Supporting Information

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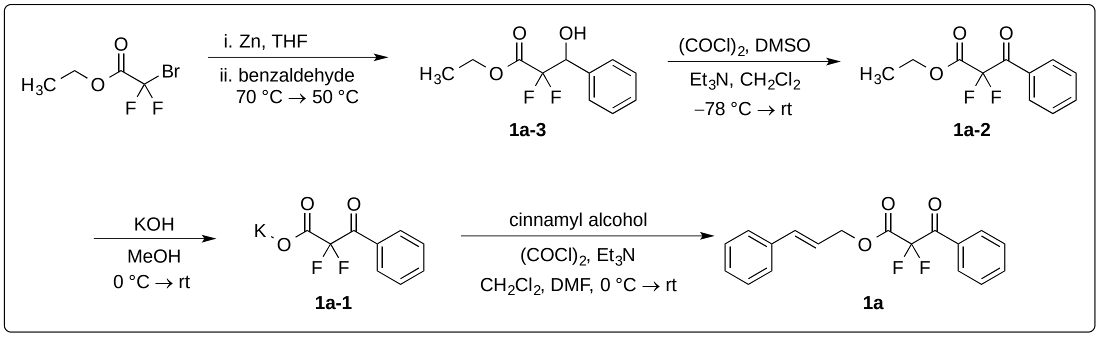
General Information

Unless otherwise noted, reactions were performed under an atmosphere of N_2 using oven-dried glassware. Palladium-catalyzed reactions were performed in 1 dram vials, which were sealed with PTFE-lined silicone septa, and all other reactions were performed in round-bottom flasks that were sealed with rubber septa. Stainless steel syringes were used to transfer air- and moisture-sensitive liquid reagents. Reactions were monitored by thin-layer chromatography (TLC) on UNIPLATE Silica Gel HLF plates, visualizing by quenching of fluorescence, or by staining with $KMnO_4$ or nihydrin. Column chromatography was conducted using an automated system. ^{19}F NMR yields and isolated yields reported in the manuscript represent an average of at least two independent runs of material deemed to be at least 95% pure by NMR. Yields reported in the supporting information refer to a single experiment.

Unless otherwise noted, reagents were purchased from commercial sources, and used as received. 1,4-Dioxane (anhydrous, 99.8%) and $Pd(OAc)_2$ (reagent grade, 98%) were purchased from Sigma Aldrich. All ligands for screening were purchased from Sigma Aldrich or Strem with the following exceptions: *t*-BuBrettPhos and PhXPhos were prepared according to previously reported syntheses.[1,2] Solvents including DMF, PhMe, CH_2Cl_2, THF, MeOH were used directly from a solvent purification system in which solvent was dried by passage through two columns of activated alumina under argon.

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker 400 AVANCE spectrometer (400 and 100 MHz, respectively) or Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane, and are referenced to proton resonance of residual $CHCl_3$ in the NMR solvent ($CHCl_3$: $\delta = 7.27$ ppm or DMSO-d_6: $\delta = 2.50$ ppm). Chemical shifts (δ) for carbon are reported in ppm downfield from tetramethylsilane, and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$: $\delta = 77.23$ ppm or DMSO-d_6: $\delta = 39.51$ ppm). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker 400 AVANCE spectrometer (376 MHz). ^{19}F NMR chemical shifts (δ) are reported in ppm upfield from trichlorofluoromethane (0 ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. Gas chromatography (GC) data were obtained via analysis using an Agilent Technologies 7890A GC system with a FID detector and an Agilent Technologies 30 m x 0.320 mm i.d. HP–5 capillary column. High-resolution mass determinations were obtained either by electrospray ionization (ESI) on a Waters LCT Premier^{TM} mass spectrometer or by atmospheric-pressure chemical ionization (APCI–hexane/PhMe) on a Waters Q-Tof Premier^{TM}, for which sample plus near mass internal exact mass standard were dissolved in hexane, and hexane or PhMe/hexane were used as ionization solvent. Infrared spectra were measured at a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer. Uncorrected melting points were measured on Thomas Hoover Capillary Melting Point apparatus.

Preparation of Compound 1a



ethyl 2,2-difluoro-3-hydroxy-3-phenylpropanoate (1a-3)

An oven-dried three-neck flask was charged with activated Zn (6.40 g, 98.4 mmol). The reaction vessel was equipped with a reflux condenser and two rubber septa, evacuated and backfilled with $N_{2(g)}$ three times. Dry THF (0.10 L) was added, followed by addition of the initiator 1,2-dibromoethane (0.50 mL, 5.8 mmol) under $N_{2(g)}$. To activate the Zn, the reaction mixture was heated with a heat gun until the THF boiled suddenly. Heating was stopped, and the mixture was cooled to rt. This heating/cooling sequence for activation of Zn was repeated four more times (5 total). Subsequently, the reaction mixture was heated to 70 °C (oil-bath), and a solution of aldehyde (5.0 mL, 49 mmol) and ethyl bromodifluoroacetate (6.4 mL, 49 mmol) was added dropwise at a rate that maintained a gentle reflux. The resulting reaction mixture was stirred at 70 °C for 1 h, and then cooled to 50 °C and stirred overnight. The reaction mixture was cooled to 0 °C, and 1 N $HCl_{(aq)}$ was added until the residual Zn was consumed (roughly 100 mL). The reaction mixture was warmed to rt, and transferred to a separation funnel. The phases were separated, and the aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (10% to 15%) for elution to provide the compound **1a-3** as a colorless oil (10.5 g, 93%). ^1H NMR ($CDCl_3$, 400 MHz) δ 7.47–7.39 (m, 5 H), 5.18 (ddd, *J* = 15.6, 8.0, 5.2 Hz, 1 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 2.66 (d, *J* = 5.2 Hz, 1 H), 1.30 (t, *J* = 7.2 Hz, 3 H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.4 (dd, *J* = 263.2, 15.4 Hz, 1 F), –113.9 (dd, *J* = 263.2, 7.9 Hz, 1 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{12}F_2O_3Na$ $[M+Na]^+$ 253.0652, found 253.0663. Spectroscopic data matched that from the previous report.[3]

ethyl 2,2-difluoro-3-oxo-3-phenylpropanoate (1a-2)

An oven-dried three-neck flask was equipped with a liquid addition funnel, a three-way valve and two rubber septa, evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (130 mL) and oxalyl chloride (6.1 mL, 71 mmol) were added sequentially at rt, and the reaction solution was cooled to –78 ºC. A solution of anhydrous DMSO (6.7 mL, 94 mmol) in dry CH_2Cl_2 (13 mL) was added dropwise at –78 ºC, and then the reaction solution was stirred at this temperature for 1 h. Next, a solution of **1a-3** (5.42 g, 23.5 mmol) dissolved in dry CH_2Cl_2 (13 mL) was added dropwise at –78 ºC, and then the resulting reaction solution was stirred at this temperature for 1 h. Et_3N (0.020 L, 0.14 mol) was added dropwise at –78 ºC, and the reaction mixture was stirred at –78 ºC for 30 min. The reaction mixture was gradually warmed to rt, and stirred at rt for 2 h. H_2O (100 mL) was added to quench the reaction, and CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 100 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (2% to 5%) for elution to afford the compound **1a-2** as a as a light yellow oil (4.40 g, 82%). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, *J* = 7.6 Hz, 2 H), 7.71–7.67 (m, 1 H), 7.56–7.52 (m, 2 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 1.33 (t, *J* = 7.2 Hz, 3 H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.6 (s, 2 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{10}F_2O_3Na$ $[M+Na]^+$ 251.0496, found 251.0490. Spectroscopic data matched that from the previous report.[4]

potassium 2,2-difluoro-3-oxo-3-phenylpropanoate (1a-1)

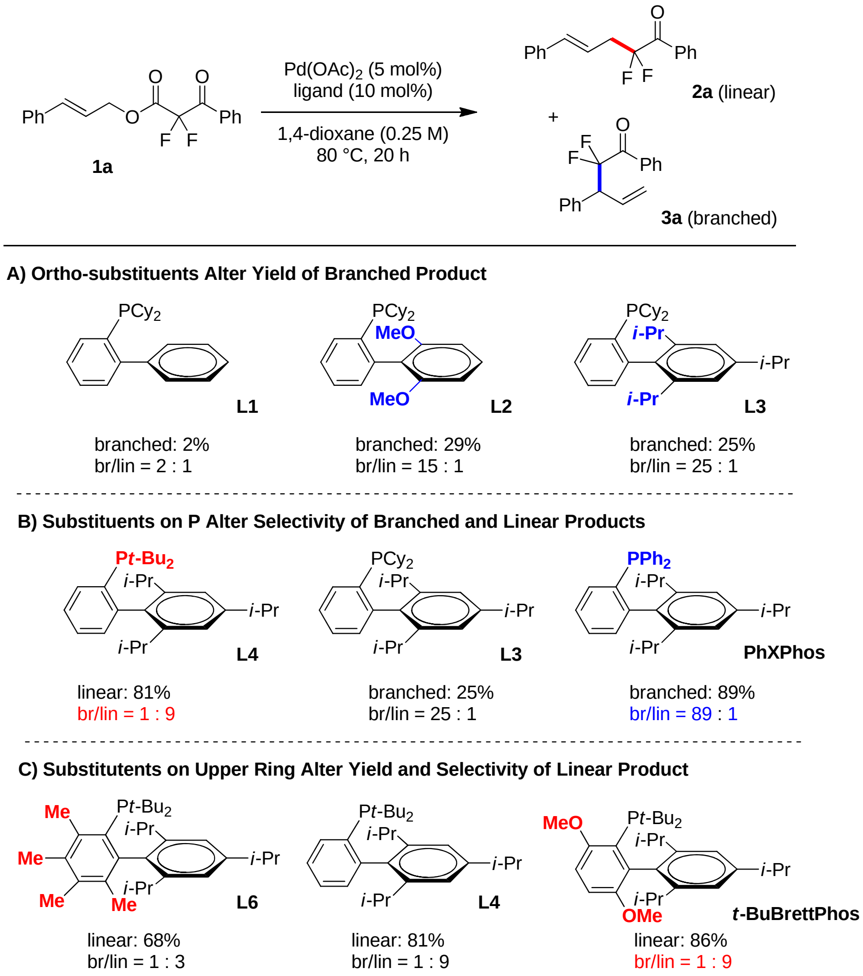
A one-neck round-bottom flask was charged with **1a-2** (3.10 g, 13.6 mmol), and MeOH (7.0 mL) was added at rt. The resulting solution was cooled to 0 ºC. A pre-cooled solution of KOH (0.760 g, 13.6 mmol) dissolved in MeOH (7.0 mL) was added dropwise, and then the reaction solution was warmed to rt, and stirred at rt for 6 h. MeOH was removed under reduced pressure. EtOAc (5 mL) and ether (5 mL) were added, and the mixture was sonicated at rt until fine solids formed. The solid was collected by filtration, washed with ether, and dried *in vacuo* to give the compound **1a-1** as a colorless solid (2.72 g, 84%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.00 (d, *J* = 8.0 Hz, 2 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 189.6 (t, *J* = 27.5 Hz), 162.4 (t, *J* = 23.8 Hz), 133.8, 132.6, 129.2, 128.5, 111.3 (t, *J* = 261.9 Hz). ^{19}F NMR (DMSO-d_6, 376 MHz) δ –105.2 (s, 2 F). IR (film) 3061, 1720, 1697, 1682, 1645, 1599, 1450, 1412, 1381, 1281, 1169, 1132, 1101, 922, 912, 816, 729, 708, 685, 584 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_9H_5F_2K_2O_3$ $[M+K]^+$ 276.9481, found 276.9492. m.p. 154–155 ºC decomposed.

cinnamyl 2,2-difluoro-3-oxo-3-phenylpropanoate (**1a**)

An oven-dried one-neck round-bottom flask was charged with potassium salt **1a-1** (3.00 g, 12.6 mmol), and the system was evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (0.040 L) and DMF (1.2 mL) were added via a syringe, and the reaction mixture was cooled to 0 ºC. Oxalyl chloride (1.2 mL, 14 mmol) was added dropwise, and then the reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. Next, a solution of cinnamyl alcohol (2.54 g, 18.9 mmol) dissolved in dry CH_2Cl_2 (2.0 mL) was added dropwise at 0 ºC followed by dropwise addition of Et_3N (2.6 mL, 19 mmol). The resulting reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. H_2O (10 mL) was added to quench the reaction, and CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 20 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (2% to 5%) for elution to furnish the compound **1a** as a as a colorless oil (3.20 g, 80%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.09 (d, *J* = 7.6 Hz, 2 H), 7.67 (t, *J* = 7.6 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.38–7.29 (m, 5 H), 6.69 (d, *J* = 15.6 Hz, 1 H), 6.23 (dt, *J* = 16, 6.8 Hz, 1 H), 4.98 (d, *J* = 6.8 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.6 (t, *J* = 27.5 Hz), 161.9 (t, *J* = 30.6 Hz), 136.5, 135.8, 135.4, 131.2, 130.2 (t, *J* = 2.5 Hz), 129.2, 128.9, 128.7, 127.0, 120.9, 110.0 (t, *J* = 263.8 Hz), 68.2. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.4 (s, 2 F). IR (film)

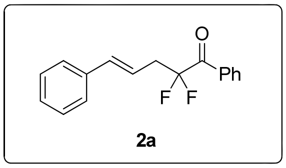
3061, 3028, 1776, 1715, 1699, 1597, 1450, 1312, 1159, 1124, 968, 922, 746, 712, 688 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{14}F_2O_3Na$ $[M+Na]^+$ 339.0809, found 339.0804.

Screening of Ligands



An oven-dried 1 dram vial was charged with substrate **1a** (47.4 mg, 0.150 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), ligand (7.0 mg, 0.0150 mmol), and a magnetic stir bar. The vial was equipped with a three-way valve, evacuated and backfilled with $N_{2(g)}$ four times. Dry 1,4-dioxane (0.60 mL) was added via a syringe under $N_{2(g)}$. The vial was sealed with a screwed-cap under $N_{2(g)}$ flow, and was stirred at rt for 5 min. Subsequently, the vial was placed on a pre-heated reaction block, and stirred at 80 °C for 20 h. The vial was cooled to rt, and the mixture was diluted with EtOAc (3 mL). Dodecane (0.020 mL, 0.088 mmol) was added as a standard, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing. A small aliquot was taken from the vial, passed through a plug of silica gel, and eluted with additional EtOAc (2 mL). The sample was analyzed using GC/FID, and the quantity of compounds **2a** and **3a** were determined using dodecane as an internal standard.

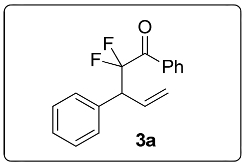
Characterization of Compounds 2a and 3a



2a

(*E*)-2,2-difluoro-1,5-diphenylpent-4-en-1-one (2a)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (dt, *J* = 8.4, 1.4 Hz, 2 H), 7.65 (tt, *J* = 7.6, 1.4 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 2 H), 7.39–7.36 (m, 2 H), 7.32 (t, *J* = 7.4 Hz, 2 H), 7.27–7.23 (m, 1 H), 6.60 (d, *J* = 15.6 Hz, 1 H), 6.22 (dt, *J* = 15.6, 7.2 Hz, 1 H), 3.14 (tdd, *J* = 17.2, 7.2, 1.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.4 (t, *J* = 31.2 Hz), 136.9, 136.4, 134.6, 132.2 (t, *J* = 2.5 Hz), 130.4 (t, *J* = 3.1 Hz), 128.9, 128.8, 128.0, 126.6, 119.0 (t, *J* = 5.6 Hz), 118.9 (t, *J* = 253.1 Hz), 38.0 (t, *J* = 23.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.9 (t, *J* = 16.9 Hz, 2 F). IR (film) 3059, 3026, 1701, 1597, 1448, 1273, 1173, 1119, 1090, 1061, 966, 947, 914, 748, 716, 688, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{15}F_2O$ $[M+H]^+$ 273.1091, found 273.1092. m.p. 45–46 ºC.

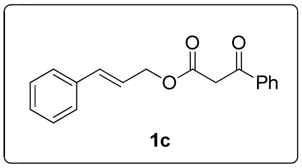


3a

2,2-difluoro-1,3-diphenylpent-4-en-1-one (3a)

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (dt, *J* = 8.8, 1.4 Hz, 2 H), 7.61 (tt, *J* = 7.6, 1.4 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 7.33–7.28 (m, 5 H), 6.22 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1 H), 5.32 (d, *J* = 10.4 Hz, 1 H), 5.23 (dt, *J* = 16.8, 1.2 Hz, 1 H), 4.32 (td, *J* = 16.4, 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.0 (t, *J* = 29.4 Hz), 135.3, 134.2, 133.1, 132.6 (t, *J* = 4.4 Hz), 130.1 (t, *J* = 3.1 Hz), 129.8, 128.8, 128.0, 120.8, 118.8 (t, *J* = 257.5 Hz), 54.2 (t, *J* = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –103.5 (dd, A of ABX, J_{AB} = 274.5 Hz, J_{AX} = 15.0 Hz, 1 F), –103.1 (dd, B of ABX, J_{AB} = 274.5 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 3065, 3032, 1701, 1597, 1448, 1267, 1178, 1049, 930, 746, 716, 698, 688 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{14}F_2ONa$ $[M+Na]^+$ 295.0910, found 295.0902.

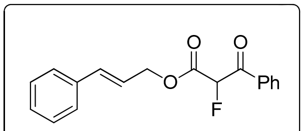
Preparation of Compounds 1b and 1c in Table 1



1c

cinnamyl 3-oxo-3-phenylpropanoate (1c)

Compound **1c** was prepared according to a previous report.[5] A mixture of cinnamyl alcohol (1.34 g, 10.0 mmol), ethyl benzoylacetate (1.73 g, 10.0 mmol), DMAP (1.22 g, 10.0 mmol) was stirred with oven-dried 4 Å molecular sieves (50 g) in dry toluene (0.080 L) at 100–105 ºC for 36 h. The reaction mixture was cooled to rt, and filtered to remove the molecular sieves. The solvents were removed under reduced pressure, and EtOAc (60 mL) and water (60 mL) were added to the residue. The layers were separated, and the organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (2% to 5%) for elution to furnish the compound **1c** as a as a yellow oil (2.08 g, 74%, ketone : enol = 4:1). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 12.53 (s, 1 H, enol), 7.98–7.96 (m, 2 H, keto), 7.82–7.79 (m, 2 H, enol), 7.61 (tt, *J* = 7.4, 1.6 Hz, 1 H, keto), 7.51–7.42 (m, 7 H, enol + keto), 7.39–7.25 (m, 8 H, enol + keto), 6.72 (d, *J* = 16.0 Hz, 1 H, enol), 6.64 (d, *J* = 16.0 Hz, 1 H, keto), 6.36 (dt, *J* = 16.0, 6.4 Hz, 1 H, enol), 6.26 (dt, *J* = 16.0, 6.4 Hz, 1 H, keto), 5.74 (s, 1 H, enol), 4.89 (dd, *J* = 6.4, 1.6 Hz, 2 H, enol), 4.83 (dd, *J* = 6.4, 1.6 Hz, 2 H, keto), 4.06 (s, 2 H, keto). HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}O_3Na$ $[M+Na]^+$ 303.0997, found 303.0996. Spectroscopic data matched that from the previous report.[6]



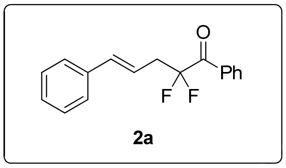
1b

cinnamyl 2-fluoro-3-oxo-3-phenylpropanoate (1b)

Compound **1b** was prepared according to a previous report.[7] Compound **1c** (1.03 g, 3.67 mmol) and $CpTiCl_3$ (39.5 mg, 0.180 mmol) were dissolved in CH_3CN (0.020 L) at rt, and selectfluor (1.40 g, 4.04 mmol) was added. The mixture was stirred at rt for 6 h, and filtered to remove solids. The filtrate was concentrated, and the crude product was purified by column chromatography using a gradient of EtOAc / hexanes (2% to 5%) for elution to furnish the compound **1b** as a as a colorless oil (0.75 g, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (dt, *J* = 8.4, 1.2 Hz, 2 H), 7.64 (tt, *J* = 7.4, 1.4 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.35–7.26 (m, 5 H), 6.62 (dt, *J* = 16.0, 1.4 Hz, 1 H), 6.21 (dt, *J* = 16.0, 6.4 Hz, 1 H), 5.94 (d, *J* = 48.8 Hz, 1 H), 4.90 (dt, *J* = 6.4, 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.6 (d, *J* = 20.0 Hz), 164.9 (d, *J* = 23.8 Hz), 135.9, 135.8, 134.7, 133.5 (d, *J* = 2.5 Hz), 129.7 (d, *J* = 3.8 Hz), 129.0, 128.8, 128.5, 126.9, 121.5, 90.2 (d, *J* = 196.2 Hz), 67.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –190.2 (d, *J* = 48.9 Hz, 1 F). IR (film) 1763, 1691, 1597, 1448, 1242, 1198, 1111, 966, 744, 690 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{15}FO_3Na$ $[M+Na]^+$ 321.0903, found 321.0894.

Experimental Procedures and Characterization of Compounds for Table 1

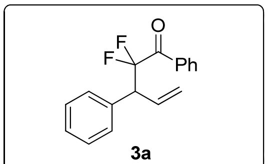
<u>General Procedure A:</u> An oven-dried 1 dram vial was charged with substrate (**1a**, **1b** or **1c**), $Pd(OAc)_2$, ligand (*t*-BuBrettPhos or PhXPhos), and a magnetic stir bar. The vial was equipped with a three-way valve, evacuated and backfilled with $N_{2(g)}$ four times. Dry 1,4-dioxane was added via a syringe under $N_{2(g)}$. The vial was sealed with a screwed-cap under $N_{2(g)}$ flow, and was stirred at rt for 5 min. Subsequently, the vial was placed on a pre-heated reaction block, and stirred at the indicated temperature for 20 h. The vial was cooled to rt, and the mixture was diluted with EtOAc. An internal standard was added, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing before checking ^{19}F or ^{1}H yields.



2a

(*E*)-2,2-difluoro-1,5-diphenylpent-4-en-1-one (2a)

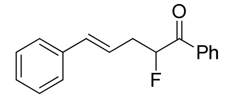
General procedure A was followed using **1a** (84.1 mg, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.0090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). α,α,α-trifluorotoluene (15 µL) was added as an internal standard to obtain a ^{19}F NMR yield of linear product **2a**. Spectral data of **2a** matched that described above.



3a

2,2-difluoro-1,3-diphenylpent-4-en-1-one (3a)

General procedure A was followed using **1a** (84.1 mg, 0.300 mmol), Pd(OAc)$_2$ (1.68 mg, 0.0075 mmol), PhXPhos (6.97 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). α,α,α-trifluorotoluene (15 µL) was added as an internal standard to obtain a ^{19}F NMR yield of branched product **3a**. Spectral data of **3a** matched that described above.

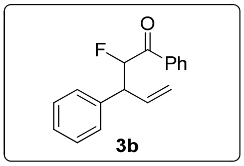


2b

(*E*)-2-fluoro-1,5-diphenylpent-4-en-1-one (2b)

General procedure A was followed using **1b** (89.5 mg, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.0090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Fluorobenzene (15 µL) was added as an internal standard to obtain ^{19}F NMR yields. After determination of the ^{19}F NMR yield, the aliquot was recombined with the reaction mixture. The total reaction mixture was passed through a plug of silica gel, and eluted with ether. Removal of the solvents and chromatographic purification provided the linear product **2b** (15.2 mg, 20%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.00 (d, *J* = 8.0 Hz, 2 H), 7.63 (tt, *J* = 7.4, 1.5 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.39–7.22 (m, 5 H), 6.53 (dt, *J* = 16.0, 1.6 Hz, 1 H), 6.27 (dt, *J* = 16.0, 7.2 Hz, 1 H), 5.69 (ddd, *J* = 49.0, 7.4, 4.8 Hz, 1 H), 3.02–2.82 (m, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 196.4 (d, *J* = 20.0 Hz), 137.0, 134.6, 134.3, 134.1, 129.2 (d, *J* = 3.8 Hz), 129.0, 128.8, 127.8, 126.5, 123.0 (d, *J* = 3.8 Hz), 93.2 (d, *J* = 185.0 Hz), 36.4 (d, *J* = 21.2

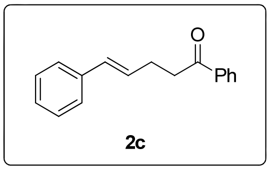
Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –187.8 (ddd, J = 48.9, 30.1, 22.5 Hz, 1 F). IR (film) 3026, 2922, 1701, 1597, 1578, 1448, 1228, 1072, 964, 744, 694 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{15}FONa$ [M+Na]$^+$ 277.1005, found 277.0995.



3b

2-fluoro-1,3-diphenylpent-4-en-1-one (3b)

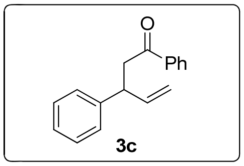
General procedure A was followed using **1b** (89.5 mg, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Fluorobenzene (15 μL) was added as an internal standard to obtain ^{19}F NMR yields. After determination of the ^{19}F yield, the aliquot was recombined with the reaction mixture. The total reaction mixture was passed through a plug of silica gel, and eluted with ether. Removal of the solvents and chromatographic purification provided the branched product **3b** as two diastereoisomers (16 mg, 21%, A : B = 2.2 : 1). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.90–7.88 (m, 2 H, isomer A), 7.79 (dt, *J* = 8.4, 1.2 Hz, 2 H, isomer B), 7.62–7.22 (m, 16 H, isomers A and B), 6.19 (ddd, *J* = 17.2, 10.2, 8.2 Hz, 1 H, isomer A), 6.16 (ddd, *J* = 17.2, 10.4, 7.6 Hz, 1 H, isomer B), 5.83 (dd, *J* = 48.4, 4.0 Hz, 1 H, isomer A), 5.78 (dd, *J* = 48.8, 5.2, 1 H, isomer B), 5.24–5.18 (m, 1 H for isomer A and 2 H for isomer B), 5.07 (dt, *J* = 17.2, 1.2 Hz, 1 H, isomer A), 4.16–4.01 (m, 4 H, isomers A and B). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 196.5 (d, *J* = 20.0 Hz, isomer B), 196.0 (d, *J* = 18.7 Hz, isomer A), 139.4 (isomer A), 137.7 (isomer B), 136.1 (d, *J* = 5.0 Hz, isomer B), 135.3 (isomer B), 135.2 (isomer A), 134.3 (d, *J* = 5.0 Hz, isomer A), 133.9 (isomer A), 133.8 (isomer B), 129.1 (isomers A and B), 129.0 (isomers A and B), 128.9 (isomers A and B), 128.8 (isomers A and B), 127.6 (isomers A and B), 119.1 (isomer A), 118.1 (isomer B), 95.9 (d, *J* = 190.0 Hz, isomer B), 95.7 (d, *J* = 191.2 Hz, isomer B), 52.6 (d, *J* = 20.0 Hz, isomer A), 52.3 (d, *J* = 20.0 Hz, isomer B). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –194.9 (dd, *J* = 48.9, 26.3 Hz, 1 F, isomer A), –191.9 (dd, *J* = 48.9, 26.3 Hz, 1 F, isomer B). IR (film) 3063, 2924, 1697, 1691, 1597, 1491, 1448, 1277, 1252, 1095, 926, 756, 698 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{15}FONa$ [M+Na]$^+$ 277.1005, found 277.0999.



2c

(*E*)-1,5-diphenylpent-4-en-1-one (2c)

General procedure A was followed using **1c** (84.1 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.0090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Dibromomethane (15 μL) was added as an internal standard to obtain ^{1}H NMR yields. Spectral data of the linear product **2c** matched that from a previous report.[8]



3c

1,3-diphenylpent-4-en-1-one (14b)

General procedure A was followed using **1c** (84.1 mg, 0.300 mmol), $Pd(OAc)_2$ (1.68 mg, 0.0075 mmol), PhXPhos (6.97 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Dibromomethane (10 μL) was added as an internal standard to obtain ^{1}H NMR yields. Spectral data of the branched product **3c** matched that from a previous report .[9]

Experimental Procedures and Characterization of Compounds for Table 2

General Procedure B: An oven-dried round-bottom flask was charged with cinnamic acid derivative (12 mmol), and dry MeOH (25 mL) was added. The mixture was cooled to 0 °C, and thionyl chloride (24 mmol) was added dropwise. The reaction mixture was warmed to rt, and then stirred at reflux for 6 h. The reaction mixture was cooled to rt, and MeOH and thionyl chloride were removed under reduced pressure. EtOAc (25 mL) and H_2O (10 mL) were added to the residue, and the solution was neutralized with $NaHCO_{3(aq)}$. The phases were separated, and the aqueous layer was extracted with EtOAc (2 x 15 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated to give the desired product without further purification.

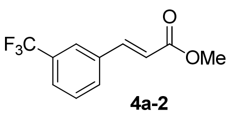
General Procedure C: An oven-dried three-neck flask was charged with cinnamic ester (8.0 mmol). The reaction vessel was equipped with a liquid addition funnel, evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (0.020 L) was added at rt, and then the solution was cooled to –78 °C. DIBAL (1.0 M in hexane, 0.020 L, 0.020 mol) was added dropwise, and then the reaction solution was gradually warmed to rt. The reaction solution was cooled to 0 °C, and 1 N HCl was added dropwise to quench the reaction until no precipitate remained. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated to give the desired product without further purification.

General Procedure D: An oven-dried one-neck round-bottom flask was charged with potassium salt **1a-1** (4.8 mmol), and the system was evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (24 mL) and DMF (1.2 mL) were added via a syringe, and the reaction mixture was cooled to 0 ºC. Oxalyl chloride (4.0 mmol) was added dropwise, and then the reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. Next, a solution of cinnamyl alcohol derivative (4.0 mmol) dissolved in dry CH_2Cl_2 (2.0 mL) was added dropwise at 0 ºC followed by dropwise addition of Et_3N (8.0 mmol). The resulting reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. H_2O (10 mL) was added to quench the reaction, and the CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 20 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography provided the desired product.

General Procedure E: Pd-Catalyzed Decarboxylation to Generate Linear Difluoroketone Product: An oven-dried 1 dram vial was charged with substrate **4a–j** (0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.0090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and a magnetic stir bar. The vial was equipped with a three-way valve, and evacuated and backfilled with $N_{2(g)}$ four times. Dry 1,4-dioxane (0.60 mL) was added via a syringe under $N_{2(g)}$. The vial was sealed with a screwed-cap under $N_{2(g)}$, and was stirred at rt for 5 min. Subsequently, the vial was placed on a pre-heated reaction block at 60 °C, and stirred for 24 h. The vial was cooled to rt, and the mixture was diluted with EtOAc (2 mL). α,α,α-Trifluorotoluene (15 µL, 0.12 mmol) or 2,2,2-trifluoroethanol (0.010 mL, 0.14 mmol) was added as a standard, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing. An aliquot was taken from the vial for ^{19}F NMR analysis. After determination of the ^{19}F yield, the aliquot was recombined with the reaction mixture. The total reaction mixture was passed through a plug of silica gel, and eluted with ether.

(In some cases, EtOAc was used for elution). Removal of the solvents and chromatographic purification provided the desired product **5a**–**j**.

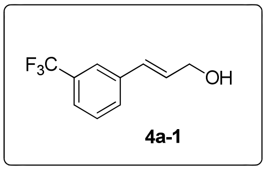
General Procedure F: Pd-Catalyzed Decarboxylation to Generate Branched Difluoroketone Product: An oven-dried 1 dram vial was charged with the substrate **4a–j** (0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.0150 mmol), and a magnetic stir bar. The vial was equipped with a three-way valve, and evacuated and backfilled with $N_{2(g)}$ four times. Dry 1,4-dioxane (3.0 mL) was added via a syringe under $N_{2(g)}$. The vial was sealed with a screwed-cap under $N_{2(g)}$, and was stirred at rt for 5 min. Subsequently, the vial was placed on a pre-heated reaction block at 90 °C, and stirred for 24 h. The vial was cooled to rt, and the mixture was diluted with EtOAc (0.50 mL α,α,α-Trifluorotoluene (15 μL, 0.12 mmol) or 2,2,2-trifluoroethanol (0.010 mL, 0.14 mmol) was added as a standard, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing. An aliquot was taken from the vial for ^{19}F NMR analysis. After determination of the ^{19}F yield, the aliquot was recombined with the reaction mixture. The total reaction mixture was passed through a plug of silica gel, and eluted with ether. (In some cases, EtOAc was used for elution). Removal of the solvents and chromatographic purification provided the desired product **6a**–**j**.



4a-2

(*E*)-methyl 3-(3-(trifluoromethyl)phenyl)acrylate (**4a-2**)

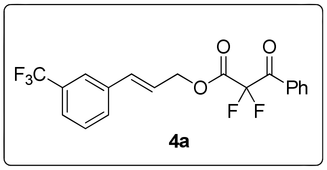
General procedure B was followed using 3-(trifluoromethyl)cinnamic acid (1.50 g, 6.94 mmol), thionyl chloride (1.0 mL, 14 mmol), and MeOH (15 mL). Workup afforded the title compound **4a-2** as a colorless solid (1.52 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77–7.69 (m, 3 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.53 (t, *J* = 7.6 Hz, 1 H), 6.52 (d, *J* = 16.0 Hz, 1 H), 3.84 (s, 3 H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.9 (s, 3 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{10}F_3O_2$ $[M+H]^+$ 231.0633, found 231.0641. Spectroscopic data matched that from the previous report.[10]



4a-1

(*E*)-3-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol (**4a-1**)

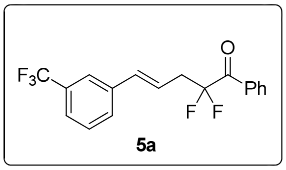
General procedure C was followed using **4a-2** (1.38 g, 6.00 mmol), DIBAL (1.0 M in hexane, 15 mL, 15 mmol), and CH_2Cl_2 (15 mL). Workup afforded the title compound **4a-1** as a light yellow oil (1.15 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (s, 1 H), 7.57–7.54 (m, 1 H), 7.51–7.49 (m, 1 H), 7.46–7.42 (m, 1 H), 6.67 (dt, *J* = 16.0, 1.6 Hz, 1 H), 6.45 (dt, *J* = 16.0, 5.4 Hz, 1 H), 4.37 (dd, *J* = 5.4, 1.6 Hz, 2 H), 1.63 (s, 3 H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –62.8 (s, 3 F). HRMS (ESI, *m/z*): calcd. for $C_{10}H_{10}F_3O$ $[M+H]^+$ 203.0684, found 203.0674. Spectroscopic data matched that from the previous report.[10]



4a

(*E*)-3-(3-(trifluoromethyl)phenyl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (**4a**)

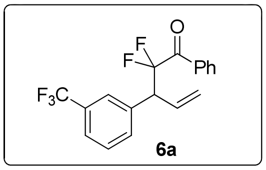
General procedure D was followed using **1a-1** (1.2 g, 4.8 mmol), oxalyl chloride (0.34 mL, 4.0 mmol), **4a-1** (0.81 g, 4.0 mmol), Et_3N (1.1 mL, 8.0 mmol), DMF (1.2 mL), and CH_2Cl_2 (24 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **4a** as a colorless oil (1.2 g, 78%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (d, *J* = 8.0 Hz, 2 H), 7.69–7.66 (m, 1 H), 7.58–7.51 (m, 5 H), 7.48–7.45 (m, 1 H), 6.70 (d, *J* = 16.0 Hz, 1 H), 6.30 (dtd, *J* = 10.0, 6.0, 1.5 Hz, 1 H), 5.00 (d, *J* = 6.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.5 (t, *J* = 27.5 Hz), 161.8 (t, *J* = 30.6 Hz), 136.6, 135.4, 134.5, 131.3 (q, *J* = 32.5 Hz), 131.1, 130.2 (t, *J* = 2.5 Hz), 130.1, 129.4, 129.2, 124.2 (q, *J* = 271.3 Hz), 125.2 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 3.8 Hz), 123.0, 110.1 (t, *J* = 263.8 Hz), 67.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.3 (s, 2 F), –62.8 (s, 3 F). IR (film) 3067, 2960, 1778, 1715, 1699, 1599, 1450, 1336, 1312, 1165, 1124, 1097, 966, 924, 793, 712, 696, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{13}F_5O_3Na$ $[M+Na]^+$ 407.0683, found 407.0611.



5a

(*E*)-2,2-difluoro-1-phenyl-5-(3-(trifluoromethyl)phenyl)pent-4-en-1-one (**5a**)

General procedure E was followed using **4a** (115.3 mg, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **5a** as a colorless oil (90.4 mg, 89%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.15 (dd, *J* = 8.2, 1.4, 2 H), 7.70–7.65 (m, 1 H), 7.62 (s, 1 H), 7.57–7.51 (m, 4 H), 7.47–7.43 (m, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 6.32 (dt, *J* = 16.0, 7.2 Hz, 1 H), 3.18 (tdd, *J* = 16.8, 7.2, 1.2 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.2 (t, *J* = 31.3 Hz), 137.6, 135.0, 134.7, 132.0 (t, *J* = 2.5 Hz), 131.2 (q, *J* = 32.5 Hz), 130.4 (t, *J* = 3.1 Hz), 129.7, 129.2, 129.0, 124.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 271.3 Hz), 123.3 (q, *J* = 3.8 Hz), 121.3 (t, *J* = 5.0 Hz), 118.8 (t, *J* = 253.1 Hz), 37.9 (t, *J* = 23.5 Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –98.7 (t, *J* = 16.9 Hz, 2 F), –62.8 (s, 3 F). IR (film) 3065, 1701, 1599, 1450, 1331, 1169, 1124, 1072, 966, 798, 716, 696 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{18}H_{14}F_5O$ [M+H]$^+$ 341.0965, found 341.0951.

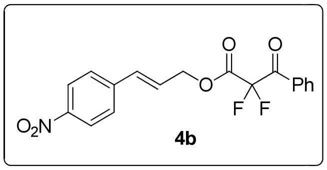


6a

2,2-difluoro-1-phenyl-3-(3-(trifluoromethyl)phenyl)pent-4-en-1-one (**6a**)

General procedure F was followed using **4a** (115 mg, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6a** as a colorless oil (86.5 mg, 85%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.99 (dd, *J* = 8.6, 1.0 Hz, 2 H), 7.66–7.61 (m, 1 H), 7.59–7.55 (m, 3 H), 7.51–7.44 (m, 3 H), 6.20 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1 H), 5.36 (dd, *J* = 10.2, 1.0 Hz, 1 H), 5.24 (d, *J* = 16.8 Hz, 1 H), 4.42 (ddd, *J* = 17.4, 14.6, 8.4 Hz, 1 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.4 (t, *J* = 29.4 Hz), 136.5, 134.5, 133.3, 132.8 (t, *J* = 2.5 Hz), 131.9 (t, *J* = 3.8

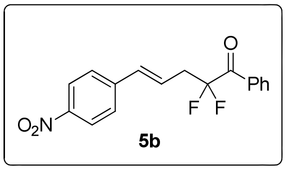
Hz), 131.1 (q, J = 31.9 Hz), 130.1 (t, J = 3.8 Hz), 129.3, 128.9, 126.7 (q, J = 3.8 Hz), 124.9 (q, J = 3.8 Hz), 124.2 (q, J = 270.0 Hz), 121.6, 118.5 (t, J = 257.5 Hz), 53.6 (t, J = 21.3 Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –103.7 (dd, A of ABX, J_{AB} = 280.1 Hz, J_{AX} = 16.9 Hz, 1 F), –102.2 (dd, B of ABX, J_{AB} = 280.1 Hz, J_{BX} = 15.0 Hz, 1 F), –62.6 (s, 3 F). IR (film) 3076, 1705, 1599, 1450, 1331, 1169, 1128, 1076, 926, 795, 716, 702, 688 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{18}H_{14}F_5O$ [M+H]$^+$ 341.0965, found 341.0971.



4b

(*E*)-3-(4-nitrophenyl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4b)

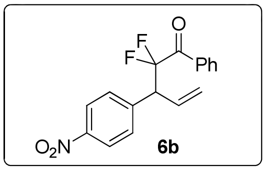
General procedure D was followed using **1a-1** (1.4 g, 5.5 mmol), oxalyl chloride (0.36 mL, 4.2 mmol), 4-nitrocinnamyl alcohol (0.75 g, 4.2 mmol), Et$_3$N (1.2 mL, 8.4 mmol), DMF (1.2 mL), and CH$_2$Cl$_2$ (0.040 L). Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **4b** as a pale yellow solid (1.2 g, 79%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.20 (d, J = 8.8 Hz, 2 H), 8.11 (d, J = 7.6 Hz, 2 H), 7.72–7.67 (m, 1 H), 7.56–7.50 (m, 4 H), 6.75 (dt, J = 16.0, 1.6 Hz, 1 H), 6.41 (dt, J = 16.0, 6.4 Hz, 1 H), 5.03 (dd, J = 6.4, 1.6 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.6 (t, J = 27.5 Hz), 161.8 (t, J = 30.6 Hz), 147.7, 142.2, 135.5, 133.2, 131.0 (t, J = 1.9 Hz), 130.2 (t, J = 2.5 Hz), 129.3, 127.6, 125.8, 124.3, 110.2 (t, J = 264.4 Hz), 67.1. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.0 (s, 2 F). IR (film) 3076, 1774, 1701, 1597, 1518, 1344, 1310, 1159, 1126, 1105, 922, 860, 822, 744, 714, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{12}F_2NO_5$ [M-H]$^+$ 360.0684, found 360.0669. m.p. 65–66 ºC.



5b

(*E*)-2,2-difluoro-5-(4-nitrophenyl)-1-phenylpent-4-en-1-one (5b)

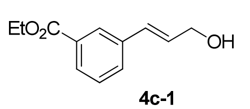
General procedure E was followed using **4b** (108 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). The reaction temperature was raised to 70 ºC. Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **5b** as a light yellow solid (41.9 mg, 44%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, *J* = 8.8 Hz, 2 H), 8.14 (dd, *J* = 8.6, 1.4 Hz, 2 H), 7.66 (tt, *J* = 7.6, 1.5 Hz, 1 H), 7.55–7.49 (m, 4 H), 6.68 (d, *J* = 16.0 Hz, 1 H), 6.43 (dt, *J* = 16.0, 7.4 Hz, 1 H), 3.20 (tdd, *J* = 16.8, 7.4, 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.9 (t, *J* = 31.2 Hz), 147.3, 143.1, 134.8, 134.4, 131.8 (t, *J* = 3.1 Hz), 130.4 (t, *J* = 3.1 Hz), 129.0, 127.1, 124.4 (t, *J* = 5.0 Hz), 124.2, 118.7 (t, *J* = 253.1 Hz), 37.9 (t, *J* = 23.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.4 (t, *J* = 16.9 Hz, 2 F). IR (film) 3076, 1697, 1597, 1514, 1344, 1202, 1111, 1032, 972, 860, 716, 687, 667 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{17}H_{14}F_2NO_3$ $[M+H]^+$ 318.0942, found 318.0935. m.p. 81–82 ºC.



6b

2,2-difluoro-3-(4-nitrophenyl)-1-phenylpent-4-en-1-one (6b)

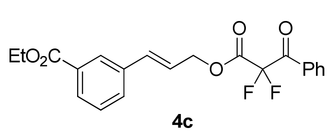
General procedure F was followed using **4b** (108 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **6b** as a yellow solid (74.4 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (d, *J* = 8.8 Hz, 2 H), 8.01 (dd, *J* = 8.2, 1.4 Hz, 2 H), 7.67–7.63 (m, 1 H), 7.56–7.48 (m, 4 H), 6.18 (ddd, *J* = 17.0, 10.4, 8.0 Hz, 1 H), 5.39 (d, *J* = 10.4 Hz, 1 H), 5.26 (d, *J* = 16.8 Hz, 1 H), 4.50 (td, *J* = 16.0, 8.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.9 (t, *J* = 30.0 Hz), 147.7, 143.1, 134.7, 132.4 (t, *J* = 2.5 Hz), 131.4 (t, *J* = 4.4 Hz), 130.8, 130.2 (t, *J* = 3.8 Hz), 129.0, 123.9, 122.0, 118.3 (t, *J* = 258.1 Hz), 53.5 (t, *J* = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.8 (dd, A of ABX, J_{AB} = 285.8 Hz, J_{AX} = 15.0 Hz, 1 F), –101.7 (dd, B of ABX, J_{AB} = 285.8 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 3084, 1701, 1599, 1524, 1448, 1348, 1176, 1053, 922, 833, 717, 694, 667 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{17}H_{14}F_2NO_3$ $[M+H]^+$ 318.0942, found 318.0927. m.p. 64–65 ºC.



4c-1

(*E*)-ethyl 3-(3-hydroxyprop-1-en-1-yl)benzoate (4c-1)

Compound **4c-1** was prepared according to a previous report.[11] An oven-dried Schlenk tube was charged with Pd(OAc)$_2$ (0.14 g, 0.60 mmol), PPh$_3$ (0.32 g, 1.2 mmol), and AgOAc (2.0 g, 12 mmol). The vessel was evacuated and backfilled with N$_{2(g)}$ three times. Dry DMF (18 mL) was added via a syringe, followed by addition of allyl alcohol (1.6 mL, 24 mmol) at rt. The reaction tube was sealed under N$_{2(g)}$ flow, placed in a pre-heated oil bath at 70 °C, and stirred for 16 h. The tube was removed from the oil bath, and allowed to cool to rt. The reaction mixture was filtered through a pad of celite. The filtrate was added with H$_2$O (15 mL), and extracted with EtOAc (3 x 25 mL). The combined organic phases were dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (20% to 40%) for elution to afford the compound **4c-1** as a as a tan oil (0.93 g, 38%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.08 (t, *J* = 2.0 Hz, 1 H), 7.93 (dd, *J* = 6.6, 1.4 Hz, 1 H), 7.57 (dd, *J* = 6.8, 1.6 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 6.67 (dt, *J* = 15.6, 1.6 Hz, 1 H), 6.46 (dt, *J* = 15.6, 5.4 Hz, 1 H), 4.42–4.36 (m, 4 H), 1.56 (br, 1 H), 1.41 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 166.7, 137.2, 131.1, 130.9, 130.2, 130.0, 128.9, 128.8, 127.7, 63.7, 61.3, 14.6. IR (film) 3458, 2982, 2868, 1716, 1443, 1367, 1288, 1261, 1198, 1105, 1022, 966, 746, 685 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for C$_{12}$H$_{15}$O$_3$ [M+H]$^+$ 207.1021, found 207.1020.

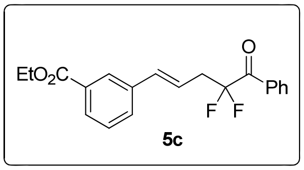


4c

(*E*)-ethyl 3-(3-((2,2-difluoro-3-oxo-3-phenylpropanoyl)oxy)prop-1-en-1-yl)benzoate (4c)

General procedure D was followed using **1a-1** (1.2 g, 4.8 mmol), oxalyl chloride (0.34 mL, 4.0 mmol), **4c-1** (0.83 g, 4.0 mmol), Et$_3$N (1.1 mL, 8.0 mmol), DMF (1.2 mL), and CH$_2$Cl$_2$ (24 mL). Workup and chromatographic purification (10% to 15% EtOAc in hexanes) afforded the title compound **4c** as a light yellow oil (1.1 g, 71%). ^{1}H

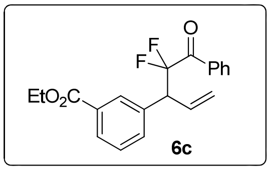
NMR ($CDCl_3$, 400 MHz) δ 8.10 (dd, *J* = 8.4, 1.6 Hz, 2 H), 8.03 (t, *J* = 1.6 Hz, 1 H), 7.97 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.69–7.65 (m, 1 H), 7.55–7.50 (m, 3 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 6.72 (d, *J* = 16.0 Hz, 1 H), 6.31 (dt, *J* = 16.0, 6.4 Hz, 1 H), 5.00 (dd, *J* = 6.4, 1.2 Hz, 1 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 1.42 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.5 (t, *J* = 27.5 Hz), 166.5, 161.9 (t, *J* = 30.0 Hz), 136.1, 135.4, 135.2, 131.2, 131.1, 130.2 (t, *J* = 2.5 Hz), 129.6, 129.2, 128.9, 128.0, 122.2, 110.0 (t, *J* = 263.8 Hz), 67.8, 61.4, 14.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.3 (s, 2 F). IR (film) 2982, 1774, 1718, 1599, 1450, 1306, 1275, 1202, 1159, 1105, 922, 748, 685 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{21}H_{18}F_2O_5Na$ $[M+Na]^+$ 411.1020, found 411.1007.



5c

(*E*)-ethyl 3-(4,4-difluoro-5-oxo-5-phenylpent-1-en-1-yl)benzoate (5c)

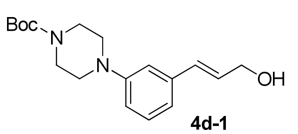
General procedure E was followed using **4c** (116 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **5c** as a colorless oil (86.0 mg, 83%). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.13 (dt, *J* = 8.4, 1.2 Hz, 2 H), 8.05 (t, *J* = 1.8 Hz, 1 H), 7.93 (dt, *J* = 7.6, 1.6 Hz, 1 H), 7.64 (tt, *J* = 7.4, 1.6 Hz, 1 H), 7.56–7.49 (m, 3 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 6.63 (d, *J* = 16.0 Hz, 1 H), 6.30 (dt, *J* = 16.0, 7.2 Hz, 1 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 3.16 (tdd, *J* = 17.2, 7.2, 1.5 Hz, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.2 (t, *J* = 31.2 Hz), 166.6, 137.1, 135.4, 134.6, 132.0 (t, *J* = 2.5 Hz), 131.0, 130.7, 130.4 (t, *J* = 3.1 Hz), 128.9, 128.8, 127.6, 120.4 (t, *J* = 5.6 Hz), 118.8 (t, *J* = 253.1 Hz), 61.2, 37.9 (t, *J* = 23.1 Hz), 14.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.8 (t, *J* = 16.9 Hz, 2 F). IR (film) 2982, 1718, 1599, 1448, 1286, 1200, 1173, 1107, 1024, 968, 752, 716, 687, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{18}F_2O_3Na$ $[M+Na]^+$ 367.1122, found 367.1104.



6c

ethyl 3-(4,4-difluoro-5-oxo-5-phenylpent-1-en-3-yl)benzoate (6c)

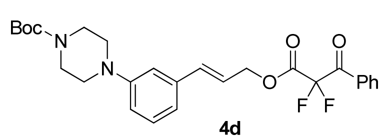
General procedure F was followed using **4c** (116 mg, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6c** as a colorless oil (86.0 mg, 83%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.03–7.97 (m, 4 H), 7.62 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.56 (d, *J* = 7.6 Hz, 1 H), 7.49–7.45 (m, 2 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 6.22 (ddd, *J* = 16.8, 10.4, 8.4 Hz, 1 H), 5.33 (dd, *J* = 10.4, 1.2 Hz, 1 H), 5.23 (dt, *J* = 17.2, 1.2 Hz, 1 H), 4.47–4.36 (m, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.6 (t, *J* = 30.0 Hz), 166.4, 135.9, 134.4, 134.2, 132.8 (t, *J* = 2.5 Hz), 132.2 (dd, *J* = 5.0, 3.8 Hz), 131.0, 130.1 (t, *J* = 3.1 Hz), 129.2, 128.9, 128.8, 121.2, 118.6 (t, *J* = 257.5 Hz), 61.3, 53.8 (t, *J*= 21.9 Hz), 14.5. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –103.8 (dd, A of ABX, J_{AB} = 278.2 Hz, J_{AX} = 18.8 Hz, 1 F), –102.3 (dd, B of ABX, J_{AB} = 278.2 Hz, J_{BX} = 11.3 Hz, 1 F). IR (film) 2984, 1718, 1597, 1448, 1367, 1282, 1180, 1107, 1051, 933, 750, 719, 694 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{18}F_2O_3Na$ [M+Na]$^+$ 367.1122, found 367.1104.



4d-1

(*E*)-tert-butyl 4-(3-(3-hydroxyprop-1-en-1-yl)phenyl)piperazine-1-carboxylate (4d-1)

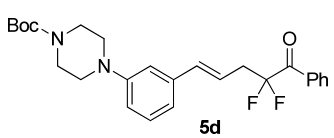
An oven-dried Schlenk tube was charged with Pd$_2$dba$_3$ (46 mg, 0.050 mmol), DavePhos (47 mg, 0.12 mmol), and 1-N-Boc-piperazine (1.1 g, 6.0 mmol). The vessel was evacuated and backfilled with $N_{2(g)}$ three times. Dry THF (5.0 mL) was added via a syringe, followed by drop wise addition of LHMDS (1.1 M in THF/ethylbenzene, 0.010 L, 11 mmol). The reaction mixture was stirred at rt for 5 min, and then a solution of (*E*)-3-(3-bromophenyl)prop-2-en-1-ol (1.1 g, 5.0 mmol) dissolved in dry THF (2.0 mL) was added. The reaction tube was sealed under $N_{2(g)}$ flow, placed in a pre-heated oil bath at 65 °C, and stirred for 7 h. The tube was removed from the oil bath, and allowed to cool to rt. The reaction mixture was diluted with EtOAc (20 mL), and washed with H$_2$O (20 mL) and brine (20 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, and concentrated. The crude product was purified by column chromatography using a gradient of EtOAc / hexanes (10% to 40%) for elution to afford the compound **4d-1** as a as a tan solid (1.0 g, 63%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.24 (t, *J* = 8.2 Hz, 1 H), 6.96–6.94 (m, 2 H), 6.85–6.83 (m, 1 H), 6.59 (dt, *J* = 16.0, 1.6 Hz, 1 H), 6.36 (dt, *J* = 16.0, 5.6 Hz, 1 H), 4.33 (d, *J* = 4.8 Hz, 2 H), 3.59 (t, *J* = 5.2 Hz, 4 H), 3.15 (t, *J* = 5.2 Hz, 4 H), 1.50 (s, 9 H). HRMS (ESI, *m/z*): calcd. for $C_{18}H_{26}N_2O_3Na$ [M+Na]$^+$ 341.1841, found 341.1827. Spectroscopic data matched that from the previous report.[10]



4d

(*E*)-tert-butyl 4-(3-(3-((2,2-difluoro-3-oxo-3-phenylpropanoyl)oxy)prop-1-en-1-yl)phenyl)piperazine-1-carboxylate (4d)

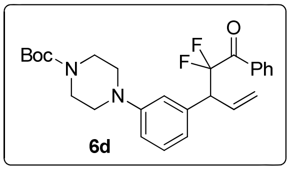
General procedure D was followed using **1a-1** (1.5 g, 5.8 mmol), oxalyl chloride (0.38 mL, 4.5 mmol), **4d-1** (1.4 g, 4.5 mmol), Et$_3$N (1.2 mL, 8.9 mmol), DMF (1.2 mL), and CH$_2$Cl$_2$ (45 mL). Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **4d** as a tan solid (1.5 g, 67%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.09 (d, *J* = 7.6 Hz, 2 H), 7.69–7.65 (m, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.24 (t, *J* = 8.0 Hz, 1 H), 6.91–6.86 (m, 3 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 6.21 (dt, *J* = 16.0, 6.8 Hz, 1 H), 4.97 (dd, *J* = 6.8, 1.2 Hz, 2 H), 3.59 (t, *J* = 5.2 Hz, 4 H), 3.14 (t, *J* = 5.2 Hz, 4 H), 1.50 (s, 9 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.6 (t, J = 27.5 Hz), 161.9 (t, J = 30.6 Hz), 154.9, 151.8, 136.8, 135.4, 131.2, 130.2 (t, J = 2.5 Hz), 129.6, 129.2, 120.9, 119.1, 117.1, 115.2, 110.1 (t, J = 263.8 Hz), 80.2, 68.2, 49.6, 43.7, 28.6. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.3 (s, 2 F). IR (film) 2976, 2822, 1774, 1693, 1597, 1450, 1421, 1242, 1163, 1124, 999, 922, 773, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{27}H_{30}F_2N_2O_5Na$ [M+Na]$^+$ 523.2020, found 523.1995. m.p. 81–82 ºC.



5d

(*E*)-tert-butyl 4-(3-(4,4-difluoro-5-oxo-5-phenylpent-1-en-1-yl)phenyl)piperazine-1-carboxylate (5d)

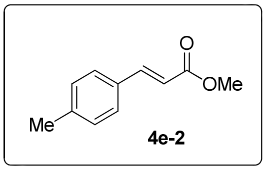
General procedure E was followed using **4d** (0.150 g, 0.300 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), *t*-BuBrettPhos (14.5 mg, 0.0300 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **5d** as a red oil (118 mg, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.13 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.67–7.63 (m, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.22 (t, *J* = 8.0 Hz, 1 H), 6.93–6.91 (m, 2 H), 6.85–6.82 (m, 1 H), 6.56 (d, *J* = 15.6 Hz, 1 H), 6.18 (dt, *J* = 15.6, 7.2 Hz, 1 H), 3.59 (t, *J* = 5.2 Hz, 4 H), 3.18–3.06 (m, 6 H), 1.50 (s, 9 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.4 (t, *J* = 31.2 Hz), 154.9, 151.8, 137.8, 136.7, 134.6, 132.2 (t, *J* = 2.5 Hz), 130.4 (t, *J* = 3.1 Hz), 129.6, 128.9, 119.0 (t, *J* = 5.6 Hz), 118.9 (t, *J* = 252.5 Hz), 118.8, 116.5, 114.9, 80.1, 49.7, 43.8, 38.0 (t, *J* = 23.8 Hz), 28.6. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –98.8 (t, *J* = 16.9 Hz, 2 F). IR (film) 2976, 1697, 1597, 1421, 1366, 1242, 1171, 1122, 997, 968, 777, 716, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{26}H_{30}F_2N_2O_3Na$ [M+Na]$^+$ 479.2122, found 479.2108.



6d

tert-butyl 4-(3-(4,4-difluoro-5-oxo-5-phenylpent-1-en-3-yl)phenyl)piperazine-1-carboxylate (6d)

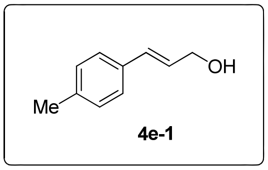
General procedure F was followed using **4d** (0.150 g, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **6d** as a yellow oil (107 mg, 78%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.94 (d, *J* = 8.0 Hz, 2 H), 7.63–7.58 (m, 1 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.23–7.19 (m, 1 H), 6.86–6.81 (m, 3 H), 6.20 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1 H), 5.30 (d, *J* = 10.0 Hz, 1 H), 5.24 (d, *J* = 17.2 Hz, 1 H), 4.26 (td, *J* = 16.4, 8.4 Hz, 1 H), 3.56 (t, *J* = 5.2 Hz, 4 H), 3.08 (t, *J* = 5.2 Hz, 4 H), 1.49 (s, 9 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 190.1 (t, *J* = 29.4 Hz), 154.9, 151.6, 136.2, 134.2, 133.2, 132.5 (t, *J* = 4.4 Hz), 130.0 (t, *J* = 3.1 Hz), 129.6, 128.8, 121.6, 120.7, 118.8 (t, *J* = 256.9 Hz), 118.2, 116.2, 80.1, 54.5 (t, *J* = 21.9 Hz), 49.5, 43.6, 28.6. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –103.8 (dd, A of ABX, J_{AB} = 270.7 Hz, J_{AX} = 15.0 Hz, 1 F), –102.6 (dd, B of ABX, J_{AB} = 270.7 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 2976, 2860, 1697, 1601, 1450, 1421, 1366, 1236, 1171, 1124, 1051, 997, 932, 868, 775, 698 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{26}H_{30}F_2N_2O_3Na$ [M+Na]$^+$ 479.2122, found 479.2130.



4e-2

(*E*)-methyl 3-(p-tolyl)acrylate (4e-2)

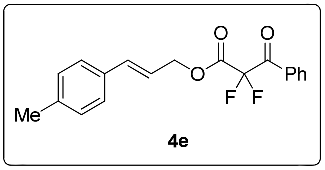
General procedure B was followed using 4-methylcinnamic acid (1.95 g, 12.0 mmol), thionyl chloride (1.7 mL, 24 mmol), and MeOH (25 mL). Workup afforded the title compound **4e-2** as a colorless solid (1.99 g, 94%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.68 (d, *J* = 16.0 Hz, 1 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 6.41 (d, *J* = 16.0 Hz, 1 H), 3.81 (s, 3 H), 2.38 (s, 3 H). Spectroscopic data of ^{1}H NMR matched that from the previous report.[12]



4e-1

(*E*)-3-(p-tolyl)prop-2-en-1-ol (4e-1)

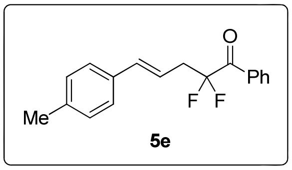
General procedure C was followed using **4e-2** (1.41 g, 8.00 mmol), DIBAL (1.0 M in hexane, 0.020 L, 0.020 mmol), and CH$_2$Cl$_2$ (0.020 L). Workup afforded the title compound **4e-1** as a colorless solid (1.15 g, 97%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.30 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.60 (dt, *J* = 16.0, 1.4 Hz, 1 H), 6.33 (dt, *J* = 16.0, 5.8 Hz, 1 H), 4.32 (td, *J* = 5.8, 1.4 Hz, 2 H), 2.36 (s, 3 H), 1.59 (t, *J* = 5.8 Hz, 1 H). Spectroscopic data of ^{1}H NMR matched that from the previous report.[13]



4e

(*E*)-3-(p-tolyl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4e)

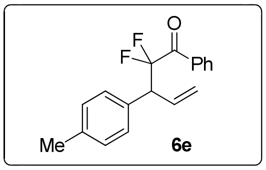
General procedure D was followed using **1a-1** (1.4 g, 5.4 mmol), oxalyl chloride (0.38 mL, 4.5 mmol), **4e-1** (0.67 g, 4.5 mmol), Et_3N (1.2 mL, 9.0 mmol), DMF (1.2 mL), and CH_2Cl_2 (25 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **4e** as a colorless oil (1.1 g, 74%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (dd, *J* = 8.8, 1.2 Hz, 2 H), 7.69–7.64 (m, 1 H), 7.54–7.49 (m, 2 H), 7.26 (d, *J* = 8.8 Hz, 2 H), 7.14 (d, *J* = 8.4 Hz, 2 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 6.18 (dt, *J* = 15.6, 6.8 Hz, 1 H), 4.96 (dd, *J* = 6.4, 1.2, 2 H), 2.36 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.6 (t, *J* = 27.5 Hz), 161.9 (t, *J* = 30.6 Hz), 138.7, 136.6, 135.3, 133.0, 131.2 (t, *J* = 1.9 Hz), 130.2 (t, *J* = 2.5 Hz), 129.5, 129.2, 126.9, 119.8, 110.0 (t, *J* = 263.1 Hz), 68.4, 21.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.4 (s, 2 F). IR (film) 3028, 2921, 1774, 1713, 1699, 1599, 1514, 1450, 1310, 1159, 1124, 1101, 970, 922, 795, 712, 685 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{16}F_2O_3Na$ $[M+Na]^+$ 353.0965, found 353.0962.



5e

(*E*)-2,2-difluoro-1-phenyl-5-(p-tolyl)pent-4-en-1-one (5e)

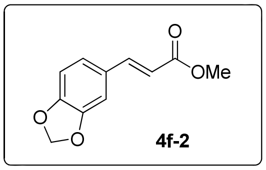
General procedure E was followed using **4e** (99.1 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **5e** as an off-white solid (75.0 mg, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (dt, *J* = 8.4, 1.2 Hz, 2 H), 7.65 (tt, *J* = 7.4, 1.5 Hz, 1 H), 7.54–7.50 (m, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.0 Hz, 2 H), 6.57 (d, *J* = 16.0 Hz, 1 H), 6.17 (dt, *J* = 16.0, 7.4 Hz, 1 H), 3.14 (tdd, *J* = 17.0, 7.4, 1.5 Hz, 2 H), 2.36 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.4 (t, *J* = 31.2 Hz), 137.8, 136.3, 134.5, 134.1, 130.4 (t, *J* = 3.1 Hz), 129.4, 128.9, 126.5, 118.9 (t, *J* = 252.5 Hz), 117.8 (t, *J* = 5.0 Hz), 38.1 (t, *J* = 23.8 Hz), 21.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –99.0 (t, *J* = 18.8 Hz, 2 F). IR (film) 3038, 2922, 1703, 1599, 1514, 1448, 1273, 1173, 1120, 968, 804, 716, 687, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{17}F_2O$ $[M+H]^+$ 287.1247, found 287.1243. m.p. 50–52 ºC.



6e

2,2-difluoro-1-phenyl-3-(p-tolyl)pent-4-en-1-one (6e)

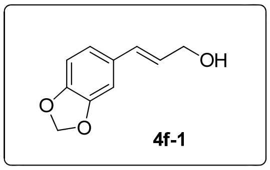
General procedure F was followed using **4e** (99.1 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6e** as a light yellow oil (77.0 mg, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (dt, J = 7.6, 1.2 Hz, 2 H), 7.61 (tt, J = 7.4, 1.4 Hz, 1 H), 7.47 (t, J = 7.8 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.14 (d, J = 8.0 Hz, 2 H), 6.22 (ddd, J = 17.2, 10.4, 8.4 Hz, 1 H), 5.30 (dd, J = 10.4, 1.2 Hz, 1 H), 5.22 (dt, J = 17.2, 1.2 Hz, 1 H), 4.29 (td, J = 16.6, 8.4 Hz, 1 H), 2.33 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.1 (t, J = 29.4 Hz), 137.8, 134.2, 133.1, 132.8 (t, J = 3.8 Hz), 132.2 (t, J = 2.5 Hz), 130.1 (t, J = 3.8 Hz), 129.6, 129.5, 128.8, 120.5, 118.8 (t, J = 256.9 Hz), 53.8 (t, J = 21.2 Hz), 21.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –103.6 (dd, A of ABX, J_{AB} = 274.5 Hz, J_{AX} = 16.9 Hz, 1 F), –103.2 (dd, B of ABX, J_{AB} = 274.5 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 3026, 2922, 1705, 1597, 1516, 1448, 1267, 1174, 1049, 924, 795, 714, 688, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2ONa$ $[M+Na]^+$ 309.1067, found 309.1064.



4f-2

(*E*)-methyl 3-(benzo[d][1,3]dioxol-5-yl)acrylate (4f-2)

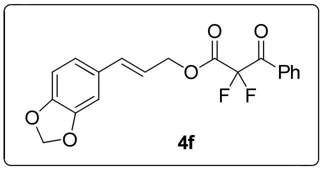
General procedure B was followed using 3,4-(methylenedioxyl)cinnamic acid (2.00 g, 10.4 mmol), thionyl chloride (1.5 mL, 21 mmol), and MeOH (15 mL). Workup afforded the title compound **4f-2** as a colorless solid (2.05 g, 96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, J = 16.0 Hz, 1 H), 7.04 (d, J = 1.6 Hz, 1 H), 7.01 (dd, J = 8.0, 1.6 Hz, 1 H), 6.82 (d, J = 8.0 Hz, 1 H), 6.28 (d, J = 16.0 Hz, 1 H), 6.02 (s, 2 H), 3.80 (s, 3 H). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{10}O_4Na$ $[M+Na]^+$ 229.0477, found 229.0494. Spectroscopic data matched that from the previous report.[14]



4f-1

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)prop-2-en-1-ol (4f-1)

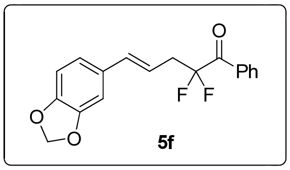
General procedure C was followed using **4f-2** (1.50 g, 7.30 mmol), DIBAL (1.0 M in hexane, 15 mL, 15 mmol), and CH_2Cl_2 (15 mL). Workup afforded the title compound **4f-1** as a colorless solid (1.27 g, 98%). ^1H NMR ($CDCl_3$, 400 MHz) δ 6.94 (d, *J* = 1.6 Hz, 1 H), 6.83 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 6.53 (dt, *J* = 16.0, 1.6 Hz, 1 H), 6.21 (dt, *J* = 16.0, 6.0 Hz, 1 H), 5.97 (s, 2 H), 4.30 (d, *J* = 6.0 Hz, 2 H), 1.45 (br, 1 H). HRMS (ESI, *m/z*): calcd. for $C_{10}H_{11}O_3$ $[M+H]^+$ 179.0708, found 179.0716. Spectroscopic data matched that from the previous report.[14]



4f

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4f)

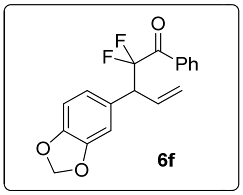
General procedure D was followed using **1a-1** (1.6 g, 6.0 mmol), oxalyl chloride (0.42 mL, 5.0 mmol), **4f-1** (0.89 g, 5.0 mmol), Et_3N (1.4 mL, 0.010 mol), DMF (1.2 mL), and CH_2Cl_2 (25 mL). Workup and chromatographic purification (10% to 20% EtOAc in hexanes) afforded the title compound **4f** as a colorless oil (1.3 g, 72%). ^1H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 8.0 Hz, 2 H), 7.67 (t, *J* = 7.4 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 6.89 (d, *J* = 1.6 Hz, 1 H), 6.82–6.75 (m, 2 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 6.05 (dt, *J* = 16.0, 6.8 Hz, 1 H), 5.98 (s, 2 H), 4.94 (d, *J* = 6.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.5 (t, *J* = 27.5 Hz), 161.9 (t, *J* = 30.6 Hz), 148.3, 148.2, 136.4, 135.3, 131.2, 130.2, 130.1 (t, *J* = 2.5 Hz), 129.2, 122.1, 118.9, 110.0 (t, *J* = 263.8 Hz), 108.5, 106.1, 101.4, 68.3. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.4 (s, 2 F). IR (film) 2895, 1774, 1711, 1699, 1504, 1491, 1448, 1308, 1252, 1159, 1040, 922, 712, 685 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{15}F_2O_5$ $[M+H]^+$ 361.0888, found 361.0897.



5f

(*E*)-5-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-1-phenylpent-4-en-1-one (5f)

General procedure E was followed using **4f** (108 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **5f** as an off-white solid (66.0 mg, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12 (dt, *J* = 8.0, 1.2 Hz, 2 H), 7.67–7.62 (m, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 6.92 (d, *J* = 1.6 Hz, 1 H), 6.81–6.74 (m, 2 H), 6.49 (d, *J* = 16.0 Hz, 1 H), 6.03 (dt, *J* = 16.0, 7.2 Hz, 1 H), 5.95 (s, 2 H), 3.10 (tdd, *J* = 17.2, 7.2, 1.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.4 (t, *J* = 30.6 Hz), 148.2, 147.5, 135.9, 134.5, 132.2 (t, *J* = 1.9 Hz), 131.4, 130.4 (t, *J* = 3.1 Hz), 128.9, 121.3, 118.9 (t, *J* = 252.5 Hz), 117.1 (t, *J* = 5.0 Hz), 108.4, 105.9, 101.3, 38.0 (t, *J* = 23.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –99.0 (t, *J* = 16.9 Hz, 2 F). IR (film) 3072, 2899, 1701, 1597, 1504, 1491, 1448, 1252, 1173, 1040, 966, 933, 804, 714, 687, 669 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{14}F_2O_3Na$ $[M+Na]^+$ 339.0809, found 339.0800. m.p. 77–78 ºC.

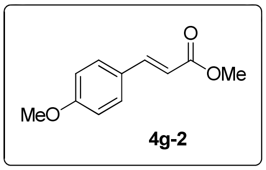


6f

3-(benzo[d][1,3]dioxol-5-yl)-2,2-difluoro-1-phenylpent-4-en-1-one (6f)

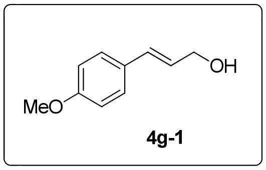
General procedure F was followed using **4f** (108.1 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **6f** as a colorless oil (77.6 mg, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (dt, *J* = 8.4, 1.2 Hz, 2 H), 7.62 (tt, *J* = 7.6, 1.4 Hz, 1 H), 7.47 (t, *J* = 8.0 Hz, 2 H), 6.84 (s, 1 H), 6.74 (s, 2 H), 6.16

(ddd, J = 16.8, 10.4, 8.2 Hz, 1 H), 5.95 (s, 2 H), 5.30 (d, J = 10.0 Hz, 1 H), 5.22 (dt, J = 16.8, 1.2 Hz, 1 H), 4.24 (td, J = 16.2, 8.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.0 (t, J = 29.4 Hz), 148.0, 147.4, 134.3, 133.1, 132.6 (t, J = 3.8 Hz), 130.1 (t, J = 3.1 Hz), 128.8, 123.4, 120.6, 118.7 (t, J = 257.5 Hz), 110.0, 108.5, 101.3, 53.7 (t, J = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.1 (dd, A of ABX, J_{AB} = 274.5 Hz, J_{AX} = 15.0 Hz, 1 F), –103.0 (dd, B of ABX, J_{AB} = 274.5 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 3076, 2893, 1705, 1597, 1504, 1489, 1446, 1250, 1182, 1040, 932, 800, 719, 688, 669 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{14}F_2O_3Na$ [M+Na]$^+$ 339.0809, found 339.0824.



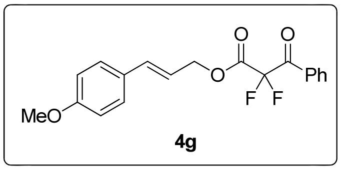
(*E*)-methyl 3-(4-methoxyphenyl)acrylate (4g-2)

General procedure B was followed using 4-methoxycinnamic acid (5.0 g, 28 mmol), thionyl chloride (4.1 mL, 56 mmol), and MeOH (45 mL). Workup afforded the title compound **4g-2** as a colorless solid (5.3 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, J = 16.0 Hz, 1 H), 7.49 (d, J = 8.8 Hz, 2 H), 6.91 (d, J = 8.4 Hz, 2 H), 6.32 (d, J = 16.0 Hz, 1 H), 3.85 (s, 3 H), 3.80 (s, 3 H). Spectroscopic data of ^{1}H NMR matched that from the previous report.[12]



(*E*)-3-(4-methoxyphenyl)prop-2-en-1-ol (4g-1)

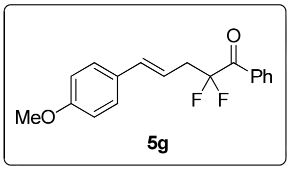
General procedure C was followed using **4g-2** (2.20 g, 11.4 mmol), DIBAL (1.0 M in hexane, 28.6 mL, 28.6 mmol), and CH_2Cl_2 (30.0 mL). Workup afforded the title compound **4g-1** as a colorless solid (1.84 g, 98%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.34 (d, J = 8.8 Hz, 2 H), 6.87 (d, J = 8.8 Hz, 2 H), 6.57 (dt, J = 16.0, 1.6 Hz, 1 H), 6.25 (dt, J = 16.0, 6.0 Hz, 1 H), 4.31 (d, J = 5.6 Hz, 2 H), 3.82 (s, 3 H), 1.42 (br, 1 H). HRMS (ESI, *m/z*): calcd. for $C_{10}H_{13}O_2$ [M+H]$^+$ 165.0916, found 165.0911. Spectroscopic data matched that from the previous report.[15]



4g

(*E*)-3-(4-methoxyphenyl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4g)

General procedure D was followed using **1a-1** (1.6 g, 6.0 mmol), oxalyl chloride (0.42 mL, 5.0 mmol), **4g-1** (0.82 g, 5.0 mmol), Et_3N (1.4 mL, 0.010 mol), DMF (1.2 mL), and CH_2Cl_2 (25 mL). Workup and chromatographic purification (10% to 20% EtOAc in hexanes) afforded the title compound **4g** as a colorless solid (0.94 g, 54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (dt, *J* = 7.6, 1.2 Hz, 2 H), 7.66 (tt, *J* = 7.6, 1.4 Hz, 1 H), 7.51 (t, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.8 Hz, 2 H), 6.64 (d, *J* = 16.0 Hz, 1 H), 6.09 (dt, *J* = 16.0, 6.8 Hz, 1 H), 4.95 (dd, *J* = 6.8, 1.2 Hz, 2 H), 3.82 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.6 (t, *J* = 27.5 Hz), 161.9 (t, *J* = 30.6 Hz), 160.1, 136.4, 135.3, 131.2 (t, *J* = 1.2 Hz), 130.2 (t, *J*= 2.5 Hz), 129.2, 128.5, 128.3, 118.5, 114.2, 110.0 (t, *J* = 263.8 Hz), 68.6, 55.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.4 (s, 2 F). IR (film) 2959, 2837, 1774, 1711, 1701, 1606, 1512, 1450, 1306, 1252, 1159, 922, 845, 711, 685 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{16}F_2O_4Na$ $[M+Na]^+$ 369.0914, found 369.0898. m.p. 36–38 ºC.

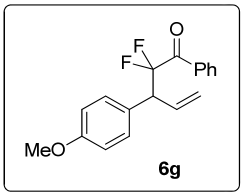


5g

(*E*)-2,2-difluoro-5-(4-methoxyphenyl)-1-phenylpent-4-en-1-one (5g)

General procedure E was followed using **4g** (104 mg, 0.300 mmol), $Pd(OAc)_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **5g** as an off-white solid (52.0 mg, 57%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (dt, *J* = 8.4, 1.2 Hz, 2 H), 7.66–7.62 (m, 1 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.31 (d, *J* = 8.8 Hz, 2 H), 6.86 (d, *J* = 8.4 Hz, 2 H), 6.53 (d, *J* = 16.0 Hz, 1 H), 6.06 (dt, *J* = 16.0, 7.2 Hz, 1 H), 3.12 (tdd, *J* = 17.2, 7.2, 1.4 Hz, 2 H), 3.81 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.5 (t, *J* = 30.6 Hz), 159.5, 135.8, 134.5, 132.2 (t, *J* =

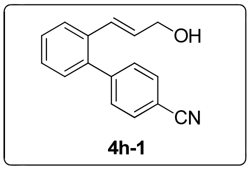
2.5 Hz), 130.4 (t, *J* = 3.1 Hz), 129.7, 128.9, 127.8, 118.9 (t, *J* = 252.5 Hz), 116.6 (t, *J* = 5.0 Hz), 114.1, 55.5, 38.1 (t, *J* = 23.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –99.0 (t, *J* = 16.9 Hz, 2 F). IR (film) 2959, 1701, 1606, 1512, 1448, 1250, 1174, 1036, 968, 837, 806, 714, 687, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2O_2Na$ $[M+Na]^+$ 325.1016, found 325.1005. m.p. 55–57 ºC.



6g

2,2-difluoro-3-(4-methoxyphenyl)-1-phenylpent-4-en-1-one (6g)

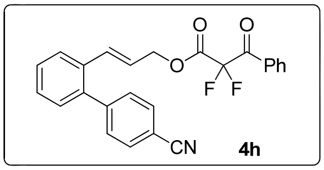
General procedure F was followed using **4g** (104 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **6g** as a colorless oil (65.1 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.61 (tt, *J* = 7.4, 1.2 Hz, 1 H), 7.46 (t, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.20 (ddd, *J* = 17.2, 10.2, 8.0 Hz, 1 H), 5.30 (d, *J* = 10.4 Hz, 1 H), 5.20 (dd, *J* = 17.2, 1.6 Hz, 1 H), 4.27 (td, *J* = 16.4, 8.0 Hz, 1 H), 3.79 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.2 (t, *J* = 30.0 Hz), 159.4, 134.2, 133.1, 132.8 (t, *J* = 4.4 Hz), 130.9, 130.1 (t, *J* = 3.8 Hz), 128.8, 127.2, 120.4, 118.8 (t, *J* =256.9 Hz), 114.2, 55.4, 53.4 (t, *J* = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.1 (dd, A of ABX, J_{AB} = 274.5 Hz, J_{AX} = 16.0 Hz, 1 F), –103.0 (dd, B of ABX, J_{AB} = 274.5 Hz, J_{BX} = 16.0 Hz, 1 F). IR (film) 2957, 1703, 1612, 1599, 1514, 1448, 1252, 1180, 1036, 922, 804, 714, 688, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2O_2Na$ $[M+Na]^+$ 325.1016, found 325.1001.



4h-1

(*E*)-2'-(3-hydroxyprop-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (4h-1)

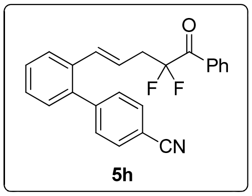
This compound was prepared according to the previously reported reaction[10] using (*E*)-2-(3-hydroxyprop-1-en-1-yl)phenyl trifluoromethanesulfonate (0.393 g, 1.39 mmol), 4-cyanophenyl boronic acid (0.324 g, 2.21 mmol), K_3PO_4 (0.633 g, 2.98 mmol) in degassed water (6.0 mL), $Pd(OAc)_2$ (6.6 mg, 0.029 mmol), XPhos (28 mg, 0.059 mmol), water (2.1 µL, 0.012 mmol), and THF (1.3 mL). Workup and chromatographic purification (0% to 30% EtOAc in hexanes) afforded the title compound **4h-1** as a pale yellow oil (0.24 g, 73%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73–7.70 (m, 2H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.48–7.45 (m, 2 H), 7.40 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.36 (td, J = 7.6, 1.6 Hz, 1 H), 7.25 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.51 (dt, *J* = 16.0, 1.4 Hz, 1 H), 6.33 (dt, *J* = 16.0, 5.4 Hz, 1 H), 4.26 (dd, *J* = 5.4, 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.9, 139.0, 134.9, 132.1, 131.0, 130.6, 130.0, 128.9, 128.7, 128.0, 126.7, 119.0, 110.0, 63.6. IR (film) 3408, 3086, 30243059, 2930, 2858, 2359, 2339, 2228, 1927, 1607, 1504, 1475, 1445, 1400, 1292, 1209, 1178, 1107, 1084, 1007, 970, 912, 843, 762, 737, 648, 575 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{12}NO$ [M-H]$^+$ 234.0919, found 234.0932.



4h

(*E*)-3-(4'-cyano-[1,1'-biphenyl]-2-yl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4h)

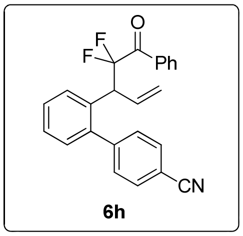
General procedure D was followed using **1a-1** (0.319 g, 1.34 mmol), oxalyl chloride (0.11 mL, 1.3 mmol), **4h-1** (0.205 g, 0.870 mmol), Et_3N (0.27 mL, 1.9 mmol), DMF (23 µL, 0.30 mmol), and CH_2Cl_2 (3.0 mL). Workup and chromatographic purification (0% to 30% EtOAc in hexanes) afforded the title compound **4h** as a yellow oil (0.32 g, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 7.6 Hz, 2 H), 7.73–7.66 (m, 3 H), 7.59–7.56 (m, 1 H), 7.53 (t, J = 7.8 Hz, 2 H), 7.44–7.39 (m, 4 H), 7.29–7.27 (m, 1 H), 6.62 (d, *J* = 16.0 Hz, 1 H), 6.22 (dt, *J* = 16.0, 6.4 Hz, 1 H), 4.90 (dd, *J* = 6.4, 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.5 (t, *J* = 28.1 Hz), 161.7 (t, *J* = 30.0 Hz), 145.3, 139.3, 135.4, 134.5, 134.0, 132.2, 132.1, 131.0, 130.6, 130.1 (t, *J* = 2.5 Hz), 130.0, 129.2, 128.8, 126.9, 123.1, 119.0, 111.3, 110.0 (t, *J* = 264.4 Hz), 67.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.2 (s, 2 F). IR 3061, 2953, 2359, 2341, 2228, 1774, 1701, 1597, 1580, 1477, 1448, 1310, 1256, 1157, 1124, 1101, 1007, 970, 922, 845, 798, 762, 712, 685, 575 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{25}H_{17}F_2NO_3Na$ [M+Na]$^+$ 440.1074, found 440.1065.



5h

(*E*)-2'-(4,4-difluoro-5-oxo-5-phenylpent-1-en-1-yl)-[1,1'-biphenyl]-4-carbonitrile (5h)

General procedure E was followed using **4h** (125.2 mg, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.0090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **5h** as a colorless solid (90.6 mg, 81%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.12 (d, *J* = 7.6 Hz, 2 H), 7.70–7.65 (m, 3 H), 7.59 (dd, *J* = 7.4, 1.8 Hz, 1 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.43 (dt, *J* = 8.0, 1.8 Hz, 2 H), 7.42–7.34 (m, 2 H), 7.26 (dd, *J* = 7.2, 2.0 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1 H), 6.15 (dt, *J* = 15.6, 7.4 Hz, 1 H), 3.06 (tdd, *J* = 16.8, 7.4, 1.3 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.1 (t, *J* = 31.2 Hz), 145.7, 138.7, 135.2, 134.9, 134.7, 132.1, 132.0 (t, *J* = 2.5 Hz), 130.7, 130.4 (t, *J* = 3.1 Hz), 129.9, 129.0, 128.8, 128.2, 127.0, 121.5 (t, *J* = 5.6 Hz), 119.1, 118.9 (t, *J* = 253.1 Hz), 111.1, 38.1 (t, *J* = 23.7 Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –98.6 (t, *J* = 16.9 Hz, 2 F). IR (film) 3061, 2924, 2361, 2330, 2228, 1701, 1597, 1477, 1448, 1273, 1173, 1122, 1103, 1084, 1022, 970, 914, 843, 762, 715, 687, 667, 575, 438 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{24}H_{17}F_2NONa$ [M+Na]$^+$ 396.1176, found 396.1176. m.p. 61 ºC.

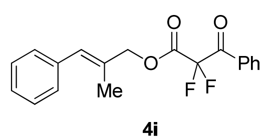


6h

2'-(4,4-difluoro-5-oxo-5-phenylpent-1-en-3-yl)-[1,1'-biphenyl]-4-carbonitrile (6h)

General procedure F was followed using **4h** (125.2 mg, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6h** as a colorless solid (58.6 mg, 52%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.71 (d, J = 7.6 Hz, 2 H), 7.67–7.62 (m, 3 H), 7.60 (tt, *J* = 7.6, 1.3 Hz, 1 H), 7.44 (td, *J* = 7.8, 1.6 Hz, 1 H), 7.39–7.33

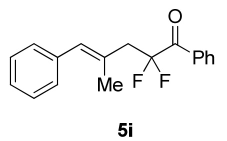
(m, 3 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 7.18 (dd, *J* = 7.4, 1.4 Hz, 1 H), 6.16 (ddd, *J* = 17.0, 10.4, 7.4 Hz, 1 H), 5.32 (d, *J* = 10.4 Hz, 1 H), 5.00 (dt, *J* = 17.2, 1.3 Hz, 1 H), 4.38 (td, *J* = 16.8, 7.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.8 (t, *J* = 28.7 Hz), 146.0, 141.5, 134.4, 132.9 (t, *J* = 3.7 Hz), 132.4, 132.3, 132.2, 130.2, 130.0, 129.8 (t, *J* = 3.1 Hz), 129.5, 128.9, 128.8, 128.0, 121.0, 118.9, 118.6 (t, *J* = 257.5 Hz), 111.4, 49.6 (t, *J* = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.6 (dd, A of A_2MX, J_{AM} = 18.8 Hz, J_{AX} = 3.8 Hz, 2 F). IR (film) 3065, 2359, 2341, 2229, 1703, 1597, 1483, 1448, 1400, 1263, 1173, 1117, 1059, 1007, 916, 845, 766, 716, 689, 667, 650, 577 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{24}H_{18}F_2NO$ [M+H]$^+$ 374.1356, found 374.1323. m.p. 94–96 ºC.



4i

(*E*)-2-methyl-3-phenylallyl 2,2-difluoro-3-oxo-3-phenylpropanoate (4i)

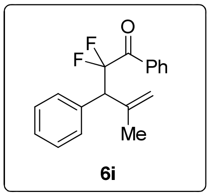
General procedure D was followed using **1a-1** (1.2 g, 4.8 mmol), oxalyl chloride (0.34 mL, 4.0 mmol), *trans*-2-methyl-3-phenyl-2-propen-1-ol (0.59 g, 4.0 mmol), Et_3N (1.1 mL, 8.0 mmol), DMF (1.2 mL), and CH_2Cl_2 (24 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **4i** as a colorless oil (0.94 g, 71%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 8.4 Hz, 2 H), 7.70–7.66 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 7.28–7.23 (m, 3 H), 6.56 (s, 1 H), 4.89 (s, 2 H), 1.83 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.6 (t, *J* = 26.9 Hz), 161.9 (t, *J* = 30.6 Hz), 136.6, 135.4, 131.2 (t, *J* = 1.9 Hz), 131.0, 130.6, 130.2 (t, *J* = 2.5 Hz), 129.2, 129.1, 128.4, 127.3, 110.0 (t, *J* = 263.1 Hz), 73.4, 15.5. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.3 (s, 2 F). IR (film) 3062, 2949, 1776, 1713, 1699, 1599, 1450, 1306, 1157, 1101, 922, 746, 698, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{16}F_2O_3Na$ [M+Na]$^+$ 353.0965, found 353.0952.



5i

(*E*)-2,2-difluoro-4-methyl-1,5-diphenylpent-4-en-1-one (5i)

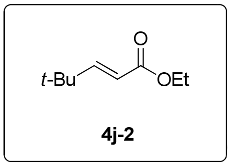
General procedure E was followed using **4i** (99.1 mg, 0.300 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *t*-BuBrettPhos (15 mg, 0.030 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **5i** as a colorless oil (67 mg, 78%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.14 (d, *J* = 7.6 Hz, 2 H), 7.66 (tt, *J* = 7.6, 1.5 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.37–7.33 (m, 2 H), 7.26–7.22 (m, 3 H), 6.41 (s, 1 H), 3.10 (t, *J* = 17.8 Hz, 2 H), 2.01 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.9 (t, *J* = 30.0 Hz), 137.6, 134.4, 132.5 (t, *J* = 1.9 Hz), 132.2, 130.3 (t, *J* = 3.1 Hz), 129.2 (t, *J* = 3.1 Hz), 129.1, 128.9, 128.3, 126.8, 119.4 (t, *J* = 253.1 Hz), 44.8 (t, *J* = 22.5 Hz), 19.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.3 (t, *J* = 18.8 Hz, 2 F). IR (film) 3059, 2922, 1703, 1599, 1448, 1277, 1176, 1113, 1061, 1028, 918, 744, 716, 698, 687 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2ONa$ $[M+Na]^+$ 309.1067, found 309.1059.



6i

2,2-difluoro-4-methyl-1,3-diphenylpent-4-en-1-one (6i)

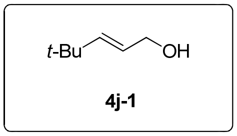
General procedure F was followed using **4i** (99.1 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6i** as a colorless oil (71 mg, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, *J* = 7.6 Hz, 2 H), 7.62 (t, *J* = 7.4 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.41–7.32 (m, 5 H), 5.08 (s, 1 H), 5.05 (s, 1 H), 4.31 (dd, *J* = 21.6, 14.4 Hz, 1 H), 1.74 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.3 (t, *J* = 30.0 Hz), 140.9 (d, *J* = 5.0 Hz), 134.5 (d, *J* = 2.5 Hz), 134.1, 133.2, 130.2, 130.0 (t, *J* = 3.1 Hz), 128.8, 128.6, 128.0, 119.1 (dd, *J* = 260.0, 253.8 Hz), 115.5 (d, *J* = 3.8 Hz), 55.7 (t, *J* = 20.6 Hz), 23.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.2 (dd, A of AMX, J_{AM} = 282.0 Hz, J_{AX} = 22.6 Hz, 1 F), –97.1 (dd, M of AMX, J_{AM} = 282.0 Hz, J_{MX} = 13.2 Hz, 1 F). IR (film) 3063, 2974, 1701, 1597, 1493, 1450, 1282, 1184, 1120, 1051, 922, 741, 717, 698, 665, 604 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2ONa$ $[M+Na]^+$ 309.1067, found 309.1069.



4j-2

(*E*)-ethyl 4,4-dimethylpent-2-enoate (4j-2)

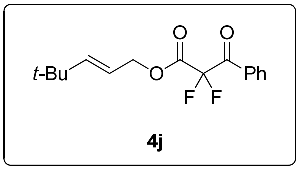
Compound **4j-2** was prepared according to a previous report[16] using pivaldehyde (1.1 mL, 10 mmol), triethyl phosphoacetate (2.4 mL, 12 mmol) and NaH (0.2661 g, 11.10 mmol, 60% dispersion in mineral oil). Workup afforded the title compound **4j-2** as a colorless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 6.97 (d, *J* = 16.0 Hz, 1 H), 5.73 (d, *J* = 16.0 Hz, 1 H), 4.19 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.08 (s, 9 H). Spectroscopic data matched that from the previous report.[16]



4j-1

(*E*)-4,4-dimethylpent-2-en-1-ol (4j-1)

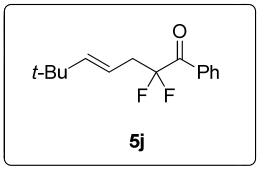
The preparation was followed according to literature report.[17] Workup and chromatographic purification (0% to 50% EtOAc in hexanes) afforded the title compound **4j-1** as a colorless liquid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 5.70 (dt, *J* = 15.6, 1.1 Hz, 1 H), 5.53 (dt, *J* = 15.6, 5.8 Hz, 1 H), 4.09 (dd, *J* = 6.4, 2.8 Hz, 2 H), 1.65 (s, 1 H), 1.01 (s, 9 H). Spectroscopic data matched that from the previous report.[17]



4j

(*E*)-4,4-dimethylpent-2-en-1-yl 2,2-difluoro-3-oxo-3-phenylpropanoate (4j)

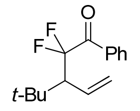
General procedure D was followed using **1a-1** (0.876 g, 3.67 mmol), oxalyl chloride (0.21 mL, 2.5 mmol), **4j-1** (0.316 g, 2.77 mmol), Et$_3$N (0.74 mL, 5.3 mmol), DMF (60 μL, 0.77 mmol), and CH$_2$Cl$_2$ (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) followed by preparative TLC (5% toluene in hexanes) provided the title compound **4j** in 95% purity as a colorless oil (0.325 g, 40%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.08 (dt, *J* = 7.2, 1.0 Hz, 2 H), 7.68 (tt, *J* = 7.6, 1.5 Hz, 1 H), 7.55–7.50 (m, 2 H), 5.82 (dt, *J* = 15.6, 1.2 Hz, 1 H), 5.42 (dt, *J* = 15.6, 6.8 Hz, 1 H), 4.76 (dd, *J* = 6.8, 1.2 Hz, 2 H), 0.98 (s, 9H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.5 (t, *J* = 26.9 Hz), 161.8 (t, *J* = 30.0 Hz), 149.6, 135.3, 131.2, 130.1 (t, *J* = 2.5 Hz), 129.2, 117.0, 109.9 (t, *J* = 263.1 Hz), 68.7, 33.3, 29.2. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.6 (s, 2 F). IR (film) 3067, 2962, 2905, 2868, 1774, 1717, 1701, 1670, 1599, 1582, 1477, 1450, 1379, 1364, 1310, 1283, 1257, 1159, 1126, 1191, 1080, 0170, 1028, 976, 924, 825, 802, 746, 712, 687, 588 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{18}F_2O_3Na$ [M+Na]$^+$ 319.1122, found 319.1121.



5j

(*E*)-2,2-difluoro-6,6-dimethyl-1-phenylhept-4-en-1-one (5j)

General procedure E was followed using **4j** (88.9 mg, 0.300 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), *t*-BuBrettPhos (15 mg, 0.030 mmol), and 1,4-dioxane (0.60 mL). The reaction was run at 100 ºC. Workup and chromatographic purification (0% to 2.5% EtOAc in hexanes) followed by preparative TLC (5% EtOAc in hexanes) afforded the title compound **5j** as a colorless viscous oil (14.8 mg, 19%, as 17:1 mixture with **6j**). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.09 (dt, *J* = 8.4, 1.2 Hz, 2 H), 7.64 (tt, *J* = 7.4, 1.5 Hz, 1 H), 7.50 (t, *J* = 8.0 Hz, 2 H), 5.63 (d, *J* = 15.6 Hz, 1 H), 5.32 (dt, *J* = 15.6, 7.2 Hz, 1 H), 2.90 (tdd, *J* = 17.0, 7.0, 1.2 Hz, 2 H), 0.97 (s, 9 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.9 (t, *J* = 30.0 Hz), 149.0, 134.4, 132.6, 130.3, 128.8, 119.1 (t, *J* = 251.9 Hz), 113.7 (t, *J* = 5.6 Hz), 38.1 (t, *J* = 23.1 Hz), 33.5, 29.5. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –99.8 (t, *J* = 16.9 Hz, 2 F). IR (film) 2961, 2905, 2868, 1703, 1599, 1580, 1477, 1460, 1450, 1425, 1364, 1271, 1234, 1198, 1175, 1119, 1088, 1032, 974, 716, 687, 602 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{15}H_{18}F_2O$ [M]$^+$ 252.1326, found 252.1321.

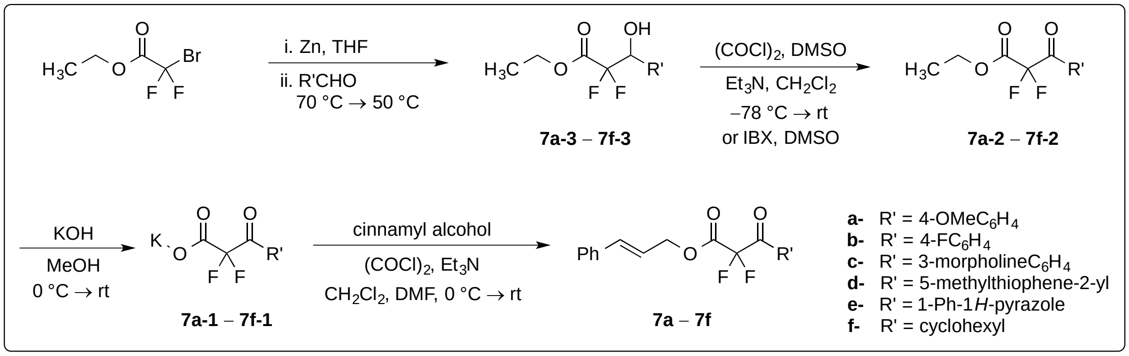


6j

3-(tert-butyl)-2,2-difluoro-1-phenylpent-4-en-1-one (6j)

General procedure F was followed using **4j** (88.9 mg, 0.300 mmol), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and *o*-xylene (3.0 mL). The reaction was run at 130 ºC. Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **6j** as a colorless solid (28.8 mg, 38%, as 18:1 mixture with **5j**). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (dd, J = 7.6, 1.6 Hz, 2 H), 7.62 (tt, J = 7.6, 1.2 Hz, 1 H), 7.49 (t, J =8.0 Hz, 2 H), 5.78–5.69 (m, 1 H), 5.17 (dt, J = 10.0, 1.6 Hz, 1 H), 4.91 (dd, J = 17.2, 1.6 Hz, 1 H), 2.86 (dt, J = 25.2, 9.8 Hz, 1 H), 1.09 (s, 9 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.4 (t, J = 29.4 Hz), 133.9, 133.4, 131.8 (dd, J = 7.5, 3.7 Hz), 130.1 (t, J = 3.7 Hz), 128.8, 121.9, 121.4 (t, J = 258.1 Hz), 57.3 (t, J = 20.6 Hz), 33.6, 29.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –106.0 (dd, A of AMX, J_{AM} = 265.1 Hz, J_{AX} = 24.4 Hz, 1 F), –98.3 (dd, M of AMX, J_{AM} = 265.1 Hz, J_{MX} = 9.4 Hz, 1 F). IR (film) 2961, 2912, 2876, 1709, 1599, 1479, 1470, 1448, 1369, 1271, 1231, 1177, 1057, 1001, 928, 883, 812, 762, 714, 689, 667 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{19}F_2O$ $[M+H]^+$ 253.1404, found 253.1407.

Experimental Procedures and Characterization of Compounds for Table 3



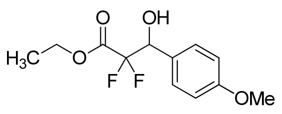
<u>General Procedure G:</u> An oven-dried three-neck flask was charged with activated Zn (3.2 g, 49 mmol). The reaction vessel was equipped with a reflux condenser and two rubber septa, evacuated and backfilled with $N_{2(g)}$ three times. Dry THF (0.050 L) was added, followed by addition of the initiator 1,2-dibromoethane (0.25 mL, 2.9

mmol) under $N_{2(g)}$. To activate the Zn, the reaction mixture was heated with a heat gun until the THF boiled suddenly. Heating was stopped, and the mixture was cooled to rt. This heating/cooling sequence for activation of Zn was repeated four more times (5 total). Subsequently, the reaction mixture was heated to 70 °C (oil-bath), and a solution of aldehyde (25 mmol) and ethyl bromodifluoroacetate (25 mmol) was added dropwise at a rate that maintained a gentle reflux. The resulting reaction mixture was stirred at 70 °C for 1 h, and then cooled to 50 °C and stirred overnight. The reaction mixture was cooled to 0 °C, and 1 N $HCl_{(aq)}$ was added until the residual Zn was consumed (roughly 100 mL). The reaction mixture was warmed to rt, and transferred to a separation funnel. The phases were separated, and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography provided the desired product.

General Procedure H: An oven-dried three-neck flask was equipped with a liquid addition funnel, three-way valve and two rubber septa, evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (0.10 L) and oxalyl chloride (59 mmol) were added sequentially at rt, and the reaction solution was cooled to –78 ºC. A solution of anhydrous DMSO (78 mmol) in dry CH_2Cl_2 (0.010 L) was added dropwise at –78 ºC, and then the reaction solution was stirred continually at this temperature for 1 h. Next, a solution of alcohol (19.5 mmol) dissolved in dry CH_2Cl_2 (0.010 L) was added dropwise at –78 ºC, and then the resulting reaction solution was stirred at this temperature for 1 h. Et_3N (117 mmol) was added dropwise at –78 ºC, and the reaction mixture was stirred at –78 ºC for 30 min. The reaction mixture was gradually warmed to rt, and stirred at rt for 2 h. H_2O (0100 mL) was added to quench the reaction, and CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 100 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography provided the desired product.

General Procedure I: A one-neck round-bottom flask was charged with β-keto ester (16 mmol), and MeOH (8.0 mL) was added at rt. The resulting solution was cooled to 0 ºC. A pre-cooled solution of KOH (16 mmol) dissolved in MeOH (8.0 mL) was added dropwise, and then the reaction solution was warmed to rt, and stirred at rt for 7 h. MeOH was removed under reduced pressure. EtOAc (8.0 mL) and ether (8.0 mL) were added, and the mixture was sonicated at rt until fine solids formed. The solid was collected by filtration, washed with ether, and dried *in vacuo* to give potassium salt.

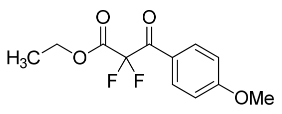
General Procedure J: An oven-dried one-neck round-bottom flask was charged with potassium salt (5.0 mmol), and the system was evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (15 mL) and DMF (0.75 mL) were added via a syringe, and the reaction mixture was cooled to 0 ºC. Oxalyl chloride (5.0 mmol) was added dropwise, and then the reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. Next, a solution of cinnamyl alcohol (6.5 mmol) dissolved in dry CH_2Cl_2 (2.0 mL) was added dropwise at 0 ºC followed by dropwise addition of Et_3N (6.0 mmol). The resulting reaction mixture was stirred at 0 ºC for 30 min, and rt for 1.5 h. H_2O (8.0 mL) was added to quench the reaction, and CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 15 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography provided the desired product.



7a-3

ethyl 2,2-difluoro-3-hydroxy-3-(4-methoxyphenyl)propanoate (7a-3)

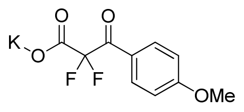
General procedure G was followed using activated Zn (3.2 g, 49 mmol), 1,2-dibromoethane (0.25 mL, 2.9 mmol), *p*-anisaldehyde (3.0 mL, 25 mmol), ethyl bromodifluoroacetate (3.2 mL, 25 mmol), and THF (0.050 L). Workup and chromatographic purification (10% to 15% EtOAc in hexanes) afforded the title compound **7a-3** as a colorless oil (5.4 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, *J* = 8.8 Hz, 2 H), 6.92 (d, *J* = 8.8 Hz, 2 H), 5.12 (ddd, *J* = 15.2, 8.0, 5.2 Hz, 1 H), 4.32 (q, *J* = 7.2 Hz, 2 H), 3.82 (s, 3 H), 2.63 (d, *J* = 5.2 Hz, 1 H), 1.31 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.8 (t, *J* = 31.2 Hz), 160.5, 129.2, 126.7, 114.1, 114.0 (dd, *J* = 257.5, 252.5 Hz), 73.6 (dd, *J* = 26.2, 23.8 Hz), 63.3, 55.5, 14.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.4 (dd, *J* = 259.4, 15.0 Hz, 1 F), –114.2 (dd, *J* = 259.4, 7.5 Hz, 1 F). HRMS (ESI, *m/z*): calcd. for $C_{12}H_{14}F_2O_4Na$ $[M+Na]^+$ 283.0758, found 283.0746. Spectroscopic data matched that from the previous report.[18]



7a-2

ethyl 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (7a-2)

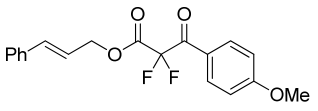
General procedure H was followed using oxalyl chloride (5.0 mL, 59 mmol), DMSO (5.5 mL, 78 mmol), **7a-3** (5.07 g, 19.5 mmol), Et_3N (16 mL, 120 mmol) and CH_2Cl_2 (120 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7a-2** as a colorless oil (4.38 g, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 8.8 Hz, 2 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 3.91 (s, 3 H), 1.33 (t, *J* = 7.2 Hz, 3 H). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.3 (s, 2 F). HRMS (ESI, *m/z*): calcd. for $C_{12}H_{12}F_2O_4Na$ $[M+Na]^+$ 281.0601, found 281.0587. Spectroscopic data matched that from the previous report.[19]



7a-1

potassium 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (7a-1)

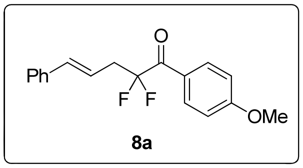
General procedure I was followed using **7a-2** (4.08 g, 15.8 mmol), KOH (0.890 g, 15.8 mmol), and MeOH (16 mL). Workup afforded the title compound **7a-1** as a colorless solid (3.68 g, 87%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.99 (d, *J* = 8.8 Hz, 2 H), 7.04 (t, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 188.0 (t, *J* = 27.5 Hz), 163.5, 162.5 (t, *J* = 23.8 Hz), 131.6, 125.5, 113.8, 111.4 (t, *J* = 261.2 Hz), 55.6. ^{19}F NMR (DMSO-d_6, 376 MHz) δ –104.9 (s, 2 F). IR (film) 2970, 2845, 1693, 1676, 1605, 1516, 1383, 1325, 1277, 1180, 1151, 1128, 1028, 922, 847, 816, 717, 613, 584 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{10}H_7F_2K_2O_4$ $[M+K]^+$ 306.9587, found 306.9574. m.p. 150–151 ºC.



7a

cinnamyl 2,2-difluoro-3-(4-methoxyphenyl)-3-oxopropanoate (7a)

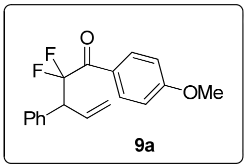
General procedure J was followed using **7a-1** (1.5 g, 5.6 mmol), oxalyl chloride (0.52 mL, 6.2 mmol), cinnamyl alcohol (1.1 g, 8.4 mmol), Et_3N (0.93 mL, 6.7 mmol), DMF (1.0 mL), and CH_2Cl_2 (0.020 L). Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **7a** as a colorless oil (1.6 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, *J* = 8.8 Hz, 2 H), 7.37–7.28 (m, 5 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 6.68 (dt, *J* = 16.0, 1.2 Hz, 1 H), 6.23 (dt, *J* = 16.0, 6.4 Hz, 1 H), 4.97 (dd, *J* = 6.4, 1.2 Hz, 2 H), 3.87 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 183.8 (t, *J* = 26.9 Hz), 165.3, 162.1 (t, *J* = 30.0 Hz), 136.3, 135.8, 132.8 (t, *J* = 2.5 Hz), 128.8, 128.6, 127.0, 124.0 (t, *J* = 1.9 Hz), 121.0, 114.5, 110.3 (t, *J* = 263.1 Hz), 68.0, 55.8. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.1 (s, 2 F). IR (film) 3028, 2960, 1774, 1701, 1690, 1601, 1574, 1512, 1427, 1312, 1269, 1157, 1099, 1026, 968, 924, 845, 746, 692, 579 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{19}H_{16}F_2O_4Na$ [M+Na]$^+$ 369.0914, found 369.0896.



8a

(*E*)-2,2-difluoro-1-(4-methoxyphenyl)-5-phenylpent-4-en-1-one (8a)

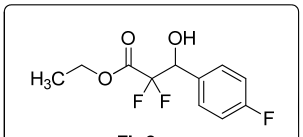
General procedure E was followed using **7a** (104 mg, 0.300 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *t*-BuBrettPhos (14.5 mg, 0.0300 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **8a** as an off-white solid (72.0 mg, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (dt, *J* = 8.8, 1.2 Hz, 2 H), 7.39–7.37 (m, 2 H), 7.32 (t, *J* = 7.4 Hz, 2 H), 7.27–7.23 (m, 1 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 6.22 (dt, *J* = 16.0, 7.2 Hz, 1 H), 3.90 (s, 3 H), 3.12 (tdd, *J* = 17.2, 7.2, 1.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.8 (t, *J* = 30.6 Hz), 164.7, 136.9, 136.2, 133.0 (t, *J* = 3.1 Hz), 128.8, 127.9, 126.6, 125.0 (t, *J* = 2.5 Hz), 119.3 (t, *J* = 5.0 Hz), 119.1 (t, *J* = 252.5 Hz), 114.2, 55.8, 38.2 (t, *J* = 23.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.5 (t, *J* = 16.9 Hz, 2 F). IR (film) 3026, 2935, 1690, 1601, 1574, 1512, 1425, 1265, 1167, 1119, 1028, 968, 845, 770, 746, 692, 619 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2O_2Na$ [M+Na]$^+$ 325.1016, found 325.0989. m.p. 41–42 ºC.



9a

2,2-difluoro-1-(4-methoxyphenyl)-3-phenylpent-4-en-1-one (9a)

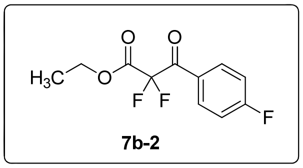
General procedure F was followed using **7a** (104 mg, 0.300 mmol), $Pd(OAc)_2$ (2.4 mg, 0.011 mmol), PhXPhos (9.8 mg, 0.021 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **9a** as a light yellow oil (76.0 mg, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99 (dt, *J* = 8.8, 1.0 Hz, 2 H), 7.33–7.28 (m, 5 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 6.23 (ddd, *J* = 17.2, 10.4, 8.0 Hz, 1 H), 5.30 (d, *J* = 10.4 Hz, 1 H), 5.22 (dt, *J* = 17.2, 1.2 Hz, 1 H), 4.31 (td, *J* = 16.4, 8.0 Hz, 1 H), 3.89 (s, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.2 (t, *J* = 29.4 Hz), 164.4, 135.6 (t, *J* = 2.5 Hz), 132.8 (t, *J* = 4.4 Hz), 132.7 (t, *J* = 3.8 Hz), 129.8, 128.8, 128.0, 125.8 (t, *J* = 1.9 Hz), 120.6, 119.0 (t, *J* = 257.5 Hz), 114.1, 55.7, 54.3 (t, *J* = 21.9 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.9 (d, A_2, *J* = 15.0 Hz, 2 F). IR (film) 3030, 2935, 1691, 1601, 1574, 1510, 1456, 1423, 1315, 1265, 1178, 1117, 1028, 924, 845, 744, 700, 619 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{16}F_2O_2Na$ $[M+Na]^+$ 325.1016, found 325.1004.



7b-3

ethyl 2,2-difluoro-3-(4-fluorophenyl)-3-hydroxypropanoate (7b-3)

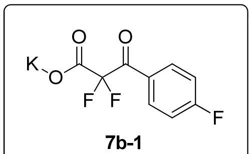
General procedure G was followed using activated Zn (3.2 g, 49 mmol), 1,2-dibromoethane (0.25 mL, 2.9 mmol), 4-fluorobenzaldehyde (2.6 mL, 25 mmol), ethyl bromodifluoroacetate (3.2 mL, 25 mmol), and THF (0.050 L). Workup and chromatographic purification (10% to 15% EtOAc in hexanes) afforded the title compound **7b-3** as a colorless oil (5.1 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46–7.42 (m, 2 H), 7.10 (t, *J* = 8.8 Hz, 2 H), 5.18 (ddd, *J* = 15.2, 8.0, 5.2 Hz, 1 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 2.71 (d, *J* = 4.8 Hz, 1 H), 1.32 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.7 (t, *J* = 31.2 Hz), 163.4 (d, *J* = 246.2 Hz), 130.4 (t, *J* = 2.5 Hz), 129.8 (d, *J* = 7.5 Hz), 115.6 (d, J = 21.2 Hz), 113.7 (dd, J = 257.5, 252.5 Hz), 73.3 (dd, J = 27.5, 23.8 Hz), 63.5, 14.0. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –120.6 (dd, J = 263.2, 15.0 Hz, 1 F), –113.8 (dd, J = 263.2, 7.5 Hz, 1 F), –112.2 (m, 1 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{11}F_3O_3Li$ $[M+Li]^+$ 255.0820, found 255.0831. Spectroscopic data matched that from the previous report.[18]



7b-2

ethyl 2,2-difluoro-3-(4-fluorophenyl)-3-oxopropanoate (7b-2)

General procedure H was followed using oxalyl chloride (5.0 mL, 58 mmol), DMSO (5.5 mL, 77 mmol), **7b-3** (4.76 g, 19.2 mmol), Et_3N (16 mL, 120 mmol) and CH_2Cl_2 (130 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7b-2** as a colorless oil (3.93 g, 83%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.16–8.13 (m, 2 H), 7.21 (t, J = 8.6 Hz, 2 H), 4.40 (q, J = 7.2 Hz, 2 H), 1.34 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 184.2 (t, J = 28.1 Hz), 167.1 (d, J = 257.5 Hz), 161.9 (t, J = 30.0 Hz), 133.2 (dt, J = 8.8, 3.1 Hz), 127.6 (m), 116.6 (d, J = 22.5 Hz), 110.0 (t, J = 262.5 Hz), 64.1, 14.0. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.5 (s, 2 F), –100.4 (m, 1 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_9F_3O_3Na$ $[M+Na]^+$ 269.0401, found 269.0411. Spectroscopic data matched that from the previous report.[20]

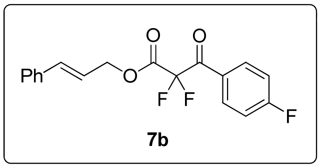


7b-1

potassium 2,2-difluoro-3-(4-fluorophenyl)-3-oxopropanoate (7b-1)

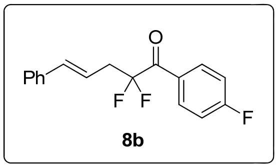
General procedure I was followed using **7b-2** (3.72 g, 15.1 mmol), KOH (0.850 g, 15.1 mmol), and MeOH (0.030 L). Workup afforded the title compound **7b-1** as a colorless solid (3.28 g, 85%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.09 (dd, J = 8.6, 5.4 Hz, 2 H), 7.37 (t, J = 9.0 Hz, 2 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 188.4 (t, J = 28.1 Hz), 165.3 (d, J = 252.5 Hz), 162.2 (t, J = 23.8 Hz), 132.3 (d, J = 10.0 Hz), 129.3 (d, J = 3.8 Hz), 115.8 (d, J =

21.2 Hz), 111.3 (t, *J* = 261.2 Hz). ^{19}F NMR (DMSO-d_6, 376 MHz) δ –105.4 (s, 2 F), –104.5 (m, 1 F). IR (film) 3086, 1718, 1678, 1645, 1605, 1512, 1404, 1300, 1250, 1161, 1099, 912, 849, 816, 764, 717, 688, 573, 521, 480 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_9H_4F_3K_2O_3$ [M+K]$^+$ 294.9387, found 294.9375. m.p. 173–174 ºC decomposed.



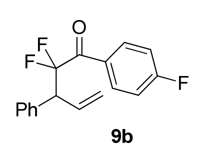
cinnamyl 2,2-difluoro-3-(4-fluorophenyl)-3-oxopropanoate (7b)

General procedure J was followed using **7b-1** (1.20 g, 4.68 mmol), oxalyl chloride (0.40 mL, 4.7 mmol), cinnamyl alcohol (0.820 g, 6.08 mmol), Et_3N (0.98 mL, 7.0 mmol), DMF (0.75 mL), and CH_2Cl_2 (16 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7b** as a colorless oil (1.14 g, 73%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.14 (dd, *J* = 8.8, 5.2 Hz, 2 H), 7.39–7.28 (m, 5 H), 7.22–7.16 (m, 2 H), 6.70 (dt, *J* = 16.0, 1.2 Hz, 1 H), 6.24 (dt, *J* = 16.0, 6.8 Hz, 1 H), 4.98 (dd, *J* = 6.8, 1.2 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 184.1 (t, *J* = 27.5 Hz), 167.1 (d, *J* = 257.5 Hz), 161.8 (t, *J* = 30.6 Hz), 136.7, 135.8, 133.2 (dt, *J* = 10.0, 2.5 Hz), 128.9, 128.8, 127.6, 127.0, 120.8, 116.6 (d, *J* = 22.5 Hz), 110.0 (t, *J* = 263.8 Hz), 68.3. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.2 (s, 2 F), –100.3 (m, 1 F). IR (film) 3082, 3028, 1774, 1701, 1599, 1508, 1308, 1244, 1161, 1124, 1101, 968, 924, 852, 746, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{13}F_3O_3Na$ [M+Na]$^+$ 357.0714, found 357.0701.



(*E*)-2,2-difluoro-1-(4-fluorophenyl)-5-phenylpent-4-en-1-one (8b)

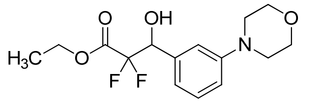
General procedure E was followed using **7b** (0.100 g, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **8b** as a light yellow oil (75.0 mg, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.18 (dd, *J* = 8.6, 5.4 Hz, 2 H), 7.39–7.37 (m, 2 H), 7.34–7.30 (m, 2 H), 7.28–7.24 (m, 1 H), 7.18 (t, *J* = 8.6 Hz, 2 H), 6.60 (d, *J* = 16.0 Hz, 1 H), 6.21 (dt, *J* = 16.0, 7.4 Hz, 1 H), 3.13 (tdd, *J* = 17.2, 7.4, 1.4 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 187.8 (t, *J* = 31.2 Hz), 166.6 (d, *J* = 256.2 Hz), 136.8, 136.5, 133.3 (dt, *J* = 10.0, 3.8 Hz), 129.8, 128.8, 128.5, 128.0, 126.6, 118.9 (t, *J* = 5.0 Hz), 118.9 (t, *J* = 252.5 Hz), 37.9 (t, *J* = 23.1 Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –102.2 (m, 1 F), –98.6 (t, *J* = 16.9 Hz, 2 F). IR (film) 3028, 1701, 1599, 1508, 1414, 1242, 1161, 966, 850, 766, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{13}F_3ONa$ [M+Na]$^+$ 313.0816, found 313.0830.



9b

2,2-difluoro-1-(4-fluorophenyl)-3-phenylpent-4-en-1-one (9b)

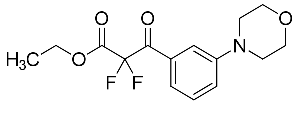
General procedure F was followed using **7b** (0.100 g, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **9b** as an off-white solid (74.8 mg, 86%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.00 (dd, *J* = 8.6, 5.4 Hz, 2 H), 7.33–7.28 (m, 5 H), 7.12 (t, *J* = 8.6 Hz, 2 H), 6.22 (ddd, *J* = 16.8, 10.4, 8.4 Hz, 1 H), 5.32 (d, *J* = 10.0 Hz, 1 H), 5.24 (d, *J* = 16.8 Hz, 1 H), 4.30 (td, *J* = 16.4, 8.4 Hz, 1 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 188.5 (t, *J* = 29.4 Hz), 166.4 (d, *J* = 256.2 Hz), 135.2 (d, *J* = 3.8 Hz), 133.0 (dt, *J* = 8.8, 3.8 Hz), 132.5 (t, *J* = 4.4 Hz), 129.8, 129.4 (d, *J* = 2.5 Hz), 128.8, 128.1, 120.9, 118.8 (t, *J* = 256.2 Hz), 116.1 (d, *J* = 21.2 Hz), 54.1 (t, *J* = 21.9 Hz). ^{19}F NMR (CDCl$_3$, 376 MHz) δ –103.4 (dd, A of ABX, J_{AB} = 276.4 Hz, J_{AX} = 16.9 Hz, 1 F), –102.6 (m, 1 F), –102.5 (dd, B of ABX, J_{AB} = 276.4 Hz, J_{BX} = 16.9 Hz, 1 F). IR (film) 3086, 1707, 1599, 1506, 1412, 1242, 1161, 1047, 926, 850, 744, 700 cm^{-1}. HRMS (APCI-hexane/PhMe, *m/z*): calcd. for $C_{17}H_{14}F_3O$ [M+H]$^+$ 291.0997, found 291.0994. m.p. 35–36 ºC.



7c-3

ethyl 2,2-difluoro-3-hydroxy-3-(3-morpholinophenyl)propanoate (7c-3)

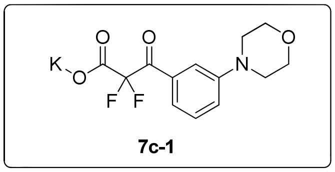
General procedure G was followed using activated Zn (1.01 g, 15.4 mmol), 1,2-dibromoethane (34 μL, 0.40 mmol), 3-morpholinobenzaldehyde[21] (1.54 g, 8.05 mmol), ethyl bromodifluoroacetate (1.1 mL, 8.6 mmol), and THF (0.040 L). Workup and chromatographic purification (0% to 30% EtOAc in hexanes) afforded the title compound **7c-3** as a white solid (1.9 g, 75%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.29 (t, *J* = 8.0 Hz, 1 H), 6.99 (s, 1 H), 6.95–6.91 (m, 2 H), 5.10 (dd, *J* = 16.0, 7.6 Hz, 1 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.86–3.84 (m, 4 H), 3.17–3.14 (m, 4 H), 1.31 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 163.8 (t, *J* = 31.2 Hz), 151.4, 135.8, 129.4, 119.6, 116.6, 115.2, 114.0 (dd, *J* = 257.5, 252.5 Hz), 74.1 (dd, *J* = 27.5, 23.7 Hz), 67.0, 63.3, 49.4, 14.1. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –120.8 (dd, *J* = 263.2, 16.9 Hz, 1 F), –113.6 (dd, *J* = 263.2, 7.5 Hz, 1 F). IR (film) 3493, 3377, 2968, 2899, 2860, 2827, 1770, 1759, 1605, 1585, 1497, 1448, 1375, 1306, 1265, 1242, 1200, 1180, 1115, 1070, 997, 974, 960, 932, 885, 854, 837, 777, 739, 714, 698, 648, 636, 557, 528 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{20}F_2NO_4$ [M+H]$^+$ 316.1360, found 316.1379.(6.0 ppm). m.p. 103–105 ºC.



7c-2

ethyl 2,2-difluoro-3-(3-morpholinophenyl)-3-oxopropanoate (7c-2)

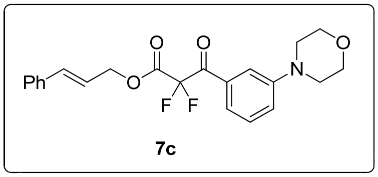
General procedure H was followed using oxalyl chloride (1.1 mL, 13 mmol), DMSO (1.3 mL, 18 mmol), **7c-3** (1.35 g, 4.28 mmol), Et$_3$N (3.6 mL, 26 mmol) and CH$_2$Cl$_2$ (71 mL). Workup and chromatographic purification (0% to 25% EtOAc in hexanes) afforded the title compound **7c-2** as a yellow solid (1.33 g, 99%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.56–7.53 (m, 2 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.22–7.19 (m, 1 H), 4.37 (q, *J* = 7.1 Hz, 2 H), 3.88–3.86 (m, 4 H), 3.22–3.19 (m, 4 H), 1.30 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.7 (t, *J* = 26.9 Hz), 162.2 (t, *J* = 30.6 Hz), 151.8, 132.0, 129.9, 122.3, 121.4 (t, *J* = 3.1 Hz), 116.0, 109.9 (t, *J* = 262.5 Hz), 66.9, 64.0, 48.9, 14.0. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.5 (s, 2F). IR (film) 3479, 3319, 3078, 2968, 2895, 2856, 2833, 2769, 2723, 2363, 2343, 1774, 1713, 1597, 1578, 1493, 1446, 1373, 1313, 1256, 1234, 1157, 1122, 1070, 1009, 999, 980, 914, 858, 833, 773, 752, 731, 704, 681, 640, 588, 527 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{15}H_{18}F_2NO_4$ $[M+H]^+$ 314.1204, found 314.1198. m.p. 61–62 ºC.



7c-1

potassium 2,2-difluoro-3-(3-morpholinophenyl)-3-oxopropanoate (7c-1)

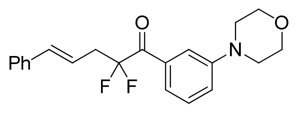
General procedure I was followed using **7c-2** (1.52 g, 4.86 mmol), KOH (0.25 g, 4.5 mmol), and MeOH (35 mL). Workup afforded the title compound **7c-1** as a bright yellow solid (0.87 g, 55%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.57–7.56 (m, 1 H), 7.46 (d, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.9 Hz, 1 H), 7.25 (dd, *J* = 8.2, 2.6 Hz, 1 H), 3.76–3.74 (m, 4 H), 3.14–3.11 (m, 4 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 189.7 (t, *J* = 26.9 Hz), 162.7 (t, *J* = 23.7 Hz), 151.0, 133.2, 129.2, 120.5, 120.1, 115.0, 111.4 (t, *J* = 261.2 Hz), 66.0, 48.2. ^{19}F NMR (DMSO-d_6, 376 MHz) δ –104.9 (s, 2 F). IR (film) 3086, 3038, 2962, 2932, 3905, 2868, 2833, 1699, 1682, 1595, 1578, 1493, 1448, 1383, 1367, 1356, 1325, 1310, 1267, 1231, 1178, 1153, 1119, 1070, 1026, 997, 978, 939, 914, 893, 868, 816, 804, 775, 748, 700, 677, 652, 598, 557, 538, 525 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{13}H_{12}F_2K_2NO_4$ $[M+2K]^+$ 362.0009, found 362.0001. m.p. 164–167 ºC decomposed.



7c

cinnamyl 2,2-difluoro-3-(3-morpholinophenyl)-3-oxopropanoate (7c)

General procedure J was followed using **7c-1** (1.67 g, 5.16 mmol), oxalyl chloride (0.43 mL, 5.1 mmol), cinnamyl alcohol (0.838 g, 6.25 mmol), Et_3N (1.5 mL, 11 mmol), DMF (0.12 mL, 1.6 mmol), and CH_2Cl_2 (25 mL). The salt and oxalyl chloride were stirred at rt for 3.5 h prior to the addition of cinnamyl alcohol at 0 °C. Workup and chromatographic purification (0% to 25% EtOAc in hexanes) afforded the title compound **7c** as a viscous yellow oil (0.84 g, 41%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58–7.56 (m, 2 H), 7.40–7.27 (m, 6 H), 7.19–7.16 (m, 1 H), 6.66 (d, J = 16.0 Hz, 1 H), 6.20 (dt, J = 16.0, 6.6 Hz, 1 H), 4.96 (d, J = 6.8 Hz, 2 H), 3.86–3.83 (m, 4 H), 3.19–3.16 (m, 4H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 185.5 (t, J = 26.9 Hz), 162.0 (t, J = 30.6 Hz), 151.7, 136.4, 135.7, 131.9, 129.9, 128.8, 128.7, 127.0, 122.3, 121.4 (t, J = 3.1 Hz), 120.8, 115.9, 109.9 (t, J = 263.1 Hz), 68.1, 66.8, 48.8. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –107.3 (s, 2F). IR (film) 2964, 2854, 2833, 1774, 1711, 1699, 1597, 1576, 1493, 1447, 1381, 1344, 1310, 1267, 1254, 1232, 1157, 1122, 1070, 999, 970, 914, 829, 798, 773, 748, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{22}H_{21}F_2KNO_4$ [M+K]$^+$ 440.1076, found 440.1057.

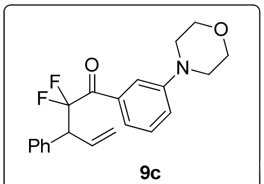


8c

(*E*)-2,2-difluoro-1-(3-morpholinophenyl)-5-phenylpent-4-en-1-one (8c)

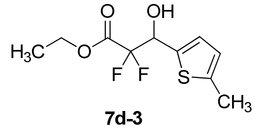
In a N$_2$-filled glovebox, an oven-dried 1 dram vial charged with substrate **7c** (30.1 mg, 0.0750 mmol) and *t*-BuBrettPhos (2.2 mg, 0.0045 mmol) and equipped with a magnetic stir bar. Subsequently, a 150 μL aliquot of a solution of Pd(OAc)$_2$ (0.0150 M in 1,4-dioxane prepared in a volumetric flask) was added to the vial. The vial was sealed with a screwed-cap, and was stirred at rt for 5 min. Subsequently, the vial was transferred out of the glove box and placed on a pre-heated reaction block at 60 ºC, and stirred for 24 h. The vial was cooled to rt, and the mixture was diluted with EtOAc (1.0 mL). α,α,α-Trifluorotoluene (3.7 μL, 0.030 mmol) was added as an internal standard, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing. An aliquot was taken from the vial for ^{19}F NMR analysis. After determination of the ^{19}F NMR yield, the aliquot was recombined with the reaction mixture. The total reaction mixture was passed through a plug of silica gel, and eluted with ether. Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **8c** in a 28:1 mixture with **9c** as a pale yellow solid (21.4 mg, 80%). The reaction was also performed at 0.3 mmol scale for the substrate **7c**, and the same result was obtained. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.64 (dt, J = 8.0, 1.4 Hz, 1 H), 7.60 (t, J = 2.0 Hz, 1 H), 7.42–7.35 (m, 3 H), 7.34–7.30 (m, 2 H), 7.27–7.23 (m, 1 H), 7.19 (dd, J = 8.2, 2.6 Hz, 1 H), 6.58 (d, J = 16.0 Hz, 1 H), 6.20 (dt, J = 16.0, 7.2 Hz, 1 H), 3.88–3.86 (m, 4 H), 3.22–3.19 (m, 4 H), 3.13 (tdd, J = 17.2, 7.2, 1.1 Hz, 2 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.7 (t, J = 30.6 Hz), 151.6, 136.8, 136.4, 133.0

(t, *J* = 2.5 Hz), 129.6, 128.8, 128.0, 126.6, 121.9 (t, *J* = 4.4 Hz), 121.7, 119.0 (t, *J* = 5.0 Hz), 118.9 (t, *J* = 253.1 Hz), 116.6 (t, *J* = 2.5 Hz), 66.9, 49.1, 38.2 (t, *J* = 23.1 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –98.7 (t, *J* = 16.9 Hz, 2 F). IR (film) 3080, 3026, 2962, 2914, 2893, 2856, 2831, 1699, 1597, 1576, 1493, 1448, 1441, 1381, 1346, 1304, 1267, 1192, 1169, 1122, 1092, 1068, 1057, 1034, 997, 968, 928, 912, 891, 752, 744, 692, 457 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{21}H_{22}F_2NO_2$ $[M+H]^+$ 358.1619, found 358.1600. m.p. 91–92 ºC.


9c

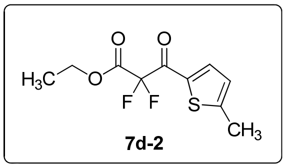
2,2-difluoro-1-(3-morpholinophenyl)-3-phenylpent-4-en-1-one (9c)

General procedure F was followed using **7c** (120.4 mg, 0.300 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), PhXPhos (13.9 mg, 0.030 mmol), and 1,4-dioxane (3.0 mL). The reaction time was 18 h. Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **9c** as a yellow oil (91.0 mg, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49 (dt, *J* = 8.0, 1.4 Hz, 1 H), 7.41 (t, *J* = 2.0 Hz, 1 H), 7.37–7.28 (m, 6 H), 7.15 (dd, *J* = 8.2, 2.6 Hz, 1 H), 6.22 (ddd, *J* = 16.8, 10.4, 8.2 Hz, 1 H), 5.31 (d, *J* = 10.0 Hz, 1 H), 5.23 (dt, *J* = 16.8, 1.2 Hz, 1 H), 3.88–3.86 (m, 4 H), 3.19–3.16 (m, 4 H), 4.33 (td, *J* = 16.4, 8.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 190.2 (t, *J* = 30.0 Hz), 151.5, 135.4 (t, *J* = 1.9 Hz), 133.8, 132.6 (t, *J* = 4.4 Hz), 129.8, 129.5, 128.8, 128.0, 121.5 (t, *J* = 4.4 Hz), 121.4, 120.7, 118.8 (t, *J* = 257.5 Hz), 116.4 (t, *J* = 2.5 Hz), 66.9, 54.2 (t, *J* = 21.9 Hz), 49.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –103.2 (dd, A of ABX, J_{AB} = 274.5 Hz, J_{AX} = 15.0 Hz, 1 F), –102.9 (dd, B of ABX, J_{AB} = 274.5 Hz, J_{BX} = 16.9 Hz, 1 F). IR (film) 3082, 3065, 3032, 2964, 2912, 2893, 2856, 2831, 1701, 1597, 1576, 1493, 1450, 1439, 1381, 1344, 1304, 1265, 1231, 1177, 1122, 1051, 997, 986, 933, 912, 864, 841, 820, 756, 727, 700, 685, 638, 517 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{21}H_{22}F_2NO_2$ $[M+H]^+$ 358.1619, found 358.1636.


7d-3

ethyl 2,2-difluoro-3-hydroxy-3-(5-methylthiophen-2-yl)propanoate (7d-3)

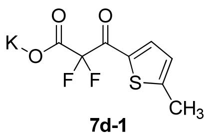
General procedure G was followed using activated Zn (1.94 g, 29.6 mmol), 1,2-dibromoethane (0.15 mL, 1.8 mmol), 5-methyl-2-thiophenecarboxaldehyde (1.6 mL, 15 mmol), ethyl bromodifluoroacetate (1.9 mL, 15 mmol), and THF (0.030 L). Workup and chromatographic purification (10% to 15% EtOAc in hexanes) afforded the title compound **7d-3** as a yellow oil (2.15 g, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.96 (d, *J* = 3.2 Hz, 1 H), 6.68 (dd, *J* = 3.4, 1.4 Hz, 1 H), 5.33 (ddd, *J* = 14.8, 8.0, 6.4 Hz, 1 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 2.60 (d, *J* = 6.0 Hz, 1 H), 2.49 (s, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.4 (dd, *J* = 32.5, 31.2 Hz), 142.2, 134.2, 128.0, 125.3, 113.4 (dd, *J* = 257.5, 253.8 Hz), 70.6 (dd, *J* = 27.5, 25.0 Hz), 63.5, 15.5, 14.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.2 (dd, *J* = 263.2, 15.0 Hz, 1 F), –114.2 (dd, *J* = 263.2, 7.5 Hz, 1 F). IR (film) 3495, 2986, 2924, 1759, 1375, 1321, 1217, 1186, 1103, 1072, 1045, 854, 793, 669 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{12}F_2O_3SNa$ [M+Na]$^+$ 273.0373, found 273.0376.



7d-2

ethyl 2,2-difluoro-3-(5-methylthiophen-2-yl)-3-oxopropanoate (7d-2)

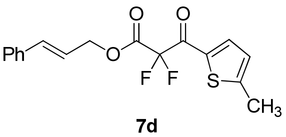
General procedure H was followed using oxalyl chloride (3.9 mL, 46 mmol), DMSO (4.4 mL, 61 mmol), **7d-3** (3.8 g, 15 mmol), Et_3N (13 mL, 92 mmol) and CH_2Cl_2 (0.11 L). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7d-2** as a yellow oil (3.2 g, 83%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87–7.86 (m, 1 H), 6.90 (dd, *J* = 4.2, 1.4 Hz, 1 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 2.60 (s, 3 H), 1.34 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 178.1 (t, *J* = 27.5 Hz), 161.9 (t, *J* = 30.6 Hz), 154.5, 137.4 (t, *J* = 4.4 Hz), 135.3, 128.2, 109.7 (t, *J* = 262.5 Hz), 64.0, 16.4, 14.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –108.2 (s, 2 F). IR (film) 2988, 2941, 1774, 1666, 1446, 1313, 1267, 1157, 1126, 1053, 868, 816, 787, 675, 580 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{10}H_{10}F_2O_3SNa$ [M+Na]$^+$ 271.0216, found 271.0221.



7d-1

potassium 2,2-difluoro-3-(5-methylthiophen-2-yl)-3-oxopropanoate (7d-1)

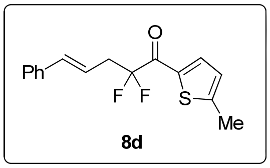
General procedure I was followed using **7d-2** (3.0 g, 12 mmol), KOH (0.67 g, 12 mmol), and MeOH (25 mL). Workup afforded the title compound **7d-1** as a colorless solid (2.6 g, 84%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 7.78 (d, J = 3.6 Hz, 1 H), 6.97 (dd, J = 4.0, 1.4 Hz, 1 H), 2.52 (s, 3 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 182.6 (t, J = 28.8 Hz), 162.1 (t, J = 23.8 Hz), 150.9, 136.8, 136.2 (t, J = 2.5 Hz), 127.8, 111.3 (t, J = 261.9 Hz), 15.6. ^{19}F NMR (DMSO-d_6, 376 MHz) δ –105.2 (s, 2 F). IR (film) 1693, 1668, 1454, 1389, 1298, 1157, 1130, 1074, 1047, 860, 818, 806, 793, 706, 615, 590, 575, 511 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_8H_5F_2K_2O_3S$ [M+K]$^+$ 296.9202, found 296.9193. m.p. 141–142 ºC decomposed.



7d

cinnamyl 2,2-difluoro-3-(5-methylthiophen-2-yl)-3-oxopropanoate (7d)

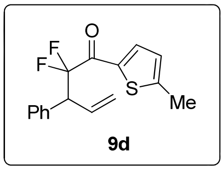
General procedure J was followed using **7d-1** (1.5 g, 5.8 mmol), oxalyl chloride (0.49 mL, 5.8 mmol), cinnamyl alcohol (1.0 g, 7.5 mmol), Et$_3$N (1.2 mL, 8.7 mmol), DMF (1.0 mL), and CH$_2$Cl$_2$ (21 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7d** as a colorless oil (1.4 g, 72%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.87–7.86 (m, 1 H), 7.39–7.29 (m, 5 H), 6.87 (dd, J = 4.0, 1.2 Hz, 1 H), 6.69 (dt, J = 16.0, 1.2 Hz, 1 H), 6.25 (dt, J = 16.0, 6.4 Hz, 1 H), 4.97 (dd, J = 6.4, 1.2 Hz, 2 H), 2.57 (s, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 177.9 (t, J = 28.1 Hz), 161.8 (t, J = 30.6 Hz), 154.6, 137.5 (t, J = 5.0 Hz), 136.4, 135.8, 135.2, 128.8, 128.7, 128.2, 127.0, 120.9, 109.7 (t, J = 263.1 Hz), 68.1, 16.4. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –108.0 (s, 2 F). IR (film) 3028, 1774, 1664, 1446, 1310, 1265, 1155, 1051, 968, 912, 812, 746, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{14}F_2O_3SNa$ [M+Na]$^+$ 359.0529, found 359.0531.



8d

(*E*)-2,2-difluoro-1-(5-methylthiophen-2-yl)-5-phenylpent-4-en-1-one (8d)

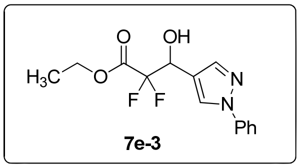
General procedure E was followed using **7d** (101 mg, 0.300 mmol), Pd(OAc)$_2$ (2.0 mg, 0.090 mmol), *t*-BuBrettPhos (8.7 mg, 0.018 mmol), and 1,4-dioxane (0.60 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **8d** as a light yellow solid (78.0 mg, 89%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.87–7.86 (m, 1 H), 7.38–7.36 (m, 2 H), 7.34–7.30 (m, 2 H), 7.26–7.22 (m, 1 H), 6.88 (dd, *J* = 3.6, 1.2 Hz, 1 H), 6.59 (d, *J* = 16.0 Hz, 1 H), 6.19 (dt, *J* = 16.0, 7.4 Hz, 1 H), 3.10 (tdd, *J* = 17.0, 7.4, 1.4 Hz, 2 H), 2.58 (s, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 182.3 (t, *J* = 31.2 Hz), 153.3, 136.9 (t, *J* = 5.0 Hz), 136.8, 136.4, 136.3, 128.7, 128.0, 127.9, 126.6, 118.9 (t, *J* = 5.0 Hz), 118.6 (t, *J* = 252.5 Hz), 38.2 (t, *J* = 23.8 Hz), 16.3. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –100.0 (t, *J* = 16.9 Hz, 2 F). IR (film) 3026, 1670, 1448, 1223, 1184, 1171, 1057, 968, 812, 758, 739, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{14}F_2OSNa$ [M+Na]$^+$ 315.0631, found 315.0643. m.p. 49–50 ºC.



9d

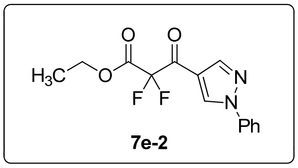
2,2-difluoro-1-(5-methylthiophen-2-yl)-3-phenylpent-4-en-1-one (9d)

General procedure F was followed using **7d** (101 mg, 0.300 mmol), Pd(OAc)$_2$ (1.7 mg, 0.0075 mmol), PhXPhos (7.0 mg, 0.015 mmol), and 1,4-dioxane (3.0 mL). The reaction time was 18 h. Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **9d** as a light yellow solid (76.0 mg, 87%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.73–7.72 (m, 1 H), 7.35–7.28 (m, 5 H), 5.81 (dd, *J* = 4.0, 1.2 Hz, 1 H), 6.22 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1 H), 5.31 (d, *J* = 10.4 Hz, 1 H), 5.24 (dt, *J* = 17.2, 1.2 Hz, 1 H), 4.26 (td, *J* = 16.6, 8.4 Hz, 1 H), 2.55 (s, 3 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 182.4 (t, *J* = 30.0 Hz), 153.2, 137.0, 136.6 (t, *J* = 5.6 Hz), 135.3 (t, *J* = 1.9 Hz), 132.4 (t, *J* = 3.8 Hz), 129.8, 128.7, 128.0, 127.8, 120.8, 118.7 (t, *J* = 257.5 Hz), 54.3 (t, *J* = 21.9 Hz), 16.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –104.8 (d, A_2, *J* = 15.0 Hz, 2 F). IR (film) 3030, 1662, 1448, 1275, 1171, 1061, 1040, 932, 812, 748, 719, 700 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{16}H_{14}F_2OSK$ [M+K]$^+$ 331.0371, found 331.0382. m.p. 55–56 ºC.


7e-3

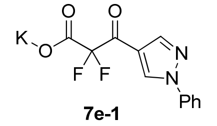
ethyl 2,2-difluoro-3-hydroxy-3-(1-phenyl-1H-pyrazol-4-yl)propanoate (7e-3)

General procedure G was followed using activated Zn (1.54 g, 23.6 mmol), 1,2-dibromoethane (0.16 mL, 1.9 mmol), 1-phenyl-1H-pyrazole-4-carbaldehyde[22] (2.70 g, 15.7 mmol), ethyl bromodifluoroacetate (2.0 mL, 15.7 mmol), and THF (80 mL). Workup and chromatographic purification (10% to 30% EtOAc in hexanes) afforded the title compound **7e-3** as a colorless solid (3.8 g, 82%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (s, 1 H), 7.74 (s, 1 H), 7.63 (dt, *J* = 7.2, 1.5 Hz, 2 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.30 (tt, *J* = 7.6, 1.4 Hz, 1 H), 5.25 (ddd, *J* = 16.0, 7.8, 2.4 Hz, 1 H), 4.34 (q, *J* = 7.2 Hz, 2 H), 3.40 (br, 1 H), 1.32 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.6 (t, *J* = 31.2 Hz), 140.3, 139.6, 129.6, 127.1, 127.0, 119.5, 118.2 (d, *J* = 2.5 Hz), 113.9 (dd, *J* = 256.2, 252.5 Hz), 66.9 (dd, *J* = 29.4, 24.4 Hz), 63.3, 13.9. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.7 (dd, J = 263.2, 15.0 Hz, 1 F), –114.1 (dd, *J* = 263.2, 7.5 Hz, 1 F). IR (film) 3325, 2986, 1759, 1599, 1568, 1504, 1406, 1321, 1213, 1074, 1007, 955, 856, 800, 758, 690 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{14}F_2N_2O_3Na$ [M+Na]$^+$ 319.0870, found 319.0865. m.p. 51–52 ºC.


7e-2

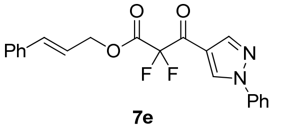
ethyl 2,2-difluoro-3-oxo-3-(1-phenyl-1H-pyrazol-4-yl)propanoate (7e-2)

IBX (3.89 g, 13.9 mmol) was added into a solution of compound **7e-3** (1.65 g, 5.57 mmol) dissolved in DMSO (0.020 L), and the solution was stirred at rt for 20 h. Water (20 mL) was added and the mixture was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with saturated $NaHCO_{3(aq)}$ (2 x 60 mL) and brine (2 x 60 mL), then dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography (10% to 20% EtOAc in hexanes) provided the title compound **7e-2** as a colorless solid (1.45g, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1 H), 8.30 (s, 1 H), 7.76–7.73 (m, 2 H), 7.55–7.50 (m, 2 H), 7.43 (tt, *J* = 7.6, 1.5 Hz, 1 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.1 (t, *J* = 28.8 Hz), 161.8 (t, *J* = 30.6 Hz), 142.9 (t, *J* = 2.5 Hz), 139.0, 131.6 (t, *J* = 4.4 Hz), 129.9, 128.5, 120.2, 118.8 (t, *J* = 2.5 Hz), 109.5 (t, *J* = 261.9 Hz), 64.1, 14.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –110.8 (s, 2 F). IR (film) 3138, 2986, 1772, 1690, 1541, 1504, 1312, 1244, 1174, 1126, 1036, 951, 889, 824, 760, 688 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{14}H_{12}F_2N_2O_3Na$ $[M+Na]^+$ 317.0714, found 317.0695. m.p. 28–29 ºC.


7e-1

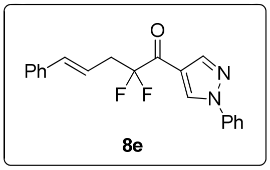
potassium 2,2-difluoro-3-oxo-3-(1-phenyl-1H-pyrazol-4-yl)propanoate (7e-1)

General procedure I was followed using **7e-2** (1.31 g, 4.45 mmol), KOH (0.250 g, 4.45 mmol), and MeOH (0.020 L). Workup afforded the title compound **7e-1** as a colorless solid (1.2 g, 89%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.04 (s, 1 H), 8.20 (s, 1 H), 7.90 (dd, *J* = 7.6, 1.6 Hz, 2 H), 7.55 (t, *J* = 8.0 Hz, 2 H), 7.41 (t, *J* = 7.2 Hz, 1 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 184.5 (t, *J* = 28.8 Hz), 162.3 (t, *J* = 2.5 Hz), 142.3, 138.7, 131.8, 129.7, 127.7, 120.4, 119.4, 111.3 (t, *J* = 261.2 Hz). ^{19}F NMR (DMSO-d_6, 376 MHz) δ –107.8 (s, 2 F). IR (film) 3126, 1693, 1682, 1543, 1506, 1385, 1267, 1167, 1126, 1084, 951, 883, 810, 752, 698, 683, 656 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{12}H_7F_2K_2N_2O_3$ $[M+K]^+$ 342.9699, found 342.9707. m.p. 139–140 ºC.


7e

cinnamyl 2,2-difluoro-3-oxo-3-(1-phenyl-1H-pyrazol-4-yl)propanoate (7e)

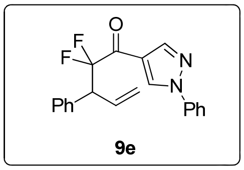
General procedure J was followed using **7e-1** (0.76 g, 2.5 mmol), oxalyl chloride (0.19 mL, 2.3 mmol), cinnamyl alcohol (0.28 g, 2.1 mmol), Et_3N (0.58 mL, 4.2 mmol), DMF (48 μL), and CH_2Cl_2 (12 mL). Workup and chromatographic purification (5% to 10% EtOAc in hexanes) afforded the title compound **7e** as a colorless solid (0.68 g, 85%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.61 (s, 1 H), 8.31 (s, 1 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.50 (t, *J* = 8.0 Hz, 2 H), 7.43–7.37 (m, 3 H), 7.35–7.28 (m, 3 H), 6.72 (d, *J* = 16.0 Hz, 1 H), 6.27 (dt, *J* = 16.0, 6.4 Hz, 1 H), 4.98 (d, *J* = 6.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.9 (t, *J* = 28.8 Hz), 161.7 (t, *J* = 30.6 Hz), 143.0 (t, *J* = 2.5 Hz), 139.0, 136.6, 135.7, 131.7 (t, *J* = 3.8 Hz), 129.9, 128.9, 128.8, 128.6, 127.0, 120.8, 120.2, 118.8, 109.6 (t, *J* = 262.5 Hz), 68.3. ^{19}H NMR ($CDCl_3$, 376 MHz) δ –110.6 (s, 2F). IR (film) 3138, 3059, 1774, 1688, 1541, 1504, 1308, 1242, 1171, 1126, 1036, 968, 951, 883, 758, 690 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{21}H_{16}F_2N_2O_3Na$ $[M+Na]^+$ 405.1027, found 405.1025. m.p. 64–65 ºC.



8e

(*E*)-2,2-difluoro-5-phenyl-1-(1-phenyl-1H-pyrazol-4-yl)pent-4-en-1-one (8e)

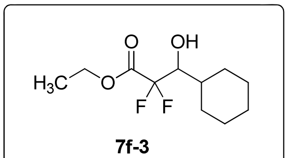
General procedure E was followed using **7e** (76.5 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), *t*-BuBrettPhos (9.7 mg, 0.020 mmol), and 1,4-dioxane (0.40 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **8e** as a colorless solid (43 mg, 64%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.56 (s, 1 H), 8.29 (s, 1 H), 7.72–7.70 (m, 2 H), 7.51 (t, *J* = 8.0 Hz, 2 H), 7.43–7.22 (m, 6 H), 6.61 (d, *J* = 16.0 Hz, 1 H), 6.19 (dt, *J* = 16.0, 7.4 Hz, 1 H), 3.10 (tdd, *J* = 17.0, 7.4, 1.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.3 (t, *J* = 31.9 Hz), 143.2 (t, *J* = 2.5 Hz), 139.2, 136.7, 136.6, 131.6 (t, *J* = 5.0 Hz), 129.9, 128.8, 128.4, 128.1, 126.6, 120.0, 119.6, 118.7 (t, *J* = 5.0 Hz), 118.5 (t, *J* = 251.2 Hz), 37.6 (t, *J* = 23.8 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –102.4 (t, *J* = 16.9 Hz, 2 F). IR (film) 1686, 1541, 1502, 1186, 1038, 951, 908, 876, 833, 756, 688 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{17}F_2N_2O$ $[M+H]^+$ 339.1309, found 339.1320. m.p. 95–97 ºC.



9e

2,2-difluoro-3-phenyl-1-(1-phenyl-1H-pyrazol-4-yl)pent-4-en-1-one (9e)

General procedure F was followed using **7e** (76.5 mg, 0.200 mmol), $Pd(OAc)_2$ (2.2 mg, 0.010 mmol), PhXPhos (9.3 mg, 0.020 mmol), and 1,4-dioxane (2.0 mL). Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **9e** as a colorless solid (49 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.38 (s, 1 H), 8.16 (s, 1 H), 7.67 (dt, *J* = 8.4, 1.9 Hz, 2 H), 7.50 (t, *J* = 8.0 Hz, 2 H), 7.42–7.25 (m, 6 H), 6.25 (ddd, *J* = 17.2, 10.4, 8.4 Hz, 1 H), 5.35 (d, *J* = 10.4 Hz, 1 H), 5.29 (dt, *J* = 16.8, 1.2 Hz, 1 H), 4.28 (td, *J* = 16.4, 8.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 184.8 (t, *J* = 31.2 Hz), 143.0 (t, *J* = 3.1 Hz), 139.1, 135.2 (d, *J* = 5.0 Hz), 132.2 (dd, *J* = 4.4, 3.1 Hz), 131.4 (t, *J* = 5.6 Hz), 129.9, 129.8, 128.8, 128.3, 128.2, 121.0, 120.4, 120.1, 118.6 (t, *J* = 255.6 Hz), 53.8 (t, *J* = 22.5 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.6 (dd, A of ABX, J_{AB} = 263.2 Hz, J_{AX} = 15.0 Hz, 1 F), –106.2 (dd, B of ABX, J_{AB} = 263.2 Hz, J_{BX} = 15.0 Hz, 1 F). IR (film) 3065, 3032, 1684, 1599, 1541, 1504, 1250, 1174, 1036, 951, 887, 758, 725, 700, 688, 658 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{20}H_{17}F_2N_2O$ $[M+H]^+$ 339.1309, found 339.1303. m.p. 81–82 ºC.

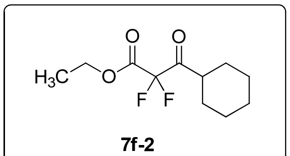


7f-3

ethyl 3-cyclohexyl-2,2-difluoro-3-hydroxypropanoate (7f-3)

General procedure G was followed using activated Zn (3.2 g, 49 mmol), 1,2-dibromoethane (0.25 mL, 2.9 mmol), cyclohexanecarboxaldehyde (3.0 mL, 25 mmol), ethyl bromodifluoroacetate (3.2 mL, 25 mmol), and THF (0.050 L). Workup and chromatographic purification (10% to 15% EtOAc in hexanes) afforded the title compound **7f-3** as a colorless oil (3.7 g, 63%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.36 (q, *J* = 7.2 Hz, 2 H), 3.89–3.79 (m, 1 H), 1.99 (d, *J* = 8.0 Hz, 1 H), 1.94–1.91 (m, 1 H), 1.82–1.65 (m, 5 H), 1.37 (t, *J* = 7.2 Hz, 3 H), 1.32–1.08 (m, 5 H). ^{13}C

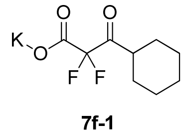
NMR ($CDCl_3$, 125 MHz) δ 164.1 (dd, *J* = 32.5, 31.2 Hz), 115.6 (dd, *J* = 256.2, 253.8 Hz), 75.4 (dd, *J* = 26.2, 23.8 Hz), 63.2, 38.4, 29.8, 27.5, 26.3, 26.2, 26.0, 14.2. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –120.1 (dd, *J* = 263.2, 15.0 Hz, 1 F), –111.6 (dd, *J* = 263.2, 7.5 Hz, 1 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{18}F_2O_3Na$ $[M+Na]^+$ 259.1122, found 259.1128. Spectroscopic data matched that from the previous report.[3]



7f-2

ethyl 3-cyclohexyl-2,2-difluoro-3-oxopropanoate (7f-2)

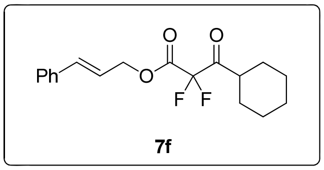
General procedure H was followed using oxalyl chloride (3.8 mL, 44 mmol), DMSO (4.2 mL, 59 mmol), **7f-3** (3.47 g, 14.7 mmol), Et_3N (12 mL, 88 mmol) and CH_2Cl_2 (95 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7f-2** as a colorless oil (3.00 g, 87%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.37 (q, *J* = 7.2 Hz, 2 H), 2.94–2.88 (m, 1 H), 1.94–1.89 (m, 2 H), 1.85–1.80 (m, 2 H), 1.73–1.69 (m, 1 H), 1.36 (t, *J* = 7.2 Hz, 3 H), 1.47–1.19 (m, 5 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.4 (t, *J* = 26.2 Hz), 161.8 (t, *J* = 30.6 Hz), 108.8 (t, *J* = 263.1 Hz), 63.8, 45.5, 28.3, 25.7, 25.5, 14.1. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –113.1 (s, 2 F). HRMS (ESI, *m/z*): calcd. for $C_{11}H_{16}F_2O_3Na$ $[M+Na]^+$ 257.0965, found 257.0959. Spectroscopic data matched that from the previous report.[3]



7f-1

potassium 3-cyclohexyl-2,2-difluoro-3-oxopropanoate (7f-1)

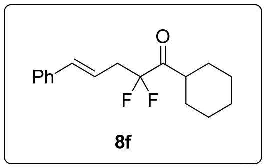
General procedure I was followed using **7f-2** (2.8 g, 12 mmol), KOH (0.67 g, 12 mmol), and MeOH (12 mL). Workup afforded the title compound **7f-1** as a colorless solid (2.5 g, 85%). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.72–2.66 (m, 1 H), 1.78–1.59 (m, 5 H), 1.27–1.11 (m, 5 H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 204.0 (t, *J* = 26.2 Hz), 162.2, 111.2 (t, *J* = 263.8 Hz), 44.8, 28.3, 25.4, 25.0. ^{19}F NMR (DMSO-d_6, 376 MHz) δ –111.1 (s, 2 F). IR (film) 2935, 2864, 1732, 1690, 1674, 1446, 1373, 1329, 1248, 1207, 1174, 1140, 1070, 964, 820, 796, 739, 631, 584 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_9H_{11}F_2K_2O_3$ $[M+K]^+$ 282.9950, found 282.9948. m.p. 188 ºC decomposed.



7f

cinnamyl 3-cyclohexyl-2,2-difluoro-3-oxopropanoate (7f)

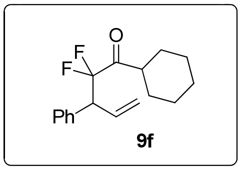
General procedure J was followed using **7f-1** (1.5 g, 6.1 mmol), oxalyl chloride (0.52 mL, 6.1 mmol), cinnamyl alcohol (1.1 g, 8.0 mmol), Et_3N (1.0 mL, 7.4 mmol), DMF (1.0 mL), and CH_2Cl_2 (20 mL). Workup and chromatographic purification (2% to 5% EtOAc in hexanes) afforded the title compound **7f** as a colorless oil (1.6 g, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.40 (m, 2 H), 7.37–7.30 (m, 3 H), 6.73 (d, *J* = 15.6 Hz, 1 H), 6.27 (dt, *J* = 15.6, 6.8 Hz, 1 H), 4.95 (d, *J* = 6.8 Hz, 2 H), 2.95–2.89 (m, 1 H), 1.94–1.89 (m, 2 H), 1.83–1.78 (m, 2 H), 1.71–1.68 (m, 1 H), 1.47–1.17 (m, 5 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 200.3 (t, *J* = 26.9 Hz), 161.7 (t, *J* = 30.6 Hz), 136.6, 135.8, 128.9, 128.8, 127.0, 120.9, 108.8 (t, *J* = 263.8 Hz), 68.1, 45.5, 28.3, 25.6, 25.4. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –112.9 (s, 2 F). IR (film) 2935, 2858, 1776, 1736, 1450, 1310, 1202, 1144, 966, 746, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{18}H_{20}F_2O_3Na$ $[M+Na]^+$ 345.1278, found 345.1284.



8f

(*E*)-1-cyclohexyl-2,2-difluoro-5-phenylpent-4-en-1-one (8f)

General procedure E was followed using **7f** (96.7 mg, 0.300 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), *t*-BuBrettPhos (14.5 mg, 0.0300 mmol), and 1,4-dioxane (0.60 mL). The reaction was run at 70 ºC, and the reaction time was extended to 36 h. Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **8f** as a light yellow oil (51.0 mg, 61%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38–7.23 (m, 5 H), 6.54 (d, *J* = 16.0 Hz, 1 H), 6.08 (dt, *J* = 16.0, 7.4 Hz, 1 H), 2.98–2.86 (m, 3 H), 1.88–1.77 (m, 4 H), 1.71–1.67 (m, 1 H), 1.42–1.19 (m, 5 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 204.3 (t, *J* = 29.4 Hz), 136.8, 136.5, 128.8, 128.0, 126.5, 118.8 (t, *J* = 5.6 Hz), 118.0 (t, *J* =253.1 Hz), 45.1, 37.2 (t, *J* = 23.8 Hz), 28.3, 25.8, 25.6. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –105.6 (t, *J* = 16.9 Hz, 2 F). IR (film) 2934, 2856, 1734, 1497, 1450, 1207, 1146, 1057, 1032, 968, 748, 692 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{20}F_2ONa$ [M+Na]$^+$ 301.1380, found 301.1388.

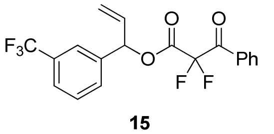


9f

1-cyclohexyl-2,2-difluoro-3-phenylpent-4-en-1-one (9f)

General procedure F was followed using **7f** (96.7 mg, 0.300 mmol), Pd(OAc)$_2$ (3.4 mg, 0.015 mmol), PhXPhos (13.9 mg, 0.0300 mmol), and 1,4-dioxane (3.0 mL). The reaction time was extended to 36 h. Workup and chromatographic purification (0% to 5% EtOAc in hexanes) afforded the title compound **9f** as a light yellow oil (61.0 mg, 73%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.36–7.28 (m, 5 H), 6.17 (ddd, *J* = 17.2, 10.0, 8.4 Hz, 1 H), 5.32 (d, *J* = 10.0 Hz, 1 H), 5.24 (d, *J* = 17.2 Hz, 1 H), 4.16–4.05 (m, 1 H), 2.63–2.56 (m, 1 H), 1.78–1.74 (m, 2 H), 1.68–1.62 (m, 2 H), 1.44–1.39 (m,1 H), 1.28–1.08 (m, 5 H). ^{13}C NMR (CDCl$_3$, 125 MHz) δ 205.0 (t, *J* = 28.8 Hz), 135.2 (d, *J* = 5.0 Hz), 132.4 (dd, *J* = 6.2, 2.5 Hz), 129.8, 128.8, 128.1, 120.8, 118.1 (t, *J* = 258.1 Hz), 53.1 (t, *J* = 21.9 Hz), 45.9, 28.1, 27.7, 25.7, 25.6, 25.5. ^{19}F NMR (CDCl$_3$, 376 MHz) δ –112.0 (dd, A of AMX, J_{AM} = 263.2 Hz, J_{AX} = 16.9 Hz, 1 F), –107.6 (dd, M of AMX, J_{AM} = 263.2 Hz, J_{MX} = 15.0 Hz, 1 F). IR (film) 2934, 2856, 1732, 1494, 1452, 1207, 1167, 1059, 1032, 966, 930, 742, 700 cm^{-1}. HRMS (ESI, *m/z*): calcd. for $C_{17}H_{20}F_2ONa$ [M+Na]$^+$ 301.1380, found 301.1378.

Preparation of Compound 15 in Figure 2B



15

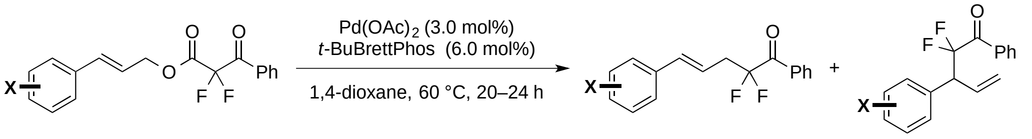
1-(3-(trifluoromethyl)phenyl)allyl 2,2-difluoro-3-oxo-3-phenylpropanoate (15)

An oven-dried one-neck round-bottom flask was charged with potassium salt **1a-1** (1.0 g, 4.2 mmol), and the system was evacuated and backfilled with $N_{2(g)}$ three times. Dry CH_2Cl_2 (21 mL) and DMF (0.10 mL) were added via a syringe, and the reaction mixture was cooled to 0 ºC. Oxalyl chloride (0.31 mL, 3.7 mmol) was added dropwise, and then the reaction mixture was stirred at 0 ºC for 30 min, and rt for 2 h. Next, a solution of 1-(3-(trifluoromethyl)phenyl)prop-2-en-1-ol[23] (0.71 g, 3.5 mmol) dissolved in dry CH_2Cl_2 (2.0 mL) was added dropwise at 0 ºC followed by dropwise addition of Et_3N (0.97 mL, 7.0 mmol). The resulting reaction mixture was stirred at 0 ºC for 30 min, and rt for 2 h. H_2O (10 mL) was added to quench the reaction, and the CH_2Cl_2 was removed under reduced pressure. The aqueous layer was extracted with ether (3 x 20 mL), and the combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by flash chromatography (0% to 15% EtOAc in hexanes) afforded the title compound **15** as a colorless oil (0.81 g, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (dd, J = 8.0, 1.4 Hz, 2 H), 7.69–7.65 (m, 1 H), 7.59 (dt, J = 6.4, 1.8 Hz, 1 H), 7.54–7.47 (m, 5 H), 6.45 (d, J = 6.0 Hz, 1 H), 5.98 (ddd, J = 17.0, 10.8, 6.2 Hz, 1 H), 5.42–5.40 (m, 1 H), 5.37 (d, J = 1.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 185.4 (t, J = 27.5 Hz), 161.0 (t, J = 30.6 Hz), 138.0, 135.4, 133.7, 131.3 (q, J = 32.5 Hz), 131.1, 130.7, 130.1 (t, J = 3.1 Hz), 129.5, 129.2, 125.8 (q, J = 3.7 Hz), 124.1 (q, J = 3.7 Hz), 124.0 (q, J = 270.9 Hz), 119.9, 109.9 (t, J = 263.7 Hz), 79.0. ^{19}F NMR ($CDCl_3$, 376 MHz) δ –107.5 (d, A of AB, J = 289.5 Hz, 1 F), –107.1 (d, B of AB, J = 289.5 Hz, 1 F), –62.7 (s, 3 F). IR (film) 3072, 1778, 1714, 1699, 1599, 1452, 1333, 1256, 1167, 1128, 1074, 926, 804, 704, 687, 580 cm^{-1}. HRMS (EI, *m/z*): calcd. for $C_{19}H_{12}F_5O_3$ [M–H$^+$] 383.0707, found 383.0698.

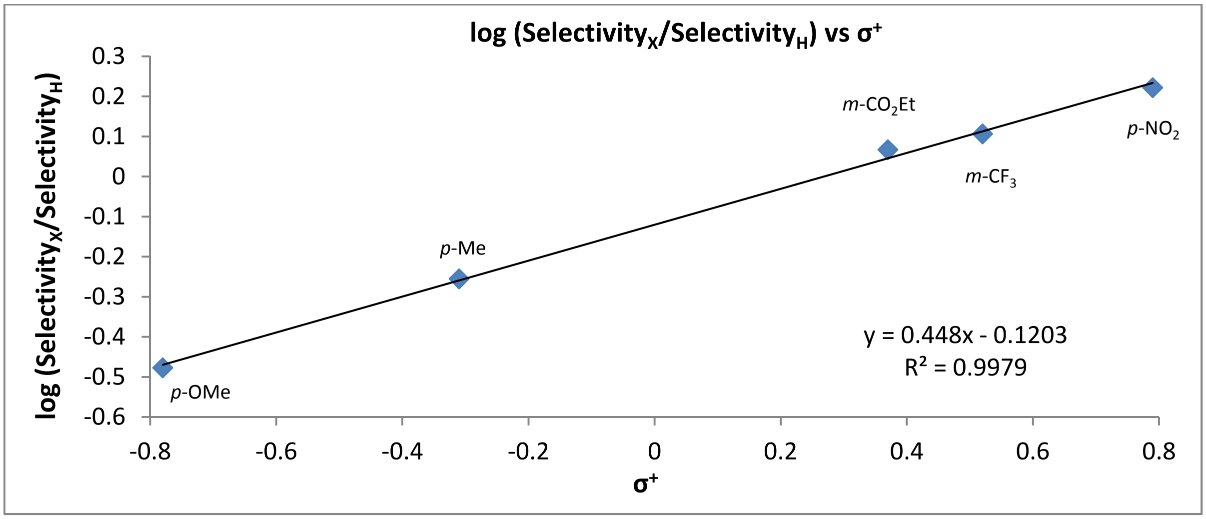
Experimental Procedures for Catalytic Reactions in Figure 2B

An oven-dried 1 dram vial was charged with substrate **15** (57.6 mg, 0.150 mmol), $Pd(OAc)_2$ (1.0 mg, 0.0045 mmol for ***catalyst system A*** or 0.8 mg, 0.0037 mmol for ***catalyst system B***), ligand (*t*-BuBrettPhos 4.4 mg, 0.0090 mmol for ***catalyst system A*** or PhXPhos 3.5 mg, 0.0075 mmol for ***catalyst system B***), and a magnetic stir bar. The vial was equipped with a three-way valve, evacuated and backfilled with $N_{2(g)}$ four times. Dry 1,4-dioxane (0.3 mL for ***catalyst system A*** or 1.5 mL for ***catalyst system B***) was added via a syringe under $N_{2(g)}$. The vial was sealed with a screwed-cap under $N_{2(g)}$ flow, and was stirred at rt for 5 min. Subsequently, the vial was placed on a pre-heated reaction block, and stirred at 60 °C for ***catalyst system A*** or 90 °C for ***catalyst system B*** for 24 h. The vial was cooled to rt, and the mixture was diluted with EtOAc (2.0 mL for ***catalyst system A*** or 0.1 mL for ***catalyst system B***). 2,2,2-trifluoroethanol (10 µL, 0.1372 mmol) was added as a standard, and the reaction mixture was stirred at rt for 30 min to ensure thorough mixing. An aliquot was taken from the vial for ^{19}F NMR analysis. ^{19}F NMR yields and selectivities reported in the manuscript represent an average of two independent runs for catalyst system A or B, respectively.

Analysis of Selectivity Data in Figure 3



1a, 4a-4c, 4e, 4g **2a, 5a-5c, 5e, 5g** **3a, 6a-6c, 6e, 6g**



Substrate	Substituent (X)	Selectivity (lin/br)	Log (Selectivity$_X$/ Selectivity$_H$)	σ^+
1a	H	18	–	–
4a	*m*-CF_3	23	0.1065	0.52
4b	*p*-NO_2	30	0.2218	0.79
4c	*m*-CO_2Et	21	0.0669	0.37
4e	*p*-Me	10	0.2553	–0.31
4g	*p*-OMe	6	0.4771	–0.78

Values for σ^+ were obtained from the literature.[24]

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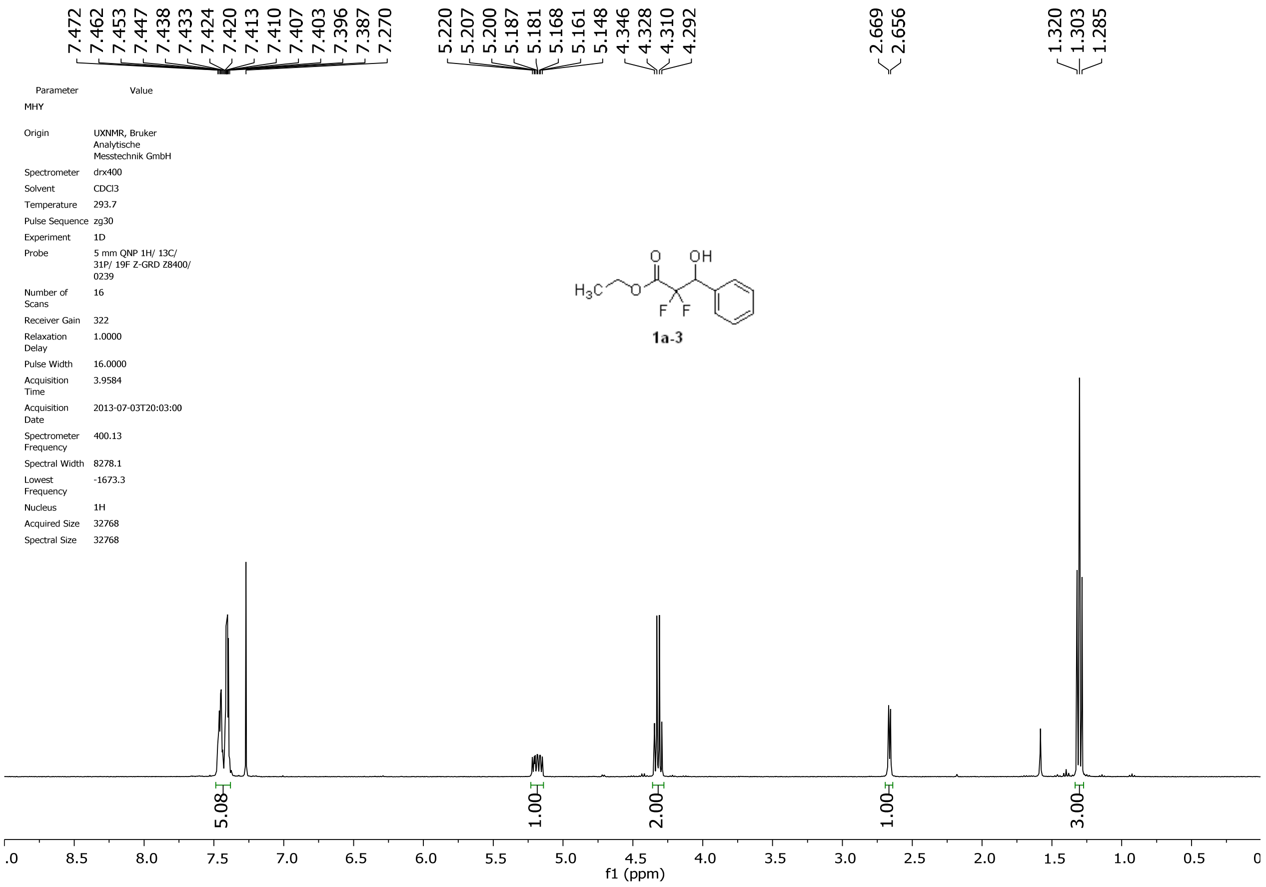

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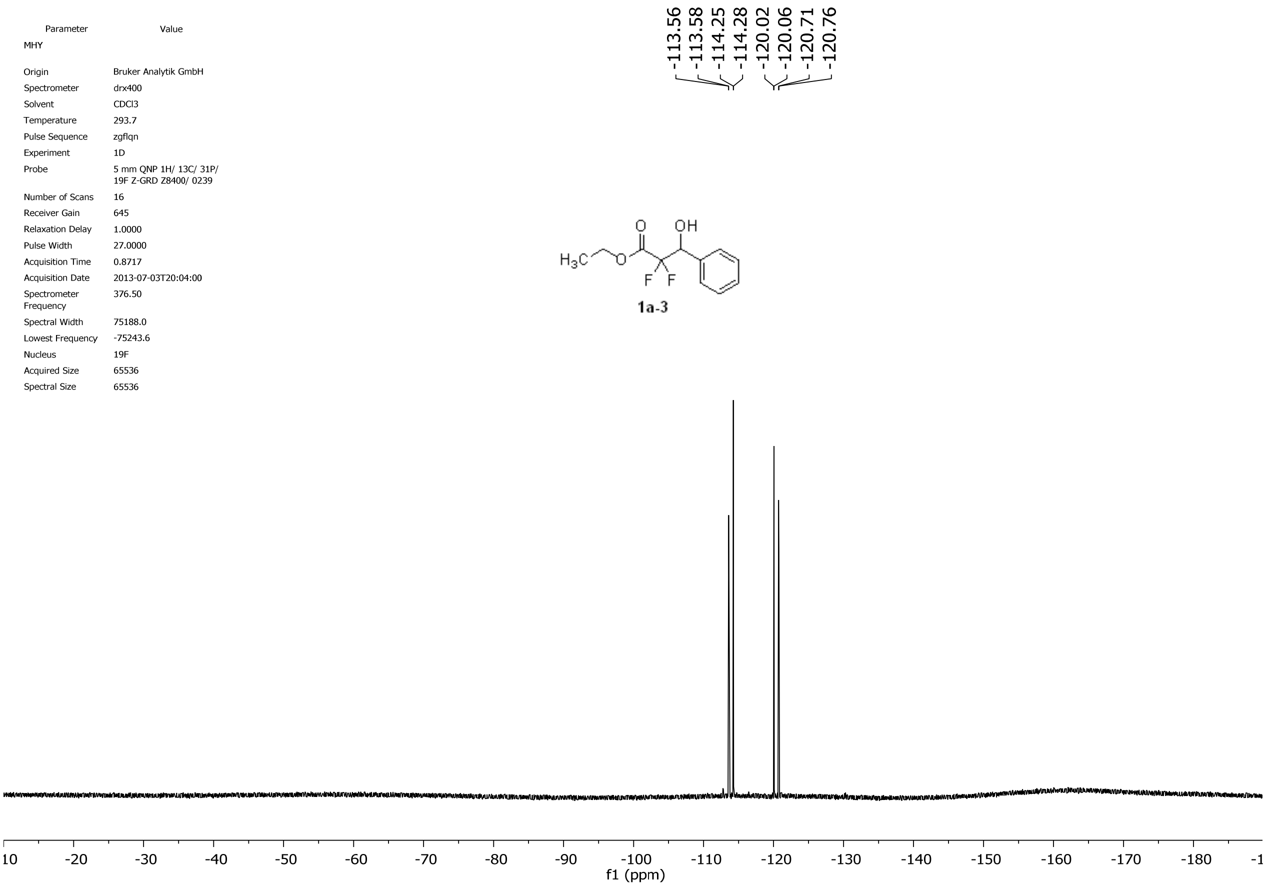

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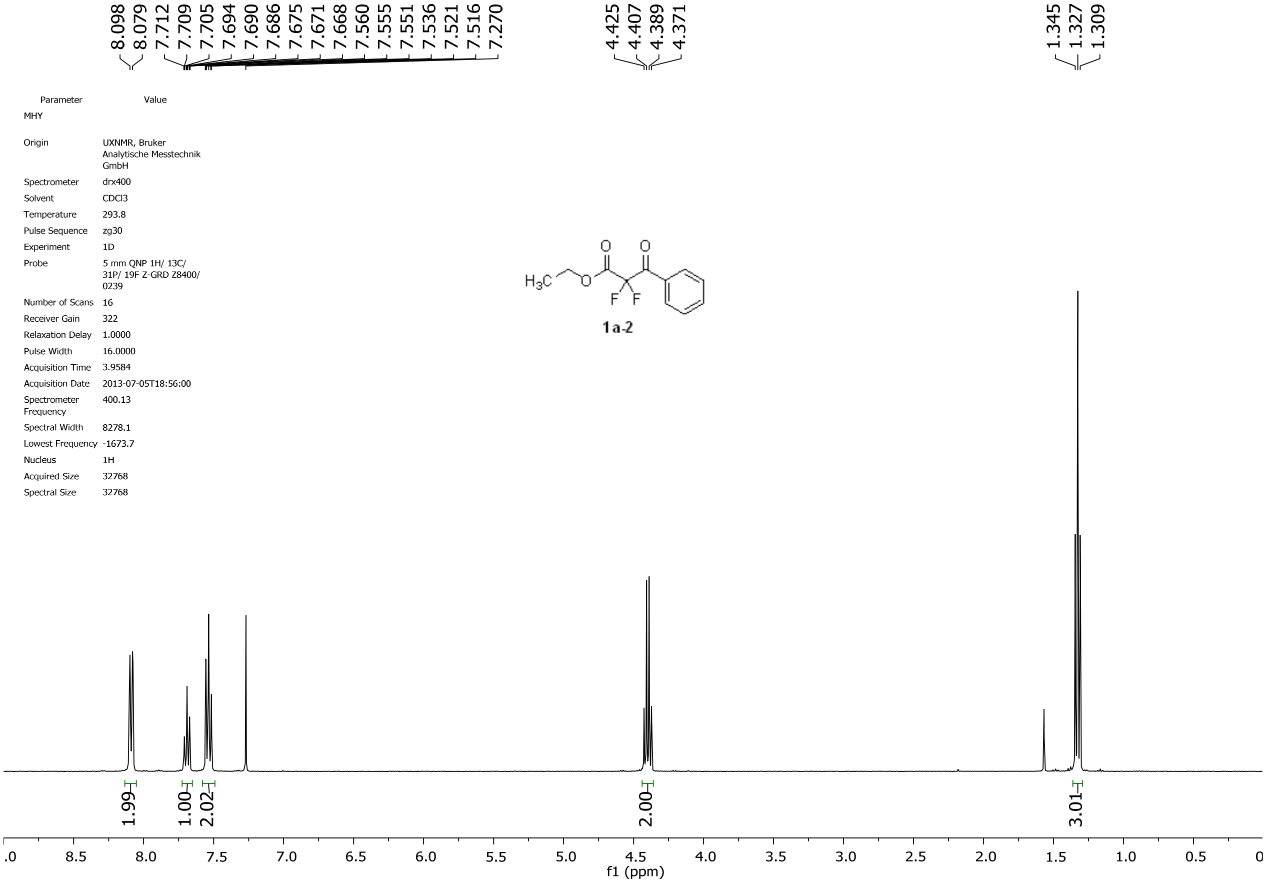

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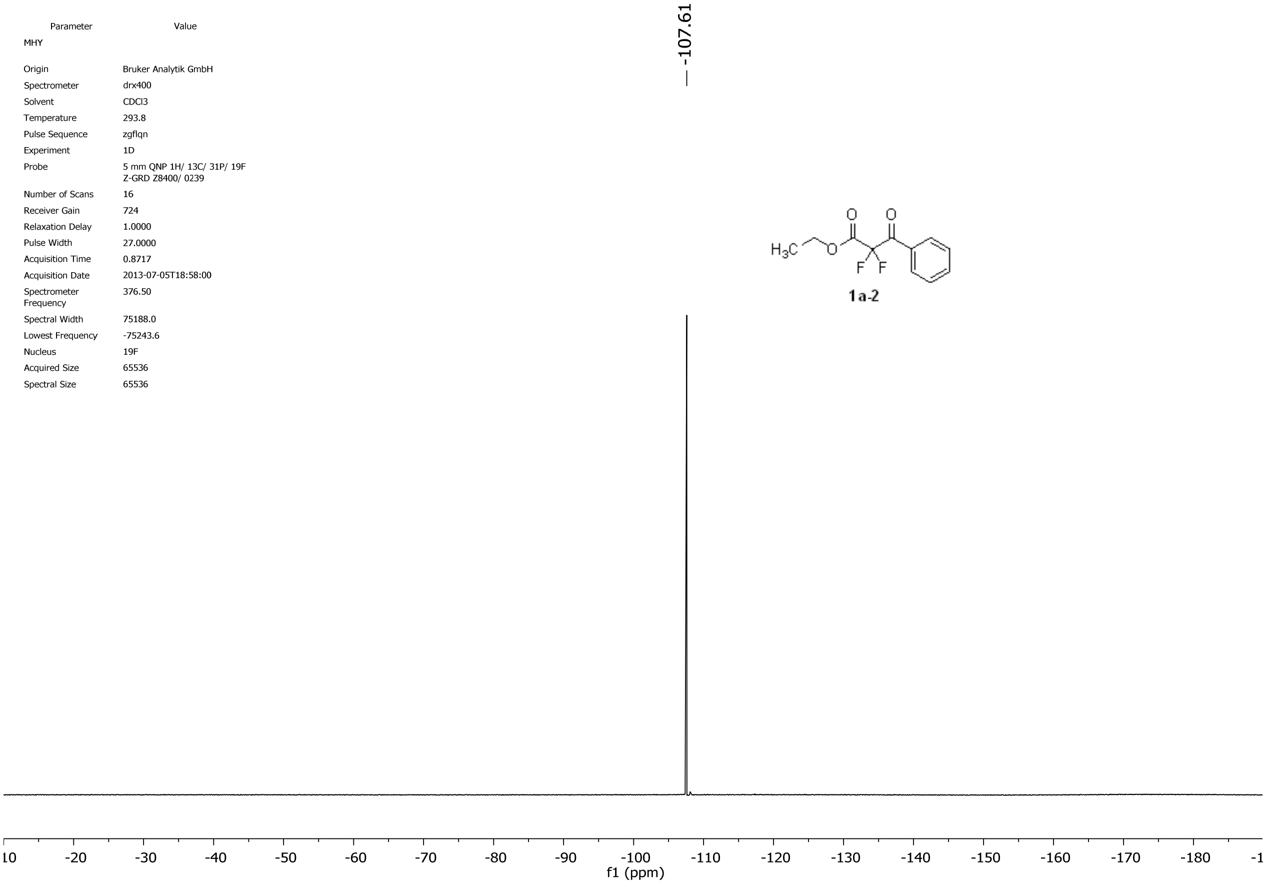

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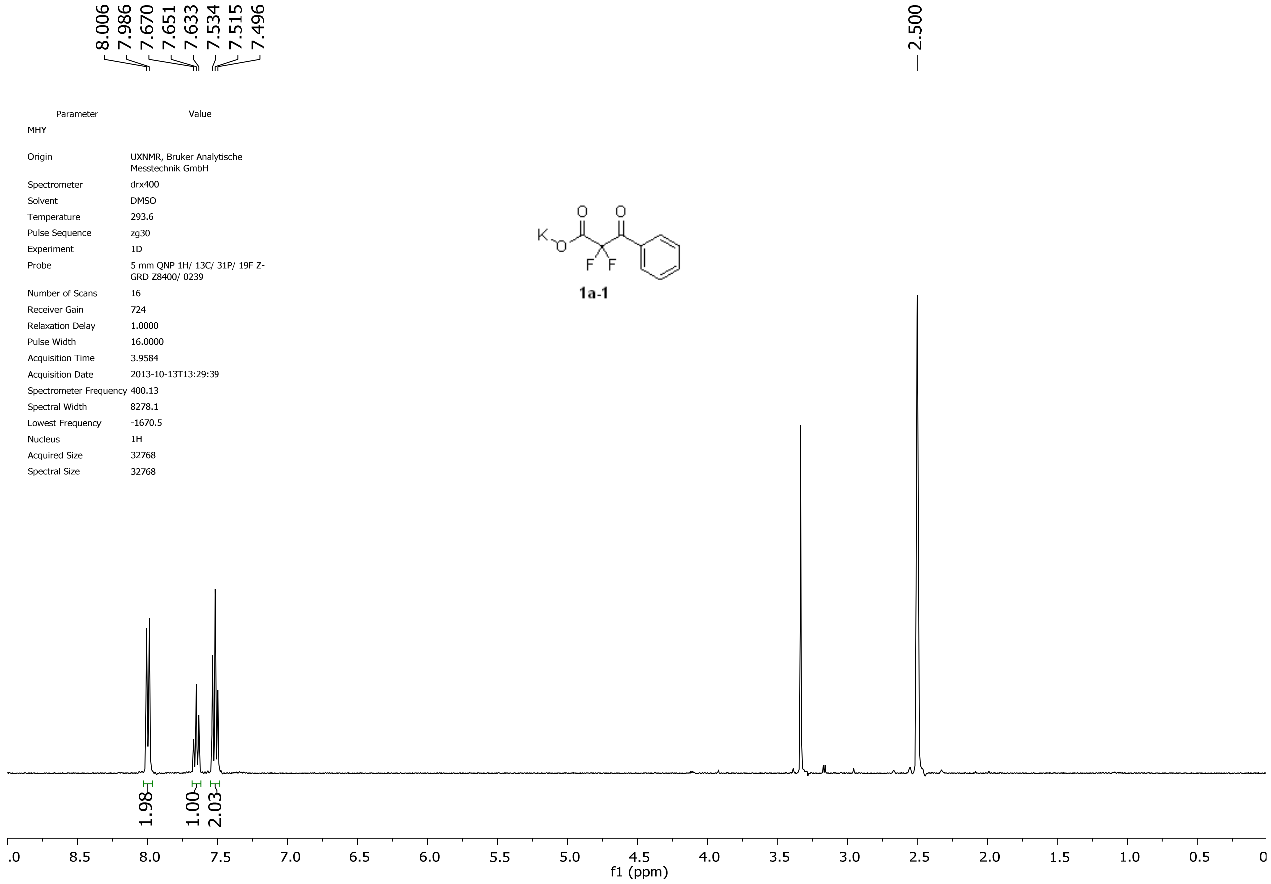

1a-1

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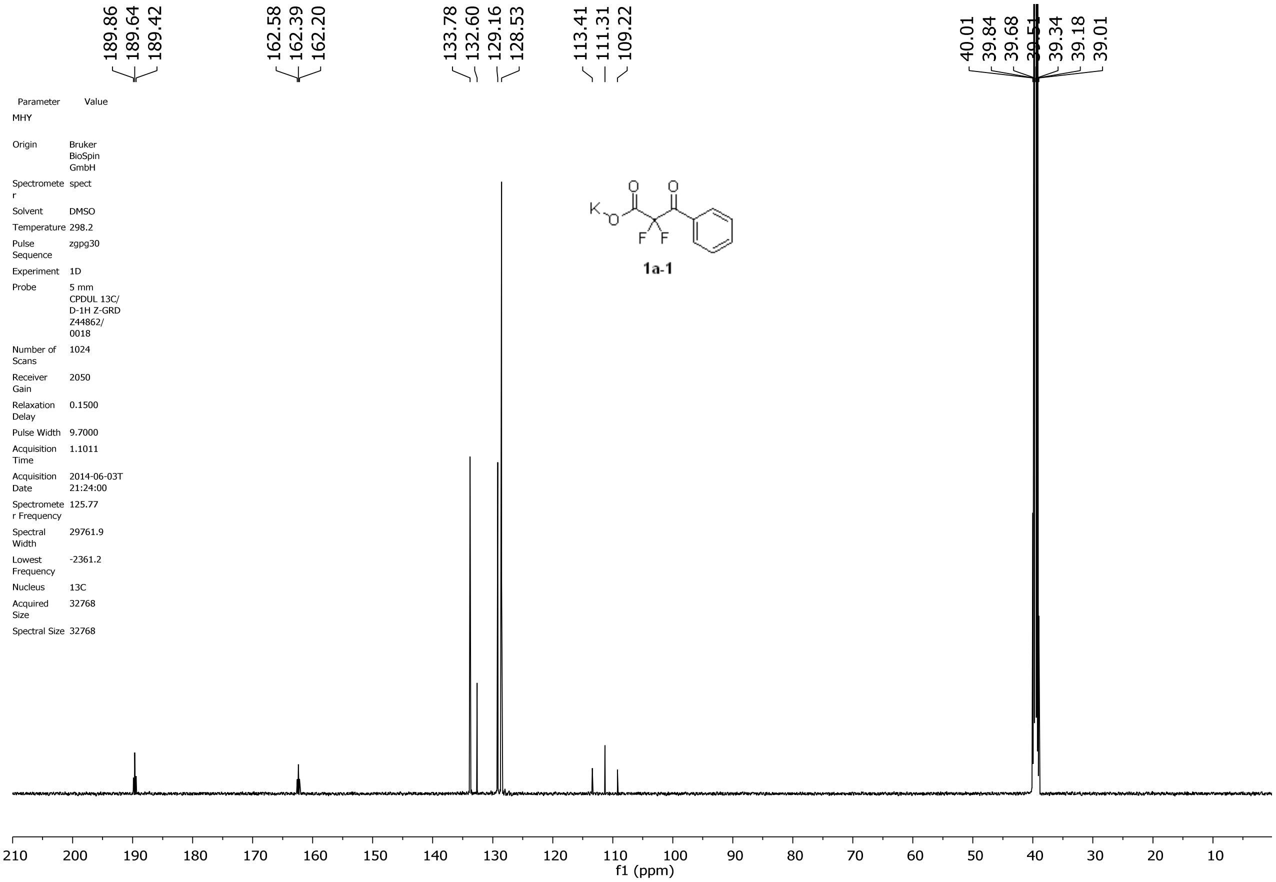

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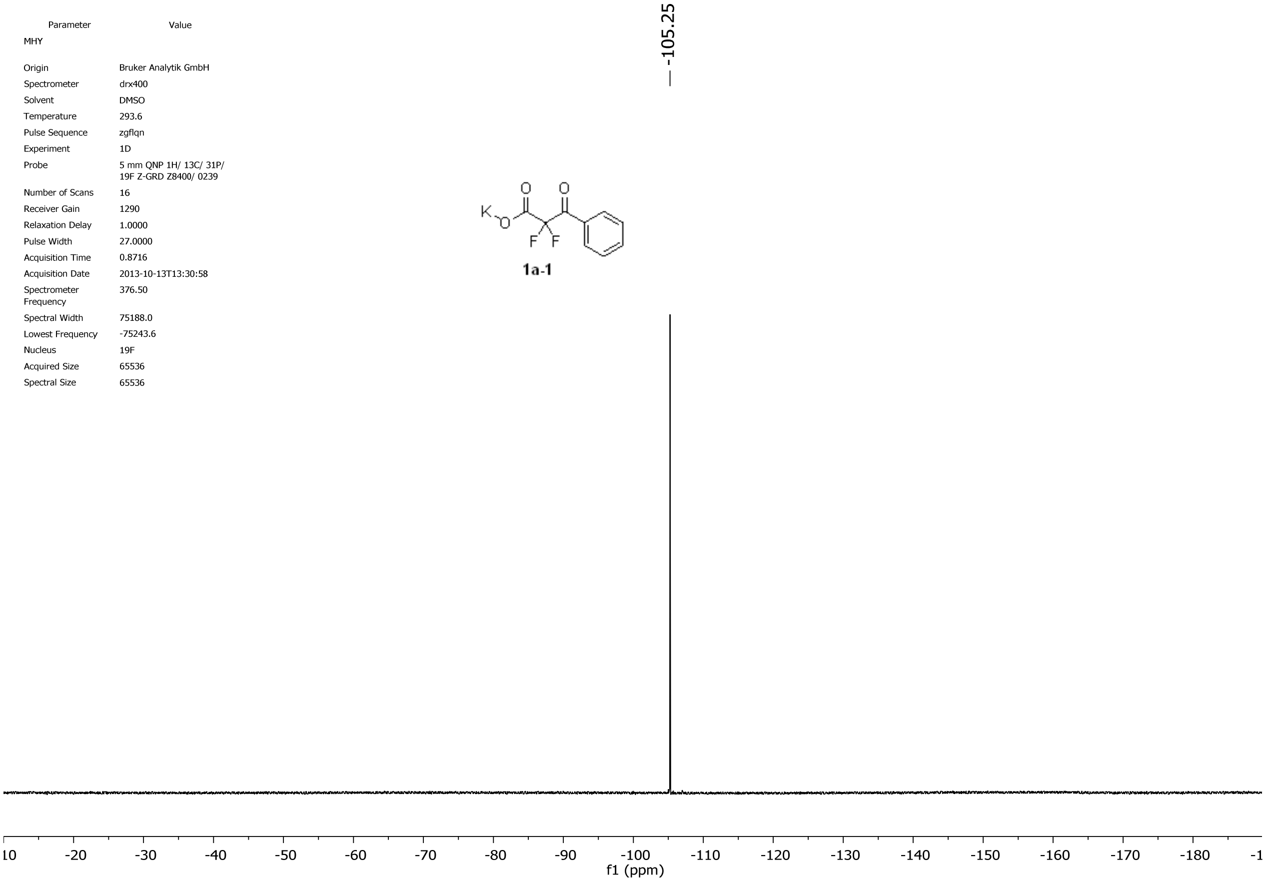

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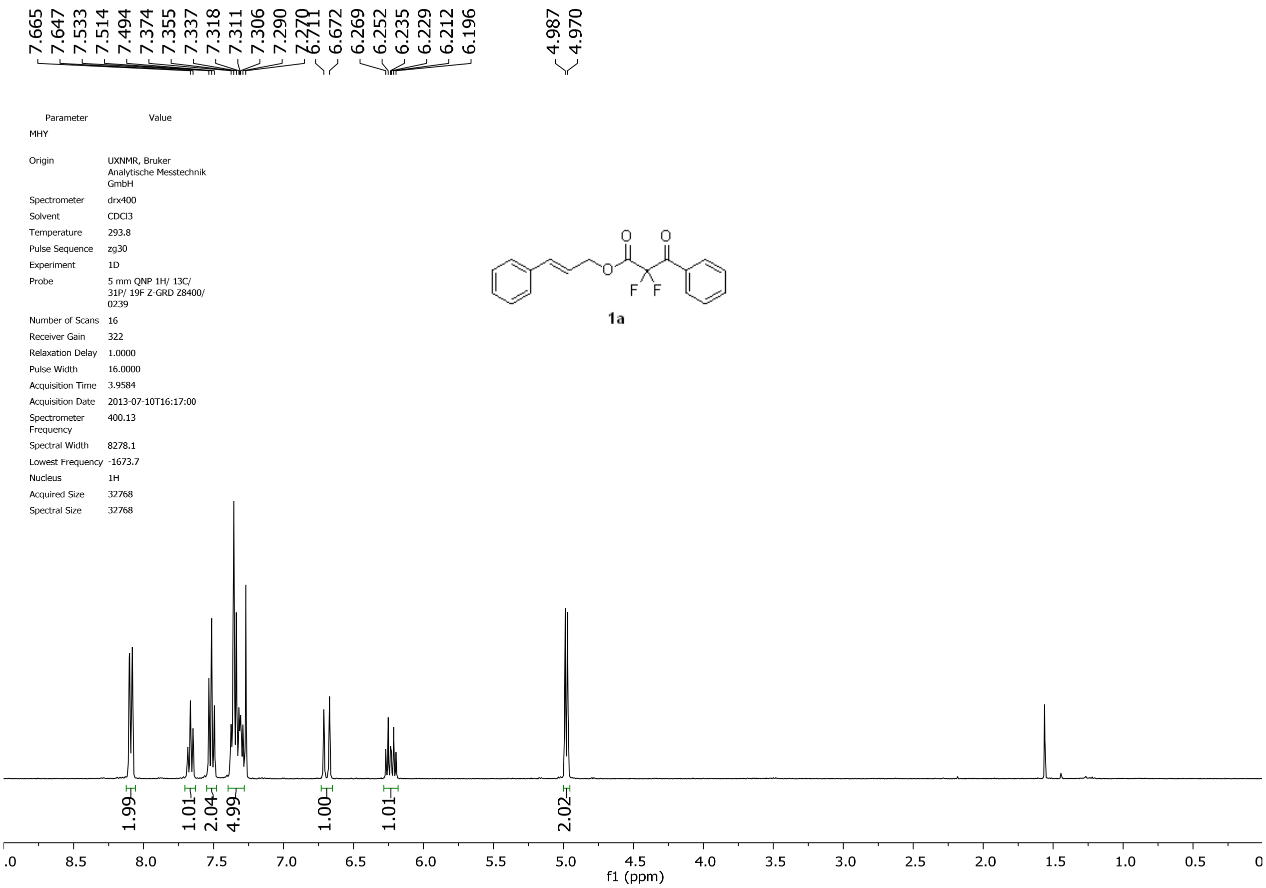

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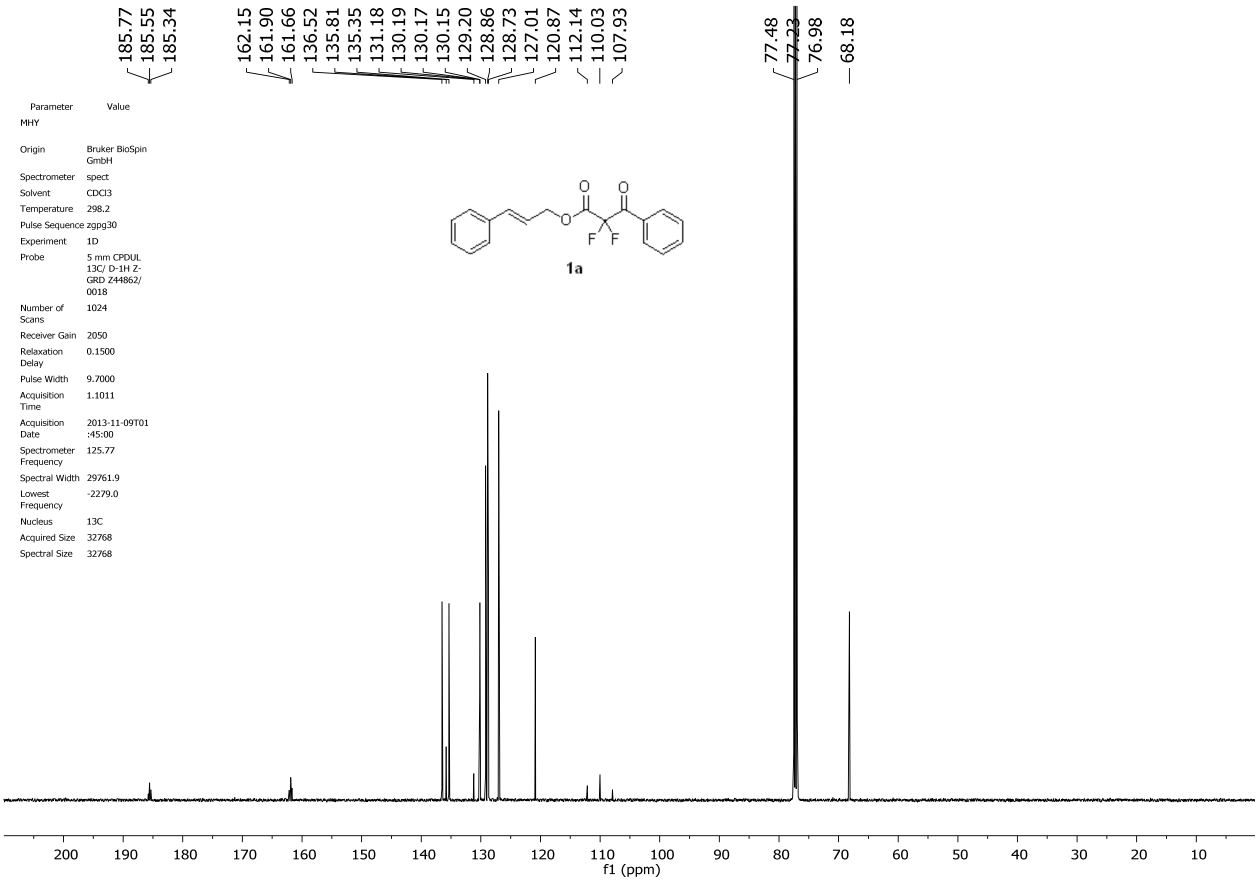

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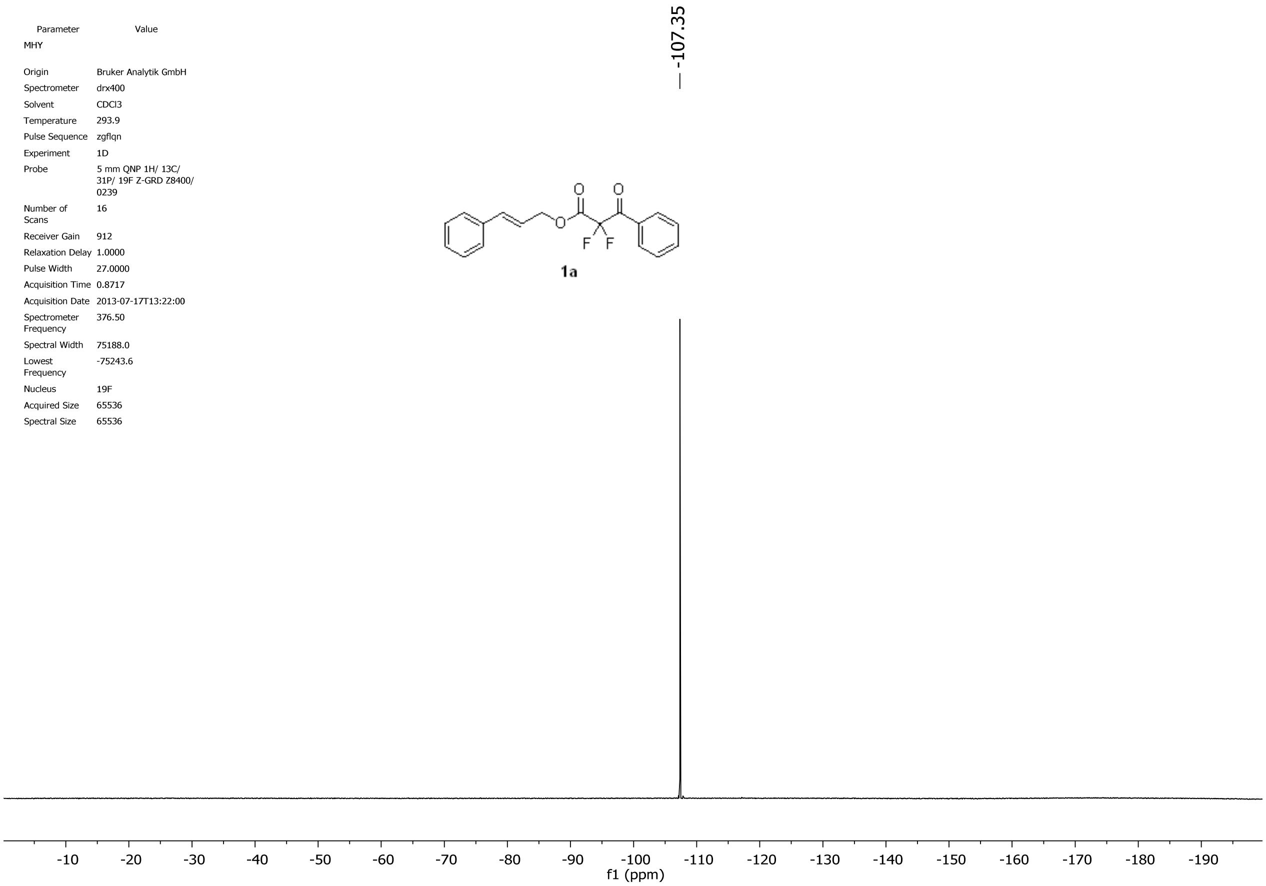

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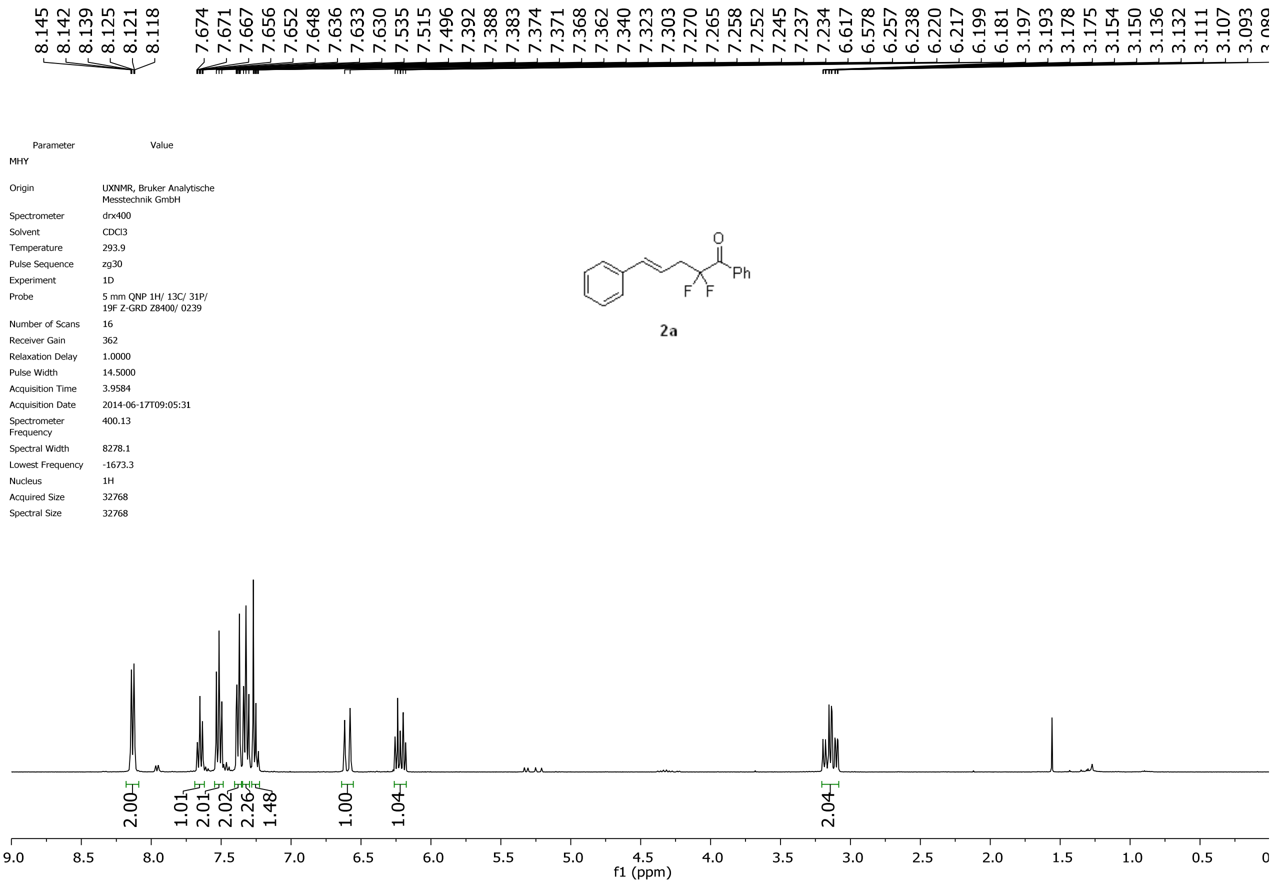

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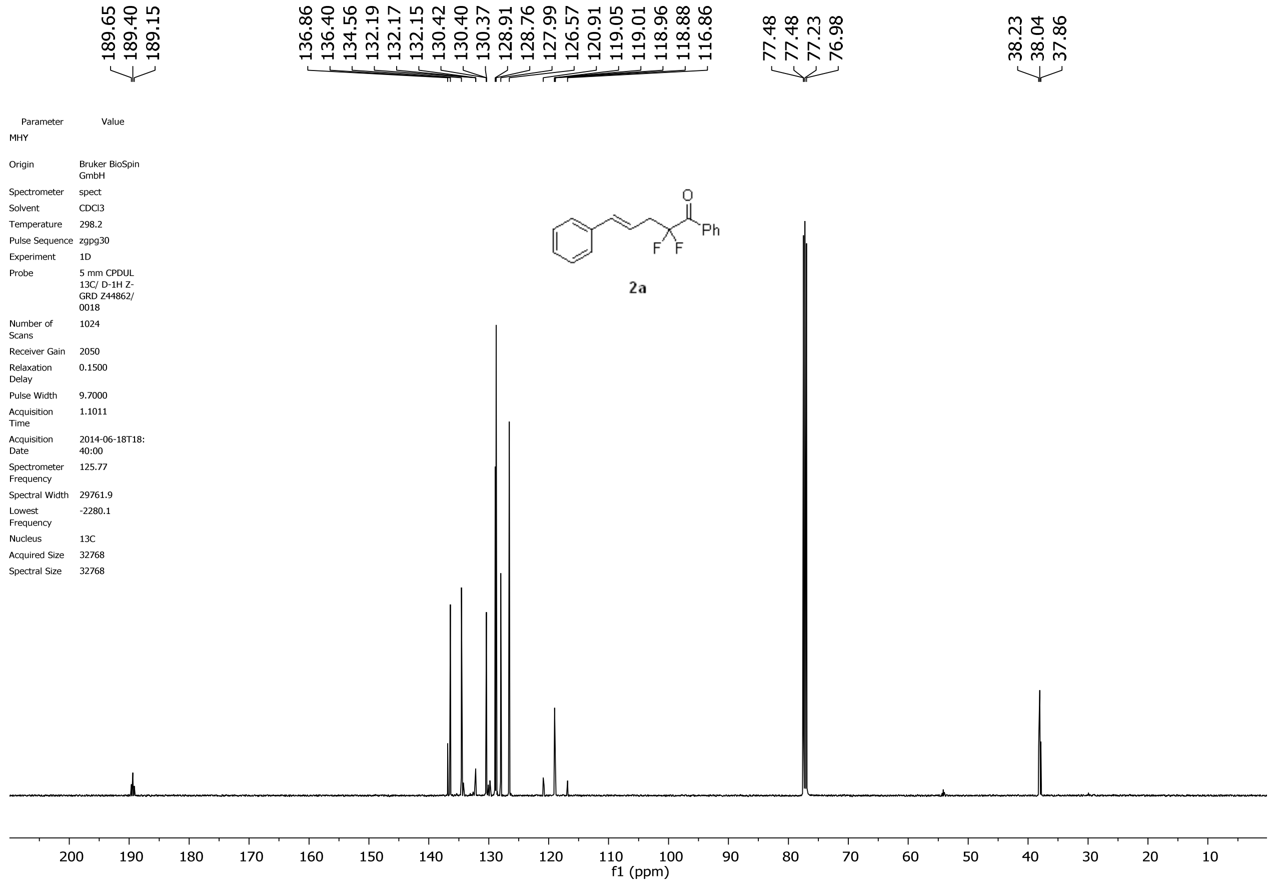

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Parameter	Value
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Parameter	Value
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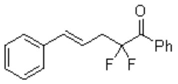
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



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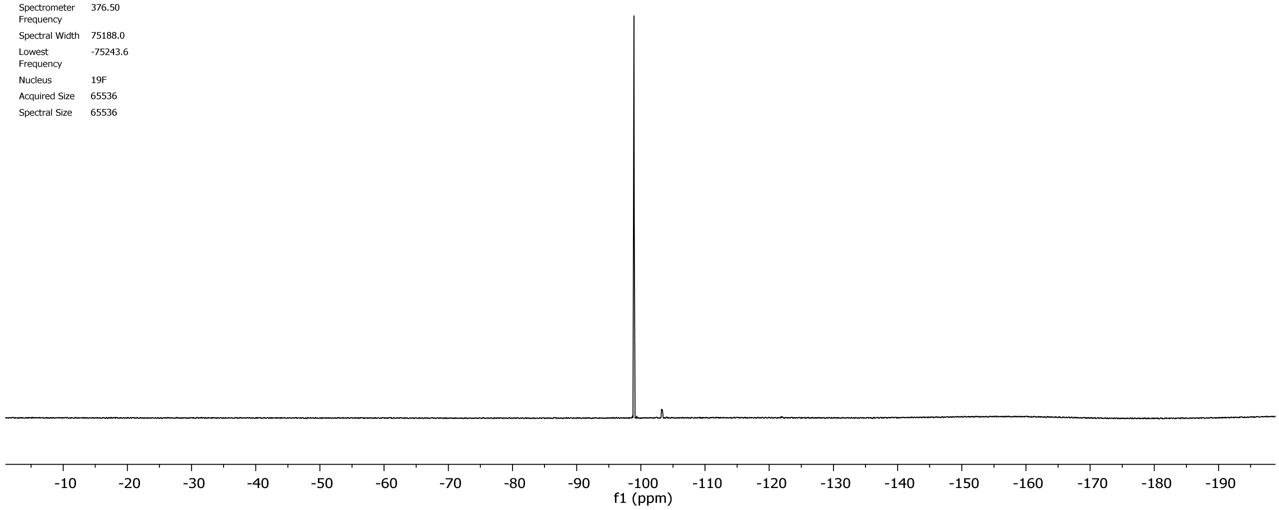
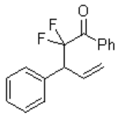


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-17T08:49:29
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



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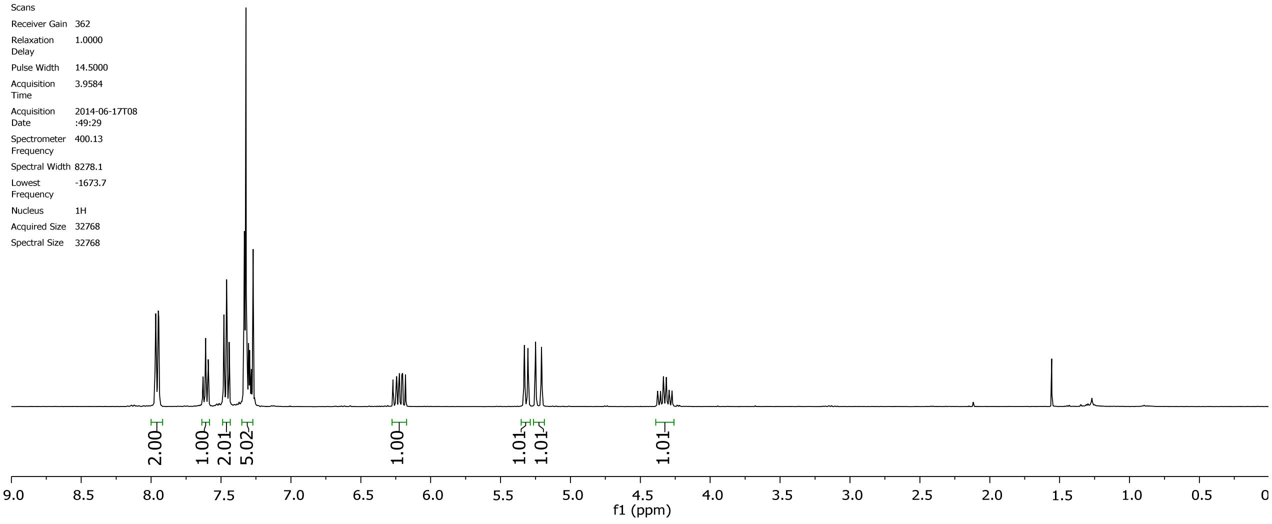
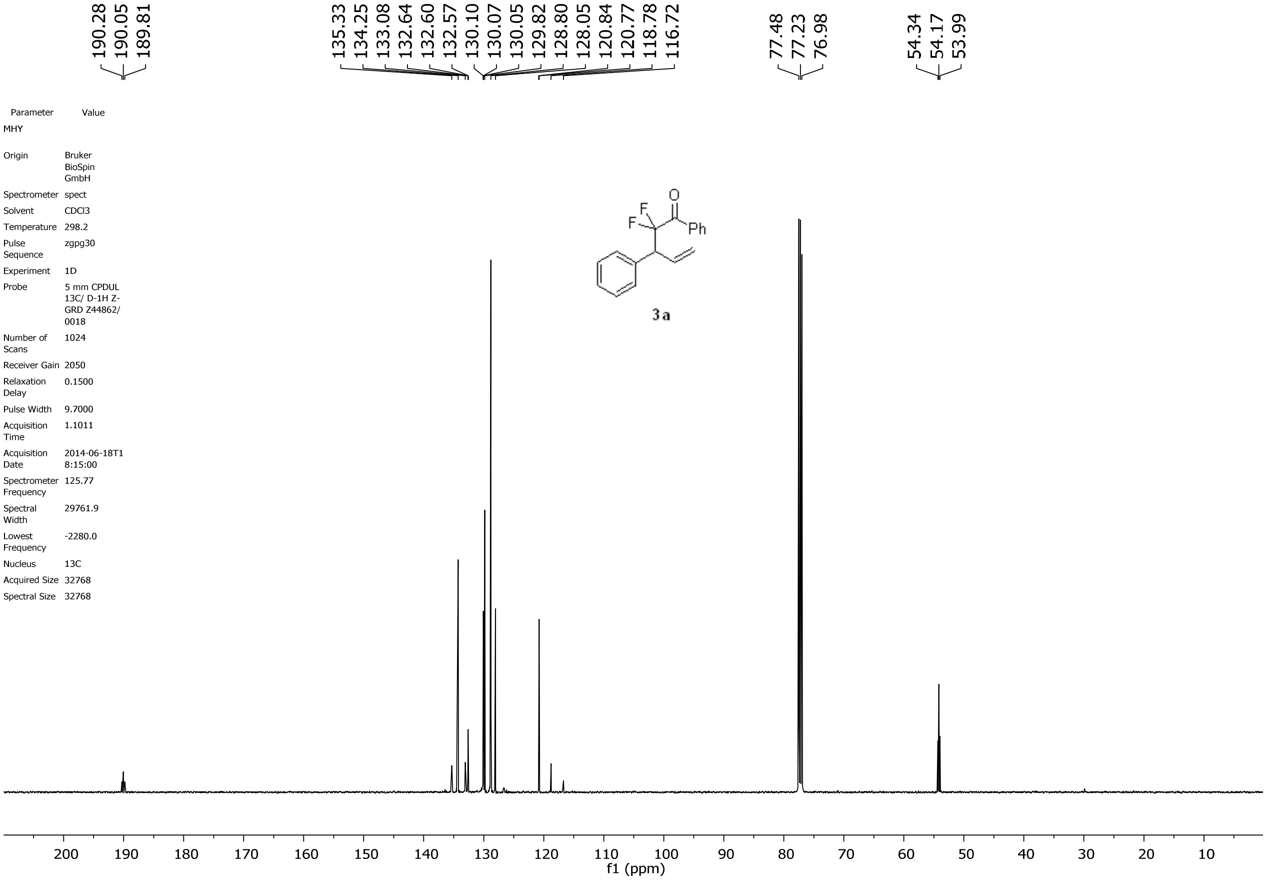
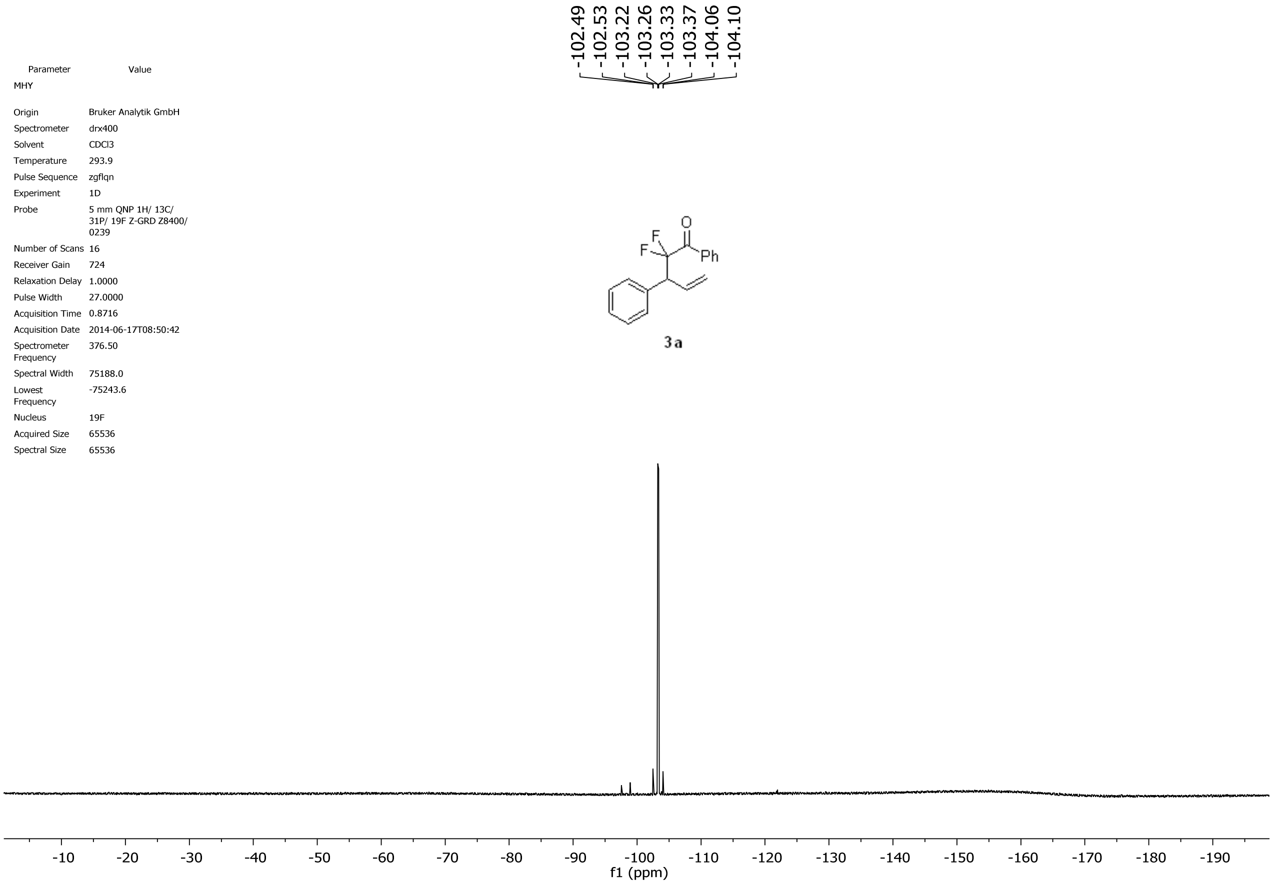




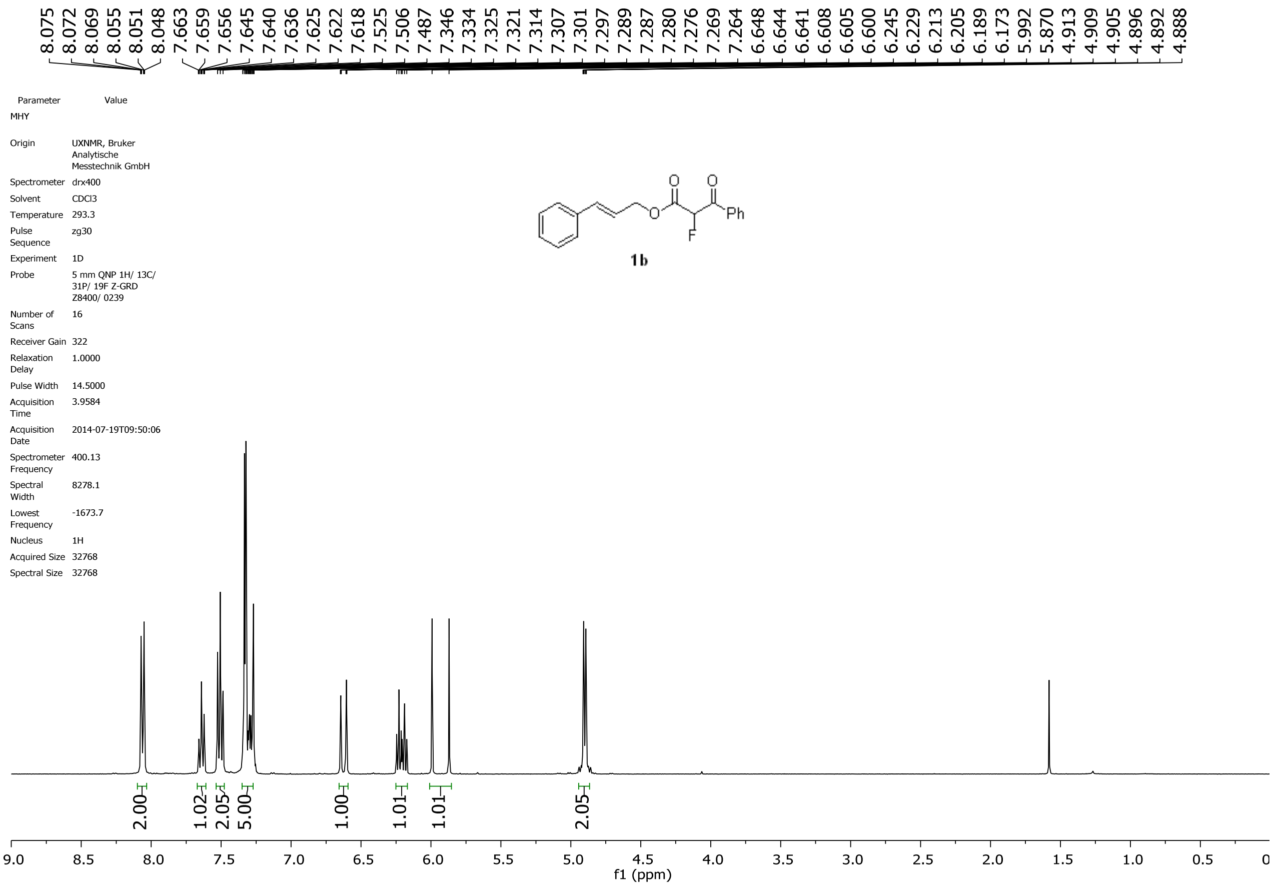
3a

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-18T18:15:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

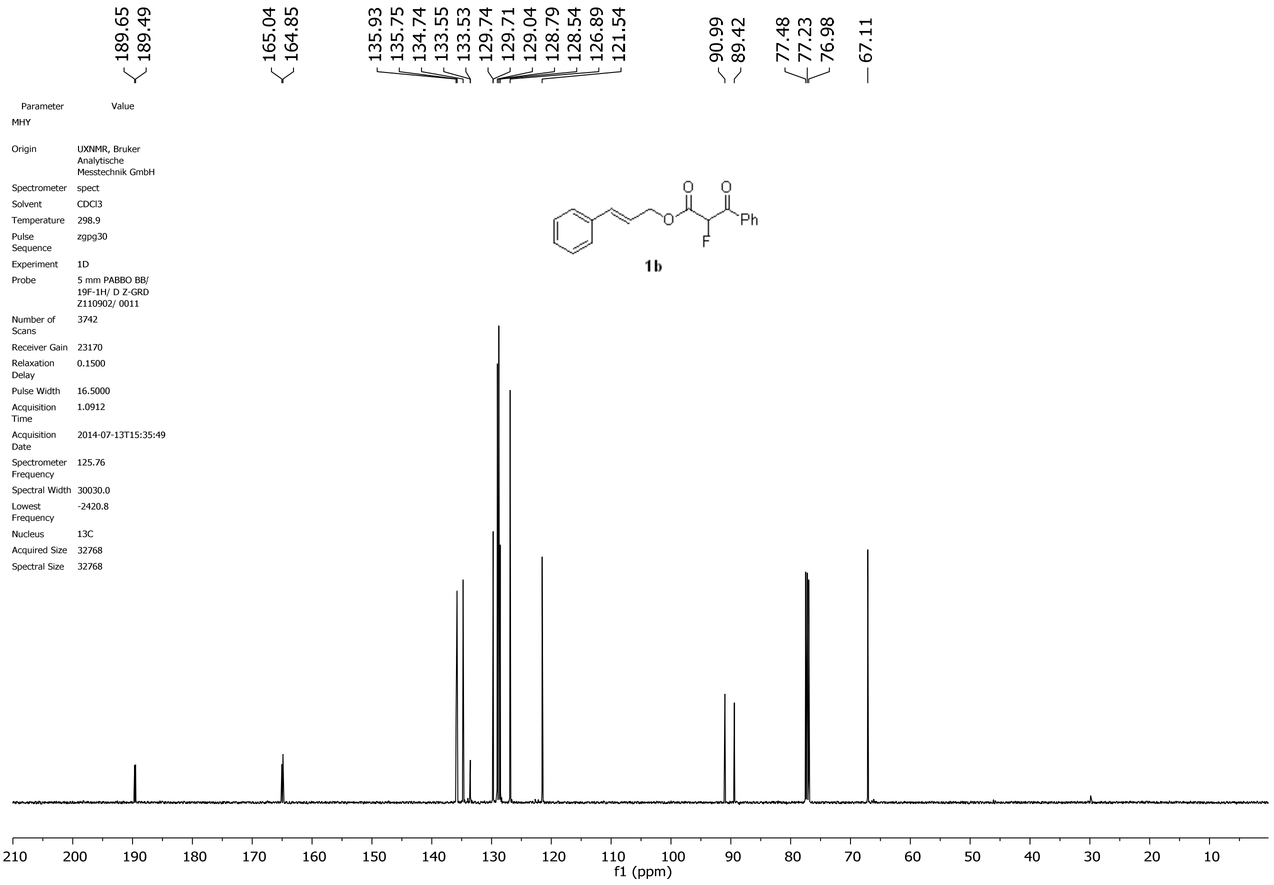


3a

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-17T08:50:42
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

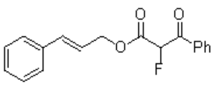


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-19T09:50:06
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

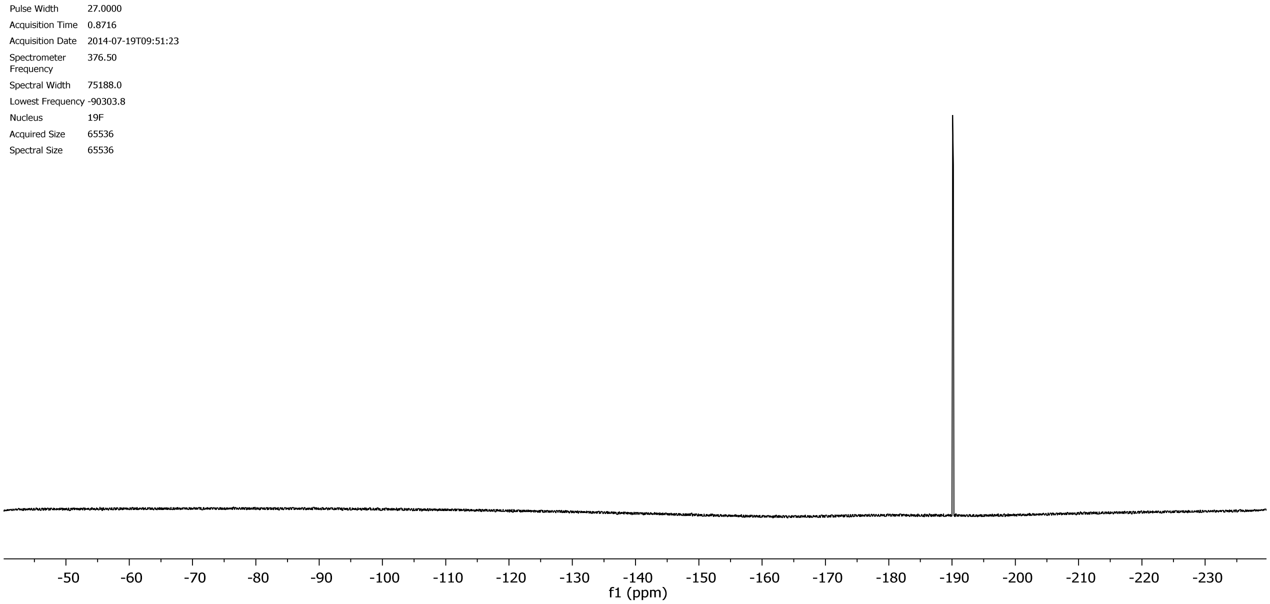


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z110902/ 0011
Number of Scans	3742
Receiver Gain	23170
Relaxation Delay	0.1500
Pulse Width	16.5000
Acquisition Time	1.0912
Acquisition Date	2014-07-13T15:35:49
Spectrometer Frequency	125.76
Spectral Width	30030.0
Lowest Frequency	-2420.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

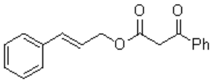
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-19T09:51:23
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-90303.8
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



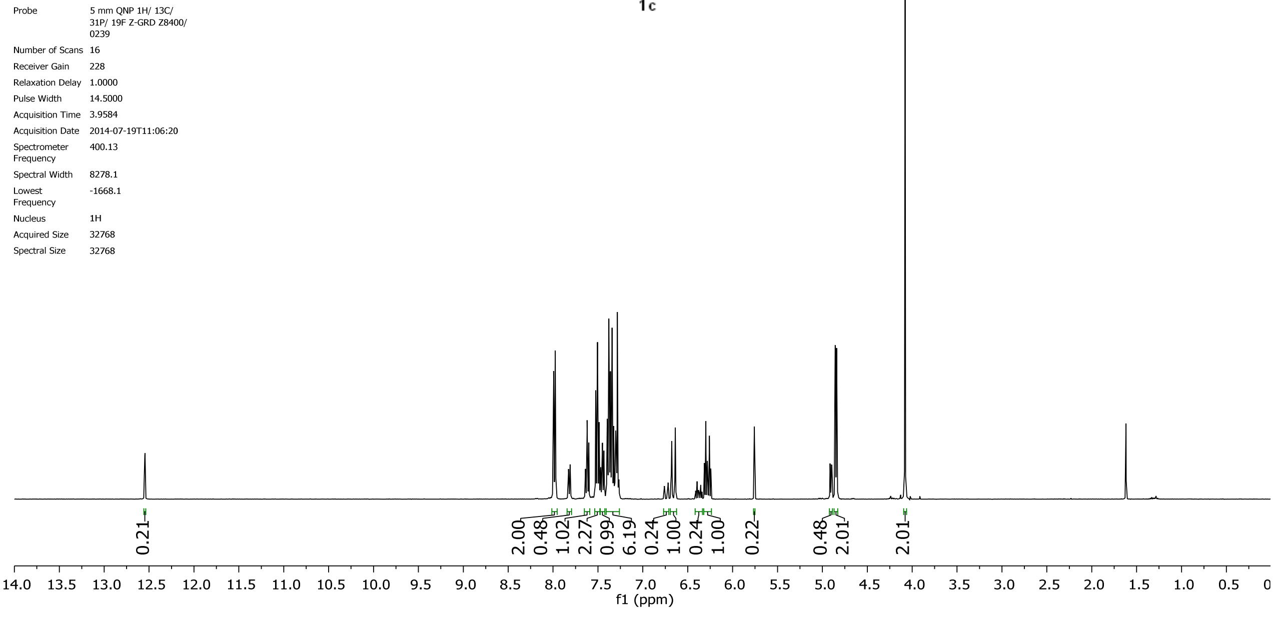
1b



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-19T11:06:20
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1668.1
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

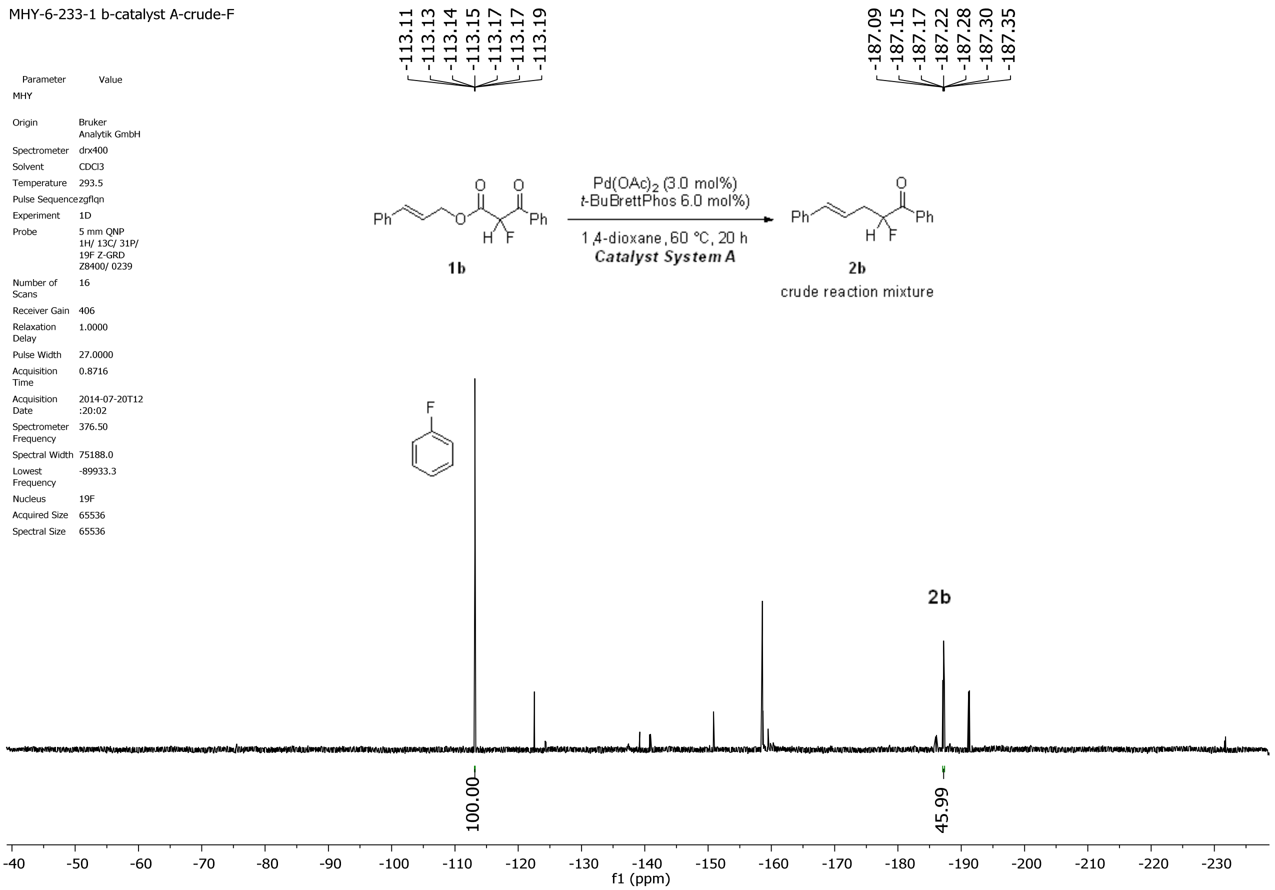


1c

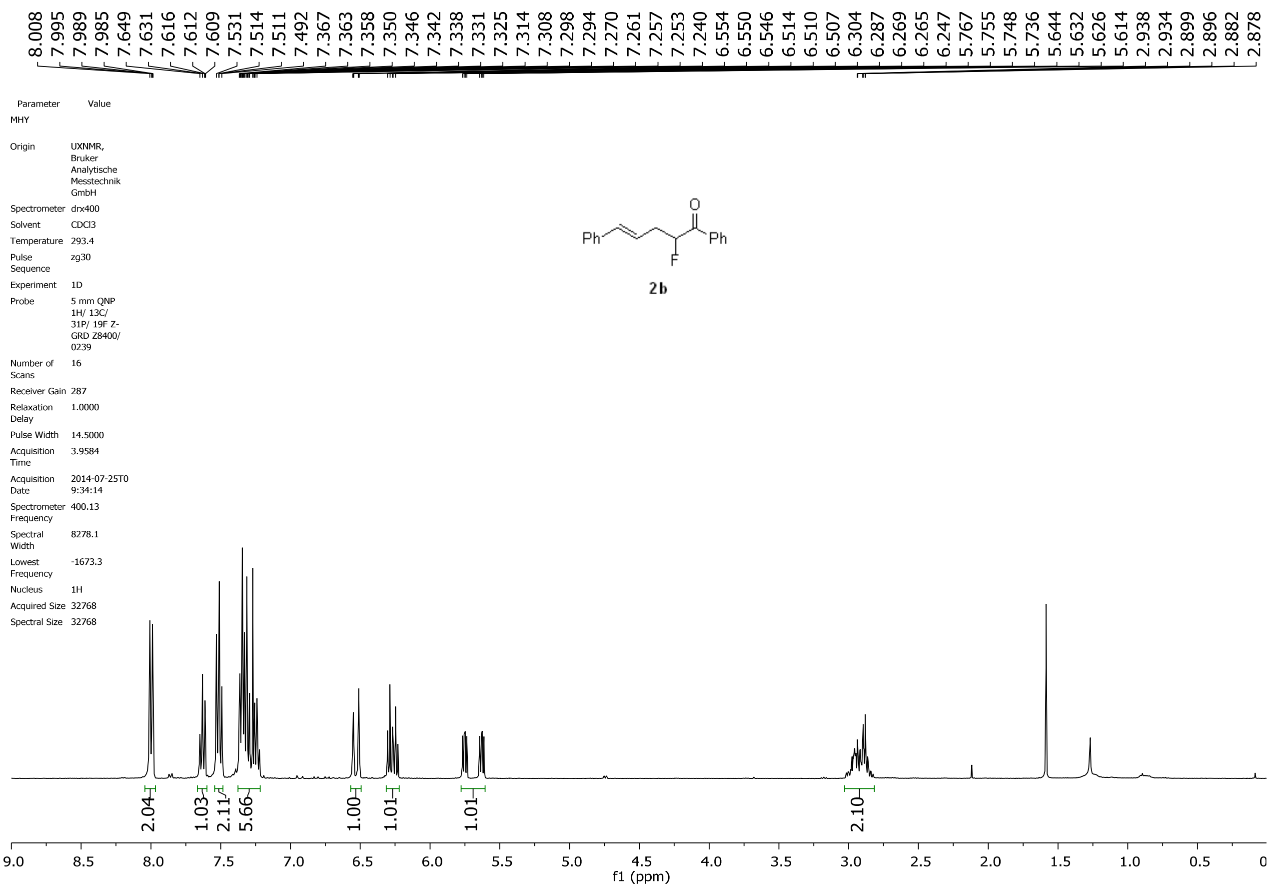


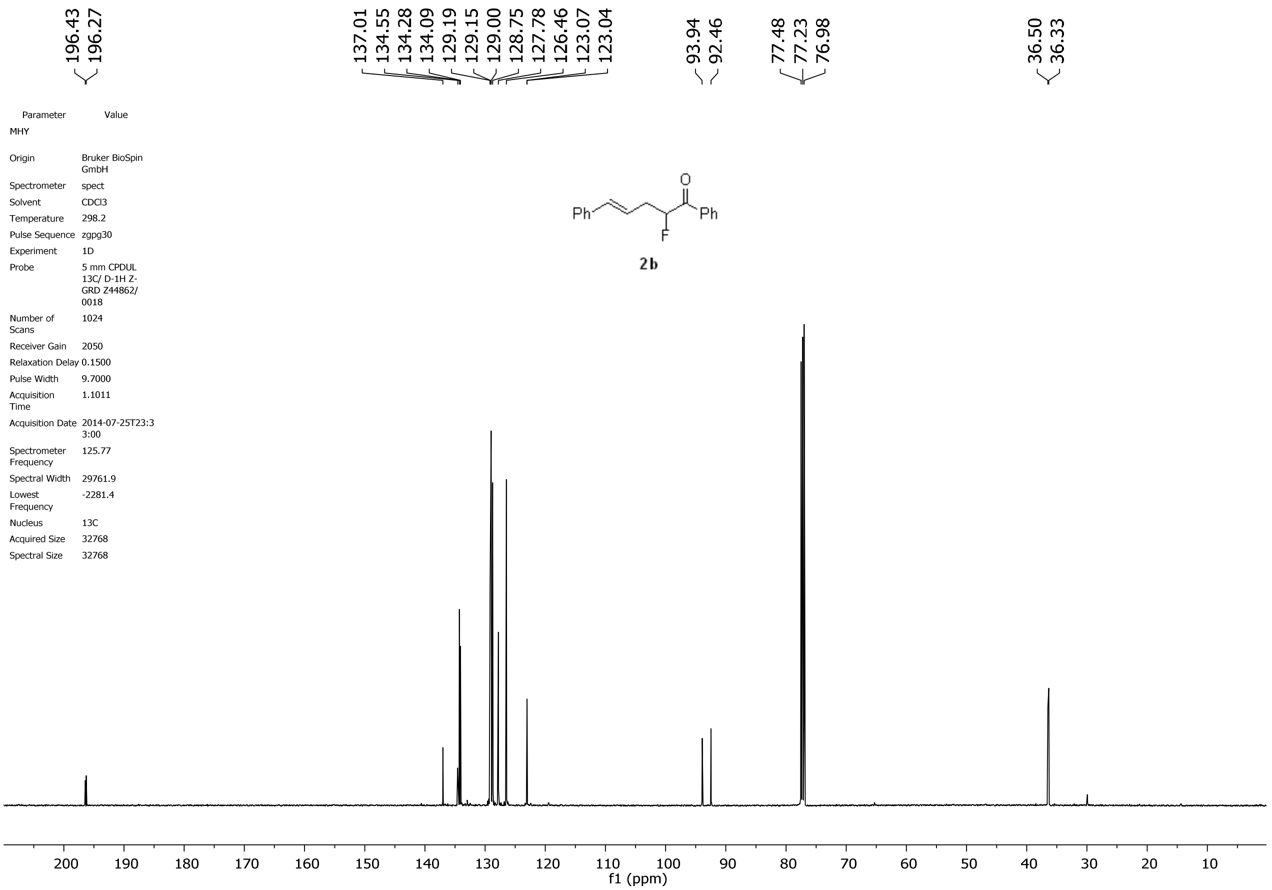
MHY-6-233-1 b-catalyst A-crude-F

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-20T12:20:02
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-89933.3
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



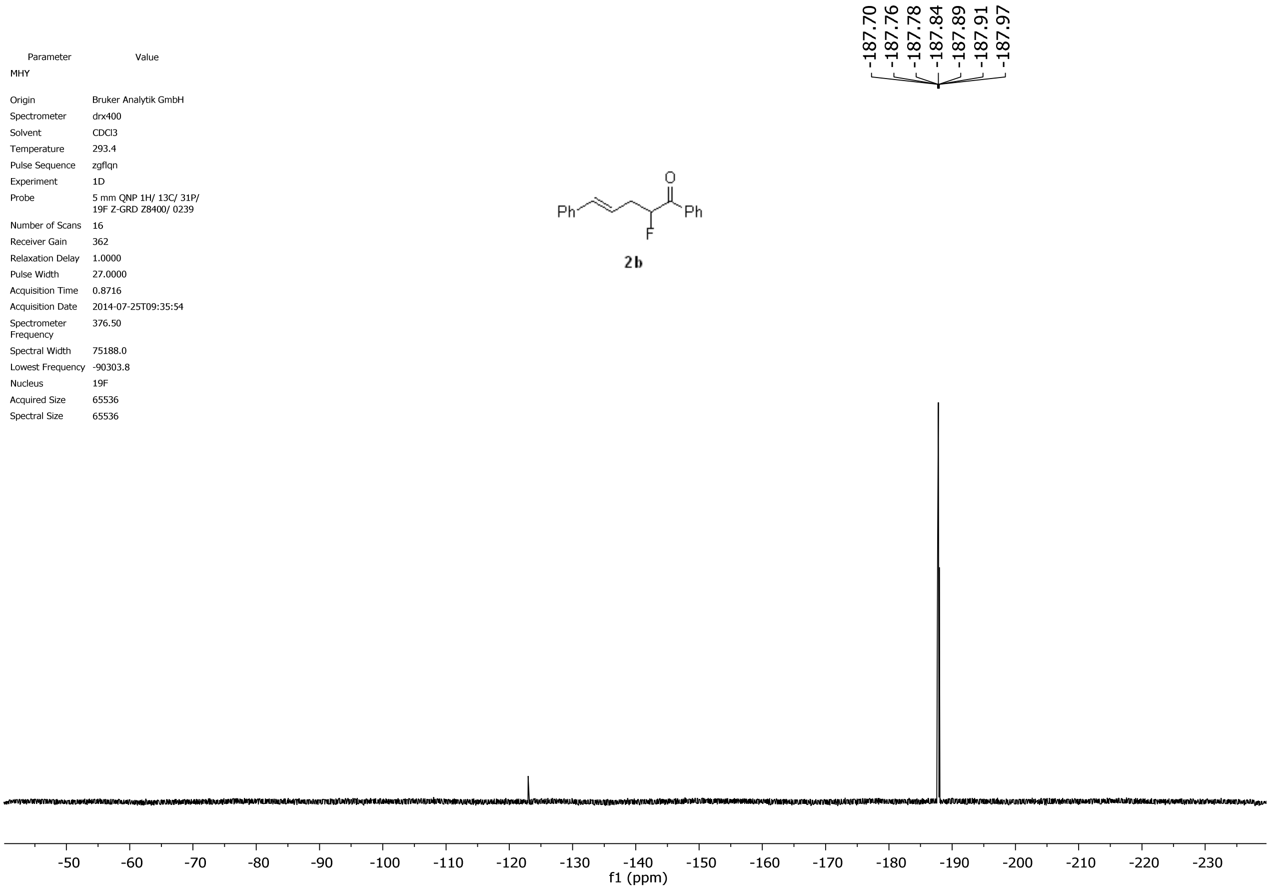
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-25T09:34:14
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768





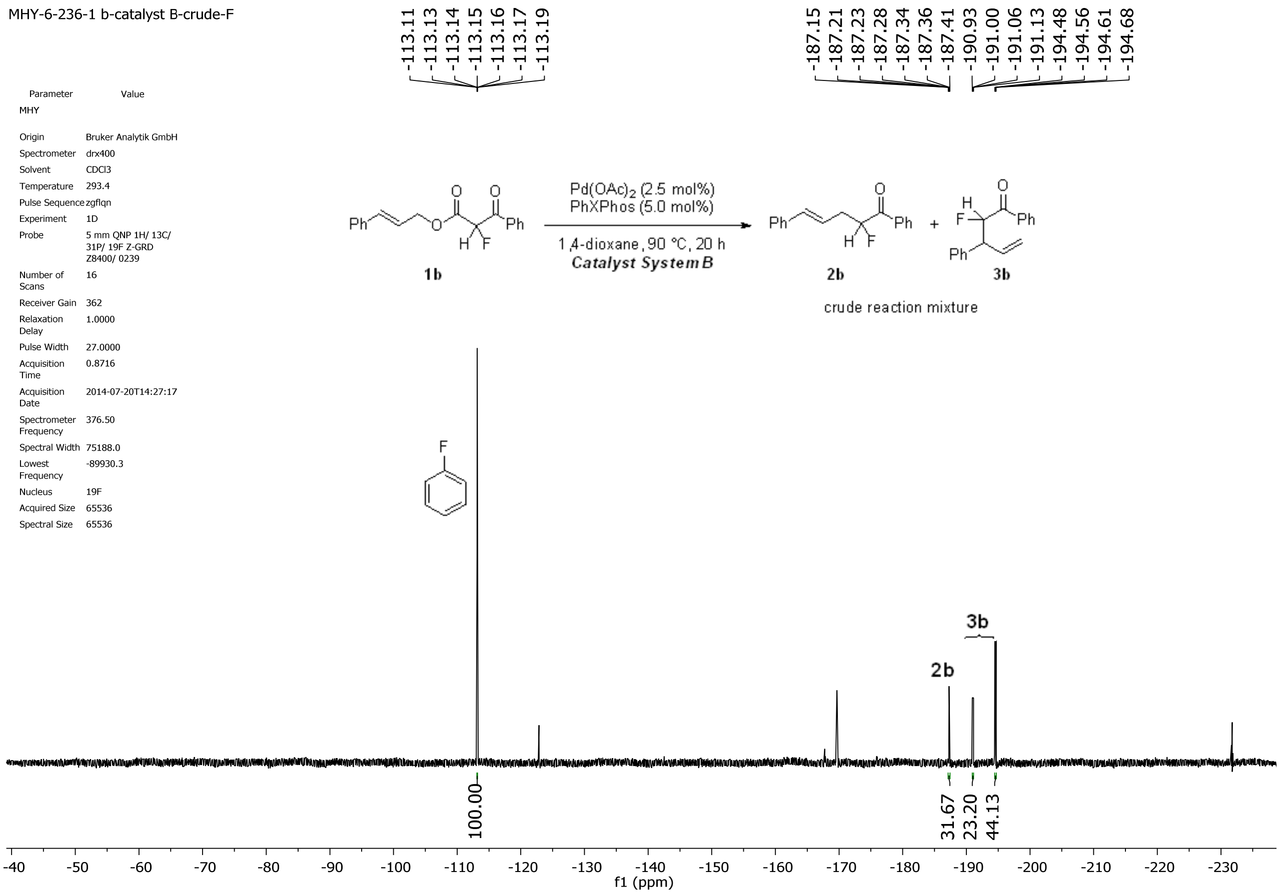
2b

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-25T23:33:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.4
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



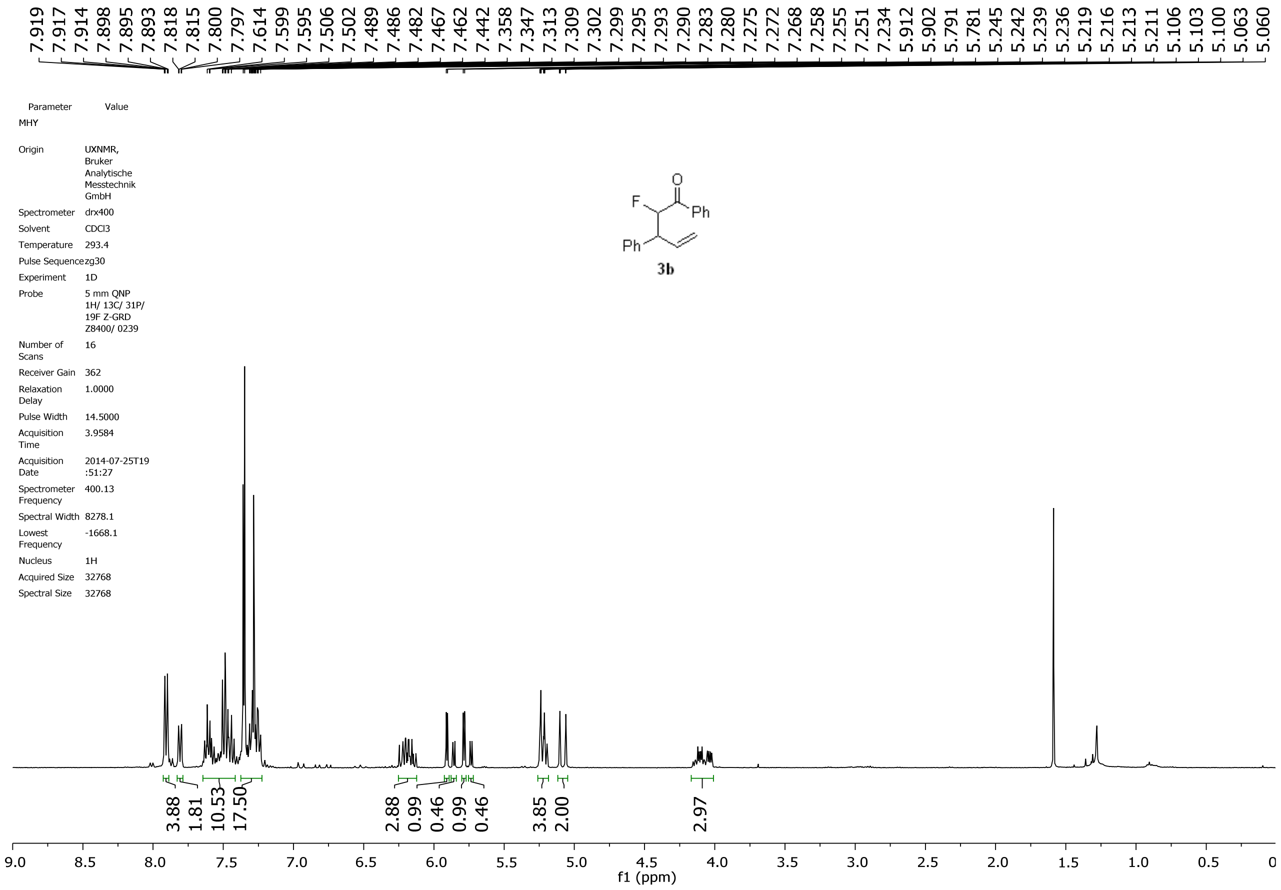
2b

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-25T09:35:54
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-90303.8
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

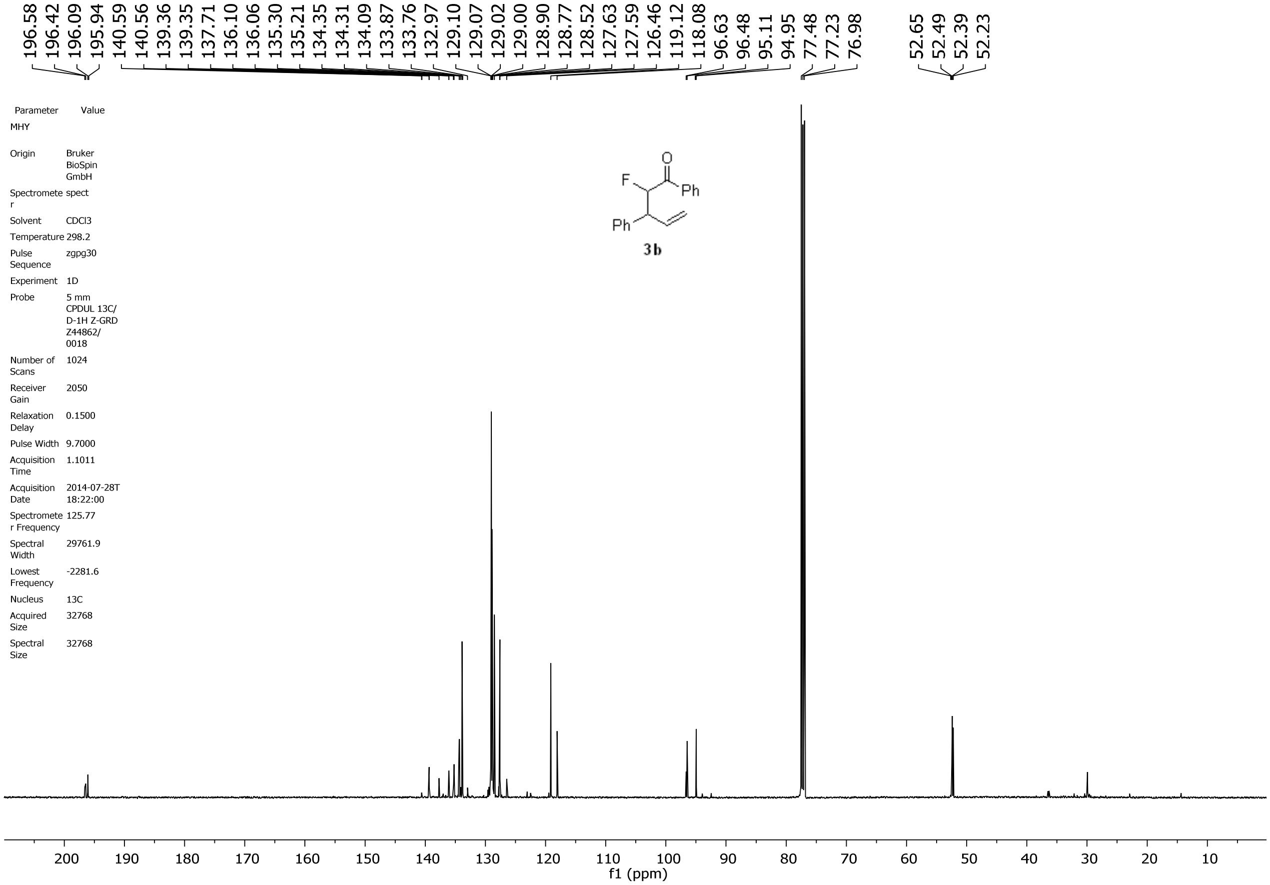


MHY-6-236-1 b-catalyst B-crude-F

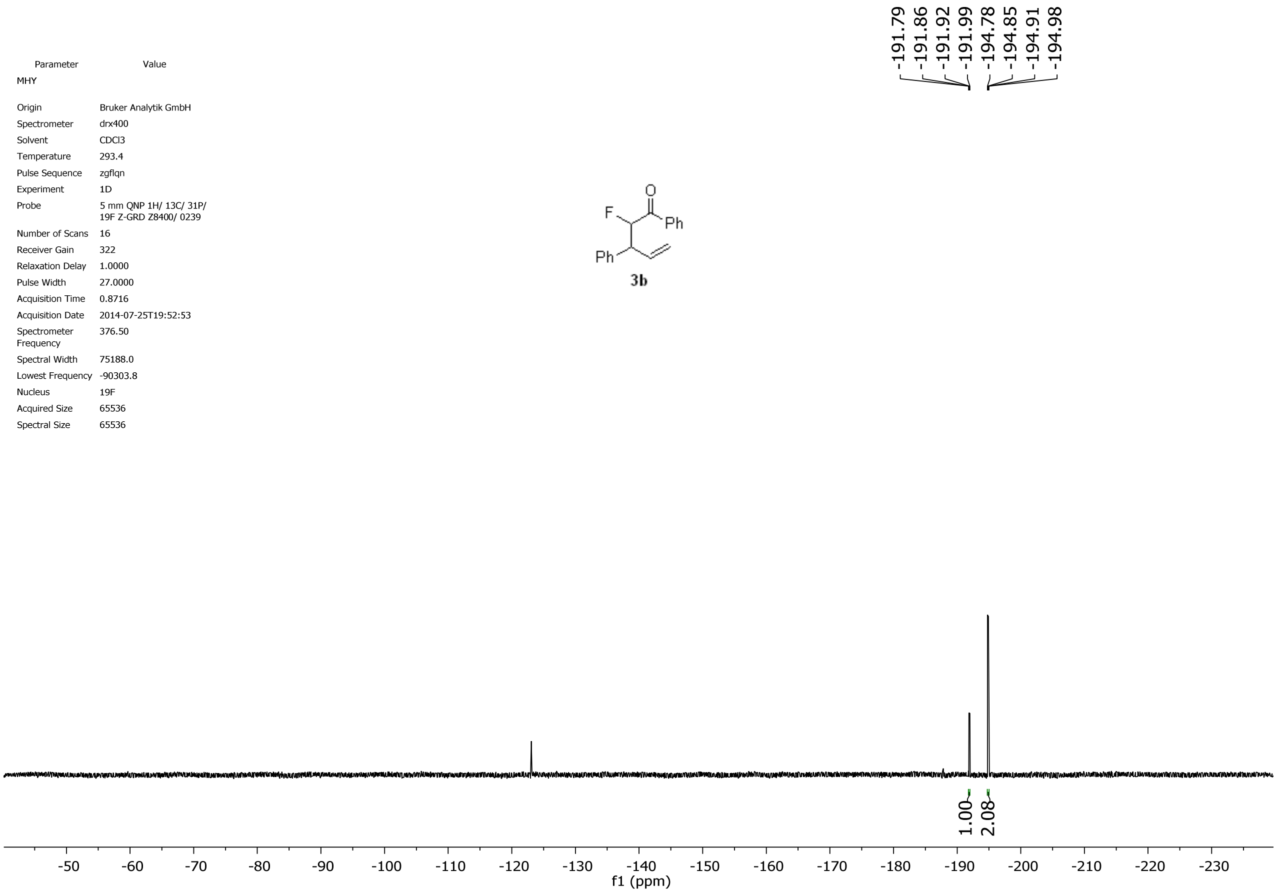
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-20T14:27:17
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-89930.3
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



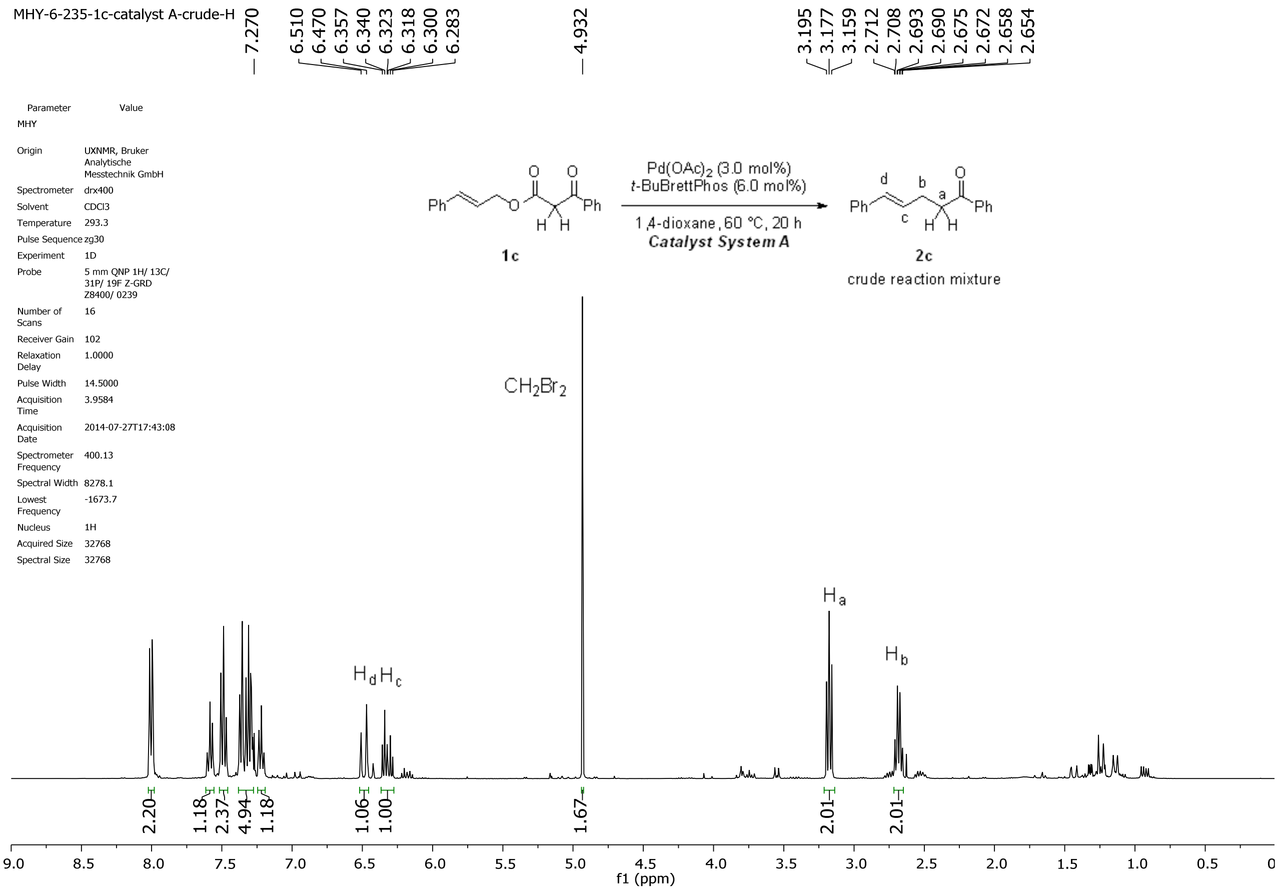
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-25T19:51:27
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1668.1
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



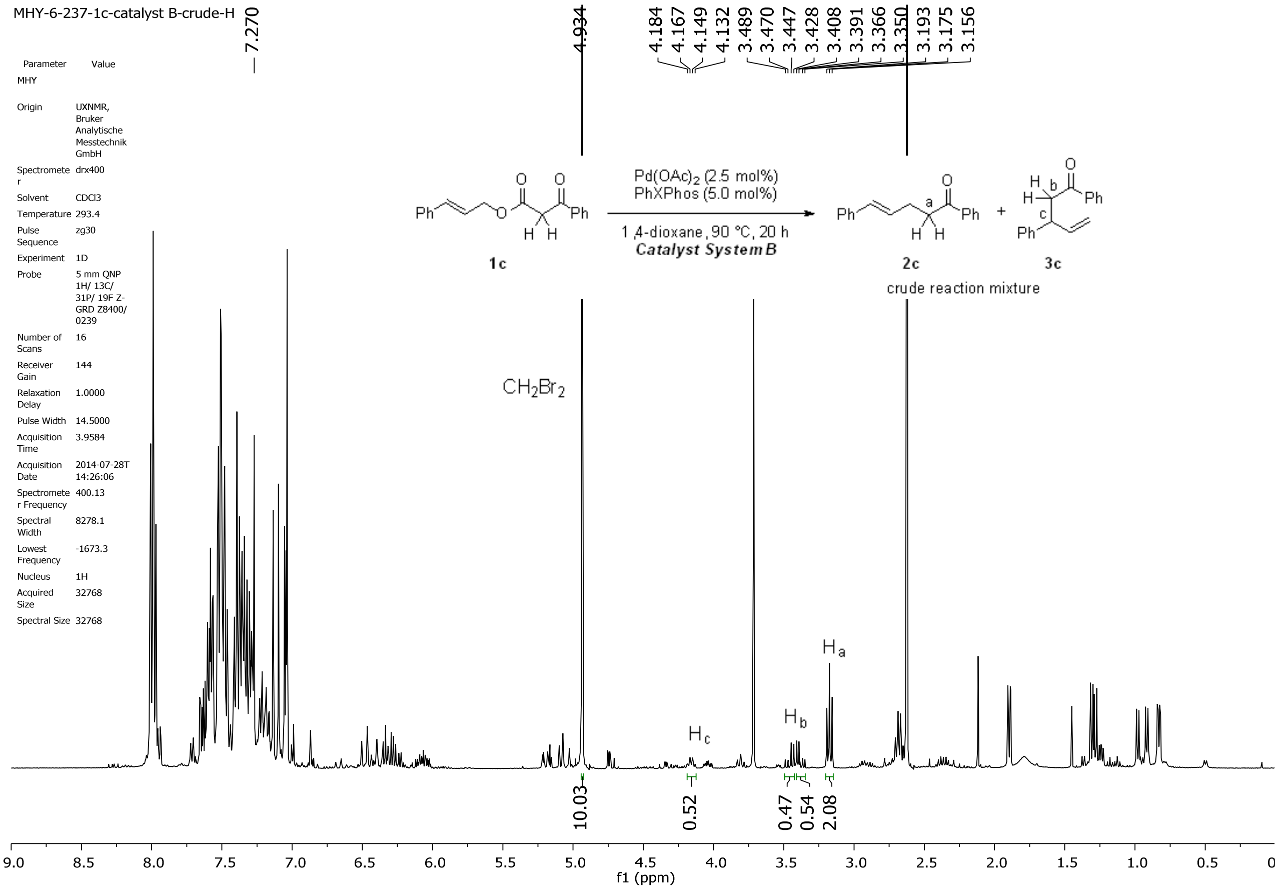
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-28T 18:22:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



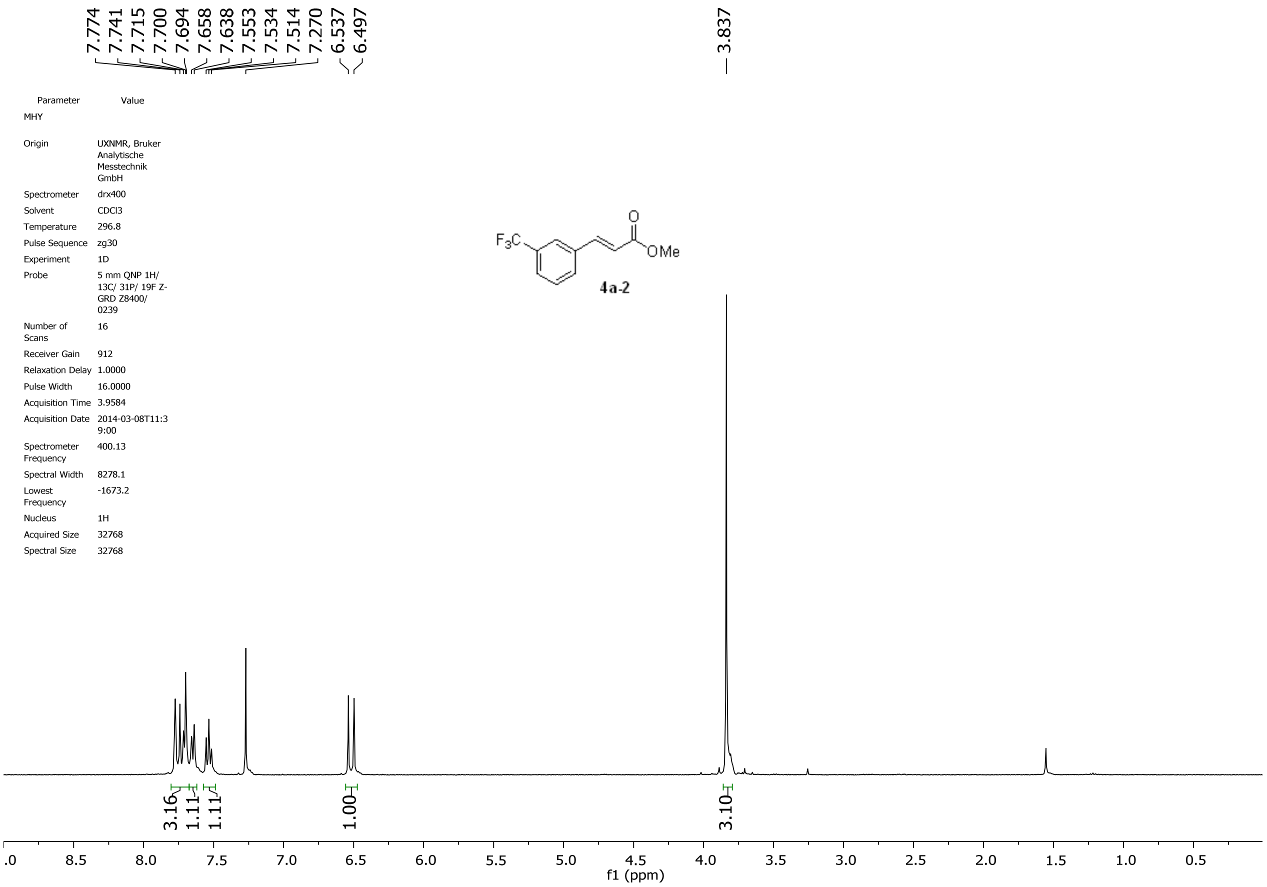
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-25T19:52:53
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-90303.8
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	102
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-27T17:43:08
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

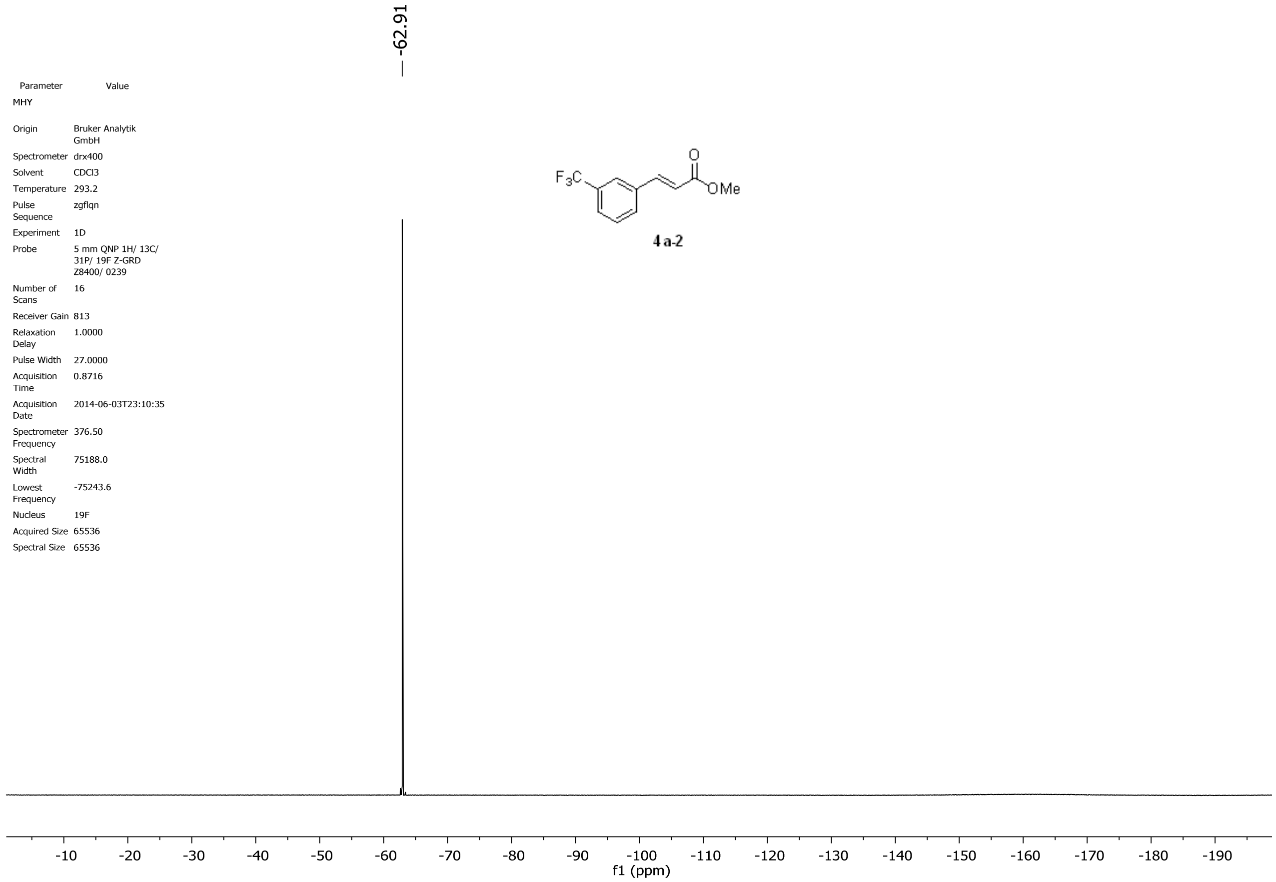


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-28T14:26:06
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



4a-2

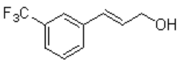
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	296.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-03-08T11:39:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.2
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



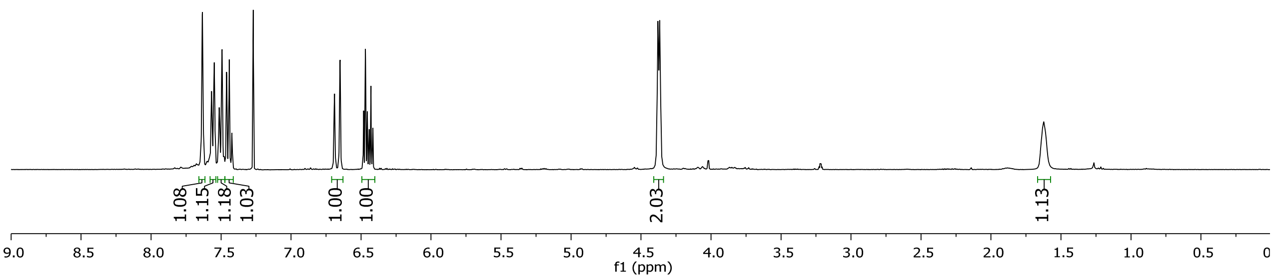
4a-2

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-03T23:10:35
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

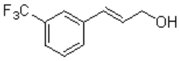
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-05T15 :34:56
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



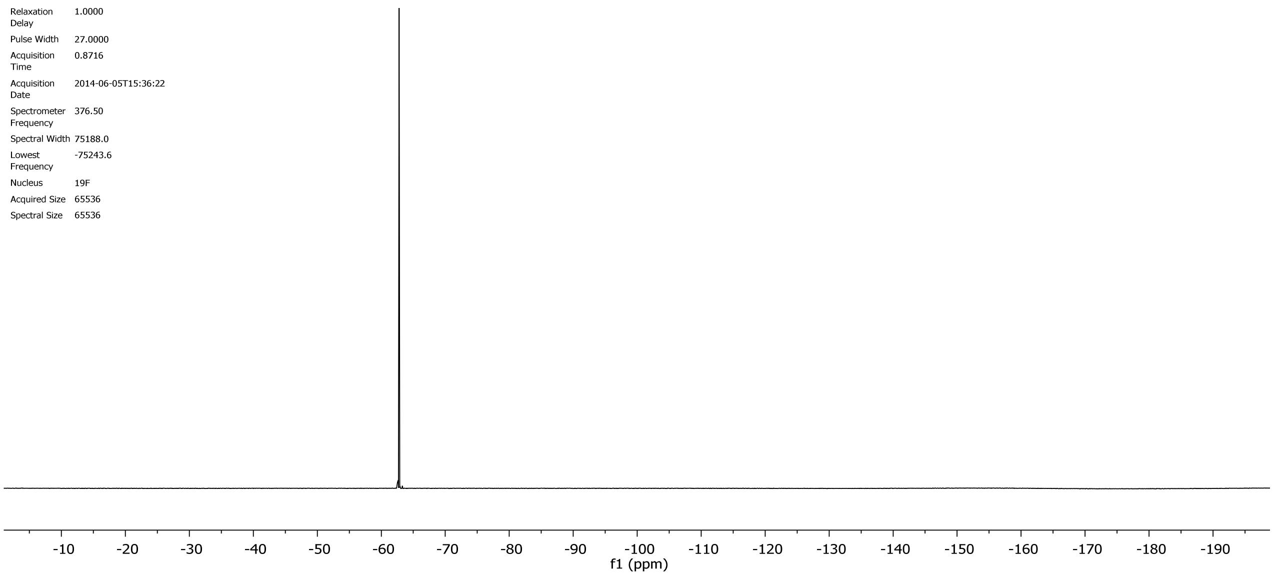
4a-1

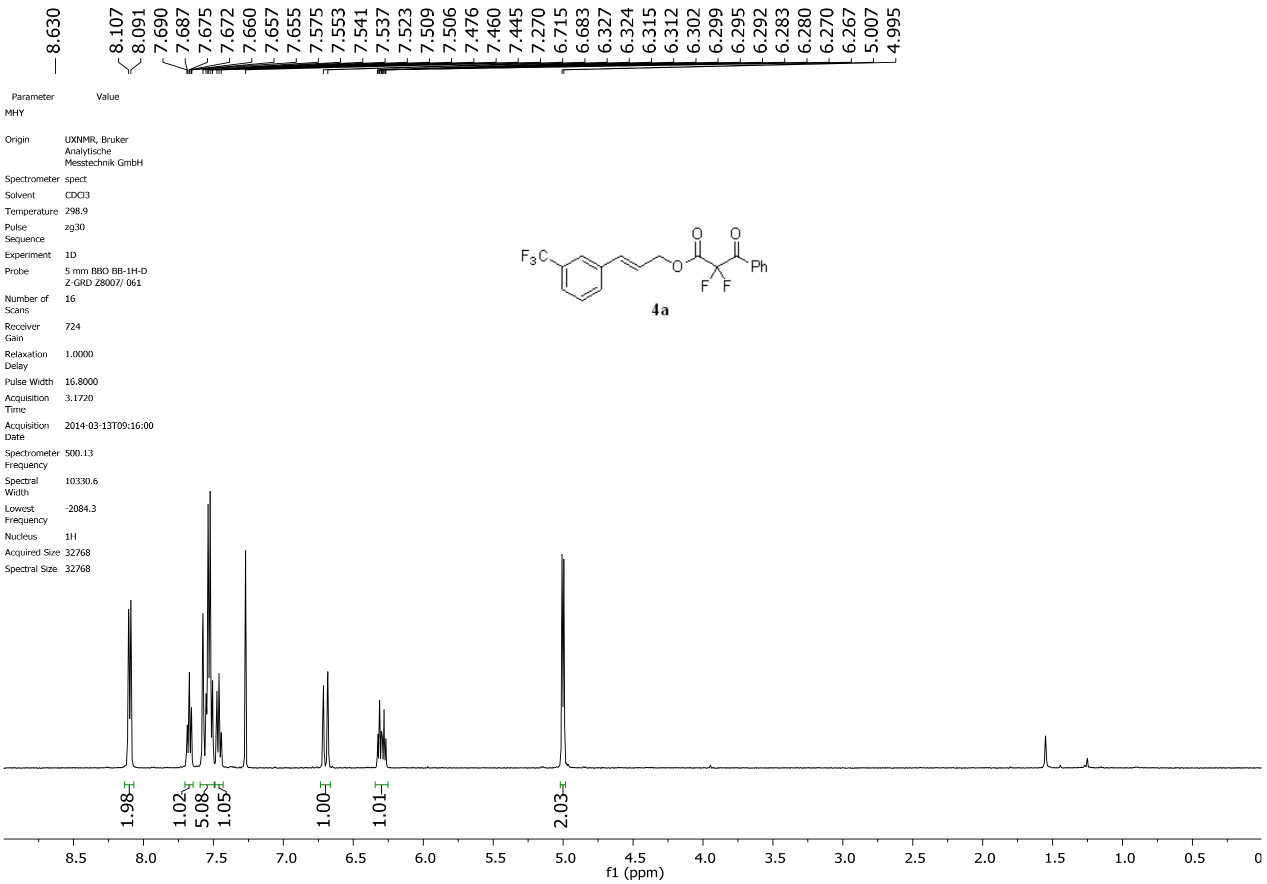


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-05T15:36:22
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



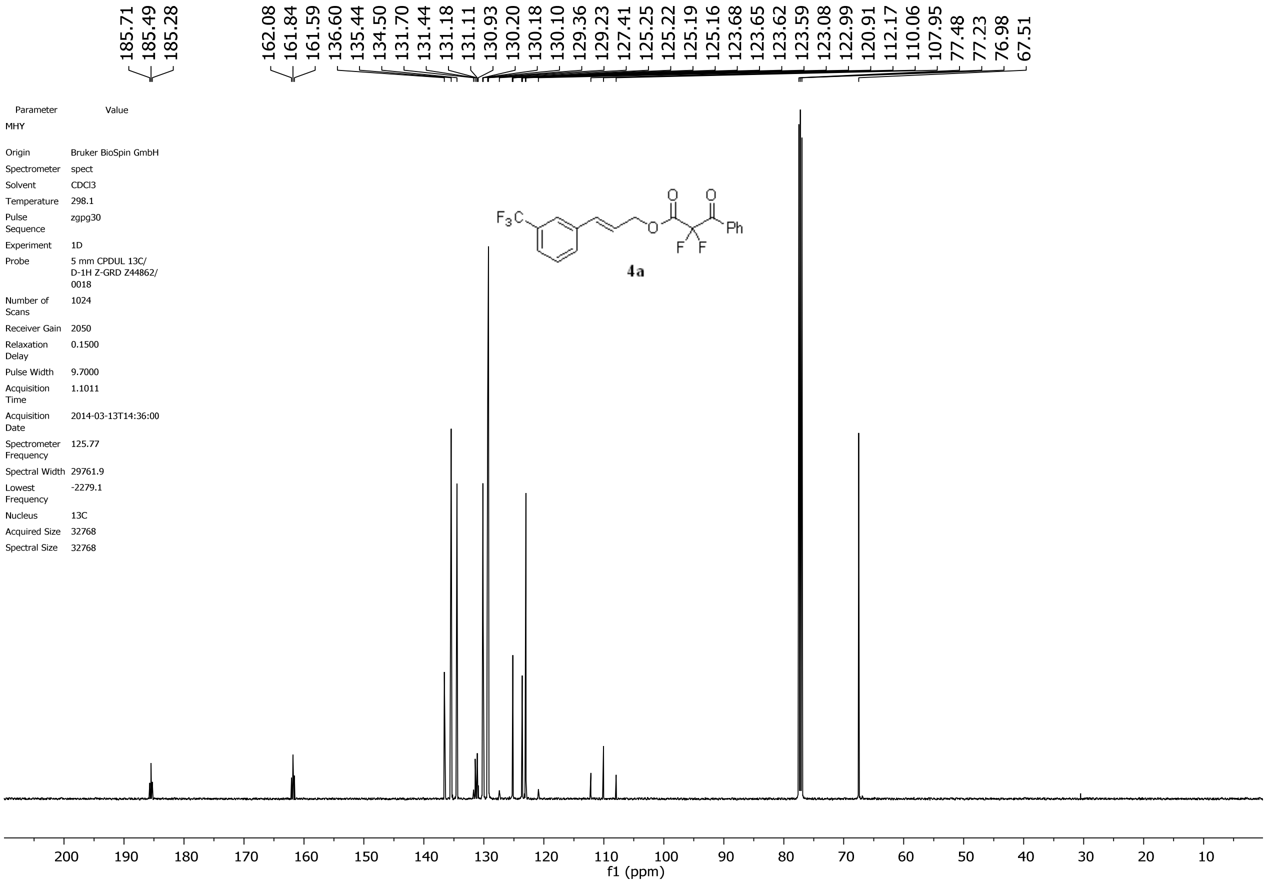
4a-1





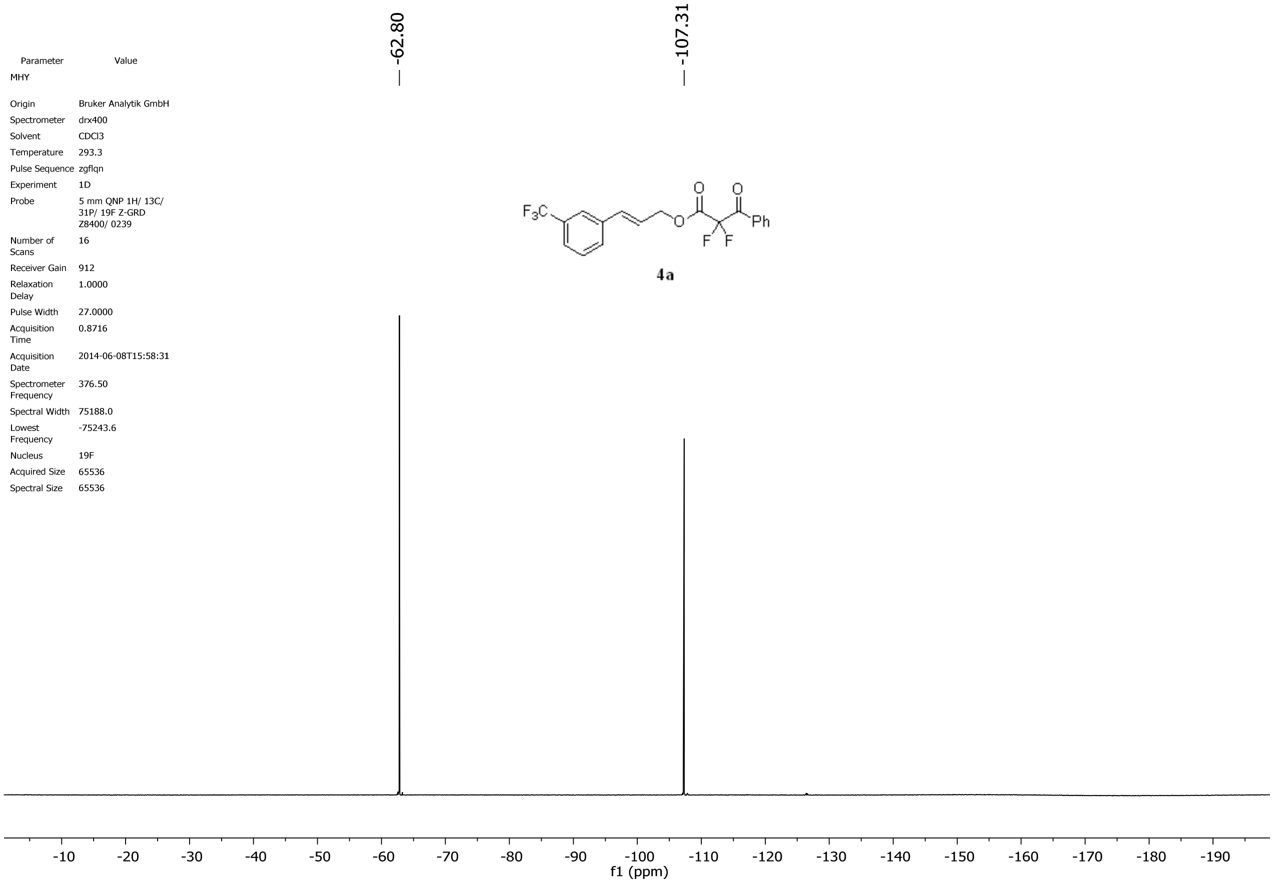
4a

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD Z8007/ 061
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	16.8000
Acquisition Time	3.1720
Acquisition Date	2014-03-13T09:16:00
Spectrometer Frequency	500.13
Spectral Width	10330.6
Lowest Frequency	-2084.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



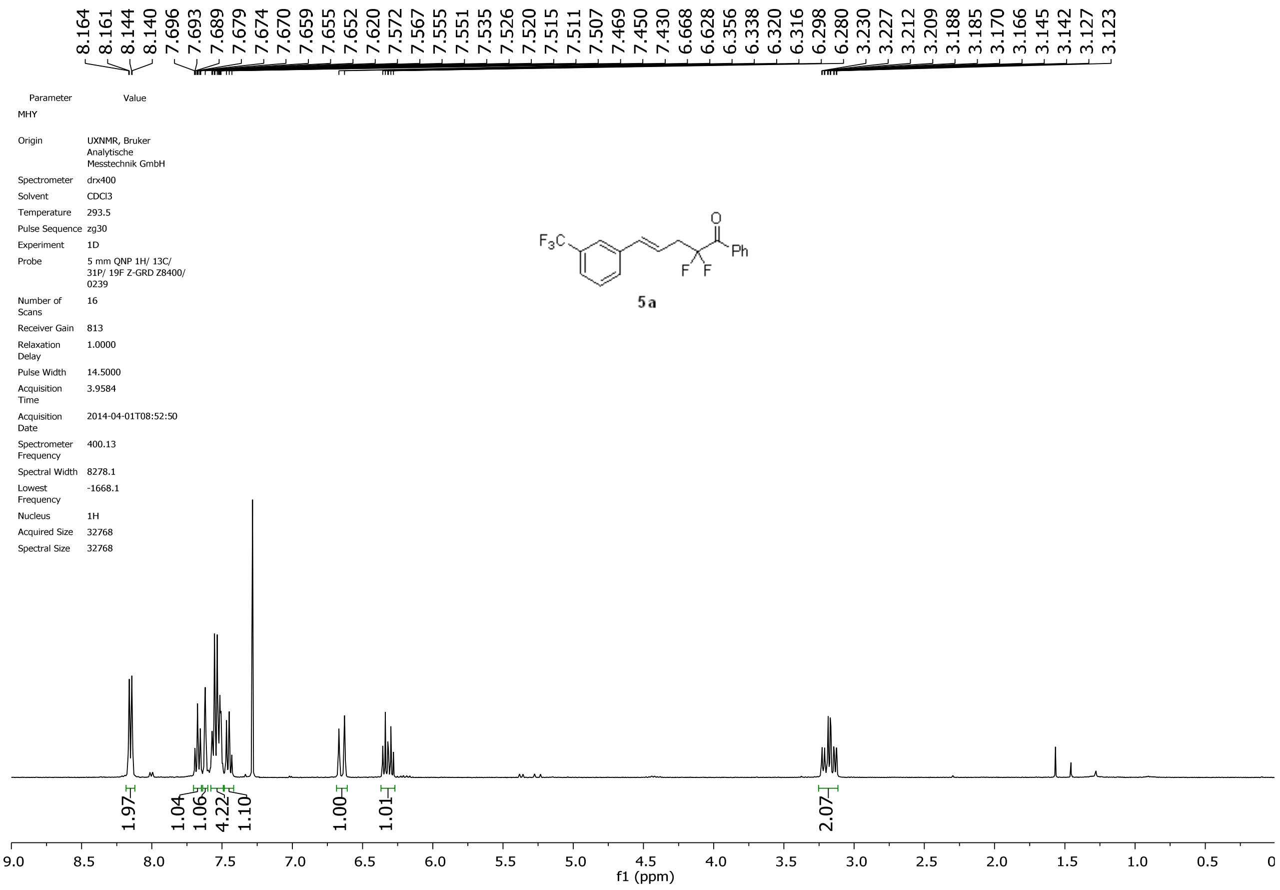
4a

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-03-13T14:36:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



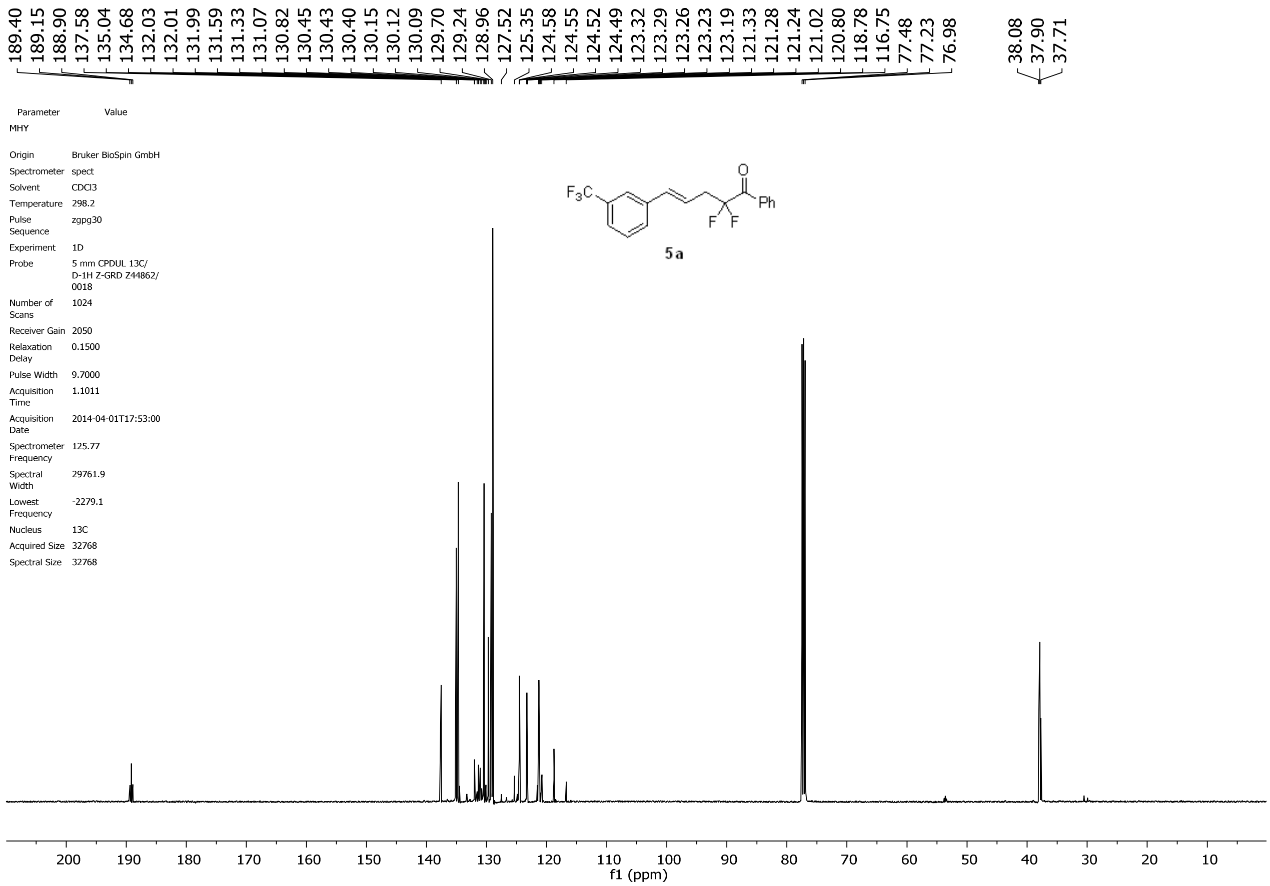
4a

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-08T15:58:31
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



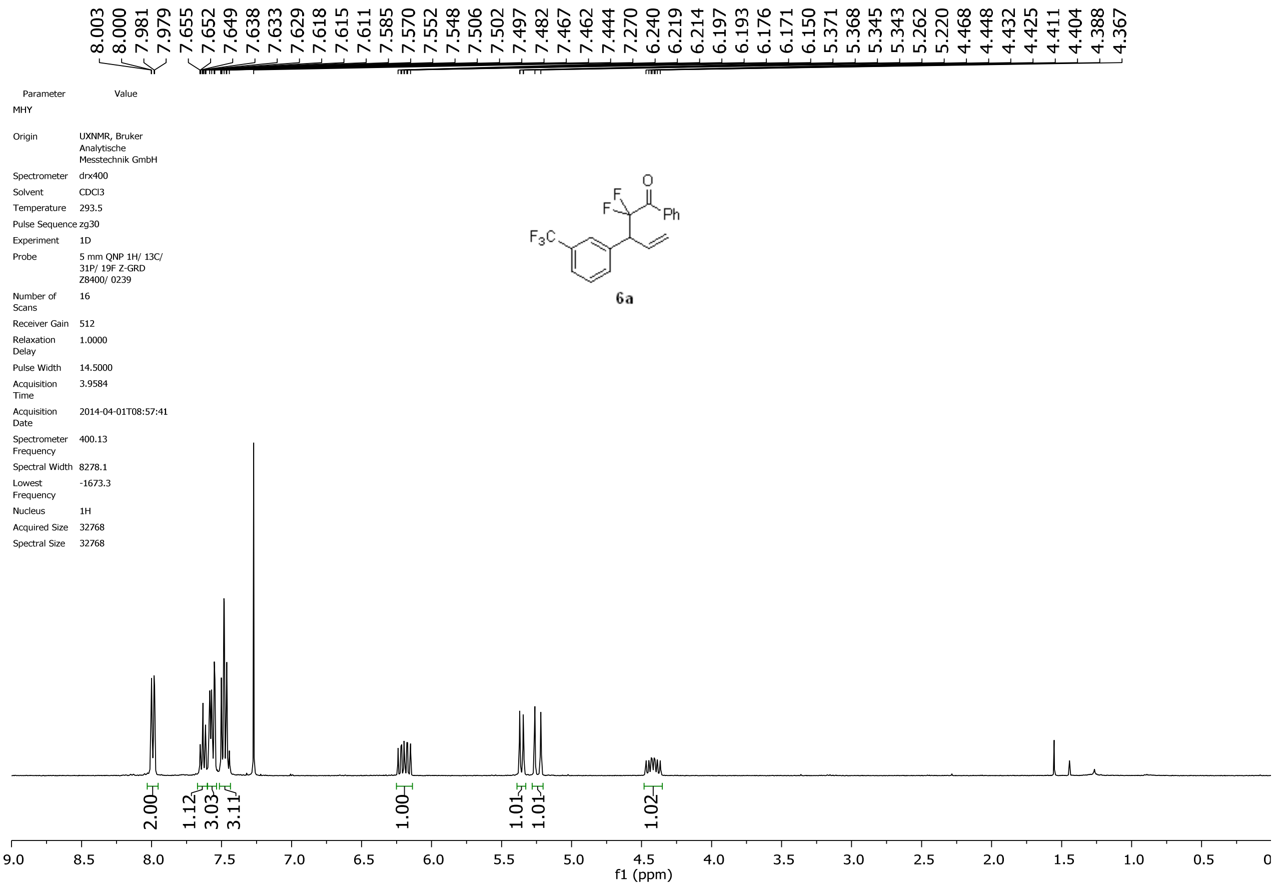
5a

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-01T08:52:50
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1668.1
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

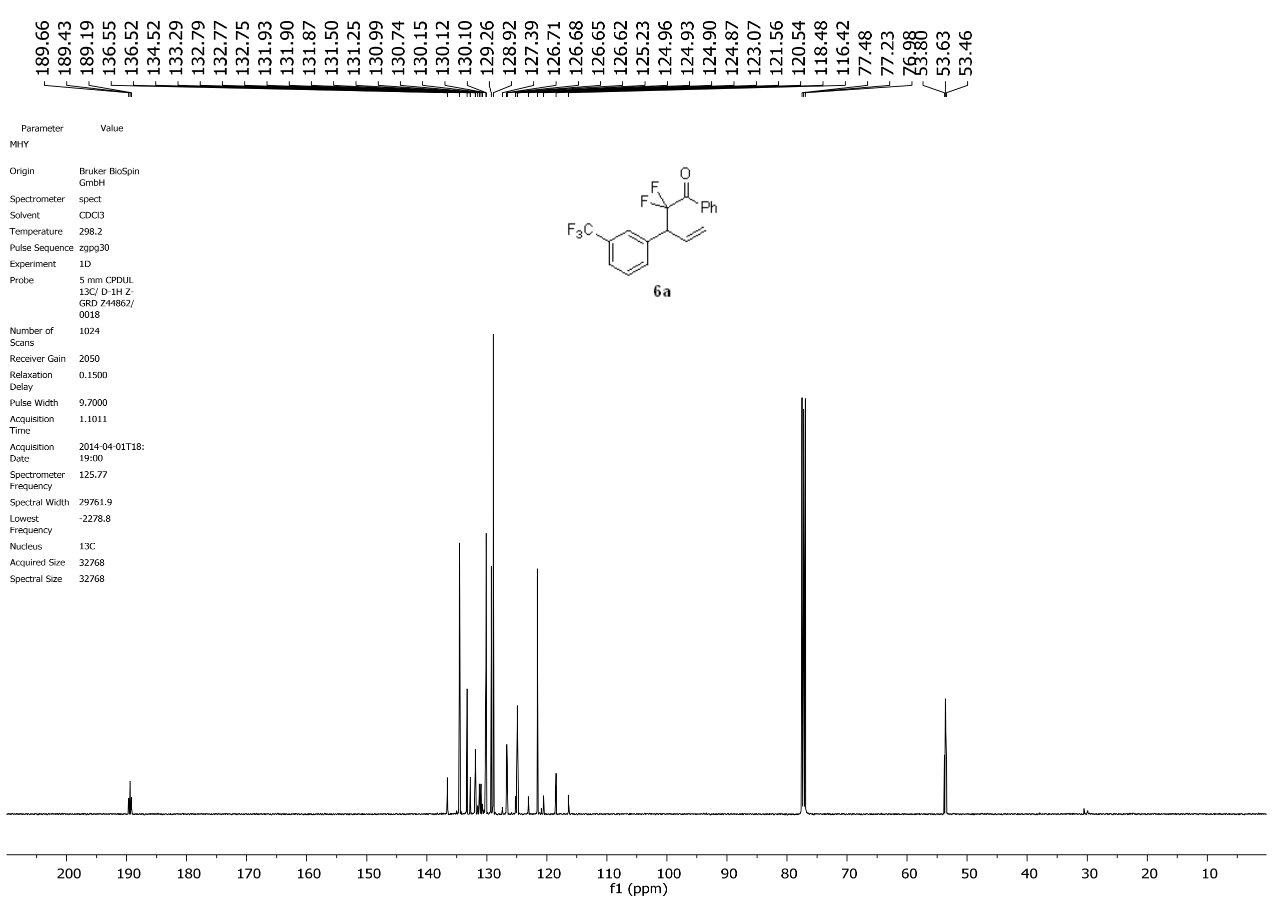


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-01T17:53:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

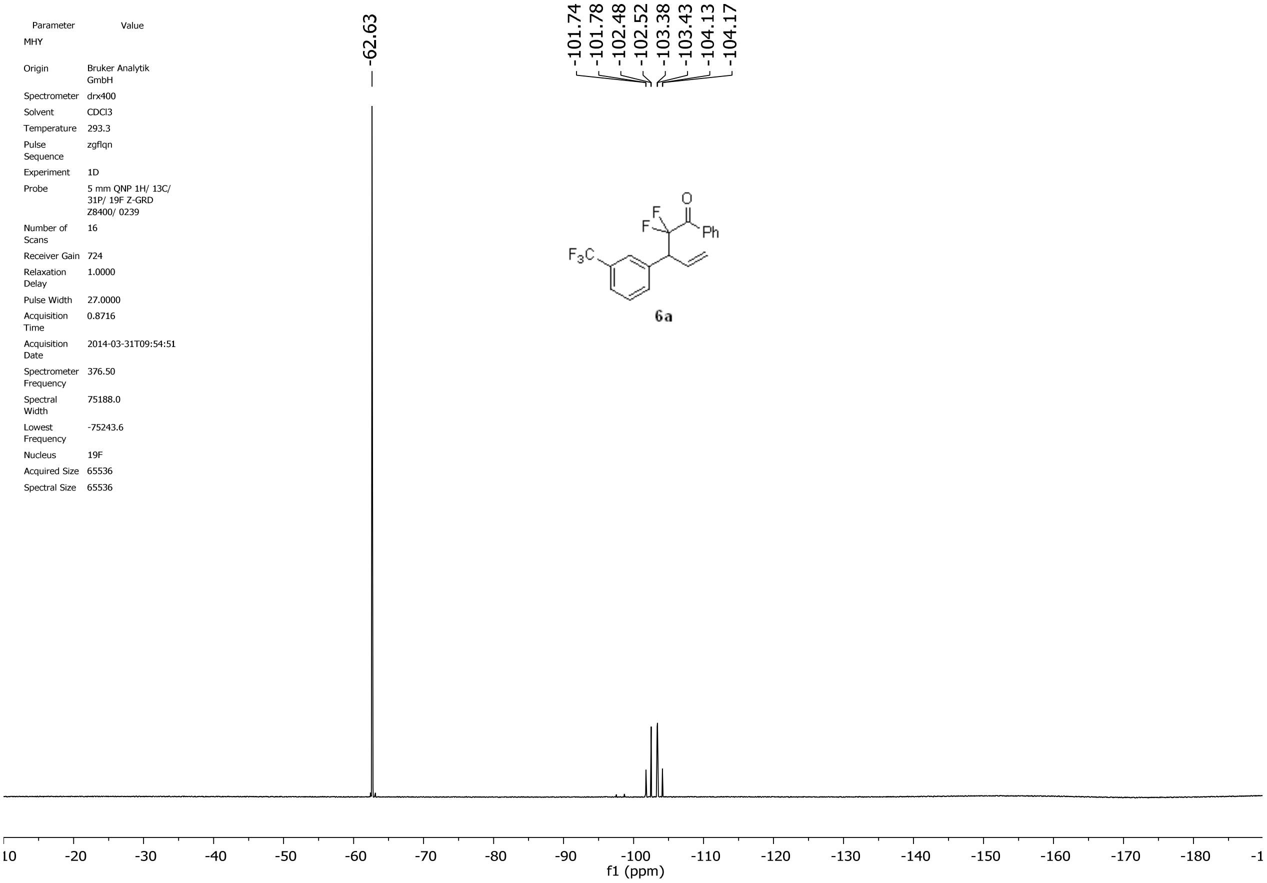
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-03-31T09:4 3:31
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



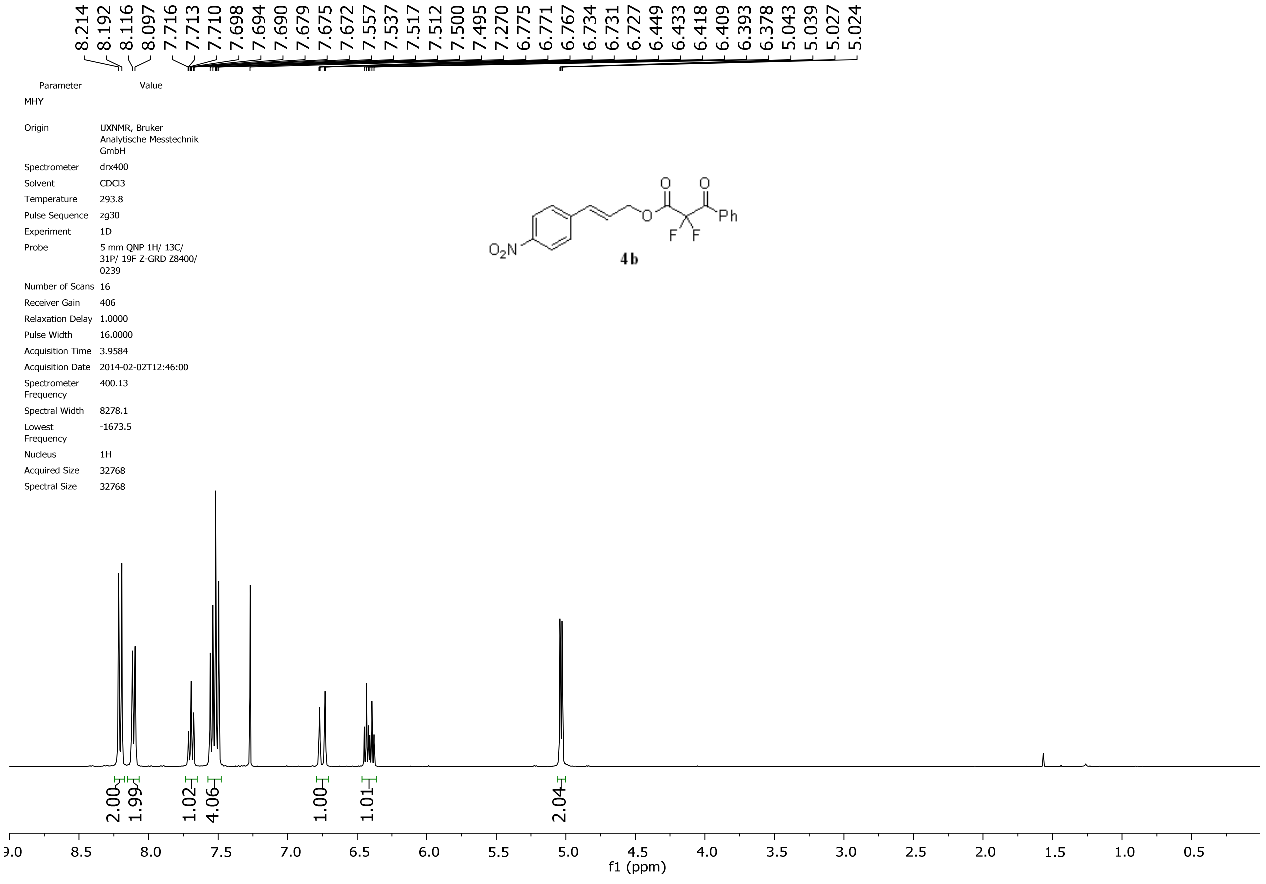
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-01T08:57:41
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



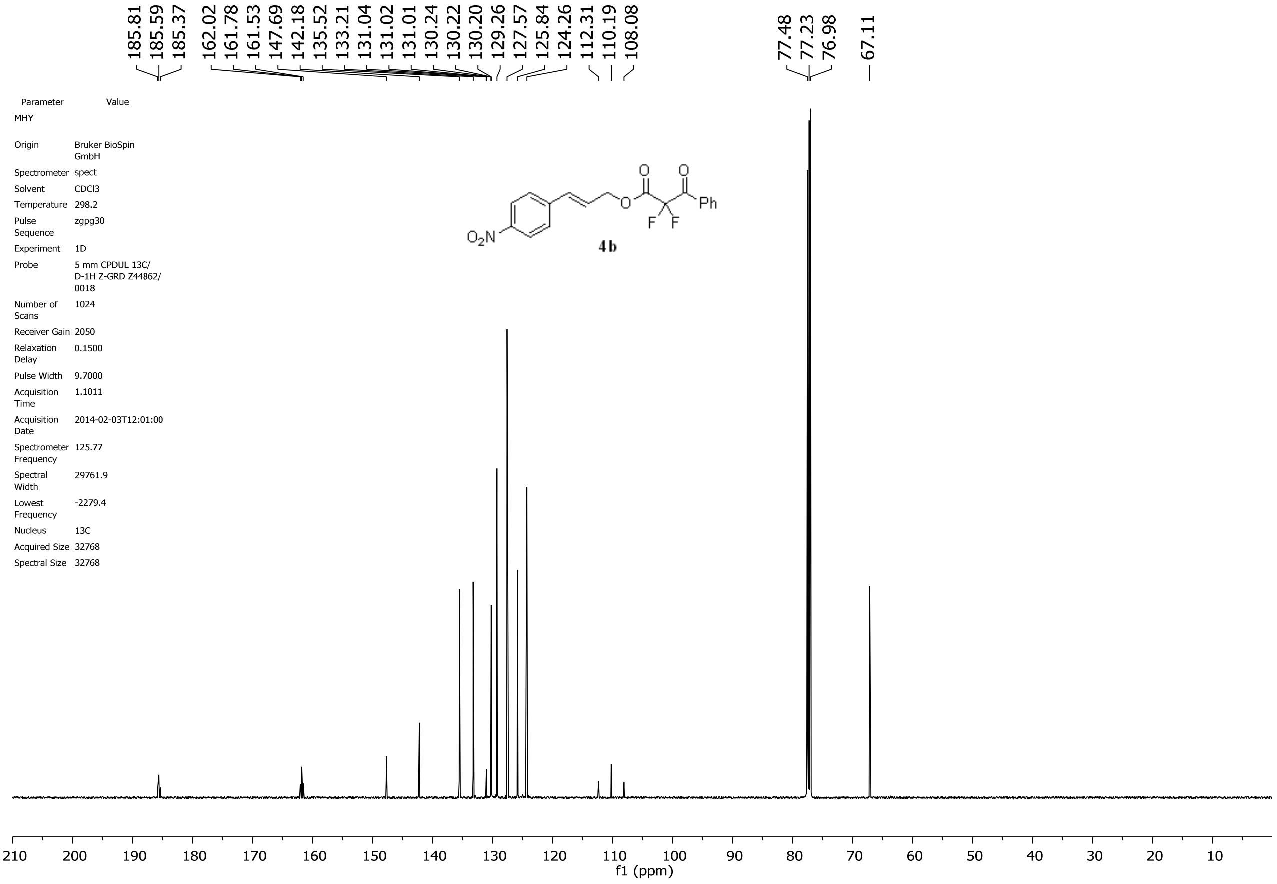
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-01T18:19:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2278.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



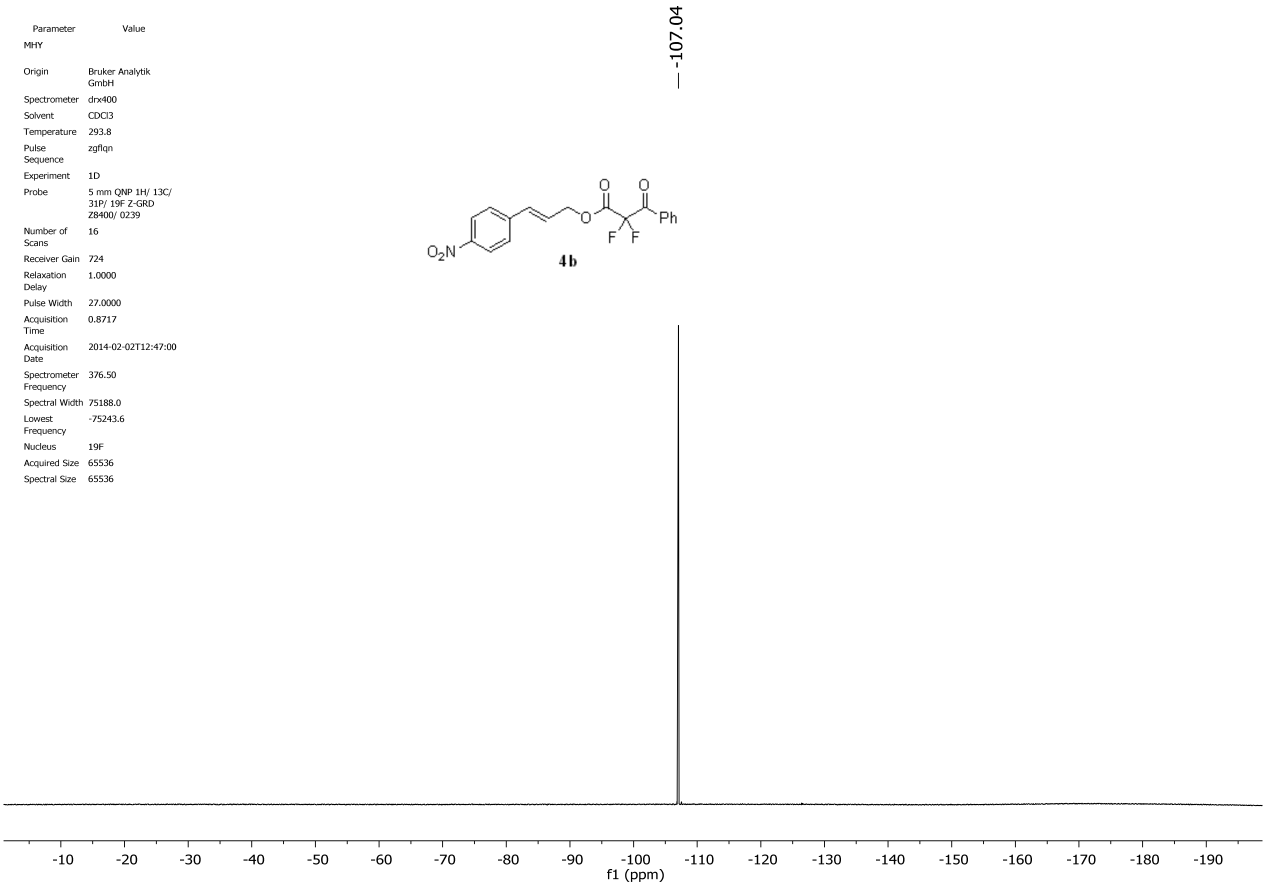
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-03-31T09:54:51
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



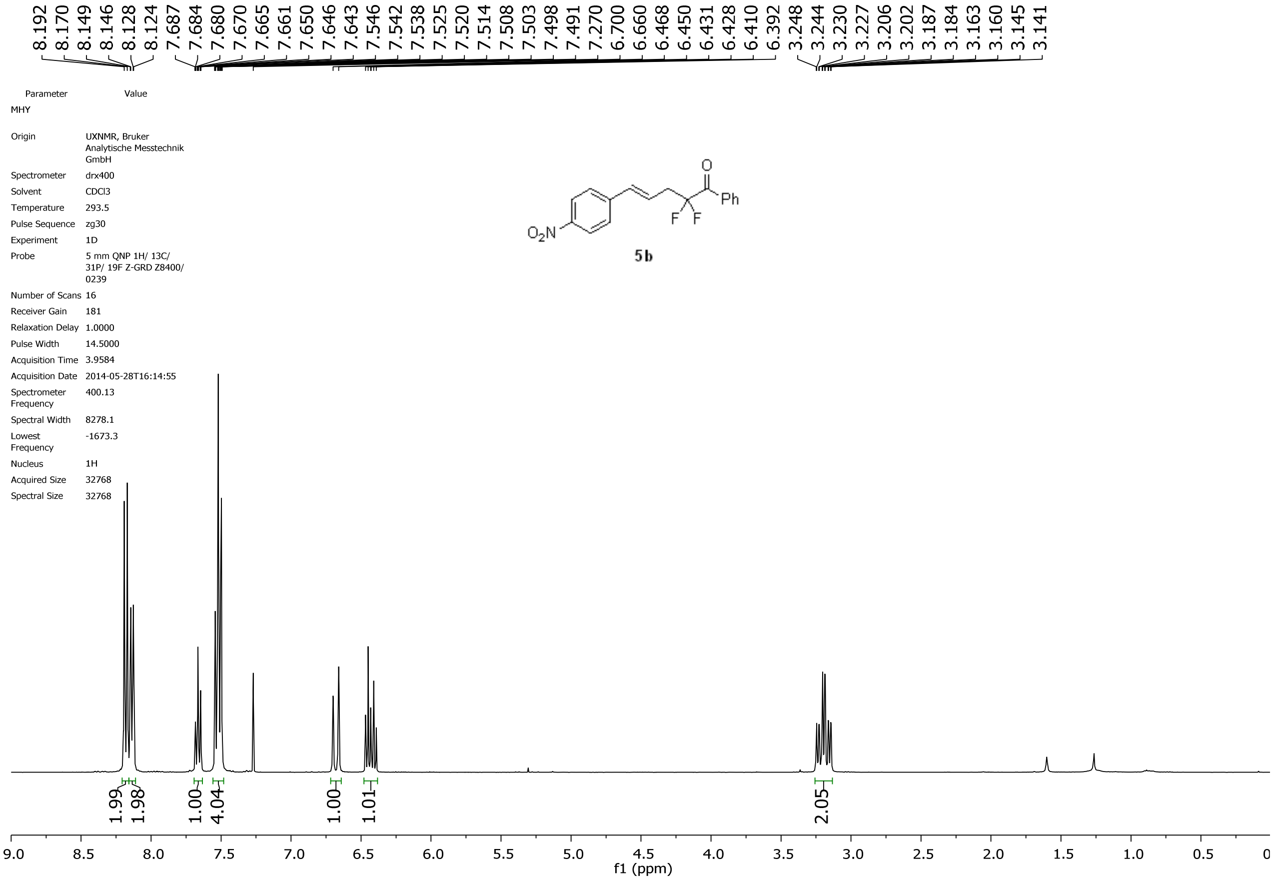
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-02T12:46:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-03T12:01:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.4
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

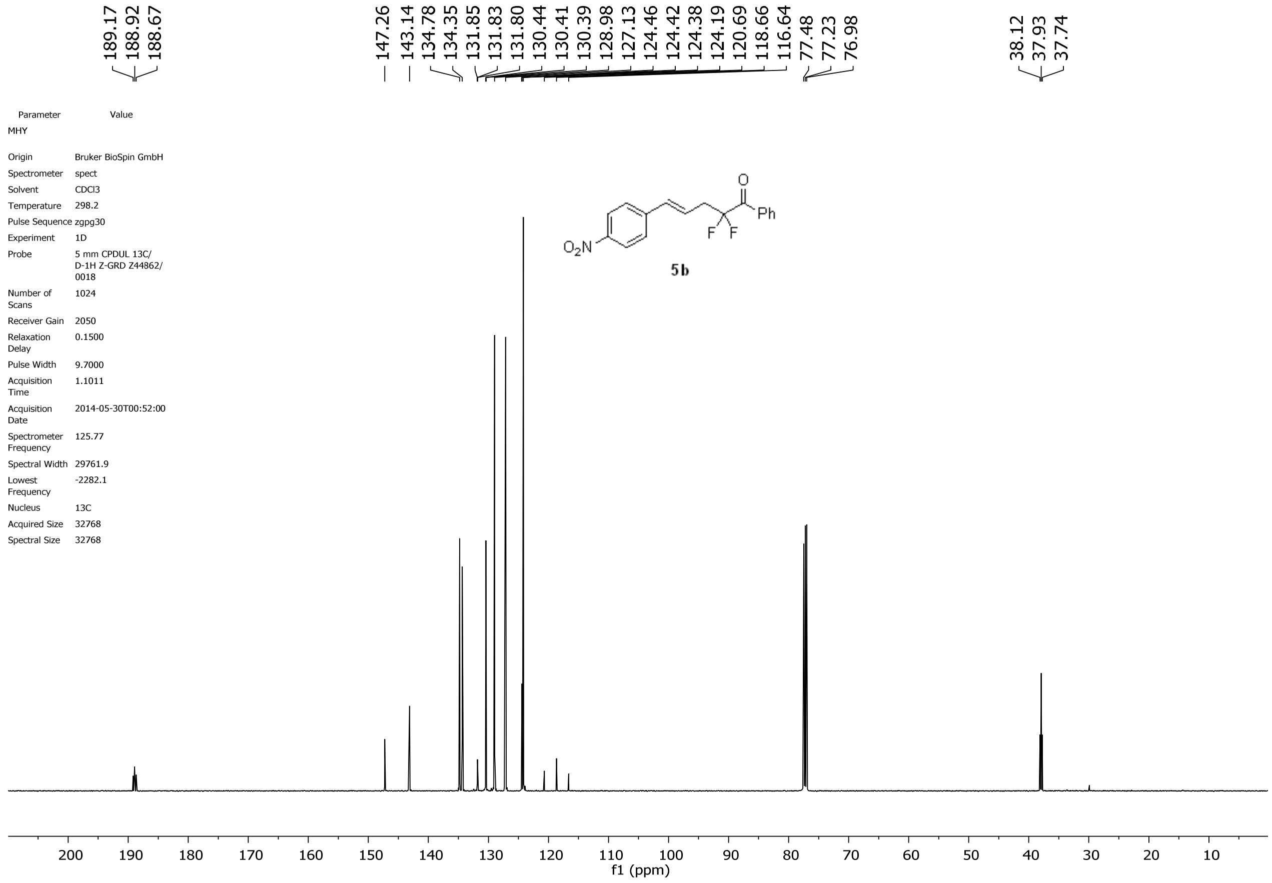


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-02-02T12:47:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



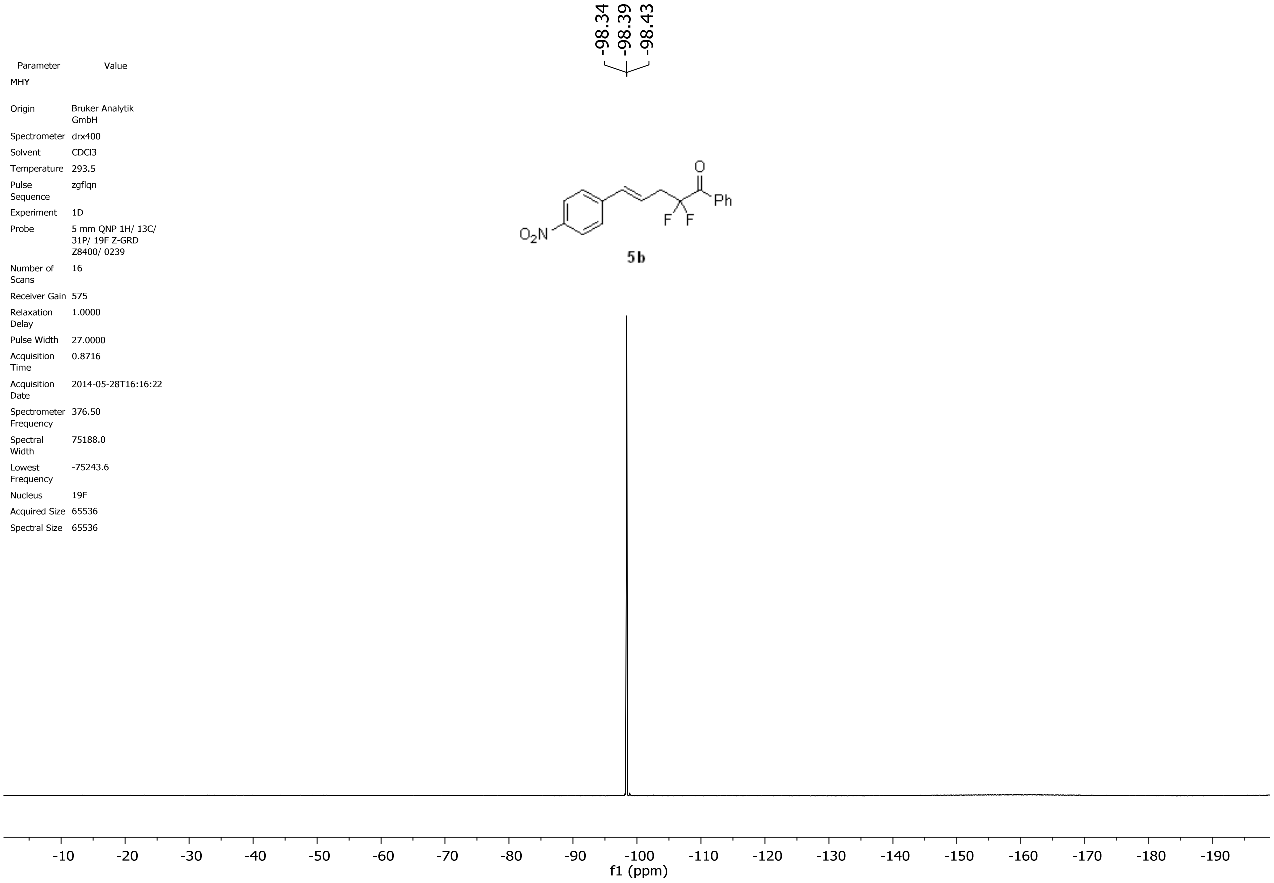
5b

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-05-28T16:14:55
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



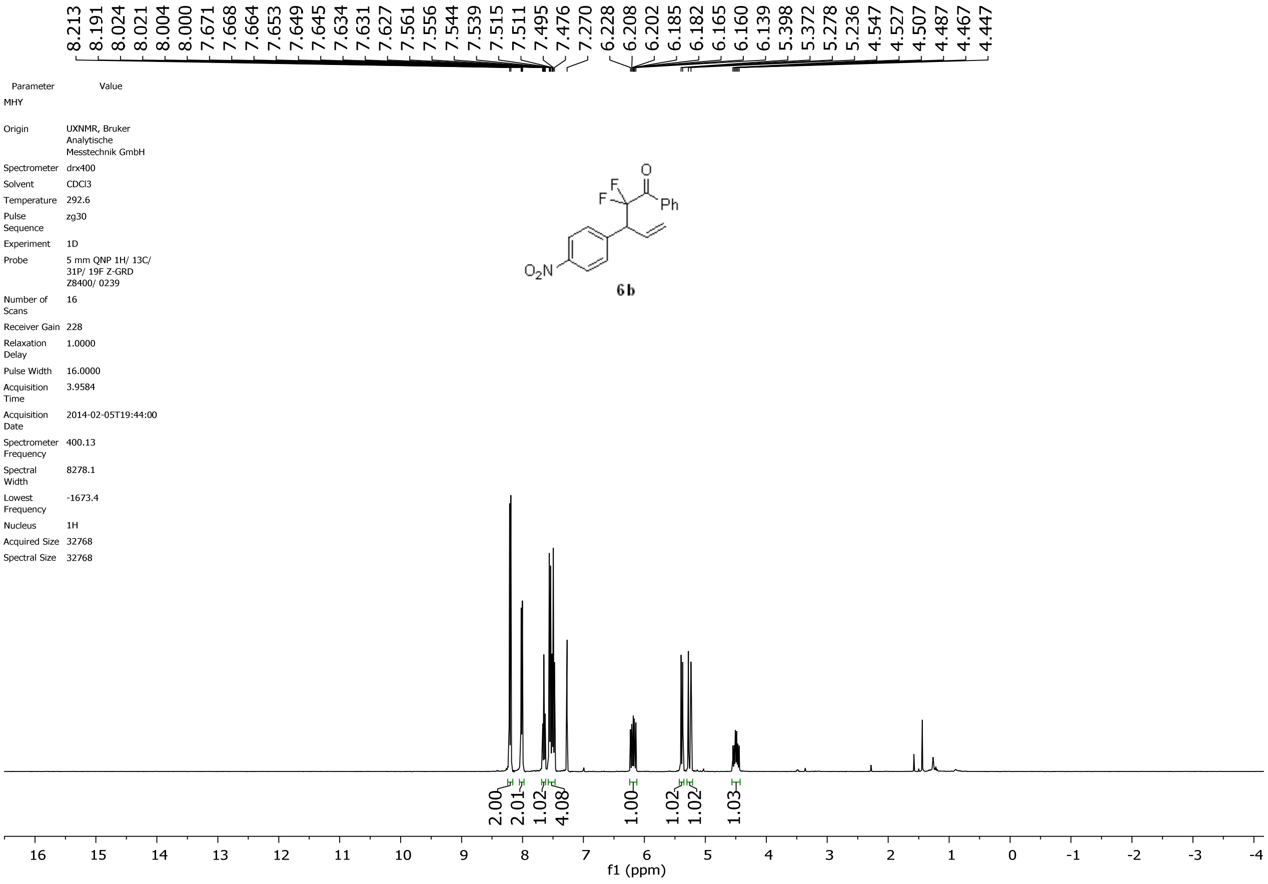
5b

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-30T00:52:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2282.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



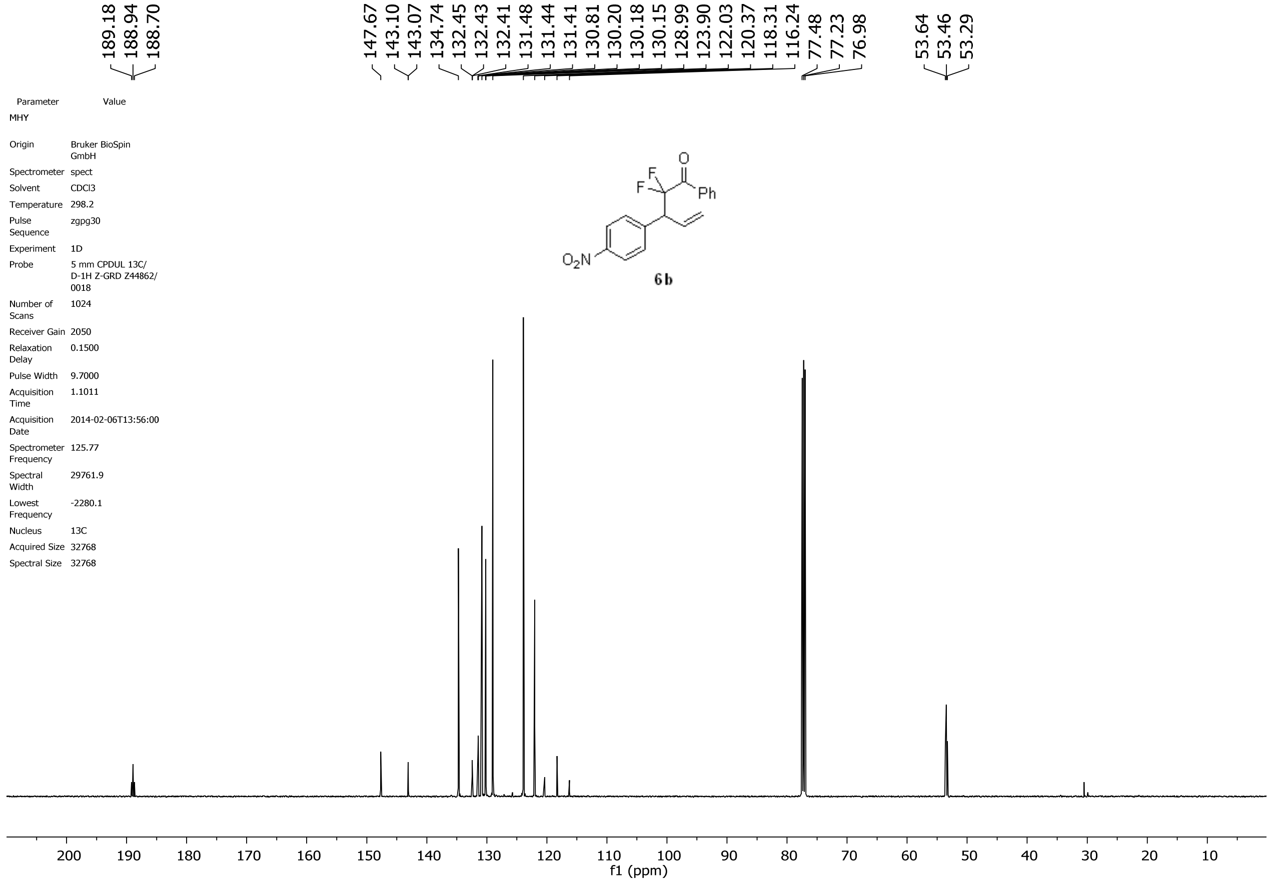
5b

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-28T16:16:22
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



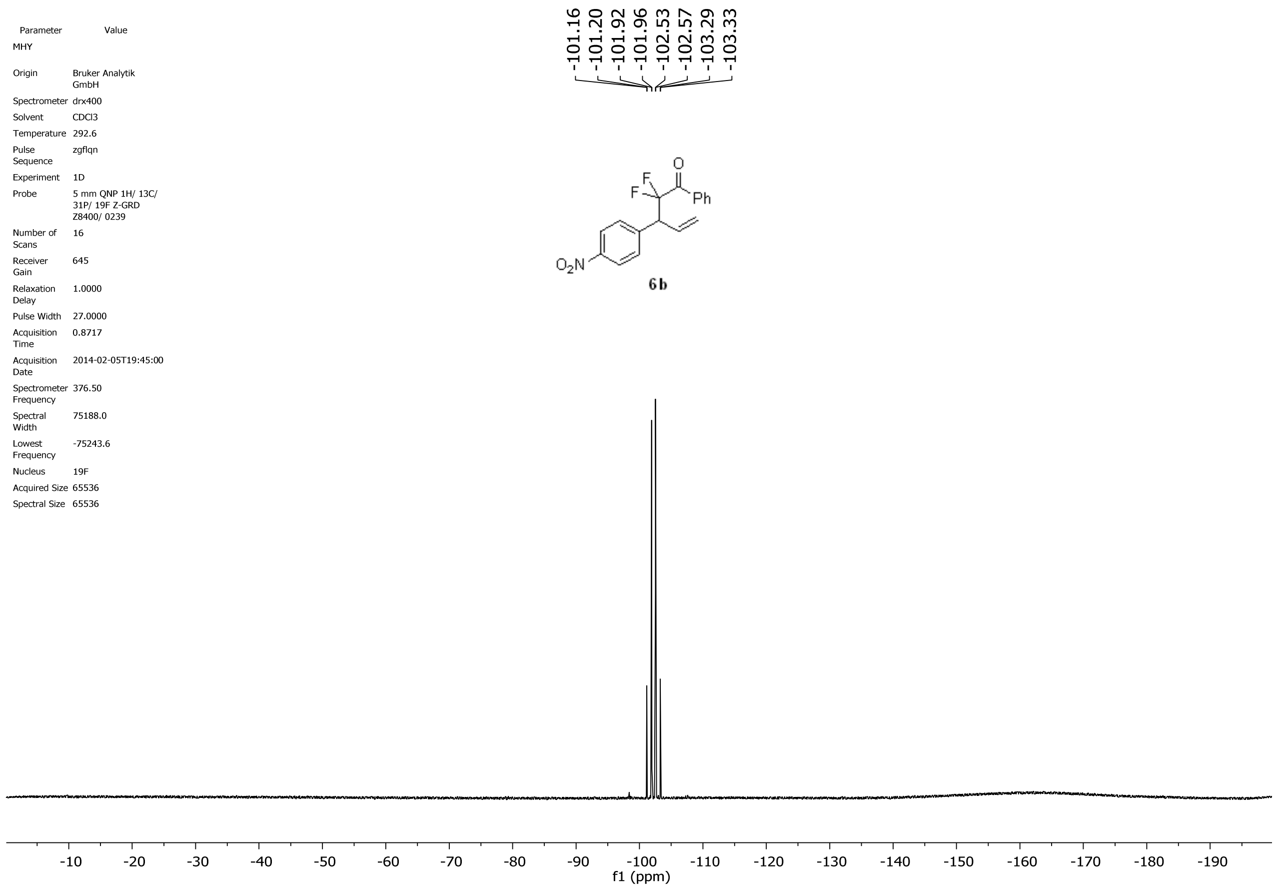
6b

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-05T19:44:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



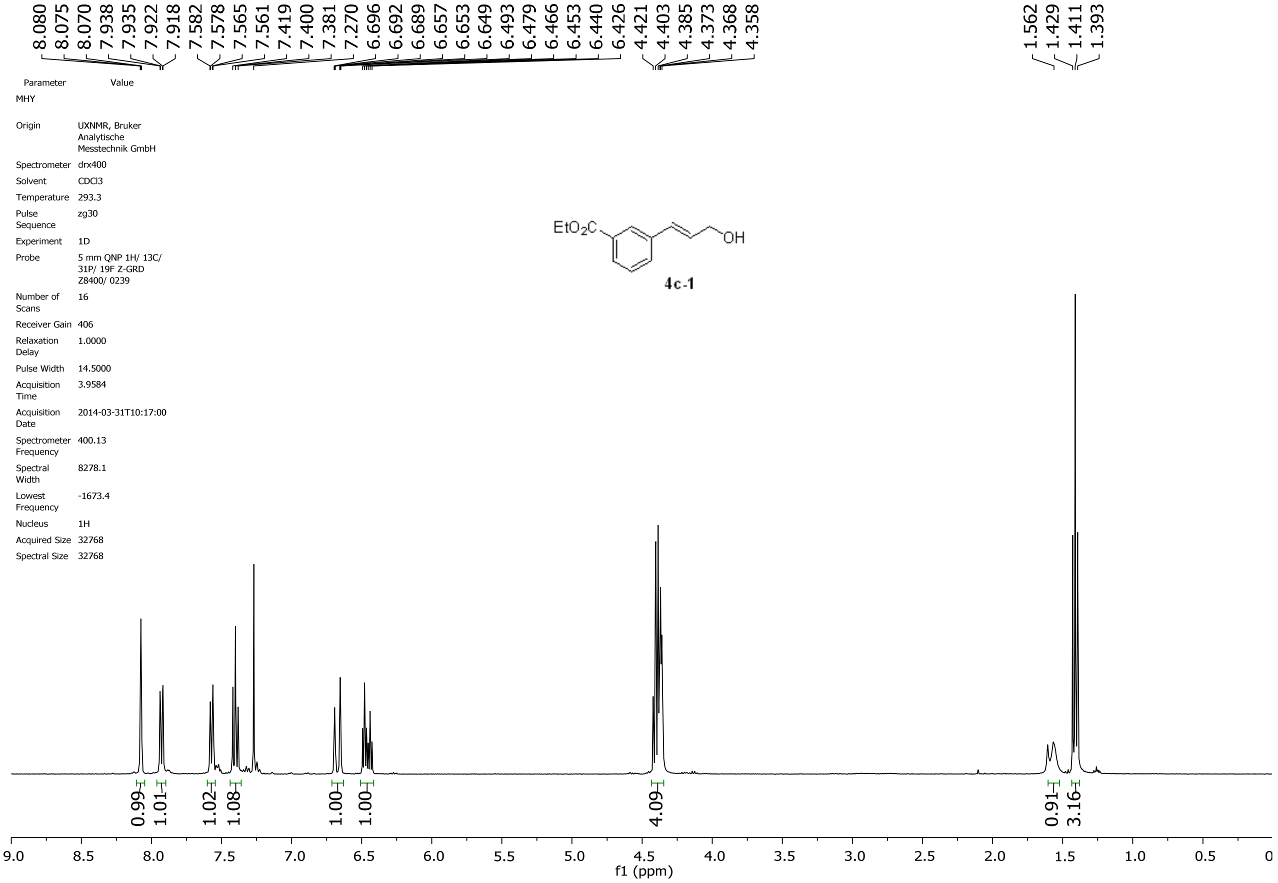
6b

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-06T13:56:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

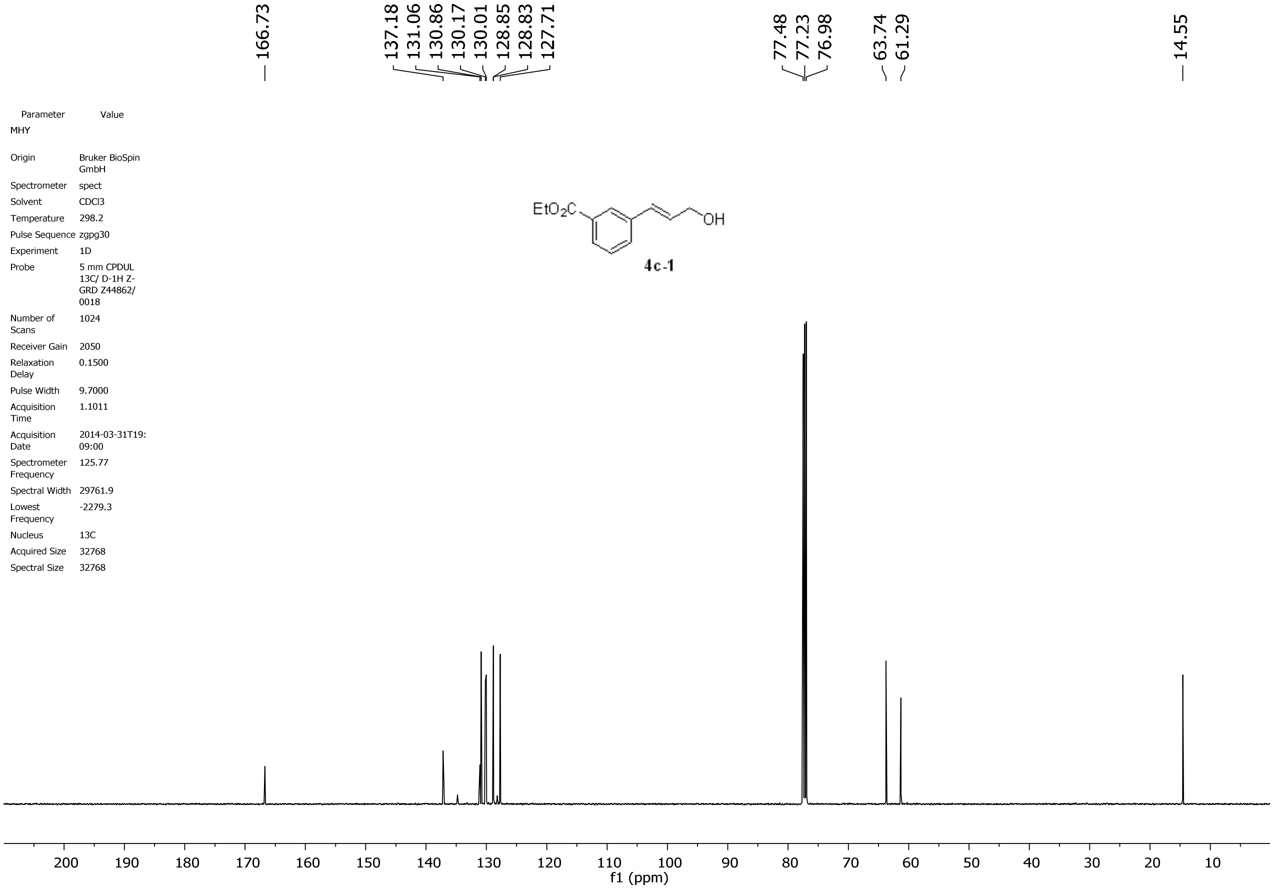


6b

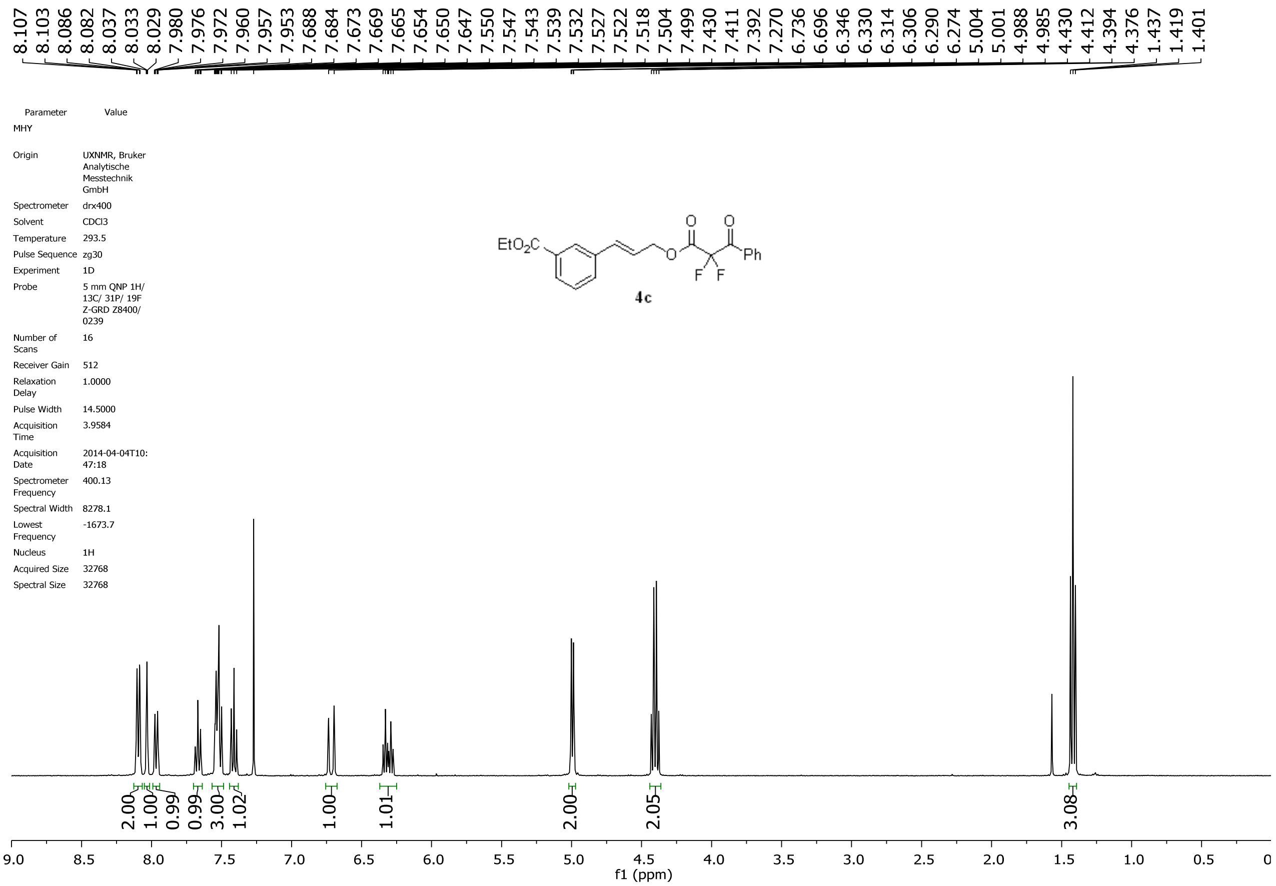
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-02-05T19:45:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



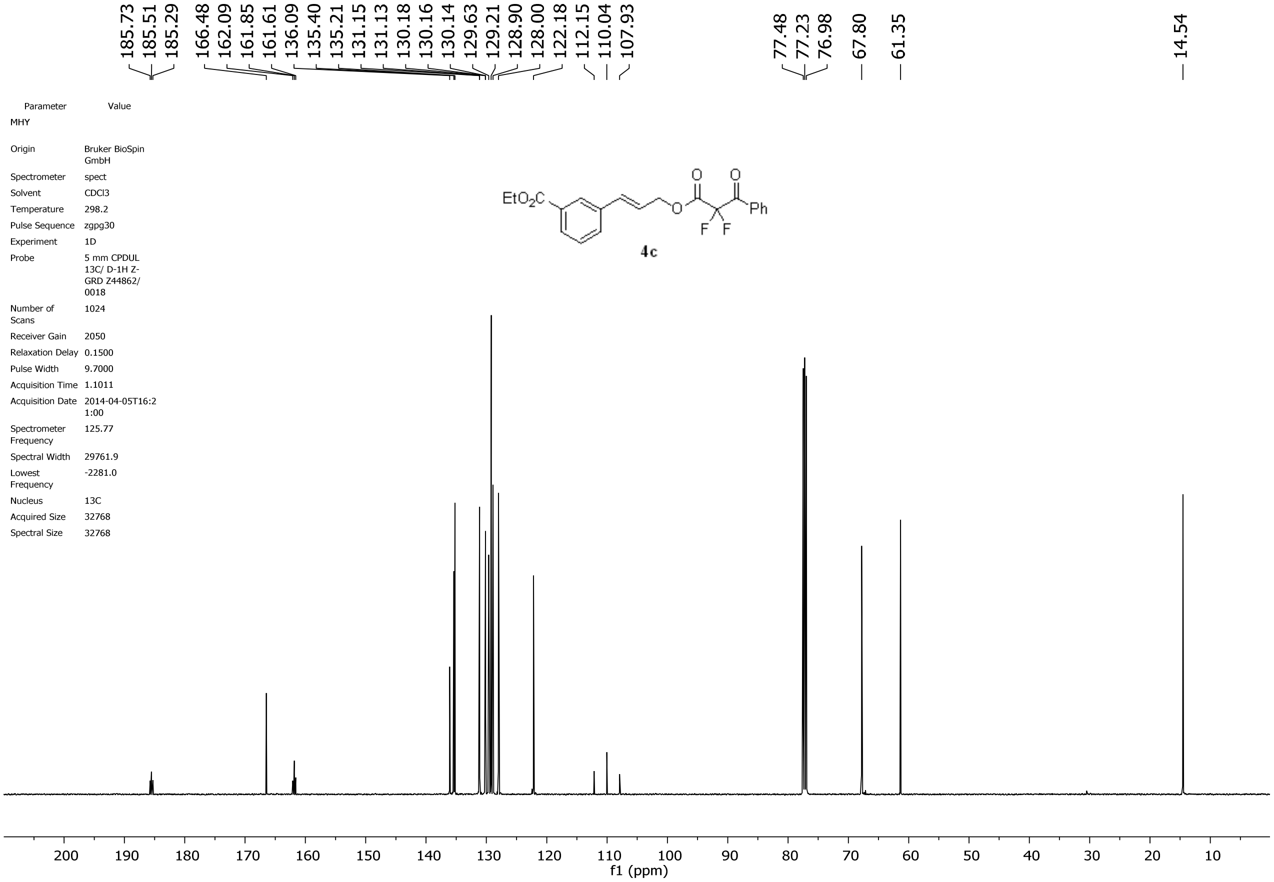
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-03-31T10:17:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-03-31T19:09:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.3
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

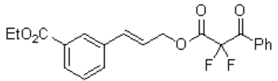


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-04T10:47:18
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-05T16:21:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-04-04T10:48:37
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



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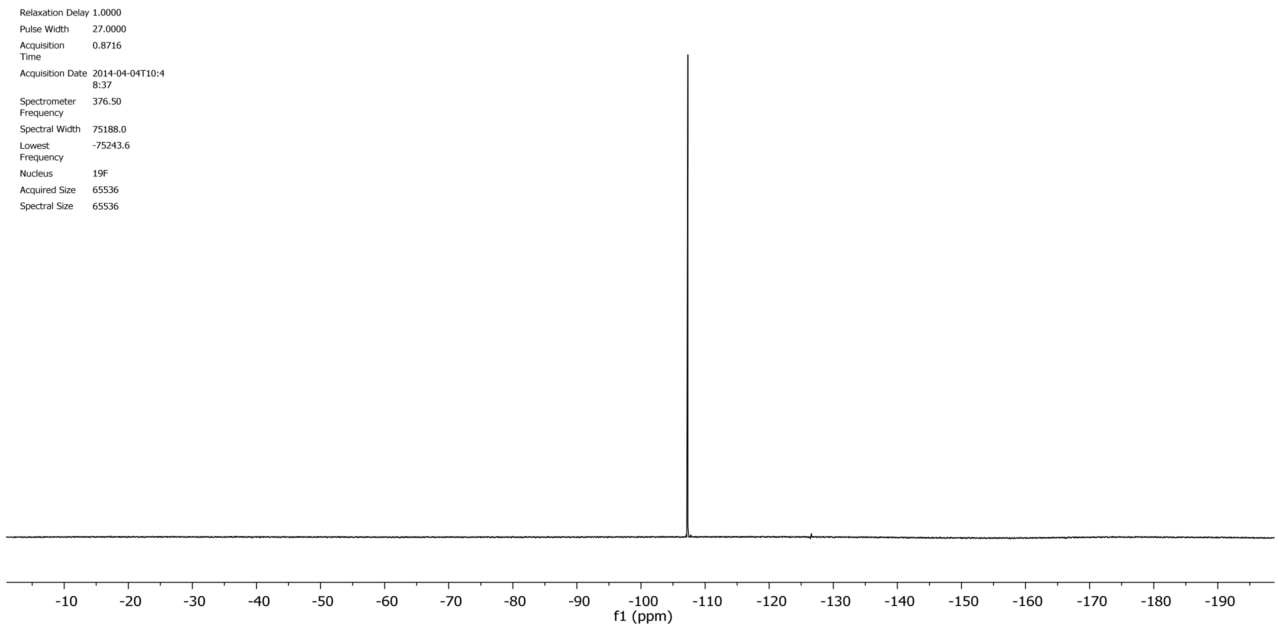
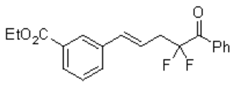


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	81
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-05-28T16:42:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



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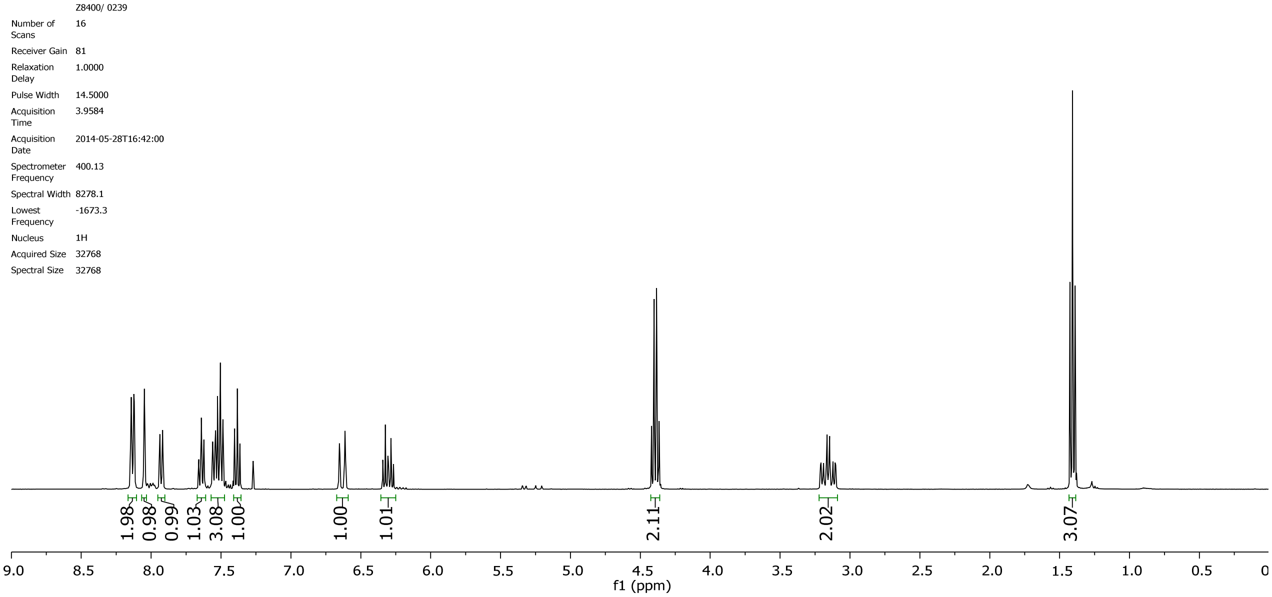
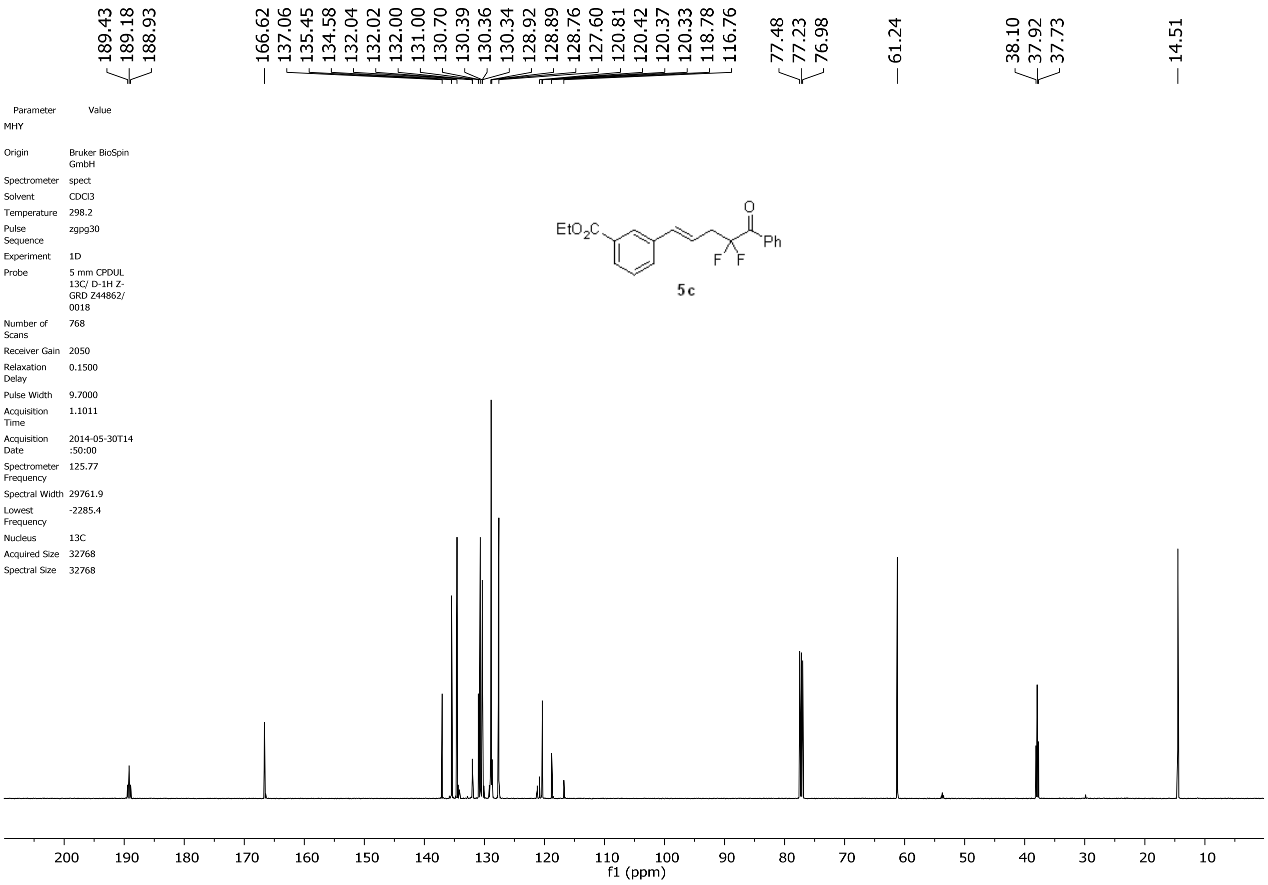
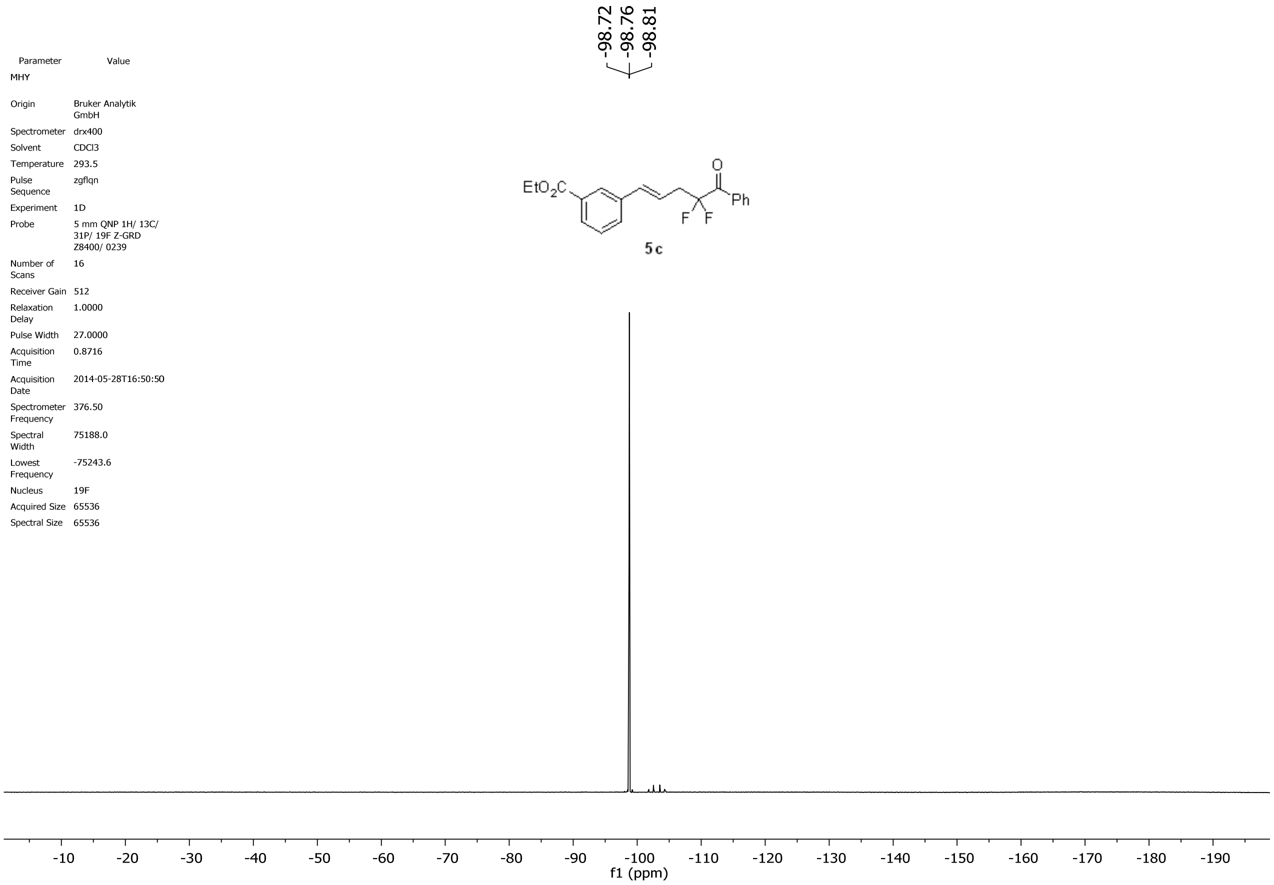
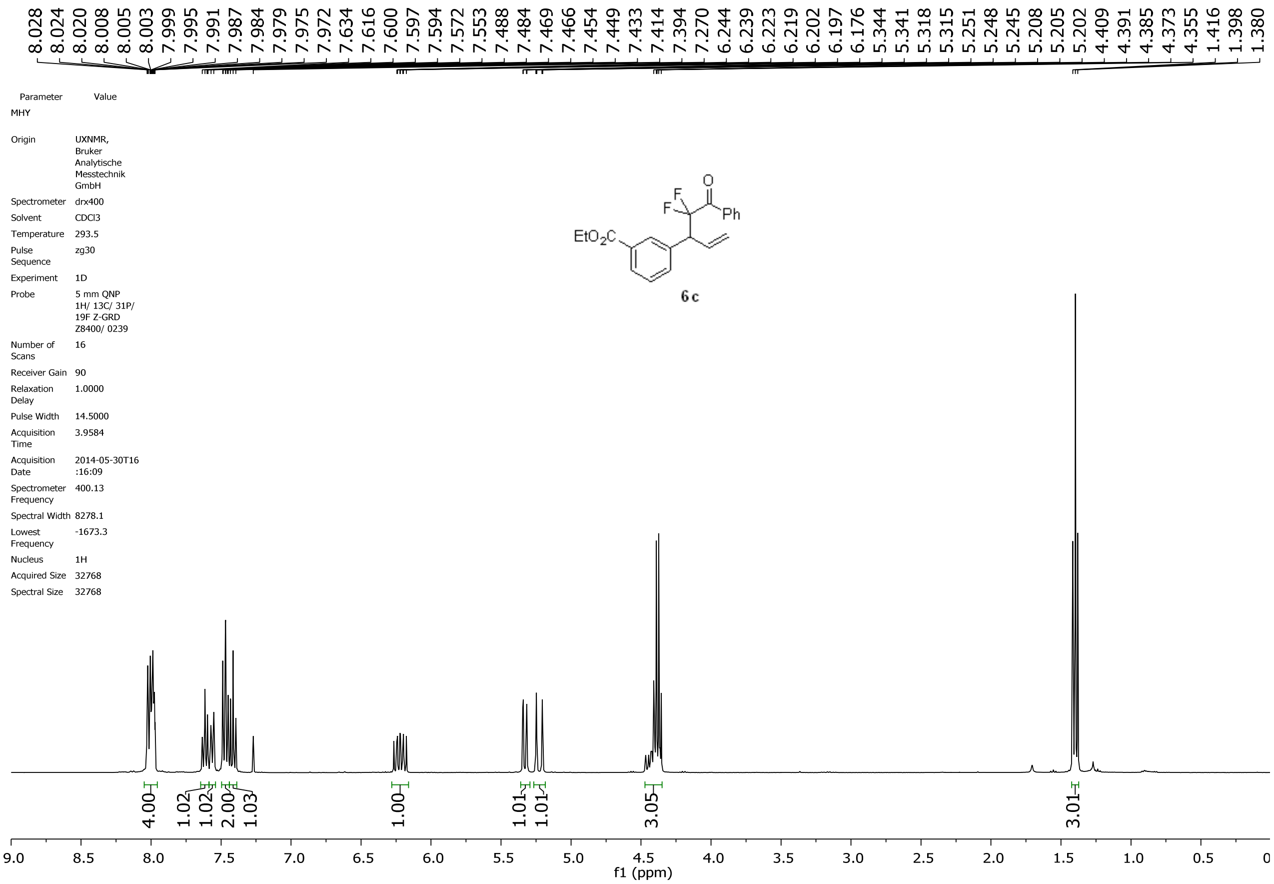




Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	768
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-30T14:50:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2285.4
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

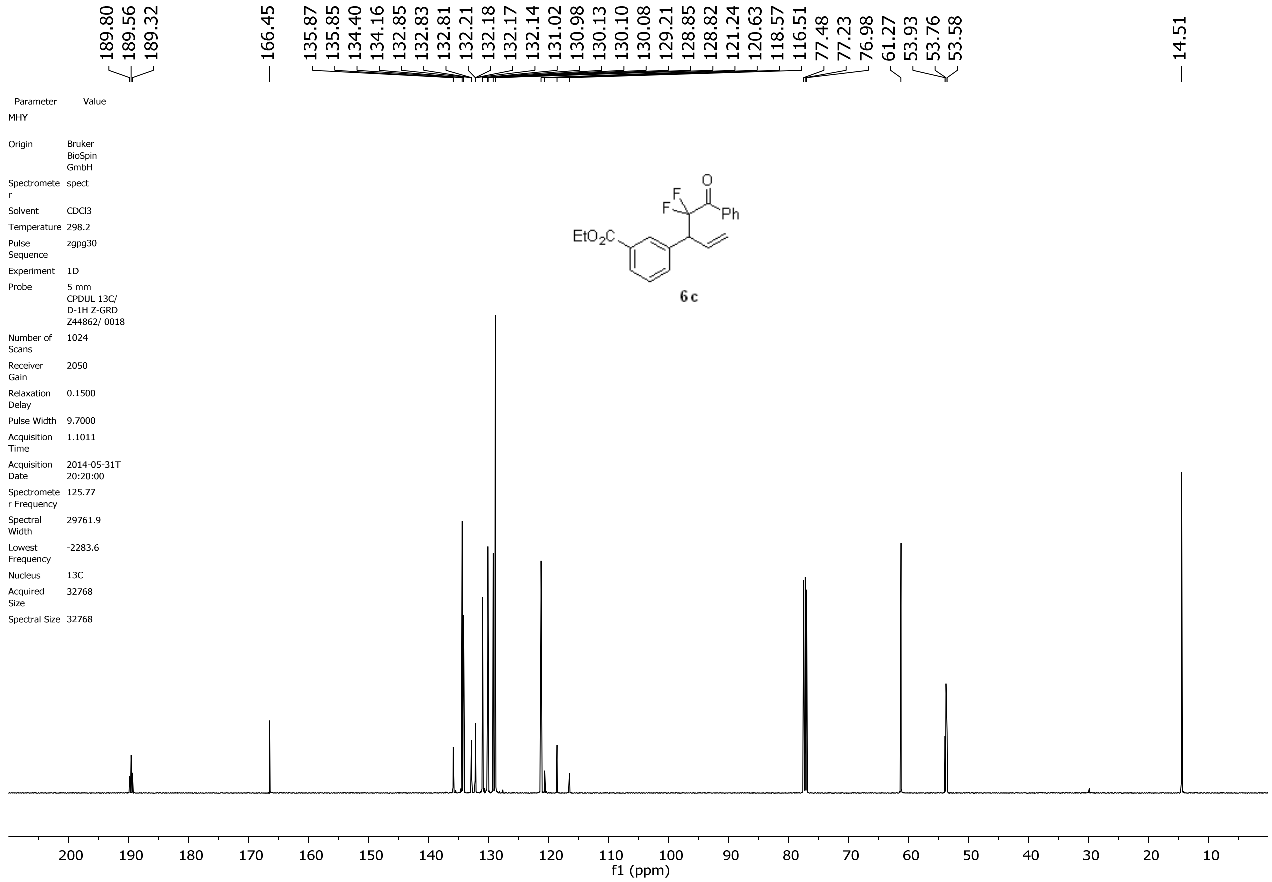


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-28T16:50:50
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



6c

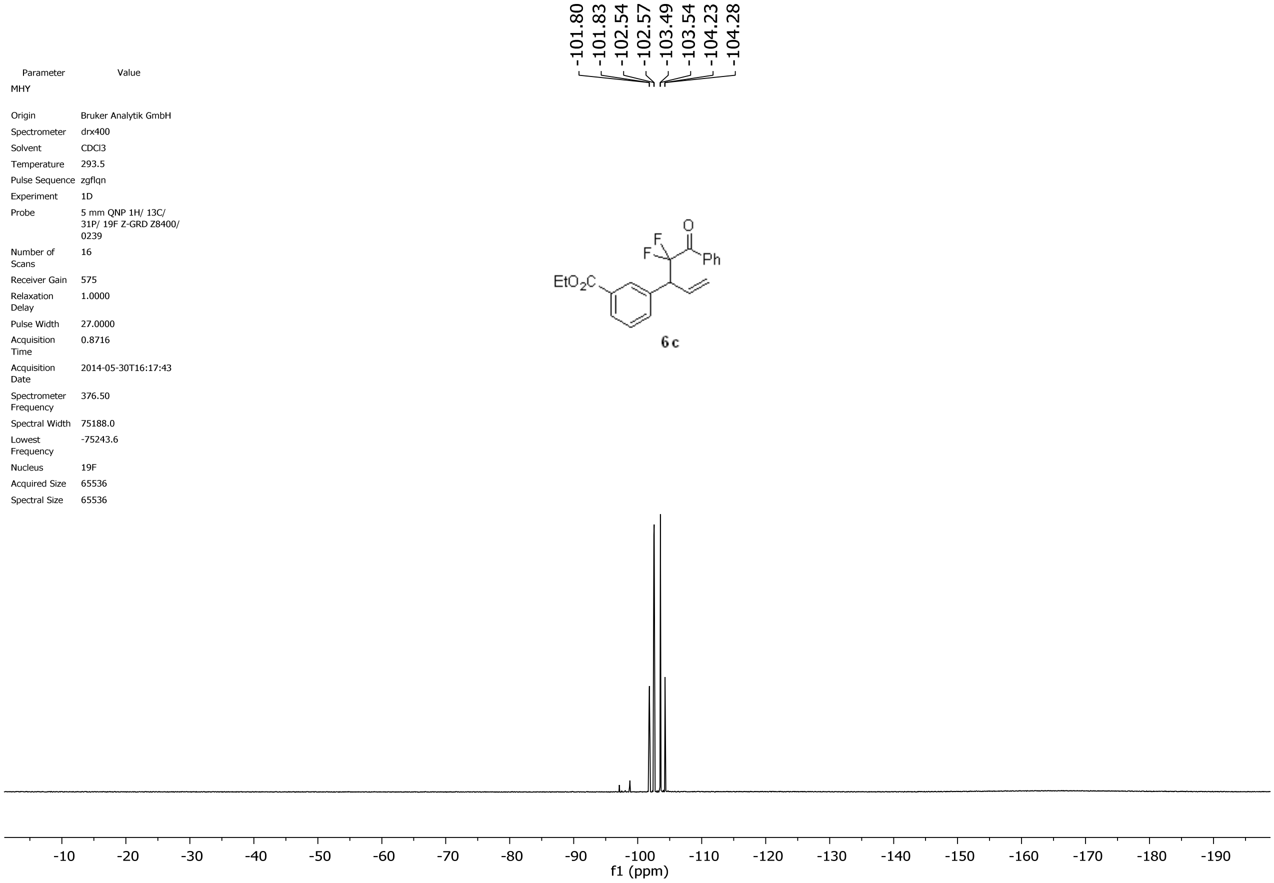
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	90
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-05-30T16 :16:09
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



6c

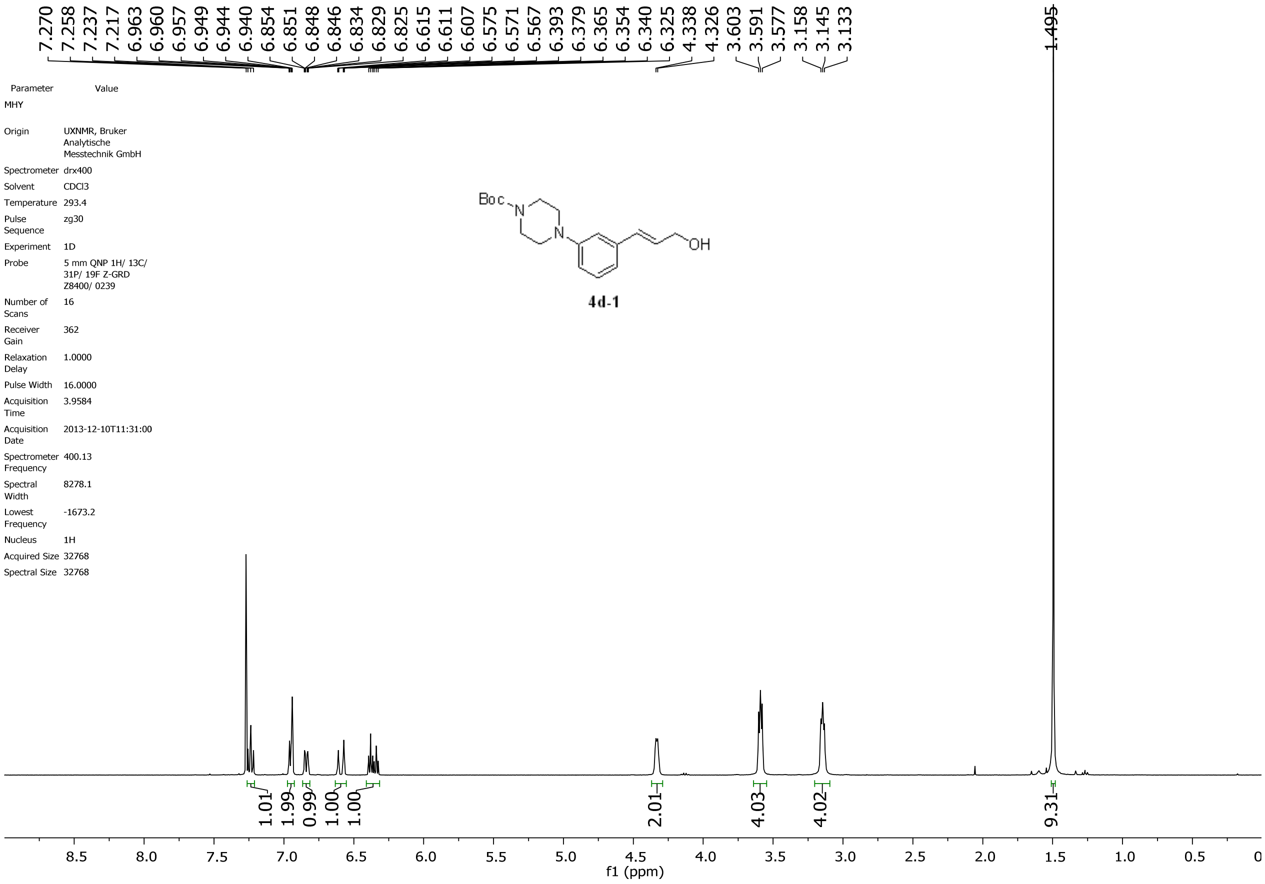
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-31T 20:20:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2283.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-30T16:17:43
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

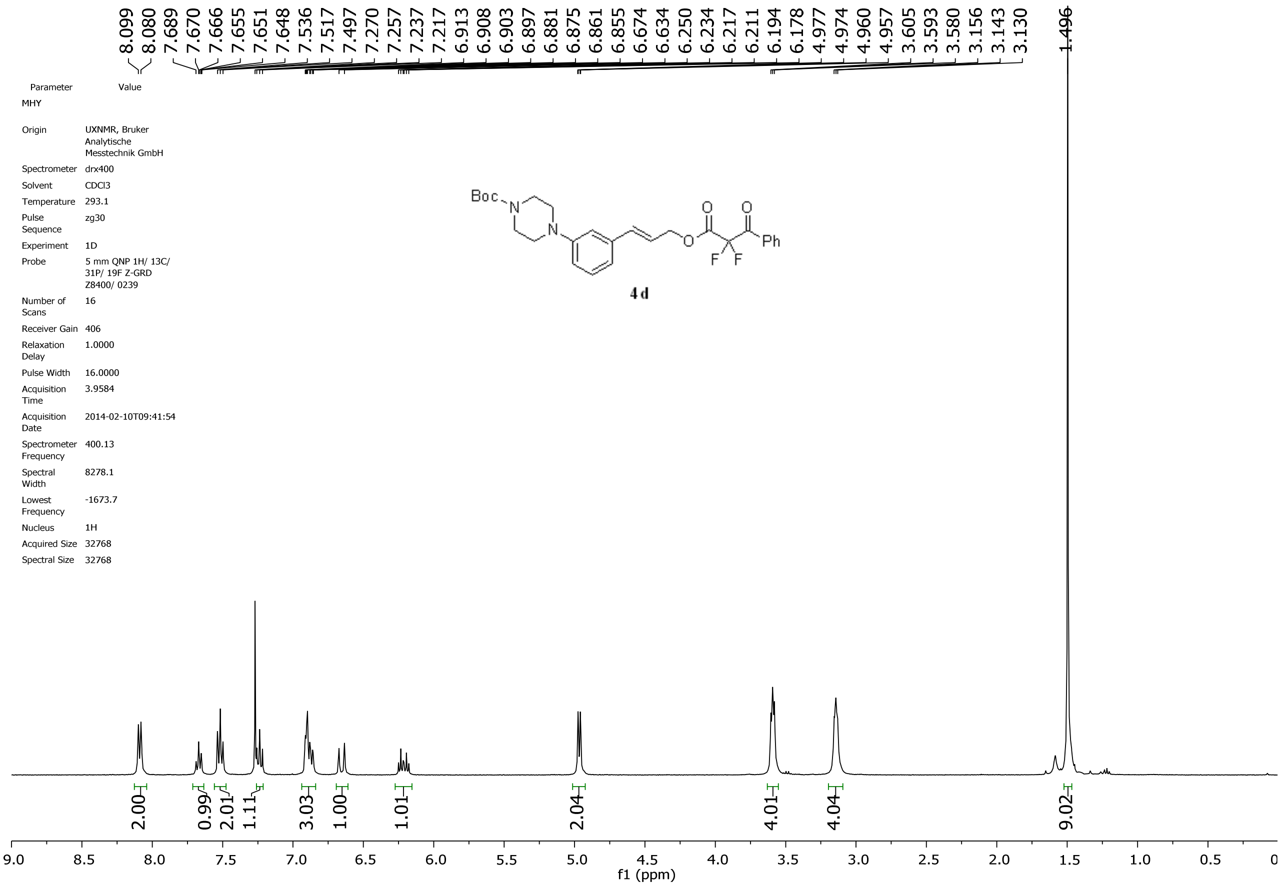


6c

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-10T11:31:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.2
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

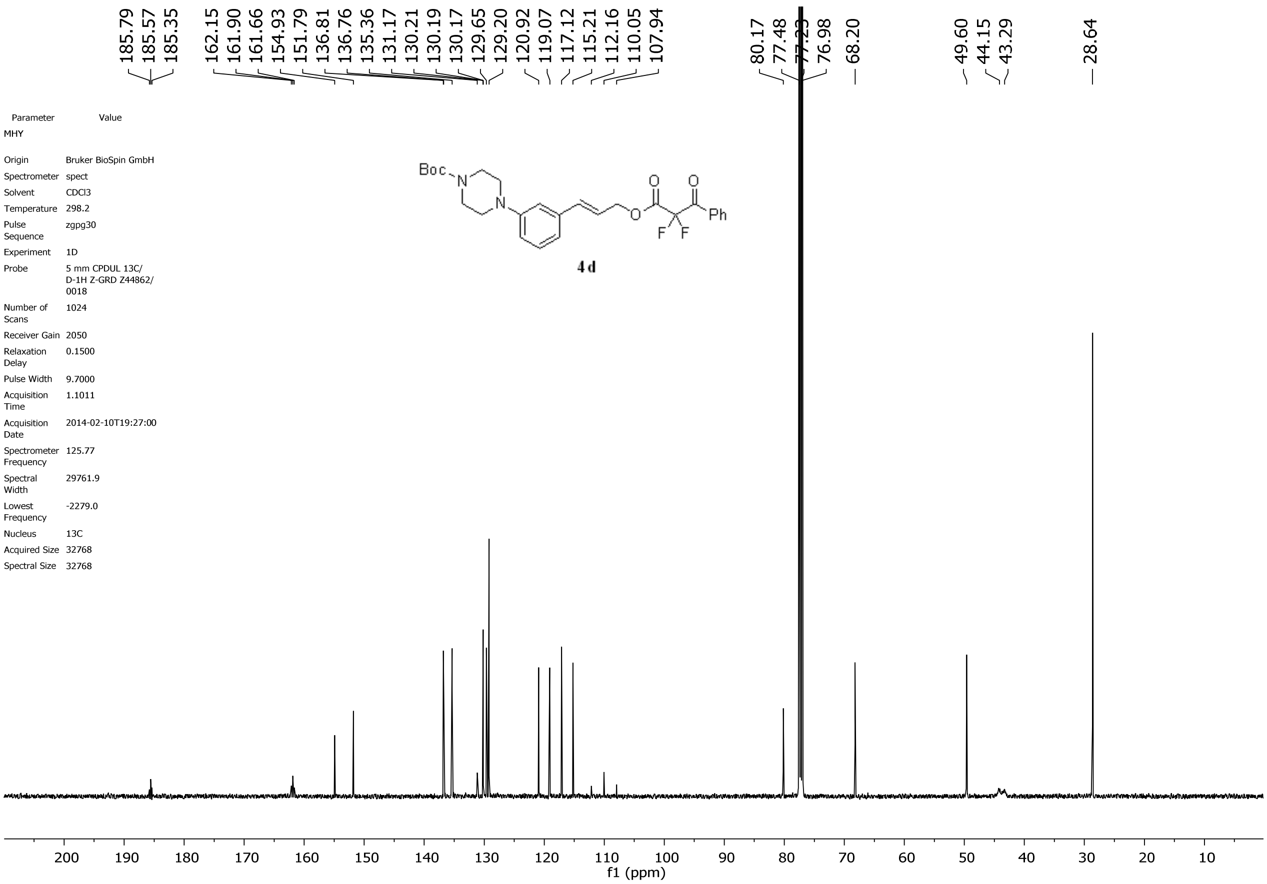


4d-1



4d

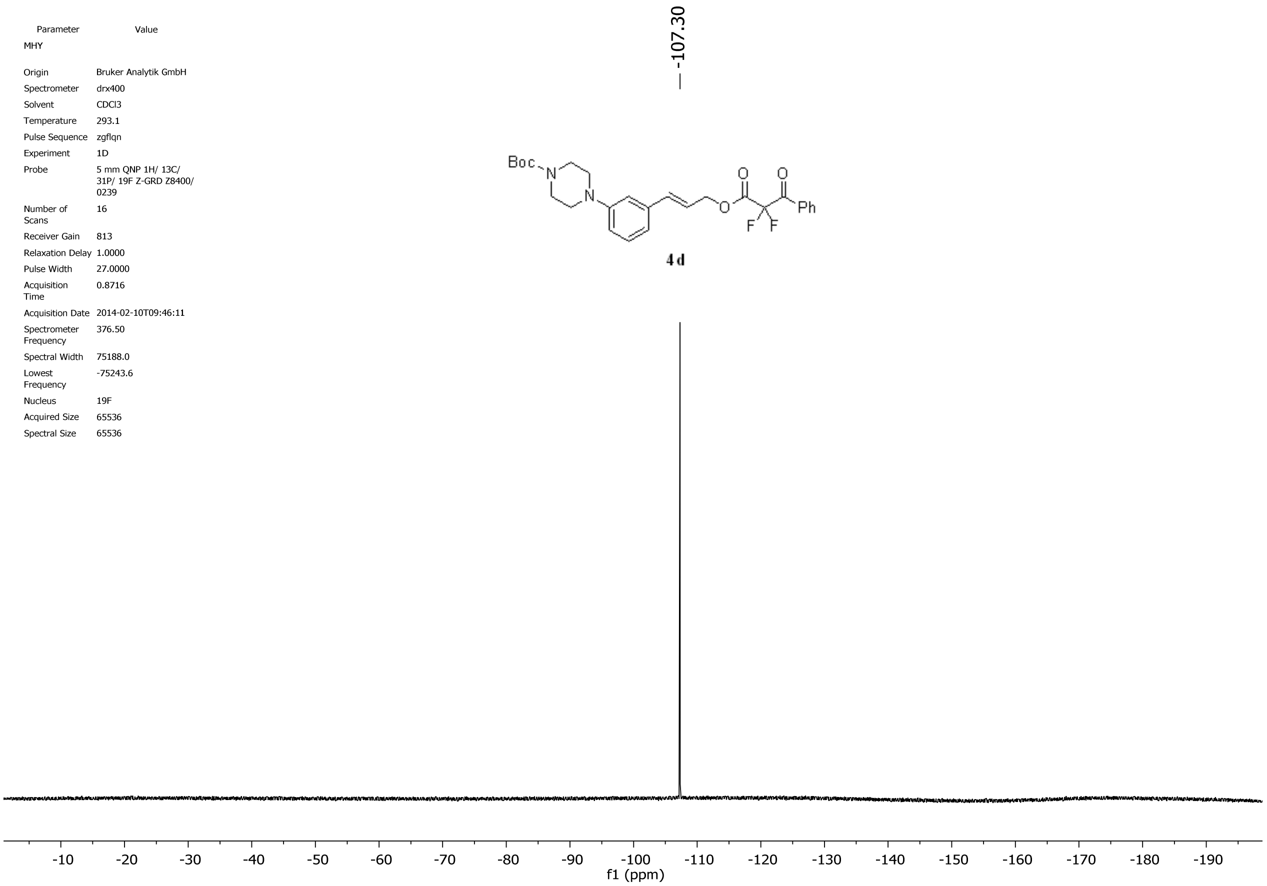
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-10T09:41:54
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



4d

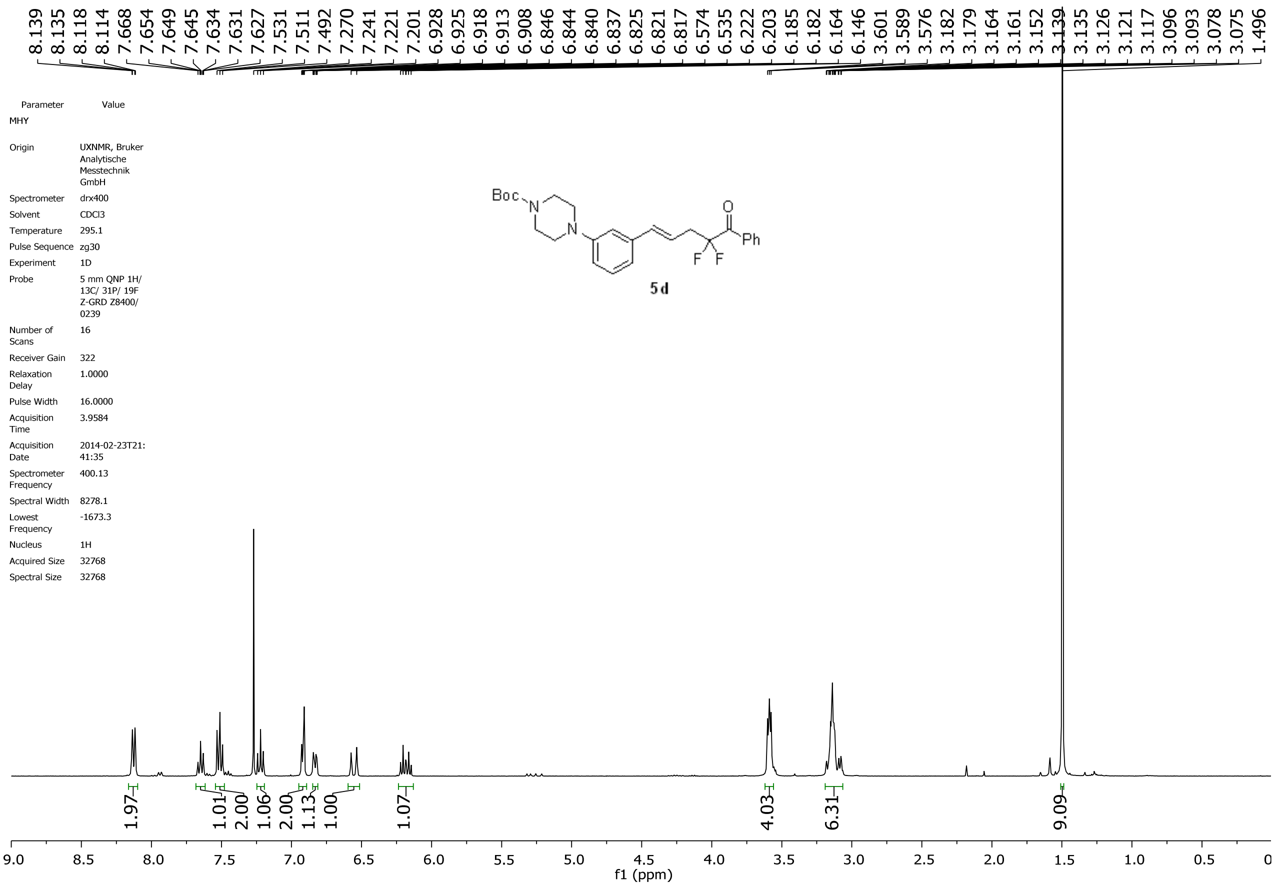
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-10T19:27:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-10T09:46:11
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

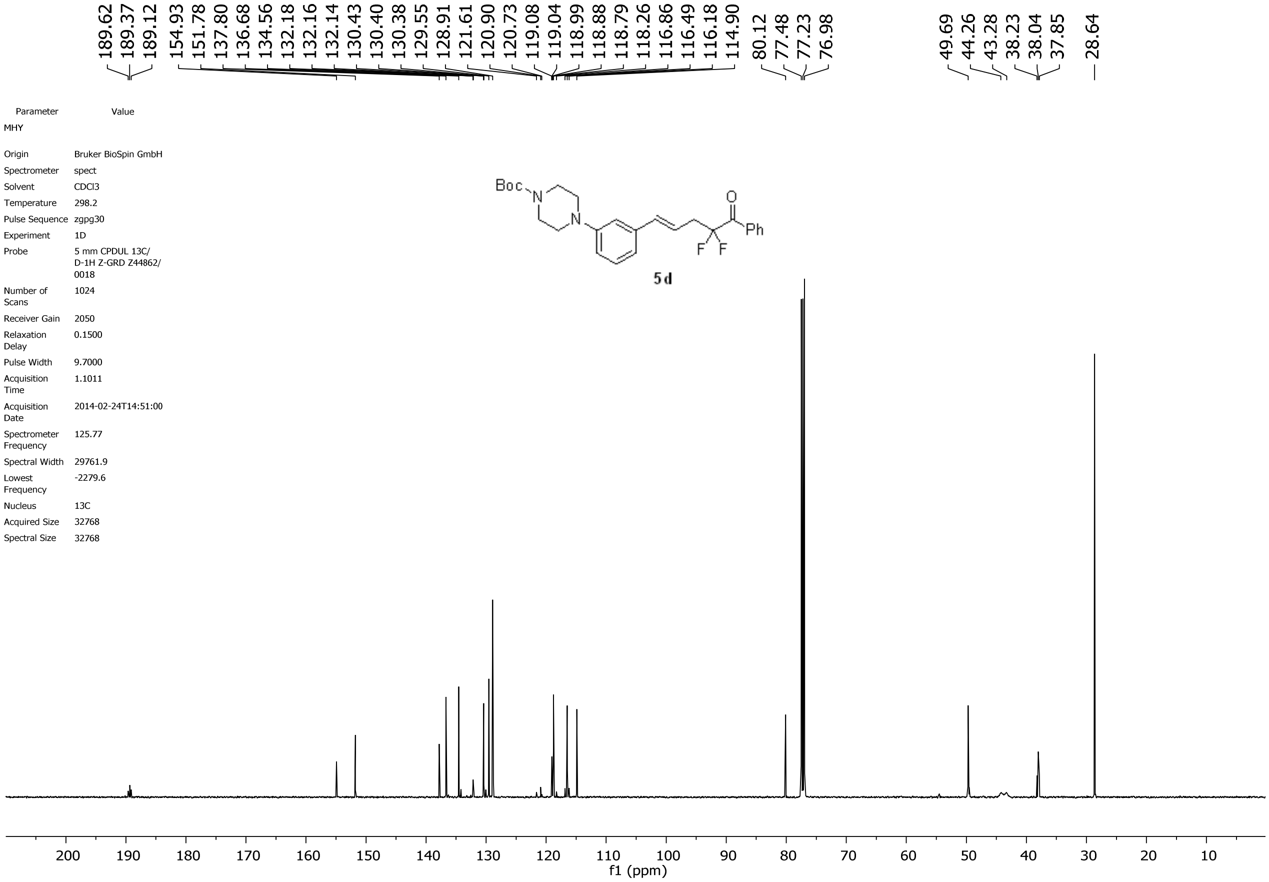


4d

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-23T21:41:35
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

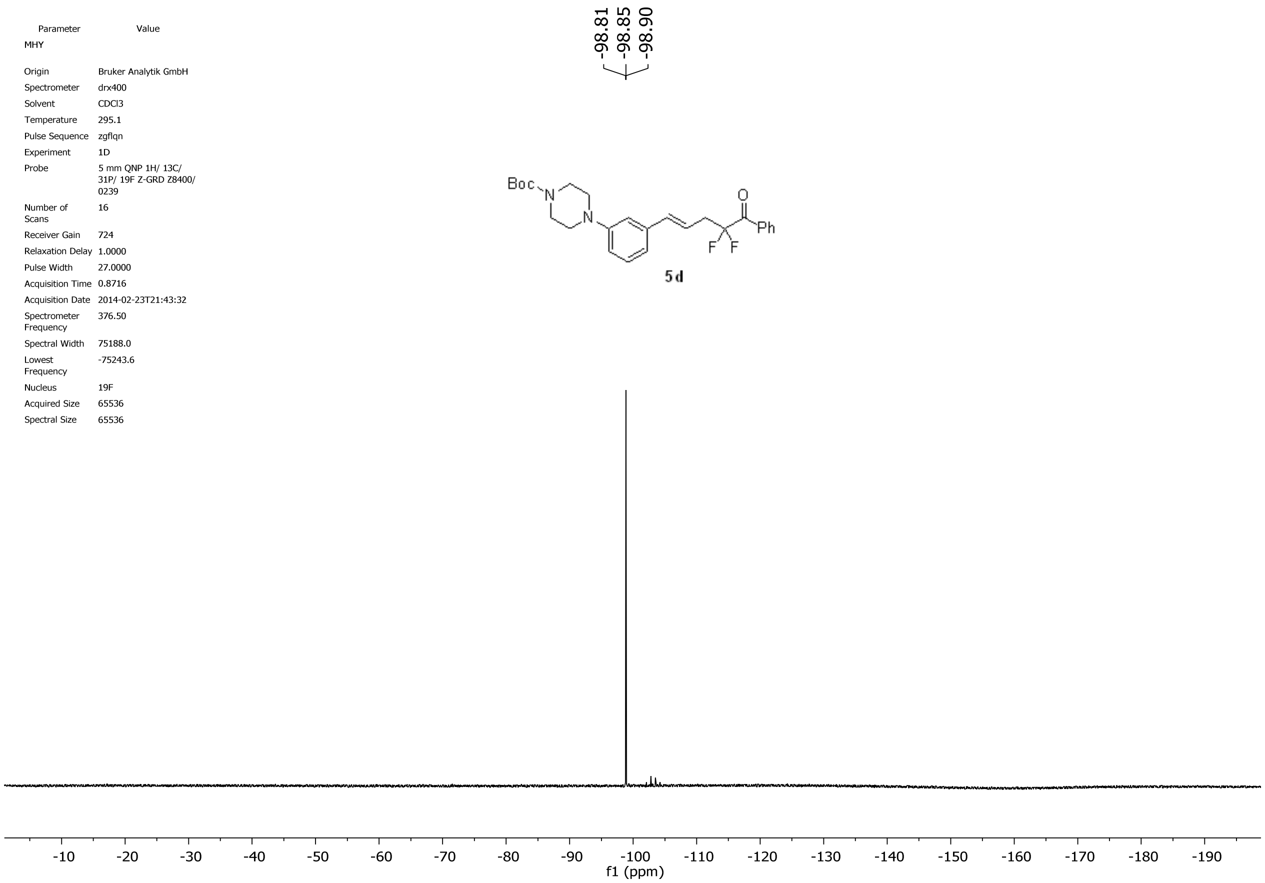


5d



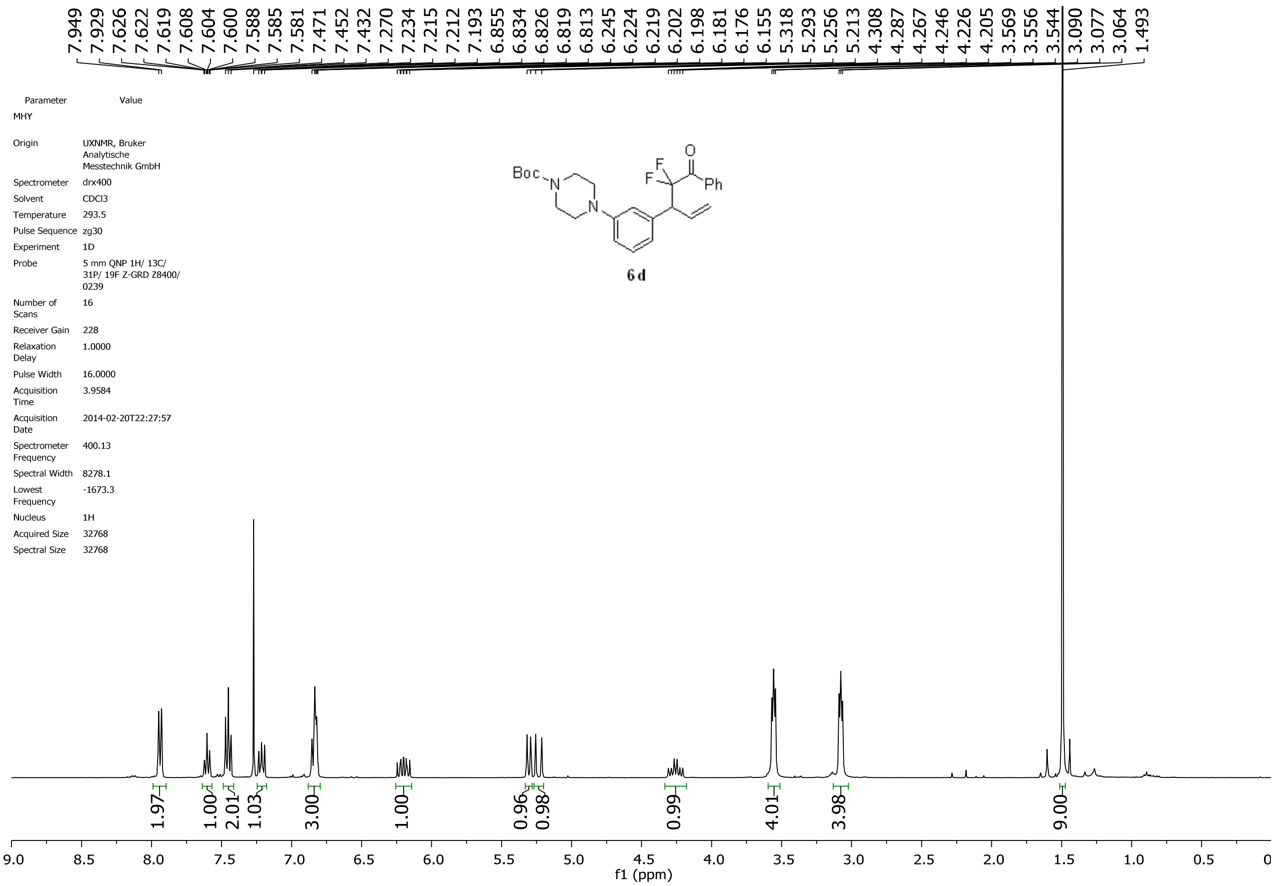
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-24T14:51:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

5d

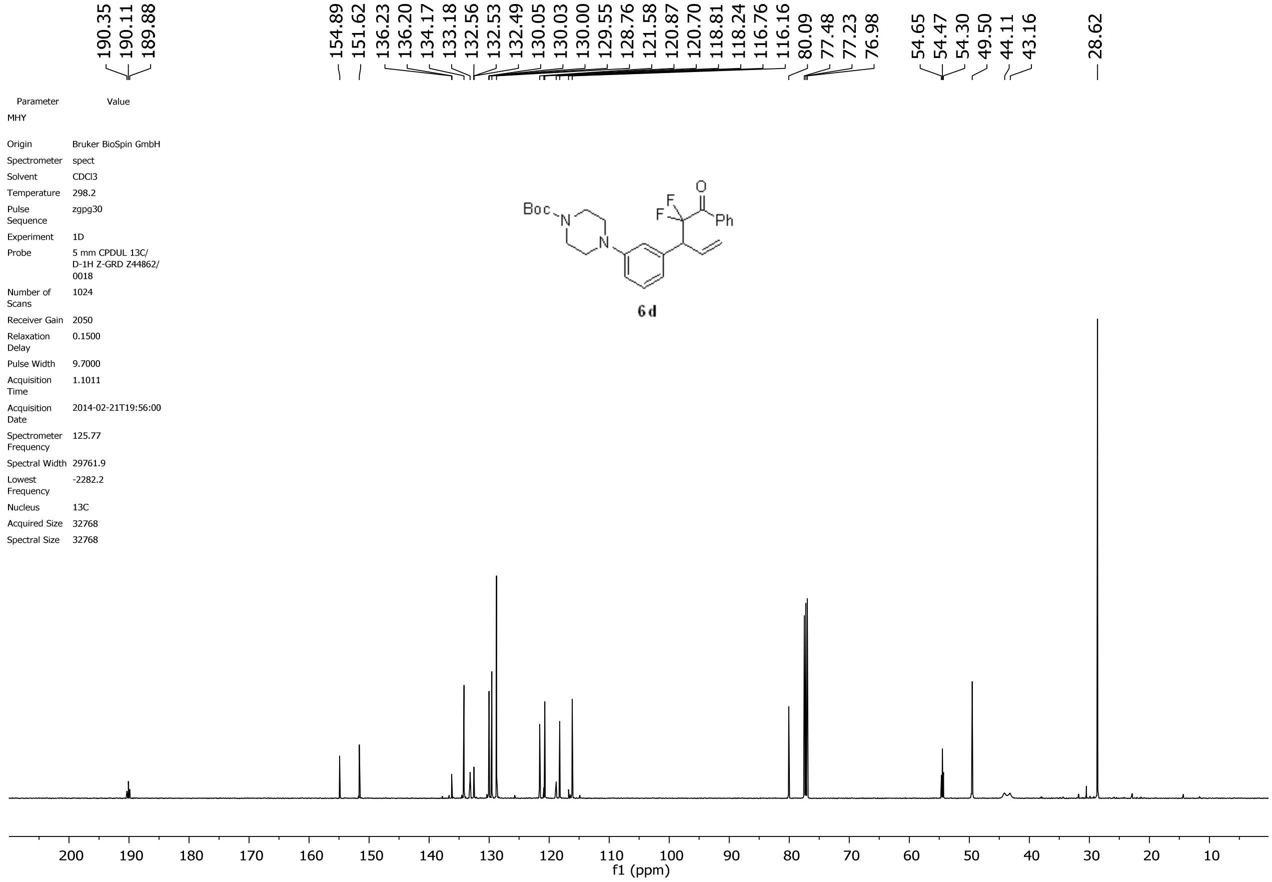


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	295.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-23T21:43:32
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

5d

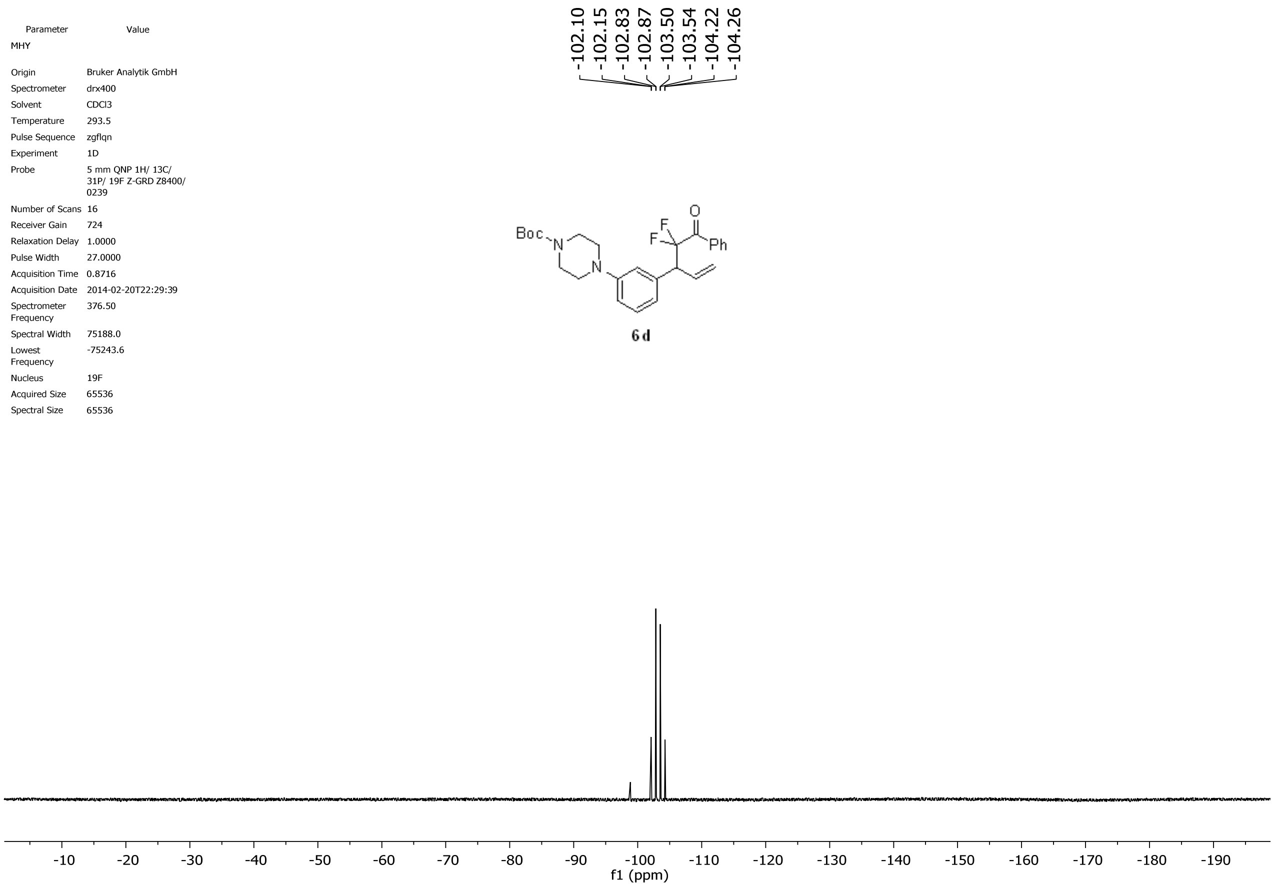


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-20T22:27:57
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



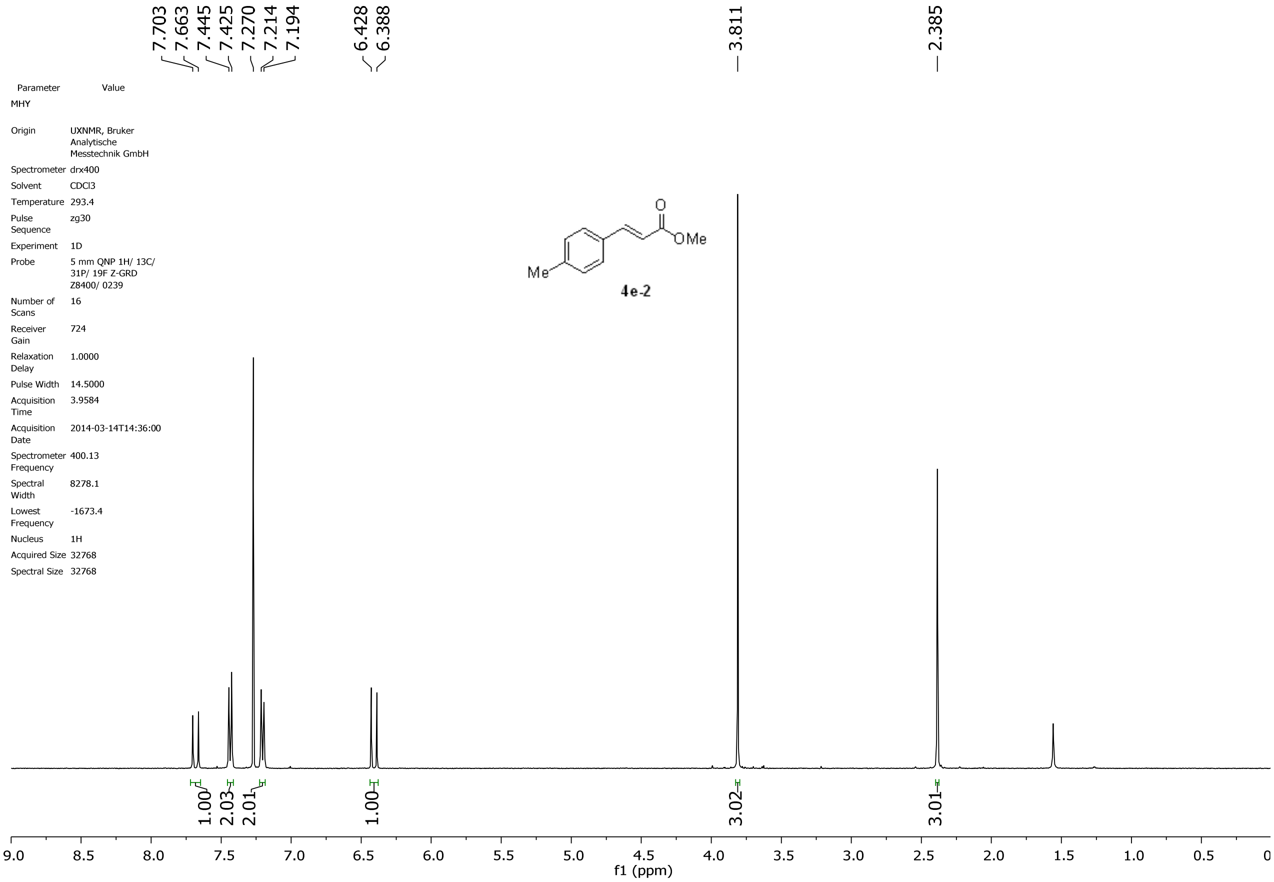
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-21T19:56:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2282.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-20T22:29:39
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

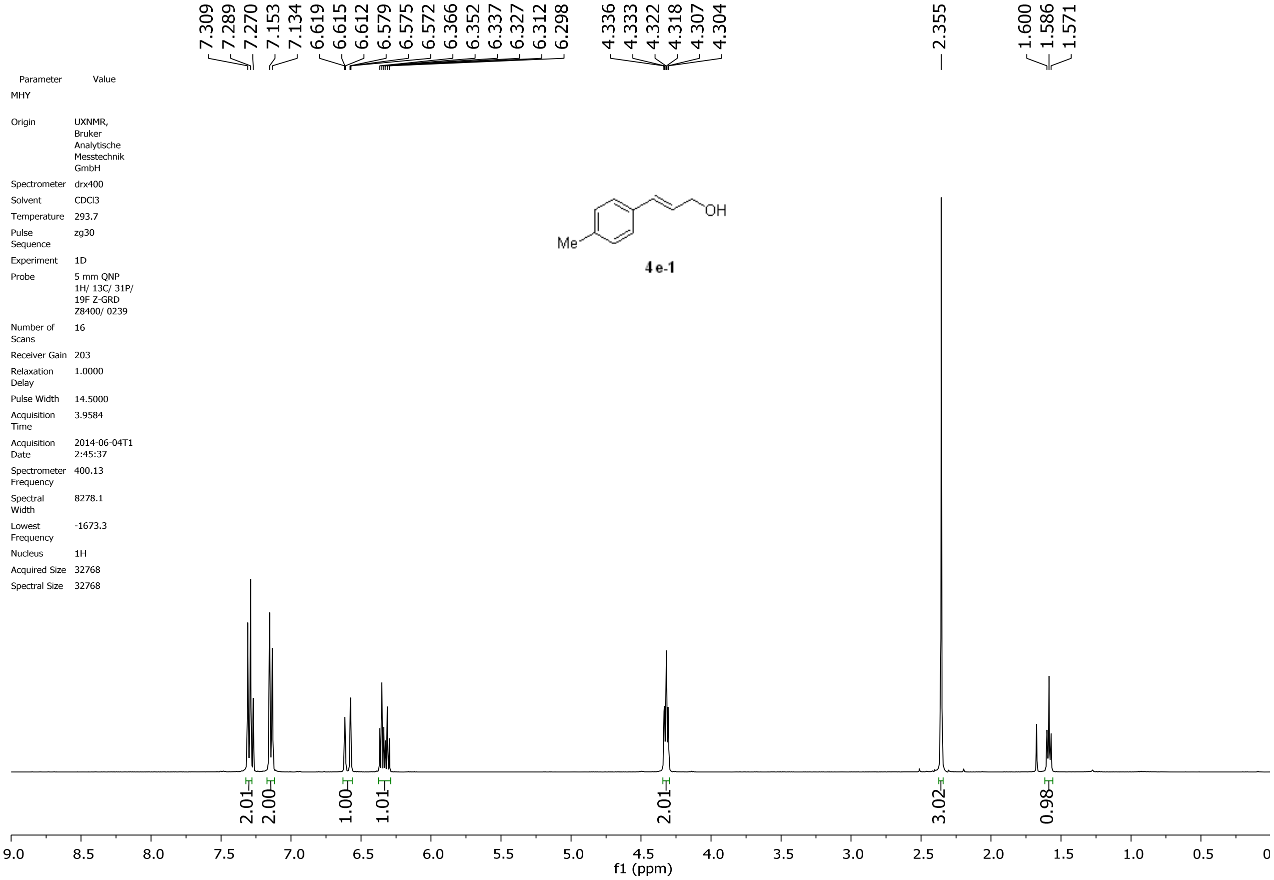


6d

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-03-14T14:36:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

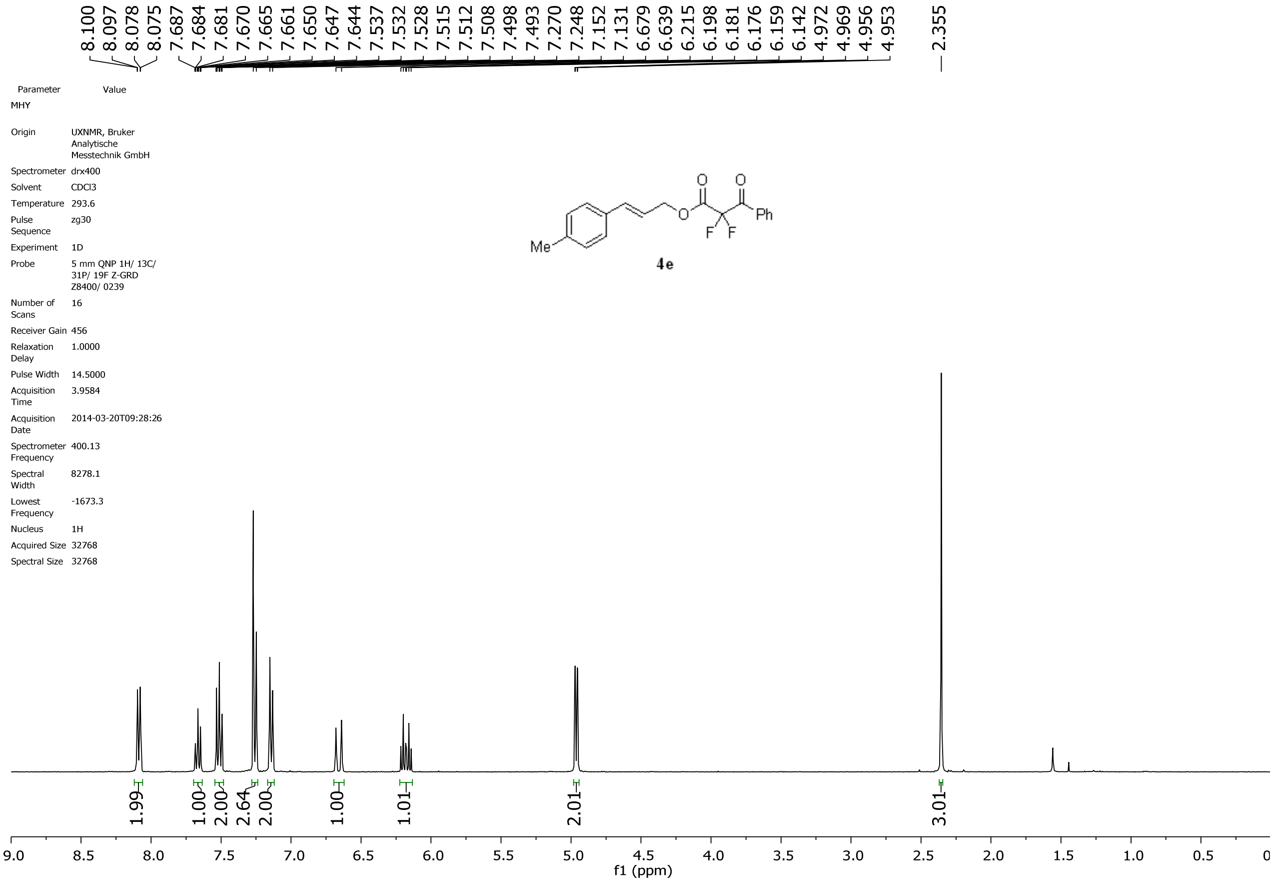


4e-2



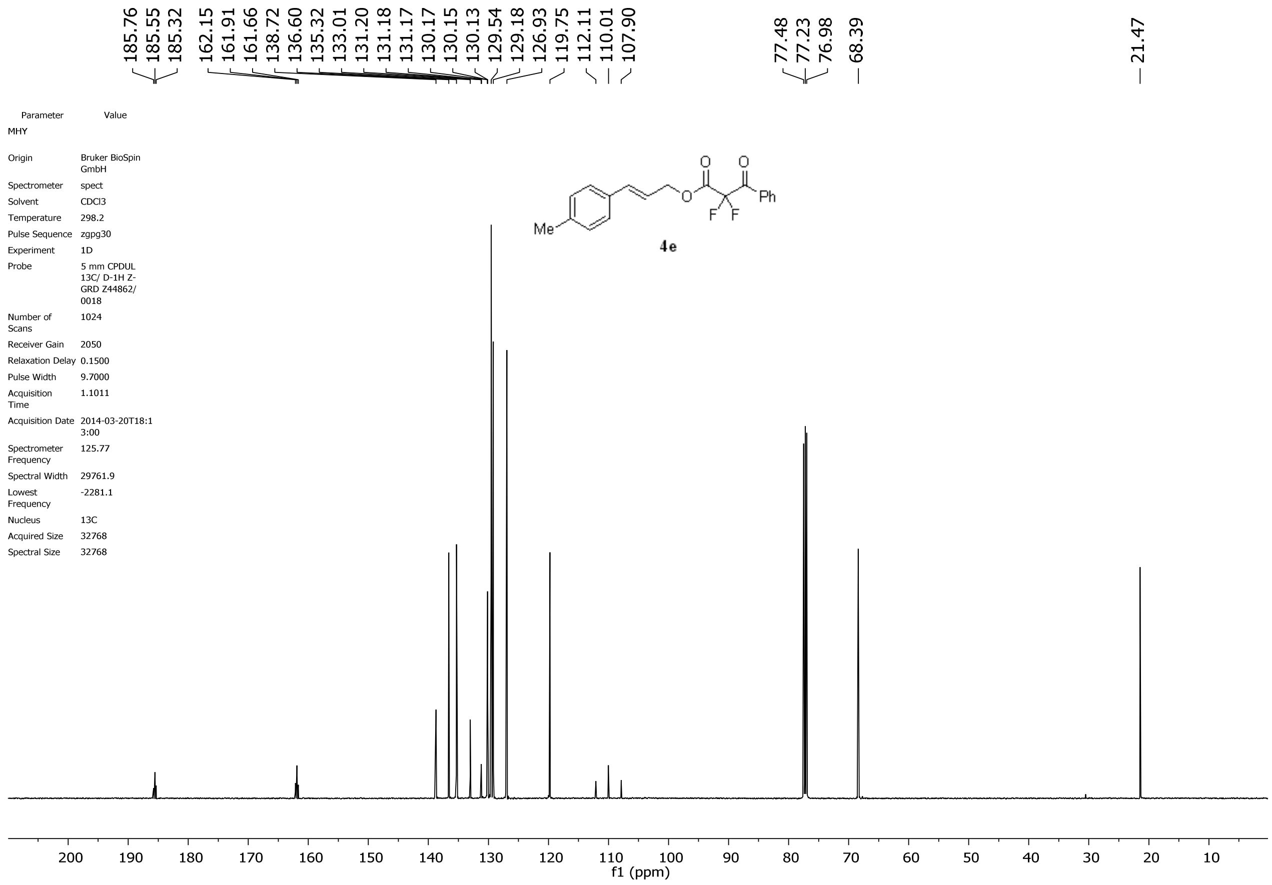
4e-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-04T1 2:45:37
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

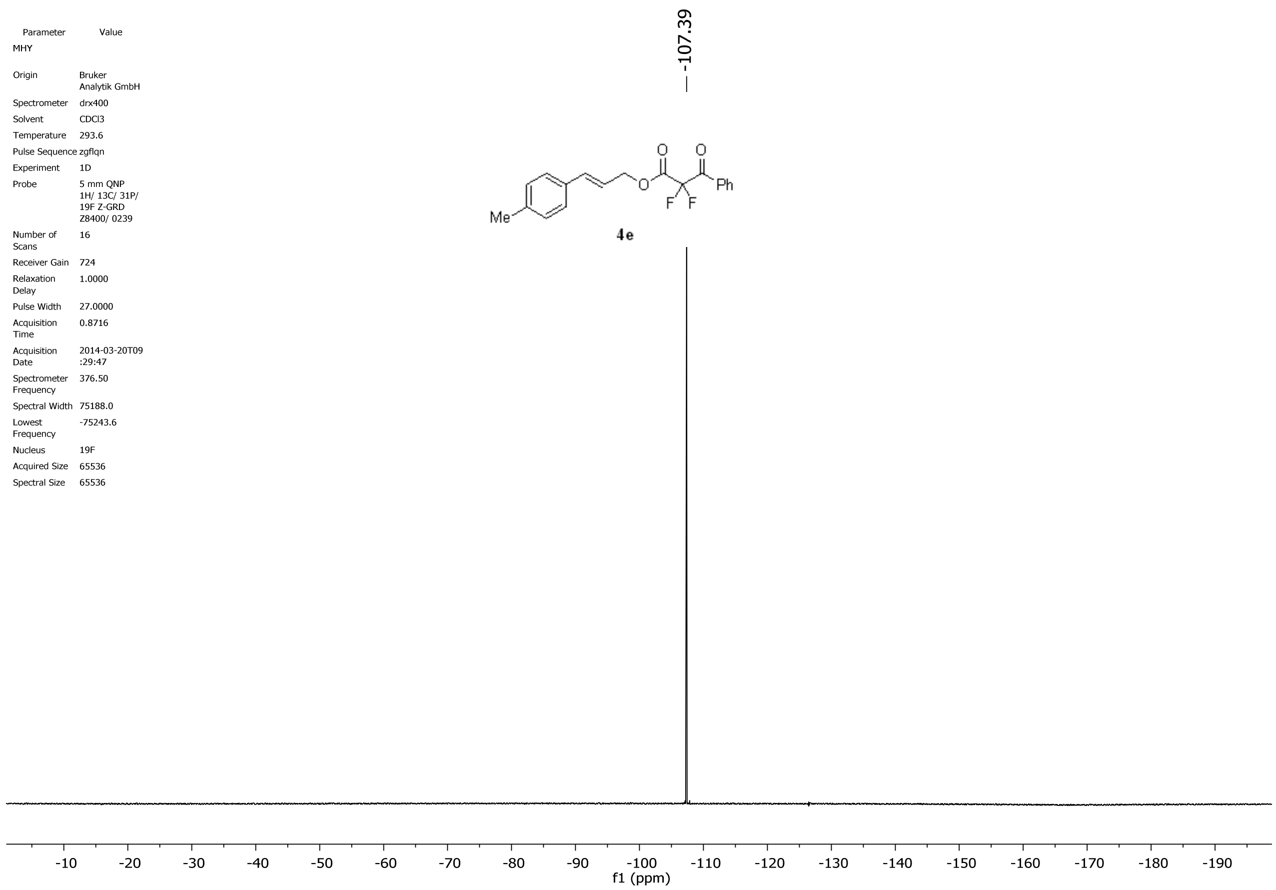


4e

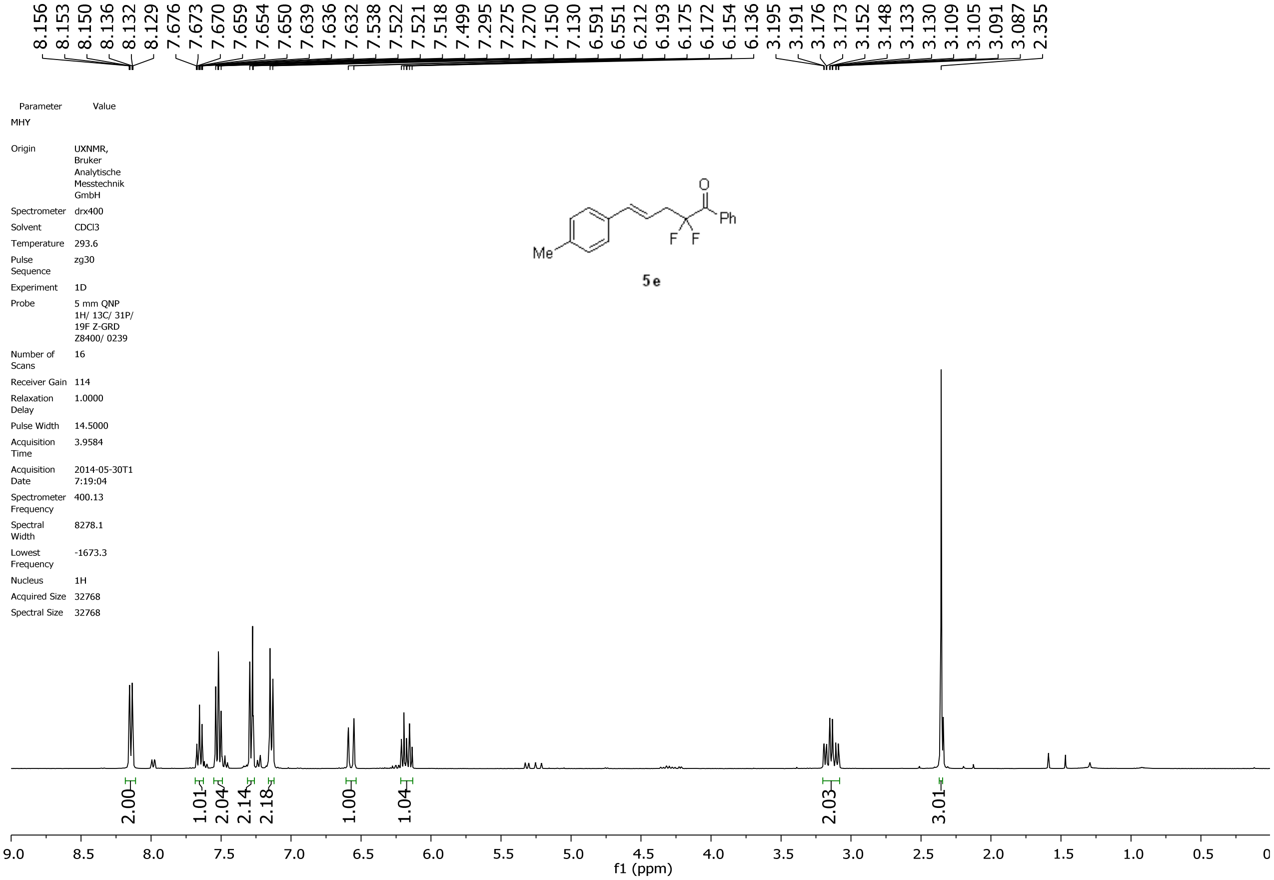
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-03-20T09:28:26
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-03-20T18:13:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

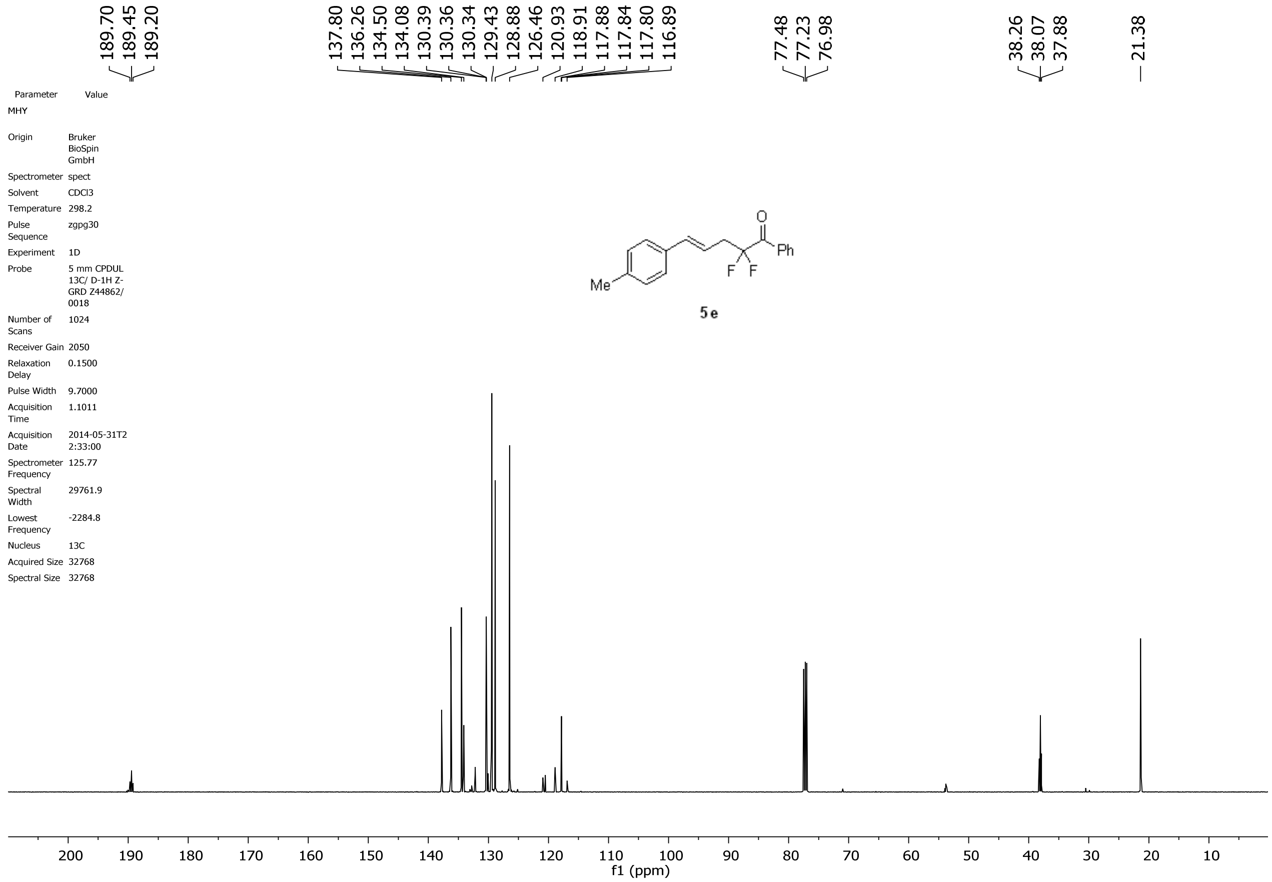


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-03-20T09:29:47
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



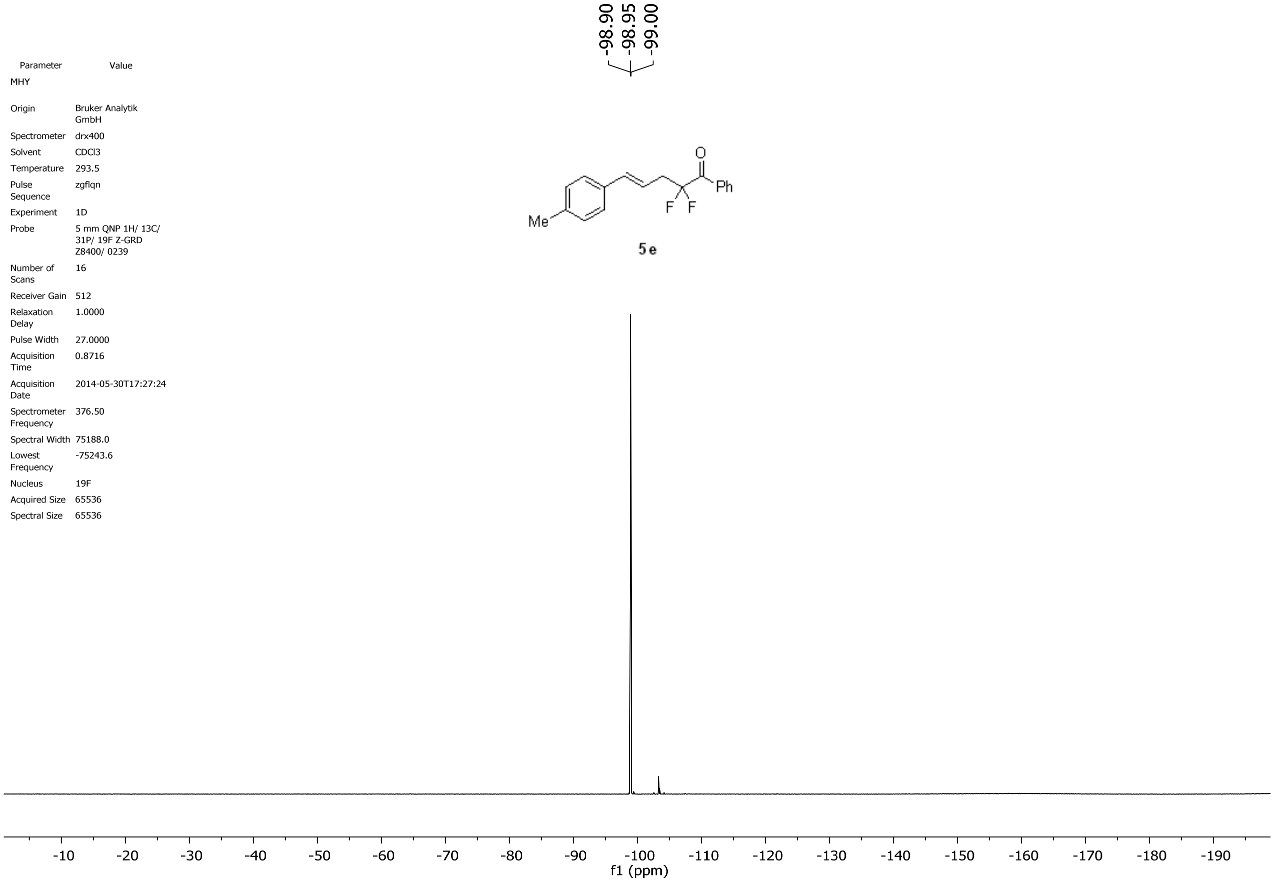
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	114
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-05-30T17:19:04
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

5e



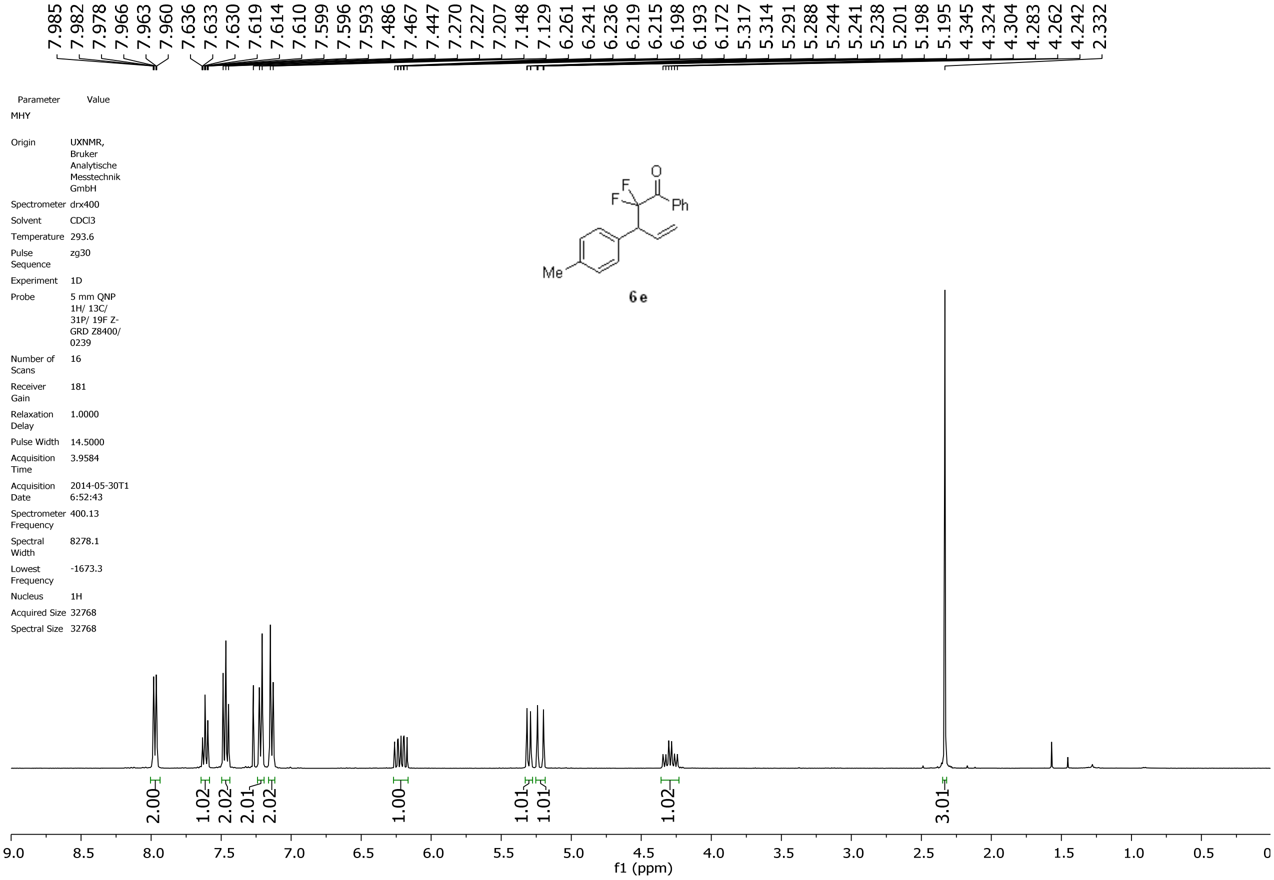
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-31T22:33:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2284.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

5e



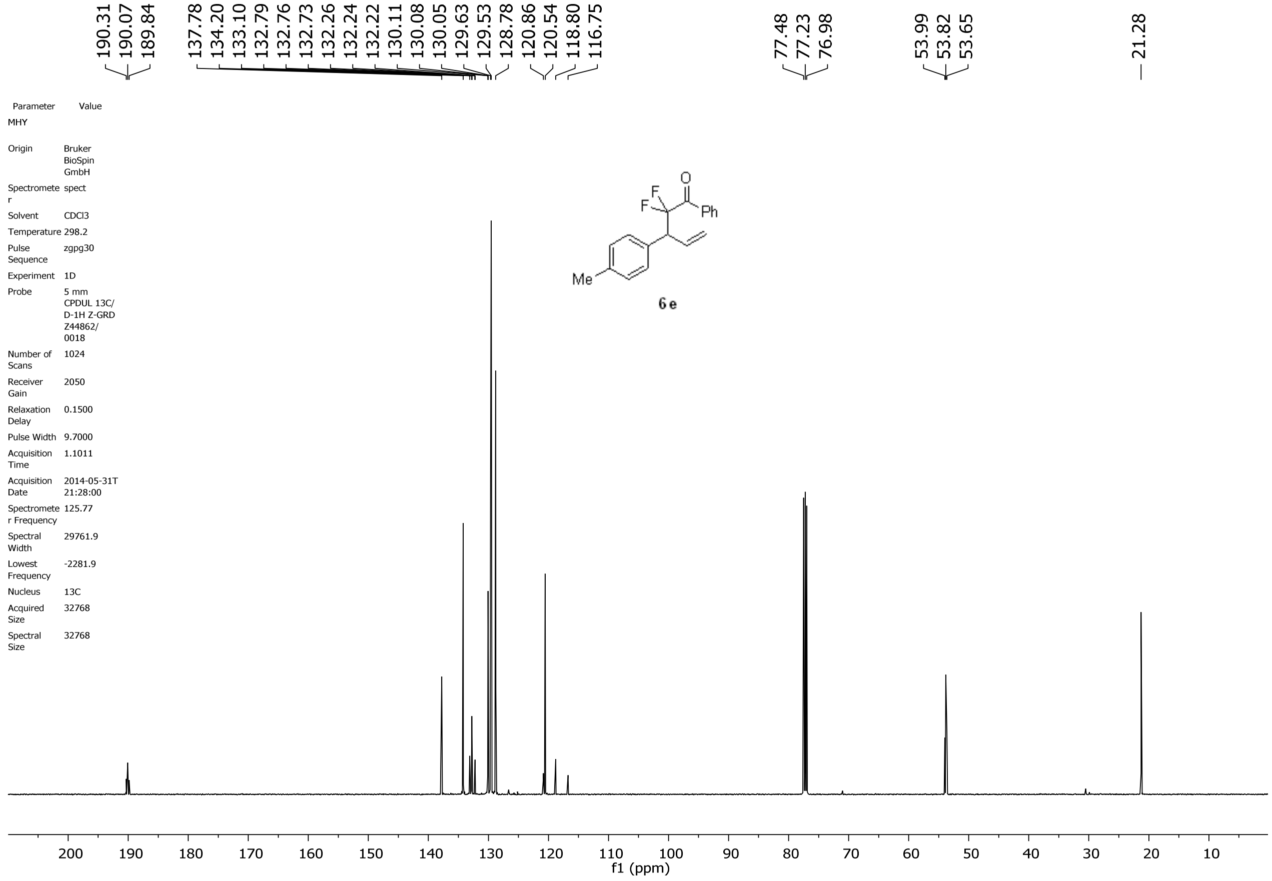
5e

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-30T17:27:24
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

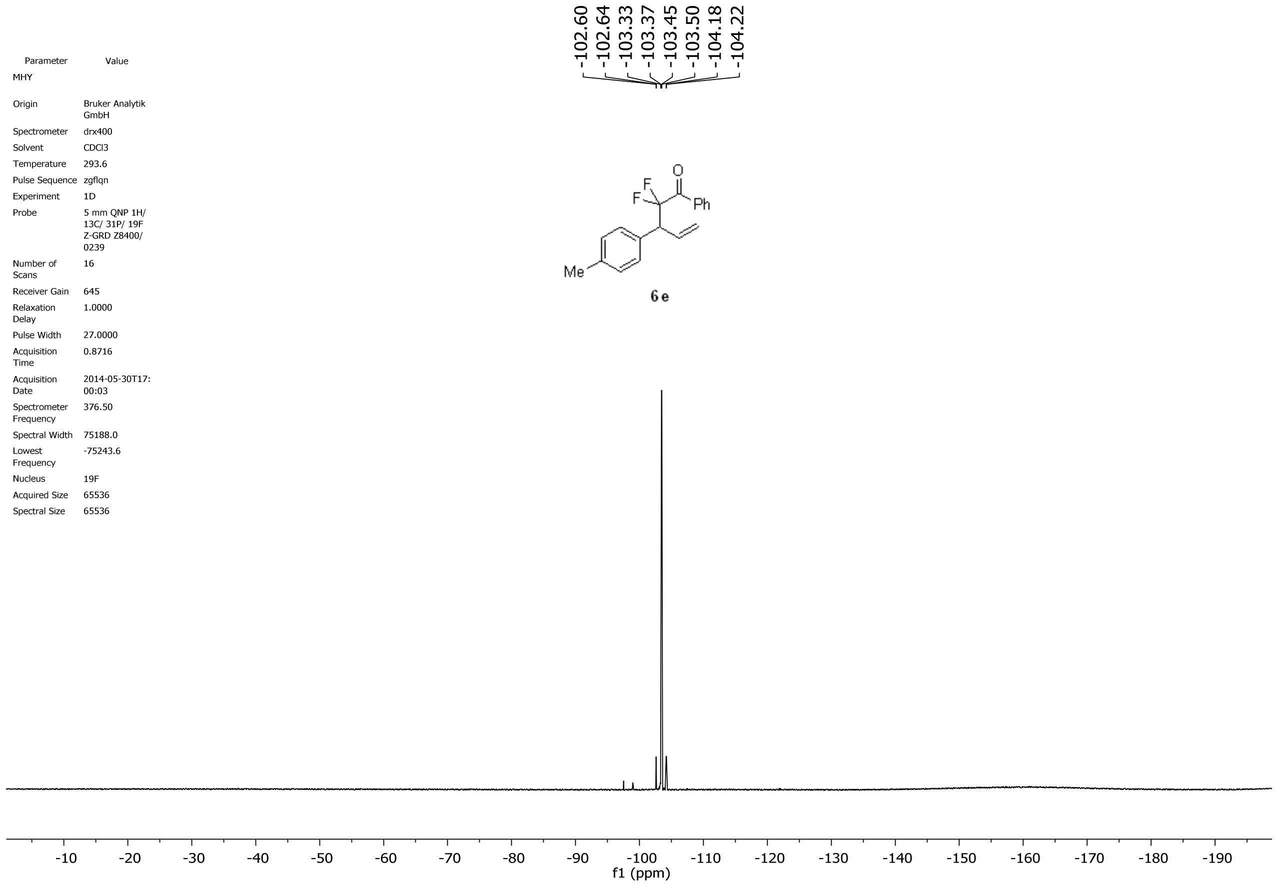


6e

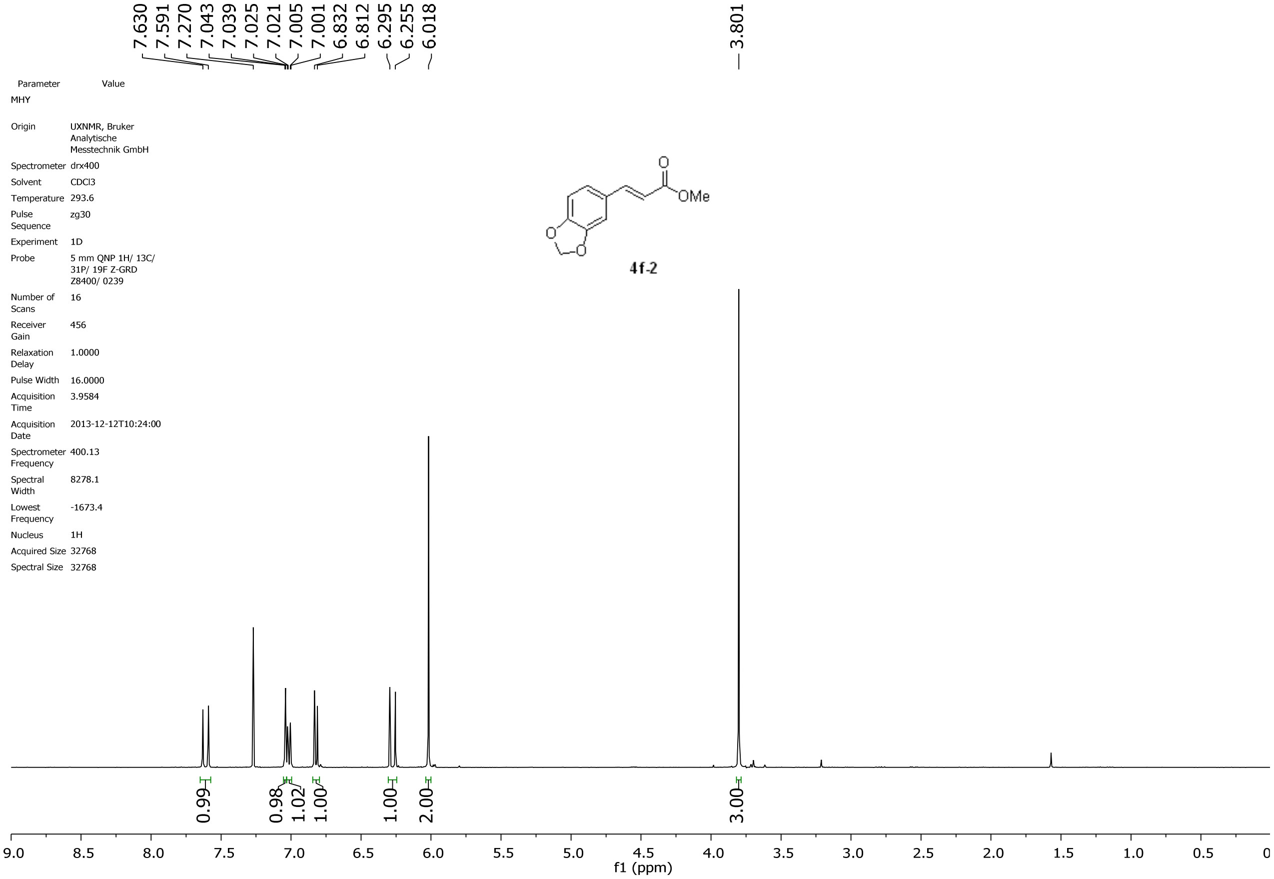
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-05-30T16:52:43
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-31T 21:28:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

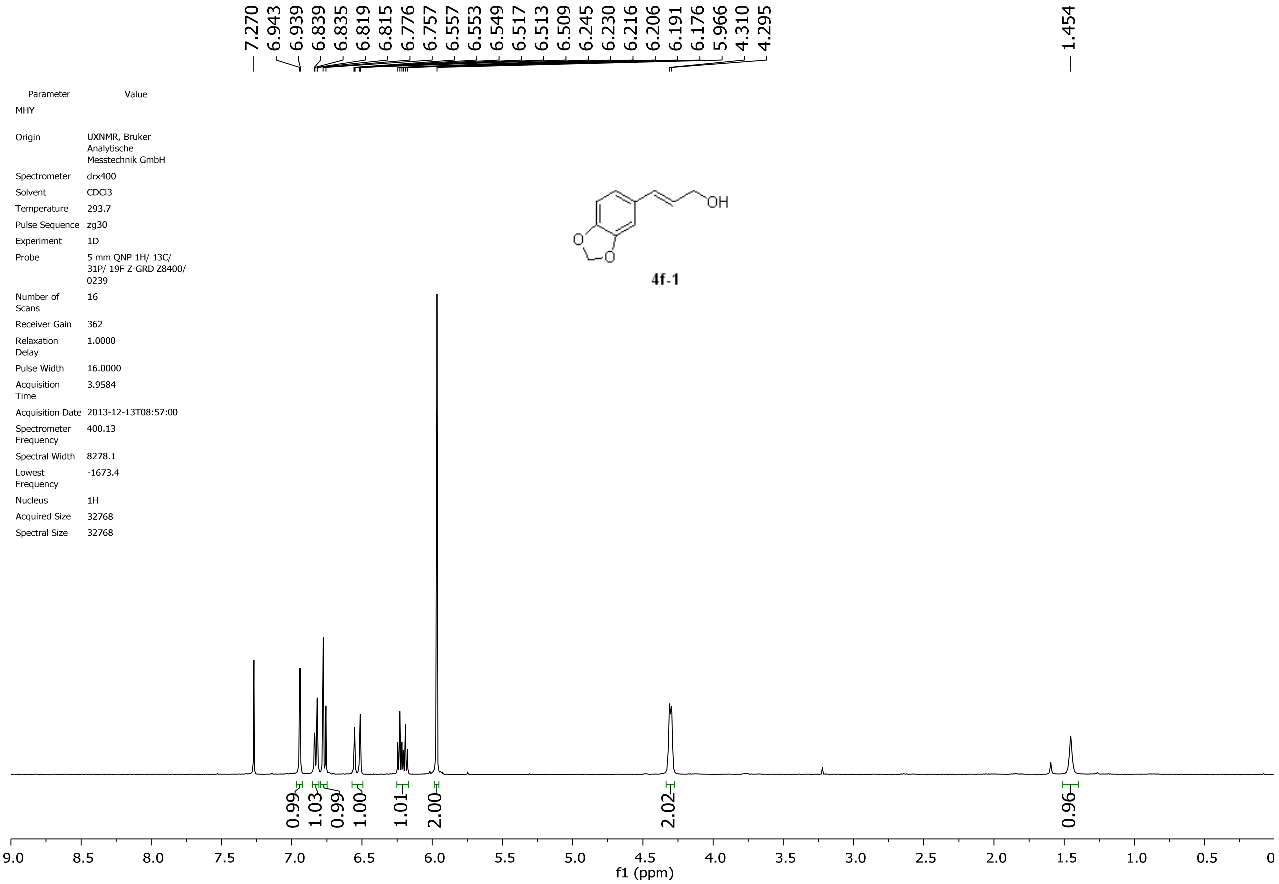


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-30T17: 00:03
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



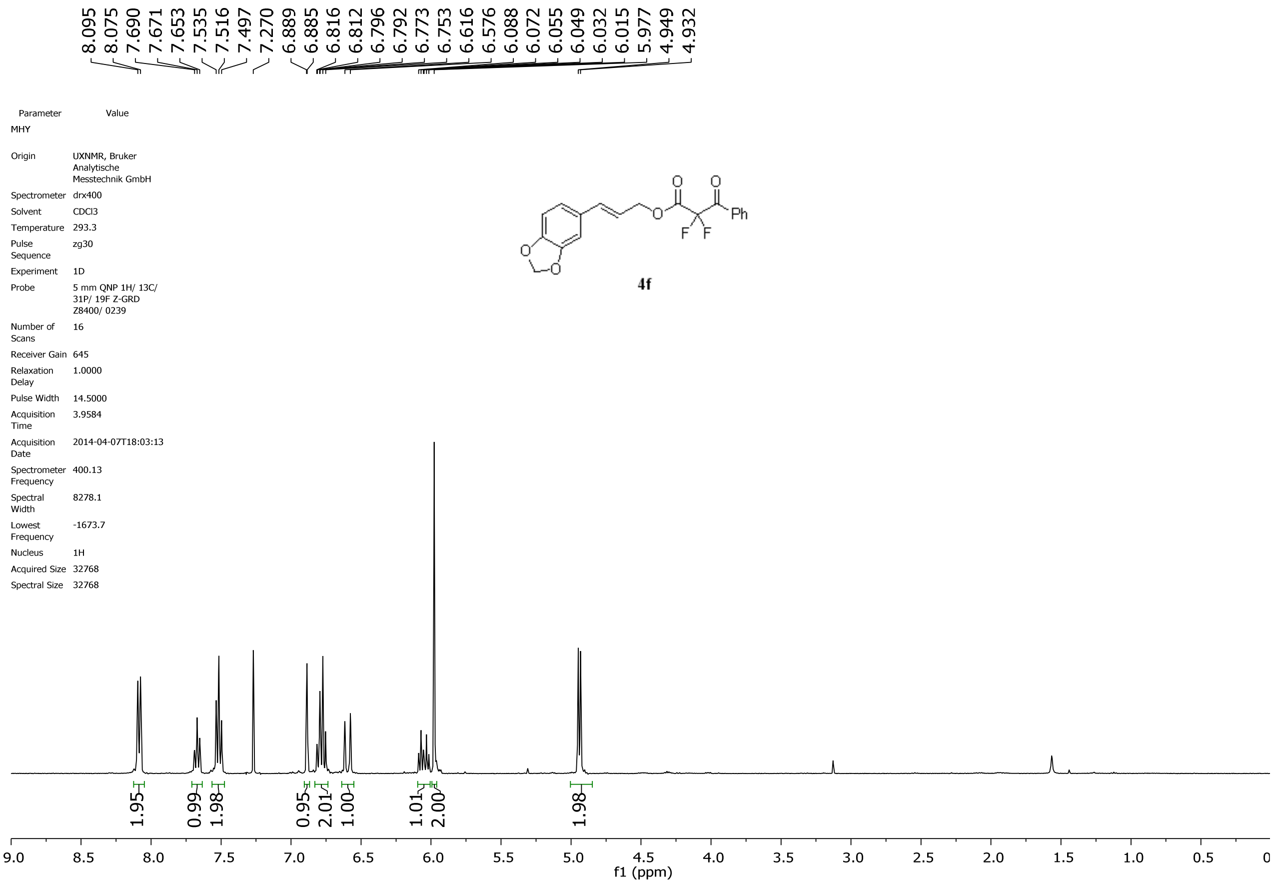
4f-2

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-12T10:24:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

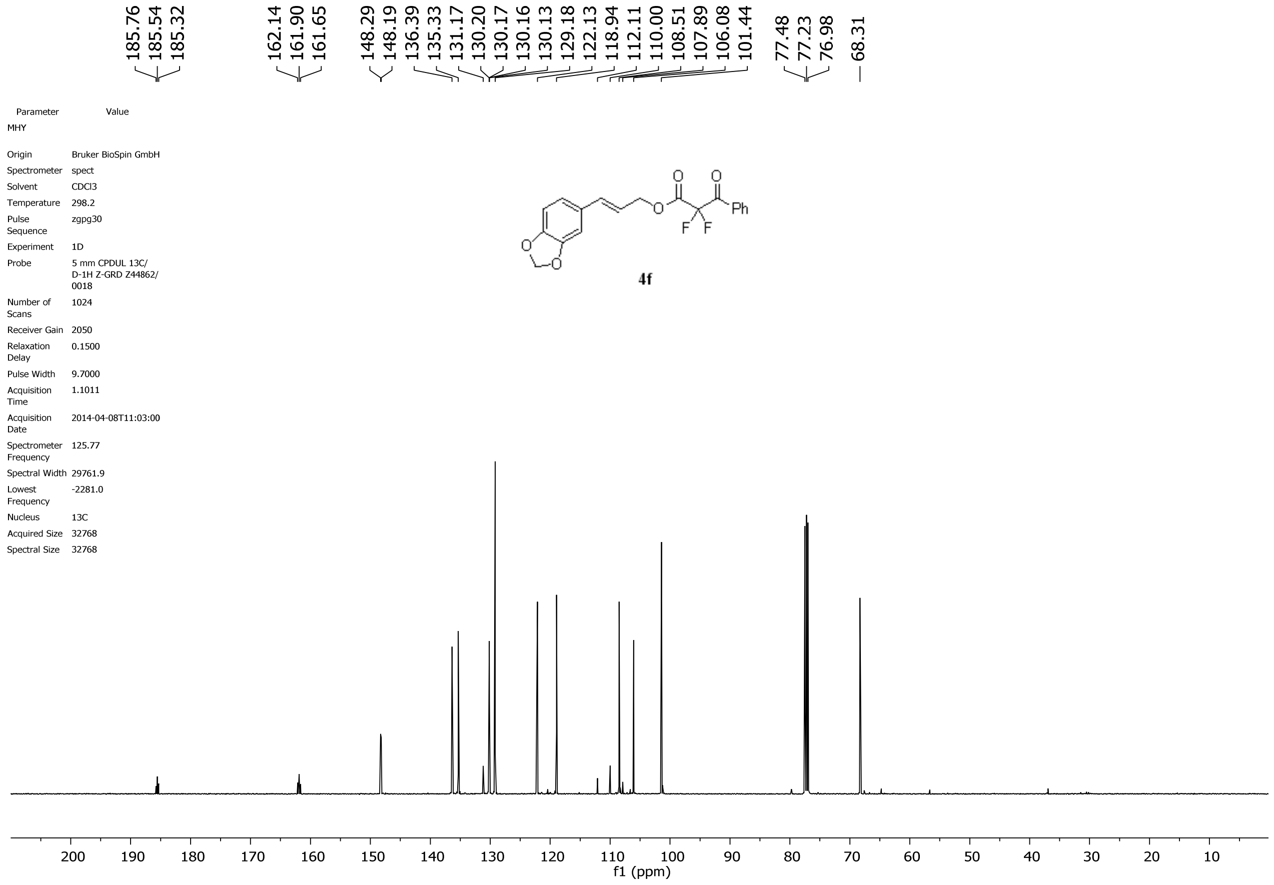


4f-1

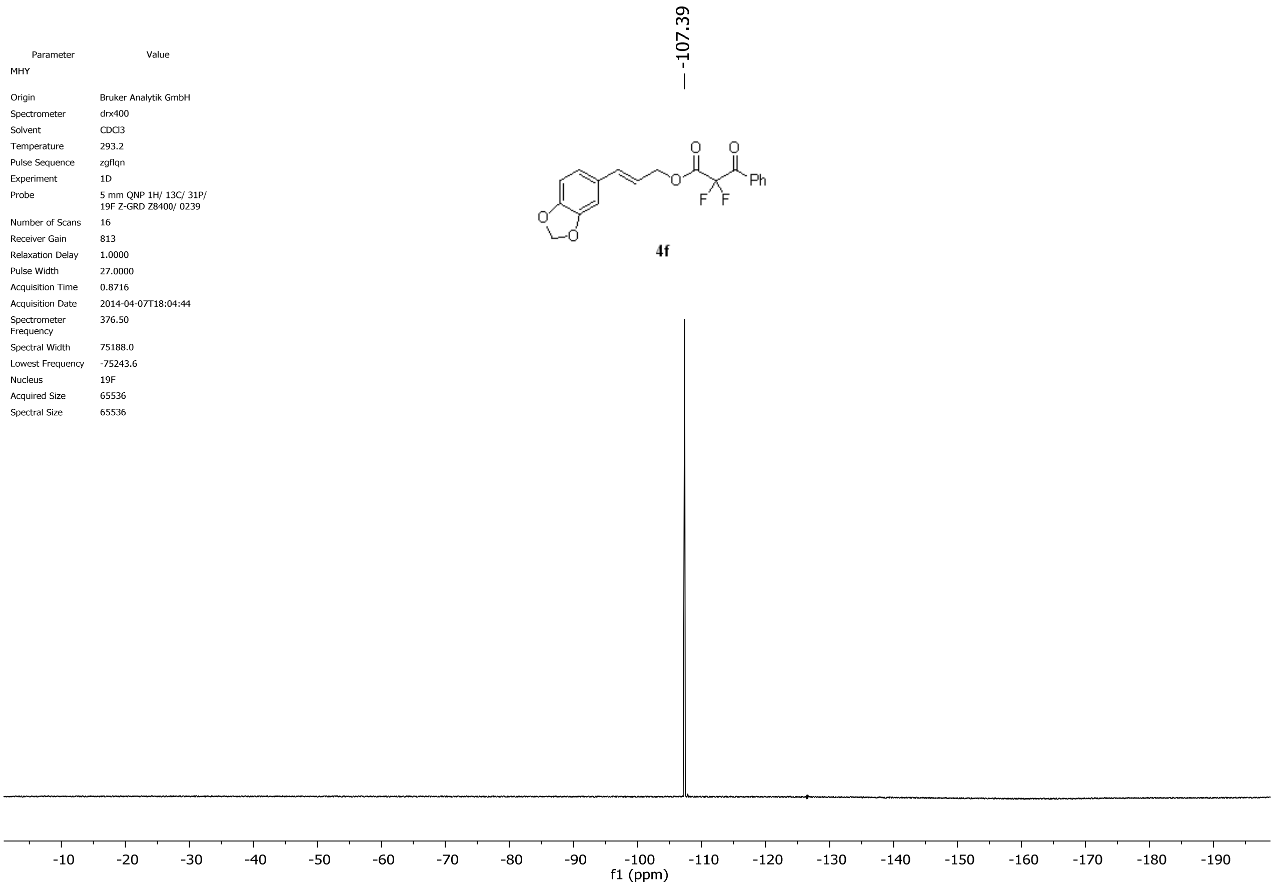
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-13T08:57:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-07T18:03:13
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

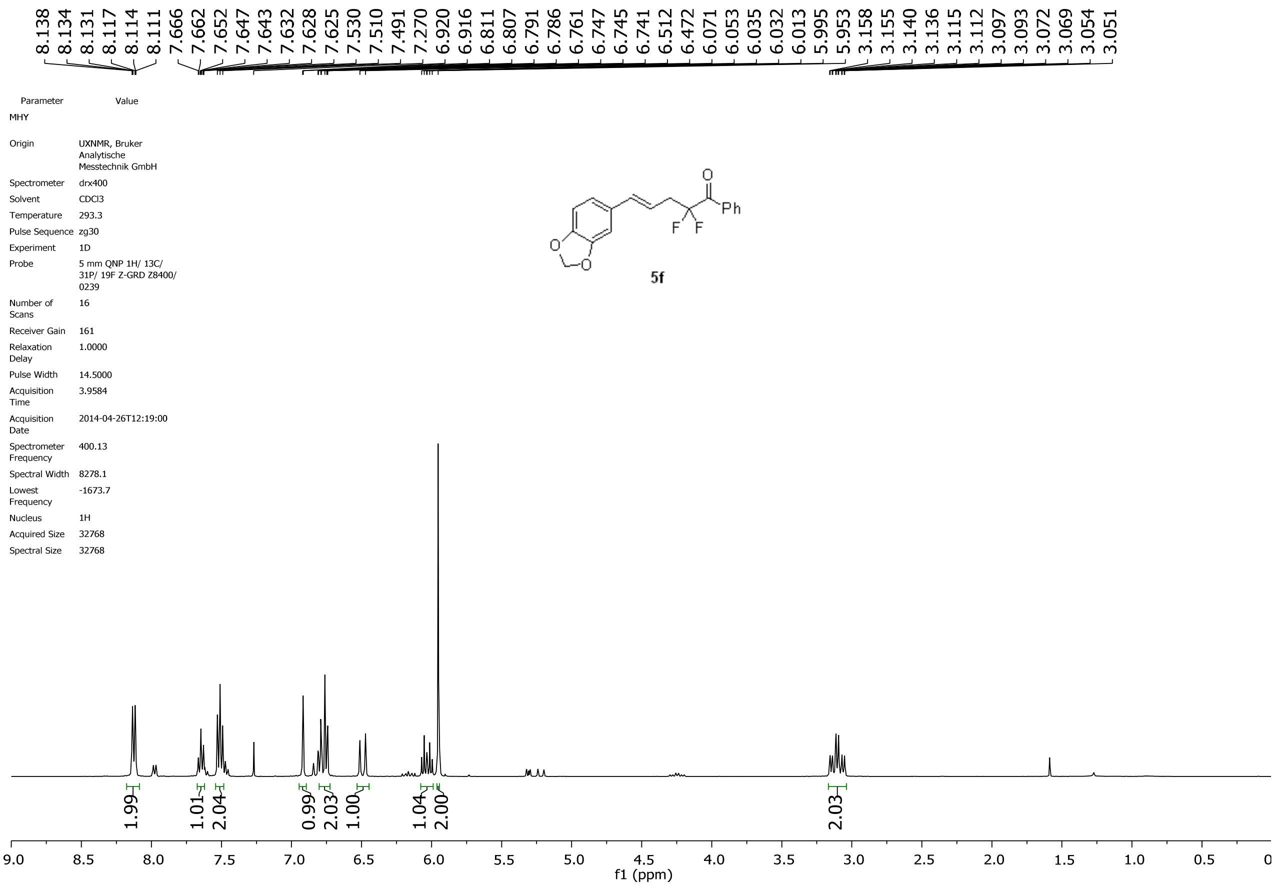


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-08T11:03:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



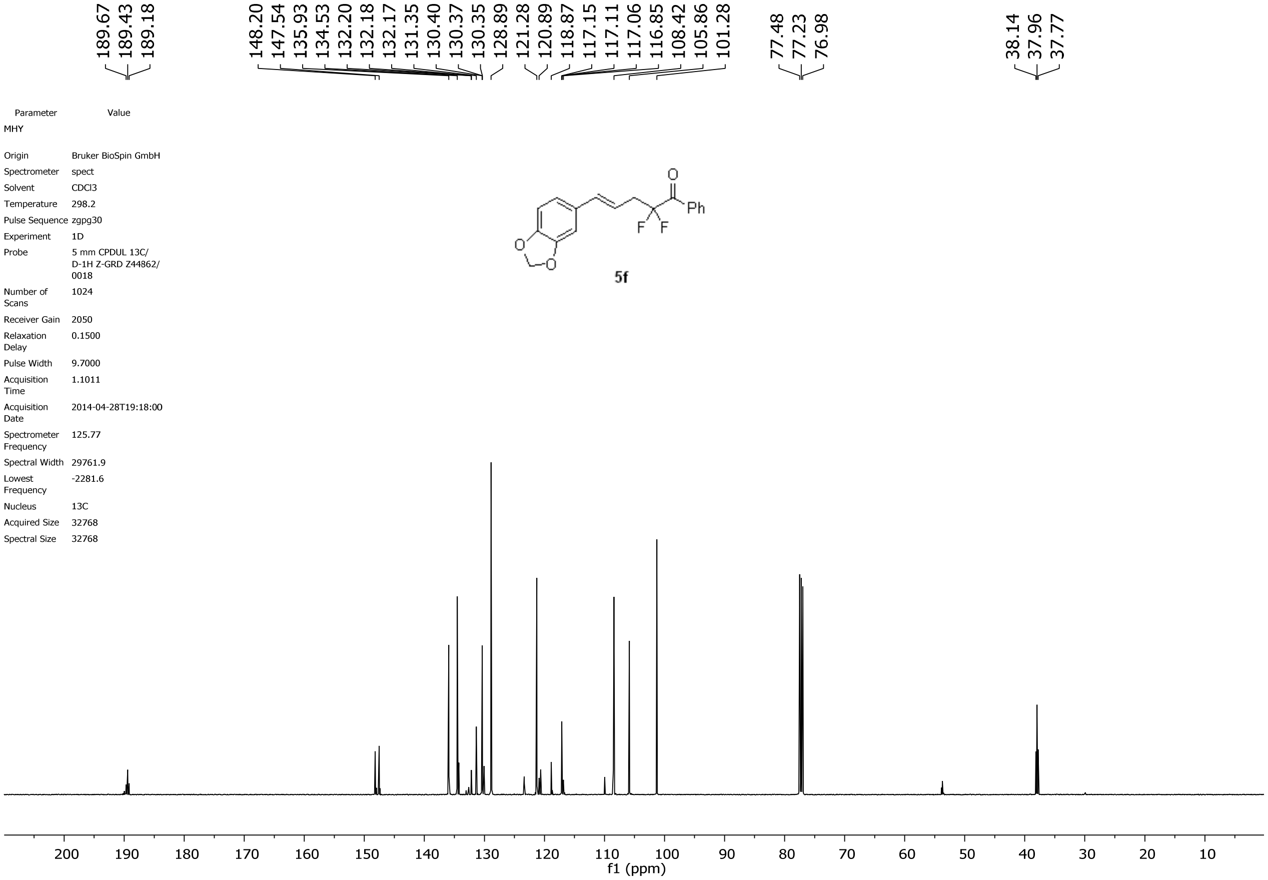
4f

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-04-07T18:04:44
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



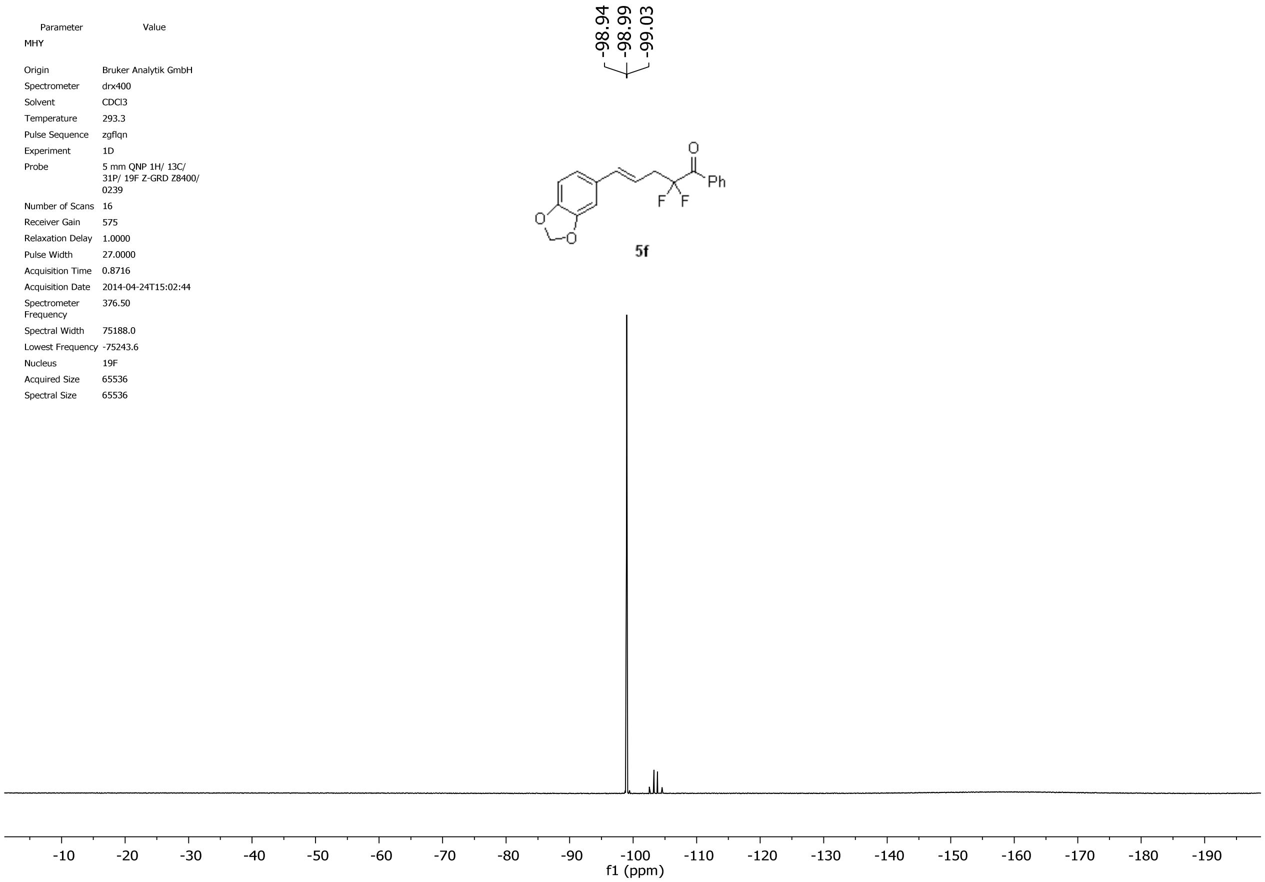
5f

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-26T12:19:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



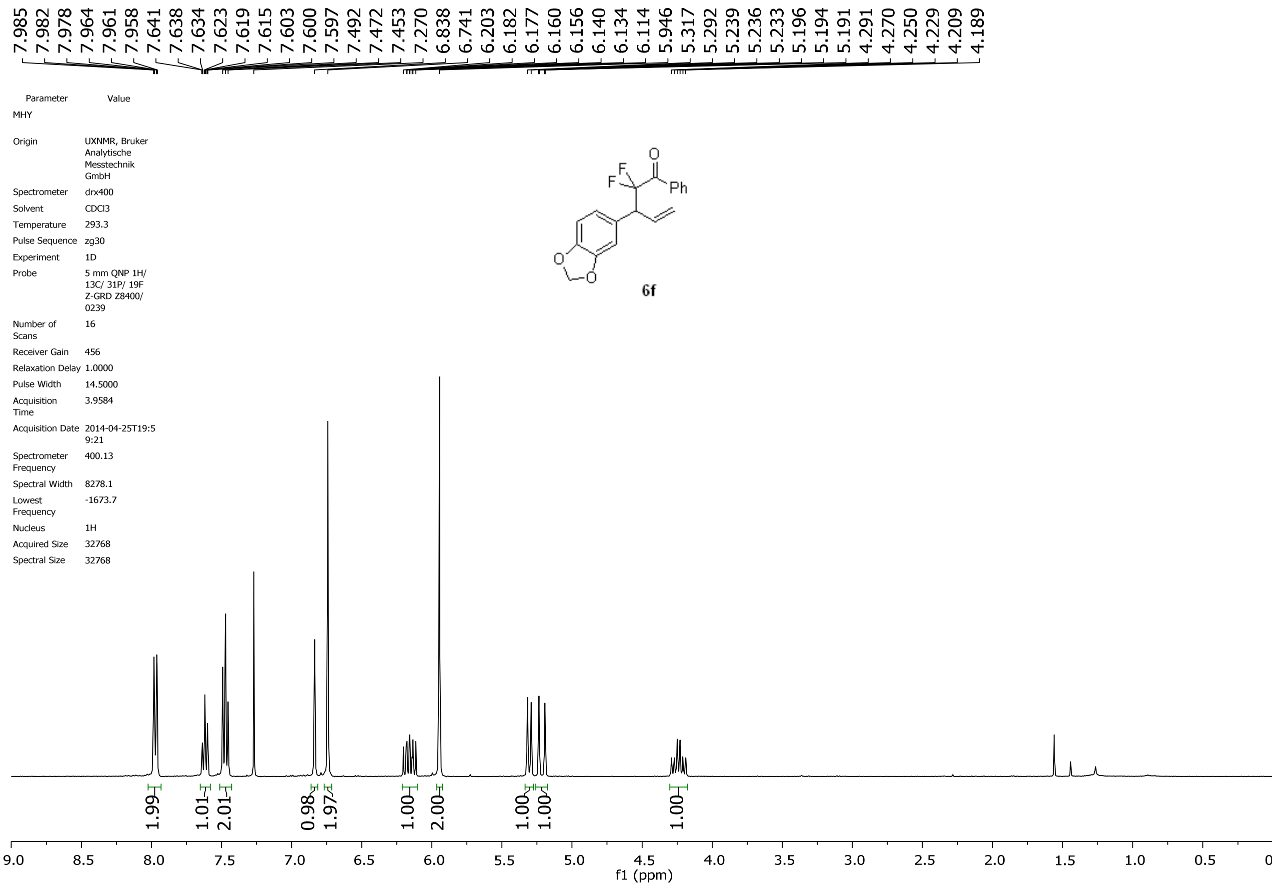
5f

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-28T19:18:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



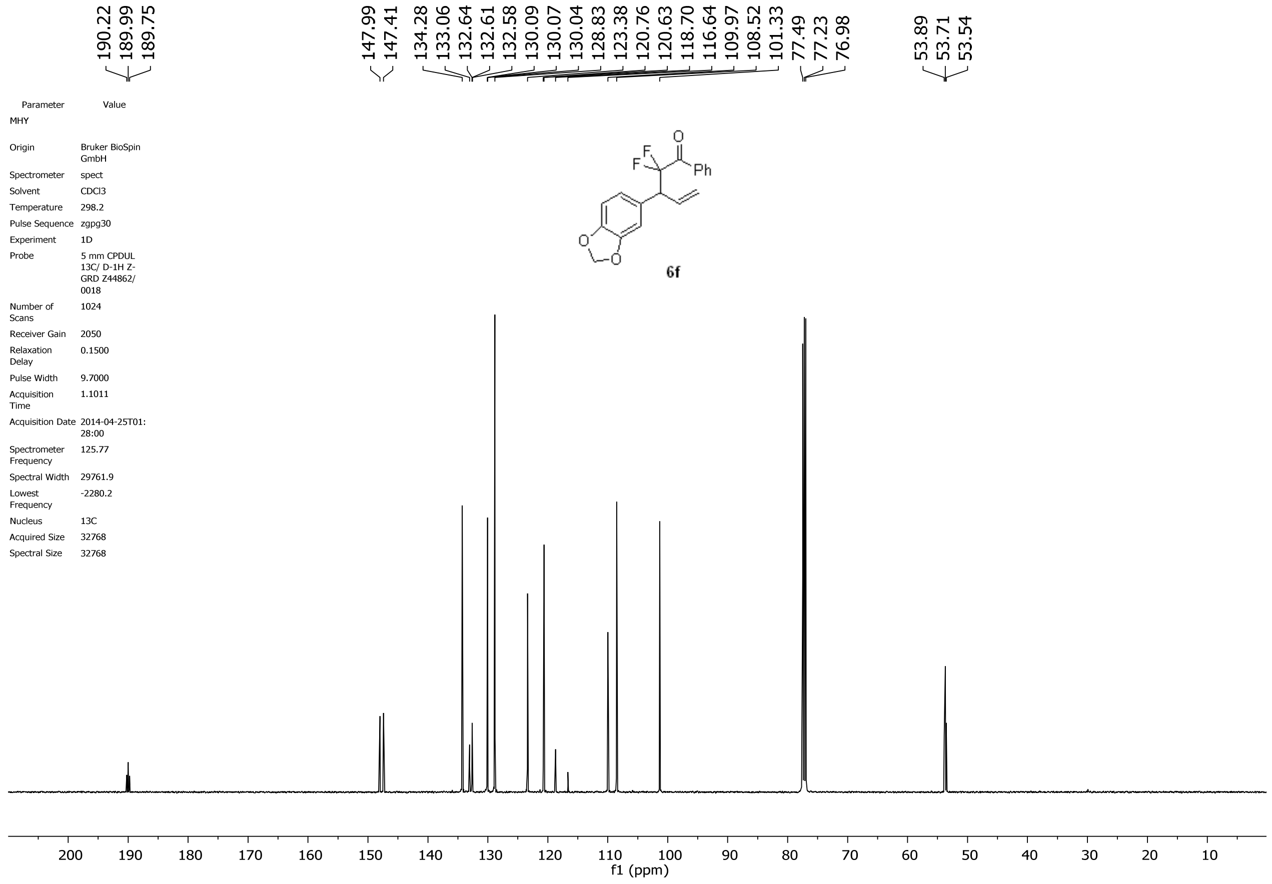
5f

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-04-24T15:02:44
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



6f

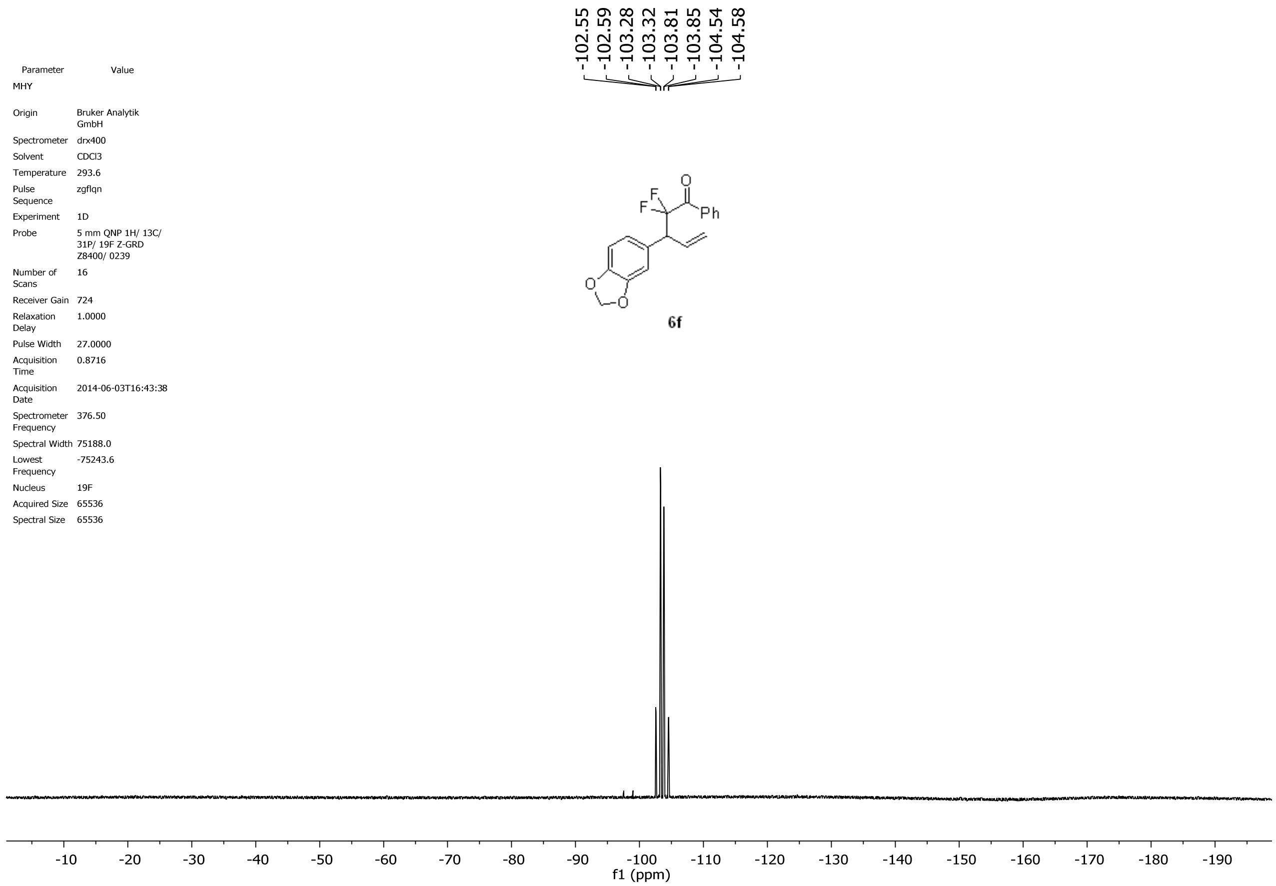
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-25T19:59:21
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



6f

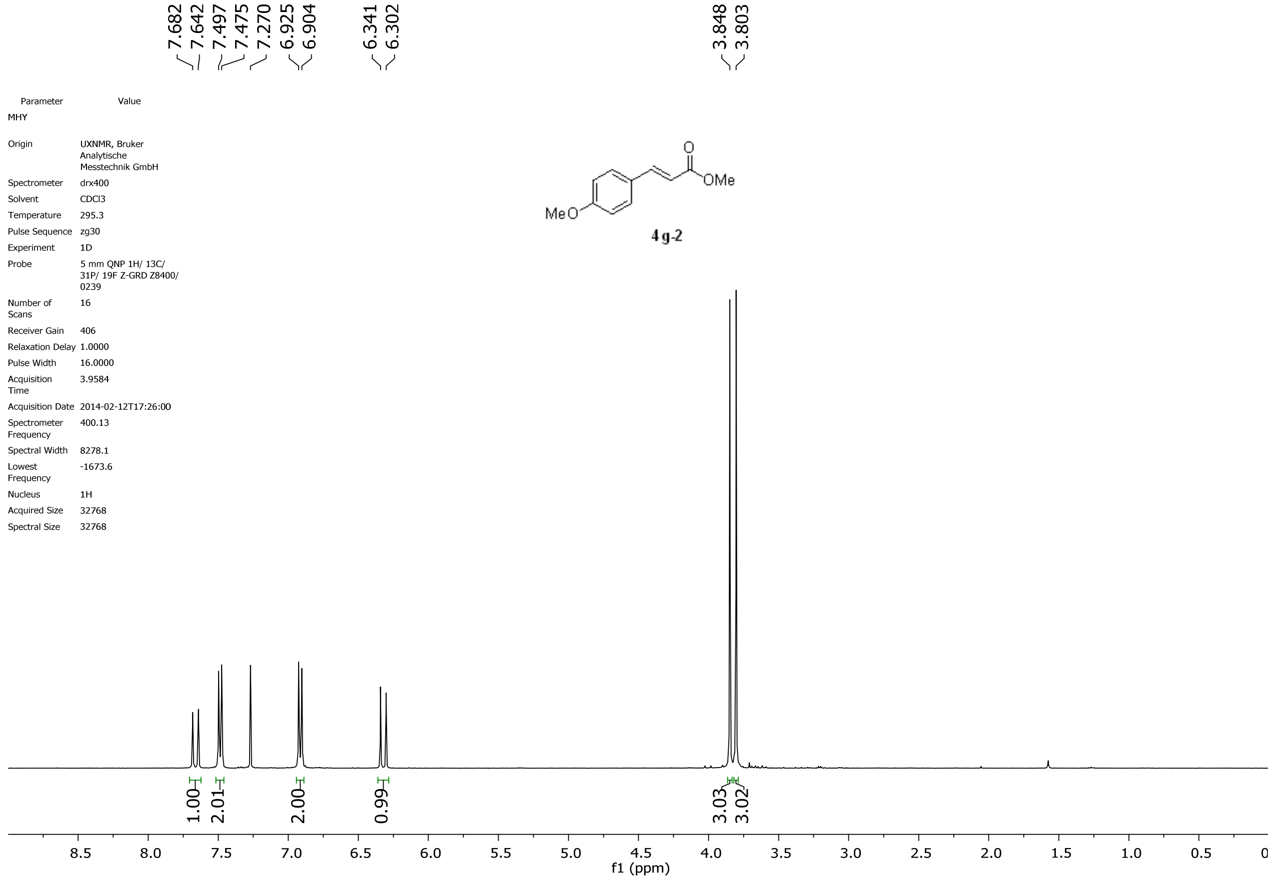
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-25T01:28:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-03T16:43:38
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

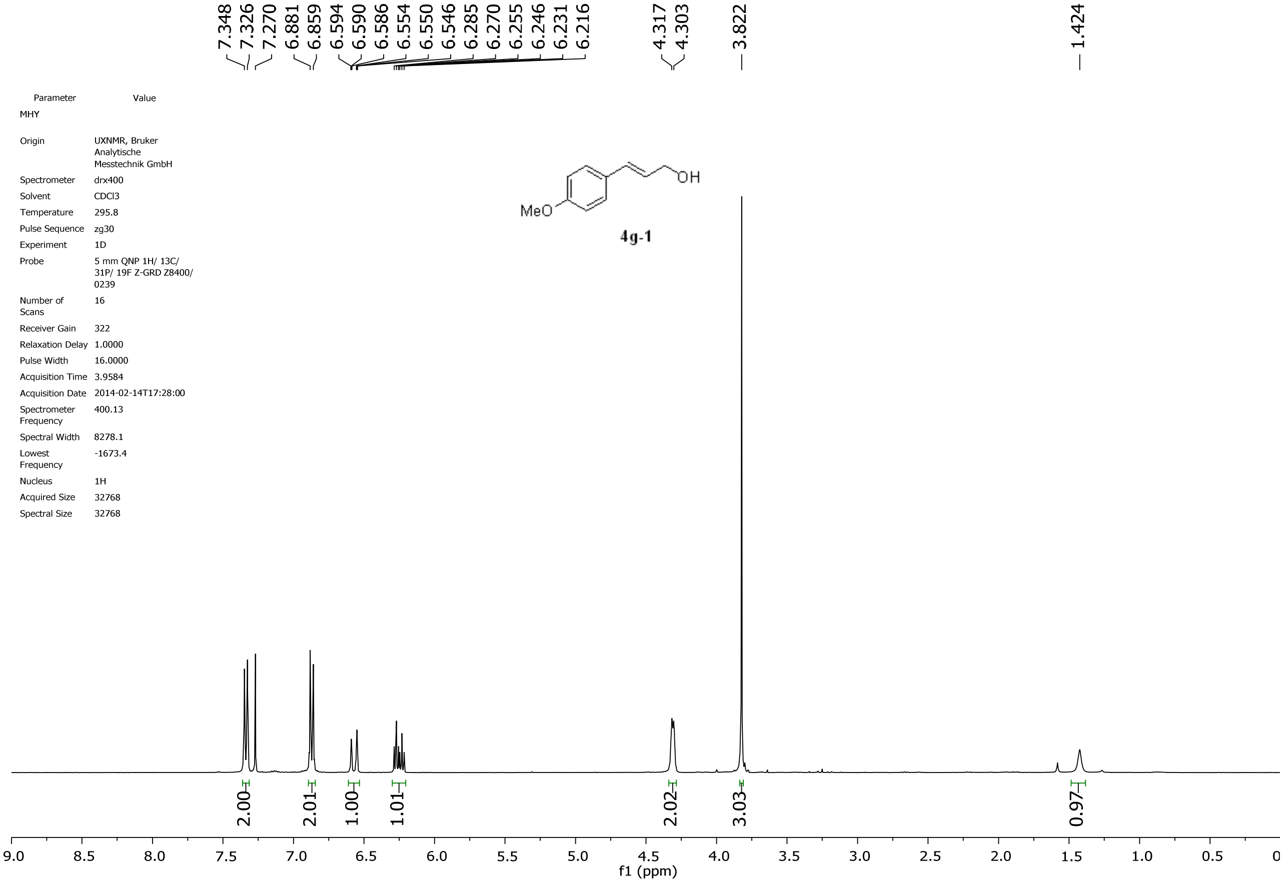


6f

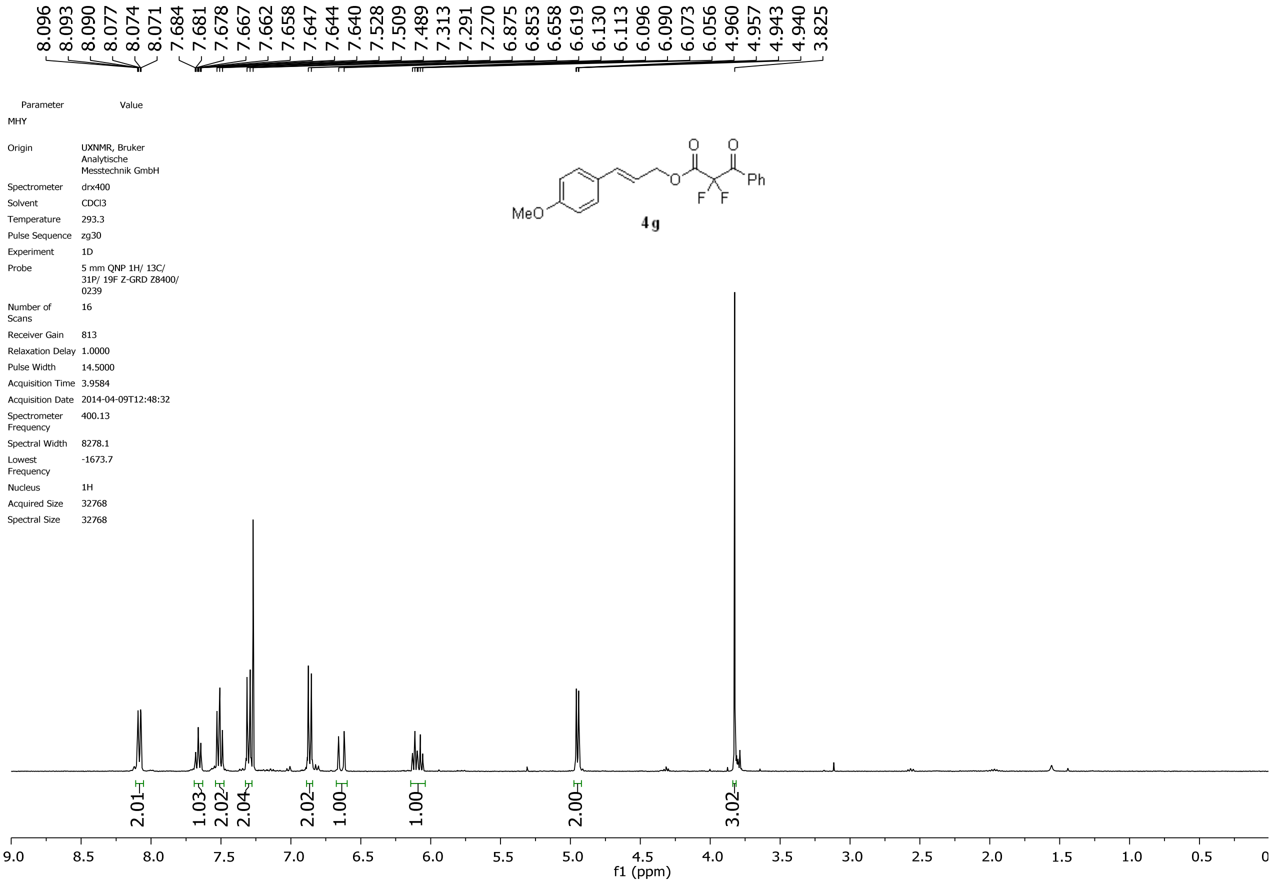
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	295.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-12T17:26:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.6
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



4g-2

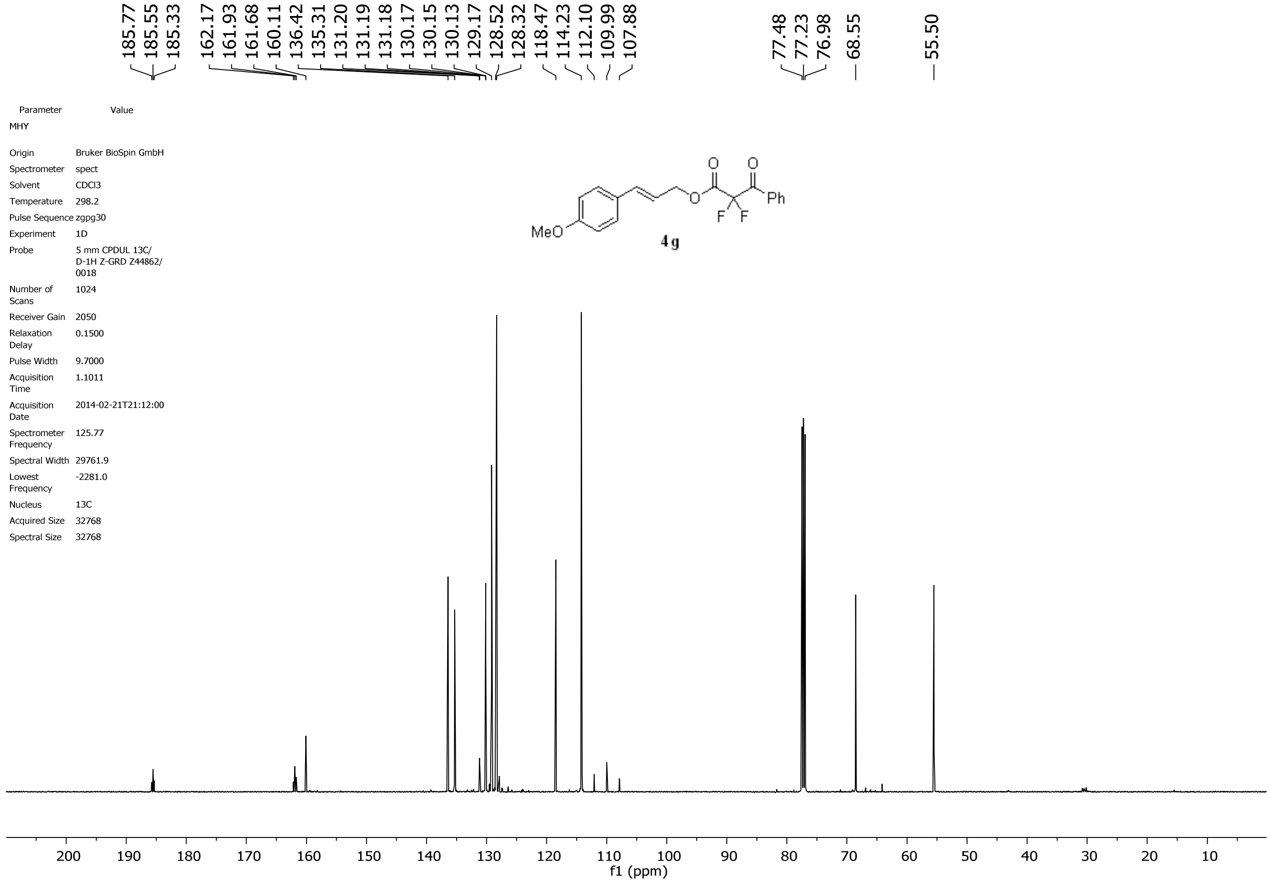


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	295.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-14T17:28:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



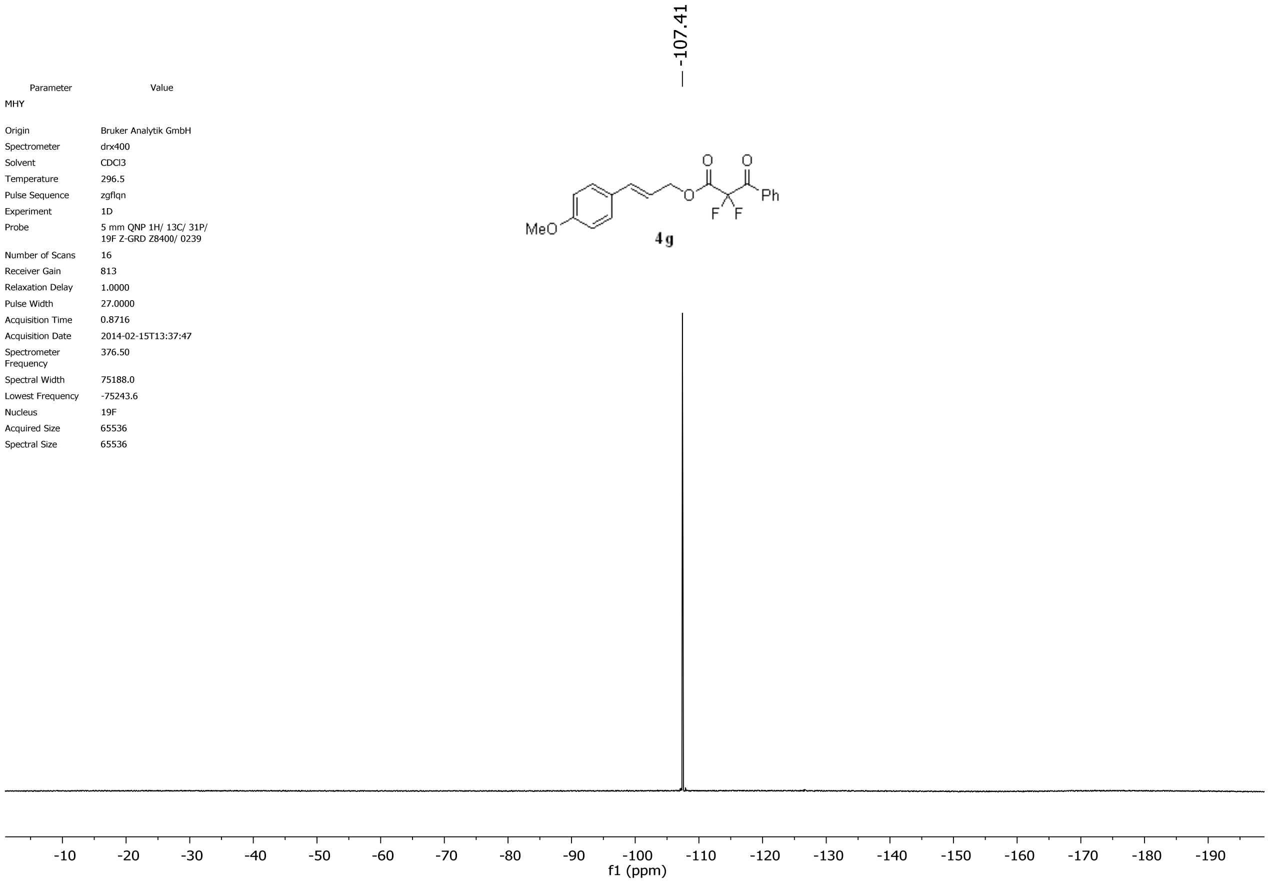
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-09T12:48:32
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-21T21:12:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

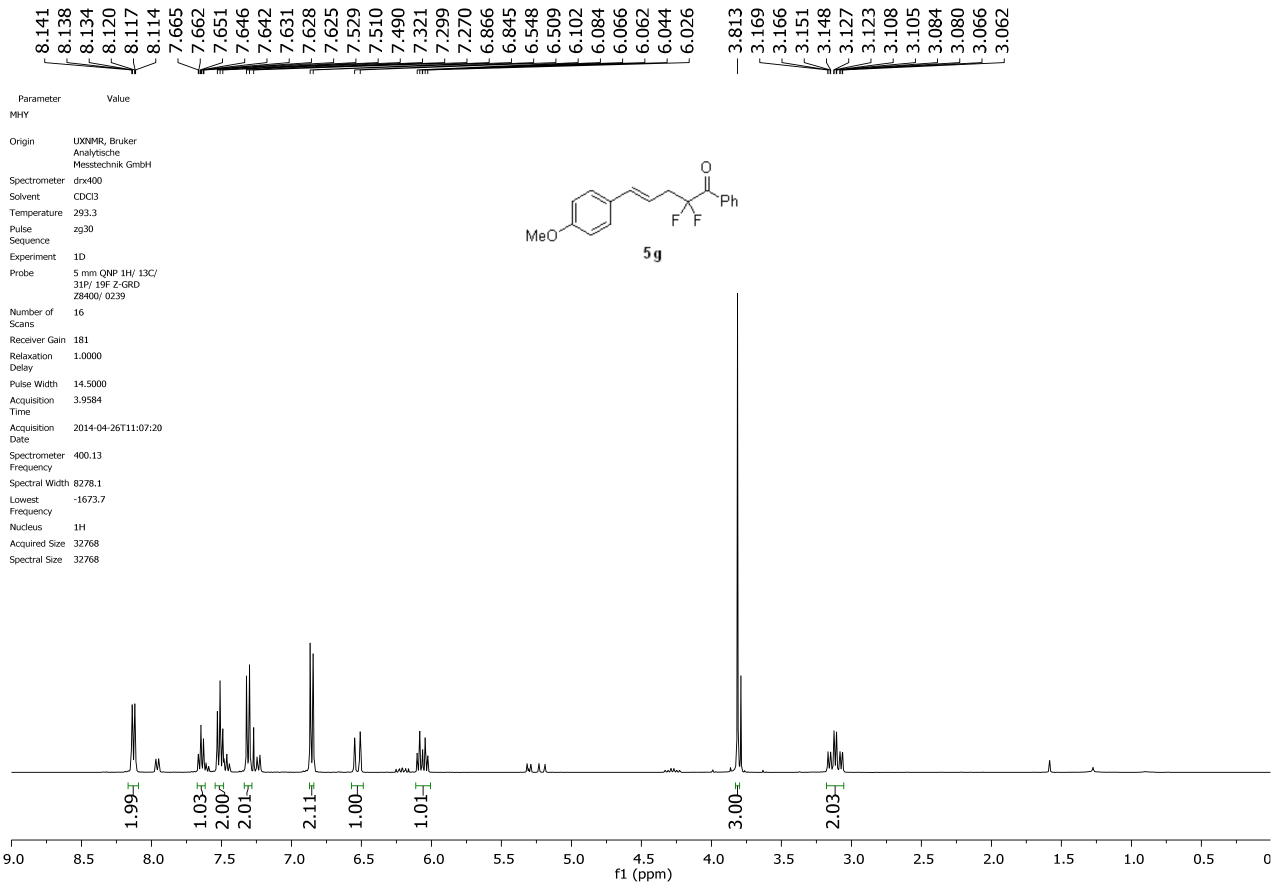


4g

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	296.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-15T13:37:47
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

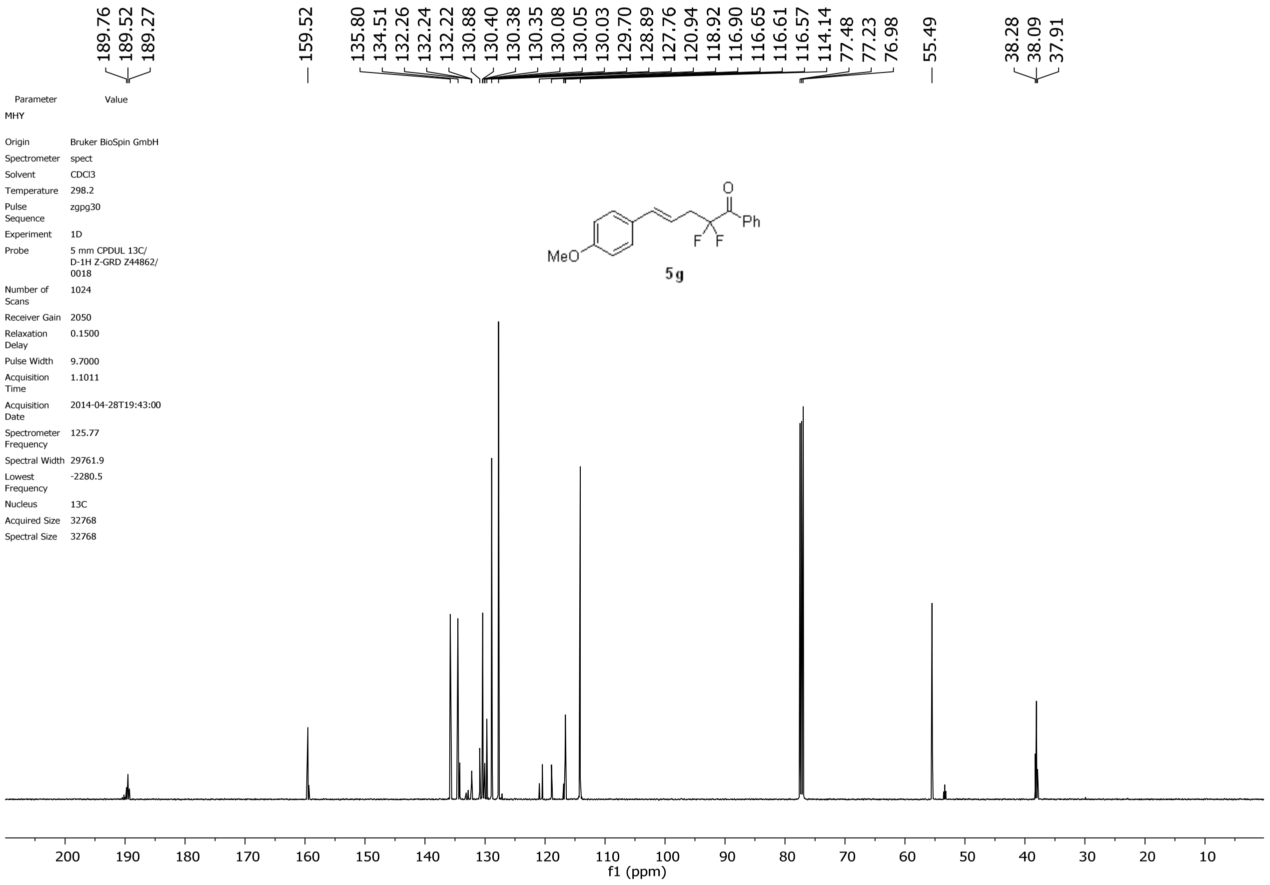


4g



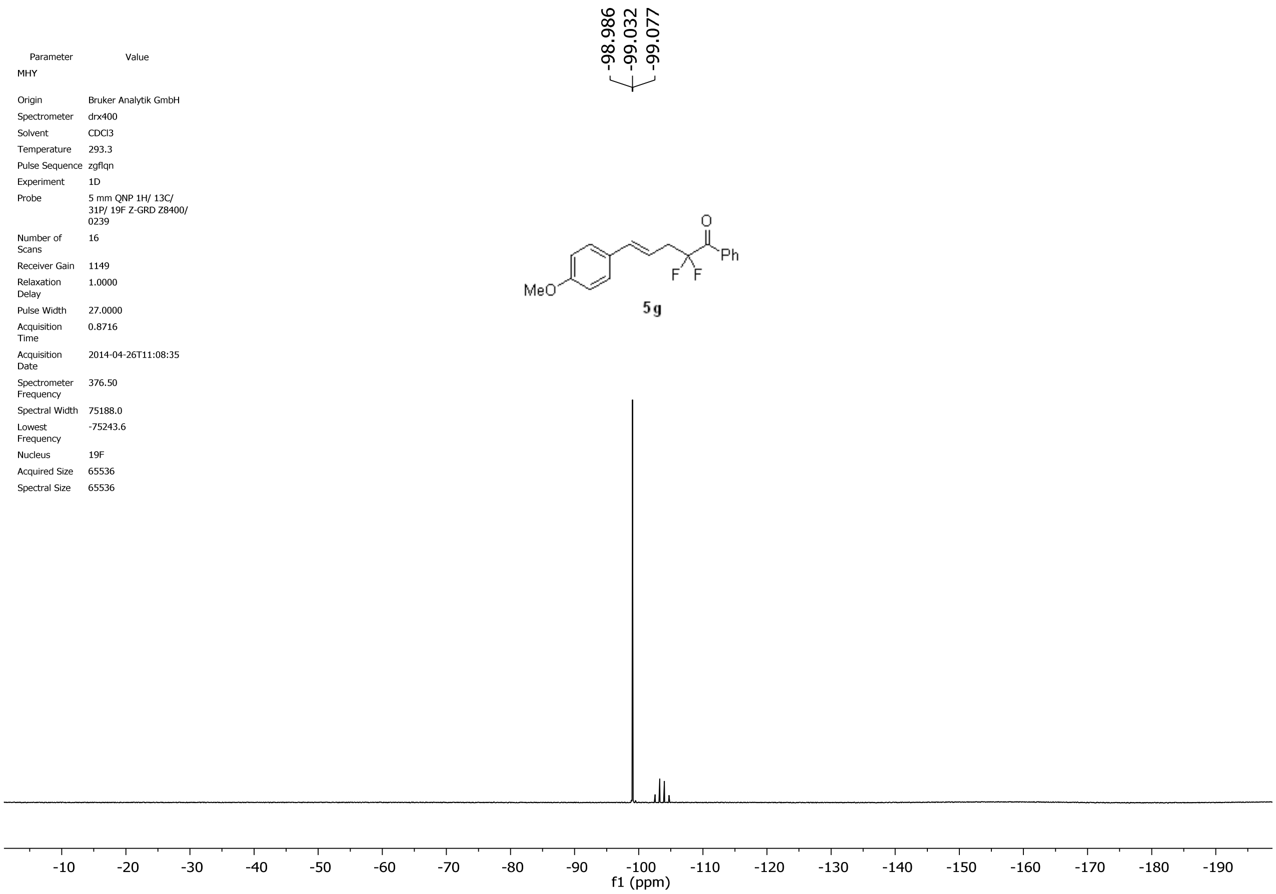
5g

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-26T11:07:20
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



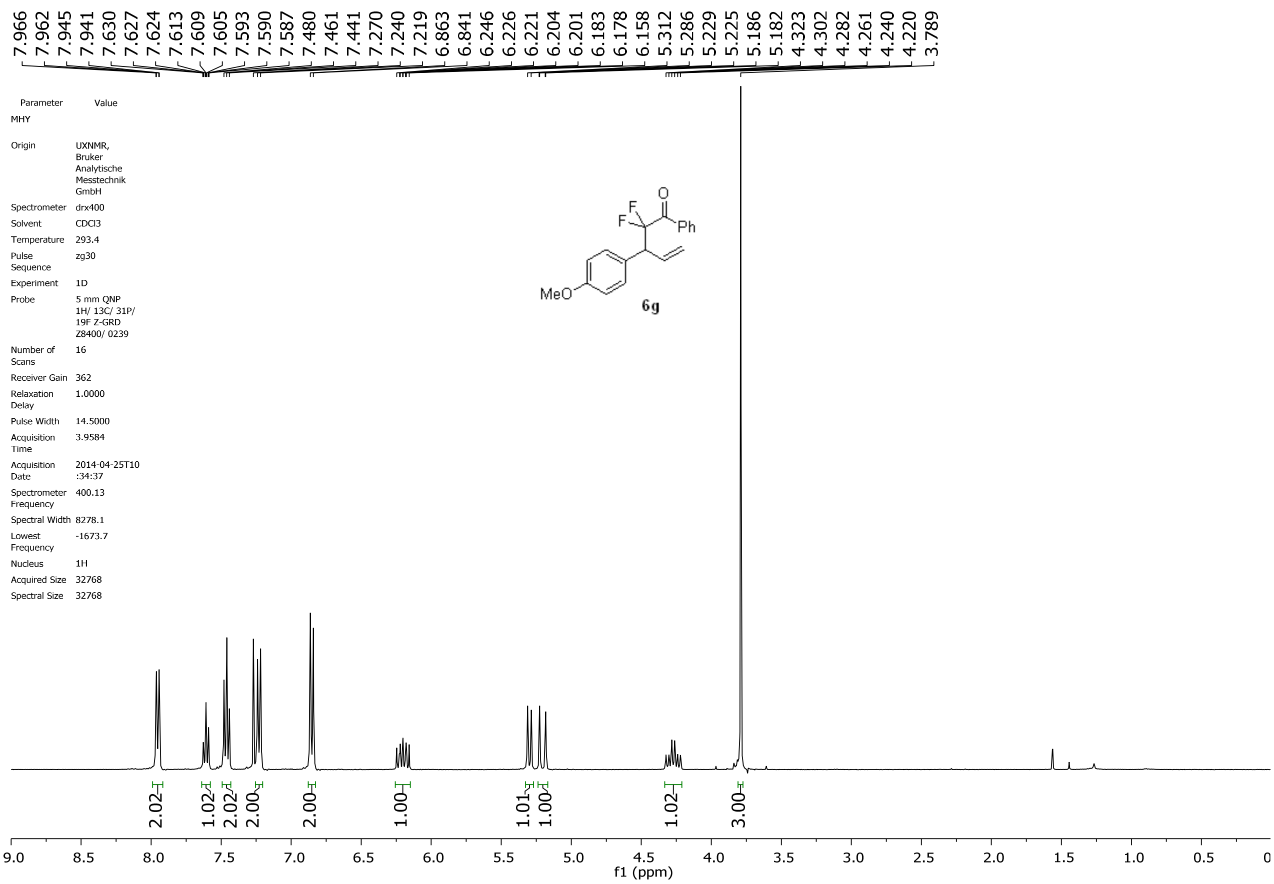
5g

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-28T19:43:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



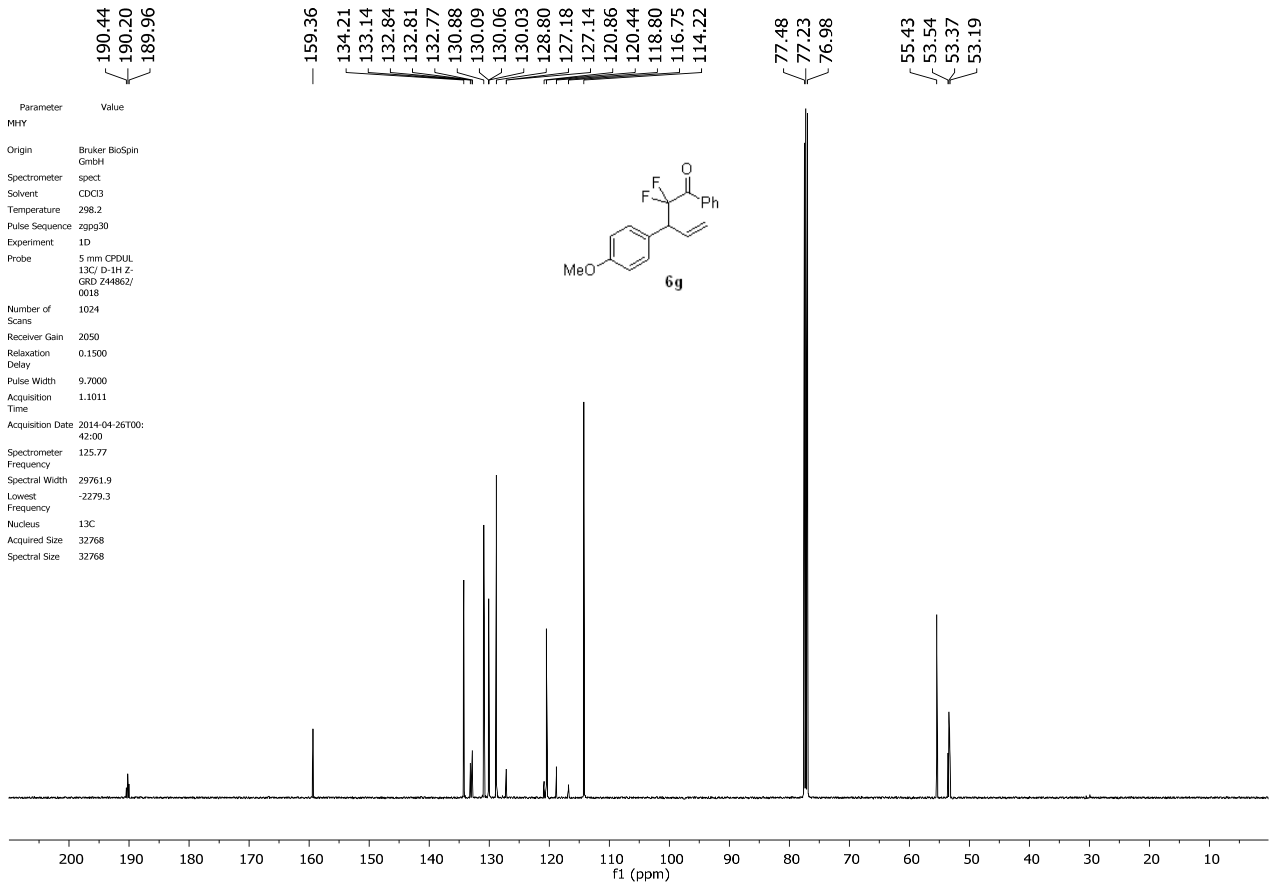
5g

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-04-26T11:08:35
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

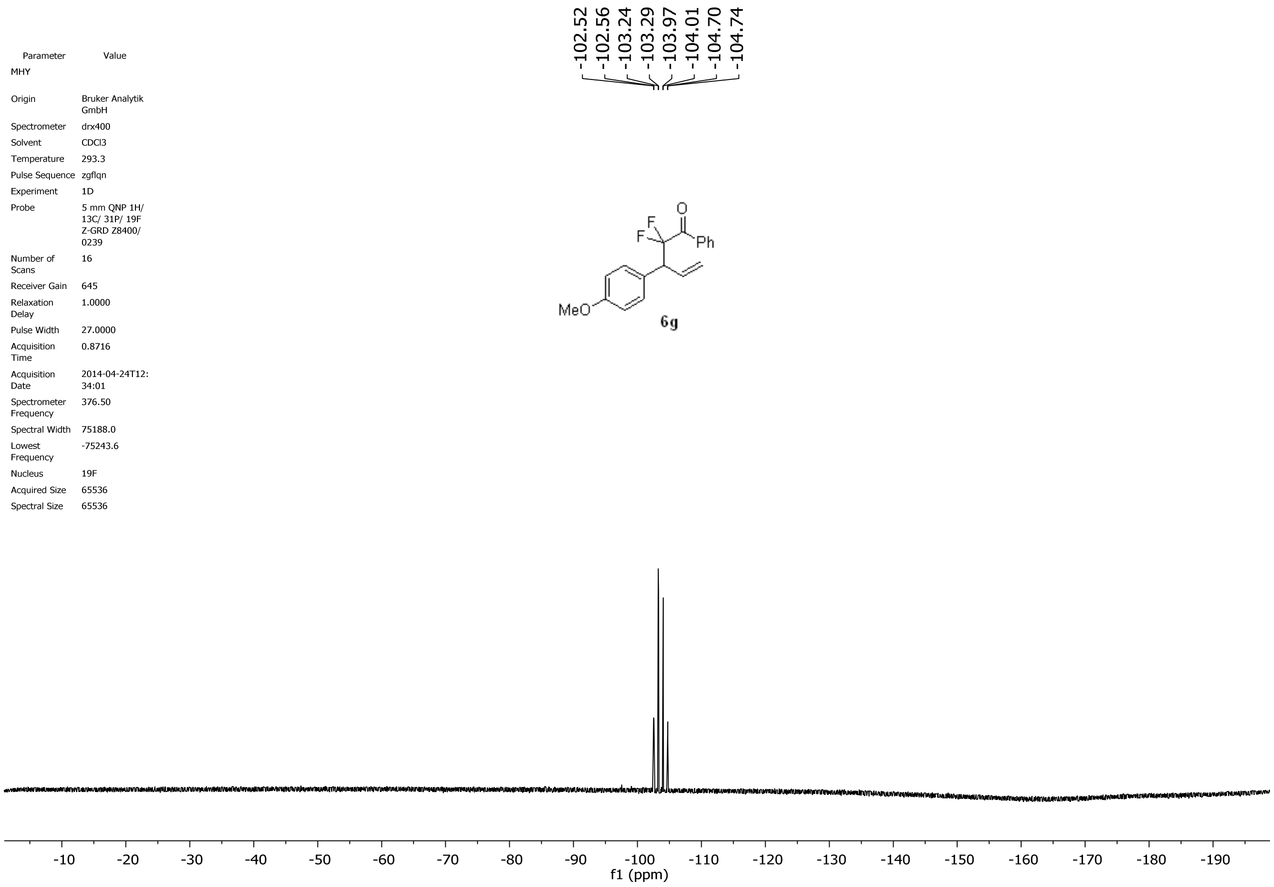


6g

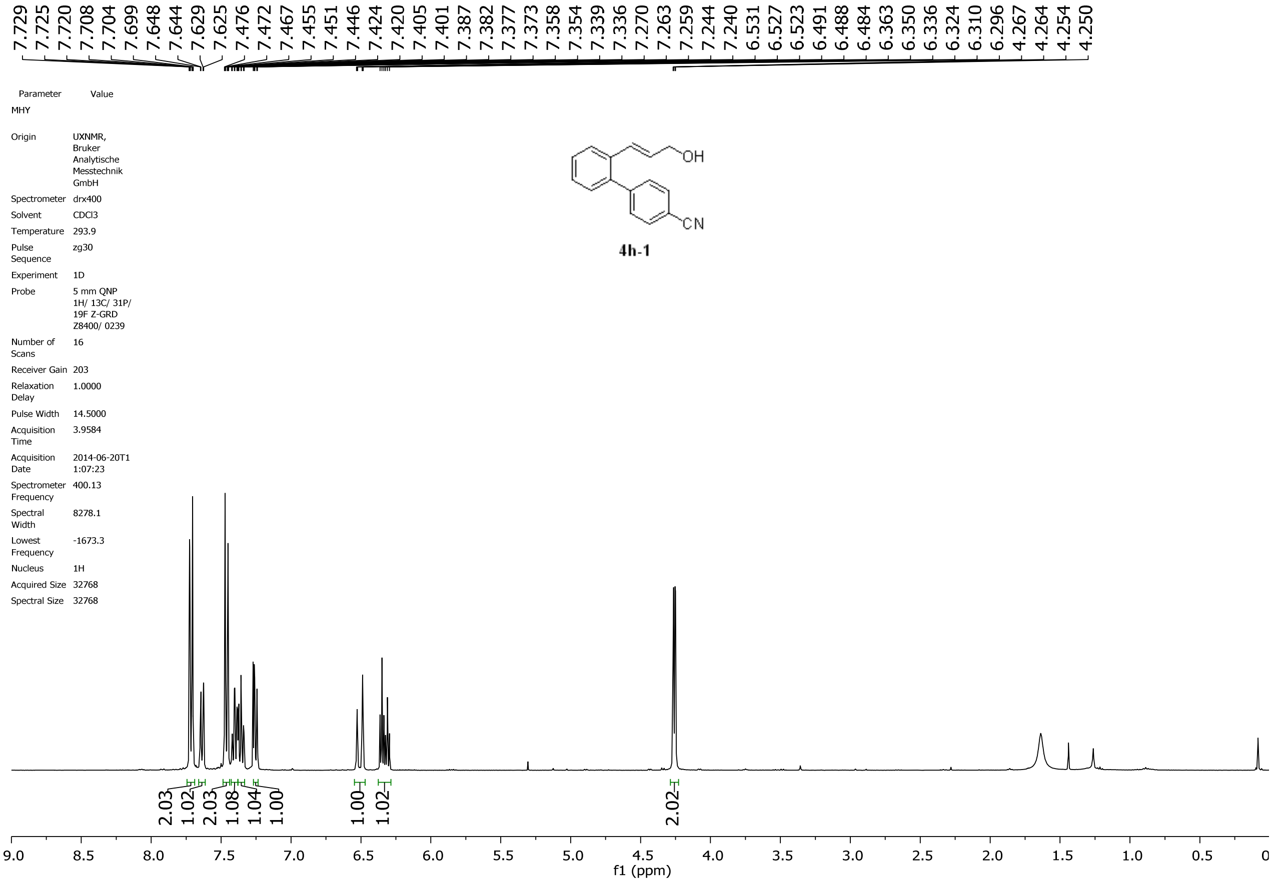
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-25T10:34:37
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-04-26T00:42:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.3
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

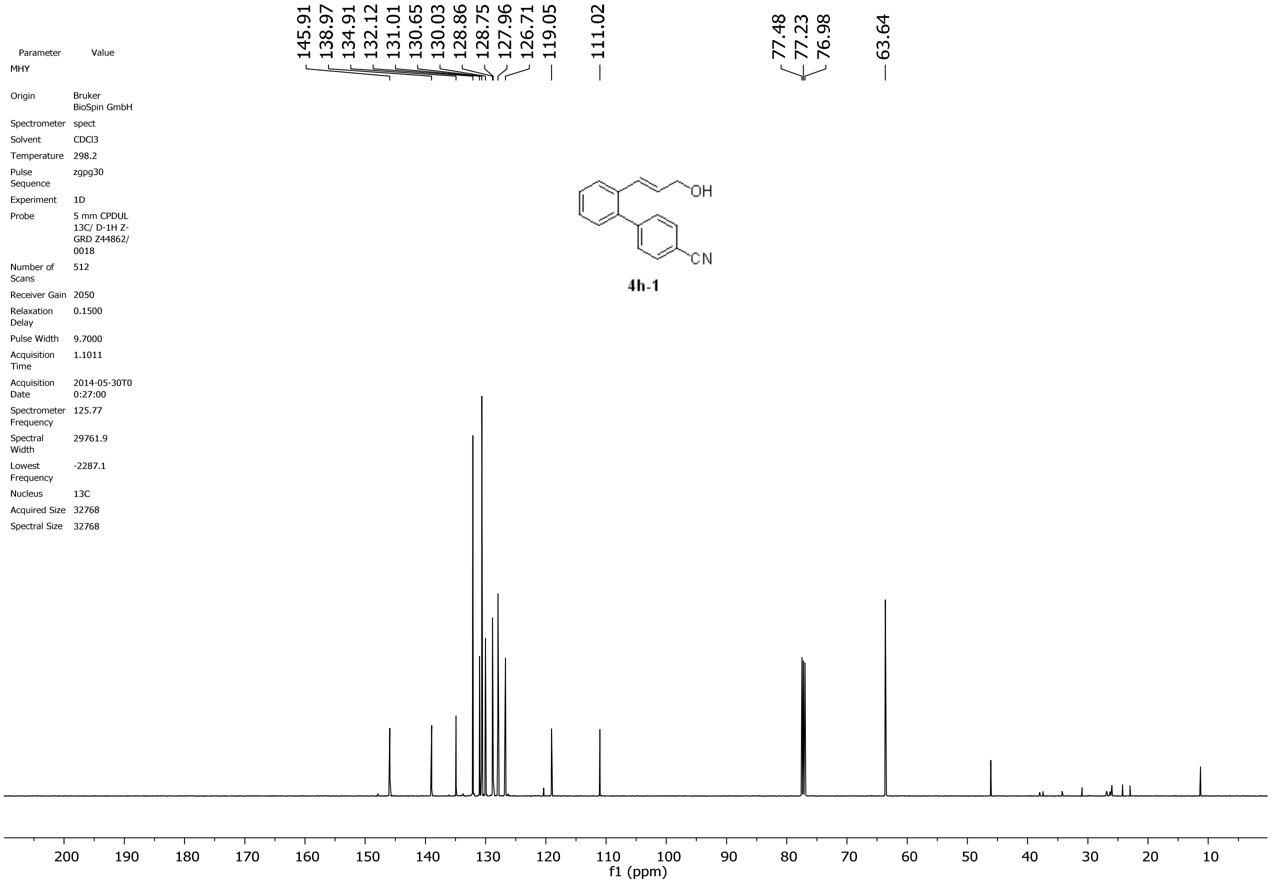


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-04-24T12:34:01
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



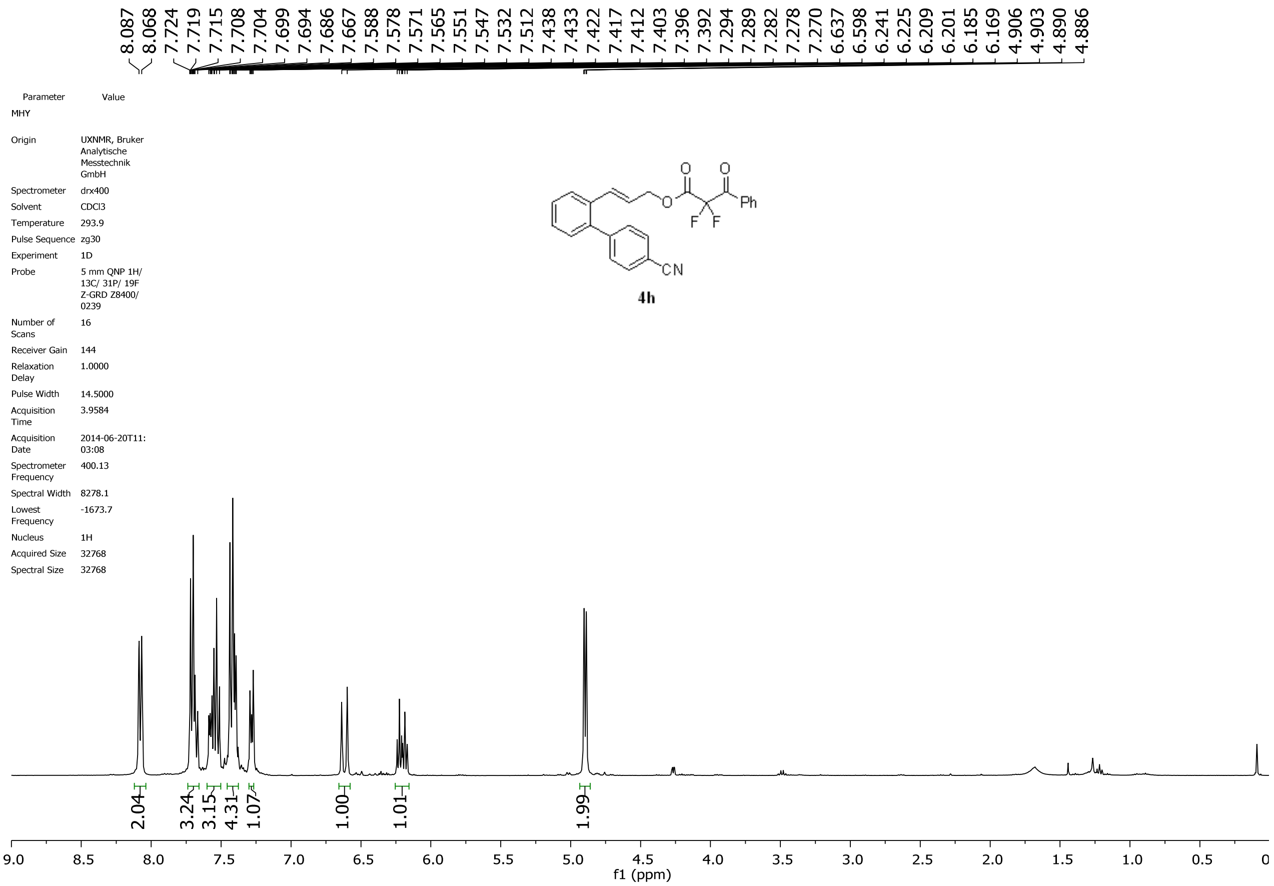
4h-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-20T11:07:23
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



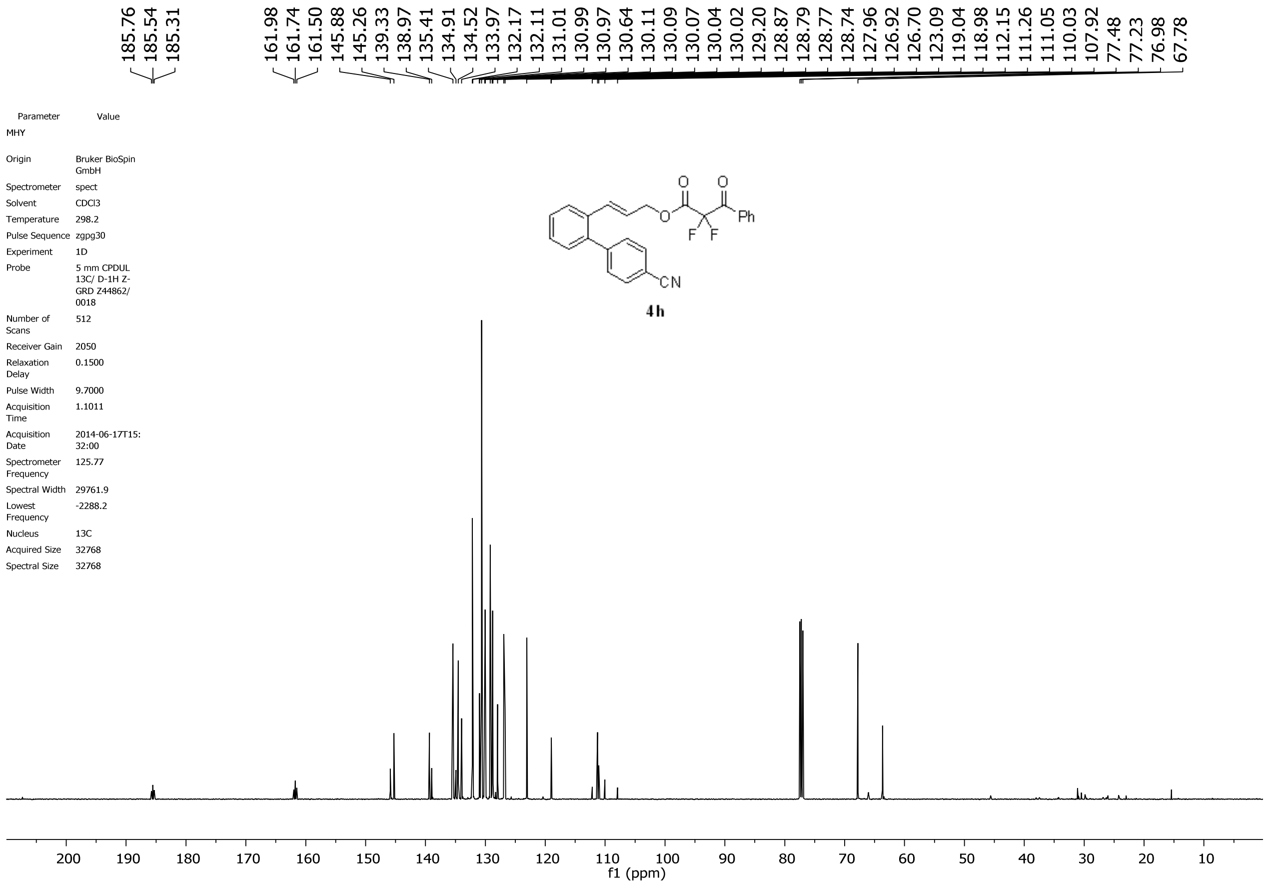
4h-1

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	512
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-30T00:27:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2287.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	144
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-20T11:03:08
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

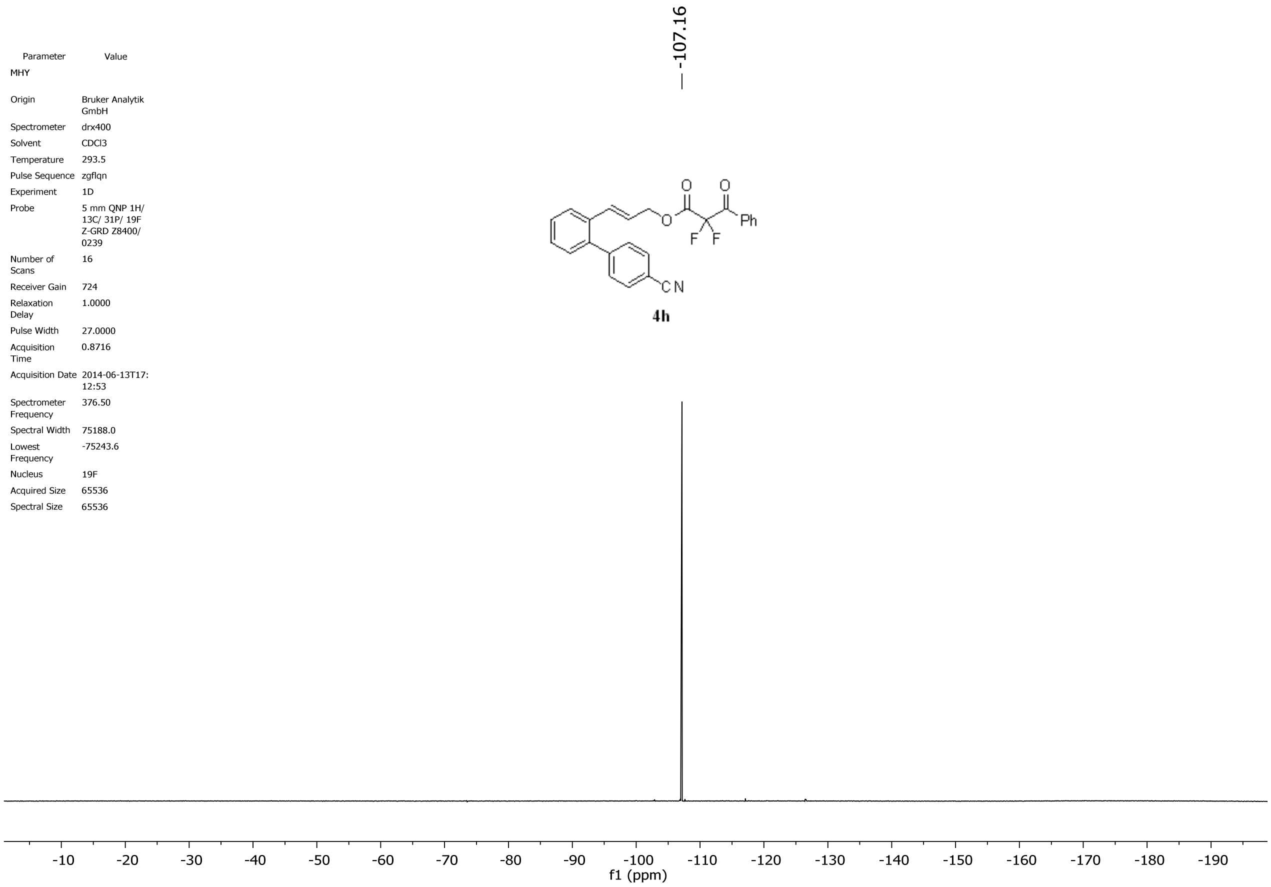
4h



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	512
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-17T15:32:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2288.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

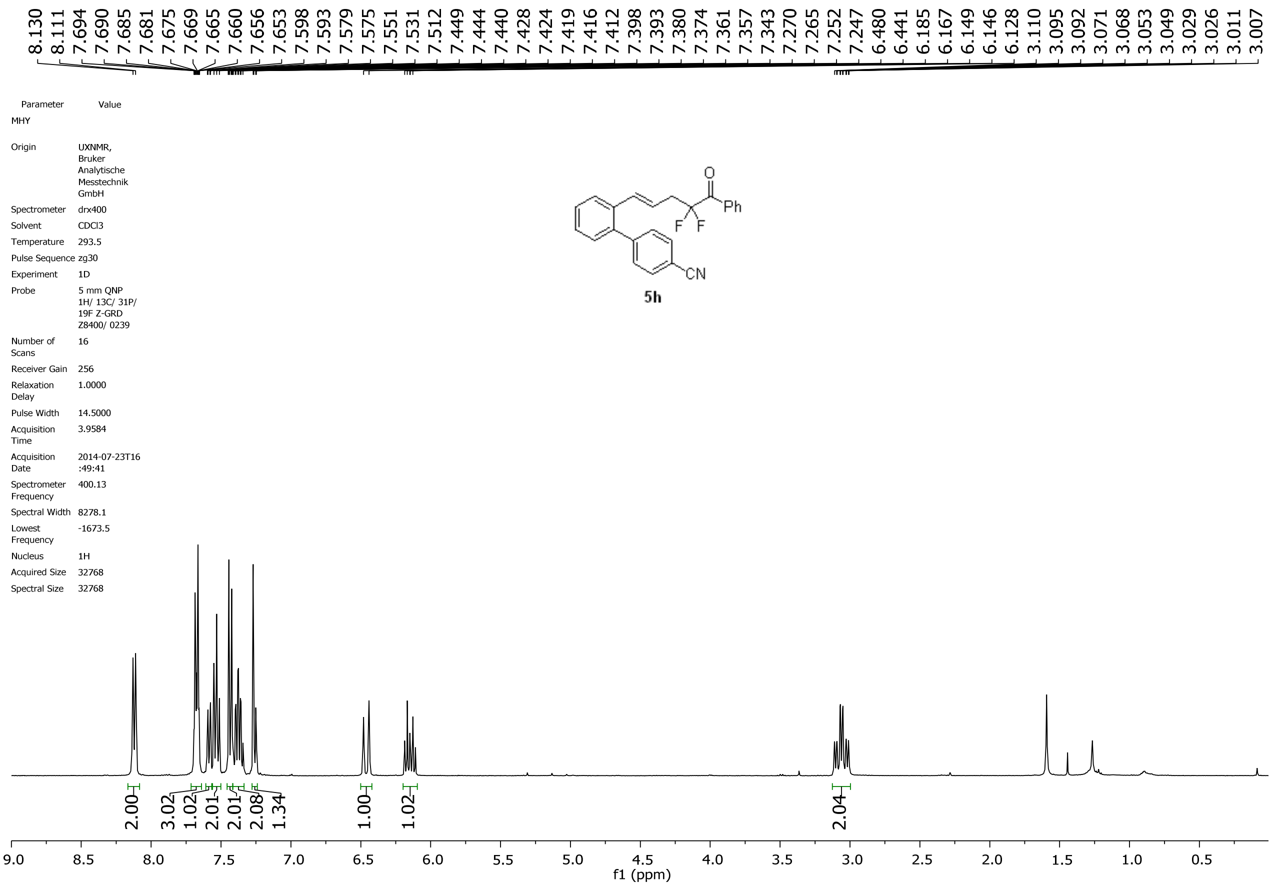
4h

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-13T17:12:53
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

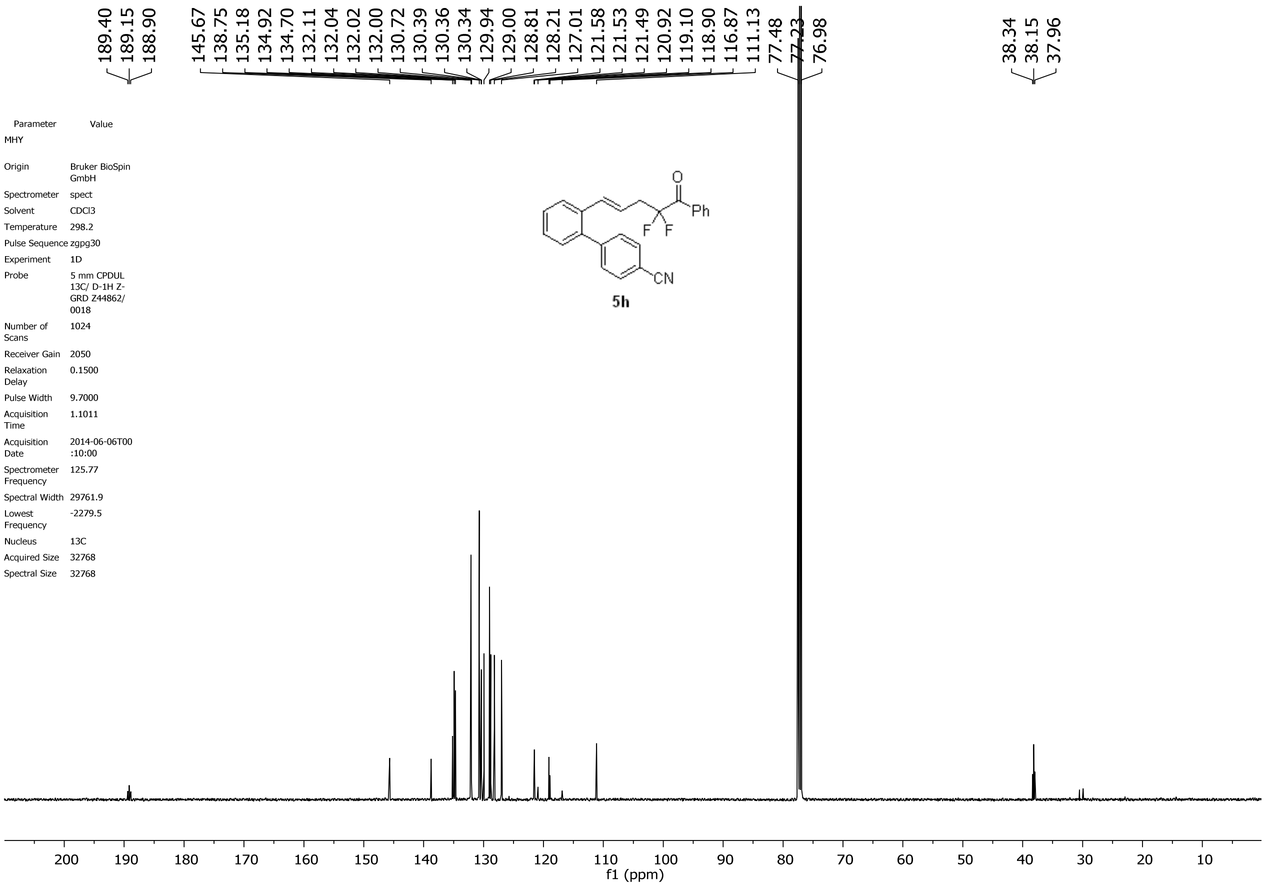


4h

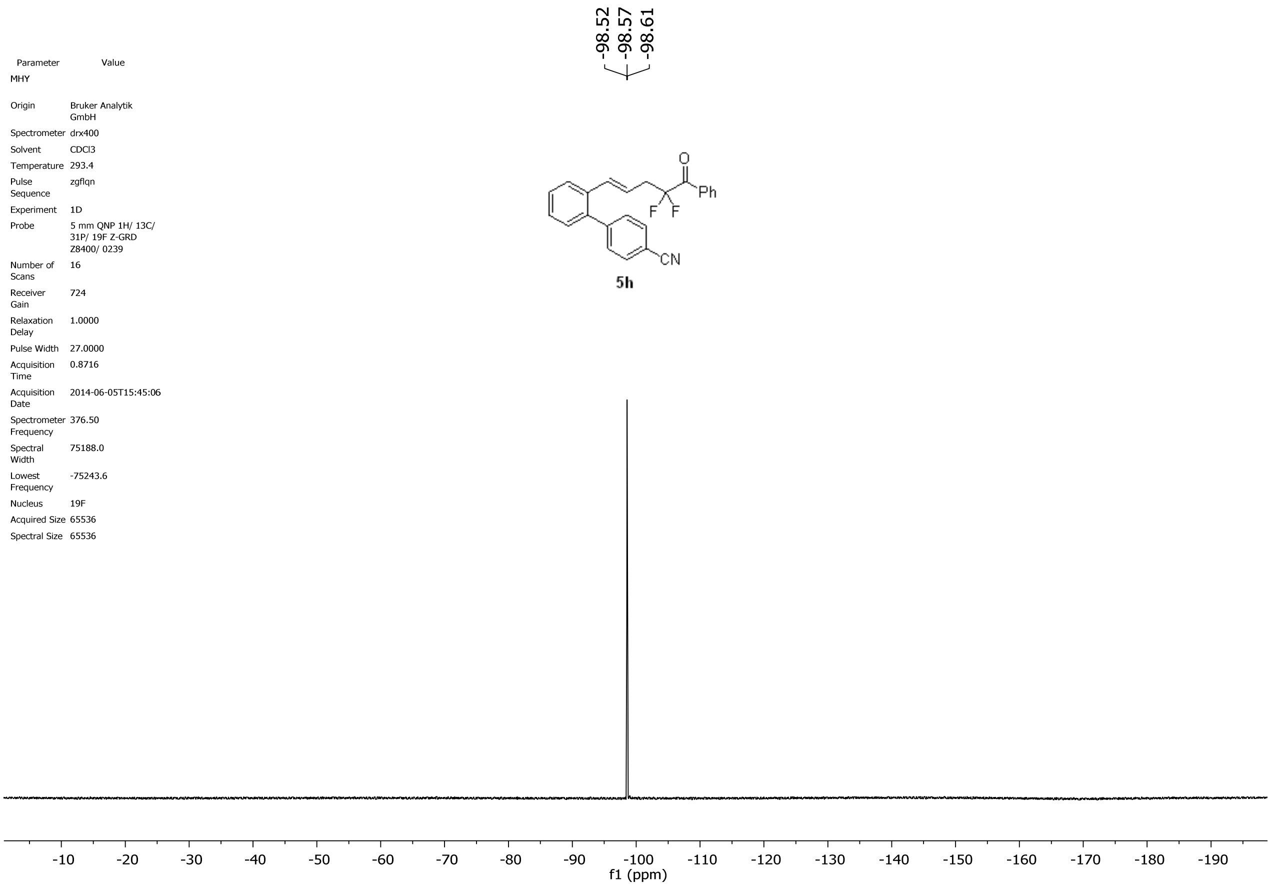
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-23T16:49:41
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



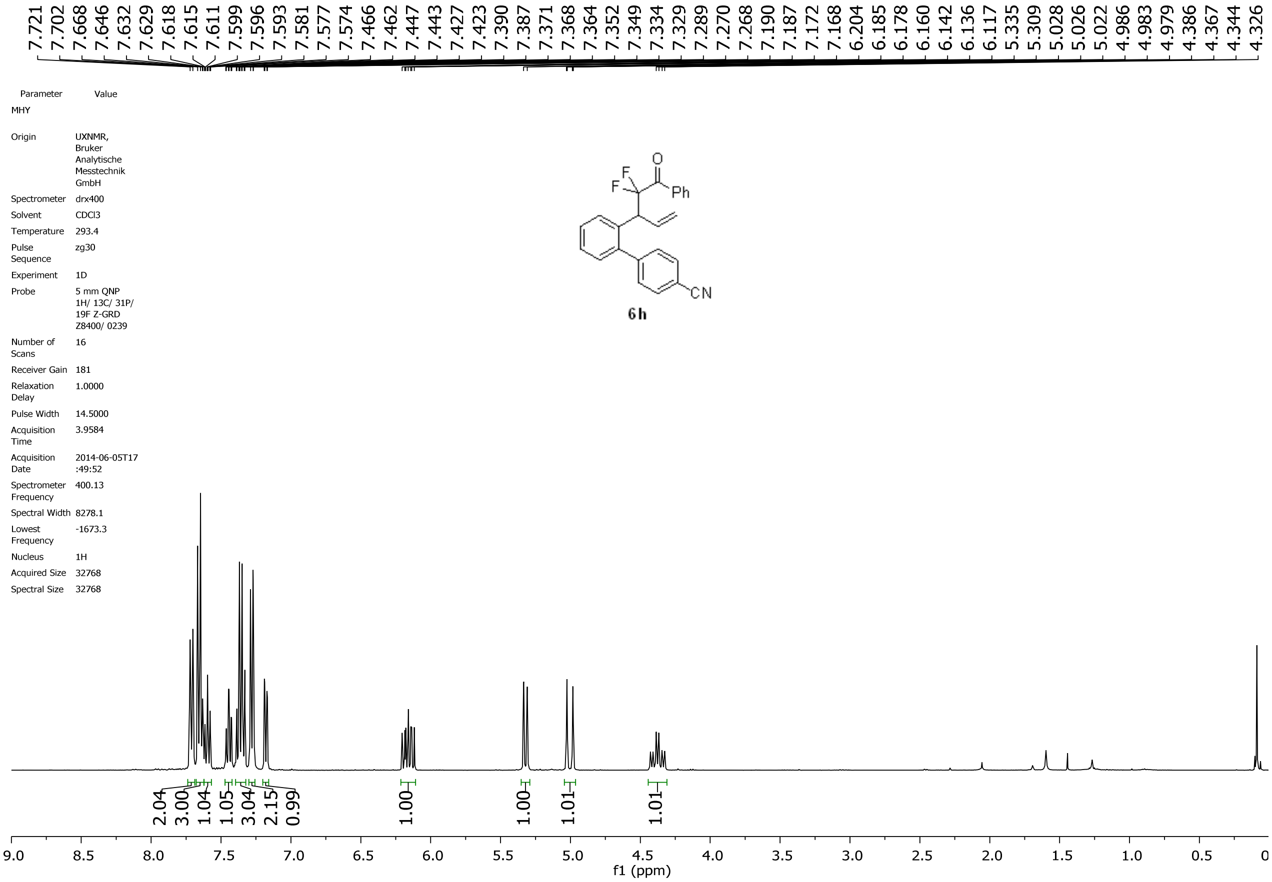
5h



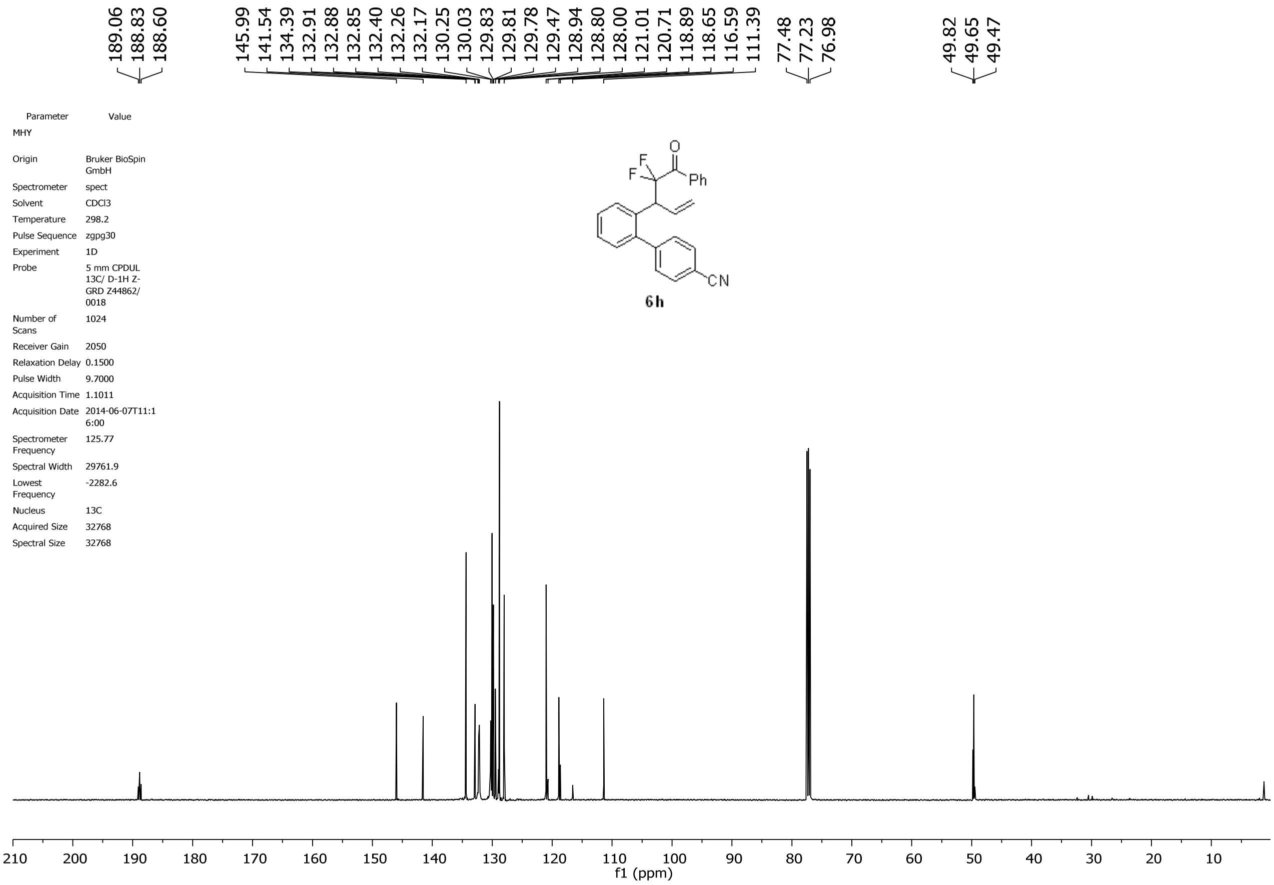
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-06T00:10:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



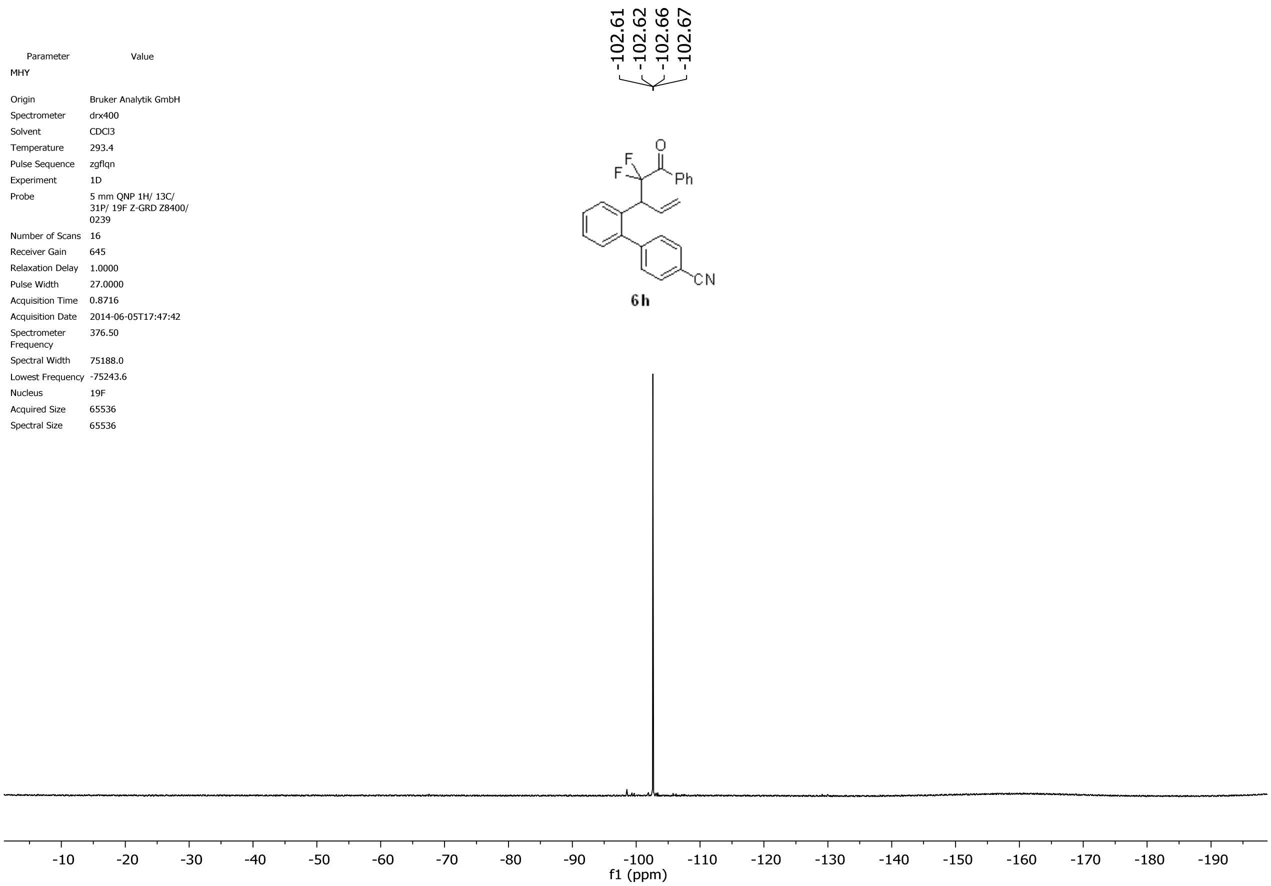
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-05T15:45:06
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-05T17:49:52
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

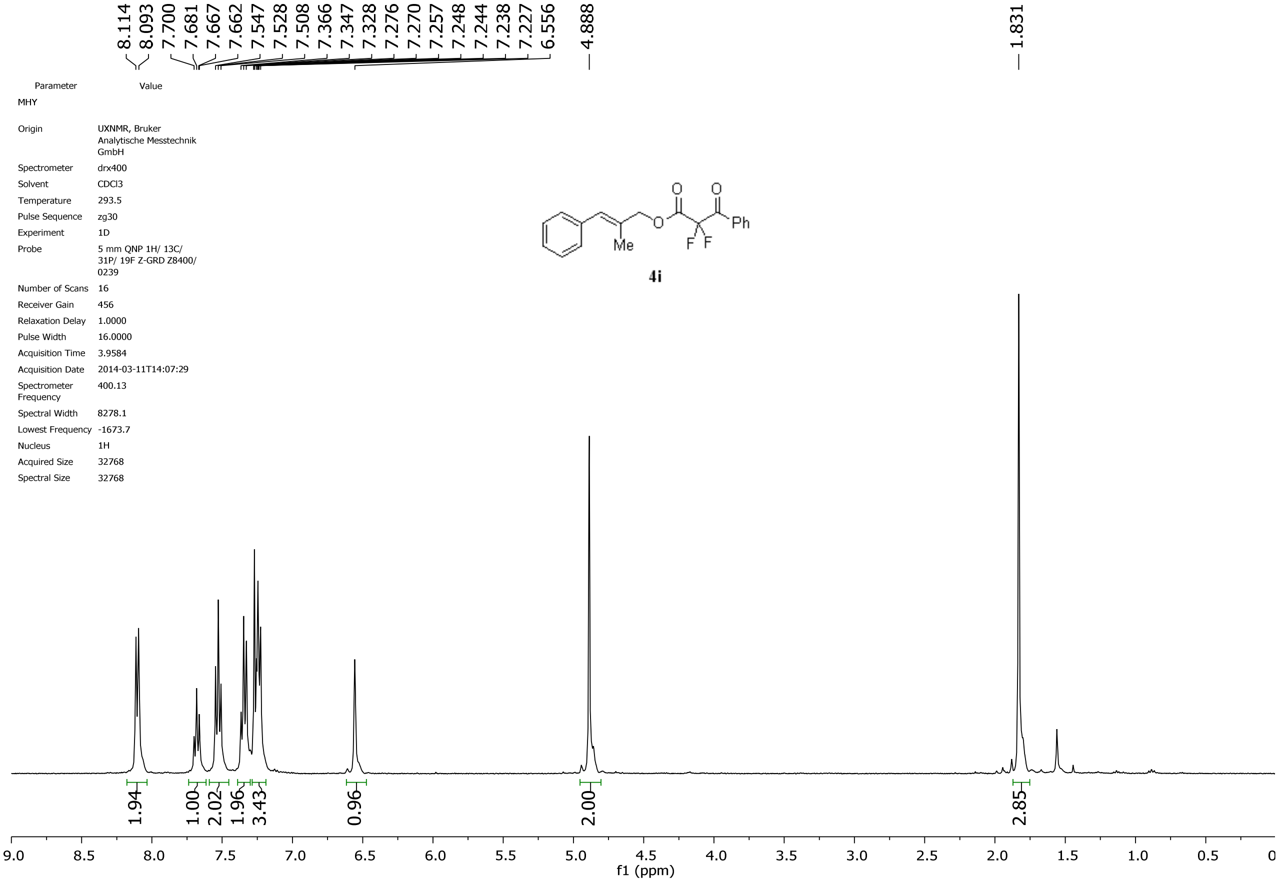


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-07T11:16:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2282.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



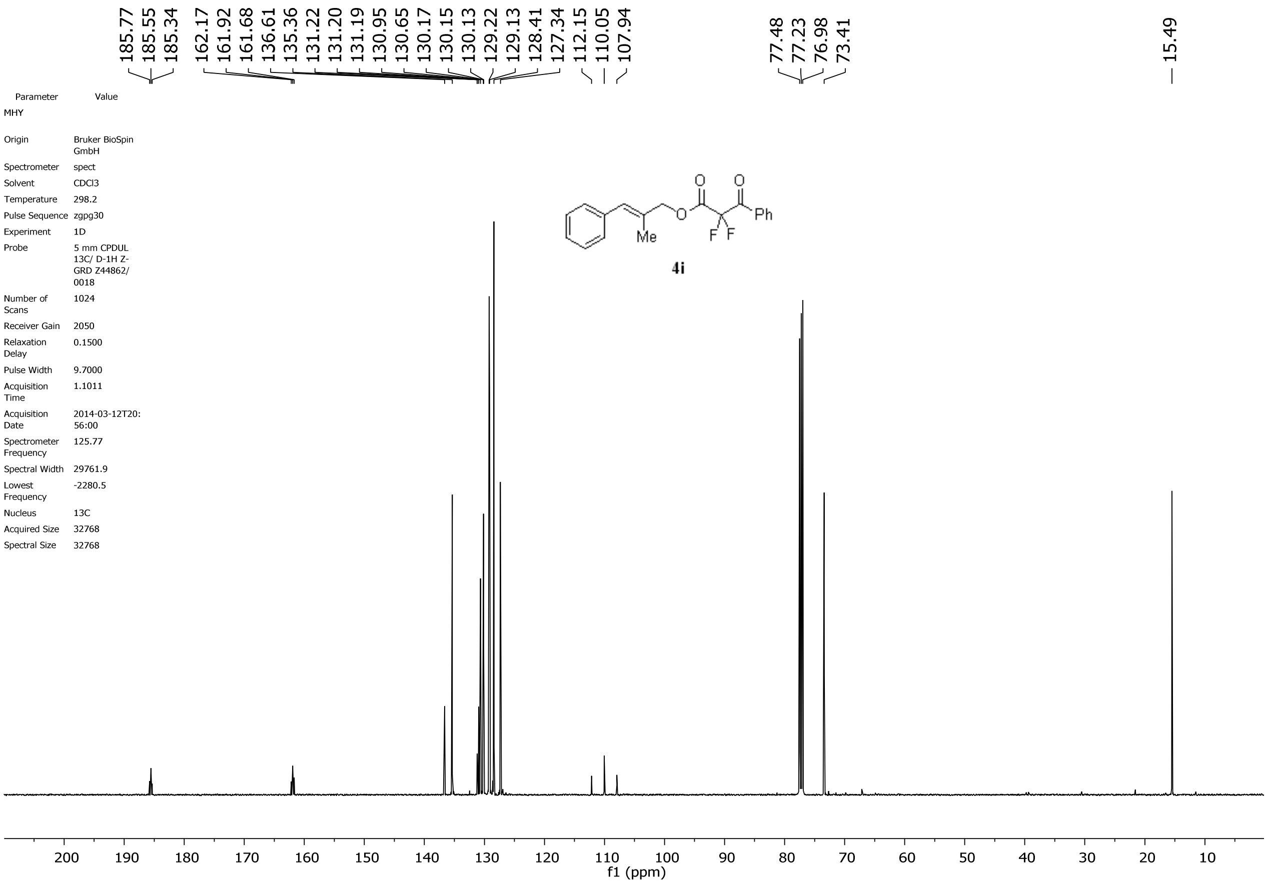
6h

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-05T17:47:42
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



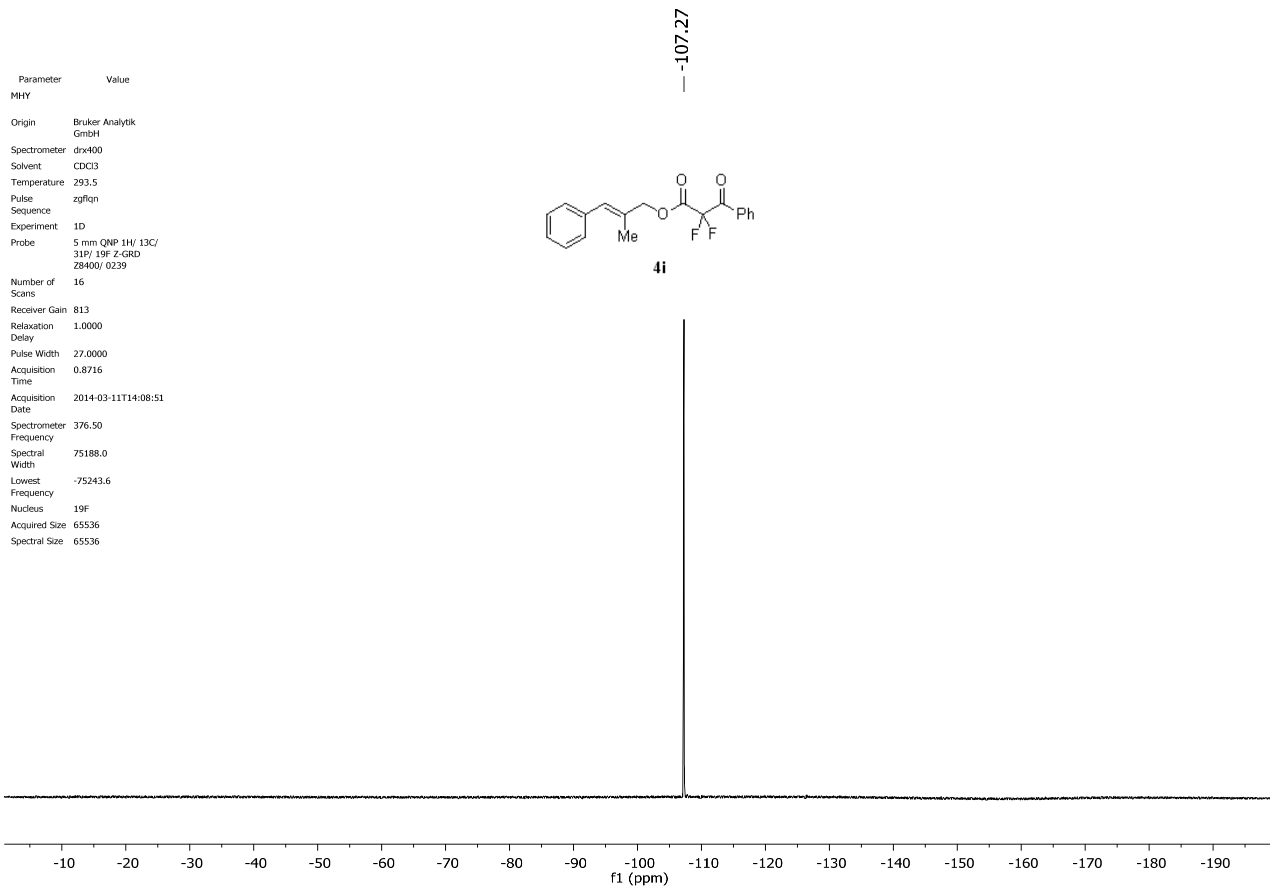
4i

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-03-11T14:07:29
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



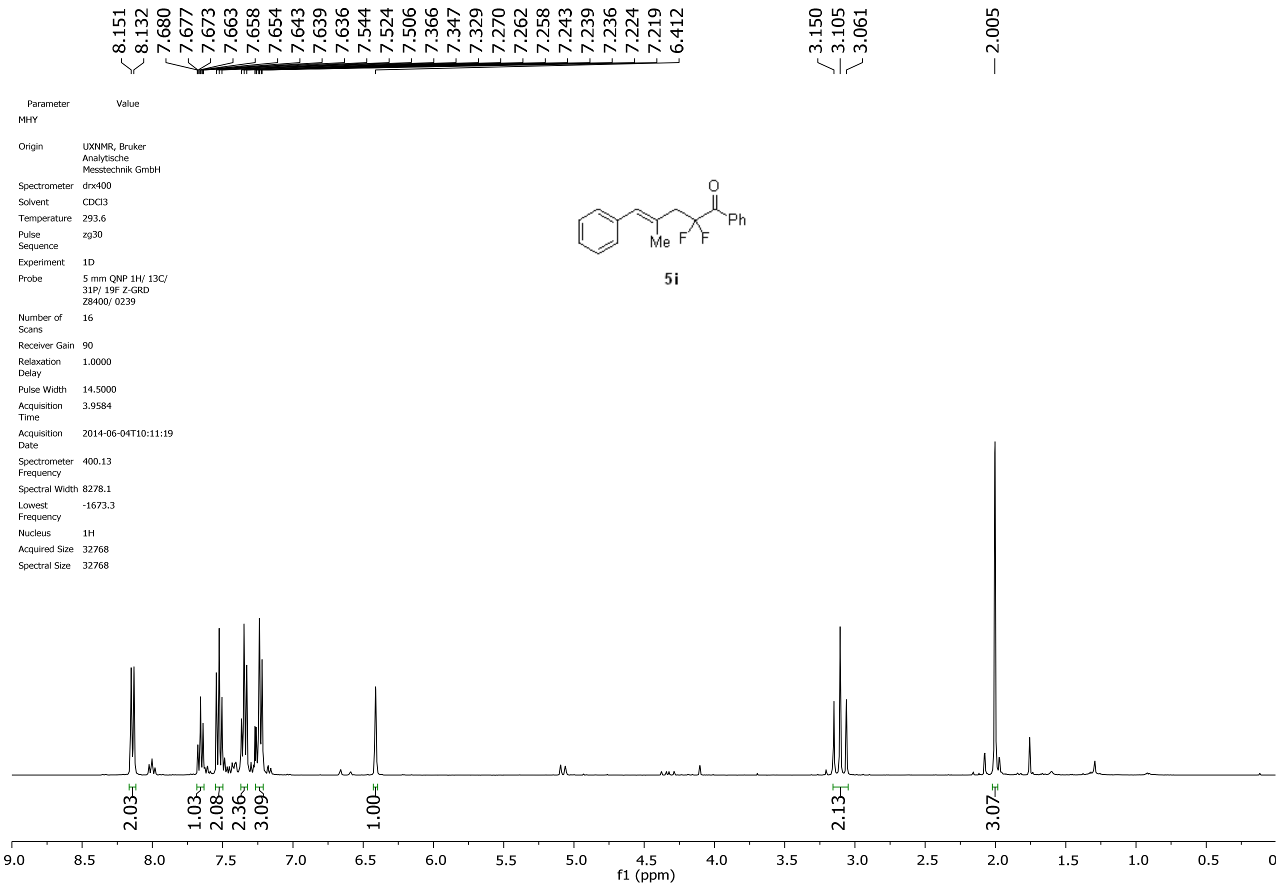
4i

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-03-12T20:56:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



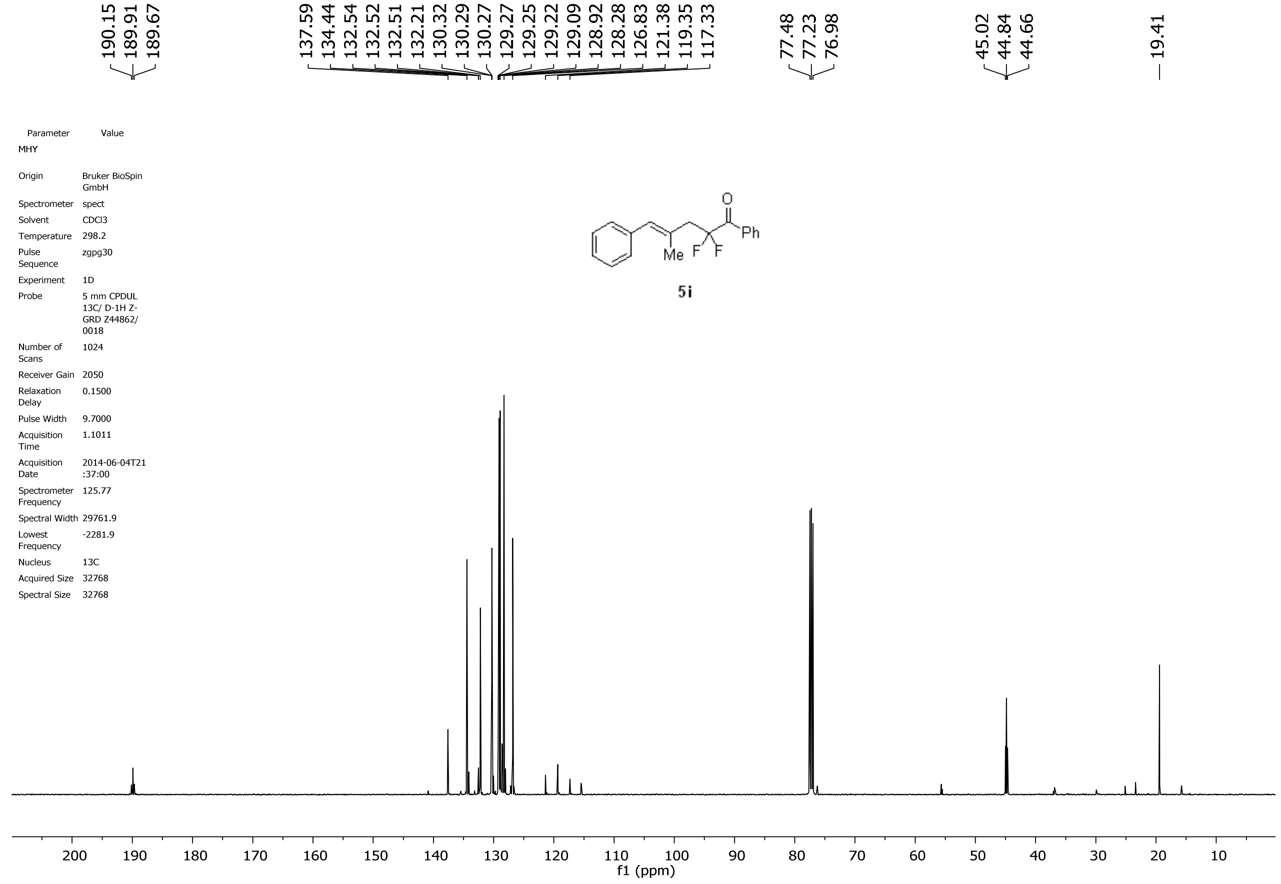
4i

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-03-11T14:08:51
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



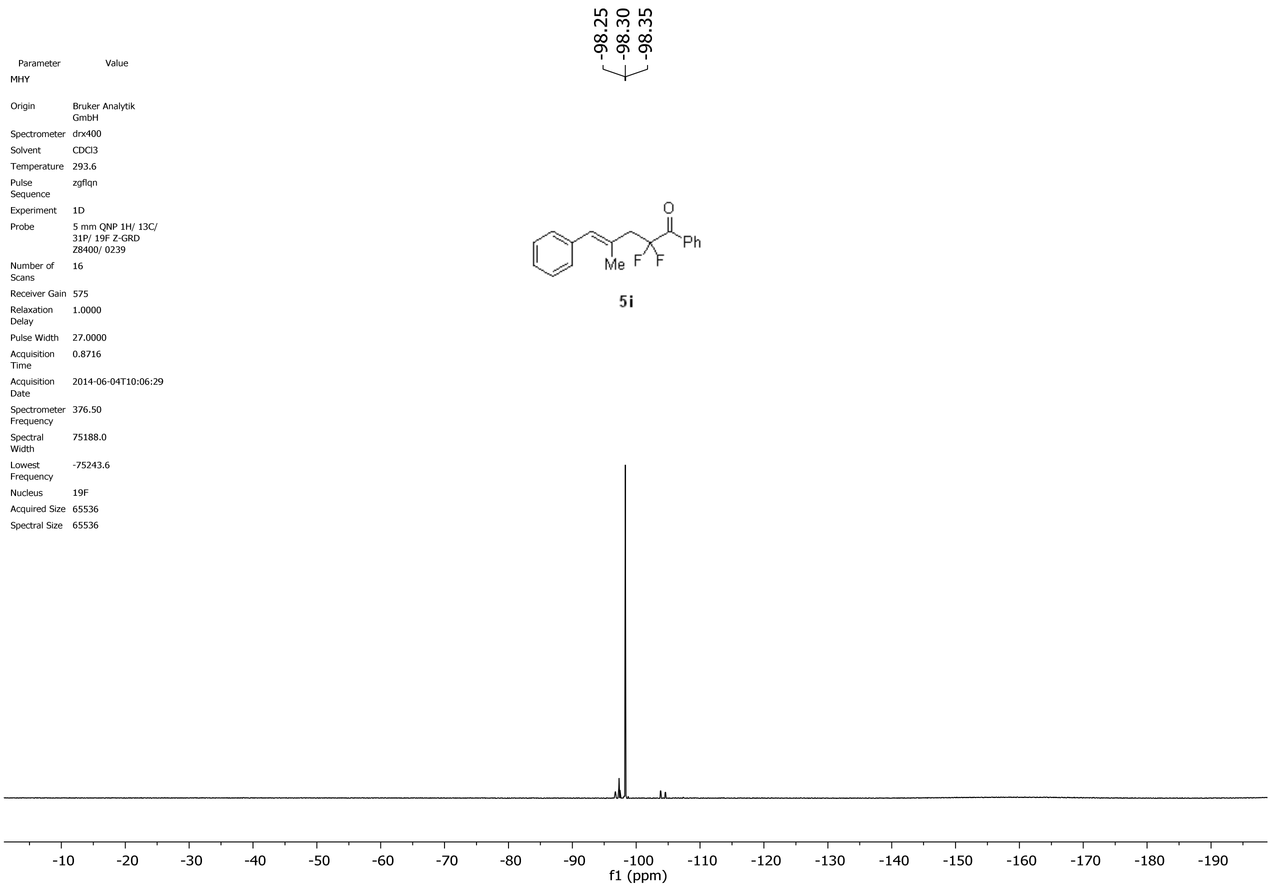
5i

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	90
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-04T10:11:19
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



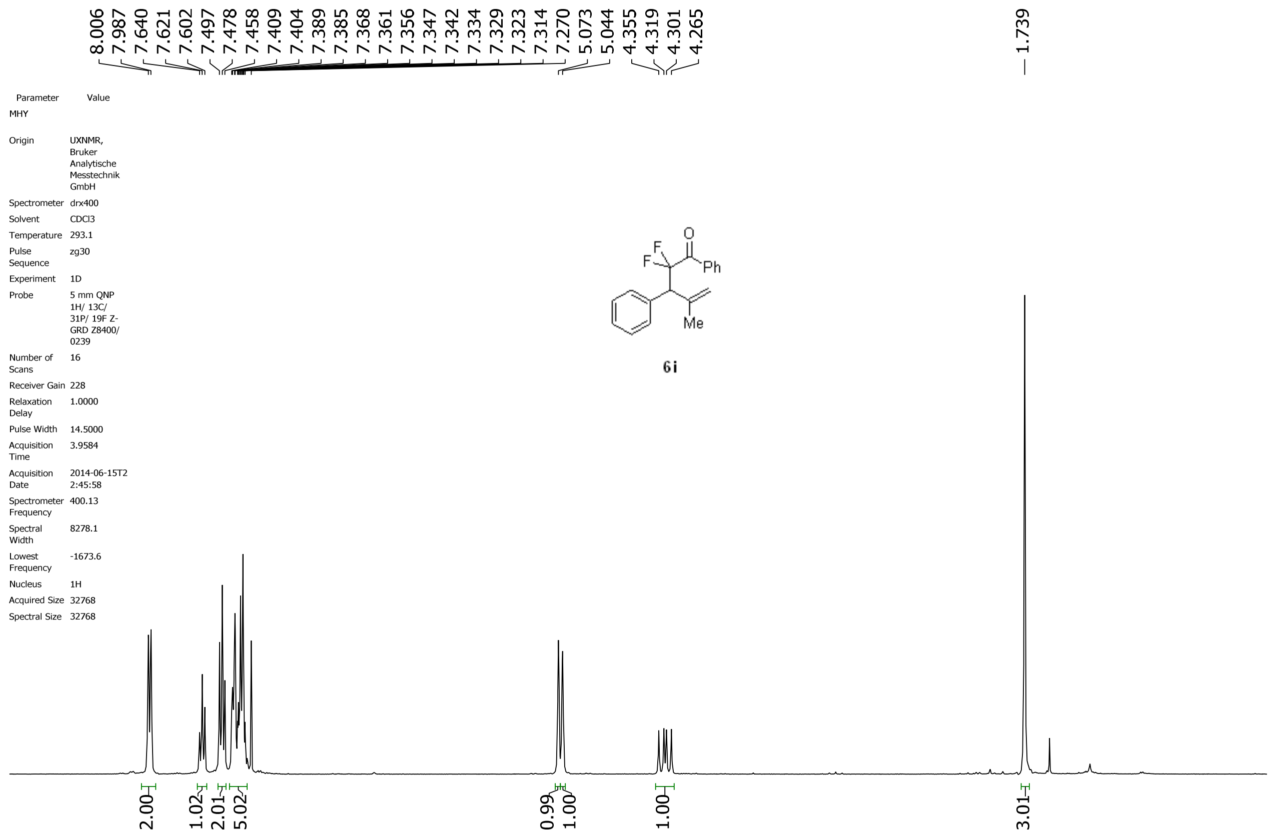
5i

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-04T21:37:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



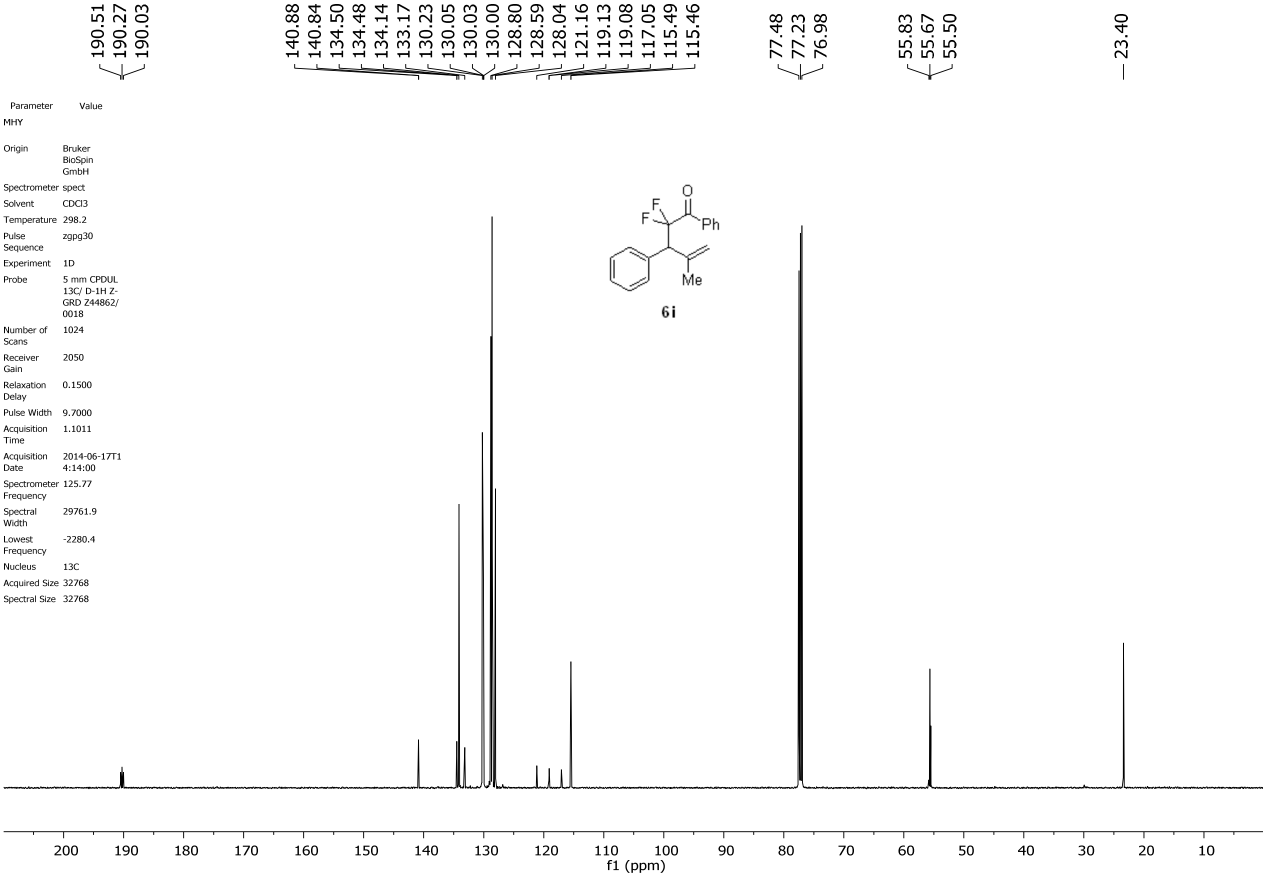
5i

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-04T10:06:29
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



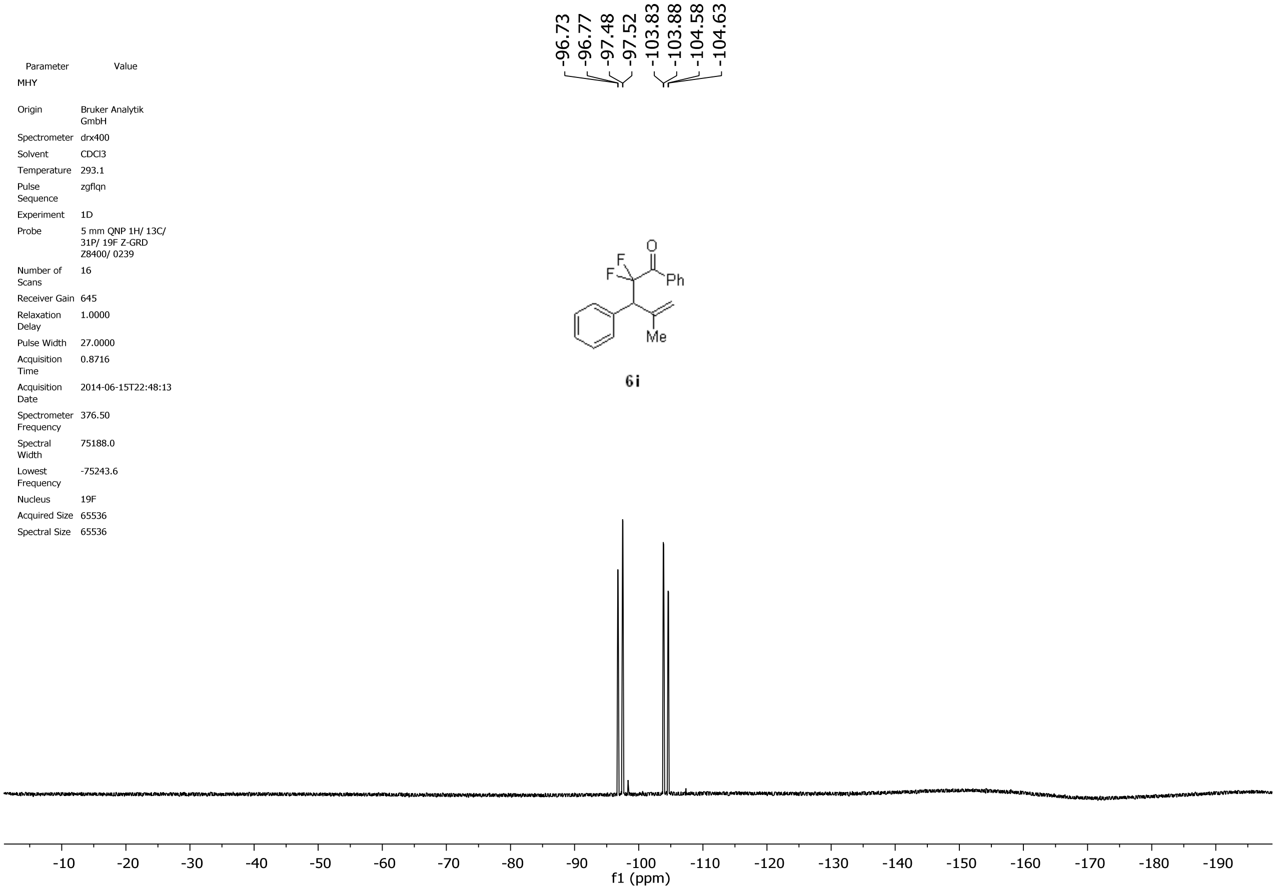
6i

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-15T2 2:45:58
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.6
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



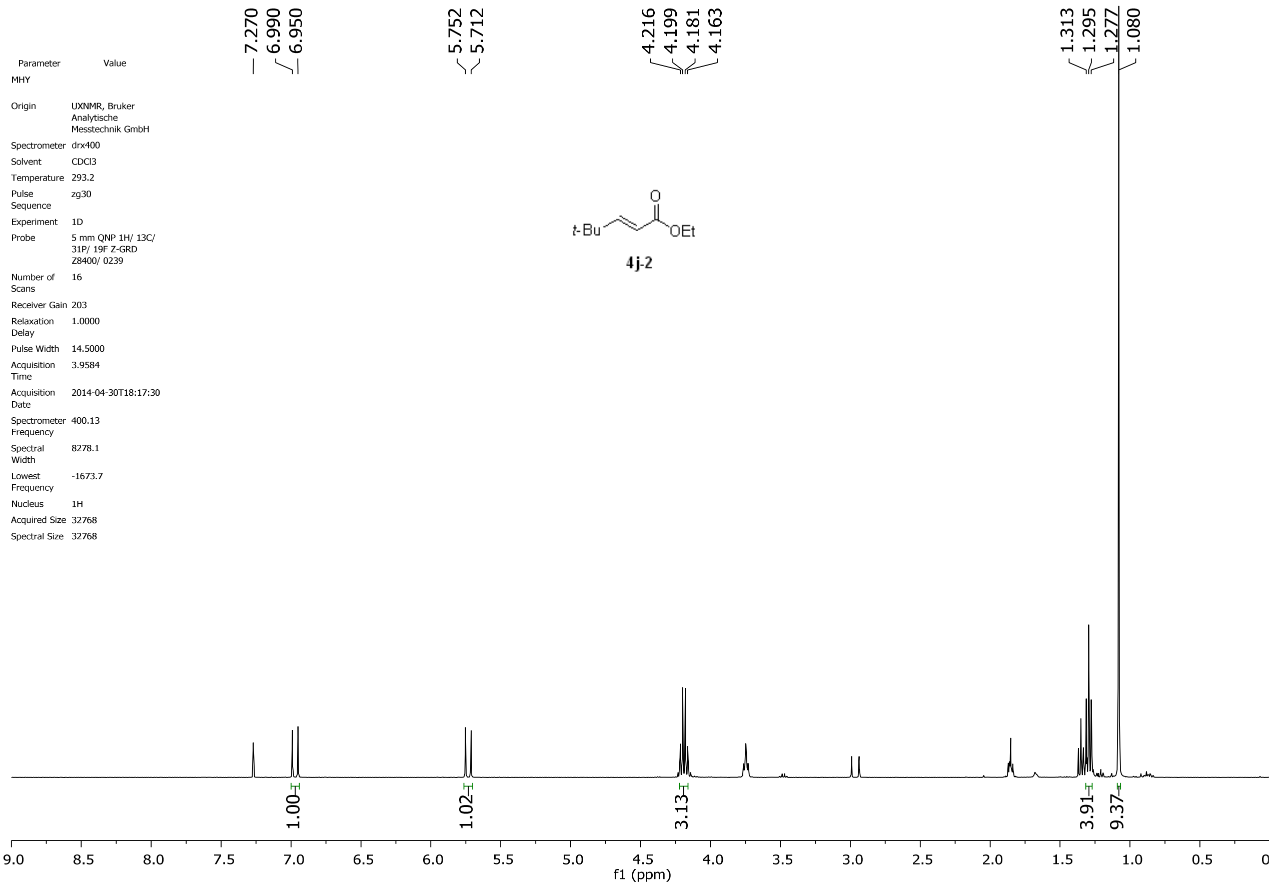
6i

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-17T14:14:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.4
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



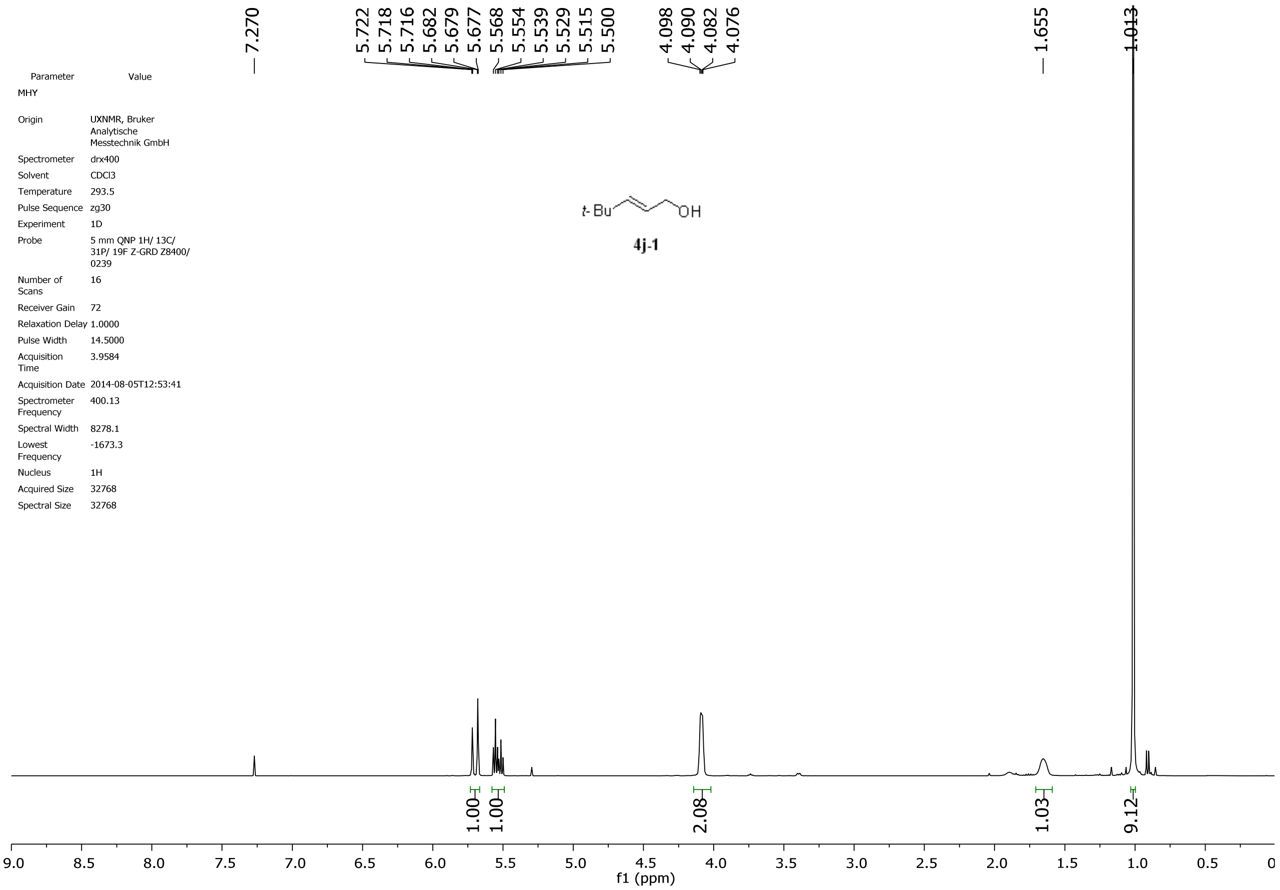
6i

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-15T22:48:13
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



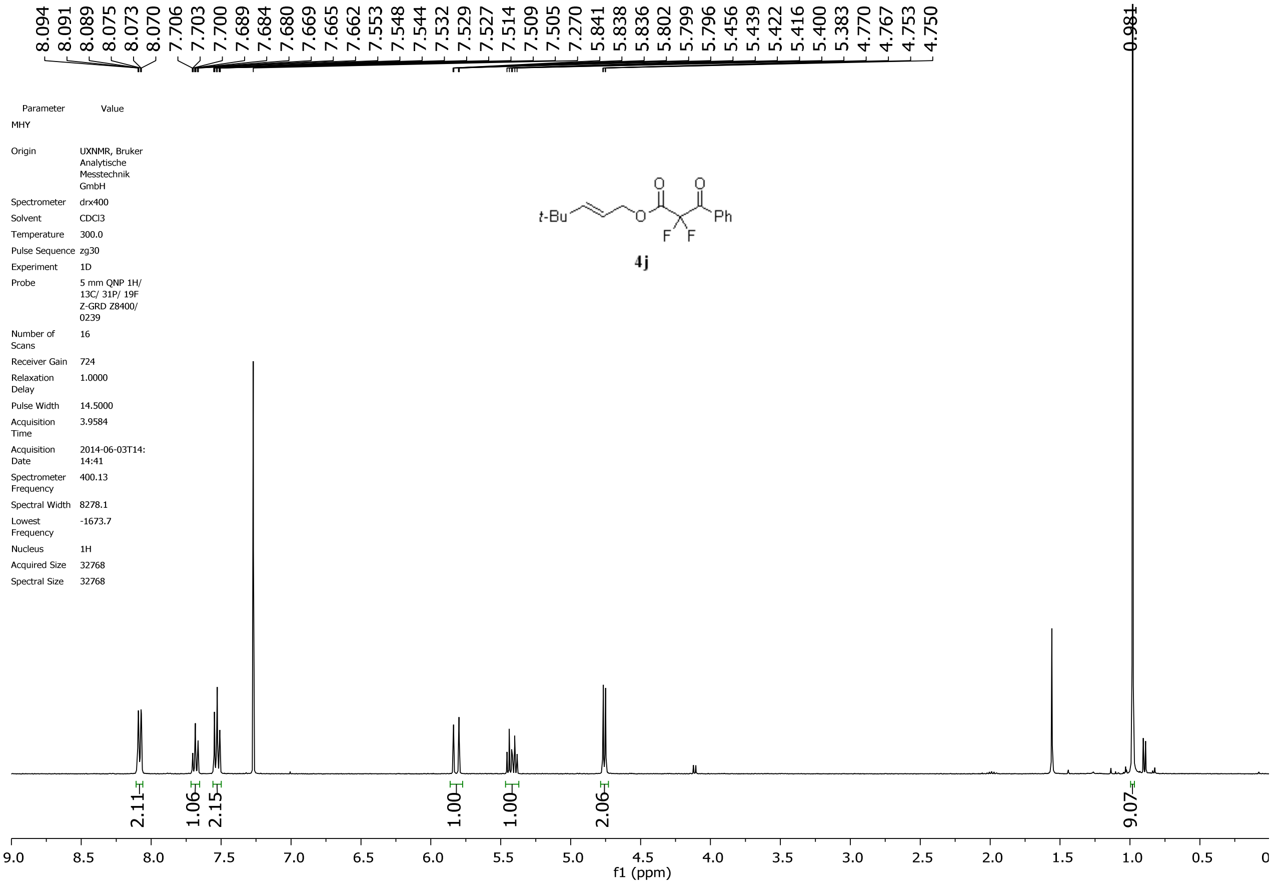
4j-2

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-04-30T18:17:30
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



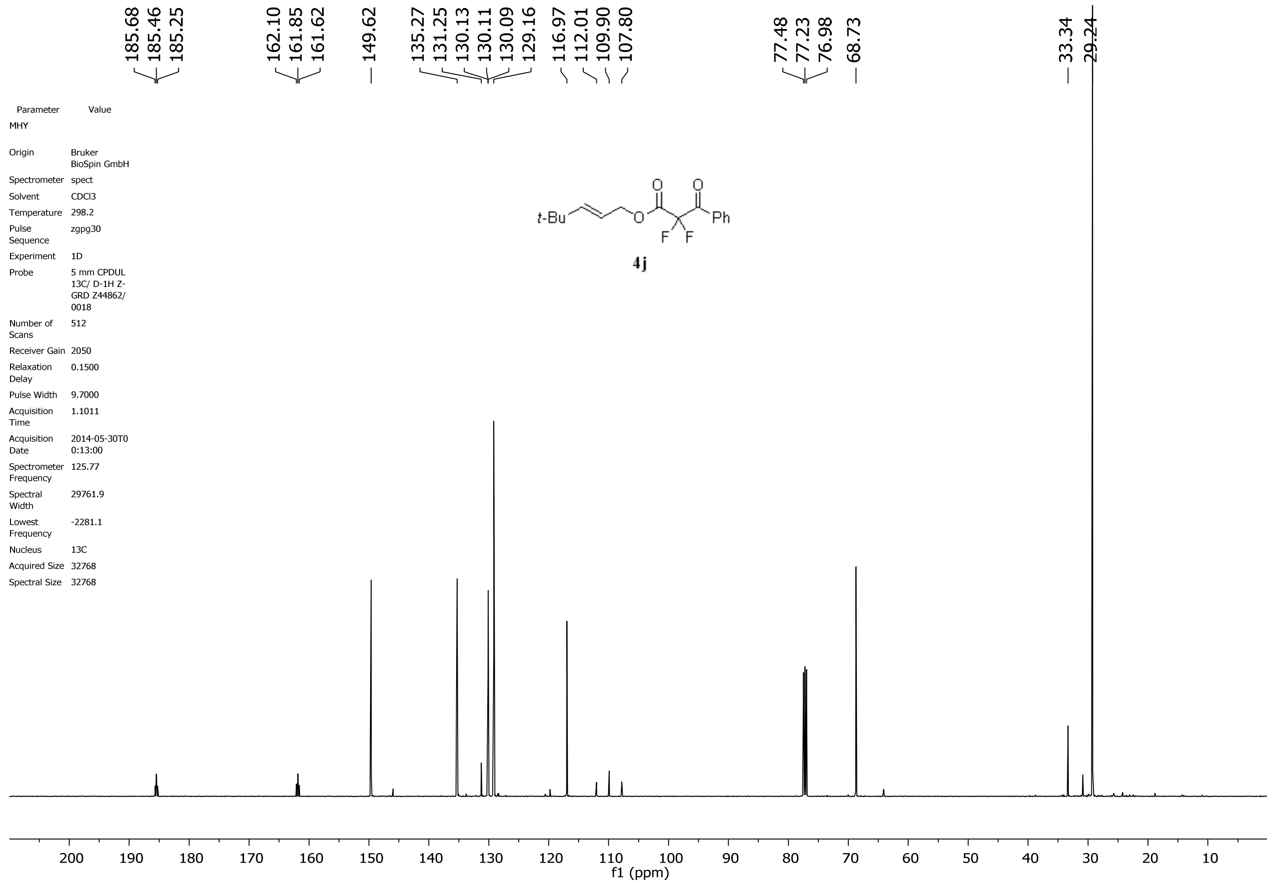
4j-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	72
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-08-05T12:53:41
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



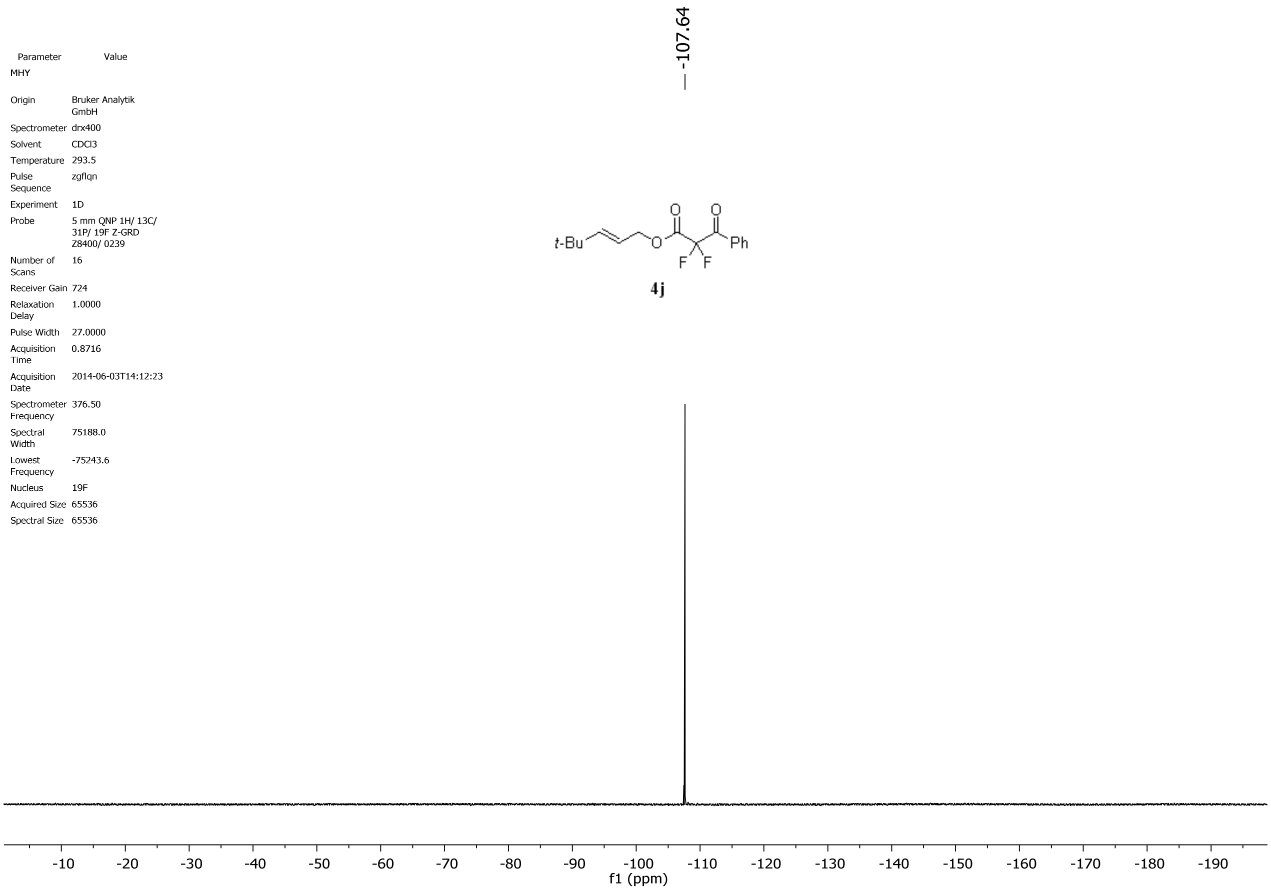
4j

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	300.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-03T14:14:41
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



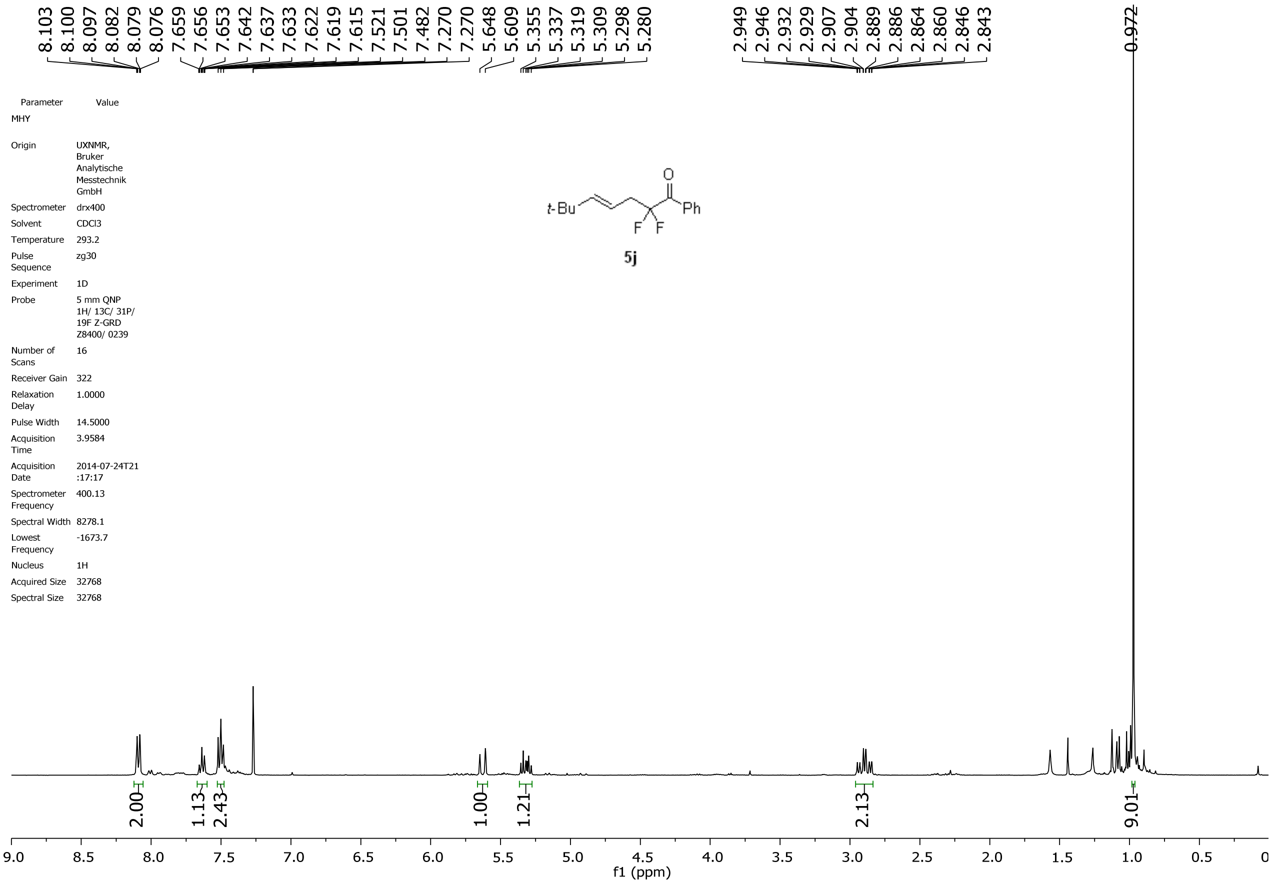
4j

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	512
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-05-30T00:13:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



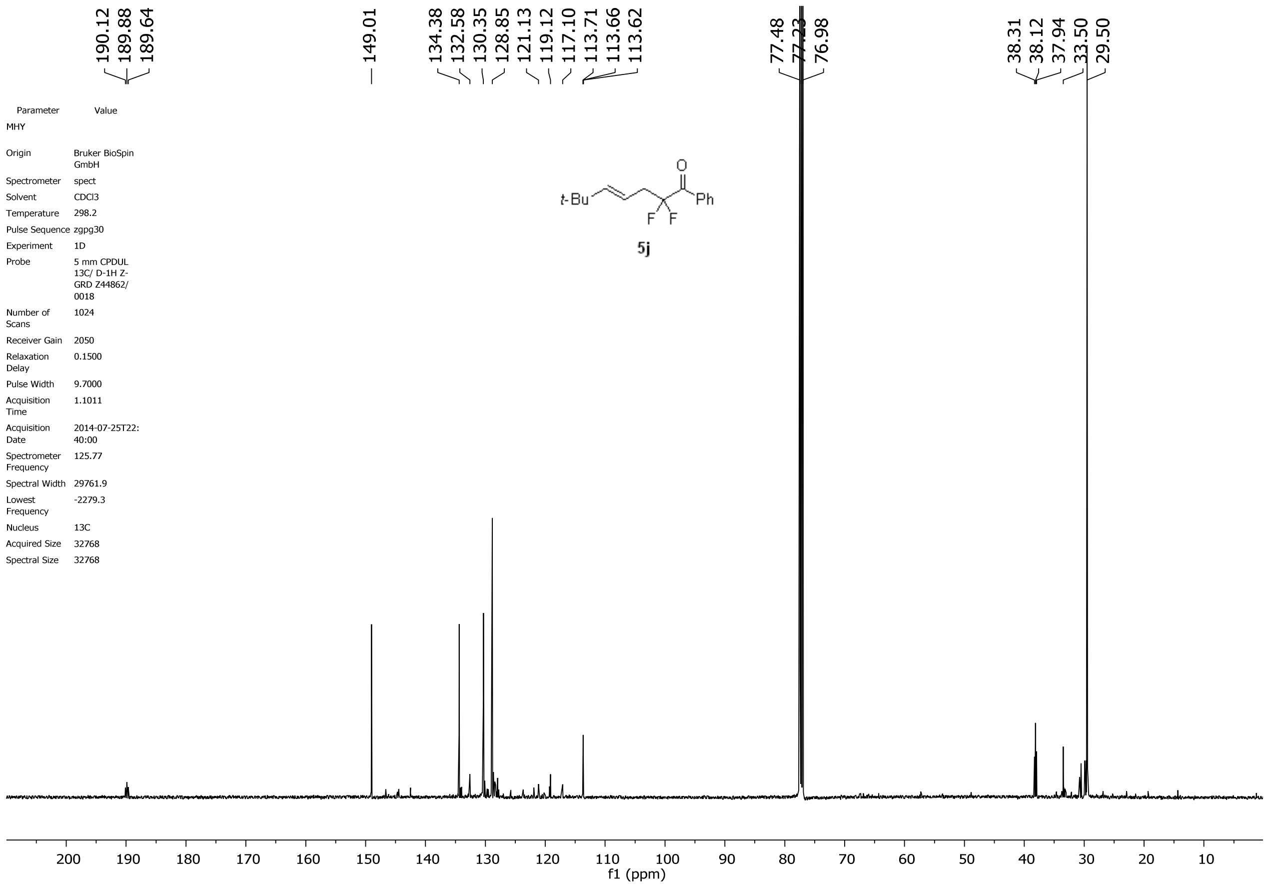
4j

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-03T14:12:23
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

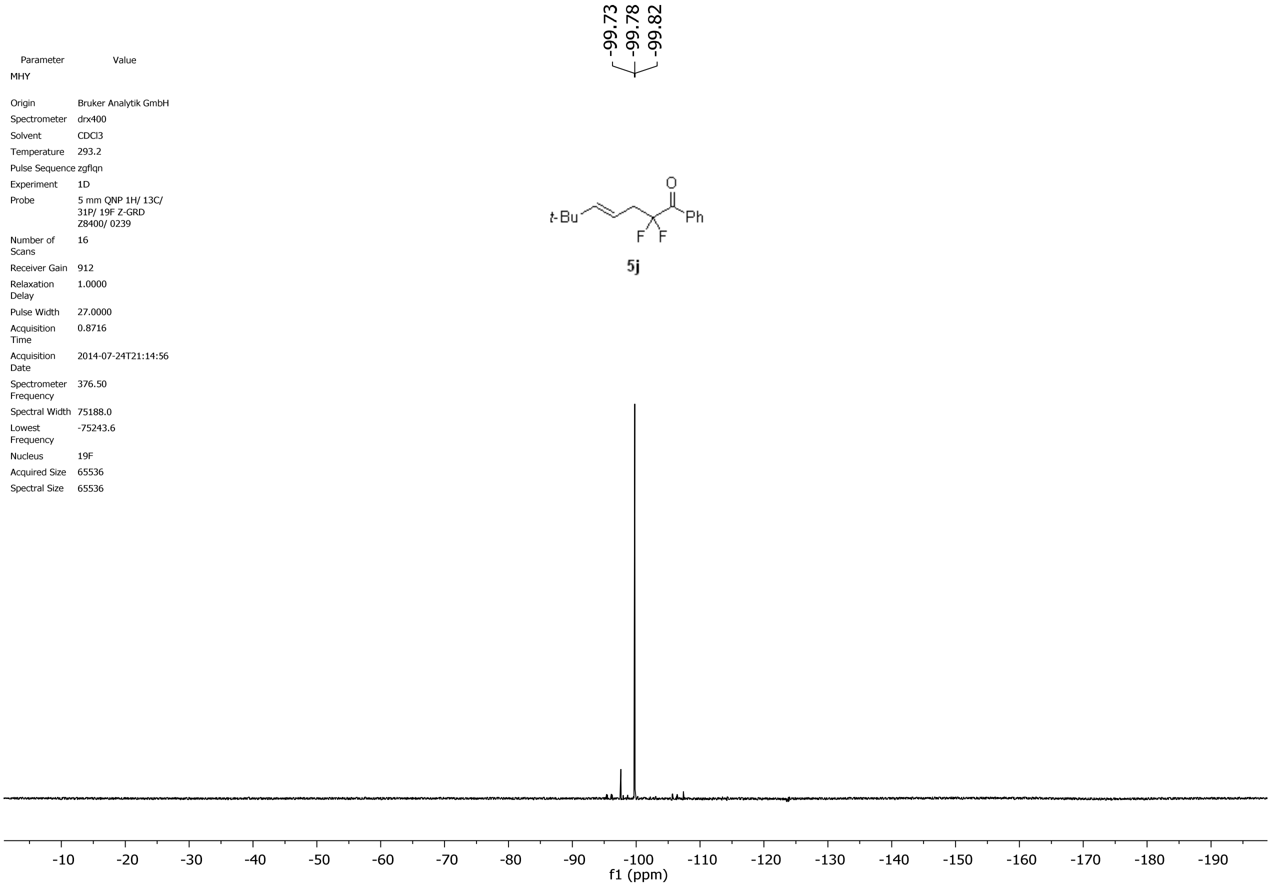


5j

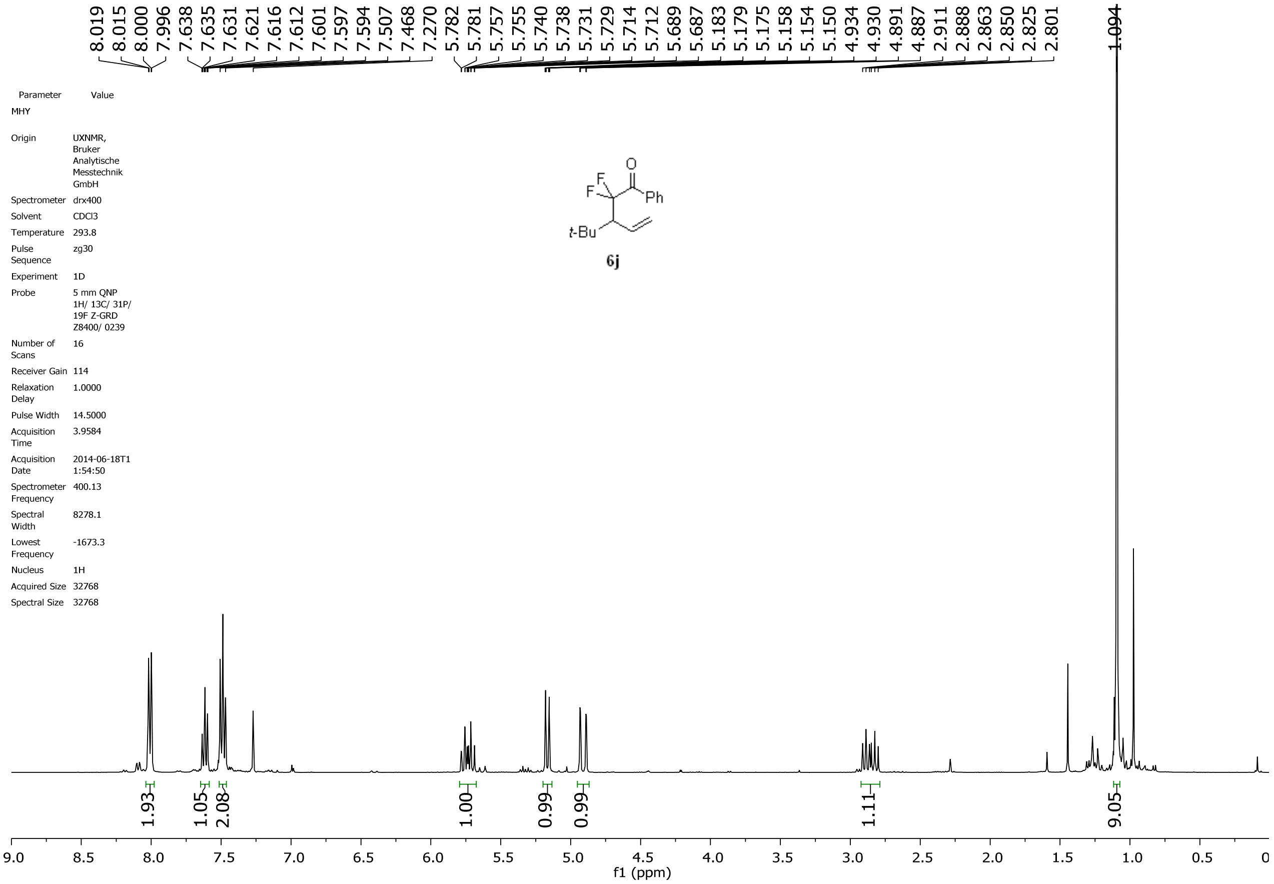
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-24T21:17:17
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-25T22:40:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.3
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

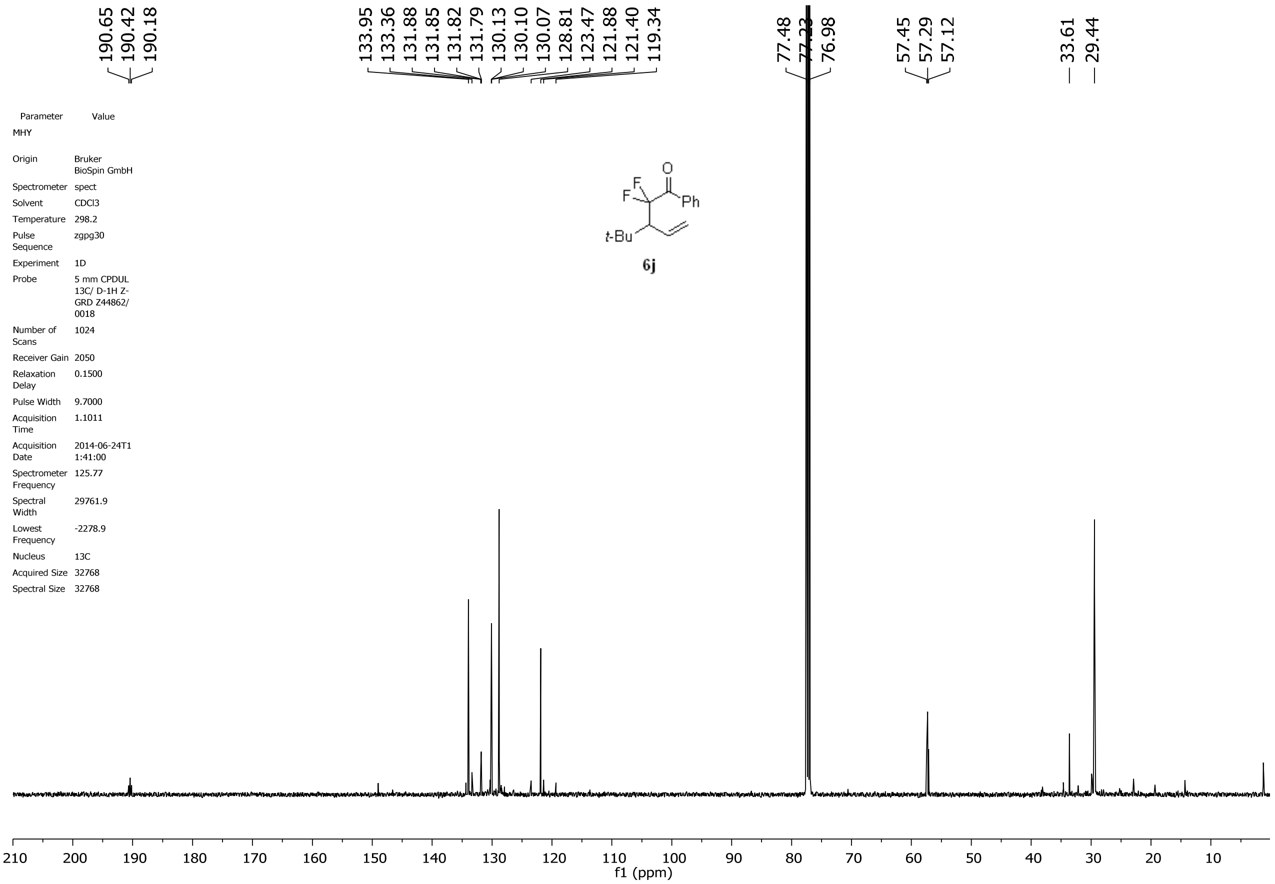


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-24T21:14:56
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



6j

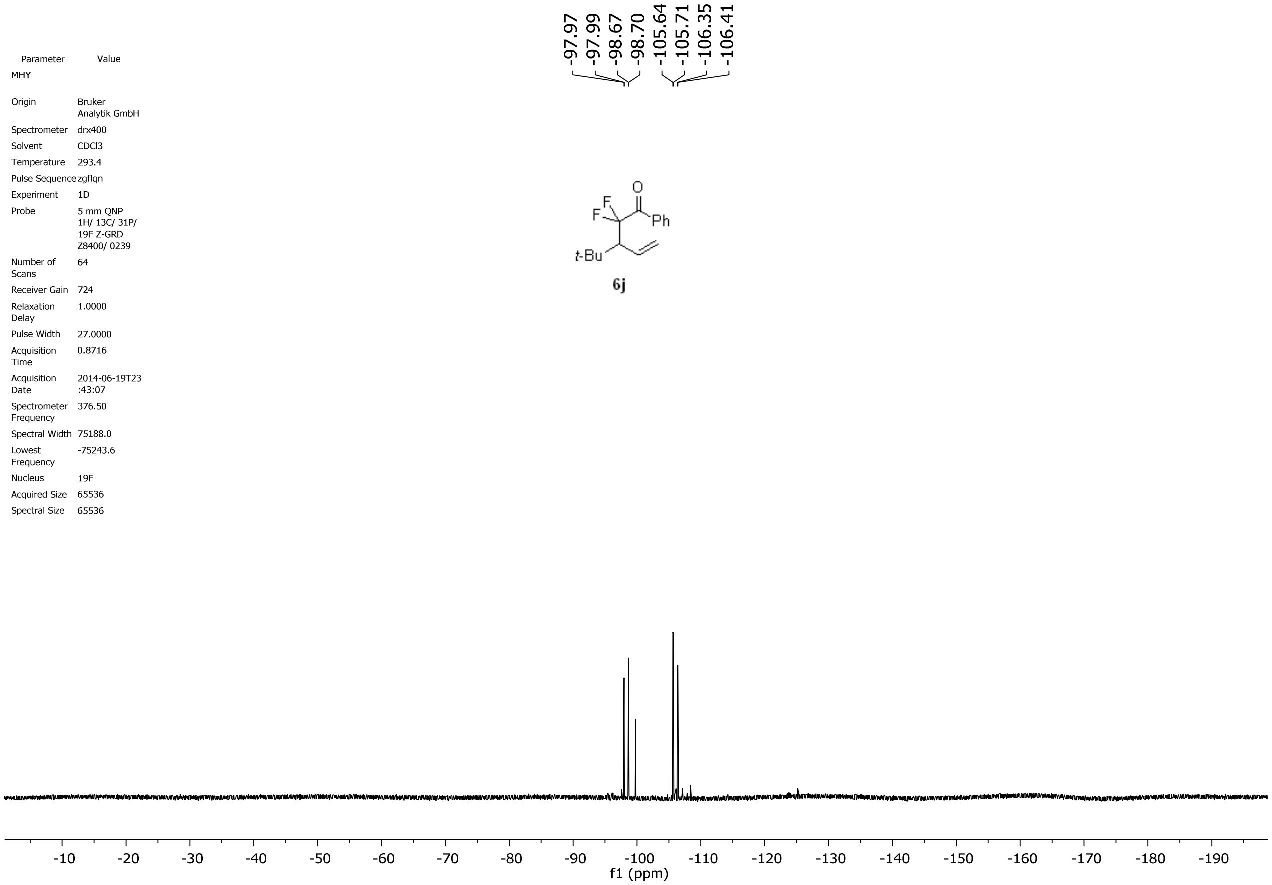
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	114
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-18T1 1:54:50
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



6j

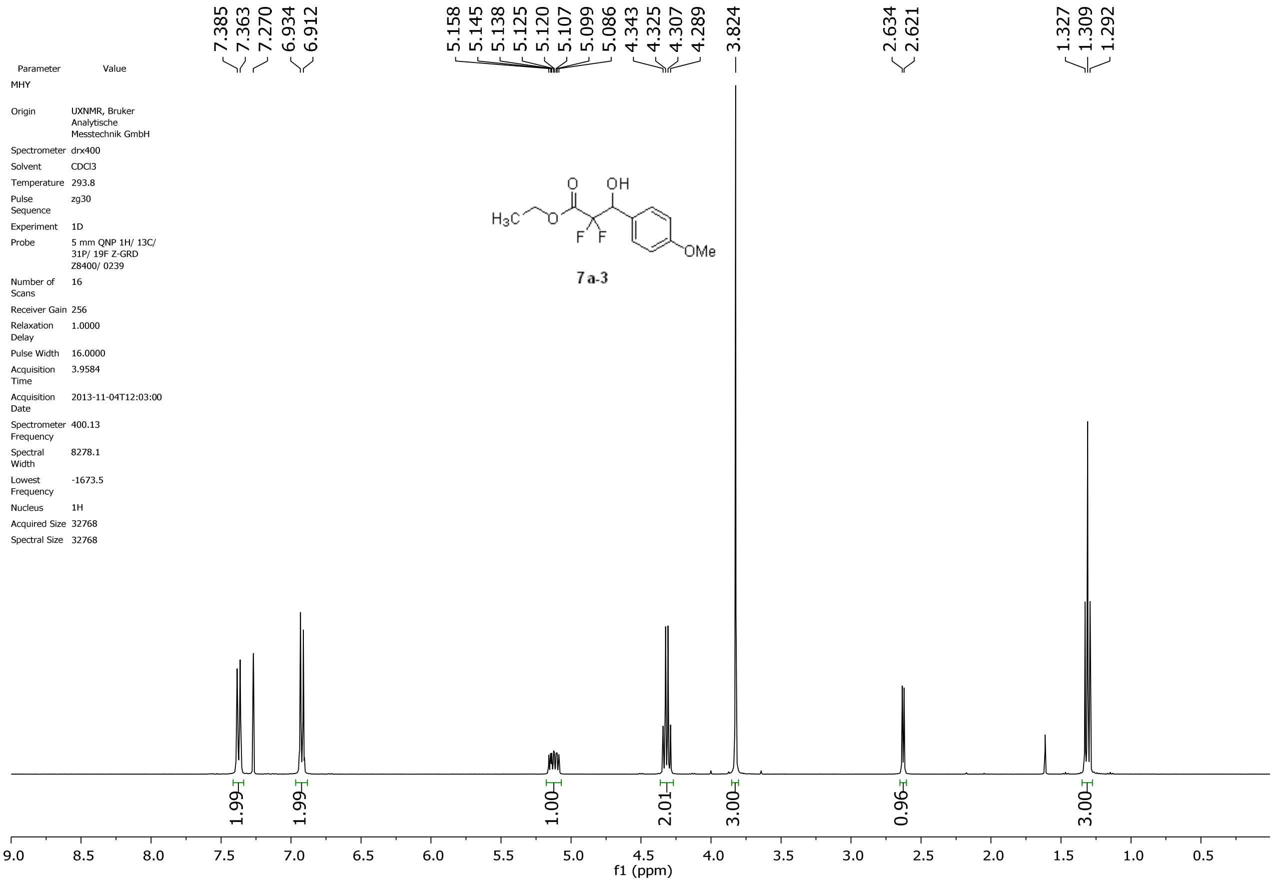
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-24T1 1:41:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2278.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	64
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-19T23:43:07
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



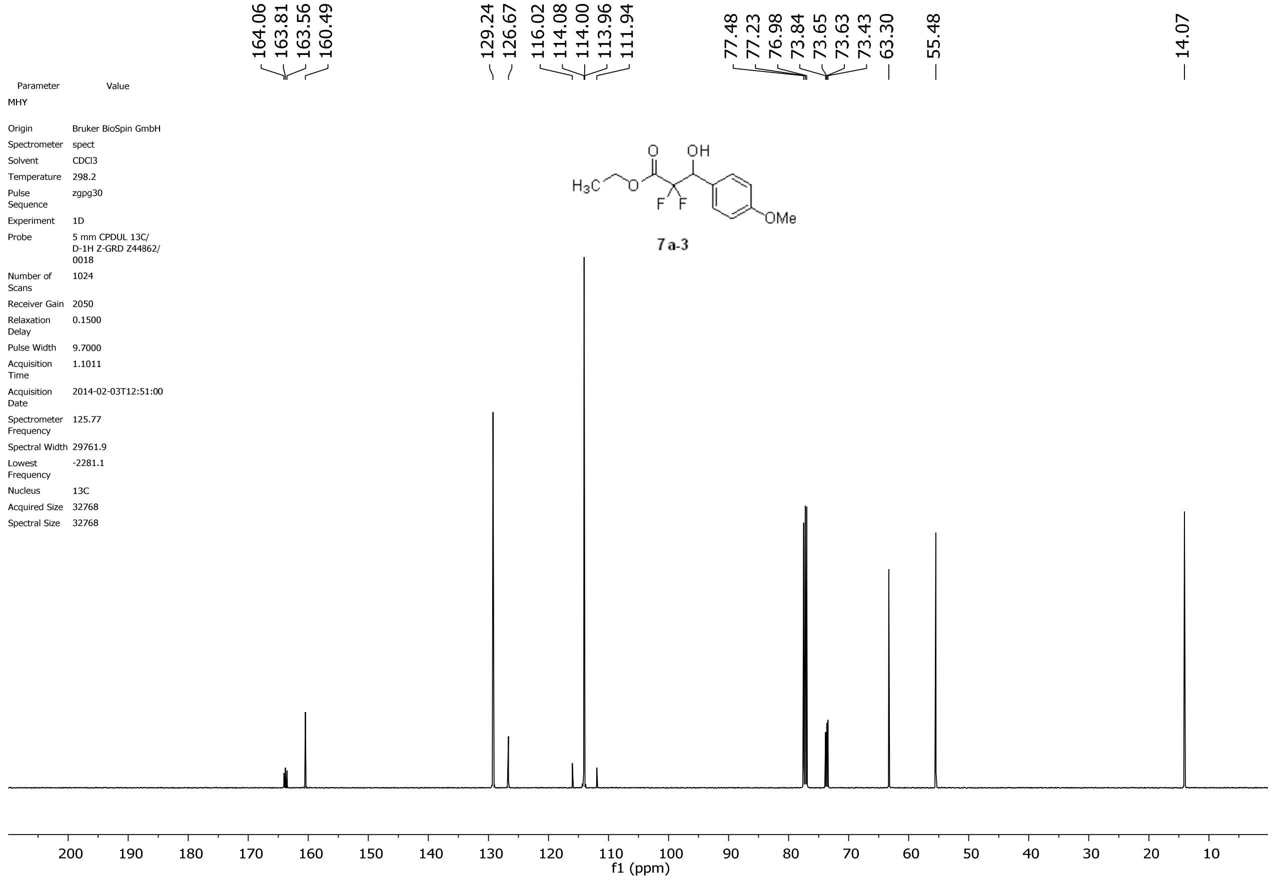
6j

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-04T12:03:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



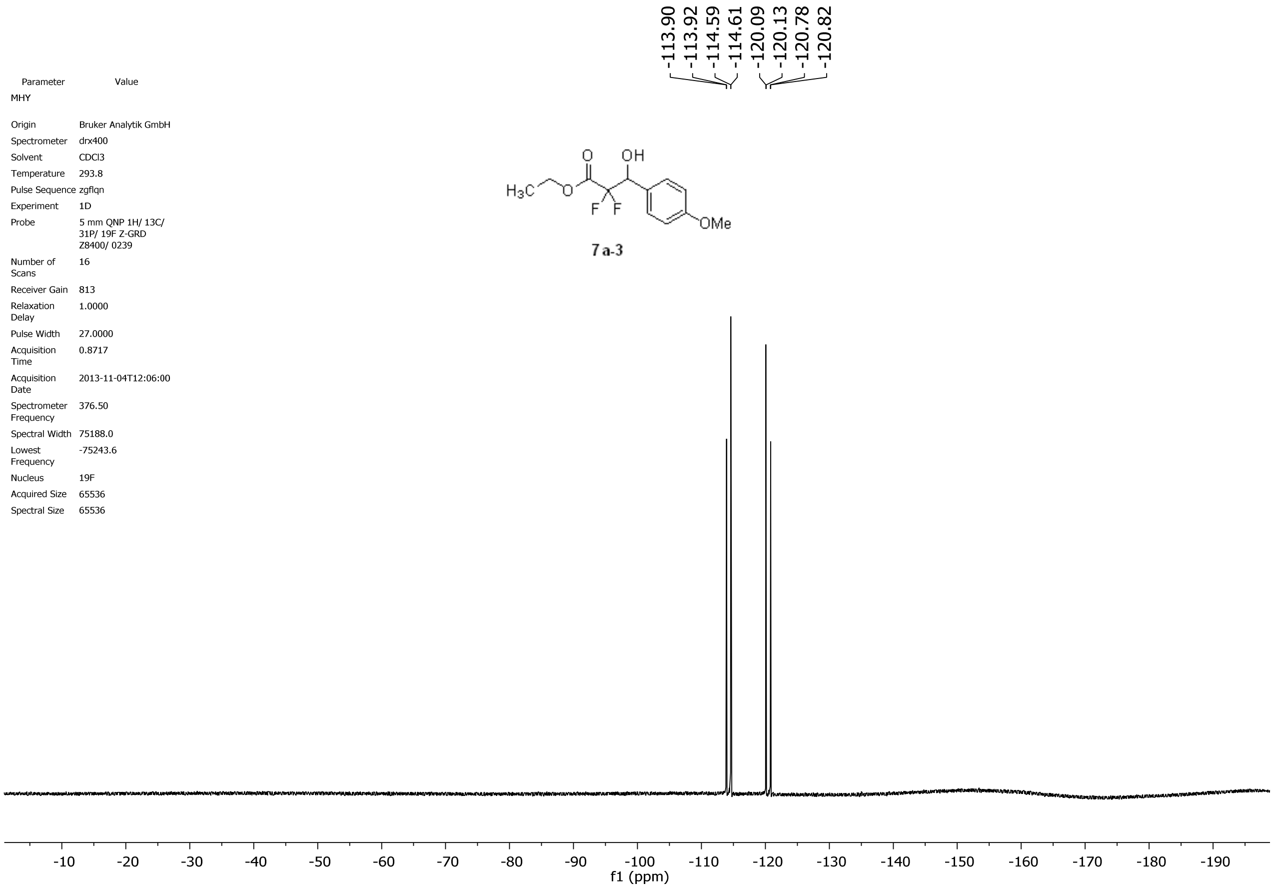
7 a-3

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-03T12:51:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

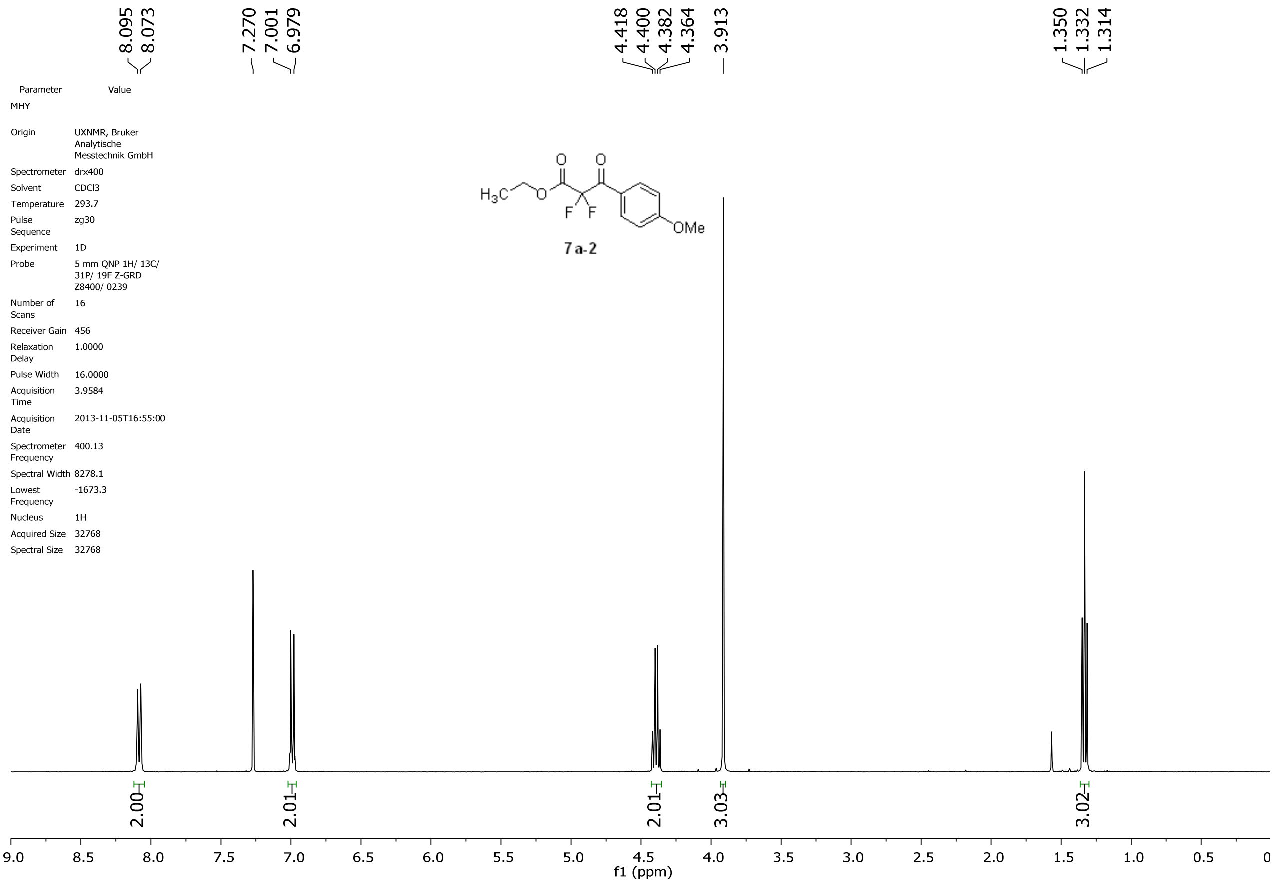


7a-3

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-04T12:06:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

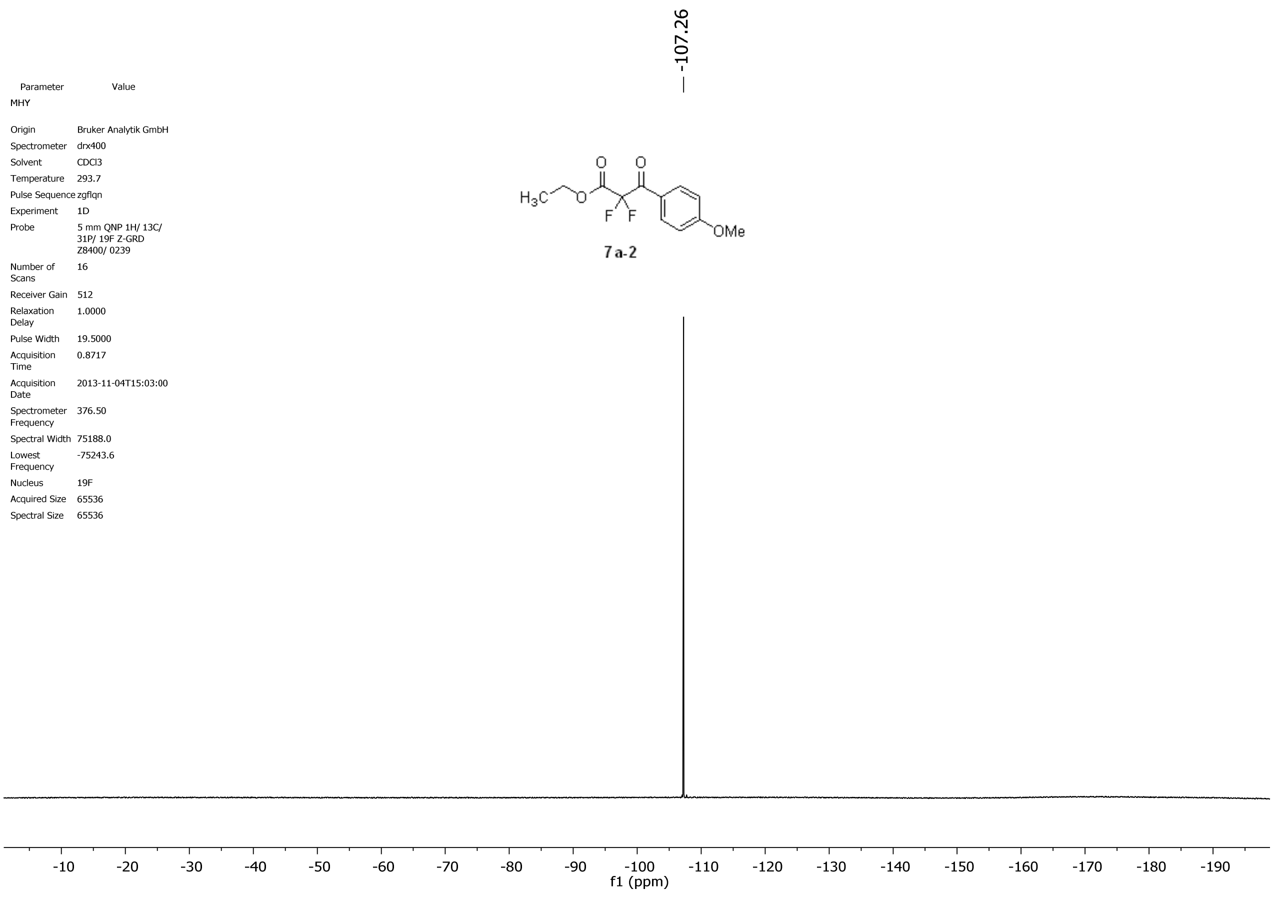


7a-3



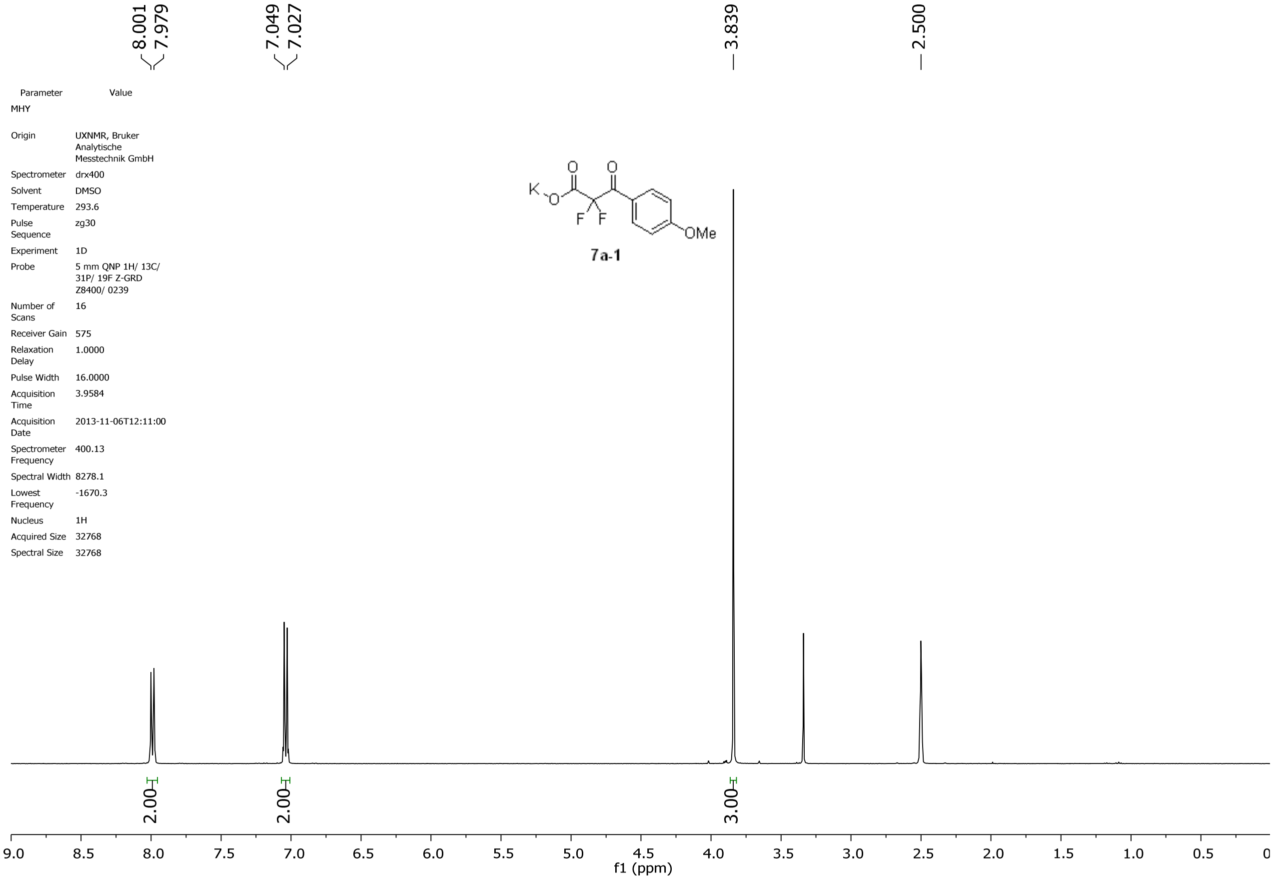
7a-2

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-05T16:55:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

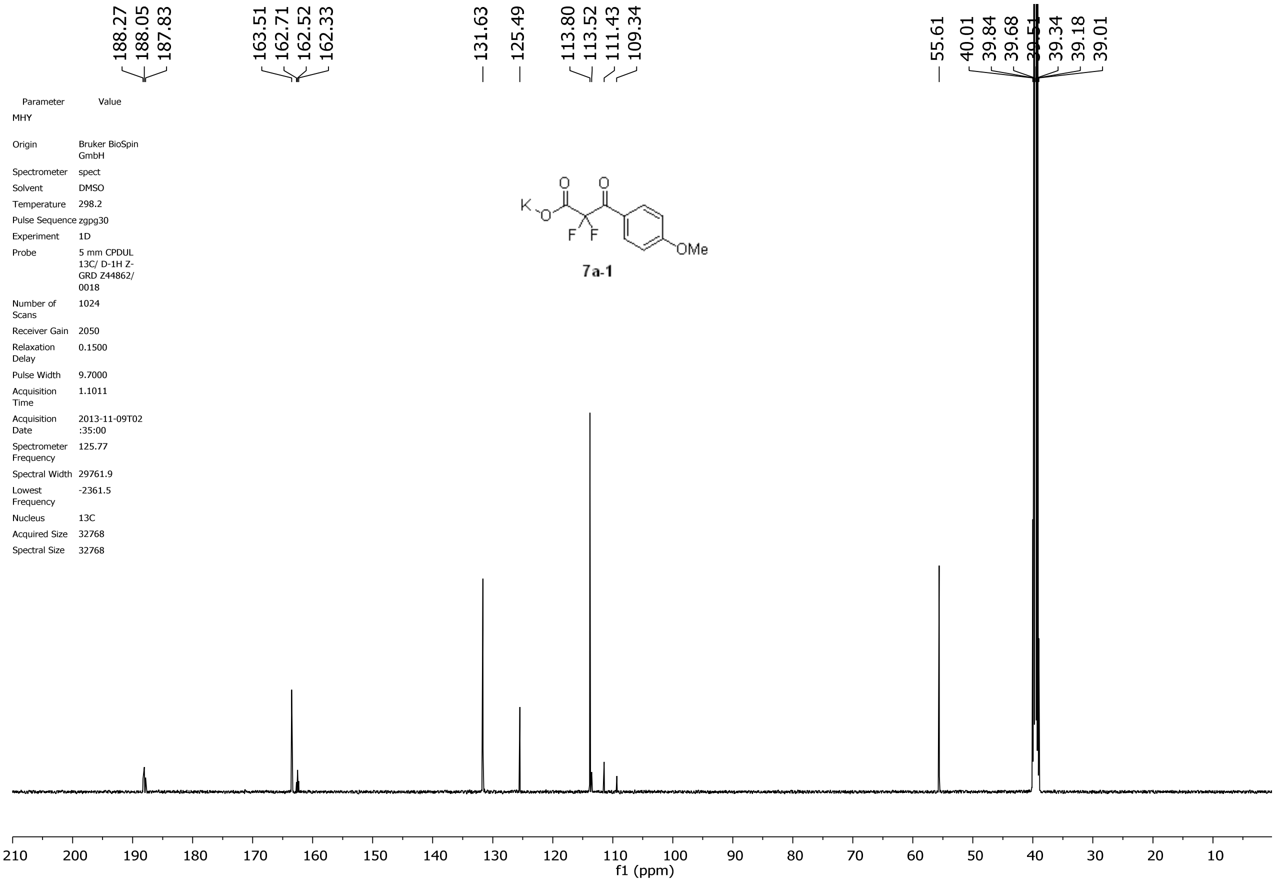


7a-2

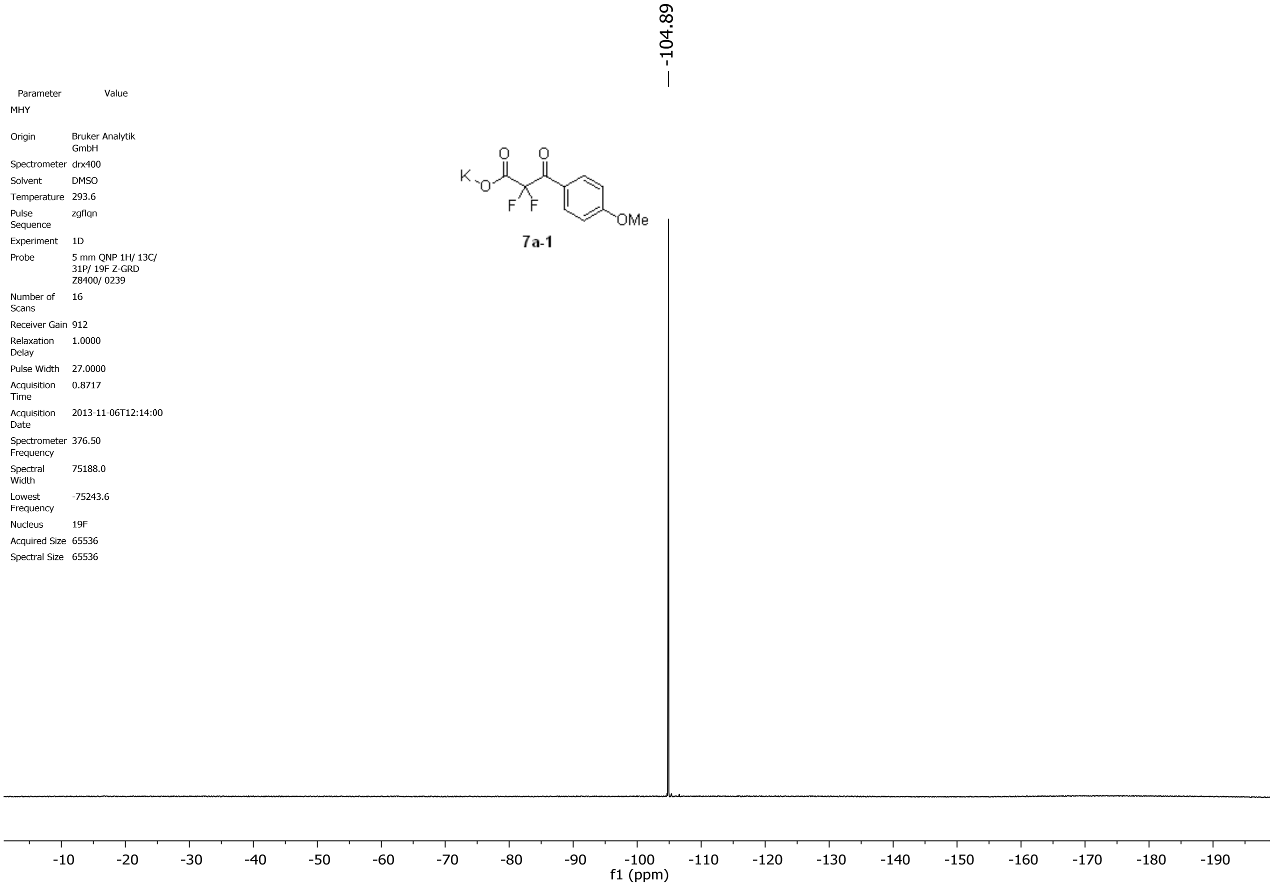
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	19.5000
Acquisition Time	0.8717
Acquisition Date	2013-11-04T15:03:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-06T12:11:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

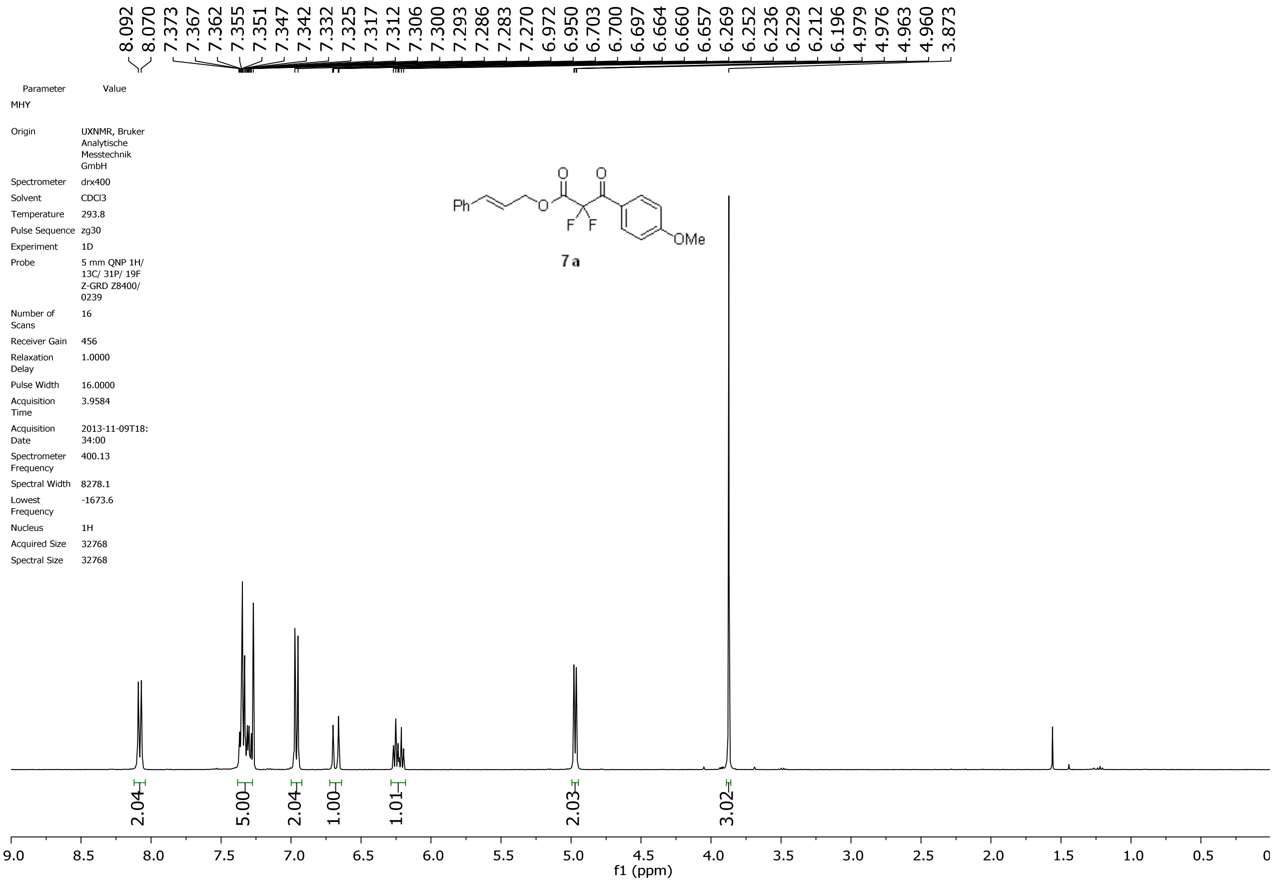


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2013-11-09T02 :35:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2361.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-06T12:14:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

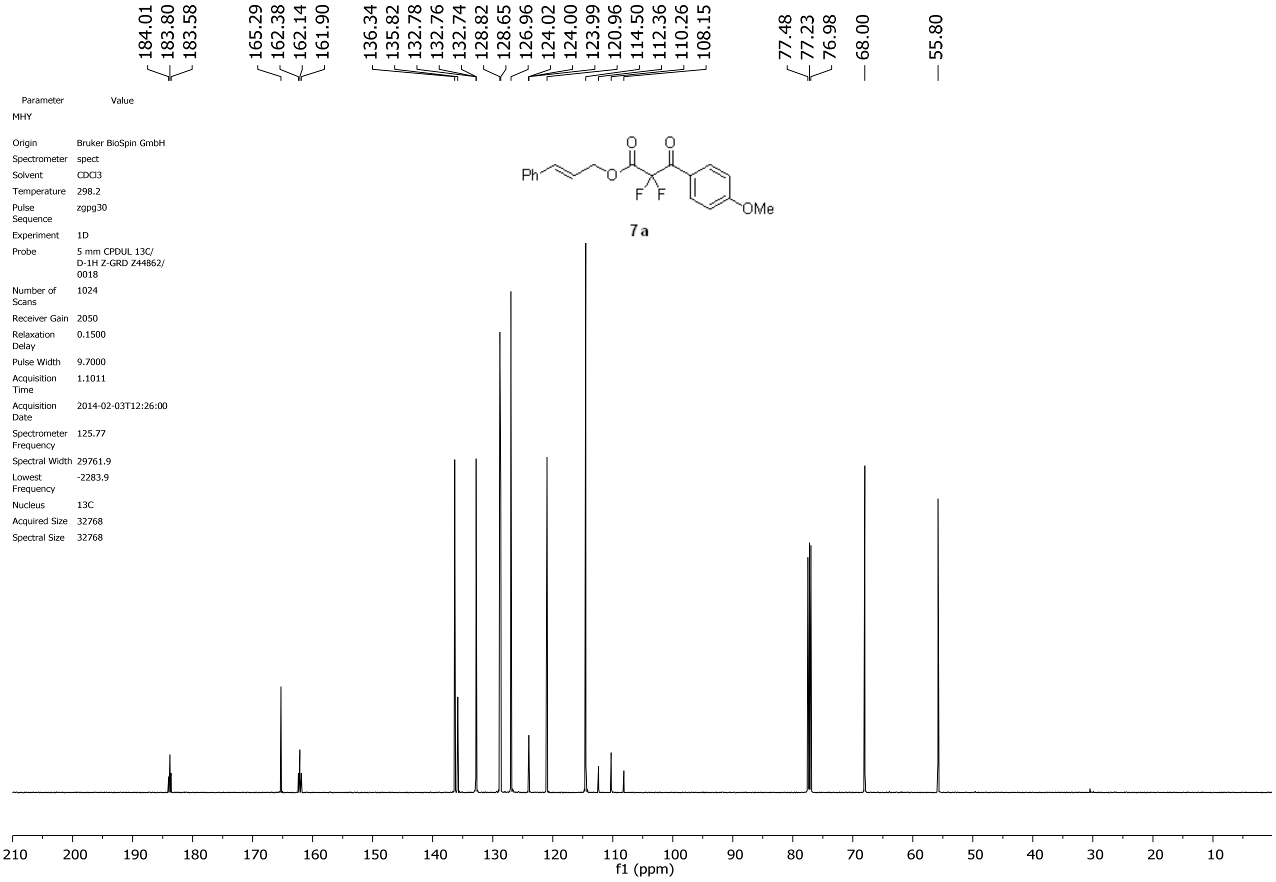
7a-1



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-09T18:34:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.6
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

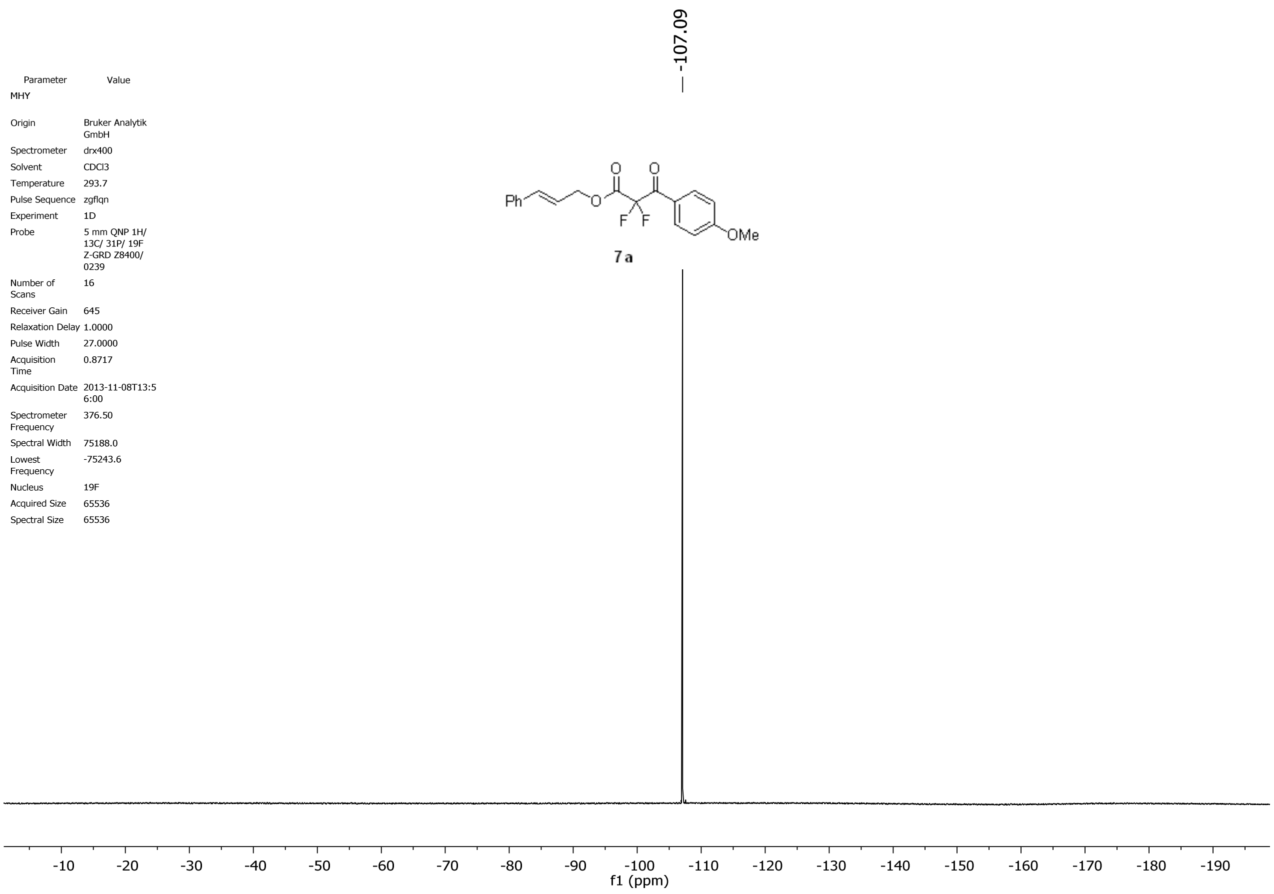
7a

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-03T12:26:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2283.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



7 a

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-08T13:5 6:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



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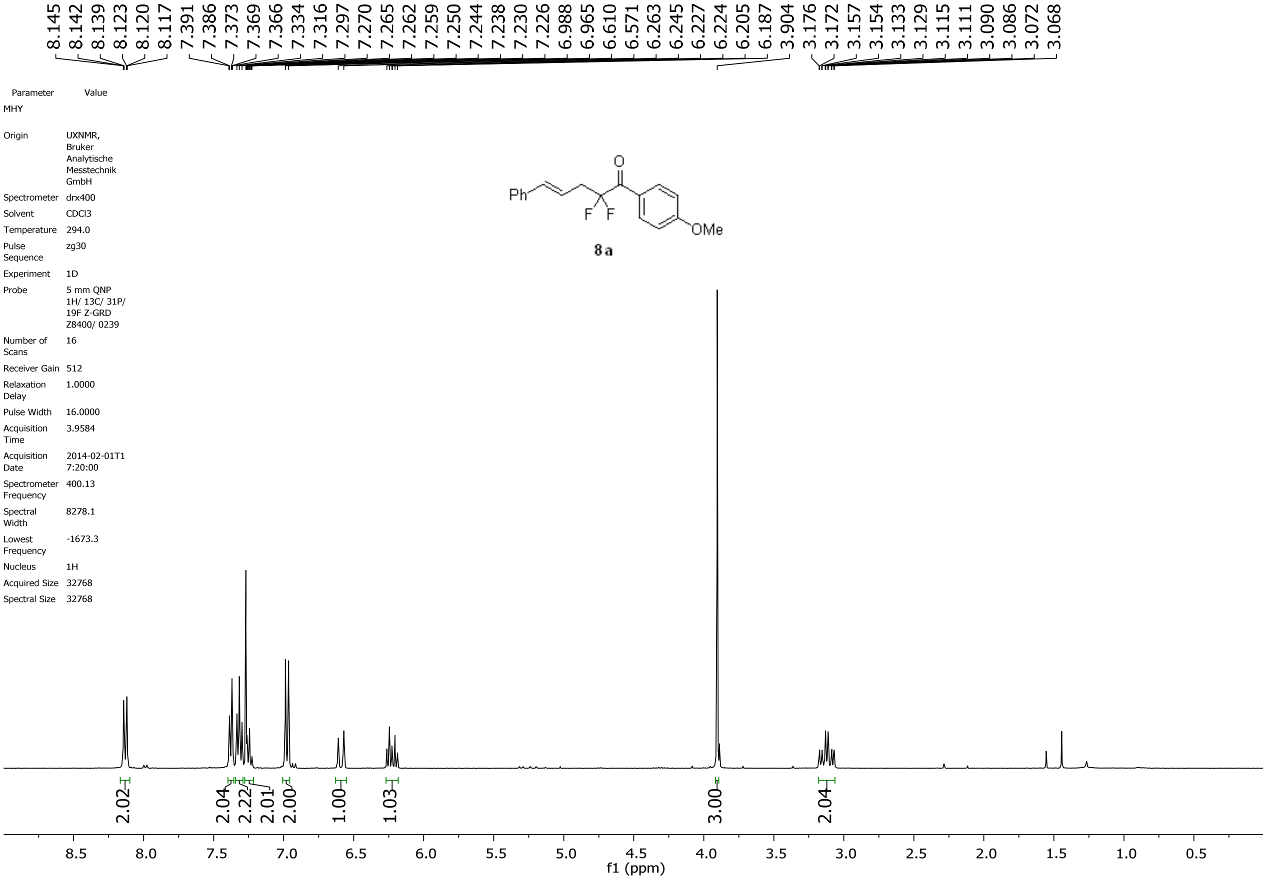
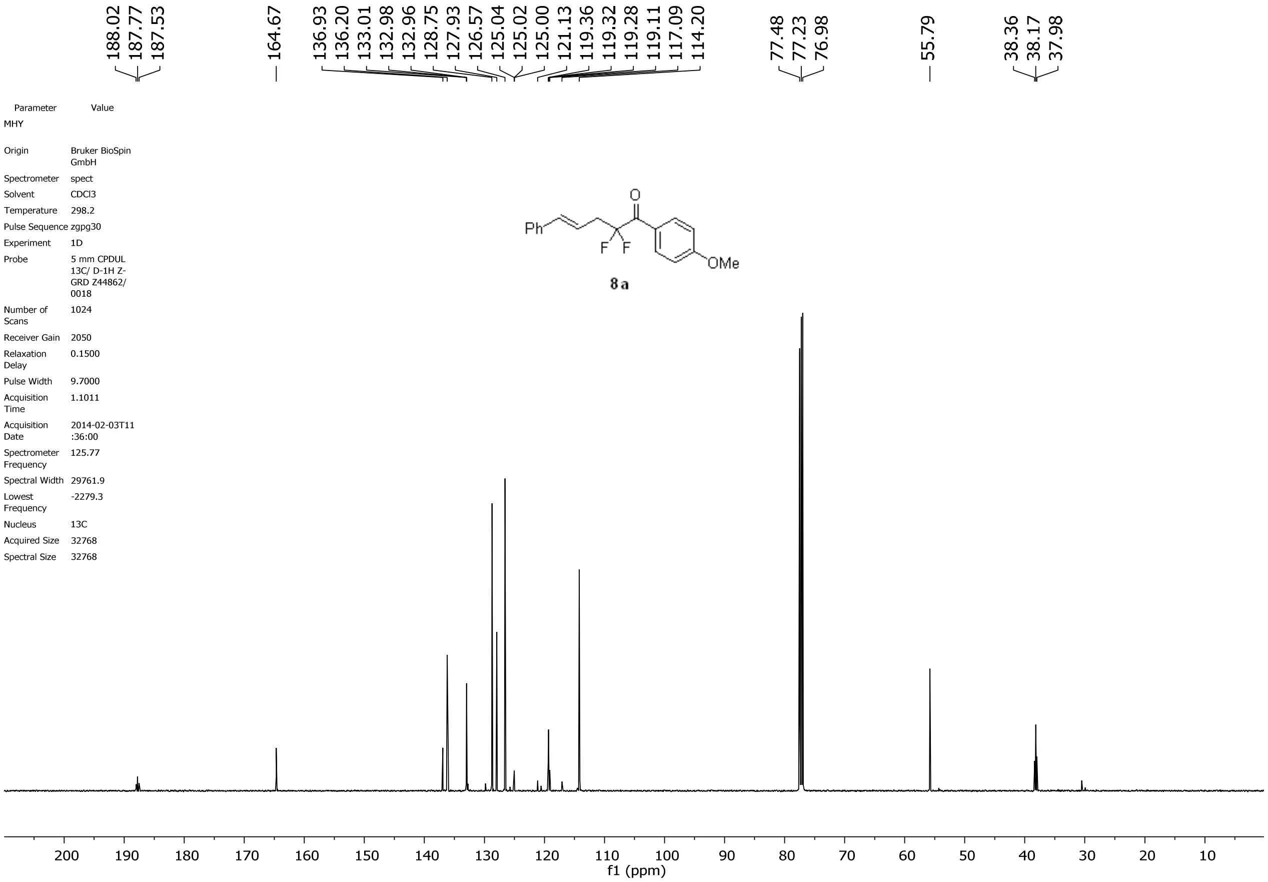


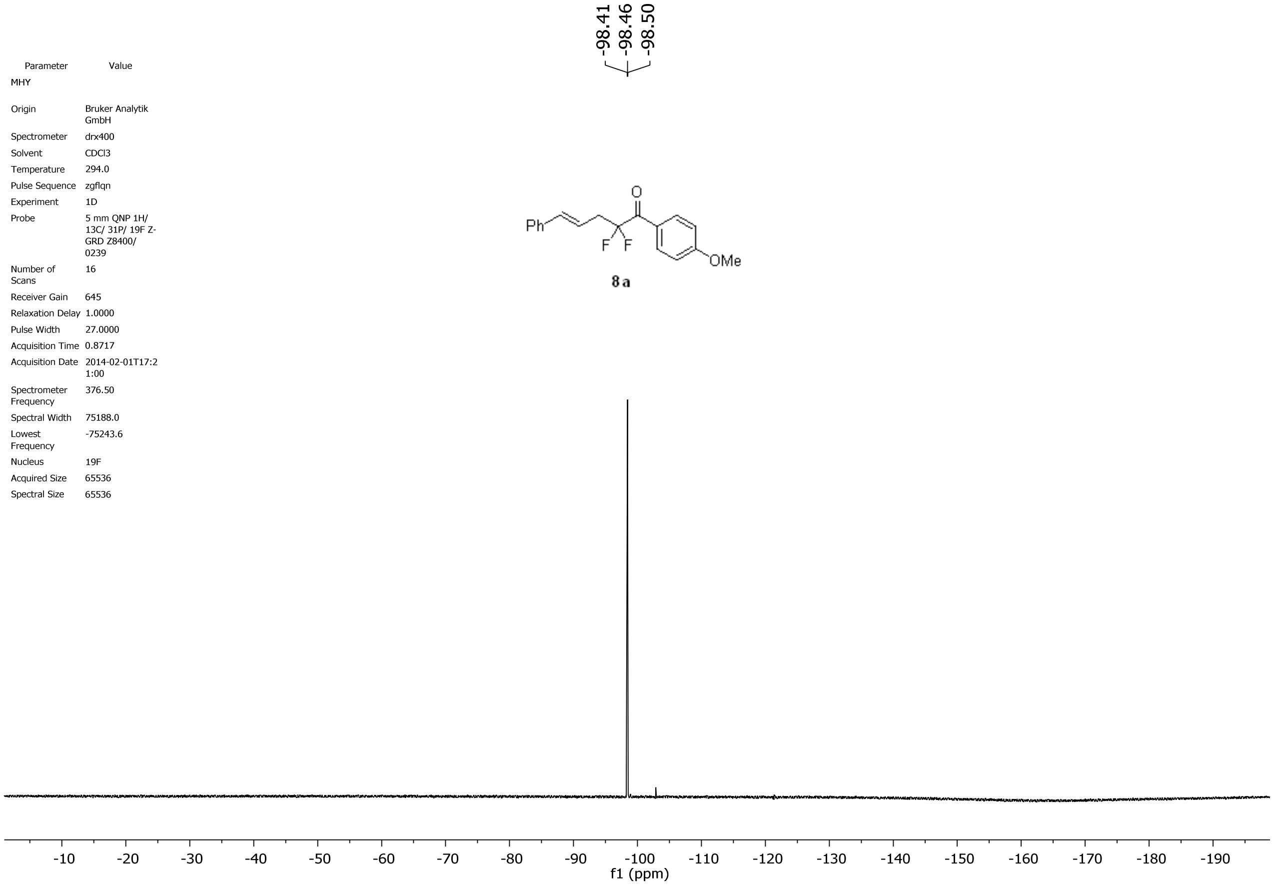
8a

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-01T17:20:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



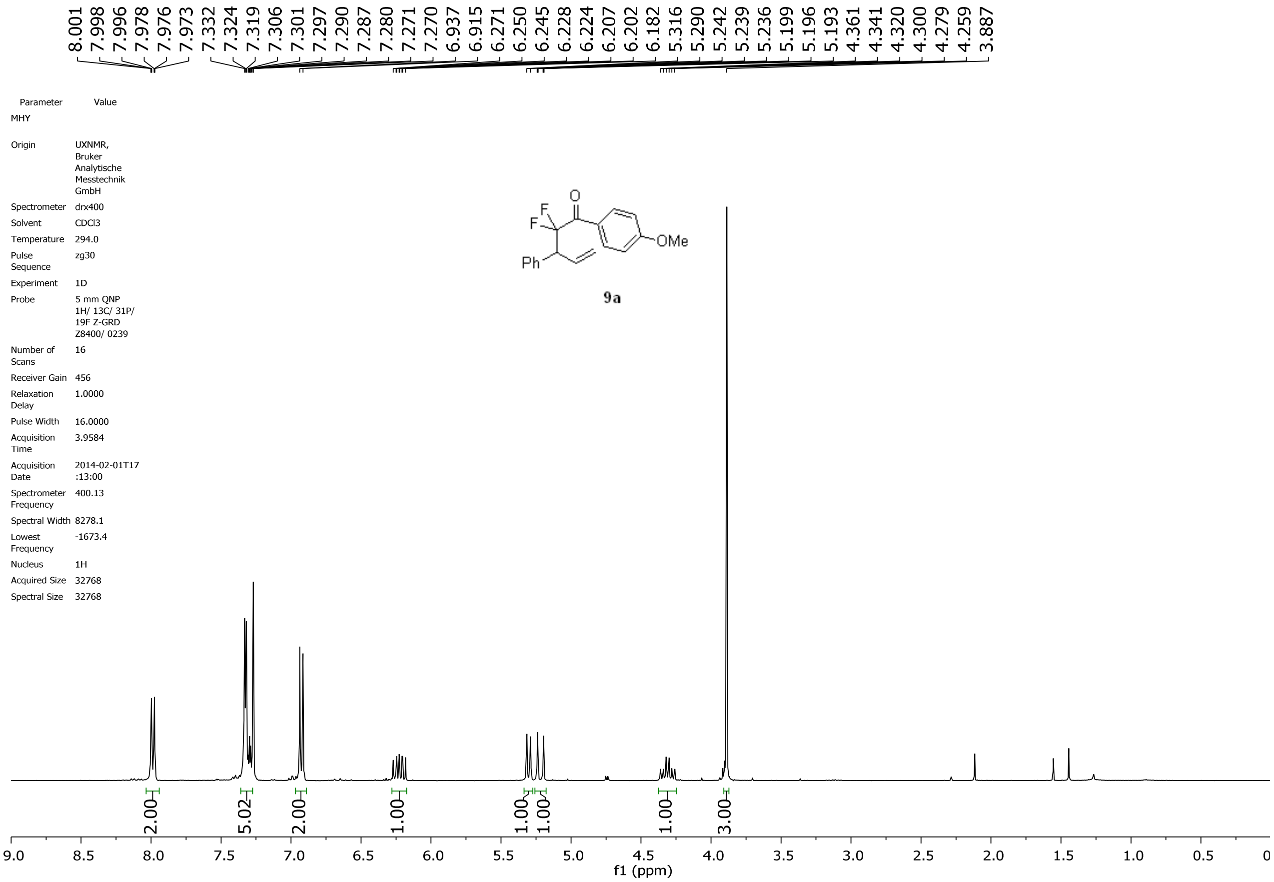
8a

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-03T11:36:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.3
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



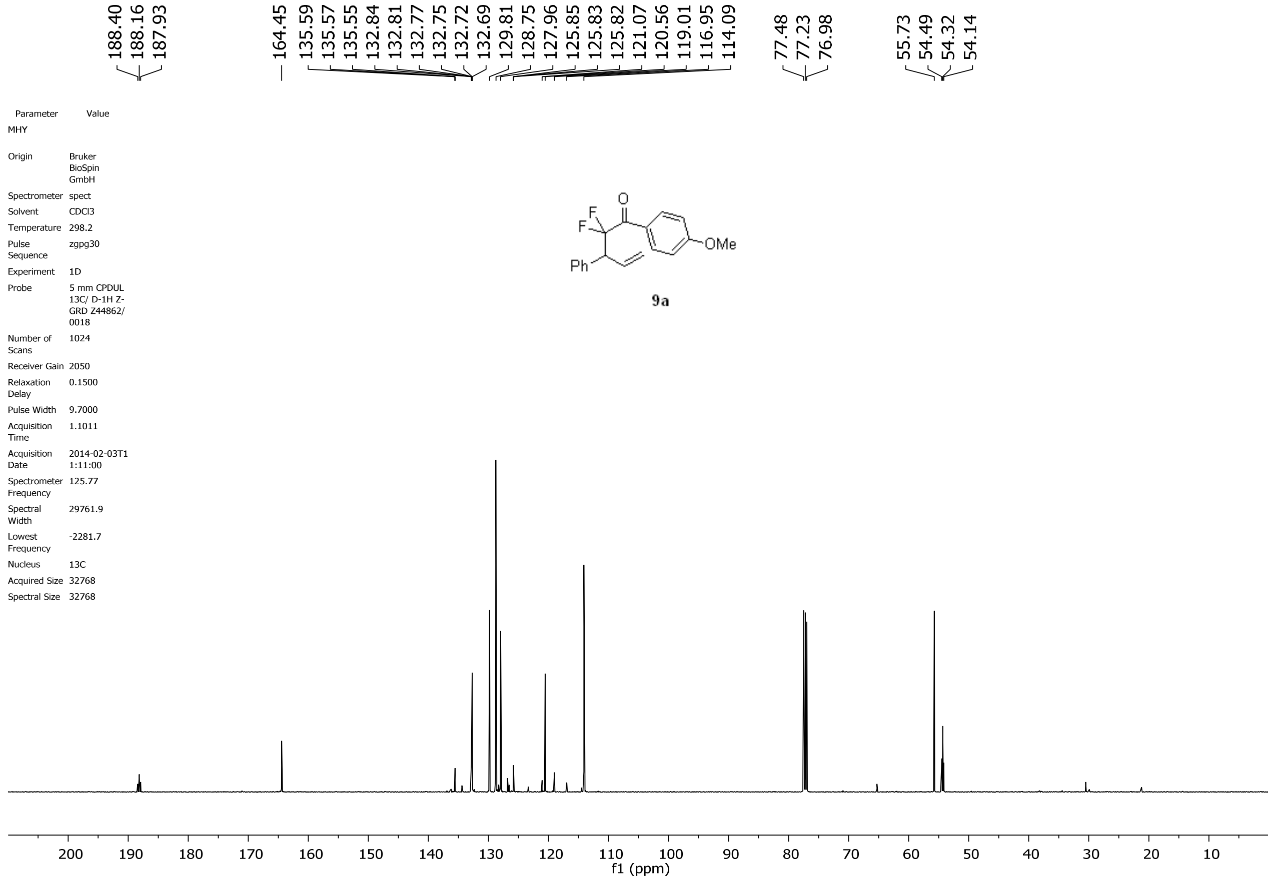
8a

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-02-01T17:21:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



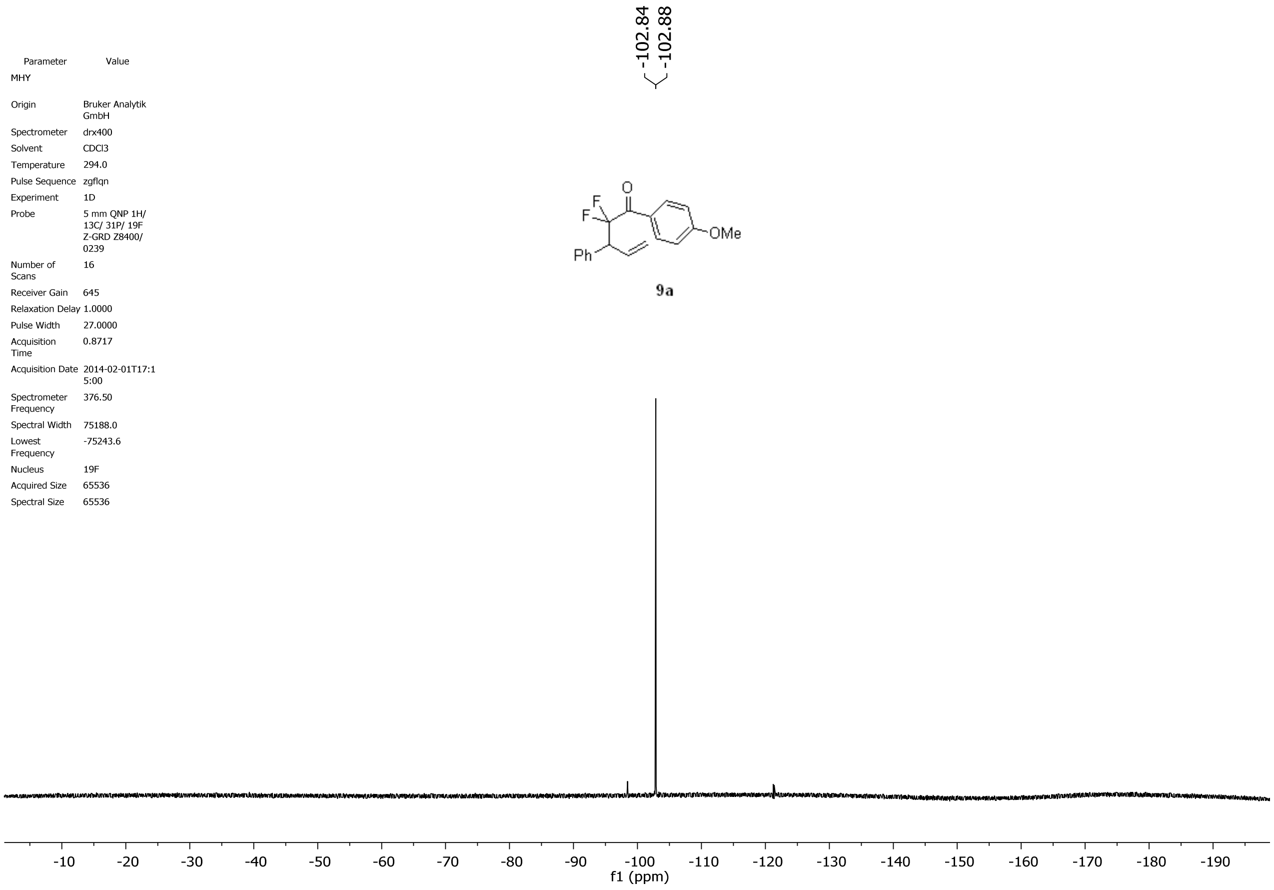
9a

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-01T17:13:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



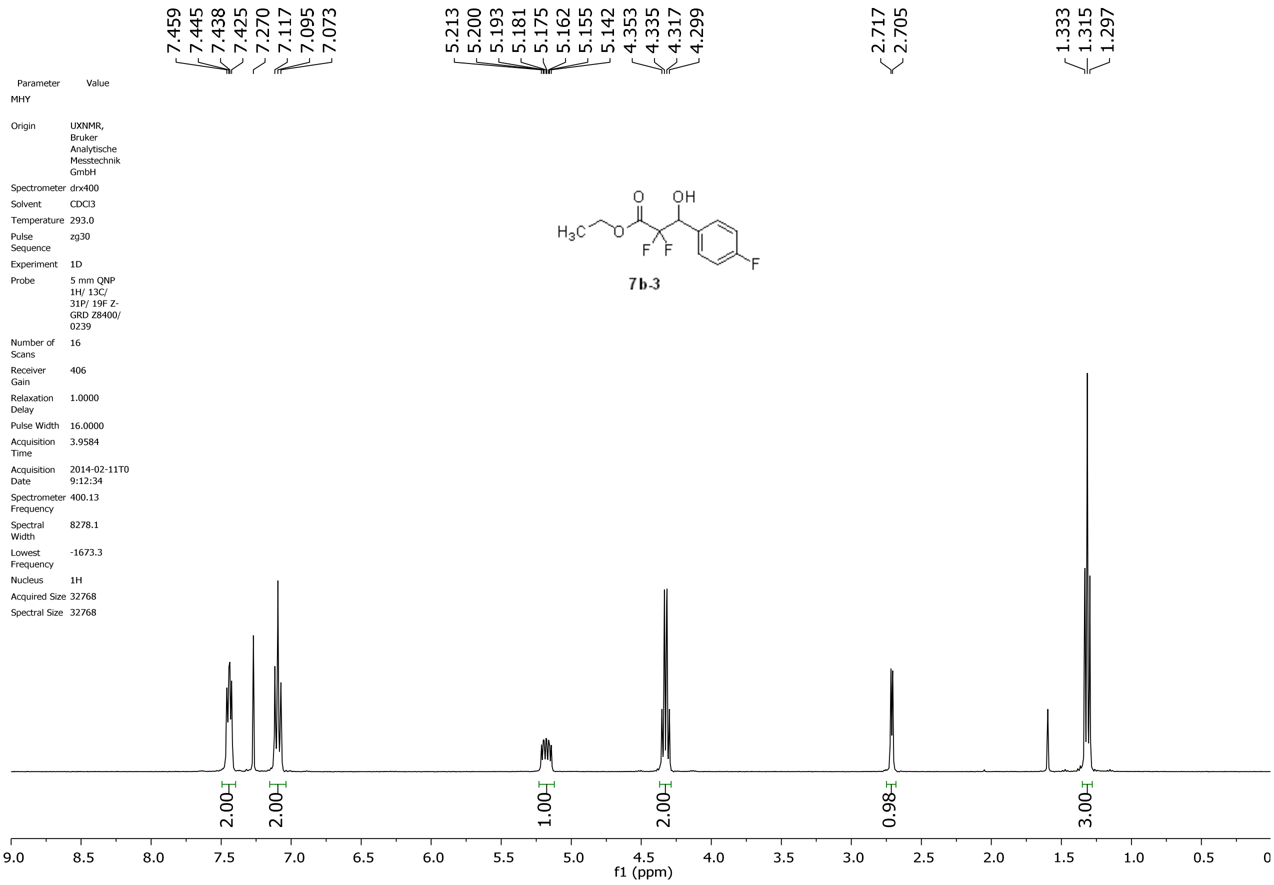
9a

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-03T11:11:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.7
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



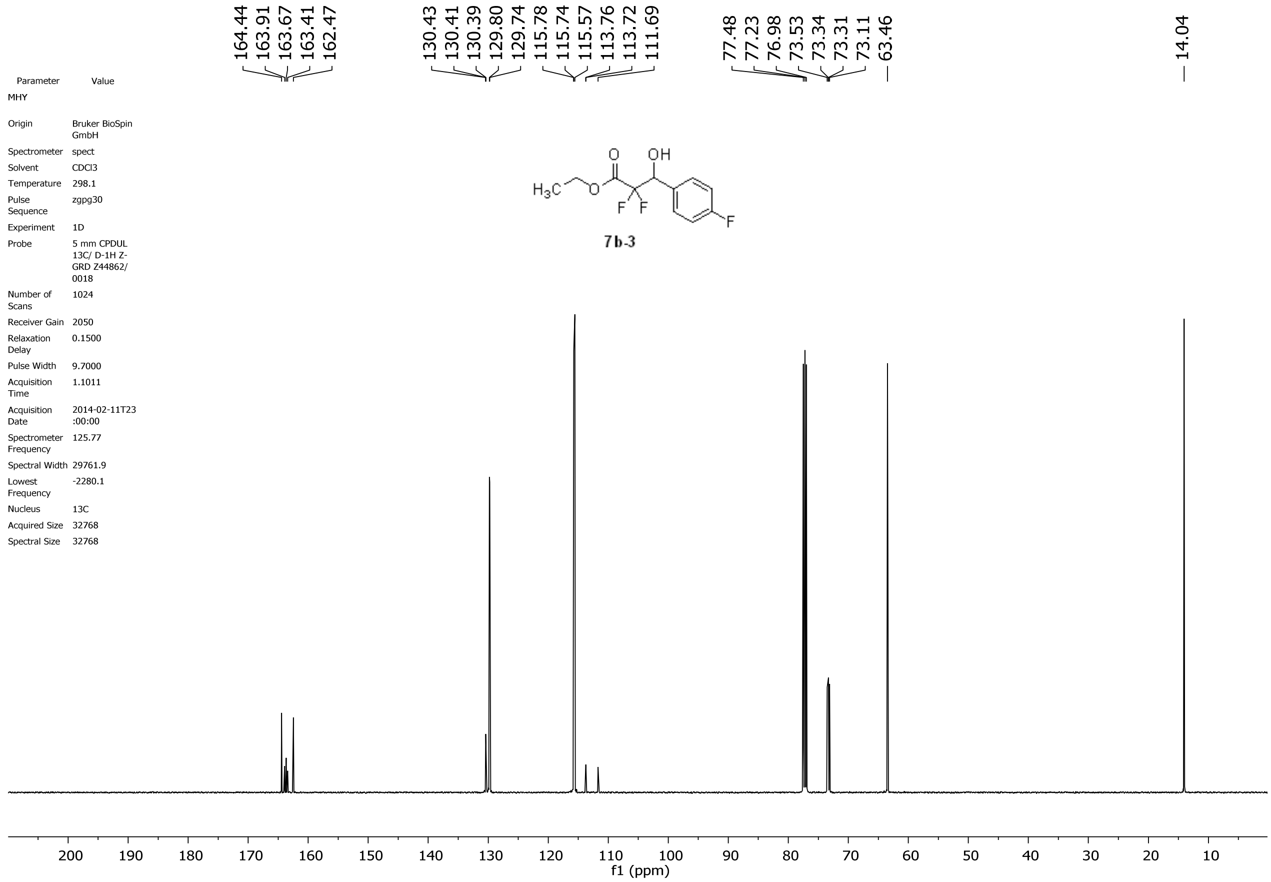
9a

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-02-01T17:15:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



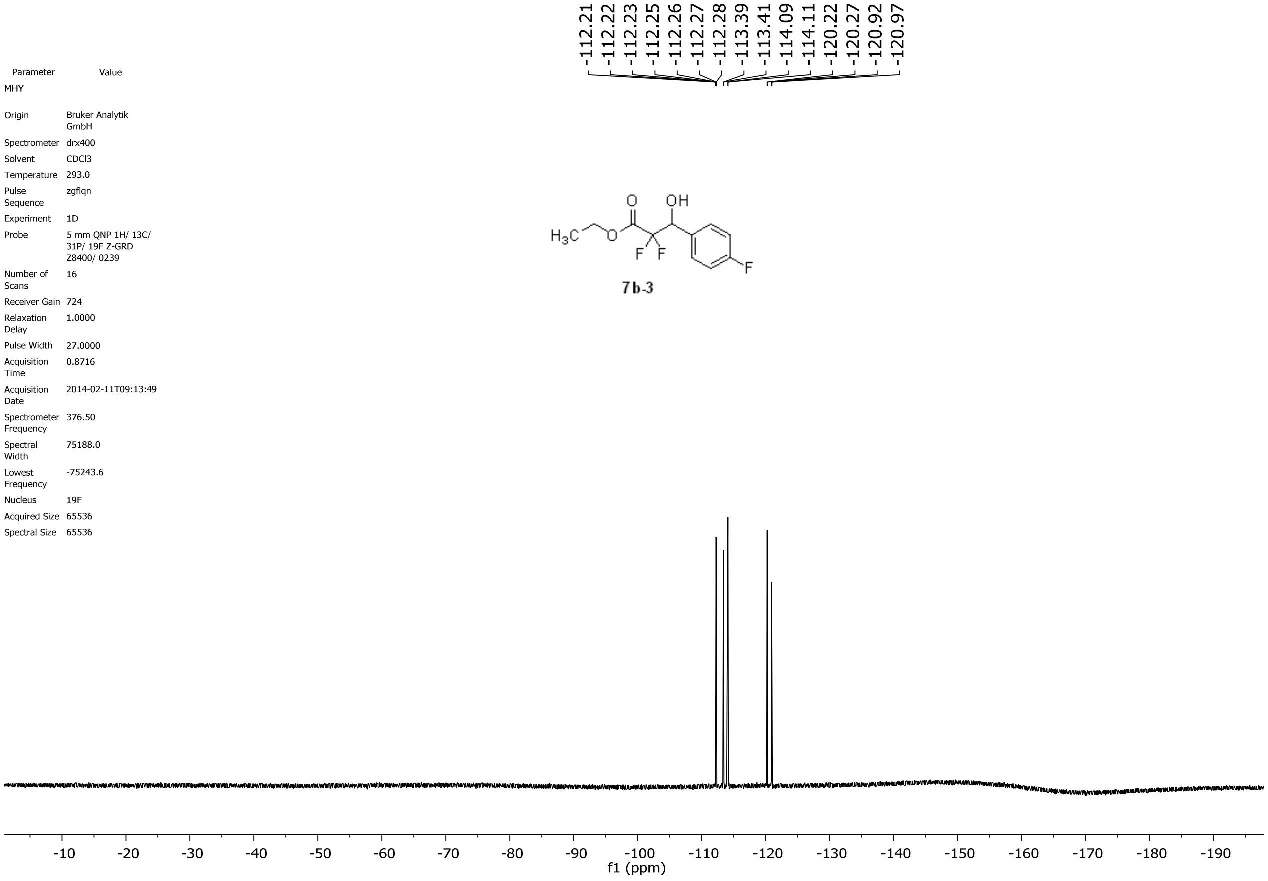
7b-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-11T09:12:34
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



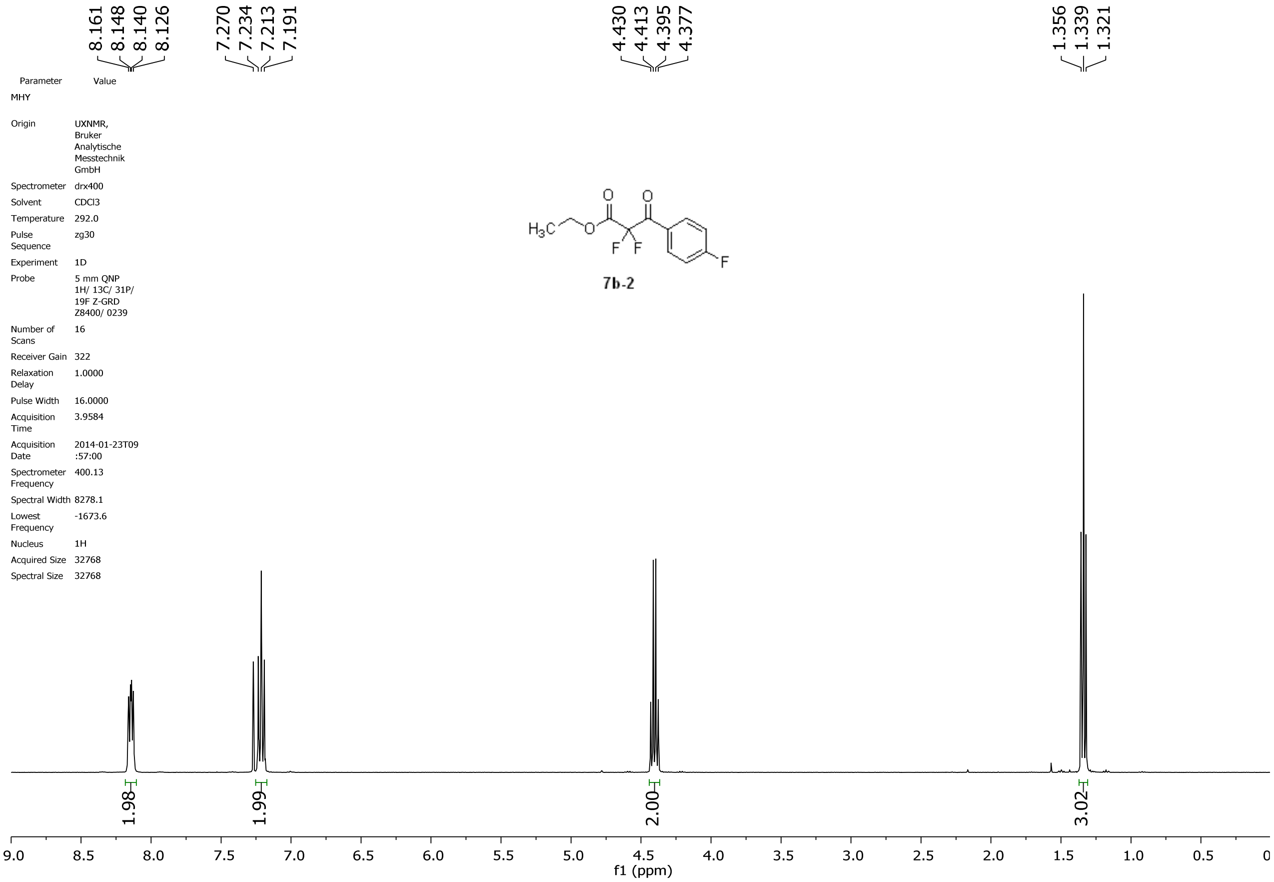
7b-3

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-11T23:00:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



7b-3

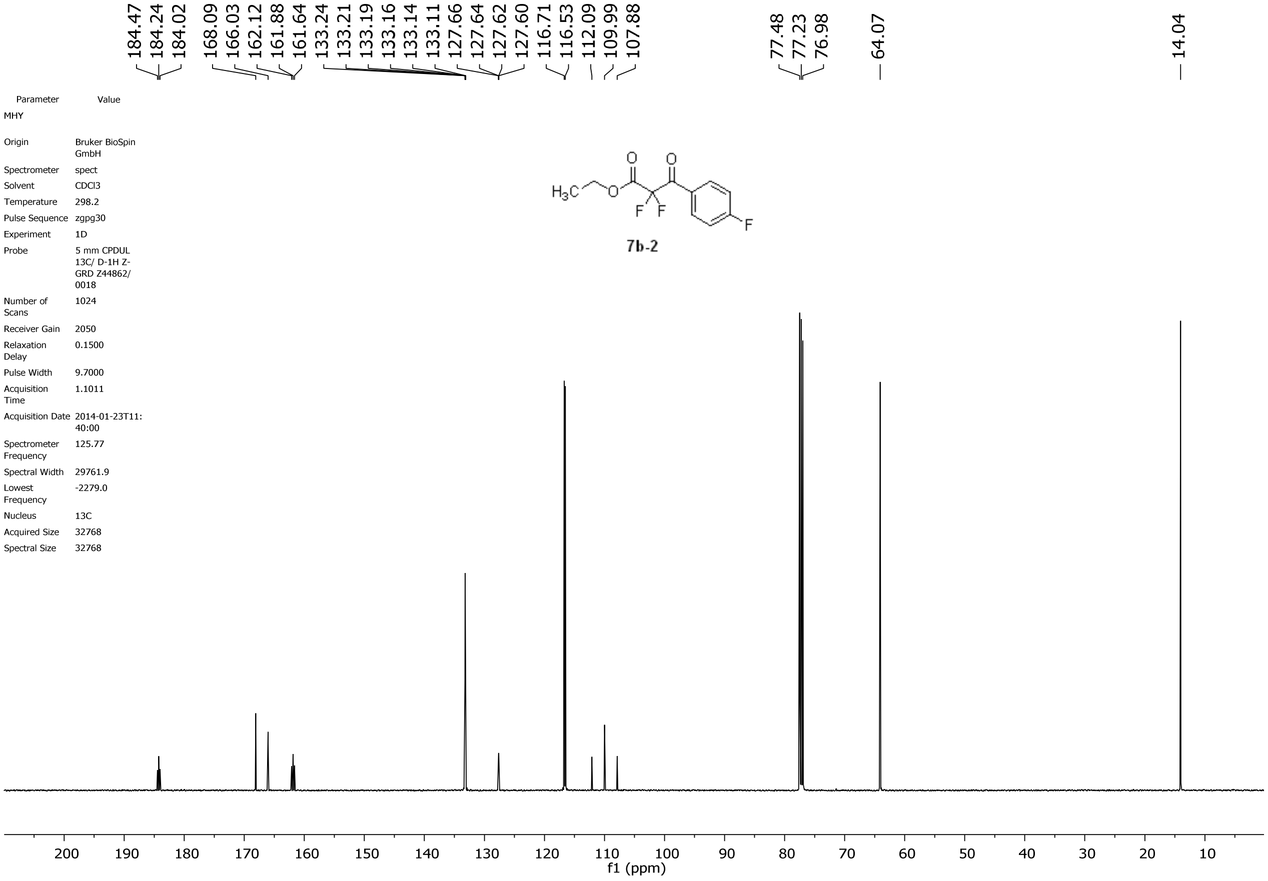
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-11T09:13:49
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



7b-2

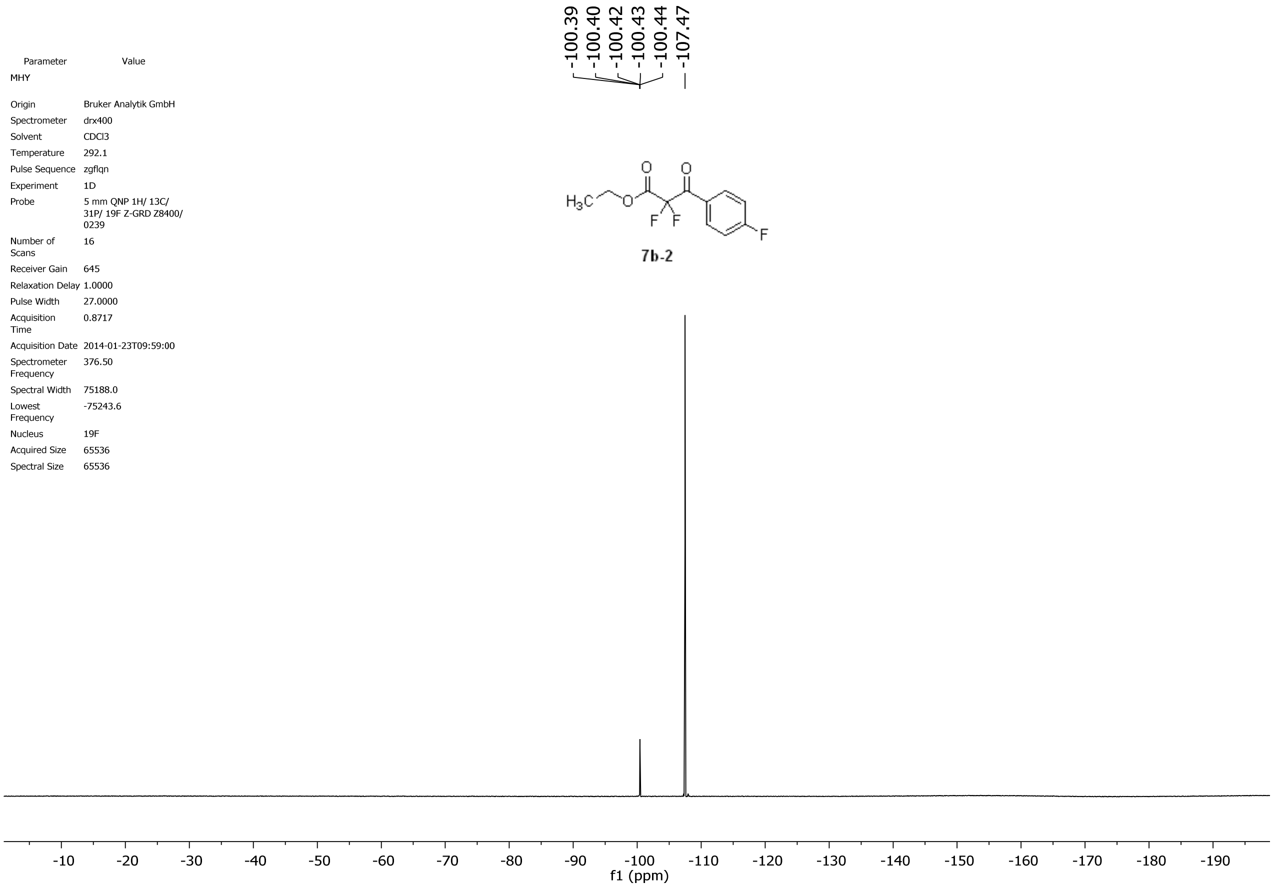
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	292.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-23T09:57:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.6
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-01-23T11:40:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

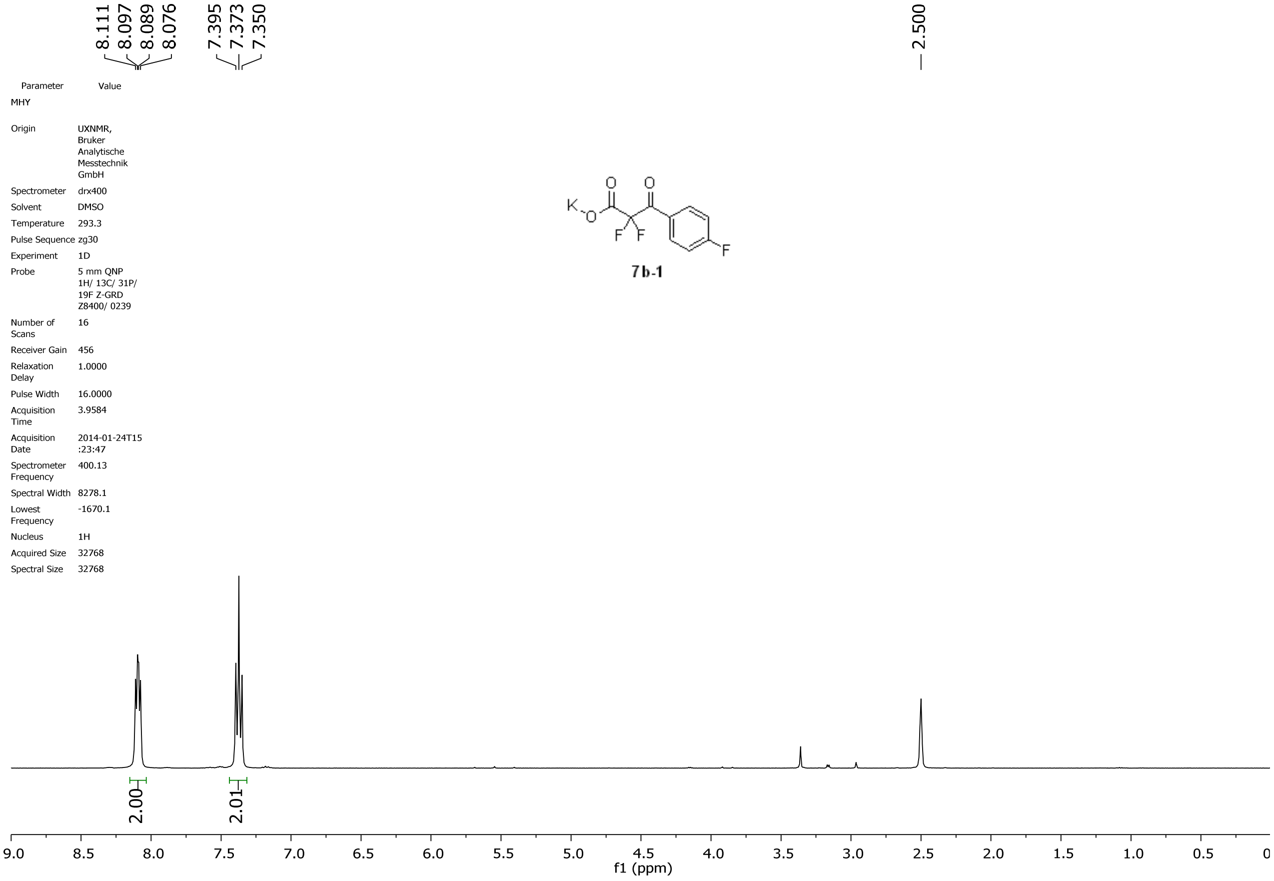


7b-2

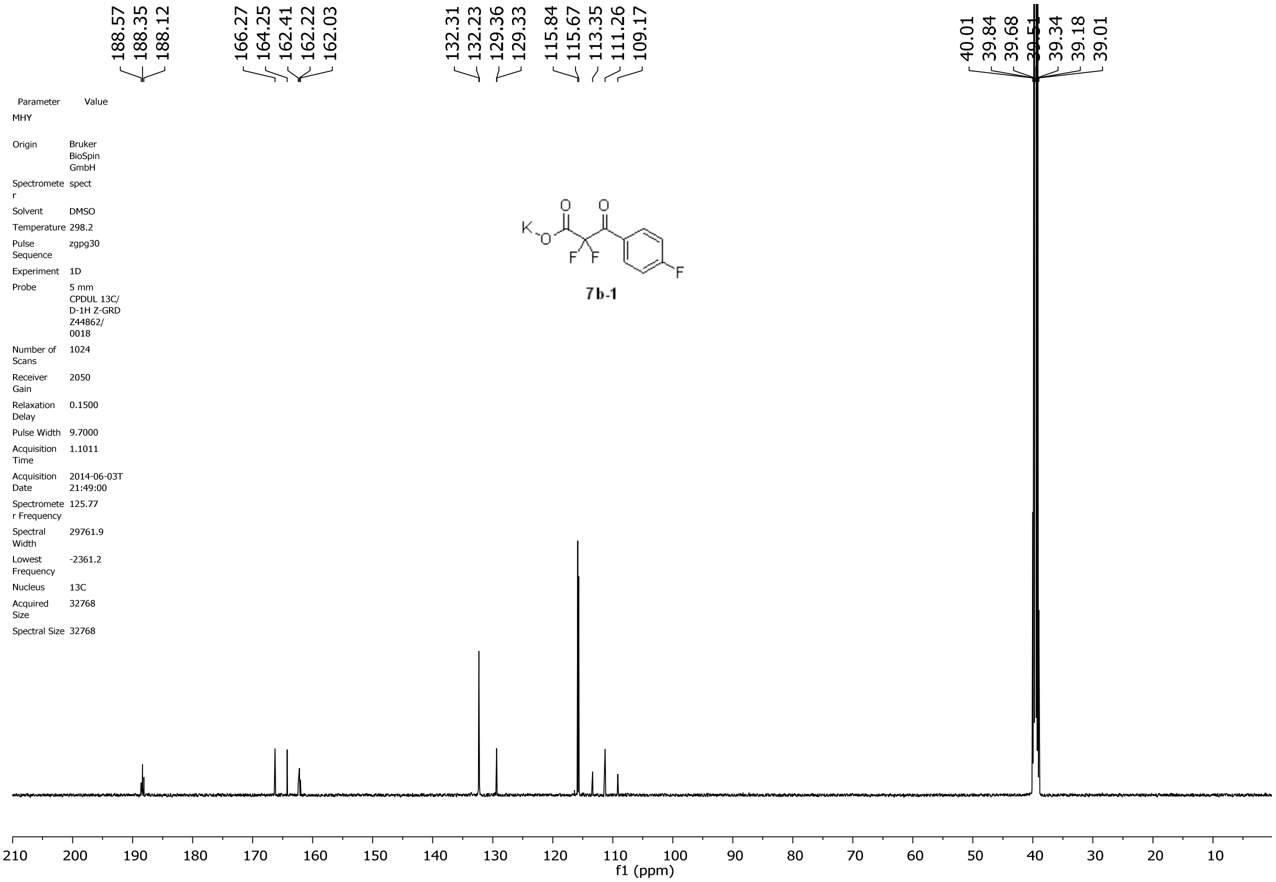
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-01-23T09:59:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



7b-2

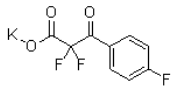


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-24T15:23:47
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.1
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

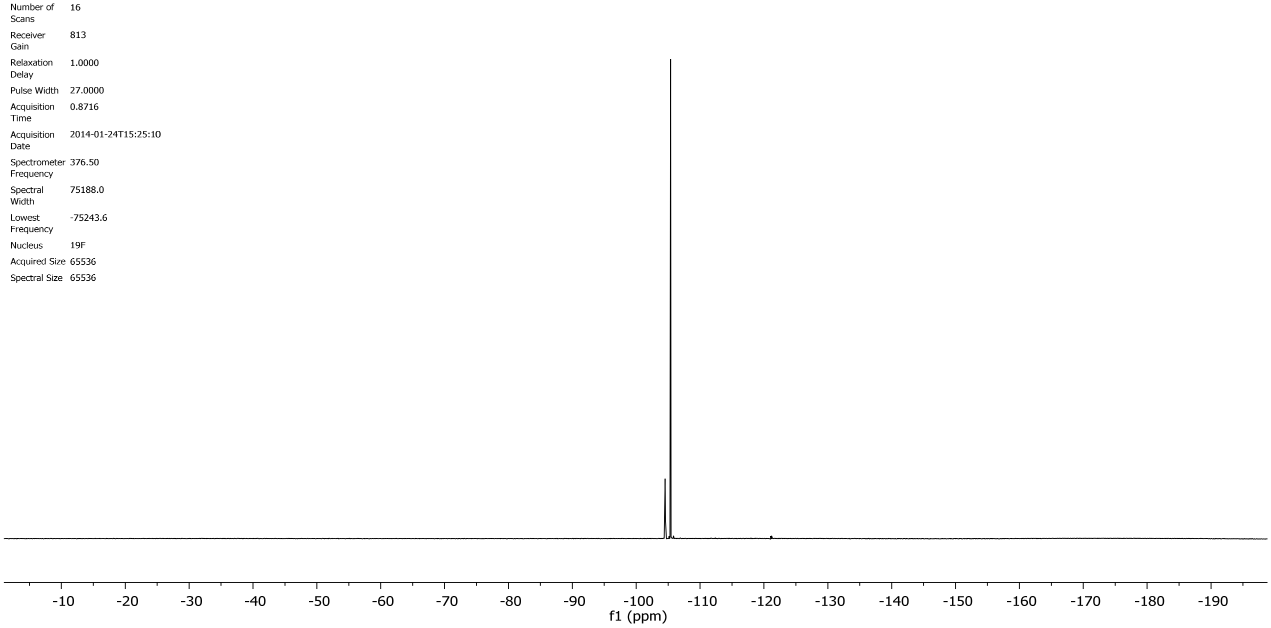


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-03T21:49:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2361.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

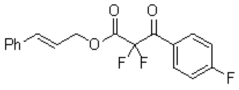
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-01-24T15:25:10
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



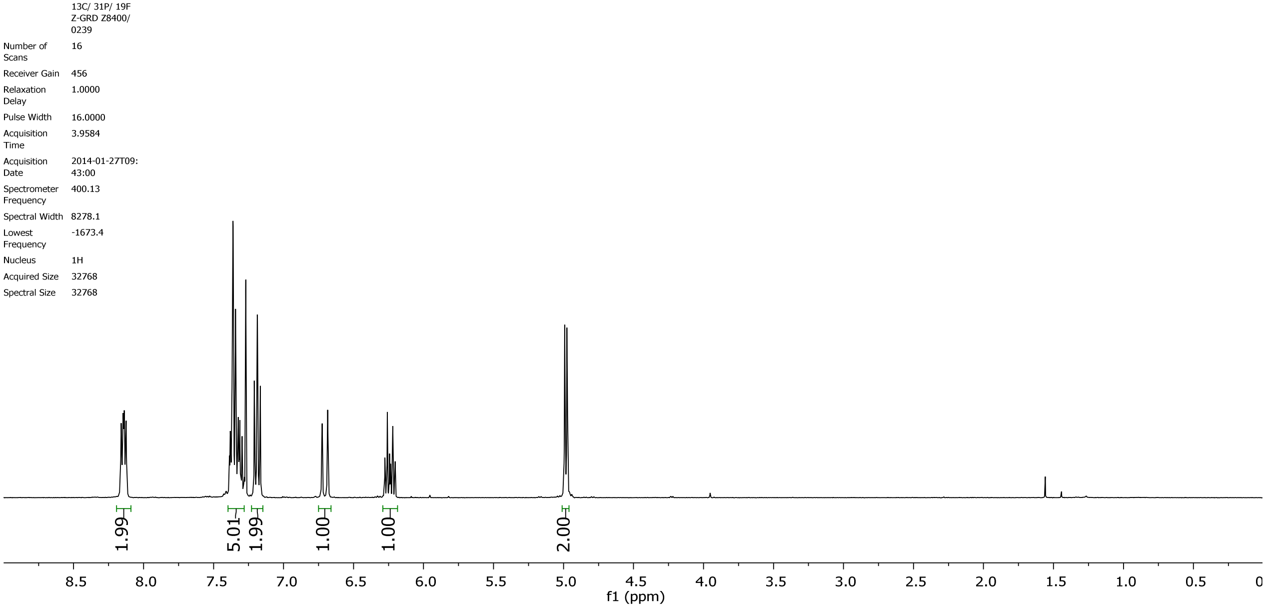
7b-1

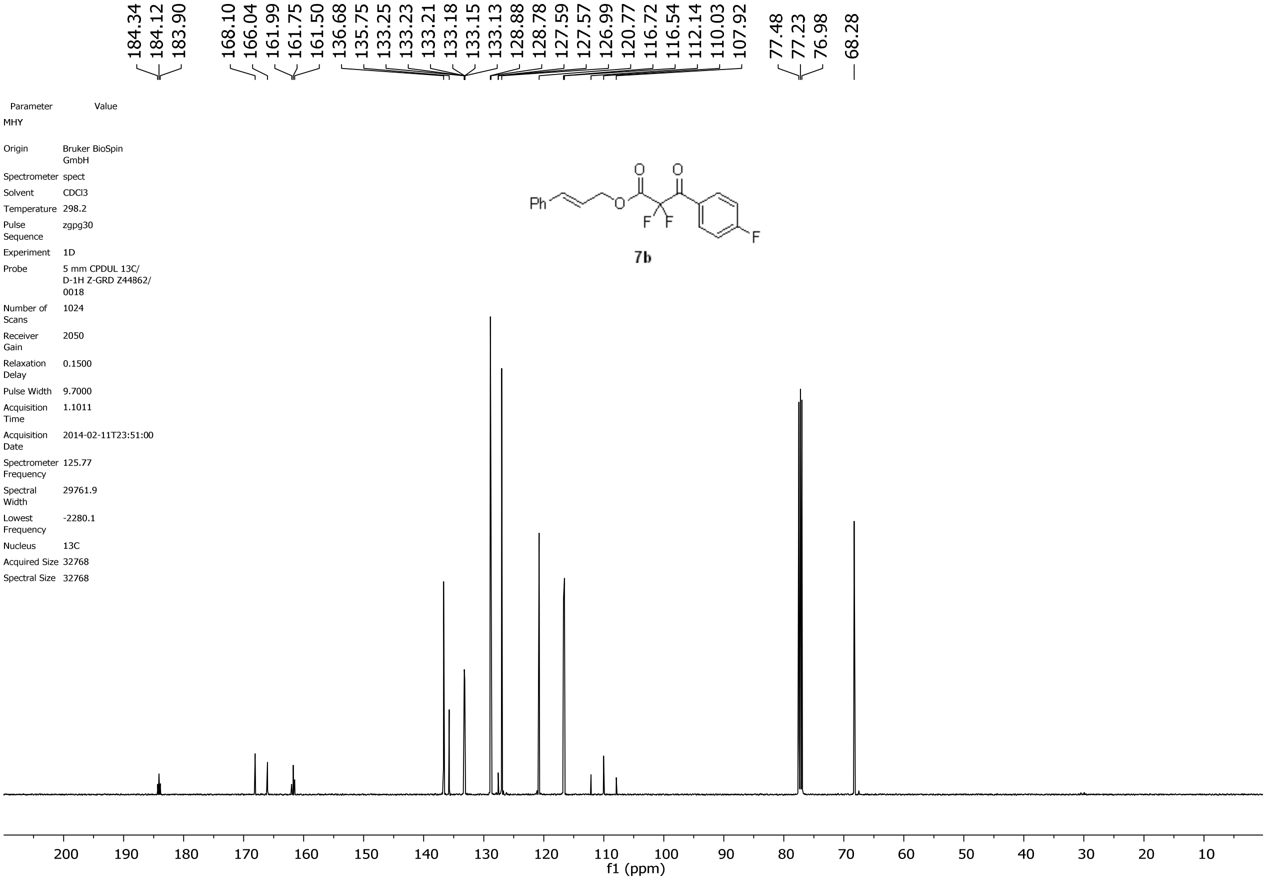


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-27T09:43:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

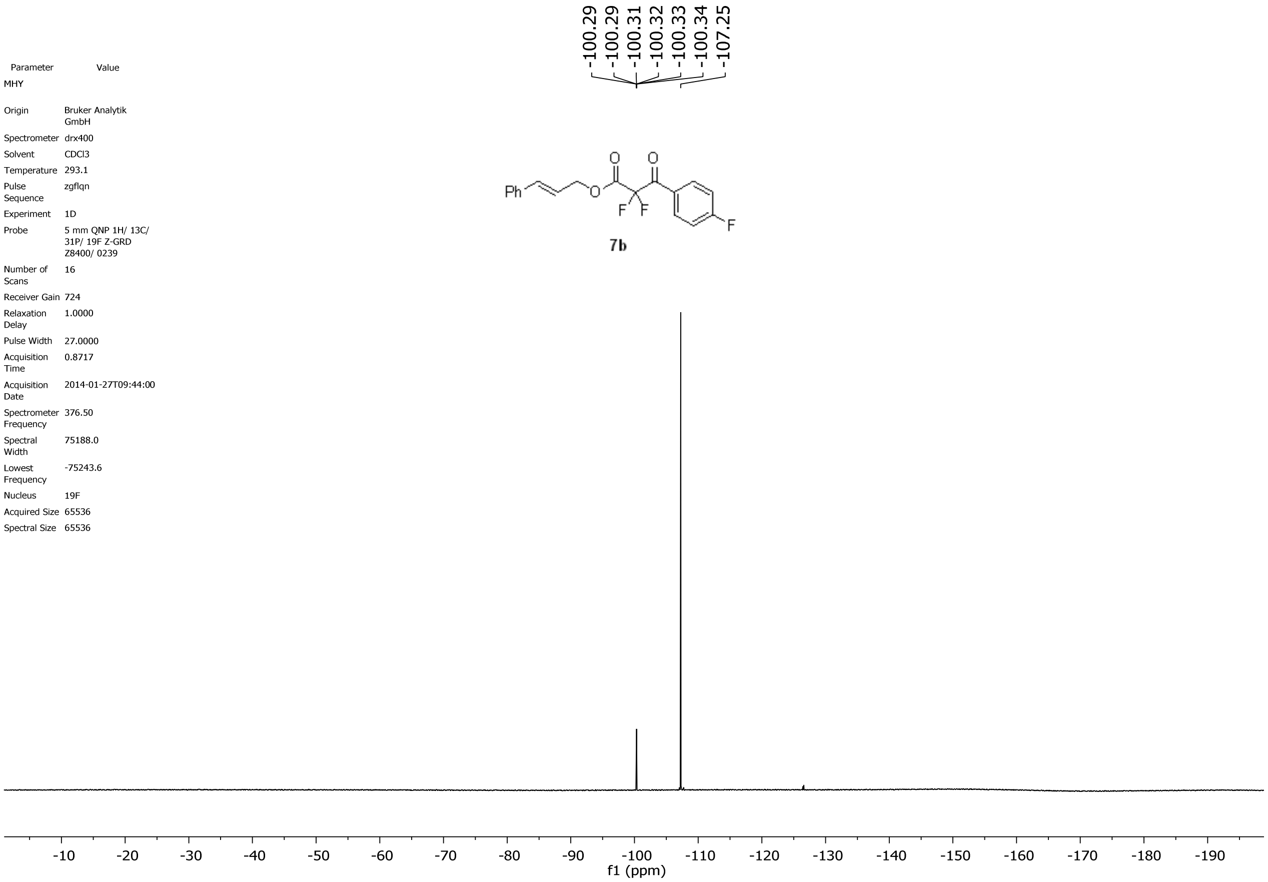


7b

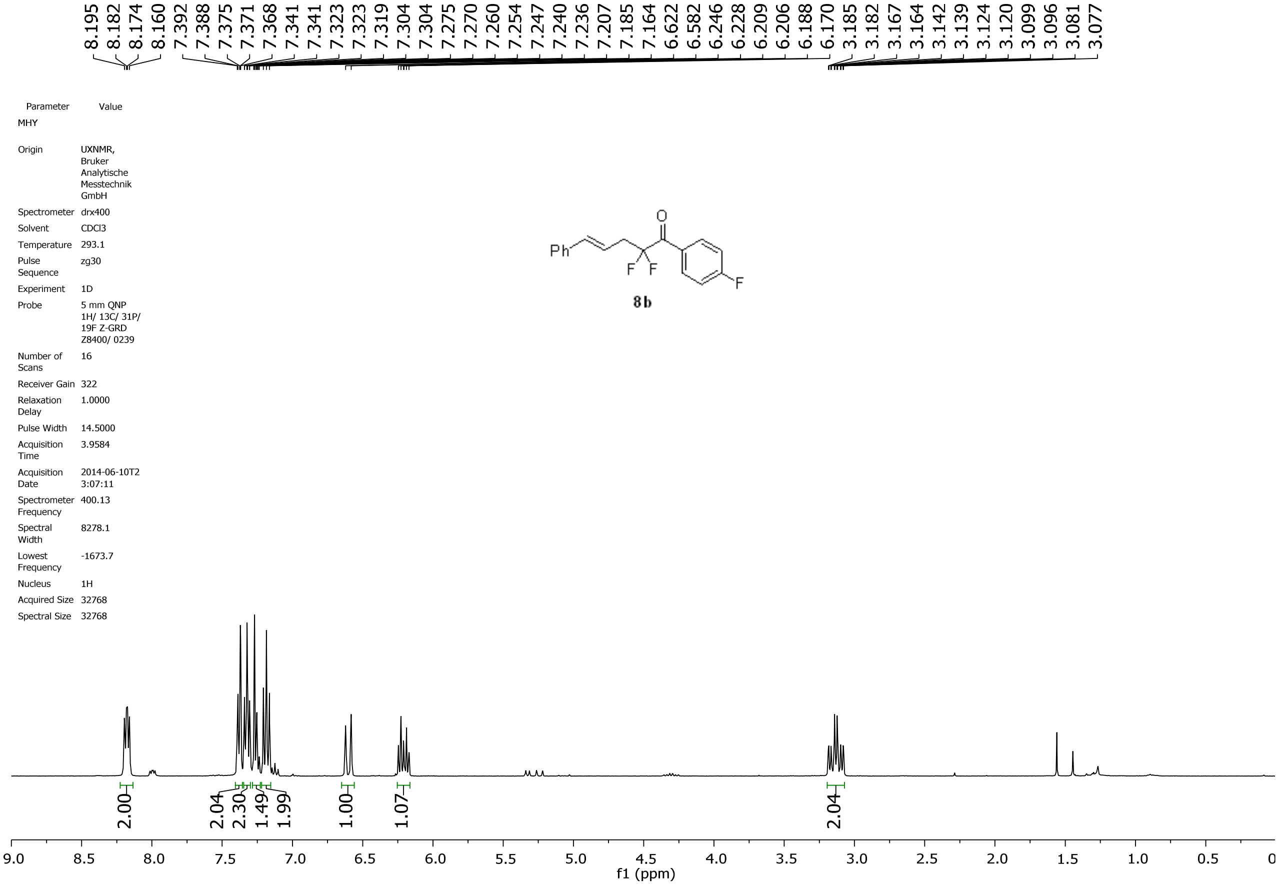




Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-11T23:51:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

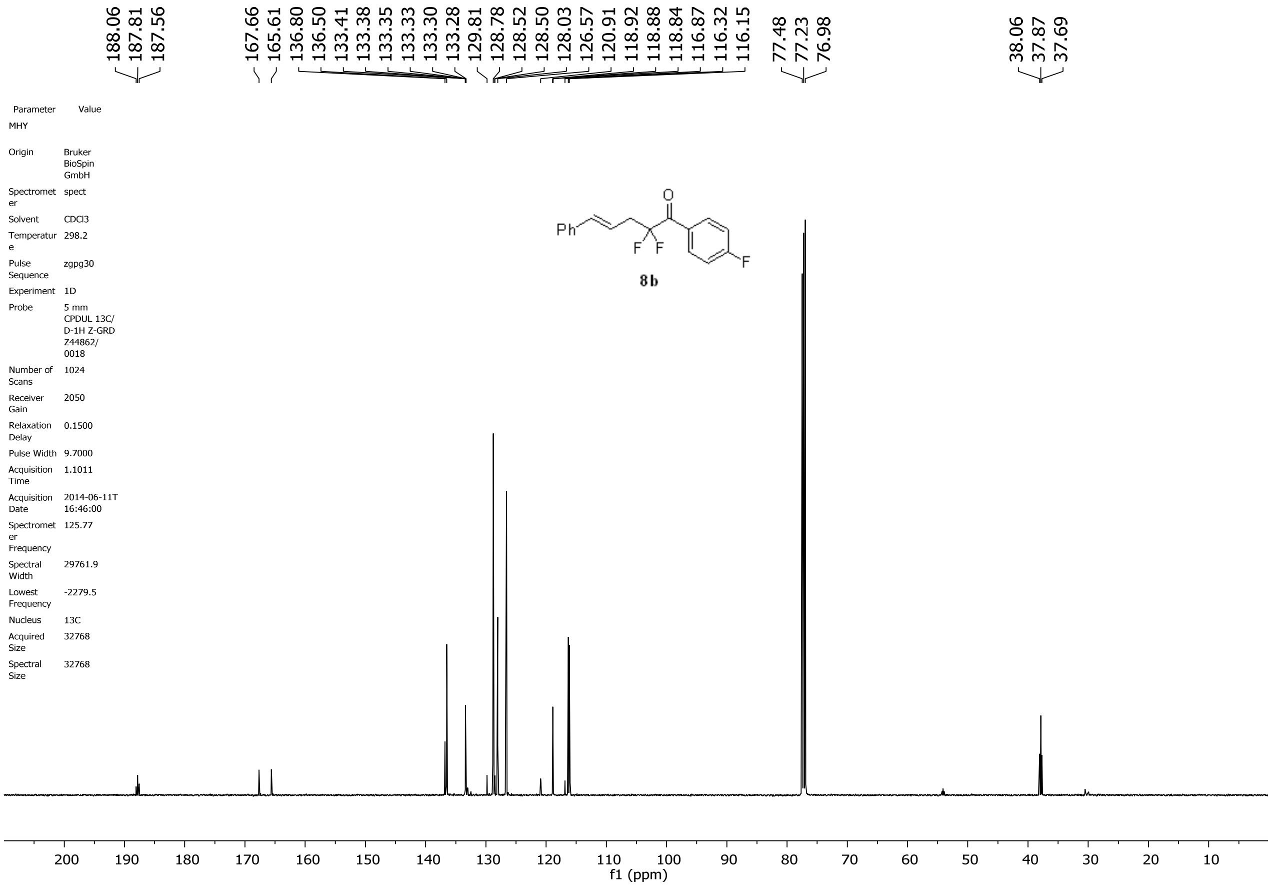


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-01-27T09:44:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



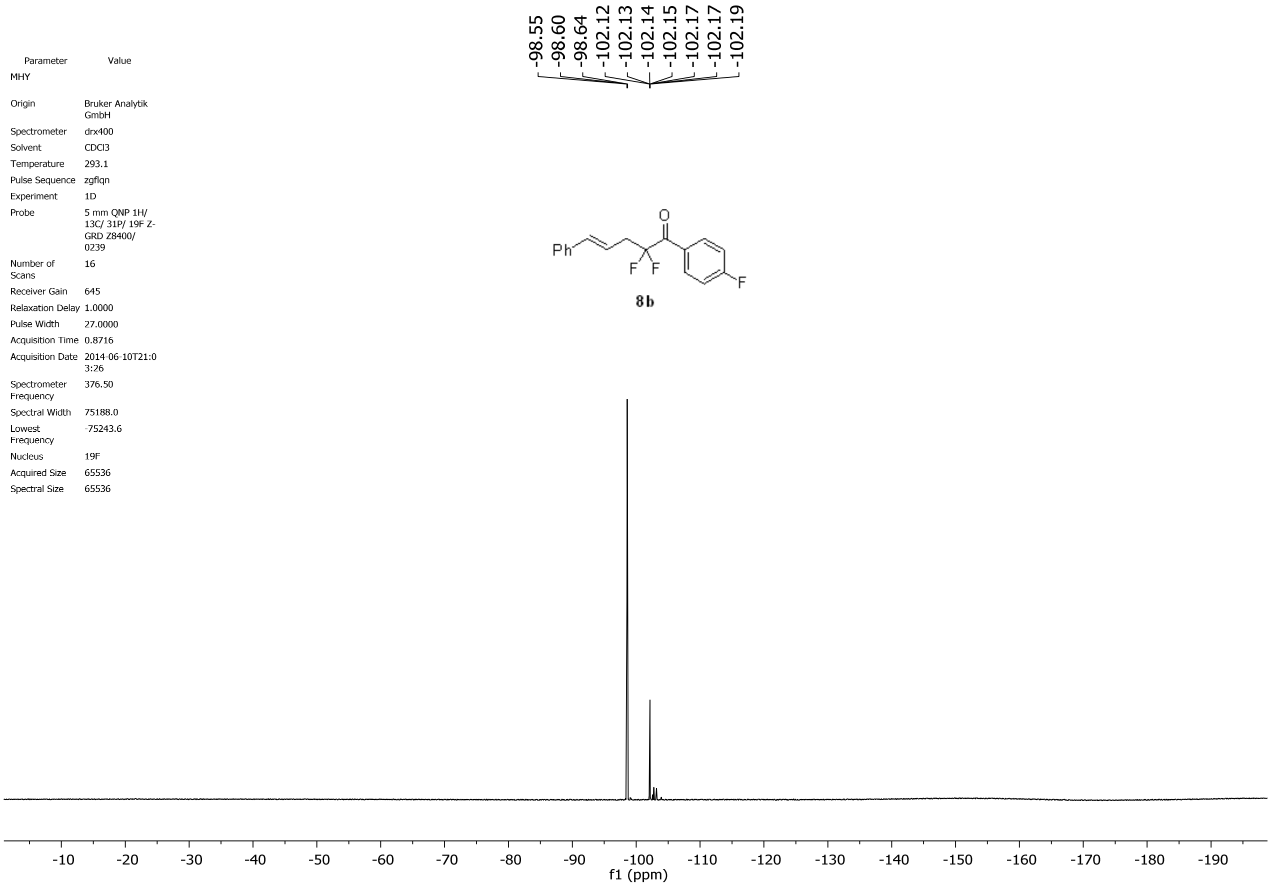
8b

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-10T23:07:11
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

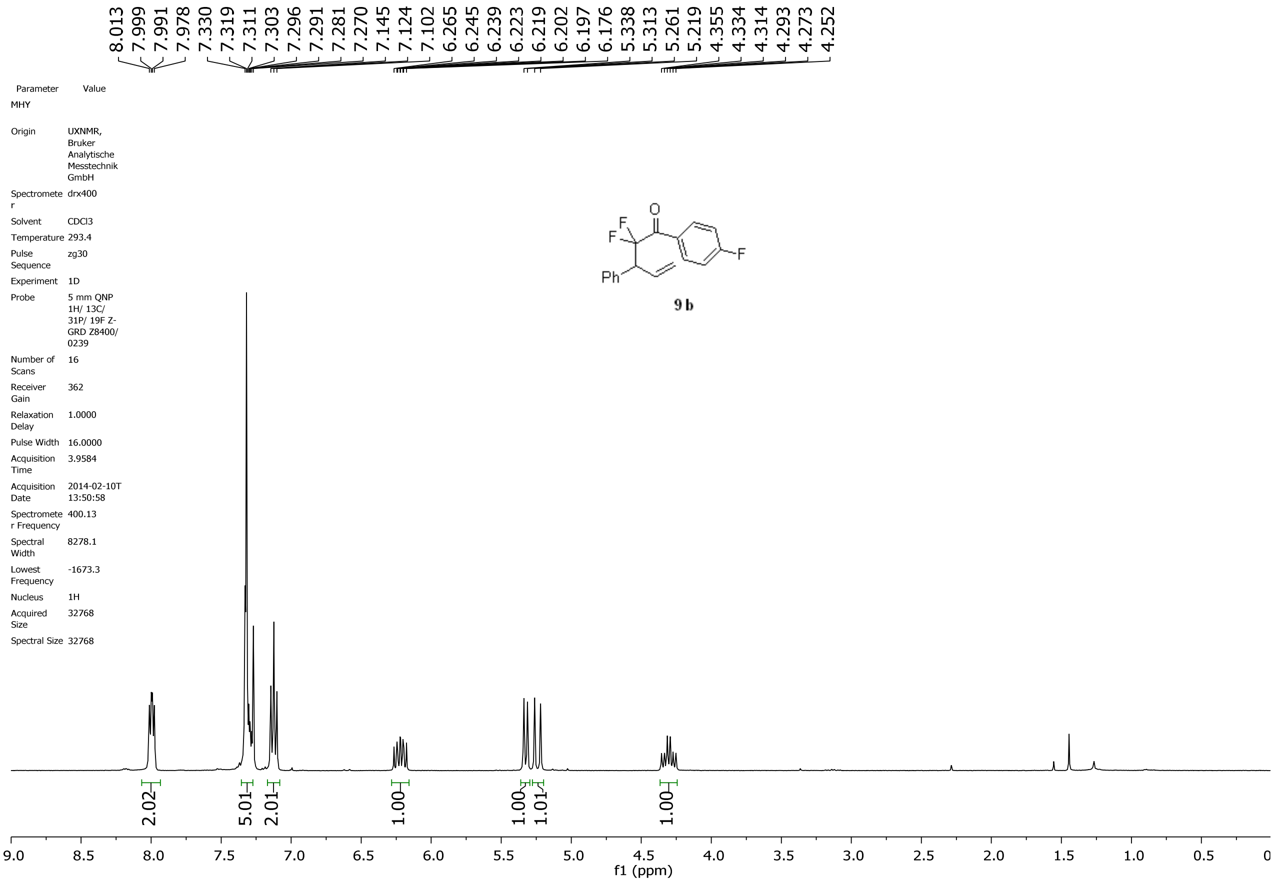


8b

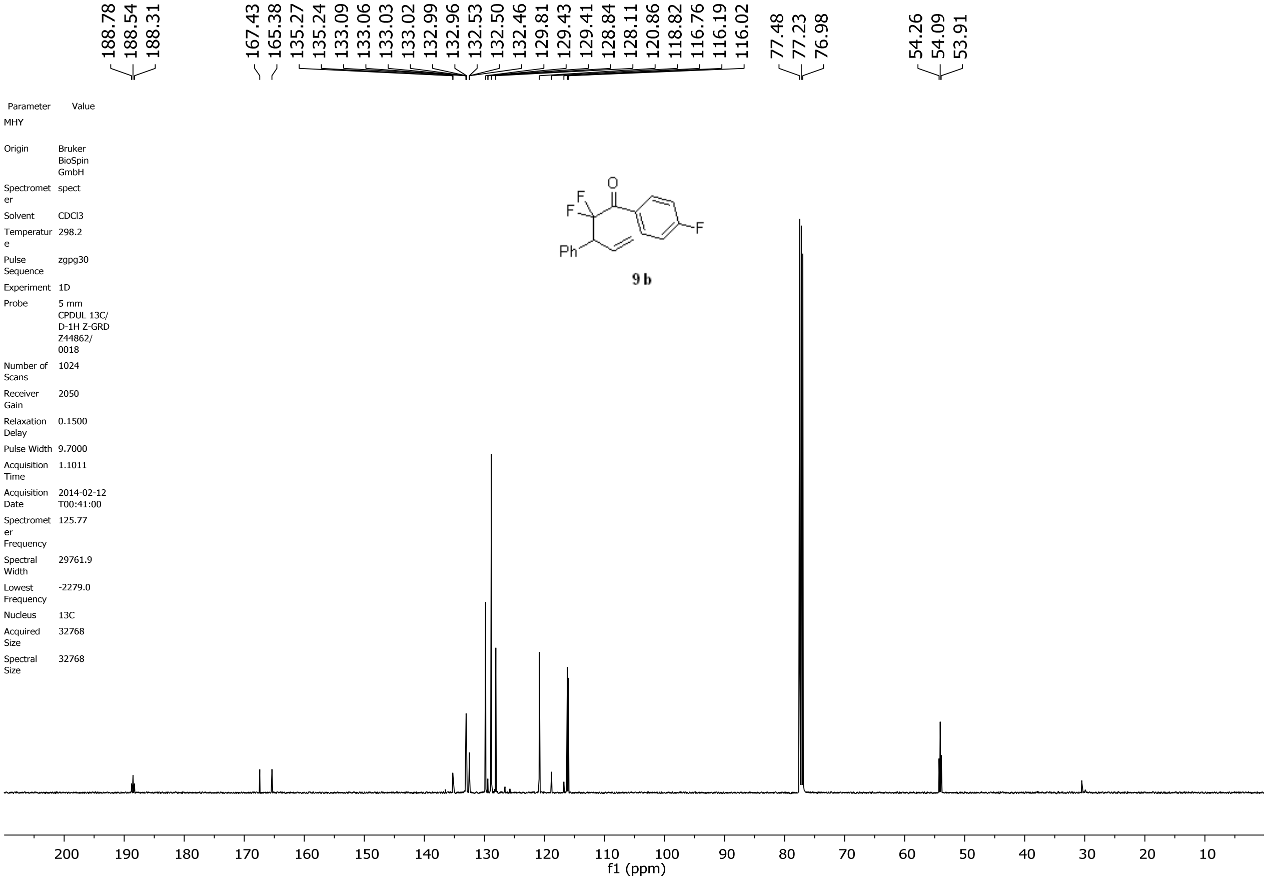
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-11T 16:46:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-10T21:03:26
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

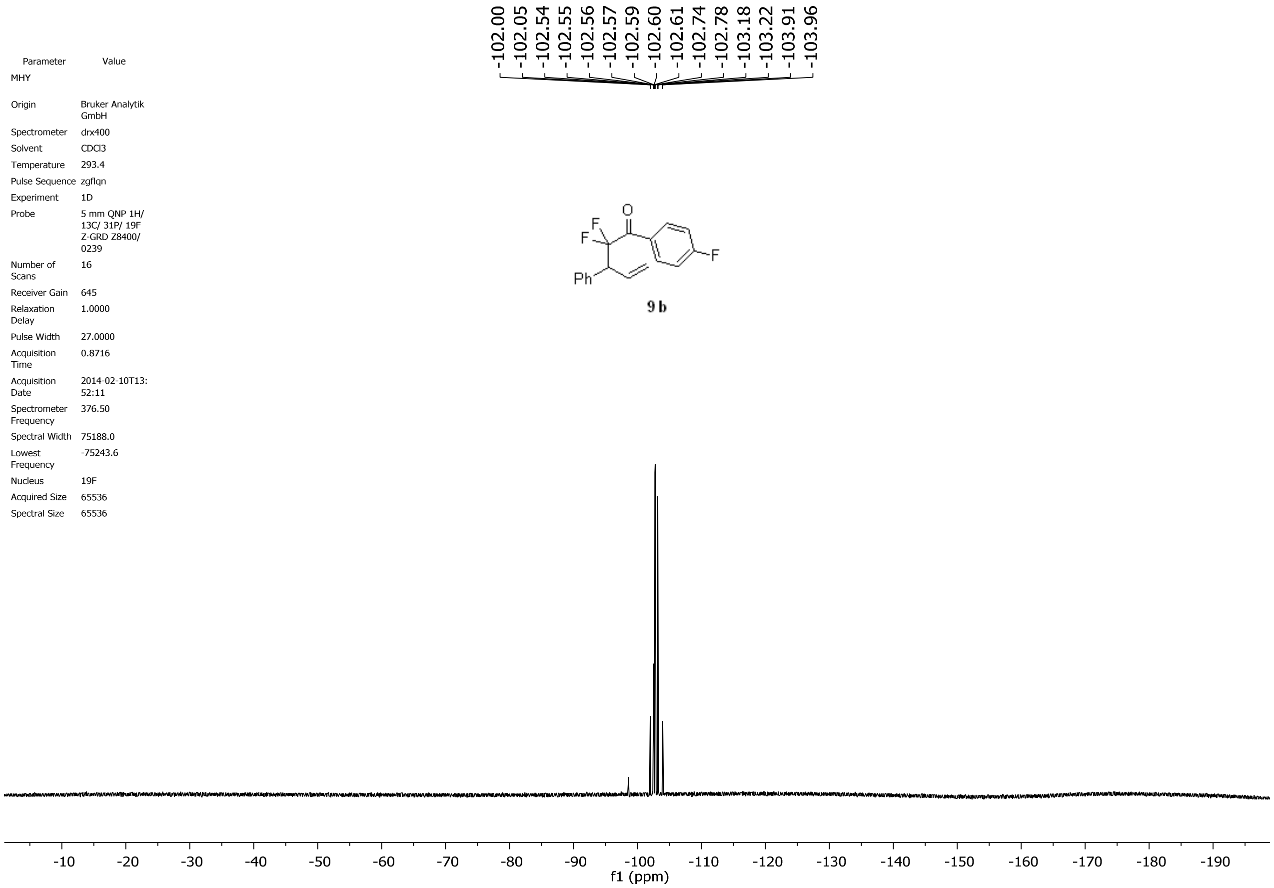


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-02-10T 13:50:58
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



9 b

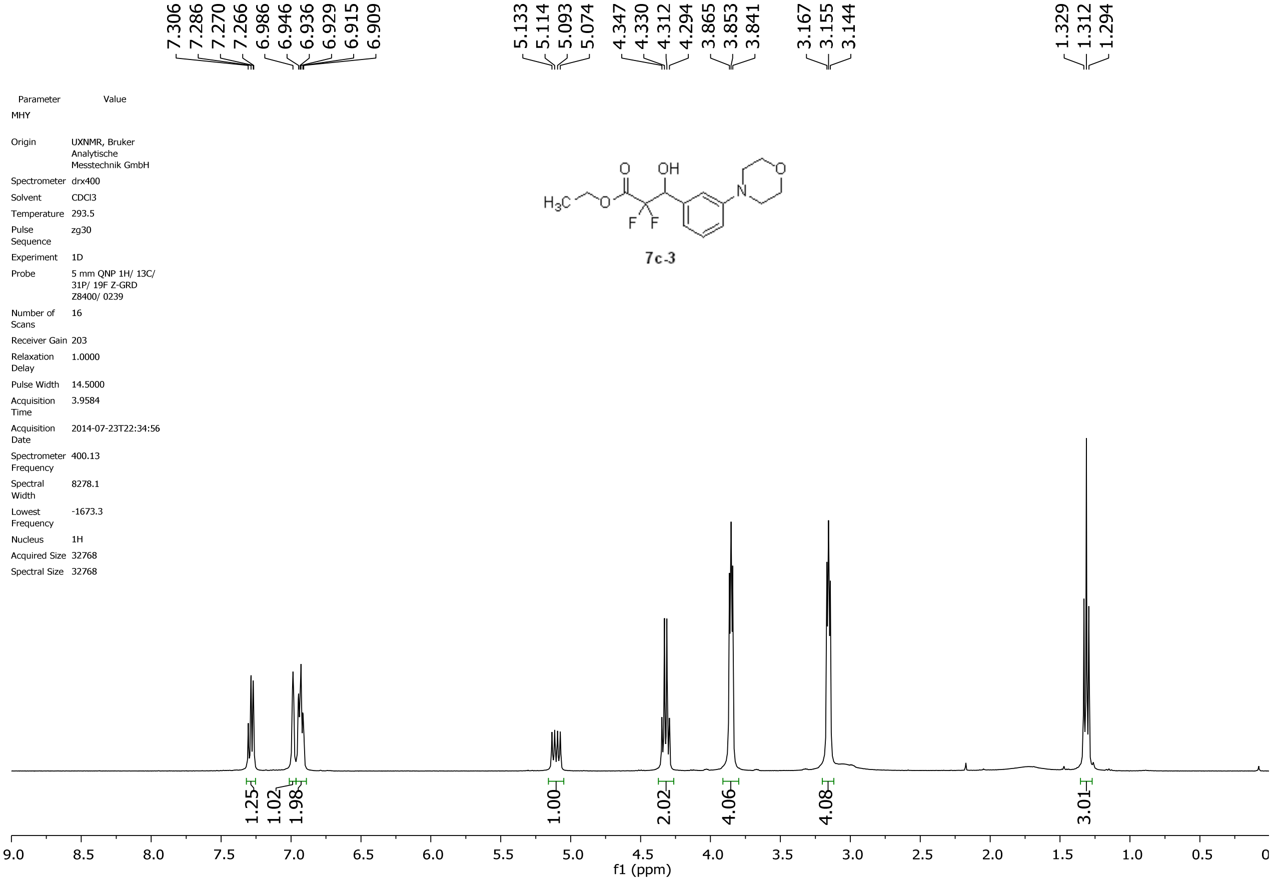
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-02-12 T00:41:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



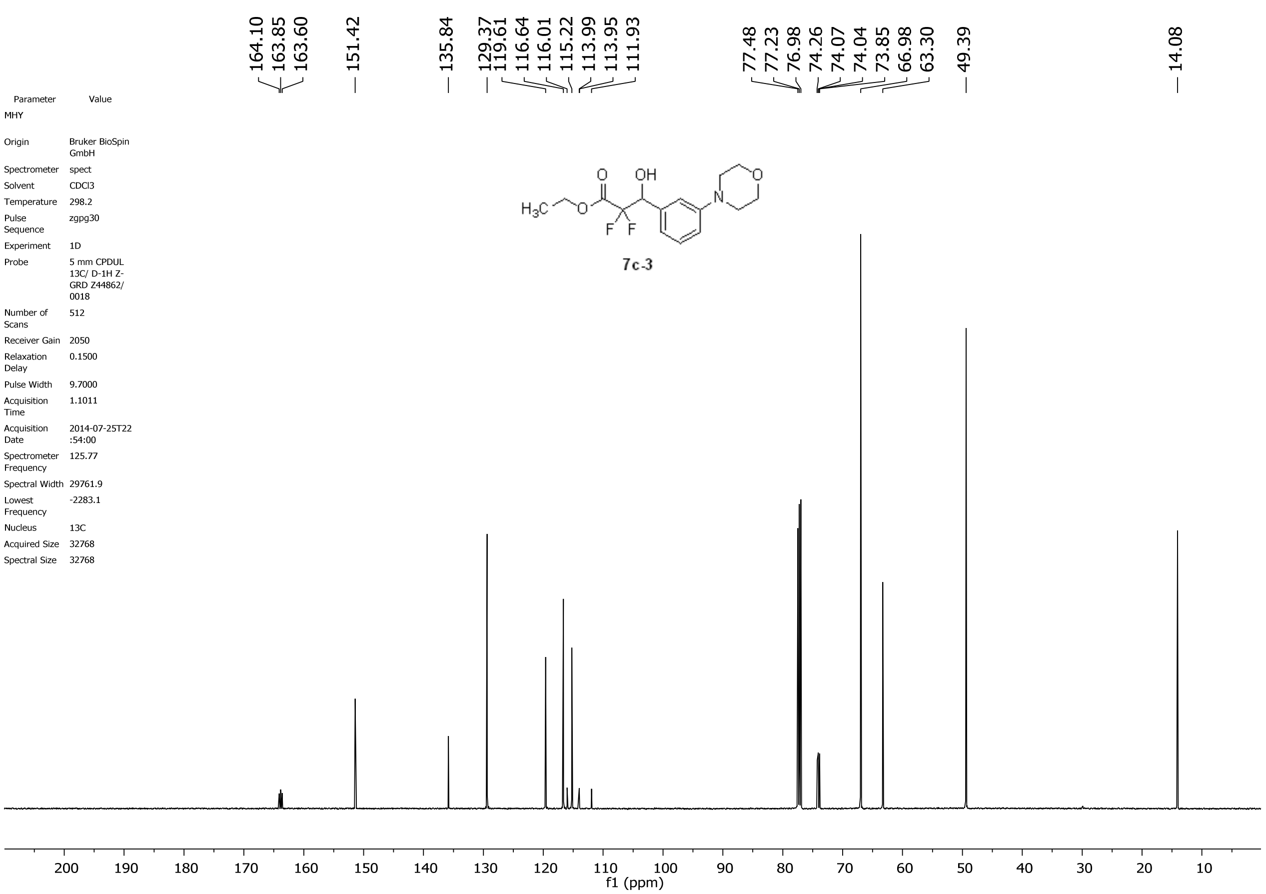
9 b

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-02-10T13:52:11
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

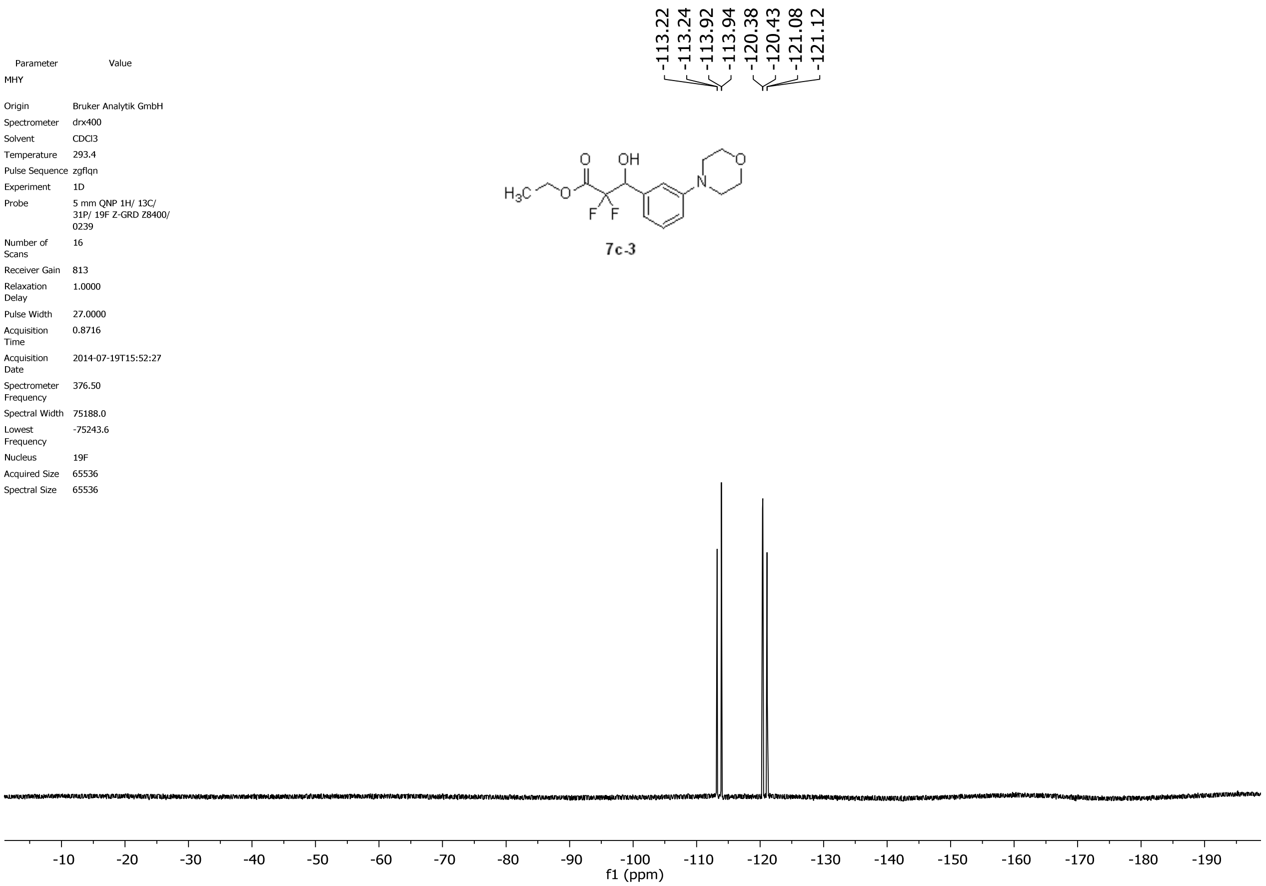
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	203
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-23T22:34:56
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	512
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-25T22 :54:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2283.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

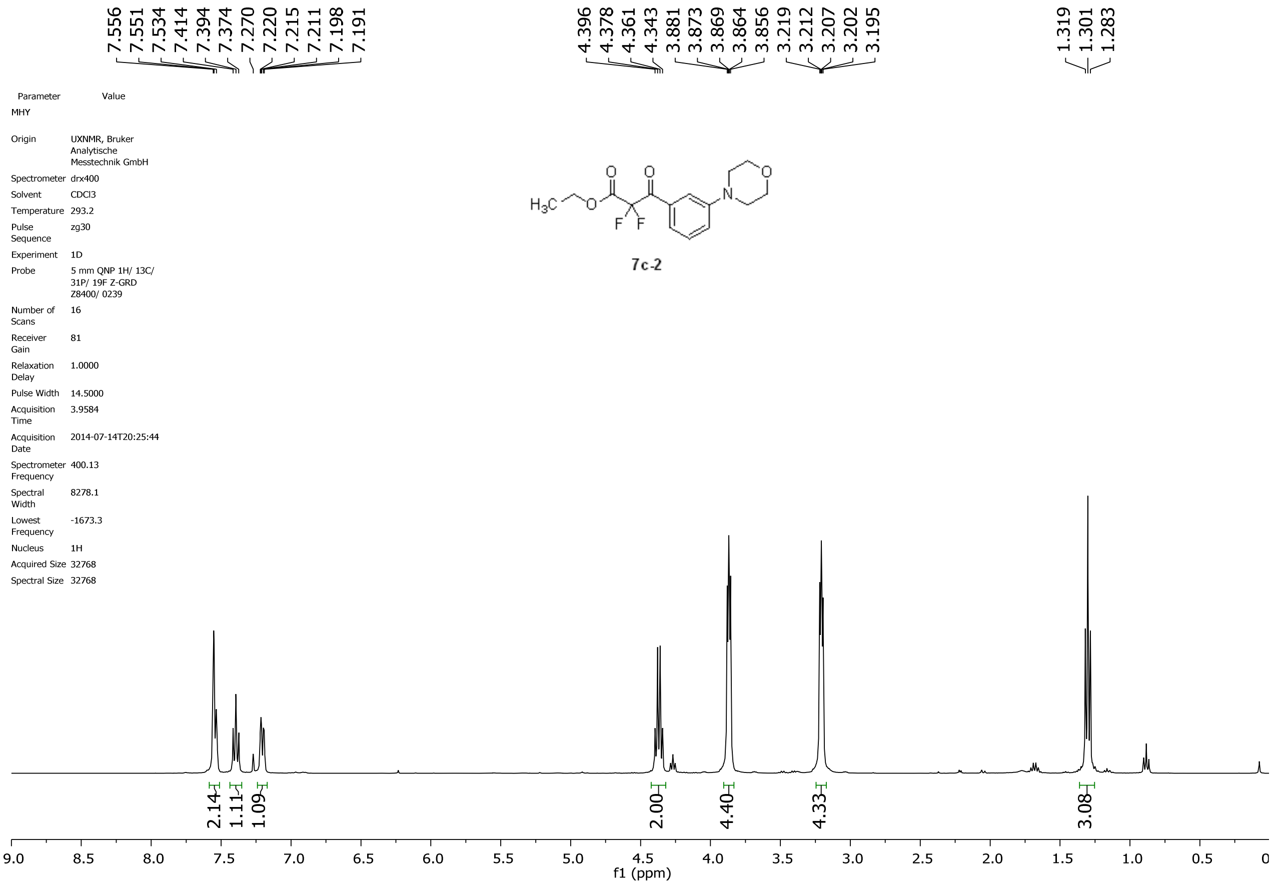


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-19T15:52:27
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

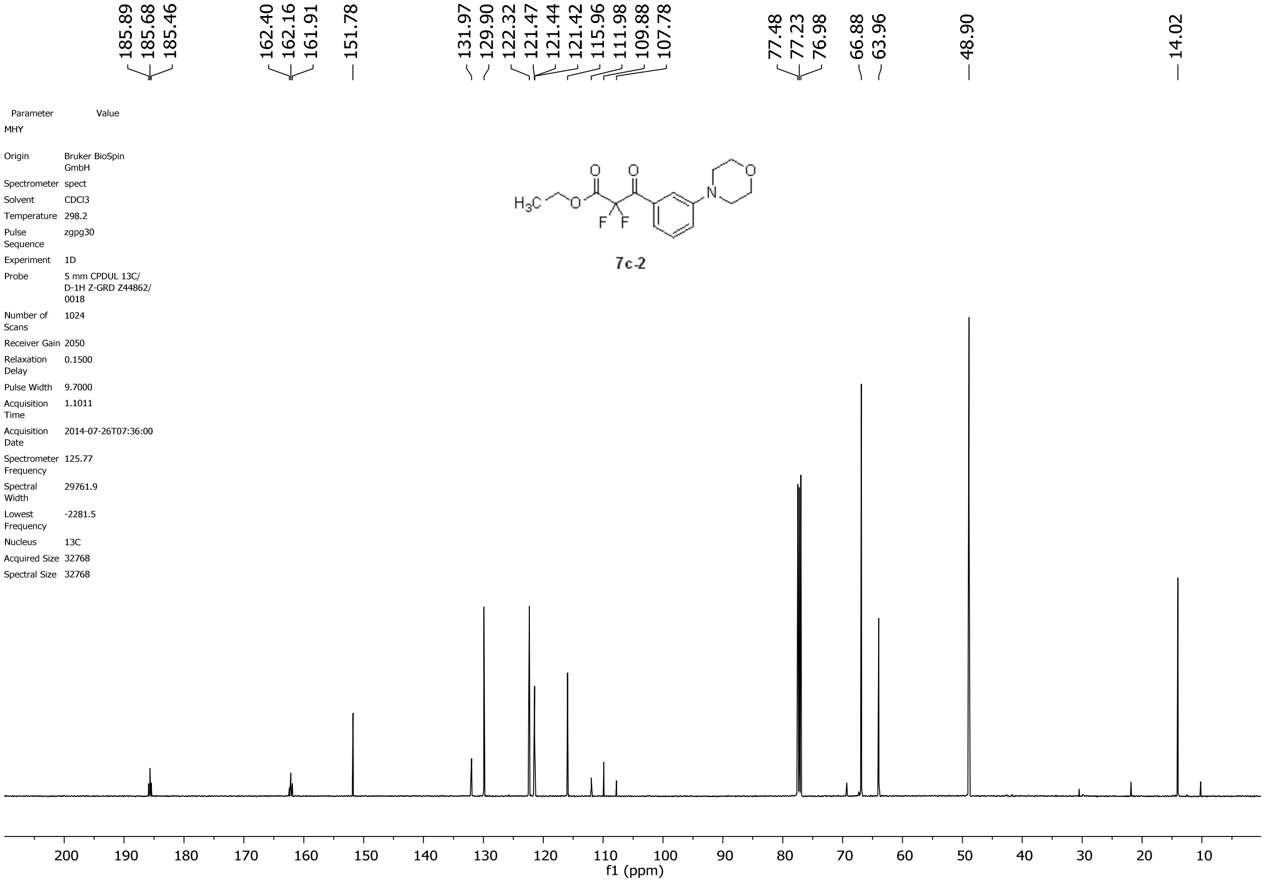


7c-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	81
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-14T20:25:44
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

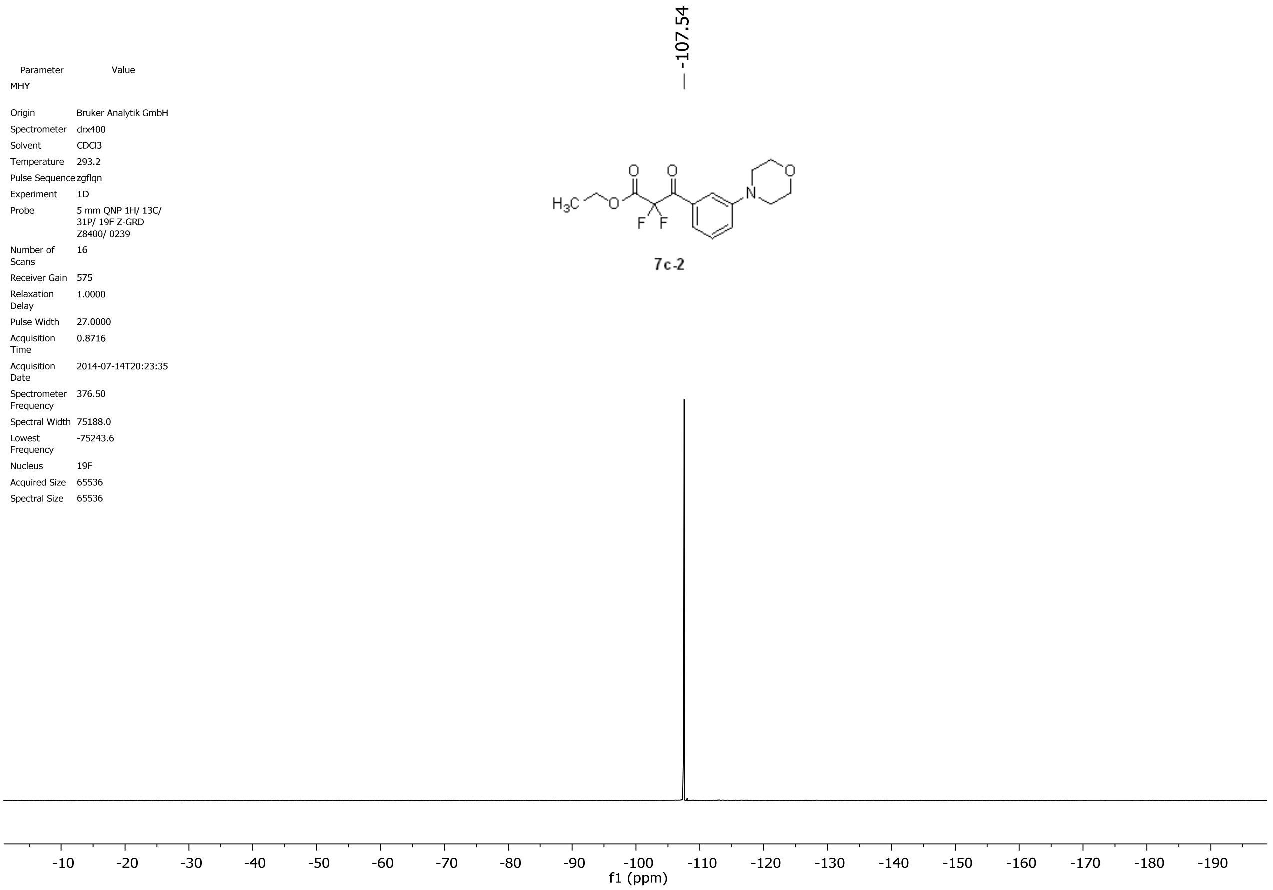


7c-2



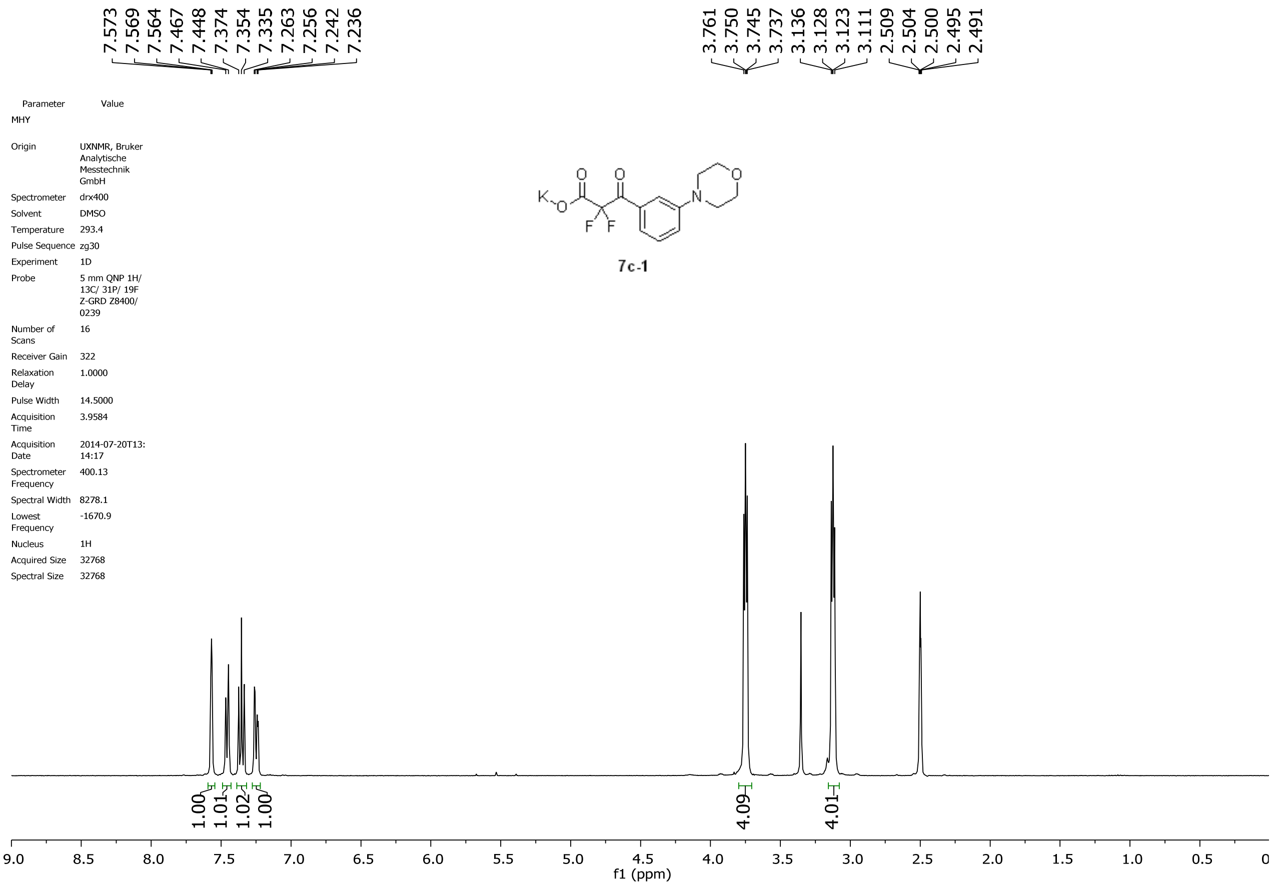
7c-2

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-26T07:36:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

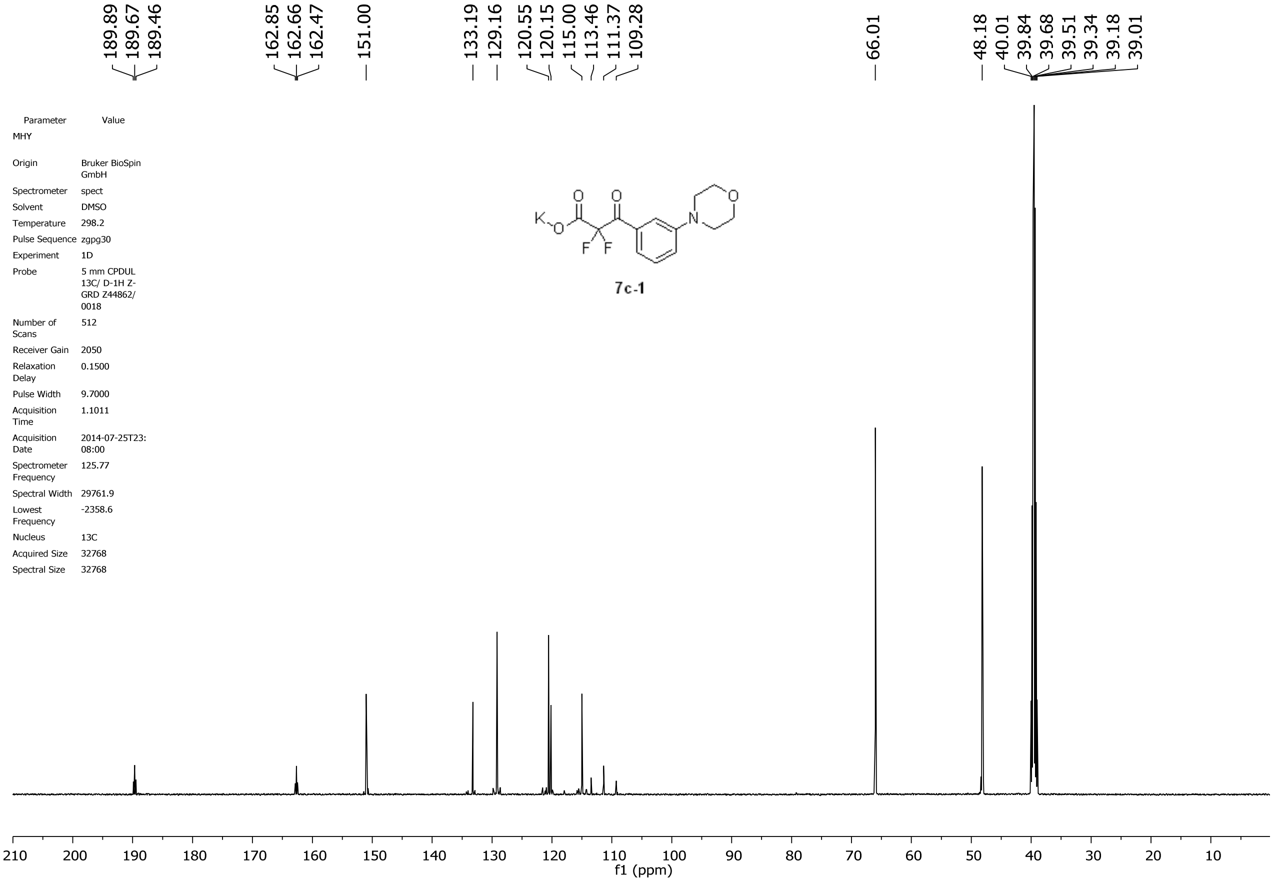


7c-2

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-14T20:23:35
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

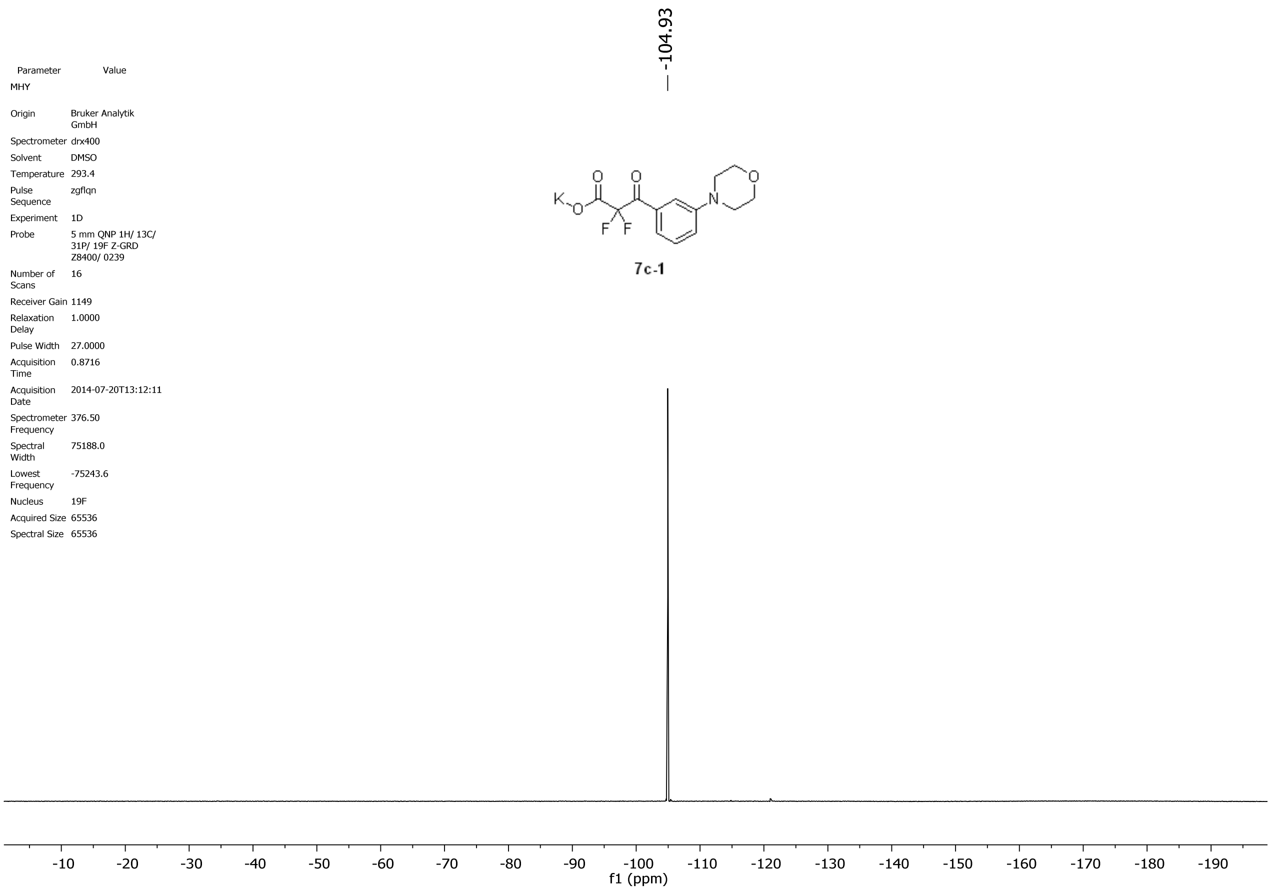


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-20T13:14:17
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.9
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



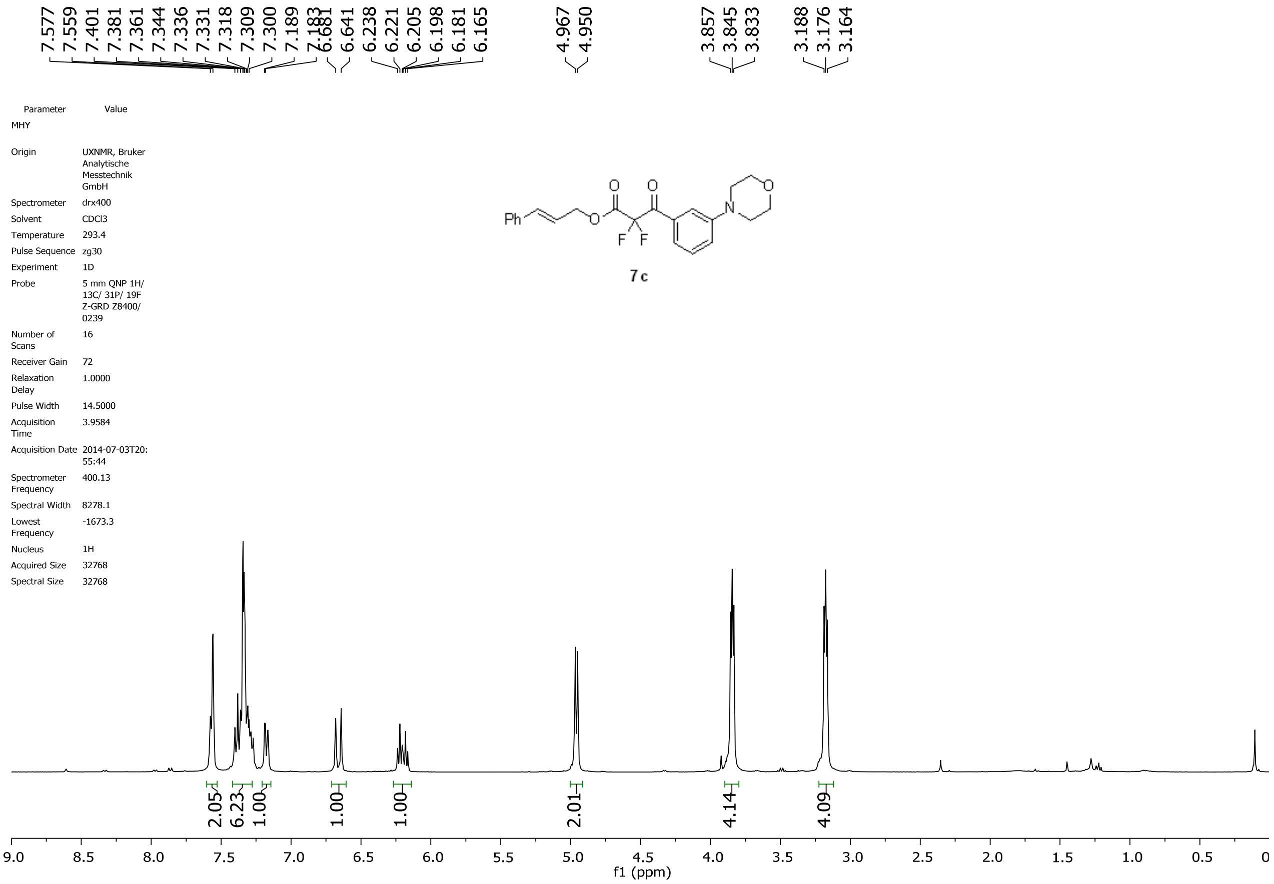
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	512
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-25T23:08:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2358.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-20T13:12:11
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

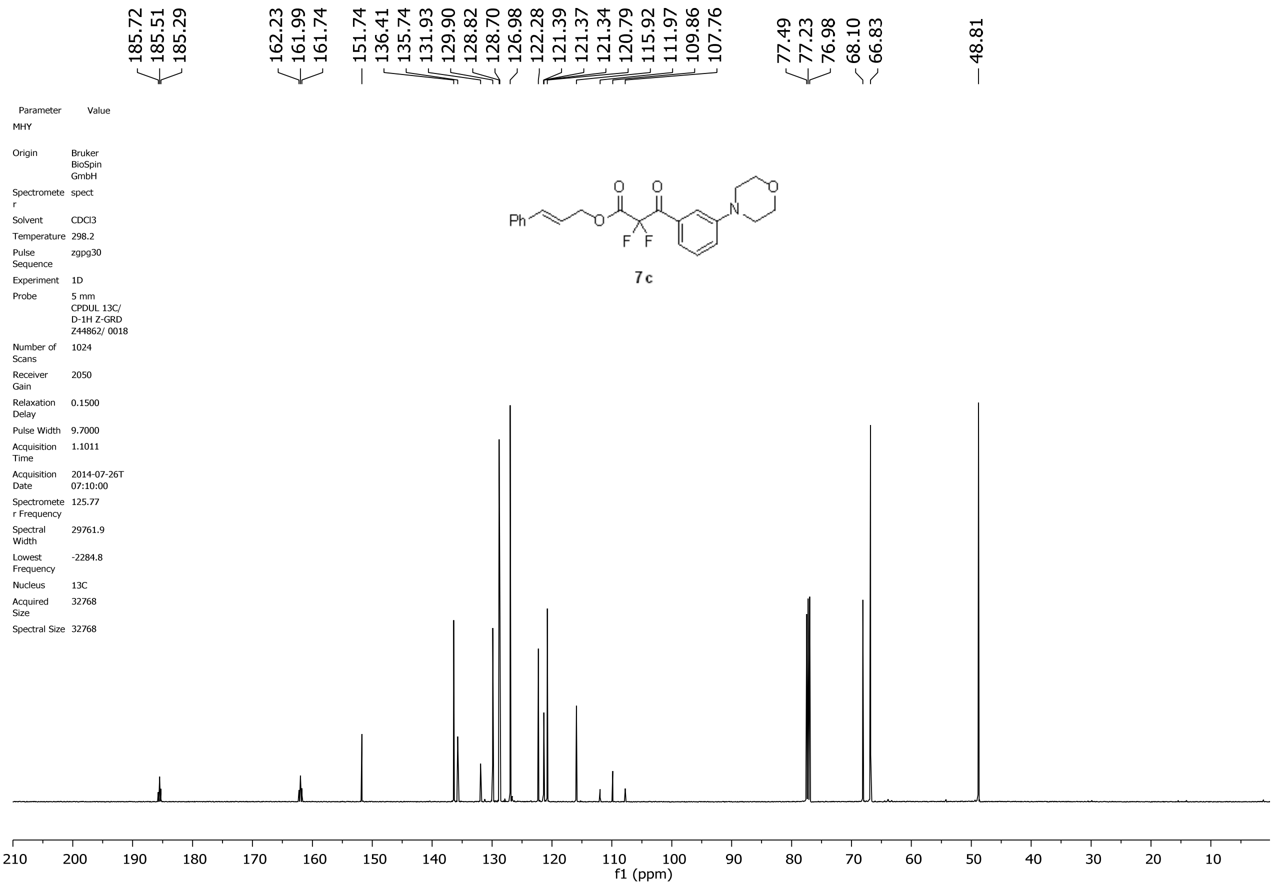


7c-1

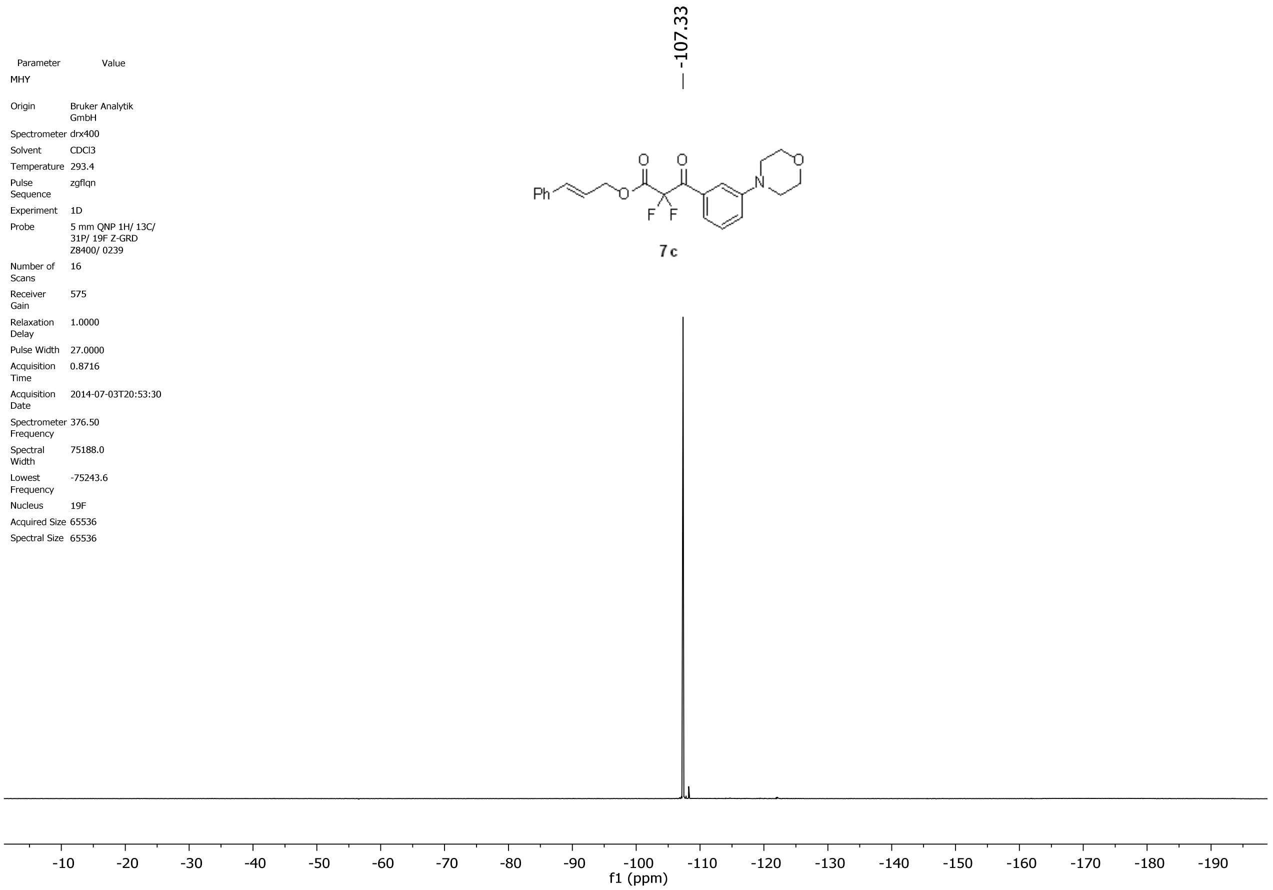
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	72
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-03T20:55:44
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



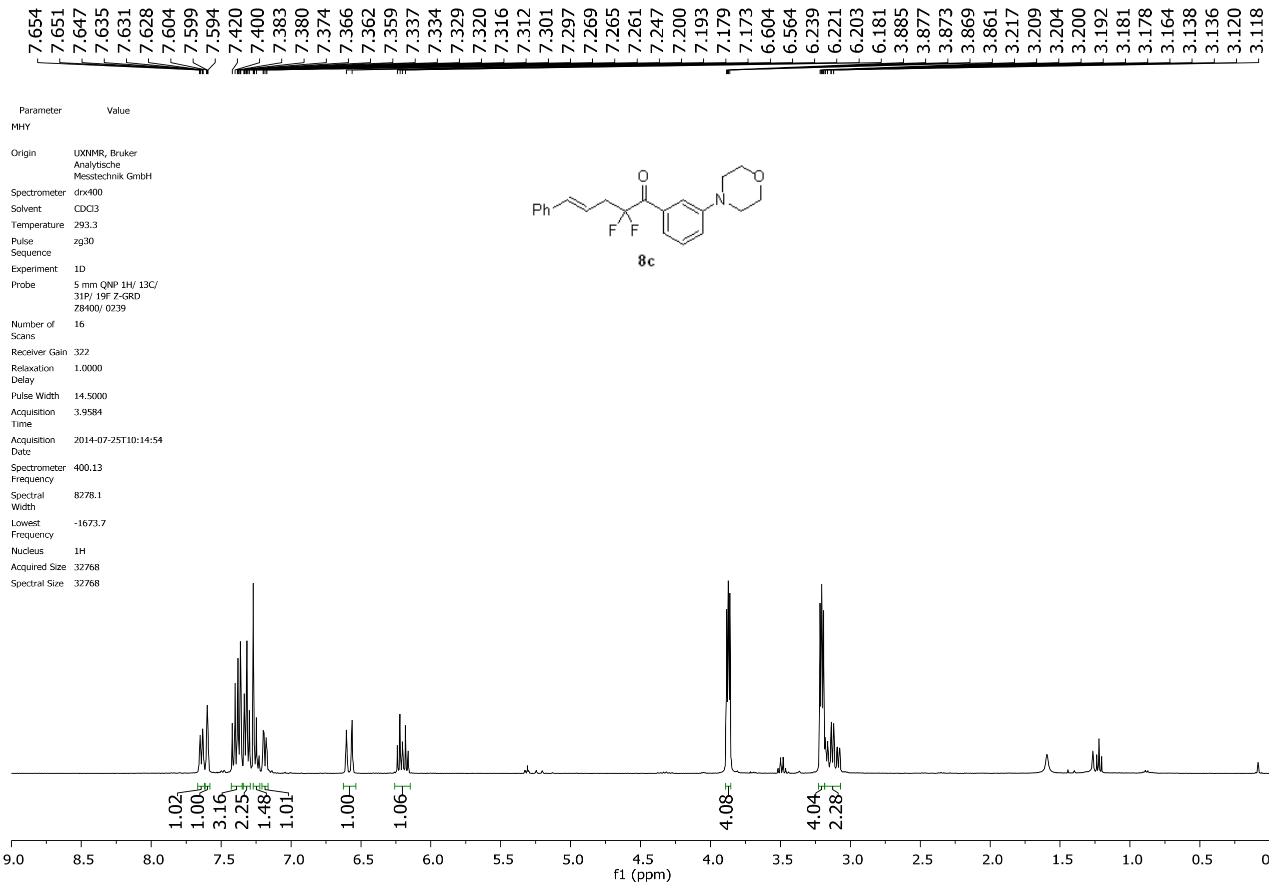
7c



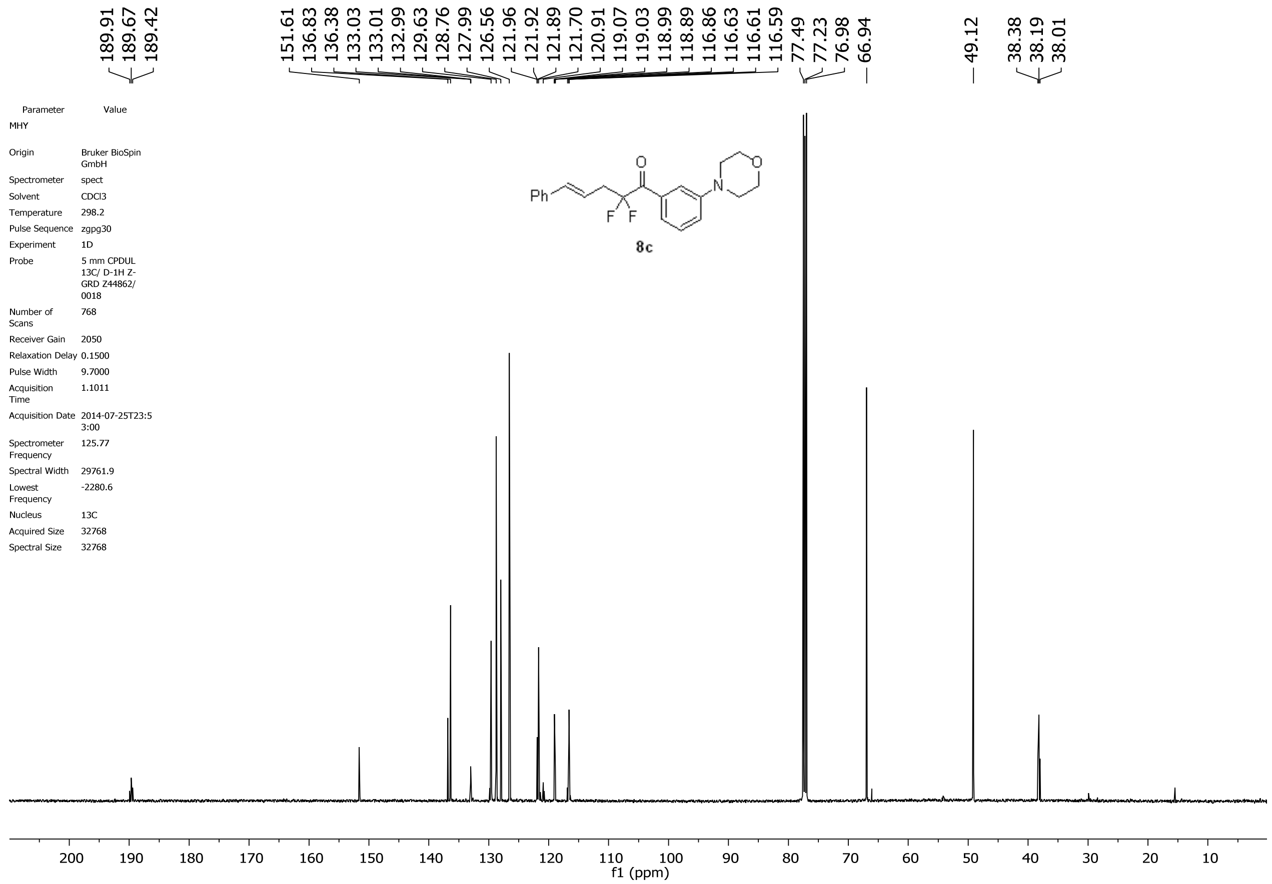
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-26T 07:10:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2284.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



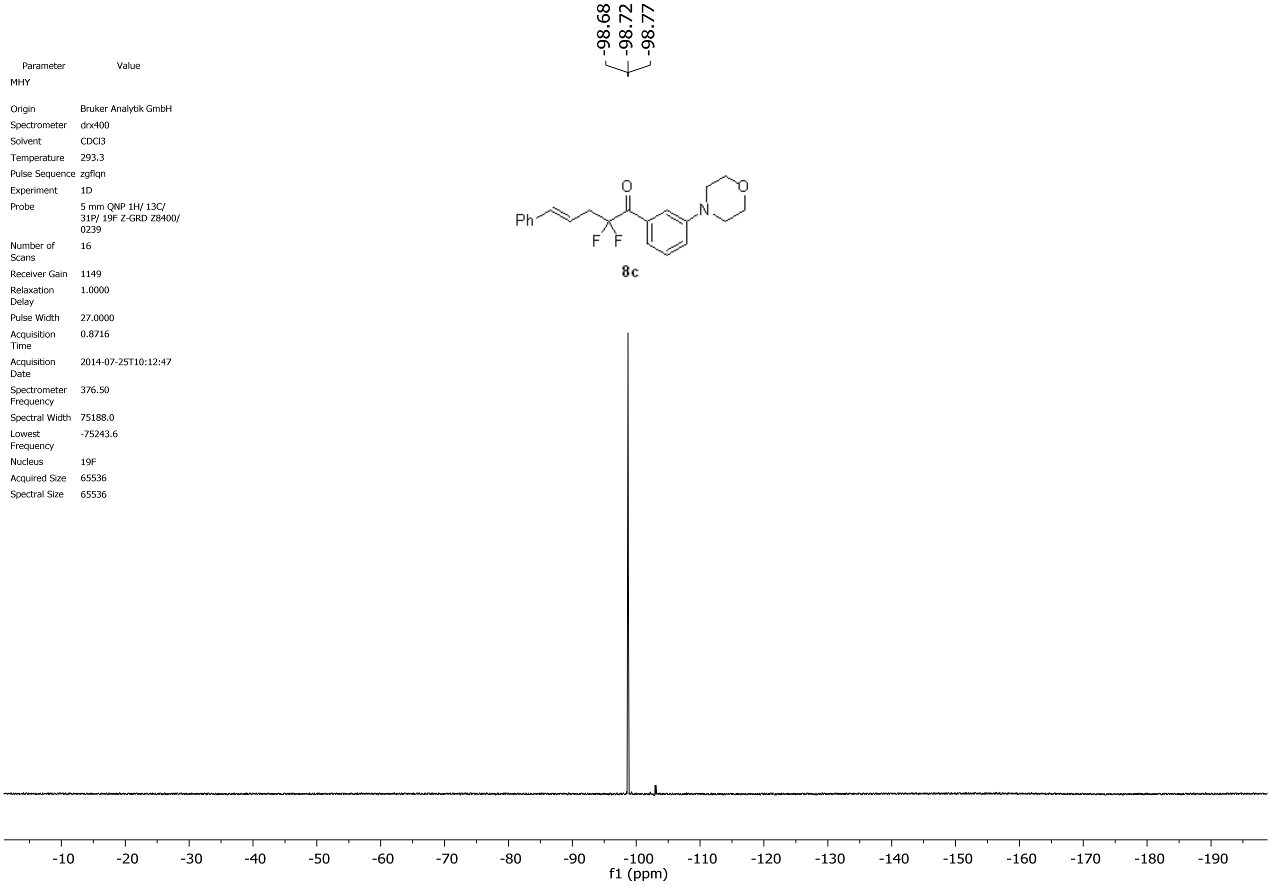
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-03T20:53:30
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



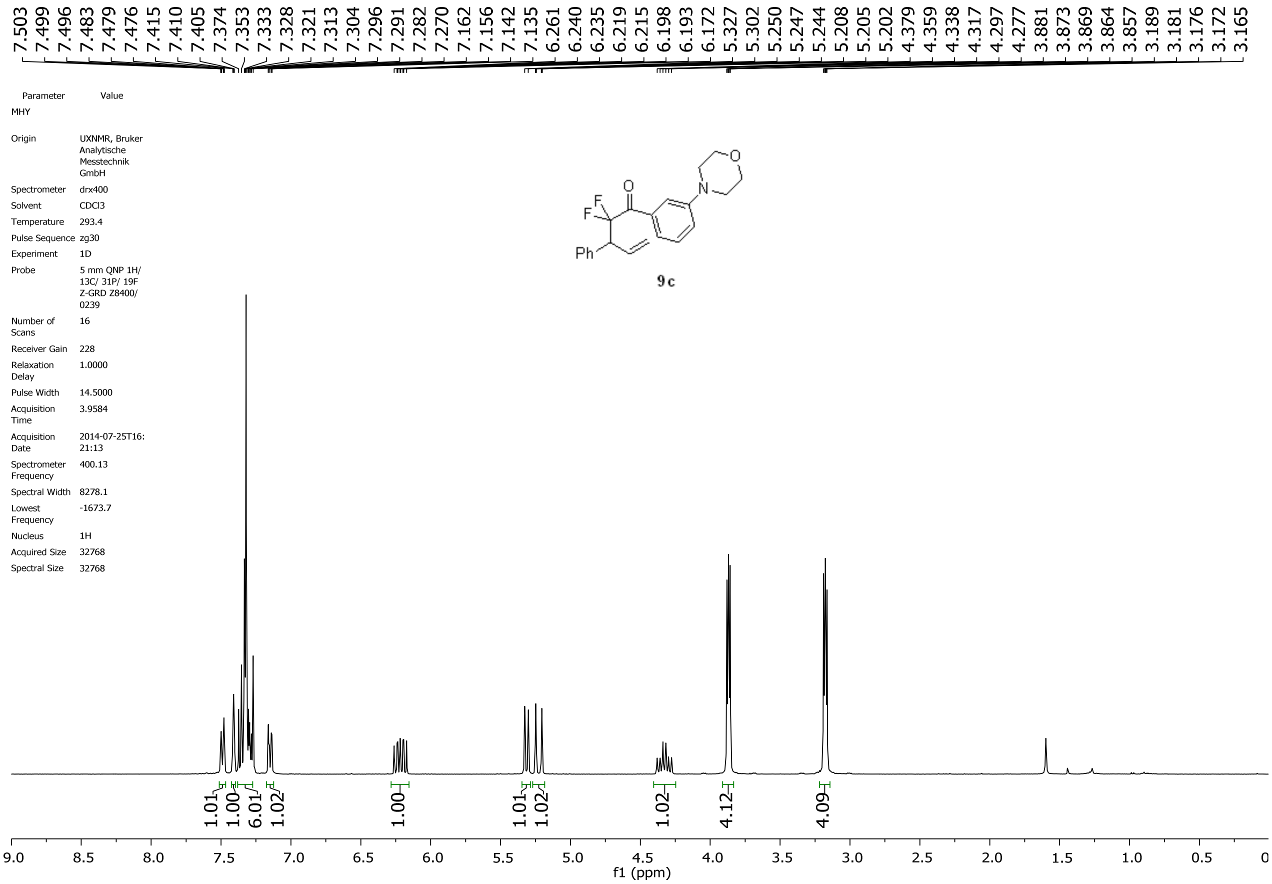
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-25T10:14:54
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



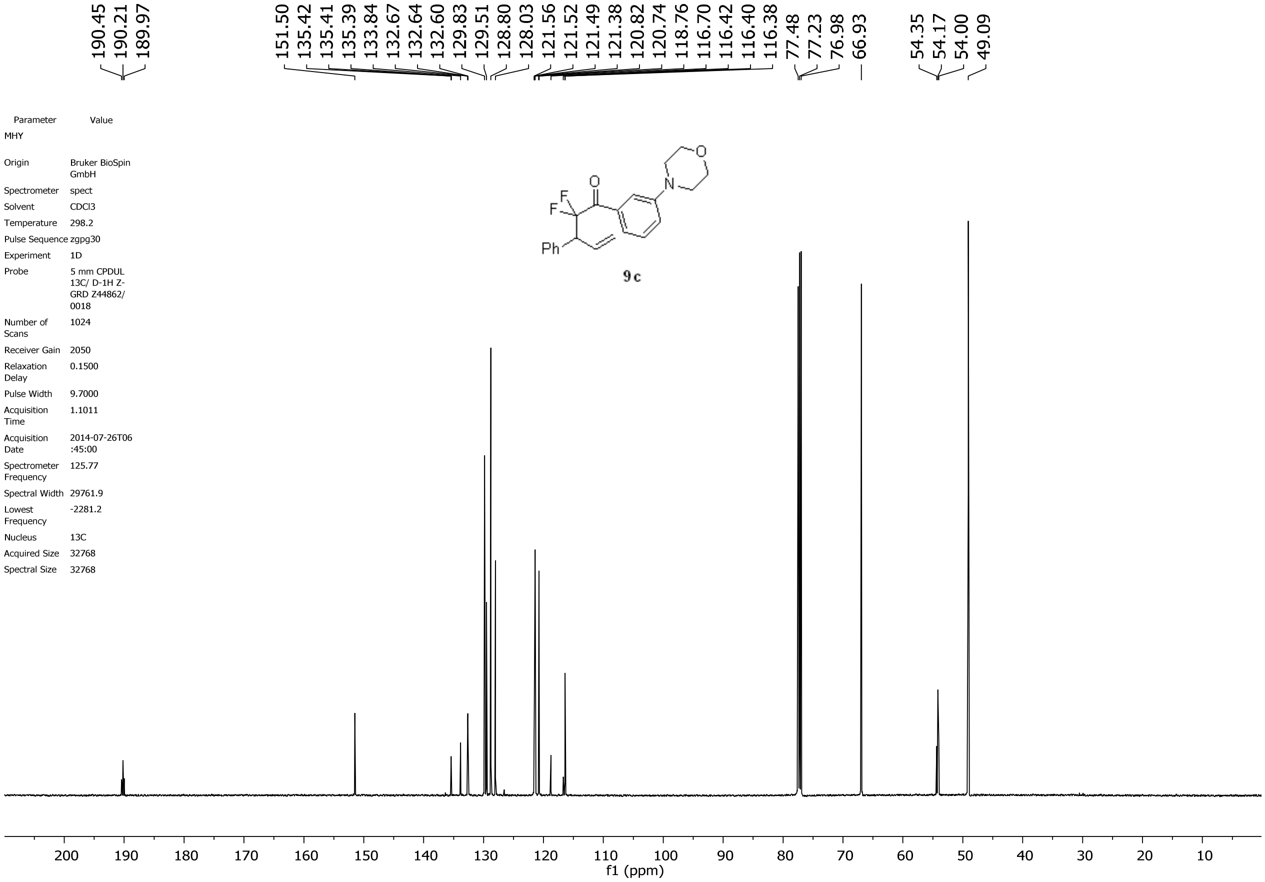
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	768
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-25T23:53:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



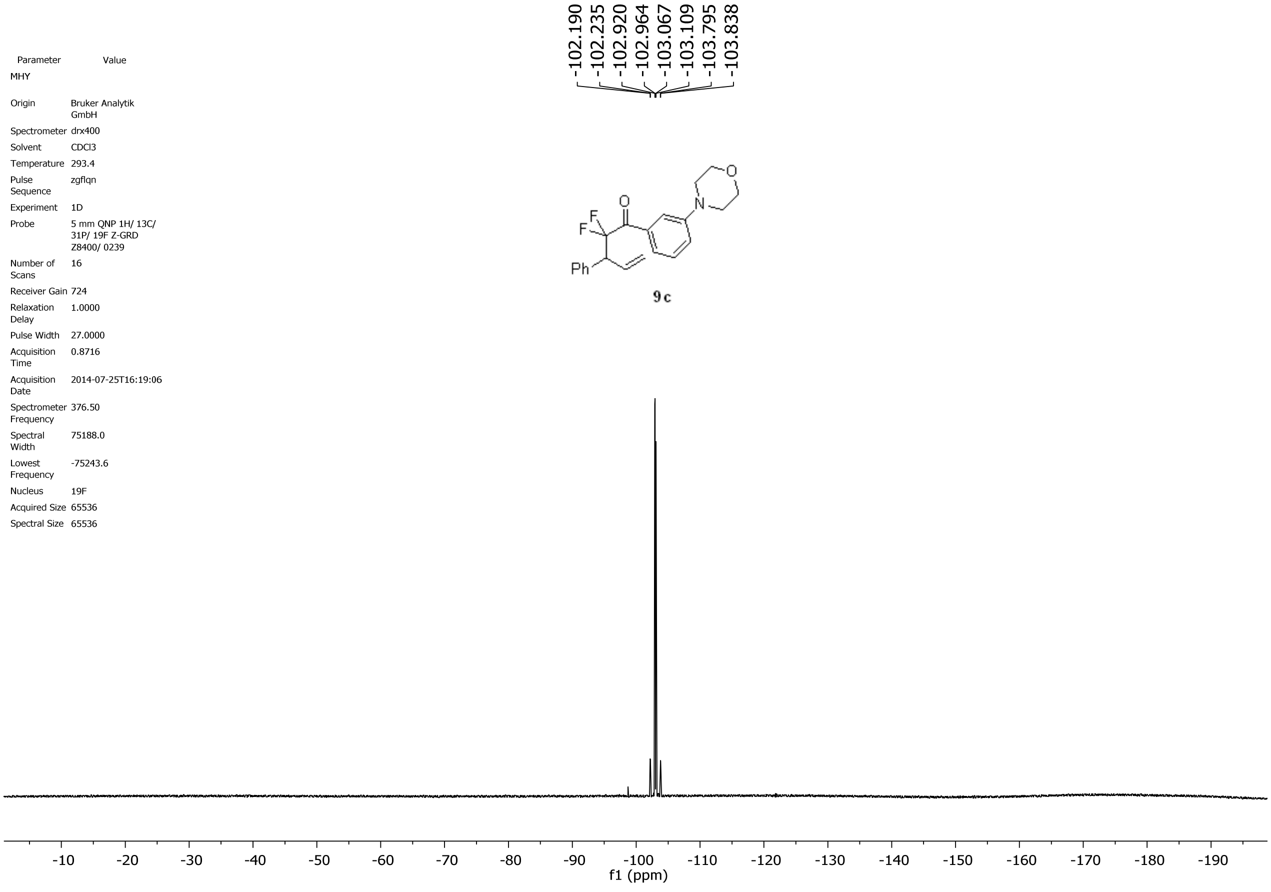
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-25T10:12:47
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



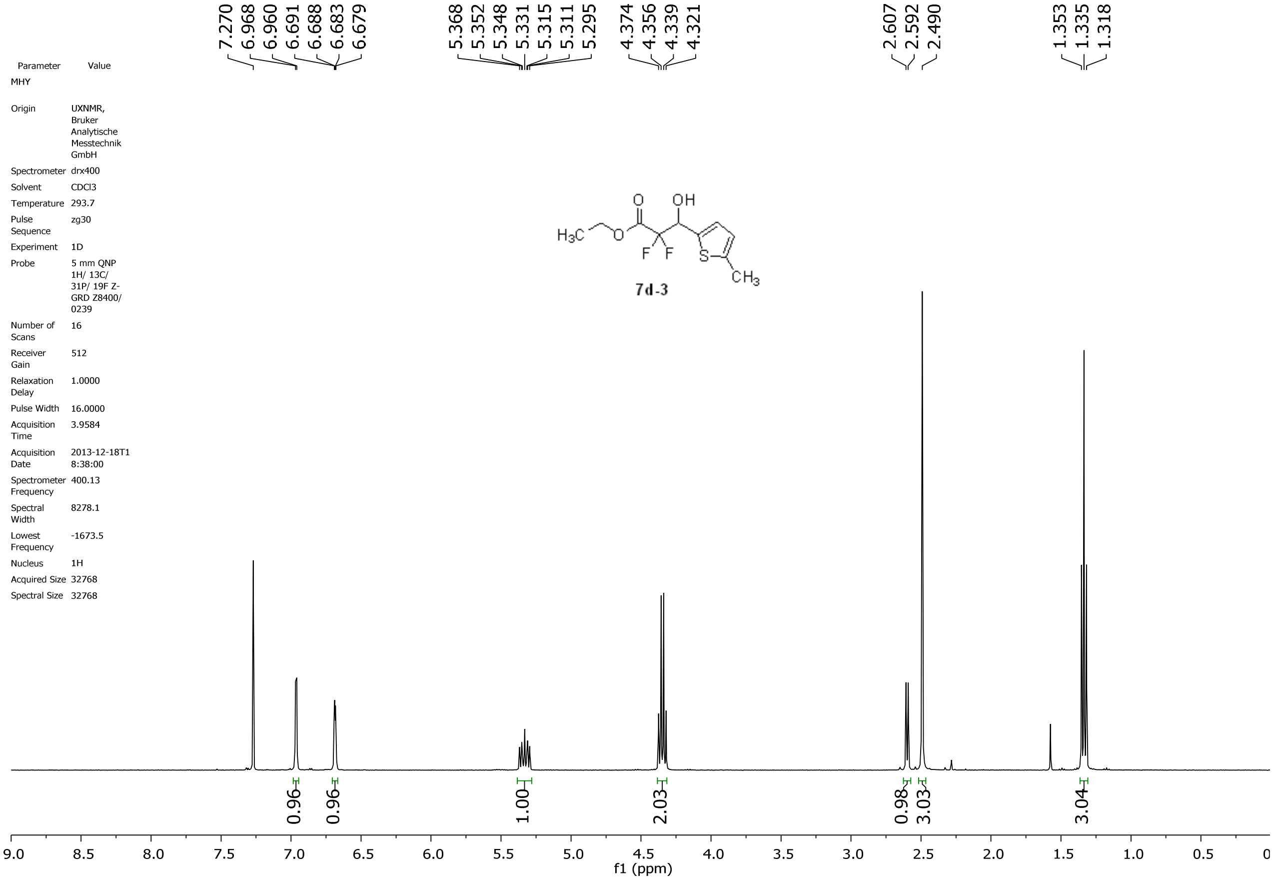
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-25T16:21:13
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-26T06 :45:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

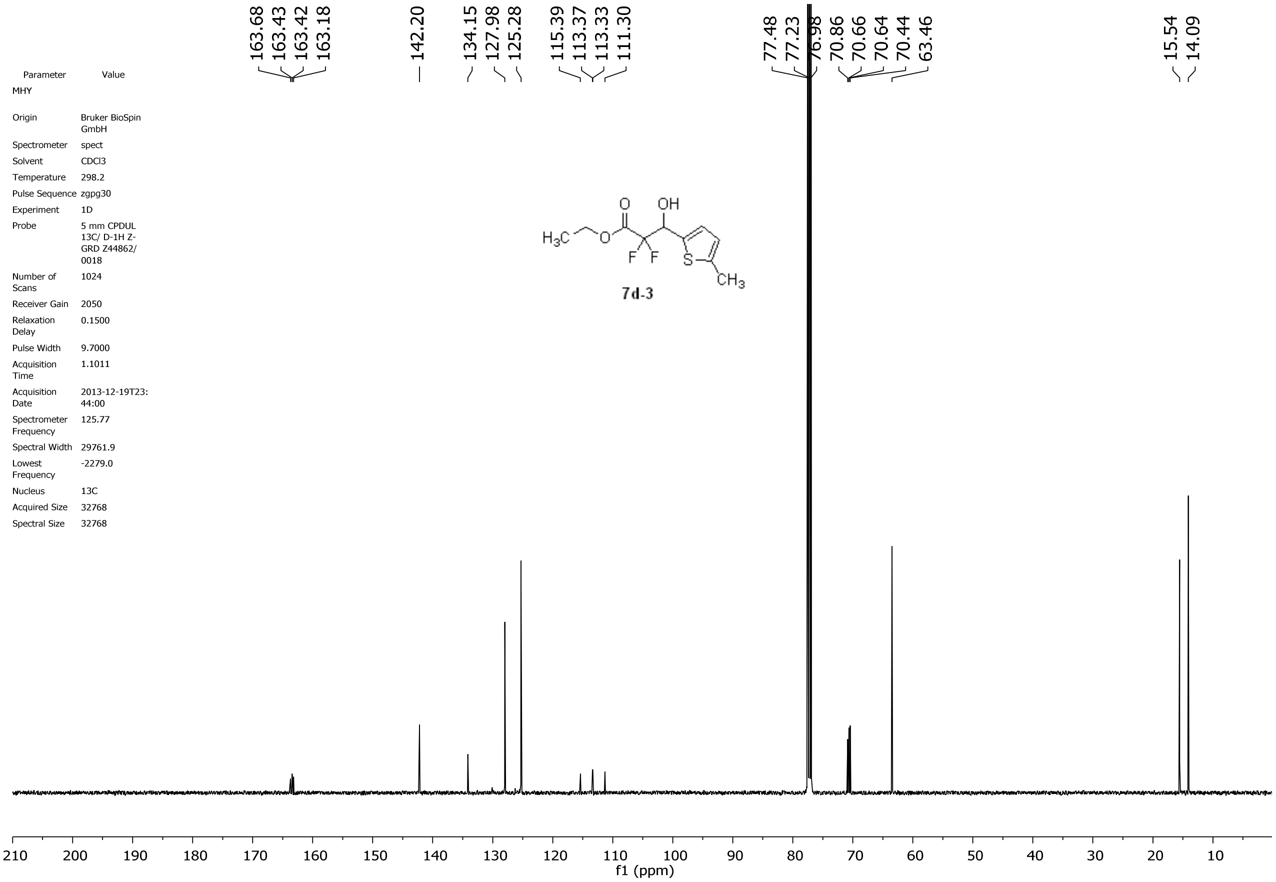


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-25T16:19:06
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



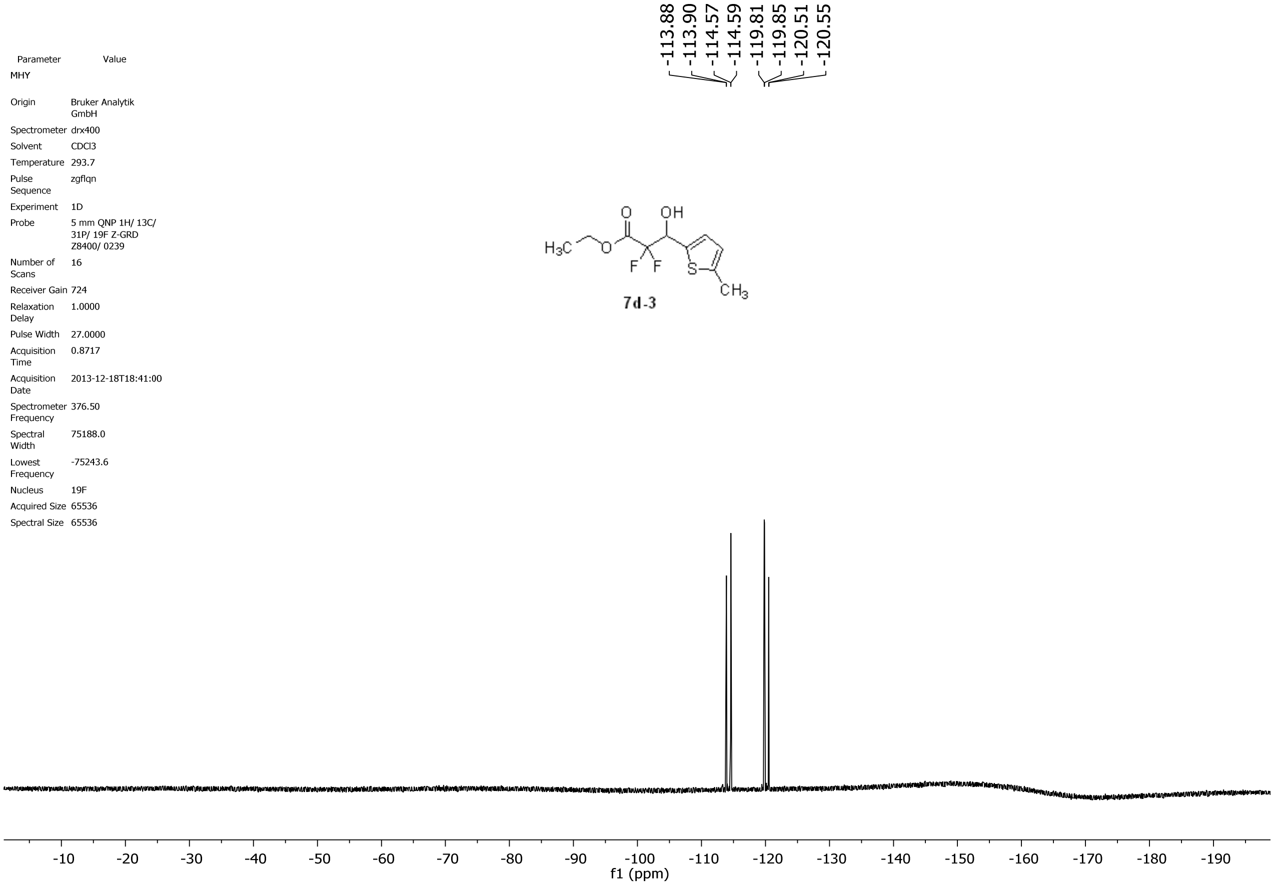
7d-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-18T18:38:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



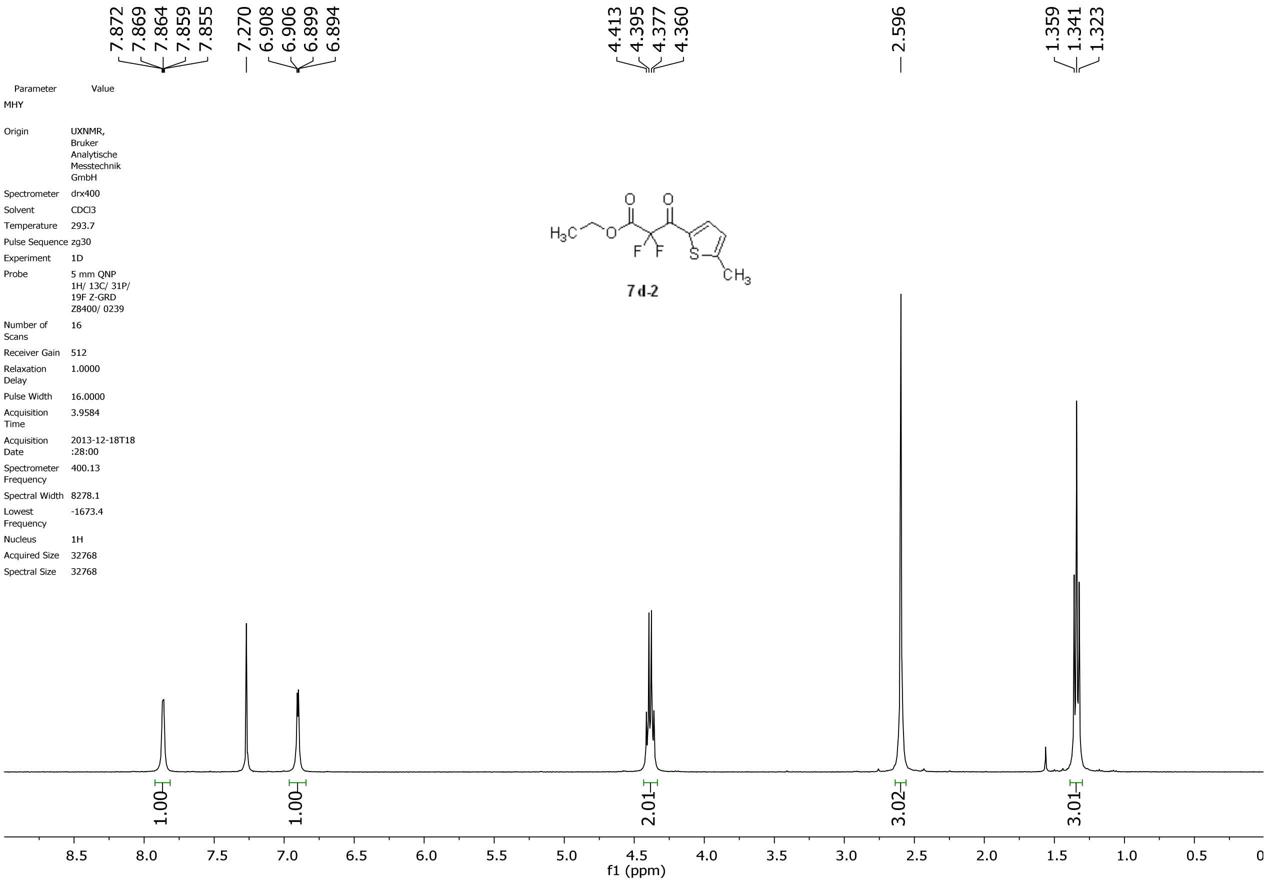
7d-3

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2013-12-19T23:44:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



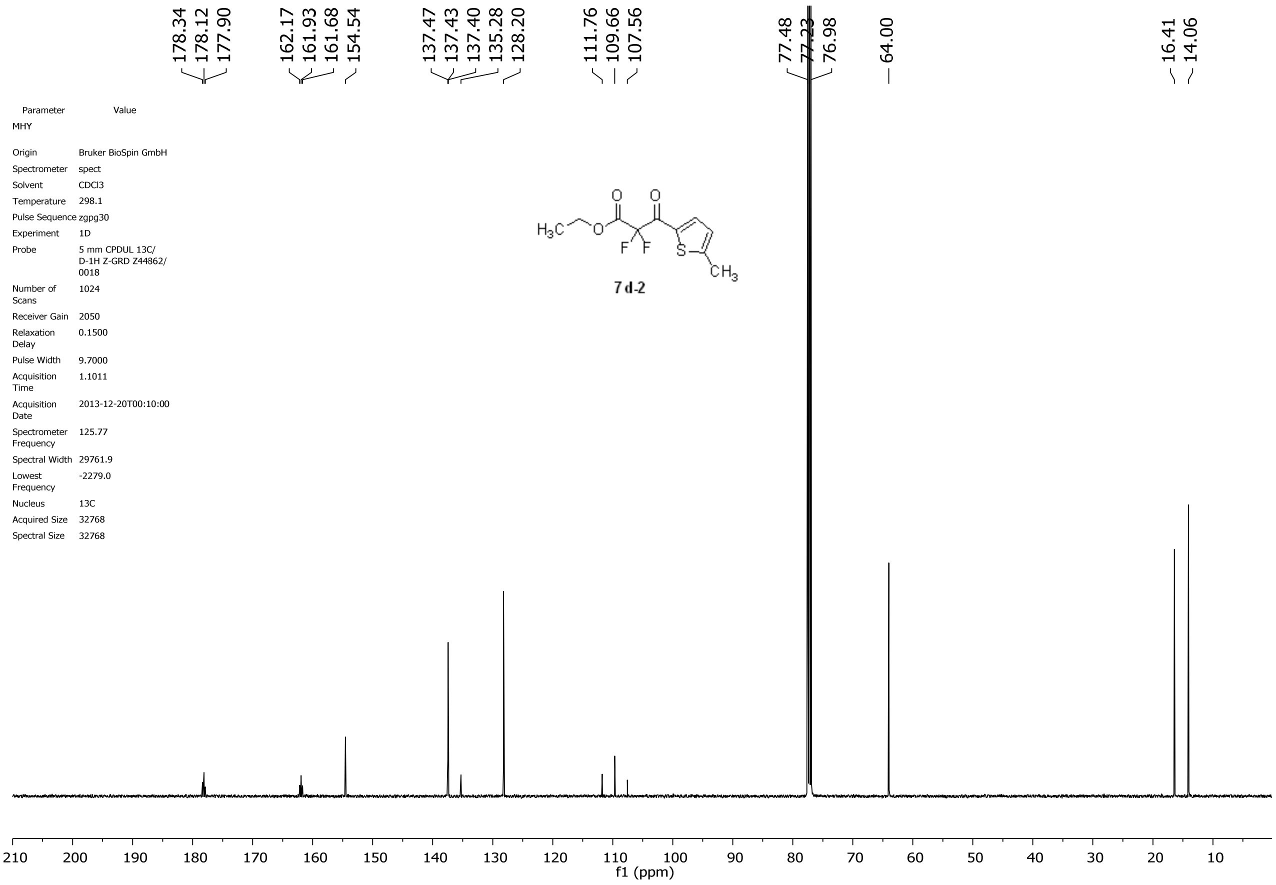
7d-3

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-12-18T18:41:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

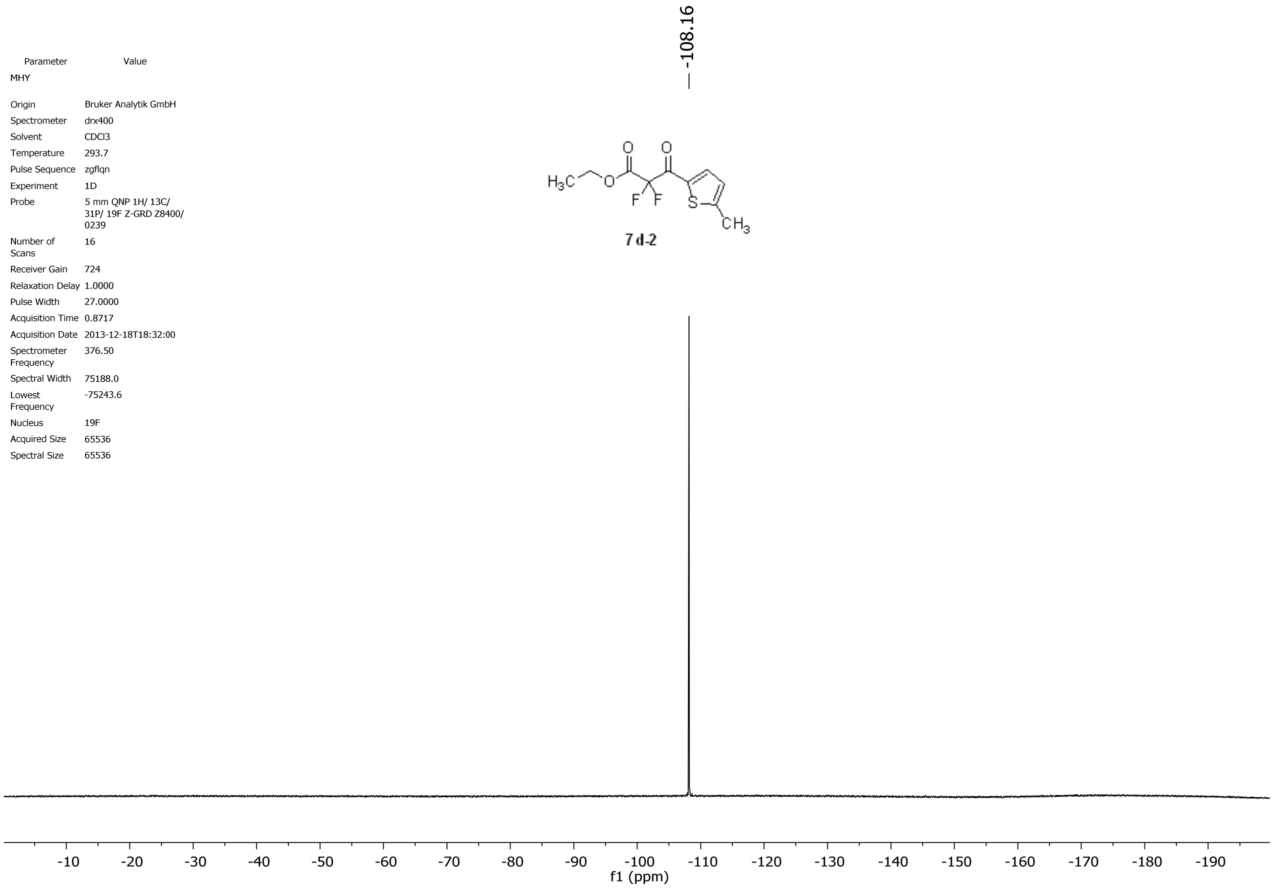


7d-2

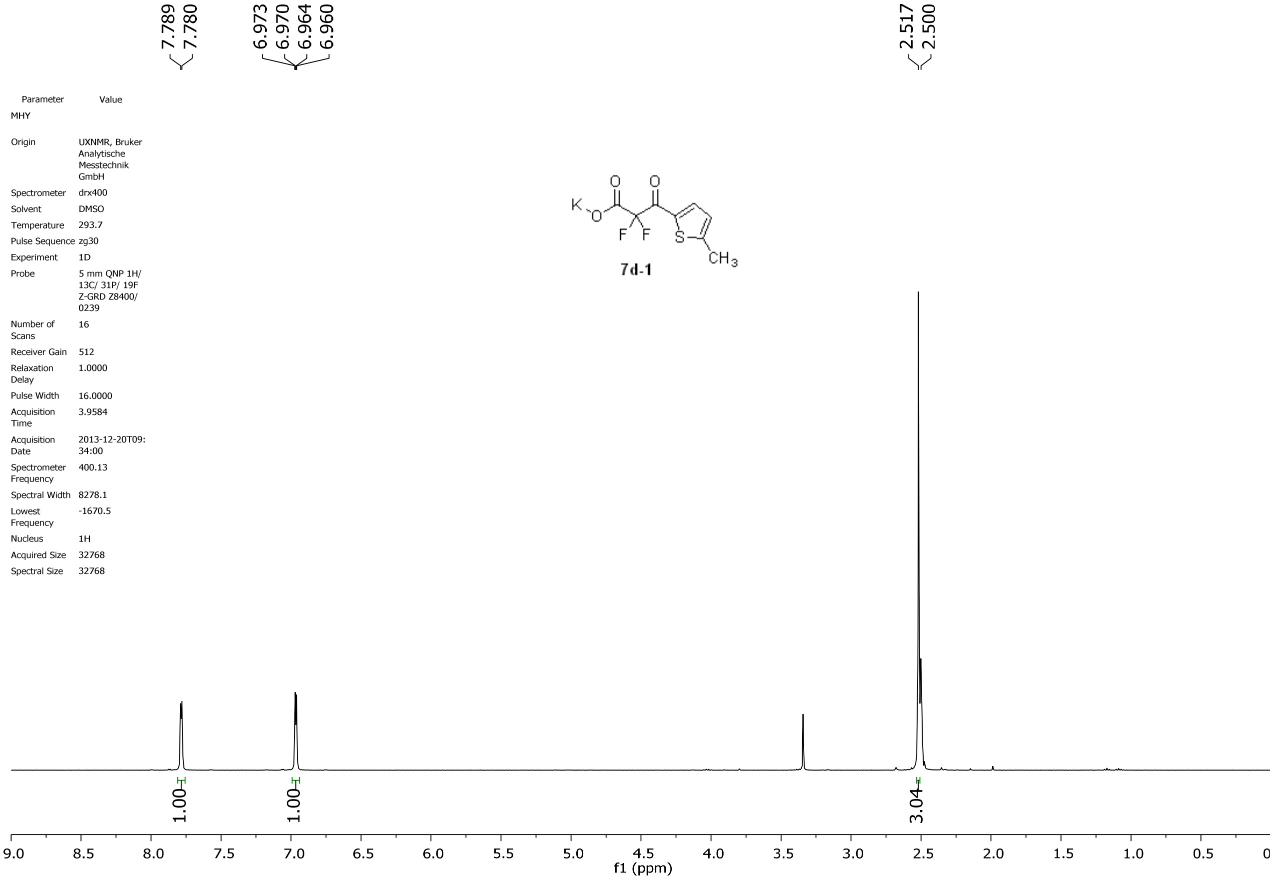
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-18T18:28:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



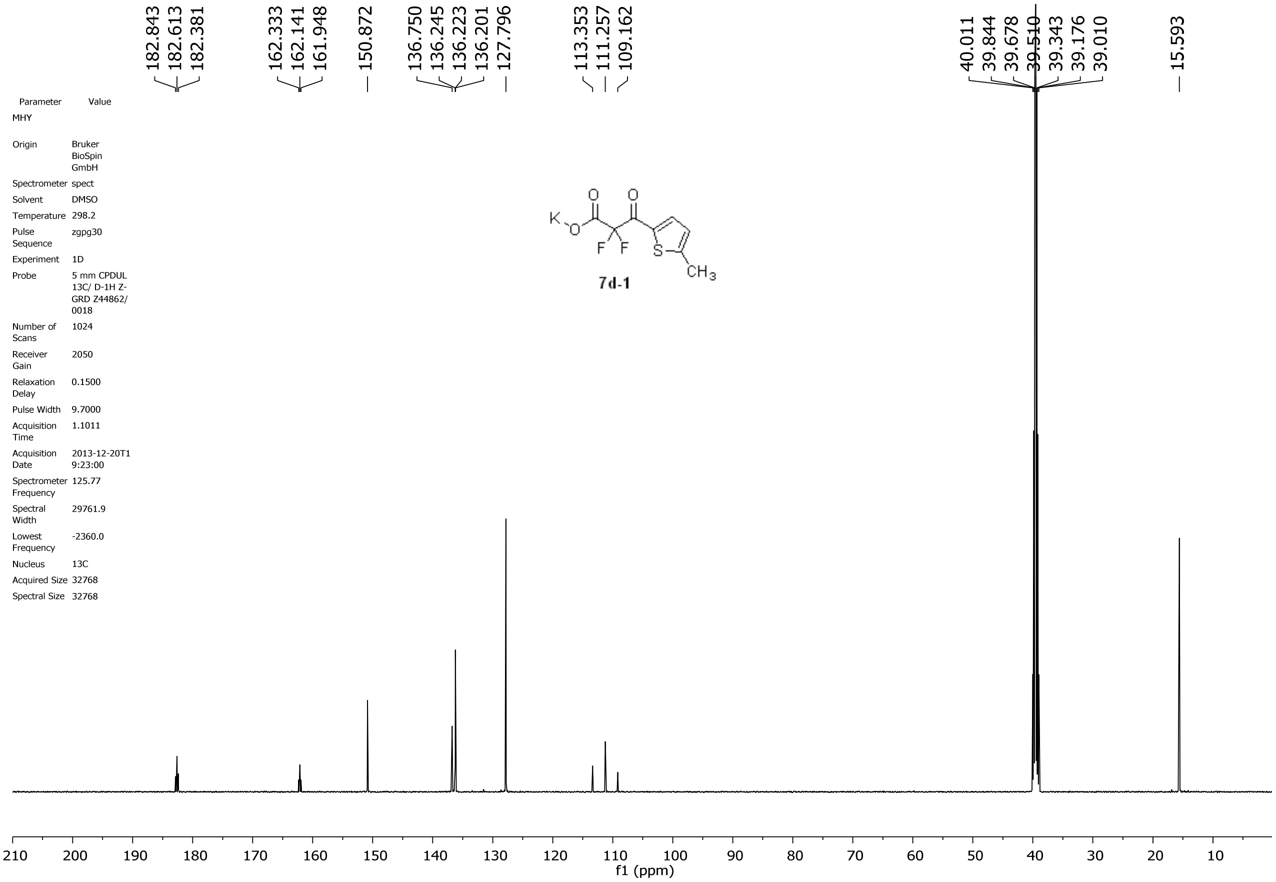
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2013-12-20T00:10:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-12-18T18:32:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

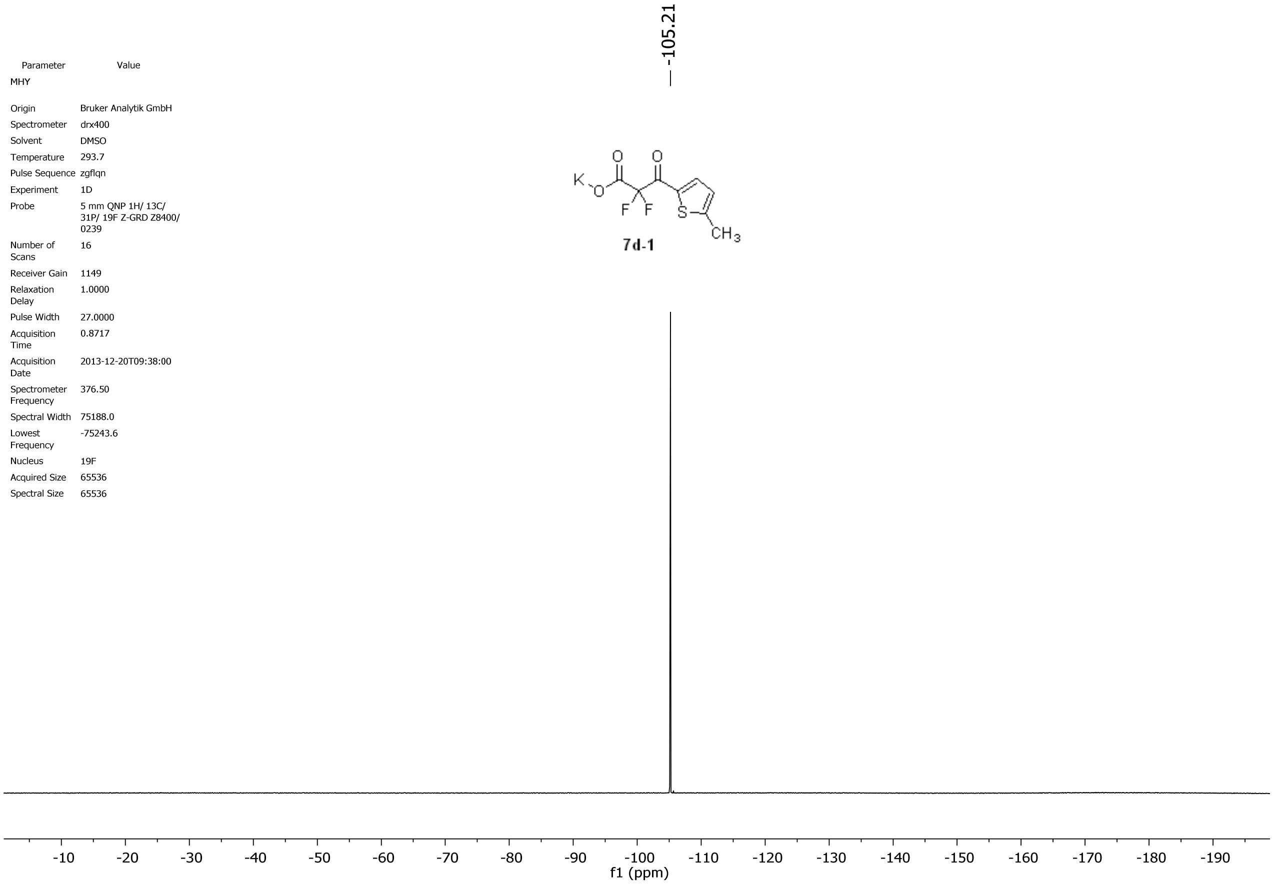


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-12-20T09:34:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



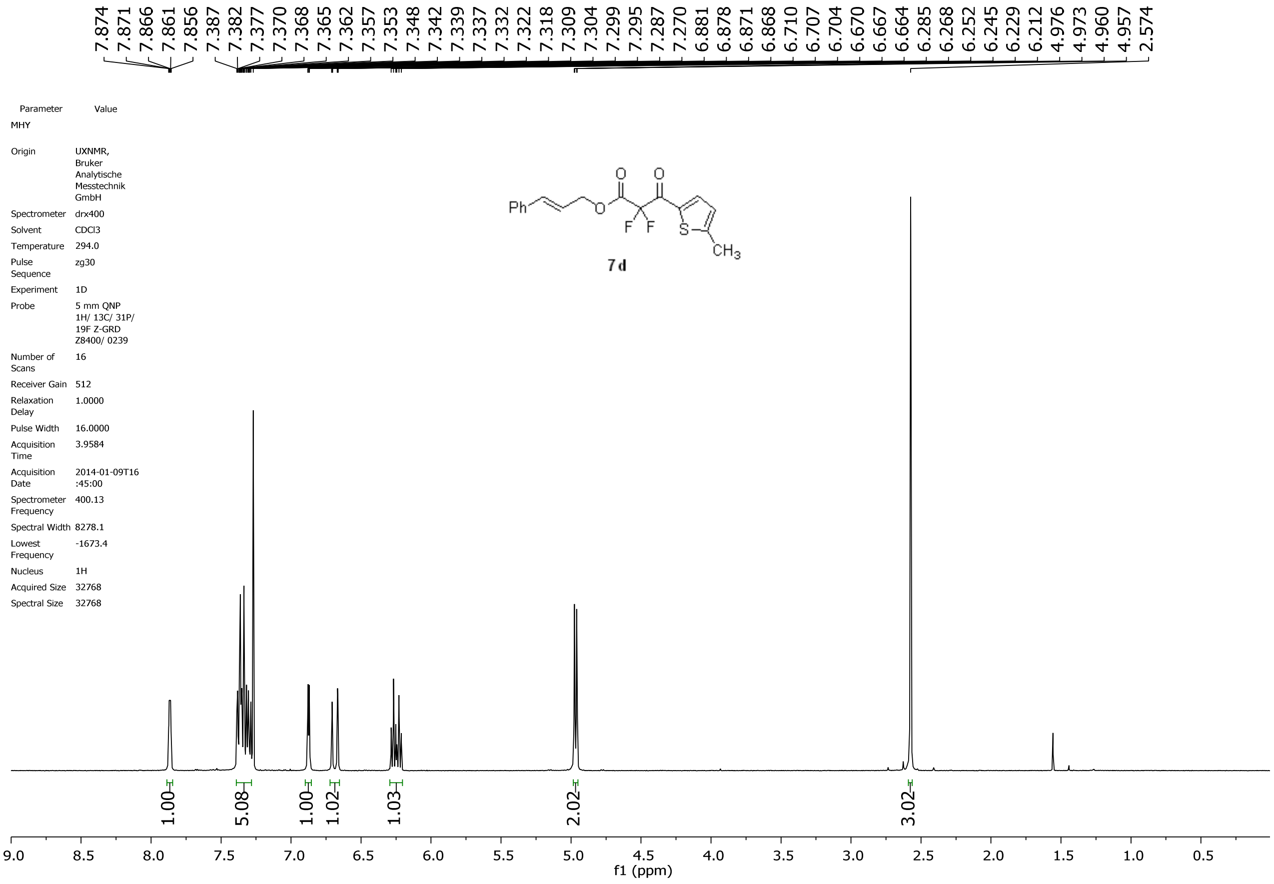
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2013-12-20T19:23:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2360.0
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-12-20T09:38:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

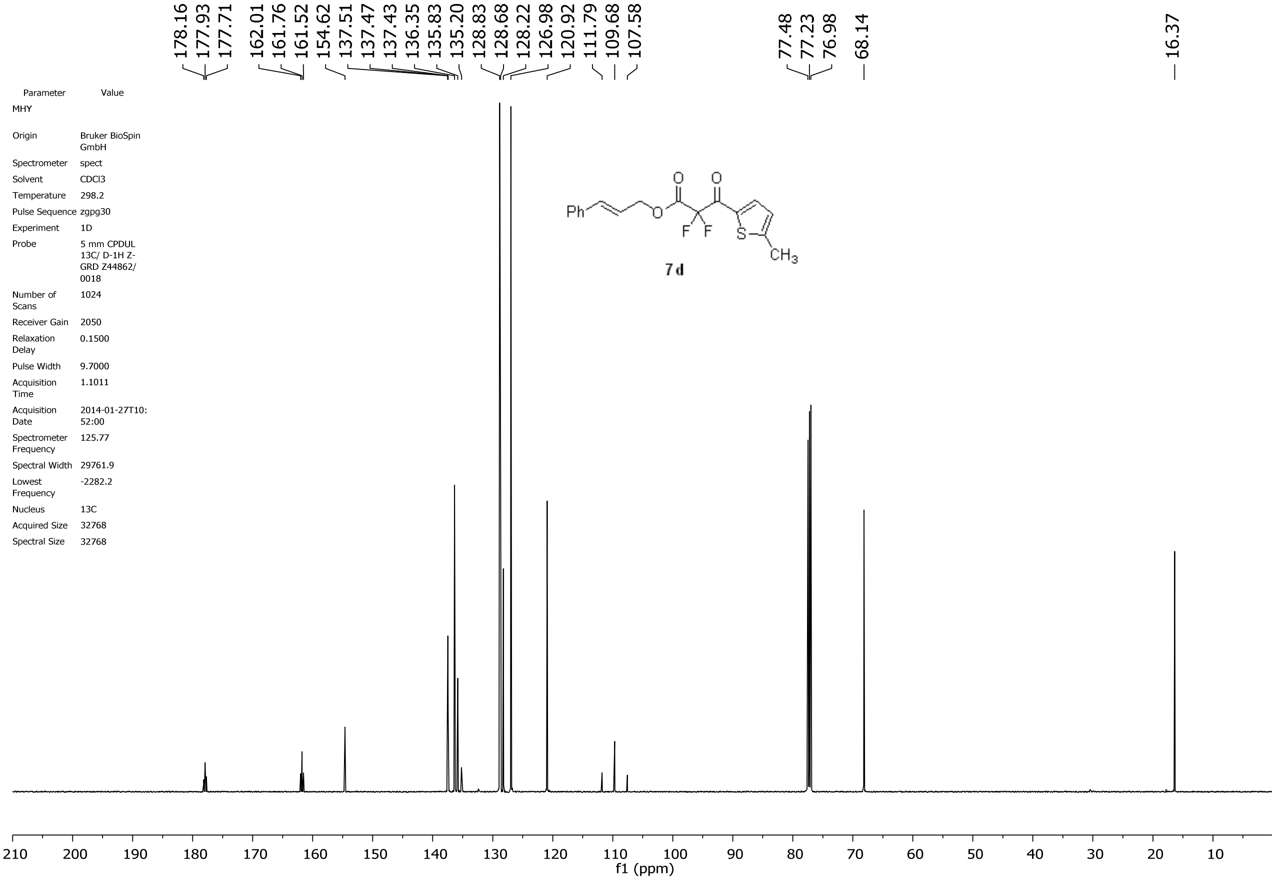


7d-1

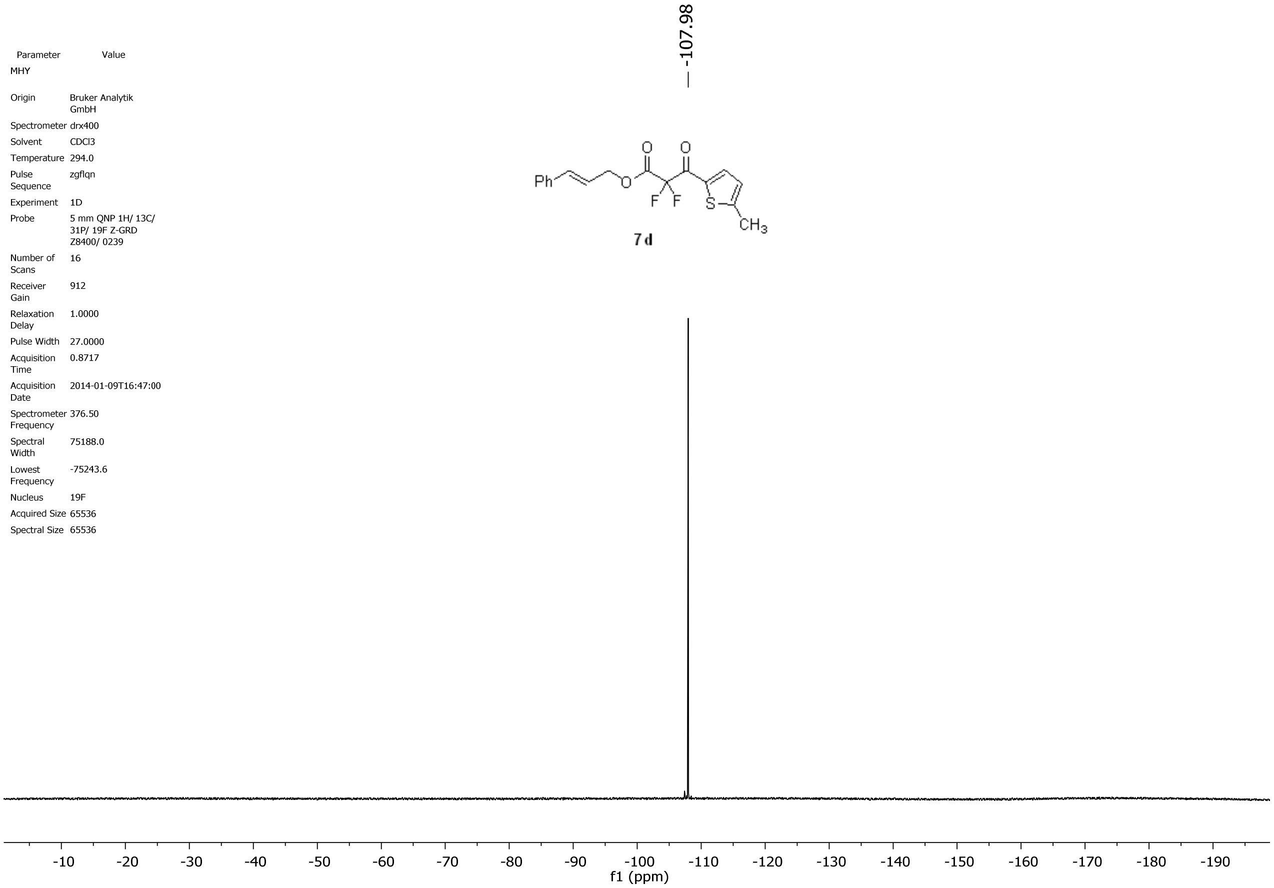
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-09T16 :45:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



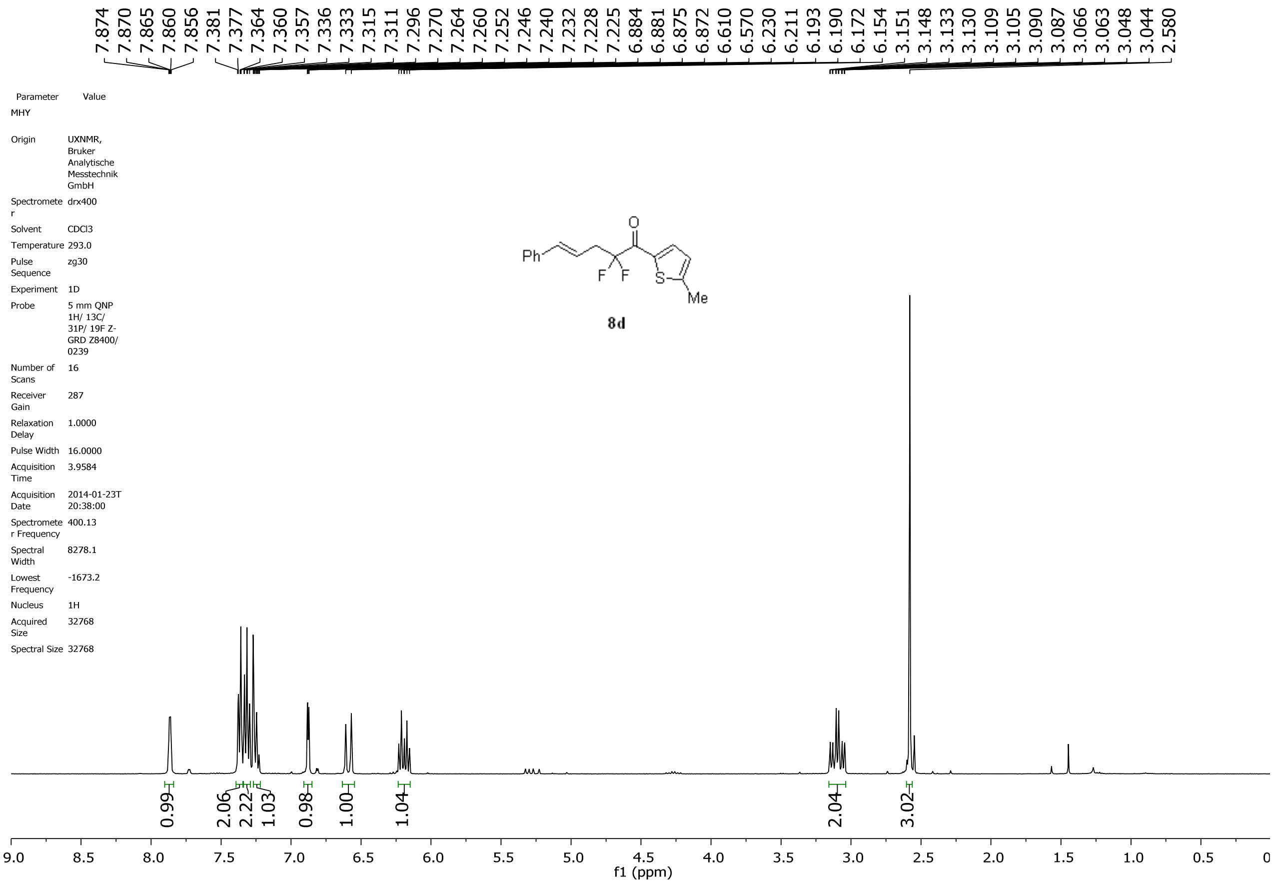
7d



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-01-27T10:52:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2282.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

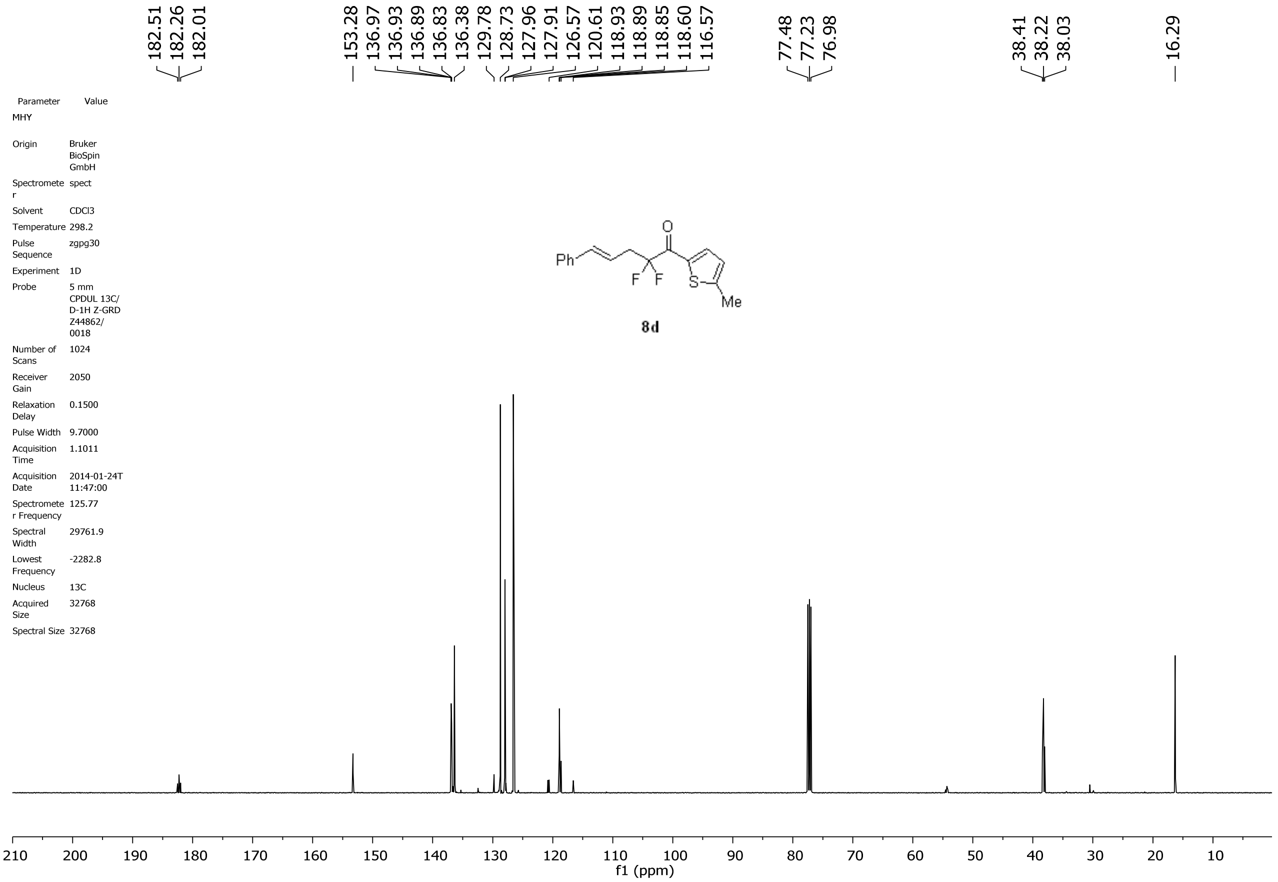


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-01-09T16:47:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



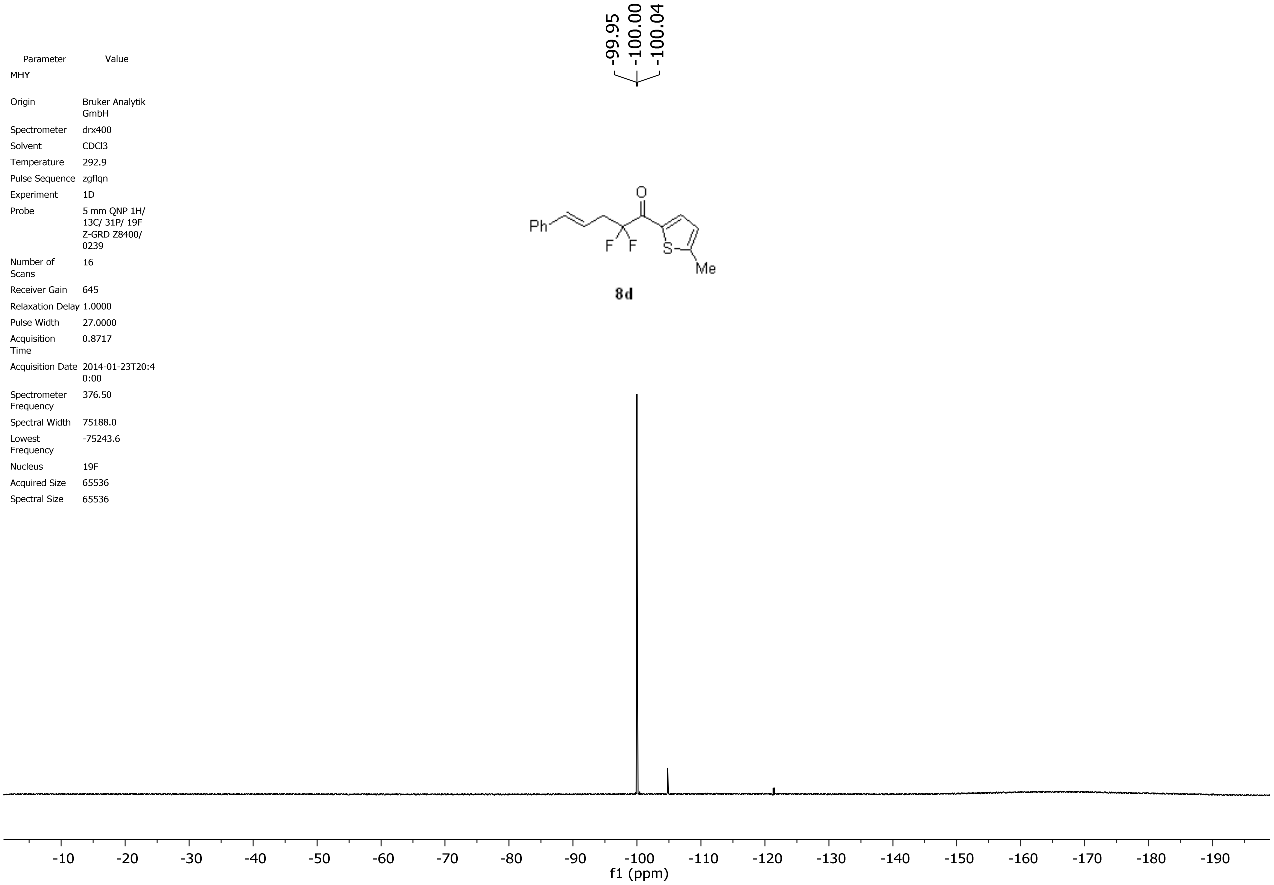
8d

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-23T 20:38:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.2
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



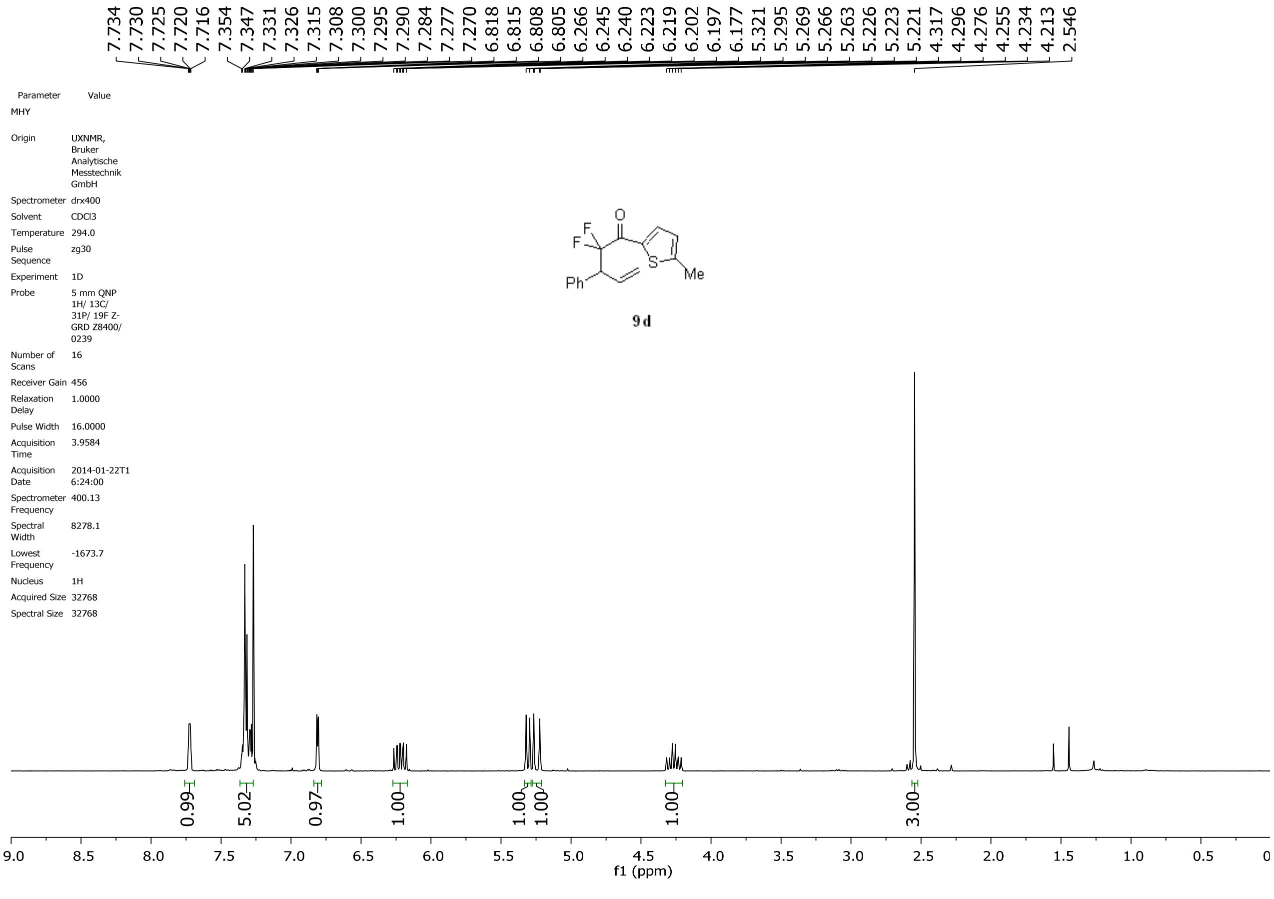
8d

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-01-24T 11:47:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2282.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



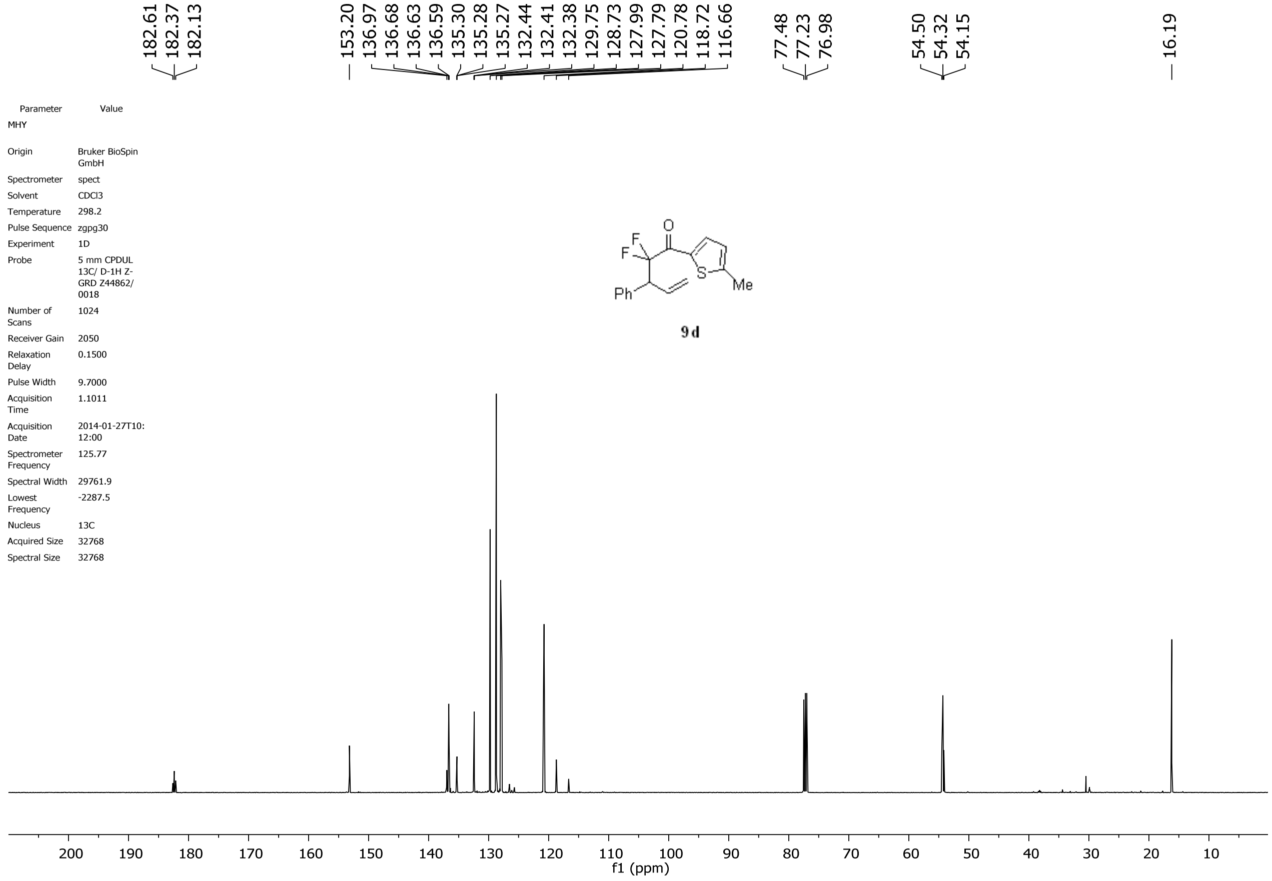
8d

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-01-23T20:40:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



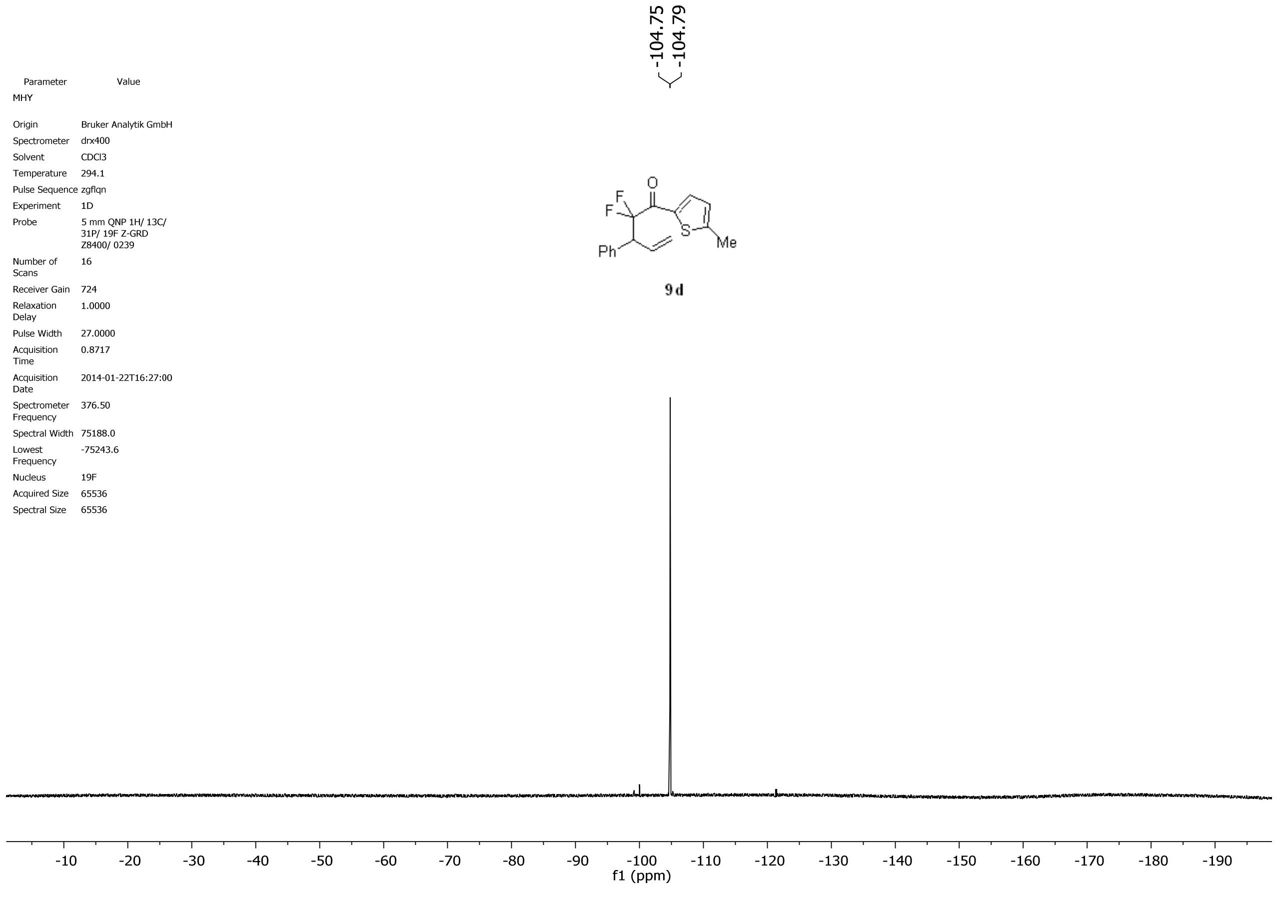
9d

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	456
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2014-01-22T16:24:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



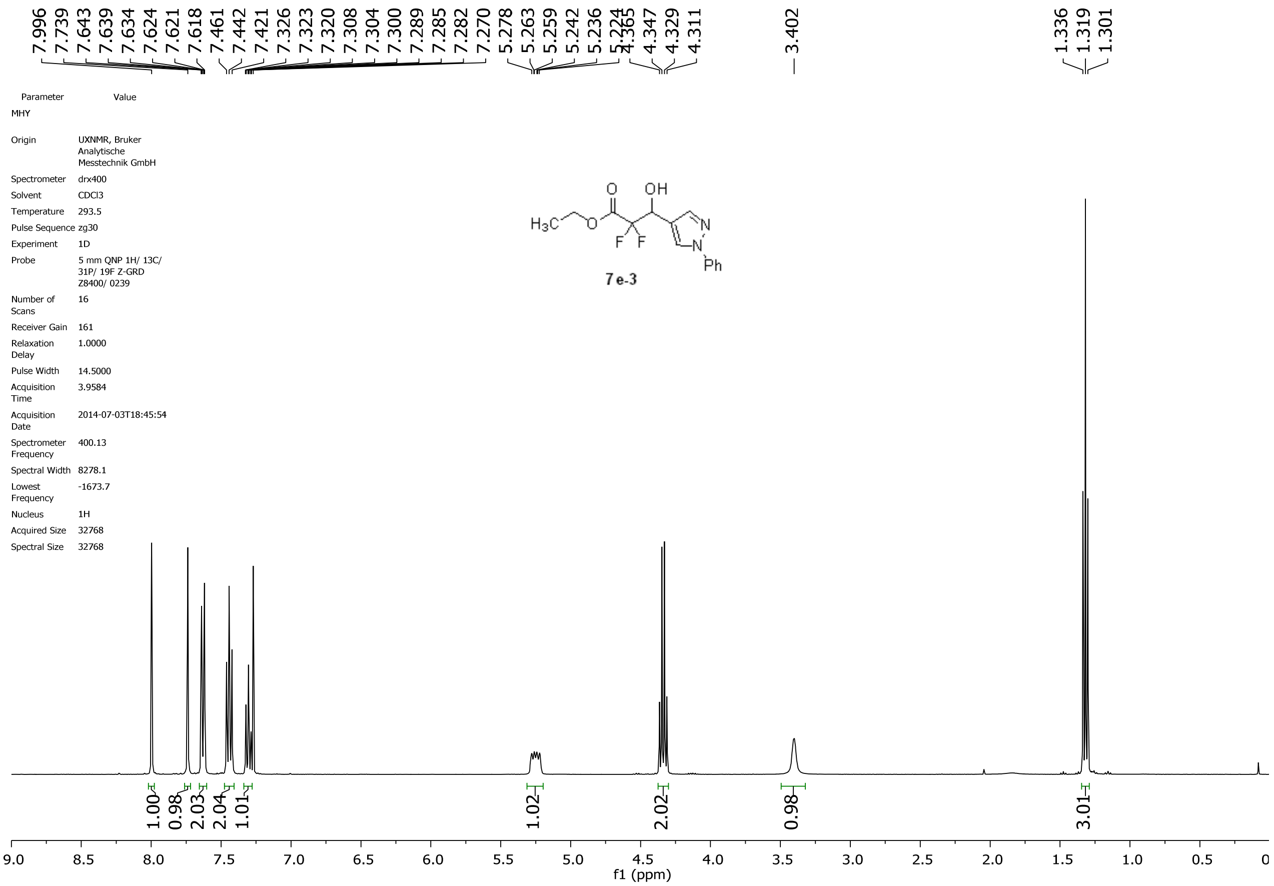
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-01-27T10:12:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2287.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

9d



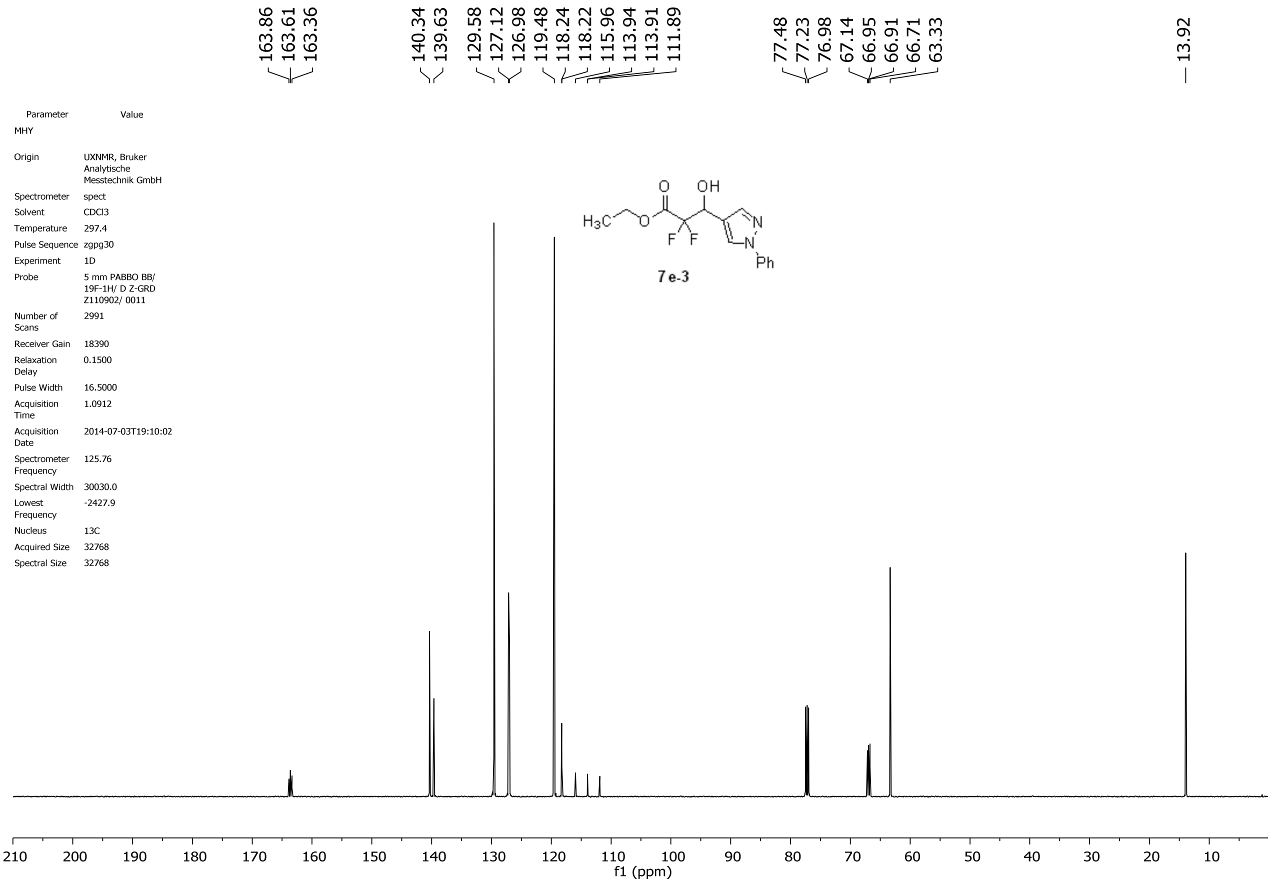
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2014-01-22T16:27:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

9d



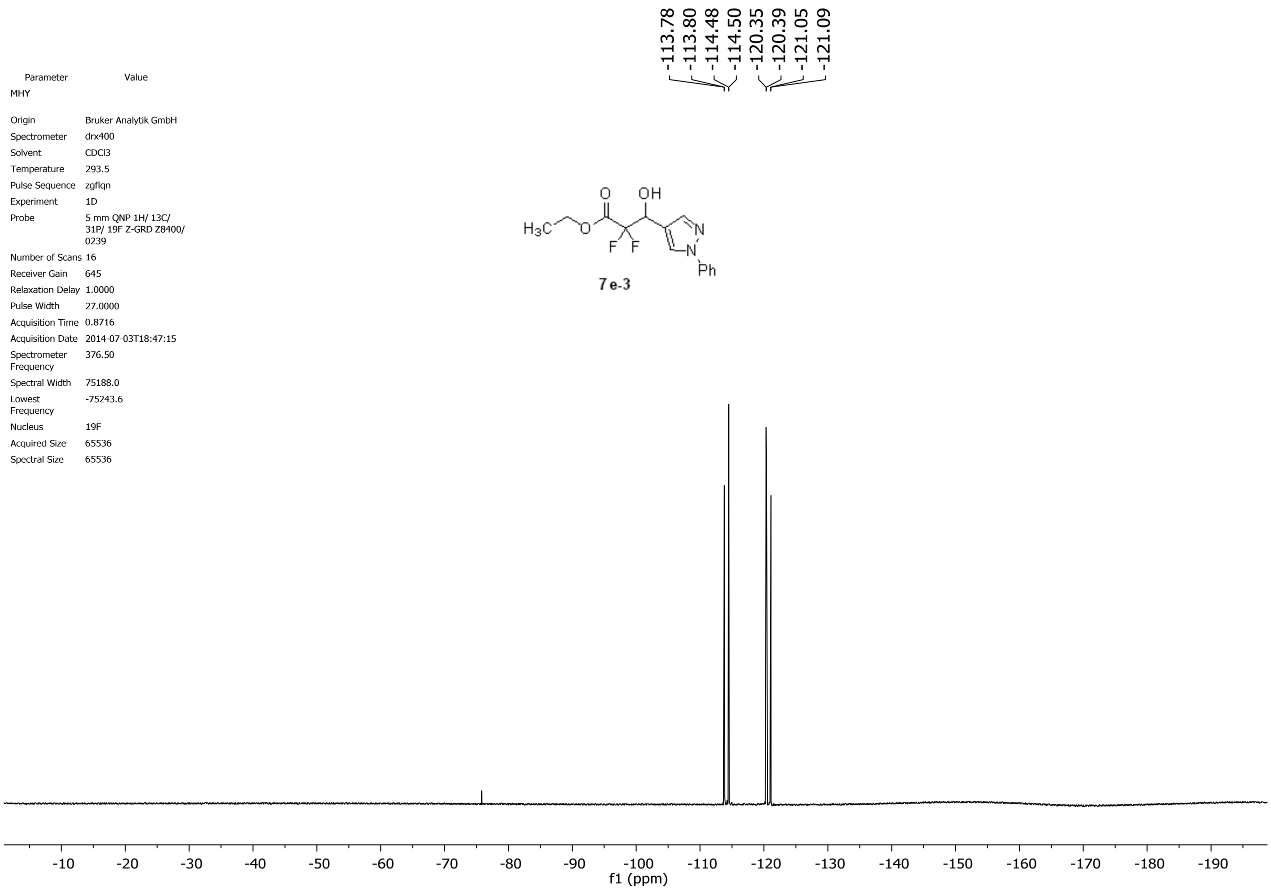
7e-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	161
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-03T18:45:54
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



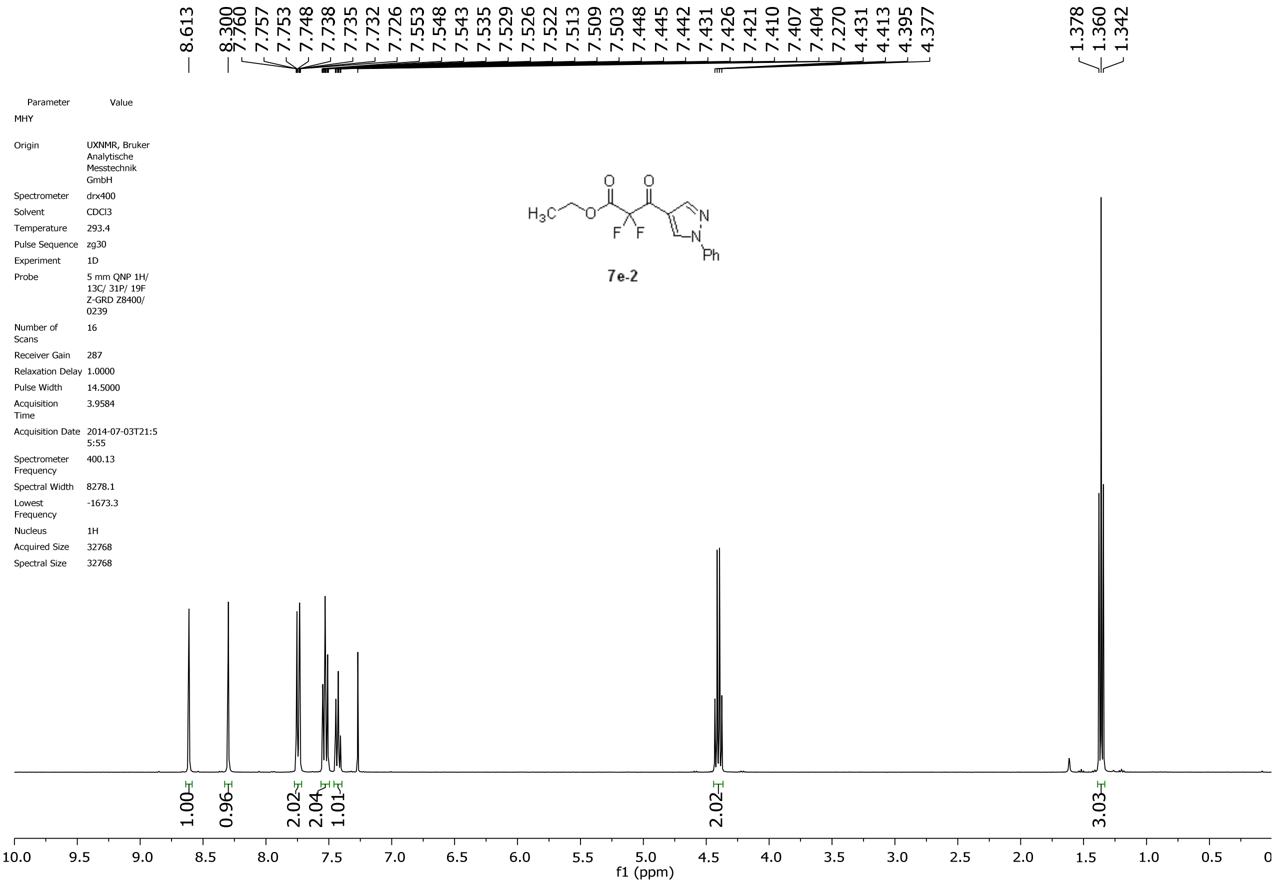
7e-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z110902/ 0011
Number of Scans	2991
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	16.5000
Acquisition Time	1.0912
Acquisition Date	2014-07-03T19:10:02
Spectrometer Frequency	125.76
Spectral Width	30030.0
Lowest Frequency	-2427.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



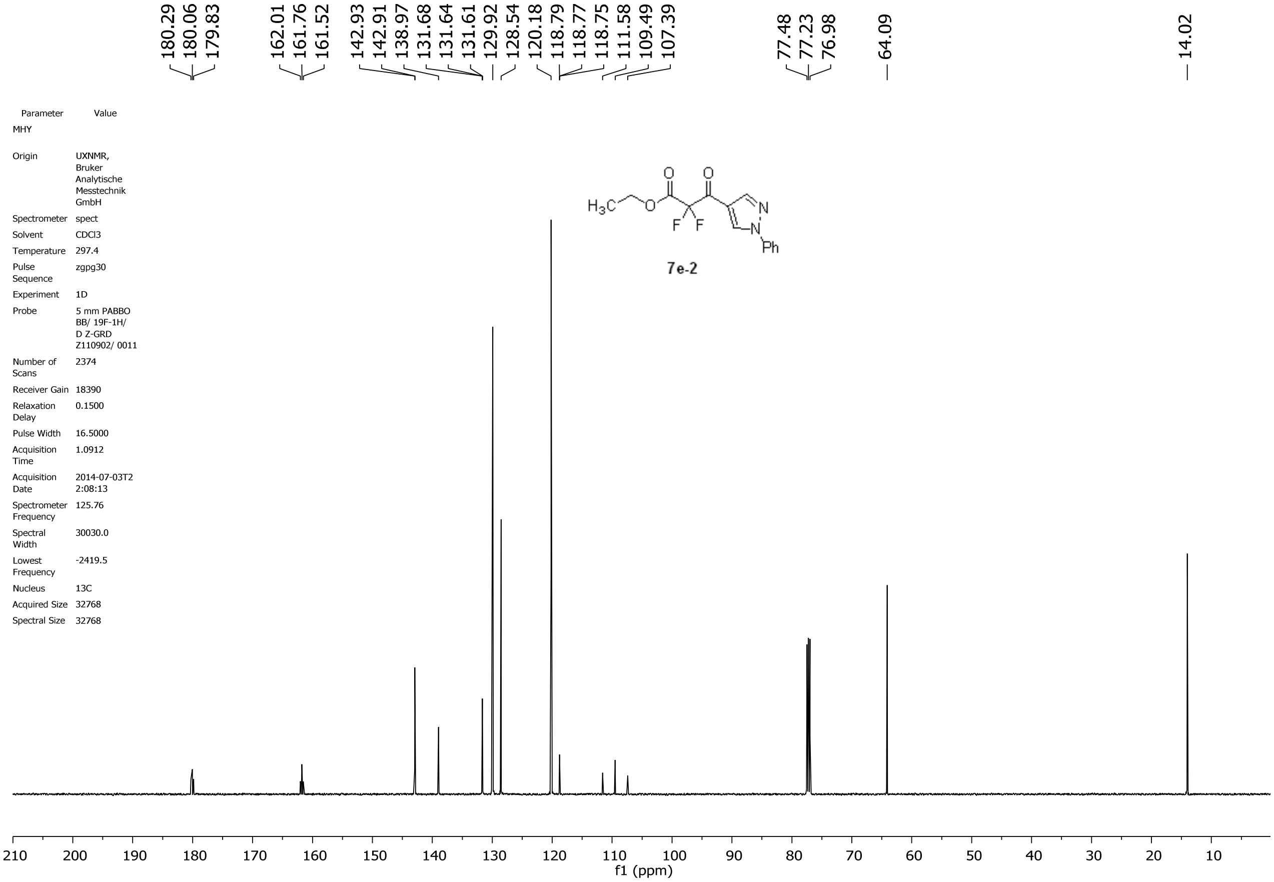
7e-3

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-03T18:47:15
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

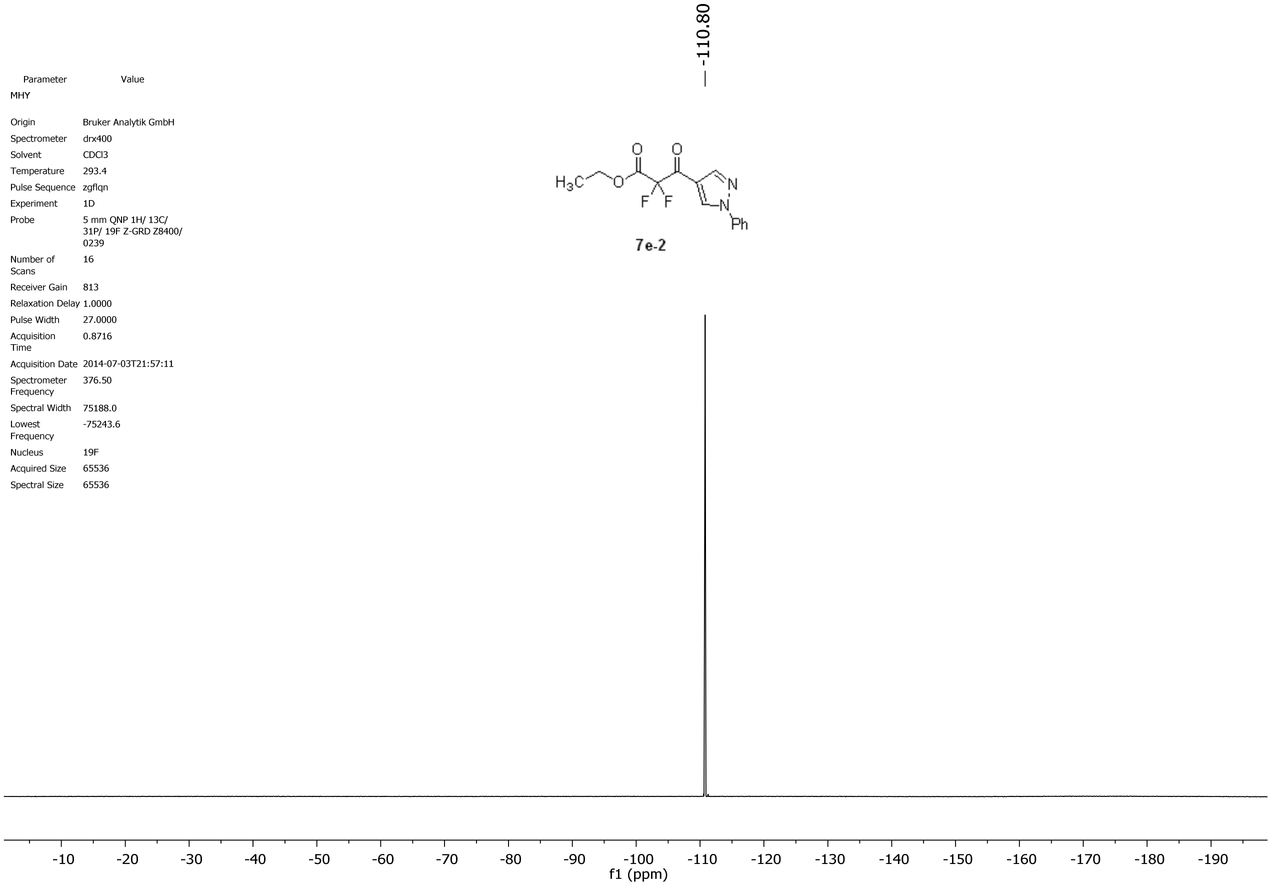


7e-2

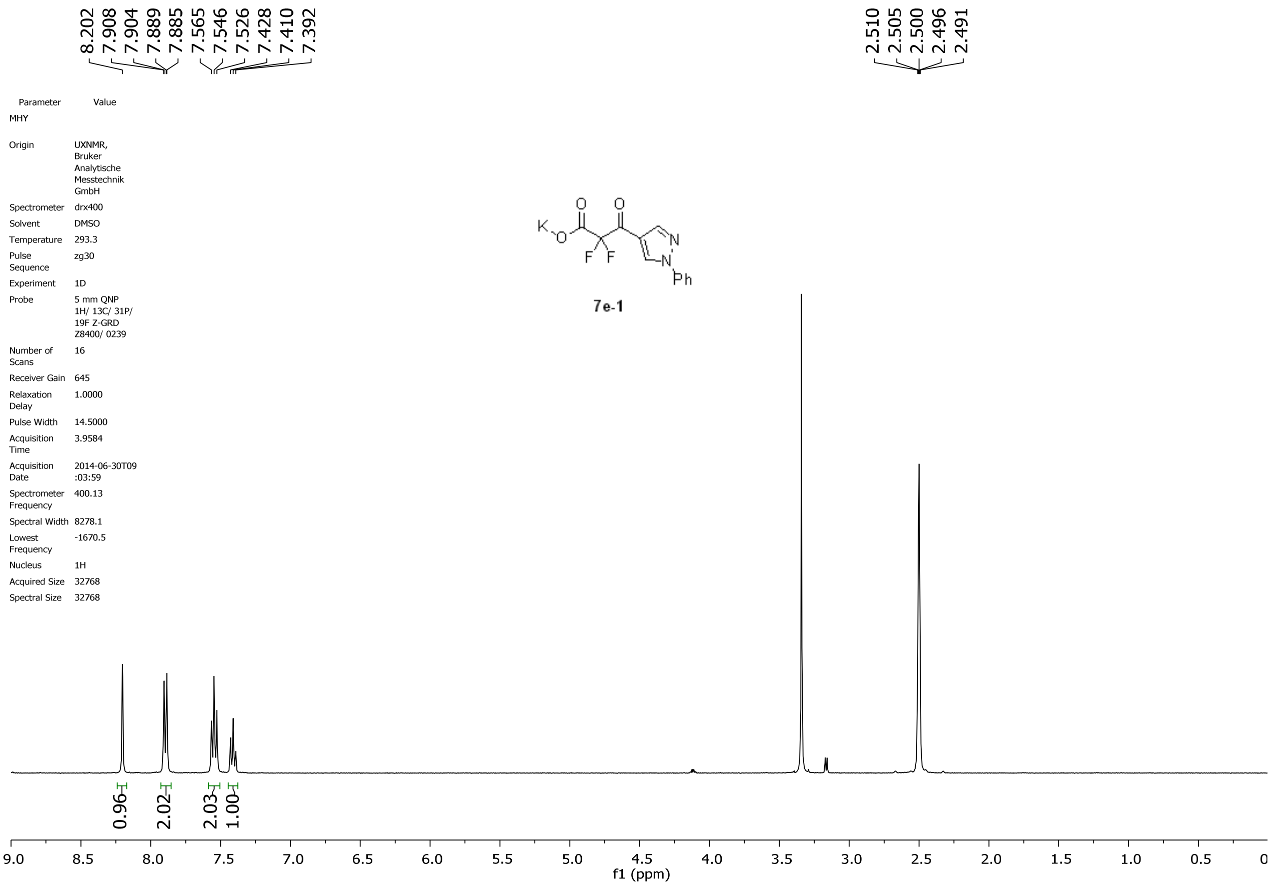
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-03T21:55:55
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z110902/ 0011
Number of Scans	2374
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	16.5000
Acquisition Time	1.0912
Acquisition Date	2014-07-03T2 2:08:13
Spectrometer Frequency	125.76
Spectral Width	30030.0
Lowest Frequency	-2419.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

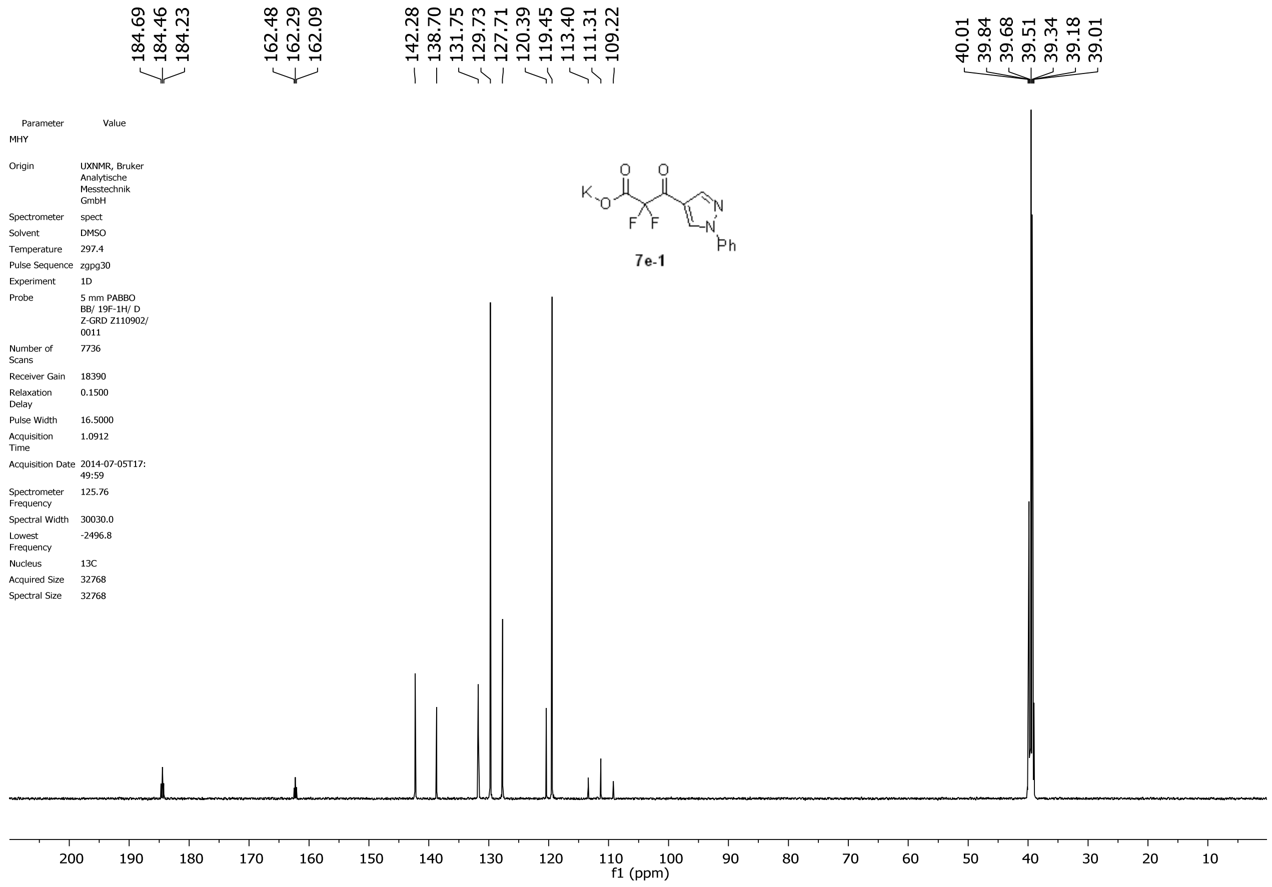


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-03T21:57:11
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



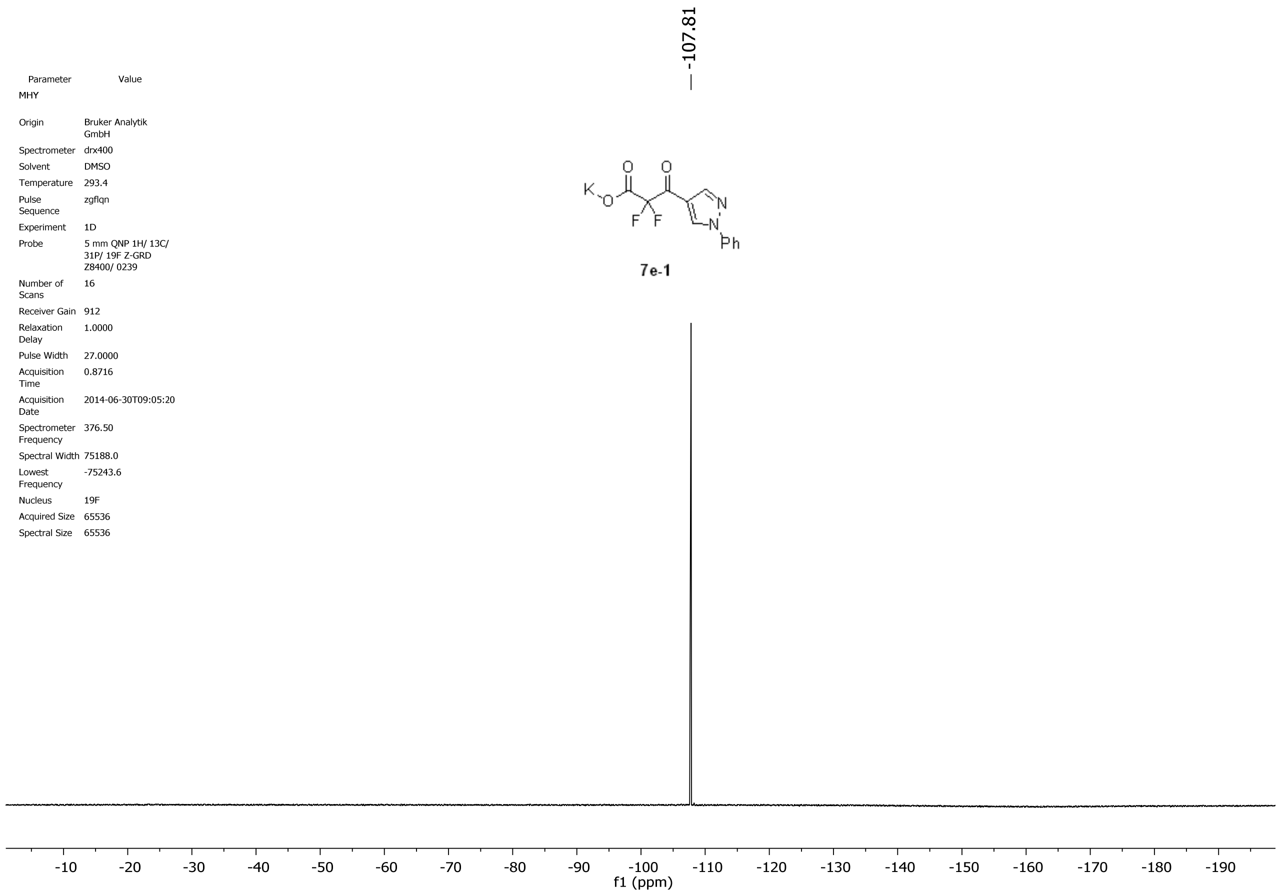
7e-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-30T09:03:59
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.5
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



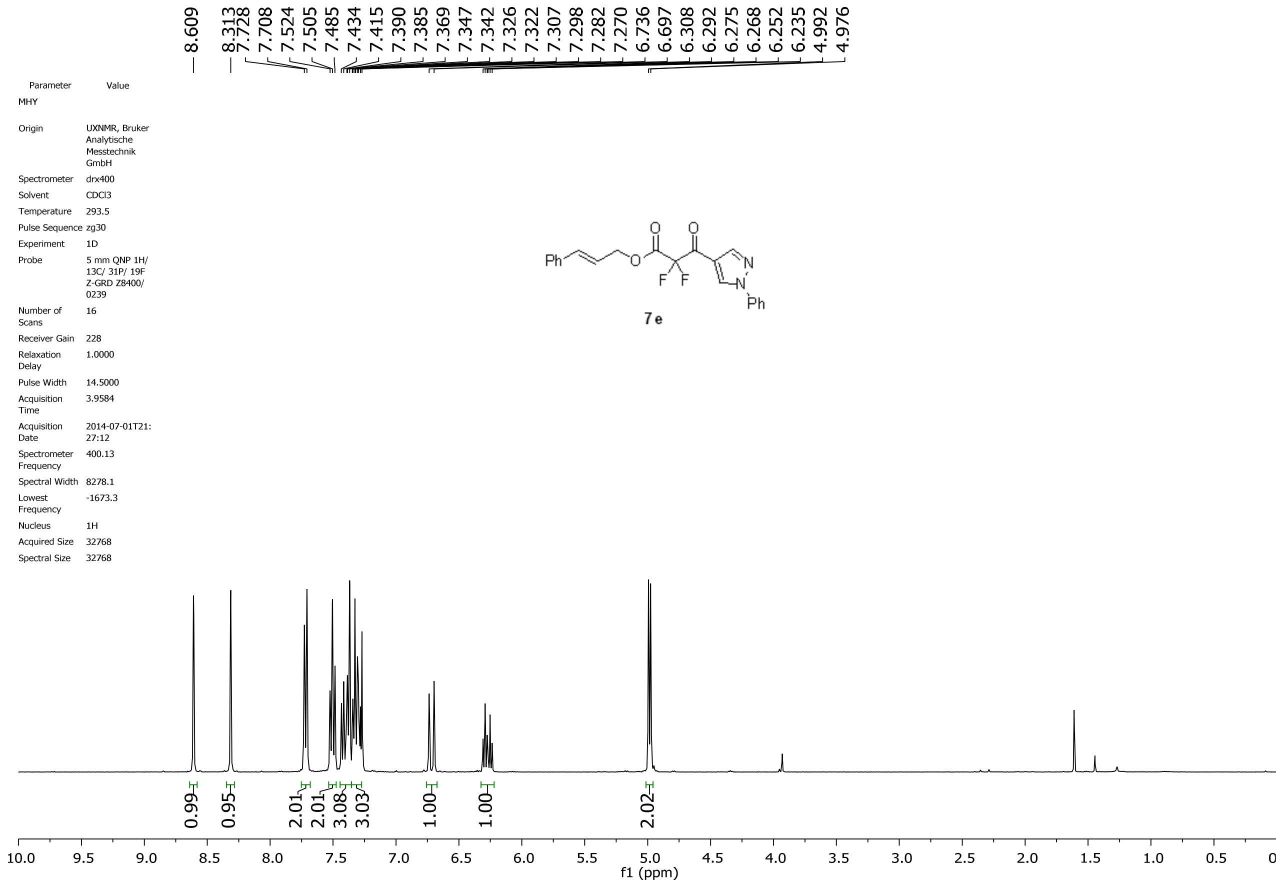
7e-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	297.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z110902/ 0011
Number of Scans	7736
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	16.5000
Acquisition Time	1.0912
Acquisition Date	2014-07-05T17:49:59
Spectrometer Frequency	125.76
Spectral Width	30030.0
Lowest Frequency	-2496.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



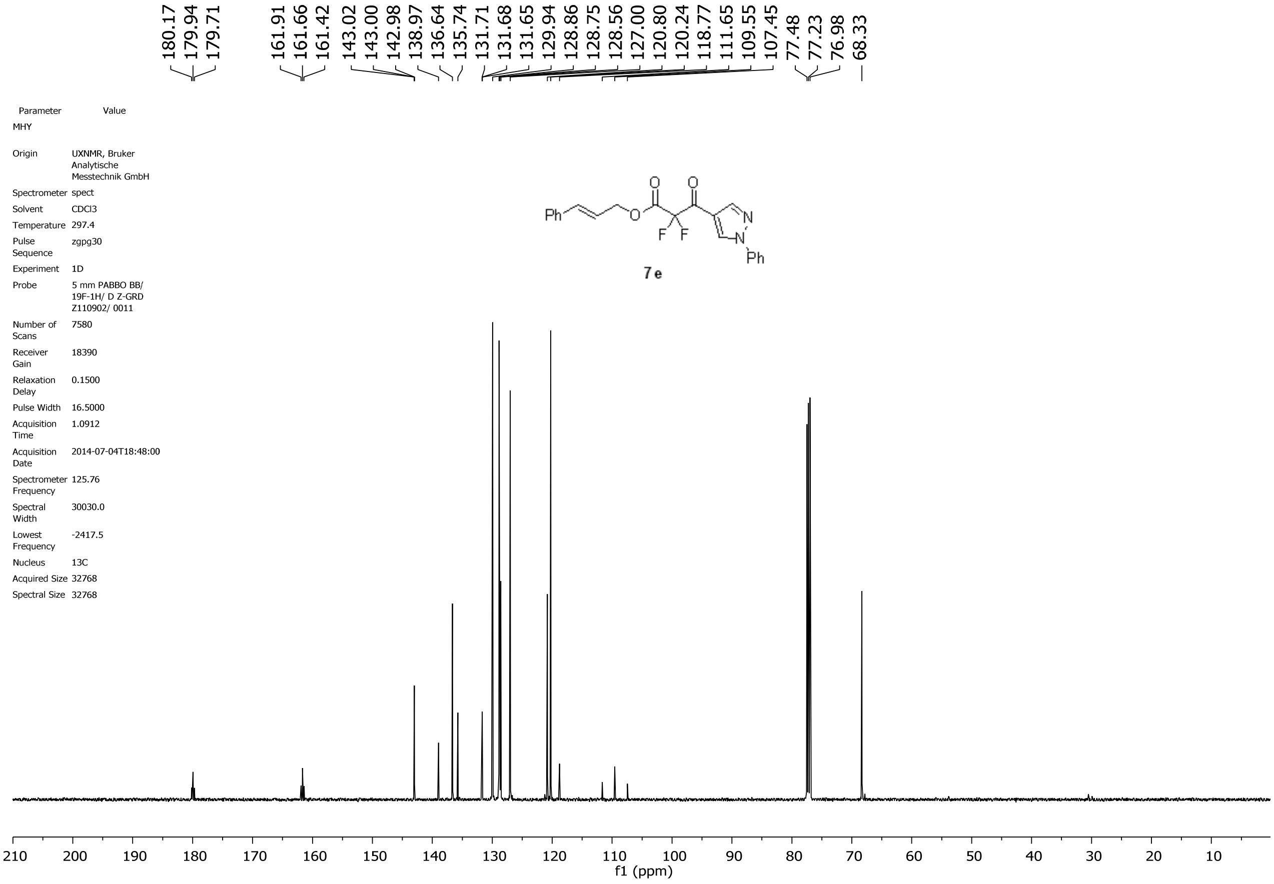
7e-1

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-30T09:05:20
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



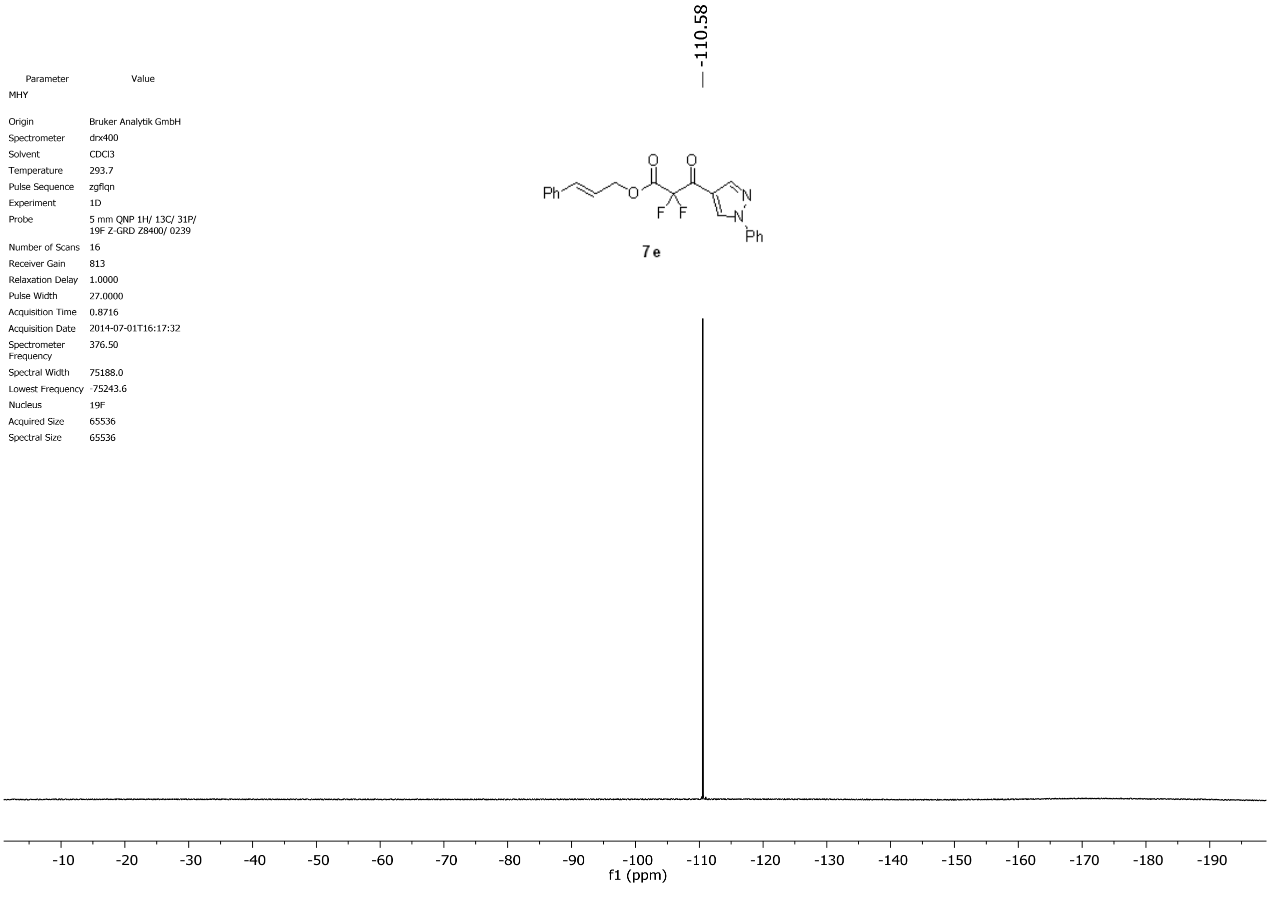
7e

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-01T21:27:12
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



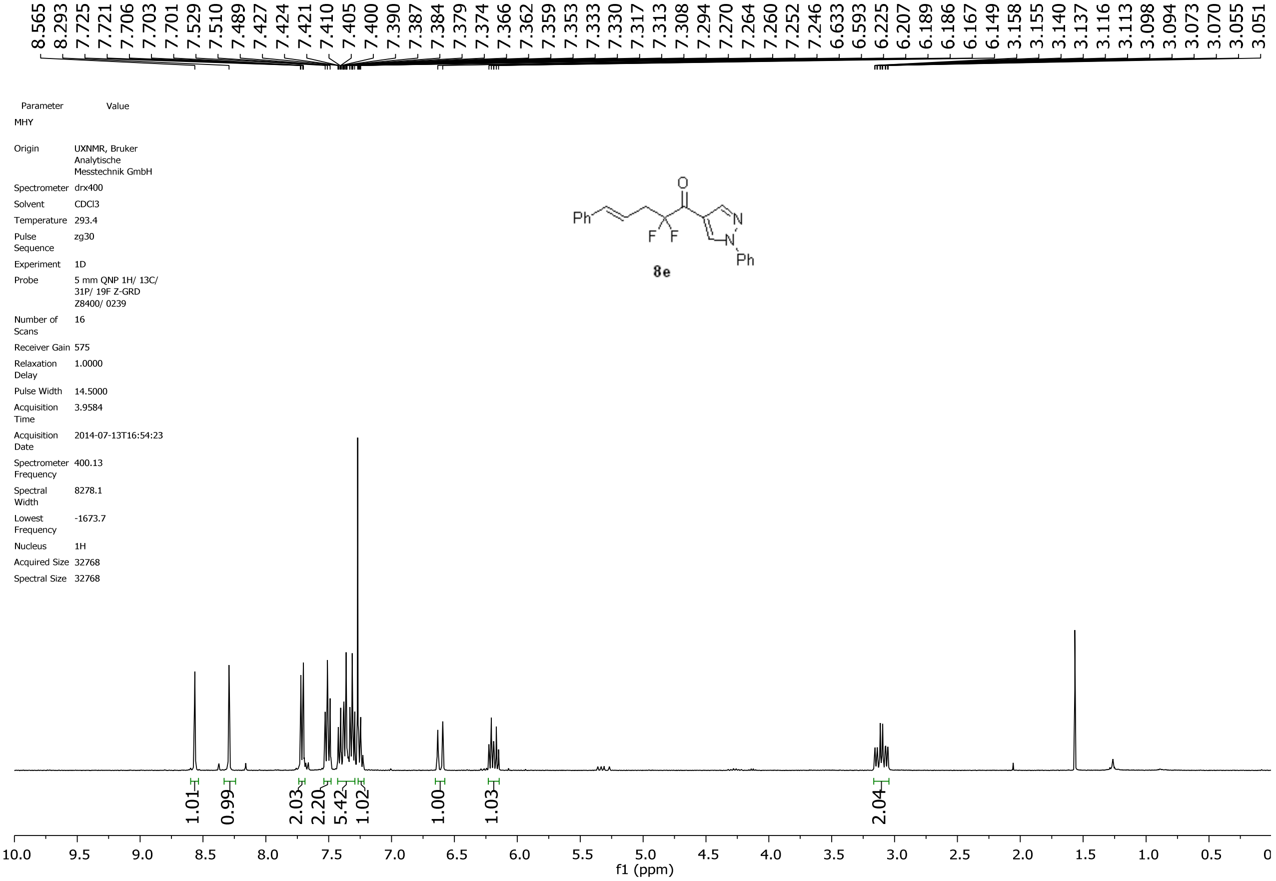
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	297.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z110902/ 0011
Number of Scans	7580
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	16.5000
Acquisition Time	1.0912
Acquisition Date	2014-07-04T18:48:00
Spectrometer Frequency	125.76
Spectral Width	30030.0
Lowest Frequency	-2417.5
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

7e



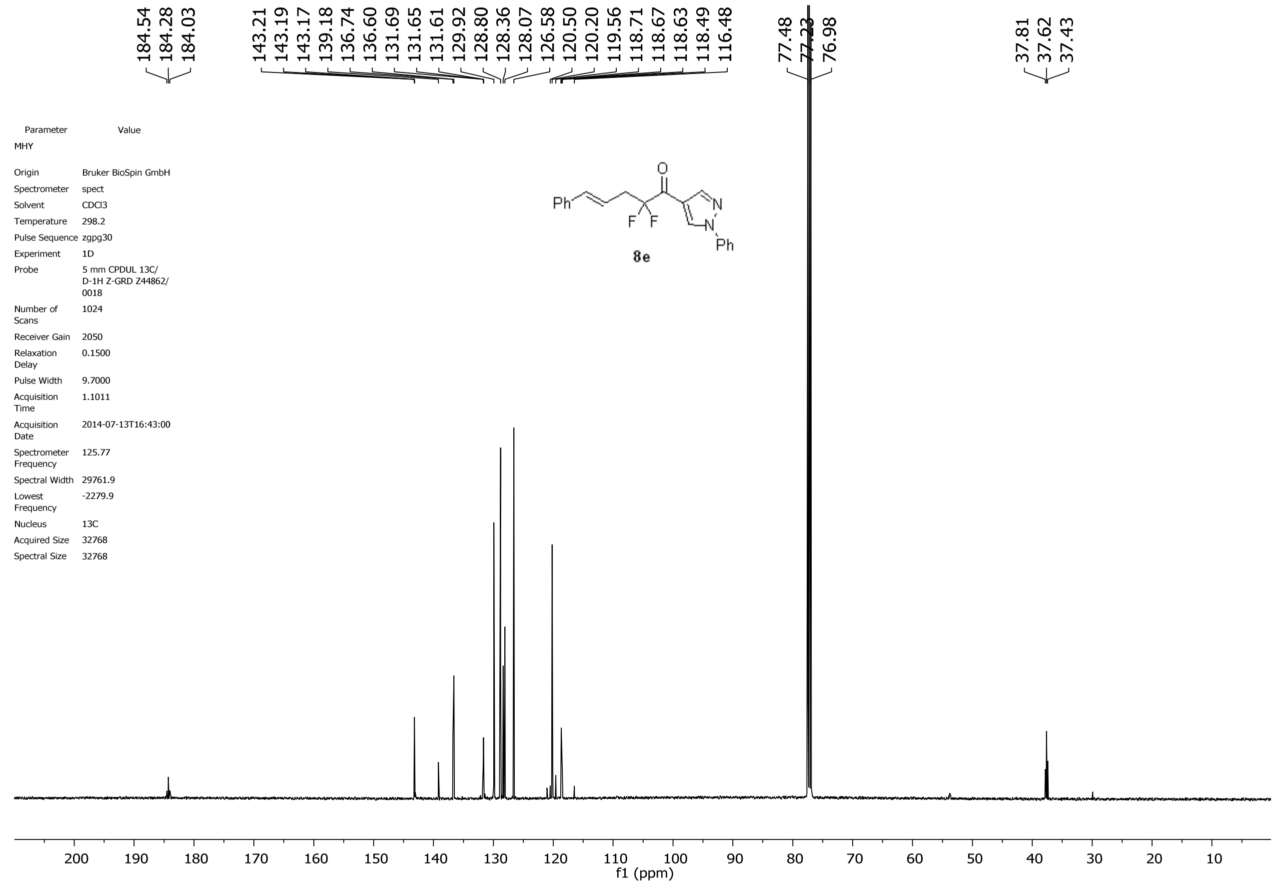
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-01T16:17:32
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

7e



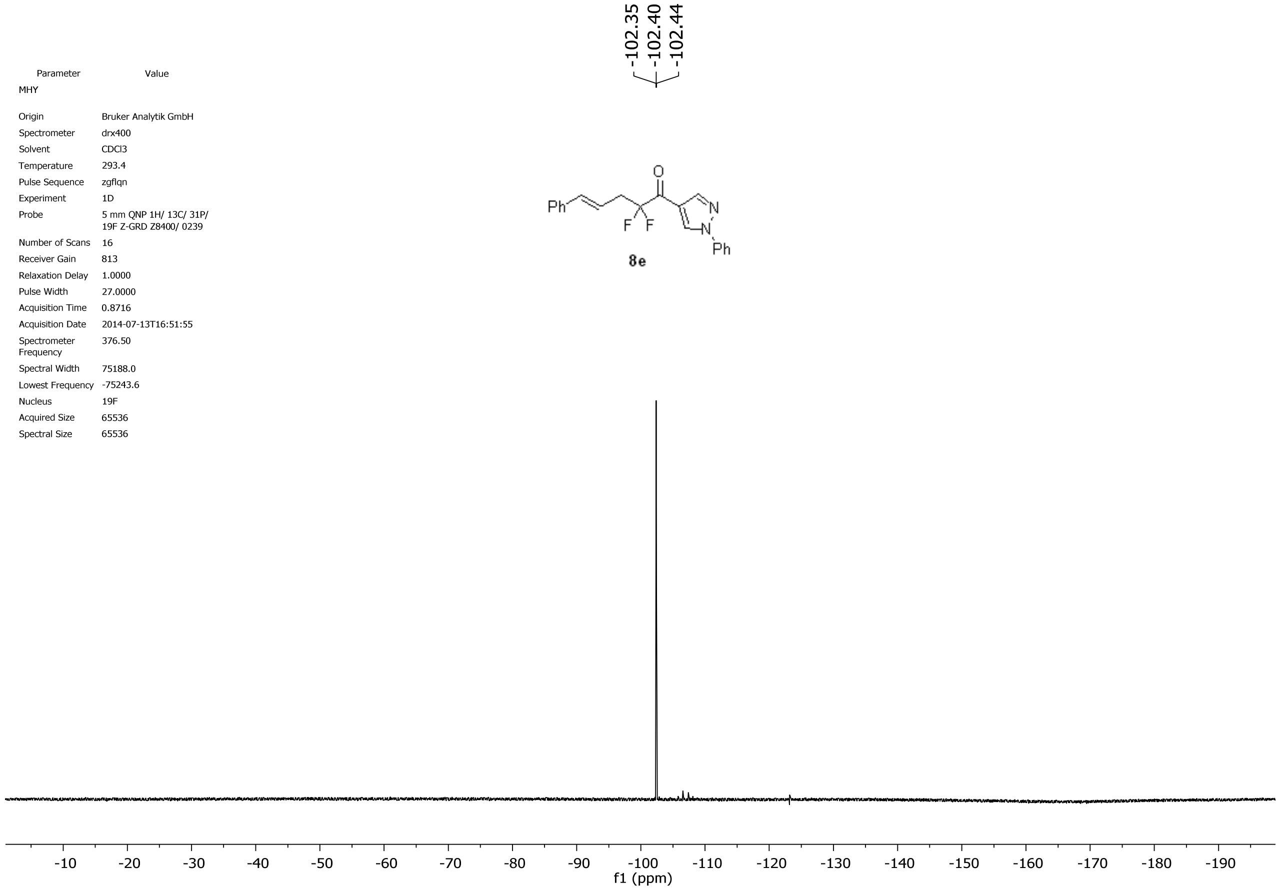
8e

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	575
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-13T16:54:23
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



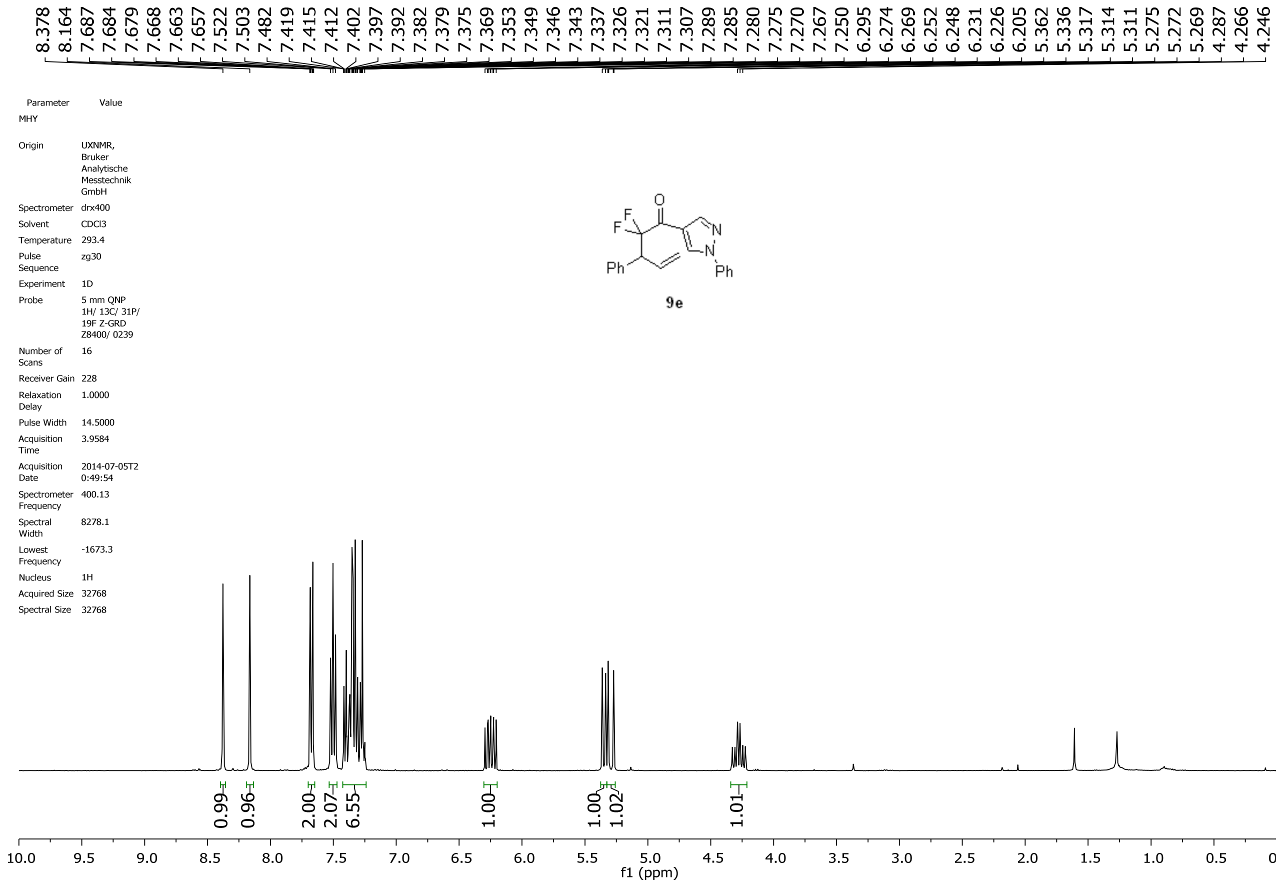
8e

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-13T16:43:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.9
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



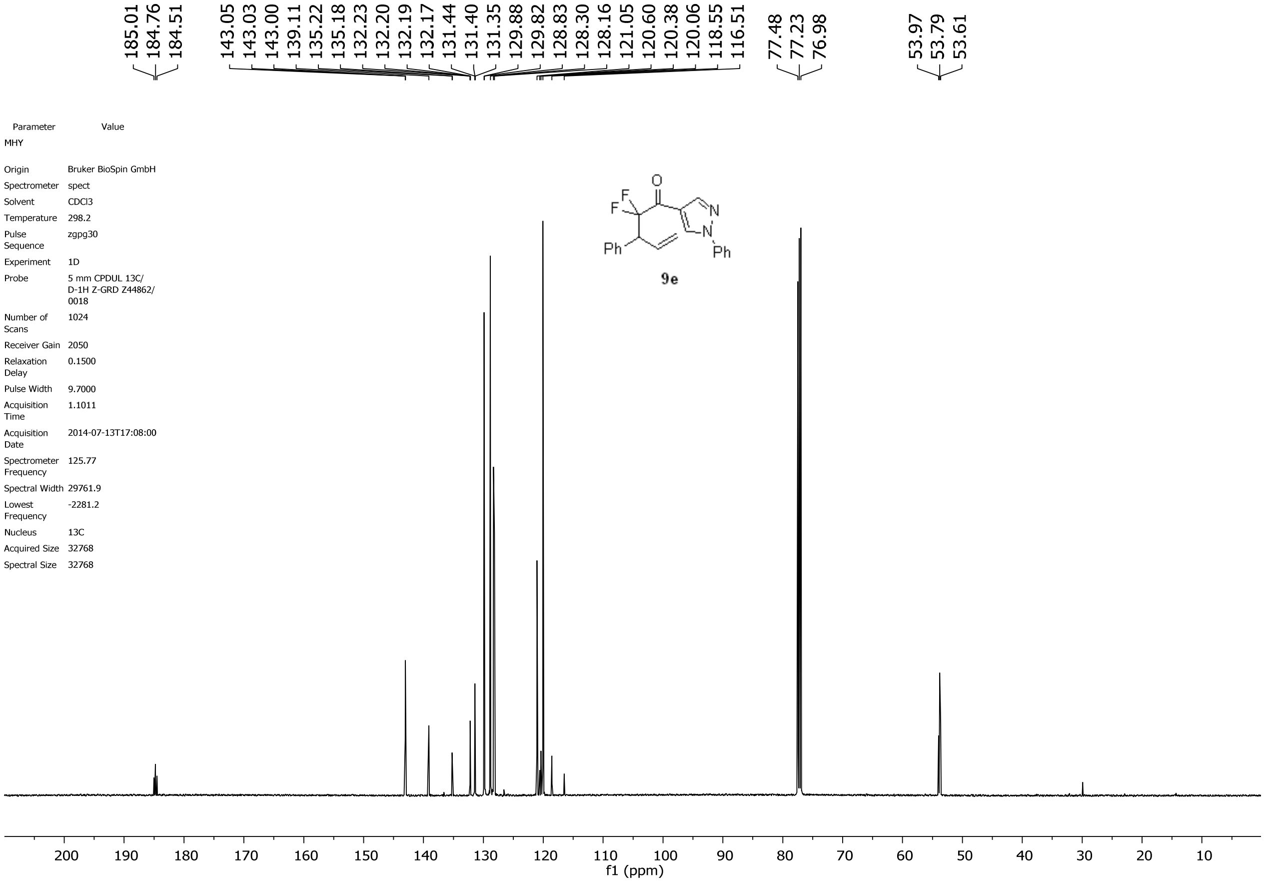
8e

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-13T16:51:55
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



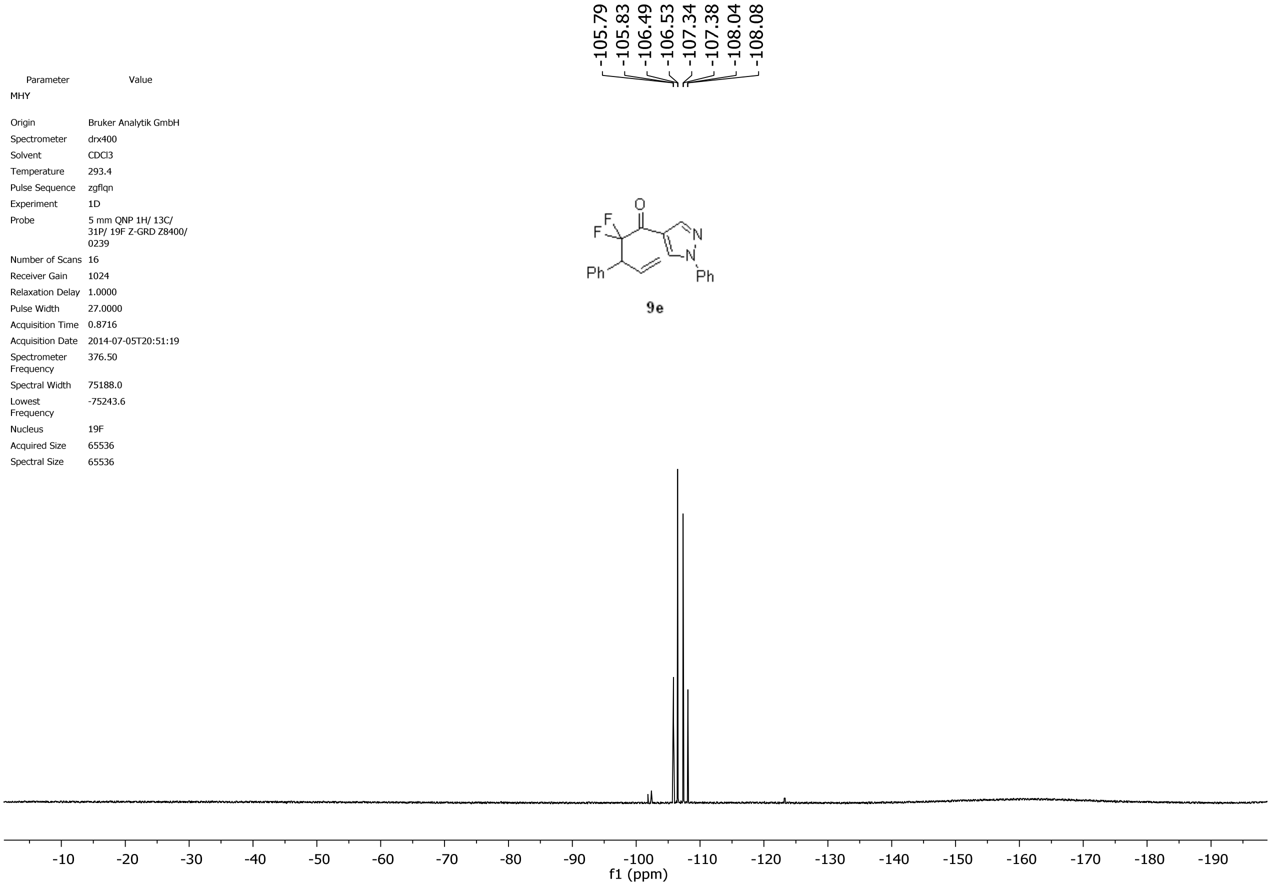
9e

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-07-05T20:49:54
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



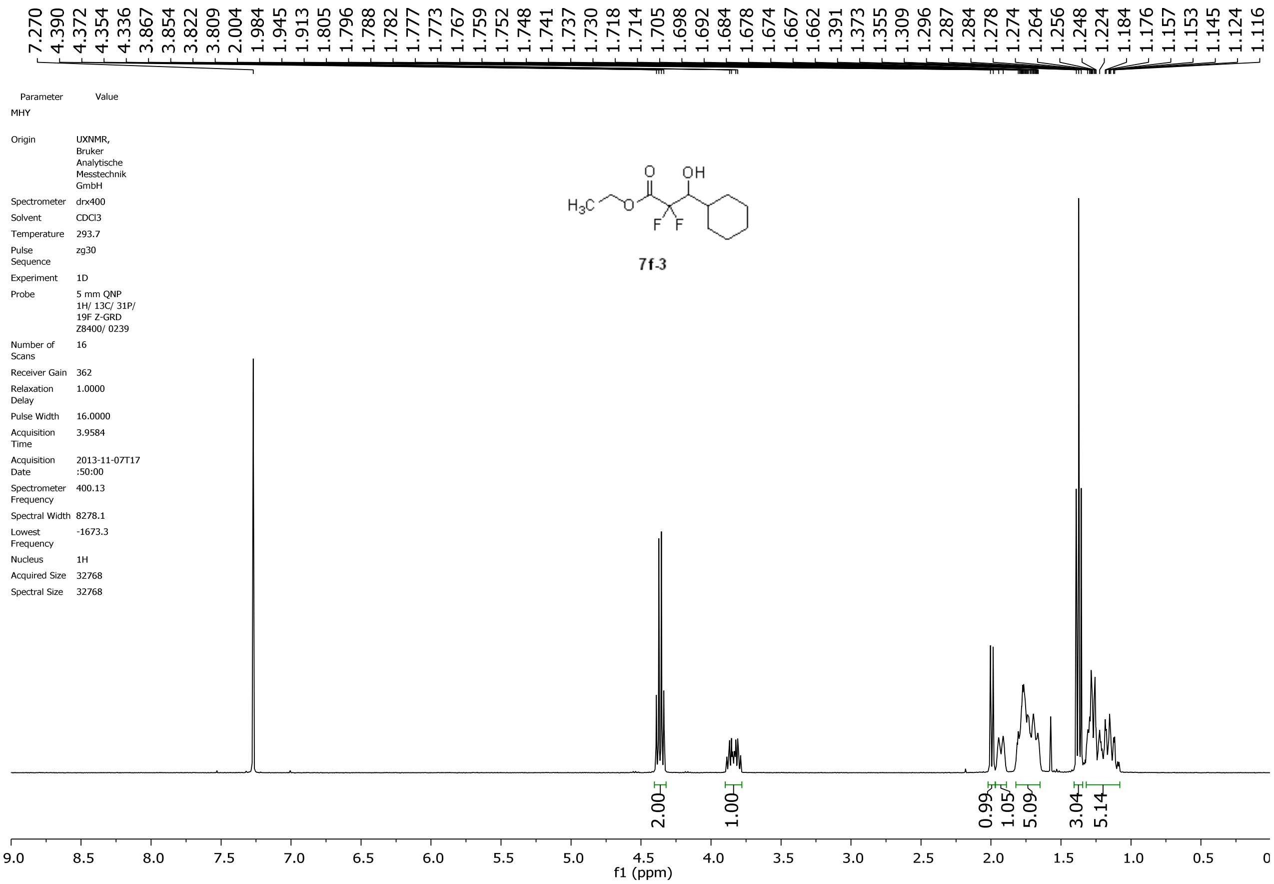
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-07-13T17:08:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2281.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

9e



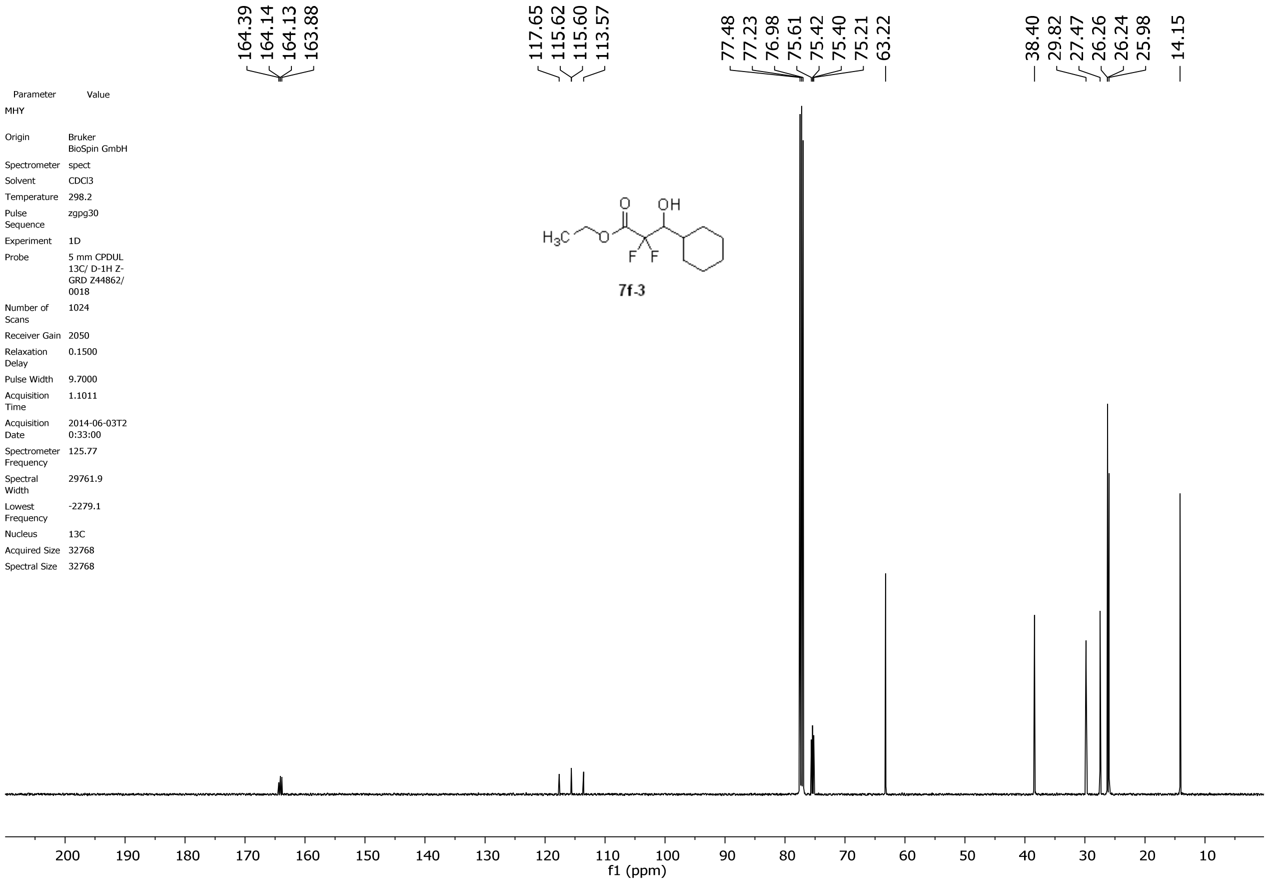
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1024
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-07-05T20:51:19
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

9e



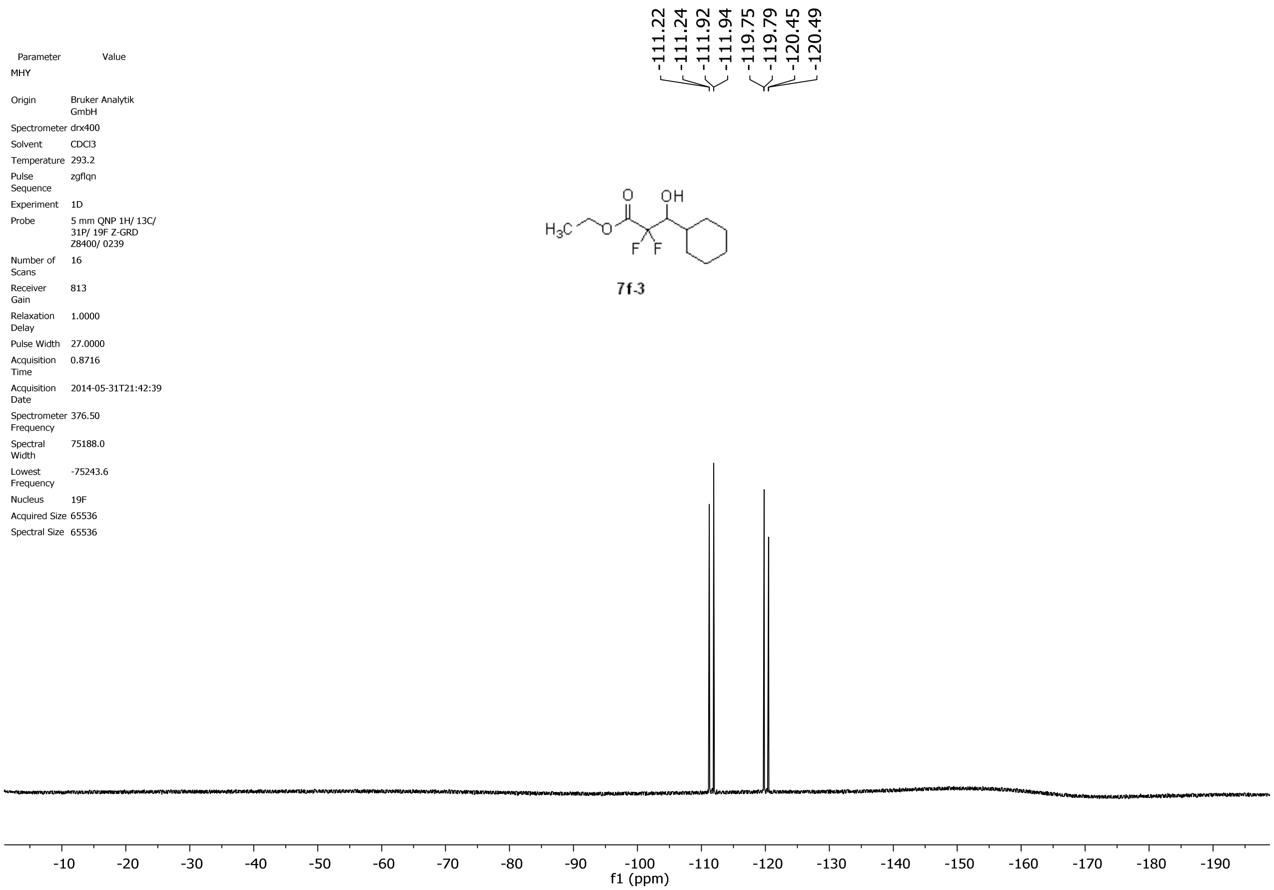
7f-3

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-07T17:50:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



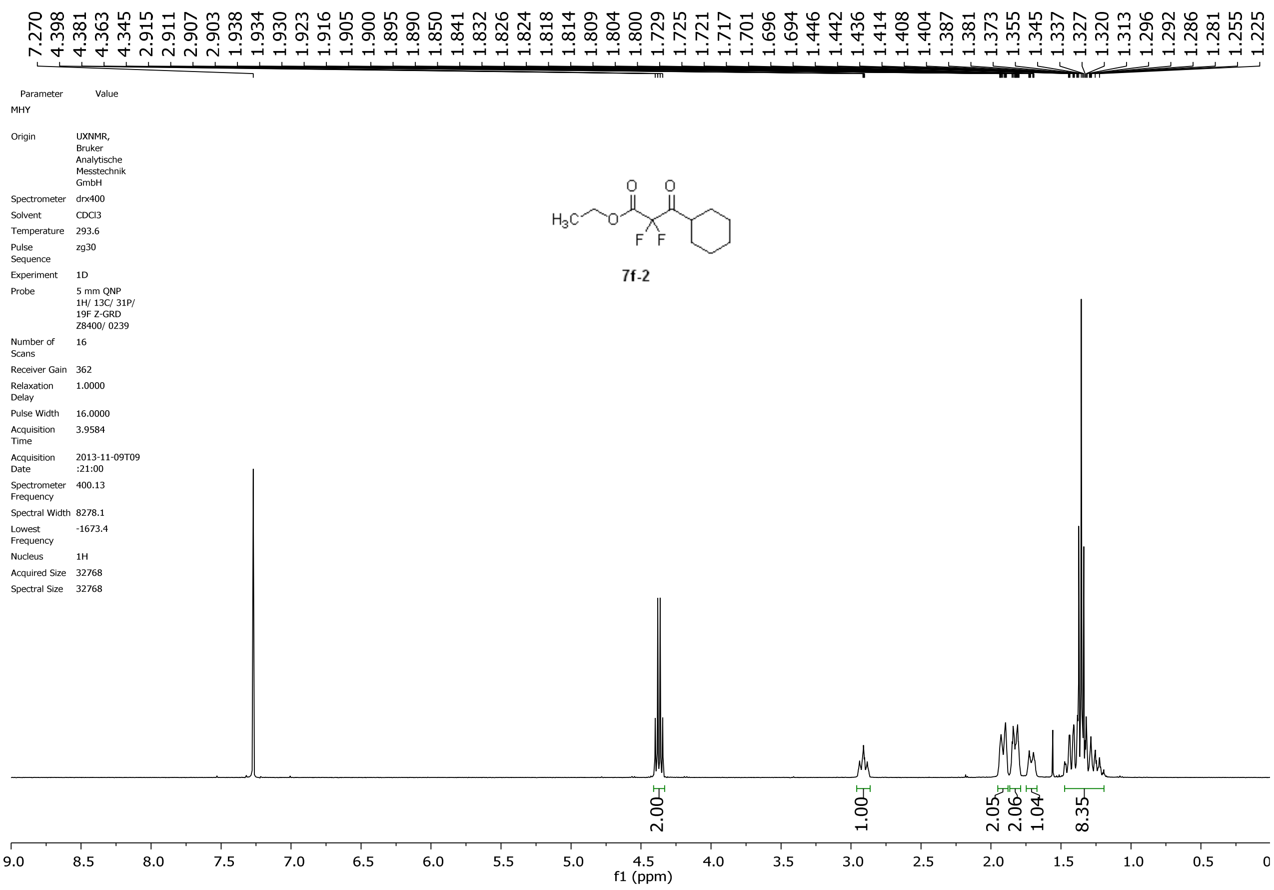
7f-3

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-03T20:33:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



7f-3

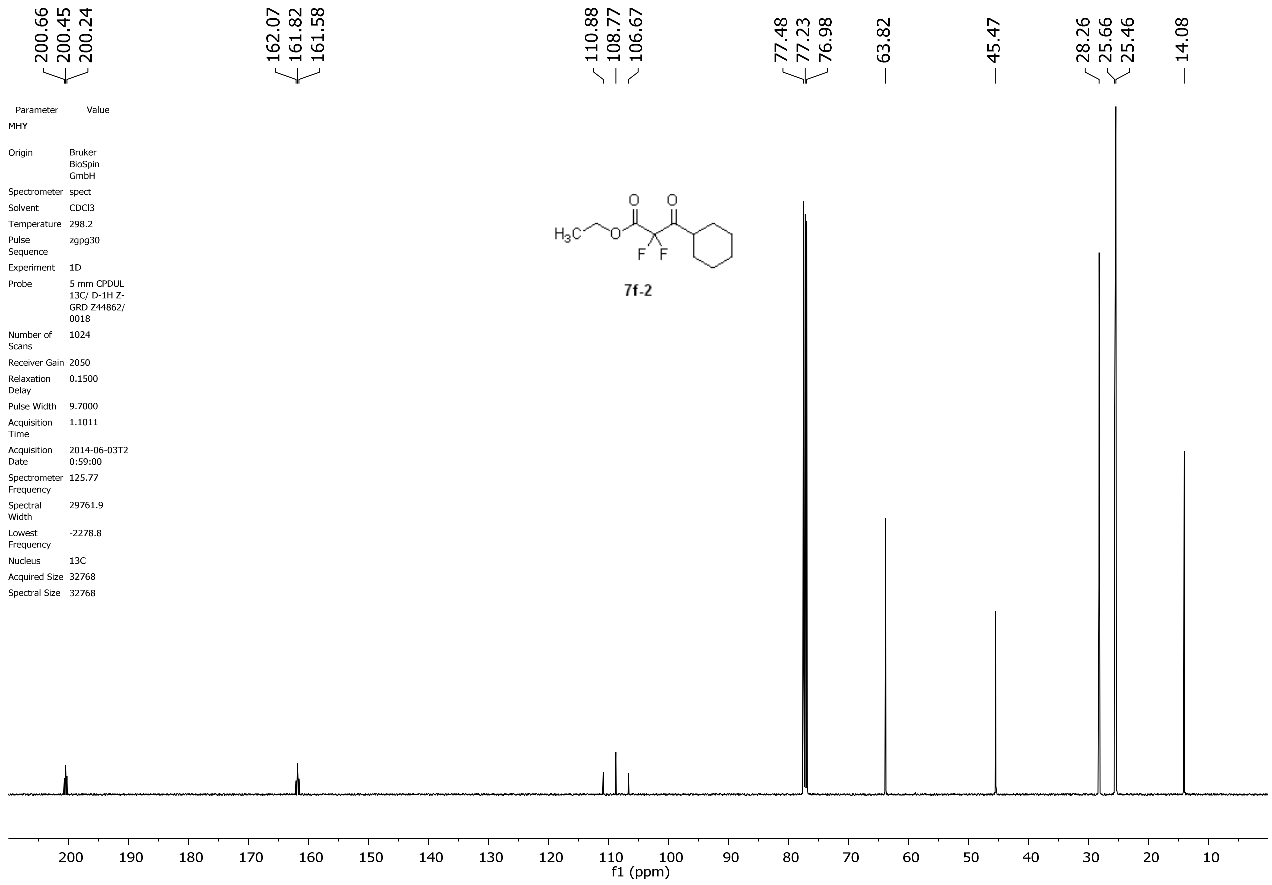
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	813
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-05-31T21:42:39
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



7f-2

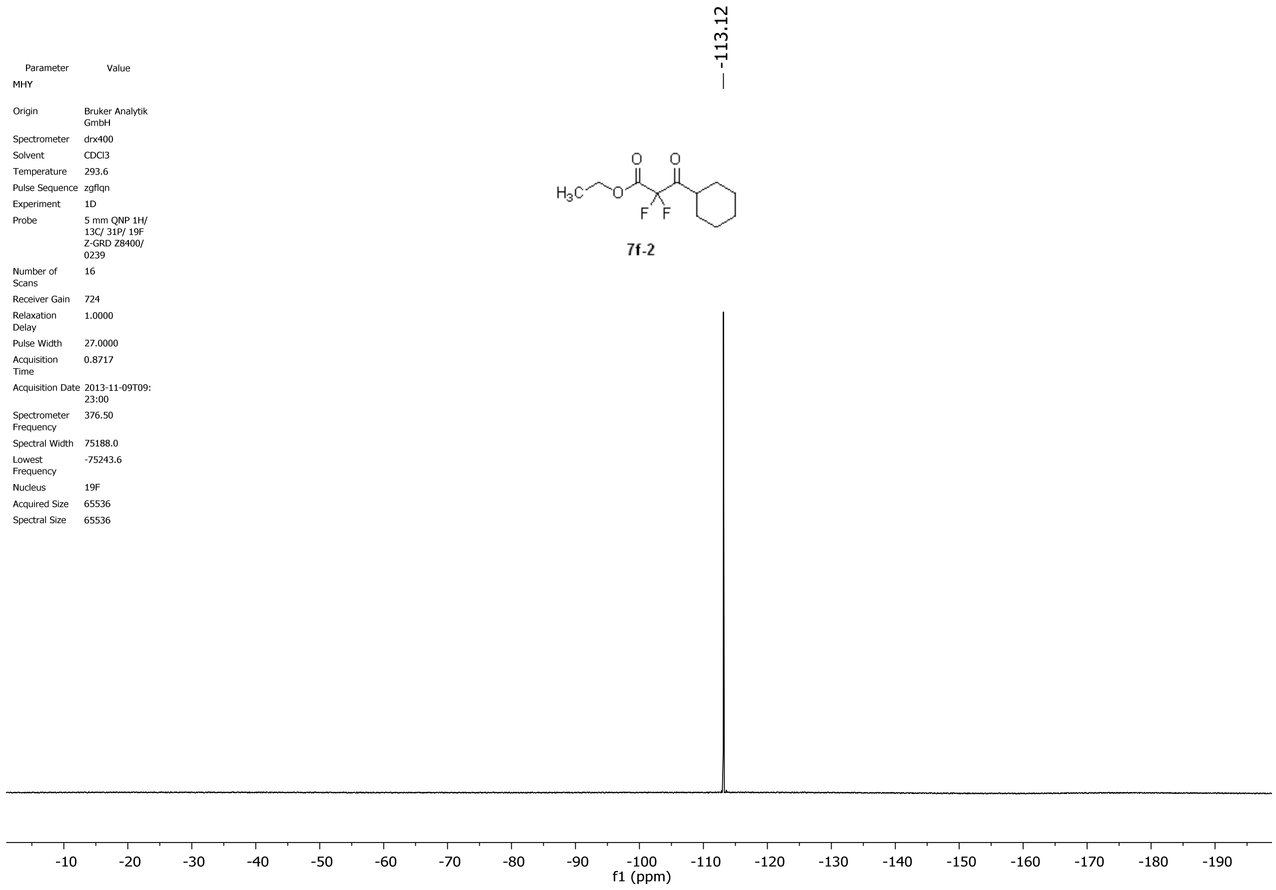
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-09T09 :21:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-03T20:59:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2278.8
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

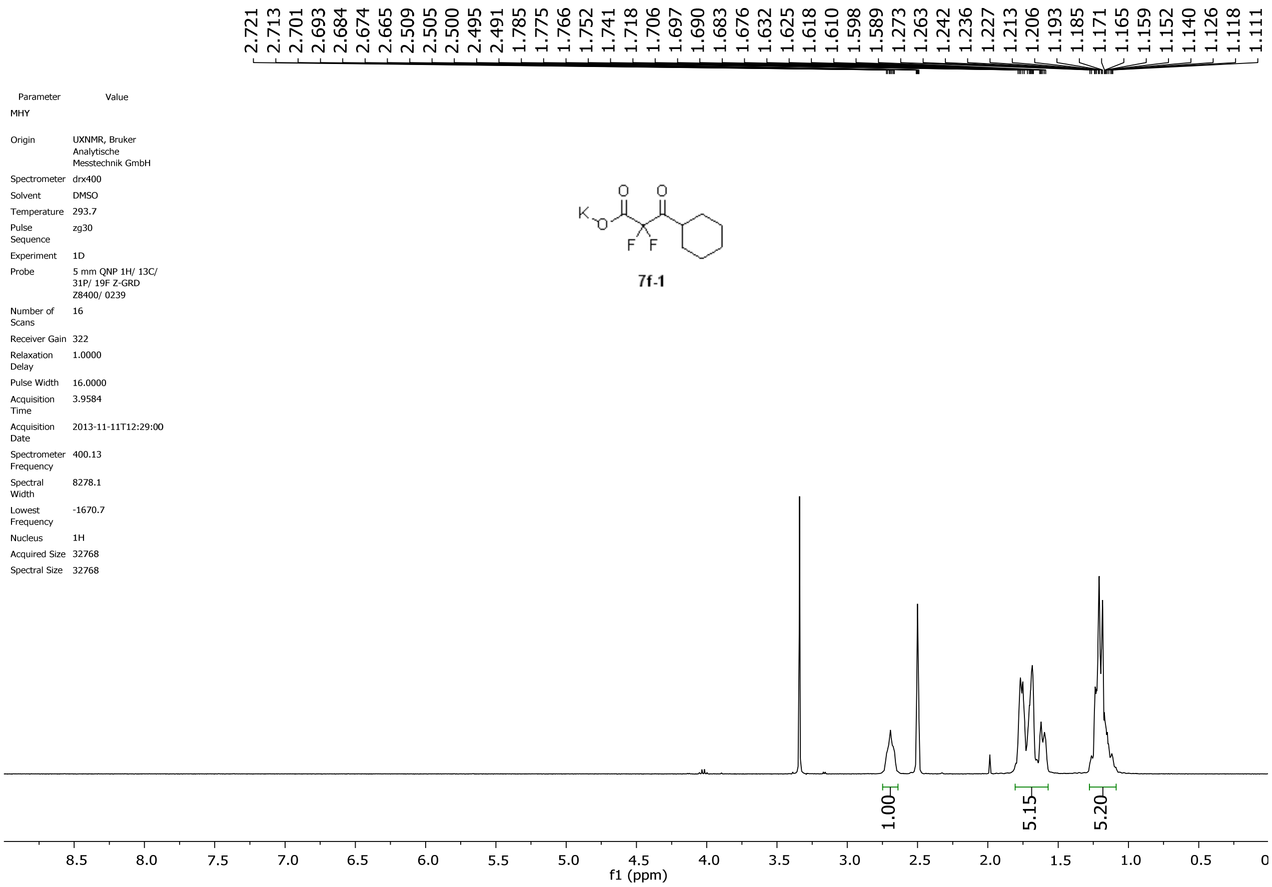


7f-2

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-09T09:23:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

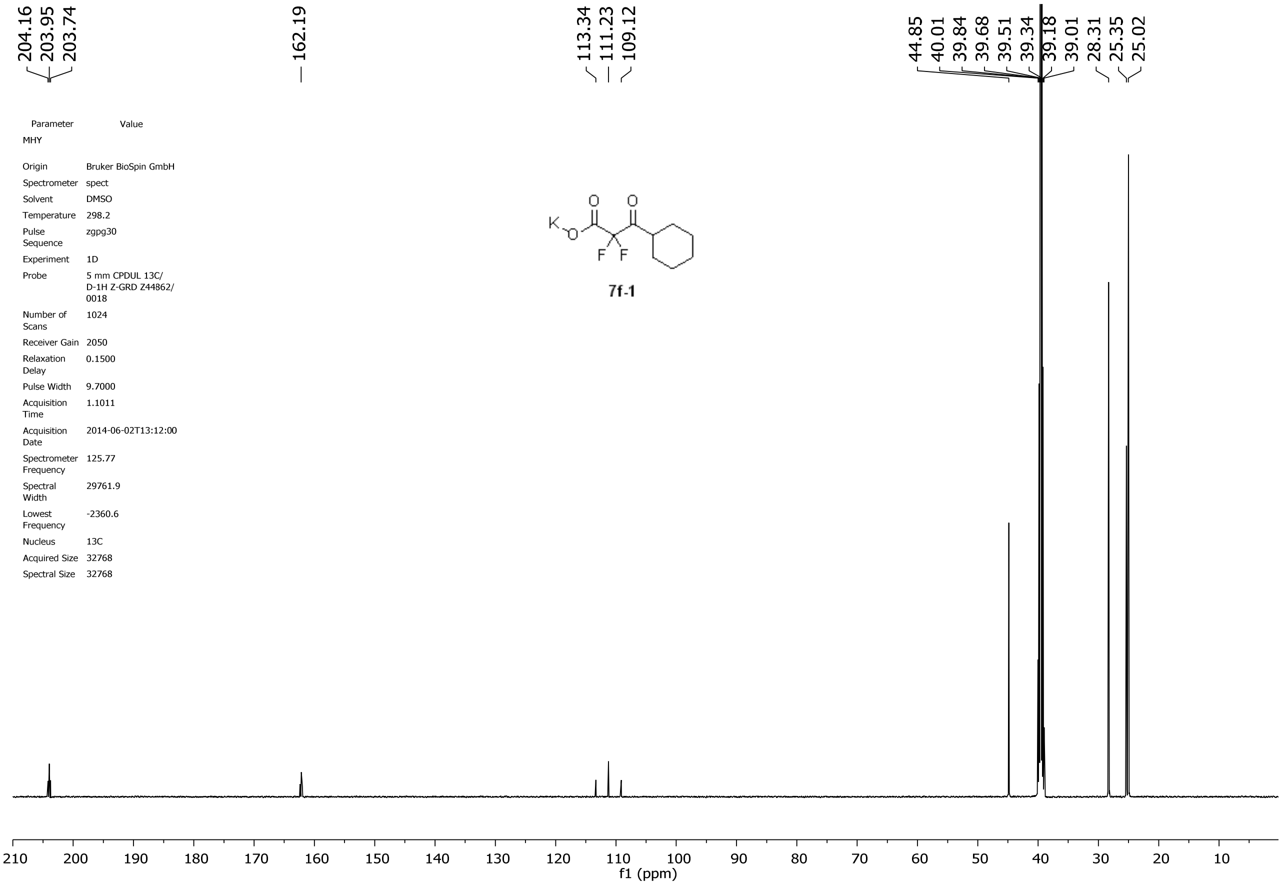


7f-2



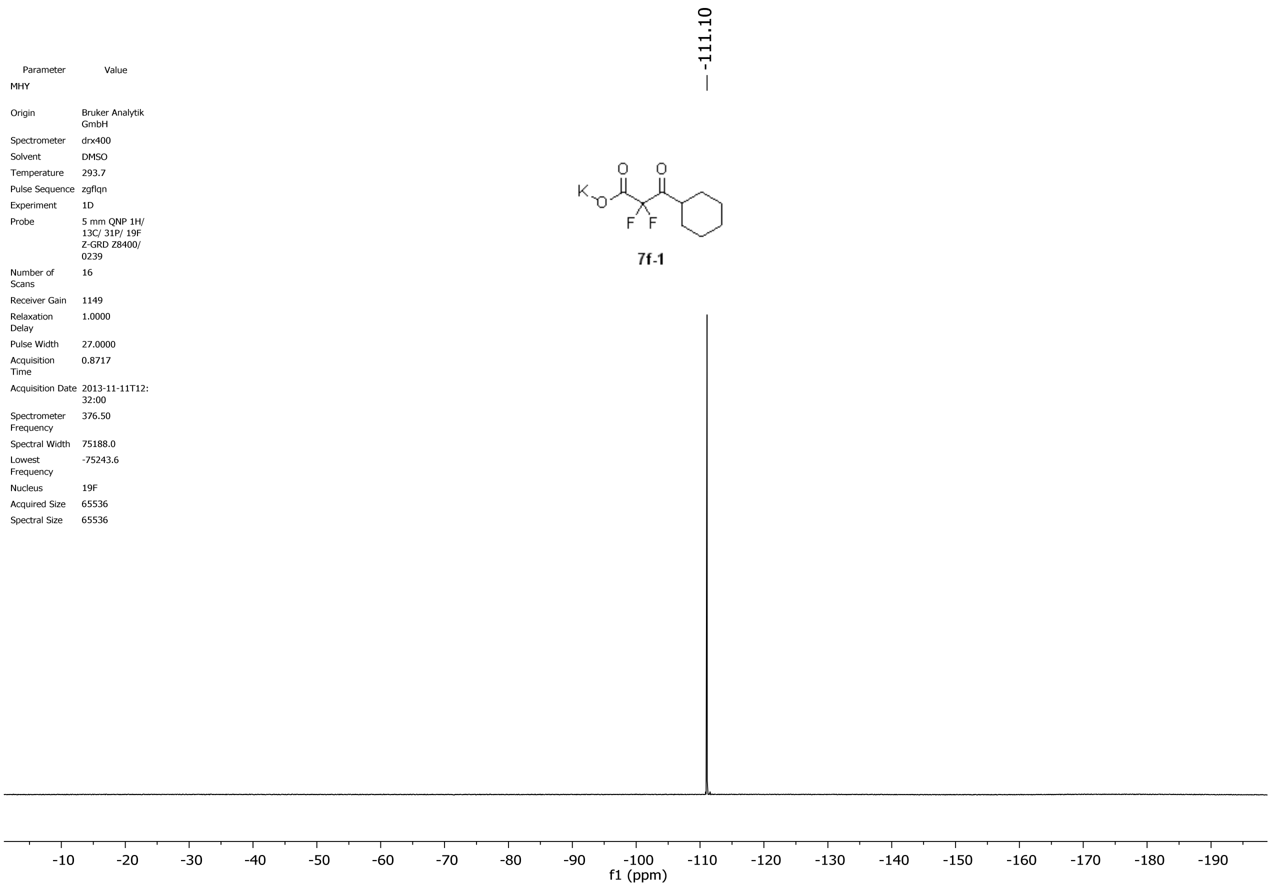
7f-1

Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-11T12:29:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1670.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

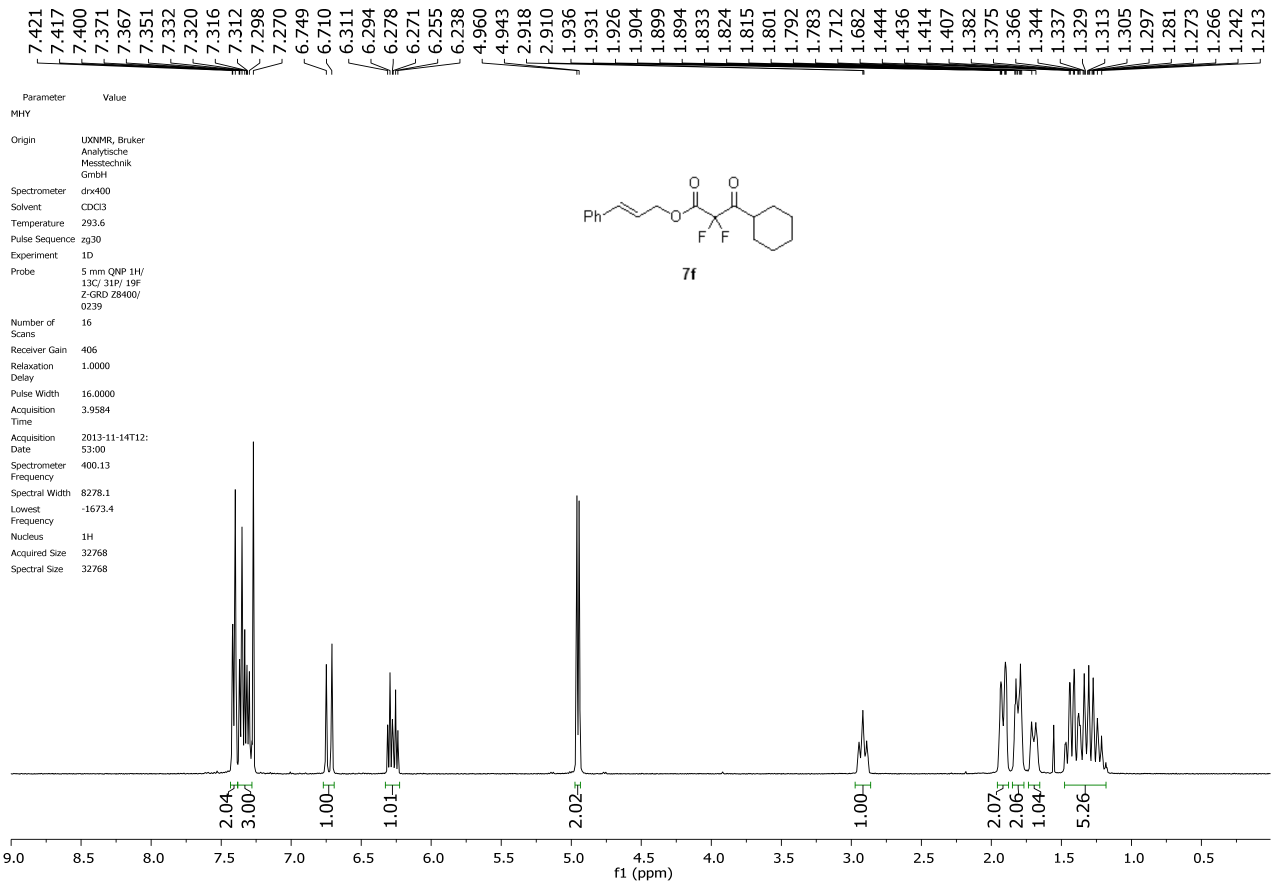


7f-1

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	DMSO
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-02T13:12:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2360.6
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

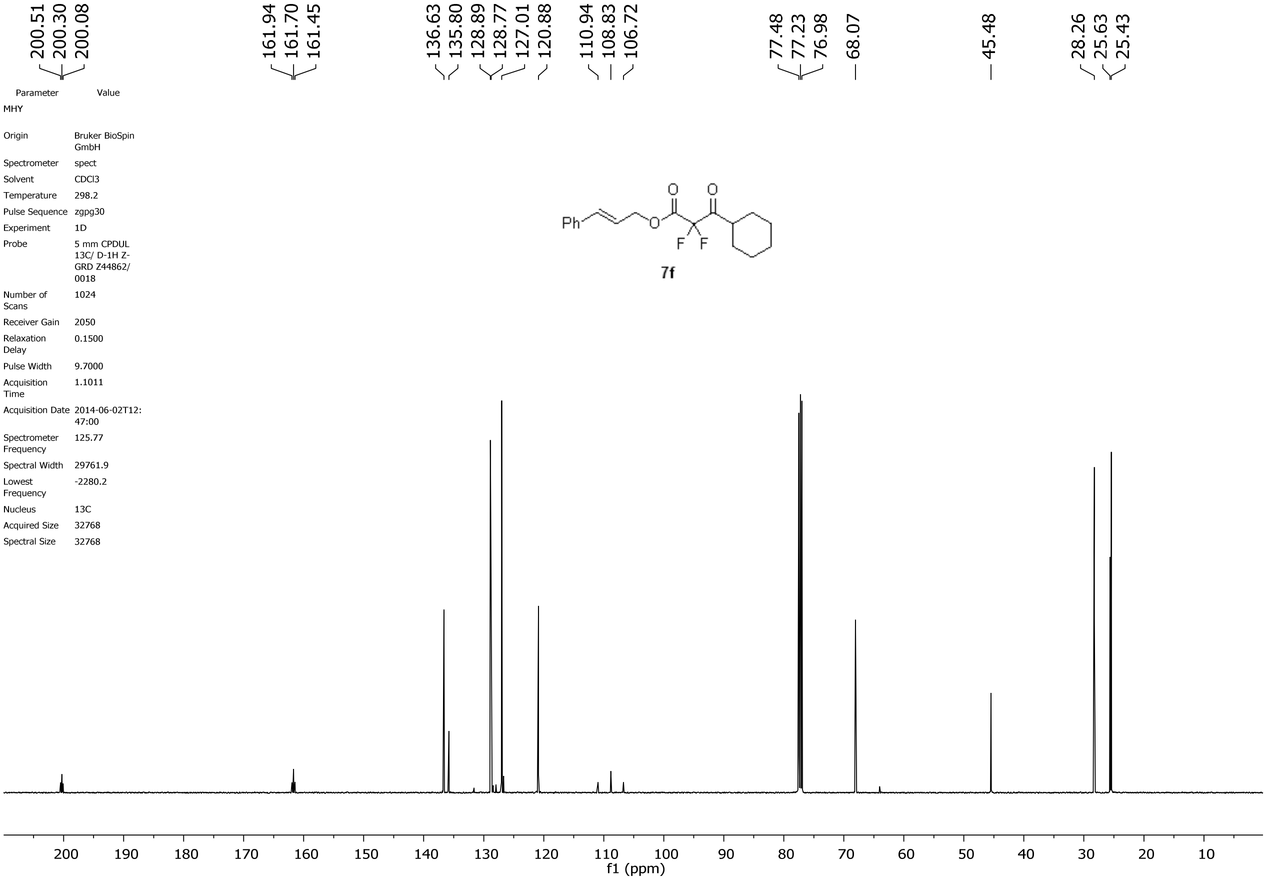


Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	DMSO
Temperature	293.7
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-11T12:32:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



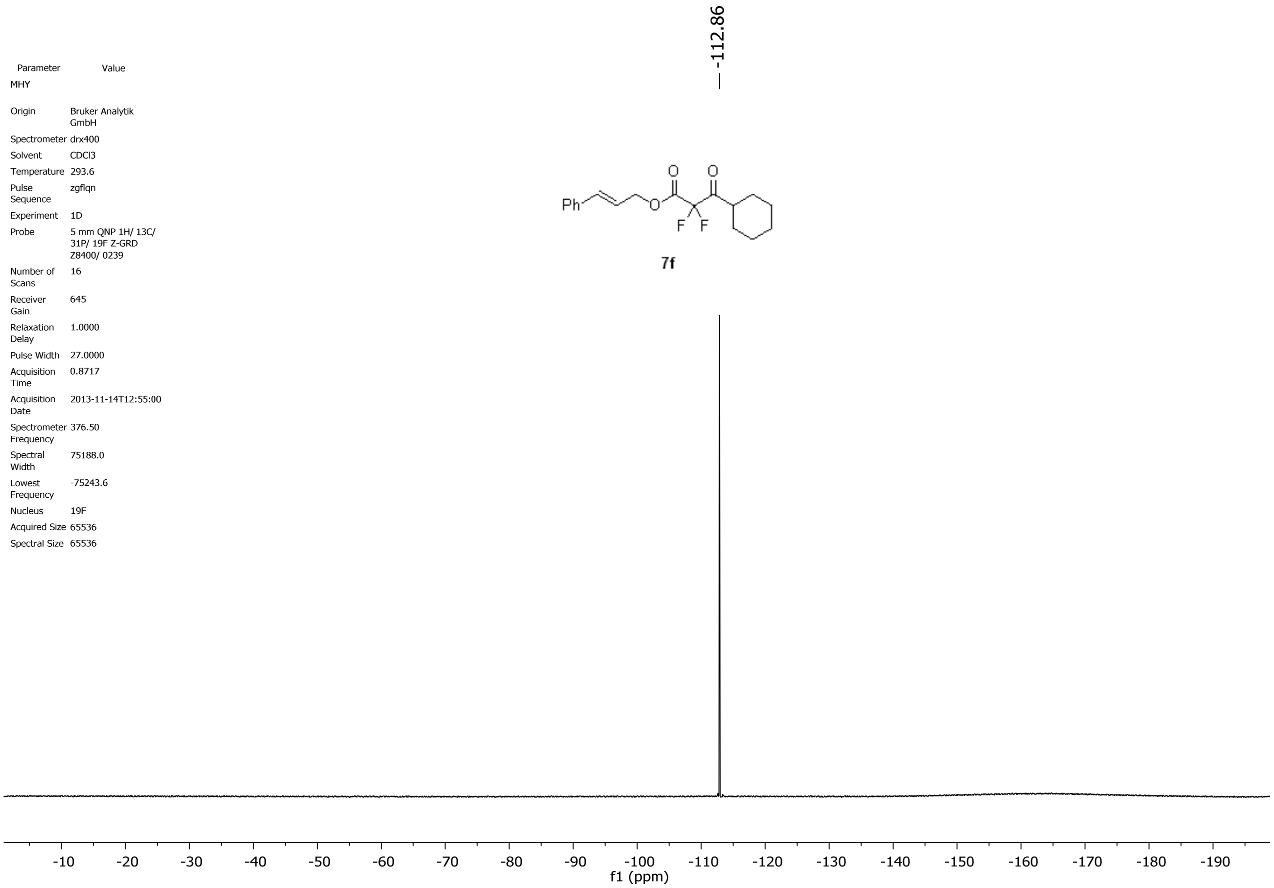
Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	406
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-11-14T12:53:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-02T12:47:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2280.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



7f

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-11-14T12:55:00
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



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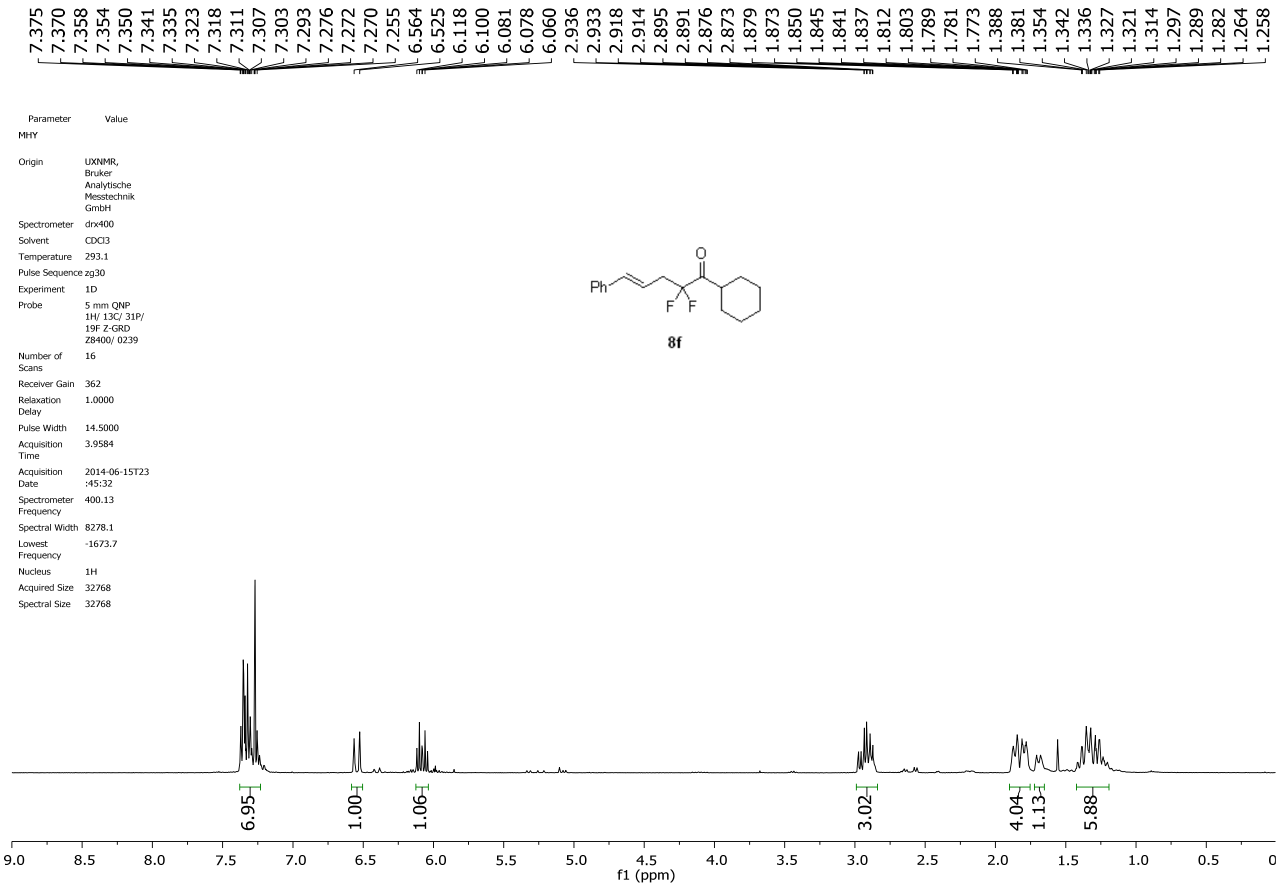
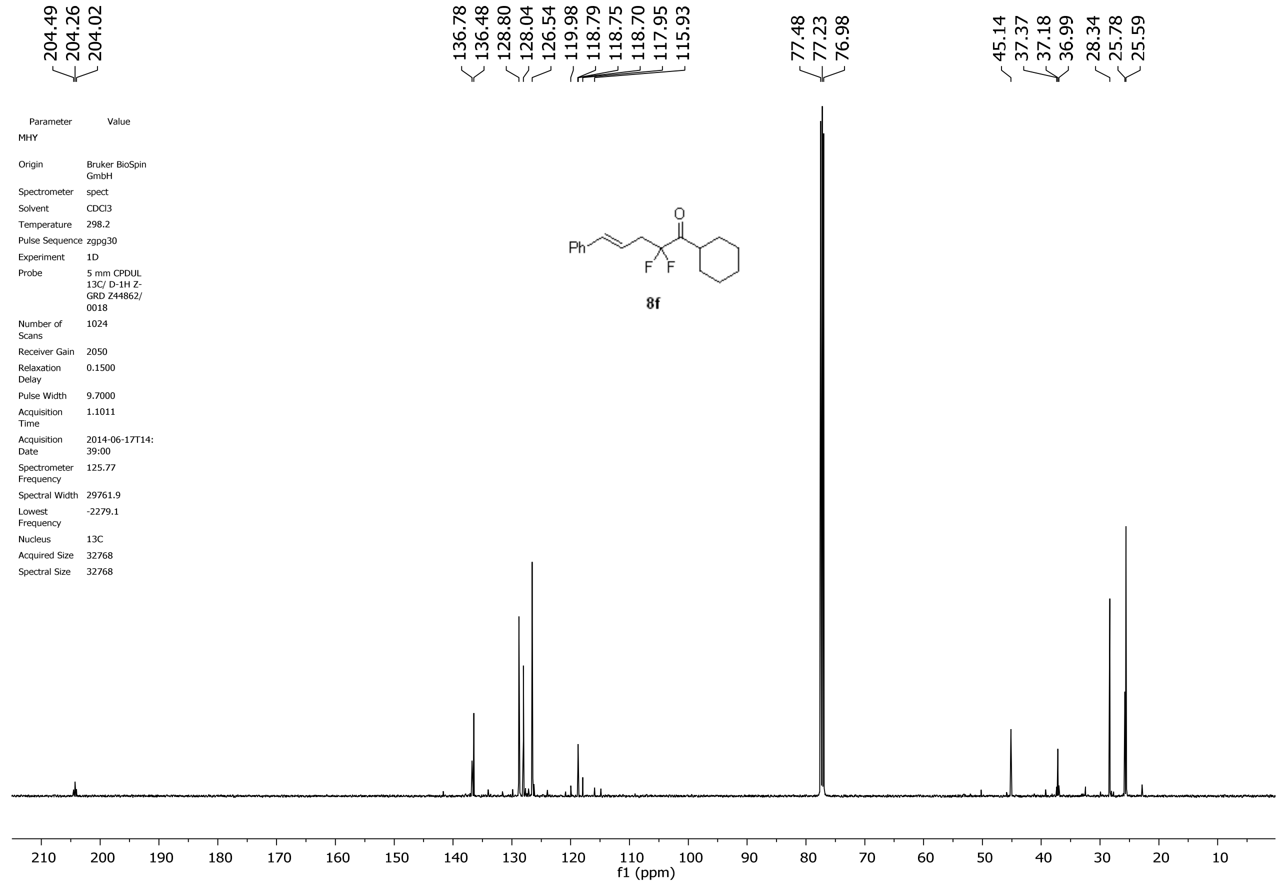
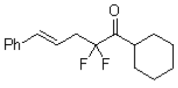


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-15T23:45:32
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-17T14:39:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	645
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-10T22:04:28
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



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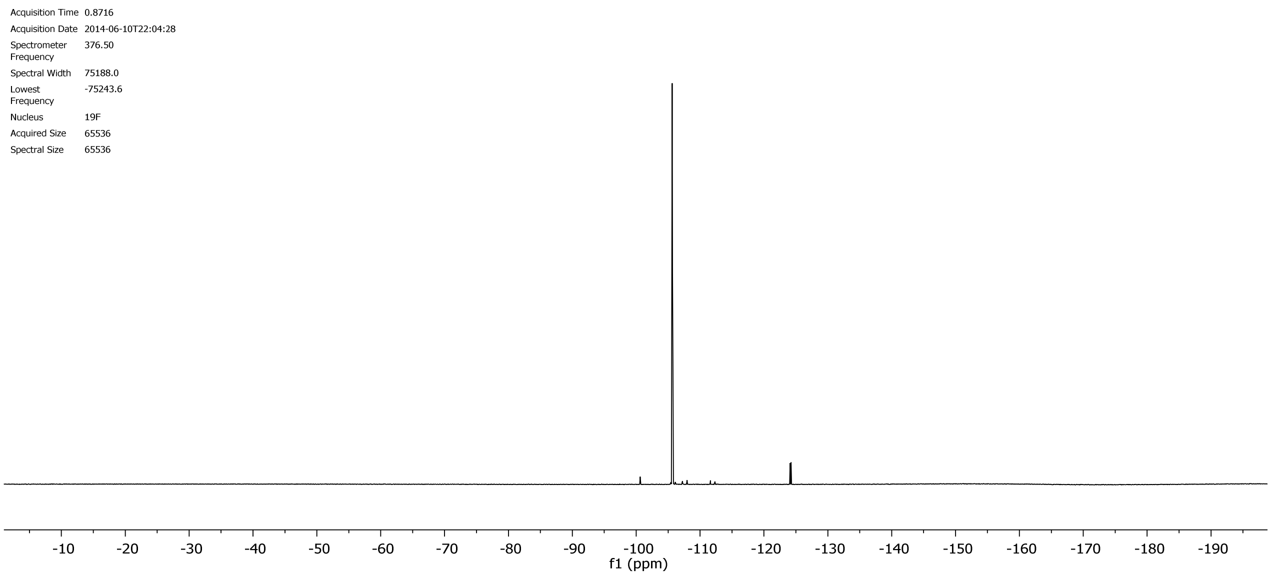
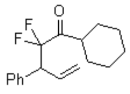


Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	3.9584
Acquisition Date	2014-06-10T22 :28:07
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768



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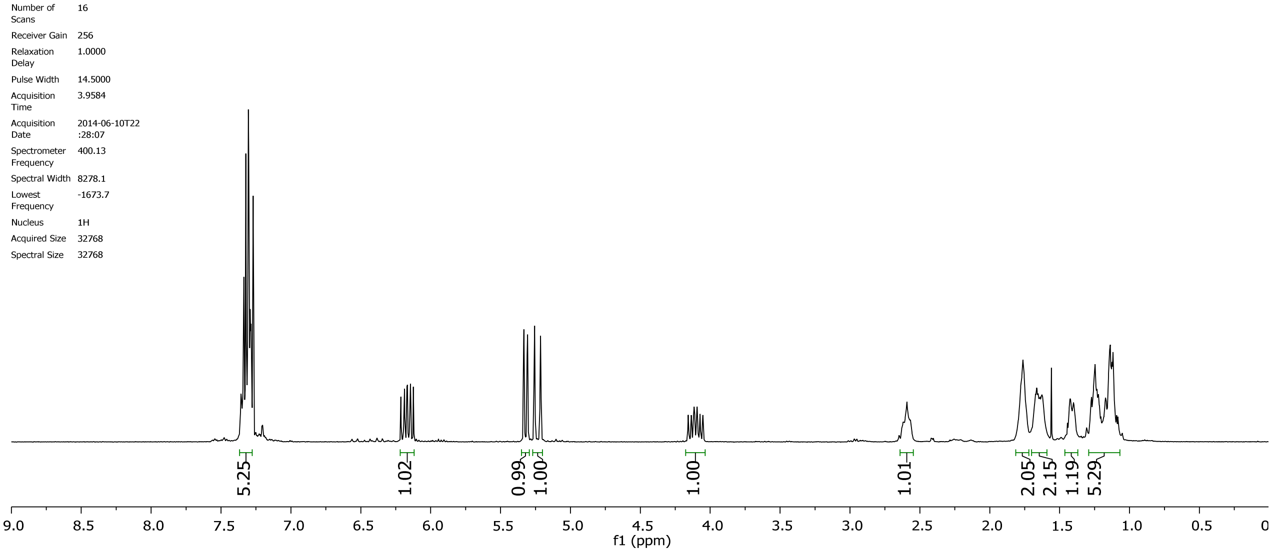

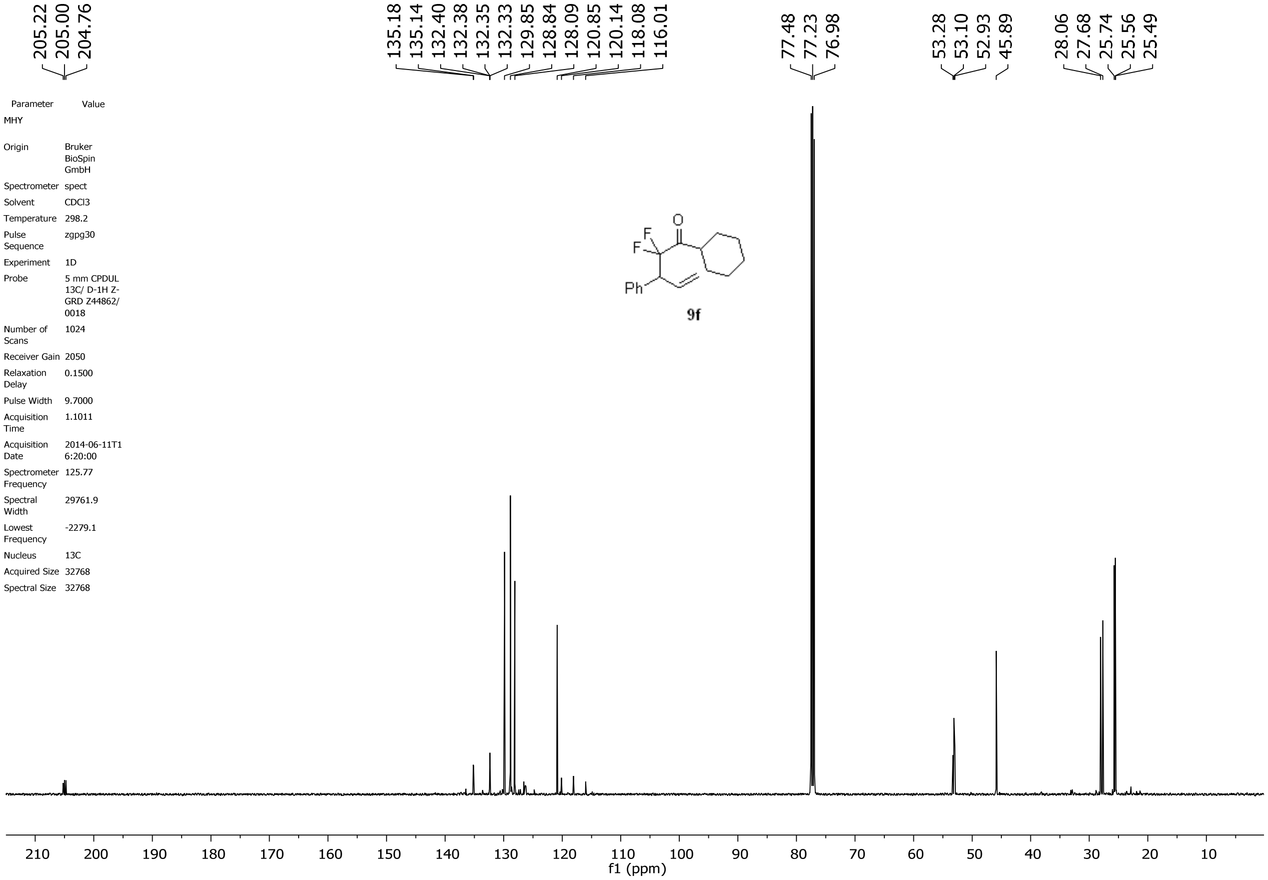

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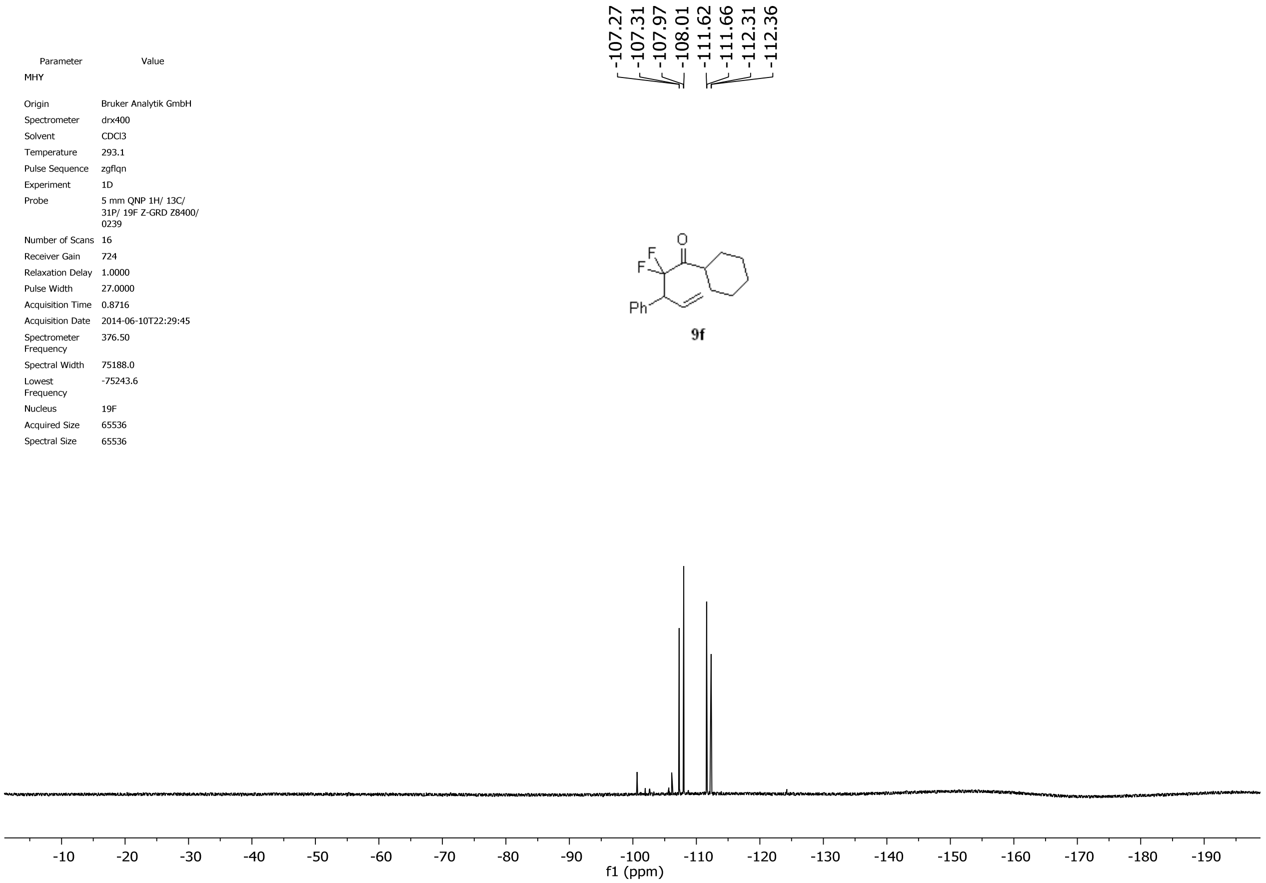
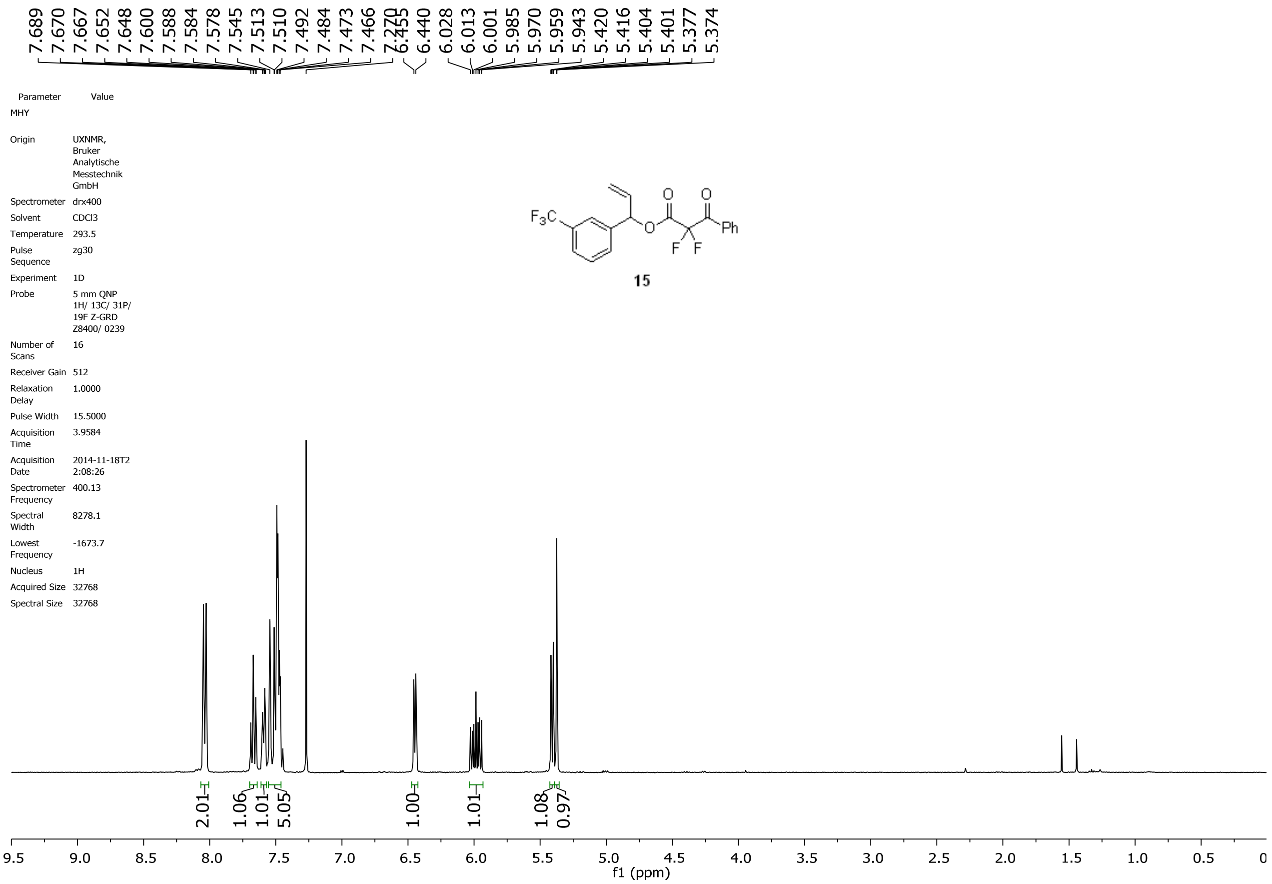
Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-06-11T16:20:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.1
Nucleus	13C
Acquired Size	32768
Spectral Size	32768

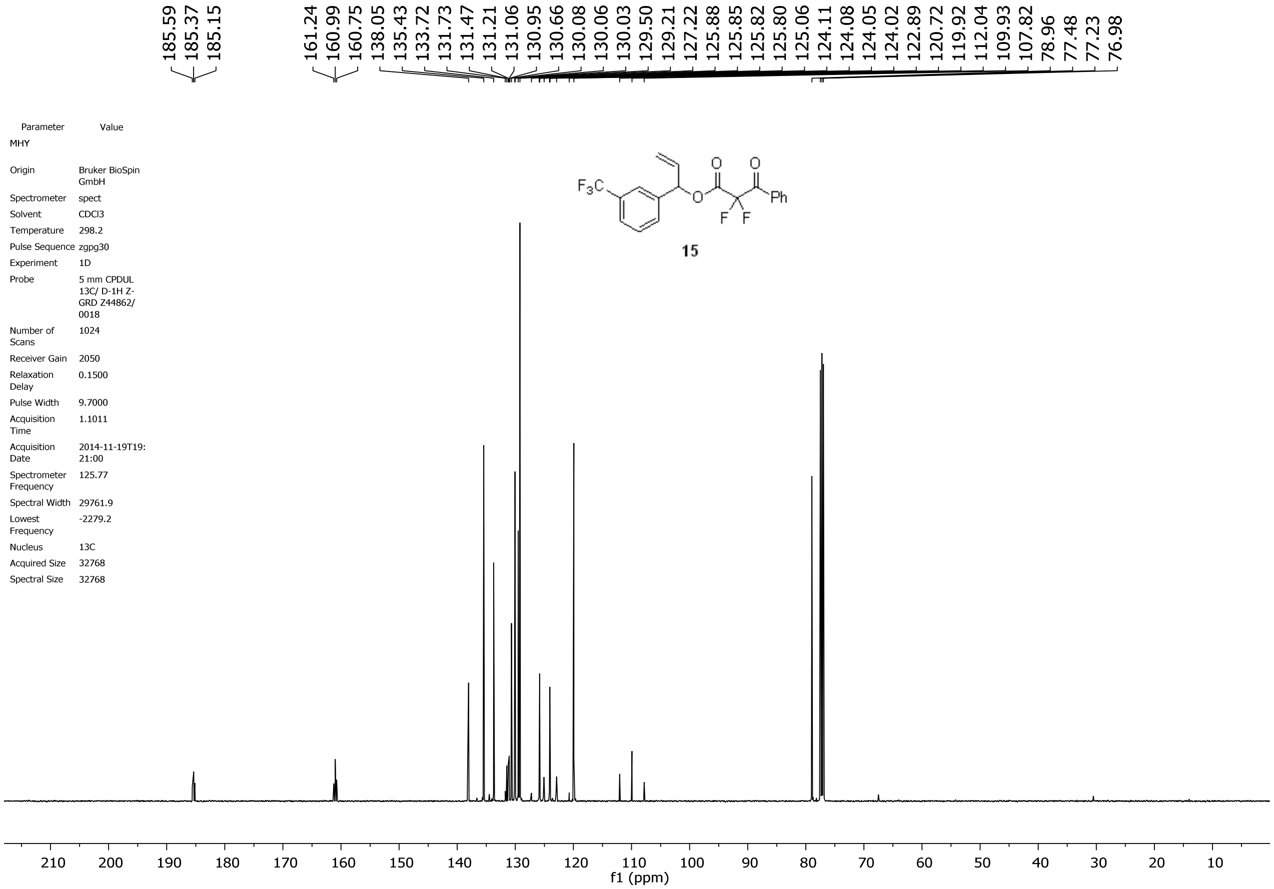


9f

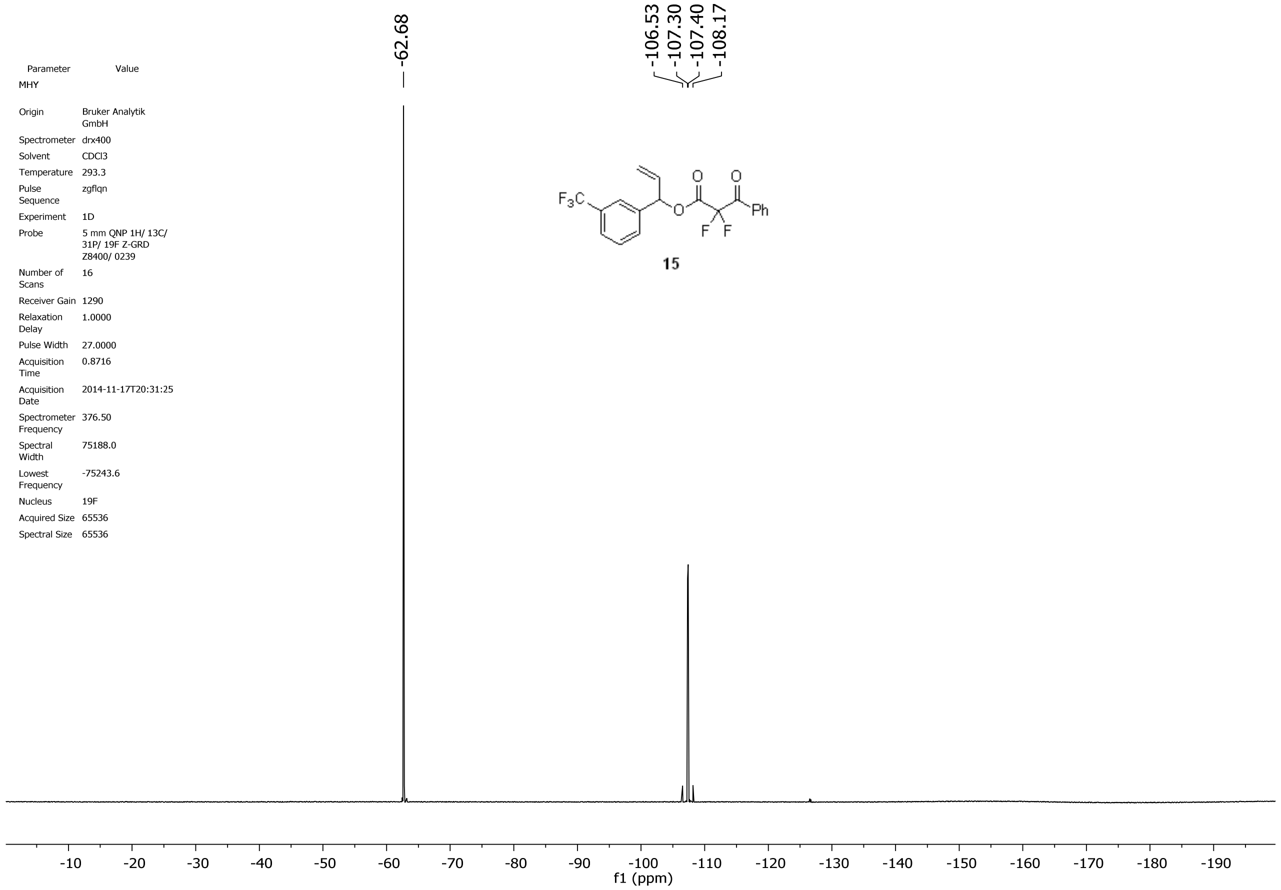
Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-06-10T22:29:45
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536



Parameter	Value
MHY	
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	512
Relaxation Delay	1.0000
Pulse Width	15.5000
Acquisition Time	3.9584
Acquisition Date	2014-11-18T22:08:26
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	32768

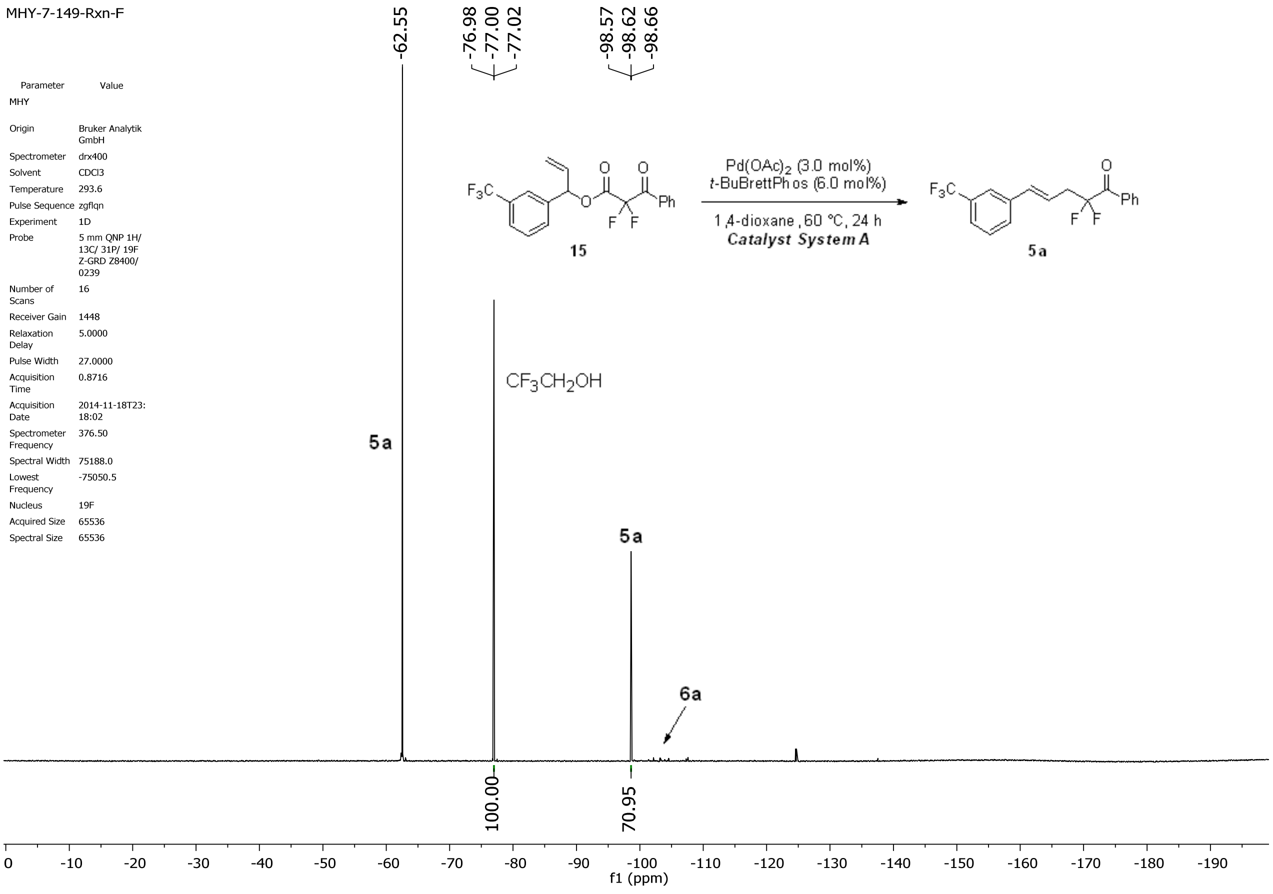


Parameter	Value
MHY	
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.7000
Acquisition Time	1.1011
Acquisition Date	2014-11-19T19:21:00
Spectrometer Frequency	125.77
Spectral Width	29761.9
Lowest Frequency	-2279.2
Nucleus	13C
Acquired Size	32768
Spectral Size	32768



Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.3
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-11-17T20:31:25
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

MHY-7-149-Rxn-F



Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1448
Relaxation Delay	5.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-11-18T23:18:02
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75050.5
Nucleus	19F
Acquired Size	65536
Spectral Size	65536

MHY-7-148-Rxn-F

Parameter	Value
MHY	
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgflqn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1149
Relaxation Delay	5.0000
Pulse Width	27.0000
Acquisition Time	0.8716
Acquisition Date	2014-11-18T23:13:51
Spectrometer Frequency	376.50
Spectral Width	75188.0
Lowest Frequency	-75070.8
Nucleus	19F
Acquired Size	65536
Spectral Size	65536