Ligand-controlled Regioselective Cu-Catalyzed Trifluoromethylation to Generate Trifluoromethylallenes

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Supporting Information

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General Considerations

Unless otherwise noted, all reactions were performed using oven-dried glassware under an atmosphere of dry N_2. Trifluoromethylation reactions were performed in resealable 15 mL screw-top vial sealed with PTFE septa. All other reactions were performed in round-bottom flasks, which were sealed with rubber septa. Stainless steel syringes were used to transfer air- or moisture-sensitive liquid reagents. Reactions were monitored by thin-layer chromatography (TLC) on UNIPLATE^{TM} Silica Gel HLF 250 micron glass plates precoated with 230–400 mesh silica impregnated with a fluorescent indicator (250 nm), visualizing by quenching of fluorescence, $KMnO_4$ solution, or *p*-anisaldehyde solution. A CombiFlash® RF–4x purification system was used for chromatographic purifications. Silica gel was purchased from Sorbent Technologies (cat. #30930M-25, 60 Å, 40–63 μm).

Unless otherwise noted, reagents were purchased from commercial sources, and used as received. Anhydrous potassium fluoride (KF) was dried in a vacuum-oven at 200 °C for at least 24 h prior to use. Anhydrous *N*,*N*′-dimethylformamide (DMF), acetonitrile (CH_3CN), methanol (MeOH), dichloromethane (DCM), tetrahydrofuran (THF), and triethylamine (NEt_3) were dispensed from a solvent purification system, in which the 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 a Bruker 500 AVANCE spectrometer (500 and 126 MHz, respectively) or a Bruker 400 AVANCE spectrometer (400 and 101 MHz, respectively). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker 400 AVANCE spectrometer (376 MHz). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane, and are referenced to the proton resonance of residual $CHCl_3$ in the NMR solvent (δ = 7.27 ppm). Chemical shifts (δ) for carbon are reported in ppm downfield from tetramethylsilane, and are referenced to the carbon resonances of the solvent peak (δ = 77.16 ppm). Chemical shifts (*δ*) for fluorine are reported in ppm, and are referenced to $PhCF_3$ (δ = –63.72 ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constant in Hertz (Hz), and integration.

Exact mass determinations were obtained by the following methods; electron impact ionization (EI) on a ZG analytical ZAB mass spectrometer, electrospray ionization (ESI) on a

Waters LCT Premier^{TM} mass spectrometer, or 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. Low-resolution mass data (CI) were recorded on a Shimadzu GCMS-QP2010 SE mass spectrometer. Infrared spectra were measured using a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer. Uncorrected melting points were measured on a Thomas Hoover Capillary Melting Point Apparatus.

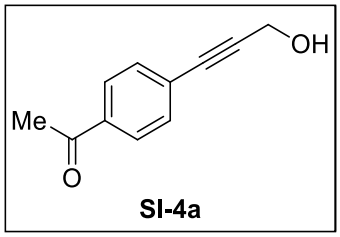
Synthesis of Propargyl Alcohols

General Procedure A:

An oven-dried Schlenk flask was charged with iodoarene (1.0 equiv), CuI (0.040 equiv), $Pd(PPh_3)_2Cl_2$ (0.020 equiv), and a magnetic stir bar. The flask was evacuated and backfilled with N_2 three times. MeCN (1 M) was injected, and the suspension was cooled to –10 °C. NEt_3 (4.5 equiv) was injected dropwise, and the mixture was stirred at –10 °C for 10 min. Propargyl alcohol (1.1 equiv) was injected dropwise, and the mixture was allowed to warm to rt. The reaction was monitored by TLC, and upon consumption of starting iodoarene (typically < 4 h), the solvent was removed *in vacuo*. The crude mixture was dissolved in EtOAc, and filtered through a pad of silica (eluted with additional EtOAc). The solvent was removed *in vacuo*, and the crude material was purified by flash chromatography to afford the 3-arylpropargyl alcohol.

General Procedure B:

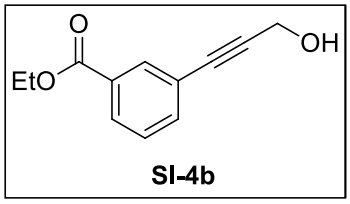
An oven-dried Schlenk flask was charged with benzaldehyde (1.0 equiv), and a magnetic stir bar. The flask was evacuated and backfilled with N_2 three times. THF was injected, and the solution was cooled to 0 °C. Ethynylmagnesium bromide (0.5 M in THF, 1.2–1.5 equiv) was injected dropwise, and the reaction was stirred at 0 °C for 1 h. The mixture was allowed to warm to rt, and monitored by TLC. After consumption of the aldehyde, the reaction was quenched with $NH_4Cl_{(aq.)}$, and diluted with EtOAc. The organic phase was washed with H_2O and brine, dried over Na_2SO_4, and filtered. The solvent was removed *in vacuo*, and chromatographic purification of the resulting residue afforded the 1-arylpropargyl alcohol.



SI-4a

1-(4-(3-Hydroxyprop-1-yn-1-yl)phenyl)ethanone[1]

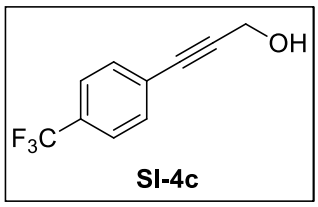
General procedure A was followed using 4-iodoacetophenone (2.46 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title product as a yellow solid (1.23 g, 71%). m.p. 74–76 °C (lit.[1] 76–77). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2 H), 7.56 – 7.49 (m, 2 H), 4.54 (s, 2 H), 2.61 (s, 3 H), 1.60 (s, 1 H).



SI-4b

Ethyl 3-(3-hydroxyprop-1-yn-1-yl)benzoate[2]

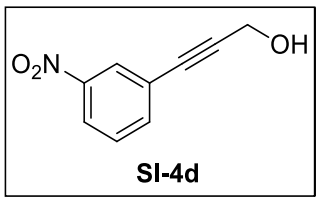
General procedure A was followed using ethyl 3-iodobenzoate (2.76 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title product as a yellow solid (1.99 g, 98%). m.p. 47–49 °C (lit.[2] 48–50 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, J = 1.7 Hz, 1 H), 8.01 (dt, J = 7.9, 1.4 Hz, 1 H), 7.61 (dt, J = 7.6, 1.4 Hz, 1 H), 7.41 (t, J = 7.8 Hz, 1 H), 4.52 (d, J = 6.1 Hz, 2 H), 4.39 (q, J = 7.2 Hz, 2 H), 1.72 (ddd, J = 7.4, 6.0, 1.7 Hz, 1 H), 1.41 (t, J = 7.1 Hz, 3 H).



SI-4c

3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-ol[1]

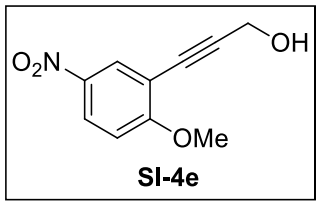
General procedure A was followed using 4-iodobenzotrifluoride (2.72 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 5:1) afforded the title product as yellow crystals (1.84 g, 92%). m.p. 35–37 °C (lit.[1] 35–36 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.54 (m, 4 H), 4.53 (s, 2 H), 1.68 (s, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.95 (s, 3 F).



SI-4d

3-(3-Nitrophenyl)prop-2-yn-1-ol[3]

General procedure A was followed using 1-iodo-3-nitrobenzene (2.49 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title product as a viscous amber oil (1.55 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (t, J = 1.9 Hz, 1 H), 8.19 (ddd, J = 8.4, 2.3, 1.1 Hz, 1 H), 7.75 (dt, J = 7.7, 1.3 Hz, 1 H), 7.52 (t, J = 8.0 Hz, 1 H), 4.54 (d, J = 6.2 Hz, 2 H), 1.73 (t, J = 6.2 Hz, 1 H).

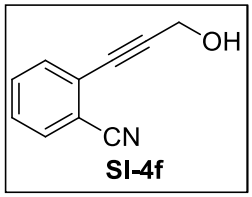


SI-4e

3-(2-methoxy-5-nitrophenyl)prop-2-yn-1-ol

General procedure A was followed using 2-iodo-4-nitroanisole (2.8 g, 0.010 mol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (15 mL) as solvent. Chromatographic purification (hexanes / EtOAc 9:1 → 3:1) afforded the title product as a pale yellow solid (1.1 g, 53%). m.p. 117–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 2.8 Hz, 1 H), 8.22 (dd, J = 9.2, 2.8 Hz, 1 H), 6.96 (d, J = 9.2 Hz, 1 H), 4.57 (d, J = 6.3 Hz, 2 H), 4.00 (s, 3 H), 1.77 (t, J = 6.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 141.2, 129.5, 126.0, 113.0, 110.4, 93.5, 79.8, 56.8, 51.8. IR (film) 3381,

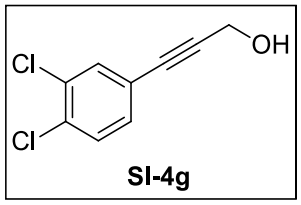
3090, 2978, 2945, 1605, 1576, 1510, 1493, 1439, 1352, 1279, 1238, 1188, 1144, 1095, 1015, 974, 899, 879, 820, 746, 723, 638 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{10}H_{10}NO_4$) requires *m/z* 208.0610, found *m/z* 208.0610 (0.0 ppm).



SI-4f

2-(3-Hydroxyprop-1-yn-1-yl)benzonitrile[4]

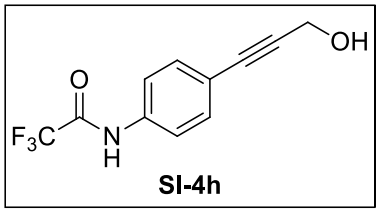
General procedure A was followed using 2-iodobenzonitrile (2.3 g, 0.010 mol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 mg, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (15 mL) as solvent. Chromatographic purification (hexanes / EtOAc 4:1 → 3:2) afforded the title product as a tan solid (1.41 g, 90%). m.p. 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 1 H), 7.59 – 7.50 (m, 2 H), 7.47 – 7.37 (m, 1 H), 4.58 (s, 2 H), 2.39 – 1.97 (m, 1 H).



SI-4g

3-(3,4-Dichlorophenyl)prop-2-yn-1-ol[5]

General procedure A was followed using 1,2-dichloro-4-iodobenzene (2.72 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 5:1) afforded the title product as a pale brown solid (1.70 g, 85%). m.p. 64–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.9 Hz, 1 H), 7.40 (d, J = 8.3 Hz, 1 H), 7.28 – 7.25 (m, 1 H), 4.50 (d, J = 6.2 Hz, 2 H), 1.65 (td, J = 6.3, 2.0 Hz, 1 H).

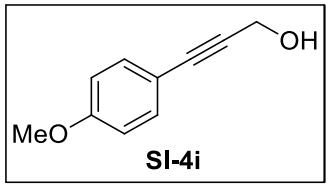


SI-4h

2,2,2-Trifluoro-*N*-(4-(3-hydroxyprop-1-yn-1-yl)phenyl)acetamide

4-Bromoaniline (2.6 g, 15 mmol) was added to an oven-dried 250 mL Schlenk flask. THF (0.050 L) and pyridine (1.8 mL, 23 mmol) were injected, and the solution was cooled to 0 °C. A solution of trifluoroacetic anhydride (2.5 mL, 18 mmol) in THF (0.010 L) was slowly injected over a 5 min period, and the reaction was stirred at 0 °C for 1.5 h. The solution was allowed to warm to rt, stirred for an additional 1.5 h, and then quenched with brine (50 mL). The mixture was extracted with EtOAc (100 mL, 2 x 50 mL), and the combined organic solution was washed with 1 N HCl (2 x 75 mL), $NaHCO_{3\ (aq.)}$ (50 mL), and brine (50 mL). The solution was dried over $MgSO_4$, and filtered through a pad of silica gel (eluted with 100 mL EtOAc). The solvent was removed *in vacuo* to provide *N*-(4-bromophenyl)-2,2,2-trifluoroacetamide as a brown solid (3.7 g, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1 H), 7.56 – 7.51 (m, 2 H), 7.51 – 7.46 (m, 2 H). *N*-(4-bromophenyl)-2,2,2-trifluoroacetamide (1.7 g, 6.4 mmol), CuI (0.12 g, 0.32 mmol), and NaI (1.9 g, 13 mmol) were added to a 50 mL Schlenk flask. The flask was evacuated and backfilled with dry N_2 (3x), and trans-*N,N'*-dimethyl-1,2-cyclohexanediamine (0.050 mL, 0.64 mmol) and 1,4-dioxane (6.4 mL) were injected. The flask was sealed with a screw-top PTFE stopper, and immersed in a 110 °C oil bath. After 16 h, the mixture was allowed to cool to rt, and poured onto 1 N HCl (25 mL). The mixture was extracted with EtOAc (3 x 25 mL), and the combined organic layers were washed with H_2O (50 mL) and brine (50 mL). The organic solution was dried over $MgSO_4$, filtered through a pad of silica gel, and the solvent was removed *in vacuo*. Analysis of the material by GC revealed a 3:1 mixture of ArI / ArBr, and the material was used without further purification. General procedure A was followed using the haloarene mixture, CuI (34 mg, 0.18 mmol), $Pd(PPh_3)_2Cl_2$ (62 mg, 0.090 mmol), NEt_3 (2.8 mL, 0.020 mol), propargyl alcohol (0.28 mL, 4.9 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (DCM / acetone 1:0 → 9:1) afforded the title product as a tan solid (0.51 g, 33% over 2 steps). m.p. 148–149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1 H), 7.58 – 7.52 (m, 2 H), 7.51 – 7.45 (m, 2 H), 4.51 (s, 2 H), 1.64 (s, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.8 (q, J = 37.7 Hz), 135.2, 132.9, 120.7, 120.3, 115.7 (q, J = 288.8 Hz), 88.1, 84.9, 51.8. ^{19}F NMR (376

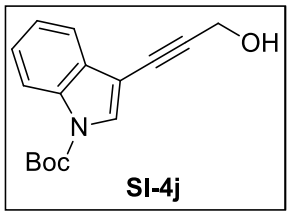
MHz, $CDCl_3$) δ –76.68 (s, 3 F). IR (film) 3421, 3308, 3200, 3074, 3065, 1720, 1609, 1549, 1510, 1412, 1358, 1281, 1244, 1215, 1182, 1153, 1014, 953, 903, 837, 741, 685 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{11}H_9NO_2F_3$) requires *m/z* 244.0585, found *m/z* 244.0585 (0.0 ppm).



SI-4i

3-(4-Methoxyphenyl)prop-2-yn-1-ol[6]

General procedure A was followed using 4-iodoanisole (2.34 g, 10.0 mmol), CuI (76 mg, 0.40 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), NEt_3 (6.3 mL, 45 mmol), propargyl alcohol (0.64 mL, 11 mmol) and MeCN (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title product as a pale yellow solid (1.56 g, 96%). m.p. 67–68 °C (lit.[6] 62.5–64.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 2 H), 6.89 – 6.81 (m, 2 H), 4.49 (d, *J* = 6.1 Hz, 2 H), 3.82 (s, 3 H), 1.64 (t, *J* = 6.1 Hz, 1 H).

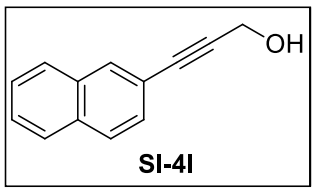


SI-4j

Tert-butyl 3-(3-hydroxyprop-1-yn-1-yl)-1H-indole-1-carboxylate

NaOH (1.7 g, 43 mmol) was added to a solution of indole (2.0 g, 17 mmol) in DMF (0.030 L). The mixture was stirred for 15 min, after which I_2 (4.4 g, 17 mmol) was added to the reaction. After 4 h of stirring at 22 °C, the mixture was poured over ice H_2O (400 mL), and the resulting precipitate was collected by filtration, washed with ice H_2O (3 x 20 mL), and dried *via* azeotropic distillation with toluene. The crude material was dissolved in DCM (0.050 L). 4-(dimethylamino)pyridine (210 mg, 1.7 mmol) and NEt_3 (3.6 mL, 26 mmol) were added. The solution was cooled to 0 °C, and di-*tert*-butyl dicarbonate (4.1 g, 19 mmol) was added. The reaction was allowed to warm to rt, and stirred for 12 h. DCM (150 mL) was added, and the mixture was washed with $NH_4Cl_{(aq.)}$ (2 x 100 mL), H_2O (100 mL), and brine (100 mL). The

organic solution was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. The material was filtered through a pad of silica (hexanes / EtOAc 19:1), and then the solvent was removed *in vacuo*. The crude material was transferred to a 50 mL Schlenk flask, and then CuI (130 mg, 0.68 mmol) and $Pd(PPh_3)_2Cl_2$ (240 mg, 0.34 mmol) were added to the flask. The system was sealed with a rubber septum, and the flask was evacuated and backfilled with N_2 three times. MeCN (25 mL) and NEt_3 (11 mL, 77 mmol) were injected into the flask, and then the solution was cooled to –10 °C. Next, propargyl alcohol (1.1 mL, 19 mmol) was added to the reaction. After 1 h, the mixture was allowed to warm to 22 °C, and stirred for 12 h. The reaction mixture was poured over $NH_4Cl_{(aq.)}$ (50 mL), and diluted with EtOAc (200 mL). The phases were separated, and the organic layer was washed with $NH_4Cl_{(aq.)}$ (100 mL), H_2O (100 mL), and brine (100 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (hexanes / EtOAc 1:0 → 7:3) afforded the title compound as a brown solid (3.2 g, 69%). m.p. 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1 H), 7.78 (s, 1 H), 7.67 (dt, *J* = 7.5, 1.0 Hz, 1 H), 7.37 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1 H), 7.30 (td, *J* = 7.5, 1.1 Hz, 1 H), 4.58 (s, 2 H), 1.87 (s, 1 H) 1.68 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 134.7, 130.5, 129.4, 125.3, 123.4, 120.1, 115.4, 102.8, 90.8, 84.6, 77.9, 52.0, 28.3. IR (film) 3396, 3153, 3053, 2978, 2932, 2866, 1734, 1609, 1558, 1474, 1450, 1373, 1308, 1275, 1232, 1155, 1099, 1049, 1034, 1013, 912, 852, 746 cm^{-1}. HRMS (EI^+) exact mass calculated for $[M]^+$ ($C_{16}H_{17}NO_3$) requires *m/z* 271.1208, found *m/z* 271.1217 (3.3 ppm).

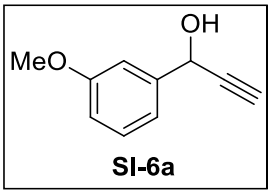


SI-4l

3-(Naphthalen-2-yl)prop-2-yn-1-ol[7]

CBr_4 (33.2 g, 0.100 mol) was added to an oven-dried 500 mL round bottom flask. DCM (75 mL) was injected, and the solution was cooled to 0 °C. A solution of PPh_3 (52.5 g, 0.200 mol) in DCM (75 mL) was added over 15 min, resulting in a brown mixture. The reaction was stirred for 10 additional minutes, after which a solution of 2-naphthaldehyde (7.81 g, 50.0 mmol) in DCM (50 mL) was slowly added. After stirring for 1 h at 0 °C, the reaction was quenched with H_2O (100 mL), and the organic phase was further washed with $NaHCO_{3\,(aq)}$ (100 mL), $NH_4Cl_{(aq)}$, and

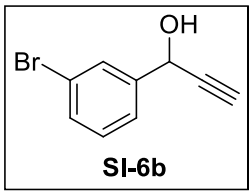
brine (100 mL). The solution was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (hexanes) provided 2-(2,2-dibromovinyl)naphthalene as a pale tan solid (12.9 g, 41.3 mmol, 83%). The material was added to an oven-dried 1 L Schlenk flask, which was sealed with a rubber septum and evacuated and backfilled with N_2 three times. THF (0.300 L) was added as solvent, and the solution was cooled to –78 °C. A solution of ^{n}BuLi (2.15 M in hexanes, 40.4 mL, 86.8 mmol) was injected over a 10 min period, and the dark brown solution was stirred at –78 °C for 1 h. The flask was placed under a positive pressure of N_2, the rubber septum was removed, and paraformaldehyde (3.72 g, 124 mmol) was added. The flask was resealed, the mixture was allowed to warm to rt and stir for an additional 12 h. The reaction was cooled to 0 °C and quenched with $NH_4Cl_{(aq.)}$ (150 mL). The aqueous phase was extracted with Et_2O (2 x 150 mL), and the organic extracts were washed with H_2O (2 x 300 mL) and brine (300 mL). The solution was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (hexanes / EtOAc 9:1 → 3:1) afforded the title compound as a pale tan solid (6.48 g, 86%). m.p. 61–63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.96 (m, 1 H), 7.85 – 7.75 (m, 3 H), 7.53 – 7.46 (m, 3 H), 4.57 (s, 2 H), 1.99 (s, 1 H).



SI-6a

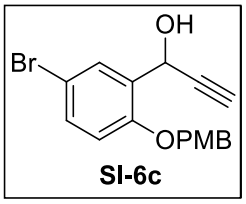
1-(3-Methoxyphenyl)prop-2-yn-1-ol[8]

General procedure B was followed using *m*-anisaldehyde (0.61 mL, 5.0 mmol), a solution of ethynylmagnesium bromide (12 mL, 0.5 M in THF, 6.0 mmol), and THF (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 9:1) afforded the title product as a yellow oil (0.67 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.9 Hz, 1 H), 7.17 – 7.10 (m, 2 H), 6.93 – 6.86 (m, 1 H), 5.46 (d, J = 2.4 Hz, 1 H), 3.84 (s, 3 H), 2.68 (d, J = 2.2 Hz, 1 H), 2.18 (s, 1 H).



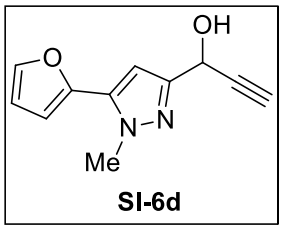
1-(3-Bromophenyl)prop-2-yn-1-ol[9]

General procedure B was followed using 3-bromobenzaldehyde (0.58 mL, 5.0 mmol), a solution of ethynylmagnesium bromide (12 mL, 0.5 M in THF, 6.0 mmol), and THF (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 9:1) afforded the title product as a yellow oil (0.80 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 1.9 Hz, 1 H), 7.48 (dd, *J* = 7.9, 1.8 Hz, 2 H), 7.27 (t, *J* = 7.9 Hz, 1 H), 5.45 (d, *J* = 2.2 Hz, 1 H), 2.71 (d, *J* = 2.3 Hz, 1 H), 2.31 (s, 1 H).



1-(5-Bromo-2-((4-methoxybenzyl)oxy)phenyl)prop-2-yn-1-ol

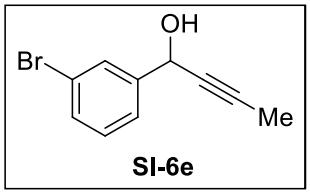
General procedure B was followed using 5-bromo-2-((4-methoxybenzyl)oxy)benzaldehyde[10] (1.61 g, 5.0 mmol), a solution of ethynylmagnesium bromide (12 mL, 0.5 M in THF, 6.0 mmol), and THF (0.010 L) as solvent. Chromatographic purification (hexanes / EtOAc 19:1 → 4:1) afforded the title product as a colorless solid (0.67 g, 83%). m.p. 89–91 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.5 Hz, 1 H), 7.40 (dd, *J* = 8.7, 2.5 Hz, 1 H), 7.38 – 7.33 (m, 2 H), 6.96 – 6.90 (m, 2 H), 6.87 (d, *J* = 8.7 Hz, 1 H), 5.67 (dd, *J* = 6.3, 2.3 Hz, 1 H), 5.07 (d, *J* = 2.1 Hz, 2 H), 3.83 (s, 3 H), 2.92 (d, *J* = 6.3 Hz, 1 H), 2.65 (d, *J* = 2.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 155.1, 132.5, 130.9, 130.8, 129.3, 128.1, 114.3, 114.2, 113.5, 82.6, 74.8, 70.7, 60.7, 55.5. IR (film) 3427, 3290, 3070, 3001, 2934, 2835, 2118, 1612, 1589, 1514, 1485, 1464, 1441, 1406, 1381, 1304, 1277, 1244, 1175, 1122, 1032, 951, 849, 822, 810, 654 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M–OH]^+$ ($C_{17}H_{14}O_2Br$) requires *m/z* 329.0177, found *m/z* 329.0176 (0.3 ppm).



SI-6d

1-(5-(Furan-2-yl)-1-methyl-1H-pyrazol-3-yl)prop-2-yn-1-ol

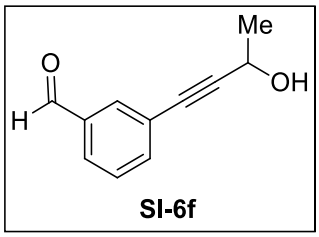
General procedure B was followed using 5-(furan-2-yl)-1-methyl-1H-pyrazole-3-carbaldehyde[11] (0.35 mL, 2.0 mmol), a solution of ethynylmagnesium bromide (5.0 mL, 0.5 M in THF, 2.5 mmol), and THF (7.0 mL) as solvent. Chromatographic purification (hexanes / EtOAc 19:1 → 14:1) afforded the title product as a yellow oil (0.37 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 1.9, 0.8 Hz, 1 H), 6.61 (s, 1 H), 6.57 (dd, *J* = 3.4, 0.8 Hz, 1 H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1 H), 5.56 (d, *J* = 2.2 Hz, 1 H), 4.03 (s, 3 H), 3.23 (s, 1 H), 2.63 (d, *J* = 2.2 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 144.5, 143.0, 135.4, 111.6, 109.0, 103.0, 83.0, 73.8, 58.9, 38.8. IR (film) 3290, 3130, 2951, 2881, 2118, 1529, 1483, 1433, 1381, 1366, 1288, 1232, 1221, 1161, 1067, 1009, 935, 901, 885, 783, 743, 665, 592 cm^{-1}. HRMS (ESI$^+$) mass calculated for $[M+Na]^+$ ($C_{11}H_{10}N_2O_2Na$) requires *m/z* 225.0640, found *m/z* 225.0636 (1.8 ppm).



SI-6e

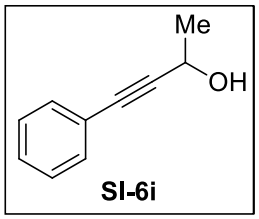
1-(3-Bromophenyl)but-2-yn-1-ol

General procedure B was followed using 3-bromobenzaldehyde (0.82 mL, 7.0 mmol), a solution of propynylmagnesium bromide (21 mL, 0.5 M in THF, 11 mmol), and THF (0.020 L) as solvent. Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title product as a yellow oil (1.5 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 1.9 Hz, 1 H), 7.48 – 7.43 (m, 2 H), 7.28 – 7.21 (m, 1 H), 5.43 – 5.37 (m, 1 H), 2.22 (d, *J* = 4.8 Hz, 1 H), 1.92 (d, *J* = 2.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 131.2, 130.1, 129.7, 125.2, 122.6, 83.8, 78.6, 64.1, 3.7. IR (film) 3346, 3061, 2959, 2918, 2853, 2226, 1593, 1572, 1472, 1427, 1377, 1313, 1298, 1275, 1258, 1188, 1138, 1092, 1070, 997, 889, 862, 766, 700, 671, 635 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{10}H_9BrO$) requires *m/z* 224.0, found *m/z* 224.0.



3-(3-Hydroxybut-1-yn-1-yl)benzaldehyde

An oven-dried Schlenk flask was charged with CuI (9.5 mg, 0.050 mmol), $Pd(PPh_3)_2Cl_2$ (0.070 g, 0.10 mmol), and a magnetic stir bar. The flask was evacuated and backfilled with N_2 three times. MeCN (0.010 mL), 3-bromobenzaldehyde (0.58 mL, 5.0 mmol), NEt_3 (0.010 mL), and but-3-yn-2-ol (0.47 mL, 6.0 mmol) were sequentially injected. The flask was placed in a 60 °C oil bath for 14 h. The reaction was allowed to cool, and the solvent was removed *in vacuo*. The residue was dissolved in Et_2O (50 mL), and washed with 1 N HCl (50 mL), H_2O (50 mL), and brine (50 mL). The organic solution was dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (hexanes / EtOAc 1:0 → 3:1) afforded the title product as a yellow oil (0.72 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.99 (s, 1 H), 7.94 – 7.90 (m, 1 H), 7.83 (dt, *J* = 7.7, 1.5 Hz, 1 H), 7.67 (dt, *J* = 7.7, 1.5 Hz, 1 H), 7.49 (t, *J* = 7.7 Hz, 1 H), 4.78 (q, *J* = 6.6 Hz, 1 H), 2.13 (s, 1 H), 1.58 (d, *J* = 6.6 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 137.3, 136.5, 133.2, 129.3, 129.2, 124.0, 92.7, 82.7, 58.9, 24.4. IR (film) 3385, 2982, 2932, 2868, 2833, 2729, 1699, 1597, 1576, 1477, 1435, 1389, 1329, 1279, 1161, 1103, 1078, 1038, 957, 903, 822, 797, 725, 685, 648 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{11}H_{11}O_2$) requires *m/z* 175.0759, found *m/z* 175.0730 (2.9 mmu).



4-Phenylbut-3-yn-2-ol

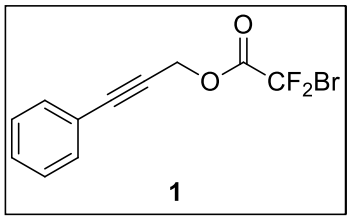
General procedure A was followed using iodobenzene (1.1 g, 0.010 mol), CuI (19 mg, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (0.14 g, 0.20 mmol), 3-butyn-2-ol (0.86 mL, 11 mmol) NEt_3 (0.010 L) and MeCN (0.010 L). Chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title

product as a brown oil (1.3 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2 H), 7.32 (dd, *J* = 5.0, 1.9 Hz, 3 H), 4.77 (q, *J* = 6.6 Hz, 1 H), 2.01 (s, 1 H), 1.57 (d, *J* = 6.6 Hz, 3 H).

Synthesis of Propargyl Bromodifluoroacetates

General Procedure C:

Bromodifluoroacetic acid (BDFA, 1.4 equiv) was added to an oven-dried round bottom flask sealed with a rubber septum. DCM was injected as solvent, and an oil bubbler was attached to the flask. DMF (0.30 equiv) and oxalyl chloride (1.3 equiv) were sequentially injected (caution: rapid evolution of noxious gases), and the solution was allowed to react for 2 h. In a separate oven-dried round bottom flask sealed with a rubber septum, substituted propargyl alcohol (1.0 equiv) was added to a solution of DCM (0.1–0.4 M), NEt_3 (2.0 equiv), and DMAP (for 2° alcohol substrates, 0.2 equiv). The solution was cooled to 0 °C, and an oil bubbler was attached to the flask. The solution of acid chloride was transferred to the solution of alcohol *via* syringe. The mixture was allowed to warm to rt, and stirred for 2–14 h. The reaction was quenched with 1 N HCl, diluted with DCM, and the organic phase was washed with H_2O and brine. The organic solution was dried over Na_2SO_4 and filtered, and the solvent was removed *in vacuo*. Chromatographic purification using a minimum amount of silica gel afforded the desired propargyl bromodifluoroacetate. [Note: some propargyl bromodifluoroacetates are prone to hydrolysis on silica gel].

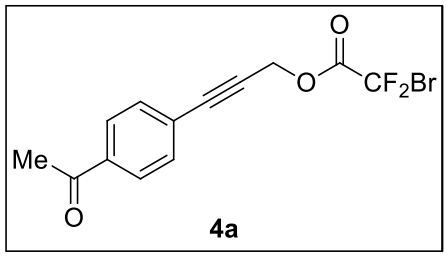


1

3-Phenylprop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

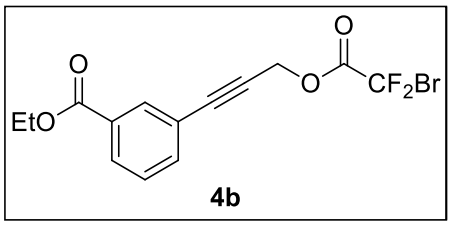
General Procedure C was followed using 3-phenylprop-2-yn-1-ol (1.2 mL, 0.010 mol), BDFA (2.5 g, 14 mmol), oxalyl chloride (1.1 mL, 13 mmol), DMF (0.23 mL, 3.0 mmol), NEt_3 (2.8 mL, 0.020 mol), with DCM (25 mL) as solvent. Workup and chromatographic purification (hexanes / EtOAc 49:1) afforded the title compound as a yellow oil (2.1 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2 H), 7.43 – 7.33 (m, 3 H), 5.19 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$)

δ 159.0 (t, J = 32.0 Hz), 132.0, 129.3, 128.4, 121.4, 108.4 (t, J = 314.3 Hz), 88.7, 80.2, 56.4.^{19}F NMR (376 MHz, $CDCl_3$) δ –61.74 (s, 2 F). IR (film) 3054, 2996, 2941, 1778, 1596, 1482, 1438, 1401, 1357, 1292, 1148, 1130, 1081, 1073, 942, 906, 850, 756, 714, 601 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{11}H_7BrF_2O_2$) requires *m/z* 288.0, found 288.0.



3-(4-Acetylphenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

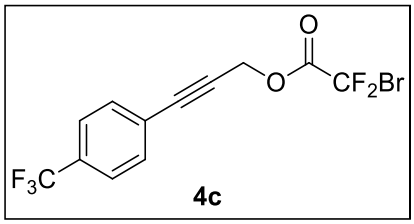
General Procedure C was followed using **SI-4a** (0.52 g, 3.00 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 49:1) afforded the title compound as a yellow oil (0.74 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2 H), 7.57 (d, J = 8.4 Hz, 2 H), 5.19 (s, 2 H), 2.62 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 159.1 (t, J = 32.1 Hz), 137.2, 132.2, 128.3, 126.2, 108.4 (t, J = 314.3 Hz), 87.8, 83.3, 56.2, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.16 (s, 2 F). IR (film) 3060, 2956, 1782, 1685, 1602, 1359, 1290, 1261, 1166, 1120, 1016, 948, 833, 707, 634 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{13}H_9BrF_2O_3$) requires *m/z* 329.9703, found *m/z* 329.9712 (2.7 ppm).



Ethyl 3-(3-(2-bromo-2,2-difluoroacetoxy)prop-1-yn-1-yl)benzoate

General Procedure C was followed using **SI-4b** (612 mg, 3.00 mmol), BDFA (735 mg, 4.20 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 19:1) afforded the title compound as a pale green oil (650 mg, 60%). ^{1}H NMR

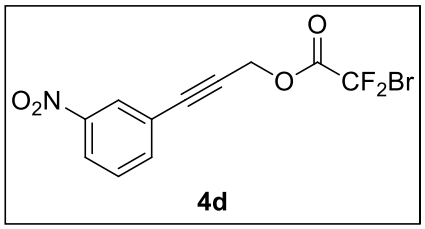
(400 MHz, $CDCl_3$) δ 8.16 (t, *J* = 1.7 Hz, 1 H), 8.05 (dt, *J* = 7.9, 1.4 Hz, 1 H), 7.65 (dt, *J* = 7.8, 1.4 Hz, 1 H), 7.43 (t, *J* = 7.8 Hz, 1 H), 5.18 (s, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 1.41 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 159.1, 136.1, 133.2, 131.0, 130.3, 128.6, 121.9, 108.4, 87.7, 81.1, 61.4, 56.3, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.35 (s, 2 F). IR (film) 3070, 2983, 1782, 1720, 1433, 1369, 1294, 1232, 1168, 1120, 1027, 952, 754, 682 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{14}H_{11}BrF_2O_4$) requires *m/z* 359.9809, found *m/z* 359.9792 (4.7 ppm).



4c

3-(4-(Trifluoromethyl)phenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

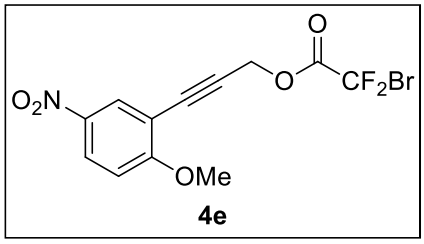
General Procedure C was followed using **SI-4c** (0.60 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes) afforded the title compound as a colorless oil (0.58 g, 54%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4 H), 5.18 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (t, *J* = 32.1 Hz), 132.4, 131.2 (q, *J* = 32.8 Hz), 125.5 (q, *J* = 3.8 Hz), 125.3 (q, *J* = 1.4 Hz), 123.9 (q, *J* = 272.3 Hz), 108.5 (t, *J* = 314.3 Hz), 87.3, 82.7, 56.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.19 (s, 2 F), –63.46 (s, 3 F). IR (film) 3062, 2952, 1782, 1616, 1569, 1438, 1406, 1375, 1325, 1124, 1068, 1018, 950, 842, 717, 702, 597 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{12}H_6BrF_5O_2$) requires *m/z* 355.9471, found *m/z* 355.9465 (1.7 ppm).



4d

3-(3-Nitrophenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

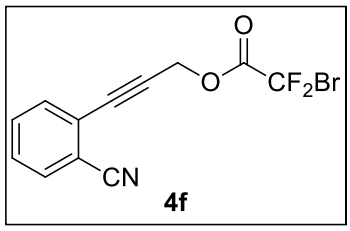
General Procedure C was followed using **SI-4d** (0.53 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 49:1) afforded the title compound as a colorless oil (0.53 g, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (t, *J* = 1.9 Hz, 1 H), 8.24 (ddd, *J* = 8.4, 2.3, 1.1 Hz, 1 H), 7.79 (dt, *J* = 7.7, 1.3 Hz, 1 H), 7.56 (t, *J* = 8.0 Hz, 1 H), 5.19 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (t, *J* = 32.2 Hz), 148.2, 137.7, 129.7, 126.9, 124.1, 123.3, 108.3 (t, *J* = 314.3 Hz), 86.1, 82.9, 55.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.40 (s, 2 H). IR (film) 3085, 2925, 1782, 1531, 1352, 1292, 1166, 1124, 1024, 952, 808, 736, 673 cm^{-1}. HRMS (EI$^+$) mass calculated for $[M]^+$ ($C_{11}H_6NBrF_2O_4$) requires *m/z* 332.9448, found *m/z* 332.9438 (3.0 ppm).



4e

3-(2-Methoxy-5-nitrophenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

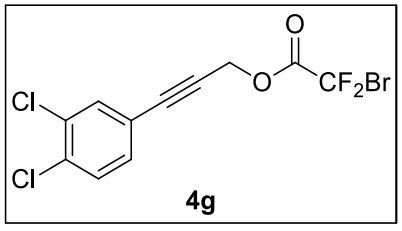
General Procedure B was followed using **SI-4e** (520 mg, 2.5 mmol), BDFA (610 mg, 3.5 mmol), oxalyl chloride (0.28 mL, 3.3 mmol), DMF (58 μL, 0.30 mmol), NEt_3 (0.70 mL, 5.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (DCM) afforded the title compound as a pale yellow solid (0.64 g, 70%). m.p. 120–121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 2.8 Hz, 1 H), 8.26 (dd, *J* = 9.2, 2.8 Hz, 1 H), 6.98 (d, *J* = 9.2 Hz, 1 H), 5.21 (s, 2 H), 4.01 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0, 159.1 (t, *J* = 32.2 Hz), 141.1, 129.7, 126.8, 111.9, 110.6, 108.5 (t, *J* = 314.3 Hz), 86.3, 82.8, 56.8, 56.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.77 (s, 2 F). IR (film) 3090, 2997, 2957, 1786, 1607, 1580, 1518, 1491, 1462, 1441, 1371, 1348, 1283, 1167, 1148, 1119, 1099, 1018, 1007, 947, 910, 885, 833, 804, 748, 727, 708, 636 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{12}H_9NO_5F_2Br$) requires *m/z* 363.9632, found *m/z* 363.9624 (2.2 ppm).



4f

3-(2-Cyanophenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure B was followed using **SI-4f** (470 mg, 3.0 mmol), BDFA (740 mg, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (10 μL, 0.9 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title compound as an orange oil (0.67 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 1 H), 7.63 – 7.56 (m, 2 H), 7.49 (ddd, *J* = 7.8, 6.9, 2.1 Hz, 1 H), 5.23 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (t, *J* = 32.3 Hz), 133.0, 132.9, 132.6, 129.6, 125.3, 117.2, 115.7, 108.4 (t, *J* = 314.3 Hz), 86.6, 84.6, 55.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.16 (s, 2 F). IR (film) 3070, 3001, 2955, 2231, 1782, 1593, 1566, 1483, 1447, 1437, 1373, 1290, 1169, 1122, 1040, 1014, 993, 951, 901, 835, 806, 764, 712, 683, 617 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{12}H_7NO_2F_2Br$) requires *m/z* 313.9628, found *m/z* 313.9631 (1.0 ppm).

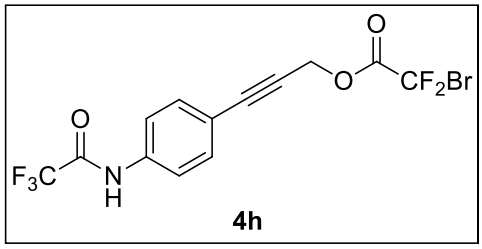


4g

3-(3,4-Dichlorophenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-4g** (0.60 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes) afforded the title compound as a pale yellow oil (0.91 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 1.9 Hz, 1 H), 7.46 – 7.39 (m, 1 H), 7.30 (dd, *J* = 8.3, 1.8 Hz, 1 H), 5.15 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (t, *J* = 32.2 Hz), 134.0, 133.7, 132.9, 131.2, 130.6, 121.4, 108.4 (t, *J* = 314.3 Hz), 86.3, 82.2, 56.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.42 (s, 2 F). IR (film) 3093, 2948,

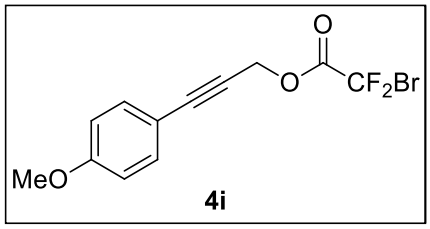
1782, 1463, 1375, 1292, 1170, 1120, 950, 819, 802, 682 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{11}H_5BrCl_2F_2O_2$) requires *m/z* 355.8818, found *m/z* 355.8817 (0.3 ppm).



4h

3-(4-(2,2,2-Trifluoroacetamido)phenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-4h** (0.35 g, 1.4 mmol), BDFA (0.35 g, 2.0 mmol), oxalyl chloride (0.16 mL, 1.9 mmol), DMF (0.033 mL, 0.43 mmol), NEt_3 (0.40 mL, 2.9 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (DCM : acetone 99:1) afforded the title compound as a tan solid (0.33 g, 58%). m.p. 116–117 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1 H), 7.61 – 7.56 (m, 2 H), 7.55 – 7.49 (m, 2 H), 5.17 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (t, *J* = 31.9 Hz), 154.8 (q, *J* = 37.7 Hz), 135.9, 133.3, 120.2, 119.3 (d, *J* = 53.8 Hz), 115.7 (d, *J* = 288.7 Hz), 108.5 (t, *J* = 314.4 Hz), 87.8, 81.1, 56.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.86 (s, 2 F), –75.67 (s, 3 F). IR (film) 3296, 3198, 3134, 2957, 1776, 1703, 1674, 1607, 1543, 1512, 1437, 1410, 1377, 1283, 1265, 1244, 1227, 1202, 1155, 1113, 1018, 945, 906, 837, 806, 741, 719, 689, 619 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{13}H_7NO_3F_5Br$) requires *m/z* 398.9529, found *m/z* 398.9529 (0.0 ppm).

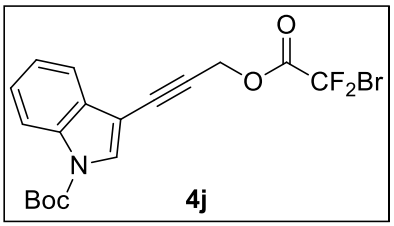


4i

3-(4-Methoxyphenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

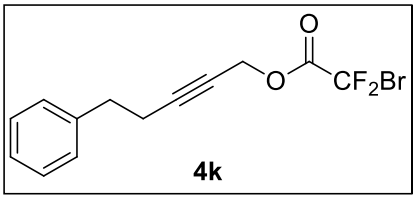
General Procedure C was followed using **SI-4i** (486 mg, 3.00 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as a colorless oil (540 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 2 H), 6.91 – 6.79 (m, 2 H), 5.16 (s, 2 H), 3.83 (s, 3 H). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 160.4, 159.2 (t, *J* = 31.9 Hz), 133.7, 114.1, 113.5, 108.6 (t, *J* = 314.4 Hz), 88.9, 79.1, 56.8, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.30 (s, 2 F). IR (film) 3010, 2839, 1780, 1606, 1510, 1290, 1249, 1172, 1120, 1031, 946, 833, 709, 603 cm^{-1}. HRMS (EI^+) exact mass calculated for $[M]^+$ ($C_{12}H_9BrF_2O_3$) requires *m/z* 317.9703, found *m/z* 317.9700 (0.9 ppm).



Tert-butyl 3-(3-(2-bromo-2,2-difluoroacetoxy)prop-1-yn-1-yl)-1H-indole-1-carboxylate

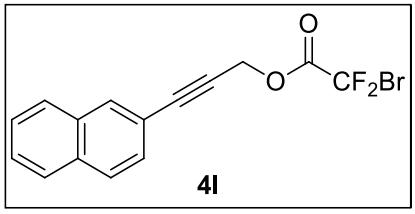
General Procedure B was followed using **SI-4j** (1.1 g, 4.2 mmol), BDFA (1.0 g, 5.8 mmol), oxalyl chloride (0.46 mL, 5.41 mmol), DMF (0.10 mL, 1.3 mmol), NEt_3 (1.2 mL, 8.3 mmol), with DCM (0.040 L) as solvent. Workup (H_2O was used in place of 1 N HCl to quench reaction) and chromatographic purification (hexanes / DCM 7:3) afforded the title compound as a tan solid (1.3 g, 73%). m.p. 49–50 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.3 Hz, 1 H), 7.85 (s, 1 H), 7.67 (ddd, *J* = 7.7, 1.4, 0.7 Hz, 1 H), 7.38 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1 H), 7.32 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1 H), 5.24 (s, 2 H), 1.68 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (t, *J* = 32.0 Hz), 149.0, 134.7, 130.5, 130.3, 125.5, 123.6, 120.1, 115.5, 108.6 (t, *J* = 314.6 Hz), 101.8, 84.8, 83.9, 81.4, 56.8, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.86 (s, 2 F). IR (film) 3153, 3055, 2982, 2935, 1782, 1742, 15558, 1475, 1452, 1371, 1277, 1234, 1155, 1121, 1101, 1051, 1032, 1014, 957, 935, 854, 746 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{18}H_{17}NO_4F_2Br$) requires *m/z* 428.0309, found *m/z* 428.0280 (2.9 mmu).



5-Phenylpent-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using 5-phenylpent-2-yn-1-ol[12] (481 mg, 3.00 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3

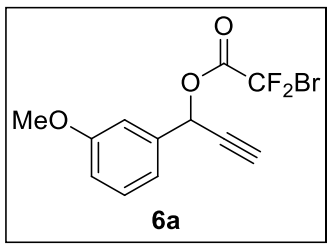
(0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 49:1) afforded the title compound as a colorless oil (752 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2 H), 7.26 – 7.20 (m, 3 H), 4.91 (t, J = 2.2 Hz, 2 H), 2.85 (t, J = 7.5 Hz, 2 H), 2.55 (tt, J = 7.5, 2.2 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1 (t, J = 31.8 Hz), 140.3, 128.6, 128.6, 126.6, 108.6 (t, J = 314.3 Hz), 89.5, 72.6, 56.5, 34.6, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.83 (s, 2 F). IR (film) 3086, 3063, 3028, 2947, 3932, 2864, 1780, 1603, 1497, 1454, 1375, 1294, 1169, 1121, 1018, 953, 839, 806, 746, 698 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{13}H_{11}O_2F_2Br$) requires *m/z* 315.9910, found *m/z* 315.9897 (4.1 ppm).



4l

3-(Naphthalen-2-yl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

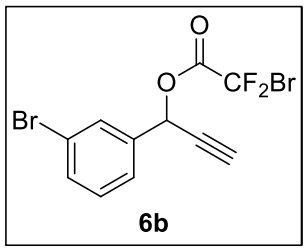
General Procedure C was followed using **SI-4l** (3.00 g, 16.5 mmol), BDFA (4.03 g, 23.0 mmol), oxalyl chloride (1.82 mL, 21.5 mmol), DMF (0.39 mL, 5.0 mmol), NEt_3 (4.60 mL, 33.0 mmol), with DCM (75 mL) as solvent. Workup and chromatographic purification (hexanes / EtOAc 49:1) afforded the title compound as a light yellow oil (4.70 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, J = 1.4 Hz, 1 H), 7.87 – 7.80 (m, 3 H), 7.57 – 7.50 (m, 3 H), 5.23 (s, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2 (t, J = 32.0 Hz), 133.4, 132.9, 132.6, 128.3, 128.3, 128.0, 127.9, 127.3, 126.9, 118.8, 108.6 (t, J = 314.4 Hz), 89.2, 80.6, 56.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.76 (s, 2 F). IR (film) 3059, 2949, 2237, 1780, 1597, 1501, 1437, 1375, 1290, 1169, 1121, 1014, 1005, 955, 939, 895, 860, 818, 746, 710 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{15}H_9O_2F_2Br$) requires *m/z* 337.9754, found *m/z* 337.9734 (2.0 mmu).



6a

1-(3-Methoxyphenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

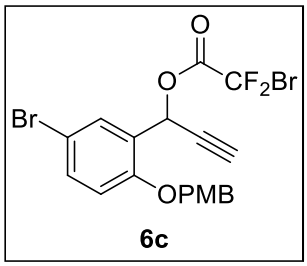
General Procedure C was followed using **SI-6a** (0.49 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (pentane / Et_2O 19:1) afforded the title compound as a colorless oil (0.90 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 1 H), 7.15 (ddt, *J* = 7.6, 1.5, 0.7 Hz, 1 H), 7.11 (dd, *J* = 2.5, 1.7 Hz, 1 H), 6.97 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1 H), 6.50 (d, *J* = 2.3 Hz, 1 H), 3.85 (s, 3 H), 2.83 (d, *J* = 2.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.0, 158.5 (t, *J* = 32.0 Hz), 135.7, 130.2, 120.2, 115.7, 113.4, 108.6 (t, *J* = 314.6 Hz), 78.0, 77.8, 69.6, 55.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ –62.06 (s, 2 F). IR (film) 3296, 3007, 2962, 2943, 2839, 2131, 1778, 1605, 1589, 1491, 1466, 1456, 1437, 1323, 1271, 1167, 1126, 1051, 1018, 957, 908, 868, 835, 785, 752, 694, 656 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{12}H_9O_3F_2Br$) requires *m/z* 317.9703, found *m/z* 317.9685 (1.8 mmu).



6b

1-(3-Bromophenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

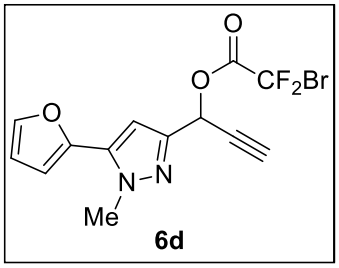
General Procedure C was followed using **SI-6b** (0.63 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as a colorless oil (1.0 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (t, *J* = 1.9 Hz, 1 H), 7.58 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1 H), 7.52 – 7.47 (m, 1 H), 7.32 (t, *J* = 7.9 Hz, 1 H), 6.47 (d, *J* = 2.3 Hz, 1 H), 2.86 (d, *J* = 2.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4 (t, *J* = 32.2 Hz), 136.3, 133.3, 131.0, 130.7, 126.6, 123.0, 108.4 (t, *J* = 314.7 Hz), 78.6, 77.2, 68.7. ^{19}F NMR (376 MHz, $CDCl_3$) ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.16 (d, *J* = 3.8 Hz, 2 F). IR (film) 3300, 3065, 2926, 2854, 2131, 1780, 1597, 1574, 1475, 1431, 1333, 1281, 1252, 1173, 1124, 1074, 1001, 957, 920, 899, 874, 812, 785, 712, 692, 673 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{11}H_6Br_2F_2O_2$) requires *m/z* 365.9, found 365.9.



6c

1-(5-Bromo-2-((4-methoxybenzyl)oxy)phenyl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-6c** (1.04 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as a tan solid (1.07 g, 71%). m.p. 65–68 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 2.5 Hz, 1 H), 7.48 (dd, J = 8.8, 2.5 Hz, 1 H), 7.30 – 7.27 (m, 2 H), 6.93 – 6.89 (m, 2 H), 6.88 – 6.85 (m, 2 H), 5.04 (s, 2 H), 3.82 (s, 3 H), 2.82 (d, J = 2.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 158.2 (t, J = 31.8 Hz), 155.3, 134.2, 132.3, 129.1, 127.8, 124.7, 114.2, 114.1, 113.2, 108.6 (t, J = 314.7 Hz), 78.2, 77.1, 70.6, 64.1, 55.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.88 (s, 2 F). IR (film) 3294, 3011, 2959, 2935, 1776, 1612, 1516, 1487, 1466, 1331, 1288, 1246, 1175, 1124, 1034, 999, 959, 905, 874, 812 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{19}H_{14}Br_2F_2O_4$) requires *m/z* 501.9, found *m/z* 501.9.

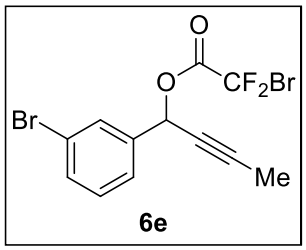


6d

1-(5-(Furan-2-yl)-1-methyl-1H-pyrazol-3-yl)prop-2-yn-1-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-6d** (1.04 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as a light yellow oil (1.07 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, J = 1.8, 0.7 Hz, 1 H), 6.71 (s, 1 H), 6.61 (dd, J = 3.4, 0.7 Hz, 1 H), 6.58 (d, J = 2.3 Hz, 1 H), 6.53 (dd, J = 3.4, 1.8 Hz, 1 H), 4.07 (s, 3 H), 2.80 (d, J = 2.3 Hz, 1 H). ^{13}C NMR

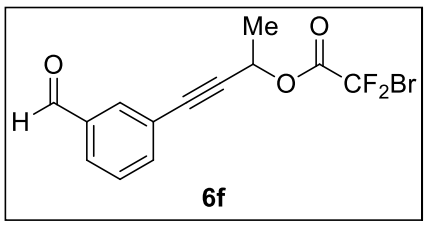
(126 MHz, $CDCl_3$) δ 158.3 (t, *J* = 32.1 Hz), 145.0, 144.0, 143.1, 135.6, 111.6, 109.2, 108.5 (t, *J* = 314.7 Hz), 104.5, 77.0, 63.9, 39.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ [–61.88] – [–61.96] (m, 2 F). IR (film) 3298, 3132, 2953, 2131, 1778, 1531, 1474, 1431, 1381, 1366, 1331, 1283, 1234, 1221, 1165, 1124, 1011, 984, 953, 903, 887, 856, 800, 775, 743, 719, 689, 654, 592 cm^{-1}. HRMS (ESI^+) mass calculated for $[M+H]^+$ ($C_{13}H_{10}BrF_2N_2O_3$) requires *m/z* 358.9843, found *m/z* 358.9839 (1.1 ppm).



6e

1-(3-Bromophenyl)but-2-yn-1-yl 2-bromo-2,2-difluoroacetate

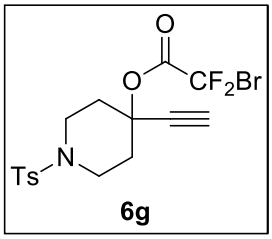
General Procedure C was followed using **SI-6e** (0.68 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), with DCM (0.010 L) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as a colorless oil (0.57 g, 50%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 1.9 Hz, 1 H), 7.55 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1 H), 7.47 (dt, *J* = 7.8, 1.3 Hz, 1 H), 7.30 (t, *J* = 7.9 Hz, 1 H), 6.45 (q, *J* = 2.3 Hz, 1 H), 1.96 (d, *J* = 2.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5 (t, *J* = 31.9 Hz), 137.6, 132.9, 131.0, 130.5, 126.6, 122.9, 108.7 (t, *J* = 314.8 Hz), 87.5, 73.2, 69.8, 4.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.99 (d, *J* = 2.1 Hz, 2 F). IR (film) 3063, 2961, 2922, 2243, 1776, 1595, 1574, 1474, 1431, 1335, 1317, 1281, 1254, 1171, 1124, 1072, 959, 918, 897, 874, 781, 708, 692 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{12}H_8O_2F_2Br_2$) requires *m/z* 379.8859, found *m/z* 379.8853 (1.6 ppm).



6f

4-(3-Formylphenyl)but-3-yn-2-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-6f** (0.70 g, 4.0 mmol), BDFA (0.98 g, 5.6 mmol), oxalyl chloride (0.44 mL, 5.2 mmol), DMF (0.093 mL, 1.2 mmol), NEt_3 (1.1 mL, 8.0 mmol), DMAP (98 mg, 0.80 mmol) with DCM (15 mL) as solvent. Workup and chromatographic purification (hexanes / EtOAc 19:1 → 9:1) afforded the title compound as a yellow oil (1.2 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.97 (td, *J* = 1.7, 0.6 Hz, 1 H), 7.88 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.71 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.53 (t, *J* = 7.7 Hz, 1 H), 5.82 (q, *J* = 6.7 Hz, 1 H), 1.75 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.4, 158.7 (t, *J* = 31.8 Hz), 137.6, 136.6, 133.4, 130.0, 129.3, 122.9, 108.7 (t, *J* = 314.7 Hz), 86.3, 85.4, 65.5, 21.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.60] – [–62.04] (m, 1 F), [–62.05] – [–62.48] (m, 1 F). IR (film) 3069, 2995, 2837, 2241, 1778, 1705, 1601, 1578, 1481, 1447, 1379, 1346, 1323, 1286, 1171, 1136, 1121, 1088, 1024, 955, 847, 797, 756, 714, 683, 604 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{13}H_9F_2BrO_3$) requires *m/z* 329.9703, found *m/z* 329.9702 (0.3 ppm).

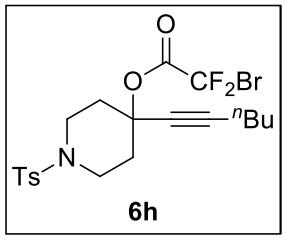


6g

4-Ethynyl-1-tosylpiperidin-4-yl 2-bromo-2,2-difluoroacetate

4-Ethynyl-1-tosylpiperidin-4-ol was prepared using a previously reported procedure.[13] General Procedure C was followed using 4-ethynyl-1-tosylpiperidin-4-ol (0.58 g, 2.1 mmol), BDFA (0.54 g, 3.1 mmol), oxalyl chloride (0.23 mL, 2.7 mmol), DMF (0.048 mL, 0.63 mmol), NEt_3 (0.58 mL, 4.2 mmol), DMAP (26 mg, 0.21 mmol) with DCM (0.010 L) as solvent. Workup and chromatographic purification (DCM) afforded the title compound as a colorless solid (0.71 g, 78%). m.p. 129–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2 H), 7.36 – 7.33 (m, 2 H), 3.27 – 3.20 (m, 2 H), 3.17 – 3.08 (m, 2 H), 2.72 (s, 1 H), 2.44 (s, 3 H), 2.38 – 2.26 (m, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9 (t, *J* = 31.8 Hz), 144.1, 132.8, 129.9, 127.9, 108.3 (t, *J* = 315.6 Hz), 79.3, 77.7, 76.6, 42.3, 35.4, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.21 (s, 2 F). IR (film) 3279, 3032, 2978, 2939, 2862, 2120, 1782, 1597, 1495, 1468, 1456, 1356, 1346, 1327, 1304, 1259, 1215, 1167, 1124, 1094, 1051, 1030, 951, 928, 872, 829, 818, 723, 650, 598, 548

cm^{-1}. HRMS (ESI^+) mass calculated for $[M+K]^+$ ($C_{16}H_{16}BrF_2NO_4SK$) requires *m/z* 473.9589, found *m/z* 473.9574 (3.2 ppm).

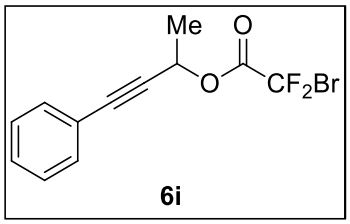


6h

4-(Hex-1-yn-1-yl)-1-tosylpiperidin-4-yl 2-bromo-2,2-difluoroacetate

1-Tosylpiperidin-4-ol was prepared using a previously reported procedure.[14] A 500 mL Schlenk flask was oven-dried was capped with a rubber septum, evacuated and backfilled with dry N_2 (3x), and attached to an oil bubbler. Oxalyl chloride (1.5 mL, 18 mmol) and DCM (0.10 L) were injected, and the solution was cooled to –78 °C. A solution of DMSO (1.9 mL, 26 mmol) in DCM (0.010 L) was injected dropwise over a 5 min period (rapid evolution of noxious gas). After 1 h, a solution of 1-tosylpiperidin-4-ol (2.3 g, 8.8 mmol) in DCM (0.020 mL) was added over a 2 min period. After an additional 1 h, NEt_3 (6.1 mL, 44 mmol) was injected, and the mixture was vigorously stirred. After 15 min, the reaction was allowed to warm to 0 °C and stirred for an additional 1 h. The reaction mixture was washed with H_2O (100 mL) and brine (100 mL). The organic solution was dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (DCM / MeOH 1:0 → 99:1) afforded 1-tosylpiperidin-4-one[15] as a colorless solid (1.9 g, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 3.39 (t, *J* = 6.2 Hz, 4 H), 2.55 (t, *J* = 6.2 Hz, 4 H), 2.45 (s, 3 H). An oven-dried 100 mL Schlenk flask was sealed with a rubber septum, and evacuated and backfilled with dry N_2 (3x). 1-Hexyne (0.45 mL, 3.9 mmol) and THF (0.010 L) were injected, and the solution was cooled to 0 °C. A solution of ^{n}BuLi (2.5 M in hexane, 1.3 mL, 3.3 mmol) was injected dropwise over a 2 min period. The solution was stirred for 30 min, and a solution of 1-tosylpiperidin-4-one (0.76 g, 3.0 mmol) in THF (0.020 L) was injected over a 5 min period. The solution was allowed to warm to rt, and after 6 h, the reaction was quenched with $NH_4Cl_{(aq)}$ (30 mL). The aqueous phase was extracted with DCM (3 x 20 mL), and the organic extracts were combined. The solution was dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (DCM / MeOH 99:1 → 49:1) provided a 4:1 mixture of 4-(hex-1-

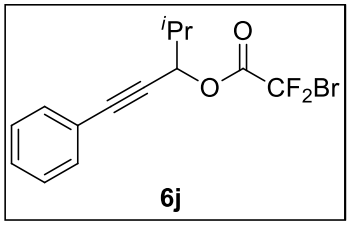
yn-1-yl)-1-tosylpiperidin-4-ol : 1-tosylpiperidin-4-one, which was used without further purification. General Procedure C was followed using BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), DMAP (73 mg, 0.60 mmol) with DCM (0.010 L) as solvent.. Workup and chromatographic purification (DCM) afforded the title compound as a colorless solid (1.0 g, 68% over two steps). m.p. 96–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 3.15 (t, *J* = 5.8 Hz, 4 H), 2.43 (s, 3 H), 2.32 – 2.20 (m, 4 H), 2.16 (t, *J* = 6.9 Hz, 2 H), 1.44 – 1.33 (m, 2 H), 1.34 – 1.24 (m, 2 H), 0.85 (t, *J* = 7.2 Hz, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9 (t, *J* = 31.3 Hz), 143.9, 132.8, 129.8, 127.9, 108.6 (t, *J* = 315.7 Hz), 90.9, 77.9, 76.0, 42.6, 35.9, 30.2, 21.9, 21.6, 18.3, 13.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.12 (s, 2 F). IR (film) 3030, 2959, 2935, 2862, 2249, 1780, 1597, 1495, 1468, 1454, 1431, 1381, 1358, 1323, 1294, 1259, 1209, 1165, 1130, 1101, 1051, 1018, 949, 912, 866, 818, 802, 731, 717, 650 cm^{-1}. HRMS (ESI^+) mass calculated for $[M+Na]^+$ ($C_{20}H_{24}BrF_2NO_4SNa$) requires *m/z* 514.0475, found *m/z* 514.0458 (3.3 ppm).



6i

4-Phenylbut-3-yn-2-yl 2-bromo-2,2-difluoroacetate

General Procedure C was followed using **SI-6i** (0.44 g, 3.0 mmol), BDFA (0.74 g, 4.2 mmol), oxalyl chloride (0.33 mL, 3.9 mmol), DMF (0.070 mL, 0.90 mmol), NEt_3 (0.84 mL, 6.0 mmol), DMAP (74 mg, 0.60 mmol) with DCM (12 mL) as solvent. Workup and chromatographic purification (hexanes / EtOAc 49:1 → 19:1) afforded the title compound as a yellow oil (0.78 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2 H), 7.39 – 7.31 (m, 3 H), 5.82 (q, *J* = 6.7 Hz, 1 H), 1.73 (d, *J* = 6.7 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8 (t, *J* = 31.6 Hz), 132.1, 129.3, 128.5, 121.7, 108.8 (t, *J* = 314.7 Hz), 87.0, 84.8, 65.9, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.57] – [–62.01] (m, 1 F) , [–62.02] – [–62.46] (m, 1 F). IR (film) 3059, 2995, 2939, 1778, 1599, 1491, 1445, 1379, 1346, 1323, 1286, 1169, 1136, 1117, 1086, 1018, 953, 914, 843, 825, 756, 717, 690, 604, 546 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{12}H_9BrF_2O_2$) requires *m/z* 302.0, found 302.0.



6j

4-Methyl-1-phenylpent-1-yn-3-yl 2-bromo-2,2-difluoroacetate

4-Methyl-1-phenylpent-1-yn-3-ol was prepared using a previously reported procedure.[16] General Procedure C was followed using 4-methyl-1-phenylpent-1-yn-3-ol (0.35 g, 2.0 mmol), BDFA (0.49 g, 2.8 mmol), oxalyl chloride (0.22 mL, 2.6 mmol), DMF (0.046 mL, 0.60 mmol), NEt_3 (0.56 mL, 4.0 mmol), DMAP (49 mg, 0.40 mmol) with DCM (8.0 mL) as solvent. Workup and chromatographic purification (hexanes / EtOAc 49:1 → 19:1) afforded the title compound as a colorless oil (0.45 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2 H), 7.39 – 7.31 (m, 3 H), 5.56 (d, *J* = 5.7 Hz, 1 H), 2.24 (pd, *J* = 6.8, 5.7 Hz, 1 H), 1.16 (d, *J* = 6.7 Hz, 3 H), 1.13 (d, *J* = 6.8 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9 (t, *J* = 31.5 Hz), 132.1, 129.2, 128.5, 121.8, 108.8 (t, *J* = 314.7 Hz), 88.1, 82.8, 74.2, 32.9, 18.1, 17.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.78 (s, 2 F). IR (film) 3059, 2970, 2934, 2878, 1778, 1491, 1470, 1445, 1391, 1364, 1340, 1292, 1169, 1124, 1099, 1070, 1030, 991, 957, 937, 895, 864, 854, 756, 690 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{14}H_{13}F_2BrO_2$) requires *m/z* 330.0067, found *m/z* 330.0047 (2.0 mmu).

Synthesis of Trifluoromethyl Allenes

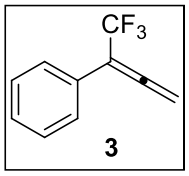
General procedure D:

KF (23 mg, 0.4 mmol) was added to a 15 mL screw-top vial, and dried in a vacuum oven for a minimum of 24 h. The vial was removed from the oven, sealed with a PTFE septum, and allowed to cool under a dry atmosphere of N_2. CuI (3.8 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), and 1,10-phenanthroline (phen, 3.6 mg, 0.020 mmol) or 2,2':6',2"-terpyridine (terpy, 4.6 mg, 0.020 mmol) were added to the vial. The system was resealed, and evacuated and backfilled with dry N_2. DMF (0.2 mL) was injected as solvent, and the mixture was placed in a 50 °C or 60 °C heating block. After 10 min, propargyl bromodifluoroactetate (0.20 mmol) was added to the vial, and heating was maintained for 14 or 24 h. The mixture was cooled to rt, diluted with EtOAc (4 mL), and α,α,α-trifluorotoluene (0.025 mL, 0.20 mmol) was injected as a standard.

After thorough mixing, an aliquot was withdrawn, and analyzed by ^{19}F NMR spectroscopy. The aliquot was recombined with the reaction mixture, which was further diluted with EtOAc (20 mL). The mixture was washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude material was subjected the silica gel chromatography to provide trifluoromethylallenes. The ratio of allene / alkyne products was determined by analysis of the ^1H NMR spectra of purified material.

General procedure E:

KF (23 mg, 0.4 mmol) was added to a 15 mL screw-top vial, and dried in a vacuum oven for a minimum of 24 h. The vial was removed from the oven, sealed with a PTFE septum, and allowed to cool under a dry atmosphere of N_2. Propargyl bromodifluoroacetate (0.2 mmol), CuI (3.8 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), and 1,10-phenanthroline (phen, 3.6 mg, 0.020 mmol) or 2,2':6',2"-terpyridine (terpy, 4.6 mg, 0.020 mmol) were added to the vial. The system was resealed, and evacuated and backfilled with dry N_2. DMF (0.2 mL) was injected as solvent, and the mixture was placed in a 50 °C or 60 °C heating block for 14 or 24 h. The mixture was cooled to rt, diluted with EtOAc (4 mL), and α,α,α-trifluorotoluene (0.025 mL, 0.20 mmol) was injected as a standard. After thorough mixing, an aliquot was withdrawn, and analyzed by ^{19}F NMR spectroscopy. The aliquot was recombined with the reaction mixture, which was further diluted with EtOAc (20 mL). The mixture was washed with H_2O (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and the solvent was removed *in vacuo*. The crude material was subjected the silica gel chromatography to afford trifluoromethylallenes. The ratio of allene / alkyne products was determined by analysis of the ^1H NMR spectra of purified material.

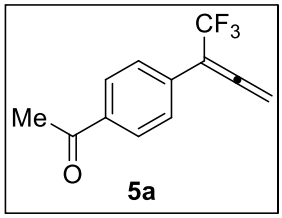


3

(1,1,1-Trifluorobuta-2,3-dien-2-yl)benzene[17]

General procedure D was followed using **2** (0.29 g, 1.0 mmol), CuI (19 mg, 0.10 mmol), phen (18 mg, 0.020 mmol), NaO_2CCF_2Br (49 mg, 0.25 mmol), KF (0.12 g, 2.0 mmol), and DMF (1.0 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (pentane) afforded the title compound as a colorless oil (0.13 g,

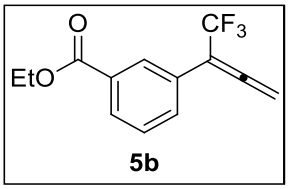
70%). Analysis of the ^{1}H NMR spectrum revealed a >100:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.8 Hz, 2 H), 7.45 – 7.39 (m, 2 H), 7.38 – 7.32 (m, 1 H), 5.57 (q, *J* = 3.4 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.43 (t, *J* = 3.7 Hz, 3 F).



5a

1-(4-(1,1,1-Trifluorobuta-2,3-dien-2-yl)phenyl)ethanone

General procedure D was followed using **4a** (66 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 49:1) afforded the title compound as a yellow oil (31 mg, 69%). Analysis of the ^{1}H NMR spectrum revealed a 33:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 5.64 (q, *J* = 3.3 Hz, 2 H), 2.62 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.2 (q, *J* = 4.1 Hz), 197.5, 136.6, 134.1, 128.8, 127.2 (q, *J* = 1.7 Hz), 123.2 (q, *J* = 273.9 Hz), 101.63 (q, *J* = 34.9 Hz), 84.5, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.41 (t, *J* = 3.4 Hz). IR (film) 3066, 2358, 2341, 1969, 2341, 1969, 1934, 1685, 1605, 1433, 1359, 1307, 1267, 1124, 1107, 935, 869, 840, 717, 609 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{12}H_9F_3O$) requires *m/z* 226.0605, found *m/z* 226.0608 (1.3 ppm).

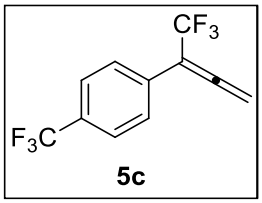


5b

Ethyl 3-(1,1,1-trifluorobuta-2,3-dien-2-yl)benzoate

General procedure D was followed using **4b** (72 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 49:1) afforded the title compound as

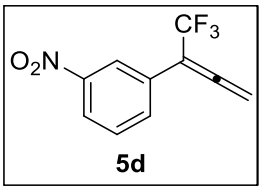
a pale yellow oil (39 mg, 76%). Analysis of the ^{1}H NMR spectrum revealed a 33:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 1 H), 8.00 (dt, *J* = 7.8, 1.4 Hz, 1 H), 7.68 – 7.59 (m, 1 H), 7.46 (t, *J* = 7.8 Hz, 1 H), 5.61 (q, *J* = 3.4 Hz, 2 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 1.41 (t, *J* = 7.1 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.7 (q, *J* = 4.0 Hz), 166.2, 131.3, 131.2 (q, *J* = 1.4 Hz), 129.8, 129.4, 128.9, 128.4, 123.3 (q, *J* = 273.8 Hz), 101.4 (q, *J* = 34.9 Hz), 84.2, 61.4, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.34 (t, *J* = 3.4 Hz, 3 F). IR (film) 3068, 2985, 1973, 1938, 1720, 1606, 1583, 1446, 1367, 1309, 1174, 1124, 1024, 873, 757, 692, 651 cm^{-1}. HRMS (EI^{+}) mass calculated for $[M]^{+}$ ($C_{13}H_{11}F_3O_2$) requires *m/z* 256.0711, found *m/z* 256.0716 (2.0 ppm).



5c

1-(1,1,1-Trifluorobuta-2,3-dien-2-yl)-4-(trifluoromethyl)benzene

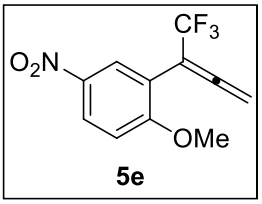
General procedure D was followed using **4c** (71 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 49:1) afforded the title compound as a colorless oil (33 mg, 66%). Analysis of the ^{1}H NMR spectrum revealed a 40:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.5 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 5.64 (q, *J* = 3.4 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.0 (q, *J* = 4.1 Hz), 133.1 (q, *J* = 1.6 Hz), 130.4 (q, *J* = 32.7 Hz), 127.4 (q, *J* = 1.6 Hz), 125.8 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 123.1 (q, *J* = 274.8 Hz), 101.3 (q, *J* = 35.0 Hz), 84.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.50 (t, *J* = 3.5 Hz, 3 F), –63.79 (s, 3 F). IR (film) 3076, 2930, 1971, 1933, 1622, 1435, 1410, 1331, 1308, 1267, 1173, 1130, 1105, 1068, 1018, 937, 868, 843, 735 cm^{-1}. HRMS (EI^{+}) mass calculated for $[M]^{+}$ ($C_{11}H_6F_6$) requires *m/z* 252.0374, found *m/z* 252.0366 (3.2 ppm).



5d

1-Nitro-3-(1,1,1-trifluorobuta-2,3-dien-2-yl)benzene

General procedure D was followed using 4**d** (67 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 9:1) afforded the title compound as a yellow oil (31 mg, 68%). Analysis of the ^{1}H NMR spectrum revealed a 29:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.23 – 8.14 (m, 1 H), 7.83 – 7.73 (m, 1 H), 7.58 (t, *J* = 8.1 Hz, 1 H), 5.71 (q, *J* = 3.3 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9 (q, *J* = 4.0 Hz), 148.7, 132.7 (q, *J* = 1.6 Hz), 131.4, 129.9, 123.1, 123.0 (q, *J* = 273.9 Hz), 122.2 (q, *J* = 1.7 Hz), 100.8 (q, *J* = 35.5 Hz), 85.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.65 (t, *J* = 3.6 Hz, 3 F). IR (film) 3078, 2995, 1974, 1930, 1531, 1350, 1309, 1182, 983, 871, 806, 707, 684 cm^{-1}. HRMS (EI^+) mass calculated for $[M]^+$ ($C_{10}H_6F_3NO_2$) requires *m/z* 229.0351, found *m/z* 229.0322 (12.7 ppm). MS (CI) mass calculated for $[M]^+$ ($C_{10}H_6F_3NO_2$) requires *m/z* 229.0, found *m/z* 229.0

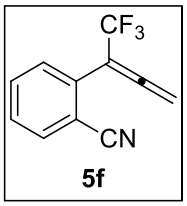


5e

1-Methoxy-4-nitro-2-(1,1,1-trifluorobuta-2,3-dien-2-yl)benzene

General procedure D was followed using 4**e** (73 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 4:1) afforded the title compound as a yellow oil (38 mg, 74%). Analysis of the ^{1}H NMR spectrum revealed a 10:1 ratio of allene / alkyne. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 9.1, 2.8 Hz, 1 H), 8.23 (d, *J* = 2.8 Hz, 1 H), 7.01 (d, *J* = 9.1 Hz, 1 H), 5.42 (q, *J* = 3.4 Hz, 2 H), 3.97 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 209.4 (q, *J* = 3.6 Hz), 162.4, 141.3, 126.7, 126.5, 122.9 (q, *J* = 273.9 Hz), 119.9, 111.0, 95.8 (q, *J*

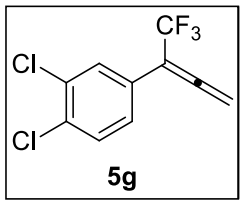
= 37.2 Hz), 82.2, 56.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.07 (t, *J* = 3.6 Hz, 3 F). IR (film) 3082, 2995, 2949, 2847, 1981, 1612, 1585, 1518, 1497, 1464, 1346, 1298, 1273, 1180, 1144, 1121, 1084, 1020, 968, 910, 868, 825, 754, 733, 694, 663, 636. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{11}H_9F_3NO_3$) requires *m/z* 260.0535, found *m/z* 260.0508 (2.7 mmu).



5f

2-(1,1,1-Trifluorobuta-2,3-dien-2-yl)benzonitrile

General procedure D was followed using **4f** (63 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 1:0 → 9:1) afforded the title compound as a colorless oil (27 mg, 64%). Analysis of the ^{1}H NMR spectrum revealed a >100:1 ratio of trifluoromethyl allene / propargyl trifluoromethane. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 1 H), 7.67 – 7.60 (m, 2 H), 7.52 – 7.47 (m, 1 H), 5.63 (q, *J* = 3.4 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.3 (q, *J* = 3.7 Hz), 134.0, 133.0, 132.9, 129.2, 129.1 (q, *J* = 1.4 Hz), 127.8 (q, *J* = 273.8 Hz), 117.2, 113.7, 98.2 (q, *J* = 36.7 Hz), 84.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.10 (t, *J* = 3.7 Hz, 3 F). IR (film) 3074, 2995, 2928, 2854, 2230, 1979, 1936, 1597, 1487, 1448, 1421, 1308, 1259, 1182, 1122, 1101, 1041, 939, 868, 766, 748, 725, 654, 609, 582, 554, 509 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{11}H_7NF_3$) requires *m/z* 210.0531, found *m/z* 210.0509 (2.2 mmu).

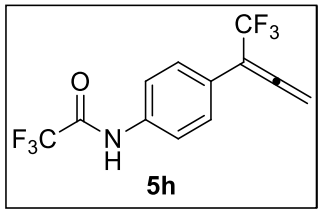


5g

1,2-Dichloro-4-(1,1,1-trifluorobuta-2,3-dien-2-yl)benzene

General procedure D was followed using **4g** (72 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and

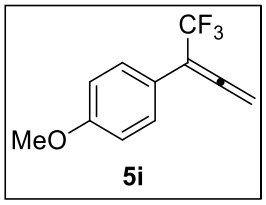
DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes) afforded the title compound as a colorless oil (41 mg, 80%). Analysis of the ^{1}H NMR spectrum revealed a 29:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.1 Hz, 1 H), 7.45 (d, *J* = 8.5 Hz, 1 H), 7.31 – 7.26 (m, 1 H), 5.63 (q, *J* = 3.3 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.6 (q, *J* = 3.9 Hz), 133.2, 132.6, 130.8, 129.4, 129.0 (q, *J* = 1.7 Hz), 126.3 (q, *J* = 1.7 Hz), 123.0 (q, *J* = 273.1 Hz), 100.6 (q, *J* = 35.3 Hz), 84.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.66 (t, *J* = 3.3 Hz, 3 F). IR (film) 3070, 2927, 1973, 1930, 1226, 1475, 1309, 1255, 1178, 1126, 1031, 958, 869, 821, 723 cm^{-1}. HRMS (EI^{+}) mass calculated for $[M]^{+}$ ($C_{10}H_5Cl_2F_3$) requires *m/z* 251.9720, found *m/z* 251.9725 (2.0 ppm).



5h

2,2,2-Trifluoro-N-(4-(1,1,1-trifluorobuta-2,3-dien-2-yl)phenyl)acetamide

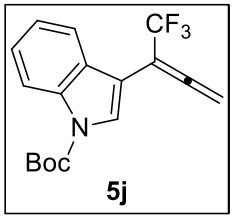
General procedure D was followed using **4h** (0.080 g, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup (wash with 1 N HCl before H_2O and brine washes) and chromatographic purification (hexanes / EtOAc 19:1 → 4:1) afforded the title compound as an amorphous tan solid (27 mg, 46%). Analysis of the ^{1}H NMR spectrum revealed an 8:1 ratio of trifluoromethyl allene / propargyl trifluoromethane. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1 H), 7.63 – 7.58 (m, 2 H), 7.51 – 7.45 (m, 2 H), 5.60 (q, *J* = 3.4 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.7 (q, *J* = 3.9 Hz), 154.9 (q, *J* = 37.5 Hz), 135.0, 133.1, 128.2 (d, *J* = 1.6 Hz), 123.3 (d, *J* = 273.9 Hz), 120.7, 115.7 (q, *J* = 288.8 Hz), 101.3 (q, *J* = 34.8 Hz), 84.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.57 (t, *J* = 3.6 Hz, 3 F), –75.70 (s, 3 F). IR (film) 3302, 2926, 1973, 1705, 1610, 1595, 1541, 1518, 1433, 1410, 1318, 1290, 1265, 1173, 1113, 966, 937, 912, 872, 837, 766, 729, 702, 660, 634, 600 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^{+}$ ($C_{12}H_7NOF_6$) requires *m/z* 295.0432, found *m/z* 295.0422 (3.4 ppm).



5i

1-Methoxy-4-(1,1,1-trifluorobuta-2,3-dien-2-yl)benzene

General procedure D was followed using **4i** (64 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / DCM 19:1) afforded the title compound as a colorless oil (32 mg, 75%). Analysis of the ^{1}H NMR spectrum revealed a >100:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2 H), 6.95 – 6.89 (m, 2 H), 5.52 (q, J = 3.4 Hz, 2 H), 3.83 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.65] – [–61.72] (m, 3 F).

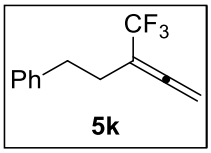


5j

Tert-butyl 3-(1,1,1-trifluorobuta-2,3-dien-2-yl)-1H-indole-1-carboxylate

General procedure E was followed using **4j** (86 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / DCM 19:1 → 9:1) afforded the title compound as a colorless oil (30 mg, 47%). Analysis of the ^{1}H NMR spectrum revealed a 100:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.3 Hz, 1 H), 7.88 (dt, J = 8.0, 1.0 Hz, 1 H), 7.74 (s, 1 H), 7.38 (ddd, J = 8.4, 7.2, 1.3 Hz, 1 H), 7.27 (dt, J = 15.2, 0.9 Hz, 1 H), 5.70 (qd, J = 2.9, 0.9 Hz, 2 H), 1.70 (s, 9 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 208.9 (q, J = 3.7 Hz), 149.5, 135.5, 128.4, 125.2, 123.3 (q, J = 274.3 Hz), 124.2 (q, J = 2.6 Hz), 123.1, 119.9, 115.5, 108.0, 95.7 (q, J = 36.1 Hz), 84.6, 84.5, 28.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.83] – [–61.87] (m, 3 F). IR (film) 3165, 3055, 2982, 2934, 1971, 1940, 1736, 1562, 1452, 1375, 1310, 1290, 1244, 1148, 1117, 1084, 1041, 1024, 883, 854, 762, 746, 729, 692 cm^{-1}. HRMS (APCI–hexane/PhMe)

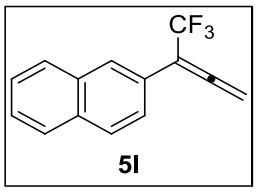
mass calculated for $[M+H]^+$ ($C_{17}H_{17}NO_2F_3$) requires *m/z* 324.1211, found *m/z* 324.1198 (4.0 ppm).



5k

(3-(Trifluoromethyl)penta-3,4-dien-1-yl)benzene

General procedure D was followed using **4k** (63 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), terpy (4.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (pentane) afforded the title compound as a colorless oil (22 mg, 51%). Analysis of the ^{1}H NMR spectrum revealed a 9:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2 H), 7.27 – 7.20 (m, 3 H), 5.19 (h, *J* = 3.5 Hz, 2 H), 2.86 – 2.75 (m, 2 H), 2.47 (ddt, *J* = 11.0, 7.2, 3.3 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6 (q, *J* = 4.3 Hz), 140.7, 128.44, 128.41, 126.2, 123.8 (q, *J* = 273.1 Hz), 98.0 (q, *J* = 33.9 Hz), 82.4, 33.5, 27.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.24 (s, 3 F). IR (film) 3088, 3065, 3030, 2928, 2860, 1985, 1954, 1605, 1497, 1454, 1333, 1263, 1202, 1155, 1119, 1082, 1055, 1030, 980, 864, 744, 700 cm^{-1}. MS (CI) mass calculated for $[M]^+$ ($C_{12}H_{11}F_3$) requires *m/z* 212.1, found *m/z* 212.1.

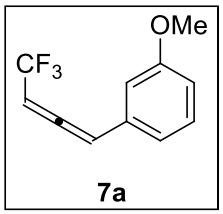


5l

2-(1,1,1-Trifluorobuta-2,3-dien-2-yl)naphthalene[17]

KF (813 mg, 14.0 mmol) and a stir bar were added to a 25 mL round-bottom flask, and placed in a 200 °C vacuum-oven. After 24 h, the flask was equipped with a 3-way flushing adaptor, and allow to cool under an atmosphere of dry N_2. The flask was charged with CuI (133 mg, 0.700 mmol), phen (126 mg, 0.700 mmol), and NaO_2CCF_2Br (345 mg, 1.75 mmol). The system was evacuated and backfilled with dry N_2 (3x), and remained under a positive pressure of N_2 during the course of the reaction. DMF (7.00 mL) was injected, and the flask was immersed in a 50 °C oil bath (Note: evolution of CO_2). After 10 min, **5l** (2.37 g, 7.00 mmol) was injected, and the

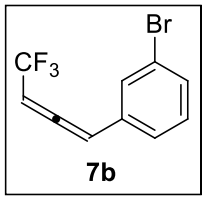
mixture was stirred for 14 h. The reaction was allowed to cool to rt, and diluted with EtOAc (100 mL). The mixture was washed with 1 N HCl (100 mL), water (100 mL), and brine (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed *in vacuo*. Chromatographic purification (hexanes / EtOAc 19:1) afforded the title compound as an amorphous yellow solid (1.33 g, 81%) Analysis of the ^{1}H NMR spectrum revealed a 40:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1 H), 7.89 – 7.80 (m, 3 H), 7.54 (dd, J = 8.8, 1.9 Hz, 1 H), 7.53 – 7.48 (m, 2 H), 5.63 (q, J = 3.3 Hz, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.21 (d, J = 4.1 Hz, 3 F).



7a

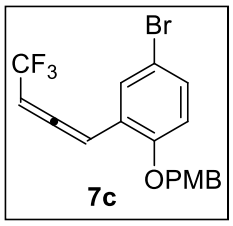
1-Methoxy-3-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene

General procedure D was followed using **6a** (64 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (pentane / Et_2O 49:1 → 19:1) afforded the title compound as a colorless oil (35 mg, 82%). Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1 H), 6.92 (dt, J = 7.8, 1.2 Hz, 1 H), 6.88 – 6.83 (m, 2 H), 6.65 (dq, J = 6.4, 3.8 Hz, 1 H), 5.89 (p, J = 5.9 Hz, 1 H), 3.83 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.1 (q, J = 5.8 Hz), 160.1, 132.2 (q, J = 1.7 Hz), 130.1, 122.5 (q, J = 271.1 Hz), 120.3, 114.4, 112.9, 101.4, 89.8 (q, J = 39.2 Hz), 55.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ [–61.15] – [–61.21] (m, 3 F). IR (film) 3007, 2962, 2943, 2839, 1969, 1599, 1583, 1493, 1470, 1441, 1414, 1398, 1306, 1286, 1263, 1225, 1130, 1047, 885, 872, 841, 785, 754, 735, 689, 648, 636 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{11}H_{10}F_3O$) requires *m/z* 215.0684, found *m/z* 215.0675 (4.2 ppm).



1-Bromo-3-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene

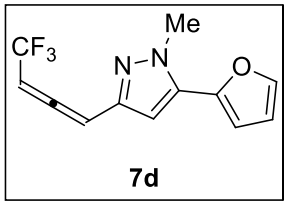
General procedure D was followed using **6b** (74 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 49:1 → 19:1) afforded the title compound as a colorless oil (39 mg, 74%). Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2 H), 7.26 – 7.22 (m, 2 H), 6.62 (dq, J = 6.4, 3.8 Hz, 1 H), 5.94 (p, J = 5.9 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.1 (q, J = 5.7 Hz), 133.1 (d, J = 1.7 Hz), 131.7, 130.6, 130.4, 126.2, 123.2, 122.3 (q, J = 271.2 Hz), 100.4, 90.3 (q, J = 39.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.34] – [–61.42] (m, 3 F). IR (film) 3069, 2957, 1967, 1705, 1593, 1572, 1475, 1429, 1416, 1371, 1348, 1259, 1192, 1163, 1132, 1074, 1018, 997, 883, 856, 787, 750, 694, 673 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{10}H_6F_3Br$) requires *m/z* 261.9605, found *m/z* 261.9589 (1.6 mmu).



4-Bromo-1-((4-methoxybenzyl)oxy)-2-(4,4,4-trifluorobuta-1,2-dien-1-yl)benzene

General procedure D was followed using **6c** (101 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / DCM 4:1) afforded the title compound as a colorless oil (32 mg, 40%). Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 2.5 Hz, 1 H), 7.36 – 7.31 (m, 3 H), 6.99 (dq, J = 6.6, 4.0 Hz, 1 H), 6.96 – 6.91 (m, 2 H), 6.84 (d, J = 8.8 Hz, 1 H), 5.82 (p, J = 5.9 Hz, 1 H), 5.02 (s, 2 H), 3.84 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.5 (q, J = 5.8 Hz), 159.6,

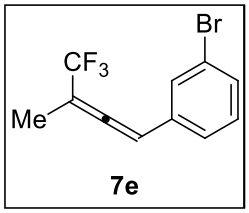
154.7, 132.3, 131.1, 129.3, 128.0, 122.4 (q, J = 271.0 Hz), 121.9 (q, J = 1.7 Hz), 114.3, 114.1, 113.3, 94.9, 89.2 (q, J = 39.1 Hz), 70.6, 55.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ [–61.23] – [–61.31] (m, 3 F). IR (film) 3016, 2957, 2935, 2837, 1967, 1612, 1587, 1516, 1491, 1466, 1416, 1404, 1379, 1304, 1246, 1175, 1130, 1036, 1001, 887, 864, 824, 806, 690, 646 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M–H]^+$ ($C_{18}H_{13}O_2F_3Br$) requires *m/z* 397.0051, found *m/z* 397.0039 (3.0 ppm).



7d

5-(Furan-2-yl)-1-methyl-3-(4,4,4-trifluorobuta-1,2-dien-1-yl)-1H-pyrazole

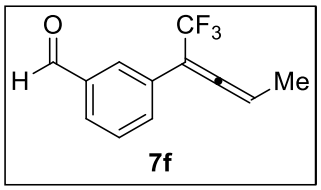
General procedure D was followed using **6d** (72 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / DCM 4:1) afforded the title compound as a colorless oil (36 mg, 70%). Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, J = 1.9, 0.8 Hz, 1 H), 6.75 (dq, J = 6.6, 3.8 Hz, 1 H), 6.59 (dd, J = 3.4, 0.8 Hz, 1 H), 6.52 (dd, J = 3.4, 1.8 Hz, 1 H), 6.49 (s, 1 H), 5.86 (dq, J = 5.8, 6.5 Hz, 1 H), 4.04 (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.8 (q, J = 5.8 Hz), 144.4, 143.1, 142.4 (q, J = 1.9 Hz), 135.8, 122.3 (q, J = 271.0 Hz), 111.7, 109.2, 103.6, 94.1, 89.3 (q, J = 39.2 Hz), 38.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ [–61.31] – [–61.35] (m, 3 F). IR (film) 3126, 3013, 2955, 1975, 1531, 1472, 1427, 1394, 1367, 1294, 1269, 1252, 1221, 1128, 1007, 903, 885, 841, 797, 741, 710, 687, 592, 571 cm^{-1}. HRMS (ESI^+) mass calculated for $[M+H]^+$ ($C_{12}H_{10}F_3N_2O$) requires *m/z* 255.0745, found *m/z* 255.0737 (3.1 ppm).



7e

1-Bromo-3-(4,4,4-trifluoro-3-methylbuta-1,2-dien-1-yl)benzene

General procedure D was followed using **6e** (76 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 50 °C for 14 h. Workup and chromatographic purification (hexanes / EtOAc 49:1) afforded the title compound as a colorless oil (39 mg, 70%). Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2 H), 7.25 – 7.20 (m, 2 H), 6.47 (hept, J = 3.1 Hz, 1 H), 1.99 (d, J = 3.0 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.2 (q, J = 4.0 Hz), 134.4, 131.3, 130.5, 130.3, 126.1, 123.5 (q, J = 273.9 Hz), 123.1, 99.1, 98.6 (q, J = 35.4 Hz), 13.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.59 (d, J = 3.2 Hz, 3 F). IR (film) 3063, 3001, 2962, 2932, 2862, 1971, 1742, 1703, 1593, 1568, 1477, 1464, 1429, 1381, 1302, 1267, 1211, 1190, 1153, 1122, 1090, 1072, 1036, 997, 976, 947, 903, 883, 862, 845, 825, 779, 760, 744, 683, 671, 646, 615 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{11}H_8F_3Br$) requires *m/z* 275.9761, found *m/z* 275.9781 (2.0 mmu).

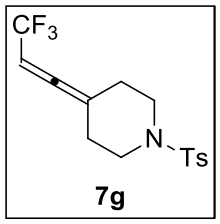


7f

3-(1,1,1-Trifluoropenta-2,3-dien-2-yl)benzaldehyde

General procedure D was followed using **6f** (66 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 60 °C for 24 h. Workup and chromatographic purification (hexanes / EtOAc 49:1 → 9:1) afforded the title compound as a yellow oil (19 mg, 43%). Analysis of the ^{1}H NMR spectrum revealed a 25:1 ratio of allene / alkyne. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.04 (s, 1 H), 7.94 – 7.91 (m, 1 H), 7.83 (dt, J = 7.7, 1.4 Hz, 1 H), 7.70 (ddt, J = 7.9, 2.0, 1.0 Hz, 1 H), 7.55 (t, J = 7.7 Hz, 1 H), 6.02 (qd, J = 7.4, 3.7 Hz, 1 H), 1.93 (d, J = 7.4 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.4 (q, J = 4.0 Hz), 192.0, 136.9, 132.8 (t, J = 1.6 Hz), 131.6, 129.5, 129.2, 128.4, 123.3 (q, J = 273.9 Hz), 100.5 (q, J = 35.0 Hz), 95.9, 13.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.53 (d, J = 3.1 Hz, 3 F). IR (film) 3067, 2961, 2930, 2853, 2822, 2729, 1961, 1707, 1601, 1583, 1485, 1443, 1398, 1373, 1310, 1246, 1194, 1157, 1121, 1070, 1034, 982, 968, 916, 837, 800, 733, 692, 681, 660, 646, 590, 538 cm^{-1}.

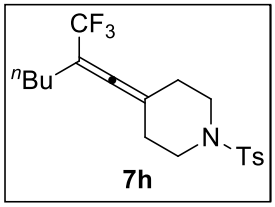
HRMS (APCI–hexane/PhMe) mass calculated for $[M+H]^+$ ($C_{12}H_{10}OF_3$) requires *m/z* 227.0684, found *m/z* 227.0671 (1.3 mmu).



7g

1-Tosyl-4-(3,3,3-trifluoroprop-1-en-1-ylidene)piperidine

General procedure E was followed using **6g** (87 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), terpy (4.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 60 °C for 24 h. Workup (DCM used in place of EtOAc for extraction) and chromatographic purification (DCM) afforded the title compound as a colorless solid (41 mg, 62%). m.p. 102–103 °C. Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 2 H), 7.37 – 7.31 (m, 2 H), 5.35 (qp, *J* = 6.4, 2.2 Hz, 1 H), 3.24 (dt, *J* = 11.3, 5.6 Hz, 2 H), 3.11 – 3.03 (m, 2 H), 2.45 (s, 3 H), 2.42 (ddt, *J* = 7.0, 3.8, 1.4 Hz, 4 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.2 (q, *J* = 5.8 Hz), 144.0, 133.4, 130.0, 127.7, 122.6 (q, *J* = 270.5 Hz), 105.2, 85.3 (q, *J* = 39.1 Hz), 46.7, 29.5 (q, *J* = 1.3 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.72 (d, *J* = 6.0 Hz, 3 F). IR (film): 3032, 2962, 2918, 2849, 1985, 1597, 1464, 1437, 1354, 1339, 1306, 1277, 1250, 1198, 1167, 1122, 1038, 1018, 976, 924, 843, 816, 725, 689, 654, 627, 563 cm^{-1}. HRMS (ESI^+) mass calculated for $[M+Na]^+$ ($C_{15}H_{16}F_3NO_2SNa$) requires *m/z* 354.0752, found *m/z* 354.0760 (2.3 ppm).

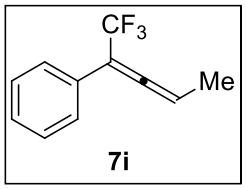


7h

1-Tosyl-4-(2-(trifluoromethyl)hex-1-en-1-ylidene)piperidine

General procedure E was followed using **6h** (0.20 g, 0.40 mmol), CuI (7.6 mg, 0.040 mmol), phen (7.2 mg, 0.040 mmol), NaO_2CCF_2Br (0.020 g, 0.10 mmol), KF (46 mg, 0.80 mmol), and

DMF (0.40 mL) as solvent. The reaction was heated at 60 °C for 24 h. Workup (DCM used in place of EtOAc for extraction) and chromatographic purification (DCM) afforded the title compound as a colorless solid (0.13 g, 81%). m.p. 73–74 °C. Alkyne-containing product was not observed by ^{1}H or ^{19}F NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 3.25 (dt, *J* = 11.2, 5.4 Hz, 2 H), 3.04 (dt, *J* = 11.7, 5.9 Hz, 2 H), 2.46 (s, 3 H), 2.39 (t, *J* = 5.7 Hz, 4 H), 2.09 (t, *J* = 7.0 Hz, 2 H), 1.42 – 1.24 (m, 4 H), 0.85 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1 (q, *J* = 4.4 Hz), 143.9, 133.5, 129.9, 127.7, 123.8 (q, *J* = 273.5 Hz), 105.1, 98.3 (q, *J* = 33.5 Hz), 47.0, 30.0, 29.6, 26.1, 22.0, 21.7, 13.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ –65.39 (s, 3 F). IR (film) 3030, 2959, 2930, 2860, 1979, 1597, 1495, 1466, 1456, 1441, 1427, 1356, 1339, 1290, 1248, 1211, 1198, 1167, 1117, 1103, 1040, 1018, 980, 970, 933, 922, 816, 800, 719, 689, 677, 654, 635 cm^{-1}. HRMS (ESI^{+}) mass calculated for $[M+Na]^{+}$ ($C_{19}H_{24}F_3NO_2SNa$) requires *m/z* 410.1378, found *m/z* 410.1367 (2.7 ppm).

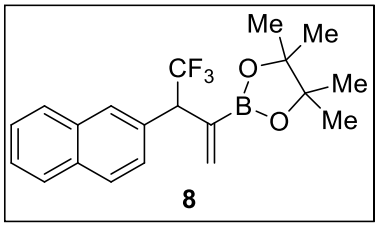


7i

(1,1,1-Trifluoropenta-2,3-dien-2-yl)benzene[18]

General procedure D was followed using **6i** (61 mg, 0.20 mmol), CuI (3.8 mg, 0.020 mmol), phen (3.6 mg, 0.020 mmol), NaO_2CCF_2Br (9.8 mg, 0.050 mmol), KF (23 mg, 0.40 mmol), and DMF (0.20 mL) as solvent. After activation, the reaction was heated at 60 °C for 24 h. Workup and chromatographic purification (pentane) afforded the title compound as a colorless oil (17 mg, 42%). Analysis of the ^{1}H NMR spectrum revealed a >100:1 ratio of allene / alkyne. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2 H), 7.40 – 7.34 (m, 2 H), 7.34 – 7.28 (m, 1 H), 5.93 (qq, *J* = 6.9, 3.2 Hz, 1 H), 1.89 (d, *J* = 7.3 Hz, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.46 (d, *J* = 3.1 Hz, 3 F).

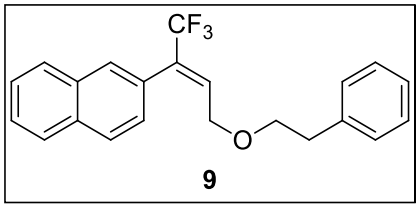
Functionalization Reactions of Trifluoromethylallenes



8

4,4,5,5-Tetramethyl-2-(4,4,4-trifluoro-3-(naphthalen-2-yl)but-1-en-2-yl)-1,3,2-dioxaborolane

In a N_2 filled glovebox, a 15 mL screw-top vial was charged with CuCl (1.0 mg, 0.010 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (4.3 mg, 0.010 mmol), NaO^{t}Bu (7.7 mg, 0.080 mmol) and THF (1.0 mL), and the solution was stirred for 1 h. Bis(pinacolato)diboron (56 mg, 0.22 mmol) was added, and the mixture was stirred for 30 min. Allene **5l** (47 mg, 0.20 mmol) and MeOH (49 μL, 1.2 mmol) were added, and the vial was sealed and removed from the glovebox and stirred for 14 h. The mixture was filtered through a pad of SiO_2, and the pad was rinsed with Et_2O (3 x 4 mL). The solvent was removed *in vacuo* to provide a brown oil. Chromatographic purification (hexanes / EtOAc 1:0 → 19:1) afforded the title compound as a colorless solid (59 mg, 82%). m.p. 84–86. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4 H), 7.53 – 7.44 (m, 3 H), 6.20 (s, 1 H), 6.07 (s, 1 H), 4.57 (q, J = 9.8 Hz, 1 H), 1.19 (s, 6 H), 1.09 (s, 6 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 133.3, 132.9, 132.2, 132.2, 129.1, 128.2, 128.1, 127.7, 127.6, 126.5 (q, J = 281.3 Hz), 126.3, 126.2, 84.1, 52.6 (q, J = 26.8 Hz), 24.8, 24.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.62 (d, J = 9.7 Hz). IR (film) 3059, 2978, 2930, 1701, 1622, 1601, 1437, 1381, 1373, 1362, 1337, 1321, 1258, 1213, 1140, 1097, 964, 872, 856, 843, 816, 746, 723 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{20}H_{22}O_2F_3B$) requires *m/z* 362.1665, found *m/z* 362.1667 (0.6 ppm).

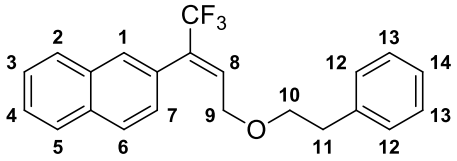


9

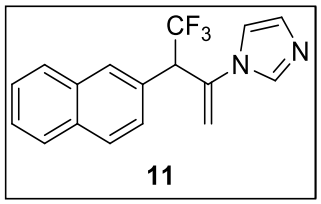
(*E*)-2-(1,1,1-Trifluoro-4-phenethoxybut-2-en-2-yl)naphthalene

In a N_2 filled glovebox, a 15 mL screw-top vial was charged with chloro[1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene]gold(I) (12 mg, 0.020 mmol), AgOTf (5.2 mg, 0.020

mmol), and PhMe (0.20 mL). The mixture was stirred for 5 min, after which a solution of allene **5l** (47 mg, 0.20 mmol) and 2-phenylethanol (26 μL, 0.22 mmol) in PhMe (0.30 mL) was injected. The vial was sealed and removed from the glovebox. After stirring for 36 h at rt, the solvent was removed *in vacuo*. Chromatographic purification (hexanes / DCM 1:0 → 4:1) afforded the title compound as a colorless oil (56 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.83 (m, 3 H), 7.72 (s, 1 H), 7.59 – 7.51 (m, 2 H), 7.35 (dd, *J* = 8.5, 1.7 Hz, 1 H), 7.32 – 7.26 (m, 2 H), 7.24 – 7.21 (m, 1 H), 7.21 – 7.17 (m, 2 H), 6.64 (tq, *J* = 5.9, 1.5 Hz, 1 H), 4.02 (dq, *J* = 6.1, 2.0 Hz, 2 H), 3.59 (t, *J* = 7.1 Hz, 2 H), 2.86 (t, *J* = 7.1 Hz, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 133.7 (q, *J* = 5.4 Hz), 133.3, 133.1 (q, *J* = 30.2 Hz), 133.0, 129.1, 129.0, 129.0, 128.5, 128.4, 128.3, 127.9, 127.0, 126.7, 126.7, 126.4, 123.3 (q, *J* = 273.4 Hz), 71.9, 67.2, 36.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ –66.81 (m, 3 F). IR (film) 3061, 3021, 2935, 2920, 2862, 1601, 1504, 1497, 1477, 1454, 1350, 1331, 1296, 1244, 1177, 1163, 1121, 999, 968, 926, 899, 860, 820, 750, 719, 698 cm^{-1}. HRMS (APCI–hexane/PhMe) mass calculated for $[M]^+$ ($C_{22}H_{19}OF_3$) requires *m/z* 356.1388, found *m/z* 356.1374 (3.9 ppm).



position	^{1}H NMR			NOESY
	□	multiplicity	*J* (Hz)	correlations
1	7.72	s	–	2, 9
2	7.87–7.83	m	–	1, 3
3	7.59–7.51	m	–	2, 4
4	7.59–7.51	m	–	3, 5
5	7.92–7.83	m	–	4, 6
6	7.92–7.83	m	–	5, 7
7	7.35	dd	8.5, 1.7	6, 9
8	6.64	tq	5.9, 1.5	9, 10
9	4.02	dq	6.1, 2.0	1, 7, 8, 10, 11
10	3.59	t	7.1	8, 9, 11, 12
11	2.86	t	7.1	9, 10, 12
12	7.21–7.17	m	–	10, 11, 13
13	7.32–7.26	m	–	12, 14
14	7.24–7.21	m	–	13



11

1-(4,4,4-Trifluoro-3-(naphthalen-2-yl)but-1-en-2-yl)-1H-imidazole

In a N_2 filled glovebox, a 15 mL screw-top vial was charged with allylpalladium(II) chloride dimer (1.8 mg, 0.0050 mmol), 1,1'-bis(diphenylphosphino)ferrocene (5.5 mg, 0.010 mmol), and THF (0.50 mL). The mixture was stirred for 5 min, after which allene **5l** (47 mg, 0.20 mmol) and imidazole (16 mg, 0.24 mmol) were added. The vial was sealed, removed from the glovebox, and placed in a 80 °C oil bath. After 24 h, the mixture was allowed to cool to rt and the solvent was removed *in vacuo*. Chromatographic purification (DCM / MeOH 1:0 → 19:1) afforded the title compound as an amorphous brown solid (41 mg, 67%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.56 – 7.44 (m, 4 H), 7.27 (s, 1 H), 7.23 – 7.17 (m, 2 H), 7.14 – 7.08 (m, 1 H), 7.01 (s, 1 H), 6.38 (t, J = 1.3 Hz, 1 H), 5.08 (m, 1 H), 4.86 (m, 1 H), 4.07 (q, J = 8.9 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.3, 136.1, 133.5, 133.3, 130.2, 129.3, 129.2, 128.4, 128.2, 127.9, 127.2, 127.0, 126.0, 124.9 (q, J = 280.4 Hz), 118.0, 111.2 (q, J = 2.1 Hz), 54.8 (q, J = 28.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ –67.34 (d, J = 8.6 Hz). IR (film) 3113, 3057, 3024, 2918, 1653, 1601, 1510, 1487, 1373, 1348, 1315, 1256, 1163, 1126, 1107, 1072, 1005, 903, 858, 818, 748, 689, 658 cm^{-1}. HRMS (ESI^+) exact mass calculated for $[M+H]^+$ ($C_{17}H_{14}F_3N_2$) requires *m/z* 303.1109, found *m/z* 303.1101 (2.6 ppm).

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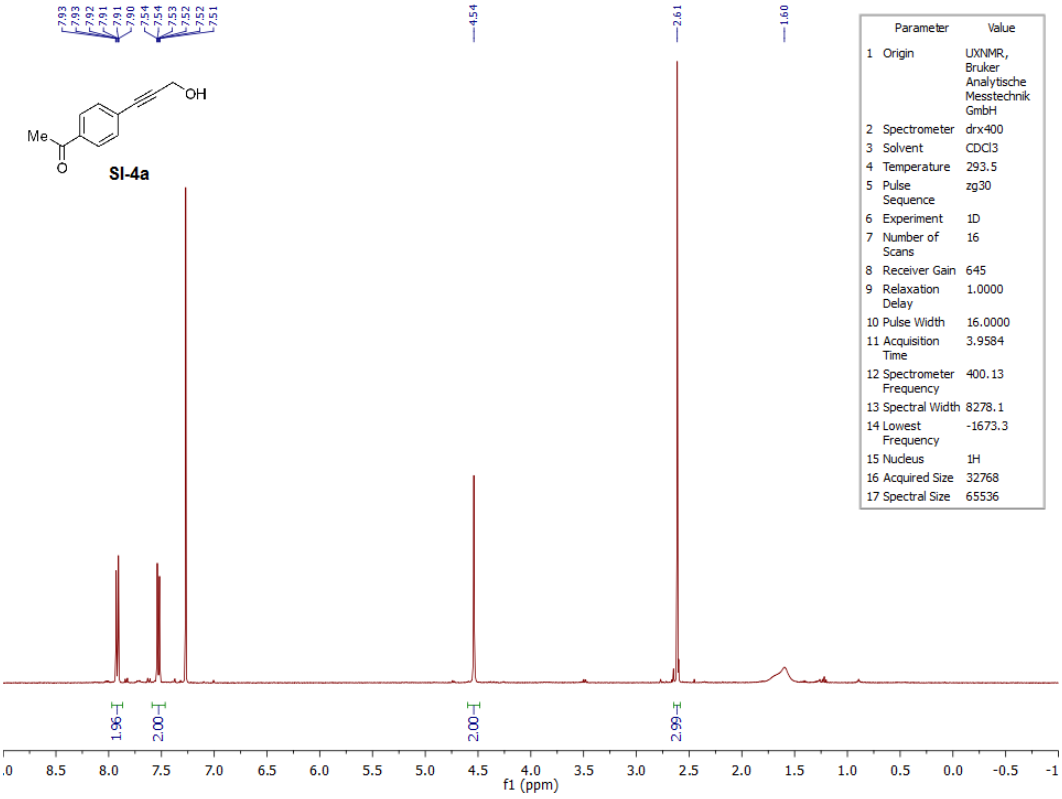
7.93
7.93
7.92
7.91
7.91
7.90
7.54
7.54
7.53
7.52
7.52
7.51
4.54
2.61
1.60
OH
Me
O
SI-4a
Parameter Value
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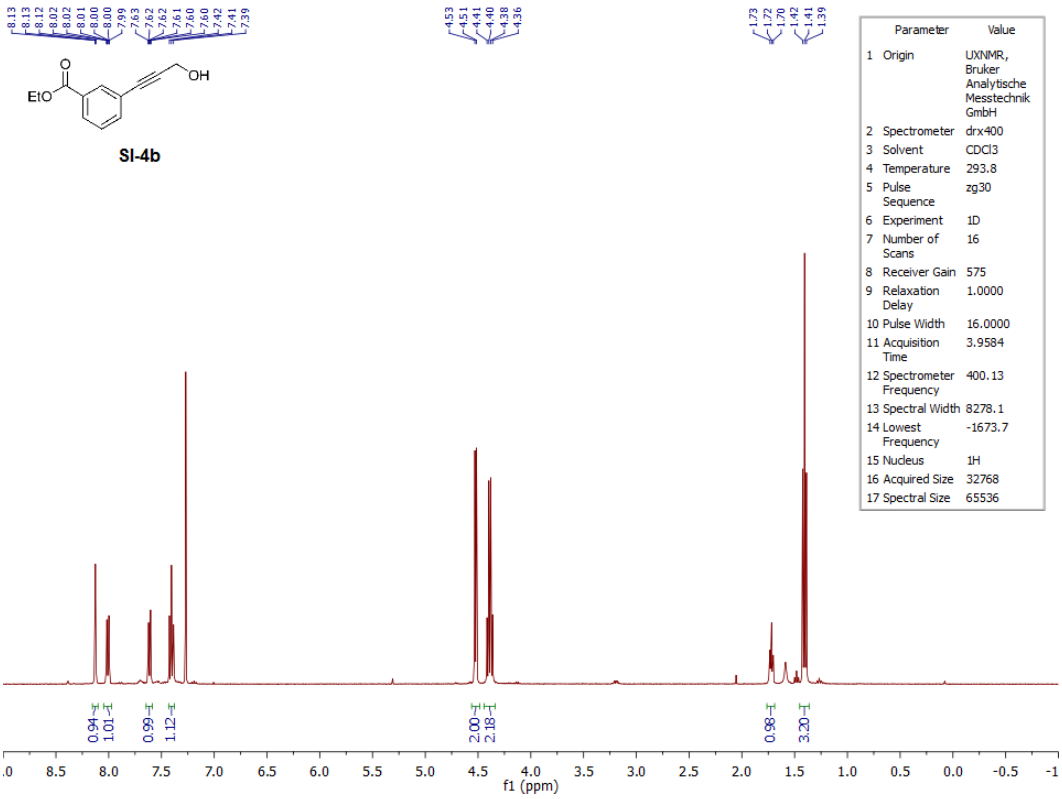
3 Solvent CDCl3
4 Temperature 293.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 645
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
1.96
2.00
2.00
2.99
f1 (ppm)


8.13
8.13
8.12
8.02
8.02
8.01
8.00
8.00
7.99
7.63
7.62
7.62
7.61
7.60
7.42
7.41
7.39
4.53
4.51
4.41
4.40
4.38
4.36
1.73
1.72
1.70
1.42
1.41
1.39
EtO
O
OH
SI-4b
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.7
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
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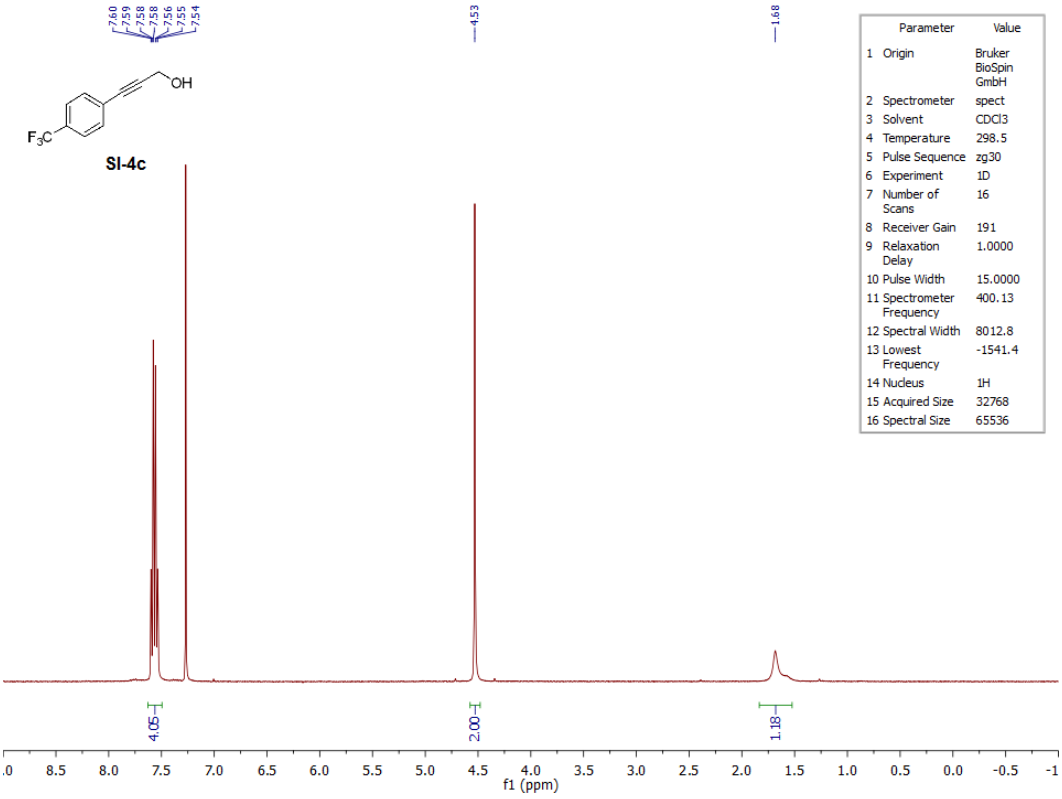
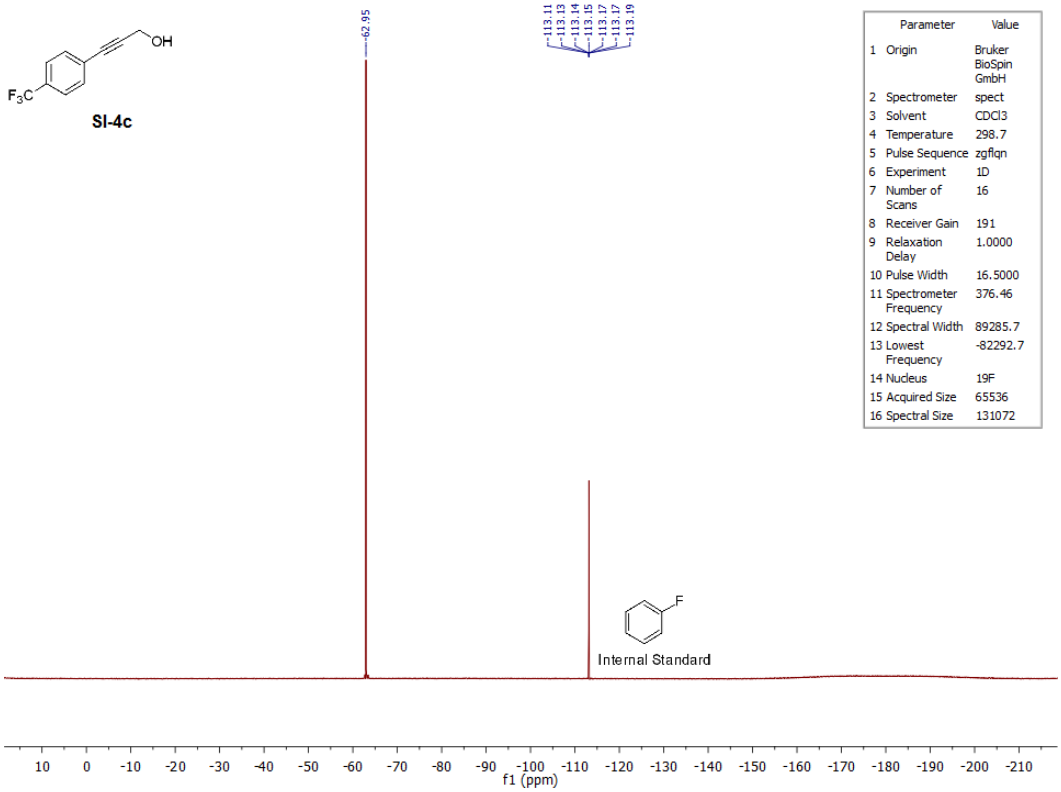
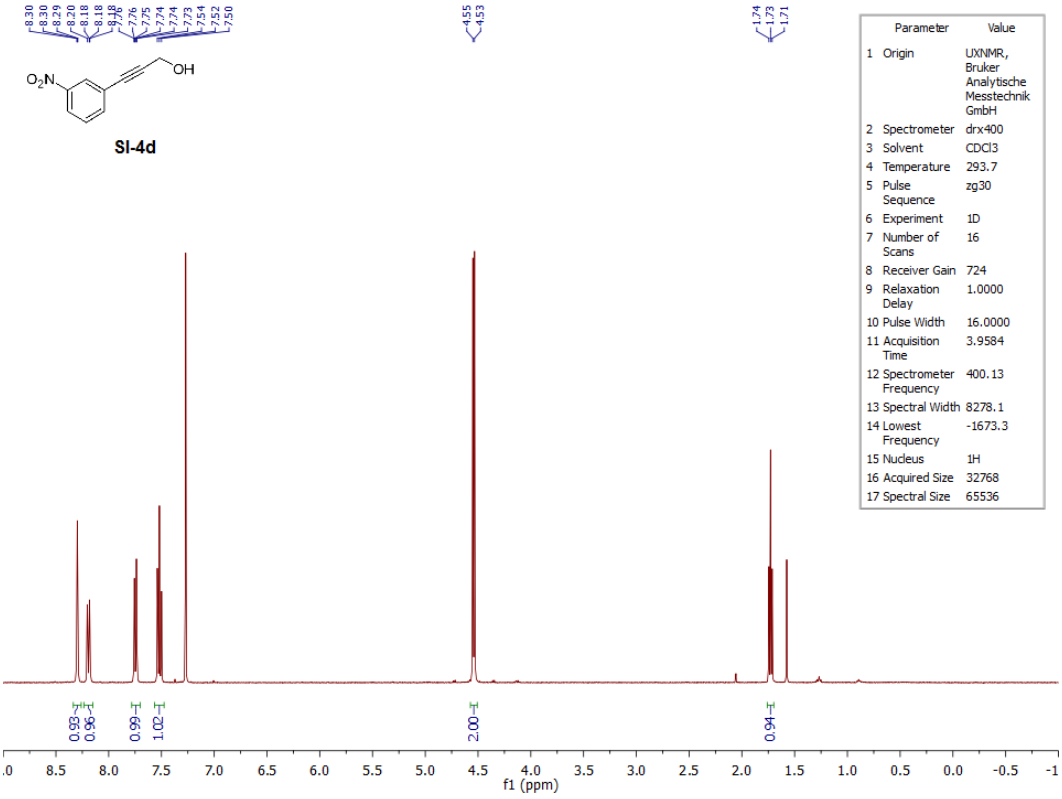
0.99
1.12
2.00
2.18
0.98
3.20
f1 (ppm)



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.5
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1541.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.7
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82292.7
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


8.30
8.30
8.29
8.20
8.18
8.18
7.76
7.75
7.74
7.74
7.73
7.54
7.52
7.50
4.55
4.53
1.74
1.73
1.71
O2N
OH
Sl-4d
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 724
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
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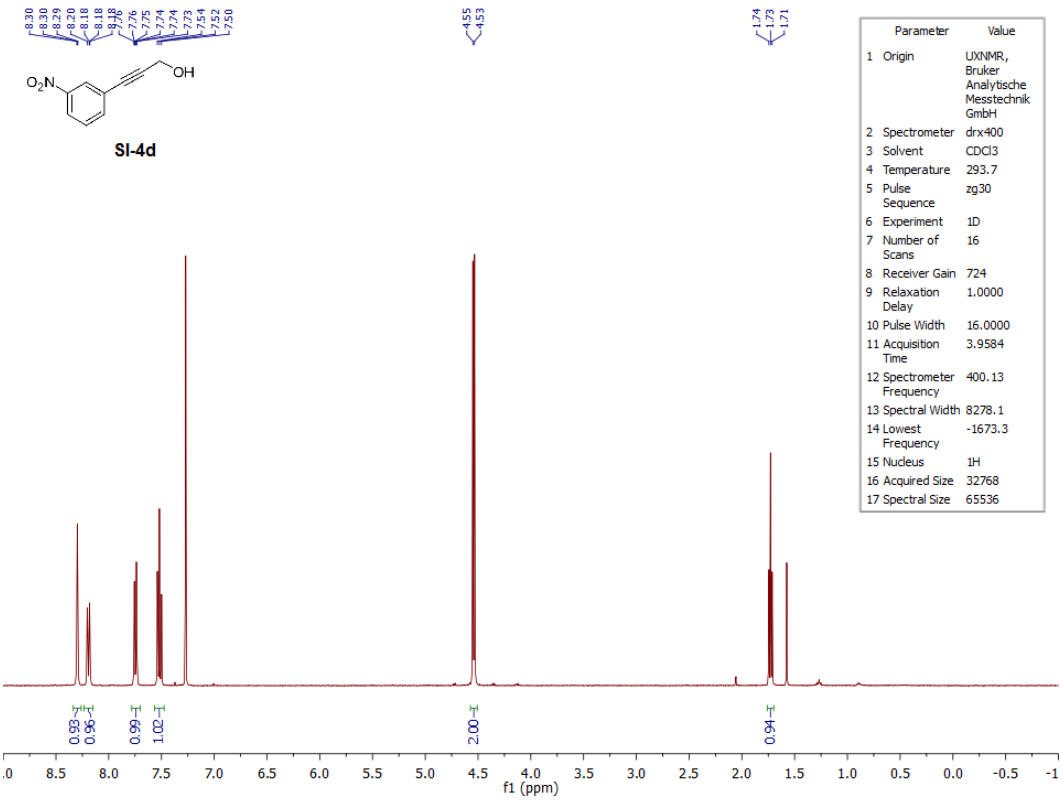
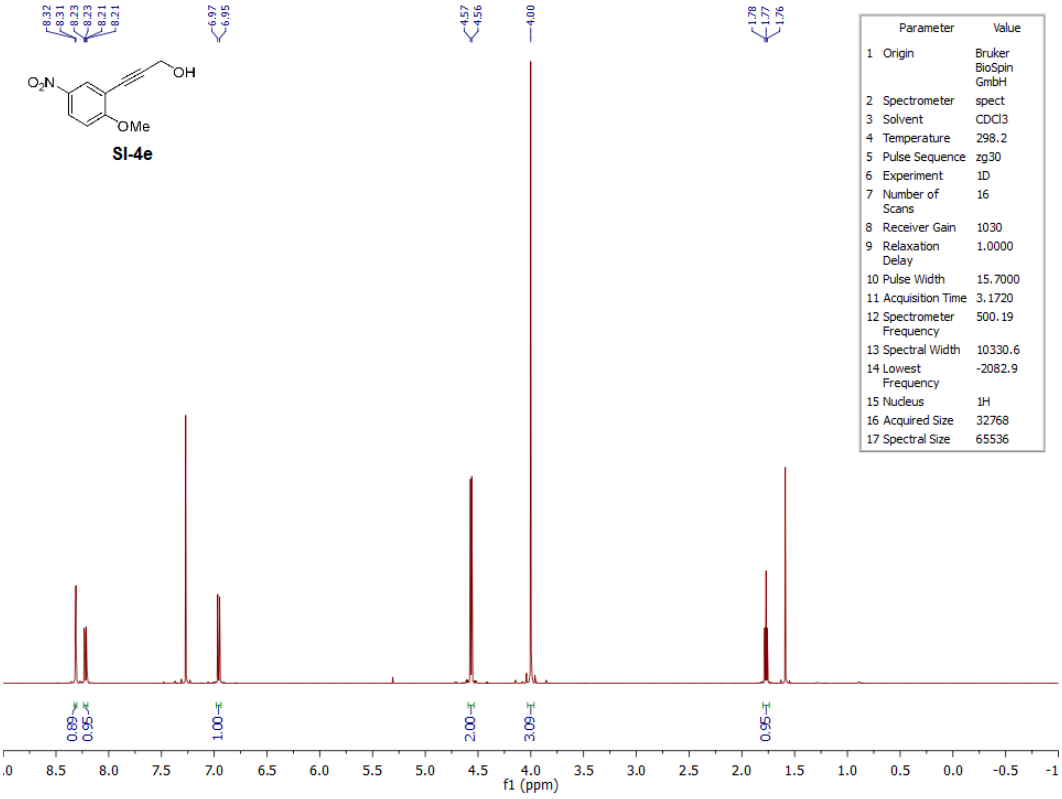
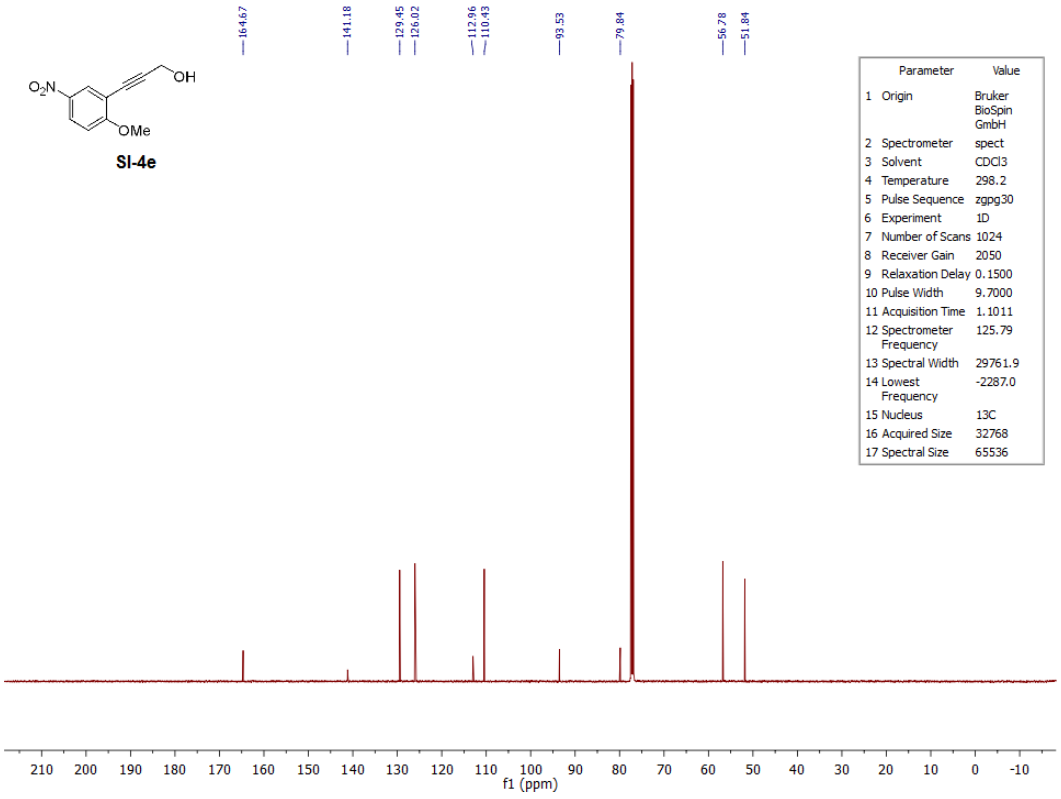
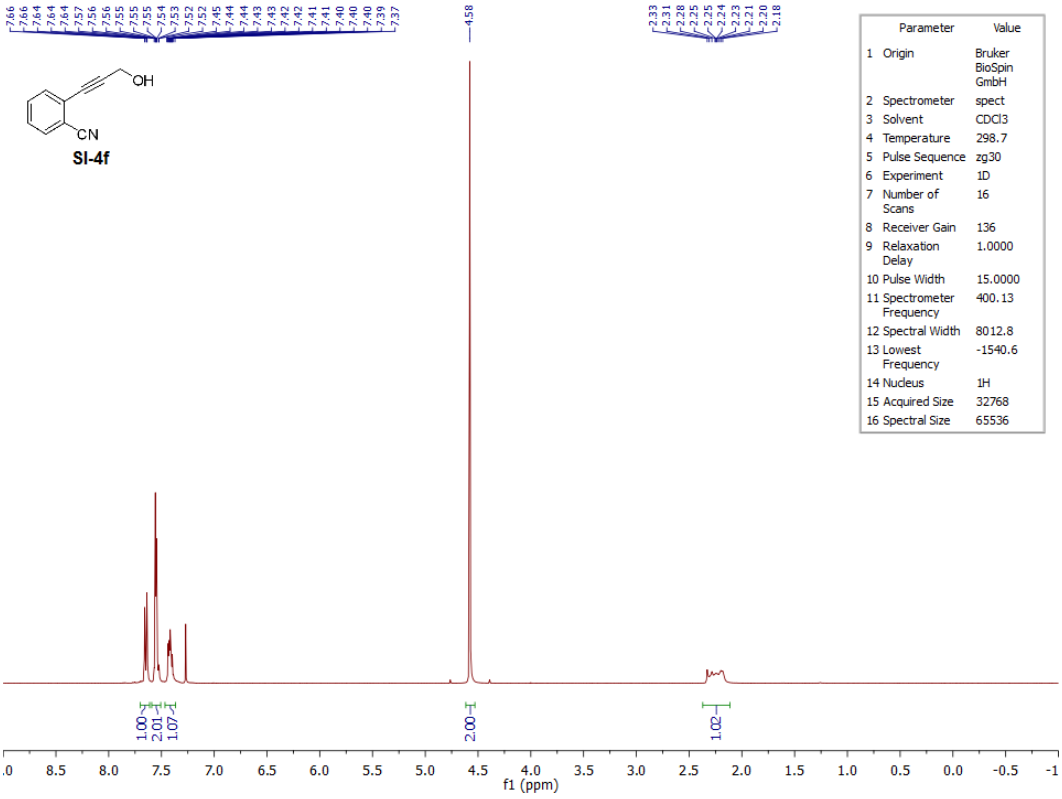
0.96
0.99
1.02
2.00
0.94
f1 (ppm)

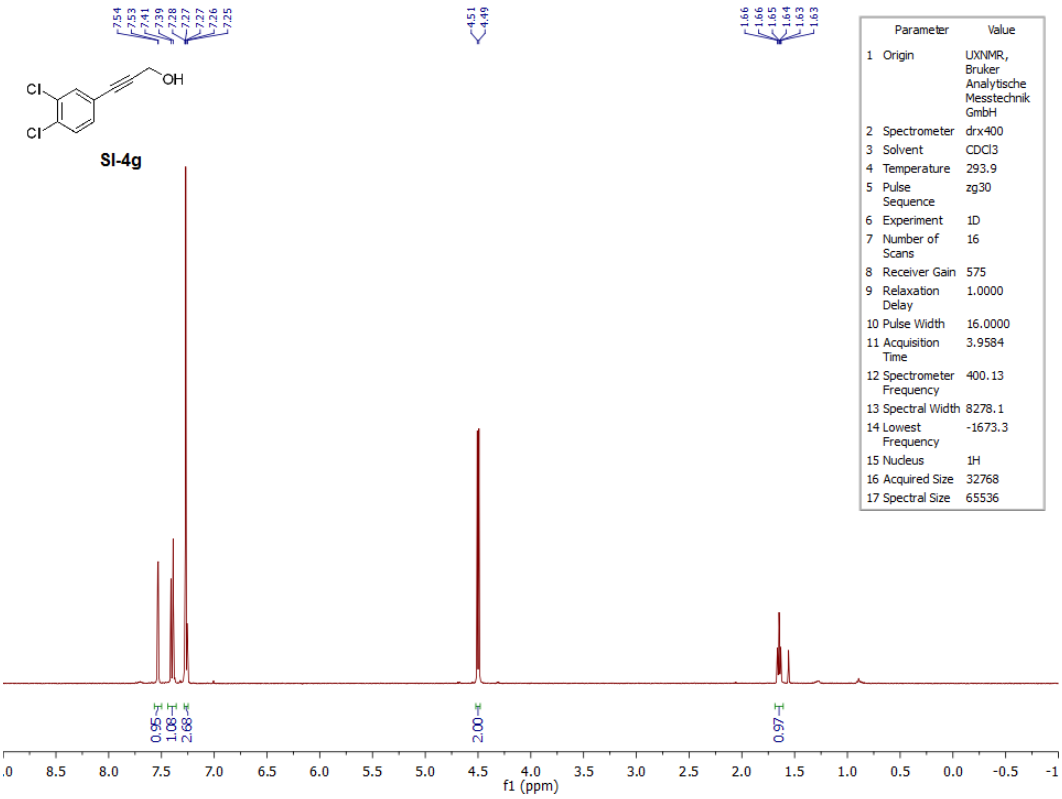

8.30
8.30
8.29
8.20
8.18
8.18
7.76
7.75
7.74
7.74
7.73
7.54
7.52
7.50
4.55
4.53
1.74
1.73
1.71
O2N
OH
Sl-4d
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 724
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.93
0.96
0.99
1.02
2.00
0.94
f1 (ppm)


8.32
8.31
8.23
8.23
8.21
8.21
6.97
6.95
4.57
4.56
4.00
1.78
1.77
1.76
OH
O2N
OMe
SI-4e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 1030
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Acquisition Time 3.1720
12 Spectrometer Frequency 500.19
13 Spectral Width 10330.6
14 Lowest Frequency -2082.9
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.89
0.95
1.00
2.00
3.09
0.95
f1 (ppm)

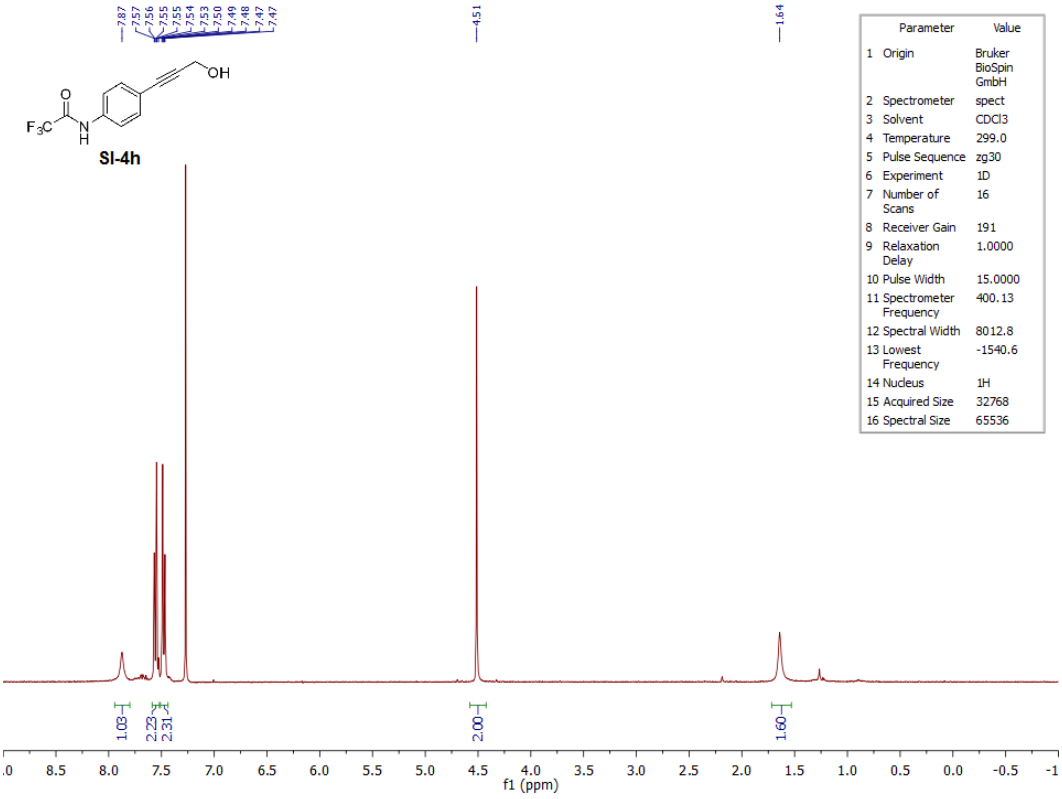

164.67
141.18
129.45
126.02
112.96
110.43
93.53
79.84
56.78
51.84
OH
O2N
OMe
SI-4e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2287.0
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)



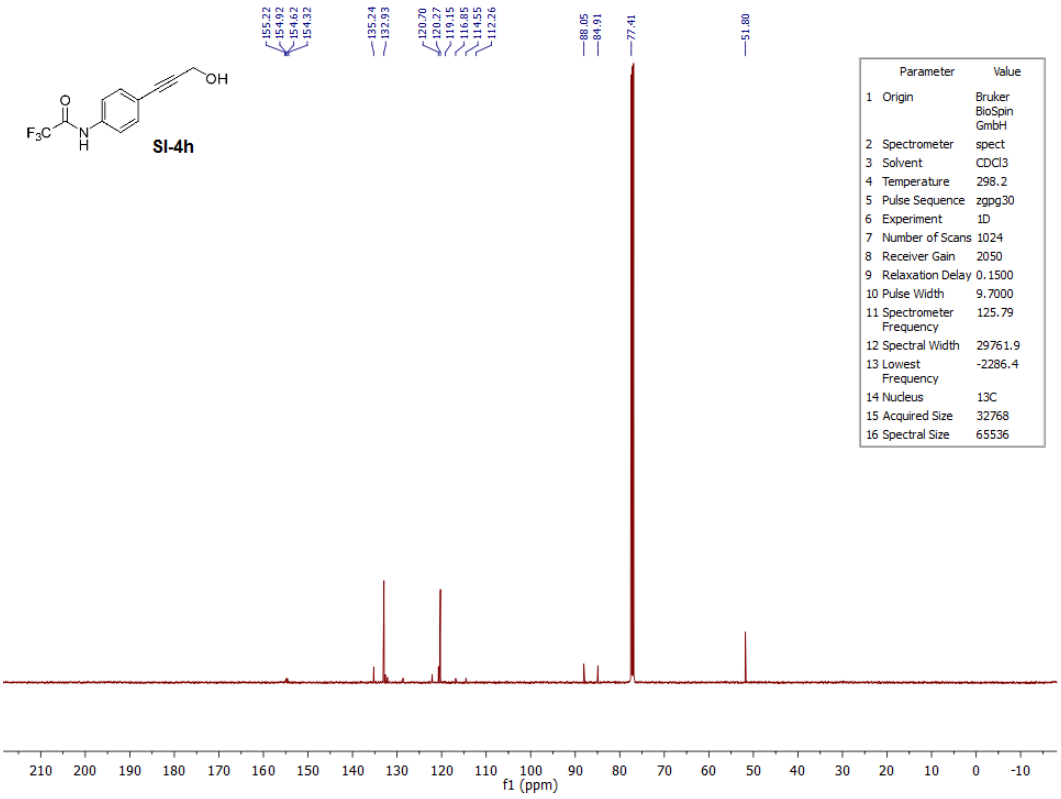
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	136
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1540.6
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



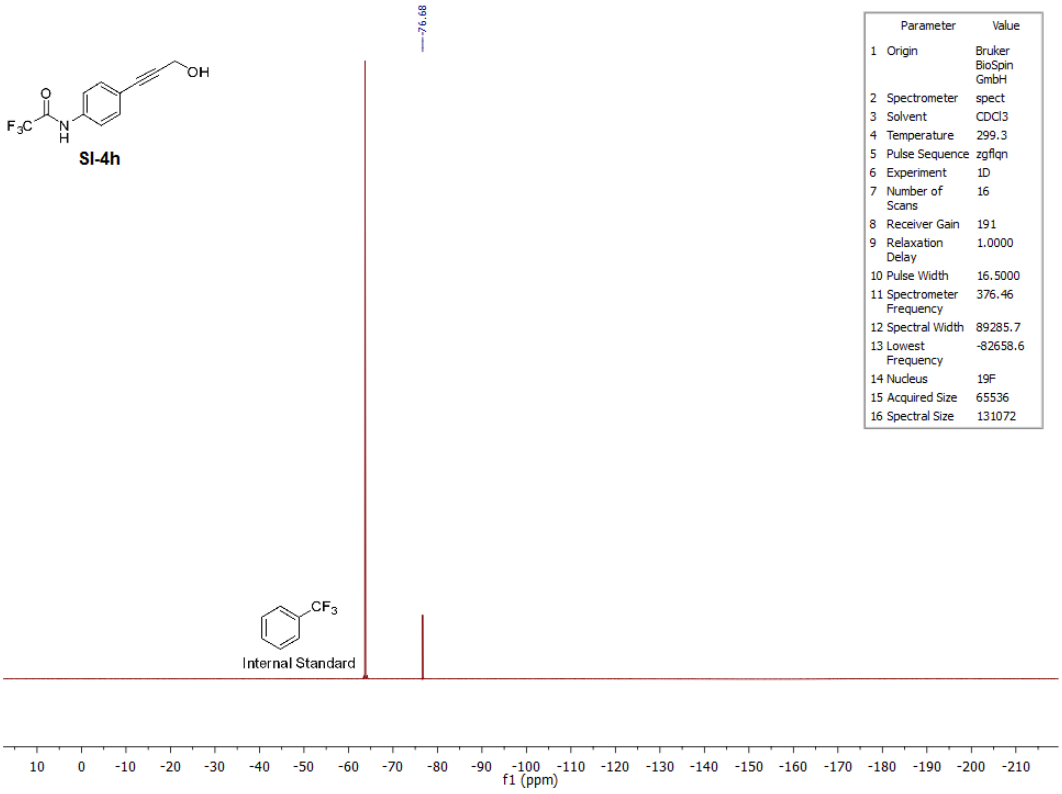
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



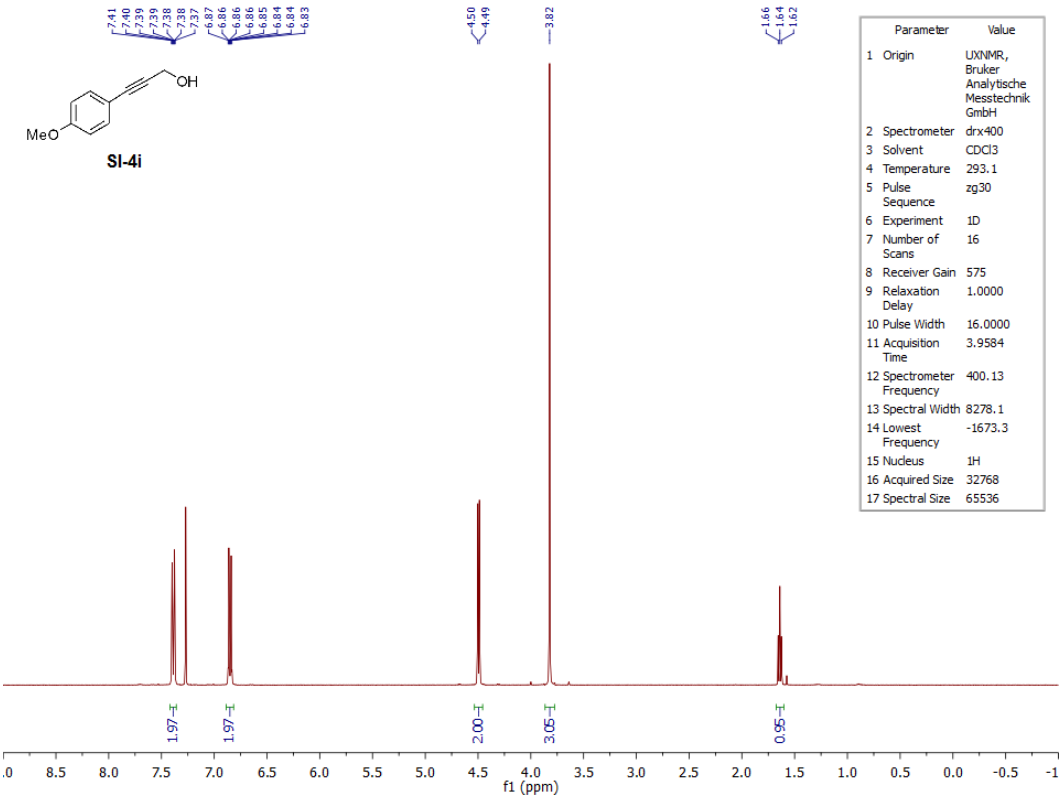
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1540.6
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



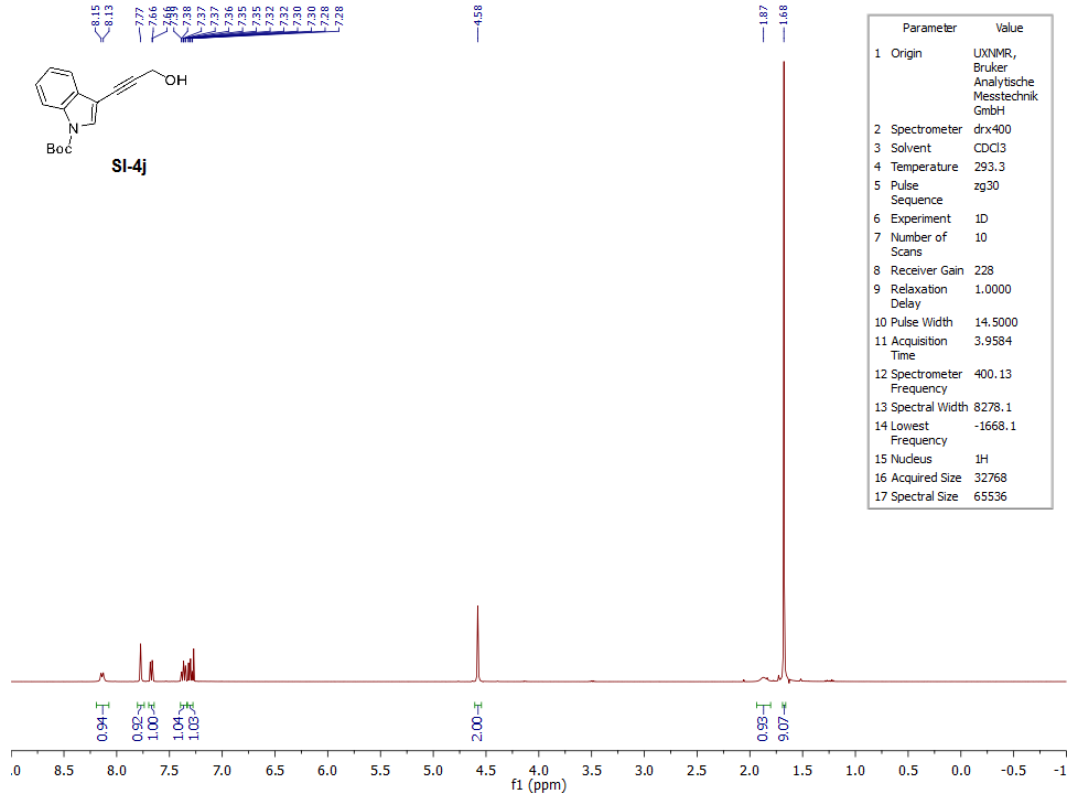
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2286.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

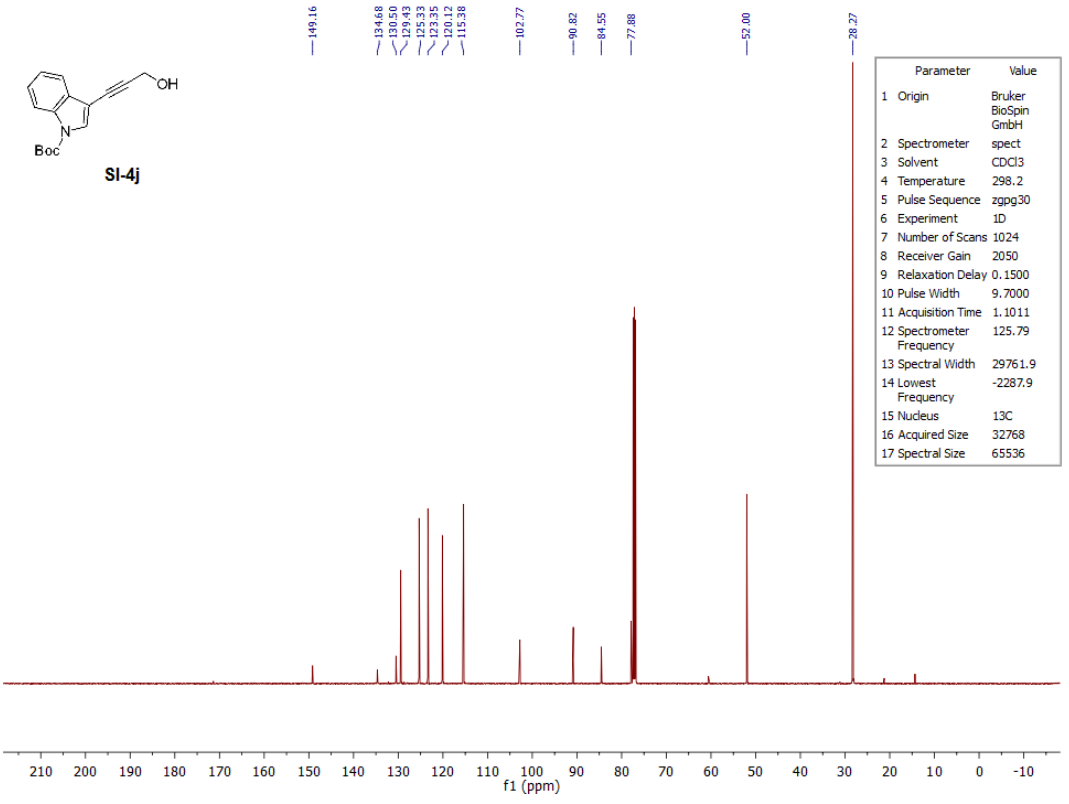


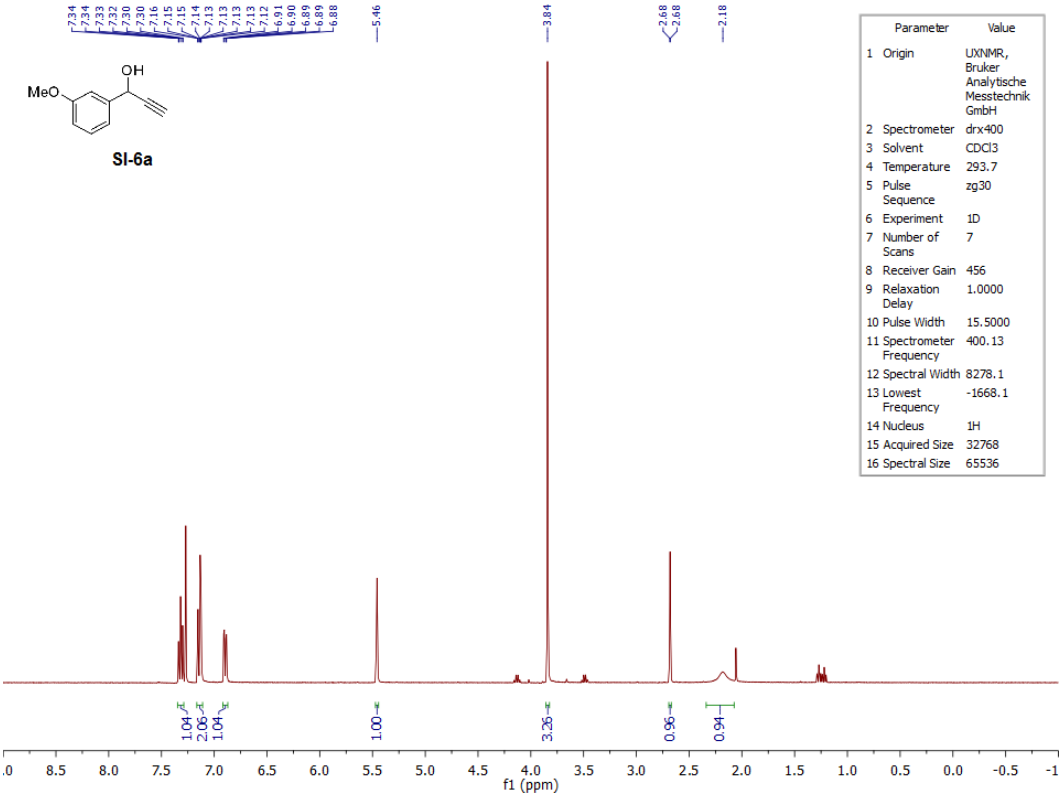
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.3
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82658.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

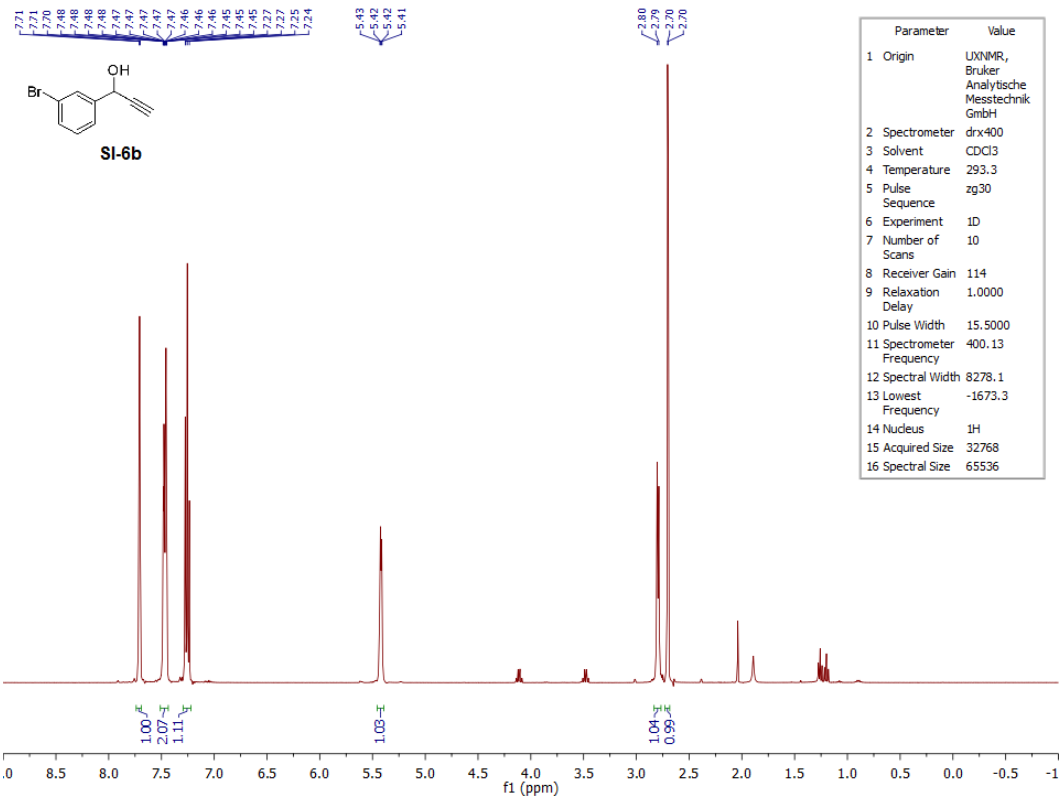


	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


8.15
8.13
7.77
7.66
7.39
7.38
7.37
7.37
7.36
7.35
7.35
7.32
7.32
7.30
7.30
7.28
7.28
4.58
1.87
1.68
OH
N
Boc
SI-4j
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 10
8 Receiver Gain 228
9 Relaxation Delay 1.0000
10 Pulse Width 14.5000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1668.1
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.94
0.92
1.00
1.04
1.03
2.00
0.93
9.07
f1 (ppm)


149.16
134.68
130.50
129.43
125.33
123.35
120.12
115.38
102.77
90.82
84.55
77.88
52.00
28.27
OH
N
Boc
SI-4j
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2287.9
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)


7.34
7.34
7.33
7.32
7.30
7.30
7.16
7.15
7.15
7.14
7.13
7.13
7.13
7.12
6.91
6.90
6.89
6.89
6.88
5.46
3.84
2.68
2.68
2.18
OH
MeO
SI-6a
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 7
8 Receiver Gain 456
9 Relaxation Delay 1.0000
10 Pulse Width 15.5000
11 Spectrometer Frequency 400.13
12 Spectral Width 8278.1
13 Lowest Frequency -1668.1
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.04
2.06
1.04
1.00
3.26
0.96
0.94
f1 (ppm)


7.71
7.71
7.70
7.48
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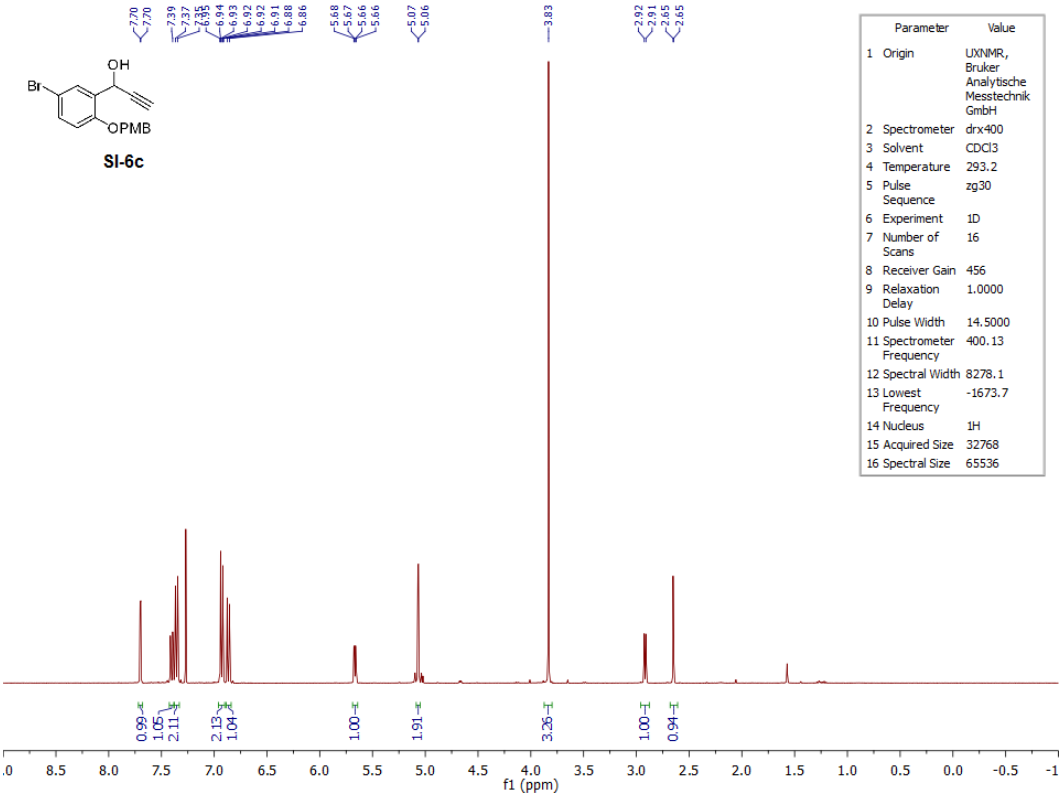
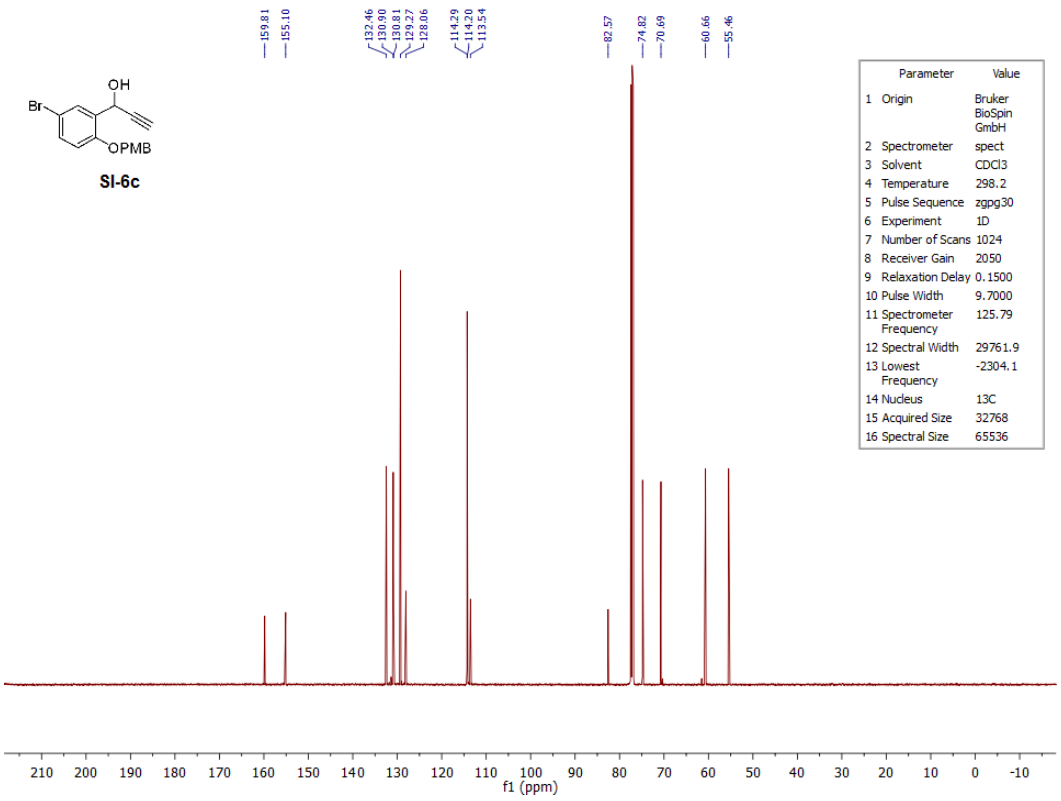
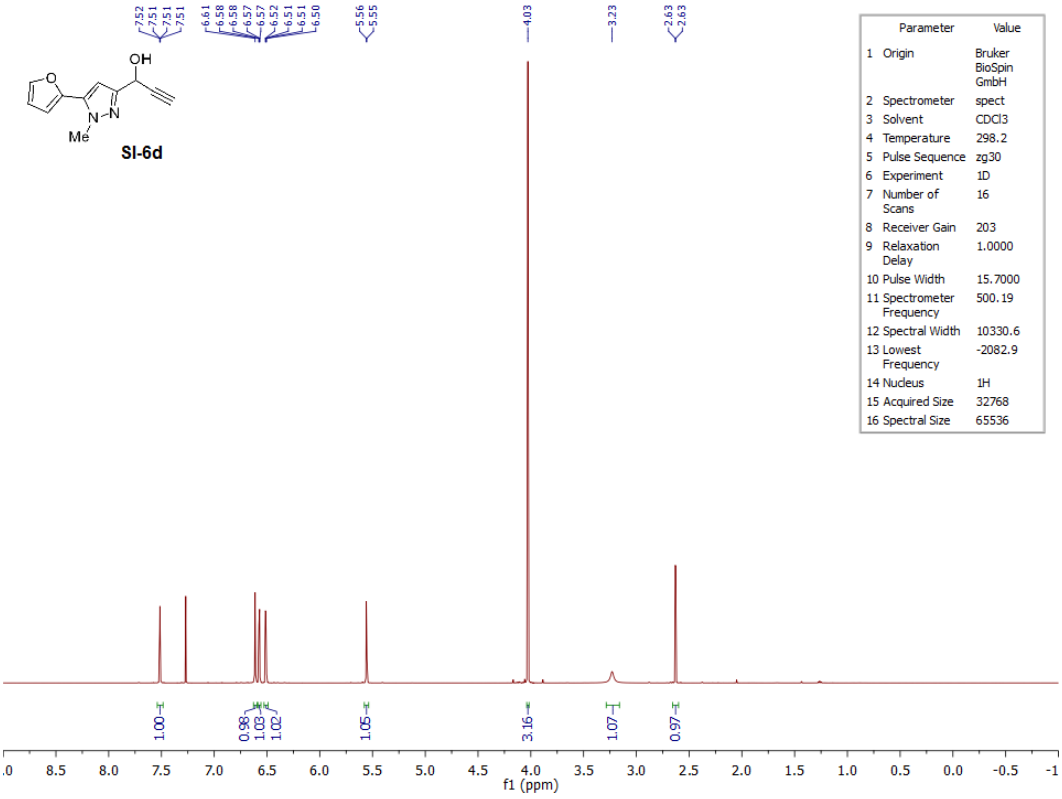
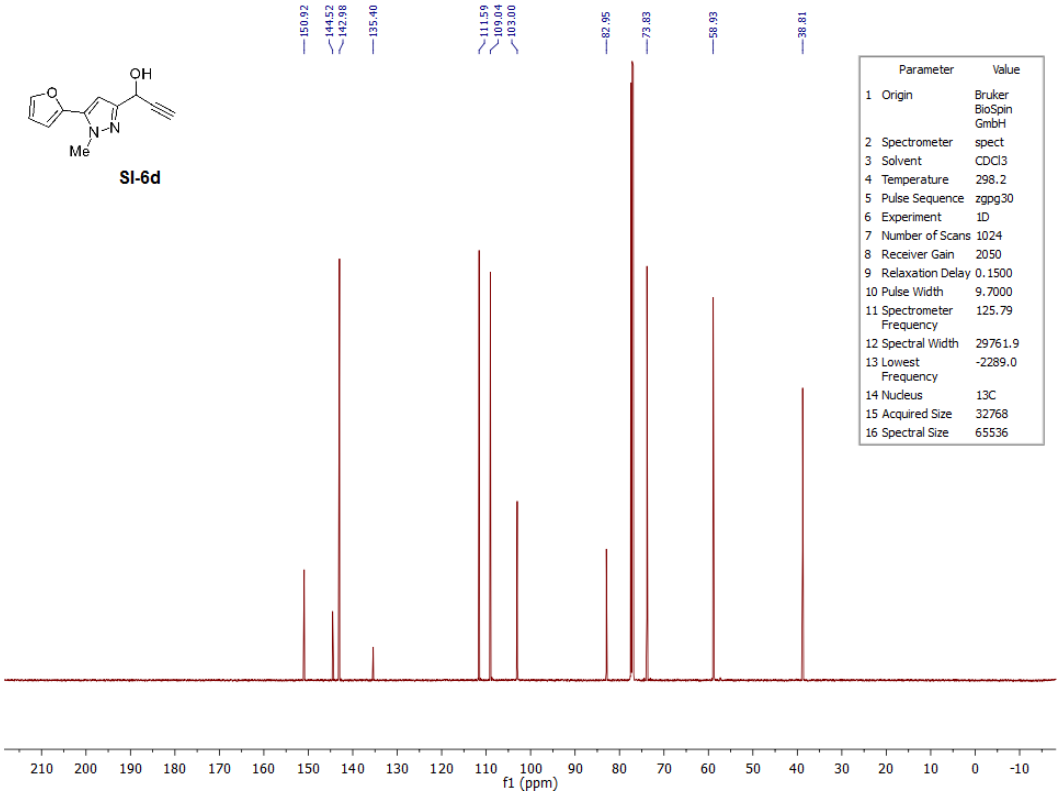
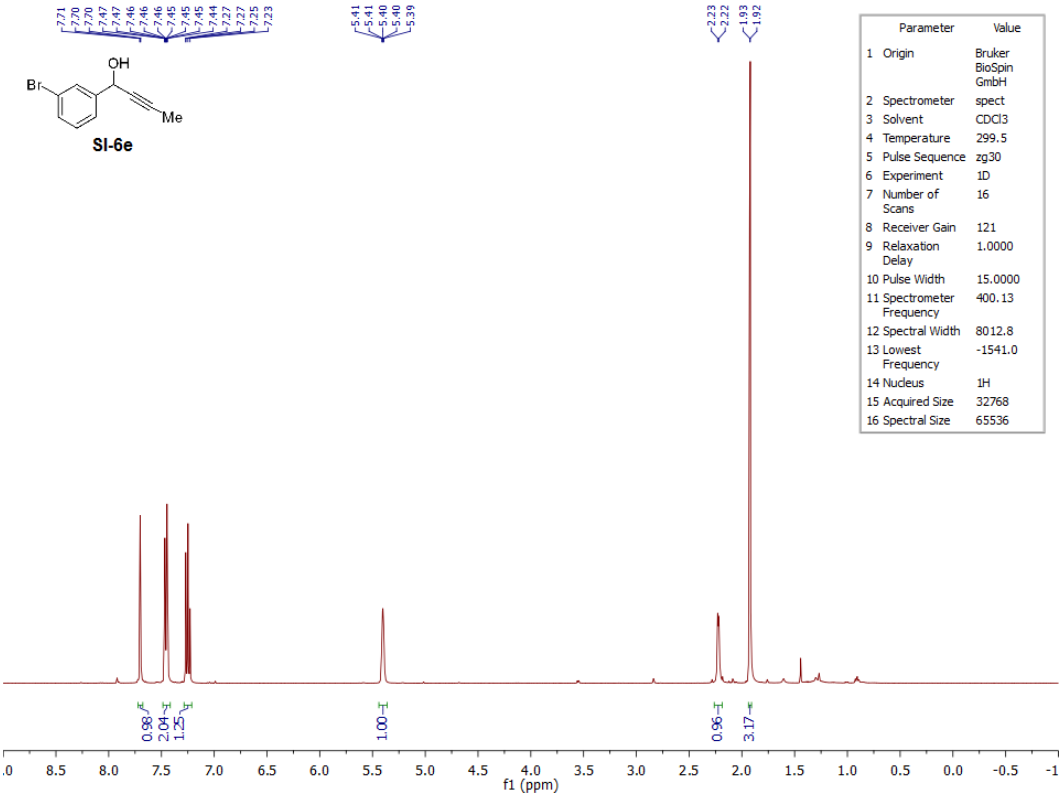
7.48
7.48
7.47
7.47
7.47
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.27
7.27
7.25
7.24
5.43
5.42
5.42
5.41
2.80
2.79
2.70
2.70
OH
Br
SI-6b
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 10
8 Receiver Gain 114
9 Relaxation Delay 1.0000
10 Pulse Width 15.5000
11 Spectrometer Frequency 400.13
12 Spectral Width 8278.1
13 Lowest Frequency -1673.3
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.00
2.07
1.11
1.03
1.04
0.99
f1 (ppm)

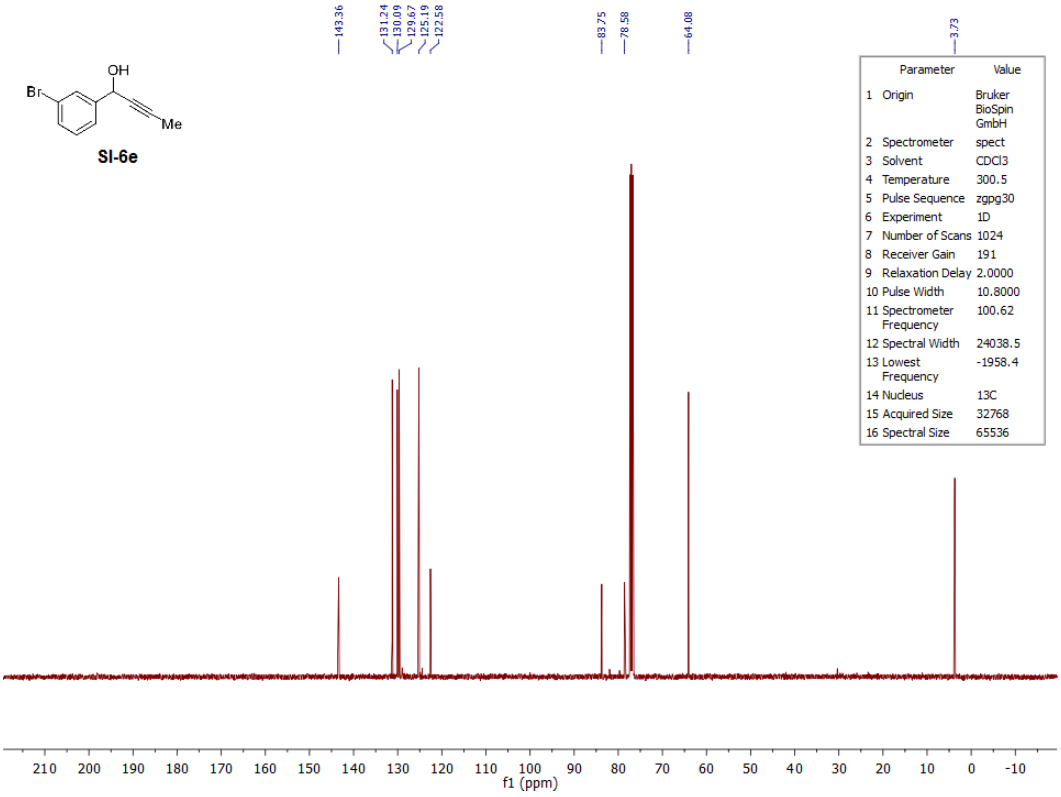

OH
Br
OPMB
SI-6c
7.70
7.70
7.39
7.37
7.35
6.95
6.94
6.93
6.92
6.92
6.91
6.88
6.86
5.68
5.67
5.66
5.66
5.07
5.06
3.83
2.92
2.91
2.65
2.65
0.99
1.05
2.11
2.13
1.04
1.00
1.91
3.26
1.00
0.94
f1 (ppm)
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 456
9 Relaxation Delay 1.0000
10 Pulse Width 14.5000
11 Spectrometer Frequency 400.13
12 Spectral Width 8278.1
13 Lowest Frequency -1673.7
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536

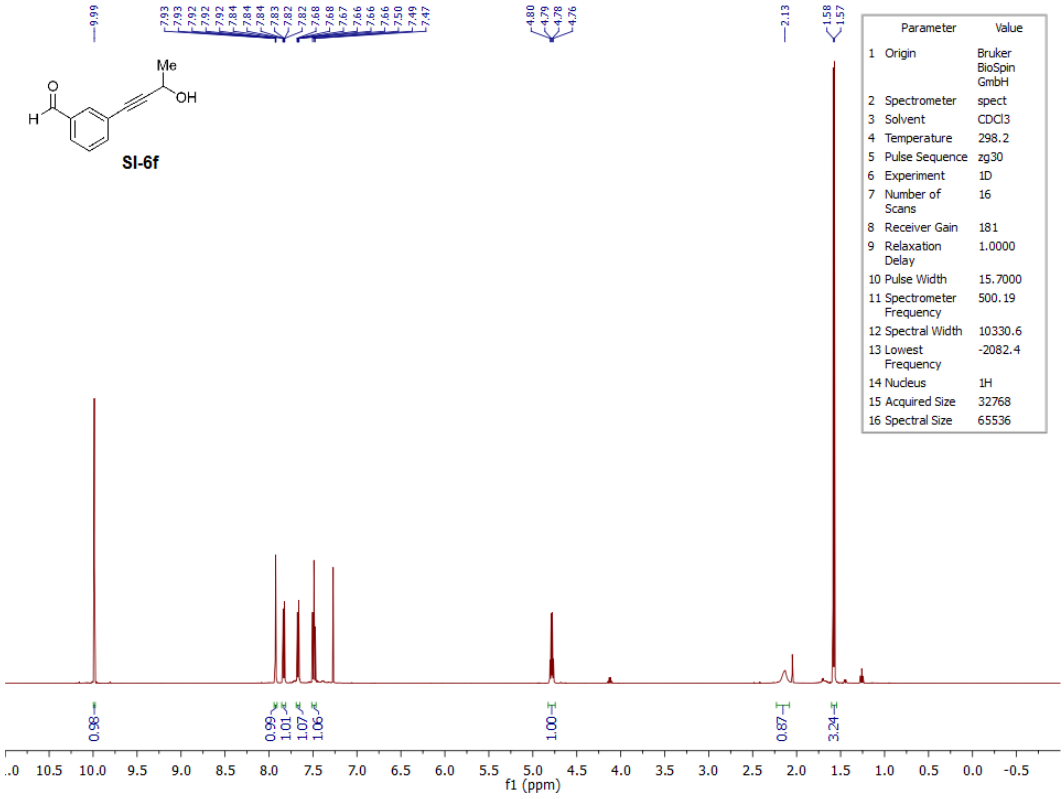

OH
Br
OPMB
SI-6c
159.81
155.10
132.46
130.90
130.81
129.27
128.06
114.29
114.20
113.54
82.57
74.82
70.69
60.66
55.46
f1 (ppm)
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2304.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536

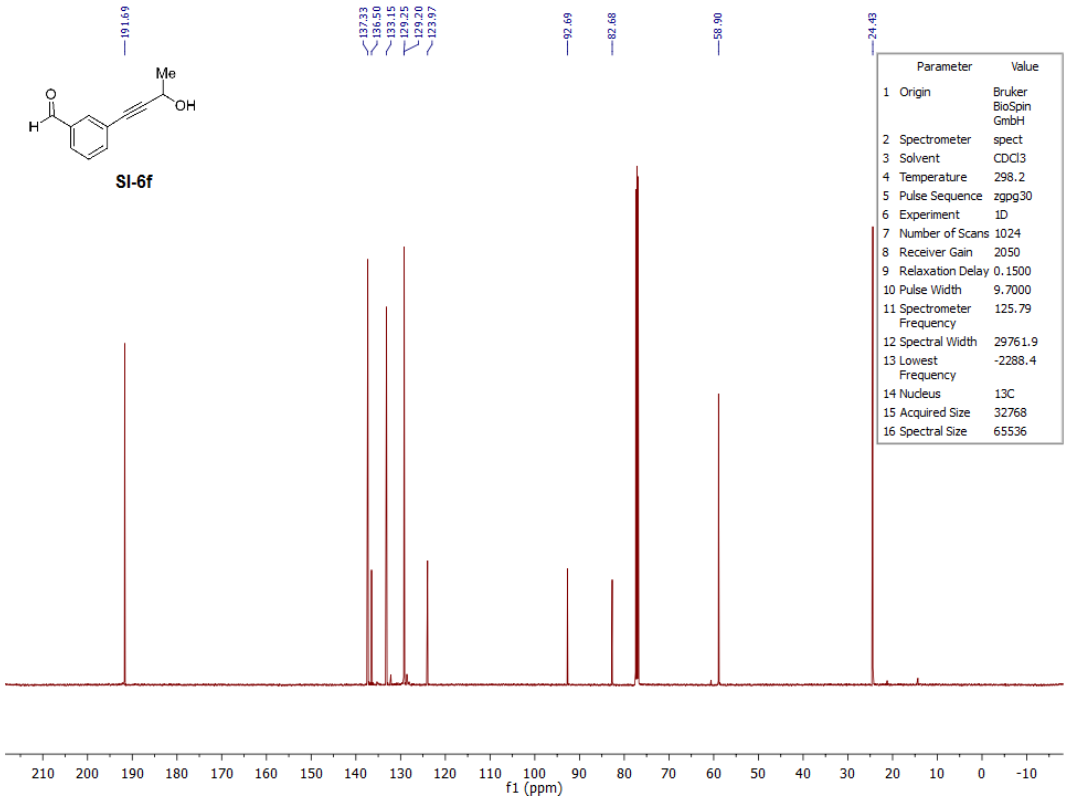

7.52
7.51
7.51
7.51
6.61
6.58
6.58
6.57
6.57
6.52
6.51
6.51
6.50
5.56
5.55
4.03
3.23
2.63
2.63
OH
O
N-N
Me
SI-6d
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 203
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2082.9
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.00
0.98
1.03
1.02
1.05
3.16
1.07
0.97
f1 (ppm)

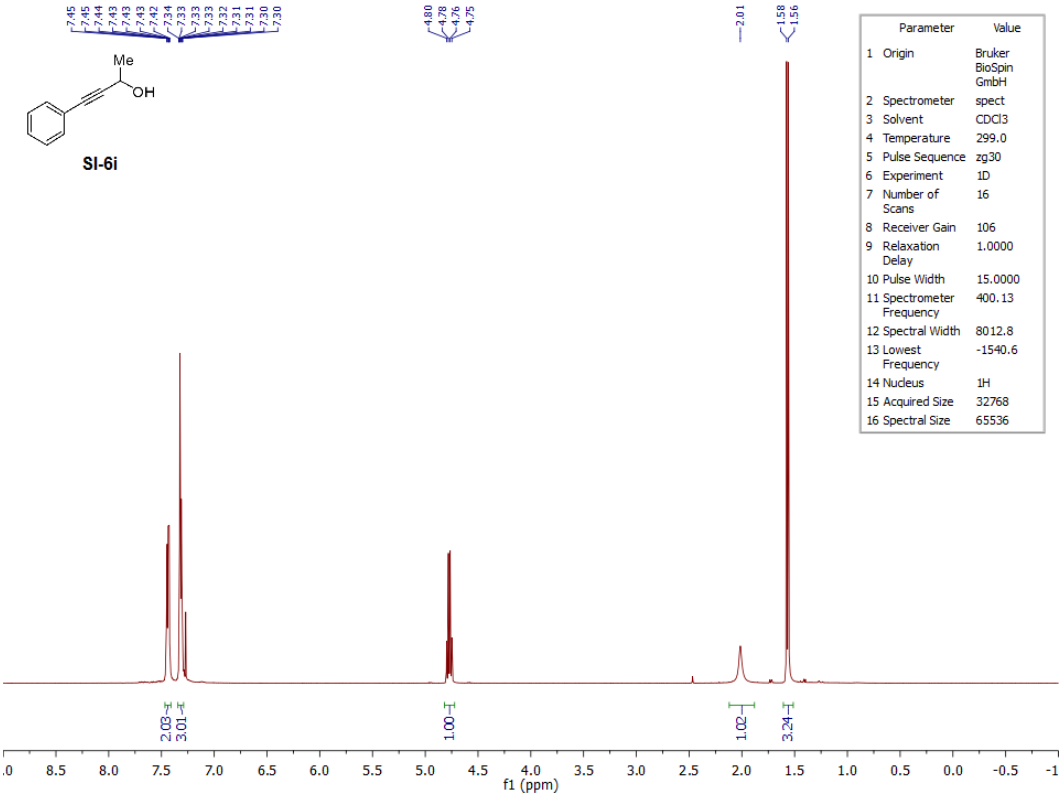

150.92
144.52
142.98
135.40
111.59
109.04
103.00
82.95
73.83
58.93
38.81
OH
O
N-N
Me
SI-6d
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2289.0
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)


7.71
7.70
7.70
7.47
7.47
7.46
7.46
7.46
7.45
7.45
7.45
7.44
7.27
7.27
7.25
7.23
5.41
5.41
5.40
5.40
5.39
2.23
2.22
1.93
1.92
OH
Br
Me
SI-6e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 121
9 Relaxation Delay 1.0000
10 Pulse Width 15.0000
11 Spectrometer Frequency 400.13
12 Spectral Width 8012.8
13 Lowest Frequency -1541.0
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
0.98
2.04
1.25
1.00
0.96
3.17
f1 (ppm)

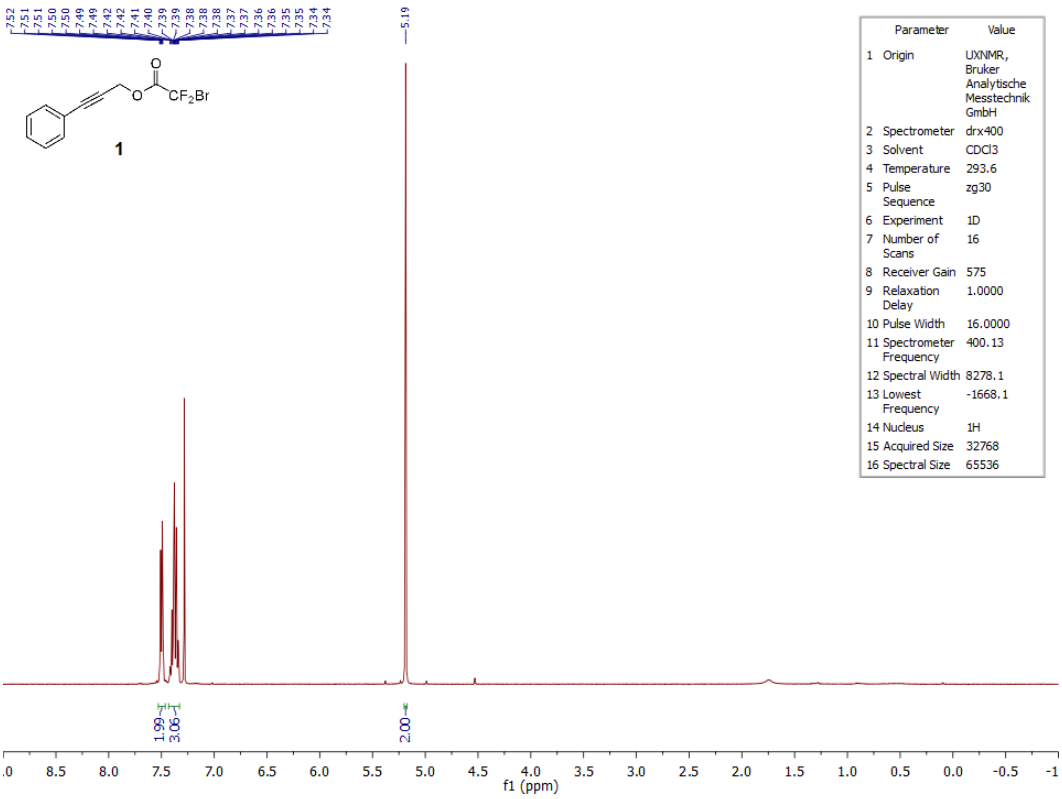

143.36
131.24
130.09
129.67
125.19
122.58
83.75
78.58
64.08
3.73
OH
Br
Me
SI-6e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 300.5
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 191
9 Relaxation Delay 2.0000
10 Pulse Width 10.8000
11 Spectrometer Frequency 100.62
12 Spectral Width 24038.5
13 Lowest Frequency -1958.4
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)


9.99
7.93
7.93
7.92
7.92
7.92
7.84
7.84
7.84
7.83
7.82
7.82
7.68
7.68
7.67
7.66
7.66
7.66
7.50
7.49
7.47
4.80
4.79
4.78
4.76
2.13
1.58
1.57
Me
OH
O
H
SI-6f
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 181
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2082.4
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
0.98
0.99
1.01
1.07
1.06
1.00
0.87
3.24
f1 (ppm)

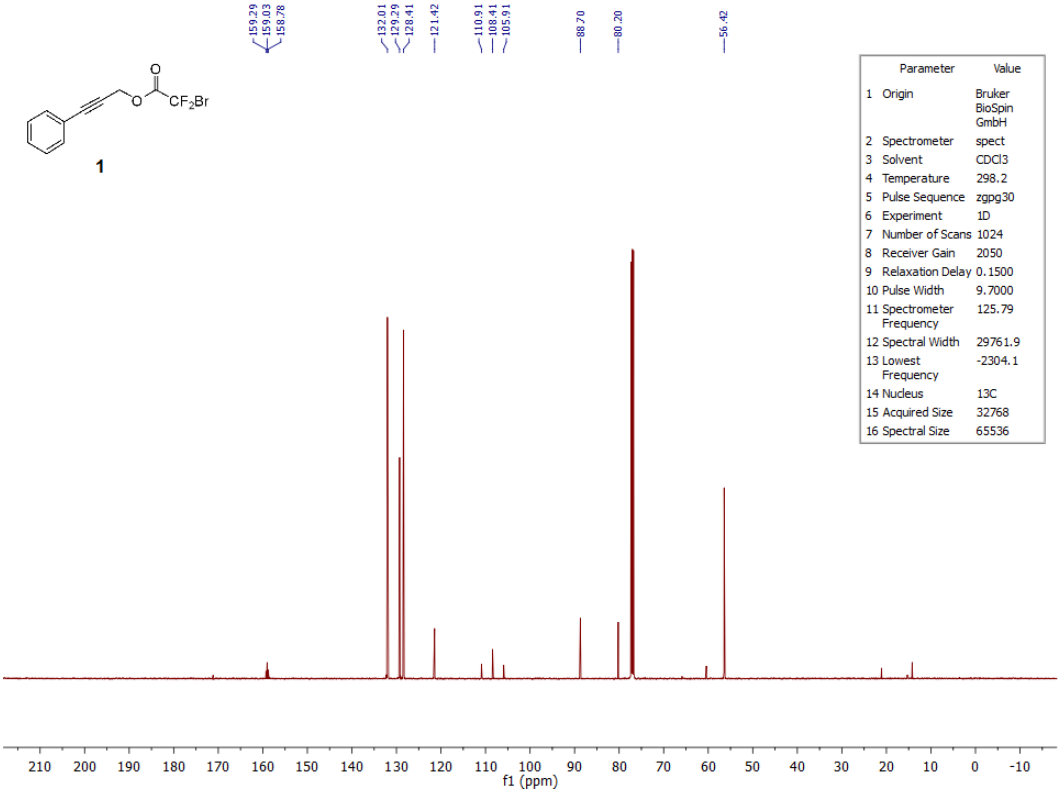

191.69
137.33
136.50
133.15
129.25
129.20
123.97
92.69
82.68
58.90
24.43
Me
OH
O
H
SI-6f
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2288.4
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

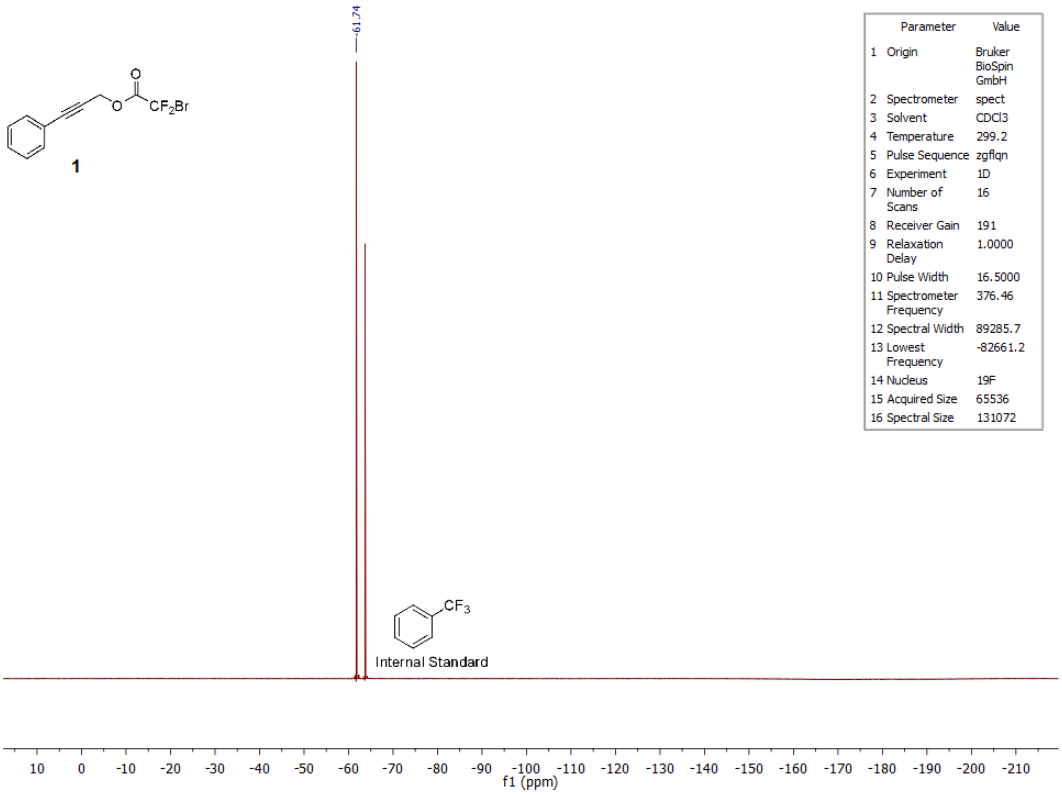


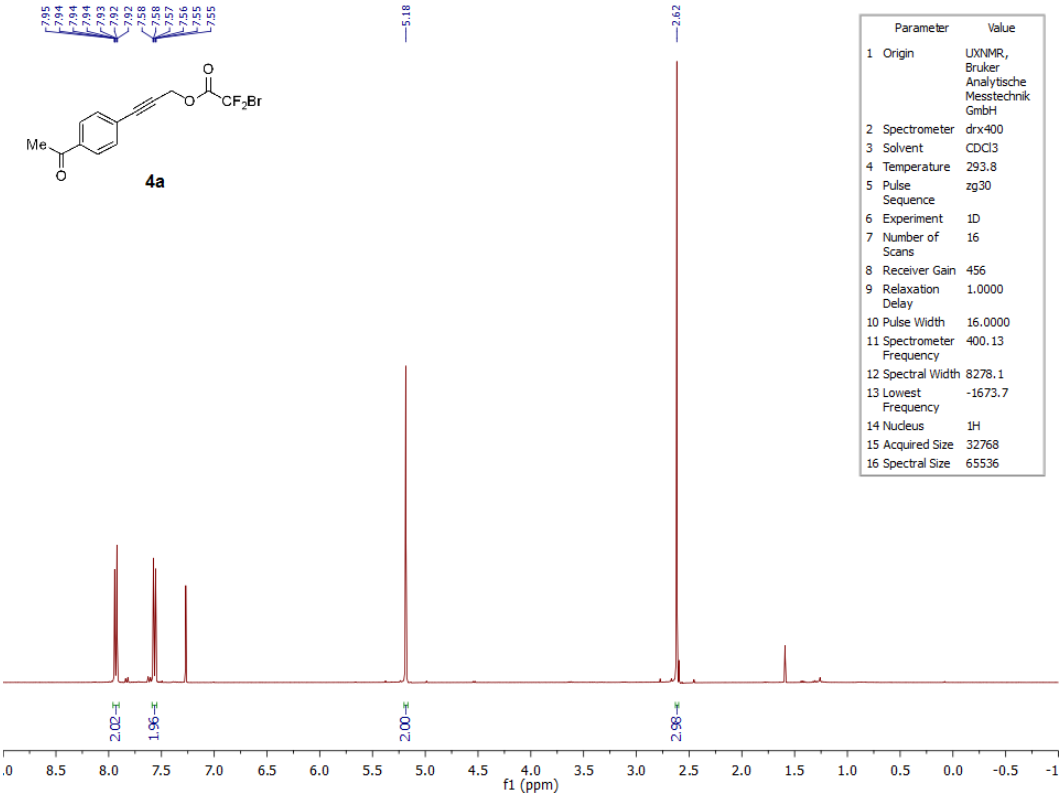
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	106
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1540.6
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

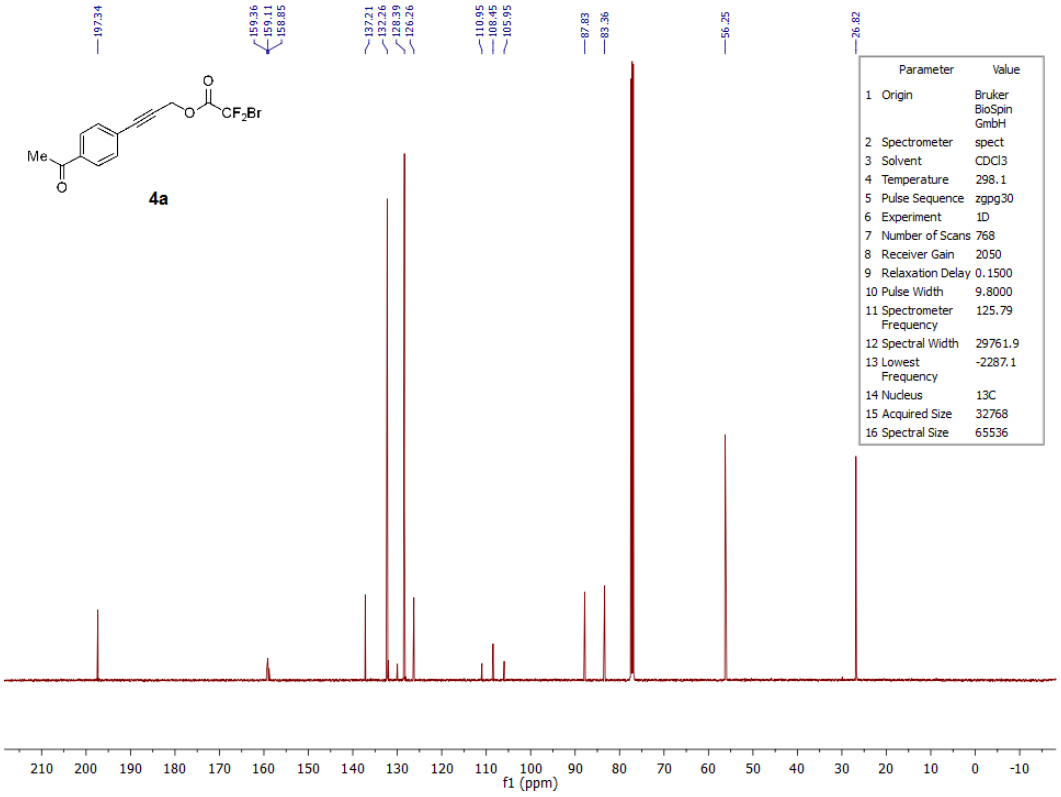


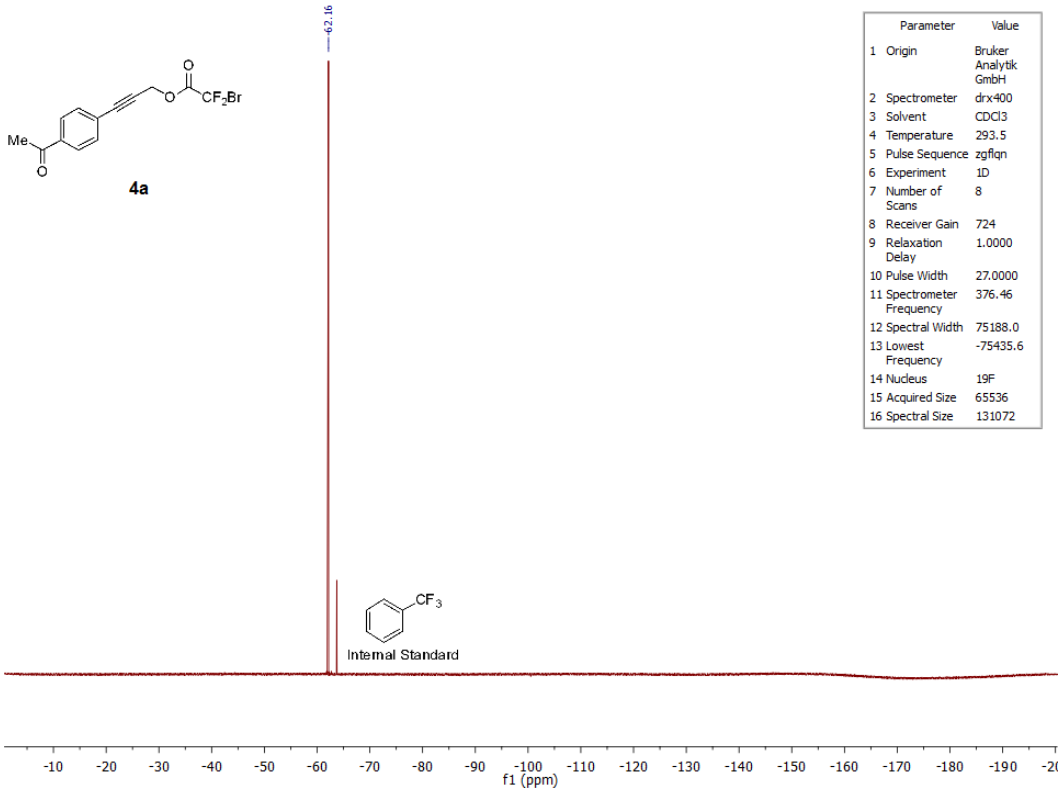
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8278.1
13	Lowest Frequency	-1668.1
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


159.29
159.03
158.78
132.01
129.29
128.41
121.42
110.91
108.41
105.91
88.70
80.20
56.42
O
O
CF2Br
1
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2304.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

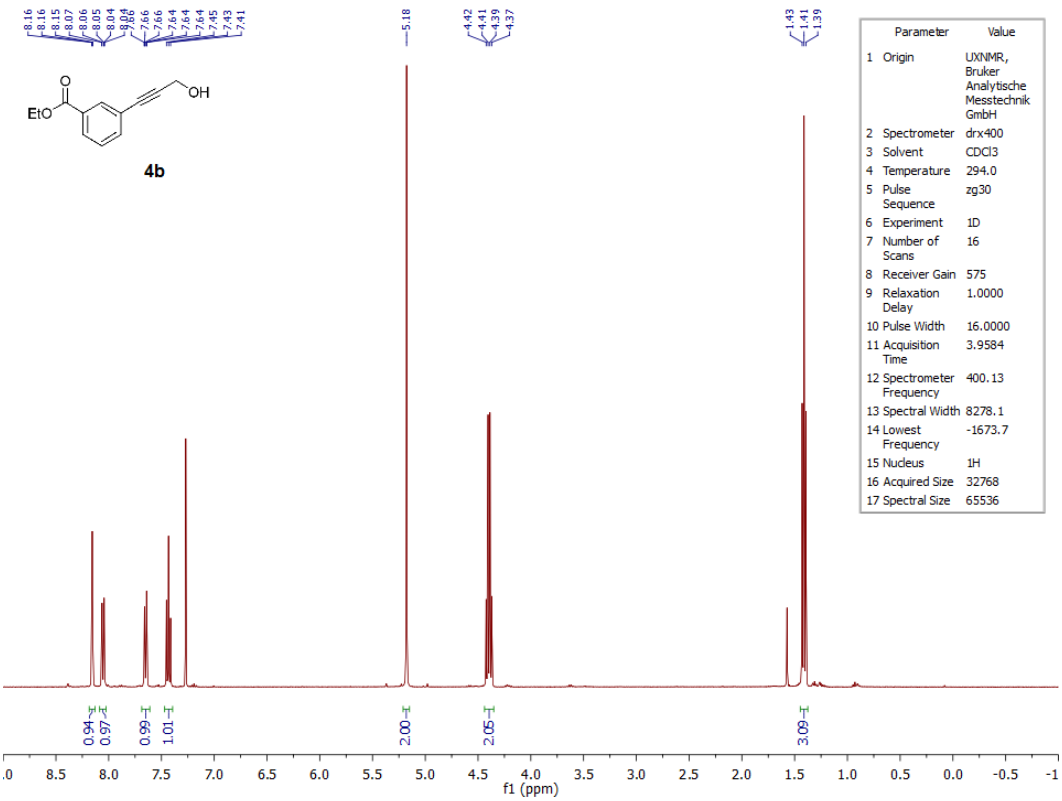

61.74
O
O
CF2Br
1
CF3
Internal Standard
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.2
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82661.2
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.95
7.94
7.94
7.94
7.93
7.92
7.92
7.58
7.58
7.57
7.56
7.55
7.55
5.18
2.62
Me
O
O
O
CF2Br
4a
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 456
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Spectrometer Frequency 400.13
12 Spectral Width 8278.1
13 Lowest Frequency -1673.7
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
2.02
1.96
2.00
2.98
f1 (ppm)

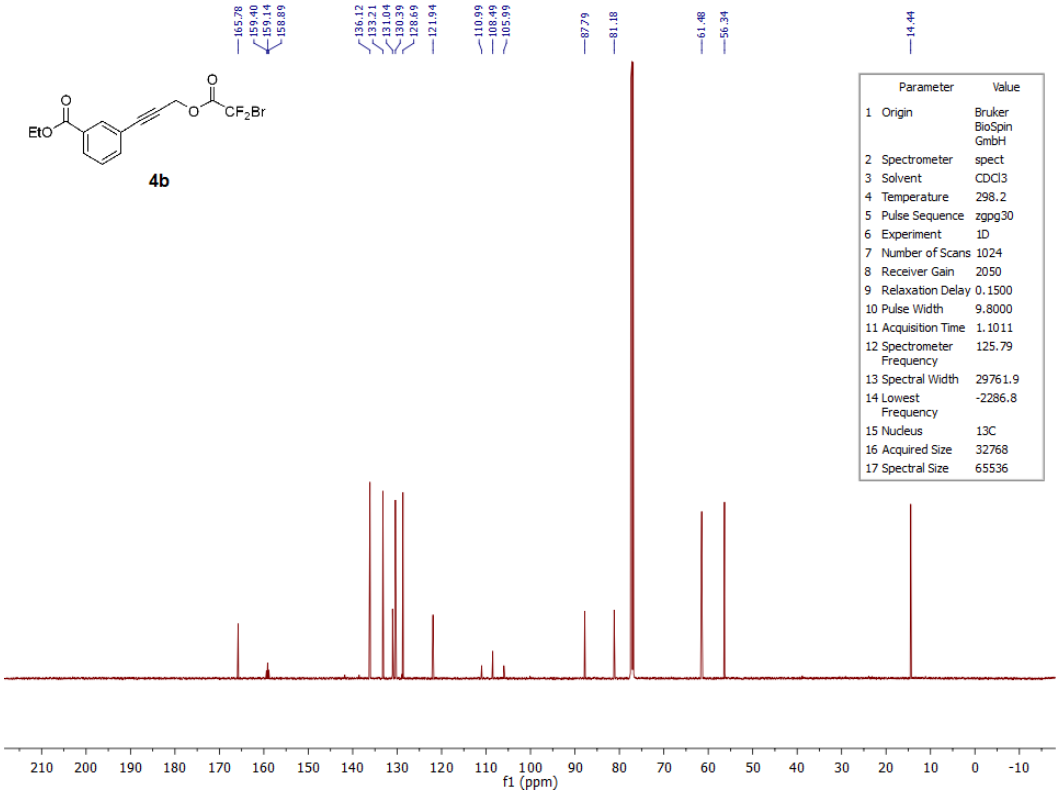

197.34
159.36
159.11
158.85
137.21
132.26
128.39
126.26
110.95
108.45
105.95
87.83
83.36
56.25
26.82
Me
O
O
O
CF2Br
4a
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 768
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.8000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2287.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

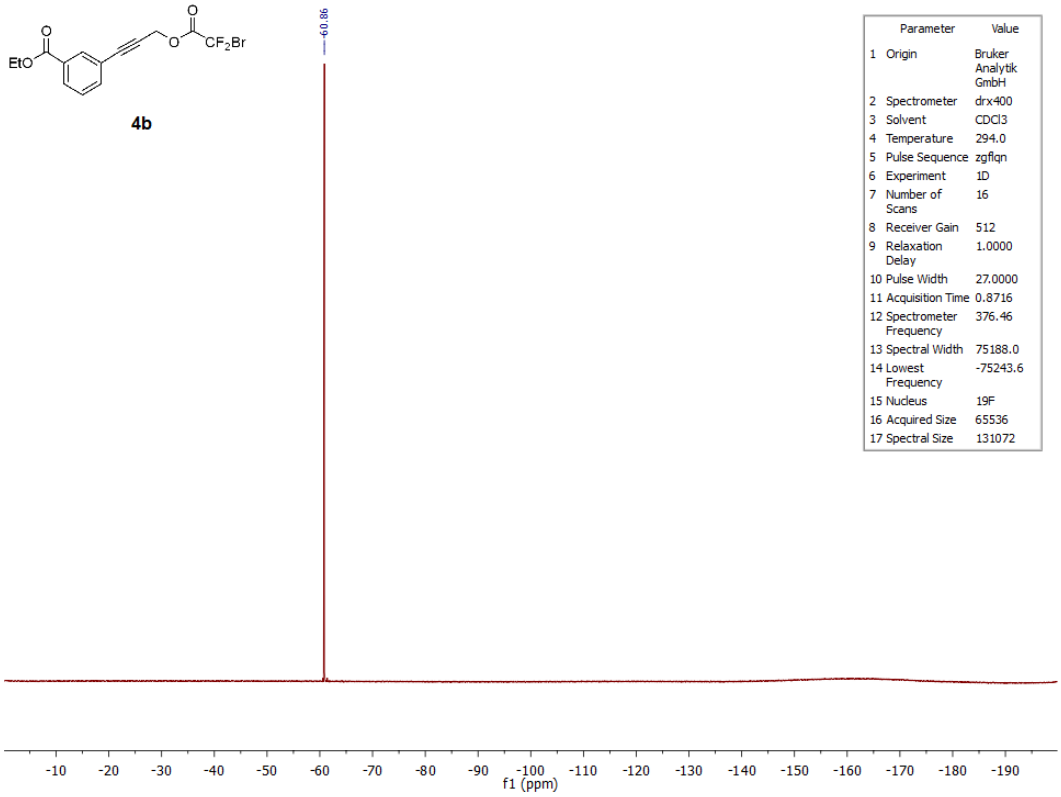


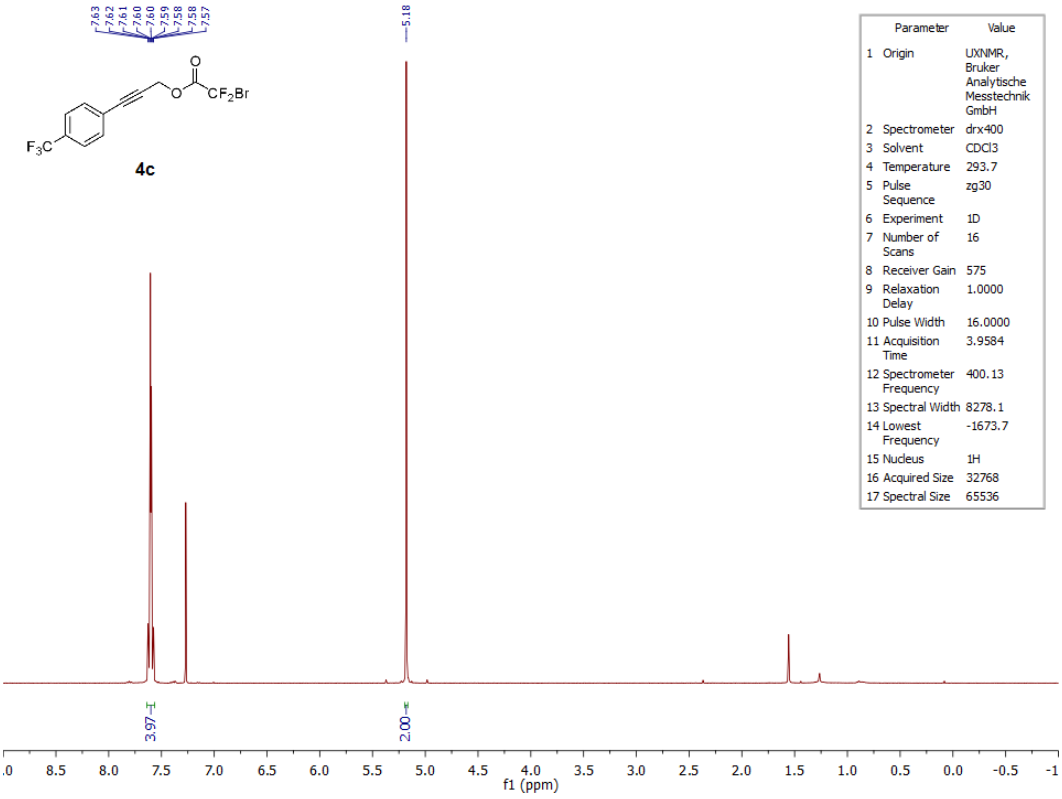
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.5
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	724
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75435.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



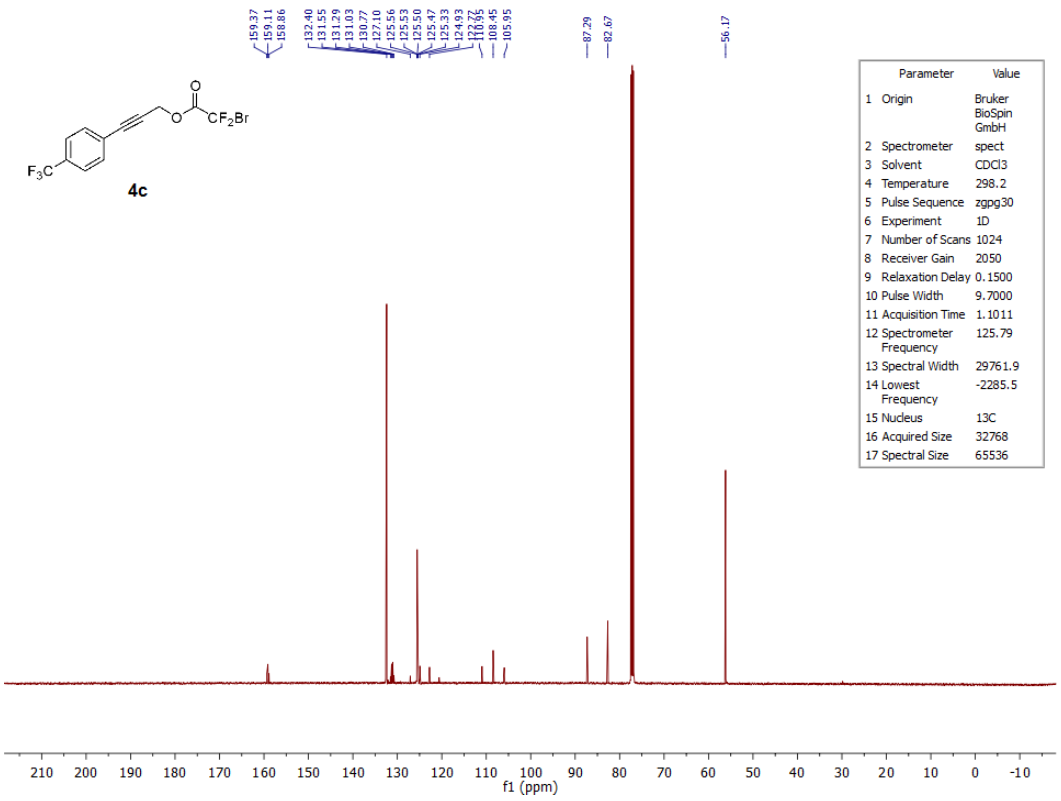
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	294.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.7
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


165.78
159.40
159.14
158.89
136.12
133.21
131.04
130.39
128.69
121.94
110.99
108.49
105.99
87.79
81.18
61.48
56.34
14.44
EtO
O
O
O
CF2Br
4b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.8000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.8
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

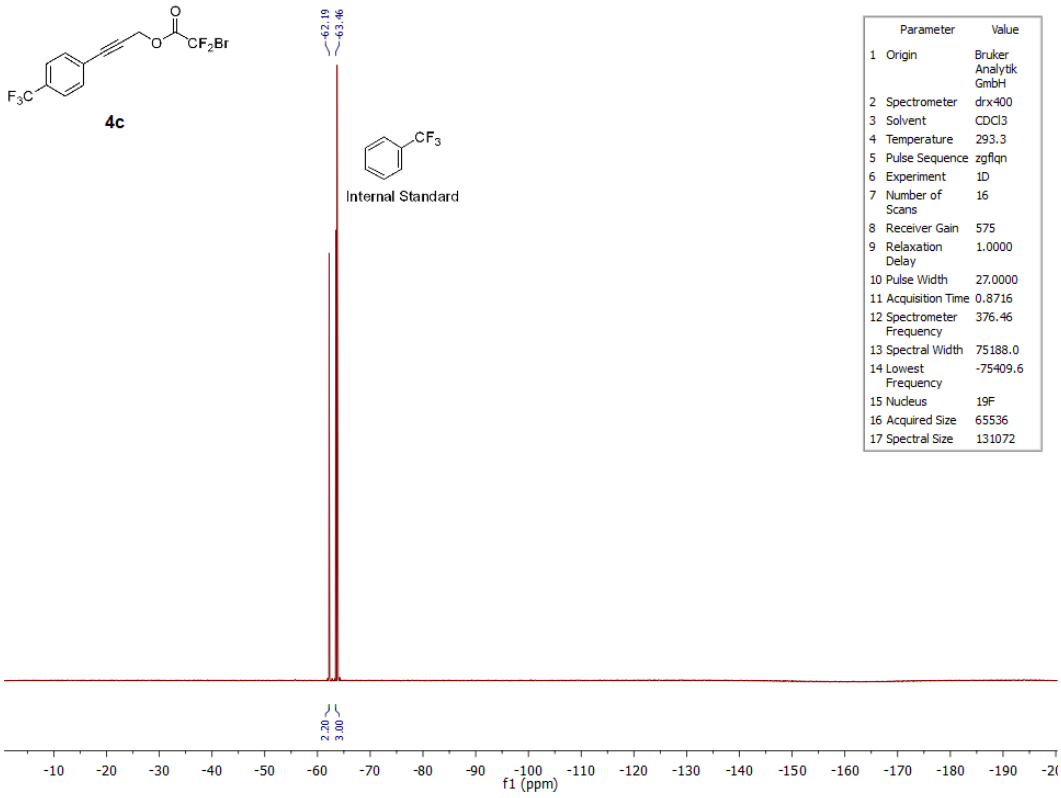

-60.86
EtO
O
O
O
CF2Br
4b
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 294.0
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 512
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Acquisition Time 0.8716
12 Spectrometer Frequency 376.46
13 Spectral Width 75188.0
14 Lowest Frequency -75243.6
15 Nucleus 19F
16 Acquired Size 65536
17 Spectral Size 131072
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



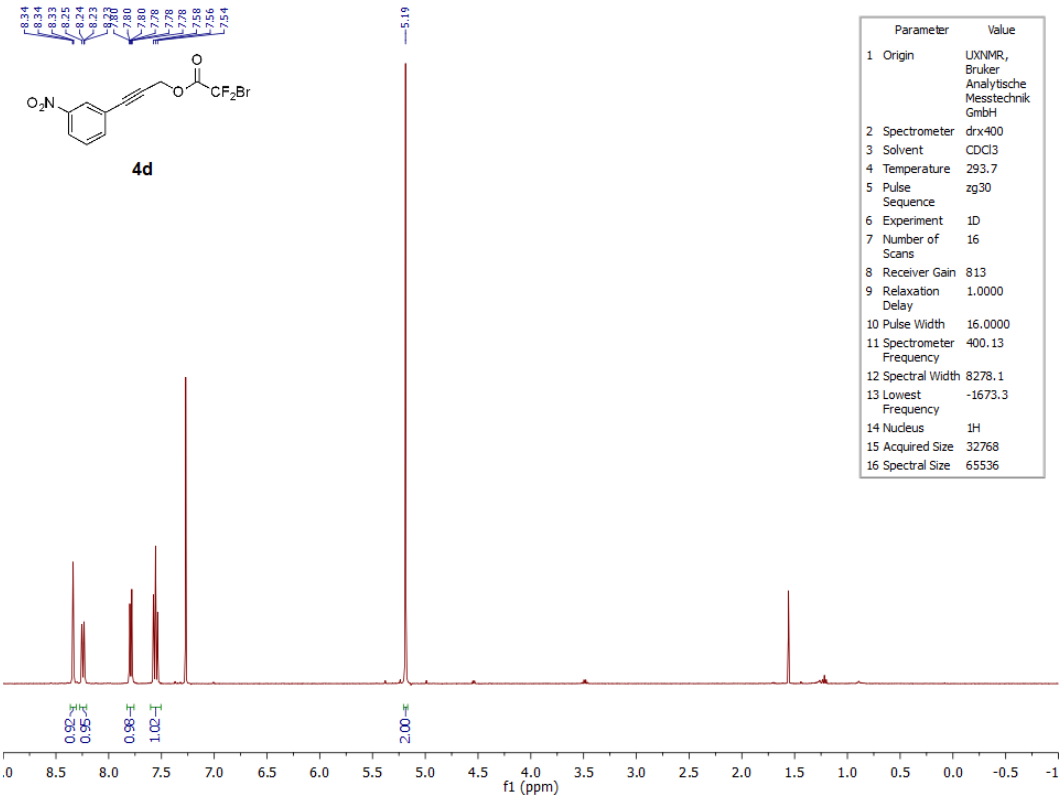
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.7
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



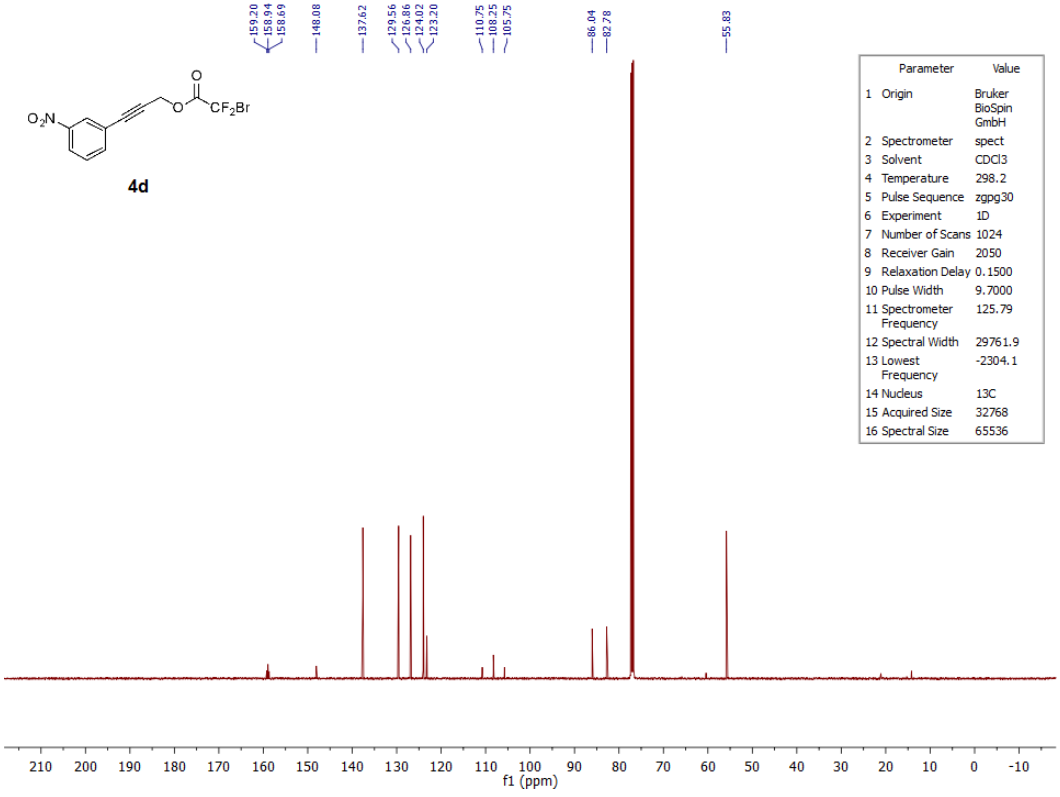
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Acquisition Time	1.1011
12	Spectrometer Frequency	125.79
13	Spectral Width	29761.9
14	Lowest Frequency	-2285.5
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536

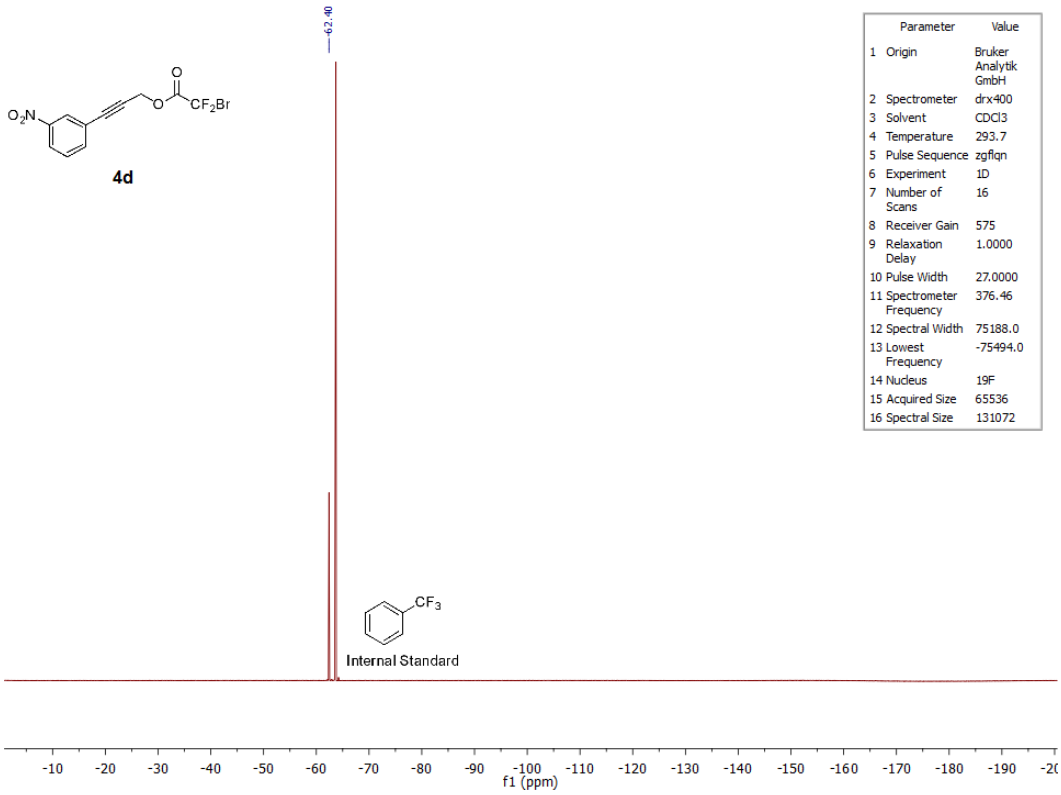


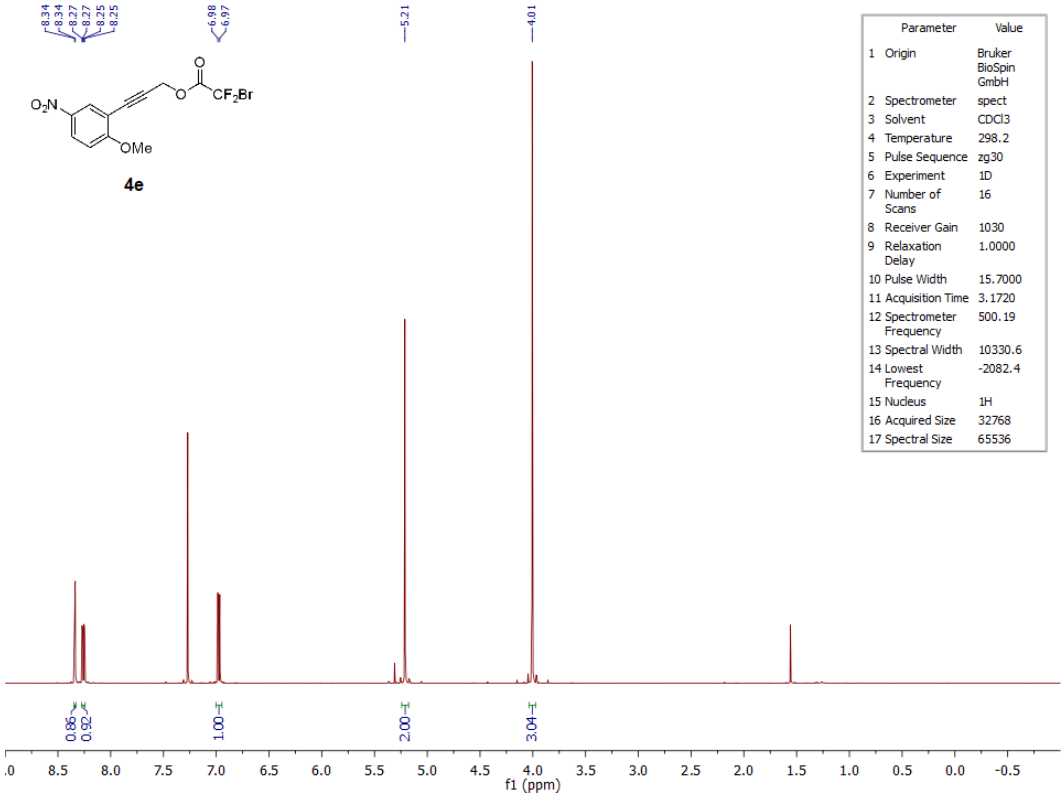
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.3
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75409.6
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



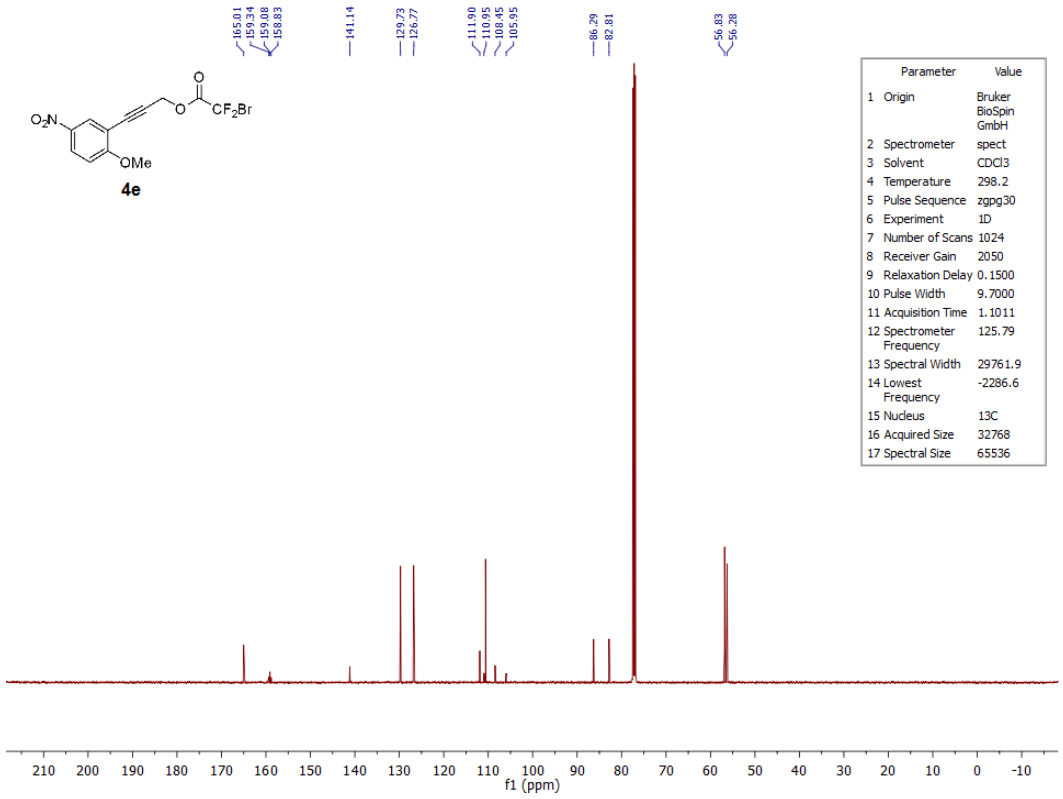
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	813
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8278.1
13	Lowest Frequency	-1673.3
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


159.20
158.94
158.69
148.08
137.62
129.56
126.86
124.02
123.20
110.75
108.25
105.75
86.04
82.78
55.83
O2N
O
O
CF2Br
4d
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2304.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

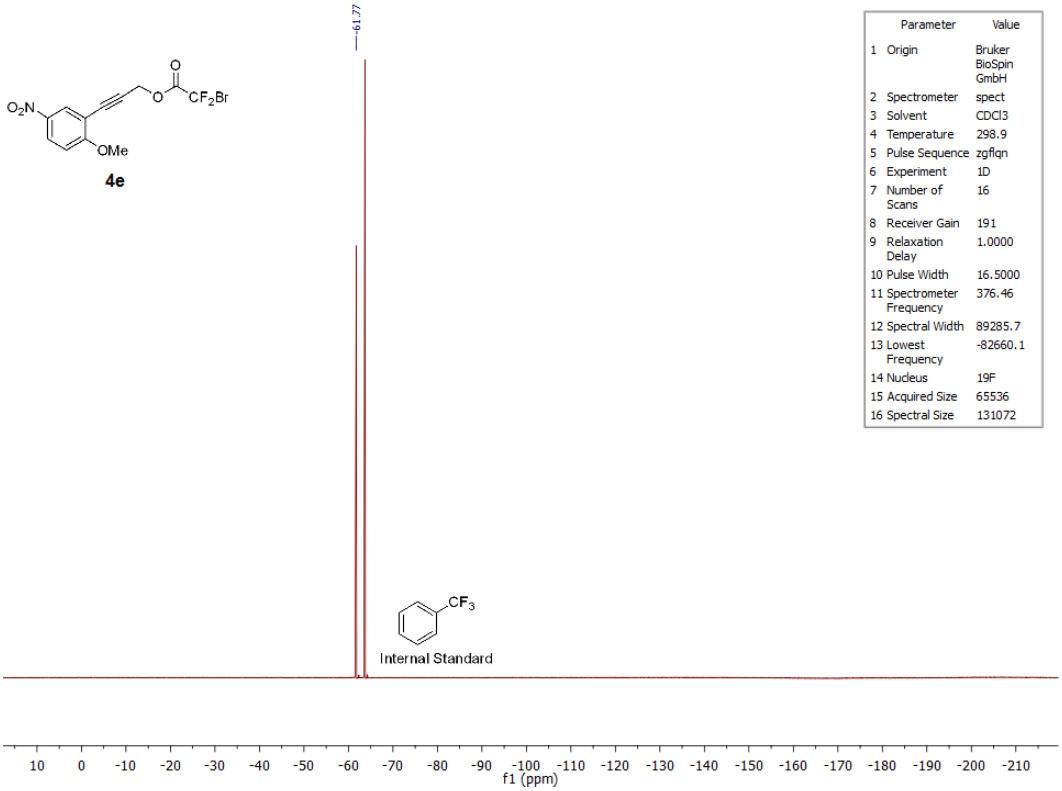

62.40
O2N
O
O
CF2Br
4d
CF3
Internal Standard
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Spectrometer Frequency 376.46
12 Spectral Width 75188.0
13 Lowest Frequency -75494.0
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)



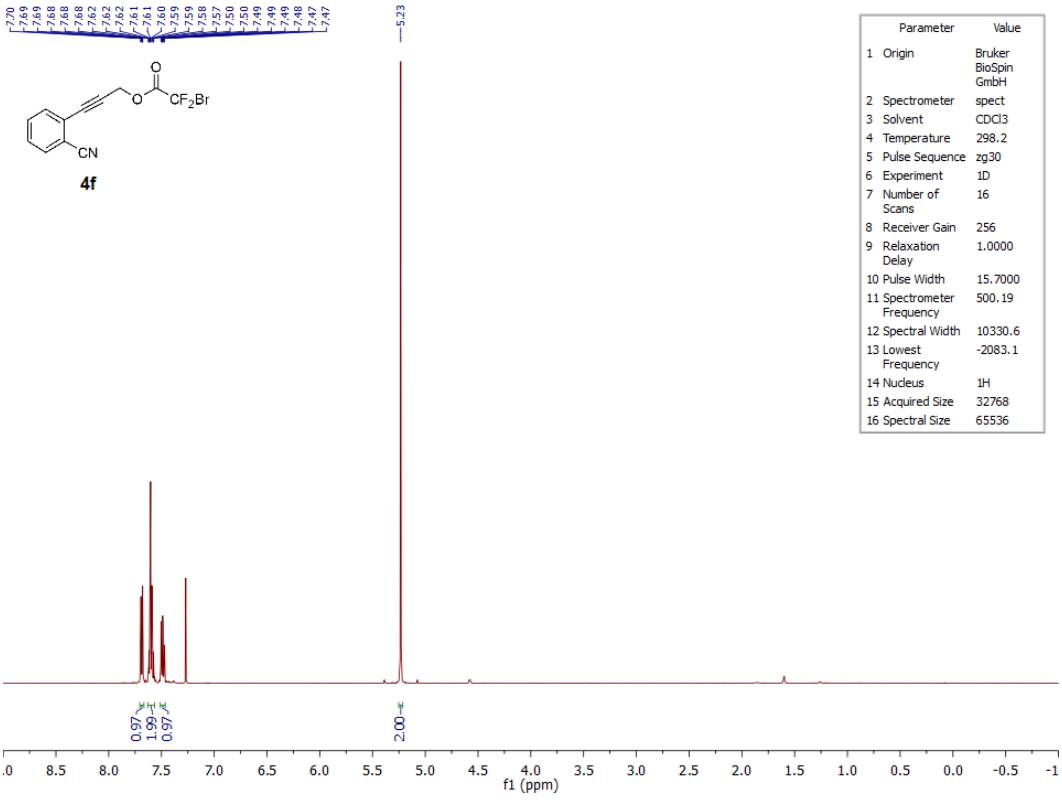
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	1030
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Acquisition Time	3.1720
12	Spectrometer Frequency	500.19
13	Spectral Width	10330.6
14	Lowest Frequency	-2082.4
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



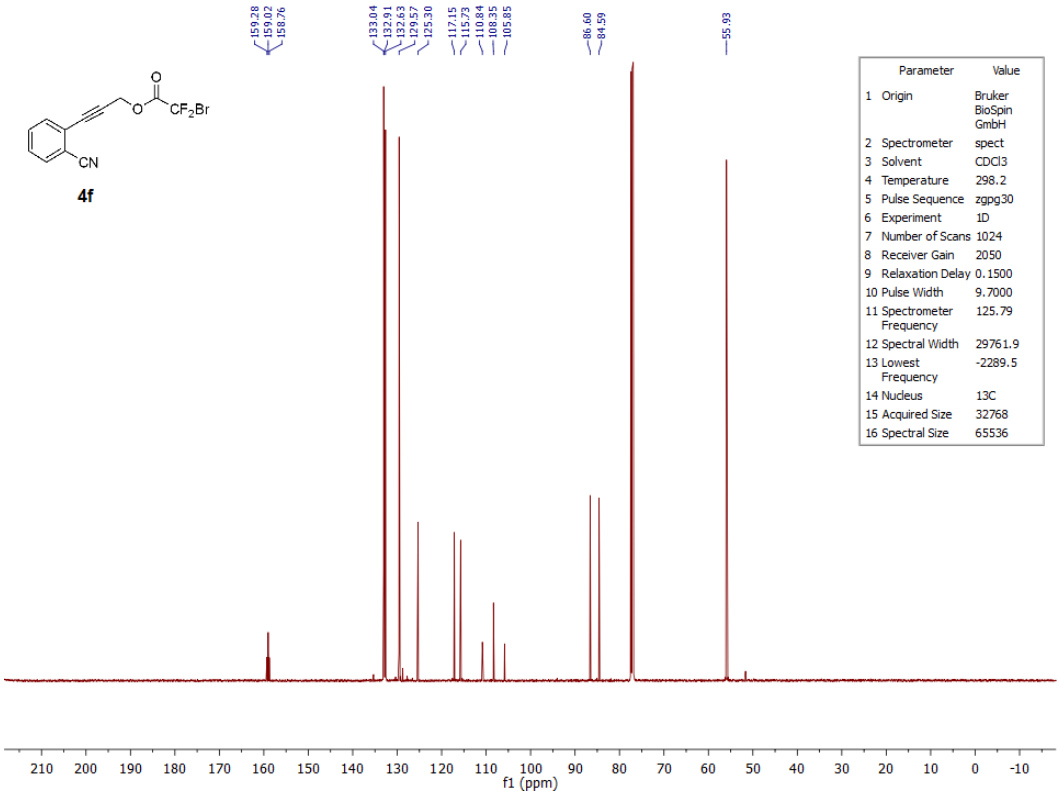
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Acquisition Time	1.1011
12	Spectrometer Frequency	125.79
13	Spectral Width	29761.9
14	Lowest Frequency	-2286.6
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536

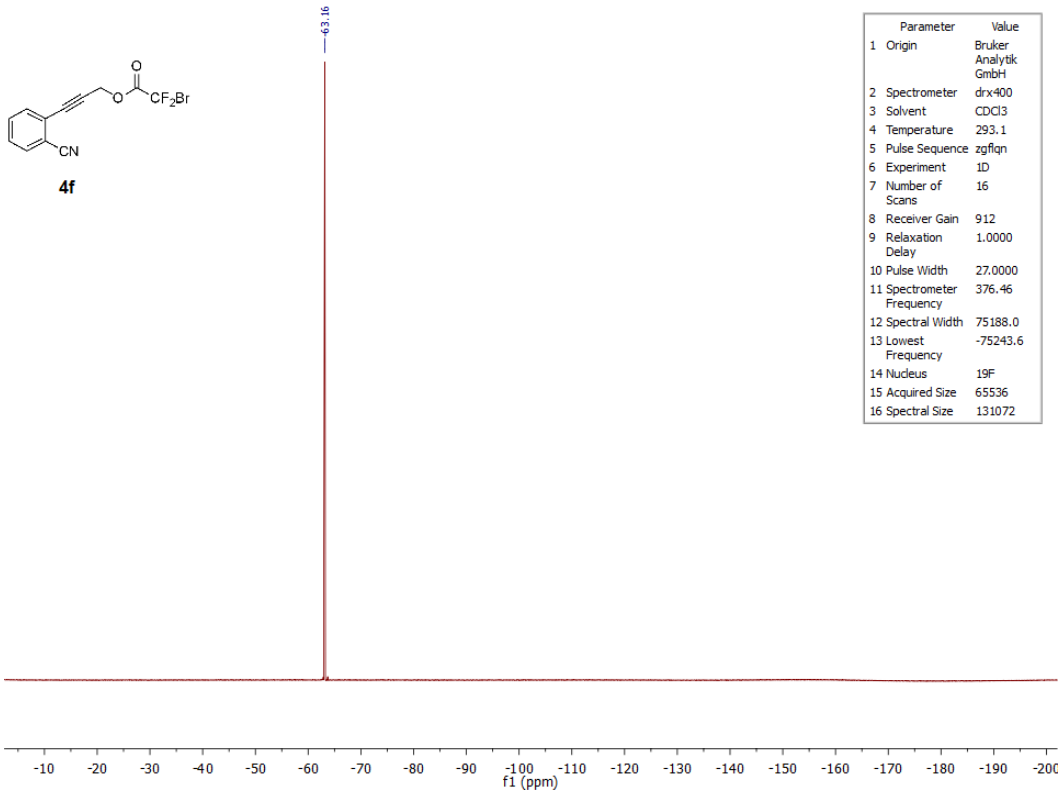


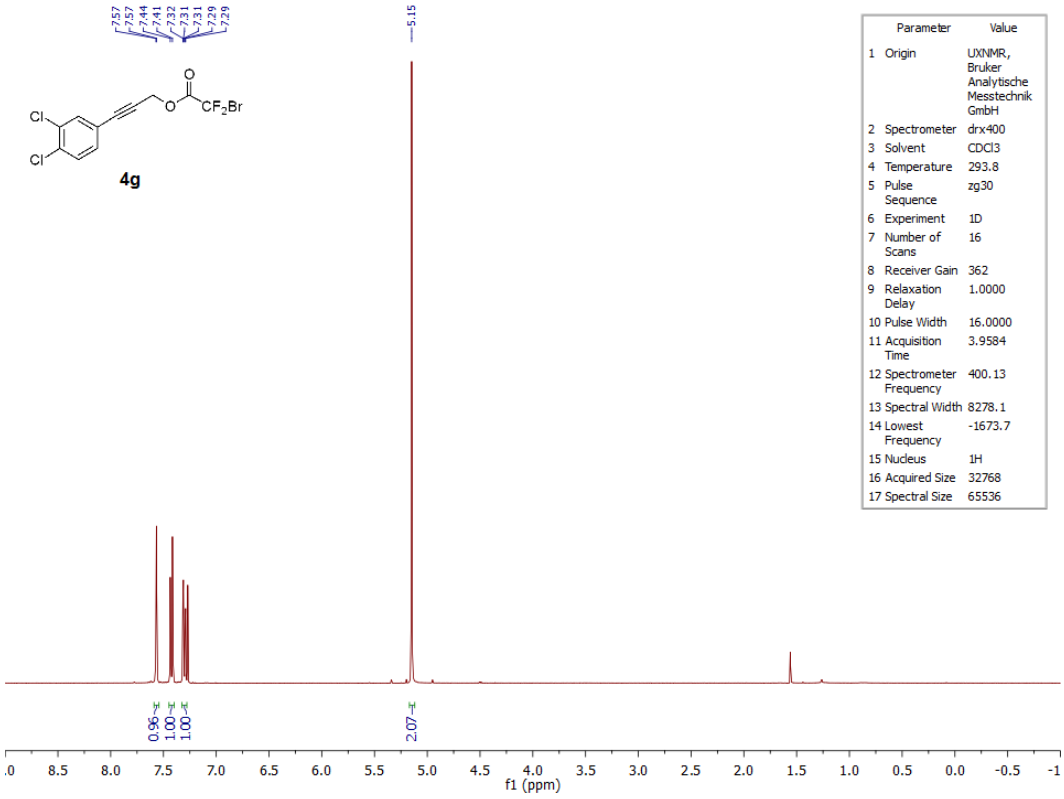
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82660.1
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



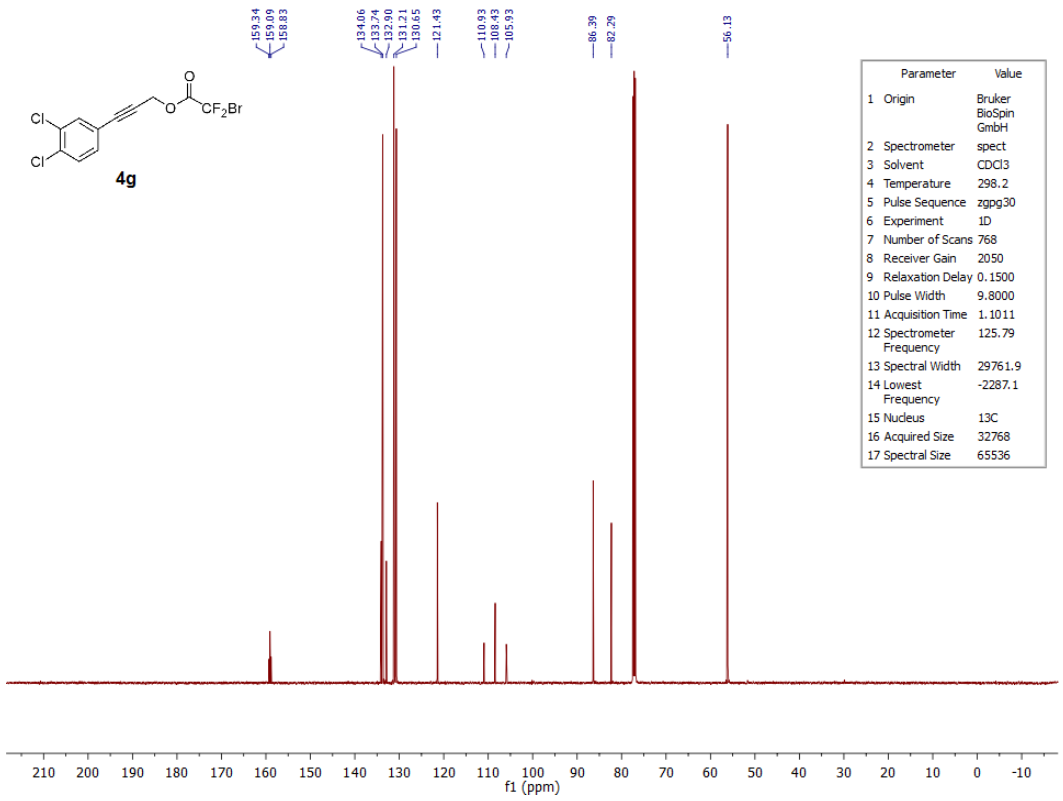
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	256
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2083.1
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


159.28
159.02
158.76
133.04
132.91
132.83
129.57
125.30
117.15
115.73
110.84
108.35
105.85
86.60
84.59
55.93
O
O
CF2Br
CN
4f
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2289.5
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

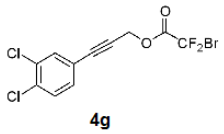

63.16
O
O
CF2Br
CN
4f
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.1
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 912
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Spectrometer Frequency 376.46
12 Spectral Width 75188.0
13 Lowest Frequency -75243.6
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.8
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	362
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.7
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536

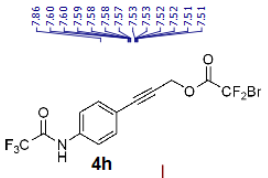


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	768
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.8000
11	Acquisition Time	1.1011
12	Spectrometer Frequency	125.79
13	Spectral Width	29761.9
14	Lowest Frequency	-2287.1
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536



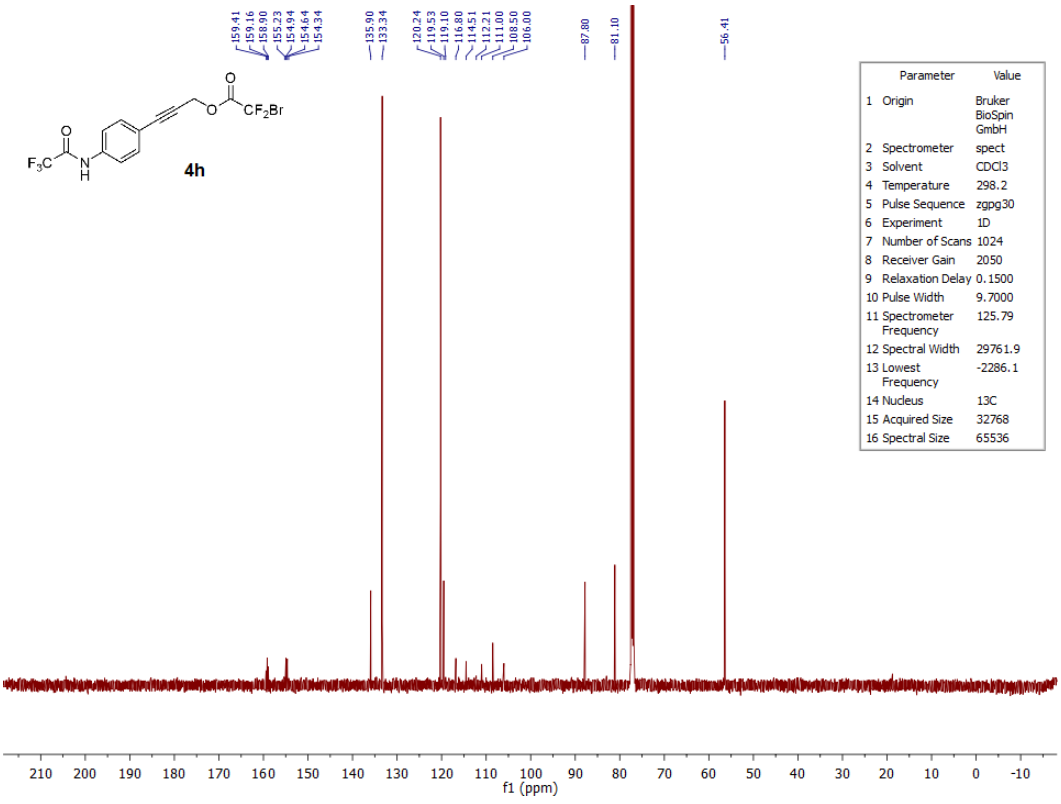
4g

	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.8
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	456
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75243.6
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072

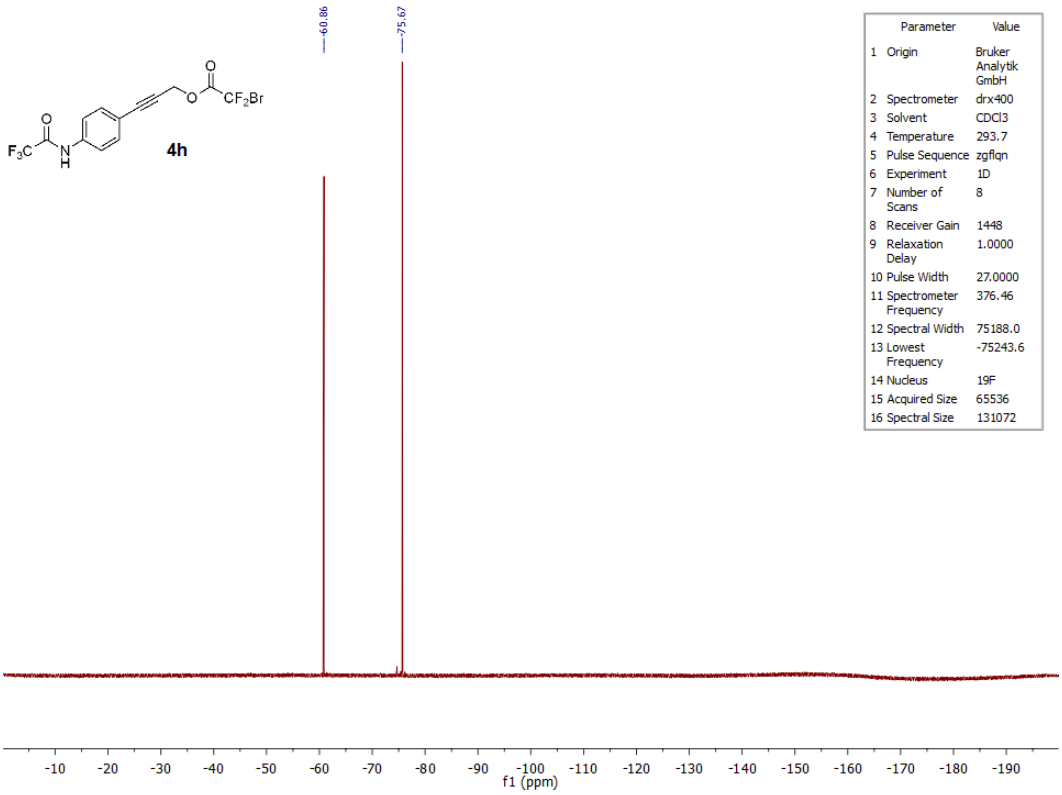


4h

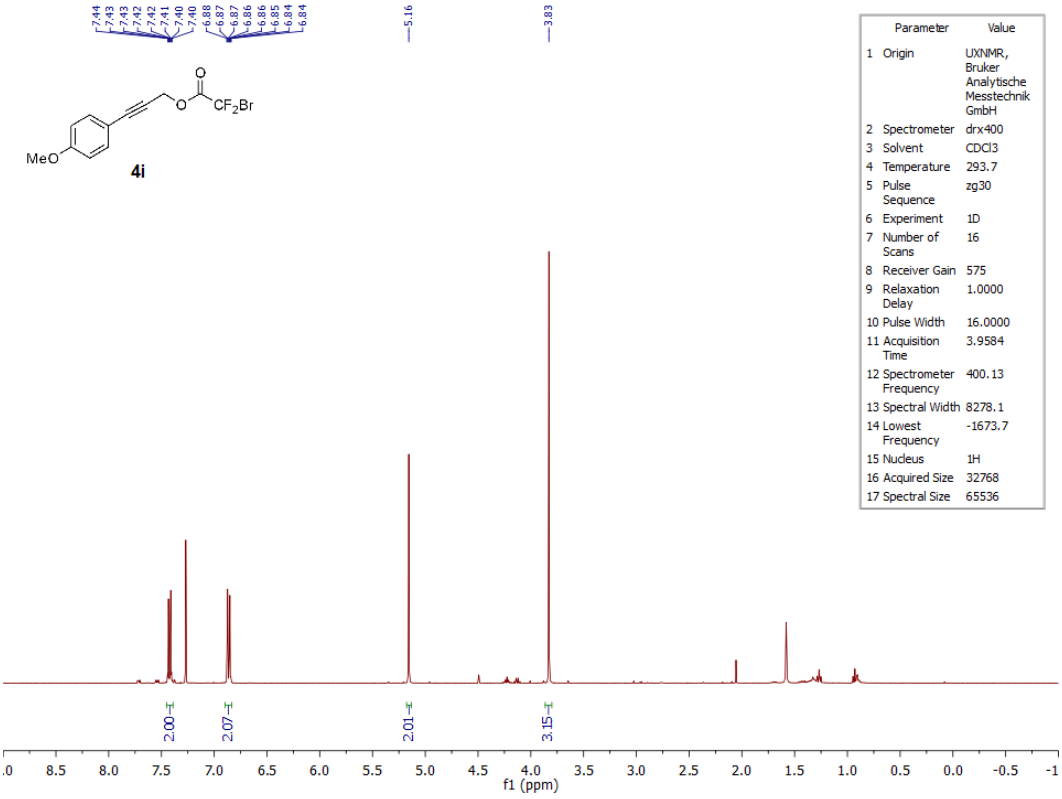
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	1620
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

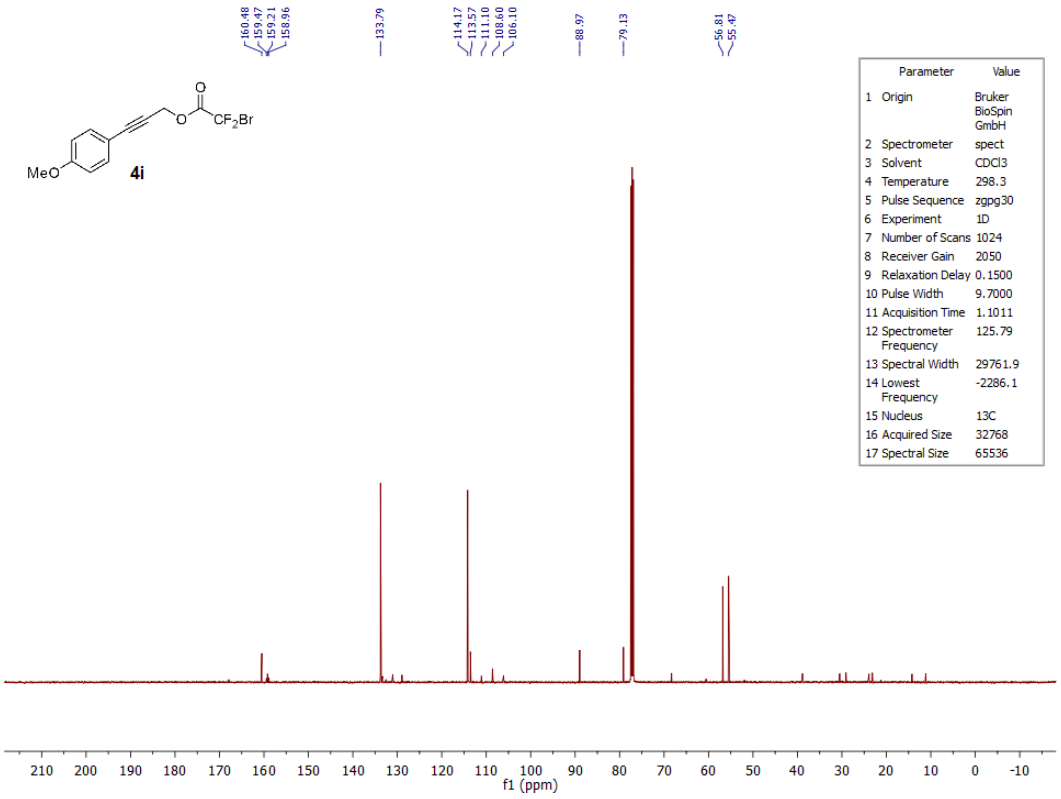


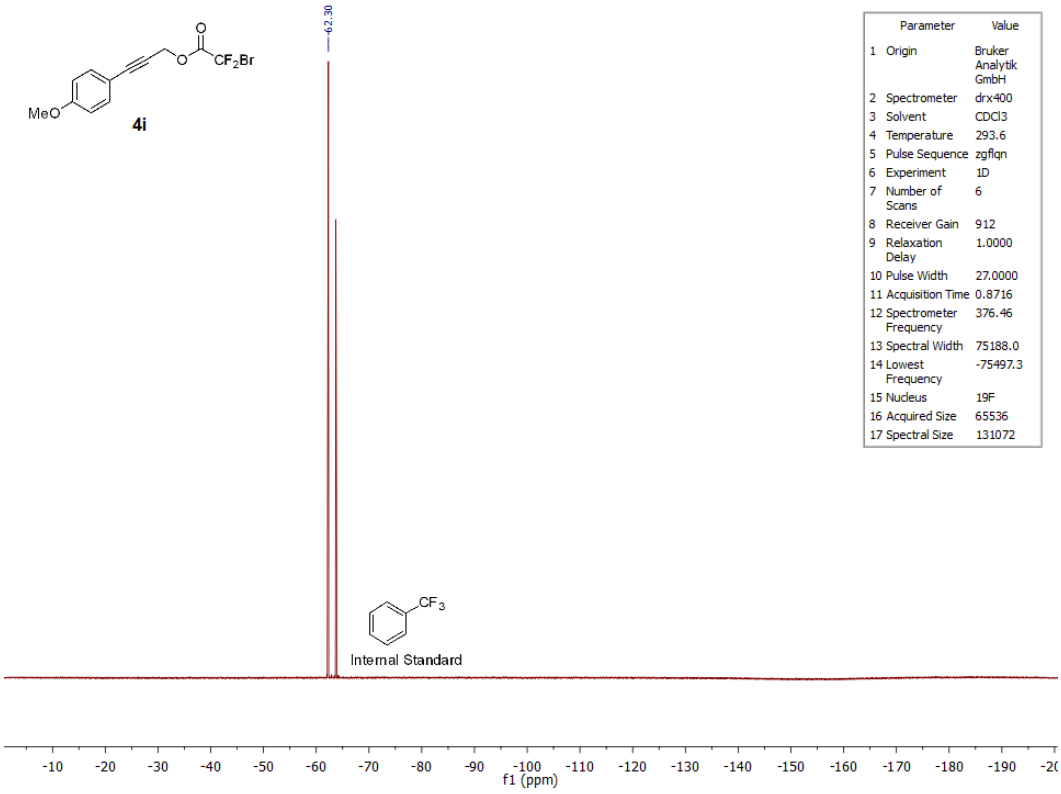
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2286.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



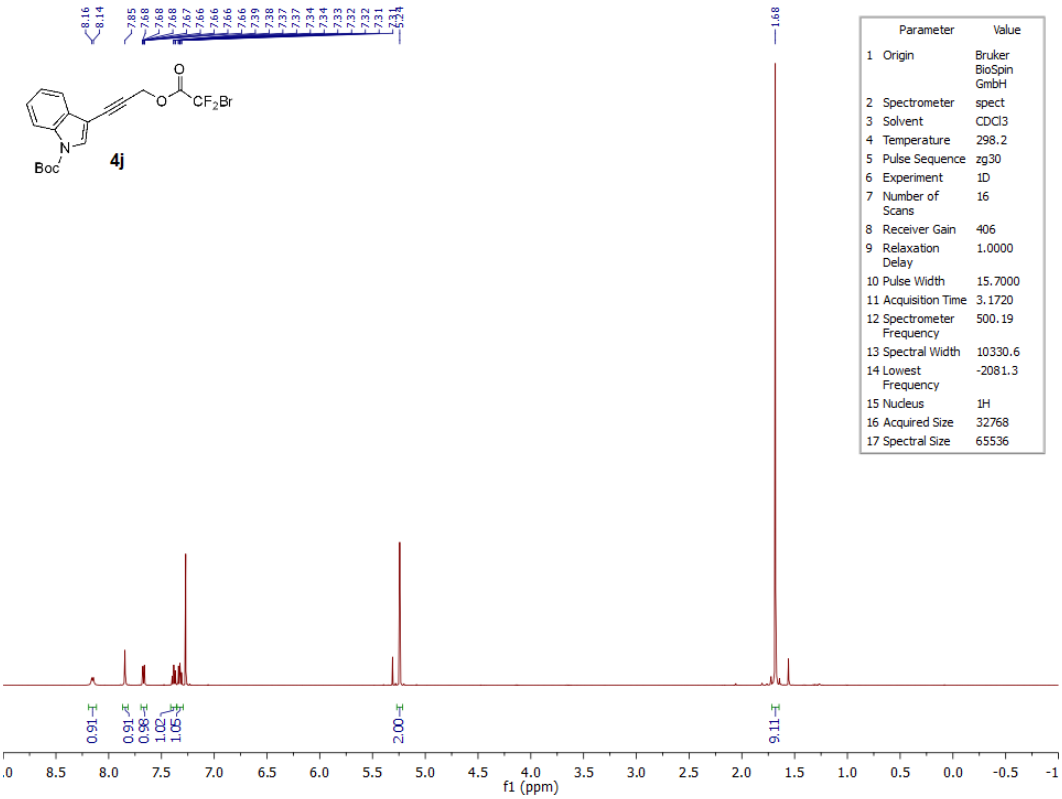
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	1448
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75243.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
6.88
6.87
6.87
6.86
6.86
6.85
6.84
6.84
5.16
3.83
O
O
CF2Br
MeO
4i
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.7
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
2.00
2.07
2.01
3.15
f1 (ppm)

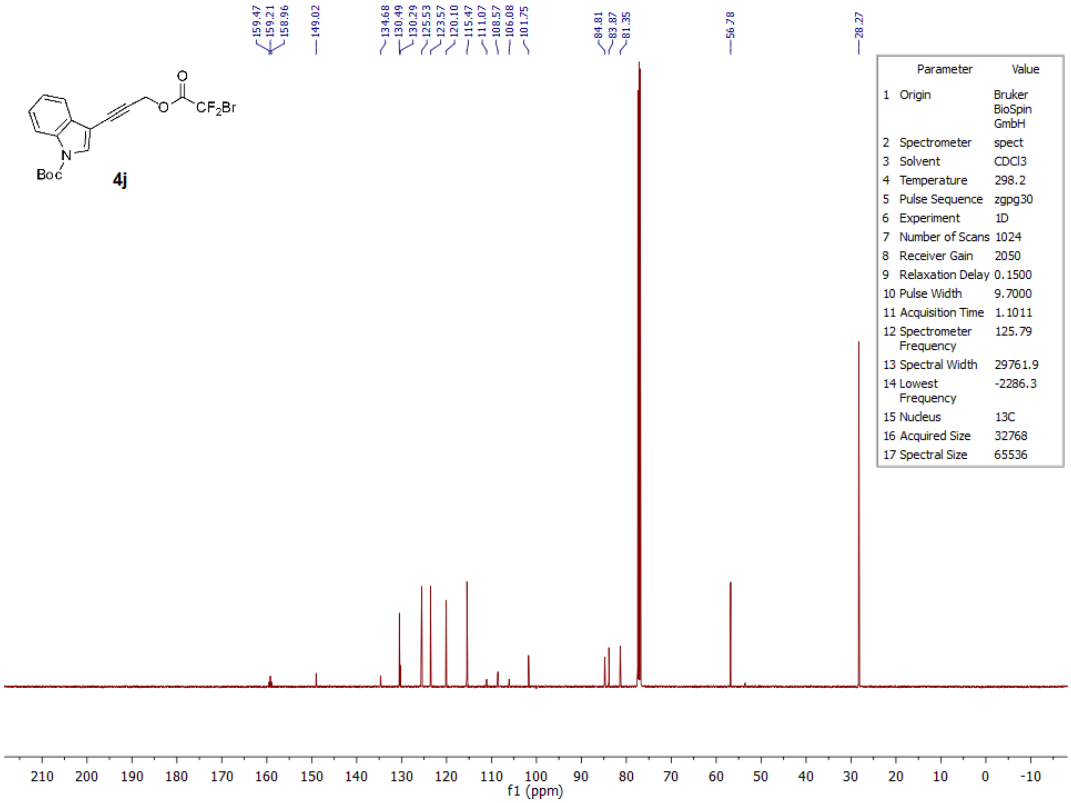

160.48
159.47
159.21
158.96
133.79
114.17
113.57
111.10
108.60
106.10
88.97
79.13
56.81
55.47
O
O
CF2Br
MeO
4i
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.3
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.1
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

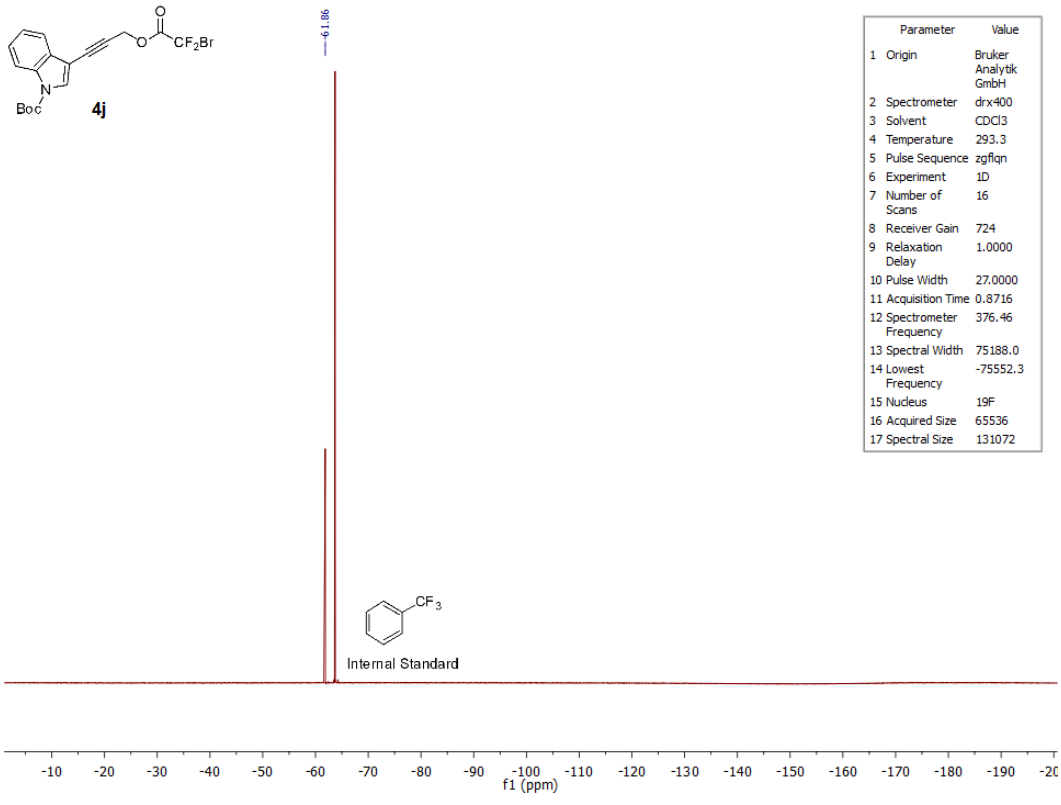


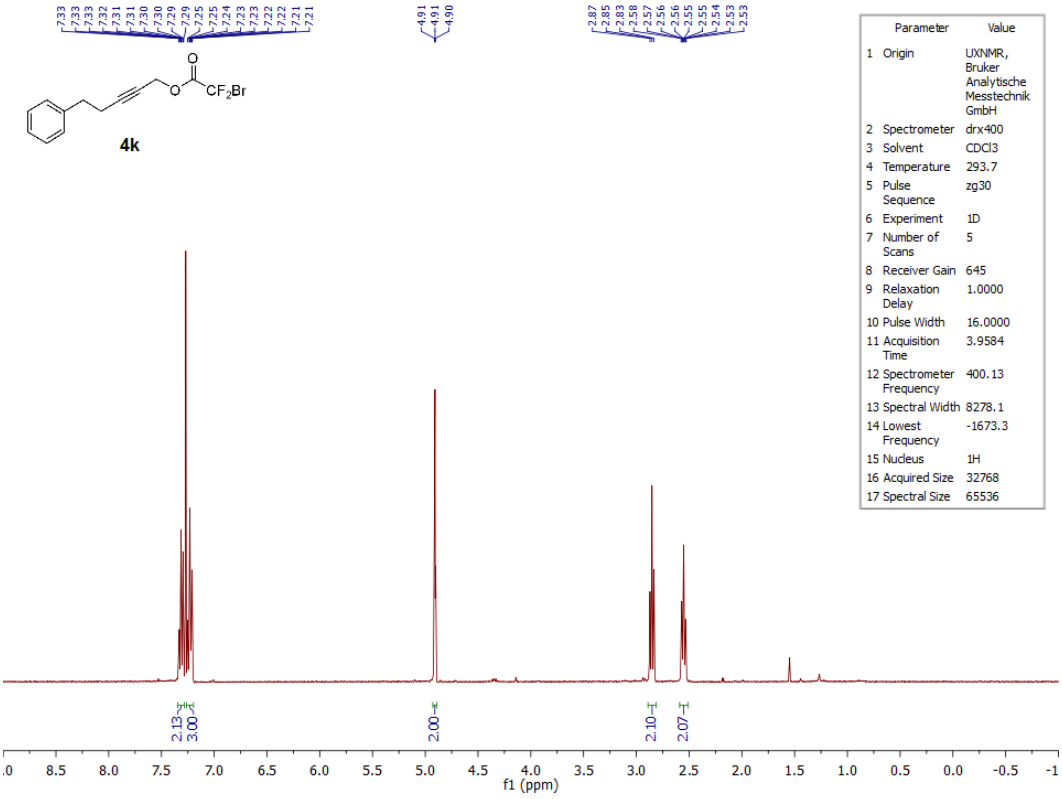
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	6
8	Receiver Gain	912
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75497.3
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072

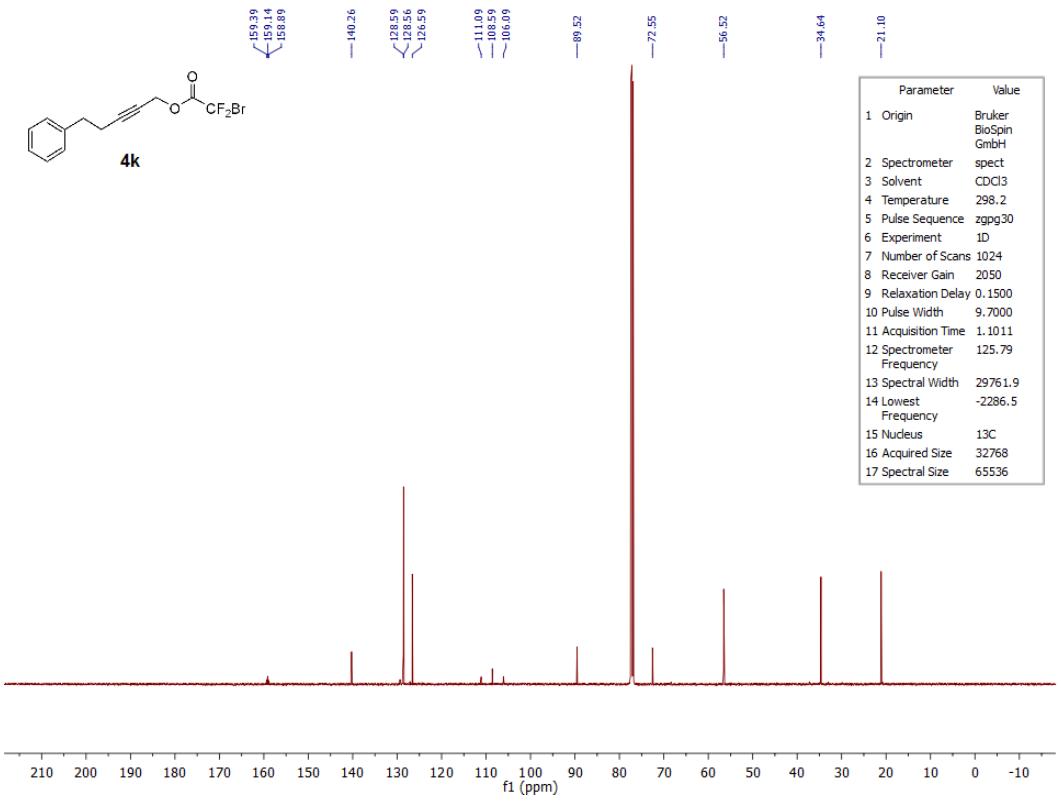


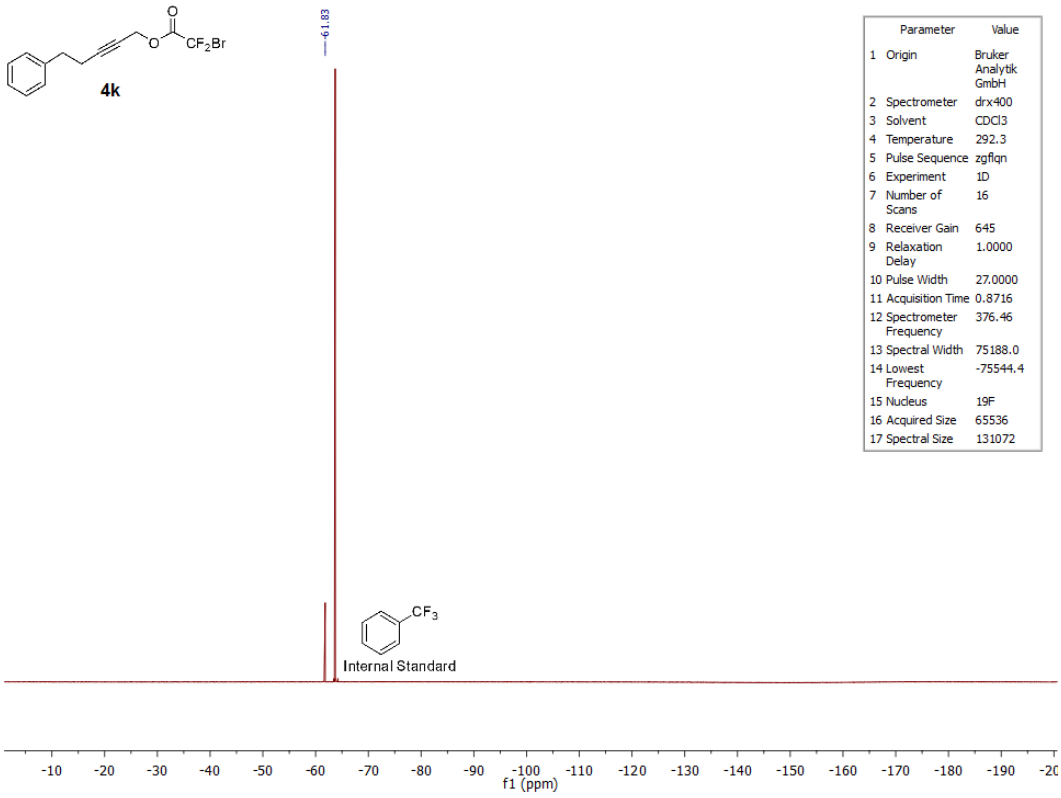
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	406
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Acquisition Time	3.1720
12	Spectrometer Frequency	500.19
13	Spectral Width	10330.6
14	Lowest Frequency	-2081.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


159.47
159.21
158.96
149.02
134.68
130.49
130.29
125.53
123.57
120.10
115.47
111.07
108.57
106.08
101.75
84.81
83.87
81.35
56.78
28.27
O
O
CF2Br
N
Boc
4j
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.3
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

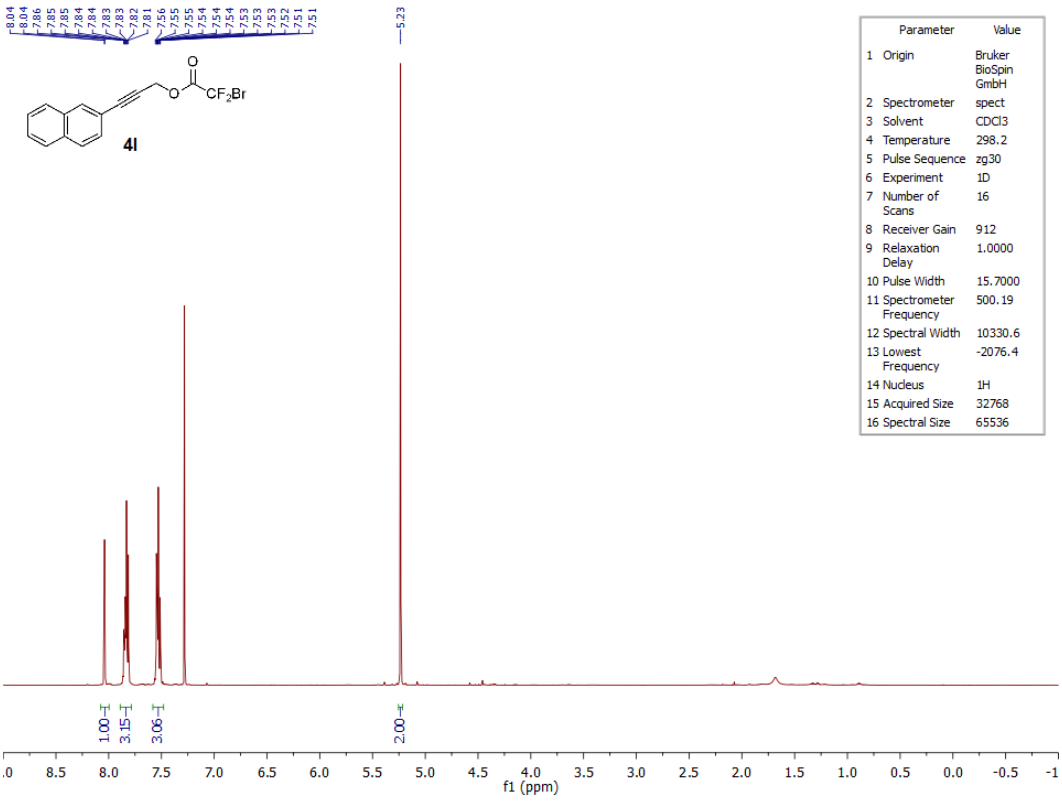

-61.86
O
O
CF2Br
N
Boc
4j
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.3
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 724
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Acquisition Time 0.8716
12 Spectrometer Frequency 376.46
13 Spectral Width 75188.0
14 Lowest Frequency -75552.3
15 Nucleus 19F
16 Acquired Size 65536
17 Spectral Size 131072
CF3
Internal Standard
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)


4k
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 5
8 Receiver Gain 645
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
2.13
3.00
2.00
2.10
2.07
f1 (ppm)

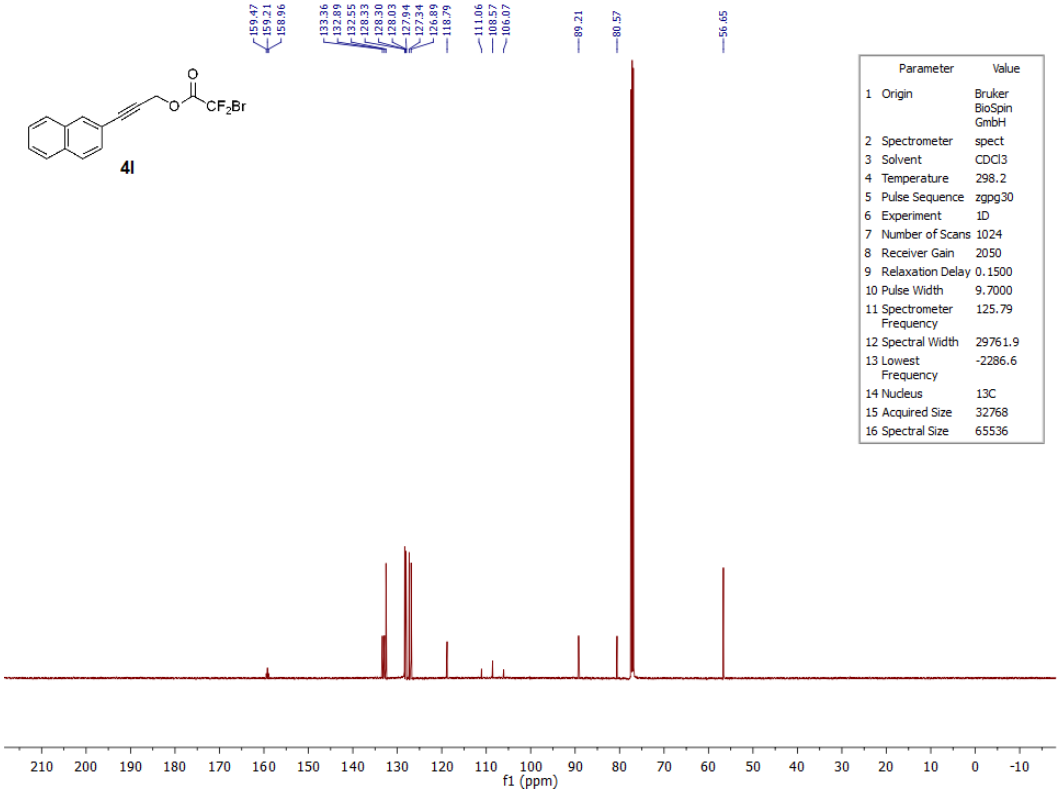

4k
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.5
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

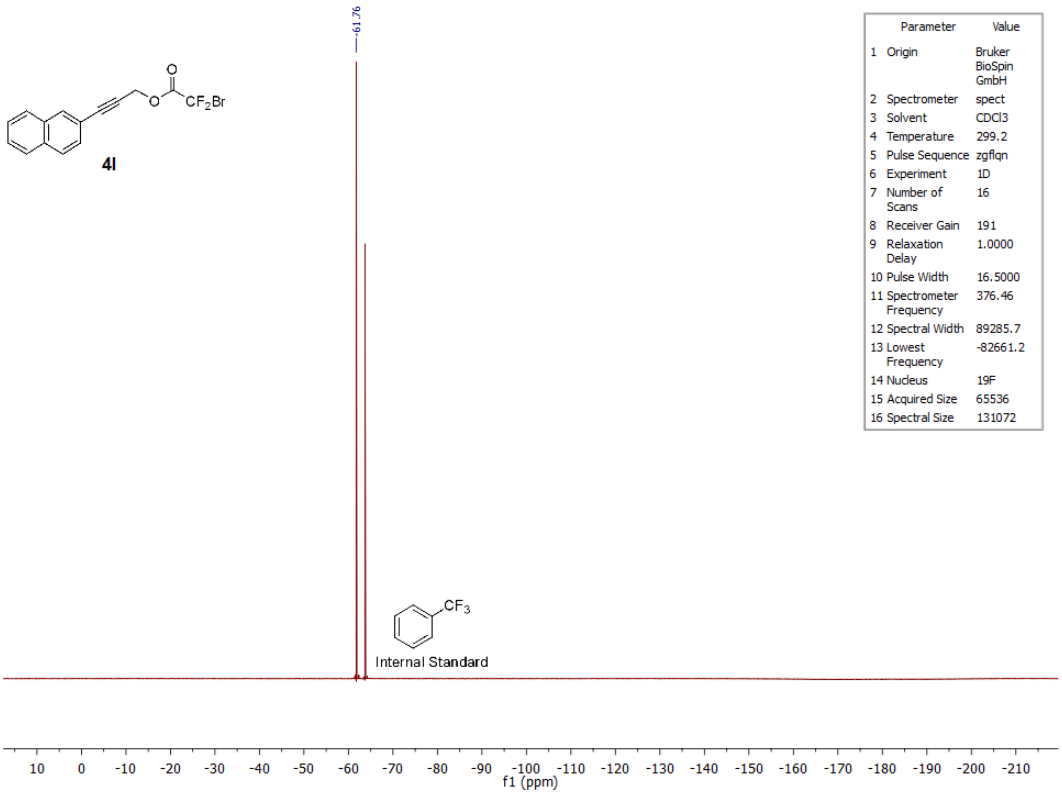


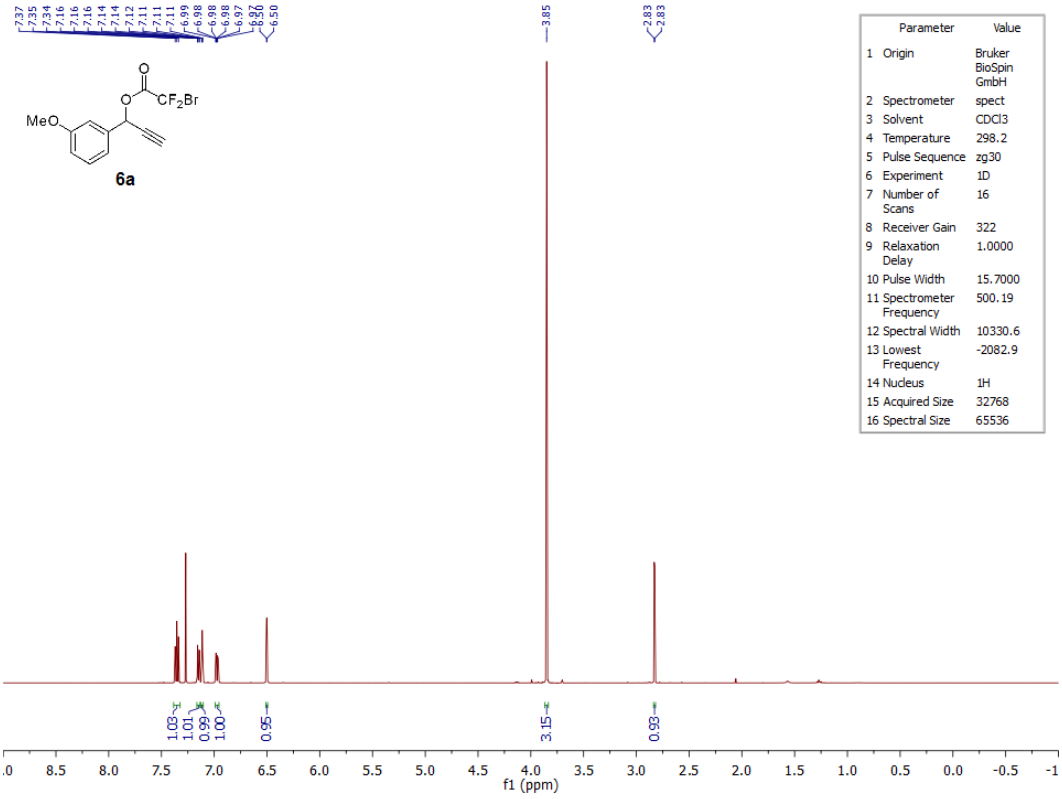
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	292.3
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75544.4
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



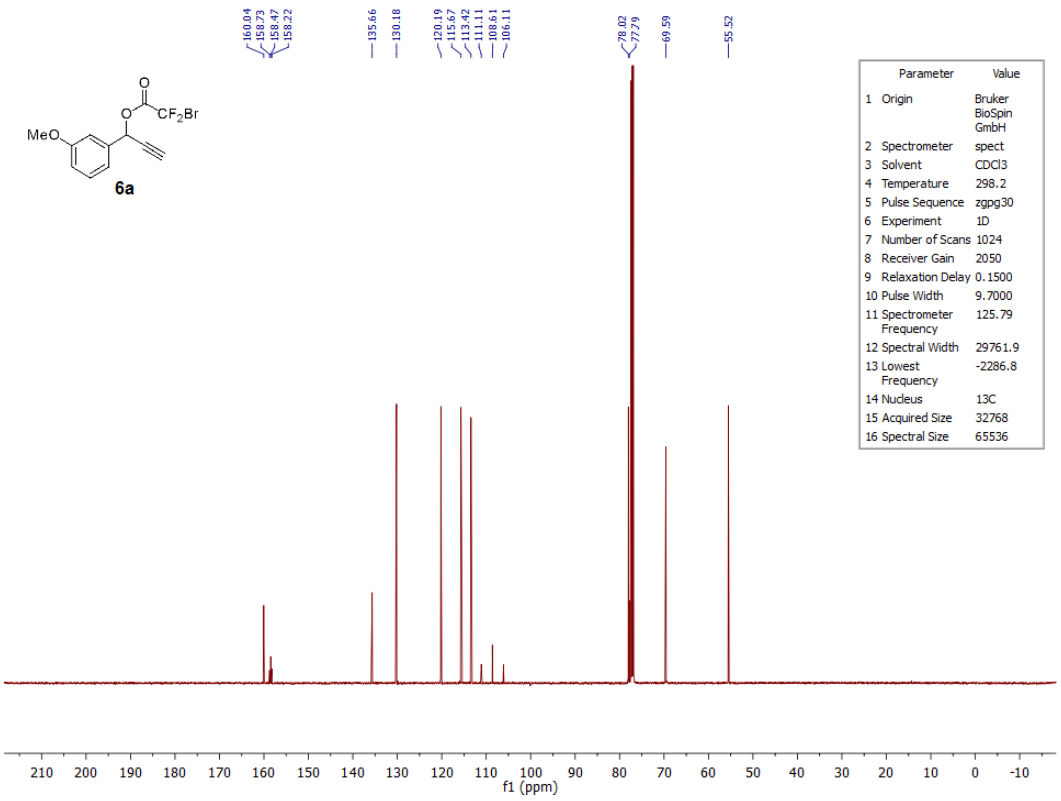
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	912
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2076.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


159.47
159.21
158.96
133.36
132.89
132.55
128.33
128.30
128.03
127.94
127.34
126.89
118.79
111.06
108.57
106.07
89.21
80.57
56.65
O
O
CF2Br
4l
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.6
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

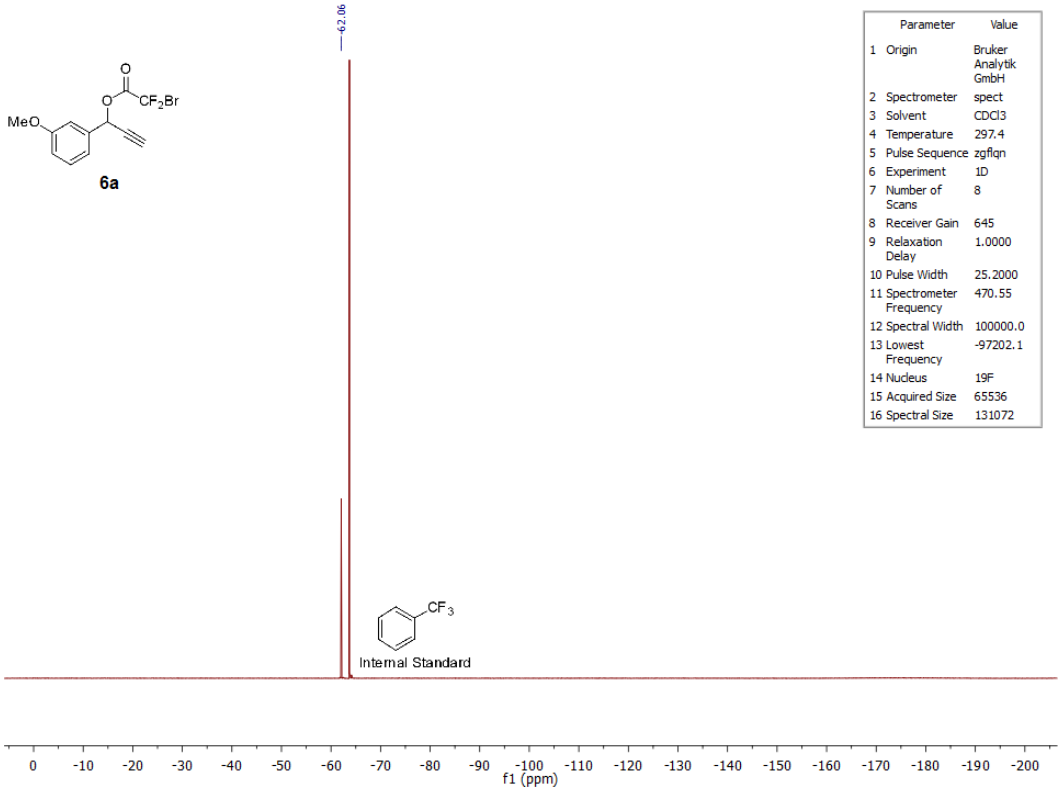

-61.76
O
O
CF2Br
4l
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.2
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82661.2
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
CF3
Internal Standard
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



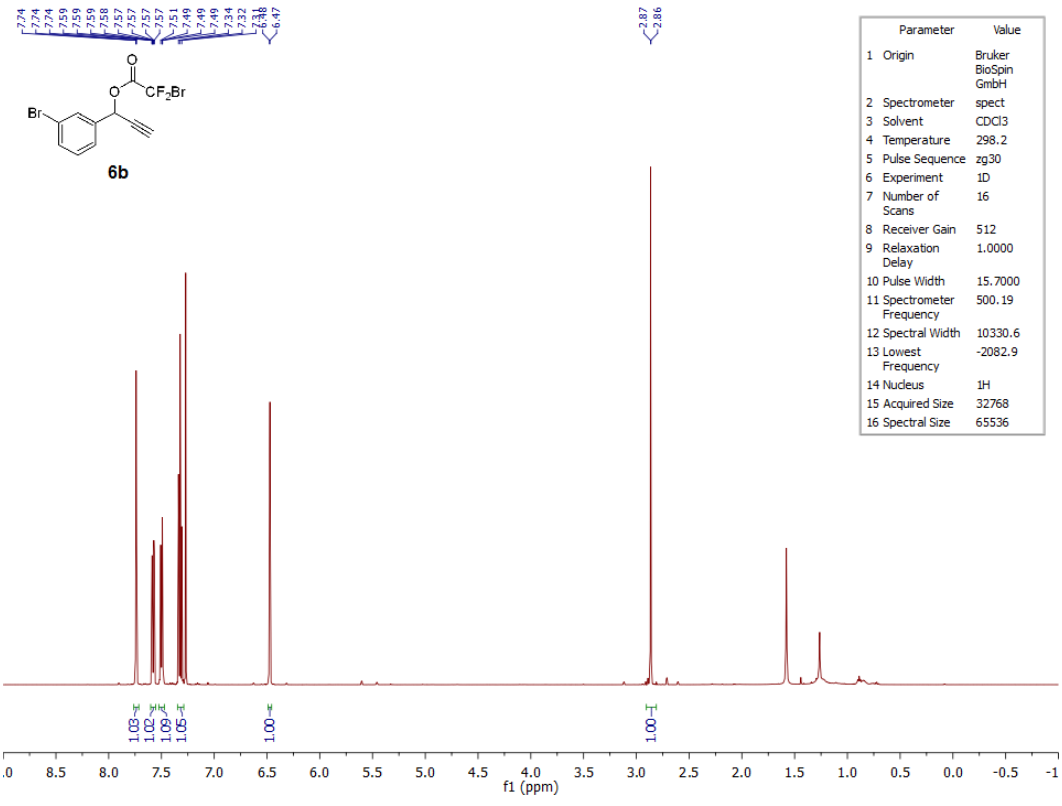
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	322
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



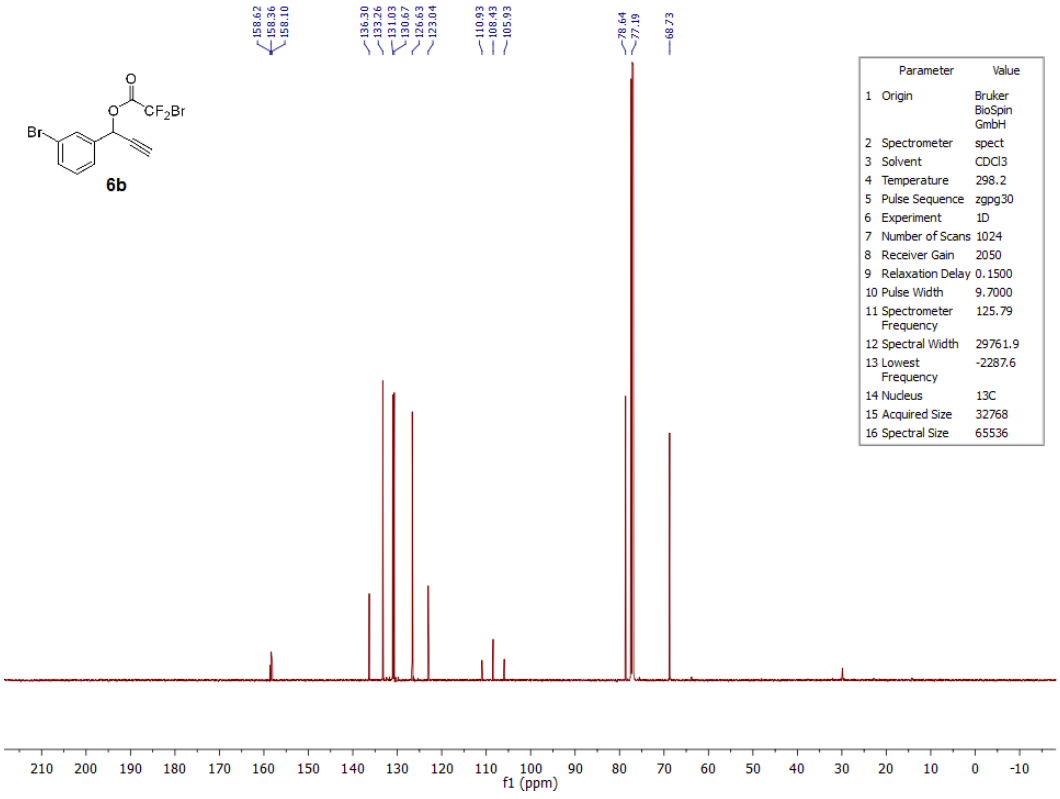
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2286.8
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	297.4
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	25.2000
11	Spectrometer Frequency	470.55
12	Spectral Width	100000.0
13	Lowest Frequency	-97202.1
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	512
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536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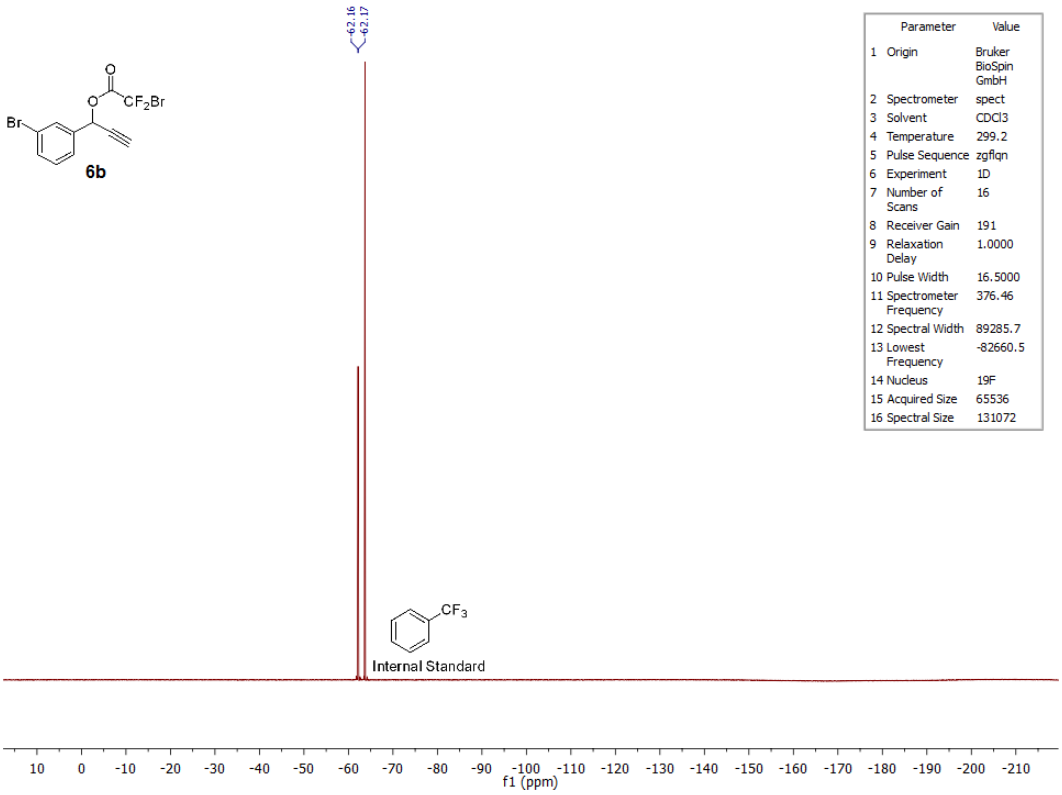
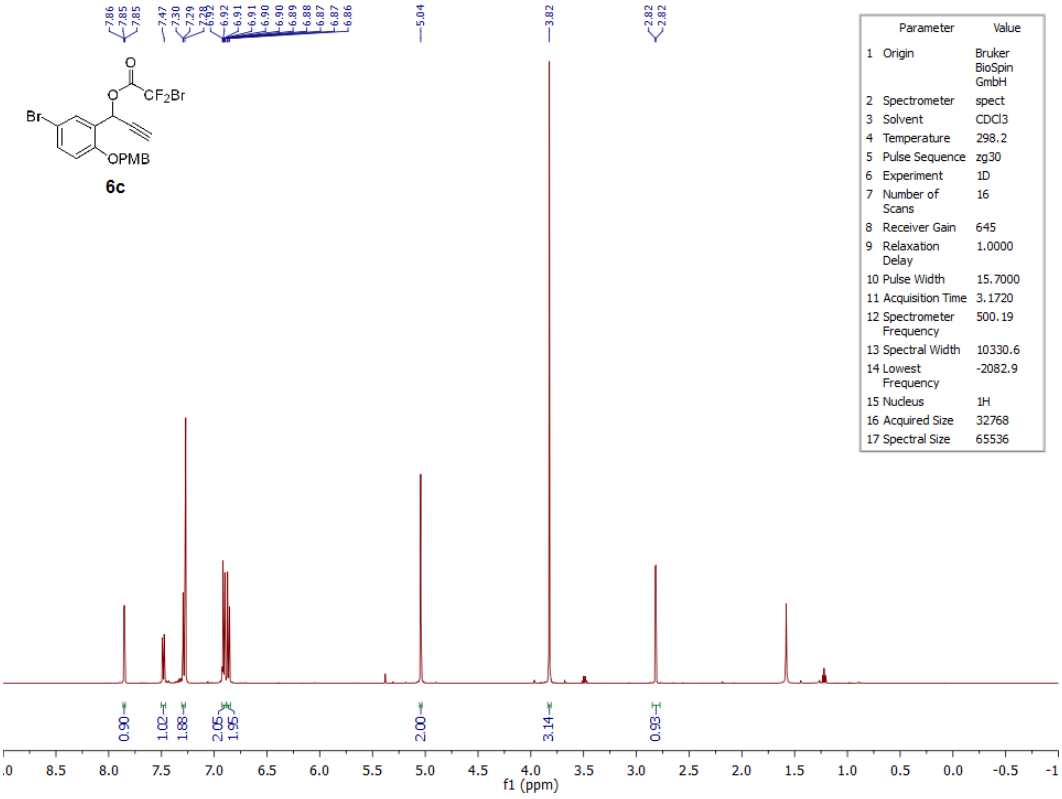
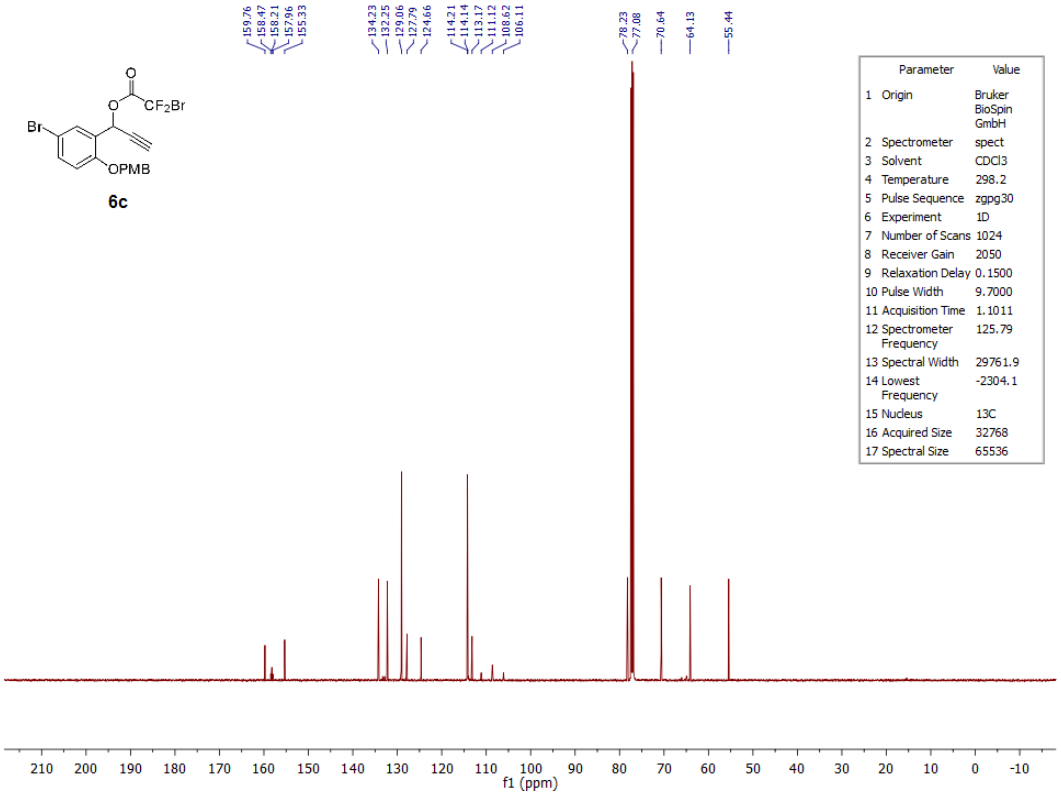
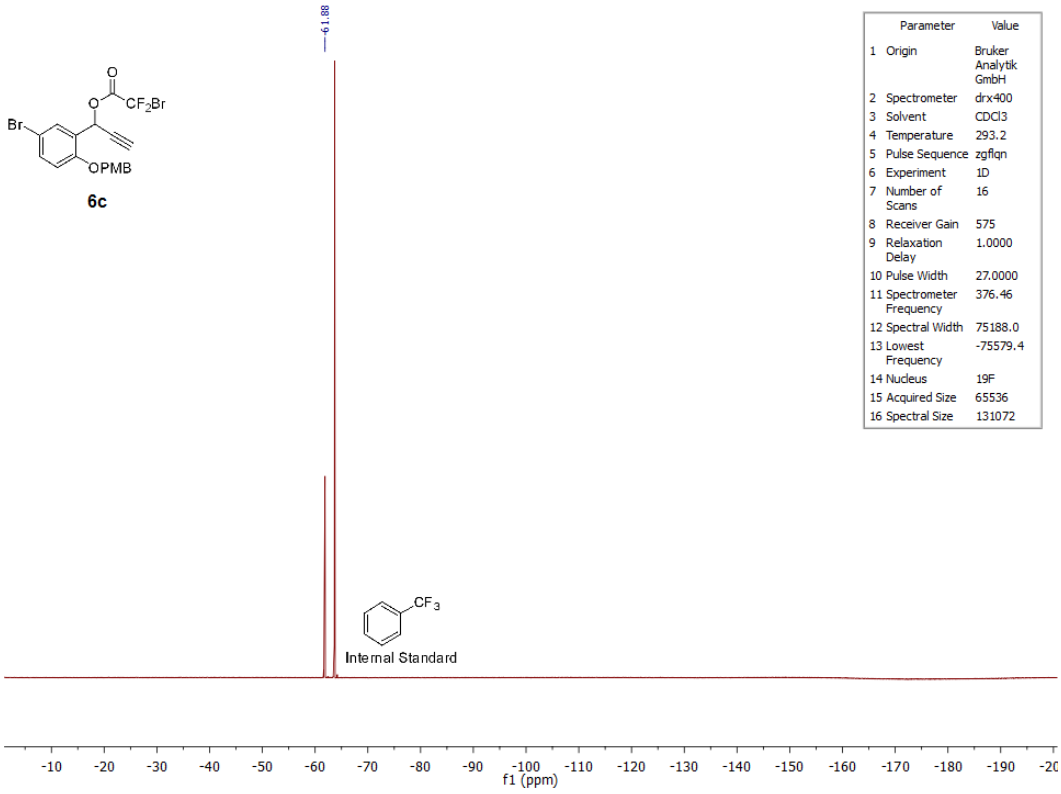
158.36
158.10
136.30
133.26
131.03
130.67
126.63
123.04
110.93
108.43
105.93
78.64
77.19
68.73
Br
O
O
CF2Br
6b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2287.6
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

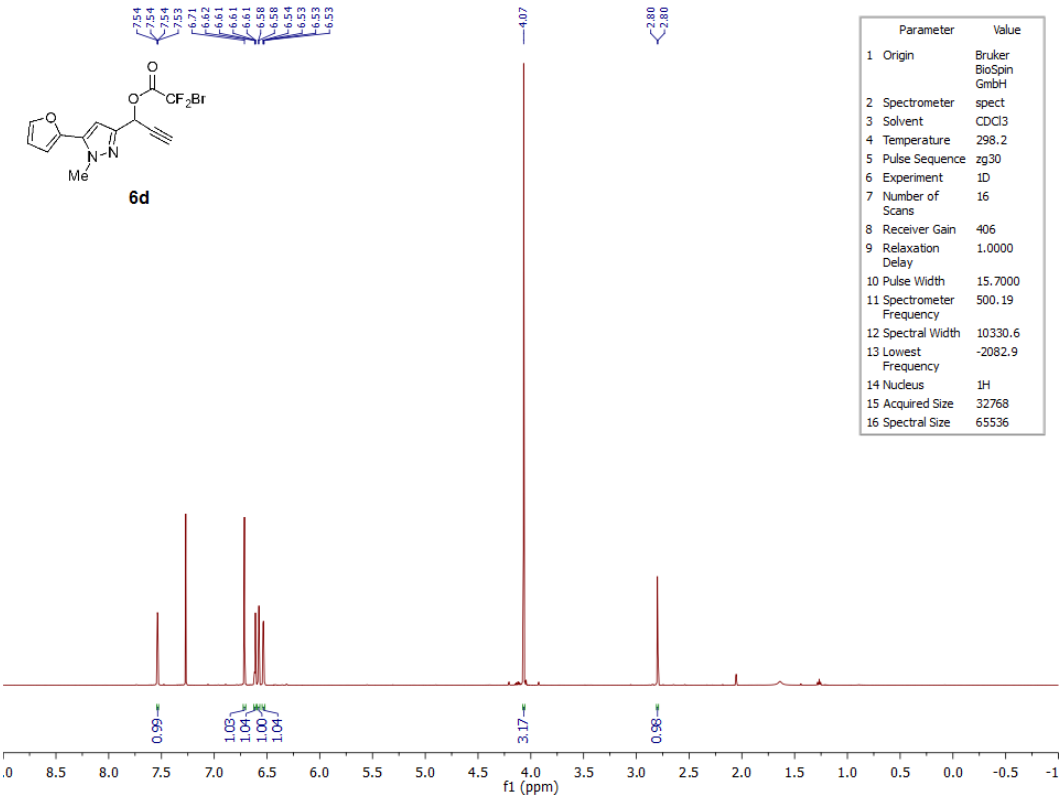

62.16
62.17
Br
O
O
CF2Br
6b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.2
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82660.5
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
CF3
Internal Standard
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.86
7.85
7.85
7.47
7.30
7.29
7.28
6.92
6.91
6.91
6.90
6.90
6.89
6.88
6.87
6.87
6.86
5.04
3.82
2.82
2.82
O
O
CF2Br
Br
OPMB
6c
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 645
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Acquisition Time 3.1720
12 Spectrometer Frequency 500.19
13 Spectral Width 10330.6
14 Lowest Frequency -2082.9
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.90
1.02
1.88
2.05
1.95
2.00
3.14
0.93
f1 (ppm)

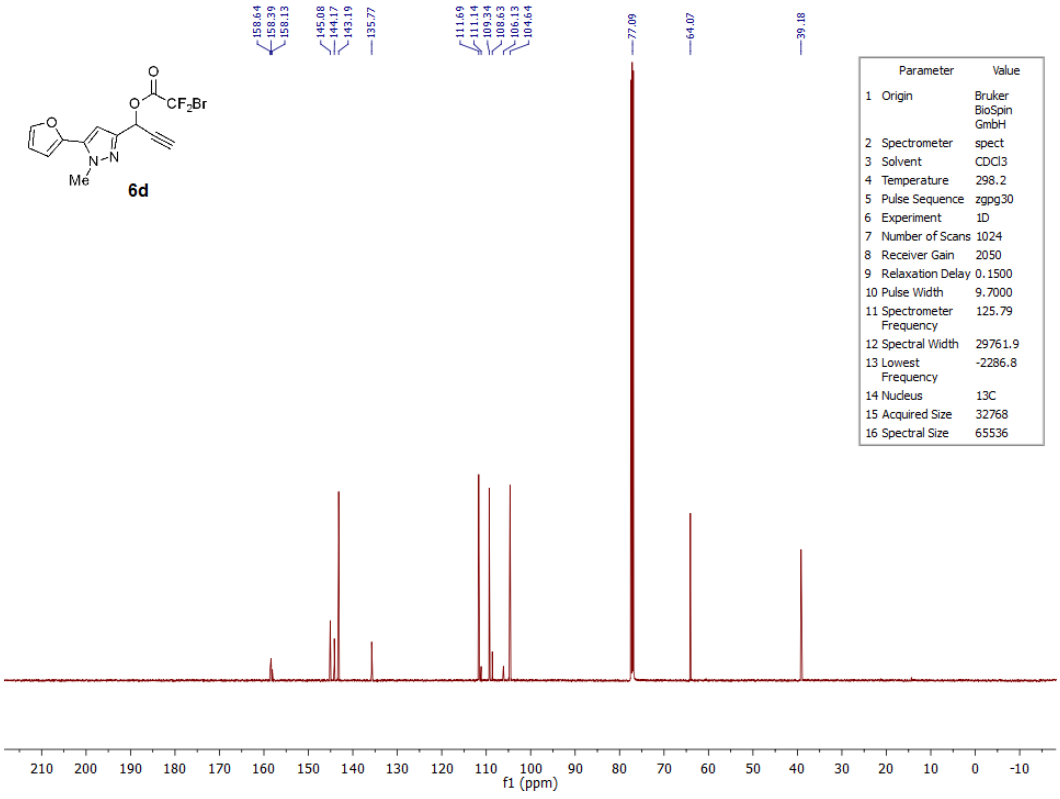

159.76
158.47
157.21
157.96
155.33
134.23
132.25
129.06
127.79
124.66
114.21
114.14
113.17
111.12
108.62
106.11
78.23
77.08
70.64
64.13
55.44
O
O
CF2Br
Br
OPMB
6c
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2304.1
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

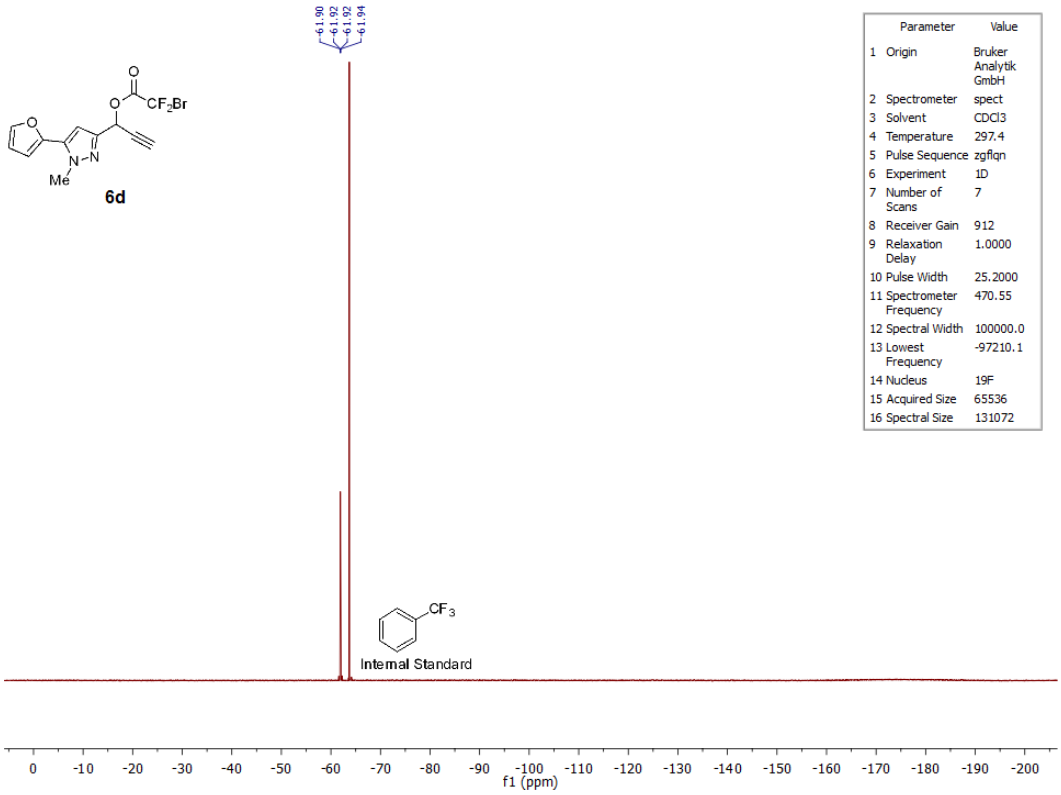


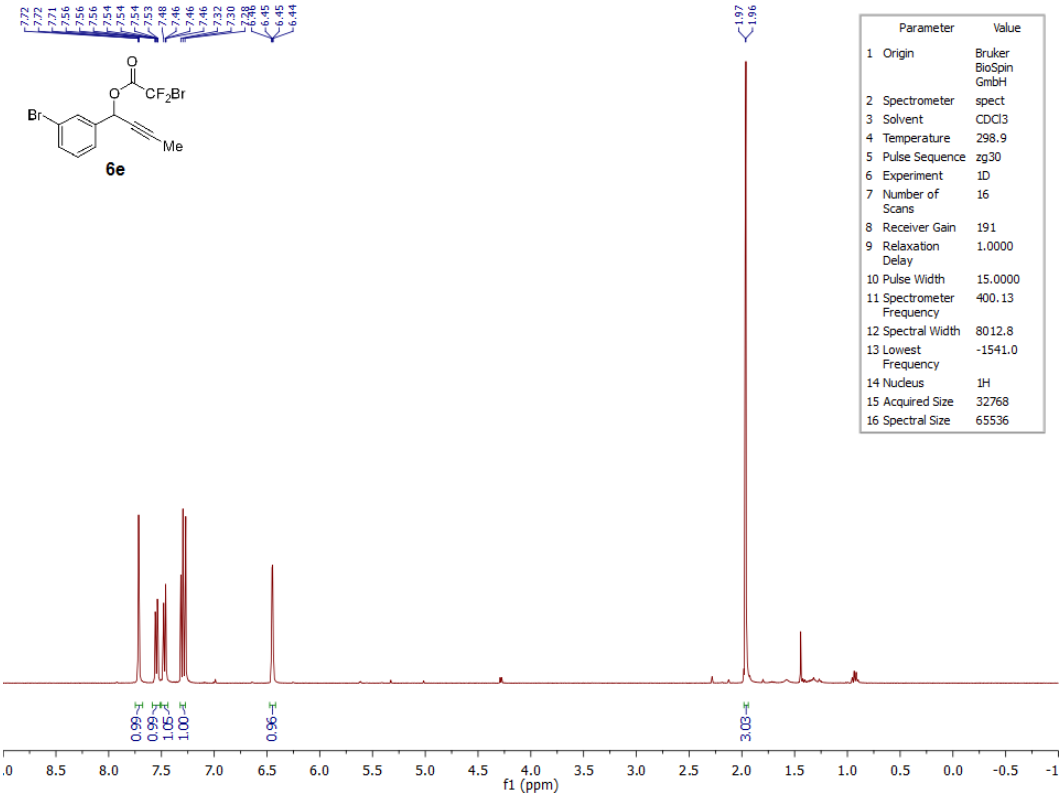
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.2
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75579.4
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072

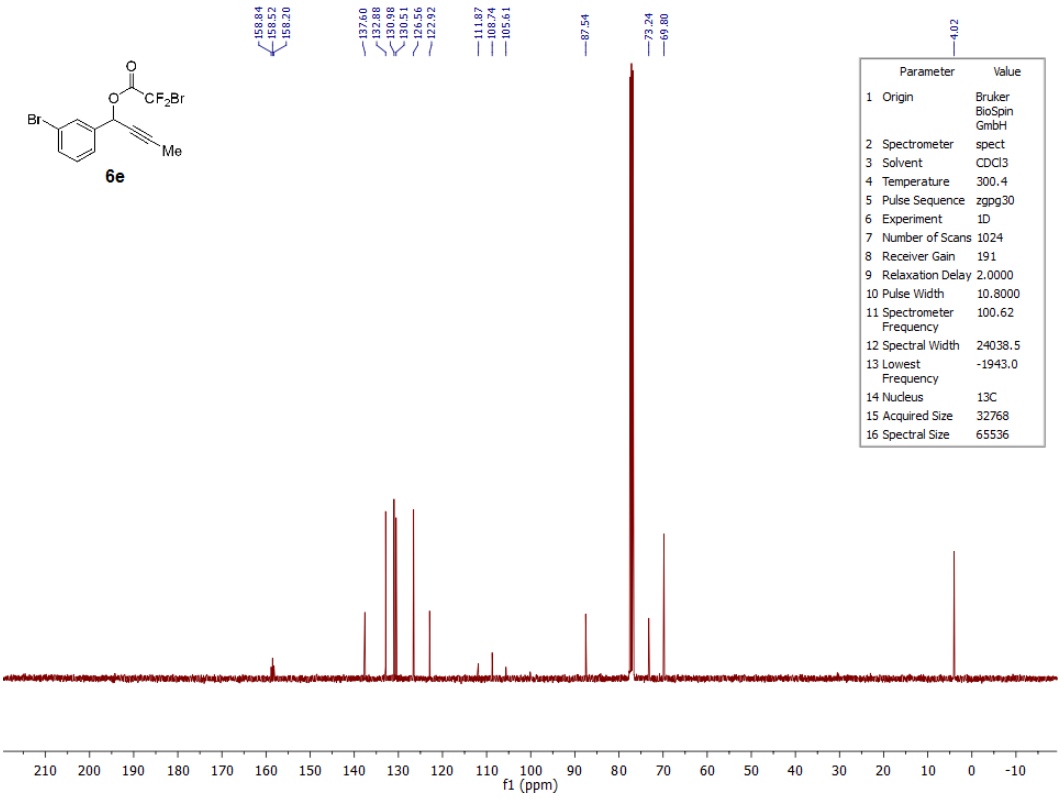


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	406
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


158.64
158.39
158.13
145.08
144.17
143.19
135.77
111.69
111.14
109.34
108.63
106.13
104.64
77.09
64.07
39.18
6d
Me
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.8
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)


-61.90
-61.92
-61.92
-61.94
6d
Me
Internal Standard
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 297.4
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 7
8 Receiver Gain 912
9 Relaxation Delay 1.0000
10 Pulse Width 25.2000
11 Spectrometer Frequency 470.55
12 Spectral Width 100000.0
13 Lowest Frequency -97210.1
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
f1 (ppm)


7.72
7.72
7.71
7.56
7.56
7.56
7.54
7.54
7.54
7.53
7.48
7.46
7.46
7.46
7.32
7.28
6.46
6.45
6.44
1.97
1.96
O
O
CF2Br
Br
Me
6e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.9
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 15.0000
11 Spectrometer Frequency 400.13
12 Spectral Width 8012.8
13 Lowest Frequency -1541.0
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
0.99
0.99
1.05
1.00
0.96
3.03
f1 (ppm)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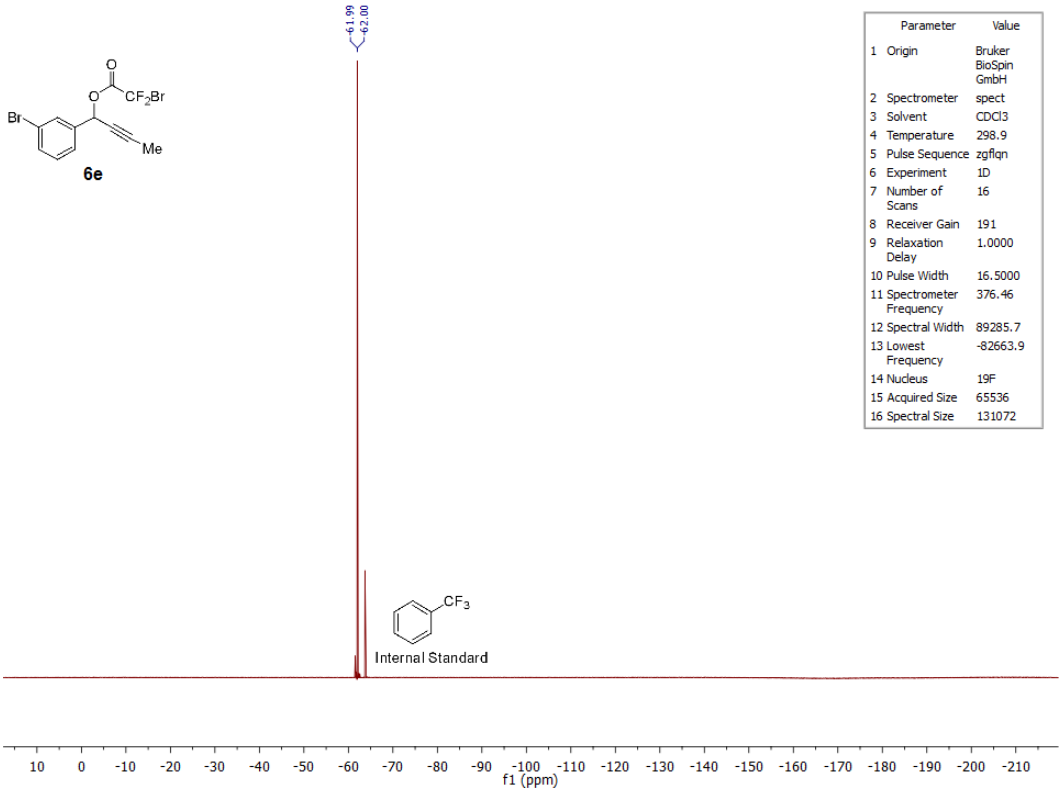
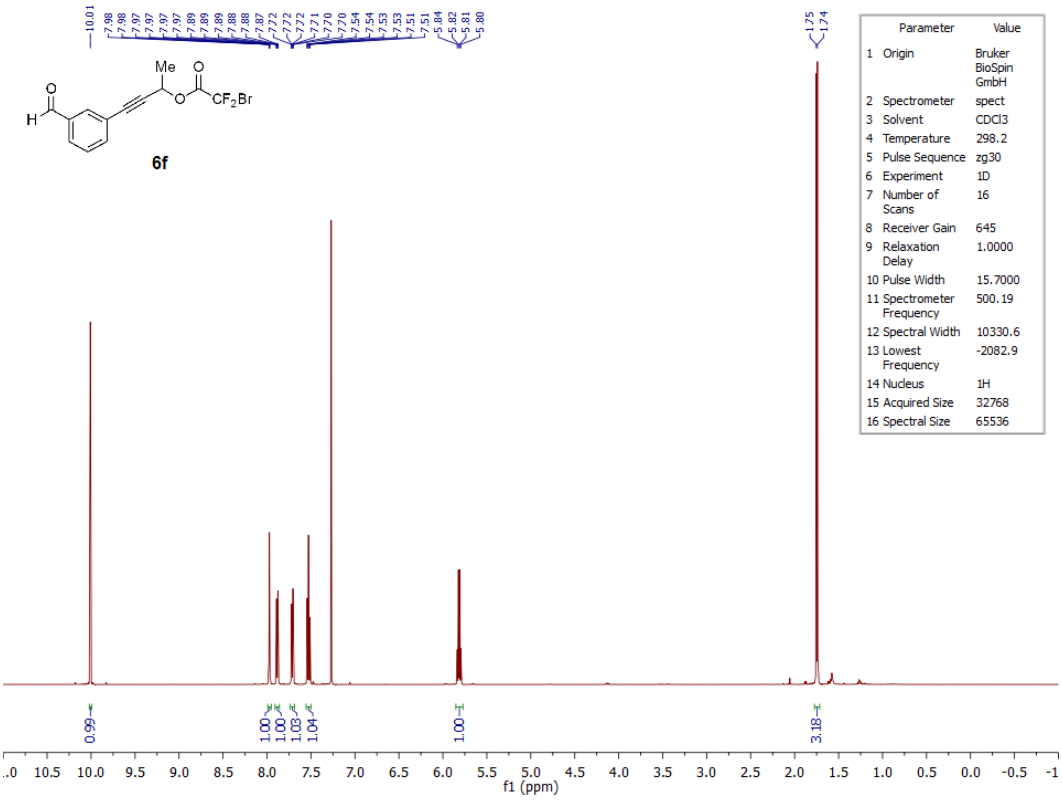
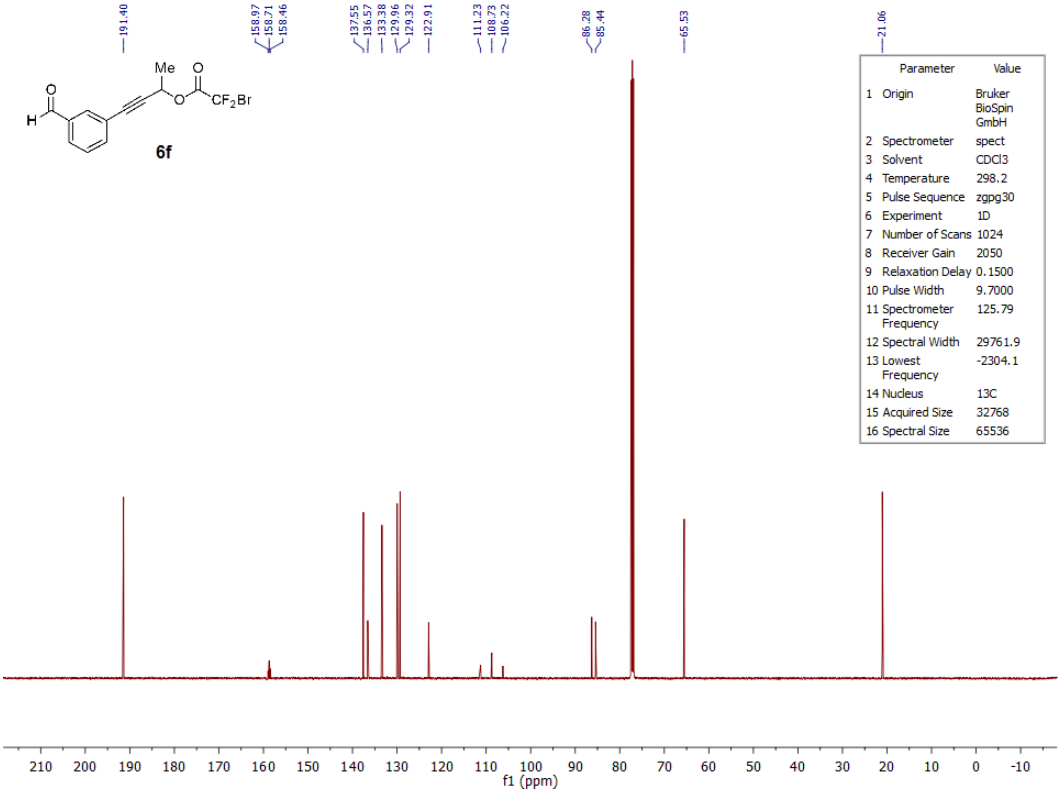
158.20
137.60
132.88
130.98
130.51
126.56
122.92
111.87
108.74
105.61
87.54
73.24
69.80
4.02
O
O
CF2Br
Br
Me
6e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 300.4
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 191
9 Relaxation Delay 2.0000
10 Pulse Width 10.8000
11 Spectrometer Frequency 100.62
12 Spectral Width 24038.5
13 Lowest Frequency -1943.0
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)



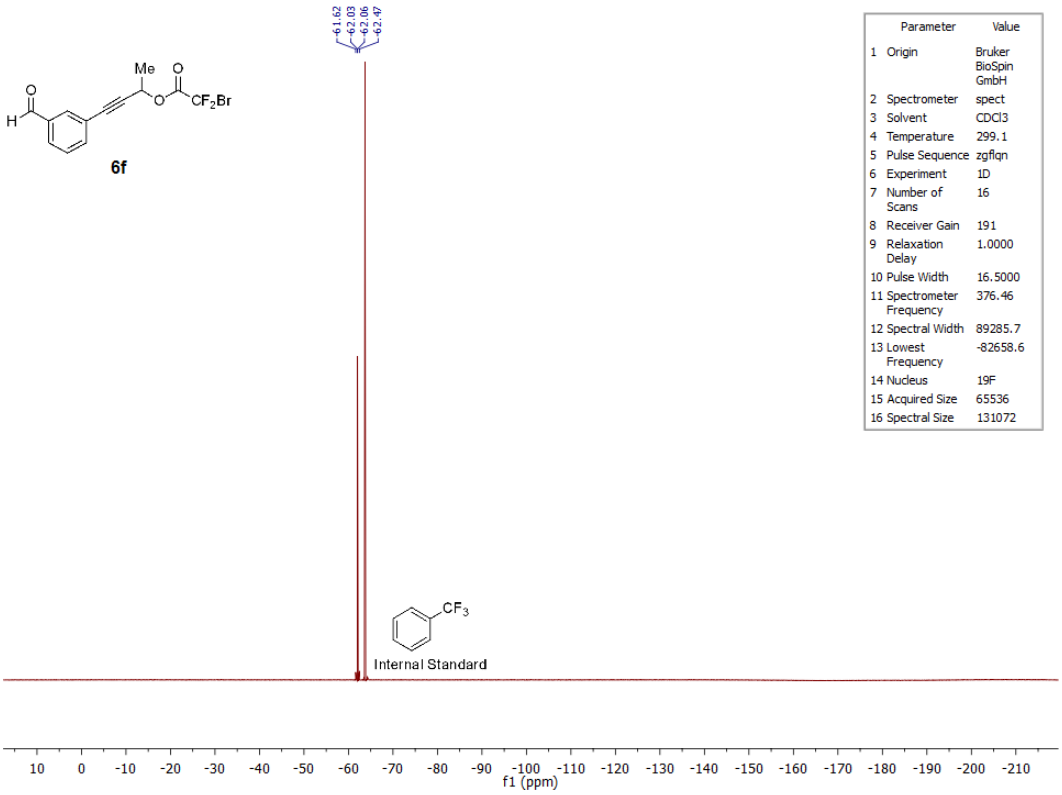
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82663.9
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



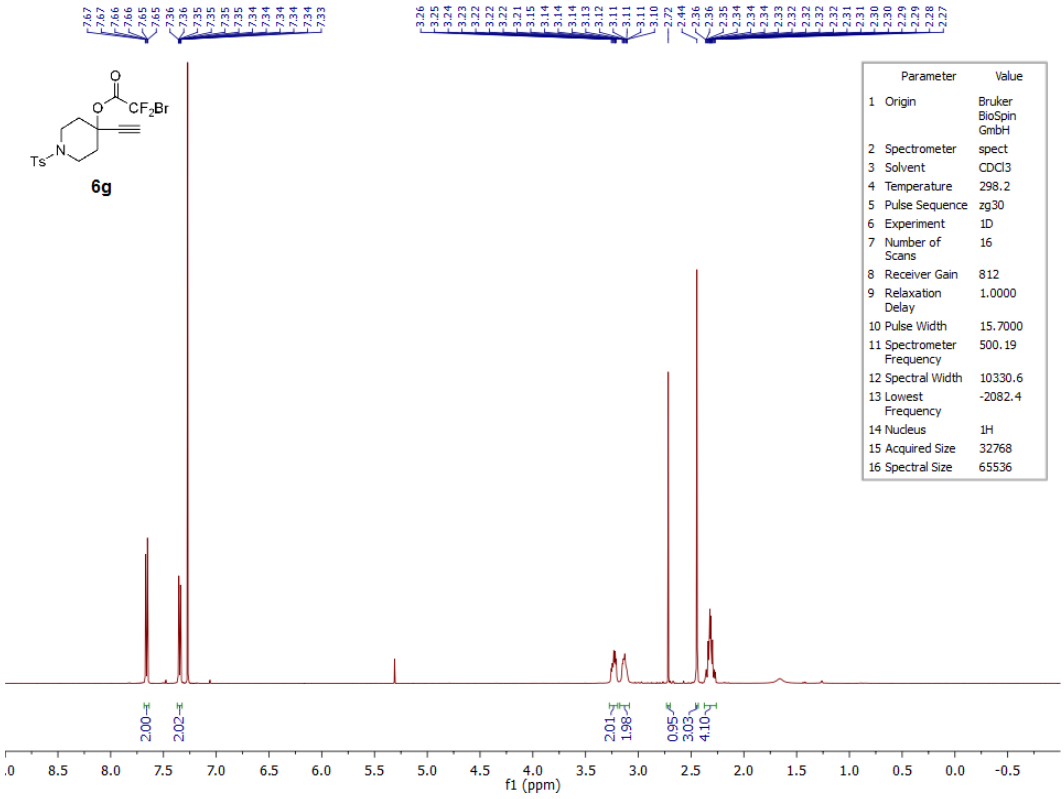
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

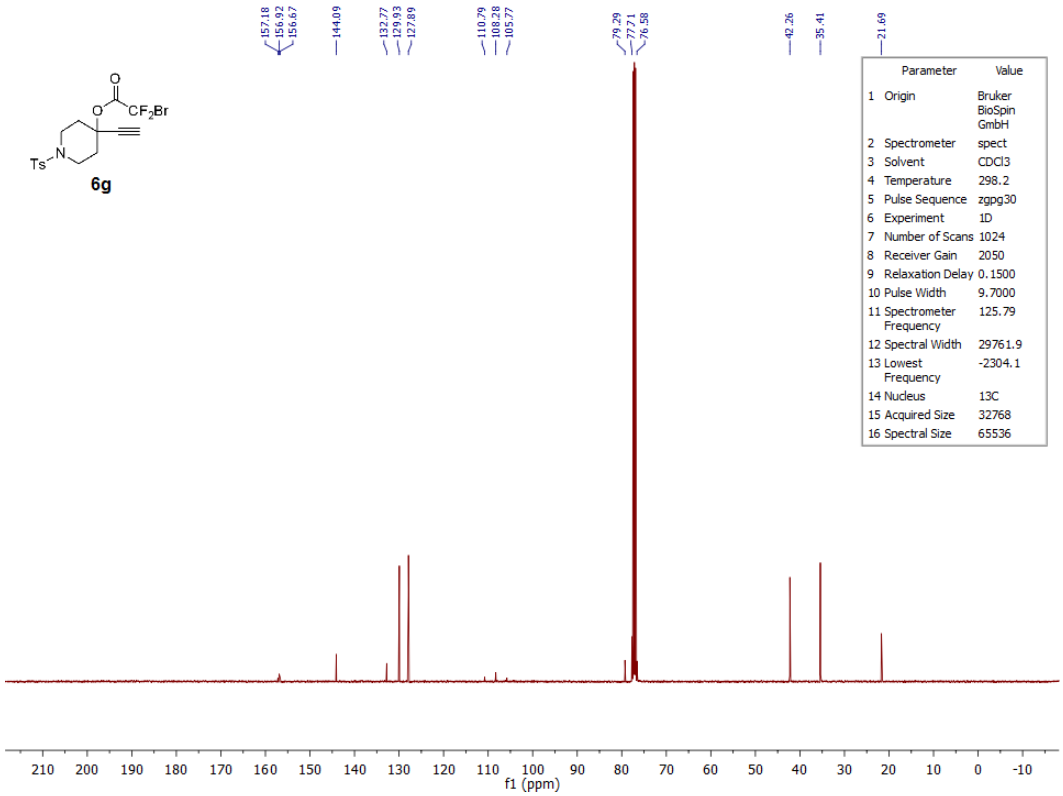


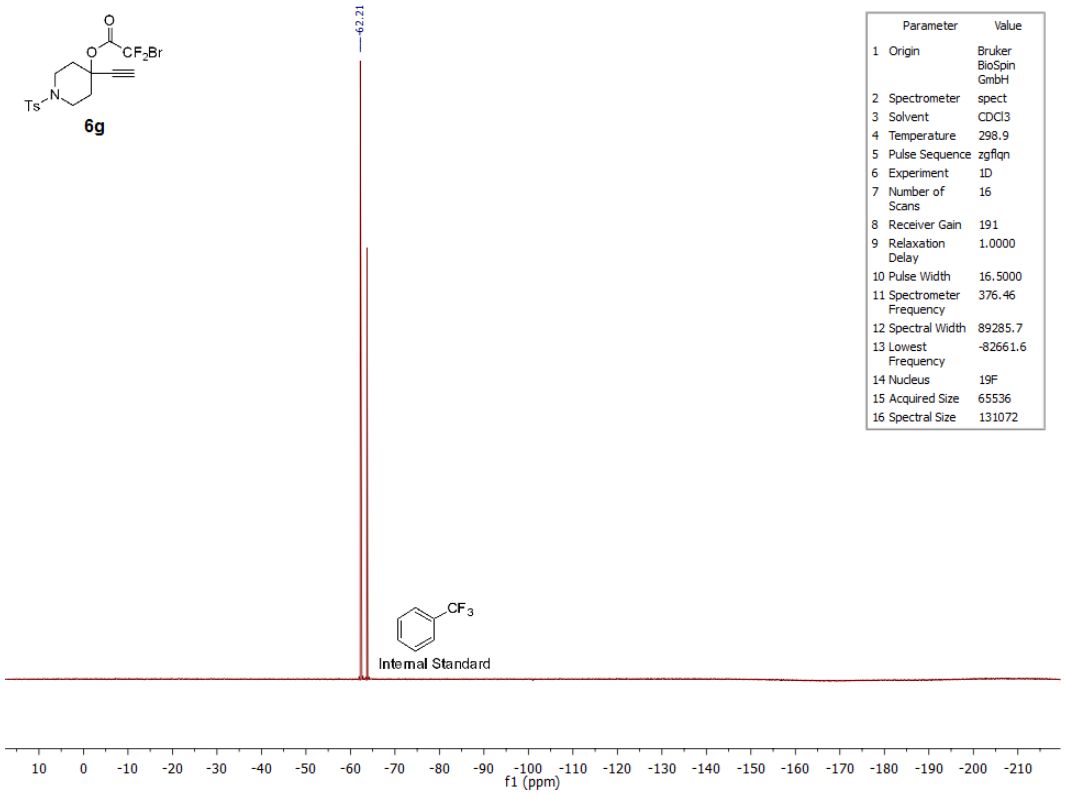
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2304.1
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



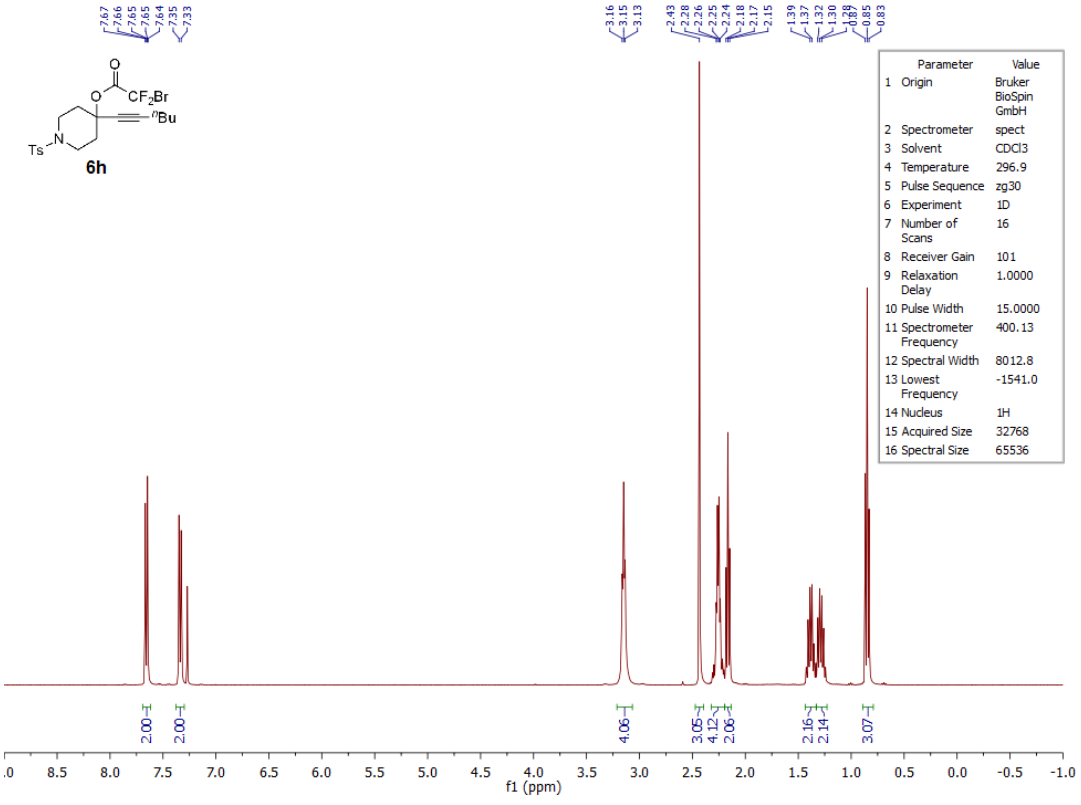
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.1
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82658.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


6g
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 812
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2082.4
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

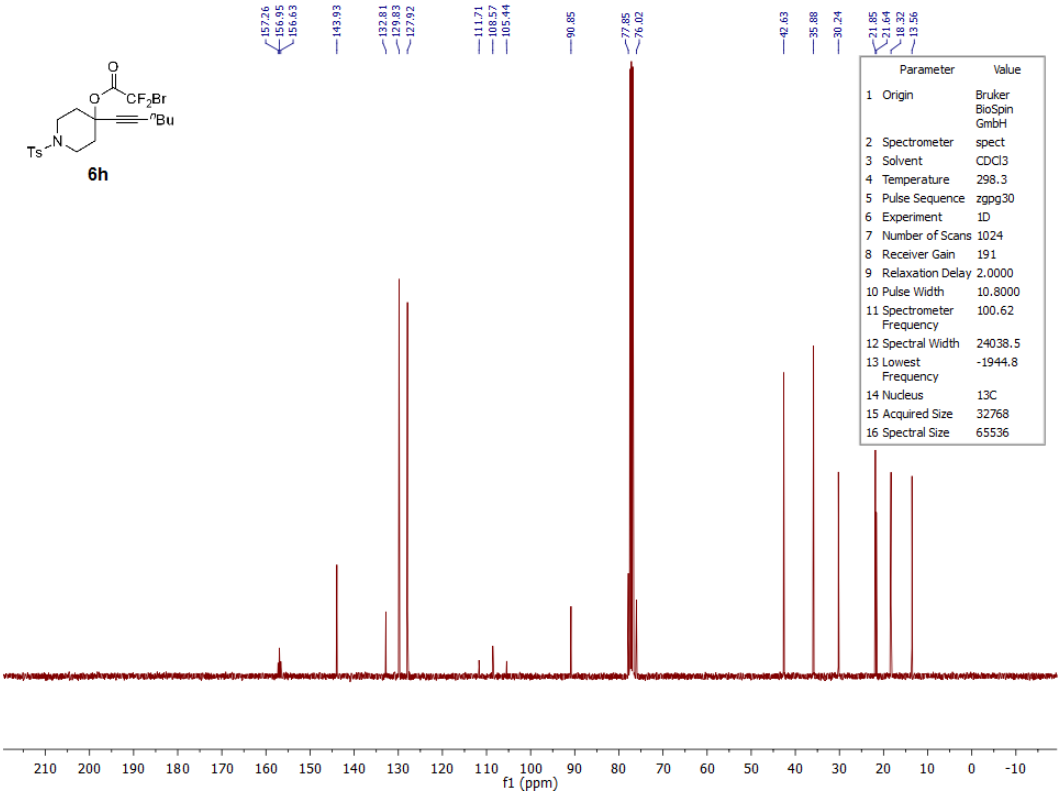

6g
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2304.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

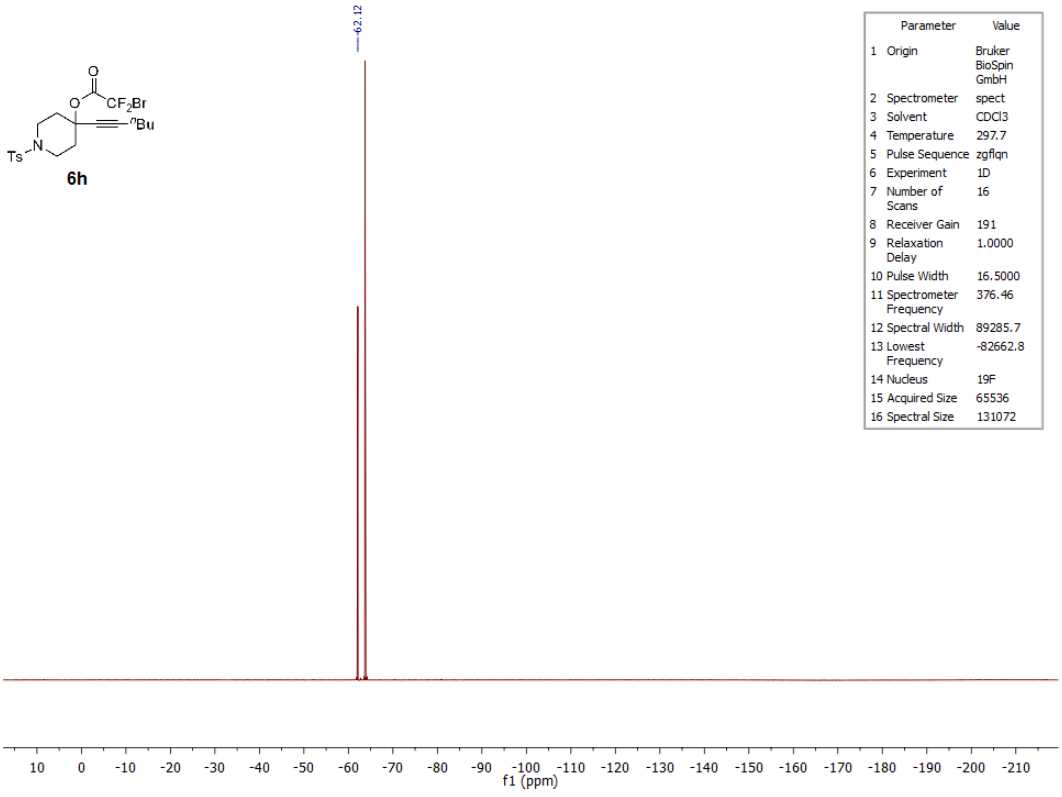


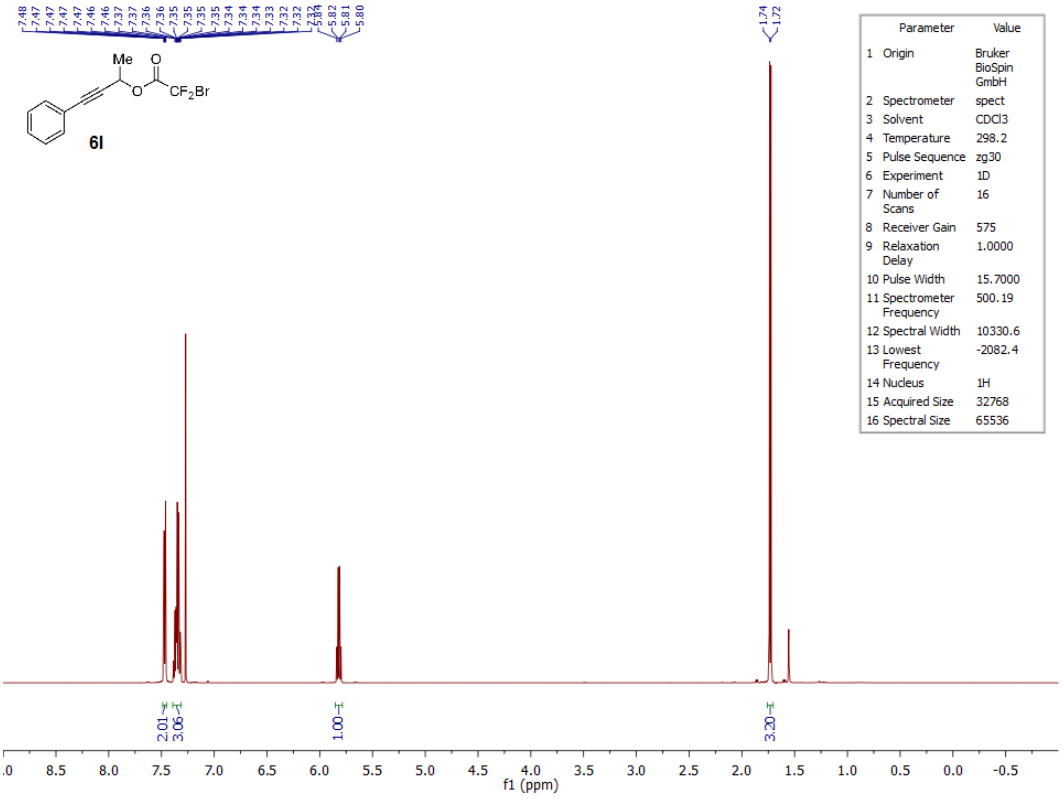
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82661.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.9
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	101
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1541.0
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


157.26
156.95
156.63
143.93
132.81
129.83
127.92
111.71
108.57
105.44
90.85
77.85
76.02
42.63
35.88
30.24
21.85
21.64
18.32
13.56
6h
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.3
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 191
9 Relaxation Delay 2.0000
10 Pulse Width 10.8000
11 Spectrometer Frequency 100.62
12 Spectral Width 24038.5
13 Lowest Frequency -1944.8
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)


62.12
6h
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 297.7
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82662.8
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
f1 (ppm)


7.48
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7.47
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7.46
7.46
7.37
7.37
7.36
7.36
7.35
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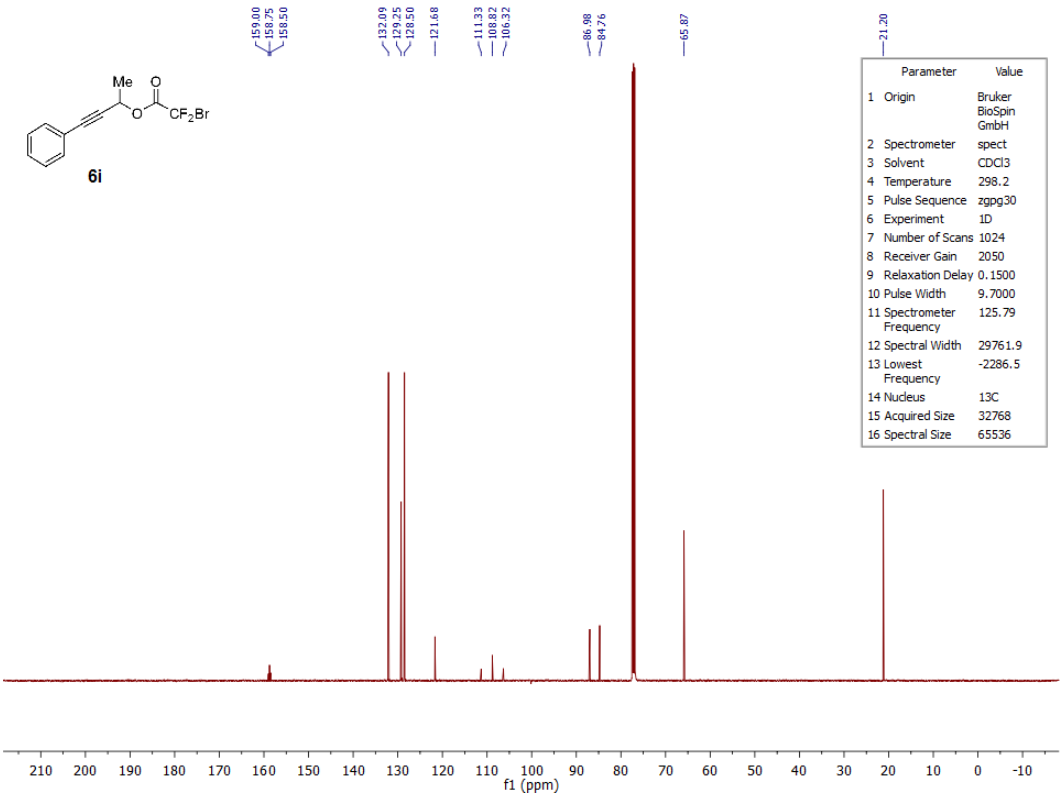
7.35
7.35
7.34
7.34
7.34
7.33
7.32
7.32
5.84
5.82
5.81
5.80
1.74
1.72
Me
O
O
CF2Br
6l
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2082.4
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
2.01
3.06
1.00
3.20
f1 (ppm)


159.00
158.75
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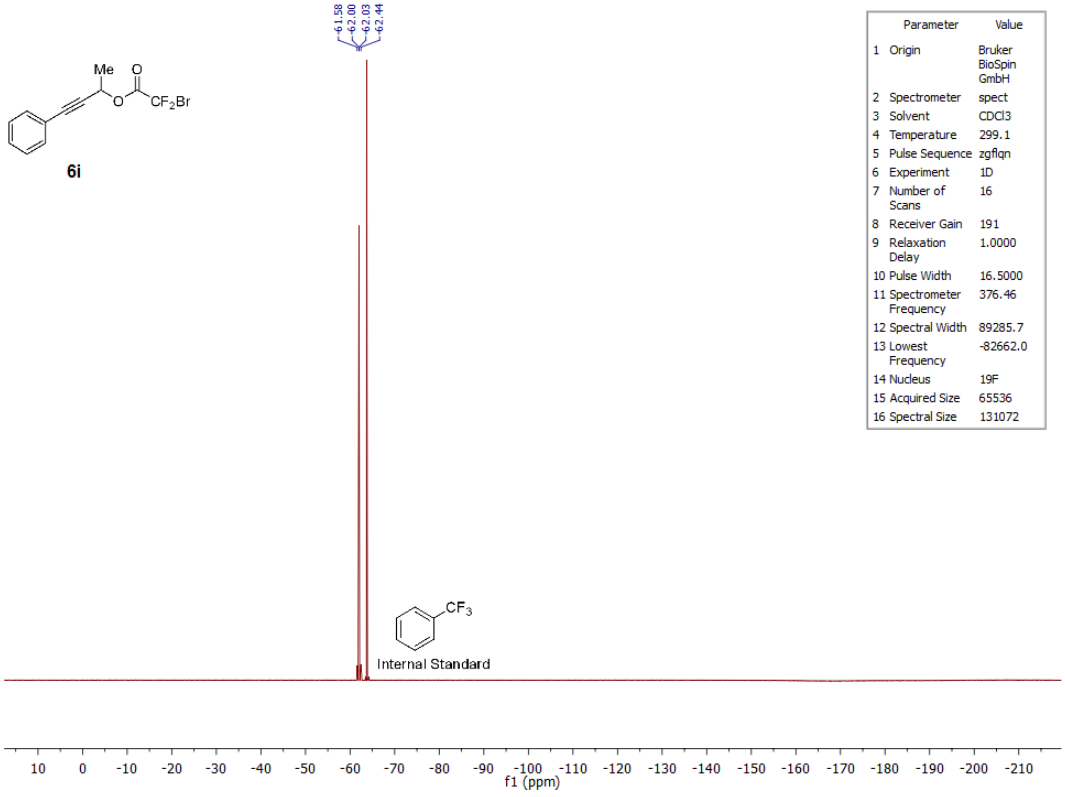
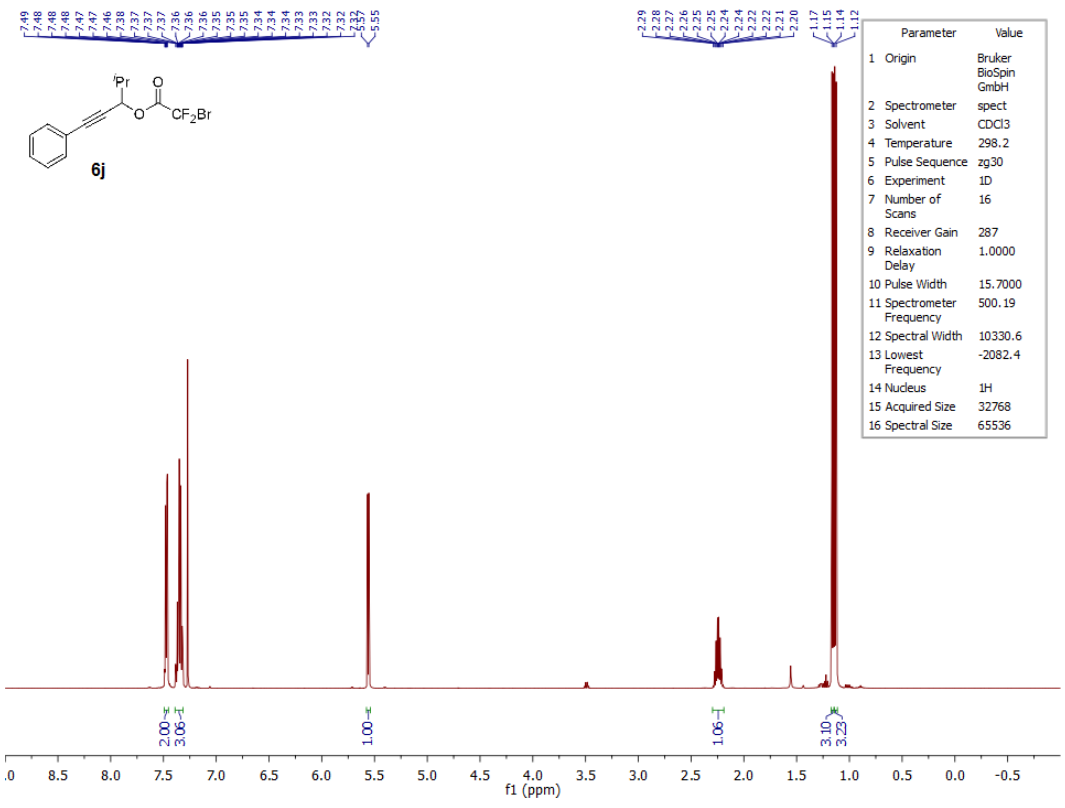
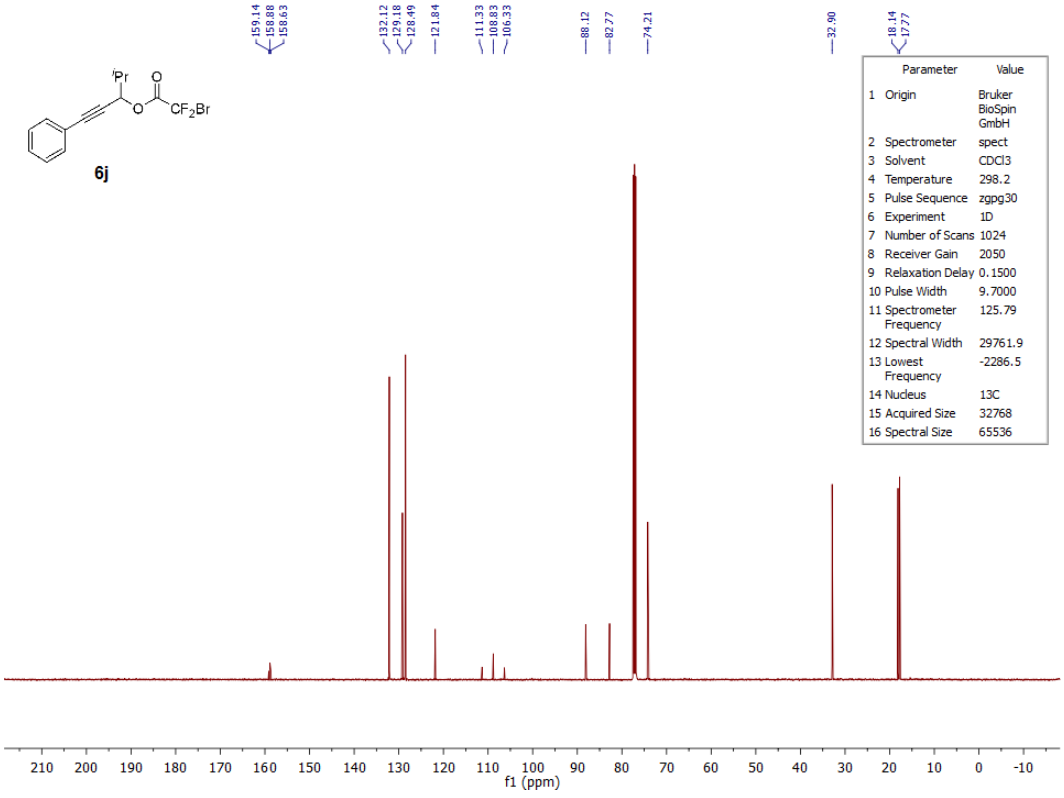
132.09
129.25
128.50
121.68
111.33
108.82
106.32
86.98
84.76
65.87
21.20
Me
O
O
CF2Br
6i
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.5
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

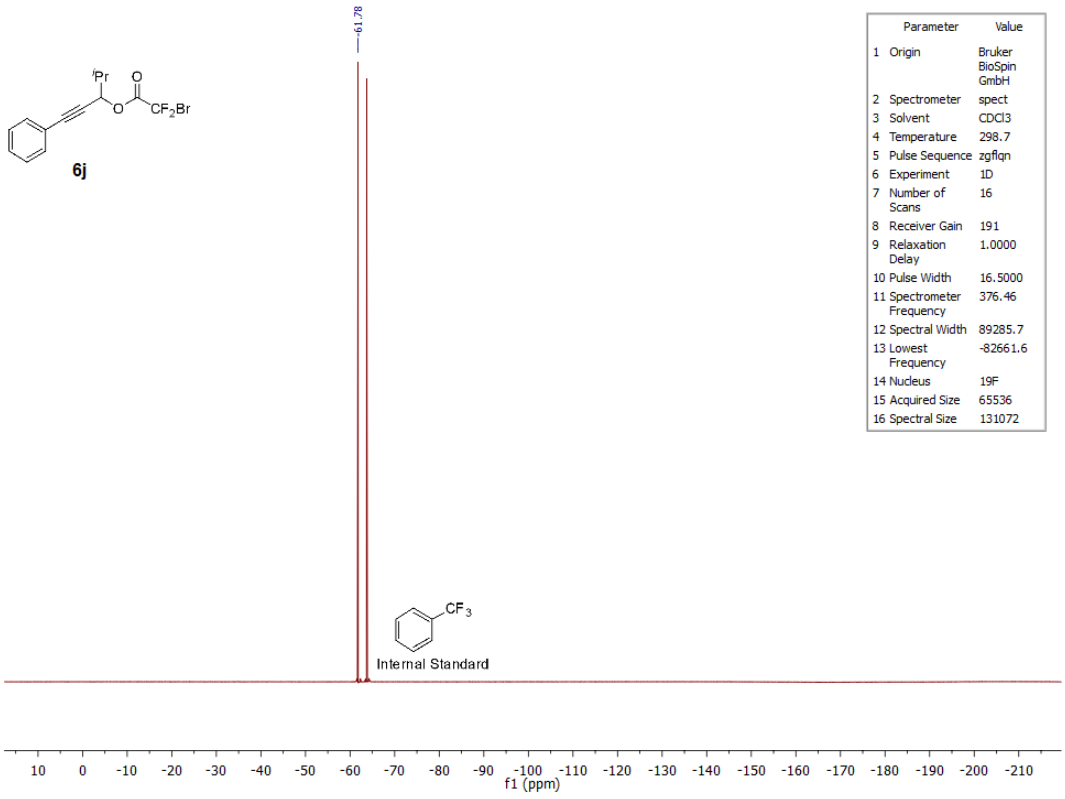


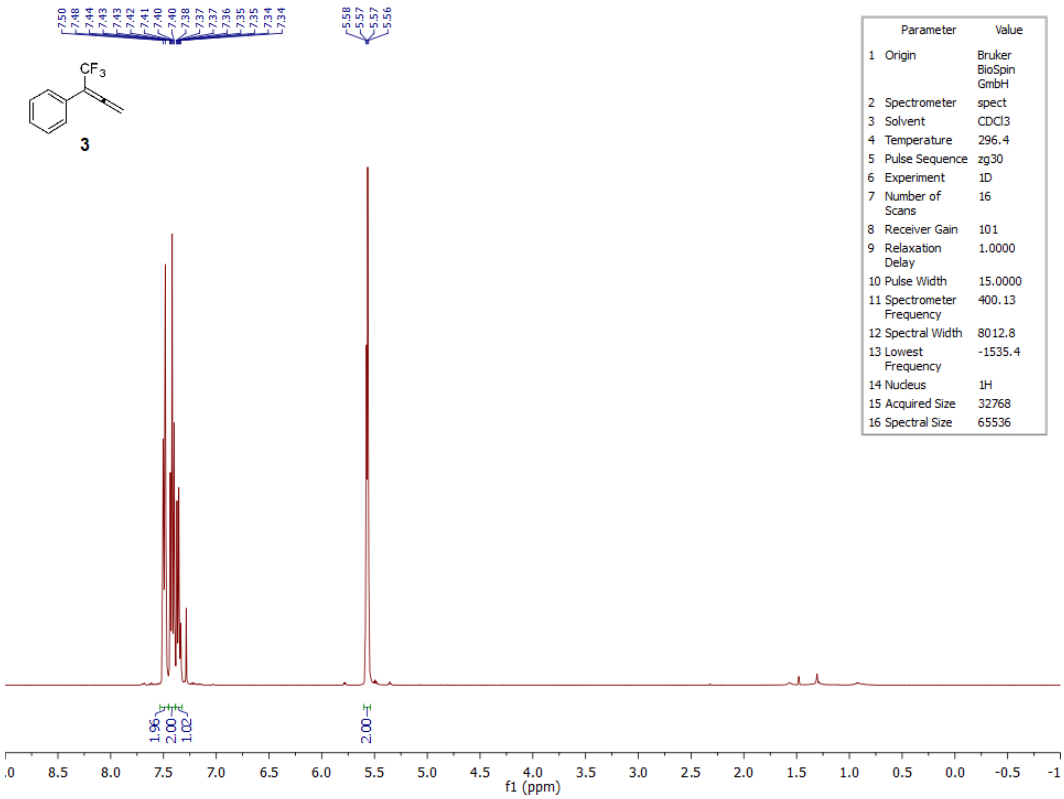
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.1
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82662.0
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



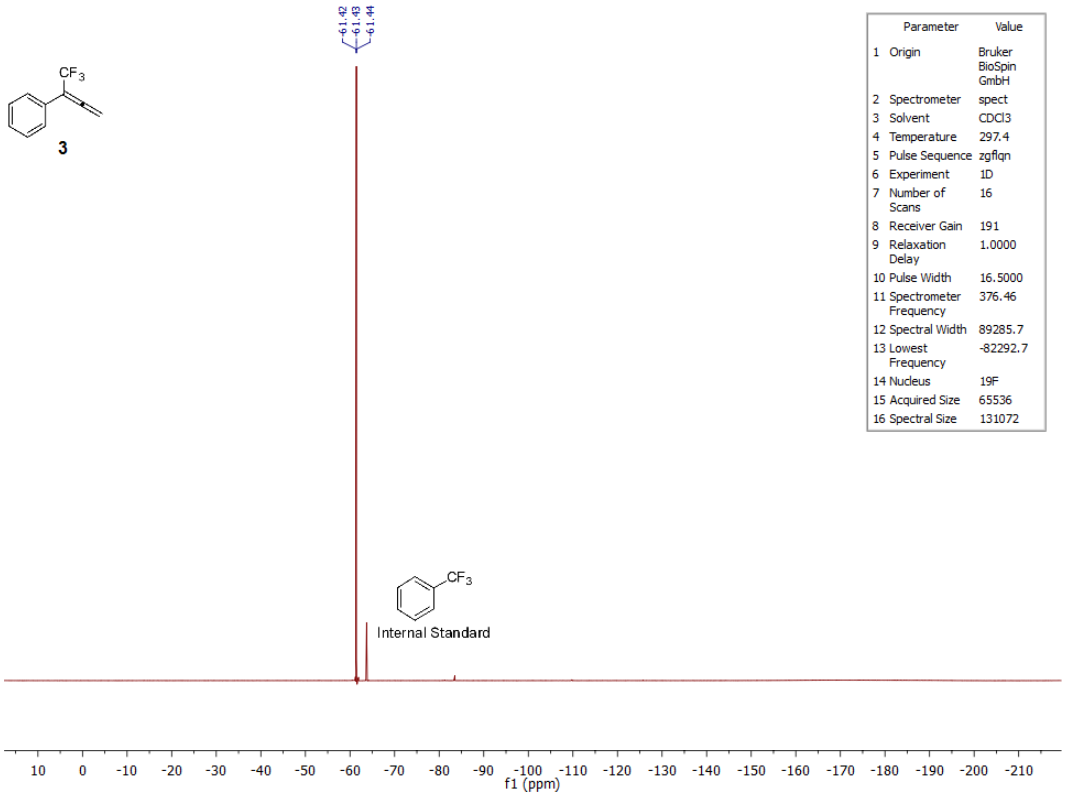
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	287
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


159.14
158.88
158.63
132.12
129.18
128.49
121.84
111.33
108.83
106.33
88.12
82.77
74.21
32.90
18.14
17.77
6j
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.5
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

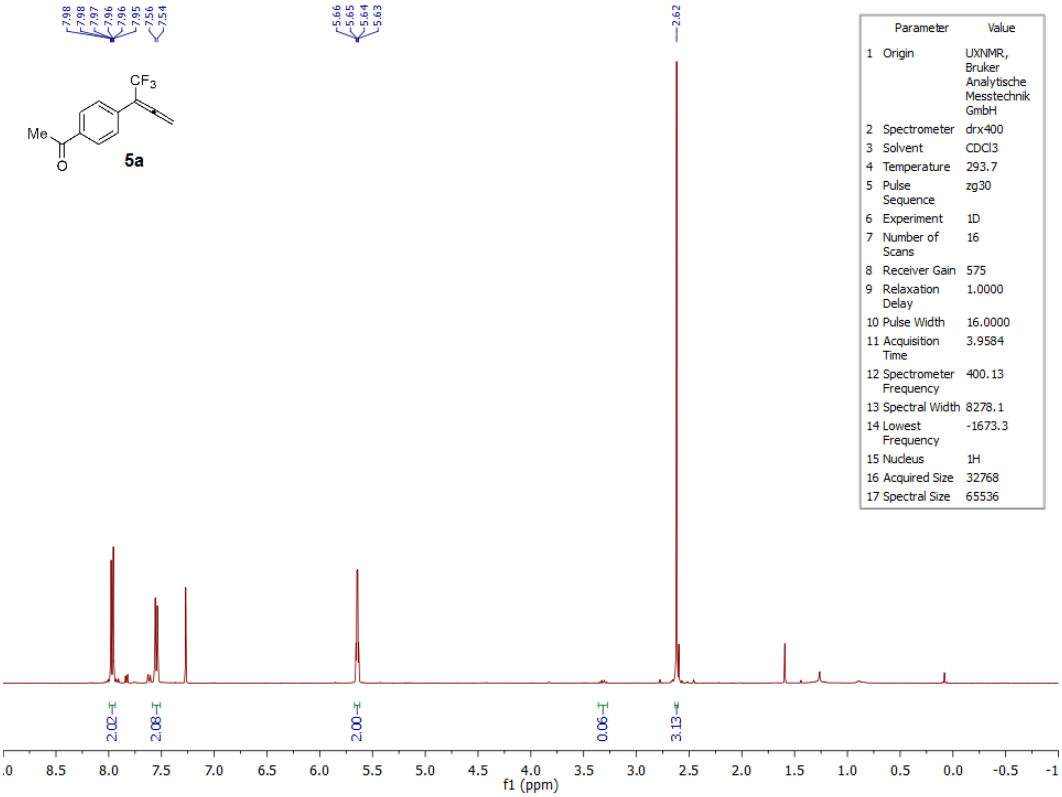

61.78
6j
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.7
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82661.6
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
Internal Standard
f1 (ppm)

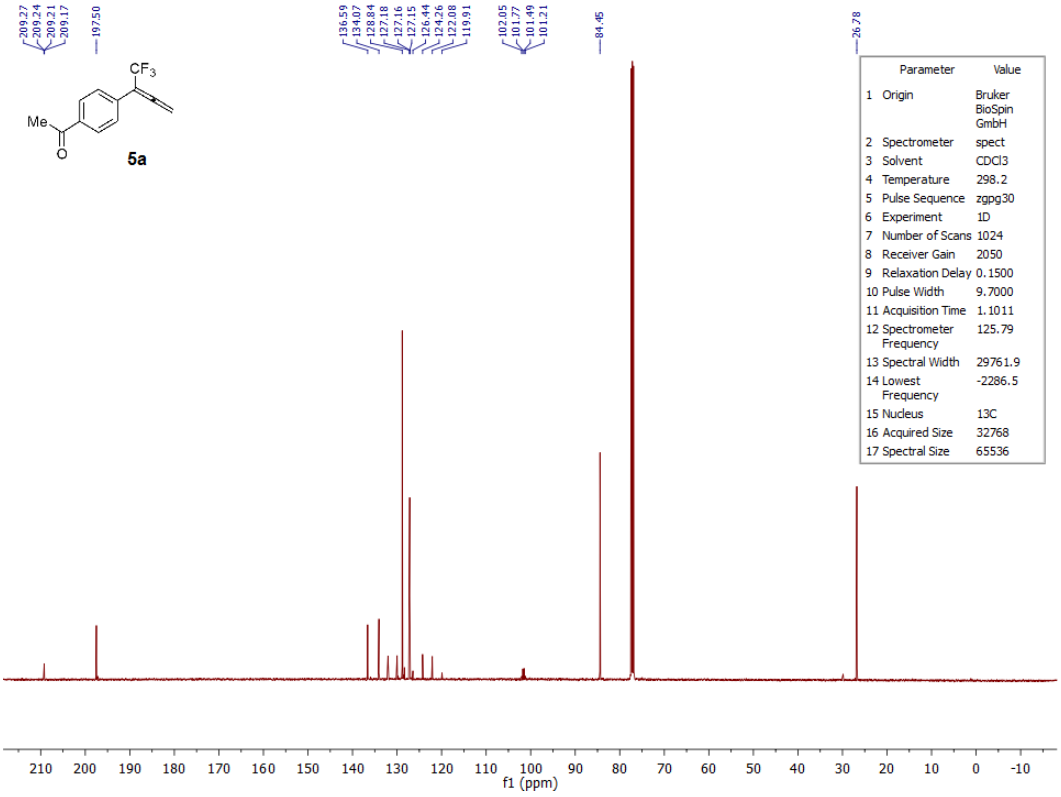


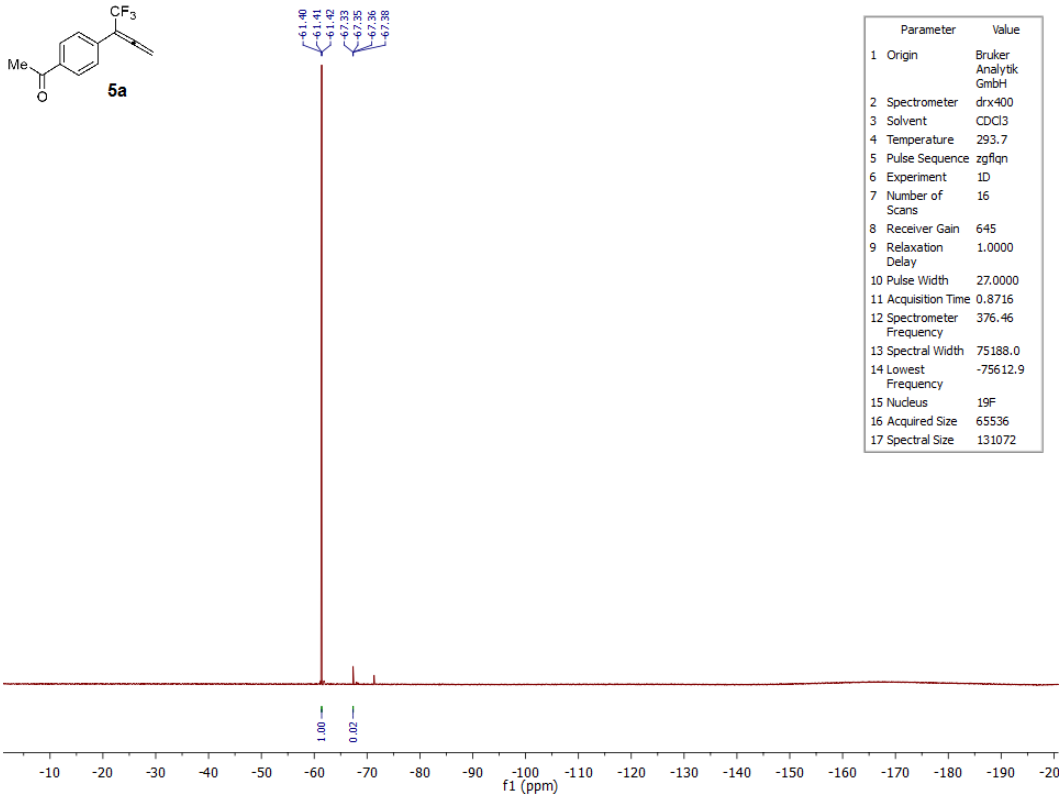
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	296.4
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	101
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1535.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



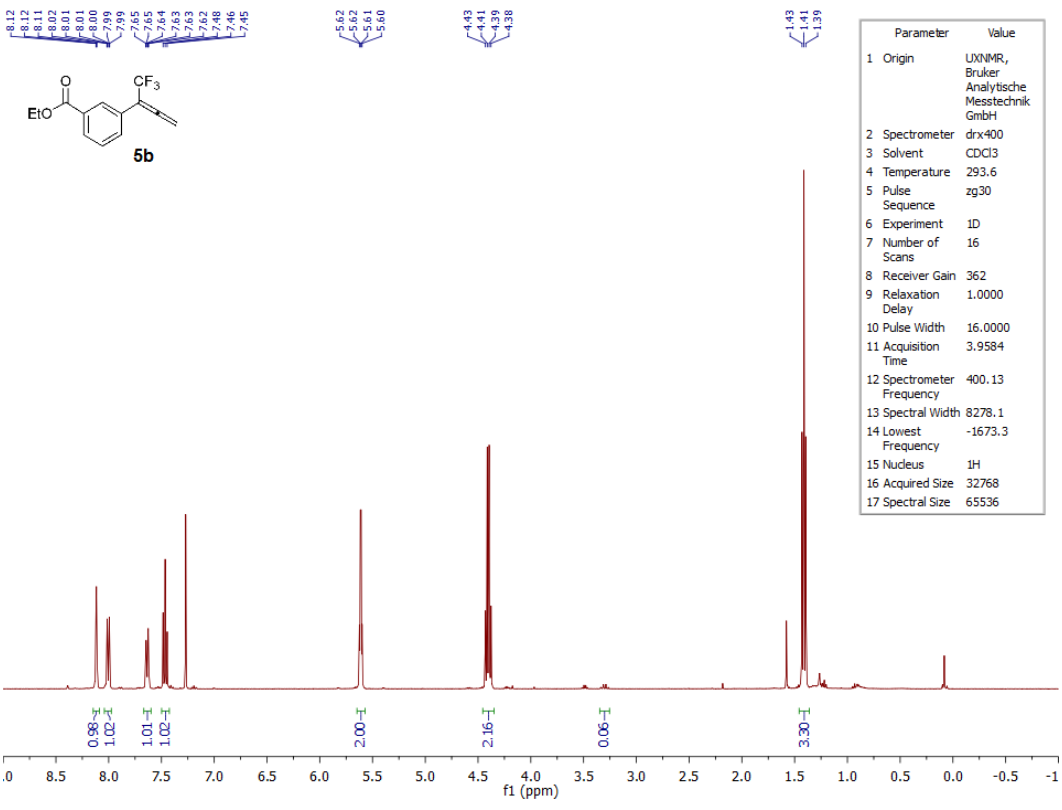
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	297.4
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82292.7
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.98
7.98
7.97
7.96
7.96
7.95
7.56
7.54
5.66
5.65
5.64
5.63
2.62
CF3
Me
O
5a
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
2.02
2.08
2.00
0.06
3.13
f1 (ppm)

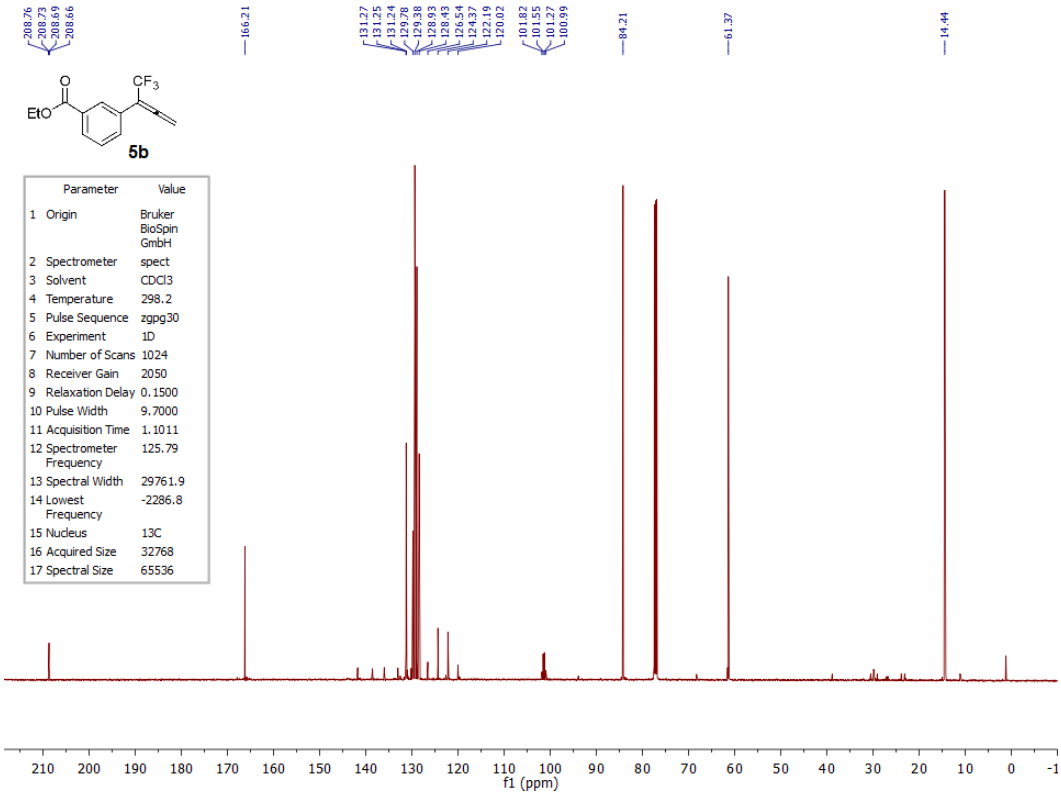

209.27
209.24
209.21
209.17
197.50
136.59
134.07
128.84
127.18
127.16
127.15
126.44
124.26
122.08
119.91
102.05
101.77
101.49
101.21
84.45
26.78
CF3
Me
O
5a
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.5
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

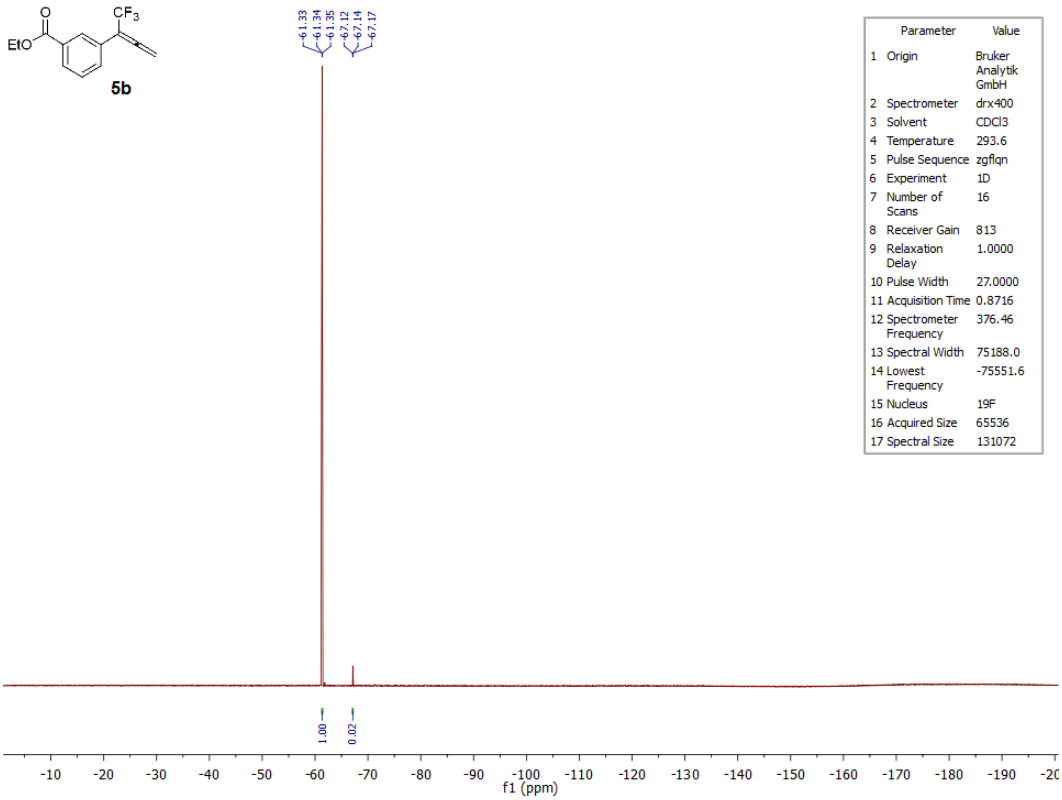


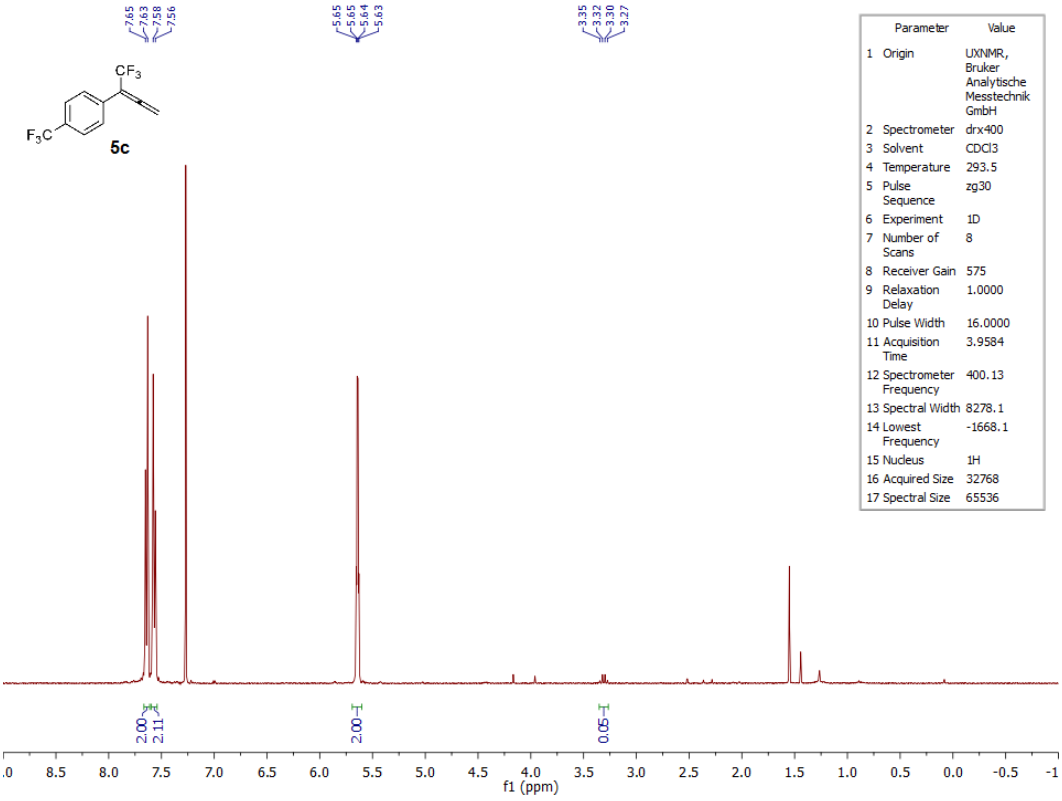
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75612.9
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072

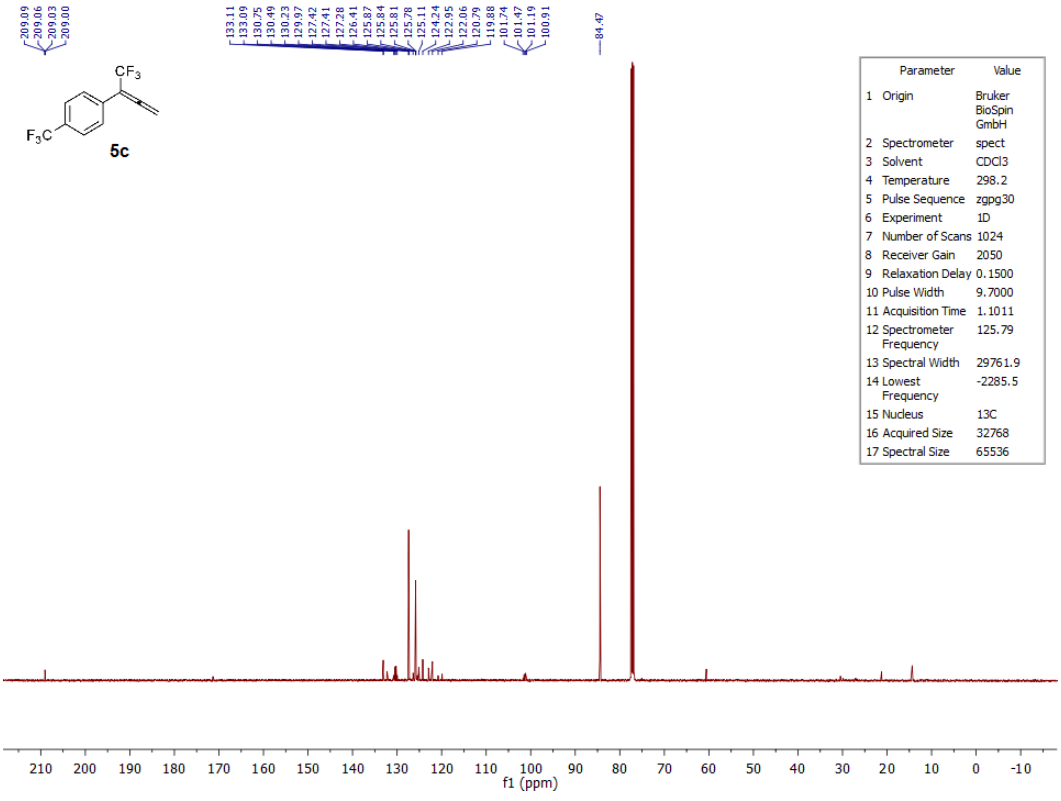


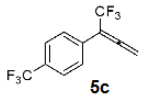
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	362
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


208.76
208.73
208.69
208.66
166.21
131.27
131.25
131.24
129.78
129.38
128.93
128.43
126.54
124.37
122.19
120.02
101.82
101.55
101.27
100.99
84.21
61.37
14.44
EtO
CF3
5b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.8
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


EtO
CF3
5b
-61.33
-61.34
-61.35
-67.12
-67.14
-67.17
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.6
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 813
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Acquisition Time 0.8716
12 Spectrometer Frequency 376.46
13 Spectral Width 75188.0
14 Lowest Frequency -75551.6
15 Nucleus 19F
16 Acquired Size 65536
17 Spectral Size 131072
1.00
0.02
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)

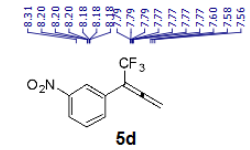

7.65
7.63
7.58
7.56
5.65
5.65
5.64
5.63
3.35
3.32
3.30
3.27
CF3
F3C
5c
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 8
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1668.1
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
2.00
2.11
2.00
0.05
f1 (ppm)


209.09
209.06
209.03
209.00
133.11
133.09
130.75
130.49
130.23
129.97
127.42
127.41
127.28
126.41
125.87
125.84
125.81
125.78
125.11
124.24
122.95
122.06
120.79
119.88
101.74
101.47
101.19
100.91
84.47
CF3
F3C
5c
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2285.5
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

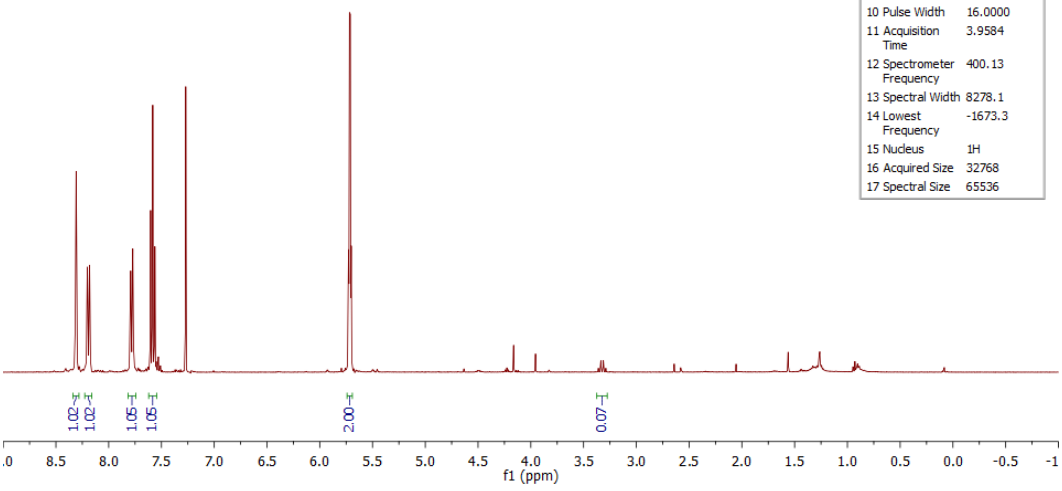


5c

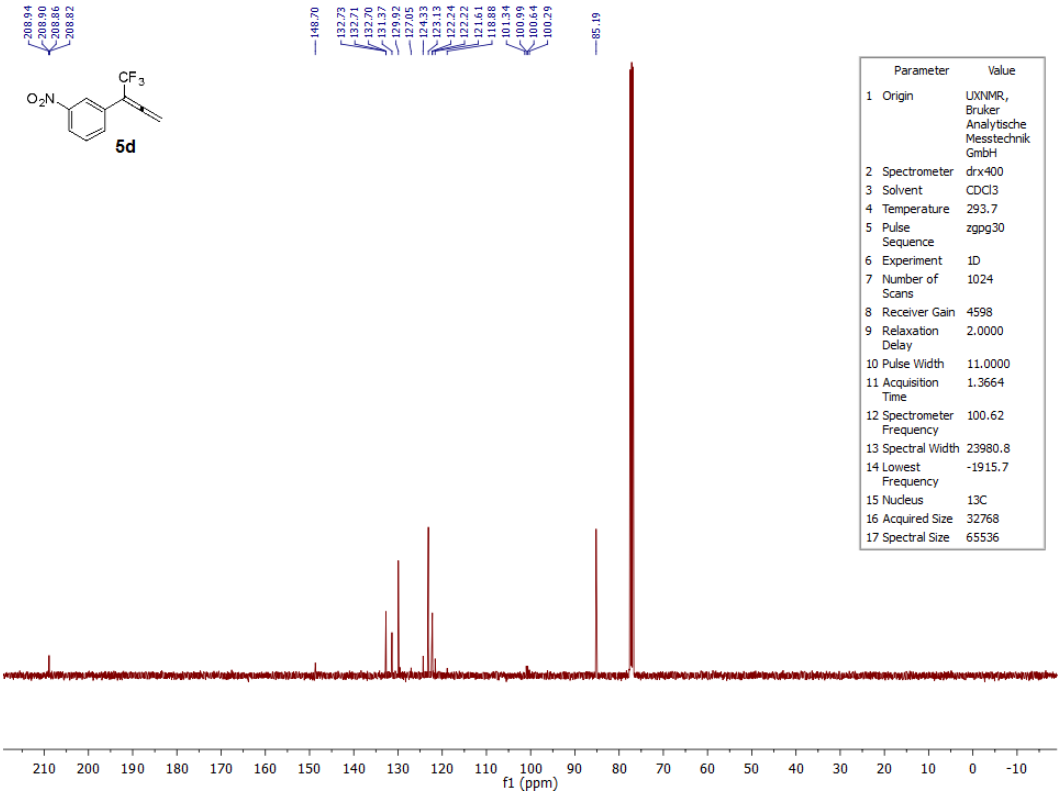
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75243.6
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



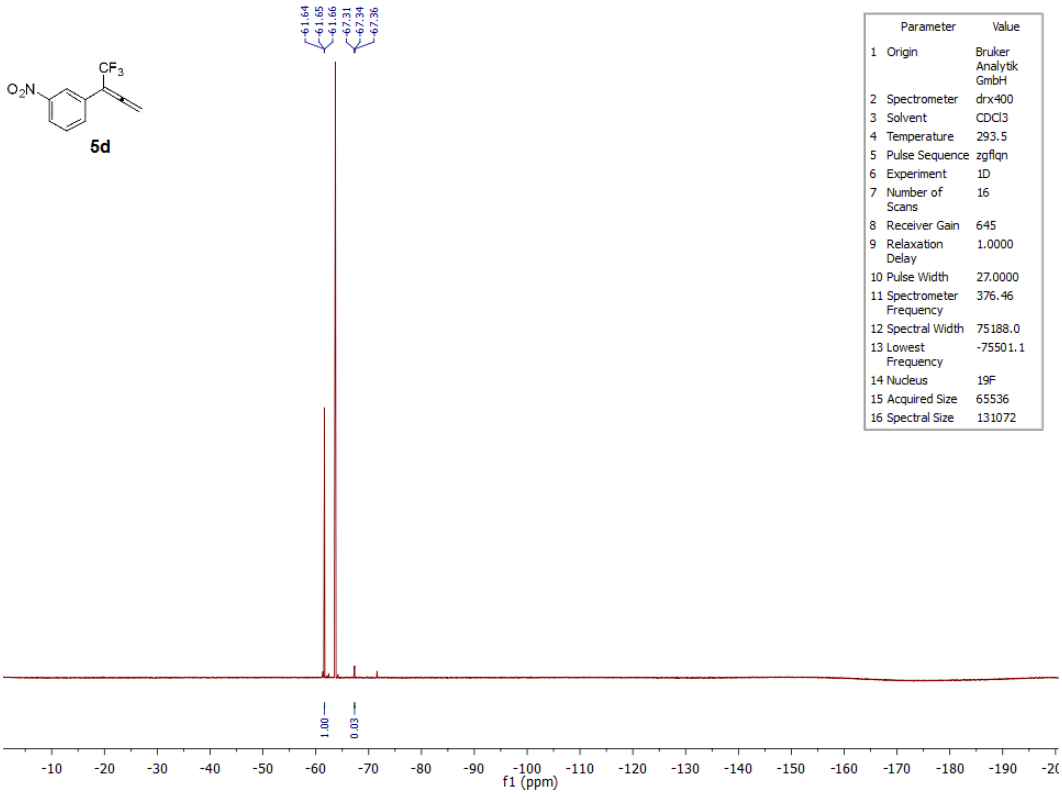
5d



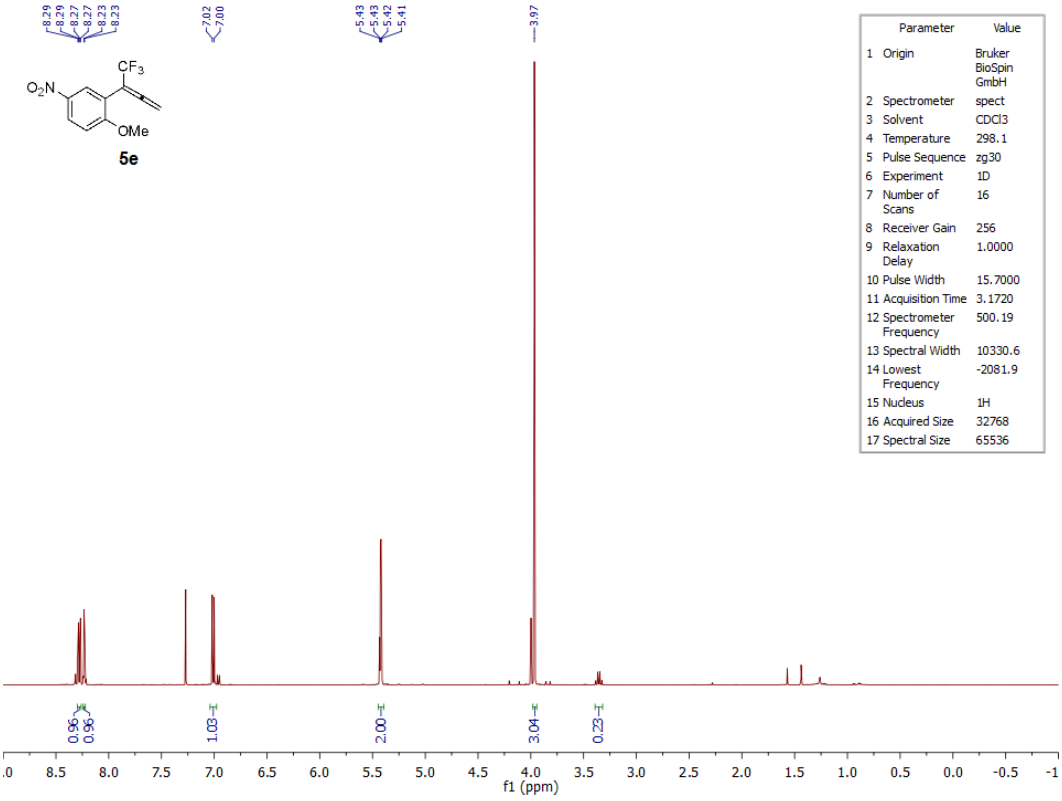
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.4
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	406
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



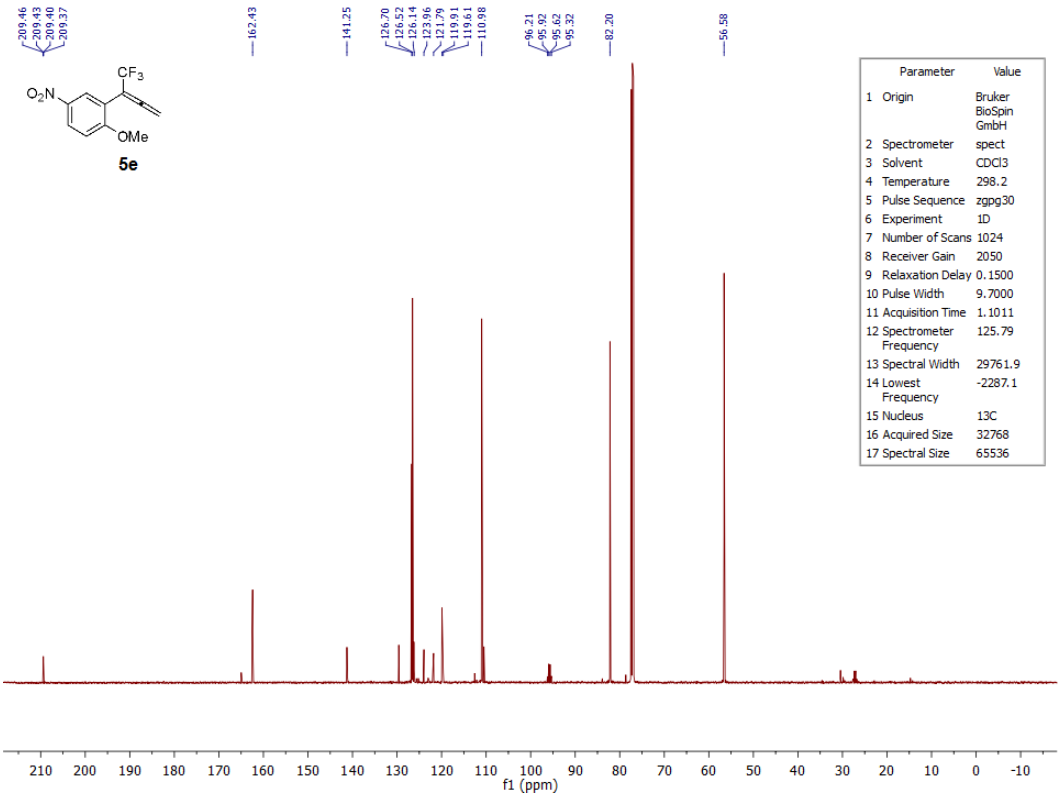
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	4598
9	Relaxation Delay	2.0000
10	Pulse Width	11.0000
11	Acquisition Time	1.3664
12	Spectrometer Frequency	100.62
13	Spectral Width	23980.8
14	Lowest Frequency	-1915.7
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536



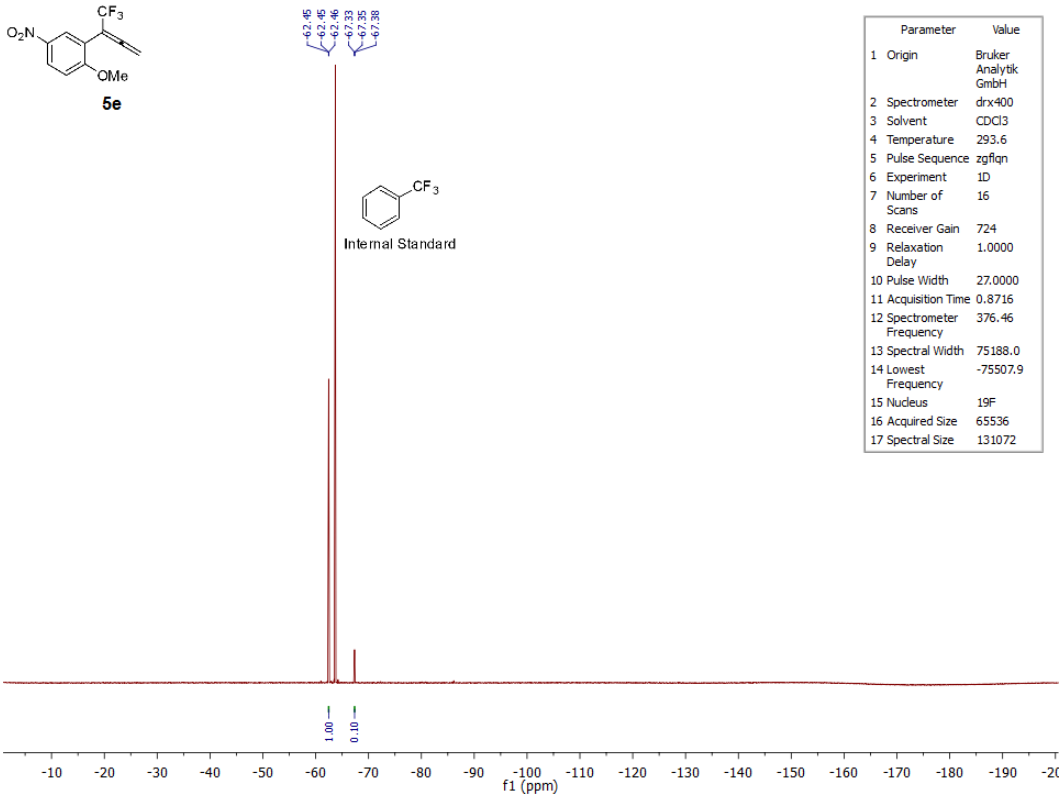
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.5
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75501.1
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



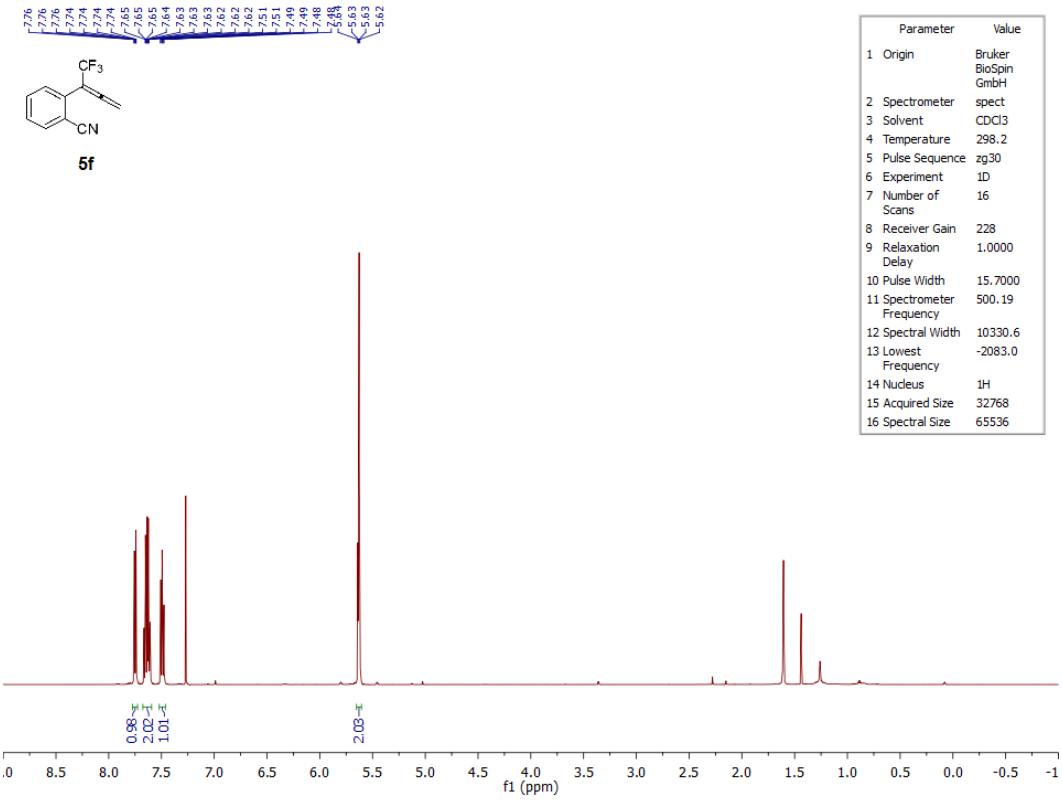
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.1
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	256
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Acquisition Time	3.1720
12	Spectrometer Frequency	500.19
13	Spectral Width	10330.6
14	Lowest Frequency	-2081.9
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



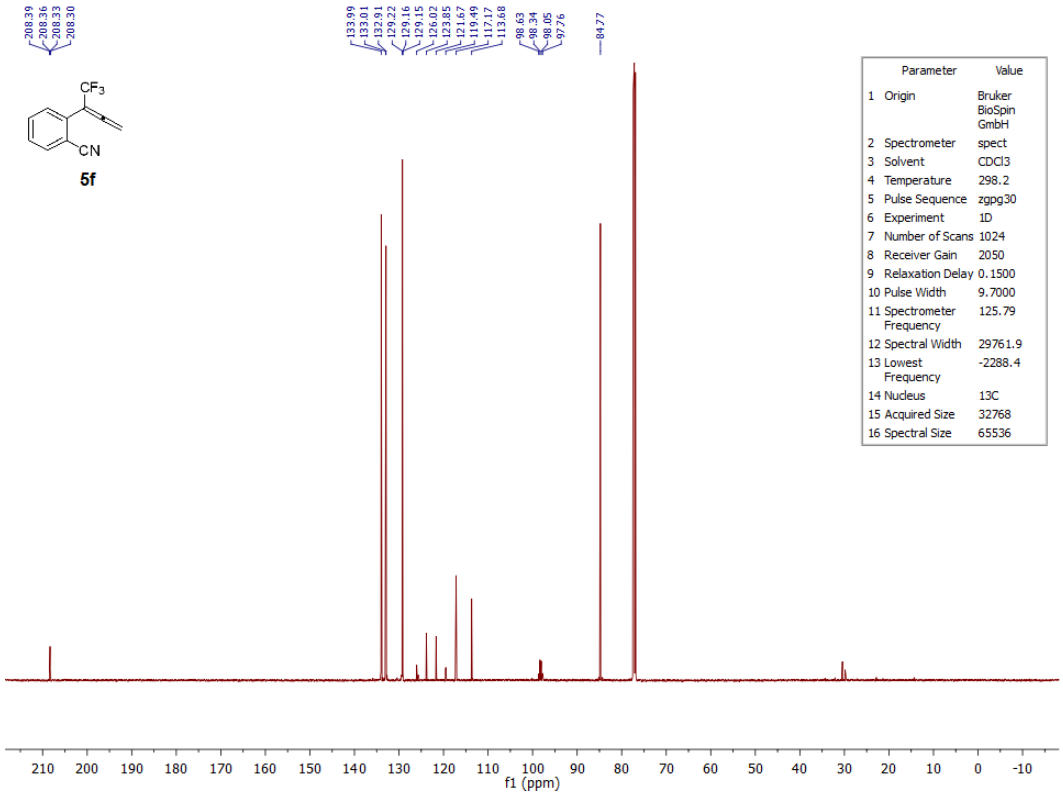
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Acquisition Time	1.1011
12	Spectrometer Frequency	125.79
13	Spectral Width	29761.9
14	Lowest Frequency	-2287.1
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536



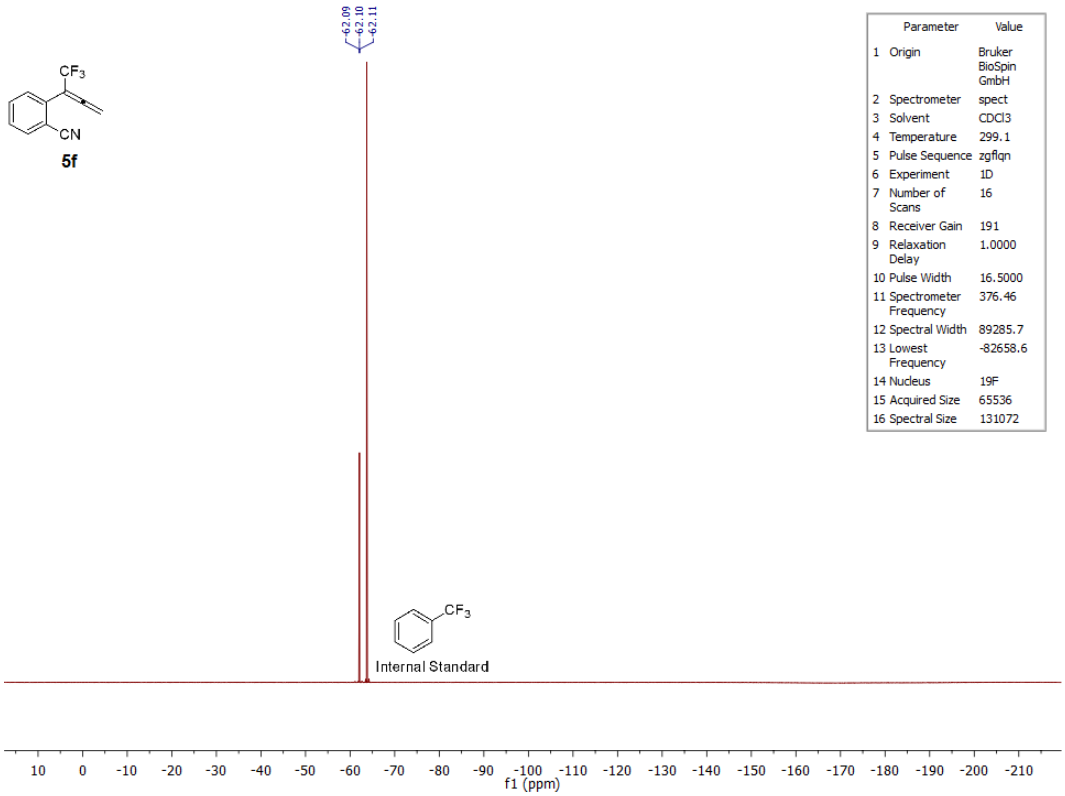
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.6
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	724
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75507.9
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



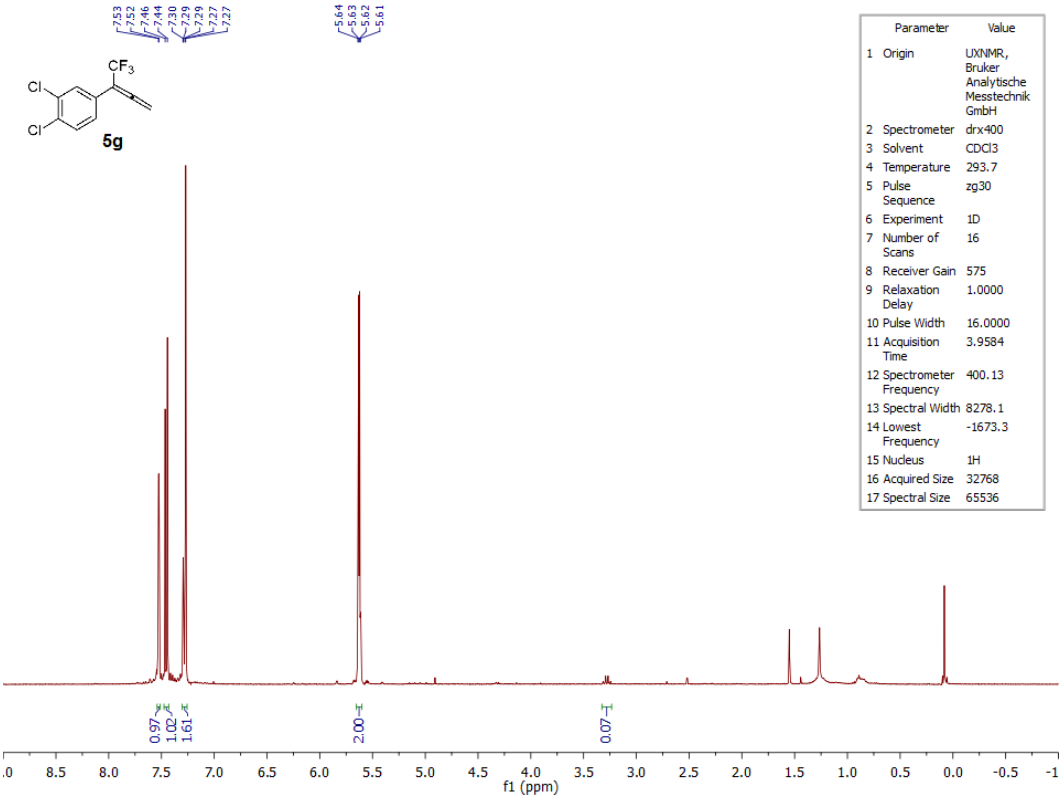
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	228
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2083.0
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

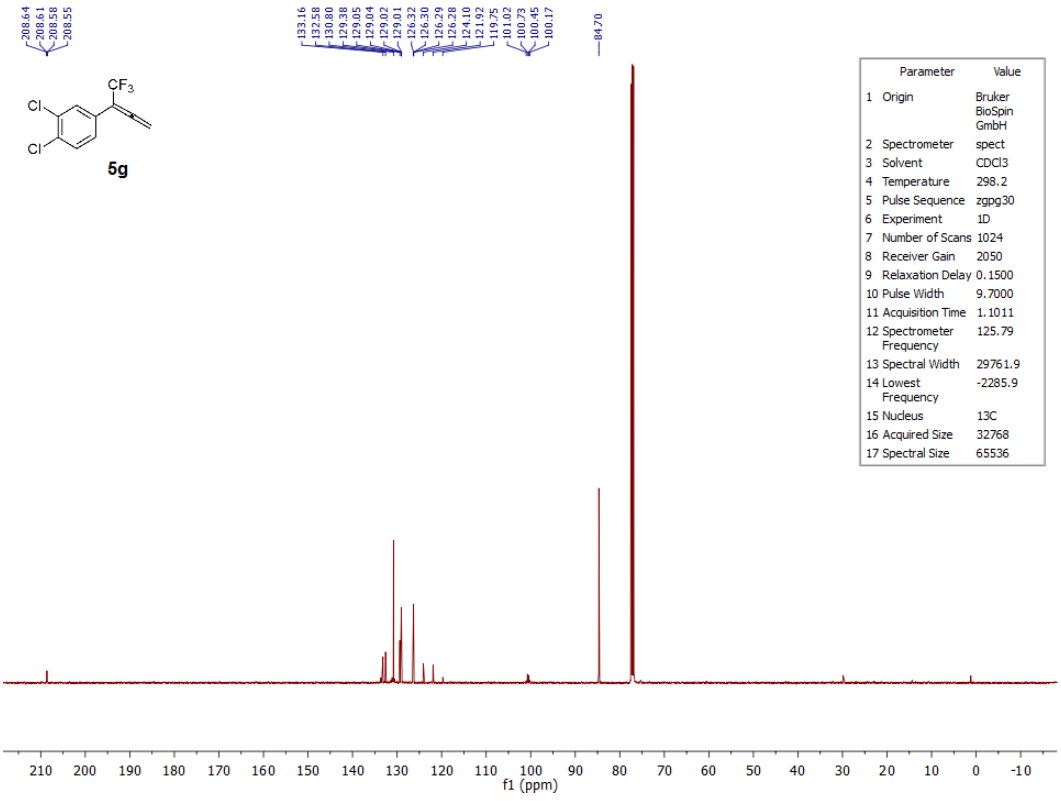


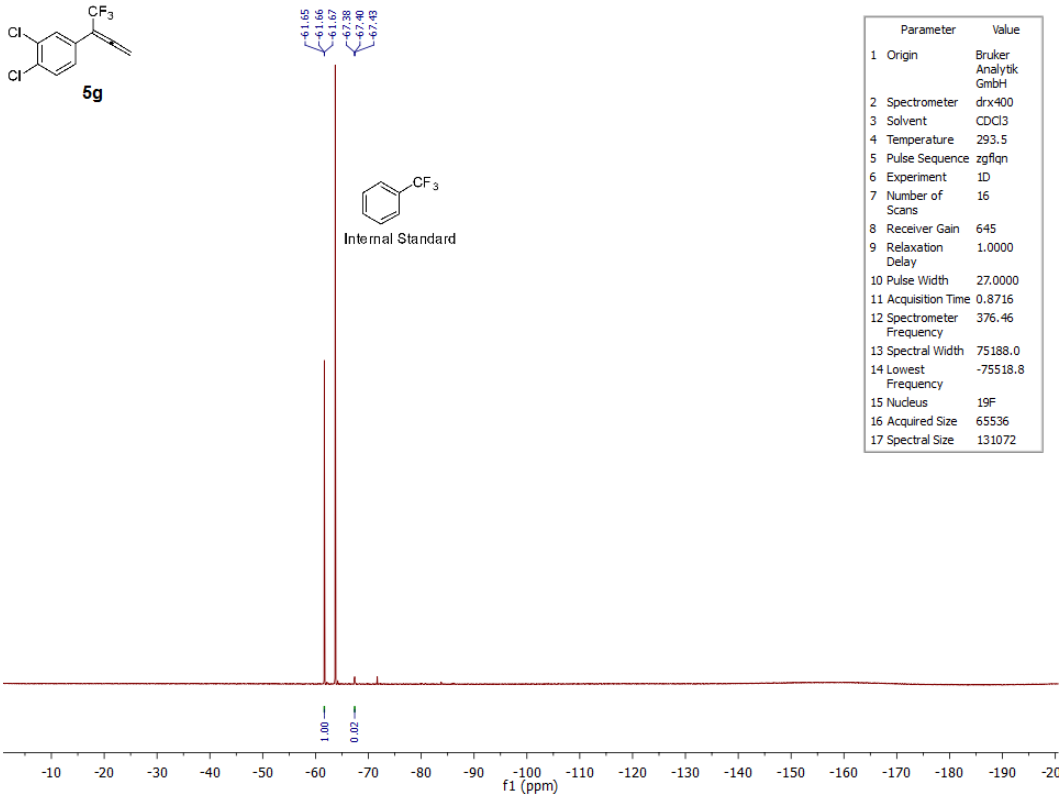
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2288.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



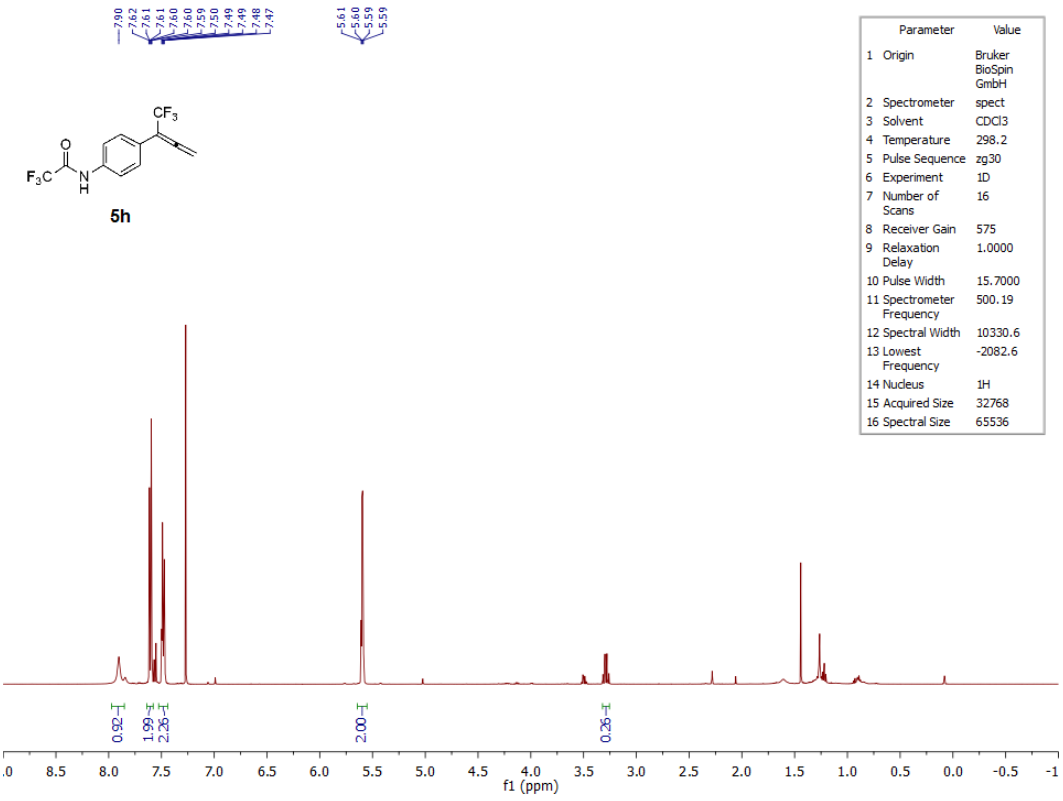
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	299.1
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82658.6
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.53
7.52
7.46
7.44
7.30
7.29
7.29
7.27
7.27
5.64
5.63
5.62
5.61
CF3
Cl
Cl
5g
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.97
1.02
1.61
2.00
0.07
f1 (ppm)

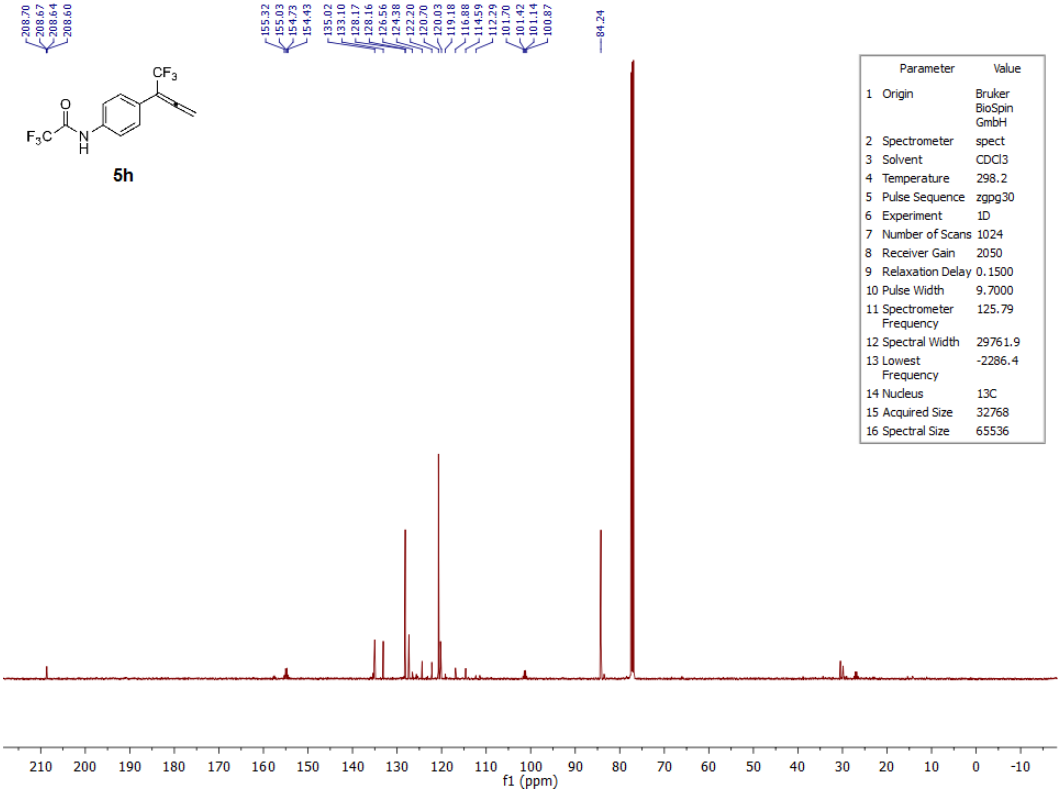

208.64
208.61
208.58
208.55
133.16
132.58
130.80
129.38
129.05
129.04
129.02
129.01
126.32
126.30
126.29
126.28
124.10
121.92
119.75
101.02
100.73
100.45
100.17
84.70
CF3
Cl
Cl
5g
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2285.9
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

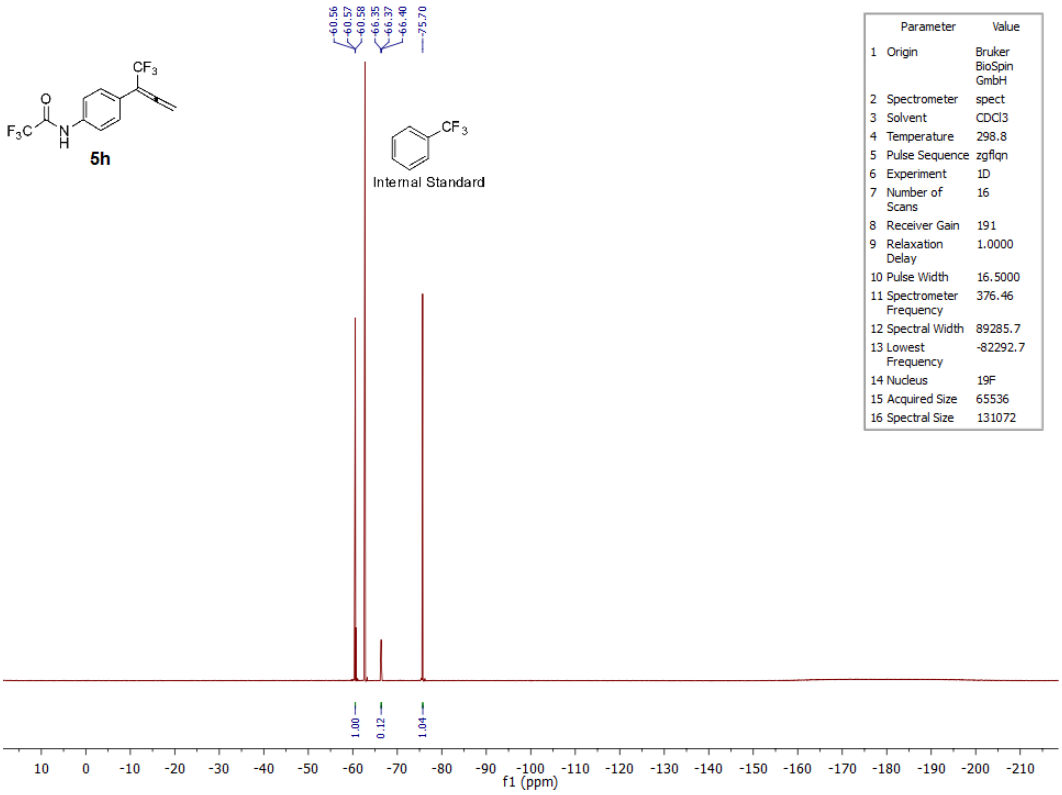


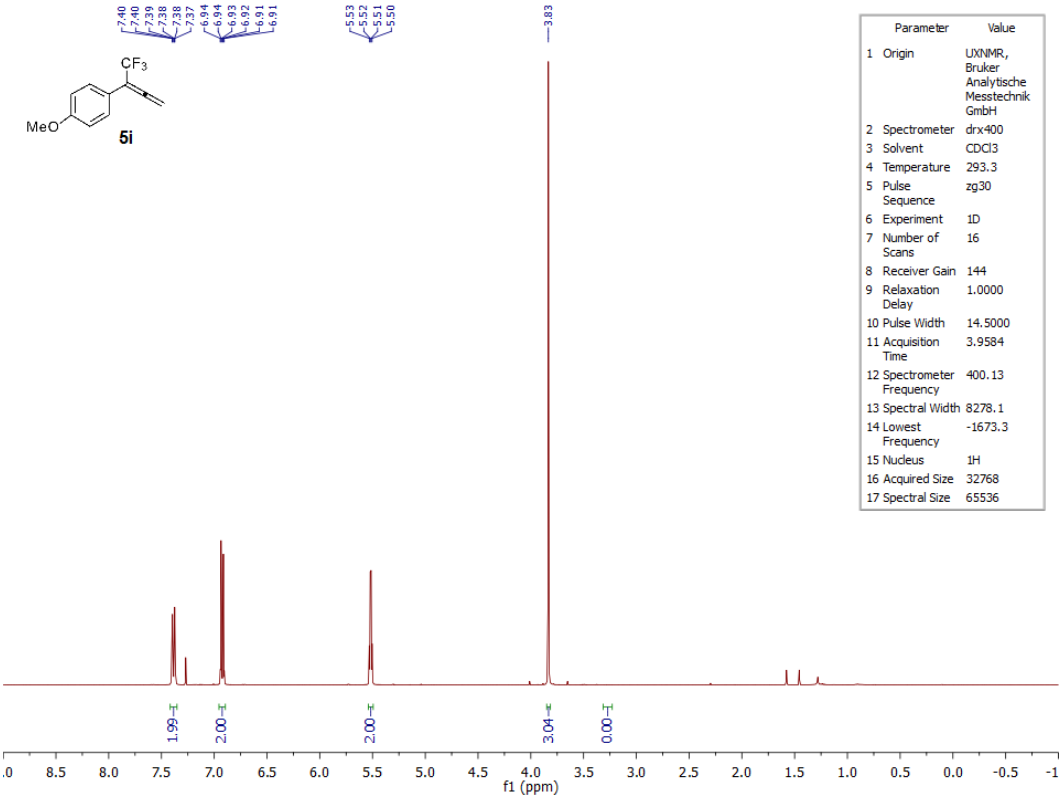
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.5
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75518.8
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



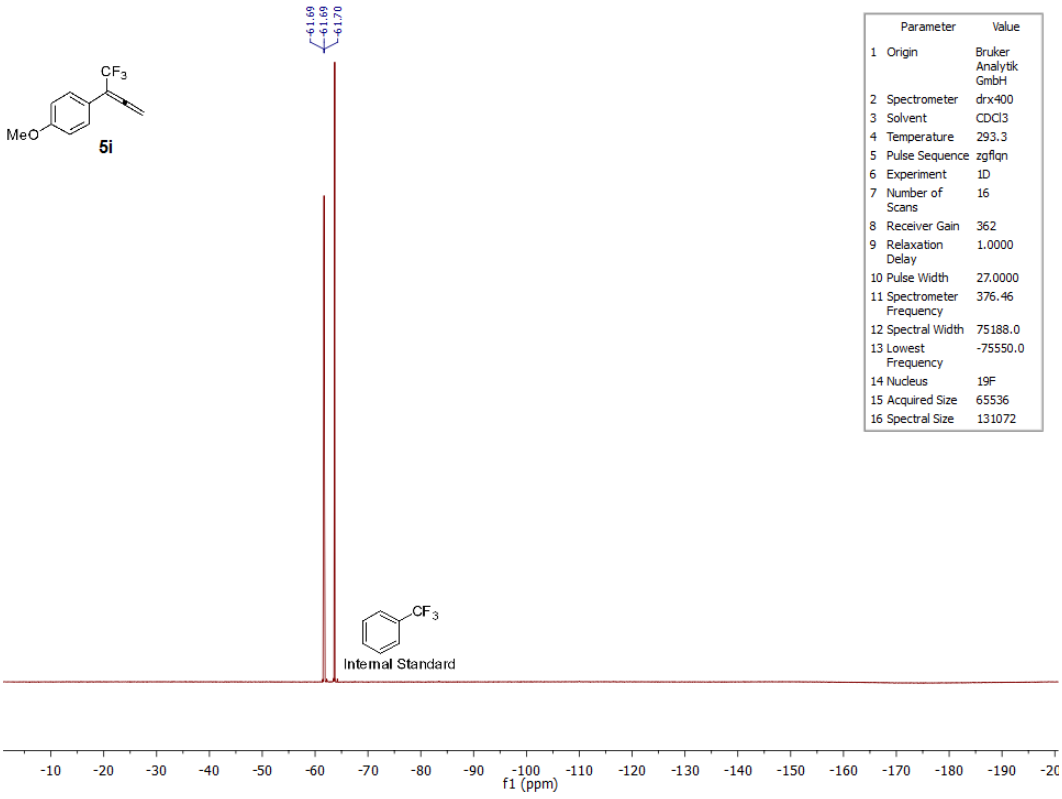
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	575
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.6
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


208.70
208.67
208.64
208.60
155.32
155.03
154.73
154.43
135.02
133.10
128.17
128.16
126.56
124.38
122.20
120.70
120.03
119.18
116.88
114.59
112.29
101.70
101.42
101.14
100.87
84.24
CF3
F3C
O
N
H
5h
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.4
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

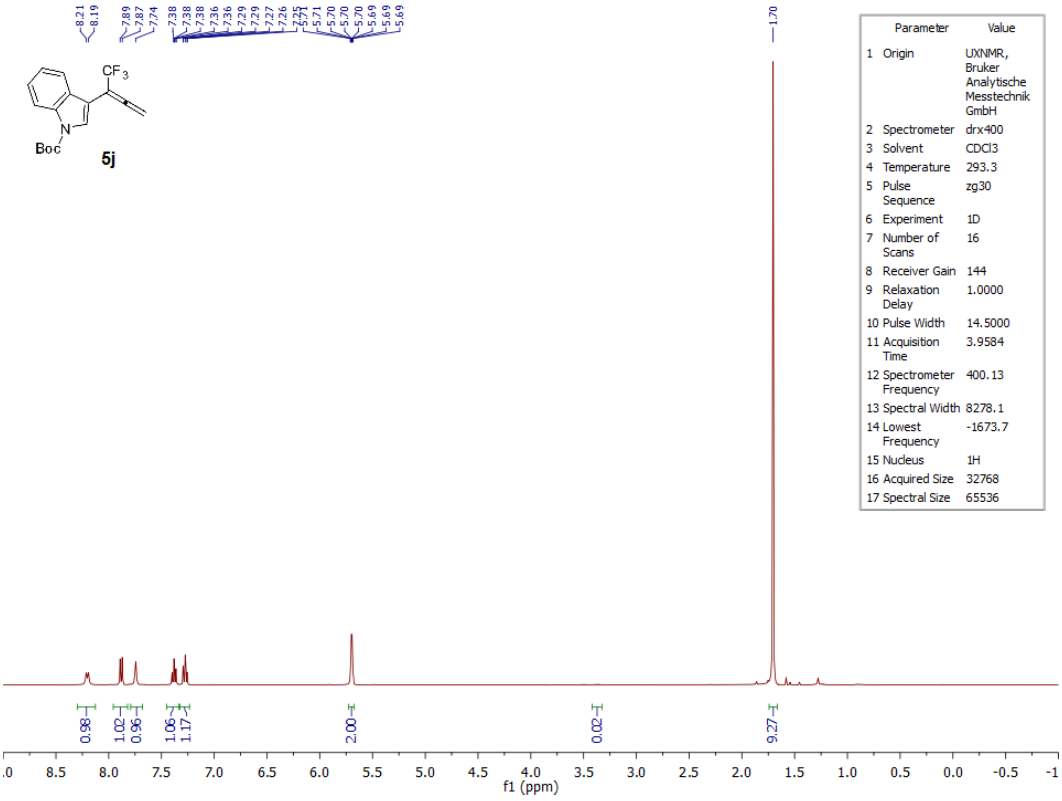

60.56
60.57
60.58
66.35
66.37
66.40
75.70
CF3
F3C
O
N
H
5h
CF3
Internal Standard
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.8
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82292.7
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
1.00
0.12
1.04
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

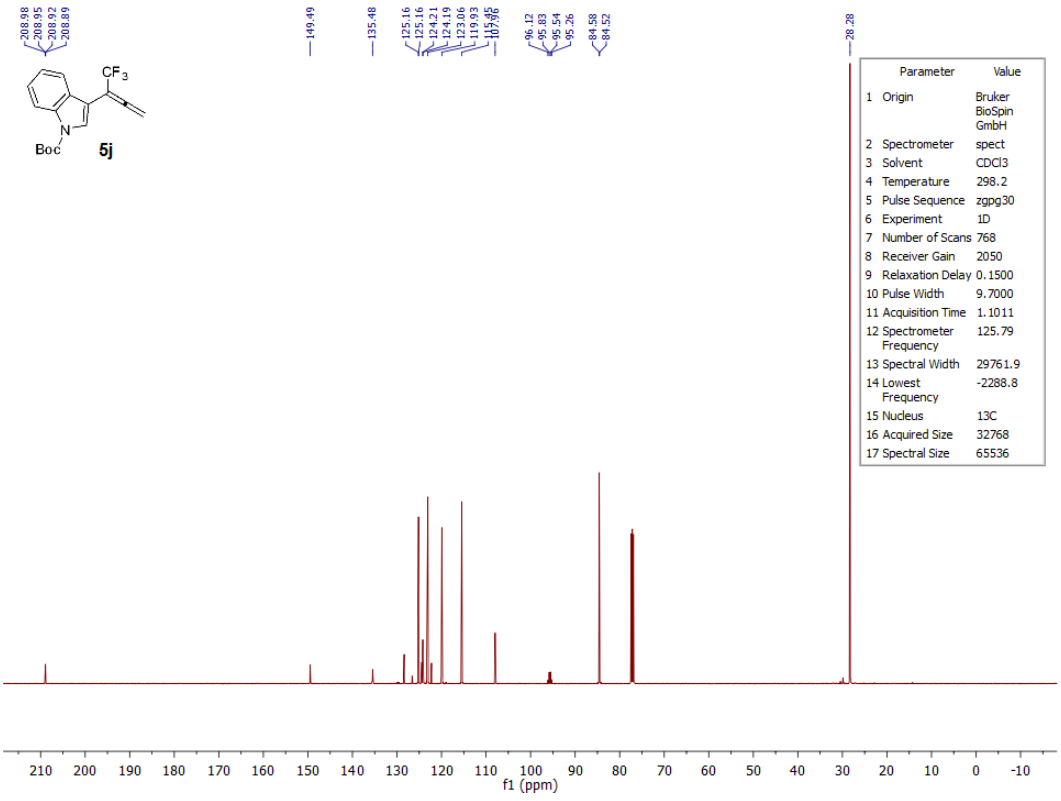


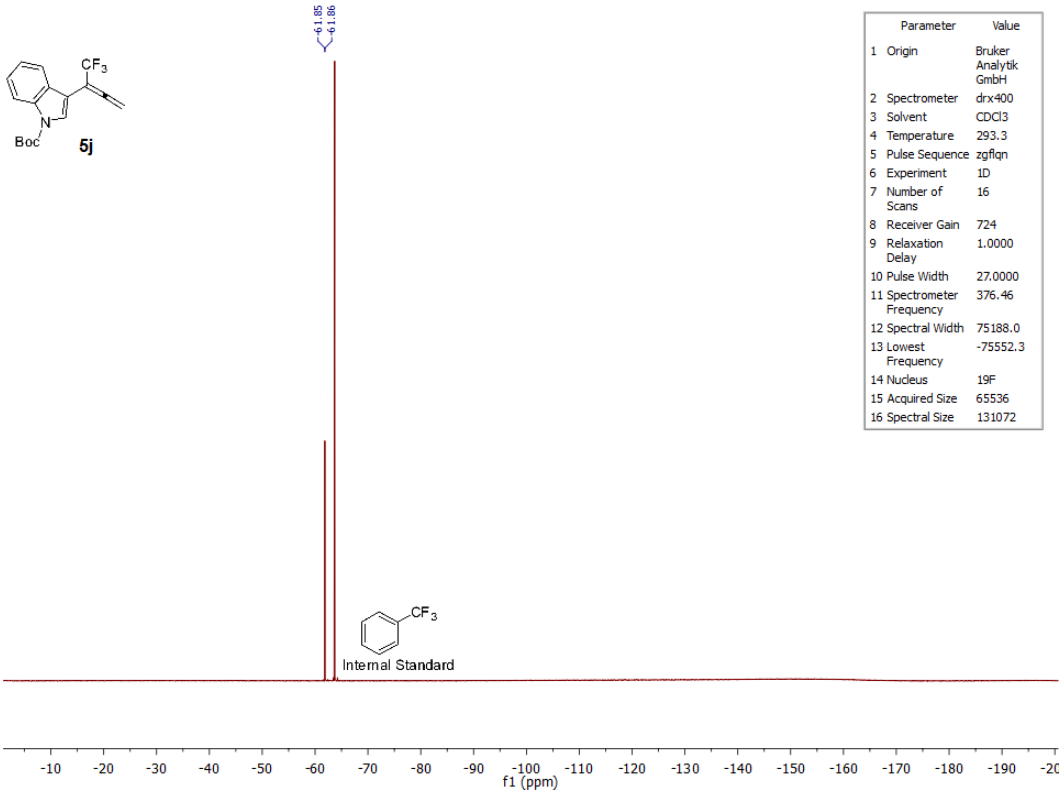
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.3
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	144
9	Relaxation Delay	1.0000
10	Pulse Width	14.5000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1673.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



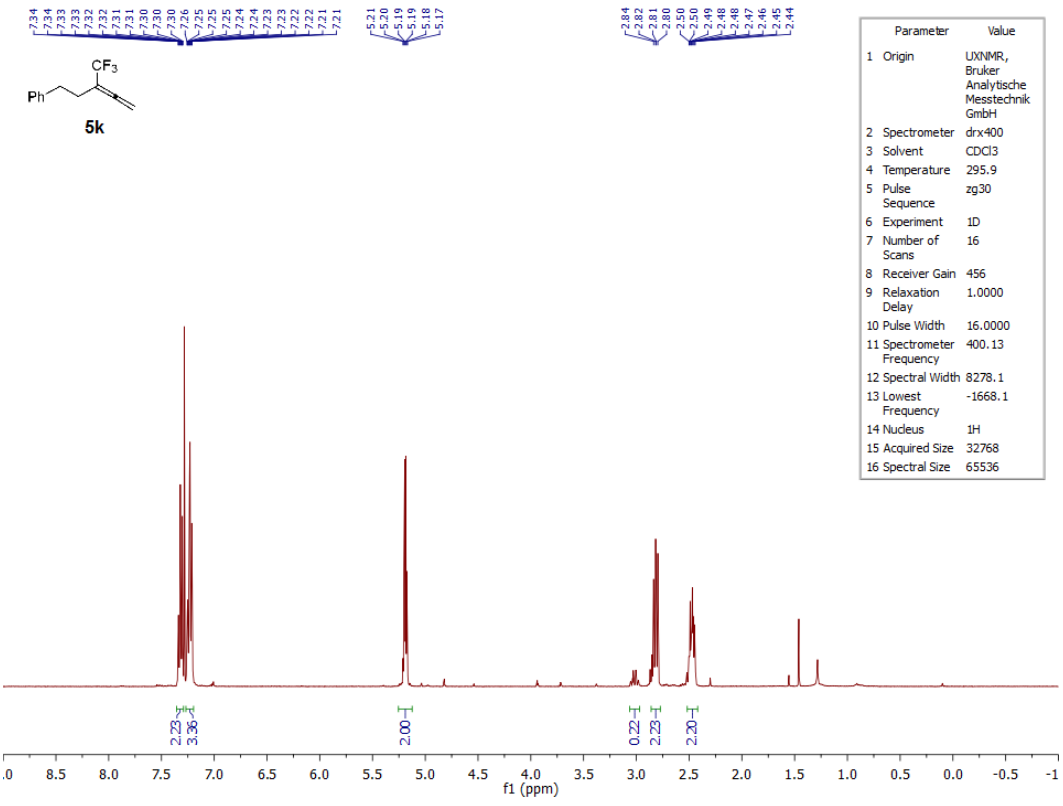
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.3
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	362
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75550.0
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


8.21
8.19
7.89
7.87
7.74
7.38
7.38
7.38
7.36
7.29
7.29
7.27
7.26
5.71
5.71
5.70
5.70
5.69
5.69
5.69
1.70
CF3
N
Boc
5j
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 144
9 Relaxation Delay 1.0000
10 Pulse Width 14.5000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.7
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
0.98
1.02
0.96
1.06
1.17
2.00
0.02
9.27
f1 (ppm)

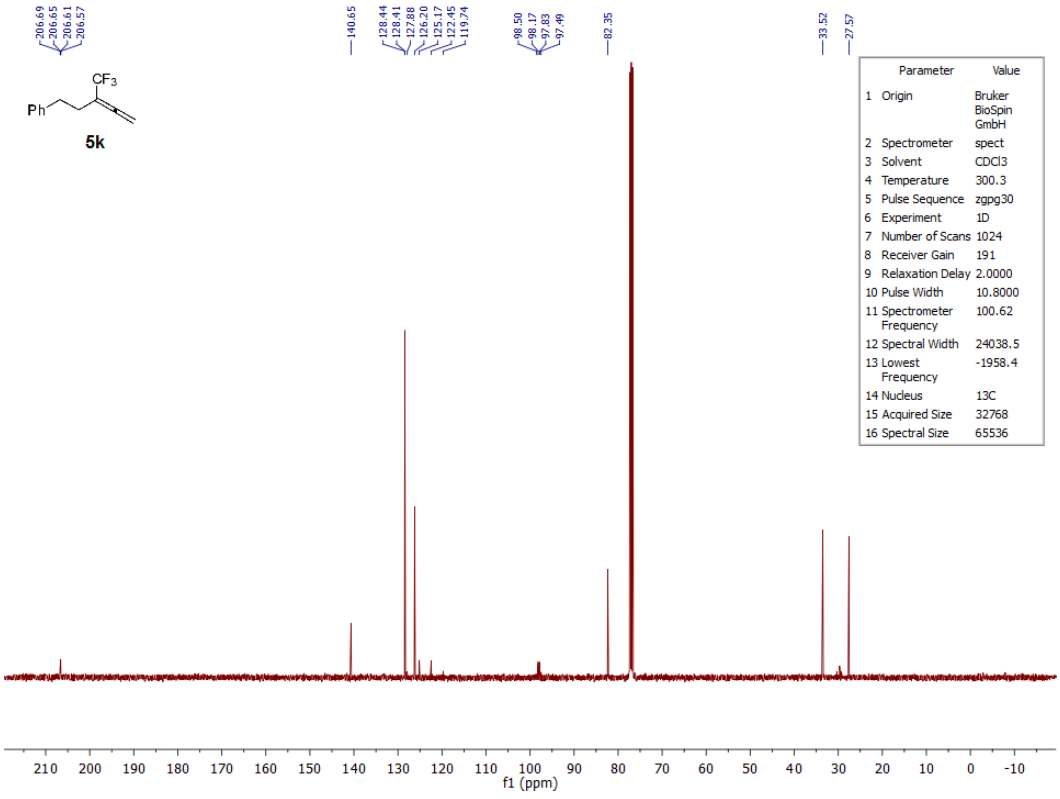

208.98
208.95
208.92
208.89
149.49
135.48
125.16
125.16
124.21
124.19
123.06
119.93
96.12
95.83
95.54
95.26
84.58
84.52
28.28
CF3
N
Boc
5j
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 768
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2288.8
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)



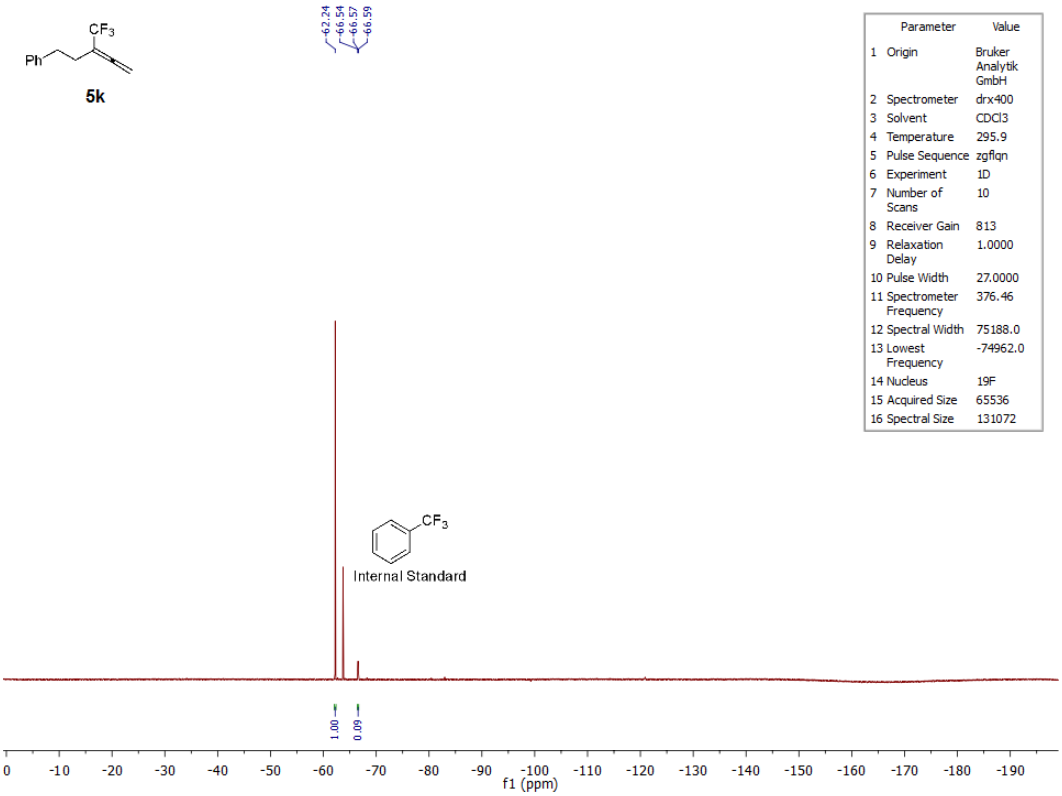
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.3
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	724
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75552.3
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



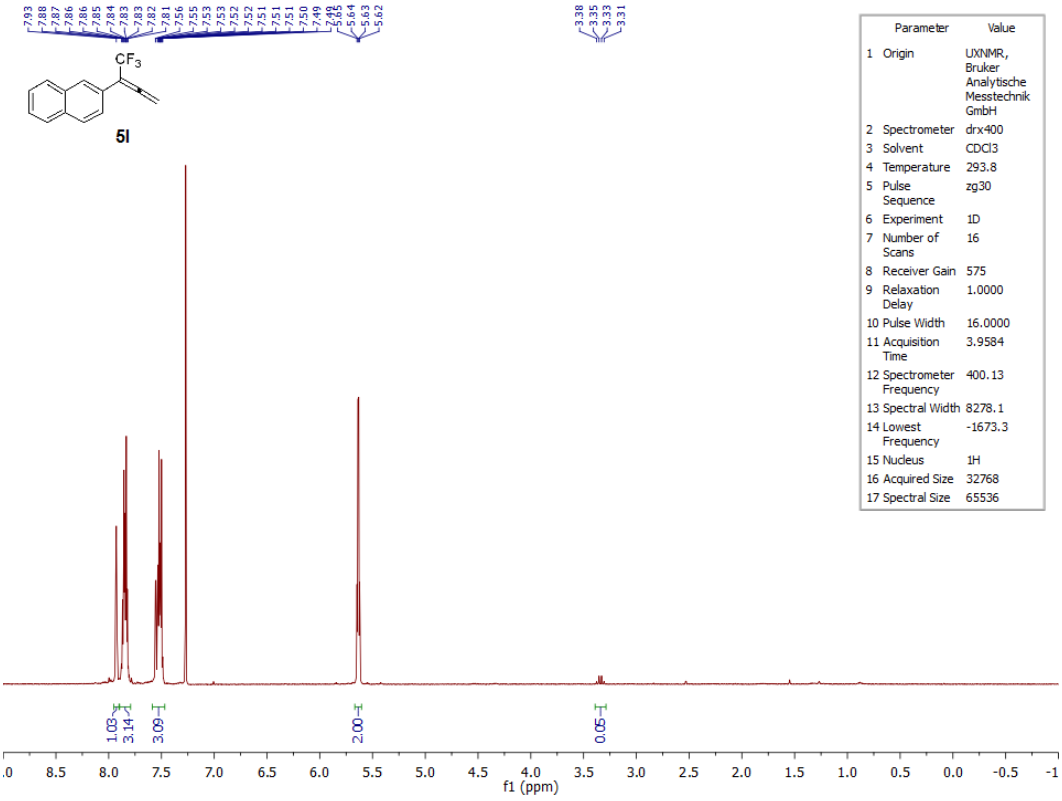
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	295.9
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	456
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8278.1
13	Lowest Frequency	-1668.1
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

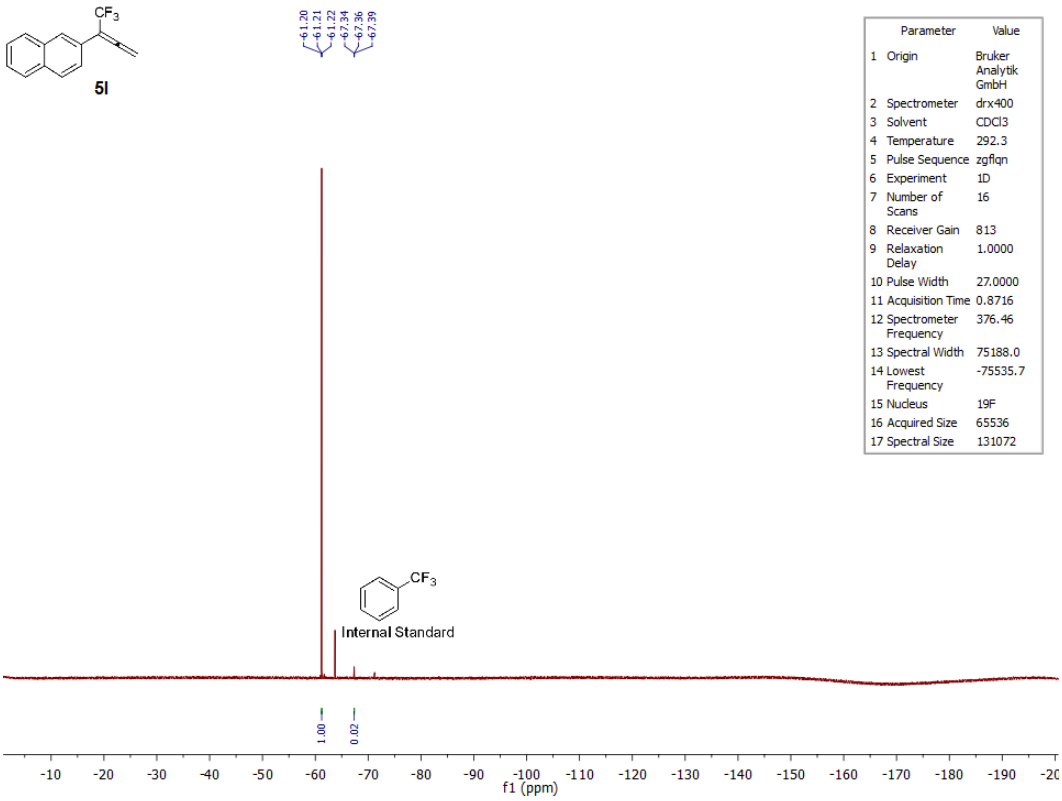


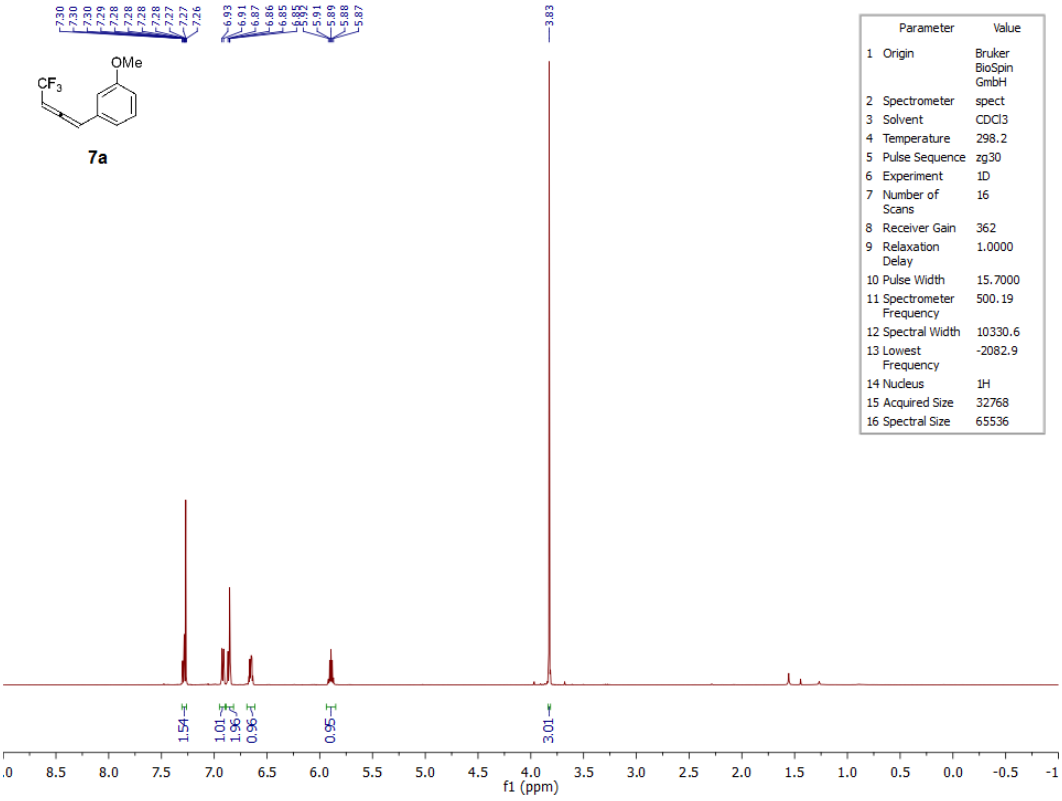
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	300.3
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	191
9	Relaxation Delay	2.0000
10	Pulse Width	10.8000
11	Spectrometer Frequency	100.62
12	Spectral Width	24038.5
13	Lowest Frequency	-1958.4
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536

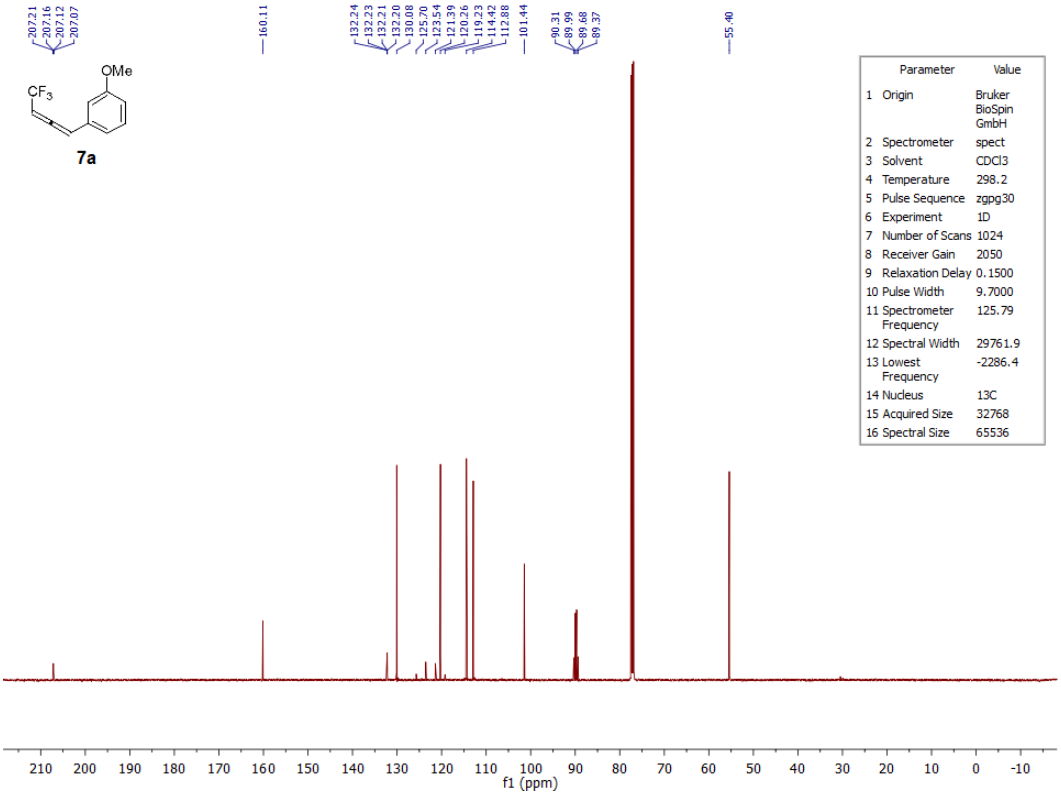


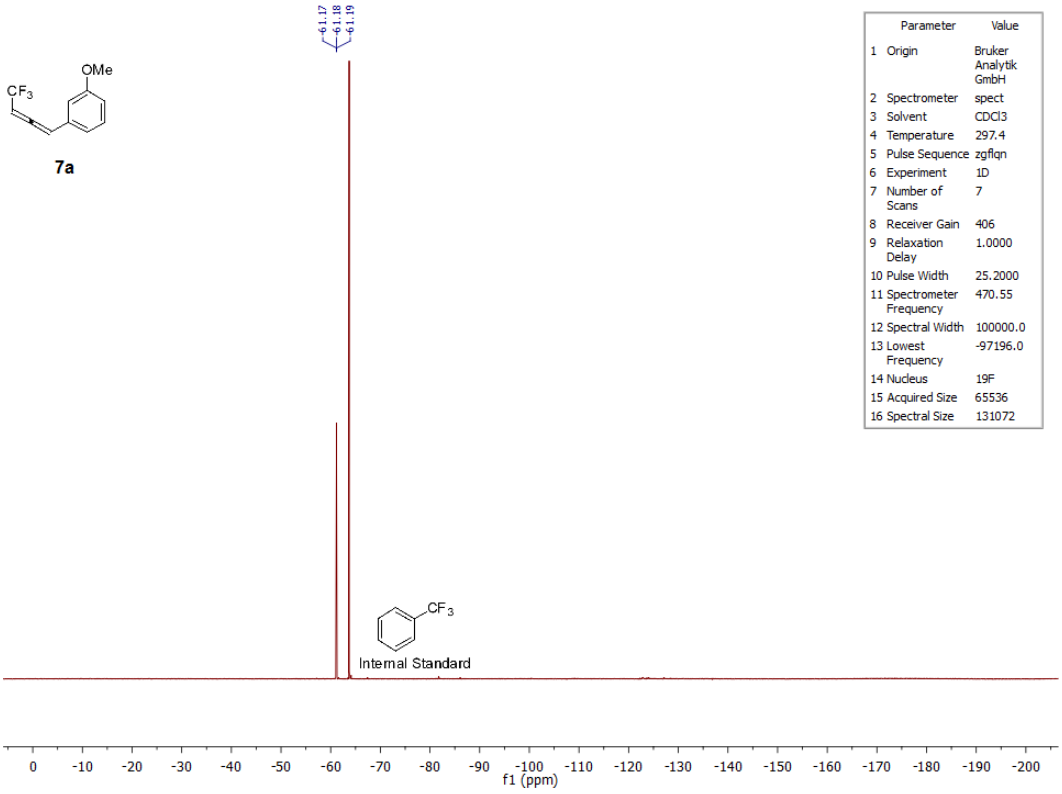
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	295.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	10
8	Receiver Gain	813
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-74962.0
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.93
7.88
7.87
7.86
7.86
7.85
7.84
7.83
7.83
7.82
7.81
7.56
7.55
7.53
7.53
7.52
7.52
7.51
7.51
7.51
7.51
7.50
7.49
5.65
5.64
5.63
5.62
3.38
3.35
3.33
3.31
CF3
5l
Parameter Value
1 Origin UXNMR, Bruker Analytische Messtechnik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 575
9 Relaxation Delay 1.0000
10 Pulse Width 16.0000
11 Acquisition Time 3.9584
12 Spectrometer Frequency 400.13
13 Spectral Width 8278.1
14 Lowest Frequency -1673.3
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
1.03
3.14
3.09
2.00
0.05
f1 (ppm)

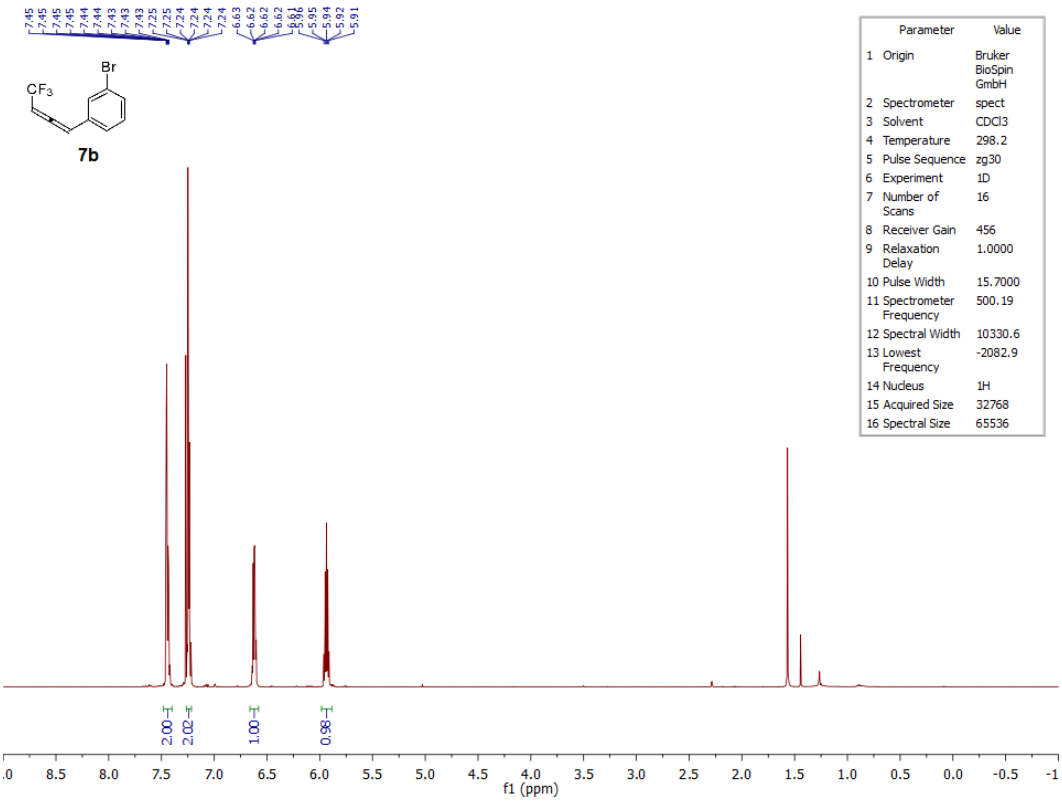

CF3
5l
-6.20
-6.21
-6.22
-7.34
-7.36
-7.39
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 292.3
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 813
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Acquisition Time 0.8716
12 Spectrometer Frequency 376.46
13 Spectral Width 75188.0
14 Lowest Frequency -75535.7
15 Nucleus 19F
16 Acquired Size 65536
17 Spectral Size 131072
CF3
Internal Standard
1.00
0.02
f1 (ppm)


7.30
7.30
7.30
7.29
7.28
7.28
7.28
7.28
7.27
7.27
7.27
7.26
6.93
6.91
6.87
6.86
6.85
5.92
5.91
5.89
5.88
5.87
3.83
OMe
CF3
7a
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 362
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2082.9
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.54
1.01
1.96
0.96
0.95
3.01
f1 (ppm)

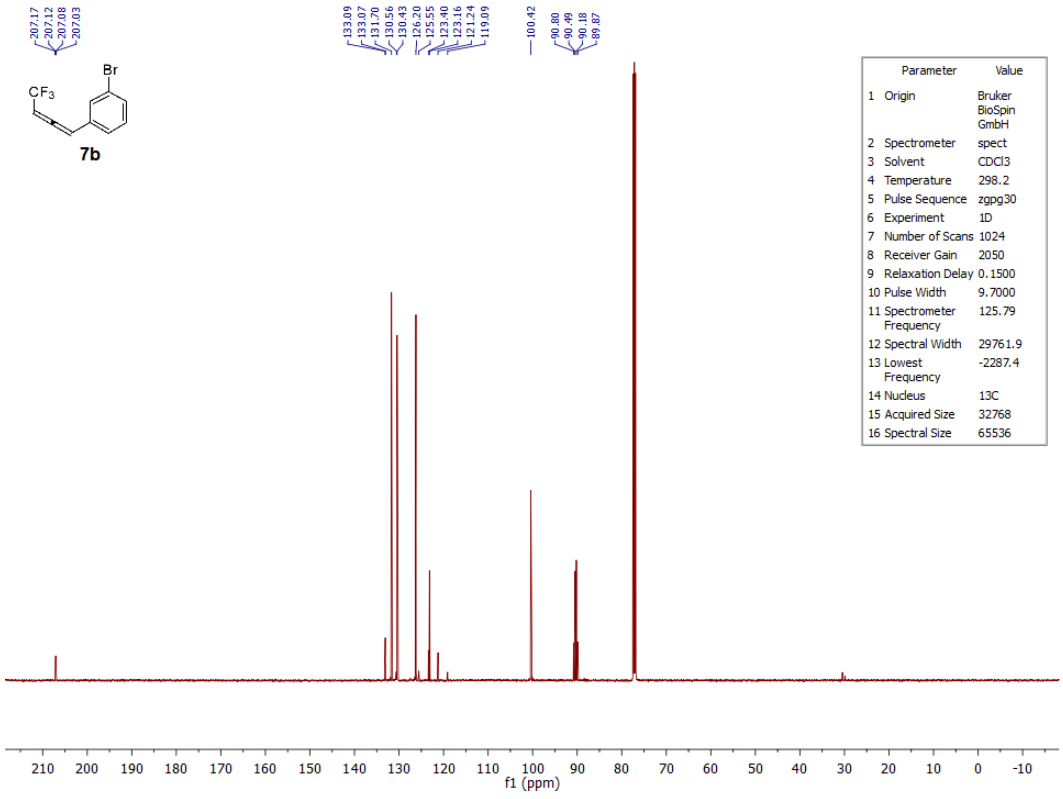

207.21
207.16
207.12
207.07
160.11
132.24
132.23
132.21
132.20
130.08
125.70
123.54
121.39
120.26
119.23
114.42
112.88
101.44
90.31
89.99
89.68
89.37
55.40
OMe
CF3
7a
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.4
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

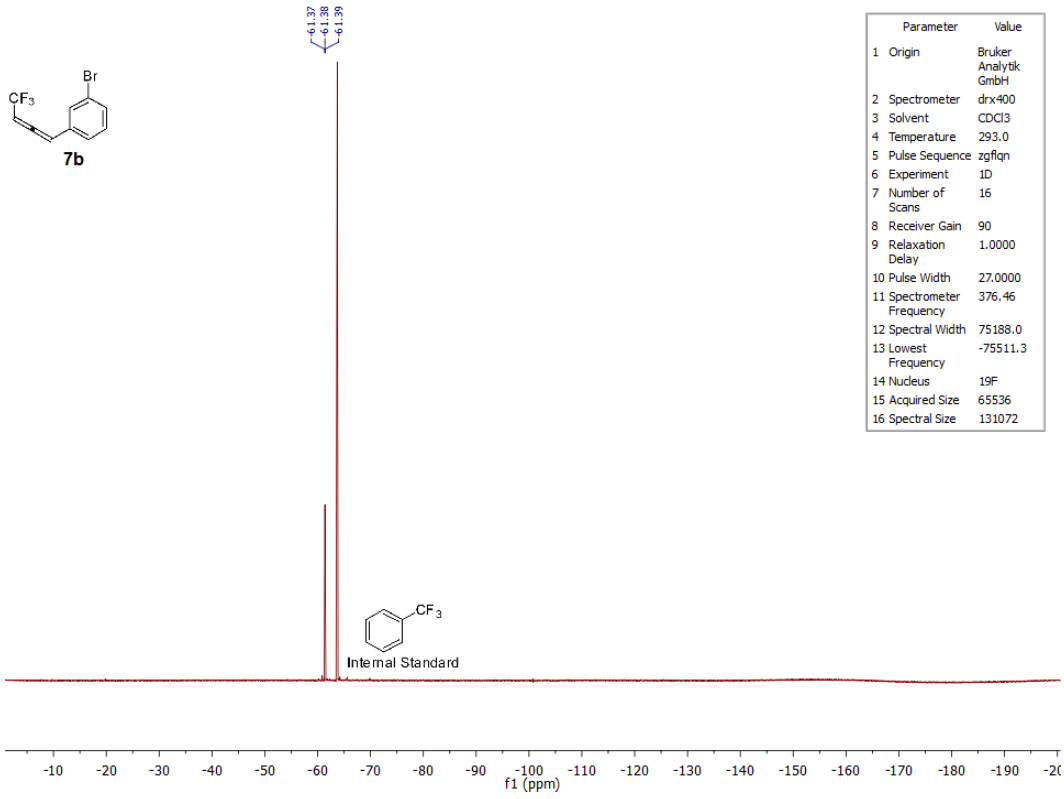


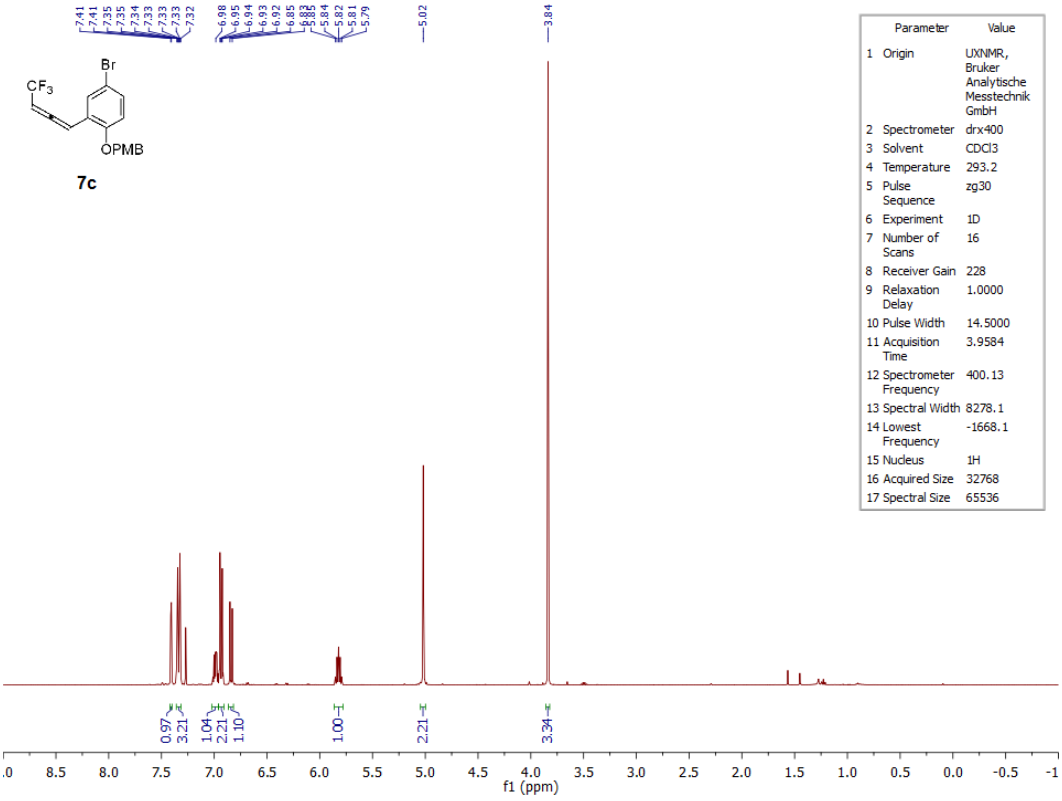
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	297.4
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	7
8	Receiver Gain	406
9	Relaxation Delay	1.0000
10	Pulse Width	25.2000
11	Spectrometer Frequency	470.55
12	Spectral Width	100000.0
13	Lowest Frequency	-97196.0
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



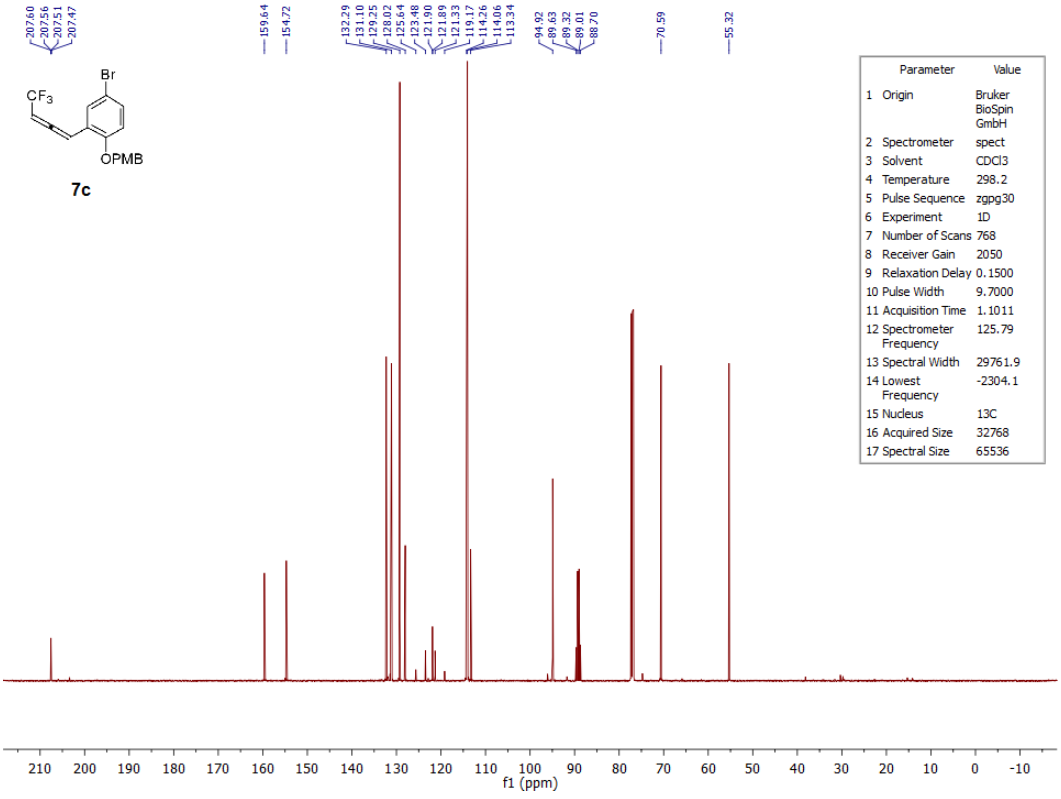
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	456
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


207.17
207.12
207.08
207.03
133.09
133.07
131.70
130.56
129.43
126.20
125.55
123.40
123.16
121.24
119.09
100.42
90.80
90.49
90.18
89.87
Br
CF3
7b
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2287.4
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

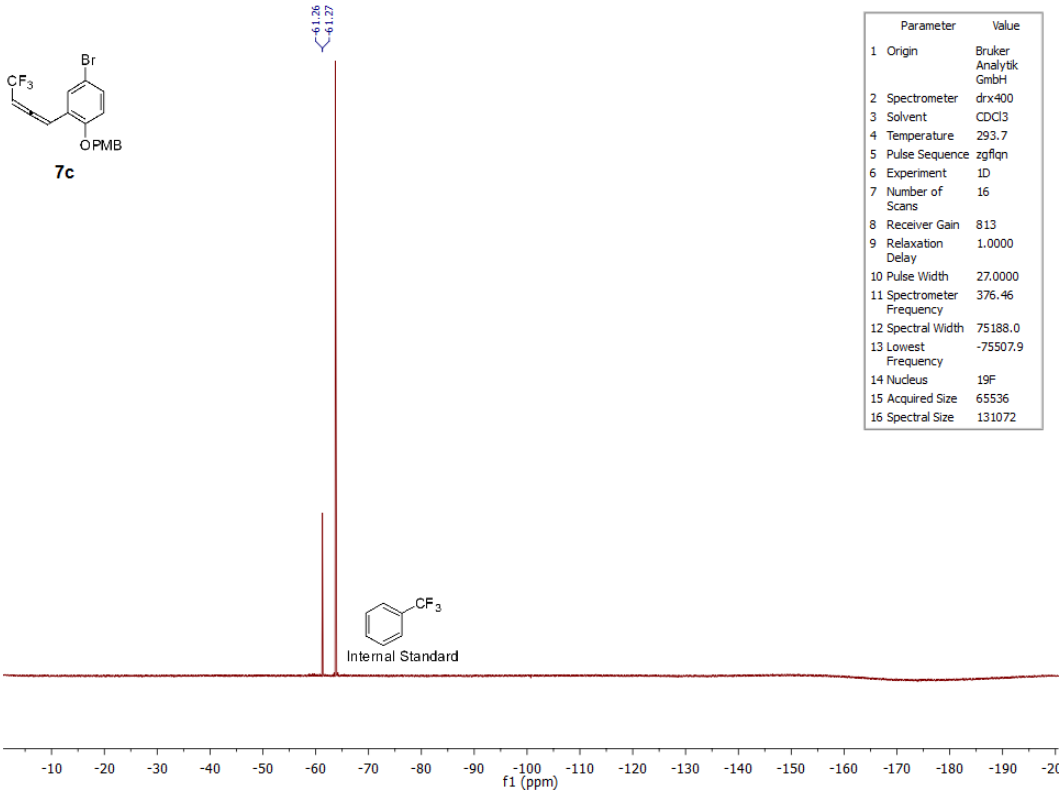

-61.37
-61.38
-61.39
Br
CF3
7b
Parameter Value
1 Origin Bruker Analytik GmbH
2 Spectrometer drx400
3 Solvent CDCl3
4 Temperature 293.0
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 90
9 Relaxation Delay 1.0000
10 Pulse Width 27.0000
11 Spectrometer Frequency 376.46
12 Spectral Width 75188.0
13 Lowest Frequency -75511.3
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
CF3
Internal Standard
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -20
f1 (ppm)



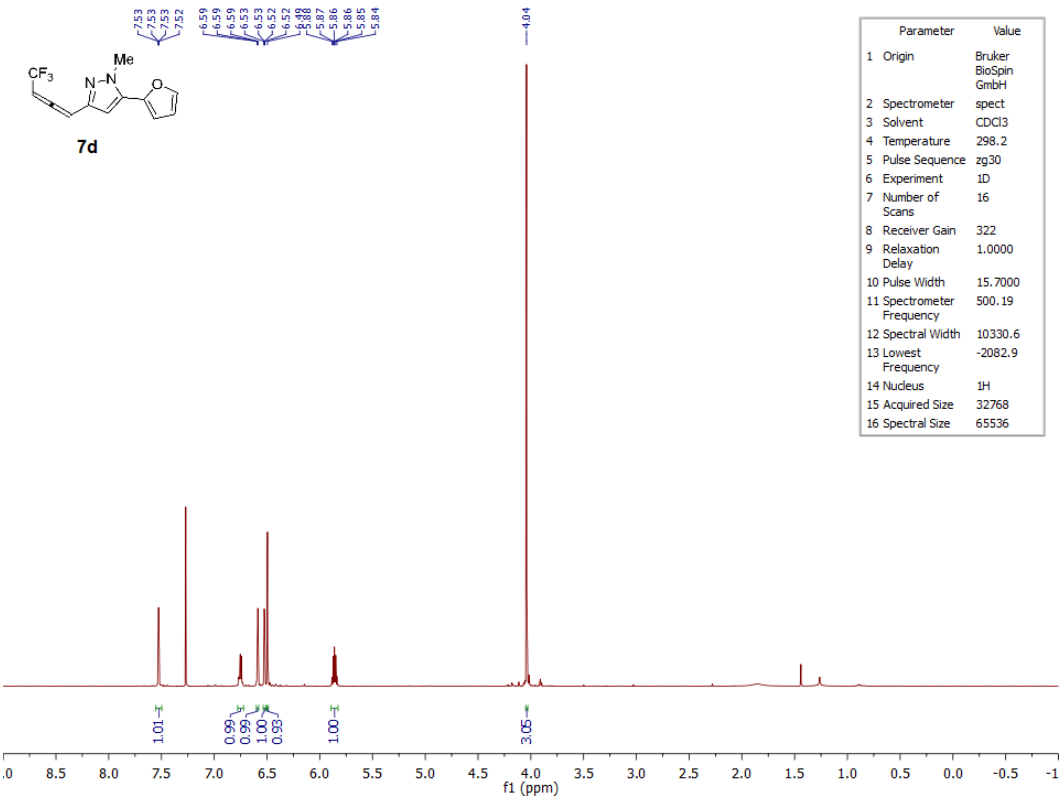
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	228
9	Relaxation Delay	1.0000
10	Pulse Width	14.5000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1668.1
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536



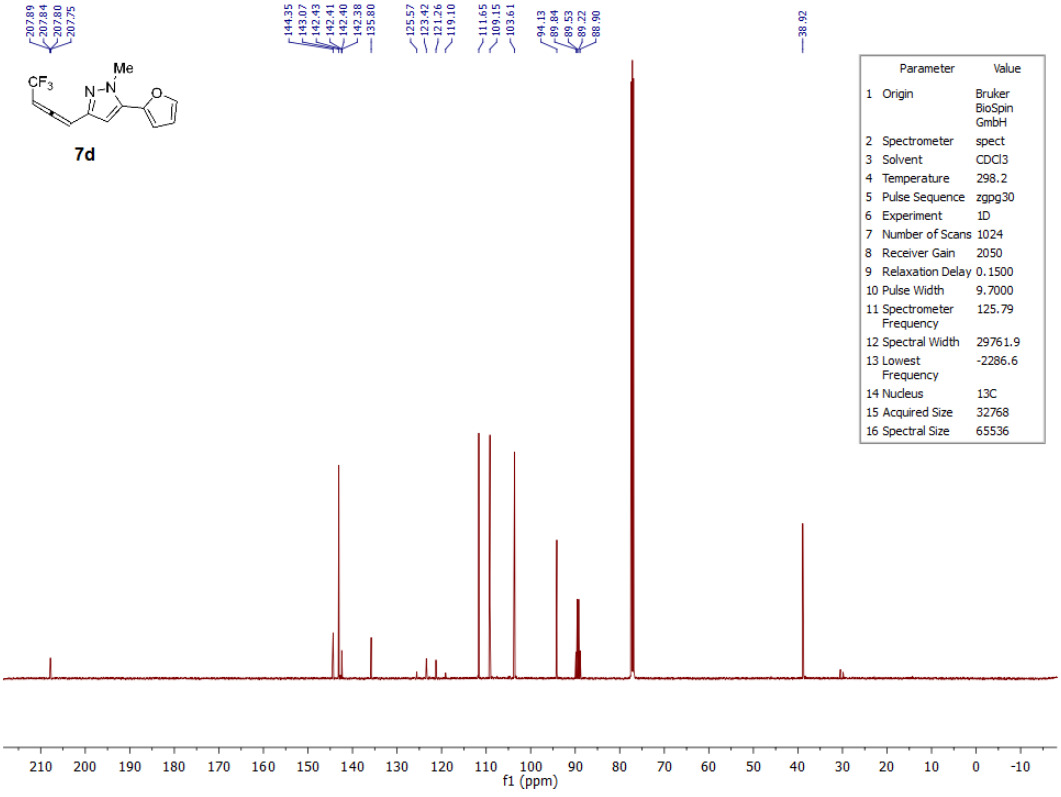
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	768
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Acquisition Time	1.1011
12	Spectrometer Frequency	125.79
13	Spectral Width	29761.9
14	Lowest Frequency	-2304.1
15	Nucleus	13C
16	Acquired Size	32768
17	Spectral Size	65536



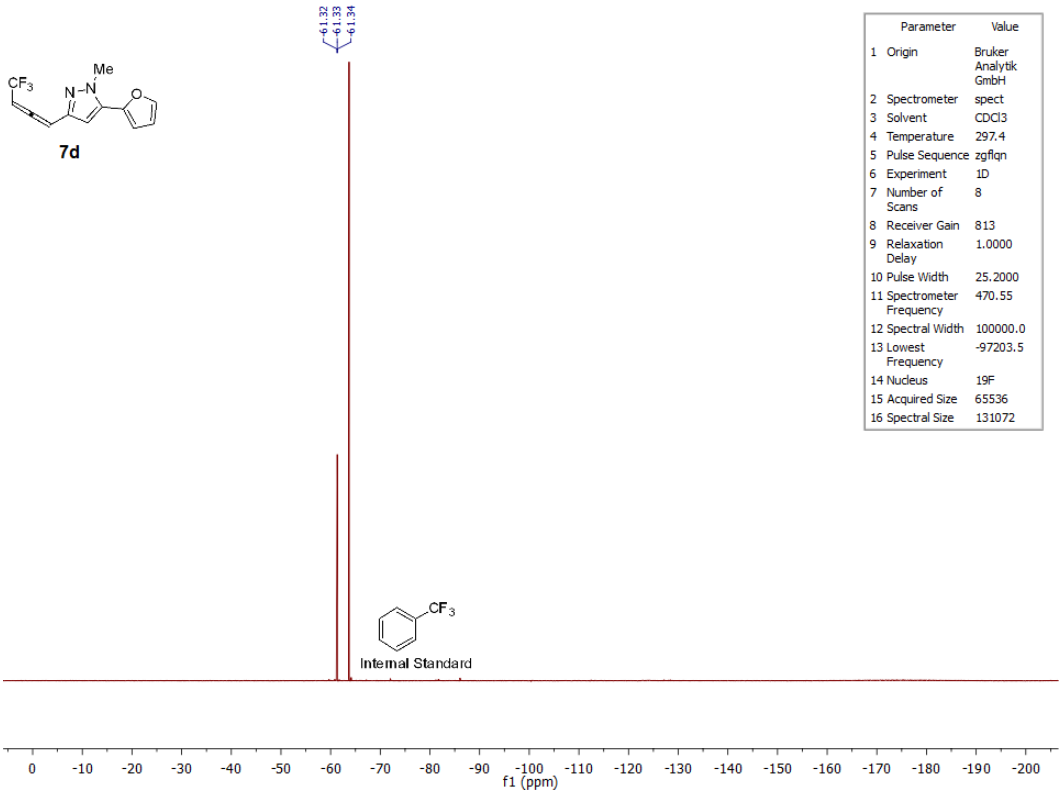
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.7
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	813
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75507.9
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



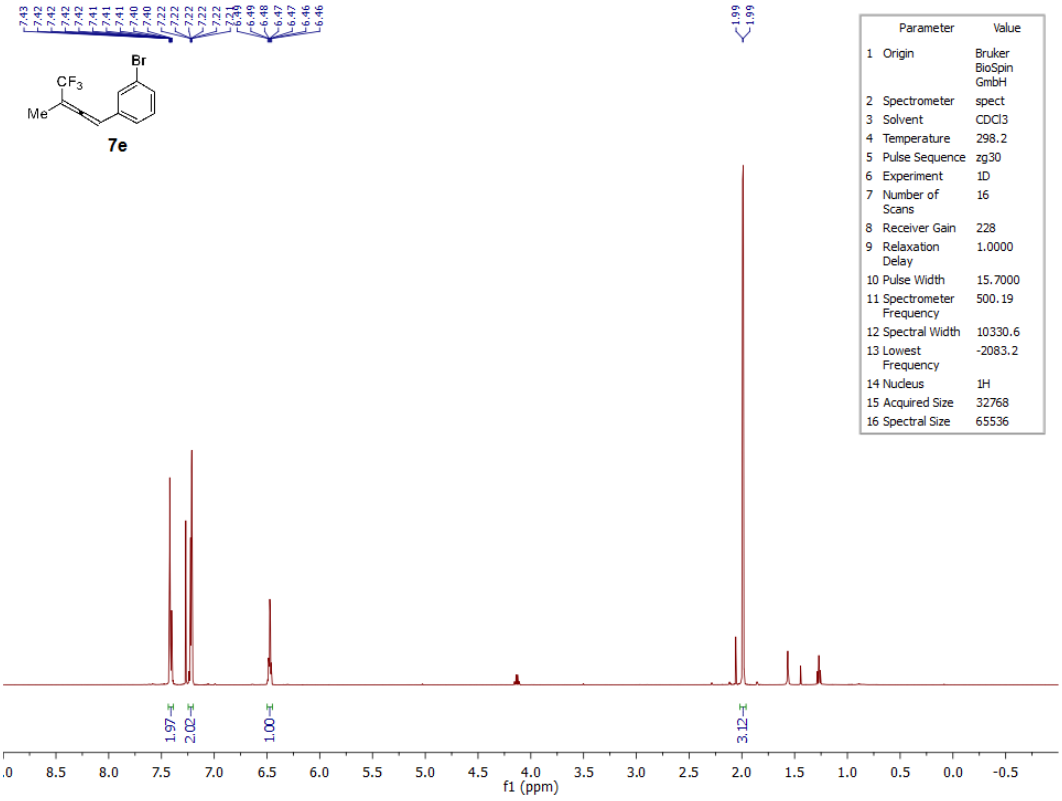
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	322
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.9
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536

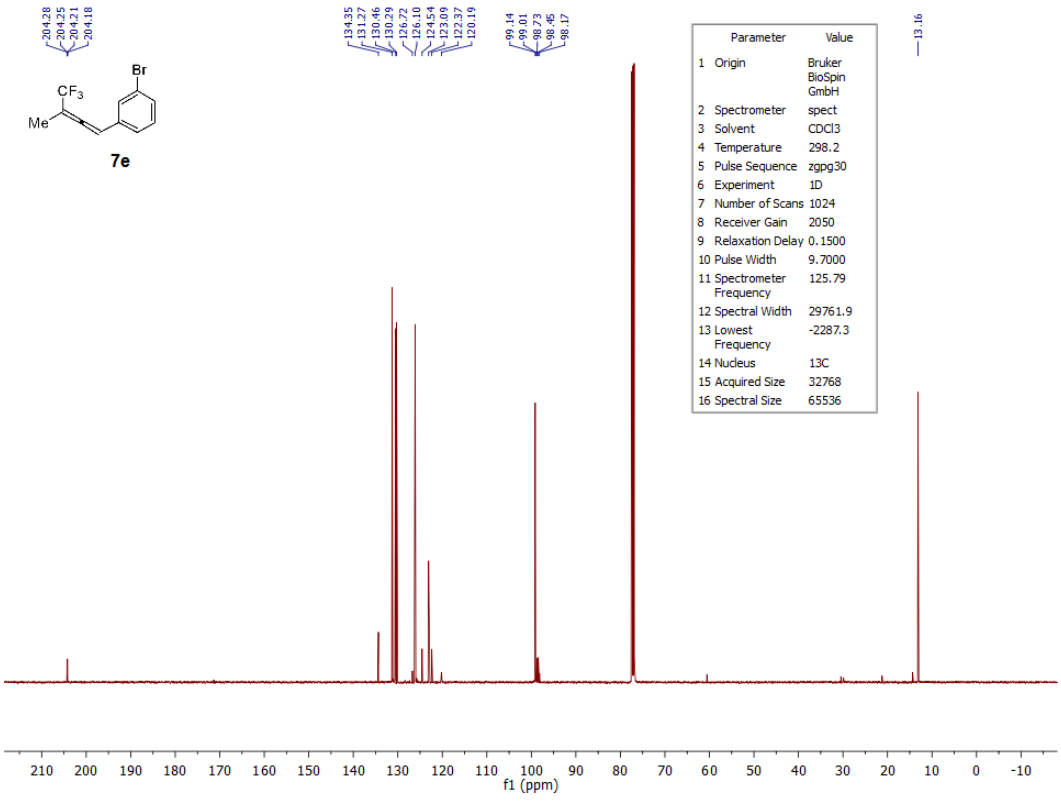


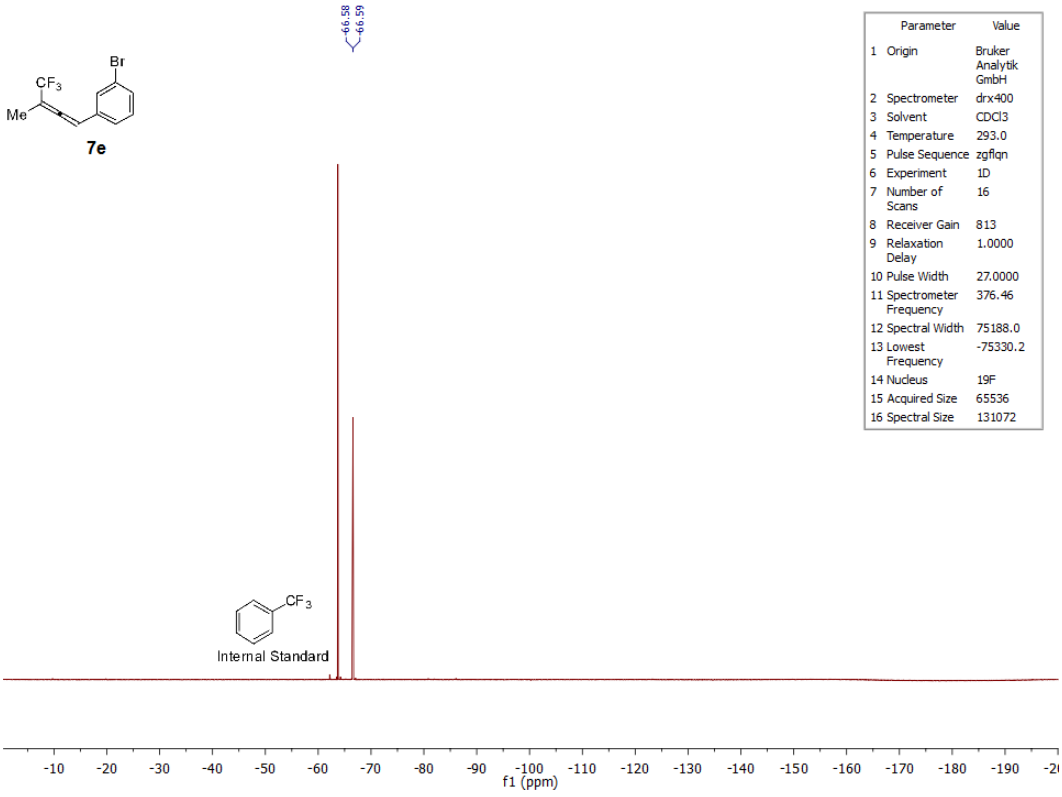
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2286.6
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



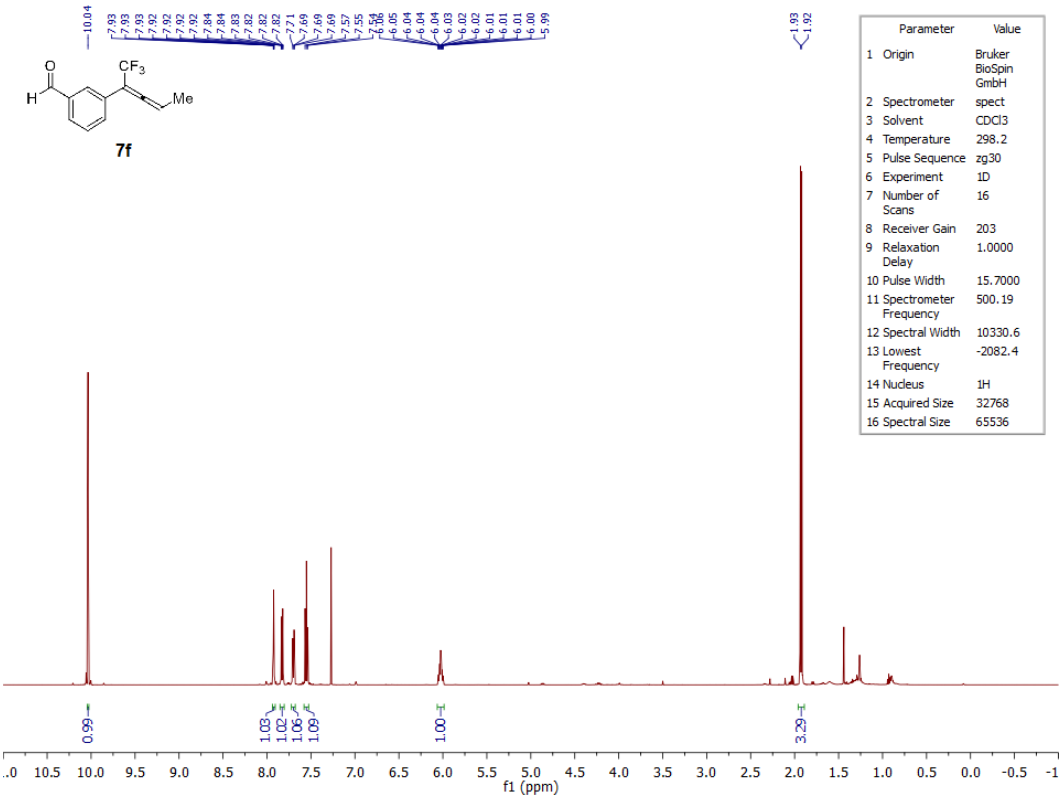
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	297.4
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	8
8	Receiver Gain	813
9	Relaxation Delay	1.0000
10	Pulse Width	25.2000
11	Spectrometer Frequency	470.55
12	Spectral Width	100000.0
13	Lowest Frequency	-97203.5
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.43
7.42
7.42
7.42
7.42
7.41
7.41
7.41
7.40
7.40
7.22
7.22
7.22
7.22
7.22
7.21
6.49
6.48
6.47
6.47
6.46
6.46
1.99
1.99
Br
CF3
Me
7e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 228
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Spectrometer Frequency 500.19
12 Spectral Width 10330.6
13 Lowest Frequency -2083.2
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.97
2.02
1.00
3.12
f1 (ppm)

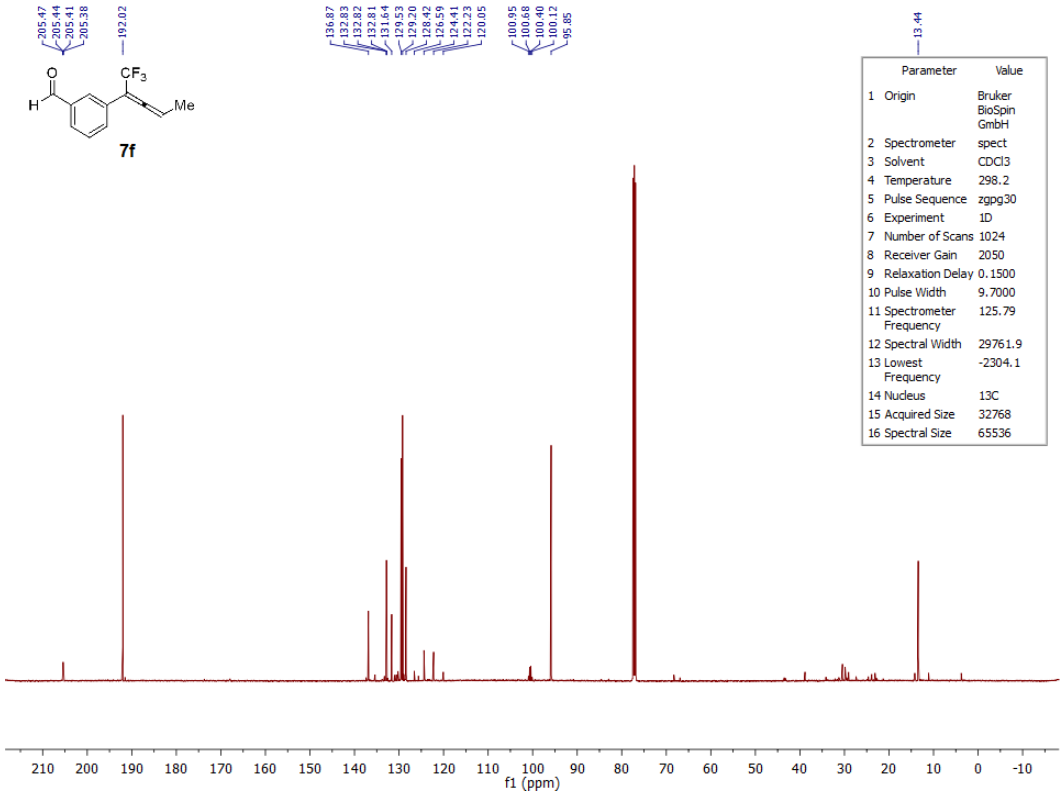

204.28
204.25
204.21
204.18
134.35
131.27
130.46
130.29
126.72
126.10
124.54
123.09
122.37
120.19
99.14
99.01
98.73
98.45
98.17
13.16
Br
CF3
Me
7e
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2287.3
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)



	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.0
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	813
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Spectrometer Frequency	376.46
12	Spectral Width	75188.0
13	Lowest Frequency	-75330.2
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	203
9	Relaxation Delay	1.0000
10	Pulse Width	15.7000
11	Spectrometer Frequency	500.19
12	Spectral Width	10330.6
13	Lowest Frequency	-2082.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536


205.47
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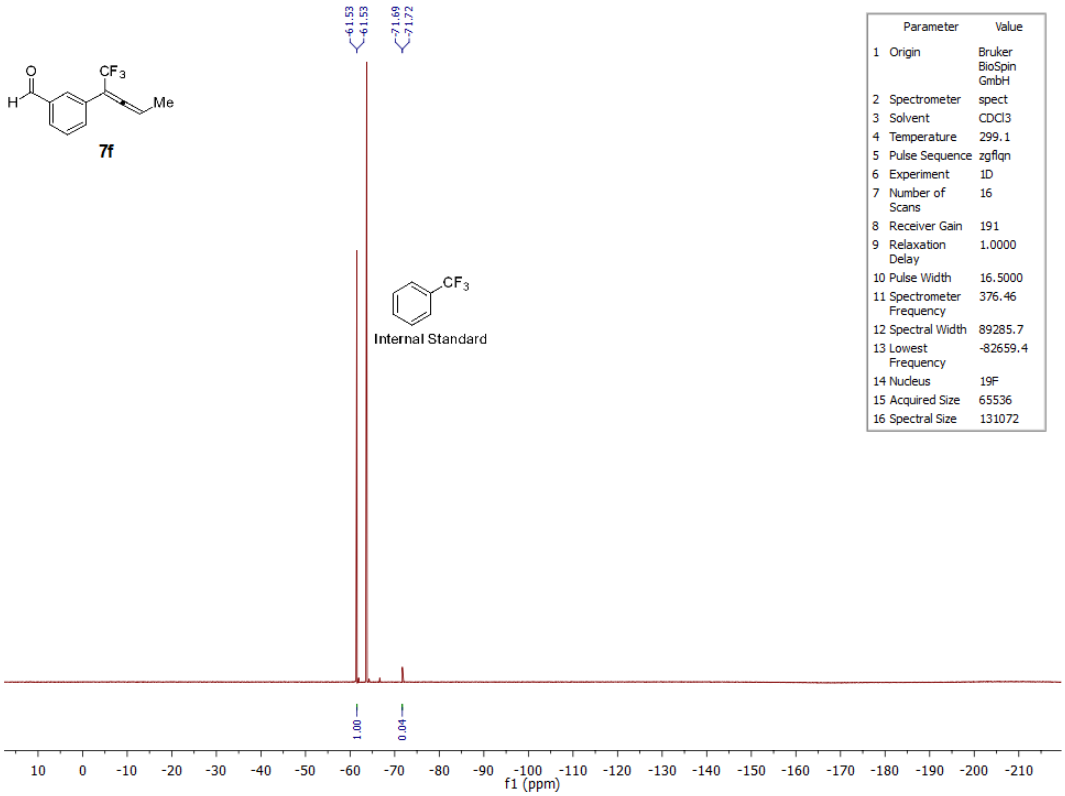
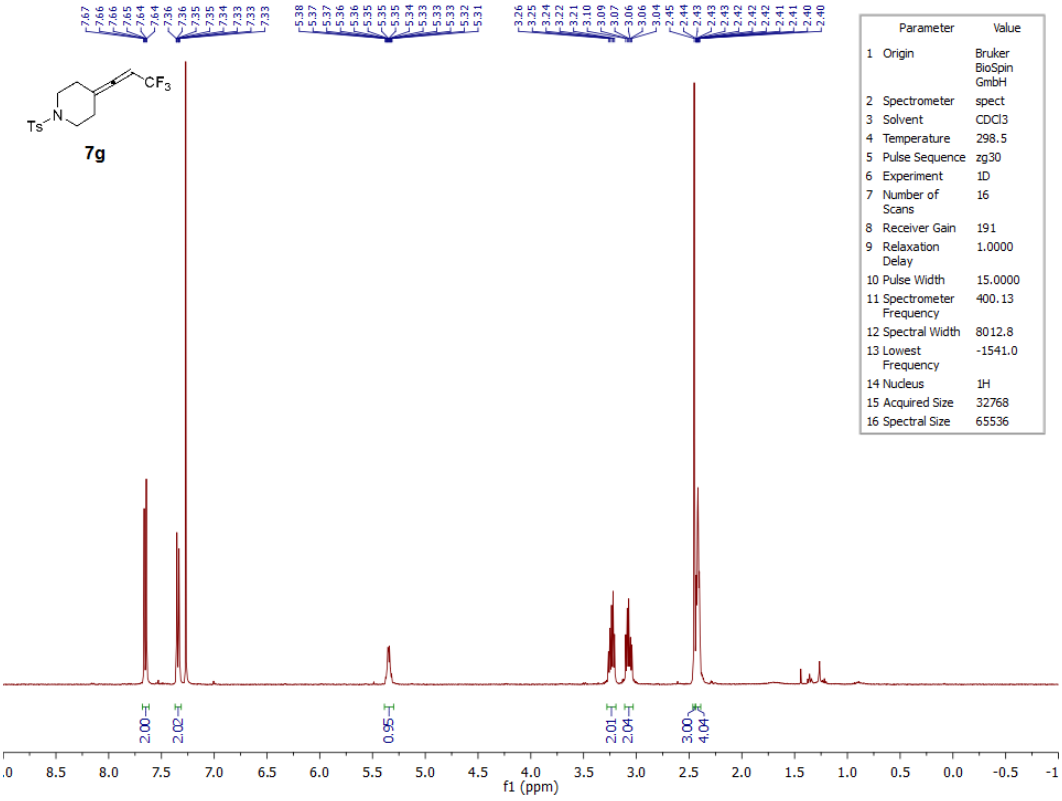
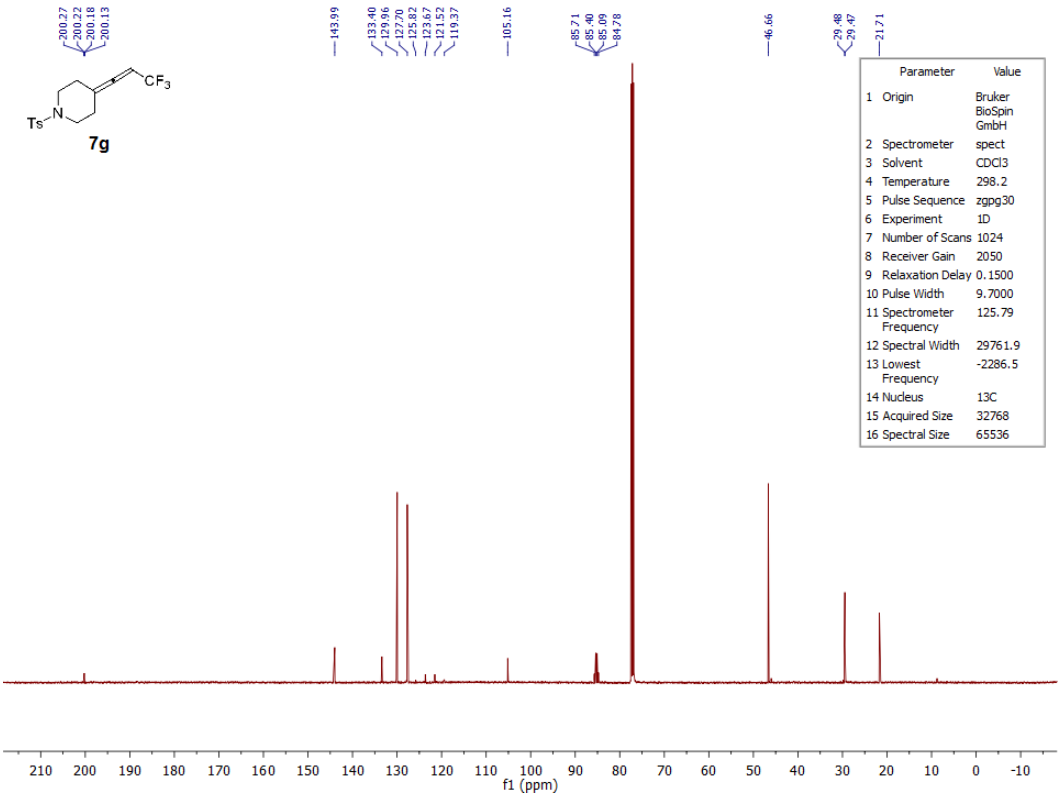
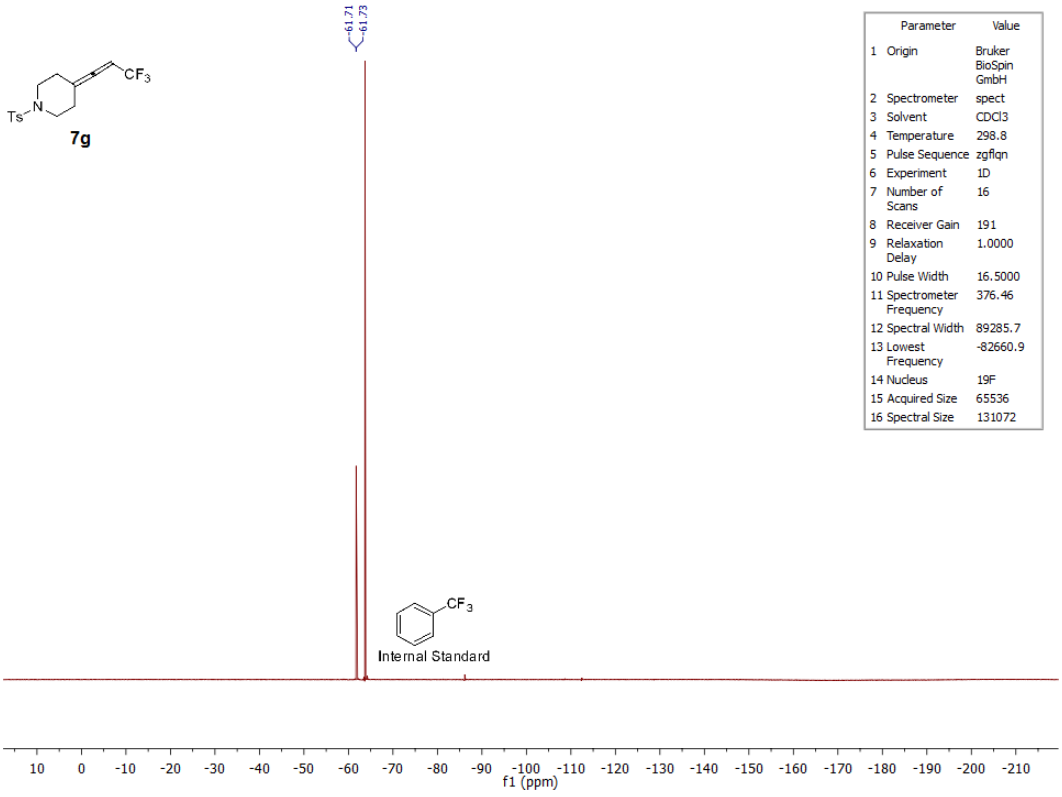
205.41
205.38
192.02
136.87
132.83
132.82
132.81
131.64
129.53
129.20
128.42
126.59
124.41
122.23
120.05
100.95
100.68
100.40
100.12
95.85
13.44
O
H
CF3
Me
7f
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2304.1
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

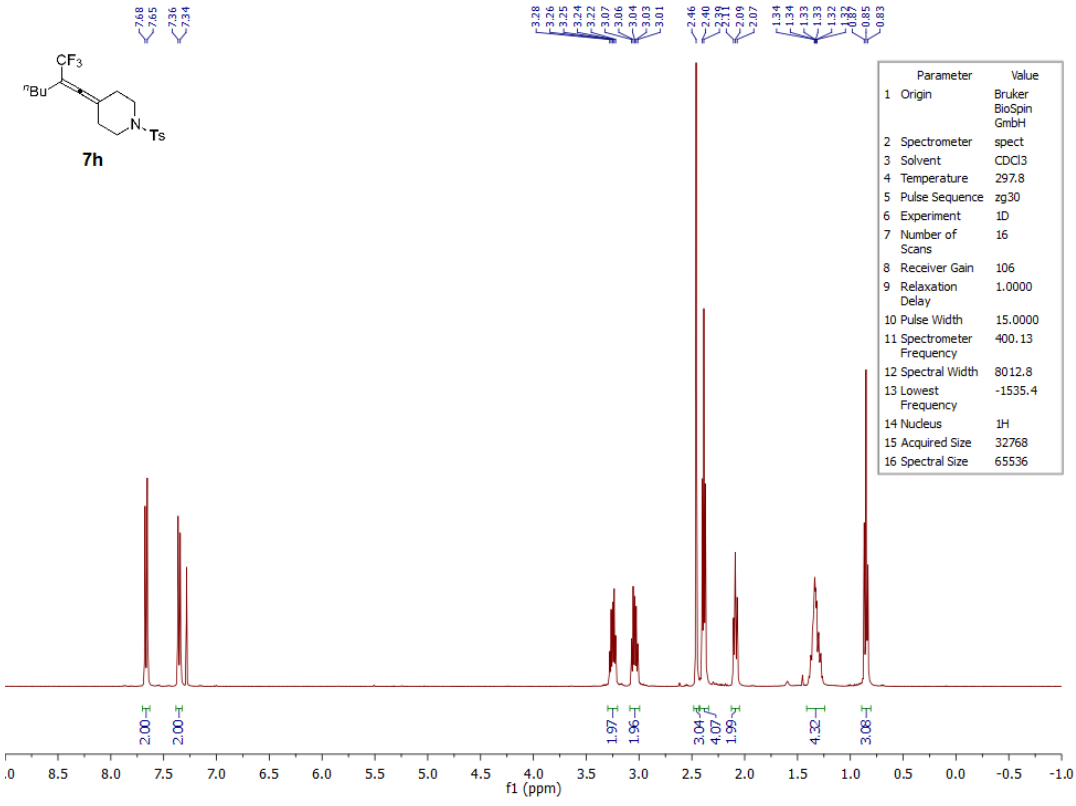

-61.53
-61.53
-71.69
-71.72
O
H
CF3
Me
7f
CF3
Internal Standard
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.1
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82659.4
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
1.00
0.04
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7g
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 15.0000
11 Spectrometer Frequency 400.13
12 Spectral Width 8012.8
13 Lowest Frequency -1541.0
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)

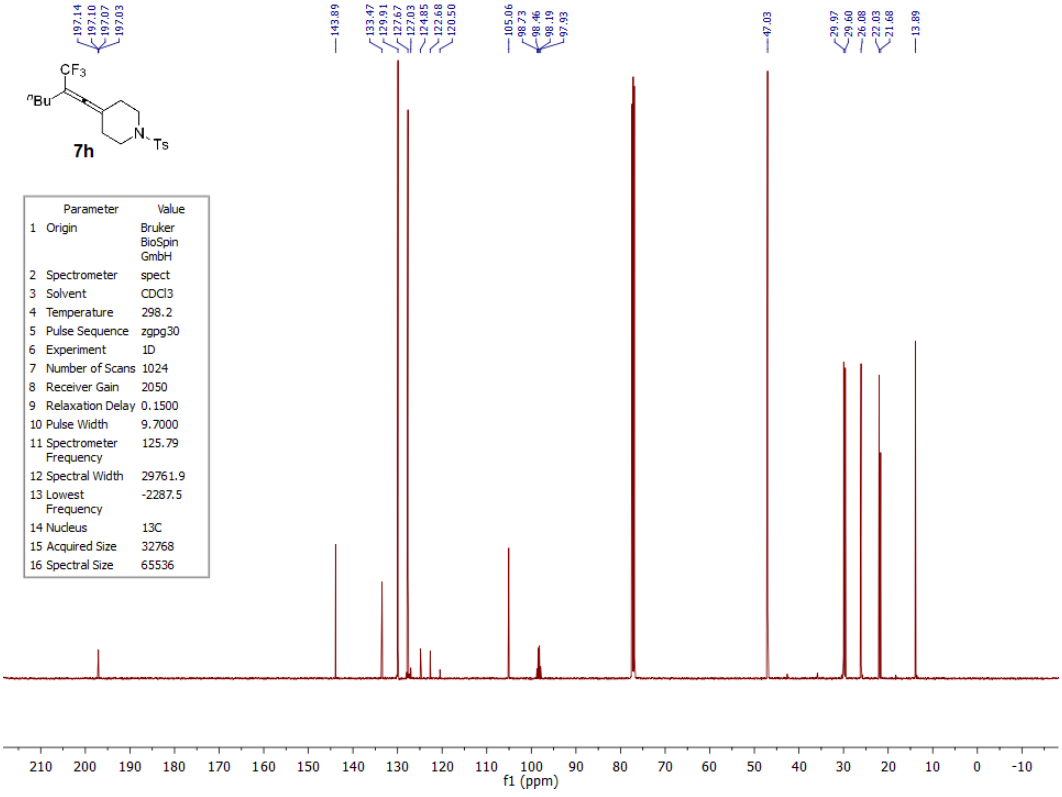

7g
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Spectrometer Frequency 125.79
12 Spectral Width 29761.9
13 Lowest Frequency -2286.5
14 Nucleus 13C
15 Acquired Size 32768
16 Spectral Size 65536
f1 (ppm)



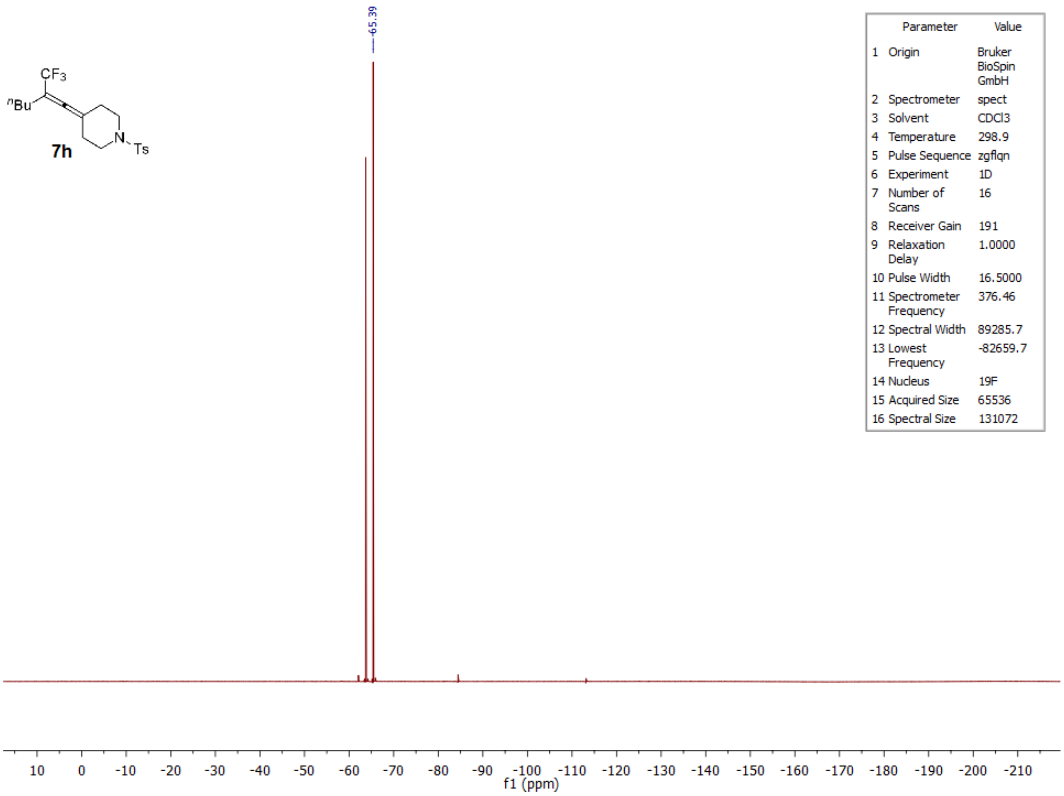
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.8
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82660.9
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072



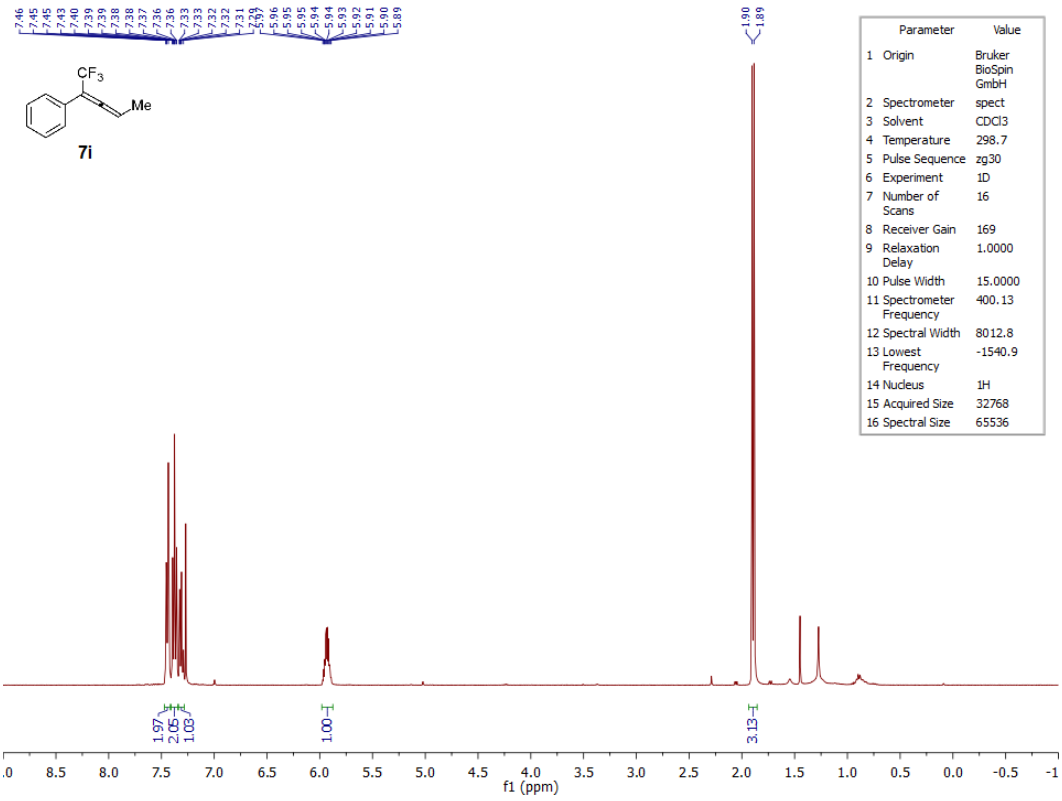
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	297.8
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	106
9	Relaxation Delay	1.0000
10	Pulse Width	15.0000
11	Spectrometer Frequency	400.13
12	Spectral Width	8012.8
13	Lowest Frequency	-1535.4
14	Nucleus	1H
15	Acquired Size	32768
16	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	1024
8	Receiver Gain	2050
9	Relaxation Delay	0.1500
10	Pulse Width	9.7000
11	Spectrometer Frequency	125.79
12	Spectral Width	29761.9
13	Lowest Frequency	-2287.5
14	Nucleus	13C
15	Acquired Size	32768
16	Spectral Size	65536



	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	191
9	Relaxation Delay	1.0000
10	Pulse Width	16.5000
11	Spectrometer Frequency	376.46
12	Spectral Width	89285.7
13	Lowest Frequency	-82659.7
14	Nucleus	19F
15	Acquired Size	65536
16	Spectral Size	131072


7.46
7.45
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7.38
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7.37
7.36
7.36
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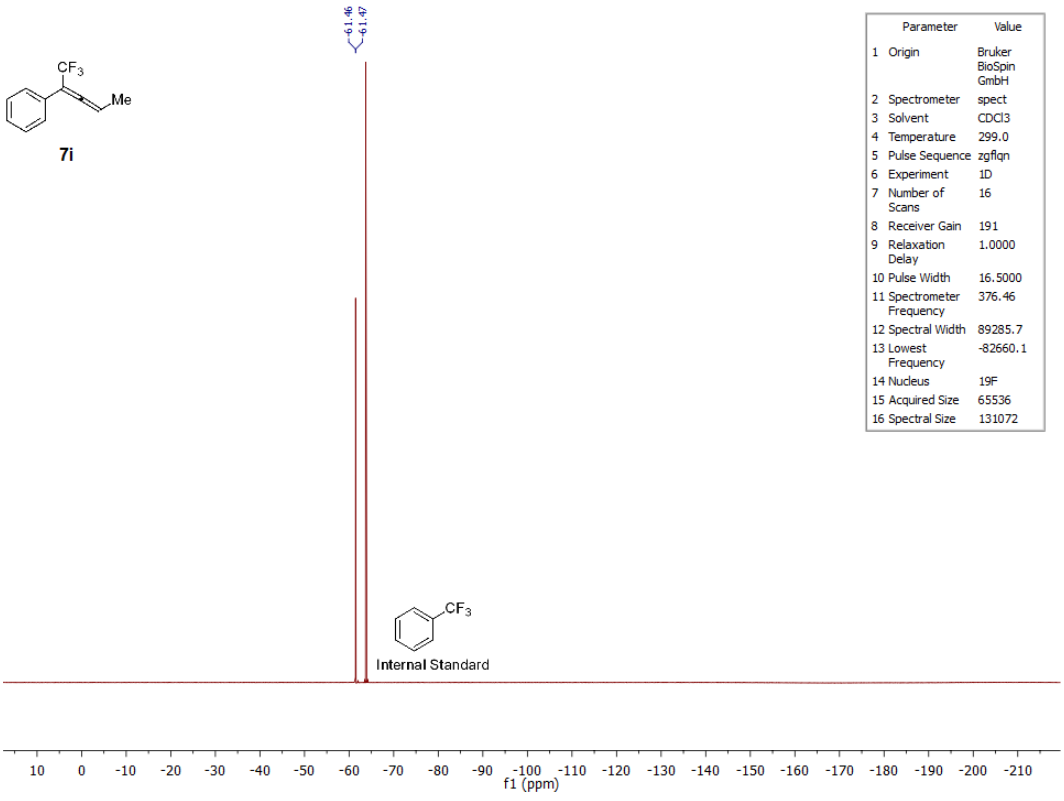
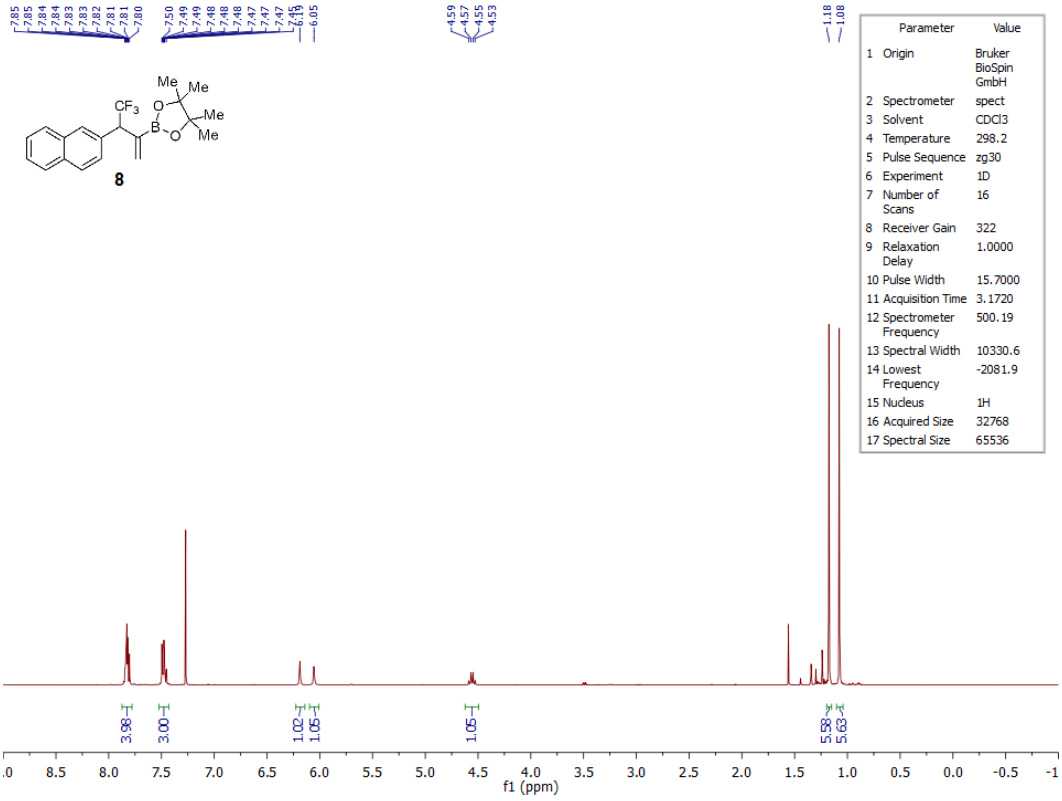
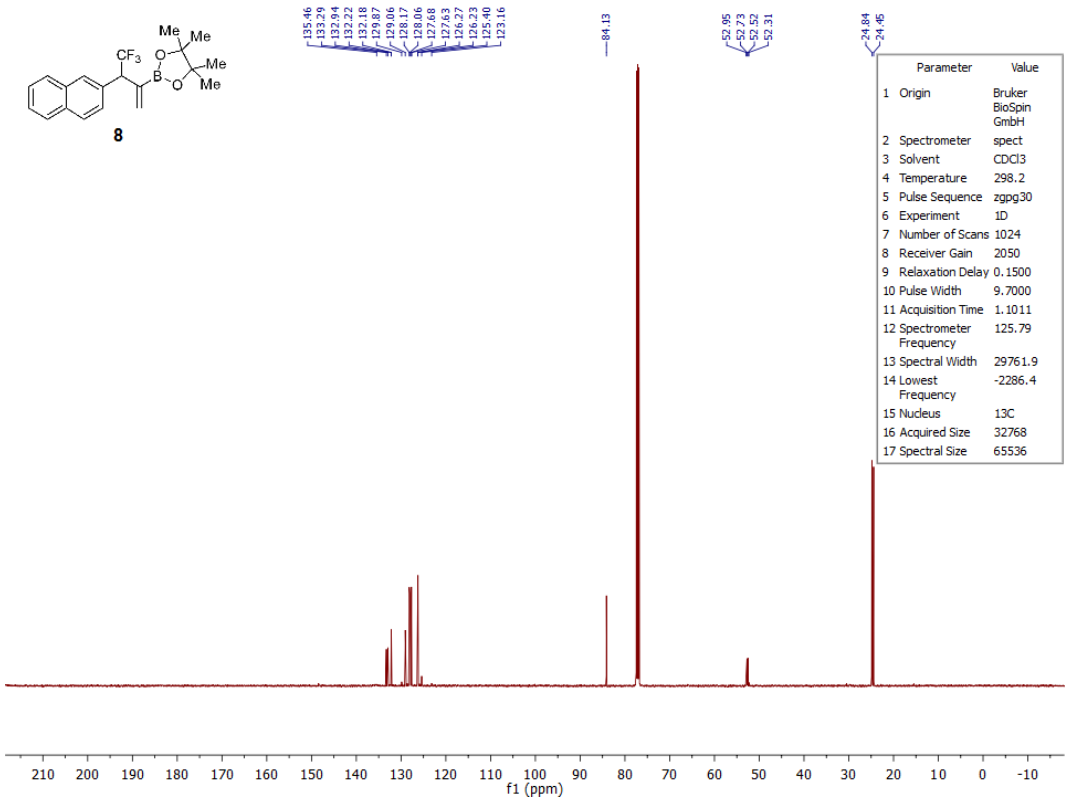
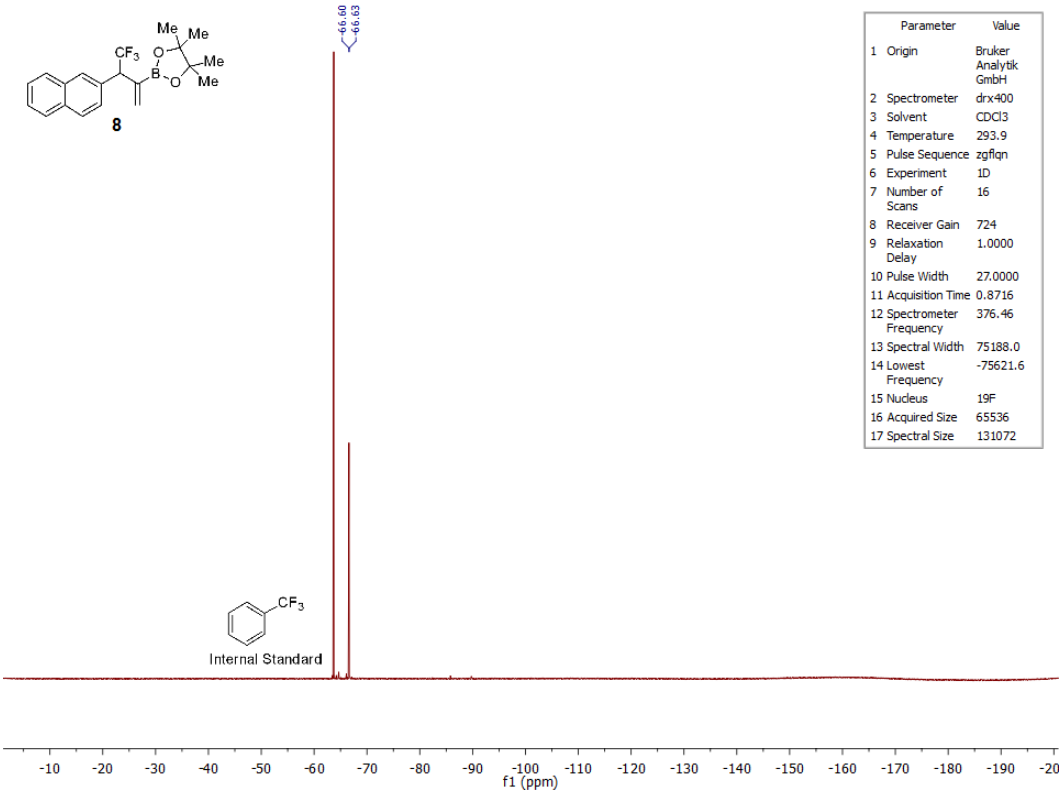
7.33
7.32
7.32
7.31
5.96
5.95
5.95
5.94
5.94
5.93
5.92
5.91
5.90
5.89
1.90
1.89
CF3
Me
7i
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 169
9 Relaxation Delay 1.0000
10 Pulse Width 15.0000
11 Spectrometer Frequency 400.13
12 Spectral Width 8012.8
13 Lowest Frequency -1540.9
14 Nucleus 1H
15 Acquired Size 32768
16 Spectral Size 65536
1.97
2.05
1.03
1.00
3.13
f1 (ppm)

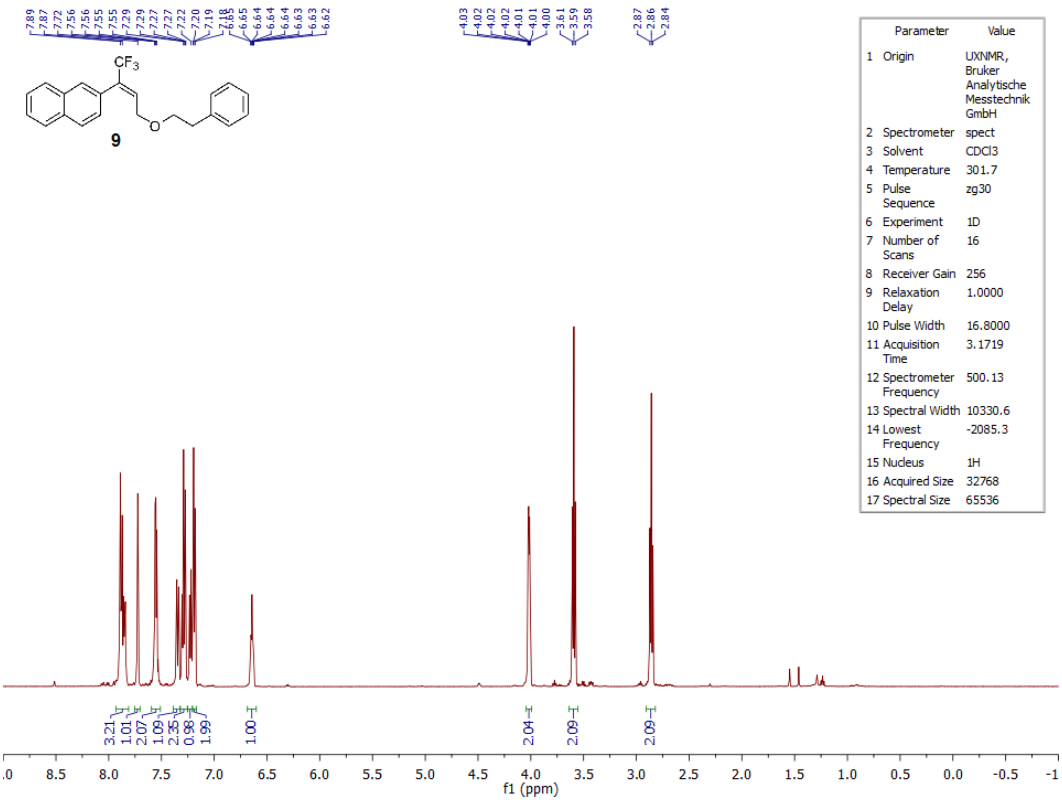

-61.46
-61.47
CF3
Me
7i
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.0
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82660.1
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
CF3
Internal Standard
f1 (ppm)


8
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 322
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Acquisition Time 3.1720
12 Spectrometer Frequency 500.19
13 Spectral Width 10330.6
14 Lowest Frequency -2081.9
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

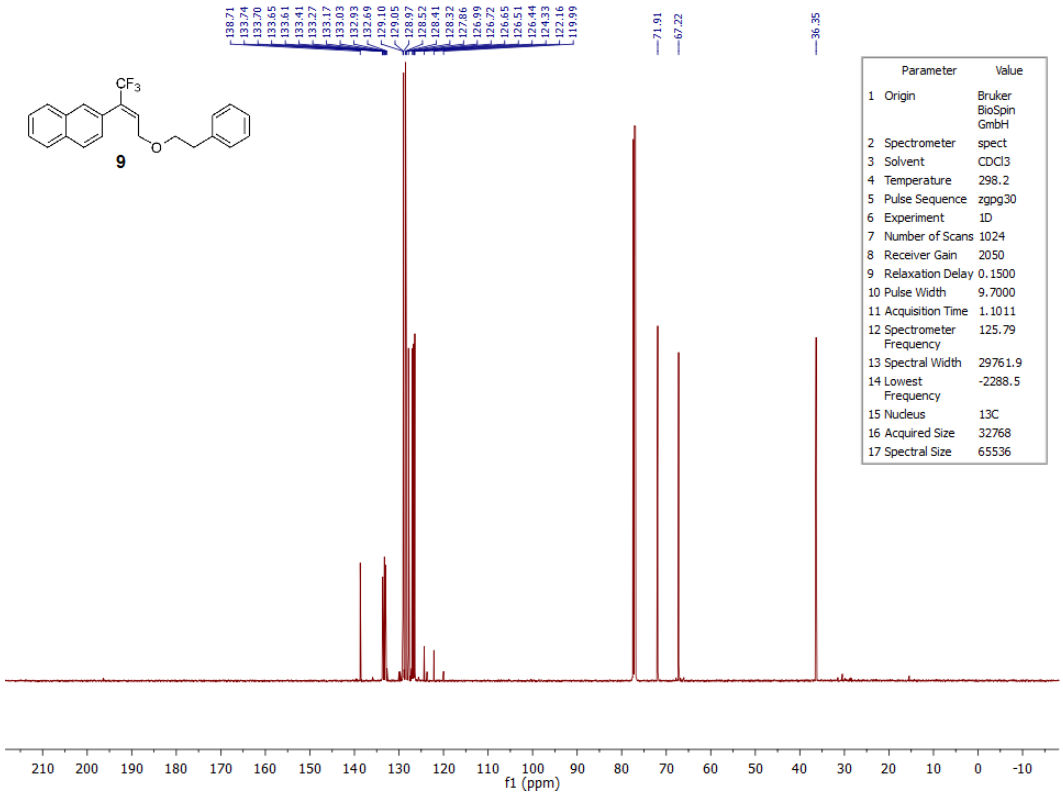

8
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2286.4
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)

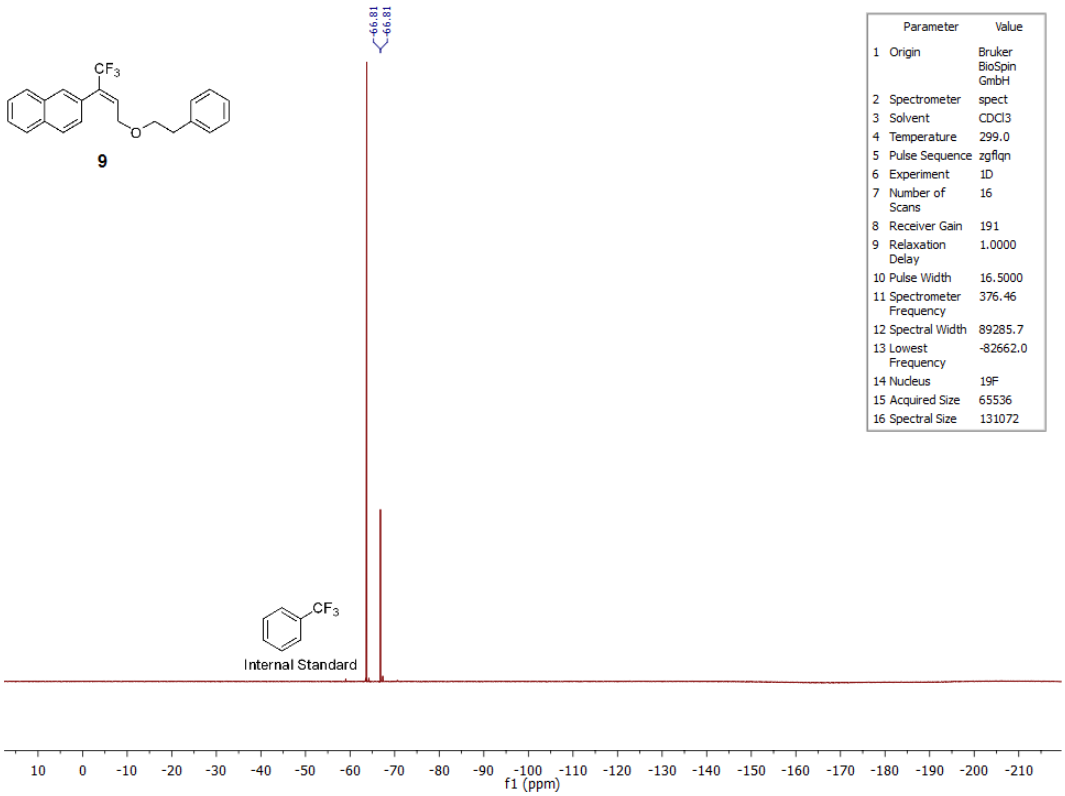


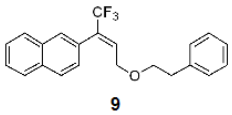
	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	724
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75621.6
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072



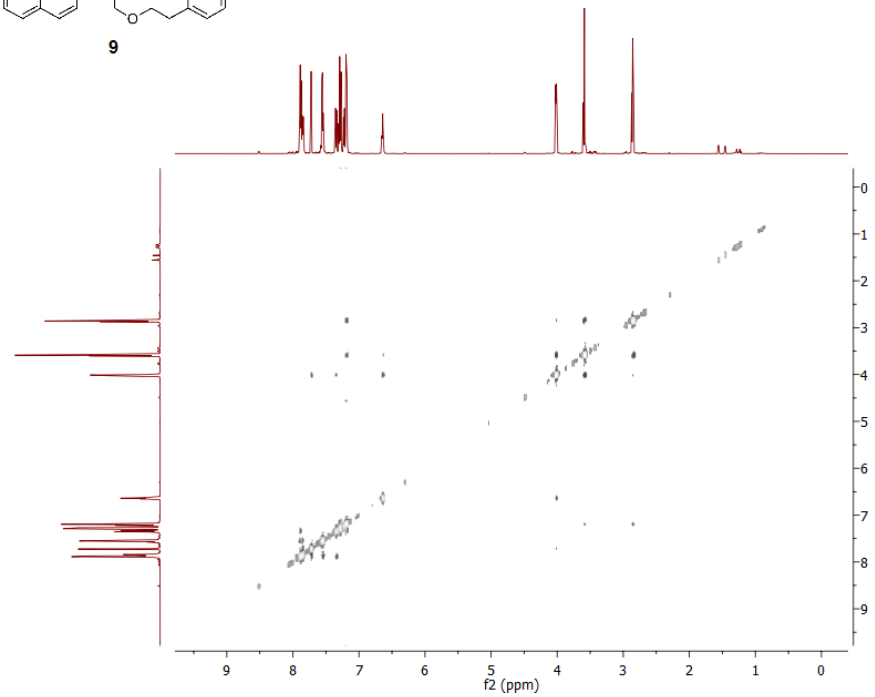
	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	301.7
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	256
9	Relaxation Delay	1.0000
10	Pulse Width	16.8000
11	Acquisition Time	3.1719
12	Spectrometer Frequency	500.13
13	Spectral Width	10330.6
14	Lowest Frequency	-2085.3
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


138.71
133.74
133.70
133.65
133.61
133.41
133.27
133.17
133.03
132.93
132.69
129.10
129.05
128.97
128.52
128.41
128.32
127.86
126.99
126.72
126.65
126.51
126.44
124.33
122.16
119.99
71.91
67.22
36.35
CF3
O
9
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2288.5
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

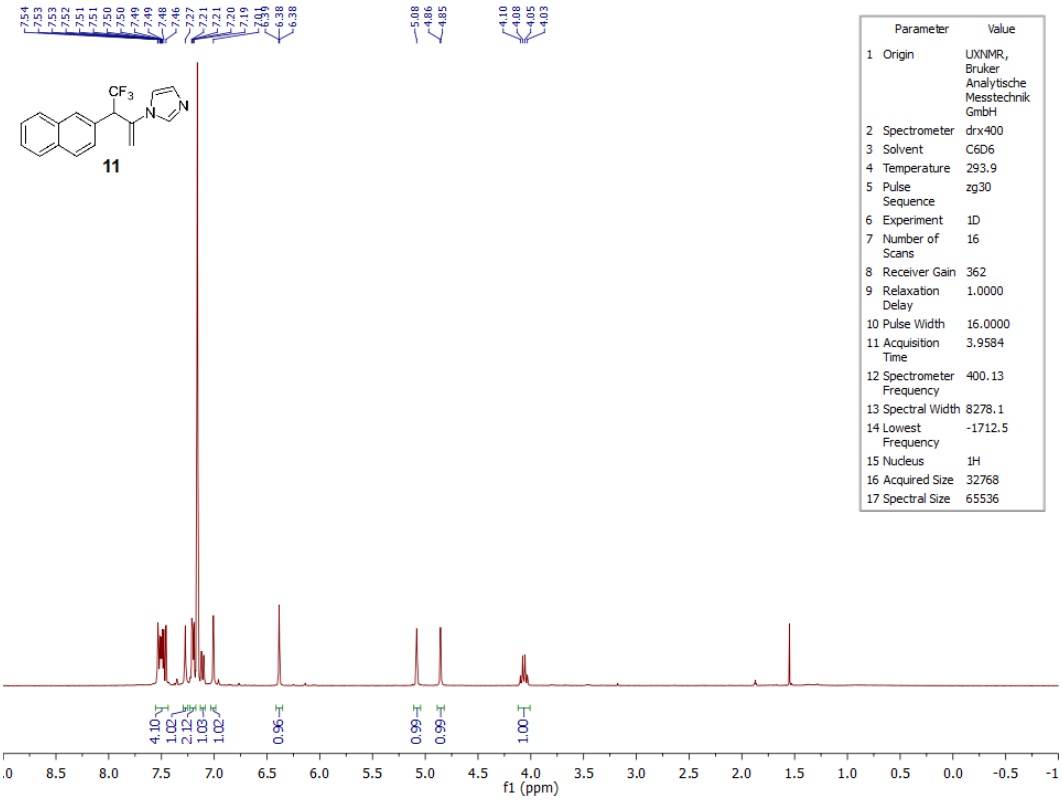

66.81
66.81
CF3
O
9
CF3
Internal Standard
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 299.0
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 191
9 Relaxation Delay 1.0000
10 Pulse Width 16.5000
11 Spectrometer Frequency 376.46
12 Spectral Width 89285.7
13 Lowest Frequency -82662.0
14 Nucleus 19F
15 Acquired Size 65536
16 Spectral Size 131072
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



9

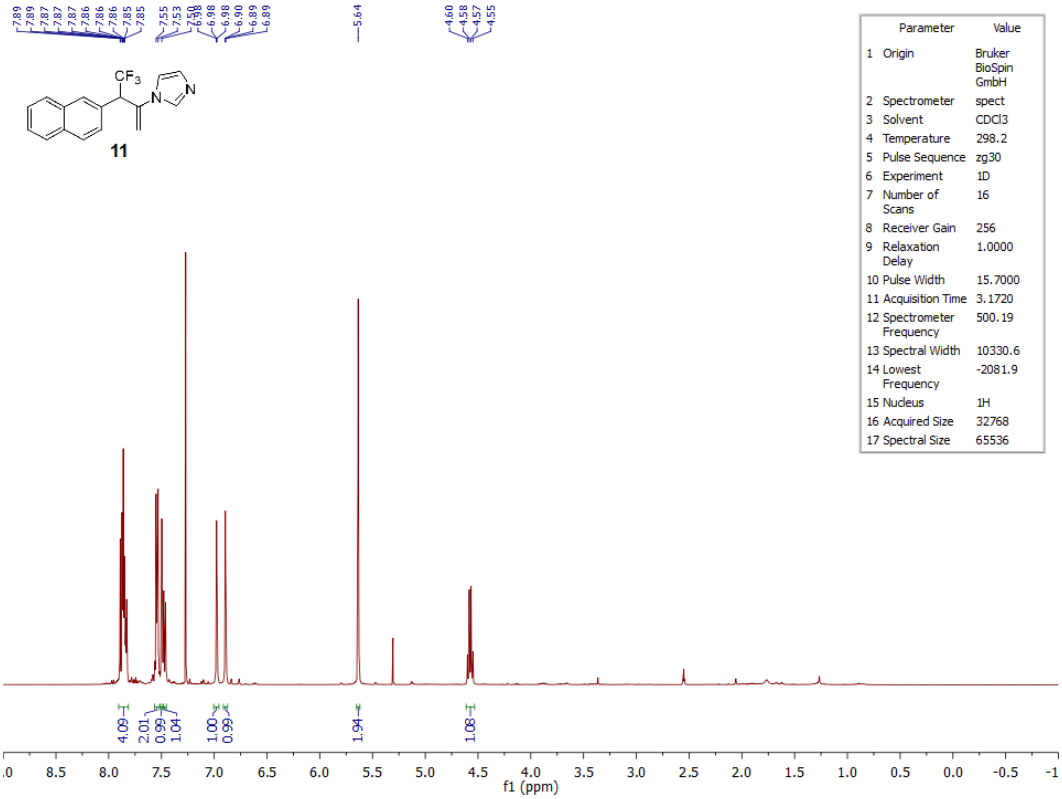


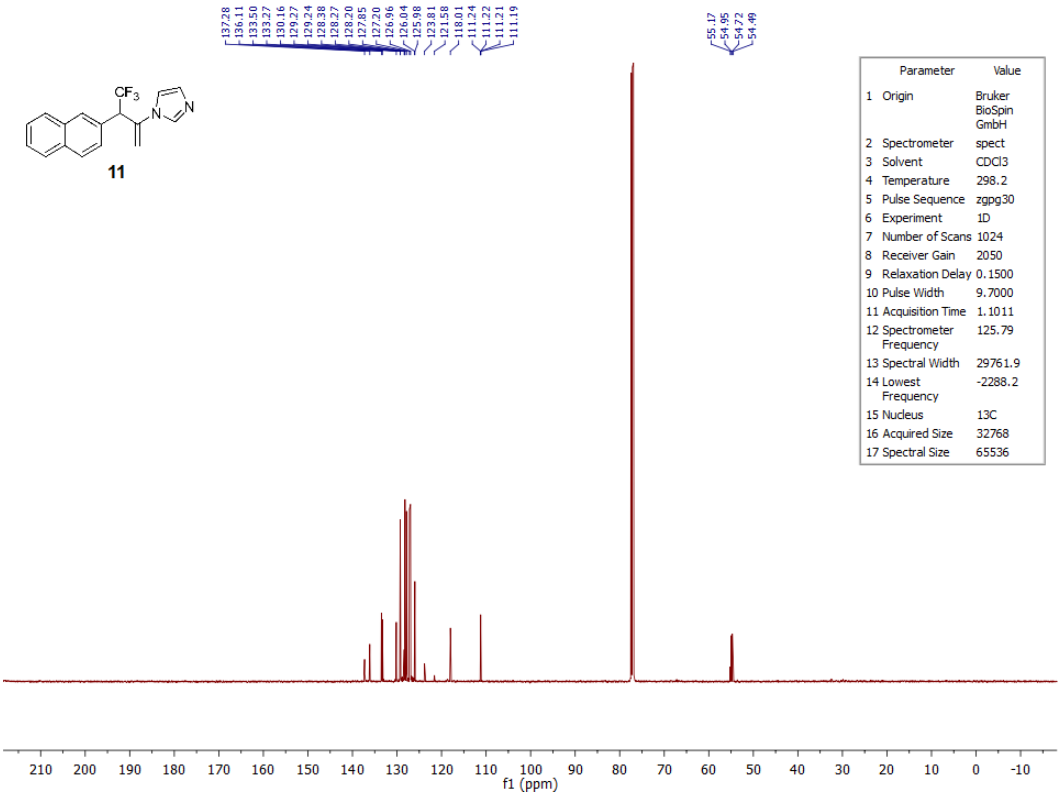
	Parameter	Value (f2, f1)
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	CDCl3
4	Temperature	298.2
5	Pulse Sequence	noesygpph
6	Experiment	NOESY
7	Number of Scans	2
8	Receiver Gain	362
9	Relaxation Delay	1.5000
10	Pulse Width	15.7000
11	Acquisition Time	0.2008
12	Spectrometer Frequency	(500.19, 500.19)
13	Spectral Width	(5102.0, 5102.8)
14	Lowest Frequency	(-206.6, -206.5)
15	Nucleus	(1H, 1H)
16	Acquired Size	(1024, 256)
17	Spectral Size	(1024, 1024)

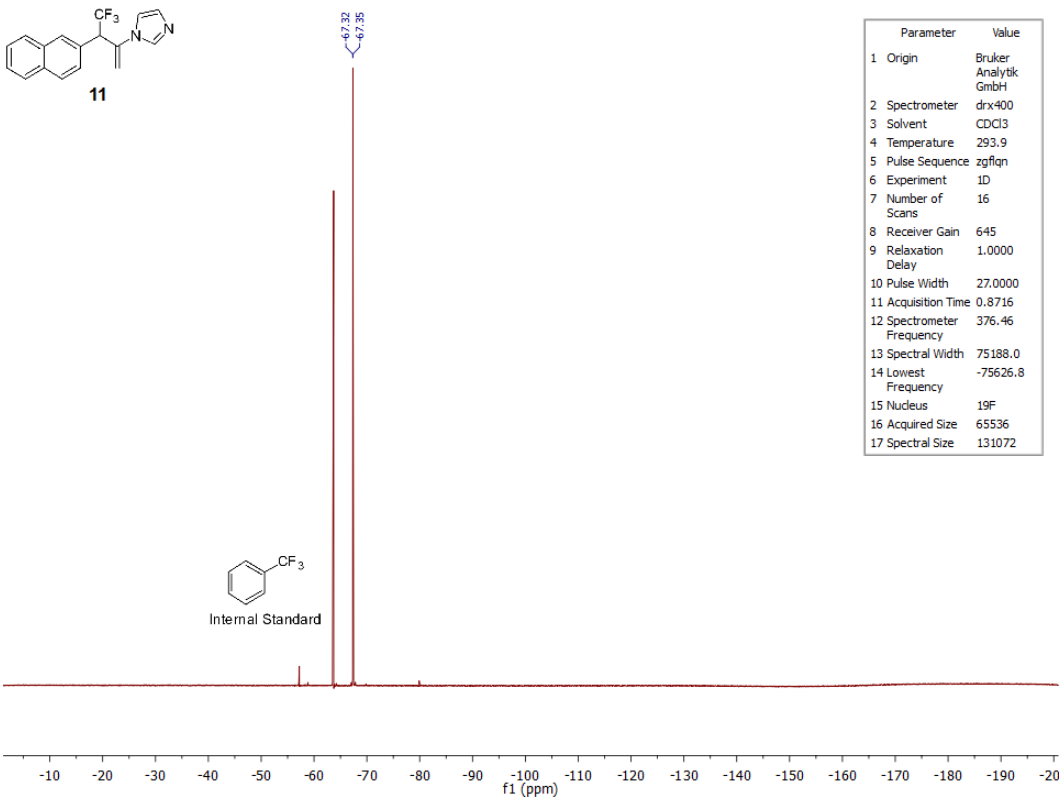


11

	Parameter	Value
1	Origin	UXNMR, Bruker Analytische Messtechnik GmbH
2	Spectrometer	drx400
3	Solvent	C6D6
4	Temperature	293.9
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	362
9	Relaxation Delay	1.0000
10	Pulse Width	16.0000
11	Acquisition Time	3.9584
12	Spectrometer Frequency	400.13
13	Spectral Width	8278.1
14	Lowest Frequency	-1712.5
15	Nucleus	1H
16	Acquired Size	32768
17	Spectral Size	65536


11
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 256
9 Relaxation Delay 1.0000
10 Pulse Width 15.7000
11 Acquisition Time 3.1720
12 Spectrometer Frequency 500.19
13 Spectral Width 10330.6
14 Lowest Frequency -2081.9
15 Nucleus 1H
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)


11
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 298.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 1024
8 Receiver Gain 2050
9 Relaxation Delay 0.1500
10 Pulse Width 9.7000
11 Acquisition Time 1.1011
12 Spectrometer Frequency 125.79
13 Spectral Width 29761.9
14 Lowest Frequency -2288.2
15 Nucleus 13C
16 Acquired Size 32768
17 Spectral Size 65536
f1 (ppm)



	Parameter	Value
1	Origin	Bruker Analytik GmbH
2	Spectrometer	drx400
3	Solvent	CDCl3
4	Temperature	293.9
5	Pulse Sequence	zgflqn
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	645
9	Relaxation Delay	1.0000
10	Pulse Width	27.0000
11	Acquisition Time	0.8716
12	Spectrometer Frequency	376.46
13	Spectral Width	75188.0
14	Lowest Frequency	-75626.8
15	Nucleus	19F
16	Acquired Size	65536
17	Spectral Size	131072