

Preparation of Fluoroalkenes via the Shapiro Reaction: Direct Access to Fluorinated Peptidomimetics

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General Information

Unless otherwise noted, reactions were performed under nitrogen atmosphere using oven-dried glassware. The Shapiro fluorination reactions were performed in the round-bottom flasks, which were sealed with three-way valves for transferring nitrogen and reagents, and all other reactions were performed in round-bottom flasks that were sealed with rubber septa. Stainless steel syringes were used to transfer air- and moisture-sensitive liquid reagents. Unless otherwise noted, reagents purchased from commercial sources were used without further purification. THF was dried by passage through activated alumina columns. All alkyllithium bases were titrated prior to each reaction using diphenylacetic acid as an indicator.¹ Reactions were monitored by thin-layer chromatography (TLC) on UNIPLATE Silica Gel HLF plates, visualizing with fluorescence quenching, KMnO_4 solution, ninhydrins, or ceric ammonium molybdate solution (CAM). ^{19}F NMR yields reported in the manuscript represent an average of at least two independent runs. Isolated yields reported in the manuscript represent either the result of one purification, or of an average of two independent purifications. Yields reported in the supporting information refer to a single experiment. Proton nuclear magnetic resonance (^1H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker 400 AVANCE spectrometer (400 and 100 MHz, respectively) or Bruker 500 AVANCE spectrometer (500 and 125 MHz, respectively). Chemical shifts (δ) for protons are reported in parts per million downfield from tetramethylsilane and are referenced to proton resonance of residual CHCl_3 in the NMR solvent ($\text{CHCl}_3 = 7.27$ ppm). Chemical shifts (δ) for carbon are reported in parts per million downfield from tetramethylsilane, and are referenced to the carbon resonances of the solvent residual peak ($\text{CDCl}_3 = 77.23$ ppm). Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded on a Bruker 400 AVANCE spectrometer (376 MHz); chemical shifts (δ) are reported in parts per millions, and are referenced to α,α,α -trifluorotoluene ($\delta = -63.72$ ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sept = septet, m = multiplet), coupling constant in Hertz (Hz), integration. High-resolution mass data were recorded on a high-resolution mass spectrometer in the ESI mode. Infrared spectra were measured at a Shimadzu FTIR-8400S Fourier Transform Infrared Spectrometer. Melting points were uncorrected and measured on Thomas Hoover Capillary Melting Point apparatus.

Preparation of 2, 4, 6-triisopropylbenzenesulfonyl hydrazide (TPSH)²

Using a syringe pump, hydrazine (2.3 mL, 2.2 mmol) was added drop wise over a period of 15 min to a pre-cooled solution of 2, 4, 6-triisopropylbenzenesulfonyl chloride (0.010 kg, 0.033 mol) in THF (0.030 L) at $-10\text{ }^{\circ}\text{C}$ (ice-salt freezing mixture). The reaction solution was warmed to $0\text{ }^{\circ}\text{C}$, and stirred for additional 3 h at this temperature. Water (0.015 L) was added to dissolve the precipitated solids. The products were then transferred to a separation funnel. The organic layer was separated, and the aqueous layer was extracted with ether (2 x 0.030 L). The organic layers were washed with ice-cold brine (2 x 0.030 L), dried over anhydrous Na_2SO_4 , filtered, and then concentrated under reduced pressure below room temperature ($25\text{ }^{\circ}\text{C}$). Pentane was added to the solid obtained, and the mixture was sonicated at rt for 3 min until fine solids formed. The solid was collected by filtration, washed with cold pentane, and dried *in vacuo* to give **TPSH** as a colorless solid (9.6 g, 97%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.21 (s, 2 H), 5.52 (s, 1 H), 4.16 (sept, $J = 6.7\text{ Hz}$, 2 H), 3.65 (br, 2 H), 2.92 (sept, $J = 6.9\text{ Hz}$, 1 H), 1.28 (d, $J = 6.7\text{ Hz}$, 12 H), 1.27 (d, $J = 6.9\text{ Hz}$, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.0, 152.0, 128.9, 124.2, 34.4, 30.0, 25.1, 23.7 ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{15}\text{H}_{27}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 299.1793, found 299.1794.

General procedure for preparation of trisylhydrazones via ketone condensation

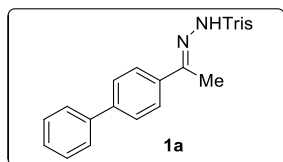
A ketone (1.0 equiv) was added to a suspension of 2, 4, 6-triisopropylbenzenesulfonyl hydrazide **TPSH** (> 1.0 equiv) in THF or MeOH (generally $c = 1.0\text{ M}$) at room temperature, and stirred for several hours (generally 1–5 h) under N_2 . In some cases, the addition of several drops of concentrated HCl or the heating facilitated the reaction.

Workup A: The reaction was quenched with a solution of aqueous NaHCO_3 , and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over anhydrous Na_2SO_4 , and concentrated to provide the crude product. The residue was triturated with MeOH (or a minimal amount of CH_2Cl_2 and a large amount of pentane) and sonicated until white solid precipitated. The solid was filtered, washed with pentane, and dried *in vacuo*.

Workup B: The extraction procedure was the same as workup A, but the crude products were purified by column chromatography using gradient elution.

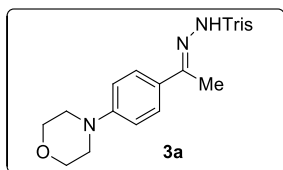
SI-5

Workup C: The solvent was removed under reduced pressure, and the residue dissolved in MeOH or pentane/CH₂Cl₂, and sonicated until solids precipitated. The solid was filtered, washed with pentane and dried *in vacuo*. (In some cases, compounds were purified by column chromatography using gradient elution).



(E)-N'-(1-([1,1'-biphenyl]-4-yl)ethylidene)-2,4,6-triisopropylbenzenesulfonohydrazide (1a)

The general procedure was followed using TPSH (3.35 g, 11.2 mmol), 4-phenylacetophenone (2.00 g, 10.2 mmol), and 4 drops of HCl with THF (0.010 L) as solvent for 1.5 h at rt. Workup A (precipitation in MeOH) afforded the title compound **1a** as a colorless solid (4.46 g, 92%). ¹H NMR (CDCl₃, 400 MHz) δ 7.72–7.74 (m, 3 H), 7.54–7.60 (m, 4 H), 7.43–7.46 (m, 2 H), 7.34–7.38 (m, 1 H), 7.19 (s, 2 H), 4.35 (sept, *J* = 6.7 Hz, 2 H), 2.91 (sept, *J* = 6.9 Hz, 1 H), 2.22 (s, 3 H), 1.32 (d, *J* = 6.7 Hz, 12 H), 1.26 (d, *J* = 6.9 Hz, 6 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 153.6, 151.6, 150.6, 142.4, 140.5, 136.4, 131.6, 129.0, 127.8, 127.2, 127.0, 126.9, 124.0, 34.4, 30.2, 25.1, 23.7, 13.3 ppm. IR (film) 3225, 2959, 1599, 1383, 1362, 1331, 1313, 1165, 1153, 1059, 1038, 910, 841, 766, 704, 660 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₂₉H₃₆N₂O₂SNa [M+Na]⁺ 499.2395, found 499.2387. m.p. 164–165 °C.

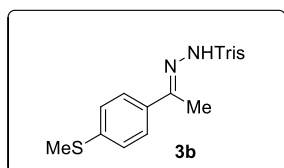


(E)-2,4,6-triisopropyl-N'-(1-(4-morpholinophenyl)ethylidene)benzenesulfonohydrazide (3a)

The general procedure was followed using TPSH (1.74 g, 5.84 mmol), 4-morpholinoacetophenone (1.00 g, 4.87 mmol) and 4 drops of HCl with MeOH (4.50 mL) as solvent for 6.0 h at rt. Workup B followed by chromatographic purification (CH₂Cl₂/MeOH) provided the title compound **3a** as a colorless solid (1.41 g, 60%). ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (d, *J* = 9.0 Hz, 2 H), 7.42 (s, 1 H), 7.16 (s, 2 H), 6.81 (d, *J* = 9.0 Hz, 2 H), 4.32 (sept, *J* = 6.8 Hz, 2 H), 3.85 (t, *J* = 4.8 Hz, 4 H), 3.19 (t, *J* = 4.8 Hz, 4 H), 2.89 (sept, *J* = 6.9 Hz, 1 H), 2.13 (s,

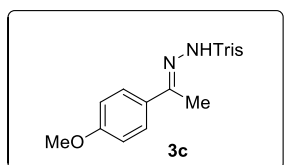
SI-6

3 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.4, 152.2, 151.5, 150.9, 131.8, 128.7, 127.6, 123.9, 114.6, 66.9, 48.7, 34.4, 30.2, 25.0, 23.7, 13.0 ppm. IR (film) 3180, 2959, 2864, 1603, 1518, 1425, 1377, 1331, 1306, 1232, 1167, 928, 739, 704 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{39}\text{N}_3\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$ 508.2610, found 508.2596. m.p. 186 °C (dec).



(E)-2,4,6-triisopropyl-N'-(1-(4-(methylthio)phenyl)ethylidene)benzenesulfonohydrazide (3b)

The general procedure was followed using TPSH (1.97 g, 6.62 mmol), 4-(methylthio)acetophenone (1.00 g, 6.02 mmol) with MeOH (7.00 mL) as solvent for 6.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **3b** as a light yellow solid (2.39 g, 89%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.56 (d, $J = 8.0$ Hz, 2 H), 7.49 (s, 1 H), 7.17 (s, 2 H), 7.16 (d, $J = 8.0$ Hz, 2 H), 4.30 (sept, $J = 6.8$ Hz, 2 H), 2.90 (sept, $J = 6.9$ Hz, 1 H), 2.48 (s, 3 H), 2.14 (s, 3 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.5, 151.6, 150.3, 140.7, 134.2, 131.6, 126.8, 125.8, 124.0, 34.4, 30.2, 25.0, 23.7, 15.6, 13.1 ppm. IR (film) 3227, 2959, 1599, 1383, 1310, 1165, 1153, 1059, 910, 820, 770, 675 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_2\text{S}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 469.1959, found 469.1955. m.p. 143–144 °C.

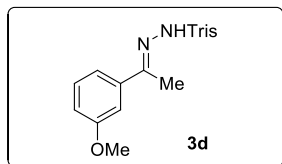


(E)-2,4,6-triisopropyl-N'-(1-(4-methoxyphenyl)ethylidene)benzenesulfonohydrazide (3c)³

The general procedure was followed using TPSH (2.20 g, 7.33 mmol), *p*-methoxyacetophenone (1.00 g, 6.66 mmol), 2 drops of HCl with THF (0.010 L) as solvent for 5.0 h at rt. Workup A (precipitation in pentane/ CH_2Cl_2) provided the title compound **3c** as a colorless solid (2.59 g, 90%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.59–7.61 (m, 3 H), 7.17 (s, 2 H), 6.83 (d, $J = 9.0$ Hz, 2 H), 4.32 (sept, $J = 6.8$ Hz, 2 H), 3.81 (s, 3 H), 2.90 (sept, $J = 6.9$ Hz, 1 H),

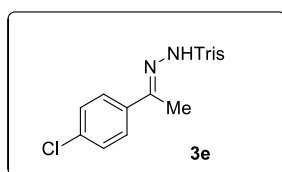
SI-7

2.15 (s, 3 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 160.9, 153.5, 151.6, 150.9, 131.7, 130.2, 127.9, 124.0, 113.7, 55.5, 34.4, 30.2, 25.0, 23.7, 13.2 ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$ 453.2188, found 453.2187.



(E)-2,4,6-triisopropyl-N'-(1-(3-methoxyphenyl)ethylidene)benzenesulfonylhydrazide (3d)

The general procedure was followed using TPSH (2.09 g, 6.99 mmol), *m*-methoxyacetophenone (1.00 g, 6.66 mmol) with MeOH (7.00 mL) as solvent for 3.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **3d** as a colorless solid (2.44 g, 85%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.61 (s, 1 H), 7.17–7.23 (m, 5 H), 6.88 (dt, $J = 2.0, 7.3$ Hz, 1 H), 4.31 (sept, $J = 6.8$ Hz, 2 H), 3.77 (s, 3 H), 2.89 (sept, $J = 6.9$ Hz, 1 H), 2.16 (s, 3 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 159.7, 153.5, 151.5, 150.5, 139.1, 131.5, 129.3, 124.0, 119.1, 115.4, 111.8, 55.4, 34.4, 30.1, 23.7, 13.5 ppm. IR (film) 3246, 2961, 2928, 1597, 1585, 1462, 1467, 1364, 1329, 1232, 1165, 1155, 1059, 856, 785, 721, 663 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{34}\text{N}_2\text{O}_3\text{SNa}$ $[\text{M}+\text{Na}]^+$ 453.2188, found 453.2194. m.p. 147–148 $^\circ\text{C}$.

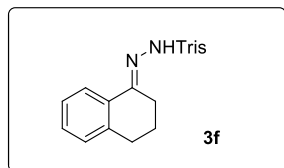


(E)-N'-(1-(4-chlorophenyl)ethylidene)-2,4,6-triisopropylbenzenesulfonylhydrazide (3e)

The general procedure was followed using TPSH (2.12 g, 7.12 mmol), 4'-chloroacetophenone (1.00 g, 6.47 mmol) with THF (6.00 mL) as solvent for 3.0 h at rt. Workup A (precipitation in pentane/ CH_2Cl_2) provided the title compound **3e** as a colorless solid (0.900 g, 32%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (br, 1 H), 7.57 (dd, $J = 1.9, 6.8$ Hz, 2 H), 7.28 (dd, $J = 1.9, 6.8$ Hz, 2 H), 7.18 (s, 2 H), 4.30 (sept, $J = 6.8$ Hz, 2 H), 2.90 (sept, $J = 6.9$ Hz, 1 H), 2.15 (s, 3 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.7,

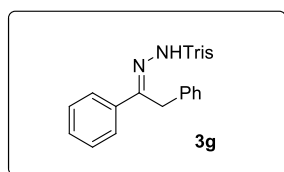
SI-8

151.6, 149.5, 136.1, 135.6, 131.5, 128.6, 127.7, 124.0, 34.4, 30.2, 25.0, 23.7, 13.3 ppm. IR (film) 3244, 2961, 2926, 1599, 1462, 1383, 1362, 1331, 1306, 1265, 1165, 1099, 908, 831, 739, 679 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{31}\text{ClN}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 457.1692, found 457.1689. m.p. 150–151 $^{\circ}\text{C}$.



(E)-N'-(3,4-dihydronaphthalen-1(2H)-ylidene)-2,4,6-triisopropylbenzenesulfonylhydrazide (3f)⁴

The general procedure was followed using TPSH (2.24 g, 7.52 mmol), alpha-tetralone (1.00 g, 6.84 mmol) with MeOH (7.00 mL) as solvent for 5.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **3f** as a colorless solid (1.40 g, 48%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.94 (dd, $J = 1.0, 7.9$ Hz, 1 H), 7.50 (s, 1 H), 7.23 (ddd, $J = 1.4, 7.4, 7.4$ Hz, 1 H), 7.17 (s, 2 H), 7.09–7.16 (m, 2 H), 4.32 (sept, $J = 6.8$ Hz, 2 H), 2.90 (sept, $J = 6.9$ Hz, 1 H), 2.74 (t, $J = 6.0$ Hz, 2 H), 2.46 (t, $J = 6.6$ Hz, 2 H), 1.90–1.97 (m, 2 H), 1.32 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.4, 151.6, 150.8, 139.7, 132.0, 131.8, 129.4, 128.5, 126.3, 125.3, 123.9, 34.3, 30.2, 29.5, 25.5, 25.0, 23.7, 21.6 ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 449.2239, found 449.2237.



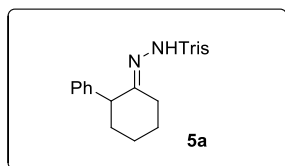
(E)-N'-(1,2-diphenylethylidene)-2,4,6-triisopropylbenzenesulfonylhydrazide (3g)⁵

The general procedure was followed using TPSH (1.67 g, 5.60 mmol), deoxybenzoin (1.00 g, 5.09 mmol), 4 drops of HCl with THF (0.010 L) as solvent for 1.5 h at rt. Workup A (precipitation in pentane/ CH_2Cl_2) provided the title compound **3g** as a colorless solid (1.14 g, 48%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.72 (d, $J = 8.0$ Hz, 2 H), 7.59 (s, 1 H), 7.27–7.35 (m, 6 H), 7.15–7.18 (m, 4 H), 4.13 (sept, $J = 6.8$ Hz, 2 H), 4.06 (s, 2 H), 2.90 (sept, $J = 7.0$ Hz, 1 H), 1.25 (d, $J = 7.0$ Hz, 6 H), 1.23 (d, $J = 6.8$ Hz, 12 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.6, 152.9,

SI-9

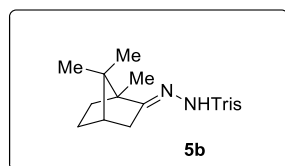
151.8, 137.3, 134.1, 131.6, 129.8, 129.7, 128.5, 128.1, 127.6, 126.8, 124.0, 34.4, 33.6, 30.4, 25.1, 23.7 ppm.

HRMS (ESI, m/z): calcd. for $C_{29}H_{36}N_2O_2SNa$ $[M+Na]^+$ 499.2395, found 499.2392.



(E)-2,4,6-triisopropyl-N'-(2-phenylcyclohexylidene)benzenesulfonohydrazide (5a)

The general procedure was followed using TPSH (1.72 g, 5.76 mmol), 2-phenylcyclohexanone (1.00 g, 5.74 mmol), 4 drops of HCl with MeOH (6.00 mL) as solvent for 3.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **5a** as a colorless solid (2.09 g, 80%). 1H NMR ($CDCl_3$, 400 MHz) δ 7.45 (s, 1 H), 7.18 (s, 2 H), 7.05–7.12 (m, 3 H), 6.87 (d, $J = 6.5$ Hz, 2 H), 4.18 (sept, $J = 6.7$ Hz, 2 H), 3.60 (t, $J = 5.0$ Hz, 1 H), 2.95 (sept, $J = 6.9$ Hz, 1 H), 2.24–2.35 (m, 2 H), 1.88–2.00 (m, 2 H), 1.60–1.78 (m, 4 H), 1.30 (dd, $J = 2.1, 6.9$ Hz, 6 H), 1.21 (d, $J = 6.7$ Hz, 6 H), 1.18 (d, $J = 6.8$ Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.2, 153.2, 151.4, 140.2, 131.7, 128.3, 127.6, 126.2, 123.8, 47.9, 34.4, 30.8, 29.9, 25.9, 24.9, 23.8, 22.5 ppm. IR (film) 3232, 2955, 2359, 1643, 1599, 1427, 1393, 1327, 1263, 1167, 1009, 926, 883, 729, 702, 669 cm^{-1} . HRMS (ESI, m/z): calcd. for $C_{27}H_{39}N_2O_2S$ $[M+H]^+$ 455.2732, found 455.2747. m.p. 130–131 $^{\circ}C$.

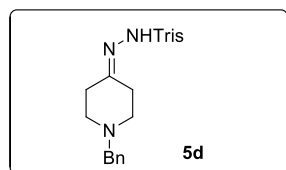


(E)-2,4,6-triisopropyl-N'-((1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)benzenesulfonohydrazide (5b)⁵

The general procedure was followed using TPSH (2.16 g, 7.23 mmol), camphor (1.00 g, 6.57 mmol), 2 drops of HCl with acetonitrile (0.010 L) as solvent for 6.0 h at rt. Workup C (precipitation in pentane/ CH_2Cl_2) provided the title compound **5b** as a colorless solid (0.860 g, 30%). 1H NMR ($CDCl_3$, 400 MHz) δ 7.15 (s, 2 H), 6.97 (br, 1 H), 4.21 (sept, $J = 6.8$ Hz, 2 H), 2.91 (sept, $J = 6.9$ Hz, 1 H), 2.23 (dt, $J = 3.6, 16.6$ Hz, 1 H), 1.96 (t, $J = 4.4$ Hz, 1 H),

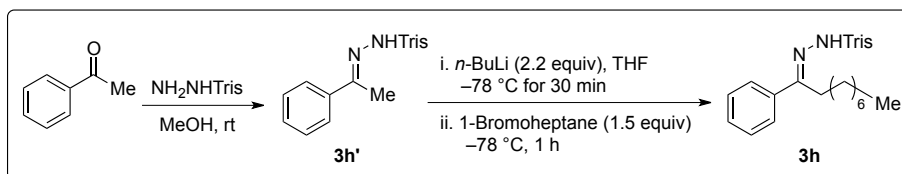
SI-10

1.78–1.85 (m, 1 H), 1.73 (d, $J = 16.7$ Hz, 1 H), 1.63 (td, $J = 4.2, 12.2$, 1 H), 1.25–1.28 (m, 19 H), 1.10–1.17 (m, 1 H), 0.87 (d, $J = 1.5$ Hz, 6 H), 0.62 (s, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 169.1, 153.1, 151.5, 131.7, 123.7, 53.0, 48.1, 44.2, 34.3, 33.8, 32.5, 30.0, 27.4, 25.0, 23.7, 19.5, 18.8, 11.1 ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{25}\text{H}_{40}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 455.2708, found 455.2692.



N'-(1-benzylpiperidin-4-ylidene)-2,4,6-triisopropylbenzenesulfonohydrazide (5d)

The general procedure was followed using TPSH (0.870 g, 2.90 mmol), N-benzyl-4-piperidone (0.500 g, 2.64 mmol) and 2 drops of HCl with THF (3.00 mL) as solvent for 3.5 h at rt. Workup B followed by chromatographic purification ($\text{CH}_2\text{Cl}_2/\text{MeOH}$) provided the title compound **5d** as a colorless solid (0.800 g, 65%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.73 (br, 1 H), 7.22–7.30 (m, 5 H), 7.15 (s, 2 H), 4.24 (sept, $J = 6.7$ Hz, 2 H), 3.48 (s, 2 H), 2.89 (sept, $J = 6.9$ Hz, 1 H), 2.50 (t, $J = 5.7$ Hz, 2 H), 2.46 (t, $J = 5.7$ Hz, 2 H), 2.31–2.36 (m, 4 H), 1.24 (d, $J = 6.6$ Hz, 18 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 156.9, 153.1, 151.4, 138.2, 131.6, 129.0, 128.4, 127.3, 123.8, 62.4, 53.5, 52.0, 34.6, 34.2, 29.9, 26.7, 24.9, 23.7 ppm. IR (film) 3236, 2959, 2868, 1599, 1458, 1425, 1364, 1319, 1165, 1151, 1032, 739, 698, 660 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{39}\text{N}_3\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 492.2661, found 492.2638. m.p. 136–138 °C.

Preparation of trisylhydrazone **3h****(E)-2,4,6-triisopropyl-N'-(1-phenylethylidene)benzenesulfonohydrazide (3h')**

The general procedure was followed using TPSH (5.96 g, 20.0 mmol), acetophenone (2.00 g, 16.7 mmol) with MeOH (0.020 L) as solvent for 3.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **3h'** as a colorless solid (4.75 g, 71%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.75 (br, 1 H), 7.63–7.66 (m, 2 H), 7.29–7.34 (m, 3 H), 7.18 (s, 2 H), 4.33 (sept, $J = 6.8$ Hz, 2 H), 2.90 (sept, $J = 6.9$ Hz, 1 H), 2.18 (s, 3 H), 1.31 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.6, 151.6, 150.9, 137.6, 131.6, 129.6, 128.4, 126.5, 124.0, 34.4, 30.2, 25.0, 23.7, 13.3 ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{32}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 423.2082, found 423.2086.

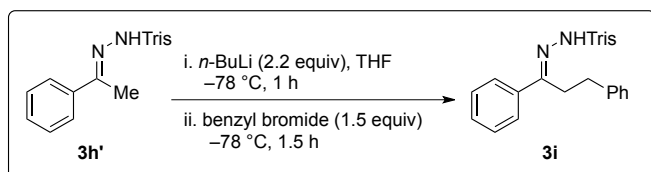
(E)-2,4,6-triisopropyl-N'-(1-phenylnonylidene)benzenesulfonohydrazide (3h)

$n\text{-BuLi}$ (2.26 ml, 5.50 mmol) was added drop wise via syringe pump over a period of 15 min to a cooled solution of **3h'** (1.00 g, 2.50 mmol) in THF (12.5 mL) at -78°C . The reaction solution was stirred at -78°C for 30 min, and then 1-bromoheptane (0.590 ml, 3.75 mmol) was added drop wise to the solution over a period of 5 min at -78°C . The resulting solution was stirred at -78°C for 1 h. Water was added at -78°C , and then the solution was allowed to warm to rt. The aqueous layer was extracted with EtOAc (2 x 0.015 L), and combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography using gradient hexane / ethyl acetate for elution to afford the compound **3h** as a colorless solid (1.50 g, 60%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.62–7.65 (m, 3 H), 7.28–7.34 (m, 3 H), 7.17 (s, 2 H), 4.29 (sept, $J = 6.8$ Hz, 2 H), 2.90 (sept, $J = 6.9$ Hz, 1 H), 2.57 (t, $J = 7.9$ Hz, 2 H), 1.49–1.56 (m, 2 H), 1.36–1.44 (m, 2 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H), 1.24–1.36 (m, 8 H), 0.89 (t, $J = 6.9$ Hz, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 154.6, 153.5, 151.7, 136.9, 131.6, 129.7, 129.5, 128.4, 127.1, 126.6, 124.0, 123.9, 38.4, 34.4, 32.0, 30.2, 29.5,

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29.3, 27.0, 26.0, 25.1, 23.7, 22.8, 21.4 ppm. IR (film) 3196, 2957, 2928, 1599, 1464, 1383, 1317, 1165, 1153, 941, 922, 764, 692, 662 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{30}\text{H}_{46}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 521.3178, found 521.3162. m.p. 97–98 $^{\circ}\text{C}$.

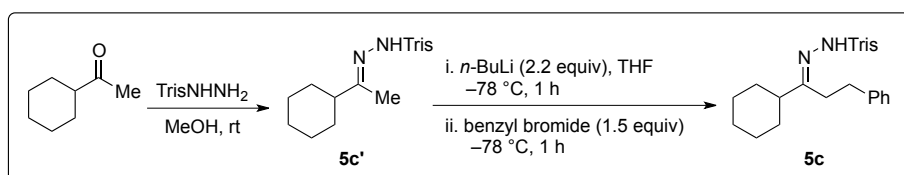
Preparation of trisylhydrazone **3i**



(*E*)-*N'*-(1,3-diphenylpropylidene)-2,4,6-triisopropylbenzenesulfonylhydrazide (**3i**)

$n\text{-BuLi}$ (3.40 ml, 8.18 mmol) was added drop wise to a solution of **3h'** (1.49 g, 3.72 mmol) in THF (20.0 mL) over a period of 15 min at -78°C via syringe pump. The reaction solution was stirred at -78°C for 1 h, and then benzyl bromide (0.670 ml, 5.58 mmol) was added drop wise to the solution over a period of 5 min at -78°C . The resulting solution was stirred at -78°C for 1.5 h, water was added at -78°C , and then the solution was recovered to rt. The aqueous layer was extracted with EtOAc (2 x 0.015 L), and combined organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by column chromatography using gradient hexane / ethyl acetate for elution to afford the compound **3i** as a colorless solid (1.25 g, 69%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.65–7.68 (m, 2 H), 7.47 (s, 1 H), 7.28–7.37 (m, 6 H), 7.22–7.24 (m, 2 H), 7.17 (s, 2 H), 4.30 (sept, $J = 6.8$ Hz, 2 H), 2.82–2.93 (m, 5 H), 1.30 (d, $J = 6.8$ Hz, 12 H), 1.25 (d, $J = 6.9$ Hz, 6 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 153.5, 151.8, 140.3, 136.6, 131.4, 129.6, 129.0, 128.5, 128.4, 126.9, 126.6, 124.0, 34.4, 31.8, 30.2, 29.0, 25.1, 23.7 ppm. IR (film) 3233, 2961, 2928, 1599, 1458, 1425, 1383, 1315, 1165, 1153, 1036, 916, 740, 694, 660 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{30}\text{H}_{38}\text{N}_2\text{O}_2\text{SNa}$ $[\text{M}+\text{Na}]^+$ 513.2552, found 513.2540. m.p. 155–157 $^{\circ}\text{C}$.

Preparation of trisylhydrazone **5c**



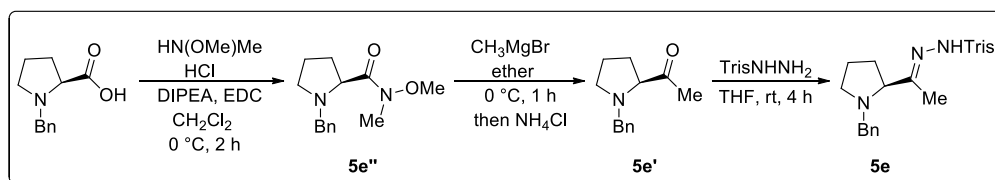
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(E)-N'-(1-cyclohexylethylidene)-2,4,6-triisopropylbenzenesulfonohydrazide (5c')⁷

The general procedure was followed using TPSH (1.28 g, 4.29 mmol), 1-cyclohexylethanone (0.540 g, 4.29 mmol) with MeOH (4.00 mL) as solvent for 5.0 h at rt. Workup C (precipitation in MeOH) provided the title compound **5c'** as a colorless solid (1.33 g, 76%). ¹H NMR (CDCl₃, 400 MHz) δ 7.16 (s, 3 H), 4.21 (sept, *J* = 6.7 Hz, 2 H), 2.91 (sept, *J* = 6.9 Hz, 1 H), 2.05–2.10 (m, 1 H), 1.73 (s, 3 H), 1.59–1.67 (m, 5 H), 1.25–1.28 (m, 18 H), 1.08–1.22 (m, 5 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 159.7, 153.2, 151.4, 131.8, 123.7, 46.8, 34.3, 30.0, 26.2, 26.0, 25.0, 23.7, 14.0 ppm. HRMS (ESI, *m/z*): calcd. for C₂₃H₄₂N₃O₂S [M+NH₄]⁺ 424.2998, found 424.2990.

(E)-N'-(1-cyclohexyl-3-phenylpropylidene)-2,4,6-triisopropylbenzenesulfonohydrazide (5c)

n-BuLi (0.480 ml, 1.08 mmol) was added drop wise to a solution of **5c'** (0.200 g, 0.490 mmol) in THF (2.50 mL) over a period of 5 min at –78 °C via syringe pump. The reaction solution was stirred at –78 °C for 1 h, and then benzyl bromide (0.090 ml, 0.74 mmol) was added drop wise to the solution over a period of 2 min at –78 °C. The resulting solution was stirred at –78 °C for 1 h. Water was added at –78 °C, and then the solution was allowed to warm to rt. The aqueous layer was extracted with EtOAc (2 x 0.003 L), and combined organic layer was dried over anhydrous Na₂SO₄ and concentrated. The crude product was purified by column chromatography using gradient hexane / ethyl acetate for elution to afford the compound **5c** as a colorless solid (0.155 g, 64%). ¹H NMR (CDCl₃, 400 MHz) δ 7.31–7.34 (m, 2 H), 7.23–7.25 (m, 1 H), 7.14–7.20 (m, 5 H), 4.19 (sept, *J* = 6.7 Hz, 2 H), 2.92 (sept, *J* = 6.9 Hz, 1 H), 2.74–2.78 (m, 2 H), 2.39–2.43 (m, 2 H), 2.01 (br, 1 H), 1.60–1.67 (m, 5 H), 1.27 (d, *J* = 6.7 Hz, 12 H), 1.26 (d, *J* = 6.9 Hz, 6 H), 1.11–1.19 (m, 5 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 162.3, 153.3, 151.6, 140.5, 131.7, 128.9, 128.3, 126.8, 123.7, 45.8, 34.4, 31.2, 30.6, 30.5, 30.1, 26.2, 25.1, 23.8 ppm. IR (film) 3236, 2959, 2928, 2866, 1601, 1454, 1383, 1323, 1163, 1153, 941, 881, 746, 700, 660 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₃₀H₄₄N₂O₂SNa [M+Na]⁺ 519.3021, found 519.3018. m.p. 135–136 °C.

Preparation of trisylhydrazone **5e****(S)-1-benzyl-N-methoxy-N-methylpyrrolidine-2-carboxamide (5e'')**

(L)-N-Benzyl-proline (2.98 g, 15.5 mmol) was suspended in CH_2Cl_2 (0.070 L), and $\text{HN}(\text{OMe})\text{Me}\cdot\text{HCl}$ (1.42 g, 14.5 mmol), diisopropylethylamine (2.40 mL, 14.5 mmol) and EDCI (2.78 g, 14.5 mmol) were added into the reaction mixture sequentially at 0 °C. The resulting reaction solution was stirred at 0 °C for 2 h, and then water was added to quench the reaction. The organic layer was collected, and the aqueous layer was extracted further with CH_2Cl_2 (2 x 0.030 L). The combined organic layer was dried over anhydrous Na_2SO_4 , concentrated, and the residue was purified by column chromatography using gradient MeOH in CH_2Cl_2 (2% to 5%) for elution to offer **5e''** as a liquid (1.41 g, 39%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.22–7.36 (m, 5 H), 3.94 (d, J = 12.8 Hz, 1 H), 3.56–3.57 (m, 4 H), 3.55 (d, J = 12.8 Hz, 1 H), 3.17 (s, 3 H), 3.08–3.13 (m, 1 H), 2.44 (q, J = 8.2 Hz, 1 H), 2.10–2.19 (m, 1 H), 1.75–1.96 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 175.0, 138.5, 129.4, 128.1, 127.0, 62.0, 61.2, 58.0, 53.0, 32.4, 29.1, 23.0 ppm. IR (film) 2964, 2939, 2874, 2359, 2341, 1663, 1454, 1387, 1312, 1177, 999, 745, 700 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 249.1603, found 249.1591.

(S)-1-(1-benzylpyrrolidin-2-yl)ethanone (5e')⁸

5e'' (1.34 g, 5.40 mmol) was dissolved in dry ether (0.050 L) and cooled to 0 °C. Methylmagnesium bromide (2.52 mL, 7.56 mmol) was added drop wise into the solution over 10 min at 0 °C. The solution was stirred at this temperature for 1 h and quenched with NH_4Cl (sat'd). The organic layer was collected and the aqueous layer was extracted further with EtOAc (2 x 0.025 L). The combined organic layer was dried over anhydrous Na_2SO_4 , concentrated, and the residue was purified by column chromatography using gradient MeOH in CH_2Cl_2 (2% to 4%) for elution to offer **5e'** as a liquid (0.930 g, 85%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.24–7.35 (m, 5 H), 3.82 (d,

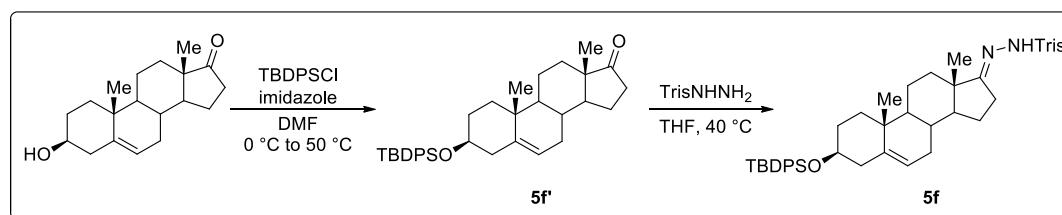
SI-15

$J = 13.0$ Hz, 1 H), 3.45 (d, $J = 13.0$ Hz, 1 H), 3.07–3.13 (m, 2 H), 2.27–2.33 (m, 1 H), 2.15 (s, 3 H), 2.06–2.13 (m, 1 H), 1.76–1.90 (m, 3 H) ppm. HRMS (ESI, m/z): calcd. for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1388, found 204.1392.

(*S,E*)-*N'*-(1-(1-benzylpyrrolidin-2-yl)ethylidene)-2,4,6-triisopropylbenzenesulfonylhydrazide (**5e**)

The general procedure was followed using TPSH (1.39 g, 4.65 mmol), **5e'** (0.860 g, 4.23 mmol) with THF (4.5 mL) as solvent for 4.0 h at rt. Workup B followed by chromatographic purification ($CH_2Cl_2/MeOH$) provided the title compound **5e** as a colorless solid (1.79 g, 88%). 1H NMR ($CDCl_3$, 400 MHz) δ 7.34 (s, 1 H), 7.18–7.23 (m, 3 H), 7.14 (s, 2 H), 7.06 (dd, $J = 2.1, 7.6$ Hz, 2 H), 4.26 (sept, $J = 6.7$ Hz, 2 H), 3.44 (d, $J = 13.4$ Hz, 1 H), 3.01–3.04 (m, 2 H), 2.88–2.93 (m, 1 H), 2.84 (sept, $J = 6.9$ Hz, 1 H), 2.12 (q, $J = 8.4$ Hz, 1 H), 1.82–1.92 (m, 1 H), 1.76 (s, 3 H), 1.61–1.75 (m, 3 H), 1.30 (d, $J = 6.7$ Hz, 6 H), 1.25 (d, $J = 6.8$ Hz, 6 H), 1.18 (t, $J = 6.7$ Hz, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 125 MHz) δ 157.3, 153.3, 151.4, 138.9, 131.5, 129.0, 128.2, 126.9, 123.8, 69.6, 57.6, 53.2, 34.3, 30.0, 28.7, 25.1, 25.0, 23.6, 23.3, 10.7 ppm. IR (film) 3231, 2959, 2868, 2359, 2341, 1599, 1458, 1425, 1383, 1364, 1323, 1165, 1153, 1038, 912, 739, 698, 667 cm^{-1} . HRMS (ESI, m/z): calcd. for $C_{28}H_{41}N_3O_2SNa$ $[M+Na]^+$ 506.2817, found 506.2793. m.p. 134–135 °C.

Preparation of trisylhydrazone **5f**



(*3S,10R,13S*)-3-((*tert*-butyldiphenylsilyl)oxy)-10,13-dimethyl-3,4,7,8,9,10,11,12,13,14,15,16-dodecahydro-1*H*-cyclopenta[*a*]phenanthren-17(2*H*)-one (**5f'**)⁹

(+)-Dehydroepiandrosterone (0.300 g, 1.04 mmol) was dissolved in dry DMF (0.010 L) at rt, and then imidazole (177 mg, 2.60 mmol) was added at 0 °C. The resulting solution was stirred at 0 °C for 15 min, and then TBDPSCI (0.540 mL, 2.08 mmol) was added drop wise. The solution was stirred at 50 °C overnight. A solution of saturated NH_4Cl (5.0 mL) was added at rt and stirred for additional 30 min. DMF was removed under reduced pressure, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The organic layer was dried over anhydrous $NaSO_4$,

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concentrated and purified by column chromatography using gradient elution (EtOAc/hexanes) to furnish **5f** as a colorless foam (500 mg, 91%). ¹H NMR (CDCl₃, 400 MHz) δ 7.68–7.71 (m, 4 H), 7.38–7.42 (m, 6 H), 5.17 (d, *J* = 5.3 Hz, 1 H), 3.52–3.59 (m, 1 H), 1.45–2.48 (m, 17 H), 1.19–1.27 (m, 2 H), 1.08 (s, 9 H), 1.03 (s, 3 H), 0.87 (s, 3 H) ppm. HRMS (ESI, *m/z*): calcd. for C₃₅H₄₇O₂Si [M+H]⁺ 527.3345, found 527.3337.

(*E*)-N'-((3*S*,10*R*,13*S*)-3-((*tert*-butyldiphenylsilyl)oxy)-10,13-dimethyl-3,4,7,8,9,11,12,13,15,16-decahydro-1*H*-cyclopenta[*a*]phenanthren-17(2*H*,10*H*,14*H*)-ylidene)-2,4,6-triisopropylbenzenesulfonohydrazide (5f**)**

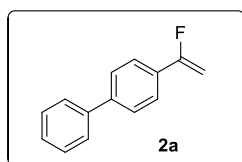
The general procedure was followed using TPSH (401 mg, 1.34 mmol), **5f** (590 mg, 1.12 mmol) with THF (1.0 mL) as solvent for 6.0 h at 40 °C. Workup C followed by chromatographic purification (EtOAc / hexanes) provided the title compound **5f** as a colorless solid (230 mg, 25%). ¹H NMR (CDCl₃, 400 MHz) δ 7.66–7.69 (m, 4 H), 7.35–7.44 (m, 6 H), 7.15 (s, 2 H), 6.92 (s, 1 H), 5.11–5.12 (m, 1 H), 4.19 (sept, *J* = 6.7 Hz, 2 H), 3.48–3.54 (m, 1 H), 2.90 (sept, *J* = 6.9 Hz, 1 H), 2.19–2.35 (m, 2 H), 2.04–2.15 (m, 2 H), 1.94–1.96 (m, 1 H), 1.76–1.86 (m, 2 H), 1.36–1.69 (m, 8 H), 1.24–1.27 (m, 19 H), 0.97–1.06 (m, 13 H), 0.80–0.86 (m, 2 H), 0.73 (s, 3 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 169.8, 153.2, 151.5, 141.7, 136.0, 135.0, 131.7, 129.7, 127.7, 123.7, 120.6, 73.3, 53.9, 50.4, 44.8, 42.6, 37.3, 36.8, 34.3, 33.8, 32.0, 31.5, 31.4, 30.1, 27.2, 26.0, 25.1, 25.0, 23.8, 23.6, 20.6, 19.6, 19.3, 16.8 ppm. IR (film) 3441, 2959, 2932, 2359, 1653, 1636, 1427, 1381, 1325, 1165, 1153, 1109, 1086, 741, 702, 667 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₅₀H₇₄N₃O₃SSi [M+NH₄]⁺ 824.5220, found 824.5190. m.p. 117–118 °C.

General procedure for the Shapiro fluorination reactions of trisylhydrazones **1a, **3a–i**, **5a–f****

An oven-dried round bottom flask was charged with the trisylhydrazone **1a**, **3a–i**, and **5a–f** (1.0 equiv) and a magnetic stir bar. The reaction vessel was equipped with a three-way valve, evacuated and back-filled with nitrogen. Dry THF (*c* = 0.20 M) was added and the mixture was stirred at room temperature until the trisylhydrazone dissolved. The solution was cooled to –78 °C, and then base (2.2 equiv) was added drop wise to the stirred solution. The resulting solution was stirred at –78 °C for 30 min to generate the dianion, and then at 0 °C for 20 min to release N₂. Subsequently, the reaction was cooled to –78 °C, and then a solution of NFSI (1.5 equiv, *c* = 0.49 ~ 0.5 M in THF) was added drop wise over 2 min. Additional THF (0.1 mL) was used to wash the

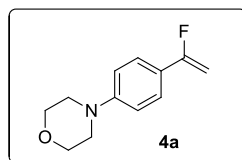
SI-17

vial, and added successively. The resulting solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, and then at rt for 2 h. A 1 N solution of α,α,α -trifluorotoluene in EtOAc (100 μL , 0.10 mmol) was added as an internal standard, and the resulting mixture was stirred at rt for 5 min. After standing for 3 min, an aliquot of the upper clear solution was removed and subjected to ^{19}F NMR analysis to determine the yield of fluoroalkene **2a**, **4a–i**, and **6a–f**. After the ^{19}F NMR analysis, the NRM sample was returned to the bulk of the reaction mixture, and the combined mixture was concentrated under reduced pressure. The resulting residue was added to a solution of NaHCO_3 (1.0 mL), stirred, and extracted with ether (3 x 5 mL). (In some cases, EtOAc was used for extraction.) The organic layers were dried over anhydrous Na_2SO_4 , and concentrated. Purification by flash chromatography provided the desired product.



4-(1-fluorovinyl)-1,1'-biphenyl (**2a**)

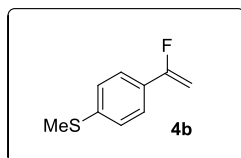
The general procedure was followed using **1a** (119 mg, 0.250 mmol), *n*-BuLi (0.240 mL, 0.550 mmol), and NFSI (118 mg, 0.375 mmol). Workup and chromatographic purification (hexanes) provided the title compound **2a** as a colorless solid (38.4 mg, 75%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.62–7.67 (m, 6 H), 7.46–7.50 (m, 2 H), 7.38–7.41 (m, 1 H), 5.10 (dd, $J = 3.5, 49.7$ Hz, 1 H), 4.90 (dd, $J = 3.5, 17.8$ Hz, 1 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 163 (d, $J = 248.5$ Hz), 142.3, 140.5, 131.1 ($J = 29.3$ Hz), 129.1, 127.9, 127.4, 127.2, 125.3 ($J = 6.9$ Hz), 89.8 ($J = 22.3$ Hz) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -107.9 (dd, $^3J_{\text{F-H}} = 18.1, 49.6$ Hz, 1 F) ppm. IR (film) 2359, 2341, 1647, 1404, 1292, 928, 843, 766, 689 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{11}\text{FNa}$ [$\text{M}+\text{Na}$] $^+$ 221.0742, found 221.0748. m.p. 120–121 $^{\circ}\text{C}$.



4-(4-(1-fluorovinyl)phenyl)morpholine (**4a**)

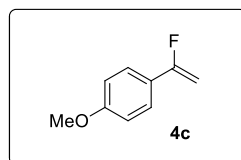
SI-18

The general procedure was followed using **3a** (121 mg, 0.250 mmol), *n*-BuLi (0.240 mL, 0.550 mmol), and NFSI (86.7 mg, 0.275 mmol). Workup and chromatographic purification (2% EtOAc in hexanes) provided the title compound **4a** as a colorless solid (35.0 mg, 68%). ¹H NMR (CDCl₃, 400 MHz) δ 7.48 (d, *J* = 8.8 Hz, 2 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 4.87 (dd, *J* = 3.4, 50.4 Hz, 1 H), 4.71 (dd, *J* = 3.4, 18.2 Hz, 1 H), 3.87 (t, *J* = 4.9 Hz, 4 H), 3.22 (t, *J* = 4.9 Hz, 4 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 163.3 (d, *J* = 247.1 Hz), 152.0, 125.9 (d, *J* = 7.0 Hz), 123.4 (d, *J* = 29.8 Hz), 114.9 (d, *J* = 1.5 Hz), 87.2 (d, *J* = 22.8 Hz), 66.9, 48.8 ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ -107.7 (dd, ³*J*_{F-H} = 18.1, 50.4 Hz, 1 F) ppm. IR (film) 2856, 2359, 1645, 1518, 1279, 1265, 1123, 920, 849, 822 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₁₂H₁₅NOF [M+H]⁺ 208.1138, found 208.1129. m.p. 111–112 °C.



(4-(1-fluorovinyl)phenyl)(methyl)sulfane (**4b**)

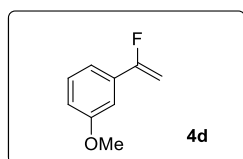
The general procedure was followed using **3b** (223 mg, 0.500 mmol), *n*-BuLi (0.470 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4b** as a light yellow solid (60.0 mg, 67%). ¹H NMR (CDCl₃, 400 MHz) δ 7.48 (d, *J* = 8.4 Hz, 2 H), 7.24 (d, *J* = 8.4 Hz, 2 H), 4.99 (dd, *J* = 3.5, 49.9 Hz, 1 H), 4.82 (dd, *J* = 3.5, 17.9 Hz, 1 H), 2.51 (s, 3 H) ppm. ¹³C NMR (CDCl₃, 125 MHz) δ 162.8 (d, *J* = 248 Hz), 140.6, 128.8 (d, *J* = 29.6 Hz), 126.1 (d, *J* = 1.5 Hz), 125.1 (d, *J* = 7.0 Hz), 89.1 (d, *J* = 22.6 Hz), 15.6 ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ -108.1 (dd, ³*J*_{F-H} = 18.1, 50.0 Hz, 1 F) ppm. IR (film) 2922, 2361, 1647, 1493, 1396, 1288, 1107, 922, 821, 739 cm⁻¹. HRMS (ESI, *m/z*): calcd. for C₉H₉FSNa [M+Na]⁺ 191.0307, found 191.0316. m.p. 48–49 °C.



1-(1-fluorovinyl)-4-methoxybenzene (**4c**)¹⁰

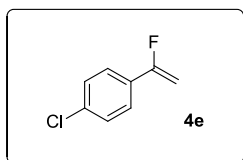
SI-19

The general procedure was followed using **3c** (215 mg, 0.500 mmol), *n*-BuLi (0.490 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4c** as a colorless liquid (41.0 mg, 54%). ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 8.8 Hz, 2 H), 6.90 (d, *J* = 8.7 Hz, 2 H), 4.89 (dd, *J* = 3.4, 50.2 Hz, 1 H), 4.74 (dd, *J* = 3.4, 18.1 Hz, 1 H), 3.84 (s, 3 H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ -107.2 (dd, ³*J*_{F-H} = 18.1, 50.0 Hz, 1 F) ppm. HRMS (ESI, *m/z*): calcd. for C₉H₁₃NOF [M+NH₄]⁺ 170.0981, found 170.0977.



1-(1-fluorovinyl)-3-methoxybenzene (**4d**)¹¹

The general procedure was followed using **3d** (86.1 mg, 0.200 mmol), *n*-BuLi (0.220 mL, 0.500 mmol), and NFSI (110 mg, 0.350 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4d** as a colorless liquid (13.0 mg, 43%). ¹H NMR (CDCl₃, 400 MHz) δ 7.28–7.32 (m, 1 H), 7.17 (d, *J* = 7.8 Hz, 1 H), 7.09–7.10 (m, 1 H), 6.92 (dd, *J* = 2.6, 8.2 Hz, 1 H), 5.04 (dd, *J* = 3.5, 49.6 Hz, 1 H), 4.87 (dd, *J* = 3.5, 17.8 Hz, 1 H), 3.84 (s, 3 H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ -107.4 (dd, ³*J*_{F-H} = 18.1, 49.6 Hz, 1 F) ppm. HRMS (ESI, *m/z*): calcd. for C₉H₁₀OF [M+H]⁺ 153.0716, found 153.0720.

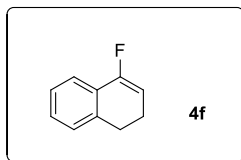


1-chloro-4-(1-fluorovinyl)benzene (**4e**)¹²

The general procedure was followed using **3e** (218 mg, 0.500 mmol), *n*-BuLi (0.470 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4e** as a colorless liquid (60.0 mg, 67%). ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (d, *J* = 8.7 Hz, 2 H), 7.36 (d, *J* = 8.7 Hz, 2 H),

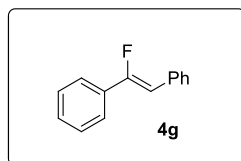
SI-20

5.03 (dd, $J = 3.6, 49.4$ Hz, 1 H), 4.89 (dd, $J = 3.6, 17.8$ Hz, 1 H) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) $\delta -107.9$ (dd, $^3J_{\text{F-H}} = 17.7, 49.3$ Hz, 1 F) ppm. HRMS (ESI, m/z): calcd. for $\text{C}_8\text{H}_6\text{ClFNa}$ $[\text{M}+\text{Na}]^+$ 179.0040, found 179.0032.



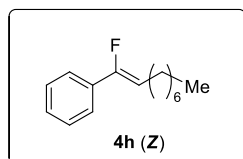
4-fluoro-1,2-dihydronaphthalene (**4f**)¹³

The general procedure was followed using **3f** (213 mg, 0.500 mmol), *n*-BuLi (0.470 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4f** as a colorless liquid (37.0 mg, 50%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.37–7.39 (m, 1 H), 7.20–7.26 (m, 2 H), 7.15–7.17 (m, 1 H), 5.49 (dt, $J = 4.6, 14.0$ Hz, 1 H), 2.84 (t, $J = 8.1$ Hz, 2 H), 2.37–2.44 (m, 2 H) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) $\delta -127.0$ (ddt, $^3J_{\text{F-H}} = 13.9$ Hz, $^4J_{\text{F-H}} = 2.1, 5.1$ Hz, 1 F) ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{10}\text{H}_9\text{FNa}$ $[\text{M}+\text{Na}]^+$ 171.0586, found 171.0593.



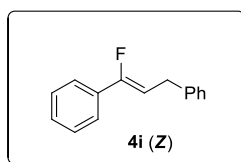
(*Z*)-(1-fluoroethene-1,2-diyl)dibenzene (**4g**)¹⁴

The general procedure was followed using **3g** (238 mg, 0.500 mmol), *s*-BuLi (1.00 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4g** as a colorless solid (82.3 mg, 83%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.67–7.69 (m, 4 H), 7.37–7.46 (m, 5 H), 7.27–7.31 (m, 1 H), 6.34 (d, $J = 39.5$ Hz, 1 H) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) $\delta -114.2$ (d, $^3J_{\text{F-H}} = 39.9$ Hz, 1 F) ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{14}\text{H}_{11}\text{FNa}$ $[\text{M}+\text{Na}]^+$ 221.0742, found 221.0749.

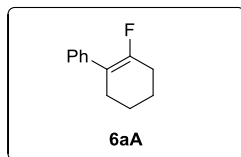


(Z)-(1-fluoronon-1-en-1-yl)benzene (4h)¹⁵

The general procedure was followed using **3h** (249 mg, 0.500 mmol), *n*-BuLi (0.45 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4h** as a colorless liquid (85.3 mg, 77%).¹⁶ ¹H NMR (CDCl₃, 400 MHz) δ 7.50–7.52 (m, 2 H), 7.28–7.38 (m, 3 H), 5.41 (dt, *J* = 7.6, 37.6 Hz, 1 H), 2.26–2.32 (m, 2 H), 1.23–1.50 (m, 10 H), 0.90 (t, *J* = 6.8 Hz, 3 H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ –121.5 (d, ³*J*_{F-H (trans)} = 37.2 Hz, 1 F, *Z* isomer), –102.8 (d, ³*J*_{F-H (cis)} = 22.9 Hz, 1 F, *E* isomer) ppm. HRMS (ESI, *m/z*): calcd. for C₁₅H₂₁FNa [M+Na]⁺ 243.1525, found 243.1531.

**(Z)-(1-fluoroprop-1-ene-1,3-diyl)dibenzene (4i)**¹⁷

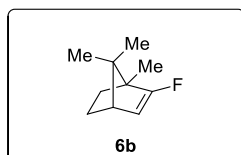
The general procedure was followed using **3i** (245 mg, 0.500 mmol), *n*-BuLi (0.49 mL, 1.10 mmol), and NFSI (237 mg, 0.750 mmol). Workup and chromatographic purification (hexanes) provided the title compound **4i** as a colorless liquid (46.0 mg, 43%).¹⁶ ¹H NMR (CDCl₃, 400 MHz) δ 7.22–7.56 (m, 10 H), 5.61 (dt, *J* = 7.7, 36.3 Hz, 1 H), 3.66 (dd, *J* = 1.4, 7.7 Hz, 2 H) ppm. ¹⁹F NMR (CDCl₃, 376 MHz) δ –121.0 (d, ³*J*_{F-H (trans)} = 36.5 Hz, 1 F, *Z* isomer), –100.1 (d, ³*J*_{F-H (cis)} = 21.4 Hz, 1 F, *E* isomer) ppm. HRMS (ESI, *m/z*): calcd. for C₁₅H₁₃FNa [M+Na]⁺ 235.0899, found 235.0891.

**6-fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (6aA)**

The general procedure was followed using **5a** (114 mg, 0.250 mmol), *t*-BuLi (0.400 mL, 0.550 mmol), and NFSI (118 mg, 0.375 mmol). Workup and chromatographic purification (hexanes) provided compound **6aA** as a colorless liquid (29.0 mg, 61%). ¹H NMR (CDCl₃, 400 MHz) δ 7.41–7.43 (m, 2 H), 7.32–7.37 (m, 2 H), 7.21–

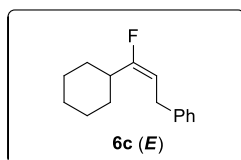
SI-22

7.26 (m, 1 H), 2.40–2.46 (m, 2 H), 2.34–2.39 (m, 2 H), 1.80–1.87 (m, 2 H), 1.71–1.78 (m, 2 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 155.8 (d, $J = 257$ Hz), 137.8, 128.2, 127.9 (d, $J = 4.3$ Hz), 126.8, 113.7 (d, $J = 6.9$ Hz), 28.4 (d, $J = 4.4$ Hz), 26.7 (d, $J = 23.9$ Hz), 23.0 (d, $J = 9.5$ Hz), 22.9 ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -104.0 (s, 1 F) ppm. IR (film) 2934, 1686, 1493, 1445, 1360, 1117, 760, 696 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{12}\text{H}_{14}\text{F}$ $[\text{M}+\text{H}]^+$ 177.1080, found 177.1078.



(1*S*,4*S*)-2-fluoro-1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (**6b**)

The general procedure was followed using **5b** (433 mg, 1.00 mmol), *s*-BuLi (1.64 mL, 2.20 mmol), and NFSI (473 mg, 1.50 mmol). Workup and chromatographic purification (pentane) provided compound **6b** as a colorless liquid (68.0 mg, 44%). ^1H NMR (CDCl_3 , 500 MHz) δ 4.96 (d, $J = 3.6$ Hz, 1 H), 2.28–2.32 (m, 1 H), 1.85–1.91 (m, 1 H), 1.59–1.64 (m, 1 H), 1.29–1.34 (m, 1 H), 1.11–1.16 (m, 1 H), 1.00 (s, 3 H), 0.94 (s, 3 H), 0.76 (s, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 168.4 (d, $J = 293.6$ Hz), 103.2 (d, $J = 2.1$ Hz), 56.3 (d, $J = 3.6$ Hz), 52.2 (d, $J = 17.6$ Hz), 49.0 (d, $J = 6.0$ Hz), 31.5 (d, $J = 4.1$ Hz), 26.7 (d, $J = 3.5$ Hz), 20.0, 19.6, 9.3 ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -131.7 (s, 1 F) ppm. HRMS (ESI, m/z): calcd. for $\text{C}_{10}\text{H}_{15}\text{FNa}$ $[\text{M}+\text{Na}]^+$ 177.1055, found 177.1053.

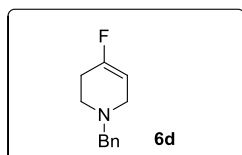


(*E*)-(3-cyclohexyl-3-fluoroallyl)benzene (**6c**)

The general procedure was followed using **5c** (124 mg, 0.250 mmol), *n*-BuLi (0.240 mL, 0.550 mmol), and NFSI (118 mg, 0.375 mmol). Workup and chromatographic purification (hexanes) provided compound **6c (E)** as a colorless liquid (25.0 mg, 46%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.29–7.33 (m, 2 H), 7.19–7.24 (m, 3 H), 5.12 (dt, $J = 8.2, 22.0$ Hz, 1 H), 3.33 (d, $J = 8.2$ Hz, 2 H), 2.51 (dtt, $J = 3.4, 11.9, 30.8$ Hz, 1 H), 1.80–1.84 (m, 2 H), 1.70–

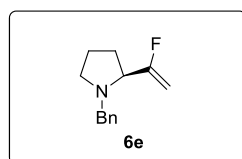
SI-23

1.74 (m, 3 H), 1.49–1.59 (m, 2 H), 1.15–1.34 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 164 (d, $J = 249.6$ Hz), 140.8, 128.7, 128.3, 126.3, 102.8 (d, $J = 24.4$ Hz), 37.4 (d, $J = 26$ Hz), 31.4 (d, $J = 10.1$ Hz), 29.6, 26.3, 25.9 ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -114.6 (dd, $J = 22.2, 30.8$ Hz, 1 F, *E* isomer), -113.8 (dd, $J = 13.9, 38.0$ Hz, 1 F, *Z* isomer) ppm. IR (film) 2930, 2855, 1693, 1493, 1450, 1148, 1130, 735, 696 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{15}\text{H}_{19}\text{FNa}$ $[\text{M}+\text{Na}]^+$ 241.1368, found 241.1366.



1-benzyl-4-fluoro-1,2,3,6-tetrahydropyridine (6d)

The general procedure was followed using **5d** (117 mg, 0.250 mmol), *n*-BuLi (0.240 mL, 0.550 mmol), and NFSI (118 mg, 0.375 mmol). Workup and chromatographic purification (10% ether in hexanes) provided compound **6d** as a colorless liquid (11.0 mg, 23%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.28–7.36 (m, 5 H), 5.17 (dtt, $J = 1.2, 7.1, 15.0$ Hz, 1 H), 3.63 (s, 2 H), 3.01–3.04 (m, 2 H), 2.69 (td, $J = 2.1, 5.8$ Hz, 2 H), 2.31–2.34 (m, 2 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 158.4 (d, $J = 256$ Hz), 138.4, 129.2, 128.5, 127.4, 100.5 (d, $J = 14.6$ Hz), 62.0 (d, $J = 2.5$ Hz), 50.3 (d, $J = 9.1$ Hz), 49.5 (d, $J = 10.1$ Hz), 26.7 (d, $J = 22.4$ Hz) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -104.3 (d, $J = 15.4$ Hz, 1 F) ppm. IR (film) 2928, 2802, 1713, 1454, 1375, 1119, 1028, 741, 700 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{12}\text{H}_{15}\text{FN}$ $[\text{M}+\text{H}]^+$ 192.1189, found 192.1186.

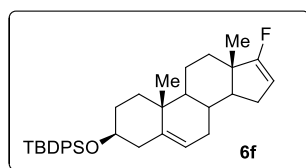


(*S*)-1-benzyl-2-(1-fluorovinyl)pyrrolidine (6e)

The general procedure was followed using **5e** (121 mg, 0.250 mmol), *n*-BuLi (0.230 mL, 0.550 mmol), and NFSI (118 mg, 0.375 mmol). Workup and chromatographic purification (hexanes) provided compound **6e** as a colorless liquid (37.0 mg, 72%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.17–7.26 (m, 5 H), 4.60 (dd, $J = 2.5, 17.1$ Hz, 1 H), 4.52

SI-24

(dd, $J = 2.5, 49.7$ Hz, 1 H), 4.02 (d, $J = 13.1$ Hz, 1 H), 3.25 (d, $J = 13.1$ Hz, 1 H), 2.99–3.07 (m, 1 H), 2.91 (t, $J = 7.9$ Hz, 1 H), 2.18 (q, $J = 8.6$ Hz, 1 H), 1.84–2.01 (m, 2 H), 1.66–1.80 (m, 2 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 166.8 (d, $J = 258.8$ Hz), 139.4, 129.0, 128.4, 127.1, 91.1 (d, $J = 18.8$ Hz), 64.5 (d, $J = 29.1$ Hz), 58.3, 53.4, 29.3, 23.0 ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -108.3 (dt, $J = 17.7, 49.6$ Hz, 1 F) ppm. IR (film) 2970, 2797, 1672, 1495, 1454, 1277, 1202, 910, 854, 739, 698 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{13}\text{H}_{16}\text{FNNa}$ $[\text{M}+\text{Na}]^+$ 228.1164, found 228.1158.



tert-butyl(((3S,10R,13S)-17-fluoro-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)diphenylsilane (6f)

The general procedure was followed using **5f** (121 mg, 0.150 mmol), *n*-BuLi (0.150 mL, 0.330 mmol), and NFSI (71 mg, 0.225 mmol). Workup and chromatographic purification (hexanes) provided compound **6f** as a colorless liquid (29.0 mg, 38%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.67–7.70 (m, 4 H), 7.35–7.45 (m, 6 H), 5.15 (d, $J = 5.3$ Hz, 1 H), 4.87–4.88 (m, 1 H), 3.50–3.58 (m, 1 H), 2.32–2.38 (m, 1 H), 2.13–2.18 (m, 1 H), 1.99–2.06 (m, 1 H), 1.80–1.97 (m, 2 H), 1.67–1.77 (m, 3 H), 1.57–1.65 (m, 2 H), 1.46–1.52 (m, 2 H), 1.34–1.41 (m, 1 H), 1.27 (br, 1 H), 1.07 (s, 9 H), 1.03 (s, 3 H), 0.97 (s, 3 H), 0.83–0.96 (m, 3 H) ppm. ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.0 (d, $J = 287.1$ Hz), 141.9, 136.0, 135.0, 129.7 (d, $J = 2.3$ Hz), 127.7 (d, $J = 2.8$ Hz), 120.8, 100.7 (d, $J = 10.1$ Hz), 73.4, 54.8 (d, $J = 5.6$ Hz), 50.9, 42.7, 42.5, 37.3, 36.9, 33.0, 32.1, 30.8, 30.1, 27.2, 27.1 (d, $J = 7.0$ Hz), 20.4, 19.5, 19.4, 15.3 (d, $J = 4.0$ Hz) ppm. ^{19}F NMR (CDCl_3 , 376 MHz) δ -131.9 (d, $J = 4.5$ Hz, 1 F) ppm. IR (film) 2932, 2856, 1651, 1462, 1427, 1371, 1109, 799, 739, 702, 613, 509 cm^{-1} . HRMS (ESI, m/z): calcd. for $\text{C}_{35}\text{H}_{45}\text{FOSiNa}$ $[\text{M}+\text{Na}]^+$ 551.3121, found 551.3145.

One-pot sequence converting ketones to fluoroalkenes 8a–c

An oven-dried round flask (25 mL) was charged with ketone **7a–c** (0.50 mmol), TPSH (0.50 mmol) and a magnetic stir bar. The reaction vessel was equipped with a three-way valve, evacuated and back-filled with

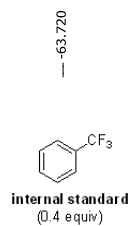
SI-25

nitrogen. A pre-prepared stock solution of TFA (0.050 mmol) in THF (1.0 mL) was added and the reaction mixture was stirred at rt for 1.5 h. Then, the reaction solution was diluted with additional THF (1.5 mL) followed by the addition of activated 4Å molecular sieves (400 mg) and stirred at rt for 10 min. The solution was cooled to $-78\text{ }^{\circ}\text{C}$, and then *n*-BuLi (1.5 mmol) was added drop wise into the pre-cooled and stirred solution at $-78\text{ }^{\circ}\text{C}$. The resulting solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min to generate the dianion and at $0\text{ }^{\circ}\text{C}$ for 20 min to release N_2 . Subsequently, the reaction solution was cooled to $-78\text{ }^{\circ}\text{C}$, and then a solution of NFSI (0.75 mmol, $c = 0.50\text{ M}$ in THF) was added drop wise over 4 min. Additional THF (0.1 mL) was used to wash the vial, and added successively. The resulting solution was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min, and then at rt for 2 h. 0.50 N α,α,α -trifluorotoluene in EtOAc (200 μL , 0.10 mmol) was added as an internal standard and the resulting mixture was stirred at rt for 5 min. After standing for 3 min, an aliquot of the upper clear solution was removed and subjected to ^{19}F NMR analysis to determine yields of fluoroalkene **8a–c**.

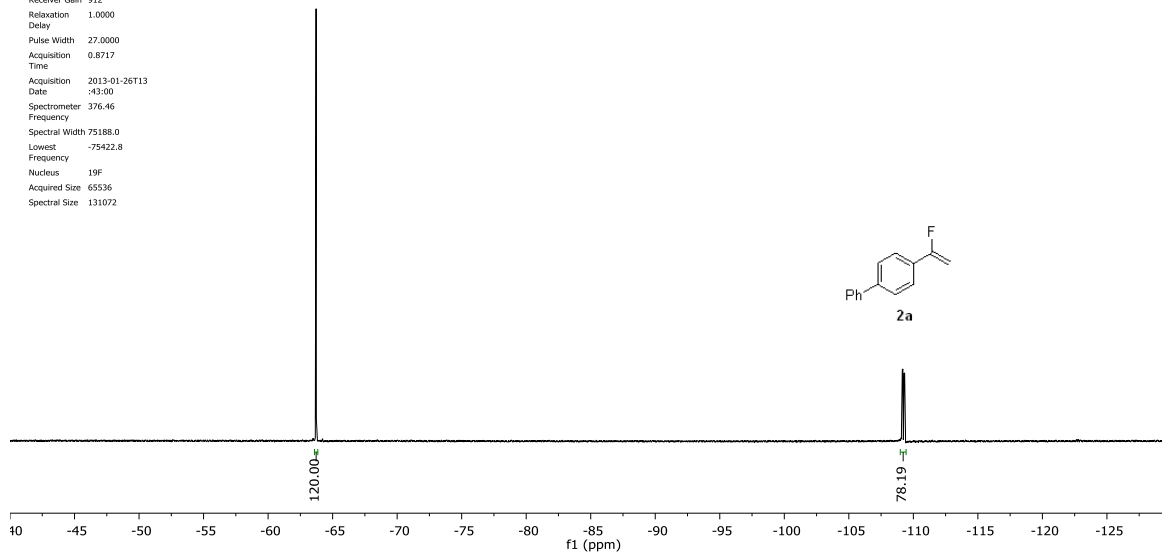
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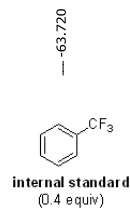
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Number of Scans	16
Receiver Gain	912
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-26T13:43:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75422.8
Nucleus	19F
Acquired Size	65536
Spectral Size	131072



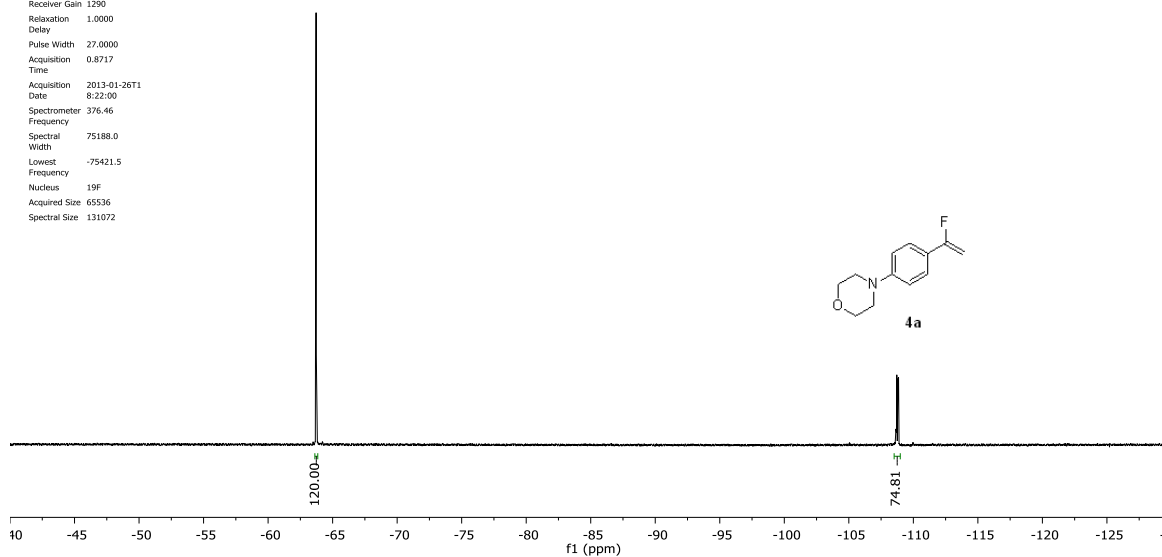
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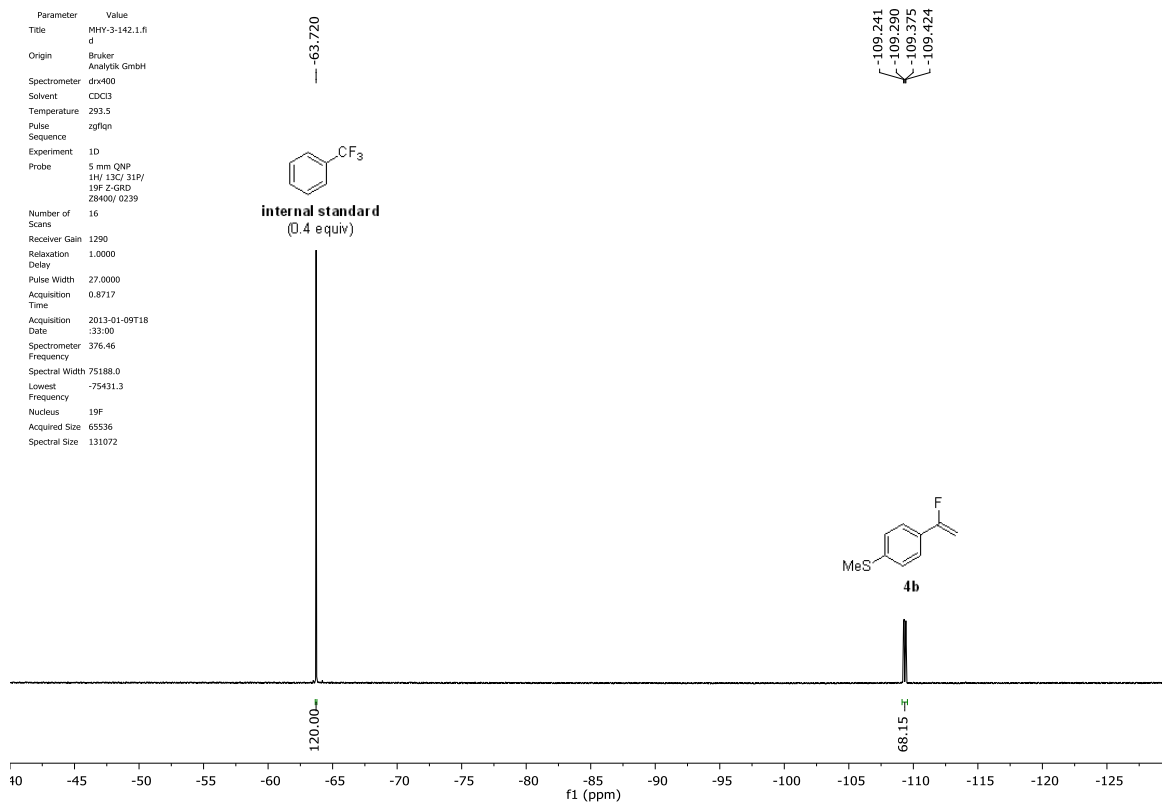
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Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-26T11:22:00
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Lowest Frequency	-75421.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072



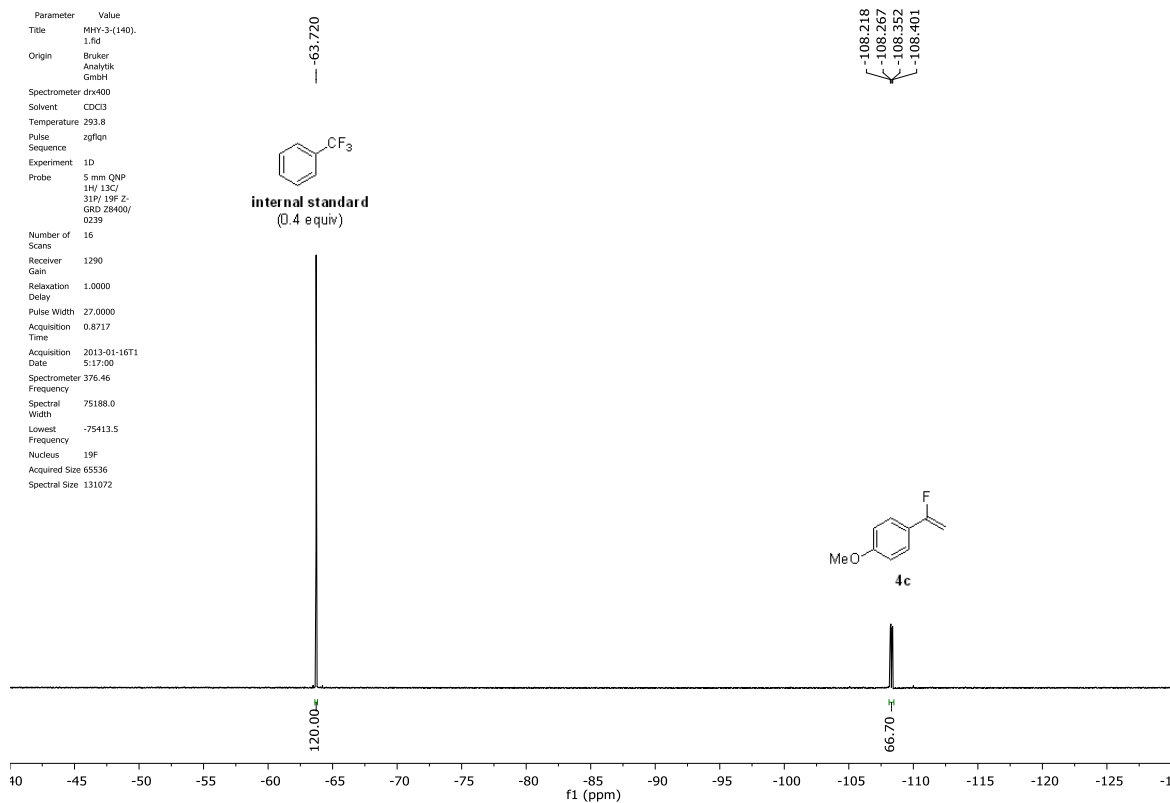
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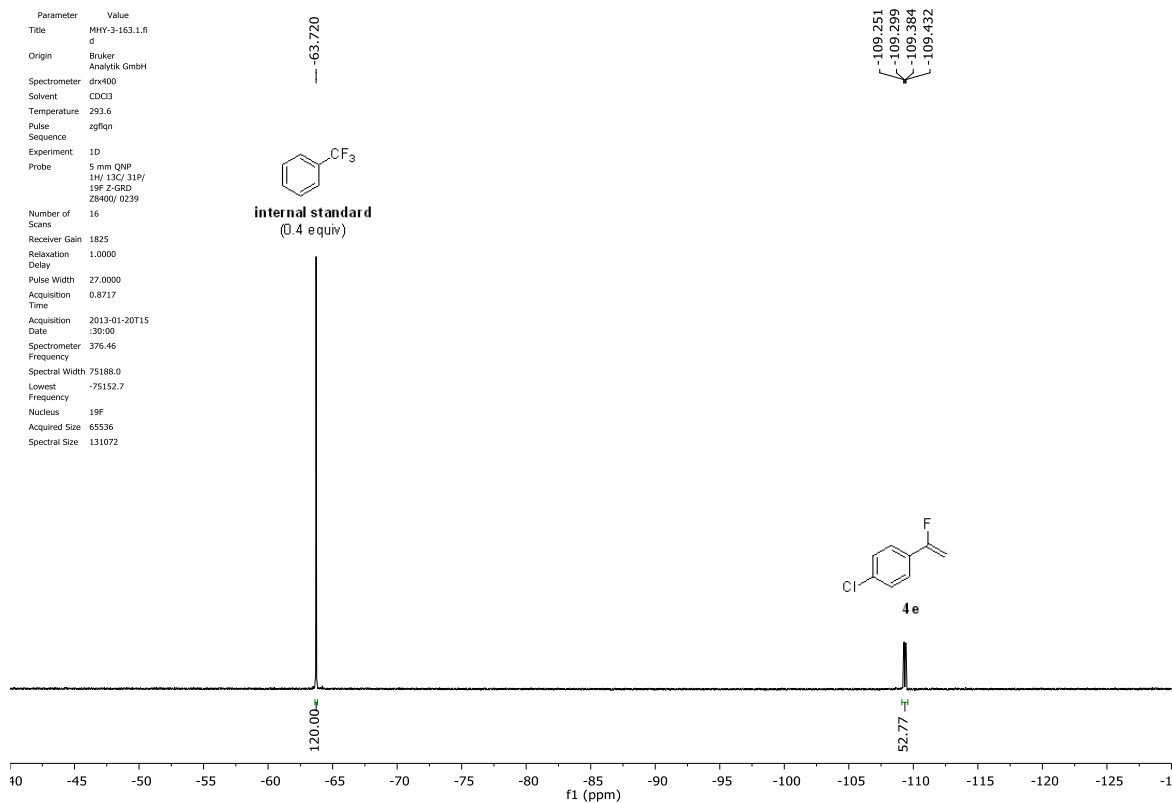
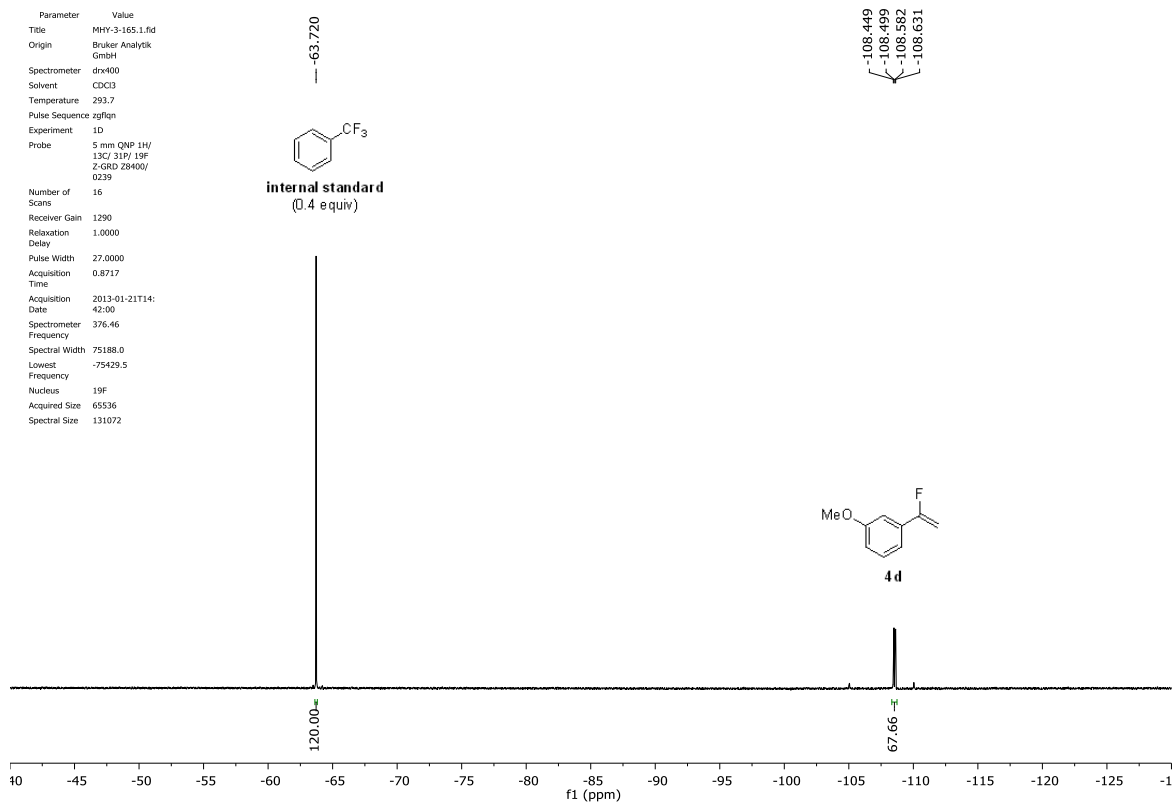


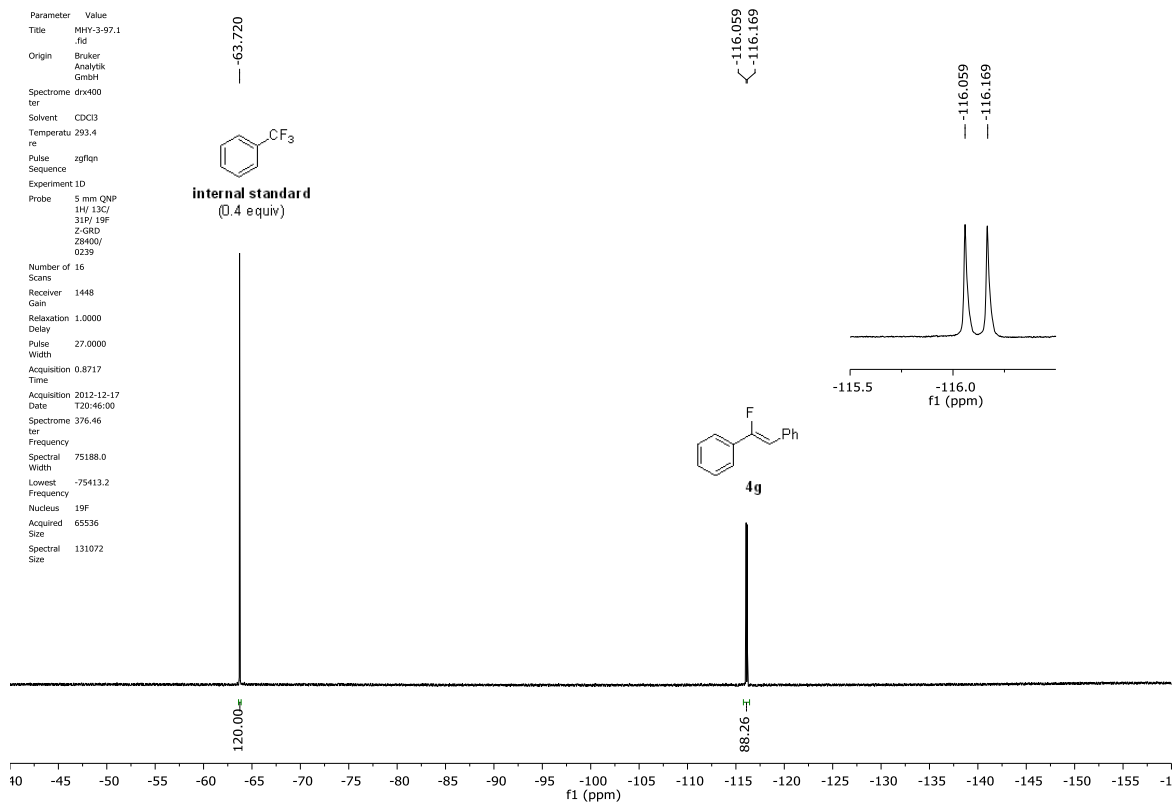
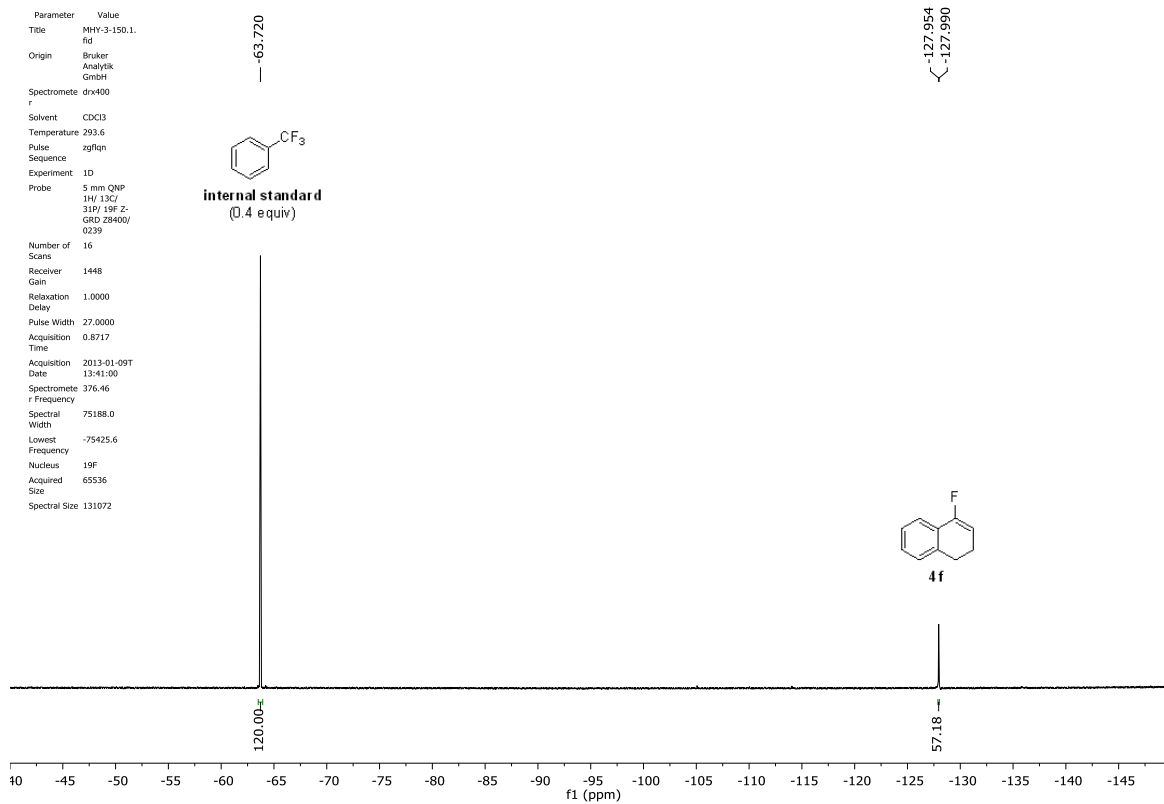
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Spectrometer	dx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgfgn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ Q239
Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-09T18:33:00
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Nucleus	19F
Acquired Size	65536
Spectral Size	131072

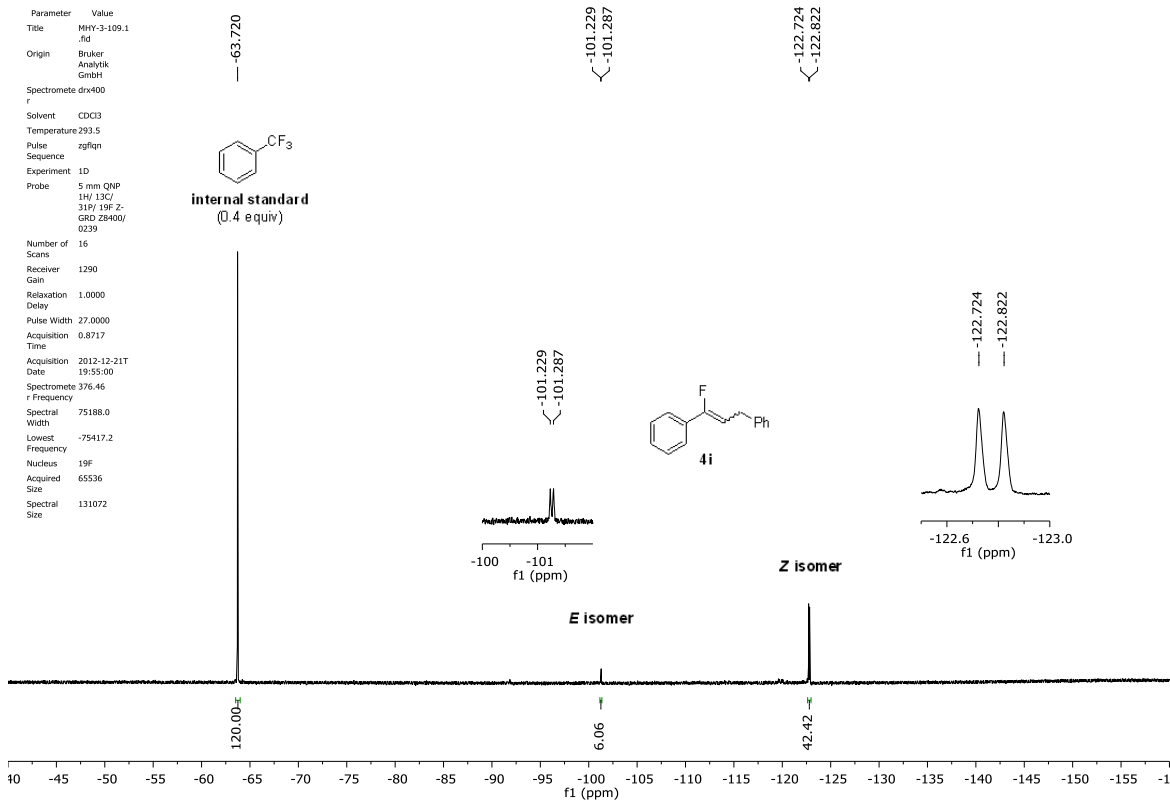
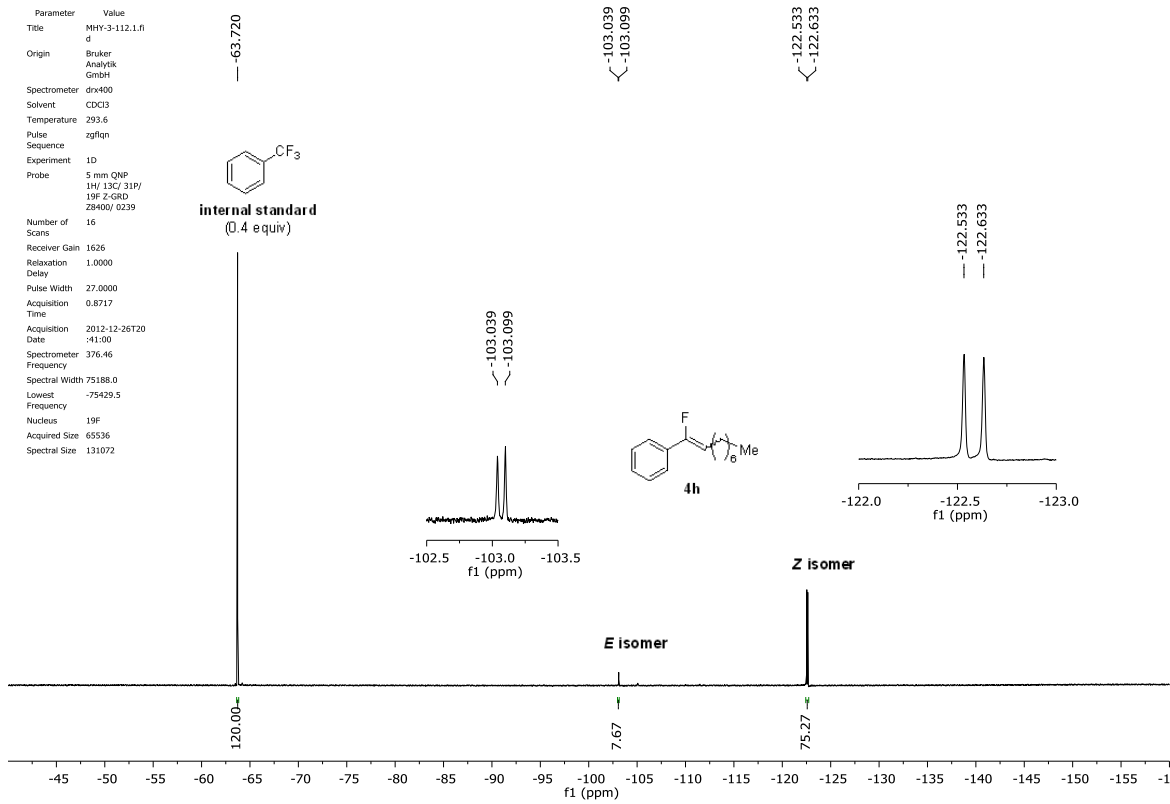


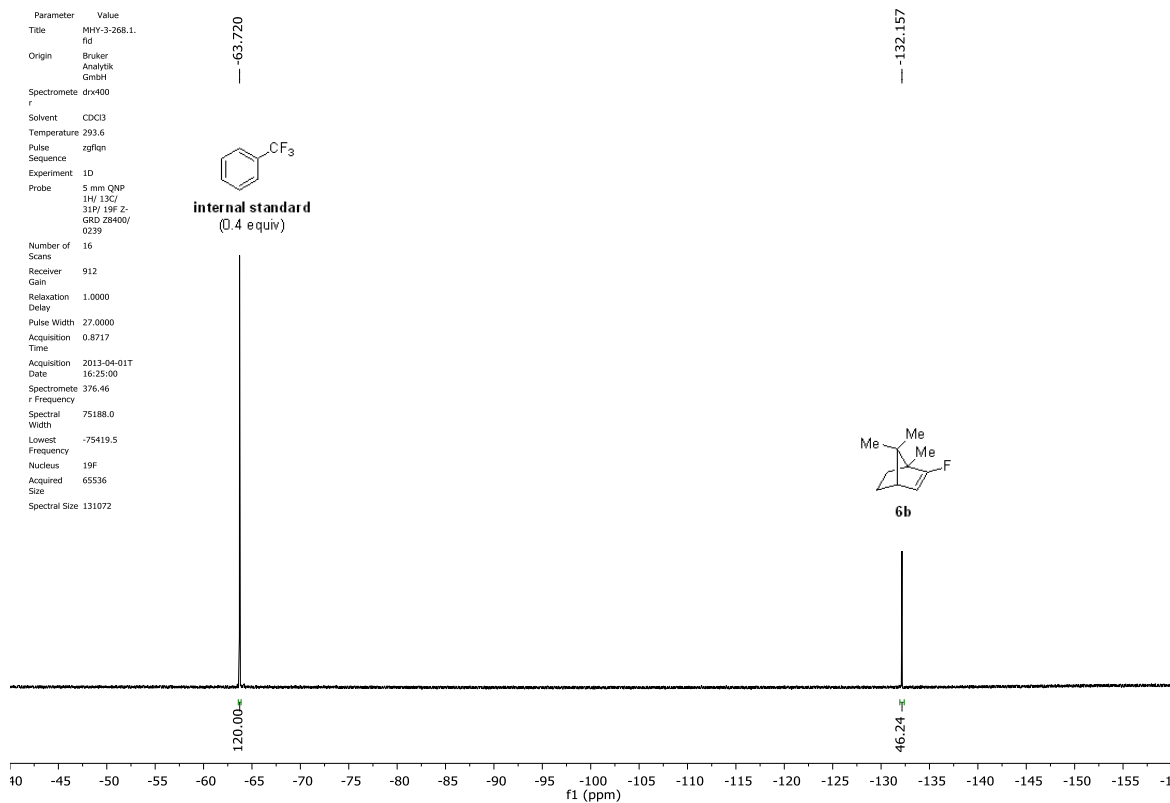
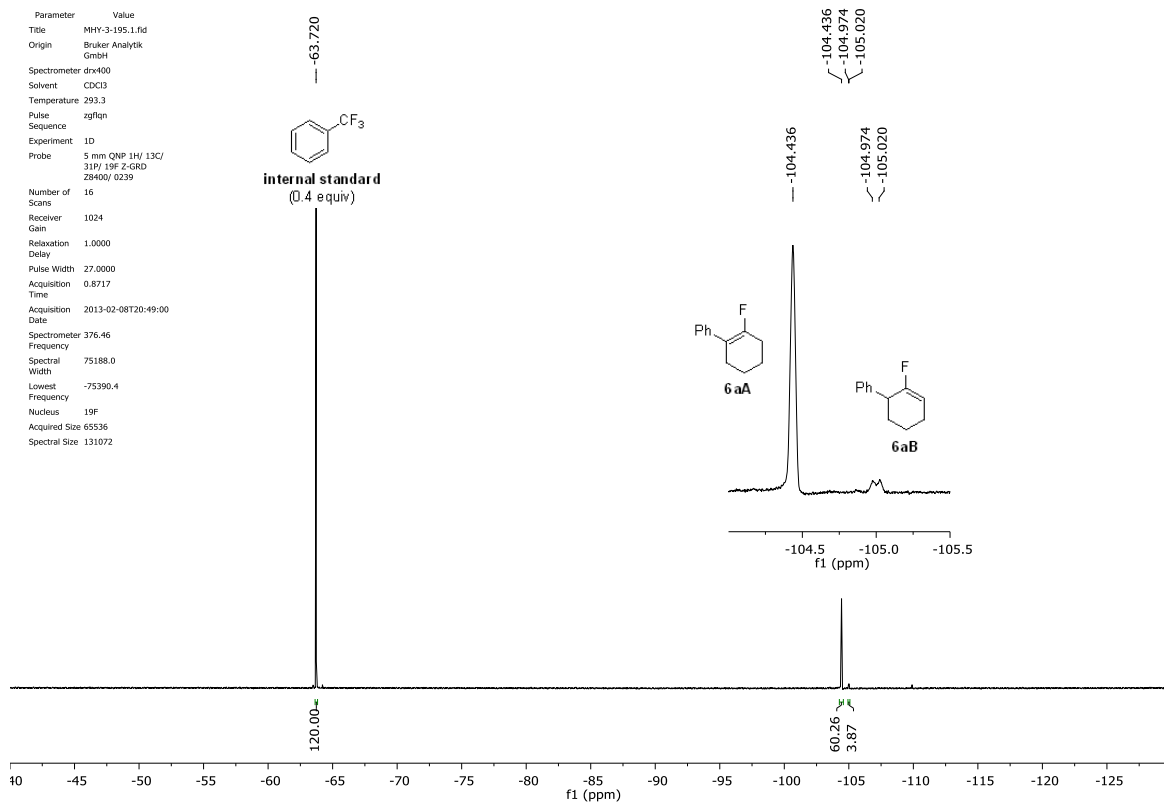
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Spectrometer	dx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zgfgn
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ Q239
Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-16T15:17:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75413.5
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

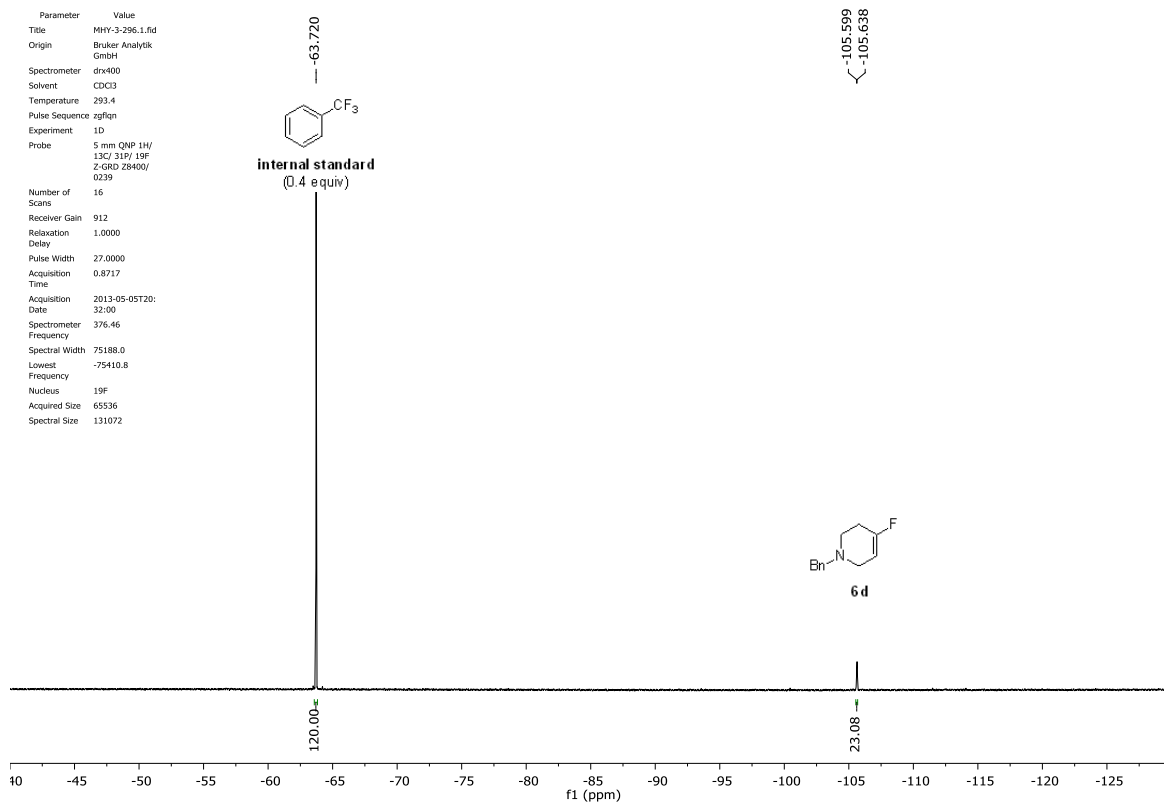
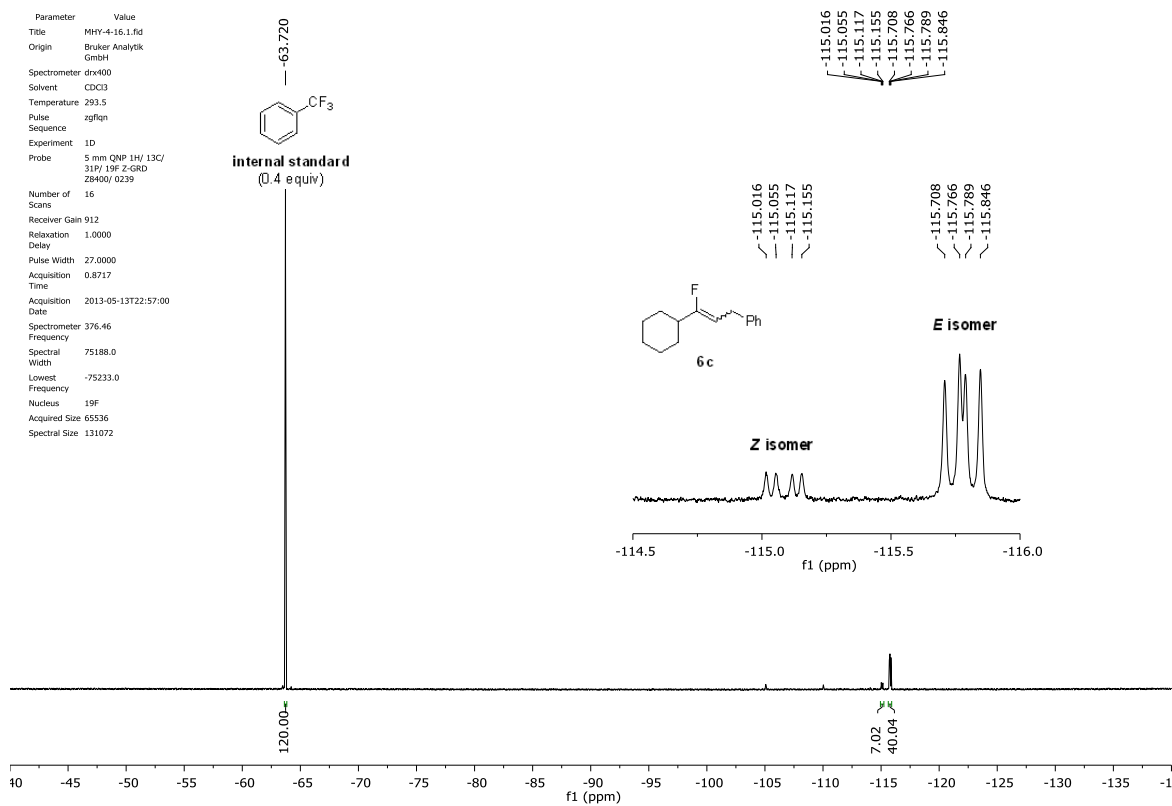




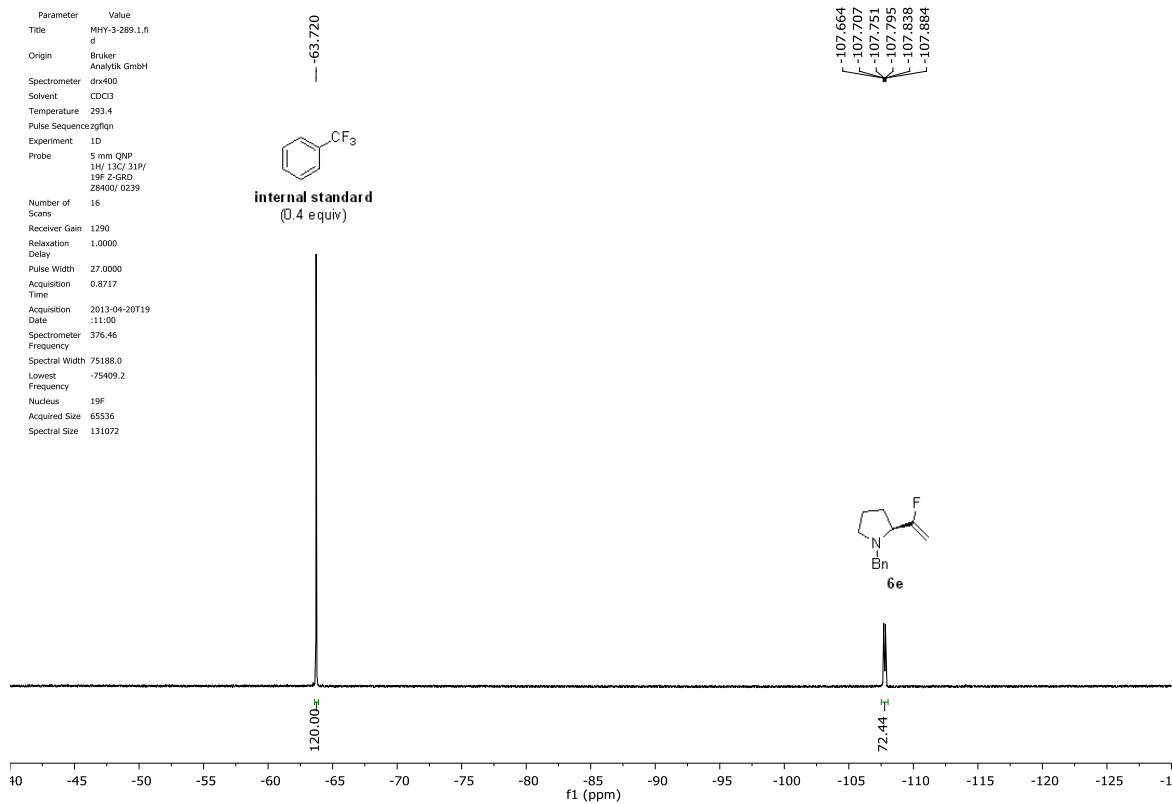




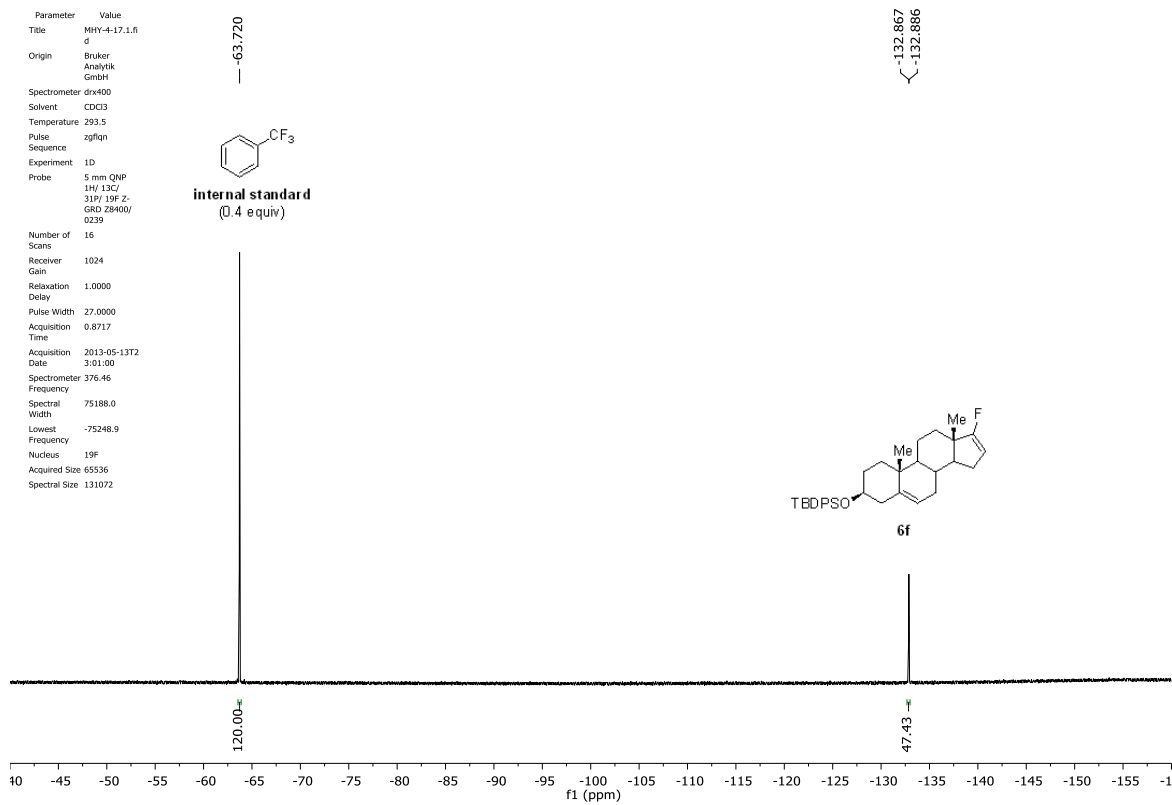


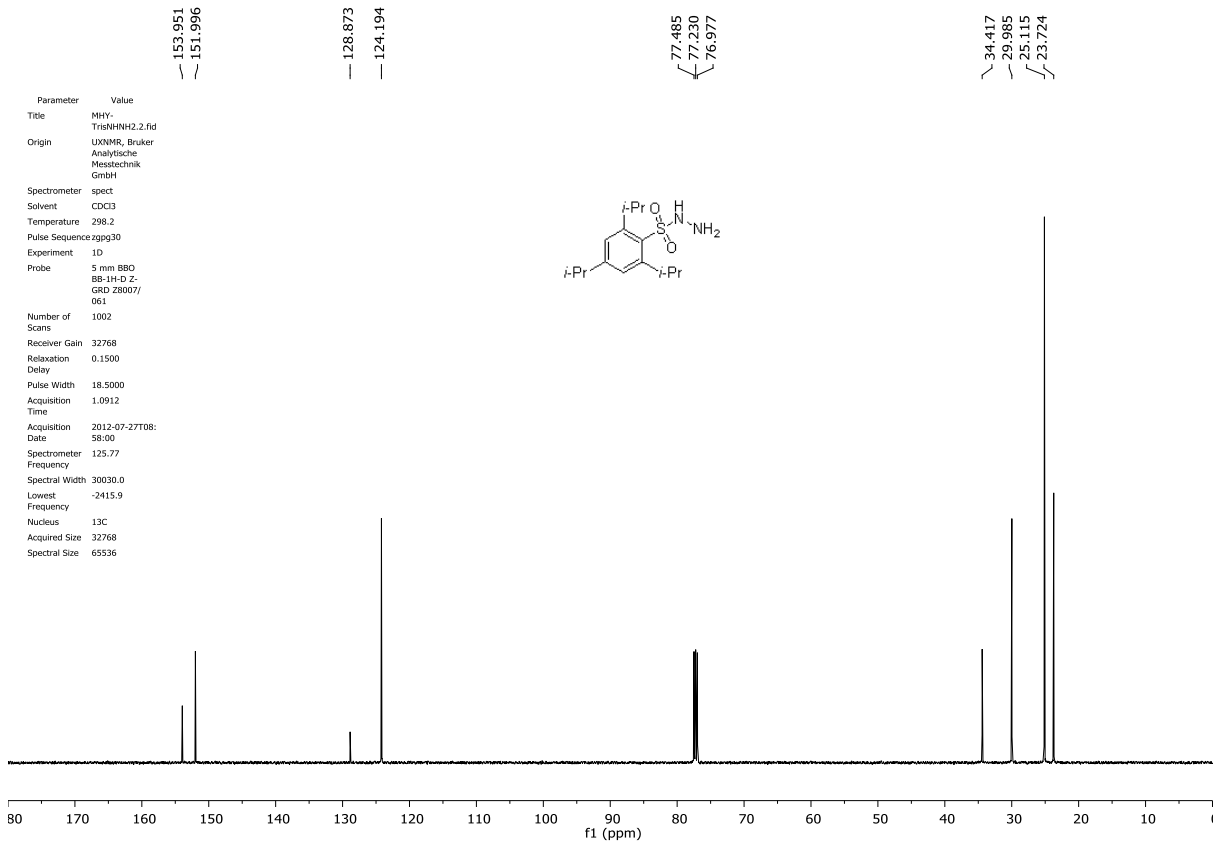
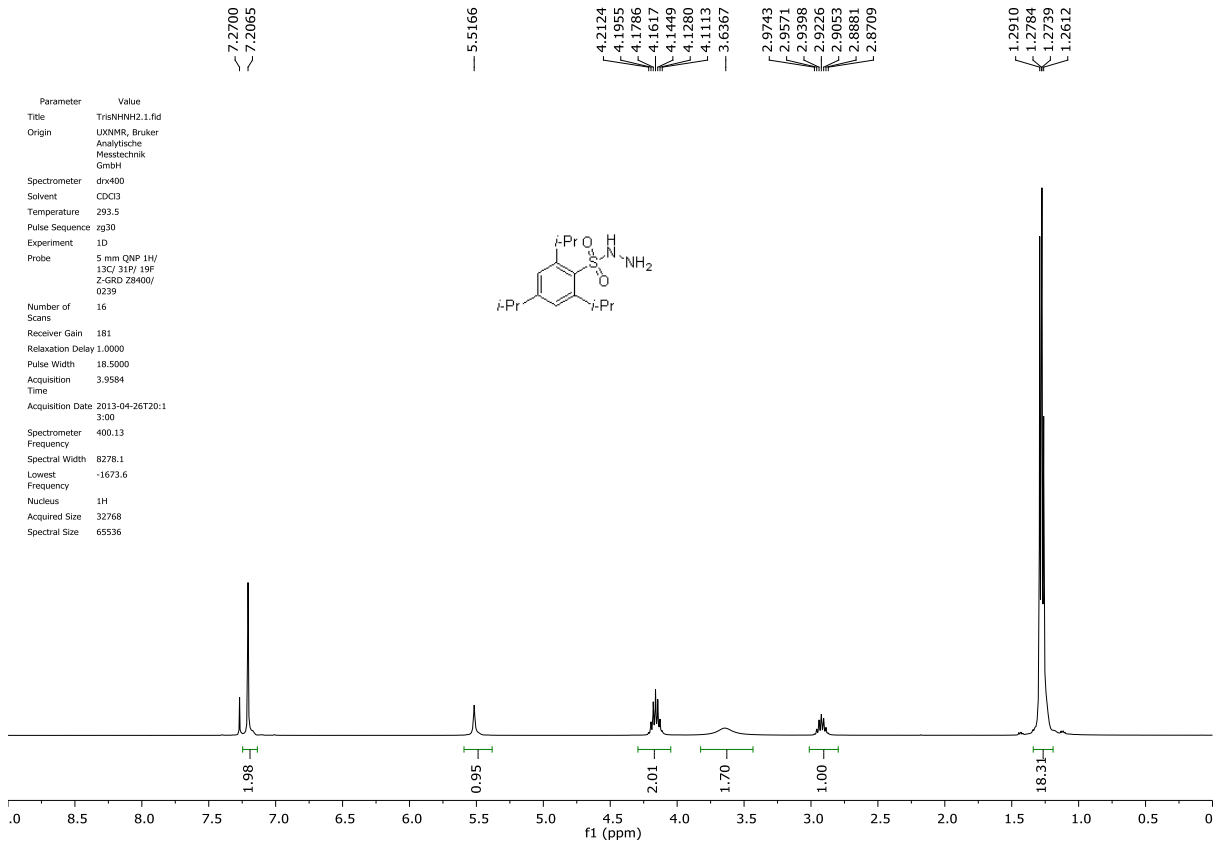


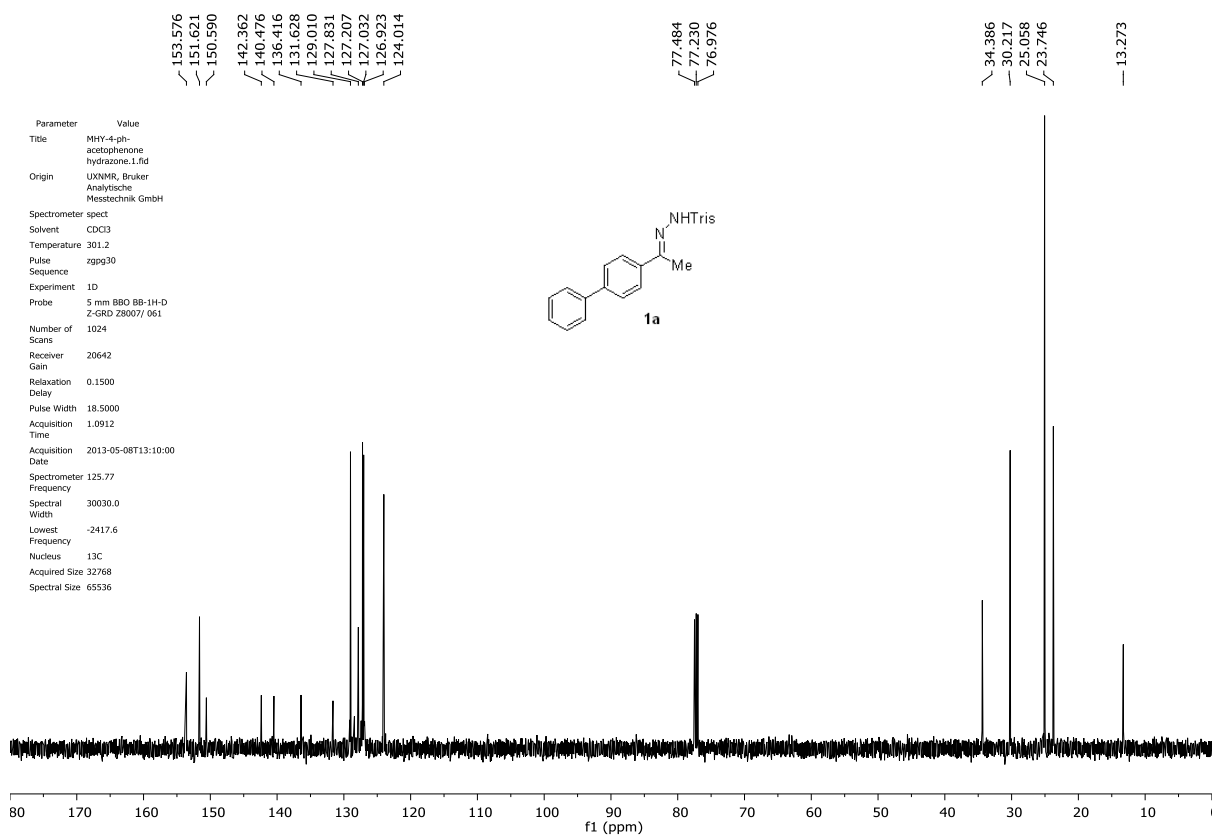
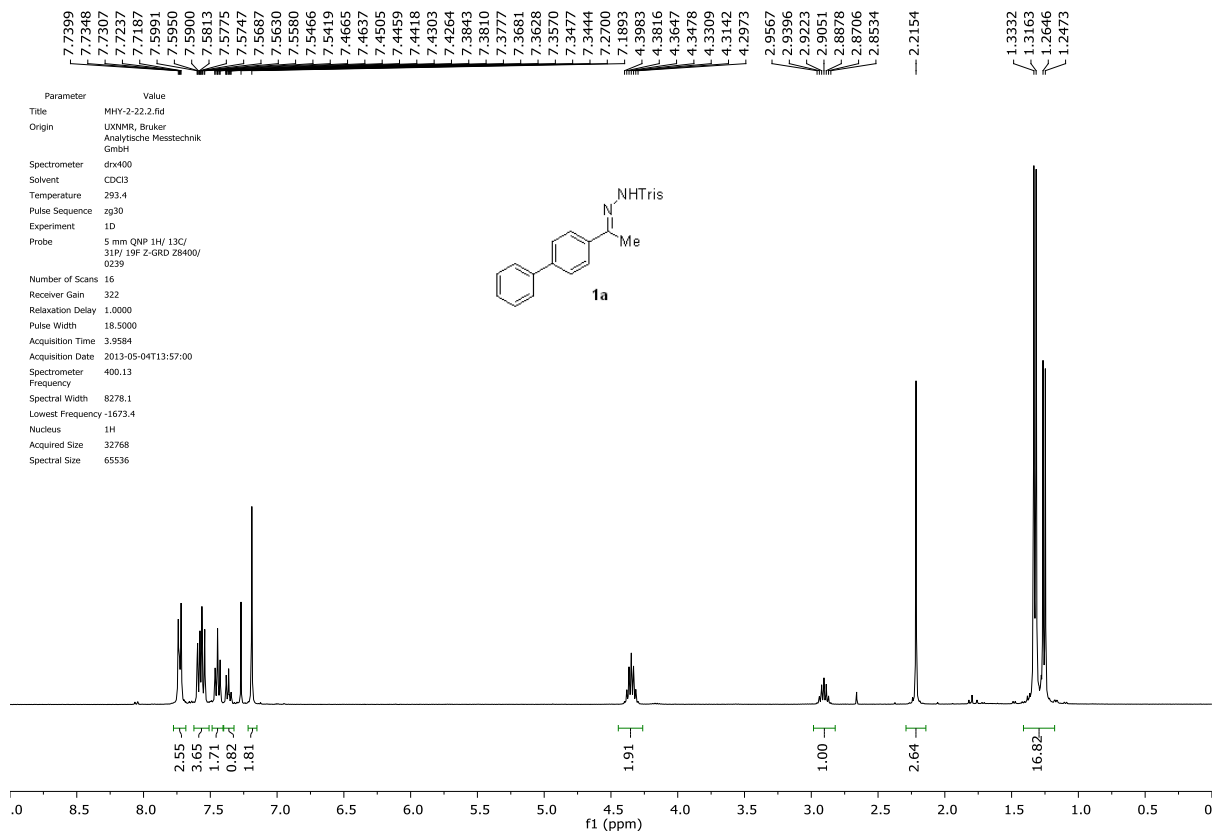
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Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgfgq
Experiment	1D
Probe	5 mm QNP 1H/13C/31P/19F Z-GRD Z8400/0239
Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-04-20T19:11:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75409.2
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

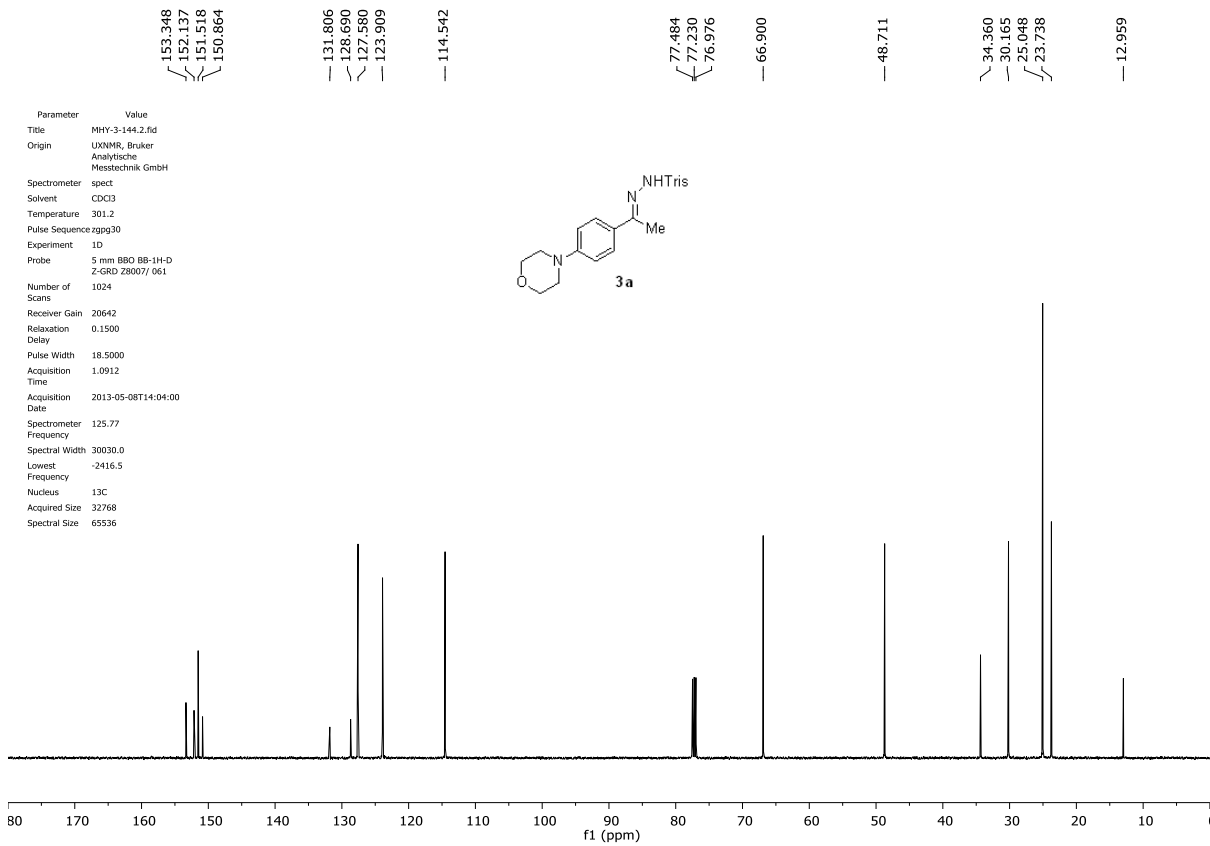
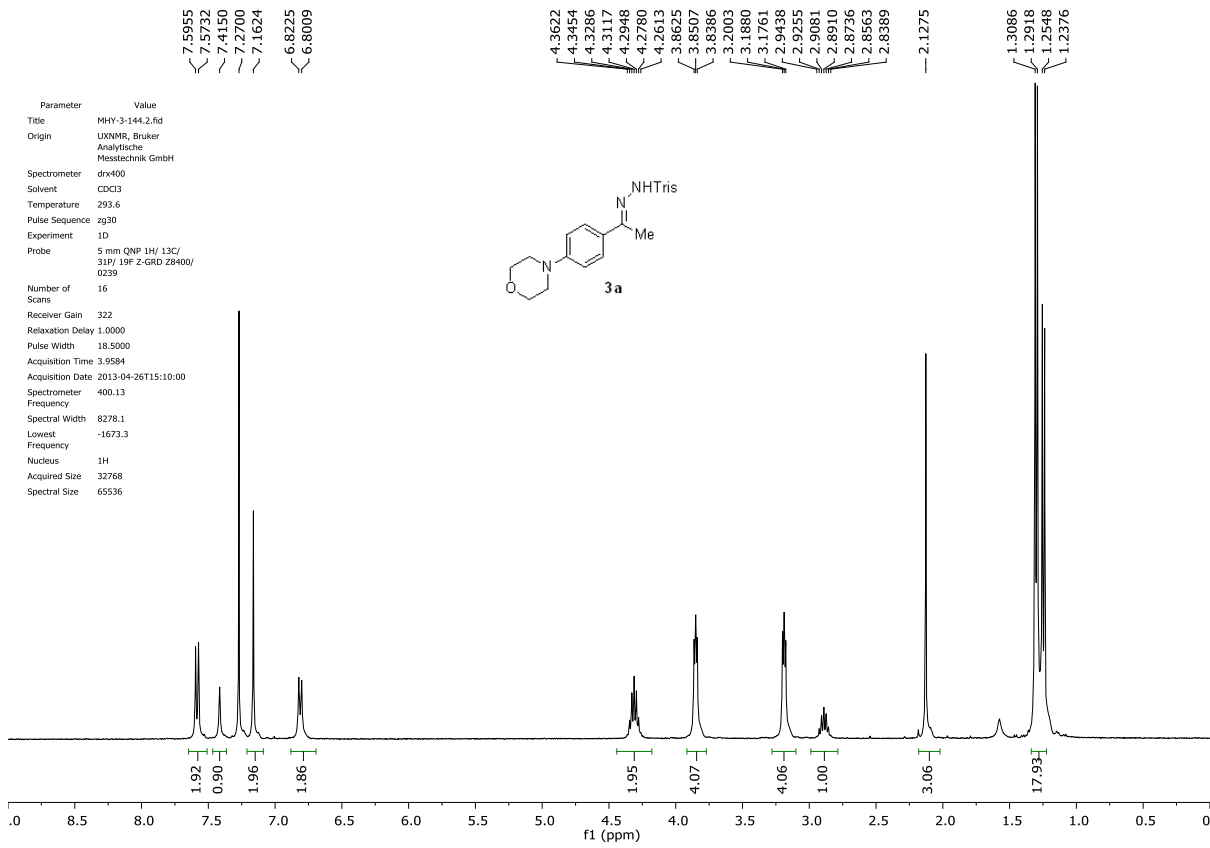


Parameter	Value
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Spectrometer	dx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgfgq
Experiment	1D
Probe	5 mm QNP 1H/13C/31P/19F Z-GRD Z8400/0239
Number of Scans	16
Receiver Gain	1024
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-05-13T2:30:00
Spectrometer Frequency	376.46
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Lowest Frequency	-75248.9
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Acquired Size	65536
Spectral Size	131072









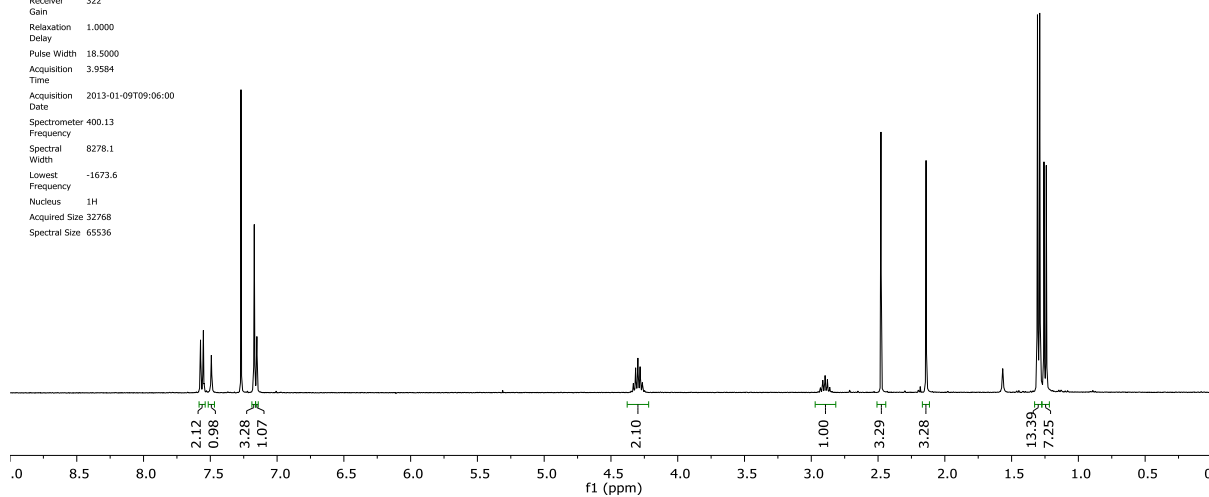
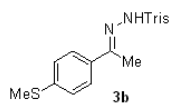
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4.2985
4.2817
4.2648
4.2480

2.9467
2.9312
2.9139
2.8965
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2.1401

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1.2399

Parameter Value
Title 4-SMe-
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Origin UXNMR, Bruker
Analytische
Messtechnik GmbH
Spectrometer dx400
Solvent CDCl3
Temperature 293.6
Pulse zg30
Sequence
Experiment 1D
Probe 5 mm QNP 1H/ 13C/
31P/ 19F 2-GRD
Z8400/ 0239
Number of
Scans 16
Receiver 322
Gain
Relaxation 1.0000
Delay
Pulse Width 18.5000
Acquisition 3.9584
Time
Acquisition 2013-01-09T09:06:00
Date
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Width
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Frequency
Nucleus 1H
Acquired Size 32768
Spectral Size 65536

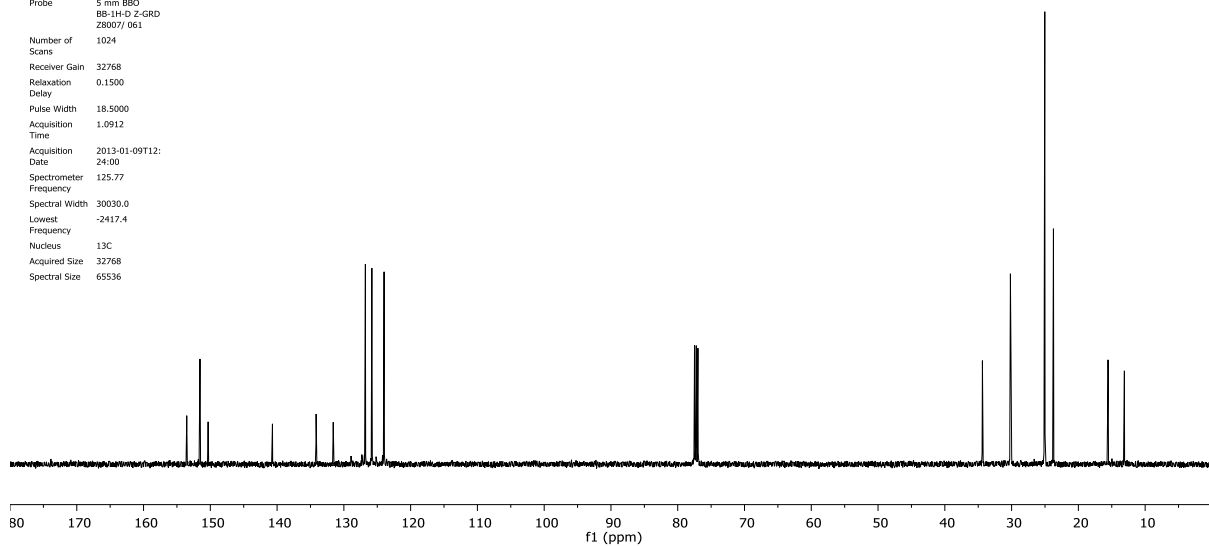
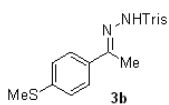


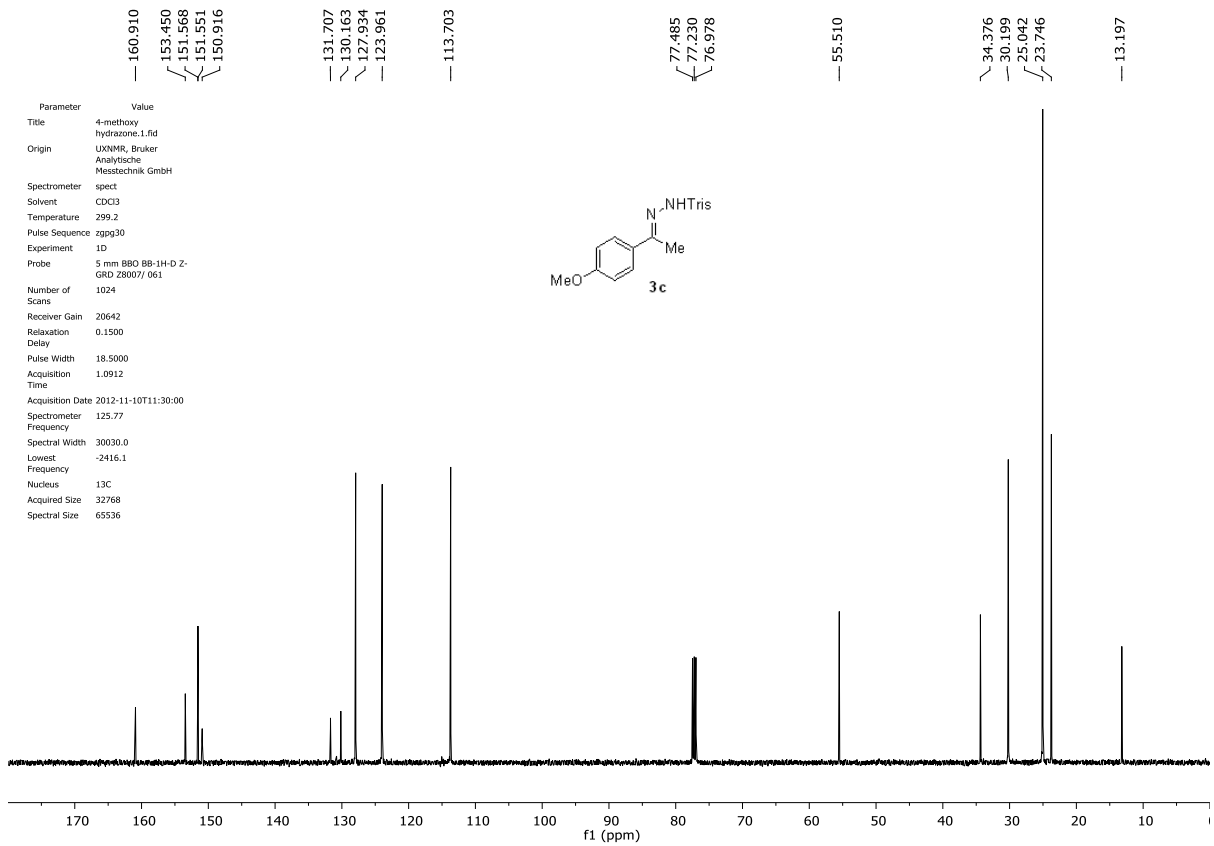
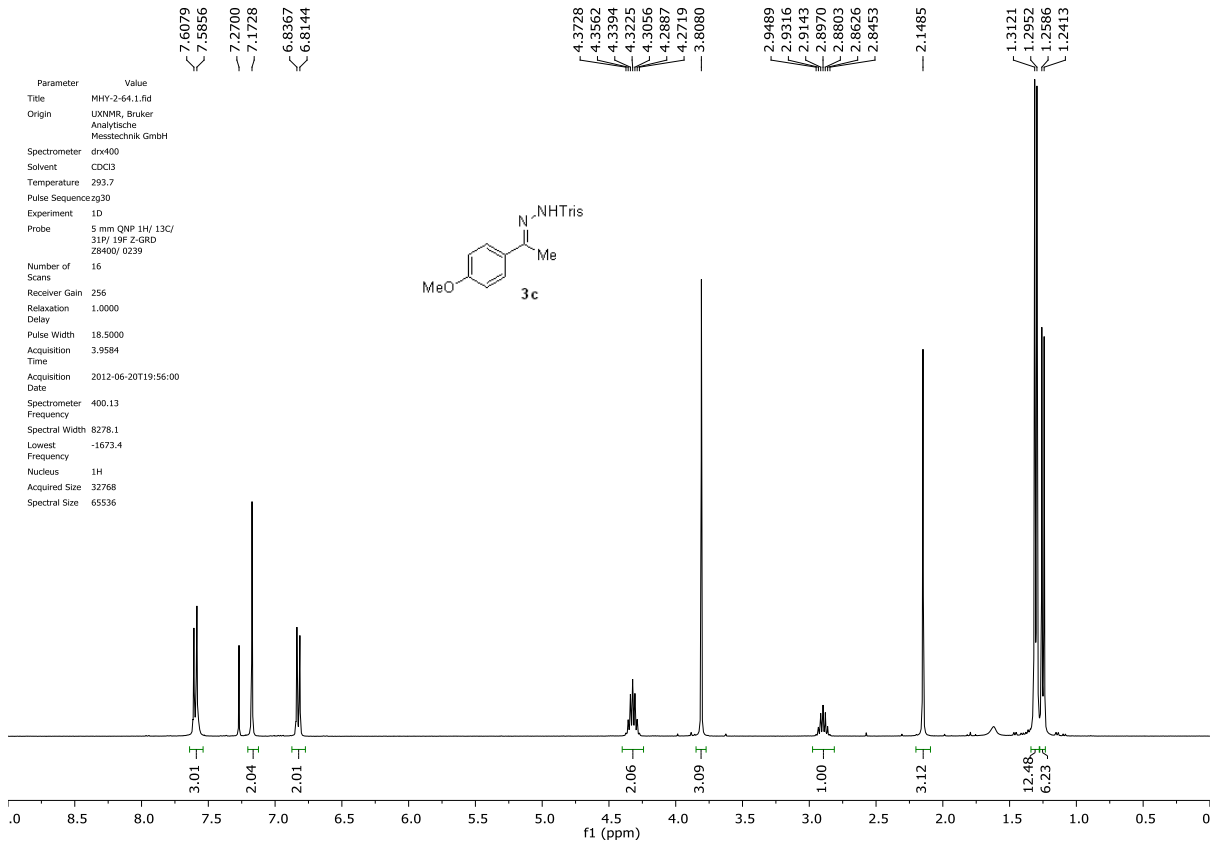
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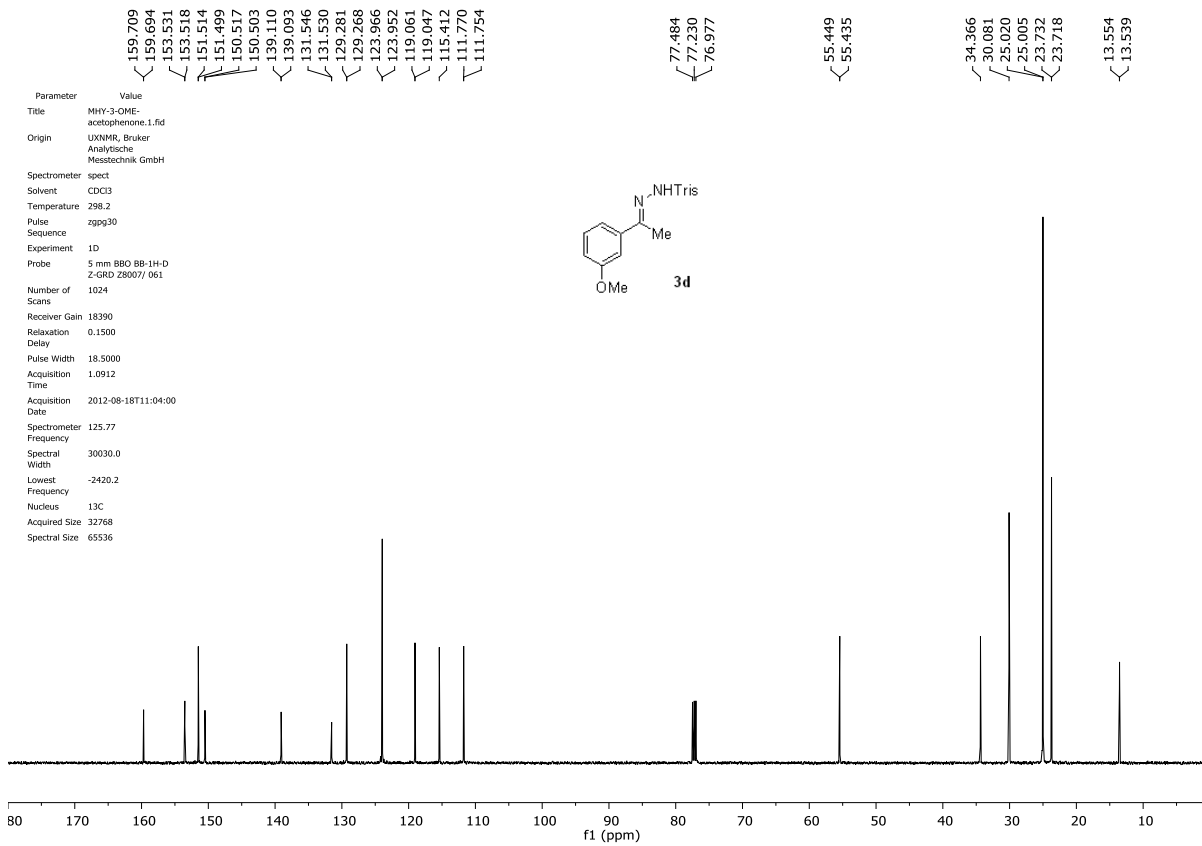
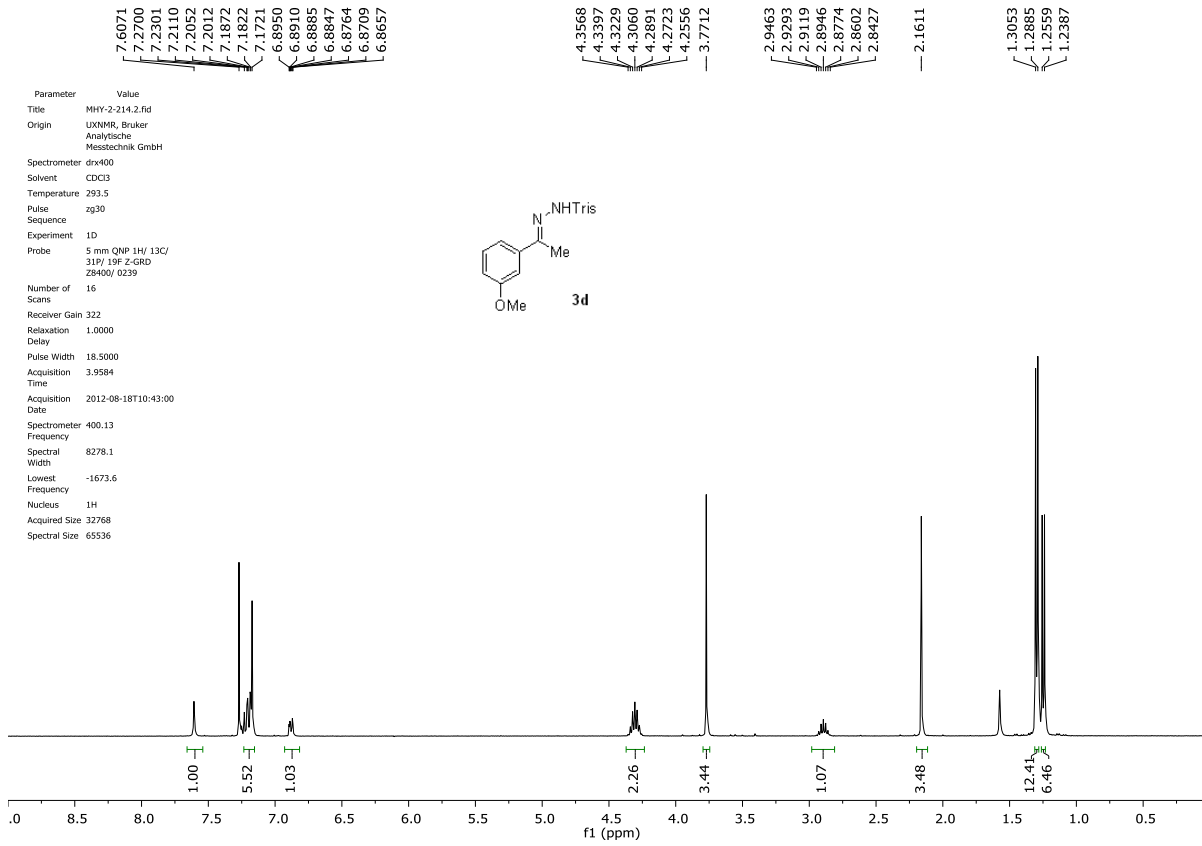
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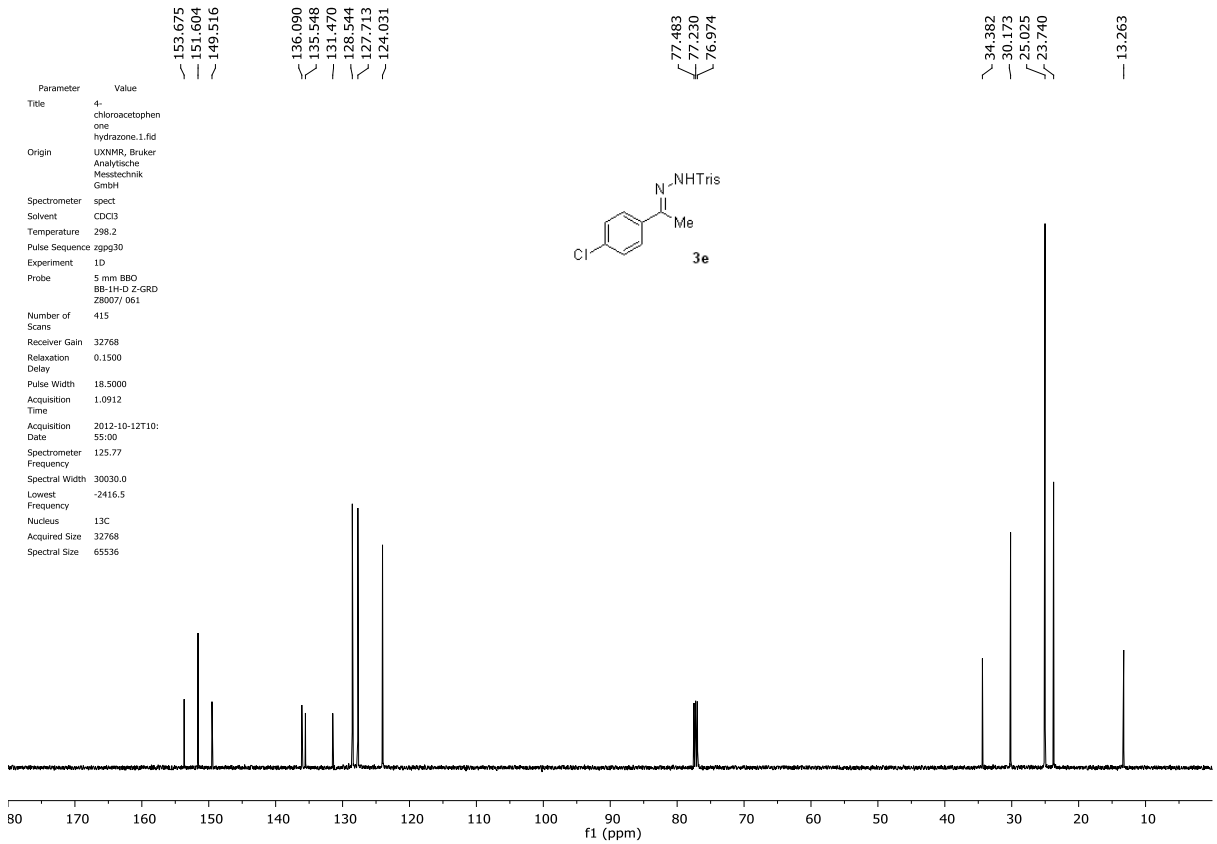
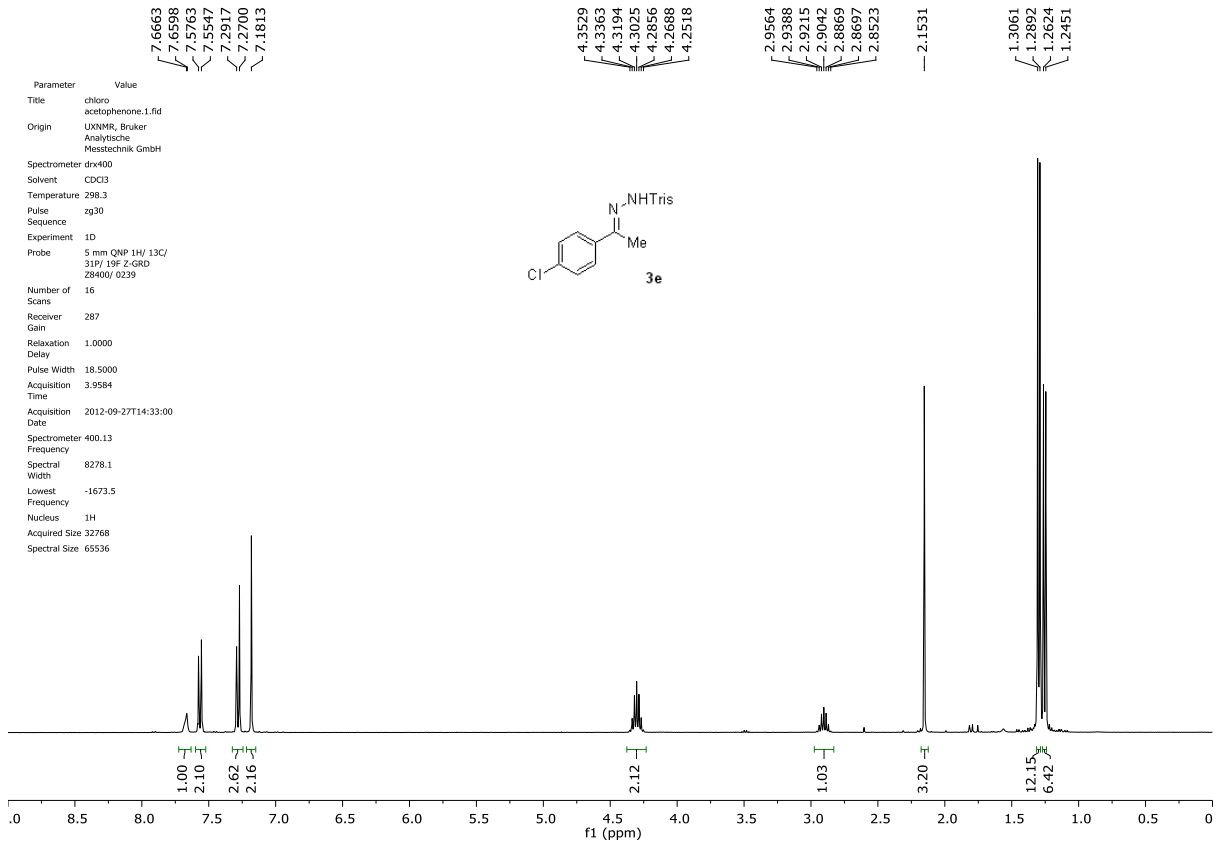
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Title 4-SMe-
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Origin UXNMR, Bruker
Analytische
Messtechnik
GmbH
Spectrometer spect
Solvent CDCl3
Temperature 299.2
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm BBO
BB-1H-D 2-GRD
Z8007/ 061
Number of
Scans 1024
Receiver Gain 32768
Relaxation 0.1500
Delay
Pulse Width 18.5000
Acquisition 1.0912
Time
Acquisition 2013-01-09T12:
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Spectral Size 65536

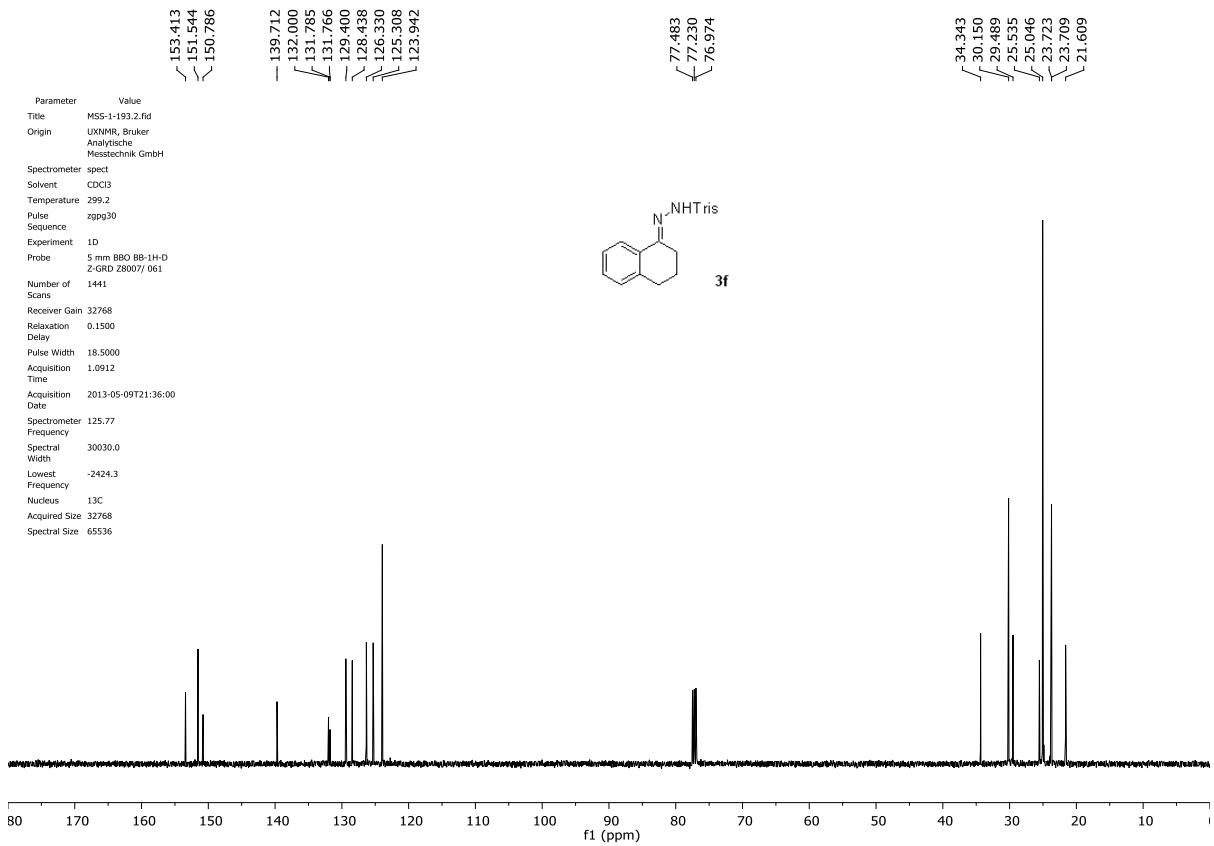
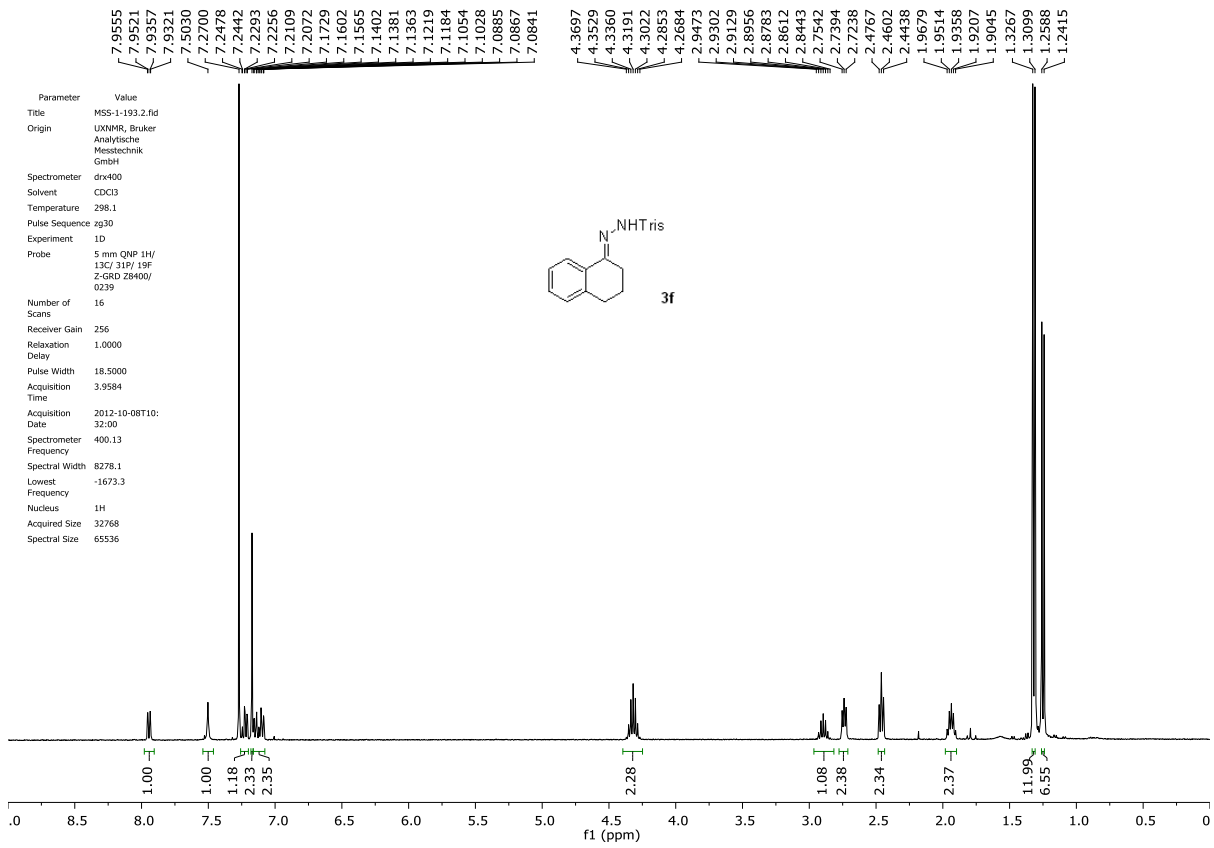


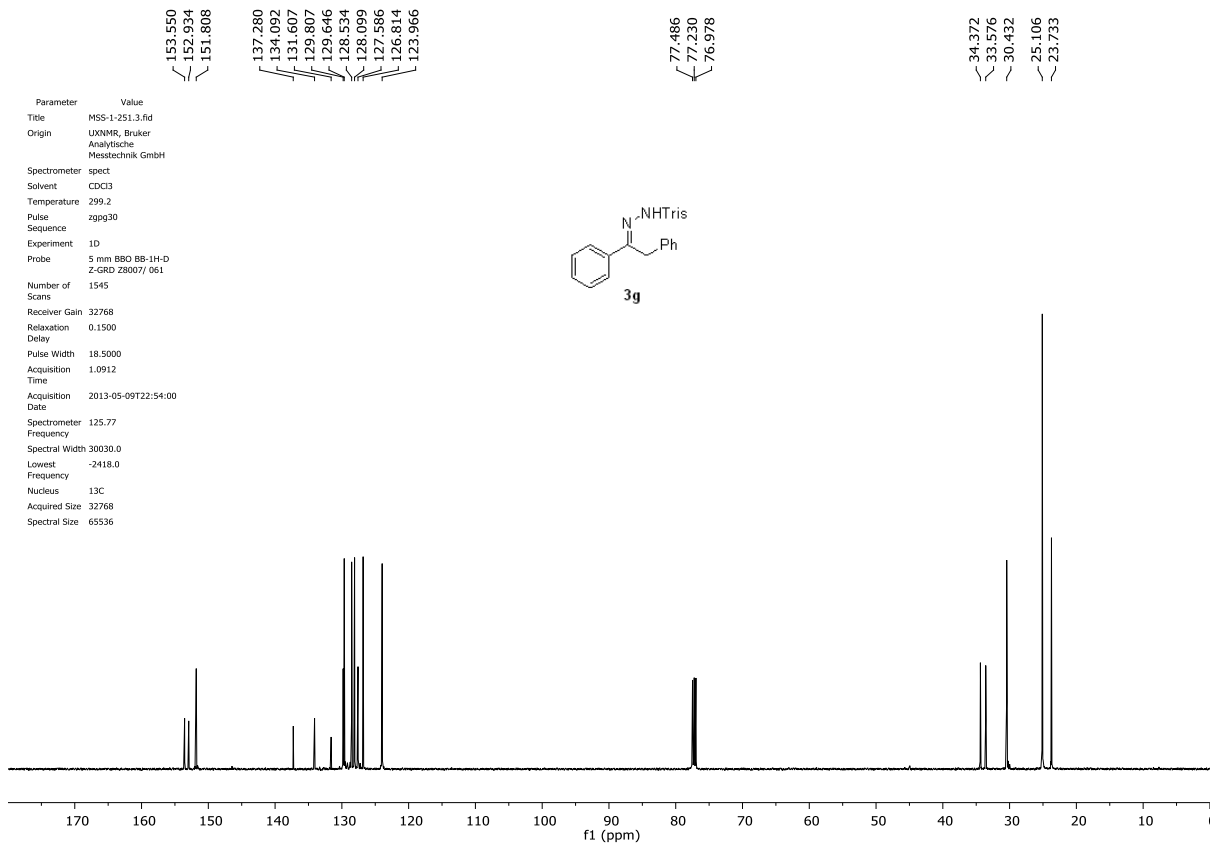
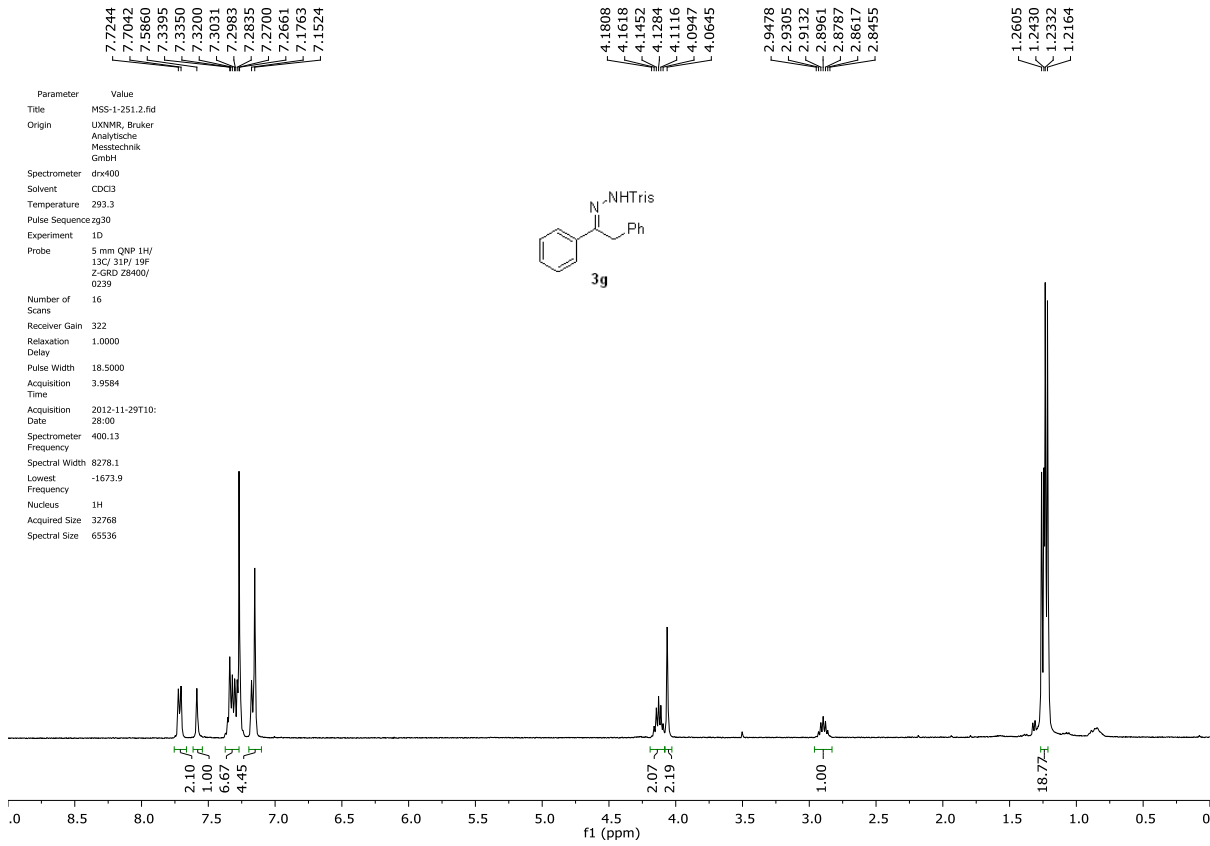


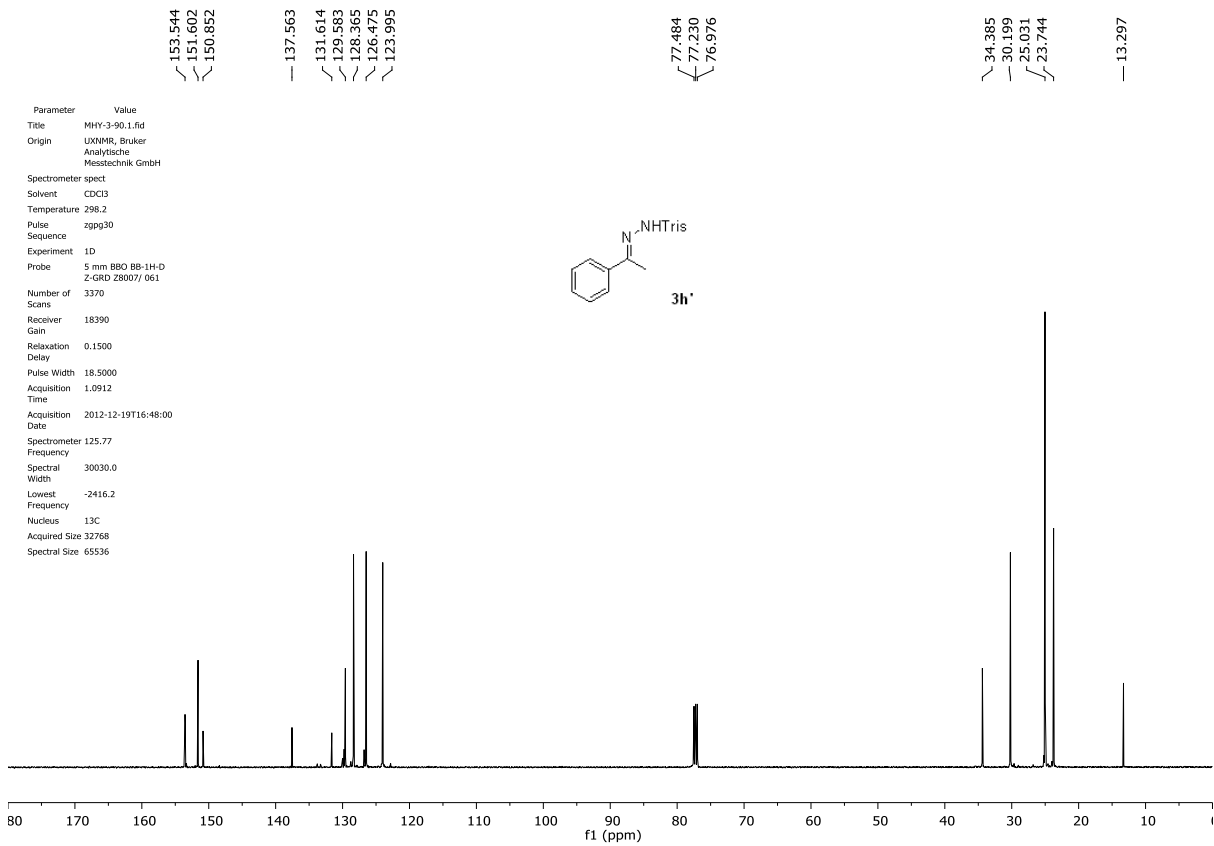
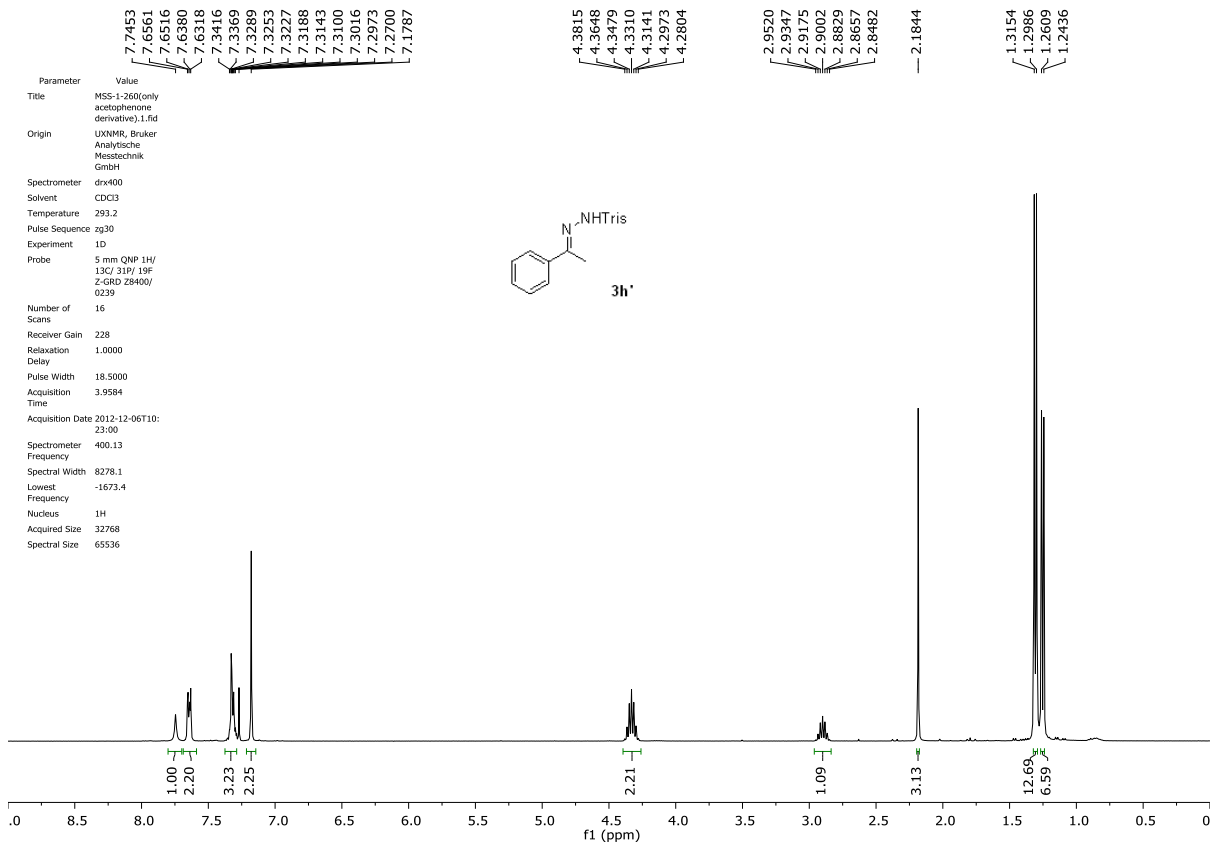
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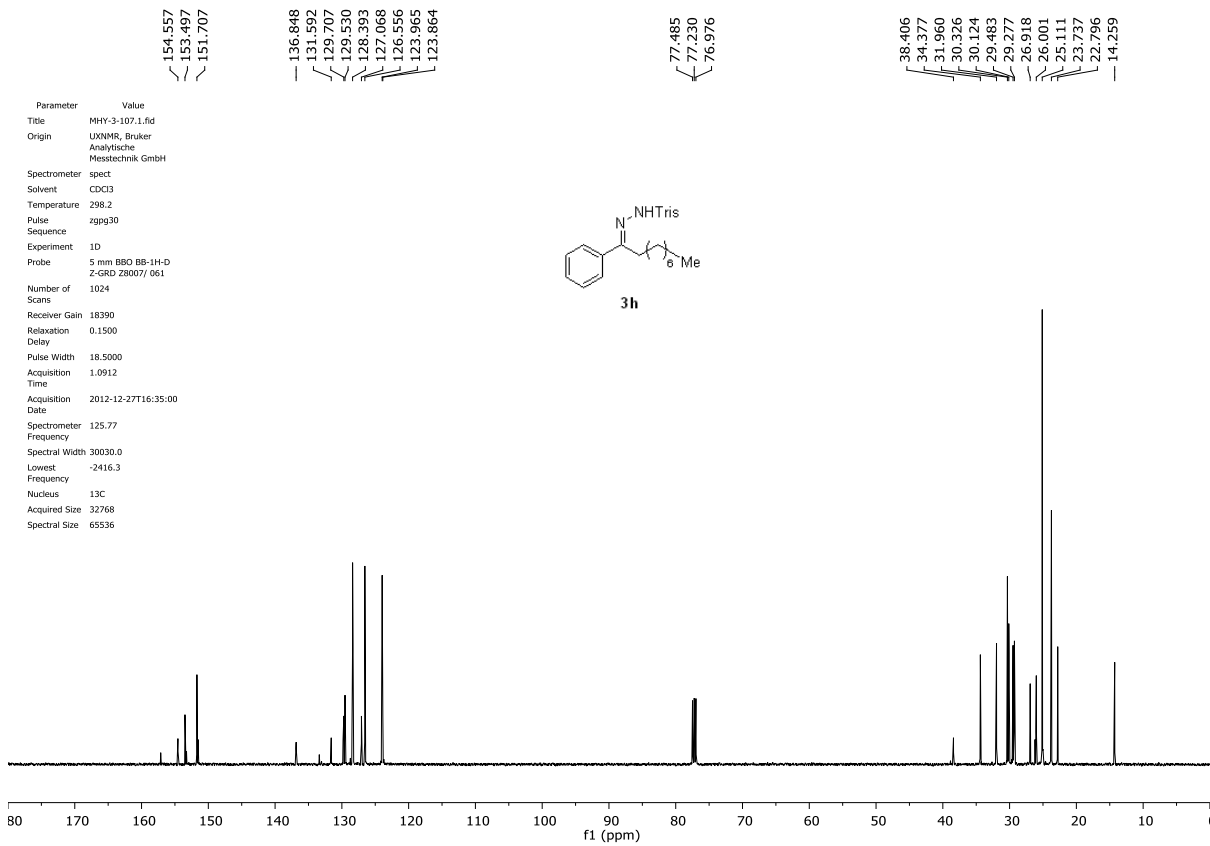
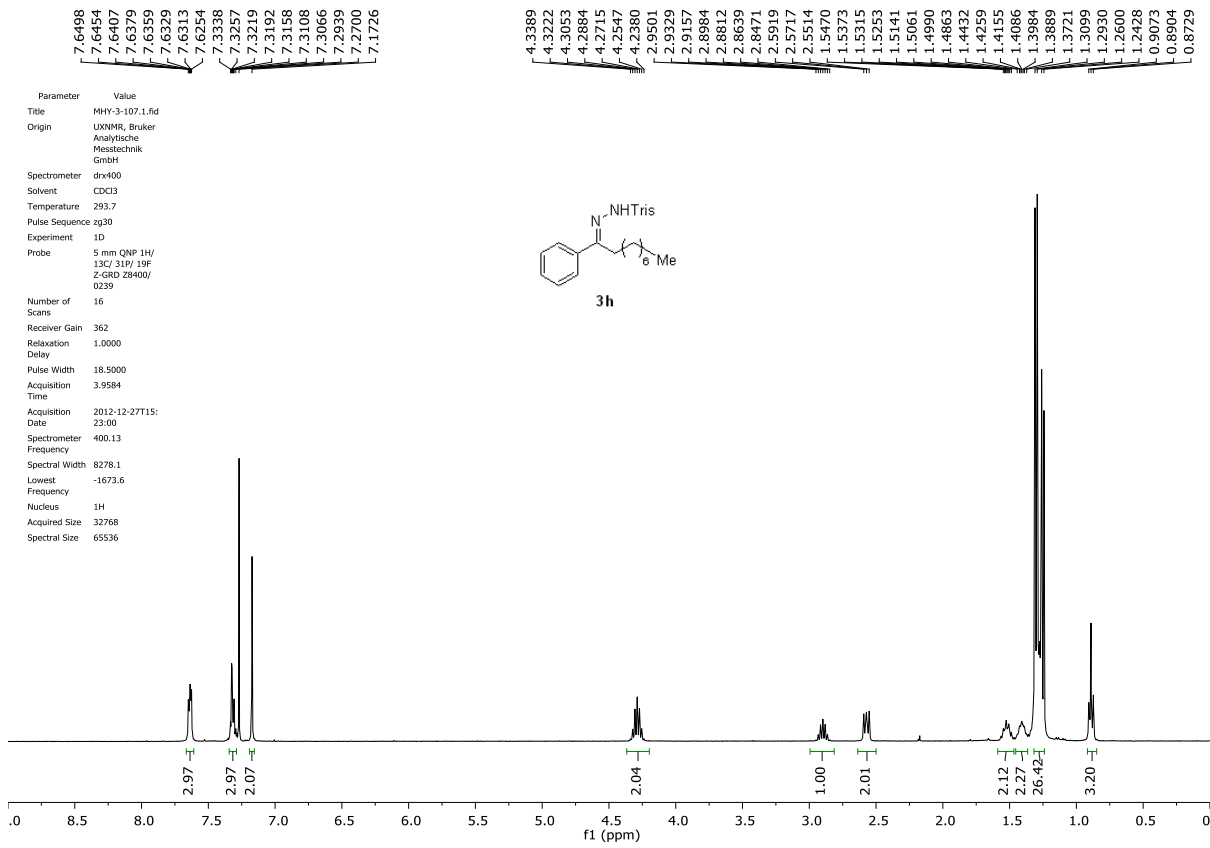












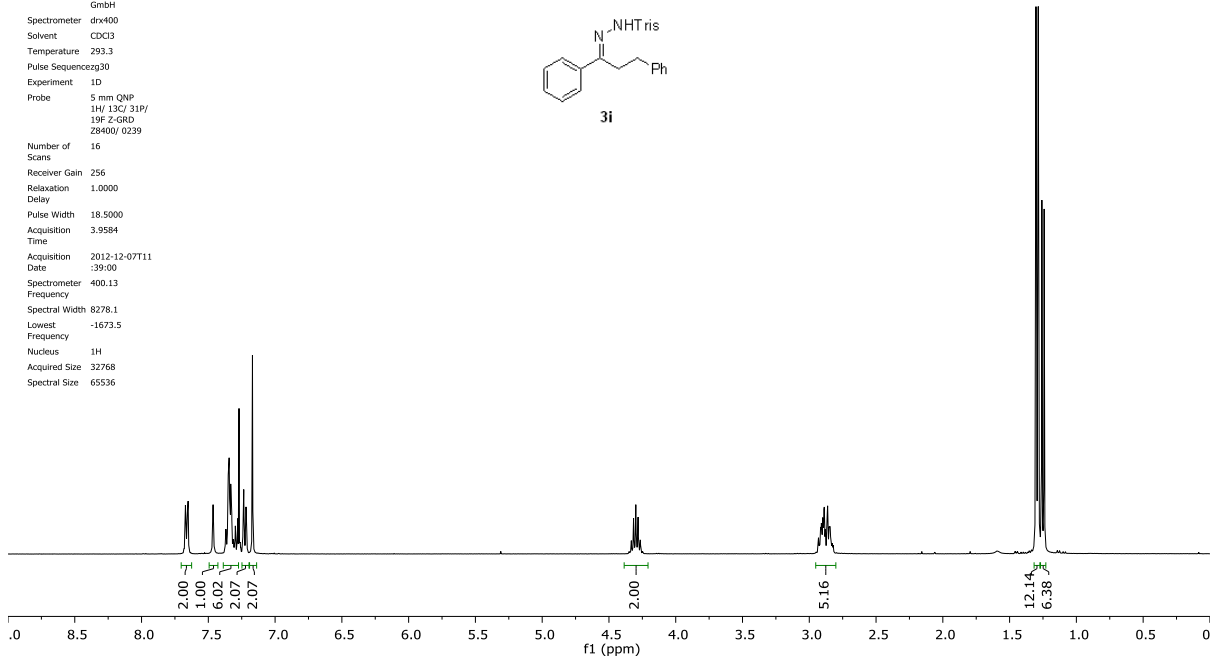
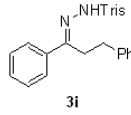
SI-46

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Parameter Value
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Solvent CDCl3
Temperature 293.3
Pulse Sequence zg30
Experiment 1D
Probe 5 mm QNP 1H/13C/31P/19F Z-GRD Z8400/0239
Number of Scans 16
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Relaxation Delay 1.0000
Pulse Width 18.5000
Acquisition Time 3.9584
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Spectral Size 65536

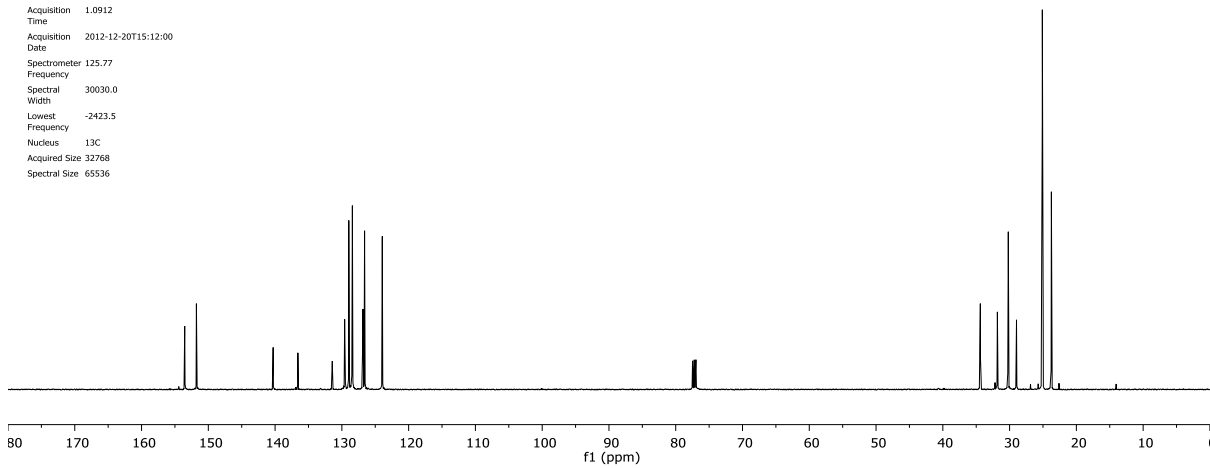
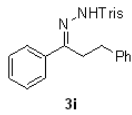


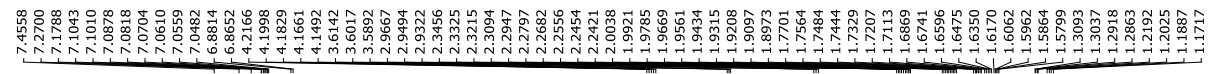
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76.976

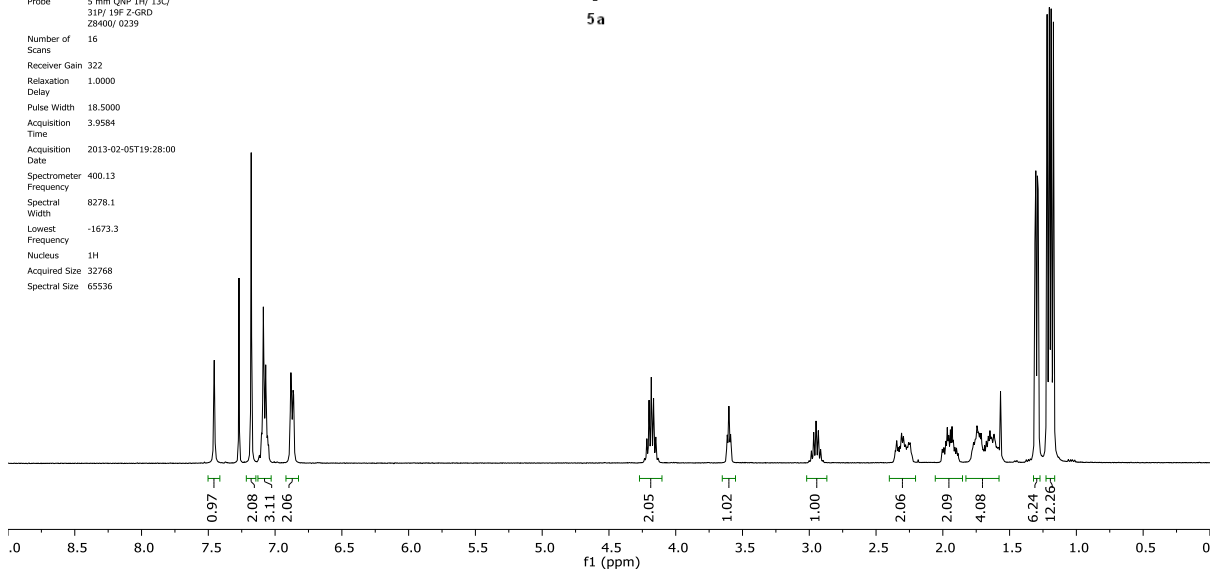
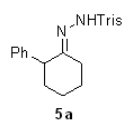
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Parameter Value
Title MHY-3-102.1.fid
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer spect
Solvent CDCl3
Temperature 298.2
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm BBO BB-1H-D Z-GRD Z80007/061
Number of Scans 2370
Receiver Gain 26008
Relaxation Delay 0.1500
Pulse Width 18.5000
Acquisition Time 1.0912
Date 2012-12-20T15:12:00
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Frequency 30030.0
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Nucleus 13C
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Spectral Size 65536

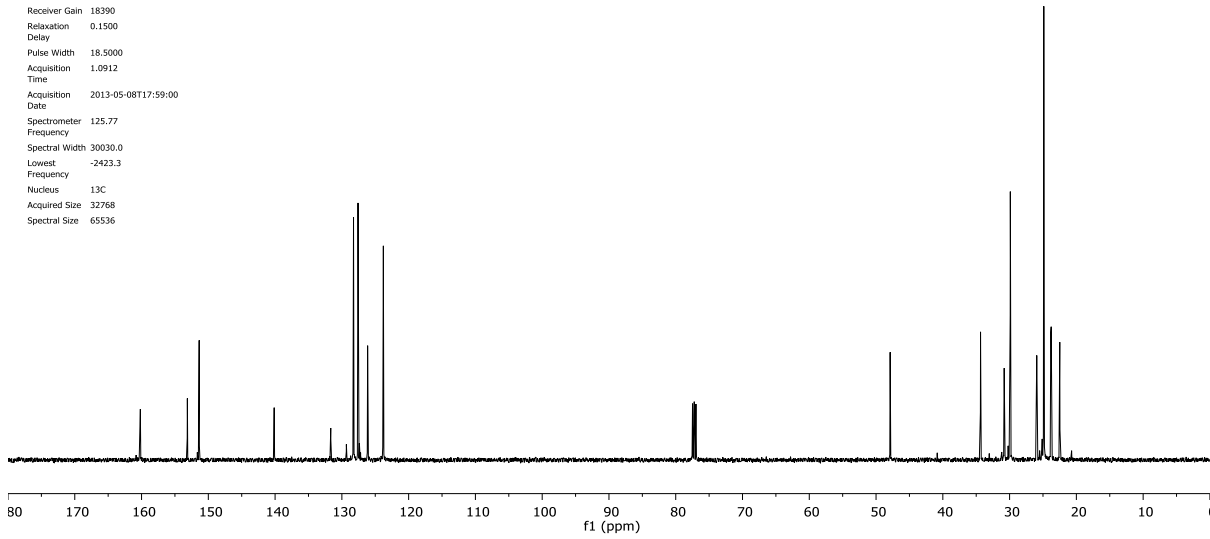
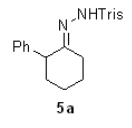


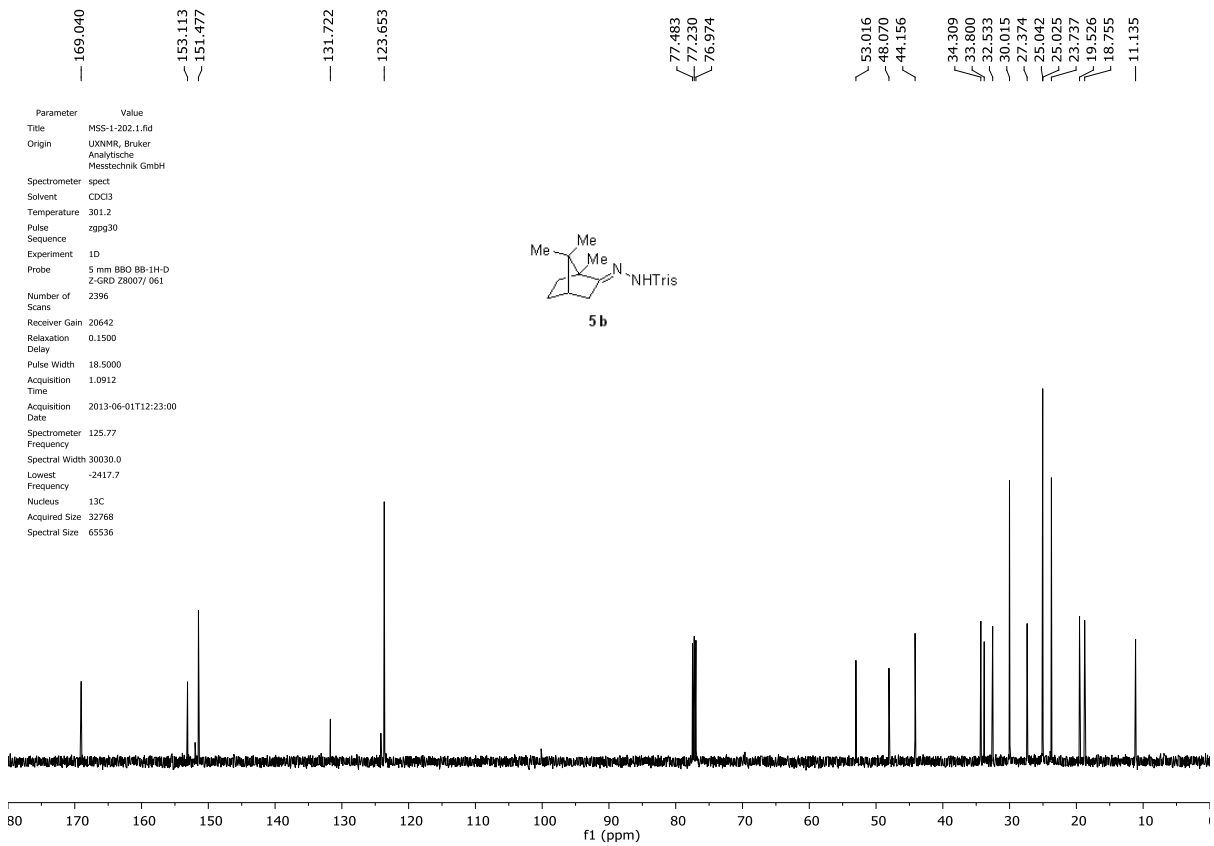
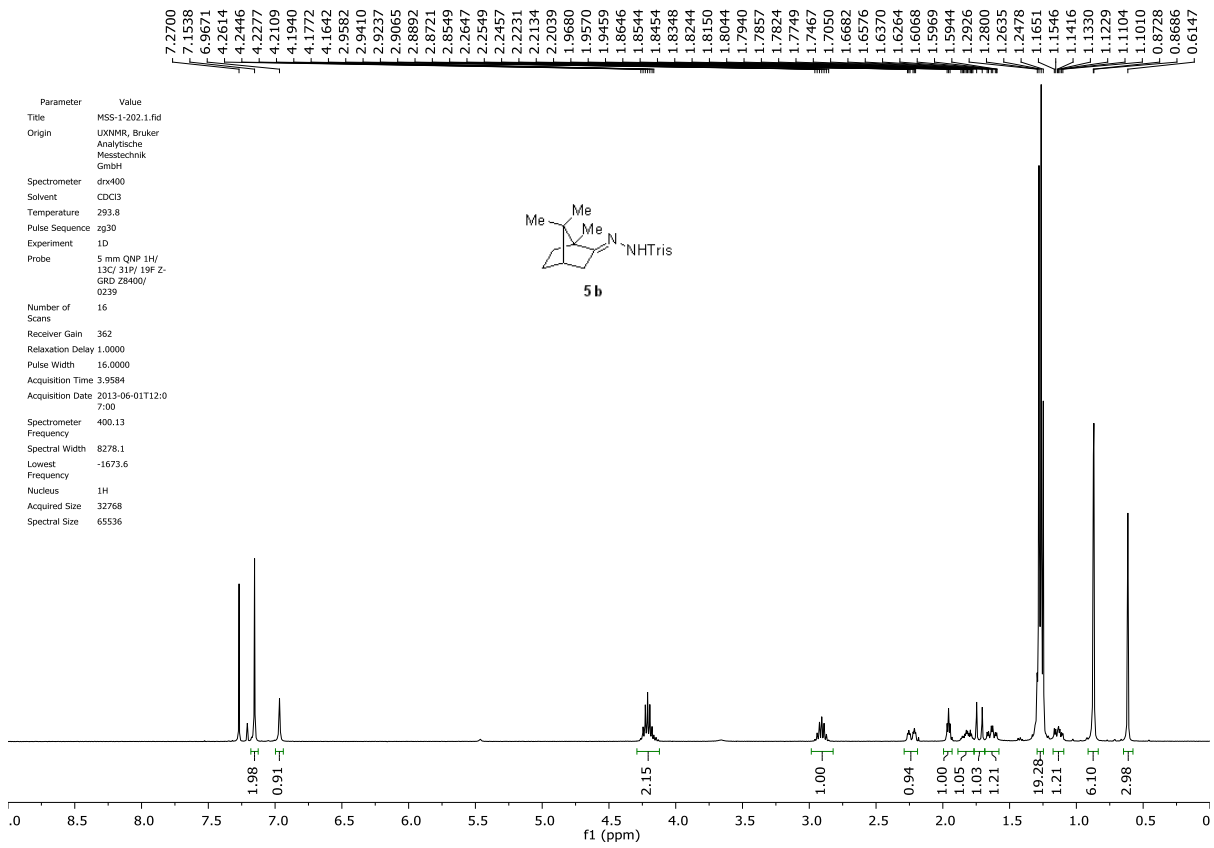


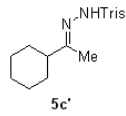
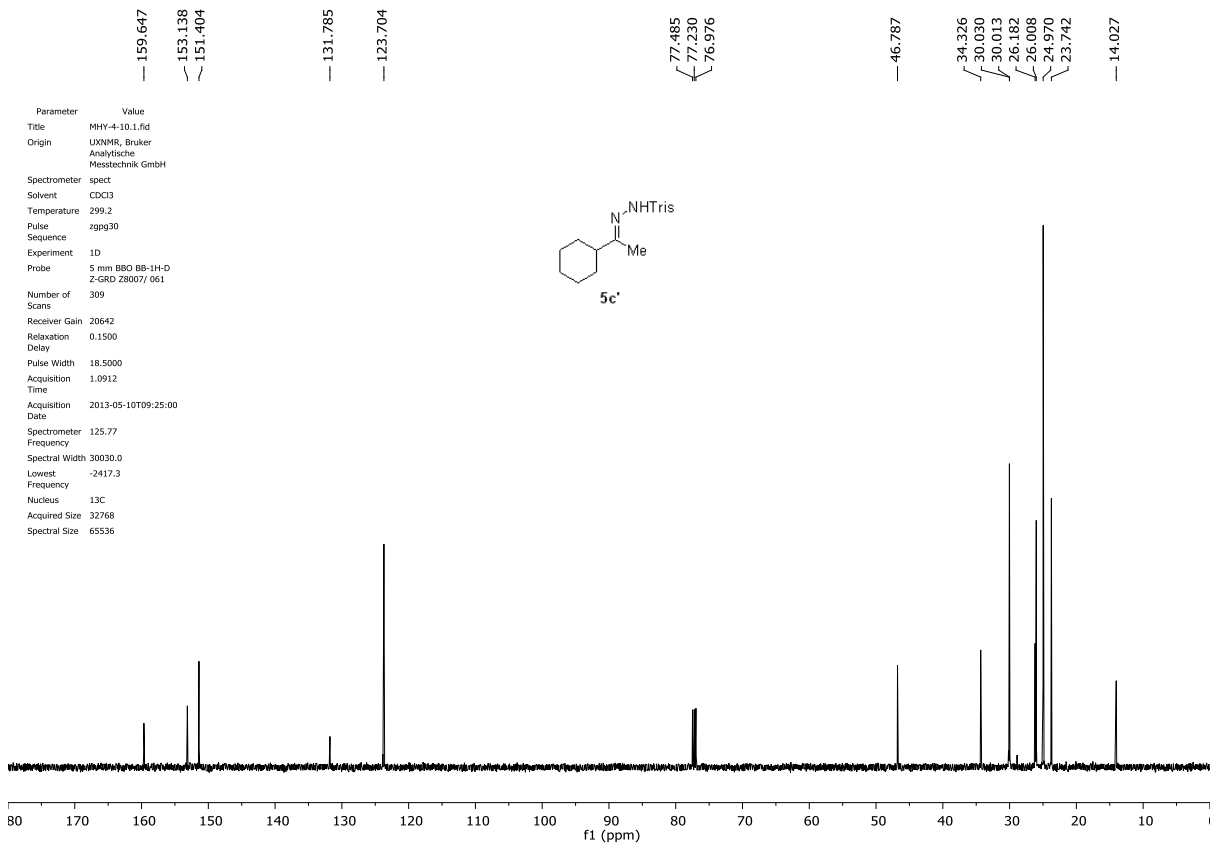
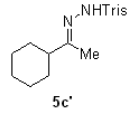
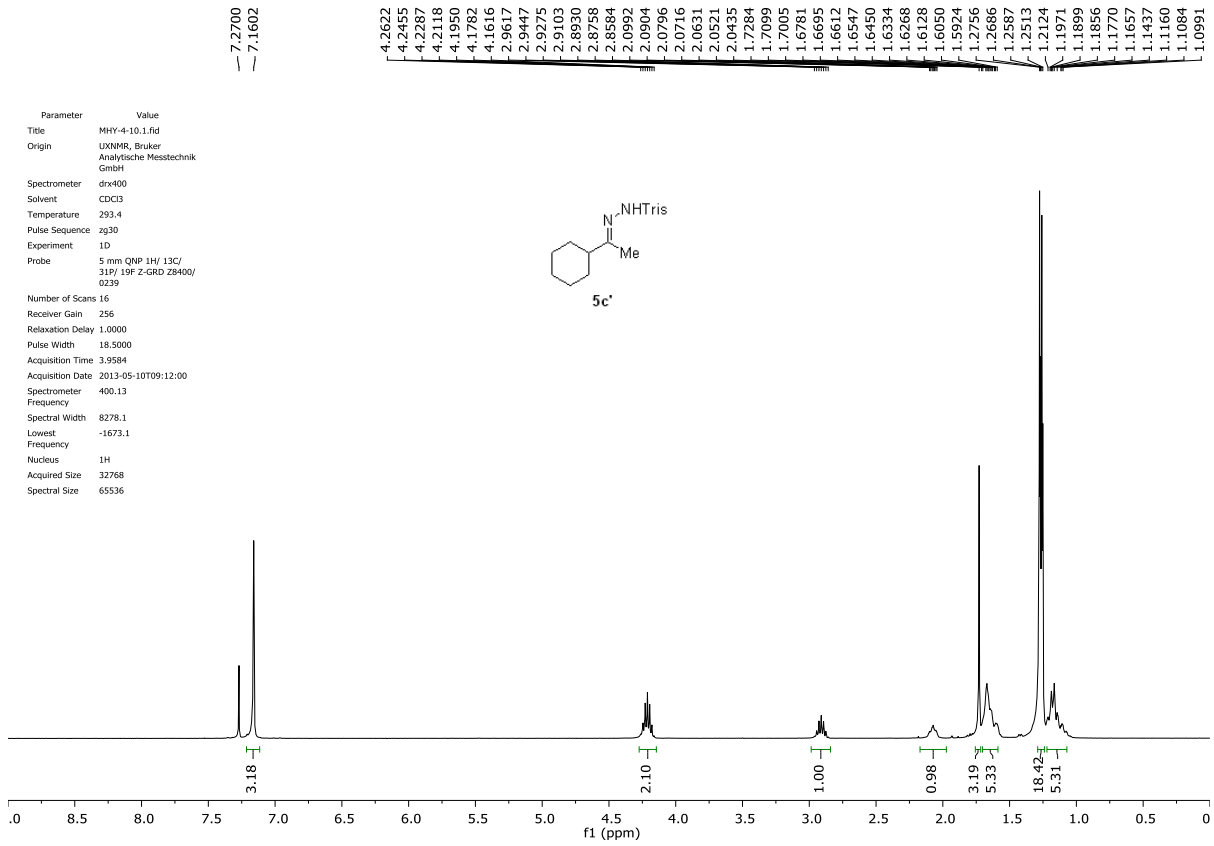
Parameter	Value
Title	2-Ph-cyclohexane-Tris.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.4
Pulse	zg30
Sequence	
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	322
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-02-05T19:28:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



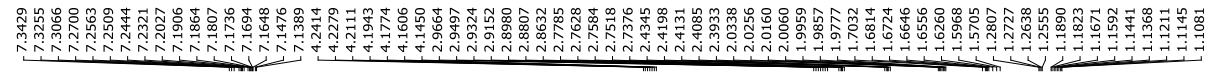
Parameter	Value
Title	MSS-1-161.7.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	300.2
Pulse	zpgg30
Sequence	
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD Z8007/ 061
Number of Scans	286
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	18.5000
Acquisition Time	1.0912
Acquisition Date	2013-05-08T17:59:00
Spectrometer Frequency	125.77
Spectral Width	30030.0
Lowest Frequency	-2423.3
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



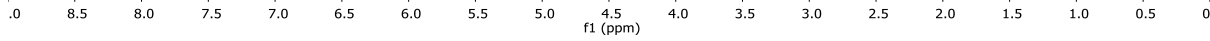
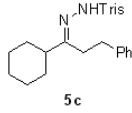




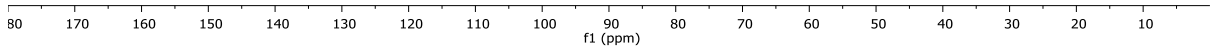
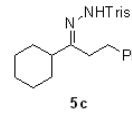
SI-50

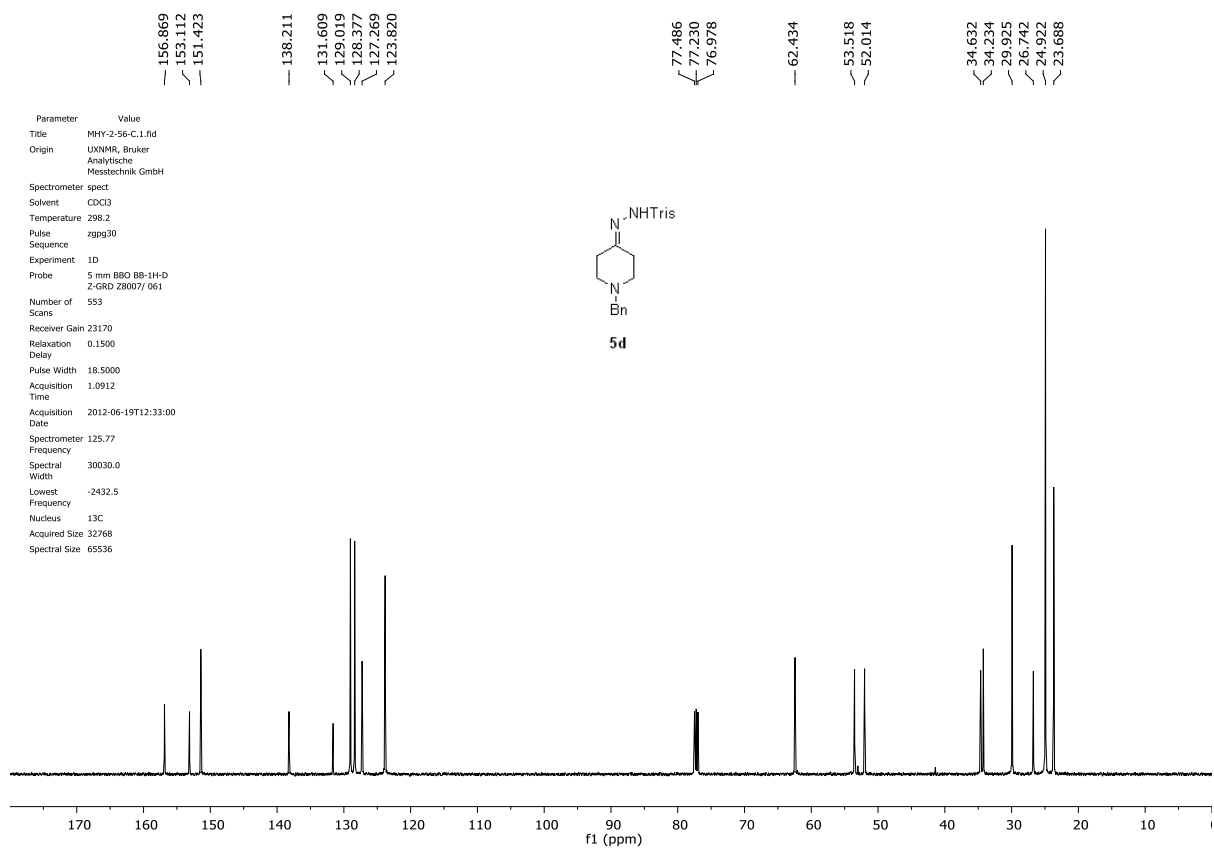
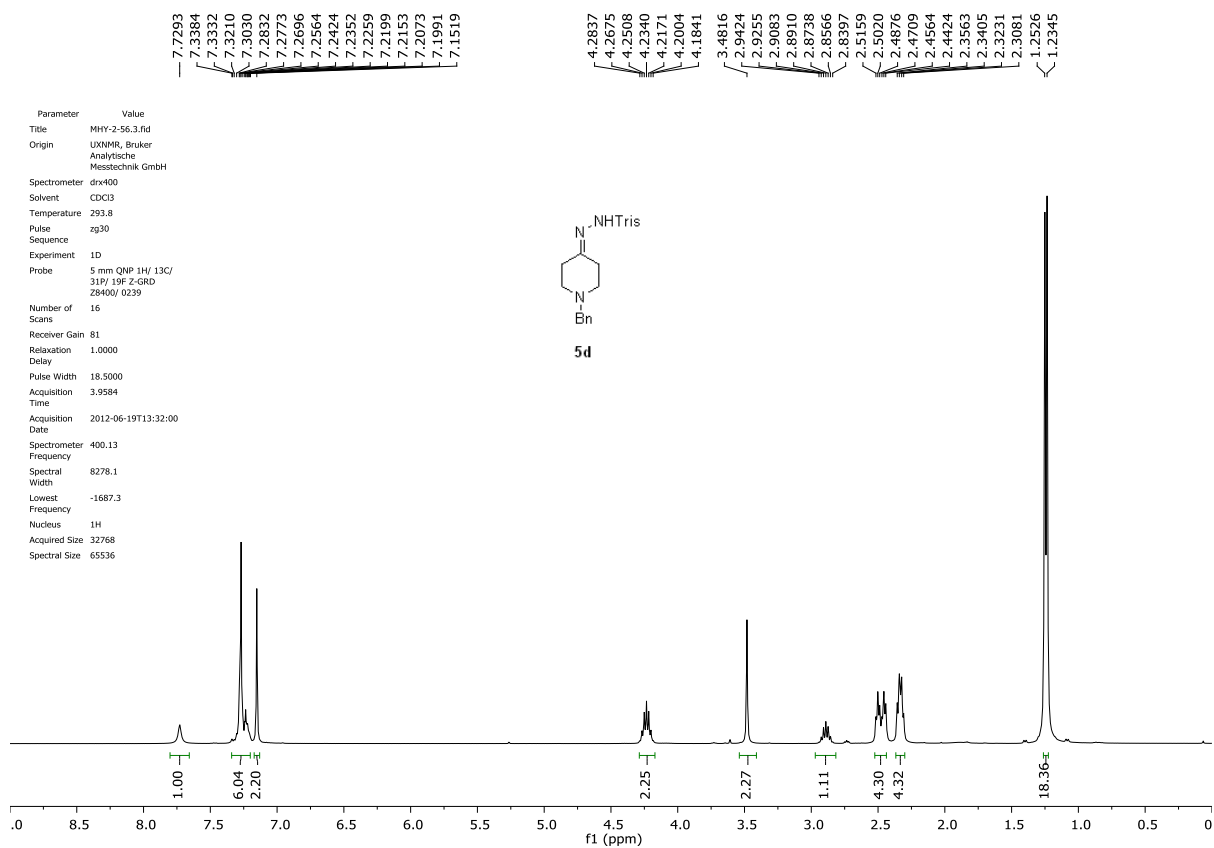


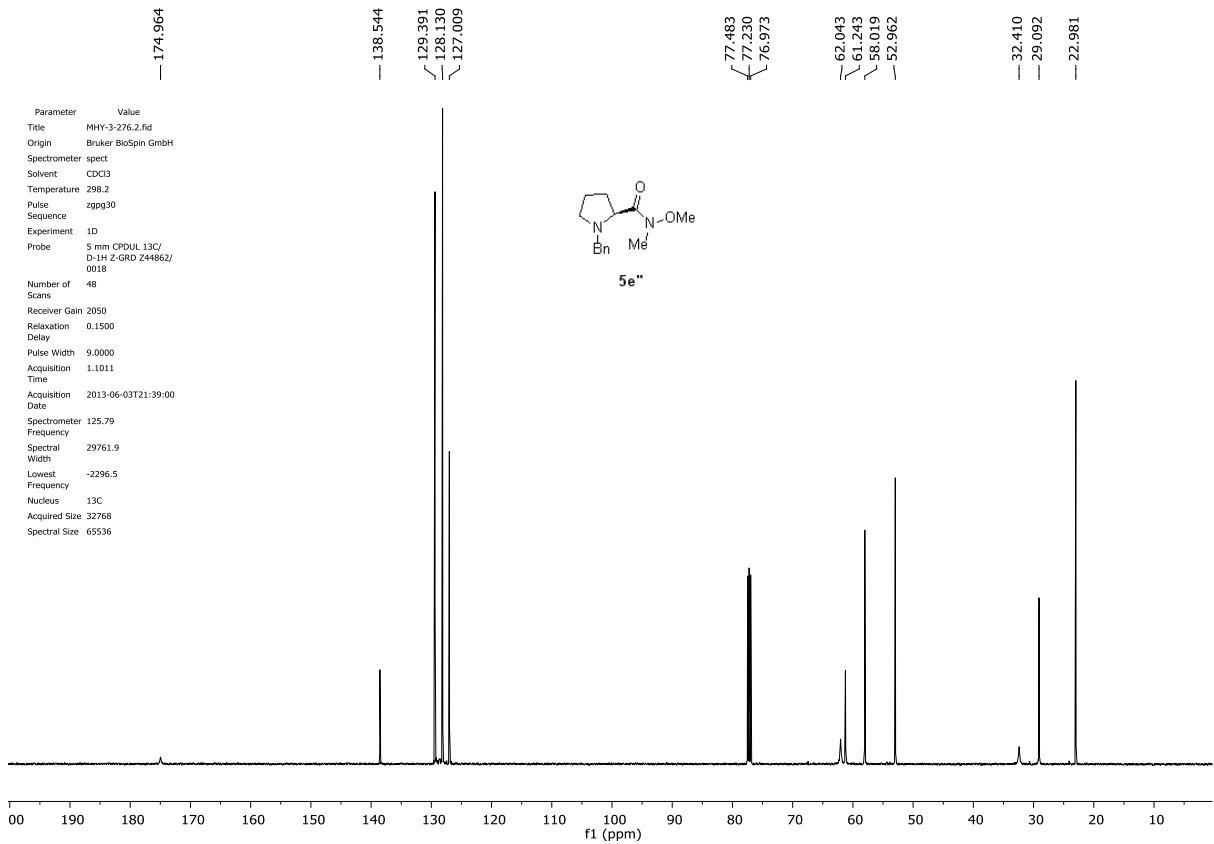
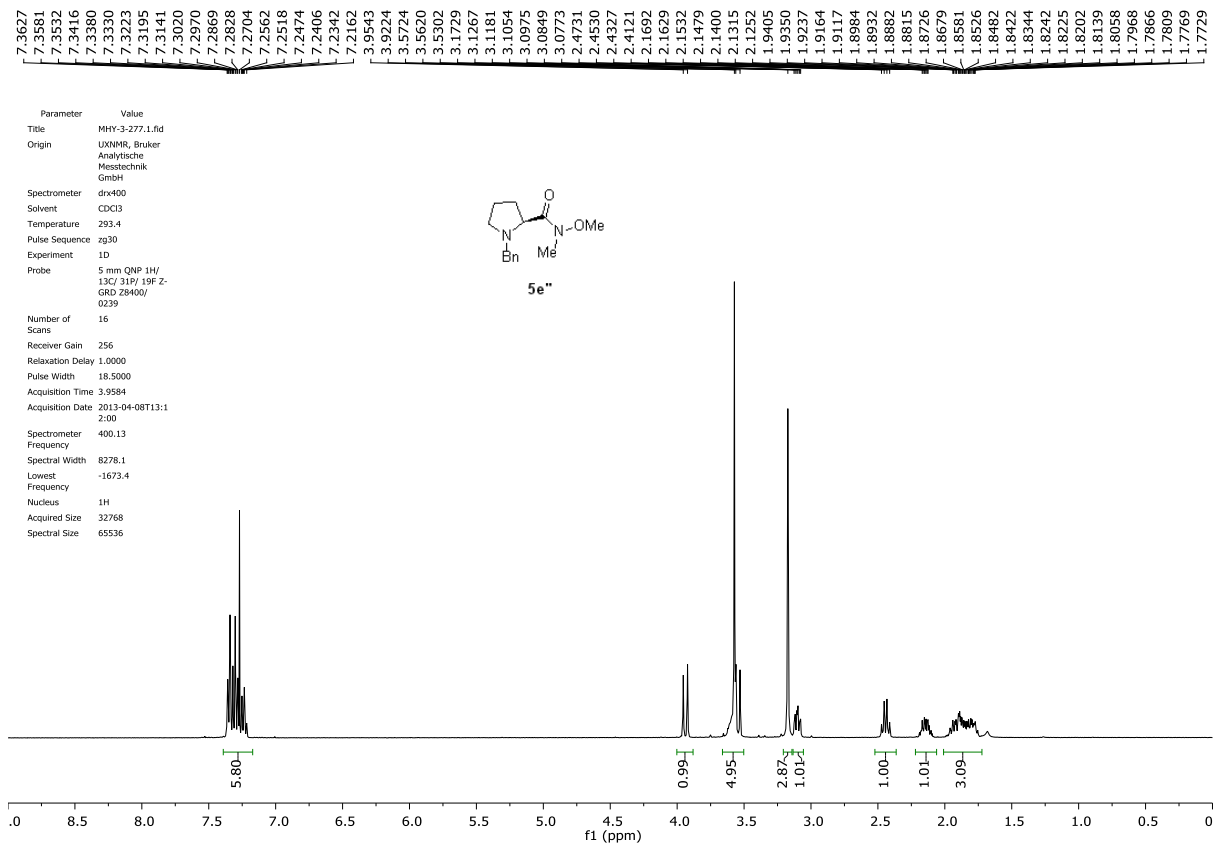
Parameter Value
 Title MHY-4-5.1.fid
 Origin UXNMR, Bruker Analytische Messtechnik GmbH
 Spectrometer drx400
 Solvent CDCl3
 Temperature 293.5
 Pulse zg30
 Sequence
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/ 31P 1H Z-GRD ZB400/ Q239
 Number of Scans 16
 Receiver Gain 287
 Relaxation 1.0000
 Delay
 Pulse Width 18.5000
 Acquisition Time 3.9584
 Date 2013-05-08T22:19:00
 Spectrometer 400.13
 Frequency 8278.1
 Width -1673.4
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536

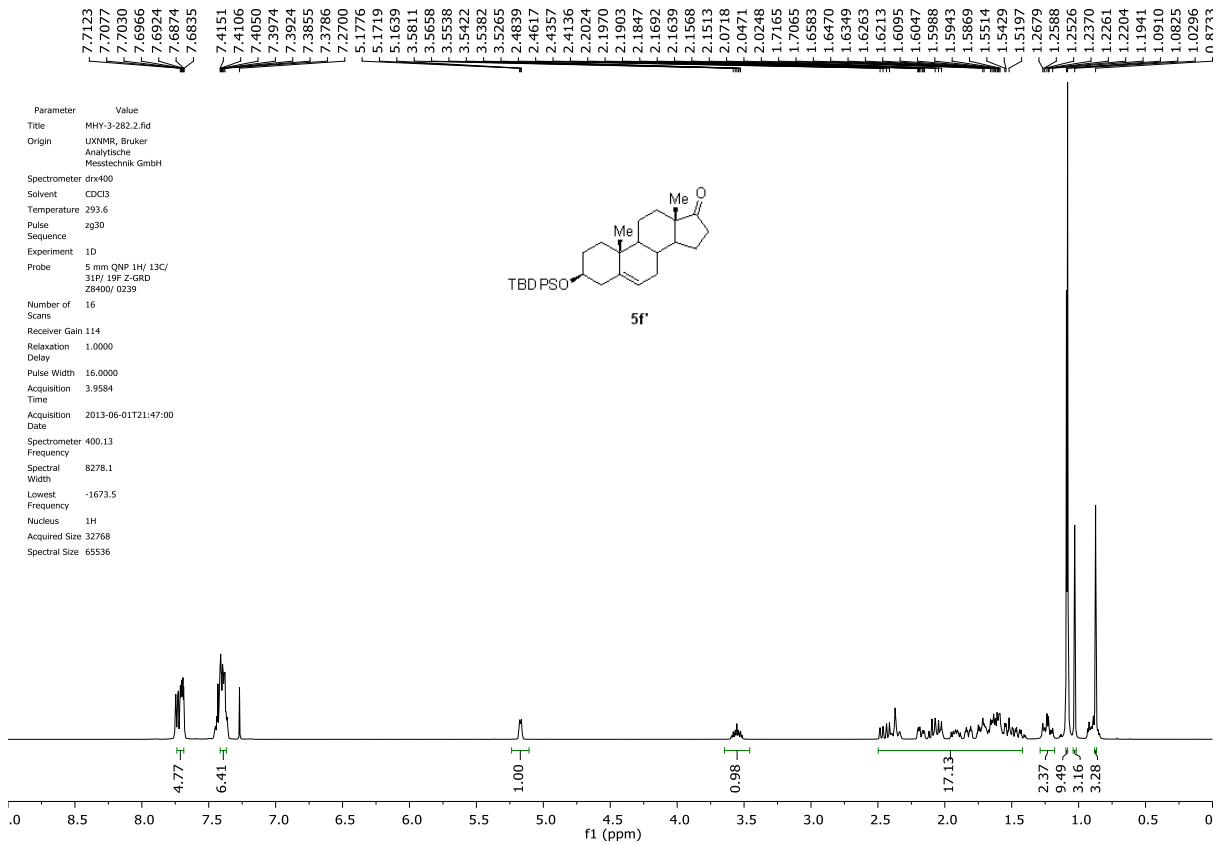
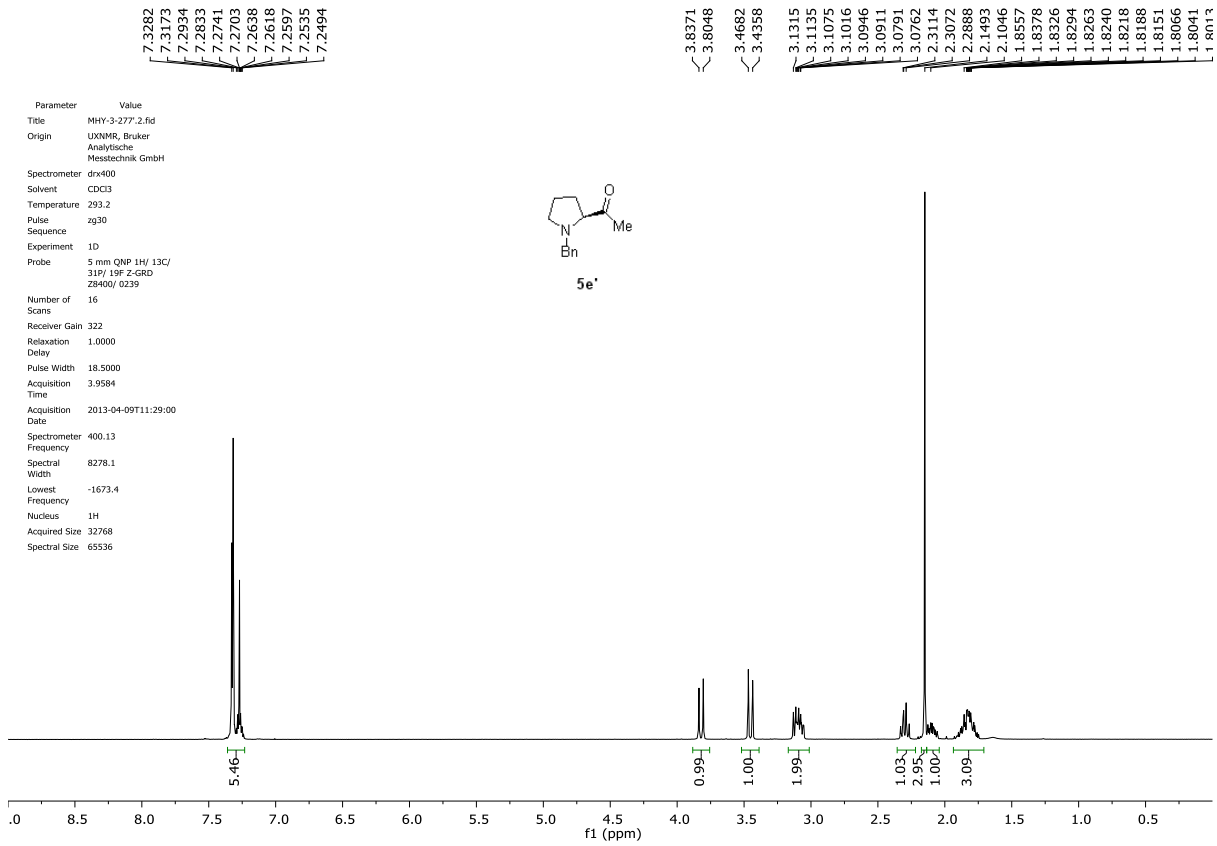


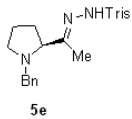
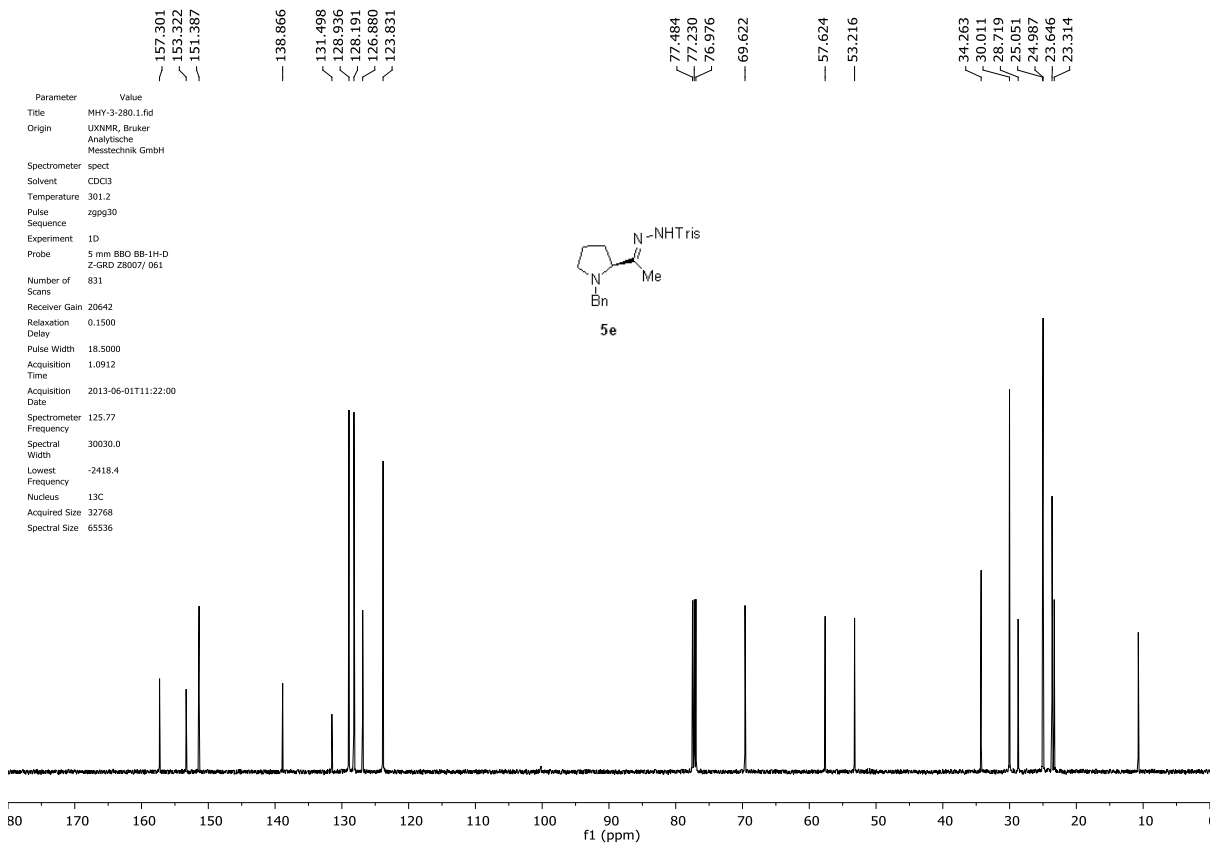
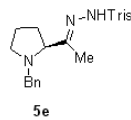
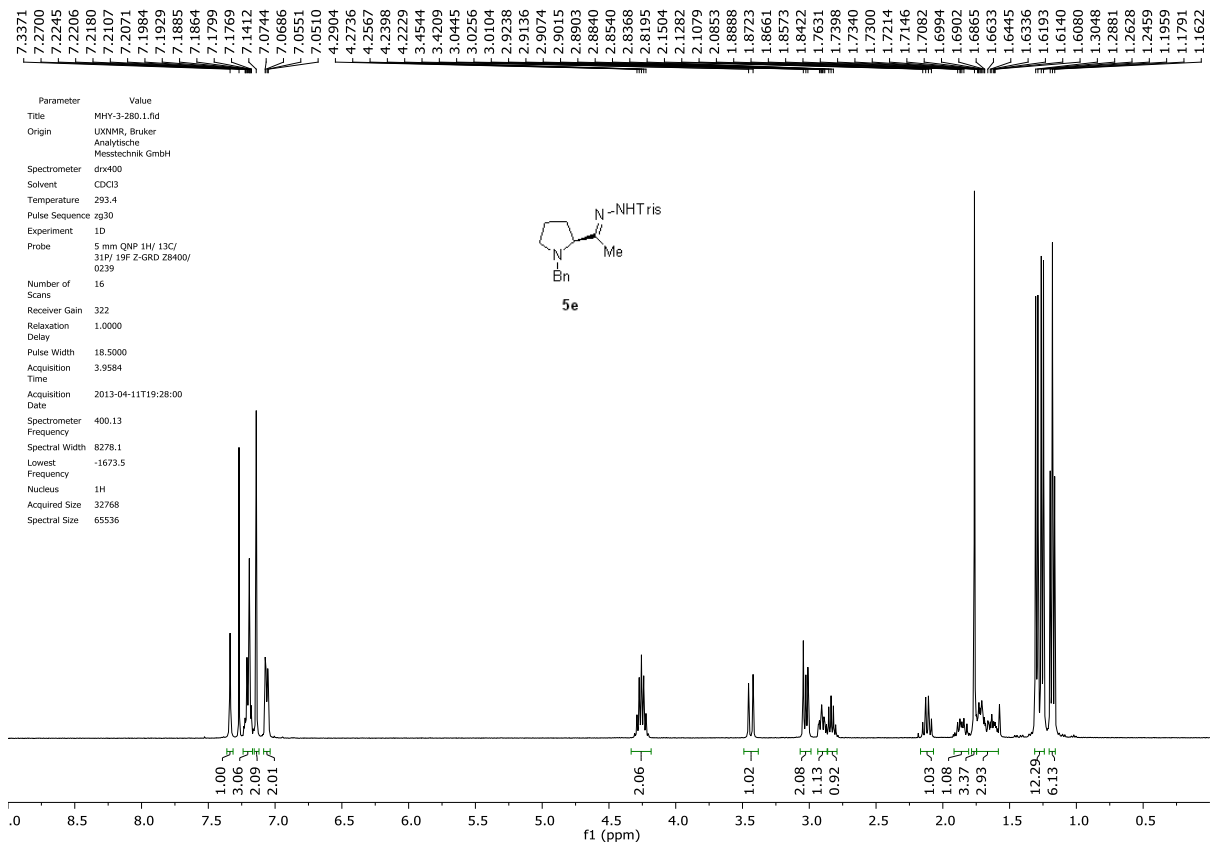
Parameter Value
 Title MHY-4-5.6.fid
 Origin UXNMR, Bruker Analytische Messtechnik GmbH
 Spectrometer spect
 Solvent CDCl3
 Temperature 301.2
 Pulse Sequence zgpg30
 Experiment 1D
 Probe 5 mm BBO BB-1H-D Z-GRD 28007/ 061
 Number of Scans 240
 Receiver Gain 20642
 Relaxation 0.1500
 Delay
 Pulse Width 18.5000
 Acquisition Time 1.0912
 Acquisition Date 2013-05-08T22:42:00
 Spectrometer 125.77
 Frequency 30030.0
 Lowest -2416.8
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

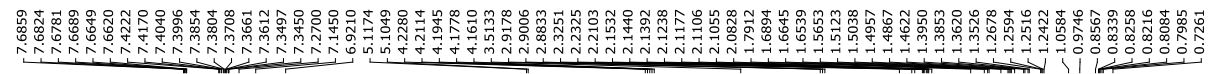




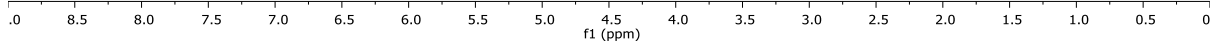
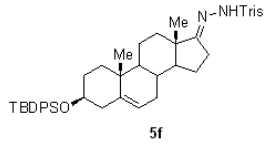




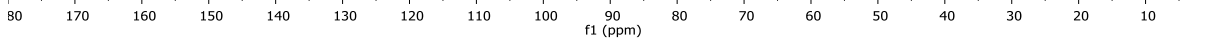
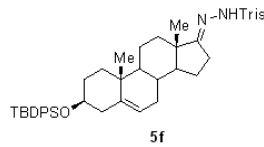


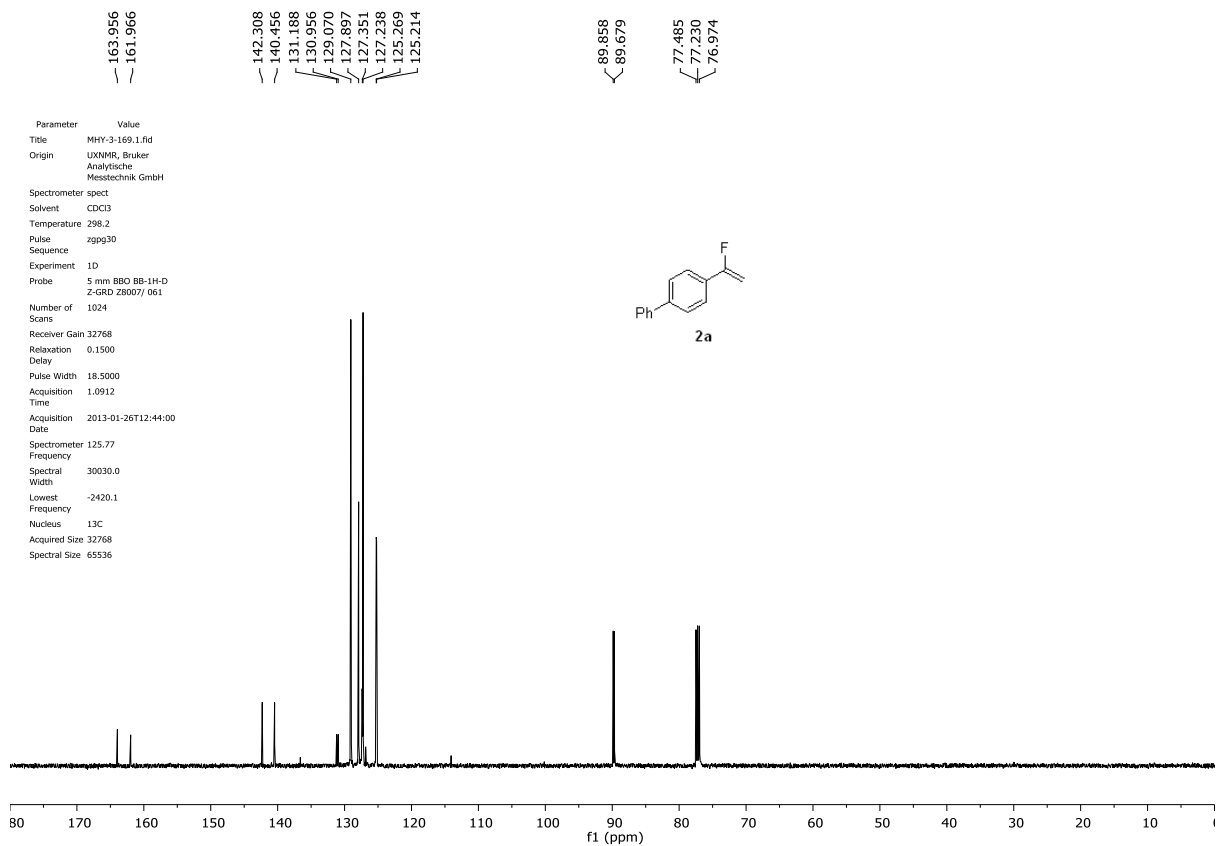
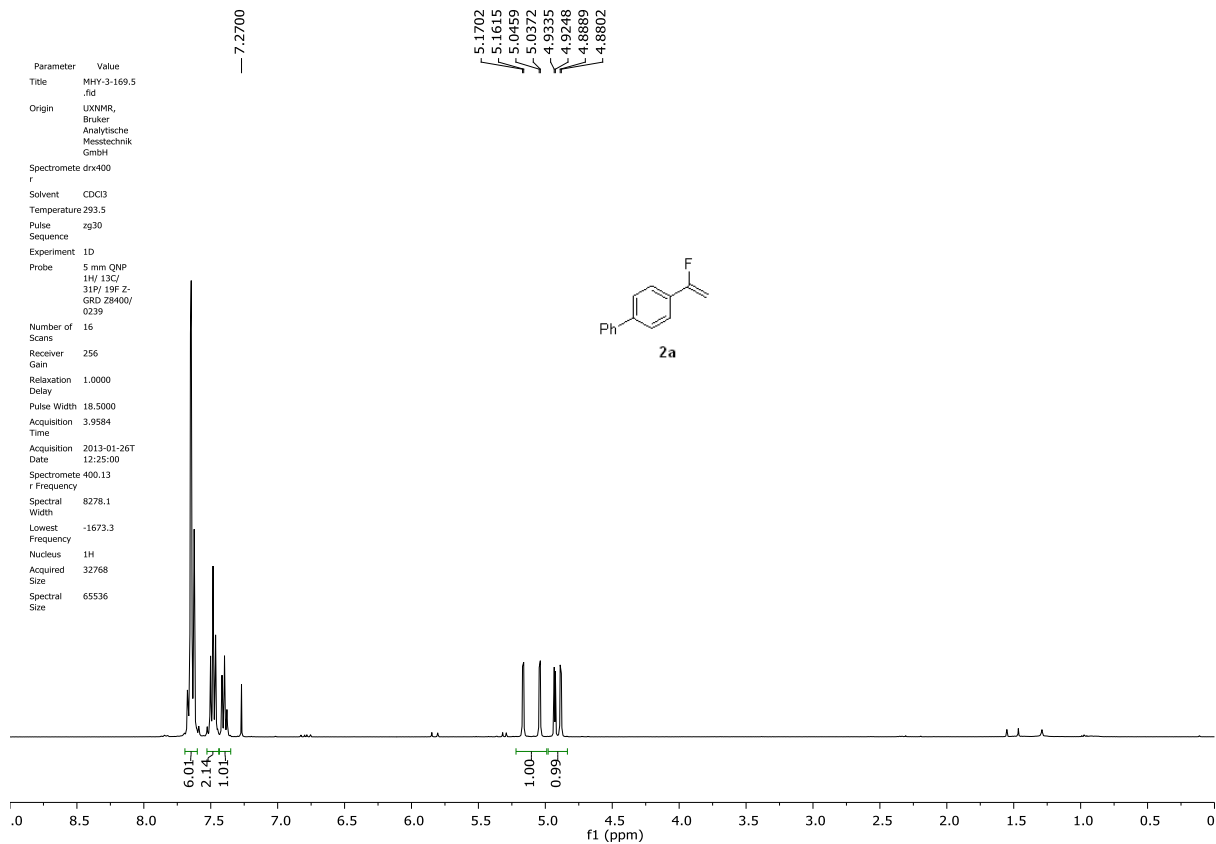


Parameter	Value
Title	MHY-3-288.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx-600
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/13C/31P/19F 2-GRD Z8400/8239
Number of Scans	16
Receiver Gain	228
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-04-20T12:24:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1873.5
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



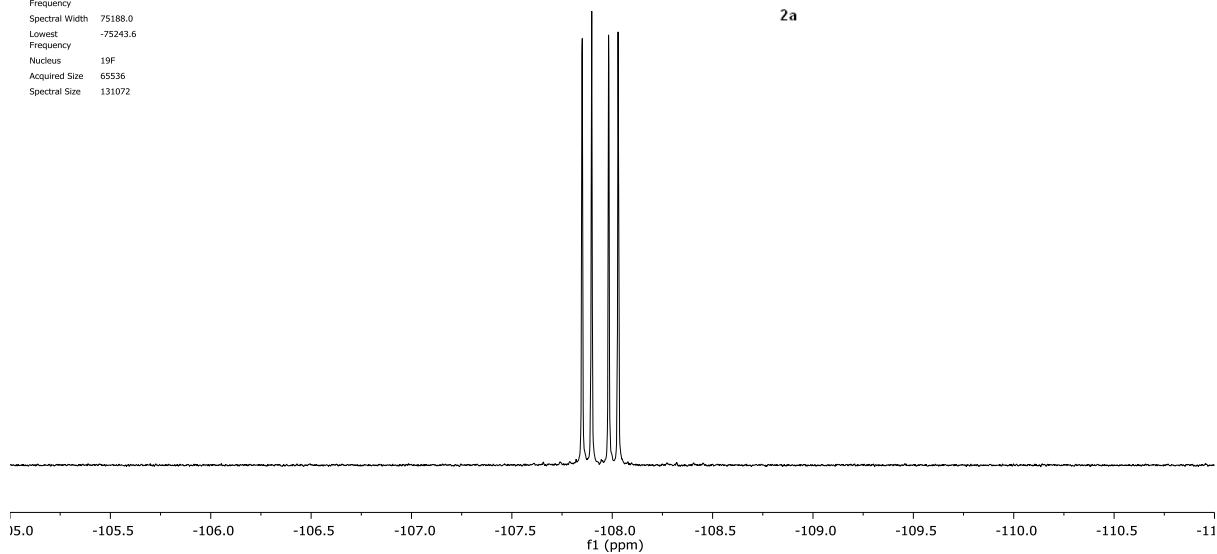
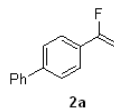
Parameter	Value
Title	MHY-3-288.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spec
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD Z8007/061
Number of Scans	1024
Receiver Gain	18390
Relaxation Delay	0.1500
Pulse Width	18.5000
Acquisition Time	1.0912
Acquisition Date	2013-04-20T13:48:00
Spectrometer Frequency	125.77
Spectral Width	30030.0
Lowest Frequency	-2415.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536





Parameter	Value
Title	MHY-3-169.3.fid
Origin	Bruker Analytik GmbH
Spectrometer	dxv400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1825
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-25T19:13:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-107.850
-107.898
-107.962
-108.030



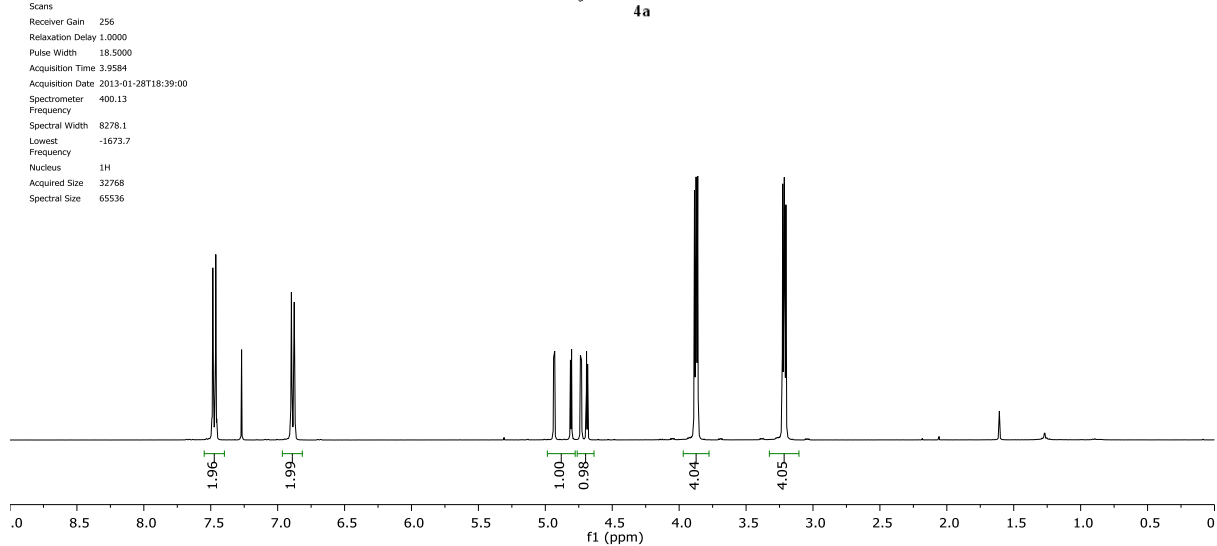
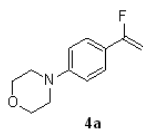
7.4846
7.4626
7.2700
6.8969
6.8767

4.9382
4.9298
4.8123
4.8039
4.7377
4.7293
4.6922
4.6838

3.8854
3.8733
3.8611

3.2267
3.2143
3.2023

Parameter	Value
Title	MHY-3-174.2.fid
Origin	UXNMR_Bruker Analytische Messtechnik GmbH
Spectrometer	dxv400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-01-28T18:39:00
Spectrometer	400.13
Frequency	8278.1
Spectral Width	8278.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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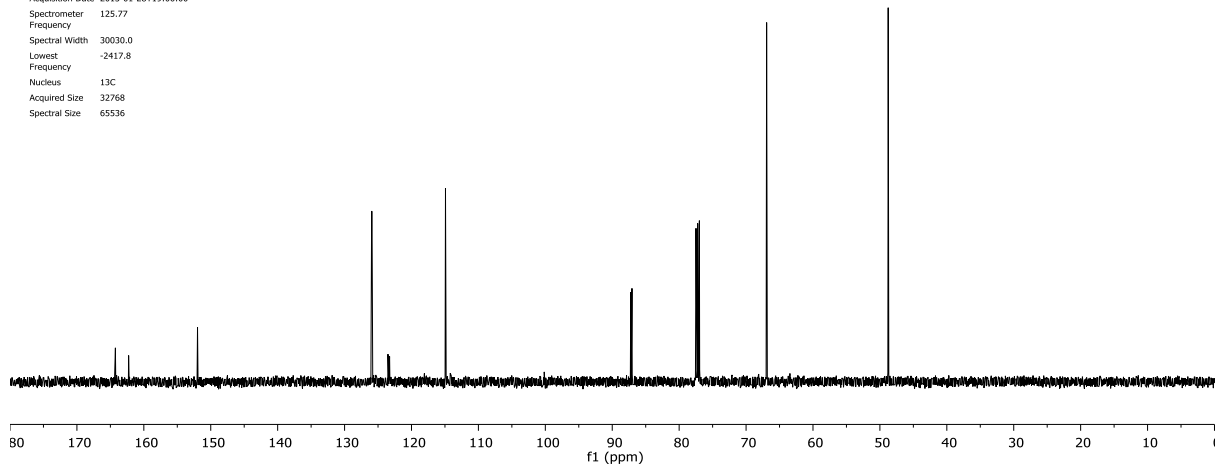
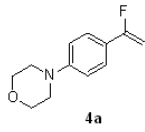
164.250
162.273
151.974

125.959
125.902
123.513
123.276
114.936
114.920

87.236
87.053
77.484
77.230
76.975
66.926

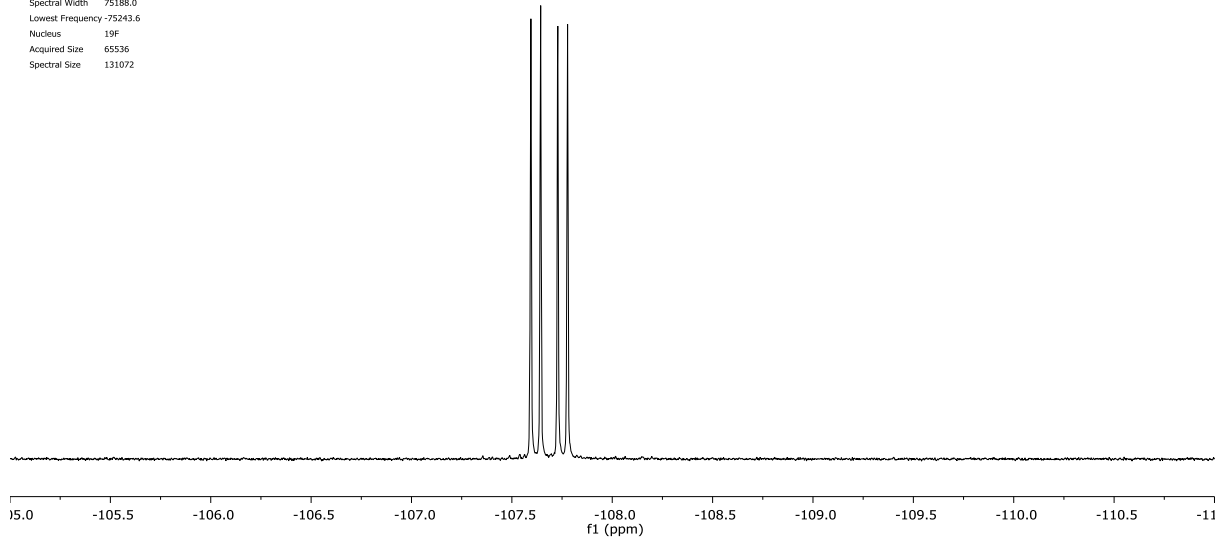
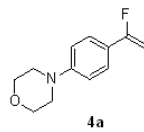
48.760

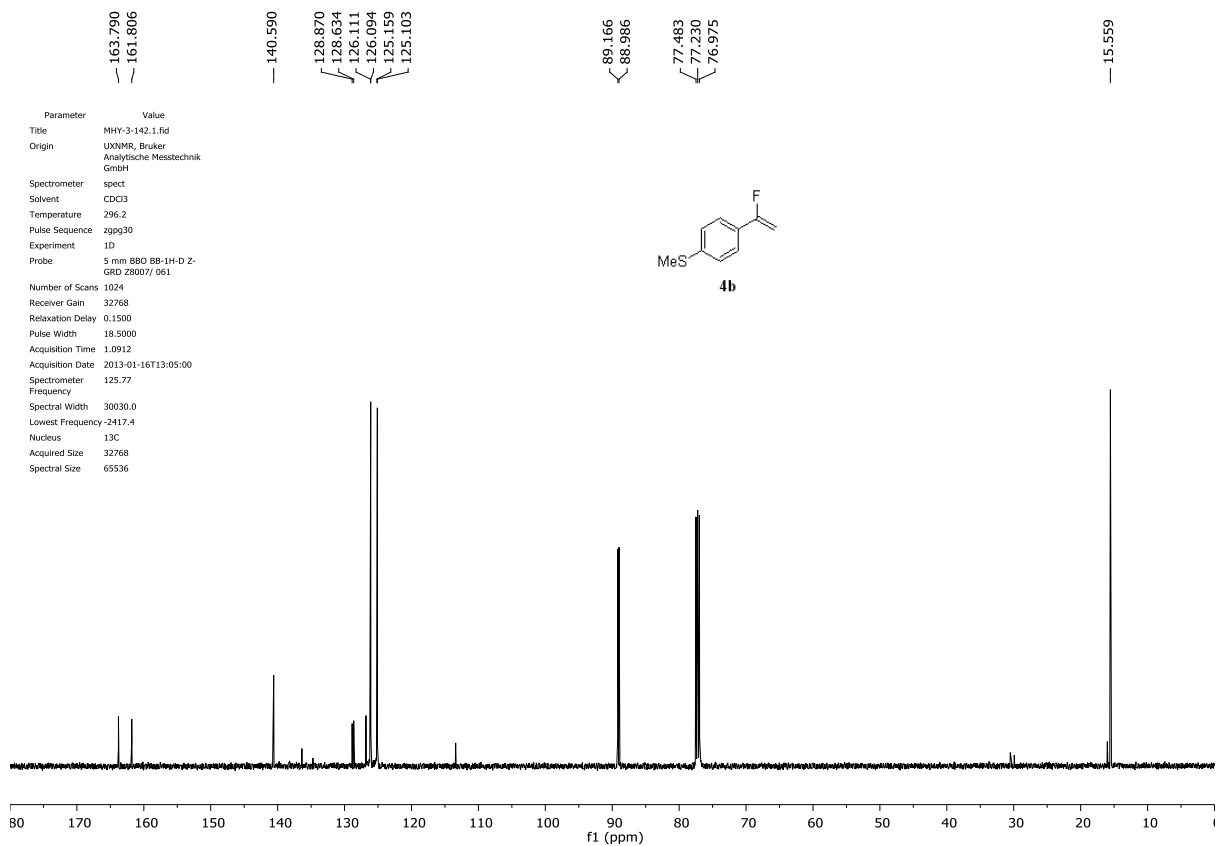
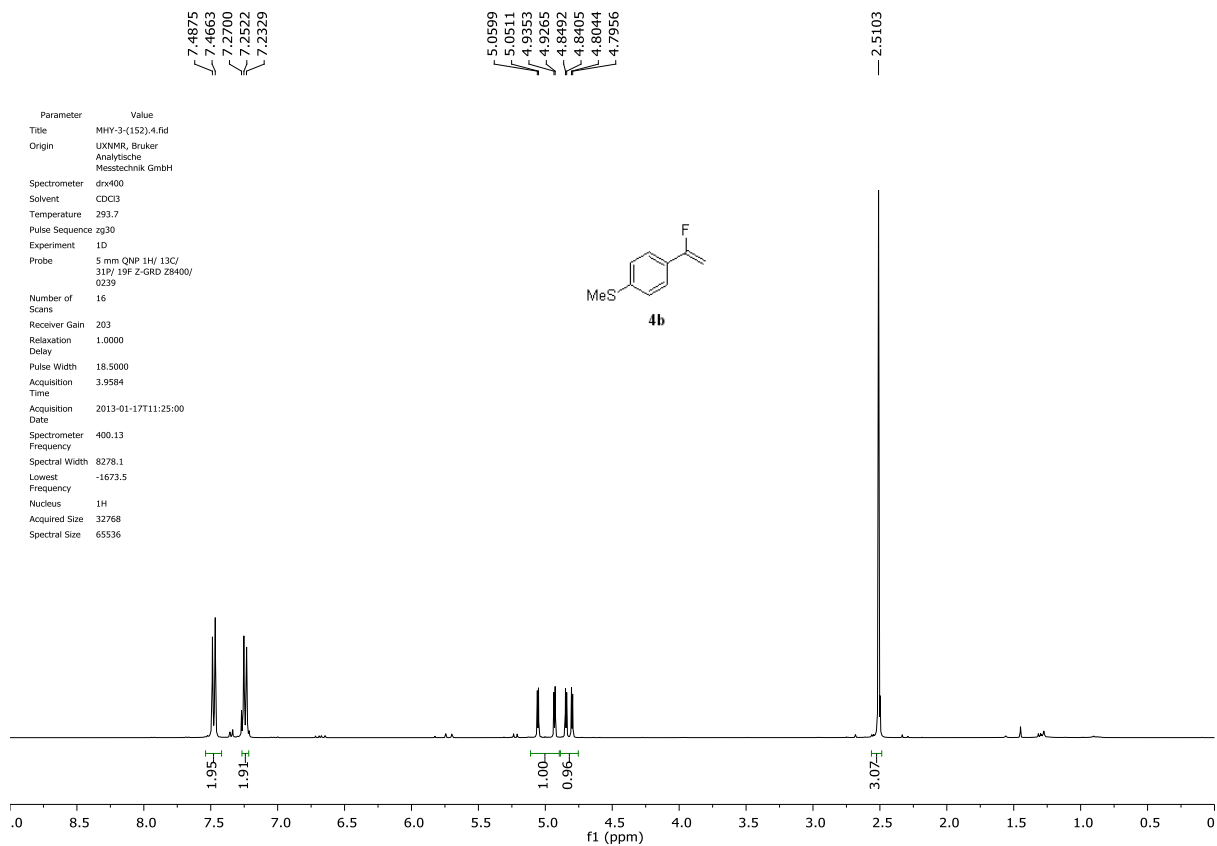
Parameter	Value
Title	MHY-3-174.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD Z8007/061
Number of Scans	1024
Receiver Gain	32768
Relaxation Delay	0.1500
Pulse Width	18.5000
Acquisition Time	1.0912
Acquisition Date	2013-01-28T19:06:00
Spectrometer Frequency	125.77
Spectral Width	30030.0
Lowest Frequency	-2417.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Title	MHY-3-174.4.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgfgan
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/0239
Number of Scans	16
Receiver Gain	1825
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-28T18:51:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-107.595
-107.643
-107.729
-107.777

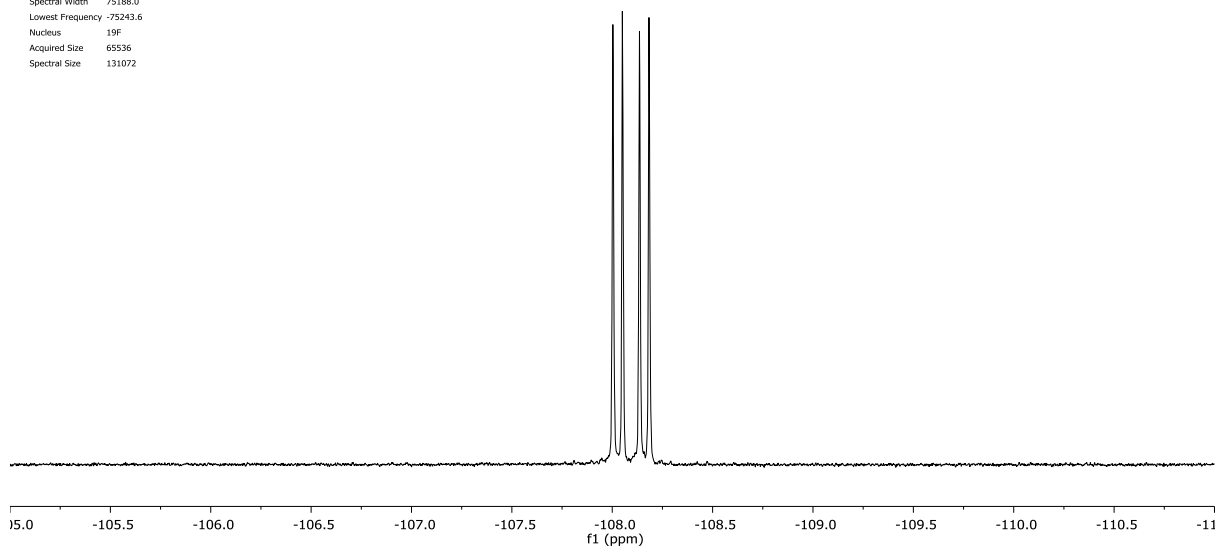
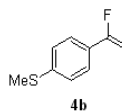




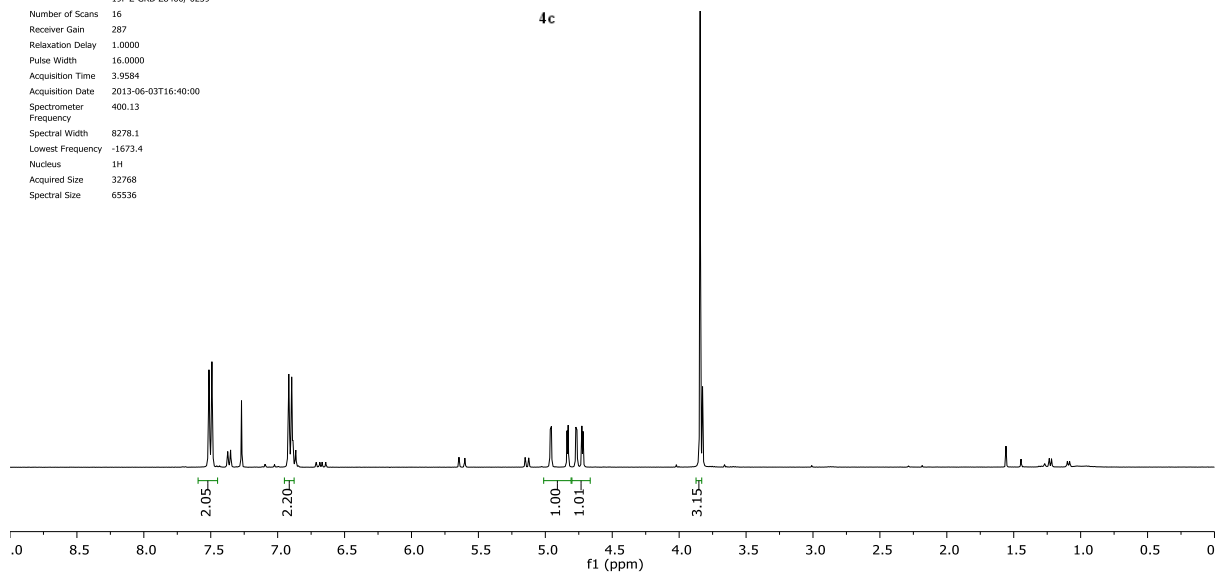
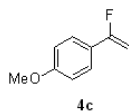
SI-60

Parameter	Value
Title	MHY-3-142.5.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ Q239
Number of Scans	16
Receiver Gain	2299
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-16T12:47:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	-75243.6
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-108.003
-108.051
-108.136
-108.184



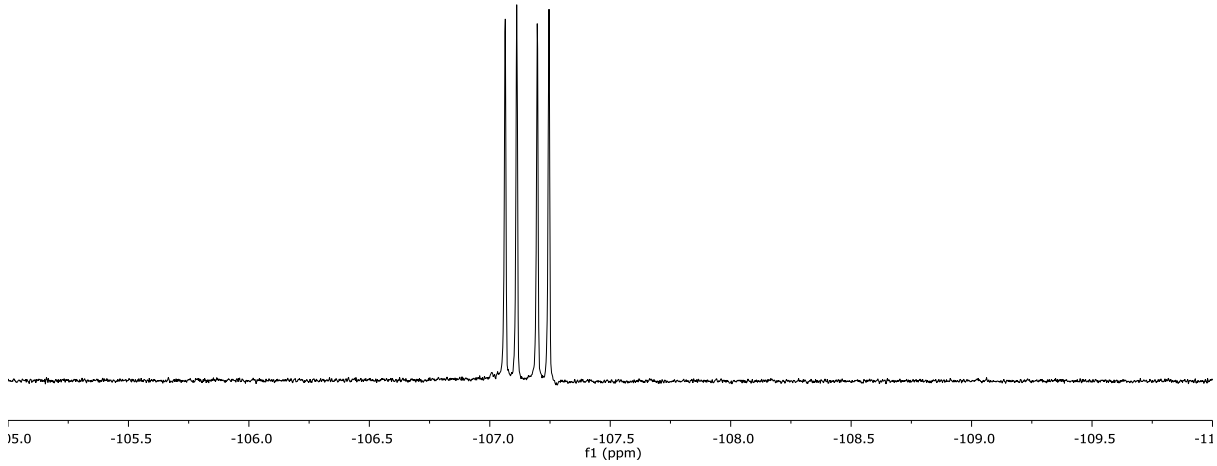
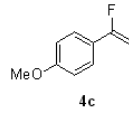
Parameter	Value
Title	MHY-4-49.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ Q239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-06-03T16:40:00
Spectrometer	400.13
Frequency	8278.1
Spectral Width	-1673.4
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



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Parameter	Value
Title	MHY-3-140.3.fid
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1290
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-09T13:21:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	-75243.6
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-107.064
-107.112
-107.197
-107.245

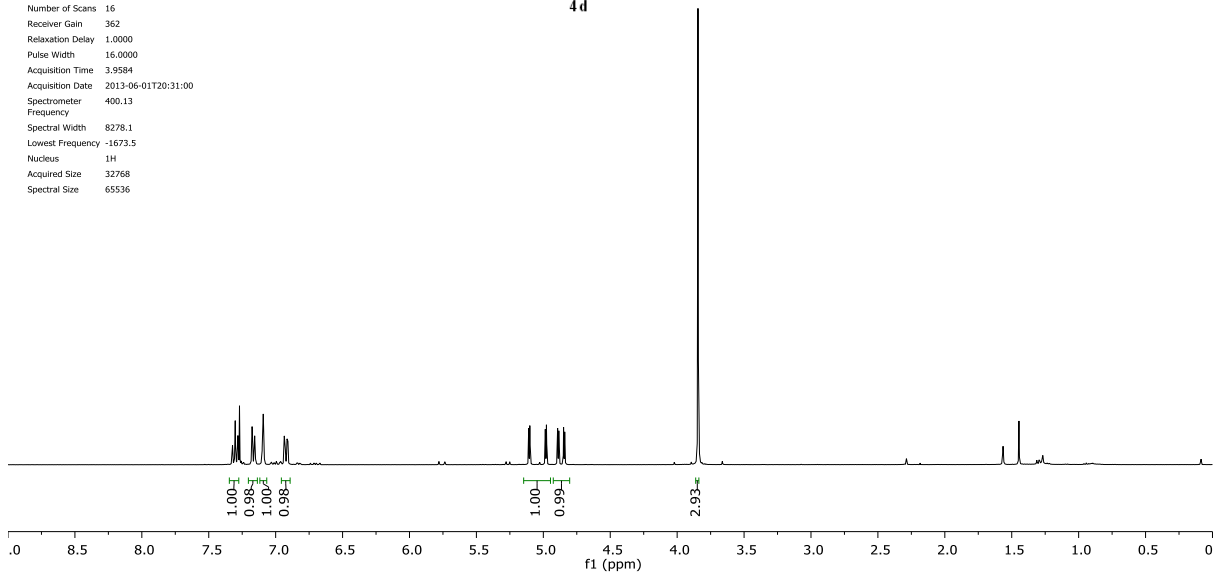
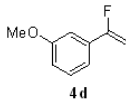


7.3222
7.3026
7.2822
7.2700
7.1762
7.1568
7.0984
7.0929
7.0887
6.9355
6.9291
6.9149
6.9085

5.1095
5.1008
4.9853
4.9767
4.8931
4.8845
4.8486
4.8400

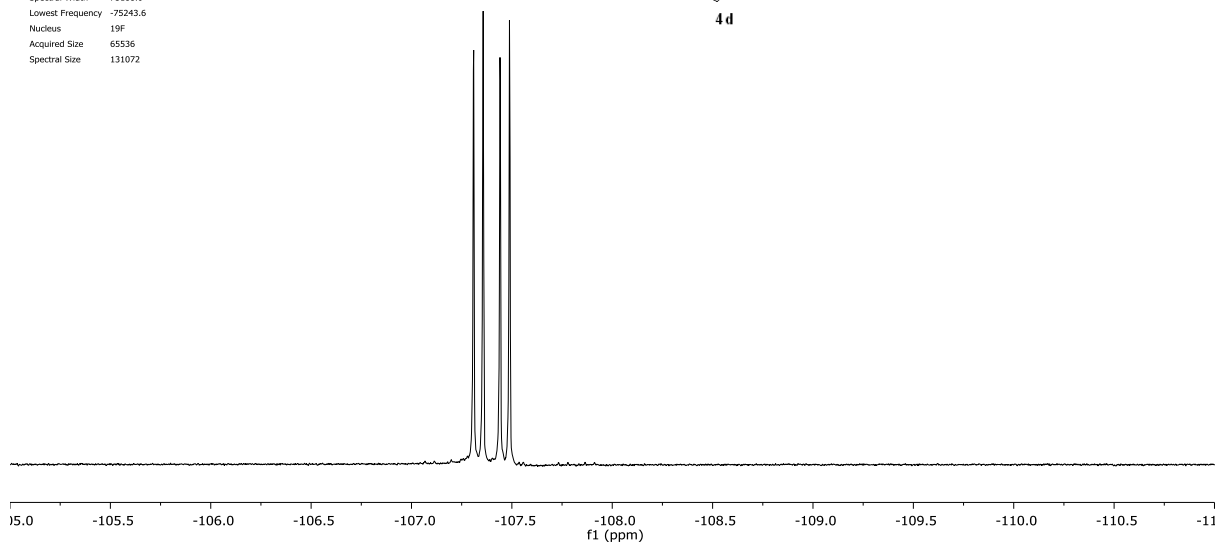
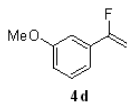
3.8445

Parameter	Value
Title	MHY-4-48.4.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	362
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-06-01T20:31:00
Spectrometer	400.13
Frequency	8278.1
Spectral Width	-1673.5
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



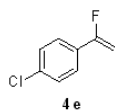
Parameter	Value
Title	MHY-4-48.3.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ 0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-06-01T20:04:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	-75243.6
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-107.309
-107.357
-107.441
-107.488

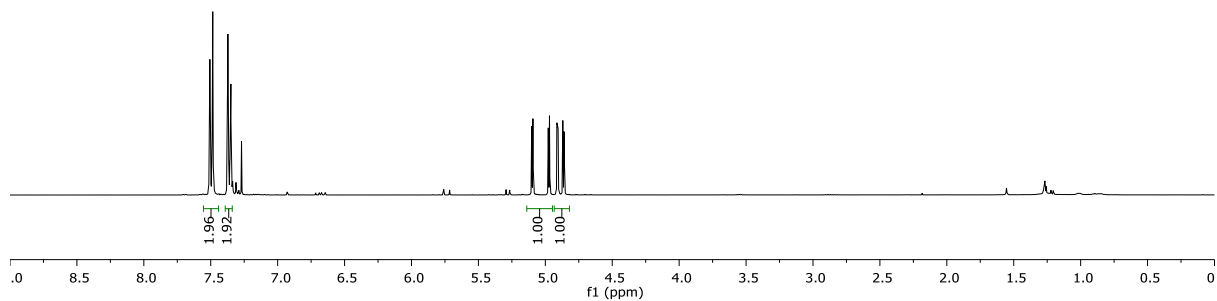


7.5064
7.4849
7.3713
7.3516
7.3495
7.2700

5.1017
5.0926
4.9783
4.9690
4.9137
4.9044
4.8691
4.8600

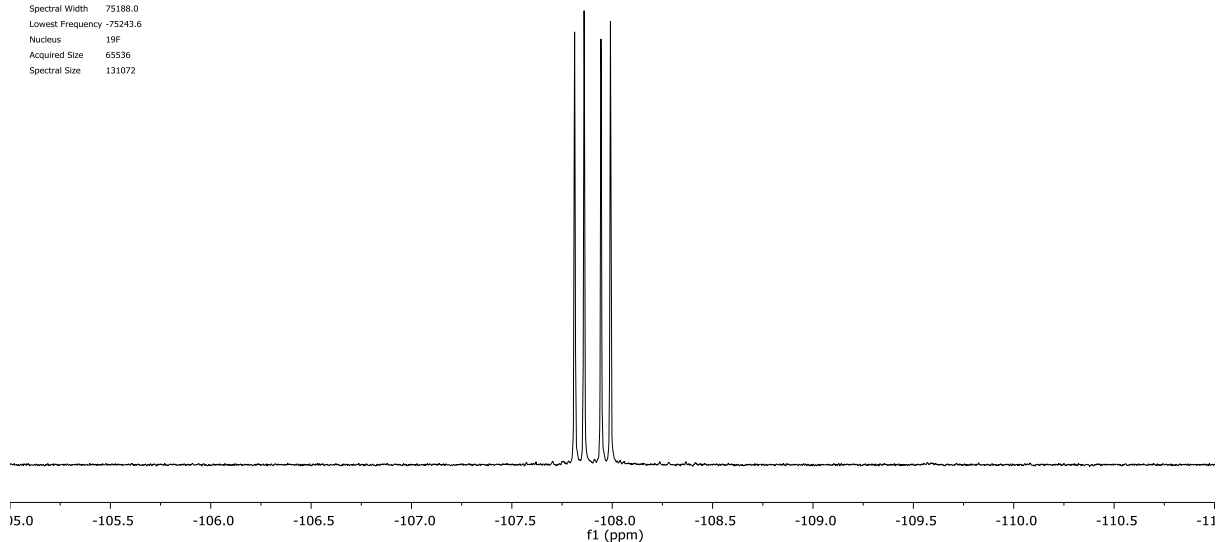
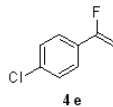


Parameter	Value
Title	MHY-3-163.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-01-22T10:46:00
Spectrometer	400.13
Frequency	8278.1
Spectral Width	-1673.6
Lowest Frequency	-1673.6
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

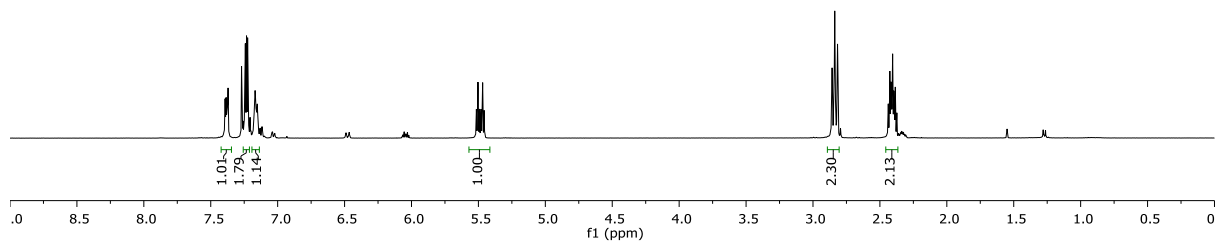
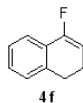


Parameter	Value
Title	MHY-3-163.3.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ 0239
Number of Scans	16
Receiver Gain	2048
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-22T10:47:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

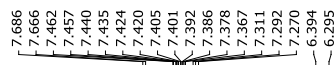
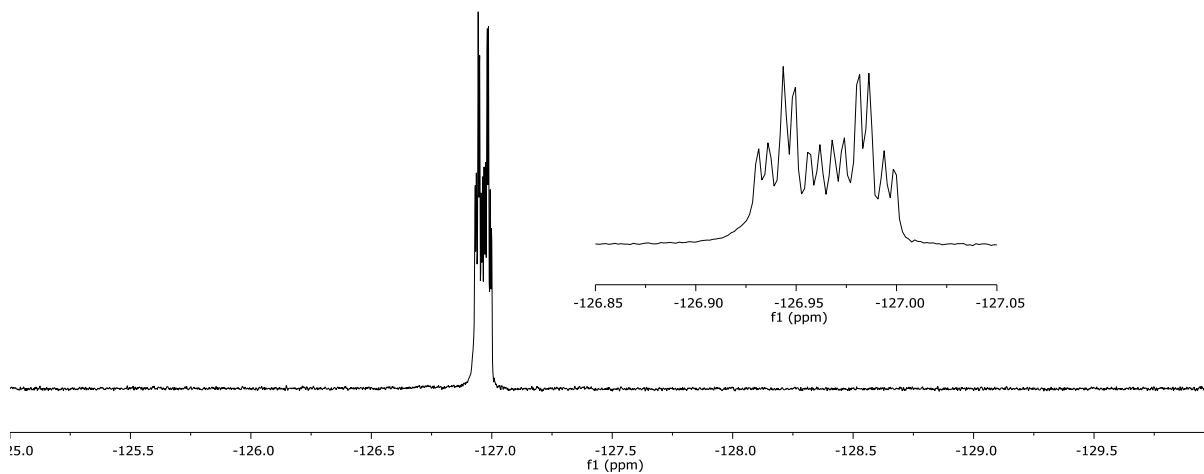
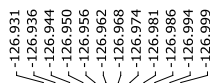
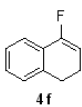
-107.813
-107.860
-107.944
-107.991



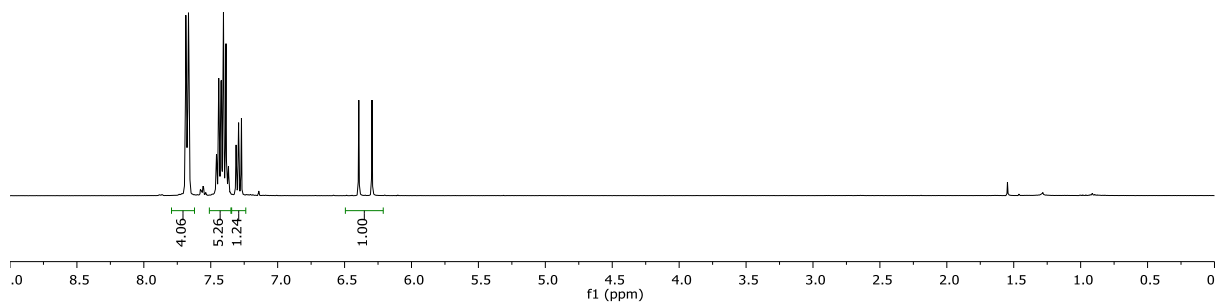
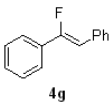
Parameter	Value
Title	MHY-3-(150).3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD ZB400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-01-15T14:44:00
Spectrometer	400.13
Frequency	8378.1
Spectral Width	8378.1
Lowest Frequency	-1673.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Title	MHY-3-(150).4.fid
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1626
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-01-15T14:48:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

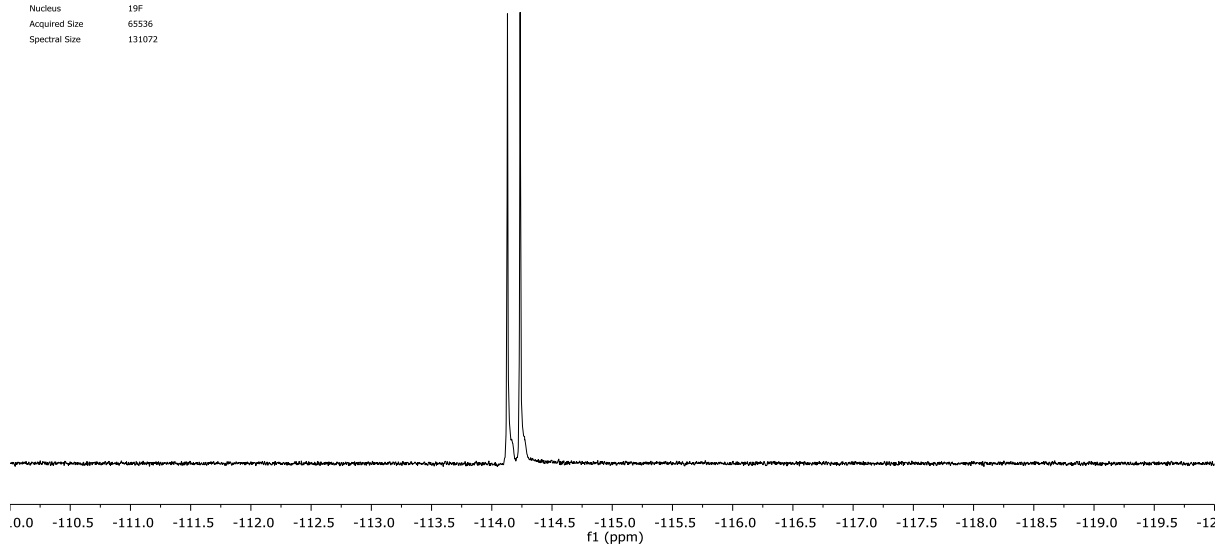
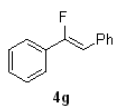


Parameter	Value
Title	MHY-3-106.9.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2012-12-24T13:39:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.4
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



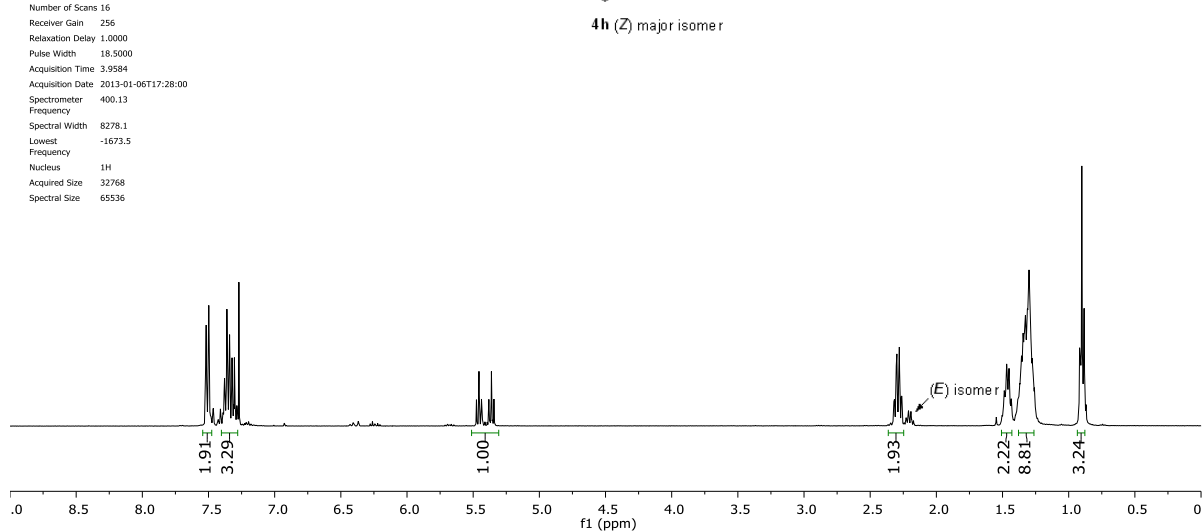
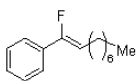
Parameter	Value
Title	MHY-3-106.13.fid
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl ₃
Temperature	293.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	2048
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-04-29T19:03:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

~114.130
~114.236

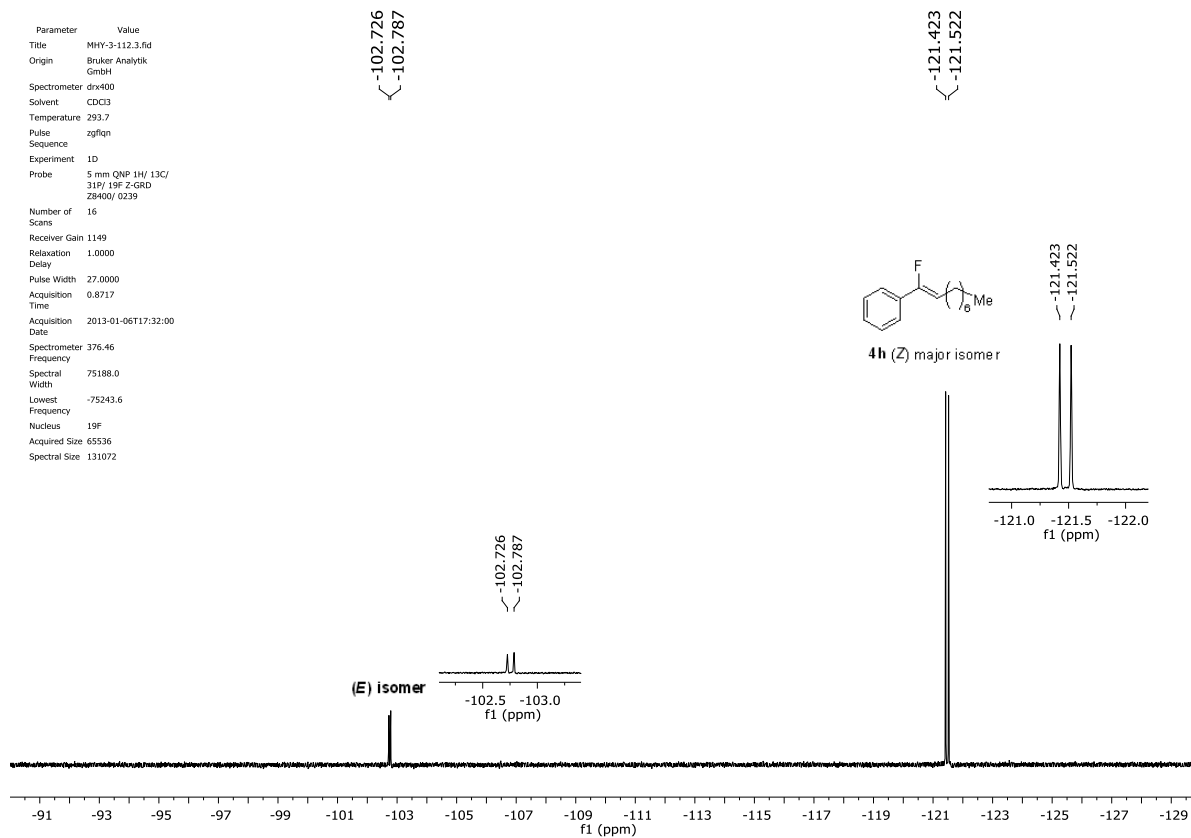


7.5216
7.5173
7.5039
7.5002
7.4972
7.3824
7.3792
7.3766
7.3605
7.3558
7.3464
7.3440
7.3407
7.3256
7.3221
7.3187
7.3037
7.2700
5.4753
5.4562
5.4372
5.3813
5.3623
5.3432
2.3211
2.3164
2.3026
2.2979
2.2844
2.2797
2.2655
2.2608
1.4690
1.4507
1.3474
1.3437
1.3378
1.3326
1.3264
1.3159
1.3131
1.3003
1.2984
1.2872
0.9178
0.8835

Parameter	Value
Title	MHY-3-112.2.fid
Origin	LIXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl ₃
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	18.5000
Acquisition Time	3.9984
Acquisition Date	2013-01-06T17:28:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.5
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

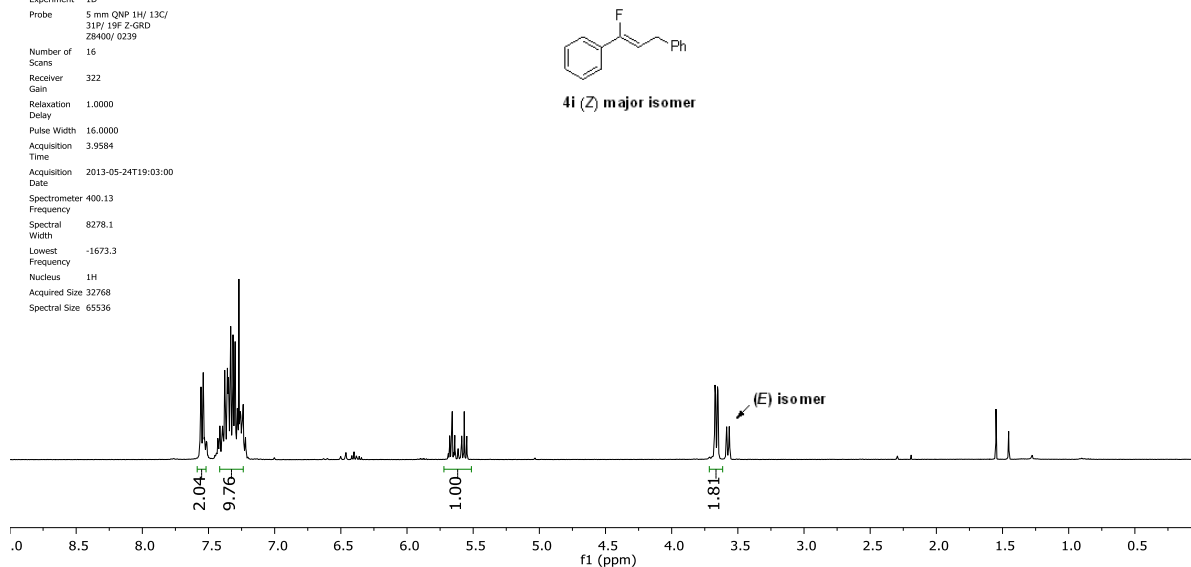


Parameter Value
 Title MHY-3-112.3.fid
 Origin Bruker Analytik GmbH
 Spectrometer dir400
 Solvent CDCl3
 Temperature 293.7
 Pulse zgpg30
 Sequence
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/ 31P/ 19F 2-GRD Z8400/ 0239
 Number of Scans 16
 Receiver Gain 1149
 Relaxation 1.0000
 Delay
 Pulse Width 27.0000
 Acquisition Time 0.8717
 Acquisition Date 2013-01-06T17:32:00
 Spectrometer 376.46
 Frequency 75188.0
 Spectral Width -75243.6
 Lowest Frequency
 Nucleus 19F
 Acquired Size 65536
 Spectral Size 131072

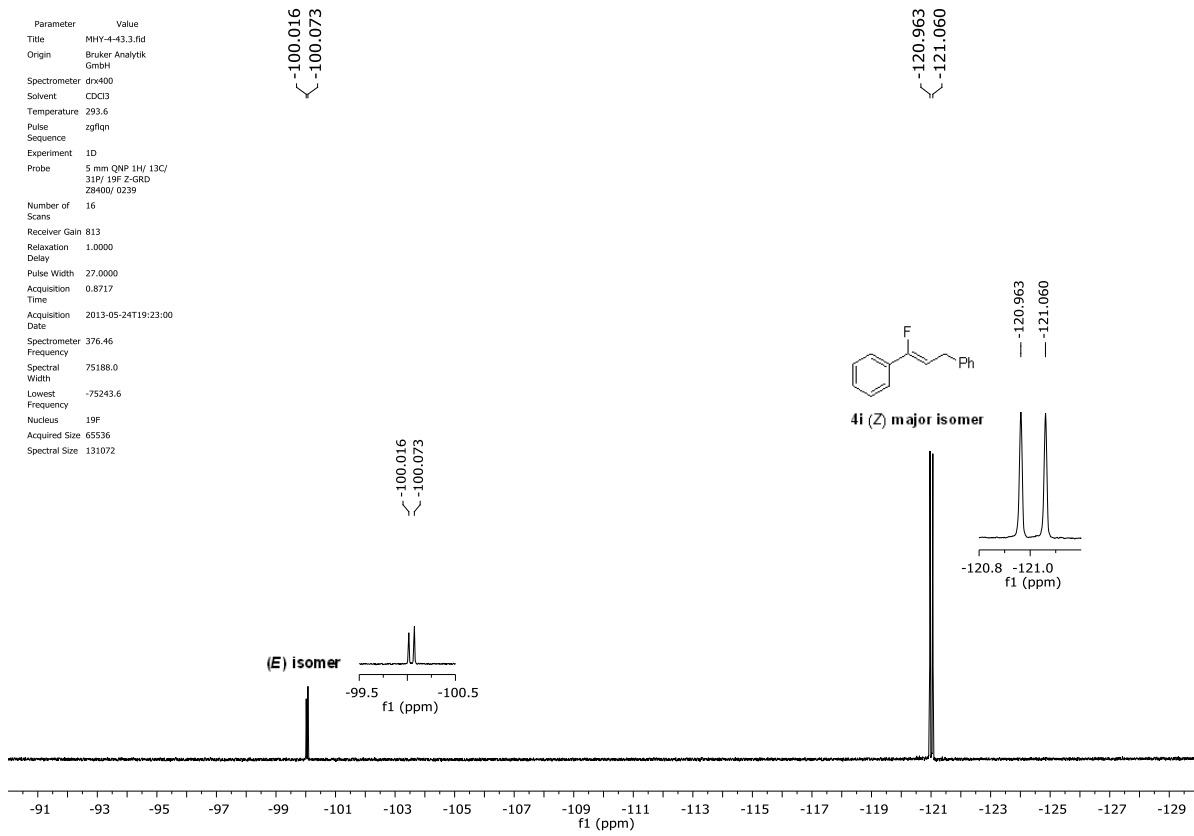


7.5614
 7.5568
 7.5401
 7.5368
 7.3775
 7.3753
 7.3714
 7.3602
 7.3572
 7.3529
 7.3489
 7.3448
 7.3384
 7.3356
 7.3316
 7.3202
 7.3140
 7.3001
 7.2700
 7.2644
 7.2593
 7.2550
 7.2478
 7.2428
 7.2377
 5.6776
 5.6583
 5.6389
 5.5867
 5.5675
 5.5481
 3.6732
 3.6688
 3.6540
 3.6496

Parameter Value
 Title MHY-4-43.2.fid
 Origin UXNMR, Bruker Analytische Messtechnik GmbH
 Spectrometer dir400
 Solvent CDCl3
 Temperature 293.6
 Pulse zg30
 Sequence
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/ 31P/ 19F 2-GRD Z8400/ 0239
 Number of Scans 16
 Receiver Gain 322
 Relaxation 1.0000
 Delay
 Pulse Width 16.0000
 Acquisition Time 3.9584
 Acquisition Date 2013-05-24T19:03:00
 Spectrometer 400.13
 Frequency 8278.1
 Spectral Width -1673.3
 Lowest Frequency
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



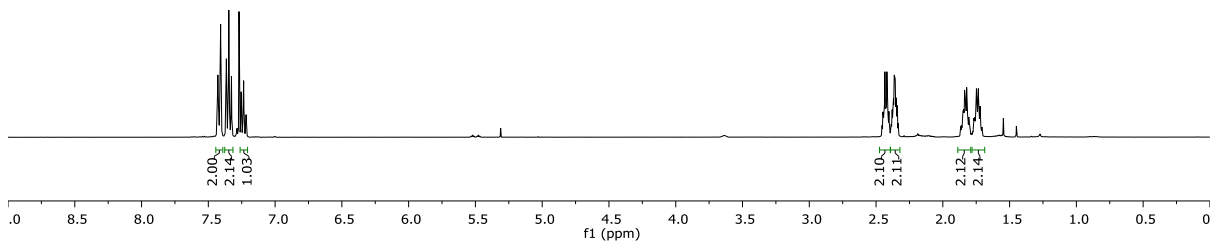
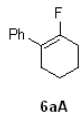
Parameter Value
 Title MHY-443.3.fid
 Origin Bruker Analytik GmbH
 Spectrometer drx400
 Solvent CDCl3
 Temperature 293.6
 Pulse Sequence zgpg30
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD 28400/ 0239
 Number of Scans 16
 Receiver Gain 813
 Relaxation Delay 1.0000
 Pulse Width 27.0000
 Acquisition Time 0.8717
 Acquisition Date 2013-05-24T19:23:00
 Spectrometer 376.46
 Frequency 75168.0
 Spectral Width -75243.6
 Lowest Frequency
 Nucleus 19F
 Acquired Size 65536
 Spectral Size 131072

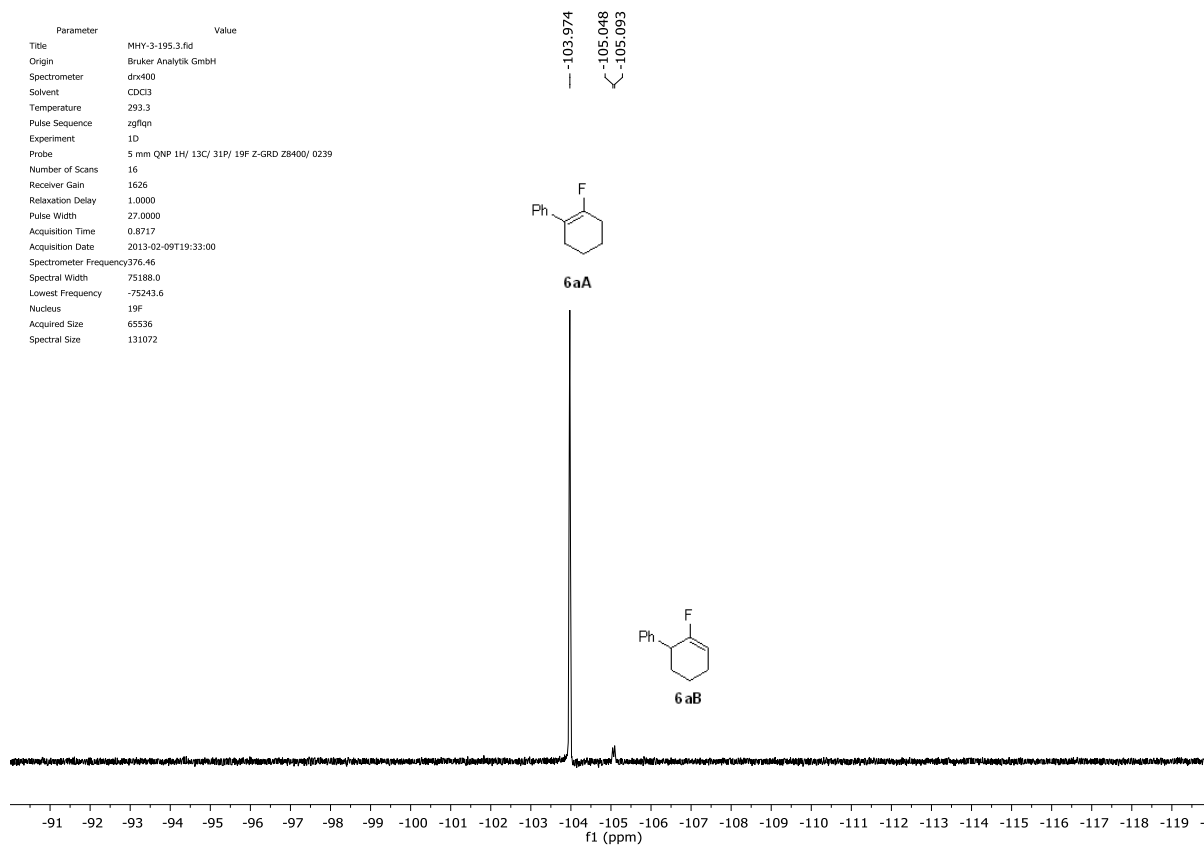
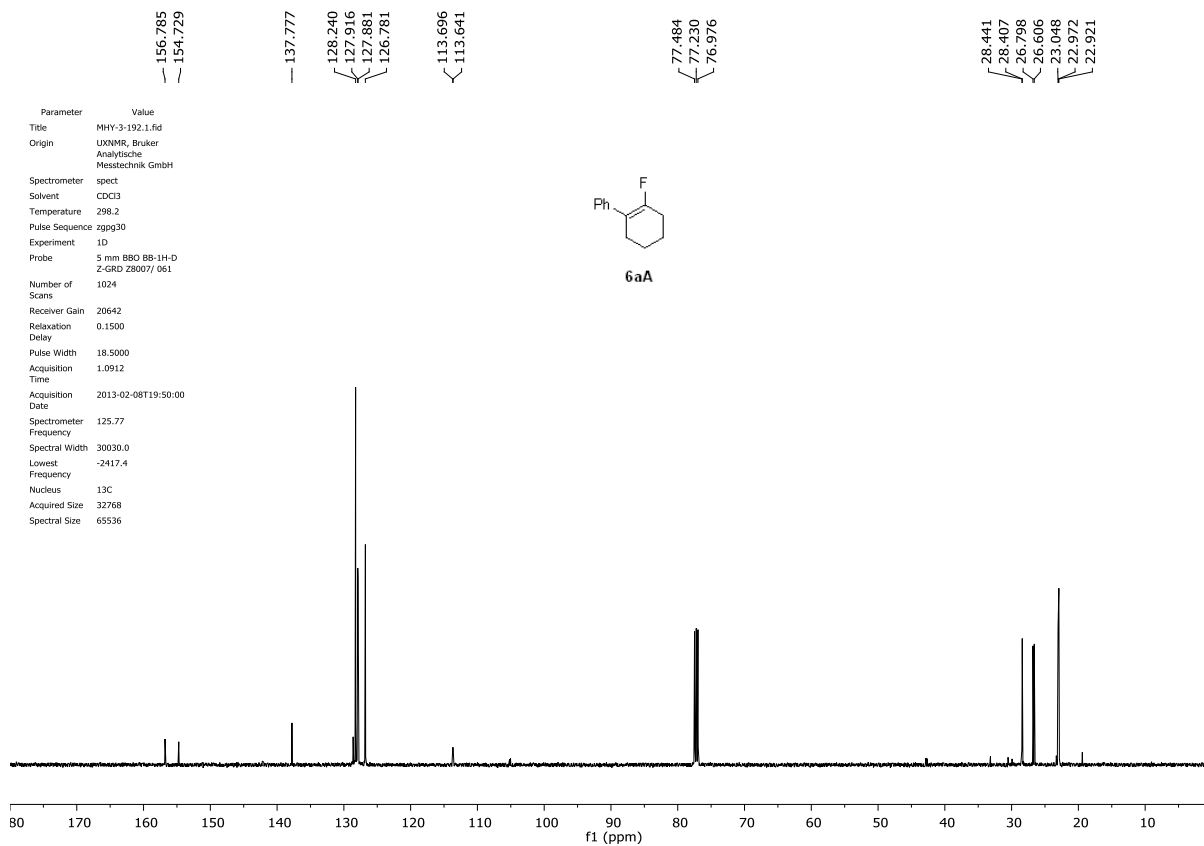


7.4286
 7.4256
 7.4130
 7.4105
 7.4077
 7.4049
 7.3654
 7.3468
 7.3425
 7.3268
 7.2704
 7.2700
 7.2571
 7.2536
 7.2503
 7.2403
 7.2355
 7.2302
 7.2206
 7.2171
 7.2137

2.4339
 2.4282
 2.4246
 2.4188
 2.4131
 2.3696
 2.3639
 2.3567
 2.3477
 1.8487
 1.8467
 1.8440
 1.8372
 1.8322
 1.8274
 1.8217
 1.8167
 1.7521
 1.7481
 1.7431
 1.7373
 1.7340
 1.7311
 1.7240
 1.7205

Parameter Value
 Title MHY-3-195.2.fid
 Origin UXNMR, Bruker Analytische Messtechnik GmbH
 Spectrometer drx400
 Solvent CDCl3
 Temperature 293.3
 Pulse Sequence zg30
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD 28400/ 0239
 Number of Scans 16
 Receiver Gain 322
 Relaxation Delay 1.0000
 Pulse Width 18.5000
 Acquisition Time 3.9584
 Acquisition Date 2013-02-09T19:28:00
 Spectrometer 400.13
 Frequency 8278.1
 Spectral Width -1673.4
 Lowest Frequency
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536





7.2700

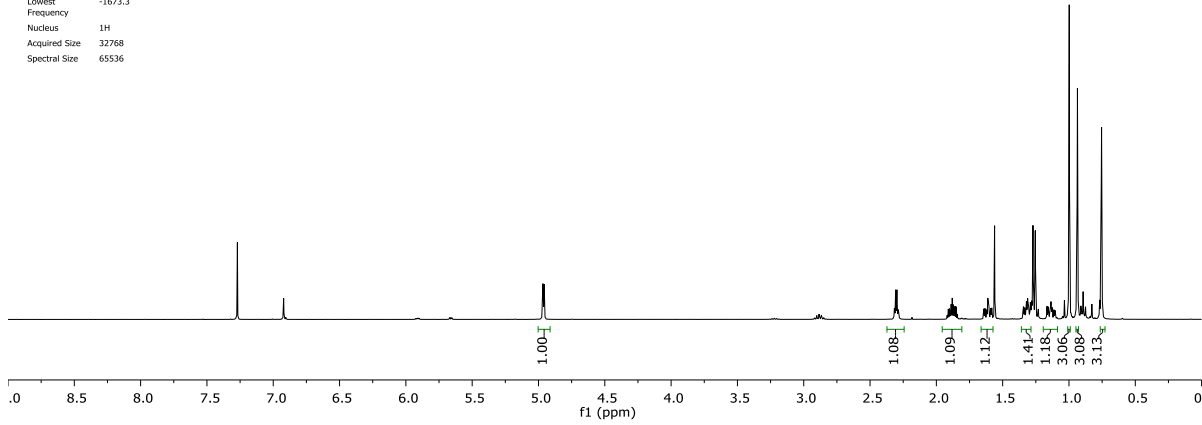
Parameter	Value
Title	MHY-3-295.9.fid
Origin	LUXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	294.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z4400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation Delay	1.0000
Pulse Width	16.0000
Acquisition Time	3.9584
Acquisition Date	2013-06-10T09:33:00
Spectrometer Frequency	400.13
Spectral Width	8278.1
Lowest Frequency	-1673.3
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

4.9664
4.9573



6b

2.3163
2.3068
2.2974
2.2879
1.9097
1.9011
1.8885
1.8801
1.8715
1.8590
1.8504
1.6420
1.6331
1.6206
1.6120
1.6033
1.5908
1.5819
1.3432
1.3207
1.3119
1.3043
1.2908
1.1659
1.1569
1.1431
1.1356
1.1277
1.1138
1.1049
0.9980
0.9363
0.7554



169.552
167.203

103.230
103.213

77.484
77.230
76.975

56.332
56.303
52.263
52.122
49.014
48.966

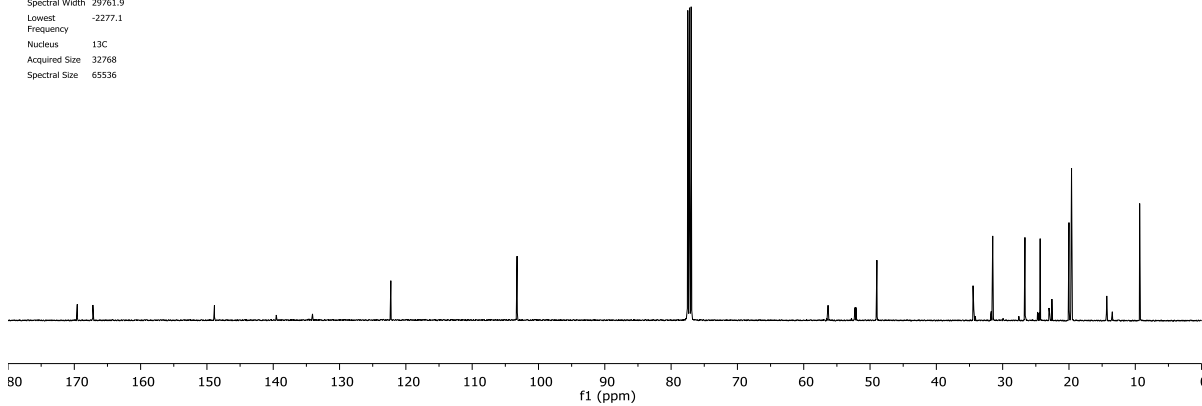
31.532
31.499
26.667
26.639
20.011
19.999
19.612

9.342

Parameter	Value
Title	MHY-3-295.11.fid
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z44862/ 0018
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	0.1500
Pulse Width	9.0000
Acquisition Time	1.1011
Acquisition Date	2013-06-09T09:45:00
Spectrometer Frequency	125.79
Spectral Width	29761.9
Lowest Frequency	-2277.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



6b



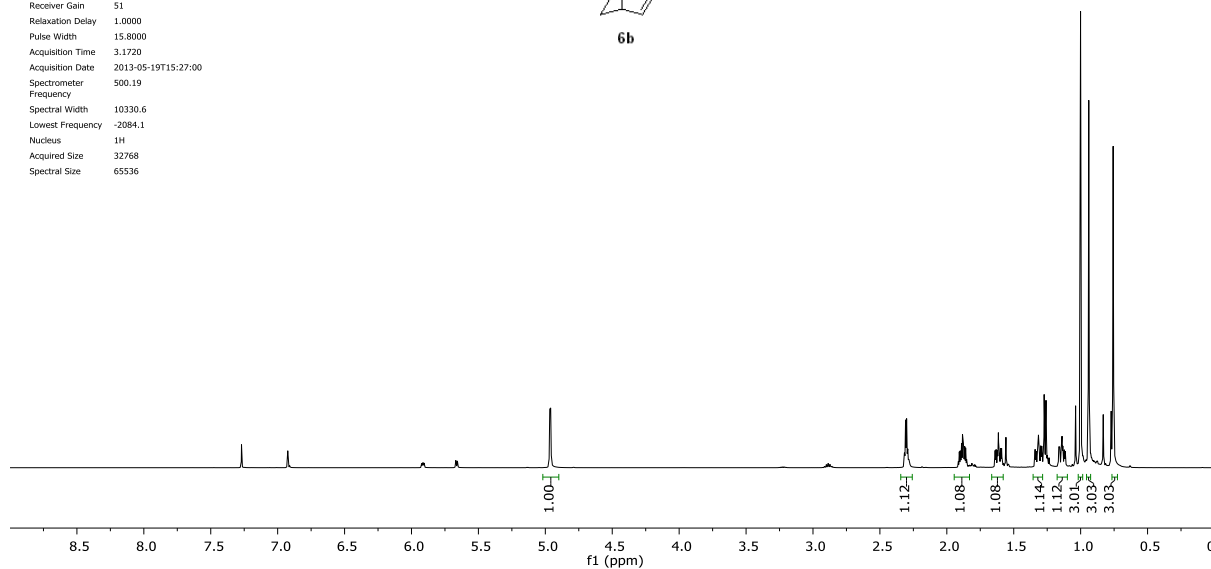
7.2700

Parameter	Value
Title	MHY-3-295.1.fid
Origin	Bruker BioSpin GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPDUL 13C/ D-1H Z-GRD Z4486Z/ 0018
Number of Scans	16
Receiver Gain	51
Relaxation Delay	1.0000
Pulse Width	15.8900
Acquisition Time	3.1720
Acquisition Date	2013-05-19T15:27:00
Spectrometer Frequency	500.19
Spectral Width	10330.6
Lowest Frequency	-2084.1
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

4.9669
4.9597
2.3157
2.3082
2.3005
2.2927
1.9067
1.6998
1.8898
1.8829
1.8761
1.8732
1.8661
1.8591
1.6387
1.6317
1.6217
1.6147
1.6078
1.5978
1.5907
1.3402
1.3328
1.3219
1.3151
1.3089
1.2981
1.2907
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1.1453
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1.1328
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1.1144
1.0008
0.9394
0.7571

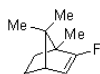


6b

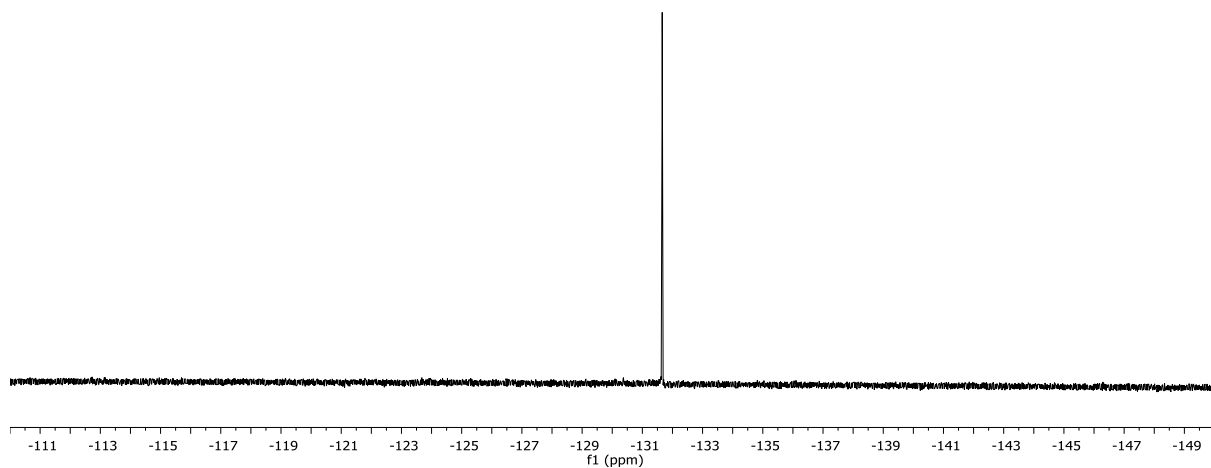


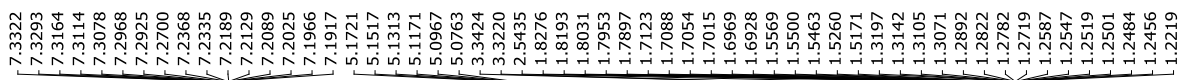
Parameter	Value
Title	MHY-3-295.7.fid
Origin	Bruker Analytik GmbH
Spectrometer	drx400
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgfgan
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	1024
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-05-05T13:36:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-131.660

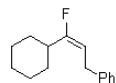


6b

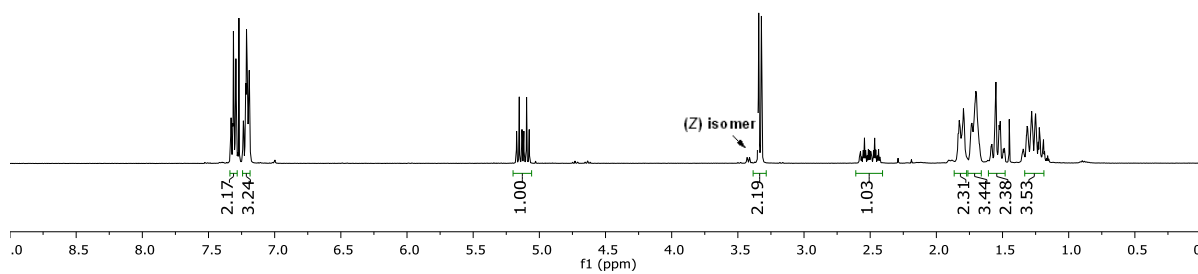




Parameter	Value
Title	MHY-4-14.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/ 0239
Number of Scans	16
Receiver Gain	287
Relaxation	1.0000
Delay	
Pulse Width	18.5000
Acquisition	3.9584
Time	
Acquisition	2013-05-13T14:34:00
Date	
Spectrometer	400.13
Frequency	
Spectral Width	8278.1
Lowest	-1673.5
Frequency	
Nucleus	1H
Acquired Size	32768
Spectral Size	65536



6c (E) major isomer



165.776
163.778

140.757
140.739

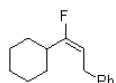
128.674
128.285
126.334

102.925
102.730

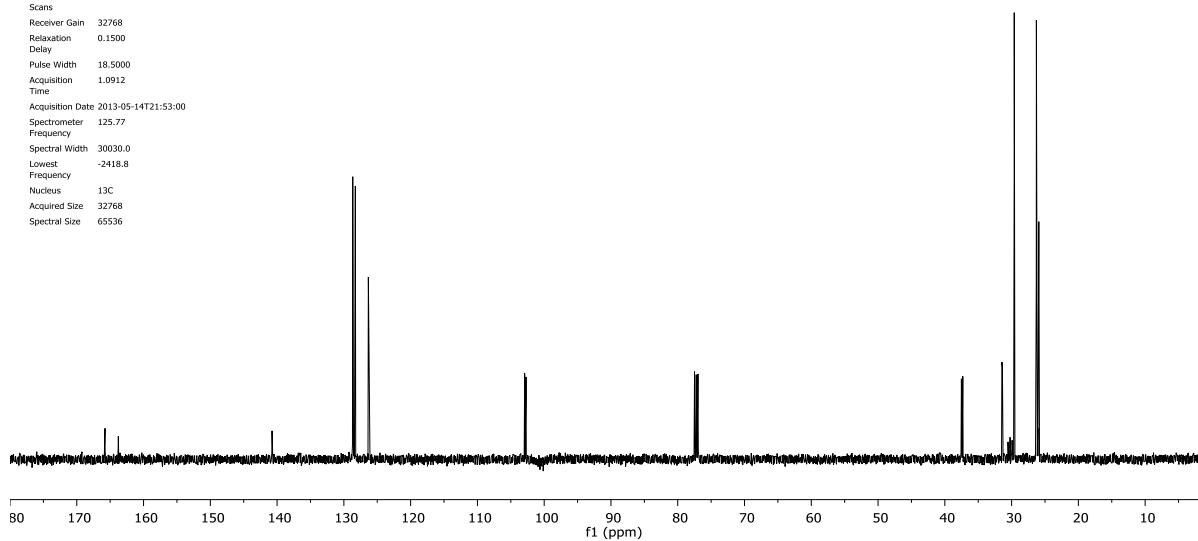
77.485
77.230
76.977

37.520
37.310
31.456
31.374
29.605
26.291
25.925

Parameter	Value
Title	MHY-4-14.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	299.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD 28007/ 061
Number of Scans	5595
Receiver Gain	32768
Relaxation	0.1500
Delay	
Pulse Width	18.5000
Acquisition	1.0912
Time	
Acquisition	2013-05-14T21:53:00
Date	
Spectrometer	125.77
Frequency	
Spectral Width	30030.0
Lowest	-2418.8
Frequency	
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

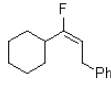


6c

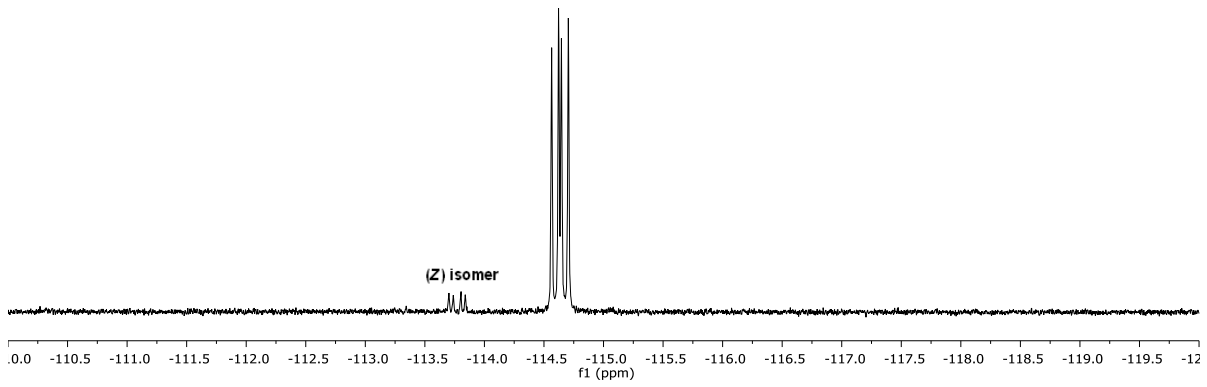


Parameter Value
 Title MHY-4-14.4.fid
 Origin Bruker Analytik GmbH
 Spectrometer drx400
 Solvent CDCl3
 Temperature 293.7
 Pulse Sequence zgpg30
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/
 31P/ 19F 2-GRD Z8400/
 0239
 Number of Scans 16
 Receiver Gain 1024
 Relaxation 1.0000
 Delay
 Pulse Width 27.0000
 Acquisition 0.8717
 Time
 Acquisition Date 2013-05-13T14:36:00
 Spectrometer 376.46
 Frequency
 Spectral Width 75188.0
 Lowest -75243.6
 Frequency
 Nucleus 19F
 Acquired Size 65536
 Spectral Size 131072

-113.701
 -113.738
 -113.802
 -113.839
 -114.564
 -114.623
 -114.646
 -114.705



6c (E) major isomer



7.3495
 7.3420
 7.3370
 7.3347
 7.2981
 7.2913
 7.2856
 7.2753
 7.2700

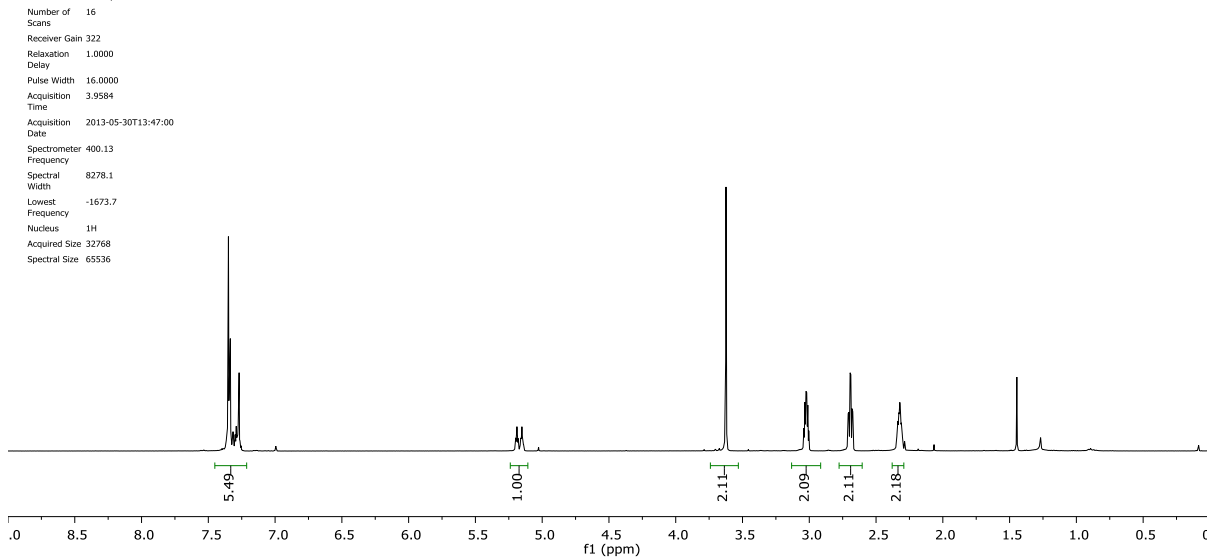
5.2010
 5.1981
 5.1926
 5.1891
 5.1858
 5.1803
 5.1773
 5.1635
 5.1606
 5.1550
 5.1517
 5.1485
 5.1427
 5.1399

3.6236
 3.0399
 3.0332
 3.0310
 3.0267
 3.0246
 3.0197
 3.0176
 3.0129
 3.0106
 3.0039
 2.77088
 2.77035
 2.6942
 2.6889
 2.6796
 2.6744
 2.3366
 2.3328
 2.3291
 2.3256
 2.3220
 2.3184
 2.3149
 2.3112

Parameter Value
 Title MHY-3-296.5.fid
 Origin UXNMR, Bruker
 Analytische Messtechnik GmbH
 Spectrometer drx400
 Solvent CDCl3
 Temperature 293.6
 Pulse zg30
 Sequence
 Experiment 1D
 Probe 5 mm QNP 1H/ 13C/
 31P/ 19F 2-GRD
 Z8400/ 0239
 Number of Scans 16
 Receiver Gain 322
 Relaxation 1.0000
 Delay
 Pulse Width 16.0000
 Acquisition 3.9584
 Time
 Acquisition Date 2013-05-30T13:47:00
 Spectrometer 400.13
 Frequency
 Spectral 8278.1
 Width
 Lowest -1673.7
 Frequency
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



6d



SI-73

159.417
157.369

138.402

129.225
128.525
127.413

100.572
100.455

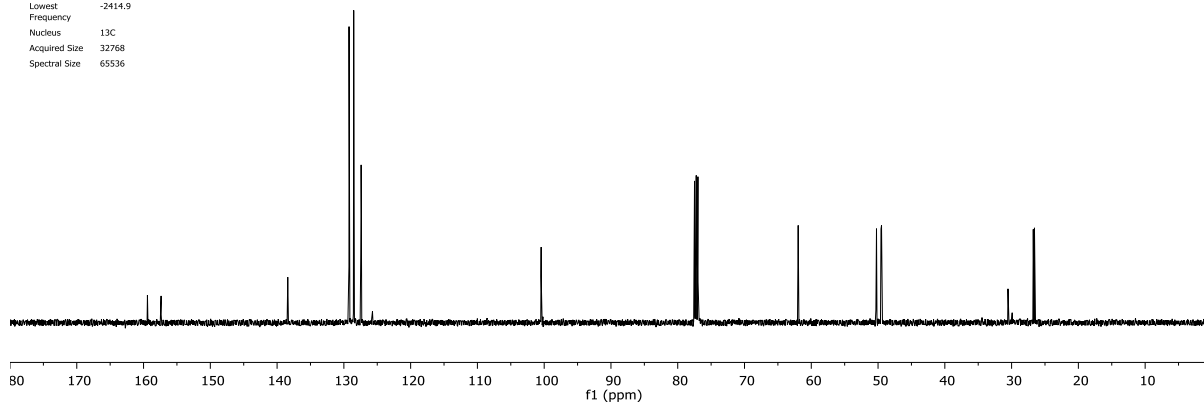
77.484
77.230
76.975

61.962
61.940

50.307
50.235
49.561
49.480

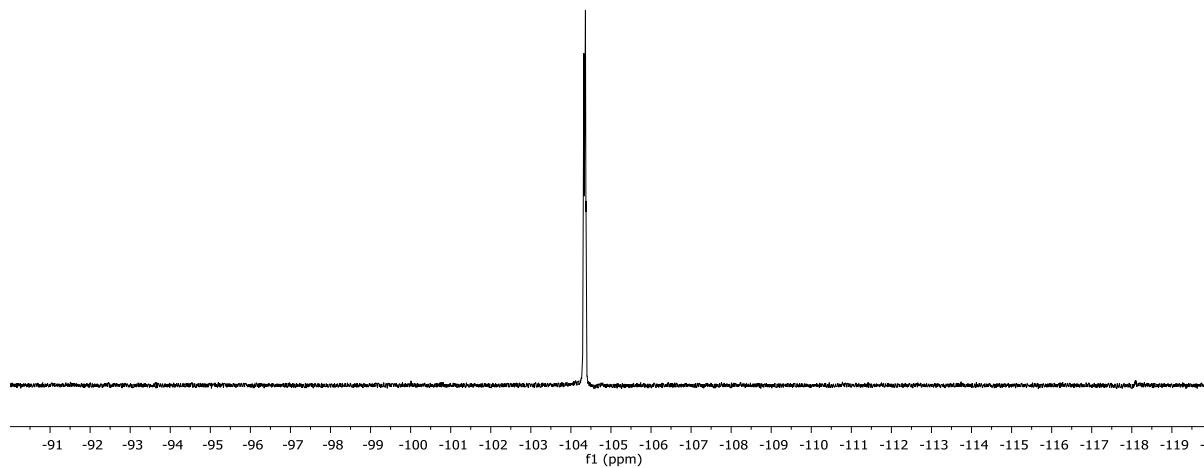
26.756
26.577

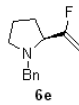
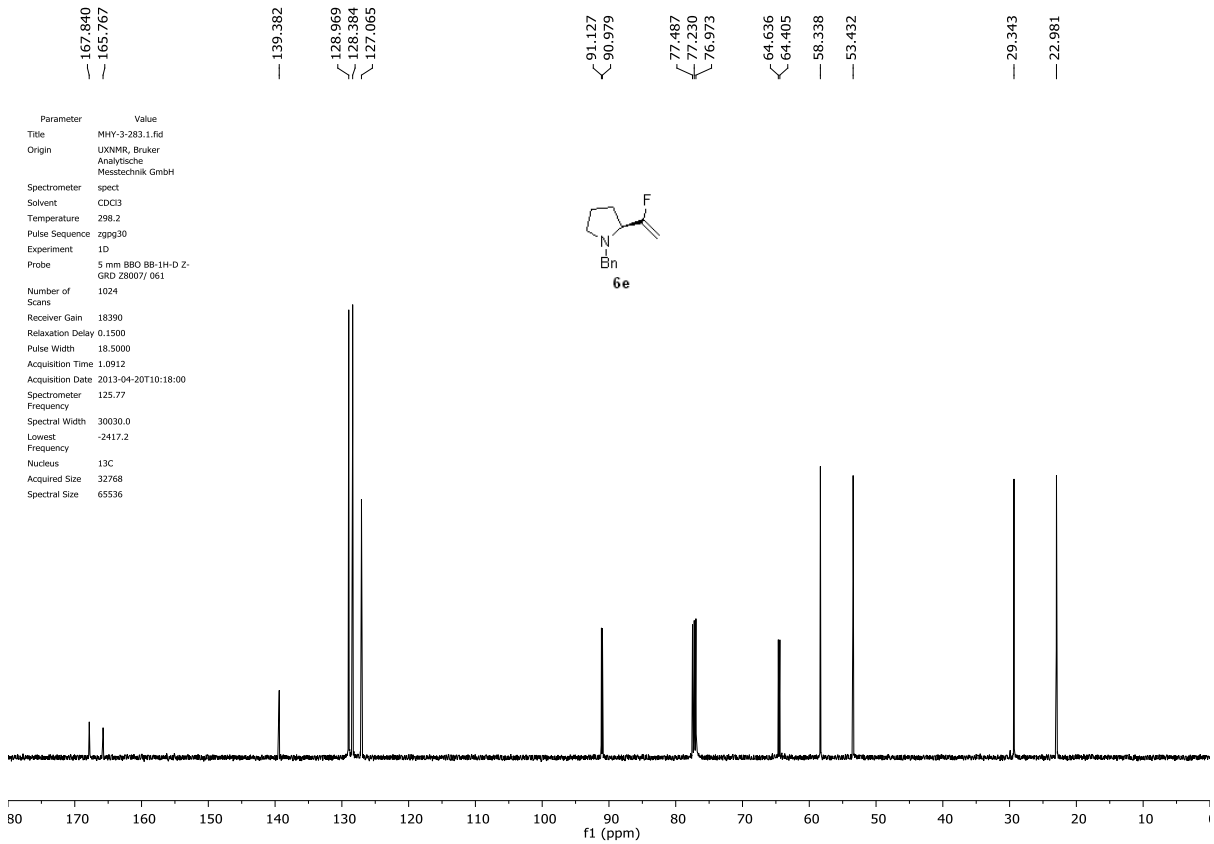
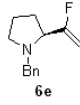
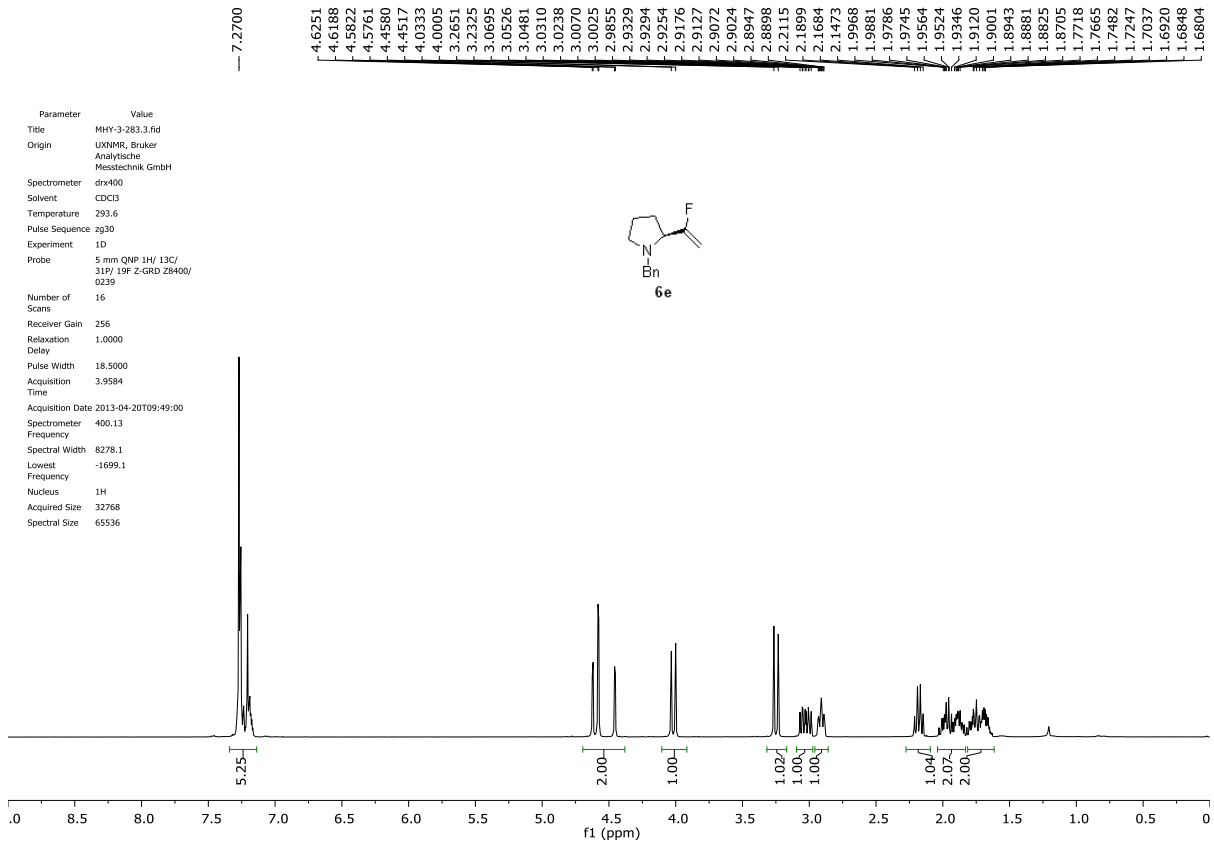
Parameter	Value
Title	MHY-4-46.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	spect
Solvent	CDCl3
Temperature	301.2
Pulse Sequence	zpgg30
Experiment	1D
Probe	5 mm BBO BB-1H-D Z-GRD Z8007/061
Number of Scans	279
Receiver Gain	32768
Relaxation Delay	0.1500
Pulse Width	18.5000
Acquisition Time	1.0912
Acquisition Date	2013-06-01T21:33:00
Spectrometer Frequency	125.77
Spectral Width	30030.0
Lowest Frequency	-2414.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



Parameter	Value
Title	MHY-3-296.6.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgfg1q
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRD Z8400/0239
Number of Scans	16
Receiver Gain	724
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-05-30T13:50:00
Spectrometer Frequency	376.46
Spectral Width	75188.0
Lowest Frequency	-75243.6
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

-104.323
-104.364

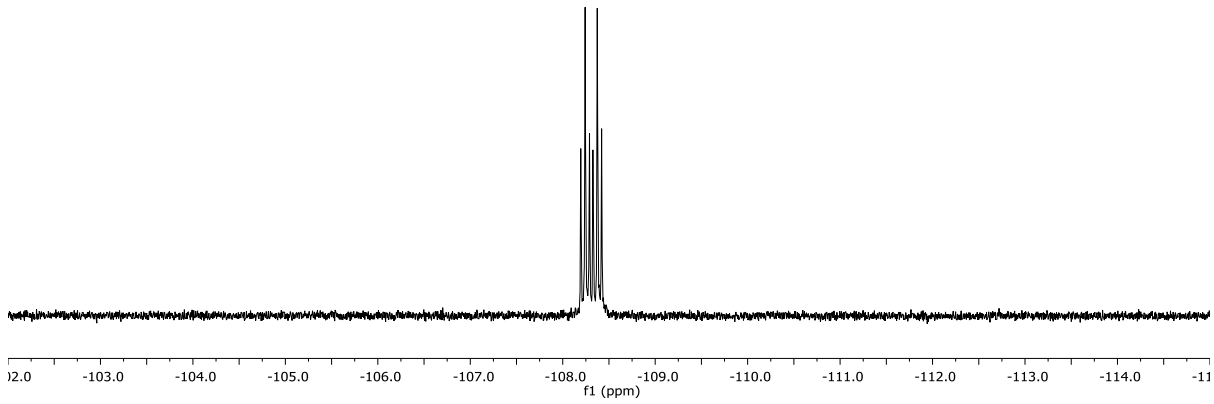
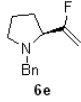




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Parameter	Value
Title	MHY-3-289.5.fid
Origin	Bruker Analytik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRO Z8400/ 0239
Number of Scans	16
Receiver Gain	1825
Relaxation Delay	1.0000
Pulse Width	27.0000
Acquisition Time	0.8717
Acquisition Date	2013-04-22T18:44:00
Spectrometer	376.46
Frequency	75188.0
Spectral Width	-75243.6
Lowest Frequency	19F
Nucleus	65536
Acquired Size	131072
Spectral Size	

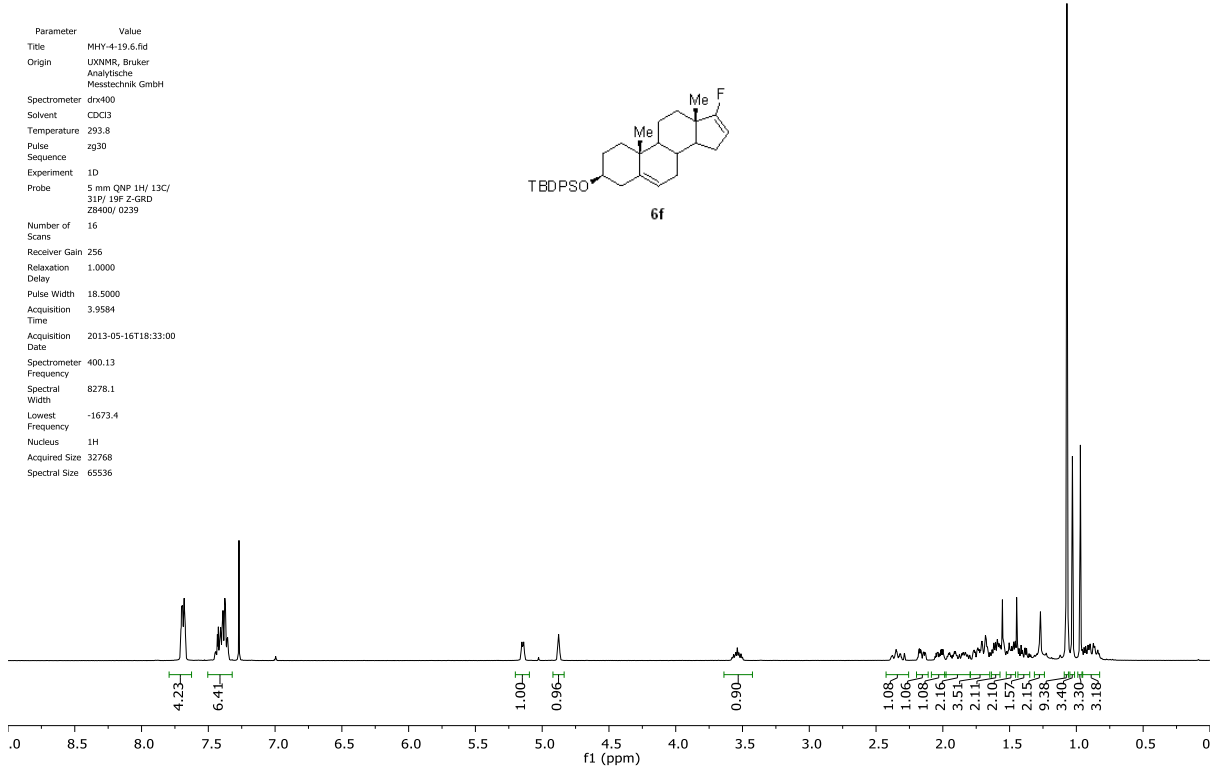
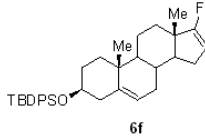
-108.195
-108.242
-108.289
-108.327
-108.374
-108.420



7.7007
7.6970
7.6930
7.6846
7.6807
7.6768
7.3959
7.3918
7.3894
7.3815
7.3784
7.3760
7.3712
7.2700

5.1517
5.1385
4.8806
4.8766
4.8726
3.5668
3.5552
3.5505
3.5392
3.5277
3.5229
3.5117
2.3569
2.3498
2.3430
2.3225
2.3157
2.2875
2.1801
2.1748
2.1679
2.1629
2.1471
2.1417
2.1344
2.1295
2.0498
2.0419
2.0341
2.0146
2.0067
1.9988
1.9551
1.9483
1.9129
1.9058
1.8517
1.8475
1.8342
1.8289
1.0708
1.0296
0.9699

Parameter	Value
Title	MHY-4-19.6.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Spectrometer	dx400
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm QNP 1H/ 13C/ 31P/ 19F Z-GRO Z8400/ 0239
Number of Scans	16
Receiver Gain	256
Relaxation Delay	1.0000
Delay	
Pulse Width	18.5000
Acquisition Time	3.9584
Acquisition Date	2013-05-16T18:33:00
Spectrometer	400.13
Frequency	8278.1
Spectral Width	-1673.4
Lowest Frequency	1H
Nucleus	32768
Acquired Size	65536
Spectral Size	



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