

SUPPORTING INFORMATION

A general synthetic method for Si-fluoresceins and Si-rhodamines

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EXPERIMENTAL INFORMATION

Page	Contents
S2	General Experimental Information for Synthesis
S2	Experimentals and Characterization Data for All Compounds
S2	Dibromide Intermediates
S12	Novel Electrophiles (17 , 70 , and 71)
S15	Si-Fluoresceins
S20	Si-Rhodamines and Related Dyes
S32	Synthesis of Rhodamines 58–60
S33	Potomac Orange (Carborhodamine 66)
S34	Optical Spectroscopy and Microscopy Methods
S37	Figures S1, S2
S38	Tables S1–S3
S42	References
S43	NMR and HPLC/MS

GENERAL EXPERIMENTAL INFORMATION FOR SYNTHESIS

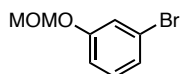
Commercial reagents were obtained from reputable suppliers and used as received. All solvents were purchased in septum-sealed bottles stored under an inert atmosphere. All reactions were sealed with septa through which a nitrogen atmosphere was introduced unless otherwise noted. Reactions were conducted in round-bottomed flasks or septum-capped crimp-top vials containing Teflon-coated magnetic stir bars. Heating of reactions was accomplished with a silicon oil bath or an aluminum reaction block on top of a stirring hotplate equipped with an electronic contact thermometer to maintain the indicated temperatures.

Reactions were monitored by thin layer chromatography (TLC) on precoated TLC glass plates (silica gel 60 F₂₅₄, 250 μ m thickness) or by LC/MS (Phenomenex Kinetex 2.1 mm \times 30 mm 2.6 μ m C18 column; 5 μ L injection; 5–98% MeCN/H₂O, linear gradient, with constant 0.1% v/v HCO₂H additive; 6 min run; 0.5 mL/min flow; ESI; positive ion mode). TLC chromatograms were visualized by UV illumination or developed with *p*-anisaldehyde, ceric ammonium molybdate, or KMnO₄ stain. Reaction products were purified by flash chromatography on an automated purification system using pre-packed silica gel columns or by preparative HPLC (Phenomenex Gemini–NX 30 \times 150 mm 5 μ m C18 column). Analytical HPLC analysis was performed with an Agilent Eclipse XDB 4.6 \times 150 mm 5 μ m C18 column under the indicated conditions. High-resolution mass spectrometry was performed by the High Resolution Mass Spectrometry Facility at the University of Iowa.

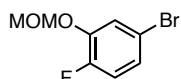
NMR spectra were recorded on a 400 MHz spectrometer. ¹H and ¹³C chemical shifts were referenced to TMS or residual solvent peaks, and ¹⁹F chemical shifts were referenced to CFCl₃. Data for ¹H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), integration. Data for ¹³C NMR spectra are reported by chemical shift (δ ppm) with hydrogen multiplicity (C, CH, CH₂, CH₃) information obtained from DEPT spectra. The characterization data for Si-fluorescein (**1**), JF₆₄₆ (**3**), SiTMR (**33**), and 3-methyl-JF₆₄₆ (**45**) matched the previously reported spectra.^{1–2} The ¹³C NMR spectra are not reported for compounds containing tetrafluoro-substituted aryl rings, as the numerous distinct fluorine couplings confounded interpretation of the spectra.

SYNTHESIS OF DIBROMIDE INTERMEDIATES

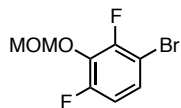
General method S1: MOM protection of phenols. The following procedure for 1-bromo-3-(methoxymethoxy)benzene (**10a**) is representative. A solution of 3-bromophenol (15.00 g, 86.7 mmol) and DIEA (22.65 mL, 130.1 mmol, 1.5 eq) in CH₂Cl₂ (200 mL) was cooled to 0 °C. Chloromethyl methyl ether (8.56 mL, 112.7 mmol, 1.3 eq) was added dropwise. The reaction was then warmed to room temperature and stirred for 4 h. It was subsequently diluted with water and extracted with CH₂Cl₂ (2 \times). The combined organic extracts were washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered, and evaporated. Flash chromatography (0–20% Et₂O/hexanes, linear gradient) afforded **10a** as a colorless oil (16.52 g, 88%).



1-Bromo-3-(methoxymethoxy)benzene (10a): The title compound (88%, colorless oil) was prepared from 3-bromophenol according to method S1. ^1H NMR (CDCl_3 , 400 MHz) δ 7.23 – 7.20 (m, 1H), 7.17 – 7.10 (m, 2H), 6.99 – 6.93 (m, 1H), 5.15 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 158.2 (C), 130.7 (CH), 125.1 (CH), 122.8 (C), 119.8 (CH), 115.2 (CH), 94.6 (CH_2), 56.2 (CH_3); HRMS (EI) calcd for $\text{C}_8\text{H}_9\text{BrO}_2$ $[\text{M}]^{++}$ 215.9786, found 215.9788.



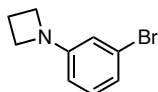
4-Bromo-1-fluoro-2-(methoxymethoxy)benzene (10b): The title compound (99%, colorless oil) was prepared from 5-bromo-2-fluorophenol according to method S1. ^1H NMR (CDCl_3 , 400 MHz) δ 7.35 (dd, $J = 7.4, 2.3$ Hz, 1H), 7.09 (ddd, $J = 8.7, 4.0, 2.4$ Hz, 1H), 6.96 (dd, $J = 10.7, 8.7$ Hz, 1H), 5.20 (s, 2H), 3.52 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -135.73 (ddd, $J_{\text{FH}} = 11.0, 7.3, 4.1$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 152.5 (d, $^1J_{\text{CF}} = 246.5$ Hz, CF), 146.0 (d, $^2J_{\text{CF}} = 11.7$ Hz, C), 125.5 (d, $^3J_{\text{CF}} = 6.9$ Hz, CH), 121.3 (d, $^3J_{\text{CF}} = 1.6$ Hz, CH), 117.7 (d, $^2J_{\text{CF}} = 20.1$ Hz, CH), 116.4 (d, $^4J_{\text{CF}} = 3.8$ Hz, C), 95.9 (CH_2), 56.6 (CH_3); HRMS (EI) calcd for $\text{C}_8\text{H}_8\text{BrFO}_2$ $[\text{M}]^{++}$ 233.9692, found 233.9684.



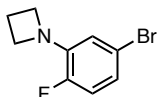
1-Bromo-2,4-difluoro-3-(methoxymethoxy)benzene (10c): The title compound (94%, colorless oil) was prepared from 3-bromo-2,6-difluorophenol according to method S1. ^1H NMR (CDCl_3 , 400 MHz) δ 7.24 (ddd, $J = 9.1, 7.2, 5.4$ Hz, 1H), 6.90 – 6.79 (m, 1H), 5.17 (s, 2H), 3.60 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -119.56 – -119.63 (m, 1F), -128.31 – -128.40 (m, 1F); ^{13}C NMR (CDCl_3 , 101 MHz) δ 155.9 (dd, $J_{\text{CF}} = 249.0, 4.1$ Hz, CF), 153.8 (dd, $J_{\text{CF}} = 248.6, 5.5$ Hz, CF), 134.3 (t, $^2J_{\text{CF}} = 15.4$ Hz, C), 127.1 (dd, $J_{\text{CF}} = 8.5, 0.7$ Hz, CH), 112.9 (dd, $J_{\text{CF}} = 20.7, 3.9$ Hz, CH), 104.7 (dd, $J_{\text{CF}} = 19.9, 4.0$ Hz, C), 99.1 (t, $^4J_{\text{CF}} = 3.5$ Hz, CH_2), 57.4 (t, $^6J_{\text{CF}} = 1.6$ Hz, CH_3); HRMS (EI) calcd for $\text{C}_8\text{H}_7\text{BrF}_2\text{O}_2$ $[\text{M}]^{++}$ 251.9597, found 251.9598.

General method S2: Synthesis of 3-bromoanilines. The following procedure for 1-(3-bromophenyl)azetidine (**29a**) is representative. An oven-dried crimp-top vial was charged with CuI (135 mg, 0.707 mmol, 0.1 eq) and K_3PO_4 (4.50 g, 21.2 mmol, 3 eq). The vial was sealed and evacuated/backfilled with nitrogen (3 \times). 1-Butanol (10 mL) was added, followed by ethylene glycol (946 μL , 17.0 mmol, 2.4 eq), 3-bromoiodobenzene (901 μL , 7.07 mmol), and azetidine (572 μL , 8.48 mmol, 1.2 eq). The reaction mixture was stirred at 100 $^\circ\text{C}$ for 18 h. It was then cooled to room temperature, diluted with saturated NH_4Cl , and extracted with EtOAc (2 \times). The combined organics

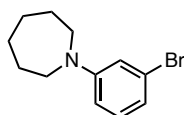
were washed with brine, dried over anhydrous MgSO_4 , filtered, and evaporated. Flash chromatography (0–10% Et_2O /hexanes, linear gradient) afforded 1.28 g (85%) of **29a** as a colorless oil.



1-(3-Bromophenyl)azetidine (29a): The title compound (85%, colorless oil) was prepared from 3-bromoiodobenzene and azetidine according to method S2. ^1H NMR (CDCl_3 , 400 MHz) δ 7.03 (t, J = 8.0 Hz, 1H), 6.84 – 6.79 (m, 1H), 6.54 (t, J = 2.0 Hz, 1H), 6.35 – 6.29 (m, 1H), 3.86 (t, J = 7.3 Hz, 4H), 2.36 (p, J = 7.2 Hz, 2H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 153.3 (C), 130.3 (CH), 123.2 (C), 120.0 (CH), 114.2 (CH), 109.9 (CH), 52.4 (CH_2), 17.0 (CH_2); HRMS (ESI) calcd for $\text{C}_9\text{H}_{11}\text{BrN}$ $[\text{M}+\text{H}]^+$ 212.0069, found 212.0076.



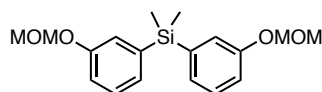
1-(5-Bromo-2-fluorophenyl)azepane (29b): The title compound (67%, colorless oil) was prepared from 4-bromo-1-fluoro-2-iodobenzene and azetidine according to method S2. ^1H NMR (CDCl_3 , 400 MHz) δ 6.82 – 6.72 (m, 2H), 6.53 (dd, J = 8.1, 2.2 Hz, 1H), 3.97 (td, J = 7.3, 2.2 Hz, 4H), 2.35 (p, J = 7.3 Hz, 2H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -135.62 – -135.72 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 151.5 (d, $^1J_{\text{CF}}$ = 241.6 Hz, CF), 141.3 (d, $^2J_{\text{CF}}$ = 12.2 Hz, C), 120.7 (d, $^3J_{\text{CF}}$ = 6.7 Hz, CH), 117.04 (d, $^2J_{\text{CF}}$ = 20.3 Hz, CH), 116.90 (d, $^4J_{\text{CF}}$ = 3.4 Hz, C), 116.89 (d, $^3J_{\text{CF}}$ = 4.8 Hz, CH), 54.0 (d, $^4J_{\text{CF}}$ = 2.4 Hz, CH_2), 18.0 (d, $^5J_{\text{CF}}$ = 2.3 Hz, CH_2); HRMS (ESI) calcd for $\text{C}_9\text{H}_{10}\text{BrFN}$ $[\text{M}+\text{H}]^+$ 229.9975, found 229.9971.



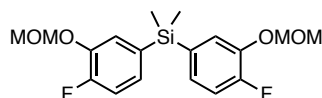
1-(3-Bromophenyl)azepane (29d): The title compound (46%, colorless oil) was prepared from 3-bromoiodobenzene and azepane according to method S2. ^1H NMR (CDCl_3 , 400 MHz) δ 7.02 (dd, J = 8.4, 7.9 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.72 (ddd, J = 7.8, 1.8, 0.8 Hz, 1H), 6.58 (ddd, J = 8.5, 2.5, 0.5 Hz, 1H), 3.46 – 3.37 (m, 4H), 1.82 – 1.72 (m, 4H), 1.57 – 1.52 (m, 4H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 150.3 (C), 130.5 (CH), 123.8 (C), 118.0 (CH), 114.0 (CH), 109.9 (CH), 49.3 (CH_2), 27.7 (CH_2), 27.2 (CH_2); HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$ 254.0539, found 254.0543.

General method S3: Preparation of diphenylsilanes 11a-c and 30a-d via addition of aryllithium reagents to Me_2SiCl_2 . The following procedure for bis(3-(methoxymethoxy)phenyl)dimethylsilane (**11a**) is representative. A solution of bromide **10a** (16.35 g, 75.3 mmol, 2.4 eq) in THF (150 mL) was cooled to -78°C under nitrogen. *n*-Butyllithium (2.65 M in hexanes, 28.42 mL, 75.3 mmol, 2.4 eq) was added, and the reaction was stirred at -78°C for 30 min. Dichlorodimethylsilane (3.79 mL, 31.4 mmol) in THF (15 mL) was then added. The dry ice bath was

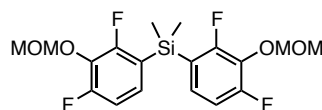
removed, and the reaction was stirred at room temperature for 3 h. It was subsequently quenched with saturated NH_4Cl , diluted with water, and extracted with EtOAc (2 \times). The combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (0–30% Et_2O /hexanes, linear gradient) afforded 10.23 g (98%) of **11a** as a colorless oil.



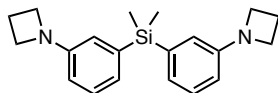
Bis(3-(methoxymethoxy)phenyl)dimethylsilane (11a): The title compound (98%, colorless oil) was prepared from **10a** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 7.31 – 7.23 (m, 2H), 7.19 – 7.13 (m, 4H), 7.05 (ddd, J = 8.2, 2.6, 1.0 Hz, 2H), 5.15 (s, 4H), 3.47 (s, 6H), 0.54 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 156.9 (C), 140.0 (C), 129.2 (CH), 127.8 (CH), 122.3 (CH), 116.8 (CH), 94.7 (CH_2), 56.1 (CH_3), -2.3 (CH_3); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{24}\text{O}_4\text{Si}$ $[\text{M}]^{++}$ 332.1444, found 332.1456.



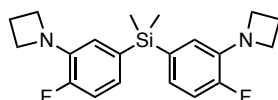
Bis(4-fluoro-3-(methoxymethoxy)phenyl)dimethylsilane (11b): The title compound (66%, colorless oil) was prepared from **10b** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 7.30 – 7.26 (m, 2H), 7.11 – 7.05 (m, 4H), 5.19 (s, 4H), 3.51 (s, 6H), 0.52 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -132.55 – -132.64 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 154.5 (d, $^1J_{\text{CF}}$ = 248.8 Hz, CF), 144.8 (d, $^2J_{\text{CF}}$ = 10.1 Hz, C), 134.4 (d, $^4J_{\text{CF}}$ = 4.5 Hz, C), 129.1 (d, $^3J_{\text{CF}}$ = 6.9 Hz, CH), 124.2 (d, $^3J_{\text{CF}}$ = 1.7 Hz, CH), 116.4 (d, $^2J_{\text{CF}}$ = 17.7 Hz, CH), 96.2 (d, $^4J_{\text{CF}}$ = 1.0 Hz, CH_2), 56.5 (CH_3), -2.1 (CH_3); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{22}\text{F}_2\text{O}_4\text{Si}$ $[\text{M}]^{++}$ 368.1255, found 368.1262.



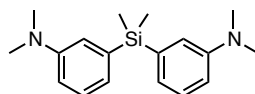
Bis(2,4-difluoro-3-(methoxymethoxy)phenyl)dimethylsilane (11c): The title compound (56%, colorless oil) was prepared from **10c** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 6.98 (dt, J = 8.1, 6.1 Hz, 2H), 6.90 (ddd, J = 9.6, 8.3, 0.9 Hz, 2H), 5.13 (s, 4H), 3.58 (s, 6H), 0.62 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -115.63 – -115.73 (m, 2F), -125.92 (td, J = 10.2, 6.4 Hz, 2F); ^{13}C NMR (CDCl_3 , 101 MHz) δ 160.8 (dd, J_{CF} = 243.5, 5.1 Hz, CF), 158.1 (dd, J_{CF} = 250.9, 5.5 Hz, CF), 132.8 (dd, J_{CF} = 18.1, 14.0 Hz, C), 129.7 (dd, J_{CF} = 13.0, 9.3 Hz, CH), 120.0 (dd, J_{CF} = 28.4, 3.6 Hz, C), 112.6 (dd, J_{CF} = 18.6, 3.1 Hz, CH), 99.0 (t, $^4J_{\text{CF}}$ = 3.4 Hz, CH_2), 57.2 (CH_3), -1.8 (t, $^4J_{\text{CF}}$ = 1.9 Hz, CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{F}_4\text{O}_4\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 427.0959, found 427.0960.



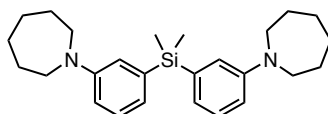
Bis(3-(azetidin-1-yl)phenyl)dimethylsilane (30a): The title compound (99%, white solid) was prepared from **29a** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 7.18 (t, $J = 7.6$ Hz, 2H), 6.89 (dt, $J = 7.1$, 0.9 Hz, 2H), 6.60 (d, $J = 2.2$ Hz, 2H), 6.45 (ddd, $J = 8.0$, 2.5, 1.0 Hz, 2H), 3.84 (t, $J = 7.2$ Hz, 8H), 2.32 (p, $J = 7.2$ Hz, 4H), 0.49 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 151.6 (C), 138.9 (C), 128.3 (CH), 123.4 (CH), 116.9 (CH), 112.2 (CH), 52.6 (CH_2), 17.2 (CH_2), -2.1 (CH_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{27}\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 323.1938, found 323.1939.



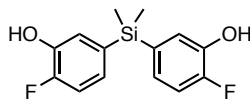
Bis(3-(azetidin-1-yl)-4-fluorophenyl)dimethylsilane (30b): The title compound (55%, colorless oil) was prepared from **29b** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 6.92 (dd, $J = 12.8$, 7.9 Hz, 2H), 6.81 (ddd, $J = 7.8$, 4.9, 1.5 Hz, 2H), 6.55 (dd, $J = 9.7$, 1.4 Hz, 2H), 3.94 (td, $J = 7.3$, 2.1 Hz, 8H), 2.32 (p, $J = 7.2$ Hz, 4H), 0.48 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -131.44 – -131.57 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 153.5 (d, $^1J_{\text{CF}} = 244.2$ Hz, CF), 139.6 (d, $^2J_{\text{CF}} = 10.0$ Hz, C), 133.8 (d, $^4J_{\text{CF}} = 4.1$ Hz, C), 124.8 (d, $^3J_{\text{CF}} = 6.3$ Hz, CH), 119.8 (d, $^3J_{\text{CF}} = 4.5$ Hz, CH), 115.3 (d, $^2J_{\text{CF}} = 17.6$ Hz, CH), 54.1 (d, $^4J_{\text{CF}} = 2.2$ Hz, CH_2), 18.2 (d, $^5J_{\text{CF}} = 2.1$ Hz, CH_2), -1.9 (CH_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{25}\text{F}_2\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 359.1750, found 359.1755.



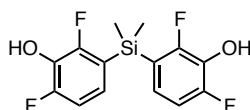
3,3'-(Dimethylsilanediyl)bis(*N,N*-dimethylaniline) (30c): The title compound (97%, colorless oil) was prepared from 3-bromo-*N,N*-dimethylaniline (**29c**) according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 7.23 (dd, $J = 8.0$, 7.2 Hz, 2H), 6.95 – 6.92 (m, 2H), 6.91 (dt, $J = 7.1$, 0.9 Hz, 2H), 6.76 (ddd, $J = 8.3$, 2.7, 0.9 Hz, 2H), 2.92 (s, 12H), 0.52 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 150.1 (C), 139.1 (C), 128.6 (CH), 122.9 (CH), 118.5 (CH), 113.7 (CH), 40.8 (CH_3), -2.0 (CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{27}\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 299.1938, found 299.1939.



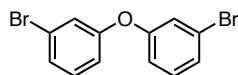
Bis(3-(azepan-1-yl)phenyl)dimethylsilane (30d): The title compound (96%, colorless oil) was prepared from **29d** according to method S3. ^1H NMR (CDCl_3 , 400 MHz) δ 7.19 (dd, $J = 8.2$, 7.2 Hz, 2H), 6.88 – 6.84 (m, 2H), 6.83 – 6.79 (m, 2H), 6.69 (ddd, $J = 8.4$, 2.8, 0.7 Hz, 2H), 3.46 – 3.37 (m, 8H), 1.80 – 1.69 (m, 8H), 1.56 – 1.48 (m, 8H), 0.51 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 148.3 (C), 139.2 (C), 128.7 (CH), 121.3 (CH), 117.0 (CH), 112.1 (CH), 49.2 (CH_2), 28.0 (CH_2), 27.4 (CH_2), -2.0 (CH_3); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{39}\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 407.2877, found 407.2884.



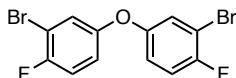
5,5'-(Dimethylsilanediyl)bis(2-fluorophenol) (13b): Silane **11b** (1.00 g, 2.71 mmol) was taken up in CH_2Cl_2 (10 mL), and trifluoroacetic acid (2.5 mL) was added. The reaction was stirred at room temperature for 2 h. Toluene (15 mL) was added, and the reaction mixture was concentrated to dryness. The resulting residue was purified by flash chromatography on silica gel (0–40% EtOAc/hexanes, linear gradient) to provide 597 mg (78%) of **13b** as a colorless, viscous oil. ^1H NMR (CDCl_3 , 400 MHz) δ 7.11 (dd, J = 9.3, 1.5 Hz, 2H), 7.06 (dd, J = 10.8, 8.0 Hz, 2H), 6.97 (ddd, J = 8.0, 5.2, 1.5 Hz, 2H), 5.06 (s, 2H), 0.50 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -140.45 – -140.55 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 152.1 (d, $^1J_{\text{CF}}$ = 240.1 Hz, CF), 143.3 (d, $^2J_{\text{CF}}$ = 13.5 Hz, C), 135.0 (d, $^4J_{\text{CF}}$ = 4.6 Hz, C), 127.0 (d, $^3J_{\text{CF}}$ = 6.3 Hz, CH), 122.9 (d, $^3J_{\text{CF}}$ = 2.0 Hz, CH), 115.5 (d, $^2J_{\text{CF}}$ = 17.0 Hz, CH), -2.2 (CH_3); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{14}\text{F}_2\text{O}_2\text{Si}$ $[\text{M}]^{+}$ 280.0731, found 280.0722.



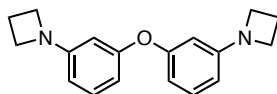
3,3'-(Dimethylsilanediyl)bis(2,6-difluorophenol) (13c): The title compound (89%, white solid) was prepared from **11c** according to the procedure described for **13b**. ^1H NMR (CDCl_3 , 400 MHz) δ 6.90 (ddd, J = 9.7, 8.4, 1.3 Hz, 2H), 6.80 (dt, J = 8.3, 6.2 Hz, 2H), 4.99 (s, 2H), 0.62 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -124.14 – -124.35 (m, 2F), -133.42 (ddd, J = 13.6, 9.7, 6.4 Hz, 2F); ^{13}C NMR (CDCl_3 , 101 MHz) δ 155.9 (dd, J_{CF} = 236.6, 4.9 Hz, CF), 153.2 (dd, J_{CF} = 245.5, 5.2 Hz, CF), 132.6 (dd, J_{CF} = 19.7, 15.1 Hz, C), 125.2 (dd, J_{CF} = 12.4, 8.5 Hz, CH), 119.4 (dd, J_{CF} = 27.3, 3.5 Hz, C), 112.2 (dd, J_{CF} = 17.3, 3.0 Hz, CH), -2.0 (t, $^4J_{\text{CF}}$ = 1.8 Hz, CH_3); HRMS (EI) calcd for $\text{C}_{14}\text{H}_{12}\text{F}_4\text{O}_2\text{Si}$ $[\text{M}]^{+}$ 316.0543, found 316.0521.



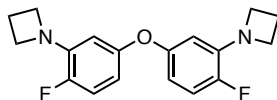
3,3'-Oxybis(bromobenzene) (55a): An oven-dried round-bottom flask was charged with 3-bromophenol (**54a**; 1.62 g, 9.34 mmol), 3-bromophenylboronic acid (3.75 g, 18.7 mmol, 2 eq), $\text{Cu}(\text{OAc})_2$ (1.70 g, 9.34 mmol, 1 eq), and 4 Å molecular sieves (8.10 g). After adding CH_2Cl_2 (80 mL) and Et_3N (6.51 mL, 46.7 mmol, 5 eq), the reaction was stirred at room temperature under ambient atmosphere for 24 h. The reaction mixture was filtered through Celite with CH_2Cl_2 and concentrated to dryness. The resultant residue was partitioned between water and Et_2O , and the aqueous layer was washed a second time with Et_2O . The combined organics were dried over anhydrous MgSO_4 , filtered, and evaporated. Flash chromatography on silica gel (100% hexanes) provided **55a** as a colorless oil (1.22 g, 40%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.29 – 7.25 (m, 2H), 7.21 (t, J = 8.0 Hz, 2H), 7.16 (t, J = 2.0 Hz, 2H), 6.94 (ddd, J = 8.0, 2.3, 1.0 Hz, 2H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 157.6 (C), 131.1 (CH), 127.1 (CH), 123.2 (C), 122.4 (CH), 117.8 (CH); HRMS (EI) calcd for $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}$ $[\text{M}]^{+}$ 327.8921, found 327.8931.



4,4'-Oxybis(2-bromo-1-fluorobenzene) (55b): The title compound (41%, white solid) was prepared from 3-bromo-4-fluorophenylboronic acid and 3-bromo-4-fluorophenol (**54b**) according to the procedure described for **55a**. ^1H NMR (CDCl_3 , 400 MHz) δ 7.18 (dd, $J = 5.6, 2.9$ Hz, 2H), 7.10 (dd, $J = 8.9, 8.0$ Hz, 2H), 6.91 (ddd, $J = 9.0, 3.8, 3.0$ Hz, 2H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -114.28 (ddd, $J_{\text{FH}} = 7.9, 5.6, 3.8$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 155.8 (d, $^1J_{\text{CF}} = 243.9$ Hz, CF), 153.3 (d, $^4J_{\text{CF}} = 2.9$ Hz, C), 123.7 (CH), 119.2 (d, $^3J_{\text{CF}} = 7.1$ Hz, CH), 117.3 (d, $^2J_{\text{CF}} = 24.2$ Hz, CH), 109.8 (d, $^2J_{\text{CF}} = 22.9$ Hz, C); HRMS (EI) calcd for $\text{C}_{12}\text{H}_6\text{Br}_2\text{F}_2\text{O}$ $[\text{M}]^{++}$ 363.8733, found 363.8726.



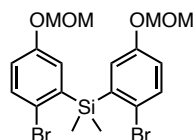
1,1'-(Oxybis(3,1-phenylene))bis(azetidine) (56a): An oven-dried round-bottom flask was charged with Pd_2dba_3 (449 mg, 0.491 mmol, 0.1 eq), XPhos (702 mg, 1.47 mmol, 0.3 eq), and Cs_2CO_3 (4.48 g, 13.7 mmol, 2.8 eq). The flask was sealed and evacuated/backfilled with nitrogen (3 \times). A solution of dibromide **55a** (1.61 g, 4.91 mmol) in dioxane (20 mL) was added, and the reaction was flushed again with nitrogen (3 \times). Following the addition of azetidine (728 μL , 10.8 mmol, 2.2 eq), the reaction was stirred at 100 $^\circ\text{C}$ for 3 h. It was then cooled to room temperature, filtered through Celite with CH_2Cl_2 , and concentrated to dryness. The crude product was purified by flash chromatography (0–25% Et_2O /hexanes, linear gradient, with constant 20% v/v CH_2Cl_2 additive) to provide a yellow solid. The solid was triturated with Et_2O , sonicated, and filtered; the filter cake was washed with additional Et_2O and dried to yield 1.18 g (86%) of **56a** as a white solid. ^1H NMR (CDCl_3 , 400 MHz) δ 7.12 (t, $J = 8.0$ Hz, 2H), 6.38 – 6.32 (m, 2H), 6.20 – 6.14 (m, 2H), 6.12 (t, $J = 2.2$ Hz, 2H), 3.84 (t, $J = 7.2$ Hz, 8H), 2.34 (p, $J = 7.2$ Hz, 4H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 158.3 (C), 153.8 (C), 129.9 (CH), 107.8 (CH), 106.3 (CH), 102.1 (CH), 52.5 (CH_2), 17.0 (CH_2); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 281.1648, found 281.1653.



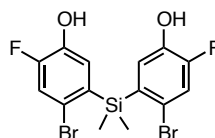
1,1'-(Oxybis(2-fluoro-5,1-phenylene))bis(azetidine) (56b): The title compound (78%, off-white solid) was prepared from **55b** according to the procedure described for **56a**. ^1H NMR (CDCl_3 , 400 MHz) δ 6.83 (dd, $J = 11.9, 8.7$ Hz, 2H), 6.22 (dt, $J = 8.7, 3.1$ Hz, 2H), 6.10 (dd, $J = 7.7, 2.9$ Hz, 2H), 3.94 (td, $J = 7.3, 2.1$ Hz, 8H), 2.33 (p, $J = 7.3$ Hz, 4H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -140.13 – -140.23 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 153.9 (d, $^4J_{\text{CF}} = 2.0$ Hz, C), 148.5 (d, $^1J_{\text{CF}} = 236.7$ Hz, CF), 141.02 (d, $^2J_{\text{CF}} = 12.7$ Hz, C), 116.0 (d, $^2J_{\text{CF}} = 20.7$ Hz, CH), 107.6 (d, $^3J_{\text{CF}} = 6.9$ Hz, CH), 104.9 (d, $^3J_{\text{CF}} = 4.7$ Hz, CH), 54.0 (d, $^4J_{\text{CF}} = 2.4$ Hz, CH_2), 18.0 (d, $^5J_{\text{CF}} = 2.3$ Hz, CH_2); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 317.1460, found 317.1464.

General method S4: Bromination with NBS. The following procedure for bis(2-bromo-5-(methoxymethoxy)phenyl)dimethylsilane (**12a**) is representative. Silane **11a** (10.22 g, 30.7 mmol) was taken up in

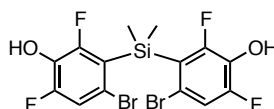
DMF (200 mL). *N*-Bromosuccinimide (10.94 g, 61.5 mmol, 2 eq) was added portion-wise over 5 min, and the reaction was then stirred at room temperature for 72 h. The reaction mixture was concentrated *in vacuo*; the resulting residue was diluted with water and extracted with EtOAc (2×). The combined organic extracts were washed with water and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Silica gel chromatography (0–30% Et₂O/hexanes, linear gradient) afforded 14.15 g (94%) of **12a** as a white solid.



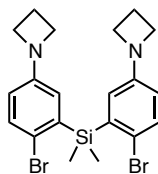
Bis(2-bromo-5-(methoxymethoxy)phenyl)dimethylsilane (12a): The title compound (94%, white solid) was prepared from **11a** according to method S4. ¹H NMR (CDCl₃, 400 MHz) δ 7.41 (d, *J* = 8.7 Hz, 2H), 7.13 (d, *J* = 3.0 Hz, 2H), 6.94 (dd, *J* = 8.7, 3.1 Hz, 2H), 5.12 (s, 4H), 3.45 (s, 6H), 0.74 (s, 6H); ¹³C NMR (CDCl₃, 101 MHz) δ 156.1 (C), 140.2 (C), 133.8 (CH), 125.9 (CH), 122.2 (C), 118.9 (CH), 94.9 (CH₂), 56.2 (CH₃), -1.1 (CH₃); HRMS (ESI) calcd for C₁₈H₂₂Br₂O₄Si [M]⁺⁺ 489.9634, found 489.9628.



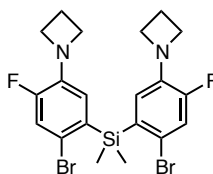
5,5'-(Dimethylsilanediyl)bis(4-bromo-2-fluorophenol) (14b): The title compound (31%, white solid) was prepared from **13b** according to method S4. ¹H NMR (CDCl₃, 400 MHz) δ 7.27 (d, ³*J*_{HF} = 10.0 Hz, 2H), 7.11 (d, ⁴*J*_{HF} = 9.9 Hz, 2H), 5.05 (d, ⁴*J*_{HF} = 3.4 Hz, 2H), 0.70 (s, 6H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -137.09 (td, *J*_{FH} = 10.1, 3.1 Hz); ¹³C NMR (DMSO-*d*₆, 101 MHz) δ 151.7 (d, ¹*J*_{CF} = 248.8 Hz, CF), 144.1 (d, ²*J*_{CF} = 10.8 Hz, C), 134.1 (d, ⁴*J*_{CF} = 4.1 Hz, C), 125.9 (d, ³*J*_{CF} = 3.5 Hz, CH), 120.7 (d, ²*J*_{CF} = 20.4 Hz, CH), 116.6 (d, ³*J*_{CF} = 7.7 Hz, C), -1.1 (CH₃); HRMS (EI) calcd for C₁₄H₁₂Br₂F₂O₂Si [M]⁺⁺ 437.8921, found 437.8944.



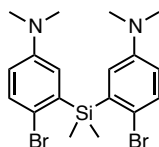
3,3'-(Dimethylsilanediyl)bis(4-bromo-2,6-difluorophenol) (14c): The title compound (93%, white solid) was prepared from **13c** according to method S4. ¹H NMR (CDCl₃, 400 MHz) δ 7.11 (dd, *J*_{HF} = 9.5, 2.0 Hz, 2H), 5.01 (s, 2H), 0.82 (t, ⁵*J*_{HF} = 3.0 Hz, 6H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -119.87 – -120.01 (m, 2F), -132.13 – -132.25 (m, 2F); ¹³C NMR (CDCl₃, 101 MHz) δ 155.9 (dd, *J*_{CF} = 240.2, 5.7 Hz, CF), 152.3 (dd, *J*_{CF} = 249.2, 6.5 Hz, CF), 132.3 (dd, *J*_{CF} = 20.9, 14.6 Hz, C), 122.2 (ddd, *J*_{CF} = 27.8, 3.8, 1.3 Hz, C), 117.7 (dd, *J*_{CF} = 20.4, 3.4 Hz, CH), 117.2 (dd, *J*_{CF} = 13.9, 10.5 Hz, C), 2.0 (t, ⁴*J*_{CF} = 5.7 Hz, CH₃); HRMS (EI) calcd for C₁₄H₁₀Br₂F₄O₂Si [M]⁺⁺ 473.8732, found 473.8713.



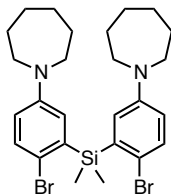
Bis(5-(azetidin-1-yl)-2-bromophenyl)dimethylsilane (31a): The title compound (95%, white solid) was prepared from **30a** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.30 (d, $J = 8.5$ Hz, 2H), 6.51 (d, $J = 2.9$ Hz, 2H), 6.31 (dd, $J = 8.5, 3.0$ Hz, 2H), 3.81 (t, $J = 7.2$ Hz, 8H), 2.33 (p, $J = 7.2$ Hz, 4H), 0.71 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 150.6 (C), 138.9 (C), 132.9 (CH), 120.4 (CH), 117.5 (C), 114.1 (CH), 52.6 (CH_2), 17.0 (CH_2), -0.9 (CH_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{25}\text{Br}_2\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 479.0148, found 479.0153.



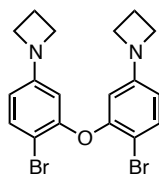
Bis(5-(azetidin-1-yl)-2-bromo-4-fluorophenyl)dimethylsilane (31b): The title compound (86%, white solid) was prepared from **30b** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.11 (d, $^3J_{\text{HF}} = 11.9$ Hz, 2H), 6.48 (d, $^4J_{\text{HF}} = 10.3$ Hz, 2H), 3.91 (td, $J = 7.3, 2.1$ Hz, 8H), 2.33 (p, $J = 7.2$ Hz, 4H), 0.69 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -129.32 – -129.45 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 152.9 (d, $^1J_{\text{CF}} = 248.9$ Hz, CF), 138.7 (d, $^2J_{\text{CF}} = 9.8$ Hz, C), 134.0 (d, $^4J_{\text{CF}} = 3.9$ Hz, C), 122.5 (d, $^3J_{\text{CF}} = 5.1$ Hz, CH), 120.3 (d, $^2J_{\text{CF}} = 21.0$ Hz, CH), 116.7 (d, $^3J_{\text{CF}} = 7.8$ Hz, C), 54.0 (d, $^4J_{\text{CF}} = 2.0$ Hz, CH_2), 18.2 (d, $^5J_{\text{CF}} = 1.9$ Hz, CH_2), -0.8 (CH_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{23}\text{Br}_2\text{F}_2\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 514.9960, found 514.9973.



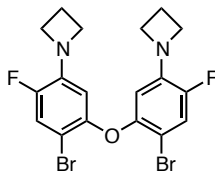
3,3'-(Dimethylsilanediyl)bis(4-bromo-N,N-dimethylaniline) (31c): The title compound (67%, white solid) was prepared from **30c** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.34 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 3.2$ Hz, 2H), 6.59 (dd, $J = 8.8, 3.2$ Hz, 2H), 2.87 (s, 12H), 0.75 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 149.0 (C), 138.9 (C), 133.1 (CH), 121.9 (CH), 116.9 (C), 115.4 (CH), 40.7 (CH_3), -0.8 (CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{25}\text{Br}_2\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 455.0148, found 455.0157.



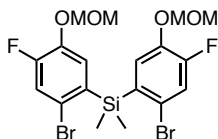
Bis(5-(azepan-1-yl)-2-bromophenyl)dimethylsilane (31d): The title compound (55%, white solid) was prepared from **30d** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.29 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 3.2 Hz, 2H), 6.54 (dd, J = 8.8, 3.3 Hz, 2H), 3.40 – 3.33 (m, 8H), 1.74 – 1.65 (m, 8H), 1.52 – 1.45 (m, 8H), 0.75 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 147.2 (C), 139.0 (C), 133.3 (CH), 120.7 (CH), 115.1 (C), 114.0 (CH), 49.5 (CH_2), 27.6 (CH_2), 27.1 (CH_2), -0.6 (CH_3); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{37}\text{Br}_2\text{N}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 563.1087, found 563.1095.



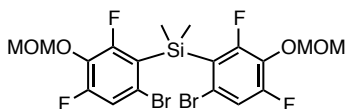
1,1'-(Oxybis(4-bromo-3,1-phenylene))bis(azetidine) (57a): The title compound (80%, white solid) was prepared from **56a** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.36 (d, J = 8.6 Hz, 2H), 6.09 (dd, J = 8.6, 2.6 Hz, 2H), 5.91 (d, J = 2.6 Hz, 2H), 3.79 (t, J = 7.3 Hz, 8H), 2.32 (p, J = 7.2 Hz, 4H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 153.8 (C), 152.8 (C), 133.6 (CH), 108.3 (CH), 102.7 (CH), 100.8 (C), 52.5 (CH_2), 16.8 (CH_2); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{19}\text{Br}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 438.9839, found 438.9838.



1,1'-(Oxybis(4-bromo-2-fluoro-5,1-phenylene))bis(azetidine) (57b): The title compound (74%, white solid) was prepared from **56b** according to method S4. ^1H NMR (CDCl_3 , 400 MHz) δ 7.15 (d, $^3J_{\text{HF}}$ = 11.3 Hz, 2H), 5.89 (d, $^4J_{\text{HF}}$ = 8.1 Hz, 2H), 3.89 (td, J = 7.3, 2.1 Hz, 8H), 2.32 (p, J = 7.3 Hz, 4H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -137.16 – -137.26 (m); ^{13}C NMR (CDCl_3 , 101 MHz) δ 150.0 (d, $^4J_{\text{CF}}$ = 2.5 Hz, C), 148.2 (d, $^1J_{\text{CF}}$ = 242.0 Hz, CF), 140.3 (d, $^2J_{\text{CF}}$ = 12.4 Hz, C), 120.1 (d, $^2J_{\text{CF}}$ = 23.3 Hz, CH), 104.6 (d, $^3J_{\text{CF}}$ = 5.2 Hz, CH), 99.5 (d, $^3J_{\text{CF}}$ = 9.0 Hz, C), 54.0 (d, $^4J_{\text{CF}}$ = 2.3 Hz, CH_2), 17.9 (d, $^5J_{\text{CF}}$ = 2.1 Hz, CH_2); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{17}\text{Br}_2\text{F}_2\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 474.9650, found 474.9670.

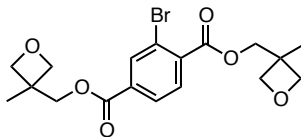


Bis(2-bromo-4-fluoro-5-(methoxymethoxy)phenyl)dimethylsilane (12b): A solution of **14b** (680 mg, 1.55 mmol) and DIEA (811 μ L, 4.66 mmol, 3 eq) in CH_2Cl_2 (10 mL) was cooled to 0 $^\circ\text{C}$. Chloromethyl methyl ether (354 μ L, 4.66 mmol, 3 eq) was added dropwise. The reaction was then warmed to room temperature and stirred for 2 h. It was subsequently diluted with water and extracted with CH_2Cl_2 (2 \times). The combined organic extracts were dried over anhydrous MgSO_4 , filtered, and evaporated. Flash chromatography (0–30% Et_2O /hexanes, linear gradient) afforded **12b** as a white solid (771 mg, 94%). ^1H NMR (CDCl_3 , 400 MHz) δ 7.285 (d, $^3J_{\text{HF}} = 10.5$ Hz, 2H), 7.277 (d, $^4J_{\text{HF}} = 9.3$ Hz, 2H), 5.15 (s, 4H), 3.49 (s, 6H), 0.73 (s, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -129.43 (dd, $J_{\text{FH}} = 10.4, 9.4$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 154.2 (d, $^1J_{\text{CF}} = 253.7$ Hz, CF), 144.0 (d, $^2J_{\text{CF}} = 9.9$ Hz, C), 134.7 (d, $^4J_{\text{CF}} = 4.3$ Hz, C), 127.3 (d, $^3J_{\text{CF}} = 2.1$ Hz, CH), 121.94 (d, $^3J_{\text{CF}} = 8.0$ Hz, C), 121.5 (d, $^2J_{\text{CF}} = 20.9$ Hz, CH), 96.4 (d, $^4J_{\text{CF}} = 1.0$ Hz, CH_2), 56.6 (CH_3), -1.0 (CH_3); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{20}\text{Br}_2\text{F}_2\text{O}_4\text{Si}$ $[\text{M}]^{+}$ 525.9445, found 525.9443.



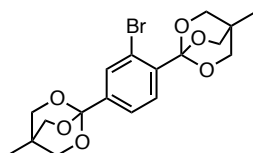
Bis(6-bromo-2,4-difluoro-3-(methoxymethoxy)phenyl)dimethylsilane (12c): The title compound (91%, colorless oil) was prepared from **14c** according to the procedure described for **12b**. ^1H NMR (CDCl_3 , 400 MHz) δ 7.11 (dd, $J_{\text{HF}} = 9.7, 2.0$ Hz, 2H), 5.11 (s, 4H), 3.57 (s, 6H), 0.82 (t, $^5J_{\text{HF}} = 3.1$ Hz, 6H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -111.16 – -111.28 (m, 2F), -125.10 (t, $J = 10.1$ Hz, 2F); ^{13}C NMR (CDCl_3 , 101 MHz) δ 160.9 (dd, $J_{\text{CF}} = 247.6, 5.9$ Hz, CF), 157.2 (dd, $J_{\text{CF}} = 254.0, 6.7$ Hz, CF), 132.4 (dd, $J_{\text{CF}} = 19.2, 13.7$ Hz, C), 123.21 – 122.67 (m, C), 122.1 (dd, $J_{\text{CF}} = 14.2, 11.2$ Hz, C), 118.2 (dd, $J_{\text{CF}} = 21.8, 3.5$ Hz, CH), 99.0 (t, $^4J_{\text{CF}} = 3.4$ Hz, CH_2), 57.4 (t, $^6J_{\text{CF}} = 1.5$ Hz, CH_3), 2.1 (t, $^4J_{\text{CF}} = 5.9$ Hz, CH_3); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{18}\text{Br}_2\text{F}_4\text{O}_4\text{Si}$ $[\text{M}]^{+}$ 561.9257, found 561.9244.

SYNTHESIS OF NOVEL ELECTROPHILES (17, 70, AND 71)

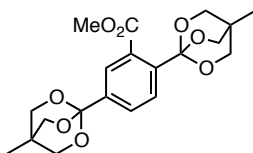


Bis((3-methyloxetan-3-yl)methyl) 2-bromoterephthalate (67): A mixture of 2-bromoterephthalic acid (6.00 g, 24.5 mmol), thionyl chloride (7.11 mL, 97.9 mmol, 4 eq), and DMF (1 drop) were stirred at reflux for 18 h. The mixture was concentrated *in vacuo* and azeotroped twice with toluene. The crude acid chloride was taken up in CH_2Cl_2 (10 mL) and added to a solution of 3-methyl-3-oxetanemethanol (9.77 mL, 97.9 mmol, 4 eq) and pyridine (15.84 mL, 195.9 mmol, 8 eq) in CH_2Cl_2 (40 mL) at 0 $^\circ\text{C}$. The ice bath was removed, and the reaction was stirred at room temperature for 3 h. It was subsequently diluted with water and extracted with CH_2Cl_2 (2 \times). The combined organics were washed with saturated NaHCO_3 and brine, dried over anhydrous MgSO_4 , filtered, and evaporated.

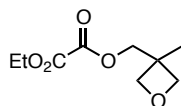
Flash chromatography (10–75% EtOAc/hexanes, linear gradient) afforded **67** as a colorless oil (8.39 g, 83%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.31 (d, J = 1.5 Hz, 1H), 8.04 (dd, J = 8.1, 1.6 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 4.622 (d, J = 6.1 Hz, 2H), 4.616 (d, J = 6.1 Hz, 2H), 4.50 – 4.43 (m, 8H), 1.44 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 165.9 (C), 164.6 (C), 136.5 (C), 135.4 (CH), 133.8 (C), 131.4 (CH), 128.4 (CH), 121.6 (C), 79.7 (CH_2), 79.6 (CH_2), 70.4 (CH_2), 70.0 (CH_2), 39.5 (C), 39.4 (C), 21.5 (CH_3), 21.3 (CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{22}\text{BrO}_6$ $[\text{M}+\text{H}]^+$ 413.0594, found 413.0599.



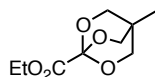
1,1'-(2-Bromo-1,4-phenylene)bis(4-methyl-2,6,7-trioxabicyclo[2.2.2]octane) (68): A solution of diester **67** (5.00 g, 12.1 mmol) in CH_2Cl_2 (40 mL) was cooled to 0 °C under nitrogen, and $\text{BF}_3 \cdot \text{OEt}_2$ (859 mg, 6.05 mmol, 0.5 eq) was added. The reaction was allowed to warm to room temperature overnight while stirring (18 h). Et_3N (5 mL) was added, and the resulting solution was stirred for 10 min. It was then concentrated *in vacuo* and directly purified by flash chromatography (0–20% EtOAc/hexanes, linear gradient, with constant 40% v/v CH_2Cl_2 and 1% v/v Et_3N additives) to afford 3.28 g (66%) of **68** as a white solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.65 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 1.6 Hz, 1H), 7.45 (dd, J = 8.2, 1.7 Hz, 1H), 4.01 (s, 6H), 3.99 (s, 6H), 0.83 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 101 MHz) δ 140.0 (C), 136.5 (C), 131.5 (CH), 127.5 (CH), 124.1 (CH), 119.8 (C), 106.0 (C), 105.8 (C), 72.4 (CH_2), 72.0 (CH_2), 30.0 (C), 29.9 (C), 13.7 (CH_3), 13.6 (CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{25}\text{BrO}_8\text{Na}$ $[\text{M}+2\text{H}_2\text{O}+\text{Na}]^+$ 471.0625, found 471.0638.



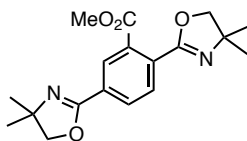
Methyl 2,5-bis(4-methyl-2,6,7-trioxabicyclo[2.2.2]octan-1-yl)benzoate (17): A solution of bromide **68** (500 mg, 1.21 mmol) in THF (15 mL) was cooled to -78 °C under nitrogen. *n*-Butyllithium (2.5 M in hexanes, 726 μL , 1.81 mmol, 1.5 eq) was added, and the reaction was stirred at -78 °C for 30 min. Methyl chloroformate (187 μL , 2.42 mmol, 2 eq) was then added. The dry ice bath was removed, and the reaction was stirred at room temperature for 1 h. It was subsequently diluted with saturated NaHCO_3 and extracted with EtOAc (2 \times). The combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (0–50% EtOAc/hexanes, linear gradient, with constant 40% v/v CH_2Cl_2 and 1% v/v Et_3N additives) afforded 314 mg (66%) of **17** as a white solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 7.59 – 7.53 (m, 2H), 7.39 – 7.36 (m, 1H), 4.01 (s, 6H), 3.95 (s, 6H), 3.77 (s, 3H), 0.82 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 101 MHz) δ 169.0 (C), 138.4 (C), 134.9 (C), 131.8 (C), 126.4 (CH), 126.3 (CH), 124.7 (CH), 106.2 (C), 106.1 (C), 72.4 (CH_2), 72.3 (CH_2), 52.1 (CH_3), 30.0 (C), 29.9 (C), 13.62 (CH_3), 13.59 (CH_3); HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{28}\text{O}_{10}\text{Na}$ $[\text{M}+2\text{H}_2\text{O}+\text{Na}]^+$ 451.1575, found 451.1572.



Ethyl ((3-methyloxetan-3-yl)methyl) oxalate (69): To a solution of 3-methyl-3-oxetanemethanol (2.74 mL, 27.5 mmol, 1.5 eq) and pyridine (2.96 mL, 36.6 mmol, 2 eq) in CH_2Cl_2 (35 mL) at 0 °C was added ethyl chlorooxoacetate (2.05 mL, 18.3 mmol). The ice bath was removed, and the reaction was stirred at room temperature for 18 h. It was subsequently diluted with water and extracted with CH_2Cl_2 (2 \times). The combined organics were washed with saturated CuSO_4 , dried with anhydrous MgSO_4 , filtered, and evaporated. Flash chromatography (0–50% EtOAc/hexanes, linear gradient) afforded **69** as a colorless oil (3.37 g, 91%). ^1H NMR (CDCl_3 , 400 MHz) δ 4.54 (d, J = 6.2 Hz, 2H), 4.43 (d, J = 6.2 Hz, 2H), 4.41 (s, 2H), 4.37 (q, J = 7.1 Hz, 2H), 1.392 (s, 3H), 1.386 (t, J = 7.1 Hz, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 158.2 (C), 157.7 (C), 79.5 (CH_2), 71.1 (CH_2), 63.4 (CH_2), 39.3 (C), 21.1 (CH_3), 14.1 (CH_3); HRMS (ESI) calcd for $\text{C}_9\text{H}_{14}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 225.0733, found 225.0734.



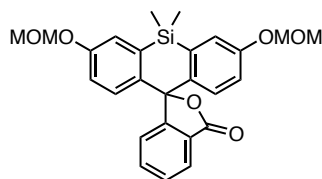
Ethyl 4-methyl-2,6,7-trioxabicyclo[2.2.2]octane-1-carboxylate (70): A solution of ester **69** (3.05 g, 15.1 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C under nitrogen, and $\text{BF}_3 \cdot \text{OEt}_2$ (535 mg, 3.77 mmol, 0.25 eq) was added. The reaction was allowed to warm to room temperature overnight while stirring (18 h). Et_3N (5 mL) was added, and the resulting solution was stirred for 10 min. It was then concentrated *in vacuo* and directly purified by flash chromatography (0–50% EtOAc/hexanes, linear gradient, with constant 1% v/v Et_3N additive) to afford 1.30 g (43%) of **70** as a white solid. ^1H NMR ($\text{DMSO}-d_6$, 400 MHz) δ 4.14 (q, J = 7.1 Hz, 2H), 3.93 (s, 6H), 1.19 (t, J = 7.1 Hz, 3H), 0.79 (s, 3H); ^{13}C NMR ($\text{DMSO}-d_6$, 101 MHz) δ 162.5 (C), 102.5 (C), 72.1 (CH_2), 61.6 (CH_2), 30.0 (C), 13.8 (CH_3), 13.3 (CH_3); HRMS (ESI) calcd for $\text{C}_9\text{H}_{14}\text{O}_5\text{Na}$ $[\text{M}+\text{Na}]^+$ 225.0733, found 225.0730.



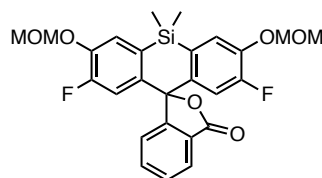
Methyl 2,5-bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)benzoate (71): The title compound (56%, colorless gum) was prepared from 2,2'-(2-bromo-1,4-phenylene)bis(4,4-dimethyl-4,5-dihydrooxazole)³ according to the procedure described for **17**. ^1H NMR (CDCl_3 , 400 MHz) δ 8.29 (d, J = 1.6 Hz, 1H), 8.06 (dd, J = 8.0, 1.7 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 4.13 (s, 2H), 4.11 (s, 2H), 3.88 (s, 3H), 1.40 (s, 6H), 1.39 (s, 6H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 167.5 (C), 161.7 (C), 160.8 (C), 132.4 (C), 131.0 (C), 130.6 (CH), 130.2 (C), 130.0 (CH), 129.0 (CH), 80.0 (CH_2), 79.5 (CH_2), 68.3 (C), 68.1 (C), 52.6 (CH_3), 28.5 (CH_3), 28.3 (CH_3); HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$ 331.1652, found 331.1651.

SYNTHESIS OF SI-FLUORESCEINS

General method S5: Preparation of Si-fluoresceins via Li/Br exchange of bis(2-bromophenyl)silanes and transmetallation with $\text{MgBr}_2 \cdot \text{OEt}_2$. The following procedure for Si-fluorescein bis(methoxymethyl ether) (**18**) is representative. A solution of dibromide **12a** (200 mg, 0.408 mmol) in THF (5 mL) was cooled to -78°C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.06 mL, 1.79 mmol, 4.4 eq) was added, and the reaction was stirred at -78°C for 30 min. It was then warmed to -10°C before adding a solution of $\text{MgBr}_2 \cdot \text{OEt}_2$ (232 mg, 0.897 mmol, 2.2 eq) in THF (5 mL). After an additional 30 min at -10°C , a solution of phthalic anhydride (**15**; 133 mg, 0.897 mmol, 2.2 eq) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was then allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH_4Cl and water and extracted with EtOAc (2 \times). The combined organic extracts were washed with saturated NaHCO_3 and brine, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. Silica gel chromatography (0–50% EtOAc/hexanes, linear gradient) afforded 113 mg (60%) of **18** as a white solid.

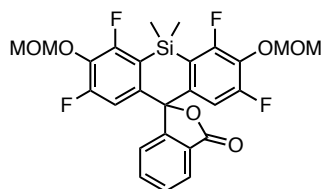


Si-Fluorescein bis(methoxymethyl ether) (18): The title compound (60%, white solid) was prepared from **12a** and phthalic anhydride (**15**) according to method S5. ^1H NMR (CDCl_3 , 400 MHz) δ 8.01 – 7.95 (m, 1H), 7.67 (td, $J = 7.6, 1.0$ Hz, 1H), 7.60 – 7.54 (m, 1H), 7.34 – 7.29 (m, 3H), 6.93 (d, $J = 8.7$ Hz, 4H), 6.89 (dd, $J = 8.8, 2.5$ Hz, 2H), 5.17 (AB quartet, $\nu_A = 2071.8$ Hz, $\nu_B = 2066.2$ Hz, $J_{AB} = 6.8$ Hz, 4H), 3.46 (s, 6H), 0.65 (s, 3H), 0.62 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 170.3 (C), 156.7 (C), 153.8 (C), 137.9 (C), 137.8 (C), 134.0 (CH), 129.3 (CH), 128.6 (CH), 126.6 (C), 126.2 (CH), 124.6 (CH), 121.4 (CH), 117.1 (CH), 94.5 (CH_2), 90.5 (C), 56.2 (CH_3), 0.3 (CH_3), -1.5 (CH_3); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{O}_6\text{Si}$ [$\text{M}+\text{H}$] $^+$ 463.1571, found 463.1590.

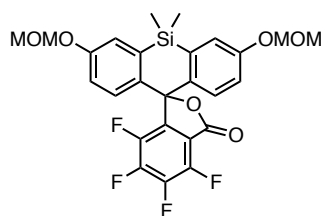


2',7'-Difluoro-Si-fluorescein bis(methoxymethyl ether) (19): The title compound (59%, white solid) was prepared from **12b** and phthalic anhydride (**15**) according to method S5. ^1H NMR (CDCl_3 , 400 MHz) δ 8.03 – 7.98 (m, 1H), 7.69 (td, $J = 7.6, 1.0$ Hz, 1H), 7.60 (td, $J = 7.5, 0.6$ Hz, 1H), 7.45 (d, $^4J_{\text{HF}} = 9.0$ Hz, 2H), 7.30 – 7.27 (m, 1H), 6.77 (d, $^3J_{\text{HF}} = 13.1$ Hz, 2H), 5.25 (s, 4H), 3.52 (s, 6H), 0.66 (s, 3H), 0.60 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -130.48 (dd, $J_{\text{FH}} = 13.0, 8.9$ Hz); ^{13}C NMR (CDCl_3 , 101 MHz) δ 169.9 (C), 153.8 (d, $^1J_{\text{CF}} = 249.3$ Hz, CF), 153.3 (C), 145.12 (d, $^2J_{\text{CF}} = 10.3$ Hz, C), 139.10 (d, $^3J_{\text{CF}} = 5.5$ Hz, C), 134.6 (CH), 132.09 (d, $^4J_{\text{CF}} = 4.4$ Hz, C), 129.8 (CH), 126.5 (CH), 125.8 (C), 124.1 (CH), 122.8 (d, $^3J_{\text{CF}} = 1.8$ Hz, CH), 115.7 (d, $^2J_{\text{CF}} = 20.2$ Hz, CH), 95.9 (CH_2), 89.0 (t, $^4J_{\text{CF}} =$

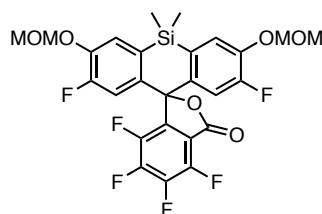
1.4 Hz, C), 56.7 (CH₃), 0.4 (CH₃), -1.0 (CH₃); HRMS (ESI) calcd for C₂₆H₂₅F₂O₆Si [M+H]⁺ 499.1383, found 499.1387.



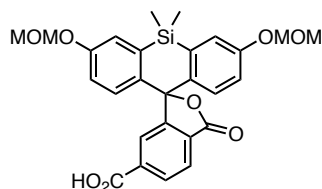
2',4',5',7'-Tetrafluoro-Si-fluorescein bis(methoxymethyl ether) (20): A solution of dibromide **12c** (250 mg, 0.445 mmol) in THF (5 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.15 mL, 1.96 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. After adding a solution of phthalic anhydride (**15**; 145 mg, 0.978 mmol, 2.2 eq) in THF (2.5 mL), the reaction was allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and water and extracted with EtOAc (2×). The combined organic extracts were washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Silica gel chromatography (0–40% EtOAc/hexanes, linear gradient) afforded **20** as a white solid (130 mg, 55%). ¹H NMR (CDCl₃, 400 MHz) δ 7.96 (d, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 6.78 (d, ³*J*_{HF} = 11.9 Hz, 2H), 5.16 (s, 4H), 3.58 (s, 6H), 0.83 (s, 3H), 0.68 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -114.36 (d, *J* = 11.2 Hz, 2F), -123.53 (t, *J* = 11.6 Hz, 2F); ¹³C NMR (CDCl₃, 101 MHz) δ 170.2 (C), 160.6 (dd, *J*_{CF} = 241.1, 5.7 Hz, CF), 157.8 (dd, *J*_{CF} = 251.5, 6.9 Hz, CF), 154.9 (C), 139.3 (dd, *J*_{CF} = 12.6, 7.9 Hz, C), 135.3 (CH), 132.7 (dd, *J*_{CF} = 18.0, 14.2 Hz, C), 129.8 (CH), 126.7 (CH), 123.2 (C), 122.9 (CH), 117.1 (dd, *J*_{CF} = 32.4, 3.1 Hz, C), 111.4 (dd, *J*_{CF} = 21.4, 2.9 Hz, CH), 98.9 (t, ⁴*J*_{CF} = 3.5 Hz, CH₂), 87.3 (C), 57.3 (CH₃), -0.8 (CH₃), -1.0 (t, ⁴*J*_{CF} = 2.7 Hz, CH₃); HRMS (ESI) calcd for C₂₆H₂₃F₄O₆Si [M+H]⁺ 535.1195, found 535.1203.



4,5,6,7-Tetrafluoro-Si-fluorescein bis(methoxymethyl ether) (21): The title compound (46%, white solid) was prepared from **12a** and tetrafluorophthalic anhydride (**16**) according to method S5. ¹H NMR (CDCl₃, 400 MHz) δ 7.32 (d, *J* = 2.7 Hz, 2H), 6.98 (dd, *J* = 8.8, 2.7 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 5.20 (AB quartet, *v*_A = 2081.5 Hz, *v*_B = 2076.1 Hz, *J*_{AB} = 6.9 Hz, 4H), 3.48 (s, 6H), 0.60 (s, 3H), 0.57 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -138.17 (td, *J* = 19.9, 9.0 Hz, 1F), -138.59 – -138.77 (m, 1F), -143.08 (ddd, *J* = 20.7, 18.5, 9.0 Hz, 1F), -150.73 – -150.88 (m, 1F); Analytical HPLC: *t*_R = 15.5 min, 97.3% purity (5 μL injection; 50–95% MeCN/H₂O, linear gradient, with constant 0.1% *v/v* TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₆H₂₃F₄O₆Si [M+H]⁺ 535.1195, found 535.1194.



2',4,5,6,7,7'-Hexafluoro-Si-fluorescein bis(methoxymethyl ether) (22): The title compound (42%, white solid) was prepared from **12b** and tetrafluorophthalic anhydride (**16**) according to method S5. ^1H NMR (CDCl_3 , 400 MHz) δ 7.45 (d, $^4J_{\text{HF}} = 8.9$ Hz, 2H), 6.73 (d, $^3J_{\text{HF}} = 12.5$ Hz, 2H), 5.27 (s, 4H), 3.53 (s, 6H), 0.59 (s, 3H), 0.55 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -129.88 (dd, $J_{\text{FH}} = 12.5, 8.9$ Hz, 2F), -136.90 (td, $J = 19.8, 9.7$ Hz, 1F), -139.38 – -139.57 (m, 1F), -141.65 (ddd, $J = 20.7, 18.4, 9.7$ Hz, 1F), -149.62 (ddd, $J = 20.5, 18.5, 4.5$ Hz, 1F); Analytical HPLC: $t_{\text{R}} = 15.3$ min, >99% purity (5 μL injection; 50–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{21}\text{F}_6\text{O}_6\text{Si}$ $[\text{M}+\text{H}]^+$ 571.1006, found 571.1013.

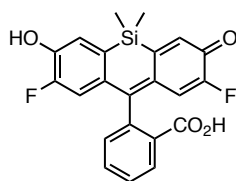


6-Carboxy-Si-fluorescein bis(methoxymethyl ether) (23): A solution of dibromide **12a** (300 mg, 0.612 mmol, 1.5 eq) in THF (15 mL) was cooled to -78 $^{\circ}\text{C}$ under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.44 mL, 2.45 mmol, 6 eq) was added, and the reaction was stirred at -78 $^{\circ}\text{C}$ for 30 min. It was then warmed to -20 $^{\circ}\text{C}$, and a solution of **17** (160 mg, 0.408 mmol) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). Following the addition of 2 N HCl (10 mL), the mixture was vigorously stirred at room temperature for 10 min. It was then diluted with water and extracted with EtOAc (2 \times). The combined organic extracts were washed with brine, dried over anhydrous MgSO_4 , filtered, and evaporated. Flash chromatography (20–100% EtOAc/hexanes, linear gradient) provided 126 mg (51%) of the 2,2-bis(hydroxymethyl)propyl ester of the title acid.

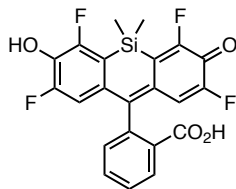
This ester (50 mg, 82.1 μmol) was taken up in 1:1 THF/MeOH (2 mL), and 1 M NaOH (164 μL , 164 μmol , 2 eq) was added. The reaction was stirred at room temperature for 18 h. It was then acidified with 1 M HCl (170 μL), diluted with water, and extracted with EtOAc (2 \times). The combined organics were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by flash chromatography (10–100% EtOAc/hexanes, linear gradient, with constant 1% v/v AcOH additive) to yield **23** as a white solid (38 mg, 91%). ^1H NMR (CDCl_3 , 400 MHz) δ 8.25 (d, $J = 8.0$ Hz, 1H), 8.06 (d, $J = 8.0$ Hz, 1H), 8.01 (s, 1H), 7.33 (d, $J = 2.2$ Hz, 2H), 6.95 (d, $J = 8.8$ Hz, 2H), 6.92 (dd, $J = 8.9, 2.4$ Hz, 2H), 5.18 (AB quartet, $\nu_{\text{A}} = 2074.4$ Hz, $\nu_{\text{B}} = 2067.6$ Hz, $J_{\text{AB}} = 6.8$ Hz, 4H), 3.46 (s, 6H), 0.69 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 169.9 (C), 169.5 (C), 156.9 (C), 154.7 (C), 137.5 (C), 137.1 (C), 134.6 (C), 130.9 (CH), 130.2 (C), 128.3 (CH), 126.4 (CH),

126.2 (CH), 121.6 (CH), 117.4 (CH), 94.4 (CH₂), 90.7 (C), 56.3 (CH₃), 0.2 (CH₃), -1.1 (CH₃); HRMS (ESI) calcd for C₂₇H₂₇O₈Si [M+H]⁺ 507.1470, found 507.1475.

General method S6: MOM deprotection. The following procedure for Si-fluorescein (**1**) is representative. Diether **18** (1.33 g, 2.88 mmol) was taken up in CH₂Cl₂ (25 mL), and trifluoroacetic acid (5 mL) was added. The reaction was stirred at room temperature for 81 h. Toluene (20 mL) was added, and the reaction mixture was concentrated to dryness. Purification by silica gel chromatography (10–100% EtOAc/hexanes, linear gradient) provided 1.04 g (96%) of **1** as a pink solid.

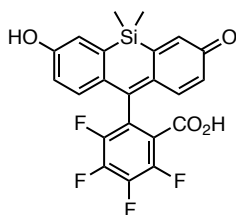


2',7'-Difluoro-Si-fluorescein (24): The title compound (94%, off-white solid) was prepared from **19** according to method S6. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.25 (s, 2H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.85 (td, *J* = 7.6, 1.0 Hz, 1H), 7.76 – 7.67 (m, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.32 (d, ⁴*J*_{HF} = 9.8 Hz, 2H), 6.55 (d, ³*J*_{HF} = 13.3 Hz, 2H), 0.60 (s, 3H), 0.51 (s, 3H); ¹⁹F NMR (DMSO-*d*₆, 376 MHz) δ -132.49 (dd, *J*_{FH} = 13.3, 9.8 Hz); ¹³C NMR (DMSO-*d*₆, 101 MHz) δ 169.1 (C), 152.7 (C), 151.4 (d, ¹*J*_{CF} = 239.7 Hz, CF), 145.0 (d, ²*J*_{CF} = 11.5 Hz, C), 135.3 (d, ³*J*_{CF} = 4.9 Hz, C), 135.2 (CH), 131.9 (d, ⁴*J*_{CF} = 4.0 Hz, C), 130.0 (CH), 125.9 (CH), 124.8 (C), 124.2 (CH), 123.0 (d, ³*J*_{CF} = 3.3 Hz, CH), 114.6 (d, ²*J*_{CF} = 19.2 Hz, CH), 88.8 (C), 0.0 (CH₃), -1.6 (CH₃); Analytical HPLC: *t*_R = 11.6 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₂H₁₇F₂O₄Si [M+H]⁺ 411.0859, found 411.0857.

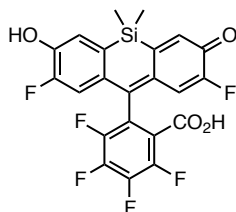


Maryland Red (2',4',5',7'-Tetrafluoro-Si-fluorescein, 25): The title compound (99%, white solid) was prepared from **20** according to method S6. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.68 (s, 2H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.75 (td, *J* = 7.6, 1.0 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 6.60 (dd, *J*_{HF} = 12.1, 1.1 Hz, 2H), 0.77 (s, 3H), 0.62 (s, 3H); ¹⁹F NMR (DMSO-*d*₆, 376 MHz) δ -118.31 (d, *J* = 16.0 Hz, 2F), -127.22 (dd, *J* = 15.9, 12.2 Hz, 2F); ¹³C NMR (DMSO-*d*₆, 101 MHz) δ 169.3 (C), 156.2 (dd, *J*_{CF} = 234.8, 6.9 Hz, CF), 154.2 (C), 153.5 (dd, *J*_{CF} = 245.2, 8.2 Hz, CF), 135.8 (CH), 133.6 (dd, *J*_{CF} = 19.5, 15.5 Hz, C), 132.8 (dd, *J*_{CF} = 11.8, 7.3 Hz, C), 129.9 (CH), 126.1 (CH), 122.9 (CH), 122.8 (C), 116.2 (dd, *J*_{CF} = 31.4, 2.5 Hz, C), 110.6 (dd, *J*_{CF} = 20.4, 2.0 Hz, CH), 87.0 (C), -1.15 (d, ⁴*J*_{CF} = 2.7 Hz, CH₃), -1.18 (CH₃); Analytical HPLC: *t*_R = 12.1 min, >99% purity (5 μL injection; 10–95%

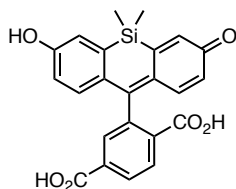
MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₂H₁₅F₄O₄Si [M+H]⁺ 447.0670, found 447.0677.



4,5,6,7-Tetrafluoro-Si-fluorescein (26): The title compound (92%, light pink solid) was prepared from **21** according to method S6. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 9.84 (s, 2H), 7.16 (d, *J* = 2.7 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.72 (dd, *J* = 8.7, 2.7 Hz, 2H), 0.55 (s, 3H), 0.47 (s, 3H); ¹⁹F NMR (DMSO-*d*₆, 376 MHz) δ -138.65 – -138.86 (m, 1F), -140.10 – -140.34 (m, 1F), -143.12 (td, *J* = 21.8, 9.0 Hz, 1F), -151.68 (td, *J* = 23.9, 22.1, 3.6 Hz, 1F); Analytical HPLC: *t*_R = 11.9 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₂H₁₅F₄O₄Si [M+H]⁺ 447.0670, found 447.0665.



2',4,5,6,7,7'-Hexafluoro-Si-fluorescein (27): The title compound (98%, off-white solid) was prepared from **22** according to method S6. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 10.38 (s, 2H), 7.34 (d, ⁴*J*_{HF} = 9.7 Hz, 2H), 6.92 (d, ³*J*_{HF} = 13.1 Hz, 2H), 0.56 (s, 3H), 0.47 (s, 3H); ¹⁹F NMR (DMSO-*d*₆, 376 MHz) δ -132.47 (dd, *J*_{FH} = 13.1, 9.7 Hz, 2F), -139.41 – -139.72 (m, 2F), -142.23 (td, *J* = 20.0, 18.4, 7.0 Hz, 1F), -151.42 – -151.60 (m, 1F); Analytical HPLC: *t*_R = 12.2 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₂H₁₃F₆O₄Si [M+H]⁺ 483.0482, found 483.0489.



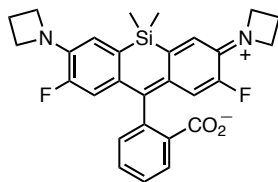
6-Carboxy-Si-fluorescein (28): The title compound (92%, pink solid) was prepared from **23** according to method S6. ¹H NMR (CD₃OD, 400 MHz) δ 8.24 (dd, *J* = 8.0, 1.1 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 – 7.85 (m, 1H), 7.15 (d, *J* = 2.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.70 (dd, *J* = 8.7, 2.7 Hz, 2H), 0.65 (s, 3H), 0.56 (s, 3H); ¹³C NMR (CD₃OD, 101 MHz) δ 171.6 (C), 168.0 (C), 158.3 (C), 156.4 (C), 138.3 (C), 137.9 (C), 135.9 (C), 131.5 (CH),

130.2 (C), 129.3 (CH), 126.8 (CH), 126.4 (CH), 121.3 (CH), 118.0 (CH), 92.6 (C), 0.0 (CH₃), -1.3 (CH₃); Analytical HPLC: t_R = 11.0 min, 97.5% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₃H₁₉O₆Si [M+H]⁺ 419.0945, found 419.0941.

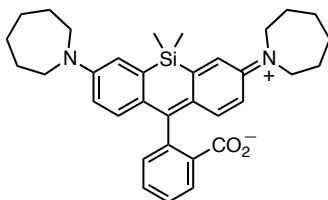
SYNTHESIS OF SI-RHODAMINES AND RELATED DYES

General method S7 (“Method A”): Preparation of Si-rhodamines via Li/Br exchange of bis(2-bromophenyl)silanes and transmetallation with MgBr₂·OEt₂. The following procedure for JF₆₄₆ (**3**) is representative. A solution of dibromide **31a** (200 mg, 0.416 mmol) in THF (10 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.08 mL, 1.83 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -10 °C before adding a solution of MgBr₂·OEt₂ (237 mg, 0.916 mmol, 2.2 eq) in THF (5 mL). After an additional 30 min at -10 °C, a solution of phthalic anhydride (**15**, 136 mg, 0.916 mmol, 2.2 eq) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was then allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and water and extracted with EtOAc (2×). The combined organic extracts were washed with saturated NaHCO₃ and brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Silica gel chromatography (0–30% EtOAc/hexanes, linear gradient, with constant 20% v/v CH₂Cl₂ additive) afforded 103 mg (55%) of JF₆₄₆ (**3**) as a white solid.

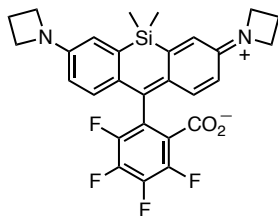
General method S8 (“Method B”): Preparation of Si-rhodamines via Li/Br exchange of bis(2-bromophenyl)silanes. The following procedure for des-carboxy-JF₆₄₆ (**44**) is representative. A solution of dibromide **31a** (200 mg, 0.416 mmol) in THF (10 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.08 mL, 1.83 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -20 °C, and a solution of methyl benzoate (125 mg, 0.916 mmol, 2.2 eq) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and water and extracted with EtOAc (2×). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting residue was redissolved in MeOH (10 mL), and AcOH (100 μ L) was added (immediate dark blue color). After stirring the blue solution at room temperature for 10 min, it was concentrated to dryness and purified by flash chromatography (0–15% MeOH/CH₂Cl₂, linear gradient, with constant 1% v/v AcOH additive) to yield 146 mg (75%) of the acetate salt of **44** as a dark blue solid. An analytically pure (>99%) sample was obtained through further purification by reverse phase HPLC (10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive); this material (the TFA salt) was used for all characterization purposes.



2',7'-Difluoro-JF₆₄₆ (32): The title compound (44%, white solid) was prepared from **31b** and phthalic anhydride (**15**) according to method S7. ¹H NMR (CDCl₃, 400 MHz) δ 7.99 – 7.95 (m, 1H), 7.66 (td, *J* = 7.5, 1.1 Hz, 1H), 7.57 (td, *J* = 7.5, 0.8 Hz, 1H), 7.26 – 7.23 (m, 1H), 6.63 (d, ⁴*J*_{HF} = 10.0 Hz, 2H), 6.50 (d, ³*J*_{HF} = 14.7 Hz, 2H), 4.00 (td, *J* = 7.3, 2.1 Hz, 8H), 2.35 (p, *J* = 7.3 Hz, 4H), 0.59 (s, 3H), 0.55 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -130.27 – -130.41 (m); ¹³C NMR (CDCl₃, 101 MHz) δ 170.3 (C), 153.9 (C), 152.8 (d, ¹*J*_{CF} = 244.3 Hz, CF), 139.7 (d, ²*J*_{CF} = 10.3 Hz, C), 134.5 (d, ³*J*_{CF} = 5.1 Hz, C), 134.3 (CH), 131.7 (d, ⁴*J*_{CF} = 3.9 Hz, C), 129.4 (CH), 126.4 (C), 126.2 (CH), 124.3 (CH), 118.6 (d, ³*J*_{CF} = 4.9 Hz, CH), 114.9 (d, ²*J*_{CF} = 19.9 Hz, CH), 90.4 (C), 54.0 (d, ⁴*J*_{CF} = 2.0 Hz, CH₂), 18.1 (d, ⁵*J*_{CF} = 1.9 Hz, CH₂), 0.5 (CH₃), -1.0 (CH₃); Analytical HPLC: *t*_R = 16.3 min, >99% purity (5 μL injection; 30–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for C₂₈H₂₇F₂N₂O₂Si [M+H]⁺ 489.1804, found 489.1813.

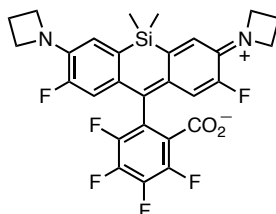


3',6'-Bis(azepanyl)-Si-rhodamine (34): The title compound (55%, light blue-green solid) was prepared from **31d** and phthalic anhydride (**15**) according to method S7. ¹H NMR (CDCl₃, 400 MHz) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 2.8 Hz, 2H), 6.70 (d, *J* = 8.9 Hz, 2H), 6.48 (dd, *J* = 8.9, 2.9 Hz, 2H), 3.49 – 3.39 (m, 8H), 1.82 – 1.69 (m, 8H), 1.57 – 1.48 (m, 8H), 0.61 (s, 3H), 0.60 (s, 3H); ¹³C NMR (CDCl₃, 101 MHz) δ 170.8 (C), 154.3 (C), 147.9 (C), 137.5 (C), 133.5 (CH), 130.9 (C), 128.7 (CH), 128.5 (CH), 127.7 (C), 125.7 (CH), 125.0 (CH), 115.6 (CH), 112.2 (CH), 92.6 (C), 49.1 (CH₂), 27.8 (CH₂), 27.2 (CH₂), 0.6 (CH₃), -1.6 (CH₃); Analytical HPLC: *t*_R = 13.6 min, >99% purity (5 μL injection; 30–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₃₄H₄₁N₂O₂Si [M+H]⁺ 537.2932, found 537.2938.

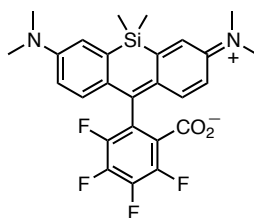


JF₆₆₉ (35): The title compound (51%, blue-green solid) was prepared from **31a** and tetrafluorophthalic anhydride (**16**) according to method S7. ¹H NMR (CDCl₃, 400 MHz) δ 6.74 (d, *J* = 8.6 Hz, 2H), 6.64 (d, *J* = 2.6 Hz, 2H), 6.31

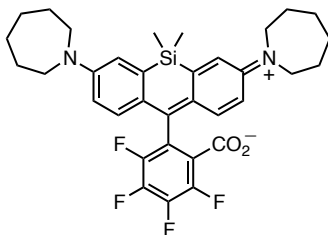
(dd, $J = 8.7, 2.6$ Hz, 2H), 3.92 (t, $J = 7.3$ Hz, 8H), 2.38 (p, $J = 7.2$ Hz, 4H), 0.55 (s, 3H), 0.53 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -138.98 – -139.14 (m, 1F), -139.22 (td, $J = 19.5, 7.6$ Hz, 1F), -144.00 – -144.18 (m, 1F), -151.91 – -152.07 (m, 1F); Analytical HPLC: $t_R = 14.3$ min, 98.9% purity (5 μL injection; 10–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{F}_4\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 525.1616, found 525.1616.



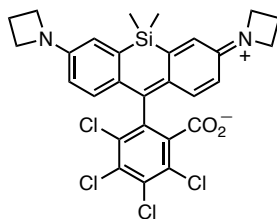
2',4,5,6,7,7'-Hexafluoro-JF₆₄₆ (36): The title compound (40%, off-white solid) was prepared from **31b** and tetrafluorophthalic anhydride (**16**) according to method S7. ^1H NMR (CDCl_3 , 400 MHz) δ 6.59 (d, $^4J_{\text{HF}} = 10.0$ Hz, 2H), 6.49 (d, $^3J_{\text{HF}} = 14.3$ Hz, 2H), 4.04 (td, $J = 7.4, 2.1$ Hz, 8H), 2.38 (p, $J = 7.3$ Hz, 4H), 0.53 (s, 3H), 0.49 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -130.17 – -130.29 (m, 2F), -138.01 (td, $J = 19.9, 9.2$ Hz, 1F), -140.03 – -140.21 (m, 1F), -142.67 (ddd, $J = 20.7, 18.5, 9.2$ Hz, 1F), -150.85 (ddd, $J = 20.7, 18.6, 4.1$ Hz, 1F); Analytical HPLC: $t_R = 17.2$ min, >99% purity (5 μL injection; 30–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 254 nm); HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{23}\text{F}_6\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 561.1428, found 561.1438.



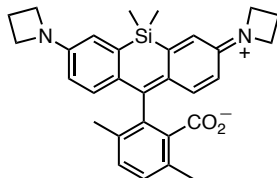
4,5,6,7-Tetrafluoro-SiTMR (37): The title compound (52%, blue solid) was prepared from **31c** and tetrafluorophthalic anhydride (**16**) according to method S7. ^1H NMR (CDCl_3 , 400 MHz) δ 6.94 (d, $J = 2.9$ Hz, 2H), 6.79 (d, $J = 8.9$ Hz, 2H), 6.61 (dd, $J = 8.9, 2.9$ Hz, 2H), 2.99 (s, 12H), 0.59 (s, 3H), 0.56 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -139.12 – -139.51 (m, 2F), -143.98 – -144.39 (m, 1F), -152.02 – -152.38 (m, 1F); Analytical HPLC: $t_R = 13.0$ min, >99% purity (5 μL injection; 10–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{25}\text{F}_4\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 501.1616, found 501.1620.



Potomac Red (4,5,6,7-Tetrafluoro-3',6'-bis(azepanyl)-Si-rhodamine, 38): The title compound (47%, light blue-green solid) was prepared from **31d** and tetrafluorophthalic anhydride (**16**) according to method S7. ^1H NMR (CDCl_3 , 400 MHz) δ 6.91 (d, $J = 2.9$ Hz, 2H), 6.73 (dd, $J = 8.9, 0.9$ Hz, 2H), 6.56 (dd, $J = 9.0, 2.9$ Hz, 2H), 3.50 – 3.43 (m, 8H), 1.83 – 1.73 (m, 8H), 1.58 – 1.53 (m, 8H), 0.57 (s, 3H), 0.55 (s, 3H); ^{19}F NMR (CDCl_3 , 376 MHz) δ -138.80 – -138.98 (m, 1F), -139.64 (td, $J = 19.9, 8.3$ Hz, 1F), -144.41 – -144.62 (m, 1F), -152.33 – -152.53 (m, 1F); Analytical HPLC: $t_R = 13.4$ min, >99% purity (5 μL injection; 30–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{37}\text{F}_4\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 609.2555, found 609.2564.

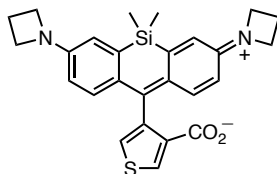


4,5,6,7-Tetrachloro-JF₆₄₆ (39): The title compound (44%, light green solid) was prepared from **31a** and tetrachlorophthalic anhydride according to method S7. ^1H NMR (CDCl_3 , 400 MHz) δ 6.62 (d, $J = 2.6$ Hz, 2H), 6.56 (d, $J = 8.7$ Hz, 2H), 6.28 (dd, $J = 8.7, 2.7$ Hz, 2H), 3.92 (t, $J = 7.3$ Hz, 8H), 2.37 (p, $J = 7.2$ Hz, 4H), 0.55 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 165.1 (C), 151.7 (C), 151.1 (C), 139.7 (C), 137.5 (C), 135.2 (C), 130.9 (C), 128.8 (C), 128.5 (C), 128.1 (CH), 124.8 (C), 115.3 (CH), 112.5 (CH), 90.8 (C), 52.2 (CH_2), 17.0 (CH_2), 0.7 (CH_3), -2.4 (CH_3); Analytical HPLC: $t_R = 15.1$ min, >99% purity (5 μL injection; 30–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{Cl}_4\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 589.0434, found 589.0433.

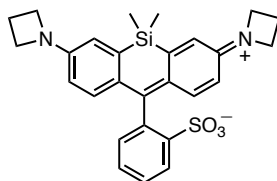


4,7-Dimethyl-JF₆₄₆ (40): The title compound (63%, white solid) was prepared from **31a** and 3,6-dimethylphthalic anhydride according to method S7. ^1H NMR (CDCl_3 , 400 MHz) δ 7.30 (d, $J = 7.7$ Hz, 1H), 7.26 (d, $J = 7.5$ Hz, 1H), 6.65 (d, $J = 2.6$ Hz, 2H), 6.57 (d, $J = 8.6$ Hz, 2H), 6.22 (dd, $J = 8.7, 2.7$ Hz, 2H), 3.89 (t, $J = 7.2$ Hz, 8H), 2.73 (s, 3H), 2.36 (p, $J = 7.2$ Hz, 4H), 1.81 (s, 3H), 0.56 (s, 3H), 0.54 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 170.7 (C),

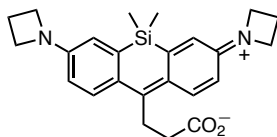
152.4 (C), 150.9 (C), 137.8 (C), 136.7 (C), 135.4 (CH), 131.82 (C), 131.77 (C), 131.2 (CH), 128.4 (CH), 125.7 (C), 115.3 (CH), 112.4 (CH), 90.7 (C), 52.3 (CH₂), 18.4 (CH₃), 17.4 (CH₃), 17.0 (CH₂), 0.9 (CH₃), -2.6 (CH₃); Analytical HPLC: t_R = 15.7 min, >99% purity (5 μ L injection; 30–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₃₀H₃₃N₂O₂Si [M+H]⁺ 481.2306, found 481.2313.



Thienyl-JF₆₄₆ (41): The title compound (30%, dark blue solid) was prepared from **31a** and thieno[3,4-*c*]furan-1,3-dione according to method S7. ¹H NMR (CD₃OD, 400 MHz) δ 8.18 (d, J = 3.3 Hz, 1H), 7.24 (d, J = 3.3 Hz, 1H), 7.20 (d, J = 9.3 Hz, 2H), 6.86 (d, J = 2.5 Hz, 2H), 6.34 (dd, J = 9.3, 2.6 Hz, 2H), 4.33 (t, J = 7.6 Hz, 8H), 2.54 (p, J = 7.7 Hz, 4H), 0.54 (s, 3H), 0.51 (s, 3H); ¹³C NMR (CD₃OD, 101 MHz) δ 169.3 (C), 154.5 (C), 148.8 (C), 142.8 (C), 142.3 (CH), 141.6 (C), 132.4 (CH), 130.1 (C), 126.6 (CH), 119.3 (CH), 112.5 (CH), 101.4 (C), 52.9 (CH₂), 16.9 (CH₂), -1.28 (CH₃), -1.33 (CH₃); Analytical HPLC: t_R = 13.5 min, >99% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₆H₂₇N₂O₂SSi [M+H]⁺ 459.1557, found 459.1564.

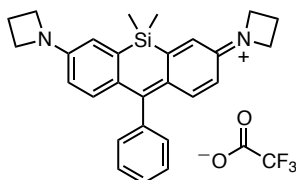


Sulfo-JF₆₄₆ (42): The title compound (32%, dark blue solid) was prepared from **31a** and 2-sulfobenzoic acid cyclic anhydride according to method S8. ¹H NMR (CD₃OD, 400 MHz) δ 8.13 (dd, J = 7.8, 1.1 Hz, 1H), 7.62 (td, J = 7.7, 1.4 Hz, 1H), 7.56 (td, J = 7.5, 1.4 Hz, 1H), 7.11 (dd, J = 7.5, 1.1 Hz, 1H), 7.01 (d, J = 9.4 Hz, 2H), 6.85 (d, J = 2.5 Hz, 2H), 6.27 (dd, J = 9.4, 2.6 Hz, 2H), 4.32 (t, J = 7.6 Hz, 8H), 2.53 (p, J = 7.6 Hz, 4H), 0.53 (s, 3H), 0.52 (s, 3H); Analytical HPLC: t_R = 12.3 min, >99% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₇H₂₉N₂O₃SSi [M+H]⁺ 489.1663, found 489.1669.

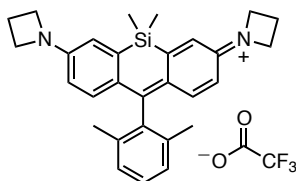


S-JF₆₄₆ (43): The title compound (9%, colorless solid) was prepared from **31a** and succinic anhydride according to method S7. ¹H NMR (CDCl₃, 400 MHz) δ 7.44 (d, J = 8.5 Hz, 2H), 6.67 (d, J = 2.5 Hz, 2H), 6.46 (dd, J = 8.5, 2.6

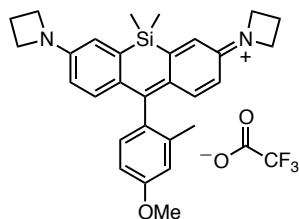
Hz, 2H), 3.90 (t, $J = 7.2$ Hz, 8H), 2.56 (t, $J = 7.9$ Hz, 2H), 2.43 – 2.30 (m, 6H), 0.55 (s, 3H), 0.44 (s, 3H); ^{13}C NMR (CDCl_3 , 101 MHz) δ 178.2 (C), 150.7 (C), 139.0 (C), 133.7 (C), 123.3 (CH), 116.5 (CH), 112.4 (CH), 88.6 (C), 52.7 (CH_2), 42.6 (CH_2), 28.9 (CH_2), 17.2 (CH_2), 0.8 (CH_3), -2.4 (CH_3); Analytical HPLC: $t_R = 10.6$ min, >99% purity (5 μL injection; 10–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 405.1993, found 405.2001.



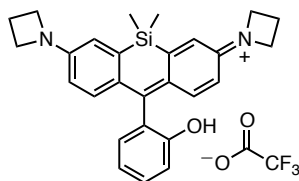
Des-carboxy-JF₆₄₆ (44): The title compound (75%, dark blue solid) was prepared from **31a** and methyl benzoate according to method S8. ^1H NMR (CD_3OD , 400 MHz) δ 7.58 – 7.52 (m, 3H), 7.26 – 7.20 (m, 2H), 7.08 (d, $J = 9.4$ Hz, 2H), 6.94 (d, $J = 2.6$ Hz, 2H), 6.34 (dd, $J = 9.4, 2.6$ Hz, 2H), 4.37 (t, $J = 7.5$ Hz, 8H), 2.55 (p, $J = 7.7$ Hz, 4H), 0.55 (s, 6H); ^{19}F NMR (CD_3OD , 376 MHz) δ -75.71 (s); ^{13}C NMR (CD_3OD , 101 MHz) δ 170.5 (C), 154.4 (C), 149.1 (C), 142.9 (CH), 140.9 (C), 130.3 (CH), 129.7 (CH), 129.3 (CH), 128.8 (C), 120.1 (CH), 112.6 (CH), 53.0 (CH_2), 16.9 (CH_2), -1.2 (CH_3); Analytical HPLC: $t_R = 13.6$ min, >99% purity (5 μL injection; 10–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{Si}$ $[\text{M}]^+$ 409.2095, found 409.2092.



3,7-Dimethyl-JF₆₄₆ (46): The title compound (4%, dark blue solid) was prepared from **31a** and methyl 2,6-dimethylbenzoate according to method S8. ^1H NMR (CD_3OD , 400 MHz) δ 7.37 – 7.32 (m, 1H), 7.24 – 7.20 (m, 2H), 7.02 (d, $J = 9.4$ Hz, 2H), 6.95 (d, $J = 2.6$ Hz, 2H), 6.36 (dd, $J = 9.4, 2.6$ Hz, 2H), 4.37 (t, $J = 7.3$ Hz, 8H), 2.56 (p, $J = 7.7$ Hz, 4H), 1.97 (s, 6H), 0.56 (s, 6H); ^{19}F NMR (CD_3OD , 376 MHz) δ -75.58 (s); ^{13}C NMR (CD_3OD , 101 MHz) δ 170.2 (C), 154.7 (C), 148.9 (C), 140.8 (CH), 139.9 (C), 136.7 (C), 129.8 (CH), 128.7 (CH), 127.8 (C), 120.1 (CH), 113.4 (CH), 53.0 (CH_2), 19.7 (CH_3), 16.9 (CH_2), -1.4 (CH_3); Analytical HPLC: $t_R = 15.1$ min, >99% purity (5 μL injection; 30–95% MeCN/ H_2O , linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{33}\text{N}_2\text{Si}$ $[\text{M}]^+$ 437.2408, found 437.2410.

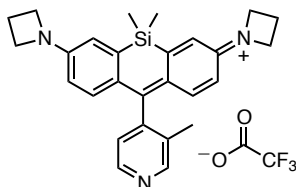


3-Methyl-5-Methoxy-JF₆₄₆ (47): The title compound (58%, dark blue solid) was prepared from **31a** and methyl 4-methoxy-2-methylbenzoate according to method S8. ¹H NMR (CD₃OD, 400 MHz) δ 7.10 (d, *J* = 9.4 Hz, 2H), 7.02 – 6.92 (m, 5H), 6.38 (dd, *J* = 9.4, 2.6 Hz, 2H), 4.38 (t, *J* = 7.6 Hz, 8H), 3.90 (s, 3H), 2.57 (p, *J* = 7.7 Hz, 4H), 1.99 (s, 3H), 0.57 (s, 3H), 0.56 (s, 3H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -75.57 (s); ¹³C NMR (CD₃OD, 101 MHz) δ 170.8 (C), 161.5 (C), 154.6 (C), 149.0 (C), 142.2 (CH), 138.5 (C), 132.4 (C), 131.3 (CH), 129.0 (C), 120.0 (CH), 116.6 (CH), 112.9 (CH), 112.3 (CH), 55.9 (CH₃), 53.0 (CH₂), 19.7 (CH₃), 16.9 (CH₂), -1.2 (CH₃), -1.4 (CH₃); Analytical HPLC: *t*_R = 13.7 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₉H₃₃N₂O₅Si [M]⁺ 453.2357, found 453.2361.

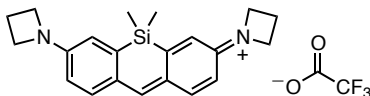


3-Hydroxy-JF₆₄₆ (48): A solution of dibromide **31a** (200 mg, 0.416 mmol) in THF (10 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.08 mL, 1.83 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -20 °C, and a solution of methyl 2-(methoxymethoxy)benzoate (180 mg, 0.916 mmol, 2.2 eq) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and water and extracted with EtOAc (2×). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting residue was redissolved in CH₂Cl₂ (10 mL), and TFA (2 mL) was added. After stirring the blue solution at room temperature for 8 h, it was diluted with toluene (10 mL), concentrated to dryness, and purified by flash chromatography (0–20% MeOH/CH₂Cl₂, linear gradient, with constant 1% v/v AcOH additive) to yield 176 mg (78%) of **48** as a dark blue solid. An analytically pure (>99%) sample was obtained through further purification by reverse phase HPLC (10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive); this material was used for all characterization purposes. ¹H NMR (CD₃OD, 400 MHz) δ 7.41 – 7.34 (m, 1H), 7.20 (d, *J* = 9.4 Hz, 2H), 7.04 – 6.95 (m, 3H), 6.91 (d, *J* = 2.5 Hz, 2H), 6.35 (dd, *J* = 9.4, 2.5 Hz, 2H), 4.36 (t, *J* = 7.5 Hz, 8H), 2.55 (p, *J* = 7.7 Hz, 4H), 0.57 (s, 3H), 0.52 (s, 3H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -75.27 (s); ¹³C NMR (CD₃OD, 101 MHz) δ 169.5 (C), 155.6 (C), 154.6 (C), 149.0 (C), 142.6 (CH), 131.5 (CH), 131.3 (CH), 129.1 (C), 127.7 (C), 120.3 (CH), 119.8 (CH), 116.6 (CH), 112.7 (CH), 52.9 (CH₂), 16.9 (CH₂), -1.0 (CH₃), -1.5 (CH₃); Analytical HPLC: *t*_R = 12.0 min, >99% purity (5 μL injection; 30–95% MeCN/H₂O,

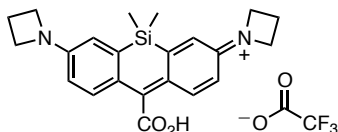
linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $C_{27}H_{29}N_2OSi [M]^+$ 425.2044, found 425.2045.



5-Aza-3-methyl-JF₆₄₆ (49): The title compound (65%, dark blue solid) was prepared from **31a** and methyl 3-methyl-4-pyridinecarboxylate according to method S8. ¹H NMR (CD₃OD, 400 MHz) δ 8.73 – 8.57 (m, 2H), 7.40 (d, J = 5.2 Hz, 1H), 6.99 (d, J = 2.5 Hz, 2H), 6.90 (d, J = 9.4 Hz, 2H), 6.39 (dd, J = 9.4, 2.6 Hz, 2H), 4.47 – 4.30 (m, 8H), 2.56 (p, J = 7.7 Hz, 4H), 2.11 (s, 3H), 0.57 (s, 3H), 0.57 (s, 3H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -75.44 (s); ¹³C NMR (CD₃OD, 101 MHz) δ 163.2 (C), 154.5 (C), 152.6 (C), 149.4 (CH), 148.8 (C), 145.7 (CH), 140.8 (CH), 135.0 (C), 126.6 (C), 126.5 (CH), 120.9 (CH), 113.5 (CH), 53.2 (CH₂), 16.8 (CH₂), 16.3 (CH₃), -1.3 (CH₃), -1.4 (CH₃); Analytical HPLC: t_R = 11.2 min, >99% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $C_{27}H_{30}N_3Si [M]^+$ 424.2204, found 424.2209.



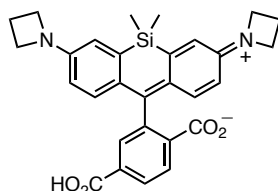
3,6-Bis(azetidiny)-Si-pyronine (50): The title compound (50%, dark blue solid) was prepared from **31a** and methyl formate according to method S8. ¹H NMR (CD₃OD, 400 MHz) δ 7.79 (bs, 1H), 7.63 (d, J = 8.9 Hz, 2H), 6.90 (dd, J = 2.4, 0.7 Hz, 2H), 6.55 (dd, J = 8.9, 2.4 Hz, 2H), 4.39 (t, J = 7.7 Hz, 8H), 2.57 (p, J = 7.7 Hz, 4H), 0.49 (s, 6H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -75.64 (s); ¹³C NMR (CD₃OD, 101 MHz) δ 160.7 (CH), 155.5 (C), 148.4 (C), 144.2 (CH), 128.7 (C), 120.2 (CH), 113.0 (CH), 53.0 (CH₂), 16.8 (CH₂), -1.5 (CH₃); Analytical HPLC: t_R = 14.1 min, >99% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for $C_{21}H_{25}N_2Si [M]^+$ 333.1787, found 333.1780.



3,6-Bis(azetidiny)-9-carboxy-Si-pyronine (51): A solution of dibromide **31a** (150 mg, 0.312 mmol) in THF (7.5 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 808 μ L, 1.37 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -20 °C, and a solution of ester **70** (139 mg, 0.687 mmol, 2.2 eq) in THF (7.5 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and

water and extracted with EtOAc (2×). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting residue was redissolved in MeOH (10 mL), and 1 M HCl (500 µL) was added. After stirring the blue solution at room temperature for 1 h, it was diluted with toluene (10 mL), concentrated to dryness, and purified by flash chromatography (0–20% MeOH/CH₂Cl₂, linear gradient, with constant 1% v/v AcOH additive) to provide the 2,2-bis(hydroxymethyl)propyl ester intermediate (118 mg, 70%, acetate salt).

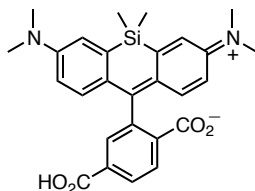
This ester (100 mg, 0.186 mmol) was taken up in MeOH (6 mL), and 1 M NaOH (1.49 mL, 1.49 mmol, 8 eq) was added. The reaction was stirred at 60 °C for 18 h. It was then acidified with AcOH (500 µL) and concentrated to dryness. The resulting residue was redissolved in MeOH, deposited onto Celite, and evaporated. Purification by flash chromatography on silica gel (0–20% MeOH/CH₂Cl₂, linear gradient, with constant 1% v/v AcOH additive; dry load with Celite) afforded the acetate salt of **51** as a dark blue solid (71 mg, 88%). An analytically pure (>99%) sample was obtained through further purification by reverse phase HPLC (10–75% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive); this material (the TFA salt) was used for all characterization purposes. ¹H NMR (CD₃OD, 400 MHz) δ 7.68 (d, *J* = 9.3 Hz, 2H), 6.90 (d, *J* = 2.5 Hz, 2H), 6.57 (dd, *J* = 9.3, 2.5 Hz, 2H), 4.40 (t, *J* = 7.7 Hz, 8H), 2.57 (p, *J* = 7.7 Hz, 4H), 0.49 (s, 6H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -75.51 (s); ¹³C NMR (CD₃OD, 101 MHz) δ 172.3 (C), 163.3 (C), 154.8 (C), 148.9 (C), 140.9 (CH), 123.8 (C), 120.5 (CH), 113.5 (CH), 53.2 (CH₂), 16.8 (CH₂), -1.4 (CH₃); Analytical HPLC: *t*_R = 12.1 min, >99% purity (5 µL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₂H₂₅N₂O₂Si [M]⁺ 377.1680, found 377.1678.



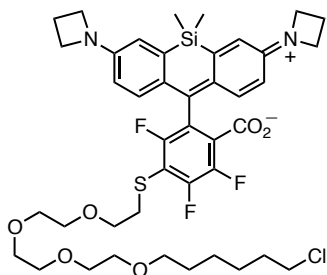
6-Carboxy-JF₆₄₆ (52): A solution of dibromide **31a** (600 mg, 1.25 mmol, 1.5 eq) in THF (30 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 2.94 mL, 5.00 mmol, 6 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -20 °C, and a solution of ester **17** (327 mg, 0.833 mmol, 1 eq) in THF (15 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). It was subsequently diluted with saturated NH₄Cl and water and extracted with EtOAc (2×). The combined organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The resulting residue was redissolved in MeOH (10 mL), and 1 M HCl (1 mL) was added. After stirring the blue solution at room temperature for 30 min, it was diluted with toluene (10 mL), deposited onto Celite, concentrated to dryness, and purified by flash chromatography (0–20% MeOH/CH₂Cl₂, linear gradient, with constant 1% v/v AcOH additive; dry load with Celite) to provide the bis(2,2-bis(hydroxymethyl)propyl) diester intermediate (401 mg, 63%, acetate salt).

This diester (75 mg, 98.6 µmol) was taken up in 2,2,2-trifluoroethanol (4.5 mL), and 25% w/v NaOH (1.5 mL) was added. The reaction was stirred at room temperature for 72 h. It was then acidified with AcOH (1.5 mL), diluted

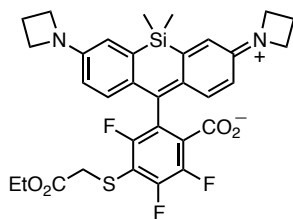
with water, and extracted with CH₂Cl₂ (2×). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Purification by flash chromatography on silica gel (10–100% EtOAc/hexanes, linear gradient, with constant 1% v/v AcOH additive) afforded 38 mg (78%) of **52** as a light blue solid. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 13.58 (s, 1H), 8.11 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.07 – 8.00 (m, 1H), 7.66 – 7.62 (m, 1H), 6.72 (d, *J* = 2.6 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.34 (dd, *J* = 8.7, 2.6 Hz, 2H), 3.83 (t, *J* = 7.3 Hz, 8H), 2.29 (p, *J* = 7.1 Hz, 4H), 0.61 (s, 3H), 0.51 (s, 3H); ¹³C NMR (DMSO-*d*₆, 101 MHz) δ 169.2 (C), 166.0 (C), 155.3 (C), 150.8 (C), 136.5 (C), 135.1 (C), 131.2 (C), 130.0 (CH), 127.9 (C), 127.0 (CH), 125.9 (CH), 124.1 (CH), 115.4 (CH), 112.8 (CH), 90.8 (C), 51.8 (CH₂), 16.3 (CH₂), -0.2 (CH₃), -0.9 (CH₃); Analytical HPLC: *t*_R = 11.1 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₉H₂₉N₂O₄Si [M+H]⁺ 497.1891, found 497.1909.



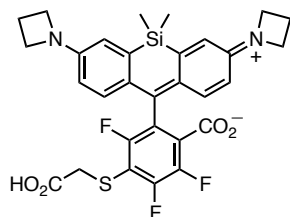
6-Carboxy-SiTMR (53): A solution of dibromide **31c** (200 mg, 0.438 mmol) in THF (10 mL) was cooled to -78 °C under nitrogen. *tert*-Butyllithium (1.7 M in hexanes, 1.13 mL, 1.93 mmol, 4.4 eq) was added, and the reaction was stirred at -78 °C for 30 min. It was then warmed to -20 °C, and a solution of ester **71** (290 mg, 0.877 mmol, 2 eq) in THF (10 mL) was added dropwise over 30 min via addition funnel. The reaction was allowed to warm to room temperature overnight (18 h). AcOH (100 μL) was added (immediate blue color), and the mixture was concentrated to dryness. The residue was taken up in 6 N HCl (10 mL) and stirred at 80 °C for 12 h. After cooling the solution to room temperature, saturated NaHCO₃ was slowly added until pH ~ 2. The resulting suspension was extracted with CH₂Cl₂ (3×). The combined organic extracts were dried over anhydrous MgSO₄, filtered, and evaporated. Flash chromatography on silica gel (10–100% EtOAc/hexanes, linear gradient, with constant 1% v/v AcOH additive) provided **53** as a blue solid (110 mg, 53%). ¹H NMR (CD₃OD, 400 MHz) δ 8.22 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 – 7.82 (m, 1H), 7.05 (d, *J* = 2.8 Hz, 2H), 6.74 (d, *J* = 9.0 Hz, 2H), 6.63 (dd, *J* = 9.0, 2.9 Hz, 2H), 2.95 (s, 12H), 0.65 (s, 3H), 0.56 (s, 3H); ¹³C NMR (CD₃OD, 101 MHz) δ 171.8 (C), 168.3 (C), 156.0 (C), 151.3 (C), 138.2 (C), 137.9 (C), 132.2 (C), 131.3 (CH), 130.9 (C), 129.4 (CH), 126.84 (CH), 126.78 (CH), 118.1 (CH), 114.9 (CH), 101.4 (C), 40.5 (CH₃), 0.3 (CH₃), -1.2 (CH₃); Analytical HPLC: *t*_R = 11.3 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₂₇H₂₉N₂O₄Si [M+H]⁺ 473.1891, found 473.1896.



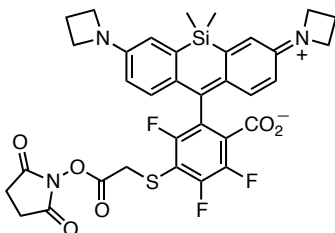
JF₆₆₉-thio-HaloTag ligand (61): To a solution of **35** (9.6 mg, 18.2 μ mol, 1.2 eq) in DMF (750 μ L) were added DIEA (5.3 μ L, 30.4 μ mol, 2 eq) and a solution of HaloTag thiol (O4) ligand (5 mg, 15.2 μ mol) in DMF (750 μ L). After stirring the reaction at room temperature for 18 h, it was concentrated to dryness and purified by silica gel chromatography (0–50% EtOAc/CH₂Cl₂, linear gradient) to afford 6.4 mg (51%) of **61** as a pale green gum. ¹H NMR (CDCl₃, 400 MHz) δ 6.73 (dd, J = 8.6, 1.2 Hz, 2H), 6.64 (d, J = 2.6 Hz, 2H), 6.29 (dd, J = 8.7, 2.6 Hz, 2H), 3.91 (t, J = 7.3 Hz, 8H), 3.69 – 3.50 (m, 16H), 3.44 (t, J = 6.6 Hz, 2H), 3.17 (t, J = 6.2 Hz, 2H), 2.38 (p, J = 7.2 Hz, 4H), 1.81 – 1.72 (m, 2H), 1.62 – 1.56 (m, 2H), 1.48 – 1.33 (m, 4H), 0.56 (s, 3H), 0.54 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -110.98 (dd, J = 21.2, 3.1 Hz, 1F), -125.79 (dd, J = 22.4, 3.2 Hz, 1F), -143.05 (t, J = 21.8 Hz, 1F); Analytical HPLC: t_R = 15.2 min, 98.9% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₄₂H₅₃ClF₃N₂O₆SSi [M+H]⁺ 833.3029, found 833.3040.



JF₆₆₉-6-SCH₂CO₂Et (62): To a solution of **35** (115 mg, 0.219 mmol) in DMF (6 mL) were added DIEA (76 μ L, 0.438 mmol, 2 eq) and ethyl thioglycolate (26 μ L, 0.241 mmol, 1.1 eq). After stirring the reaction at room temperature for 2 h, it was concentrated to dryness and purified by silica gel chromatography (0–40% EtOAc/toluene, linear gradient) to afford 109 mg (80%) of **62** as a blue-green solid. ¹H NMR (CDCl₃, 400 MHz) δ 6.74 (dd, J = 8.6, 1.4 Hz, 2H), 6.65 (d, J = 2.6 Hz, 2H), 6.28 (dd, J = 8.6, 2.6 Hz, 2H), 4.07 (q, J = 7.1 Hz, 2H), 3.91 (t, J = 7.3 Hz, 8H), 3.65 (s, 2H), 2.38 (p, J = 7.2 Hz, 4H), 1.14 (t, J = 7.1 Hz, 3H), 0.56 (s, 3H), 0.55 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -110.32 (dd, J = 21.4, 1.7 Hz, 1F), -125.48 (dd, J = 22.2, 1.9 Hz, 1F), -142.55 (t, J = 21.9 Hz, 1F); Analytical HPLC: t_R = 10.9 min, >99% purity (5 μ L injection; 30–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₃₂H₃₂F₃N₂O₄SSi [M+H]⁺ 625.1799, found 625.1805.

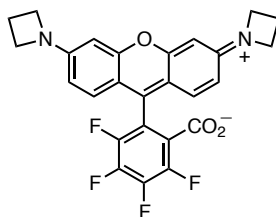


JF₆₆₉-6-SCH₂CO₂H (63): To a solution of sulfide **62** (99 mg, 158 mmol) in 1:1 MeOH/THF (6 mL) was added 1 M NaOH (317 μ L, 317 μ mol, 2 eq). The reaction was stirred at room temperature for 2 h. It was subsequently acidified with 1 M HCl (350 μ L), diluted with water, and extracted with EtOAc (2 \times). The organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography on silica gel (25–100% EtOAc/hexanes, linear gradient, with constant 1% v/v AcOH additive) provided **63** (50 mg, 53%) as a dark blue-green solid. ¹H NMR (CD₃OD, 400 MHz) δ 6.95 (dd, J = 9.0, 1.0 Hz, 2H), 6.85 (d, J = 2.6 Hz, 2H), 6.39 (dd, J = 9.1, 2.6 Hz, 2H), 4.18 (t, J = 7.5 Hz, 8H), 3.75 (s, 2H), 2.48 (p, J = 7.4 Hz, 4H), 0.58 (s, 3H), 0.49 (s, 3H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -110.81 (dd, J = 17.2, 2.3 Hz, 1F), -127.53 (dd, J = 22.3, 2.3 Hz, 1F), -143.48 – -143.99 (m, 1F); Analytical HPLC: t_R = 11.9 min, >99% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₃₀H₂₈F₃N₂O₄SSi [M+H]⁺ 597.1486, found 597.1492.

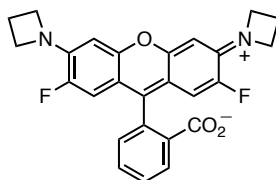


JF₆₆₉-NHS (64): To a solution of sulfide **62** (30 mg, 48.0 μ mol) in 1:1 MeOH/THF (2 mL) was added 1 M NaOH (96 μ L, 96.0 μ mol, 2 eq). The reaction was stirred at room temperature for 1 h. It was subsequently acidified with 1 M HCl (110 μ L), diluted with water, and extracted with EtOAc (2 \times). The organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude acid was combined with TSTU (22 mg, 72.0 μ mol, 1.5 eq) in DMF (2 mL), and DIEA (25 μ L, 144 μ mol, 3 eq) was added. After stirring the reaction at room temperature for 2 h, it was diluted with 10% w/v citric acid and extracted with EtOAc (2 \times). The combined organics were washed with brine, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. Flash chromatography on silica gel (0–100% EtOAc/toluene, linear gradient) afforded **64** as a pale green solid (20 mg, 59%). ¹H NMR (CDCl₃, 400 MHz) δ 6.70 (dd, J = 8.6, 1.6 Hz, 2H), 6.66 (d, J = 2.6 Hz, 2H), 6.25 (dd, J = 8.6, 2.6 Hz, 2H), 3.94 (s, 2H), 3.91 (t, J = 7.3 Hz, 8H), 2.80 (s, 4H), 2.37 (p, J = 7.2 Hz, 4H), 0.57 (s, 3H), 0.56 (s, 3H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -108.84 (d, J = 21.6 Hz, 1F), -123.65 (d, J = 22.2 Hz, 1F), -141.72 (t, J = 21.9 Hz, 1F); Analytical HPLC: t_R = 12.5 min, 97.9% purity (5 μ L injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 650 nm); HRMS (ESI) calcd for C₃₄H₃₁F₃N₃O₆SSi [M+H]⁺ 694.1649, found 694.1658.

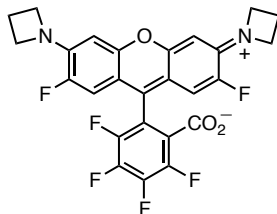
SYNTHESIS OF RHODAMINES 58–60



JF₅₇₁ (58): The title compound (45%, dark purple solid) was prepared from **57a** and tetrafluorophthalic anhydride (**16**) according to method S7. ¹H NMR (CD₃OD, 400 MHz) δ 7.29 (d, *J* = 9.0 Hz, 2H), 6.64 (dd, *J* = 9.2, 2.2 Hz, 2H), 6.48 (d, *J* = 2.2 Hz, 2H), 4.32 (t, *J* = 7.7 Hz, 8H), 2.56 (p, *J* = 7.6 Hz, 4H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -139.12 (ddd, *J* = 21.0, 12.5, 3.8 Hz, 1F), -140.88 (ddd, *J* = 22.2, 12.5, 3.6 Hz, 1F), -153.58 (ddd, *J* = 22.7, 19.2, 4.0 Hz, 1F), -157.77 (ddd, *J* = 21.3, 19.5, 3.7 Hz, 1F); Analytical HPLC: *t_R* = 12.0 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 550 nm); HRMS (ESI) calcd for C₂₆H₁₉F₄N₂O₃ [M+H]⁺ 483.1326, found 483.1328.

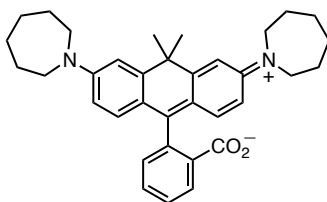


JF₅₅₂ (59): The title compound (60%, pink solid) was prepared from **57b** and phthalic anhydride (**15**) according to method S7. ¹H NMR (CDCl₃, 400 MHz) δ 8.03 – 7.98 (m, 1H), 7.67 (td, *J* = 7.4, 1.2 Hz, 1H), 7.61 (td, *J* = 7.5, 0.9 Hz, 1H), 7.20 – 7.13 (m, 1H), 6.24 (d, ³*J*_{HF} = 12.6 Hz, 2H), 6.21 (d, ⁴*J*_{HF} = 7.9 Hz, 2H), 4.01 (td, *J* = 7.4, 2.0 Hz, 8H), 2.37 (p, *J* = 7.3 Hz, 4H); ¹⁹F NMR (CDCl₃, 376 MHz) δ -138.07 – -138.17 (m); ¹³C NMR (CDCl₃, 101 MHz) δ 169.3 (C), 152.6 (C), 148.63 (d, ⁴*J*_{CF} = 1.2 Hz, C), 148.61 (d, ¹*J*_{CF} = 239.1 Hz, CF), 142.2 (d, ²*J*_{CF} = 13.2 Hz, C), 135.1 (CH), 129.9 (CH), 127.2 (C), 125.2 (CH), 124.1 (CH), 113.6 (d, ²*J*_{CF} = 21.4 Hz, CH), 106.7 (d, ³*J*_{CF} = 6.3 Hz, C), 100.8 (d, ³*J*_{CF} = 4.8 Hz, CH), 84.4 (C), 53.9 (d, ⁴*J*_{CF} = 2.3 Hz, CH₂), 17.8 (d, ⁵*J*_{CF} = 2.2 Hz, CH₂); Analytical HPLC: *t_R* = 11.6 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 550 nm); HRMS (ESI) calcd for C₂₆H₂₁F₂N₂O₃ [M+H]⁺ 447.1515, found 447.1515.



JF₅₇₄ (60): The title compound (34%, dark purple solid) was prepared from **57b** and tetrafluorophthalic anhydride (**16**) according to method S7. ¹H NMR (CD₃OD, 400 MHz) δ 7.07 (d, ³J_{HF} = 12.7 Hz, 2H), 6.55 (d, ⁴J_{HF} = 7.3 Hz, 2H), 4.49 (t, *J* = 7.1 Hz, 8H), 2.57 (p, *J* = 7.7 Hz, 4H); ¹⁹F NMR (CD₃OD, 376 MHz) δ -130.52 (dd, *J*_{FH} = 12.6, 7.4 Hz, 2F), -139.22 (ddd, *J* = 21.0, 12.8, 4.4 Hz, 1F), -140.48 (ddd, *J* = 22.2, 12.7, 4.3 Hz, 1F), -152.63 (ddd, *J* = 23.1, 19.2, 4.5 Hz, 1F), -156.45 – -156.67 (m, 1F); Analytical HPLC: *t*_R = 12.2 min, >99% purity (5 μL injection; 10–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 550 nm); HRMS (ESI) calcd for C₂₆H₁₇F₆N₂O₃ [M+H]⁺ 519.1138, found 519.1145.

SYNTHESIS OF POTOMAC ORANGE (CARBORHODAMINE 66)



Potomac Orange (3',6'-bis(azepanyl)-carborhodamine, 66): A vial was charged with carbofluorescein ditriflate⁴ (100 mg, 161 μmol), Pd₂dba₃ (14.7 mg, 16.1 μmol, 0.1 eq), XPhos (23.0 mg, 48.2 μmol, 0.3 eq), and Cs₂CO₃ (147 mg, 450 μmol, 2.8 eq). The vial was sealed and evacuated/backfilled with nitrogen (3×). Dioxane (1.5 mL) was added, and the reaction was flushed again with nitrogen (3×). Following the addition of hexamethyleneimine (43.4 μL, 386 μmol, 2.4 eq), the reaction was stirred at 100 °C for 2 h. It was then cooled to room temperature, diluted with CH₂Cl₂, deposited onto Celite, and concentrated to dryness. Purification by silica gel chromatography (10–100% EtOAc/hexanes, linear gradient; dry load with Celite) afforded **66** (76 mg, 91%) as a blue solid. ¹H NMR (CDCl₃, 400 MHz) δ 8.00 – 7.95 (m, 1H), 7.58 (td, *J* = 7.4, 1.3 Hz, 1H), 7.53 (td, *J* = 7.4, 1.1 Hz, 1H), 7.13 – 7.08 (m, 1H), 6.84 (d, *J* = 2.5 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 6.46 (dd, *J* = 8.9, 2.6 Hz, 2H), 3.51 – 3.42 (m, 8H), 1.84 (s, 3H), 1.83 – 1.76 (m, 8H), 1.75 (s, 3H), 1.60 – 1.49 (m, 8H); ¹³C NMR (CDCl₃, 101 MHz) δ 171.0 (C), 155.4 (C), 149.3 (C), 147.3 (C), 134.3 (CH), 129.2 (CH), 128.8 (CH), 127.7 (C), 124.9 (CH), 124.2 (CH), 118.7 (C), 110.6 (CH), 108.1 (CH), 49.3 (CH₂), 38.7 (C), 35.9 (CH₃), 32.4 (CH₃), 27.9 (CH₂), 27.2 (CH₂); Analytical HPLC: *t*_R = 11.9 min, >99% purity (5 μL injection; 30–95% MeCN/H₂O, linear gradient, with constant 0.1% v/v TFA additive; 20 min run; 1 mL/min flow; ESI; positive ion mode; detection at 600 nm); HRMS (ESI) calcd for C₃₅H₄₁N₂O₂ [M+H]⁺ 521.3163, found 521.3172.

OPTICAL SPECTROSCOPY AND MICROSCOPY METHODS

General. Fluorescent and fluorogenic molecules were prepared as stock solutions in DMSO and diluted such that the final DMSO concentration did not exceed 1% v/v.

UV–Vis and Fluorescence Spectroscopy. Spectroscopy was performed using 1-cm path length, 3.5-mL quartz cuvettes from Starna Cells. All measurements were taken at ambient temperature (22 ± 2 °C), and spectra are uncorrected. Absorption spectra were recorded on a Cary Model 100 spectrometer (Varian), and fluorescence spectra were recorded on a Cary Eclipse fluorometer (Varian; slit widths at 5 nm). The spectra, maximum absorption wavelength (λ_{max}), extinction coefficient (ϵ), and quantum yield (Φ) were taken in 0.1 M NaOH (Si-fluoresceins) or 10 mM HEPES pH 7.3 (all other dyes, unless otherwise specified); the reported values for ϵ are averages ($n = 3$).

Quantum Yield Determination. Absolute quantum yields (Φ) were measured using a Quantaaurus-QY spectrometer (model C11374) from Hamamatsu. This instrument uses an integrating sphere to determine photons absorbed and emitted by a sample. Measurements were carried out using dilute samples ($A < 0.1$) and self-absorption corrections were performed using the instrument software.⁵

pK_a Determination (Figure 2c,d). The pK_a values for compounds **1**, **24–28** were determined in buffers containing 150 mM NaCl and 10 mM buffer. The following buffer systems were used: citrate (pH 4.0–6.2); phosphate (pH 5.8–8.0); tris (pH 7.8–9.0); carbonate (pH 9.2–10.0). Buffer solutions containing 5 μ M fluorophore were prepared (36 samples from pH 4.0–10.0, in duplicate). Absorbance values were read on Cary Model 100 spectrometer and plotted using GraphPad Prism software. The points were fitted to a sigmoidal dose response curve with a variable slope to determine the Hill coefficient (h).

Stability study of JF₆₆₉ (35, Figure S2). To a solution of PBS containing 10 mM β -mercaptoethanol was added JF₆₆₉ (**35**, 10 μ M). This sample was analyzed immediately (0 h) and after 1, 2, and 4 h at ambient temperature using an Agilent 1200 analytical HPLC/MS system equipped with an autosampler and photodiode array detector. Using the HPLC autosampler, 25 μ L of this solution was injected onto a Phenomenex Gemini–NX 30 \times 150 mm 5 μ m C18 column eluting with a gradient of 10–95% v/v MeCN/H₂O (constant v/v 0.1% TFA) over 20 min. The resulting chromatograms at 670 nm are collected in Figure S2 and show <1% conversion to the substitution (S_NAr) product after 4 h.

General cell culture and fluorescence microscopy. COS7 were maintained in phenol red-free DMEM supplemented with 10% (v/v) fetal bovine serum and 2 mM GlutaMAX (ThermoFisher) at 37°C in a humidified 5% (v/v) CO₂ incubator; COS7[H2B-Halo] stably expresses the H2B-HaloTag fusion. Cells were imaged with either a Zeiss 710 LSM inverted confocal microscope or an 880 LSM using a W Plan APO 20x/0.8 or a C APO 40x/1.2 W Corr FCS M27 objective with appropriate filter sets for each dye. U2OS cells (ATCC) were cultured in FluoroBrite

Dulbecco's modified Eagle medium (DMEM, phenol red-free; Thermo Fisher Scientific) supplemented with 10% (v/v) fetal bovine serum (Thermo Fisher Scientific), 2 mM GlutaMAX (Thermo Fisher Scientific), 1X Antibiotic-Antimycotic solution (10,000 µg/mL penicillin, 10,000 µg/mL streptomycin, and 25 µg/mL Amphotericin B; Thermo Fisher Scientific) and maintained at 37 °C in a humidified 5% (v/v) CO₂ environment. The cells have integrated a histone H2B–HaloTag expressing plasmid via the piggyback transposase, under the selection of 500 µg/ml Geneticin (Life Technologies). This ‘H2B–Halo’ cell line undergoes regular mycoplasma testing by the Janelia Cell Culture Facility. Cells were imaged live on a confocal microscope in the Janelia Imaging Facility (Zeiss 800, Plan-Apochromat 63X/1.40 Oil DIC M27) using 640 nm Ex/650-700 nm Em.

Co-staining of JF₆₆₉-thio-HaloTag ligand (61) and Hoechst 33342 in cells (Figure 3b–d). U2OS cells stably expressing H2B-HaloTag were sequentially stained, first for 2 hrs with 100 nM JF₆₆₉-thio-HaloTag ligand (61) then 30 min with 5 µM Hoechst 33342 at 37 °C. The cells were washed twice with fresh media and imaged live. The nuclear co-staining of these cells by the JF₆₆₉-thio-HaloTag ligand and Hoechst 33342 dye is displayed as a maximum intensity projection of a confocal image stack using Fiji.

Cell immunolabeling (Figure 3e,f). JF₆₆₉-NHS (64) and Alexa Fluor 660 NHS were conjugated to a polyclonal goat anti-mouse IgG (H +L) secondary antibody (ThermoFisher #31160) at pH 8.3, and purified by gel filtration. The initial molar dye:protein ratio for the coupling was 20:1 and 10:1 for JF₆₆₉ and AF660, respectively. The conjugation yielded approximately six molecules of dye/IgG for each of the two reactions. For immunolabeling, COS7 cells were grown in 35 mm MatTek glass bottom dishes to appropriate density. Cells were washed twice with 60 mM PIPES, 25 mM HEPES, 10 mM EGTA, 2 mM MgCl₂ (PHEM), followed by fixation with fresh 4% paraformaldehyde for 10 min at ambient temperature, followed by three additional washes with PHEM for 10 min each. Cells were then permeabilized with 0.3% Triton X-100 for 10 min and washed 3 times with PHEM for 5 min each. Incubating in PBS with 3% bovine serum albumin (BSA) for 30 min blocked nonspecific protein binding sites. A primary monoclonal antibody against alpha-tubulin (DM1A, ThermoFisher) was bound to the cells at 4 µg/ml in PBS, 3% BSA for 50 min with shaking. After three 10 min washes with PBS, the secondary antibody was applied at 1 µg/ml for 50 min as above. Cells were washed and counterstained with 2 µg/ml Hoechst 33342 for 15 min. After another three 10 min washes with PBS, cells were imaged.

Photostability comparison of JF₆₆₉ and Alexa Fluor 660 (Figure 3g). The photostability comparison between JF₆₆₉ and Alexa Fluor 660 was performed on COS7 cells that had been immunolabeled with secondary antibodies conjugated to each of the two dyes. Bleaching and images were obtained via confocal Z-stacks (1 µm x 19). Each cycle of bleaching consisted of 10 bleaching iterations, followed by collection of an image stack, which was repeated for 30 cycles. The 633 nm excitation power for both imaging and bleaching of JF₆₆₉ was 720 µW, measured at the objective. For Alexa Fluor 660, the 633 nm power was reduced to 320 µW to correct for the increased absorbance of this dye at 633 nm relative to JF₆₆₉. Image stacks for each cycle were summed, and the mean fluorescence was calculated after background subtraction.

Dye staining (Figure 4). COS7 were grown in 35 mm glass bottom dishes (MatTek), washed and fixed with 4% paraformaldehyde in 0.1 M phosphate pH 7.2 for 30 min. After washing with PBS, cells were stained with 5 μ M dye (Potomac Yellow (**65**), Potomac Orange (**66**)) for 30 min followed by 3 additional PBS washes. For comparison of Si-rhodamine **34** and Potomac Red (**38**), cells were stained with 2 μ M dye for 60 min, washed and fixed as above.

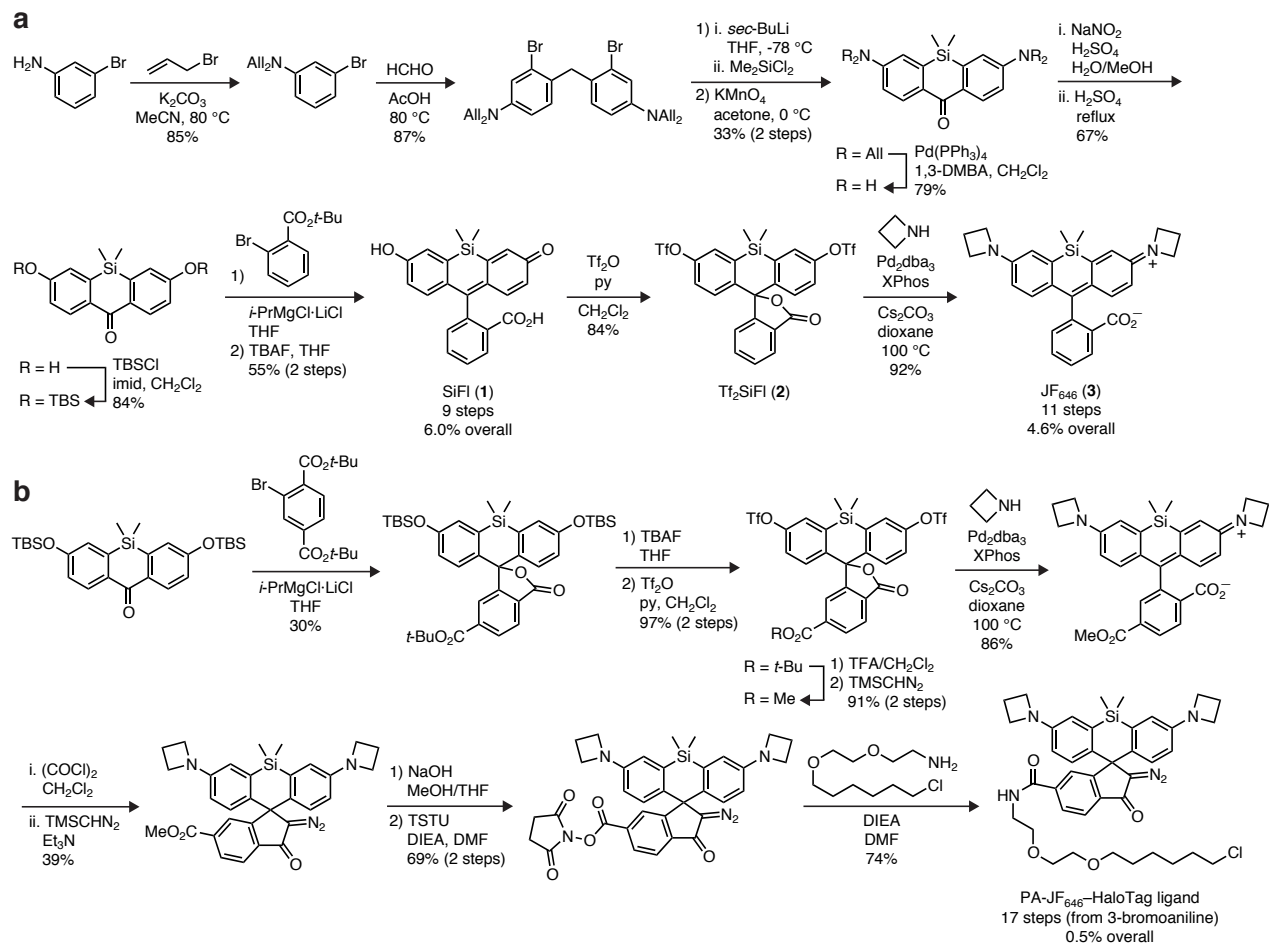


Figure S1. Previously reported syntheses of JF₆₄₆ probes. (a) Synthesis of SiFI (**1**) and JF₆₄₆ (**3**) via the Si-anthrone described by Nagano et al.^{1,6} (b) Synthesis of PA-JF₆₄₆-HaloTag ligand.²

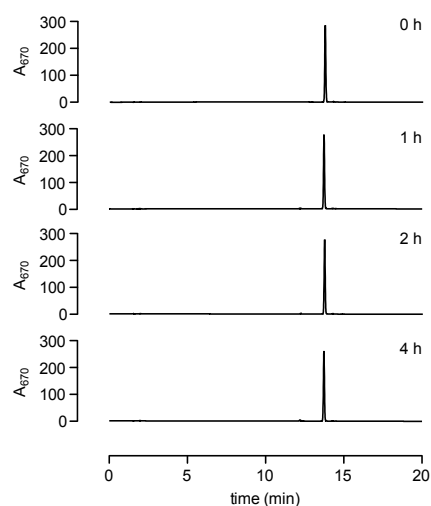
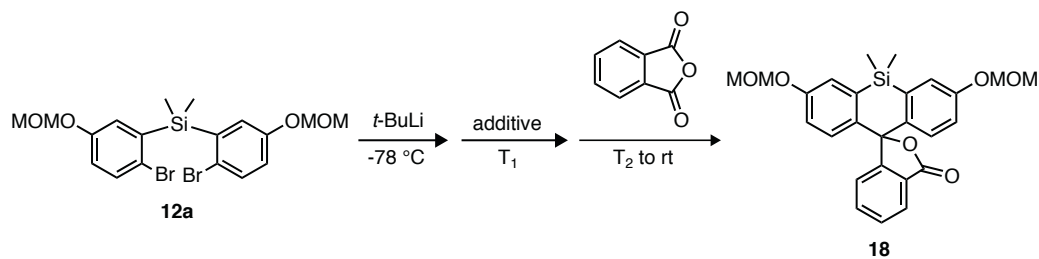


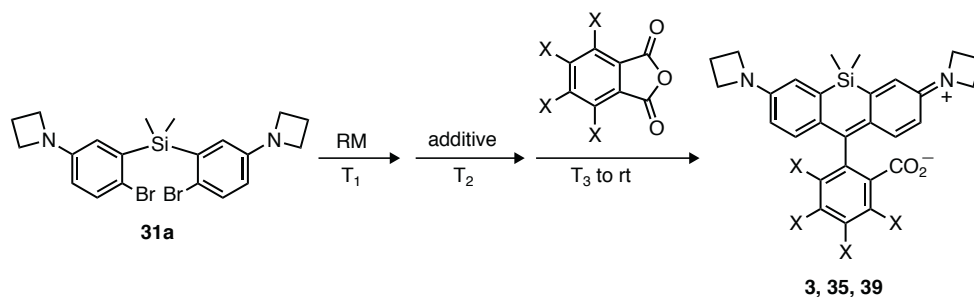
Figure S2. HPLC traces of JF₆₆₉ (**35**) incubated for 0, 1, 2, and 4 h in PBS containing 10 mM β-mercaptoethanol.

Table S1. Optimization of reaction conditions for the synthesis of **18** via Li/Br exchange of **12a** and addition to phthalic anhydride.



additive	T ₁ (°C)	T ₂ (°C)	anhydride addition	yield (%)
none	–	-78	fast (<1 min)	40
none	–	-20	slow (30 min)	49
MgBr ₂ (2.2 eq)	-10	-78	fast (<1 min)	57
MgBr ₂ ·OEt ₂ (2.2 eq)	-10	-10	slow (30 min)	60

Table S2. Optimization of reaction conditions for the synthesis of JF₆₄₆ analogs via Li/Br exchange of **31a** and addition to phthalic anhydrides.



RM	T ₁ (°C)	additive	T ₂ (°C)	T ₃ (°C)	X	anhydride addition	yield (%)
<i>sec</i> -BuLi (2.2 eq)	-78	none	–	-78	H	fast (<1 min)	28
<i>sec</i> -BuLi	-78	none	–	-20	H	slow (30 min)	38
<i>t</i> -BuLi (4.4 eq)	-78	none	–	-78	H	fast (<1 min)	34
<i>t</i> -BuLi	-78	none	–	-20	H	slow (30 min)	46
<i>t</i> -BuLi	-78	MgBr ₂ (2.2 eq)	-78	-78	H	fast (<1 min)	29
<i>t</i> -BuLi	-78	MgBr ₂	-10	-10	H	slow (30 min)	53
<i>t</i> -BuLi	-78	MgBr ₂ ·OEt ₂ (2.2 eq)	-10	-10	H	slow (30 min)	55
<i>i</i> -PrBu ₂ MgLi (2.4 eq)	0	none	–	0	H	slow (30 min)	21
<i>i</i> -PrBu ₂ MgLi	-78	none	20	-78	H	slow (30 min)	14
<i>t</i> -BuLi	-78	none	–	-20	F	slow (30 min)	24
<i>t</i> -BuLi	-78	MgBr ₂ ·OEt ₂	-10	-10	F	slow (30 min)	51
<i>sec</i> -BuLi	-78	none	–	-78	Cl	fast (<1 min)	0
<i>t</i> -BuLi	-78	MgBr ₂ ·OEt ₂	-10	-10	Cl	slow (30 min)	44

Table S3. Full spectroscopic properties of rhodamine dyes.

structure	dye	λ_{max} (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϵ_{water} ($\text{M}^{-1} \text{cm}^{-1}$)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$) ^a	Φ
	3 (JF ₆₄₆)	646	646	664	5,600	152,000	0.52
	32^b	—	—	—	—	101,000	—
	35 (JF ₆₆₉)	669	669	682	112,000	116,000	0.37
	36	695	695	707	2,000	149,000	— ^c
	62	668	668	681	119,000	145,000	0.38
	63	667	668	681	130,000	147,000	0.38
	39	674	673	685	9,870	84,500	0.14
	40	649	649	660	<500	7,200	— ^c
	41	650	651	667	113,000	149,000	0.40
	42	654	655	670	124,000	139,000	0.51
	43	652	652	668	21,200	126,000	0.25

structure	dye	λ_{max} (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϵ_{water} ($\text{M}^{-1} \text{cm}^{-1}$)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$) ^a	Φ
	33	643	643	662	28,200	141,000	0.41
	37	667	667	682	132,000	139,000	0.31
	34	657	657	674	2,200	185,000	— ^c
	38	683	682	698	15,500	215,000	0.10
	44	648	648	662	116,000	—	0.20
	45	649	649	663	118,000	—	0.47
	46	651	651	664	89,600	—	0.51
	47	649	649	664	110,000	—	0.49
	48	651	651	666	136,000	—	0.48
	49	656	656	670	133,000	—	0.48
	50	636	636	649	97,100	—	0.62
	51	641	641	657	120,000	—	0.26

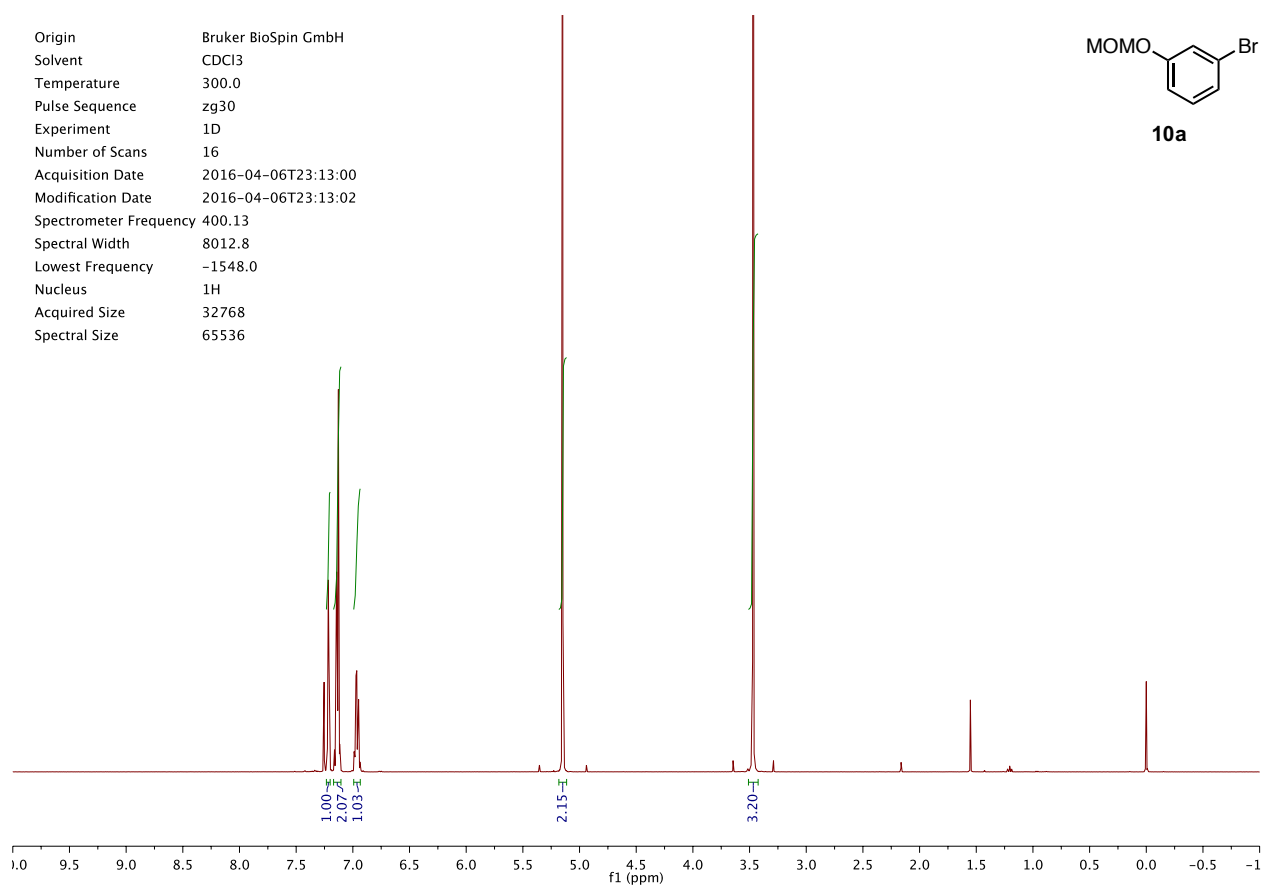
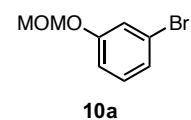
structure	dye	λ_{max} (nm)	λ_{ex} (nm)	λ_{em} (nm)	ϵ_{water} ($\text{M}^{-1} \text{cm}^{-1}$)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$) ^a	Φ
	JF₅₄₉	549	549	571	101,000	134,000	0.88
	58 (JF₅₇₁)	571	571	590	101,000	125,000	0.78
	59 (JF₅₅₂)	552	552	575	95,200	129,000	0.83
	60 (JF₅₇₄)	574	574	594	103,000	132,000	0.78

All measurements taken in 10 mM HEPES pH 7.3 unless otherwise noted. ^a Extinction coefficients measured in EtOH with 0.1% trifluoroacetic acid or 2,2,2-trifluoroethanol with 0.1% trifluoroacetic acid. ^b Dye **32** was strongly shifted to the closed form in water, making it essentially non-fluorescent. ^c Could not determine quantum yield in water due to modest aqueous solubility and dominance of the closed form in water.

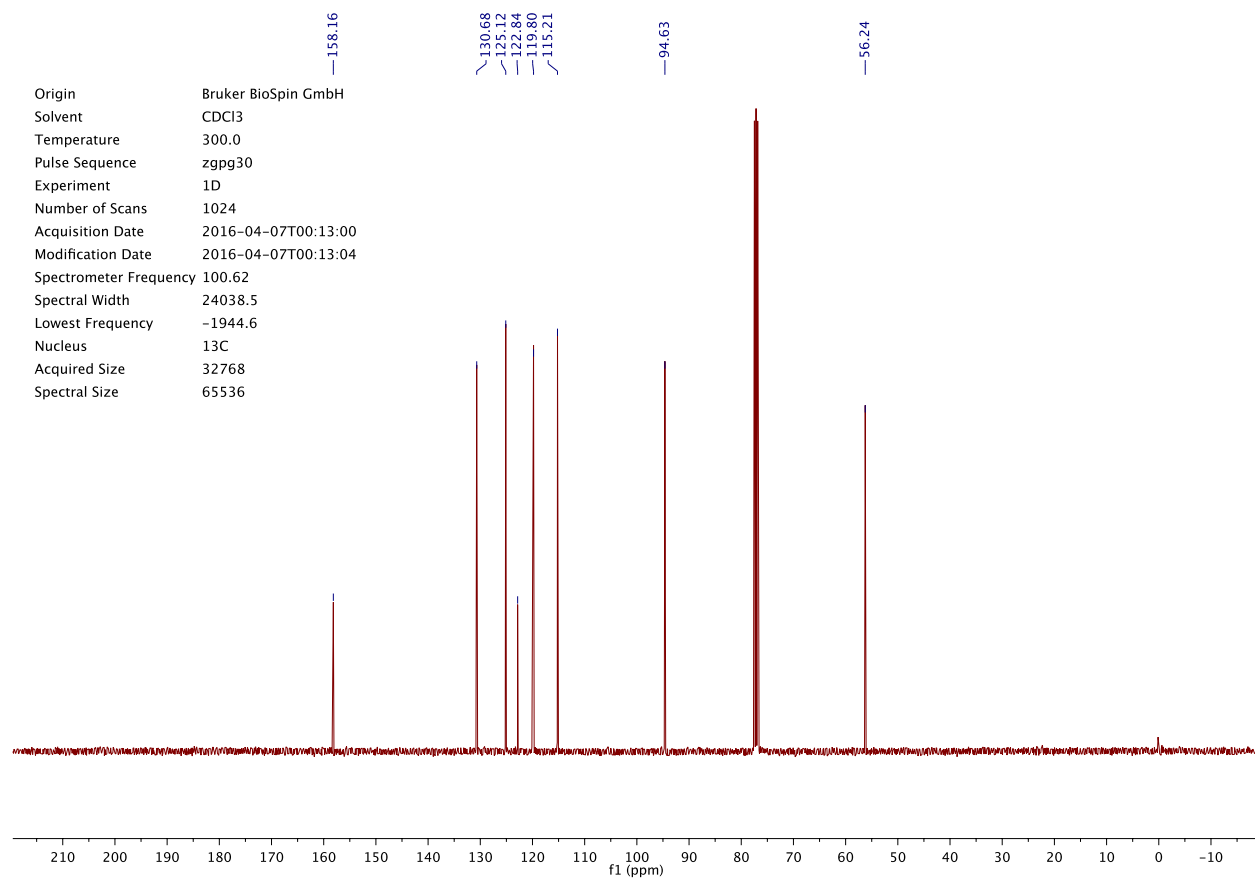
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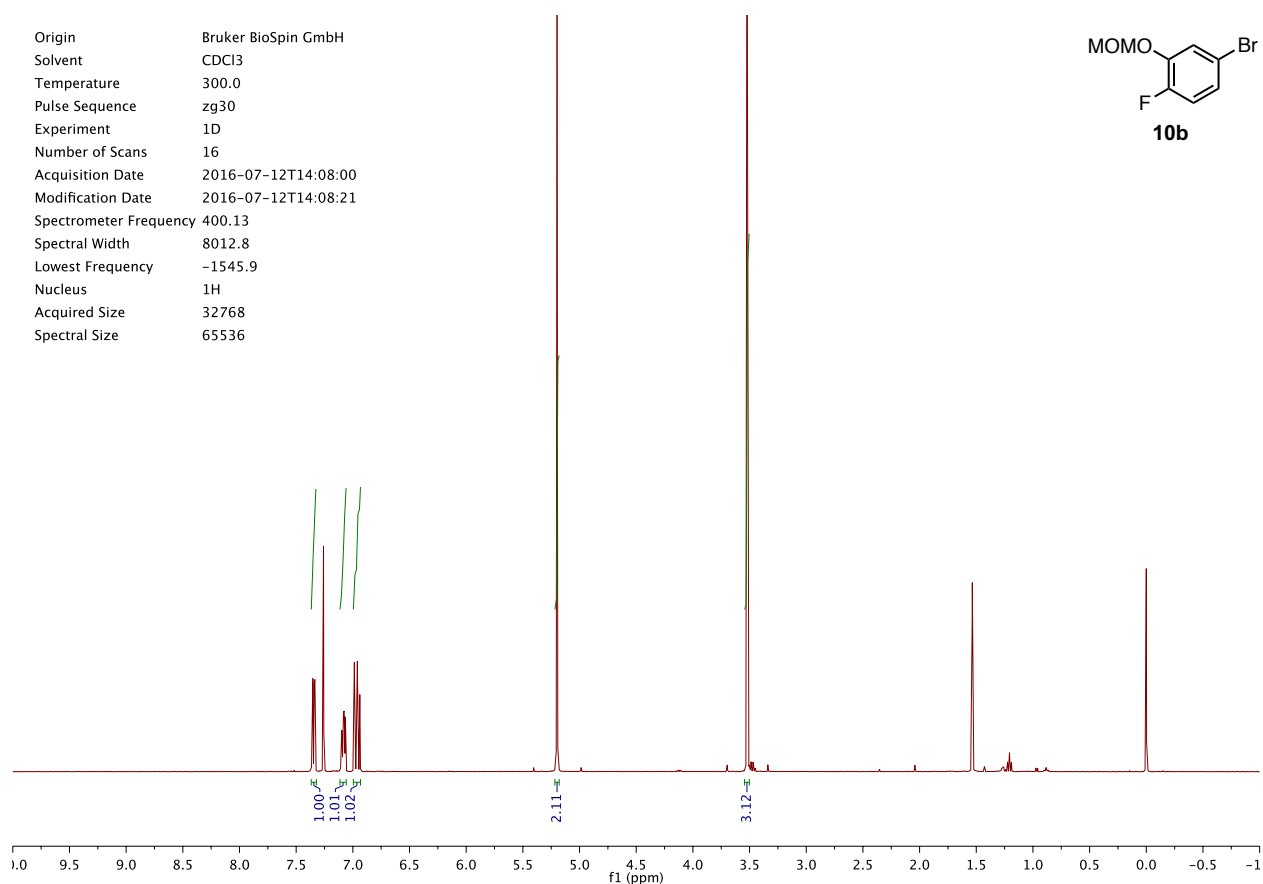
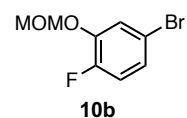
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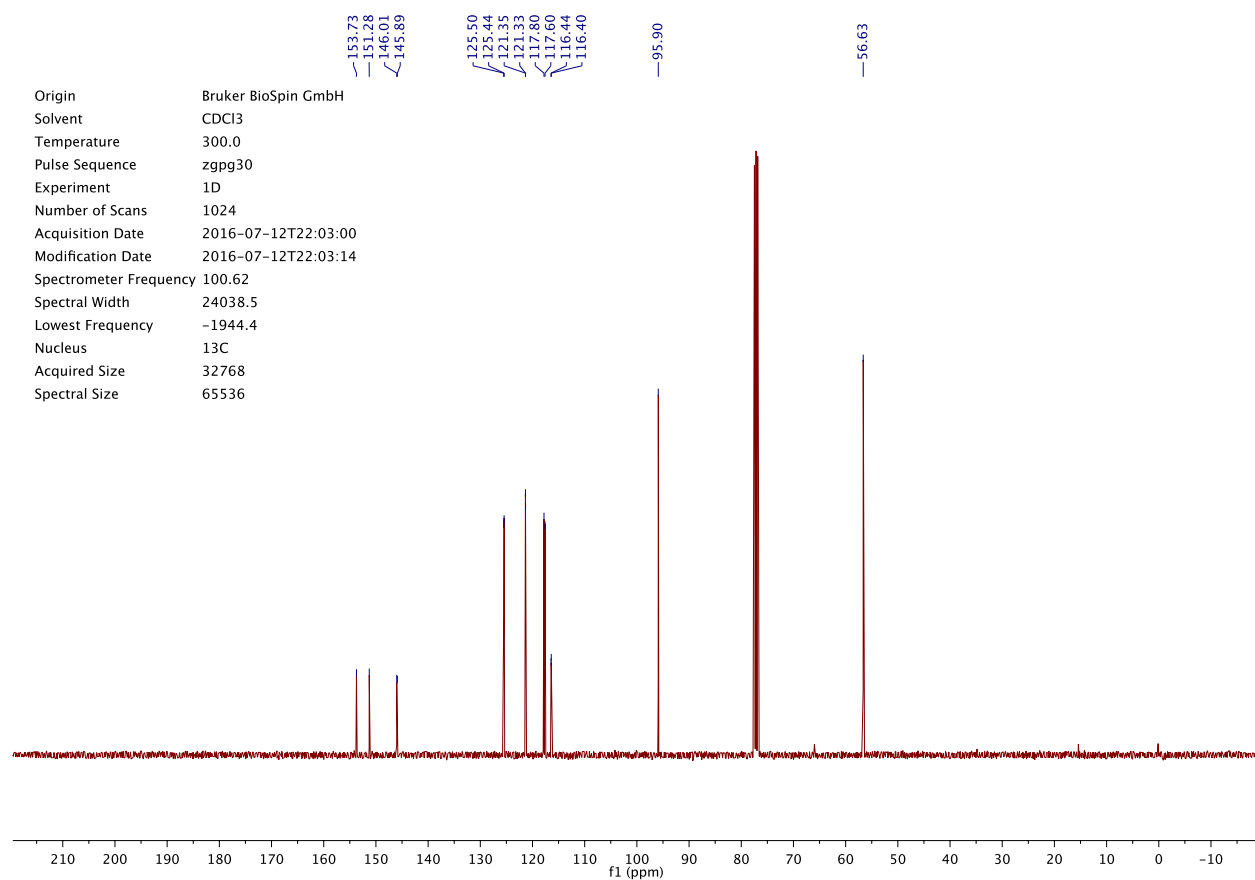
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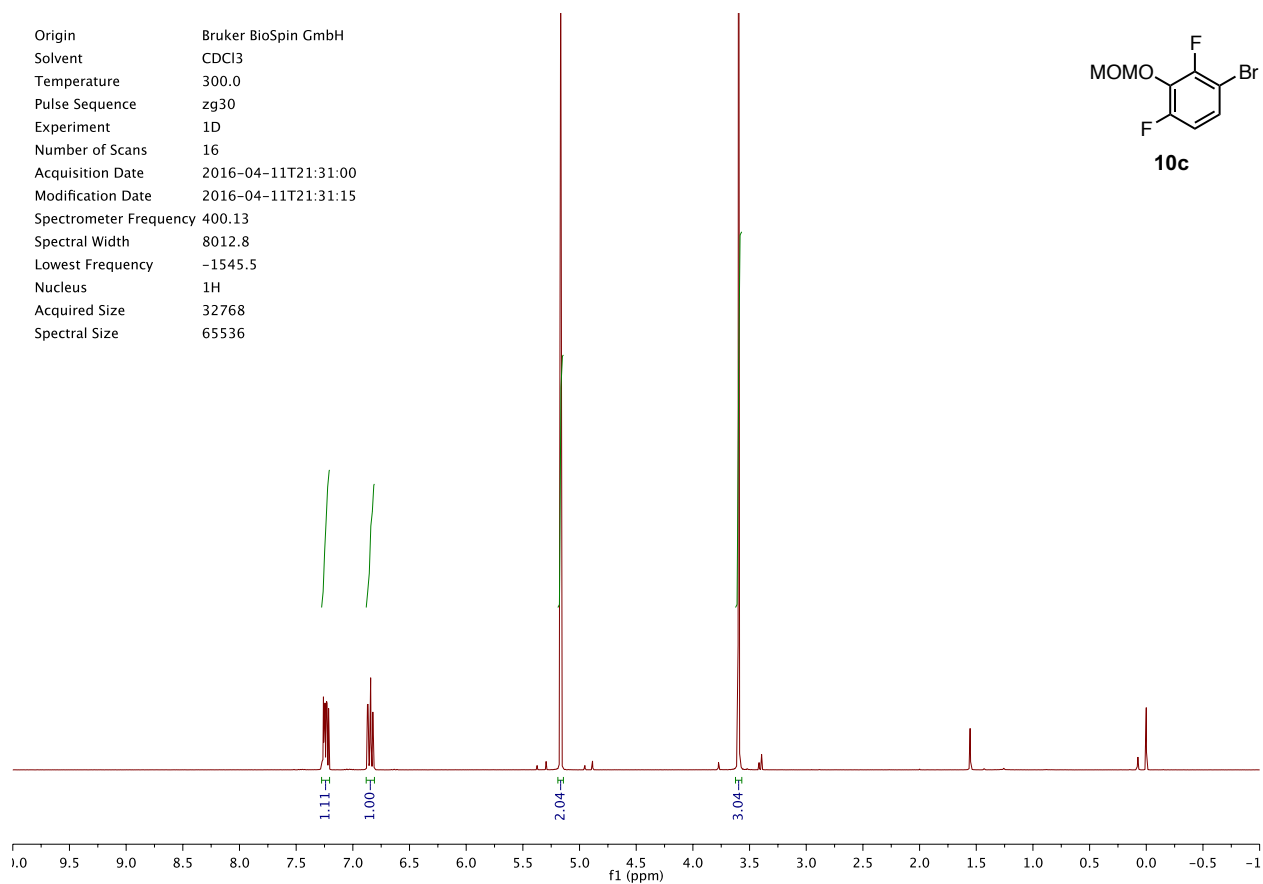
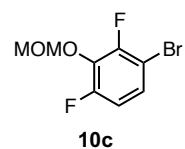
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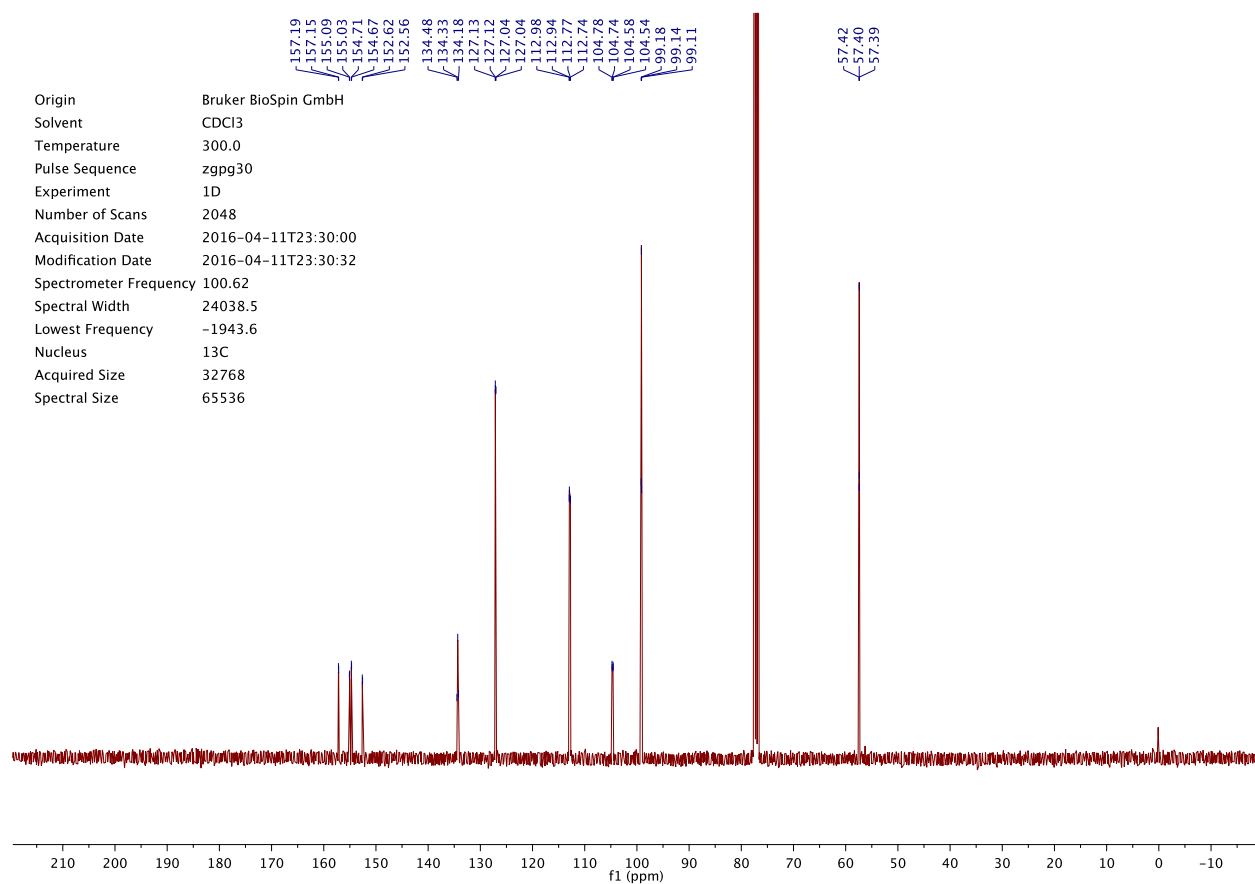
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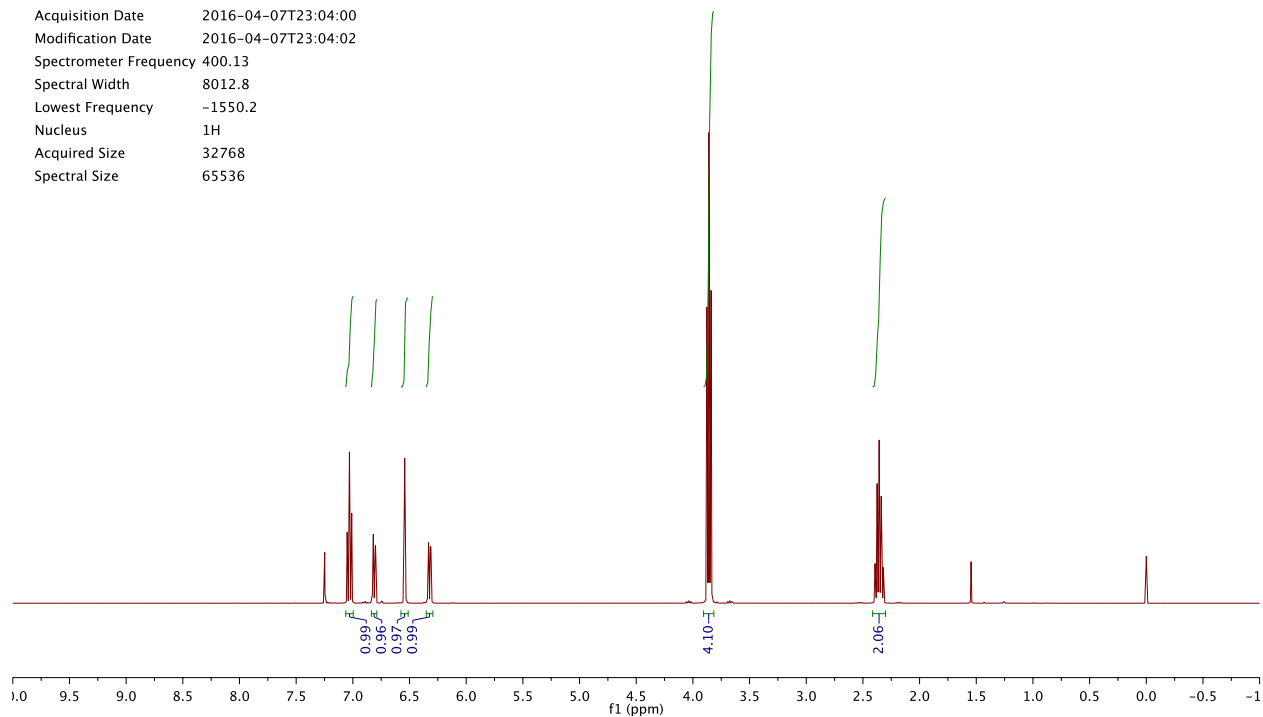
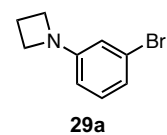
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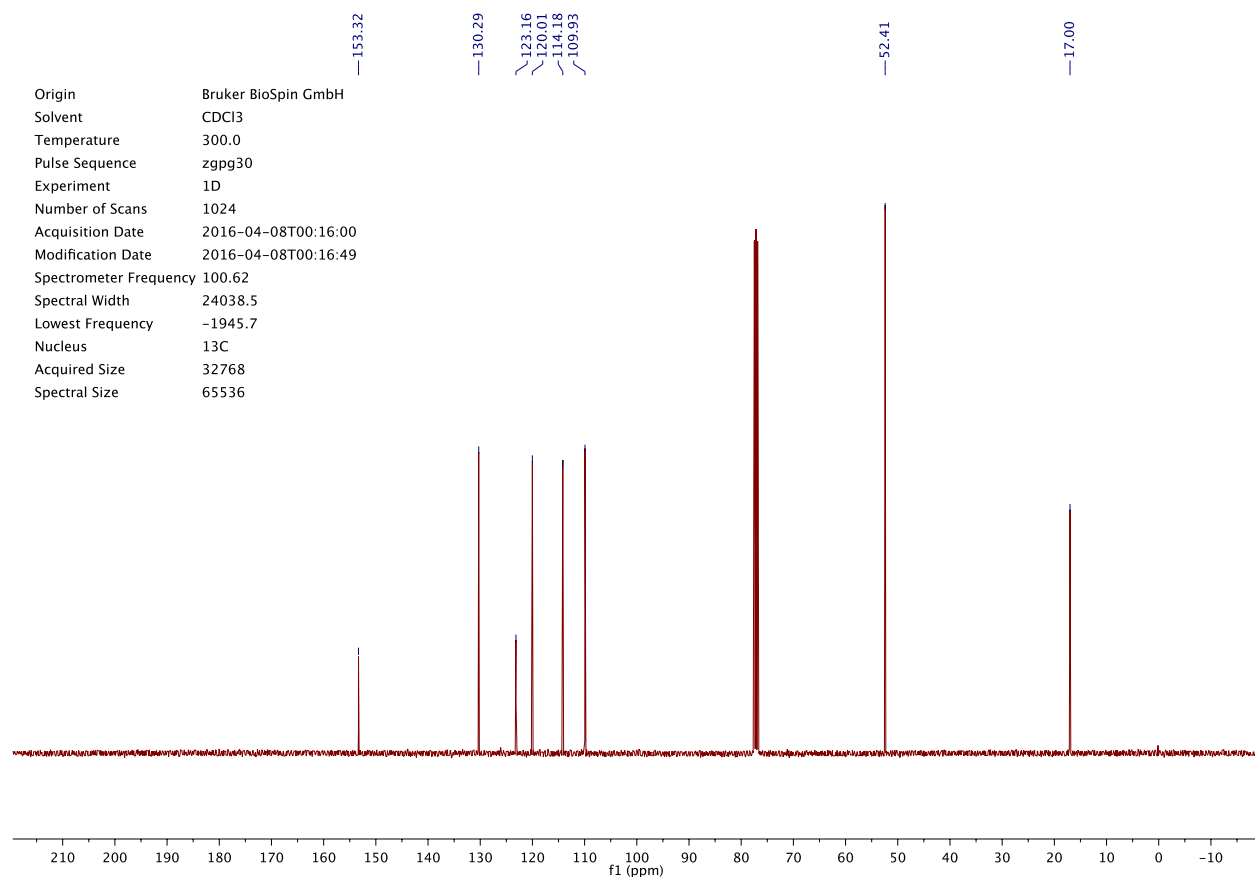
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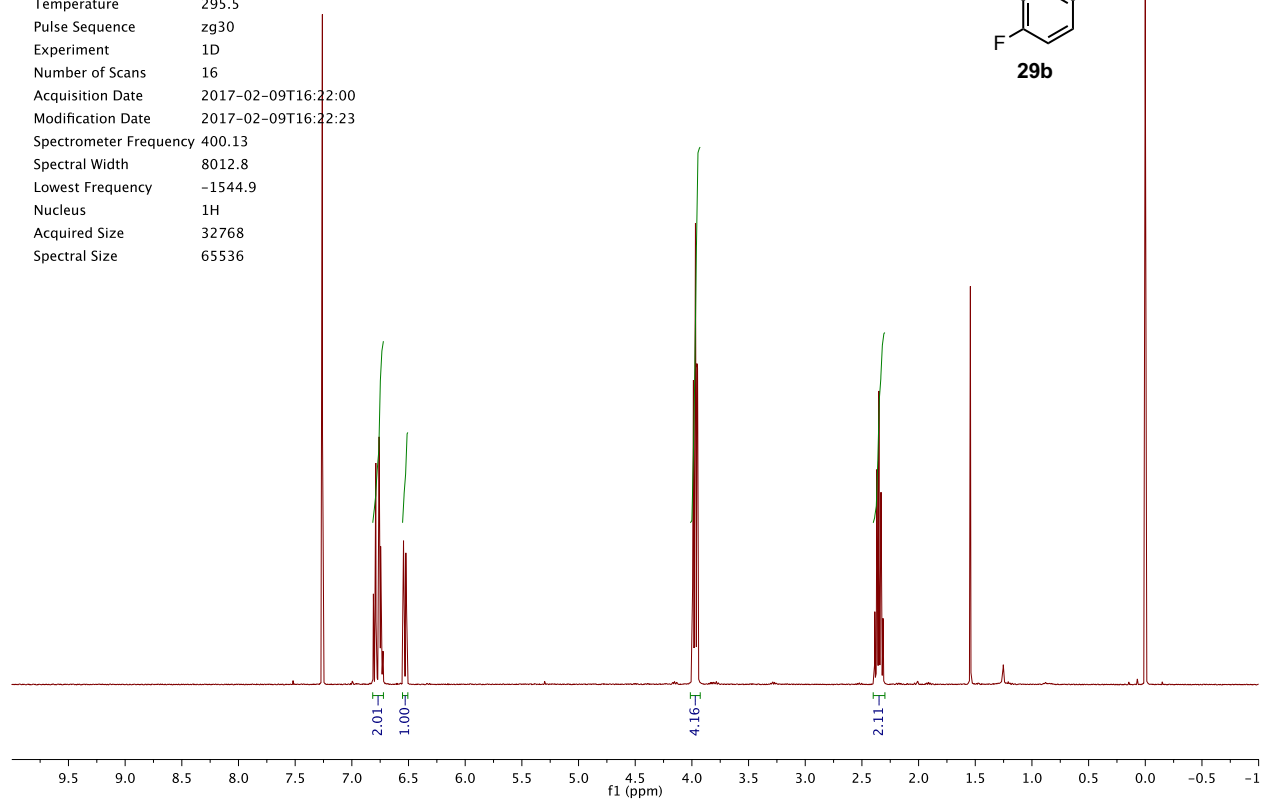
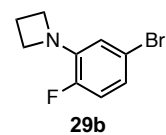
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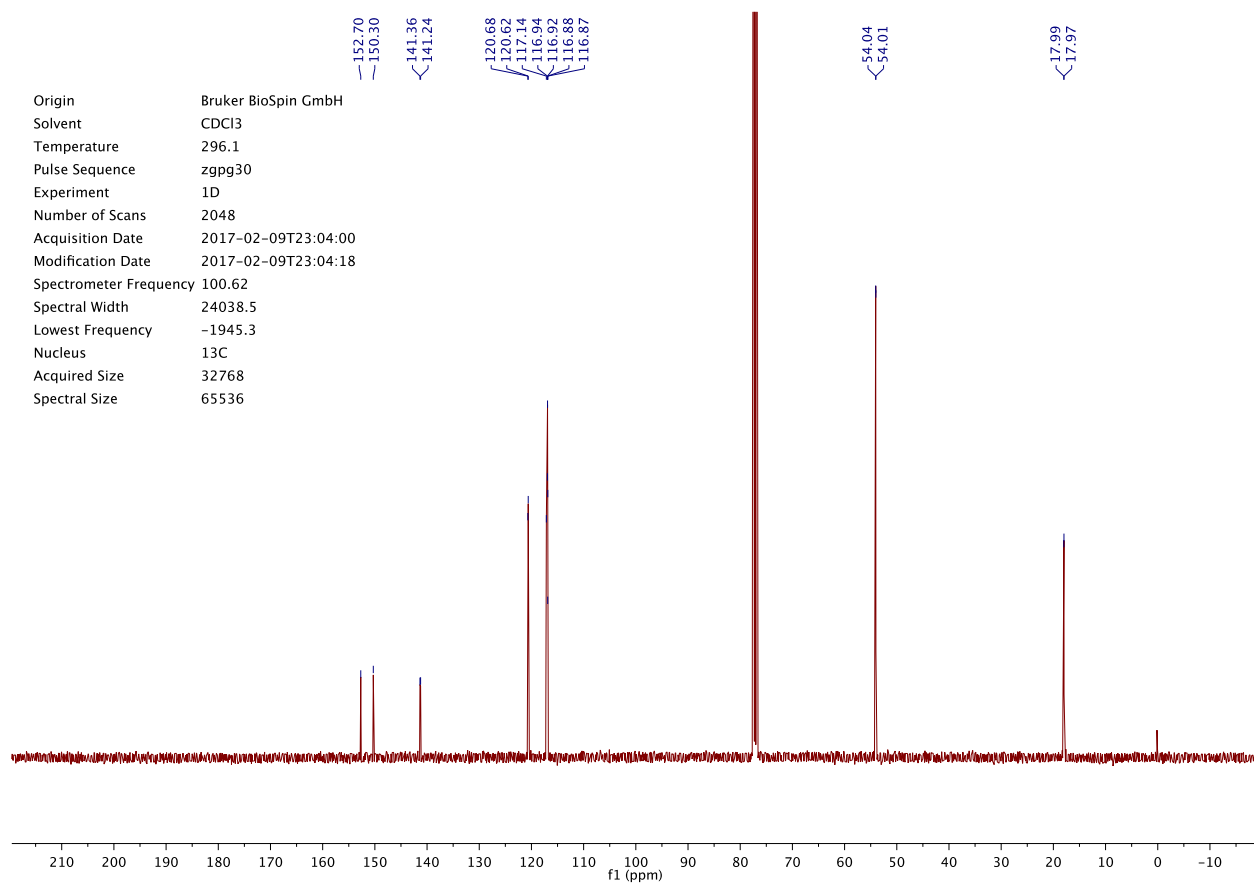
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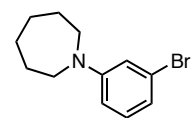
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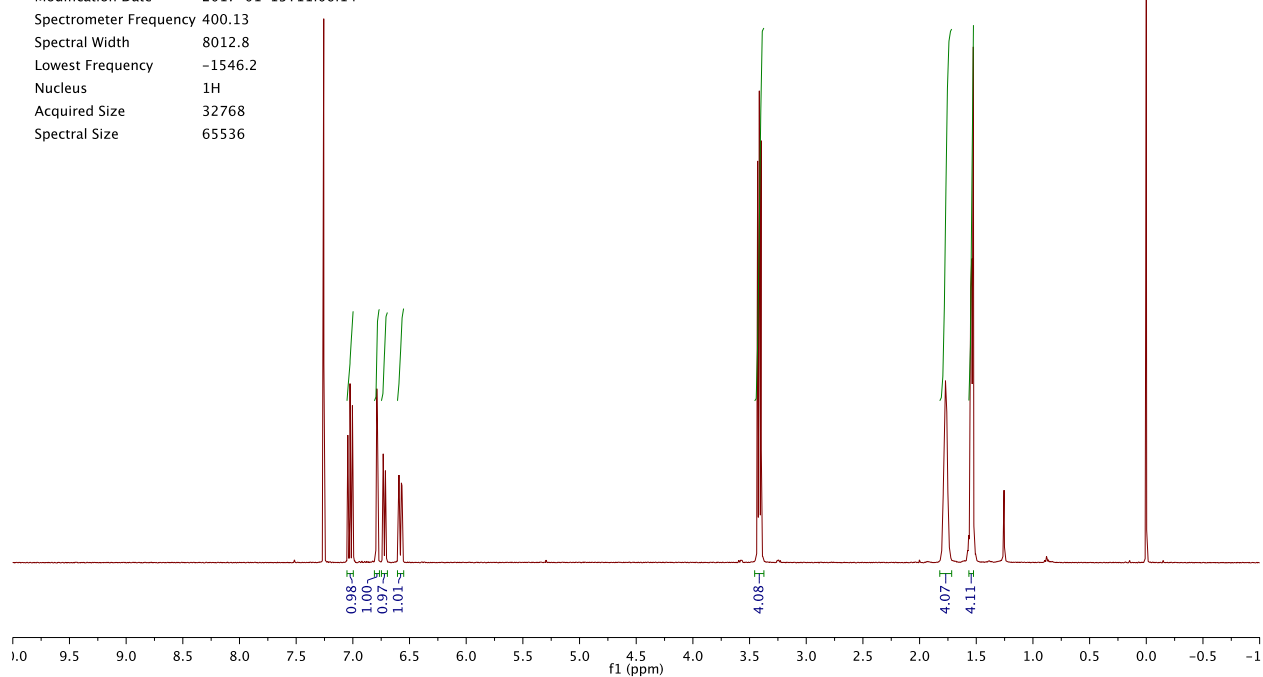
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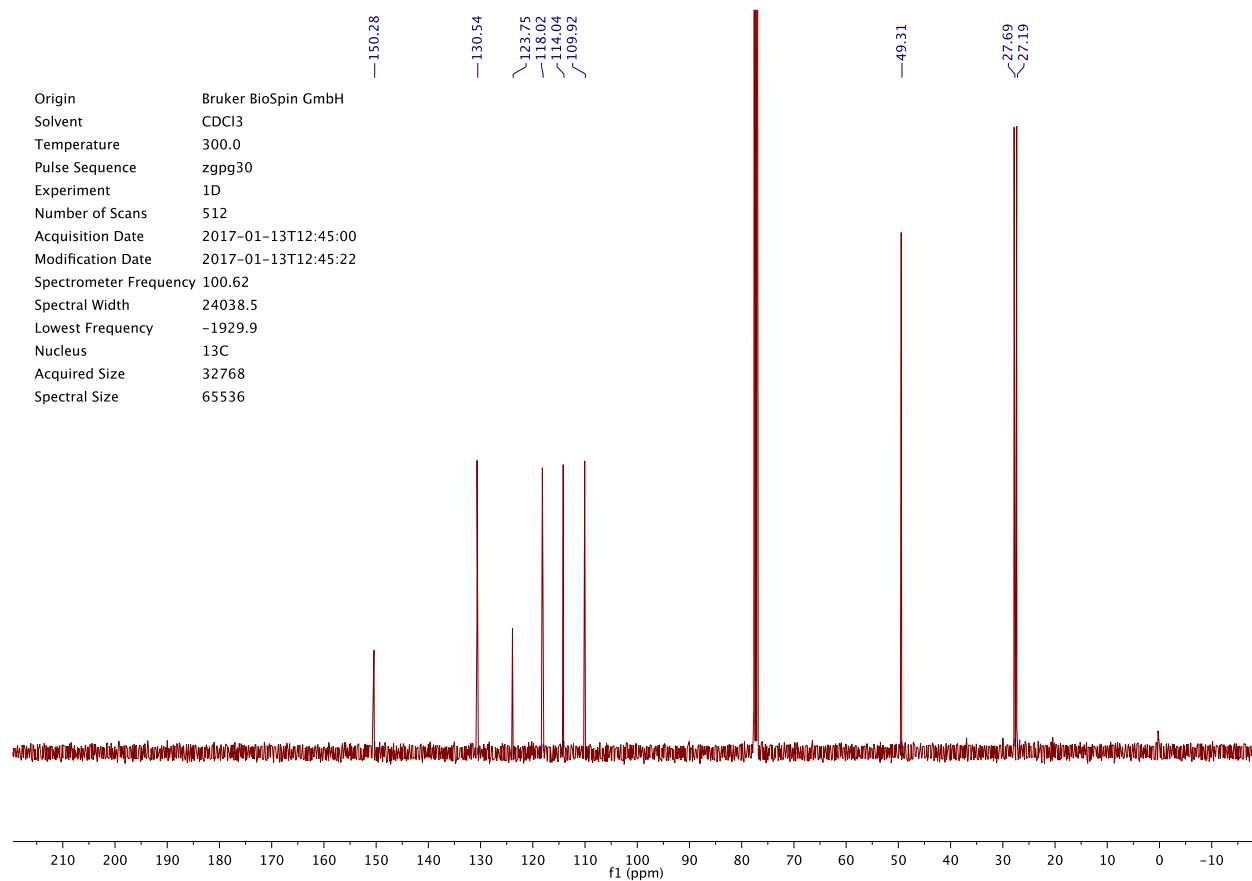
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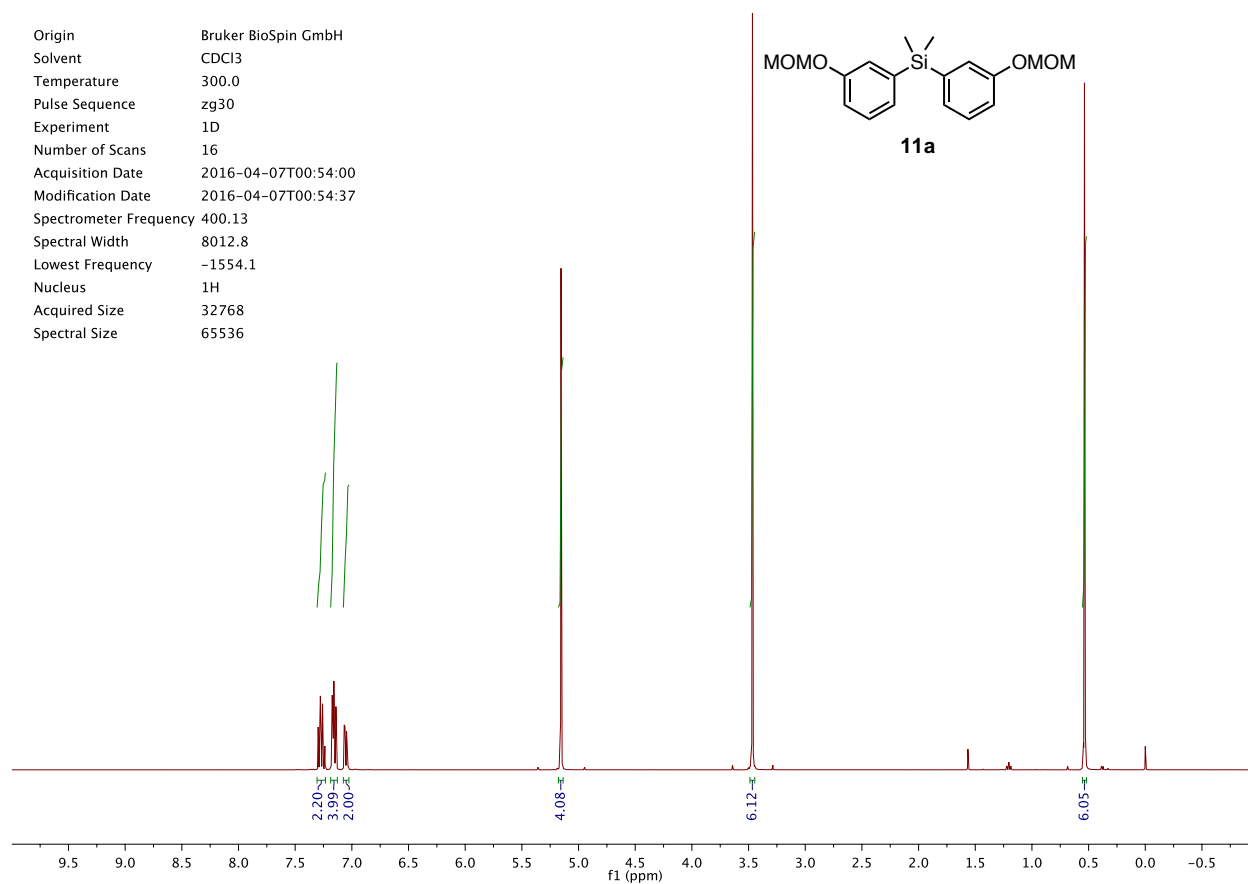
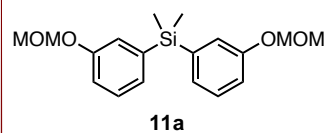
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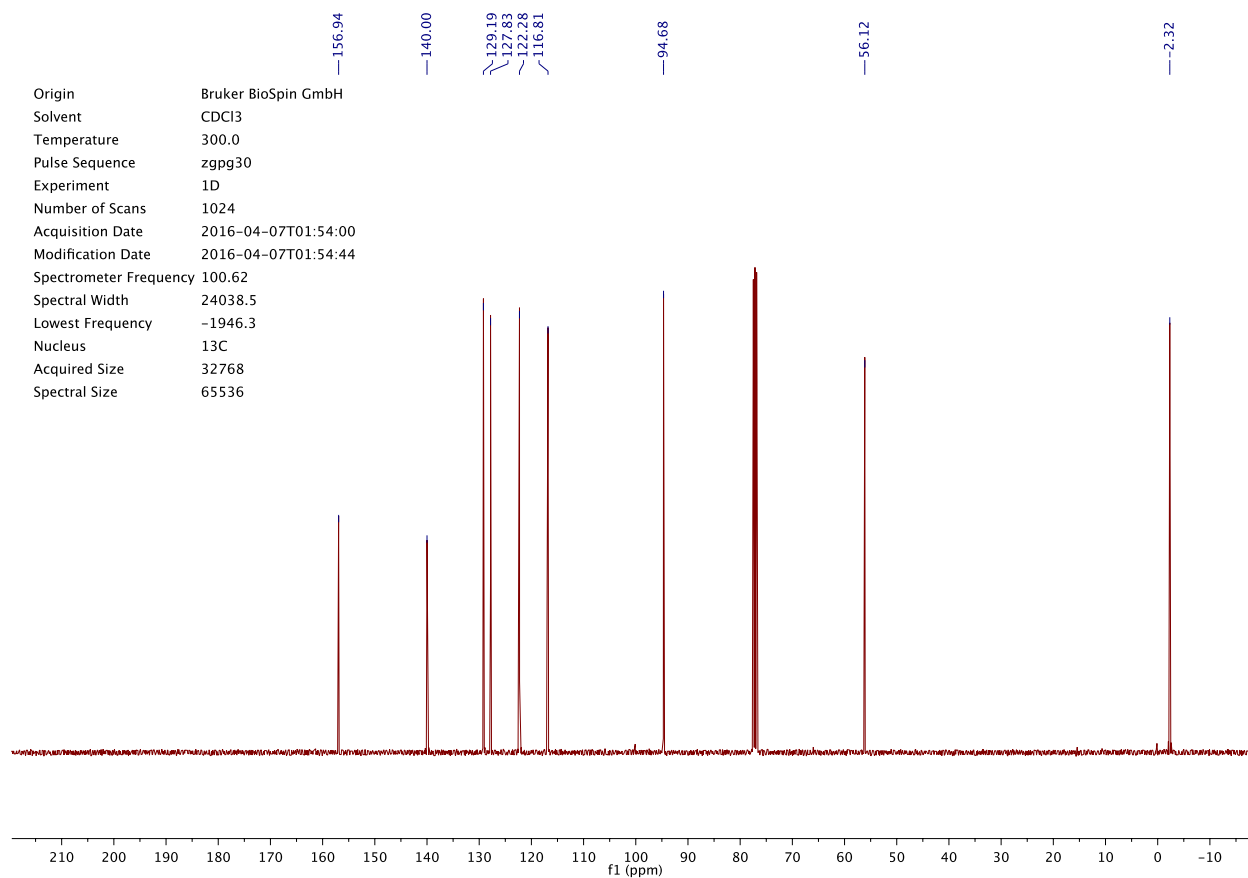
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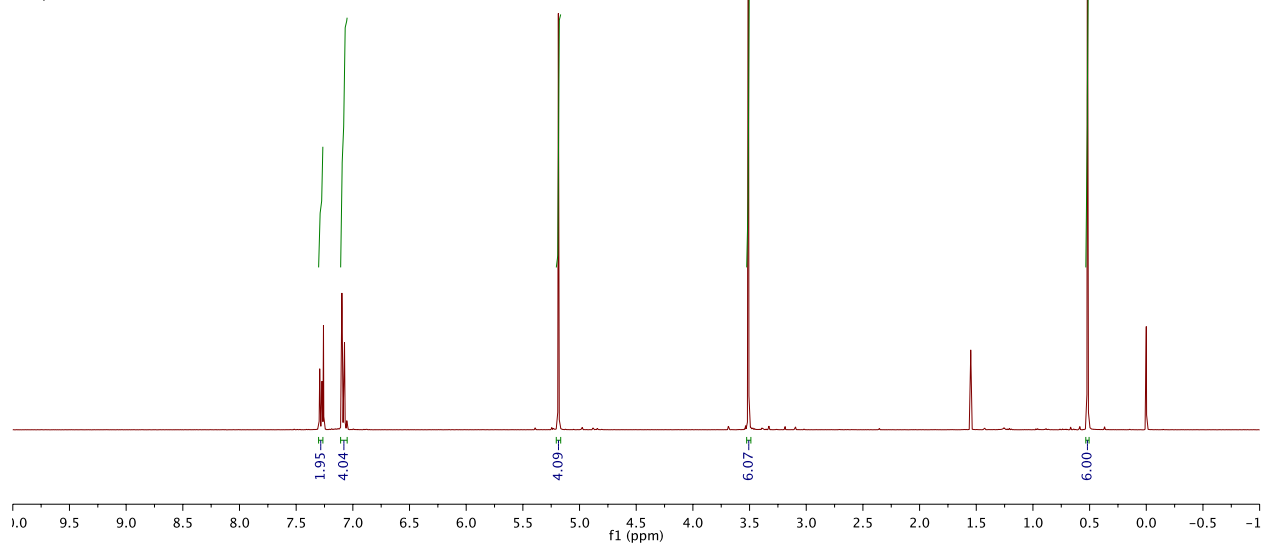
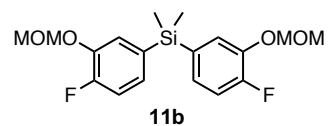
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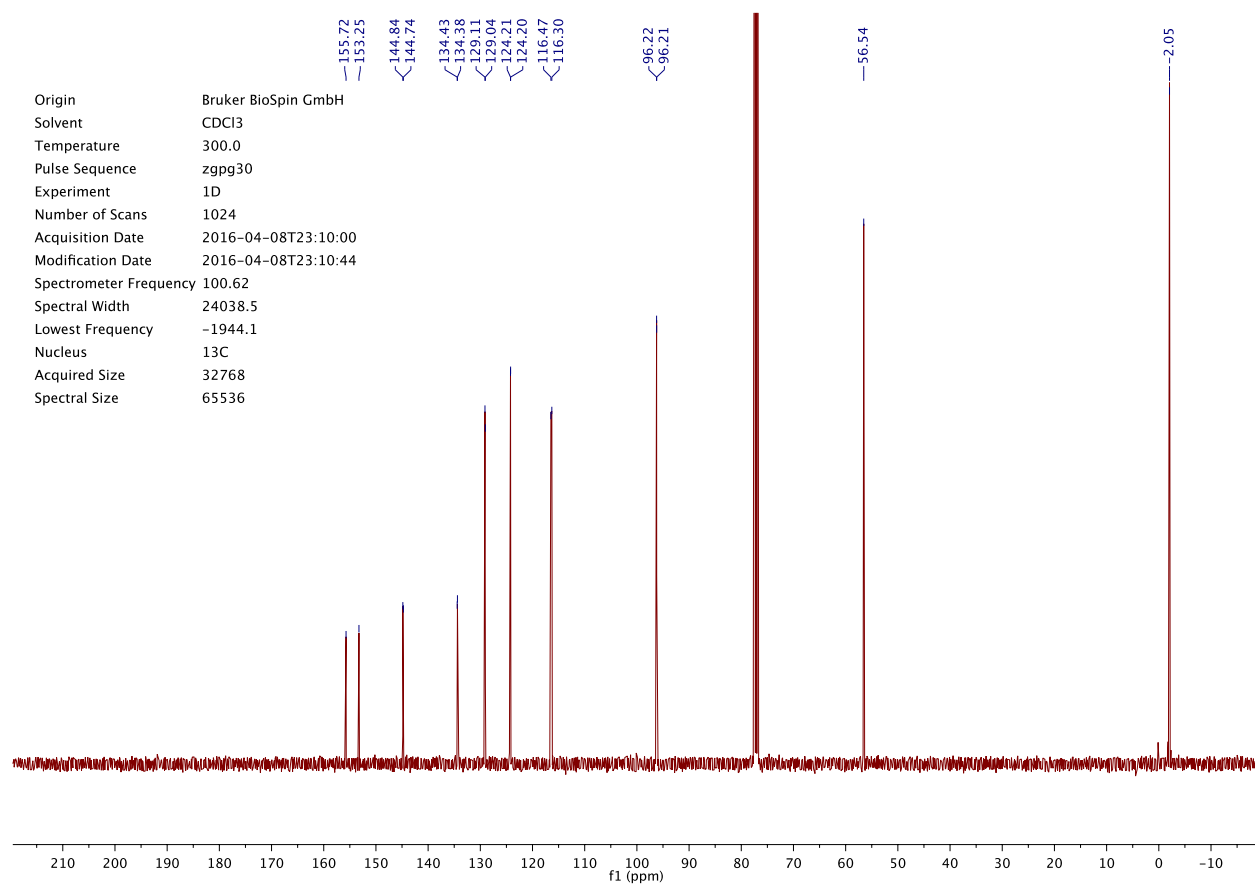
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 Lowest Frequency -1946.3
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



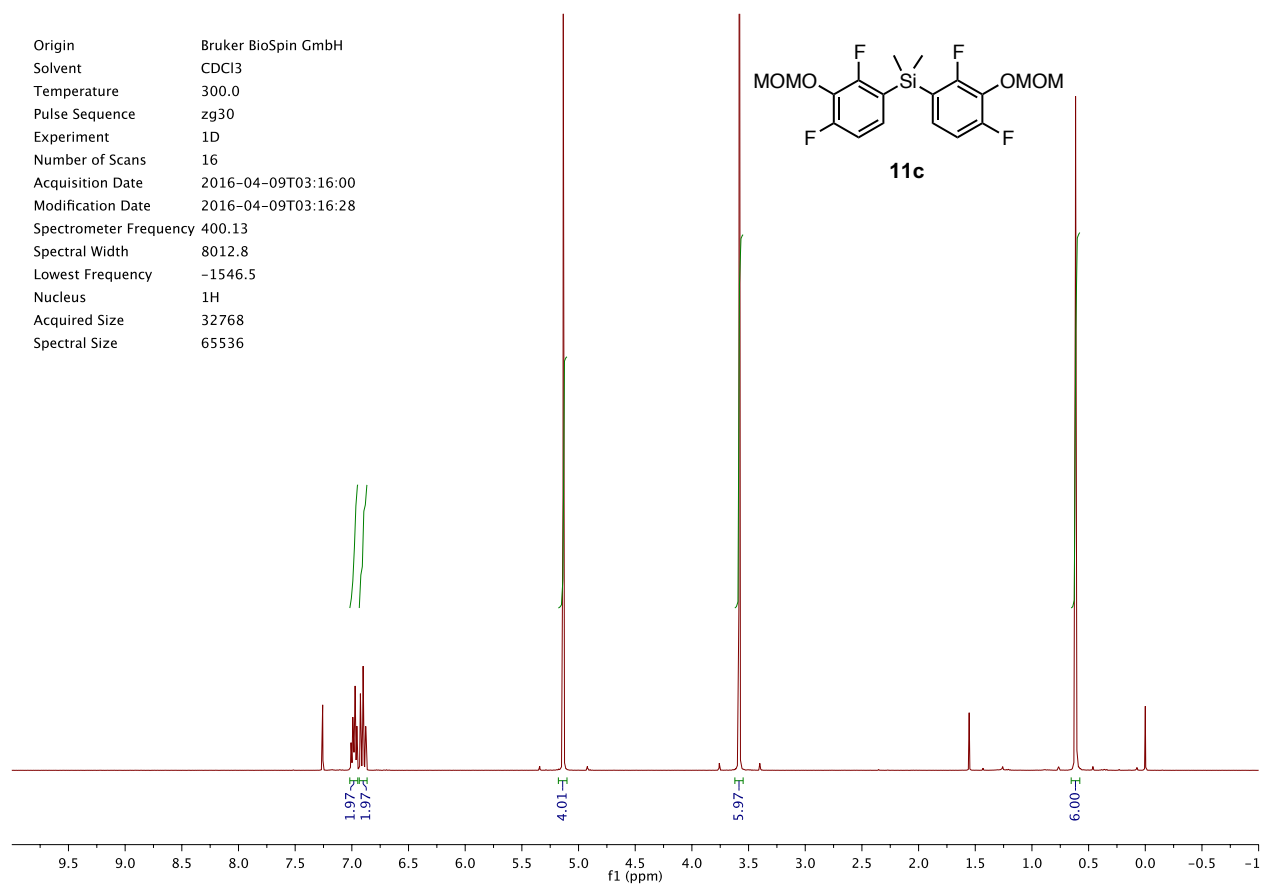
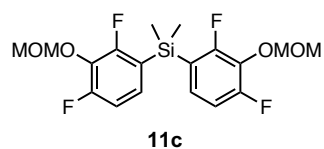
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 Temperature 295.6
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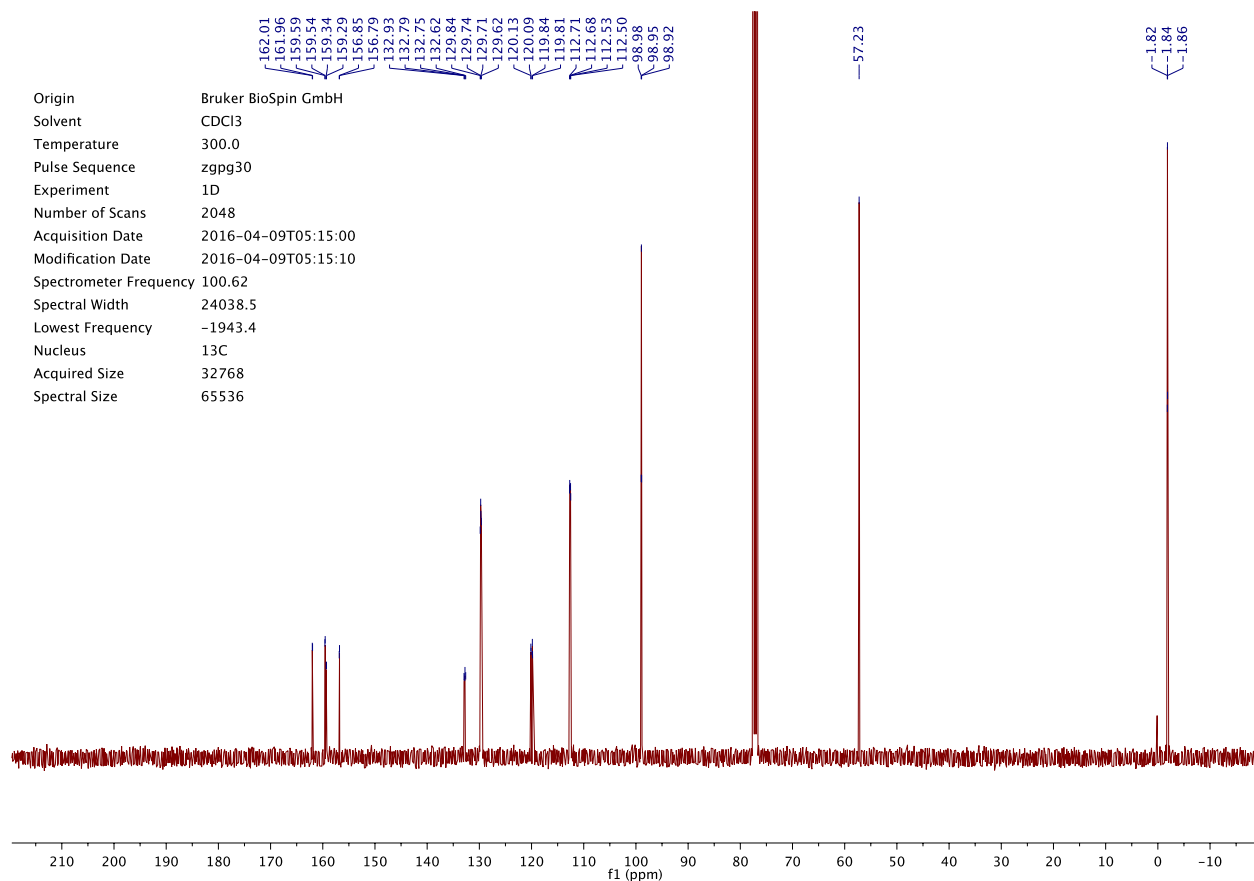
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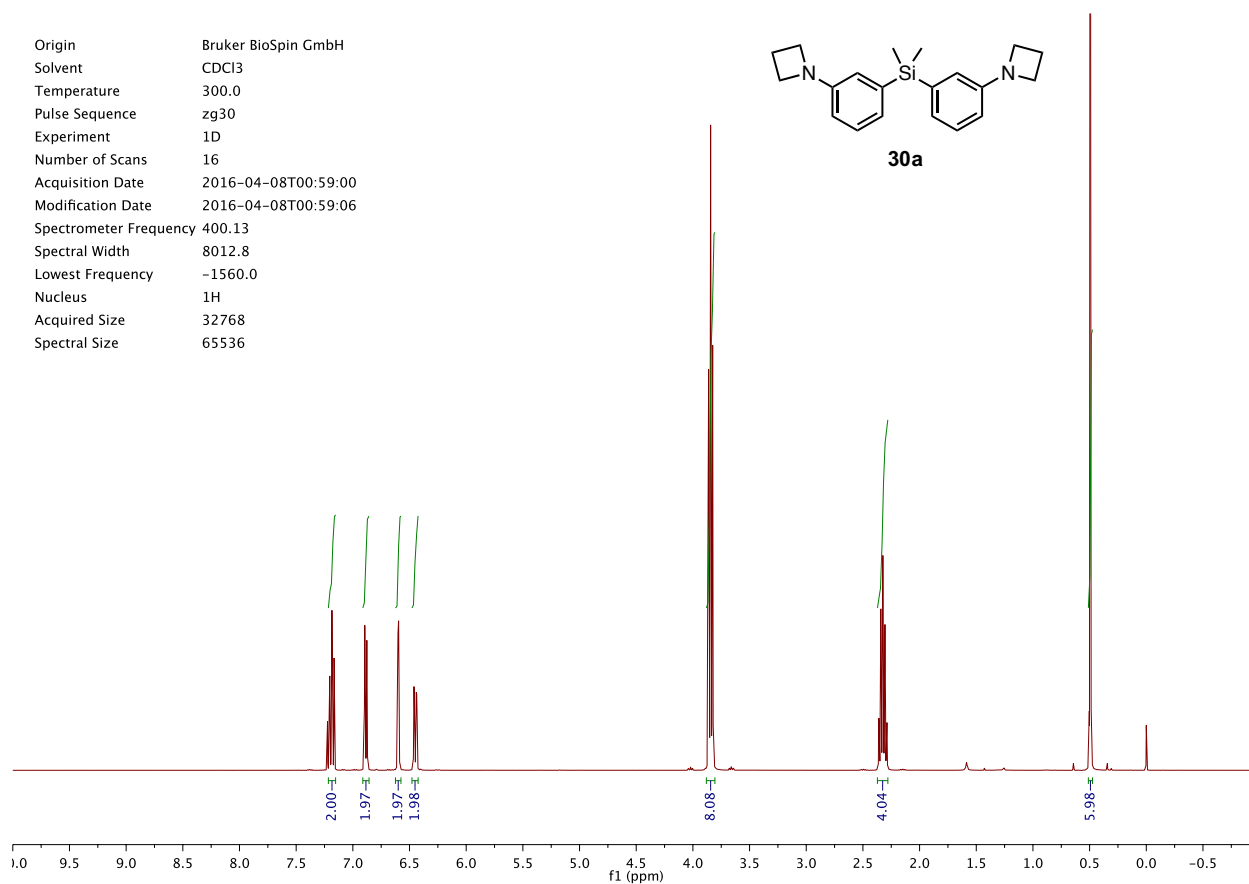
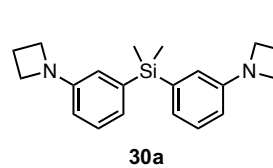
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 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



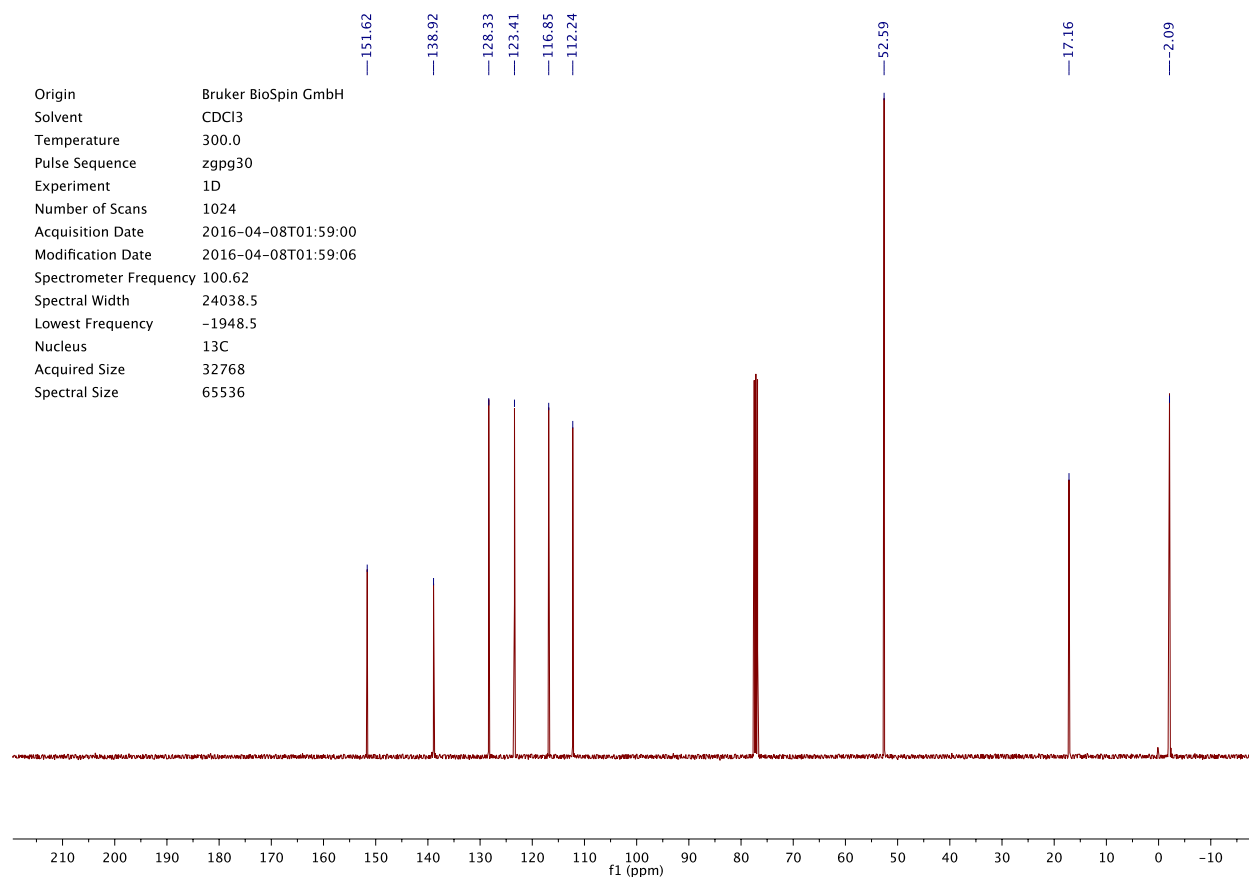
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 Nucleus ¹³C
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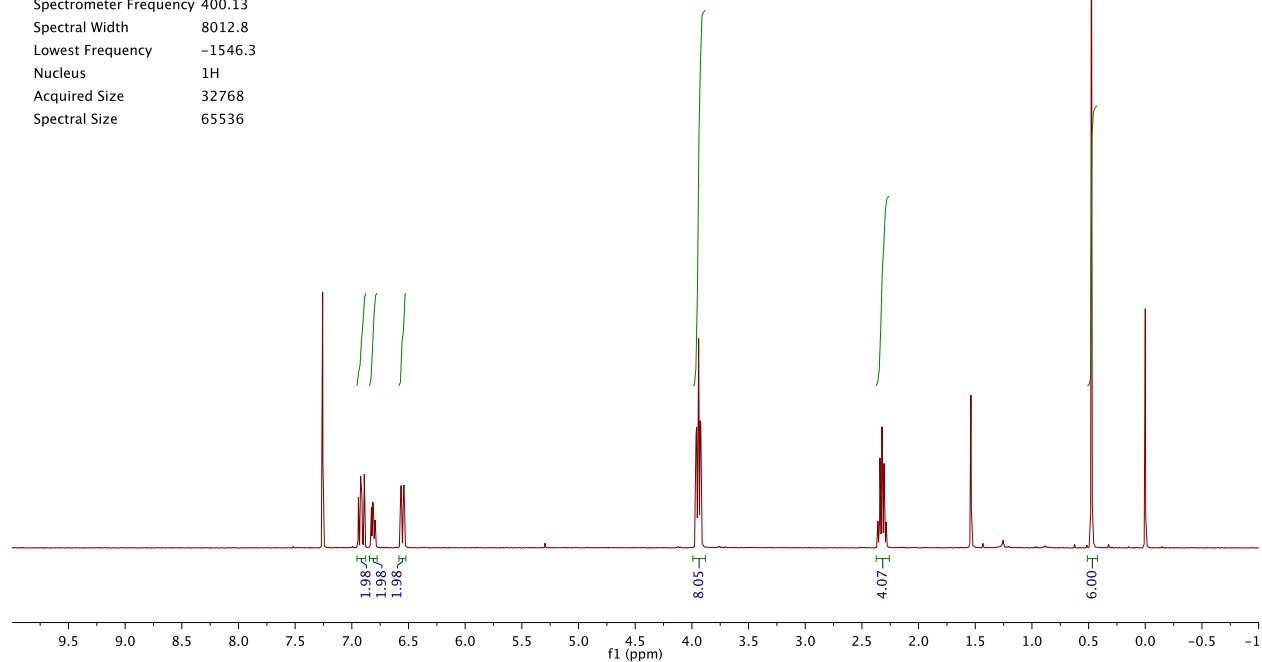
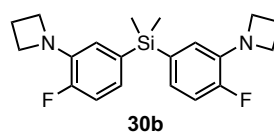
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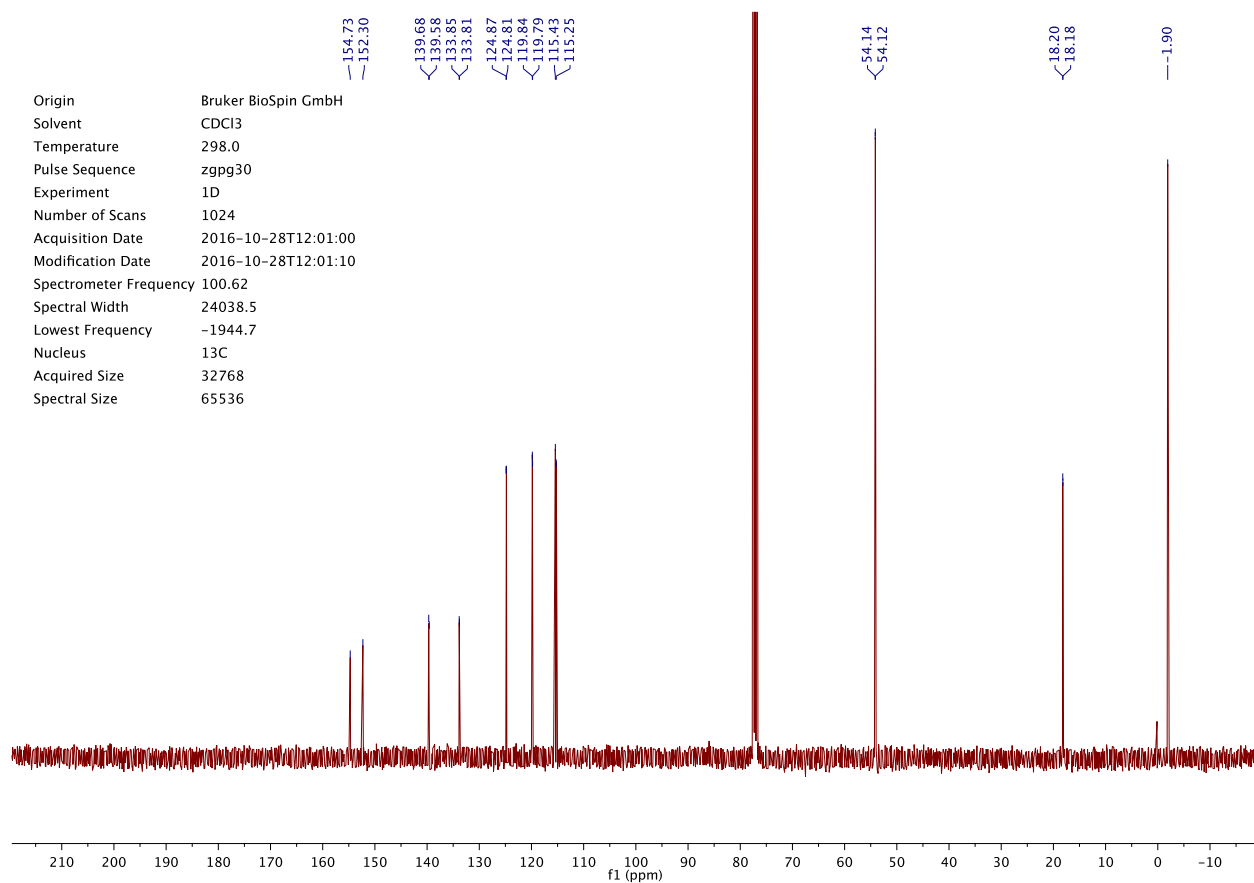
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 Spectral Size 65536



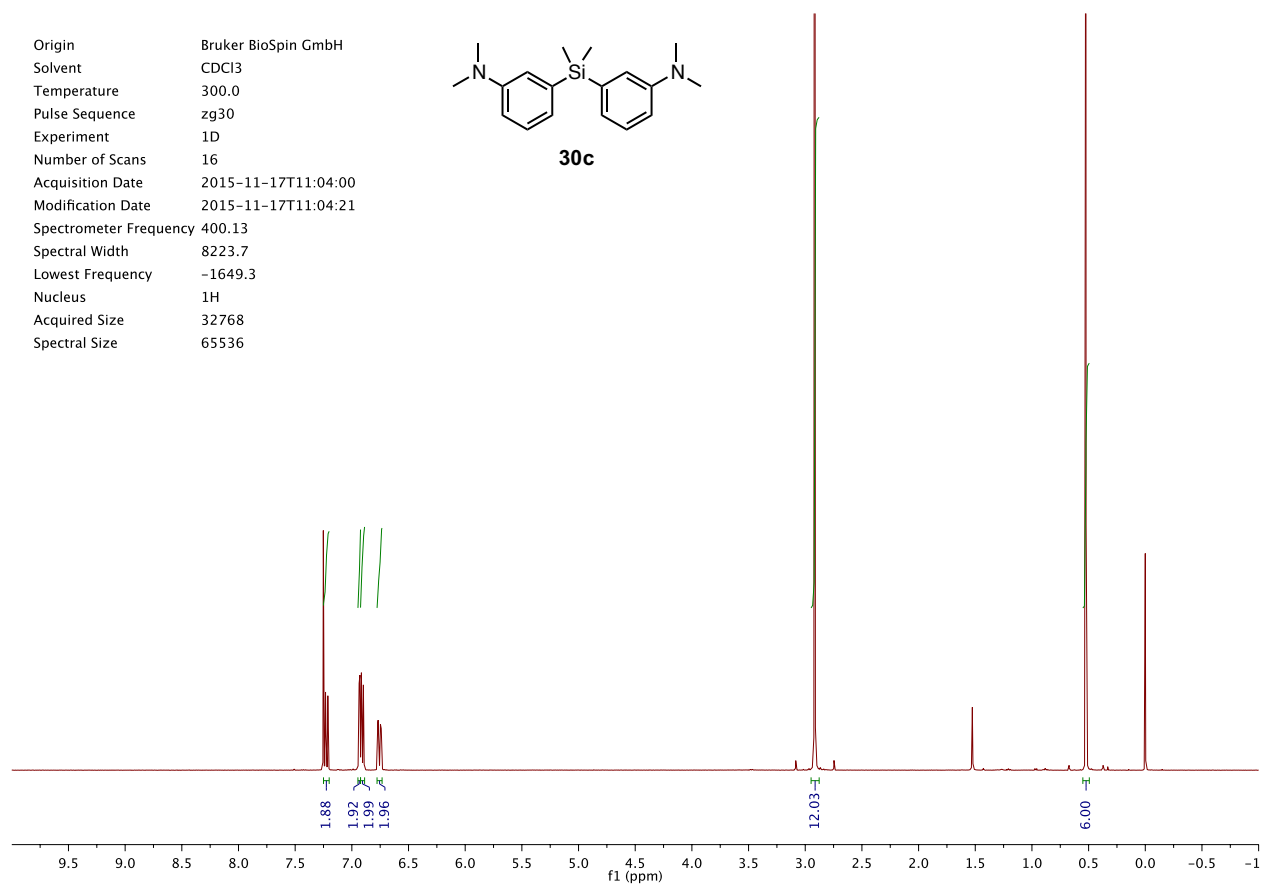
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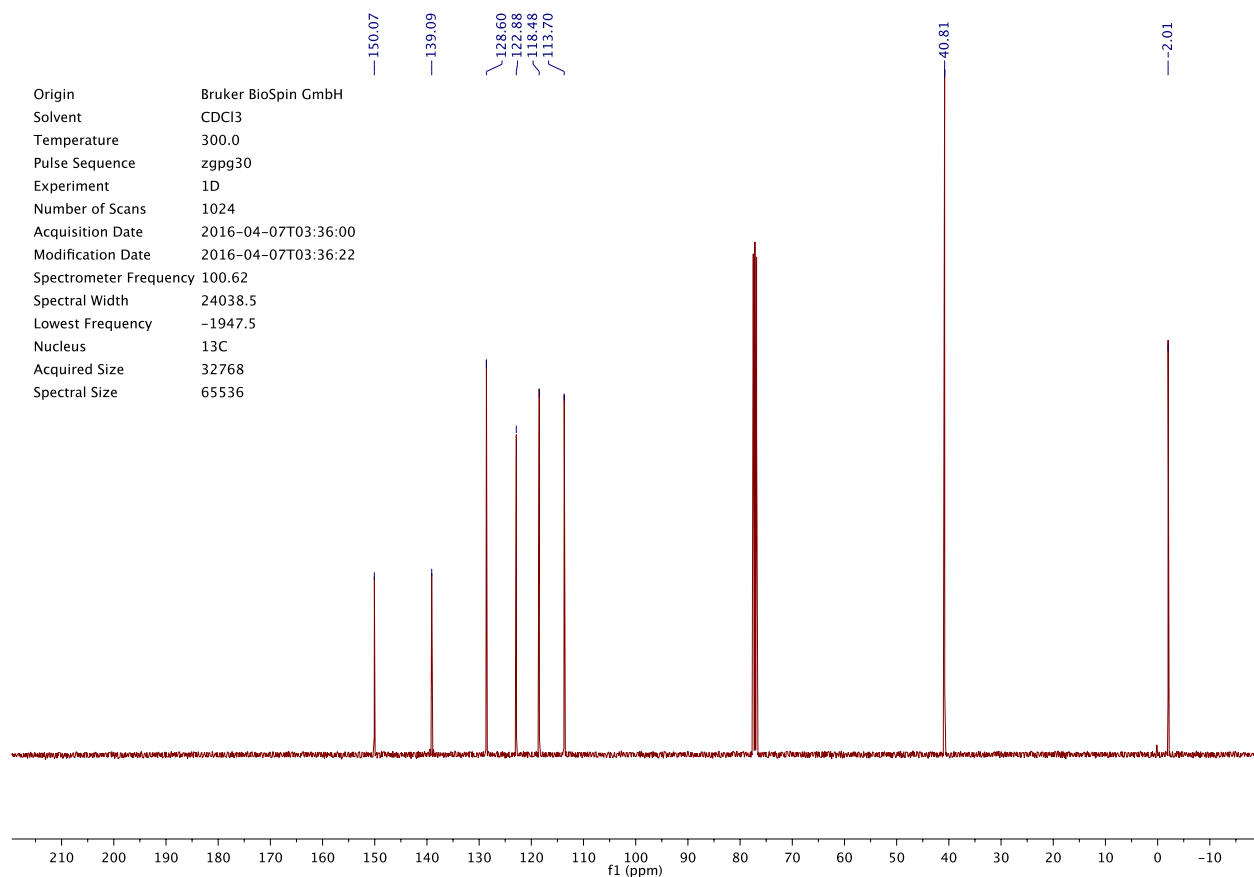
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 Spectral Size 65536



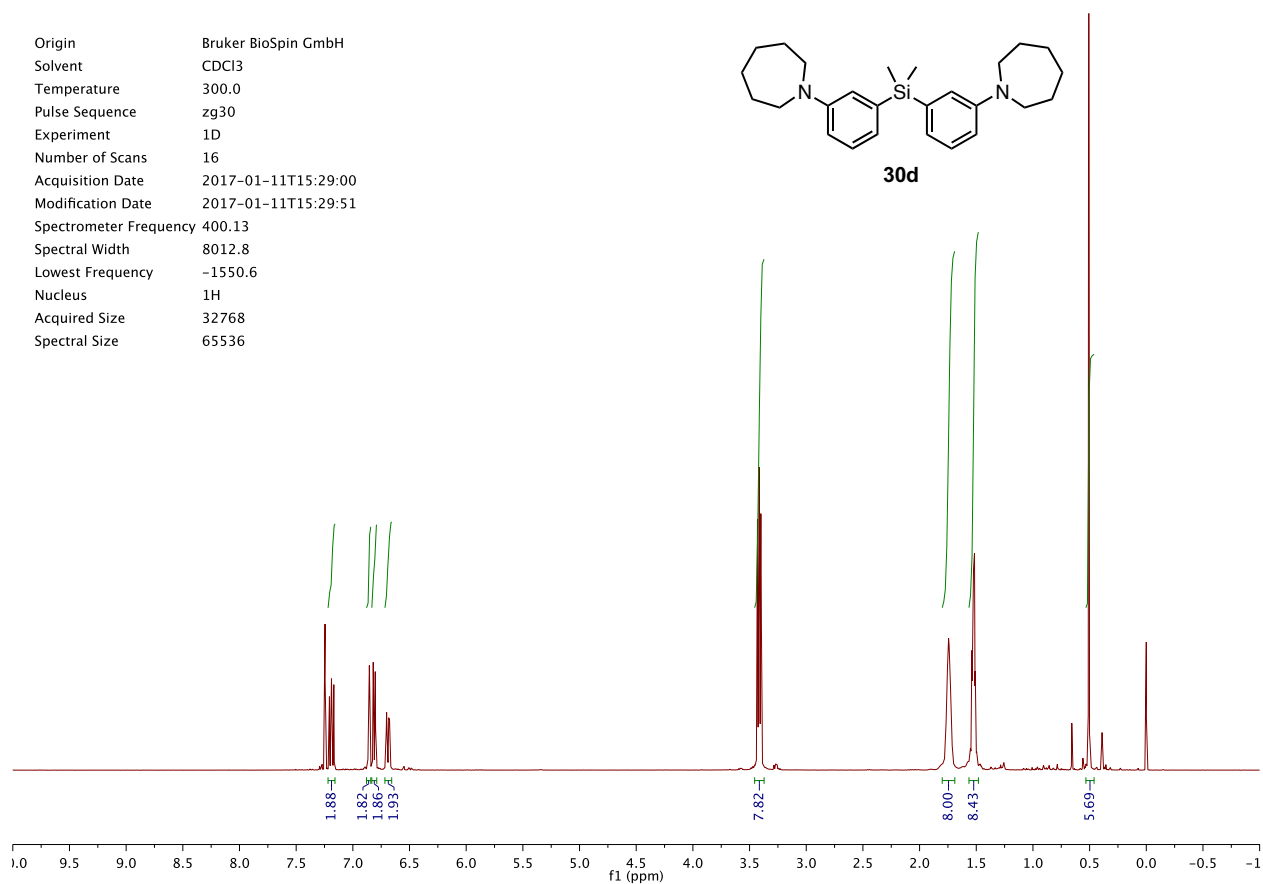
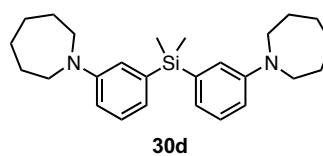
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 Spectral Size 65536



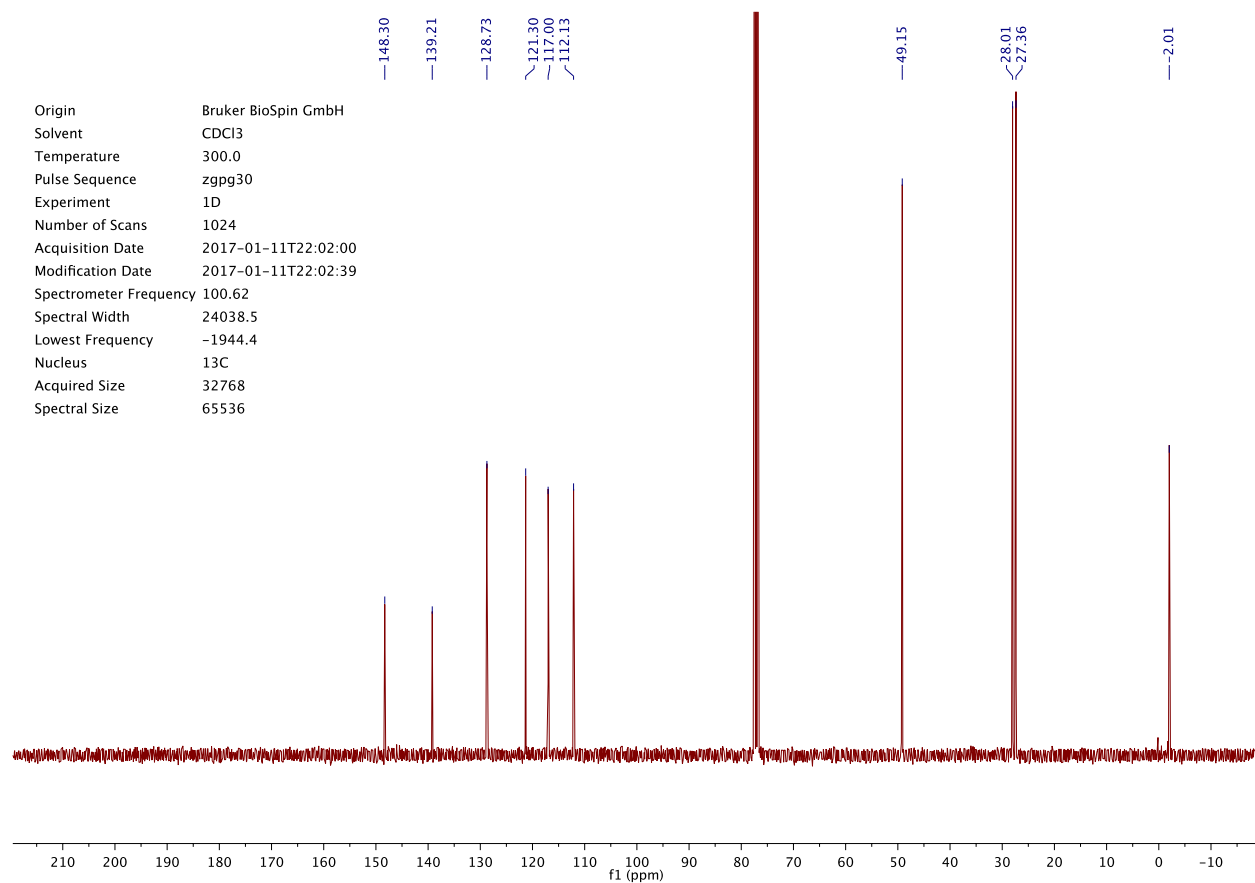
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 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



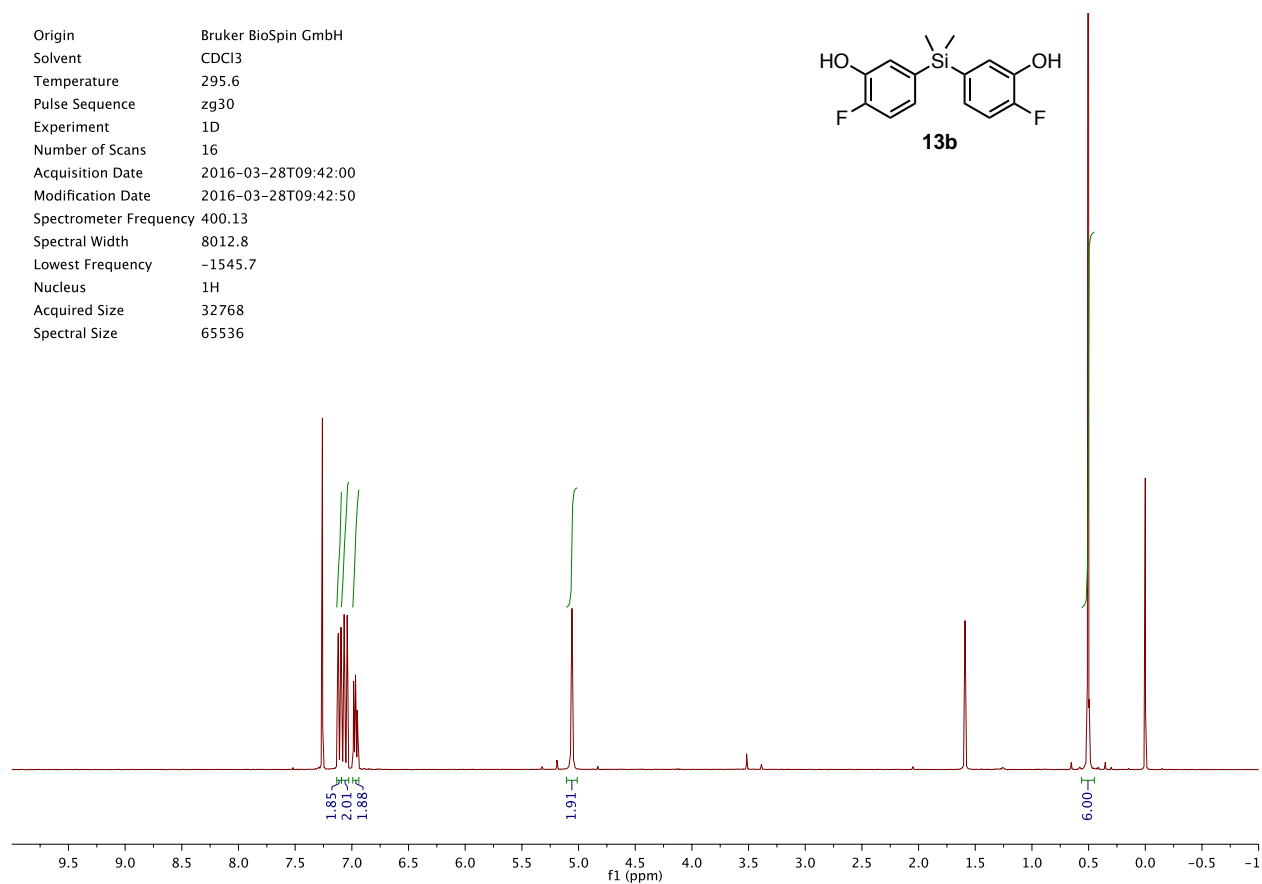
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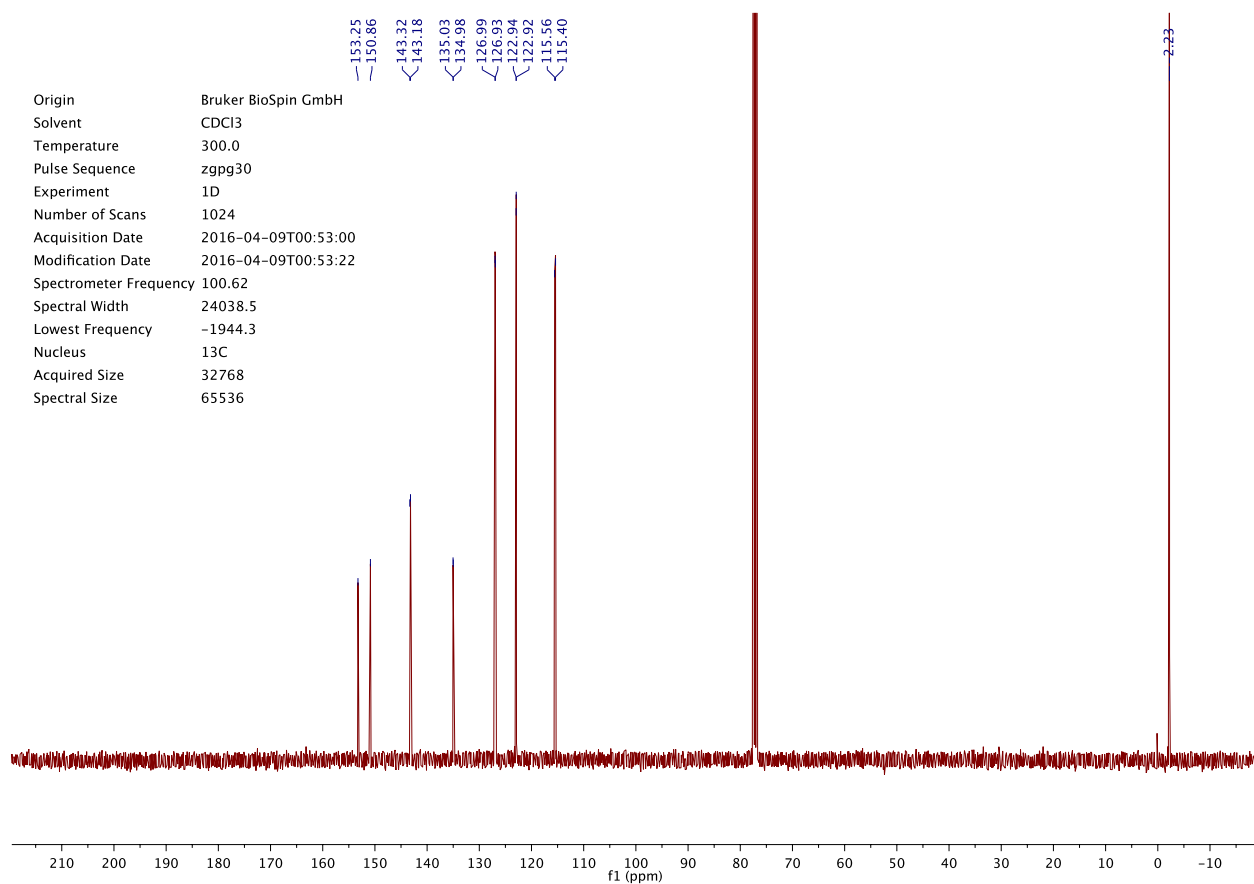
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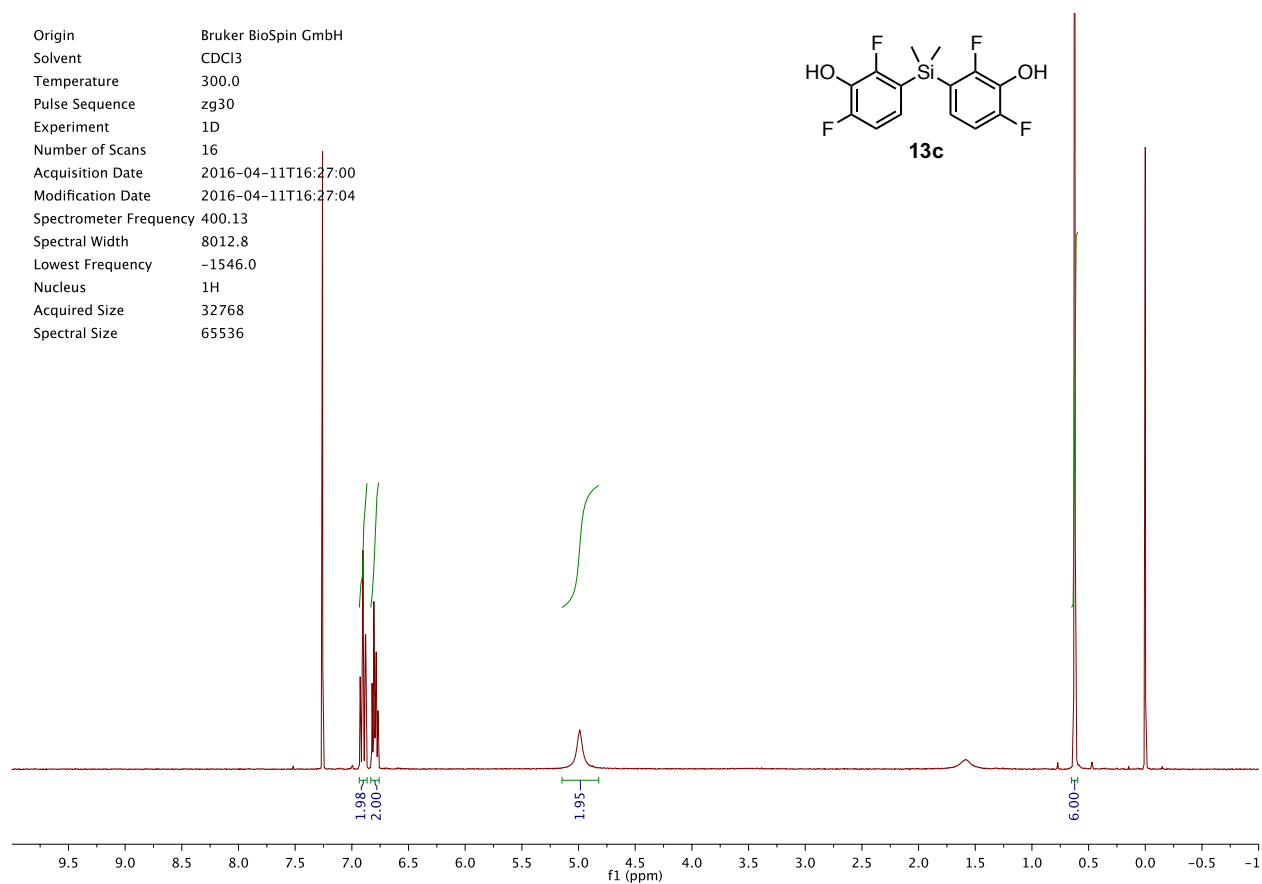
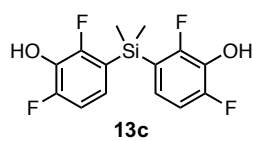
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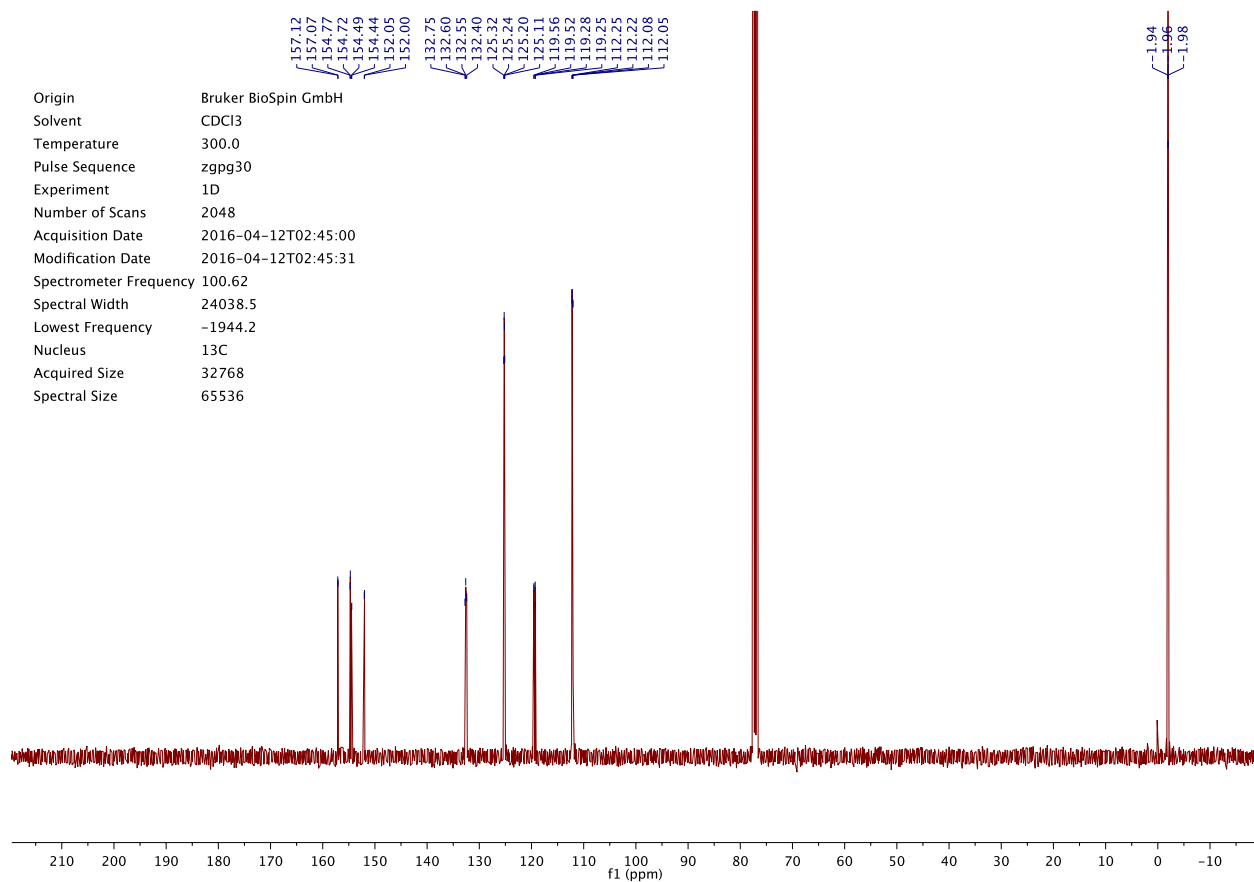
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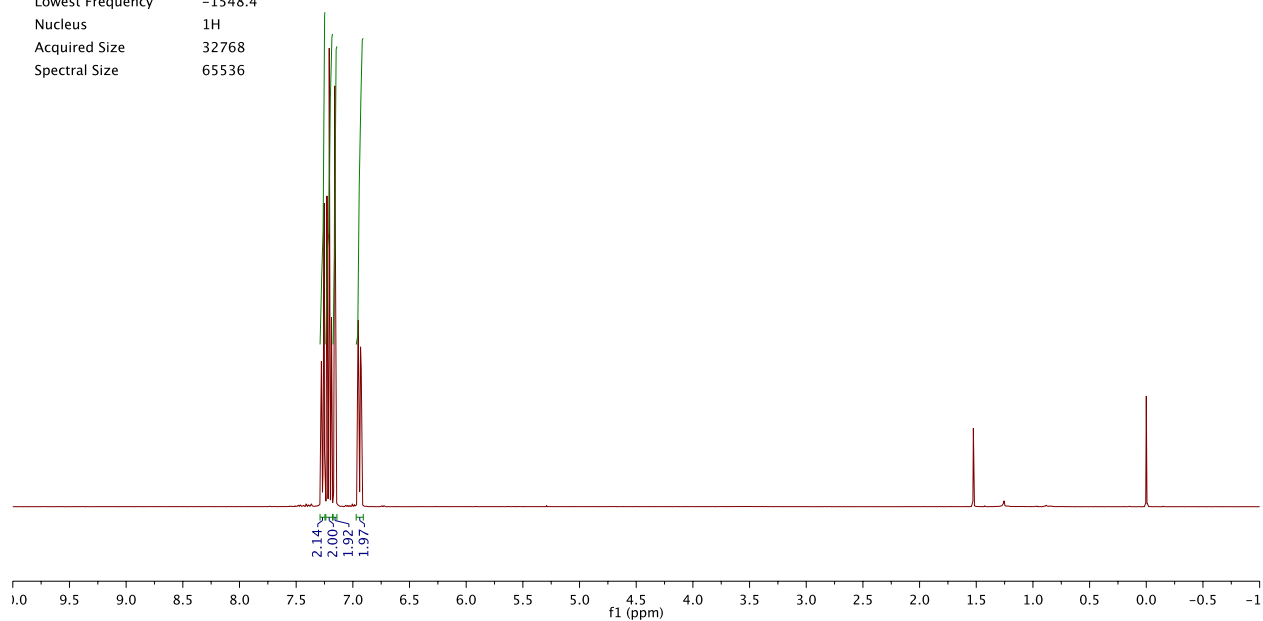
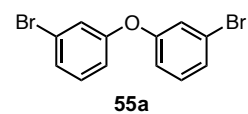
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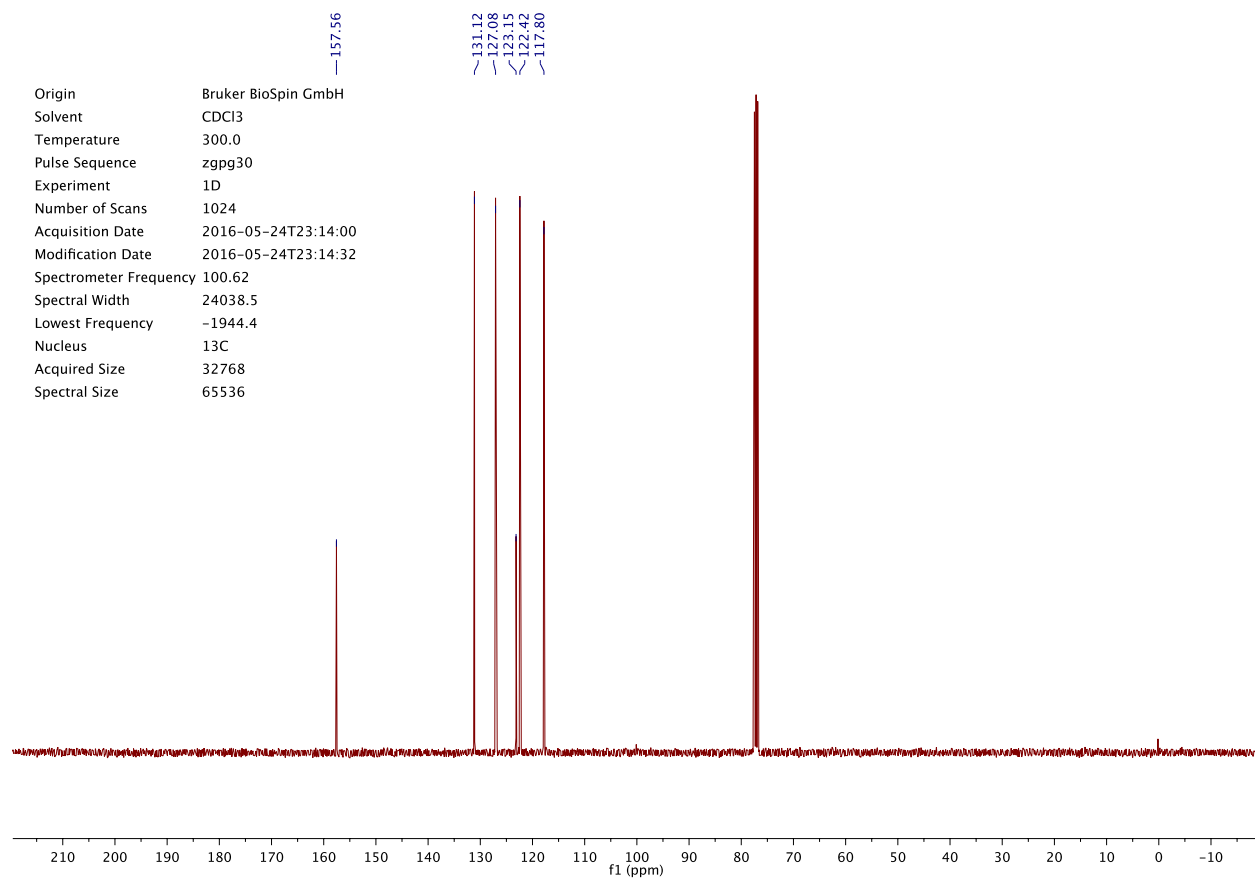
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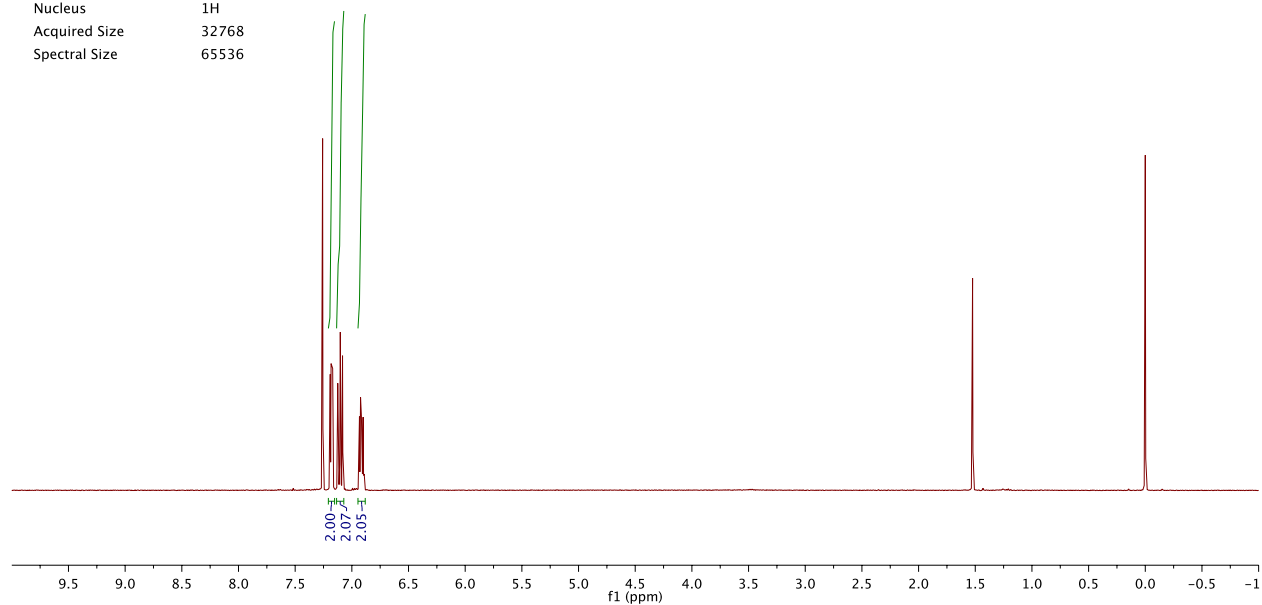
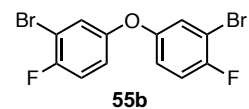
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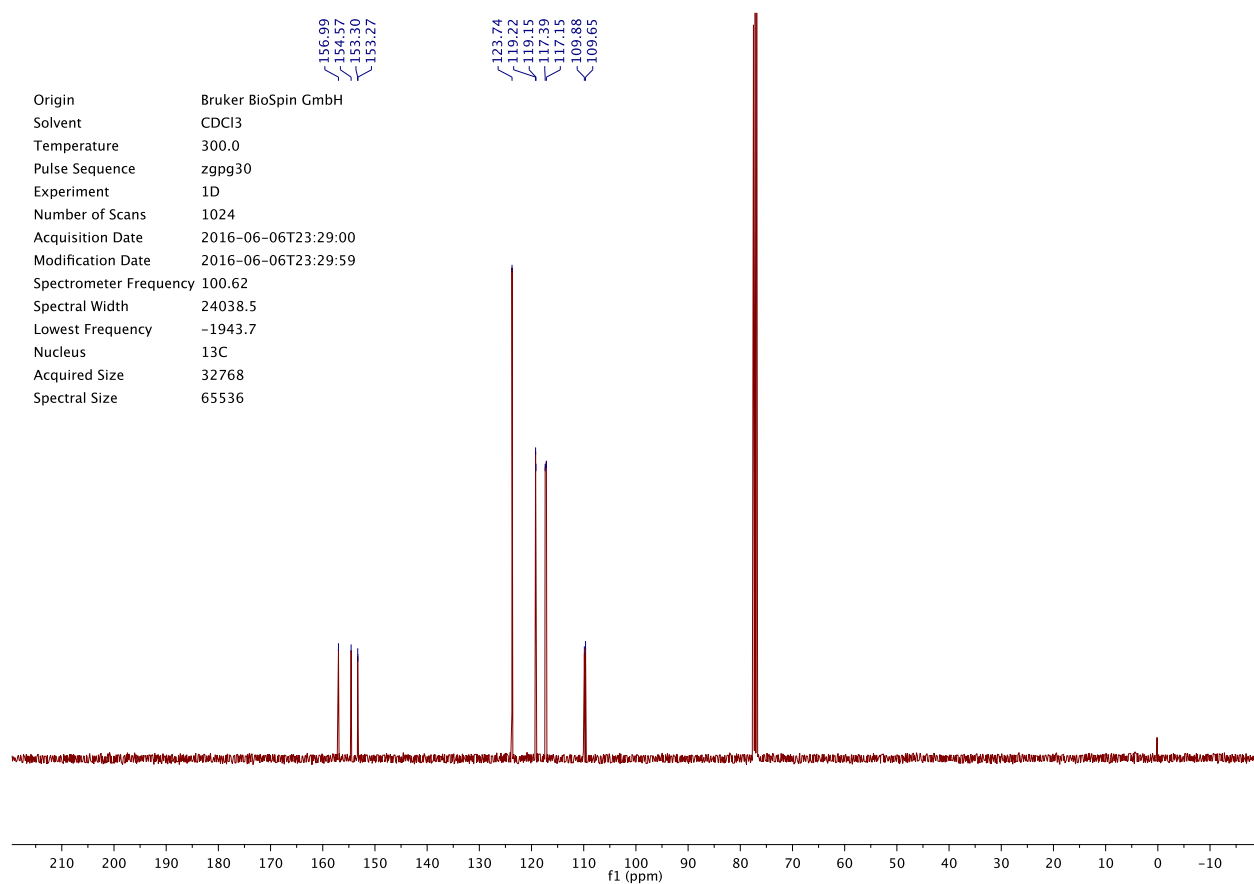
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 Nucleus ¹³C
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 Spectral Size 65536



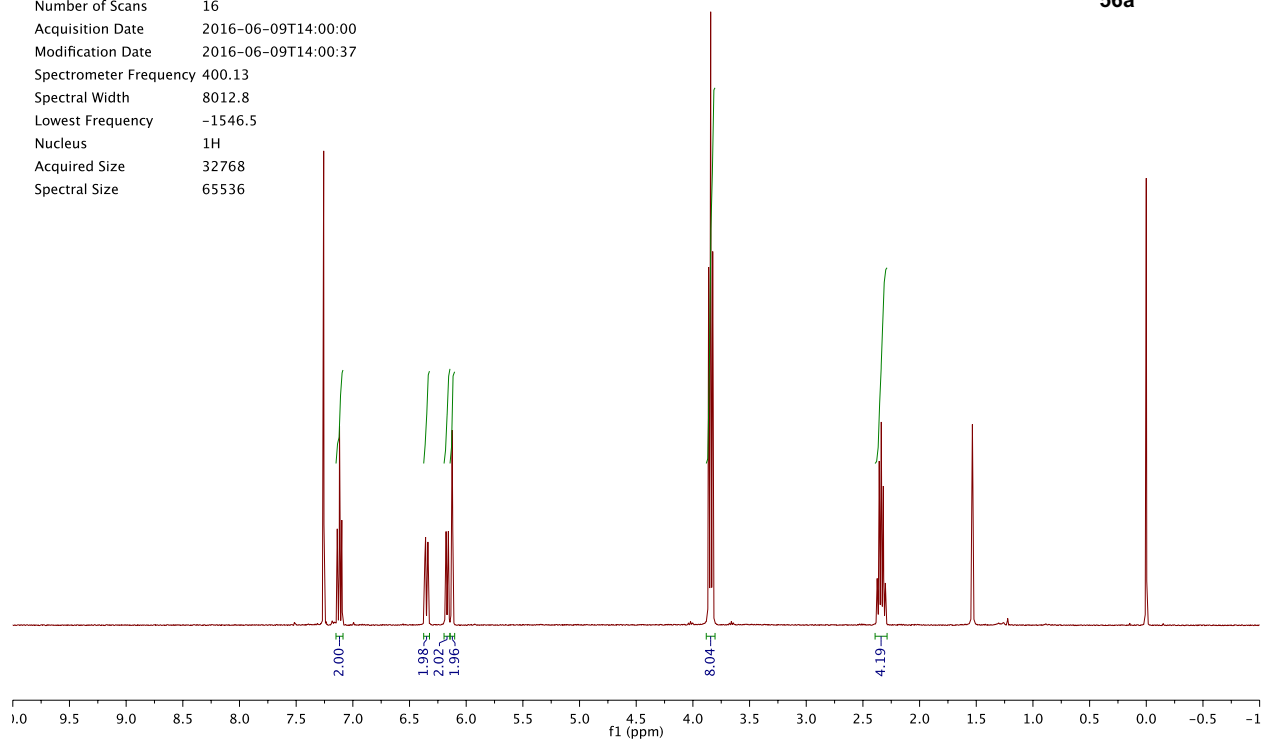
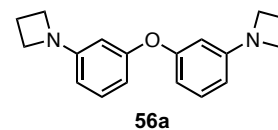
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 Nucleus ¹H
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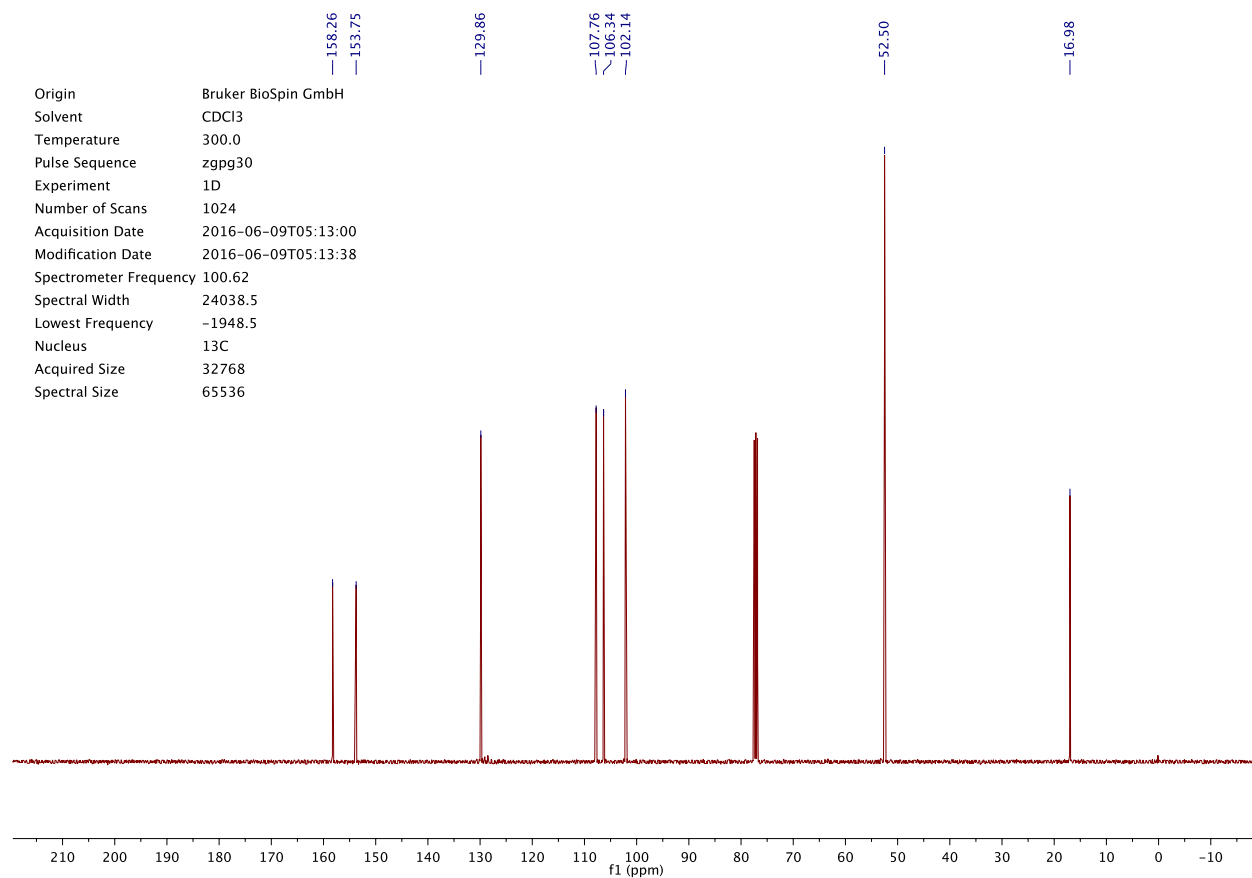
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 Acquired Size 32768
 Spectral Size 65536



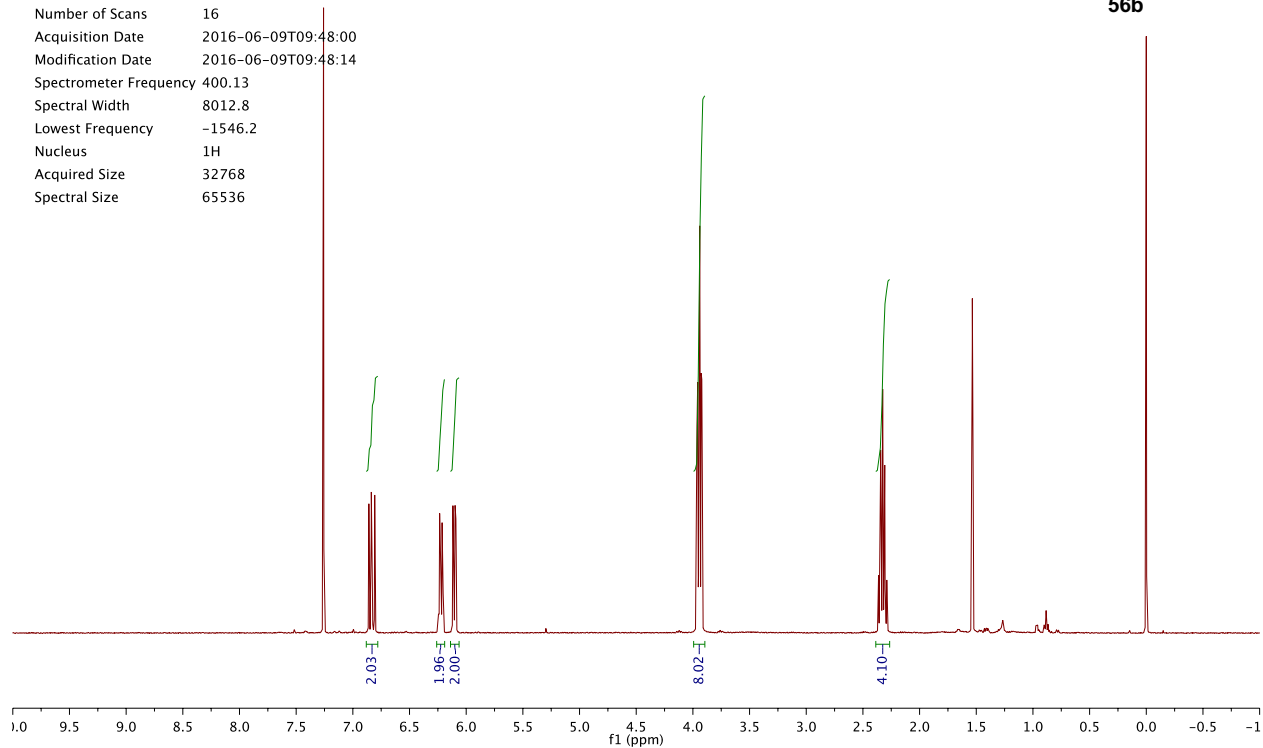
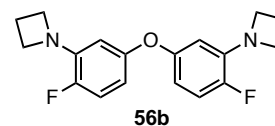
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 Spectral Size 65536



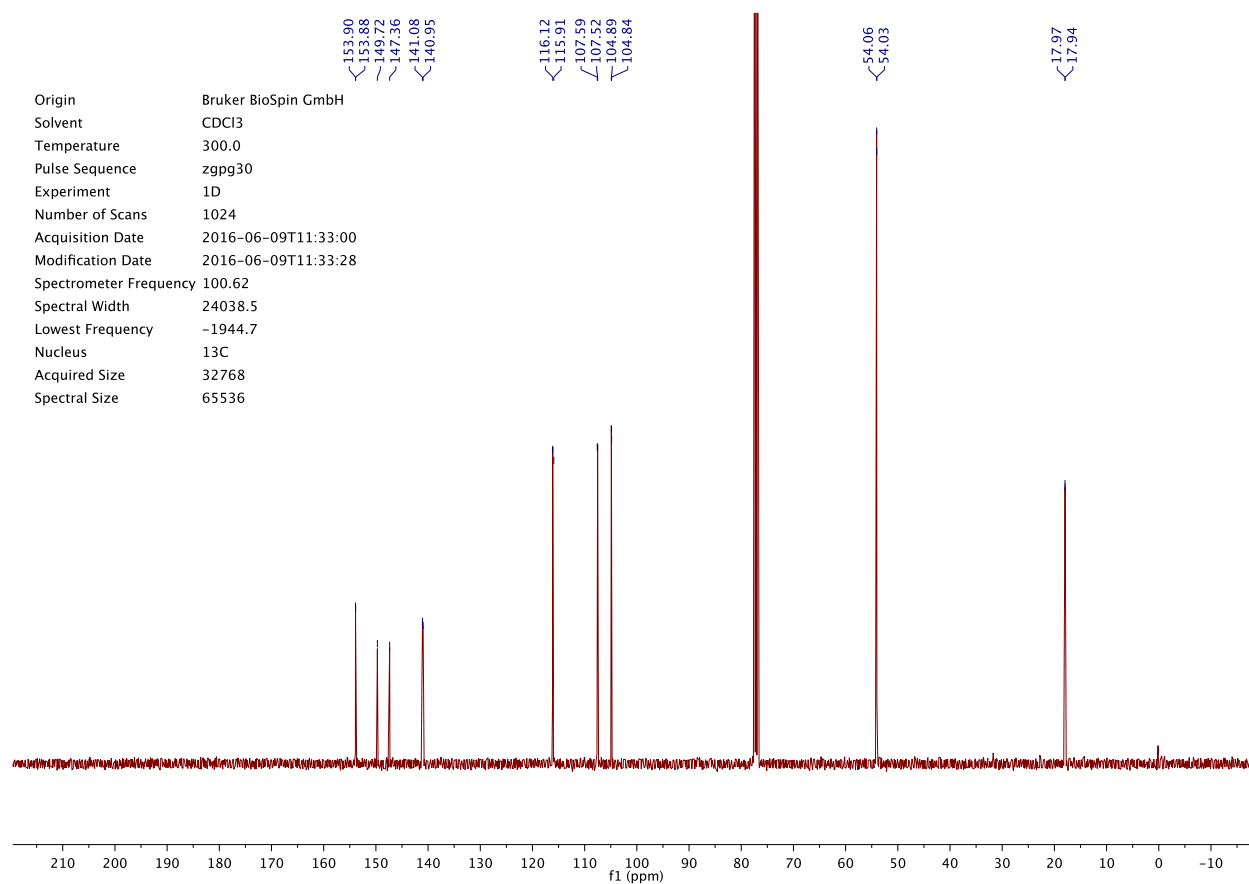
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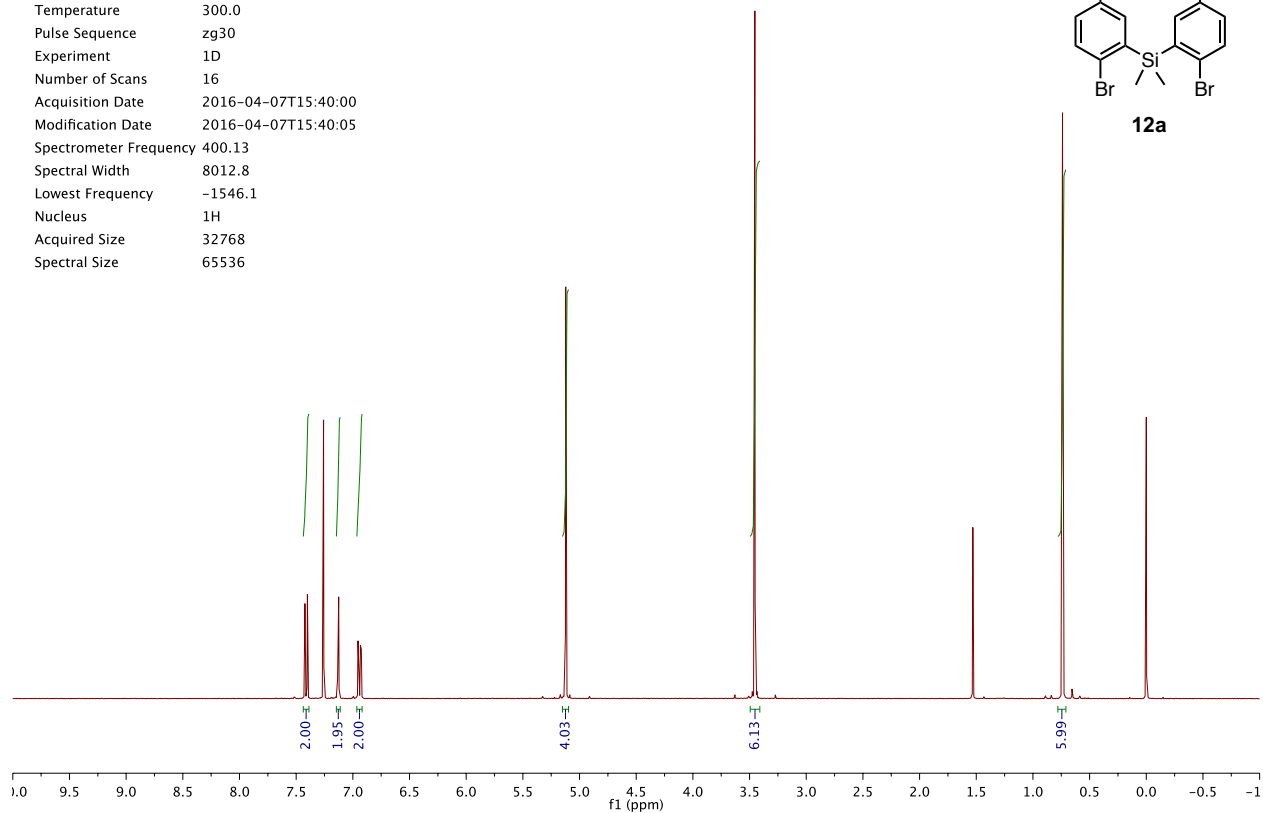
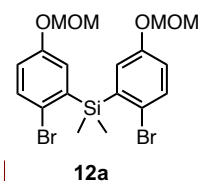
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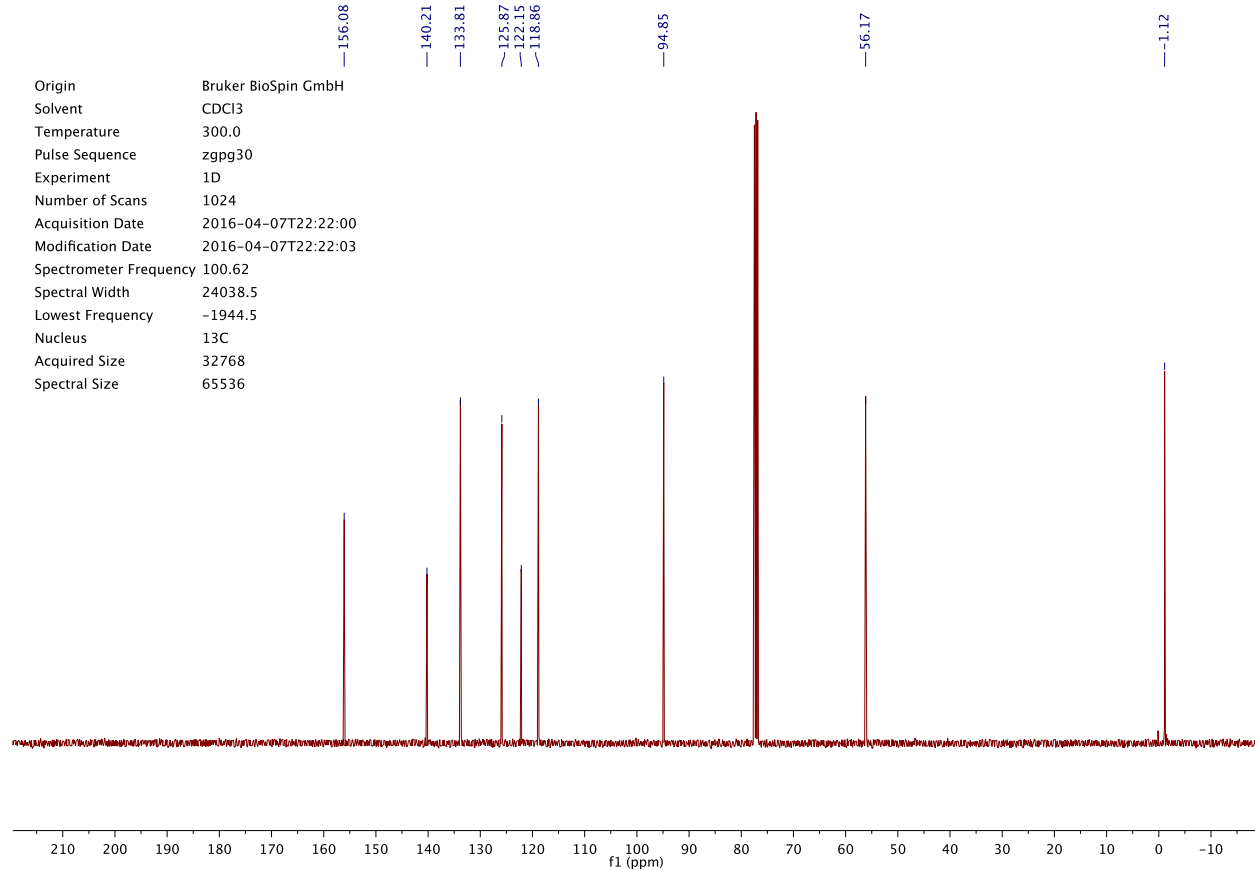
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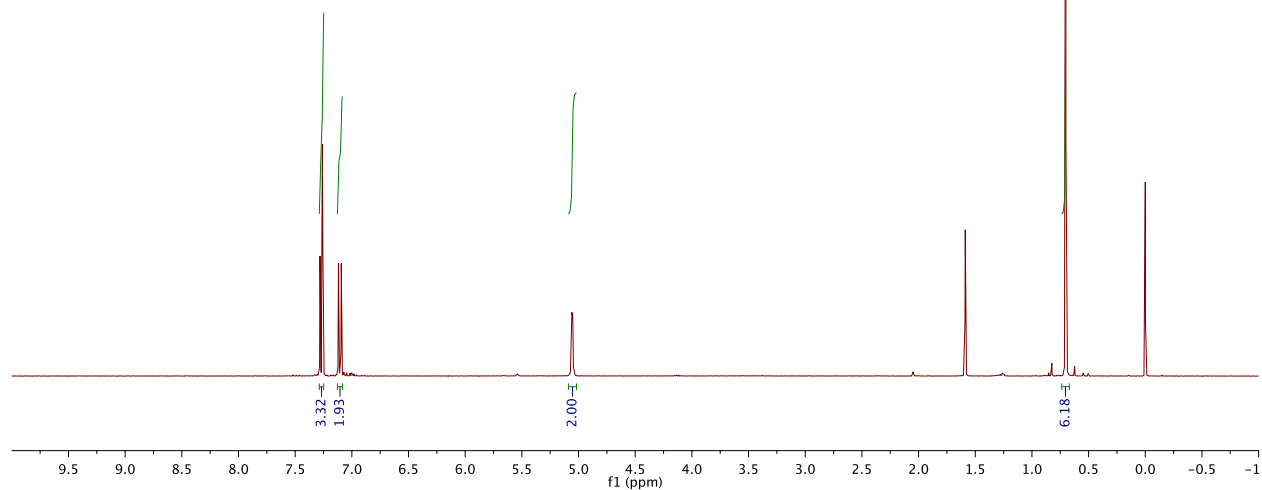
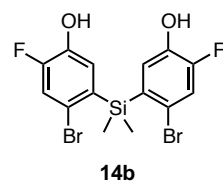
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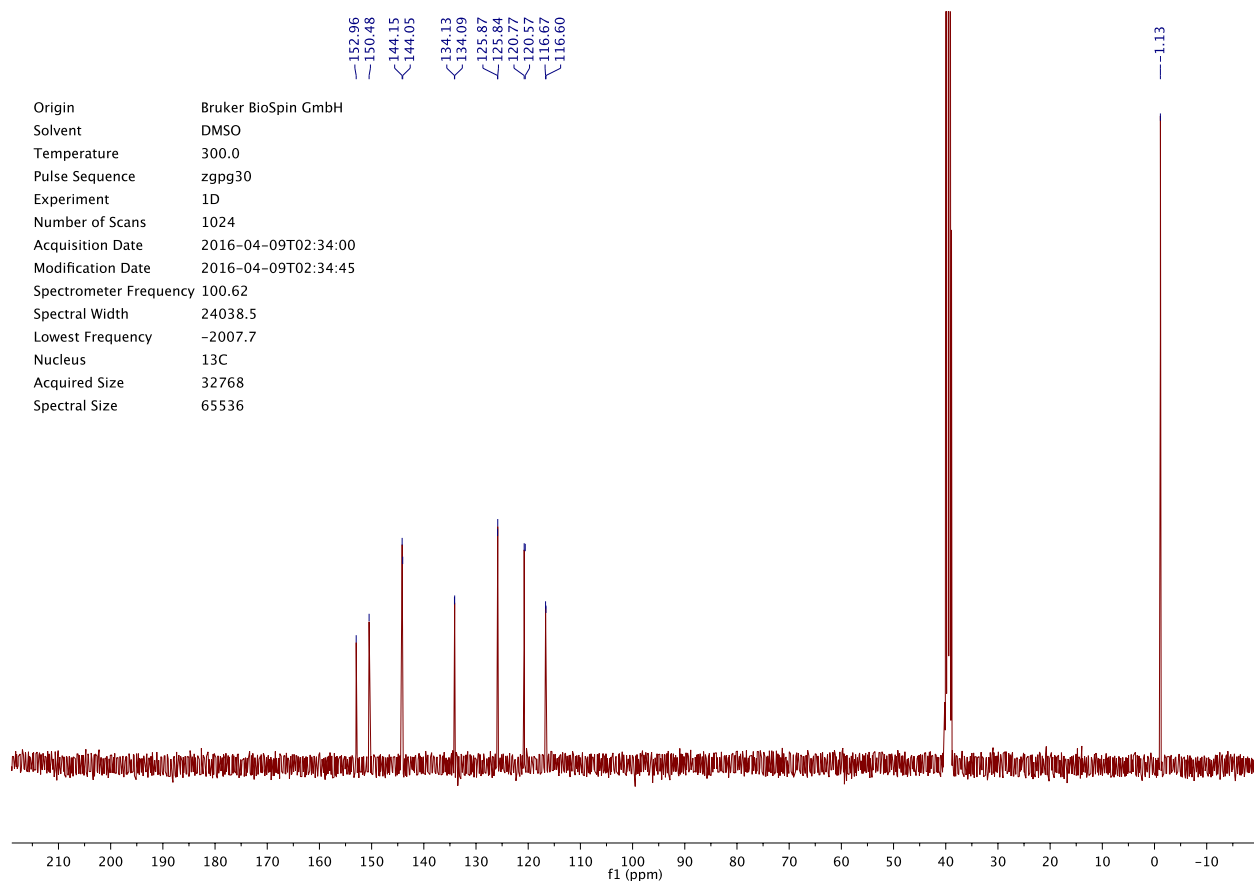
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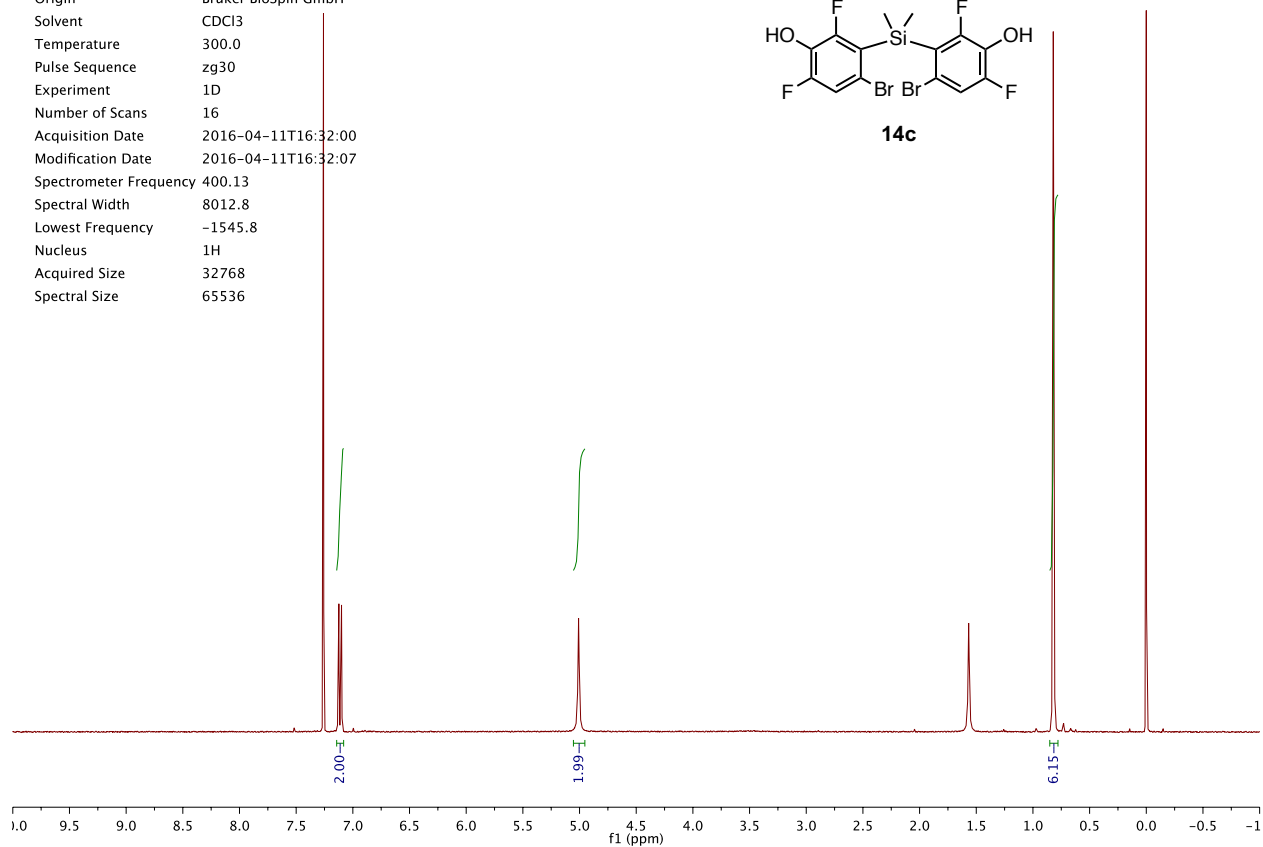
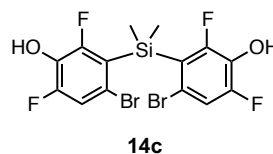
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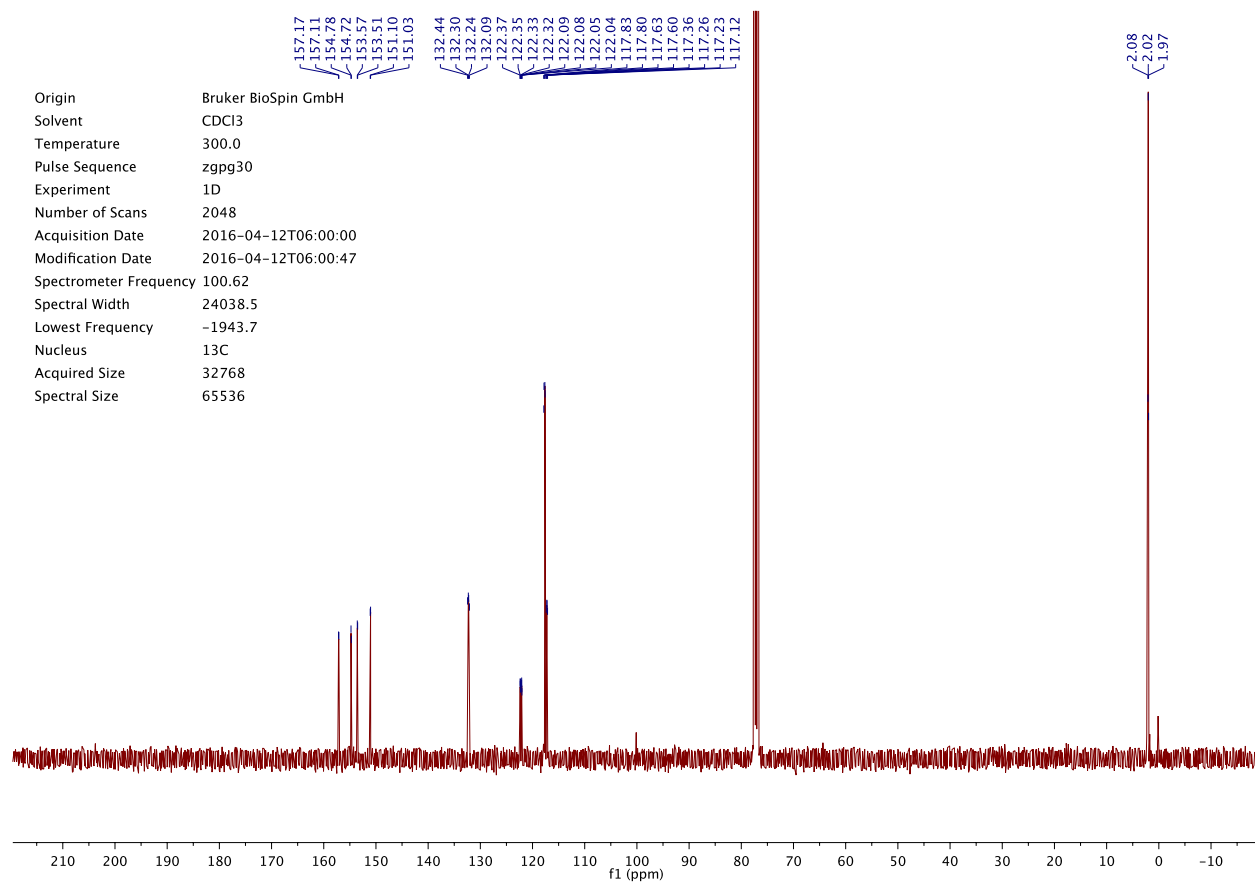
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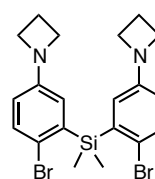
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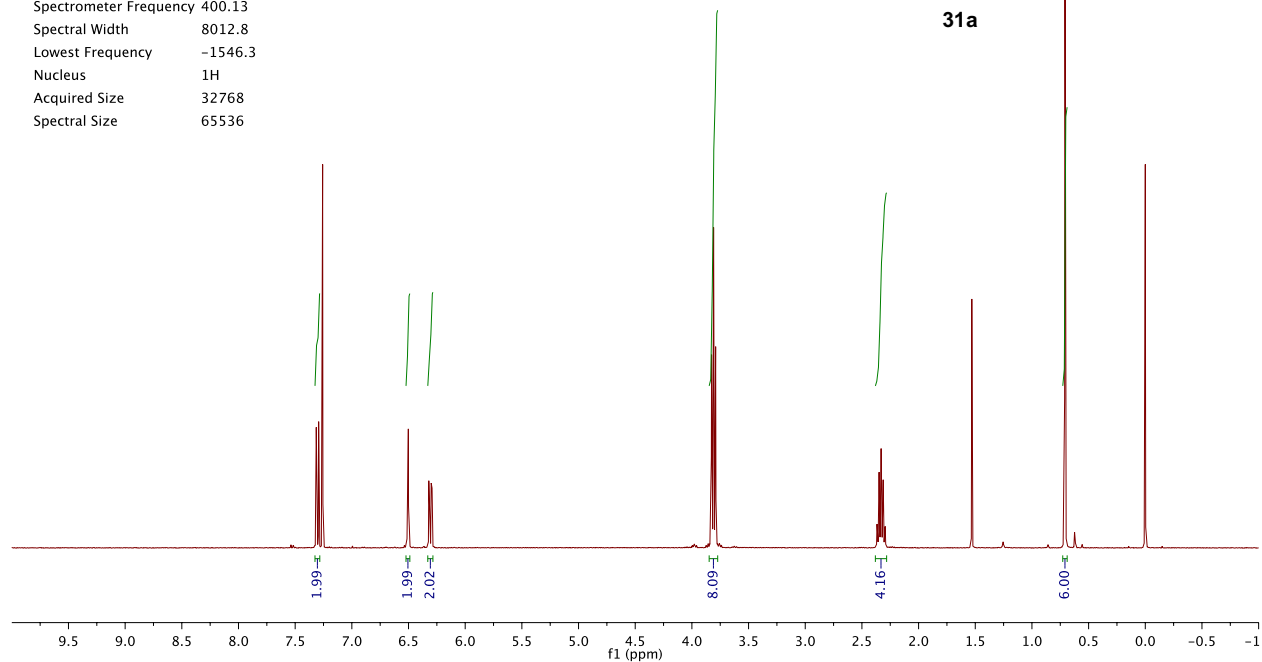
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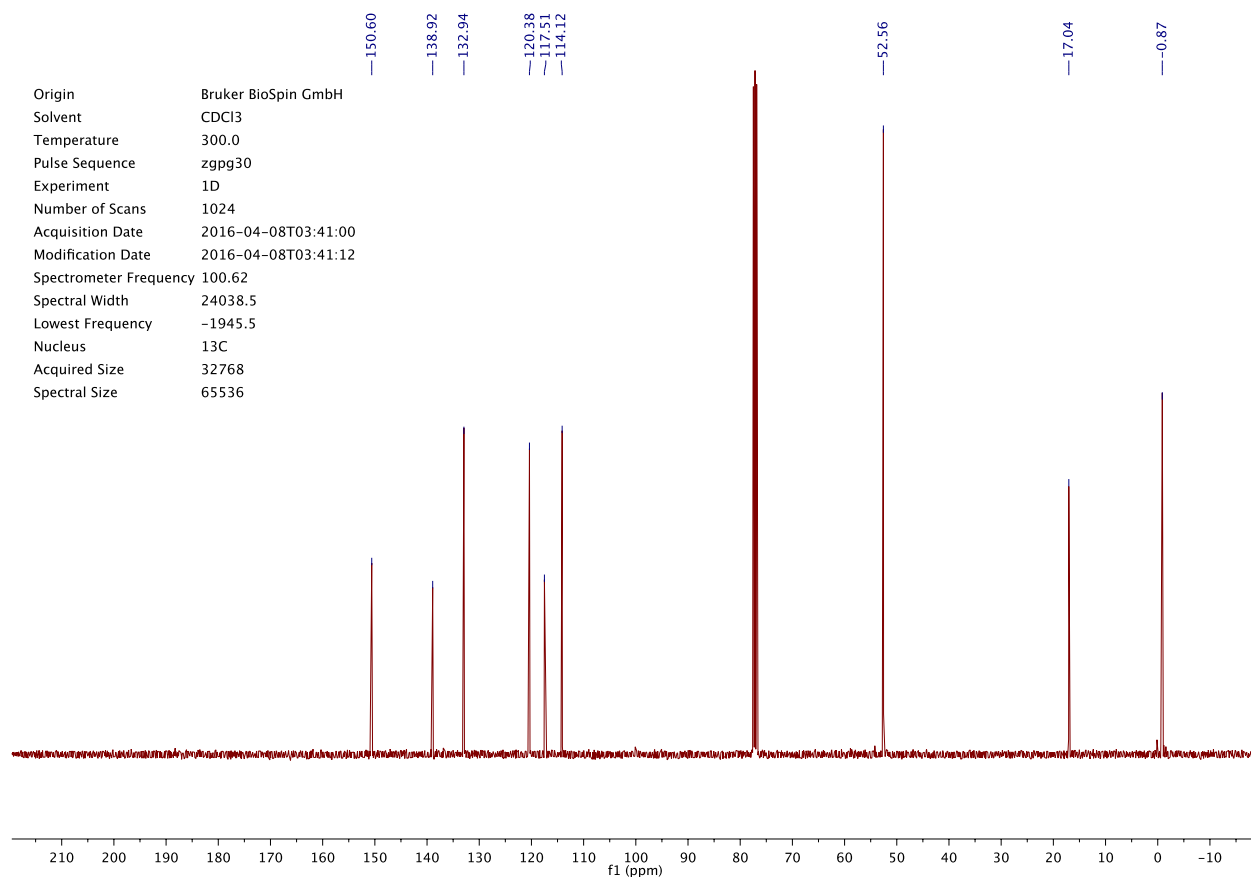
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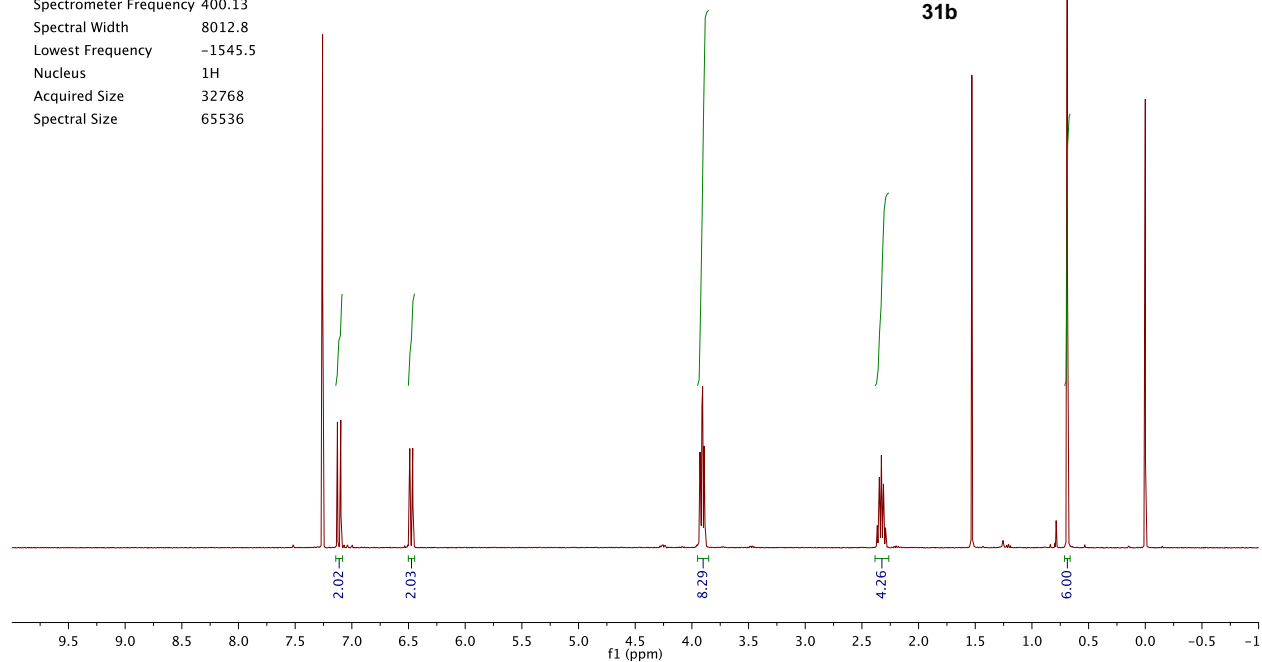
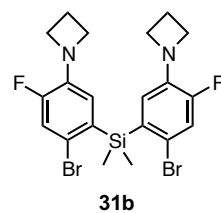
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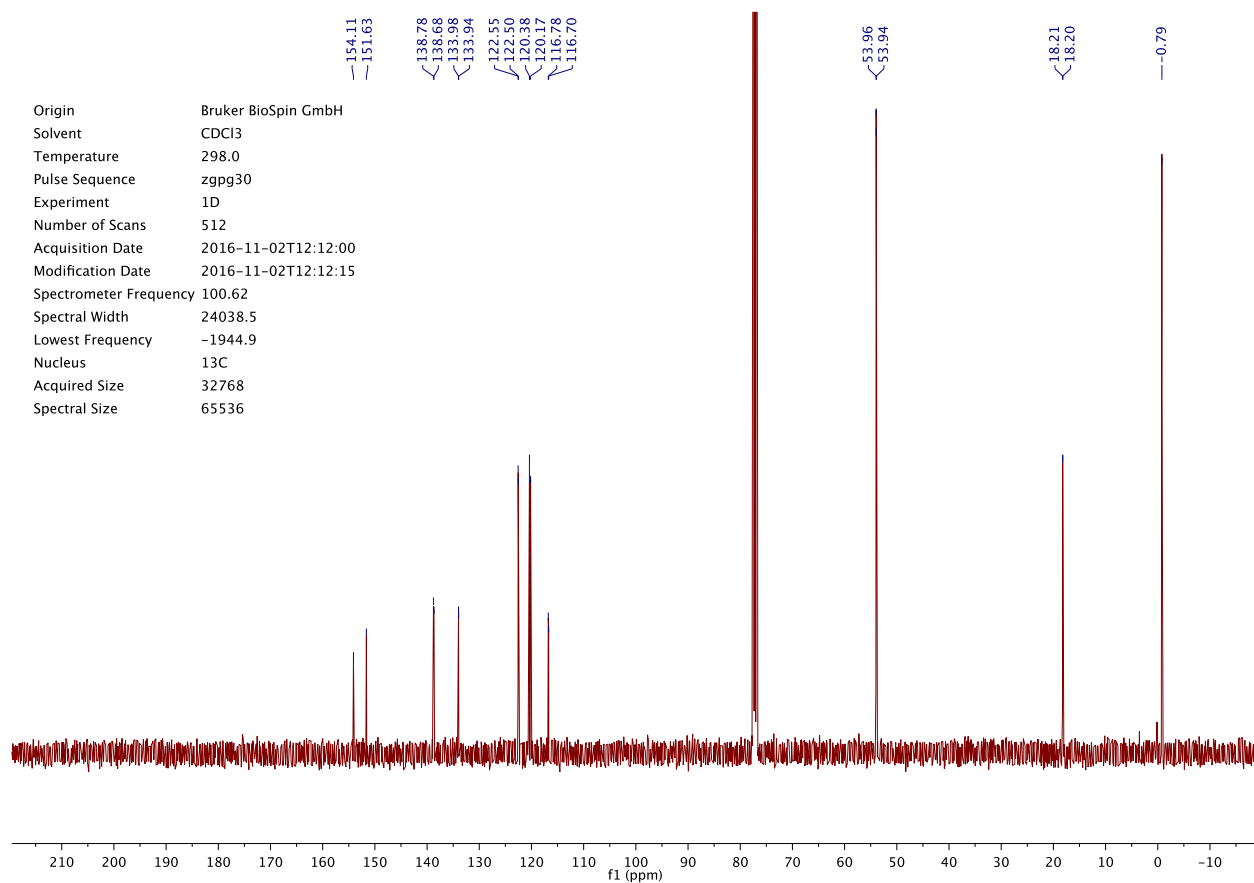
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 Solvent CDCl₃
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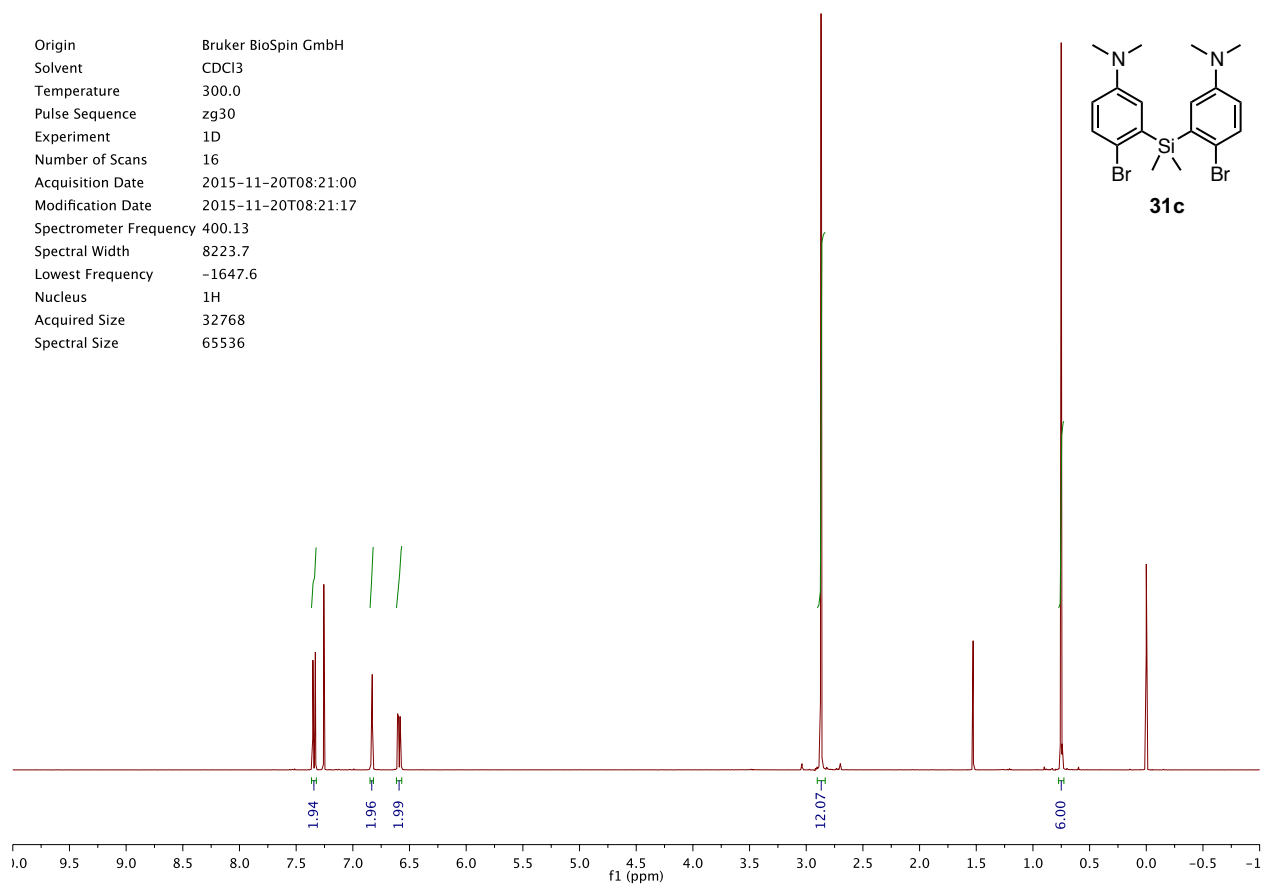
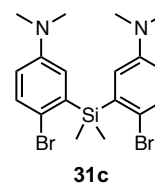
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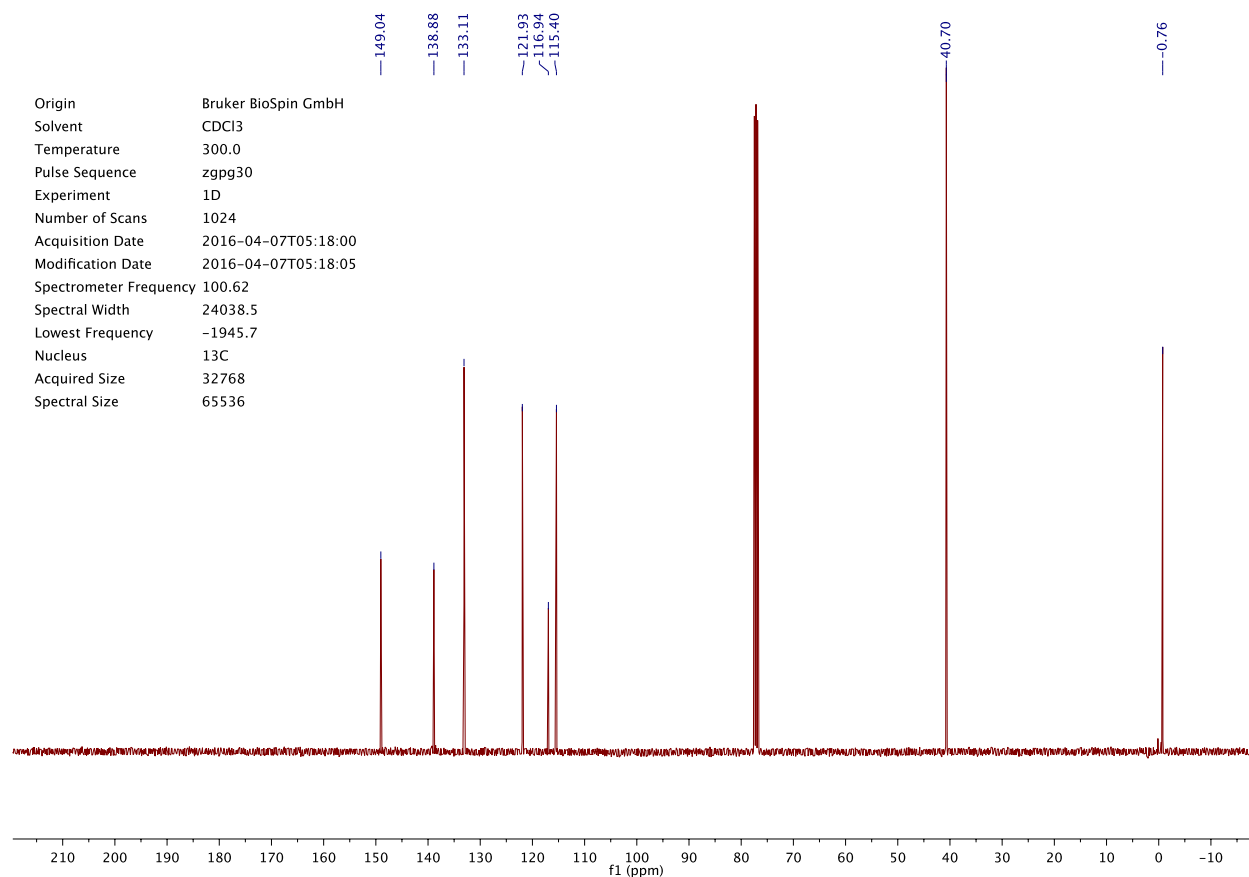
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 Spectrometer Frequency 100.62
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 Lowest Frequency -1944.9
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



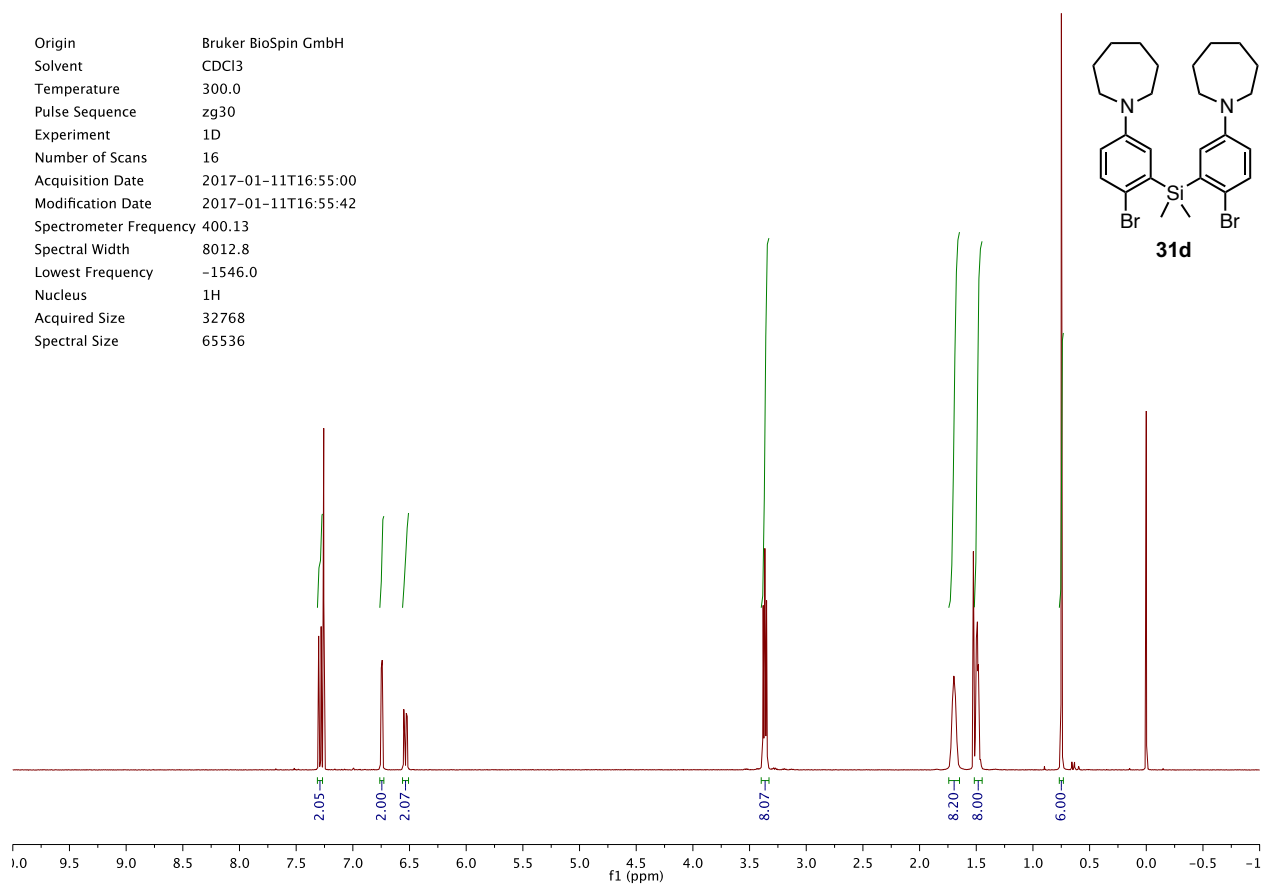
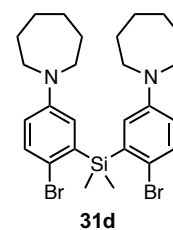
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 Solvent CDCl₃
 Temperature 300.0
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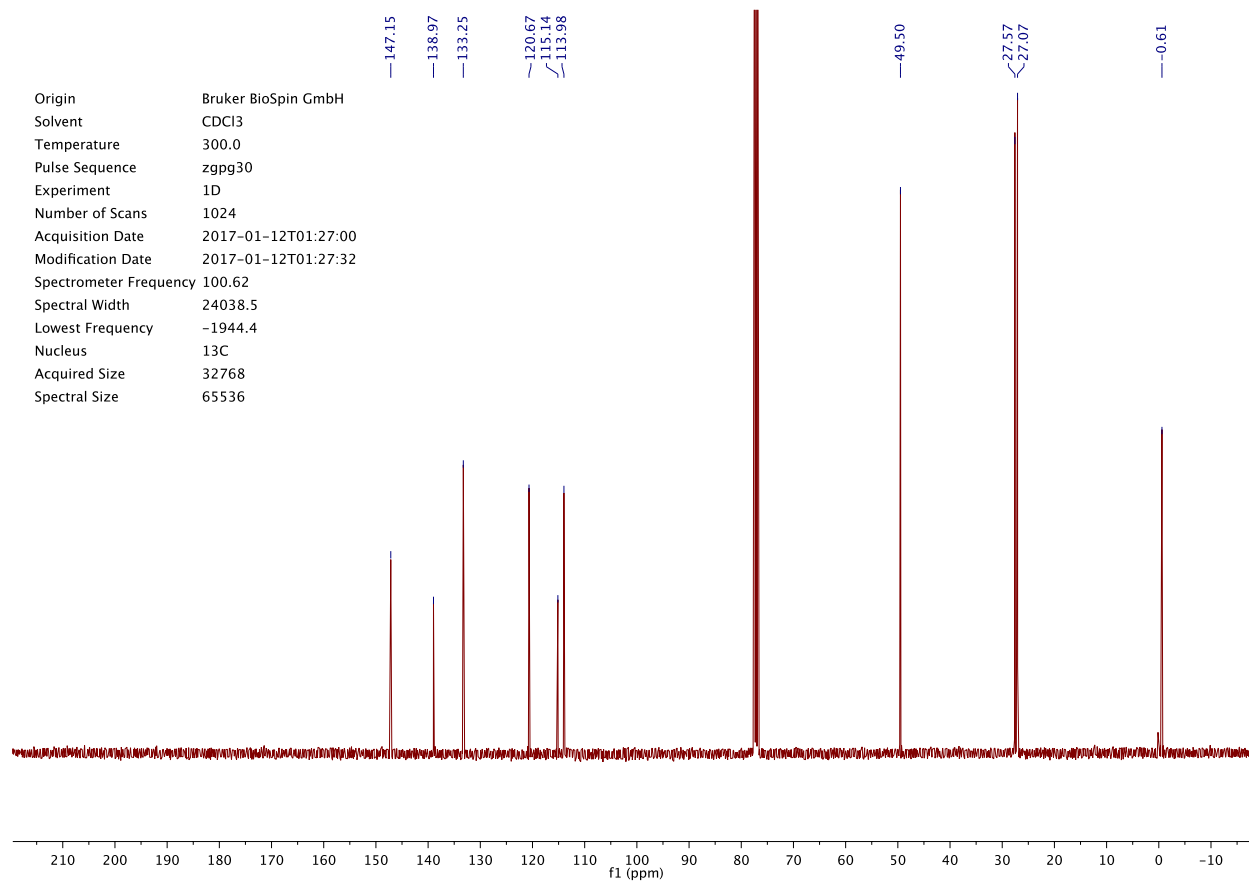
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 Nucleus ¹³C
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 Spectral Size 65536



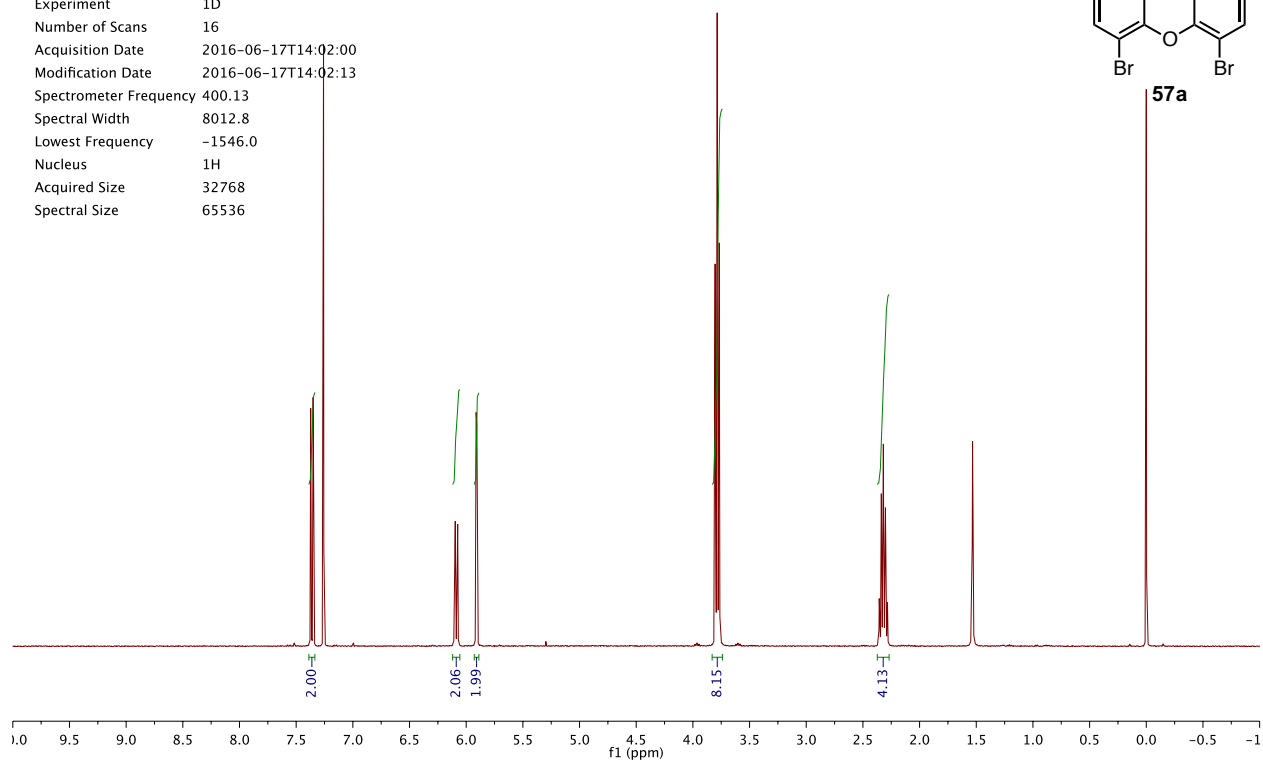
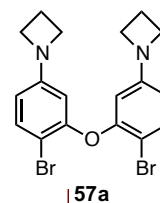
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 Lowest Frequency -1546.0
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



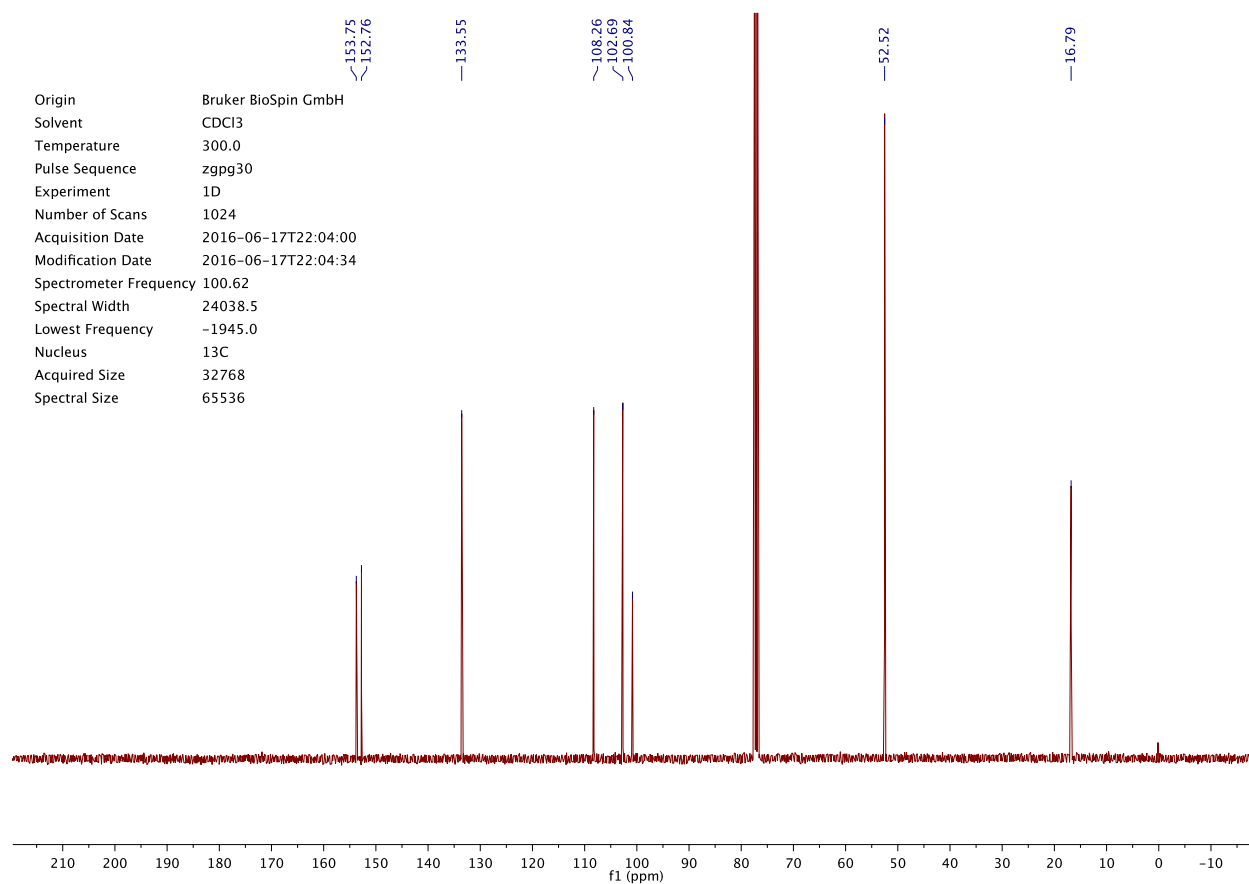
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 Spectral Size 65536



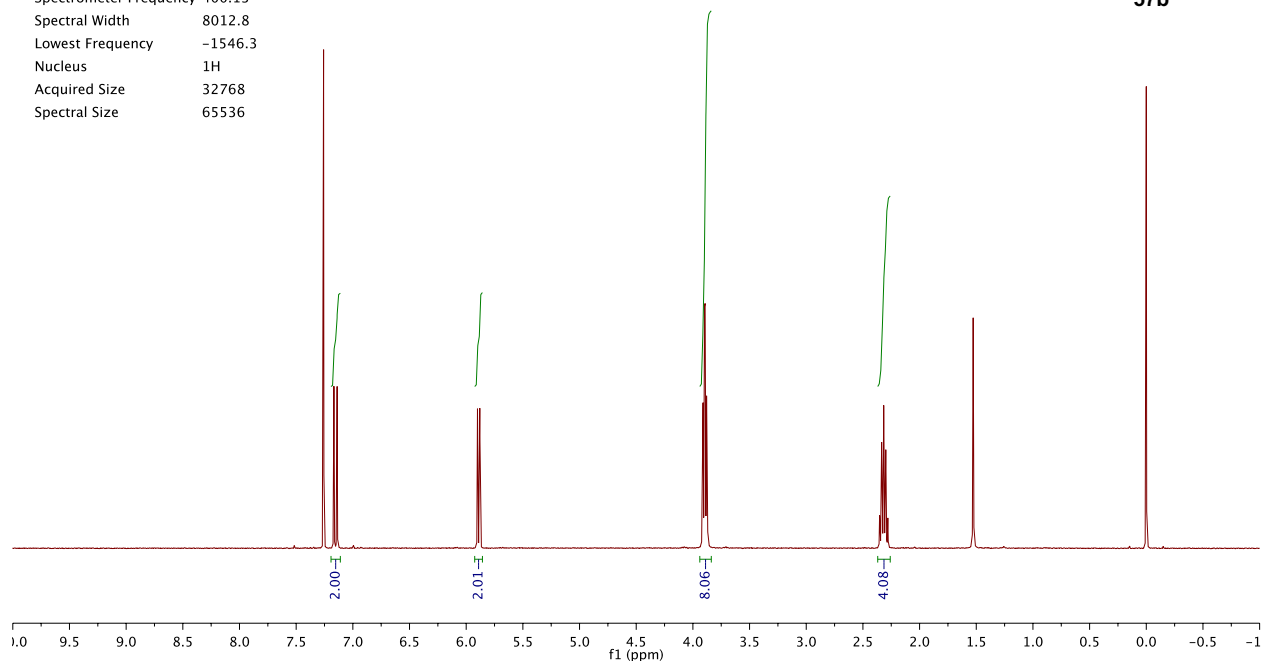
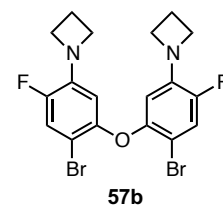
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 Lowest Frequency -1546.0
 Nucleus ¹H
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 Spectral Size 65536



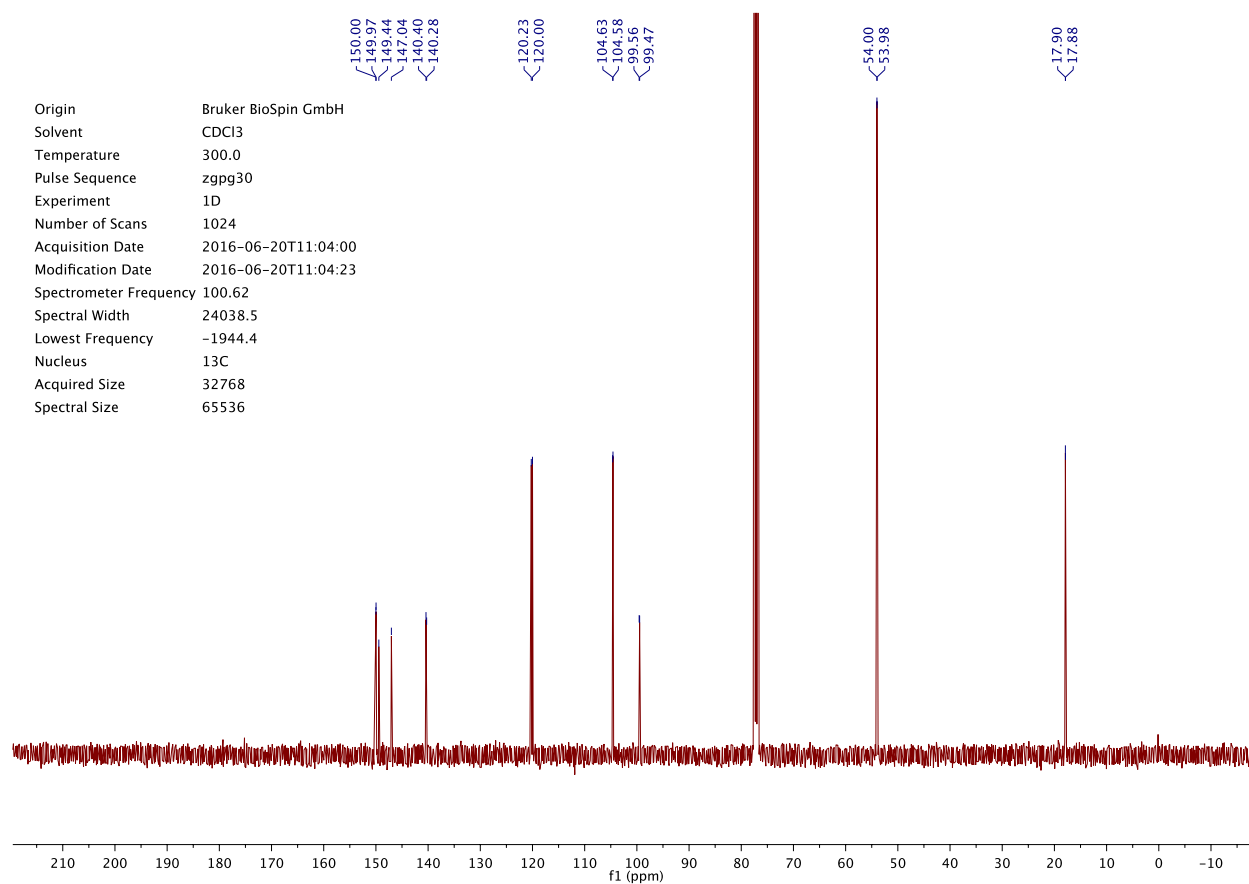
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 Spectral Size 65536



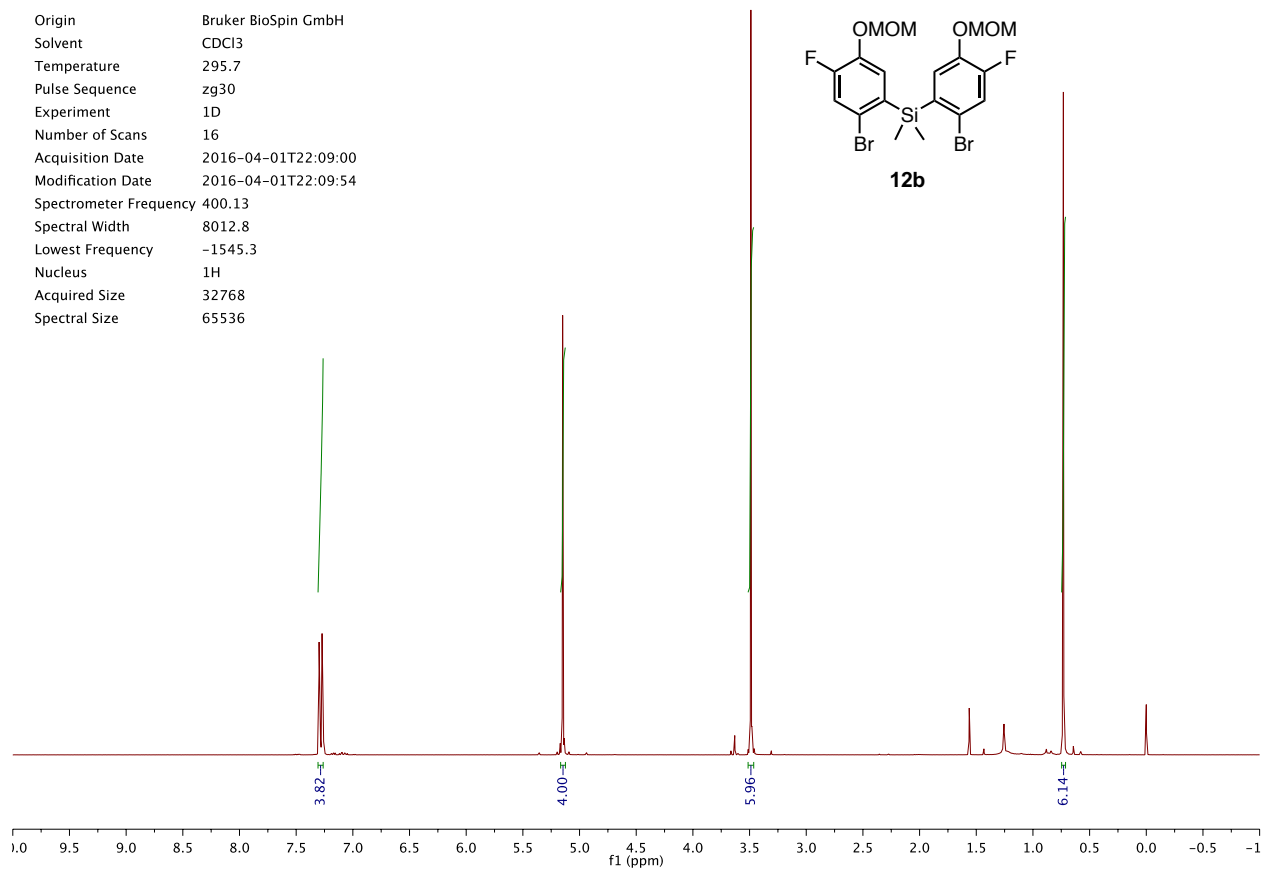
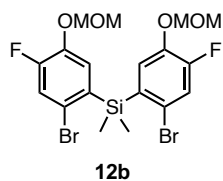
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 Nucleus ¹H
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 Spectral Size 65536



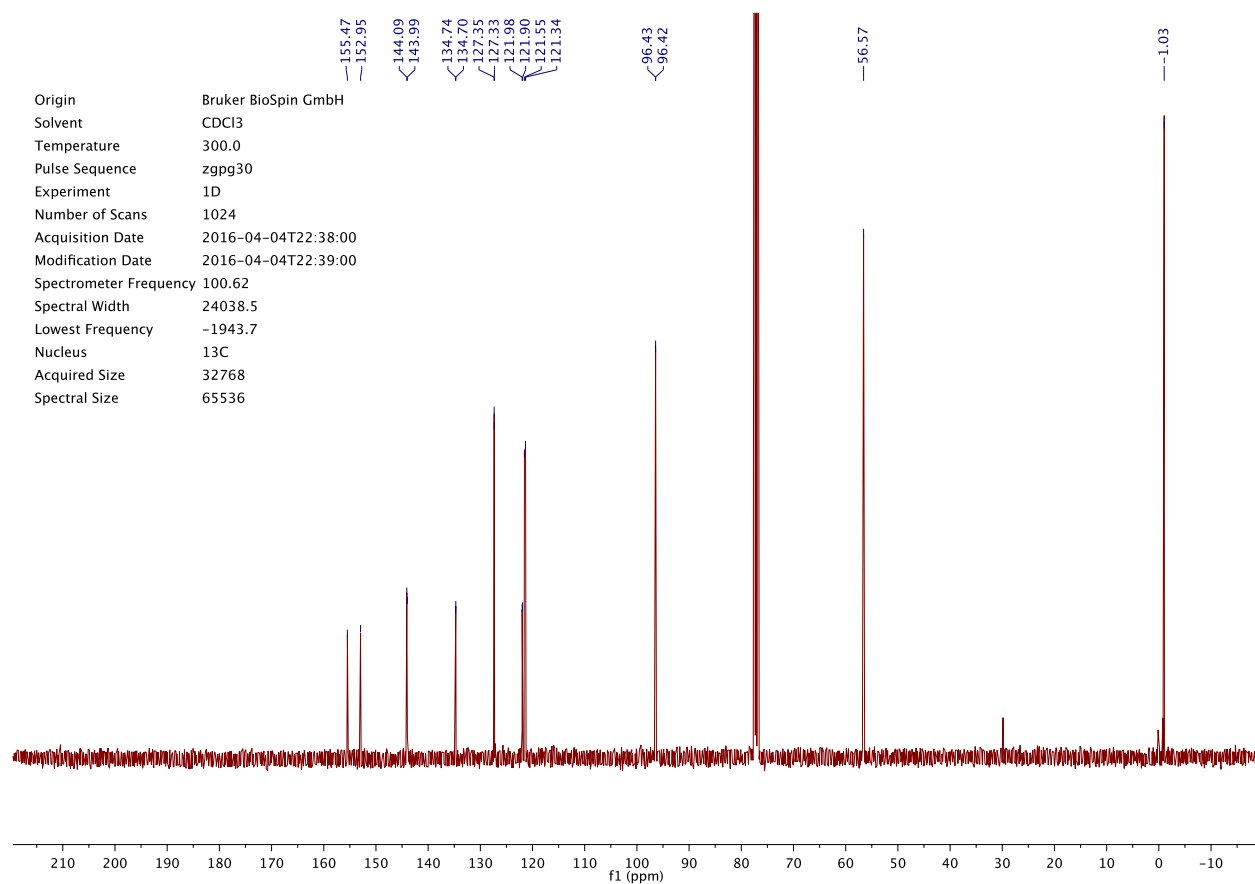
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 Spectral Size 65536



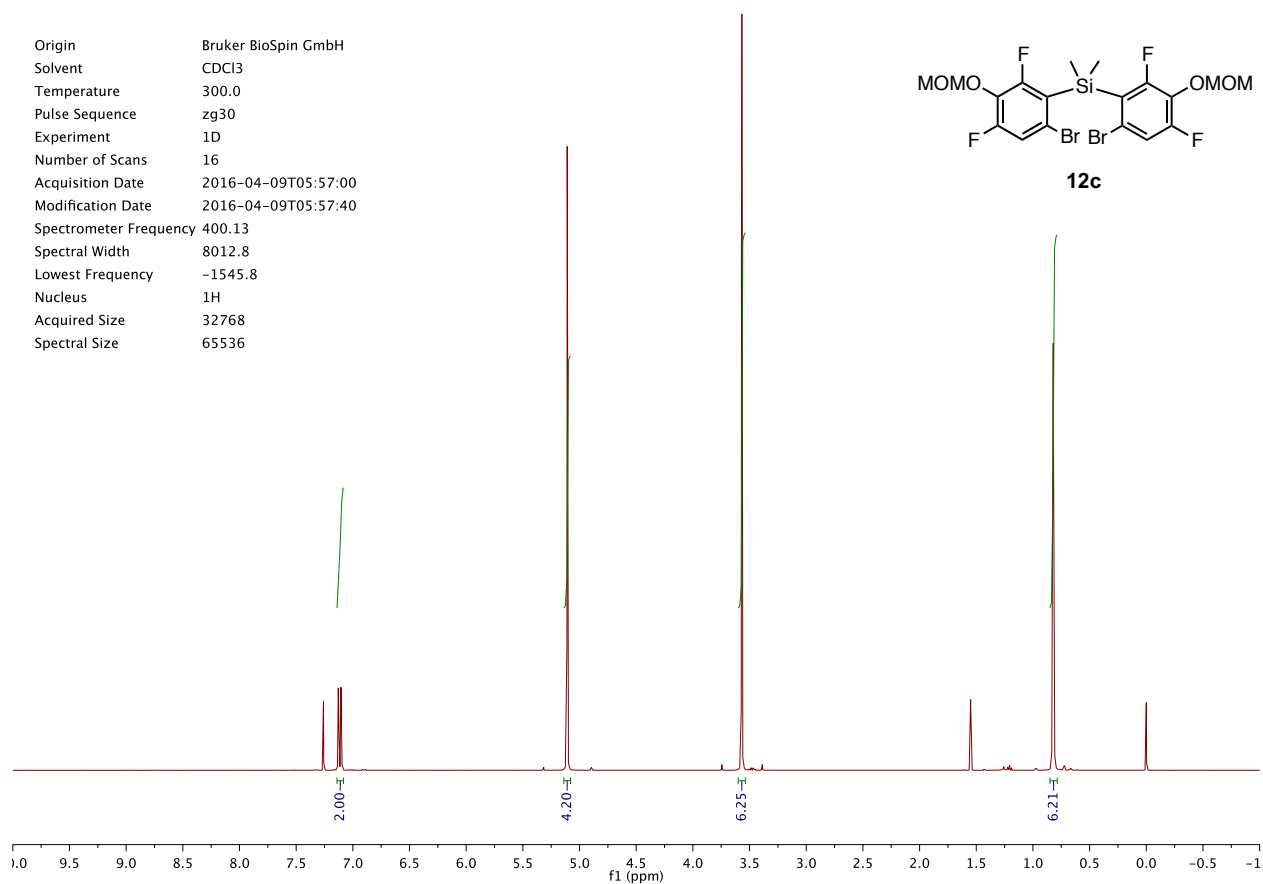
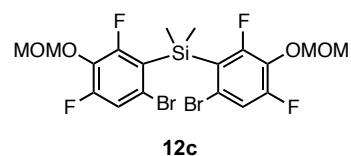
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 Lowest Frequency -1545.3
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



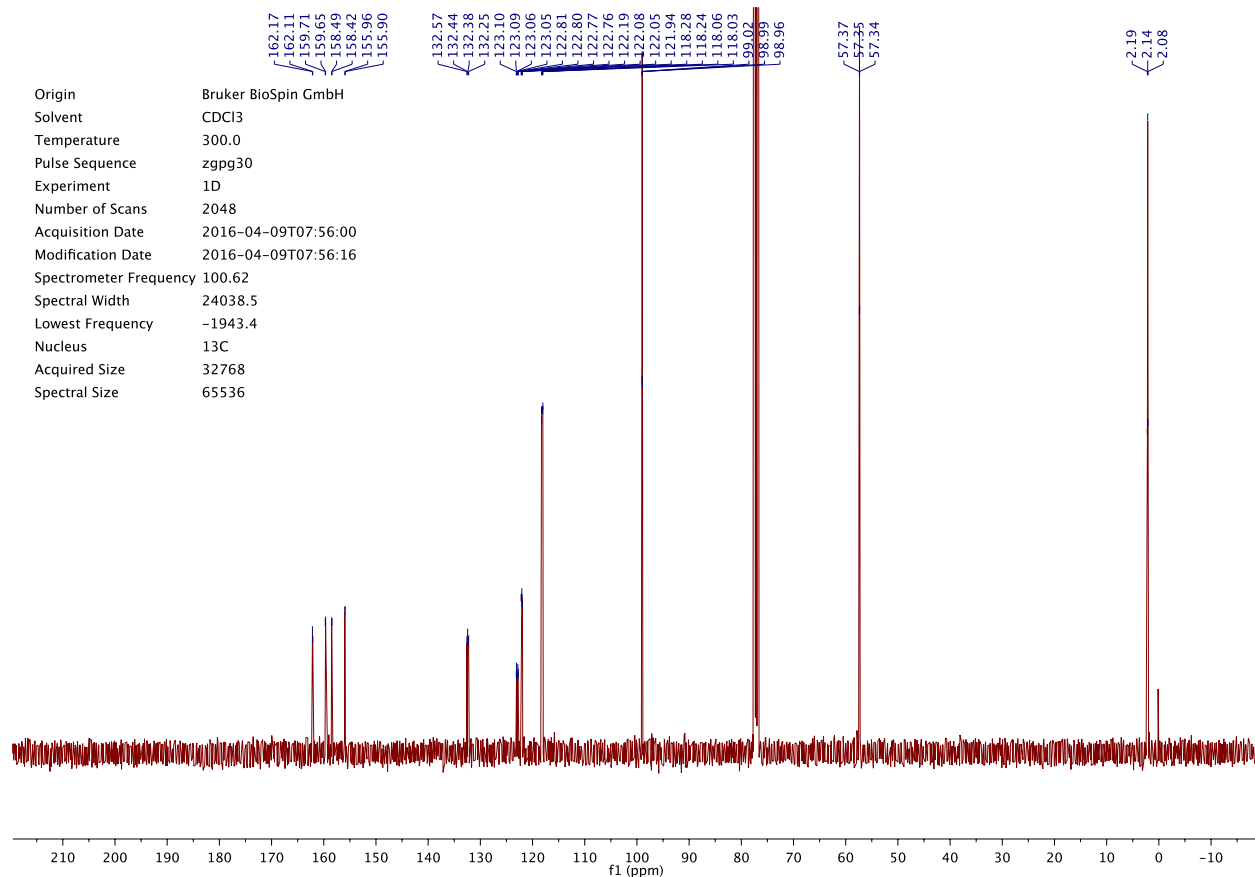
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 Spectral Size 65536



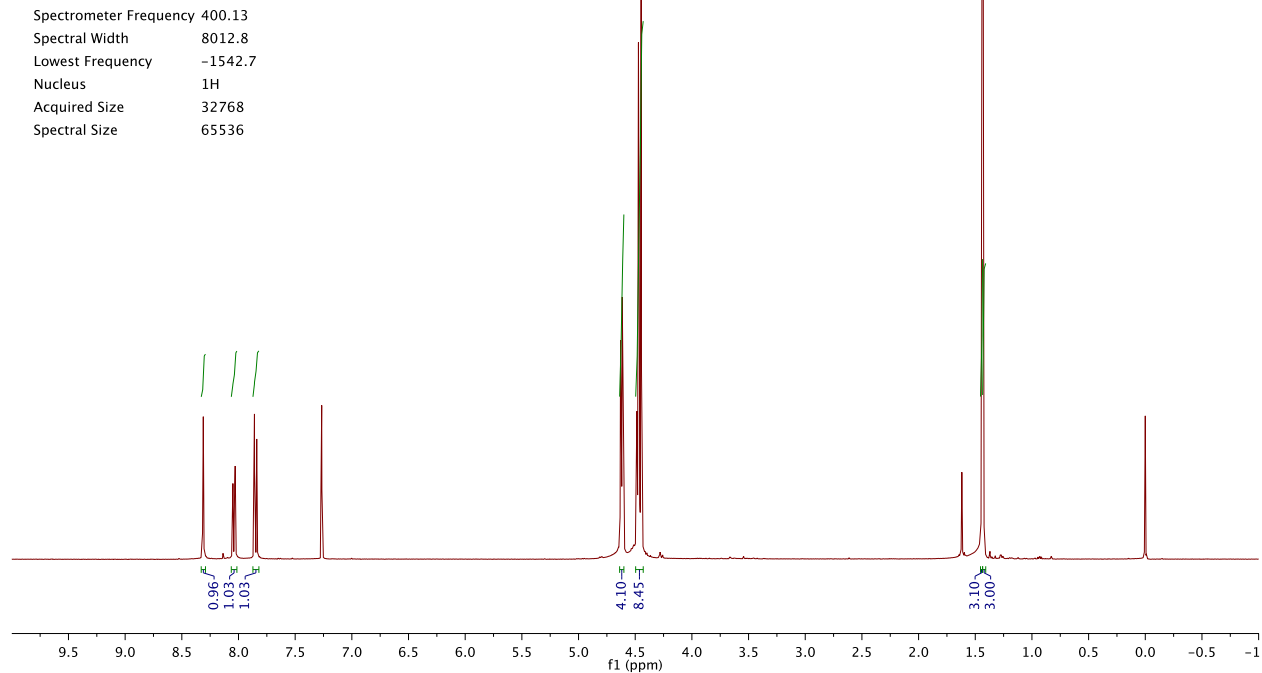
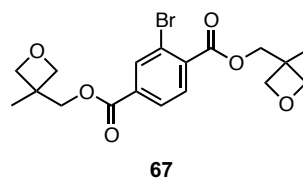
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 Solvent CDCl₃
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 Lowest Frequency -1545.8
 Nucleus ¹H
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 Spectral Size 65536



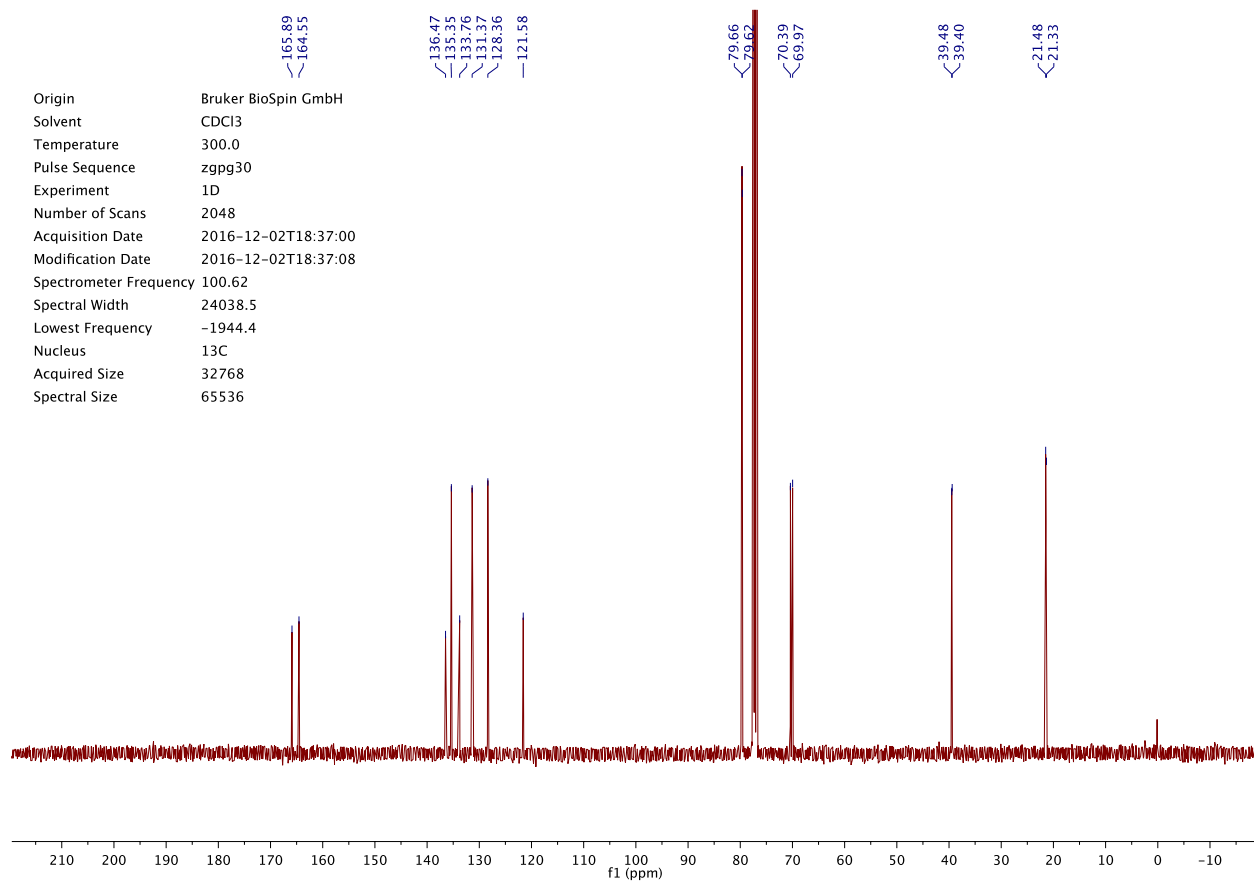
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 Spectral Size 65536



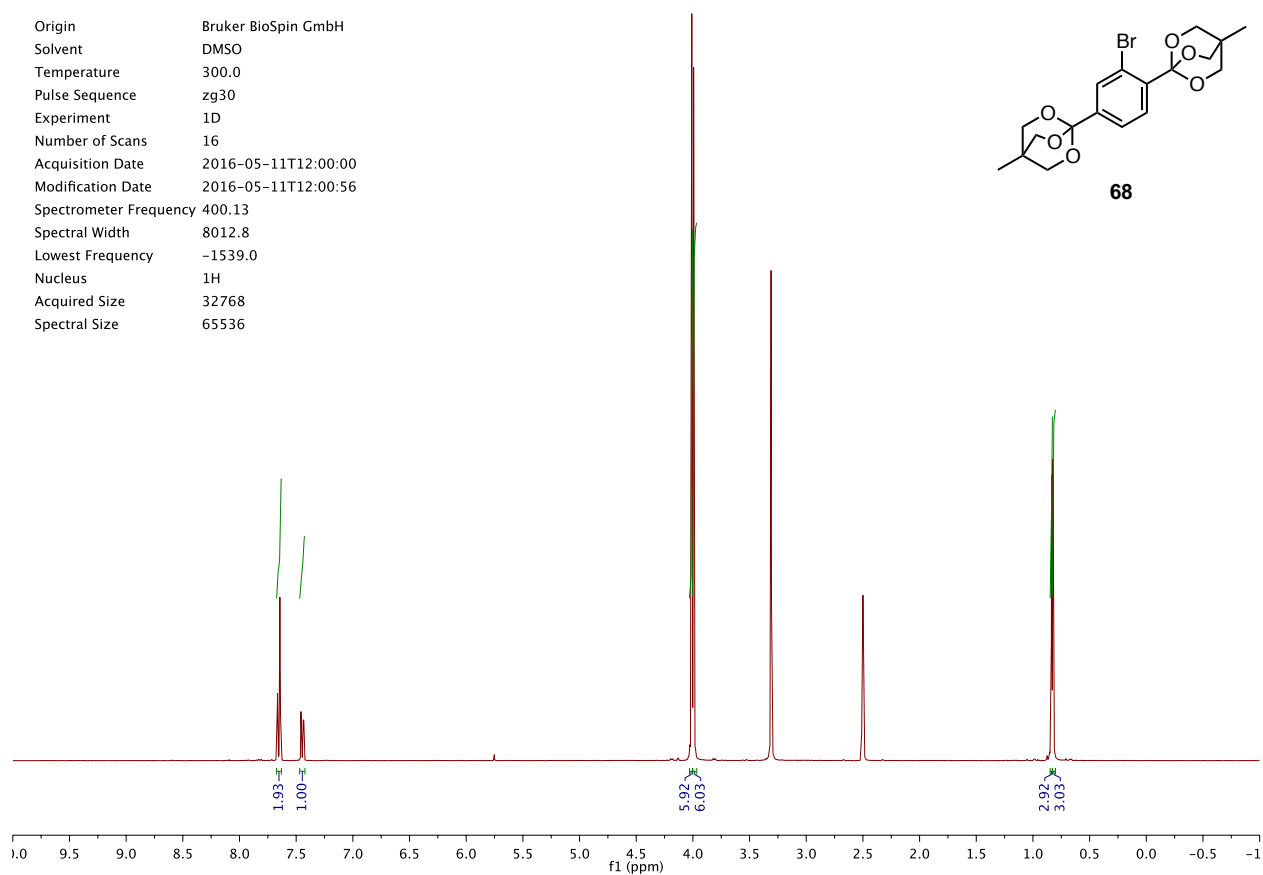
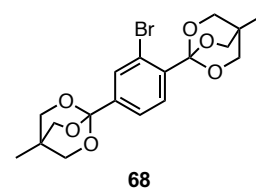
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 Solvent CDCl₃
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 Spectral Size 65536



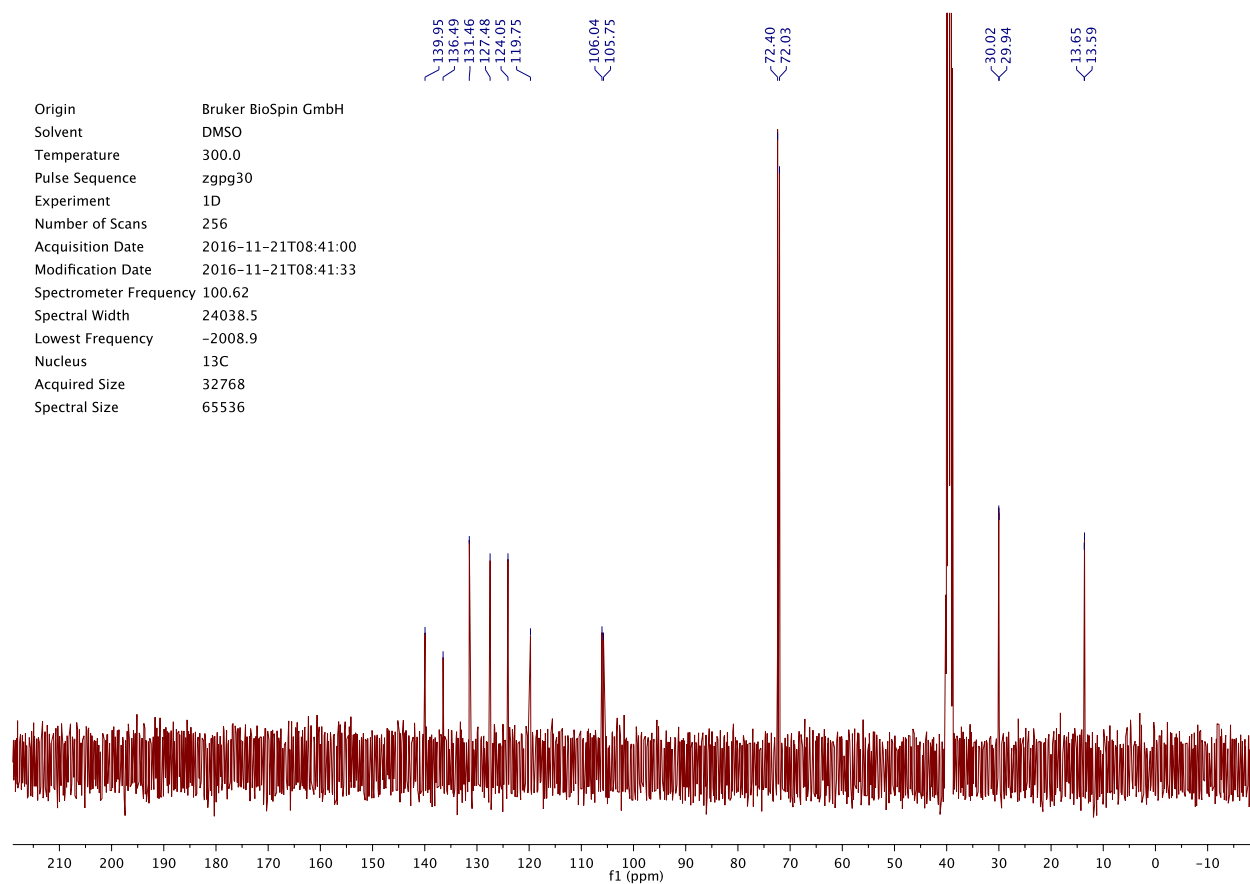
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 Lowest Frequency -1944.4
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



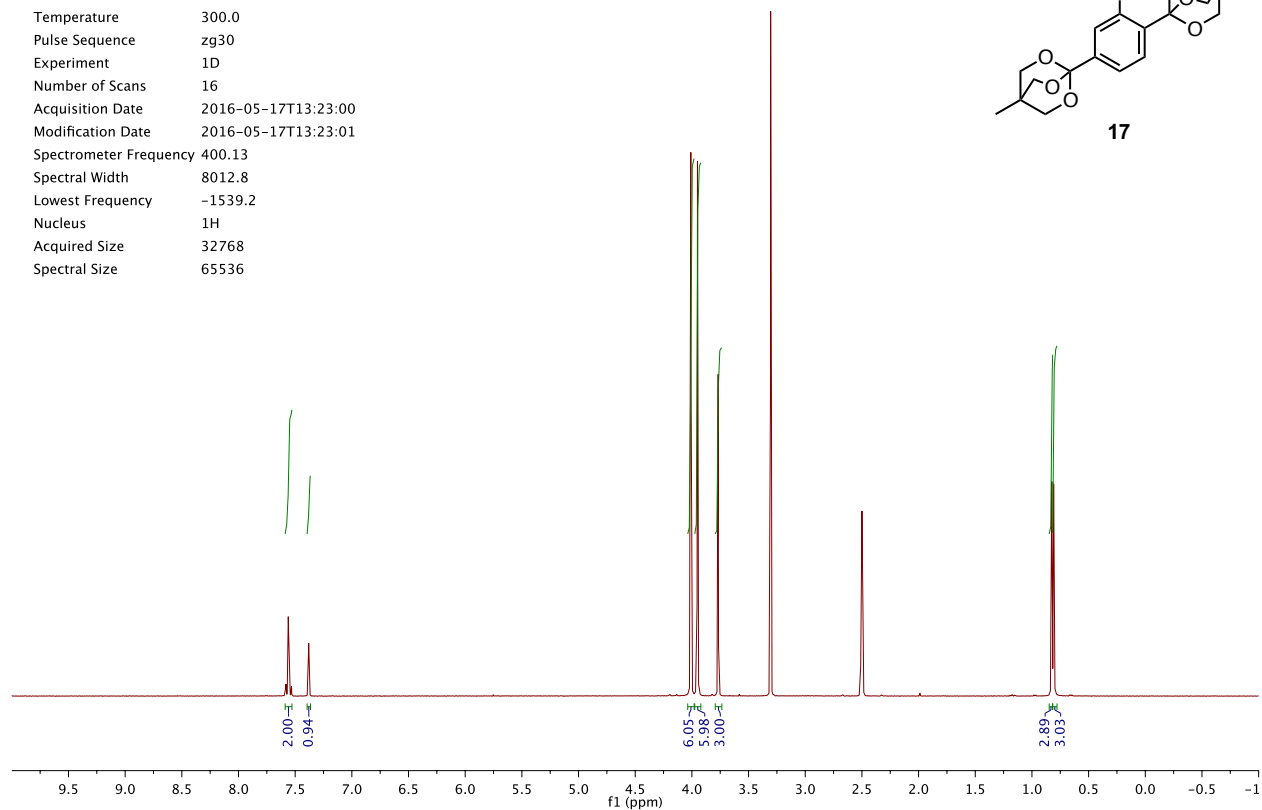
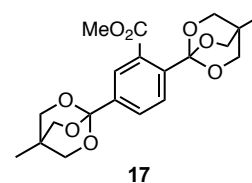
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 Spectral Size 65536



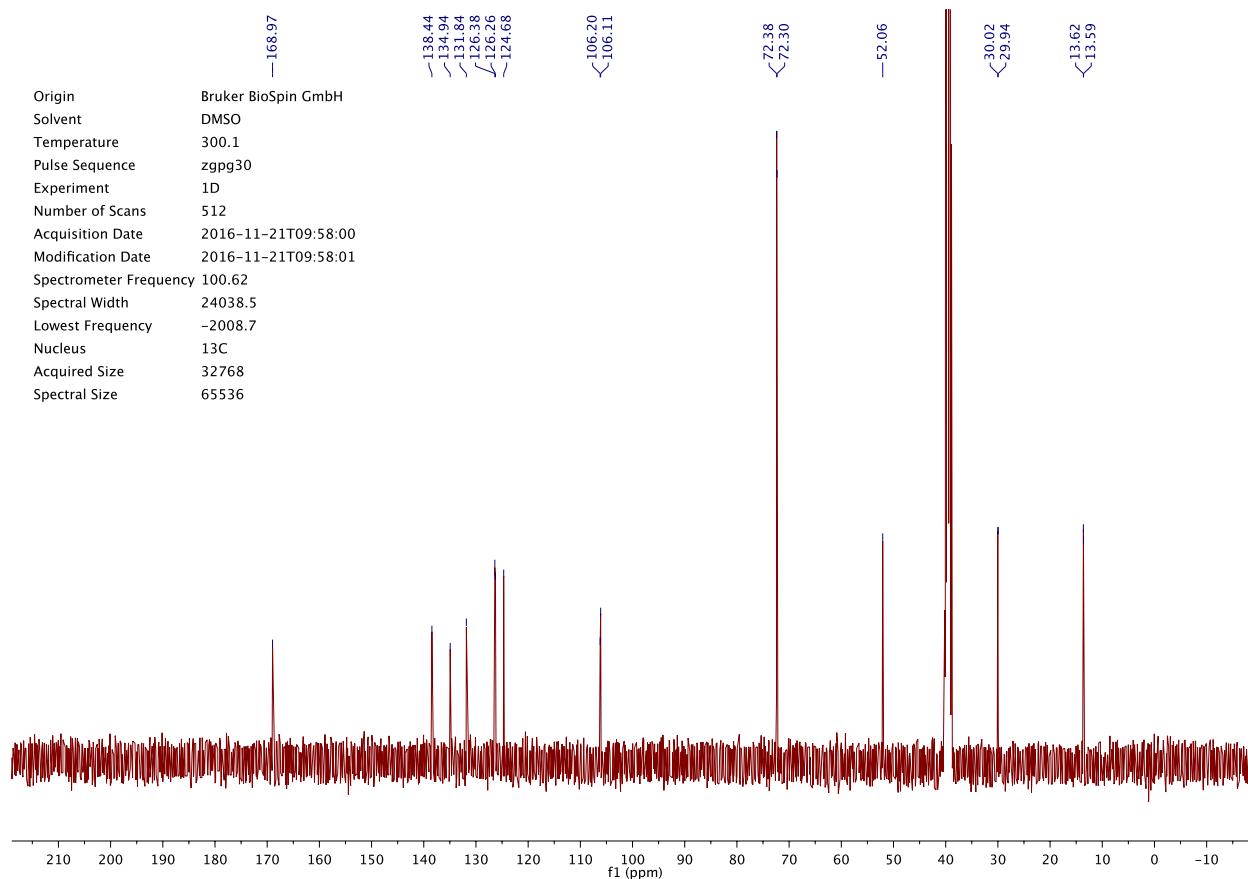
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 Lowest Frequency -2008.9
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536



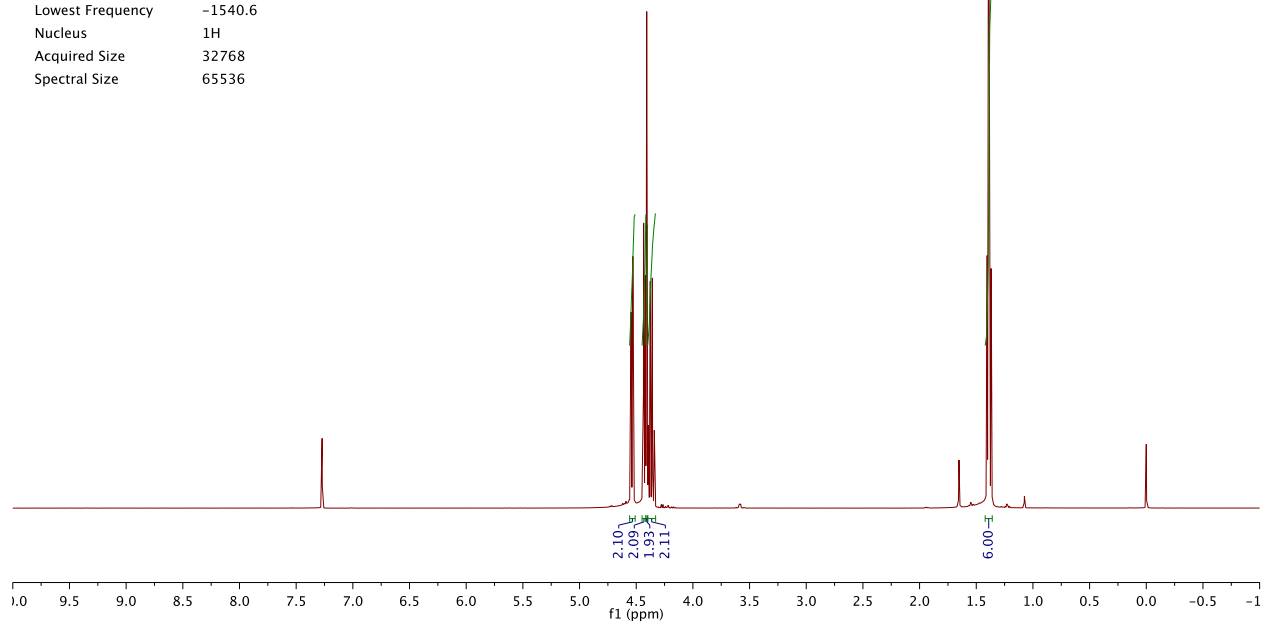
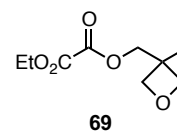
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 Modification Date 2016-05-17T13:23:01
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 Lowest Frequency -1539.2
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



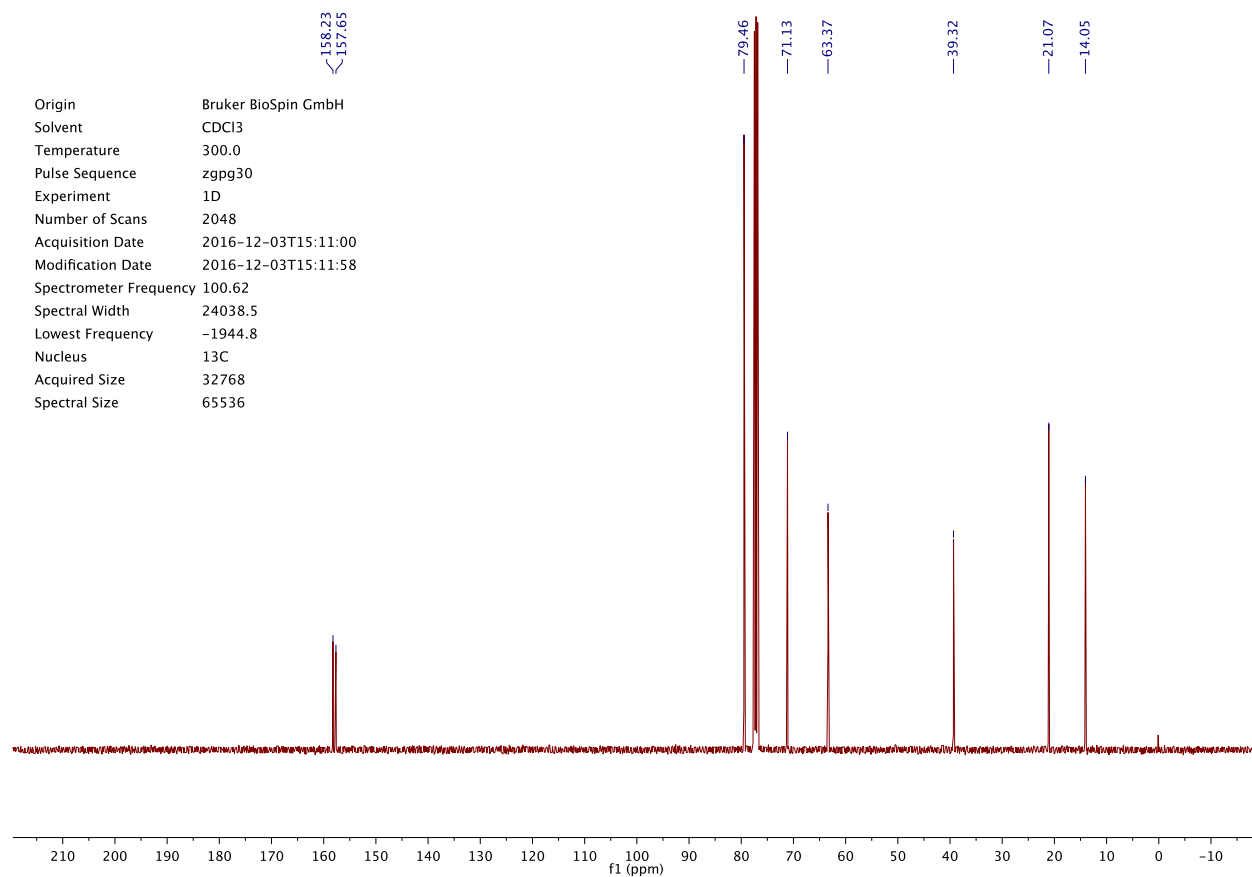
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 Lowest Frequency -2008.7
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536



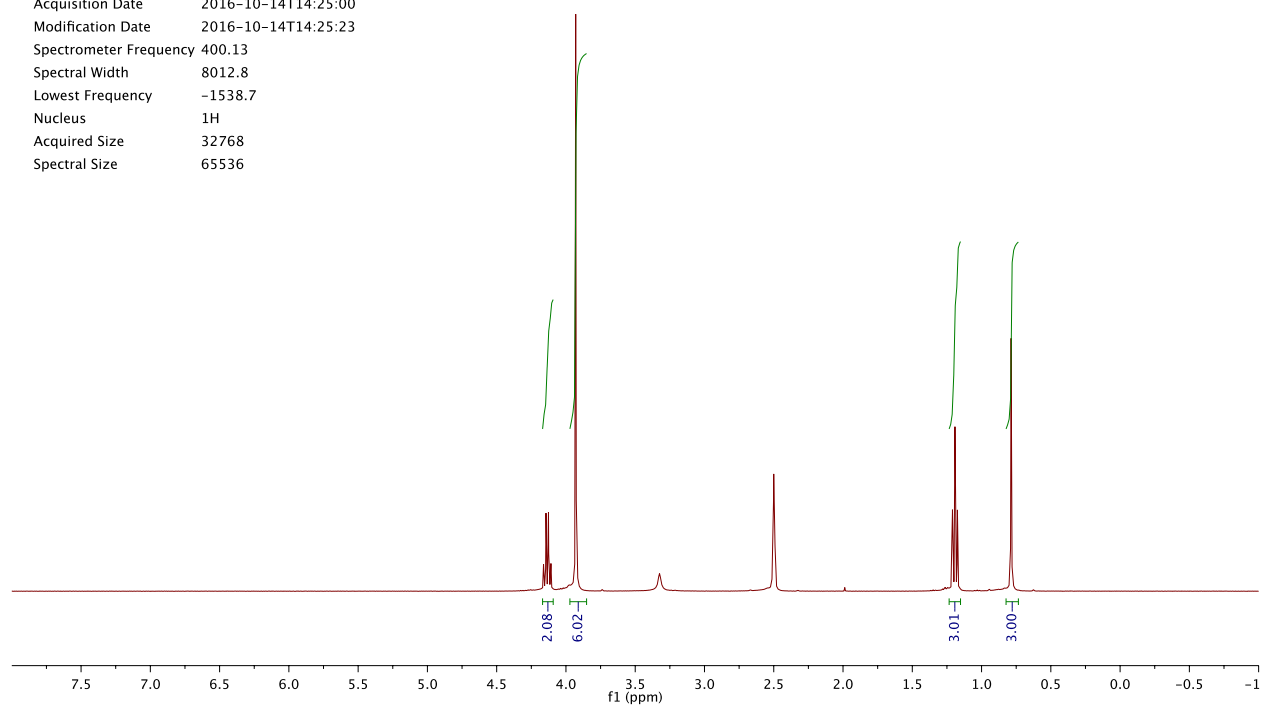
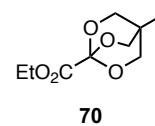
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 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



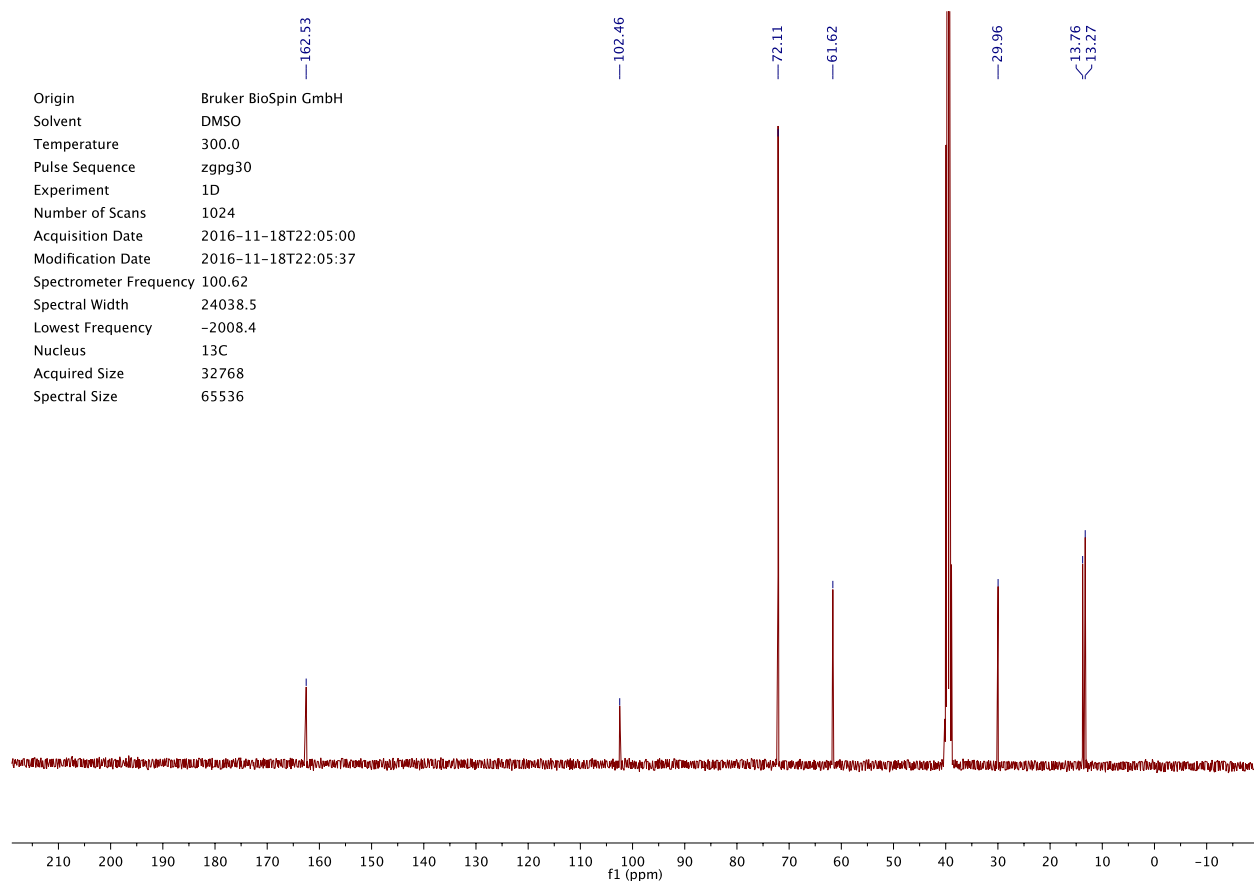
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 Acquired Size 32768
 Spectral Size 65536



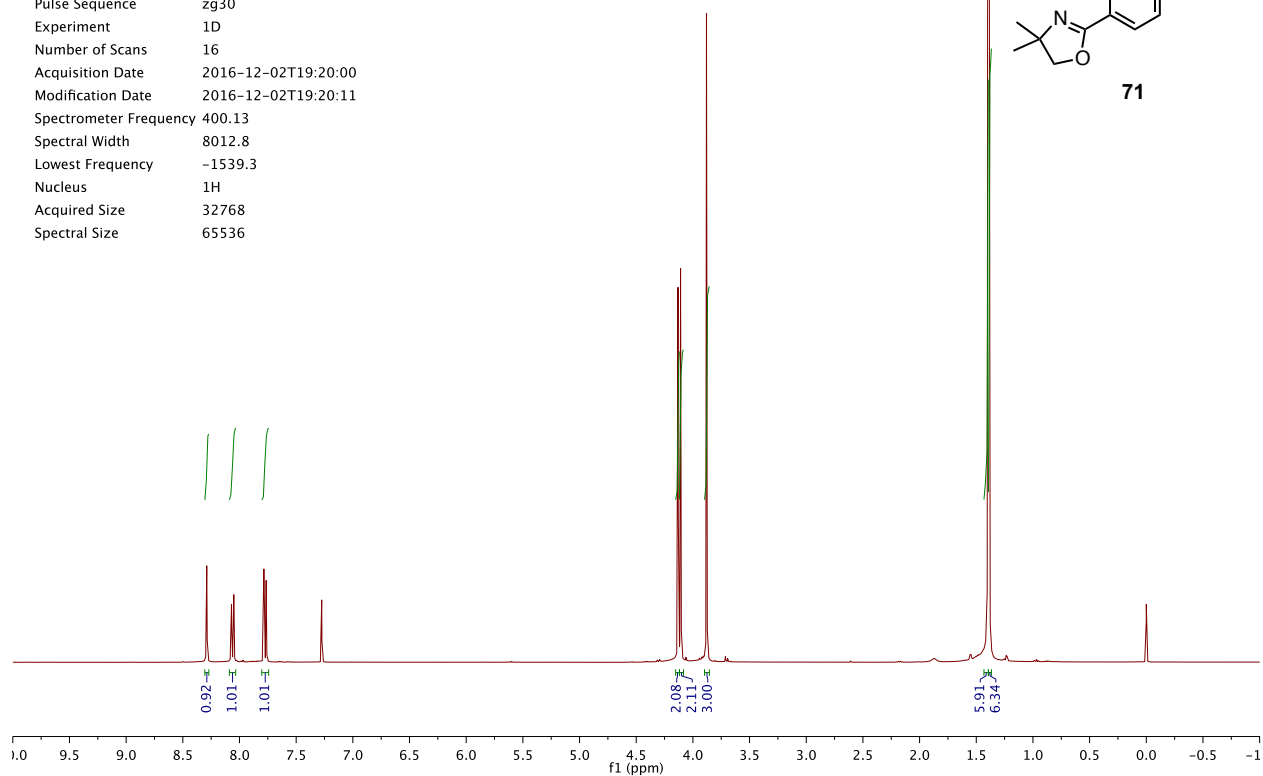
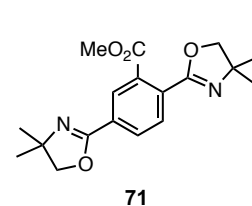
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 Nucleus 1H
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 Spectral Size 65536



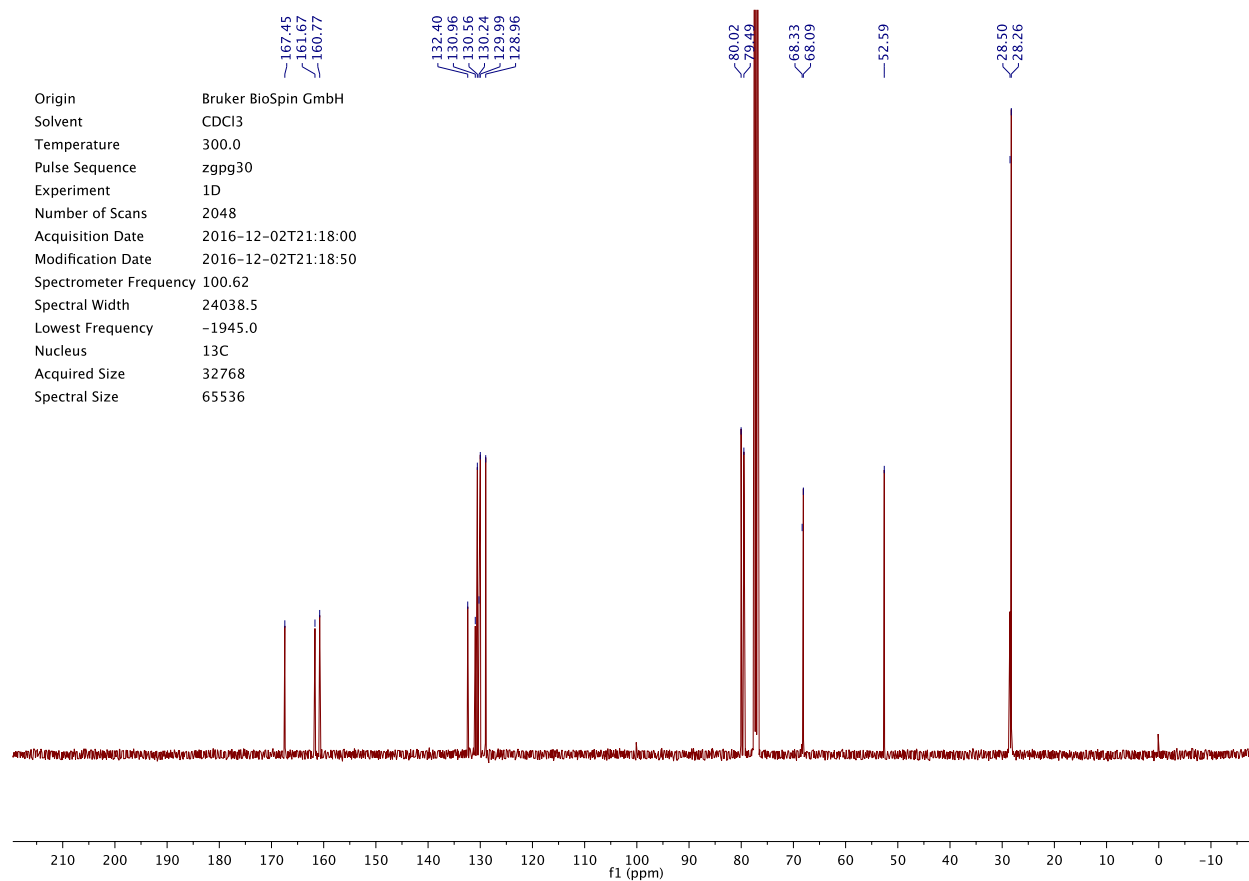
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 Spectral Size 65536



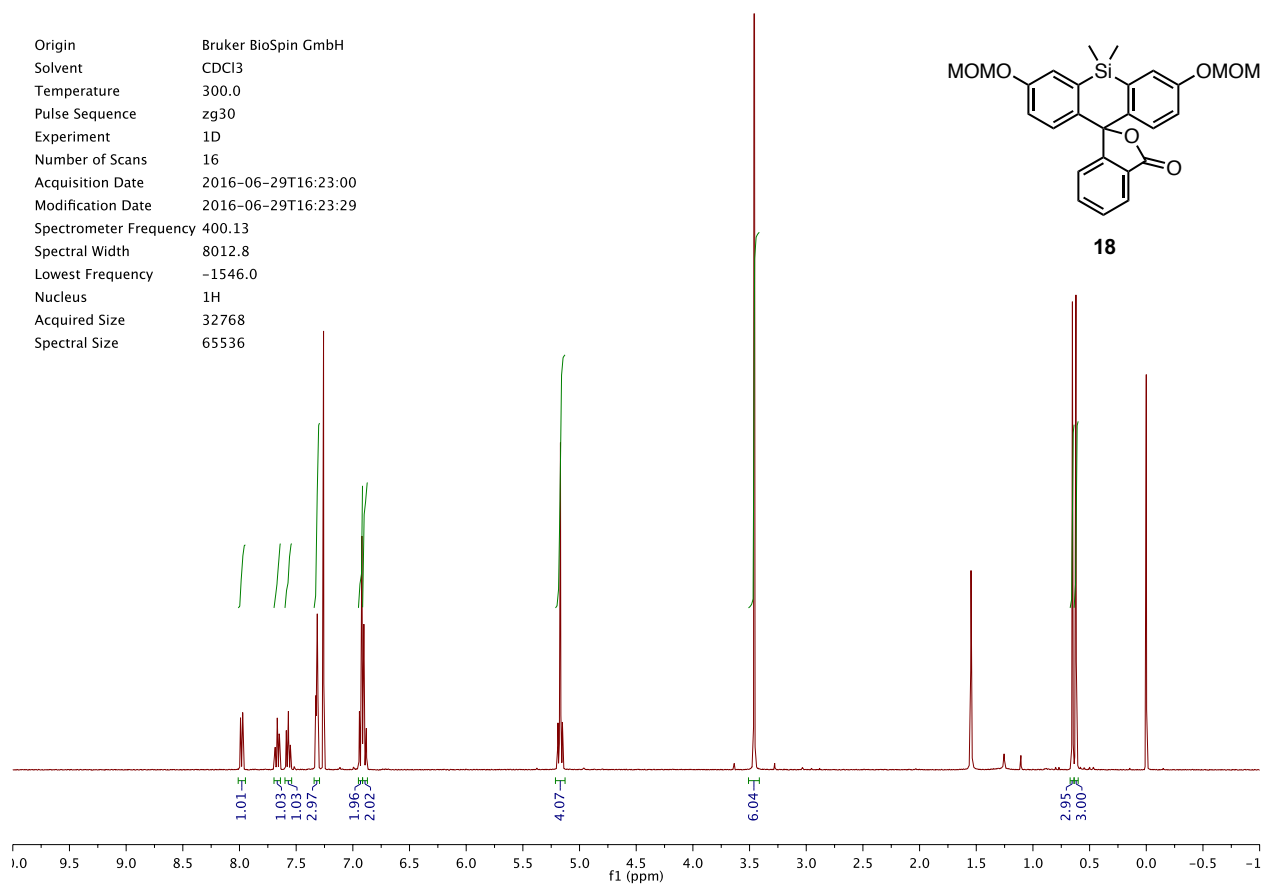
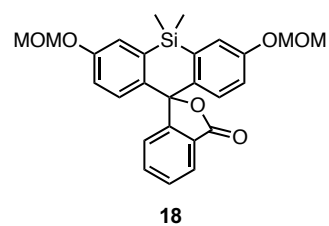
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 Spectral Size 65536



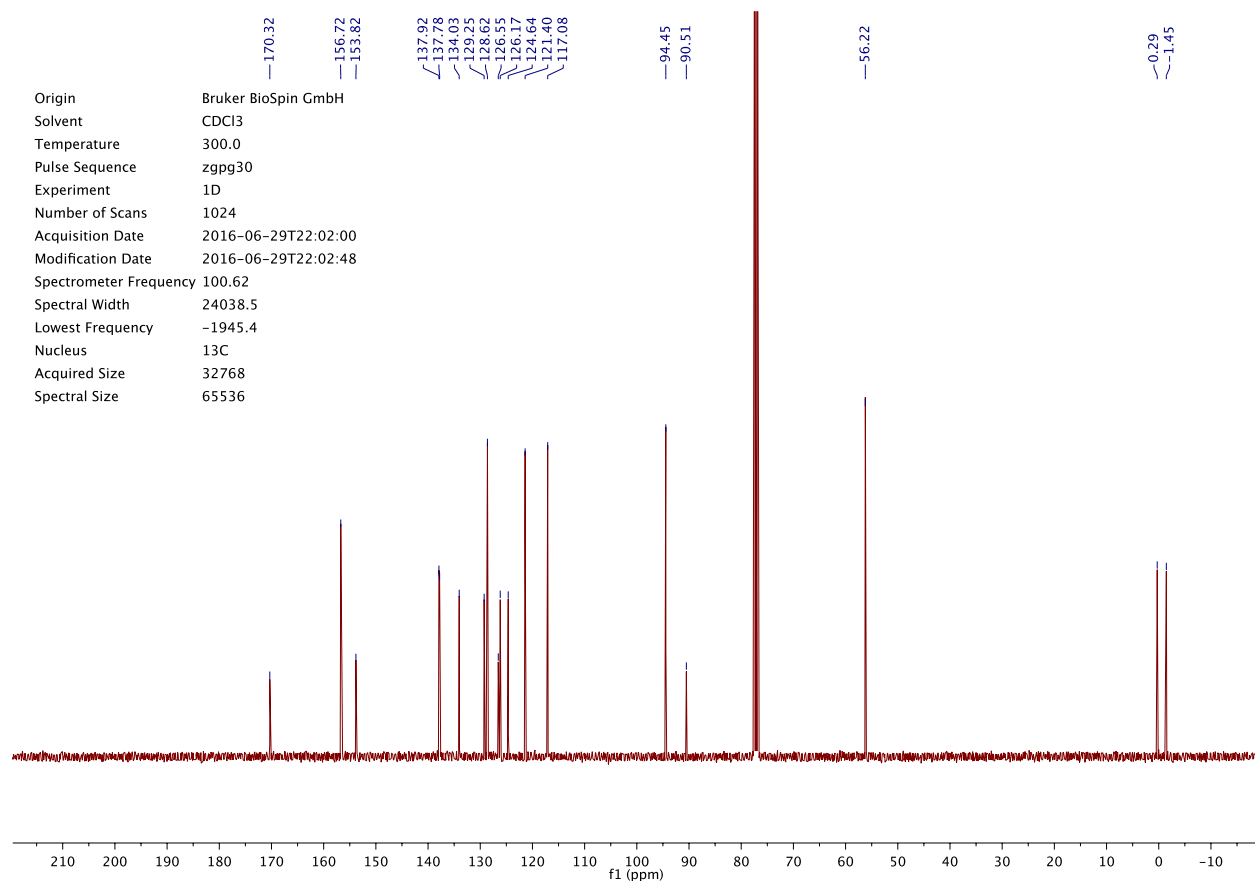
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 Nucleus ¹³C
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 Spectral Size 65536



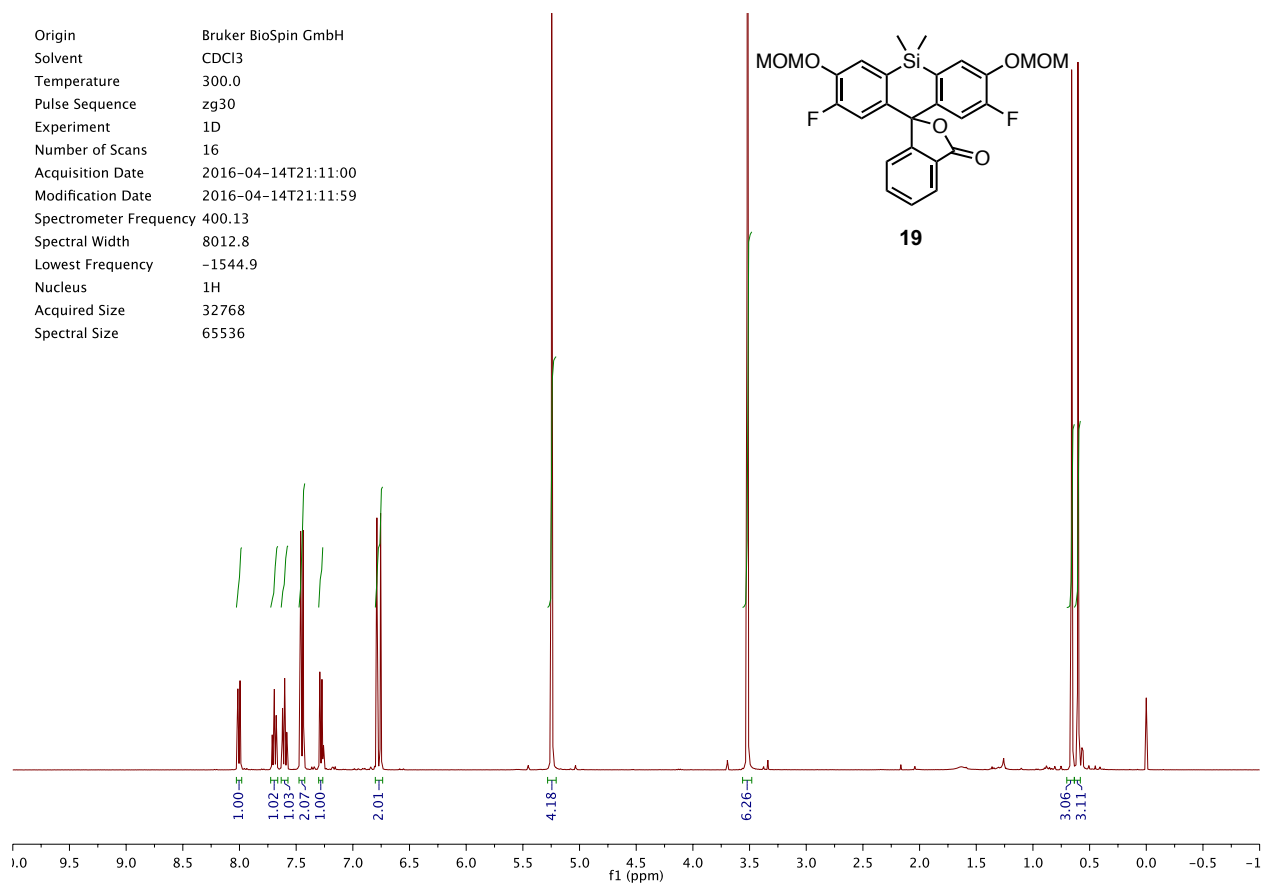
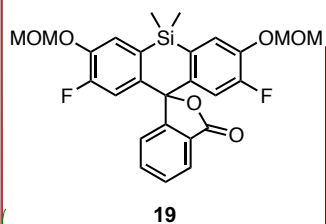
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 Nucleus ¹H
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 Spectral Size 65536



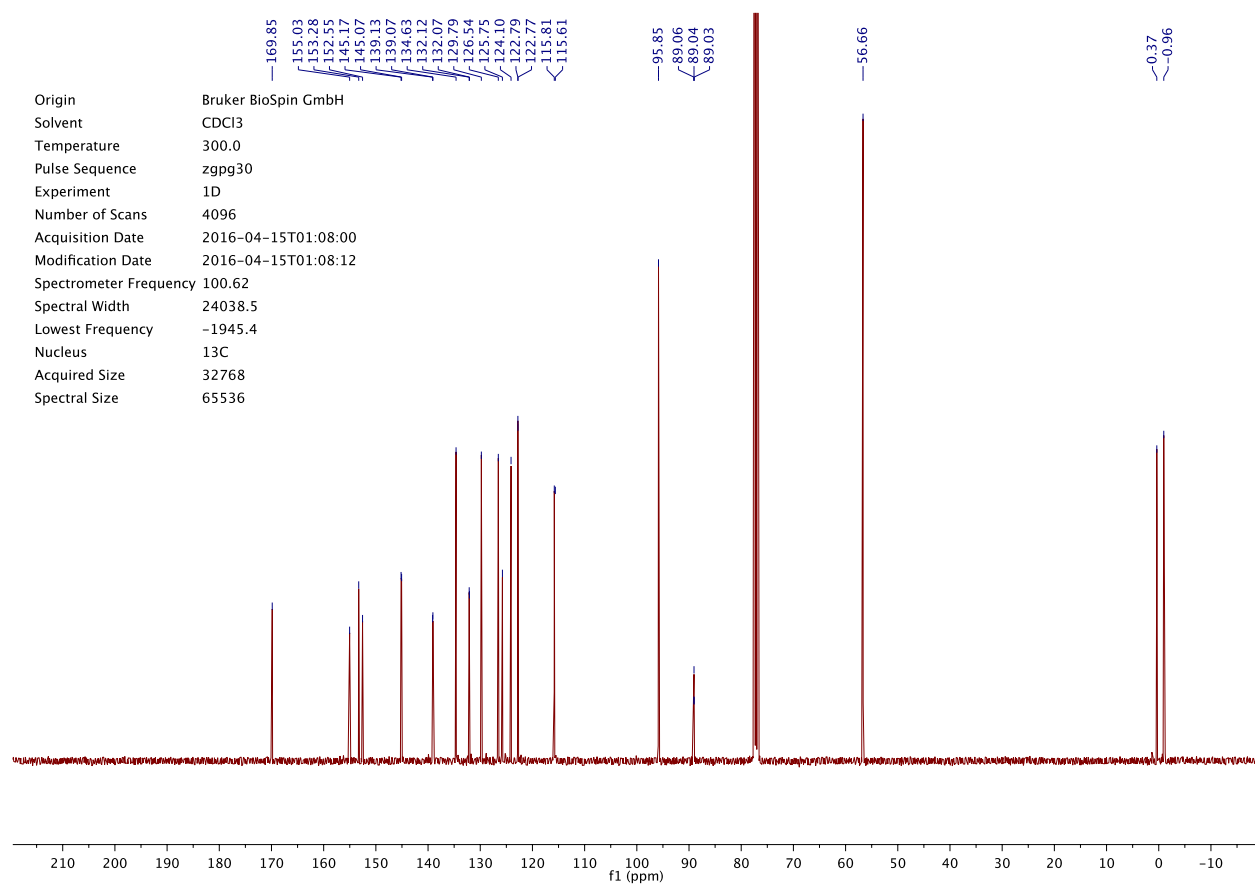
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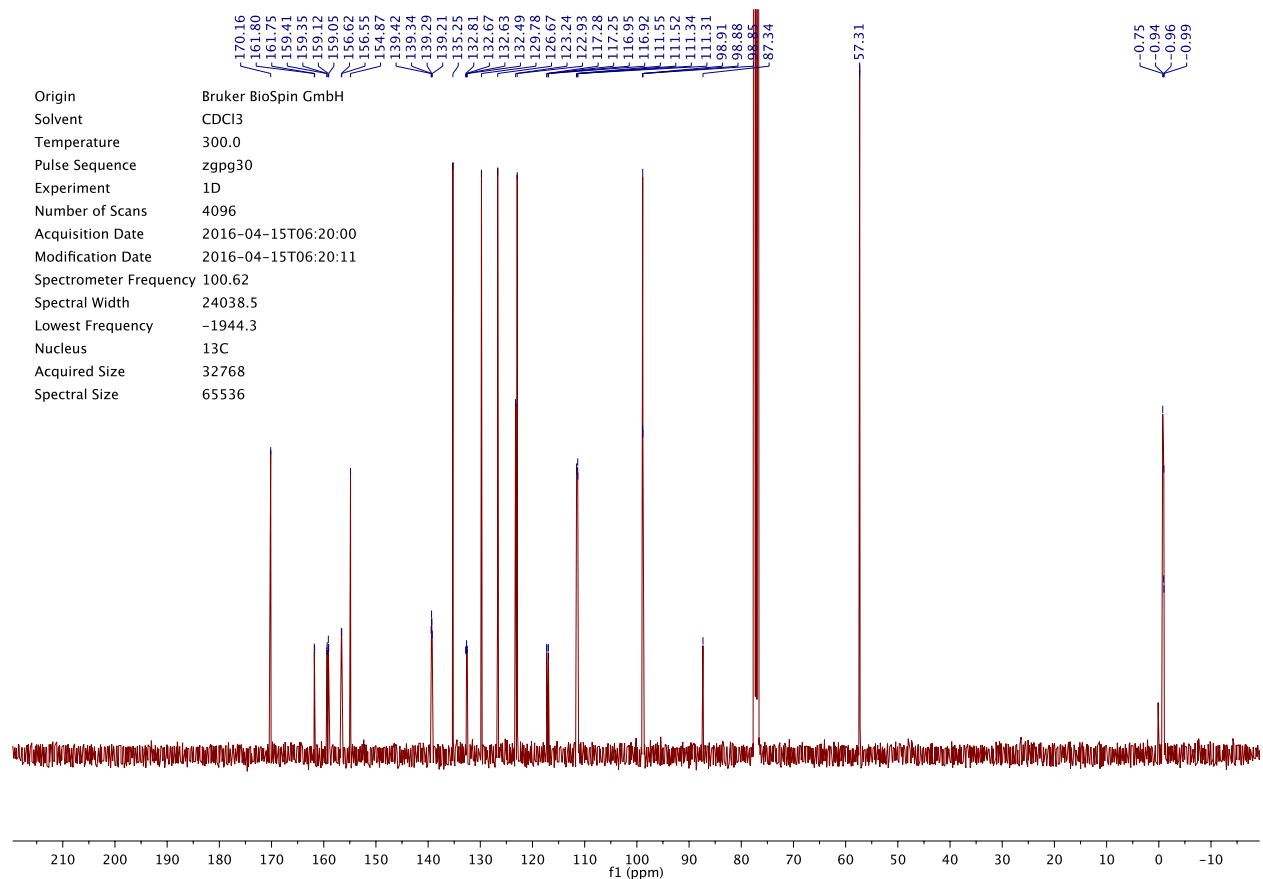
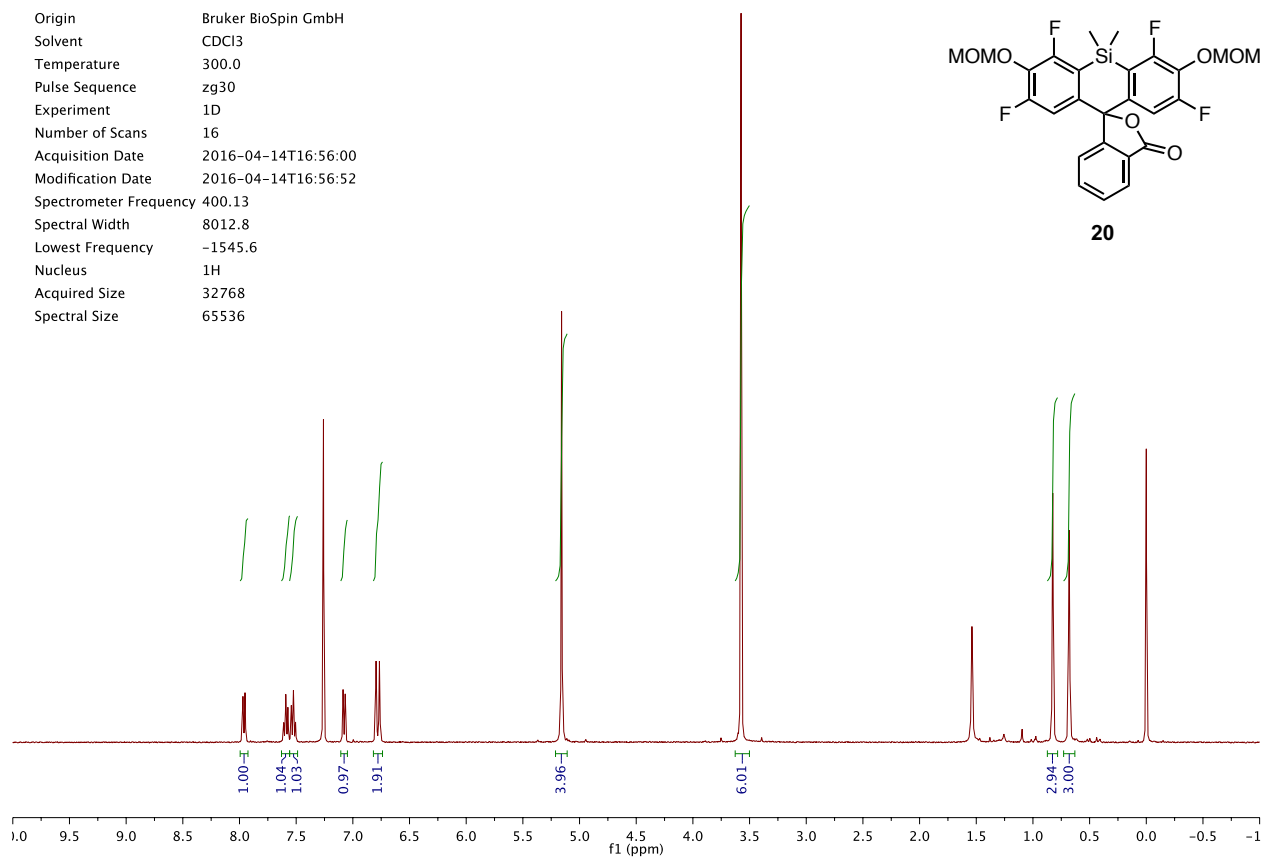
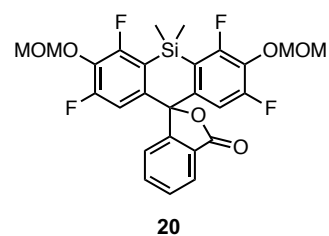
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 Spectral Size 65536



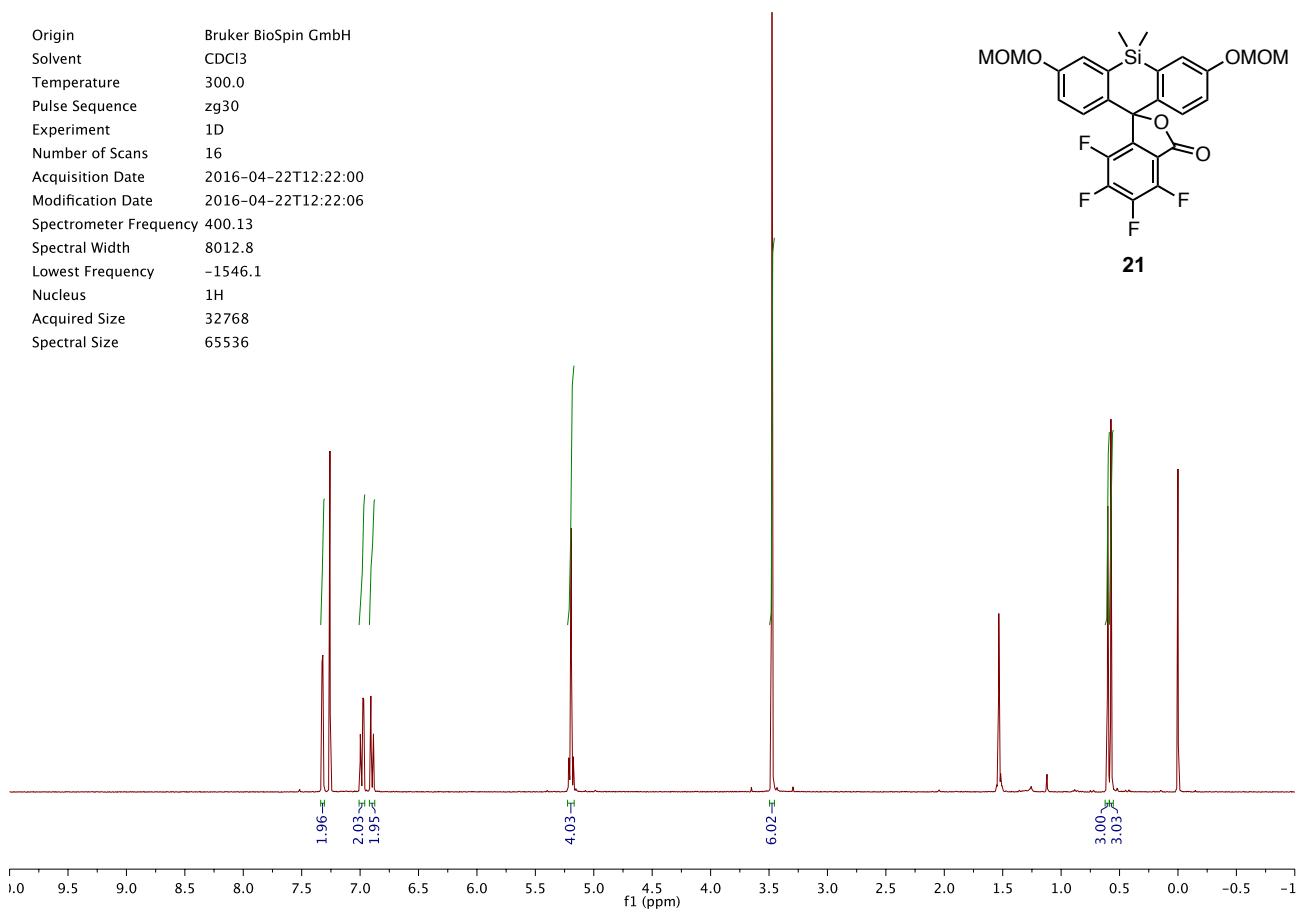
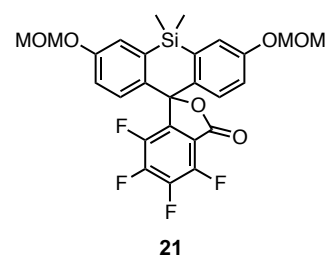
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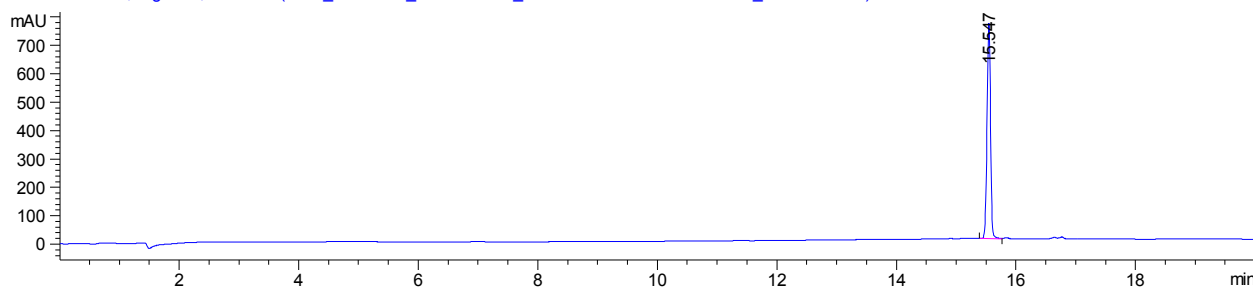
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 Nucleus ¹H
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 Spectral Size 65536



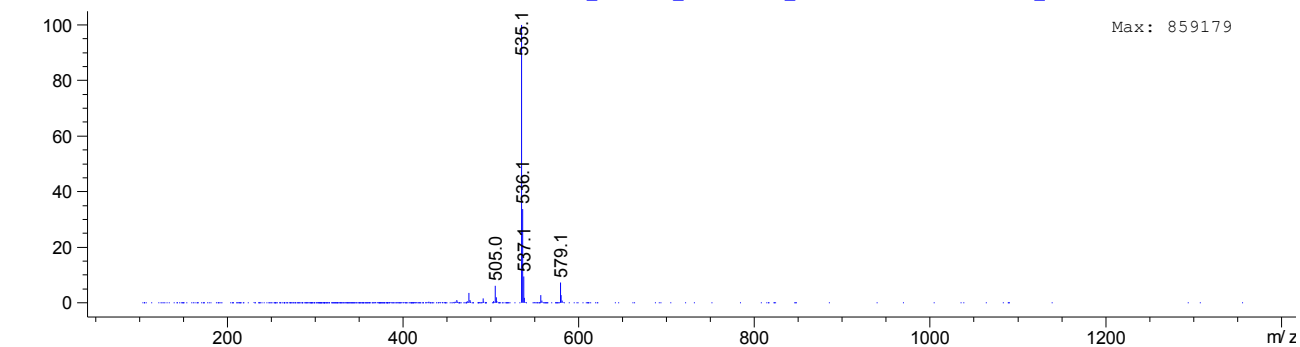
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 Solvent CDCl₃
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 Experiment 1D
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 Lowest Frequency -1546.1
 Nucleus ¹H
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 Spectral Size 65536



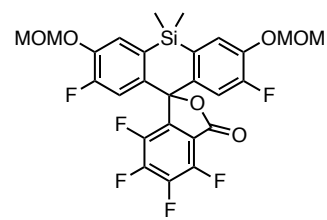
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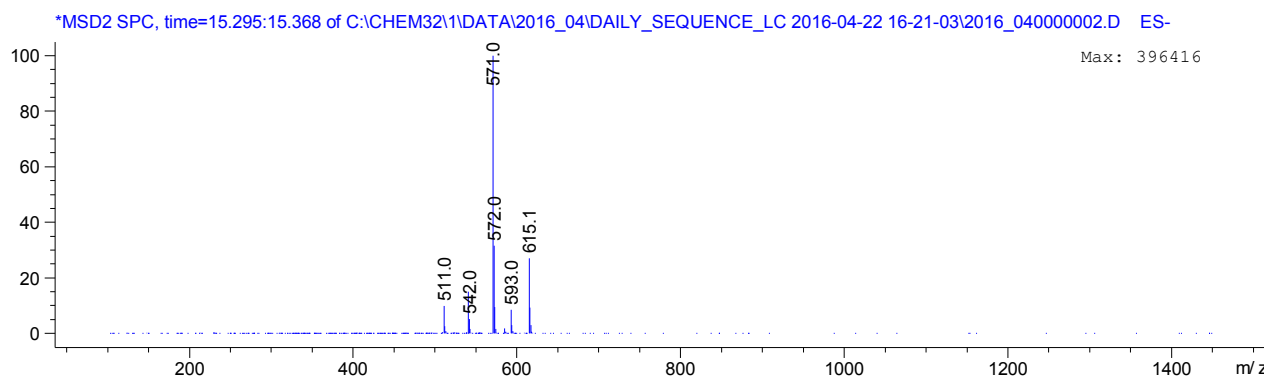
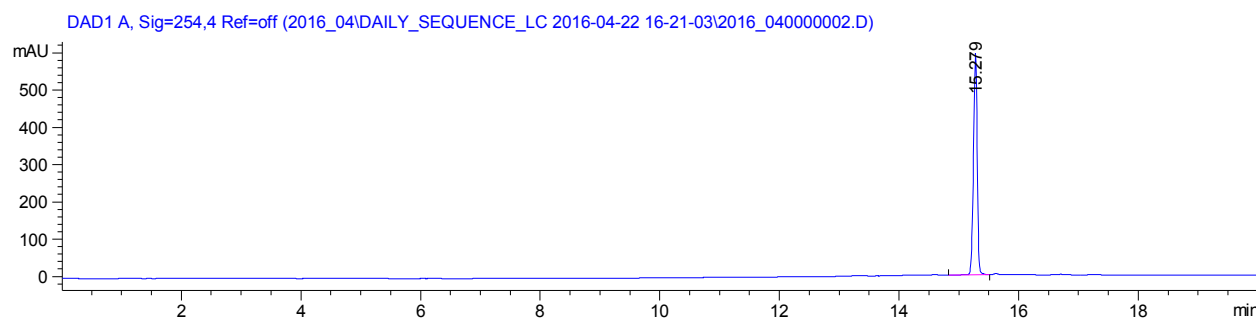
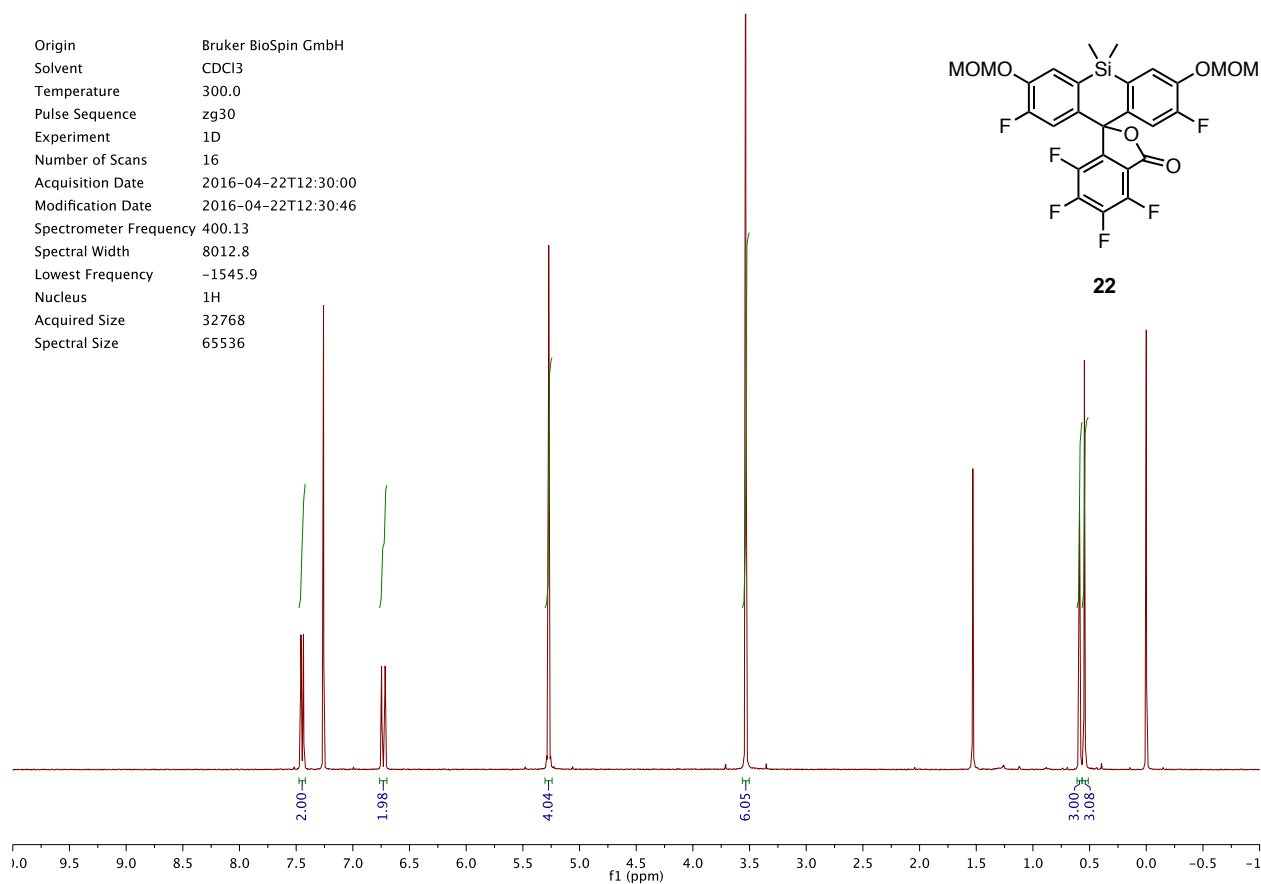
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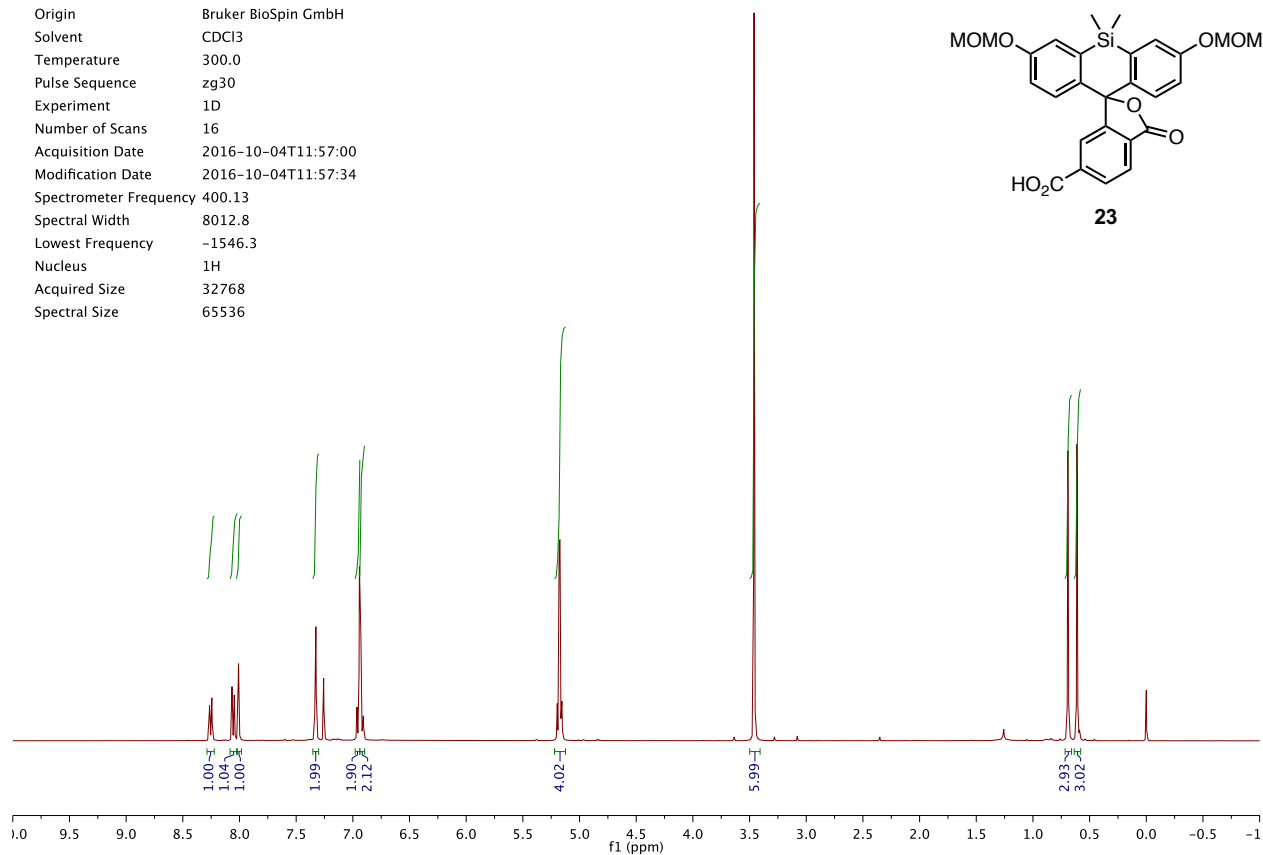
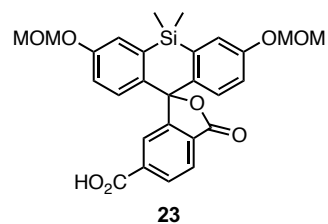
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 Spectral Width 8012.8
 Lowest Frequency -1545.9
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



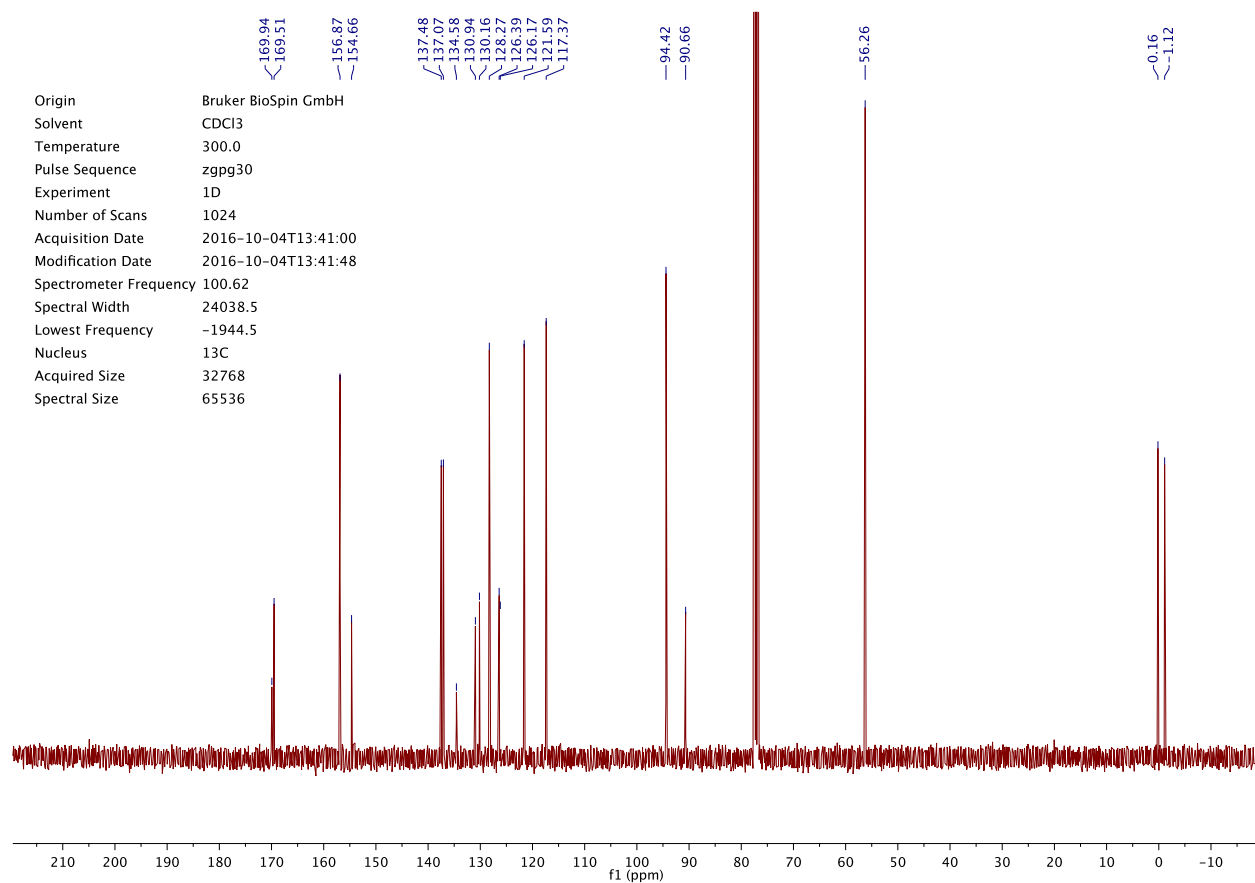
22



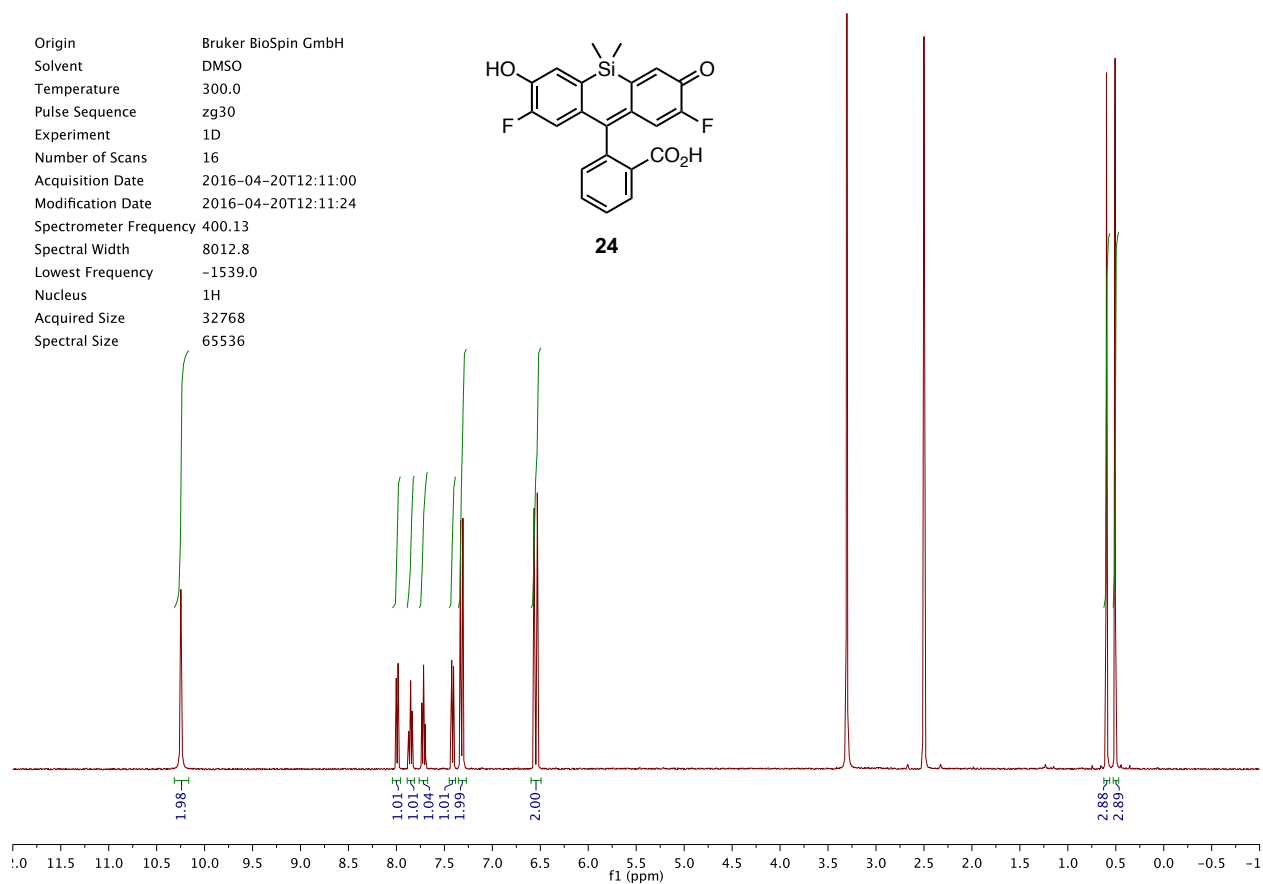
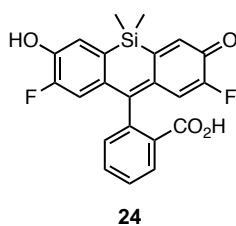
Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-10-04T11:57:00
 Modification Date 2016-10-04T11:57:34
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1546.3
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



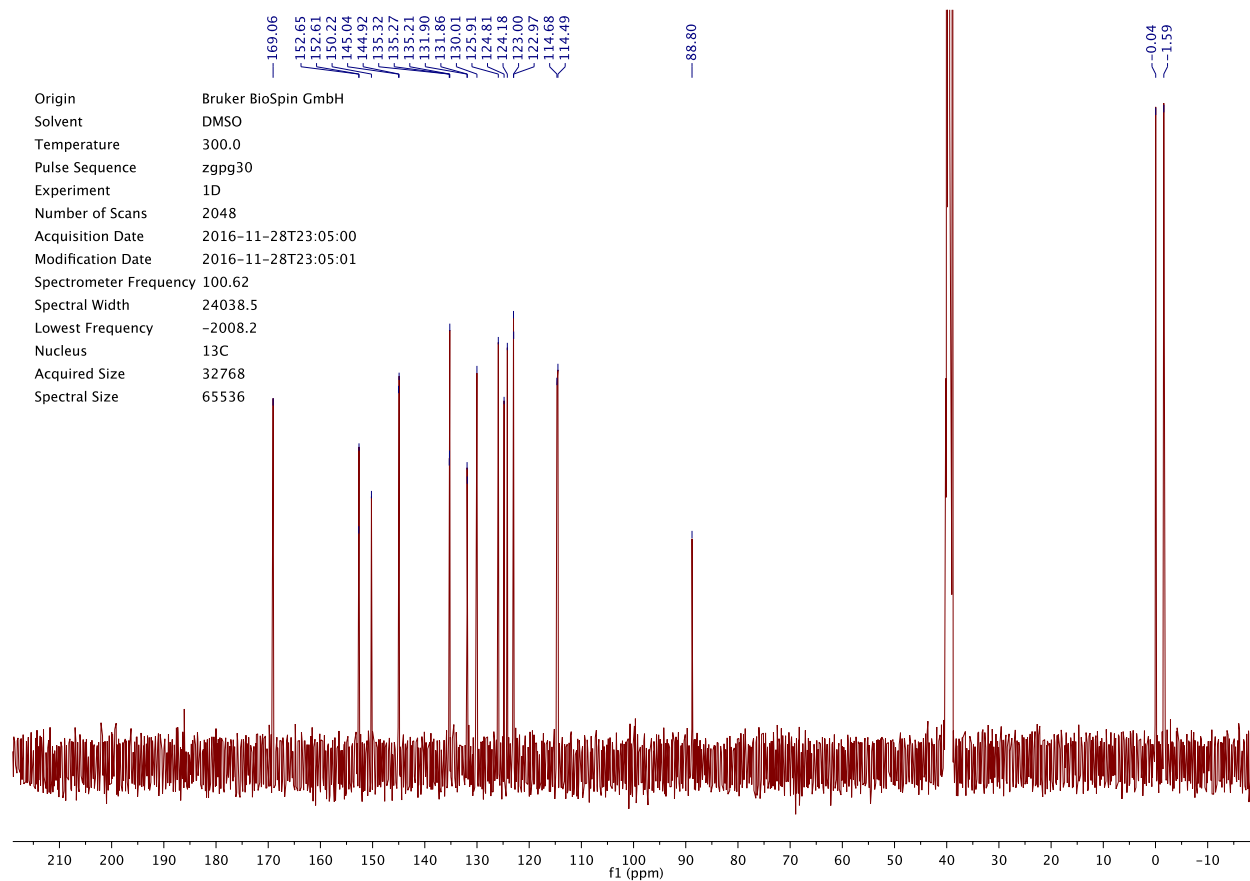
Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 1024
 Acquisition Date 2016-10-04T13:41:00
 Modification Date 2016-10-04T13:41:48
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1944.5
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

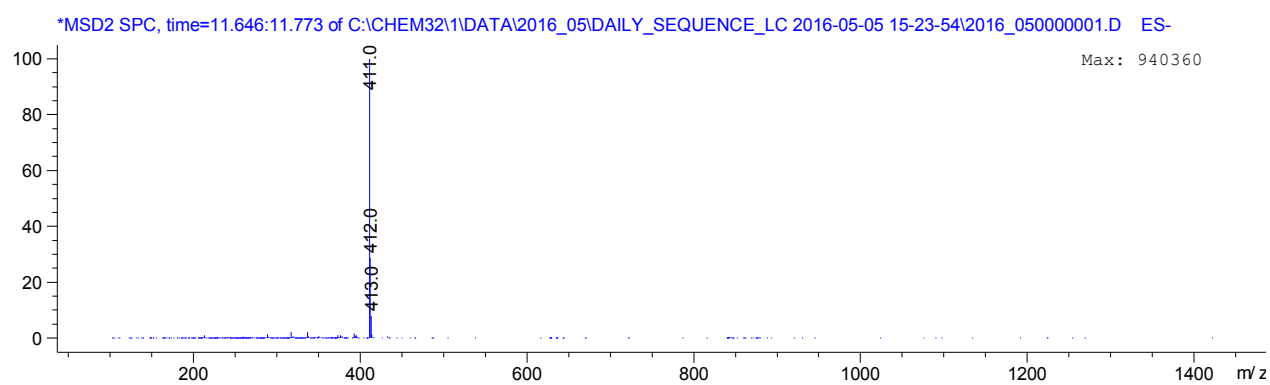
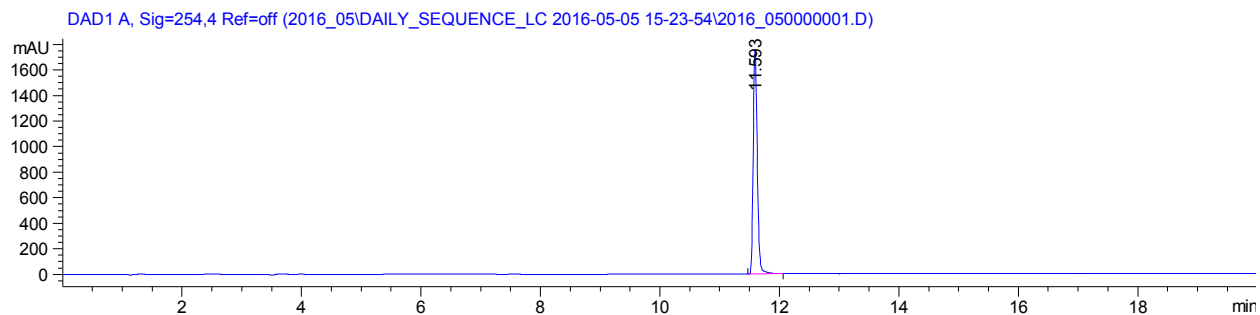
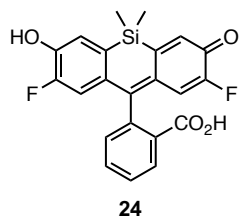


Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-04-20T12:11:00
 Modification Date 2016-04-20T12:11:24
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1539.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536

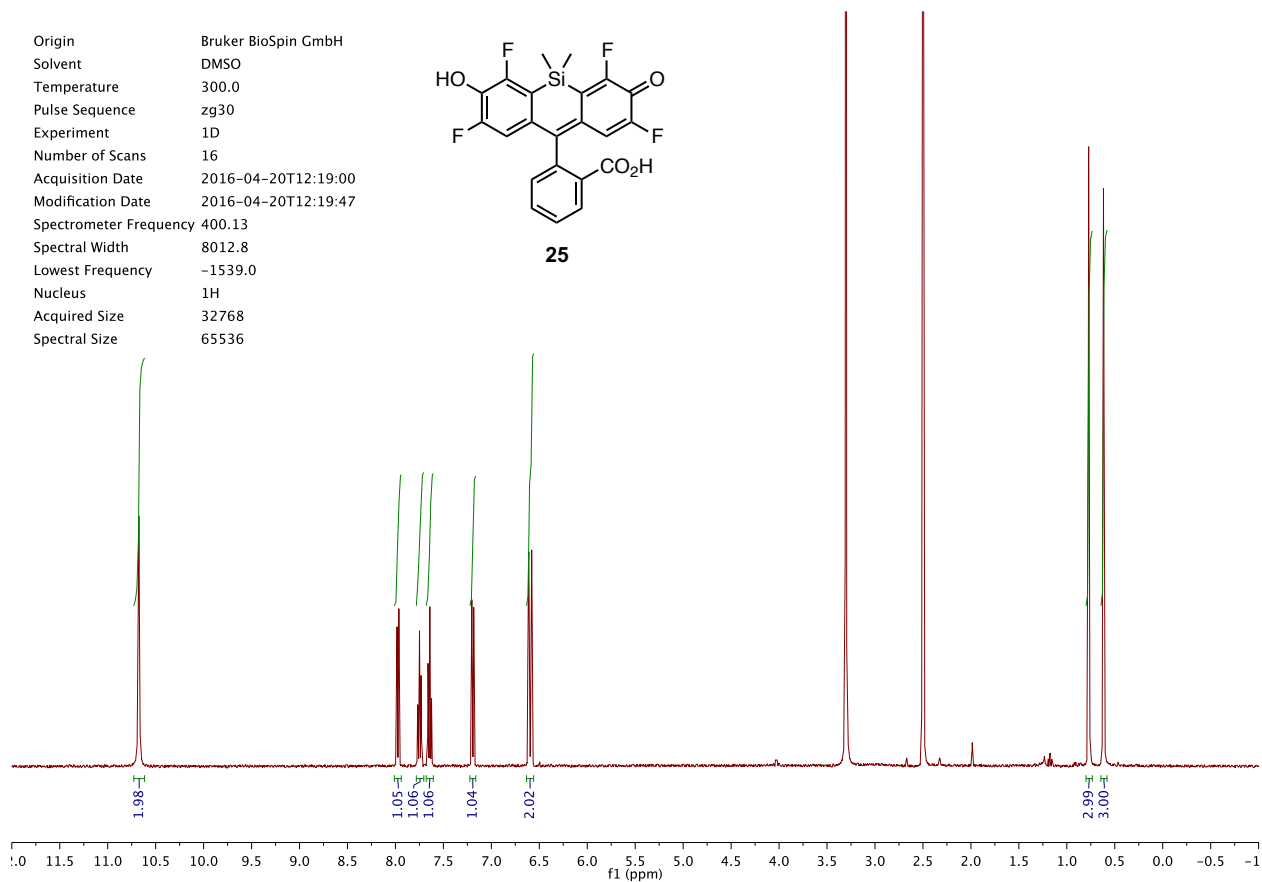
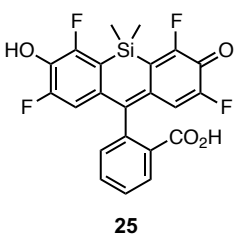


Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-28T23:05:00
 Modification Date 2016-11-28T23:05:01
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -2008.2
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

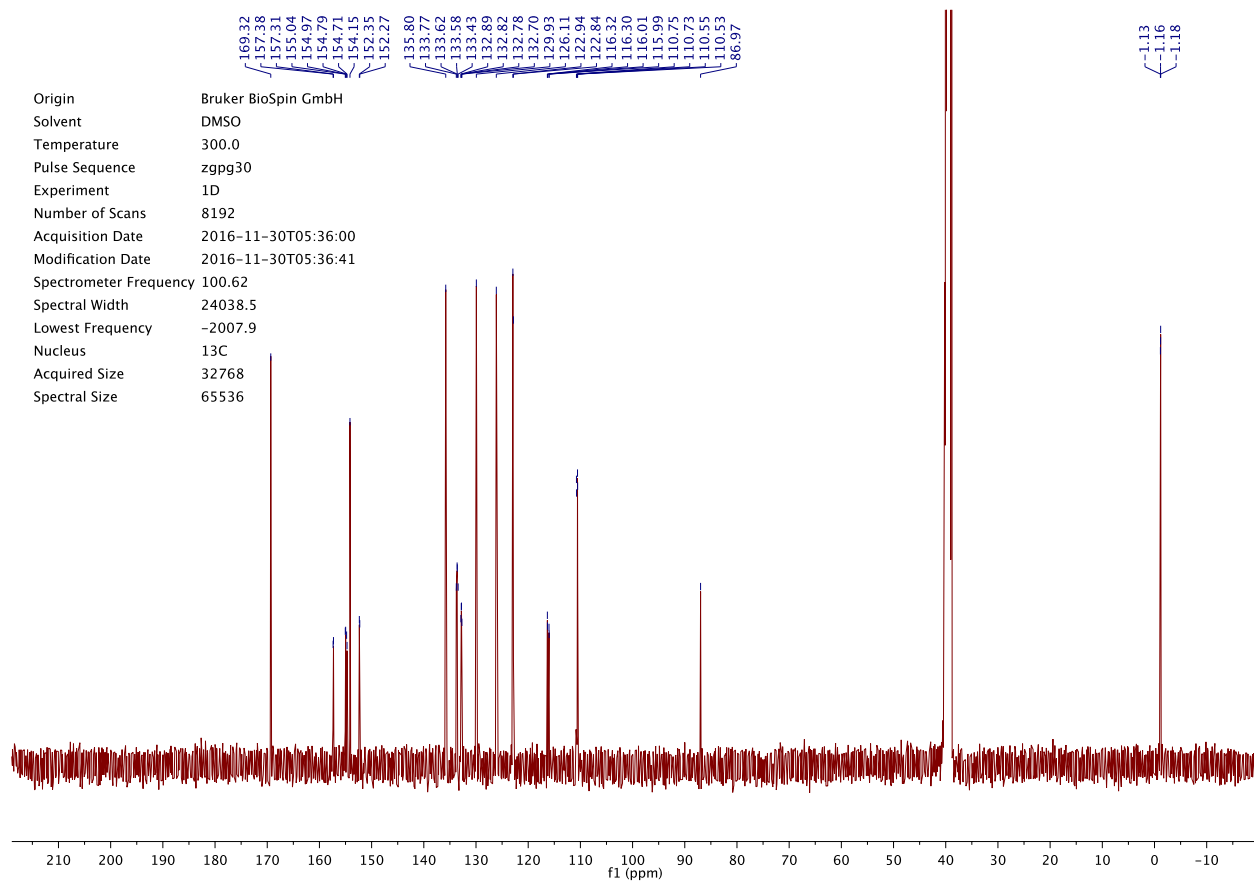


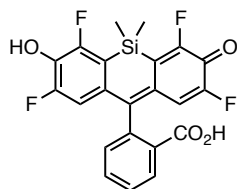


Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-04-20T12:19:00
 Modification Date 2016-04-20T12:19:47
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1539.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536

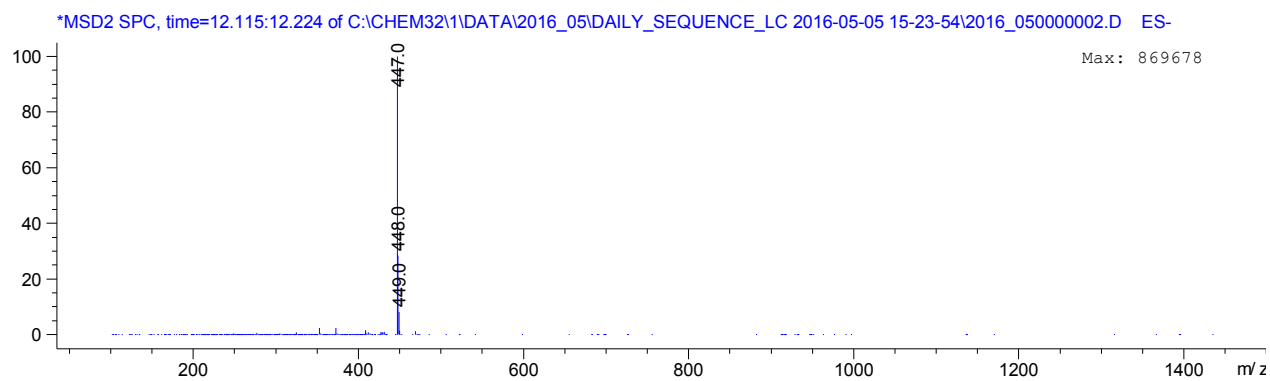
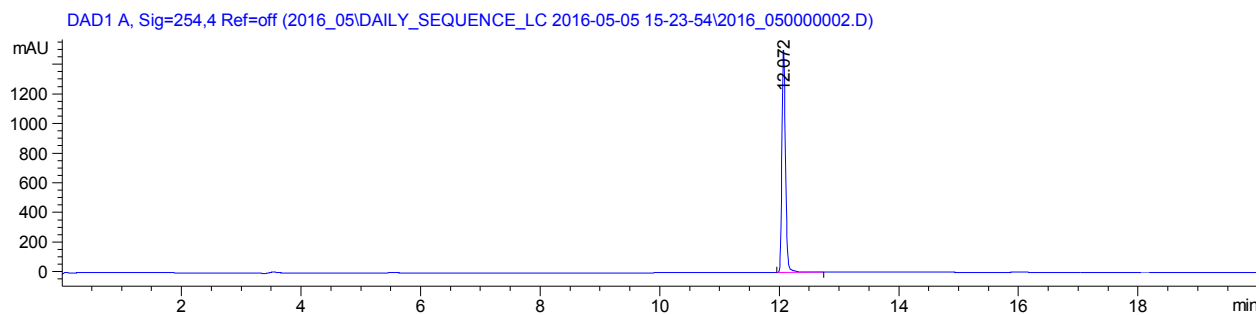


Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 8192
 Acquisition Date 2016-11-30T05:36:00
 Modification Date 2016-11-30T05:36:41
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -2007.9
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

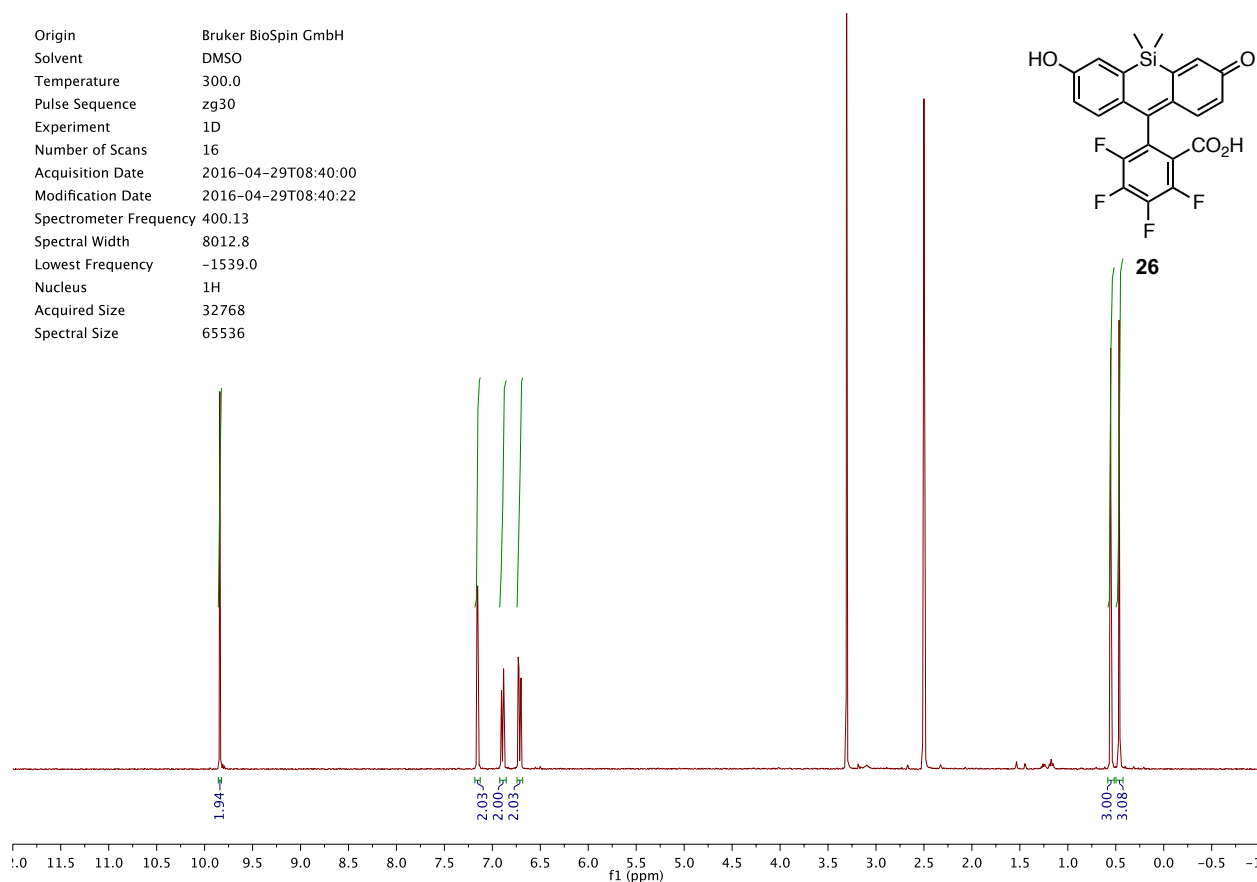
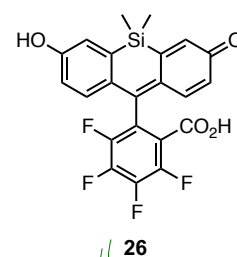




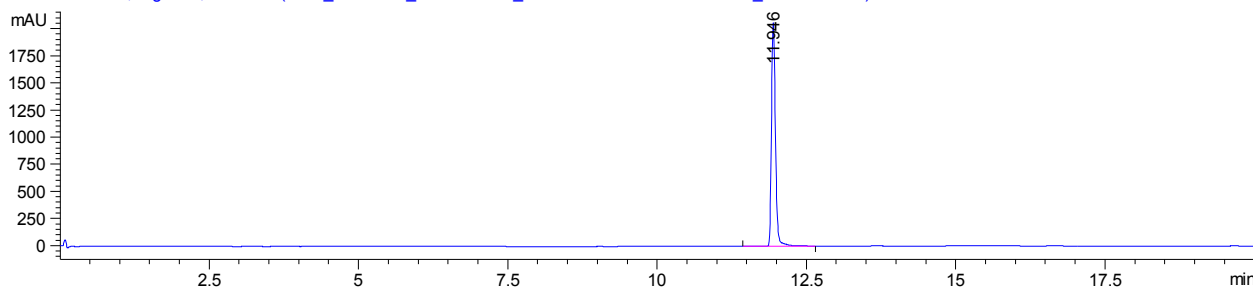
25



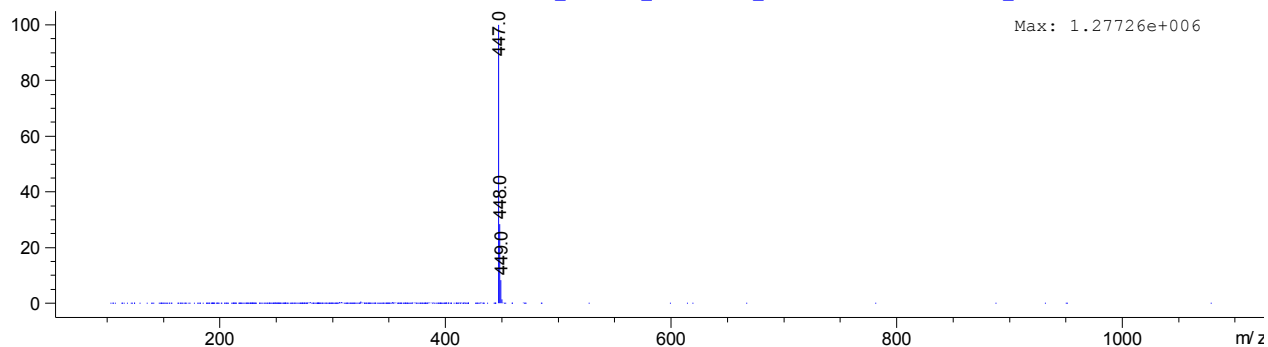
Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-04-29T08:40:00
 Modification Date 2016-04-29T08:40:22
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1539.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



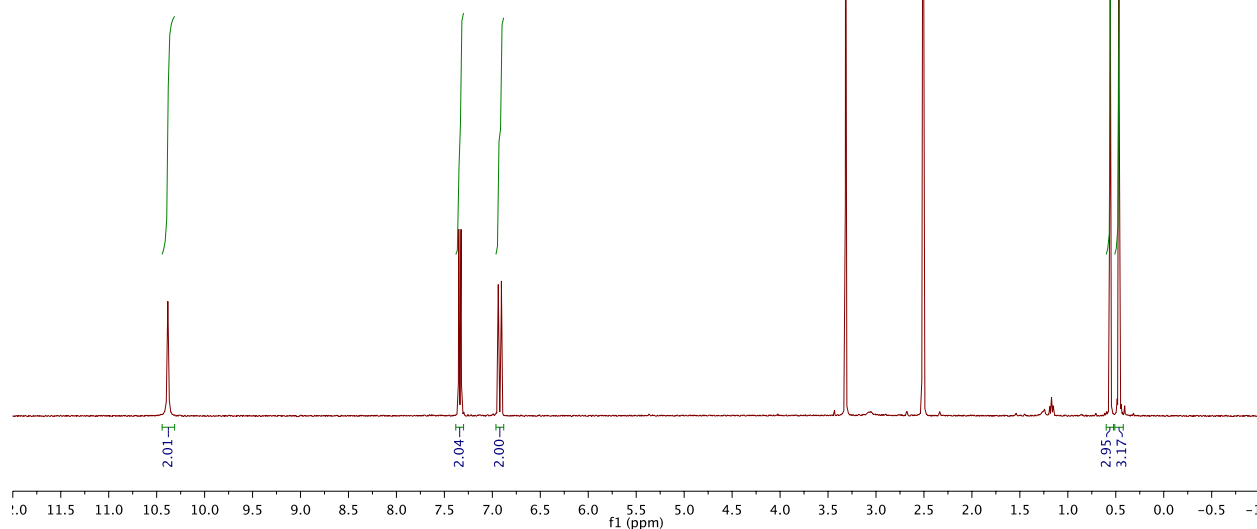
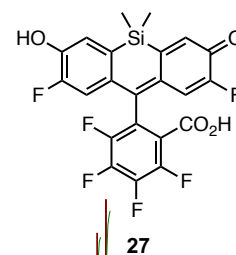
DAD1 A, Sig=254,4 Ref=off (2016_05/DAILY_SEQUENCE_LC 2016-05-05 15-23-54/2016_050000003.D)



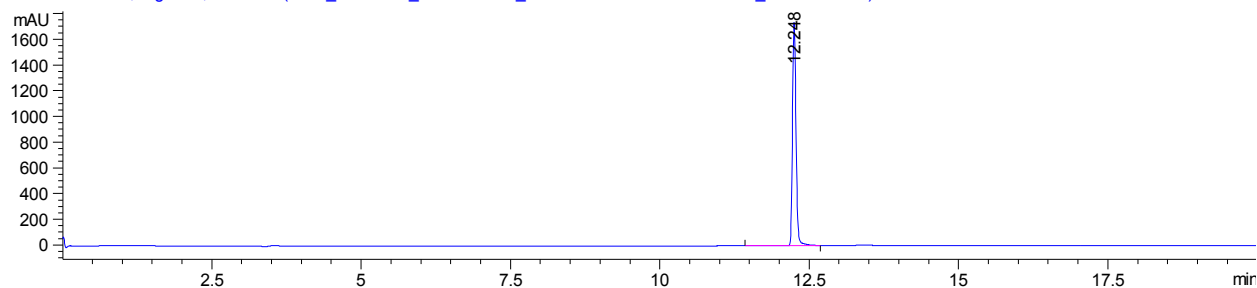
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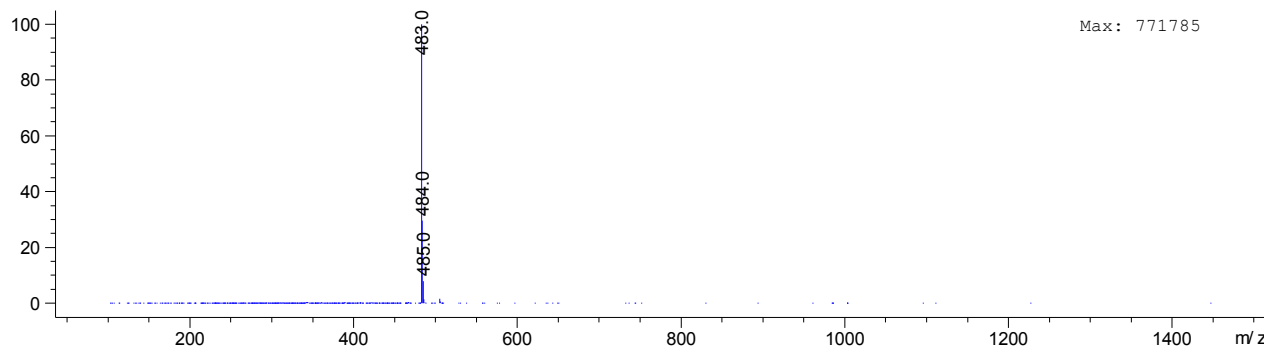
Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-04-29T08:44:00
 Modification Date 2016-04-29T08:44:40
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1535.4
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



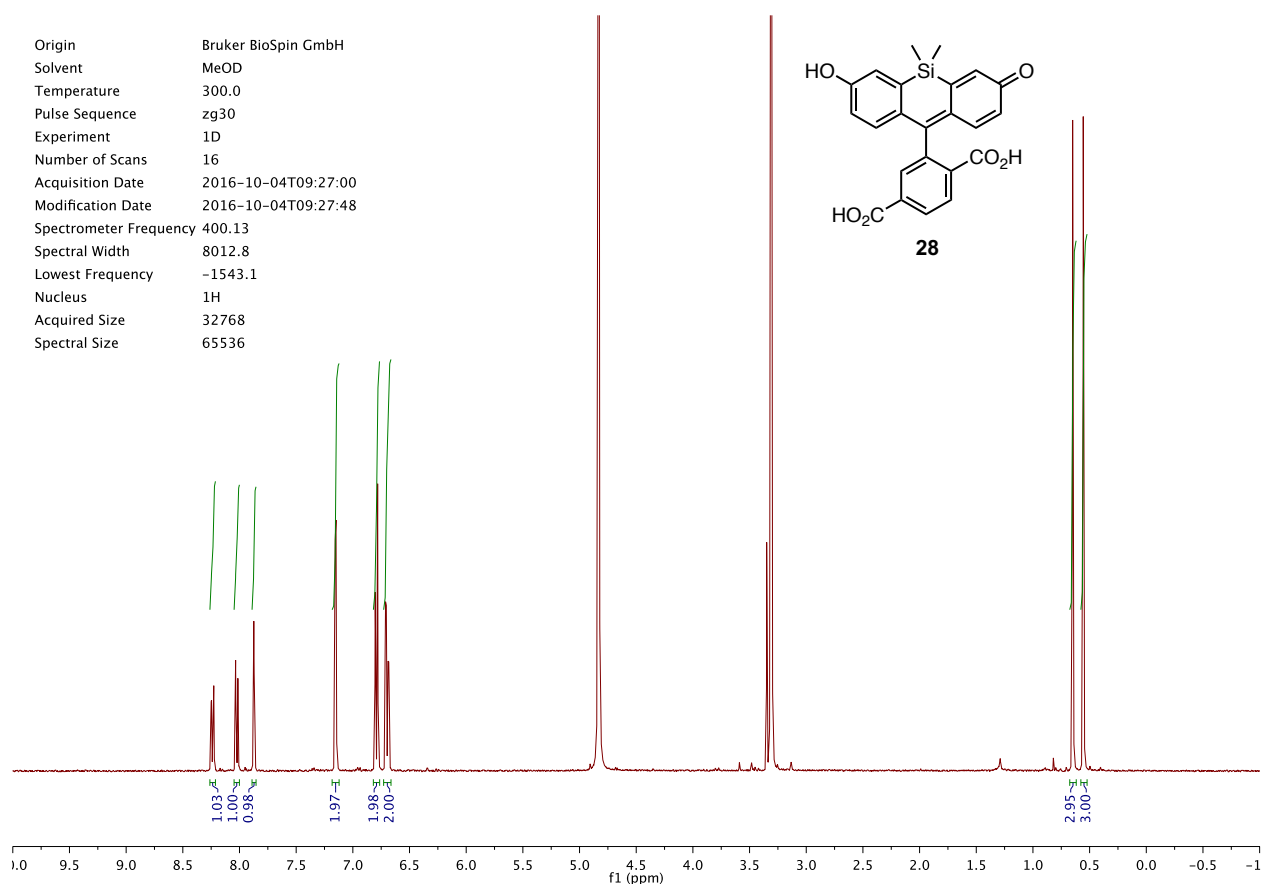
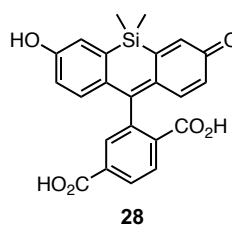
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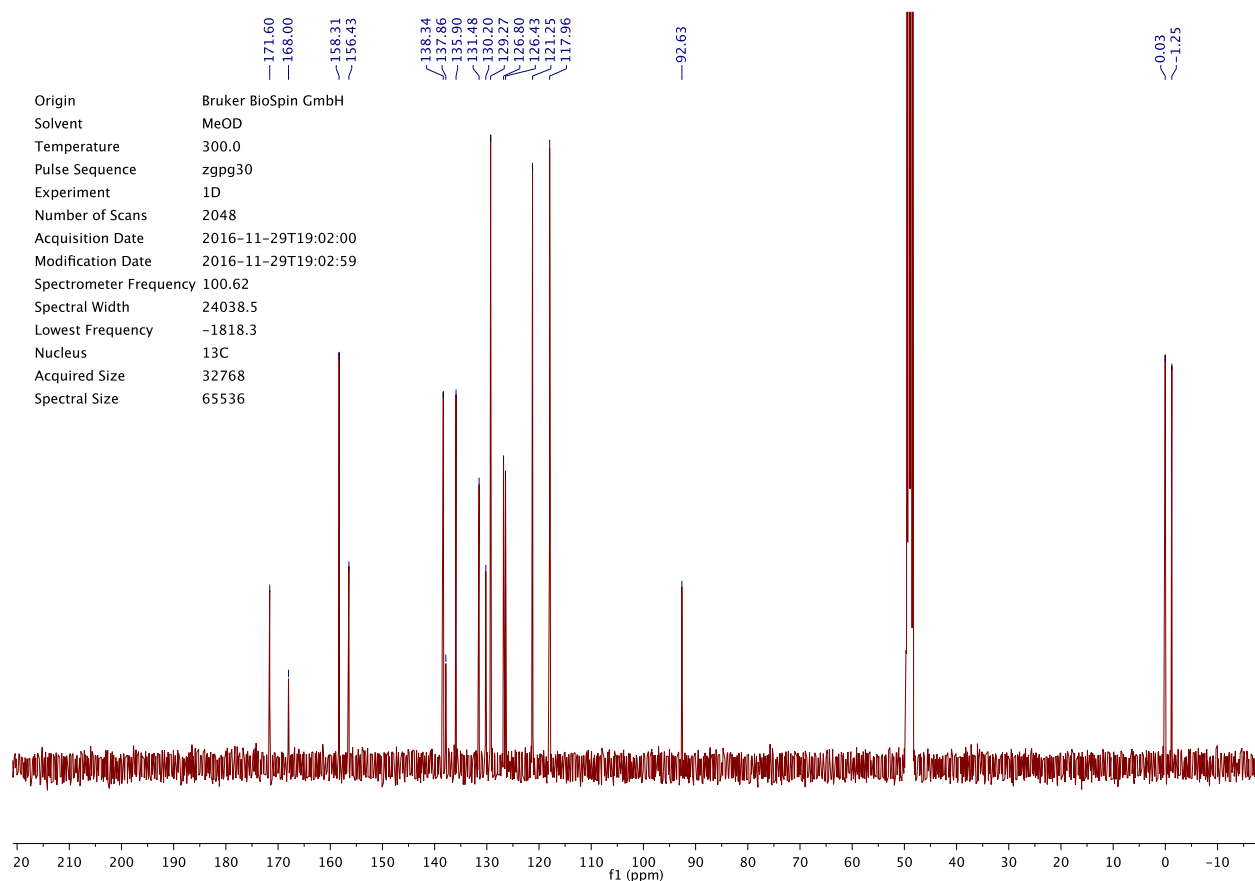
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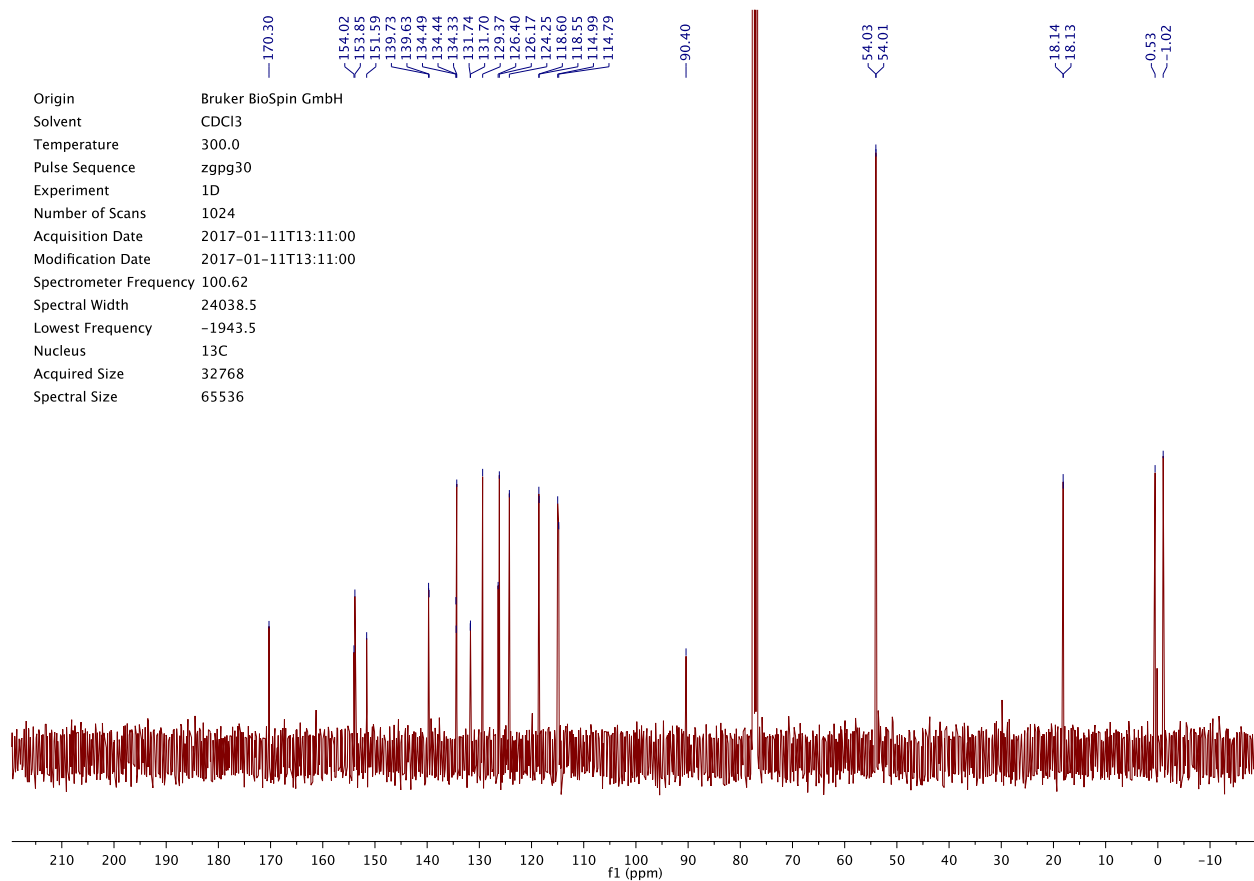
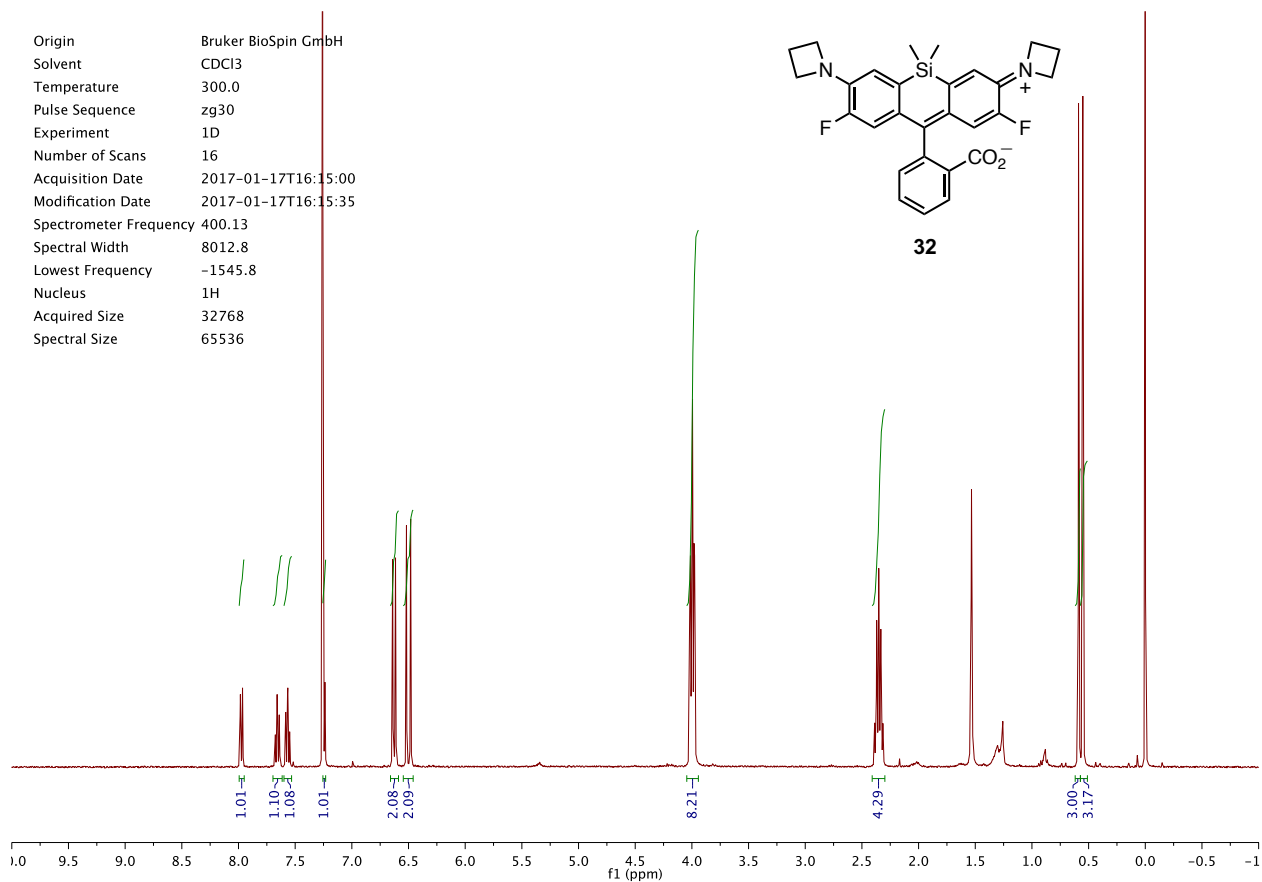


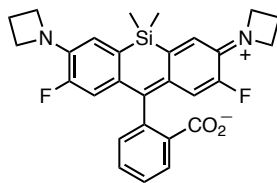
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-10-04T09:27:00
 Modification Date 2016-10-04T09:27:48
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.1
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-29T19:02:00
 Modification Date 2016-11-29T19:02:59
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1818.3
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

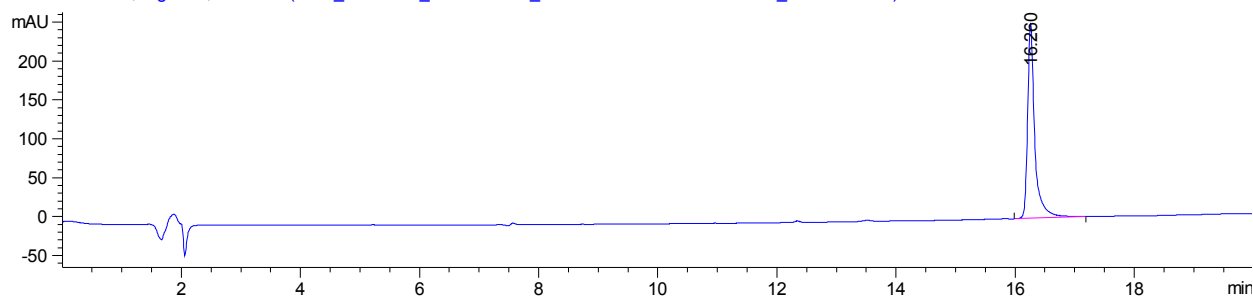




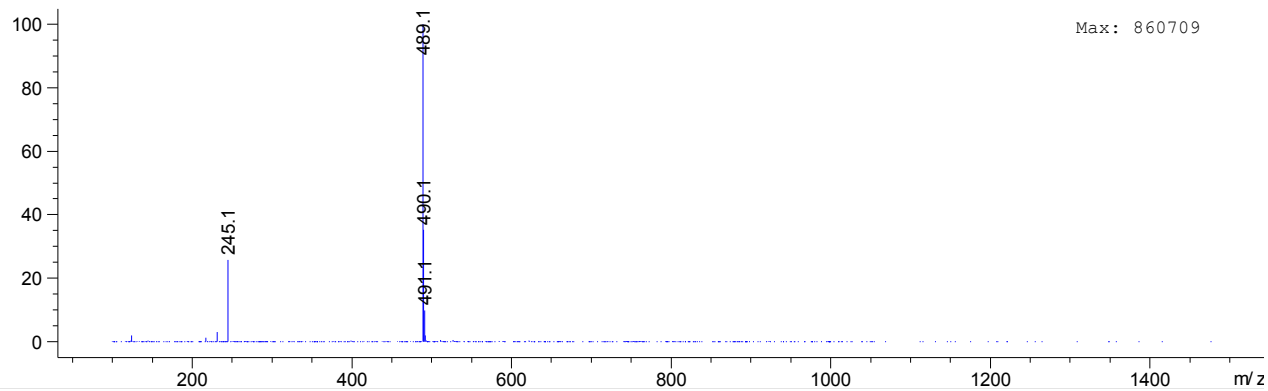


32

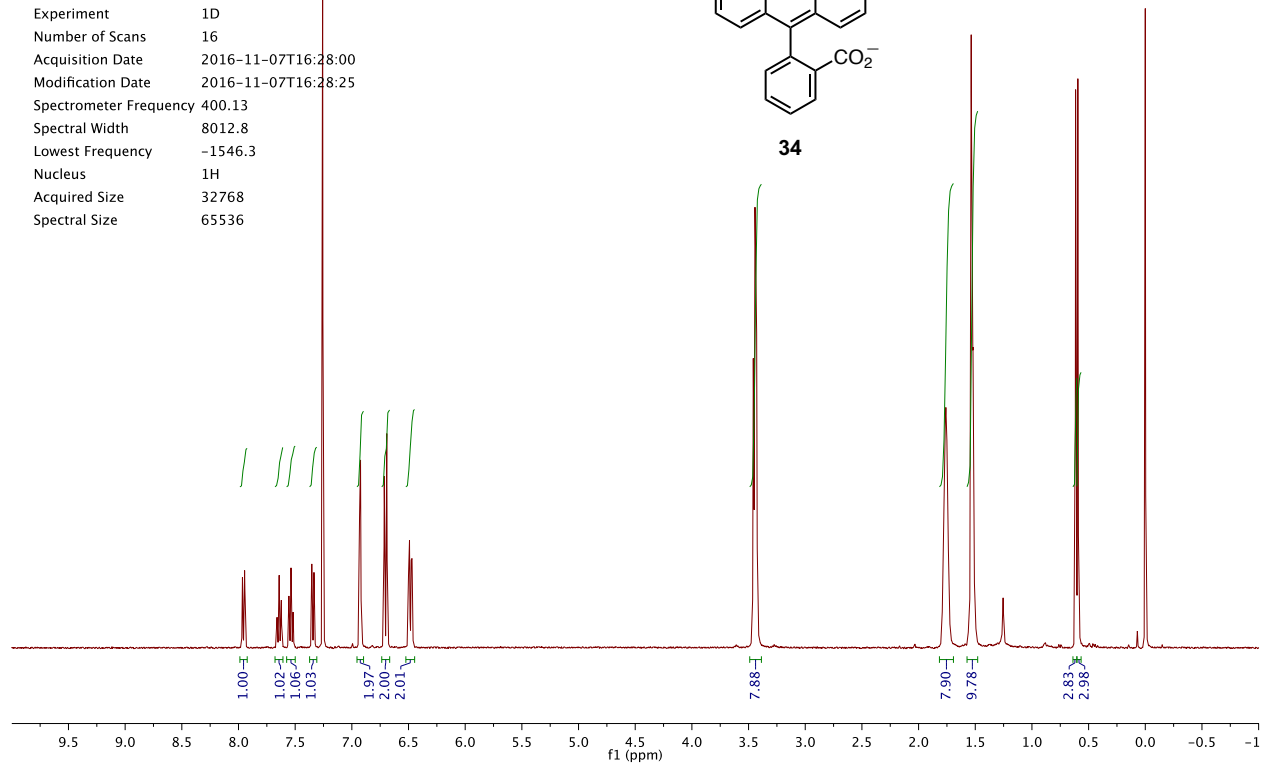
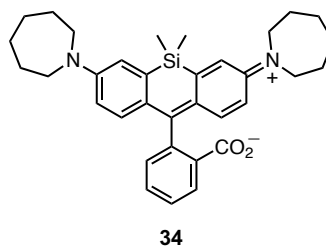
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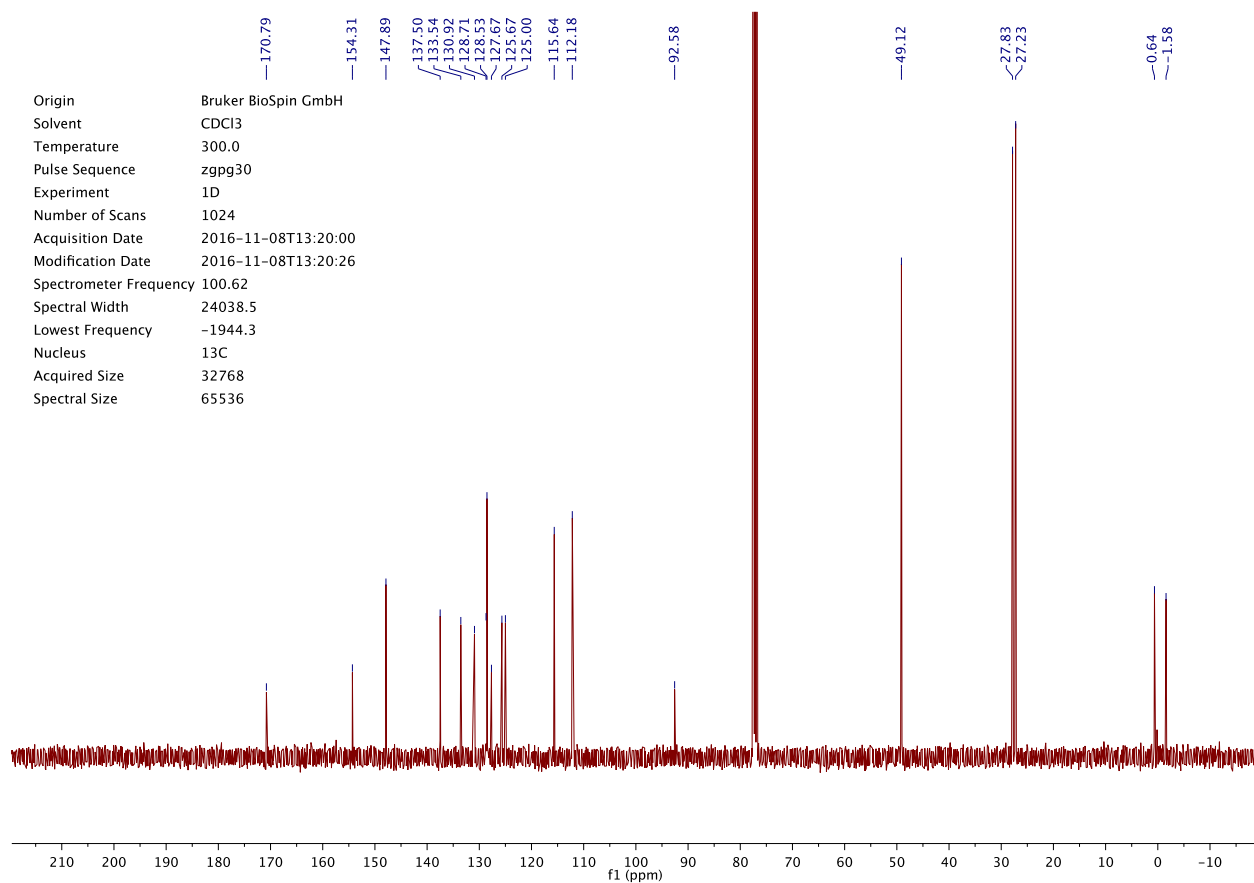
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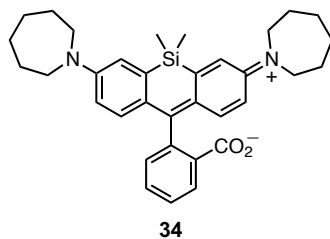


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-11-07T16:28:00
 Modification Date 2016-11-07T16:28:25
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1546.3
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

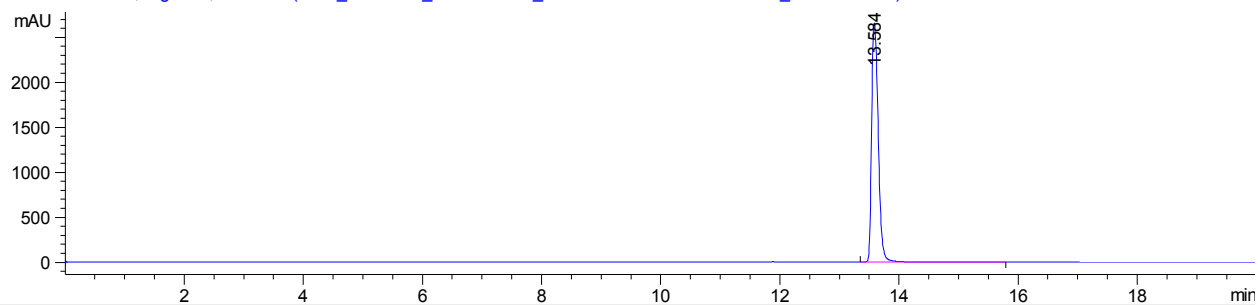


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 1024
 Acquisition Date 2016-11-08T13:20:00
 Modification Date 2016-11-08T13:20:26
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1944.3
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

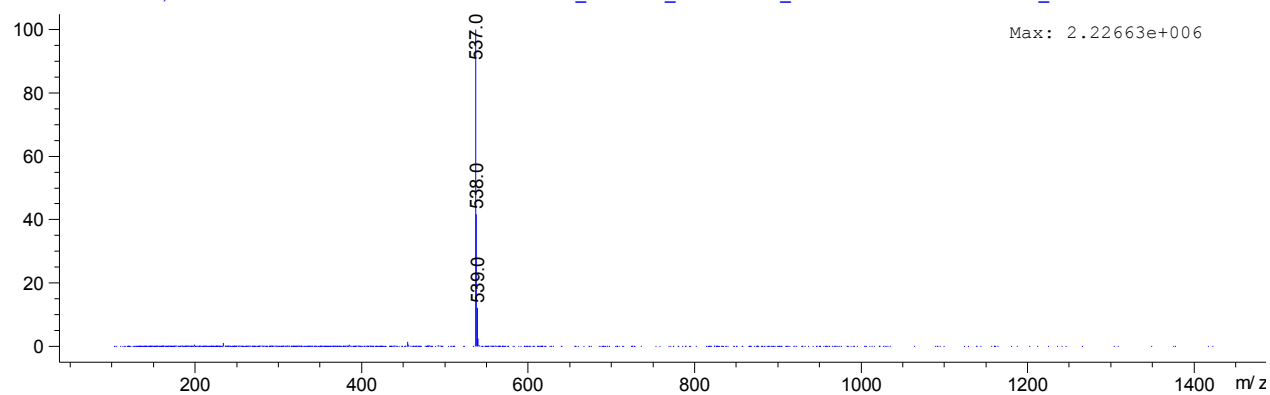




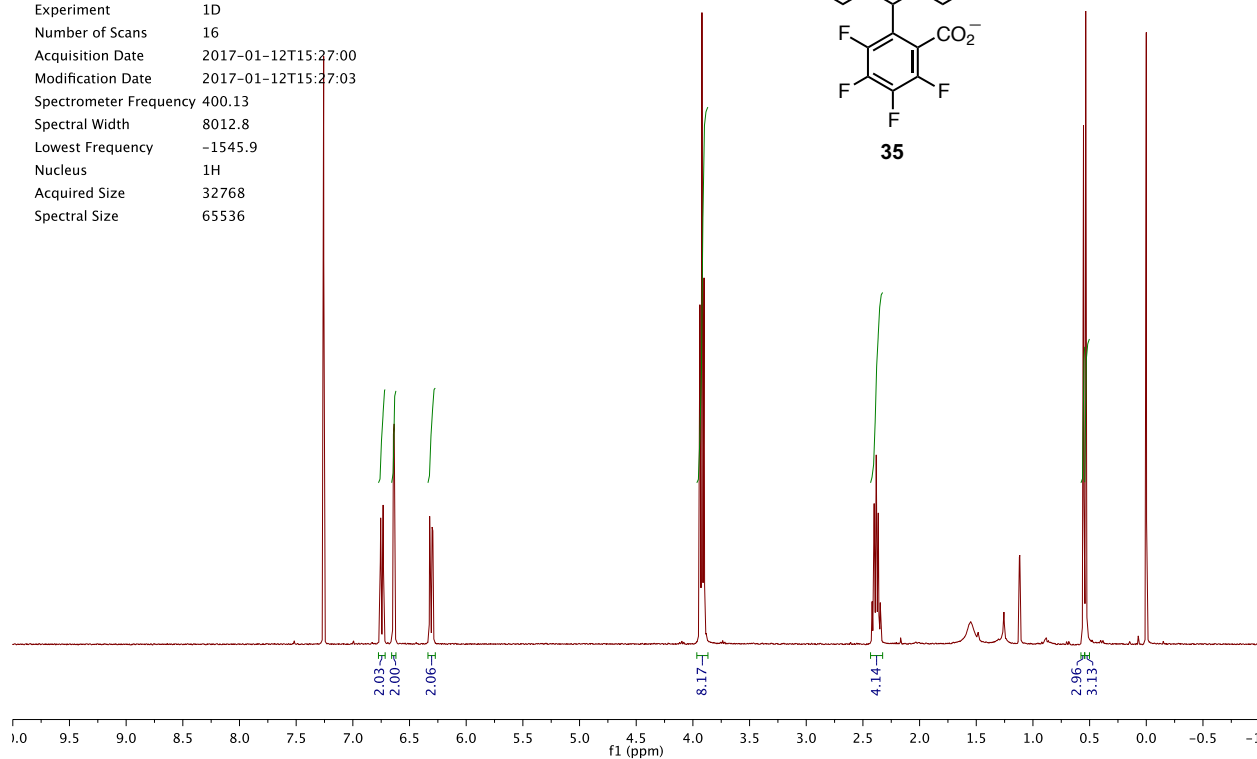
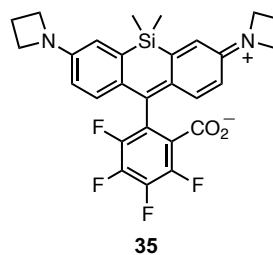
DAD1 E, Sig=650,4 Ref=off (2016_10\DAIY_SEQUENCE_LC 2016-11-04 13-18-38\2016_100000002.D)



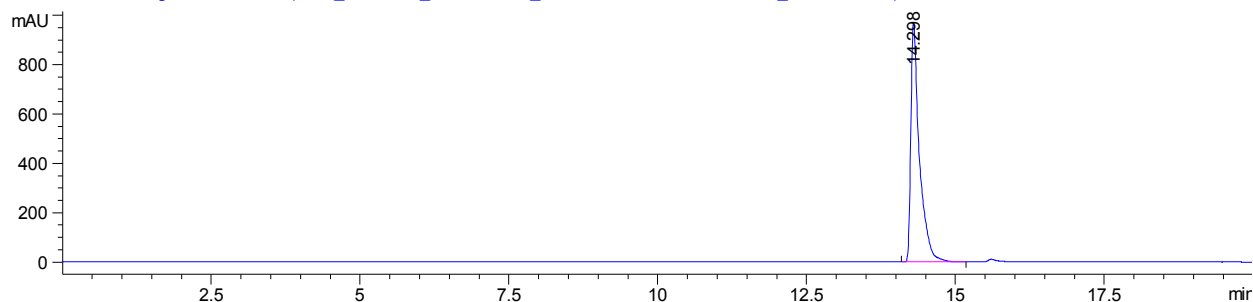
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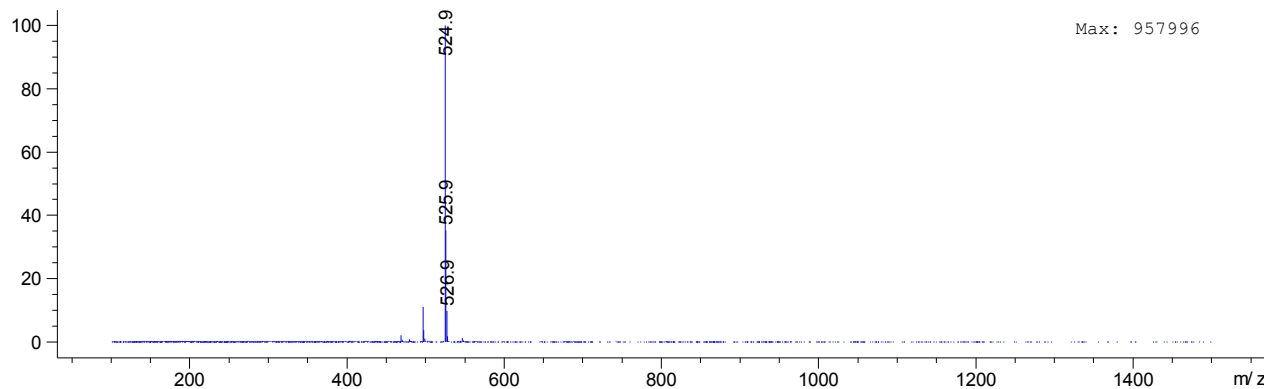
Origin Bruker BioSpin GmbH
 Solvent CDCl3
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-12T15:27:00
 Modification Date 2017-01-12T15:27:03
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1545.9
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



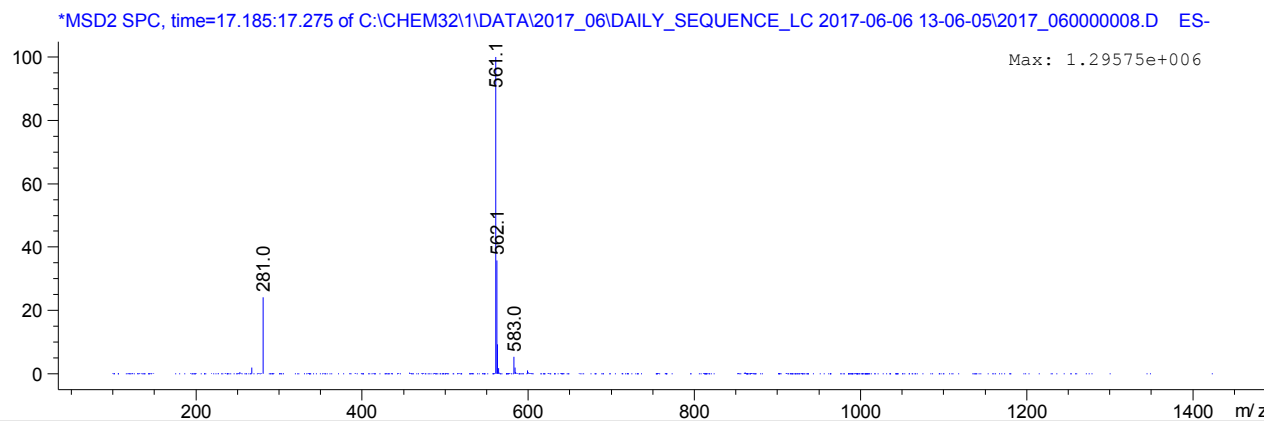
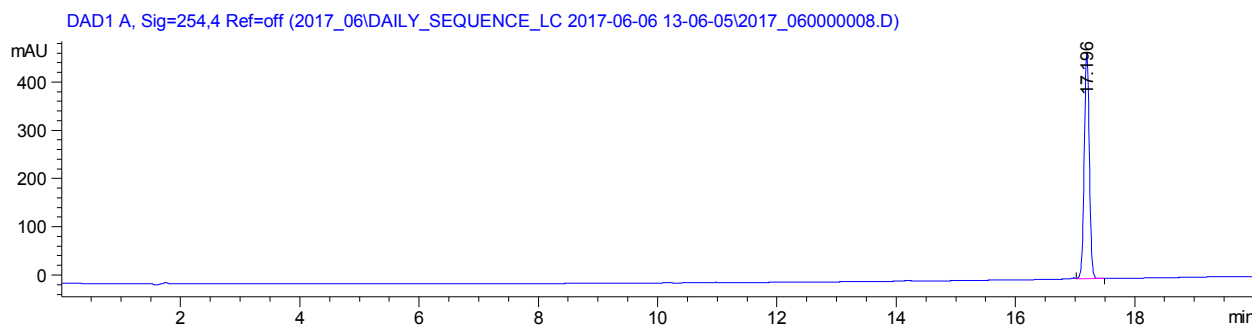
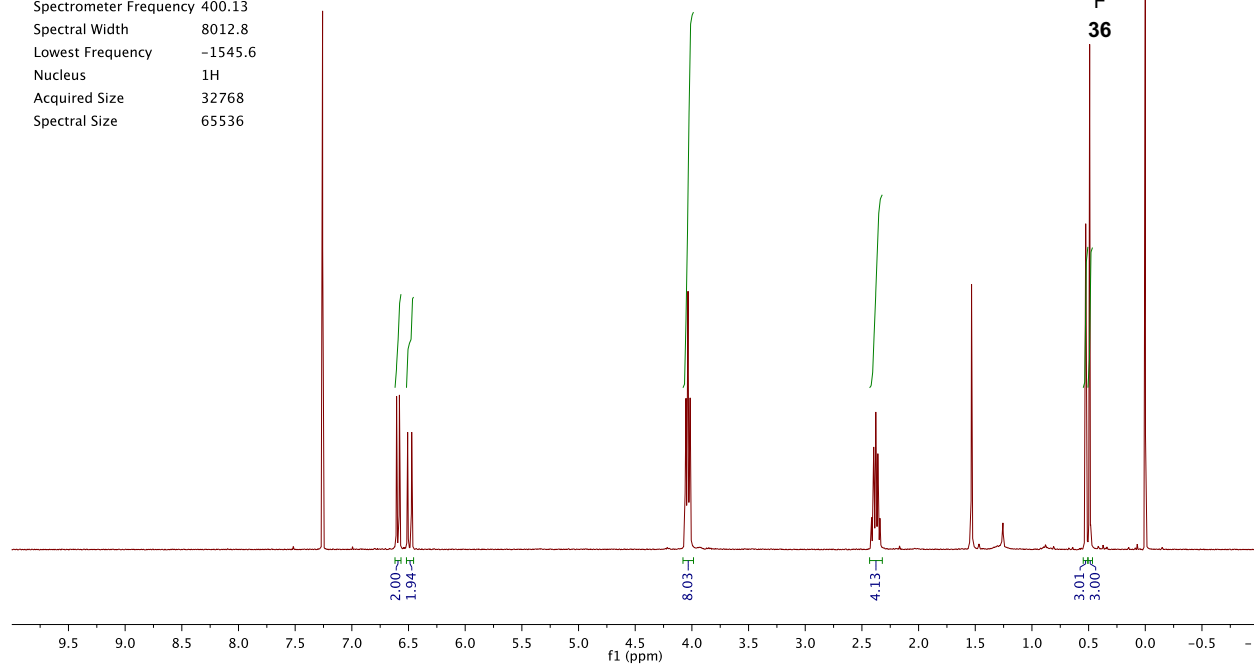
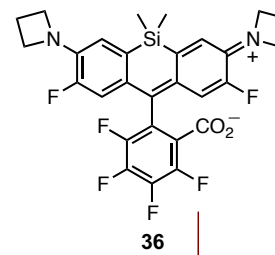
DAD1 E, Sig=650,4 Ref=off (2016_11\DAIY_SEQUENCE_LC 2016-11-23 11-45-02\2016_110000022.D)



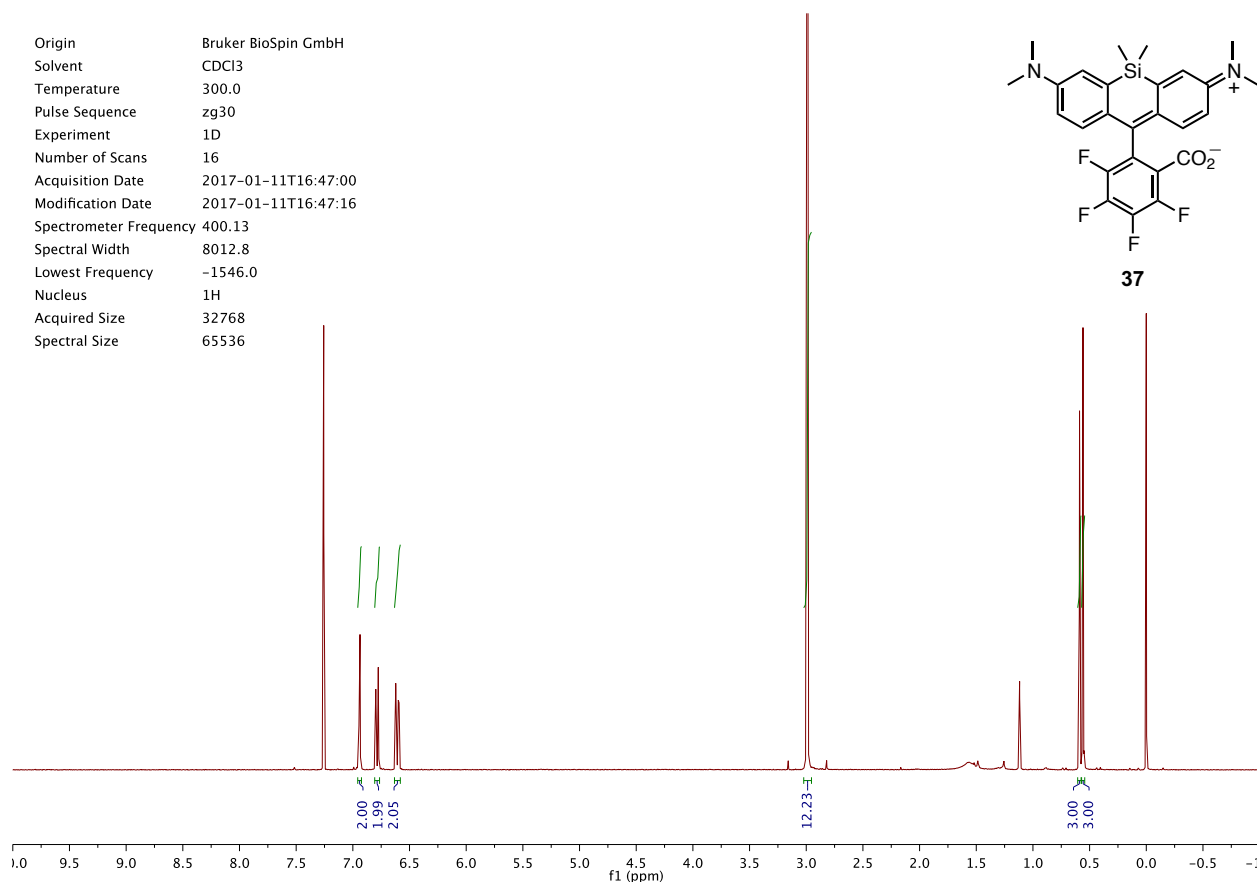
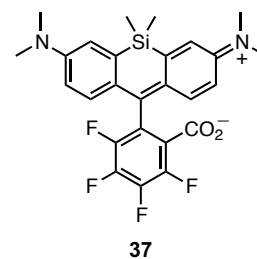
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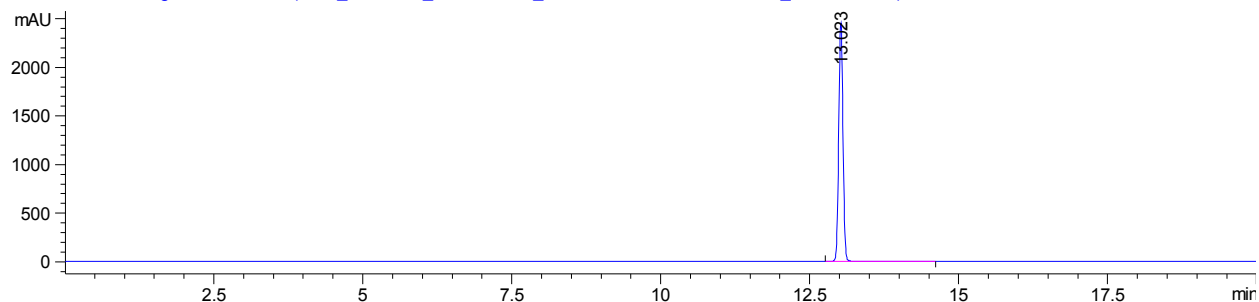
Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-12T15:35:00
 Modification Date 2017-01-12T15:35:53
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1545.6
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



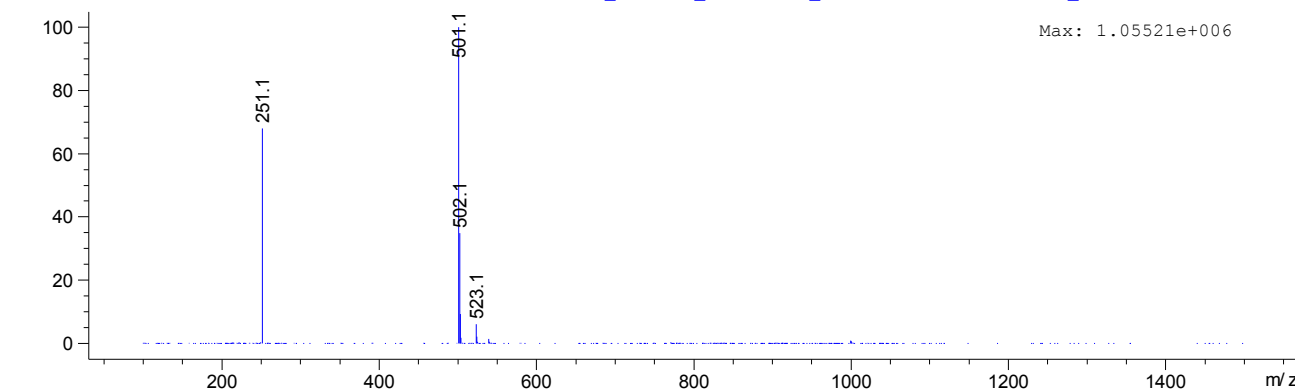
Origin Bruker BioSpin GmbH
 Solvent CDCl3
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-11T16:47:00
 Modification Date 2017-01-11T16:47:16
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1546.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



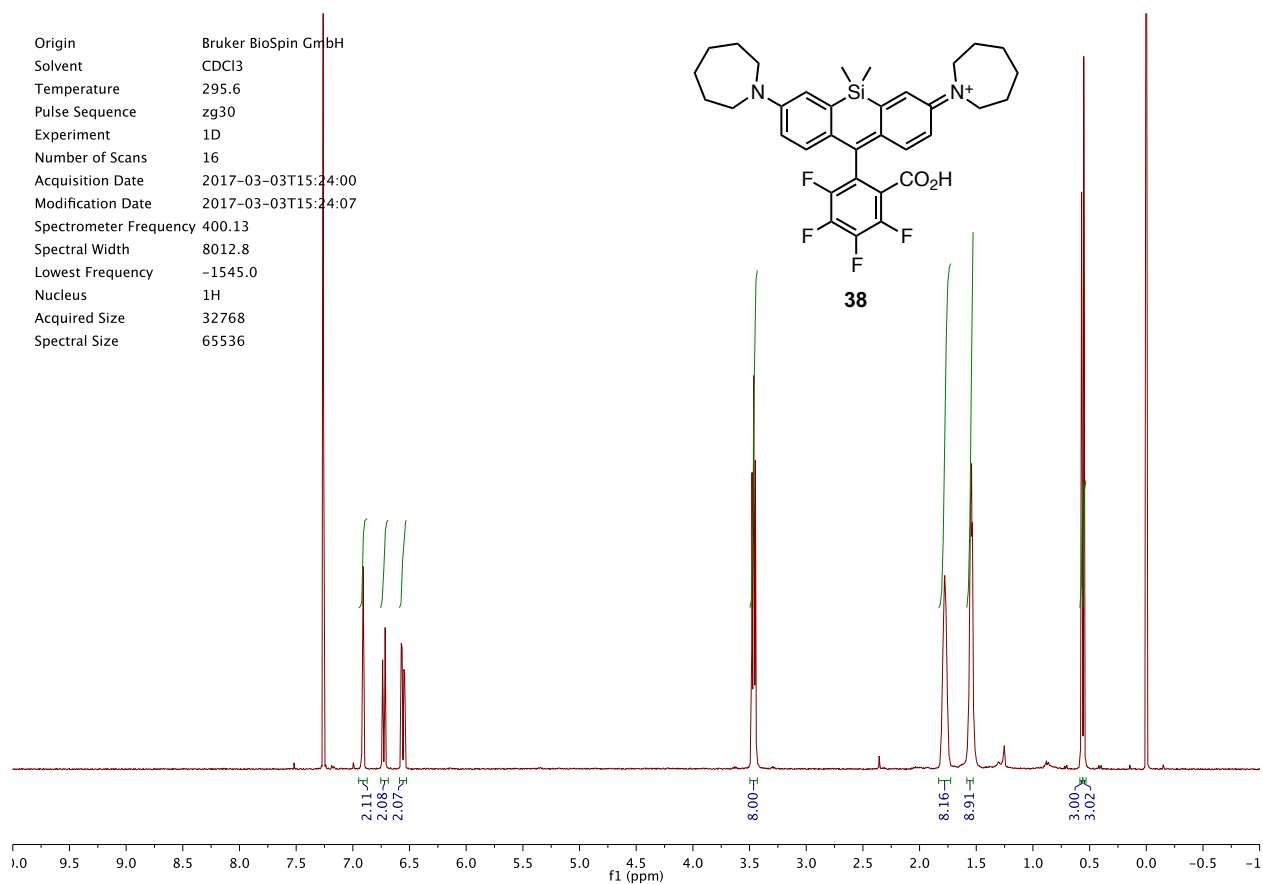
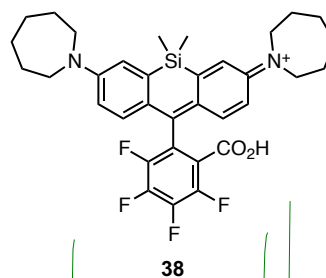
DAD1 E, Sig=650.4 Ref=off (2017_06\DAIY_SEQUENCE_LC 2017-06-06 13-06-05\2017_060000002.D)



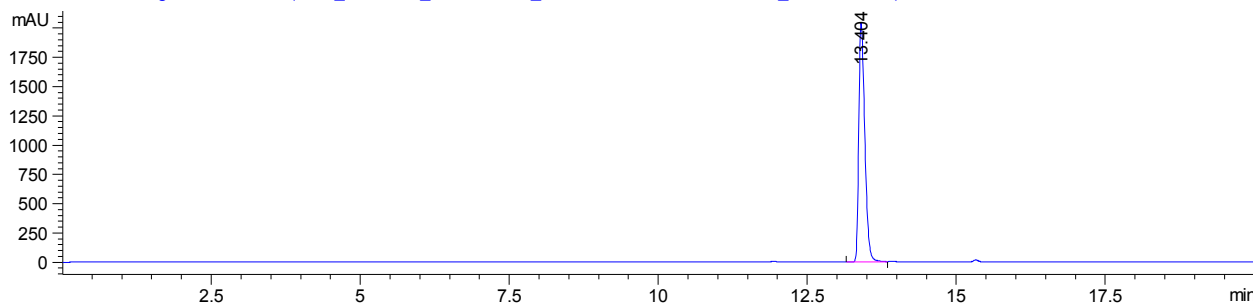
*MSD2 SPC, time=13.024:13.097 of C:\CHEM32\1\DATA\2017_06\DAIY_SEQUENCE_LC 2017-06-06 13-06-05\2017_060000002.D ES-



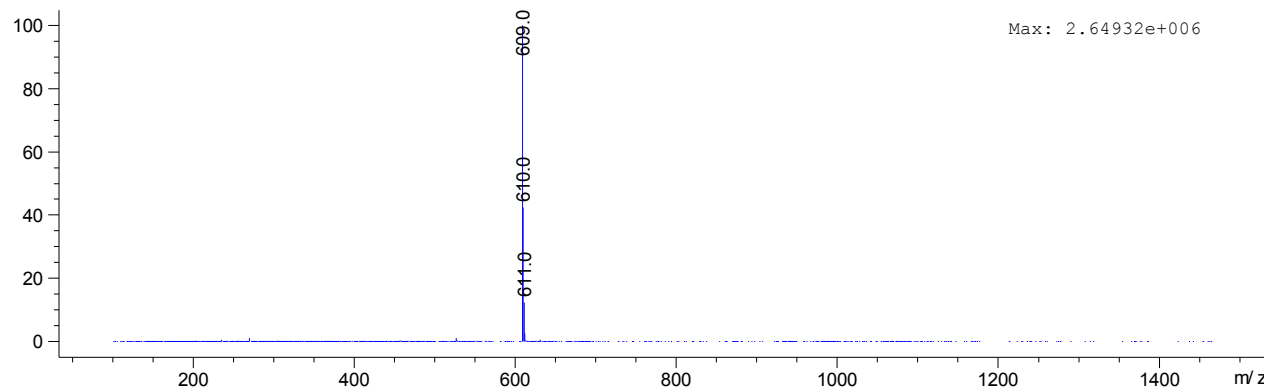
Origin Bruker BioSpin GmbH
 Solvent CDCl3
 Temperature 295.6
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-03-03T15:24:00
 Modification Date 2017-03-03T15:24:07
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1545.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



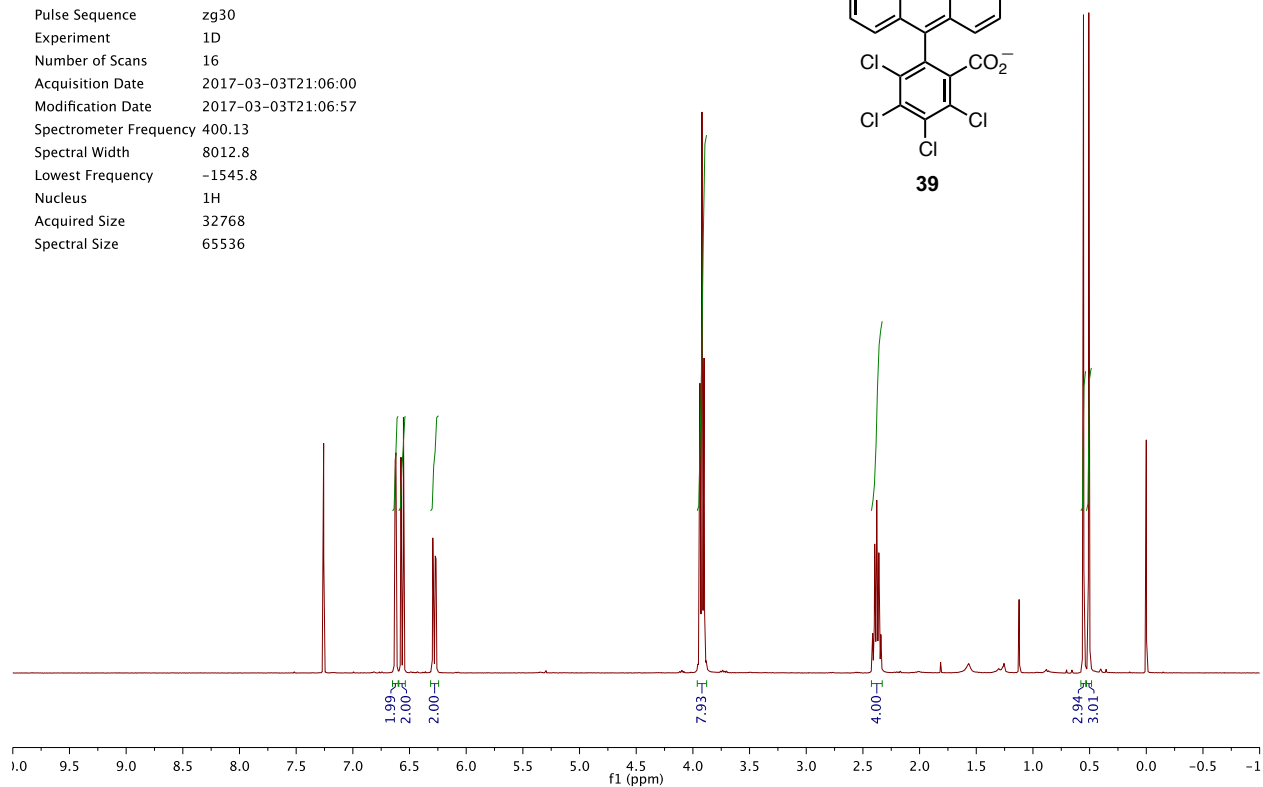
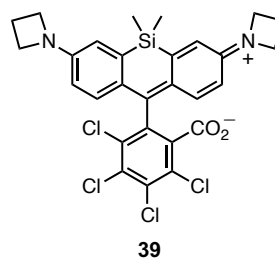
DAD1 E, Sig=650.4 Ref=off (2016_10\DAIY_SEQUENCE_LC 2016-11-04 16-33-32\2016_100000002.D)



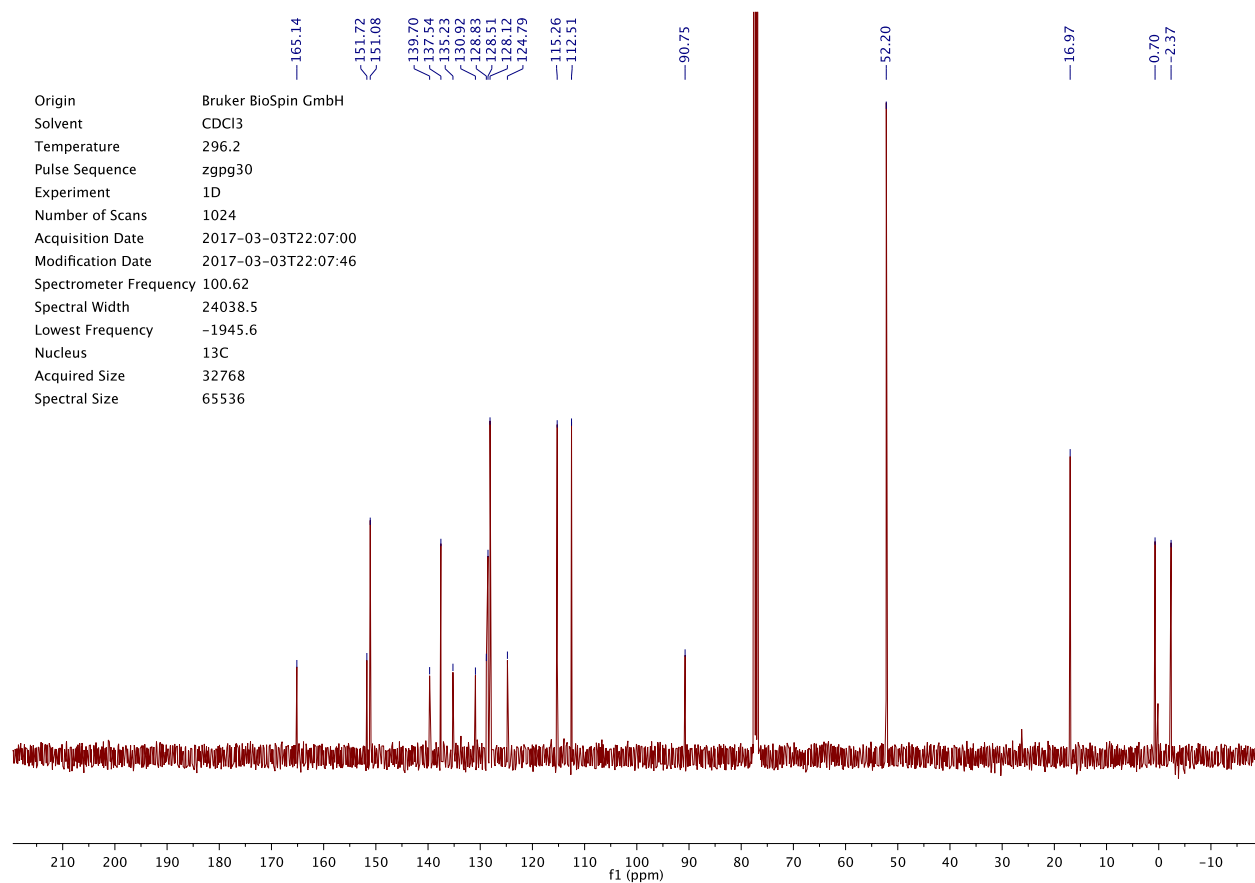
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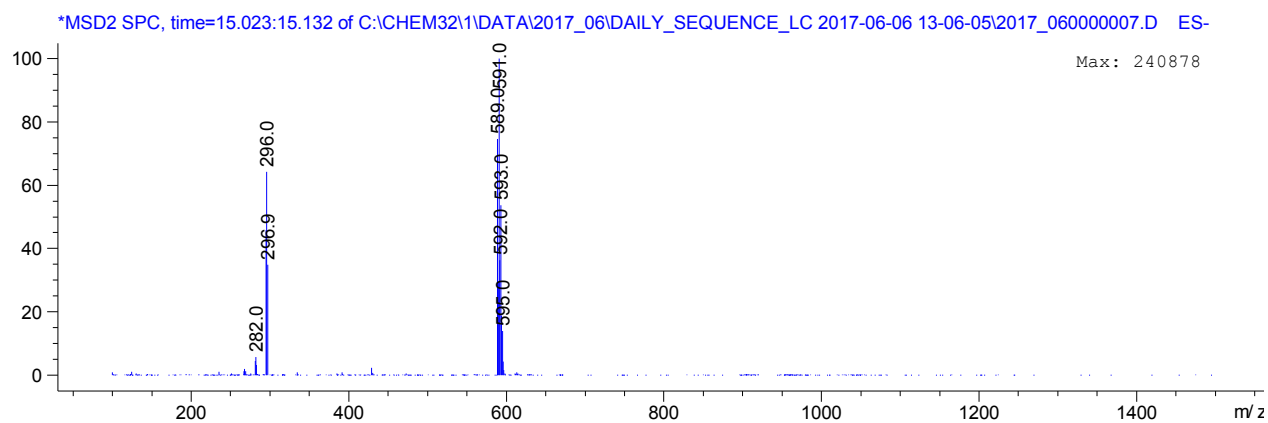
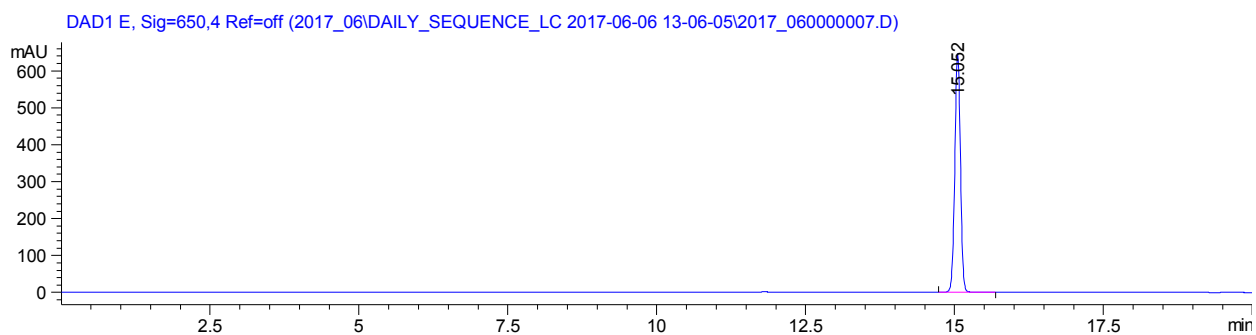
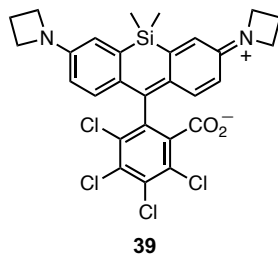


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 295.5
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-03-03T21:06:00
 Modification Date 2017-03-03T21:06:57
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1545.8
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

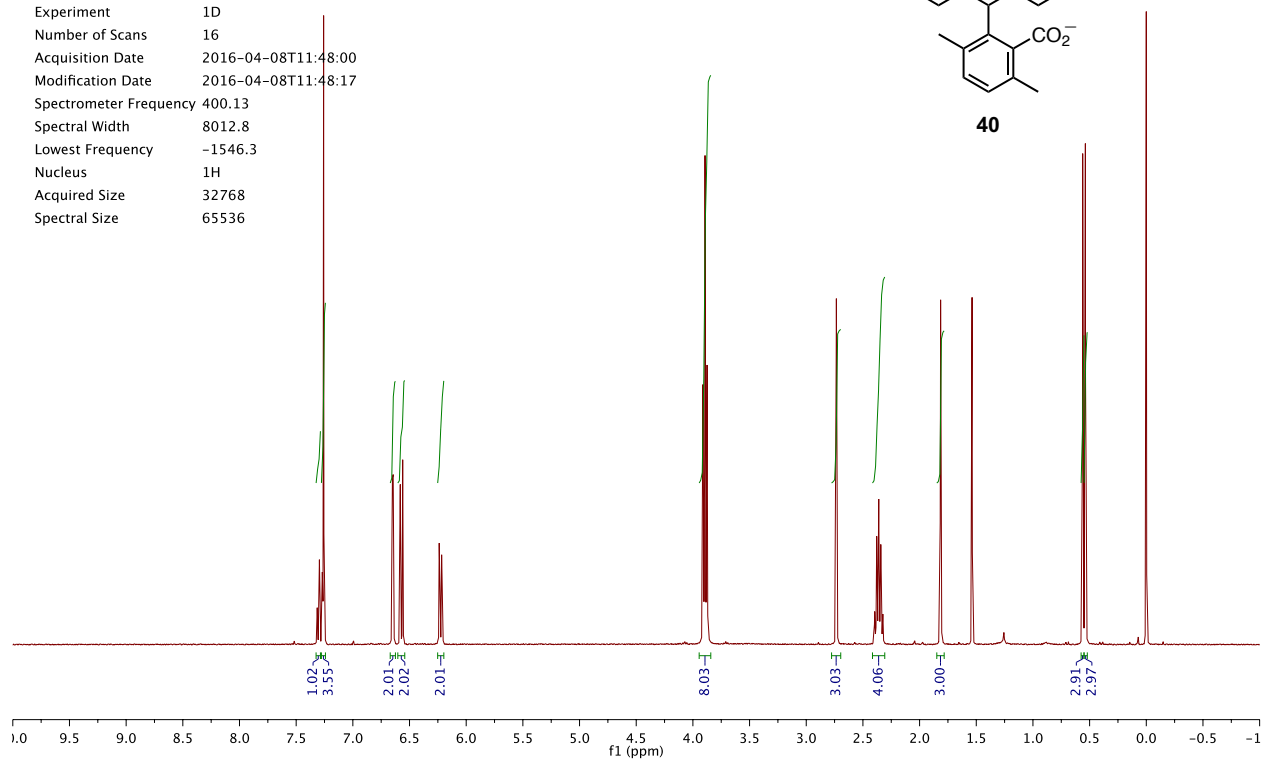
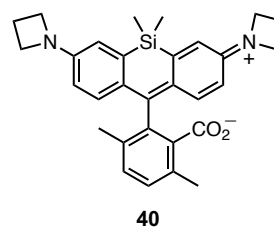


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 296.2
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 1024
 Acquisition Date 2017-03-03T22:07:00
 Modification Date 2017-03-03T22:07:46
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1945.6
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

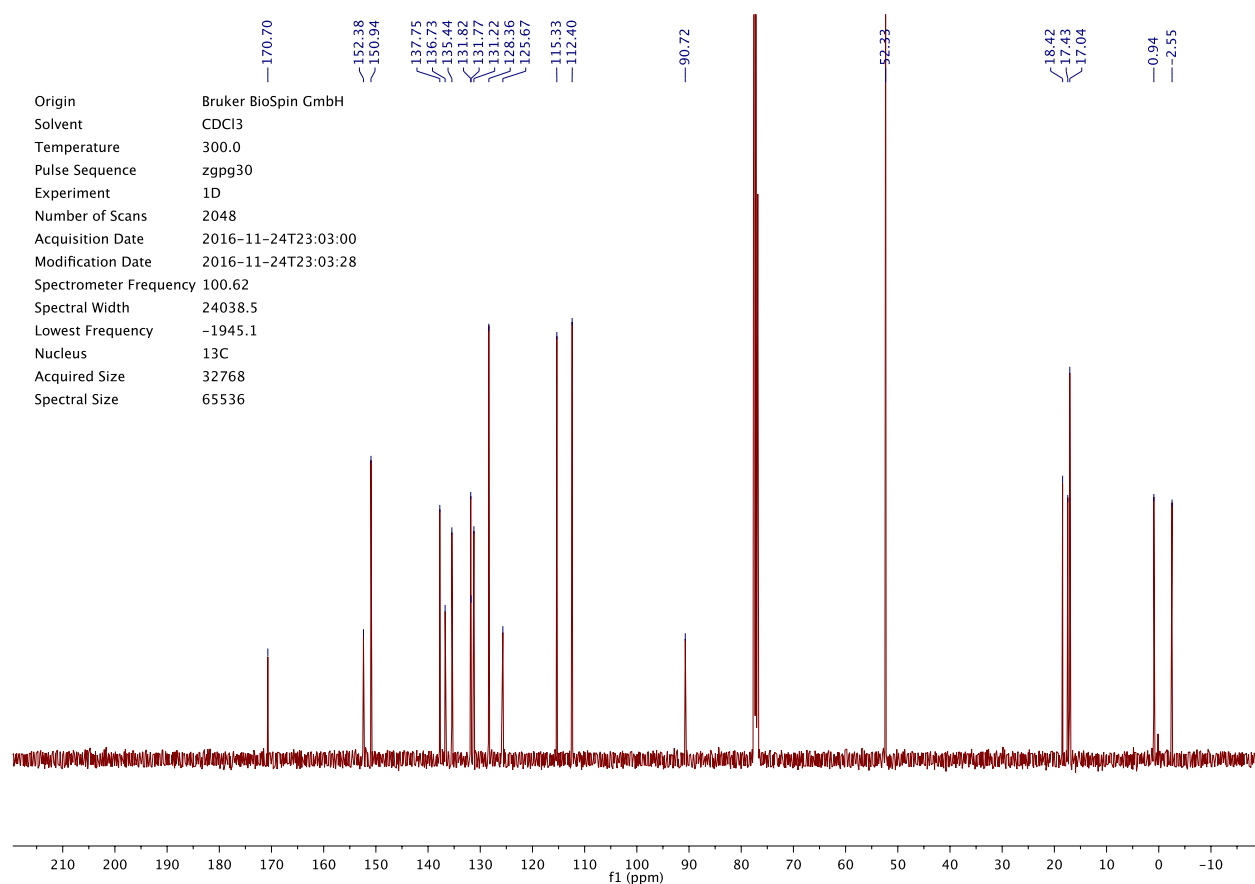


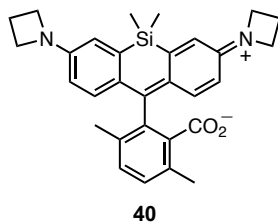


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-04-08T11:48:00
 Modification Date 2016-04-08T11:48:17
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1546.3
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

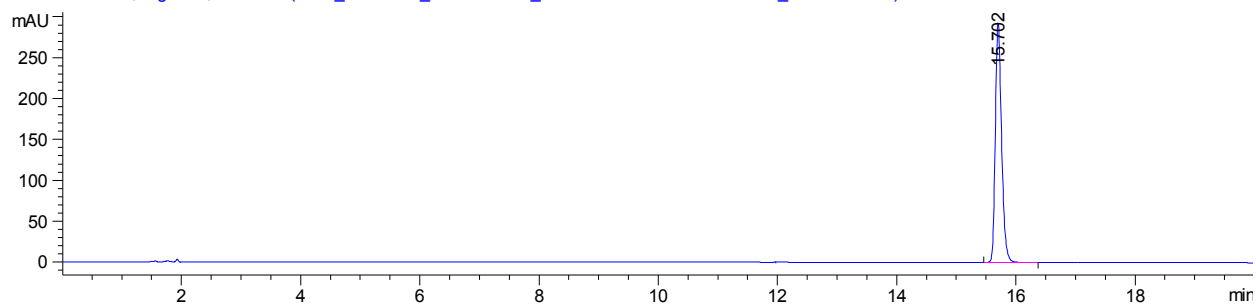


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-24T23:03:00
 Modification Date 2016-11-24T23:03:28
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1945.1
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

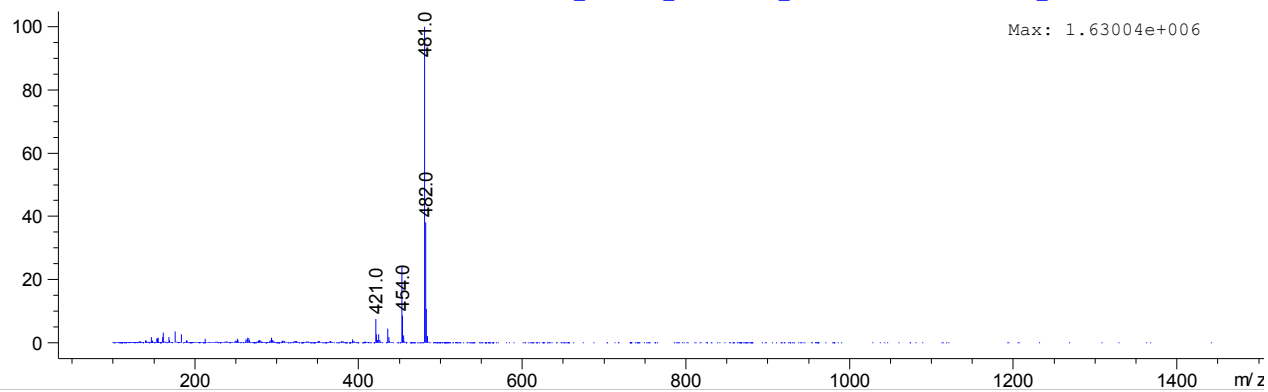




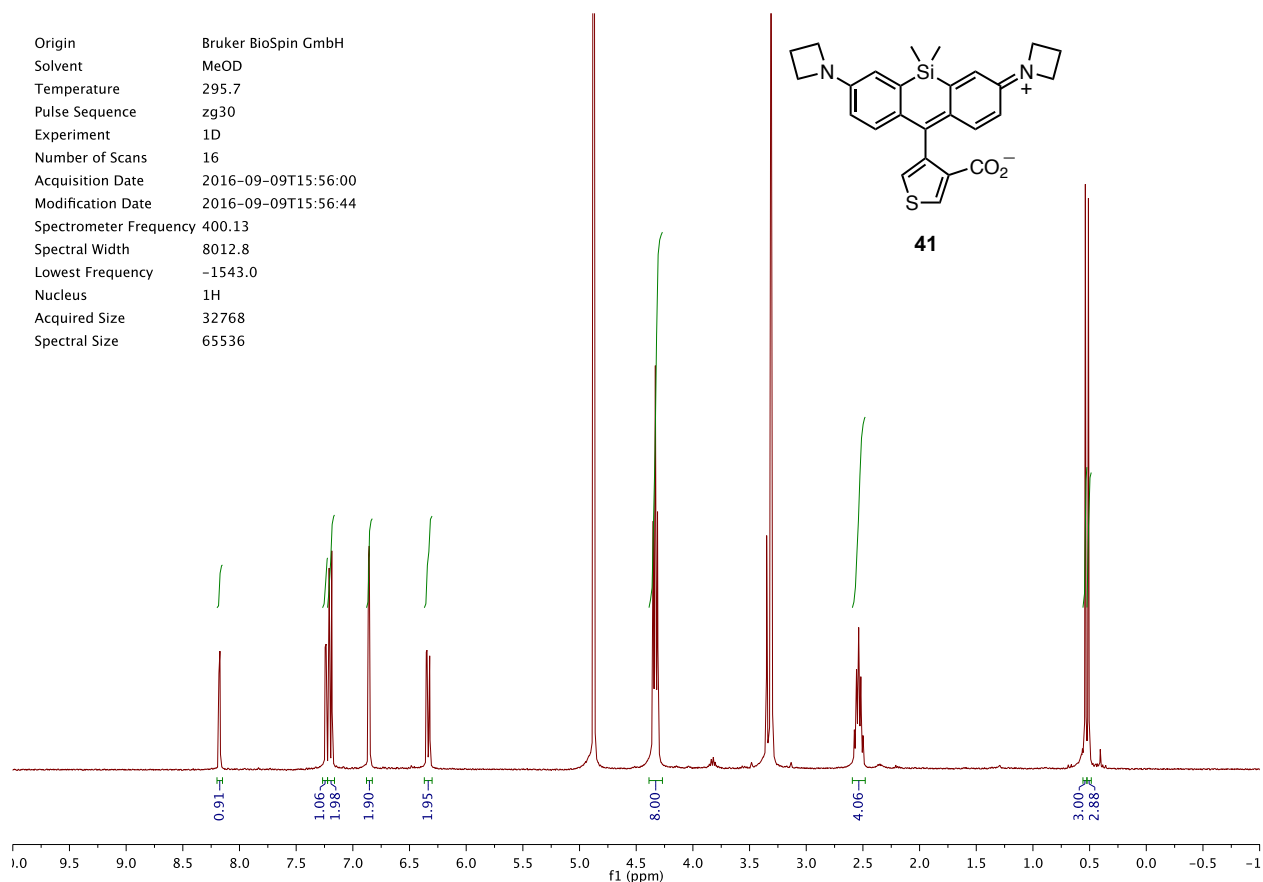
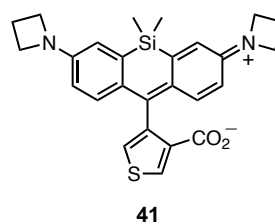
DAD1 E, Sig=650,4 Ref=off (2016_11\DAIY_SEQUENCE_LC 2016-11-23 11-45-02\2016_110000018.D)



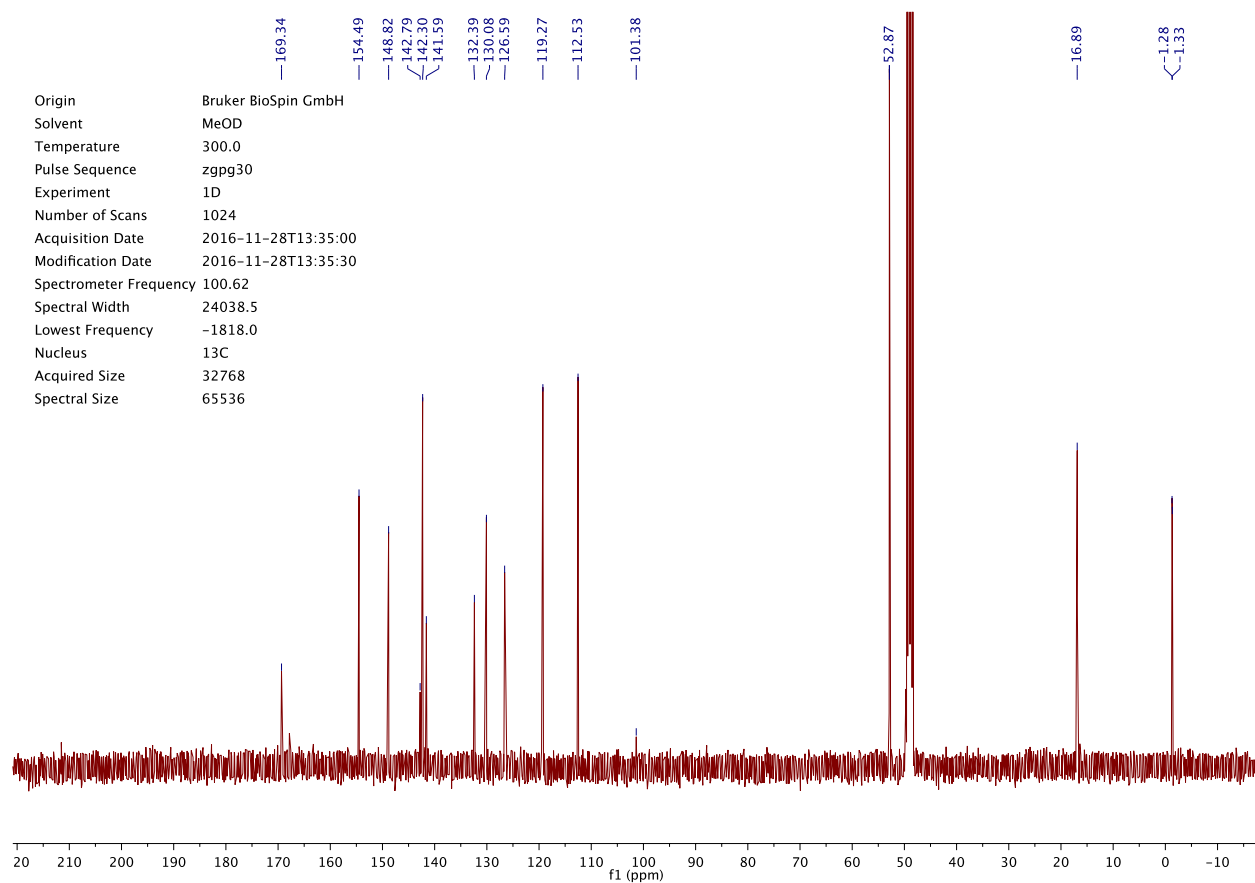
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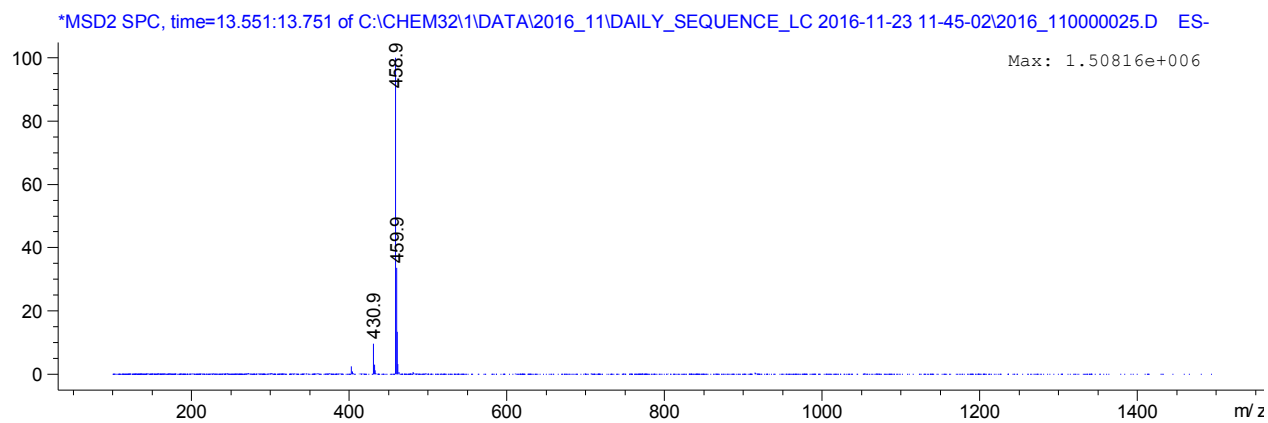
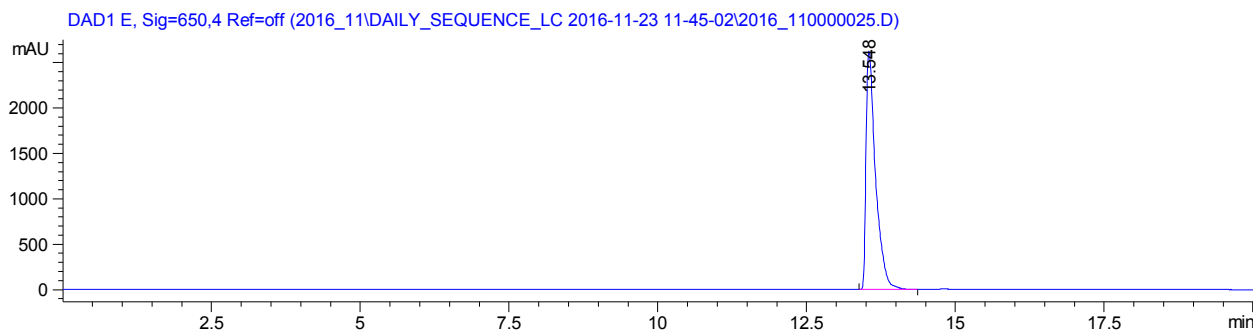
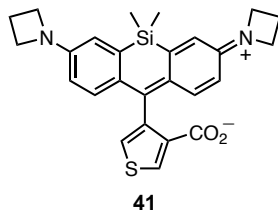


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 295.7
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-09-09T15:56:00
 Modification Date 2016-09-09T15:56:44
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus ^1H
 Acquired Size 32768
 Spectral Size 65536

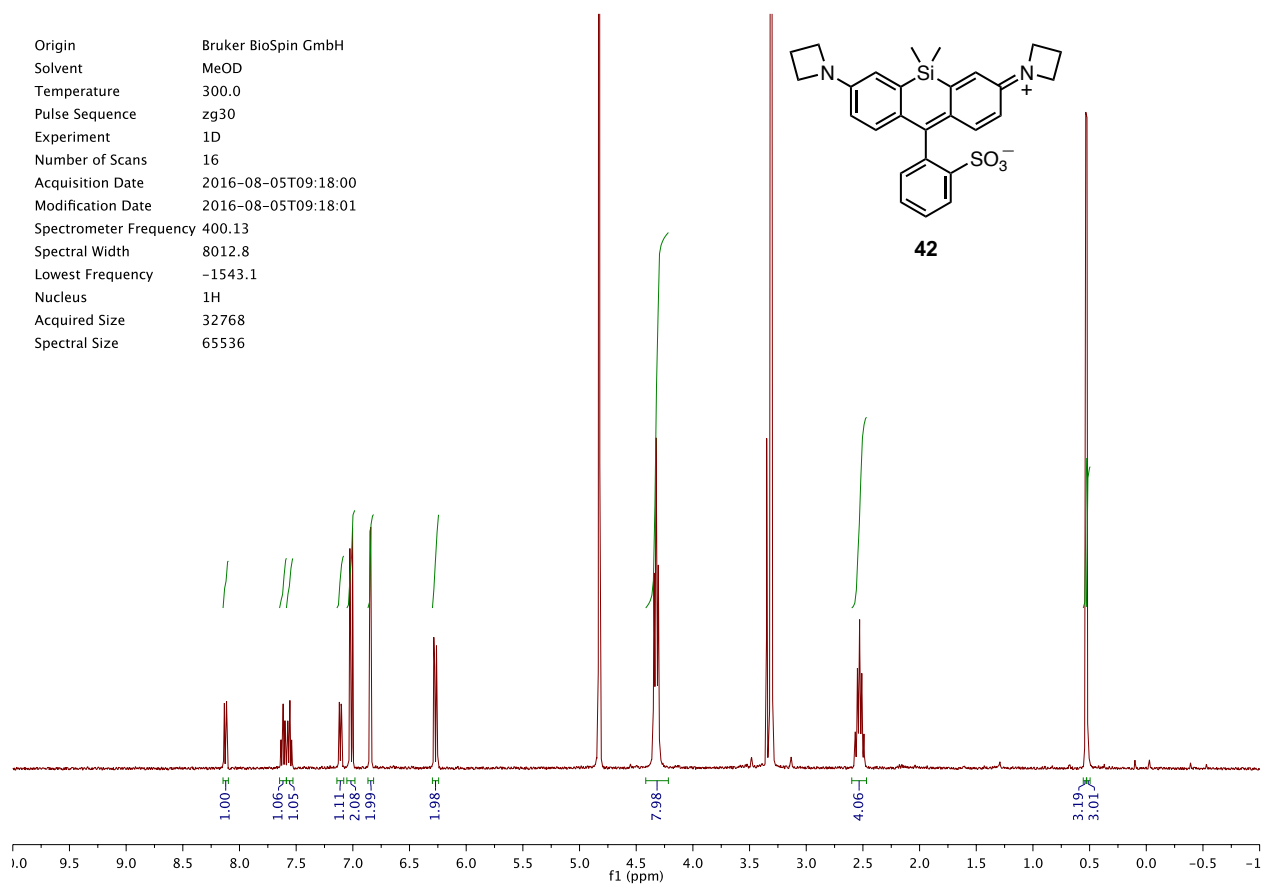
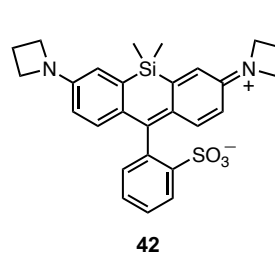


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 1024
 Acquisition Date 2016-11-28T13:35:00
 Modification Date 2016-11-28T13:35:30
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1818.0
 Nucleus ^{13}C
 Acquired Size 32768
 Spectral Size 65536

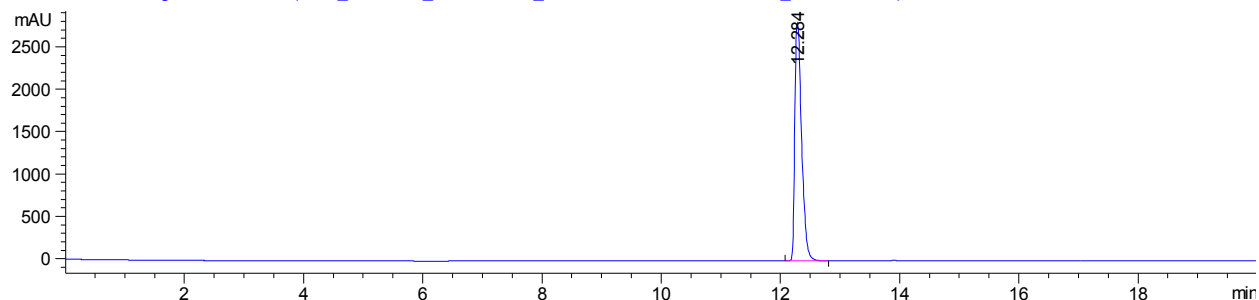




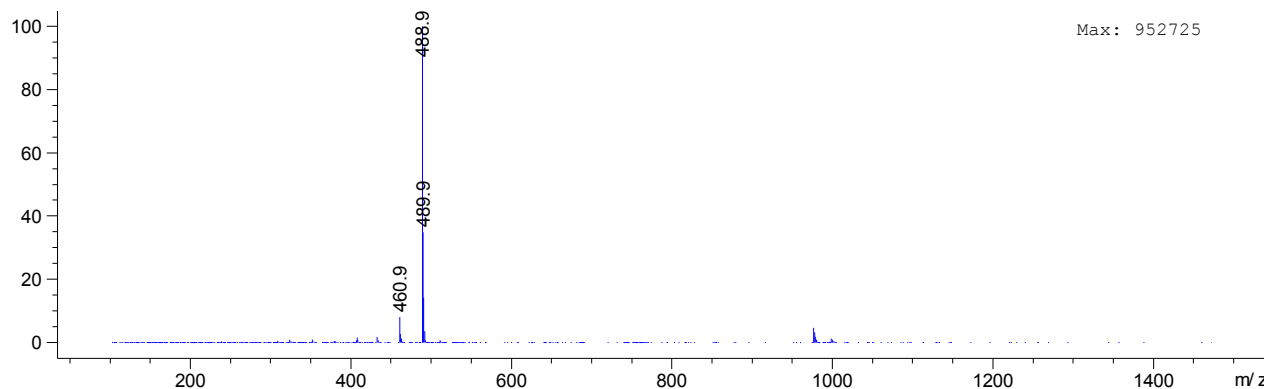
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-08-05T09:18:00
 Modification Date 2016-08-05T09:18:01
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.1
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



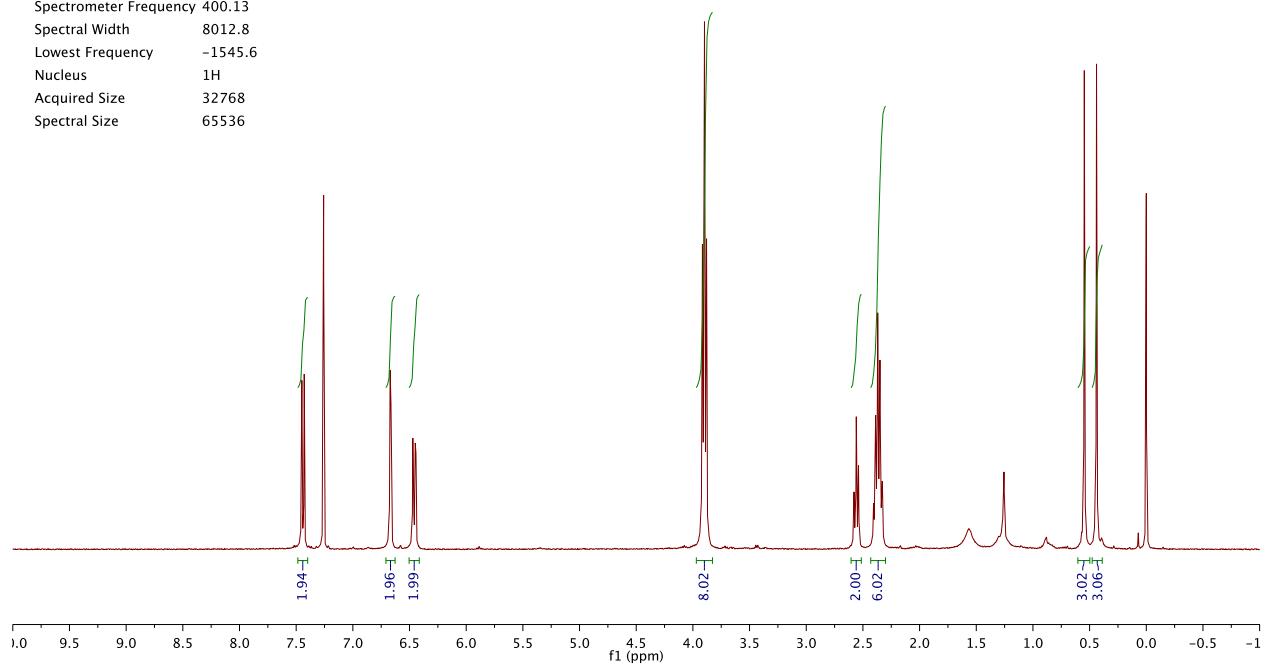
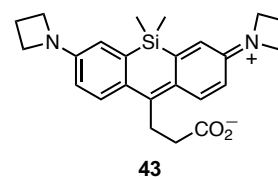
DAD1 E, Sig=650,4 Ref=off (2016_11\DAI\SEQUENCE_LC 2016-11-22 15-28-20\2016_110000001.D)



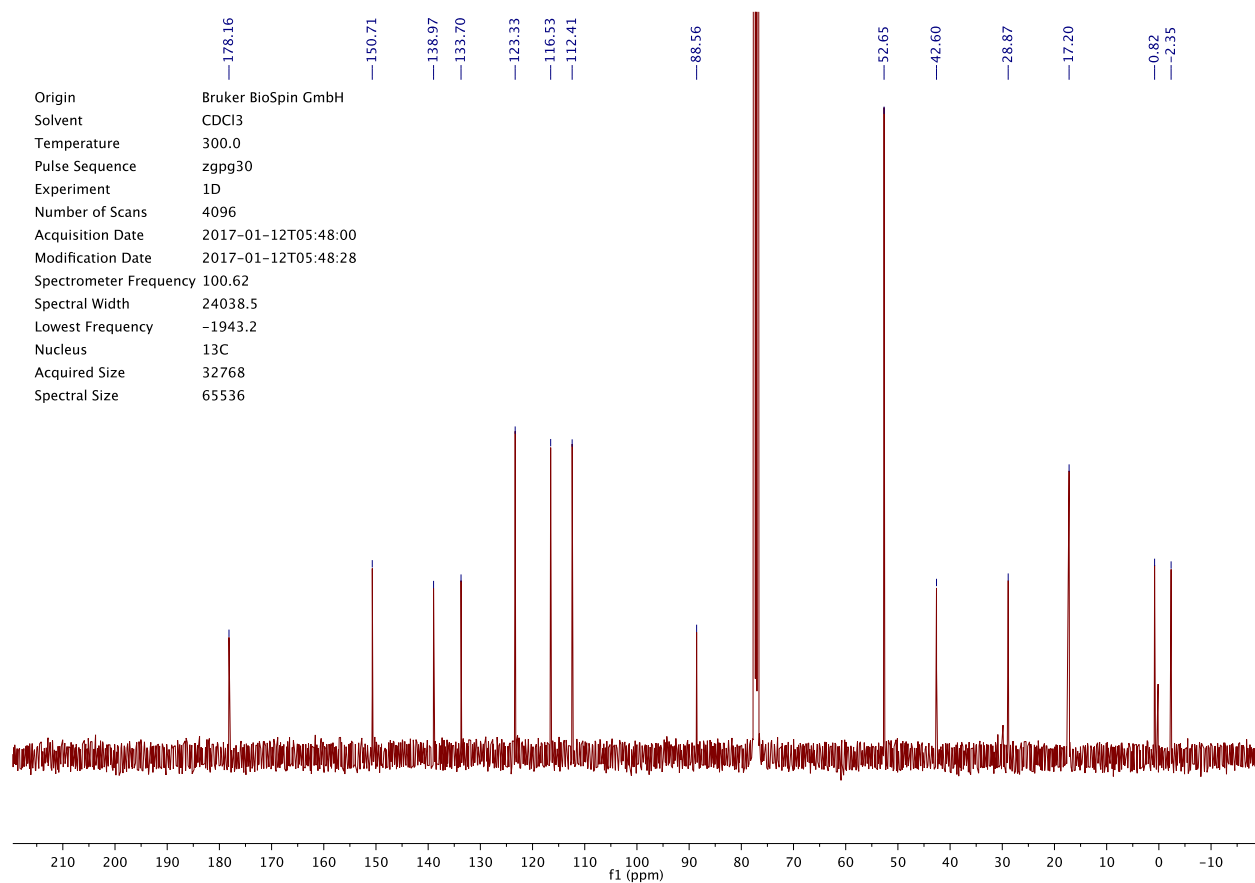
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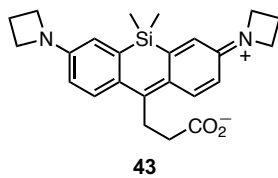


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-12T01:52:00
 Modification Date 2017-01-12T01:52:34
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1545.6
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

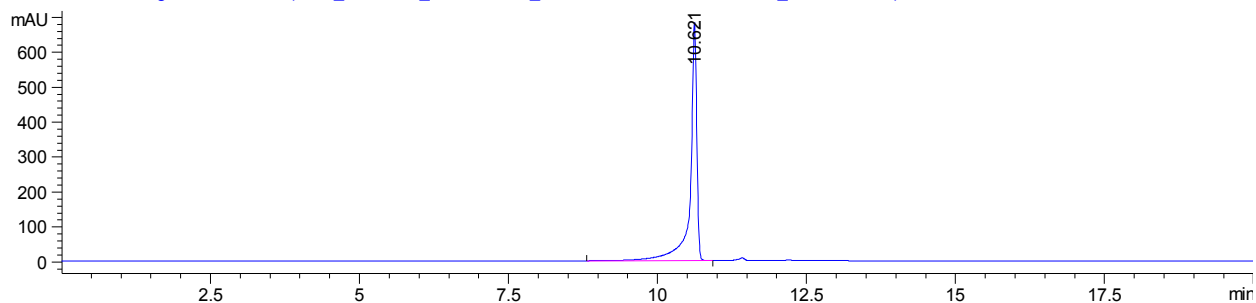


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 4096
 Acquisition Date 2017-01-12T05:48:00
 Modification Date 2017-01-12T05:48:28
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1943.2
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

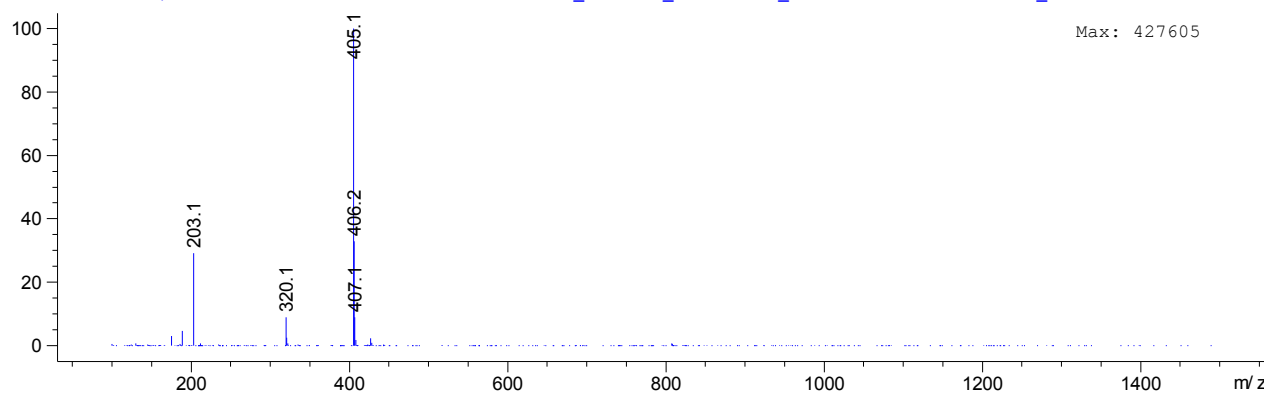




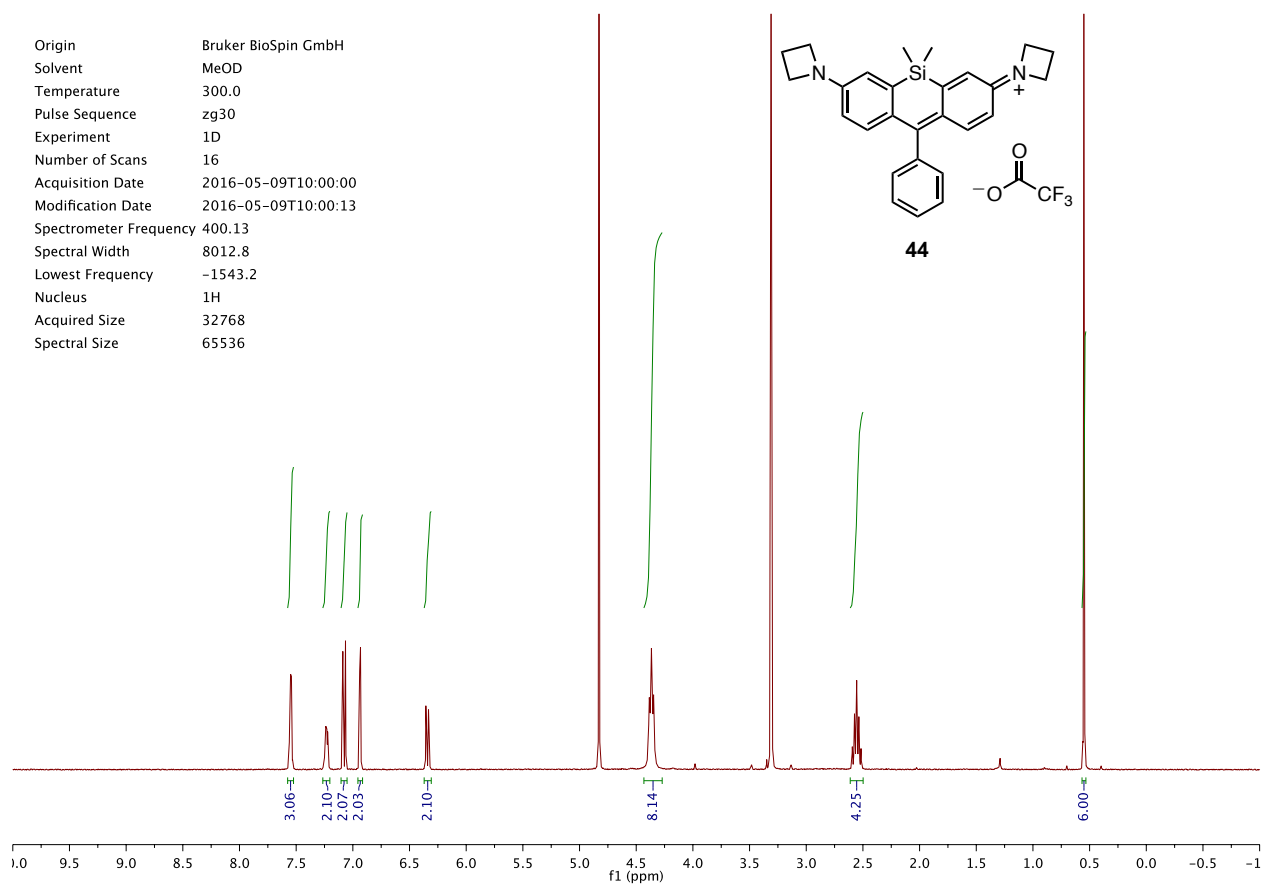
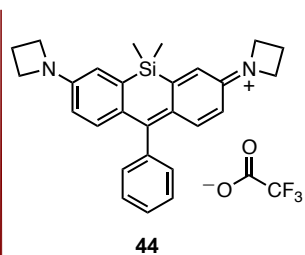
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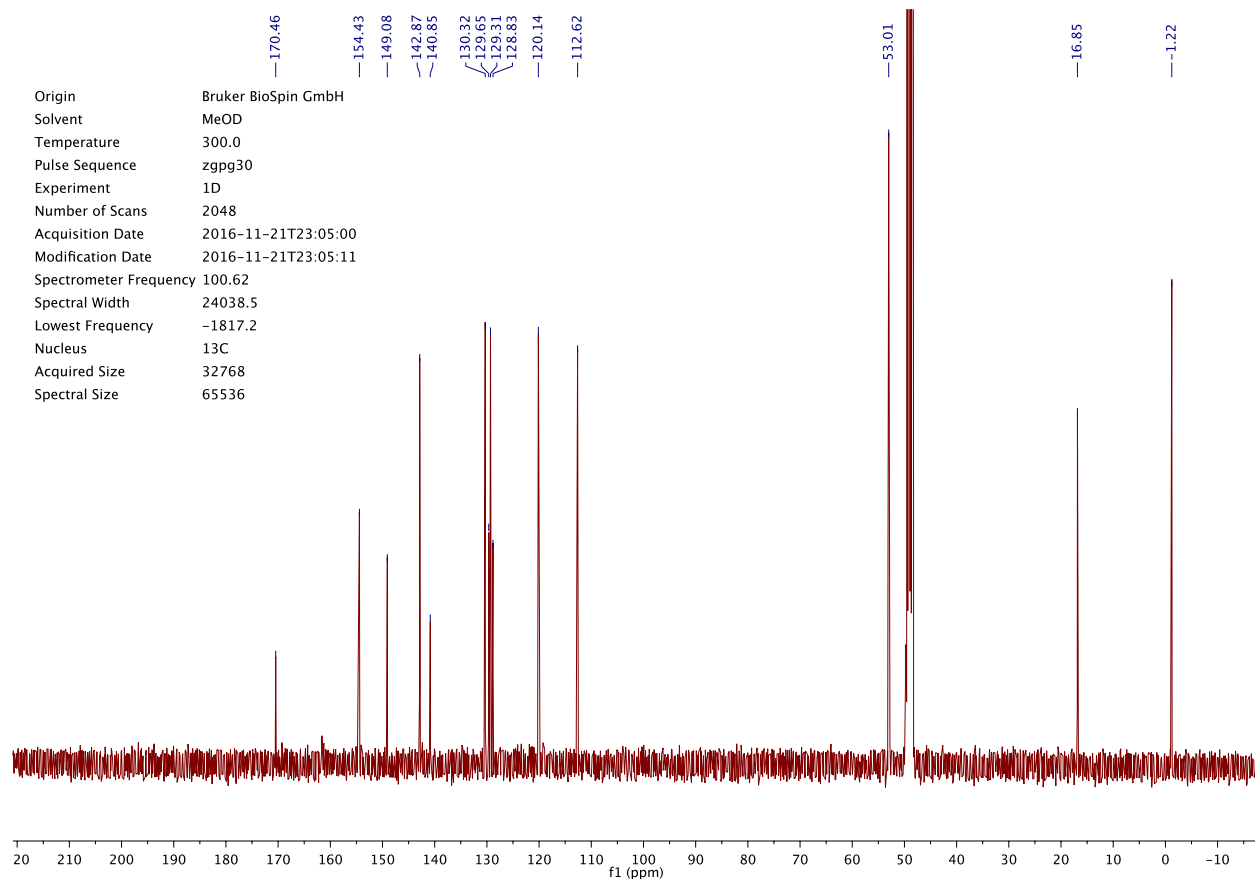
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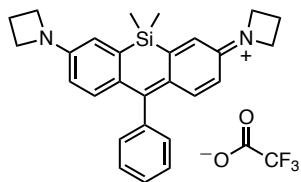


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-05-09T10:00:00
 Modification Date 2016-05-09T10:00:13
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.2
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



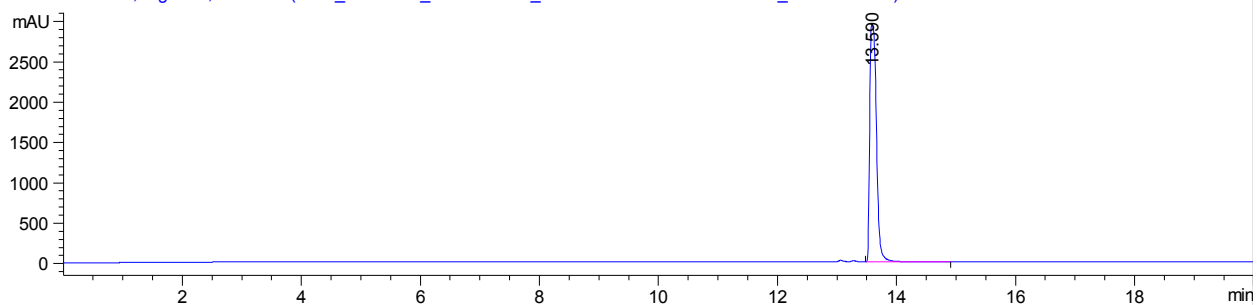
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-21T23:05:00
 Modification Date 2016-11-21T23:05:11
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.2
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536



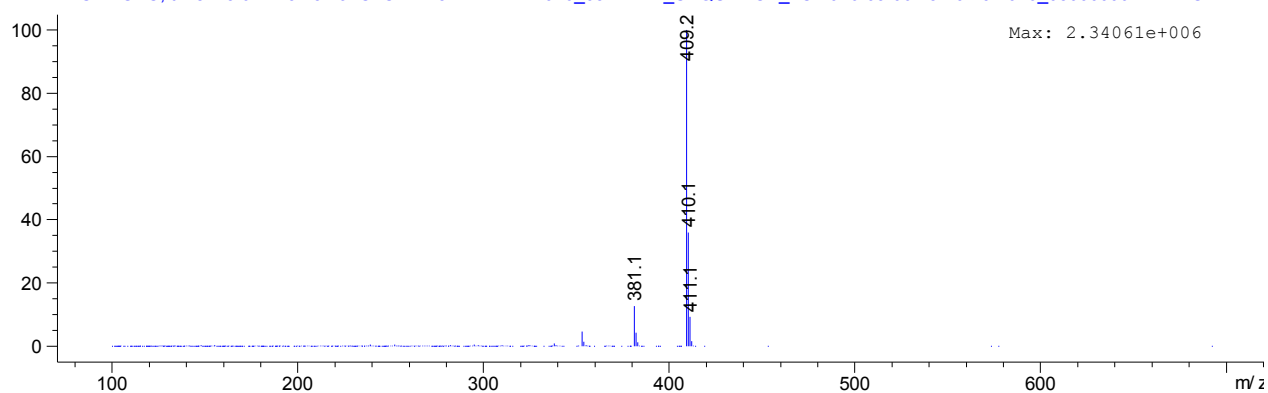


44

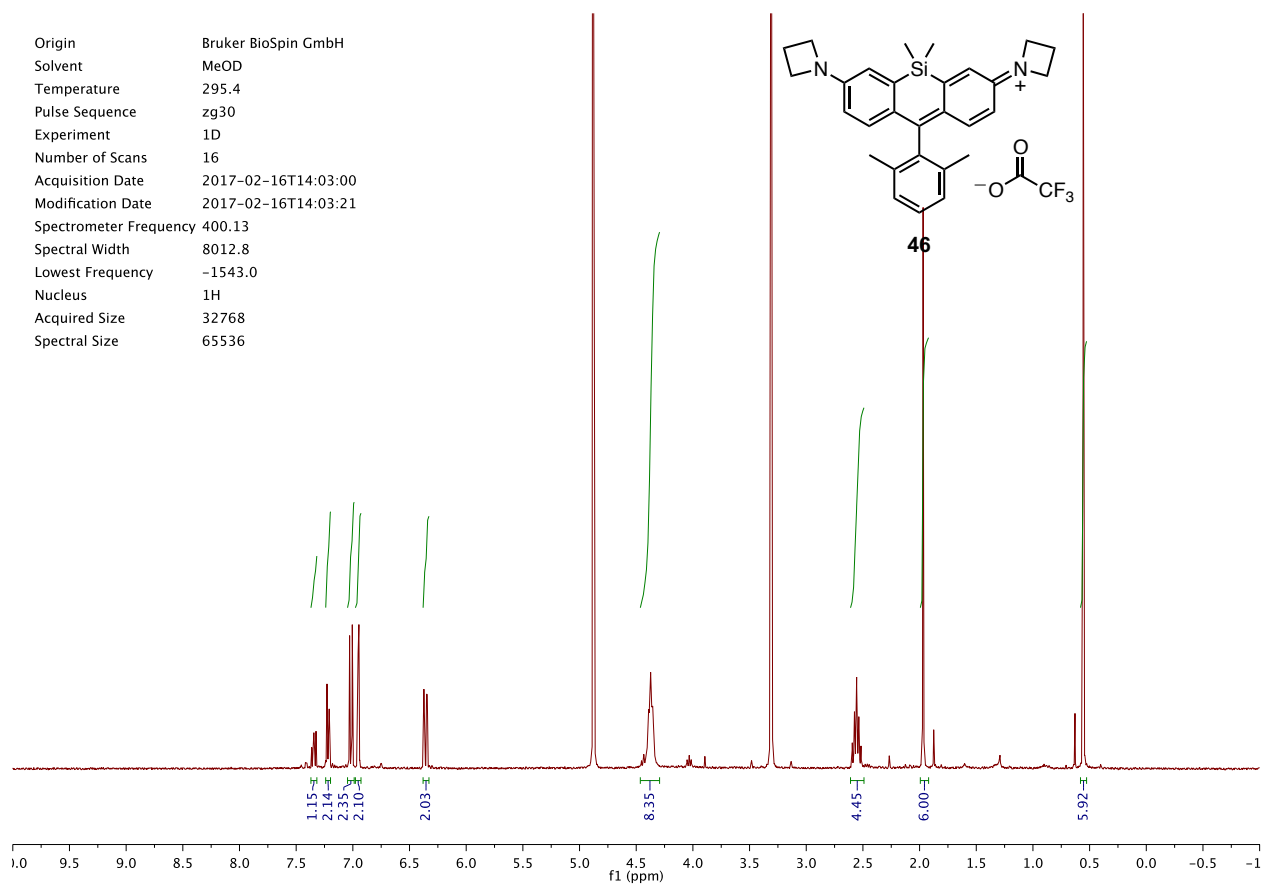
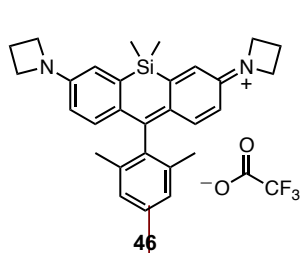
DAD1 E, Sig=650,4 Ref=off (2016_05\DAIY_SEQUENCE_LC 2016-05-06 15-10-19\2016_050000001.D)



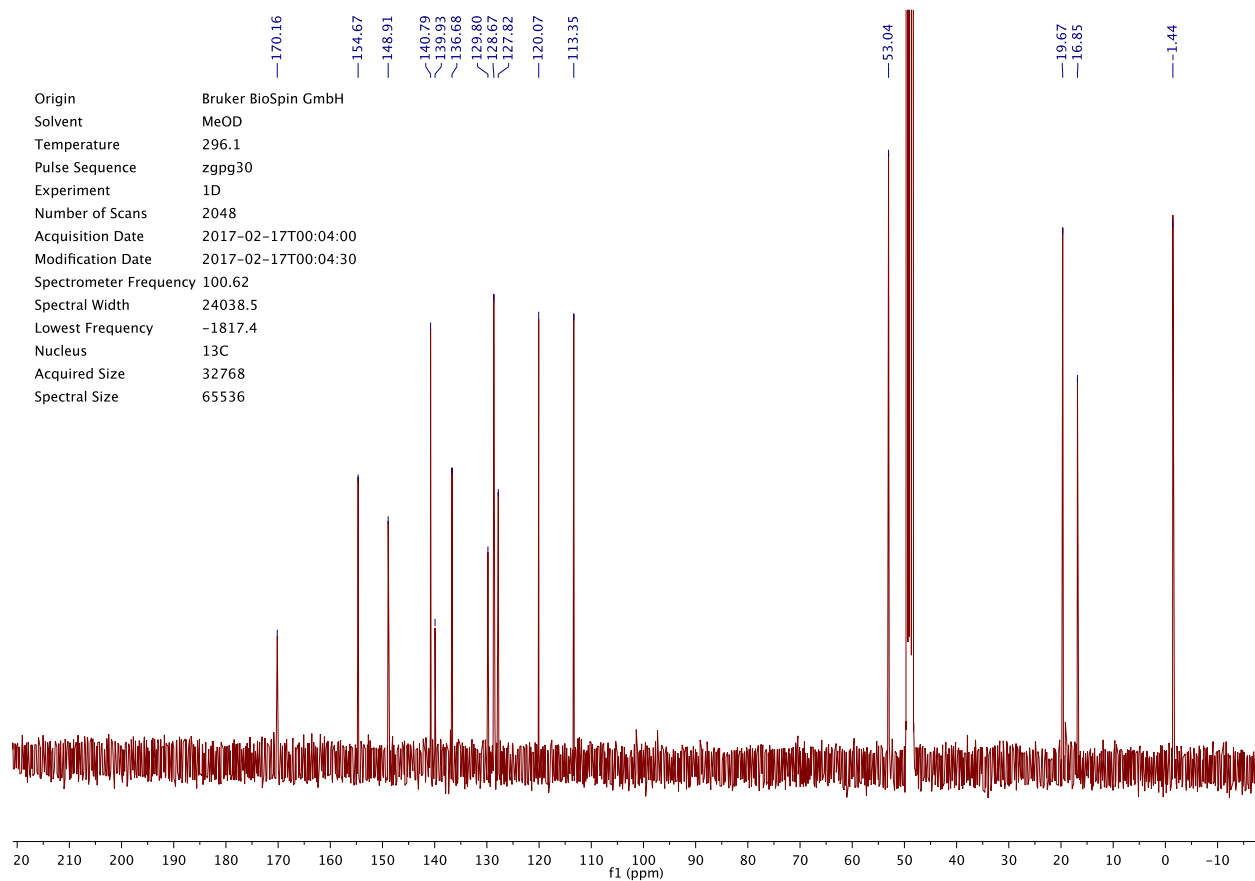
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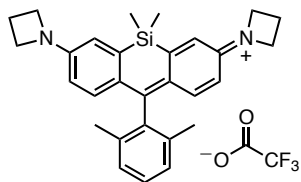


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 295.4
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-02-16T14:03:00
 Modification Date 2017-02-16T14:03:21
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



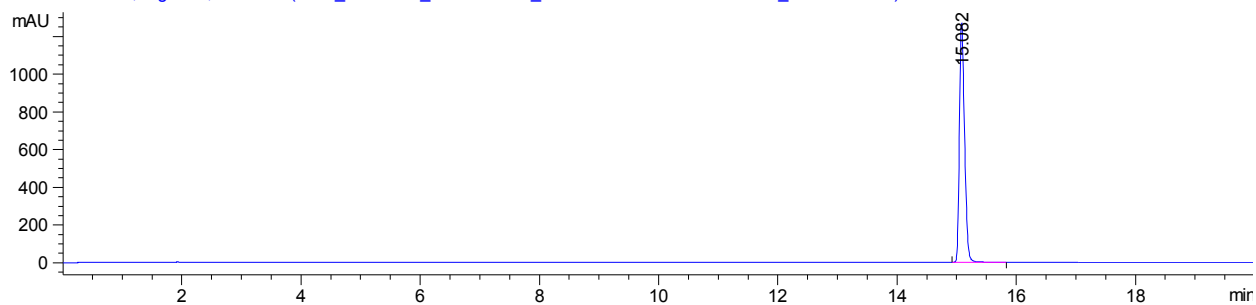
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 296.1
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2017-02-17T00:04:00
 Modification Date 2017-02-17T00:04:30
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.4
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536



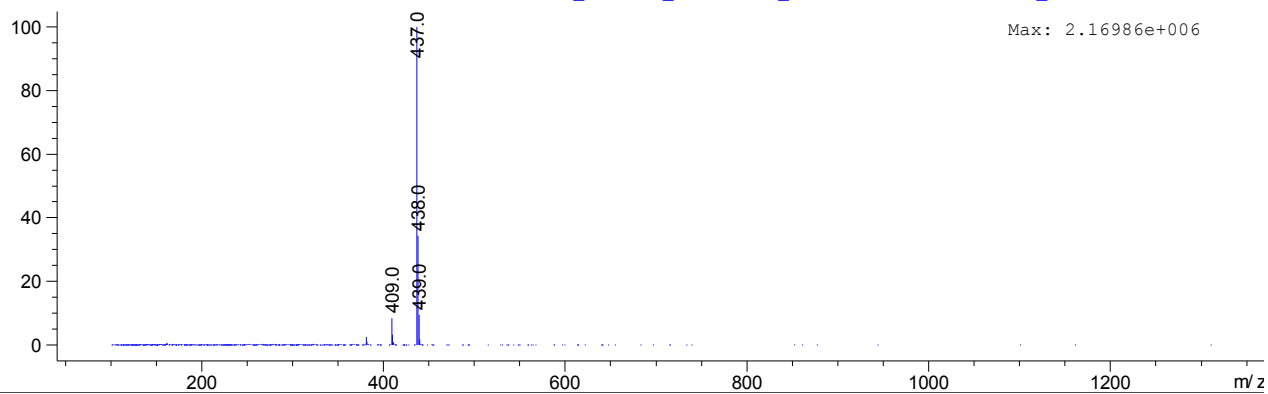


46

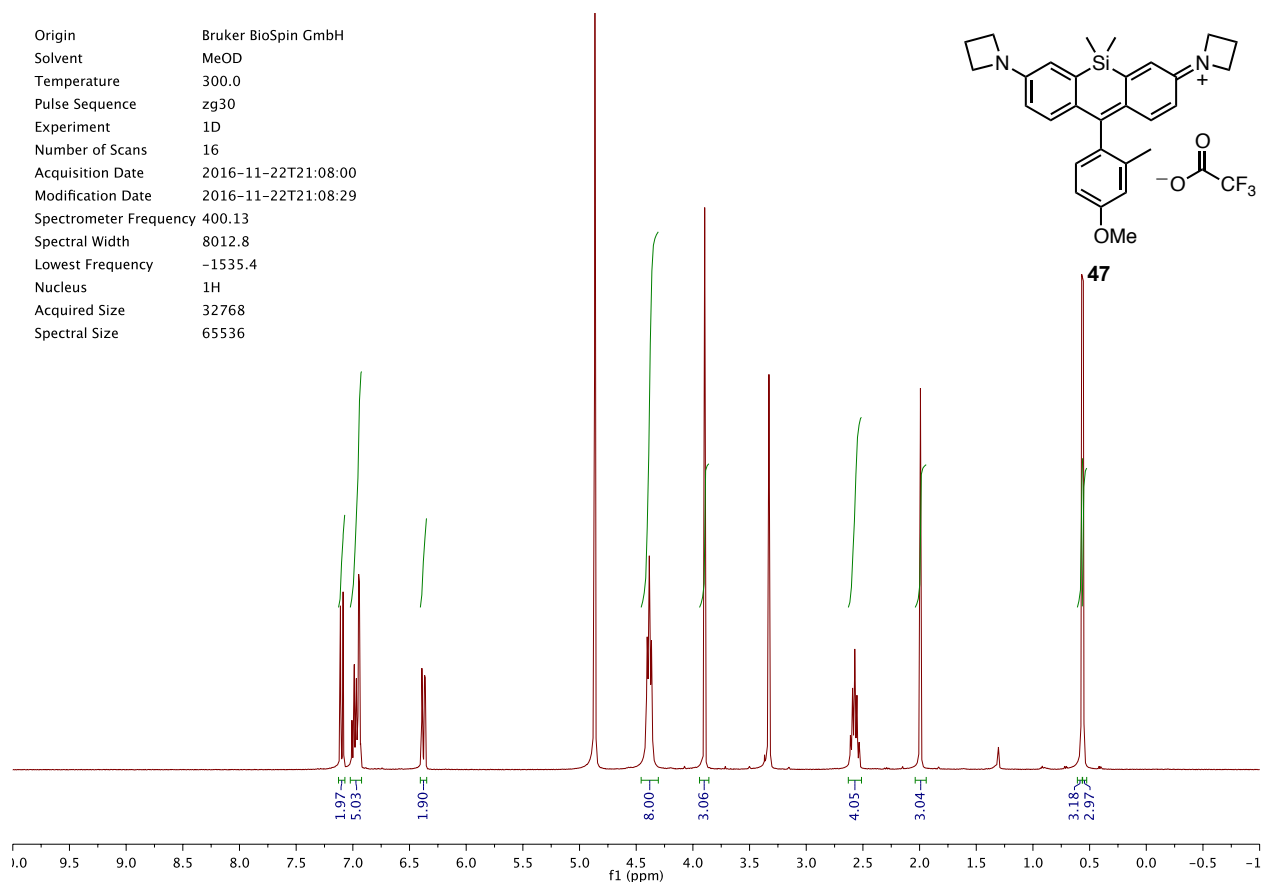
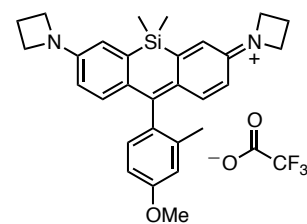
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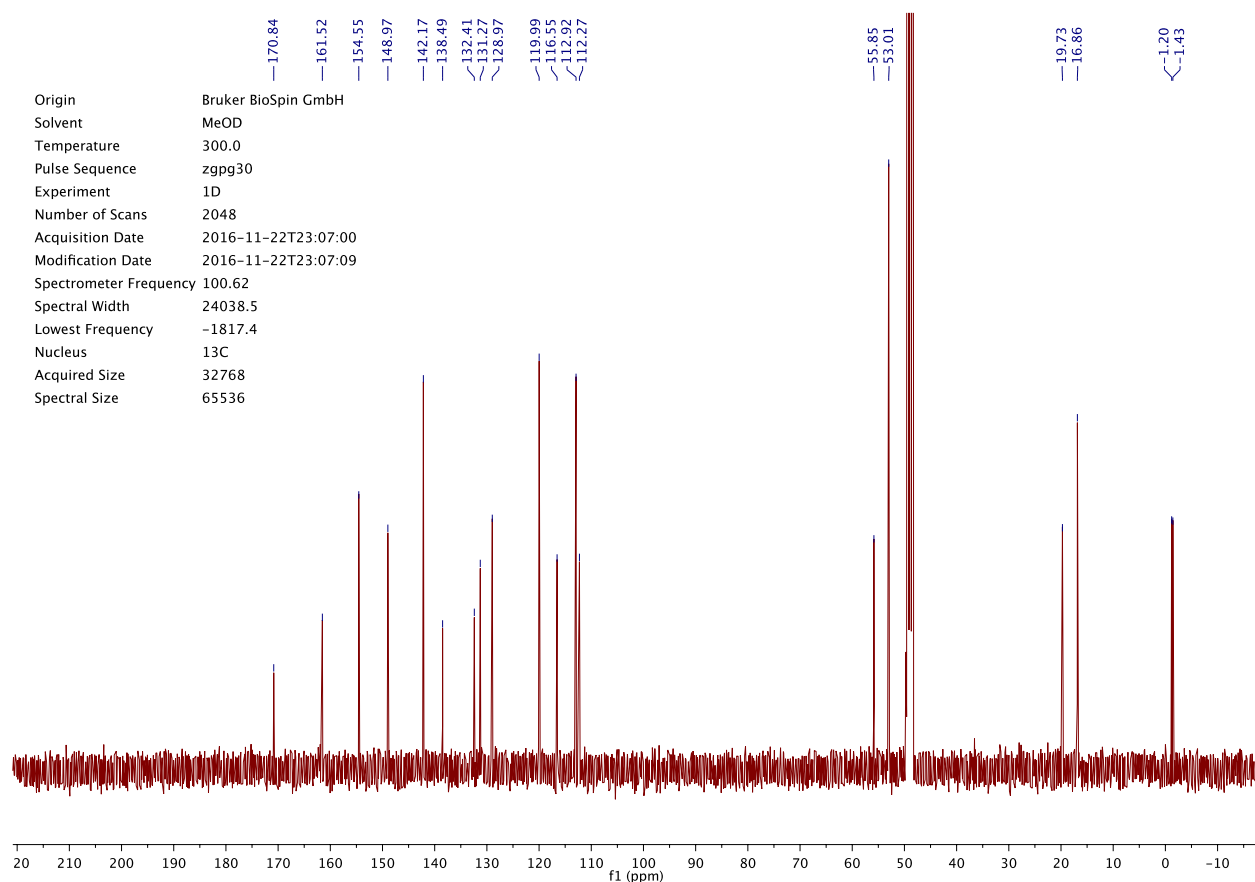
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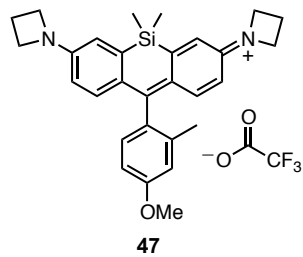


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-11-22T21:08:00
 Modification Date 2016-11-22T21:08:29
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1535.4
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536

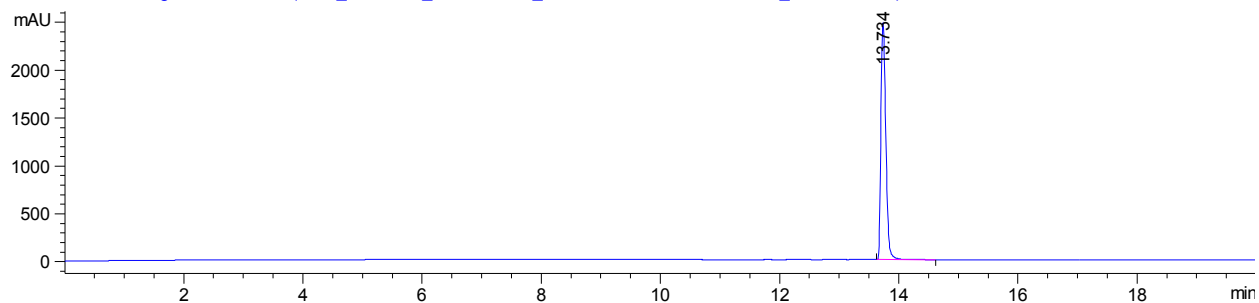


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-22T23:07:00
 Modification Date 2016-11-22T23:07:09
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.4
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

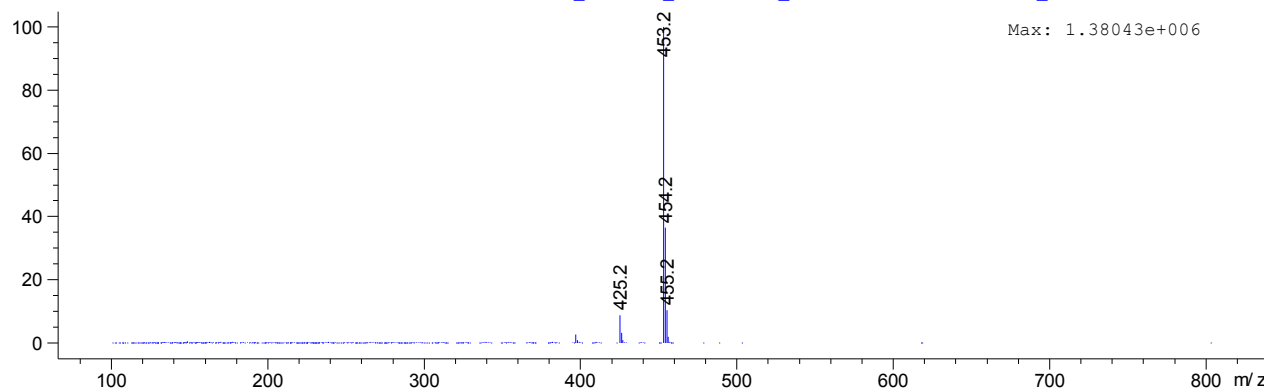




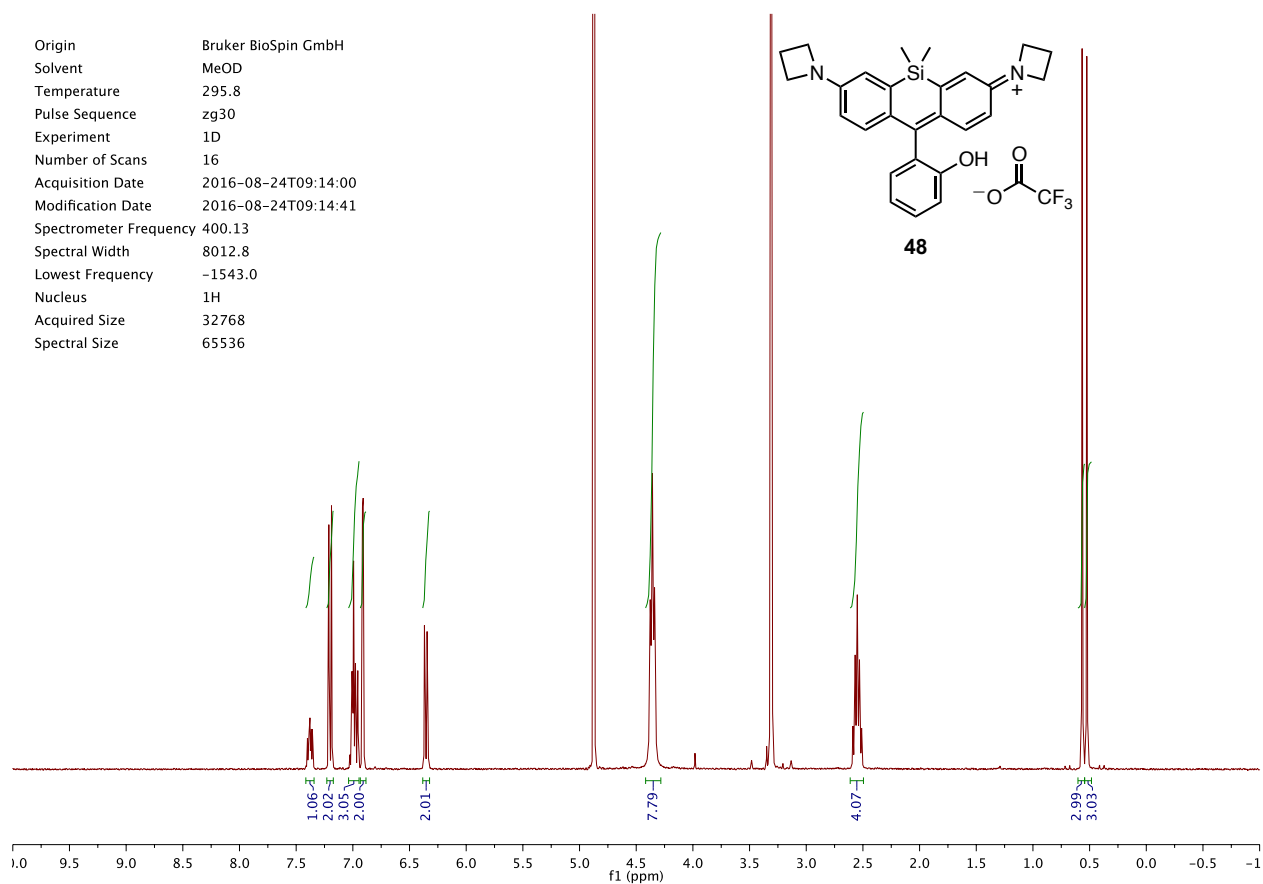
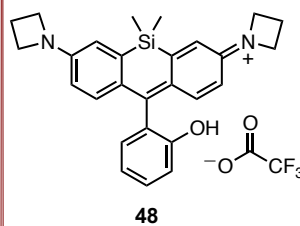
DAD1 E, Sig=650,4 Ref=off (2016_05\DAIY_SEQUENCE_LC 2016-05-05 12-30-42\2016_050000001.D)



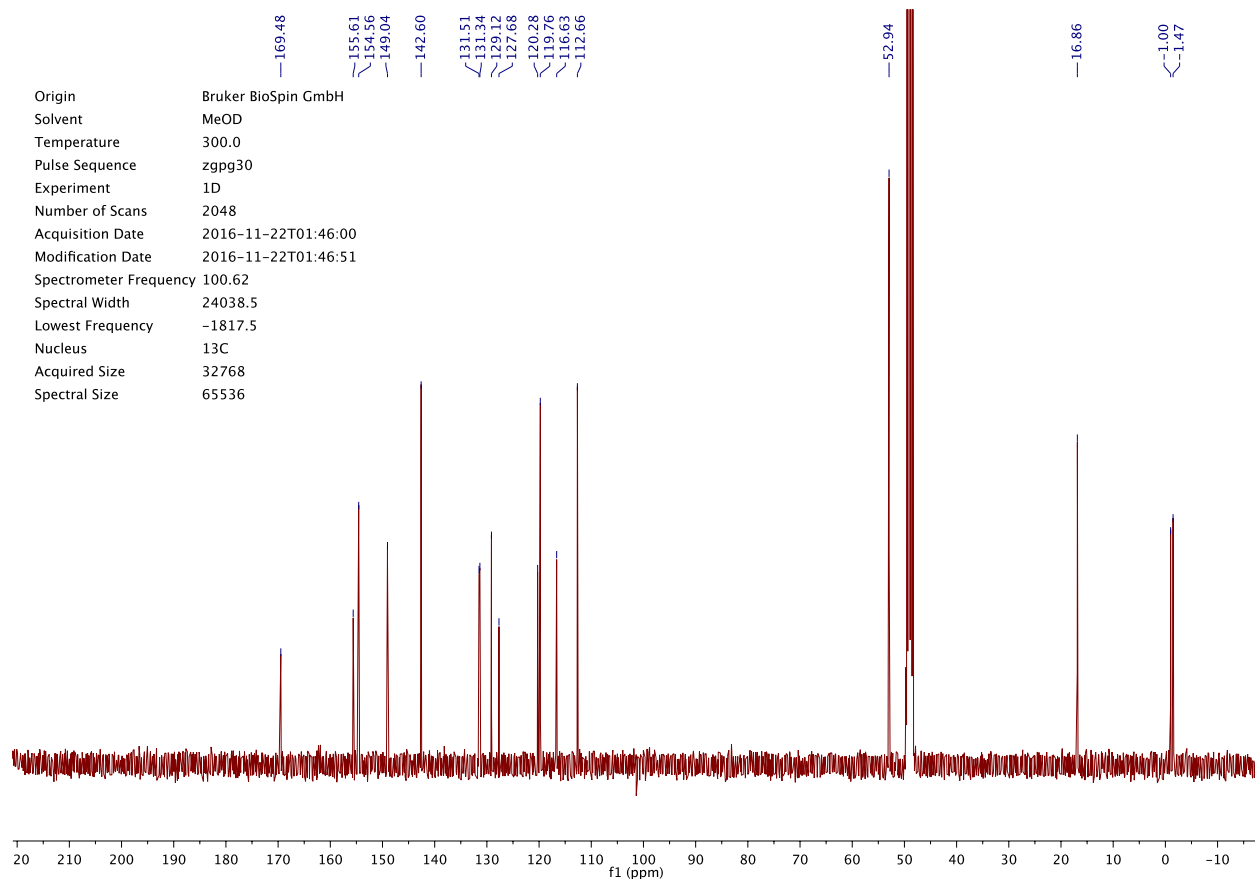
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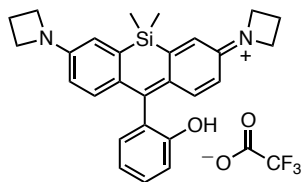


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 295.8
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-08-24T09:14:00
 Modification Date 2016-08-24T09:14:41
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



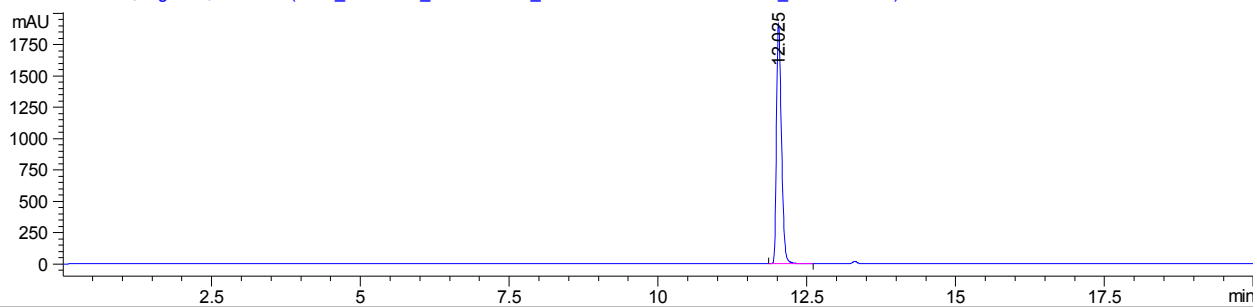
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-22T01:46:00
 Modification Date 2016-11-22T01:46:51
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.5
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536



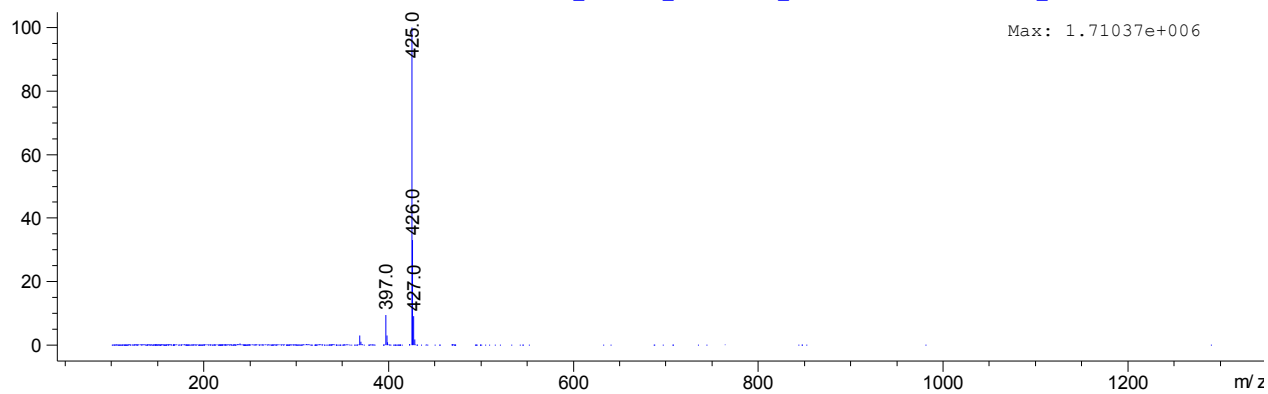


48

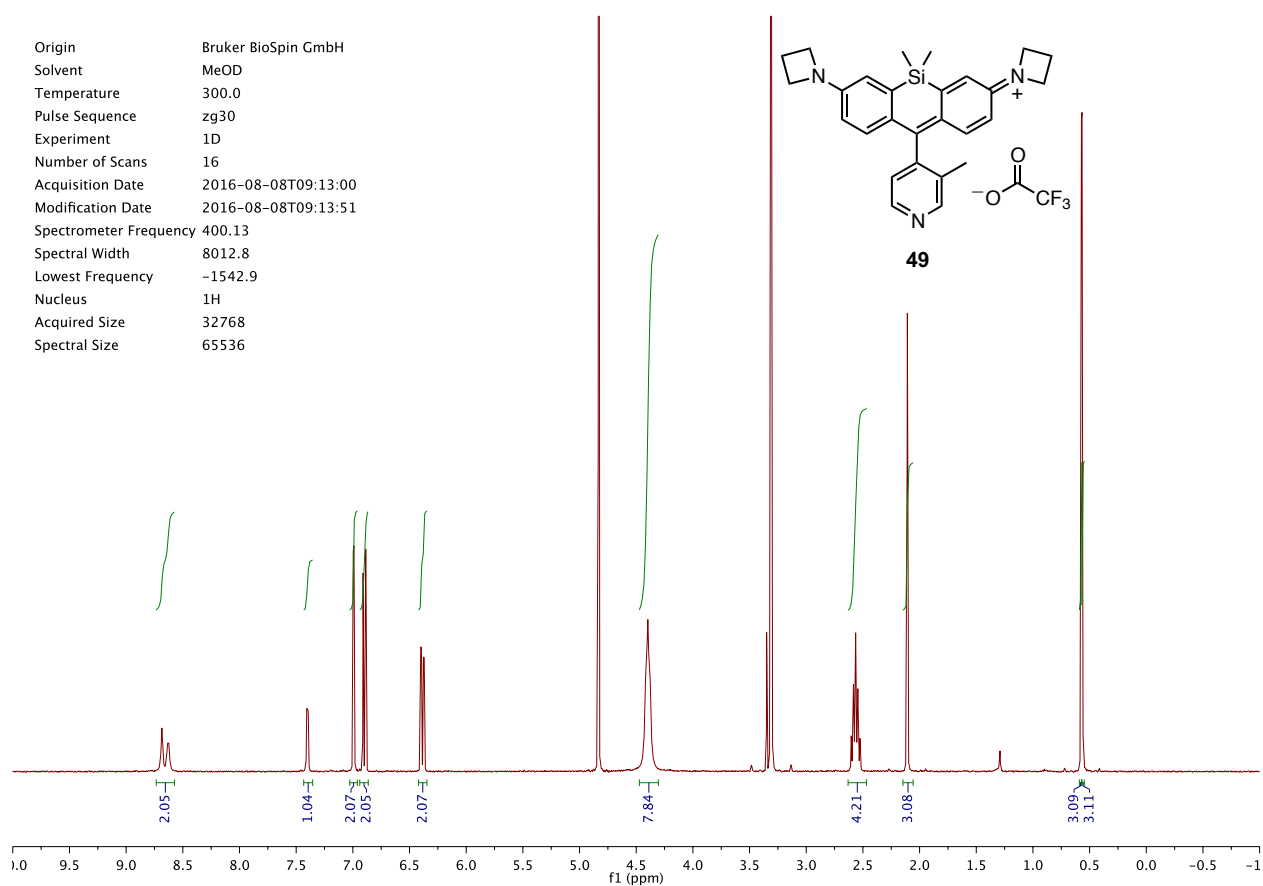
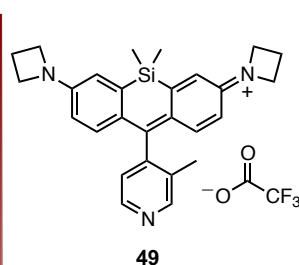
DAD1 E, Sig=650,4 Ref=off (2016_08\DAIY_SEQUENCE_LC 2016-08-22 12-03-19\2016_080000002.D)



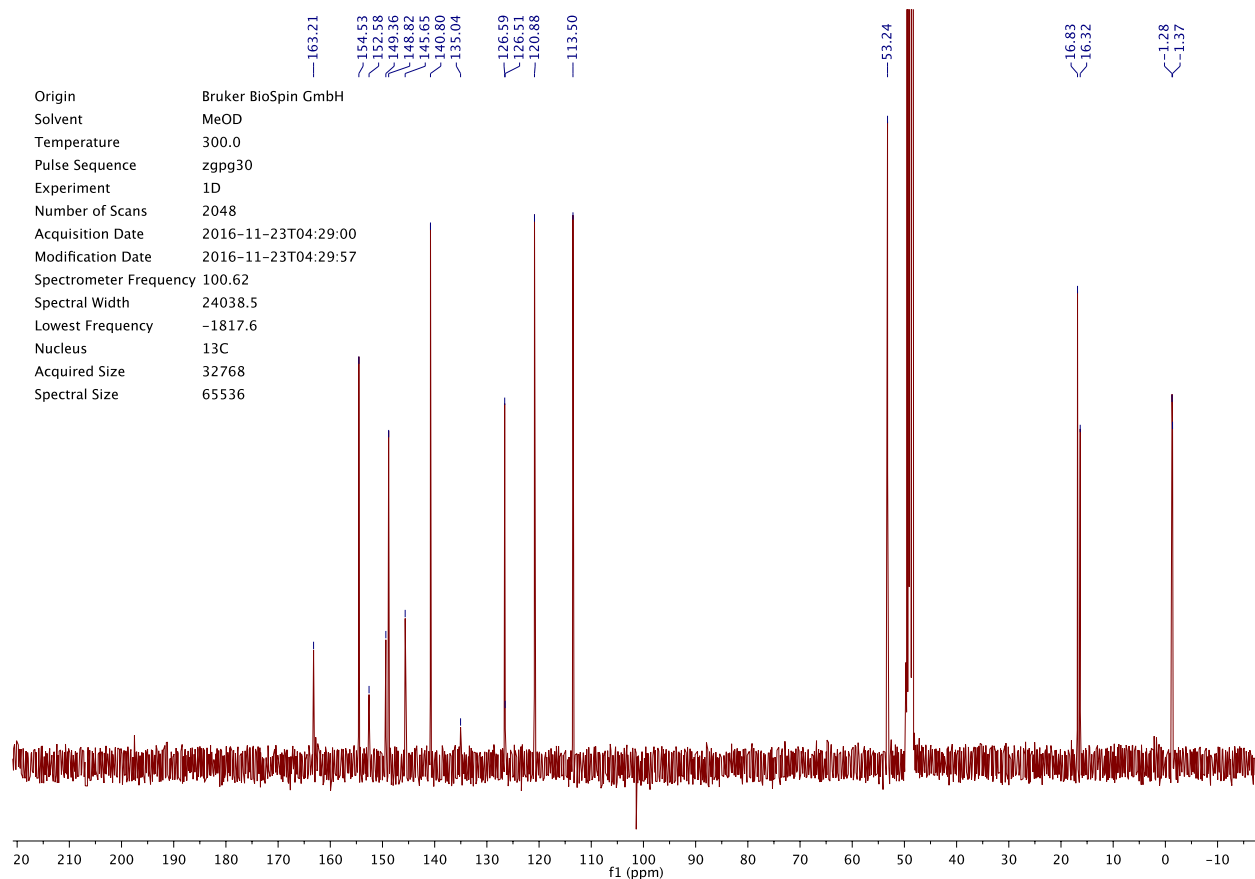
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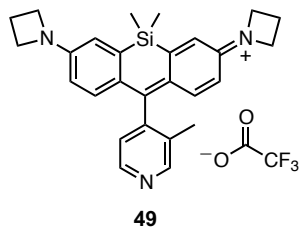


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-08-08T09:13:00
 Modification Date 2016-08-08T09:13:51
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1542.9
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

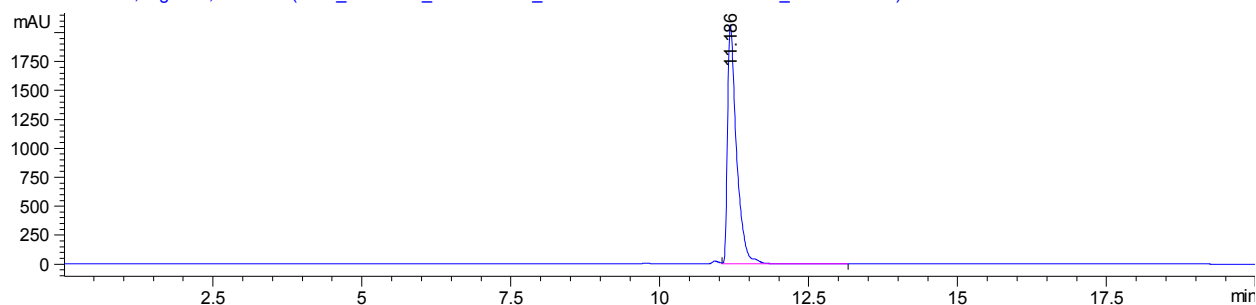


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-23T04:29:00
 Modification Date 2016-11-23T04:29:57
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.6
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

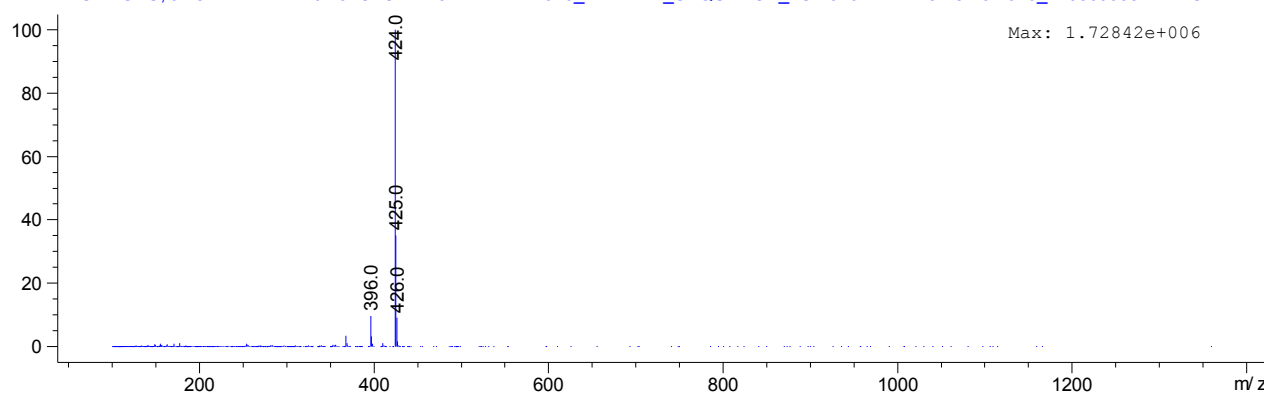




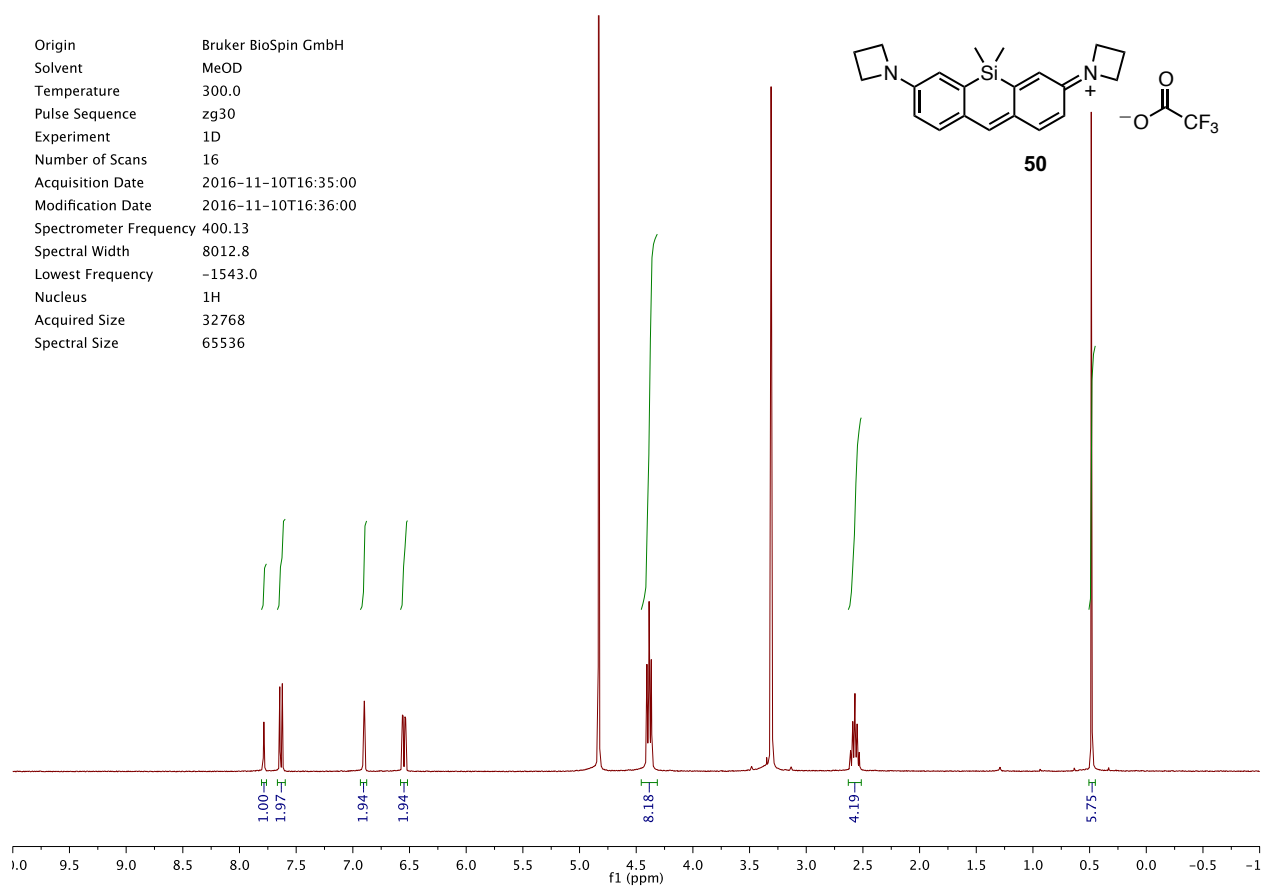
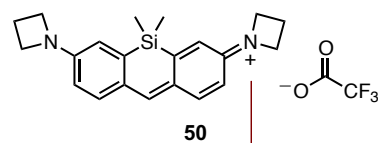
DAD1 E, Sig=650,4 Ref=off (2016_11\DAIY_SEQUENCE_LC 2016-11-22 15-28-20\2016_110000005.D)



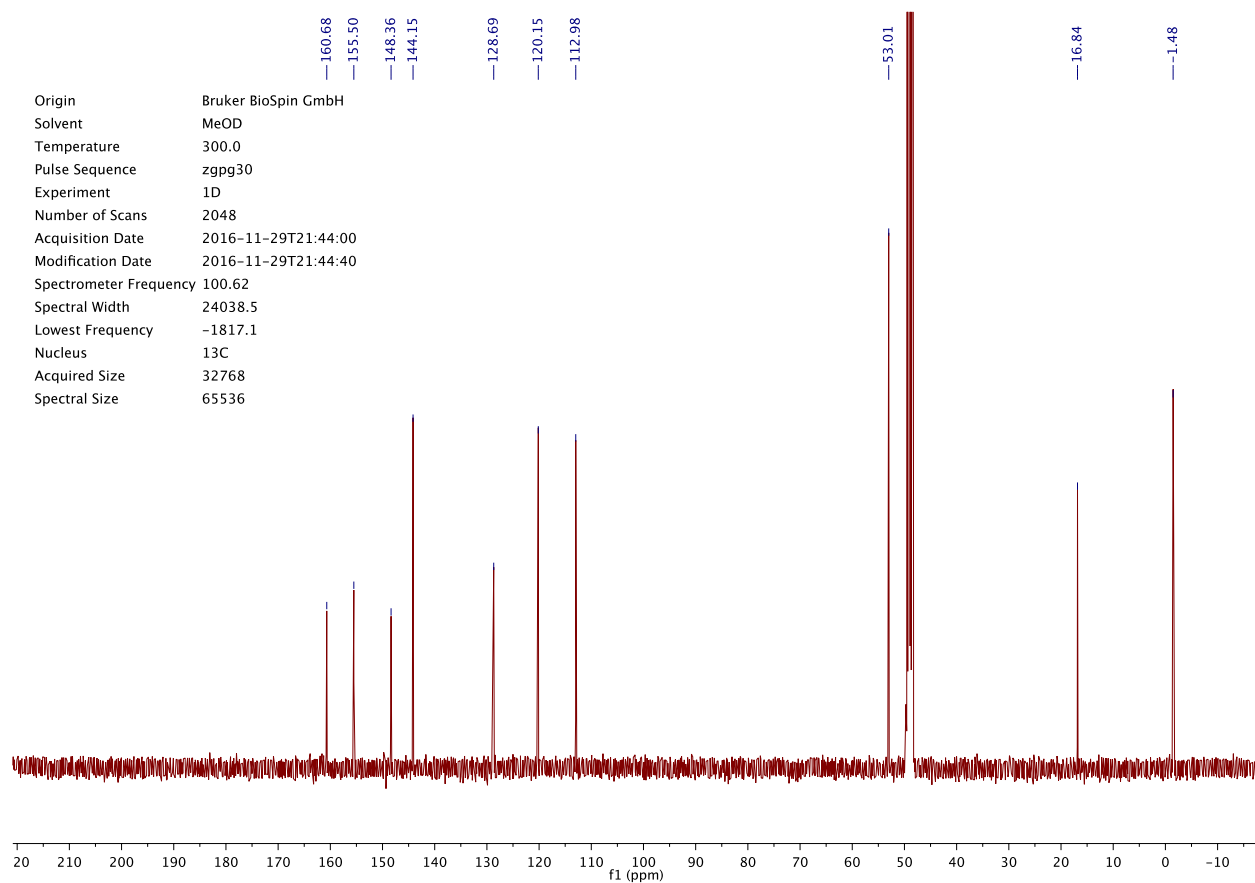
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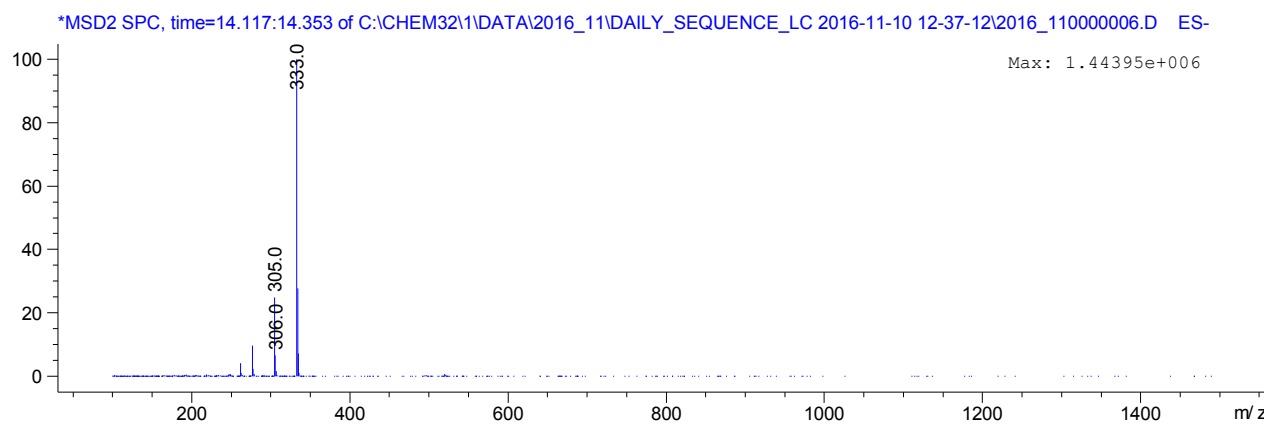
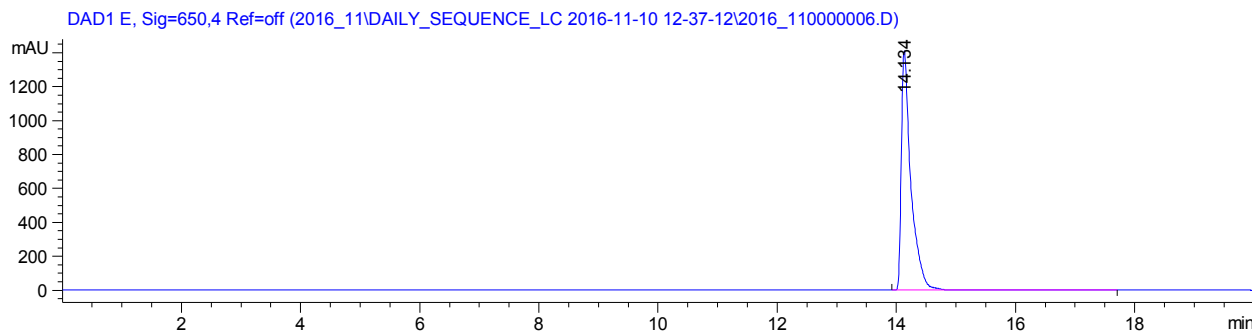
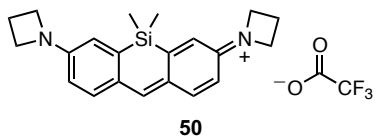


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-11-10T16:35:00
 Modification Date 2016-11-10T16:36:00
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536

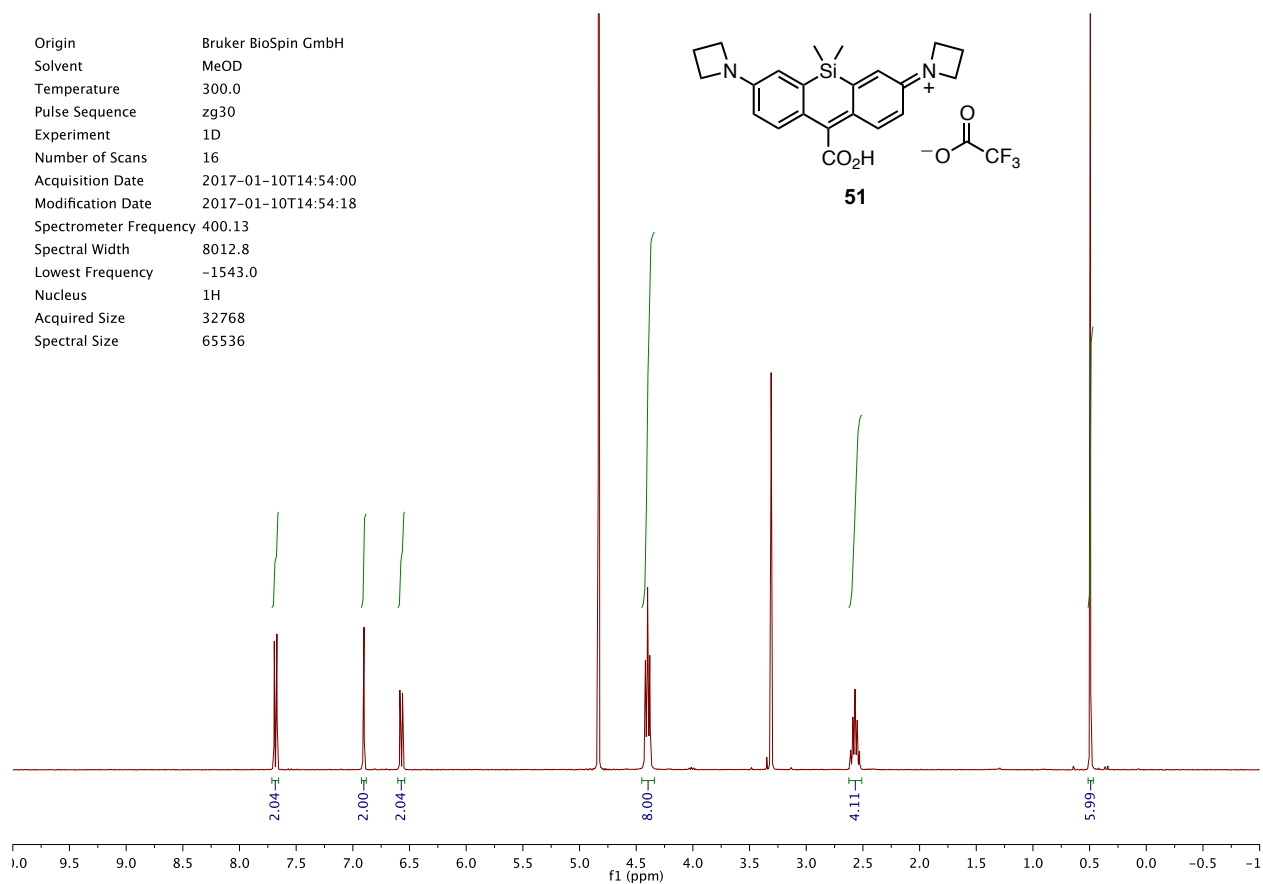
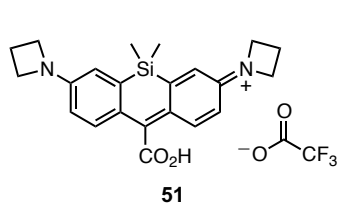


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-29T21:44:00
 Modification Date 2016-11-29T21:44:40
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.1
 Nucleus 13C
 Acquired Size 32768
 Spectral Size 65536

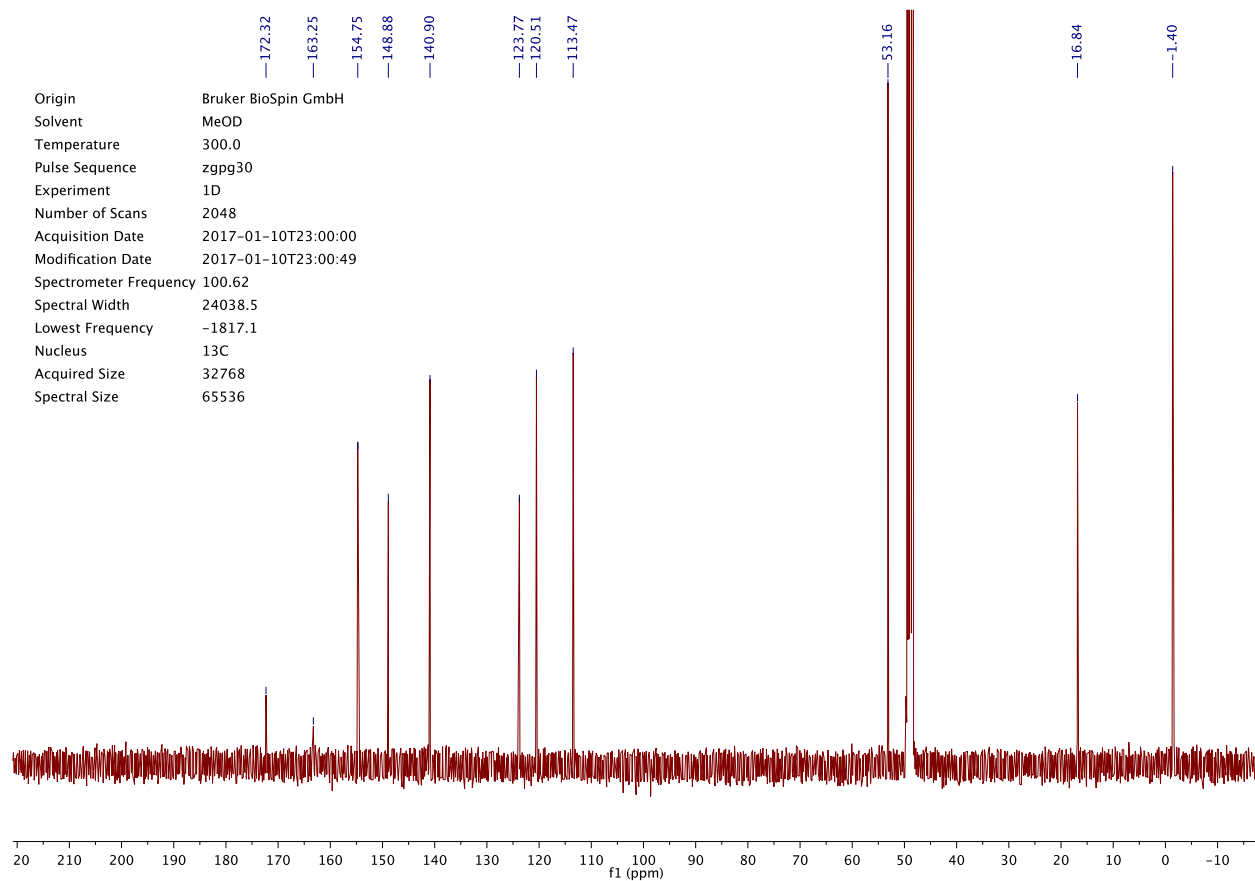


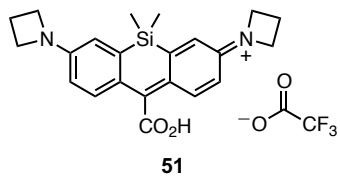


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-10T14:54:00
 Modification Date 2017-01-10T14:54:18
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

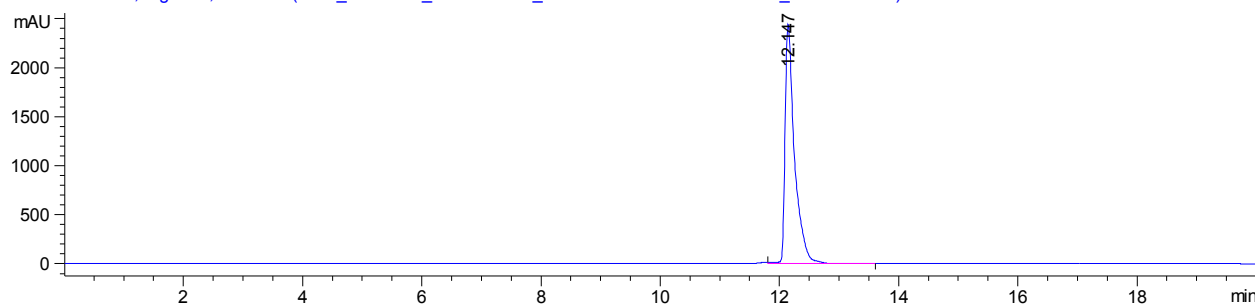


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2017-01-10T23:00:00
 Modification Date 2017-01-10T23:00:49
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1817.1
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

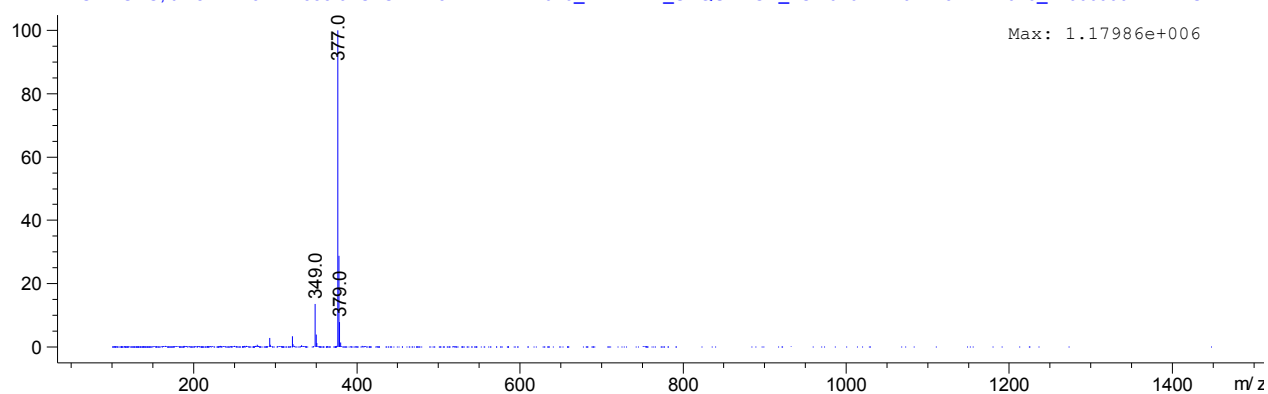




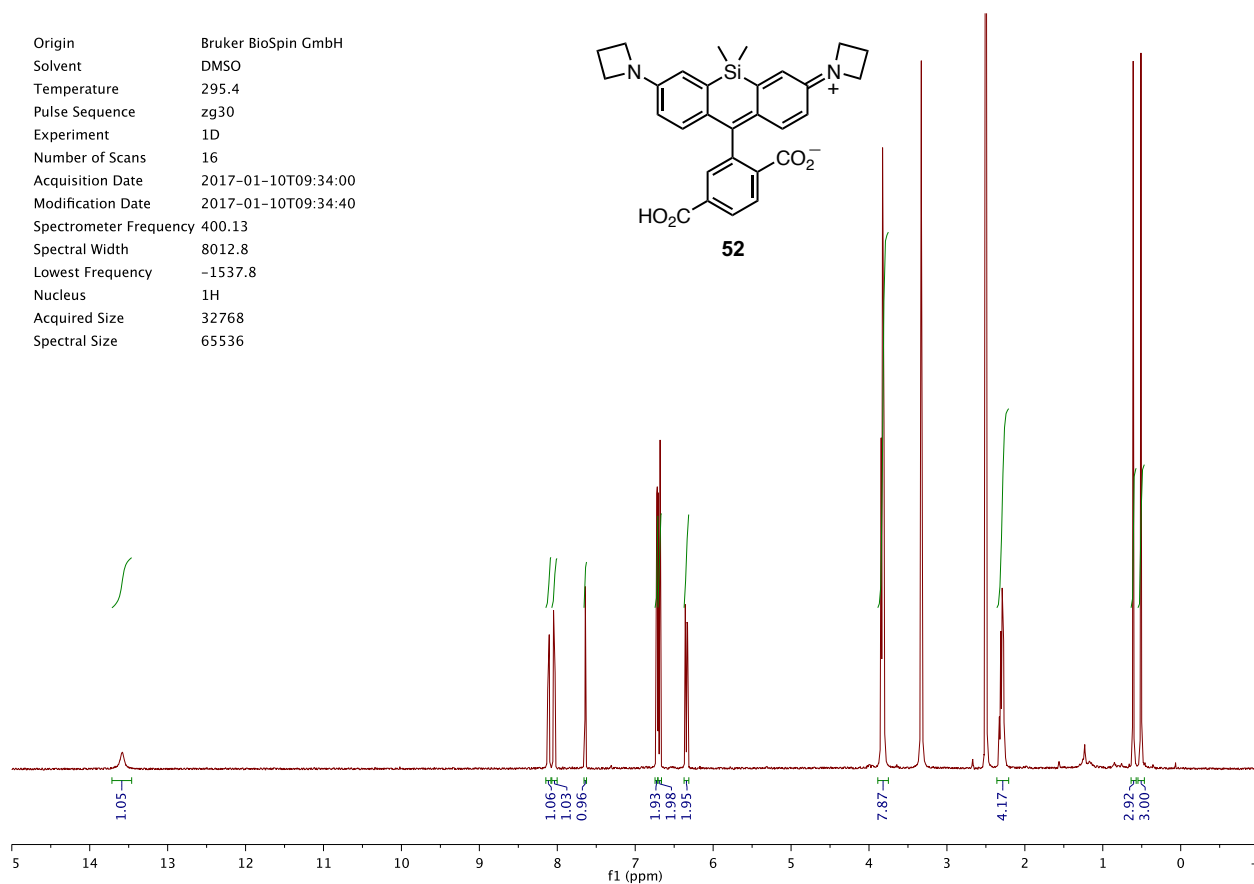
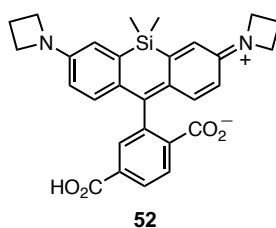
DAD1 E, Sig=650,4 Ref=off (2016_11\DAIY_SEQUENCE_LC 2016-11-10 12-37-12\2016_110000004.D)



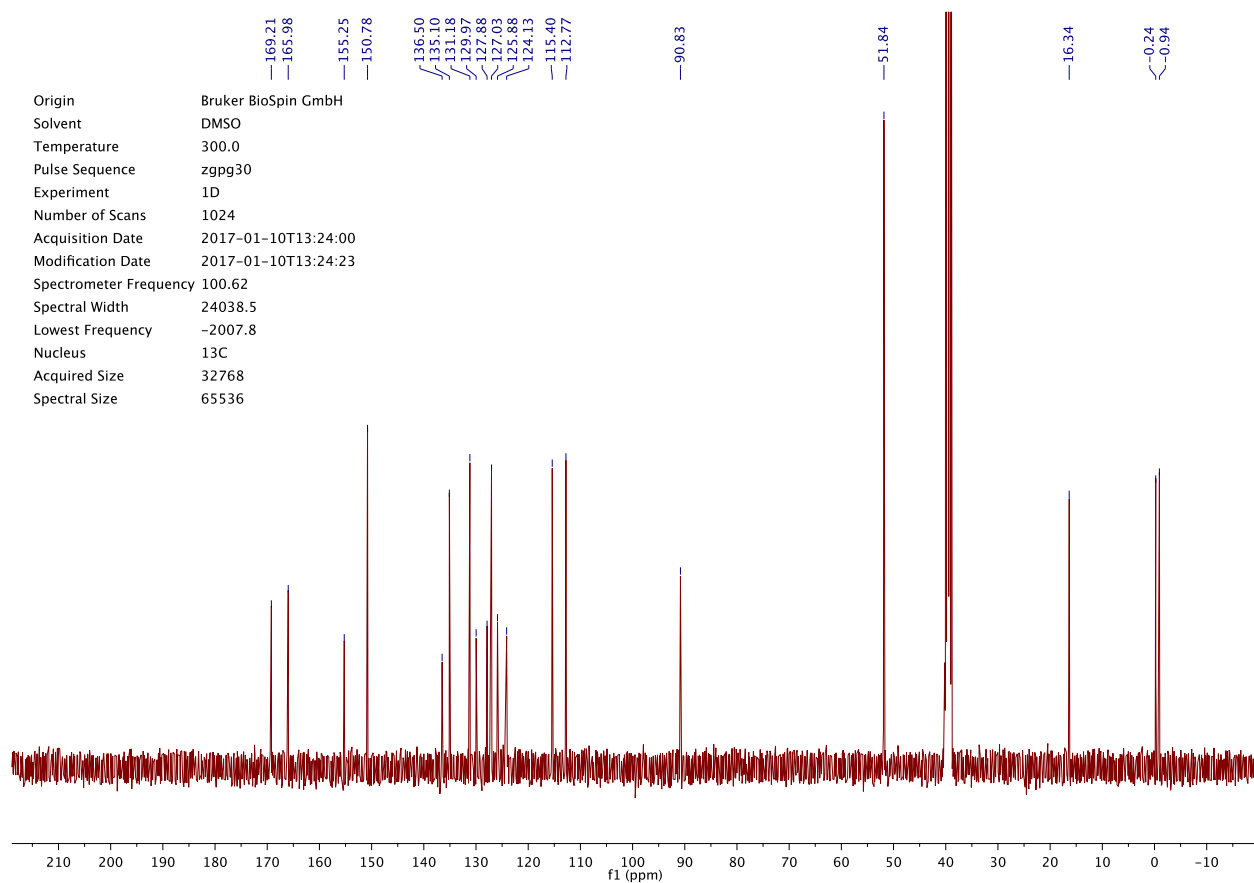
*MSD2 SPC, time=12.137:12.355 of C:\CHEM32\1\DATA\2016_11\DAIY_SEQUENCE_LC 2016-11-10 12-37-12\2016_110000004.D ES-

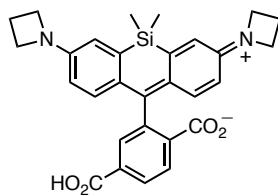


Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 295.4
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-01-10T09:34:00
 Modification Date 2017-01-10T09:34:40
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1537.8
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



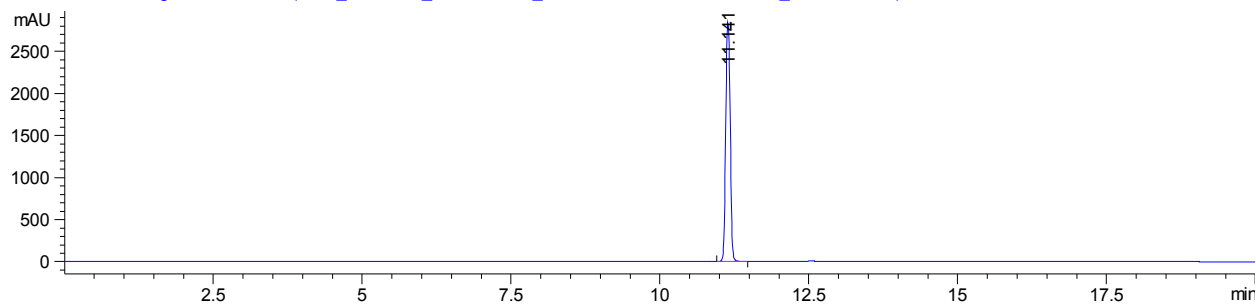
Origin Bruker BioSpin GmbH
 Solvent DMSO
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 1024
 Acquisition Date 2017-01-10T13:24:00
 Modification Date 2017-01-10T13:24:23
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -2007.8
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



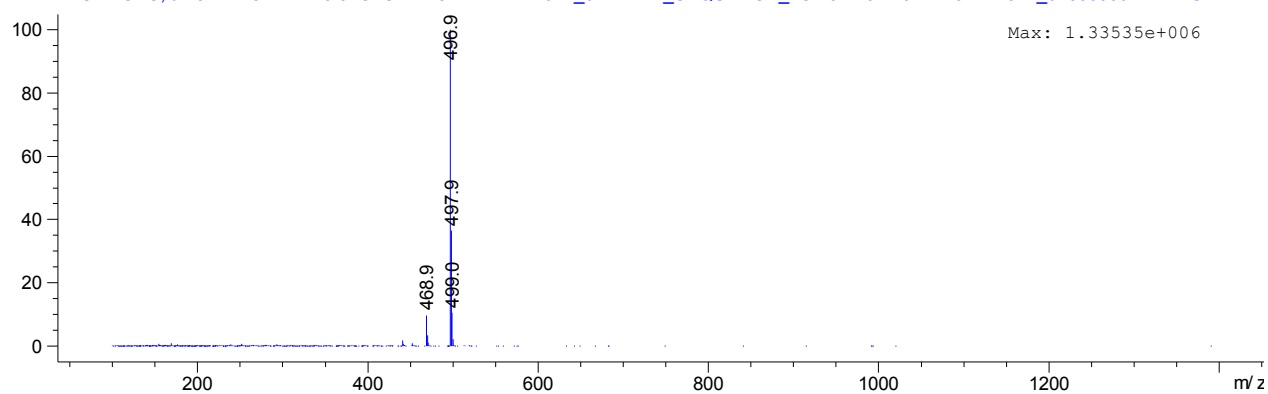


52

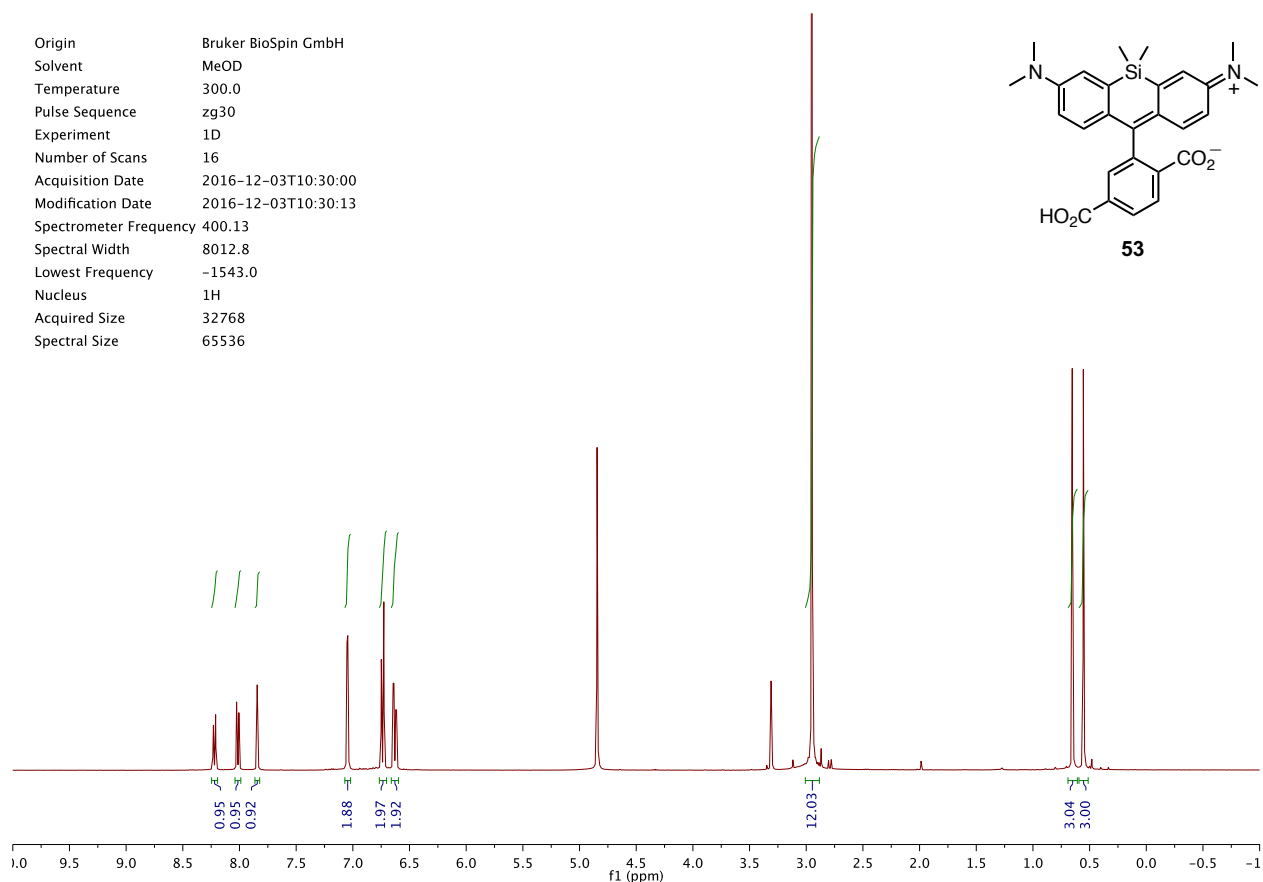
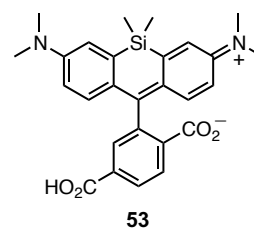
DAD1 E, Sig=650,4 Ref=off (2017_01\DAIY_SEQUENCE_LC 2017-01-19 14-40-14\2017_010000004.D)



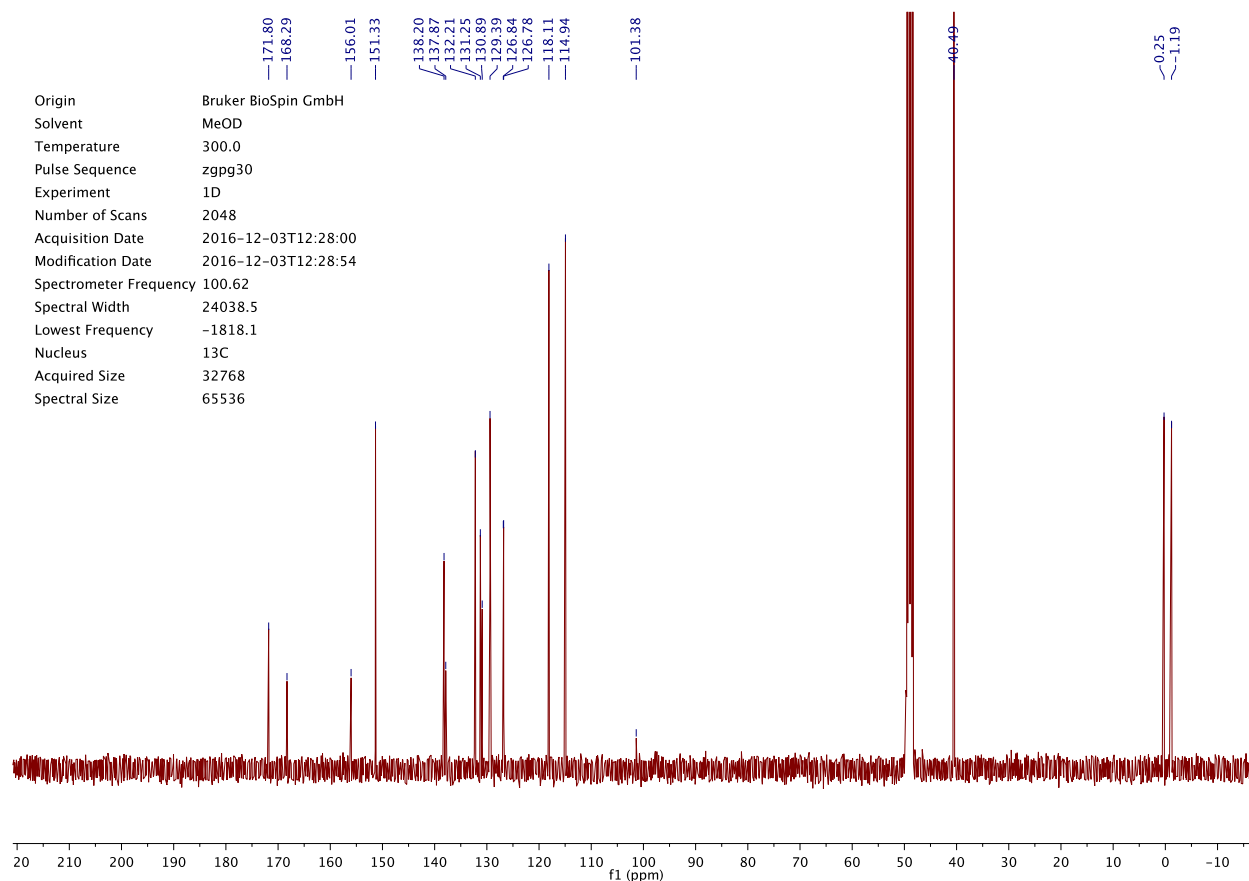
*MSD2 SPC, time=11.152:11.243 of C:\CHEM32\1\DATA\2017_01\DAIY_SEQUENCE_LC 2017-01-19 14-40-14\2017_010000004.D ES-

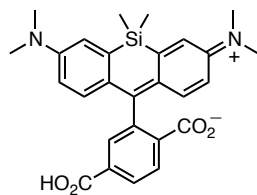


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-12-03T10:30:00
 Modification Date 2016-12-03T10:30:13
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536

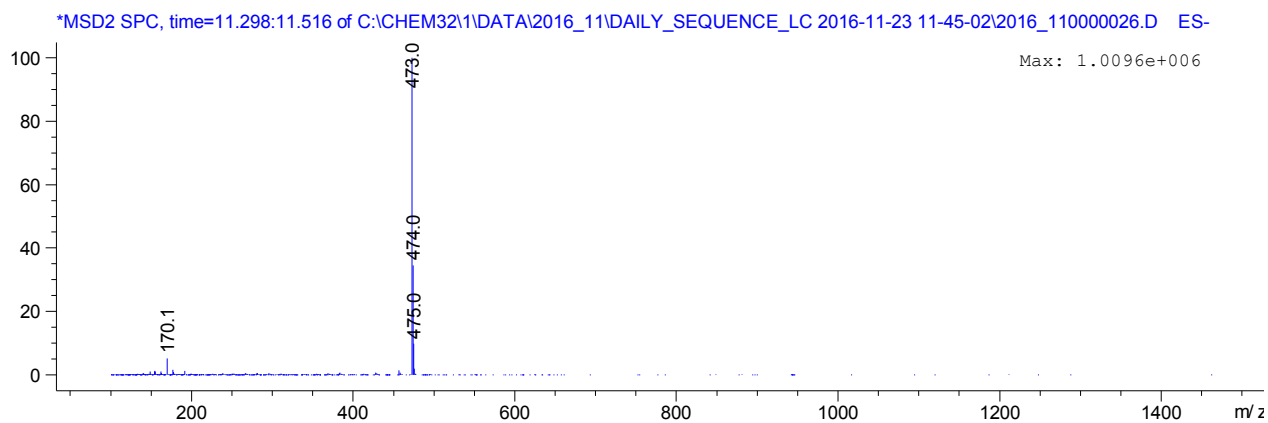
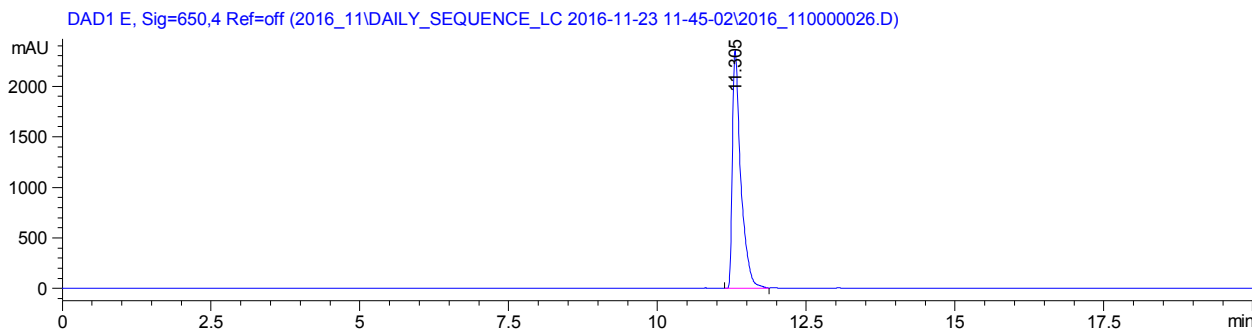


Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-12-03T12:28:00
 Modification Date 2016-12-03T12:28:54
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1818.1
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536

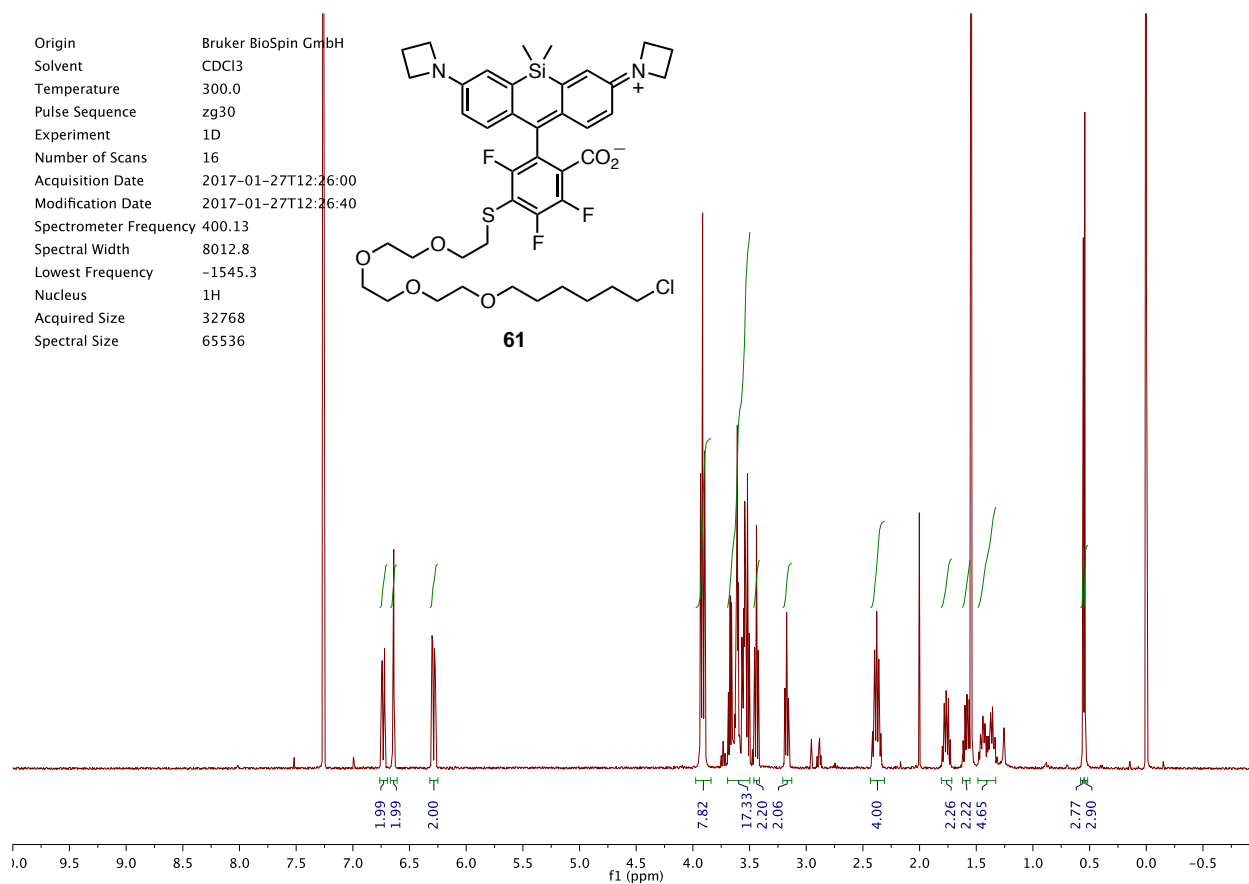
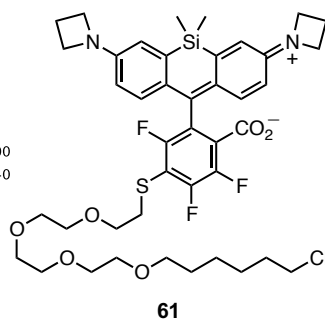




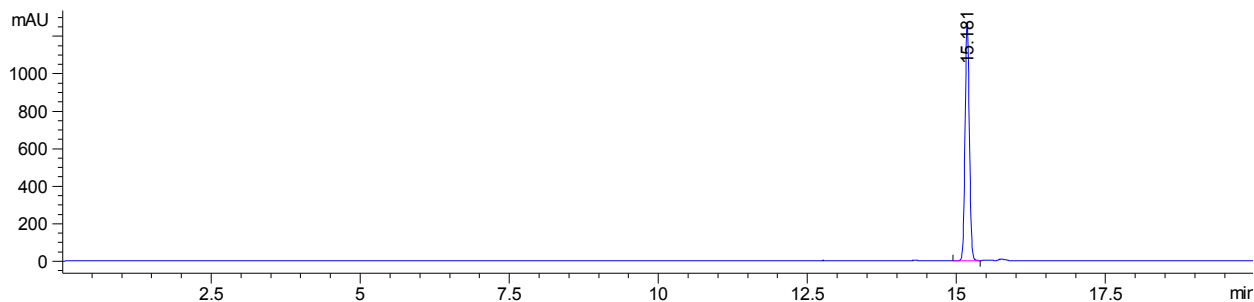
53



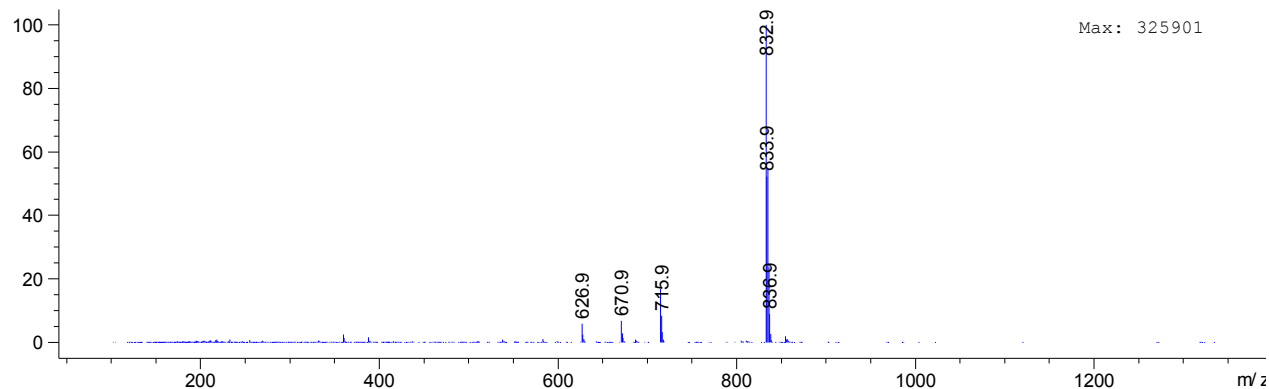
Origin: Bruker BioSpin GmbH
 Solvent: CDCl₃
 Temperature: 300.0
 Pulse Sequence: zg30
 Experiment: 1D
 Number of Scans: 16
 Acquisition Date: 2017-01-27T12:26:00
 Modification Date: 2017-01-27T12:26:40
 Spectrometer Frequency: 400.13
 Spectral Width: 8012.8
 Lowest Frequency: -1545.3
 Nucleus: ¹H
 Acquired Size: 32768
 Spectral Size: 65536



DAD1 E, Sig=650.4 Ref=off (2017_01\DAIY_SEQUENCE_LC 2017-01-26 14-20-01\2017_010000002.D)



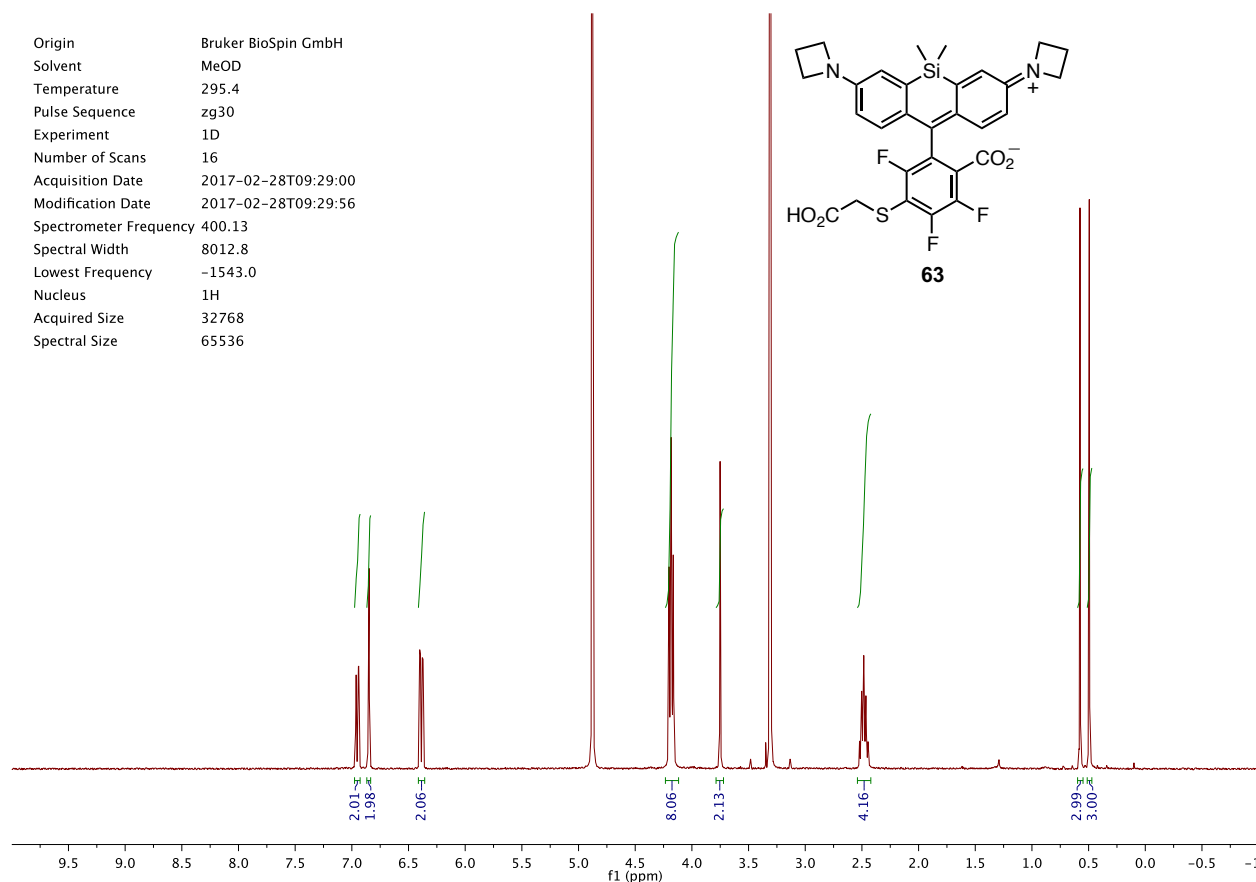
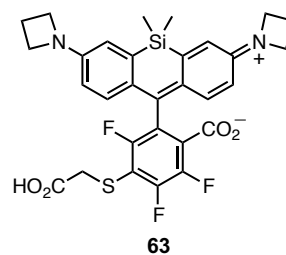
*MSD2 SPC, time=15.204:15.277 of C:\CHEM32\1\DATA\2017_01\DAIY_SEQUENCE_LC 2017-01-26 14-20-01\2017_010000002.D ES-



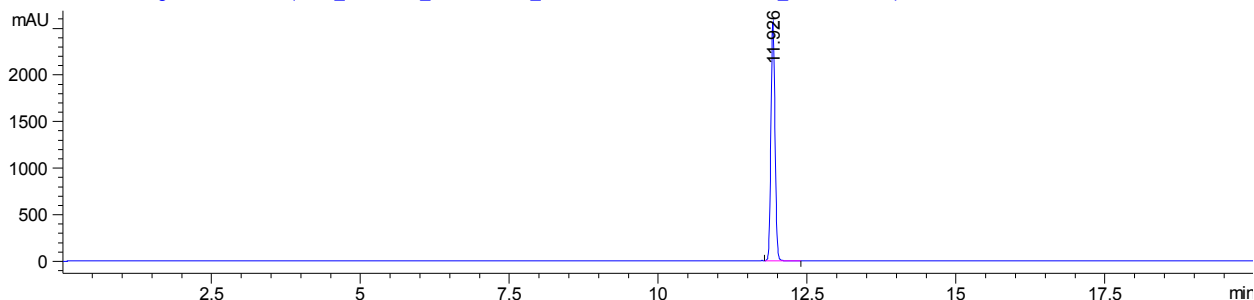
62



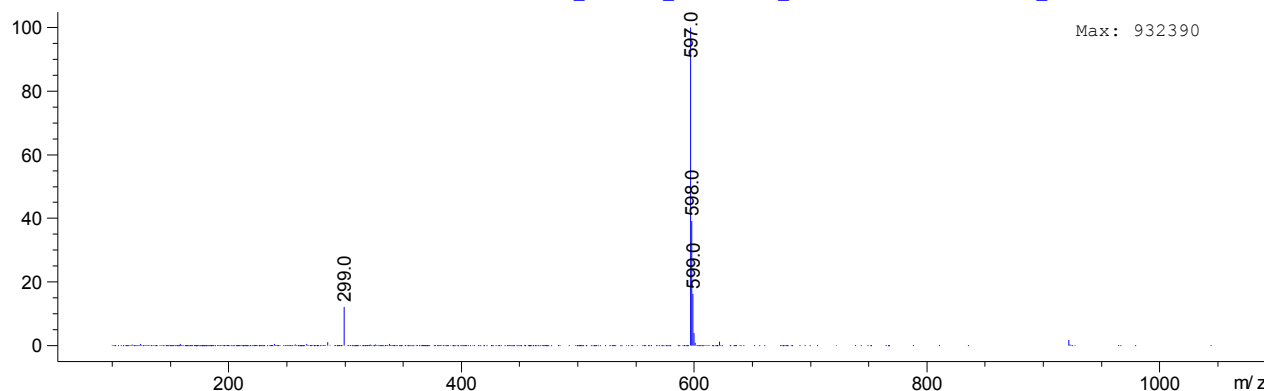
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 295.4
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-02-28T09:29:00
 Modification Date 2017-02-28T09:29:56
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



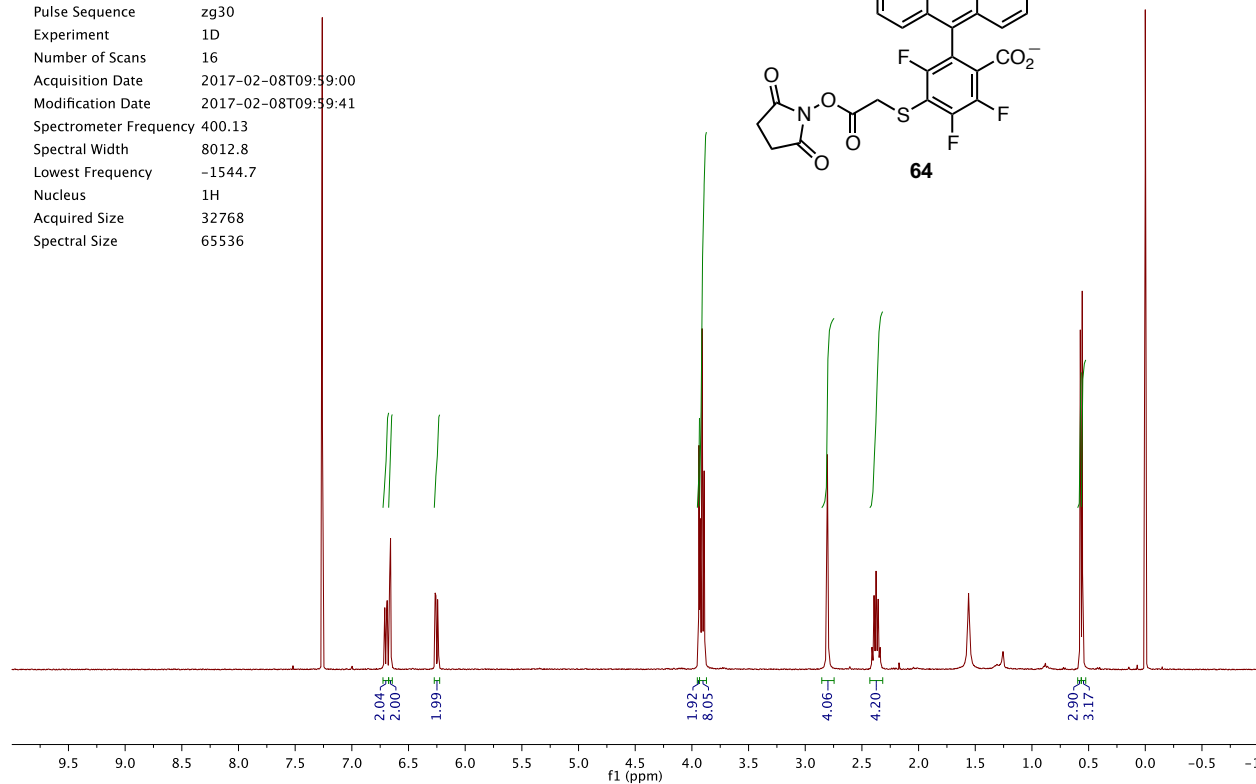
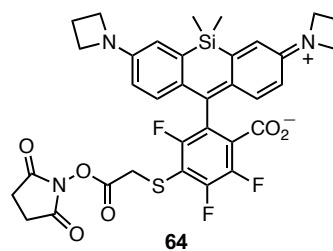
DAD1 E, Sig=650.4 Ref=off (2017_02\DAIY_SEQUENCE_LC 2017-02-27 16-10-57\2017_020000002.D)



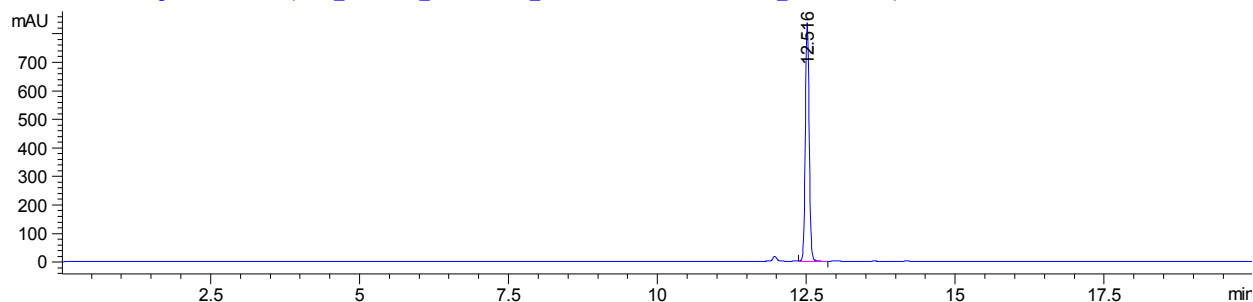
*MSD2 SPC, time=11.934:12.006 of C:\CHEM32\1\DATA\2017_02\DAIY_SEQUENCE_LC 2017-02-27 16-10-57\2017_020000002.D ES-



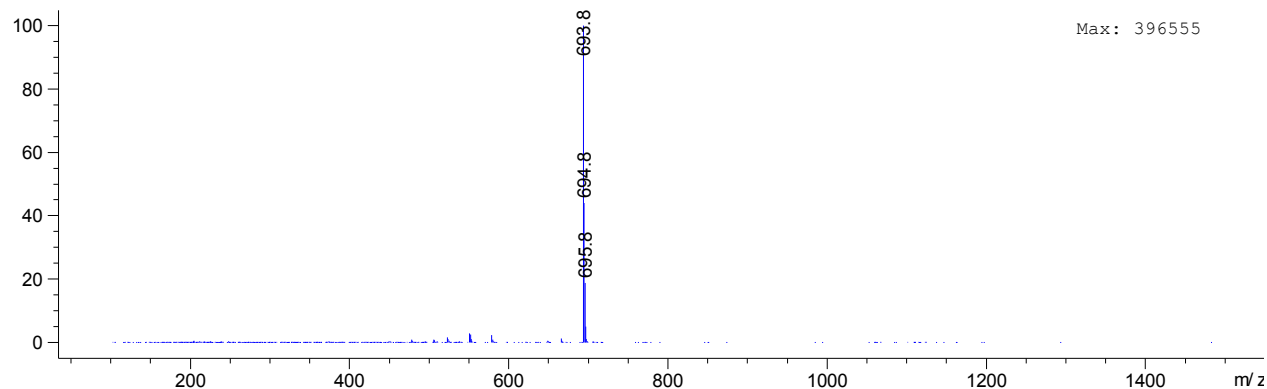
Origin Bruker BioSpin GmbH
 Solvent CDCl3
 Temperature 295.6
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2017-02-08T09:59:00
 Modification Date 2017-02-08T09:59:41
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1544.7
 Nucleus 1H
 Acquired Size 32768
 Spectral Size 65536



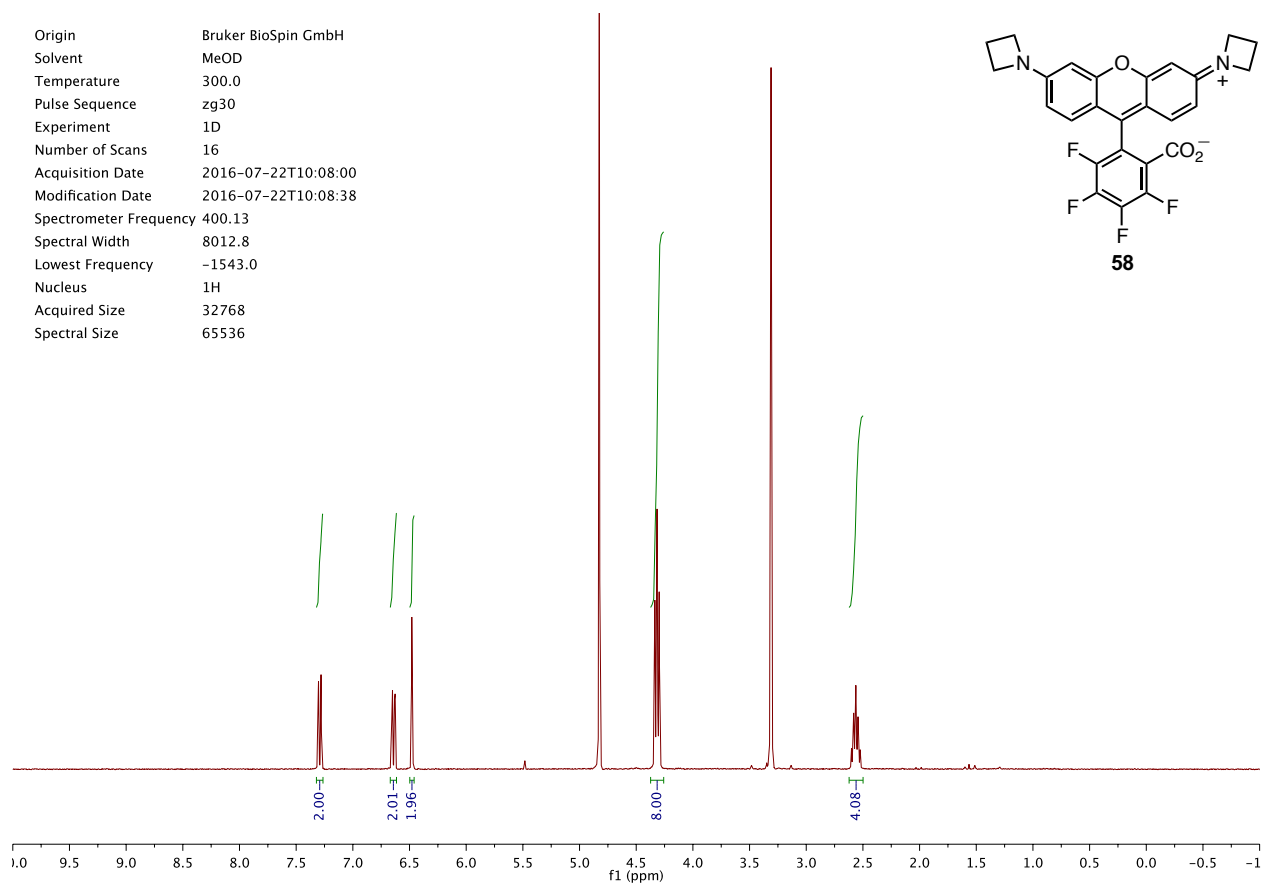
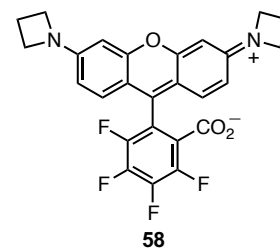
DAD1 E, Sig=650,4 Ref=off (2017_02\DAIY_SEQUENCE_LC 2017-02-07 16-04-30\2017_020000002.D)



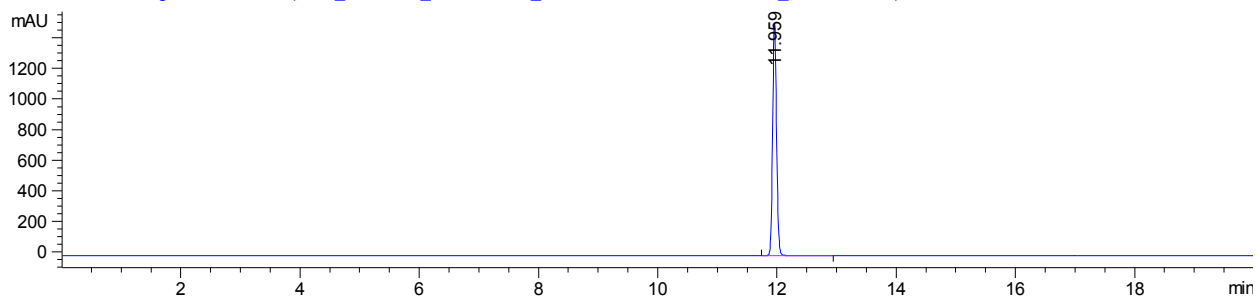
*MSD2 SPC, time=12.533:12.624 of C:\CHEM32\1\DATA\2017_02\DAIY_SEQUENCE_LC 2017-02-07 16-04-30\2017_020000002.D ES-



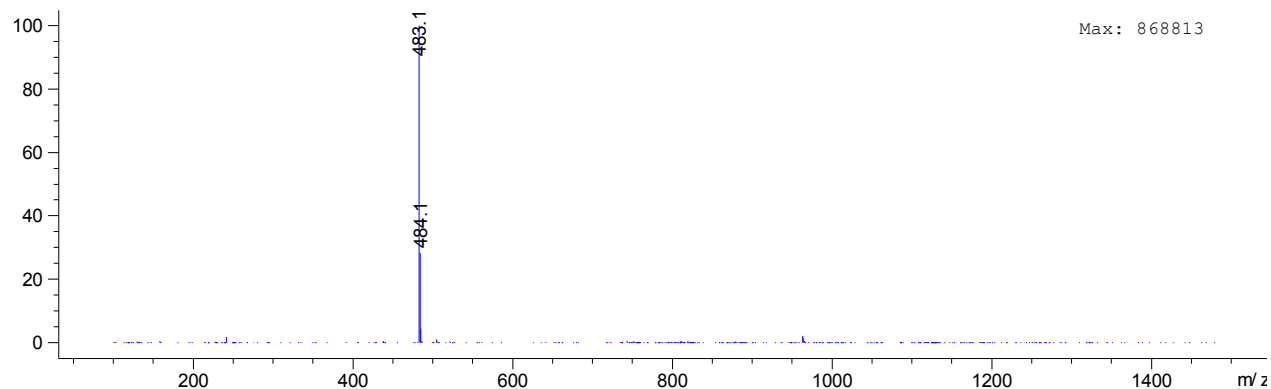
Origin Bruker BioSpin GmbH
 Solvent MeOD
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-07-22T10:08:00
 Modification Date 2016-07-22T10:08:38
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1543.0
 Nucleus ^1H
 Acquired Size 32768
 Spectral Size 65536



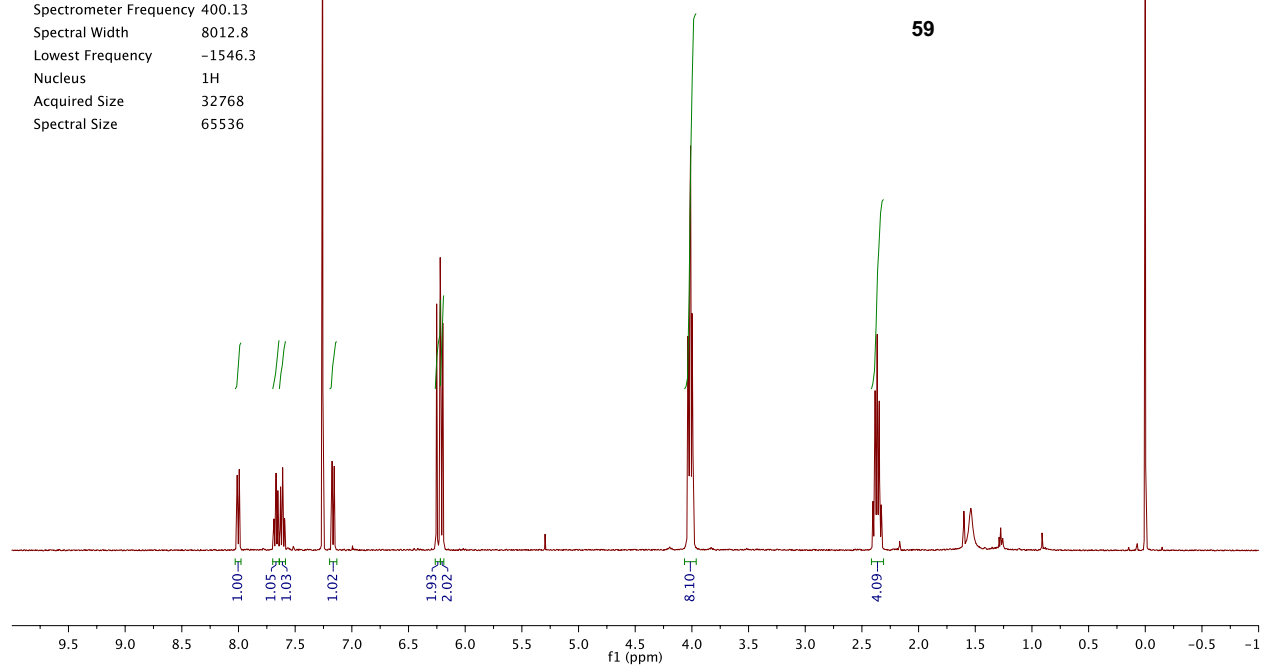
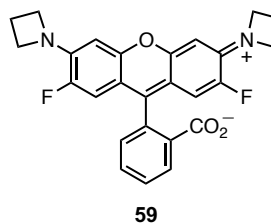
DAD1 C, Sig=550.4 Ref=off (2017_06DAILY_SEQUENCE_LC 2017-06-06 10-45-47\2017_060000005.D)



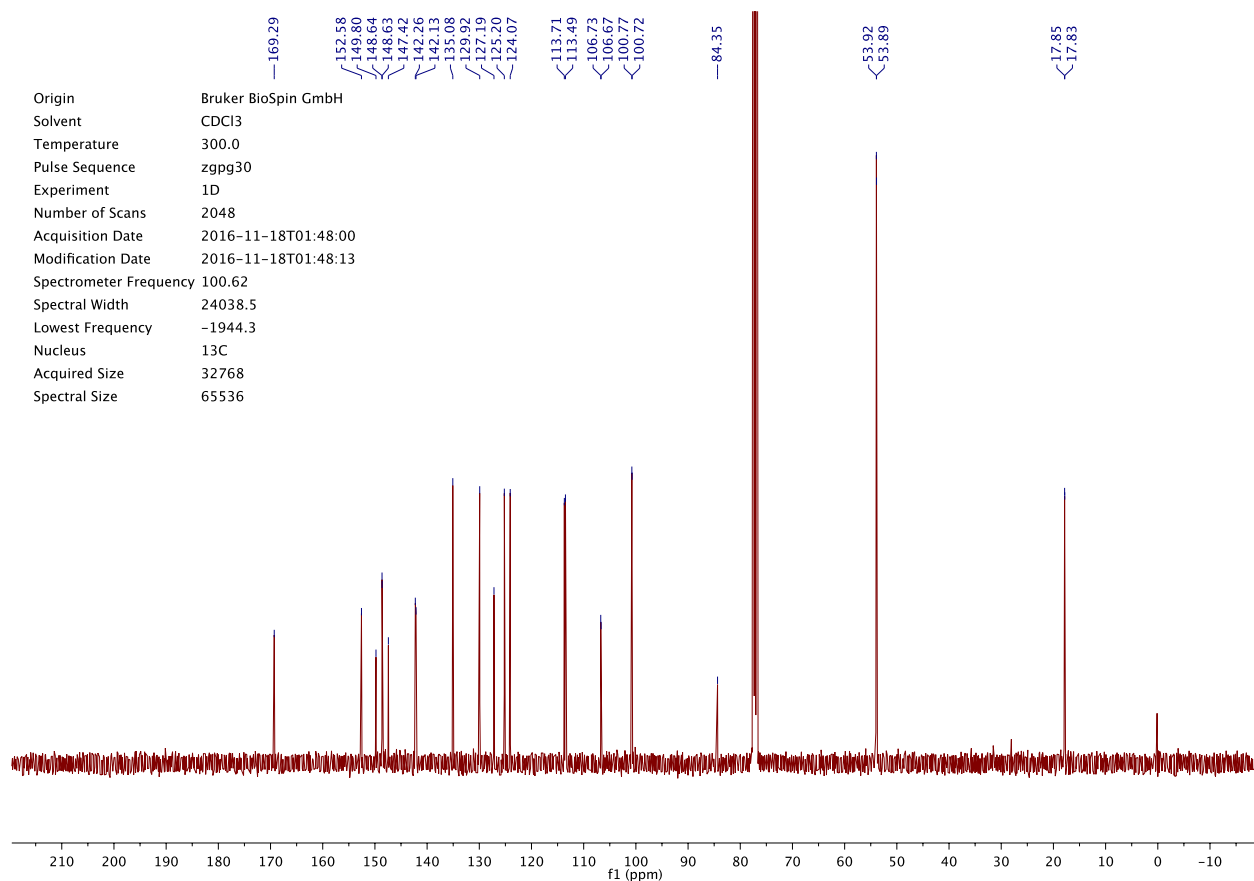
*MSD2 SPC, time=11.955:12.028 of C:\CHEM32\1\DATA\2017_06DAILY_SEQUENCE_LC 2017-06-06 10-45-47\2017_060000005.D ES-

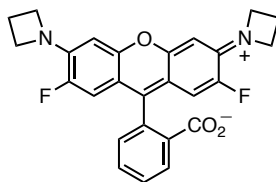


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2016-07-25T15:18:00
 Modification Date 2016-07-25T15:18:20
 Spectrometer Frequency 400.13
 Spectral Width 8012.8
 Lowest Frequency -1546.3
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



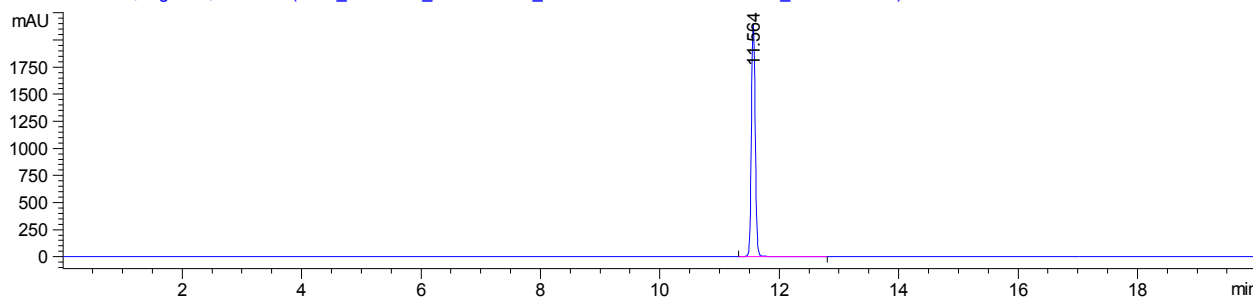
Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2016-11-18T01:48:00
 Modification Date 2016-11-18T01:48:13
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1944.3
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536



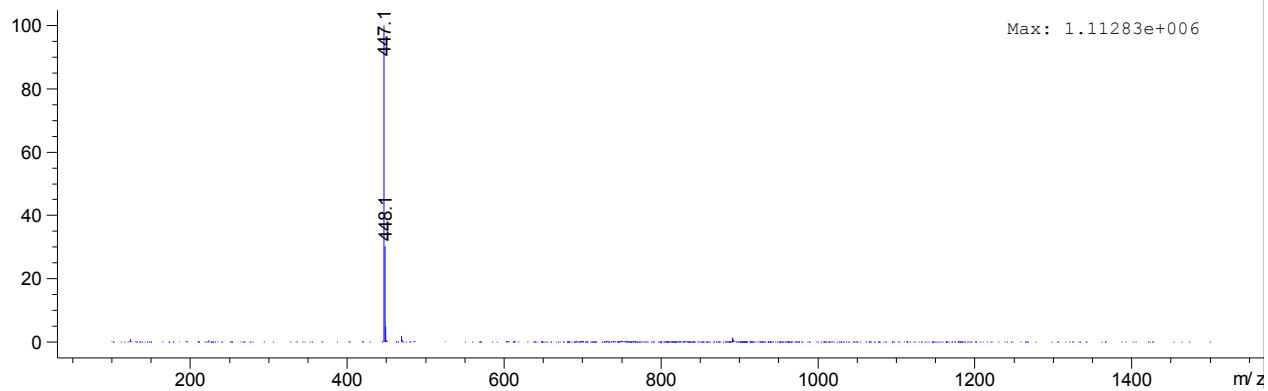


59

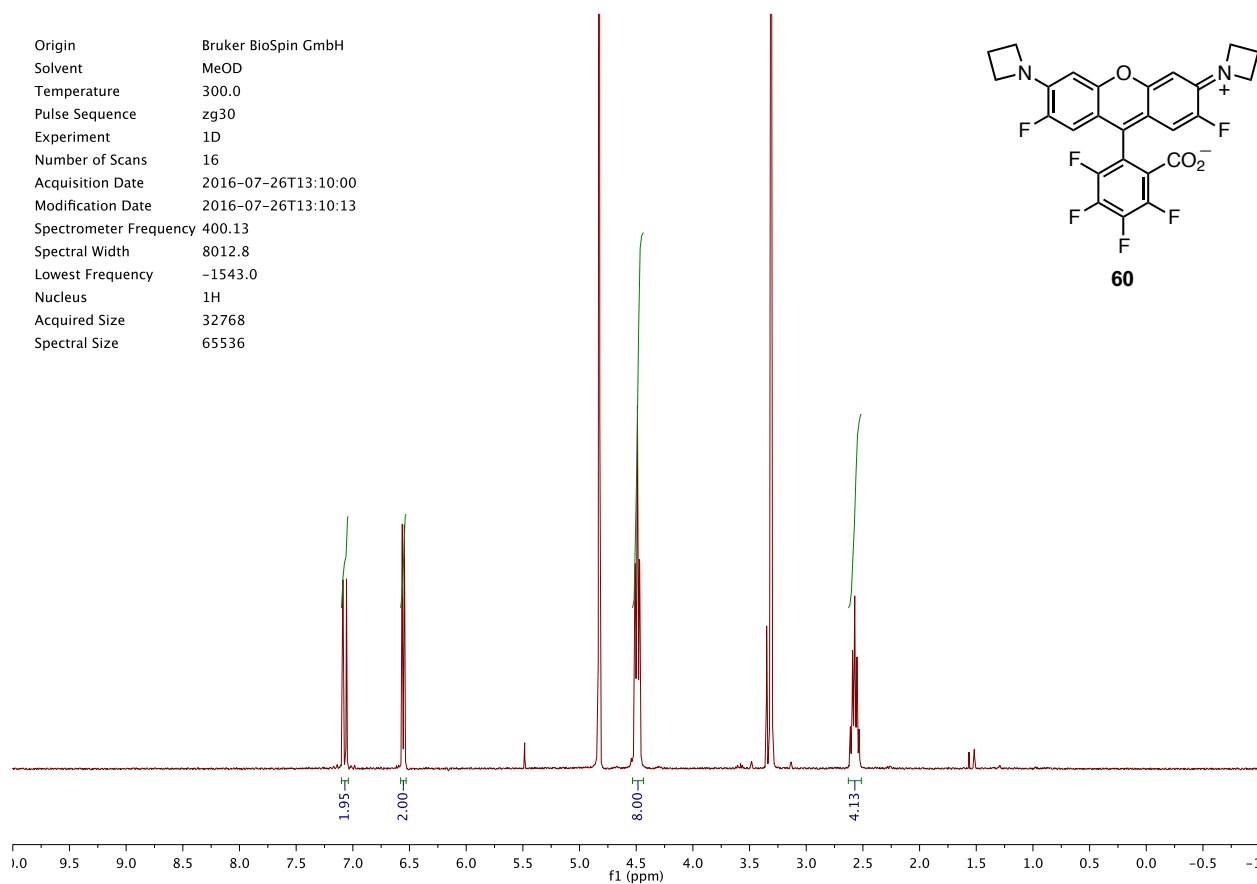
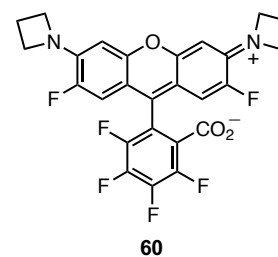
DAD1 C, Sig=550,4 Ref=off (2017_07\DAIY_SEQUENCE_LC 2017-07-11 14-47-28\2017_070000002.D)



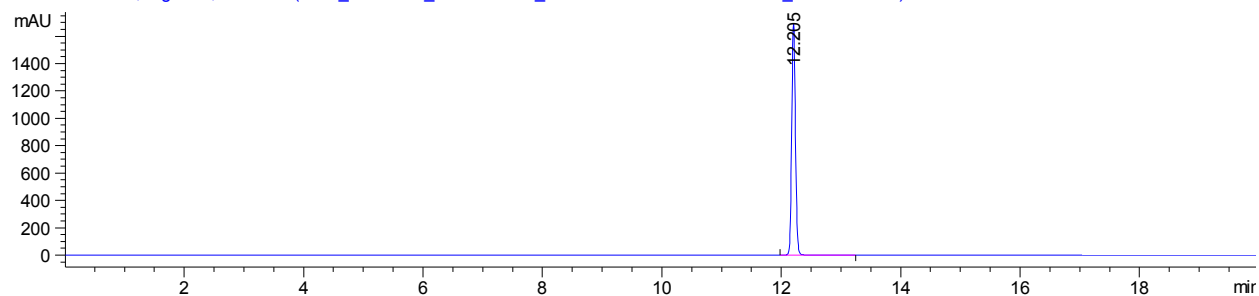
*MSD2 SPC, time=11.570:11.643 of C:\CHEM32\1\DATA\2017_07\DAIY_SEQUENCE_LC 2017-07-11 14-47-28\2017_070000002.D ES-



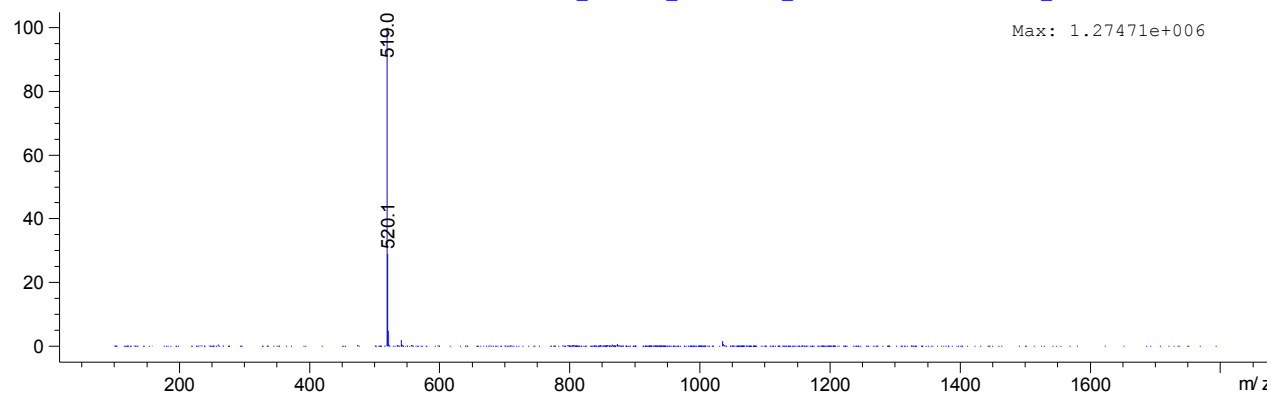
Origin: Bruker BioSpin GmbH
 Solvent: MeOD
 Temperature: 300.0
 Pulse Sequence: zg30
 Experiment: 1D
 Number of Scans: 16
 Acquisition Date: 2016-07-26T13:10:00
 Modification Date: 2016-07-26T13:10:13
 Spectrometer Frequency: 400.13
 Spectral Width: 8012.8
 Lowest Frequency: -1543.0
 Nucleus: ^1H
 Acquired Size: 32768
 Spectral Size: 65536



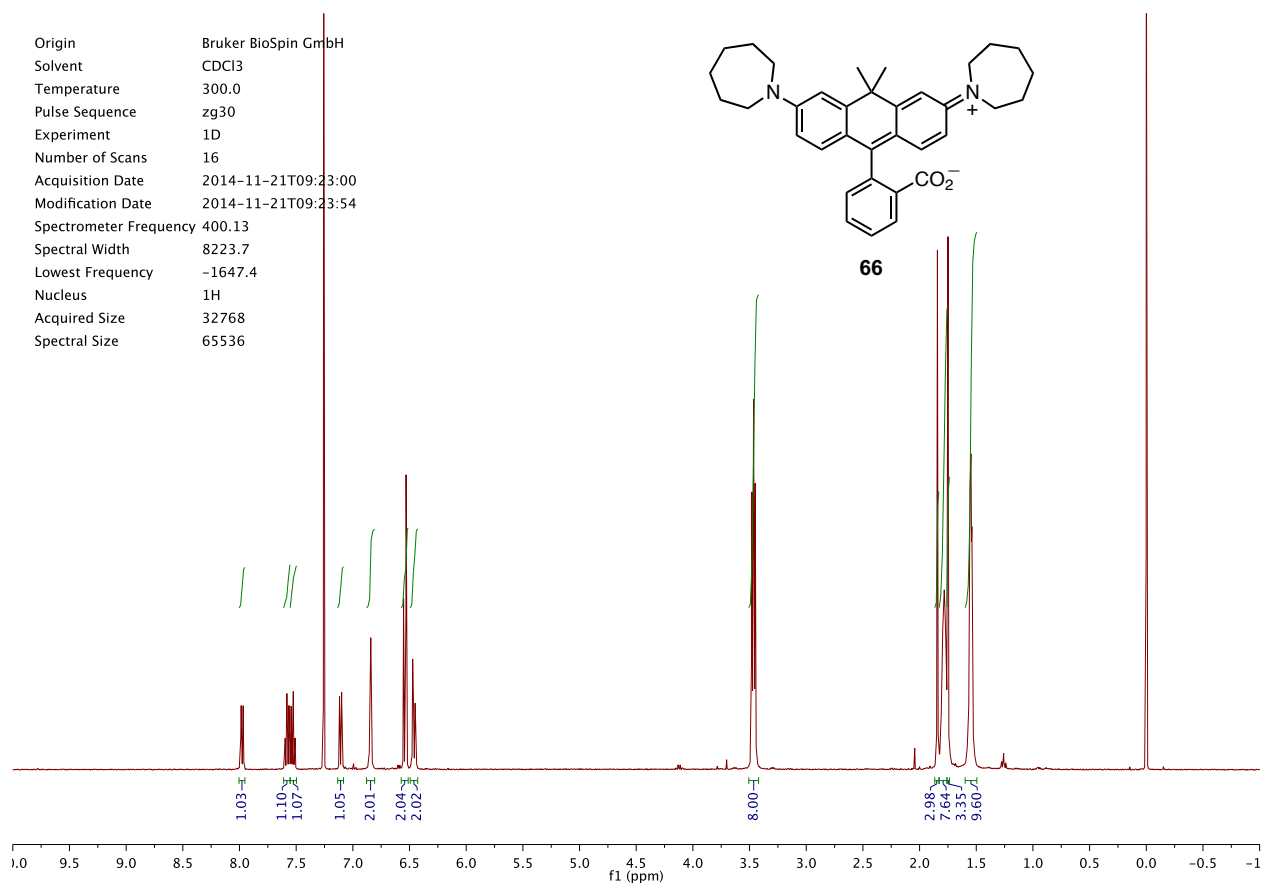
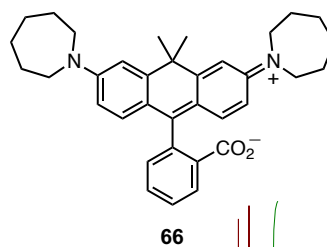
DAD1 C, Sig=550,4 Ref=off (2017_07\DAI\SEQUENCE_LC 2017-07-10 13-53-21\2017_070000007.D)



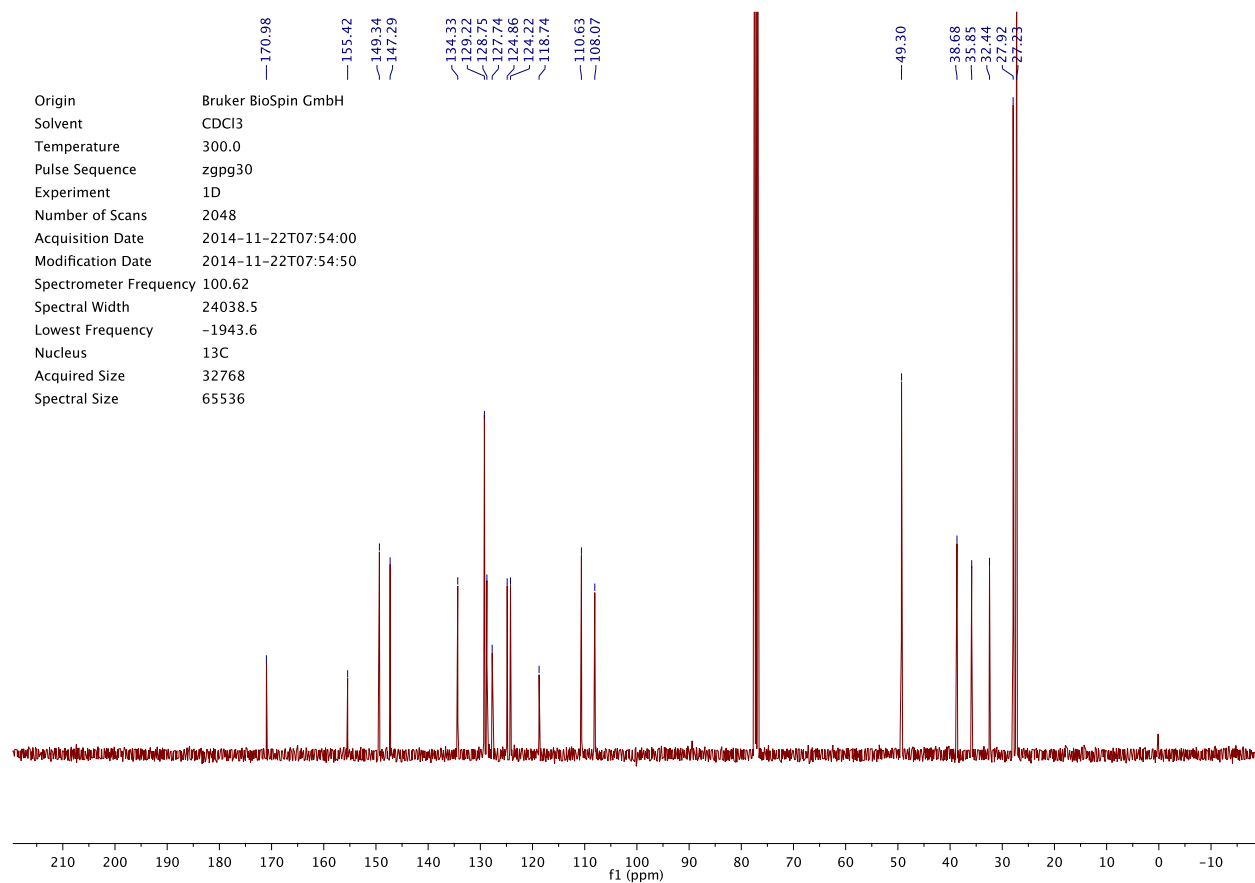
*MSD2 SPC, time=12.201:12.283 of C:\CHEM32\1\DATA\2017_07\DAI\SEQUENCE_LC 2017-07-10 13-53-21\2017_070000007.D ES-

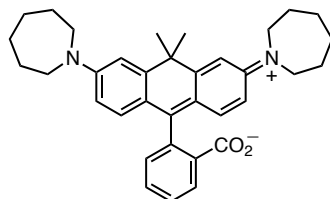


Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zg30
 Experiment 1D
 Number of Scans 16
 Acquisition Date 2014-11-21T09:23:00
 Modification Date 2014-11-21T09:23:54
 Spectrometer Frequency 400.13
 Spectral Width 8223.7
 Lowest Frequency -1647.4
 Nucleus ¹H
 Acquired Size 32768
 Spectral Size 65536



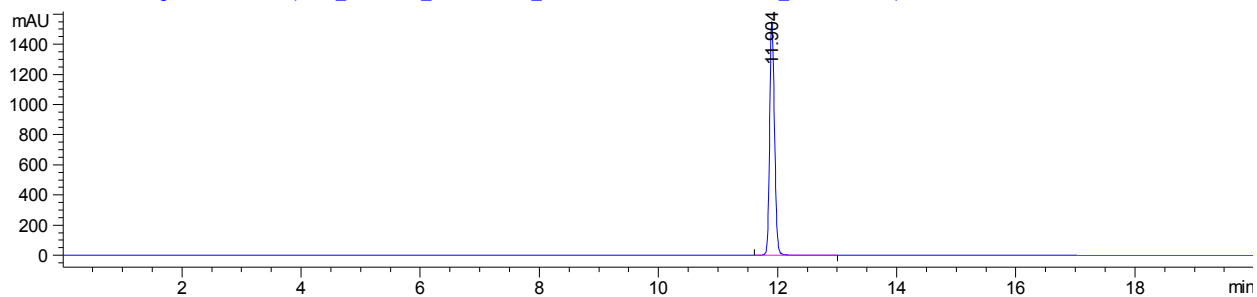
Origin Bruker BioSpin GmbH
 Solvent CDCl₃
 Temperature 300.0
 Pulse Sequence zgpg30
 Experiment 1D
 Number of Scans 2048
 Acquisition Date 2014-11-22T07:54:00
 Modification Date 2014-11-22T07:54:50
 Spectrometer Frequency 100.62
 Spectral Width 24038.5
 Lowest Frequency -1943.6
 Nucleus ¹³C
 Acquired Size 32768
 Spectral Size 65536





66

DAD1 D, Sig=600,4 Ref=off (2017_01\DAIY_SEQUENCE_LC 2017-01-25 10-16-26\2017_010000003.D)



*MSD2 SPC, time=11.916:12.025 of C:\CHEM32\1\DATA\2017_01\DAIY_SEQUENCE_LC 2017-01-25 10-16-26\2017_010000003.D ES-

