Supporting information of

Remote Hydroamination of Disubstituted Alkenes by a Combination of Isomerization and Regioselective N-H Addition

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1. General Information

1.1 General Experimental Procedures

All manipulations were performed in a nitrogen-filled glovebox or on a Schlenk manifold unless otherwise noted. Glassware was dried at 150 °C for at least 4 h before use. All liquid alkenes were stored over 4 Å molecular sieves in the glovebox for at least 12 h prior to use. All solid alkenes were used as received without further purification. All aminopyridines were purified by column chromatography to remove oxidized impurities prior to use. All catalytic reactions were assembled in a nitrogen-filled glovebox with oven-dried glassware and were stirred with Teflon-coated magnetic stirring bars.

1.2 Reagents and Solvents

DCM, Et_2O, THF, and hexanes were collected from a solvent purification system containing a 0.33 m column of activated alumina under nitrogen and stored over 4 Å molecular sieves for at least 12 h prior to use. Anhydrous 1,4-dioxane was purchased from Acros, stored in a glovebox, and stored over 4 Å molecular sieves for at least 12 h prior to use. Phosphine ligands were used as received from Takasago or Strem. Aminopyridines was purchased from Aldrich, columned with ethyl acetate/hexanes, and stored in a glovebox. $[Ir(coe)_2Cl]_2$ was used as received from Strem.

1.3 Chromatography and Data Analysis

Flash column chromatography was carried out with a Teledyne Isco CombiFlash Rf system using RediSep Rf Gold columns.

^{1}H, ^{13}C and ^{19}F NMR Spectra were recorded on a Bruker 500 or 600 MHz spectrometer. ^{1}H chemical shifts are reported in parts per million, relative residual protiated solvent as a reference. ^{13}C chemical shifts are reported in parts per million, relative to the deuterated solvent as a reference. ^{19}F chemical shifts were reported in parts per million, relative to an external standard of $CFCl_3$. ^{31}P chemical shifts were reported in parts per million, relative to an 85% H_3PO_4 external standard.

High-resolution mass spectral (HRMS) data were obtained with PerkinElmer AxION 2 TOF (ESI and APCI), Thermo LTQ-FTICR (ESI) and Waters Autospec Premier (EI) mass spectrometers at the QB3/Chemistry Mass Spectrometry Facility at UC Berkeley at the LBNL Catalysis Facility.

Gas Chromatography (GC) was performed on an Agilent 7890 GC with an FID detector.

Liquid Chromatography (LC) was performed on a Waters ACQUITY UPLC System with a UV detector.

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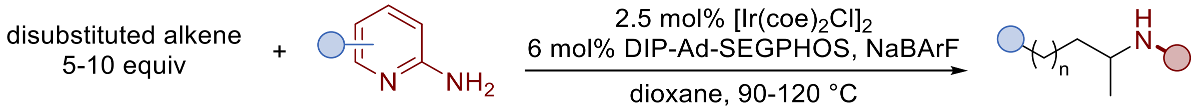
1.4 Naming of Compounds

Compound names are those generated by ChemDraw 16.0 software (PerkinElmer), following the IUPAC nomenclature.

2. General Procedures for the Remote Hydroamination of Alkenes



Condition A: In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with $[Ir(coe)_2Cl]_2$ (2.3 mg, 2.5 µmol, 2.5 mol%), aminopyridine (0.10 mmol, 1.0 equiv), DIP-Ad-SEGPHOS (7.3 mg, 6.0 µmol, 6.0 mol%), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (5.4 mg, 6.0 µmol, 6.0 mol%), alkene (0.50 to 1.0 mmol, 5.0 to 10 equiv) 1,4-dioxane (0.2 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 90 to 120 °C in an aluminium heating block. The ratio between the product and aminopyridine was monitored by ^{1}H NMR spectroscopy periodically, and the reaction was diluted with 1 mL of DCM after this ratio was great than 10:1 or this ratio remained unchanged for two consecutive aliquots. The last aliquot was analyzed by GC or LC to determine the regioselectivity of the reaction. The crude material was concentrated in vacuo and purified by flash column chromatography to afford the product.

3. Reaction Development for the Remote Hydroamination of Alkenes

In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with $[Ir(coe)_2Cl]_2$ (2.3 mg, 2.5 μmol, 2.5 mol%), aminopyridine (0.10 mmol, 1.0 equiv), ligand (6.0 μmol, 6.0 mol%), additive (6.0 μmol, 6.0 mol%), 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol), cis-4-octene (**1a**) (16 to 78 μL, 0.10 to 0.50 mmol, 1.0 to 5.0 equiv) solvent (0.2 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at the designated temperature in an aluminium heating block. An aliquot (5 μL) was then taken from the reaction and analyzed by ^{1}H NMR spectroscopy and GC.

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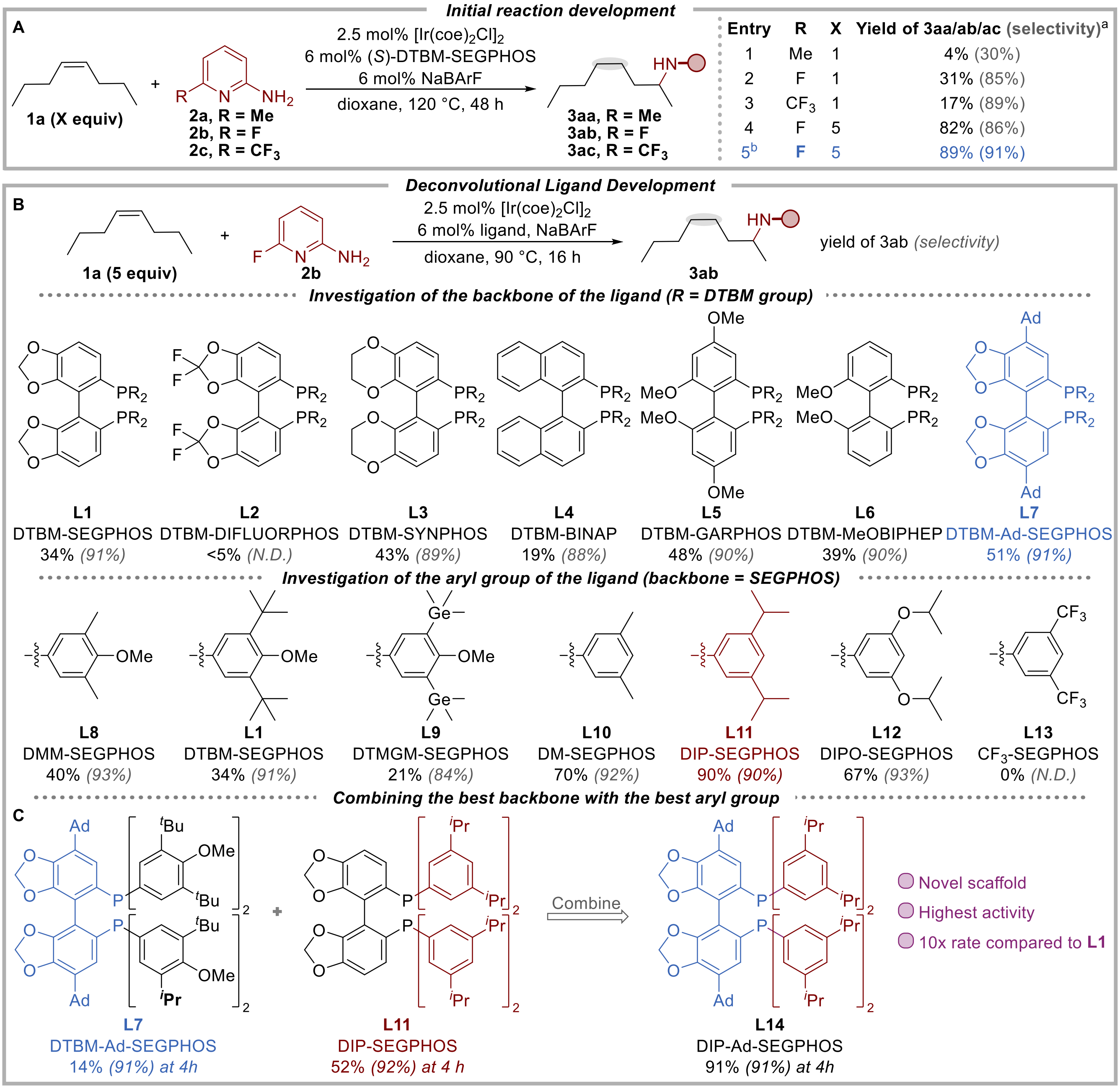
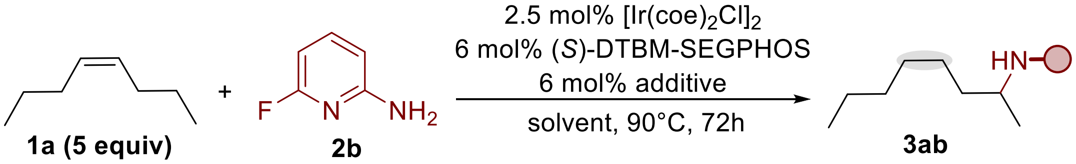


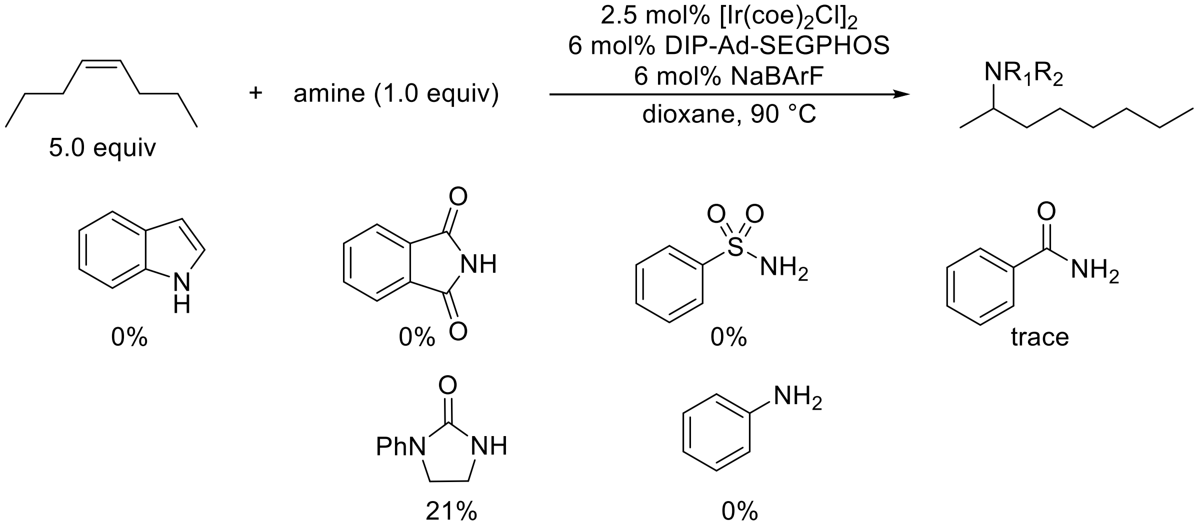
Figure S1. (A) Identification of suitable aminopyridine of the remote hydroamination of *cis*-4-octene. (B) Investigation effect of backbones and aryl fragments of the bisphosphine ligand on the remote hydroamination of *cis*-4-octene. (C) Identification of suitable ligand for the remote hydroamination of *cis*-4-octene. [a]Yield represents the yield of 2-amine with respect to 2-aminopyridine as the limiting reagent. selectivity = 2-amine/all amines. [b]The reaction was performed at 90 °C for 72 h.



Entry	solvent	Additive	Yield of 3ab (selectivity)[a]
1	dioxane	NaBArF	89% (91%)
2	dioxane	$NaNTf_2$	7% (92%)
3	dioxane	NaOTf	0% (N.D.)
4	PhF	NaBArF	83% (88%)
5	PhCl	NaBArF	82% (88%)
6	$PhCF_3$	NaBArF	83% (85%)
7	THF	NaBArF	13% (89%)
8	2-Me-THF	NaBArF	14% (89%)
9	DME	NaBArF	7% (85%)
10	CPME	NaBArF	23% (89%)

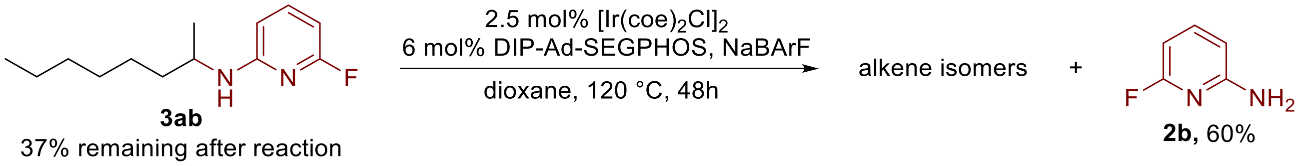
Figure S2. Investigation of the reaction conditions for the remote hydroamination of *cis*-4-octene. [a]Yield represents the yield of 2-amine with respect to 2-aminopyridine as the limiting reagent. selectivity = 2-amine/all amines.

4. Investigation of Other N-H donors for Remote Hydroamination



In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with $[Ir(coe)_2Cl]_2$ (2.3 mg, 2.5 µmol, 2.5 mol%), aminopyridine (0.10 mmol, 1.0 equiv), DIP-Ad-SEGPHOS (7.3 mg, 6.0 µmol, 6.0 mol%), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (5.4 mg, 6.0 µmol, 6.0 mol%), *cis*-4-octene (78 µL, 0.50 mmol, 5.0 equiv) 1,4-dioxane (0.2 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 90 °C in an aluminium heating block for 48 h. The crude material was analyzed by ^1H NMR, concentrated in vacuo, and purified by flash column chromatography to afford the product.

5. Investigation for the Possibility of Reversible Hydroamination



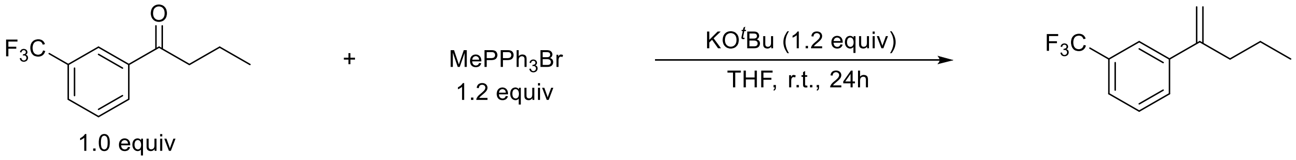
In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with $[Ir(coe)_2Cl]_2$ (2.3 mg, 2.5 µmol, 2.5 mol%), aminopyridine 6-fluoro-N-(octan-2-yl)pyridin-2-amine (**3ab**) (22 mg, 0.10 mmol, 1.0 equiv), DIP-Ad-SEGPHOS (7.3 mg, 6.0 µmol, 6.0 mol%), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (5.4 mg, 6.0 µmol, 6.0 mol%), 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol), dioxane (0.2 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 120 °C in an aluminium heating block for 72 h. The reaction was cooled to room temperature, and a 5 µL aliquot was taken. The aliquot was analyzed by ^{1}H NMR spectroscopy. Analysis by what type ^{1}H NMR spectroscopy showed that **2b** was formed in 60% yield along with the formation of octene isomers. 37% of **3ab** was detected after the reaction.

6. Synthesis of Substrates and DIP-Ad-SEGPHOS

6.1 Alkene Substrates

Condition B: An oven-dried flask was charged with dry DCM (15 mL), carboxylic acid (1.0 to 1.1 equiv), 4-dimethylamino pyridine (DMAP) (0.10 equiv), alcohol (1.0 to 1.1 equiv), *N,N'*-diisopropylcarbodiimide (DIC) (1.0 equiv), and a magnetic stir bar. The reaction mixture was allowed to stir at room temperature for 24 h, before filtering and concentrating under reduced pressure. The crude residue was directly purified by flash column chromatography to yield pure ester. **Notes:** No attempts were made to optimize for yield.

Compound 1f



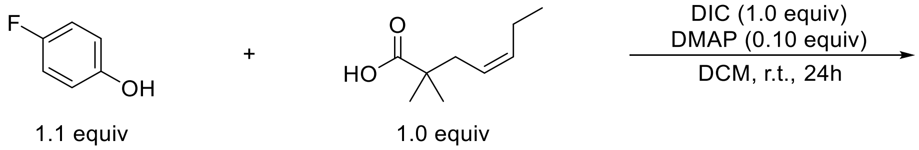
An oven-dried flask was charged with dry THF (15 mL), MePPh$_3$Br (2.6 g, 7.4 mmol), and a magnetic stir bar. At 0 °C, a dry THF solution (20 ml) of potassium *tert*-butoxide (830 mg, 7.4 mmol) was added dropwise. The mixture was warmed to room temperature and stirred for 1 h. At room temperature, A THF solution (20 ml) of 1-(3-(trifluoromethyl)phenyl)butan-1-one (1.3 g, 6.2 mmol) was added dropwise. The reaction mixture was allowed to stir at room temperature for 24 h, before concentrating under reduced pressure. The product was purified by flash column chromatography (SiO$_2$; Hexanes) to afford the corresponding alkene **1f** (944 mg, 72%) as a colorless oil. Note: Contains 15% of an inseparable trisubstituted isomer.

^{1}H NMR 1H NMR (600 MHz, CDCl$_3$) δ 7.65 (app-s, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.42 (t, J = 7.7 Hz, 1H), 5.33 (d, J = 1.3 Hz, 1H), 5.15 (q, J = 1.3 Hz, 1H), 2.51 (td, J = 7.8, 1.2 Hz, 2H), 1.49 (h, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 147.51, 142.49, 132.07, 130.82 (q, J = 32.0 Hz) 128.83, 124.40 (q, J = 272.0 Hz), 124.07 (q, J = 3.7 Hz), 123.05 (q, J = 3.9 Hz), 113.88, 37.40, 21.34, 13.81.

HRMS (*m/z*): (EI) calc'd [M]$^+$: 214.0969, found: 214.0972.

Compound 1k



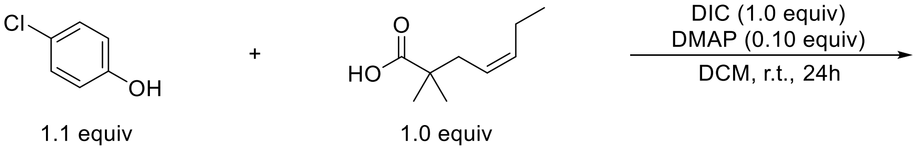
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid[1] (313 mg, 2.00 mmol) and 4-fluorophenol (247 mg, 2.20 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 95:5 Hexanes:EA) to afford the corresponding ester **1k** (413 mg, 66%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 – 6.95 (m, 4H), 5.59 – 5.50 (m, 1H), 5.42 – 5.35 (m, 1H), 2.43 (d, J = 7.5 Hz, 2H), 2.08 (p, J = 7.5 Hz, 2H), 1.33 (s, 6H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.32, 160.14 (d, J = 243.95 Hz) 146.89 (d, J = 3.0 Hz), 134.87, 123.64, 122.91 (d, J = 8.4 Hz), 115.97 (d, J = 23.4 Hz), 42.77, 37.69, 24.82, 20.68, 14.14.

HRMS (*m/z*): (EI) calc'd for $[M]^+$: 250.1369, found: 250.1371.

Compound 1l



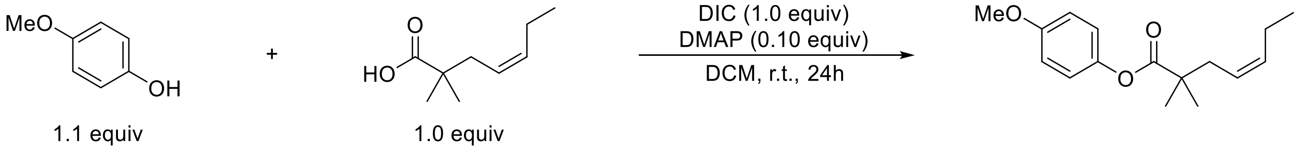
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid (391 mg, 2.50 mmol) and 4-chlorophenol (354 mg, 2.75 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 95:5 Hexanes:EA) to afford the corresponding ester **1l** (320 mg, 48%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 2H), 7.04 – 6.86 (m, 2H), 5.67 – 5.49 (m, 1H), 5.43 – 5.33 (m, 1H), 2.53 – 2.30 (d, J = 7.6 Hz, 2H), 2.08 (p, J = 7.5, 2H), 1.32 (s, 6H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.06, 149.56, 134.92, 130.96, 129.39, 123.58, 122.94, 42.83, 37.68, 24.80, 20.68, 14.14.

HRMS (*m/z*): (EI) calc'd for $[M]^+$: 266.1074, found: 266.1077.

Compound 1m



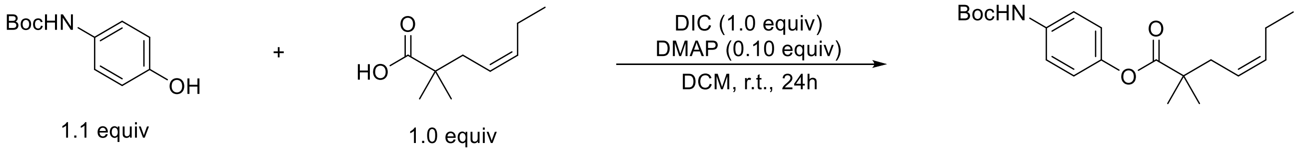
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid (391 mg, 2.50 mmol) and 4-methoxyphenol (341 mg, 2.75 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 95:5 Hexanes:EA) to afford the corresponding ester **1m** (395 mg, 56%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 – 6.91 (m, 2H), 6.91 – 6.76 (m, 2H), 5.61 – 5.47 (m, 1H), 5.45 – 5.34 (m, 1H), 3.79 (s, 3H), 2.43 (d, J = 7.6 Hz, 2H), 2.09 (p, J = 7.5 Hz, 2H), 1.32 (s, 6H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.63, 157.10, 144.58, 134.73, 123.83, 122.26, 114.39, 55.60, 42.71, 37.72, 24.86, 20.68, 14.16.

HRMS (*m/z*): (EI) calc'd $[M]^+$: 262.1569, found: 262.1572.

Compound 1n



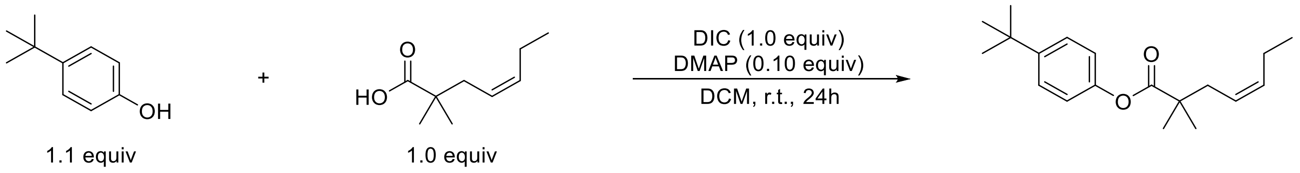
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid (391 mg, 2.50 mmol) and tert-butyl (4-hydroxyphenyl)carbamate (575 mg, 2.75 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 90:10 Hexanes:EA) to afford the corresponding ester **1n** (576 mg, 66%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.4 Hz, 2H), 7.00 – 6.90 (m, 2H), 6.47 (s, 1H), 5.57 – 5.50 (m, 1H), 5.44 – 5.35 (m, 1H), 2.42 (d, J = 7.6 Hz, 2H), 2.08 (p, J = 7.5 Hz, 2H), 1.51 (s, 9H), 1.31 (s, 6H), 0.96 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.42, 152.72, 146.41, 135.82, 134.78, 123.76, 121.92, 119.31, 42.74, 37.70, 28.34, 24.83, 20.68, 14.15.

HRMS (*m/z*): (ESI) calc'd for $[2M+Na]^+$: 717.4086, found: 717.4088.

Compound 1o



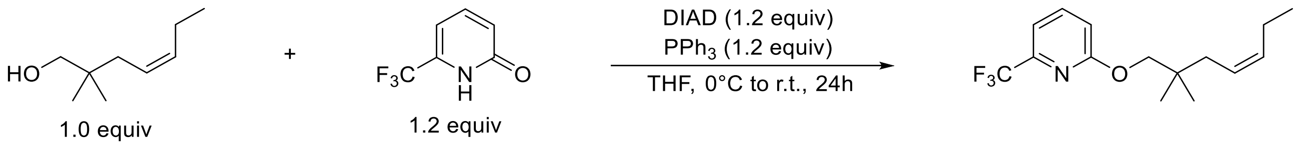
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid (391 mg, 2.50 mmol) and 4-(tert-butyl)phenol (413 mg, 2.75 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 95:5 Hexanes:EA) to afford the corresponding ester **1o** (296 mg, 41%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.01 – 6.94 (m, 2H), 5.64 – 5.48 (m, 1H), 5.44 – 5.37 (m, 1H), 2.43 (d, J = 7.6 Hz, 2H), 2.09 (p, J = 7.4 Hz, 2H), 1.33 (s, 6H), 1.31 (s, 9H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.42, 148.72, 148.38, 134.71, 126.22, 123.86, 120.81, 42.75, 37.71, 34.46, 31.43, 24.86, 20.69, 14.17.

HRMS (*m/z*): (EI) calc'd $[M]^+$: 288.2089, found: 288.2089.

Compound 1p



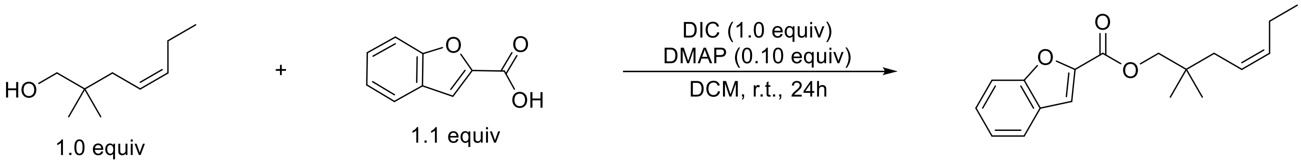
An oven-dried flask was charged with (Z)-2,2-dimethylhept-4-en-1-ol (370 mg, 2.62 mmol), triphenylphosphine (824 mg 3.16 mmol), 6-(trifluoromethyl)pyridin-2(1H)-one (512 mg, 3.16 mmol), 15 mL of dry THF, and a magnetic stir bar. The solution was cooled to 0 °C, and diisopropyl azodicarboxylate (DIAD) (617 µL, 3.14 mmol) was added dropwise. The resulting mixture was slowly warmed to room temperature. After stirring for 24 h, the reaction was concentrated under reduced pressure. The crude material was purified by flash column chromatography (SiO$_2$; 97:3 Hexanes:EA) to afford the corresponding ether **1p** (540 mg, 72%) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (t, J = 7.8 Hz, 1H), 7.22 (d, J = 7.2 Hz, 1H), 6.91 (d, J = 8.4 Hz, 1H), 5.51 – 5.44 (m, 1H), 5.43 – 5.36 (m, 1H), 4.04 (s, 2H), 2.13 (d, J = 7.7 Hz, 2H), 2.03 (p, J = 7.4, 2H), 1.01 (s, 6H), 0.91 (t, J = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.32, 145.49 (q, J = 34.5 Hz), 139.08, 133.99, 124.53, 121.42 (q, J = 273.6 Hz), 114.58, 112.89 (q, J = 3.2 Hz), 74.14, 36.19, 34.78, 24.37, 20.51, 14.13.

HRMS (*m/z*): (ESI) calc'd for [M+Na]$^+$: 300.1389, found: 300.1399.

Compound 1q



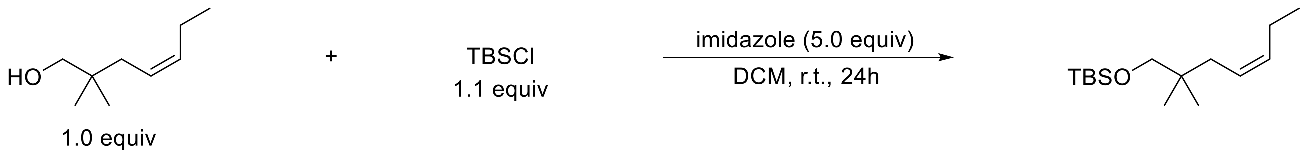
According to **Condition B**, benzofuran-2-carboxylic acid (446 mg, 2.75 mmol) and (Z)-2,2-dimethylhept-4-en-1-ol (356 mg, 2.50 mmol) were coupled, and the product was purified by flash column chromatography (SiO$_2$; 90:10 Hexanes:EA) to afford the corresponding ester **1q** (626 mg, 87%) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.69 (dt, J = 8.0, 1.0 Hz, 1H), 7.60 (dq, J = 8.4, 0.9 Hz, 1H), 7.51 (d, J = 1.0 Hz, 1H), 7.45 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 7.31 (ddd, J = 8.0, 7.2, 0.9 Hz, 1H), 5.59 – 5.47 (m, 1H), 5.44 – 5.37 (m, 1H), 4.11 (s, 2H), 2.14 (d, J = 7.6 Hz, 2H), 2.07 (pd, J = 7.5, 1.6 Hz, 2H), 1.03 (s, 6H), 0.94 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 159.85, 155.94, 145.82, 134.57, 127.68, 127.13, 124.13, 123.91, 122.92, 113.65, 112.56, 72.96, 36.34, 34.99, 24.38, 20.70, 14.32.

HRMS (*m/z*): (EI) calc'd for [M]$^+$: 286.1569, found: 286.1566.

Compound 1s



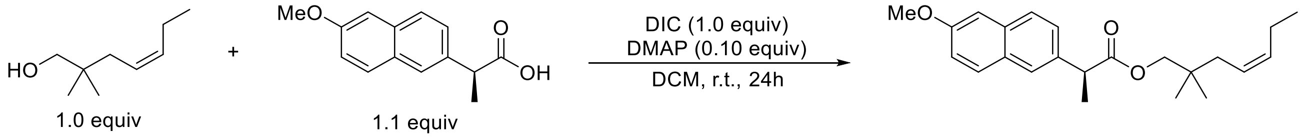
An oven-dried flask was charged with dry DCM (15 mL), TBSCl (332mg, 2.20 mmol), (Z)-2,2-dimethylhept-4-en-1-ol (284 mg, 2.00 mmol), imidazole (681 mg, 10.0 mmol) and a magnetic stir bar. The reaction mixture was allowed to stir at room temperature for 24 h, before concentrating under reduced pressure. The crude residue was directly purified by flash column chromatography (SiO_2; Hexanes) to afford the corresponding ether **1s** (415 mg, 81%) as a colorless oil. Note: Contains 7% of inseparable TBS siloxane.

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.47 – 5.38 (m, 1H), 5.37 – 5.30 (m, 1H), 3.21 (s, 2H), 2.02 (p, J = 7.5 Hz, 2H), 1.95 (d, J = 7.8 Hz, 2H), 0.92 (t, J = 7.5 Hz, 3H), 0.87 (s, 9H), 0.80 (s, 6H), 0.00 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 133.44, 125.61, 71.49, 36.19, 35.87, 26.07, 24.06 (two carbons), 20.67, 14.43, -5.34.

HRMS (*m/z*): (EI) calc'd $[M-CH_3]^+$: 241.1988, found: 241.1988.

Compound 1u



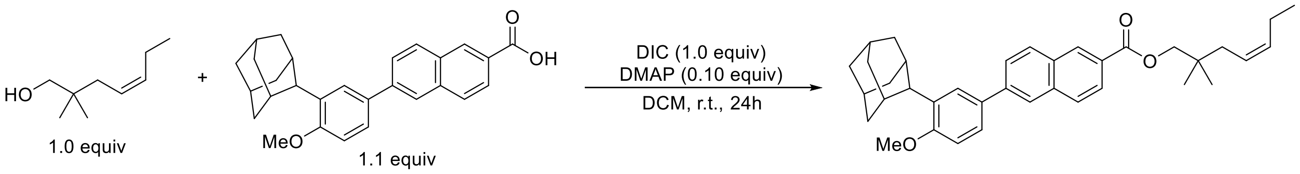
According to **Condition B**, naproxen (507 mg, 2.20 mmol) and (Z)-2,2-dimethylhept-4-en-1-ol (284 mg, 2.00 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 85:15 Hexanes:EA) to afford the corresponding ester **1u** (547 mg, 77%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 2H), 7.68 – 7.66 (m, 1H), 7.42 (dd, J = 8.4, 1.9 Hz, 1H), 7.17 – 7.08 (m, 2H), 5.44 – 5.36 (m, 1H), 5.29 – 5.20 (m, 1H), 3.91 (s, 3H), 3.88 (q, J = 7.2 Hz, 1H), 3.84 – 3.73 (m, 2H), 1.94 – 1.80 (m, 4H), 1.60 (d, J = 7.1 Hz, 3H), 0.85 (t, J = 7.5 Hz, 3H), 0.81 (d, J = 6.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.61, 157.60, 135.75, 134.12, 133.68, 129.27, 128.94, 127.03, 126.41, 126.00, 124.13, 118.92, 105.59, 72.28, 55.30, 45.68, 36.02, 34.65, 24.07, 24.02, 20.41, 18.29, 14.13.

HRMS (*m/z*): (EI) calc'd for $[M]^+$: 354.2195, found: 354.2189.

Compound 1v



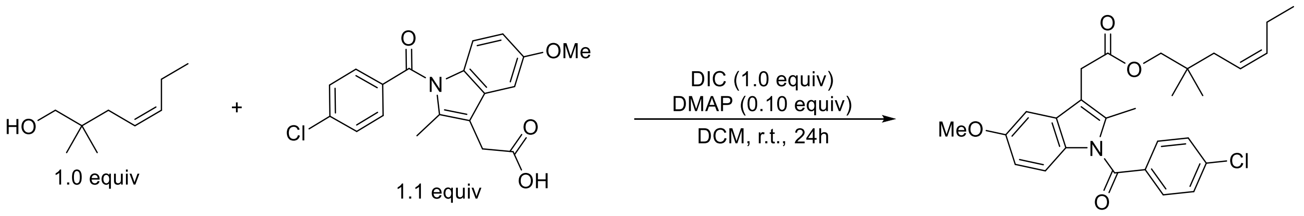
According to **Condition B**, adapalene (991 mg, 2.40 mmol) and (Z)-2,2-dimethylhept-4-en-1-ol (311 mg, 2.18 mmol) were coupled, and the product was purified by flash column chromatography (SiO_2; 90:10 Hexanes:EA) to afford the corresponding ester **1v** (871 mg, 74%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.09 (dd, J = 8.5, 1.7 Hz, 1H), 8.03 – 8.01 (m, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.81 (dd, J = 8.5, 1.8 Hz, 1H), 7.62 (d, J = 2.4 Hz, 1H), 7.55 (dd, J = 8.4, 2.4 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 5.57 – 5.50 (m, 1H), 5.49 – 5.41 (m, 1H), 4.13 (s, 2H), 3.91 (s, 3H), 2.22 – 2.18 (m, 8H), 2.14 – 2.05 (m, 5H), 1.81 (app-s, 6H), 1.08 (s, 6H), 0.95 (t, J = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.83, 158.94, 141.37, 139.03, 135.96, 134.31, 132.59, 131.29, 130.72, 129.72, 128.24, 127.31, 126.48, 126.00, 125.75, 125.57, 124.76, 124.24, 112.13, 72.64, 55.18, 40.63 (two carbons), 37.24, 37.15 (two carbons), 36.40, 34.91, 29.14 (two carbons), 24.45, 20.61, 14.21.

HRMS (*m/z*): (EI) calc'd for $[M]^+$: 536.3290, found: 536.3290.

Compound 1w



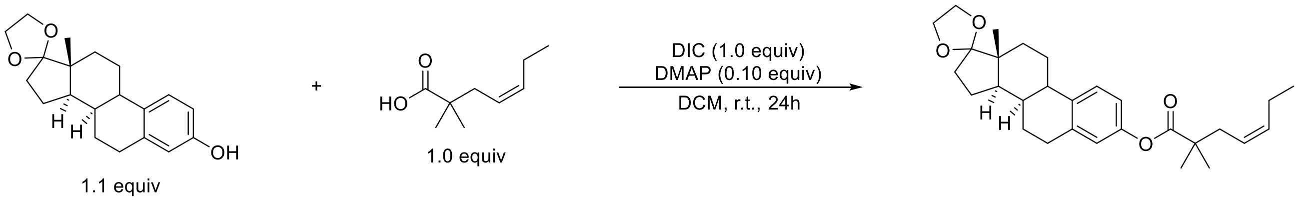
According to **Condition B**, indomethacin (787 mg, 2.20 mmol) and (Z)-2,2-dimethylhept-4-en-1-ol (284 mg, 2.00 mmol) were coupled, and the product was purified by flash column chromatography (SiO$_2$; 85:15 Hexanes:EA) to afford the corresponding ester **1w** (317 mg, 33%) as a yellow oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 – 7.59 (m, 2H), 7.49 – 7.43 (m, 2H), 6.97 (d, J = 2.6 Hz, 1H), 6.87 (d, J = 9.0 Hz, 1H), 6.67 (dd, J = 9.0, 2.6 Hz, 1H), 5.48 – 5.39 (m, 1H), 5.32 – 5.23 (m, 1H), 3.83 (s, 3H), 3.82 (s, 2H), 3.68 (s, 2H), 2.40 (s, 3H), 1.97 – 1.88 (m, 4H), 0.89 (t, J = 7.6 Hz, 3H), 0.85 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 170.87, 168.28, 156.09, 139.26, 135.74, 134.26, 133.95, 131.17, 130.80, 130.64, 129.12, 123.98, 114.97, 112.78, 111.85, 101.19, 72.63, 55.69, 36.06, 34.52, 30.47, 24.09, 20.45, 14.17, 13.34.

HRMS (*m/z*): (EI) calc'd for [2M+Na]$^+$: 985.3932, found: 985.3941.

Compound 1x



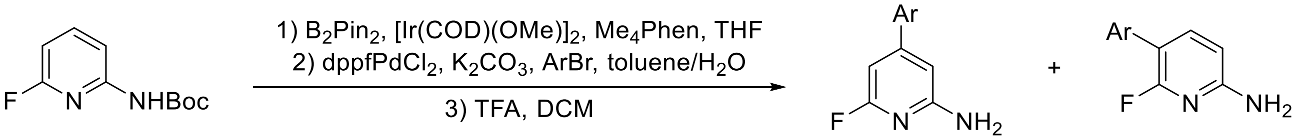
According to **Condition B**, (Z)-2,2-dimethylhept-4-enoic acid (391 mg, 2.50 mmol) and (8R,13R,14R)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17, 2' [1,3]dioxolan]-3-ol (847 mg, 2.75 mmol) were coupled, and the product was purified by flash column chromatography (SiO$_2$; 95:5 Hexanes:EA) to afford the corresponding ester **1x** (552 mg, 49%) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.27 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.5 Hz, 1H), 6.75 (s, 1H), 5.61 – 5.51 (m, 1H), 5.45 – 5.36 (m, 1H), 4.01 – 3.85 (m, 4H), 2.91 – 2.79 (m, 2H), 2.42 (d, J = 7.6 Hz, 2H), 2.37 – 2.22 (m, 2H), 2.14 – 2.07 (m, 2H), 2.07 – 1.99 (m, 1H), 1.86 – 1.80 (m, 4H), 1.70 – 1.33 (m, 6H), 1.32 (s, 6H), 0.97 (t, J = 7.5 Hz, 3H), 0.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.50, 148.77, 138.18, 137.79, 134.69, 126.29, 123.89, 121.41, 119.41, 118.49, 65.28, 64.60, 49.41, 46.12, 43.83, 42.72, 38.73, 37.70, 34.24, 30.70, 29.54, 26.82, 26.01, 24.86 (two carbons), 22.38, 20.68, 14.33, 14.17.

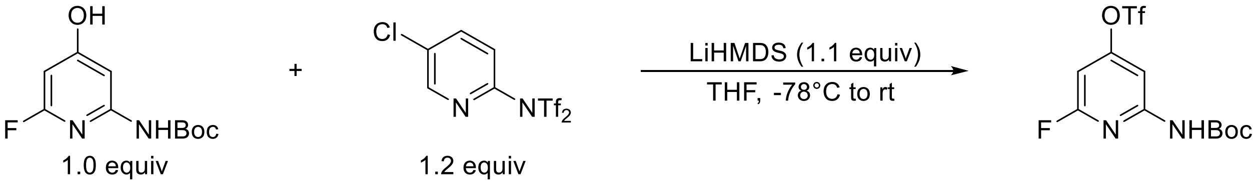
HRMS (*m/z*): (ESI) calc'd for $[2M+Na]^+$: 927.5746, found: 927.5724.

6.2 Aminopyridine Substrates



Condition C^2: In a nitrogen-filled glovebox, a 20mL vial was charged sequentially with $[Ir(COD)(OMe)]_2$ (6.6 mg, 0.010 mmol, 1.0 mol%), tetramethylphenanthroline (5.2 mg, 0.022 mmol, 2.2 mol%), B_2pin_2 (380 mg, 1.5 mmol, 1.5 equiv), HBpin (20 μL), dried THF (2.0 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 80 °C for 0.5 h and brought back into the glovebox. Tert-butyl (6-fluoropyridin-2-yl)carbamate (210 mg, 1.0 mmol, 1.0 equiv) was added and the vial was capped and removed from the glovebox. The reaction was heated at 50 °C for 0.75 h, brought back into the glovebox, filtered, and concentrated in vacuo. Aryl bromide (1.2 mmol, 1.2 equiv), $dppfPdCl_2$ (37 mg, 0.050 mmol, 5 mol%), K_2CO_3 (350 mg, 2.5 mmol, 2.5 equiv), toluene (2.0 mL), and water (0.2 mL) were then added. The vial was capped and removed from the glovebox. The reaction was heated at 100 °C for 24 h, filtered, concentrated under reduced pressure, and redissolved in DCM (2.0 mL). At room temperature, TFA (766 μL, 10.0 mmol, 10.0 equiv) was added dropwise. The reaction mixture was allowed to stir overnight before quenched with $NaHCO_3$ and extracted with DCM. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (SiO_2) to afford correspond arylated aminopyridines as yellow solids.

Compound 2g-NHBoc



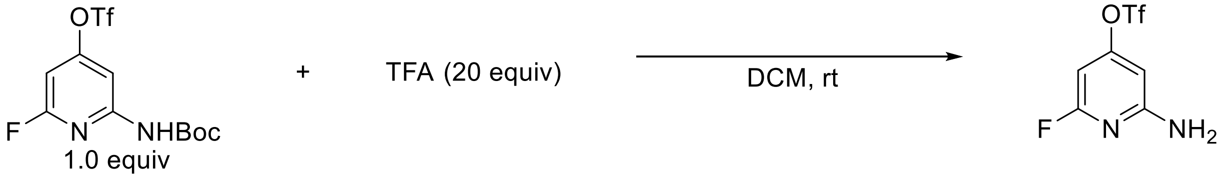
An oven-dried flask was charged with dry THF (15 mL), tert-butyl (6-fluoro-4-hydroxypyridin-2-yl)carbamate (84 mg, 0.37 mmol) and a magnetic stir bar. At -78 °C, LiHMDS (1M solution, 410 µL, 0.41 mmol) was added dropwise. The reaction mixture was allowed to stir -78 °C for 0.5 h and a THF solution of Comin's reagent (170 mg, 0.44 mmol) was added dropwise -78 °C. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction mixture was concentrated under reduced pressure and the crude residue was directly purified by flash column chromatography (SiO_2; 95:5 Hexanes:EA) to afford compound **2g-NHBoc** (120 mg, 93%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.31 (s, 1H), 6.53 (s, 1H), 1.53 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.56 (d, J = 241.5 Hz), 159.85 (d, J = 11.6 Hz), 152.10 (d, J = 18.3 Hz), 151.33, 118.56 (q, J = 321.0 Hz), 101.70 (d, J = 5.4 Hz), 96.37 (d, J = 40.9 Hz), 82.62, 28.11.

HRMS (*m/z*): (ESI) calc'd for $[M+Na]^+$: 383.0295, found: 383.0292.

Compound 2g



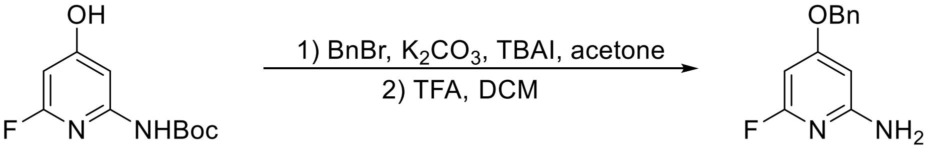
A 20mL vial was charged with DCM (0.5 mL), compound **2g-NHBoc** (90 mg, 0.25 mmol) and a magnetic stir bar. At room temperature, TFA (380 µL, 5.0 mmol, 20 equiv) was added dropwise. The reaction mixture was allowed to stir overnight before quenched with $NaHCO_3$ and extracted with DCM. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (SiO_2; 75:25 Hexanes:EA) to afford compound **2g** (59 mg, 90%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.24 (s, 1H), 6.17 (s, 1H), 4.89 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.98 (d, J = 239.1 Hz), 159.80 (d, J = 12.9 Hz), 158.67 (d, J = 20.2 Hz), 118.70 (q, J = 320.9 Hz), 96.74 (d, J = 5.5 Hz), 91.01 (d, J = 42.0 Hz).

HRMS (*m/z*): (ESI) calc'd for $[2M+K]^+$: 558.9390, found: 558.9377.

Compound 2i



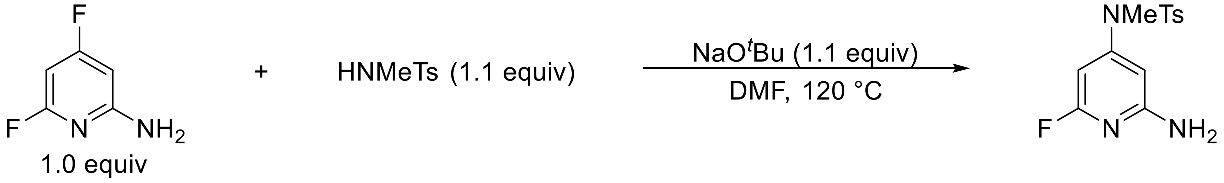
A 20mL vial was charged with dry acetone (2.0 mL), compound **2g-NHBoc** (69 mg, 0.30 mmol), TBAI (5.5 mg, 0.015 mmol, 5 mol%), BnBr (38 µL, 0.32 mmol, 1.1 equiv), K_2CO_3 (62 mg, 0.45 mmol, 3.0 equiv) and a magnetic stir bar. The reaction mixture was allowed to stir overnight and extracted with EA. The reaction mixture was filtered, concentrated under reduced pressure, and redissolved in DCM (0.5 mL). At room temperature, TFA (460 µL, 6.0 mmol, 20 equiv) was added dropwise. The reaction mixture was allowed to stir overnight before quenched with $NaHCO_3$ and extracted with DCM. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (SiO_2; 75:25 Hexanes:EA) to afford compound **2i** (56 mg, 85%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 5H), 5.88 (app-s, 2H), 5.04 (app-s, 2H), 4.51 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.97 (d, J = 12.7 Hz), 164.68 (d, J = 233.0 Hz), 158.37 (d, J = 21.0 Hz), 135.73, 128.86, 128.52, 127.57, 90.36 (d, J = 4.2 Hz), 85.66 (d, J = 40.9 Hz), 70.38.

HRMS (*m/z*): (ESI) calc'd for $[M+Na]^+$: 241.0747, found: 241.0736.

Compound 2j



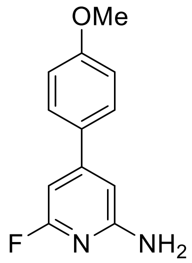
In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with 4,6-difluoropyridin-2-amine (33 mg, 0.25 mmol, 1.0 equiv), N,4-dimethylbenzenesulfonamide (55 mg, 0.27 mmol, 1.1 equiv), (NaO^{t}Bu) (24 mg, 0.27 mmol, 1.1 equiv), DMF (2.5 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 120 °C for 24 h. The crude material was extracted with EA/H_2O 5 times to remove residual DMF, concentrated in vacuo, and purified by flash column chromatography (SiO_2; 95:5 DCM:EA) to afford compound **2j** (58 mg, 78%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.8 Hz, 2H), 6.35 (s, 1H), 6.04 (s, 1H), 4.59 (s, 2H), 3.20 (s, 3H), 2.43 (s, 3H).

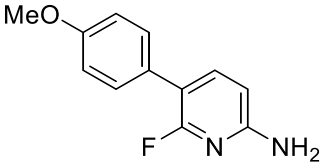
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.70 (d, J = 234.8 Hz), 157.66 (d, J = 19.6 Hz), 154.08 (d, J = 11.4 Hz), 144.42, 133.73, 129.76, 127.39, 98.75 (d, J = 4.4 Hz), 91.48 (d, J = 40.5 Hz), 36.61, 21.58.

HRMS (*m/z*): (ESI) calc'd for $[M+ACN+H]^+$: 337.1129, found: 337.1120.

Compound 2o and 2r



2o



2r

According to **Condition C**, 1-bromo-4-methoxybenzene (220 mg, 1.2 mmol) was used as the aryl bromide coupling partner, and the product was purified by flash column chromatography (SiO_2; 50:50 Hexanes:ether) to afford compound **2o** (57 mg, 26%) as a yellow solid and **2r** (90 mg, 41%) as a yellow solid.

Compound 2o

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.00 – 6.96 (m, 2H), 6.49 (s, 1H), 6.42 (s, 1H), 4.54 (s, 2H), 3.86 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.14 (d, J = 235.9 Hz), 160.80, 157.86 (d, J = 18.1 Hz), 154.92 (d, J = 9.1 Hz), 130.40 (d, J = 3.6 Hz), 128.24, 114.52, 102.01 (d, J = 3.9 Hz), 95.29 (d, J = 37.2 Hz), 55.55.

HRMS (*m/z*): (ESI) calc'd $[M+ACN+H]^+$: 260.1193, found: 260.1187.

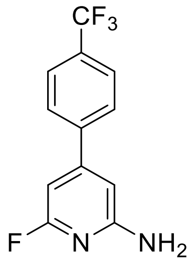
Compound 2r

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (t, J = 10.1 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 6.43 (d, J = 8.0 Hz, 1H), 4.61 (s, 2H), 3.86 (s, 3H).

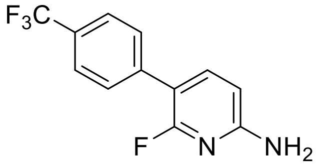
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.38 (d, J = 238.8 Hz), 158.84, 156.10 (d, J = 16.5 Hz), 142.03 (d, J = 5.2 Hz), 129.42 (d, J = 3.2 Hz), 127.07 (d, J = 5.0 Hz), 114.03, 111.34 (d, J = 27.1 Hz), 105.34 (d, J = 4.4 Hz), 55.33.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 241.0747, found: 241.0746.

Compound 2p and 2s



2p



2s

According to **Condition C**, 1-bromo-4-trifluoromethylbenzene (270 mg, 1.2 mmol) was used as the aryl bromide coupling partner,, and the product was purified by flash column chromatography (SiO_2; 80:20 Hexanes:EA) to afford compound **2p** (87 mg, 34%) as a yellow solid and **2s** (77 mg, 30%) as a yellow solid.

Compound 2p

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 6.54 (s, 1H), 6.46 (s, 1H), 4.72 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.94 (d, J = 237.1 Hz), 157.98 (d, J = 17.8 Hz), 153.76 (d, J = 8.8 Hz), 141.59, 131.23 (q, J = 32.7 Hz), 127.34, 125.96 (q, J = 3.7 Hz), 123.94 (q, J = 272.4 Hz), 102.73 (d, J = 4.3 Hz), 95.74 (d, J = 37.6 Hz).

HRMS (*m/z*): (ESI) calc'd $[2M+ACN+Na]^+$: 576.1406, found: 576.1433.

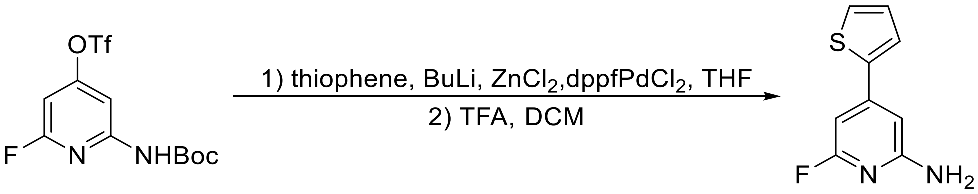
Compound 2s

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 3H), 7.63 (t, J = 8.1 Hz, 2H), 6.47 (dd, J = 8.2, 1.6 Hz, 1H), 4.83 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.70 (d, J = 239.8 Hz), 157.42 (d, J = 17.3 Hz), 142.22 (d, J = 4.6 Hz), 138.48 (d, J = 5.3 Hz), 129.19 (q, J = 32.6 Hz), 128.57 (d, J = 3.6 Hz), 125.59 (q, J = 3.7 Hz), 124.33 (q, J = 272.0 Hz), 110.00 (d, J = 26.9 Hz), 105.67 (d, J = 4.3 Hz).

HRMS (*m/z*): (ESI) calc'd $[M+ACN+Na]^+$: 320.0782, found: 320.0772.

Compound 2q



An oven-dried flask was charged with dry THF (3.0 mL), thiophene (76 mg, 0.90 mmol) and a magnetic stir bar. At -78 °C, BuLi (2.5M solution, 400 μL, 1.0 mmol, 1.1 equiv) was added dropwise. The reaction mixture was allowed to stir -78 °C for 0.5 h, and a THF suspension of $ZnCl_2$ (240 mg, 1.8 mmol, 2.0 equiv) was added dropwise -78 °C. The reaction mixture was allowed to slowly warm to 0 °C, stirred for 0.5 h, and brought into the glovebox. In a nitrogen-filled glovebox, a 20mL vial was charged sequentially $dppfPdCl_2$ (11 mg, 0.015 mmol, 5.0 mol%), compound **2g-NHBoc** (110 mg, 0.3 mmol), and the arylzinc solution. The vial was capped and removed from the glovebox. The reaction was heated at 65 °C for 24 h, filtered, concentrated under reduced pressure, and redissolved in DCM (2.0 mL). At room temperature, TFA (766 μL, 10.0 mmol, 10.0 equiv) was added dropwise. The reaction mixture was allowed to stir overnight before quenched with $NaHCO_3$ and extracted with DCM. The reaction mixture was concentrated under reduced pressure and purified by flash column chromatography (SiO_2; 75:25 Hexanes:EA) to afford compound **2q** (36 mg, 62%) as a yellow solid.

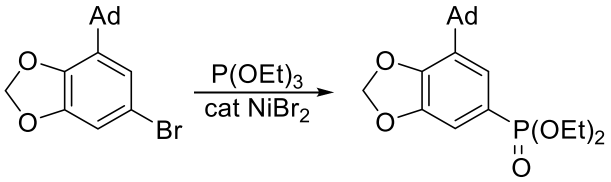
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 2H), 7.13 (app-s, 1H), 6.56 (s, 1H), 6.49 (s, 1H), 4.34 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.10 (d, J = 236.3 Hz), 157.98 (d, J = 17.9 Hz), 147.86 (d, J = 9.5 Hz), 140.96 (d, J = 4.0 Hz), 128.36, 127.24, 125.70, 100.98 (d, J = 3.9 Hz), 94.31 (d, J = 38.5 Hz).

HRMS (*m/z*): (ESI) calc'd $[M+K]^+$: 232.9946, found: 232.9952.

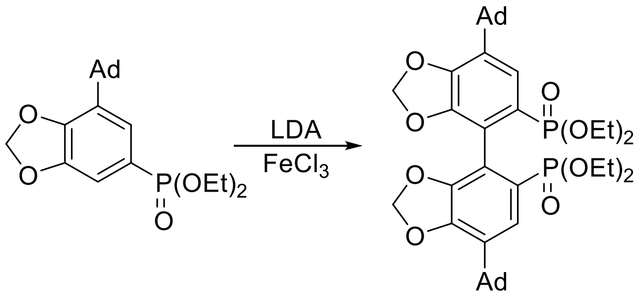
6.3 DIP-Ad-SEGPHOS Synthesis

diethyl (7-((3r,5r,7r)-adamantan-1-yl)benzo[d][1,3]dioxol-5-yl)phosphonate



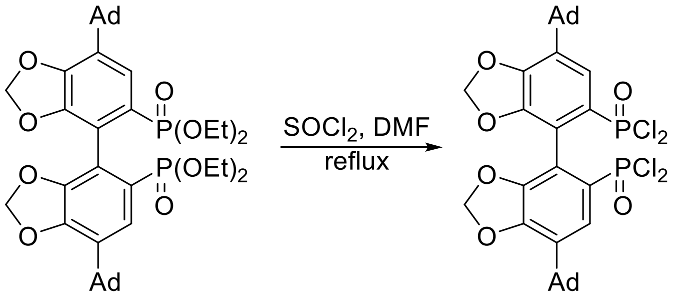
Adapted from a reported procedure[3]: 4-((3r,5r,7r)-adamantan-1-yl)-6-bromobenzo[d][1,3]dioxole[4] (4.7 g, 14 mmol) and nickel dibromide (180 mg, 1.4 mmol, 10 mol%) were placed in a two-necked flask provided with a distillation apparatus and a dropping funnel. The suspension was heated at 160 °C, after what triethylphosphite (2.9 mL, 17 mmol, 1.2 equiv) was added dropwise over 1 h. The reaction mixture was stirred at 160 °C for 1 h. The ethyl bromide formed was continuously distilled all along the reaction. After cooling down the mixture, 50 mL of diethyl ether and 50 mL of ethyl acetate were added and the precipitate was filtered off. The filtrate was concentrated under reduced pressure and the crude oil was purified by flash column chromatography (SiO_2; 50:50 hexanes:EA) to afford the target compound (4.2 g, 76%) as a yellow oil. The NMR spectra of the target compound matched those reported in the literature.[5]

Ad-SEGPHOS-POEt$_2$



Adapted from a reported procedure[3]: To a solution of diethyl (7-((3r,5r,7r)-adamantan-1-yl)benzo[d][1,3]dioxol-5-yl)phosphonate (4.8 g, 12 mmol) in dry THF (15 mL) was added dropwise a solution of freshly prepared LDA (13 mmol, 1.1 equiv) at -78 °C. The reaction mixture was stirred at -78 °C for 15 minutes and at -15°C for 15 minutes. The mixture was cooled to -78 °C and a THF solution of anhydrous $FeCl_3$ (2.7 g, 16 mmol, 1.3 equiv) was added dropwise. The reaction temperature was allowed to rise to r.t and the mixture was stirred overnight. The solution was concentrated in vacuum, and the brown residue was diluted with CH_2Cl_2 (50 mL) and treated with 50 mL of 2 M aqueous NaOH. After stirring for 1 h, the resulting suspension was filtered on celite. The organic layer was washed with water and brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The obtained brown solid was purified by flash column chromatography (SiO_2; 90:10 DCM:MeOH) to afford the target compound (4.1 g, 87%) as white solid. The NMR spectra of the target compound matched those reported in the literature.[5]

Ad-SEGPHOS-POCl₂



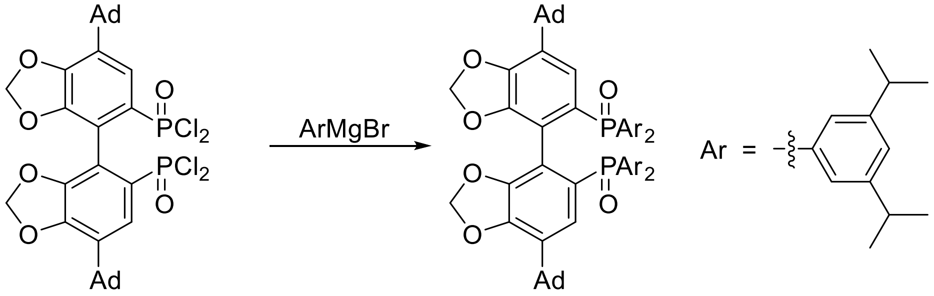
Adapted from a reported procedure[6]: In a nitrogen-filled glovebox, an oven dried round-bottom flask (50 ml) was charged **Ad-SEGPHOS-POEt₂** (2.0 g, 2.5 mmol) and a magnetic stir bar. A reflux condenser was attached to the flask. Thionyl chloride was added to the flask via syringe (18 mL, 250 mmol), followed by dropwise addition of DMF (1.9 ml, 25 mmol). The solution was allowed to reflux (96 °C) for 17 h. Upon completion, the flask was allowed to cool to room temperature, and the solvents were distilled away under high vacuum to yield a brown solid. The flask was taken into the glovebox, and the solid was redissolved in DCM and dried under high vacuum for 48 h to yield the title compound as a pale solid (1.8 g, 98% yield). Note: The crude solid was used directly for the next step without further purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 22.6 Hz, 2H), 6.09 (d, J = 1.5 Hz, 2H), 6.03 (d, J = 1.4 Hz, 2H), 2.13 – 2.08 (m, 6H), 2.08 – 2.04 (m, 12H), 1.82 – 1.75 (m, 12H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 33.68.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 765.0633, found: 765.0633.

Ad-SEGPHOS-POAr$_2$



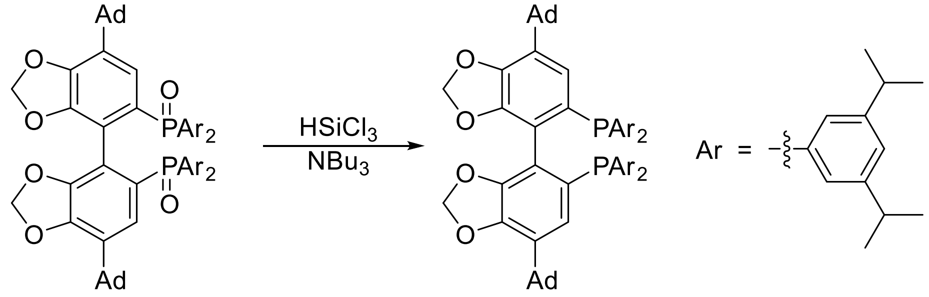
Adapted from a reported procedure[6]: In a nitrogen-filled glovebox, a 20 ml vial was charged with Mg turnings (350 mg, 14 mmol), 1-bromo-3,5-diisopropylbenzene (2.9 g, 12 mmol), a crystal of iodine, THF (5.0 mL) and a magnetic stir bar. The vial was capped and stirred at 65 °C for 3 h. The Grignard was then brought back into the back and was added dropwise to a 20 ml vial containing a THF solution (5 mL) of **Ad-SEGPHOS-POCl$_2$** (890 mg, 1.2 mmol) at -35 °C. The reaction was heated at 65 °C for 24 h. Upon completion, the reaction was allowed to cool to room temperature, quenched with NH_4Cl (aq), extracted with EA and concentrated under high vacuum. The obtained crude solid was purified by flash column chromatography (SiO_2; 70:30 Hexanes:EA) to afford the target compound (1.1 g, 70%) as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (dd, J = 11.9, 1.7 Hz, 4H), 7.26 (dd, J = 12.3, 1.7 Hz, 4H), 7.13 (s, 2H), 7.03 (s, 2H), 6.78 (d, J = 15.2 Hz, 2H), 5.82 (d, J = 1.8 Hz, 2H), 5.61 (d, J = 1.8 Hz, 2H), 2.87 (hept, J = 6.9 Hz, 4H), 2.69 (hept, J = 6.9 Hz, 4H), 1.95 (app-s, 6H), 1.87 – 1.79 (m, 12H), 1.71 – 1.62 (m, 12H), 1.20 (dd, J = 6.9, 4.8 Hz, 24H), 1.05 (dd, J = 8.5, 6.9 Hz, 24H).

^{31}P NMR (243 MHz, $CDCl_3$) δ 30.50.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 1247.7381, found: 1247.7404.

DIP-Ad-SEGPHOS (Ad-SEGPHOS-PAr$_2$)



Adapted from a reported procedure[6]: In a nitrogen-filled glovebox, a 40 ml vial was charged with **Ad-SEGPHOS-POAr$_2$** (2.0 g, 1.6 mmol) and a magnetic stir bar. Dry mesitylene (5.0 ml) and dry Bu$_3$N (4.6 mL, 19 mmol) were added to the vial. Trichlorosilane (1.9 mL, 19 mmol) was added dropwise to the solution. Once the evolution of gas ceased, the vial was sealed with a Teflon-lined cap and placed in a 120 °C heating block. After 24 h, the vial was removed from the heating block and the reaction mixture was transferred into a 250 mL round-bottom flask placed in an ice bath. Under a stream of nitrogen and vigorous stirring, an aqueous solution of NaOH (25%, 10 ml) was added to the flask dropwise. The reaction was stirred at room temperature for 1 h, quenched with HCl (aq), extracted with EA and concentrated under high vacuum. The obtained crude solid was purified by flash column chromatography (SiO$_2$; 97:3 Hexanes:EA) to afford the target compound (1.5 g, 83%) as white solid.

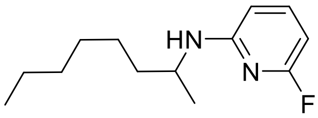
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.26 (s, 1H), 7.00 – 6.96 (m, 7H), 6.95 – 6.93 (m, 2H), 6.91 – 6.89 (m, 2H), 6.63 – 6.58 (m, 2H), 5.74 (d, J = 1.7 Hz, 2H), 5.14 (d, J = 1.7 Hz, 2H), 2.80 (hept, J = 6.9 Hz, 4H), 2.72 (hept, J = 6.9 Hz, 4H), 1.95 – 1.91 (m, 6H), 1.87 – 1.78 (m, 12H), 1.72 – 1.61 (m, 12H), 1.17 (dd, J = 6.9, 3.7 Hz, 24H), 1.12 (dd, J = 6.9, 5.9 Hz, 24H).

^{31}P NMR (243 MHz, CDCl$_3$) δ -13.90.

HRMS (*m/z*): (ESI) calc'd [M+H]$^+$: 1215.7483, found: 1215.7477.

7. Scope of Hydroamination

Compound 3ab



From *cis*-4-octene: According to **Condition A** at 90 °C for 4.5 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ab** (20 mg, 91%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC.

From *trans*-4-octene: According to **Condition A** at 90 °C for 44 h. *trans*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ab** (20 mg, 91%) as a yellow oil. The regioselectivity of the reaction was determined to be 90% by GC. Note: 4-NMe_2-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS.

From an equimolar mixture of *cis*-4-octene, *cis*-3-octene, and *cis*-2-octene: According to **Condition A** at 90 °C for 5 h. *cis*-4-octene (26 µL, 0.17 mmol), *cis*-3-octene (26 µL, 0.17 mmol), *cis*-2-octene (26 µL, 0.17 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ab** (20 mg, 89%) as a yellow oil. The regioselectivity of the reaction was determined to be 92% by GC.

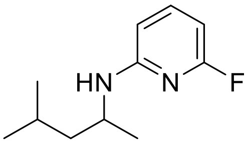
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (q, J = 8.1 Hz, 1H), 6.14 (dd, J = 8.1, 2.4 Hz, 1H), 6.07 (dd, J = 7.8, 2.3 Hz, 1H), 4.38 (s, 1H), 3.70 (h, J = 6.4 Hz, 1H), 1.56 – 1.41 (m, 2H), 1.40 – 1.31 (m, 2H), 1.31 – 1.22 (m, 6H), 1.17 (d, J = 6.6 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.43 (d, J = 236.0 Hz), 157.75 (d, J = 16.9 Hz), 141.71 (d, J = 8.7 Hz), 102.54 (d, J = 4.0 Hz), 95.09 (d, J = 36.6 Hz), 47.48, 37.21, 31.90, 29.37, 26.08, 22.71, 20.90, 14.17.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.72.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 225.1762, found: 225.1758.

Compound 3bb



According to **Condition A** at 90 °C for 14 h. alkene **1b** (92 µL, 0.75 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3bb** (16 mg, 80%) as a yellow oil. The regioselectivity of the reaction was determined to be 93% by GC. Note: 4-NMe_2-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS.

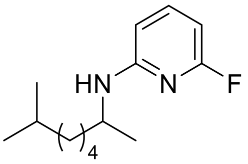
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (q, J = 8.1 Hz, 1H), 6.15 (d, J = 8.1 Hz, 1H), 6.08 (d, J = 7.7 Hz, 1H), 4.33 (s, 1H), 3.79 (h, J = 6.4 Hz, 1H), 1.75 – 1.66 (m, 1H), 1.47 – 1.37 (m, 1H), 1.33 – 1.22 (m, 1H), 1.17 (d, J = 6.3 Hz, 3H), 0.92 (dd, J = 12.8, 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.45 (d, J = 236.0 Hz), 157.73 (d, J = 16.8 Hz), 141.77 (d, J = 8.7 Hz), 102.47 (d, J = 3.9 Hz), 95.15 (d, J = 36.8 Hz), 46.82, 45.65, 25.16, 22.86, 22.82, 21.36.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.67.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 197.1449, found: 197.1446.

Compound 3cb



According to **Condition A** at 90 °C for 24 h. alkene **1c** (94 mg, 0.75 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3cb** (20 mg, 84%) as a yellow oil. The regioselectivity of the reaction was determined to be 85% by GC. Note: 4-NMe_2-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS.

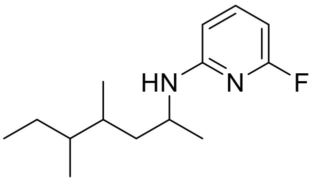
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (q, J = 8.1 Hz, 1H), 6.07 (d, J = 8.1 Hz, 1H), 6.01 (d, J = 7.7 Hz, 1H), 4.31 (d, J = 8.4 Hz, 1H), 3.70 – 3.55 (m, 1H), 1.48 – 1.36 (m, 3H), 1.31 – 1.19 (m, 4H), 1.13 – 1.05 (m, 5H), 0.78 (d, J = 6.6 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.33 (d, J = 236.0 Hz), 157.63 (d, J = 16.8 Hz), 141.60 (d, J = 8.7 Hz), 102.40 (d, J = 4.4 Hz), 95.00 (d, J = 36.9 Hz), 47.37, 38.92, 37.14, 27.91, 27.34, 26.25, 22.61(two carbons), 20.81.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.74.

HRMS (*m/z*): (ESI) calc'd $[2M+K]^+$: 515.3322, found: 515.3313.

Compound 3db



According to **Condition A** at 100 °C for 13 h. 3-methyl-4-methyleneheptane (250 mg, 2.0 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3db** (19 mg, 80%) as a yellow oil. The regioselectivity of the reaction was determined to be 95% by GC. The d.r. of the product was determined to be 7:17:16:10 by GC. Notes: Contain 4% inseparable isomers.

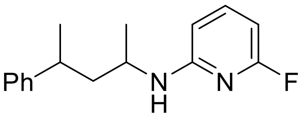
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 1H), 6.20 – 6.13 (m, 1H), 6.13 – 6.05 (m, 1H), 4.39 (s, 1H), 4.02 – 3.59 (m, 1H), 1.69 – 1.53 (m, 1H), 1.46 – 1.26 (m, 4H), 1.23 – 1.18 (m, 3H), 1.18 – 1.08 (m, 1H), 0.98 – 0.88 (m, 3H), 0.88 – 0.76 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.49 (d, J = 235.8 Hz, all diastereomers), 157.65 (d, J = 16.2 Hz, two diastereomers), 157.55 (d, J = 16.0 Hz, two diastereomers), 141.77 (d, J = 8.7 Hz, two diastereomers), 141.75 (d, J = 8.8 Hz, two diastereomers), 102.49 (d, J = 3.5 Hz, two diastereomers), 102.47 (d, J = 3.5 Hz, two diastereomers), 95.24 (d, J = 37.0 Hz, two diastereomers), 95.18 (d, J = 37.1 Hz, two diastereomers), 46.01 (two diastereomers), 45.72 (two diastereomers), 42.77 (two diastereomers), 40.55 (two diastereomers), 39.74 (two diastereomers), 38.68 (two diastereomers), 34.34 (two diastereomers), 33.33 (two diastereomers), 27.50 (two diastereomers), 25.71 (two diastereomers), 21.03 (two diastereomers), 20.67 (two diastereomers), 16.89 (two diastereomers), 15.88 (two diastereomers), 14.63 (two diastereomers), 14.11 (two diastereomers), 12.38 (two diastereomers), 12.30 (two diastereomers).

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.66 (diastereomer 1), -69.68 (diastereomer 2), -69.70 (diastereomer 3), -69.72 (diastereomer 4).

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 239.1918, found: 239.1919.

Compound 3eb



According to **Condition A** at 90 °C for 24 h. alkene **1e** (73 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3eb** (22 mg, 86%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. The d.r. of the product was determined to be 1:1 by GC.

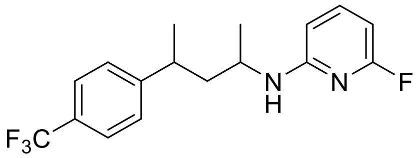
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (p, J = 8.3 Hz, 2H, both diastereomers), 7.35 (t, J = 7.6 Hz, 2H, diastereomer 1), 7.32 – 7.28 (m, 2H, diastereomer 2), 7.27 – 7.20 (m, 4H, both diastereomers), 7.18 (d, J = 7.5 Hz, 2H, both diastereomers), 6.12 (ddd, J = 8.2, 6.4, 2.3 Hz, 2H, both diastereomer), 5.98 (dd, J = 8.0, 2.4 Hz, 1H, diastereomer 1), 5.94 (dd, J = 8.1, 2.4 Hz, 1H, diastereomer 2), 4.38 (d, J = 8.8 Hz, 2H, both diastereomers), 3.63 (hept, J = 6.9 Hz, 1H, diastereomer 1), 3.56 (h, J = 6.5, 5.9 Hz, 1H, diastereomer 2), 3.01 – 2.92 (m, 1H, diastereomer 2), 2.91 – 2.82 (m, 1H, diastereomer 1), 1.99 – 1.90 (m, 1H, diastereomer 1), 1.86 – 1.75 (m, 2H, both diastereomers), 1.74 – 1.65 (m, 1H, diastereomer 2), 1.31 (dd, J = 8.9, 6.9 Hz, 6H, both diastereomers), 1.24 (d, J = 6.4 Hz, 3H, diastereomer 1), 1.17 (d, J = 6.4 Hz, 3H, diastereomer 2).

^{13}C NMR 13C NMR (151 MHz, $CDCl_3$) δ 163.38 (d, J = 236.1 Hz, diastereomer 1), 163.36 (d, J = 236.0 Hz, diastereomer 2), 157.66 (d, J = 16.7 Hz, diastereomer 1), 157.51 (d, J = 16.8 Hz, diastereomer 2), 146.92 (diastereomer 1), 146.79 (diastereomer 2), 141.76 (d, J = 8.8 Hz, diastereomer 1), 141.73 (d, J = 8.7 Hz, diastereomer 2), 128.68 (diastereomer 1), 128.59 (diastereomer 2), 127.19 (diastereomer 1), 127.04 (diastereomer 2), 126.36 (diastereomer 1), 126.29 (diastereomer 2), 102.39 (d, J = 4.3 Hz, diastereomer 1), 102.32 (d, J = 3.9 Hz, diastereomer 2), 95.29 (d, J = 36.7 Hz, both diastereomers), 46.25 (diastereomer 1), 45.94 (diastereomer 2), 45.76 (diastereomer 1), 45.74 (diastereomer 2), 37.13 (diastereomer 1), 36.90 (diastereomer 2), 22.88 (diastereomer 1), 22.67 (diastereomer 2), 21.38 (diastereomer 1), 21.05 (diastereomer 2).

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.72 (diastereomer 1), -69.78 (diastereomer 2).

HRMS (*m/z*): (ESI) calc'd $[2M+ACN+Na]^+$: 580.3222, found: 580.3239.

Compound 3fb



According to **Condition A** at 90 °C for 48 h. alkene **1f** (110 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3fb** (29 mg, 88%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. The d.r. of the product was determined to be 1:1 by GC.

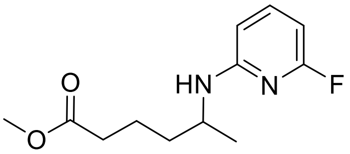
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.30 (m, 10H, both diastereomers), 6.16 – 6.04 (m, 2H, both diastereomers), 6.00 – 5.88 (m, 2H, both diastereomers), 4.32 (dd, J = 14.6, 9.0 Hz, 2H, both diastereomers), 3.65 (p, J = 7.0 Hz, 1H, diastereomer 1), 3.51 (p, J = 6.9 Hz, 1H, diastereomer 2), 2.99 (h, J = 7.2 Hz, 1H, diastereomer 2), 2.92 (h, J = 7.1 Hz, 1H, diastereomer 1), 1.91 (dt, J = 14.7, 7.6 Hz, 1H, diastereomer 1), 1.78 (t, J = 7.1 Hz, 2H, both diastereomers), 1.71 – 1.63 (m, 1H, diastereomer 2), 1.29 (dd, J = 10.0, 6.9 Hz, 6H, both diastereomers), 1.20 (d, J = 6.4 Hz, 3H, diastereomer 2), 1.13 (d, J = 6.3 Hz, 3H, diastereomer 1).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.43 (d, J = 236.1 Hz, diastereomer 1), 163.39 (d, J = 236.2 Hz, diastereomer 2), 157.54 (d, J = 14.0 Hz, diastereomer 1), 157.42 (d, J = 14.0 Hz, diastereomer 2), 147.98 (diastereomer 1), 147.69 (diastereomer 2), 141.88 (d, J = 8.5 Hz, diastereomer 1), 141.79 (d, J = 8.6 Hz, diastereomer 2), 130.61 (both diastereomers), 129.12 (diastereomer 1), 129.02 (diastereomer 2), 124.39 (q, J = 272.1 Hz, diastereomer 1), 124.38 (q, J = 272.1 Hz, diastereomer 1), 124.02 (q, J = 3.8 Hz, diastereomer 2), 123.67 (q, J = 3.7 Hz, diastereomer 1), 123.24 (q, J = 3.6 Hz, diastereomer 2), 102.55 (d, J = 3.7 Hz, diastereomer 1), 102.37 (d, J = 3.7 Hz, diastereomer 2), 95.65 (d, J = 10.8 Hz, diastereomer 1), 95.41 (d, J = 10.7 Hz, diastereomer 2), 46.17 (diastereomer 2), 45.71 (diastereomer 1), 45.55 (both diastereomers), 37.13 (diastereomer 1), 36.88 (diastereomer 2), 22.71 (diastereomer 1), 22.42 (diastereomer 2), 21.54 (diastereomer 1), 21.17 (diastereomer 2).

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.48 (diastereomer 1), -62.52 (diastereomer 2), -69.66 (diastereomer 1), -69.74 (diastereomer 2).

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 349.1298, found: 349.1285.

Compound 3gb



According to **Condition A** at 120 °C for 44 h. alkene **1g** (130 mg, 1.0 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 90:10 hexanes:EA) to afford compound **3gb** (14 mg, 58%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC. Note: 4-NMe_2-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS. 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

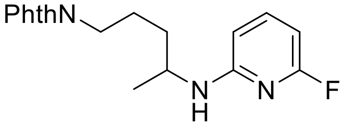
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 6.15 (dd, J = 8.0, 2.4 Hz, 1H), 6.08 (dd, J = 7.8, 2.3 Hz, 1H), 4.38 (s, 1H), 3.79 (q, J = 6.4 Hz, 1H), 3.66 (s, 3H), 2.33 (t, J = 7.3 Hz, 2H), 1.77 – 1.63 (m, 2H), 1.59 – 1.46 (m, 2H), 1.20 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.88, 163.31 (d, J = 236.1 Hz), 157.49 (d, J = 16.6 Hz), 141.60 (d, J = 8.5 Hz), 102.77 (d, J = 4.0 Hz), 95.18 (d, J = 36.9 Hz), 51.54, 46.96, 36.33, 33.79, 21.39, 20.84.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.70.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 241.1347, found: 241.1346.

Compound 3hb



According to **Condition A** at 100 °C for 40 h. alkene **1h** (110 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 95:5 DCM:MeCN) to afford compound **3hb** (30 mg, 92%) as a yellow oil. The regioselectivity of the reaction was determined to be 93% by GC.

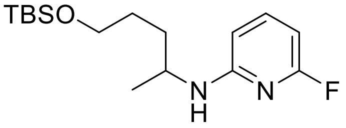
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (dd, J = 5.4, 3.0 Hz, 2H), 7.73 – 7.65 (m, 2H), 7.40 (q, J = 8.1 Hz, 1H), 6.14 (dd, J = 8.0, 2.3 Hz, 1H), 6.05 (dd, J = 7.7, 2.3 Hz, 1H), 4.42 (s, 1H), 3.83 (q, J = 6.5 Hz, 1H), 3.69 (t, J = 7.1 Hz, 2H), 1.85 – 1.69 (m, 2H), 1.60 – 1.48 (m, 2H), 1.17 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.54, 163.38 (d, J = 236.1 Hz), 157.54 (d, J = 17.0 Hz), 141.68 (d, J = 8.7 Hz), 134.04, 132.18, 123.32, 102.92 (d, J = 3.9 Hz), 95.28 (d, J = 36.9 Hz), 47.02, 37.95, 34.13, 25.40, 21.07.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.66.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 328.1456, found: 328.1455.

Compound 3ib



According to **Condition A** at 90 °C for 44 h. alkene **1i** (100 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 95:5 hexanes:EA) to afford compound **3ib** (16 mg, 50%) as a yellow oil. The regioselectivity of the reaction was determined to be 81% by GC. Note: 4-NMe_2-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS. 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

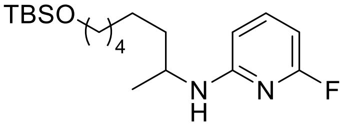
^{1}**H NMR** (600 MHz, CDCl$_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 6.15 (dd, J = 8.0, 2.4 Hz, 1H), 6.08 (dd, J = 7.8, 2.3 Hz, 1H), 4.44 (s, 1H), 3.76 (q, J = 6.2 Hz, 1H), 3.66 – 3.59 (m, 2H), 1.65 – 1.51 (m, 4H), 1.20 (d, J = 6.4 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}**C NMR** (151 MHz, CDCl$_3$) δ 163.30 (d, J = 236.0 Hz), 157.57 (d, J = 16.7 Hz), 141.58 (d, J = 8.5 Hz), 102.57 (d, J = 3.9 Hz), 95.04 (d, J = 36.6 Hz), 62.91, 47.17, 33.28, 29.20, 25.95, 20.86, 18.33, -5.30.

^{19}**F NMR** (565 MHz, CDCl$_3$) δ -69.75.

HRMS (*m/z*): (ESI) calc'd [M+H]$^+$: 313.2106, found: 313.2107.

Compound 3jb



According to **Condition A** at 90 °C for 21 h. alkene **1j** (130 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO$_2$; 95:5 hexanes:EA) to afford compound **3jb** (20 mg, 77%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC. Note: 4-NMe$_2$-3,5-DIP-MeOBIPHEP was used as the ligand instead of DIP-Ad-SEGPHOS.

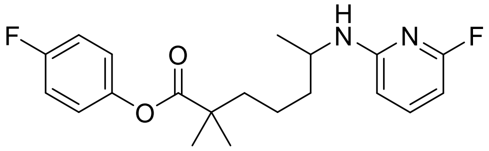
^{1}**H NMR** (600 MHz, CDCl$_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 6.14 (dd, J = 8.0, 2.4 Hz, 1H), 6.08 (dd, J = 7.8, 2.3 Hz, 1H), 4.36 (s, 1H), 3.71 (q, J = 6.4 Hz, 1H), 3.58 (t, J = 6.6 Hz, 2H), 1.59 – 1.44 (m, 4H), 1.40 – 1.35 (m, 2H), 1.33 – 1.28 (m, 4H), 1.18 (d, J = 6.3 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

^{13}**C NMR** (151 MHz, CDCl$_3$) δ 163.43 (d, J = 236.1 Hz), 157.73 (d, J = 16.9 Hz), 141.76 (d, J = 8.6 Hz), 102.56 (d, J = 4.3 Hz), 95.16 (d, J = 36.8 Hz), 63.36, 47.48, 37.17, 32.92, 29.52, 26.12 (two carbons), 25.89, 20.94, 18.51, -5.13.

^{19}**F NMR** (565 MHz, CDCl$_3$) δ -69.72.

HRMS (*m/z*): (ESI) calc'd [M+H]$^+$: 369.2732, found: 369.2733.

Compound 3kb



According to **Condition A** at 120 °C for 24 h. alkene **1k** (130 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 90:10 hexanes:EA) to afford compound **3kb** (28 mg, 77%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

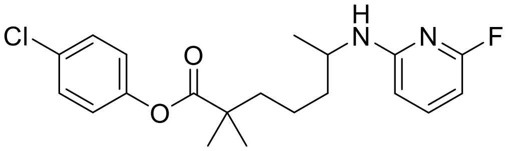
^{1}H NMR 1H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 7.07 – 6.98 (m, 2H), 6.97 – 6.91 (m, 2H), 6.14 (dd, J = 8.0, 2.4 Hz, 1H), 6.09 (dd, J = 7.7, 2.3 Hz, 1H), 4.36 (s, 1H), 3.80 (q, J = 6.4 Hz, 1H), 1.73 – 1.62 (m, 2H), 1.59 – 1.48 (m, 2H), 1.48 – 1.37 (m, 2H), 1.30 (d, J = 2.0 Hz, 6H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.59, 163.44 (d, J = 236.1 Hz), 160.25 (d, J = 244.0 Hz), 157.66 (d, J = 16.8 Hz), 146.91 (d, J = 2.8 Hz), 141.75 (d, J = 8.5 Hz), 122.98 (d, J = 8.4 Hz), 116.12 (d, J = 23.3 Hz), 102.80 (d, J = 4.2 Hz), 95.31 (d, J = 36.9 Hz), 47.13, 42.73, 40.61, 37.58, 25.25 (two carbons), 21.66, 21.04.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.62.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 363.1879, found: 363.1878.

Compound 3lb



According to **Condition A** at 120 °C for 24 h. alkene **1l** (130 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 90:10 hexanes:EA) to afford compound **3lb** (32 mg, 84%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 5 mol% $[Ir(coe)_2Cl]_2$, 12 mol% ligand, and 12 mol% NaBArF were used.

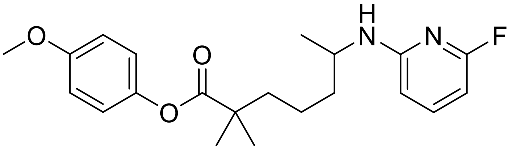
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.0 Hz, 1H), 7.30 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.3 Hz, 2H), 6.19 – 6.13 (m, 1H), 6.11 – 6.05 (m, 1H), 4.35 (s, 1H), 3.80 (q, J = 6.5 Hz, 1H), 1.73 – 1.63 (m, 2H), 1.60 – 1.51 (m, 2H), 1.47– 1.37 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.34, 163.45 (d, J = 236.0 Hz), 157.66 (d, J = 16.6 Hz), 149.59, 141.76 (d, J = 8.6 Hz), 131.11, 129.54, 123.01, 102.82 (d, J = 4.4 Hz), 95.33 (d, J = 36.7 Hz), 47.12, 42.79, 40.58, 37.57, 29.84, 25.24, 21.66, 21.06.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.61.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 379.1583, found: 379.1584.

Compound 3mb



According to **Condition A** at 120 °C for 24 h. alkene **1m** (130 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 85:15 hexanes:EA) to afford compound **3mb** (30 mg, 80%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

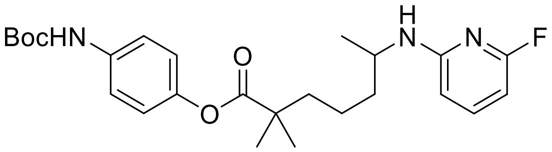
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 6.90 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 6.14 (dd, J = 8.0, 2.3 Hz, 1H), 6.08 (dd, J = 7.7, 2.3 Hz, 1H), 4.38 (s, 1H), 3.79 (s, 4H), 1.72 – 1.60 (m, 2H), 1.59 – 1.48 (m, 2H), 1.48 – 1.38 (m, 2H), 1.30 (s, 3H), 1.29 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.79, 163.31 (d, J = 236.0 Hz), 157.55 (d, J = 16.9 Hz), 157.12, 144.47, 141.64 (d, J = 8.5 Hz), 122.21, 114.43, 102.65 (d, J = 3.9 Hz), 95.15 (d, J = 36.6 Hz), 55.59, 47.07, 42.55, 40.55, 37.46, 25.21, 25.16, 21.55, 20.88.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.66.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 375.2078, found: 375.2079.

Compound 3nb



According to **Condition A** at 120 °C for 48 h. alkene **1n** (170 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 85:15 hexanes:EA) to afford compound **3nb** (28 mg, 61%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

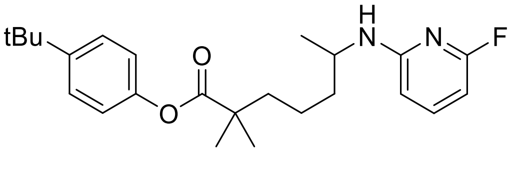
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 6.52 (s, 1H), 6.14 (dd, J = 8.1, 2.3 Hz, 1H), 6.08 (dd, J = 7.7, 2.2 Hz, 1H), 4.38 (s, 1H), 3.78 (q, J = 6.4 Hz, 1H), 1.72 – 1.62 (m, 2H), 1.57 – 1.48 (m, 11H), 1.47 – 1.38 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H), 1.19 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.59, 163.27 (d, J = 236.1 Hz), 157.52 (d, J = 16.7 Hz), 152.74, 146.30, 141.67 (d, J = 8.6 Hz), 135.88, 121.84, 119.37, 102.68 (d, J = 3.9 Hz), 95.14 (d, J = 36.7 Hz), 47.07, 42.58, 40.50, 37.44, 29.71, 28.34, 25.18, 25.13, 21.53, 20.86.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.69.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 460.2606, found: 460.2609.

Compound 3ob



According to **Condition A** at 120 °C for 48 h. alkene **1o** (140 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 92:8 hexanes:EA) to afford compound **3ob** (19 mg, 47%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 5 mol% [Ir(coe)$_2$Cl]$_2$, 12 mol% ligand, and 12 mol% NaBArF were used.

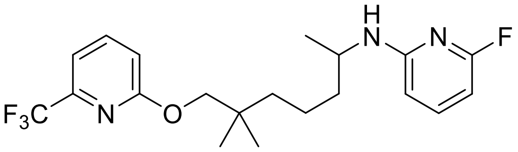
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 (q, J = 8.1 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.05 (dd, J = 8.0, 2.4 Hz, 1H), 5.99 (dd, J = 7.8, 2.3 Hz, 1H), 4.28 (s, 1H), 3.73 – 3.64 (m, 1H), 1.63 – 1.54 (m, 2H), 1.50 – 1.39 (m, 2H), 1.39 – 1.29 (m, 2H), 1.21 (s, 9H), 1.21 (s, 3H), 1.20 (s, 3H), 1.10 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 176.56, 163.31 (d, J = 236.1 Hz), 157.53 (d, J = 16.7 Hz), 148.61, 148.42, 141.63 (d, J = 8.5 Hz), 126.26, 120.75, 102.62 (d, J = 4.0 Hz), 95.17 (d, J = 36.9 Hz), 47.10, 42.59, 40.57, 37.47, 34.45, 31.42, 25.21, 25.17, 21.56, 20.88.

^{19}F NMR (565 MHz, CDCl$_3$) δ -69.66.

HRMS (*m/z*): (ESI) calc'd [M+H]$^+$: 401.2599, found: 401.2698.

Compound 3pb



According to **Condition A** at 120 °C for 24 h. alkene **1p** (140 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO$_2$; 97:3 hexanes:EA) to afford compound **3pb** (26 mg, 65%) as a yellow oil. The regioselectivity of the reaction was determined to be 87% by GC. Note: 3.75 mol% [Ir(coe)$_2$Cl]$_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

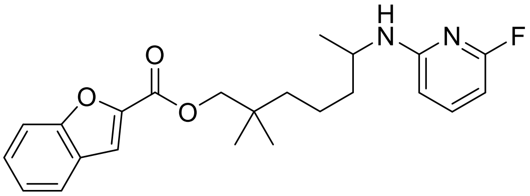
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.66 (t, J = 7.9 Hz, 1H), 7.43 (q, J = 8.1 Hz, 1H), 7.21 (d, J = 7.3 Hz, 1H), 6.87 (d, J = 8.5 Hz, 1H), 6.14 (d, J = 8.0 Hz, 1H), 6.08 (d, J = 7.7 Hz, 1H), 4.36 (s, 1H), 4.03 (s, 2H), 3.74 (q, J = 6.5 Hz, 1H), 1.55 – 1.43 (m, 2H), 1.41 – 1.34 (m, 4H), 1.17 (d, J = 6.3 Hz, 3H), 0.97 (s, 6H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.29, 163.28 (d, J = 235.9 Hz), 157.58 (d, J = 16.9 Hz), 145.42 (q, J = 34.6 Hz), 141.62 (d, J = 8.7 Hz), 139.13, 121.42 (q, J = 273.5 Hz), 114.63, 112.93 (q, J = 3.3 Hz), 102.49 (d, J = 4.0 Hz), 95.05 (d, J = 36.8 Hz), 74.32, 47.24, 39.05, 37.93, 34.08, 24.48, 24.45, 20.83, 20.39.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.42, -69.74.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 400.2007, found: 400.2007.

Compound 3qb



According to **Condition A** at 120 °C for 24 h. alkene **1q** (140 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 90:10 hexanes:EA) to afford compound **3qb** (28 mg, 70%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

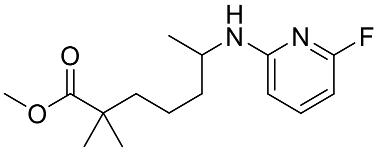
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.49 (s, 1H), 7.44 (t, J = 8.4 Hz, 1H), 7.40 (q, J = 8.1 Hz, 1H), 7.33 – 7.27 (m, 1H), 6.13 (dd, J = 8.1, 2.3 Hz, 1H), 6.06 (dd, J = 7.7, 2.3 Hz, 1H), 4.37 (s, 1H), 4.09 (s, 2H), 3.77 (q, J = 6.4 Hz, 1H), 1.56 – 1.44 (m, 2H), 1.45 – 1.31 (m, 4H), 1.19 (d, J = 6.4 Hz, 3H), 0.99 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.29 (d, J = 236.0 Hz), 159.71, 157.57 (d, J = 16.9 Hz), 155.80, 145.60, 141.61 (d, J = 8.7 Hz), 127.57, 126.98, 123.78, 122.81, 113.60, 112.40, 102.60 (d, J = 4.2 Hz), 95.09 (d, J = 36.6 Hz), 73.12, 47.19, 39.08, 37.86, 34.17, 24.29 (two carbons), 20.88, 20.38.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.69.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 399.2078, found: 399.2076.

Compound 3rb



According to **Condition A** at 120 °C for 58 h. alkene **1r** (85 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 90:10 hexanes:EA) to afford compound **3rb** (22 mg, 76%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC.

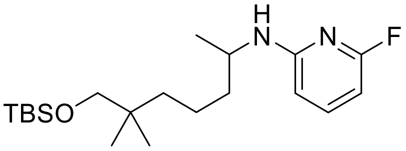
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.0 Hz, 1H), 6.18 – 6.10 (m, 1H), 6.10 – 6.02 (m, 1H), 4.36 (s, 1H), 3.73 (q, J = 6.4 Hz, 1H), 3.62 (s, 3H), 1.55 – 1.40 (m, 4H), 1.35 – 1.21 (m, 2H), 1.16 (d, J = 6.5 Hz, 3H), 1.14 (d, J = 3.1 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 178.52, 163.42 (d, J = 235.9 Hz), 157.67 (d, J = 16.9 Hz), 141.74 (d, J = 8.6 Hz), 102.70 (d, J = 3.9 Hz), 95.20 (d, J = 36.8 Hz), 51.78, 47.21, 42.39, 40.68, 37.52, 25.31, 25.26, 21.56, 20.90.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.73.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 283.1816, found: 283.1815.

Compound 3sb



According to **Condition A** at 120 °C for 24 h. alkene **1s** (130 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97:3 hexanes:EA) to afford compound **3sb** (22 mg, 58%) as a yellow oil. The regioselectivity of the reaction was determined to be 88% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

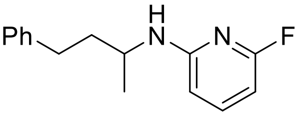
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (q, J = 8.1 Hz, 1H), 6.14 (dd, J = 8.1, 2.4 Hz, 1H), 6.08 (dd, J = 7.8, 2.3 Hz, 1H), 4.38 (s, 1H), 3.72 (q, J = 6.4 Hz, 1H), 3.21 (s, 2H), 1.54 – 1.38 (m, 2H), 1.36 – 1.27 (m, 2H), 1.21 (d, J = 8.6 Hz, 2H), 1.18 (d, J = 6.5 Hz, 3H), 0.88 (s, 9H), 0.80 (s, 6H), 0.01 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.30 (d, J = 236.1 Hz), 157.59 (d, J = 16.8 Hz), 141.62 (d, J = 8.7 Hz), 102.39 (d, J = 4.1 Hz), 95.02 (d, J = 36.6 Hz), 71.44, 47.40, 38.70, 38.08, 35.21, 25.89, 24.12, 24.10, 20.78, 20.41, 18.28, -5.53.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.75.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 369.2732, found: 369.2734.

Compound 3tb



According to **Condition A** at 90 °C for 24 h. (Z)-but-1-en-1-ylbenzene (44 mg, 0.34 mmol), (E)-but-2-en-1-ylbenzene (44 mg, 0.34 mmol), (E)-but-1-en-1-ylbenzene (44 mg, 0.34 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3tb** (19 mg, 79%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

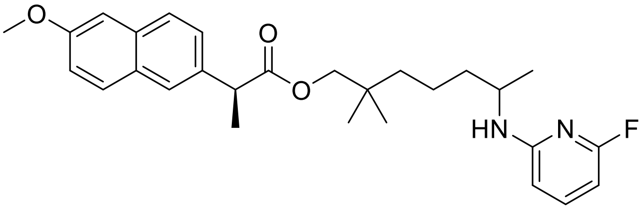
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (q, J = 8.1 Hz, 1H), 7.28 (t, J = 7.6 Hz, 2H), 7.21 – 7.15 (m, 3H), 6.17 – 6.09 (m, 1H), 6.09 – 6.05 (m, 1H),, 4.42 (d, J = 8.9 Hz, 1H), 3.81 – 3.75 (m, 1H), 2.75 – 2.67 (m, 2H), 1.89 – 1.78 (m, 2H), 1.24 (d, J = 6.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.32 (d, J = 236.1 Hz), 157.53 (d, J = 16.7 Hz), 141.73 (d, J = 4.1 Hz), 141.66, 128.44, 128.39, 125.94, 102.49 (d, J = 4.0 Hz), 95.29 (d, J = 36.9 Hz), 46.91, 38.78, 32.39, 20.90.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.67.

HRMS (*m/z*): (ESI) calc'd $[2M+ACN+H]^+$: 530.3090, found: 530.3077.

Compound 3ub



According to **Condition A** at 120 °C for 48 h. alkene **1u** (180 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 95:5 hexanes:EA) to afford compound **3ub** (38 mg, 81%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. The d.r. of the product was determined to be 1:1 by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used. Note: The two diastereomers have identical NMR chemical shifts.

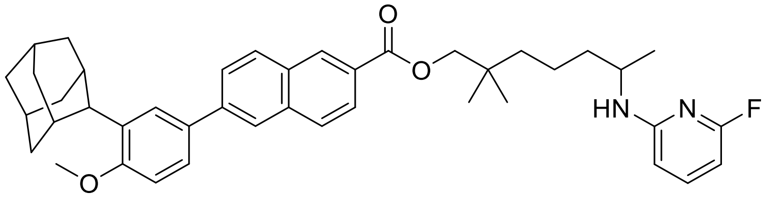
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 3H), 7.42 – 7.38 (m, 2H), 7.15 – 7.11 (m, 1H), 7.11 (s, 1H), 6.09 – 6.04 (m, 2H), 4.22 (s, 1H), 3.92 – 3.85 (m, 4H), 3.82 (dd, J = 10.8, 2.8 Hz, 1H), 3.71 (dd, J = 10.8, 3.0 Hz, 1H), 3.62 – 3.52 (m, 1H), 1.59 (d, J = 7.2 Hz, 3H), 1.29 – 1.08 (m, 5H), 1.06 – 1.02 (m, 4H), 0.80 (s, 3H), 0.77 (d, J = 3.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.59, 163.31 (d, J = 235.7 Hz), 157.64, 157.55 (d, J = 16.7, 2.5 Hz), 141.57 (d, J = 8.7, 2.6 Hz), 135.83, 133.69, 129.27, 128.93, 127.03, 126.43, 126.00, 118.98, 105.61, 102.54 (d, J = 8.3, 3.9 Hz), 95.00 (d, J = 36.9, 2.1 Hz), 72.26, 55.30, 47.10, 45.63, 38.77, 37.68, 33.89, 24.44, 24.17, 20.70, 20.24, 18.05.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.72.

HRMS (*m/z*): (ESI) calc’d $[M+H]^+$: 467.2704, found: 467.2702.

Compound 3vb



According to **Condition A** at 120 °C for 24 h. alkene **1v** (270 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 80:20 hexanes:EA) to afford compound **3vb** (58 mg, 89%) as a white solid. The regioselectivity of the reaction was determined to be >95% by LCMS. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

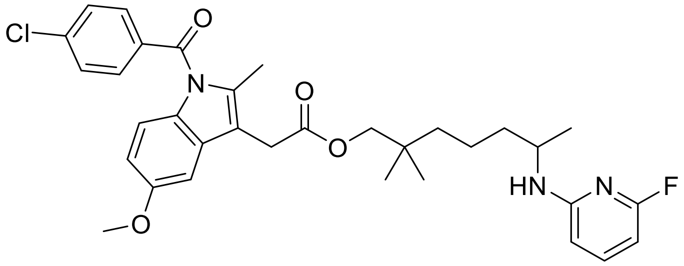
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.03 (s, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.81 (dd, J = 8.6, 1.8 Hz, 1H), 7.63 (d, J = 2.4 Hz, 1H), 7.55 (dd, J = 8.3, 2.3 Hz, 1H), 7.39 (q, J = 8.1 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 6.13 (dd, J = 8.1, 2.3 Hz, 1H), 6.07 (dd, J = 7.7, 2.2 Hz, 1H), 4.44 (s, 1H), 4.12 (s, 2H), 3.91 (s, 3H), 3.79 (q, J = 6.4 Hz, 1H), 2.21 (s, 6H), 2.12 (s, 3H), 1.89 – 1.77 (m, 6H), 1.61 – 1.36 (m, 6H), 1.20 (d, J = 6.4 Hz, 3H), 1.06 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.90, 163.39 (d, J = 236.0 Hz), 159.04, 157.68 (d, J = 16.7 Hz), 141.68 (d, J = 8.7 Hz), 141.45, 139.11, 136.05, 132.63, 131.36, 130.80, 129.81, 128.35, 127.33, 126.56, 126.04, 125.83, 125.62, 124.80, 112.23, 102.66 (d, J = 4.4 Hz), 95.14 (d, J = 36.9 Hz), 73.00, 67.18, 55.25, 47.33, 40.72, 39.41, 38.00, 37.32, 37.24, 34.29, 29.80, 29.22 (two carbons), 24.61, 24.57, 20.94, 20.56.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.69.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 649.3800, found: 649.3810.

Compound 3wb



According to **Condition A** at 120 °C for 24 h. alkene **1w** (240 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 80:20 hexanes:EA) to afford compound **3wb** (52 mg, 87%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by LCMS. Note: 5 mol% $[Ir(coe)_2Cl]_2$, 12 mol% ligand, and 12 mol% NaBArF were used.

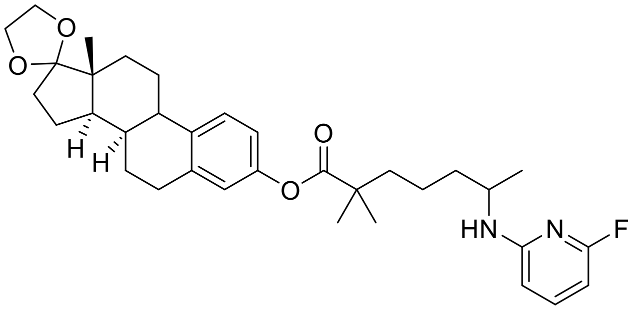
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.41 (q, J = 8.2 Hz, 1H), 6.98 (d, J = 2.5 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.66 (dd, J = 8.9, 2.6 Hz, 1H), 6.11 (dd, J = 7.9, 2.3 Hz, 1H), 6.06 (dd, J = 7.8, 2.3 Hz, 1H), 4.35 (s, 1H), 3.82 (s, 3H), 3.79 (s, 2H), 3.66 (s, 3H), 2.39 (s, 3H), 1.28 – 1.24 (m, 4H), 1.14 – 1.07 (m, 5H), 0.81 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.83, 168.30, 163.32 (d, J = 235.7 Hz), 157.62 (d, J = 16.7 Hz), 156.05, 141.55 (d, J = 8.8 Hz), 139.31, 135.75, 133.89, 131.17, 130.83, 130.65, 129.13, 114.95, 112.85, 111.69, 102.68 (d, J = 3.9 Hz), 101.44, 94.98 (d, J = 36.8 Hz), 72.56, 55.71, 47.11, 38.82, 37.78, 33.80, 30.48, 24.29, 24.20, 20.87, 20.32, 13.33.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.70.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 594.2529, found: 594.2534.

Compound 3xb



According to **Condition A** at 120 °C for 19 h. alkene **1x** (230 mg, 0.50 mmol) and aminopyridine **2b** (11 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 80:20 hexanes:EA) to afford compound **3xb** (33 mg, 58%) as a yellow oil. The regioselectivity of the reaction was determined to be >95% by GC. The d.r. of the product was determined to be 1:1 by GC. Note: The two diastereomers have identical NMR chemical shifts.

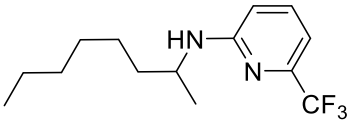
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (q, J = 8.1 Hz, 1H), 7.25 (d, J = 8.9 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 6.71 (s, 1H), 6.14 (d, J = 8.0 Hz, 1H), 6.08 (d, J = 7.7 Hz, 1H), 4.39 (s, 1H), 4.04 – 3.83 (m, 4H), 3.79 (q, J = 6.6 Hz, 1H), 2.84 (t, J = 8.1 Hz, 2H), 2.40 – 2.19 (m, 2H), 2.08– 1.98 (m, 1H), 1.96 – 1.81 (m, 2H), 1.81 – 1.72 (m, 2H), 1.72 – 1.60 (m, 3H), 1.60 – 1.32 (m, 9H), 1.29 (d, J = 3.8 Hz, 6H), 1.19 (d, J = 6.4 Hz, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.65, 163.30 (d, J = 236.1 Hz), 157.54 (d, J = 16.9 Hz), 148.68, 141.62 (d, J = 8.6 Hz), 138.21, 137.83, 126.32, 121.34, 119.39, 118.41, 102.65 (d, J = 3.9 Hz), 95.13 (d, J = 36.7 Hz), 65.27, 64.59, 49.40, 47.10, 46.12, 43.83, 42.56, 40.53, 38.73, 37.47, 34.24, 30.71, 29.53, 26.81, 26.01, 25.24, 25.16, 22.38, 21.55, 20.85, 14.33.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.65.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 565.3436, found: 565.3431.

Compound 3ac



According to **Condition A** at 100 °C for 36 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2c** (16 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 98:2 hexanes:EA) to afford compound **3ac** (16 mg, 56%) as a yellow oil. The regioselectivity of the reaction was determined to be 94% by GC. Note: 5 mol% $[Ir(coe)_2Cl]_2$, 12 mol% ligand, and 12 mol% NaBArF were used.

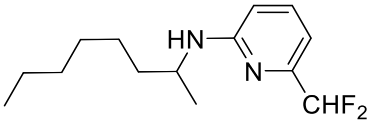
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (t, J = 7.9 Hz, 1H), 6.87 (d, J = 7.4 Hz, 1H), 6.48 (d, J = 8.5 Hz, 1H), 4.61 (d, J = 8.1 Hz, 1H), 3.74 (hept, J = 6.6 Hz, 1H), 1.60 – 1.44 (m, 2H), 1.41 – 1.33 (m, 2H), 1.33 – 1.24 (m, 6H), 1.20 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.17, 146.74 (q, J = 33.7 Hz), 138.10, 121.66 (q, J = 274.1 Hz), 109.28, 108.38 (q, J = 3.3 Hz), 47.37, 37.08, 31.77, 29.24, 25.98, 22.59, 20.69, 14.04.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.84.

HRMS (*m/z*): (ESI) calc’d $[M+K]^+$: 313.1289, found: 313.1276.

Compound 3ad



According to **Condition A** at 100 °C for 18 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2d** (14 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ad** (15 mg, 67%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC.

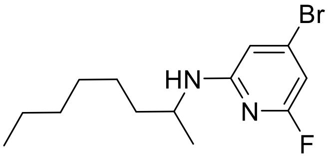
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 (t, J = 7.8 Hz, 1H), 6.75 (d, J = 7.3 Hz, 1H), 6.34 (d, J = 8.4 Hz, 1H), 6.32 (t, J = 55.9 Hz, 1H), 4.42 (d, J = 8.4 Hz, 1H), 3.66 (p, J = 6.7 Hz, 1H), 1.53 – 1.37 (m, 2H), 1.34 – 1.26 (m, 2H), 1.25 – 1.16 (m, 6H), 1.12 (d, J = 6.4 Hz, 3H), 0.81 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.08, 151.30 (t, J = 24.9 Hz), 138.21, 114.03 (t, J = 240.0 Hz), 108.17 (t, J = 3.7 Hz), 47.29, 37.14, 31.78, 29.7 (t, J = 319.1 Hz) 29.27, 26.01, 22.60, 20.77, 14.06.

^{19}F NMR (565 MHz, $CDCl_3$) δ -116.65 (app-d, J = 55.3 Hz).

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 279.1643, found: 279.1663.

Compound 3ae



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2e** (19 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ae** (23 mg, 75%) as a yellow oil. The regioselectivity of the reaction was determined to be 92% by GC.

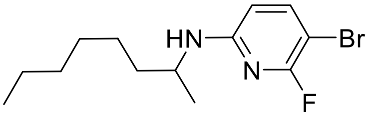
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.31 (s, 1H), 6.27 (s, 1H), 4.48 (d, J = 8.4 Hz, 1H), 3.68 (hept, J = 6.8 Hz, 1H), 1.54 – 1.43 (m, 2H), 1.40 – 1.22 (m, 8H), 1.18 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.29 (d, J = 238.4 Hz), 157.77 (d, J = 19.1 Hz), 135.79 (d, J = 10.9 Hz), 105.50, 99.16 (d, J = 40.9 Hz), 47.66, 37.10, 31.89, 29.33, 26.03, 22.72, 20.85, 14.19.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.66.

HRMS (*m/z*): (ESI) calc'd $[2M+H]^+$: 605.1661, found: 605.1671.

Compound 3af



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2f** (19 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3af** (17 mg, 61%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC.

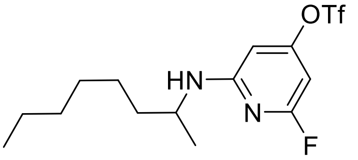
^{1}H NMR 1H NMR (600 MHz, $CDCl_3$) δ 7.53 (t, J = 8.7 Hz, 1H), 6.09 (d, J = 8.5 Hz, 1H), 4.40 (d, J = 8.3 Hz, 1H), 3.77 – 3.63 (m, 1H), 1.55 – 1.41 (m, 2H), 1.39 – 1.21 (m, 8H), 1.17 (d, J = 6.4 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.73 (d, J = 233.2 Hz), 156.36 (d, J = 15.9 Hz), 144.10 (d, J = 2.8 Hz), 104.59 (d, J = 4.4 Hz), 86.93 (d, J = 37.9 Hz), 47.60, 36.99, 31.76, 29.22, 25.92, 22.58, 20.71, 14.05.

^{19}F NMR (565 MHz, $CDCl_3$) δ -67.25.

HRMS (*m/z*): (ESI) calc'd $[2M+H]^+$: 605.1661, found: 605.1671.

Compound 3ag



According to **Condition A** at 100 °C for 18 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2g** (26 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ag** (20 mg, 54%) as a yellow oil. The regioselectivity of the reaction was determined to be 91% by GC. Note: 3.75 mol% $[Ir(coe)_2Cl]_2$, 9 mol% ligand, and 9 mol% NaBArF were used.

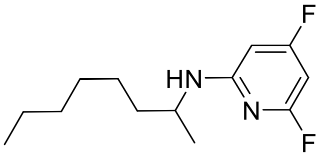
^{1}H NMR 1H NMR (600 MHz, $CDCl_3$) δ 6.04 (s, 1H), 6.02 (s, 1H), 4.71 (d, J = 8.3 Hz, 1H), 3.75 – 3.66 (m, 1H), 1.56 – 1.45 (m, 2H), 1.40 – 1.22 (m, 8H), 1.20 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.85 (d, J = 237.5 Hz), 159.54 (d, J = 13.2 Hz), 158.16 (d, J = 20.5 Hz), 118.58 (q, J = 320.8 Hz), 94.65, 88.87 (d, J = 43.0 Hz), 47.80, 36.83, 31.71, 29.15, 25.88, 22.55, 20.54, 14.01.

^{19}F NMR (565 MHz, $CDCl_3$) δ -64.23, -72.85.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 395.1023, found: 395.1020.

Compound 3ah



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2h** (13 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3ah** (17 mg, 71%) as a yellow oil. The regioselectivity of the reaction was determined to be 93% by GC.

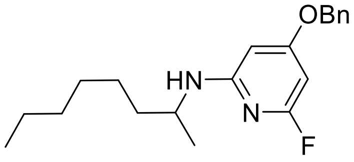
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.86 (s, 1H), 5.84 (t, J = 2.8 Hz, 1H), 4.56 (d, J = 8.3 Hz, 1H), 3.65 – 3.58 (m, 1H), 1.54 – 1.42 (m, 2H), 1.38 – 1.23 (m, 8H), 1.18 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.63 (dd, J = 255.8, 14.1 Hz), 164.29 (dd, J = 234.6, 17.4 Hz), 158.53 (dd, J = 21.2, 14.2 Hz), 89.30 (dd, J = 22.9, 5.3 Hz), 85.00 (dd, J = 42.2, 24.6 Hz), 47.82, 37.08, 31.90, 29.34, 26.05, 22.72, 20.80, 14.18.

^{19}F NMR (565 MHz, $CDCl_3$) δ -66.22 (d, J = 22.8 Hz), -98.96.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 243.1668, found: 243.1663.

Compound 3ai



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2i** (22 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97:3 hexanes:EA) to afford compound **3ai** (29 mg, 88%) as a yellow oil. The regioselectivity of the reaction was determined to be 90% by GC.

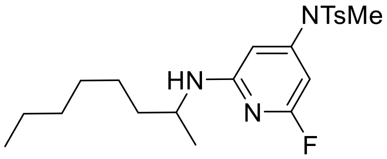
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 4.4 Hz, 4H), 7.37 – 7.32 (m, 1H), 5.78 (d, J = 1.7 Hz, 1H), 5.72 (s, 1H), 5.05 (s, 2H), 4.37 (d, J = 8.3 Hz, 1H), 3.59 (p, J = 6.7 Hz, 1H), 1.52 – 1.42 (m, 2H), 1.39 – 1.20 (m, 8H), 1.16 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.85 (d, J = 13.0 Hz), 164.70 (d, J = 231.8 Hz), 158.21 (d, J = 21.1 Hz), 135.96, 128.85, 128.47, 127.64, 88.14 (d, J = 4.2 Hz), 83.72 (d, J = 41.8 Hz), 70.31, 47.67, 37.17, 31.91, 29.38, 26.07, 22.72, 20.86, 14.19.

^{19}F NMR (565 MHz, $CDCl_3$) δ -69.20.

HRMS (*m/z*): (ESI) calc'd $[2M+Na]^+$: 683.4106, found: 683.4096.

Compound 3aj



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2j** (30 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 91:9 hexanes:EA) to afford compound **3aj** (31 mg, 77%) as a yellow oil. The regioselectivity of the reaction was determined to be 92% by GC.

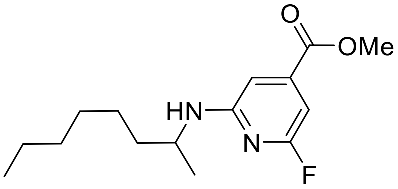
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 7.8 Hz, 2H), 6.99 (d, J = 7.4 Hz, 2H), 5.91 (s, 1H), 5.55 (s, 1H), 4.18 (d, J = 8.3 Hz, 1H), 3.43 – 3.31 (m, 1H), 2.90 (s, 3H), 2.14 (s, 3H), 1.26 – 1.14 (m, 2H), 1.14 – 0.96 (m, 8H), 0.89 (d, J = 6.4 Hz, 3H), 0.61 (t, J = 6.8 Hz, 3H).

^{13}C NMR 13C NMR (151 MHz, $CDCl_3$) δ 163.73 (d, J = 233.5 Hz), 157.54 (d, J = 19.8 Hz), 153.70 (d, J = 11.6 Hz), 144.23, 133.83, 129.66, 127.45, 97.60, 89.77 (d, J = 41.3 Hz), 47.45, 36.99, 36.70, 31.78, 29.25, 25.90, 22.59, 21.56, 20.69, 14.06.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.72.

HRMS (*m/z*): (ESI) calc'd $[2M+ACN+H]^+$: 878.4244, found: 878.4236.

Compound 3ak



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2k** (17 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97:3 hexanes:EA) to afford compound **3ak** (18 mg, 65%) as a yellow oil. The regioselectivity of the reaction was determined to be 90% by GC.

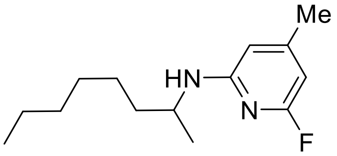
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (s, 1H), 6.59 (s, 1H), 4.57 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H), 3.79 (t, J = 7.0 Hz, 1H), 1.56 – 1.43 (m, 2H), 1.41 – 1.23 (m, 8H), 1.19 (d, J = 6.4 Hz, 3H), 0.87 (t, J = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.42 (d, J = 4.3 Hz), 163.90 (d, J = 236.4 Hz), 158.06 (d, J = 17.4 Hz), 143.39 (d, J = 9.0 Hz), 103.34, 94.88 (d, J = 39.7 Hz), 52.76, 47.65, 37.15, 31.89, 29.35, 26.04, 22.72, 20.91, 14.18.

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.83.

HRMS (*m/z*): (ESI) calc'd $[M+ACN+Na]^+$: 346.1902, found: 349.1905.

Compound 3al



According to **Condition A** at 100 °C for 24 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2l** (12 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 98:2 hexanes:EA) to afford compound **3al** (17 mg, 69%) as a yellow oil. The regioselectivity of the reaction was determined to be 92% by GC.

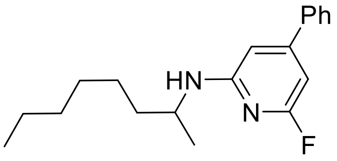
^{1}H NMR (600 MHz, $CDCl_3$) δ 5.96 (s, 1H), 5.93 (s, 1H), 4.29 (d, J = 8.5 Hz, 1H), 3.68 (app-dq, J = 8.2, 6.3 Hz, 1H), 2.23 (s, 3H), 1.53 – 1.42 (m, 2H), 1.39 – 1.32 (m, 2H), 1.30 – 1.23 (s, 6H), 1.17 (d, J = 6.4 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.79 (d, J = 234.5 Hz), 157.59 (d, J = 17.8 Hz), 153.45 (d, J = 8.9 Hz), 102.89 (d, J = 3.6 Hz), 96.32 (d, J = 36.6 Hz), 47.46, 37.28, 31.92, 29.40, 26.09, 22.73, 21.35 (d, J = 3.5 Hz), 21.00, 14.20.

^{19}F NMR (565 MHz, $CDCl_3$) δ -72.35.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 239.1918, found: 239.1909.

Compound 3am



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2m** (19 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3am** (22 mg, 72%) as a yellow oil. The regioselectivity of the reaction was determined to be 89% by GC. Notes: Contain 10% inseparable isomers.

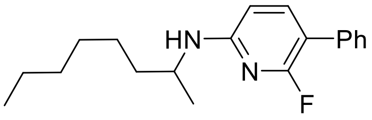
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.48 – 7.38 (m, 3H), 6.35 (s, 1H), 6.32 (s, 1H), 4.47 (d, J = 8.3 Hz, 1H), 3.84 – 3.76 (m, 1H), 1.58 – 1.47 (m, 2H), 1.42 – 1.35 (m, 2H), 1.34 – 1.24 (m, 6H), 1.22 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.17 (d, J = 234.8 Hz), 157.94 (d, J = 18.3 Hz), 154.97 (d, J = 9.0 Hz), 138.79 (d, J = 3.5 Hz), 129.17, 129.04, 127.06, 100.75 (d, J = 3.9 Hz), 93.96 (d, J = 38.0 Hz), 47.61, 37.28, 31.93, 29.42, 26.11, 22.74, 21.03, 14.20.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.71.

HRMS (*m/z*): (ESI) calc'd $[M+K]^+$: 339.1634, found: 339.1635.

Compound 3an



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2n** (19 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3an** (24 mg, 80%) as a yellow oil. The regioselectivity of the reaction was determined to be 90% by GC. Notes: Contain 10% inseparable isomers.

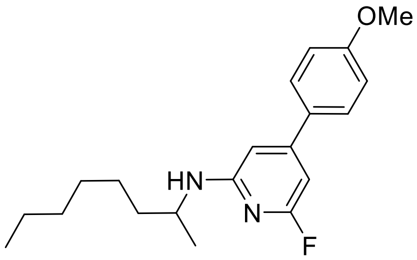
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (dd, J = 10.1, 8.2 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.40 (t, J = 7.6 Hz, 2H), 7.32 – 7.27 (m, 1H), 6.27 (dd, J = 8.2, 1.8 Hz, 1H), 4.44 (s, 1H), 3.77 (p, J = 6.1 Hz, 1H), 1.60 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 – 1.25 (m, 6H), 1.22 (d, J = 6.2 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR 13C NMR (151 MHz, $CDCl_3$) δ 160.46, 158.88, 156.59 (d, J = 17.1 Hz), 141.81 (d, J = 5.1 Hz), 135.14 (d, J = 5.4 Hz), 128.48, 126.76, 109.58 (d, J = 27.7 Hz), 103.30 (d, J = 4.1 Hz), 47.52, 37.16, 31.79, 29.27, 25.99, 22.61, 20.91, 14.07.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.27.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 323.1894, found: 323.1887.

Compound 3ao



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2o** (22 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 95:5 hexanes:EA) to afford compound **3ao** (20 mg, 61%) as a yellow oil. The regioselectivity of the reaction was determined to be 87% by GC.

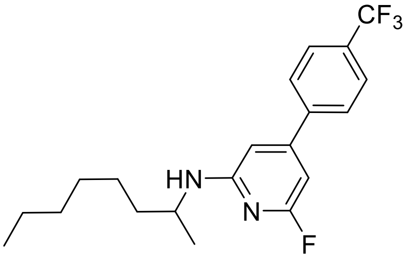
^{1}H NMR 1H NMR (600 MHz, CDCl$_3$) δ 7.54 – 7.50 (m, 2H), 6.99 – 6.95 (m, 2H), 6.31 (s, 1H), 6.29 (s, 1H), 4.46 (s, 1H), 3.85 (s, 3H), 3.78 (q, J = 6.4 Hz, 1H), 1.59 – 1.45 (m, 2H), 1.56 – 1.46 (m, 2H), 1.34 – 1.24 (m, 6H), 1.22 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.17 (d, J = 234.7 Hz), 160.63, 157.88 (d, J = 18.0 Hz), 154.45 (d, J = 9.1 Hz), 131.02 (d, J = 3.4 Hz), 128.23, 114.44, 100.06 (d, J = 3.4 Hz), 93.42 (d, J = 37.7 Hz), 55.52, 47.61, 37.29, 31.93, 29.42, 26.12, 22.74, 21.03, 14.20.

^{19}F NMR (565 MHz, CDCl$_3$) δ -71.17.

HRMS (*m/z*): (ESI) calc'd [M+ACN+Na]$^+$: 394.2264, found: 394.2266.

Compound 3ap



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 μL, 0.50 mmol) and aminopyridine **2p** (26 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO$_2$; 97.5:2.5 hexanes:EA) to afford compound **3ap** (17 mg, 47%) as a yellow oil. The regioselectivity of the reaction was determined to be 93% by GC.

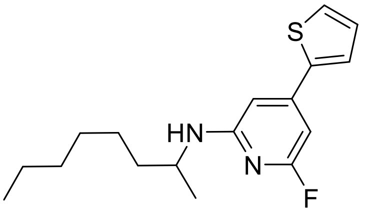
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.71 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 6.30 (s, 1H), 4.52 (d, J = 8.2 Hz, 1H), 3.83 – 3.76 (m, 1H), 1.58 – 1.49 (m, 2H), 1.44 – 1.36 (m, 2H), 1.34 – 1.24 (m, 6H), 1.23 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.06 (d, J = 235.5 Hz), 157.92 (d, J = 18.1 Hz), 153.26 (d, J = 9.1 Hz), 142.22 (d, J = 3.1 Hz), 131.01 (q, J = 32.6 Hz), 127.34, 125.88 (q, J = 3.8 Hz), 123.99 (q, J = 272.1 Hz), 100.88, 93.85 (d, J = 38.4 Hz), 47.50, 37.11, 31.78, 29.26, 25.97, 22.60, 20.85, 14.05.

^{19}F NMR (565 MHz, CDCl$_3$) δ -62.64, -69.78.

HRMS (*m/z*): (ESI) calc'd [M+H]$^+$: 369.1949, found: 369.1951.

Compound 3aq



According to **Condition A** at 100 °C for 12 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2q** (19 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3aq** (15 mg, 49%) as a yellow oil. The regioselectivity of the reaction was determined to be 86% by GC.

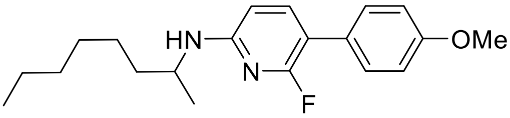
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 3.6 Hz, 1H), 7.37 (d, J = 5.0 Hz, 1H), 7.10 (dd, J = 5.1, 3.7 Hz, 1H), 6.35 (s, 1H), 6.33 (s, 1H), 4.45 (d, J = 8.4 Hz, 1H), 3.79 (p, J = 6.7 Hz, 1H), 1.58 – 1.46 (m, 2H), 1.42 – 1.34 (m, 2H), 1.34 – 1.23 (m, 6H), 1.21 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR 13C NMR (151 MHz, $CDCl_3$) δ 164.12 (d, J = 234.3 Hz), 157.89 (d, J = 18.5 Hz), 147.14 (d, J = 9.8 Hz), 141.47 (d, J = 4.4 Hz), 128.10, 126.67, 125.21, 99.03, 92.31 (d, J = 39.1 Hz), 47.44, 37.14, 31.79, 29.28, 25.97, 22.61, 20.89, 14.07.

^{19}F NMR (565 MHz, $CDCl_3$) δ -70.54.

HRMS (*m/z*): (ESI) calc'd $[2M+Na]^+$: 635.3024, found: 635.3037.

Compound 3ar



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2r** (22 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 95:5 hexanes:EA) to afford compound **3ar** (15 mg, 46%) as a yellow oil. The regioselectivity of the reaction was determined to be 92% by GC.

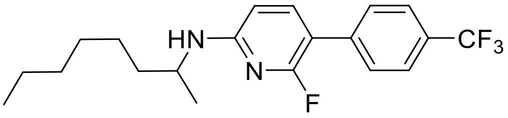
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (t, J = 10.2 Hz, 1H), 7.42 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.4 Hz, 2H), 6.26 (dd, J = 8.2, 1.8 Hz, 1H), 3.83 (s, 3H), 3.75 (q, J = 6.4 Hz, 1H), 1.56 – 1.45 (m, 2H), 1.43 – 1.34 (m, 2H), 1.34 – 1.24 (m, 7H), 1.21 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR 13C NMR (151 MHz, $CDCl_3$) δ 159.60 (d, J = 238.0 Hz), 158.73, 156.31 (d, J = 16.7 Hz), 141.75 (d, J = 5.3 Hz), 129.43 (d, J = 3.0 Hz), 127.64 (d, J = 5.1 Hz), 114.12, 109.47 (d, J = 27.8 Hz), 103.40 (d, J = 4.2 Hz), 55.45, 47.68, 37.28, 31.93, 29.41, 26.12, 22.74, 21.03, 14.20.

^{19}F NMR (565 MHz, $CDCl_3$) δ -73.73.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 353.1999, found: 353.2004.

Compound 3as



According to **Condition A** at 100 °C for 6 h. *cis*-4-octene (78 µL, 0.50 mmol) and aminopyridine **2s** (26 mg, 0.10 mmol) was allowed to react, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **3as** (17 mg, 47%) as a yellow oil. The regioselectivity of the reaction was determined to be 93% by GC.

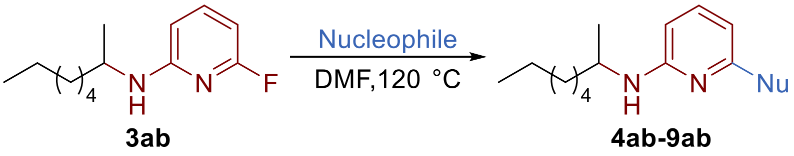
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 – 7.52 (m, 5H), 6.29 (d, J = 8.3 Hz, 1H), 4.55 (s, 1H), 3.79 (p, J = 6.2 Hz, 1H), 1.57 – 1.48 (m, 2H), 1.42 – 1.35 (m, 2H), 1.34 – 1.26 (m, 6H), 1.23 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.75 (d, J = 238.9 Hz), 157.15 (d, J = 17.5 Hz), 141.55 (d, J = 4.8 Hz), 138.81 (d, J = 5.3 Hz), 128.66 (q, J = 32.5 Hz), 128.26 (d, J = 3.4 Hz), 125.41 (q, J = 3.8 Hz), 124.28 (q, J = 271.9 Hz), 107.96 (d, J = 27.3 Hz), 103.61, 47.55, 37.10, 31.78, 29.25, 25.98, 22.60, 20.86, 14.06.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.44, -72.49.

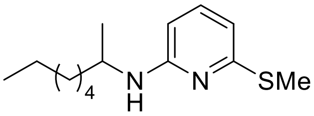
HRMS (*m/z*): (ESI) calc'd $[2M+H]^+$: 737.3825, found: 737.3846.

8. Product Derivatization by S_NAr



Condition D: In a nitrogen-filled glovebox, a 1-dram vial was charged sequentially with 6-fluoro-N-(octan-2-yl)pyridin-2-amine (**3ab**) (22 mg, 0.10 mmol, 1.0 equiv), nucleophile (0.30 to 1.0 mmol, 3.0 to 10.0 equiv), DMF (0.2 mL), and a magnetic stir bar. The vial was capped and removed from the glovebox. The reaction was heated at 120 to 130 °C in an aluminium heating block. The crude material was extracted with ether/H_2O 5 times to remove residual DMF, concentrated in vacuo, and purified by flash column chromatography to afford the product.

Compound 4ab



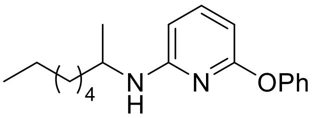
According to **Condition D** at 120 °C for 18 h. sodium methanethiolate (NaSMe) (71 mg, 1.0 mmol) was used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **4ab** (21 mg, 83%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (t, J = 7.8 Hz, 1H), 6.43 (d, J = 7.5 Hz, 1H), 6.02 (d, J = 8.2 Hz, 1H), 4.33 (s, 1H), 3.73 (h, J = 7.4, 7.0 Hz, 1H), 2.49 (s, 3H), 1.58 – 1.51 (m, 1H), 1.50 – 1.41 (m, 1H), 1.40 – 1.33 (m, 2H), 1.32 – 1.25 (m, 6H), 1.18 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.11, 158.06, 137.50, 109.24, 101.66, 47.34, 37.38, 31.95, 29.47, 26.23, 22.75, 21.01, 14.20, 13.41.

HRMS (*m/z*): (ESI) calc'd $[2M+ACN+Na]^+$: 568.3478, found: 568.3472.

Compound 5ab



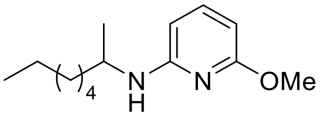
According to **Condition D** at 120 °C for 36 h. potassium phenoxide (KOPh) (39 mg, 0.30 mmol) was used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **5ab** (24 mg, 80%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (q, J = 7.8 Hz, 3H), 7.17 – 7.12 (m, 3H), 6.03 (d, J = 8.0 Hz, 1H), 5.97 (d, J = 7.8 Hz, 1H), 4.30 (d, J = 8.1 Hz, 1H), 3.62 (hept, J = 6.5 Hz, 1H), 1.53 – 1.46 (m, 1H), 1.44 – 1.37 (m, 1H), 1.36 – 1.20 (m, 8H), 1.14 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.28, 157.85, 154.86, 140.54, 129.51, 124.17, 121.17, 100.30, 97.54, 47.45, 37.30, 31.95, 29.44, 26.15, 22.74, 20.93, 14.21.

HRMS (*m/z*): (ESI) calc'd $[2M+Na]^+$: 619.3982, found: 619.3962.

Compound 6ab



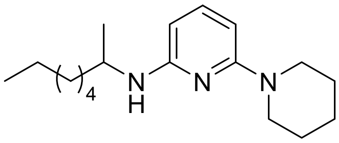
According to **Condition D** at 130 °C for 36 h. lithium methoxide (LiOMe) (11 mg, 0.30 mmol) was used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **4ab** (18 mg, 77%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, J = 7.9 Hz, 1H), 5.97 (d, J = 7.8 Hz, 1H), 5.89 (d, J = 7.9 Hz, 1H), 4.20 (s, 1H), 3.84 (s, 3H), 3.71 (hept, J = 6.6 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.48 – 1.42 (m, 1H), 1.41 – 1.34 (m, 2H), 1.32 – 1.24 (m, 6H), 1.19 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.81, 157.51, 140.02, 97.78, 96.78, 53.15, 47.43, 37.43, 31.97, 29.49, 26.26, 22.76, 21.06, 14.21.

HRMS (*m/z*): (ESI) calc'd $[M+Na]^+$: 259.1781, found: 259.1768.

Compound 7ab



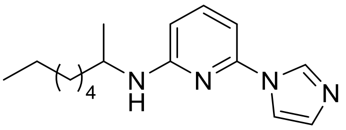
According to **Condition D** at 130 °C for 18 h. piperidine (29 μL, 0.30 mmol) and sodium *tert*-butoxide (NaO^tBu) (29 mg, 0.30 mmol) were used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **7ab** (21 mg, 72%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (app-d, J = 7.8 Hz, 1H), 5.92 (d, J = 7.8 Hz, 1H), 5.86 (d, J = 7.9 Hz, 1H), 4.05 (s, 1H), 3.75 (q, J = 6.5 Hz, 1H), 1.56 (s, 10H), 1.48 – 1.40 (m, 1H), 1.39 – 1.33 (m, 2H), 1.33 – 1.24 (m, 7H), 1.18 (d, J = 6.4 Hz, 3H), 0.88 (d, J = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.37, 157.13, 139.53, 100.26, 98.35, 78.74, 47.34, 37.49, 31.98, 29.50, 29.11, 26.32, 22.76, 21.19, 14.21.

HRMS (*m/z*): (ESI) calc'd $[M+ACN+Na]^+$: 353.2676, found: 535.2666.

Compound 8ab



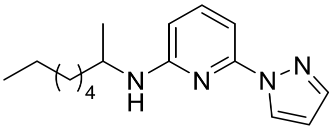
According to **Condition D** at 130 °C for 24 h. imidazole (20 mg, 0.30 mmol) and sodium *tert*-butoxide (NaO^tBu) (29 mg, 0.30 mmol) were used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **8ab** (25 mg, 92%) as a yellow oil.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.26 (s, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.09 (s, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.28 (d, J = 8.3 Hz, 1H), 4.57 (d, J = 8.2 Hz, 1H), 3.89 (hept, J = 6.6 Hz, 1H), 1.60 – 1.55 (m, 1H), 1.55 – 1.46 (m, 1H), 1.40 – 1.35 (m, 2H), 1.34 – 1.26 (m, 6H), 1.22 (d, J = 6.4 Hz, 3H), 0.88 (t, J = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 158.33, 148.32, 139.93, 135.20, 129.98, 116.54, 105.49, 99.43, 47.55, 37.46, 32.24, 29.72, 26.50, 23.02, 20.95, 14.24.

HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 273.2074, found: 273.2075.

Compound 9ab



According to **Condition D** at 130 °C for 24 h. pyrazole (20 mg, 0.30 mmol) and sodium *tert*-butoxide (NaO^tBu) (29 mg, 0.30 mmol) were used as the nucleophile, and the product was purified by flash column chromatography (SiO_2; 97.5:2.5 hexanes:EA) to afford compound **9ab** (25 mg, 93%) as a yellow oil.

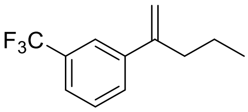
^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.30 (d, J = 2.6 Hz, 1H), 7.48 (s, 1H), 7.32 (t, J = 7.9 Hz, 1H), 6.94 (d, J = 7.7 Hz, 1H), 6.23 (t, J = 2.1 Hz, 1H), 6.08 (d, J = 8.2 Hz, 1H), 4.27 (s, 1H), 3.70 (p, J = 6.3 Hz, 1H), 1.42 (ddt, J = 12.3, 9.3, 6.1 Hz, 1H), 1.37 – 1.29 (m, 1H), 1.23 (hept, J = 5.9 Hz, 2H), 1.19 – 1.08 (m, 6H), 1.05 (d, J = 6.4 Hz, 3H), 0.70 (t, J = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.43, 150.50, 141.58, 139.79, 126.91, 107.01, 104.32, 99.76, 47.40, 37.35, 31.96, 29.47, 26.26, 22.76, 21.00, 14.20.

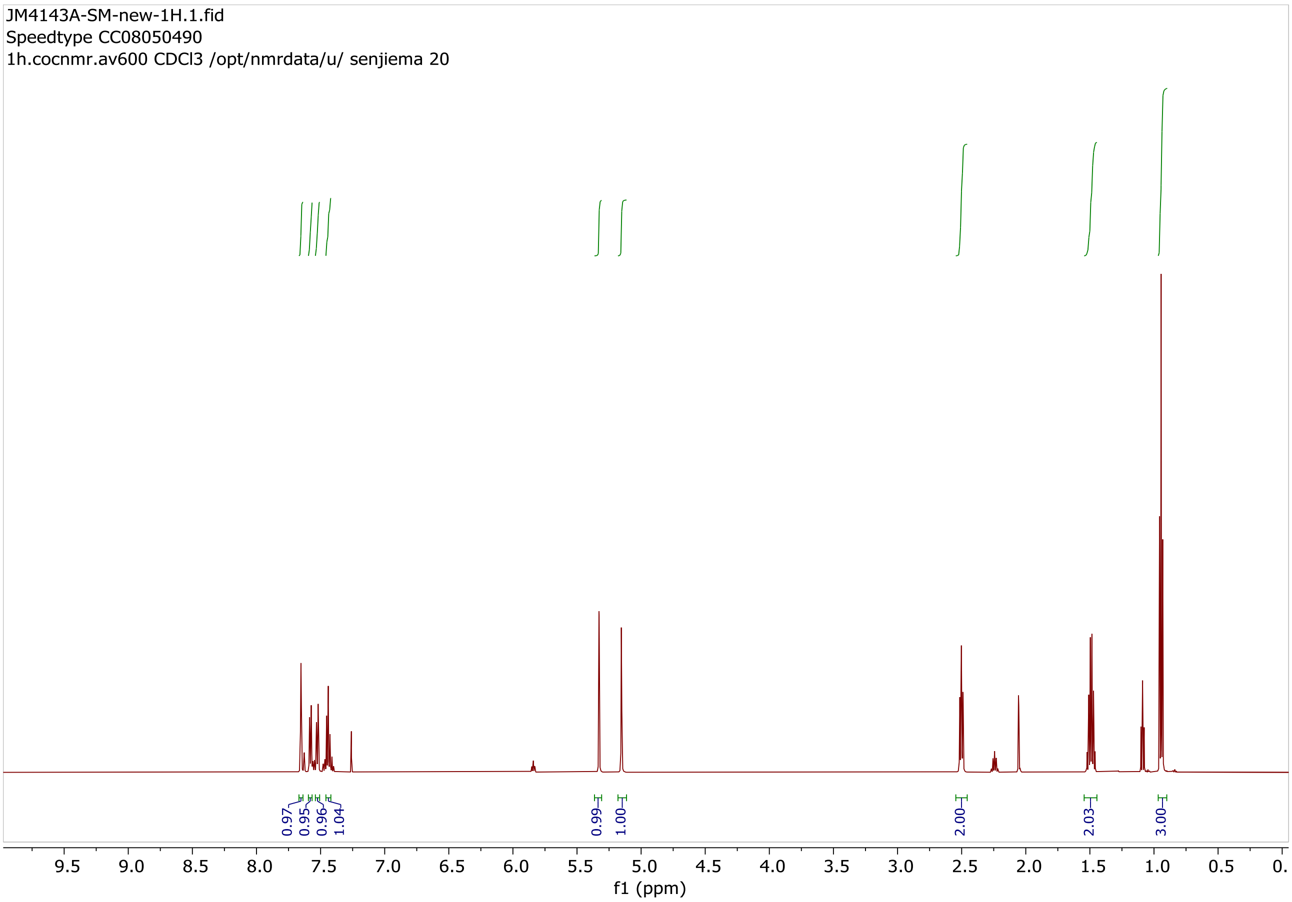
HRMS (*m/z*): (ESI) calc'd $[M+H]^+$: 273.2074, found: 273.2077.

9. NMR Spectra

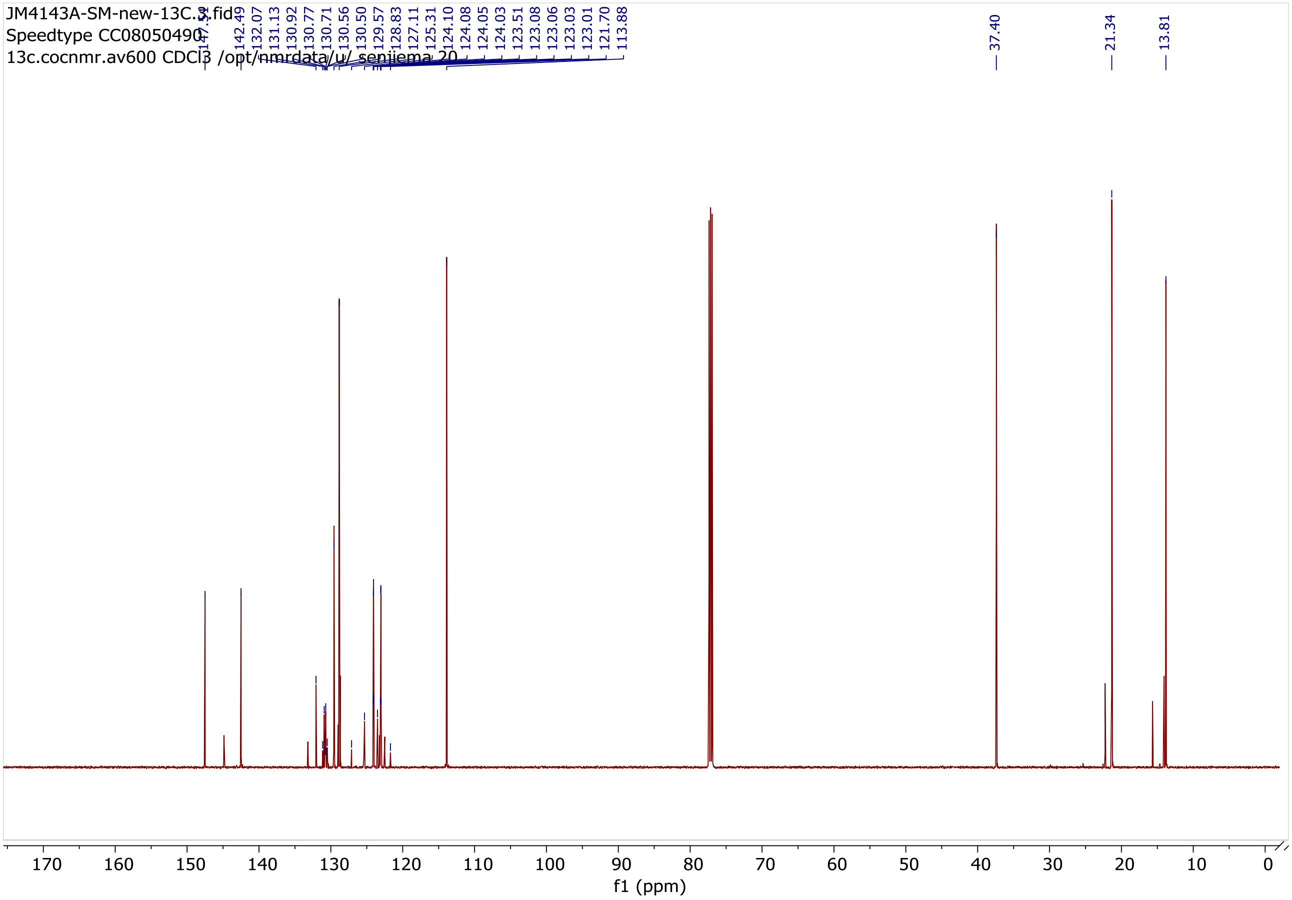
Compound 1f



^{1}H NMR



^{13}C NMR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13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 20
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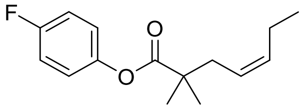
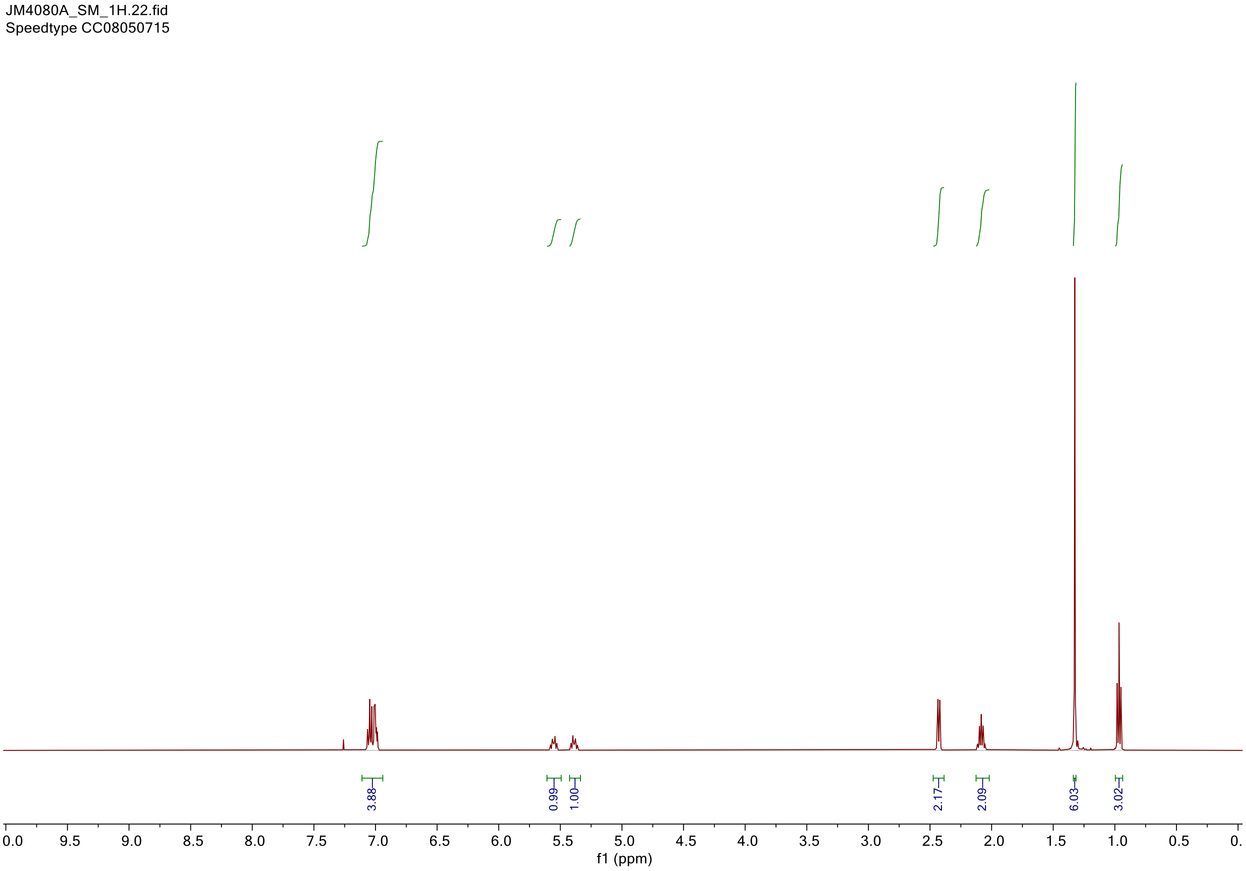
142.49
132.07
131.13
130.92
130.77
130.71
130.56
130.50
129.57
128.83
127.11
125.31
124.10
124.08
124.05
124.03
123.51
123.08
123.06
123.03
123.01
121.70
113.88
37.40
21.34
13.81
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

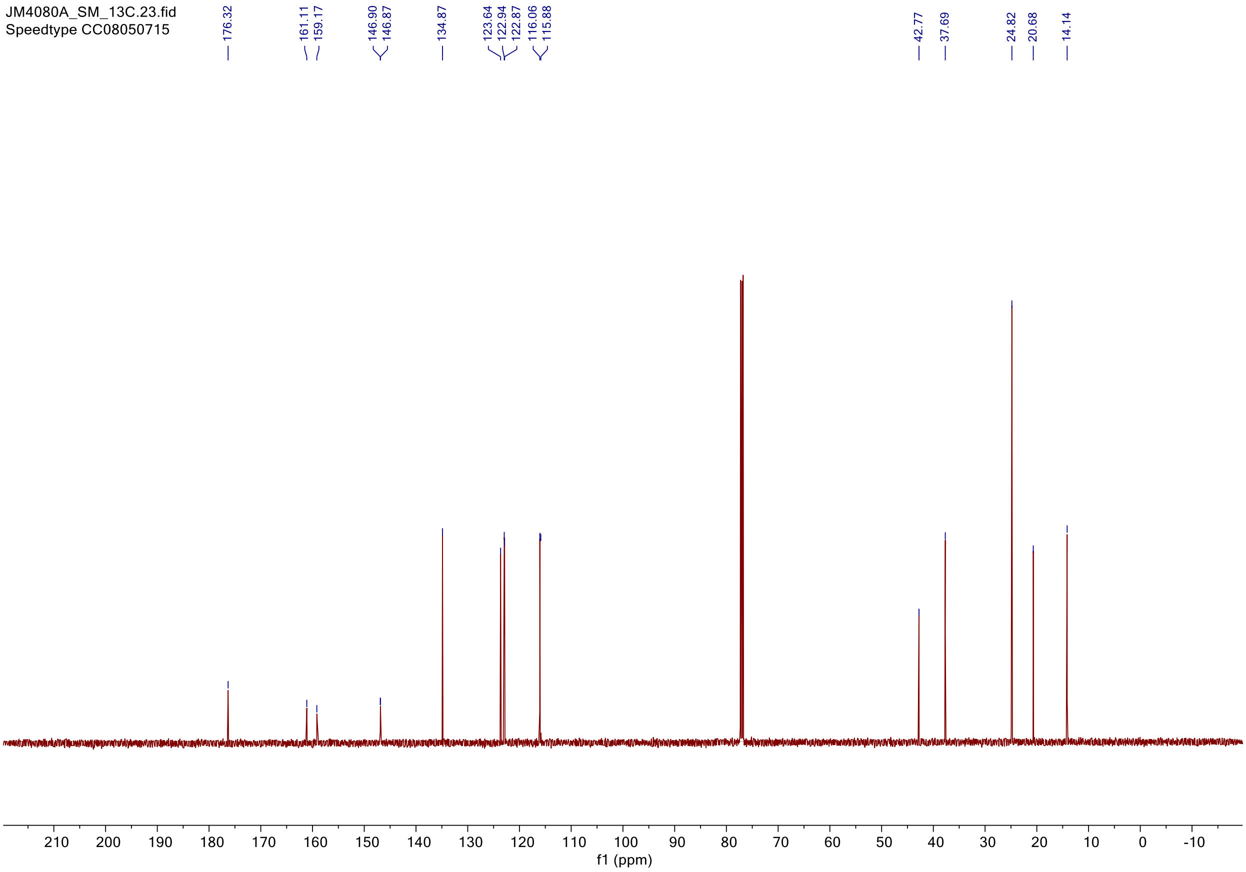
Compound 1k



^{1}H NMR



^{13}C NMR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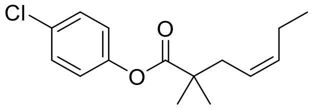
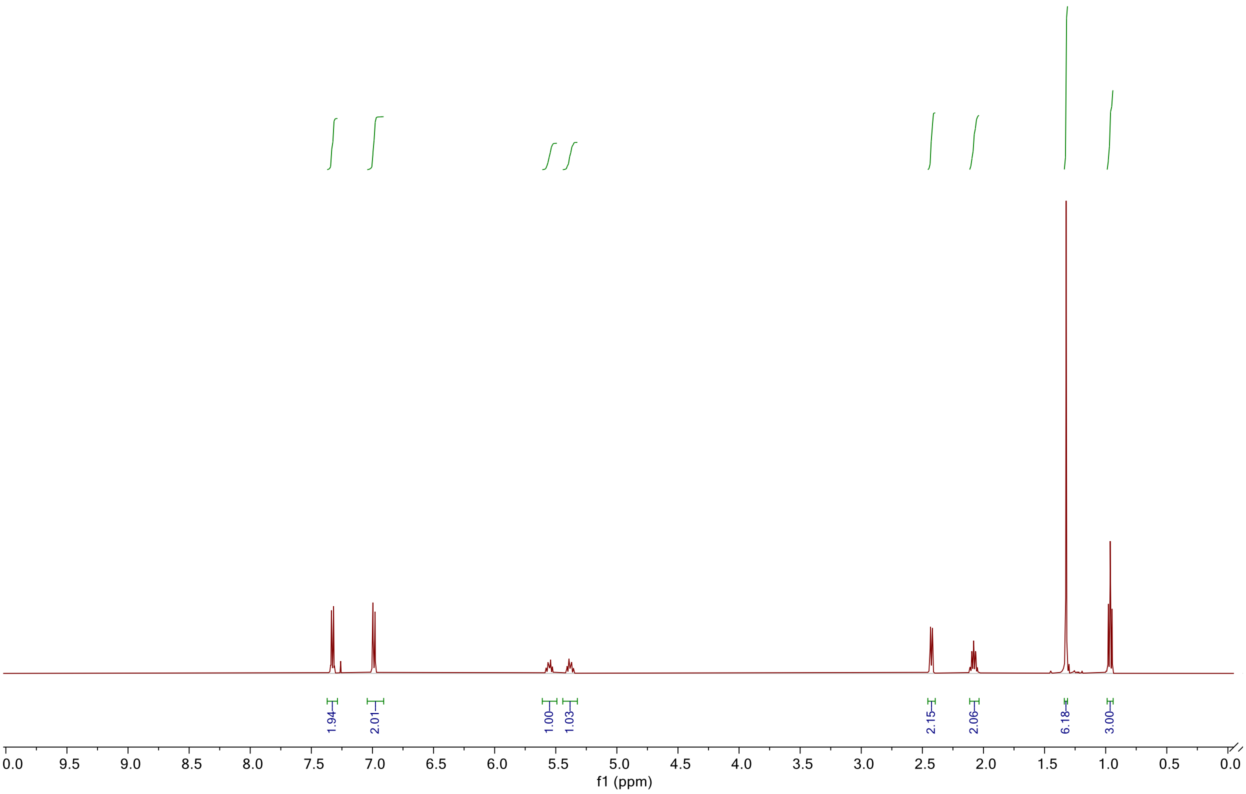
122.87
116.06
115.88
42.77
37.69
24.82
20.68
14.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 1l



^{1}H NMR

JM4087A_SM_1H.22.fid
Speedtype CC08050715



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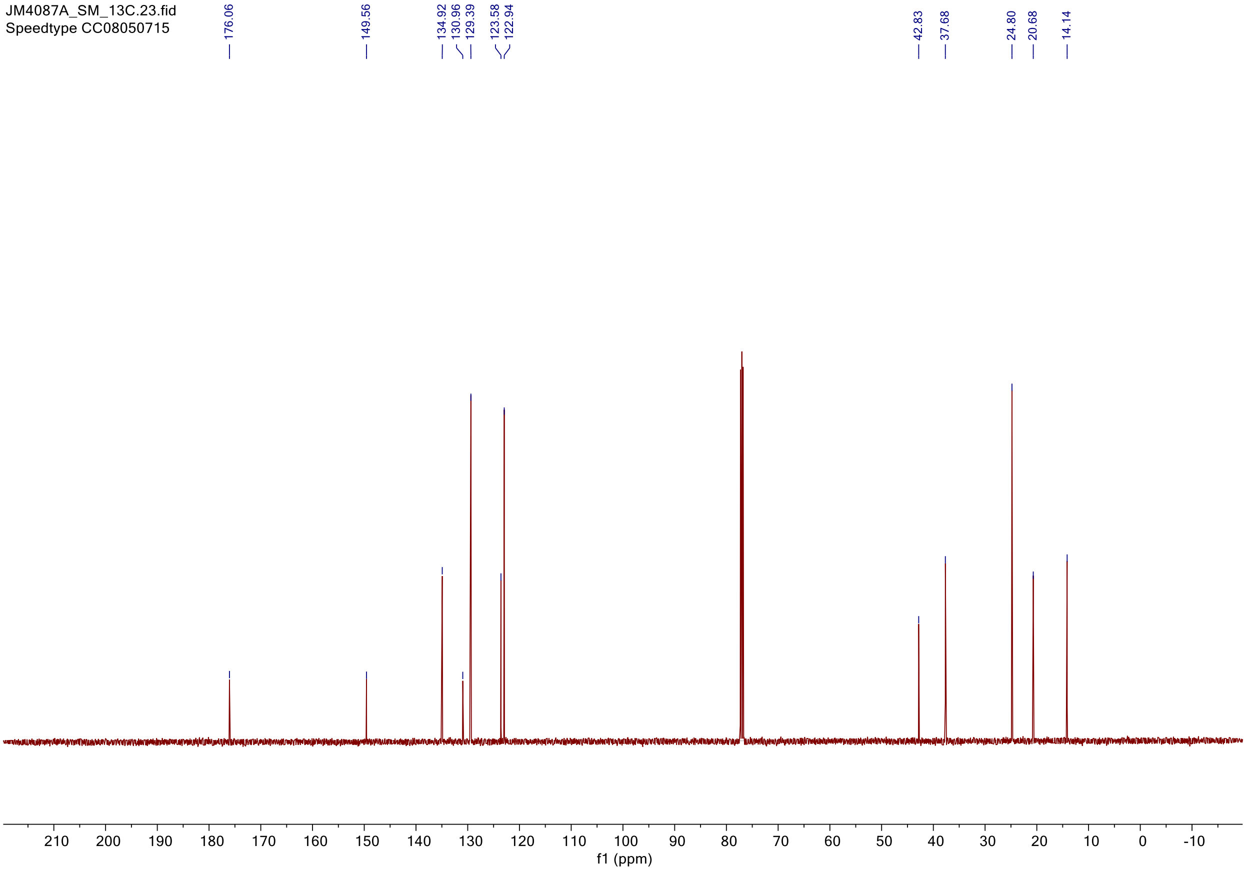
^{13}C NMR



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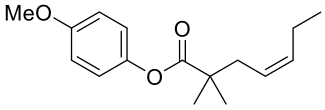
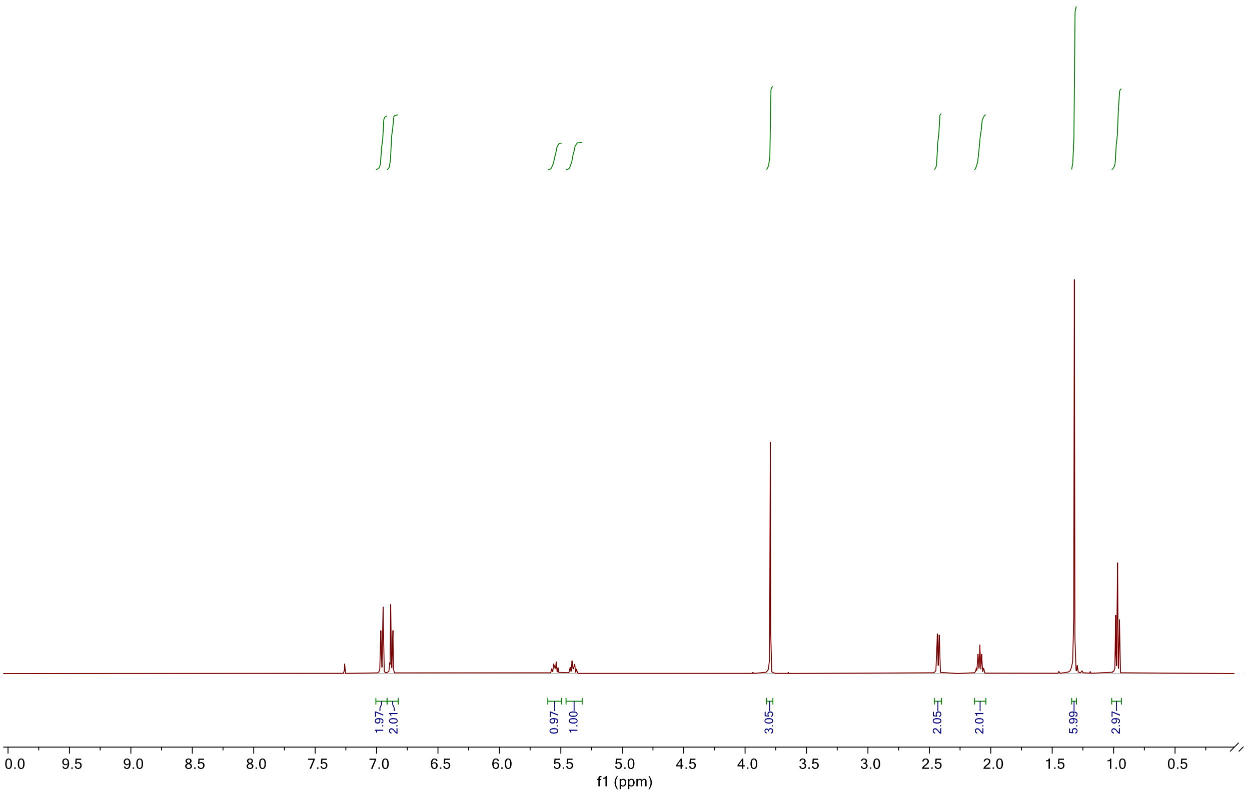
Compound 1m



^{1}H NMR

JM4080B_SM_1H.22.fid
Speedtype CC08050715



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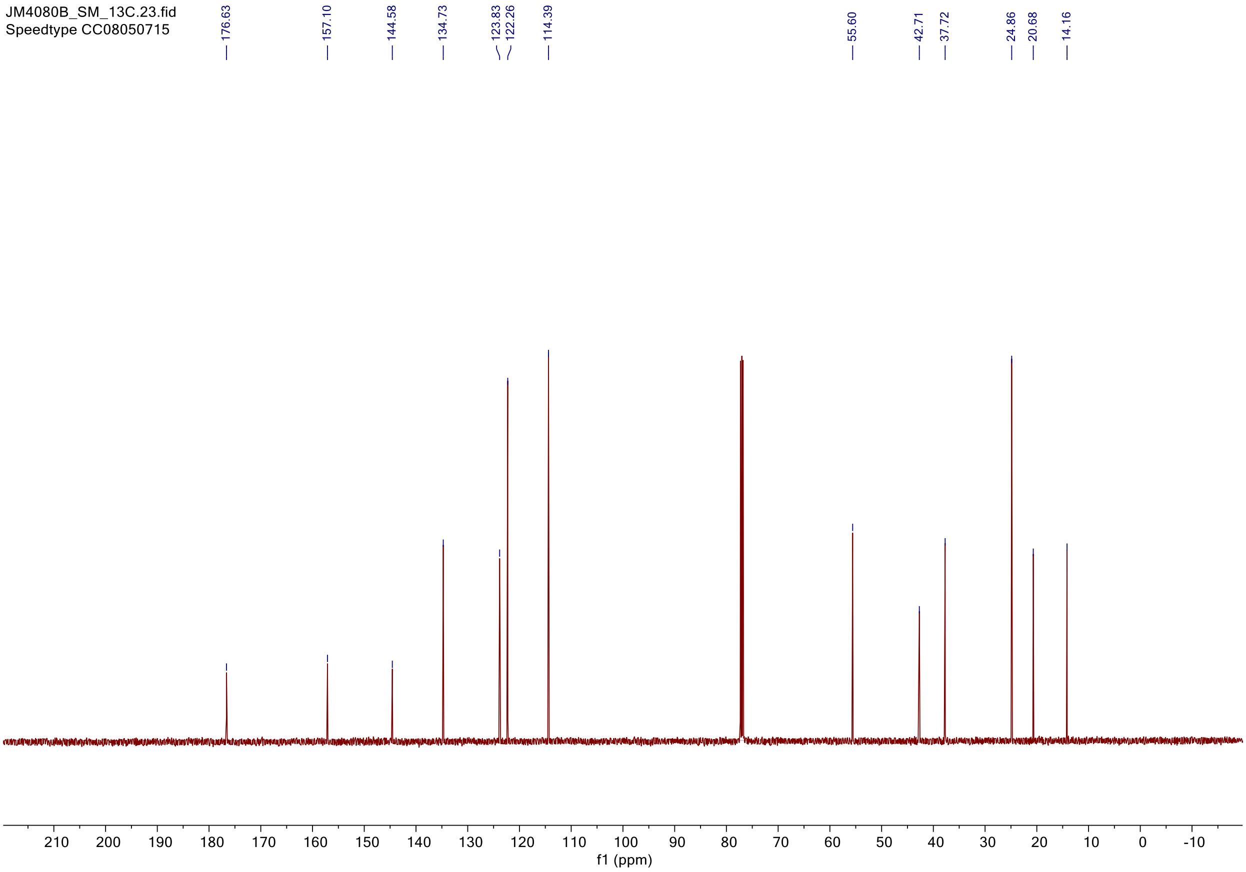
^{13}C NMR



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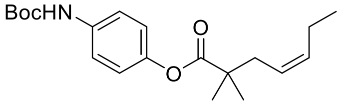
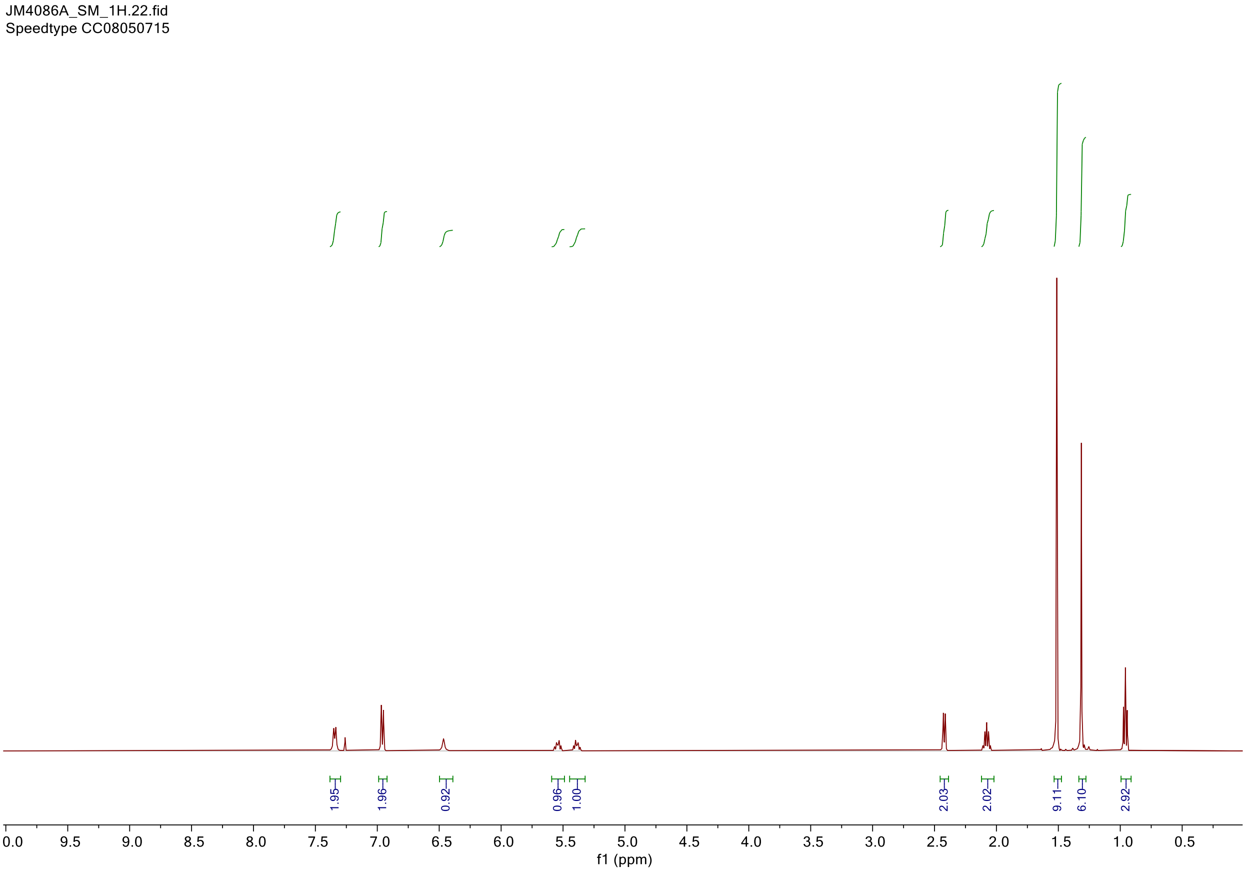
Compound 1n



^{1}H NMR



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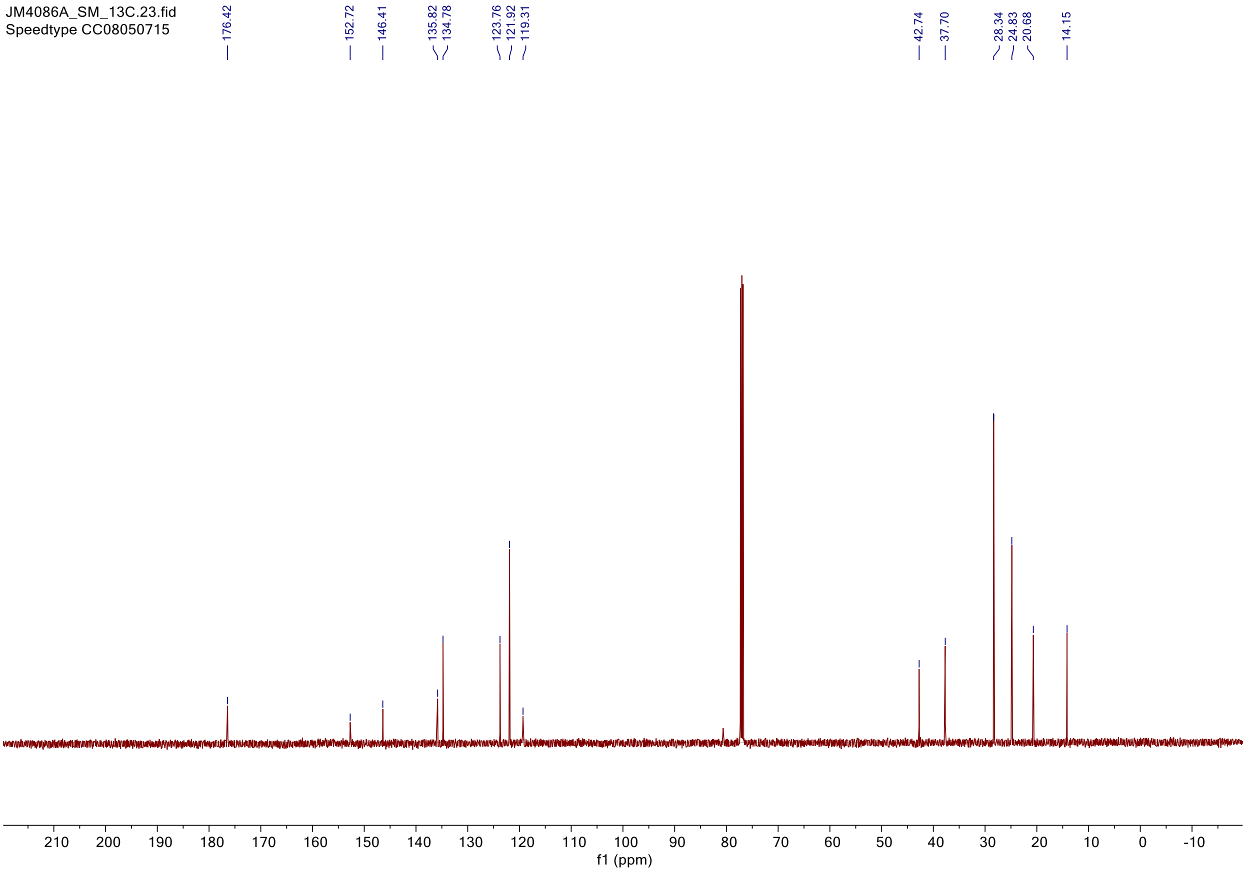
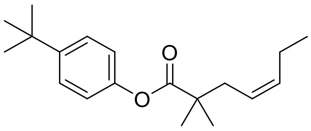
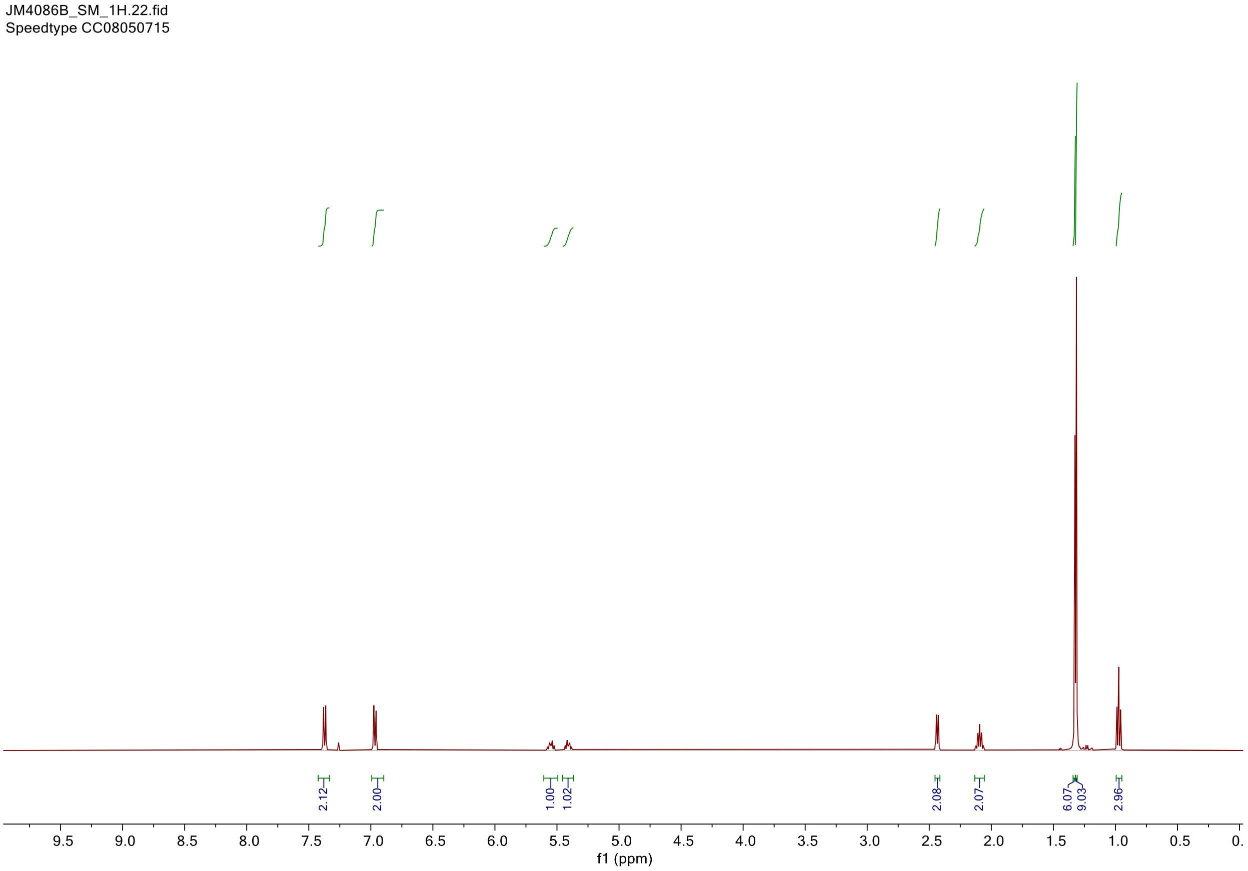
^{13}C NMR



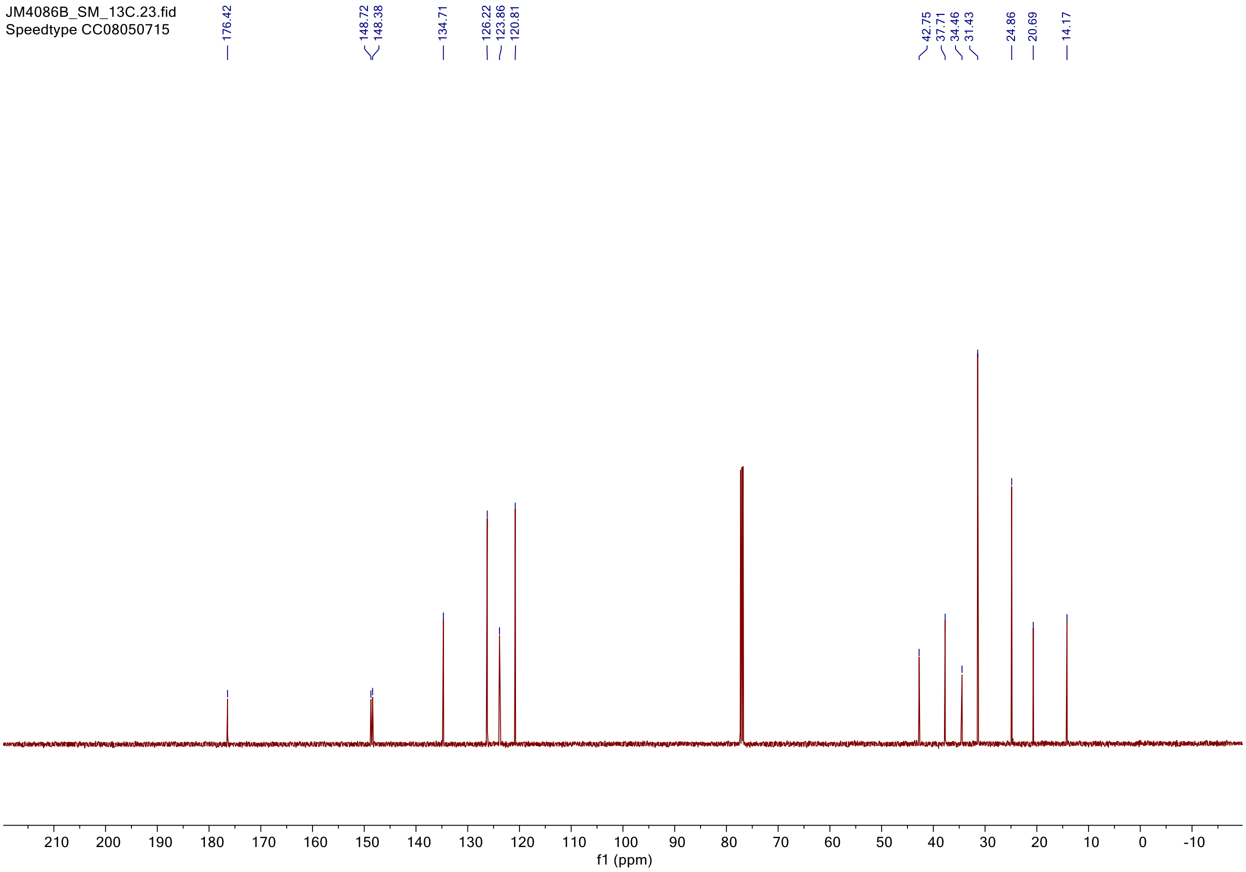
Compound 1o



^{1}H NMR



^{13}C NMR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134.71
126.22
123.86
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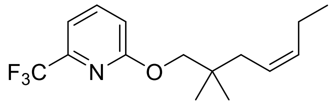
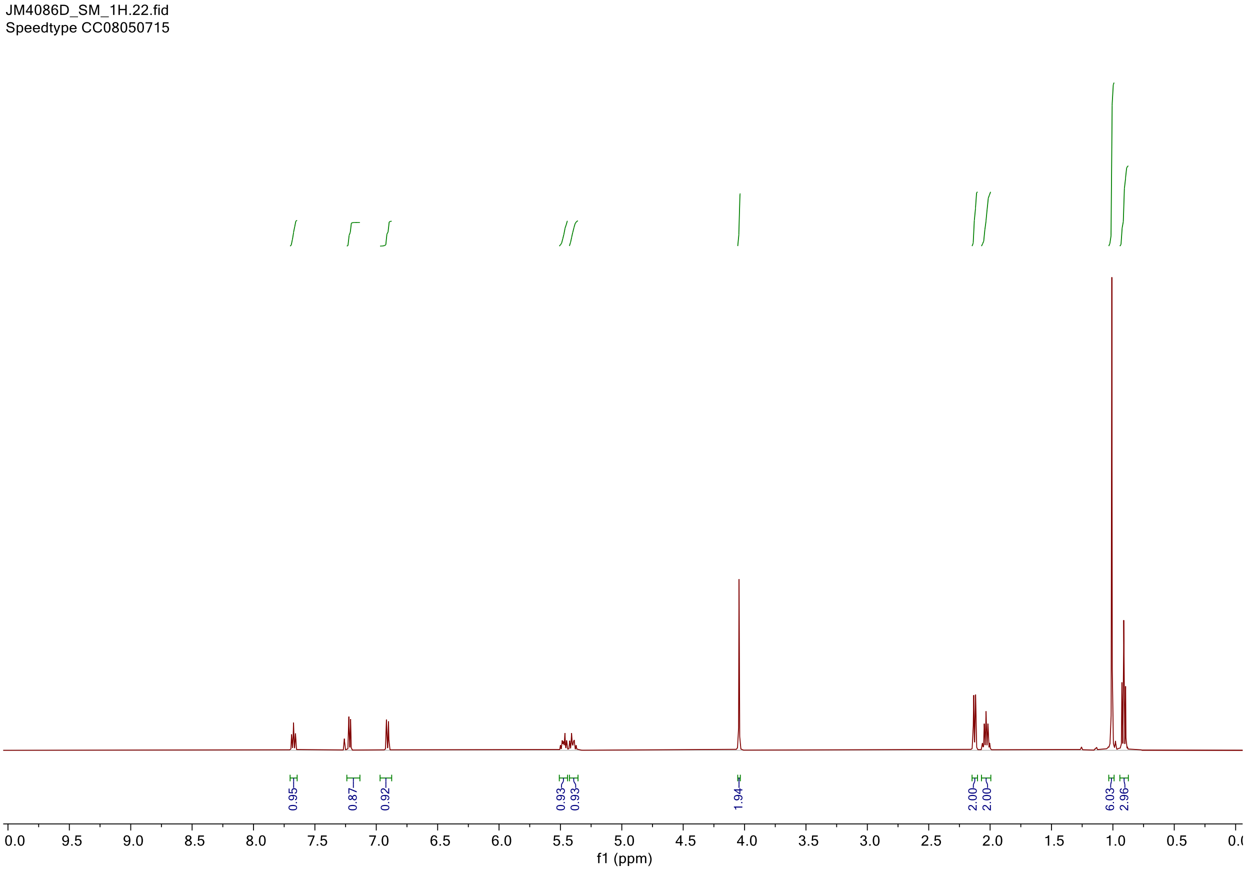
31.43
24.86
20.69
14.17
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 1p



^{1}H NMR



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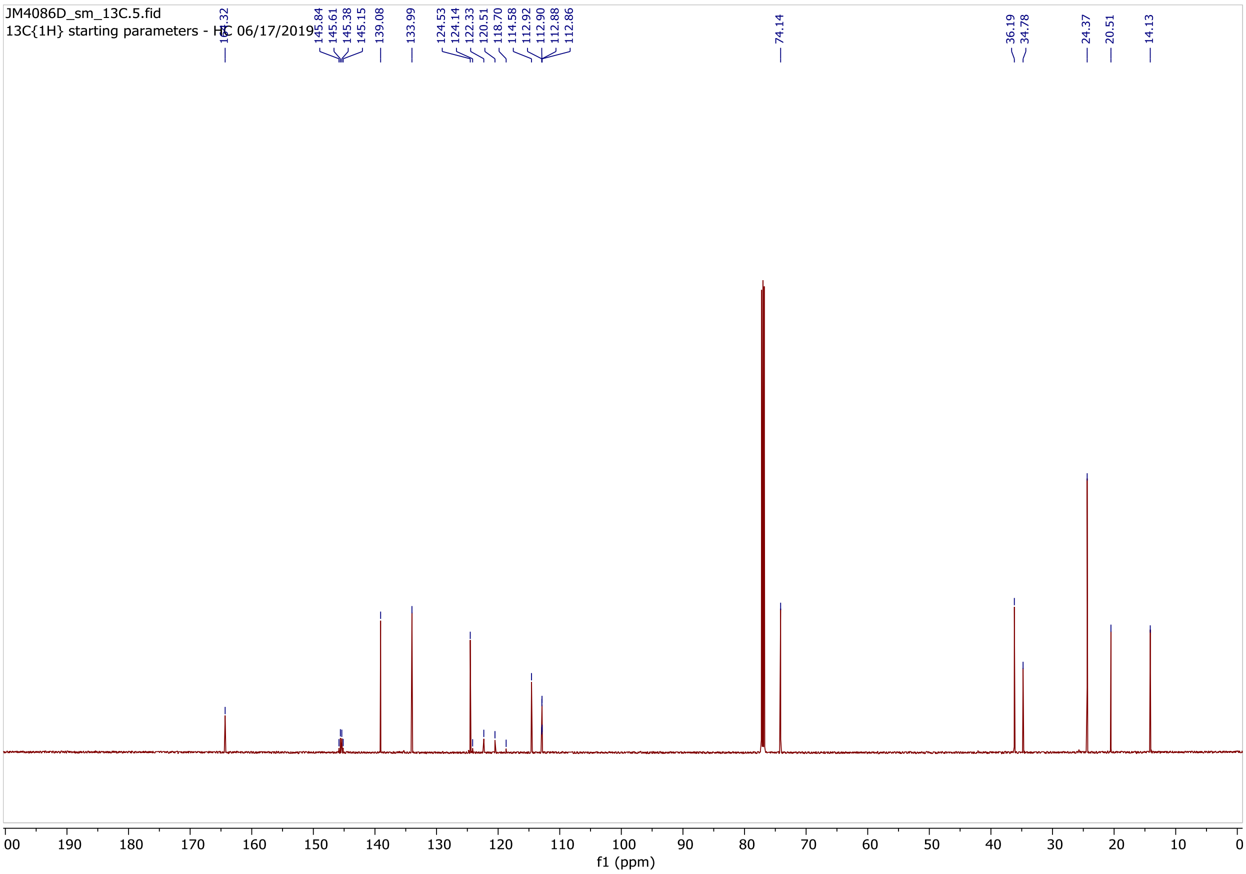
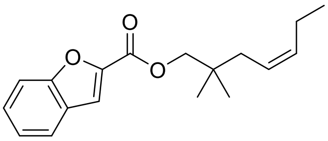
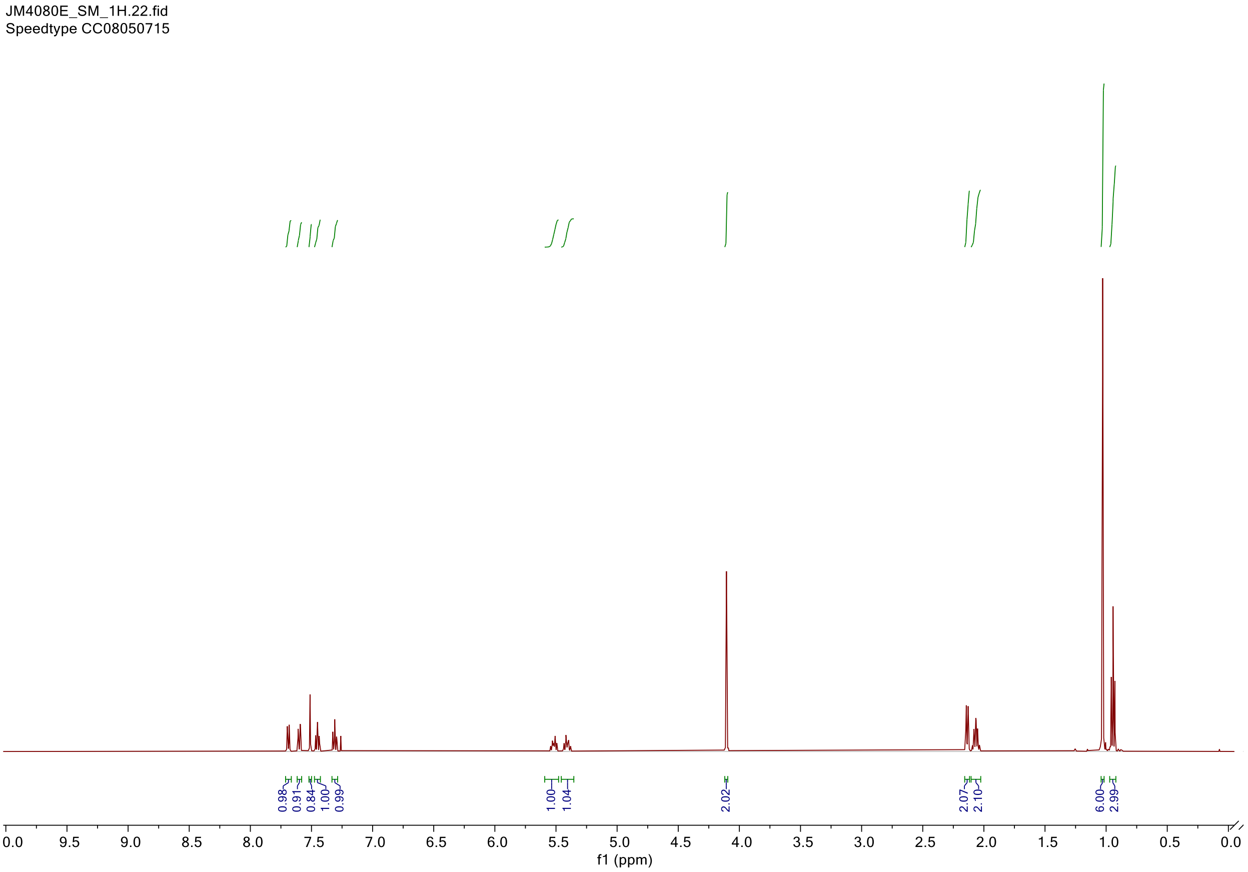
^{13}C NMR



Compound 1q



^{1}H NMR



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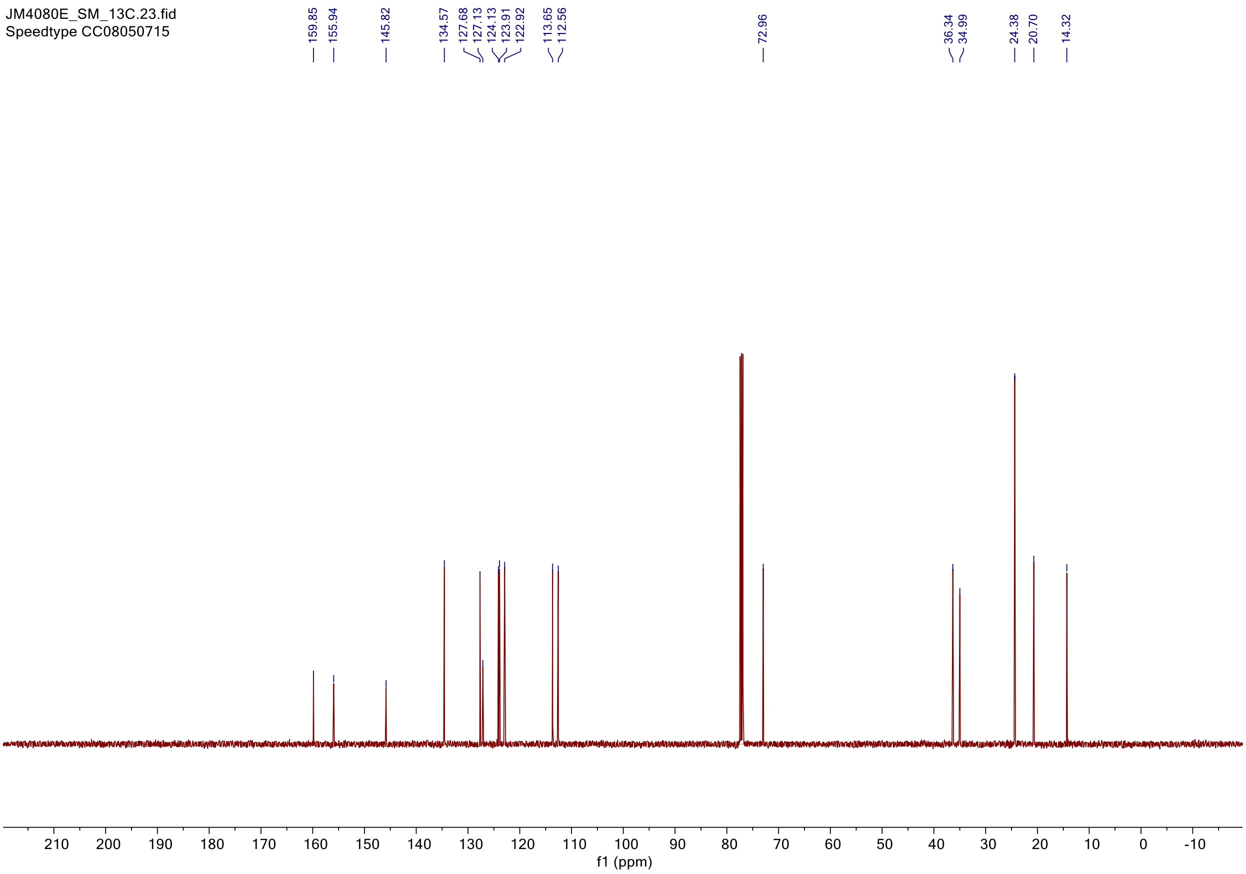
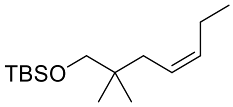
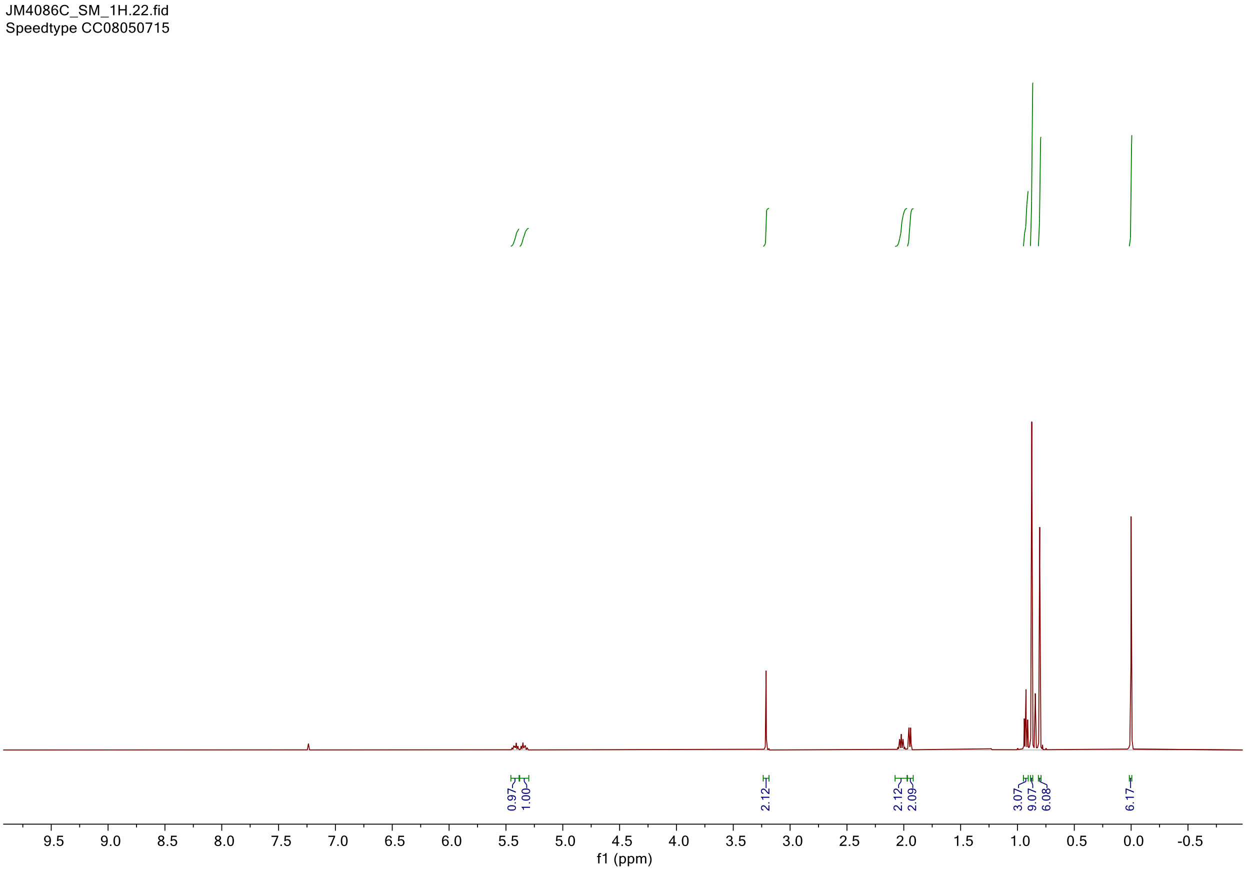
^{13}C NMR



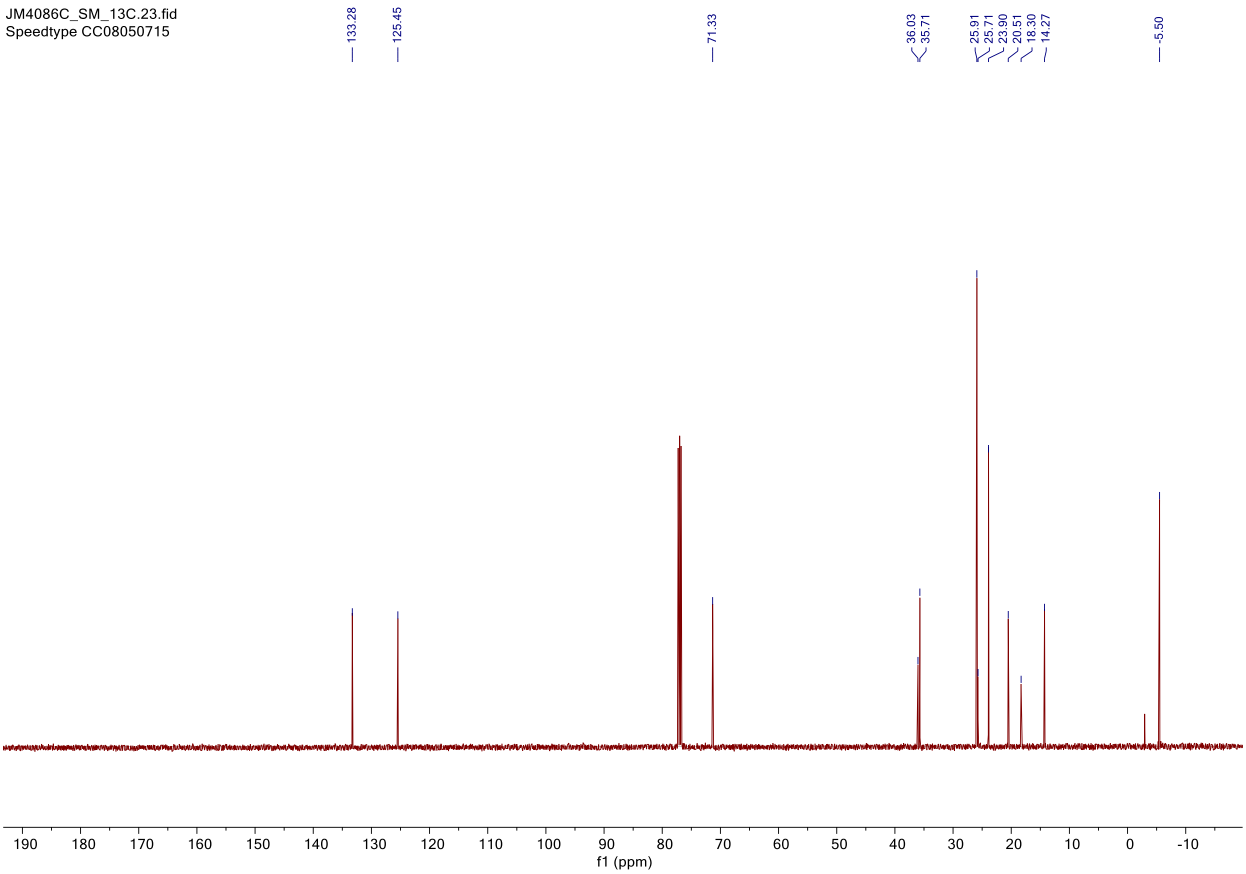
Compound 1s



^{1}H NMR



^{13}C NMR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71.33
36.03
35.71
25.91
25.71
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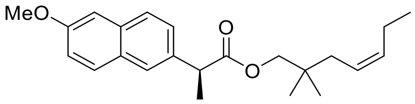
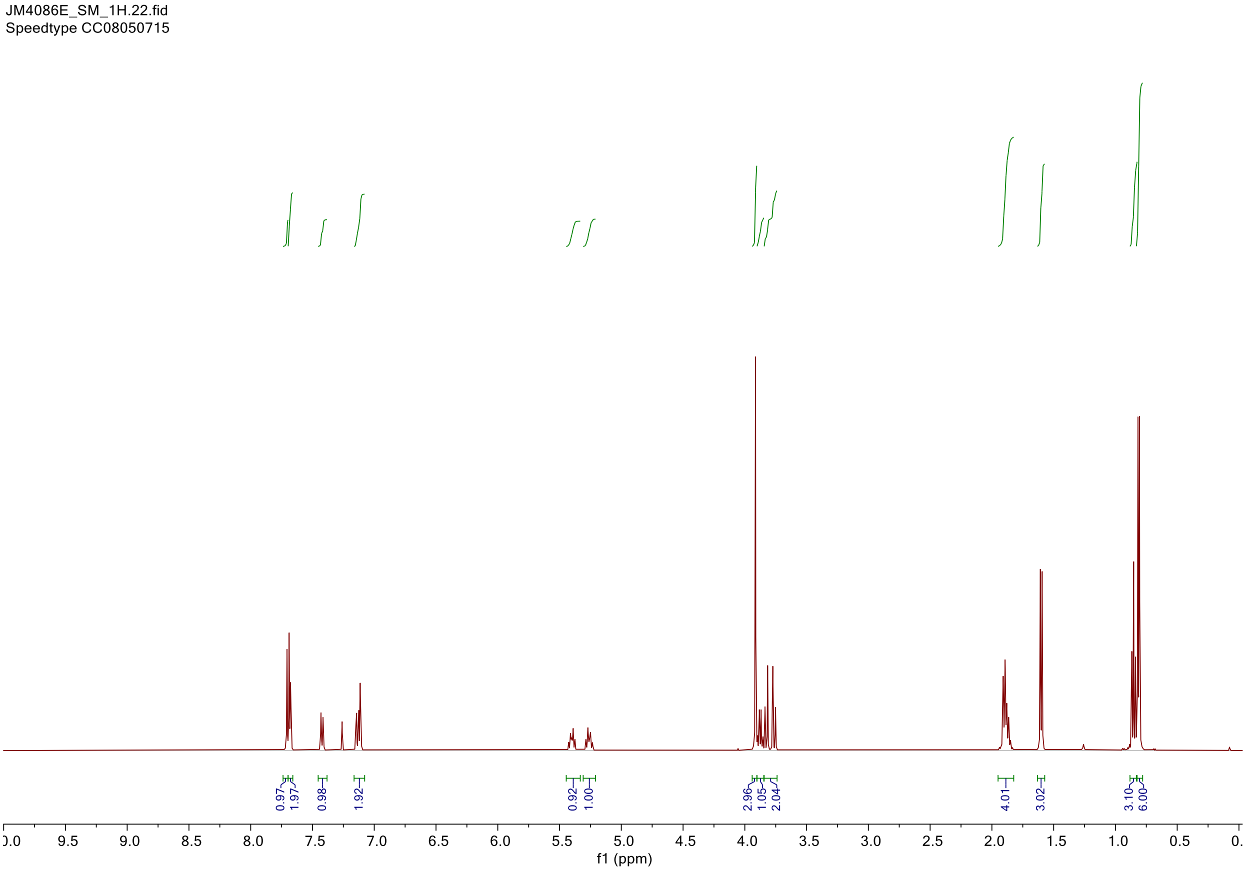
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 1u



^{1}H NMR



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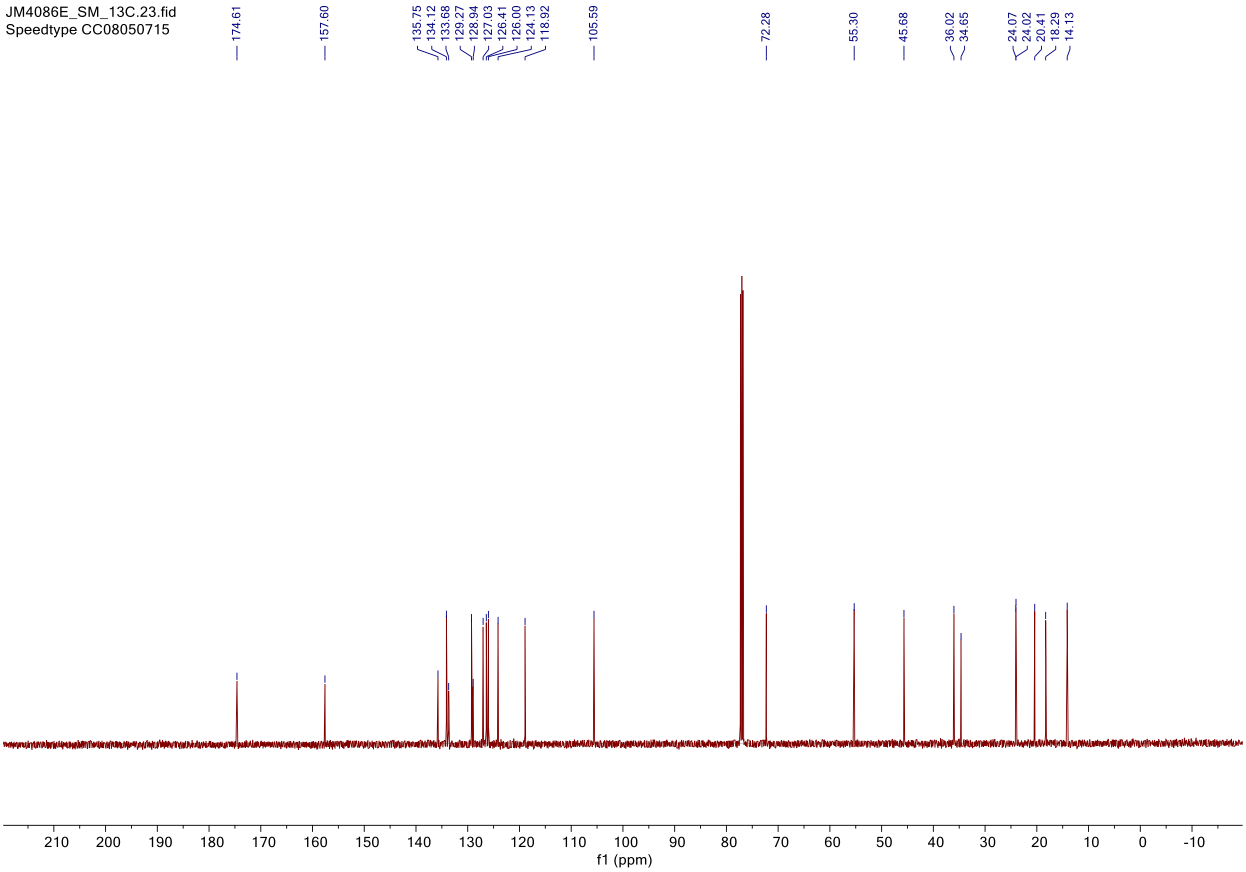
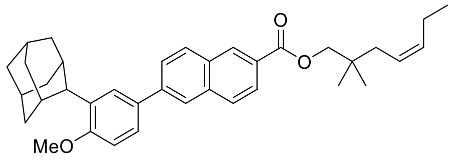
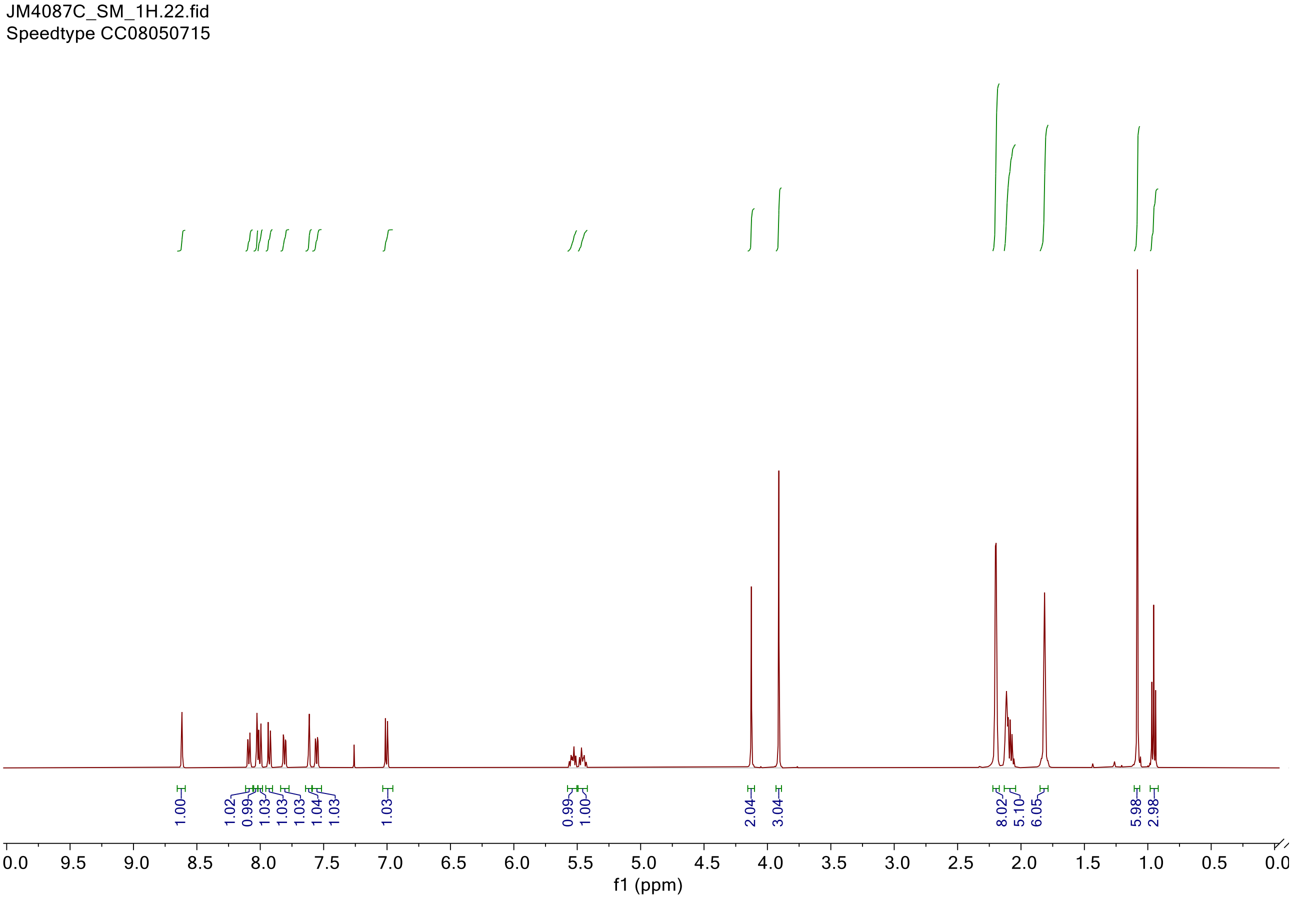
^{13}C NMR



Compound 1v



^{1}H NMR



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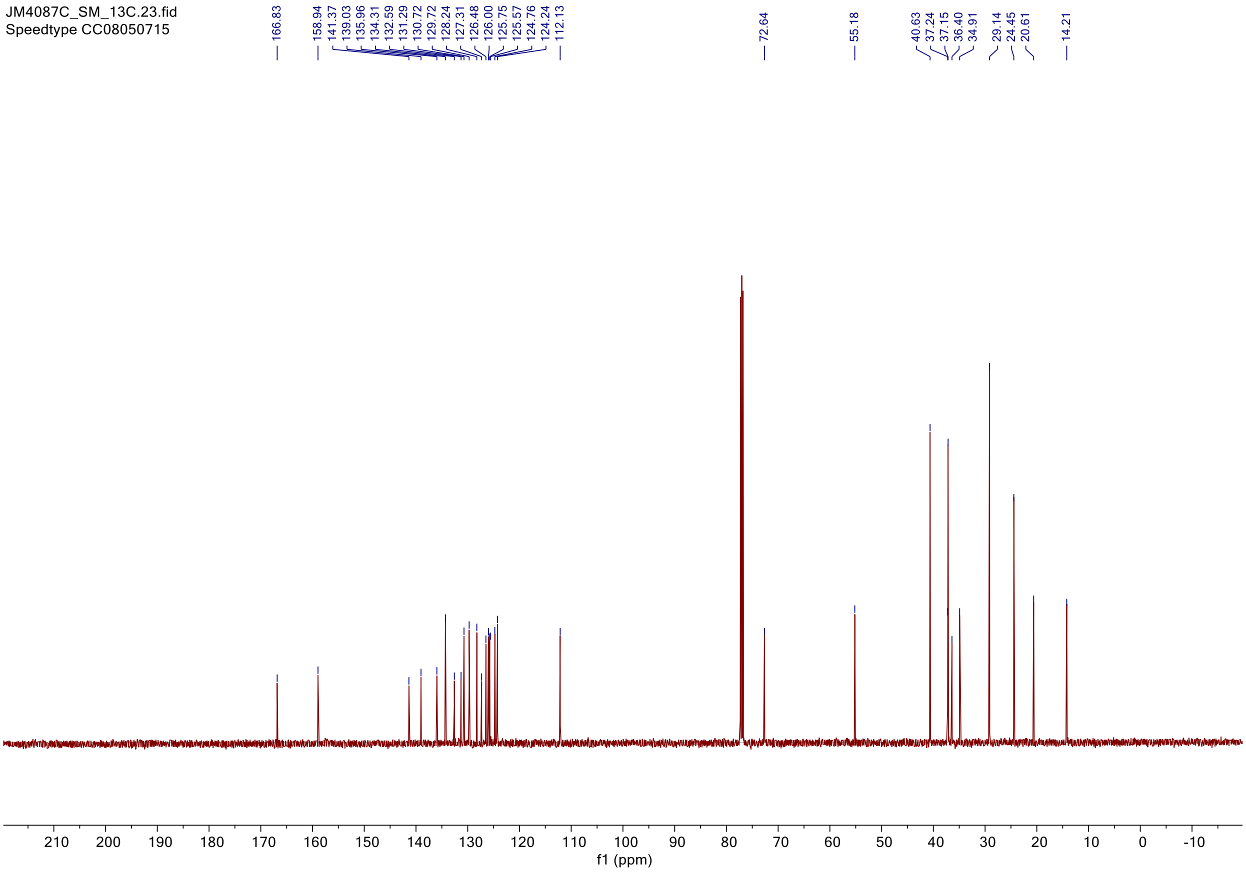
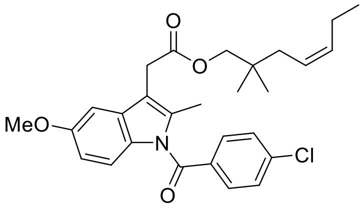
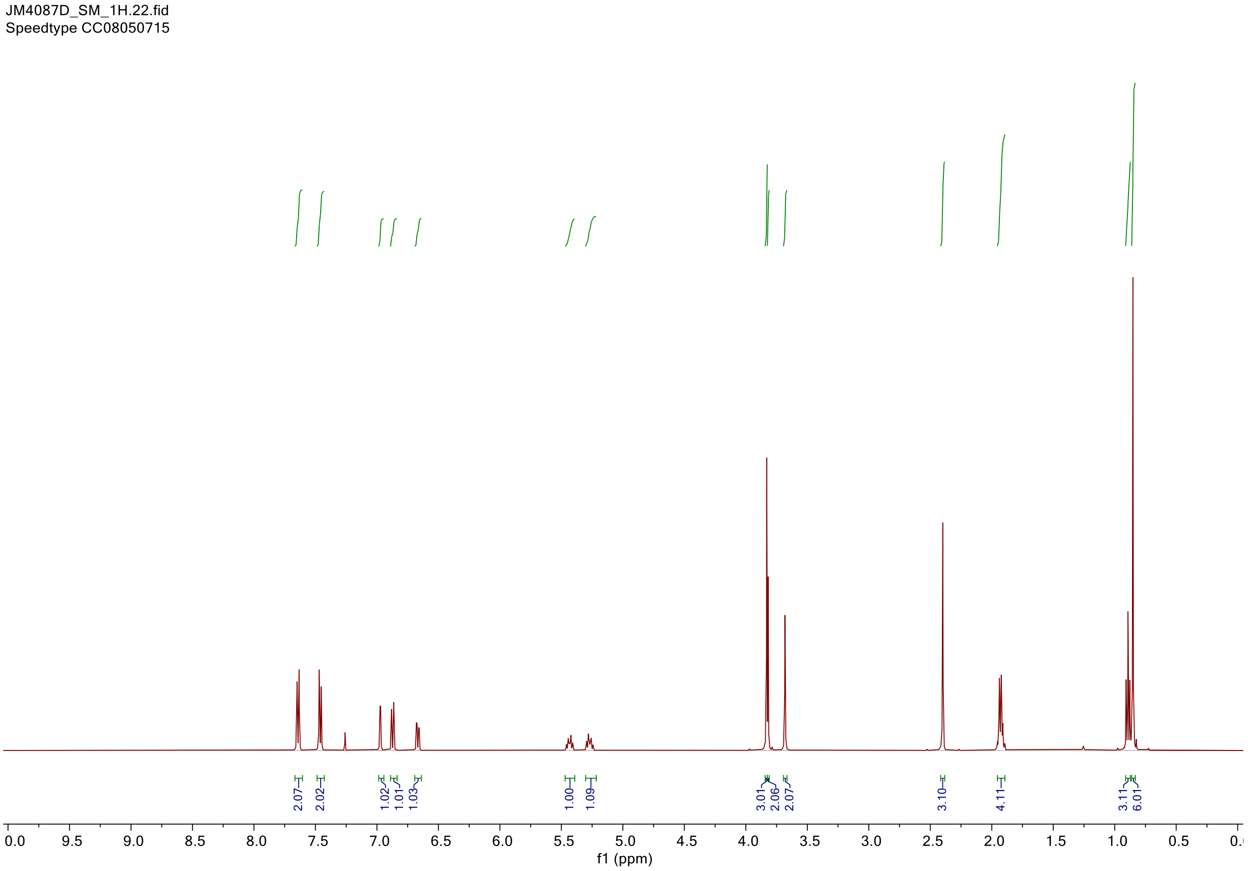
^{13}C NMR



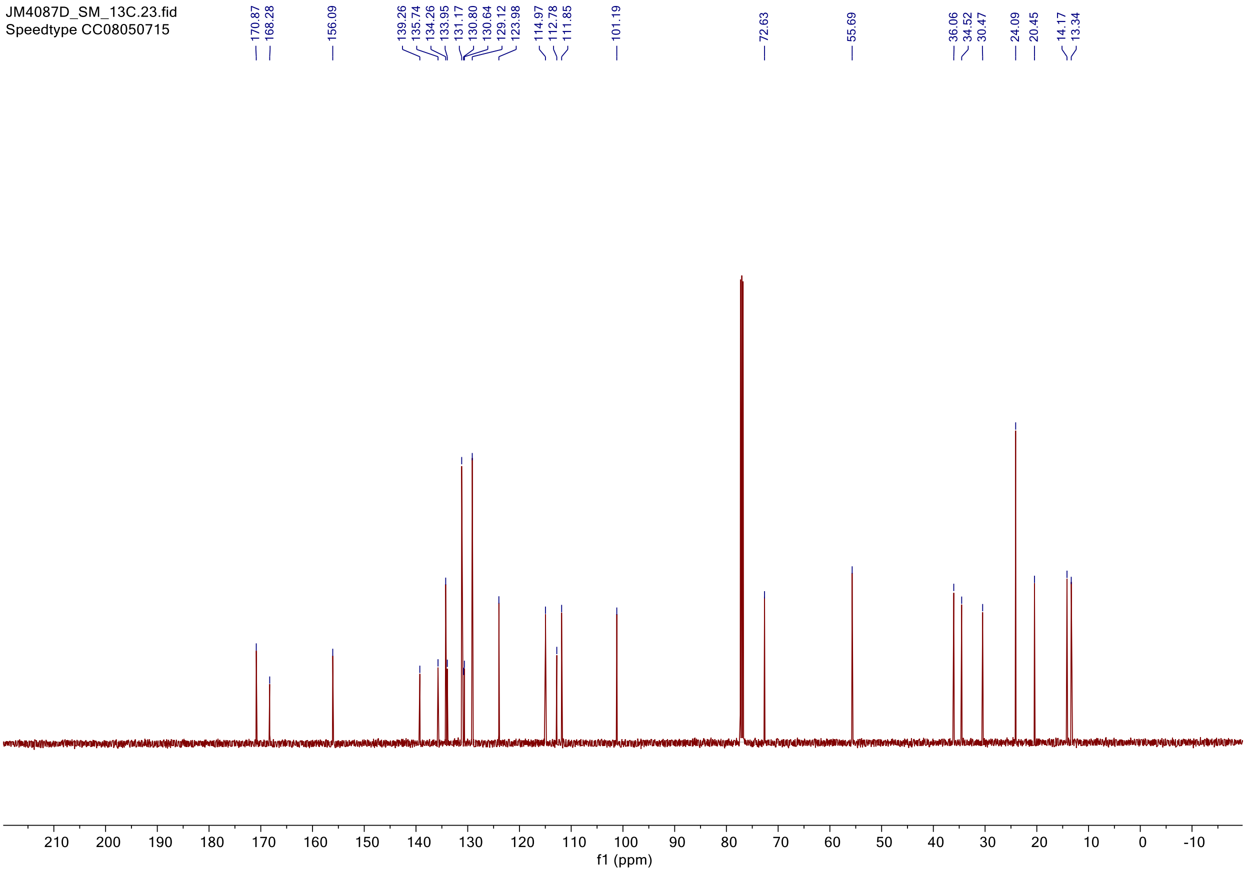
Compound 1w



^{1}H NMR



^{13}C NMR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168.28
156.09
139.26
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134.26
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131.17
130.80
130.64
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123.98
114.97
112.78
111.85
101.19
72.63
55.69
36.06
34.52
30.47
24.09
20.45
14.17
13.34
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200
190
180
170
160
150
140
130
120
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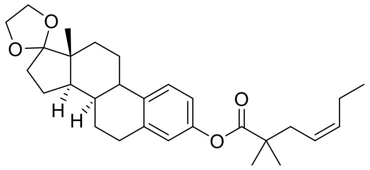
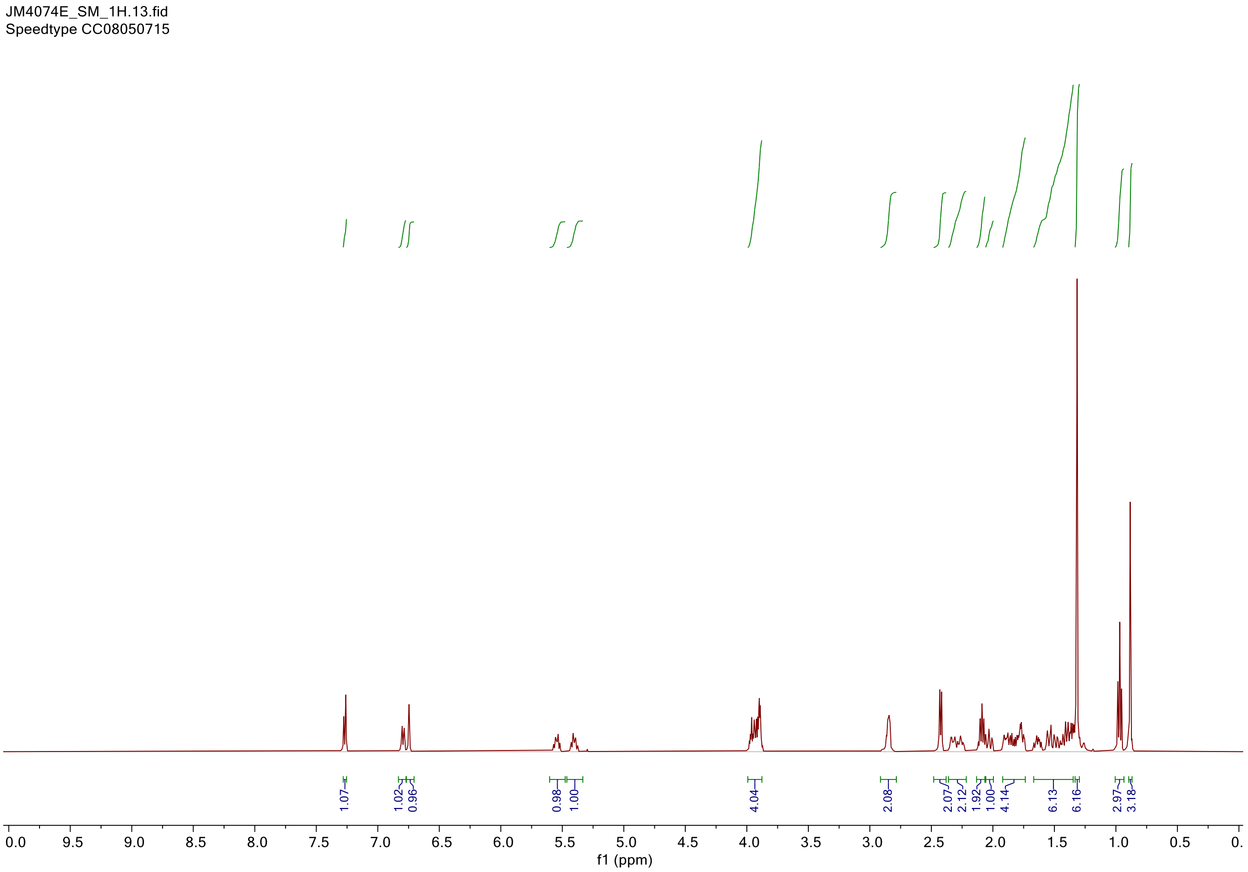
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

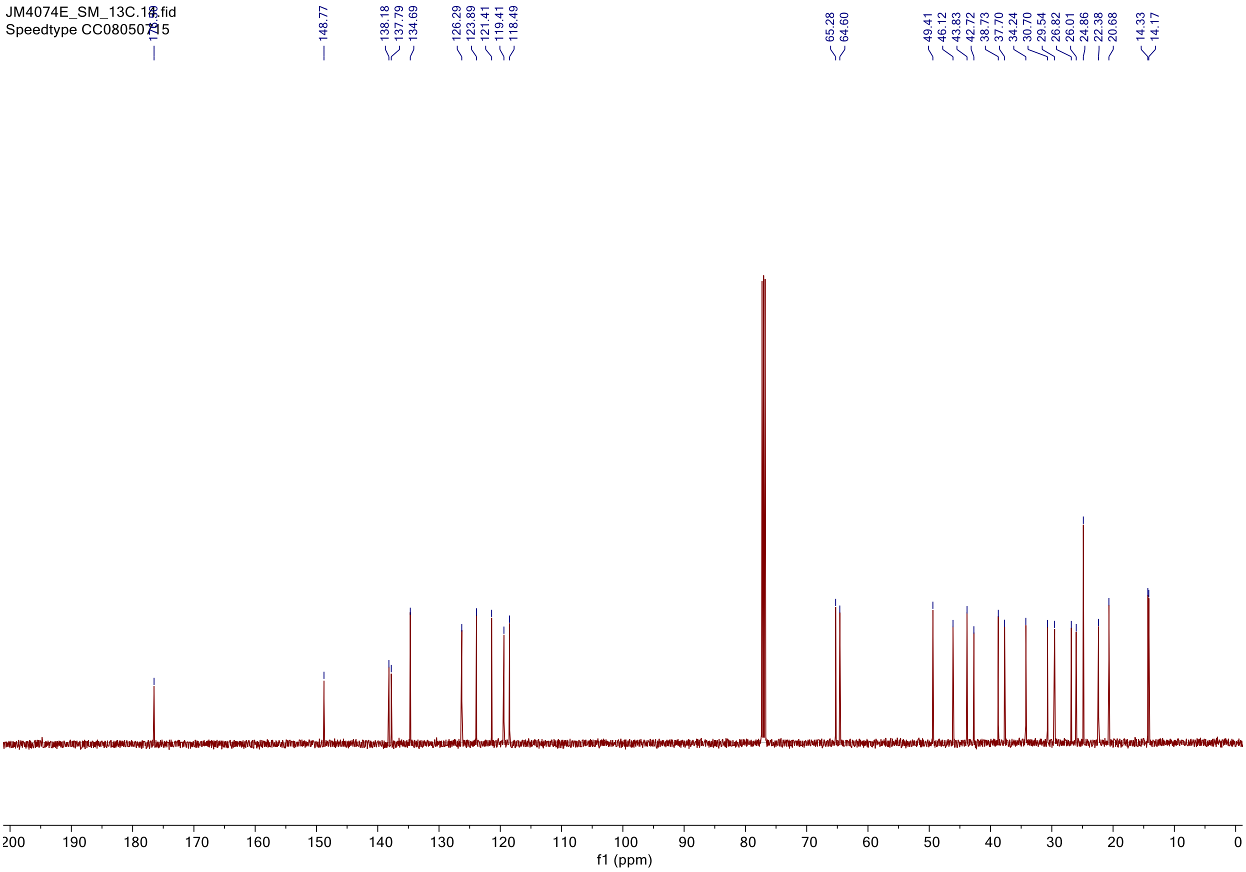
Compound 1x



^{1}H NMR



^{13}C NMR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137.79
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65.28
64.60
49.41
46.12
43.83
42.72
38.73
37.70
34.24
30.70
29.54
26.82
26.01
24.86
22.38
20.68
14.33
14.17
200
190
180
170
160
150
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130
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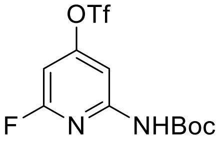
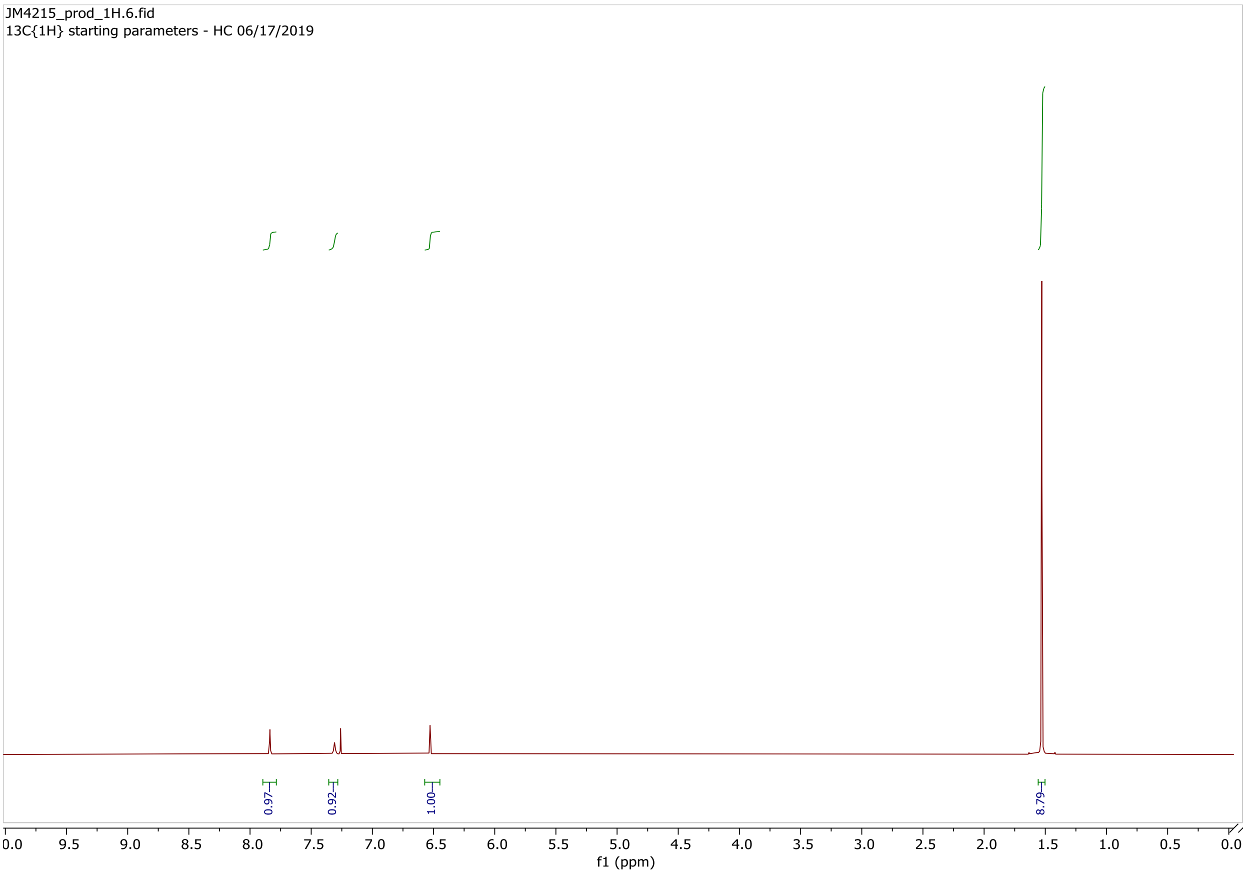
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Compound 2g-NHBoc



^{1}H NMR



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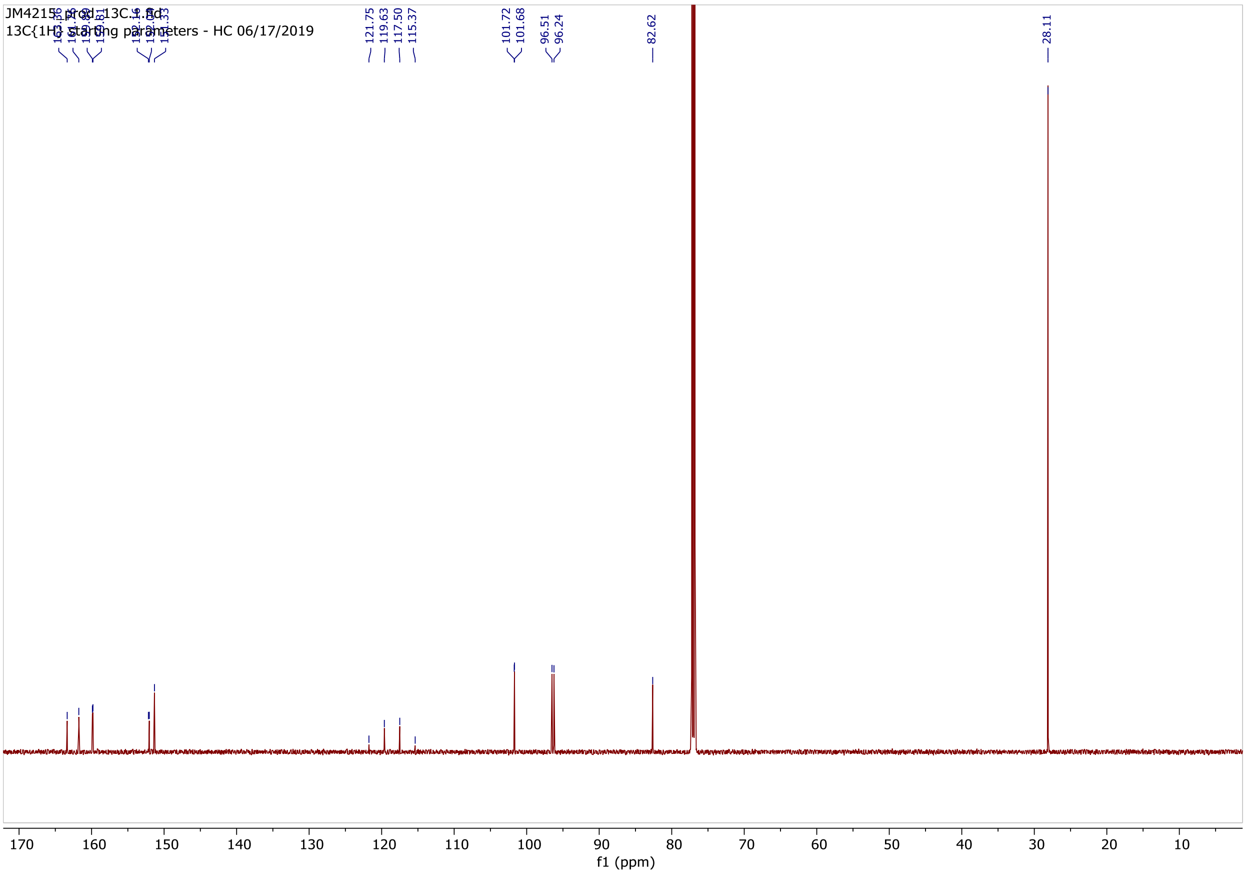
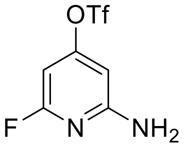
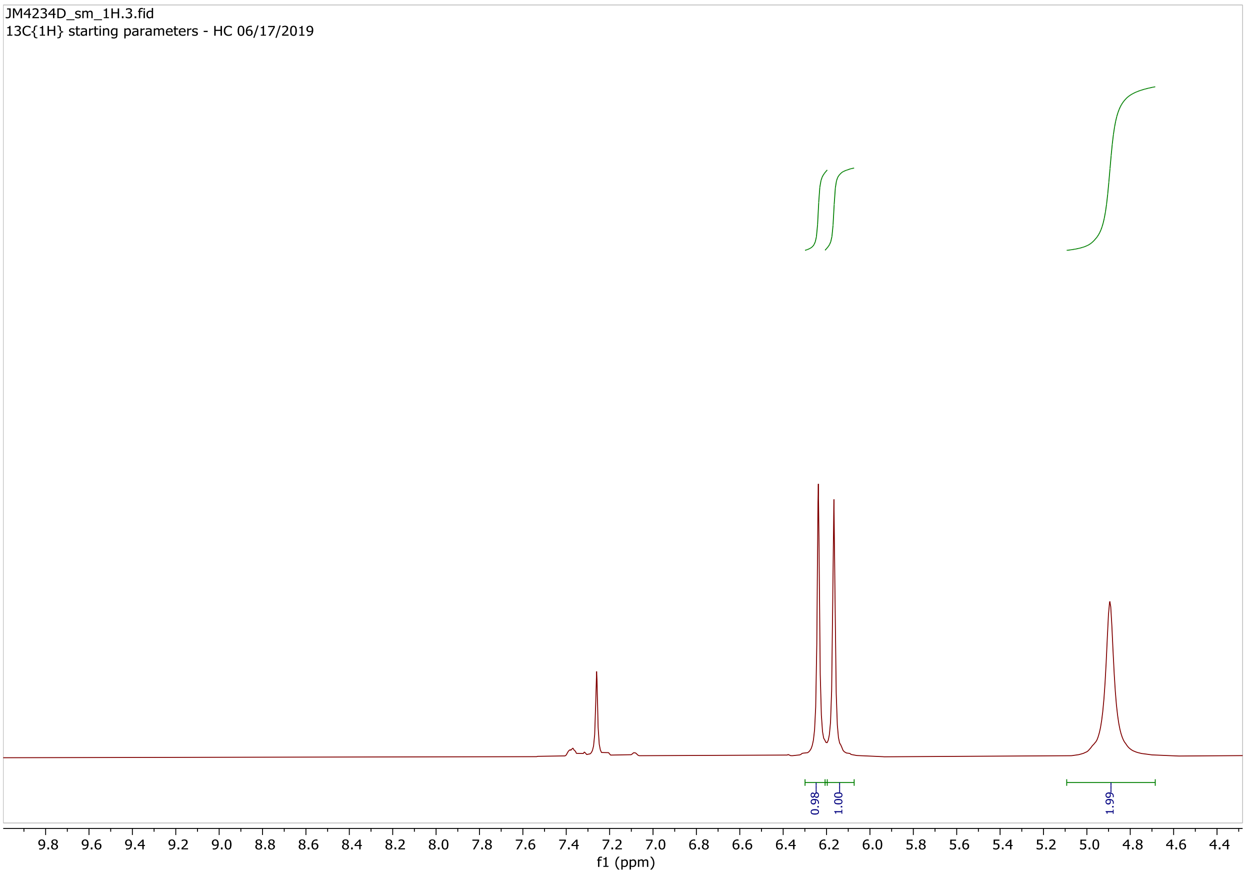
^{13}C NMR



Compound 2g



^{1}H NMR



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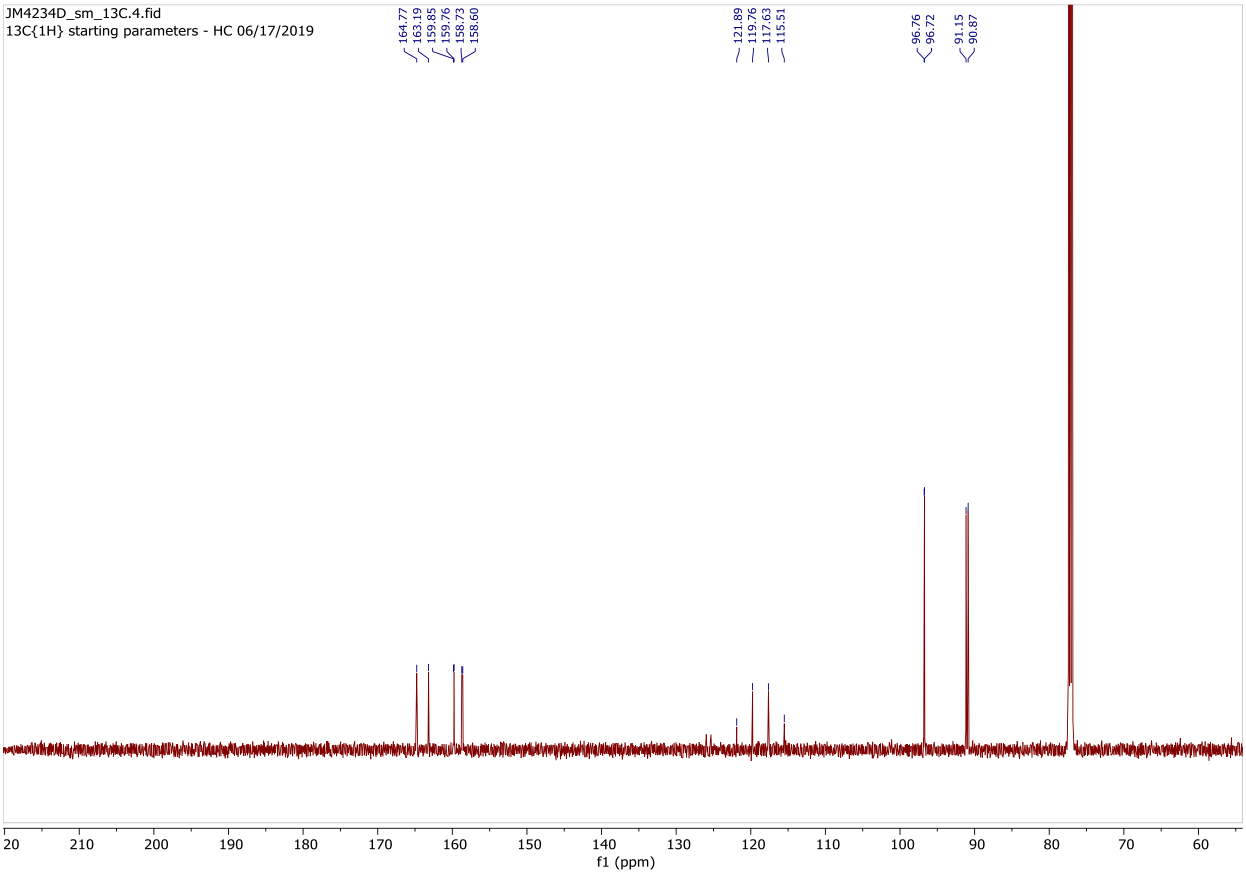
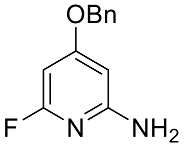
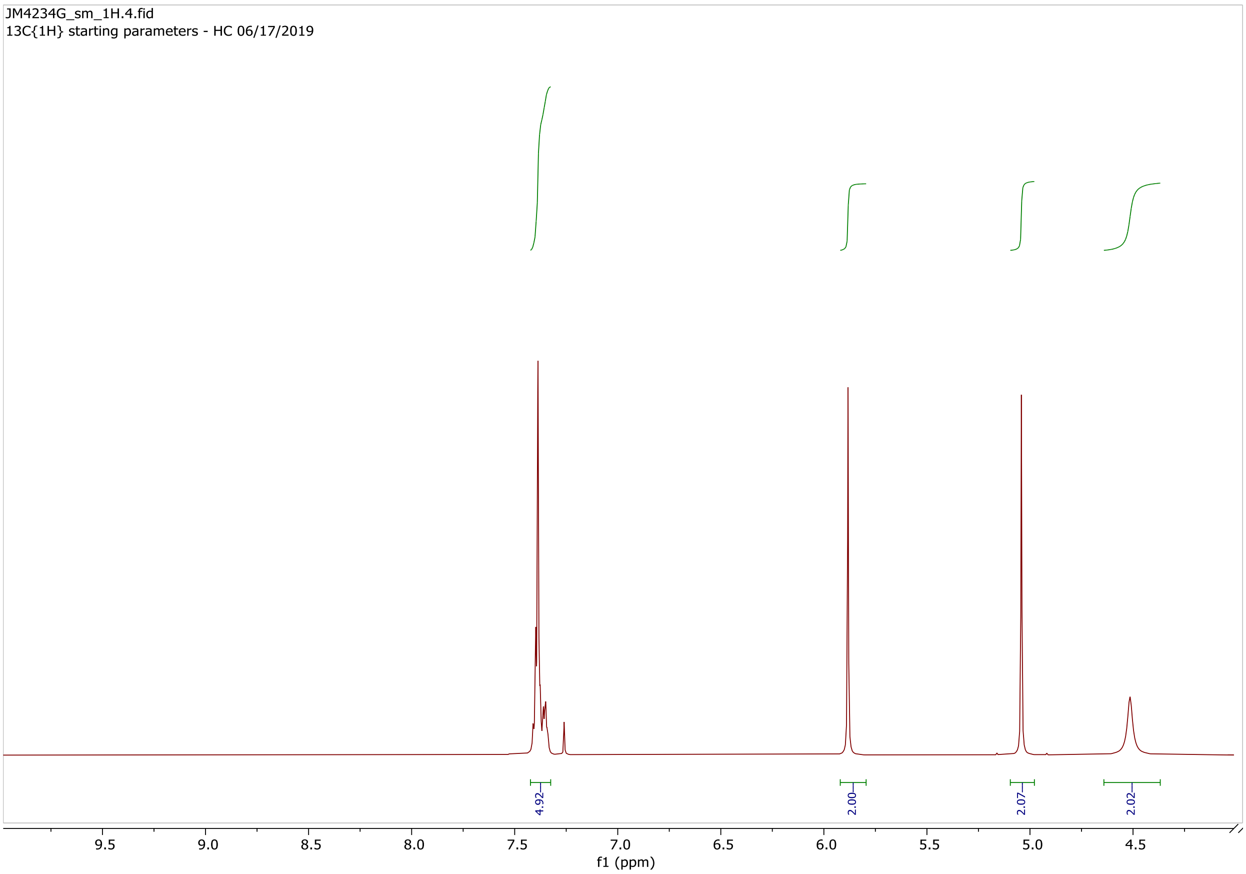
^{13}C NMR



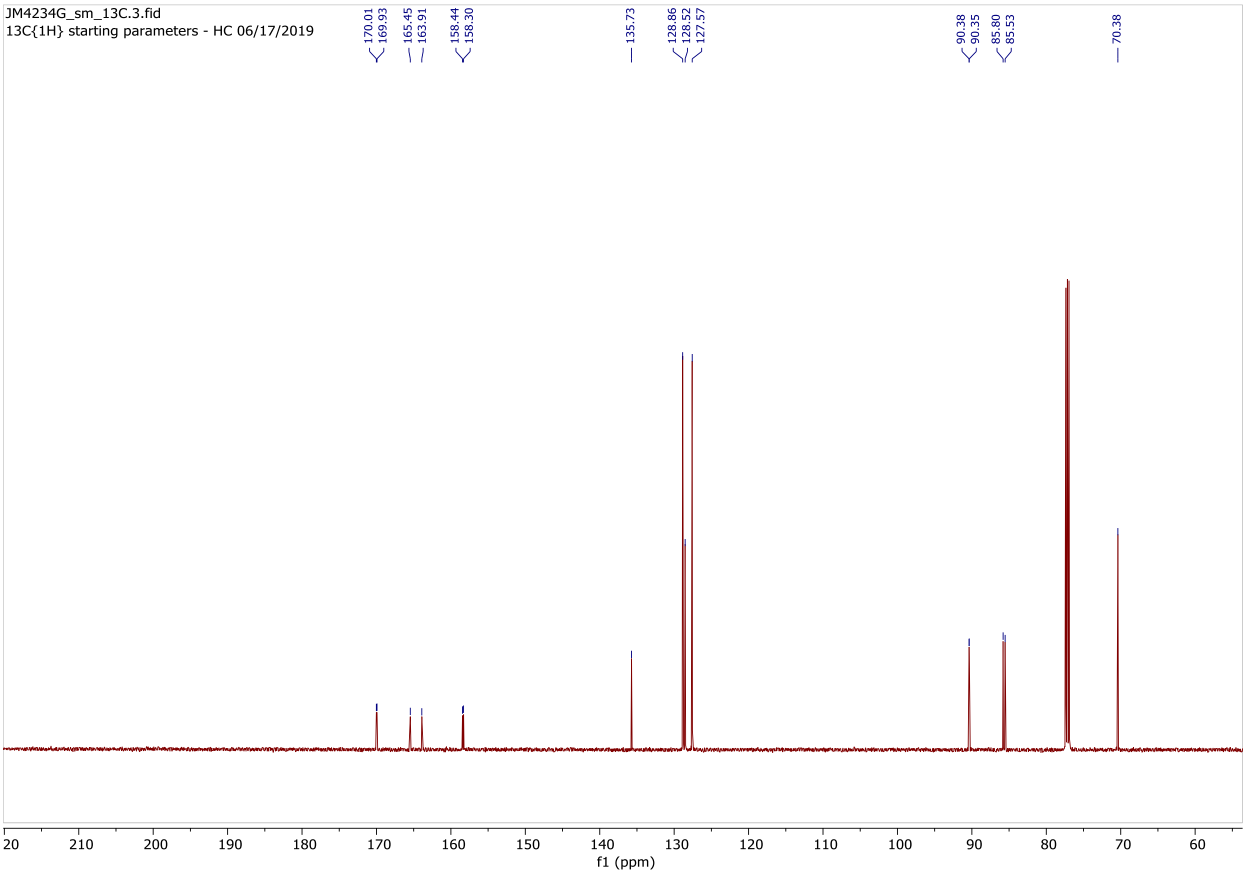
Compound 2i



^{1}H NMR



^{13}C NMR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169.93
165.45
163.91
158.44
158.30
135.73
128.86
128.52
127.57
90.38
90.35
85.80
85.53
70.38
20
210
200
190
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170
160
150
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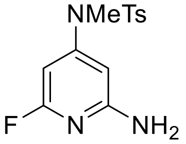
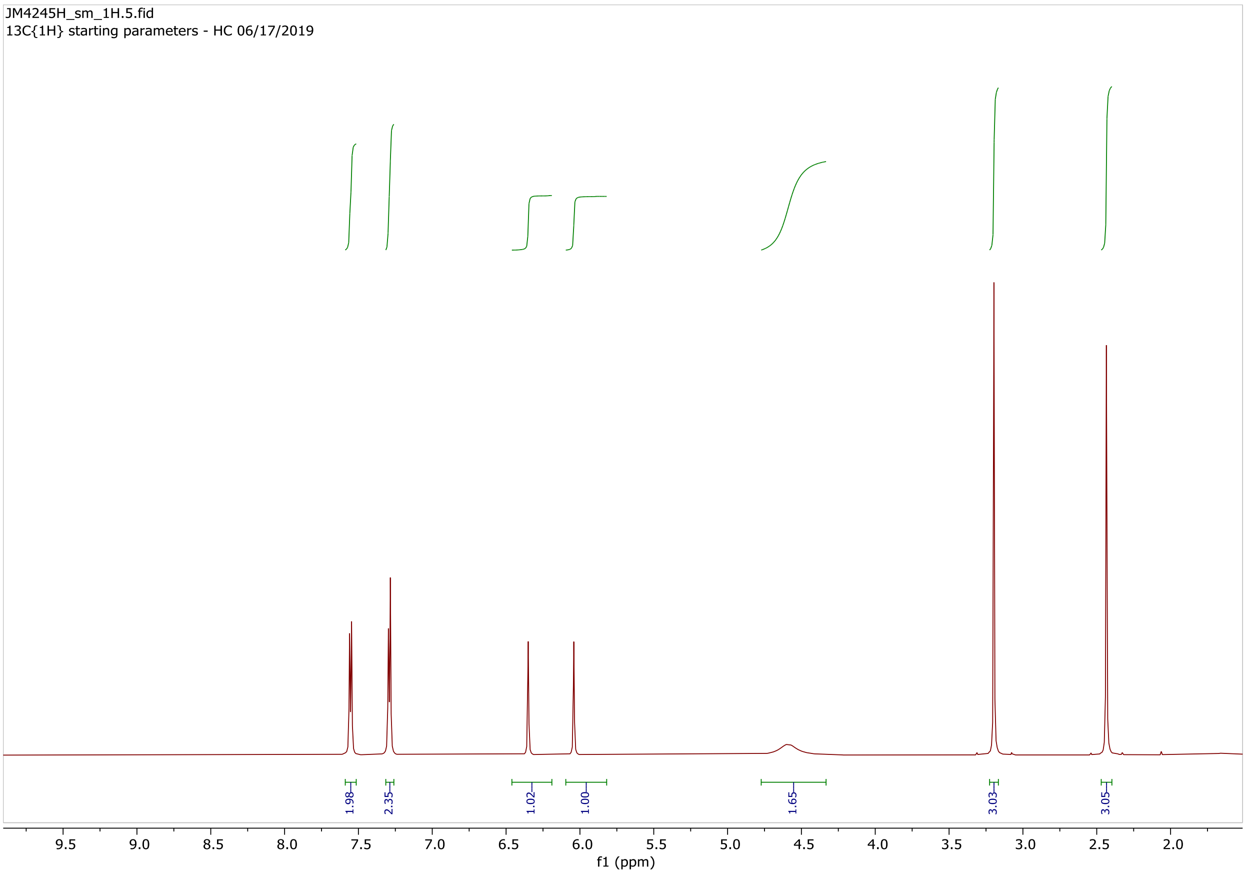
130
120
110
100
90
80
70
60
f1 (ppm)

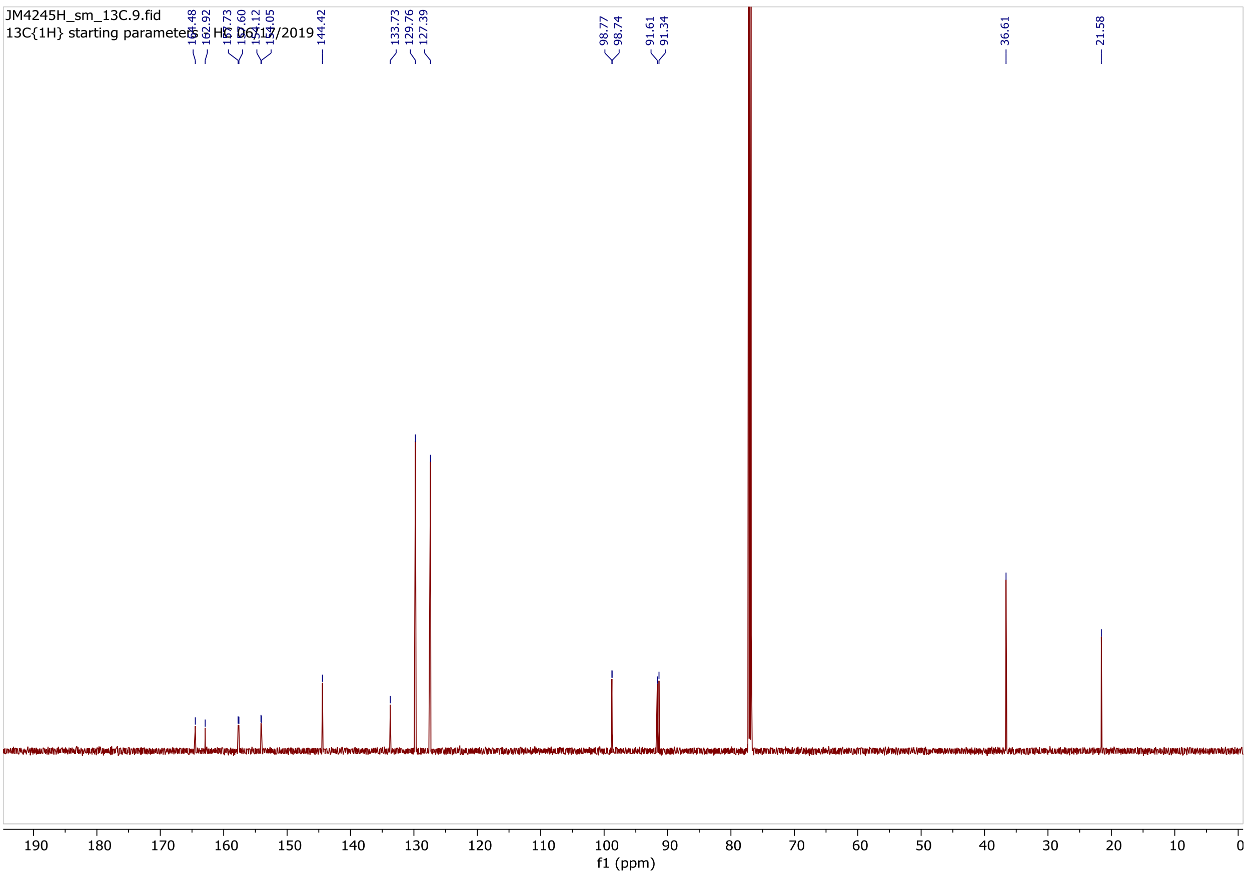
Compound 2j



^{1}H NMR



^{13}C NMR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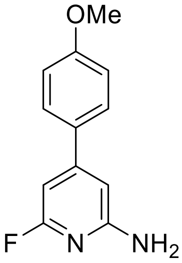
127.39
98.77
98.74
91.61
91.34
36.61
21.58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

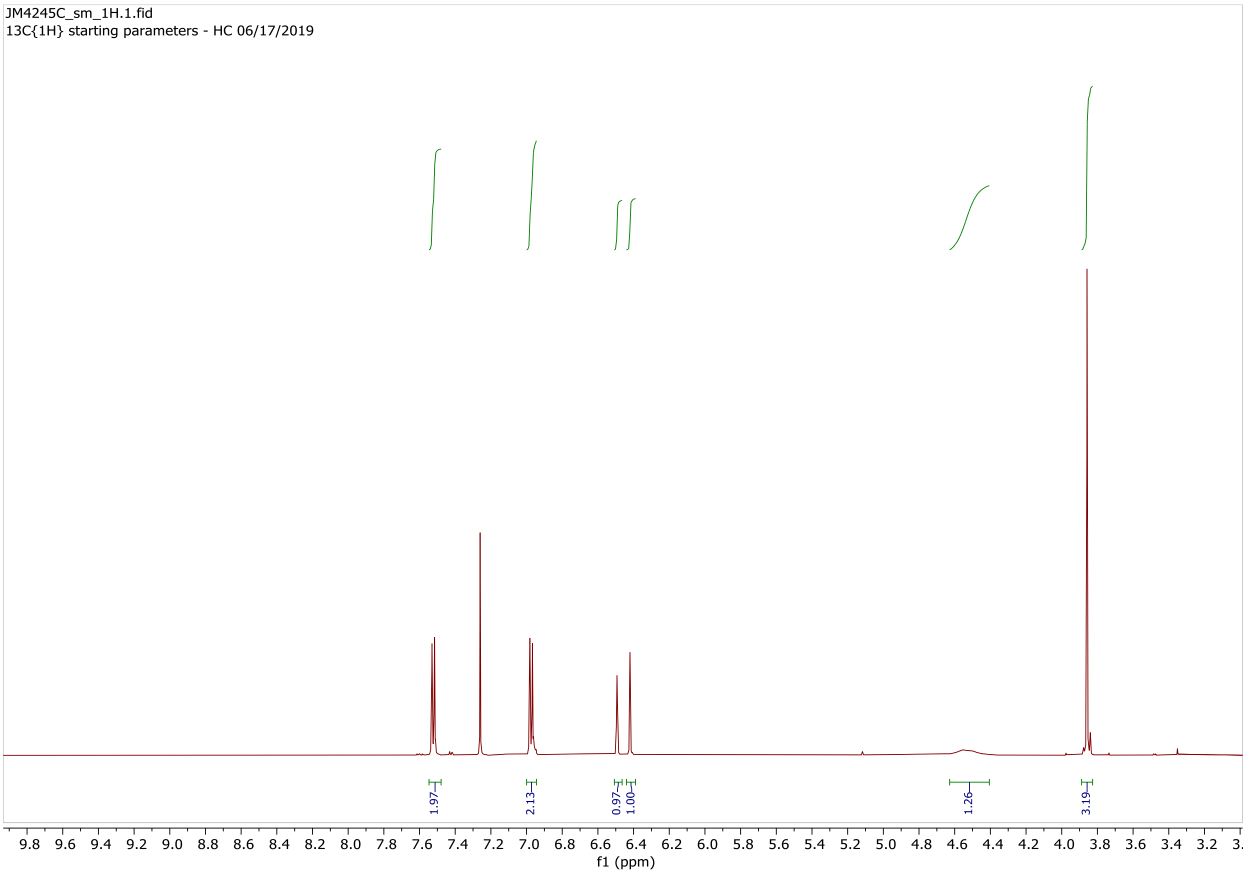
[*Return to table of contents*]

Compound 2o



2o

^{1}H NMR



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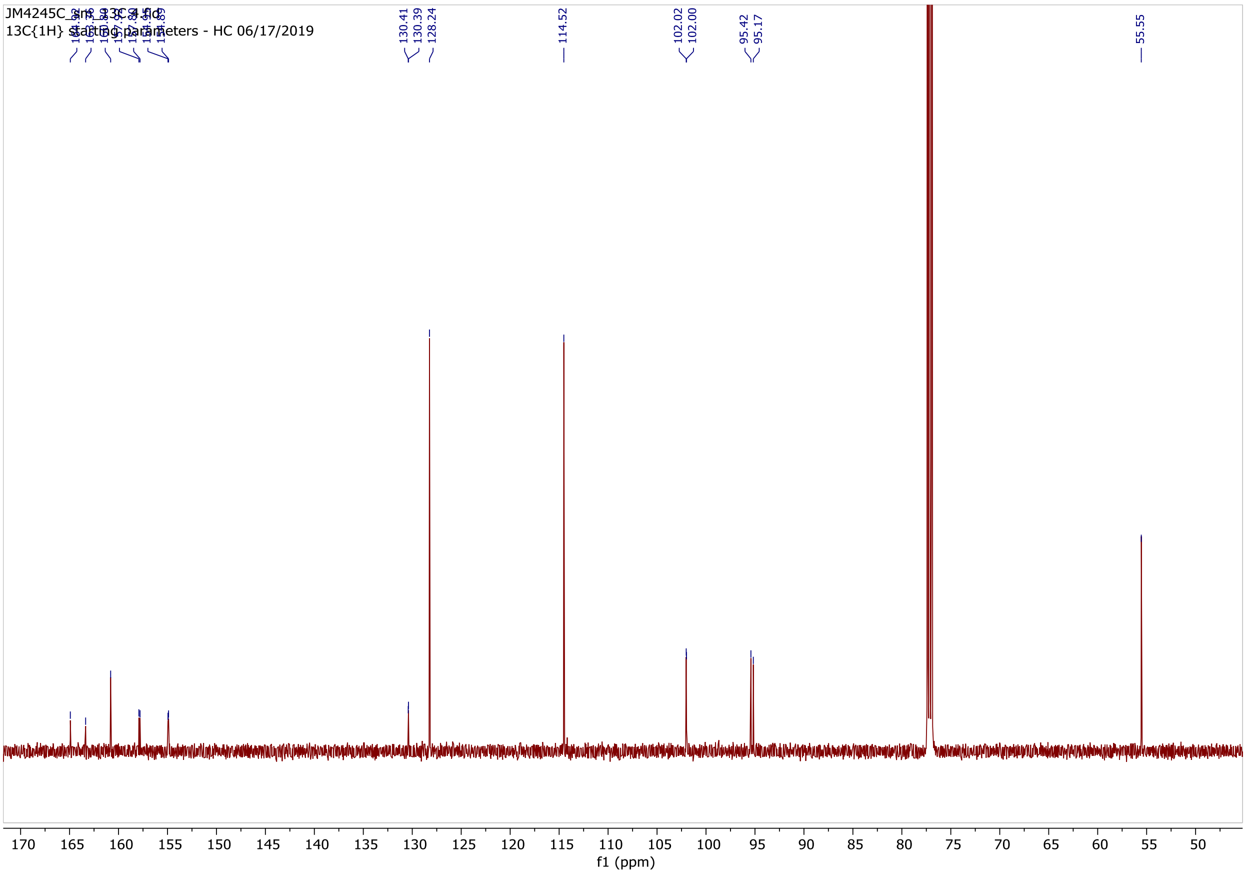
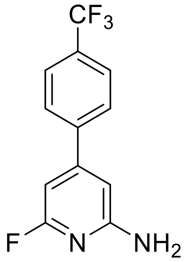
^{13}C NMR

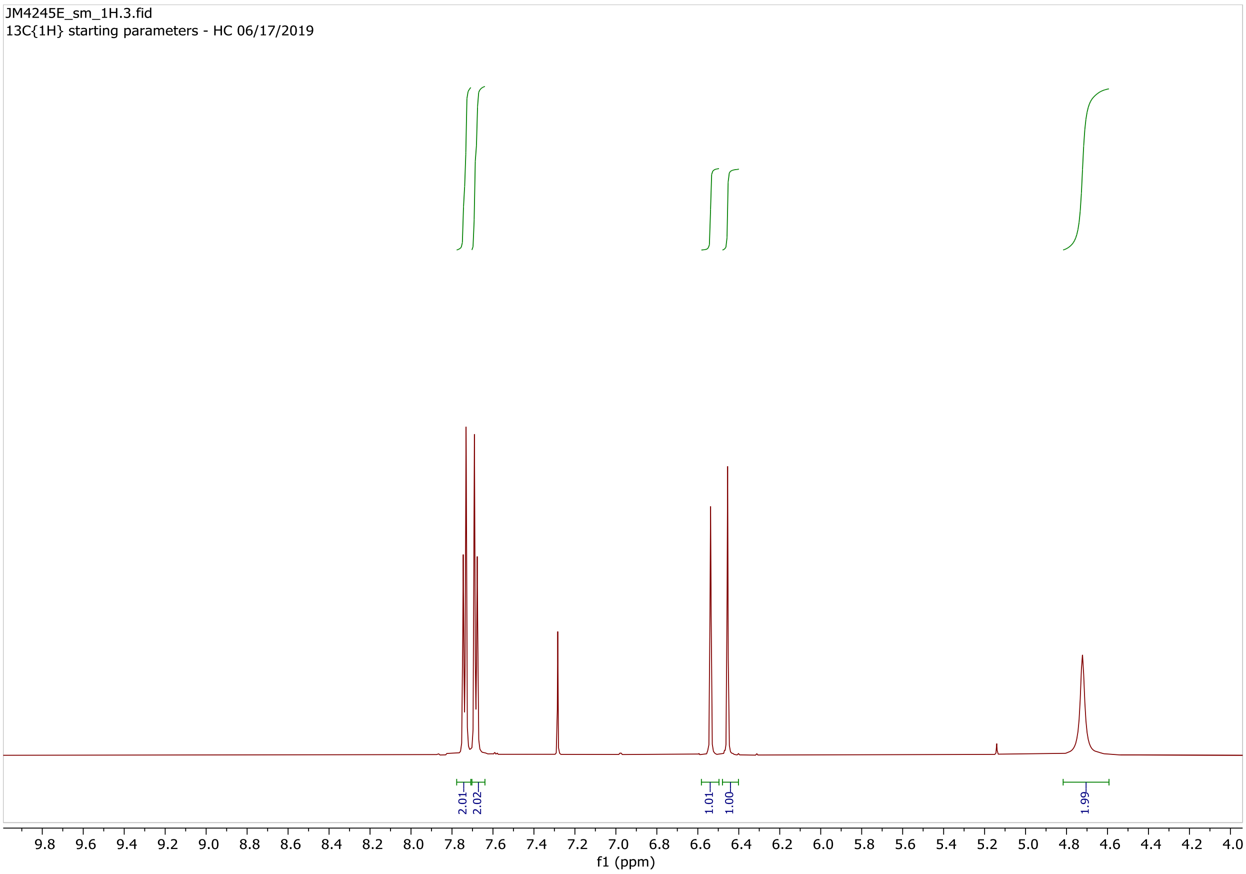


Compound 2p

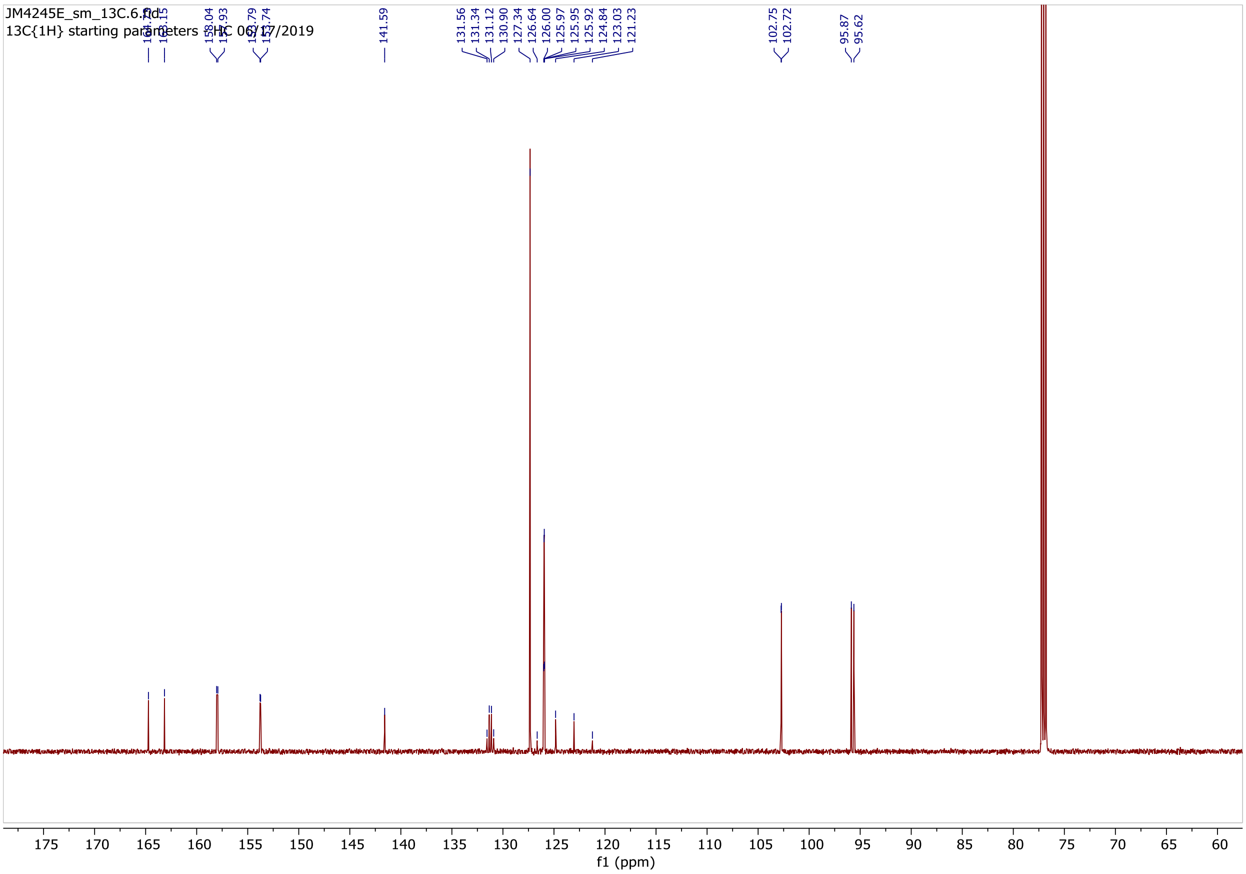


2p

^{1}H NMR

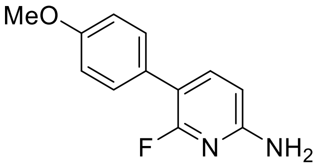


^{13}C NMR


JM4245E_sm_13C.6.fid
13C{1H} starting parameters - HC 06/17/2019
164.7
163.15
158.04
157.93
153.79
153.74
141.59
131.56
131.34
131.12
130.90
127.34
126.64
126.00
125.97
125.95
125.92
124.84
123.03
121.23
102.75
102.72
95.87
95.62
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
f1 (ppm)

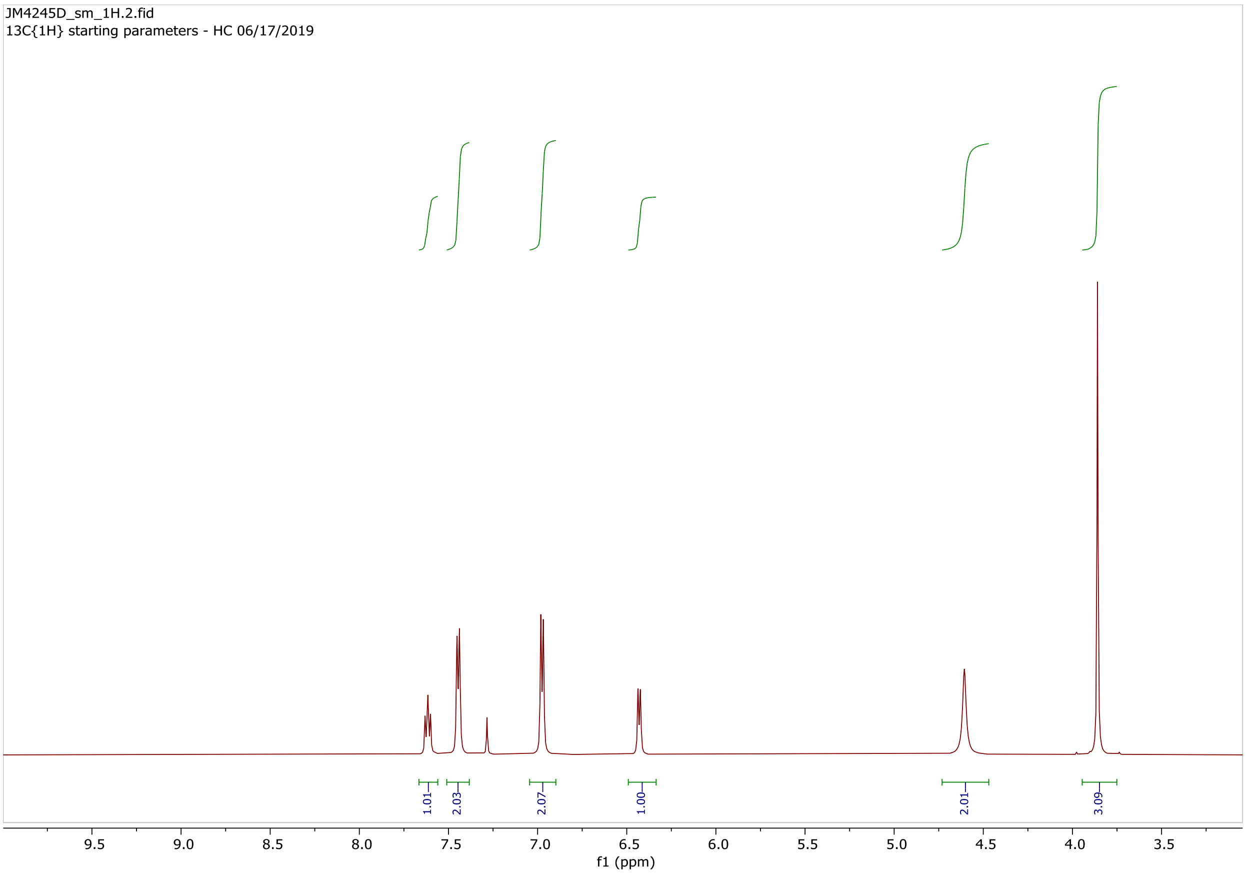
[*Return to table of contents*]

Compound 2r

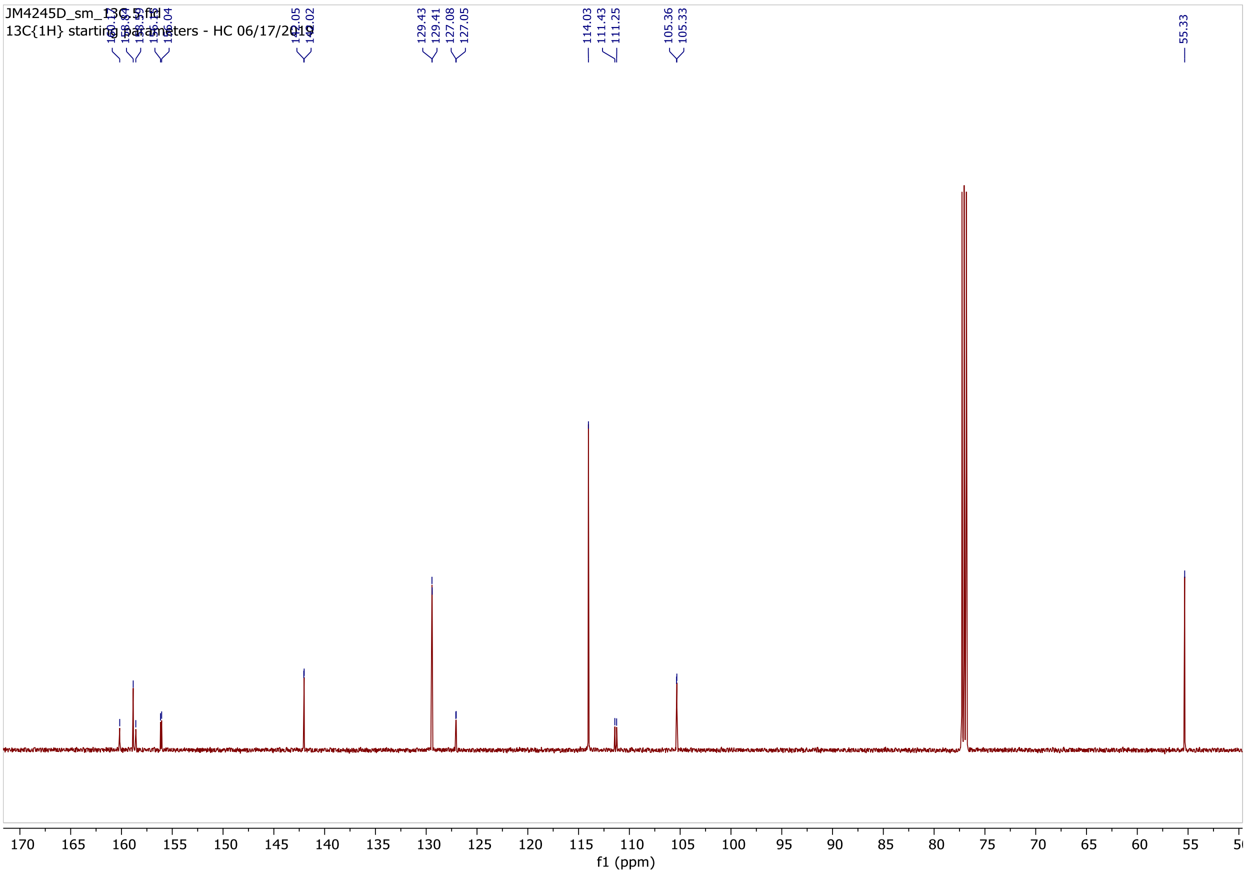


2r

^{1}H NMR



^{13}C NMR


JM4245D_sm_13C.5.fid
13C{1H} starting parameters - HC 06/17/2019
160.17
158.84
158.59
156.15
156.04
142.05
142.02
129.43
129.41
127.08
127.05
114.03
111.43
111.25
105.36
105.33
55.33
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
f1 (ppm)

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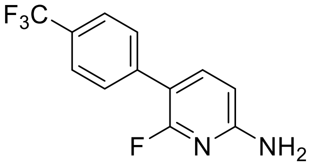
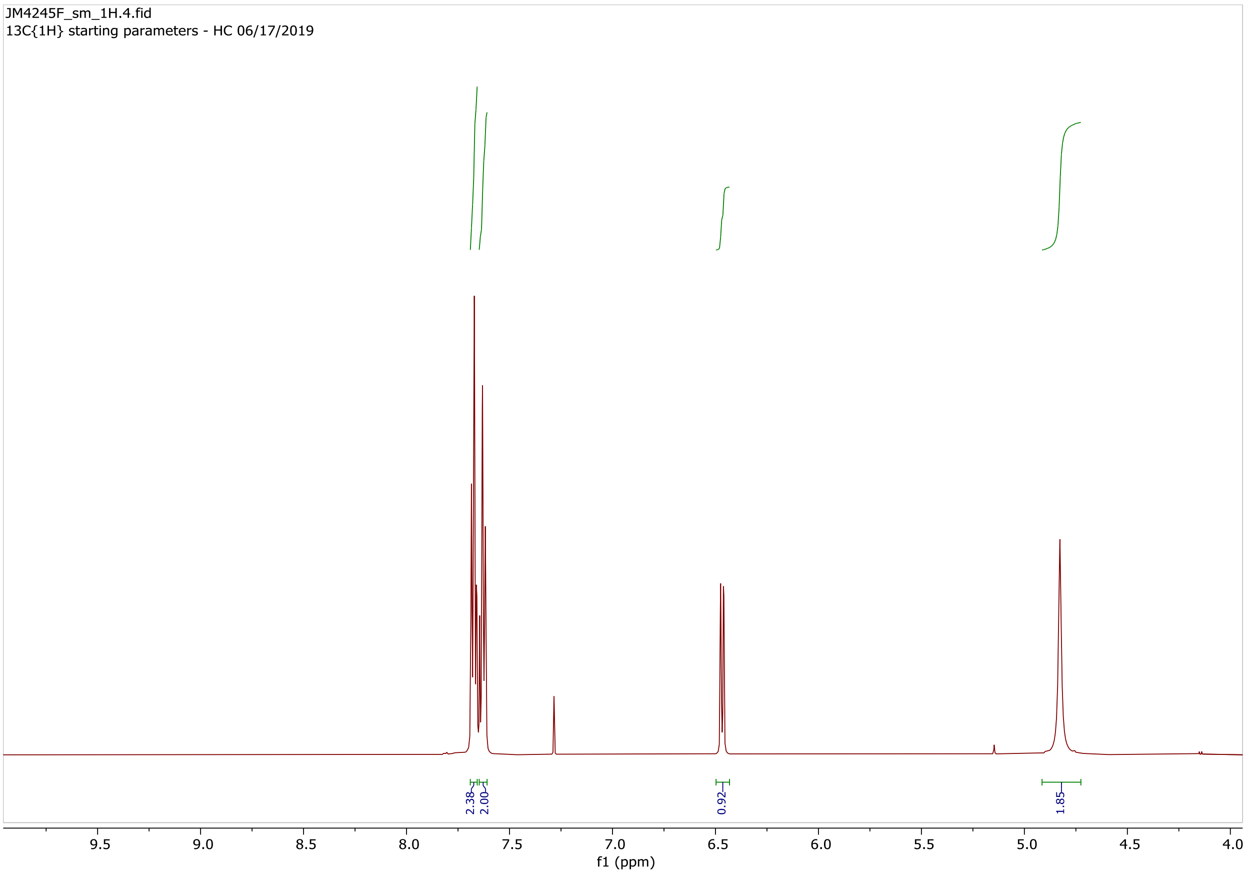
Compound 2s



2s

^{1}H NMR



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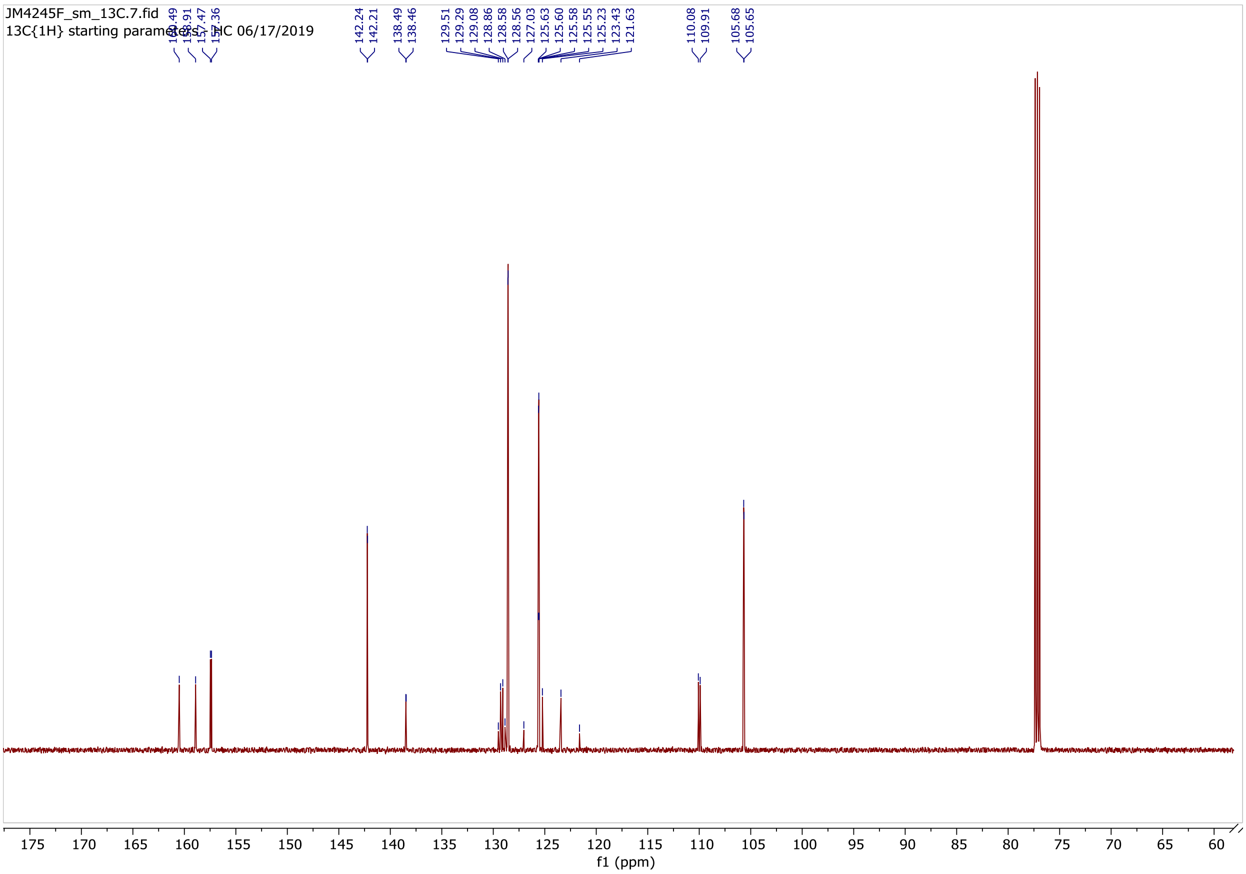
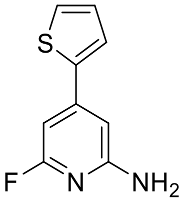
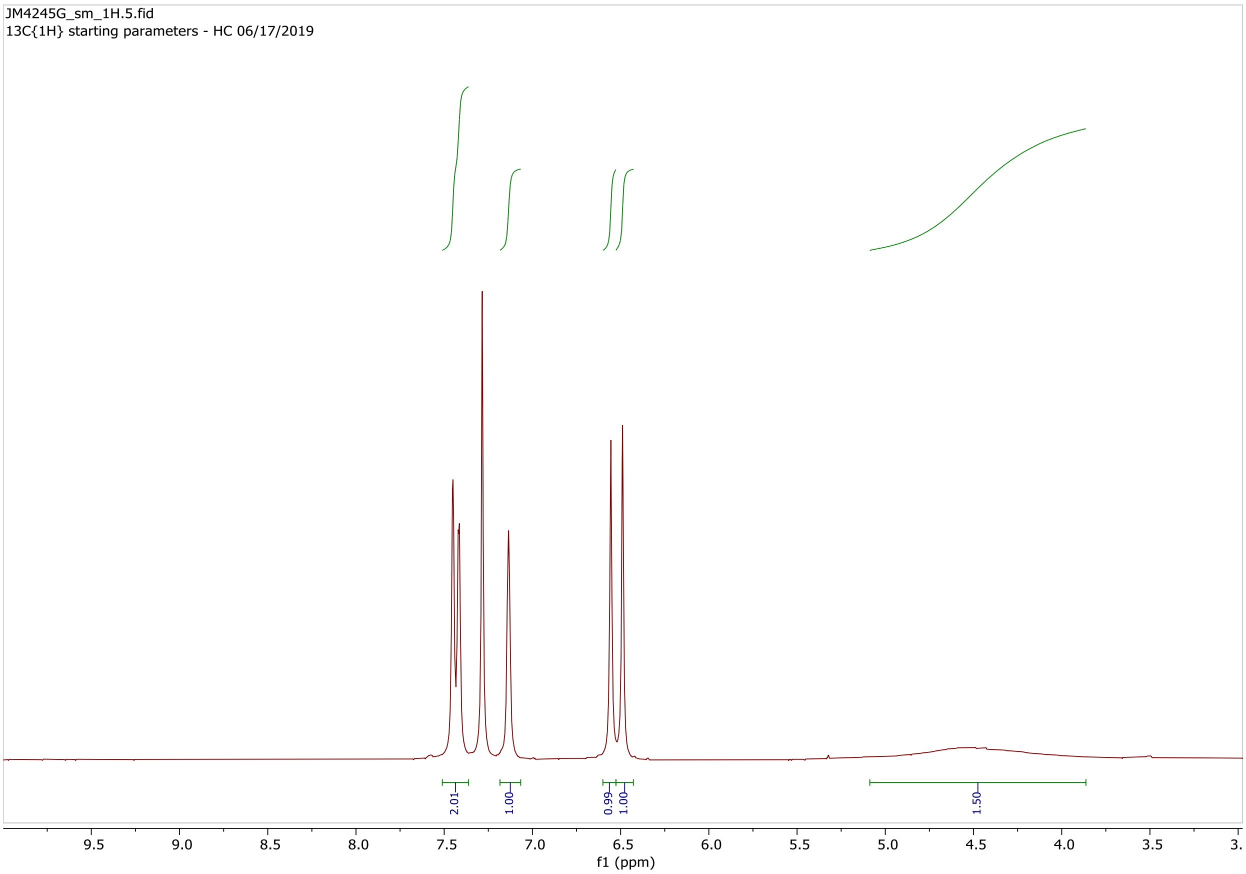
^{13}C NMR



Compound 2q



^{1}H NMR



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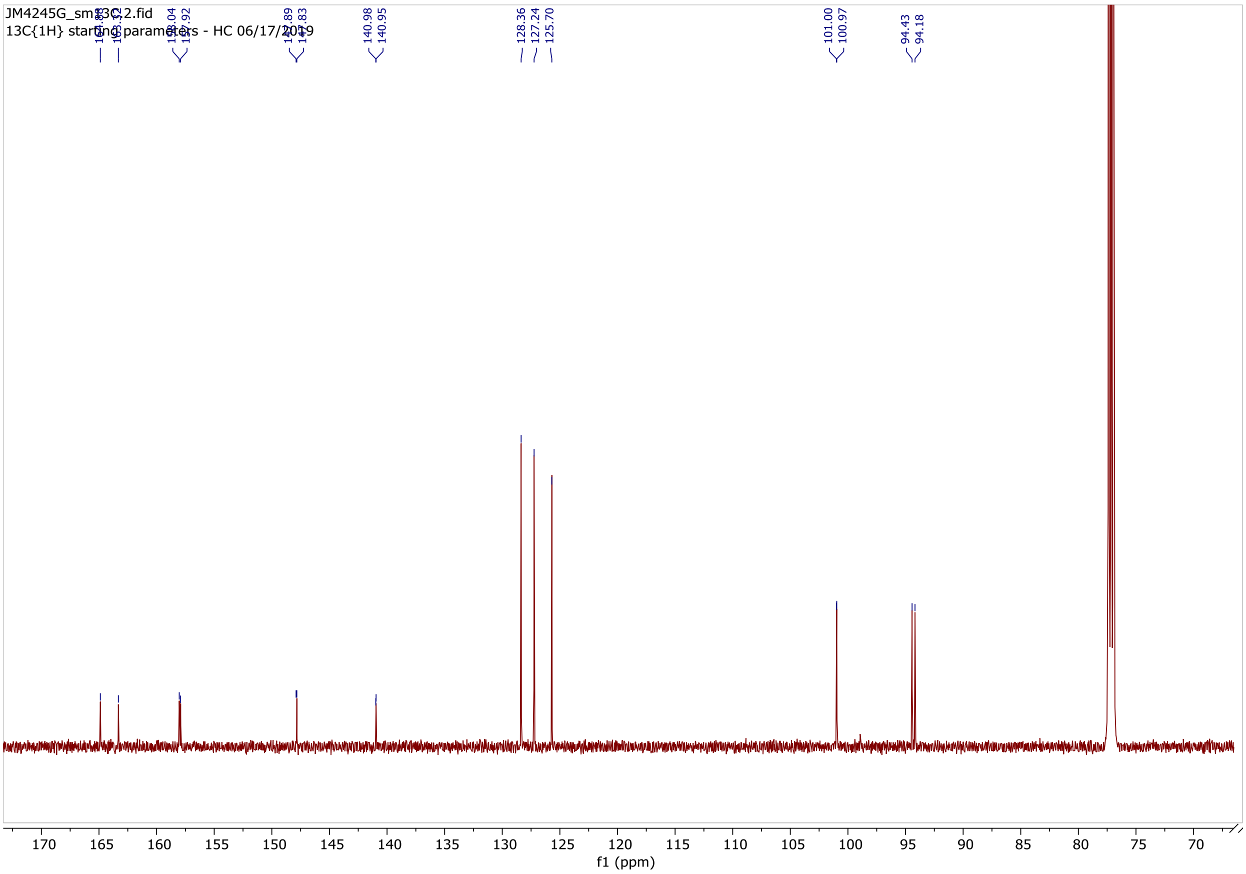
^{13}C NMR



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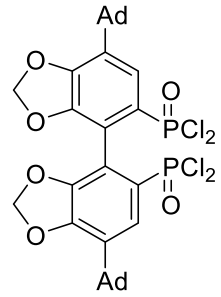
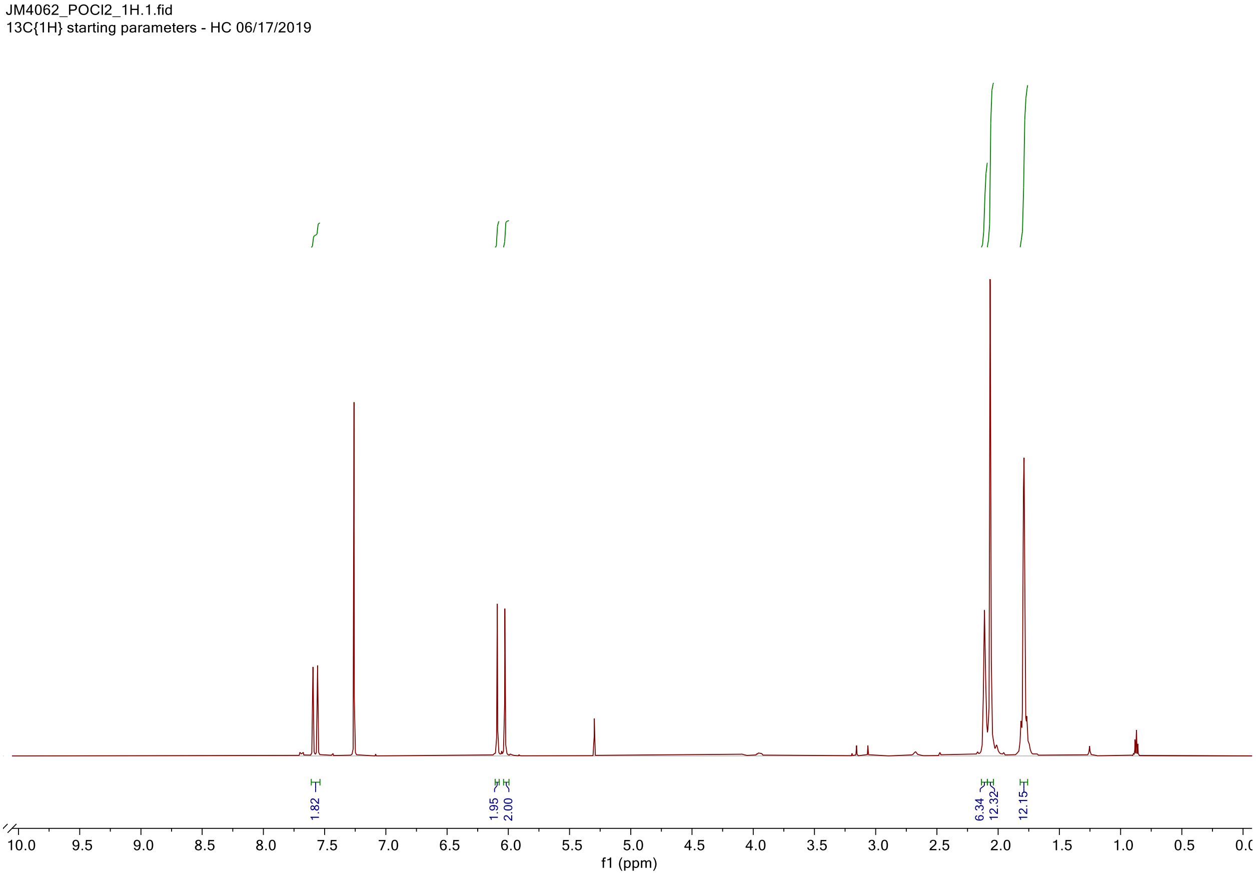
Ad-SEGPHOS-POCl₂



^{1}H NMR



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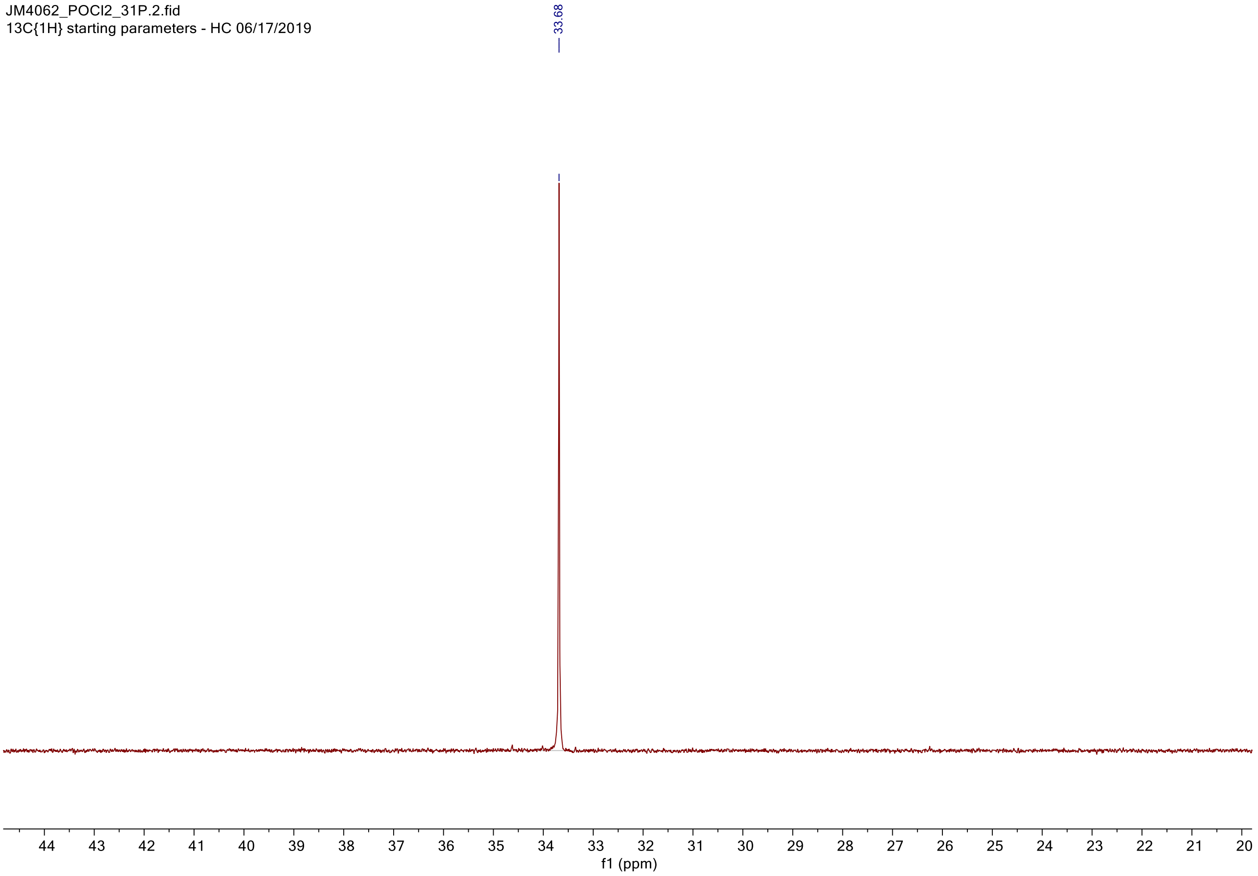
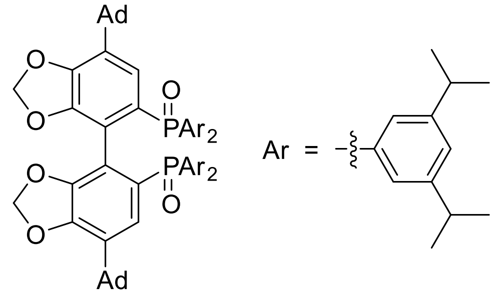
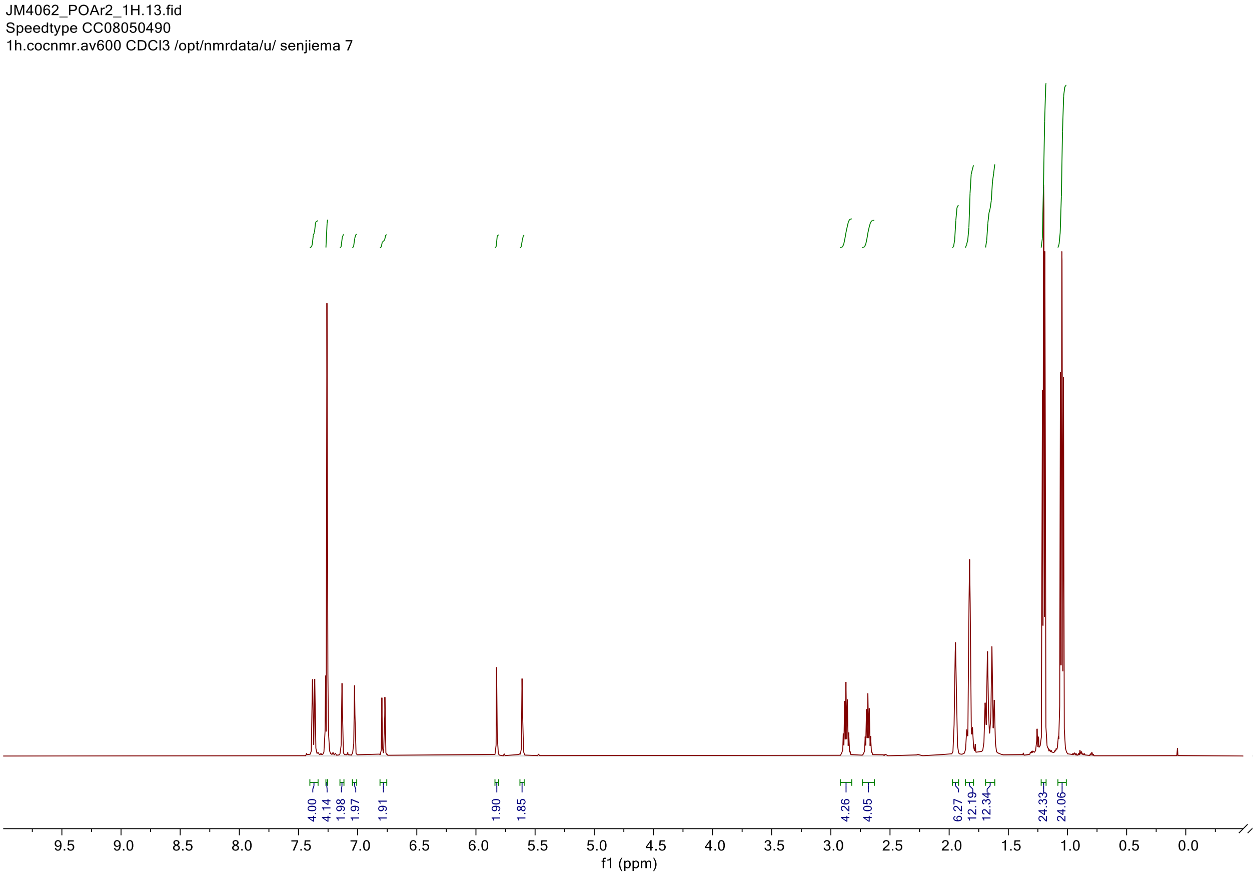
^{31}P NMR



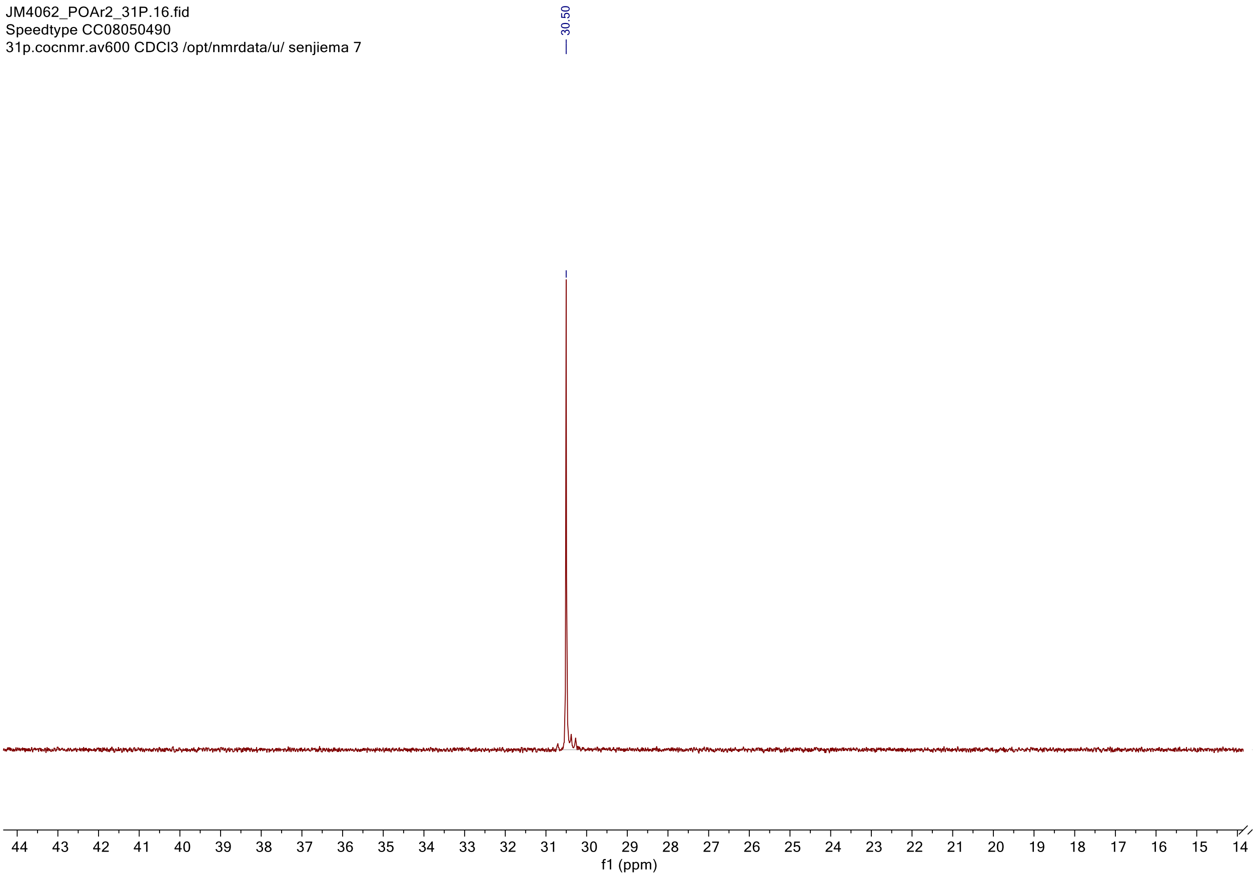
Ad-SEGPHOS-POAr$_2$



^{1}H NMR



^{31}P NMR


JM4062_POAr2_31P.16.fid
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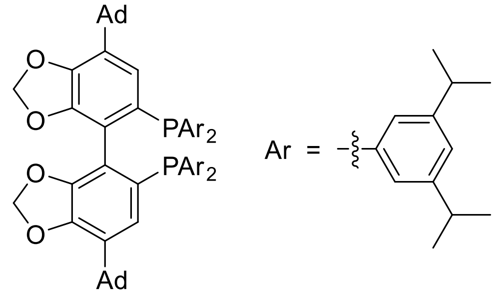
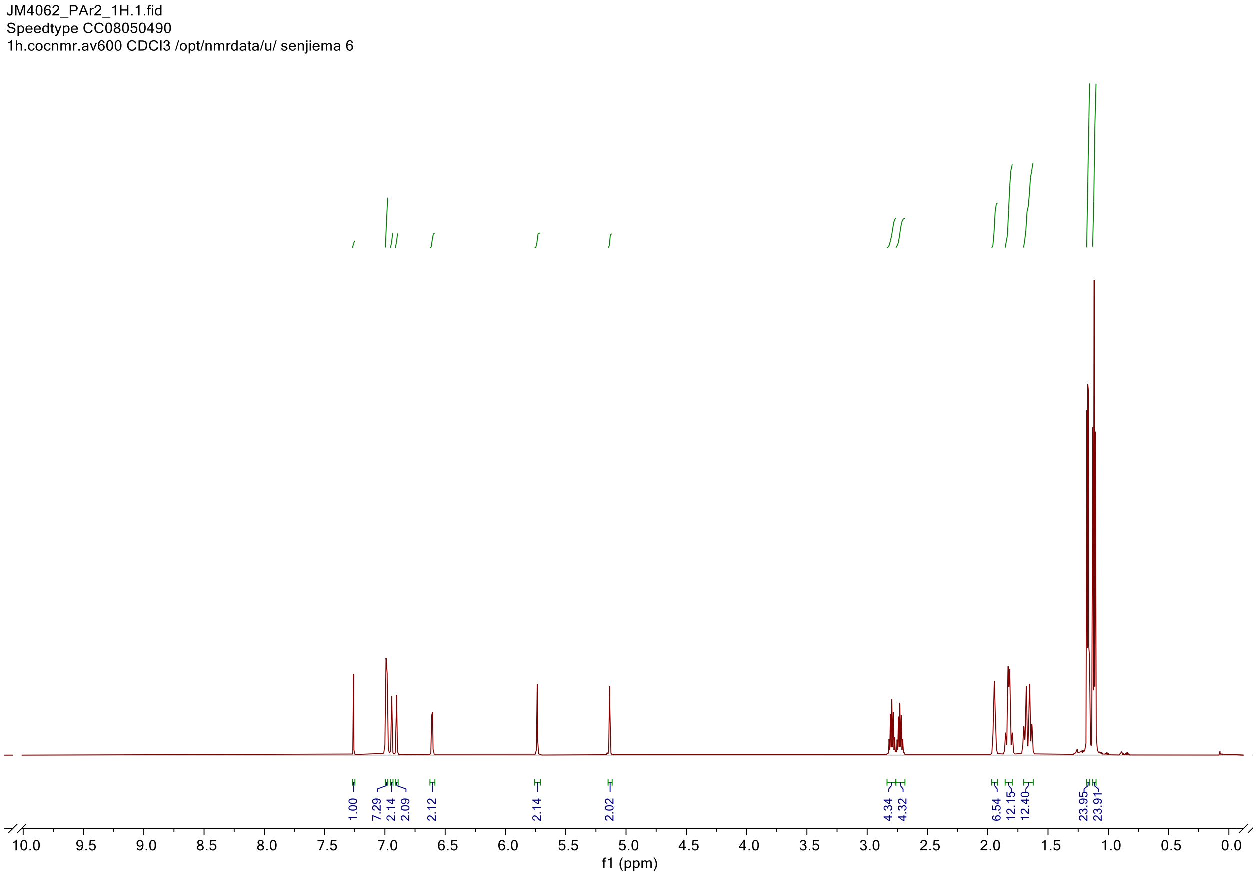
31p.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 7
30.50
44 43 42 41 40 39 38 37 36 35 34 33 32 31 30 29 28 27 26 25 24 23 22 21 20 19 18 17 16 15 14
f1 (ppm)

DIP-Ad-SEGPHOS (Ad-SEGPHOS-PAr$_2$)



^{1}H NMR



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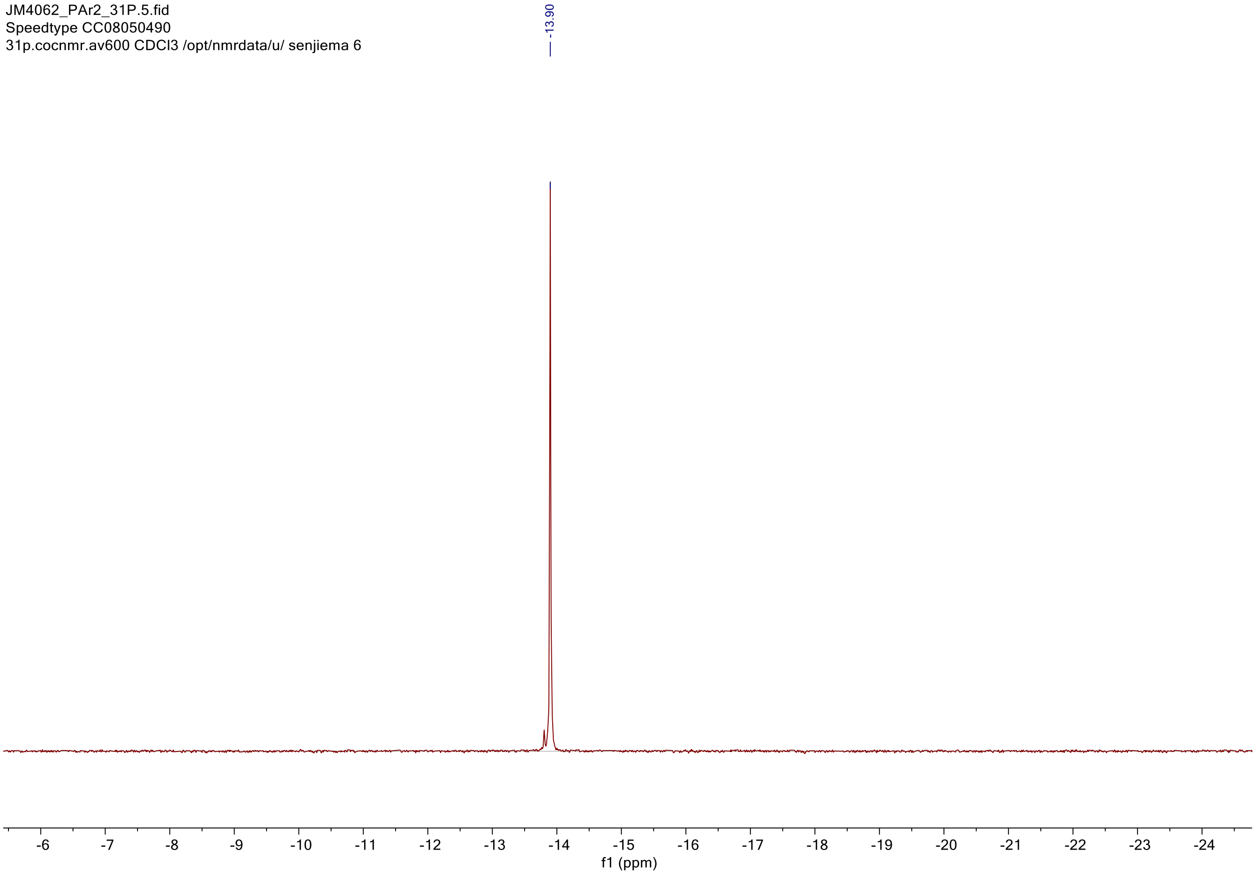
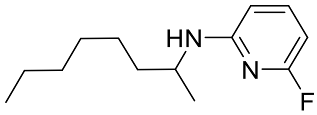
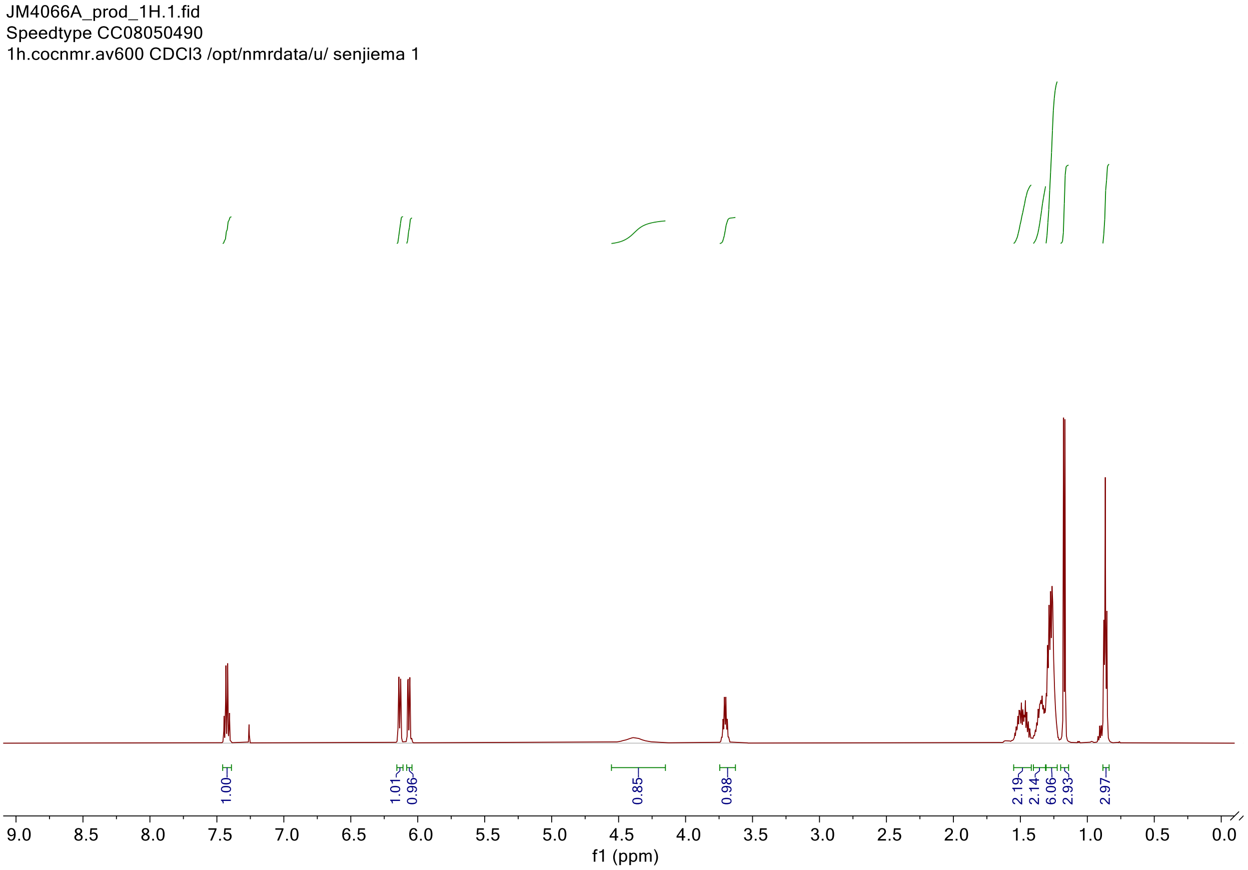
^{31}P NMR



Compound 3ab



^{1}H NMR



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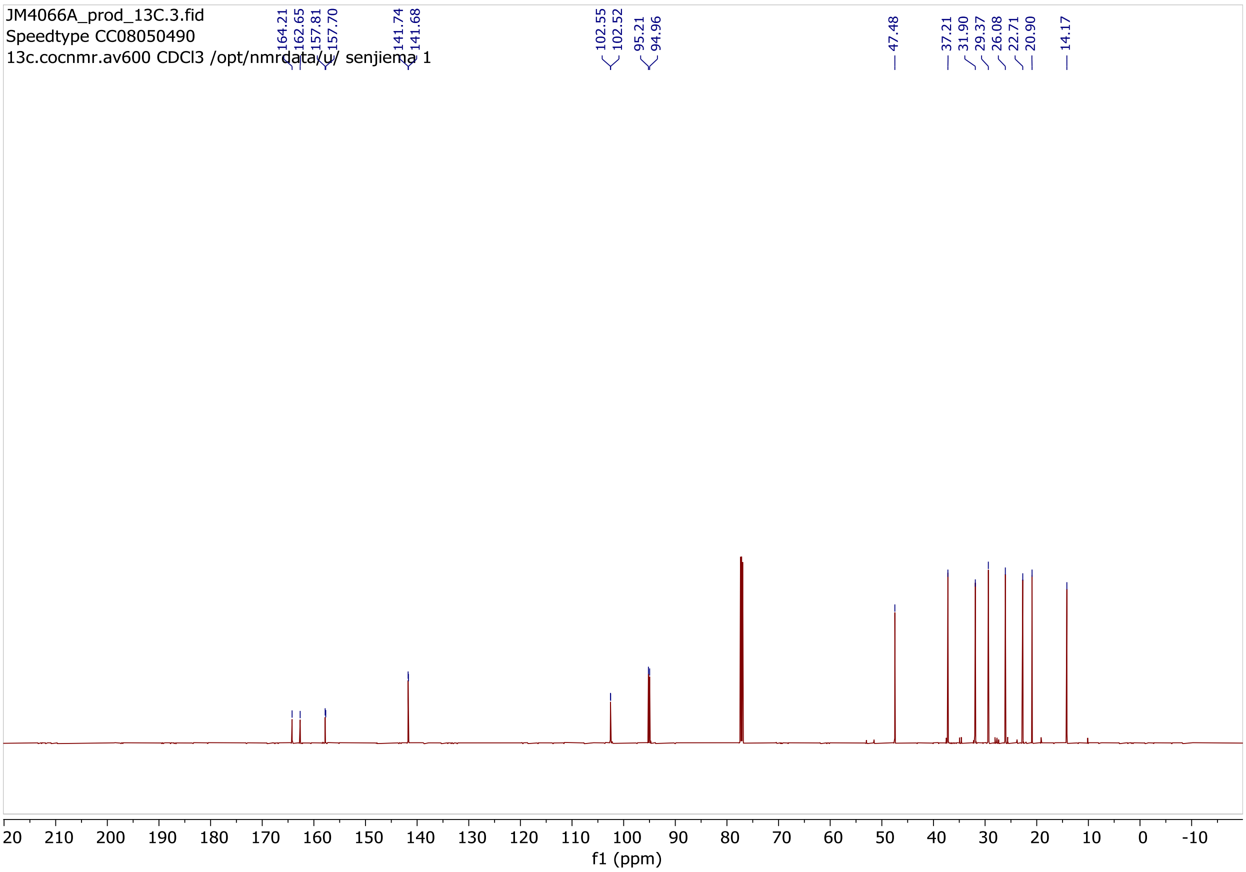
^{13}C NMR



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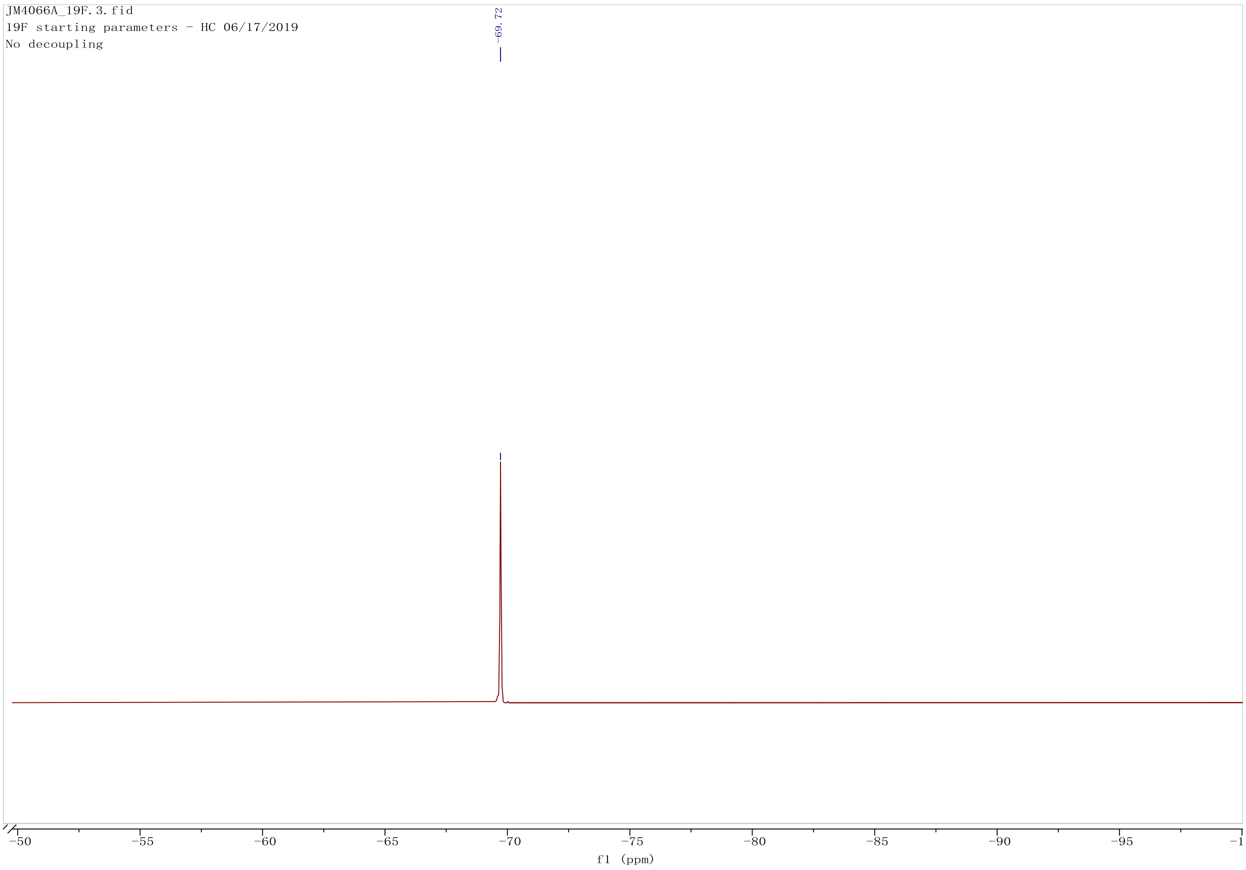
^{19}F NMR



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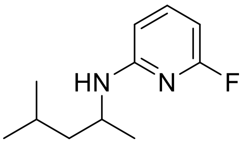
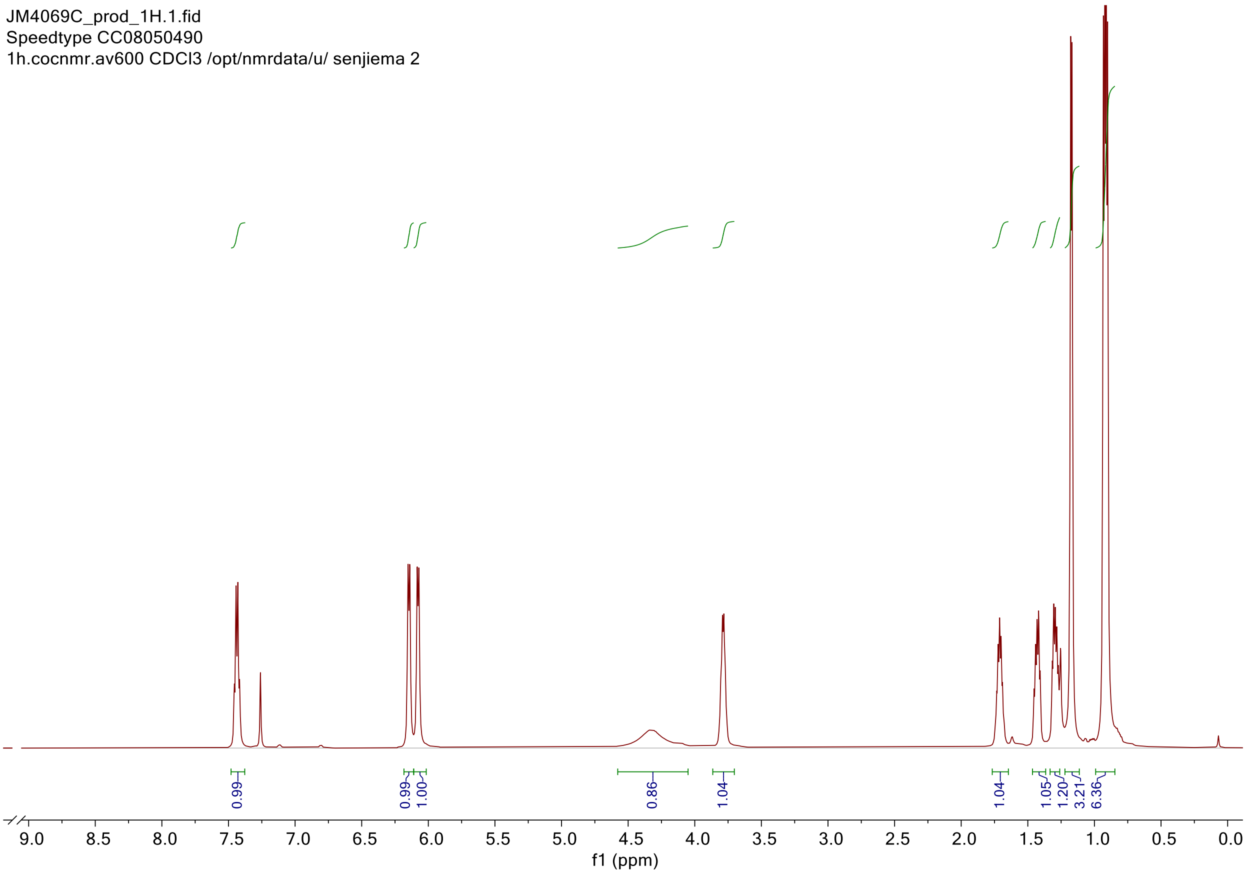
Compound 3bb



^{1}H NMR



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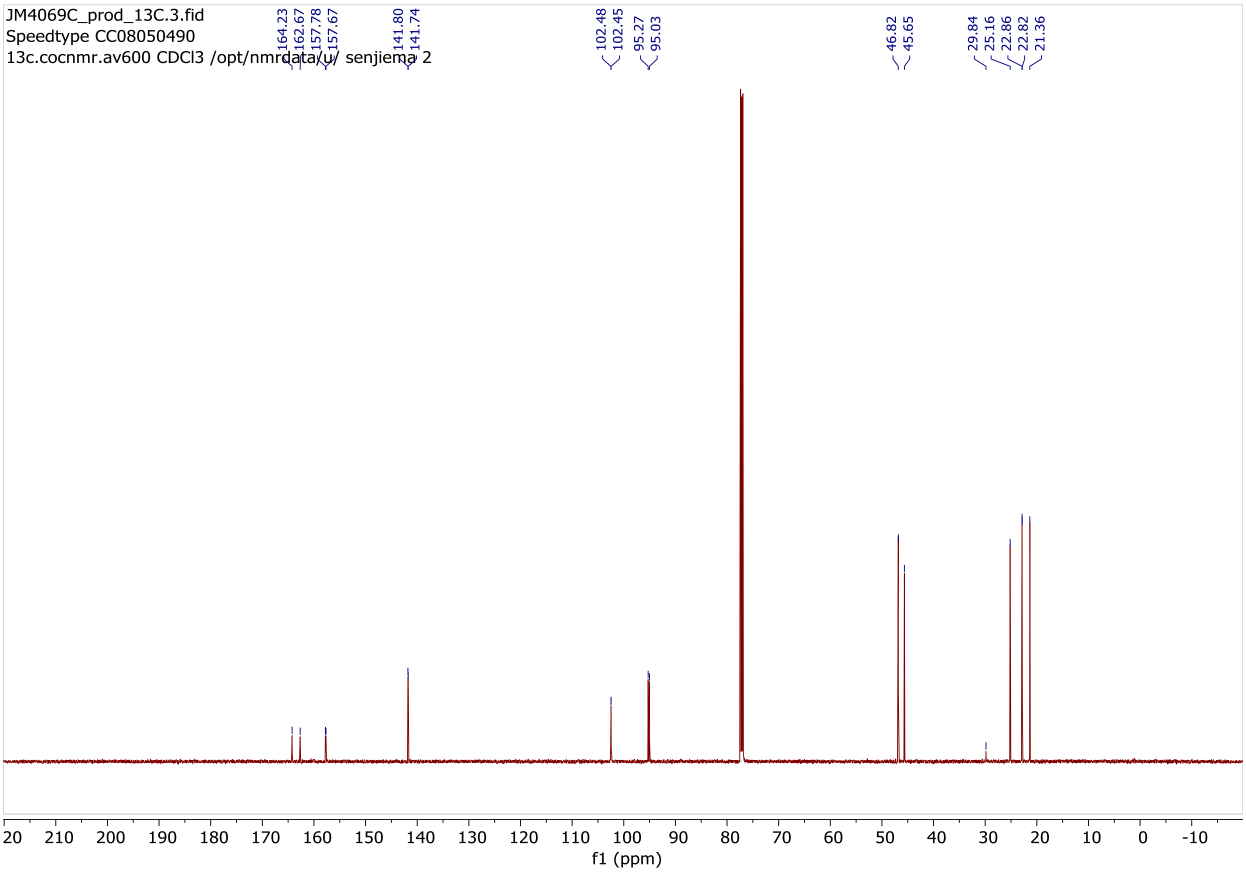
^{13}C NMR



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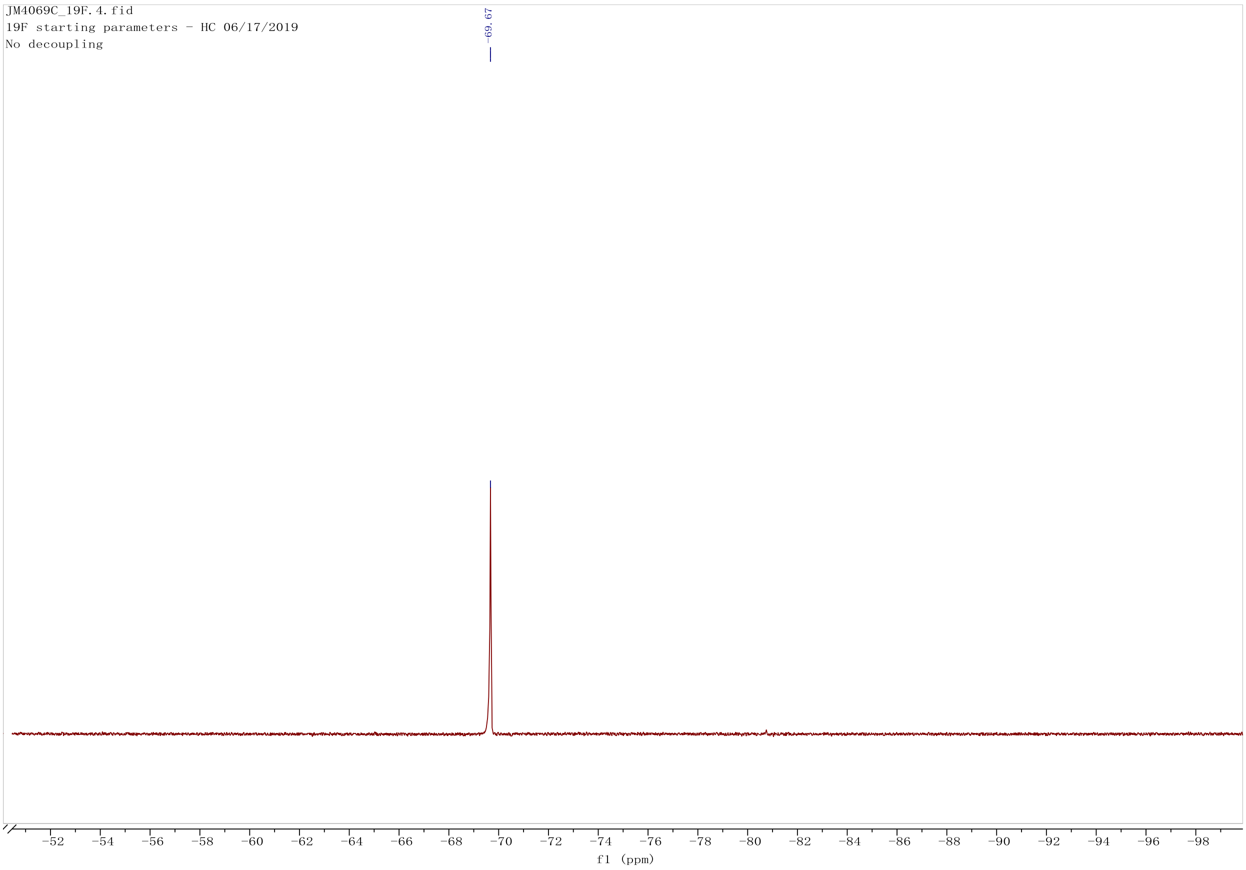
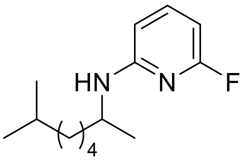
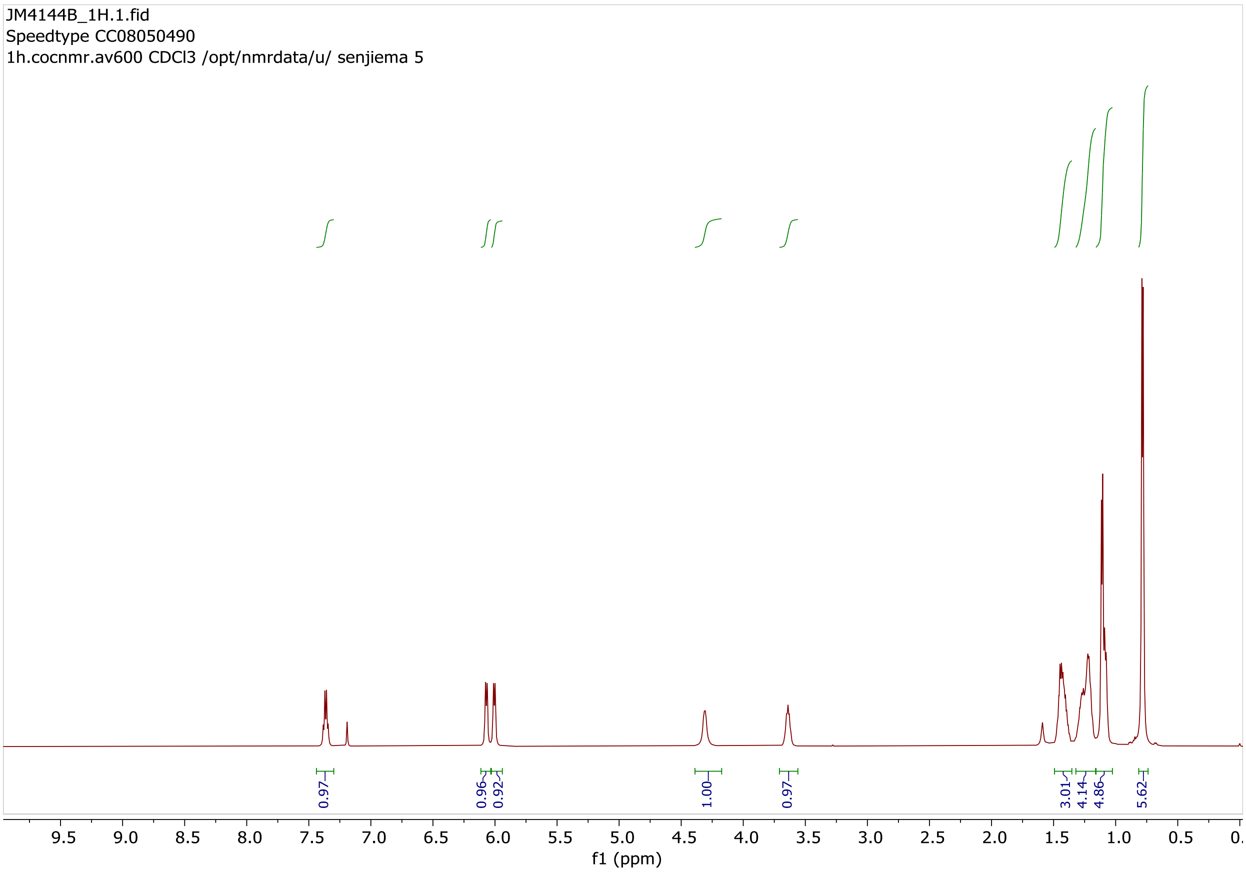
^{19}F NMR



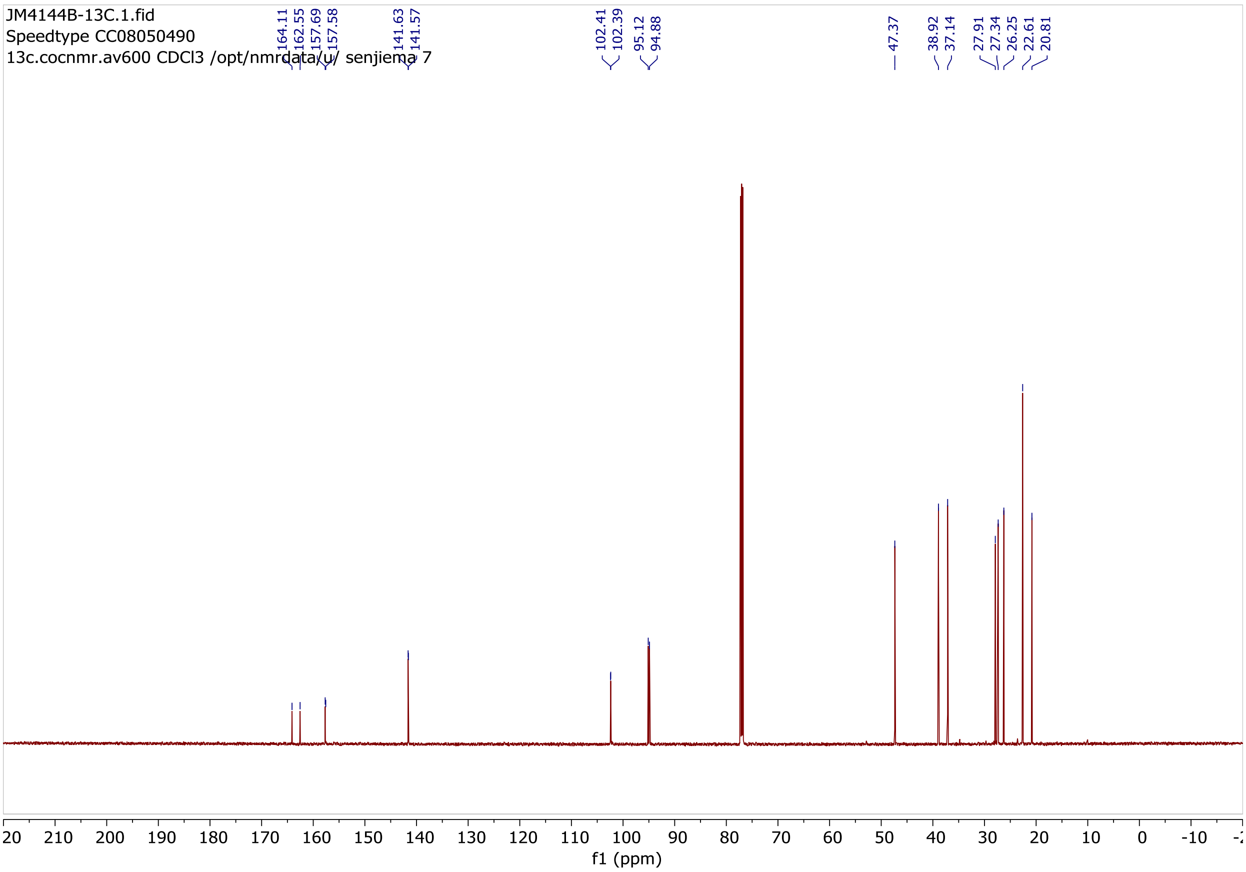
Compound 3cb



^{1}H NMR



^{13}C NMR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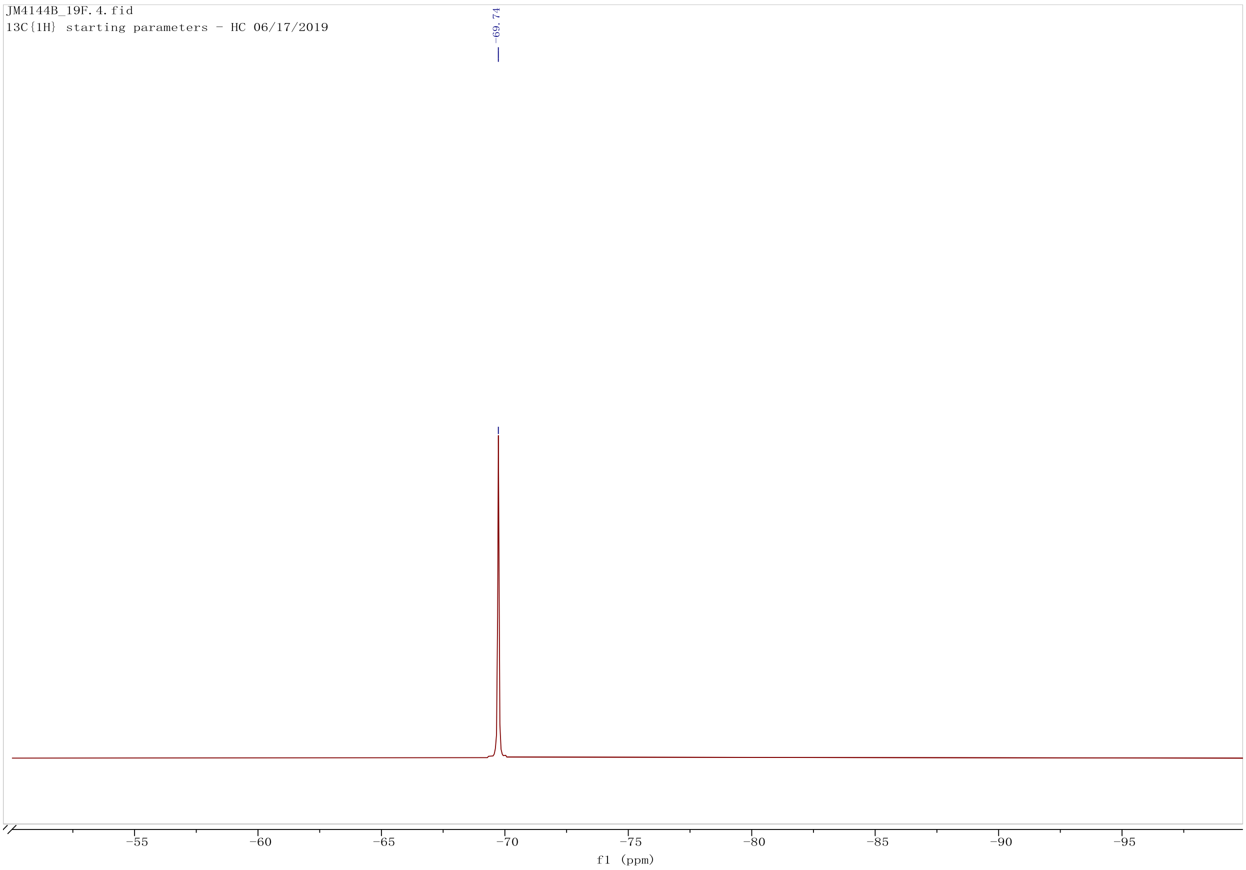
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 7
164.11
162.55
157.69
157.58
141.63
141.57
102.41
102.39
95.12
94.88
47.37
38.92
37.14
27.91
27.34
26.25
22.61
20.81
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

[*Return to table of contents*]

^{19}F NMR



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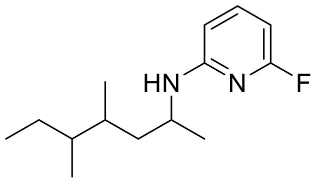
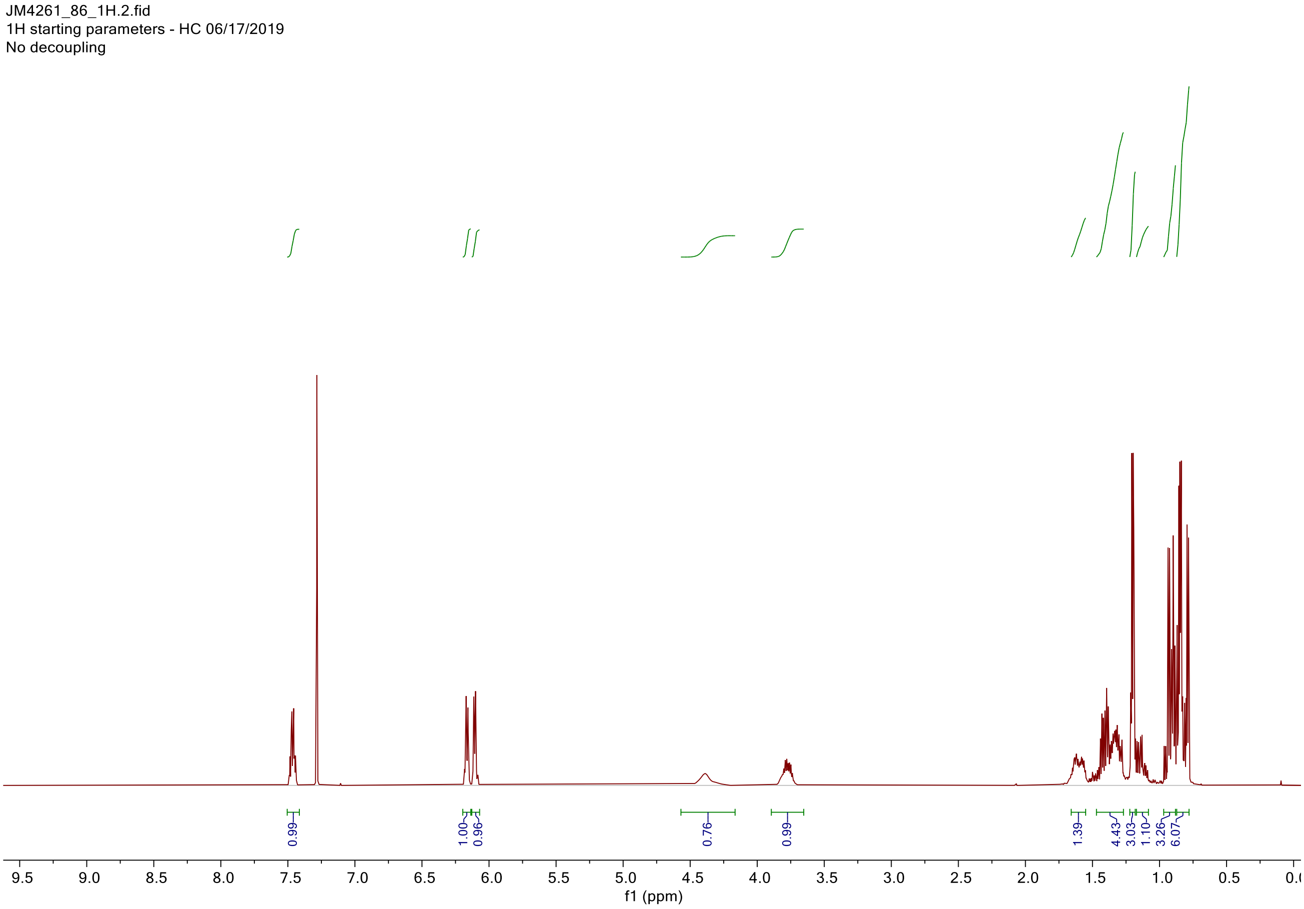
Compound 3db



^{1}H NMR



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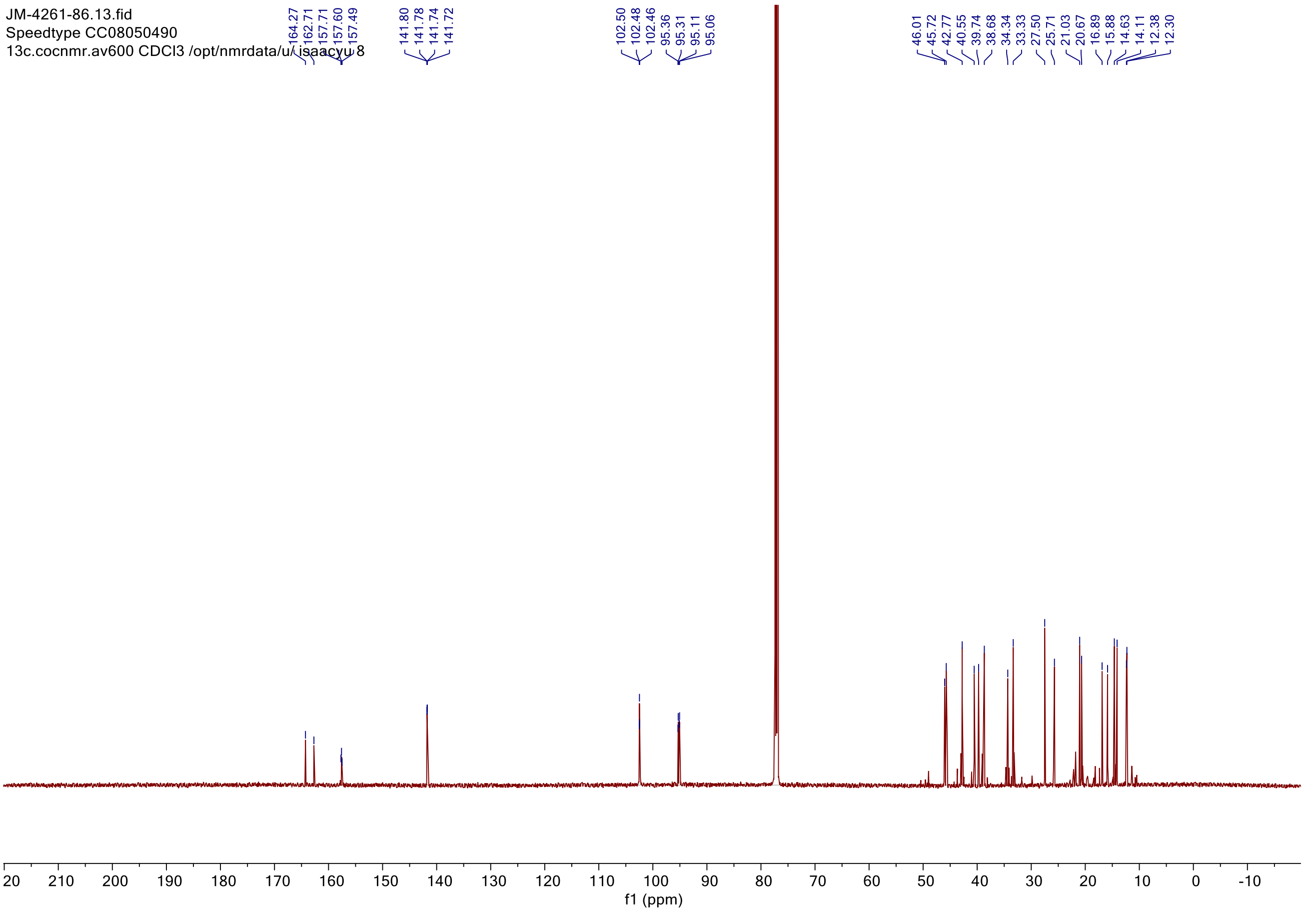
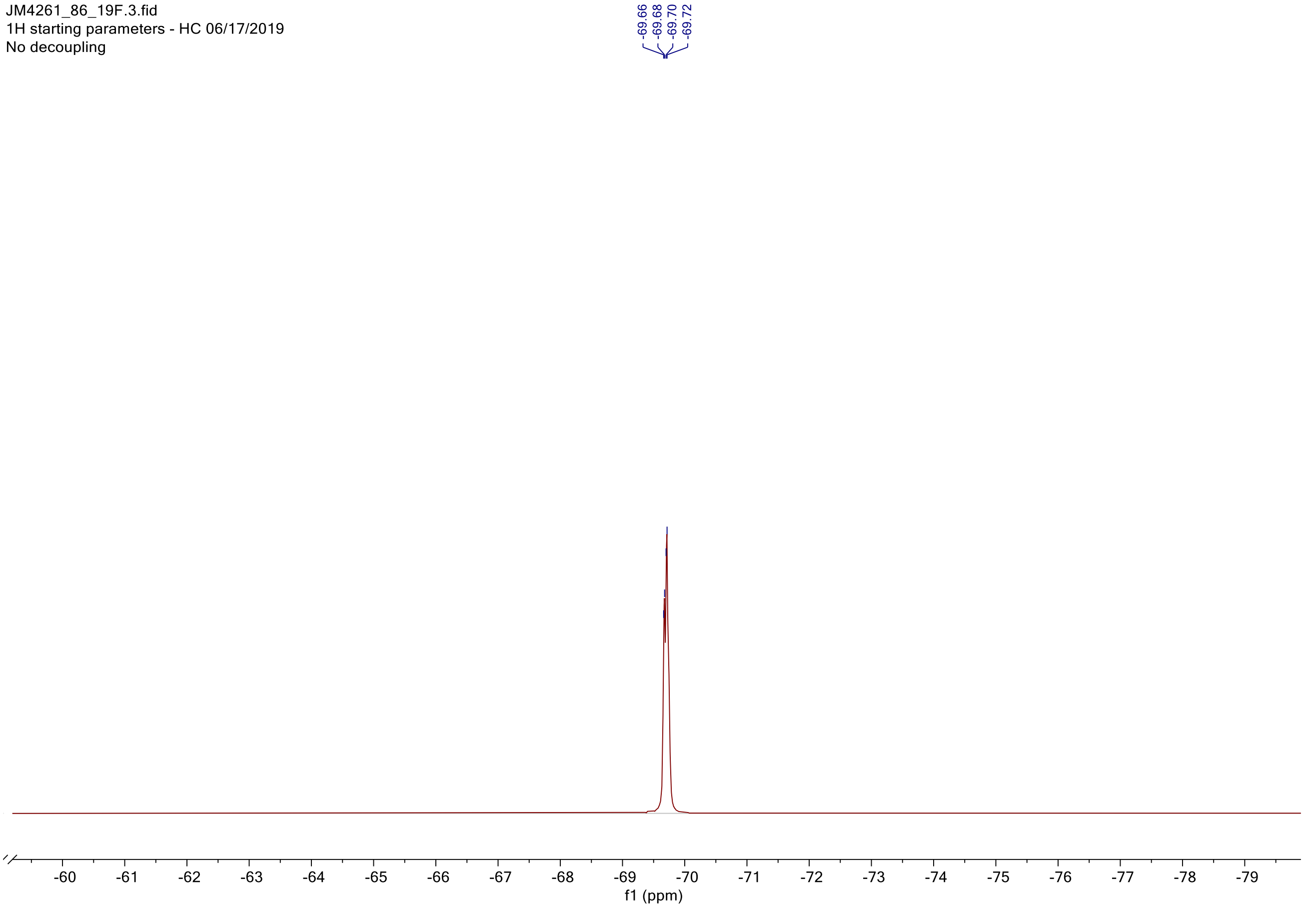
^{13}C NMR



^{19}F NMR

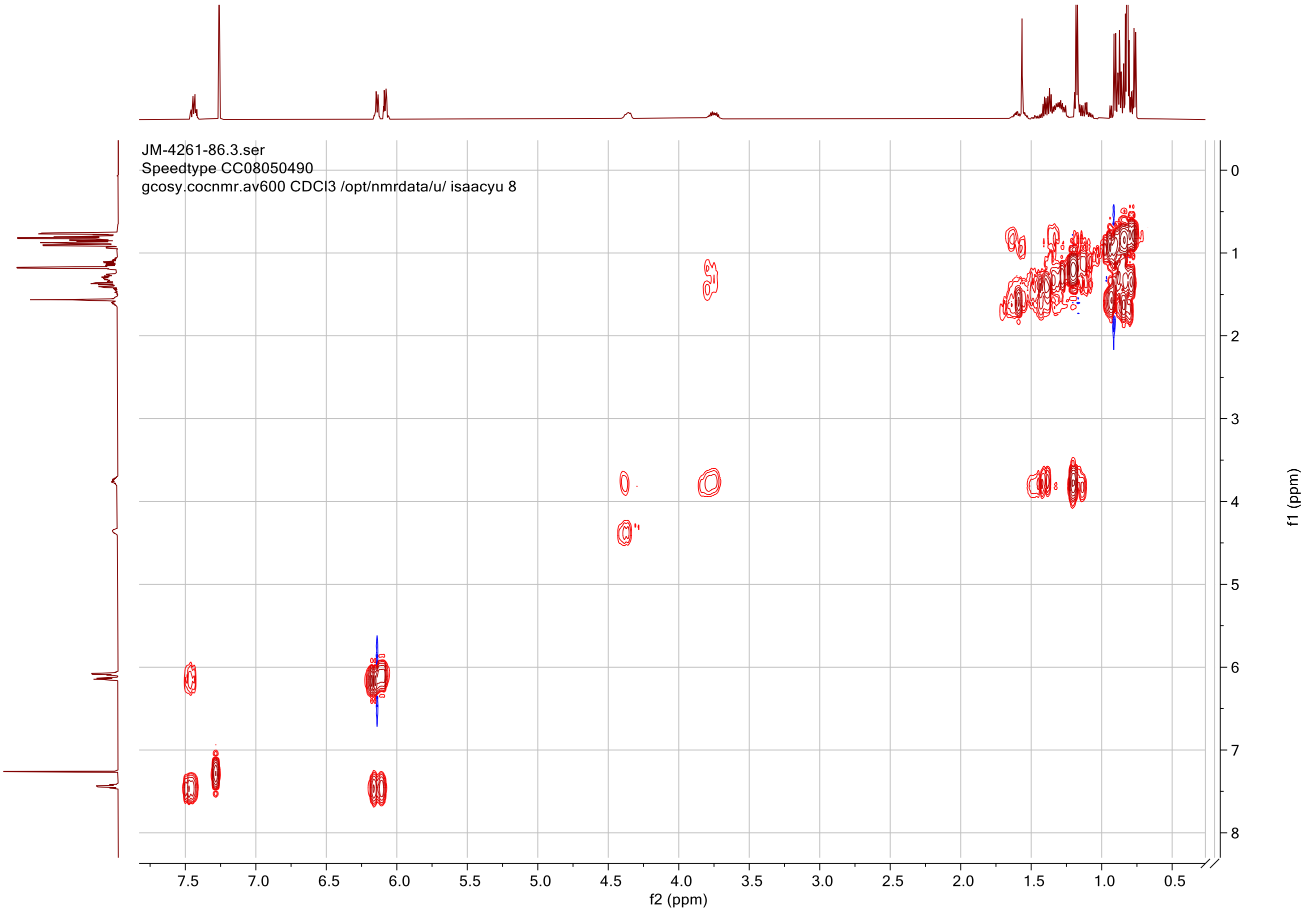

JM4261_86_19F.3.fid
1H starting parameters - HC 06/17/2019
No decoupling
-69.66
-69.68
-69.70
-69.72
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
f1 (ppm)

[*Return to table of contents*]

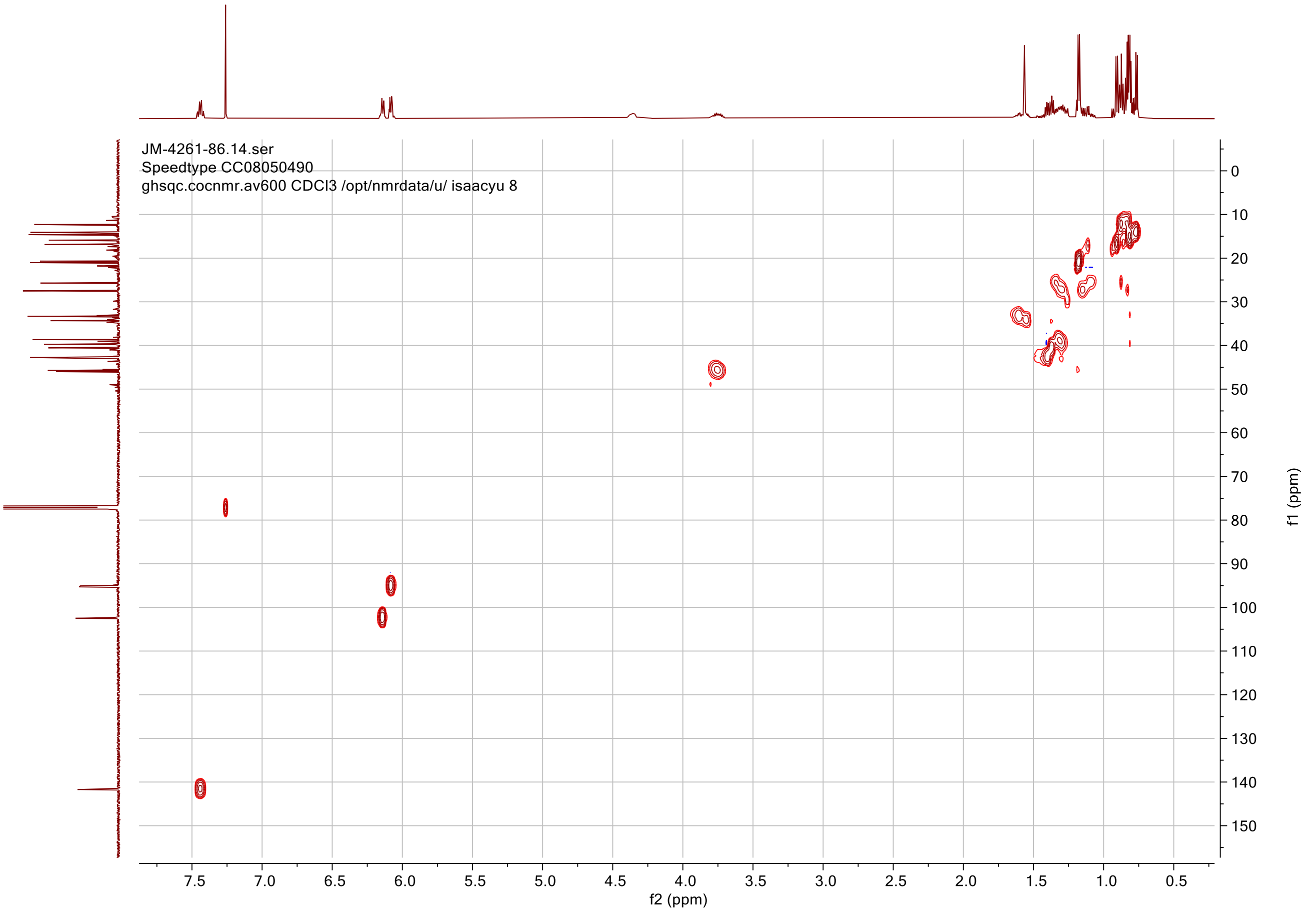
DEPT-135 ^{13}C NMR

[*Return to table of contents*]

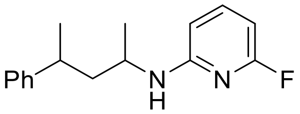
COSY NMR



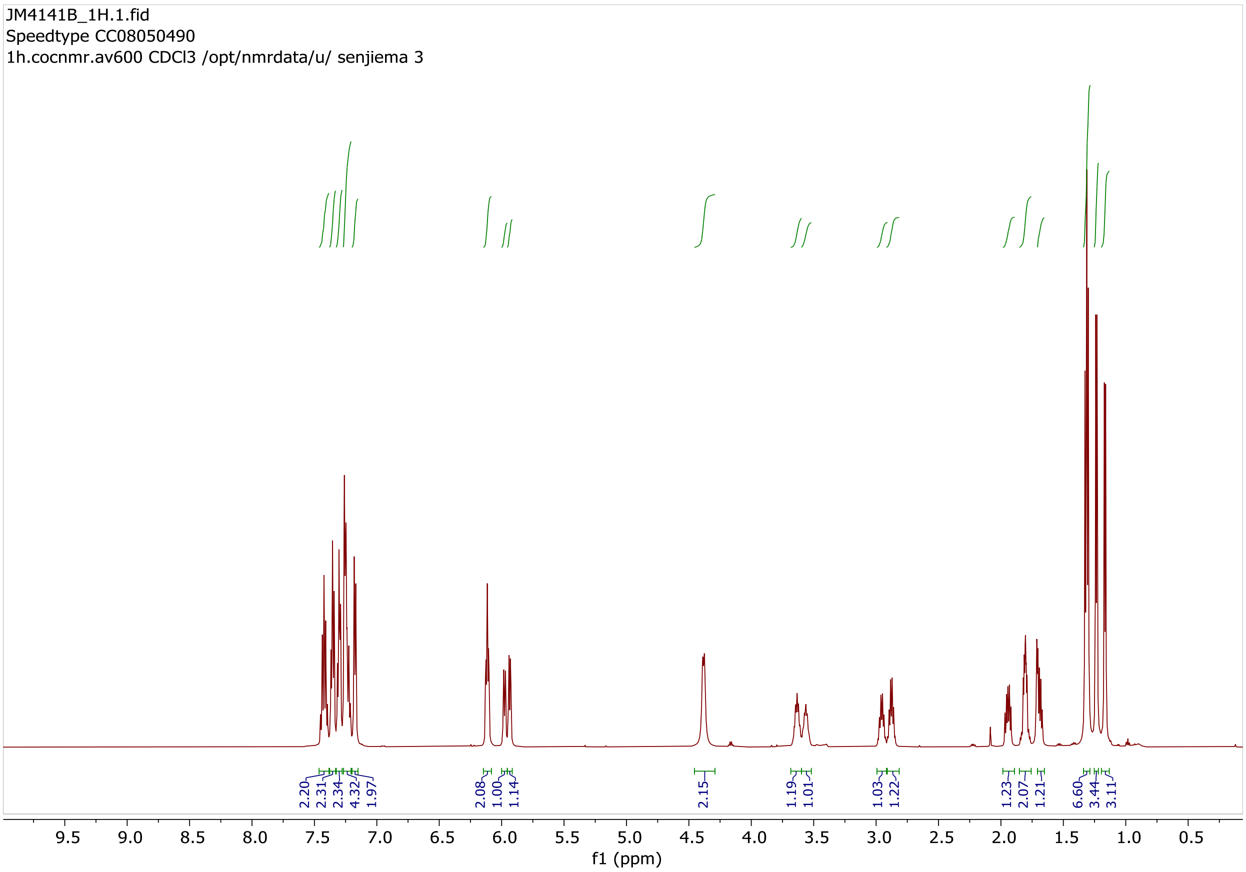
HSQC NMR


JM-4261-86.14.ser
Speedtype CC08050490
ghsqc.cocnmr.av600 CDCl3 /opt/nmrdata/u/ isaacyu 8
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
f1 (ppm)

Compound 3eb



^{1}H NMR



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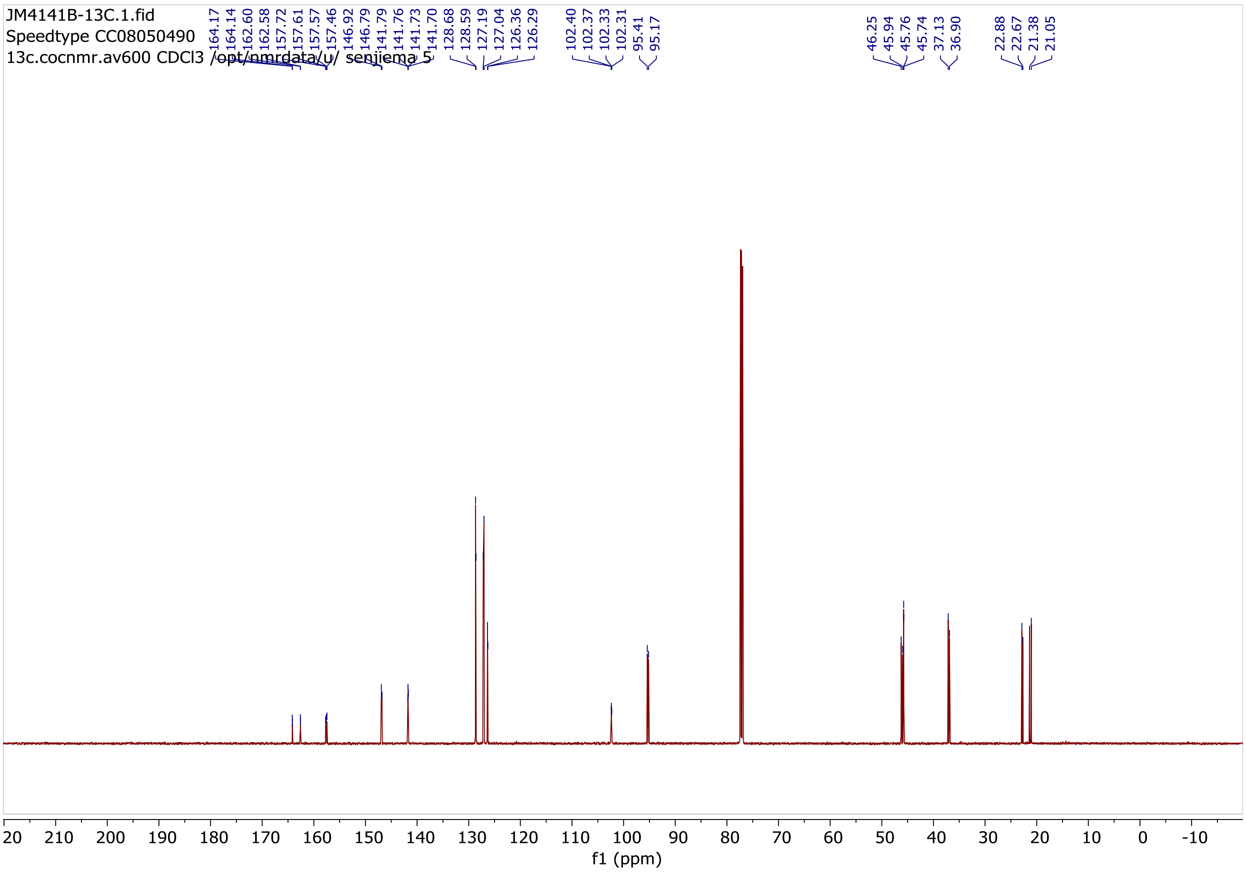
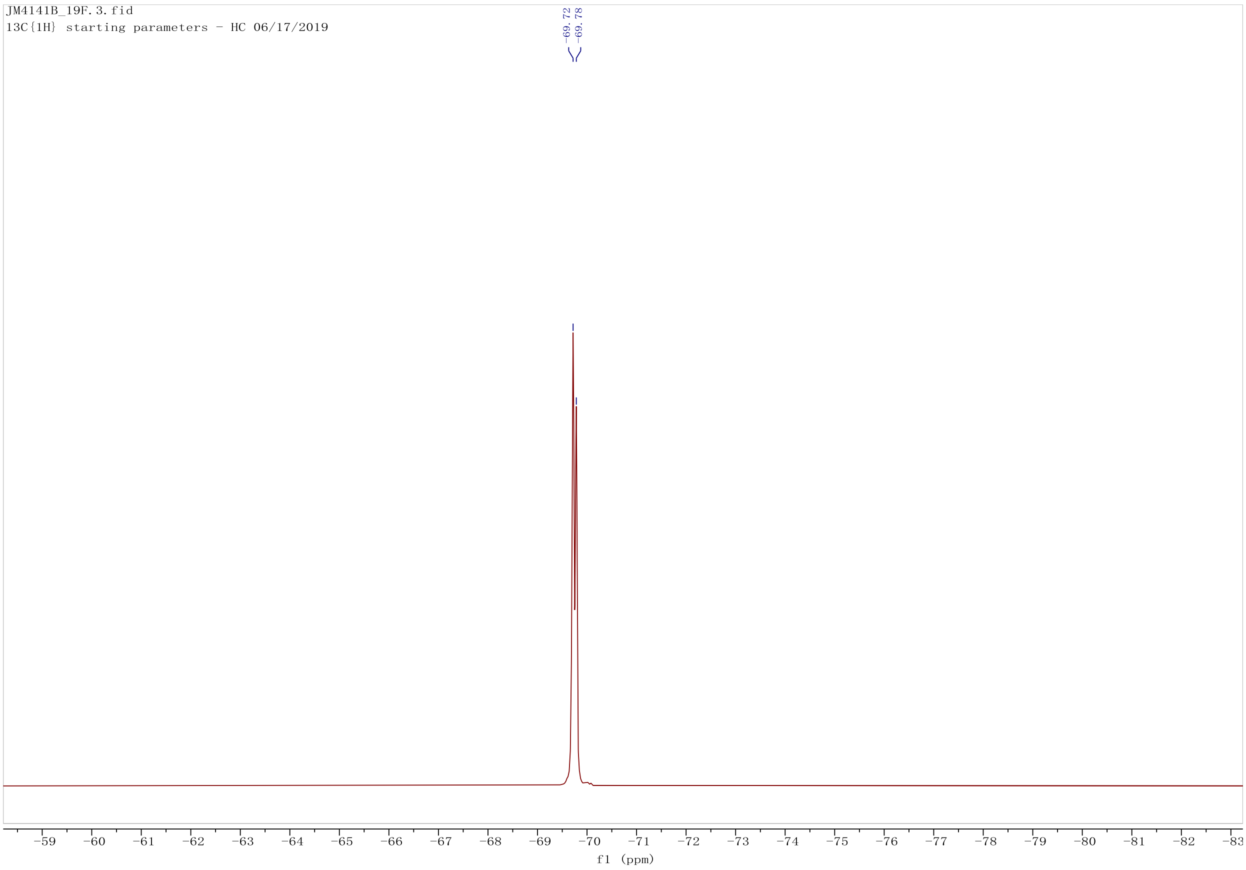
^{13}C NMR



^{19}F NMR


JM4141B_19F.3.fid
13C{1H} starting parameters - HC 06/17/2019
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-69.78
-59
-60
-61
-62
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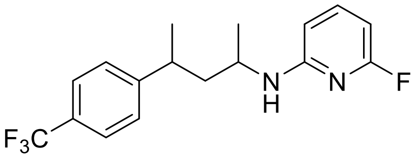
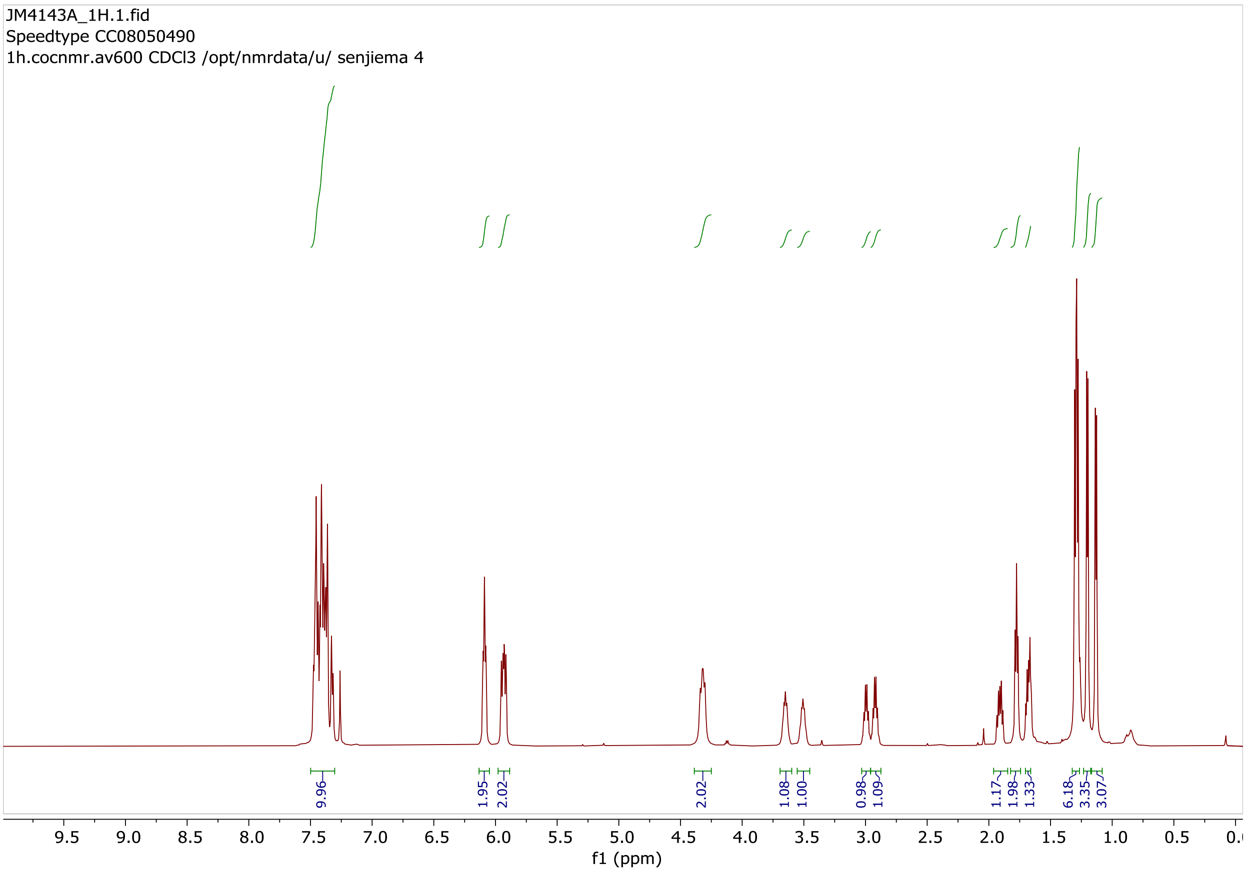
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
-81
-82
-83
f1 (ppm)

Compound 3fb



^{1}H NMR



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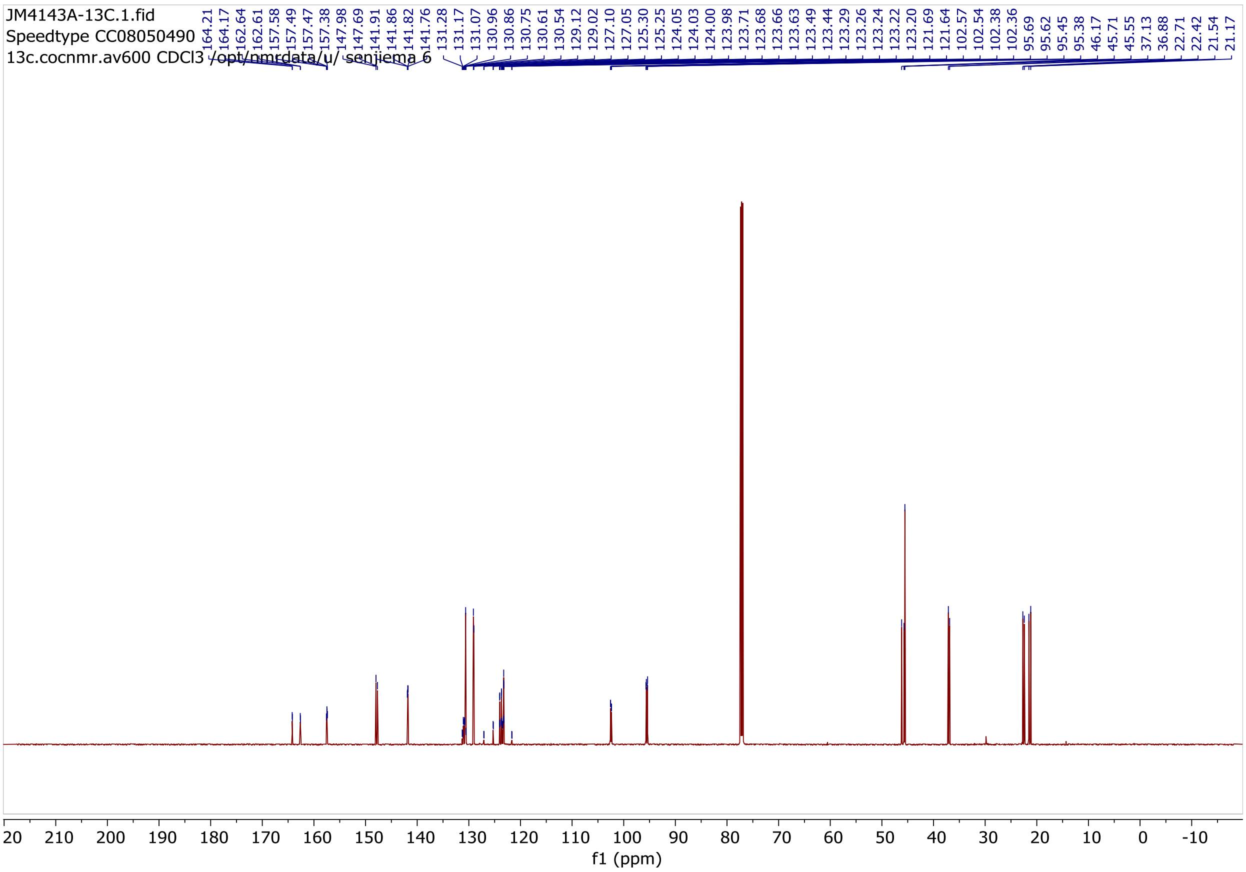
^{13}C NMR



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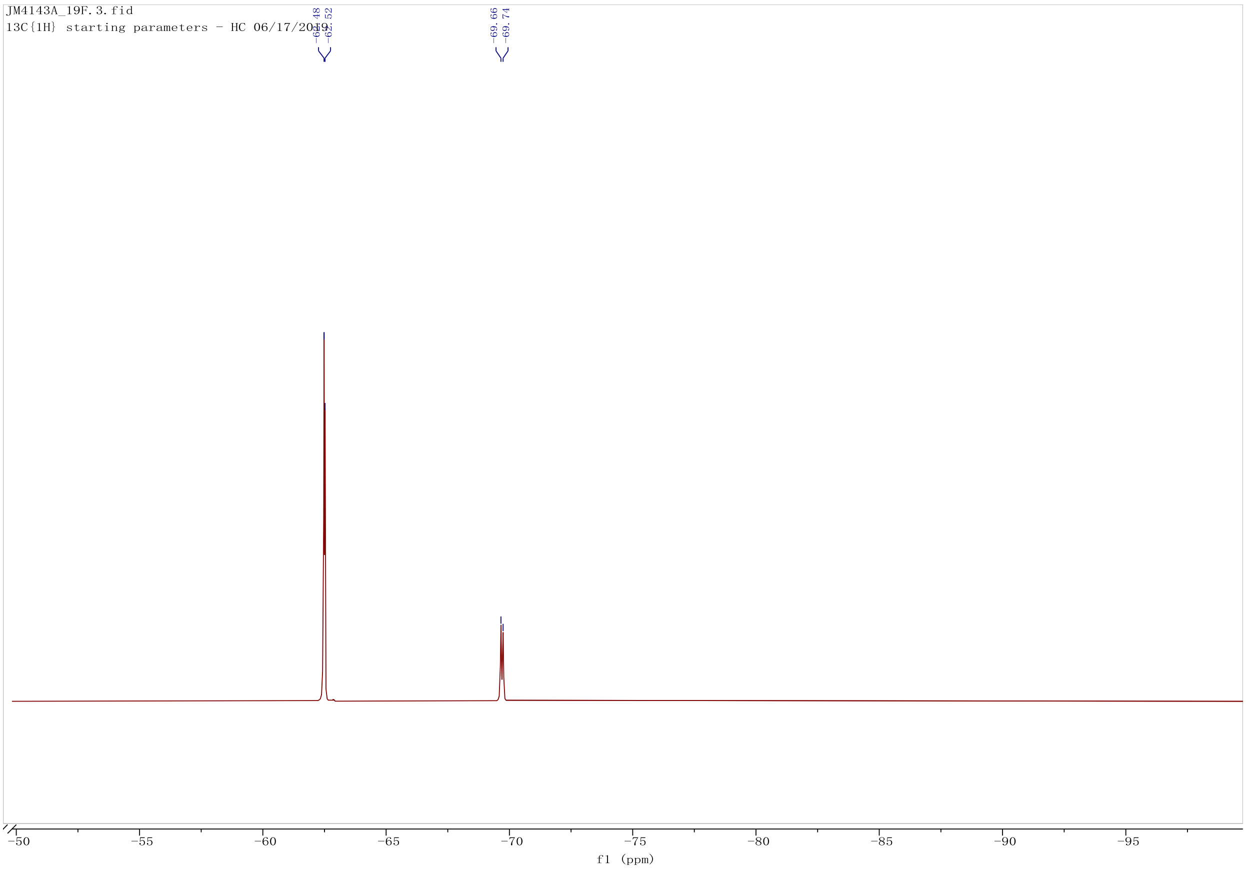
^{19}F NMR



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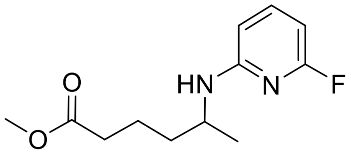
Compound 3gb



^{1}H NMR

JM4082F_prod_new_1H.12.fid
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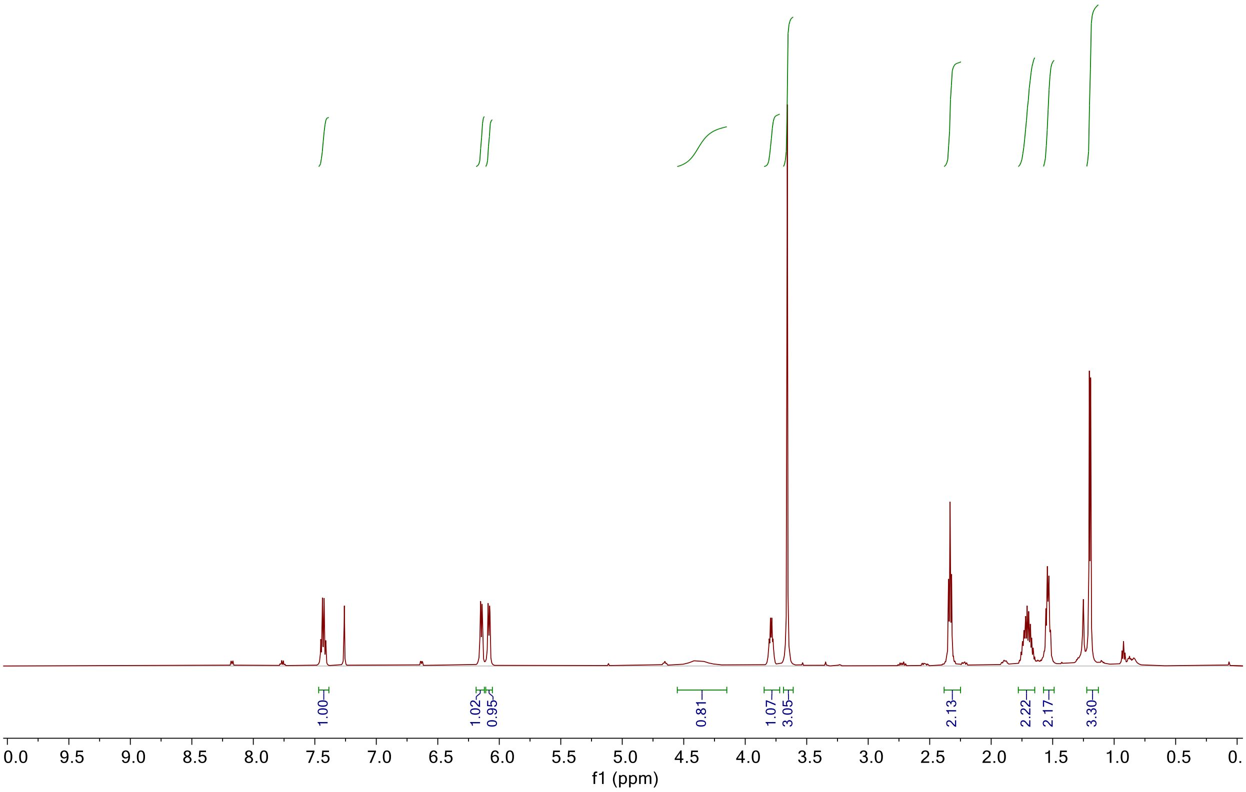
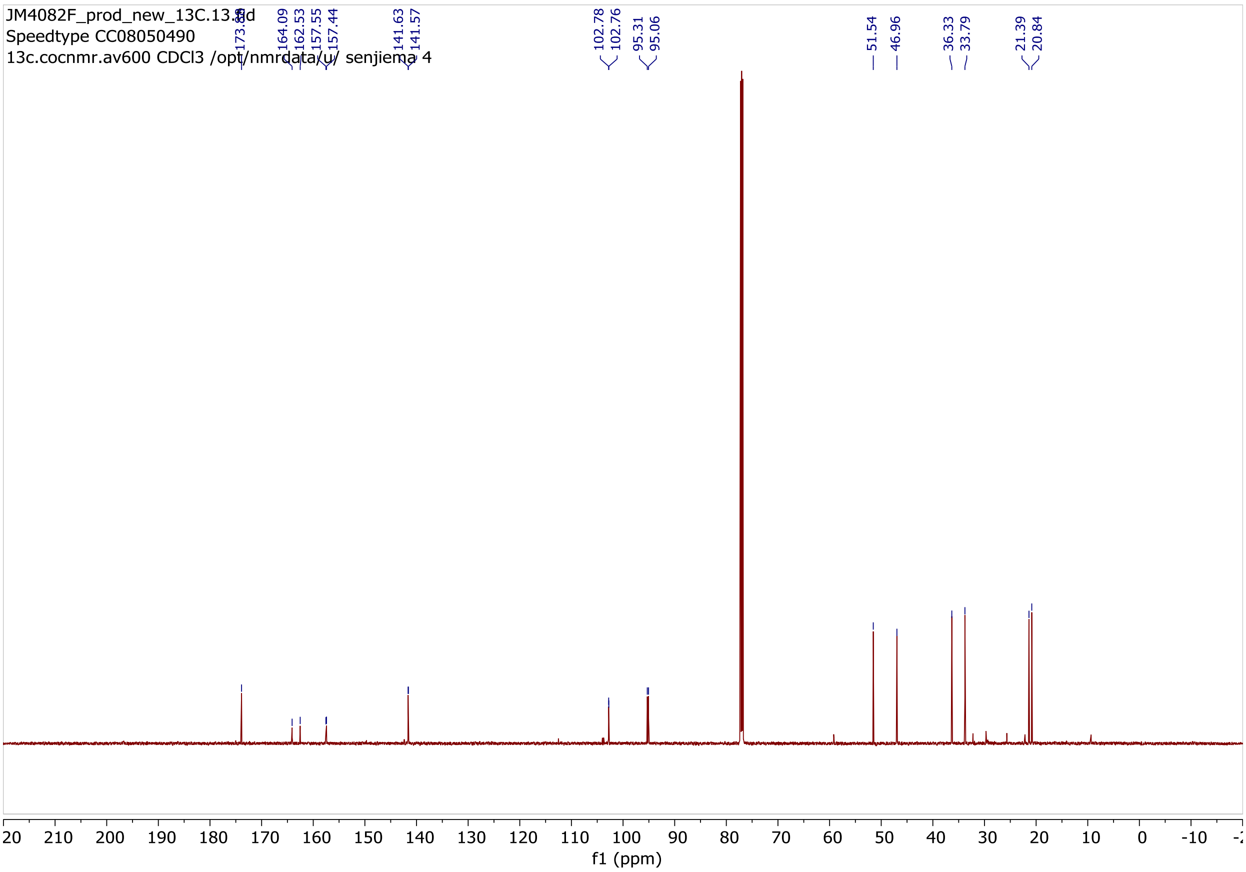
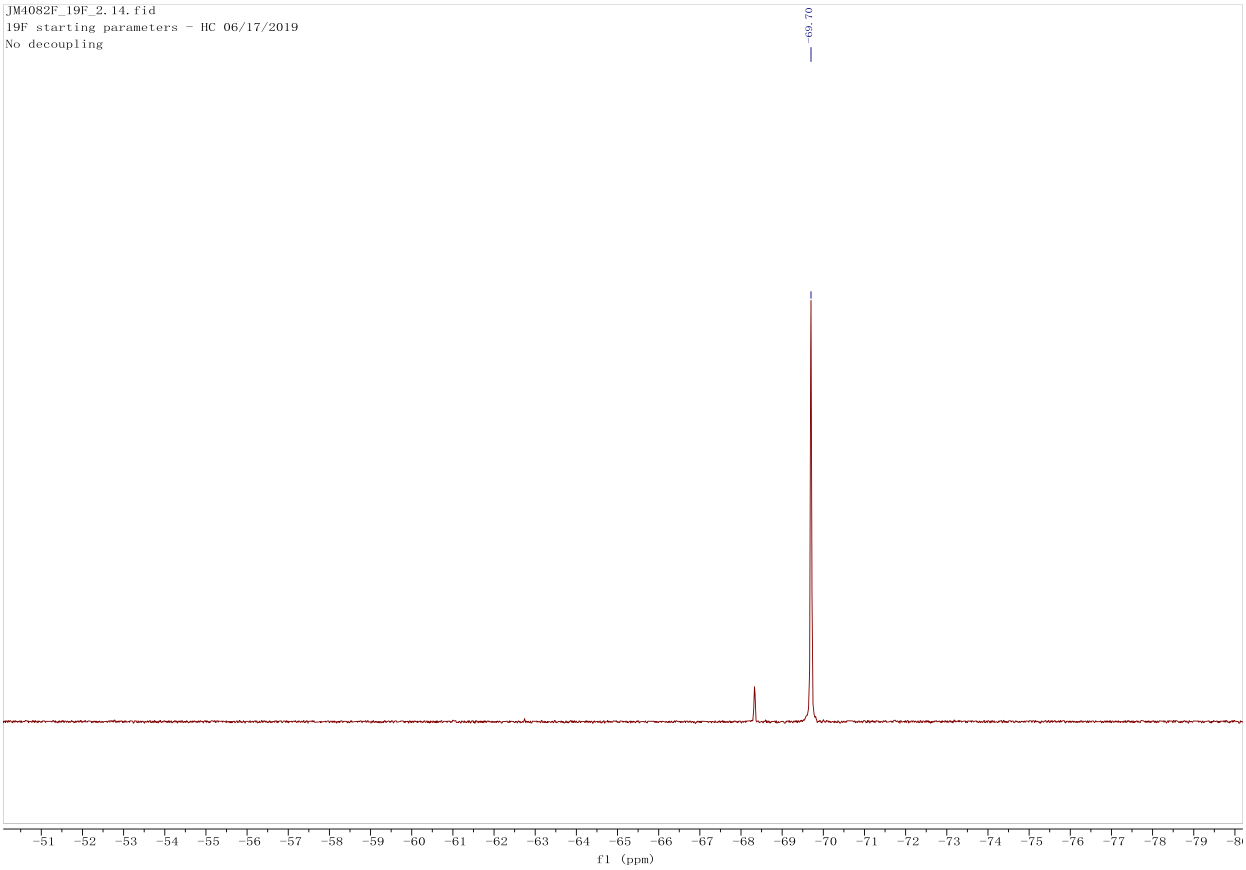


^{13}C NMR


JM4082F_prod_new_13C.13.fid
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 4
173.88
164.09
162.53
157.55
157.44
141.63
141.57
102.78
102.76
95.31
95.06
51.54
46.96
36.33
33.79
21.39
20.84
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-
f1 (ppm)

^{19}F NMR


JM4082F_19F_2.14.fid
19F starting parameters - HC 06/17/2019
No decoupling
-69.70
-51
-52
-53
-54
-55
-56
-57
-58
-59
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
f1 (ppm)

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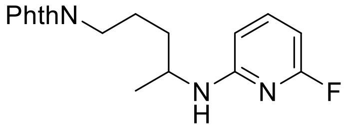
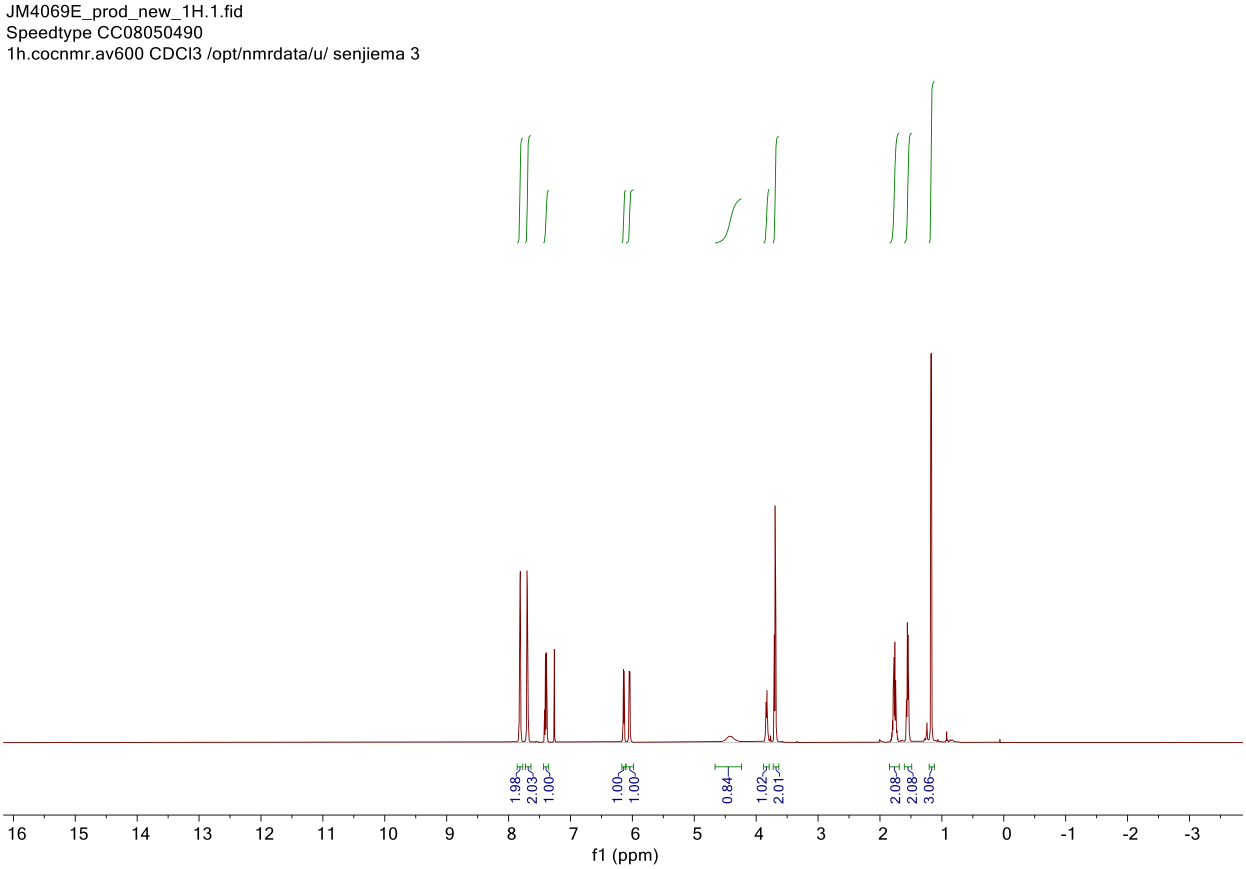
Compound 3hb



^{1}H NMR



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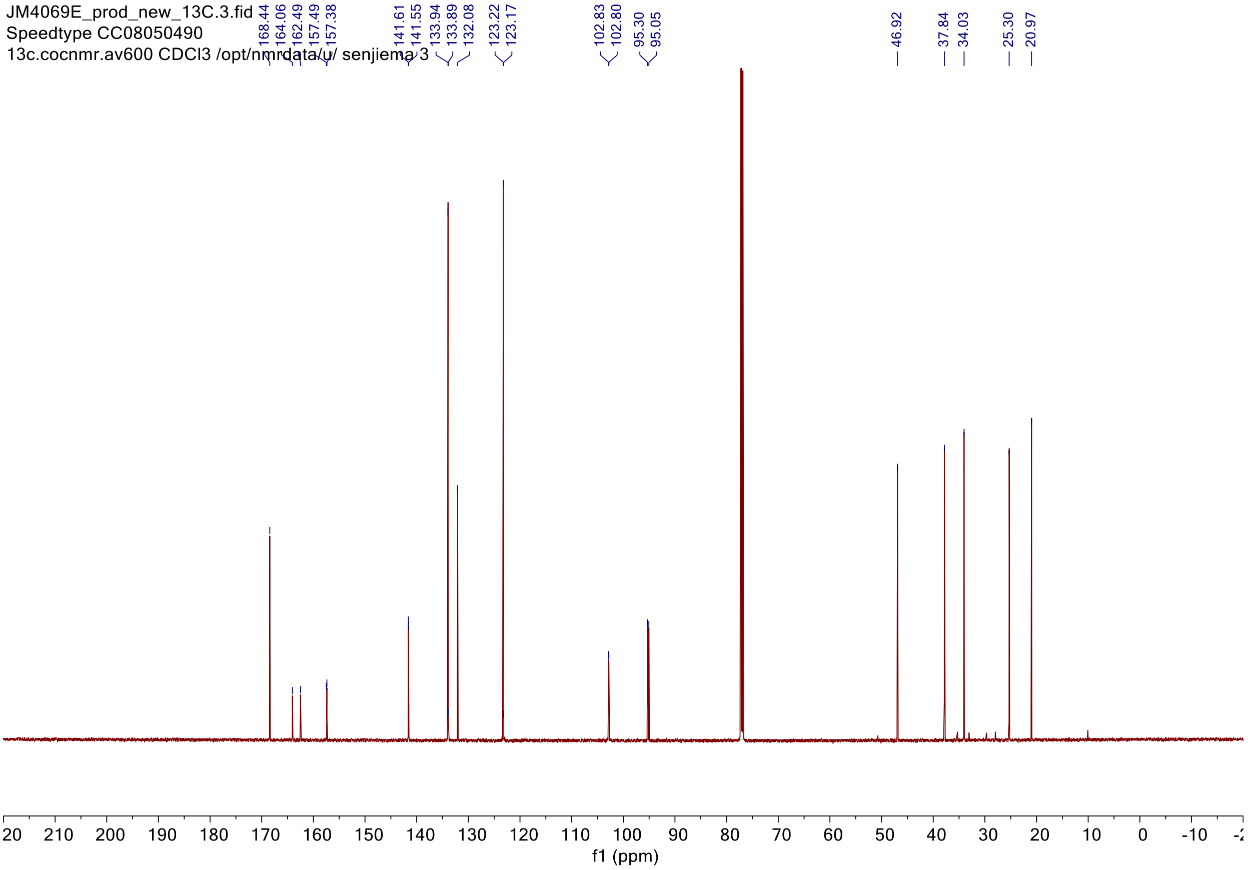
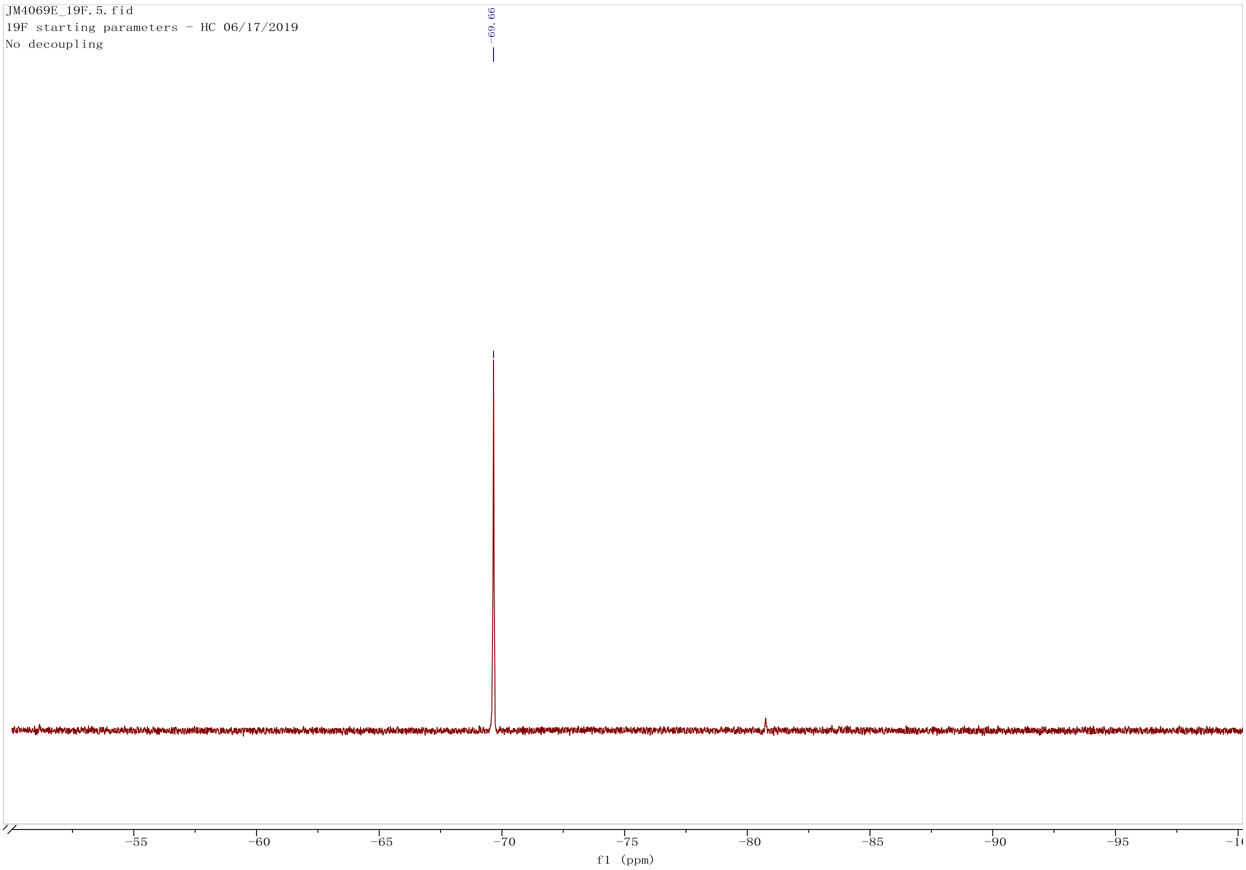
^{13}C NMR

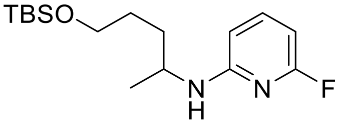


^{19}F NMR

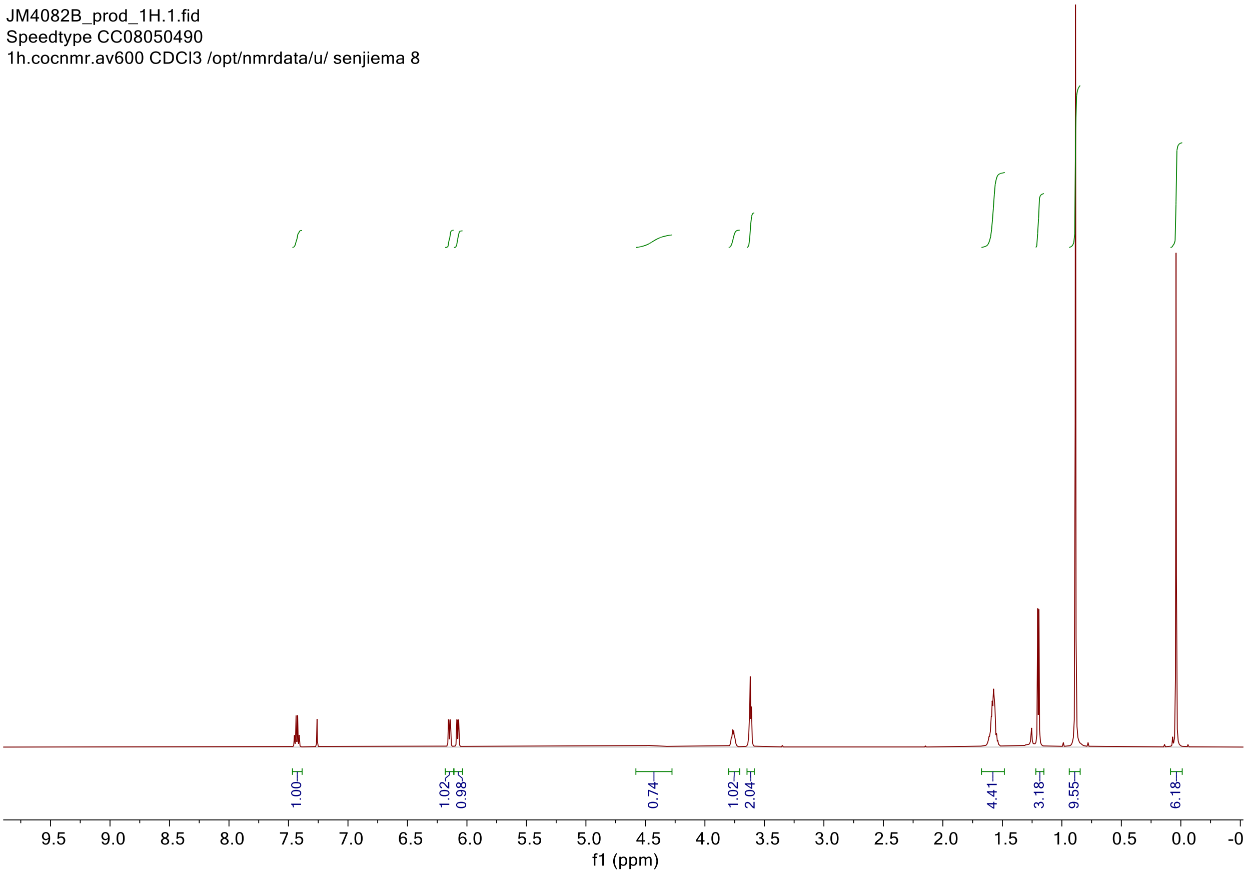

JM4069E_19F.5.fid
19F starting parameters - HC 06/17/2019
No decoupling
−69.66
−55
−60
−65
−70
−75
−80
−85
−90
−95
f1 (ppm)

[*Return to table of contents*]

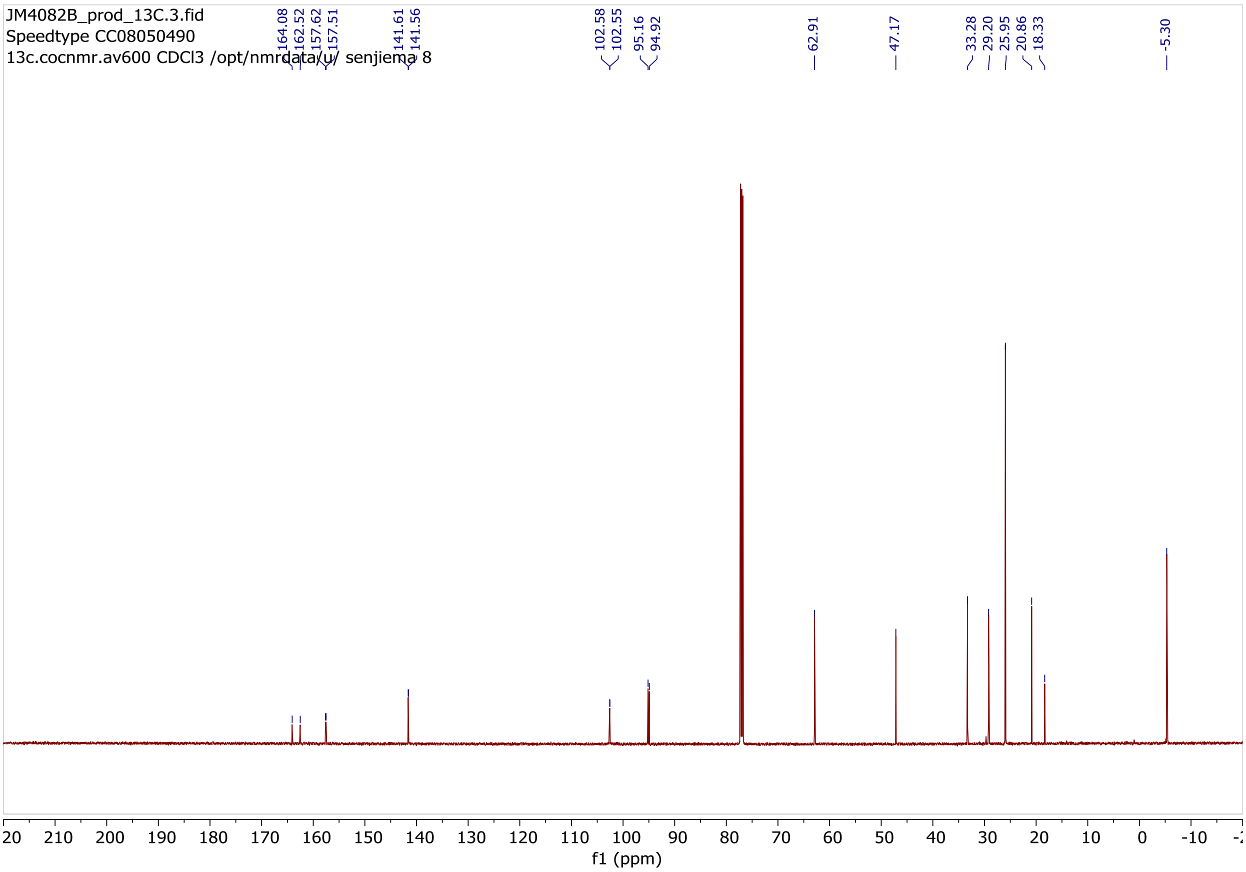
Compound 3ib



^{1}H NMR



^{13}C NMR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162.52
157.62
157.51
141.61
141.56
102.58
102.55
95.16
94.92
62.91
47.17
33.28
29.20
25.95
20.86
18.33
-5.30
20
210
200
190
180
170
160
150
140
130
120
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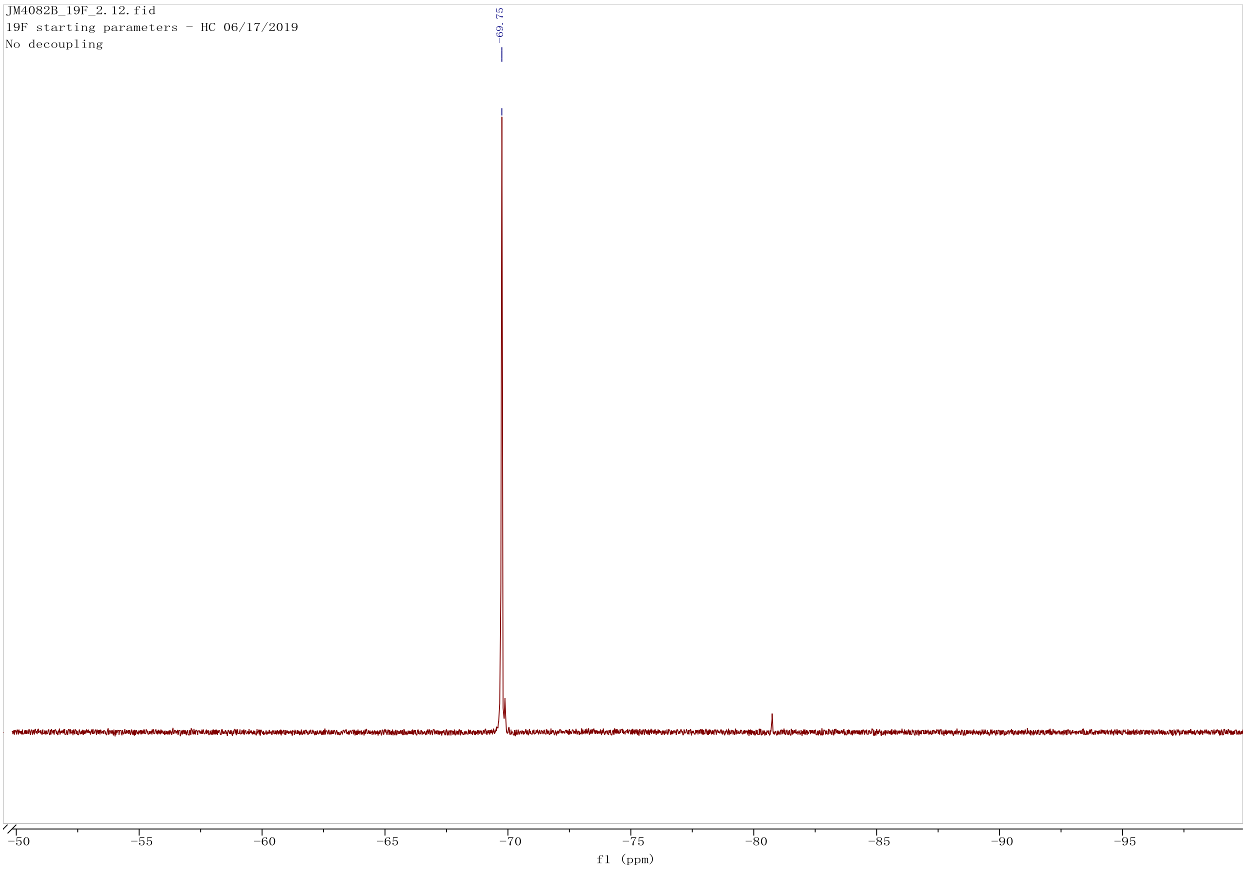
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


JM4082B_19F_2.12.fid
19F starting parameters - HC 06/17/2019
No decoupling
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-60
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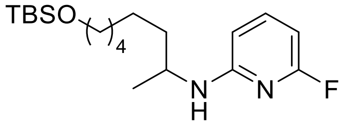
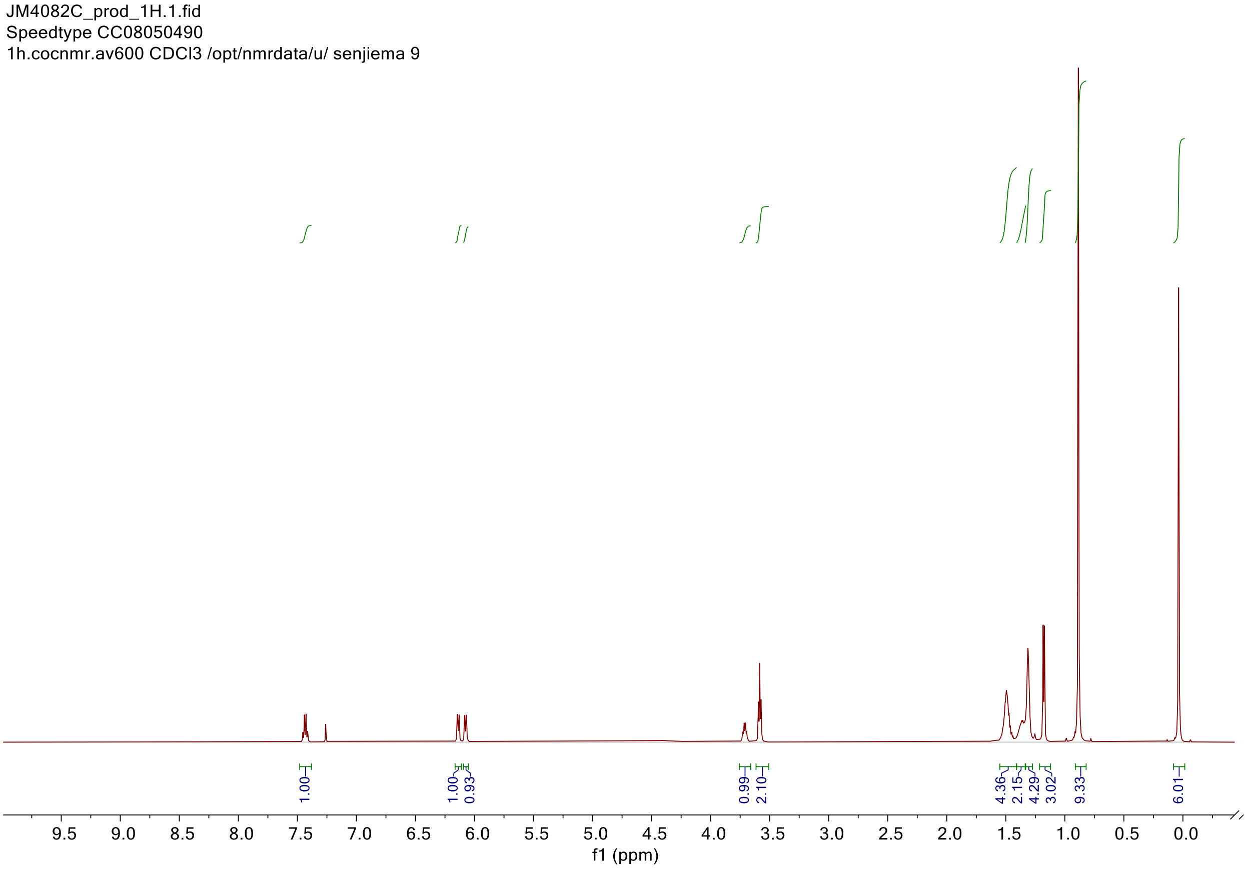
-90
-95
f1 (ppm)

Compound 3jb



^{1}H NMR



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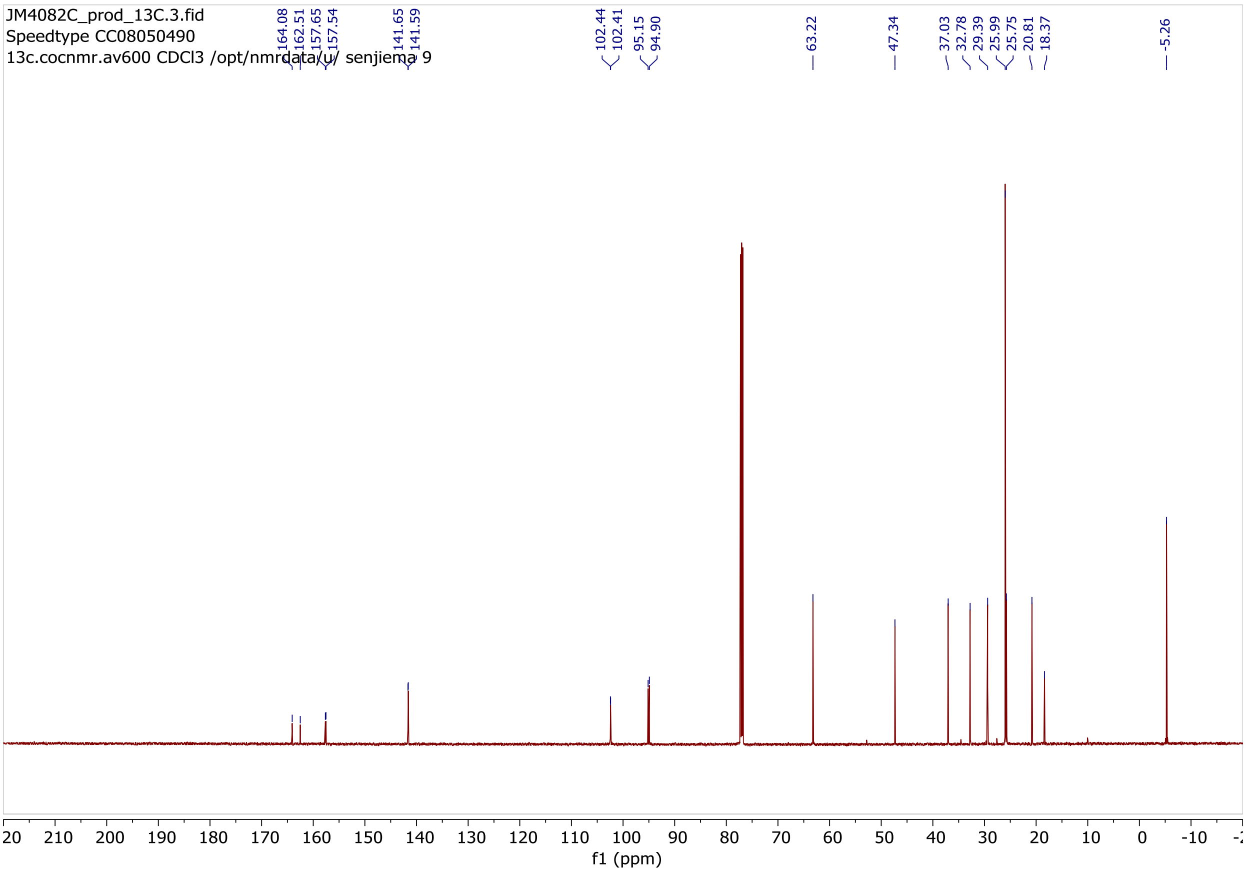
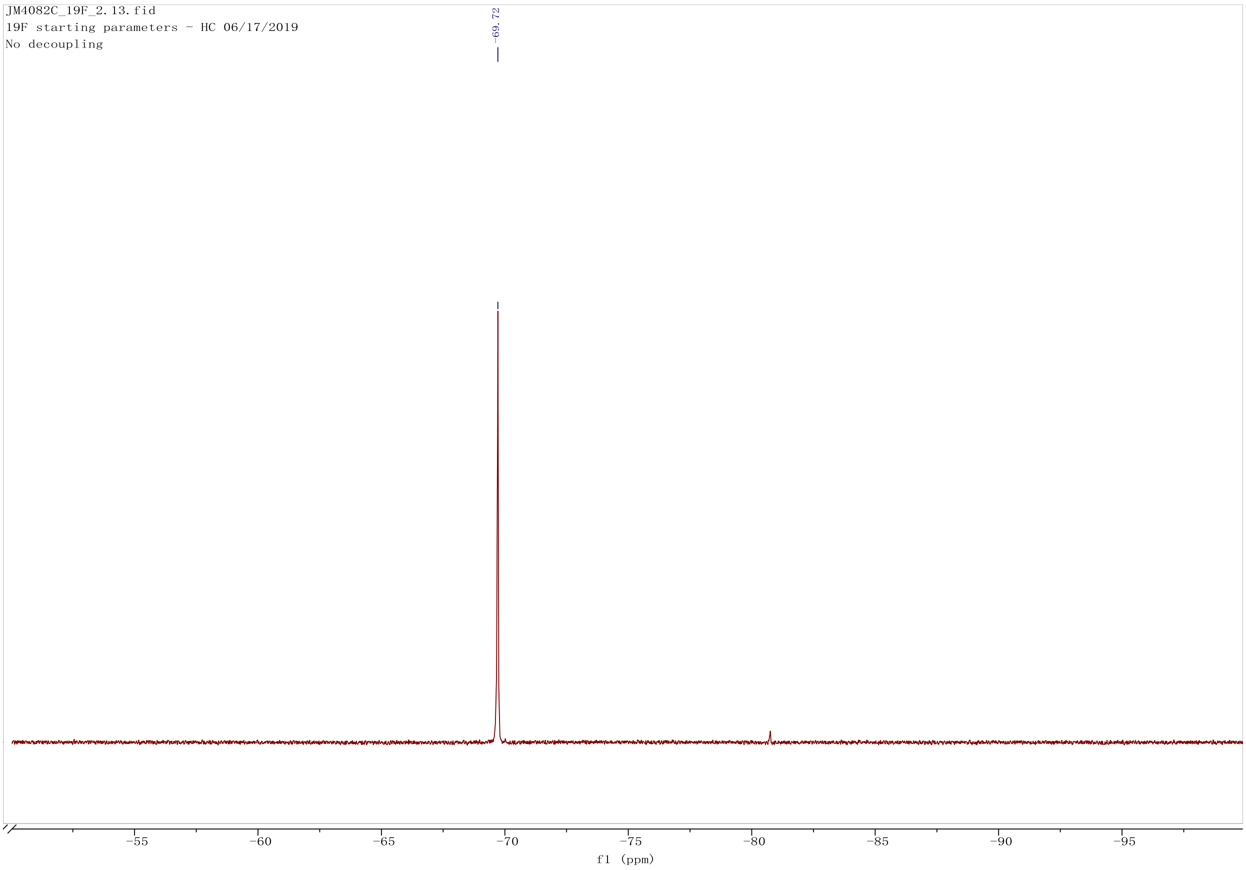
^{13}C NMR



^{19}F NMR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-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

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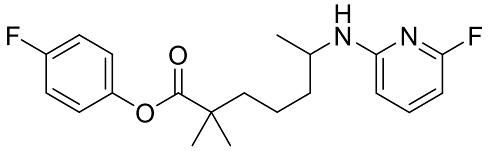
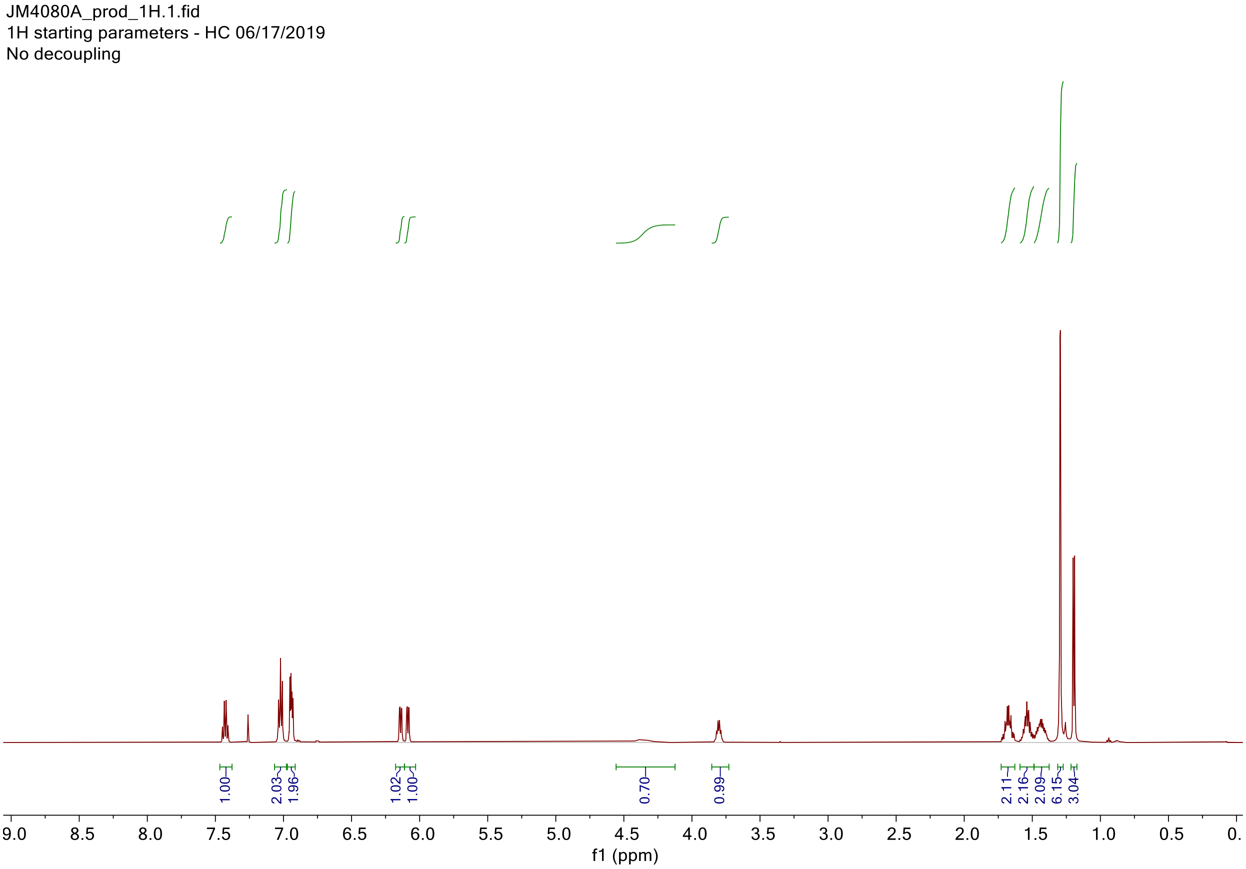
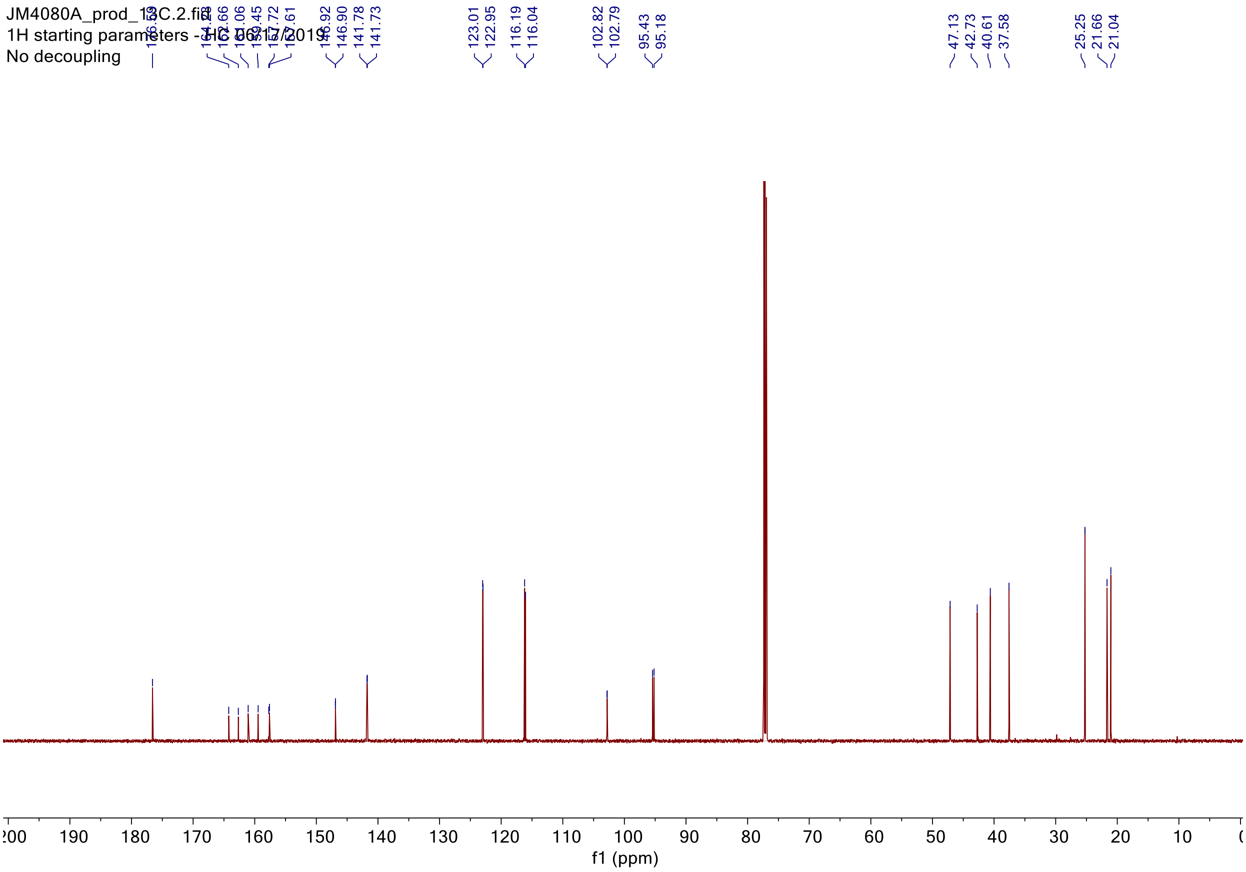
Compound 3kb



^{1}H NMR



^{13}C NMR


JM4080A_prod_13C.2.fid
1H starting parameters - HC 06/17/2019
No decoupling
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162.66
161.06
159.45
157.72
157.61
146.92
146.90
141.78
141.73
123.01
122.95
116.19
116.04
102.82
102.79
95.43
95.18
47.13
42.73
40.61
37.58
25.25
21.66
21.04
200
190
180
170
160
150
140
130
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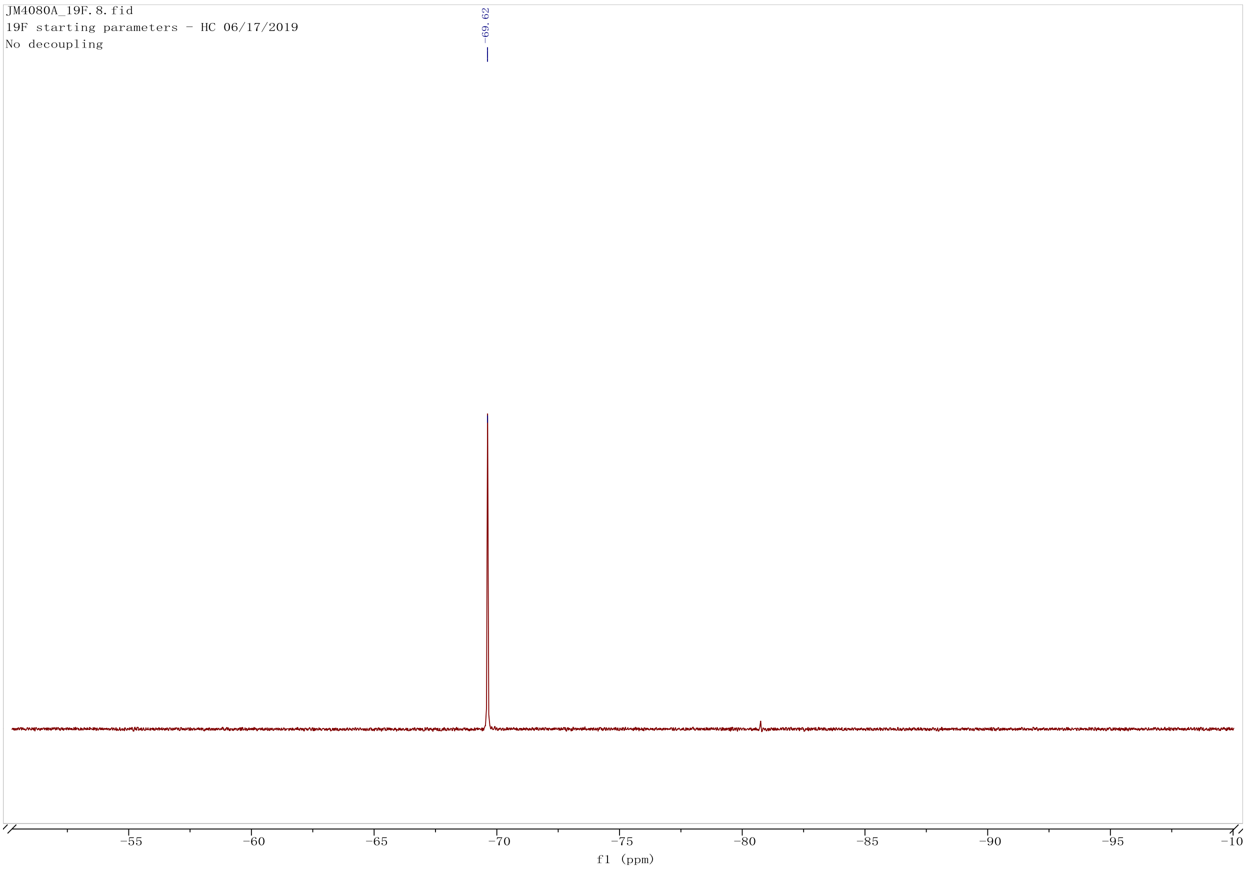
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR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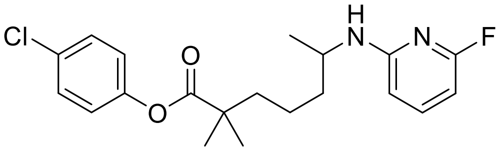
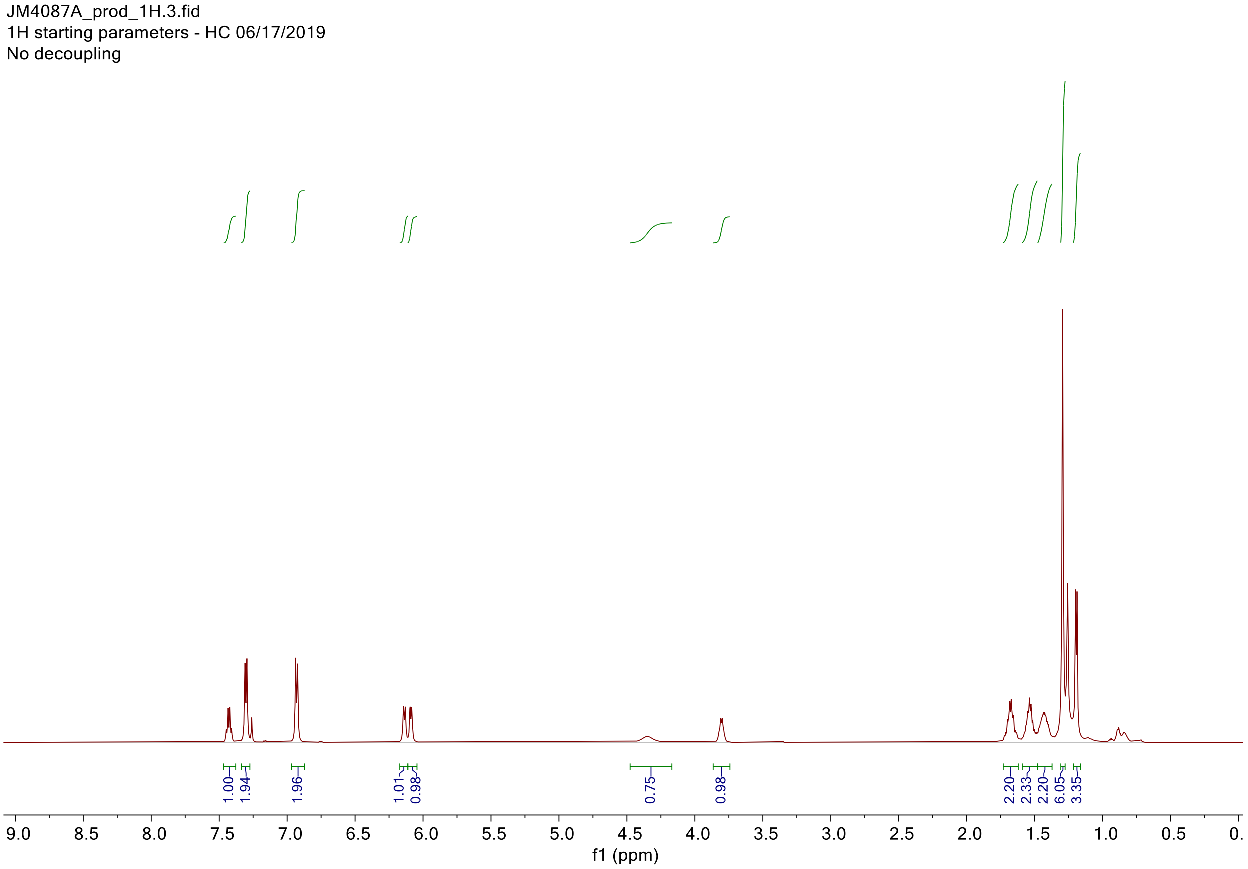
-85
-90
-95
-10
f1 (ppm)

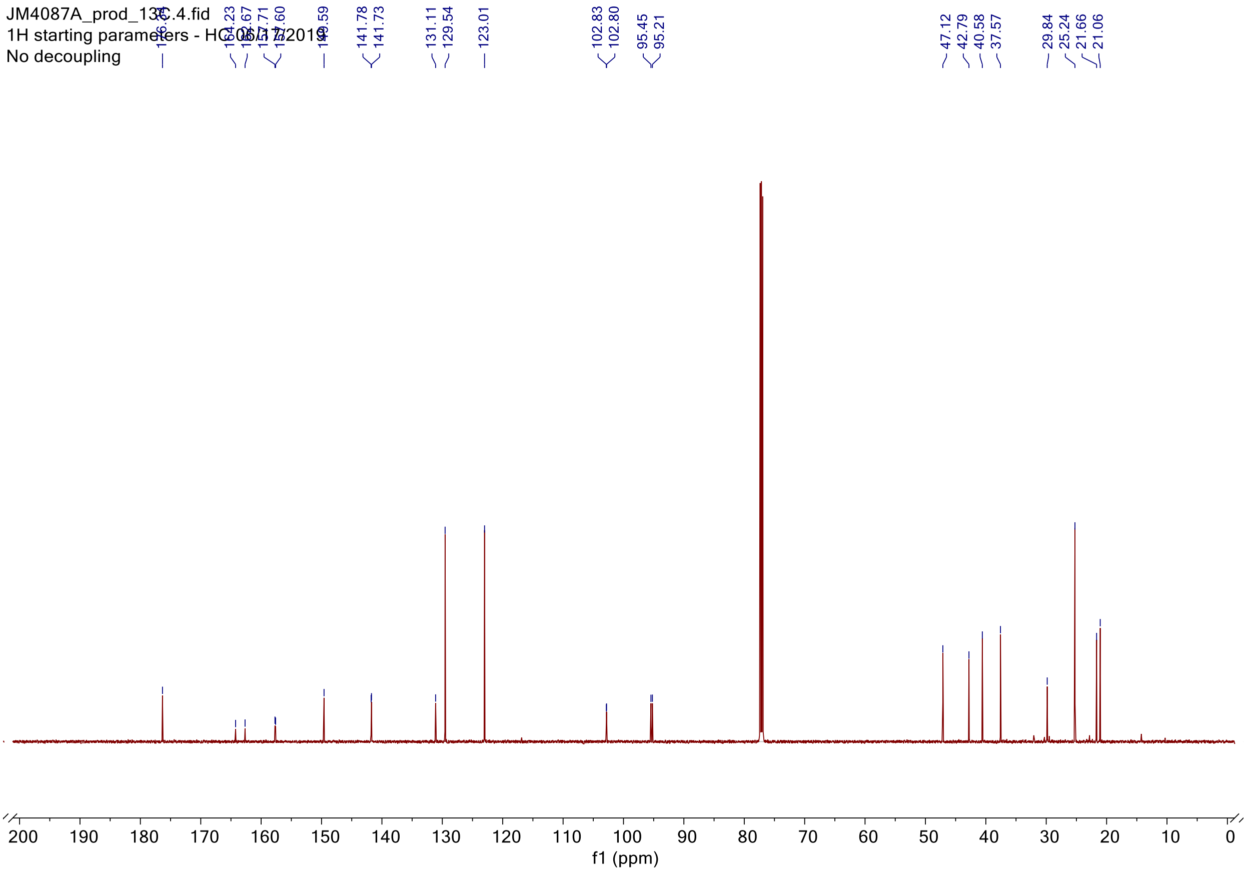
Compound 3lb



^{1}H NMR



^{13}C NMR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No decoupling
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141.78
141.73
131.11
129.54
123.01
102.83
102.80
95.45
95.21
47.12
42.79
40.58
37.57
29.84
25.24
21.66
21.06
200
190
180
170
160
150
140
130
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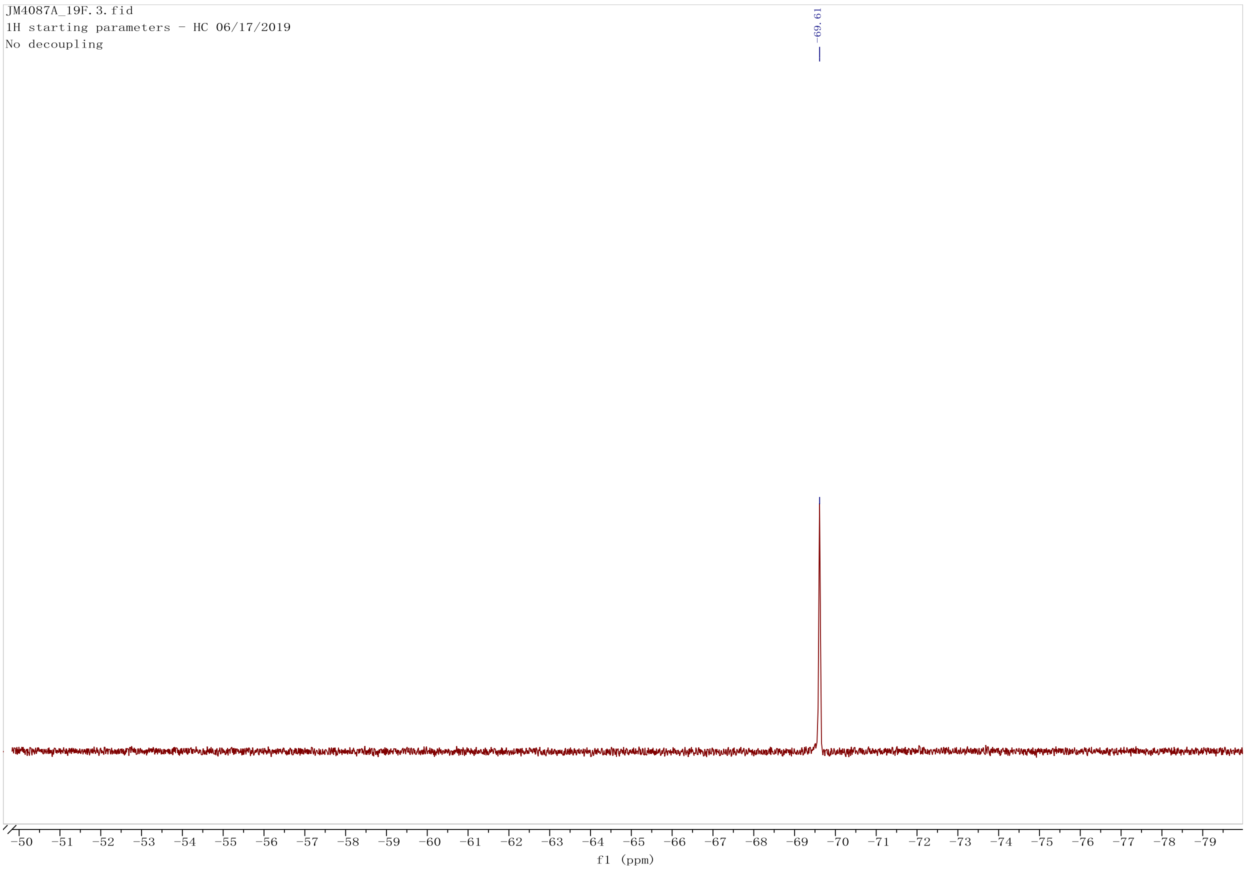
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{19}F NMR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No decoupling
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-51
-52
-53
-54
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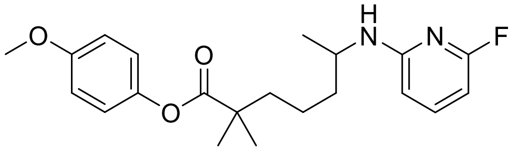
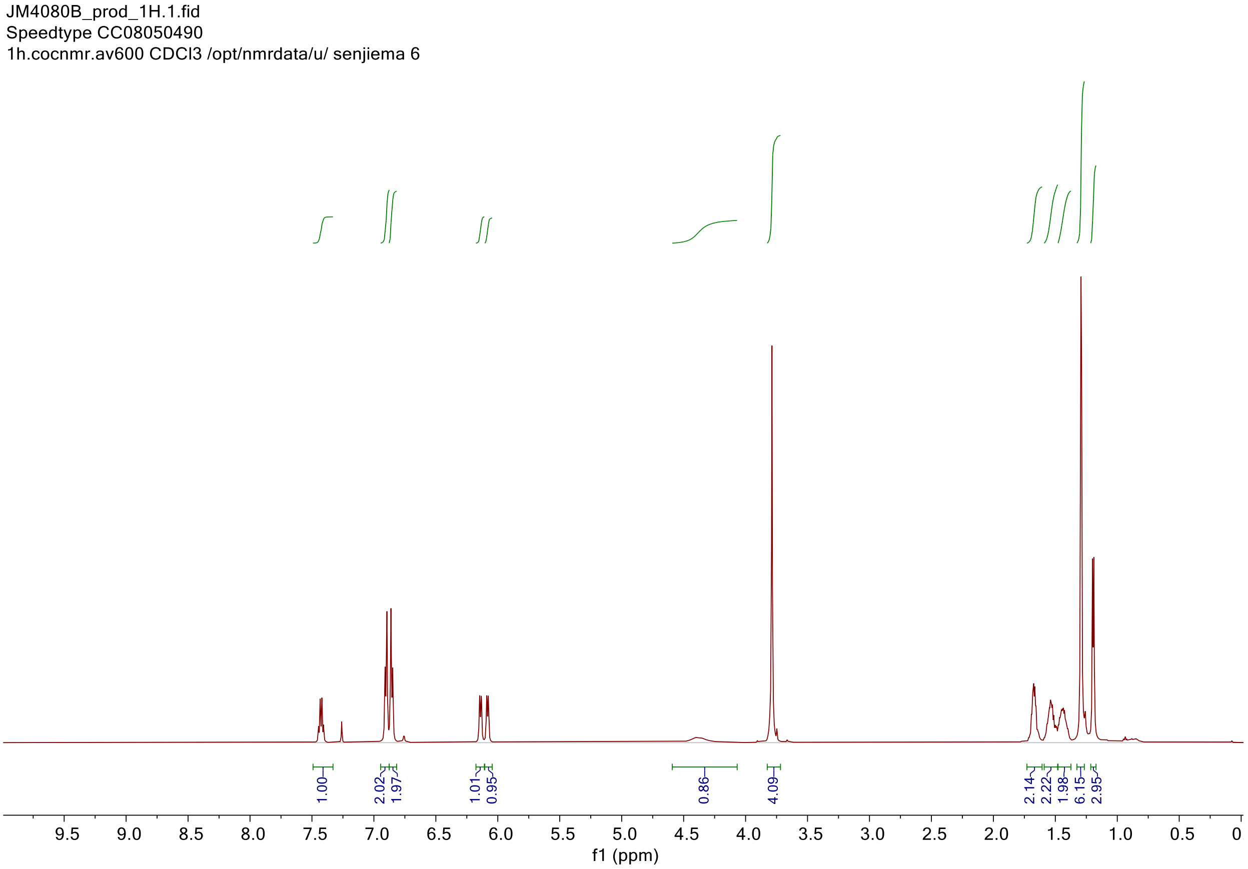
-60
-61
-62
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
f1 (ppm)

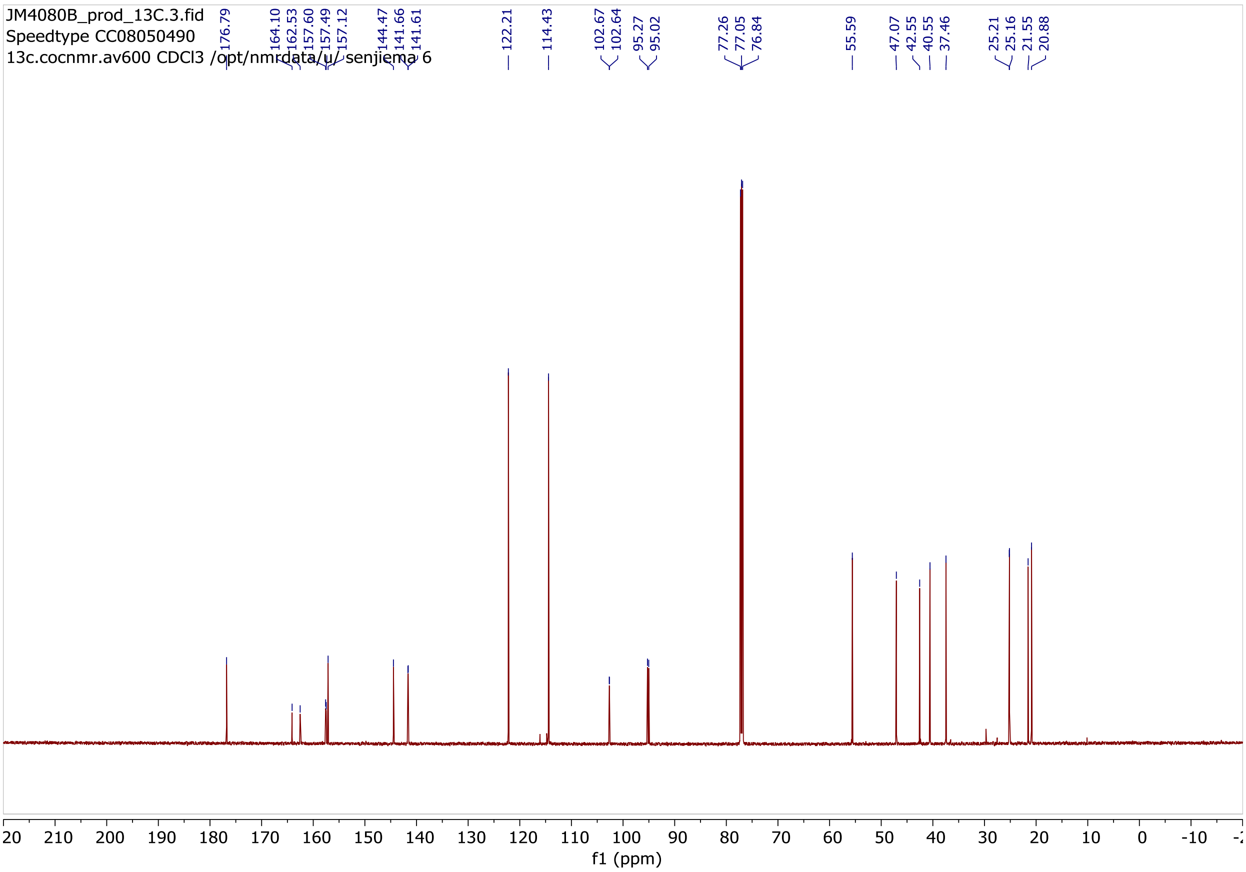
Compound 3mb



^{1}H NMR



^{13}C NMR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164.10
162.53
157.60
157.49
157.12
144.47
141.66
141.61
122.21
114.43
102.67
102.64
95.27
95.02
77.26
77.05
76.84
55.59
47.07
42.55
40.55
37.46
25.21
25.16
21.55
20.88
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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20
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0
-10
f1 (ppm)

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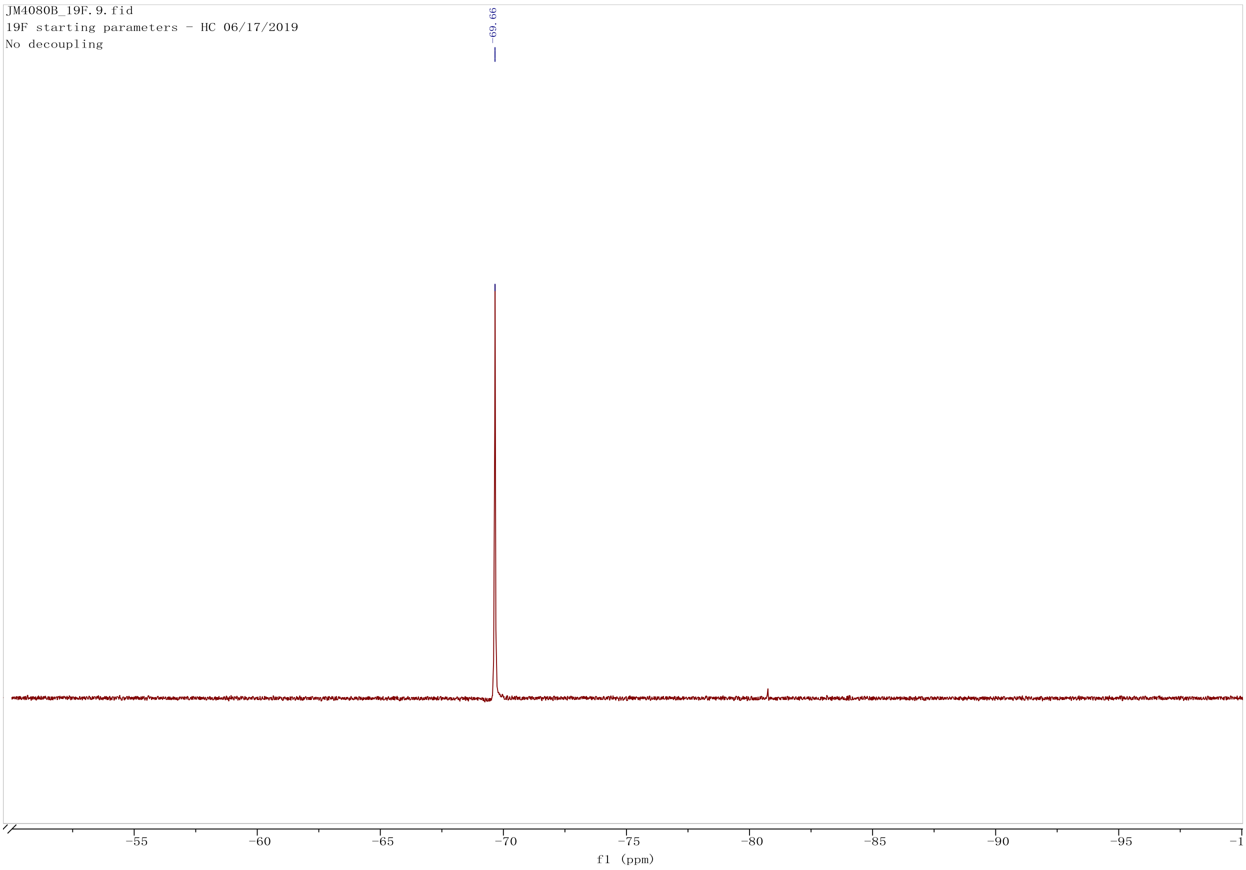
^{19}F NMR



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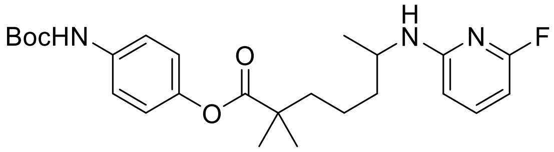
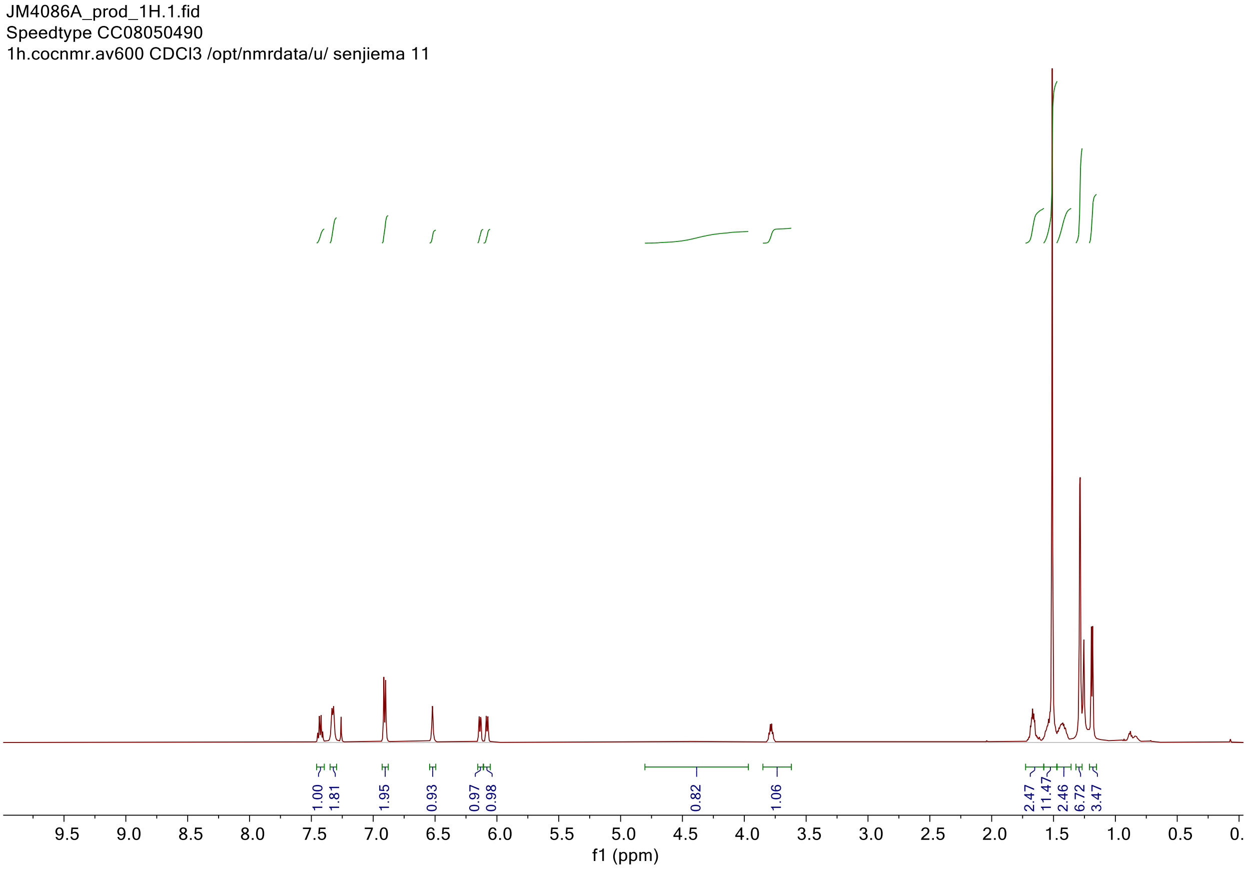
Compound 3nb



^{1}H NMR



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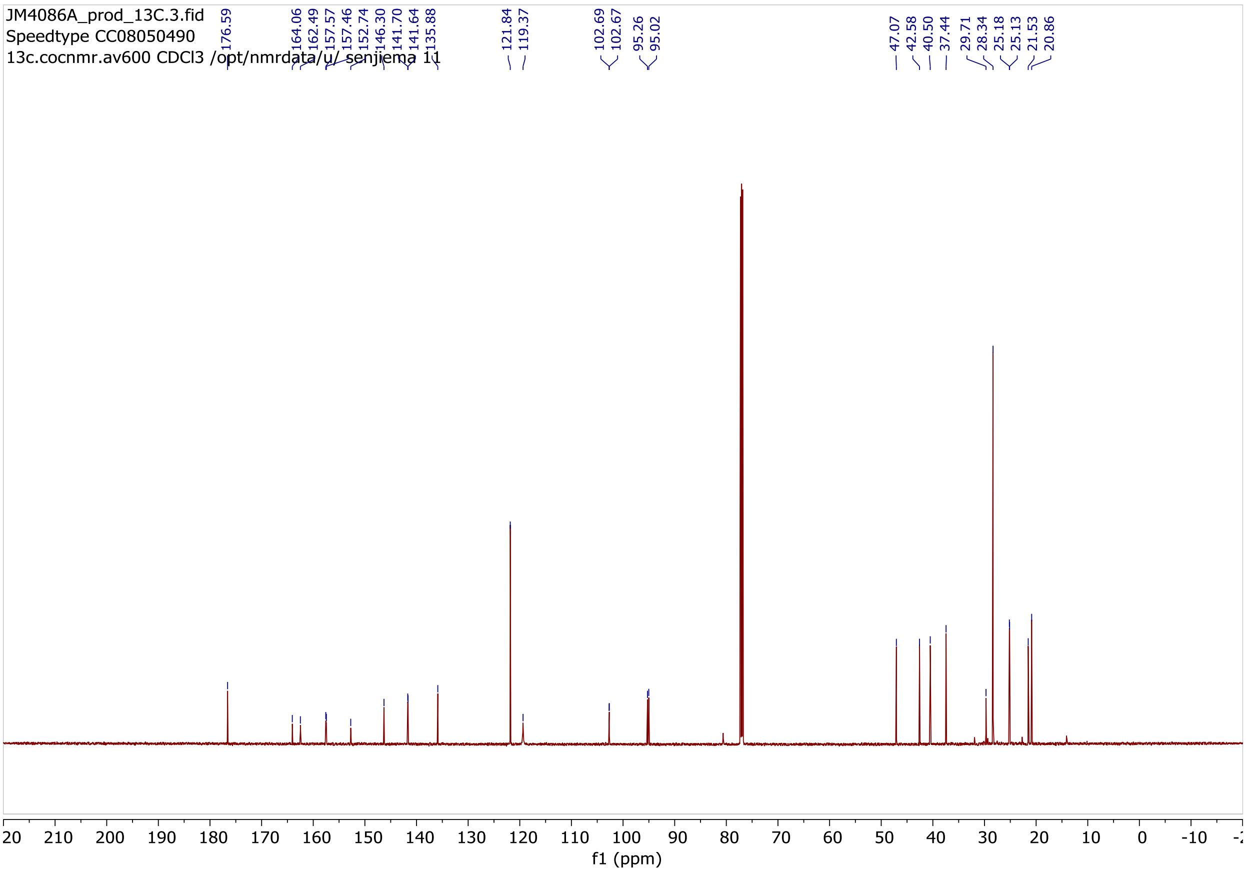
1^3C NMR



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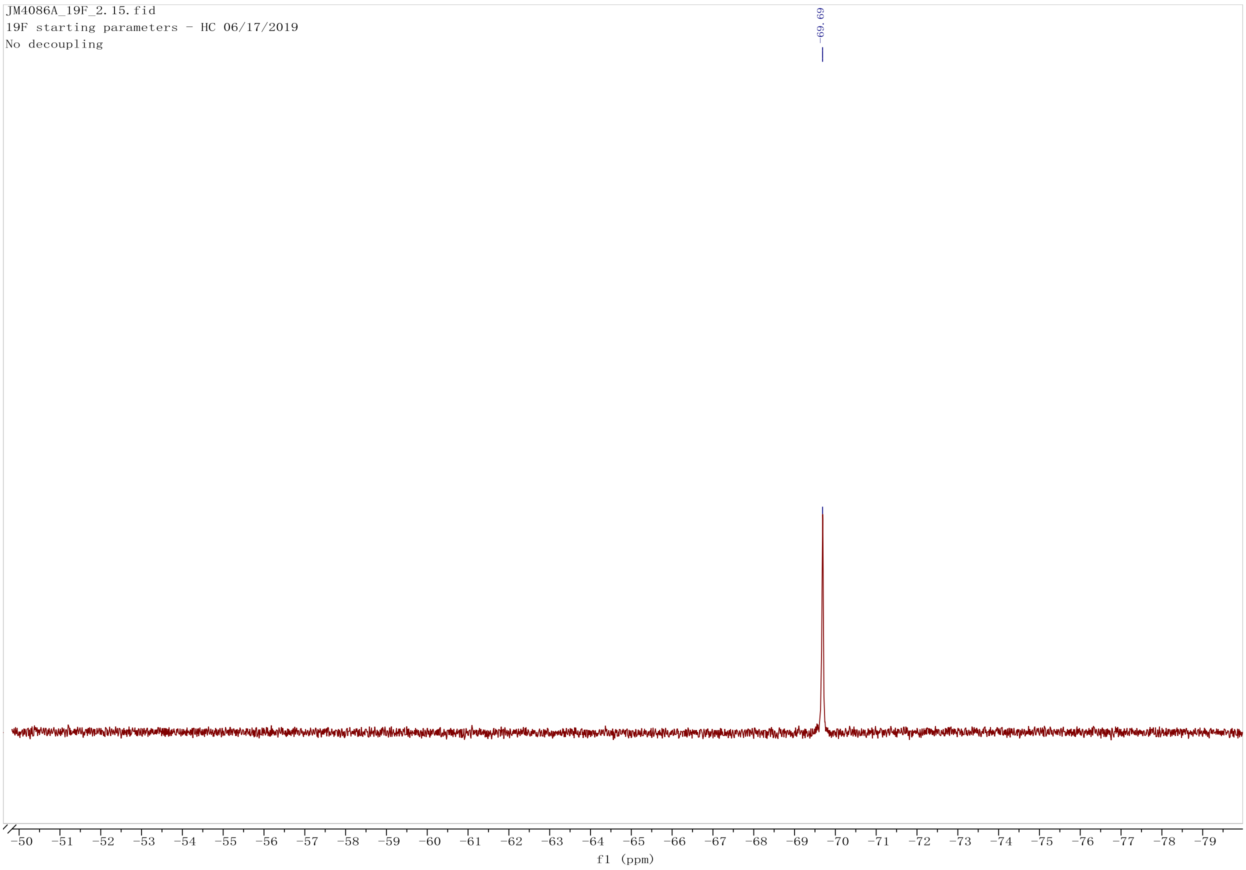
^{19}F NMR



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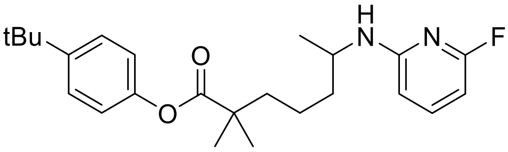
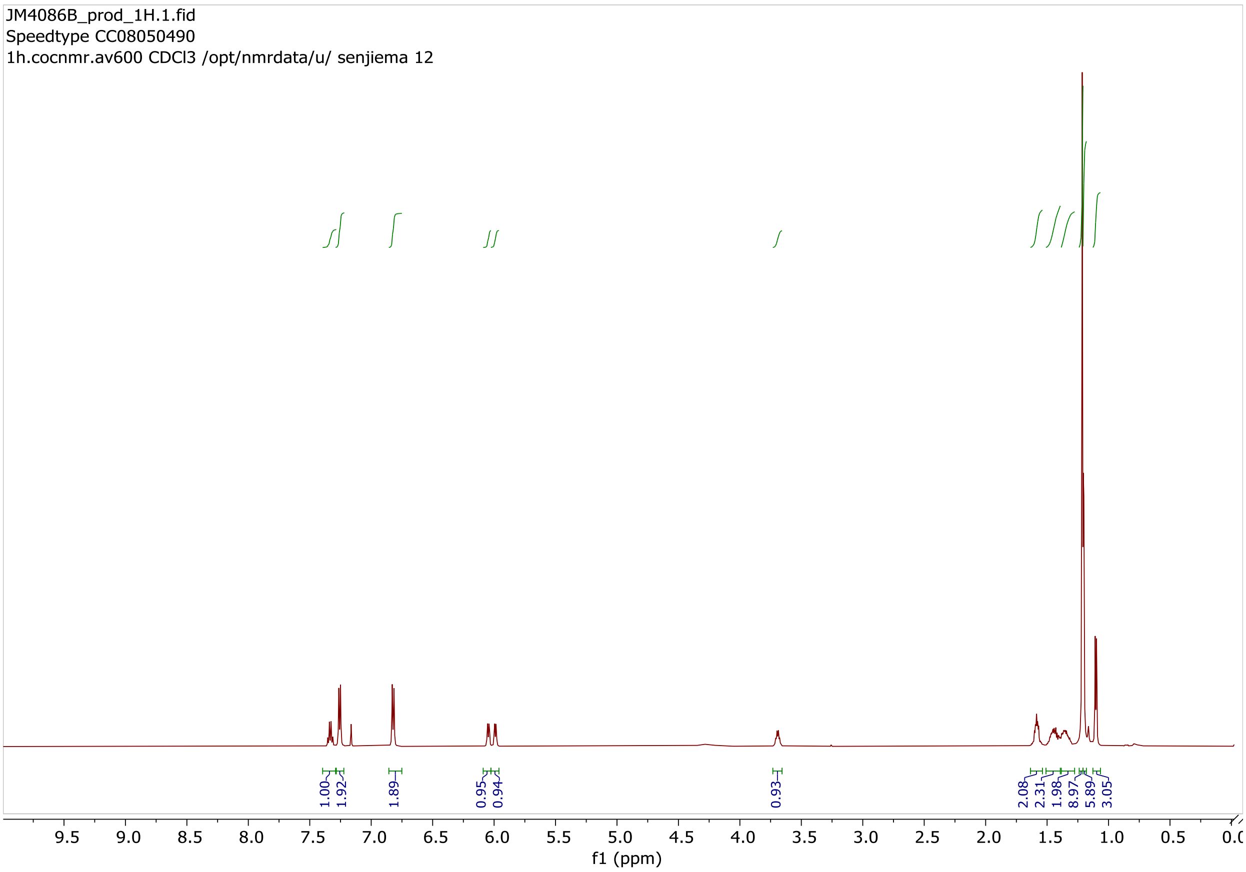
Compound 3ob



^{1}H NMR



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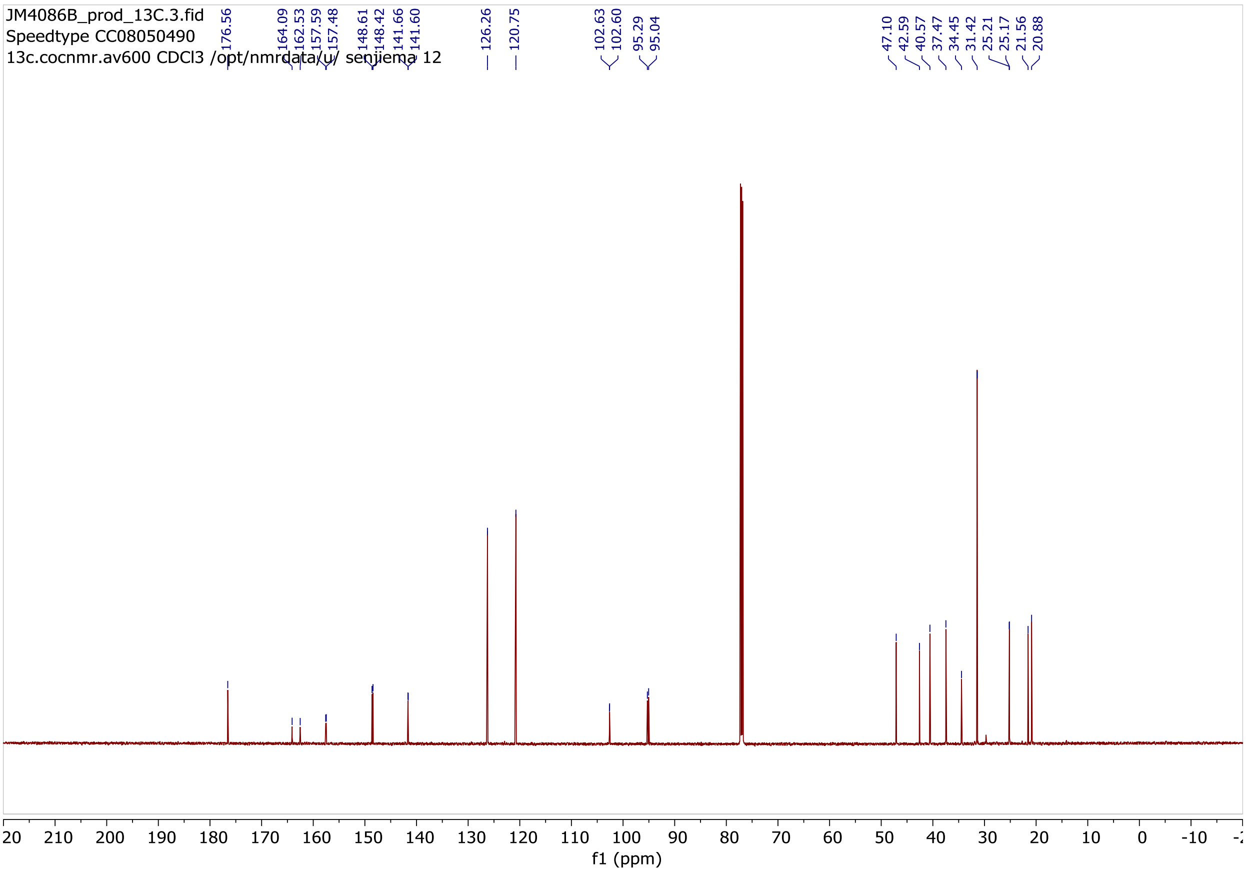
^{13}C NMR



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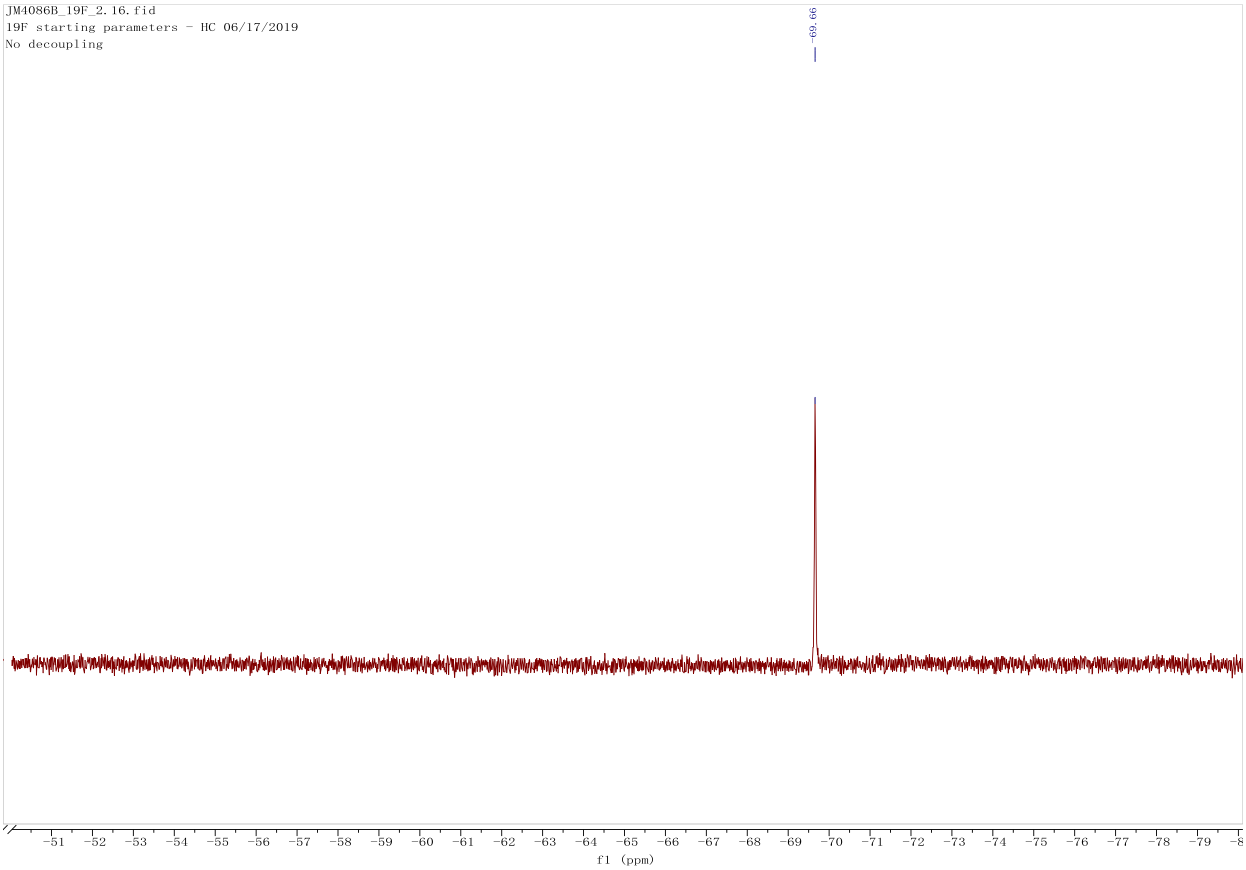
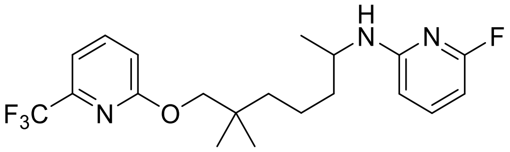
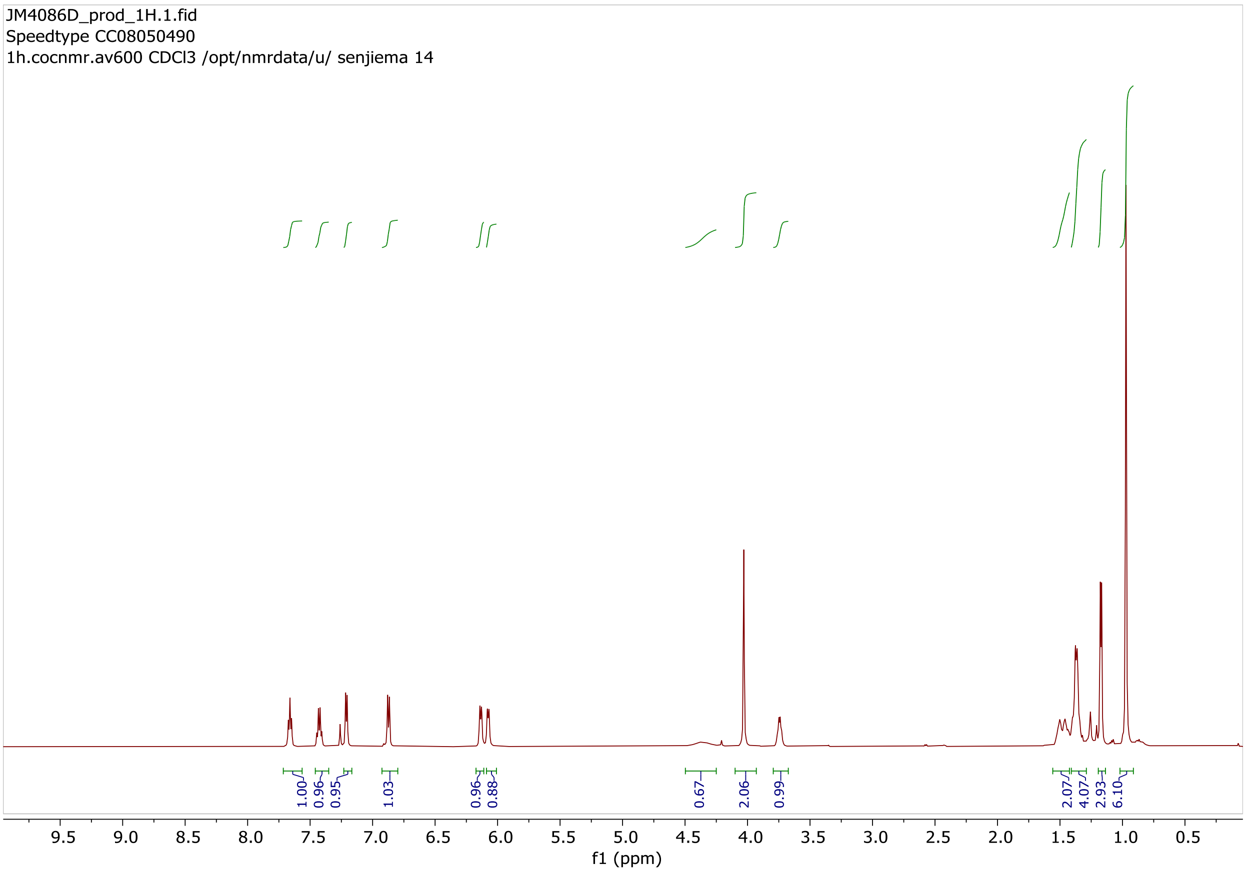
^{19}F NMR



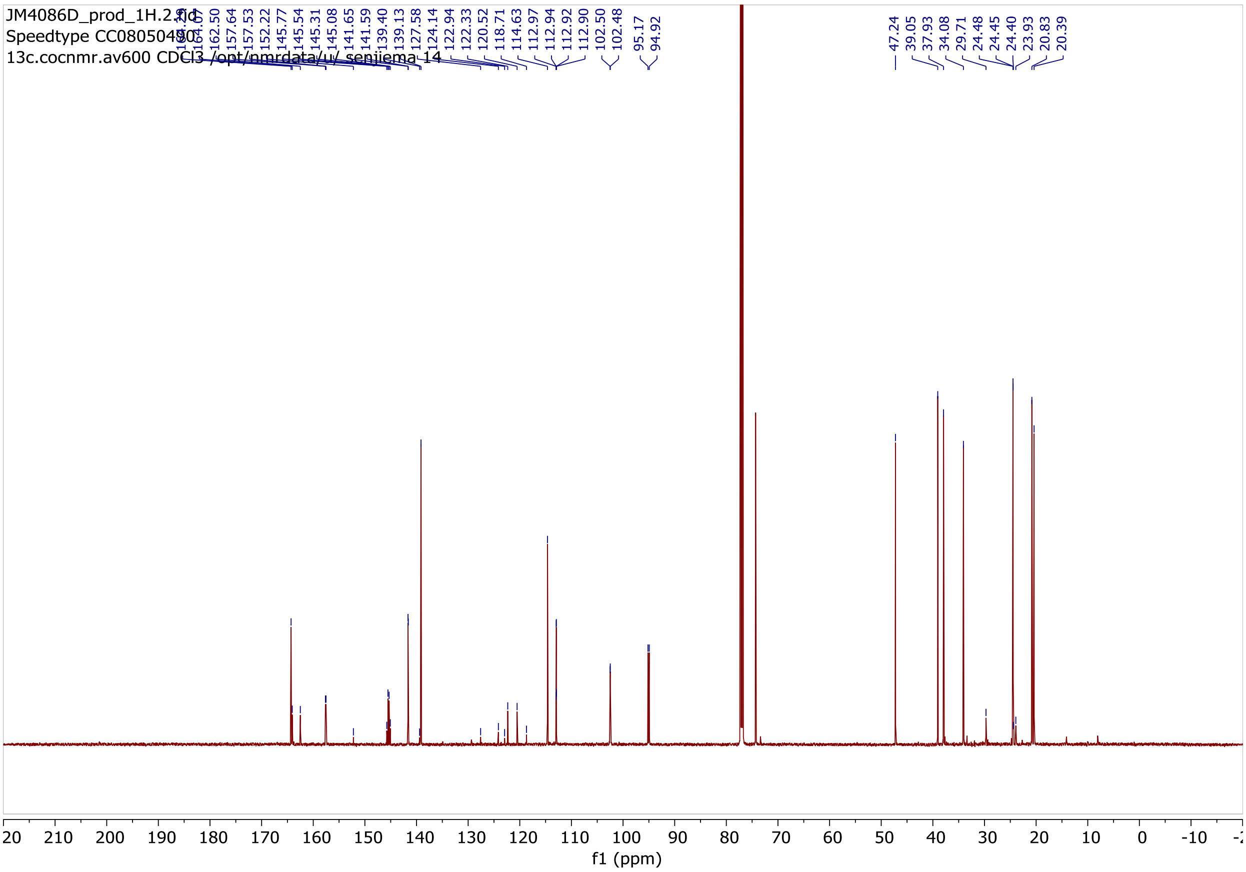
Compound 3pb



^{1}H NMR



^{13}C NMR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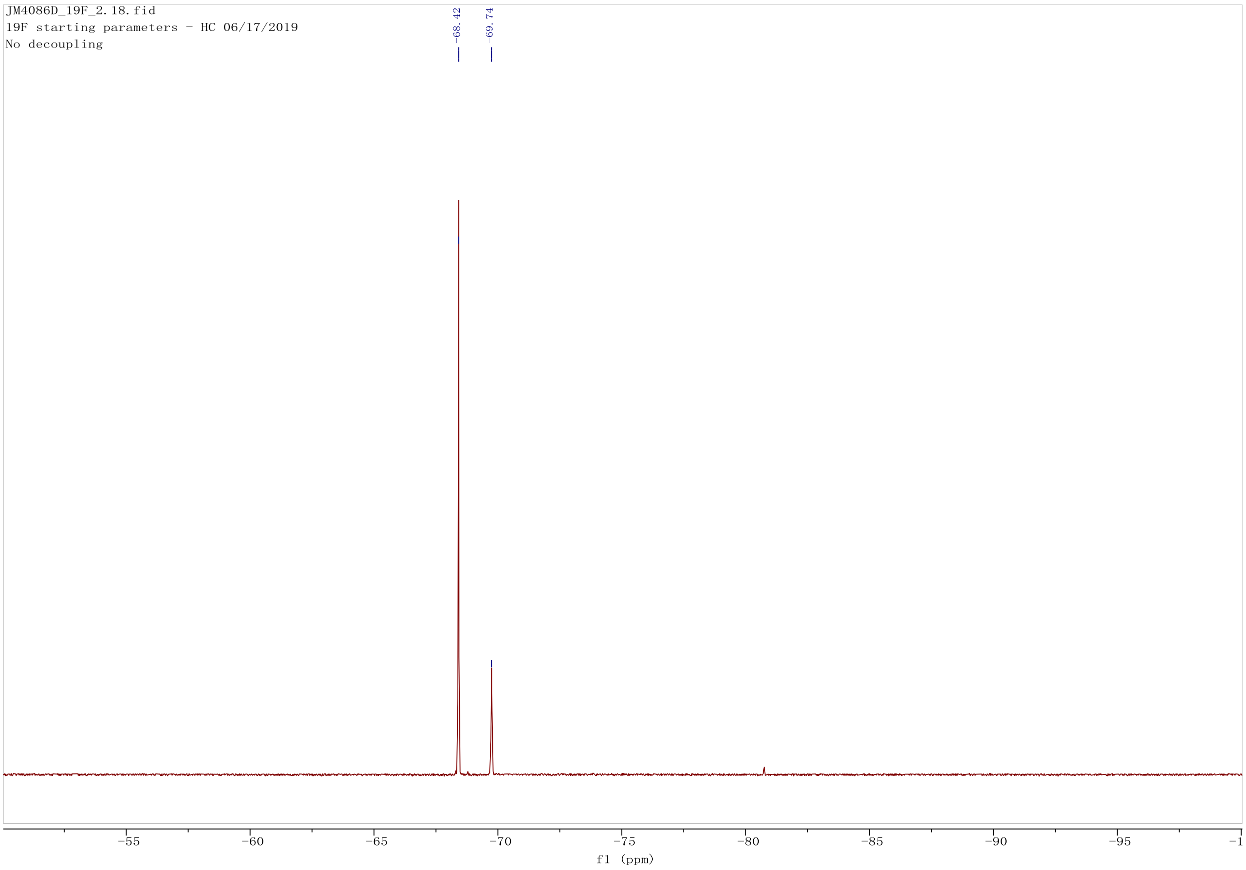
162.50
157.64
157.53
152.22
145.77
145.54
145.31
145.08
141.65
141.59
139.40
139.13
127.58
124.14
122.94
122.33
120.52
118.71
114.63
112.97
112.94
112.92
112.90
102.50
102.48
95.17
94.92
47.24
39.05
37.93
34.08
29.71
24.48
24.45
24.40
23.93
20.83
20.39
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR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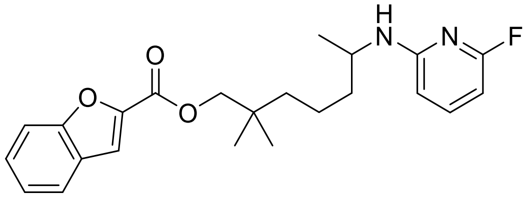
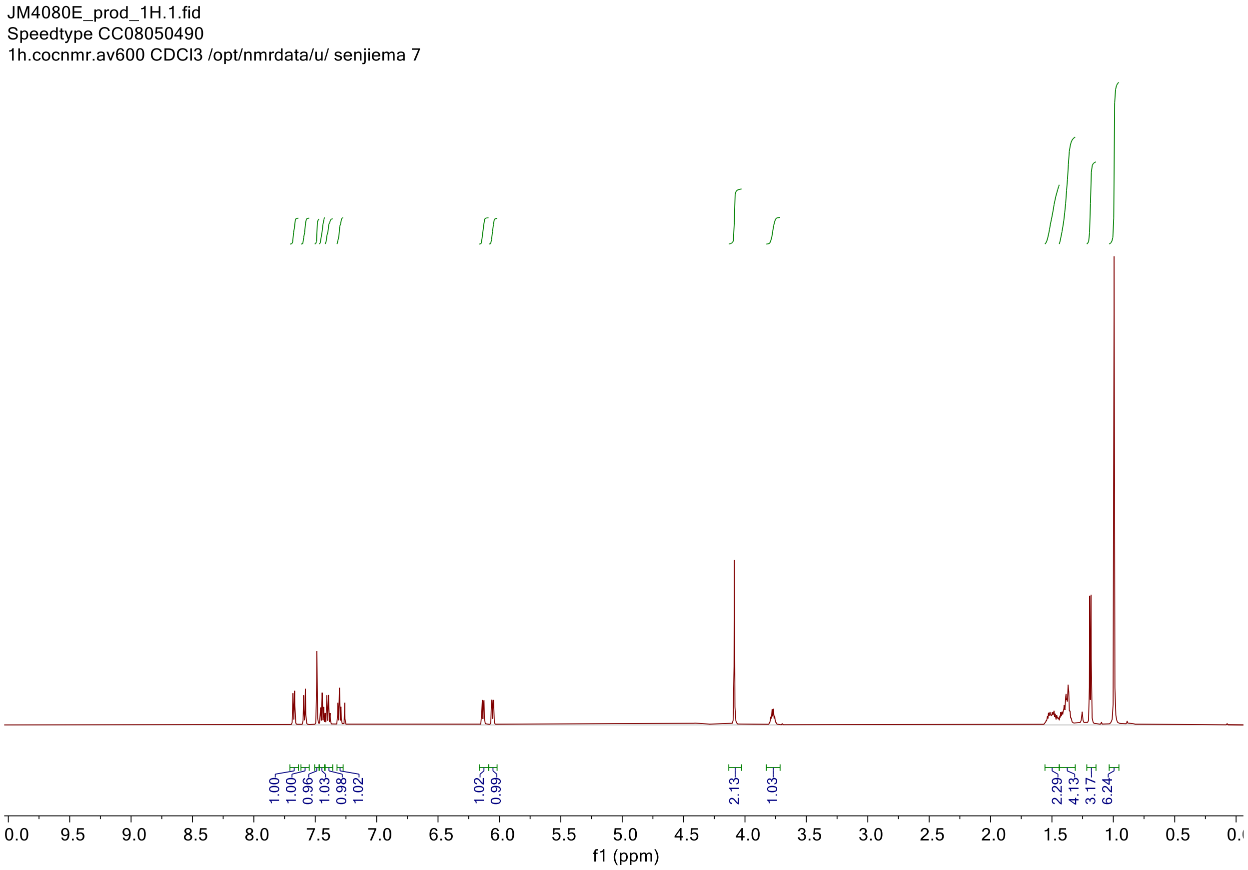
-70
-75
-80
-85
-90
-95
-1
f1 (ppm)

Compound 3qb



^{1}H NMR



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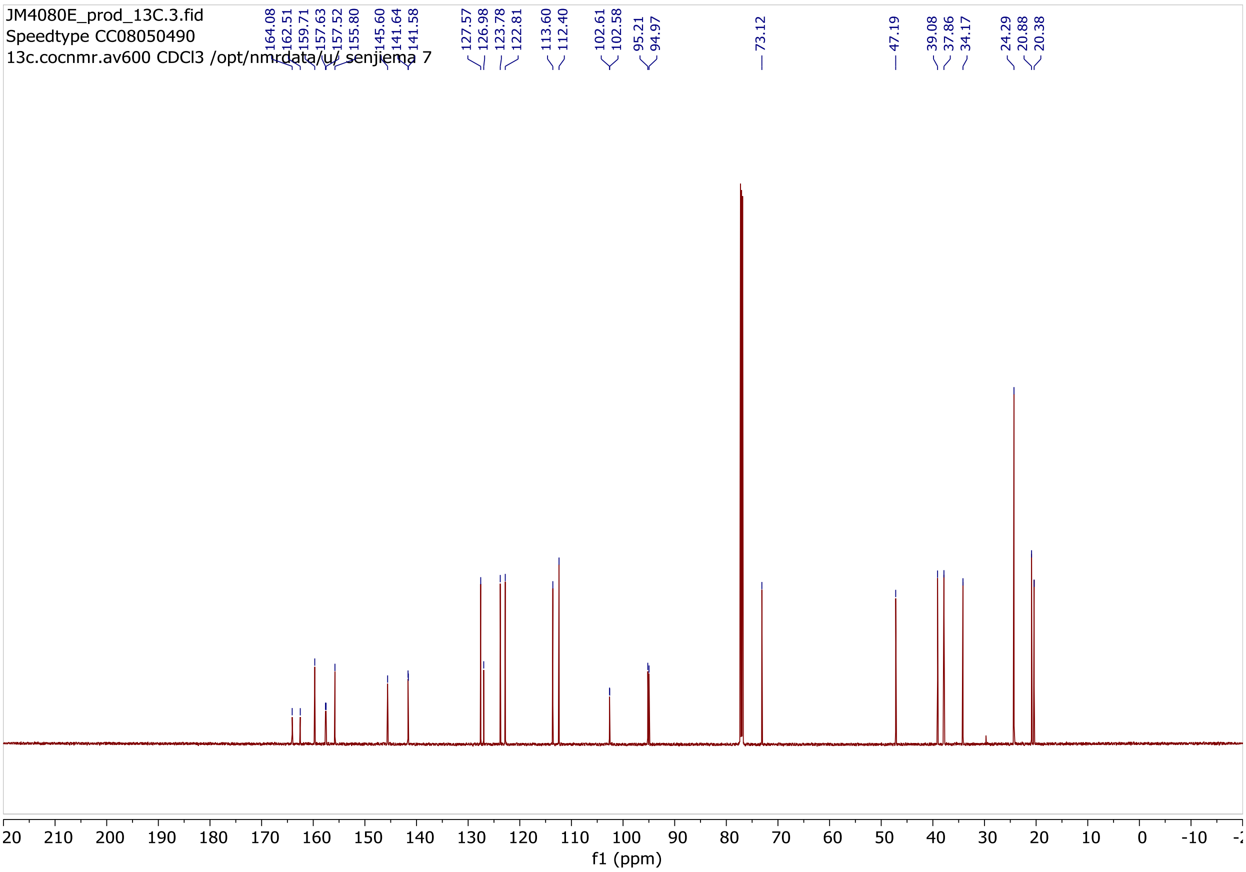
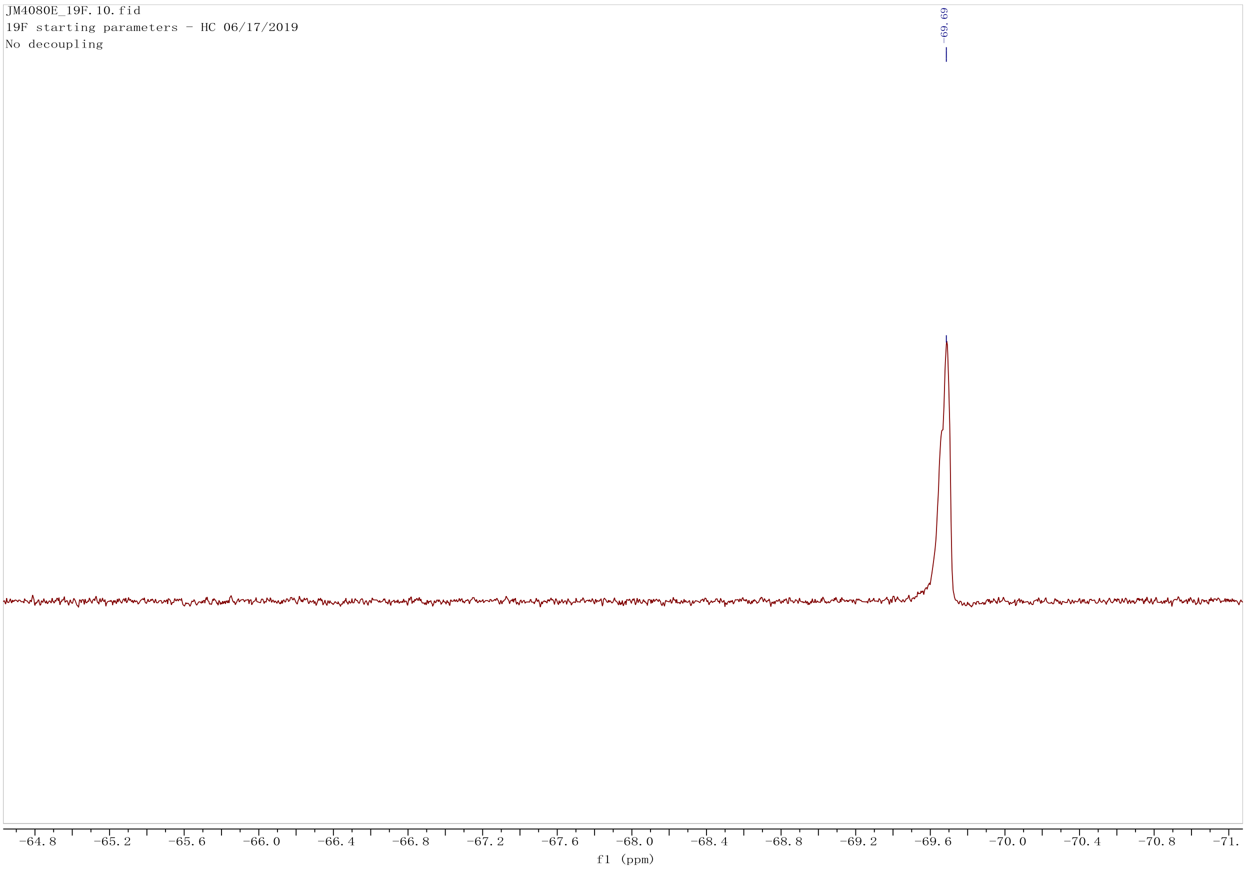
^{13}C NMR



^{19}F NMR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19F starting parameters - HC 06/17/2019
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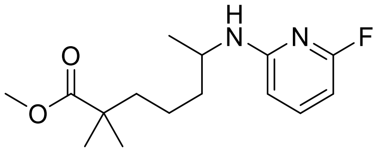
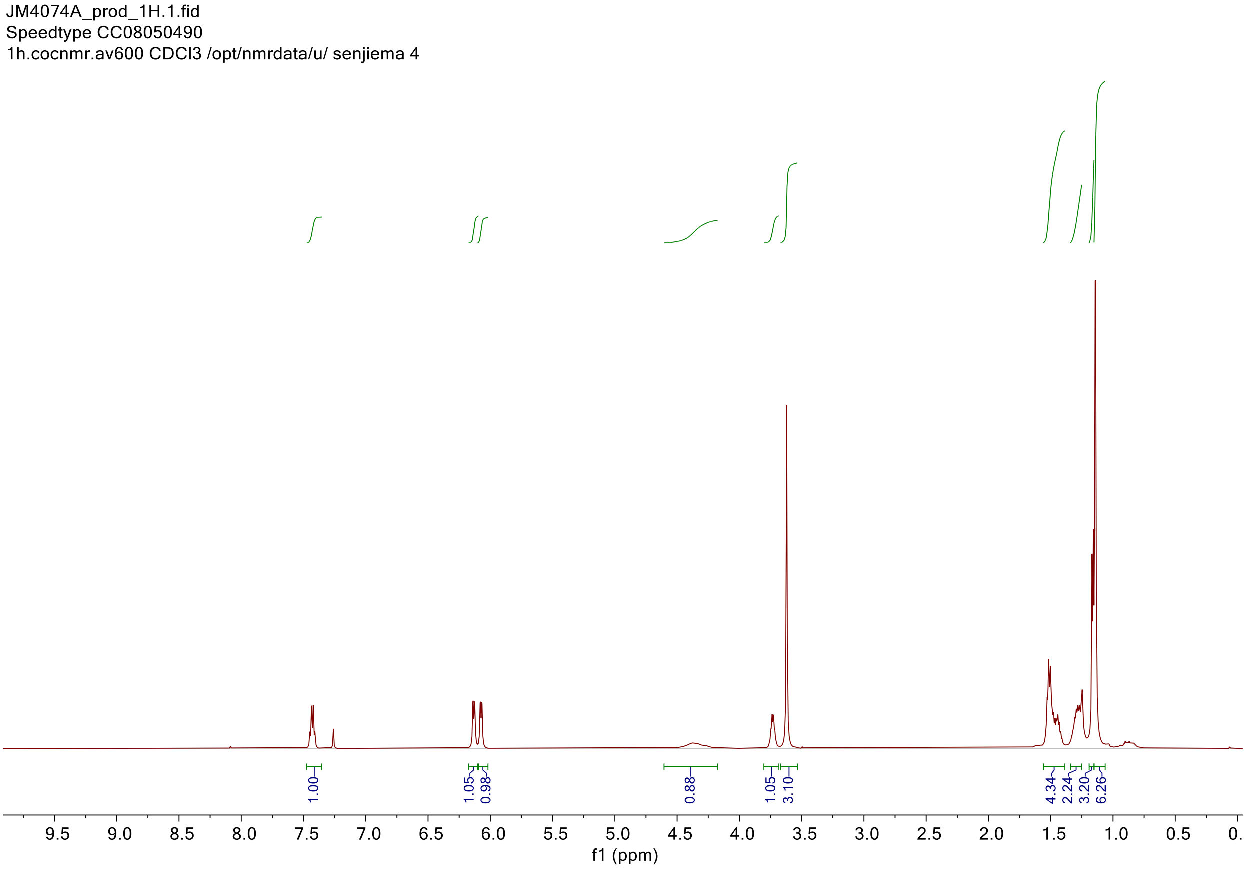
-65.6
-66.0
-66.4
-66.8
-67.2
-67.6
-68.0
-68.4
-68.8
-69.2
-69.6
-70.0
-70.4
-70.8
-71.
f1 (ppm)

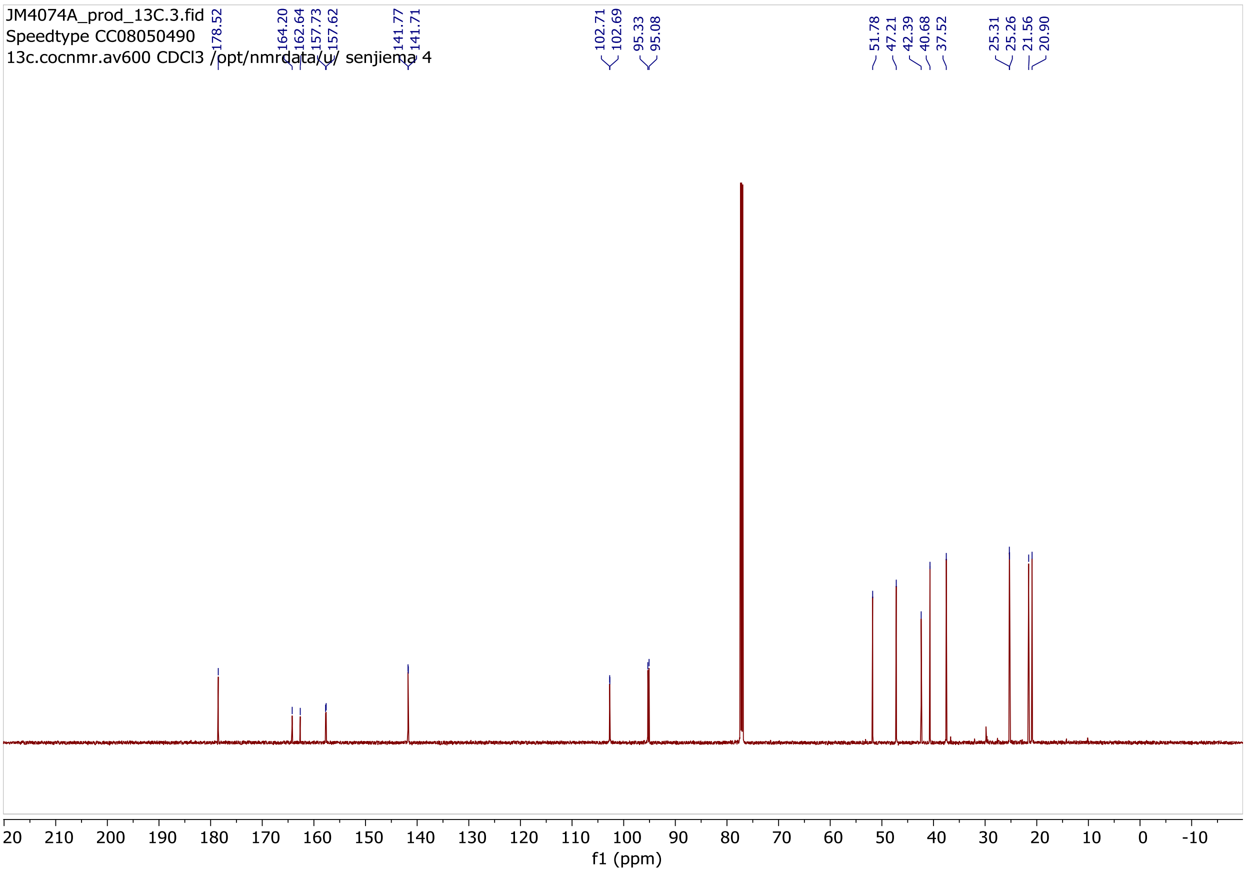
Compound 3rb



^{1}H NMR



^{13}C NMR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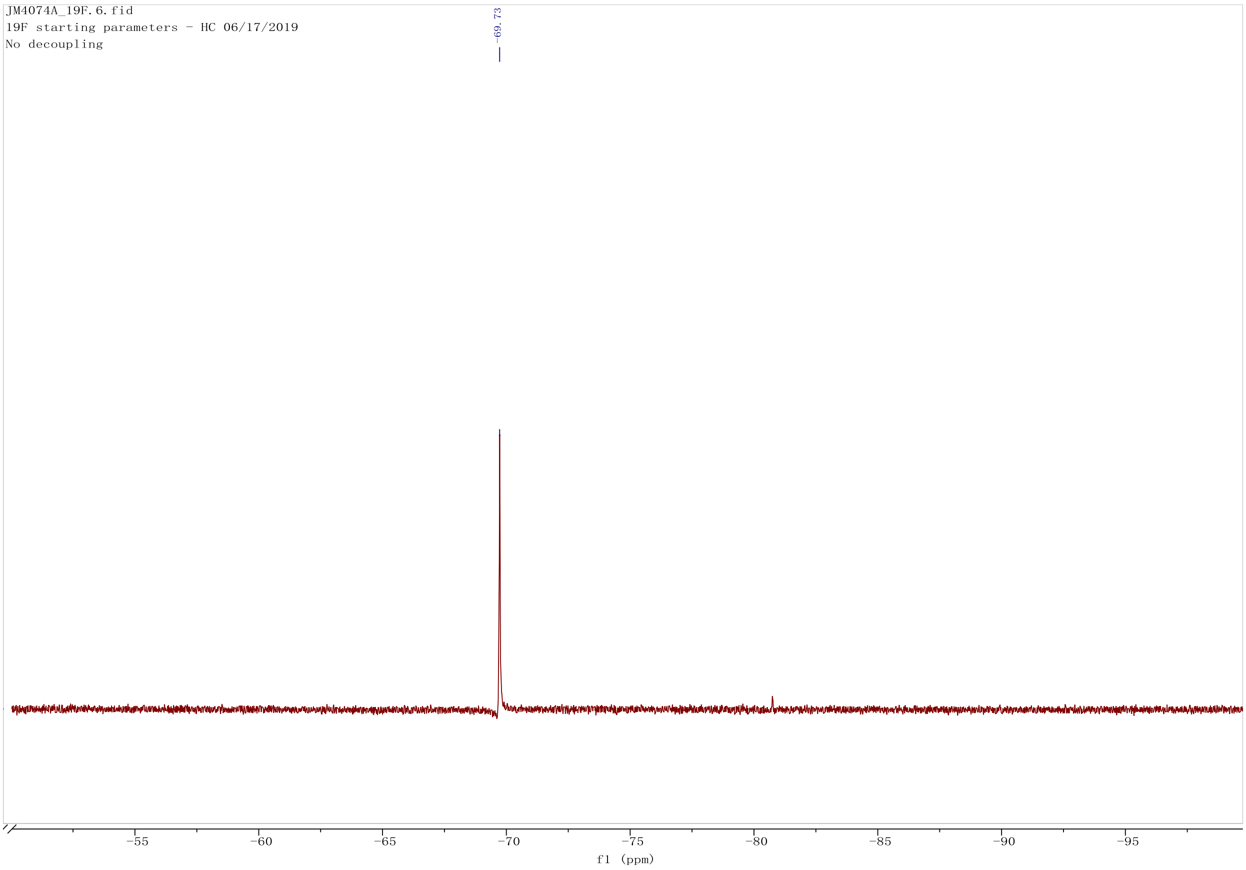
157.62
141.77
141.71
102.71
102.69
95.33
95.08
51.78
47.21
42.39
40.68
37.52
25.31
25.26
21.56
20.90
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


JM4074A_19F.6.fid
19F starting parameters - HC 06/17/2019
No decoupling
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-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

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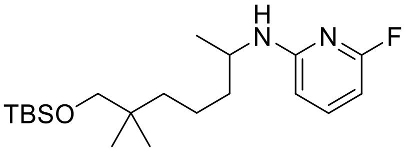
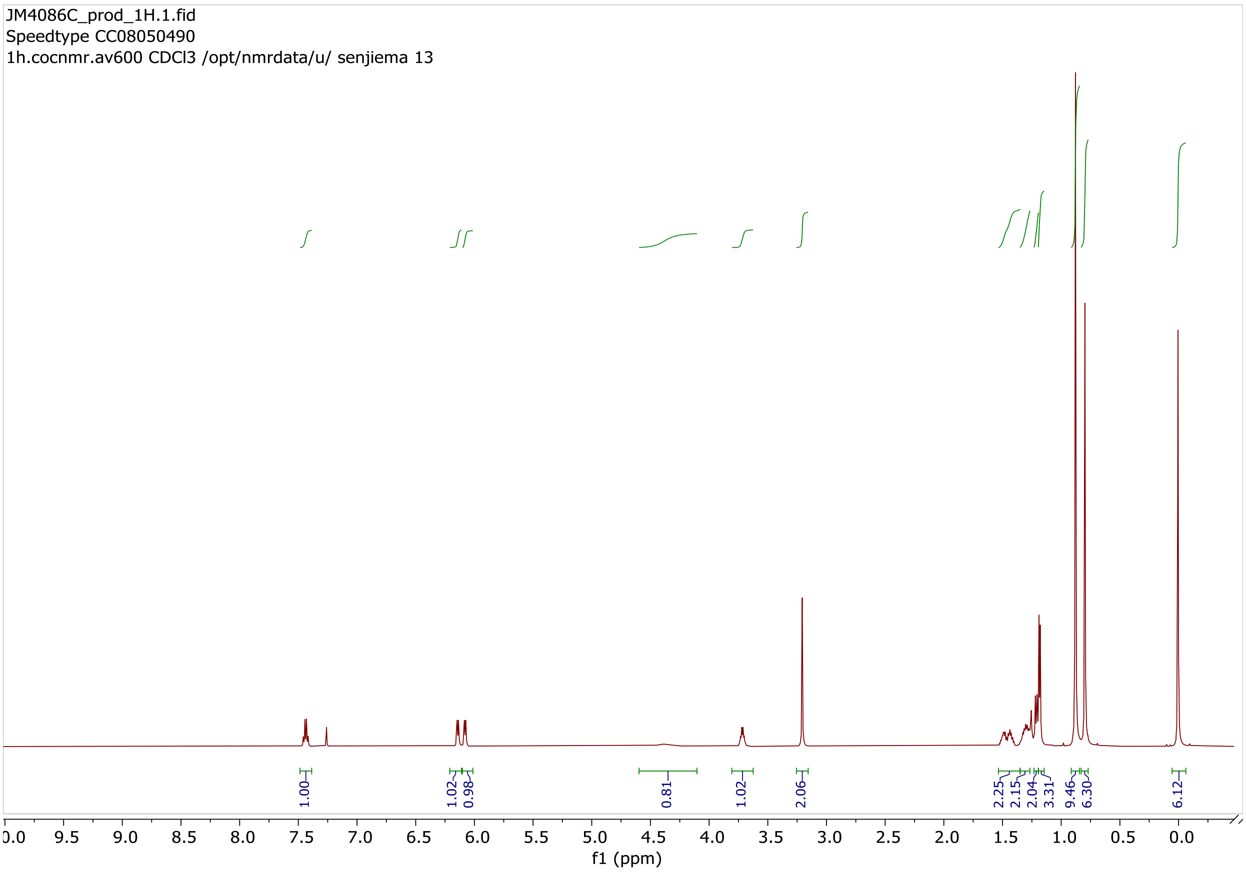
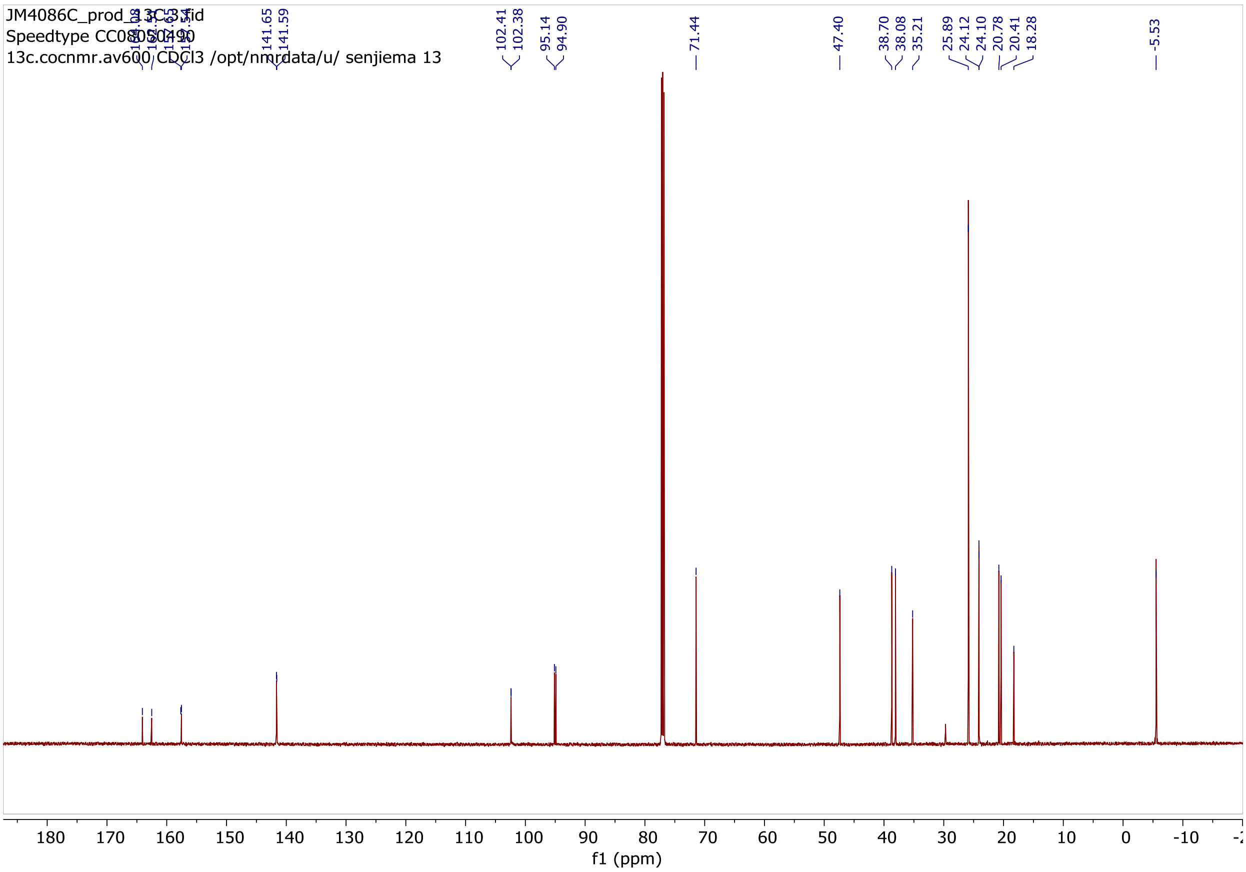
Compound 3sb



^{1}H NMR



^{13}C NMR


JM4086C_prod_13C.3.fid
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 13
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157.54
141.65
141.59
102.41
102.38
95.14
94.90
71.44
47.40
38.70
38.08
35.21
25.89
24.12
24.10
20.78
20.41
18.28
-5.53
180
170
160
150
140
130
120
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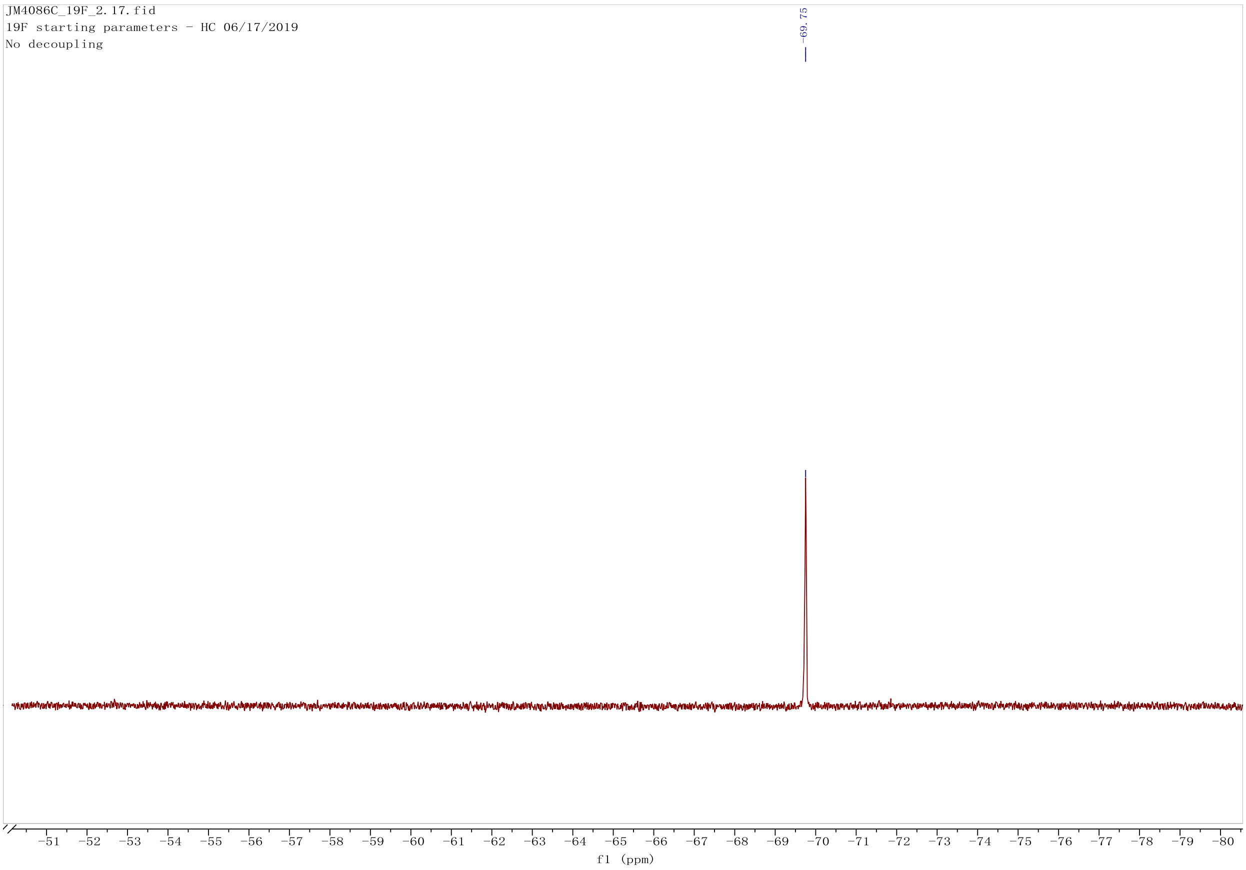
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


JM4086C_19F_2.17.fid
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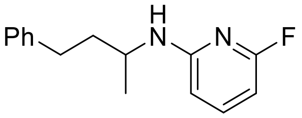
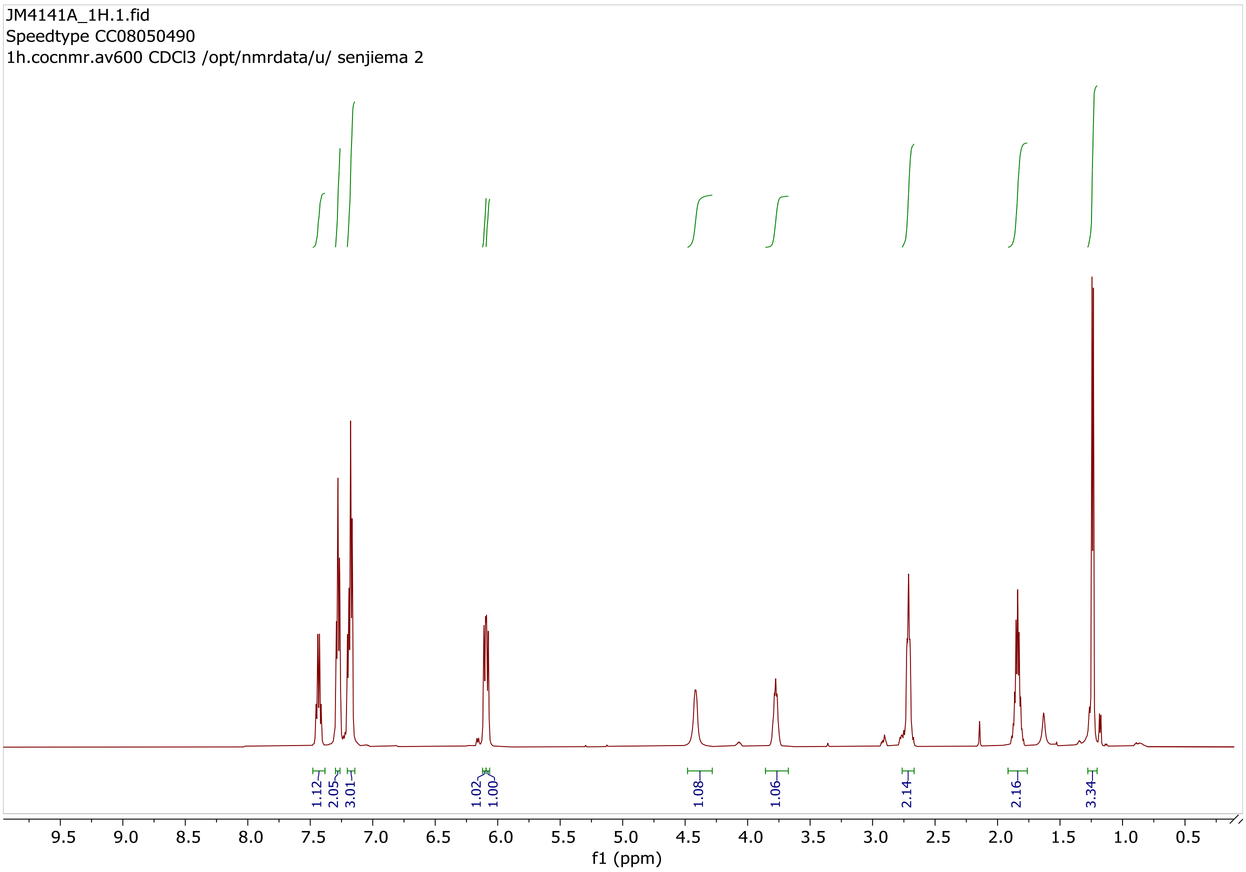
-63
-64
-65
-66
-67
-68
-69
-70
-71
-72
-73
-74
-75
-76
-77
-78
-79
-80
f1 (ppm)

Compound 3tb



^{1}H NMR



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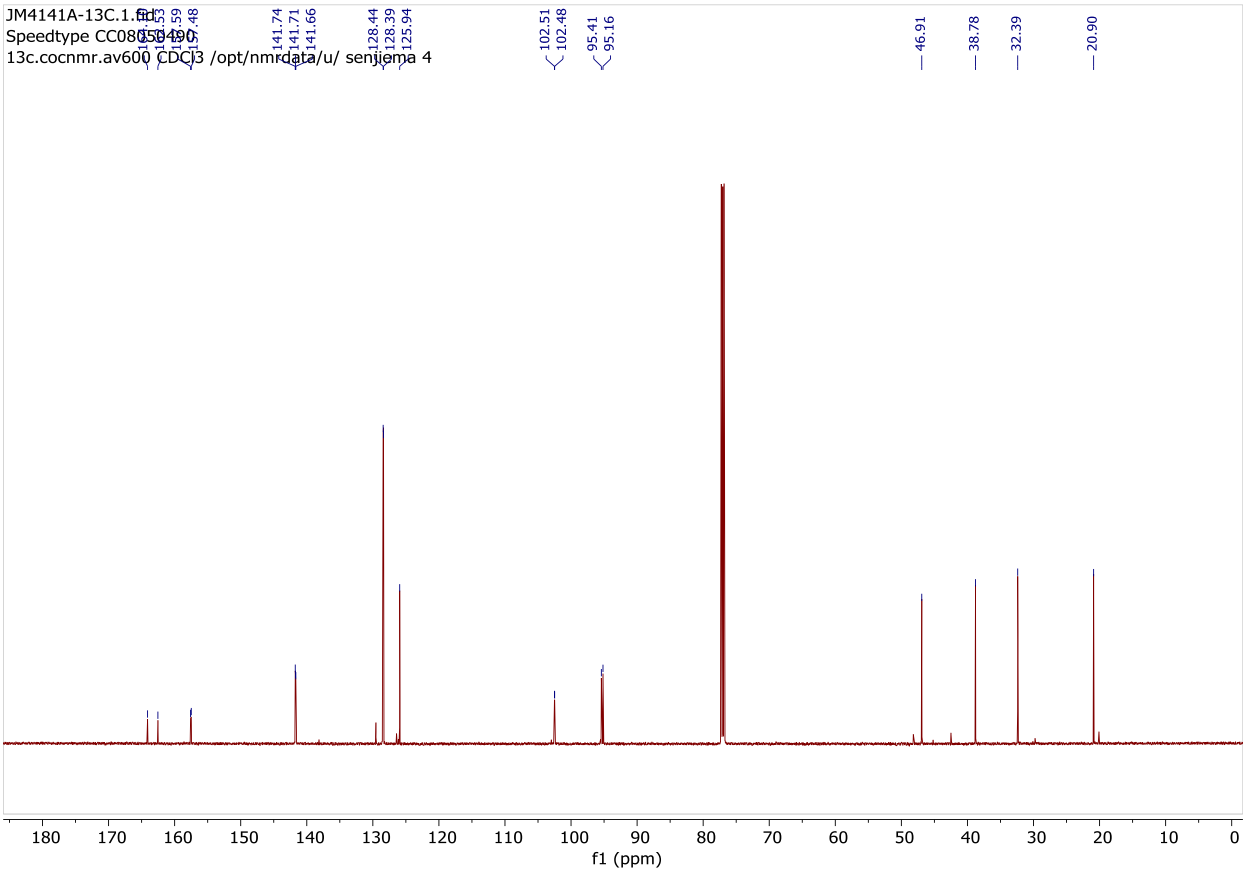
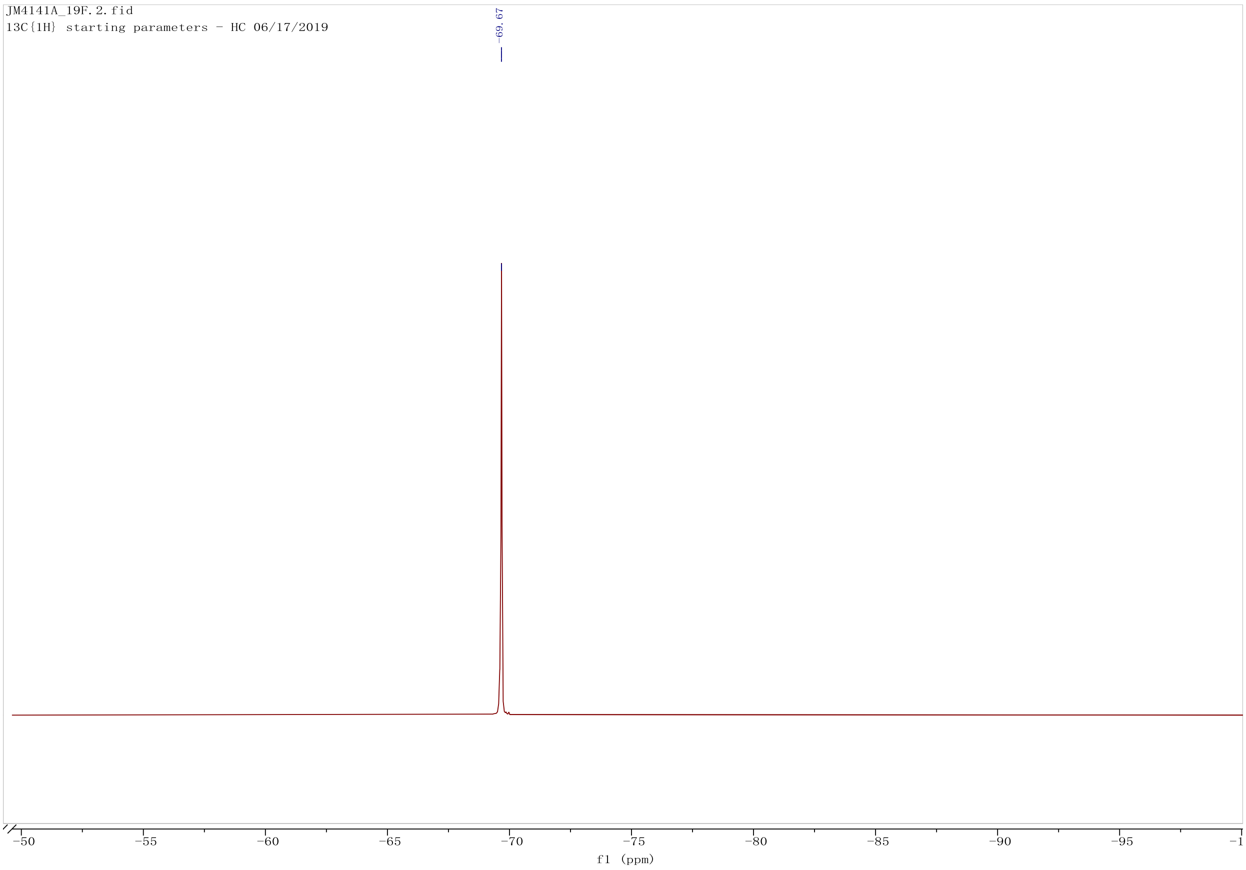
^{13}C NMR

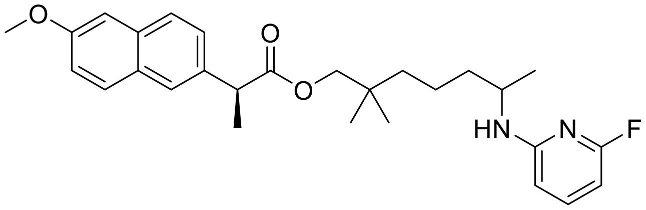


^{19}F NMR

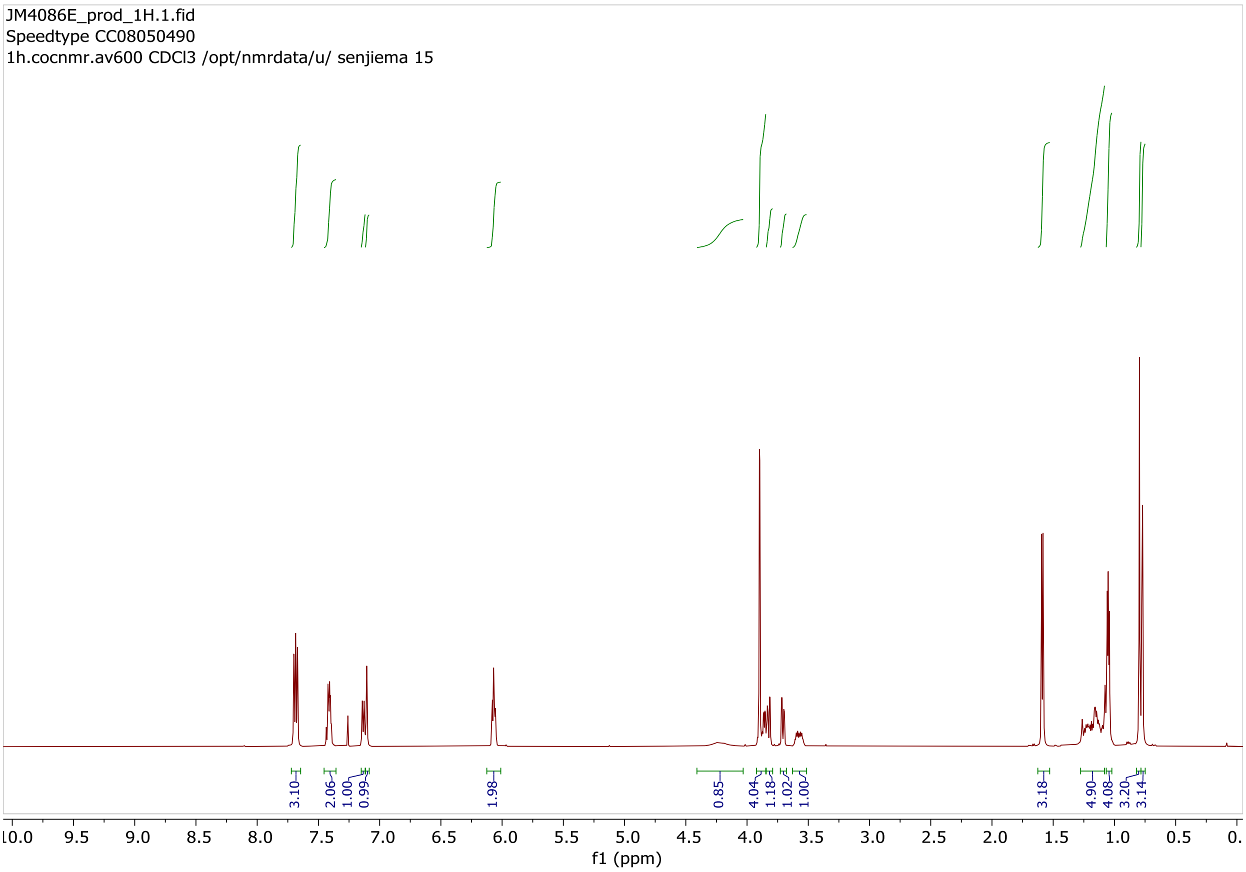

JM4141A_19F.2.fid
13C{1H} starting parameters - HC 06/17/2019
-69.67
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-1
f1 (ppm)

[*Return to table of contents*]

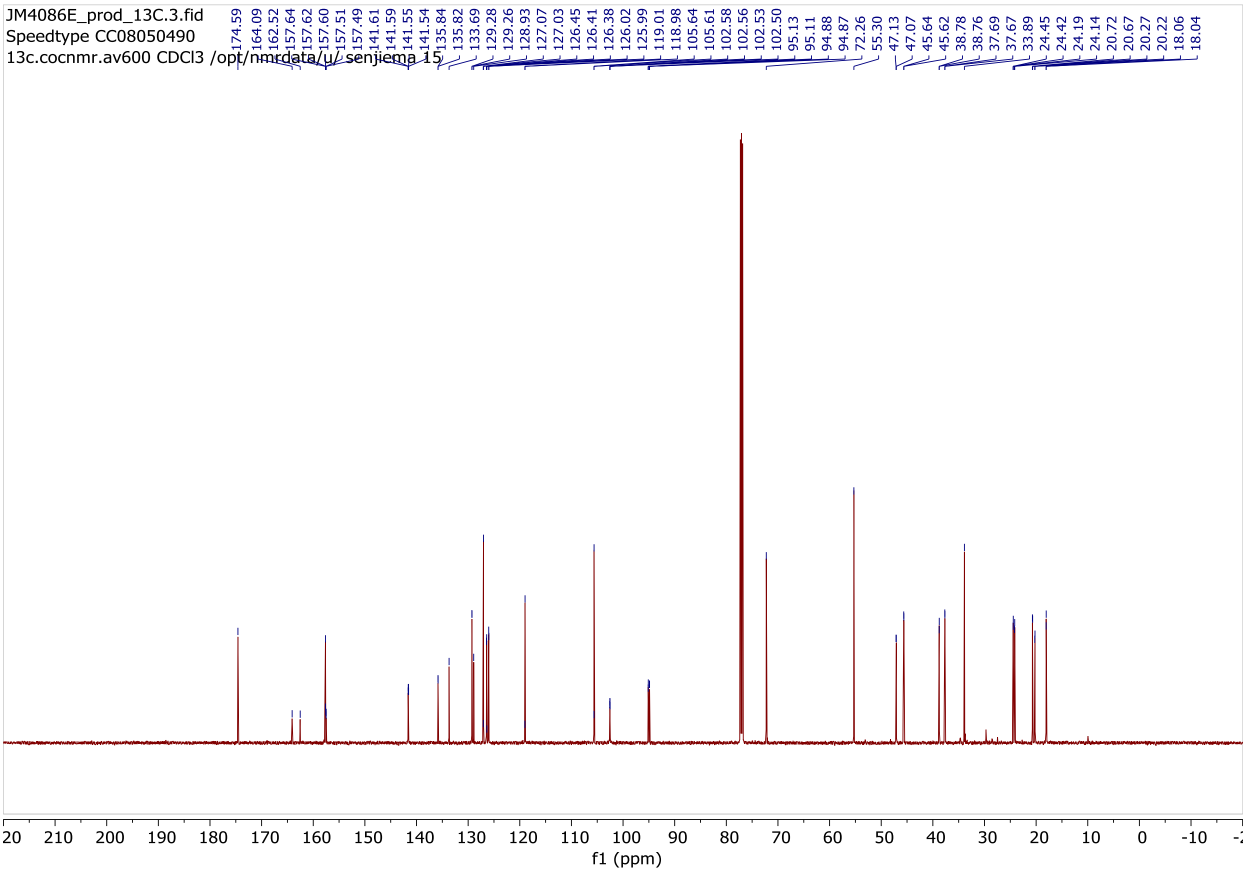
Compound 3ub



^{1}H NMR



^{13}C NMR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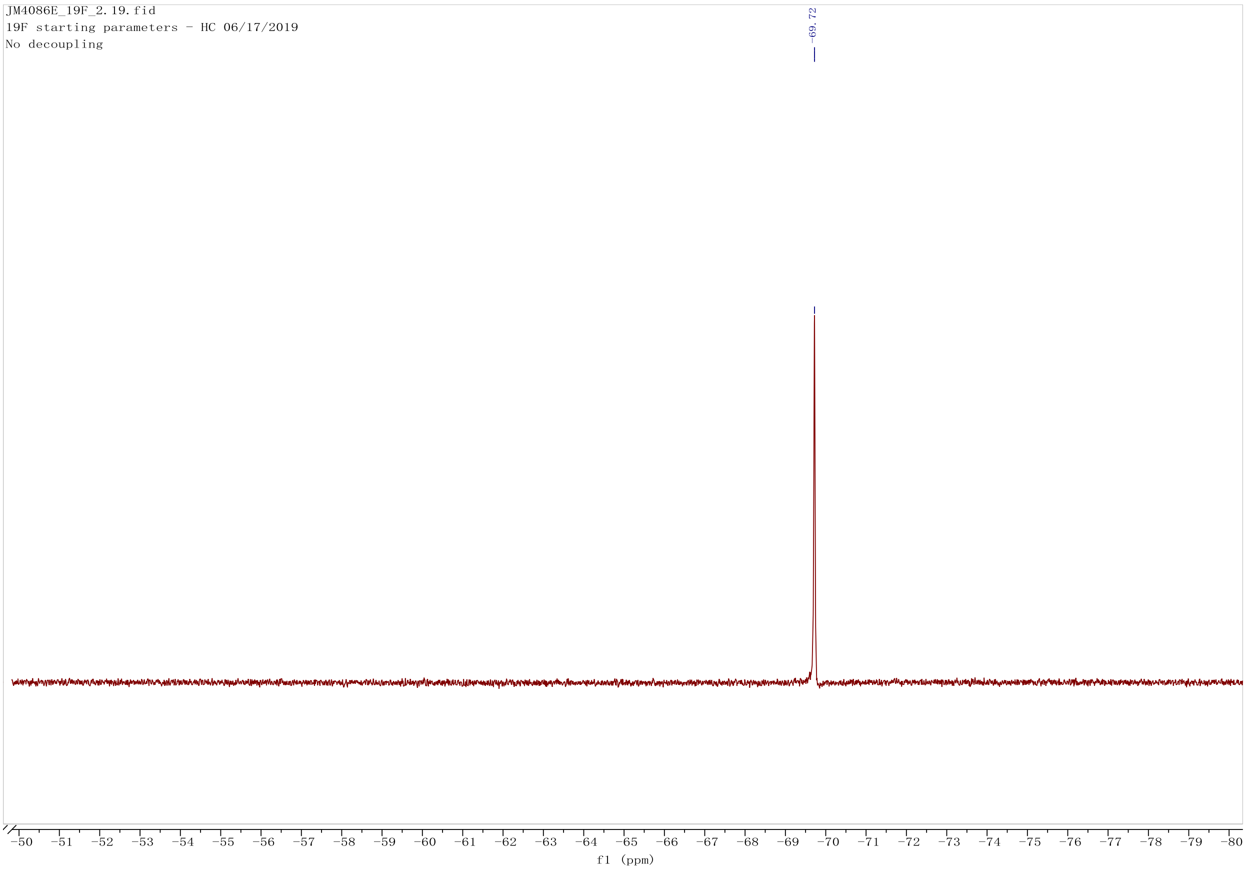
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 15
174.59
164.09
162.52
157.64
157.62
157.60
157.51
157.49
141.61
141.59
141.55
141.54
135.84
135.82
133.69
129.28
129.26
128.93
127.07
127.03
126.45
126.41
126.38
126.02
125.99
119.01
118.98
105.64
105.61
102.58
102.56
102.53
102.50
95.13
95.11
94.88
94.87
72.26
55.30
47.13
47.07
45.64
45.62
38.78
38.76
37.69
37.67
33.89
24.45
24.42
24.19
24.14
20.72
20.67
20.27
20.22
18.06
18.04
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)

^{19}F NMR


JM4086E_19F_2.19.fid
19F starting parameters - HC 06/17/2019
No decoupling
—69.72
−50
−51
−52
−53
−54
−55
−56
−57
−58
−59
−60
−61
−62
−63
−64
−65
−66
−67
−68
−69
−70
−71
−72
−73
−74
−75
−76
−77
−78
−79
−80
f1 (ppm)

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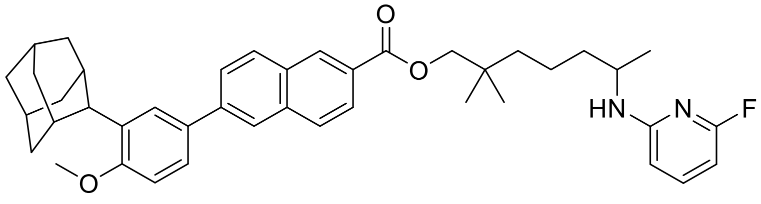
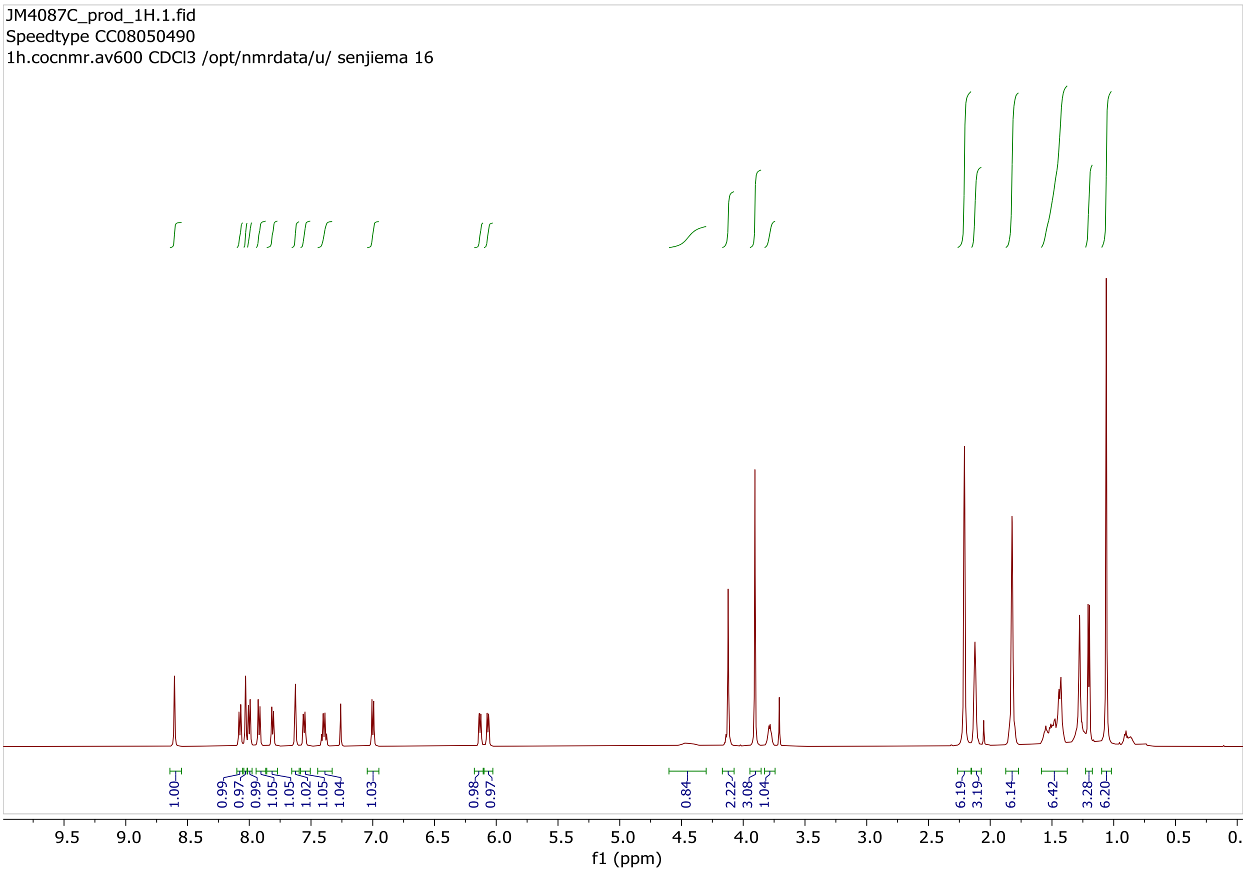
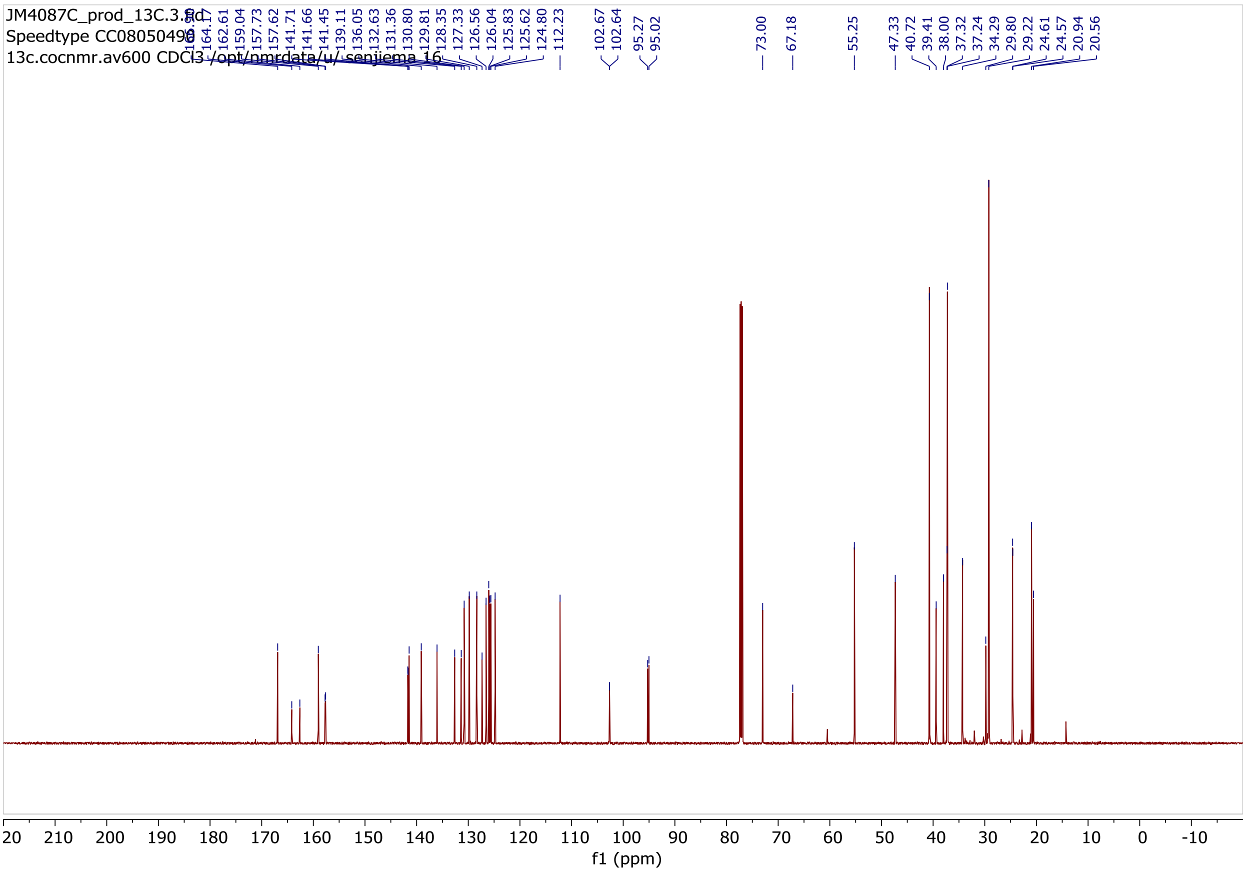
Compound 3vb



^{1}H NMR



^{13}C NMR


JM4087C_prod_13C.3.fid
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 16
166.90
164.17
162.61
159.04
157.73
157.62
141.71
141.66
141.45
139.11
136.05
132.63
131.36
130.80
129.81
128.35
127.33
126.56
126.04
125.83
125.62
124.80
112.23
102.67
102.64
95.27
95.02
73.00
67.18
55.25
47.33
40.72
39.41
38.00
37.32
37.24
34.29
29.80
29.22
24.61
24.57
20.94
20.56
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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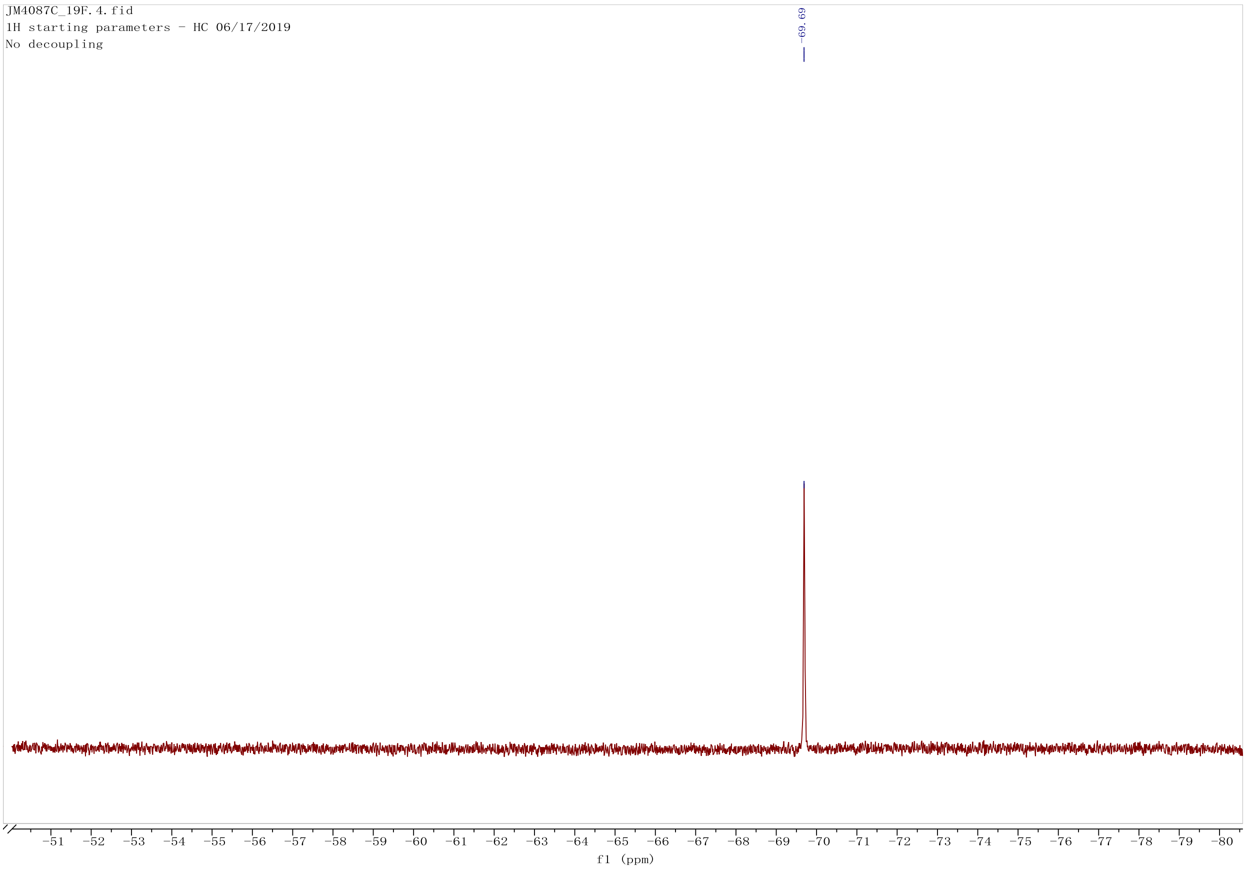
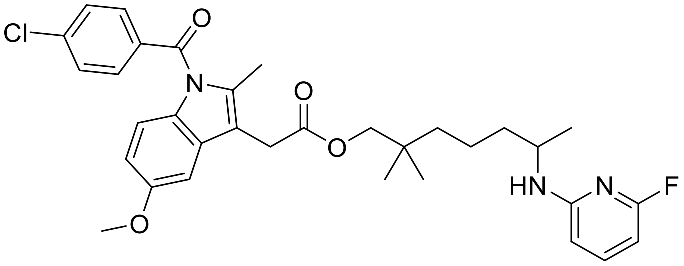
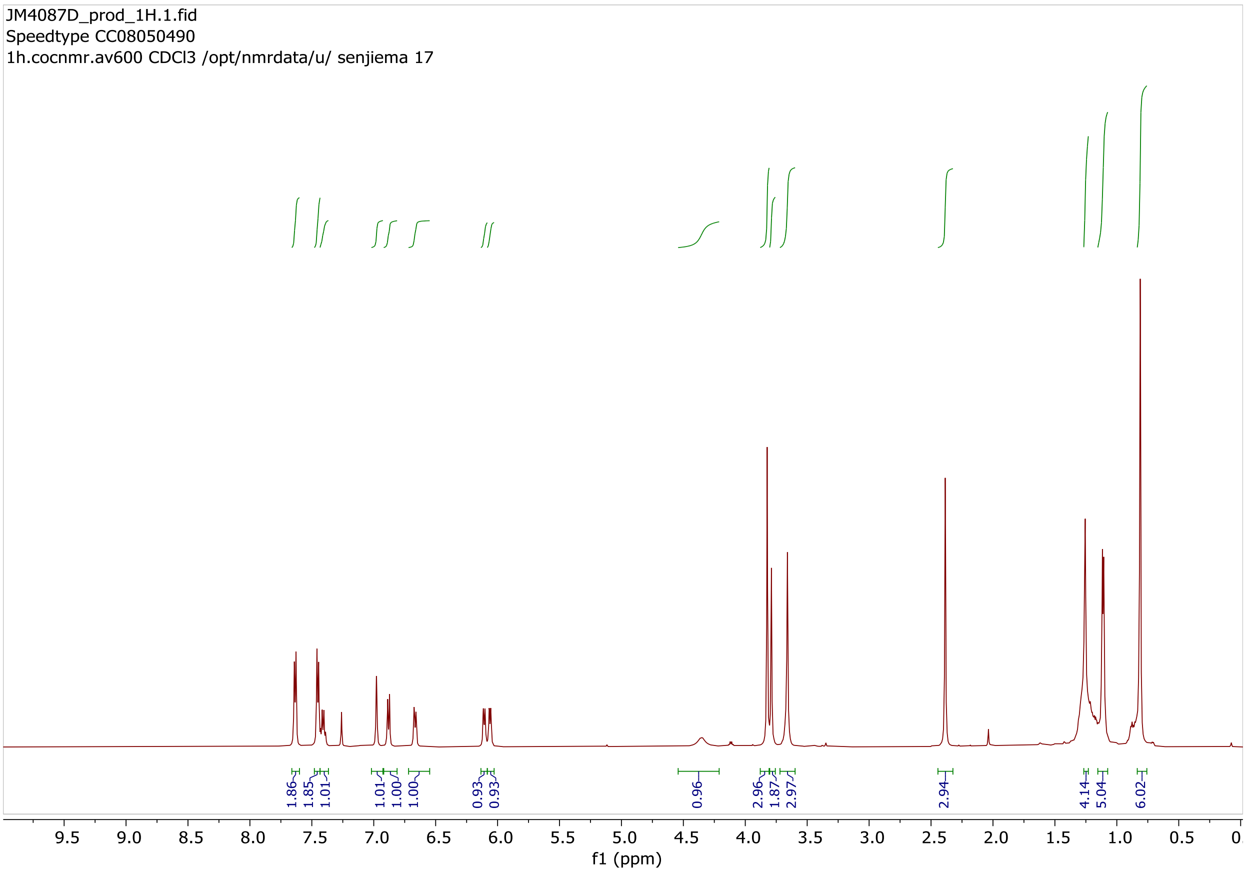
^{19}F NMR



Compound 3wb



^{1}H NMR



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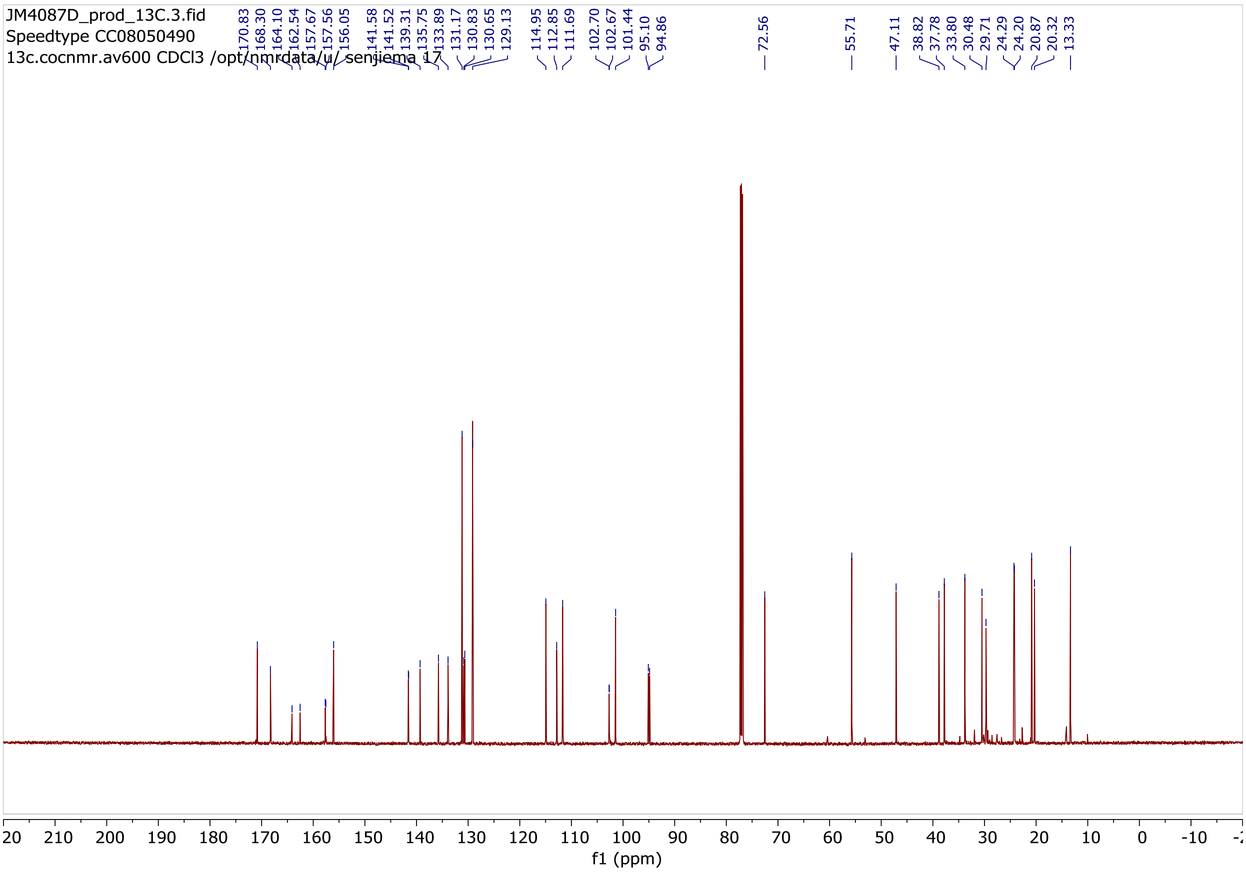
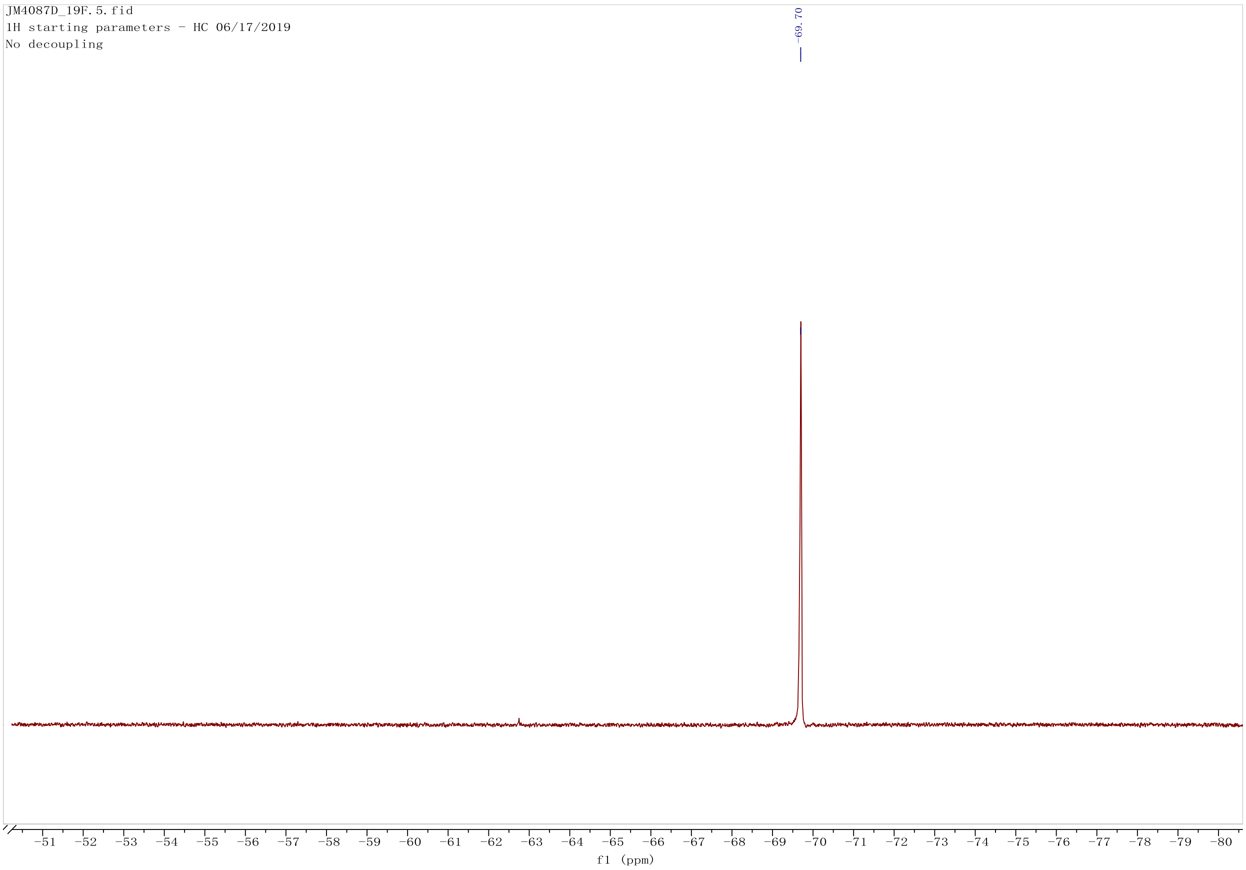
^{13}C NMR



^{19}F NMR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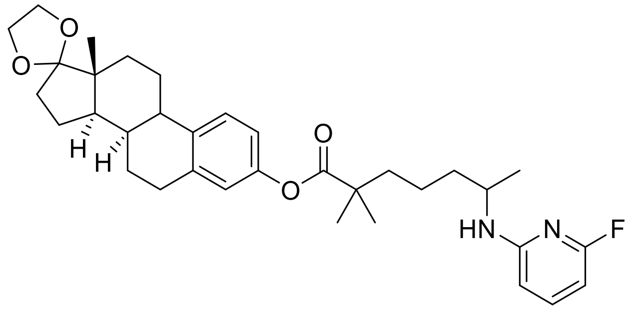
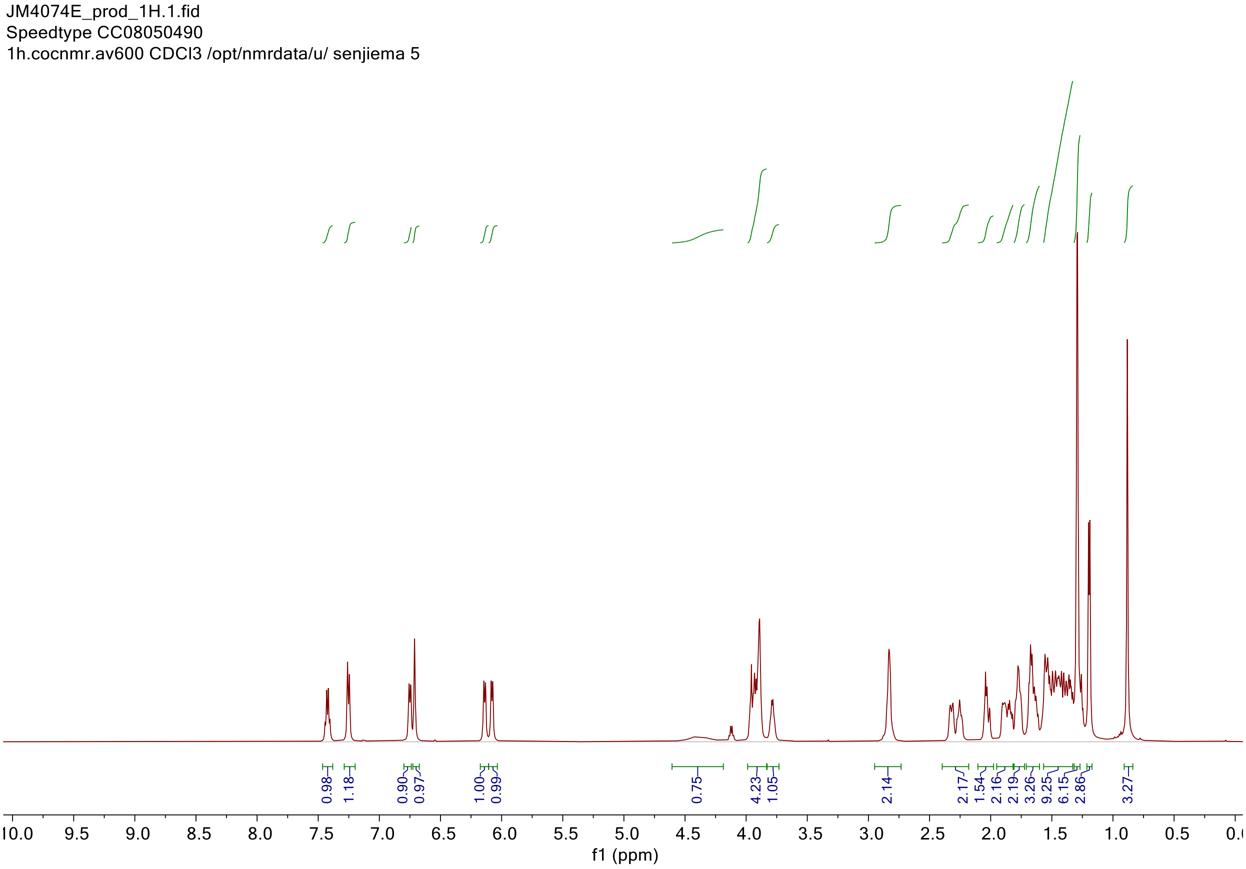
1H starting parameters - HC 06/17/2019
No decoupling
−69.70
−51
−52
−53
−54
−55
−56
−57
−58
−59
−60
−61
−62
−63
−64
−65
−66
−67
−68
−69
−70
−71
−72
−73
−74
−75
−76
−77
−78
−79
−80
f1 (ppm)

Compound 3xb



^{1}H NMR



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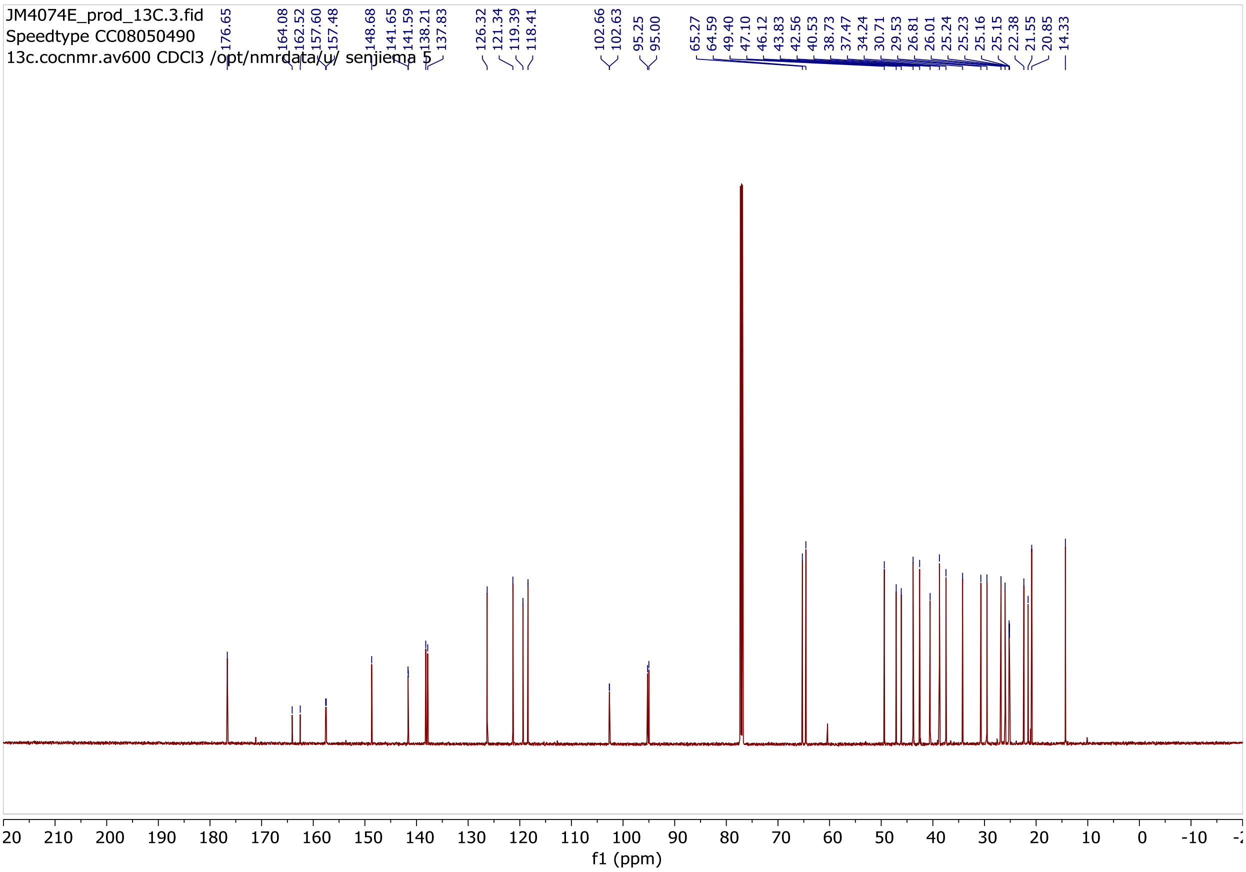
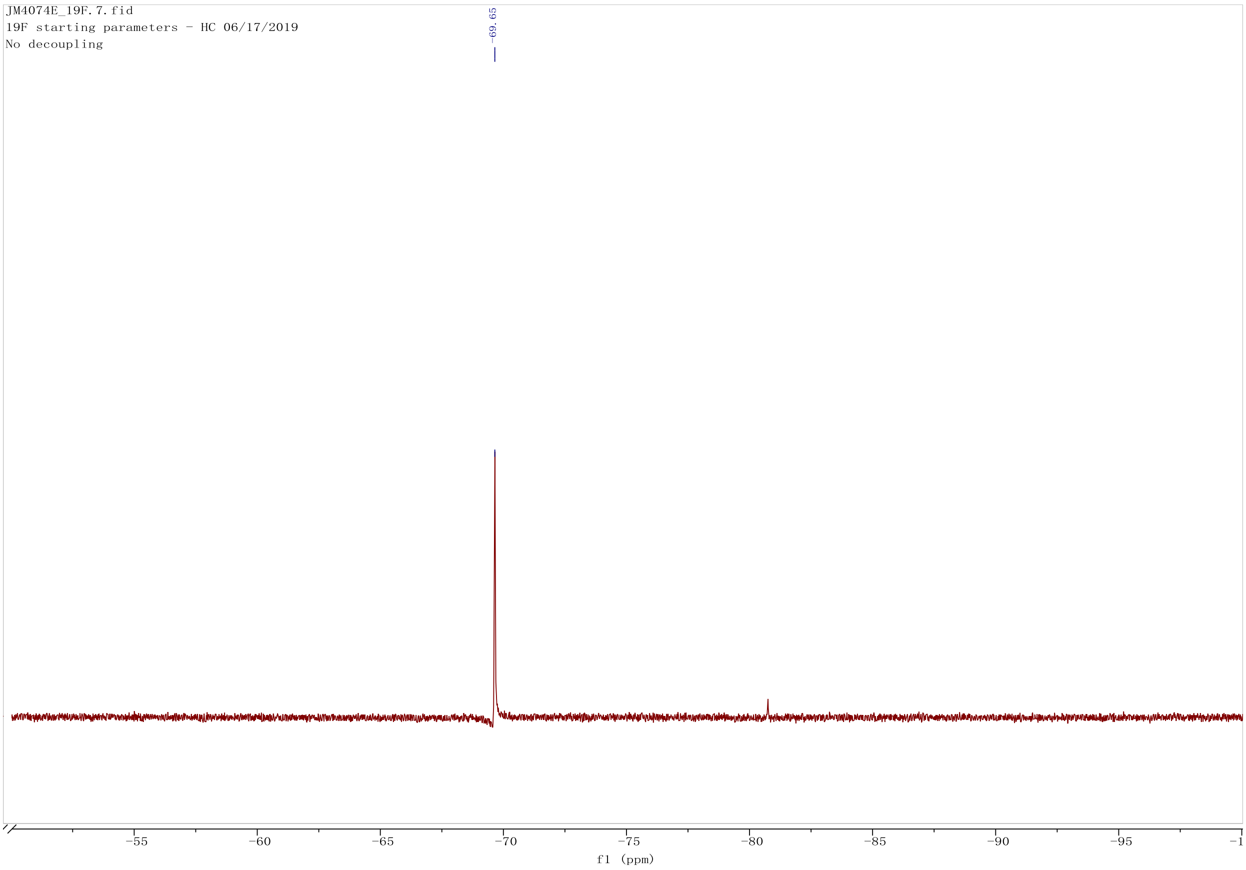
^{13}C NMR



^{19}F NMR


JM4074E_19F.7.fid
19F starting parameters - HC 06/17/2019
No decoupling
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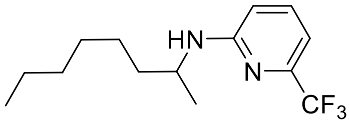
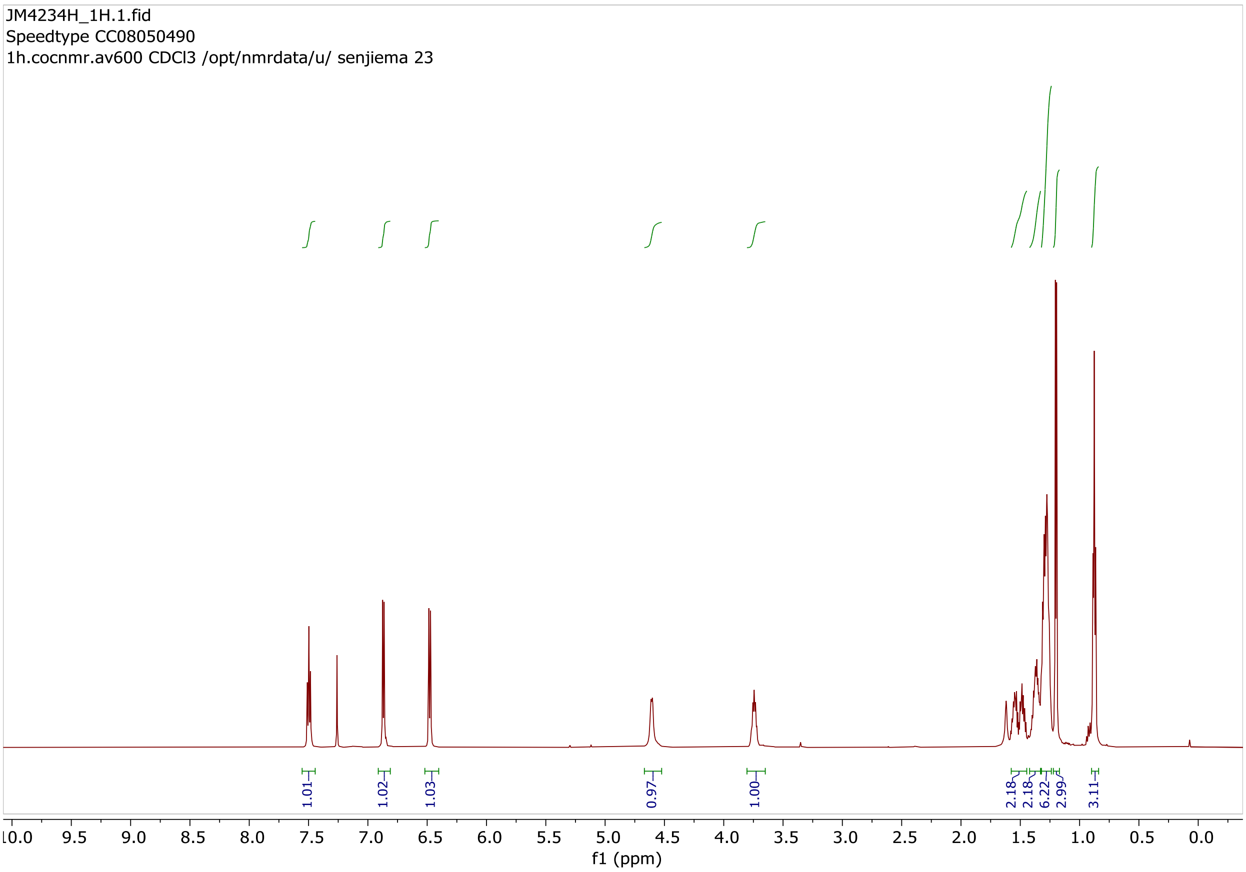
-55
-60
-65
-70
-75
-80
-85
-90
-95
-1
f1 (ppm)

Compound 3ac



^{1}H NMR



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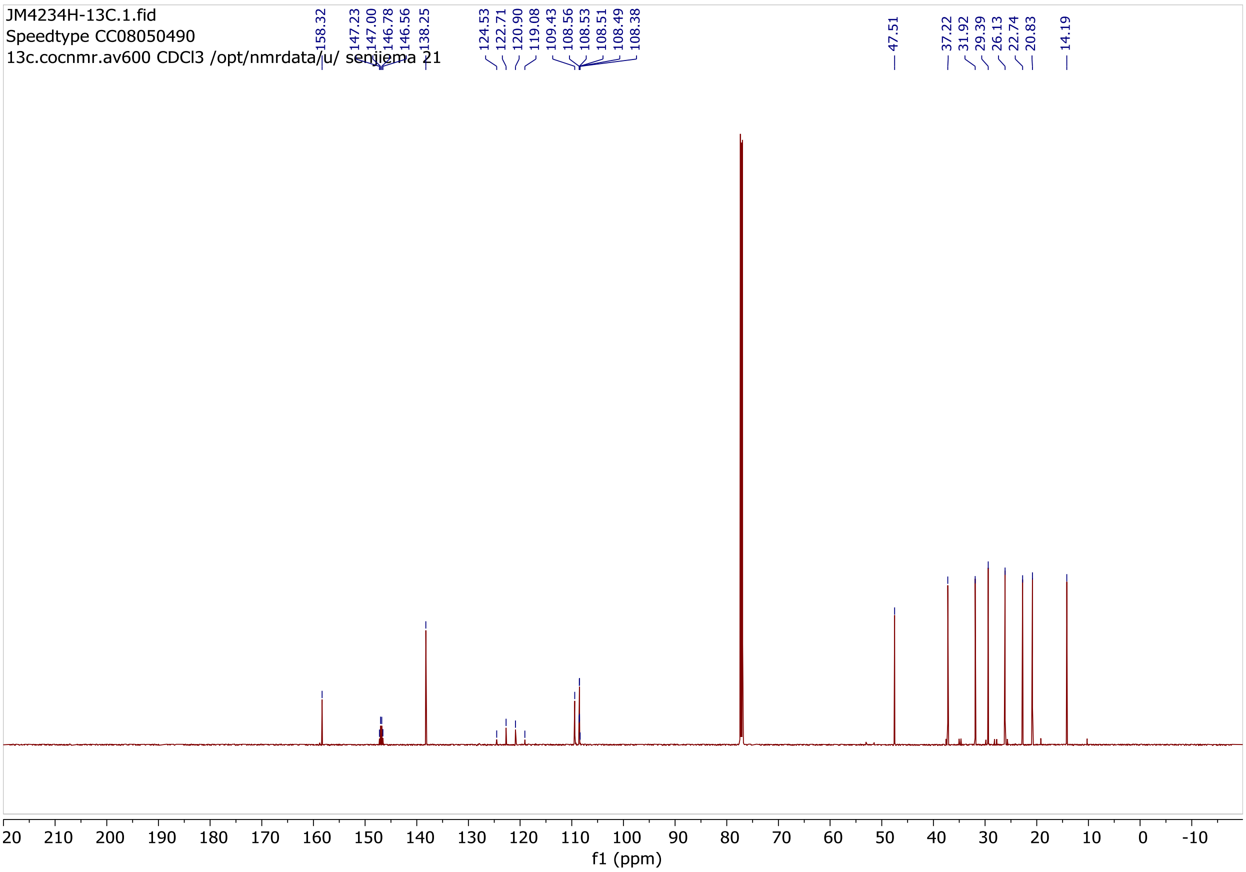
^{13}C NMR



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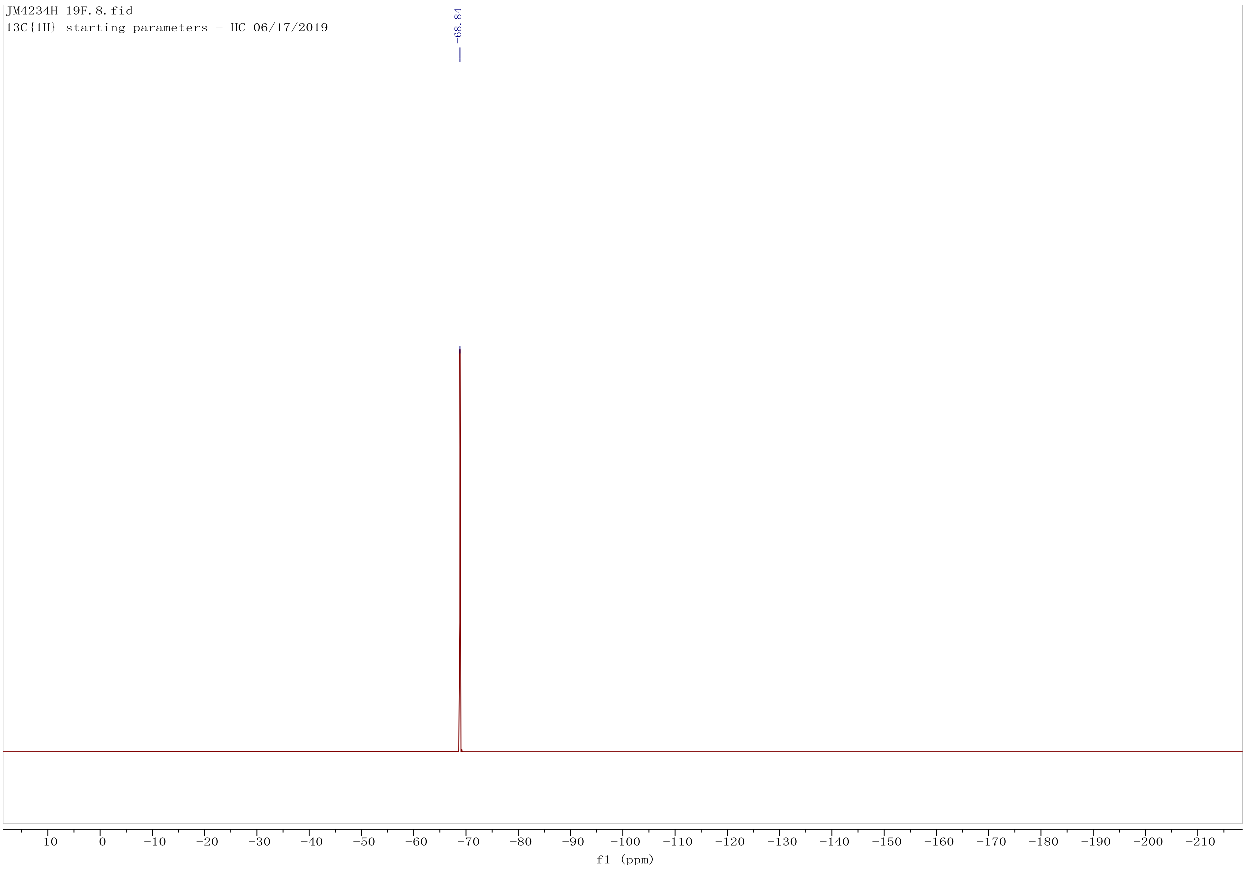
^{19}F NMR



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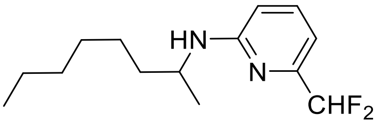
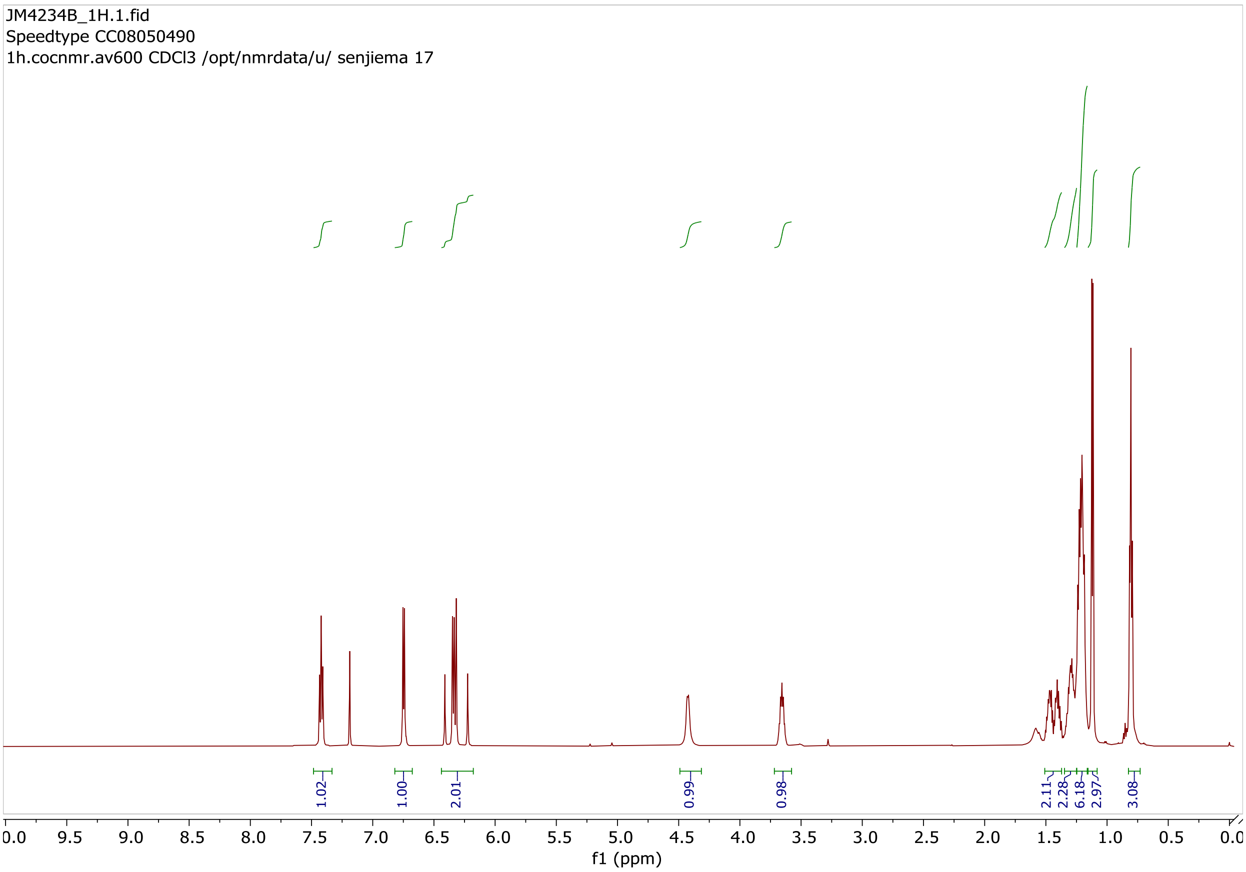
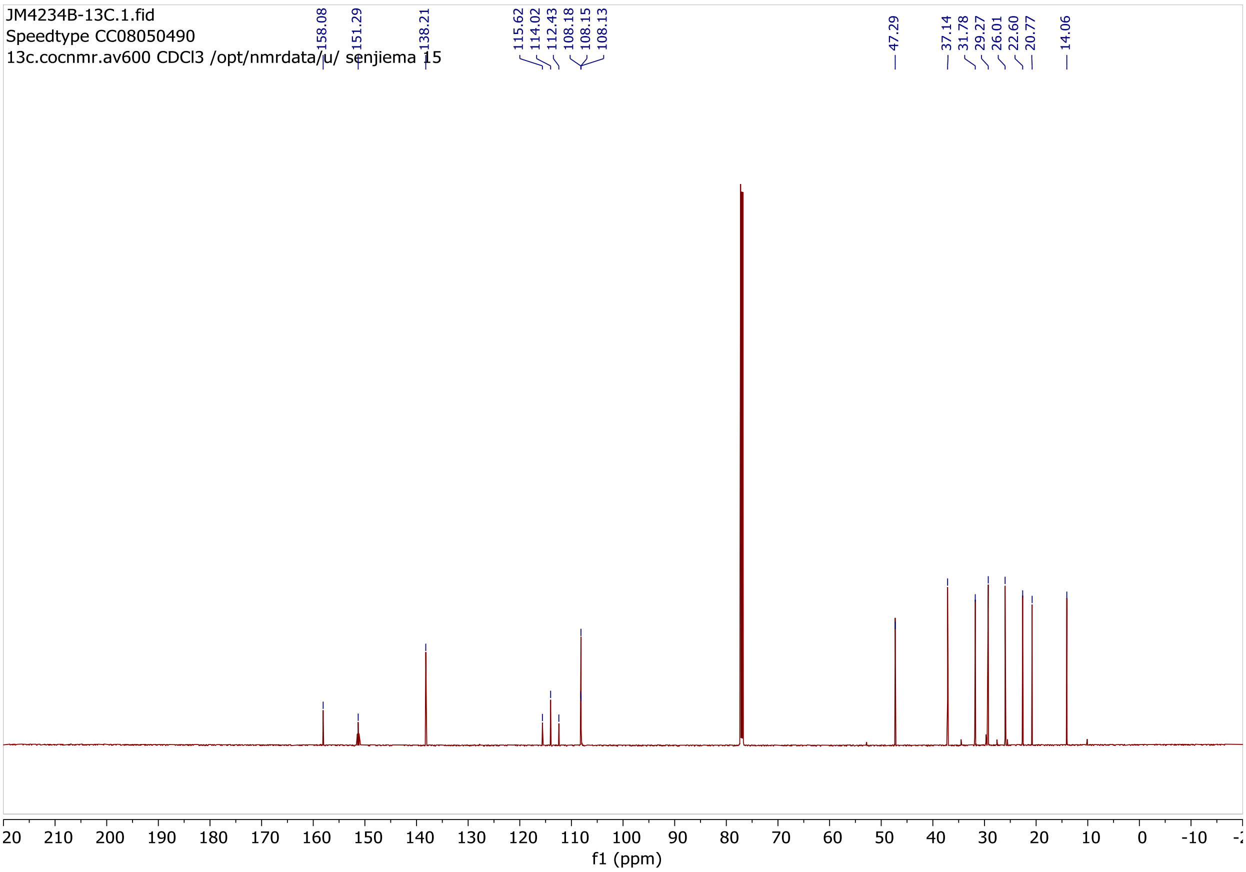
Compound 3ad



^{1}H NMR



^{13}C NMR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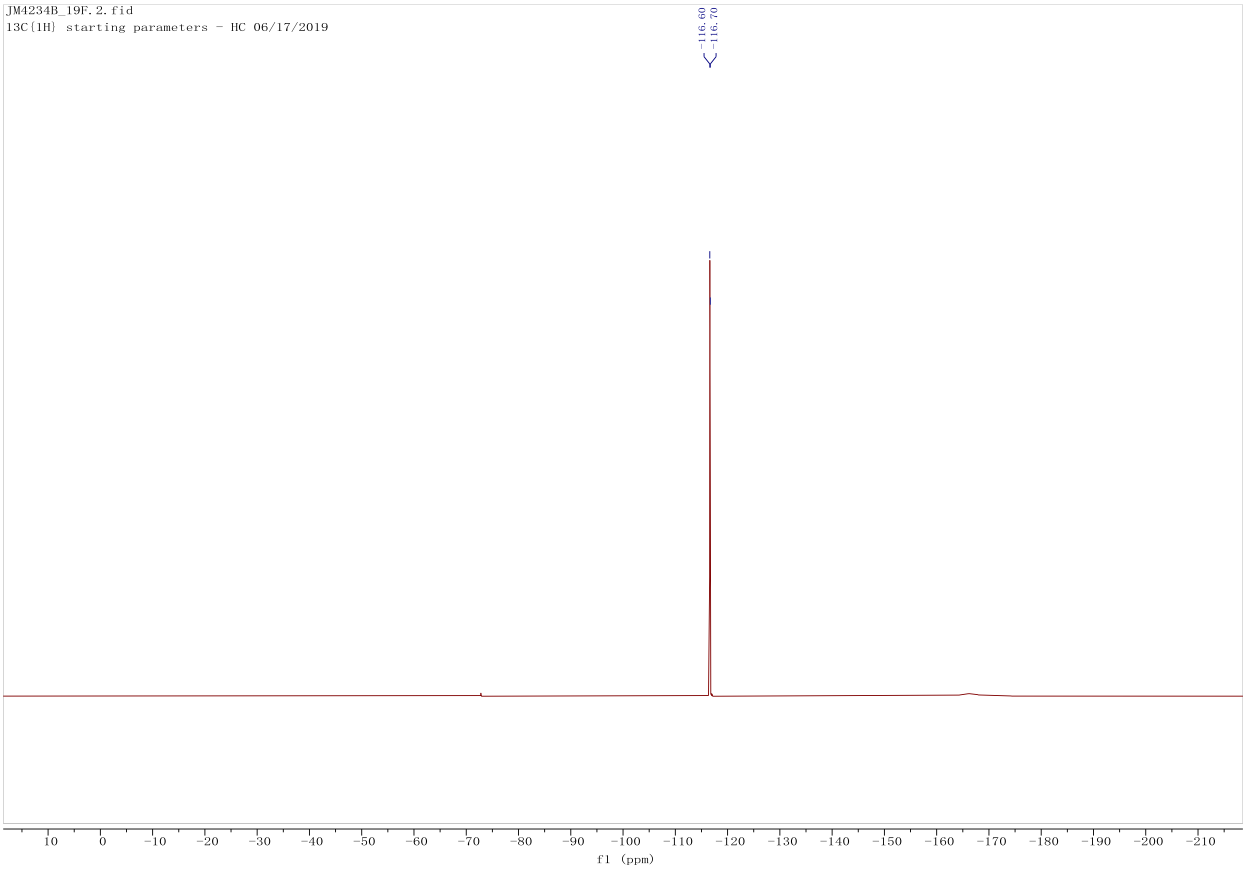
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 15
158.08
151.29
138.21
115.62
114.02
112.43
108.18
108.15
108.13
47.29
37.14
31.78
29.27
26.01
22.60
20.77
14.06
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


JM4234B_19F.2.fid
13C{1H} starting parameters - HC 06/17/2019
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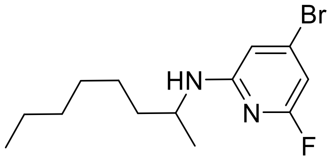
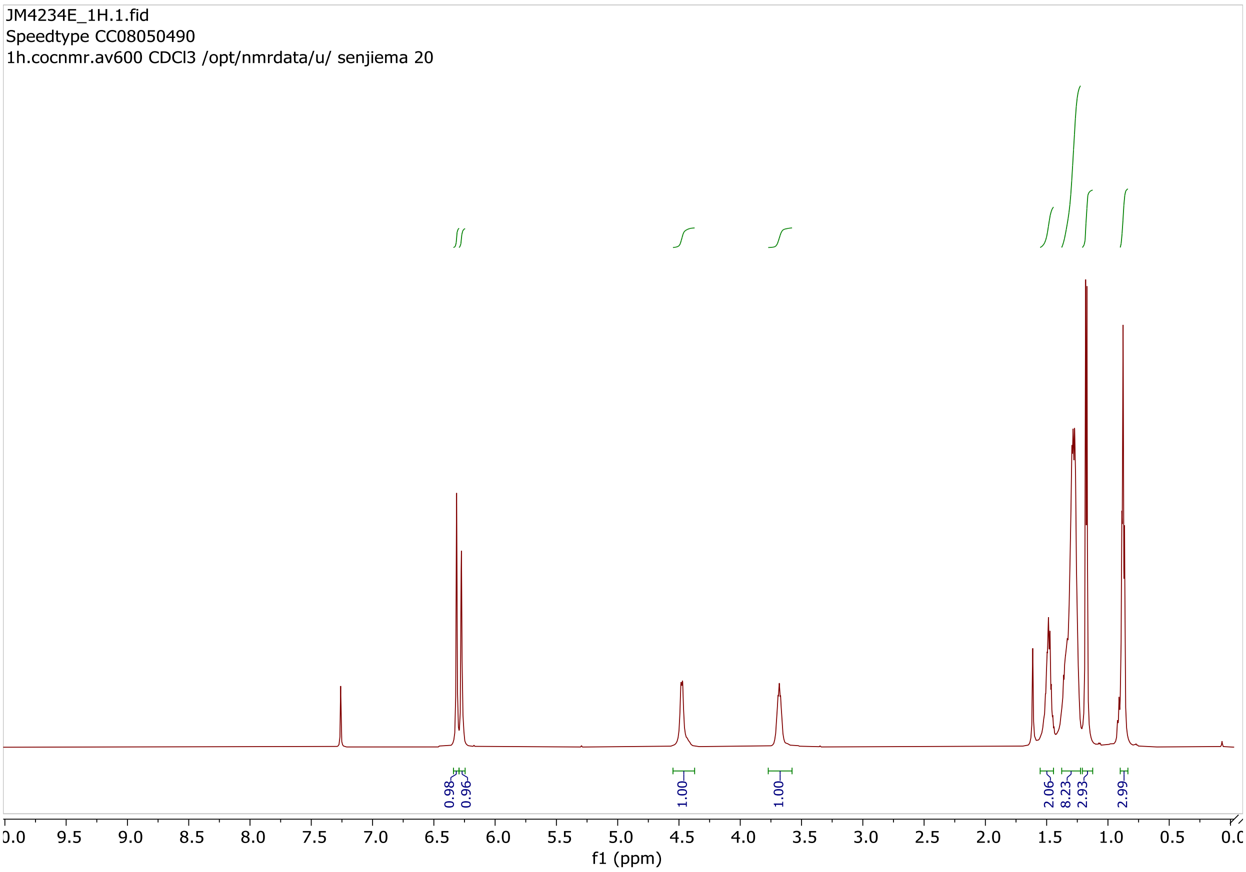
-116.70
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

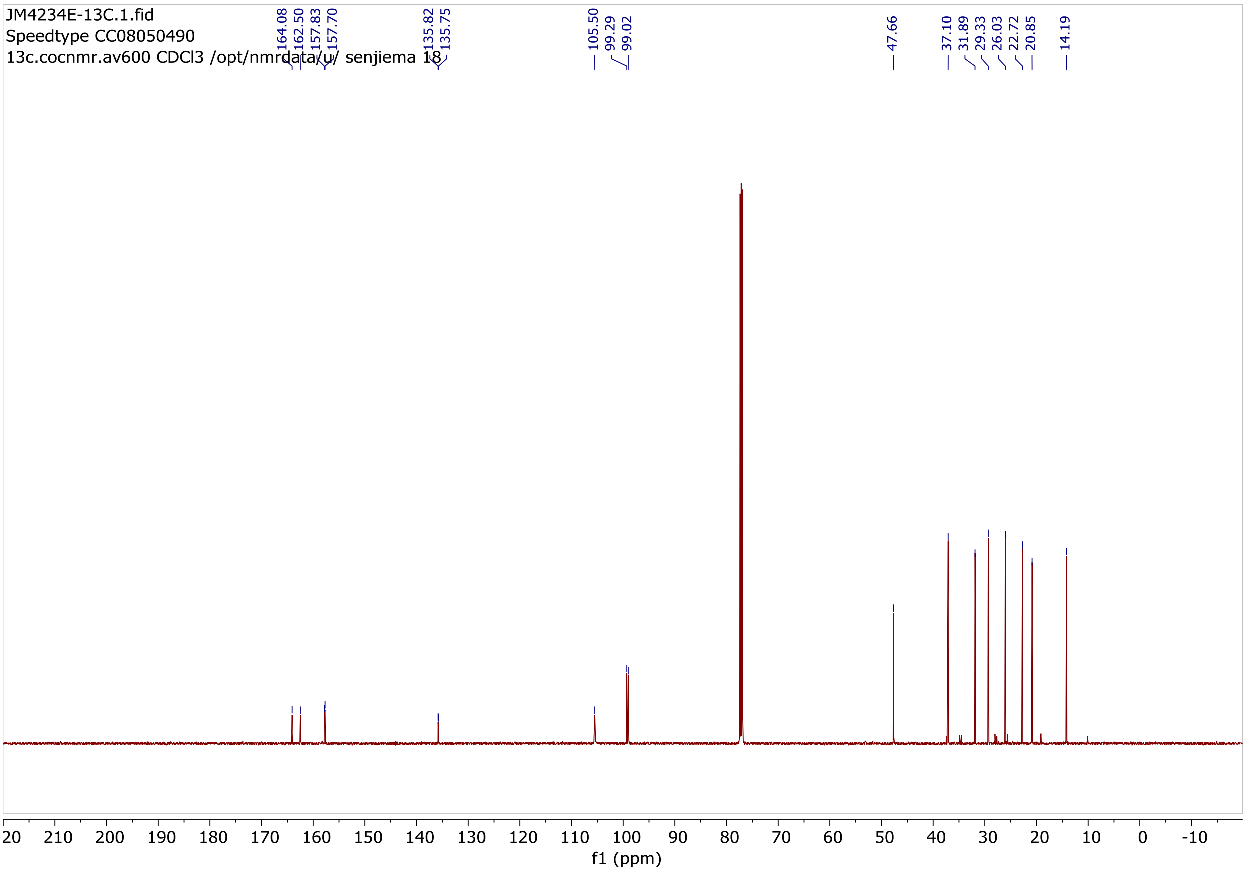
Compound 3ae



^{1}H NMR



^{13}C NMR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164.08
162.50
157.83
157.70
135.82
135.75
105.50
99.29
99.02
47.66
37.10
31.89
29.33
26.03
22.72
20.85
14.19
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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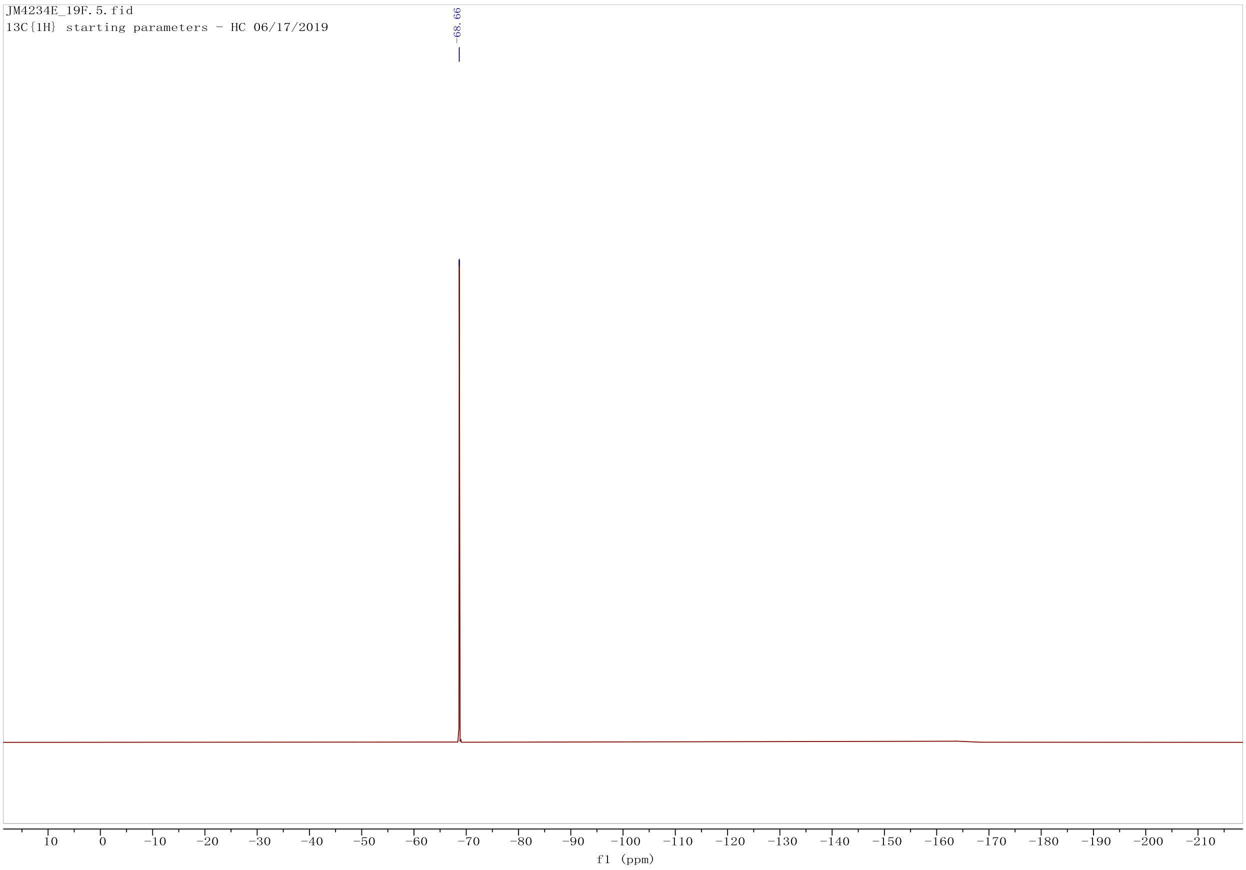
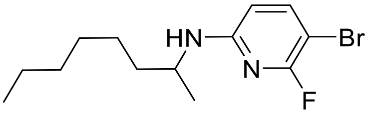
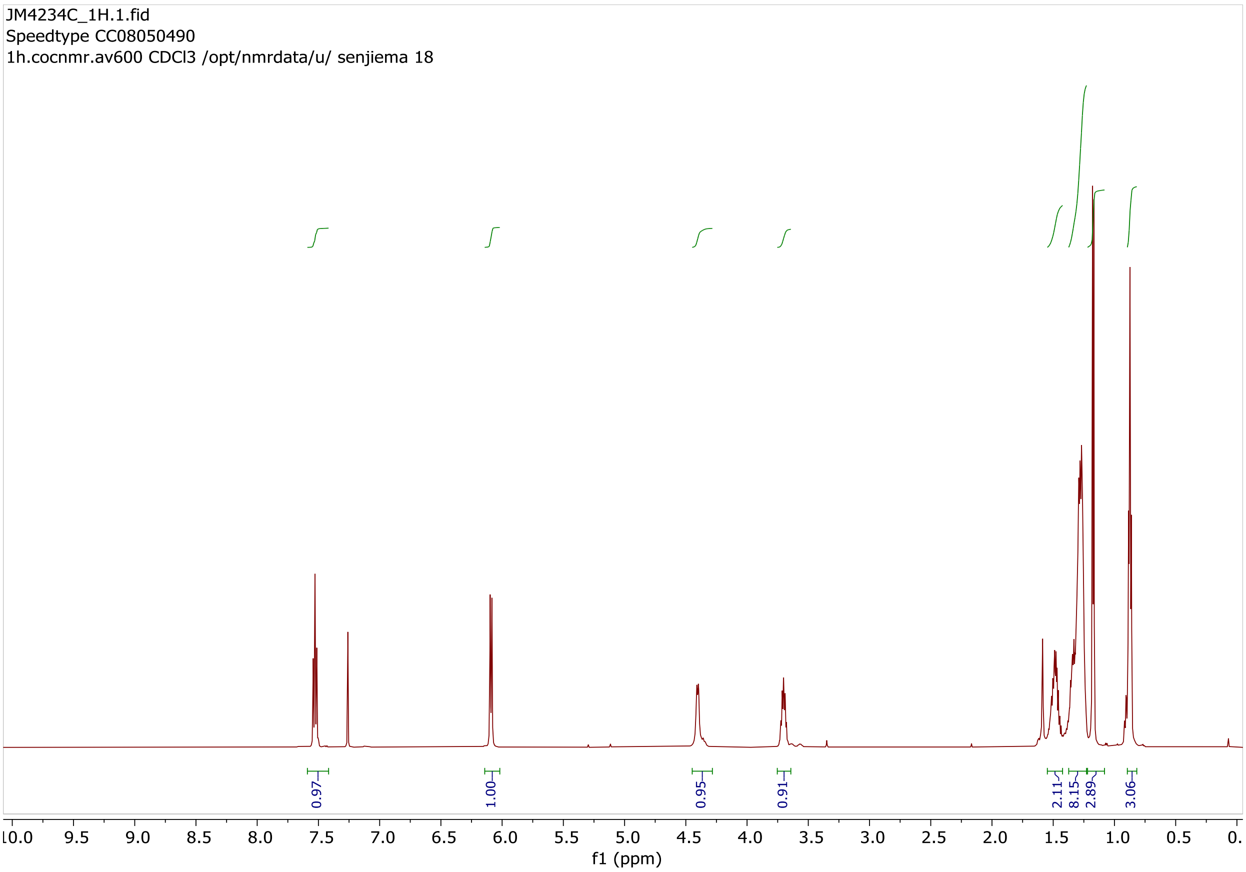
^{19}F NMR



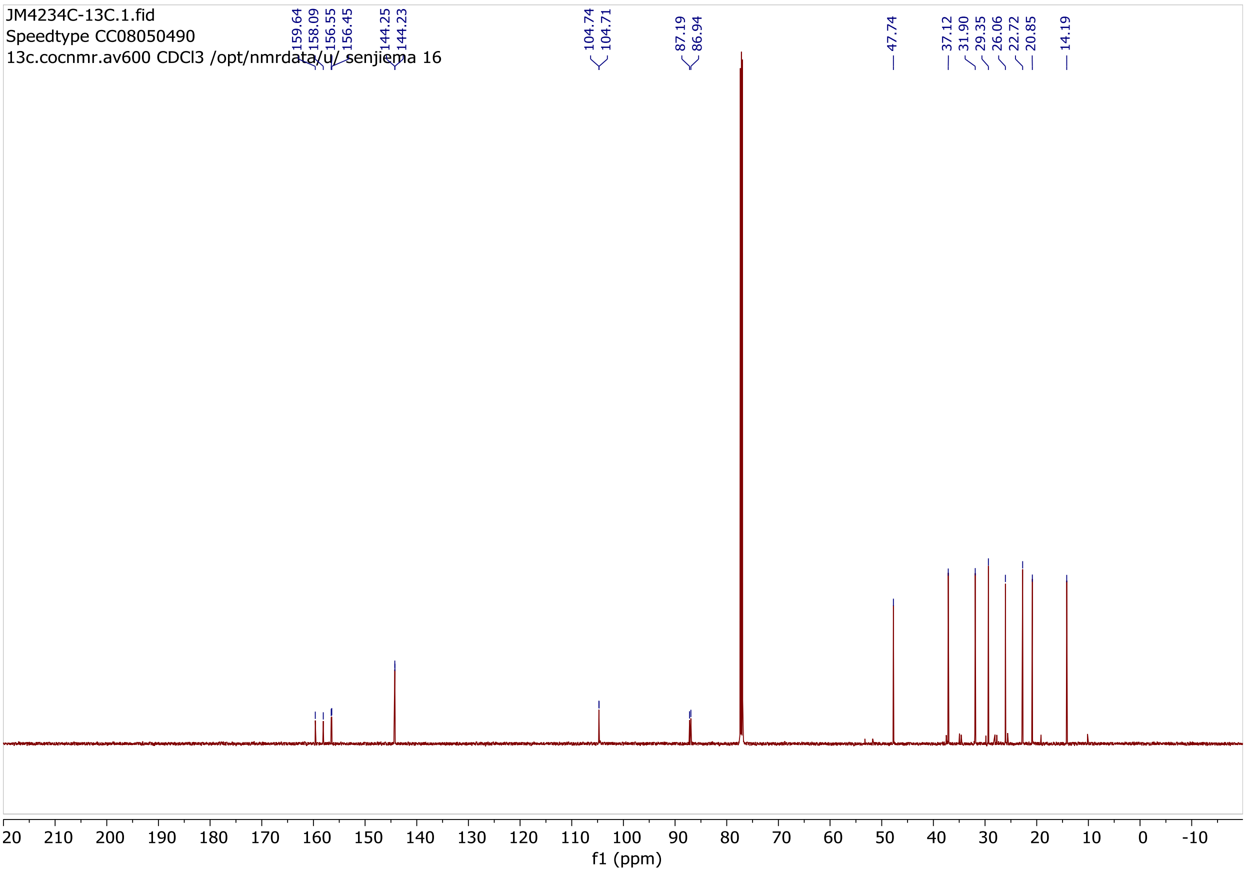
Compound 3af



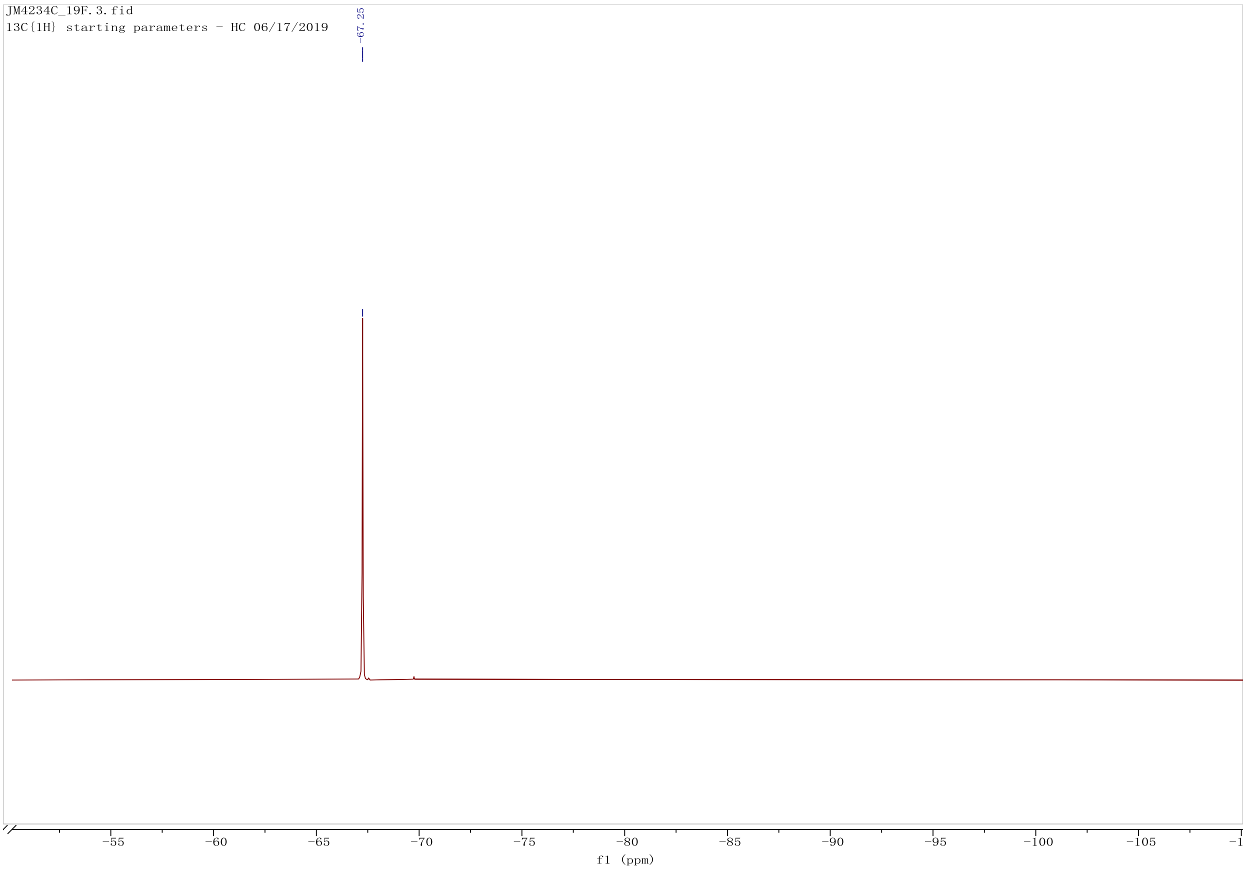
^{1}H NMR



^{13}C NMR


JM4234C-13C.1.fid
Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 16
159.64
158.09
156.55
156.45
144.25
144.23
104.74
104.71
87.19
86.94
47.74
37.12
31.90
29.35
26.06
22.72
20.85
14.19
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{19}F NMR


JM4234C_19F.3.fid
13C{1H} starting parameters - HC 06/17/2019
−67.25
−55
−60
−65
−70
−75
−80
−85
−90
−95
−100
−105
f1 (ppm)

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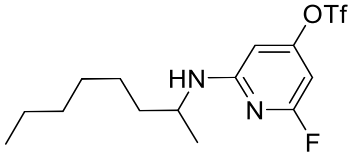
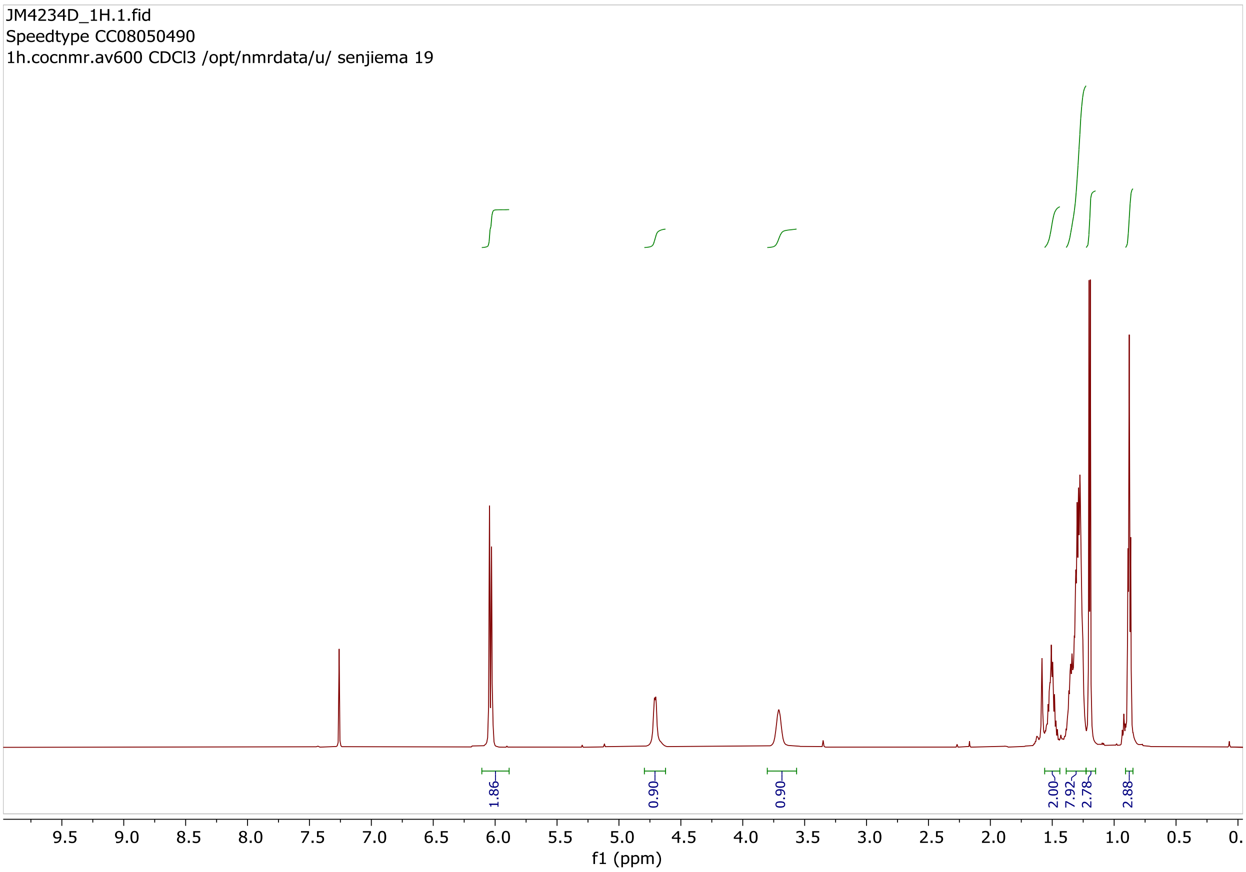
Compound 3ag



^{1}H NMR



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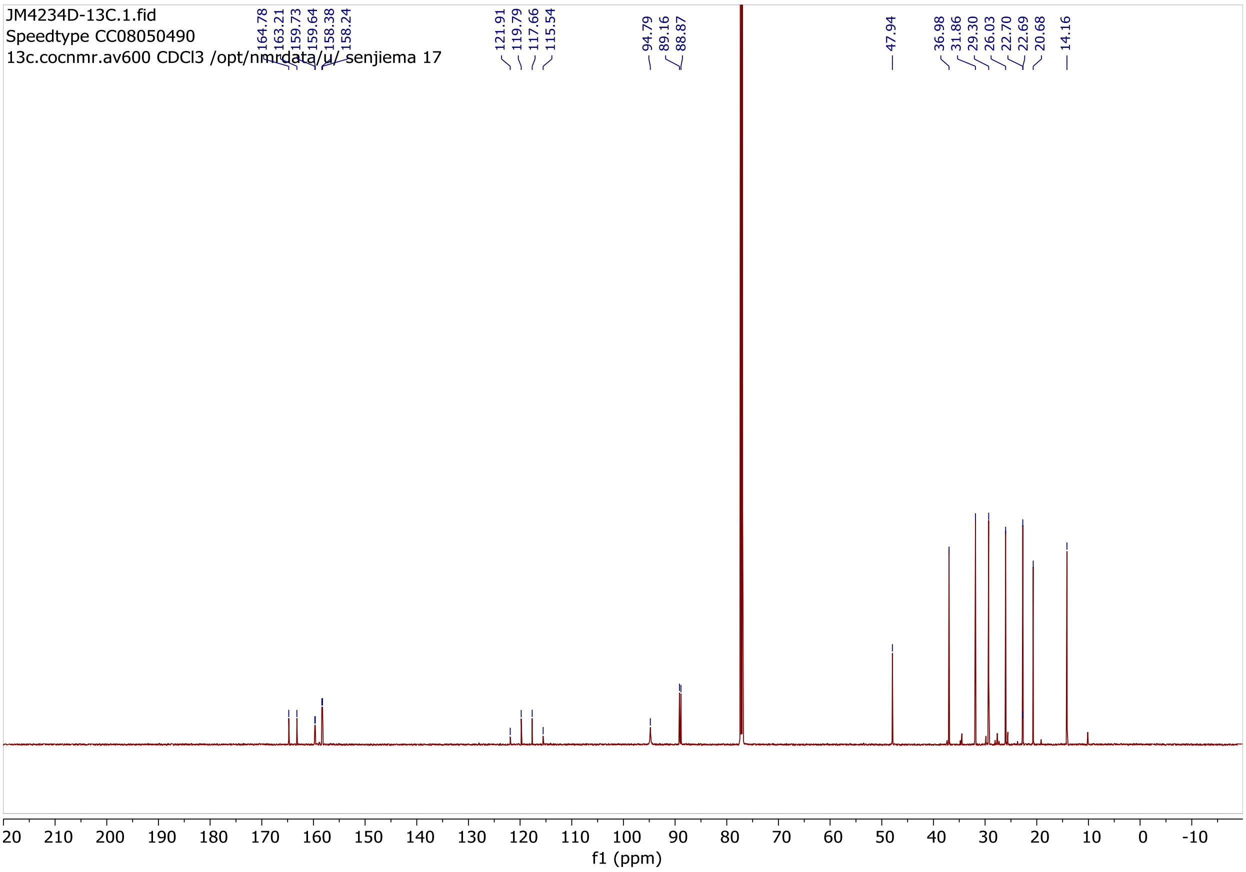
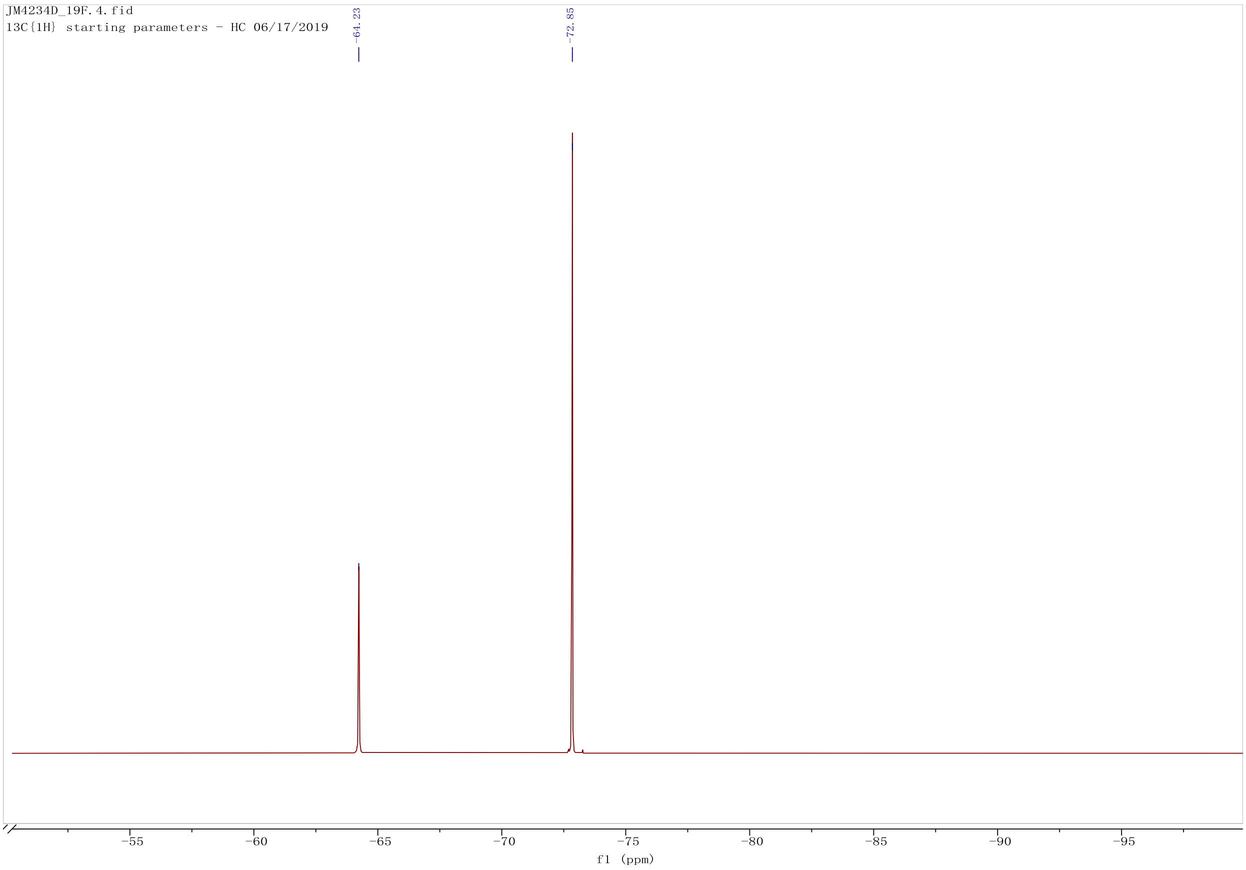
^{13}C NMR



^{19}F NMR


JM4234D_19F.4.fid
13C{1H} starting parameters - HC 06/17/2019
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-72.85
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

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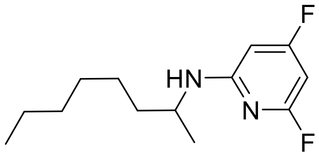
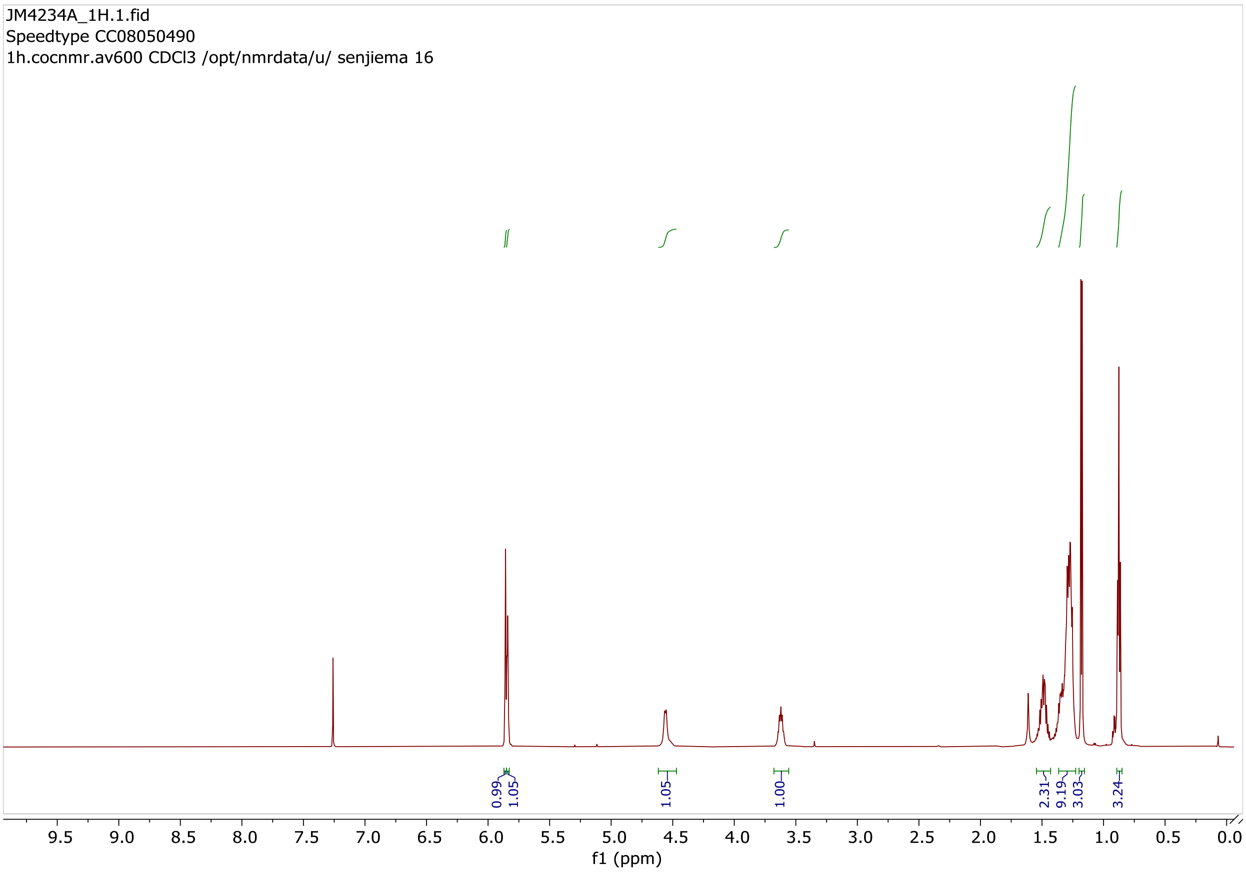
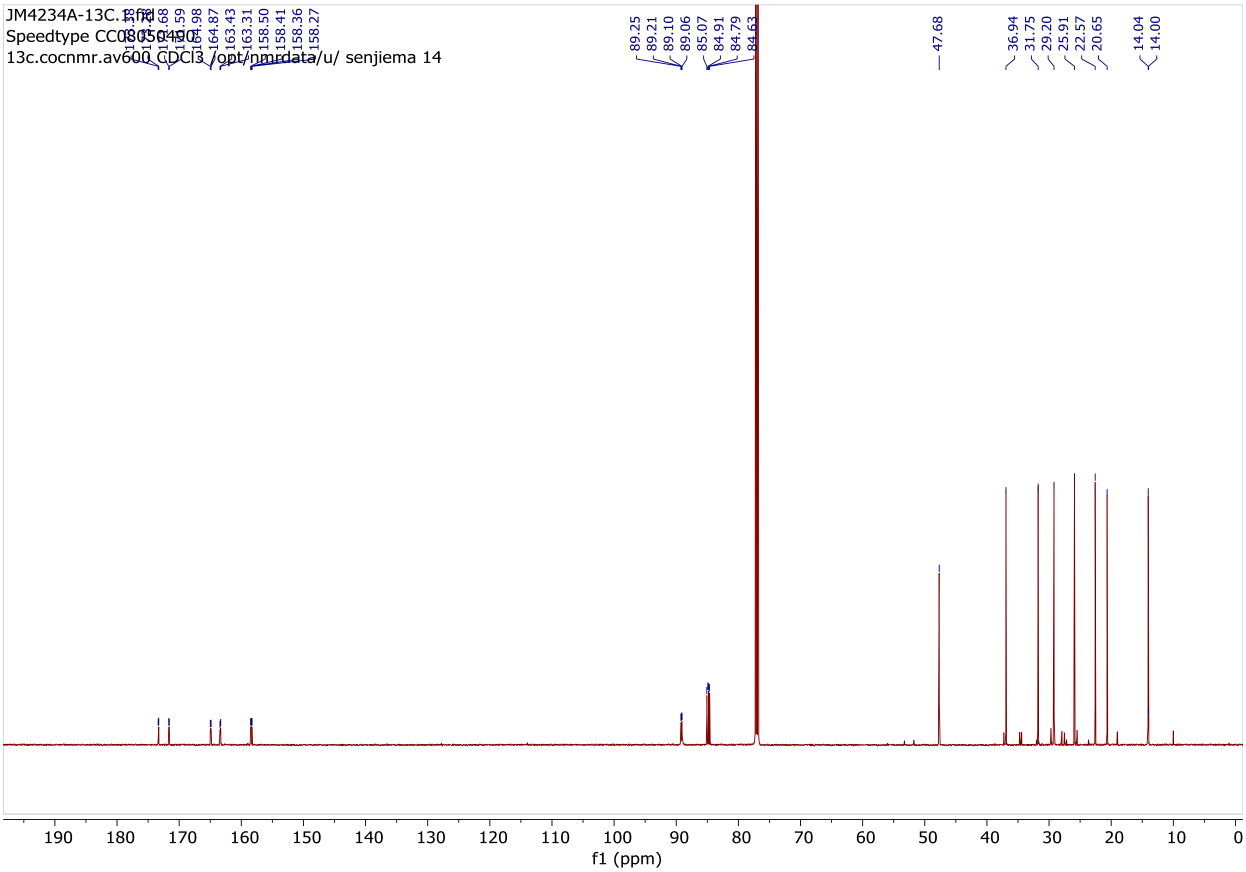
Compound 3ah



^{1}H NMR



^{13}C NMR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Speedtype CC08050490
13c.cocnmr.av600 CDCl3 /opt/nmrdata/u/ senjiema 14
173.38
173.28
171.68
171.59
164.98
164.87
163.43
163.31
158.50
158.41
158.36
158.27
89.25
89.21
89.10
89.06
85.07
84.91
84.79
84.63
47.68
36.94
31.75
29.20
25.91
22.57
20.65
14.04
14.00
190
180
170
160
150
140
130
120
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80
70
60
50
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f1 (ppm)

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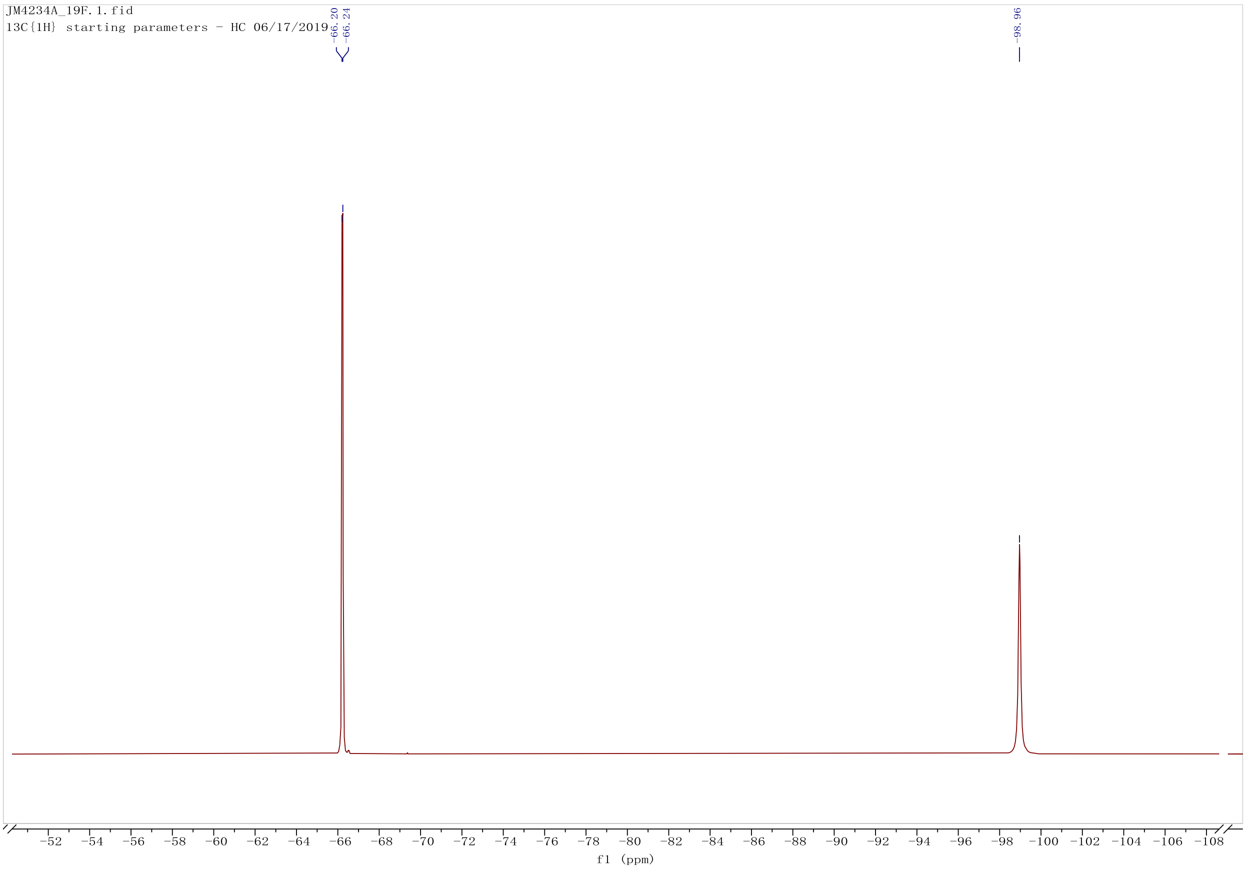
^{19}F NMR



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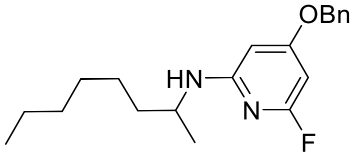
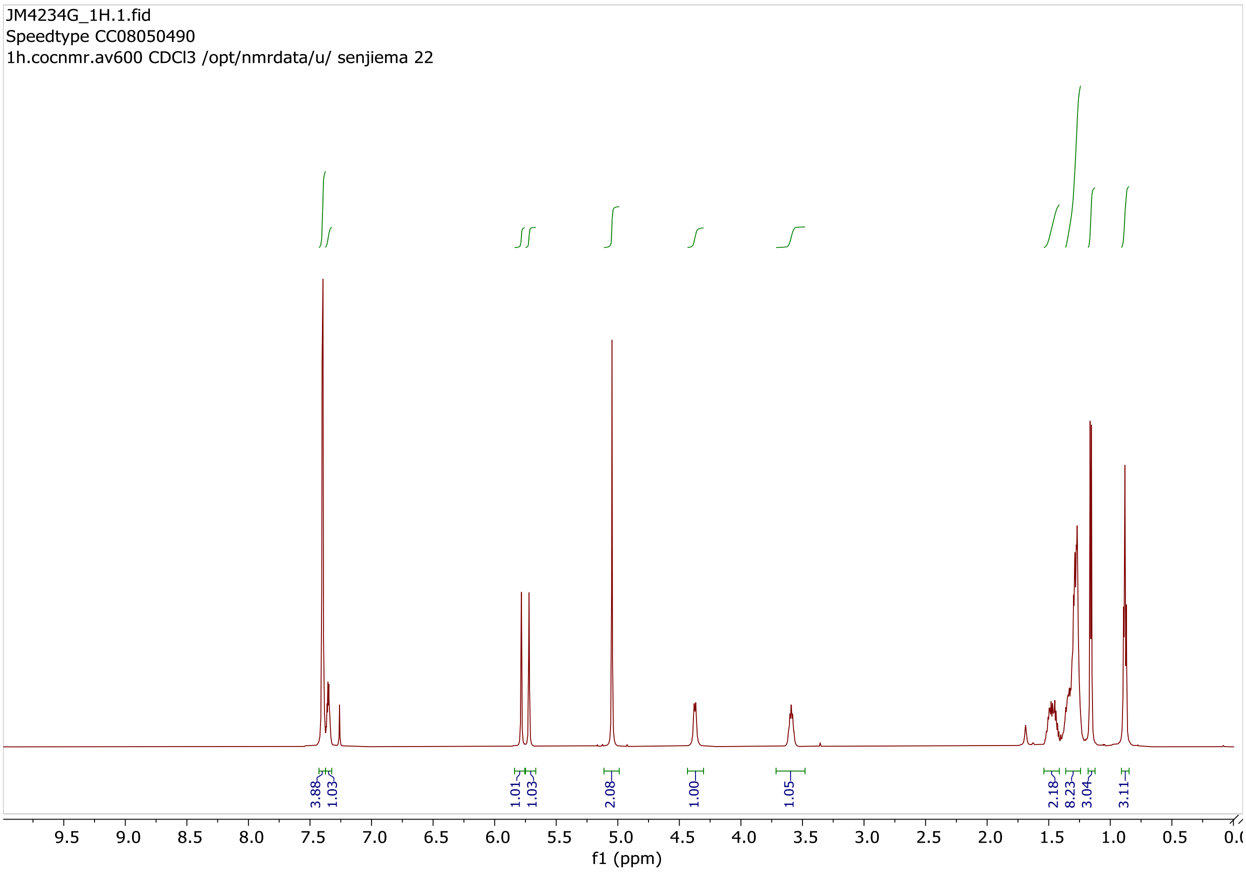
Compound 3ai



^{1}H NMR



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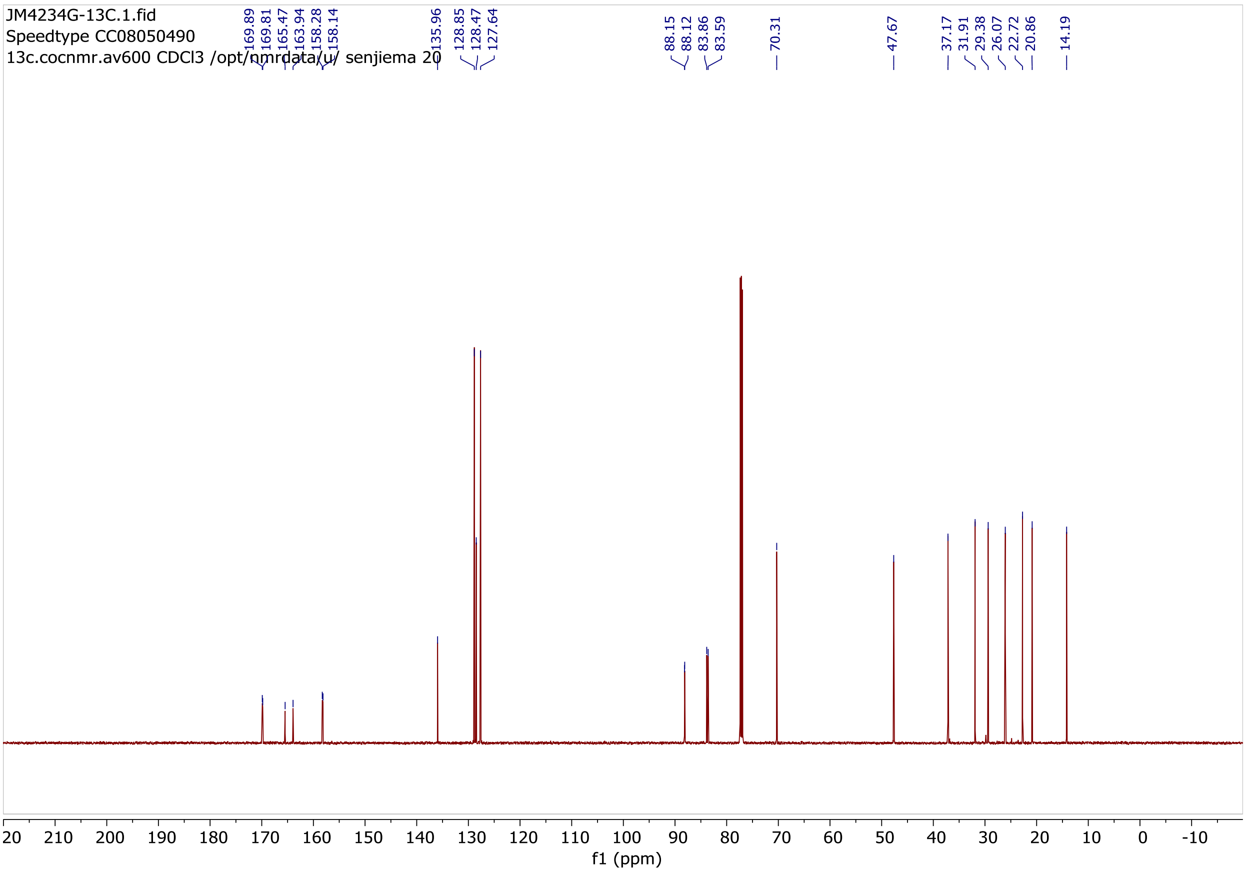
^{13}C NMR



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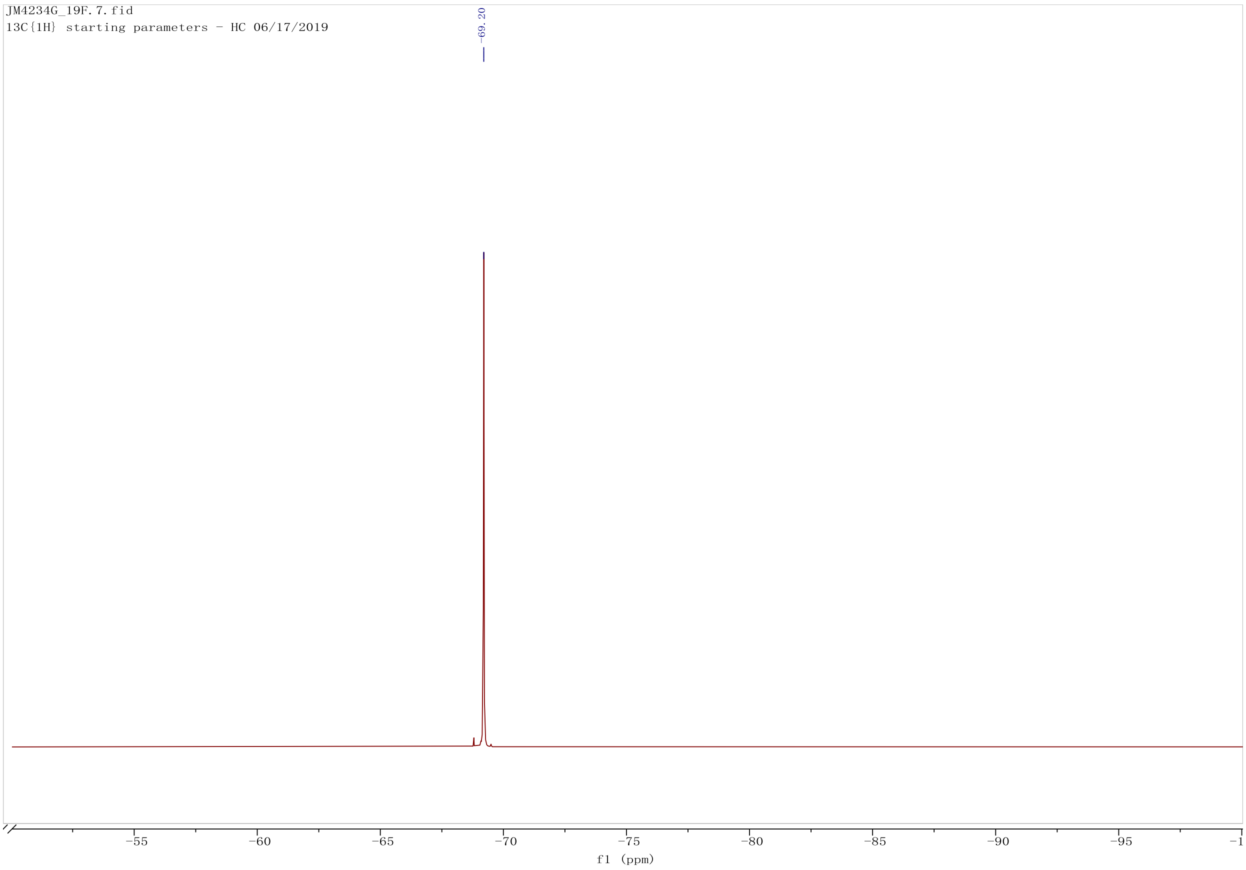
^{19}F NMR



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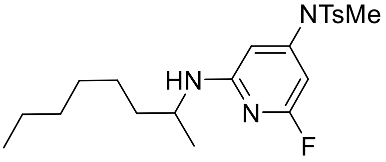
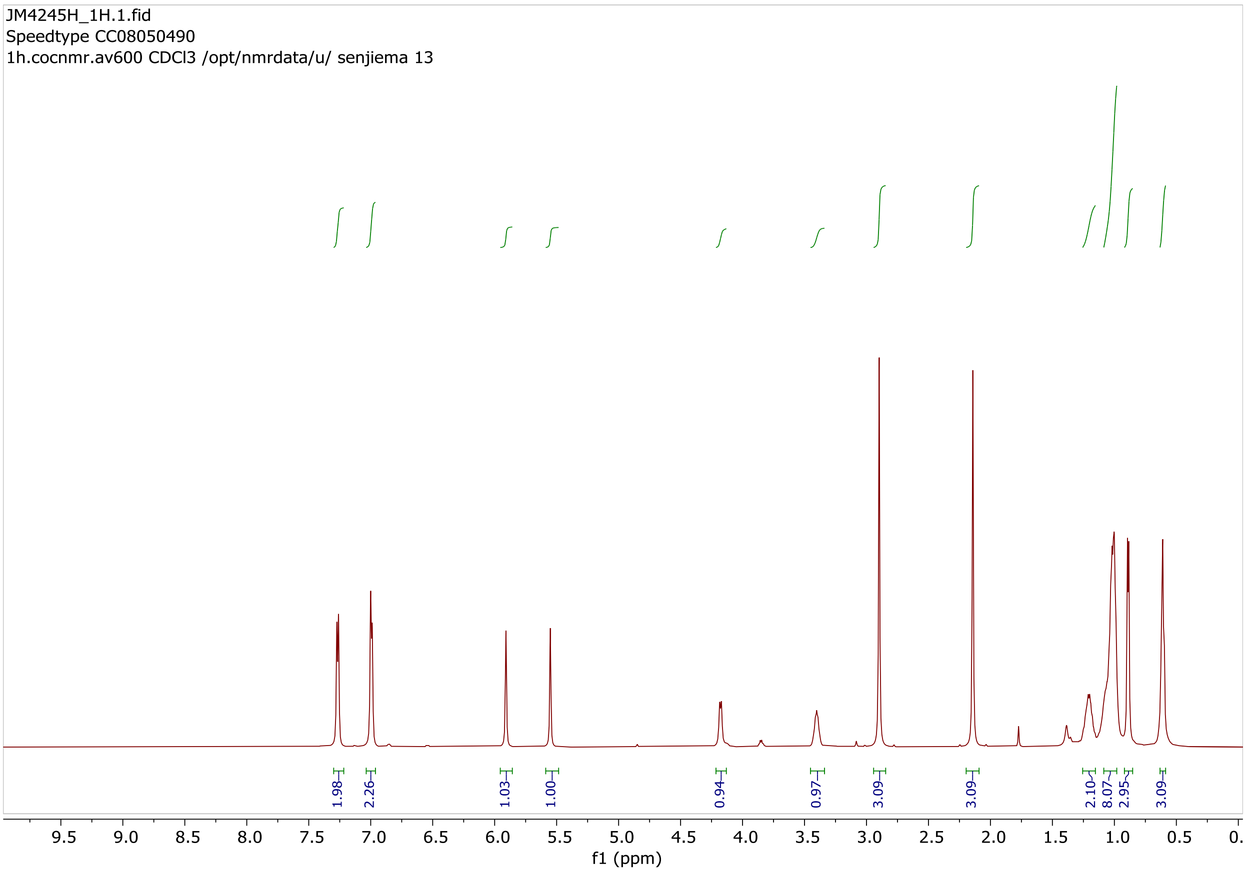
Compound 3aj



^{1}H NMR



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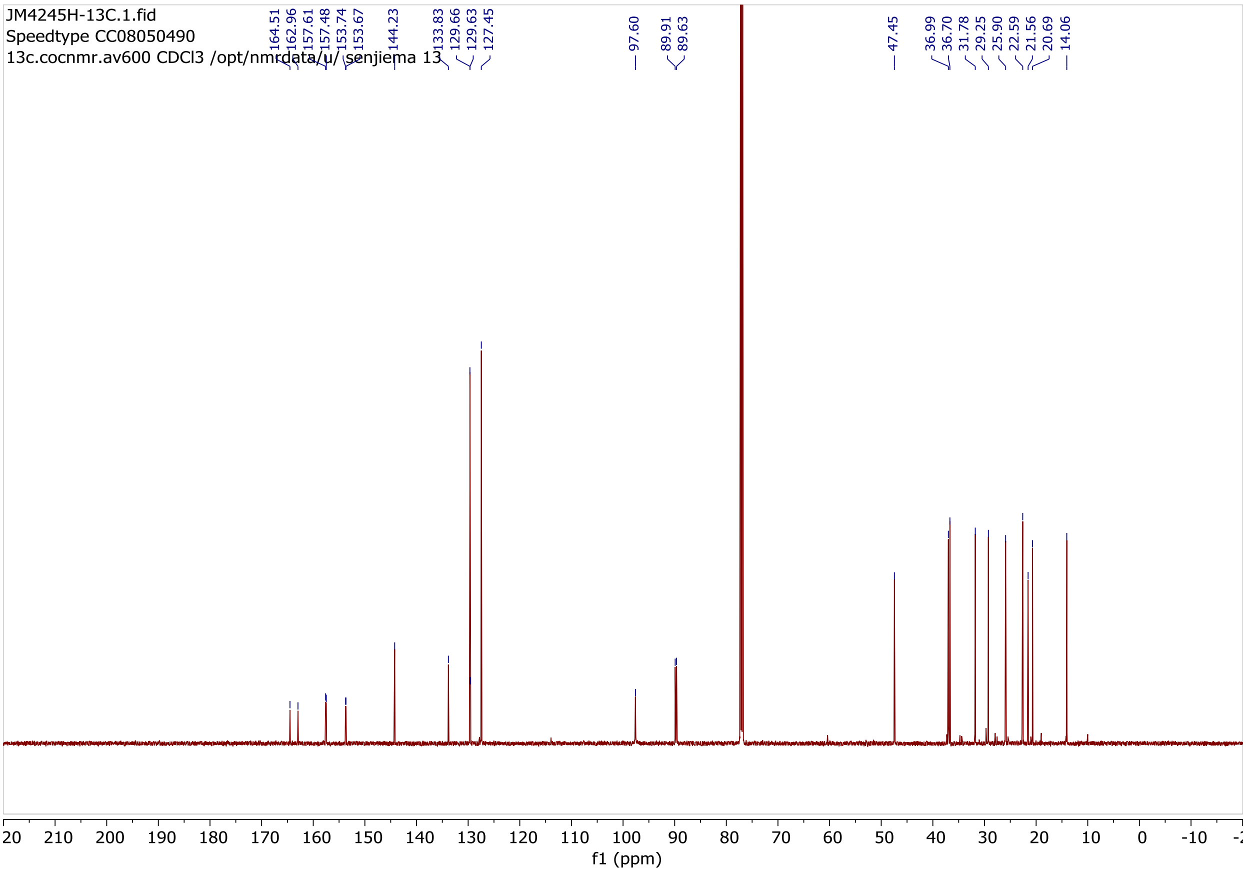
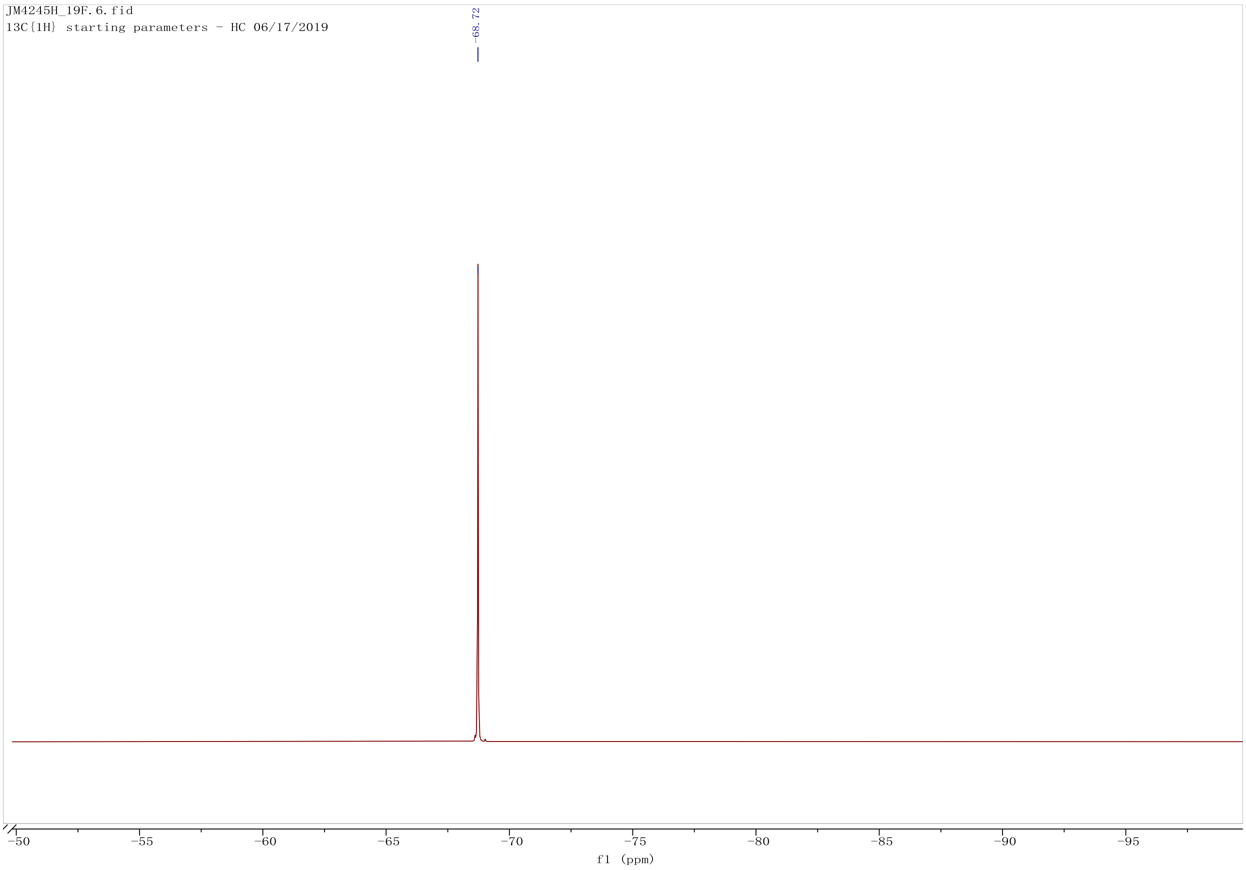
^{13}C NMR



^{19}F NMR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13C{1H} starting parameters - HC 06/17/2019
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-50
-55
-60
-65
-70
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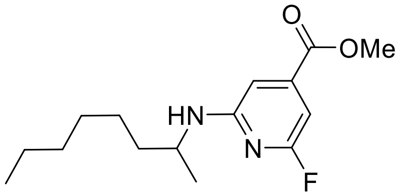
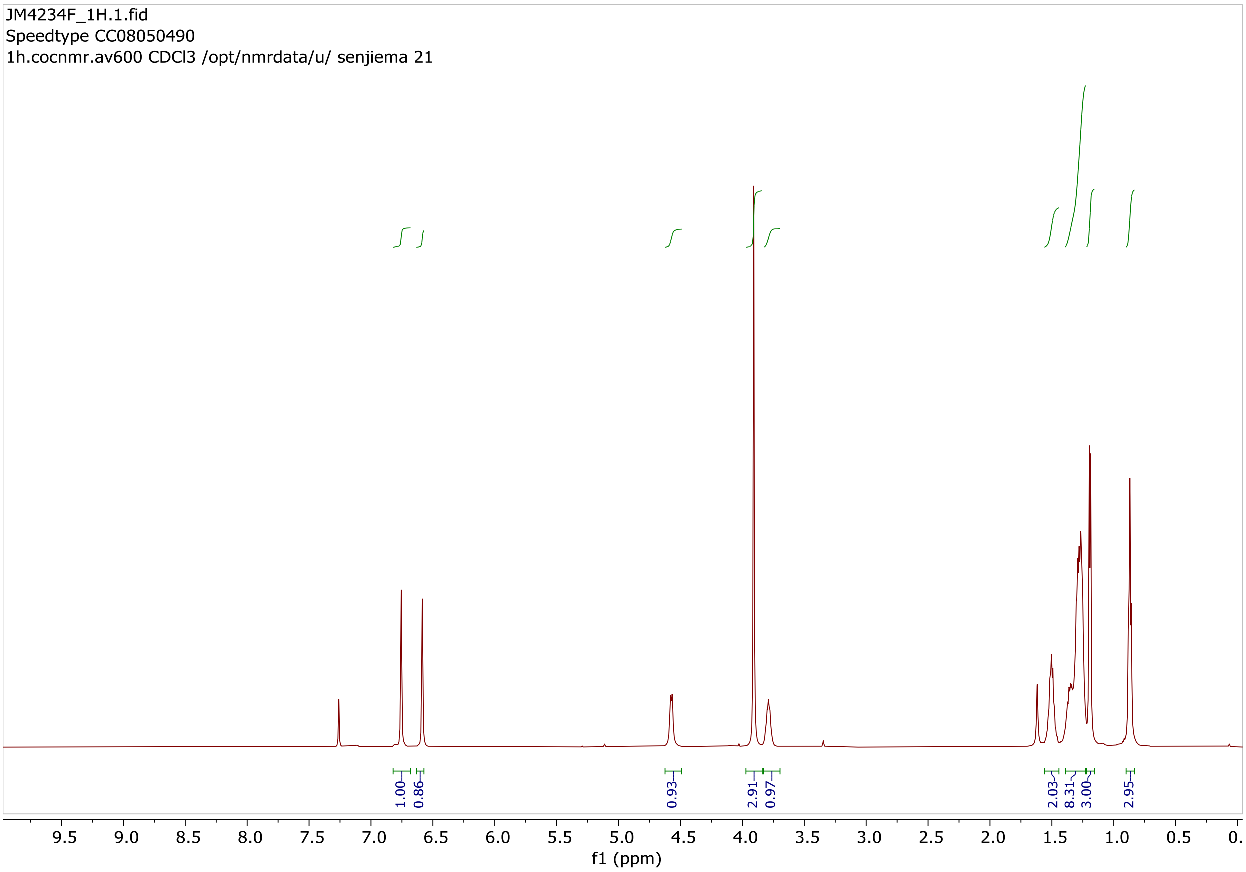
-85
-90
-95
f1 (ppm)

Compound 3ak



^{1}H NMR



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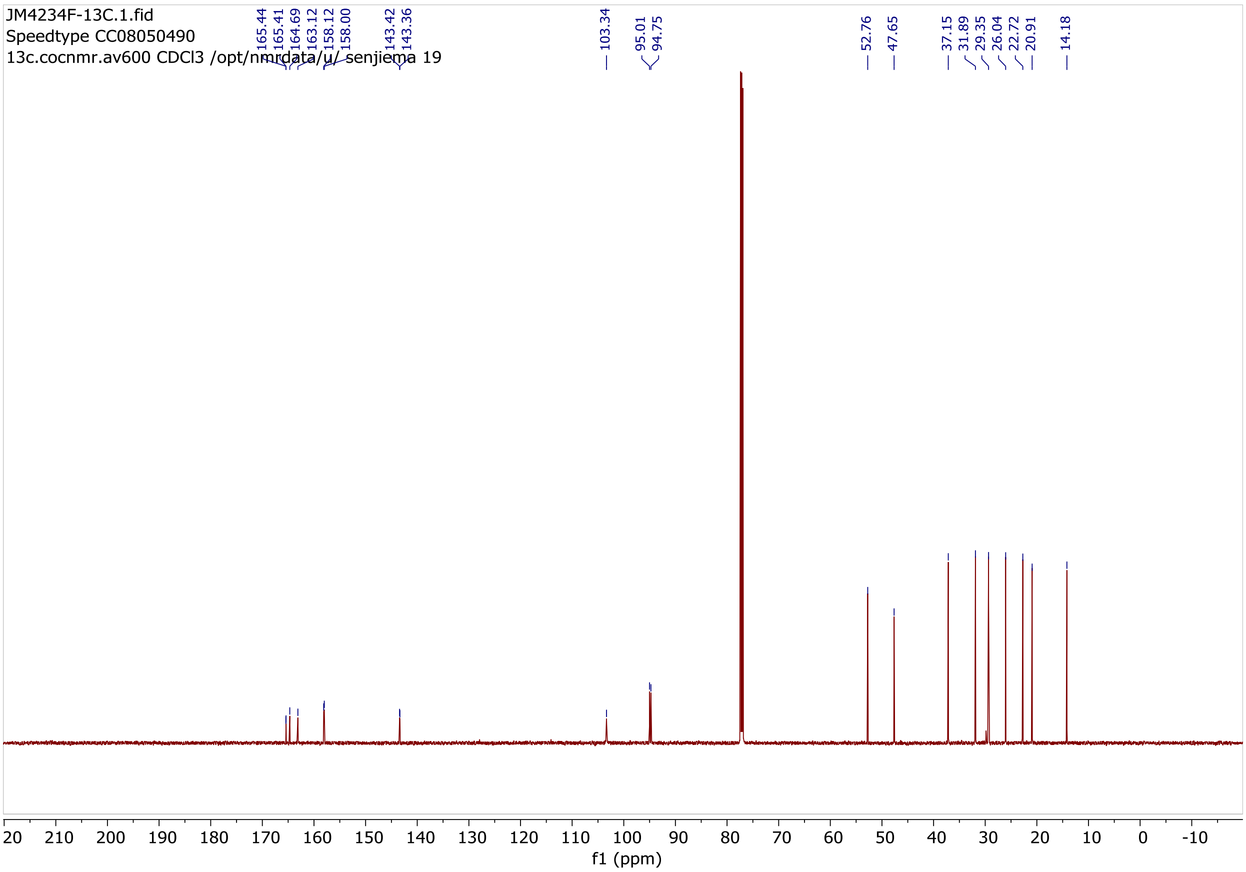
^{13}C NMR



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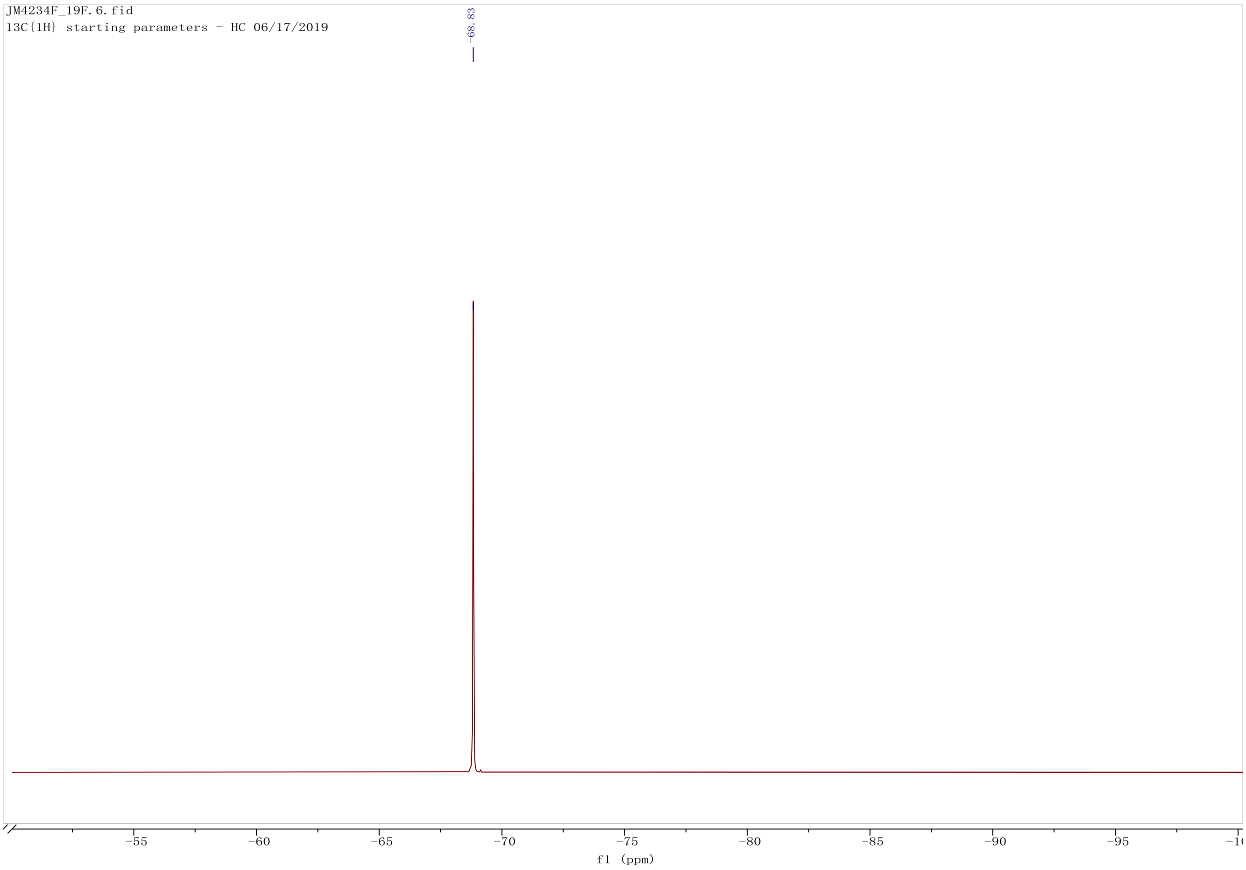
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-70
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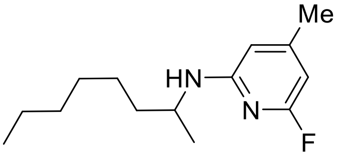
-80
-85
-90
-95
f1 (ppm)

Compound 3al



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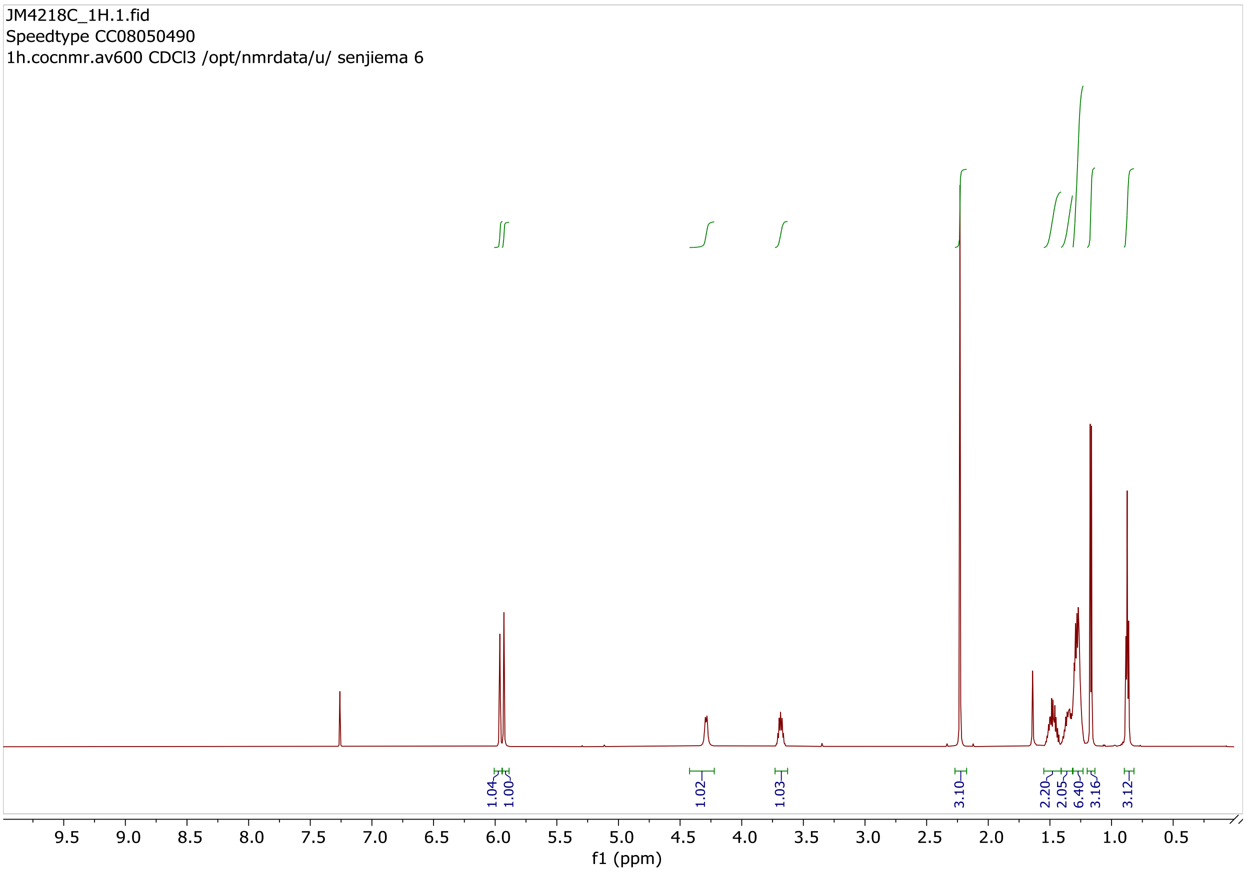

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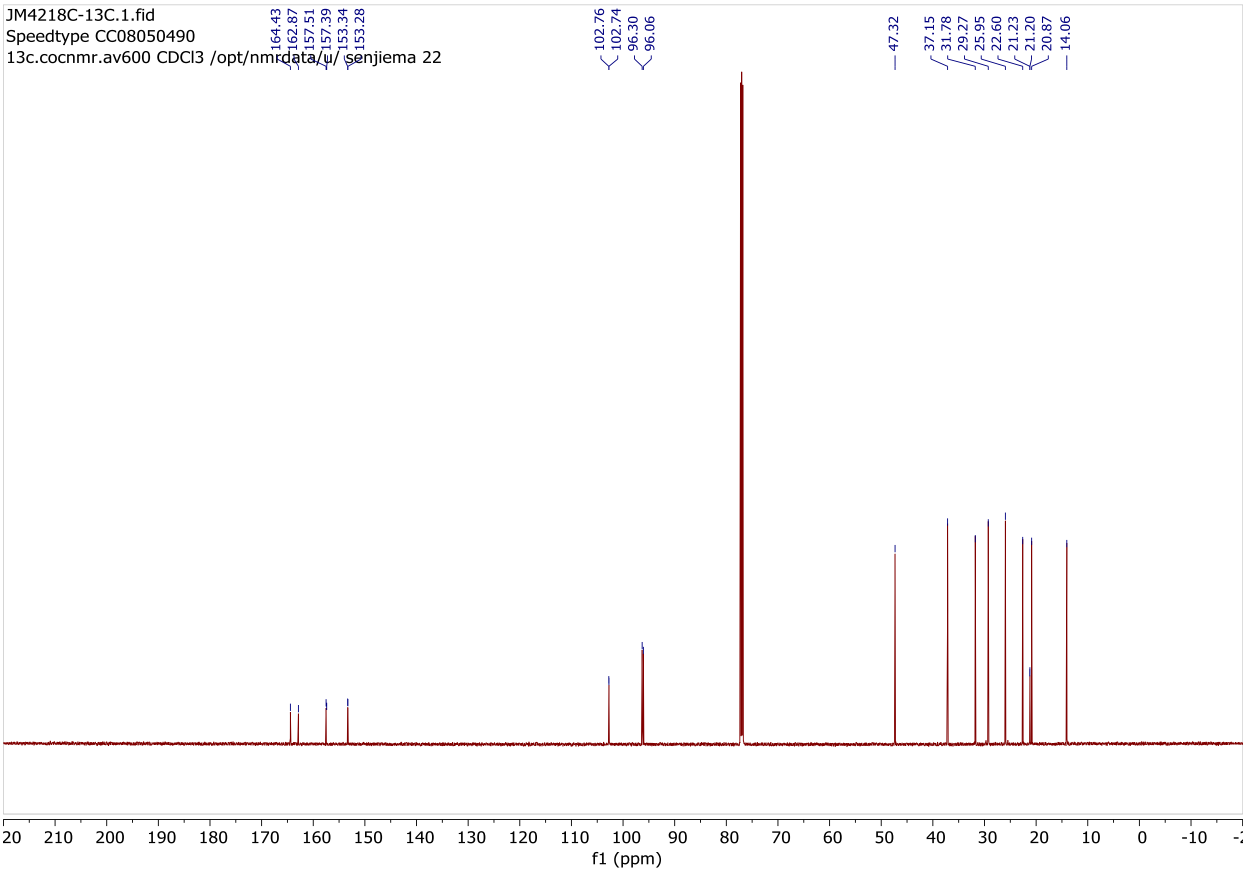

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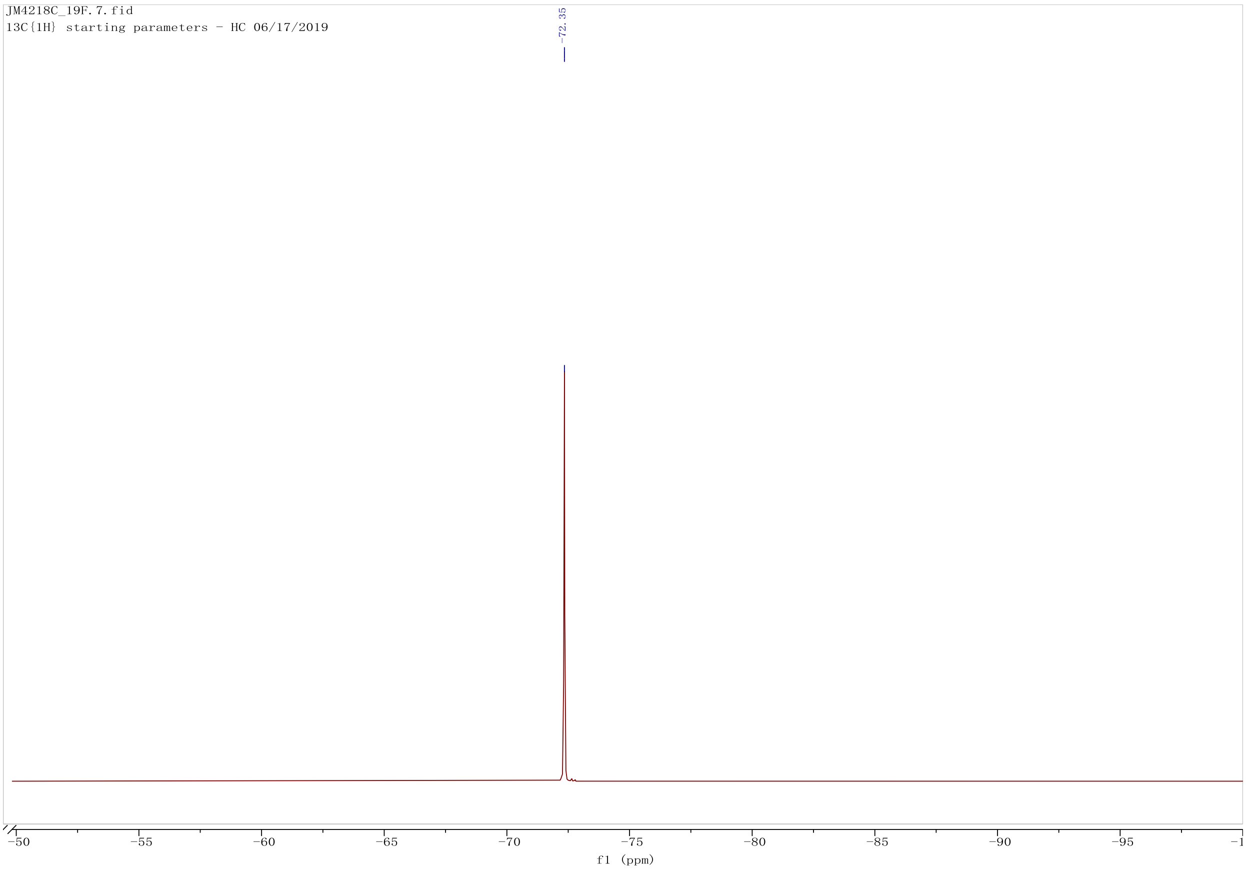
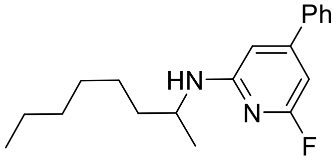
^{19}F NMR



Compound 3am



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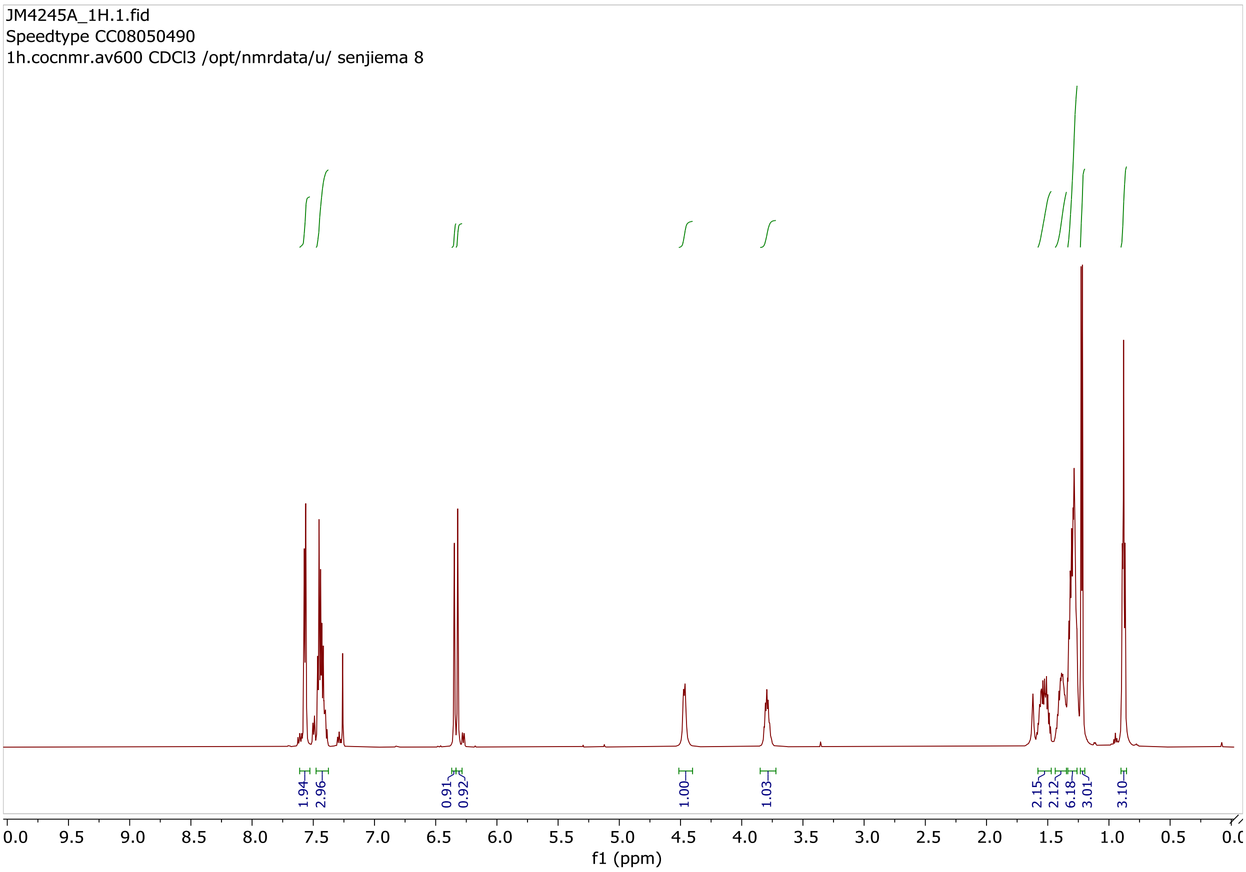

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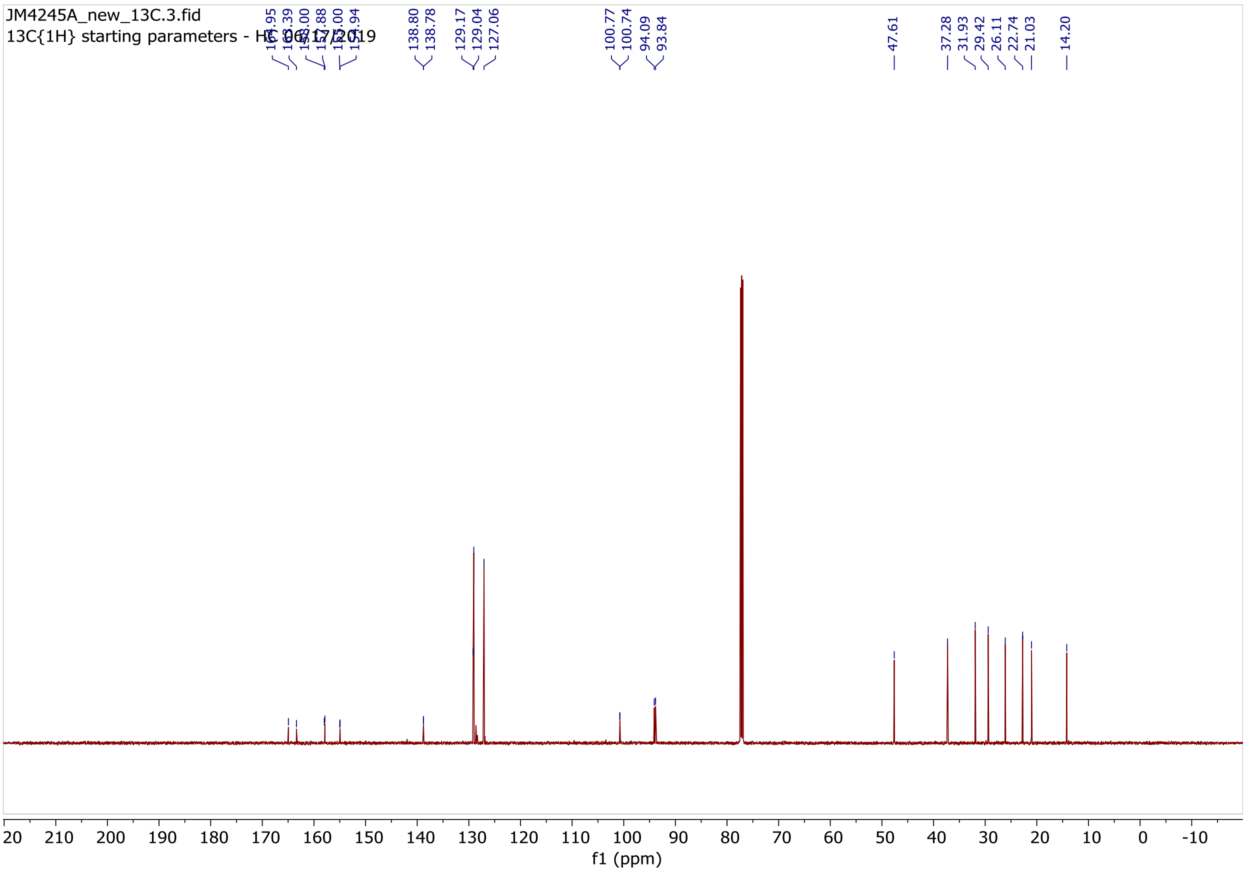

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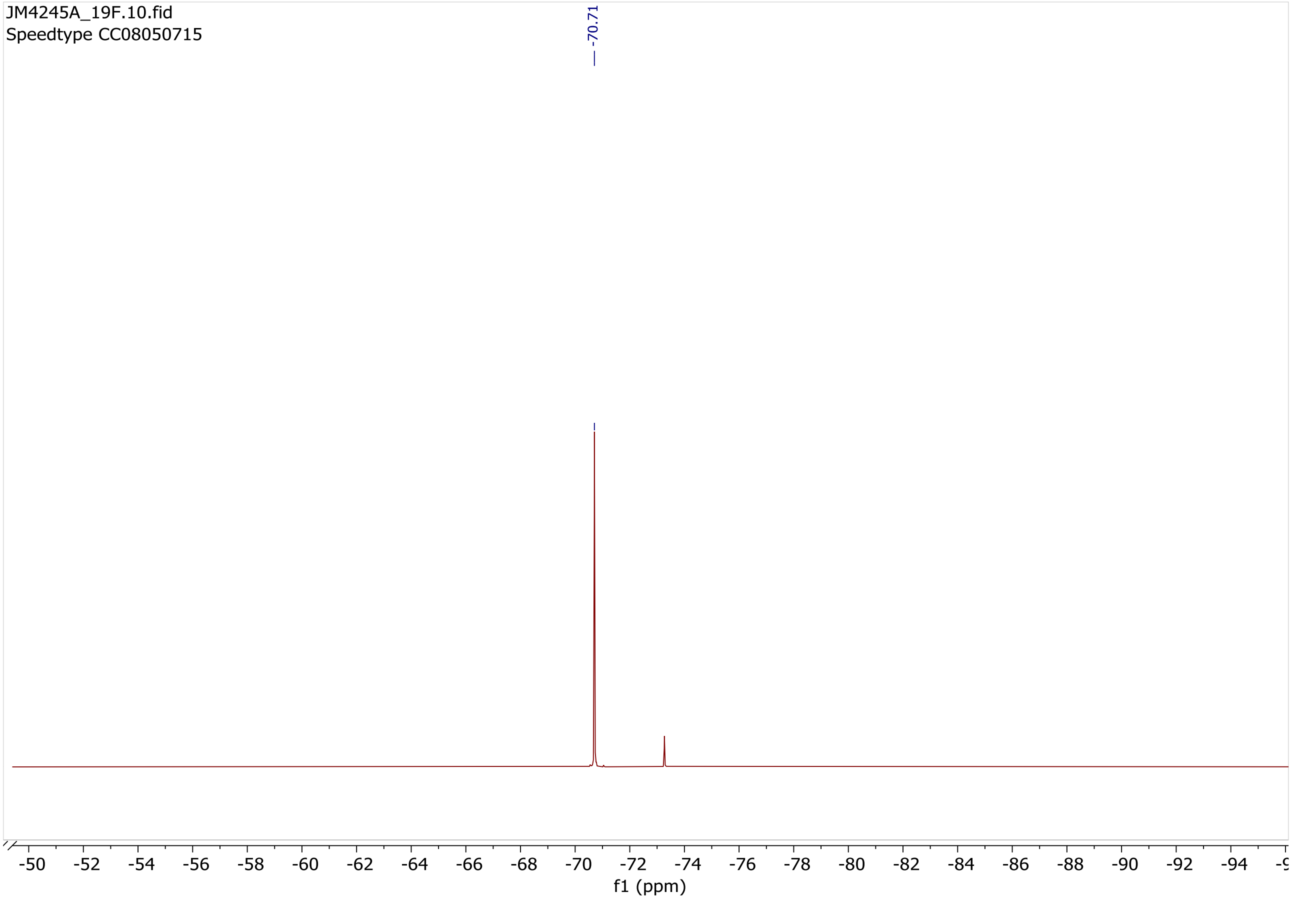
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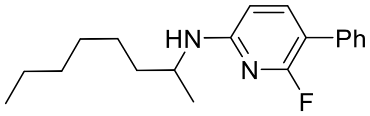
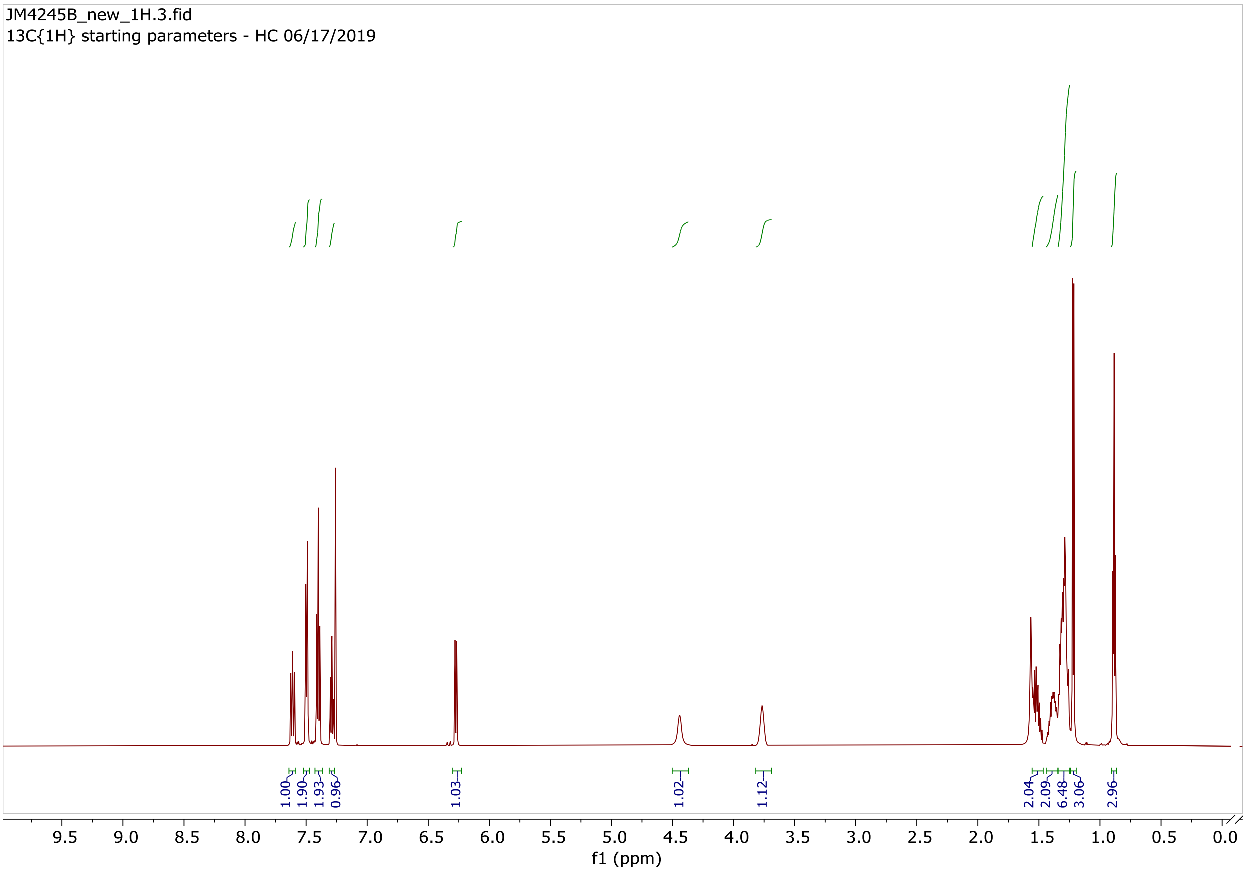
-50
-52
-54
-56
-58
-60
-62
-64
-66
-68
-70
-72
-74
-76
-78
-80
-82
-84
-86
-88
-90
-92
-94
f1 (ppm)

Compound 3an



^{1}H NMR



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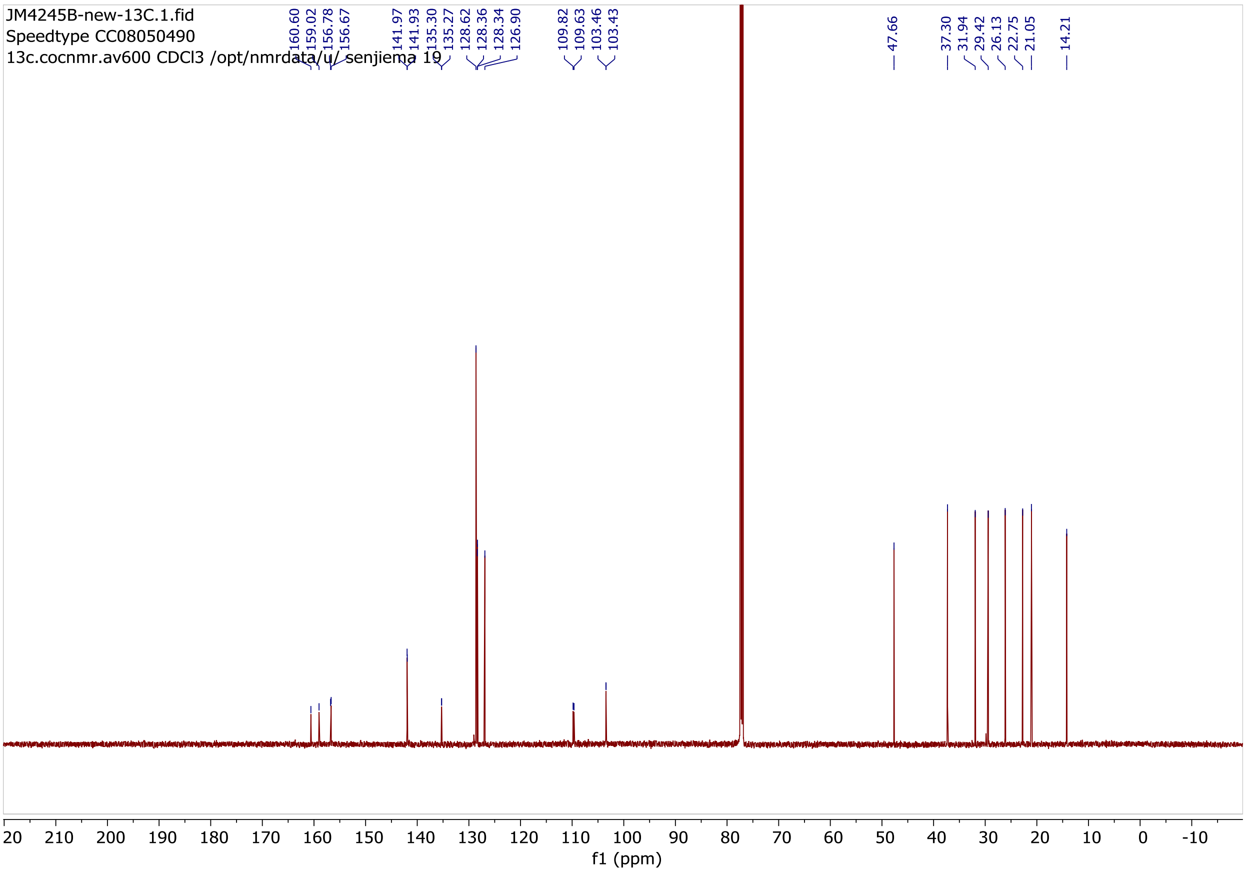
^{13}C NMR



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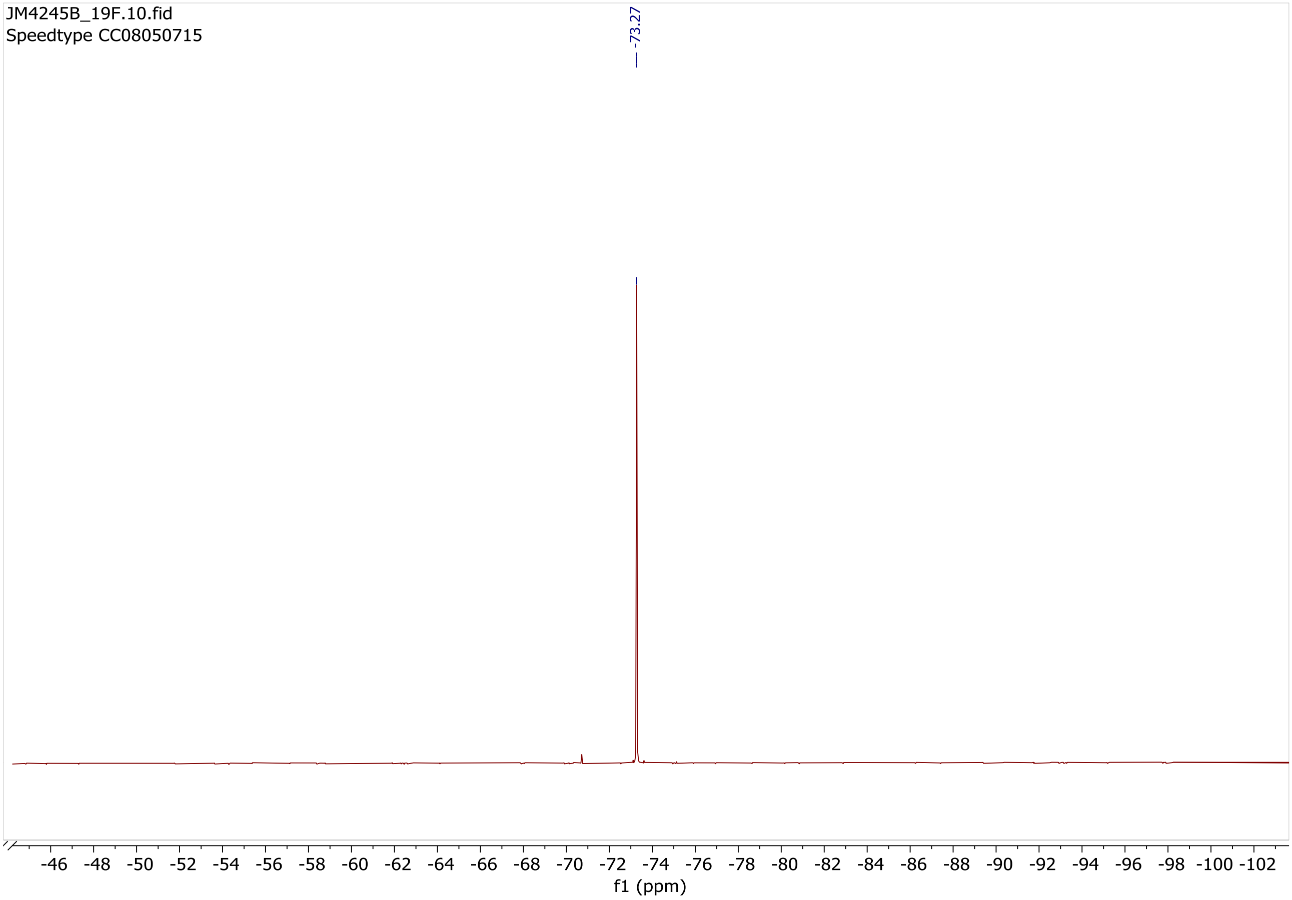
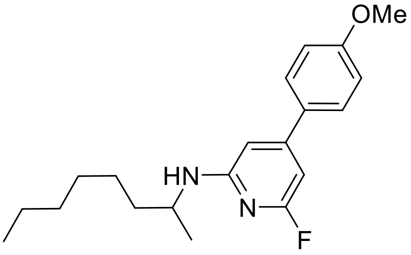
^{19}F NMR



Compound 3ao



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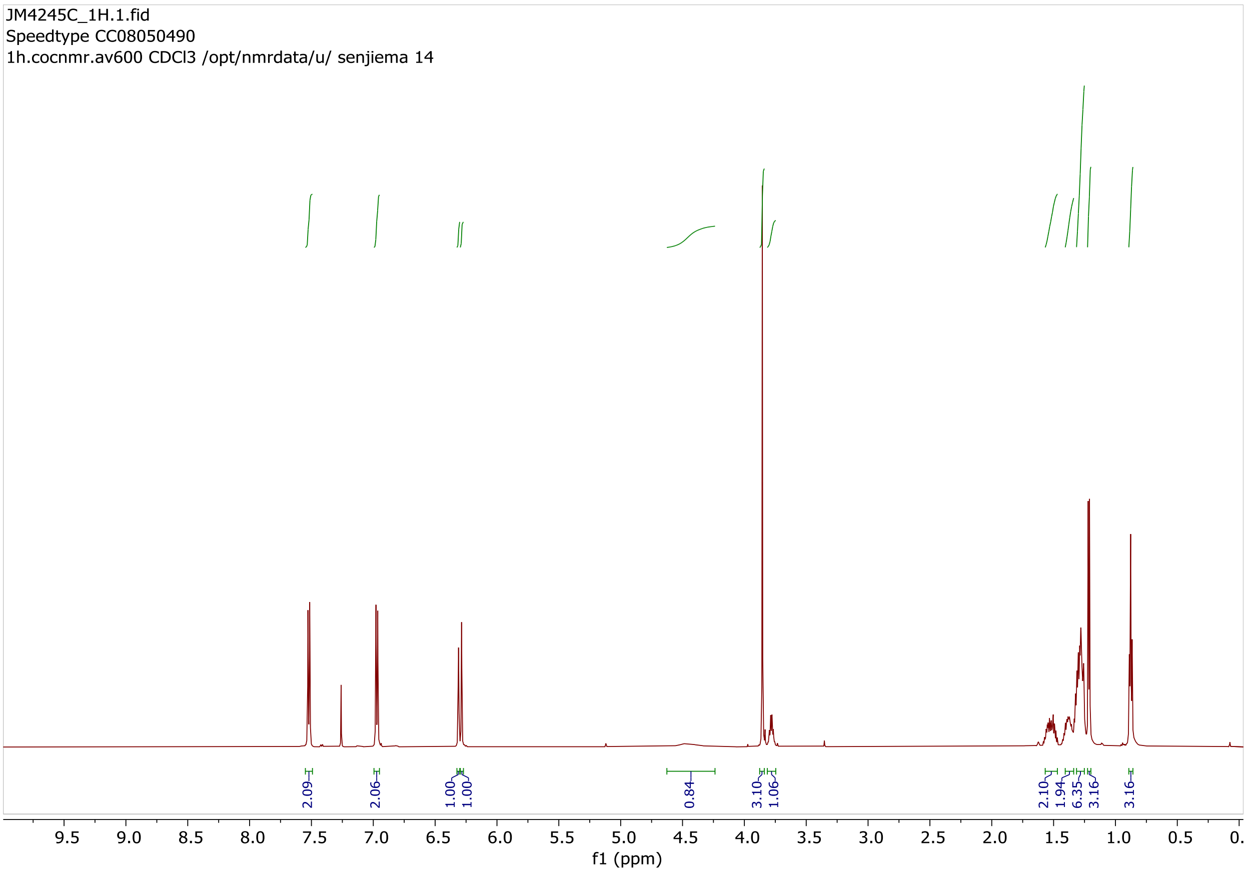

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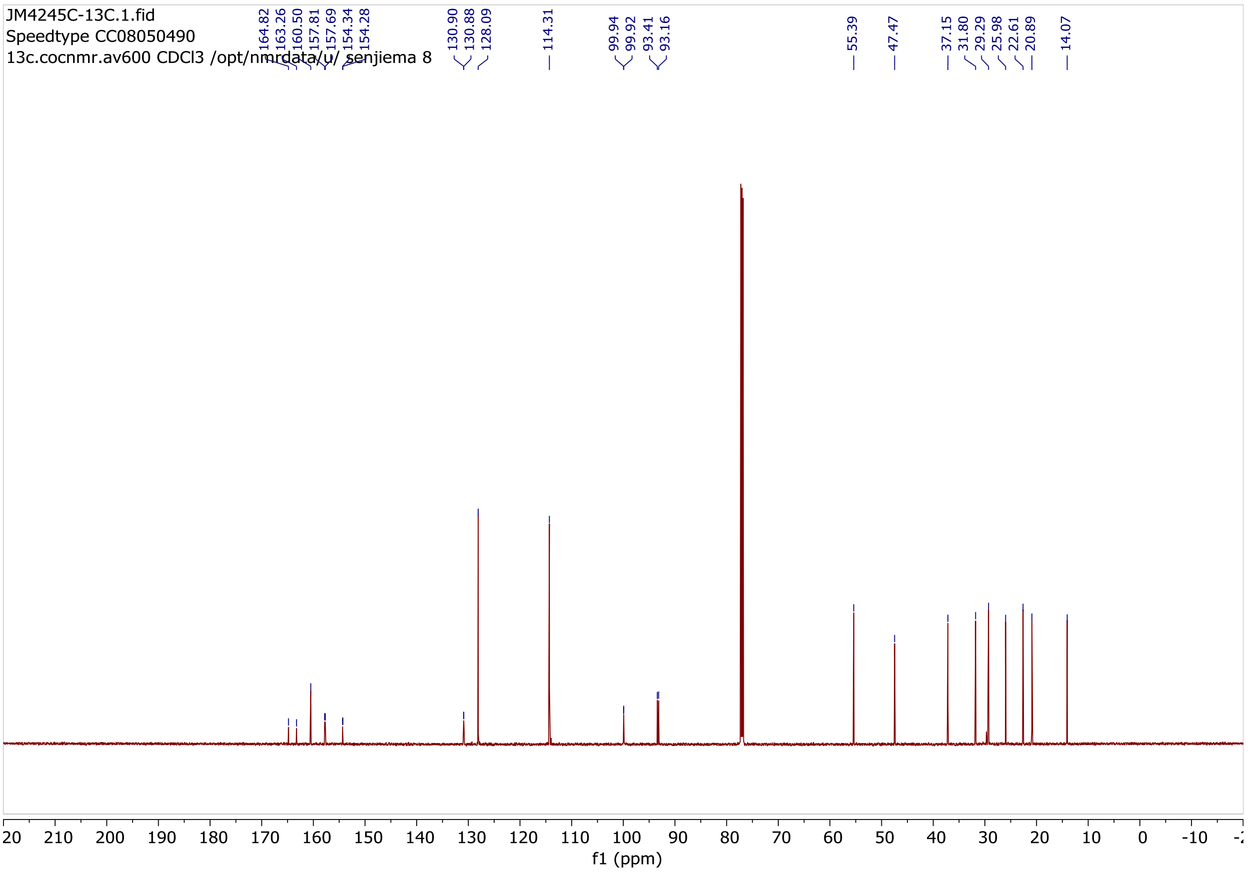
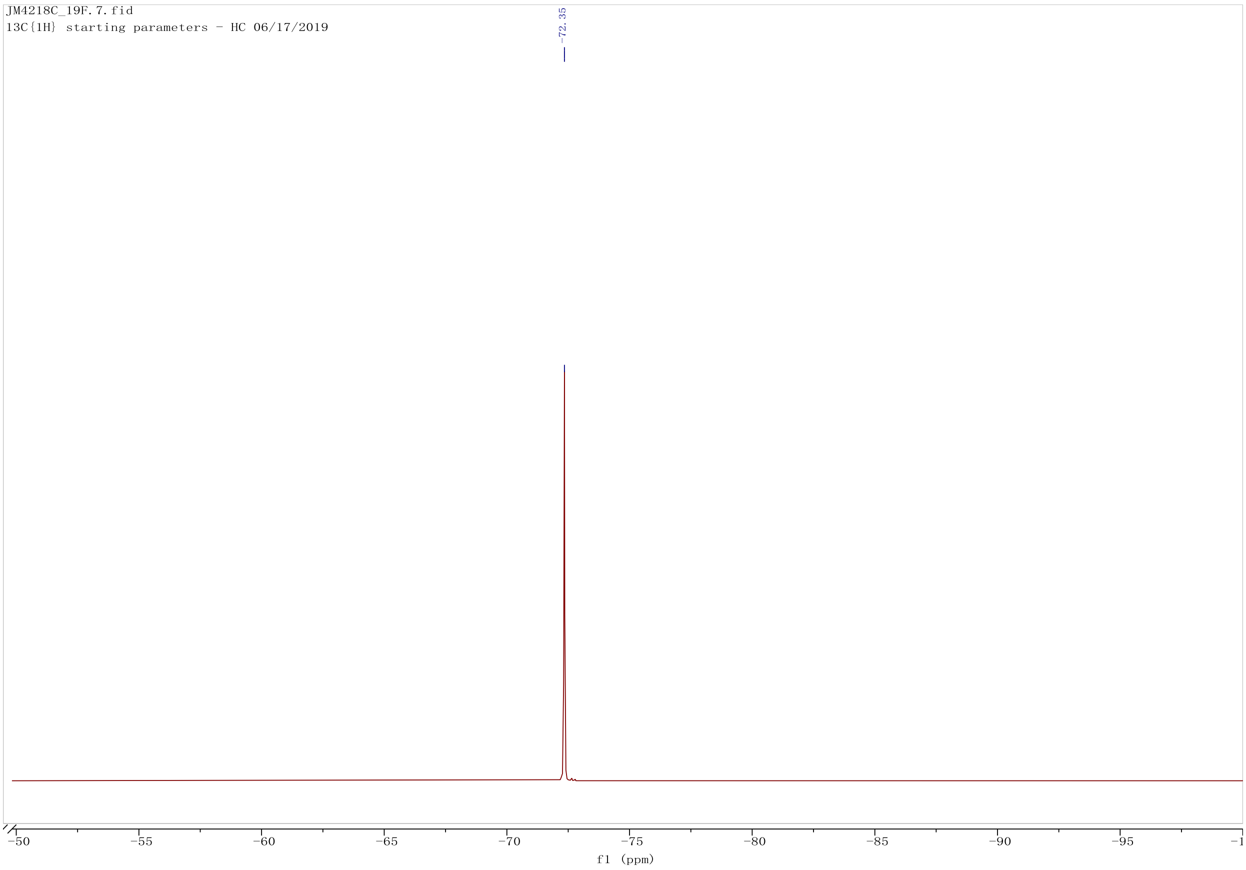
^{13}C NMR



^{19}F NMR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-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-1
f1 (ppm)

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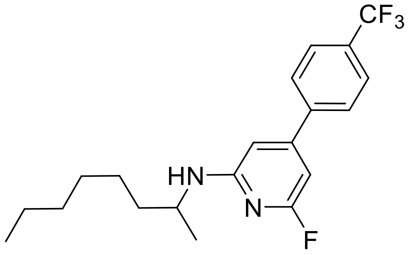
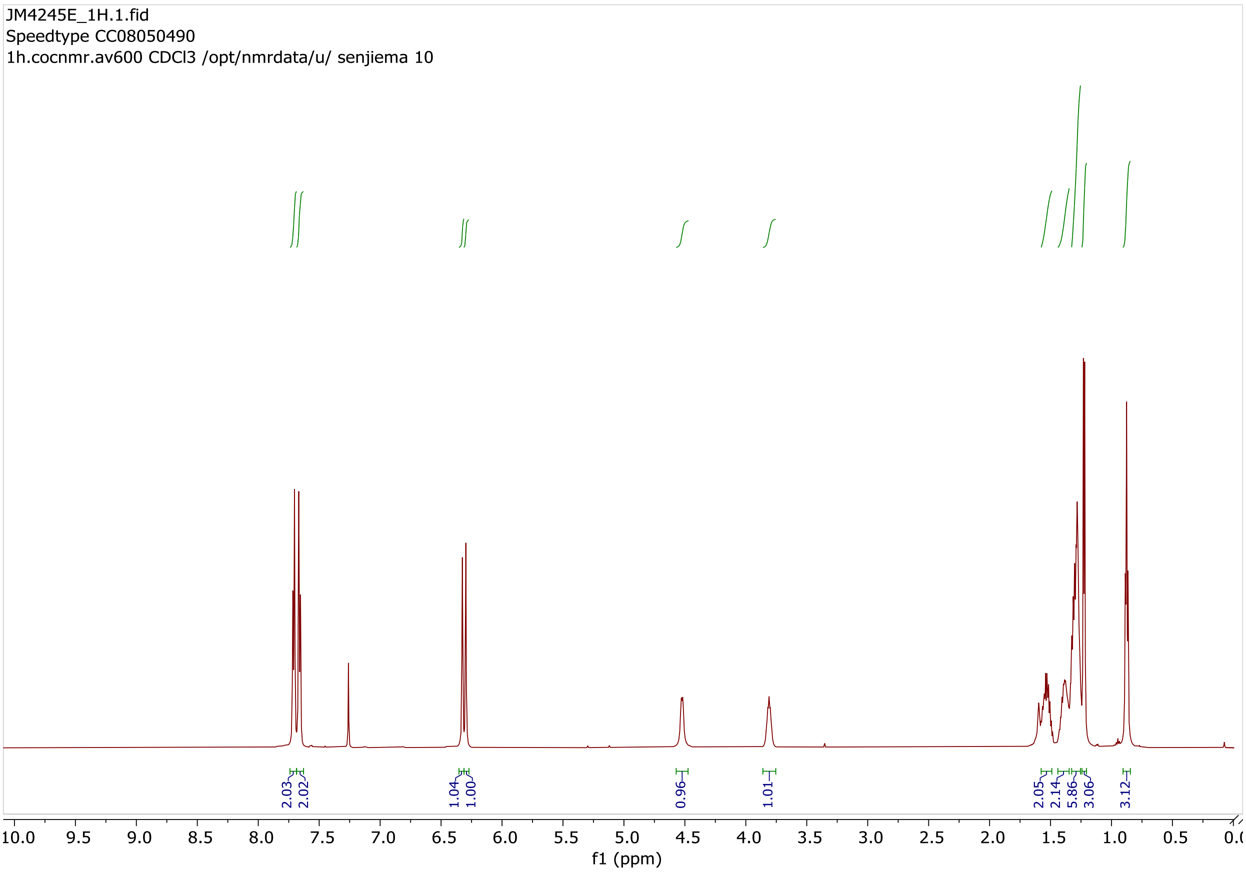
Compound 3ap



^{1}H NMR



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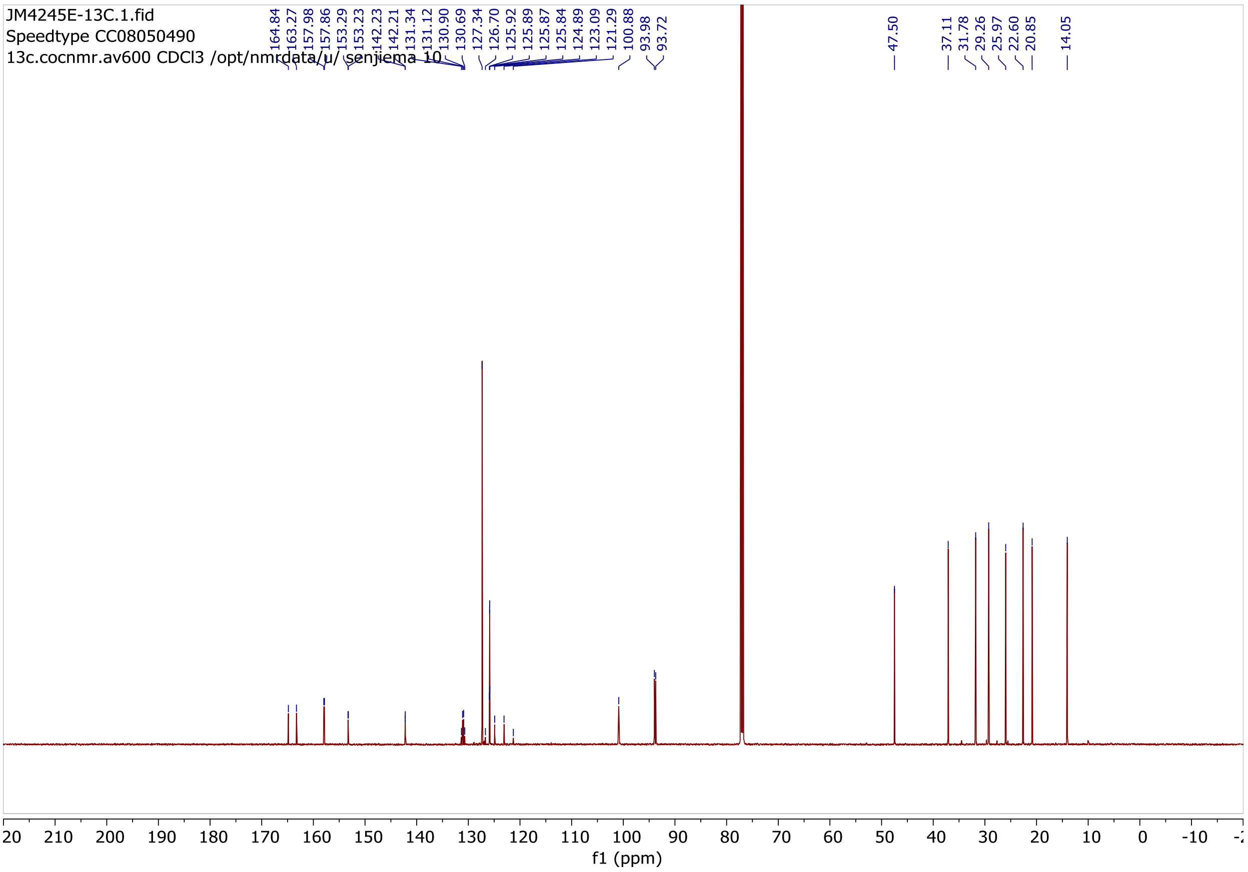
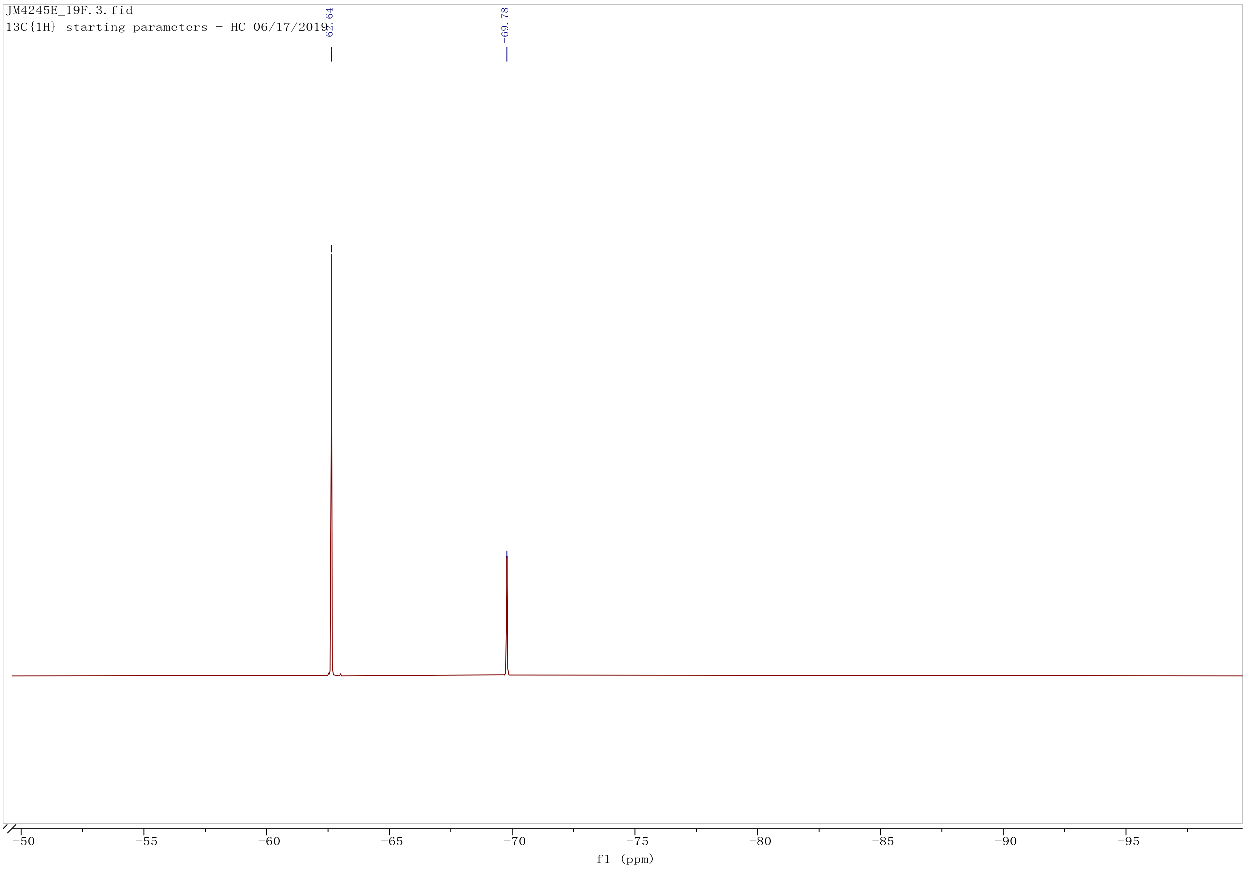
^{13}C NMR



^{19}F NMR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-69.78
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

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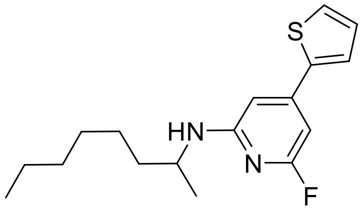
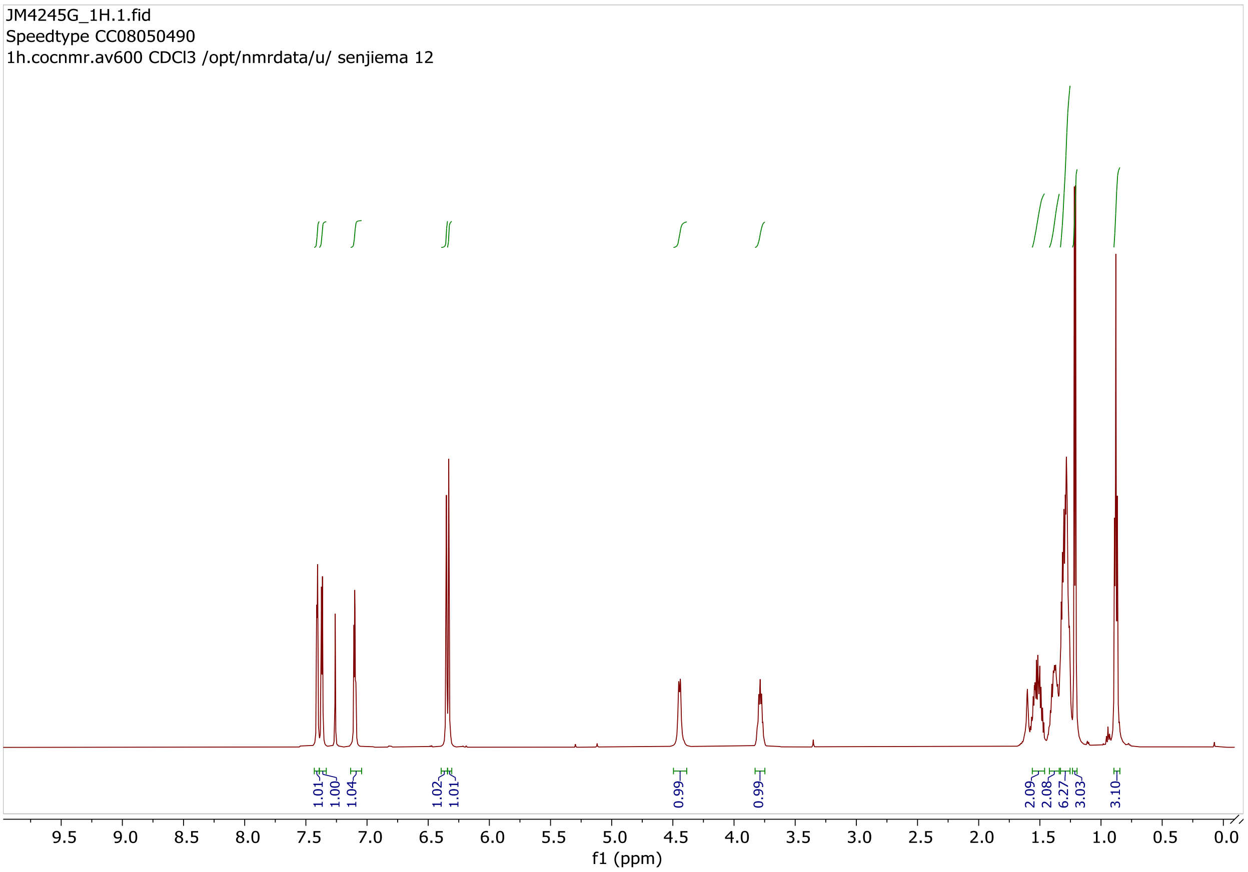
Compound 3aq



^{1}H NMR



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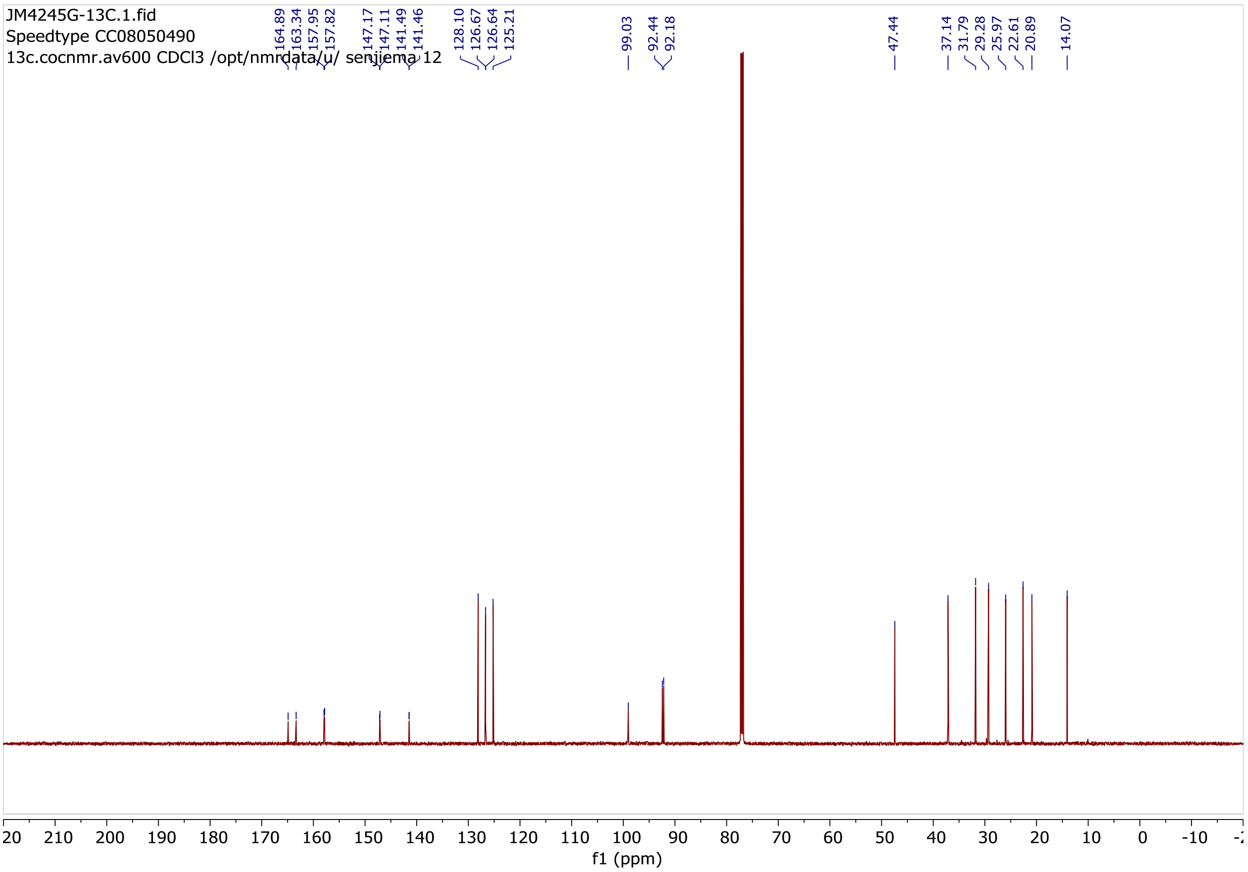
^{13}C NMR



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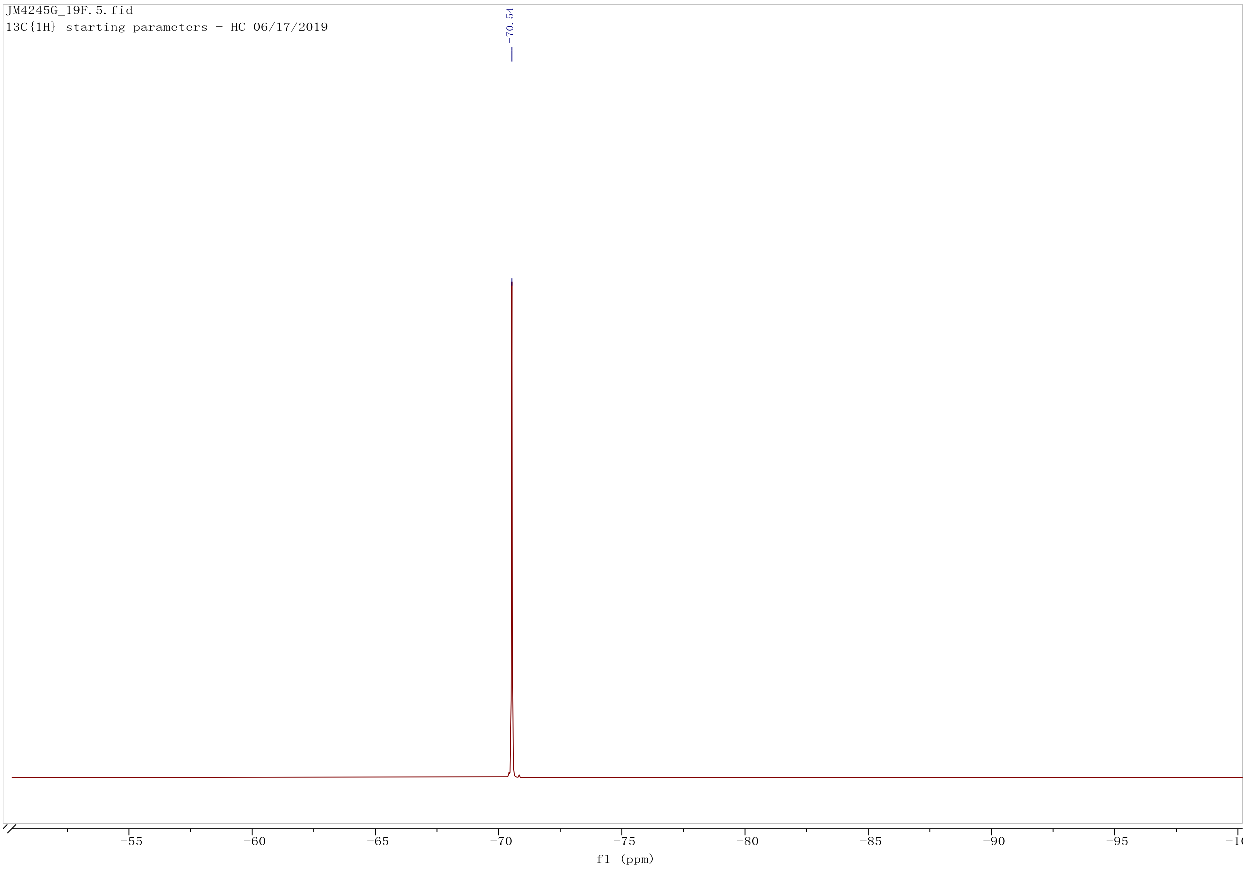
^{19}F NMR



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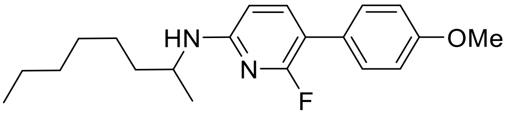
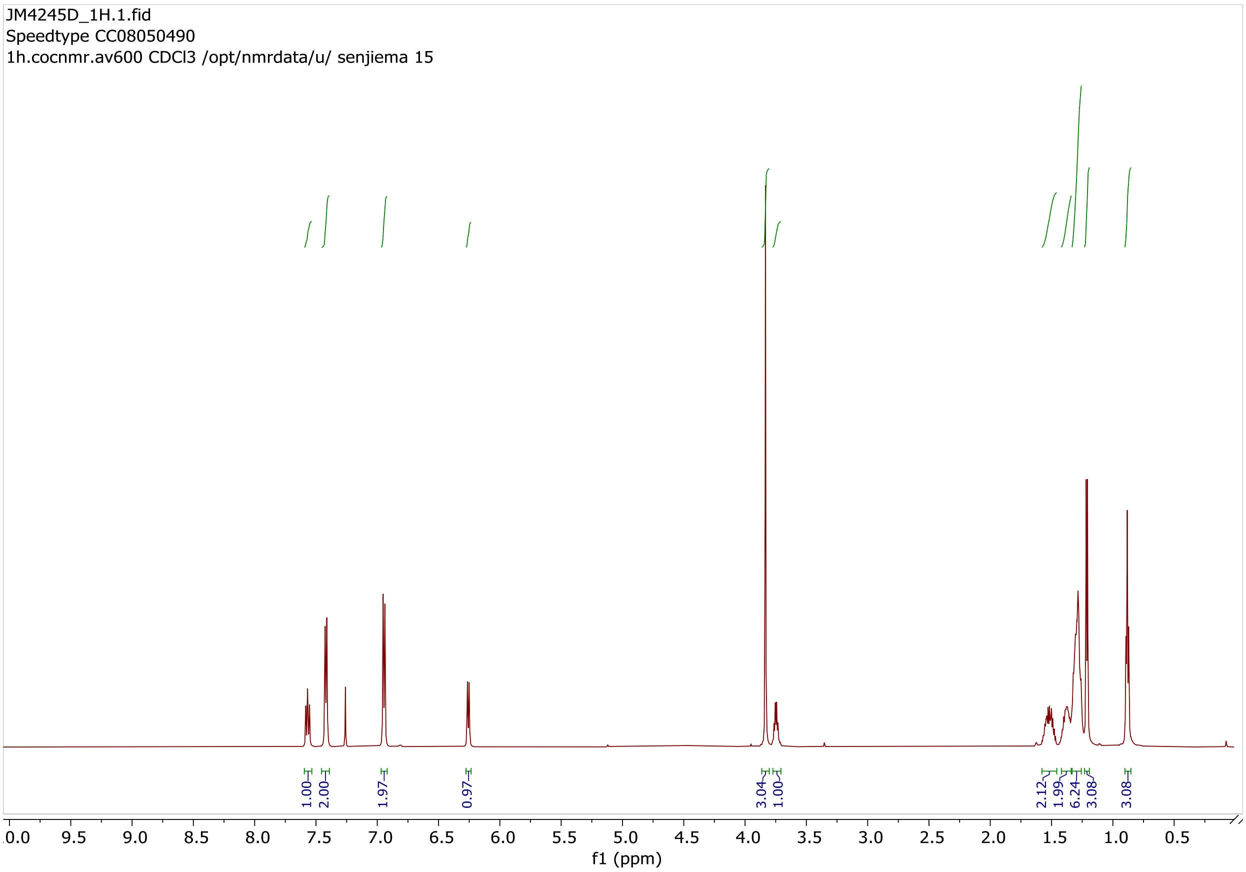
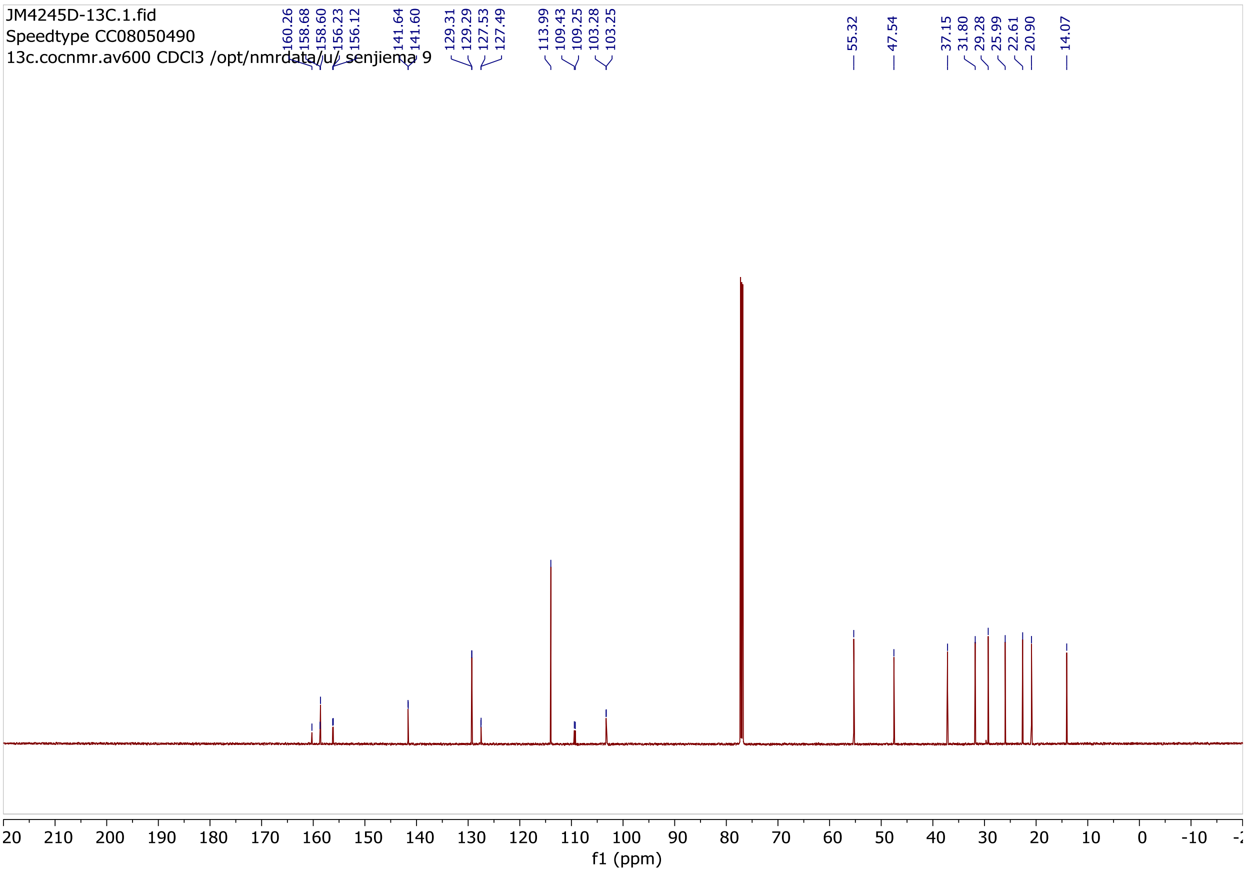
Compound 3ar



^{1}H NMR



^{13}C NMR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158.68
158.60
156.23
156.12
141.64
141.60
129.31
129.29
127.53
127.49
113.99
109.43
109.25
103.28
103.25
55.32
47.54
37.15
31.80
29.28
25.99
22.61
20.90
14.07
f1 (ppm)

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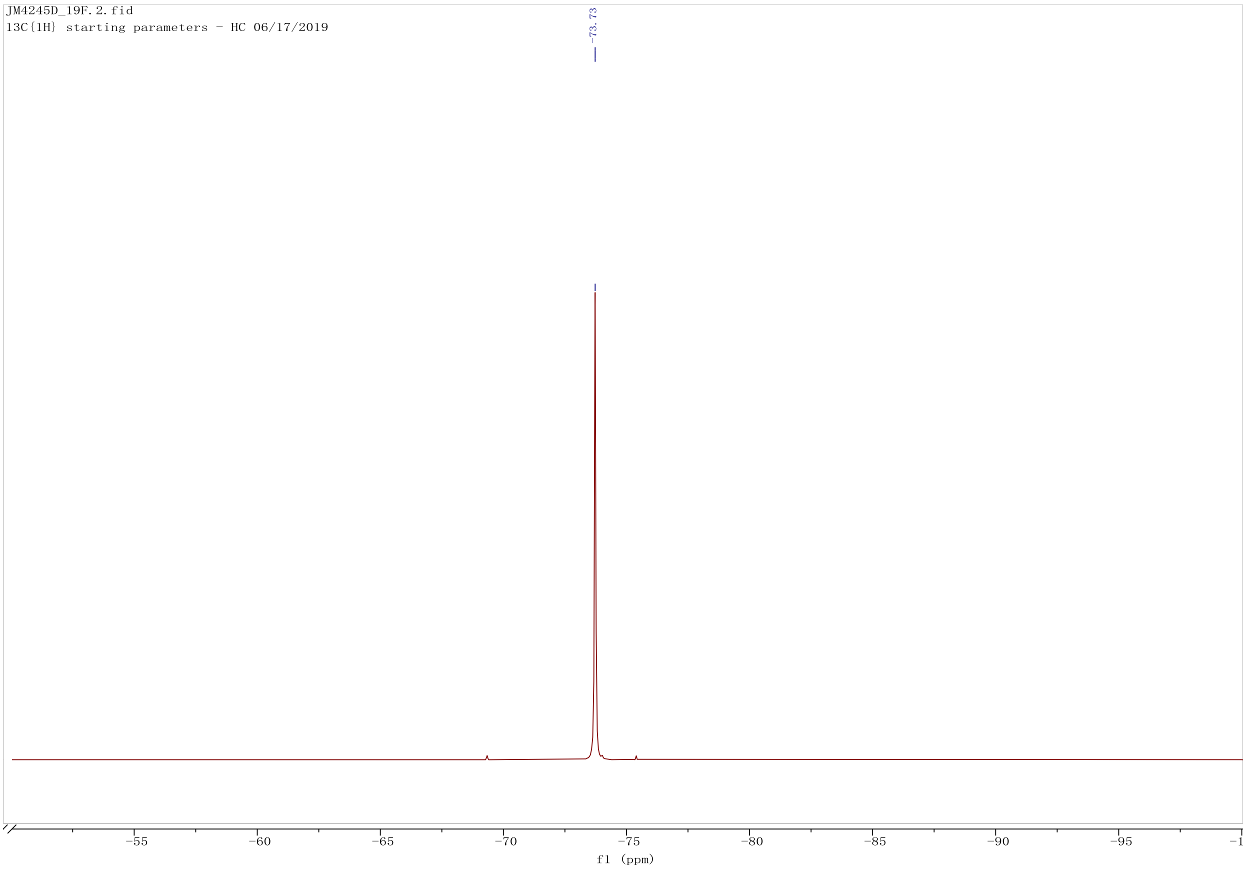
^{19}F NMR



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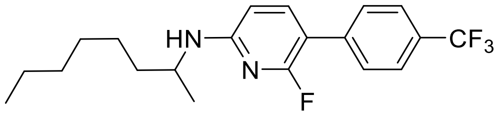
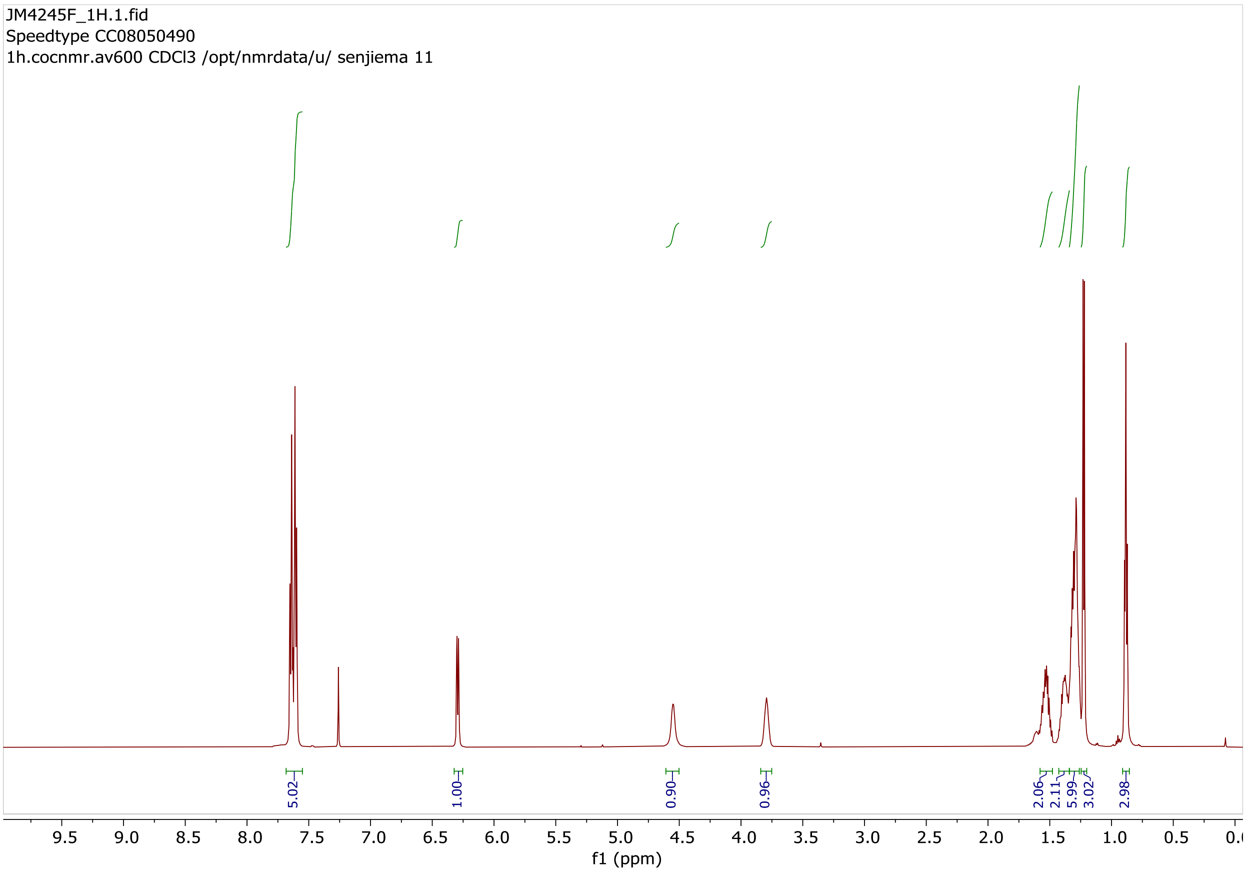


^{1}H NMR



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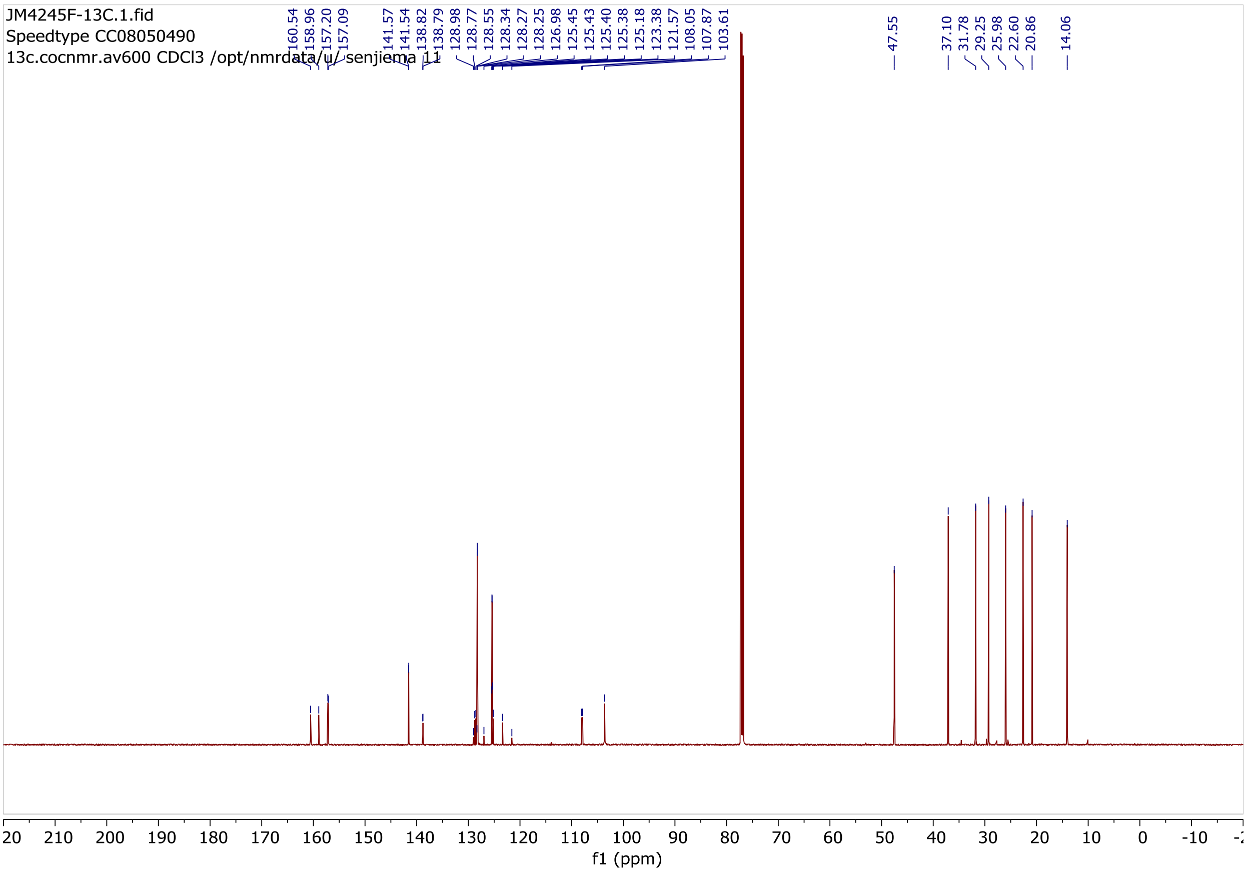
^{13}C NMR



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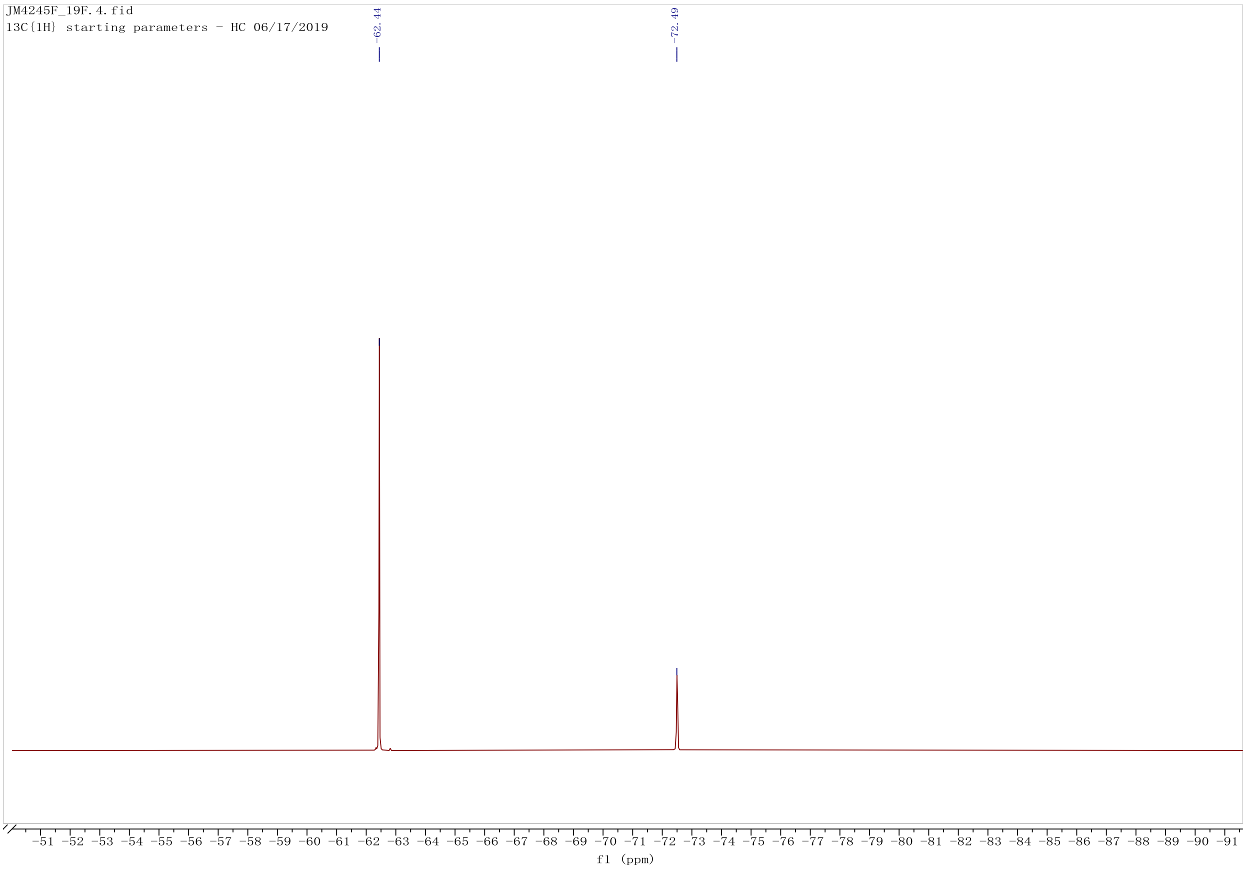
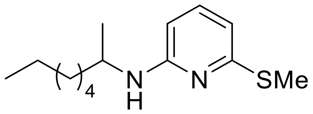
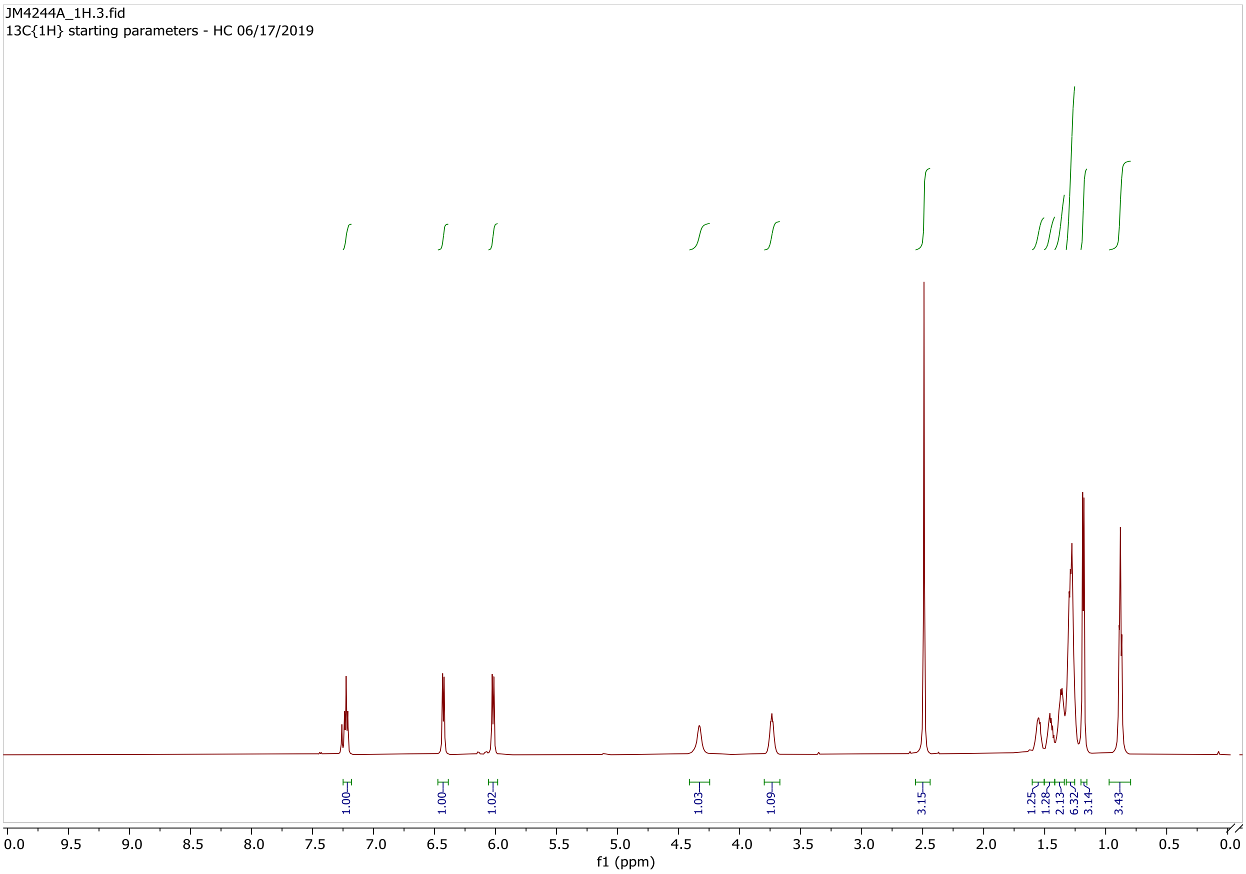


Compound 4ab



^{1}H NMR



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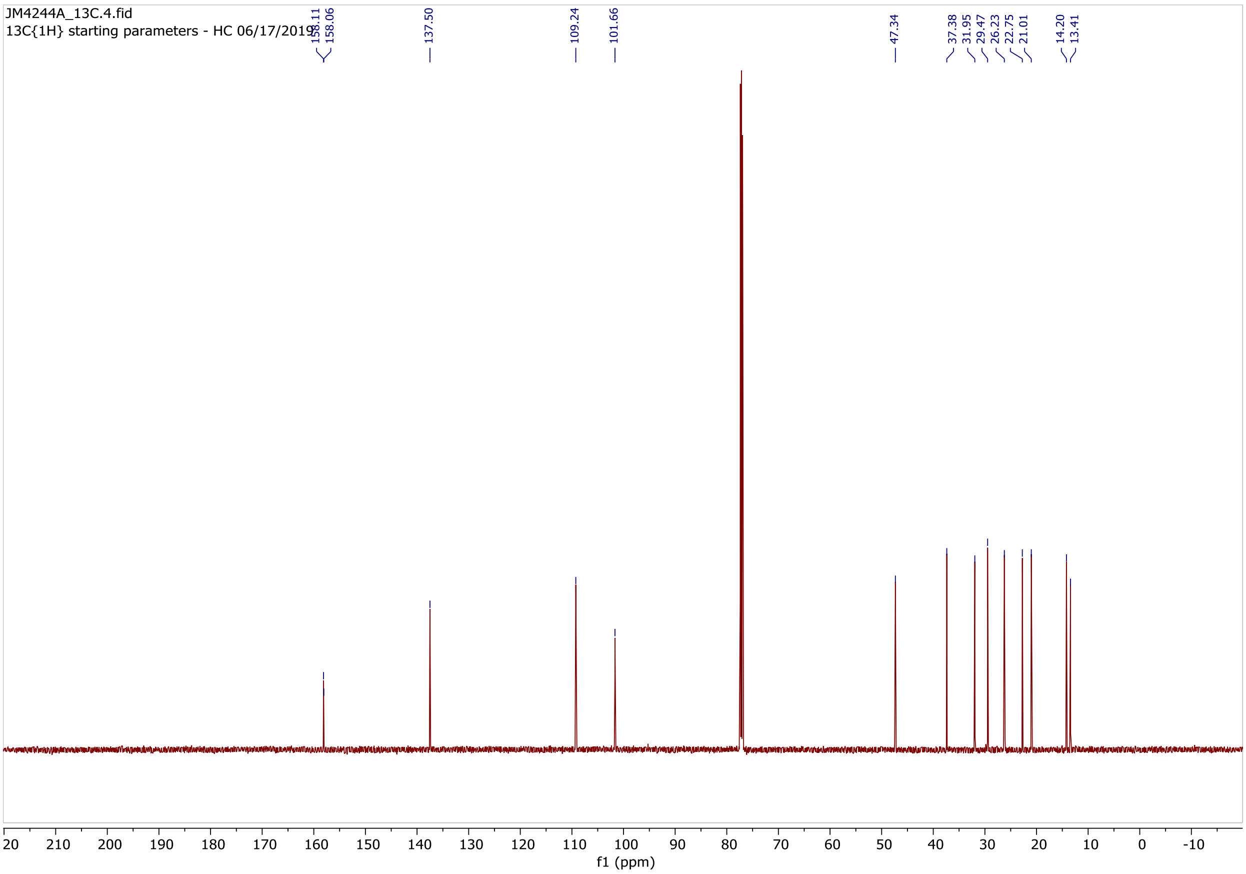
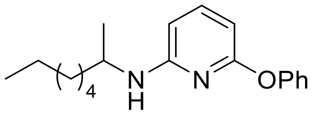
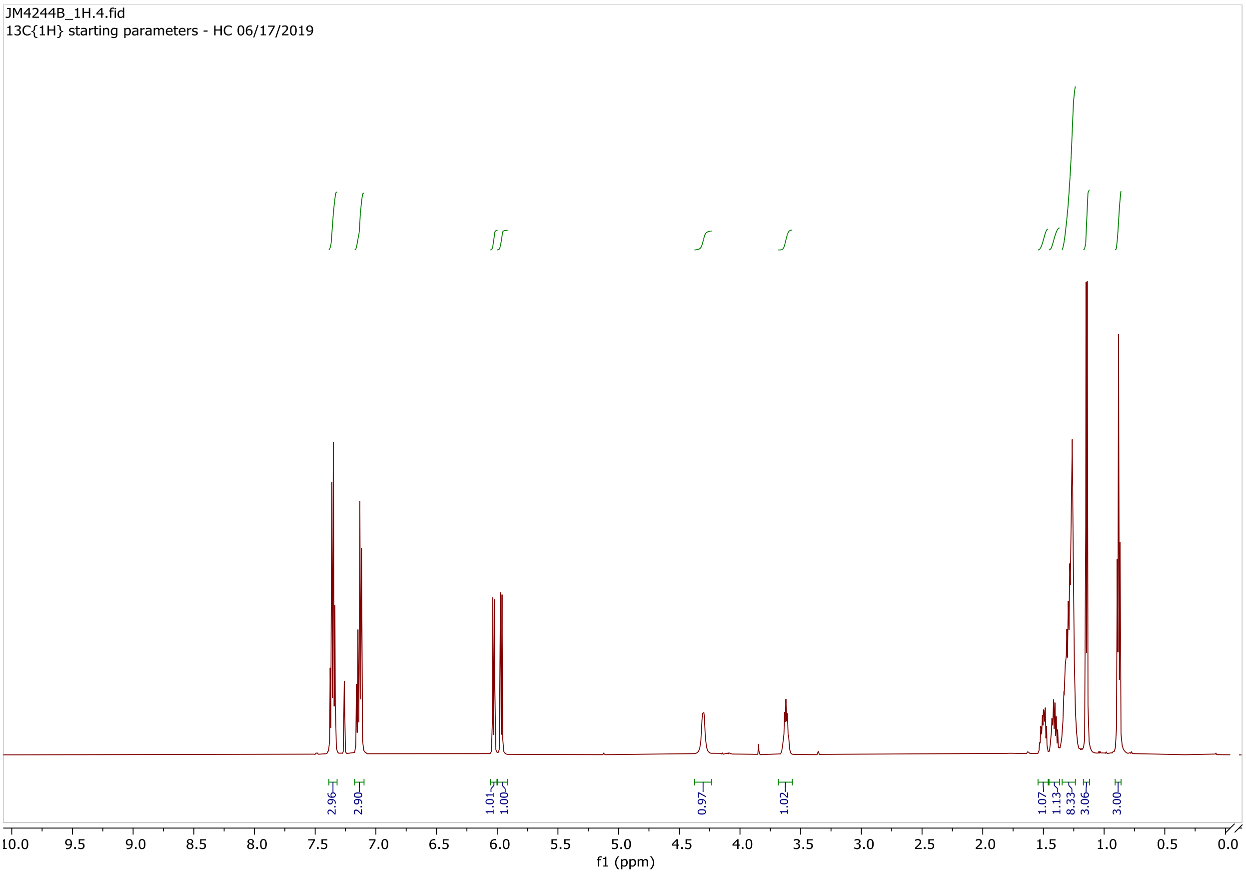
^{13}C NMR



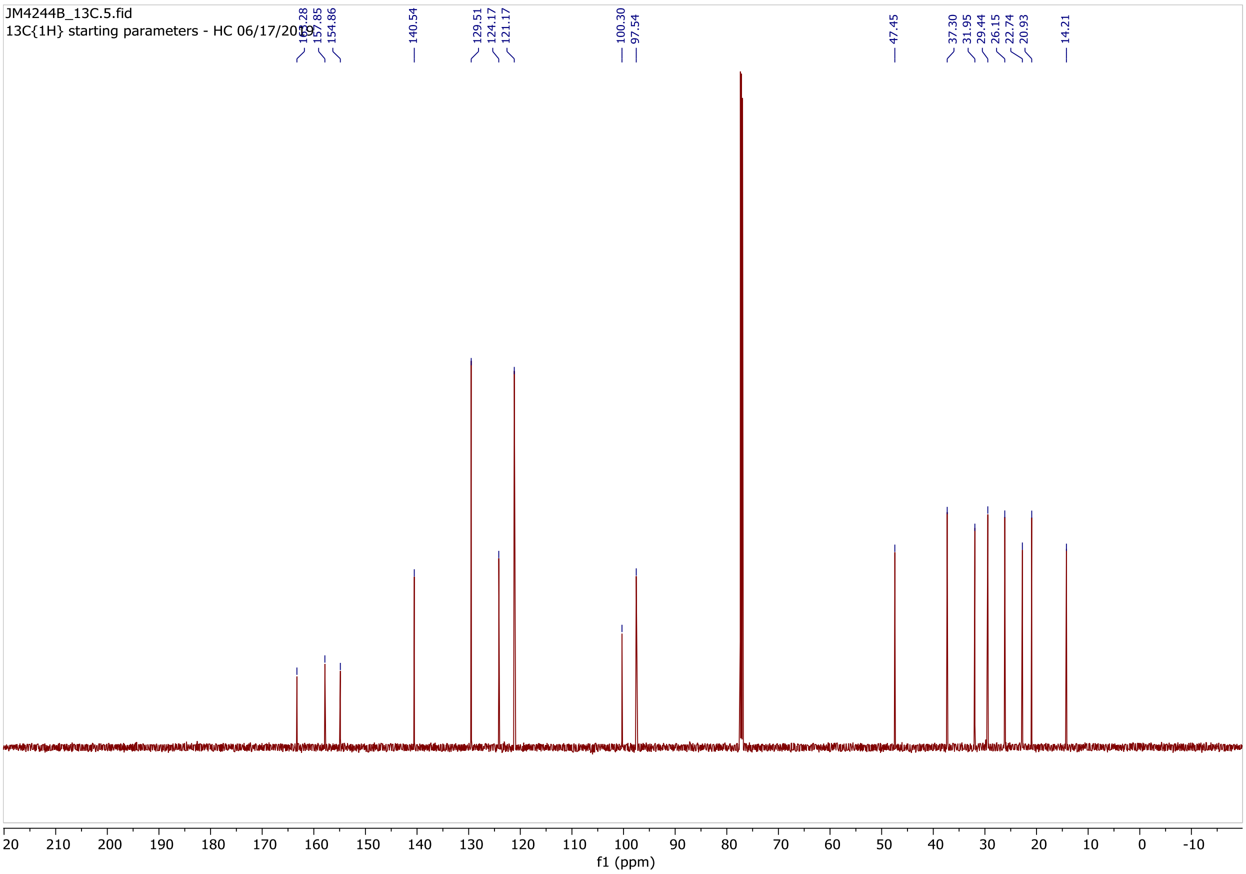
Compound 5ab



^{1}H NMR



^{13}C NMR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154.86
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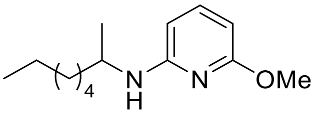
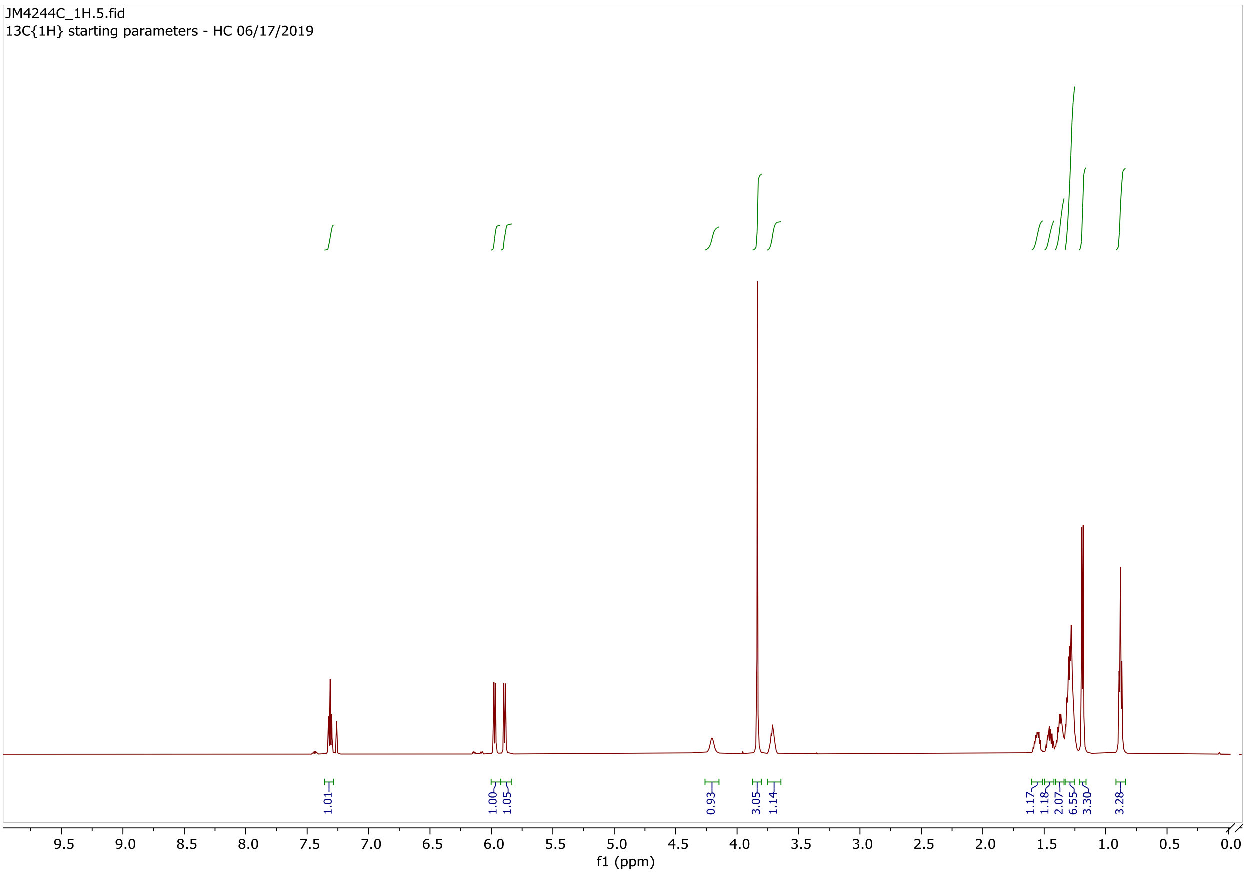
129.51
124.17
121.17
100.30
97.54
47.45
37.30
31.95
29.44
26.15
22.74
20.93
14.21
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

Compound 6ab



^{1}H NMR



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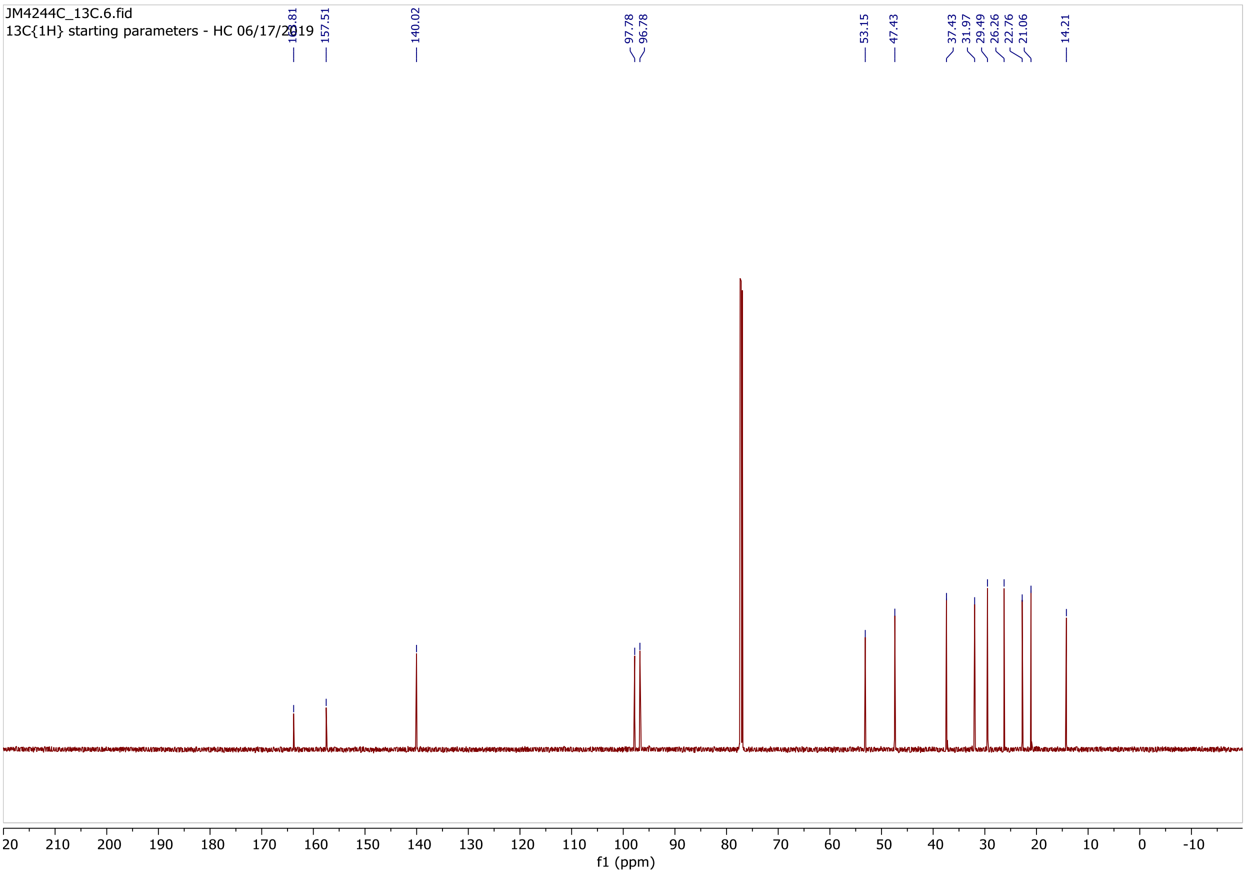
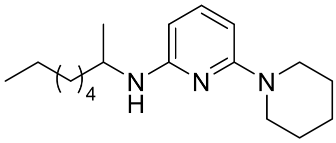
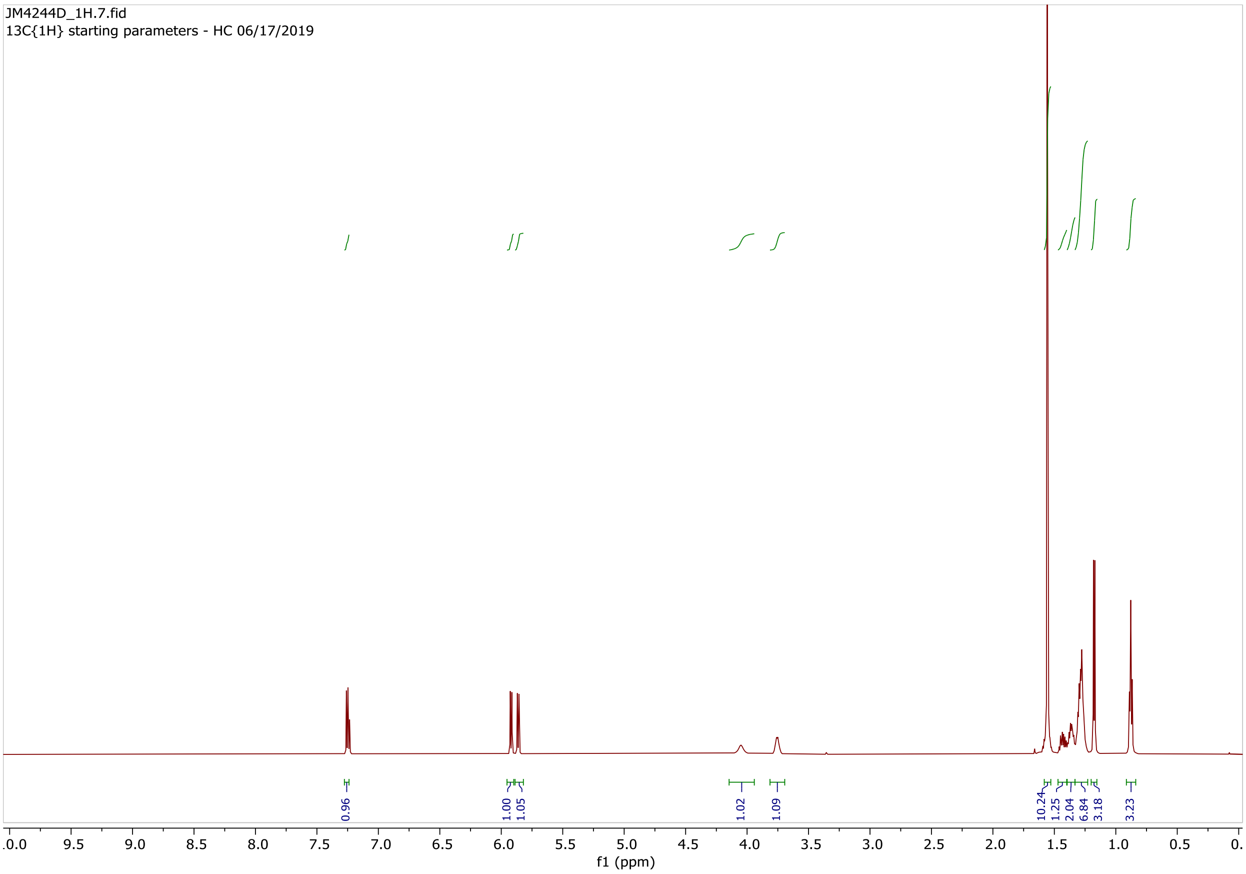
^{13}C NMR



Compound 7ab



^{1}H NMR



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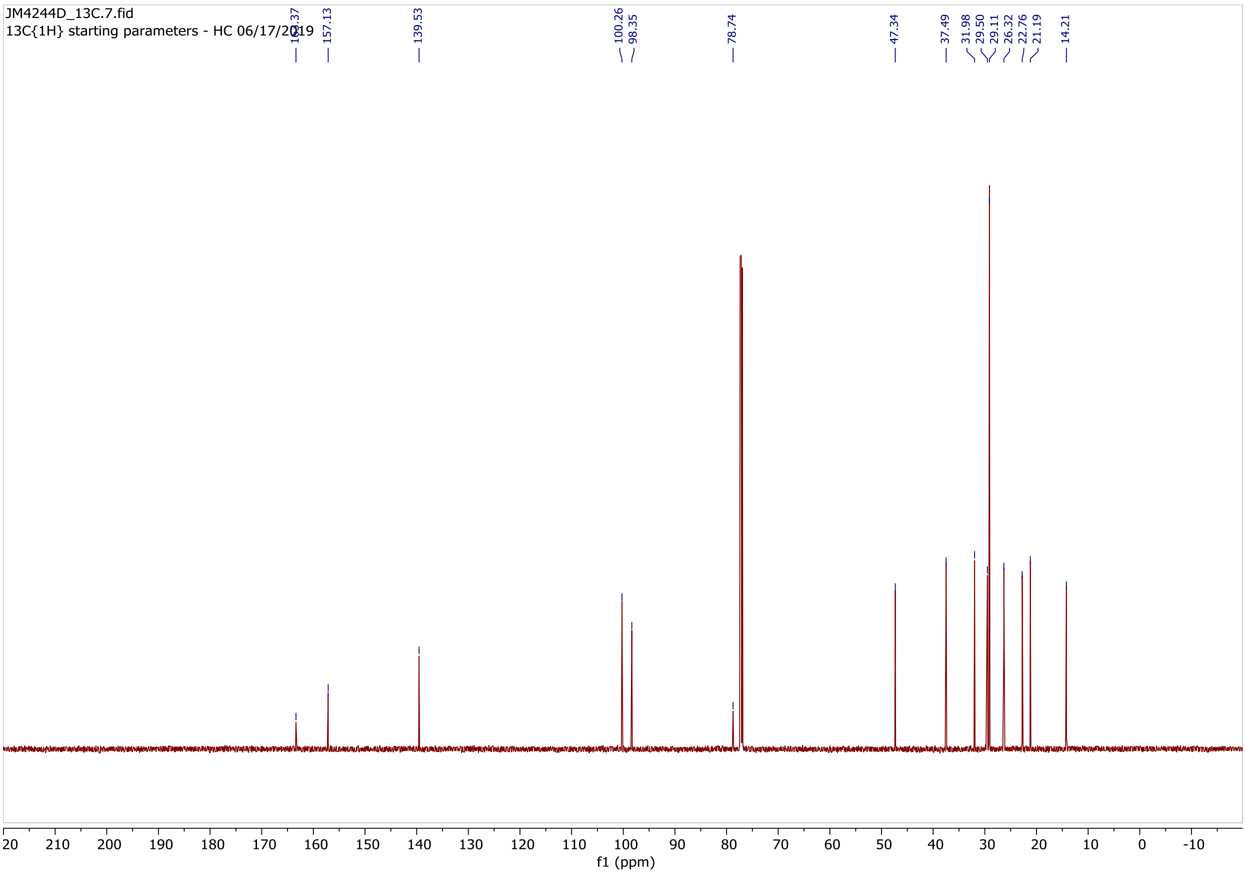
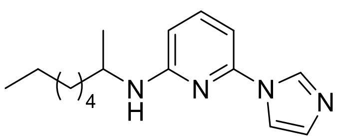
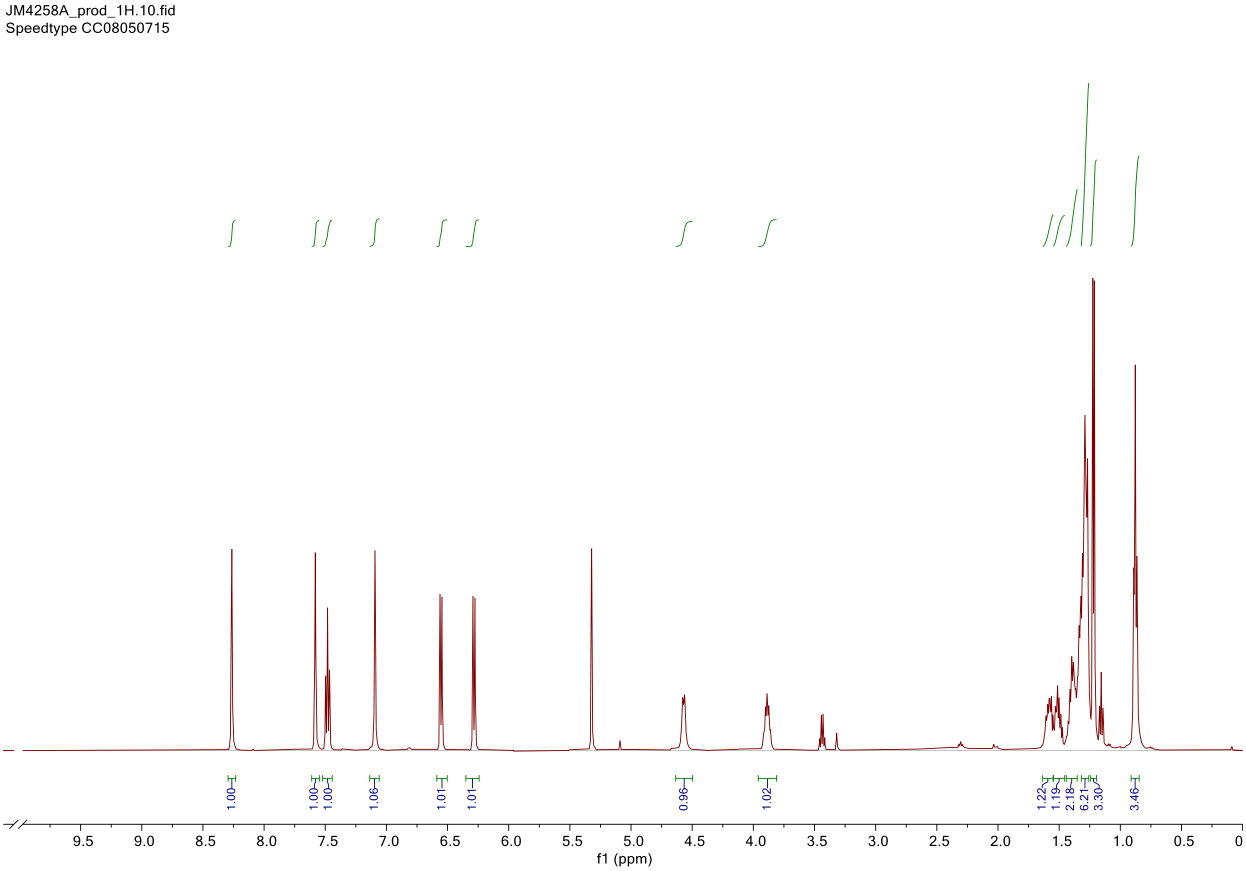
^{13}C NMR



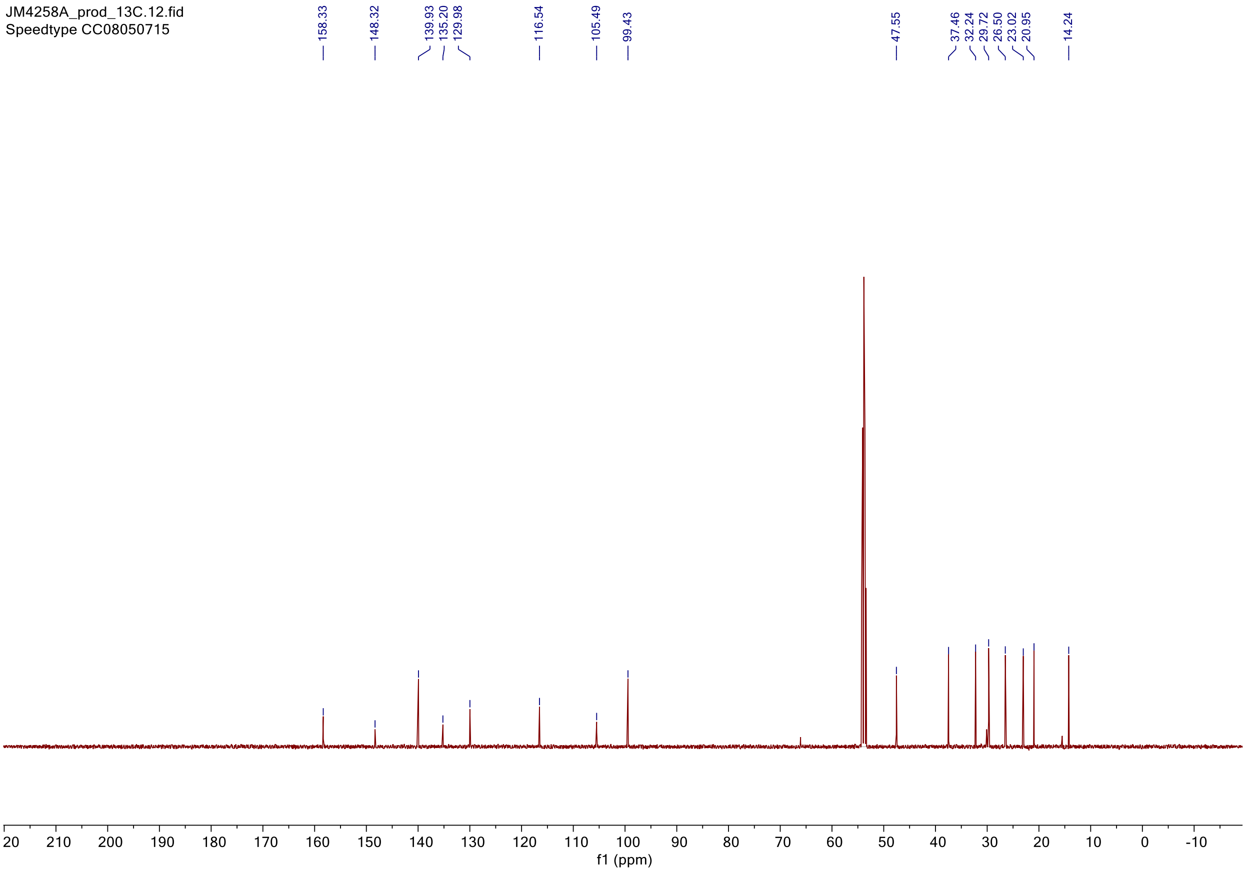
Compound 8ab



^{1}H NMR



^{13}C NMR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20.95
14.24
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200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

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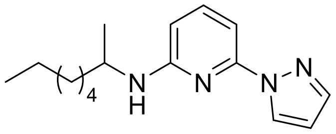
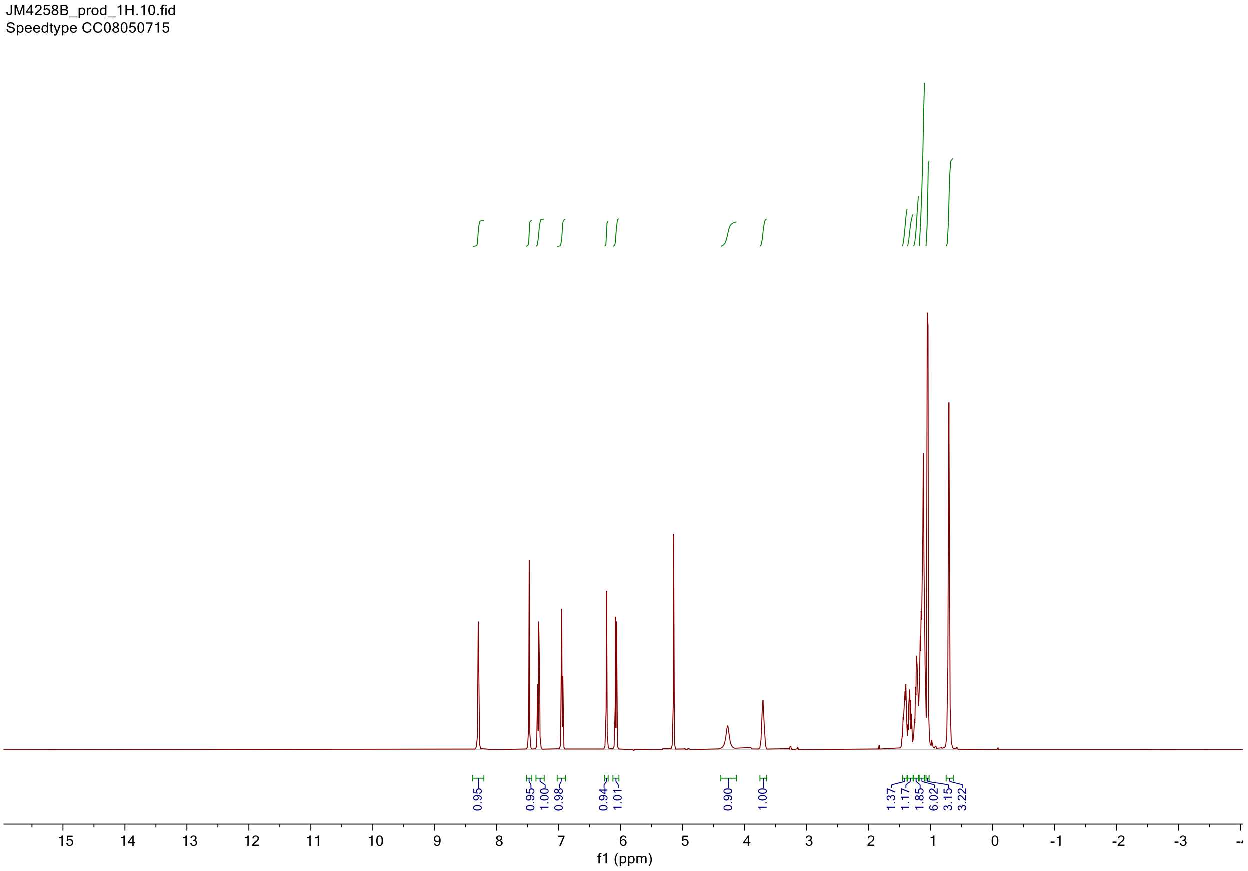
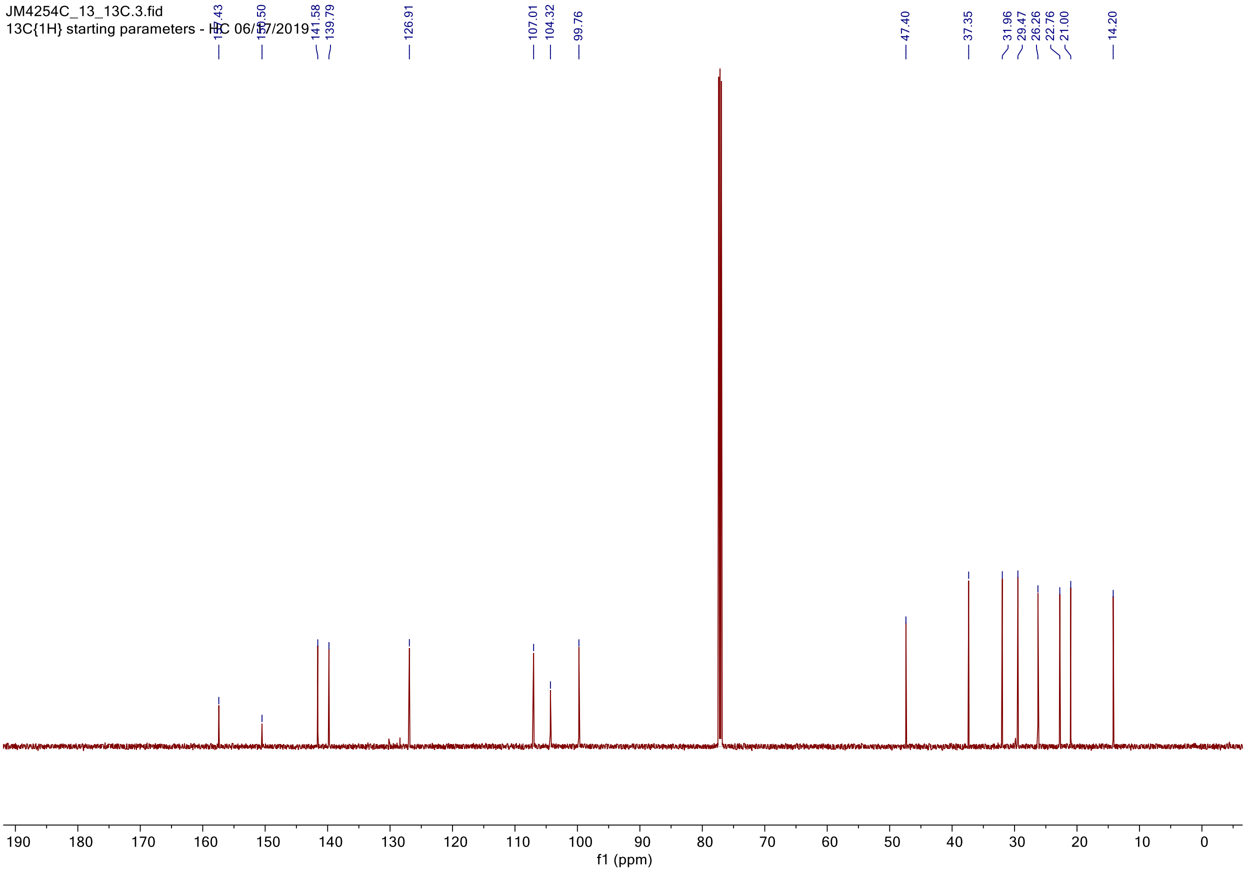
Compound 9ab



^{1}H NMR



^{13}C NMR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139.79
126.91
107.01
104.32
99.76
47.40
37.35
31.96
29.47
26.26
22.76
21.00
14.20
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

10. References

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