Reaction of Dearomatized Heterocycles with Sulfur Hexafluoride (SF_6) and the Pentafluorosulfanyl (SF_5) Group

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Contents

General Experimental Considerations

Unless specified otherwise all reactions conducted under nitrogen atmosphere, or the reagents were mixed under nitrogen before the introduction of sulfur hexafluoride. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were acquired at 300 K on a Bruker AV-400 or AV-500 MHz NMR spectrometer in $CDCl_3$, C_6D_6, CD_3CN or $(CD_3)_2SO$ using standard NMR tubes and caps. ^{1}H spectra in deuterated chloroform are referenced to the residual non-deuterated chloroform (7.26 ppm) or to TMS standard (0.00 ppm) in the deuterated chloroform. ^{1}H spectra in deuterated benzene are referenced to the C_6D_5H peak (7.16 ppm). ^{13}C NMR spectra in deuterated chloroform are referenced using the central peak associated with $CDCl_3$ (77.16 ppm). Spectra in non-deuterated solvents were acquired using the SMART program on the AV-400 and AV-500 instruments. Mass spectrometric data was obtained by Xiao Feng in the Mass Spectrometry Laboratory at Dalhousie University. Procedures inside the glove box were conducted in a 2001 issue IT Glovebox under a nitrogen atmosphere. The Kessil PR160L-390nm LED lamp was used in irradiated reactions.

Sulfur hexafluoride (SF_6) was purchased from Air Liquide in a cylinder containing 10 lbs of SF_6. The cylinder had a fill date of June 9th, 2018.

For non-pressurized reactions, SF_6 was dispensed into a 1L Restek Multi-Layer Foil gas-sampling bag, fitted with a Luer lock, then dispensed from the gas-sampling bag into the reactions. A picture and rationalization for use of gas-sampling bags is shown on page S5. Non-pressurized reactions were conducted in 20 mL Thermo Scientific Clear VOA Vials with 0.125 inch septa caps and generously taped with electrical tape, both around the cap, and over the puncture holes to further seal the vessel.

Pressurized reactions were conducted at 80 psi in a Q-Tube gas purging set, obtained from Aldrich (Product number Z757993). Rather than having a proportional pressure relief valve, the Q-Tube has an internal septum, which will deform in an over-pressure scenario, and contact a pressure-releasing needle. In the set-up we used, this needle was placed in a position where pressure would be relieved around 120 PSI. We did not observe any significant autogenous pressure generation in these reactions.

Note regarding the ^{1}H NMR spectra: During the time this research was conducted Halifax Nova Scotia experienced extended periods of high humidity. Thus, unavoidably signals corresponding to the presence of water are observed in some of ^{1}H NMR spectra.

Solvents

3Å molecular sieves were purchased from Sigma Aldrich and dried for 12 hours in a round-bottom flask, with an external heating mantle measured at 240 ^{o}C with thermocouple, under

approximately 1 torr vacuum. The activated sieves were stored under nitrogen in a glovebox and used to further day solvents stored within the glove box.

Acetonitrile was purchased from Sigma-Aldrich in a Sure/seal ® bottle (anhydrous, catalogue number 271004) and stored over 3Å molecular sieves under nitrogen, in the glovebox.

Diethyl ether was purchased as ACS grade from Fisher and was used as received.

Dimethyl sulfoxide was purchased as anhydrous >99.9% ACS grade from Sigma-Aldrich in a Sure/seal ® bottle (catalogue number 276855) and used as received.

Ethanol was purchased as ACS grade from Fisher and was used as received.

Ethyl acetate was purchased as ACS grade from Fisher and was used as received.

Hexanes was purchased as ACS grade from Fisher and was used as received.

Reagents

Sodium 4-methylbenzenesulfinate, benzyl nicotinate and butyl nicotinate was purchased from AmBeed and used directly as received.

p-Tolylsulfur pentafluoride, o-fluorophenylsulfur pentafluoride, diethyl 1,4-dihydro-2,6-dimethyl-3,5-pyridinedicarboxylate, 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane, 3,5-dibromopyridine and methyl nicotinate were purchased from Oakwood Chemical and used directly as received.

3-Acetylpyridine, α-methylstyrene (containing a 15 ppm p-tert-butylcatechol inhibitor, n-butyllithium solution in hexanes (2.5 M), 1,3,5 trimethoxybenzene, benzaldehyde, and 2-aminothiophenol were purchased from Sigma-Aldrich and used directly as received.

Cesium carbonate was purchased from Sigma-Aldrich and was dried by stirring the powder under vacuum at 100 ^{o}C for 72 hours and stored at ambient temperature under a nitrogen atmosphere inside of a glove box. For these reactions, the undried powdered cesium carbonate used as received had comparable performance.

3-Ethyl 5-methyl 4-(2,3-dichlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, 4-ethoxyanisole, isoquinoline, and 3,5-diethyoxycarbonyl-1,4-dihydro-2,4,6-collidine were purchased from Combi-Blocks and used directly as received.

Sodium hydride was purchased from Aldrich and stored as a 55% dispersion in mineral oil.

Experimental Procedures and Tabulated Data

General procedure for Pressurized Sulfur Hexafluoride (SF_6) Reactions: An oven dried glass pressure tube and stir bar were brought into the glove box where the substrate and base were added. The solvent was as added, the pressure tube was closed with a rubber septa and it brought out of the glove box. The tube's septum was removed and the tube was immediately attached to the pressure head of the Q-Tube. The tube was then pressurized with SF_6 to 80 psi and placed in front of a 390 nm LED to stir for 18 hours. The irradiation was done in a fumehood, with an amber-tinted film coating the fumehood, to minimize escape of the near-UV light.

Figure S1 Photograph of irradiation of non-pressurized reactions (two outer vials), and pressurized Q-tube (centre of photograph)

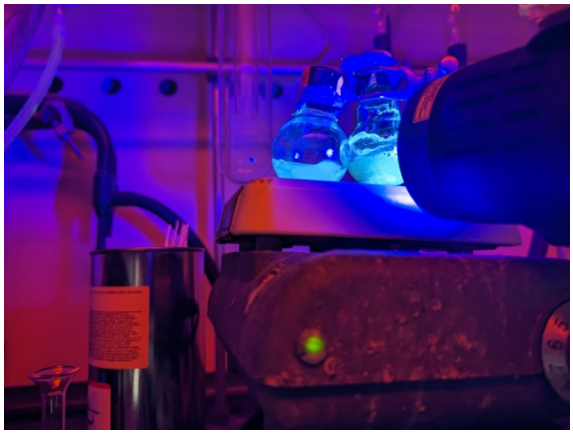


Figure S2 Photograph of irradiation of Hantzsch esters in DMSO under SF_6. Note a variation of this image was used (without explanation of what reaction it was), as the 2024 cover image for the Canadian Journal of Chemistry.

General procedure for Non-Pressurized Sulfur Hexafluoride (SF_6) Reactions: In the glovebox, the substrate, and base (if applicable), was added to an oven dried 5-dram vial containing a stir bar. Solvent was dispensed into the vial, it was capped with a septa vial cap, the junction between the cap and vial was overwrapped with electrical tape and the vial was removed from the glove box. Using a disposable needle as an outlet and an oven dried 1 foot needle attached to a prefilled bag of SF_6, the SF_6 was bubbled through the reaction mixture for approximately 45 seconds. The exposed septum was covered with electrical tape and the vial itself was further sealed with electrical tape to prevent SF_6 leakage. The vial was placed in front of the 390 nm LED, with stirring for 18 hours.

Note on use of Gas Sampling Bags for SF_6 Chemistry:

In our previous work on SF_6 degradation,[1] we had used standard latex balloons to dispense SF_6. Upon attempts to use the same charge of a balloon to introduce SF_6 to multiple reactions over a several day time-period, we noted latex balloons were inappropriate for storage of SF_6, even for several hours. Upon having a balloon partially filled with SF_6, we noticed a visible increase in the diameter of the balloon over time. We assumed this is because the balloon is permeable to atmospheric gases, and less permeable to SF_6, so atmospheric gases diffuse into the balloon towards equalization of the partial pressure, resulting in contamination of the SF_6.

In 2021, in a conversation with Prof. Rachel Chang (Dalhousie Department of Physics and Atmospheric Science) and a Twitter conversation with Prof. Nadine Bourduas-Dedekind (University of British Columbia Chemistry Department), we became aware of the use of Gas sampling bags in atmospheric science, and their suitability for sampling F-gases. We found Restek Multi-Layer Foil Gas Sampling Bags (Supplier number 22950), and Restek Tedlar® Sampling Bags (a fluoropolymer) are both well-suited for long-term storage of SF_6. Several samples of SF_6 stored for over 4 years in such gas-sampling bags have shown no change in the volume of the gas sampling bag.

Figure S3. Photo of Restek Tedlar gas-sampling bag filled with SF_6.

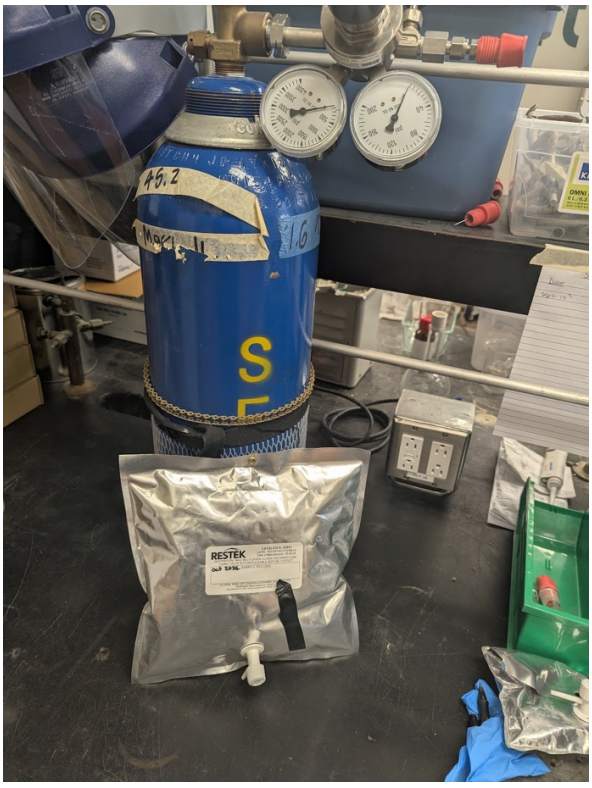
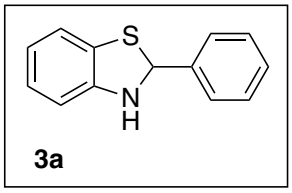


Figure S4. Photo of Restek Multi-layer Foil Gas Sampling bag filled with SF_6.

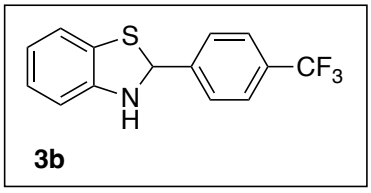
Dearomatized Substrates



3a

Compound **3a:** 2-Aminothiophenol (1.5 mL, 14 mmol, 1 equiv.), benzaldehyde (1.42 mL, 14 mmol, 1 equiv.) and ethanol (10 mL) were mixed in a 5-dram vial. The mixture was placed in the freezer for 3 hrs where a white precipitation formed. The solid was collected via a Buchner filtration and the solid was rinsed with a minimal amount of cold ethanol. The resulting solid was dried under vacuum to afford **3a** (1.82 g, 8.53 mmol, 61%) as a white solid. **3a** may undergo thermal decomposition over prolonged periods of time and begin appearing yellow in color. **3a** should be kept at 2–4°C under a nitrogen atmosphere. Samples of **3a** prepared in our lab in 2018 had undergone complete decomposition by 2024. The parent 2-aminothiophenol is also prone to decomposition, as observed for a sample of the same age, even upon storage in a refrigerator, and should be checked by ^{1}H NMR spectroscopy before use.

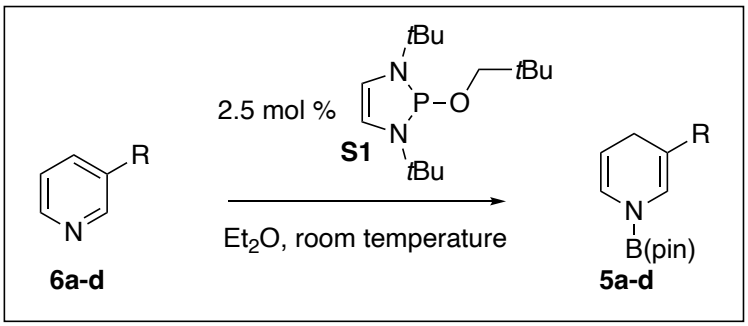
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.37–7.30 (m, 3H), 7.04 (ap. dd, *J* = 7.7 Hz, 1.1 Hz, 1H), 6.94 (td, *J* = 7.3 Hz, 1.1 Hz, 1H), 6.76 (td, *J* = 7.5 Hz, 1.1 Hz, 1H), 6.65 (ap. dd, *J* = 7.7 Hz, 0.9 Hz, 1H), 6.37 (d, *J* = 3.2 Hz, 1H), 4.34 (br. s, 1H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 146.4, 141.8, 128.9, 128.9, 126.7, 125.6, 121.8, 120.8, 109.9, 70.2.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{13}H_{12}NS$: 214.0685 found: 214.0683.



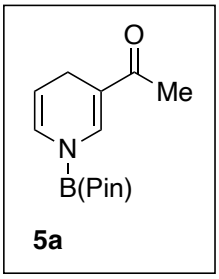
3b

Compound **3b**: 4-Trifluoromethylbenzaldehyde (1.2 mL, 8.97 mmol, 1 equiv.), 2-amino-thiophenol (0.96 mL, 8.97 mmol, 1 equiv.) and ethanol (8 mL) were mixed in a 5-dram vial. A yellowish white precipitate formed and the mixture was placed in the freezer for 3 hrs. The solid was collected via a Buchner filtration and the solid was rinsed with a minimal amount of cold ethanol. The resulting solid was dried under vacuum to afford **3b** (1.45 g, 5.16 mmol, 58%) as a white solid. Compound **3b** may undergo thermal decomposition over prolonged periods of time and begin appearing yellow in color. Compound **3b** should be kept at 2–4°C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65–7.60 (m, 4H), 7.05 (dd, *J* = 7.6 Hz, 1.0 Hz, 1H), 6.97 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.79 (dt, *J* = 7.6 Hz, 1.2 Hz, 1H), 6.70 (dd, *J* = 7.8 Hz, 0.9 Hz, 1H), 6.39 (s, 1H), 4.41 (br. s, 1H).
^{19}F NMR (470 MHz, $CDCl_3$): δ -62.6.
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 146.1, 131.0 (q, $^{2}J_{CF}$ = 32.5 Hz), 127.0, 126.3, 125.9 (m), 124.1 (q, $^{1}J_{CF}$ = 273.3 Hz), 121.9, 121.3, 110.3, 69.1.

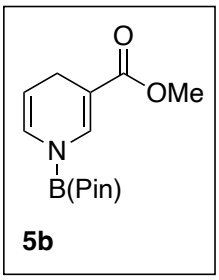


Scheme S1: General scheme for preparation of dearomatized pyridines.



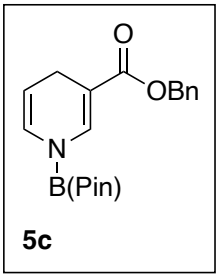
Compound **5a**: Prepared according to the literature procedure (Scheme S1) using 3-acetylpyridine (**6a**) (0.22 mL, 2 mmol, 1 equiv.), diazaphospholene catalyst **S1** (14 mg, 0.05 mmol, 0.025 equiv.), 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (0.32 mL, 2.2 mmol, 1.1 equiv.) and ether (2 mL) yielding **5a** (196 mg, 0.79 mmol, 39%) as a yellow solid.[2]

^{1}H NMR (400 MHz, C_6D_6): δ 7.37–7.37 (m, 1H), 6.37–6.34 (m, 1H), 4.77 (dt, *J* = 8.2 Hz, 3.5 Hz, 1H), 3.20–3.18 (m, 2H), 1.89 (s, 3H), 0.97 (s, 12H).
^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 195.0, 138.5, 125.1, 107.5, 84.3, 24.5, 24.1, 21.9.
^{11}B NMR (128 MHz, C_6D_6): δ 24.1.



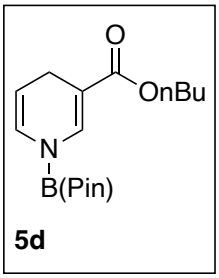
Compound **5b**: Prepared according to the literature procedure using methyl nicotinate **6b** (274 mg, 2 mmol, 1 equiv.), catalyst **S1** (14 mg, 0.05 mmol, 0.025 equiv.), 4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (0.32 mL, 2.2 mmol, 1.1 equiv.) and ether (2 mL) yielding **5b** (440 mg, 1.66 mmol, 83%) as a yellow solid.

^{1}H NMR (500 MHz, C_6D_6): δ 7.87 (ap. s, 1H), 6.36– 6.33(m, 1H), 4.71–4.67 (m, 1H), 3.40 (s, 3H), 3.23–3.21 (m, 2H), 0.91 (s, 12H).
^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 167.8, 137.9, 125.5, 106.4, 105.4, 84.2, 50.8, 24.4, 22.6.
^{11}B NMR (128 MHz, C_6D_6): δ 24.1.



Compound **5c**: Prepared from benzyl nicotinate **6c** (0.48 mL, 2.5 mmol, 1 equiv.), catalyst **S1** (18 mg, 0.06 mmol, 2.5 mol %) and diethyl ether (2 mL). These were added to a 5-dram vial with a stir bar inside the glove box. Pinacolborane (0.4 mL, 2.75 mmol, 1.1 equiv.) was added, vial was capped and the mixture was left to stir for 2 days. The reaction mixture was then concentrated via vacuo resulting in **5c** (0.81 g, 2.25 mmol, 94%) as a yellow thick oil. The values reported are for the major regioisomer, and another inseparable regioisomer was evident in the spectra.

^{1}H NMR (400 MHz, C_6D_6): δ 7.91 (ap. s, 1H), 7.19–7.15 (m, 2H), 7.08–7.01 (m, 3H), 6.33 (ap. dq, *J* = 8.2 Hz, 1.3 Hz, 1H), 5.09 (s, 2H), 4.67 (dt, *J* = 8.1 Hz, 3.5 Hz, 1H), 3.19–3.18 (m, 2H), 0.89 (s, 12H).
^{13}C{^{1}H} NMR (100 MHz, C_6D_6): δ 167.8, 138.8, 138.1, 129.1, 128.9, 128.4, 126.0, 107.0, 105.9, 84.7, 66.1, 24.9, 23.2.
^{11}B NMR (128 MHz, C_6D_6): δ 24.1 ppm.

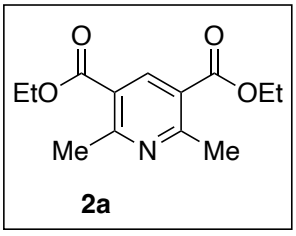


5d

Compound **5d**: Butyl nicotinate **6d** (0.42 mL, 2.5 mmol, 1 equiv.), catalyst **S1** (18 mg, 0.06 mmol, 2.5 mol %) and diethyl ether (2 mL) were added to a 5-dram vial with a stir bar inside the glove box. Pinacolborane (0.4 mL, 2.75 mmol, 1.1 equiv.) was added, vail was capped and the mixture was left to stir for 2 days. The reaction mixture was then concentrated in vacuo resulting **in 5d** (0.70 g, 2.3 mmol, 92 %) as a yellow thick oil. The values reported are for the major regioisomer, and another inseparable regioisomer was evident in the spectra.

^{1}H NMR (400 MHz, C_6D_6): δ 7.89 (m, 1H), 6.36 (ap. dq, *J* = 8.2 Hz, 1.8 Hz, 1H), 4.71 (dt, *J* = 8.1 Hz, 3.1 Hz, 1H), 4.07 (t, *J* = 6.8 Hz, 2H), 3.25–3.23 (m, 2H), 1.41–1.34 (m, 2H), 1.20–1.11 (m, 2H), 0.92 (s, 12H), 0.72 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 167.4, 137.7, 125.6, 106.4, 105.8, 84.2, 63.7, 31.2, 24.4, 22.7, 19.5, 13.9.
^{11}B NMR (128 MHz, C_6D_6): δ 24.1 ppm.

Aromatized Products



2a

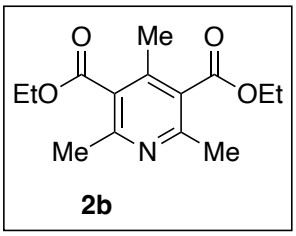
Compound **2a**: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using 3,5-diethyl 1,4-dihydro-3,5-pyridinedicarboxylate **1a** (127 mg, 0.5 mmol, 1 equiv.), cesium carbonate (163 mg, 0.5 mmol, 1 equiv.) and DMSO (5 mL). The reaction mixture was extracted with 4 x 8 mL hexanes, the combined hexane layers were dried over sodium sulfate, and it was concentrated via rotary evaporator. Compound **2a** (114 mg, 0.45 mmol, 90% yield) was isolated as a white solid via column chromatography (30% ethyl acetate, and 70% hexanes).

A replicate of this reaction produced 1.13 mmol (2.26 equivalents) of CsF, when analyzed by ^{19}F NMR spectroscopy, using sodium trifluoroacetate as an internal standard.

Procedure without base: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using 3,5-diethyl 1,4-dihydro-3,5-pyridinedicarboxylate **1a** (127 mg, 0.5 mmol, 1 equiv.) and DMSO (5 mL). The reaction mixture was extracted with 4 x 8 mL hexanes, the combined hexane layers were dried over sodium sulfate, and it was concentrated via rotary evaporator. Residual

DMSO was removed with a silica plug rinsing with a 30% ethyl acetate and 70% hexanes mixture. **2a** (105 mg, 0.42 mmol, 83% yield) was isolated as a white solid. The characterization data below is presented for the reactions prepared with base, but the material from this procedure had matching NMR spectra.

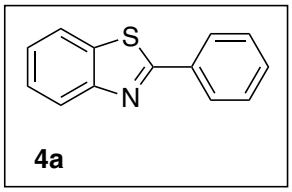
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.68 (s, 1H), 4.40 (q, *J* = 7.2 Hz, 4H), 2.85 (s, 6H), 1.42 (t, *J* = 7.0 Hz, 6H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.1, 162.3, 141.0, 123.2, 61.5, 25.1, 14.4.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{13}H_{18}NO_4$: 252.12303 found: 252.1228.



2b

Compound **2b**: Prepared according to **General procedure for Pressurized Sulfur Hexafluoride (SF_6) Reactions** using 3,5-diethyoxycarbonyl-1,4-dihydro-2,4,6-collidine **1b** (133 mg, 0.5 mmol, 1 equiv.), sodium hydride (60 mg, 2.5 mmol, 5 equiv.) and DMSO (5 mL). The reaction was mixed for 48 hours. The reaction mixture was extracted with 9 x 8 mL hexanes, the combine hexane layers were dried over sodium sulfate, and it was concentrated via rotary evaporator. Note the extraction process should be repeated until all **2b** was removed from the DMSO layer. Compound **2b** (44 mg, 0.17 mmol, 33% yield) was isolated via column chromatography (25% ethyl acetate, and 75% hexanes).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.41 (q, *J* = 7.0 Hz, 4H), 2.52 (s, 6H), 2.27 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 6H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 168.5, 155.1, 142.2, 127.7, 61.7, 23.1, 17.08, 14.3.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{14}H_{20}NO_4$: 266.1387 found: 266.1393.

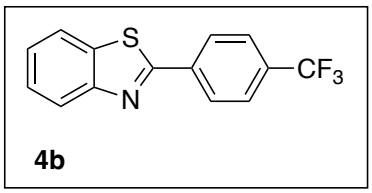


4a

Compound 4a: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **3a** (53 mg, 0.25 mmol, 1 equiv.), cesium carbonate (81 mg, 0.25 mmol, 1 equiv.) and MeCN (2.5 mL). The reaction mixture was filtered over celite, rinsing with MeCN and the filtrate was concentrated via rotary evaporator. The resulting solid was dried under vacuum to afford **4a** (42 mg, 0.2 mmol, 80%). For this substrate, the aromatization reaction did not work well in DMSO, with only an 8% yield.

Procedure without base: The above procedure (still in MeCN) at the same scale except without cesium carbonate led to **4a** (51 mg, 0.24 mmol, 97 %). The characterization data below is for the batch with base, but a representative proton NMR spectrum of the material without base is included on page **S25**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11–8.07(m, 3H), 7.91 (ap. d, *J* = 7.7 Hz, 1H), 7.51–7.48 (m, 4H), 7.41–7.37 (m, 1H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 168.2, 154.3, 135.2, 133.8, 131.1, 129.2, 127.7, 126.5, 125.3, 123.4, 121.8.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{13}H_{10}NS$: 212.0528 found: 212.0534.

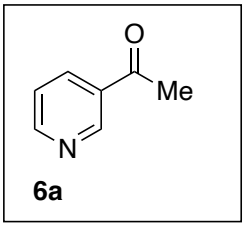


4b

Compound 4b: Prepared according to **General Procedure for Bubbled SF_6 Reactions** from **3b** (141 mg, 0.5 mmol, 1 equiv.),[3] cesium carbonate (489 mg, 1.5 mmol, 3 equiv.) and DMSO (5 mL). Upon completion, the reaction mixture was extracted with 4 x 8 mL hexanes; the combined hexane layers were dried over sodium sulfate and then concentrated via rotary evaporator. The mixture was redissolved in a 50% ethyl acetate 50% hexanes solution and filtered over a silica plug to remove residue DMSO. The filtrate was concentrated via rotary evaporator to yield **4b** (71 mg, mmol, 51%) as a white solid. Unlike **4a**, this reaction gave comparable yield in either CH_3CN or DMSO as solvents.

Reaction without base: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **4b** (50 mg, 0.18 mmol, 1 equiv.) and MeCN (2 mL). The reaction mixture what filtered over celite rinsing with MeCN and the filtrate was concentrated via rotary evaporator. The resulting solid was dried under vacuum to afford **4a** (49 mg, 0.17 mmol, 99%). The characterization data was obtained for material obtained from the reaction in DMSO with base, however a proton NMR of the reaction without base is included on page **S28**.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.55–7.51 (m, 1H), 7.45–7.42 (m, 1H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 166.2, 154.2, 136.9, 135.4, 132.6 (q, $^2J_{CF}$ = 32.2 Hz), 127.9, 126.8, 126.2 (q, $^3J_{CF}$ = 3.7 Hz), 125.9, 123.9 (q, $^1J_{CF}$ = 272.8 Hz), 123.8, 121.9.
^{19}F NMR (470 MHz, $CDCl_3$): δ -62.9.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{14}H_9F_3NS$: 280.0402 found: 280.0410.

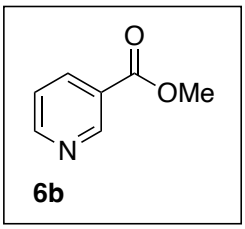


6a

Compound **6a**: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **5a** (65.3 mg, 0.26 mmol, equiv. 1), cesium carbonate (256 mg, 0.79 mmol, 3 equiv.) and MeCN (2.5 mL) and yielded **6a** (0.078 mmol, NMR yield 31 %). 1,3,5-Trimethoxybenzene was used as an internal standard to estimate the yield as all attempts to further purify **6a** led to significant product loss. This reaction was also conducted in DMSO, and aromatization was observed, however the product was poorly soluble in DMSO.

Partial characterization data (from crude reaction mixture):

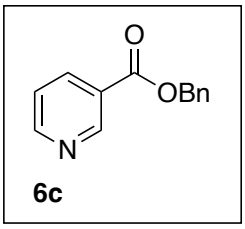
^{1}H NMR (500 MHz, CH_3CN): 9.13 (dd, *J* = 2.4 Hz, 0.7 Hz, 1H), 8.76 (dd, *J* = 4.7 Hz, 1.5 Hz, 1H), 8.25 (ddd, *J* = 7.9 Hz, 2.3 Hz, 1.7 Hz, 1H), 7.48 (ddd, *J* = 8.0 Hz, 4.8 Hz, 0.9 Hz, 1H), 2.61 (s, 3H).



6b

Compound **6b**: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **5b** (66.3 mg, 0.25 mmol, equiv. 1), cesium carbonate (244 mg, 0.75 mmol, 3 equiv.) and MeCN (3 mL) and yielded **6b** (0.15 mmol, NMR yield 60 %). 1,3,5-Trimethoxybenzene as used as an internal standard to determine the qualitative yield as all attempts to further purify **6b** led to significant product loss. The reaction gave a 56% yield, also estimated by internal standard, in DMSO.

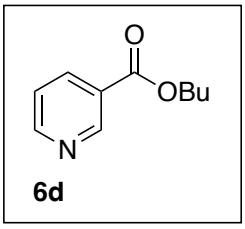
Partial characterization data (from crude reaction mixture):
^{1}H NMR (500 MHz, CH_3CN): 9.14 (dd, *J* = 2.3 Hz, 0.7 Hz, 1H), 8.77 (dd, *J* = 4.8 Hz, 1.7 Hz, 1H), 8.28 (ddd, *J* = 8.0 Hz, 2.2 Hz, 1.8 Hz, 1H), 7.47 (ddd, *J* = 8.0 Hz, 4.8 Hz, 0.9 Hz, 1H), 3.92 (s, 3H).



6c

Compound **6c:** Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **5c** (0.1 g, 0.29 mmol, 1 equiv.), cesium carbonate (0.29 g, 0.88 mmol, 3 equiv.) and MeCN (3 mL). The reaction mixture was filtered over celite rinsing with MeCN, and the filtrate was concentrated via rotary evaporator to yield an orange liquid. After column chromatography (25% ethyl acetate, and 75% hexanes), **6c** (55 mg, 0.26 mmol, 89%) was obtained as a yellow liquid. Conducting the reaction in DMSO resulted in a 62% NMR yield, using 1,3,5-trimethoxybenzene as an internal standard. Attempts to further purify **6c** made in DMSO led to significant product loss.

^{1}H NMR (500 MHz, $CDCl_3$): 9.27 (ap. dd, *J* = 2.2 Hz, 0.8 Hz, 1H), 8.78 (dd, *J* = 4.9 Hz, 1.8 Hz, 1H), 8.32 (dt, *J* = 8.0 Hz, 1.9 Hz, 1H), 7.46–7.45 (m, 2H), 7. 42–7.36 (m, 4H), 5.40 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.2, 153.7, 151.2, 137.3, 135.6, 128.8, 128.6, 128.5, 126.2, 123.4, 67.3.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{13}H_{12}NO_2$: 214.0863 found: 214.0867 .

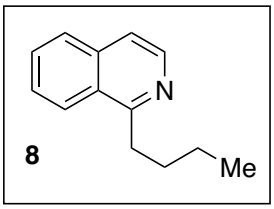


6d

Compound **6d**: Prepared according to **General Procedure for Bubbled SF_6 Reactions** using **5d** (0.11 g, 0.35 mmol, equiv. 1), cesium carbonate (0.35 g, 1.1 mmol, 3 equiv.) and MeCN (3 mL). The reaction mixture was filtered over celite rinsing with MeCN, and the filtrate was concentrated via rotary evaporator to yield an orange liquid. After column chromatography (25% ethyl acetate, and 75% hexanes), **6d** (30 mg, 0.17 mmol, 47%) was

obtained as a yellow liquid. Conducting the reaction in DMSO resulted in a 70% yield was estimated by using 1,3,5-trimethoxybenzene as an NMR internal standard. . Attempts to further purify **6d** made in DMSO led to significant product loss.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.23 (ap. d, *J* = 1.6 Hz, 1H), 8.78 (dd, *J* = 4.9 Hz , 1.7 Hz, 1H), 8.30 (dt, *J* = 7.9Hz, 2.1Hz, 1H), 7.39 (ddd, *J* = 7.9 Hz, 4.9 Hz, 0.8 Hz, 1H), 4.37 (t, *J* = 6.6 Hz, 2H), 1.80–1.74 (m, 2H), 1.52–1.45 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.5, 153.4, 151.0, 137.1, 126.5, 123.4, 65.4, 30.8, 19.3, 13.8.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{10}H_{14}NO_2$: 180.1019 found: 180.1020 .

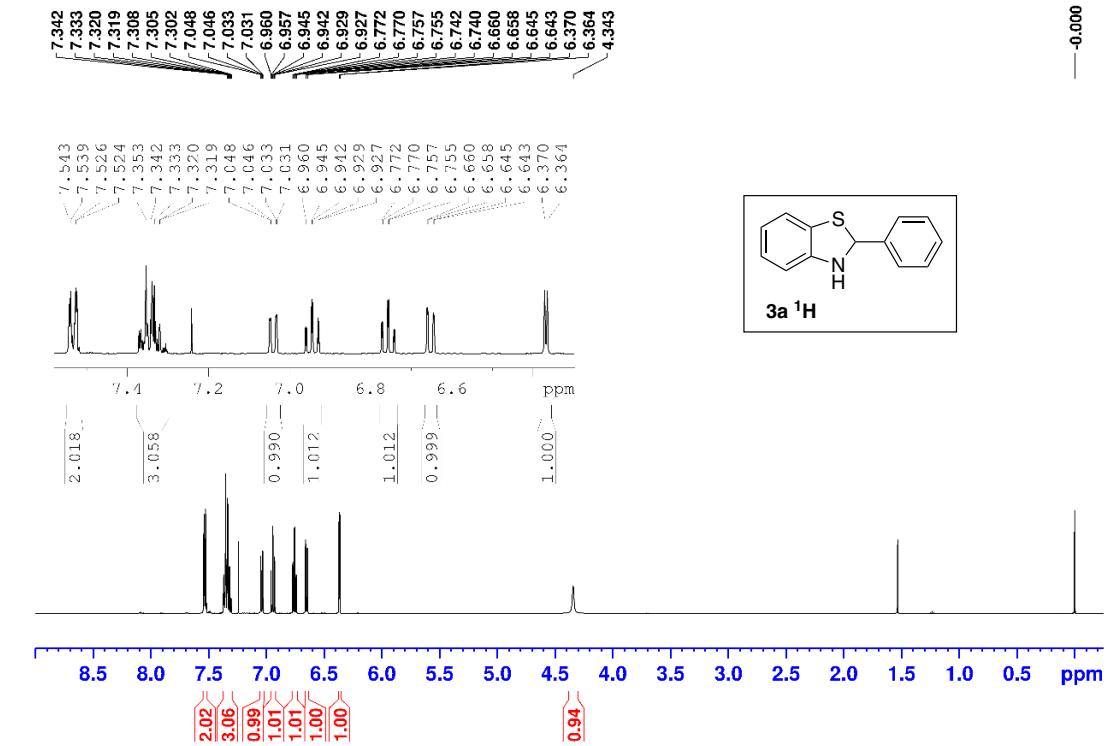


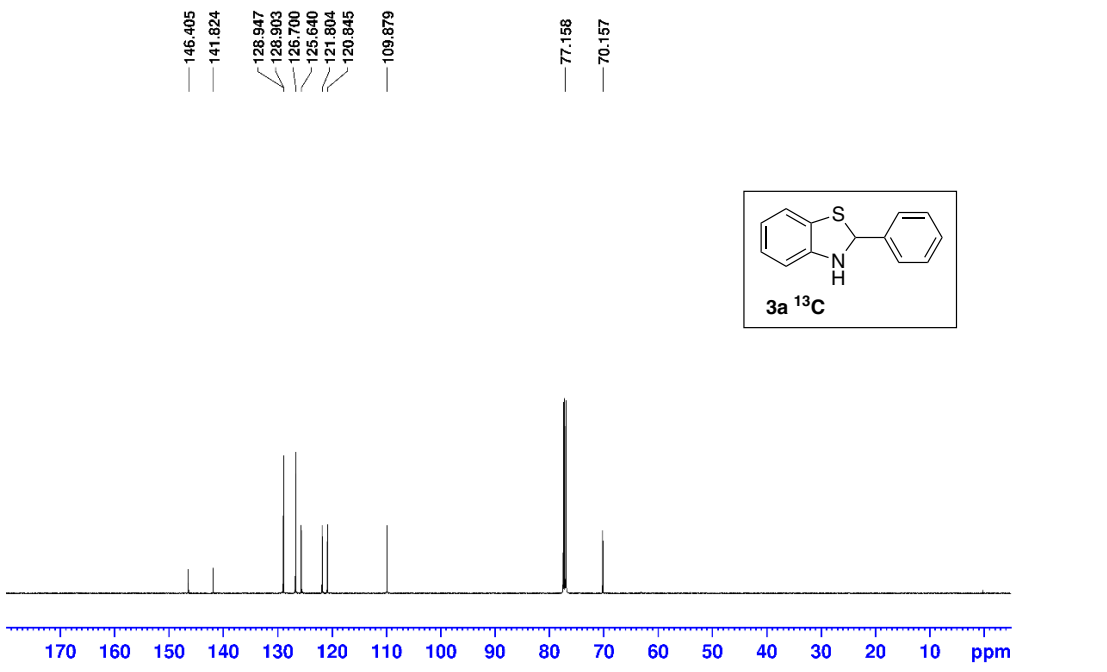
Compound **8:** Prepared according to **General Procedure for Bubbled SF_6 Reactions,** with the exclusion of a base, using **7**. Compound **7** was prepared according to the literature procedure.[4] In the glovebox, **7** (39 mg, 0.20mmol, 1 equiv.) was dissolved in MeCN (2.5 mL), and the general procedure for bubbled SF_6 reactions was completed. The reaction mixture was filtered over celite rinsing with MeCN, and the filtrate was concentrated via rotary evaporator to yield a brown liquid. Product **8** (22 mg, 0.12 mmol, 60%) was obtained as a brown liquid after column chromatography (15% ethyl acetate, and 85% hexanes). When the procedure was done with DMSO as the solvent, a 52% yield was obtained.

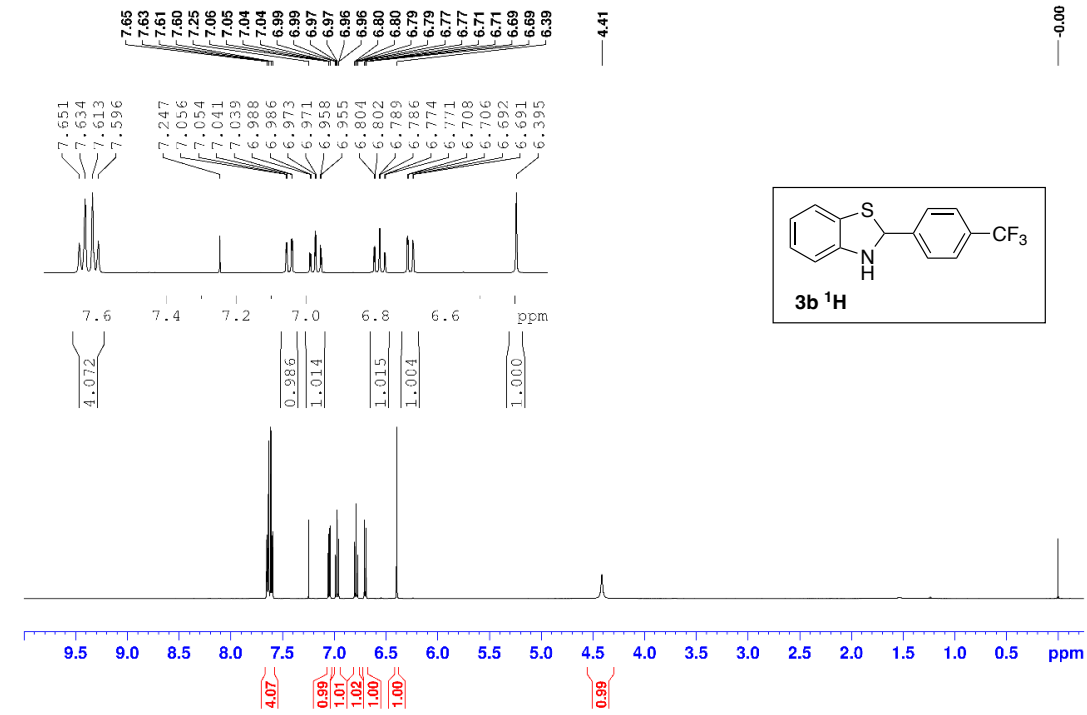
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, *J* = 5.7 Hz, 1H), 8.17–8.15 (m, 1H), 7.81 (ap. d, *J* = 8.2 Hz, 1H), 7.67–7.64 (m, 1H), 7.60–7.57 (m, 1H), 7.49 (d, *J* = 5.7 Hz, 1H), 3.31–3.28 (m, 2H), 1.88–1.82 (m, 2H), 1.54–1.47 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.6, 142.0, 136.4, 129.9, 127.5, 127.0, 125.5, 119.3, 35.4, 32.1, 23.1, 14.1.
HRMS(ESI): *m/z* $(M+H)^+$ calculated for $C_{13}H_{16}N$: 186.12773 found: 186.1279.

Characterized NMR Spectra

Dearomatized Substrates



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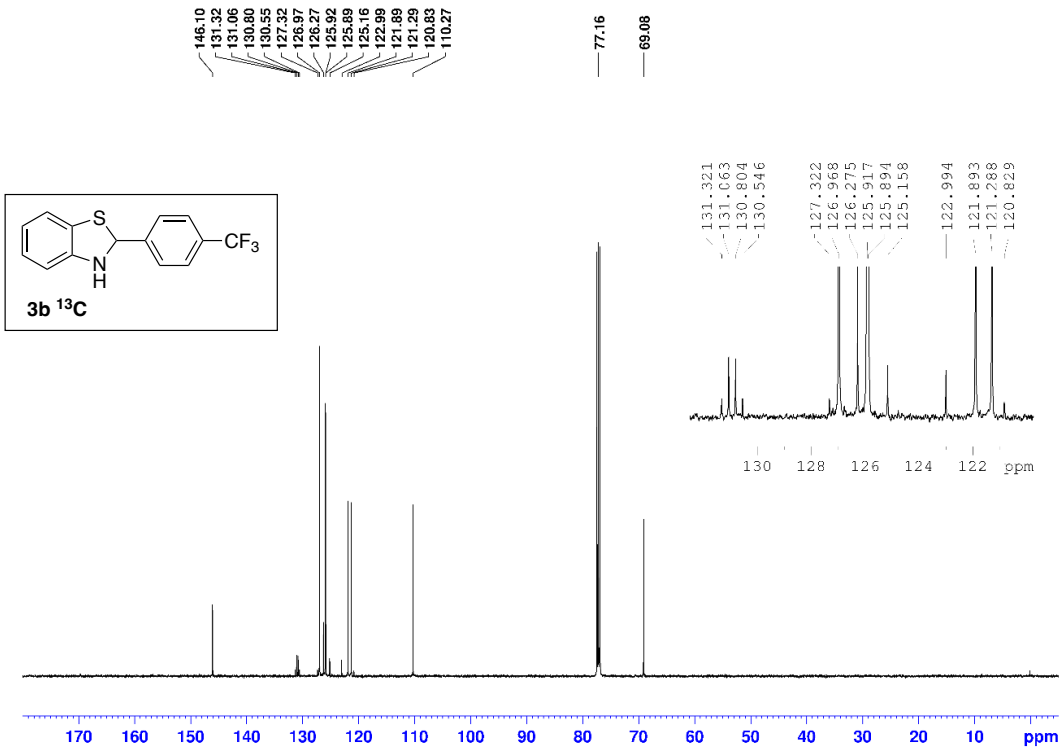
4.41
-0.00
7.651 7.634 7.613 7.596
7.247 7.056 7.054 7.041 7.039 6.988 6.986 6.973 6.971 6.958 6.955 6.804 6.802 6.789 6.786 6.774 6.771 6.708 6.706 6.692 6.691 6.395
7.6 7.4 7.2 7.0 6.8 6.6 ppm
4.072 0.986 1.014 1.015 1.004 1.000
S
N
H
CF3
3b 1H
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.07 0.99 1.01 1.02 1.00 1.00 0.99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77.16
69.08
131.321 131.663 130.804 130.546
127.322 126.968 126.275 125.917 125.894 125.158
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130 128 126 124 122 ppm
S
N
H
CF3
3b 13C
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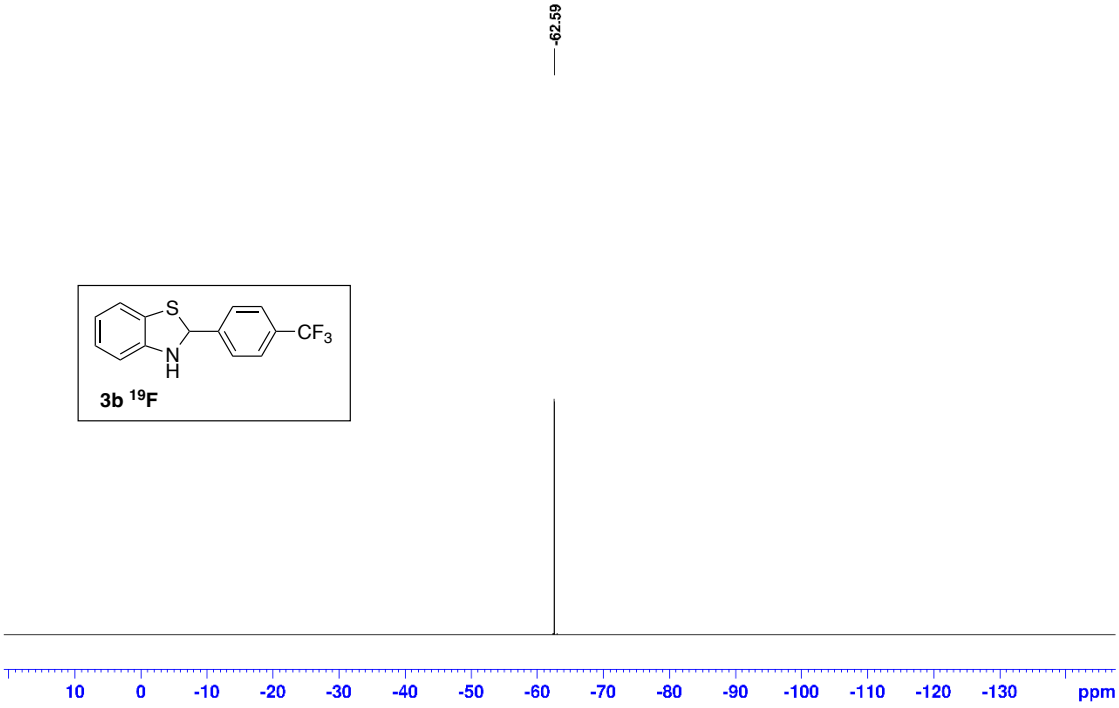
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N
H
CF3
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-80
-90
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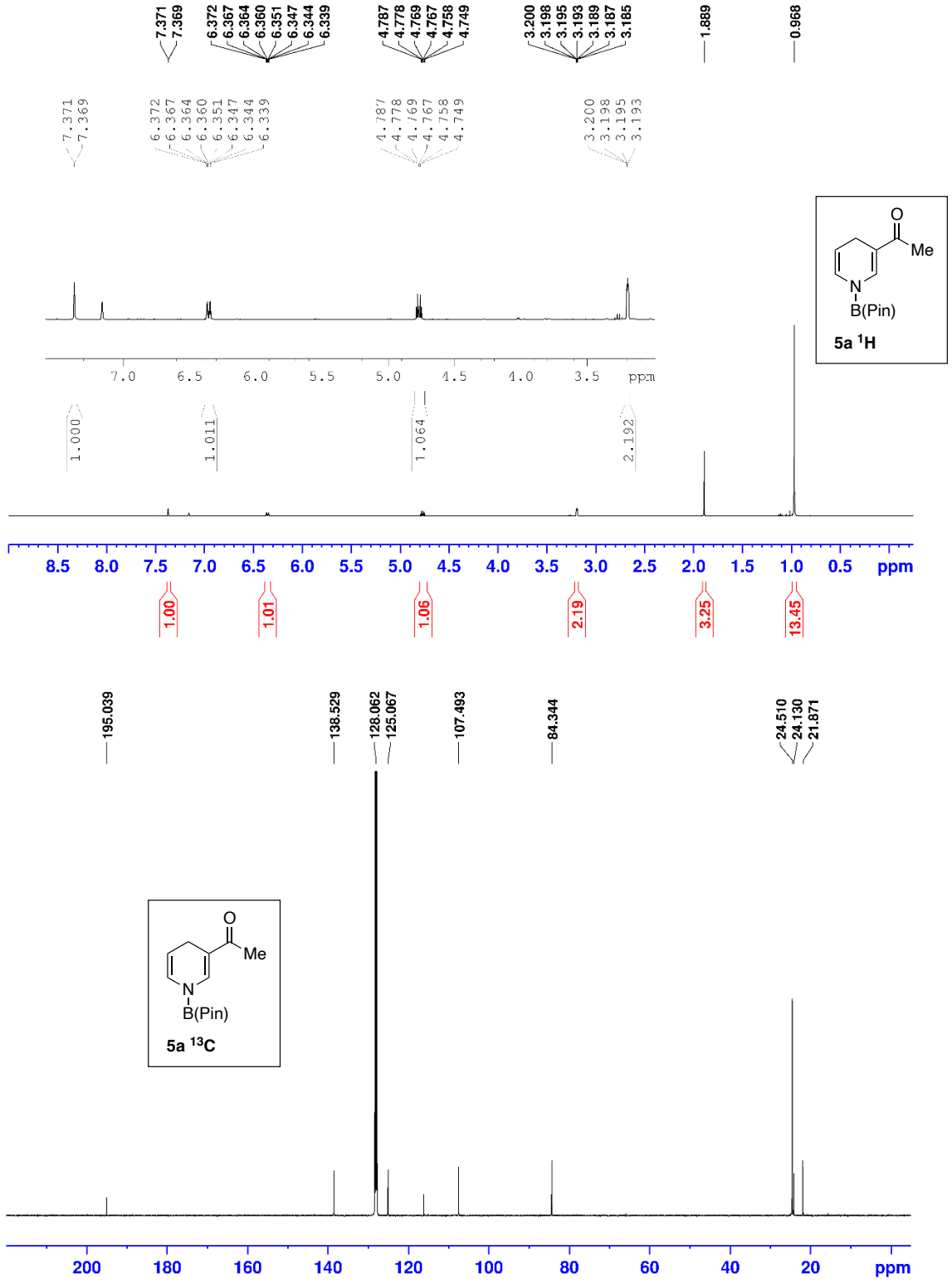
-110
-120
-130
ppm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4.769
4.767
4.758
4.749
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3.198
3.195
3.193
3.189
3.187
3.185
1.889
0.968
1.000
1.011
1.064
2.192
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
ppm
O
Me
N
B(Pin)
5a ^{1}H
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.01
1.06
2.19
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13.45
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24.130
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140
120
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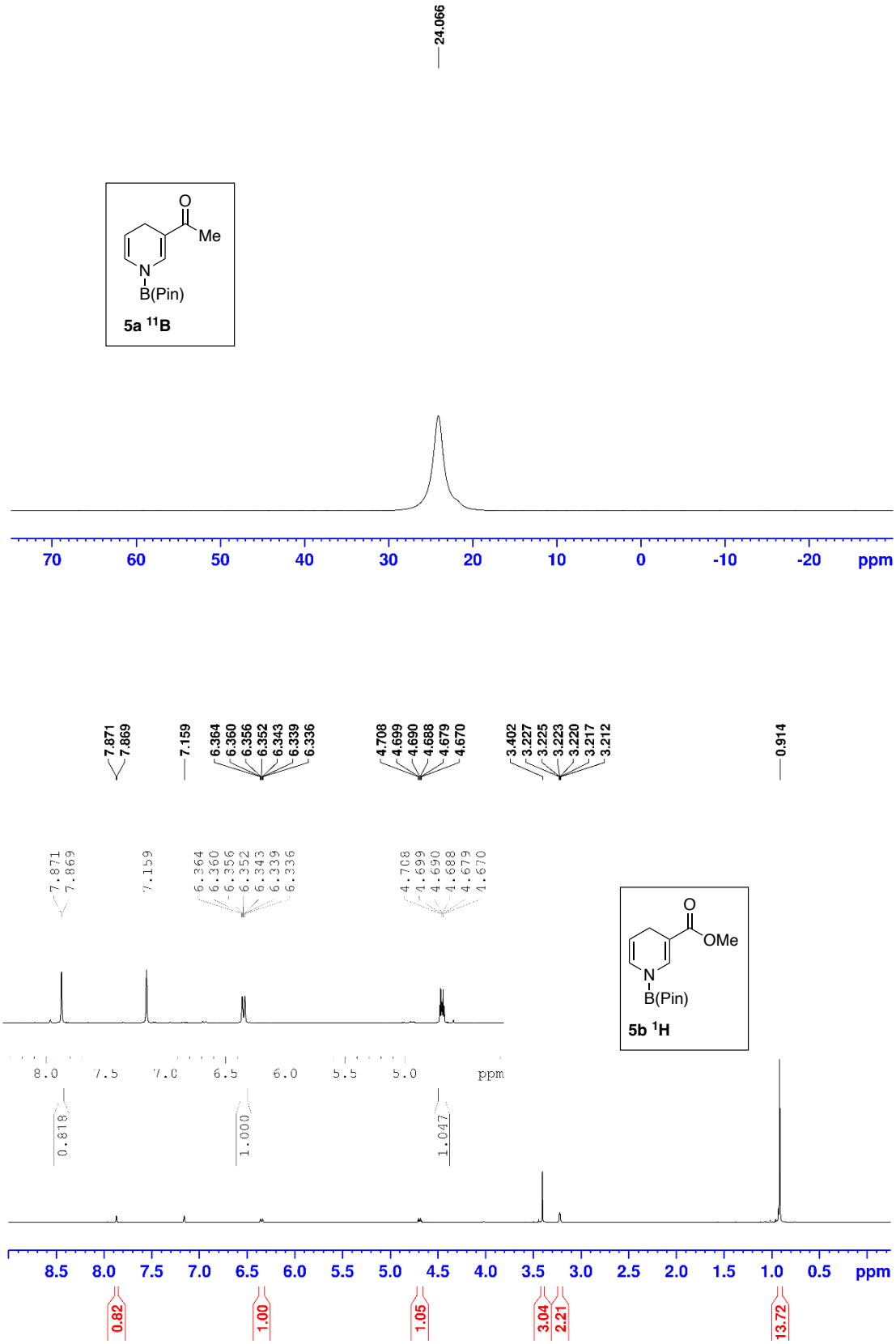
80
60
40
20
ppm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7.869
7.159
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6.360
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6.352
6.343
6.339
6.336
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4.699
4.690
4.688
4.679
4.670
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3.225
3.223
3.220
3.217
3.212
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OMe
N
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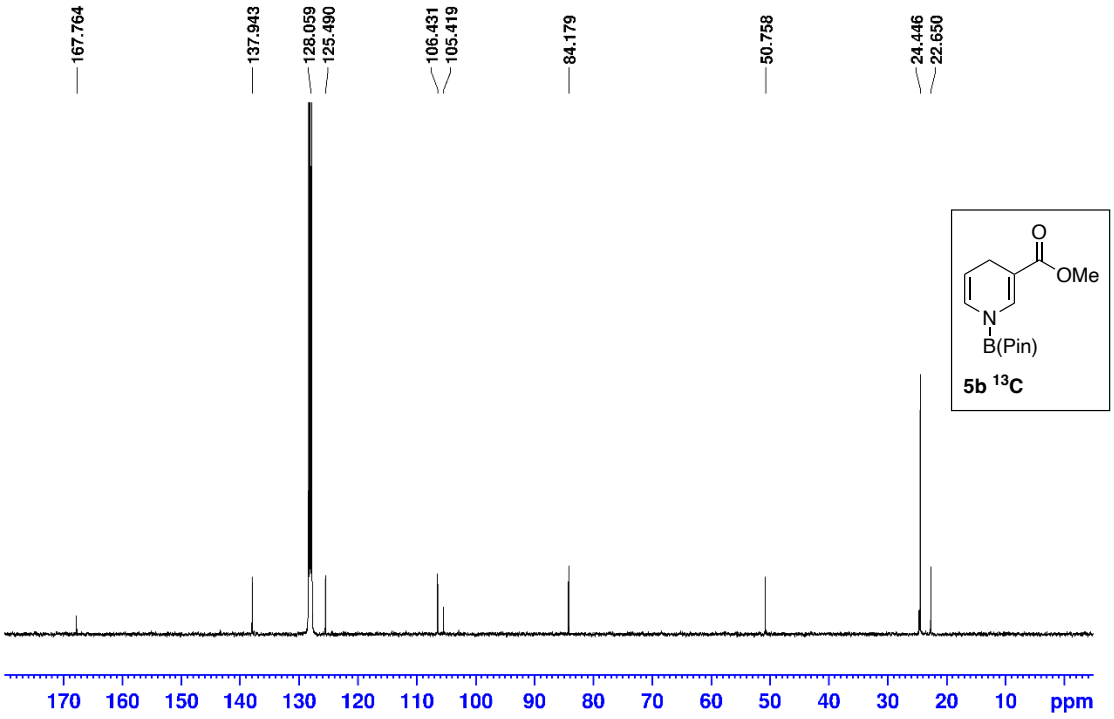
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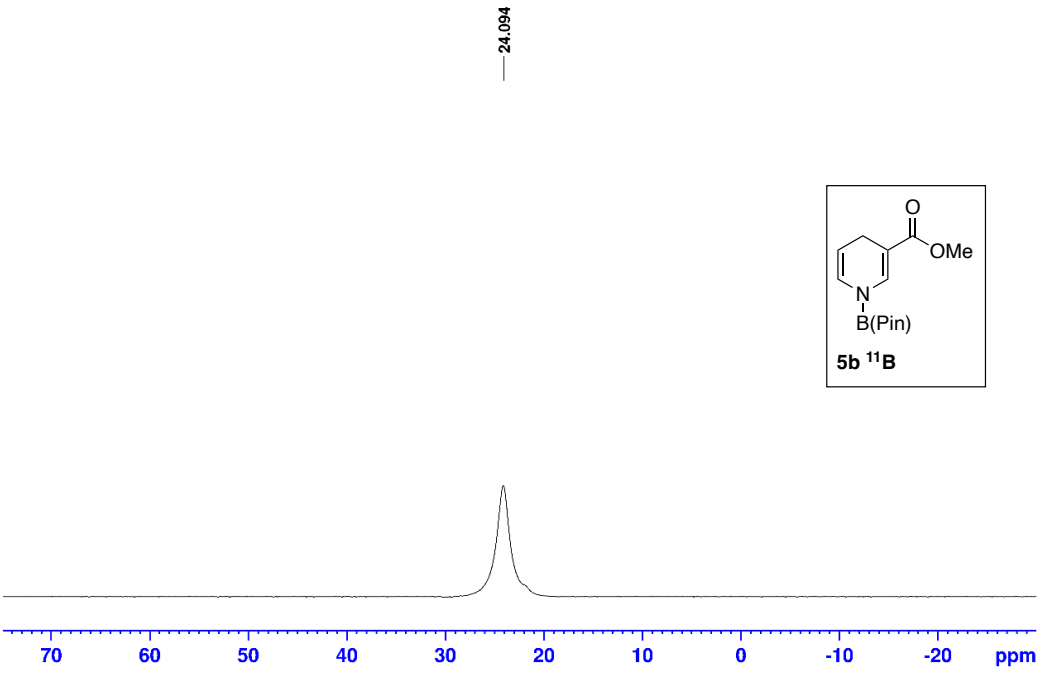
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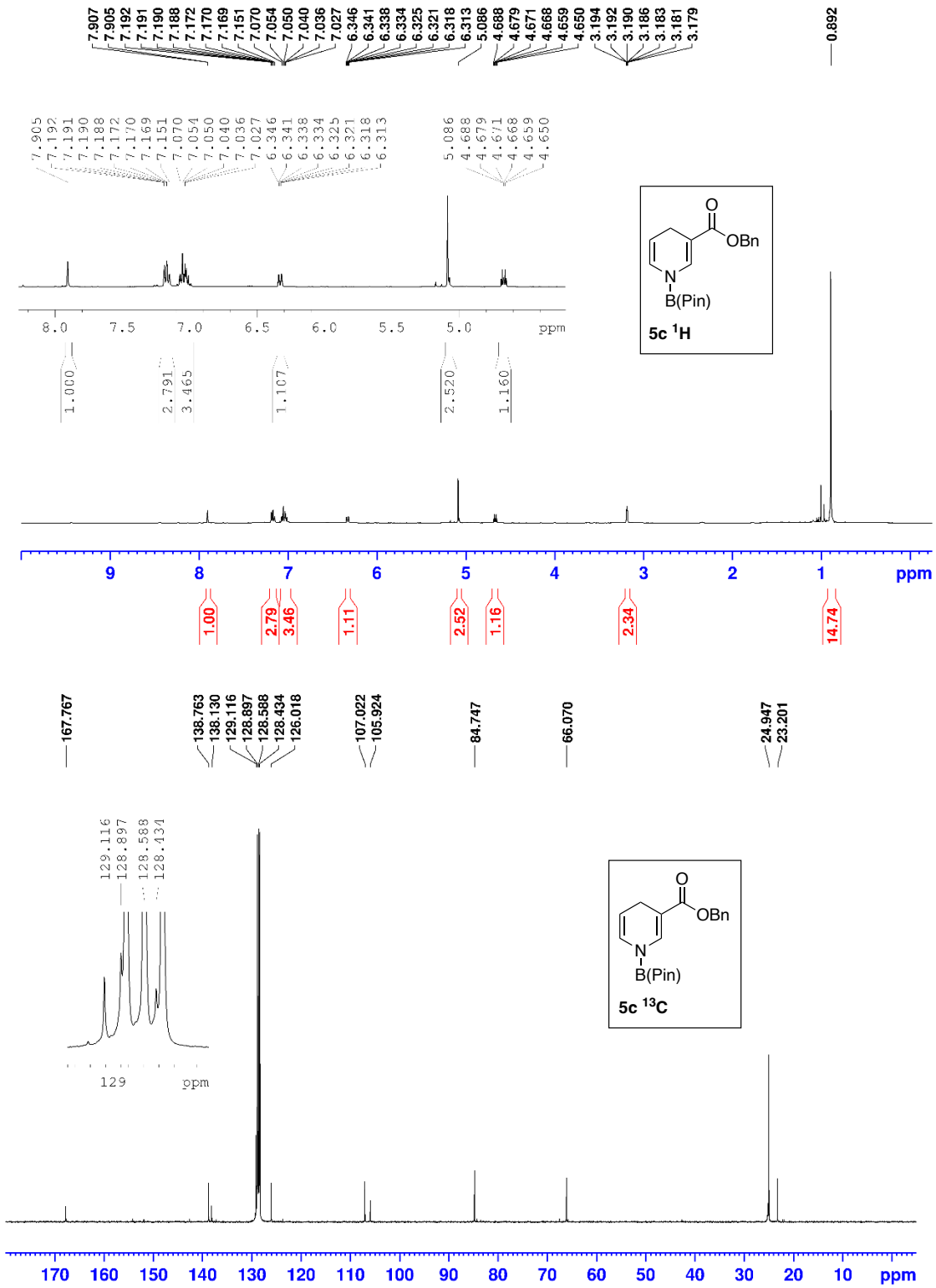
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7.040
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7.027
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6.334
6.325
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6.313
5.086
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4.668
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3.181
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138.763
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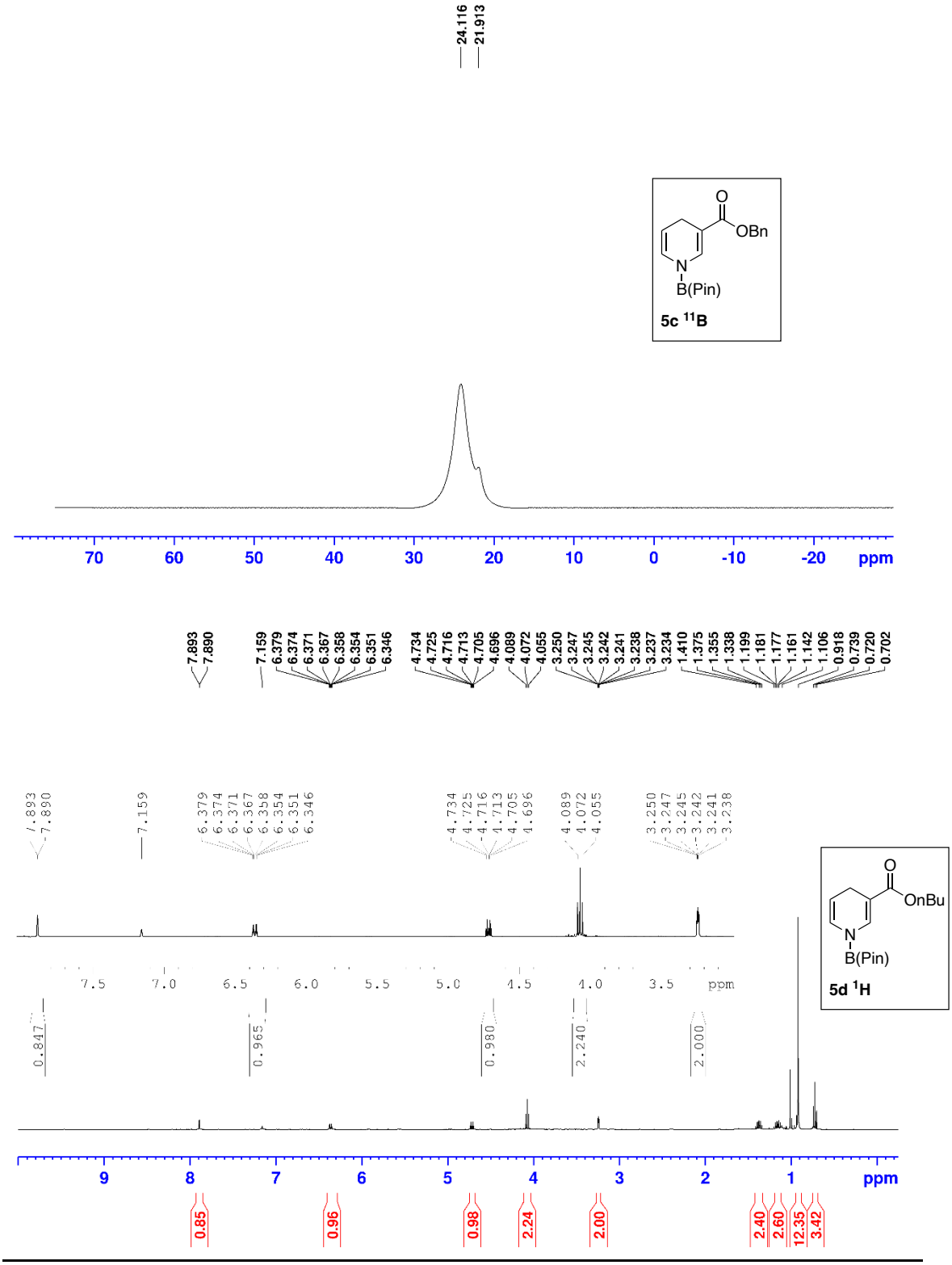
5c ^{13}C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6.374
6.371
6.367
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6.354
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1.410
1.375
1.355
1.338
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1.181
1.177
1.161
1.142
1.106
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0.739
0.720
0.702
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N
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6.0
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ppm
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0.980
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2.000
9
8
7
6
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3
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1
ppm
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2.00
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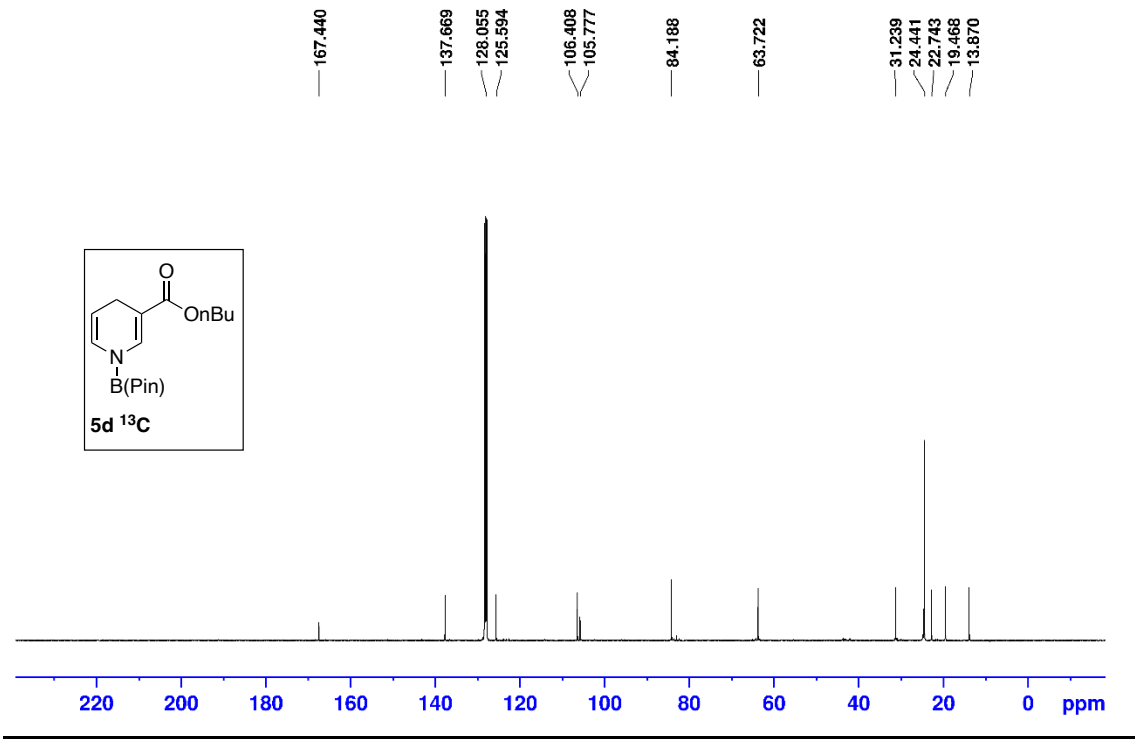
12.35
3.42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120
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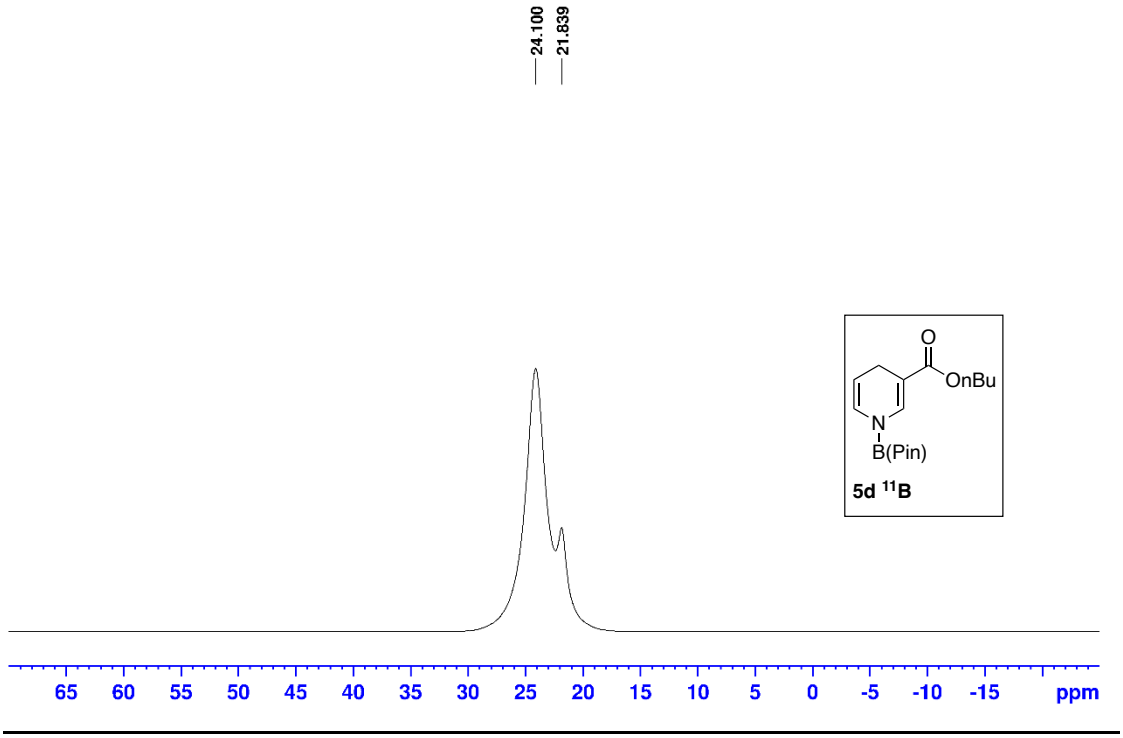
0
ppm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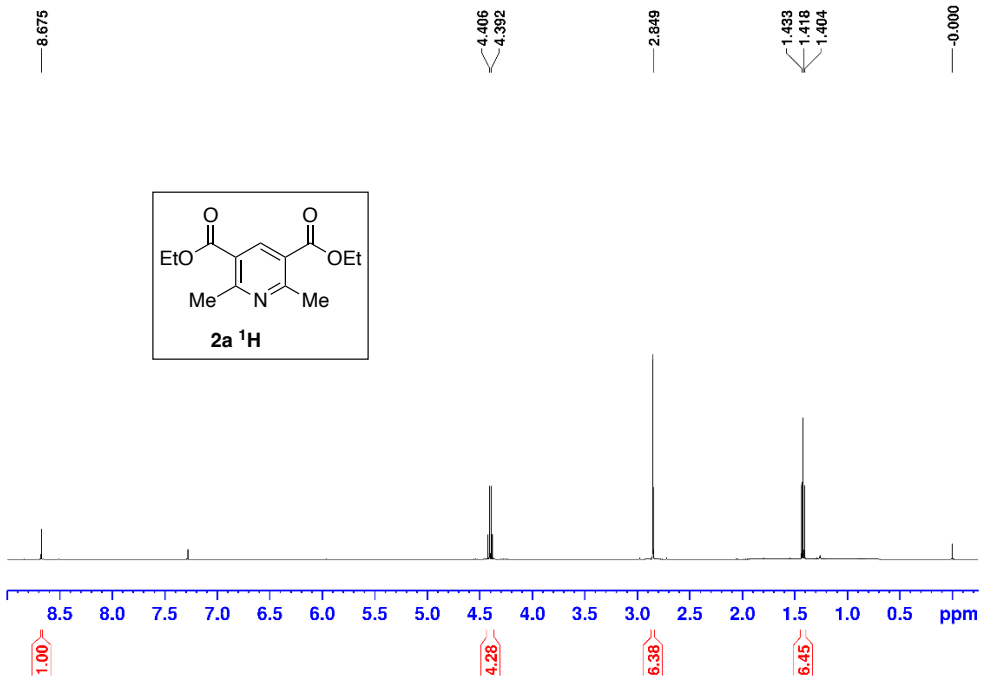
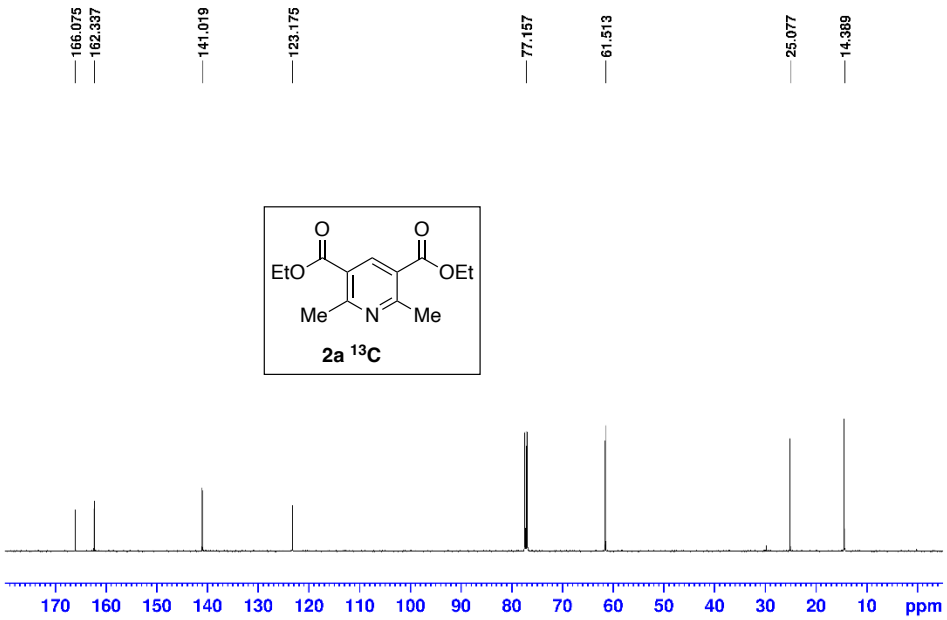
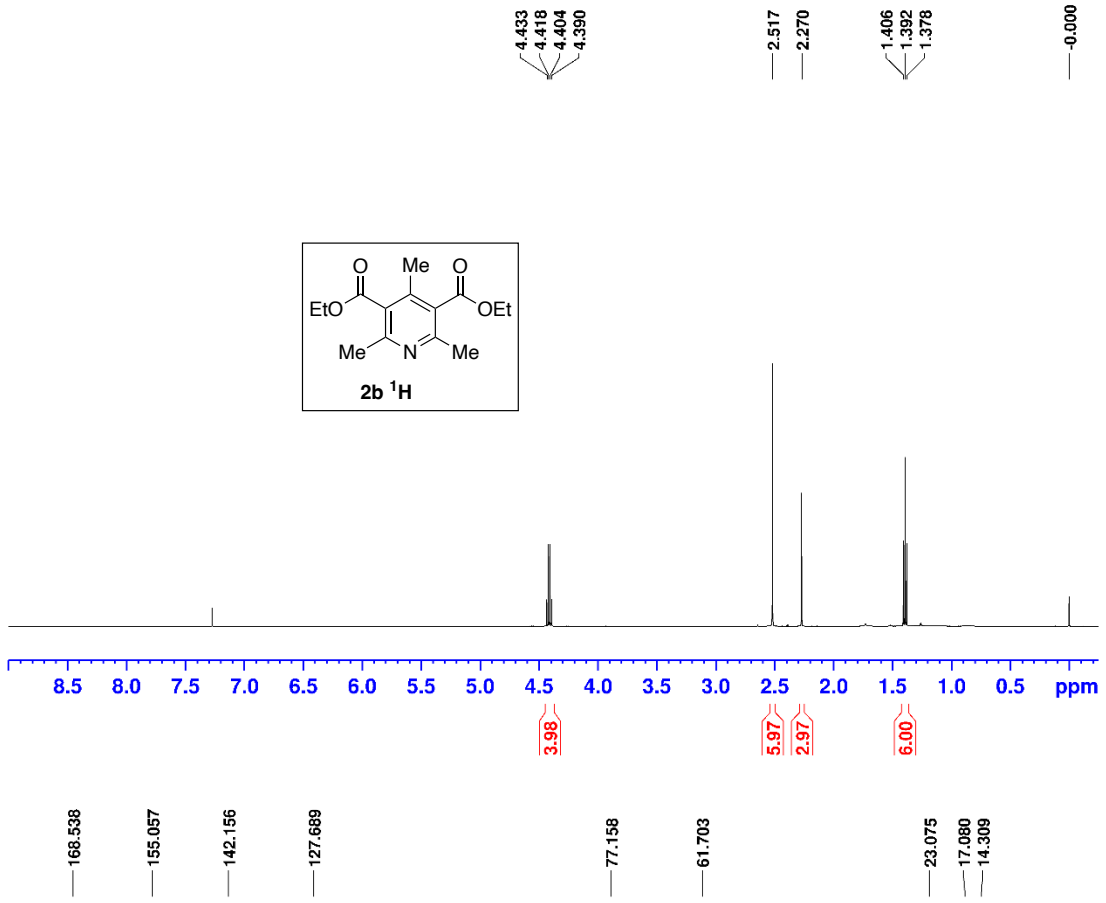
-15
ppm

Aromatized Products



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1.392
1.378
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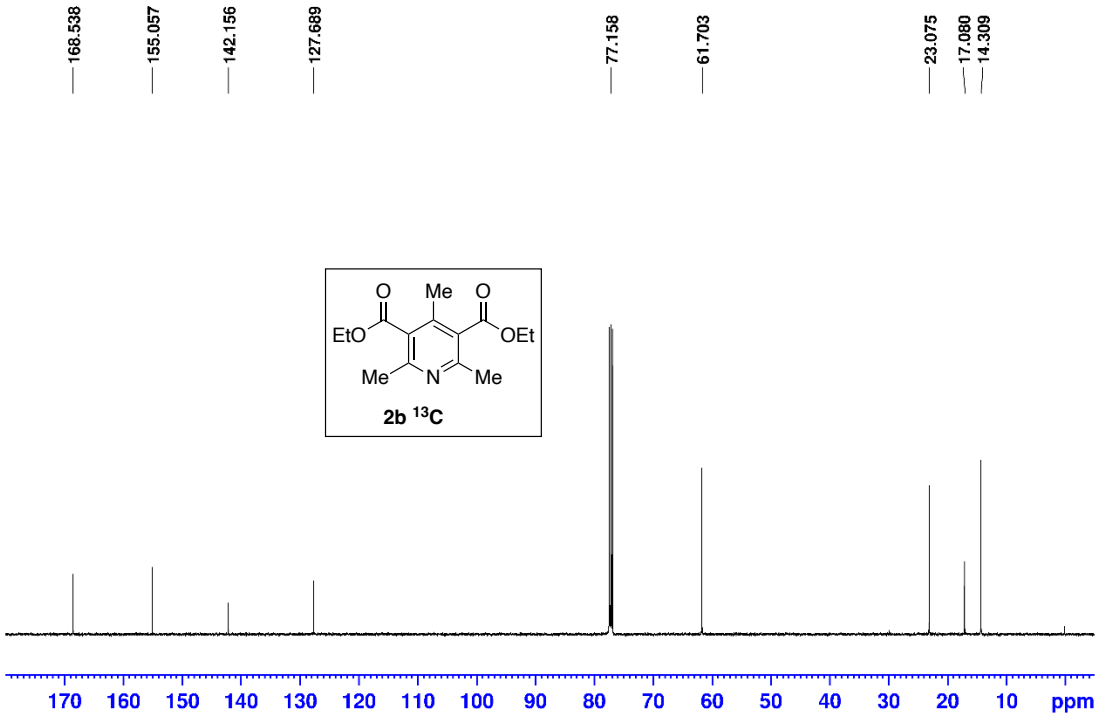
O
Me
O
EtO
OEt
Me
N
Me
2b ^{1}H
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.98
5.97
2.97
6.00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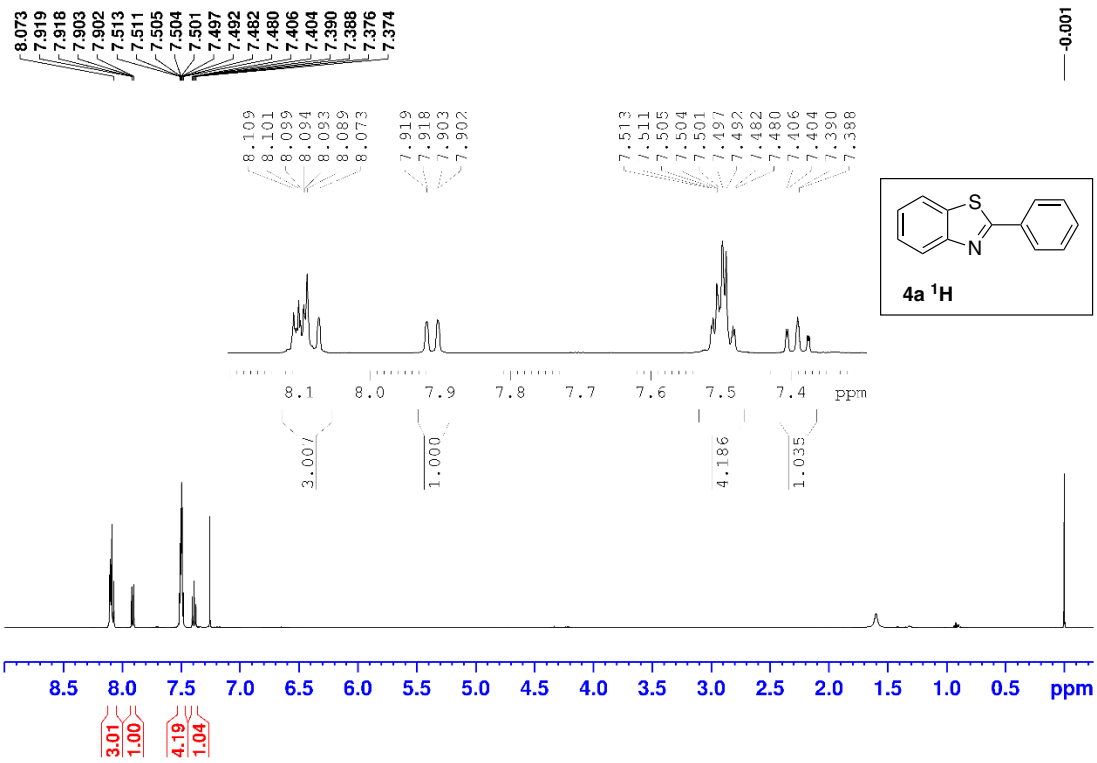
Me
O
EtO
OEt
Me
N
Me
2b ^{13}C
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.902
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7.505
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7.497
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7.482
7.480
7.406
7.404
7.390
7.388
7.376
7.374
-0.001
8.109
8.101
8.099
8.094
8.093
8.089
8.073
7.919
7.918
7.903
7.902
7.513
7.511
7.505
7.504
7.501
7.497
7.492
7.482
7.480
7.406
7.404
7.390
7.388
S
N
4a 1H
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
ppm
3.00
1.000
4.186
1.035
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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1.5
1.0
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1.00
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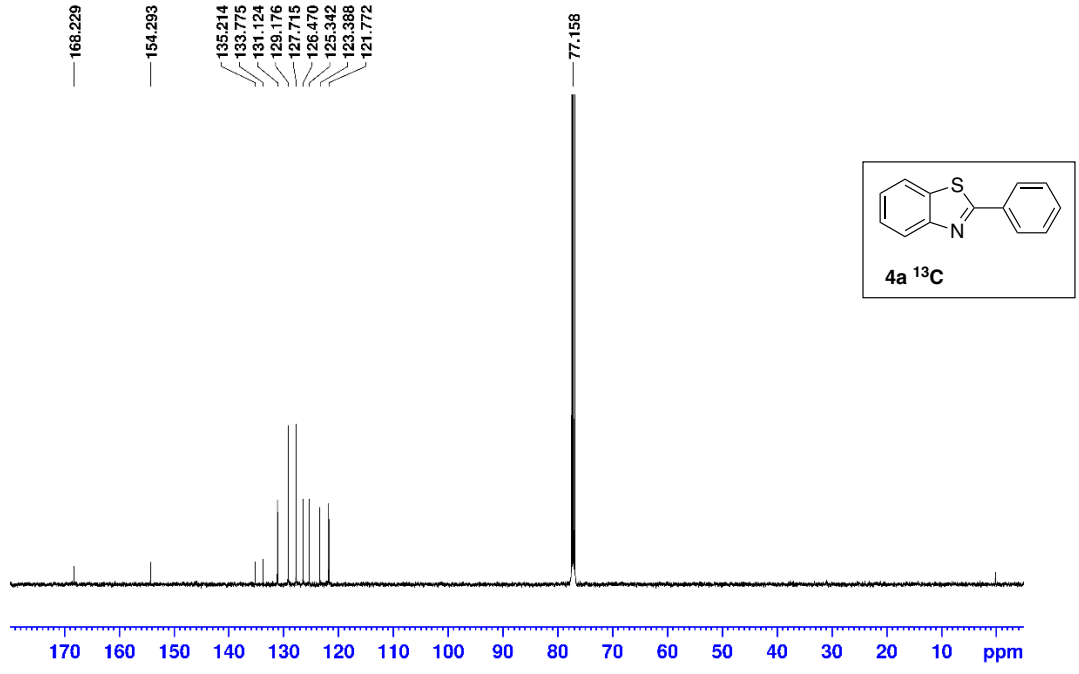
1.04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129.176
127.715
126.470
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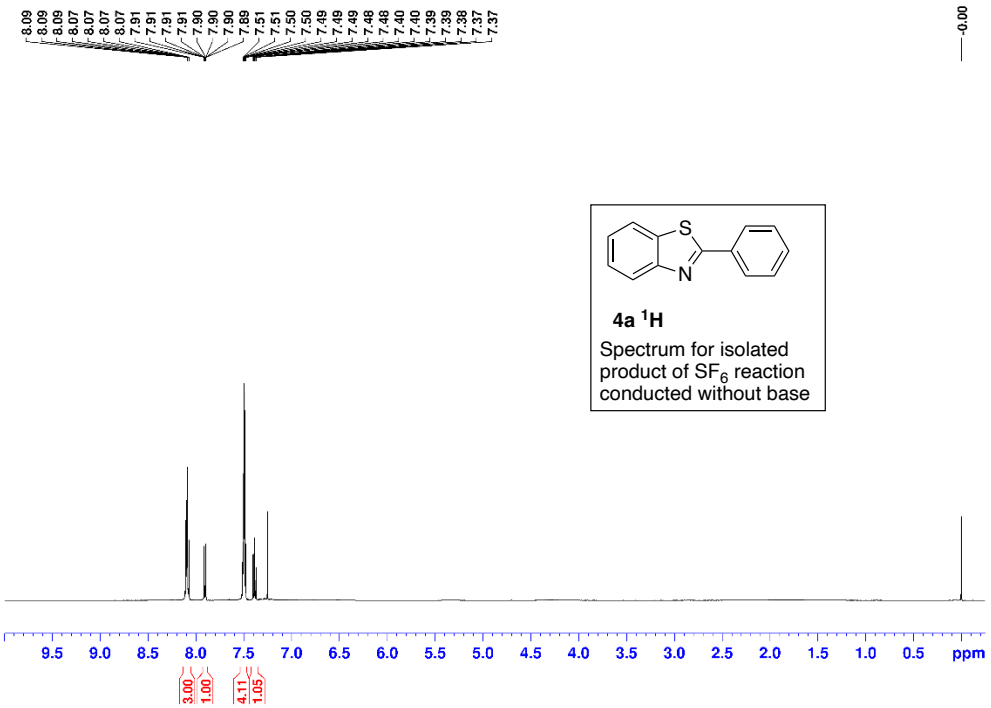
123.388
121.772
77.158
S
N
4a 13C
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.90
7.89
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.40
7.40
7.39
7.39
7.38
7.37
7.37
-0.00
S
N
4a ^{1}H
Spectrum for isolated product of SF_6 reaction conducted without base
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
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1.5
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ppm
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1.00
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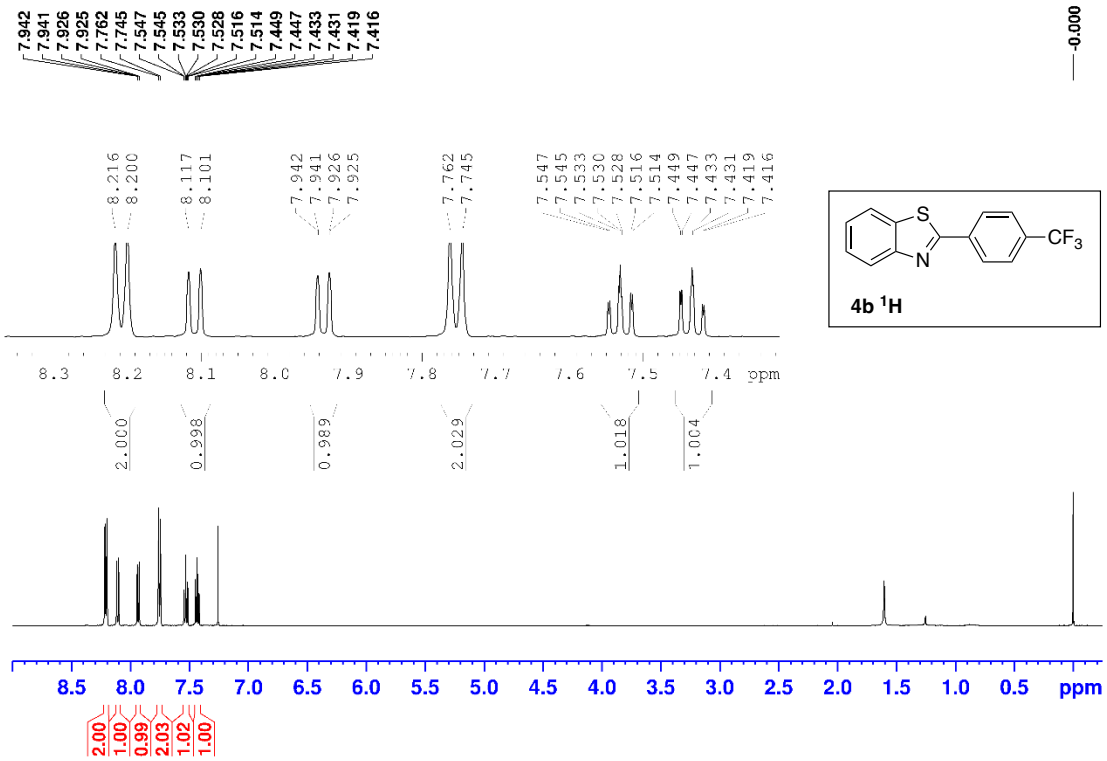
1.05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7.926
7.925
7.762
7.745
7.547
7.545
7.533
7.530
7.528
7.516
7.514
7.449
7.447
7.433
7.431
7.419
7.416
-0.000
8.216
8.200
8.117
8.101
7.942
7.941
7.926
7.925
7.762
7.745
7.547
7.545
7.533
7.530
7.528
7.516
7.514
7.449
7.447
7.433
7.431
7.419
7.416
S
N
CF3
4b 1H
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4 ppm
2.000
0.998
0.989
2.029
1.018
1.004
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
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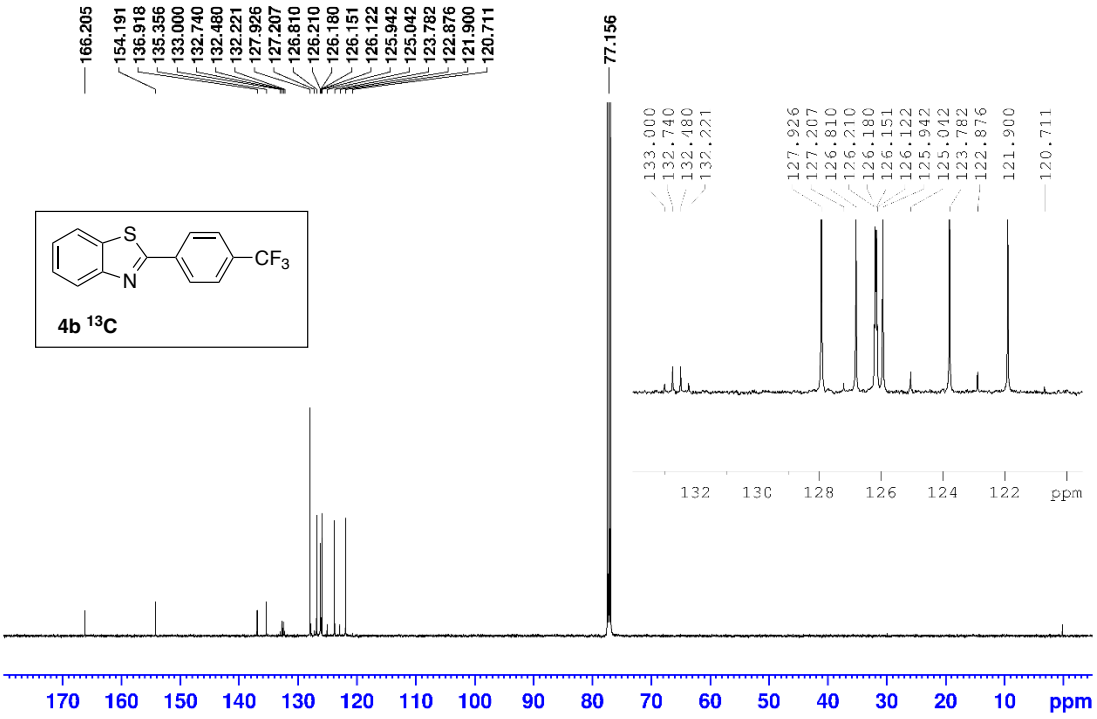
2.03
1.02
1.00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133.000
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132.480
132.221
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127.207
126.810
126.210
126.180
126.151
126.122
125.942
125.042
123.782
122.876
121.900
120.711
77.156
133.000
132.740
132.480
132.221
127.926
127.207
126.810
126.210
126.180
126.151
126.122
125.942
125.042
123.782
122.876
121.900
120.711
S
N
CF3
4b 13C
132
130
128
126
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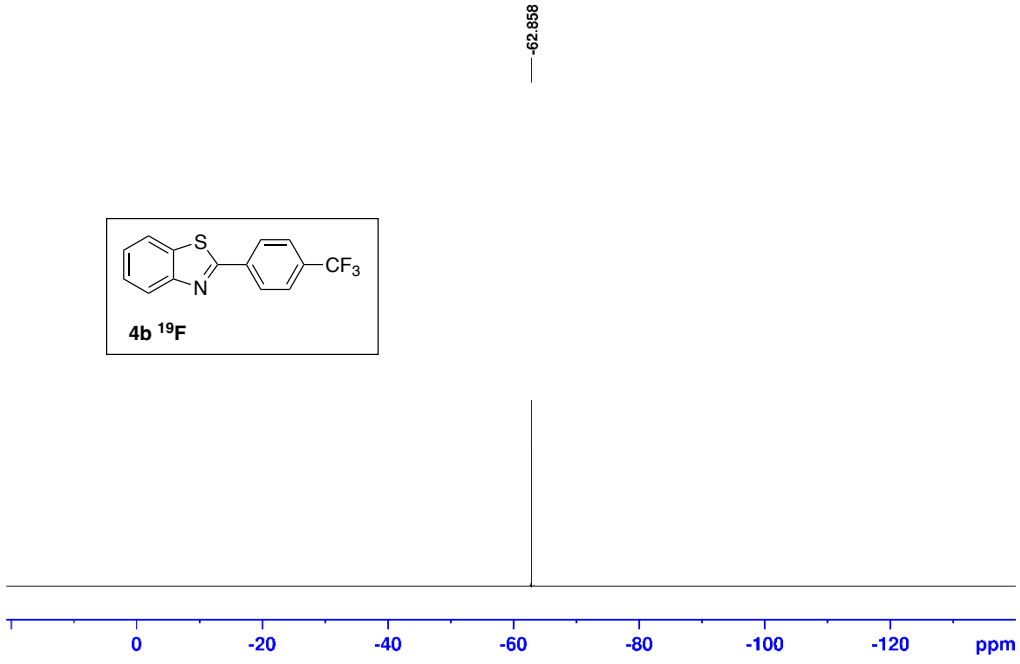
80
70
60
50
40
30
20
10
ppm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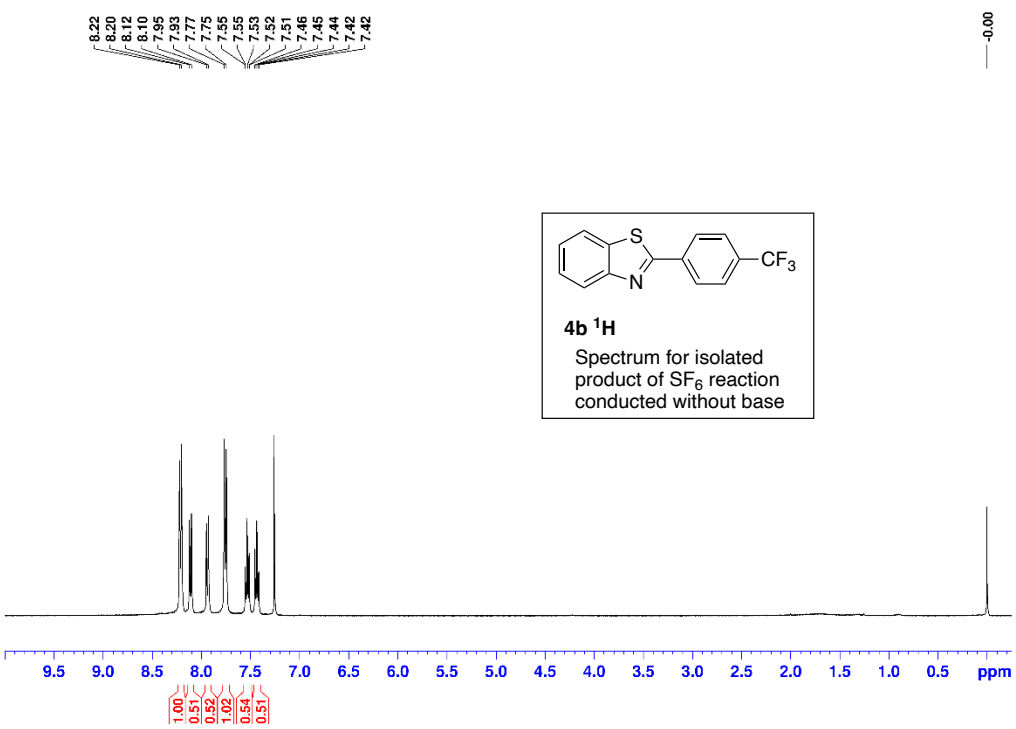
N
CF3
4b 19F
0
-20
-40
-60
-80
-100
-120
ppm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7.75
7.55
7.53
7.52
7.51
7.46
7.45
7.44
7.42
7.42
-0.00
S
N
CF3
4b 1H
Spectrum for isolated product of SF6 reaction conducted without base
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
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1.5
1.0
0.5
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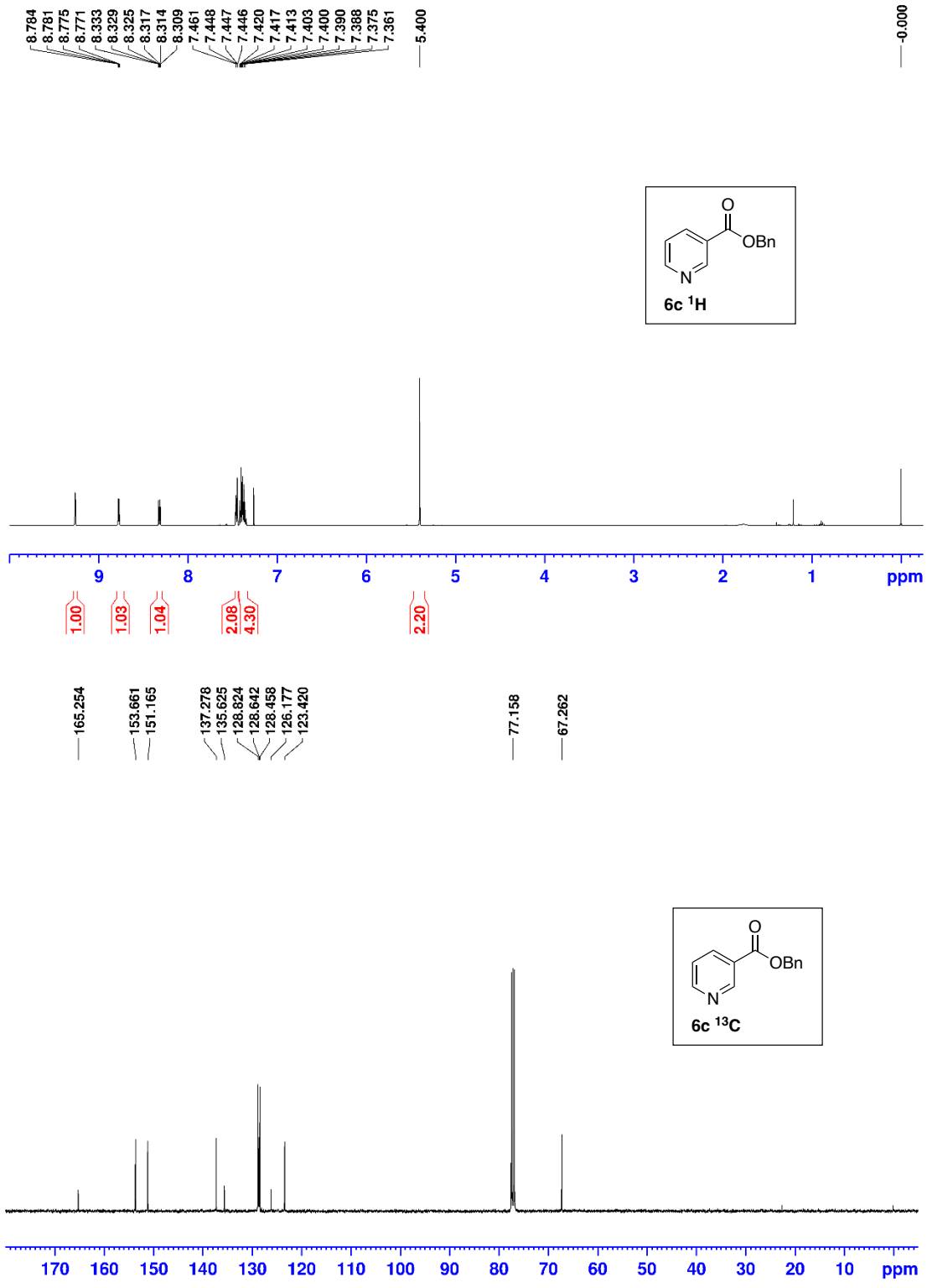
0.52
1.02
0.54
0.51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7.446
7.420
7.417
7.413
7.403
7.400
7.390
7.388
7.375
7.361
5.400
0.000
O
OBn
N
6c 1H
9
8
7
6
5
4
3
2
1
ppm
1.00
1.03
1.04
2.08
4.30
2.20
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151.165
137.278
135.625
128.824
128.642
128.458
126.177
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67.262
O
OBn
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150
140
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120
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90
80
70
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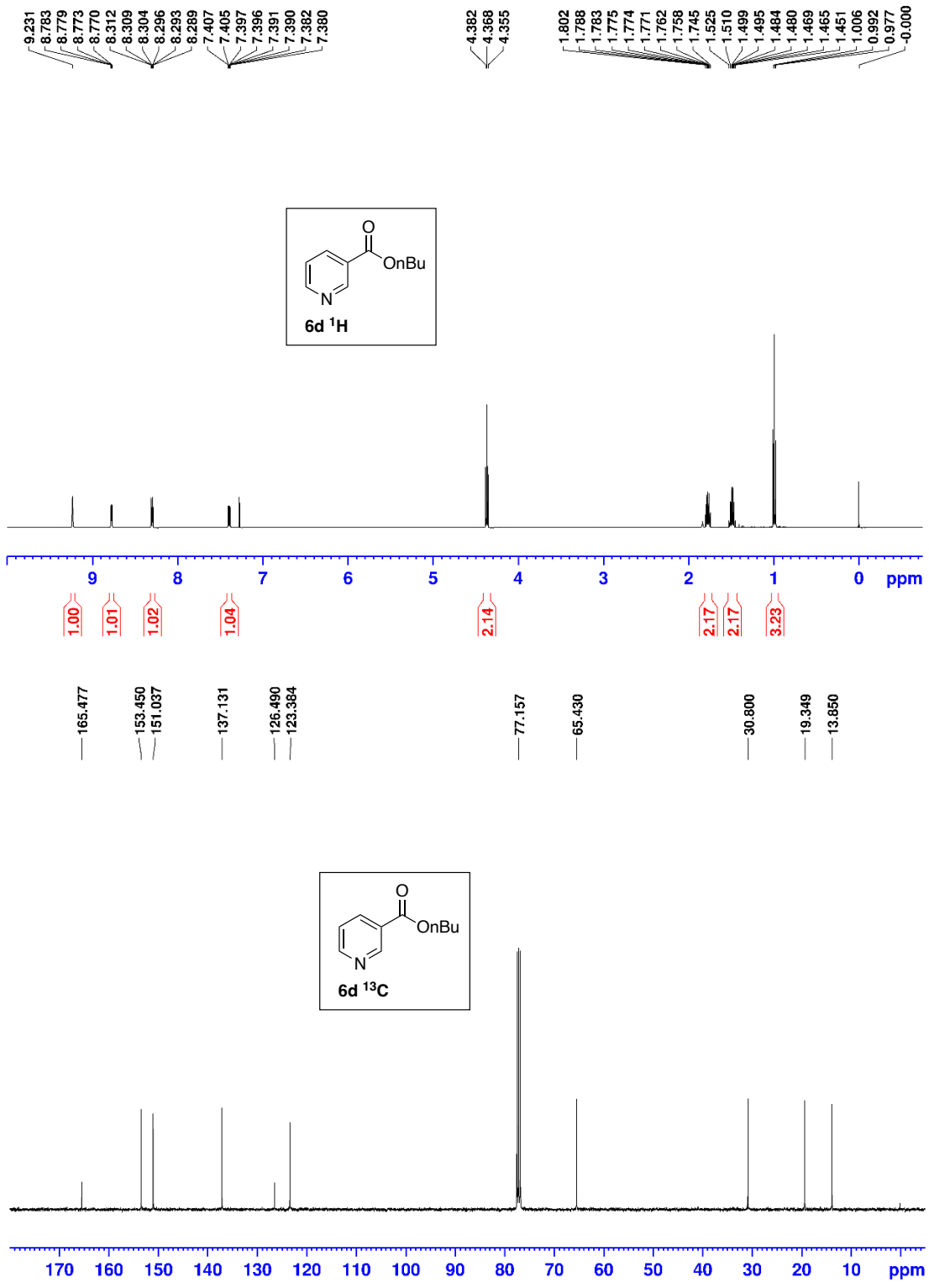
50
40
30
20
10
ppm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7.397
7.396
7.391
7.390
7.382
7.380
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4.368
4.355
1.802
1.788
1.783
1.775
1.774
1.771
1.762
1.758
1.745
1.525
1.510
1.499
1.495
1.484
1.480
1.469
1.465
1.451
1.006
0.992
0.977
-0.000
O
OnBu
N
6d 1H
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.01
1.02
1.04
2.14
2.17
2.17
3.23
165.477
153.450
151.037
137.131
126.490
123.384
77.157
65.430
30.800
19.349
13.850
O
OnBu
N
6d 13C
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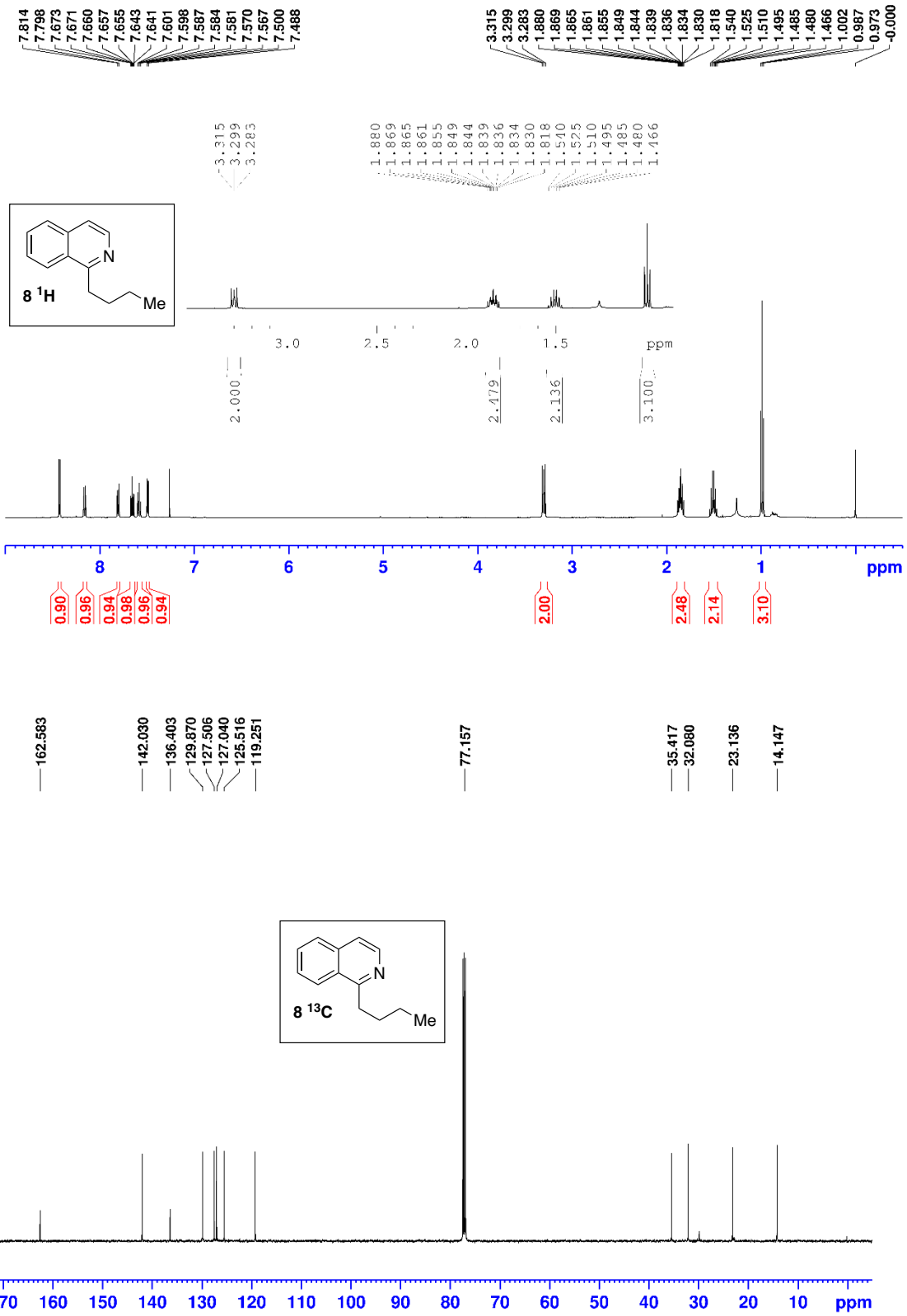
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.641
7.601
7.598
7.587
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7.581
7.570
7.567
7.500
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3.299
3.283
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1.869
1.865
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1.855
1.849
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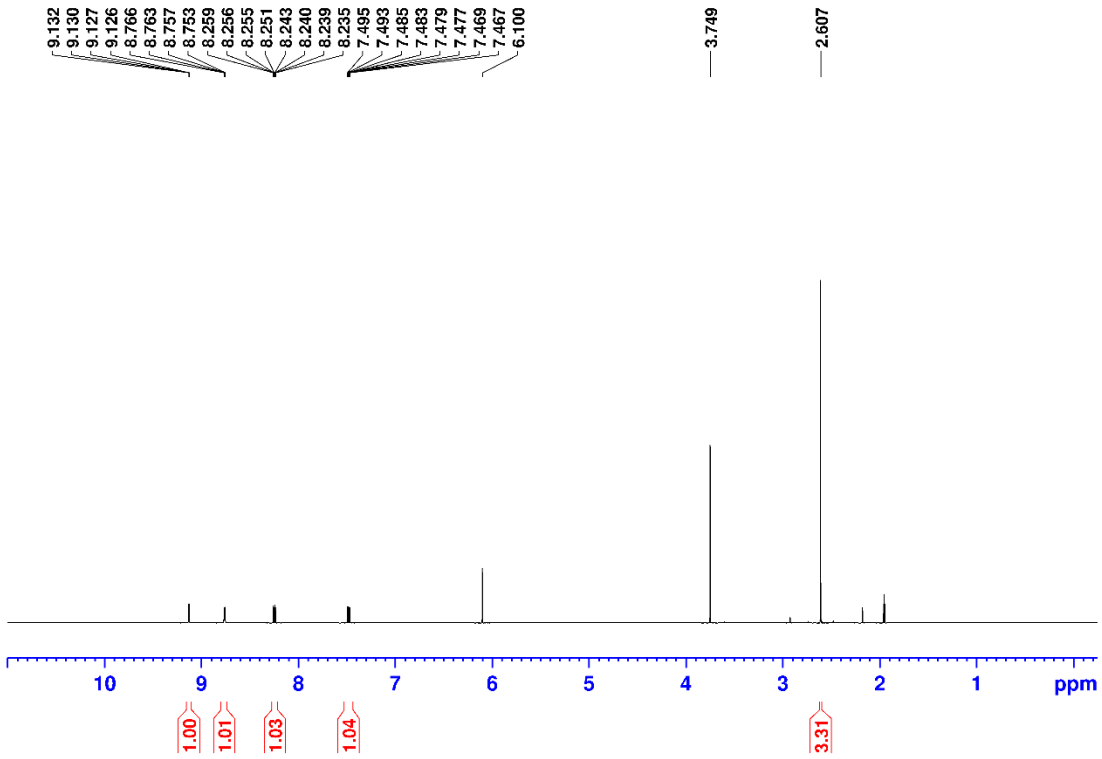
1.836
1.834
1.830
1.818
1.540
1.525
1.510
1.495
1.485
1.480
1.466
1.002
0.987
0.973
-0.000
8 1H
Me
3.0
2.5
2.0
1.5
ppm
2.000
2.479
2.136
3.100
8
7
6
5
4
3
2
1
ppm
0.90
0.96
0.94
0.98
0.96
0.94
2.00
2.48
2.14
3.10
162.583
142.030
136.403
129.870
127.506
127.040
125.516
119.251
77.157
35.417
32.080
23.136
14.147
8 13C
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

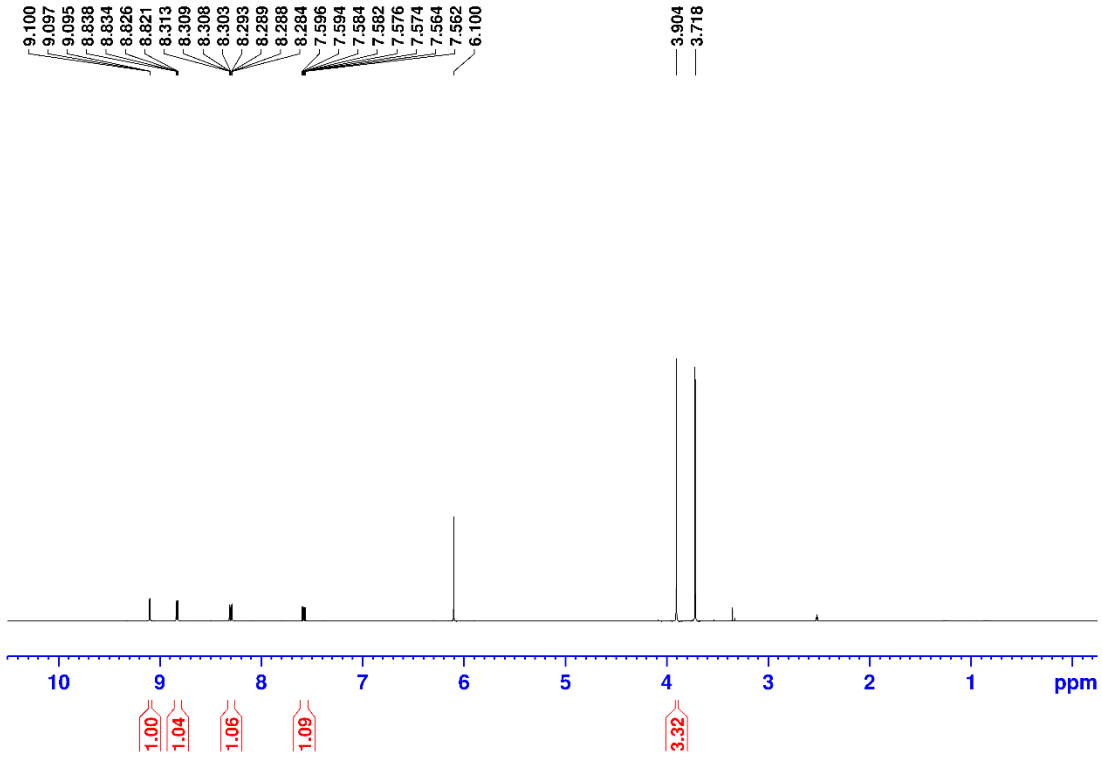
Internal Standard ^{1}H NMR Spectra 6a-6b

H^{1} NMR reference mixtures for 6a-6b below are of 1: 0.33 ratios of 1,3,5-trimethoxybenzene (TMB) and the commercial samples of **6a-6b**. Samples in DMSO-d_6 were calibrated to the TMB peak at 6.1 ppm as reported in the Reference Material Certificate for TMB. Samples in MeCN-d_3 were calibrated to the TMB peak at 6.1 ppm as reported in the Reference Material Certificate for TMB. The singlet peak at 3.7 ppm corresponds to the three methoxy CH_3 groups in TMB. NMR spectra were acquired at 300 K on a Bruker AV-500 MHz NMR spectrometer.

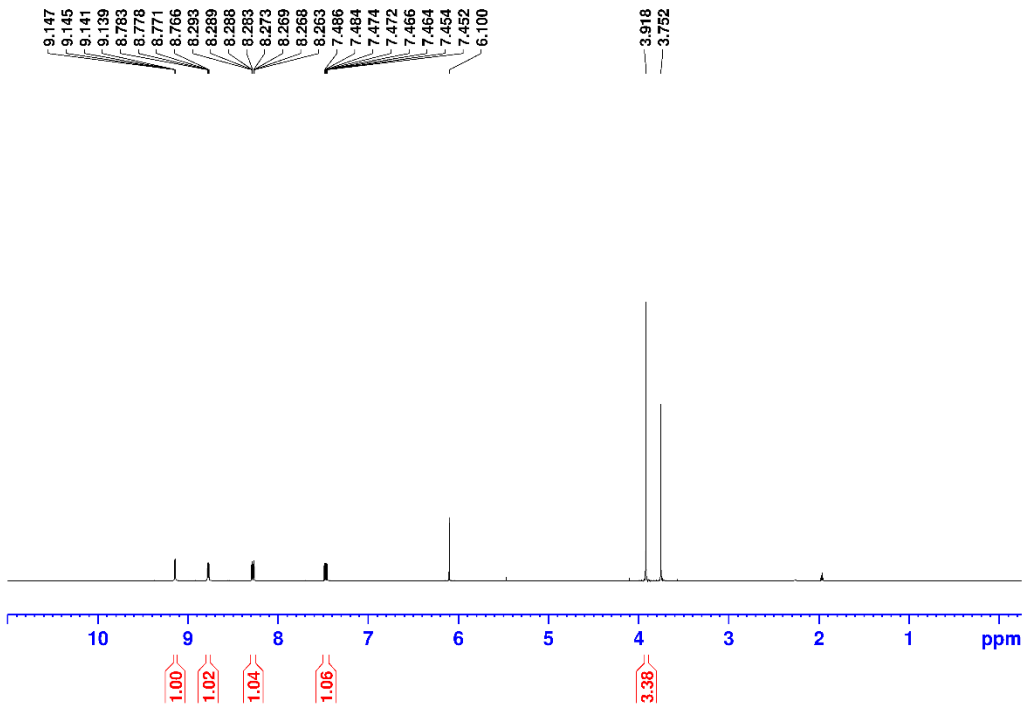
6a (3-acetylpyridine) and TMB in MeCN-d_3 reference sample



6b (methyl nicotinate) and TMB in DMSO-d_6 reference sample



6b (methylnicotinate) and TMB in MeCN-d_3 reference sample



H^1 NMR spectra of reaction mixtures with IS for 6a-6d are calibrated to TMB. Reaction mixtures in non deuterated DMSO were calibrated to the TMB peak at 6.1 ppm as reported in the Reference Material Certificate for TMB. Reaction mixtures in non deuterated MeCN were calibrated to the TMB peak at 6.1 ppm as reported in the Reference Material Certificate for TMB. Integrations shown were used for NMR calculations. NMR spectra were acquired at 300 K on a Bruker AV-400 MHz NMR spectrometer.

Reaction mixtures were removed from irradiation and TMB and 5 mL of distilled water were added. The reaction was left to stir for 1 hour and settle for 10 minutes. An NMR aliquot was taken from the resulting mixture.

6a-6d calculation:

I = ^{1}H NMR peak integration of product (P) or Internal Standard (IS)

H = Number of hydrogen atoms associated with the ^{1}H NMR peak for product (P) or Internal Standard (IS)

M = mmol of product (P) or Internal Standard (IS)

A re arranged and simplified version of equation 1 was used for **6a-6d** NMR yield determination,

(1) $$\frac{I_P}{I_{IS}} = \frac{H_P}{H_{IS}} \frac{M_P}{M_{IS}}$$

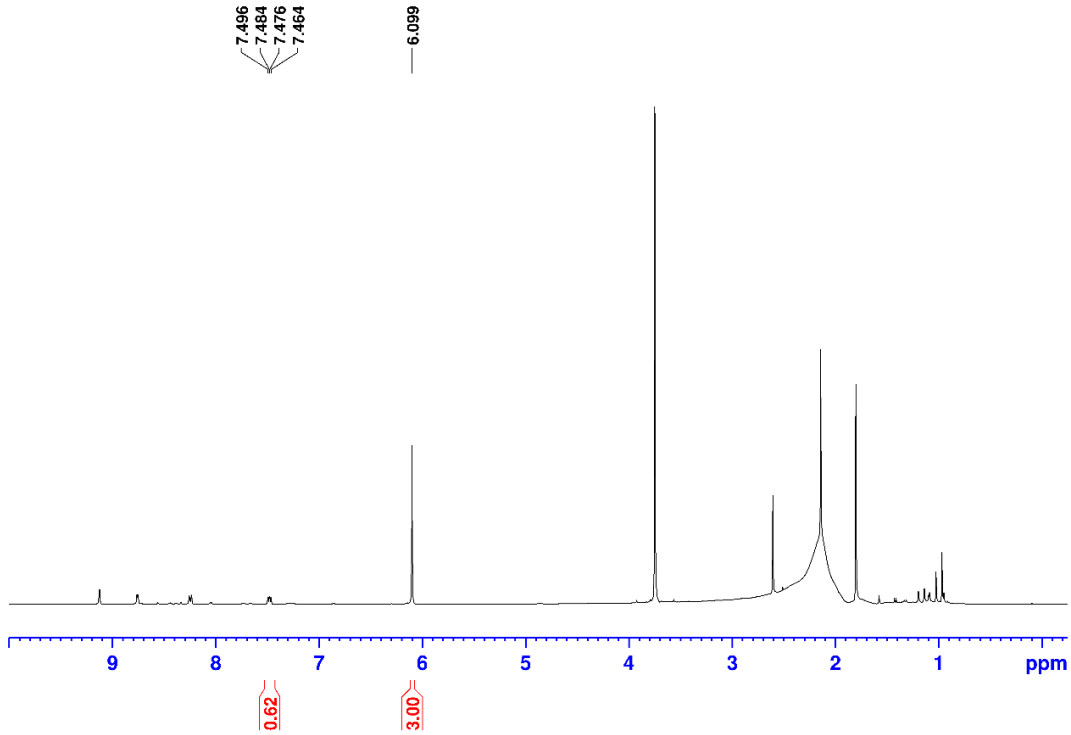
Equation 1 can be rearranged to Equation 2,

(2) $$M_P = \frac{I_P}{I_{IS}} \frac{H_{IS}}{H_P} M_{IS}$$

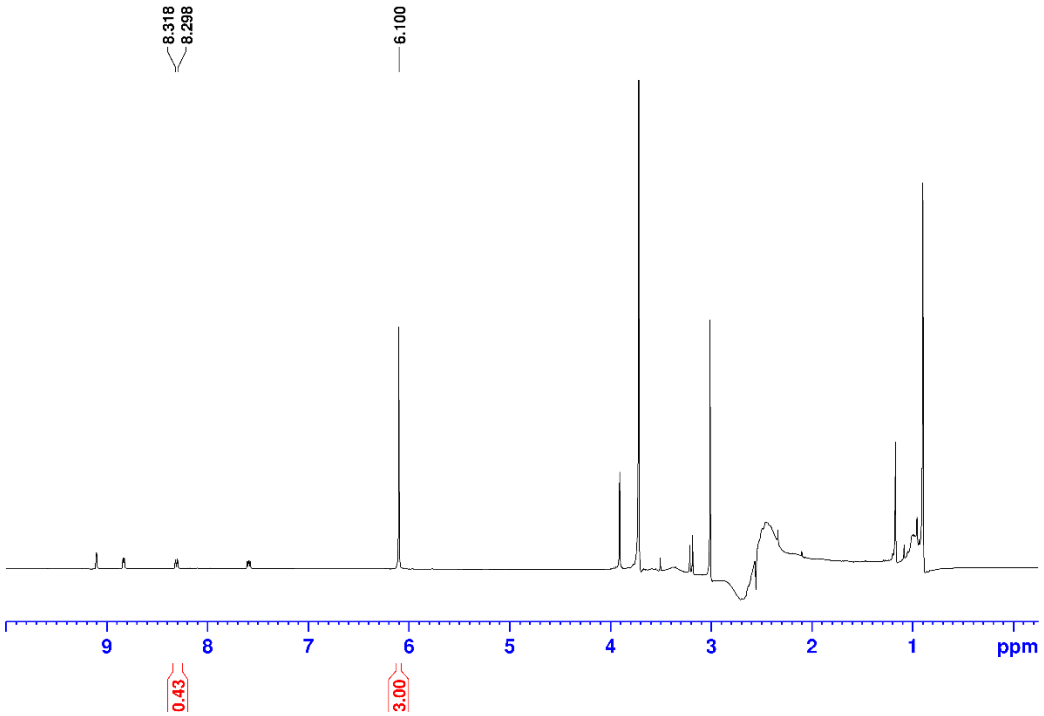
The IS ^{1}H NMR peak integration was set to 3 (I_{IS} = 3), the number of hydrogen atoms associated with the IS peak is 3 (H_{IS} = 3). The peak chosen for product integration corresponds with 1 hydrogen atom (H_P = 1). Therefore, equation 2 can be simplified to,

(3) $$M_P = I_P M_{IS}$$

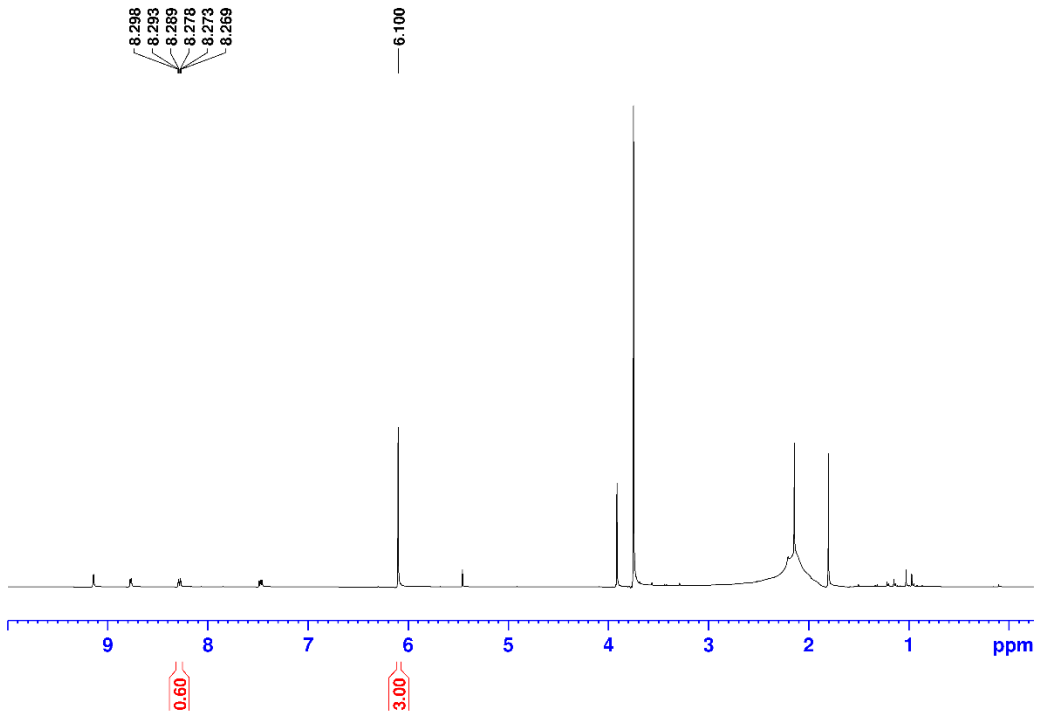
6a (acetylpyridine) and 0.125 mmol of TMB in MeCN reaction mixture:



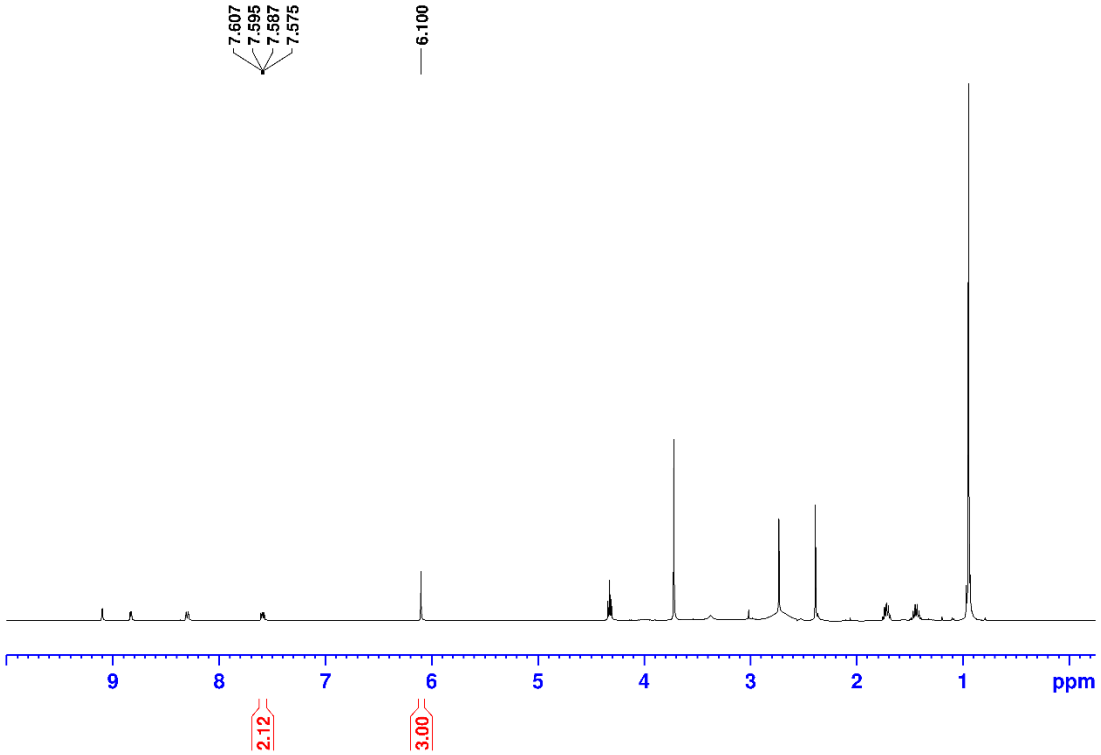
6b (methyl nicotinate) and 0.119 mmol TMB in DMSO reaction mixture:



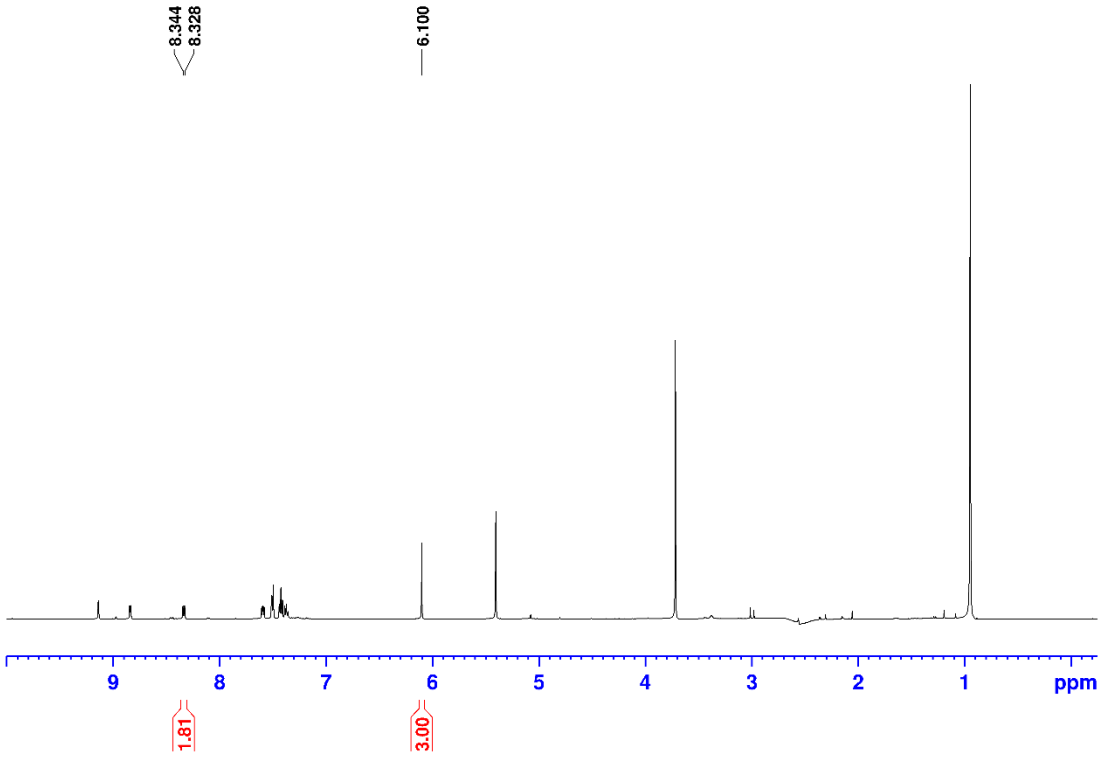
6b (methyl nicotinate) and 0.25 mmol of TMB in MeCN reaction mixture:



6d (Butyl nicotinate) and 0.108 mmol TMB in DMSO reaction mixture:



6c (Benzyl nicotinate) and 0.101 TMB in DMSO reaction mixture:



Internal Standard ^{19}F NMR Spectra

To determine CsF NMR yield for reactions producing **2a**, the reaction mixture was prepared according to the **General Procedure for Bubbled SF_6 Reactions**. The reaction mixture was removed from irradiation and sodium trifluoroacetate, and 10 mL of distilled water were added. The reaction was left to stir for 1 hour and NMR yield of CsF was calculated using ^{19}F NMR integrations shown below, with the sodium trifluoroacetate peak calibrated to 1.

CsF calculation:

I = ^{19}F NMR peak integration of cesium fluoride (CsF) or Internal Standard (IS)

F = Number of Fluorine atoms associated with the ^{19}F NMR peak for cesium fluoride (CsF) or Internal Standard (IS)

M = mmol of cesium fluoride (CsF) or Internal Standard (IS)

A re arranged and simplified version of equation 1 was used for CsF NMR yield determination,

(1) $$\frac{I_{CsF}}{I_{IS}} = \frac{F_{CsF}}{F_{IS}} \frac{M_{CsF}}{M_{IS}}$$

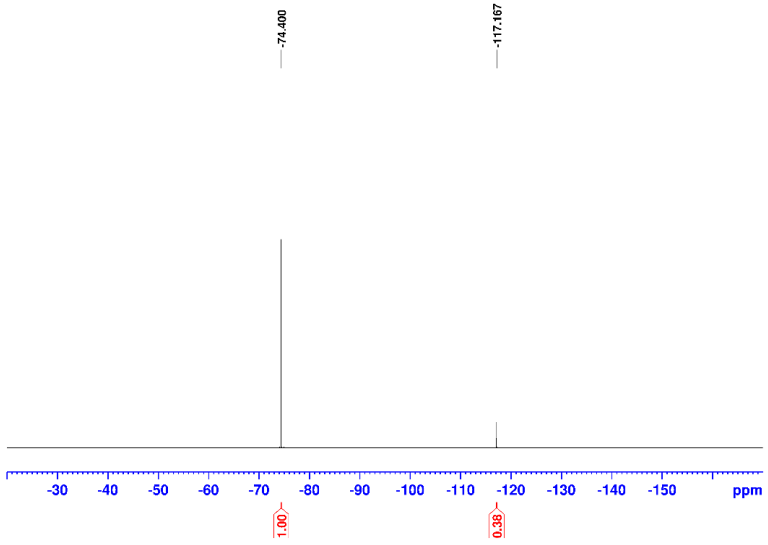
Equation 1 can be rearranged to Equation 2,

(2) $$M_{CsF} = \frac{I_{CsF}}{I_{IS}} \frac{F_{IS}}{F_{CsF}} M_{IS}$$

The IS ^{19}F NMR peak integration was set to 1 (I_{IS} = 1), the number of fluorine atoms associated with the IS fluorine peak is 3 (F_{IS} = 3) and the number of fluorine atoms associated with the CsF fluorine peak is 1 (F_{CsF} = 1). Therefore, equation 2 can be simplified to,

(3) $$M_{CsF} = 3 I_{CsF} M_{IS}$$

^{19}F NMR Spectrum for reaction mixture **1a** with 1 mmol of IS:



Speciation of Sulfur:

We attempted to determine the fate of the sulfur. Attempts to conduct qualitative analysis (for example precipitation of sulfite with barium salts) were complicated by the presence of DMSO, fluoride, and carbonate in the reaction mixture.

Low-resolution MS data of the reaction mixture from page **S8** showed the presence of a peak consistent with bisulfite (HSO_3^-, m/z expected= 80.9652) however we were unable to obtain high-resolution mass spectra in this range due to technical limitations. Further attempts to quantify the presence of sulfite as a formaldehyde adduct were not successful, potentially due to competing presence of fluoride, carbonate, DMSO, and **2a**.

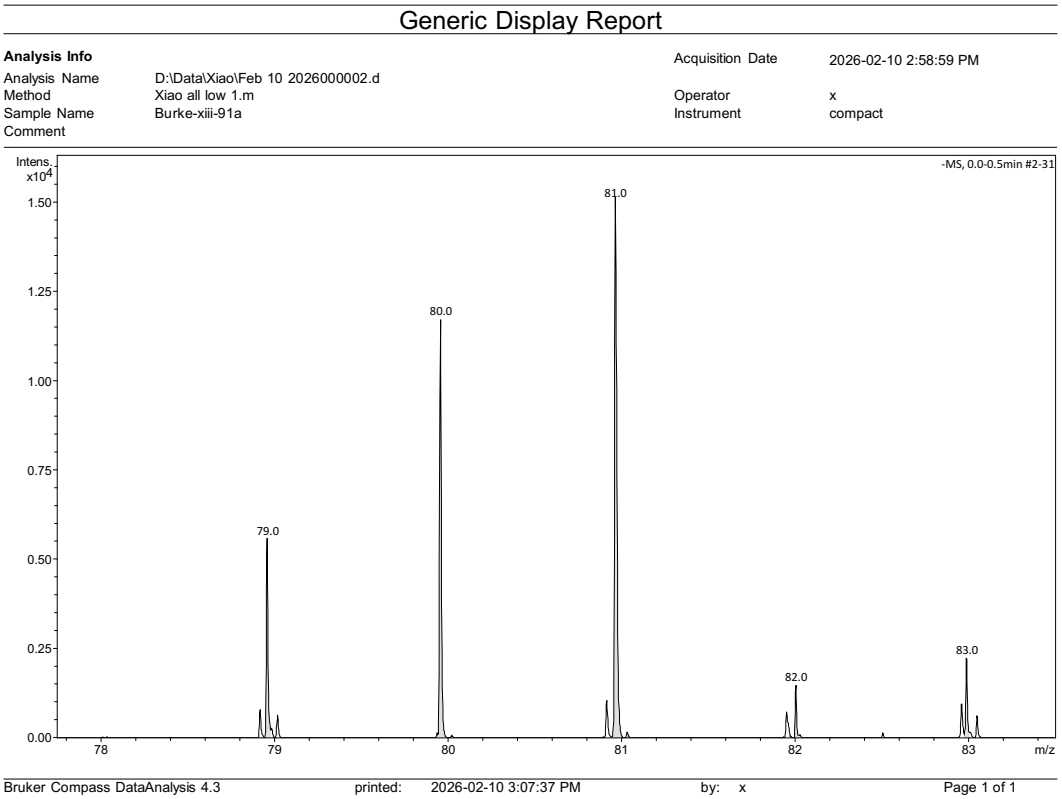
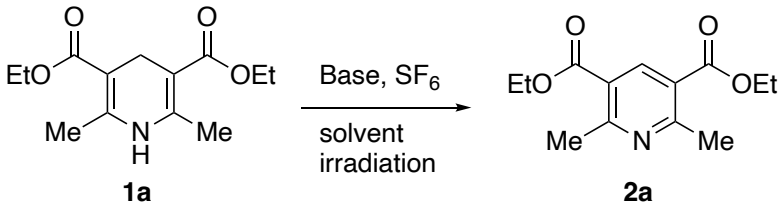


Figure S5: Potential detection of HSO_3^- by mass-spectrometry.

HEH Optimization Table

Table S1:

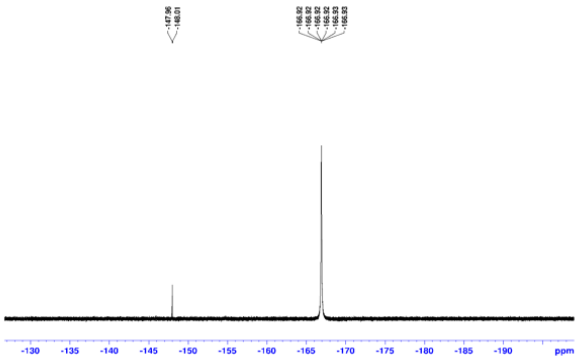


1a **2a**

HEH 1a	Base	Solvent	Irradiation	SF_6	Yield 2a
1 equiv.	Cs_2CO_3 (1 equiv.)	MeCN	390nm	Bubbled	33%
1 equiv.	Cs_2CO_3 (1 equiv.)	Toluene	390nm	Bubbled	29%
1 equiv.	Cs_2CO_3 (1 equiv.)	DMSO	390nm	Bubbled	86%
1 equiv.	K_2CO_3 (1 equiv.)	DMSO	390nm	Bubbled	37%
1 equiv.	NEt_3 (1 equiv.)	DMSO	390nm	Bubbled	12%
1 equiv.	NaH* (1 equiv.)	DMSO	390nm	Bubbled	59%
1 equiv.	CsF (3 equiv.)	DMSO	390nm	Bubbled	63%
1 equiv.	Cs_2CO_3 (3 equiv.)	DMSO	390nm	Bubbled	90%
1 equiv.	Cs_2CO_3 (3 equiv.)	MeCN	390nm	80 psi	76%
1 equiv.	Cs_2CO_3 (3 equiv.)	DMSO	427nm	Bubbled	71%
1 equiv.	Cs_2CO_3 (3 equiv.)	DMSO	456nm	Bubbled	57%
1 equiv.	Cs_2CO_3 (1 equiv.)	DMSO	390nm	N/A	39%, No F-detected
N/A	Cs_2CO_3 (1 equiv.)	DMSO	390nm	Bubbled	No F-detected
1 equiv.	Cs_2CO_3 (3 equiv.)	DMSO	N/A (dark)	Bubbled	17%
1 equiv	none	DMSO	390 nm	Bubbled	83%

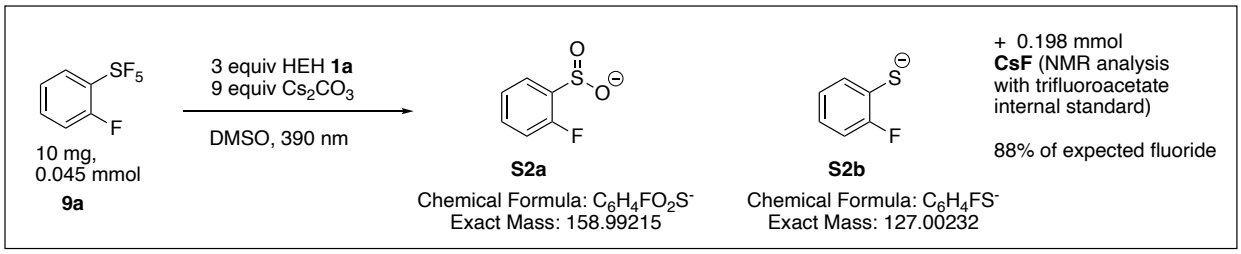
*NaH from a 55 % mixture suspended in mineral oil

The following ^{19}F spectrum is from the crude reaction mixture of aromatization of **1a** with SF_6 conducted *without base* in DMSO, on page **S8**, consistent with HF in DMSO.[5]



Ar-SF_5 Experiments and Mass Spectrometry Data

General Procedure for Ar-SF_5 Decomposition Experiments: In the glove box, the Ar-SF_5 compound **9a** or **9b** (10 mg, 1 equiv.) was placed in a 1-dram vial with a stir bar. 3,5-Diethyl 1,4-dihydro-3,5-pyridinedicarboxylate (3 equiv.), cesium carbonate (9 equiv.) and DMSO (1.5 mL) were then placed in the vial, and the vial was capped and sealed with electrical tape. The vial was immediately removed from the glovebox and irradiated with a 390 nm LED and stirred for 18 hours. The reaction mixture was submitted for NMR and mass spectroscopic analysis.



Scheme S2: Decomposition of SF_5 group in **9a**

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Xiao\Oct 03 2025000010.d	Acquisition Date	2025-10-03 11:43:12 AM
Method	Xiao all 1.m		
Sample Name	Burke-xiii-28 neg	Operator	x
Comment		Instrument	compact 8255754.20059

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

Meas. m/z	Ion Formula	m/z	err [ppm]
127.0023	C6H4FS	127.0023	0.5

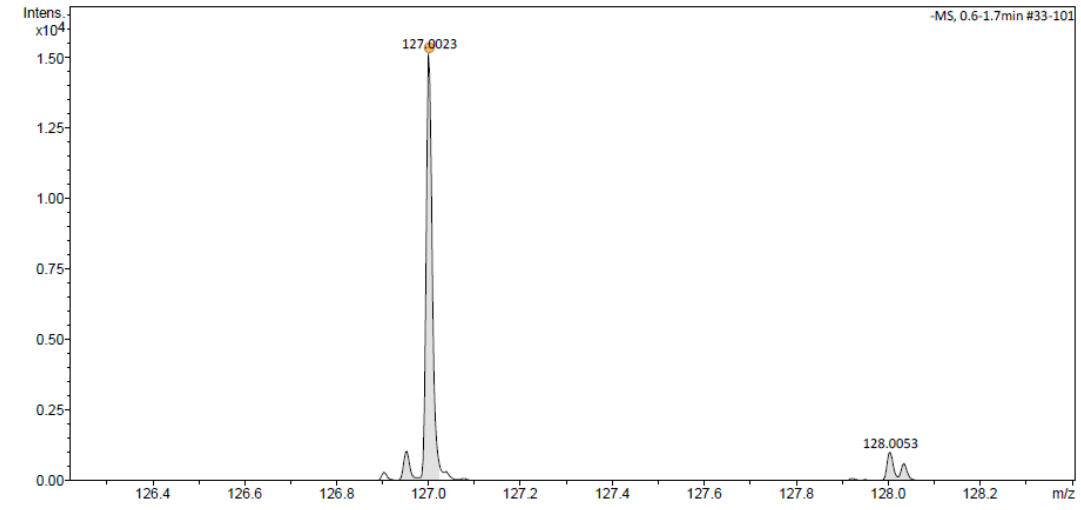


Figure S6: Detection of **S2b** (thiolate) using ESI in negative mode:

Mass Spectrum SmartFormula Report

Analysis Info

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Method	Xiao all 1.m		
Sample Name	Burke-xiii-28 neg	Operator	x
Comment		Instrument	compact 8255754.20059

Acquisition Parameter

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Focus	Not active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

Meas. m/z	Ion Formula	m/z	err [ppm]
158.9924	C6H4FO2S	158.9922	-1.8

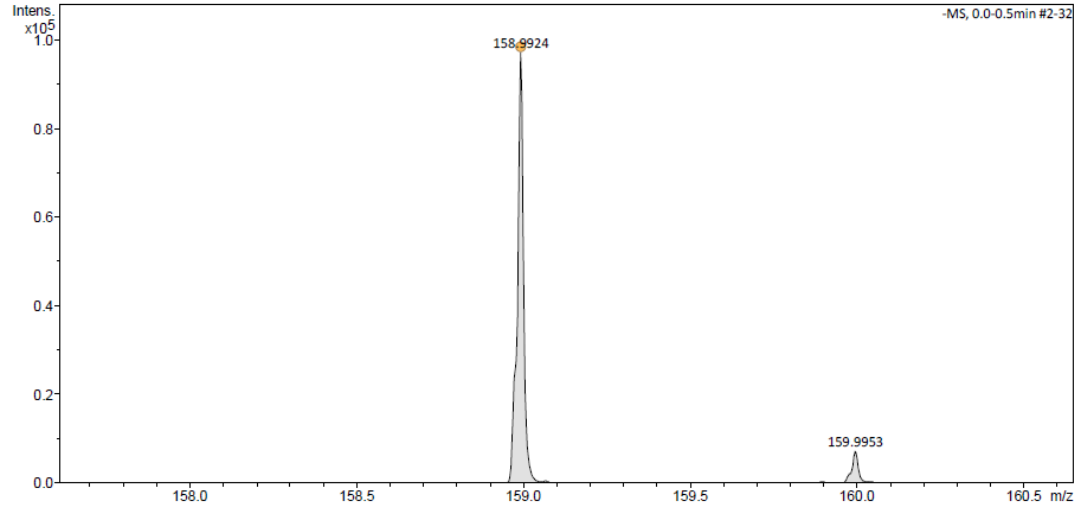
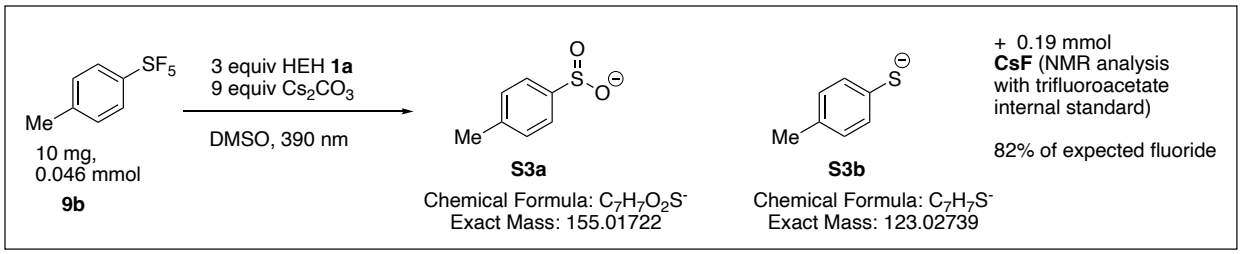


Figure S7: Detection of **S2a** (sulfinate) using ESI in negative mode:



Scheme S3: Decomposition of SF_5 group of **9b**

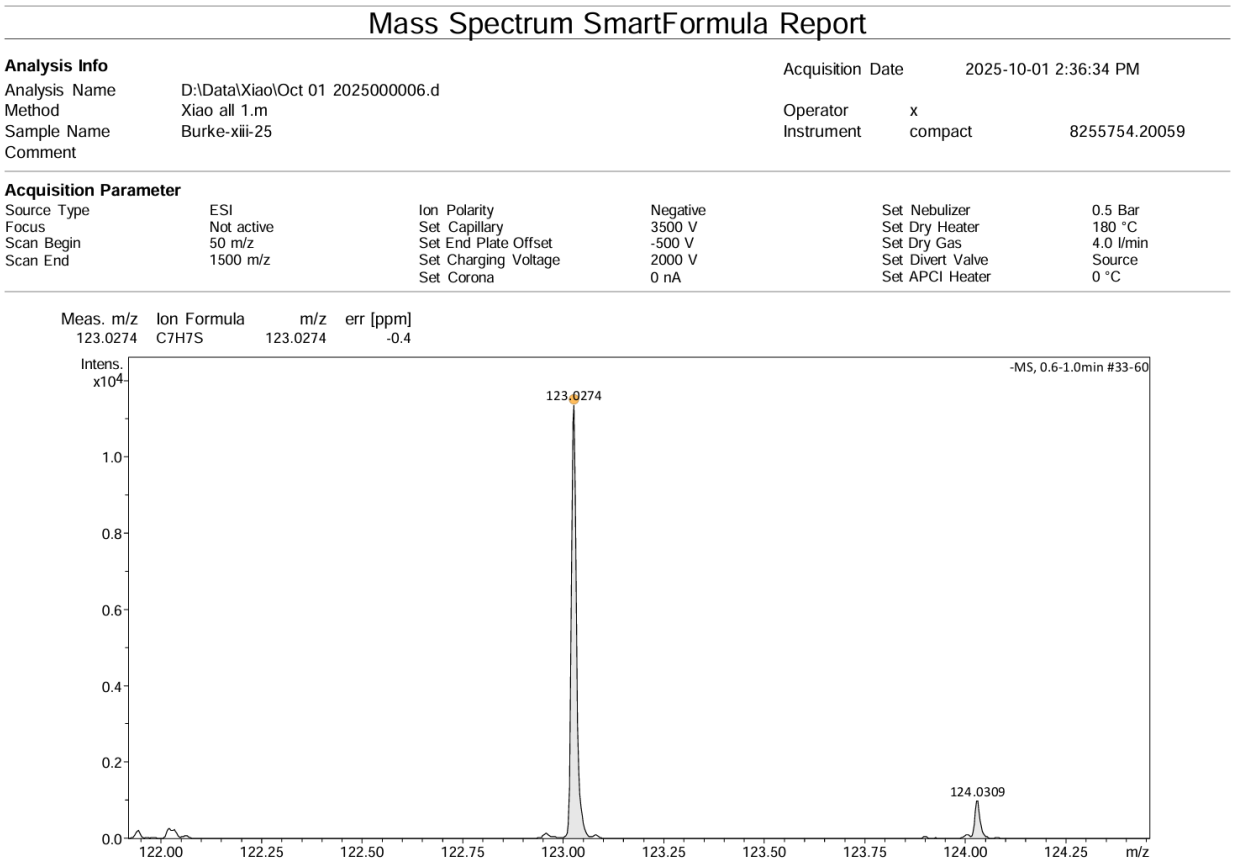


Figure S8: Detection of **S3b** (thiolate) using ESI in negative mode:

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Xiao\Oct 01 2025000006.d	Acquisition Date	2025-10-01 2:36:34 PM
Method	Xiao all 1.m	Operator	x
Sample Name	Burke-xiii-25	Instrument	compact 8255754.20059
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.5 Bar
Focus	Not active	Set Capillary	3500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

Meas. m/z	Ion Formula	m/z	err [ppm]
123.0274	C7H7S	123.0274	-0.4
155.0168	C7H7O2S	155.0172	2.5

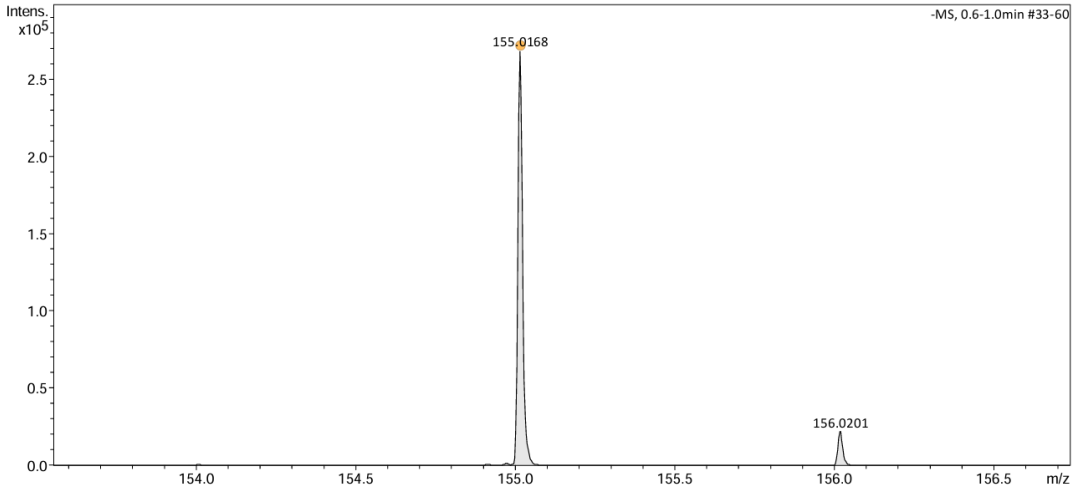


Figure S9: Detection of **S3b** (sulfinate) using ESI in negative mode:

To determine CsF NMR yields for the SF_5 decomposition reactions, the samples were prepared according to the **General procedure for Ar-SF_5 Decomposition Experiments** except 3 mL of DMSO was used. The reaction mixture was removed from irradiation and sodium trifluoroacetate, and 5 mL of distilled water were added. The reaction was left to stir for 1 hour and NMR yield of CsF was calculated using ^{19}F NMR integrations shown below, with the sodium trifluoroacetate peak calibrated to 1.

CsF calculation:

I = ^{19}F NMR peak integration of cesium fluoride (CsF) or Internal Standard (IS)

F = Number of Fluorine atoms associated with the ^{19}F NMR peak for cesium fluoride (CsF) or Internal Standard (IS)

M = mmol of cesium fluoride (CsF) or Internal Standard (IS)

A re arranged and simplified version of equation 1 was used for CsF NMR yield determination,

(1) $$\frac{I_{CsF}}{I_{IS}} = \frac{F_{CsF}}{F_{IS}} \frac{M_{CsF}}{M_{IS}}$$

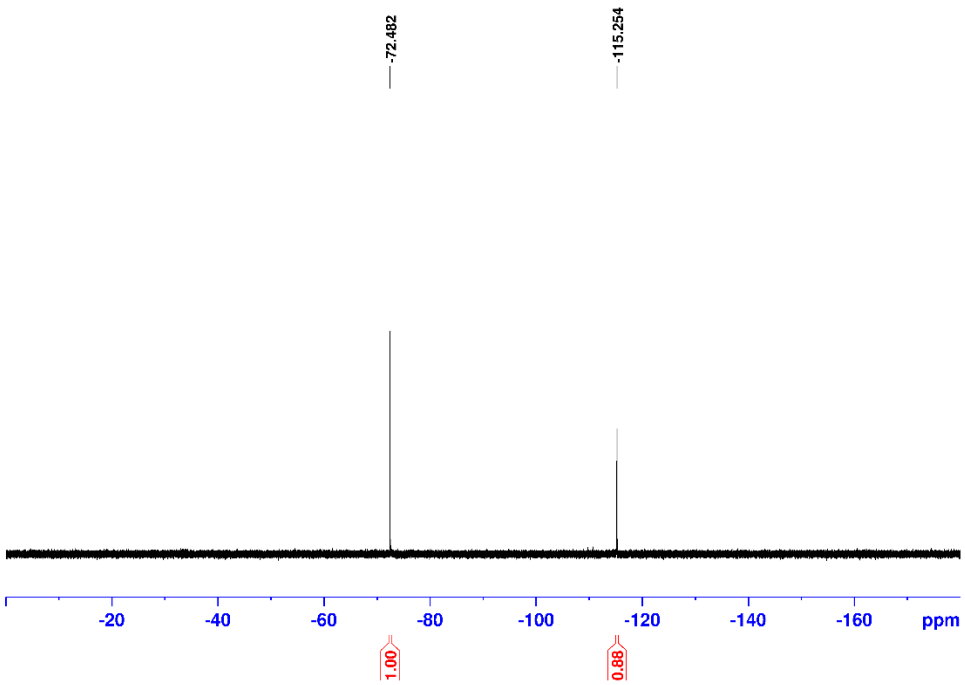
Equation 1 can be rearranged to Equation 2,

(2) $$M_{CsF} = \frac{I_{CsF}}{I_{IS}} \frac{F_{IS}}{F_{CsF}} M_{IS}$$

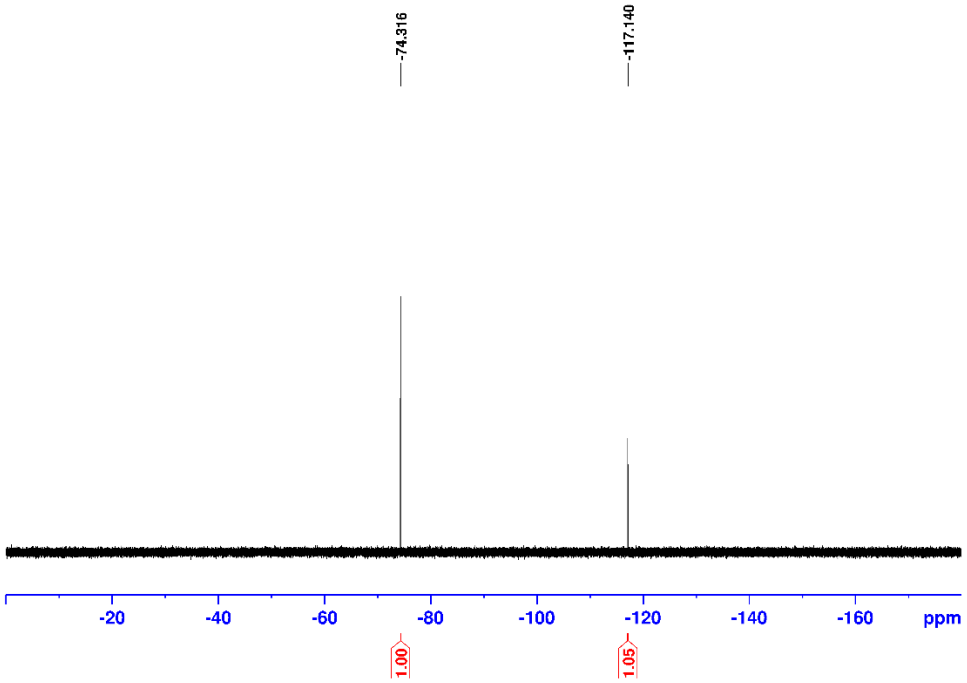
The IS ^{19}F NMR peak integration was set to 1 (I_{IS} = 1), the number of fluorine atoms associated with the IS fluorine peak is 3 (F_{IS} = 3) and the number of fluorine atoms associated with the CsF fluorine peak is 1 (F_{CsF} = 1). Therefore, equation 2 can be simplified to,

(3) $$M_{CsF} = 3 I_{CsF} M_{IS}$$

Compound **9a** – 0.198 mmol of fluoride obtained, 4.4 equiv. of CsF (10.2 mg of IS was added)



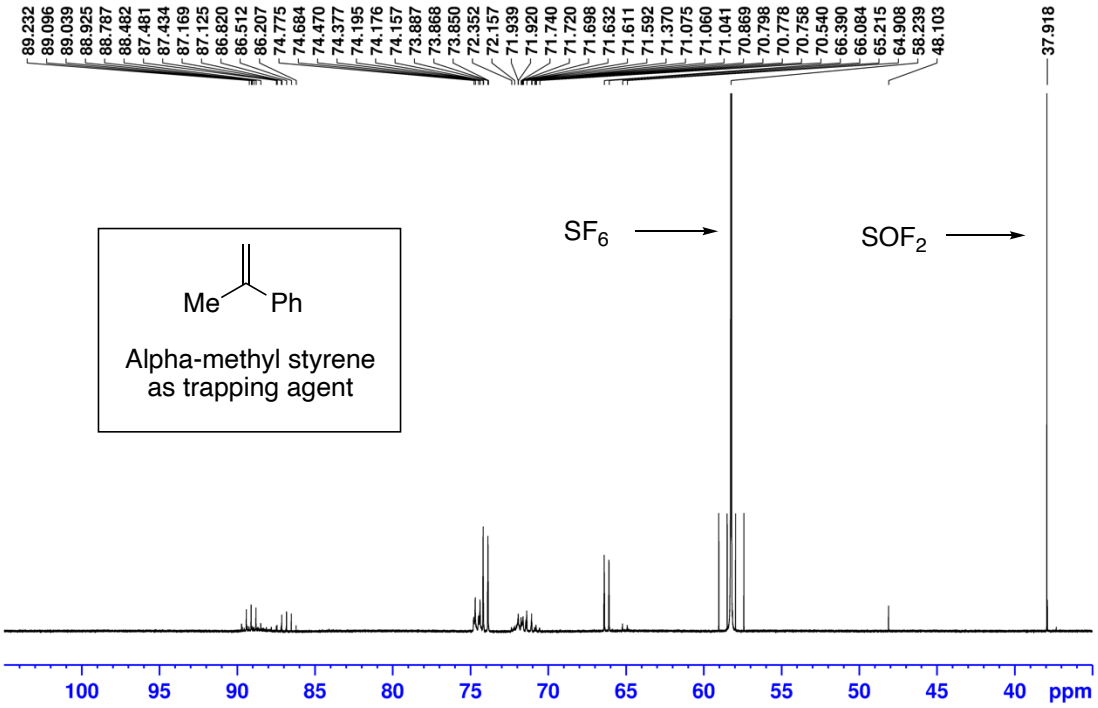
Compound **9b** – 0.19 mmol of fluoride was obtained, 4.1 equiv. CsF (8.2 mg of IS was added)



Trapping Experiments

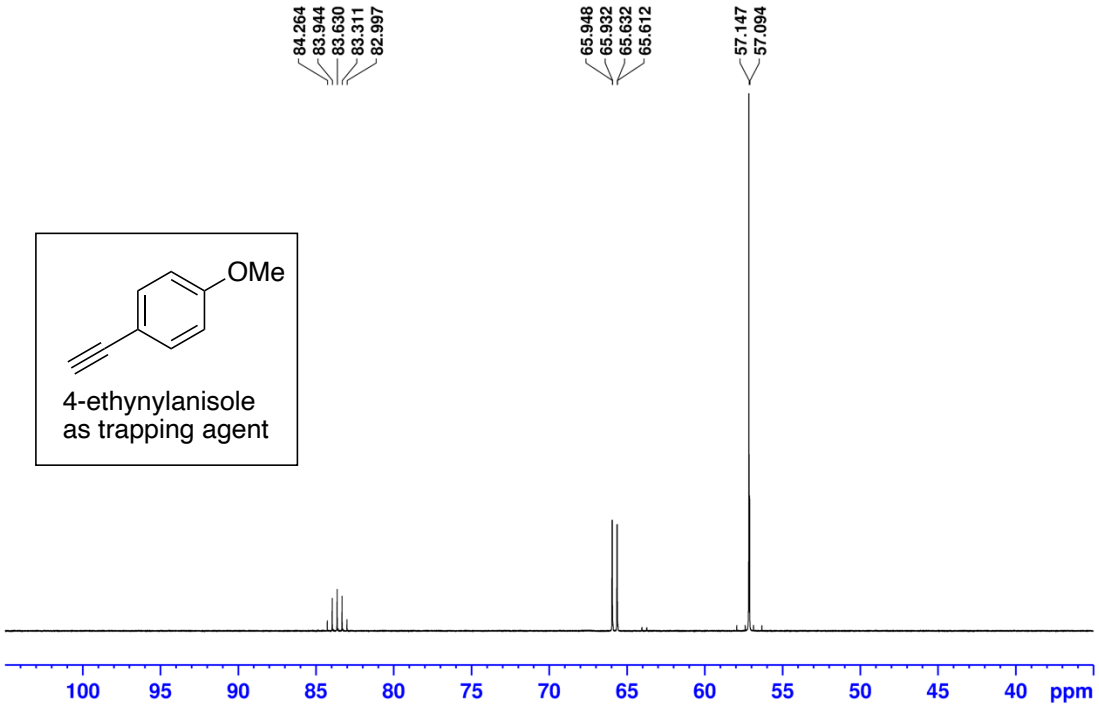
We attempted to identify the intermediacy of the SF_5 radical via addition of alkenes or alkynes to the Hantzsch ester/ cesium carbonate mixture to act as a radical trap.

Addition of alpha-methyl styrene (15 equivalents) to a 1:1 mixture of Hantzsch ester and cesium carbonate in CH_3CN, with 390 nm irradiation, under 80 psi of SF_6 resulted in the formation of a complex mixture of SF_5 containing products, with characteristic doublets around +70 ppm (the 4 equatorial fluorides), and pentets around +85 ppm (the apical SF_5 fluoride). Further analysis of this complex mixture was not feasible, potentially due to low yield, and product volatility. However, this trapping experiment provides evidence of the intermediacy of the SF_5 radical, which is known to add to alpha-methyl styrene.[6] The partial reduction product thionyl fluoride (SOF_2 was also observed).



Interestingly, conducting the reaction in methanol, with 1 equivalent of 4-ethynylanisole, 1 equivalent of **1a**, and 1 equivalent of Cs_2CO_3, led to the formation of one predominant product, with signals characteristic of a vinyl-SF_5 compound.[7] The yield for this transformation was not high, and no attempt was made to isolate the product. Wagenknecht and Rombach reported the trapping of SF_5 radicals generated by an iridium photocatalyst with 4-ethynylanisole in

methanol, during the preparation of this manuscript.[8] Repeating the same conditions in acetonitrile resulted in no SF_5 product formation.



UV-Vis Absorption and Fluorescence Data and Stern-Volmer Attempts

UV-vis samples were made under N_2 atmosphere within the glove box in quartz cuvettes. Samples were taped and removed from the glovebox and promptly submitted for spectral analysis.

The UV-Vis Absorption (Figure **S10**) and fluorescence (Figure **S11**) spectra was collected from a 0.05M solution of the deprotonated 3,5-diethyl 1,4-dihydro-3,5-pyridinedicarboxylate species (Cs^+ HEH^-). The excitation wavelength used to collect the fluorescence spectrum was 390 nm.

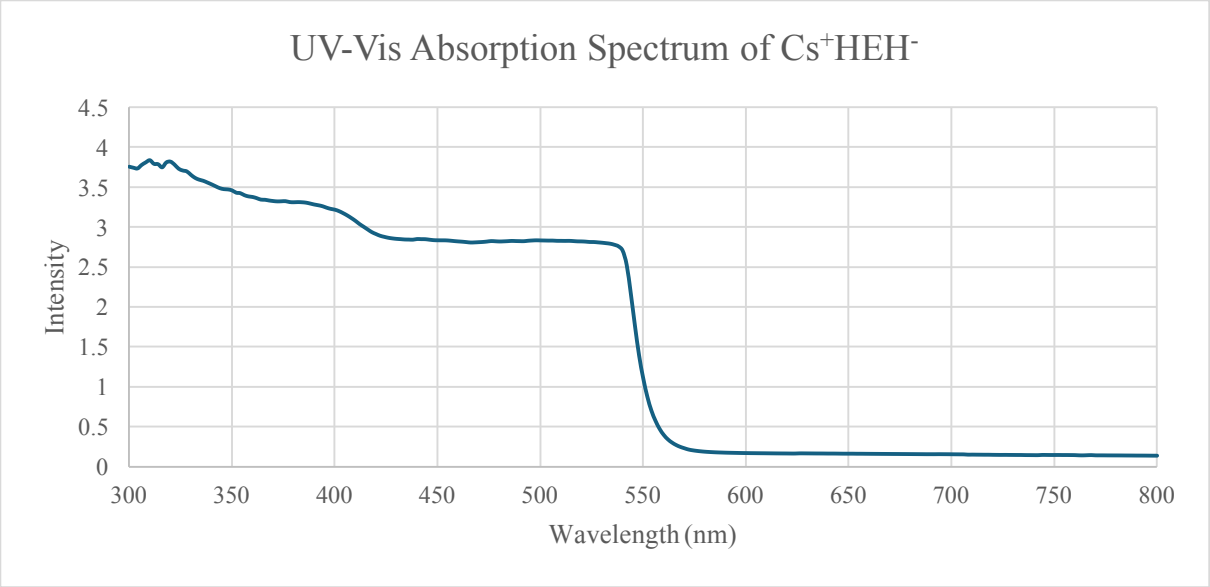


Figure S10: UV-Vis Absorption Spectrum of **1a** and Cs_2CO_3 in DMSO.

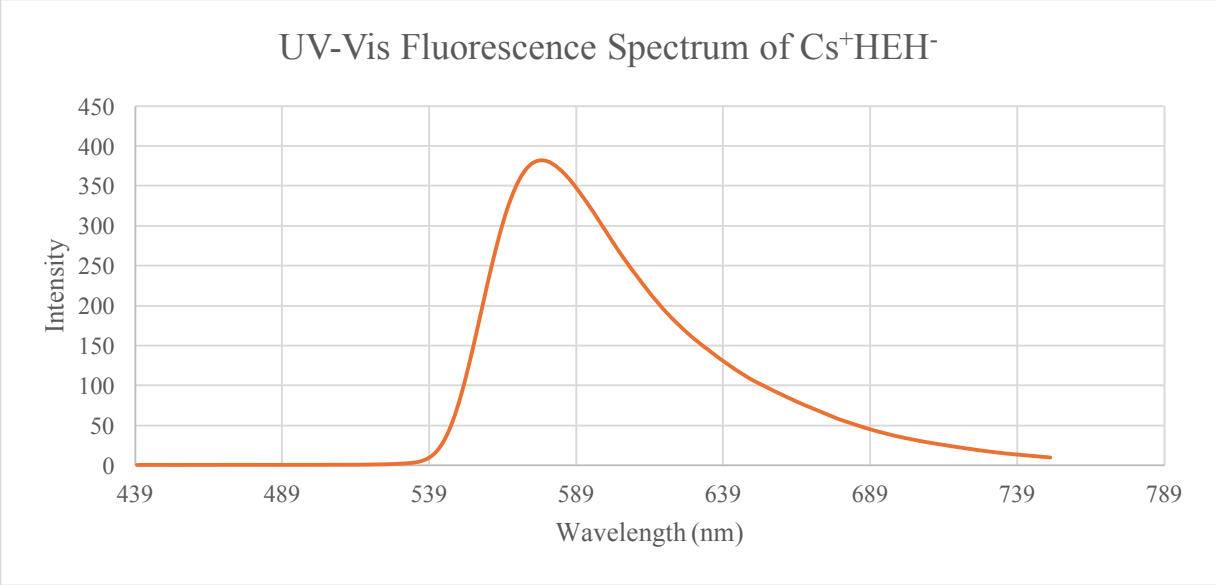


Figure S11: Fluorescence Spectrum of **1a** and Cs_2CO_3 in DMSO.

To analyze change in fluorescence of the Cs+HEH species in the absence and presence of an aryl SF_5 compound (Figure S11) a 0.05M sample of Cs^+HEH^- was made in DMSO and the fluorescence spectrum was recorded (orange plot). With the sample brought back inside the glove box under, 1 drop of aryl-SF5 compound **9a** was added to the sample and the fluorescence spectrum was recorded again (blue plot). The excitation wavelength used to collect the fluorescence spectrum was 390 nm.

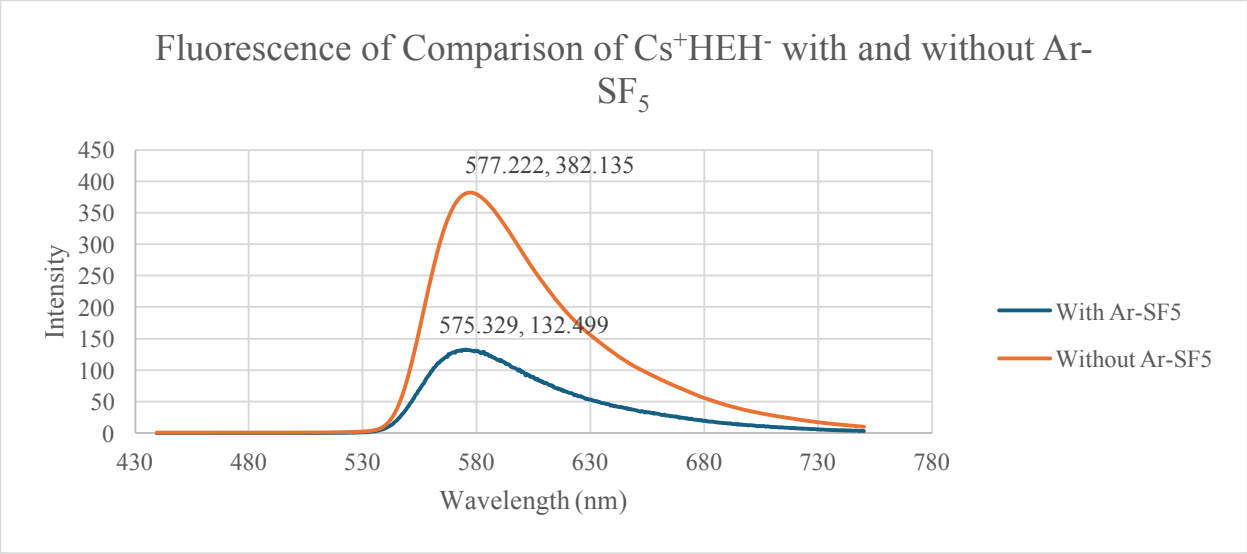


Figure S12: Change in Fluorescence Spectrum of **1a** and Cs_2CO_3 in DMSO upon addition of aryl SF_5 compound **9a**

Additionally, to analyze the change in fluorescence of the Cs^+HEH^- species in the absence and presence of SF_6 (Figure S12) a 0.05M sample of Cs^+HEH^- was made in DMSO and the fluorescence spectrum was recorded (orange plot). Outside the glove box, SF_6 was then bubbled through the sample mixture for 30 seconds and the fluorescence spectrum was recorded again (blue plot). The excitation wavelength used to collect the fluorescence spectrum was 390 nm.

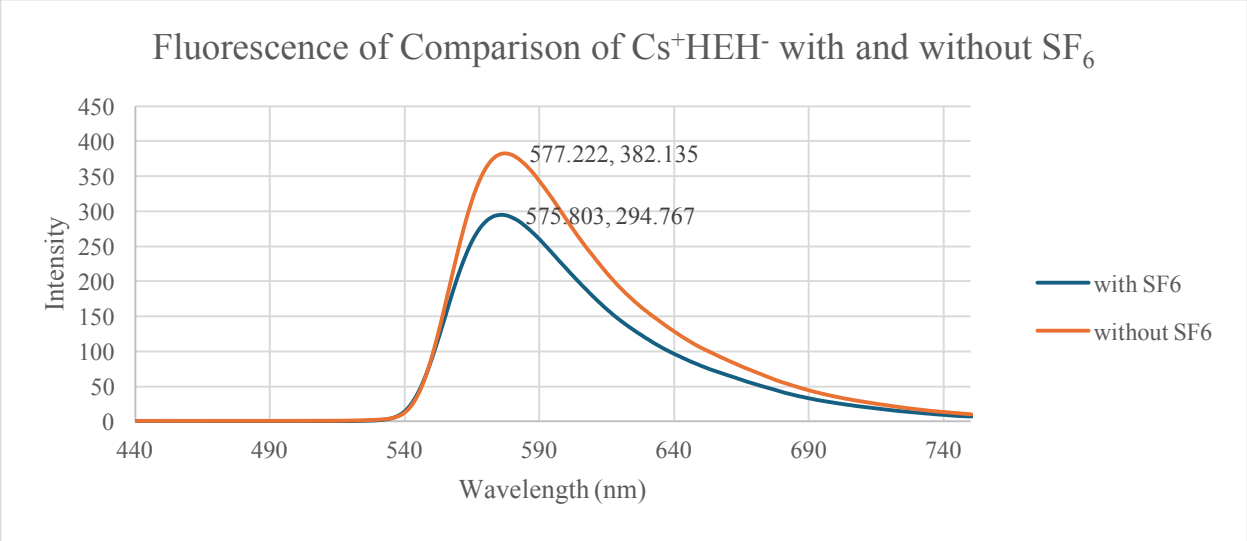


Figure S13: Change in Fluorescence Spectrum of **1a** and Cs_2CO_3 in DMSO upon sparging the sample with SF_6.

Attempts at making a **Stern-Volmer plot** were made. These did show a trend that increased amounts of aryl-SF_5 **9a** resulted in a decrease in fluorescence of the Hantzsch-ester Cs_2CO_3 mixture, however we encountered technical issues that resulted in some poor-quality data points.

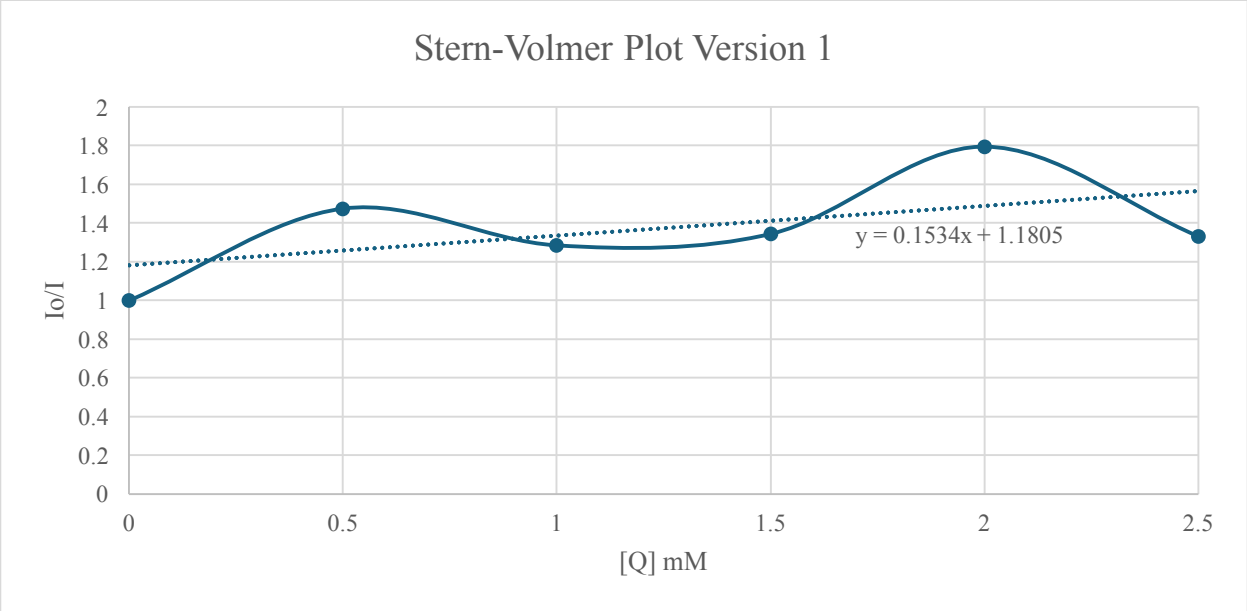
Namely due to the expense of aryl SF_5 compounds, and requirement of excess aryl SF_5 quencher, we conducted the reaction at a lower concentration of Hantzsch ester than the above single-point plots. We observed that at lower concentrations, the Hantzsch ester underwent observable bleaching in the DMSO alone over a time scale of several minutes. Because the samples were prepared in the glovebox at a significant distance from the spectrophotometer, and because we did not have unlimited access to the spectrophotometer, we were unable to consistently measure each sample in the same timeframe. However, despite the poor quality of the data points, we chose to include the data, as a trend is visible, and there is clearly a reaction that consumes aryl SF_5 when **1a** is present.

<u>Version 1:</u>

A serial dilution was done to make a 0.1 mM solution of Na^+ HEH^- in DMSO (Solution A) from a 0.1M solution of Na^+ HEH^- in DMSO within the glovebox. A 15 mM stock solution of the quencher [Q] Ar-SF_5 (ortho-F) (Solution B) was also made within the glove box.

Stern-Volmer solutions were made up:

1) 2 mL of Solution A, 1 mL of DMSO
2) 2 mL of Solution A, 0.1 mL of Solution B, 0.9 mL of DMSO
3) 2 mL of Solution A, 0.2 mL of Solution B, 0.8 mL of DMSO
4) 2 mL of Solution A, 0.3 mL of Solution B, 0.7 mL of DMSO
5) 2 mL of Solution A, 0.4 mL of Solution B, 0.6 mL of DMSO
6) 2 mL of Solution A, 0.5 mL of Solution B, 0.5 mL of DMSO

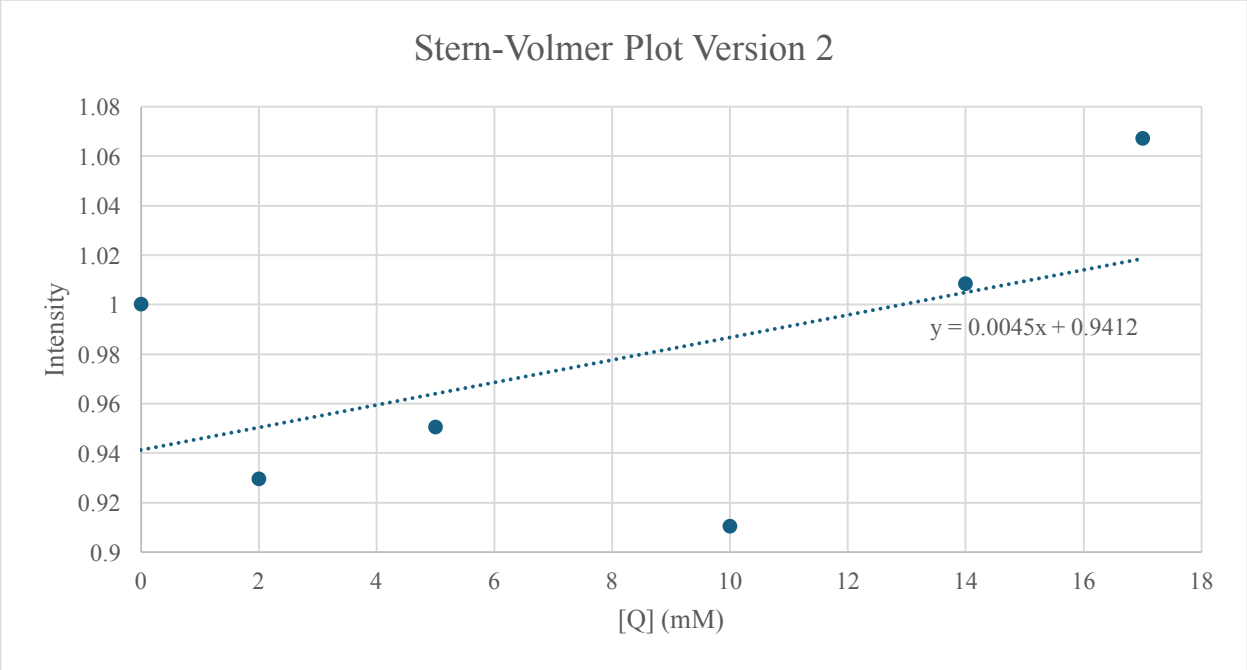


Version 2:

A serial dilution was done to make a 0.1 mM solution of Na^+ HEH^- in DMSO (Solution A) from a 0.1M solution of Na^+ HEH^- in DMSO within the glovebox. Quencher [Q] Ar-SF_5 (ortho-F) was added as a neat liquid (Solution B) using a micro syringe.

Stern-Volmer solutions were made up:

1) 2.9 mL of Solution A, 0.1 mL of DMSO
2) 2.9 mL of Solution A, 2 µL of Solution B, 98 µL of DMSO
3) 2.9 mL of Solution A, 5 µL of Solution B, 95 µL of DMSO
4) 2.9 mL of Solution A, 10 µL of Solution B, 90 µL of DMSO
5) 2.9 mL of Solution A, 14 µL of Solution B, 85 µL of DMSO
6) 2.9 mL of Solution A, 17 µL of Solution B, 83 µL of DMSO



References:

[1] B. S. N. Huchenski, A. W. H. Speed, *Chem. Commun.,* 2021, **57**, 7128.
[2] T. Hynes, E. N. Welsh, R. McDonald, M. J. Ferguson, A. W. H. Speed, *Organometallics*, 2018, **37**, 841.
[3] C. Zhu, T. Akiyama, *Org. Lett.,* 2009, **11**, 4180.
[4] F. Calogero, L. Wilczek, E. Pinosa, A. Gualandi, R. Dorta, A. Herrera, Y. Dai, A. Rossignol, F. Negri, Z. Ziani, A. Fermi, P. Ceroni, P. G. Cozzi, *Angew. Chem., Int. Ed.,* 2024, **63**, e202411074
[5] M. Hudlicky, *J. Fluor. Chem.*, 1985, **28**, 461.
[6] D. Rombach, H.-A. Wagenknecht, *ChemCatChem*, 2018, **10**, 2955.
[7] M. Birepinte, P. A. Champagne, J.-F. Paquin, *Angew. Chem., Int. Ed.*, 2022, **61**, e202112575.

[8] M. Flügge, S. Klehenz, S. Leidenheimer, D. Rombach, H.-A. Wagenknecht, *ChemRxiv*, 2025, DOI: 10.26434/chemrxic-2025-vbvcz