Supplementary Information

Pulsed-light-induced photochemical reactions: a case study on trifluoromethylation reactions of 1,3-dimethoxybenzene

Mayaka Maeno,[*a] Toshifumi Nishida,[b] Morihiro Kitamura[b] and Katsuyuki Morii[*a,b]

[a]*Nippon Shokubai Research Alliance Laboratory, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan*

[b]*Nippon Shokubai Co. Ltd., 5-8 Nishi Otabi-Cho, Suita, Osaka, 564-8512, Japan*

Email: mayaka_maeno@kumamoto-u.ac.jp

Email: katsuyuki_morii@shokubai.co.jp

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General Information

All reactions were performed in dried glassware under a positive pressure of nitrogen. Commercially available chemicals were obtained from Merck & Co., TCI, Wako, Nacalai, BLD pharma and used as received unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) performed with 0.25 mm Silica gel (70-F254) TLC Plate-Wako. The TLC plates were visualized with UV light (254 nm) and *p*-anisaldehyde in ethanol/heat. ^{1}H (400 or 500 or 600 MHz), ^{13}C NMR (125 or 151 MHz) and ^{19}F (376 or 471 MHz) NMR spectra for solution in $CDCl_3$ were recorded on JEOL JNM-ECS400, JEOL JNM-ECX500 and Bruker AVANCE III. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane (δH = 0.00 ppm) or $CHCl_3$ (δH = 7.26 ppm and δC = 77.0 ppm) or hexafluorobenzene (δF = −162.9 ppm). The following abbreviations were used to show the multiplicities; s: singlet, d: doublet, t: triplet, q: quartet, sep: septet, m: multiplet. The wave numbers ($\tilde{\nu}$) of recorded IR-signals are quoted in cm^{-1} on JASCO FT/IR 6200. High resolution mass spectrometry (HRMS) was carried out on an electrospray ionization mass spectrometer with a micro-TOF analyzer. Emission spectra were recorded by Fluorescence Spectrophotometer F-7000 (Hitachi High-Tech Corporation).

Optimization of the reaction conditions

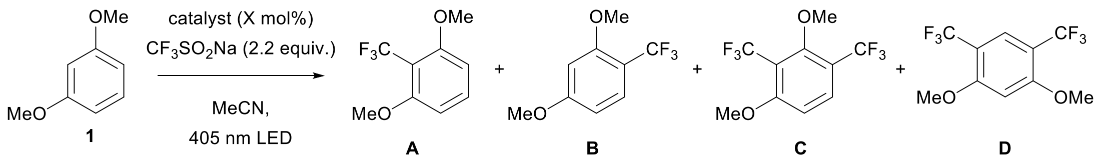


Table S1. Optimization of catalysts.[a]

entry	catalyst (X)	light condition	yield (%)[b]	A/B/C/D[b]
1	AQN-2-COOH (5)	Continuous light	92	22/61/3.0/6.3
2	AQN-2-COOH (5)	Pulsed light (10^5 Hz, duty ratio = 0.1)	85	22/58/1.2/3.3
3	9,10-dicyanoanthracene (5)	Continuous light	85	17/55/3.6/9.3
4	9,10-dicyanoanthracene (5)	Pulsed light (10^5 Hz, duty ratio = 0.1)	20	5.6/14/0/0
5	$[Ru(phen)_3]Cl_2$ (1.5)	Continuous light	N.R.	—
6	$[Ru(phen)_3]Cl_2$ (1.5)	Pulsed light (10^5 Hz, duty ratio = 0.1)	N.R.	—
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.5)	Continuous light	50	7.6/37/3.6/2.0
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (1.5)	Pulsed light (10^5 Hz, duty ratio = 0.1)	89	20/61/2.4/5.4
9	Titanium oxide (5)	Continuous light	10	2.6/7.3/0/0
10	Titanium oxide (5)	Pulsed light (10^5 Hz, duty ratio = 0.1)	N.R.	—

[a] Reaction condition: **1** (0.25 mmol), CF_3SO_2Na (0.55 mmol) and catalyst (X mol%) in acetonitrile (2.5 mL) at 15 °C was irradiated 405 nm LED for 20 h. [b] determined by ^{19}F NMR.

Evaluation of wavelength of LED

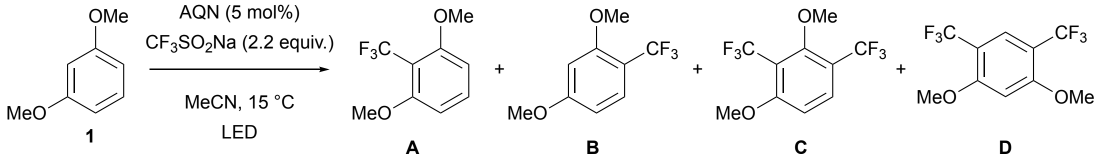


Table S2. Evaluation of wavelength of LED[a]

entry	wavelength (nm)	yield (%)[b]	A/B/C/D[b]
1	365	83	16/49/4.6/13
2	385	86	15/49/7.2/15
s3	405	90	18/57/4.4/1

[a] Reaction condition: **1** (0.25 mmol), CF_3SO_2Na (0.55 mmol) and AQN (0.0125 mmol) in acetonitrile (2.5 mL) at 15 °C was irradiated continuous LED for 20 h. [b] Determined by ^{19}F NMR spectroscopys

Evaluation of frequency of pulsed light

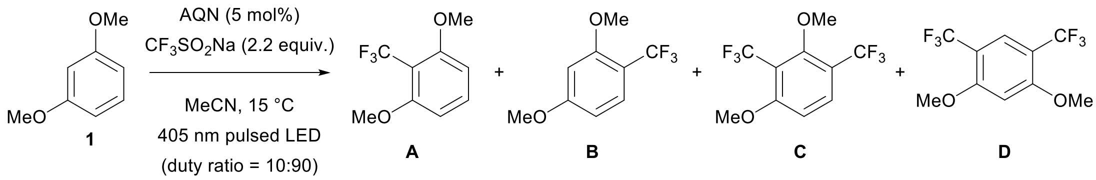


Table S3. Evaluation of frequency of pulsed light[a]

entry	frequency (Hz)	ON/OFF (s)[b]	yield (%)[c,d]	A/B/C/D[c,d]
1	1.4×10^{-5} (CW, 2 h)	7200/64800	31	5.0/25/0/0.8
2	10^{-4}	1000/9000	59	14/43/0.3/1.8
3	10^{-3}	100/900	69	18/49/0/2.3
4	10^{-2}	10/90	72	17/52/1.3/3.0
5	10^{-1}	1/9	77	17/53/1.4/3.9
6	10^{0}	100m/900m	89	18/62/1.9/5.5
7	10^{1}	10m/90m	88	18/59/2.1/6.5
8	10^{2}	1m/9m	84	19/58/2.1/6.2
9	10^{3}	100μ/900μ	94	20/60/2.4/5.5
10	10^{4}	10μ/90μ	90	19/59/2.3/6.2
11	10^{5}	1μ/9μ	94	20/65/2.2/6.7

[a] Reaction condition: **1** (0.25 mmol), CF_3SO_2Na (0.55 mmol) and AQN (0.0125 mmol) in acetonitrile (2.5 mL) at 15 °C was irradiated 405 nm pulsed LED for 20 h. [b] per 1 cycle. [c] determined by ^{19}F NMR. [d] the results for all reactions are averages of 2 experiments.

Pulsed LED photoreaction set-up

We used a continuous light photoreactor (AMP-V1) and a custom-made pulse-driven photoreactor purchased from Techno Sigma Co., Ltd. for our reactions. The pulse waveform was controlled by a function generator which was connected to pulse-driven light reaction system. The light intensity of light source was measured by using a photodiode sensor. The light source was positioned 20 mm from the surface of the reaction solution and the reaction temperature was maintained using a water bath connected to circulation cooling system.

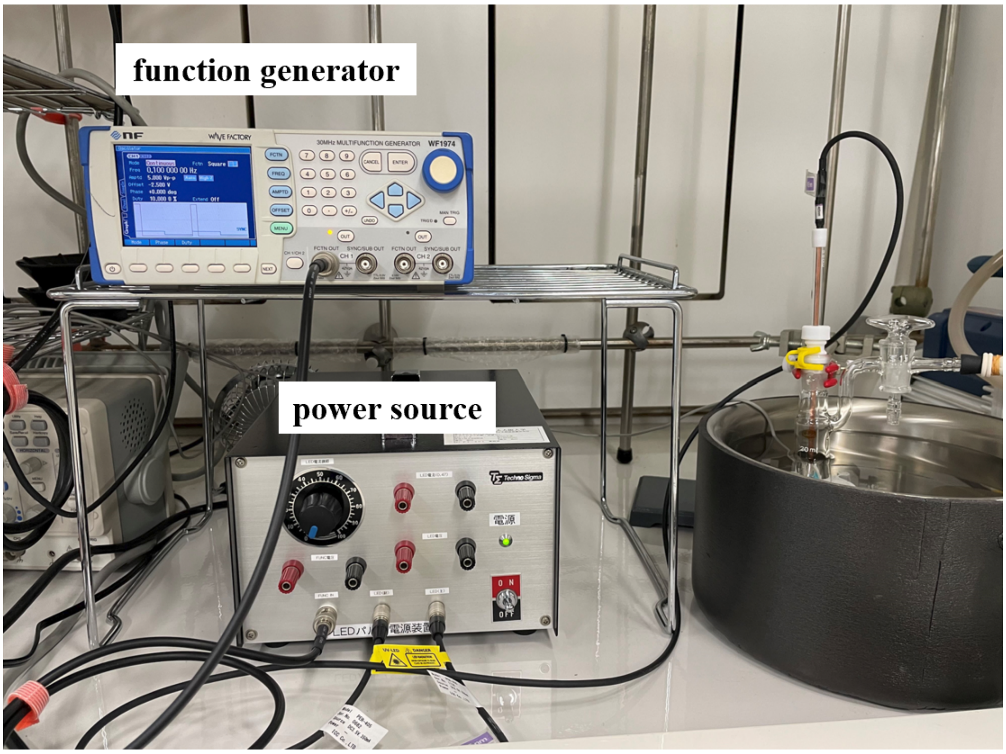


Fig. S1 Pulsed-driven photoreactor.

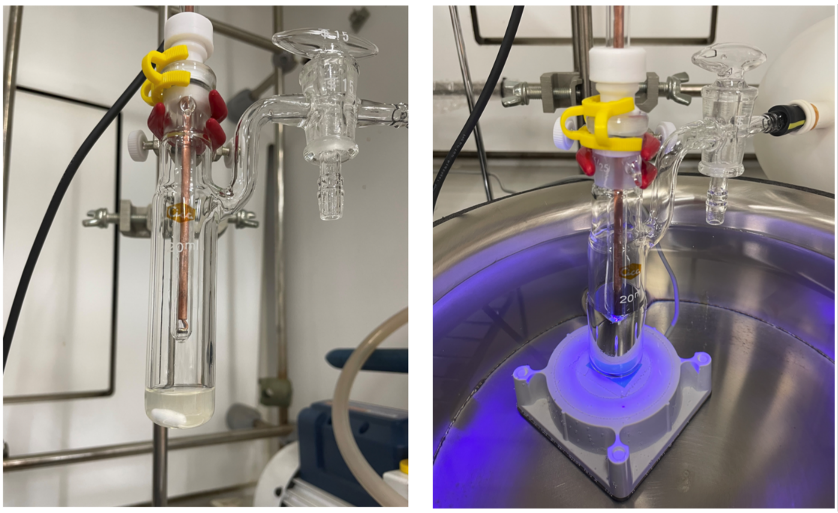
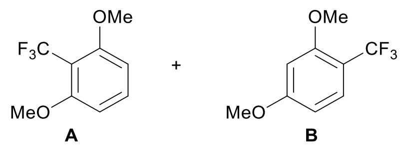


Fig. S2 Reaction set-up.

General procedure for the pulsed light induced trifluoromethylation reaction

The reaction was conducted by slightly modified reported procedure.[1] To an oven dried schlenk tube equipped with stirring bar added CF_3SO_2Na (0.55 mmol, 2.2 equiv.), anthraquinone (0.0125 mmol, 5 mol%) and acetonitrile (2.5 mL, 0.1M) in nitrogen filled glovebox. Then moving from glovebox, dimethoxyarene (0.25 mmol) was added and irradiated 405 nm LED from the surface of the reaction solution with stirring at 15 °C for appropriate time. After completion of the reaction, saturated $NaHCO_3$ aqueous solution was added and extracted with ethyl acetate (×3). The combined organic layers were dried over $MgSO_4$. The yield and product ratio were determined by ^{19}F NMR spectroscopy using hexafluorobenzene as an internal standard. The crude products were purified by preparative TLC (NH_2 modified silica-gel for compounds **E**, **F**, **I**, **J**, **K and L**) to measure the chemical properties. Spectroscopic data of **A** and **B** were in agreement with the literature.[1,2,3]

1,3-Dimethoxy-2-(trifluoromethyl)benzene (A) and 2,4-Dimethoxy-1-(trifluoromethyl)benzene (B)



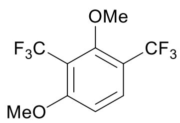
Data for **A**

Colorless liquid. R_f = 0.27 (*n*-hexane/dichloromethane = 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.38 (t, 1H, *J* = 8.6 Hz), 6.61 (d, 2H, *J* = 9.2 Hz), 3.86 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −56.1 (s, 3F). ^{19}F NMR data was in agreement with the literature.[3]

Data for **B**.

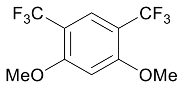
Colorless liquid. R_f = 0.27 (*n*-hexane/dichloromethane = 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.48 (d, 1H, *J* = 8.8 Hz), 6.52 - 6.47 (m, 3H), 3.88 (s, 3H), 3.85 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −62.5 (s, 3F). ^{19}F NMR data was in agreement with the literature.[3]

1,3-Dimethoxy-2,4-bis(trifluoromethyl)benzene (C)



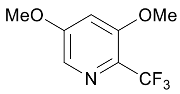
Colorless liquid. R_f = 0.30 (*n*-hexane/dichloromethane = 9/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, 1H, *J* = 9.2 Hz), 6.83 (d, 1H, *J* = 9.2 Hz), 3.94 (s, 3H), 3.89 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −58.5 (s, 3F), −61.6 (s, 3F). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 162.1, 158.9 - 158.8 (m), 131.3 (q, *J* = 5.4 Hz), 123.3 (q, *J* = 271.7 Hz), 122.9 (q, *J* = 275.1 Hz), 118.2 (q, *J* = 31.4 Hz), 113.9 (q, *J* = 30.0 Hz), 107.2, 64.9, 56.6. **IR (KBr)**: ν˜ = 1605, 1514, 1495, 1418, 1345, 1301, 1289, 1272, 1228, 1116, 1085, 1060, 817, 632 cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{10}H_8F_6O_2$ 274.0428; Found 274.0423. ^{19}F NMR data was in agreement with the literature.[3]

1,5-Dimethoxy-2,4-bis(trifluoromethyl)benzene (D)



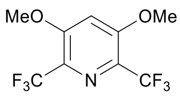
White solid. R_f = 0.43 (*n*-hexane/ethyl acetate = 4/1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (s, 1H), 6.56 (s, 1H), 3.97 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ −62.9 (s, 3F). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 161.7, 126.5 (sep, *J* = 4.5 Hz), 123.3 (q, *J* = 271.3 Hz), 110.5 (q, *J* = 32.2 Hz), 96.2, 56.2. **IR (neat)**: $\tilde{\nu}$ = 1626, 1585, 1513, 1442, 1322, 1255, 1218, 1131, 1061, 1021, 917, 826, 648 cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_{10}H_8F_6O_2$ 274.0428; Found 274.0426. ^{19}F NMR data was in agreement with the literature.[3]

3,5-Dimethoxy-2-(trifluoromethyl)pyridine (E)



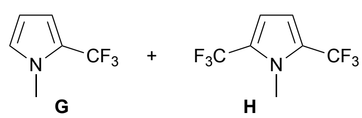
Off-white solid. R_f = 0.38 (*n*-hexane/ethyl acetate = 7/3). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.92 (d, 1H, *J* = 2.2 Hz), 6.86 (d, 1H, *J* = 2.0 Hz), 3.93 (s, 3H), 3.91 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 159.1, 155.3, 129.2 (q, *J* = 34.3 Hz), 126.7, 121.9 (q, *J* = 273.0 Hz), 105.8, 56.1, 55.9. **^{19}F NMR** (376 MHz, $CDCl_3$): δ −66.7 (s, 3F). **IR (neat)**: $\tilde{\nu}$ = 1582, 1413, 1342, 1270, 1201, 1187, 1146, 1113, 1069, 1012, 848, 709, 646 cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_8H_8F_3NO_2$ 207.0507; Found 207.0506.

3,5-Dimethoxy-2,6-bis(trifluoromethyl)pyridine (F)



Off-white solid. R_f = 0.24 (*n*-hexane/ethyl acetate = 7/3). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 6.94 (s, 1H), 4.01 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 157.8, 127.1 (q, *J* = 35.3 Hz), 121.0 (q, *J* = 273.6 Hz), 103.7, 56.4. **^{19}F NMR** (376 MHz, $CDCl_3$): δ −66.9 (s, 3F). **IR (neat)**: $\tilde{\nu}$ = 1594, 1433, 1335, 1218, 1188, 1157, 1122, 1071, 1009, 855, 710, 650 cm^{-1}. **HRMS** (EI) m/z: $[M]^+$ Calcd. for $C_9H_7F_6NO_2$ 275.0381; Found 275.0377.

1-Methyl-2-(trifluoromethyl)-1*H*-pyrrole (G) and 1-Methyl-2,5-bis(trifluoromethyl)-1*H*-pyrrole (H)



The product was highly volatile and isolation could not be performed.

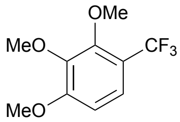
Data for **G**

^{19}F NMR (471 MHz, $CDCl_3$): δ −59.6 (s, 3F). NMR data were in agreement with the literature.[4]

Data for **H**

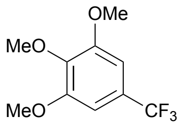
^{19}F NMR (471 MHz, $CDCl_3$): δ −60.5 (s, 3F). NMR data were in agreement with the literature.[4]

1,2,3-trimethoxy-4-(trifluoromethyl)benzene (I)



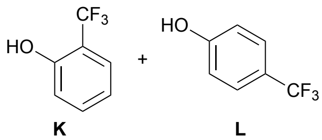
Yellow liquid. R_f = 0.38 (*n*-hexane/dichloromethane = 6/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.26 (d, *J* = Hz, 1H), 6.68 (d, *J* = Hz, 1H), 3.69 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ −61.9 (s, 3F). NMR data was in agreement with the literature.[5]

1,2,3-trimethoxy-5-(trifluoromethyl)benzene (J)



Off-white solid. R_f = 0.24 (*n*-hexane/dichloromethane = 6/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 6.83 (s, 2H), 3.90 (s, 6H), 3.88 (s, 3H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ −63.3 (s, 3F). NMR data was in agreement with the literature.[5]

2-Trifluoromethylphenol (K) and 4-Trifluoromethylphenol (L)



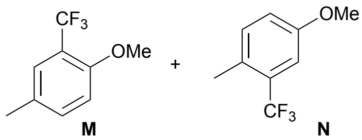
Data for **K**

Slightly yellow liquid. R_f = 0.20 (*n*-hexane/diethyl ether = 1/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.53-7.51 (m, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 5.60 (bs, 1H). **^{19}F NMR** (MHz, $CDCl_3$): δ – 62.7 (s, 3F). NMR data were in agreement with the literature.[6]

Data for **L**

Slightly yellow liquid. R_f = 0.20 (*n*-hexane/diethyl ether = 1/1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 5.06 (bs, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$): δ −62.1 (s, 3F). NMR data were in agreement with the literature.[7]

1-methoxy-4-methyl-2-(trifluoromethyl)benzene (M) and 4-Mmethoxy-1-methyl-2-(trifluoromethyl)benzene (N)



The product was highly volatile and isolation could not be performed.

Data for **M**

^{19}F NMR (471MHz, $CDCl_3$): δ – 63.0 (s, 3F). NMR data were in agreement with the literature.[8]

Data for **N**

^{19}F NMR (471MHz, $CDCl_3$): δ −62.7 (s, 3F). NMR data were in agreement with the literature.[8]

Emission spectra of AQN

Fluorescence emission measurement was carried out in MeCN containing AQN (2.0 mM). The mixed solution of AQN and 1,3-dimethoxybenzene (0.05 mM) in MeCN was prepared from a 0.1 mM MeCN solution of 1,3-dimethoxybenzene and a 4.0 mM MeCN solution of AQN.

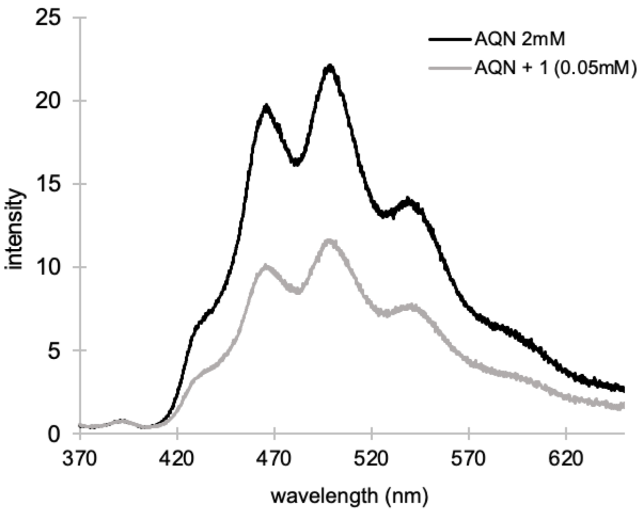


Fig. S3 Fluorescence emission spectra of AQN solution and AQN + 1,3-dimethoxybenzene solution

DFT calculation studies

Theoretical calculations to estimate the activation energies for all processes of trifluoromethyl radical addition and hydrogen abstraction were performed using the Gaussian 16 Revision B.01 software package.[3] All the computations employed in this study were performed using density functional theory (DFT) with the wB97X-D functional. Geometrical optimizations and energy calculations were performed using the 6-311+G(2d,p) basis set.

Energy change of the second trifluoromethylation reaction

Fig. S3 shows the free energy profiles for the second trifluoromethylation reaction. The second $\cdot CF_3$ addition, which is sterically hindered by the rotational barriers of the methoxy groups, has higher activation energies in both route 1 and route 2 (47.2 vs. 52.1 or 56.1 kJ/mol, Fig. 2(b) and (c)). The result suggested that the second ·CF3 addition reaction is less favorable.

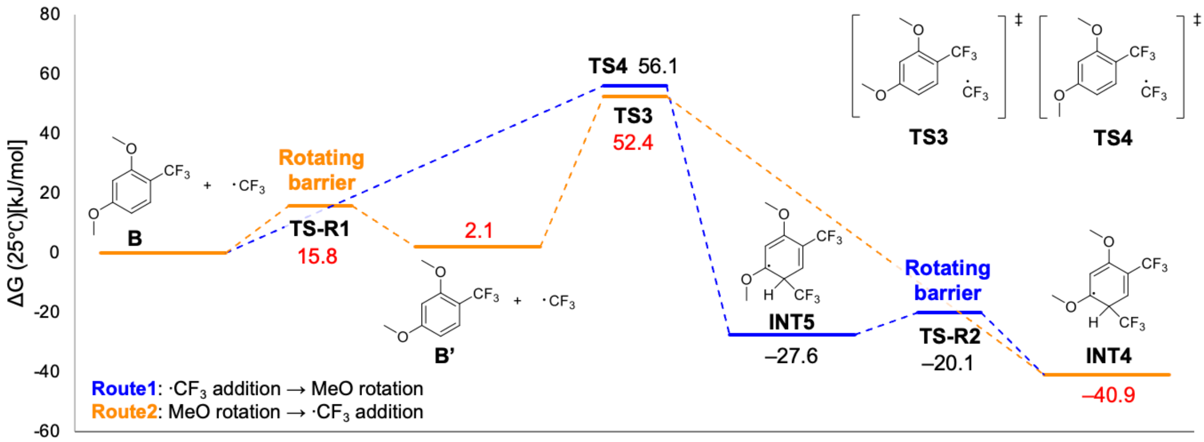
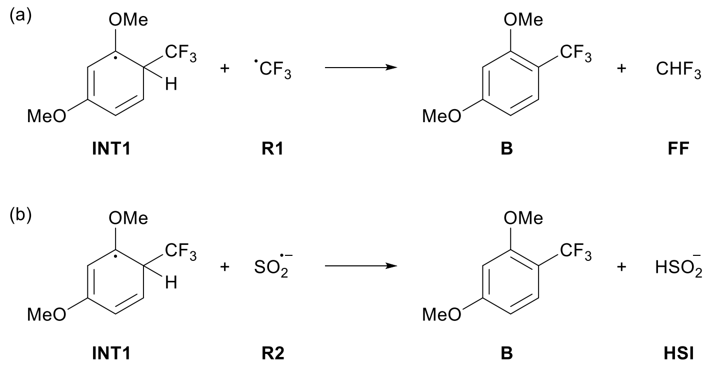


Fig. S4 Free energy profiles of the second trifluoromethylation reactions.

Energy change of hydrogen abstraction reaction

Fig. S4 shows the free energy profiles for the hydrogen radical abstraction reactions by trifluoromethyl radical (·CF_3) or sulfoxylate anion radical (SO_2^{-}·) in which provide 1,3-dimethoxy-4-(trifluoromethyl)benzene from monotrifluoromethylated intermediate. The results suggested that hydrogen abstractions are easily proceed because free energies decrease monotonically in both cases.



Scheme S1. Hydrogen abstraction from monotrifluoromethylated intermediate (a) by ·CF_3 and (b) by SO_2·$^{-}$.

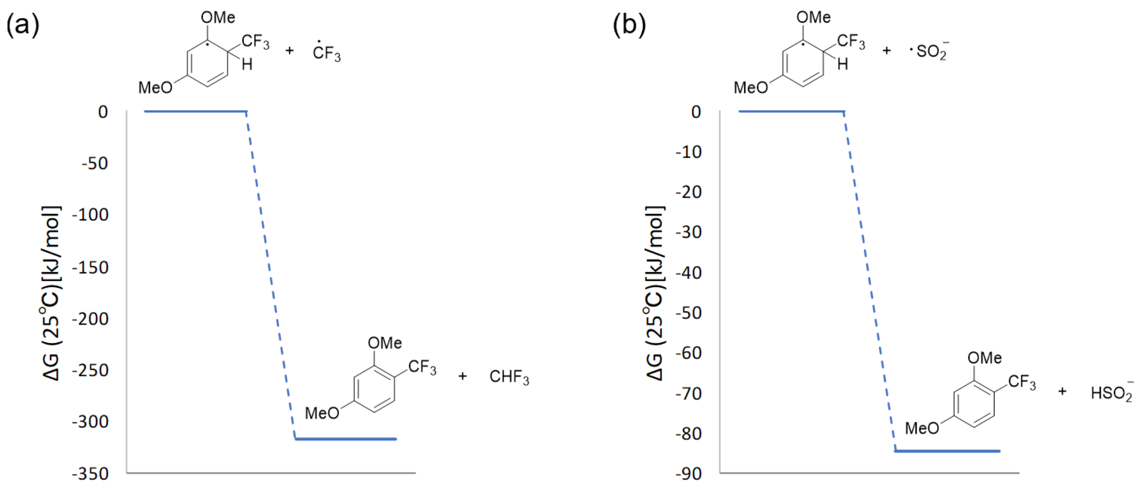
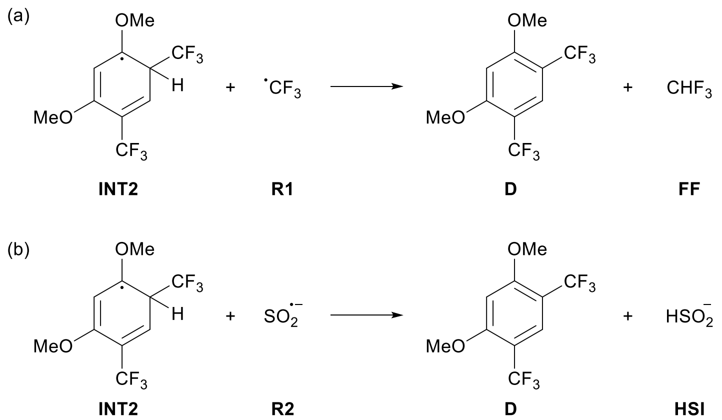


Fig. S5 Free energy profile for hydrogen abstraction reactions (a) by ·CF_3. (b) by SO_2·$^{-}$.

Fig. S5 shows the free energy profiles for the hydrogen radical abstraction reactions by trifluoromethyl radical ($\cdot CF_3$) or sulfur dioxide radical anion ($SO_2\cdot^-$) in which provide 1,5-dimethoxy-2,4-bis(trifluoromethyl)benzene from bistrifluoromethylated intermediate. The results suggested that hydrogen abstractions are easily proceed because free energies also decrease monotonically in both cases.



Scheme S2. Hydrogen abstraction from bistrifluoromethylated intermediate (a) by $\cdot CF_3$. and (b) by $SO_2\cdot^-$.

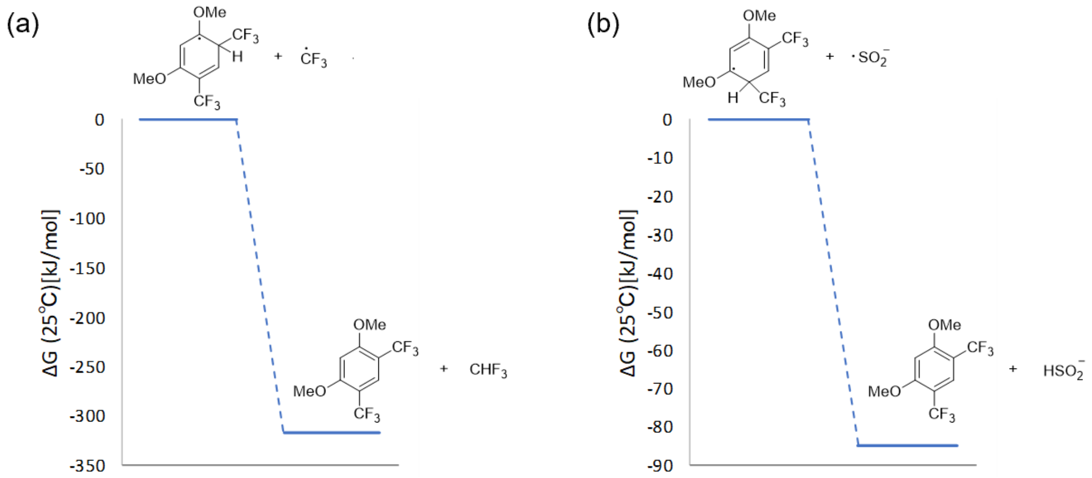
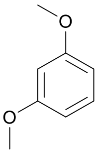


Fig. S6 Free energy profile for hydrogen abstraction reactions (a) by $\cdot CF_3$. and (b) by $SO_2\cdot^-$.

Structural information



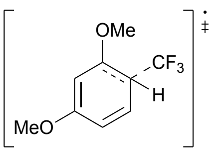
1

	X	Y	Z
C	1.589736	-1.111665	0.000000
C	1.310755	0.258509	0.000000
C	0.000000	0.703999	0.000000
C	-1.044955	-0.223650	0.000000
C	-0.783395	-1.585535	0.000000
C	0.545580	-2.008431	0.000000
H	2.621609	-1.437514	0.000000
O	-2.288389	0.319503	0.000000
H	-1.579659	-2.315866	0.000000
H	0.758314	-3.071152	0.000000
C	-3.392116	-0.556840	0.000000
H	-0.257531	1.753636	0.000000
H	-3.399356	-1.189787	0.893275
H	-3.399356	-1.189787	-0.893275
H	-4.278435	0.074347	0.000000
O	2.389256	1.078945	0.000000
C	2.165218	2.470497	0.000000
H	1.616577	2.786407	0.893239
H	1.616577	2.786407	-0.893239
H	3.149390	2.934418	0.000000

$\cdot CF_3$

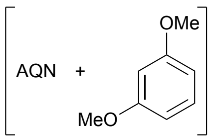
R1

	X	Y	X
C	0.000000	0.000000	0.323740
F	0.000000	1.253698	-0.071942
F	-1.085734	-0.626849	-0.071942
F	1.085734	-0.626849	-0.071942



TS1

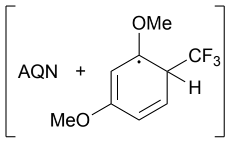
	X	Y	Z
C	0.626434	-0.103317	1.223860
C	0.230890	1.076730	0.538132
C	-0.999229	1.148946	-0.073050
C	-1.897491	0.078255	0.042232
C	-1.576326	-1.041244	0.805069
C	-0.339090	-1.099453	1.423735
H	1.498306	-0.047210	1.863880
O	-3.067096	0.247804	-0.613049
H	-2.278272	-1.852080	0.936632
H	-0.087855	-1.958084	2.033478
C	-4.025851	-0.786157	-0.546078
H	-1.313929	2.011345	-0.643229
H	-4.363120	-0.949721	0.482079
H	-3.629726	-1.720798	-0.954570
H	-4.866566	-0.455376	-1.151902
O	1.162439	2.049680	0.506990
C	0.887437	3.210929	-0.247627
H	0.016987	3.743669	0.147721
H	0.719495	2.964513	-1.300350
H	1.768624	3.842168	-0.159466
C	1.921839	-1.010332	-0.332204
F	3.066992	-0.350348	-0.482682
F	1.276936	-1.033949	-1.493239
F	2.189587	-2.260642	0.041453



INT1

	X	Y	Z
C	-2.332055	0.693877	2.471475
C	-1.232355	1.388321	2.001524
C	-0.126882	0.697725	1.519444
C	-0.126808	-0.699479	1.518919
C	-1.232212	-1.390549	2.000478
C	-2.331982	-0.696572	2.470955
C	1.029134	1.469224	0.989975
C	1.029305	-1.470459	0.988900

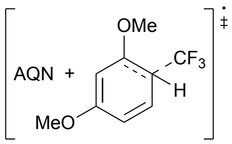
C	2.190657	-0.698253	0.463690
C	2.190586	0.697537	0.464223
C	3.276417	1.389309	-0.059598
H	3.253263	2.471747	-0.051124
C	4.353799	0.695613	-0.582699
C	4.353865	-0.695308	-0.583241
C	3.276549	-1.389514	-0.060682
H	-3.197311	1.235602	2.833887
H	-1.215910	2.470423	1.986489
H	-1.215647	-2.472639	1.984663
H	-3.197180	-1.238659	2.832964
H	5.197834	1.237348	-0.992626
H	5.197954	-1.236643	-0.993586
H	3.253503	-2.471960	-0.053038
O	1.028444	-2.684024	0.976572
O	1.028225	2.682799	0.978740
C	-0.444592	-1.211002	-1.937839
C	-1.724739	-1.201477	-1.382210
C	-2.364009	0.000934	-1.119113
C	-1.724312	1.203306	-1.381374
C	-0.444165	1.212776	-1.936987
C	0.169564	0.000874	-2.210225
H	0.077586	-2.135394	-2.137979
O	-2.412622	2.318684	-1.040213
H	0.078339	2.137132	-2.136457
H	1.170382	0.000846	-2.627001
C	-1.750670	3.563312	-1.146700
H	-3.346739	0.000950	-0.666697
H	-1.507182	3.797075	-2.188080
H	-0.839760	3.580424	-0.540805
H	-2.451324	4.306444	-0.770970
O	-2.413478	-2.316856	-1.041894
C	-1.751826	-3.561618	-1.148745
H	-0.840992	-3.579181	-0.542747
H	-1.508264	-3.795080	-2.190175
H	-2.452718	-4.304708	-0.773373



INT2

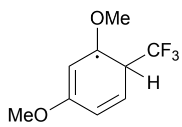
	X	Y	Z
C	4.326015	-0.759750	1.605702
C	3.256840	0.053975	1.935722
C	2.463331	0.602600	0.934673
C	2.744609	0.326590	-0.404617
C	3.829767	-0.479458	-0.729108
C	4.616135	-1.021700	0.271111
C	1.324363	1.481237	1.317233
C	1.888512	0.861317	-1.499396
C	0.759966	1.751771	-1.116851
C	0.489296	2.044255	0.221629
C	-0.585085	2.863906	0.550103
H	-0.780683	3.067744	1.594971
C	-1.386581	3.387066	-0.449346
C	-1.120433	3.092416	-1.783314
C	-0.052983	2.277411	-2.114999
H	4.940732	-1.188358	2.388064
H	3.020031	0.281386	2.967571
H	4.037428	-0.671792	-1.774133
H	5.459067	-1.652013	0.014115
H	-2.225568	4.022298	-0.191660
H	-1.752837	3.498701	-2.563551
H	0.167188	2.028335	-3.145218
O	2.103985	0.576944	-2.660068
O	1.089254	1.734561	2.480459
C	-2.271577	-0.250218	-0.199443
C	-1.392069	-0.646280	0.955952
C	-0.288264	-1.410322	0.798029
C	0.132975	-1.828472	-0.495997
C	-0.566871	-1.414330	-1.634868
C	-1.687496	-0.645122	-1.522357
C	-3.688166	-0.831939	-0.056033
O	1.239312	-2.605299	-0.502332

H	-0.208204	-1.668852	-2.622858
H	-2.202118	-0.301928	-2.408868
C	1.757851	-3.005019	-1.754455
H	0.331460	-1.692216	1.638115
H	2.018288	-2.138833	-2.370090
H	1.044130	-3.637111	-2.292289
H	2.656291	-3.578796	-1.536740
O	-1.833519	-0.140649	2.117698
C	-1.174377	-0.534266	3.307855
H	-0.138846	-0.186882	3.315218
H	-1.211211	-1.621709	3.423054
H	-1.719371	-0.059935	4.120341
F	-4.346976	-0.339851	0.998325
F	-3.677455	-2.164490	0.064555
F	-4.426085	-0.535202	-1.141511
H	-2.427928	0.837368	-0.157769



TS2

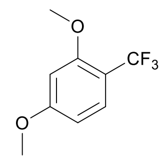
	X	Y	Z
C	4.235713	-1.421343	1.312378
C	3.283038	-0.525542	1.764654
C	2.582234	0.261981	0.859445
C	2.834678	0.140851	-0.508070
C	3.802686	-0.750822	-0.954856
C	4.500533	-1.529330	-0.048127
C	1.564846	1.220575	1.372802
C	2.071426	0.939414	-1.508673
C	1.059879	1.902458	-0.992876
C	0.818706	2.035307	0.375694
C	-0.150071	2.926068	0.825020
H	-0.329286	3.004546	1.889356
C	-0.873162	3.677839	-0.082830
C	-0.630786	3.547914	-1.446746
C	0.331933	2.664229	-1.899971
H	4.778312	-2.036087	2.020427
H	3.065705	-0.419865	2.819956
H	3.989629	-0.820475	-2.019364
H	5.253253	-2.224824	-0.399998
H	-1.632137	4.365877	0.269608
H	-1.199253	4.137716	-2.155954
H	0.532570	2.541672	-2.956800
O	2.265100	0.803072	-2.697652
O	1.354929	1.333742	2.562710
C	-2.079382	0.169597	-0.412045
C	-1.566829	-0.204978	0.858437
C	-0.589267	-1.168657	0.959900
C	-0.050231	-1.737742	-0.202641
C	-0.463477	-1.311573	-1.461619
C	-1.440438	-0.334269	-1.551017
H	-2.667615	1.076917	-0.469812
O	0.899837	-2.673704	0.012049
H	-0.016368	-1.703482	-2.363483
H	-1.743787	0.026259	-2.525620
C	1.438566	-3.342104	-1.109135
H	-0.197260	-1.495541	1.912440
H	1.948379	-2.646197	-1.781190
H	0.658985	-3.879542	-1.657860
H	2.162823	-4.051524	-0.714585
O	-2.132879	0.426587	1.902061
C	-1.738178	0.046450	3.208444
H	-0.677871	0.253239	3.372586
H	-1.949869	-1.012439	3.384649
H	-2.336385	0.651164	3.886266
C	-3.997495	-0.964549	-0.380086
F	-3.790204	-2.200527	0.059503
F	-4.458274	-1.018609	-1.628604
F	-4.907661	-0.373710	0.389939



INT3

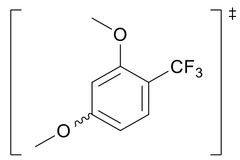
	X	Y	Z
C	-0.839378	-0.353085	-0.790131

C	-0.292717	0.977401	-0.349278
C	0.990850	1.137597	0.039670
C	1.917571	0.059033	-0.040932
C	1.535886	-1.154200	-0.624300
C	0.249420	-1.355265	-1.036404
C	-1.842522	-0.912755	0.235604
O	3.155336	0.346610	0.424735
H	2.260958	-1.941999	-0.780473
H	-0.032671	-2.285277	-1.510292
C	4.138894	-0.662842	0.363839
H	1.367514	2.090202	0.385807
H	4.355326	-0.945676	-0.671259
H	3.832545	-1.549214	0.928048
H	5.034077	-0.239796	0.814600
O	-1.224958	1.946439	-0.401889
C	-0.854674	3.240479	0.023013
H	-0.043691	3.639073	-0.594818
H	-0.544506	3.233157	1.072328
H	-1.740363	3.860989	-0.09111
F	-2.92033	-0.134115	0.379879
F	-1.294196	-1.063889	1.446427
F	-2.286343	-2.120116	-0.156129
H	-1.444368	-0.200954	-1.693688



B

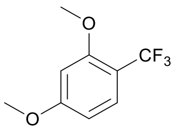
	X	Y	Z
C	0.536720	0.608657	0.000000
C	-0.812735	0.210100	0.000000
C	-1.131484	-1.135807	0.000000
C	-0.118845	-2.096725	0.000000
C	1.215395	-1.714644	0.000000
C	1.519625	-0.359304	0.000000
C	0.893698	2.064873	0.000000
O	-0.547915	-3.377203	0.000000
H	2.015685	-2.439738	0.000000
H	2.556934	-0.052596	0.000000
C	0.421029	-4.405085	0.000000
H	-2.154984	-1.481309	0.000000
H	1.049929	-4.357155	0.893953
H	1.049929	-4.357155	-0.893953
H	-0.134476	-5.340104	0.000000
O	-1.727688	1.195825	0.000000
C	-3.096179	0.849504	0.000000
H	-3.359492	0.277244	0.894453
H	-3.359492	0.277244	-0.894453
H	-3.640262	1.790888	0.000000
F	0.421029	2.710637	1.078142
F	0.421029	2.710637	-1.078142
F	2.226576	2.245868	0.000000



TS-R1

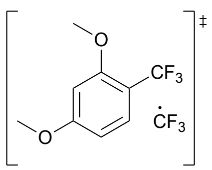
	X	Y	Z
C	-0.692881	-0.499710	-0.052198
C	-0.035349	0.739828	-0.092224
C	1.346883	0.776413	-0.223645
C	2.063761	-0.411024	-0.315710
C	1.423869	-1.636503	-0.280586
C	0.043869	-1.666418	-0.149227
C	-2.187631	-0.550482	0.088599
O	3.421330	-0.355466	-0.479094
H	2.001423	-2.547395	-0.365990
H	-0.472003	-2.616721	-0.123763
C	4.143572	-0.265138	0.737966
H	1.888811	1.710321	-0.272814
H	3.955319	-1.139711	1.369359
H	3.872722	0.640702	1.290850
H	5.198690	-0.226908	0.473145
O	-0.809838	1.835926	-0.003046
C	-0.194893	3.105522	-0.049494
H	0.329645	3.257382	-0.997534
H	0.502181	3.239026	0.783348
H	-1.001890	3.829112	0.036423

F	-2.818713	0.062511	-0.924277
F	-2.613710	0.026788	1.222767
F	-2.638026	-1.816455	0.110755



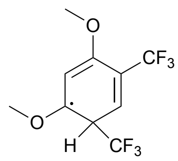
B'

	X	Y	Z
C	-0.725367	-0.552102	0.000000
C	-0.005186	0.646803	0.000000
C	1.387299	0.627061	0.000000
C	2.058957	-0.593293	0.000000
C	1.348482	-1.789077	0.000000
C	-0.030434	-1.753059	0.000000
C	-2.224433	-0.532785	0.000000
O	3.404918	-0.703792	0.000000
H	1.889504	-2.725512	0.000000
H	-0.587100	-2.680468	0.000000
C	4.181396	0.474092	0.000000
H	1.937852	1.554286	0.000000
H	3.992801	1.075997	0.894605
H	3.992801	1.075997	-0.894605
H	5.219252	0.148832	0.000000
O	-0.727144	1.783197	0.000000
C	-0.054227	3.022293	0.000000
H	0.564553	3.139159	-0.895139
H	0.564553	3.139159	0.895139
H	-0.832200	3.782013	0.000000
F	-2.732708	0.086495	-1.078019
F	-2.732708	0.086495	1.078019
F	-2.732708	-1.777913	0.000000



TS3

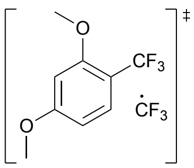
	X	Y	Z
C	-2.135905	-1.489235	0.530201
F	-3.455021	-1.482891	0.367097
F	-1.833115	-0.887004	1.674674
F	-1.705978	-2.745542	0.568537
C	1.189663	-0.247583	-0.410378
C	0.916650	1.042737	0.073220
C	-0.343058	1.613390	-0.123762
C	-1.335857	0.886236	-0.756466
C	-1.116275	-0.459435	-1.133205
C	0.193796	-0.958838	-1.041817
C	2.565624	-0.830409	-0.258191
O	-2.571434	1.350205	-1.009054
H	-1.825547	-0.918575	-1.810304
H	0.408757	-1.944119	-1.430705
C	-2.911500	2.648759	-0.567720
H	-0.534732	2.620238	0.211758
H	-2.285721	3.406985	-1.048257
H	-2.823264	2.729155	0.519747
H	-3.948250	2.800884	-0.857643
O	1.924766	1.675561	0.693634
C	1.711770	2.973332	1.207097
H	0.913883	2.975992	1.955614
H	1.474944	3.682089	0.407894
H	2.648402	3.262308	1.677366
F	2.927869	-0.953876	1.027037
F	3.505407	-0.084852	-0.860884
F	2.642550	-2.056370	-0.800460



INT4

	X	Y	Z
C	-1.294506	-0.643078	-0.691739
C	-1.407915	0.841545	-0.507468
C	-0.367301	1.601318	-0.073747
C	0.916695	1.034937	0.106961
C	1.148710	-0.305086	-0.290789
C	0.133725	-1.092732	-0.722584

C	-2.056143	-1.406456	0.409988
H	0.330981	-2.100509	-1.056164
H	-0.507581	2.658363	0.094491
O	-2.632661	1.297197	-0.819534
C	-2.892568	2.676238	-0.661183
H	-2.230143	3.275168	-1.294092
H	-2.776519	2.977816	0.384209
H	-3.924378	2.825659	-0.969306
F	-3.367240	-1.147051	0.392662
F	-1.603324	-1.104011	1.631139
F	-1.913996	-2.730374	0.243528
H	-1.809781	-0.926692	-1.617784
C	2.555608	-0.845146	-0.266290
O	1.974126	1.717971	0.585959
C	1.801178	3.061380	0.979382
H	1.043290	3.150562	1.763577
H	1.530497	3.693758	0.128067
H	2.763606	3.382629	1.370438
F	3.065751	-0.857825	0.972182
F	3.385529	-0.121435	-1.032129
F	2.613658	-2.105484	-0.721828



TS4

	X	Y	Z
C	1.184387	-0.246649	-0.411426
C	1.079995	1.057992	0.122632
C	-0.116485	1.751933	0.013837
C	-1.223782	1.155442	-0.570165
C	-1.186307	-0.205726	-0.961065
C	0.084363	-0.832360	-0.976958
C	2.501041	-0.969268	-0.375760
O	-2.321993	1.925673	-0.660124
H	-1.948188	-0.596178	-1.622544
H	0.168380	-1.824167	-1.398584
C	-3.458816	1.424978	-1.341734
H	-0.217423	2.769825	0.361236
H	-3.863567	0.537957	-0.850225
H	-3.221844	1.197465	-2.385066
H	-4.197243	2.222319	-1.307444
O	2.187833	1.560479	0.686502
C	2.144661	2.864466	1.229613
H	1.396793	2.934948	2.024571
H	1.933551	3.607428	0.455151
H	3.133381	3.044682	1.644052
F	2.936588	-1.170962	0.875766
F	3.466181	-0.300885	-1.025936
F	2.414524	-2.178035	-0.954528
C	-2.175268	-1.187593	0.703773
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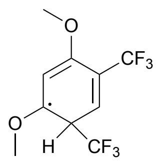
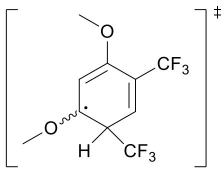


INT5

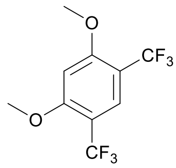
	X	Y	Z
C	-1.341603	-0.413244	-0.557733
C	-1.310431	1.075502	-0.343759
C	-0.177763	1.719042	0.048478
C	1.055028	1.050152	0.146603
C	1.142867	-0.299597	-0.294488
C	0.041388	-0.980665	-0.681104
C	-2.087027	-1.132164	0.586188
H	0.129861	-1.994998	-1.041397
H	-0.254498	2.779228	0.246982
O	-2.450525	1.800811	-0.429340
C	-3.348854	1.508887	-1.488558
H	-3.867794	0.561230	-1.330552
H	-2.825885	1.495850	-2.449871
H	-4.078921	2.315183	-1.489576
F	-3.368846	-0.746303	0.670156
F	-1.523427	-0.907769	1.773156

F	-2.092064	-2.458224	0.382091
H	-1.922769	-0.669470	-1.452113
C	2.495281	-0.962168	-0.368061
O	2.196827	1.624237	0.566464
C	2.160771	2.967026	1.002098
H	1.459945	3.093716	1.832373
H	1.890576	3.641450	0.184079
H	3.168545	3.196707	1.339474
F	3.074385	-1.048874	0.835788
F	3.336813	-0.295665	-1.170940
F	2.412317	-2.211599	-0.849627



TS-R2

	X	Y	Z
C	-1.365829	-0.470390	-0.566798
C	-1.374705	0.991949	-0.230740
C	-0.262752	1.647122	0.196761
C	0.991644	1.011970	0.237604
C	1.112113	-0.311469	-0.281581
C	0.029994	-1.001512	-0.699467
C	-2.138294	-1.300988	0.475654
H	0.148046	-1.992323	-1.113599
H	-0.366030	2.686542	0.479250
O	-2.572546	1.628132	-0.344759
C	-2.708451	2.448570	-1.496549
H	-2.592069	1.858912	-2.411980
H	-1.971941	3.257590	-1.494058
H	-3.712039	2.868161	-1.461717
F	-3.424111	-0.950659	0.544063
F	-1.616757	-1.173821	1.699373
F	-2.099703	-2.605486	0.155497
H	-1.925217	-0.634459	-1.497836
C	2.482854	-0.931466	-0.392395
O	2.118932	1.584965	0.693476
C	2.052319	2.896459	1.213078
H	1.355444	2.952330	2.054370
H	1.758976	3.613612	0.440530
H	3.056493	3.130535	1.557813
F	3.065689	-1.070473	0.804456
F	3.303047	-0.194930	-1.155422
F	2.434490	-2.152092	-0.945289



D

	X	Y	Z
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C	0.000000	1.206048	0.976505
C	0.000000	0.000000	1.670785
C	0.000000	-1.206048	0.976505
C	0.000000	-1.207630	-0.423192
C	0.000000	0.000000	-1.095550
C	0.000000	2.504046	-1.179680
O	0.000000	-2.403785	1.578546
H	0.000000	0.000000	-2.175973
C	0.000000	-2.467753	2.989717
H	0.000000	0.000000	2.748709
H	-0.895788	-1.998573	3.406982
H	0.895788	-1.998573	3.406982
H	0.000000	-3.526353	3.236720
O	0.000000	2.403785	1.578546
C	0.000000	2.467753	2.989717
H	0.895788	1.998573	3.406982
H	-0.895788	1.998573	3.406982
H	0.000000	3.526353	3.236720
F	1.078106	3.254691	-0.906405
F	-1.078106	3.254691	-0.906405
F	0.000000	2.296885	-2.506215
C	0.000000	-2.504046	-1.179680
F	-1.078106	-3.254691	-0.906405
F	1.078106	-3.254691	-0.906405
F	0.000000	-2.296885	-2.506215

CHF_3

FF

	X	Y	Z
C	0.000000	0.000000	0.338274
F	0.000000	1.249426	-0.128080
F	-1.082034	-0.624713	-0.128080
F	1.082034	-0.624713	-0.128080
H	0.000000	0.000000	1.428509

$SO_2^{\bullet-}$

R2

	X	Y	Z
S	0.000000	0.000000	0.409498
O	0.000000	1.271300	-0.409498
O	0.000000	-1.271300	-0.409498

HSO_2^-

HSI

	X	Y	Z
H	-1.295136	0.844391	0.000000
S	0.040473	0.385324	0.000000
O	0.040473	-0.438098	1.261449
O	0.040473	-0.438098	-1.261449

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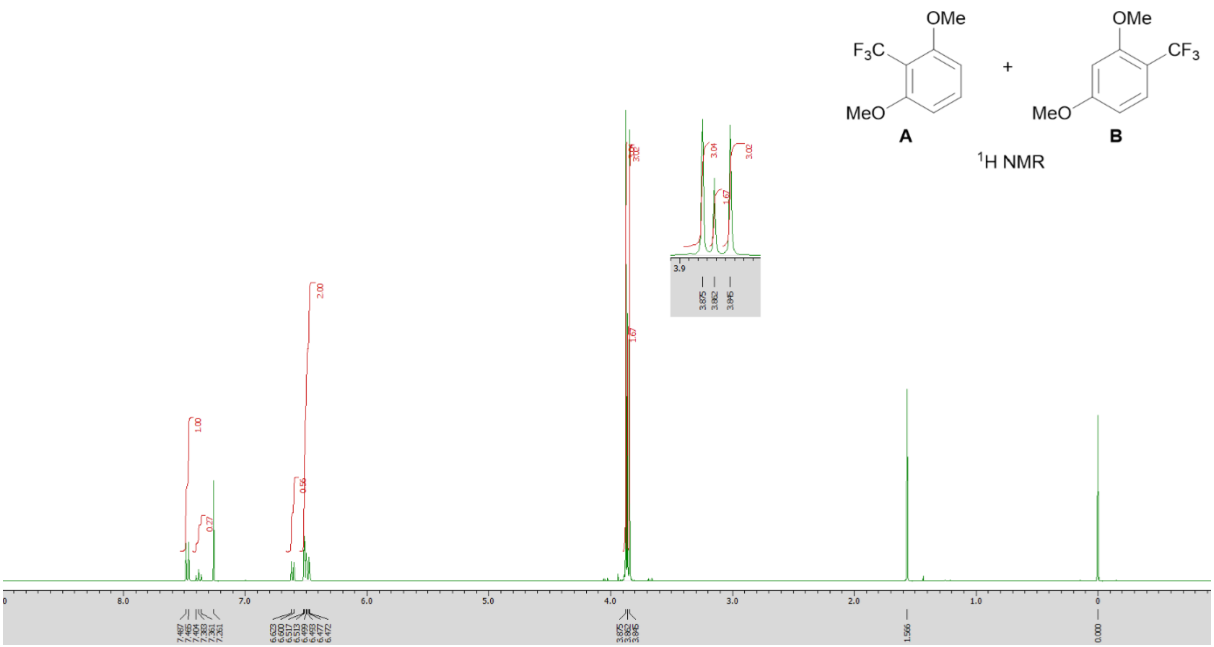
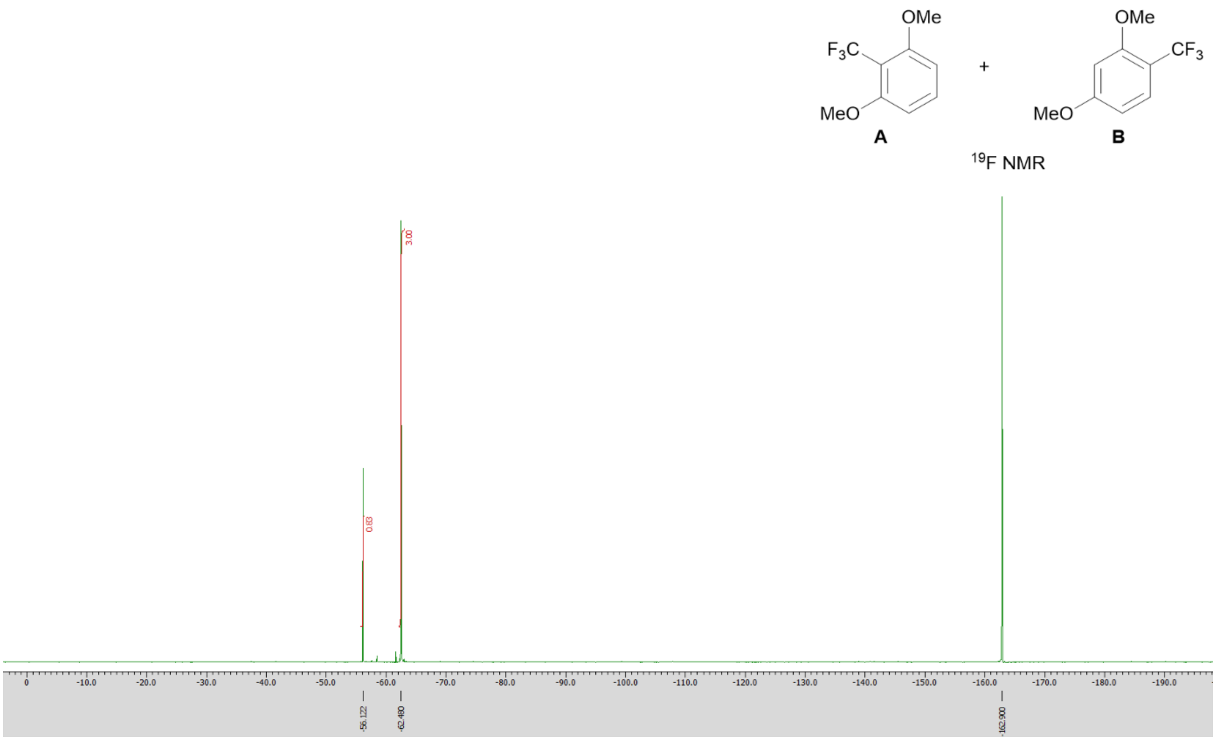
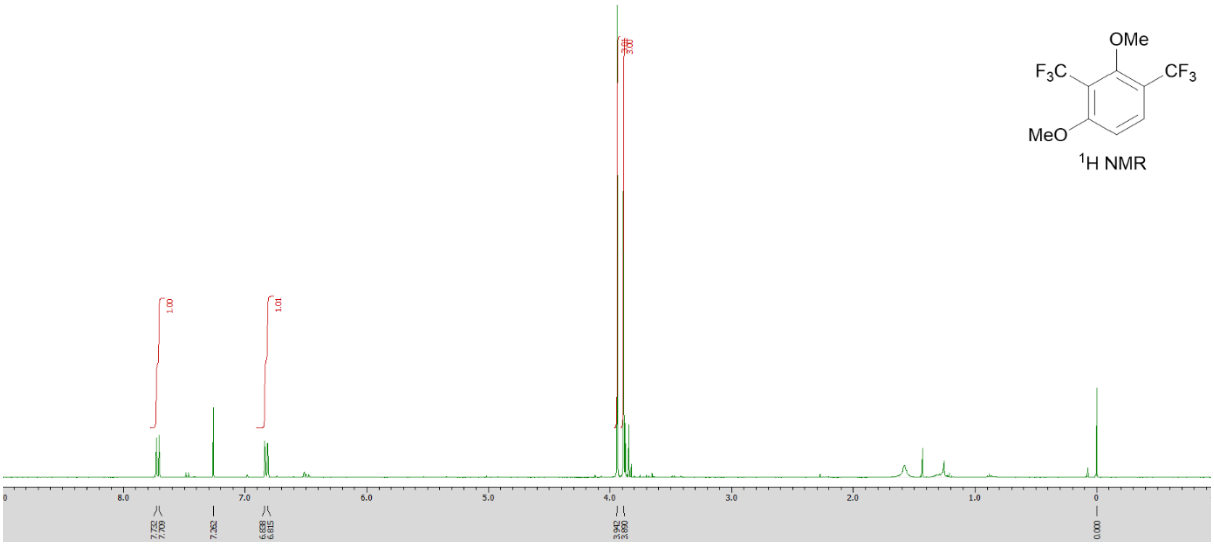
Copies of ^{1}H, ^{19}F and ^{13}C NMR spectra



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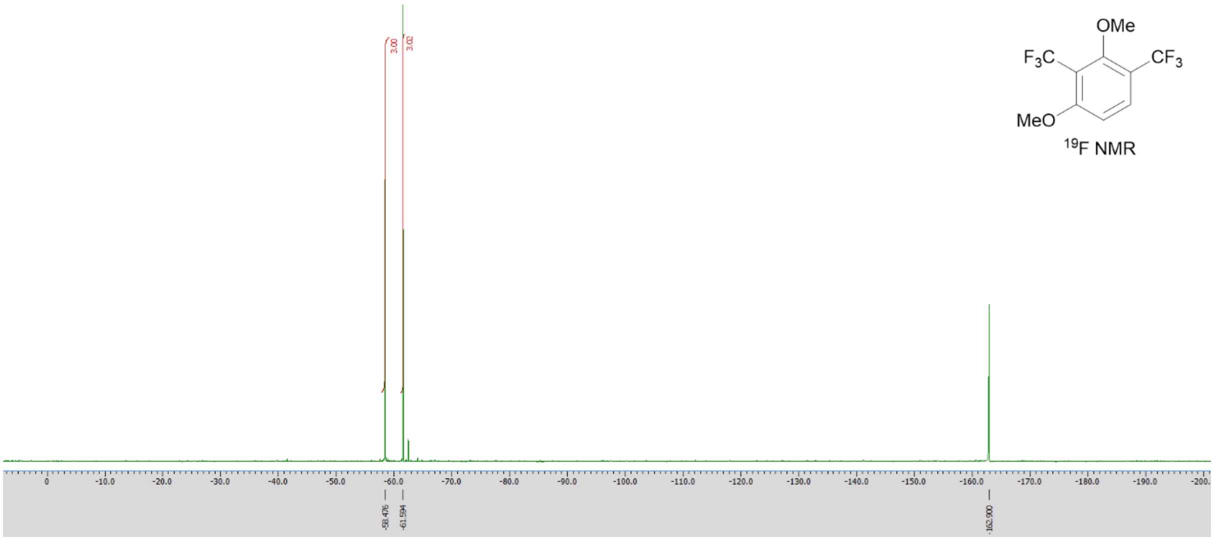
CF3
MeO
1H NMR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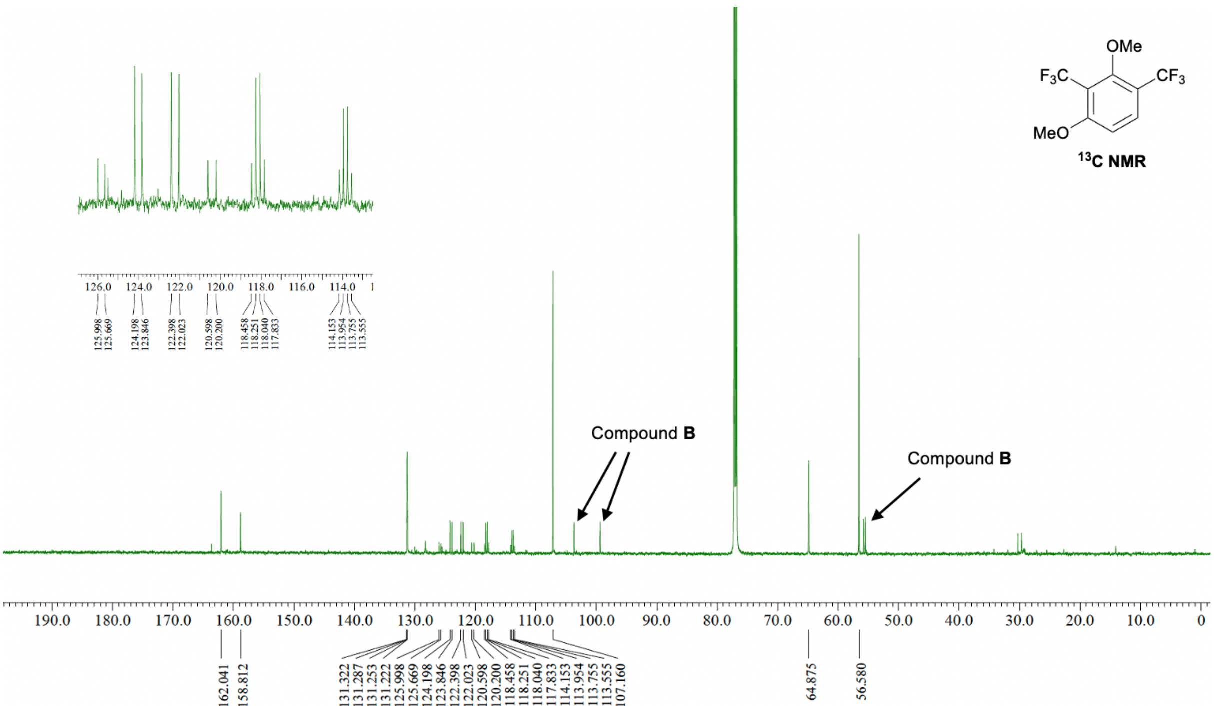
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Compound B
Compound B
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124.198
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122.398
122.023
120.598
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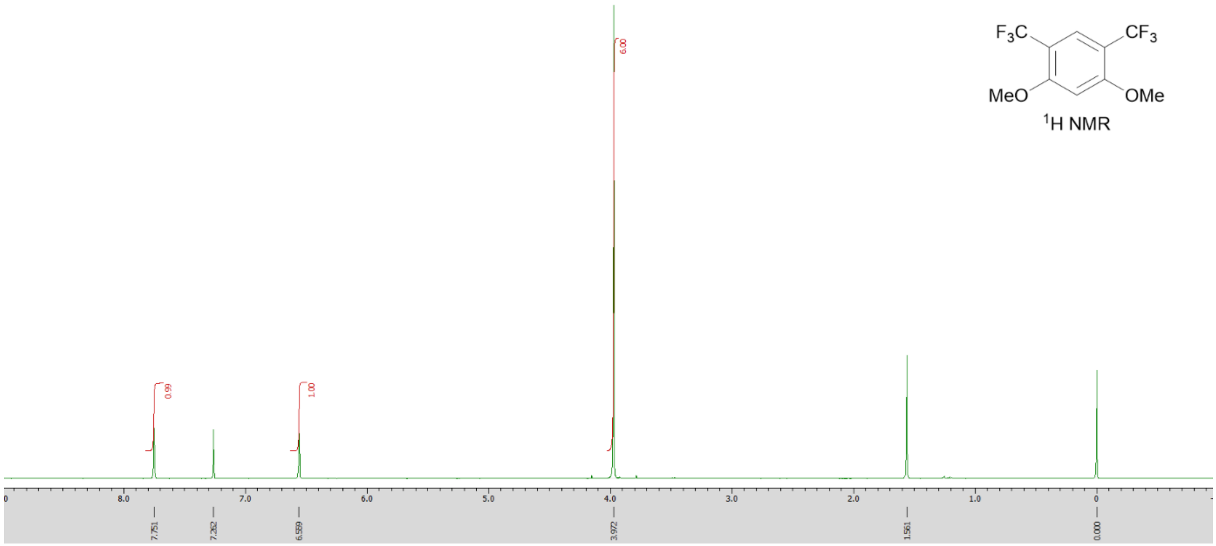
56.580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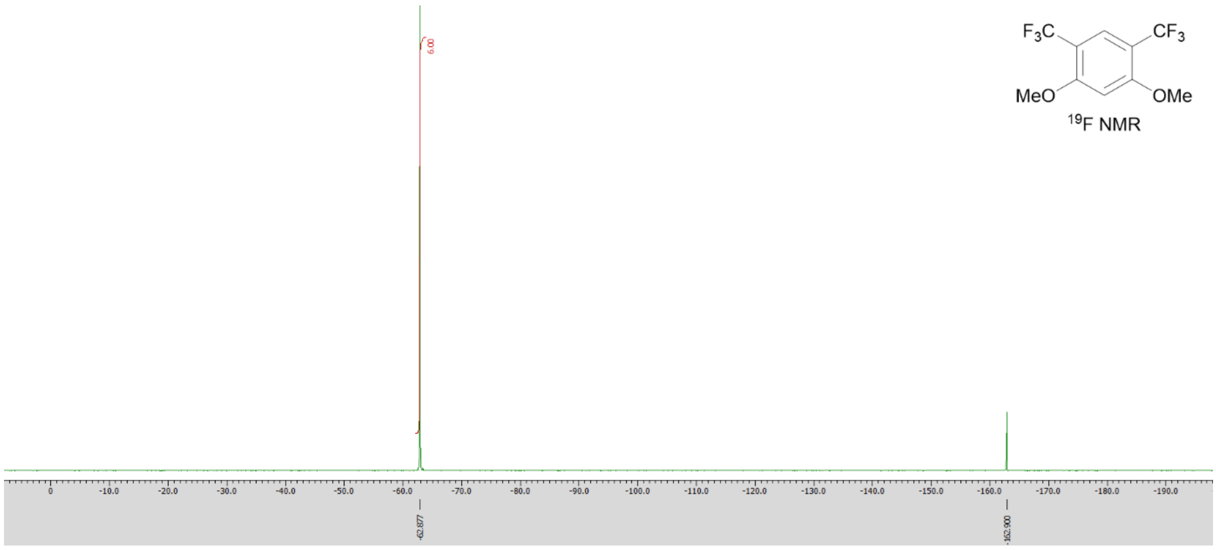
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CF3
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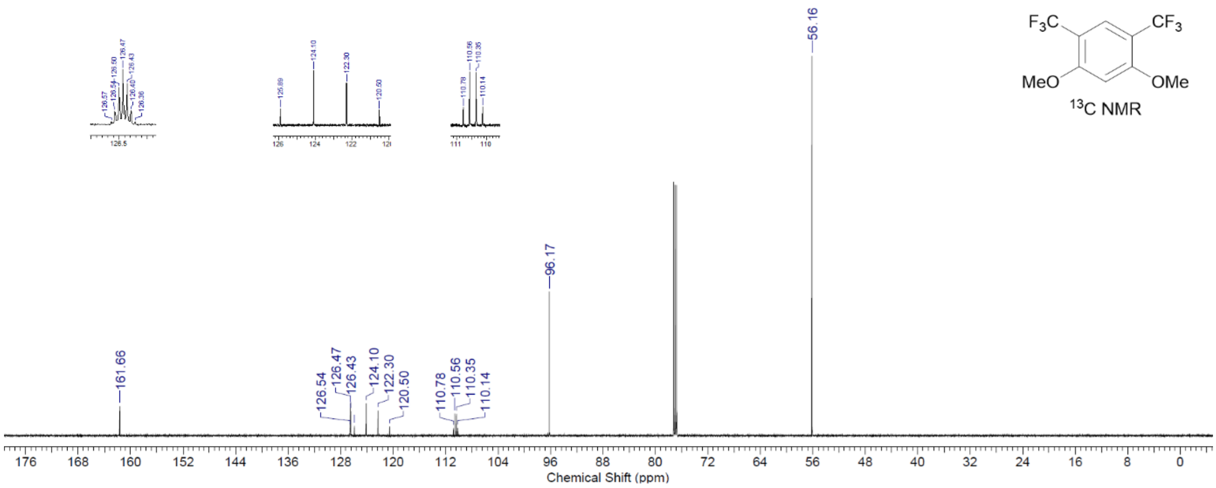
-162.900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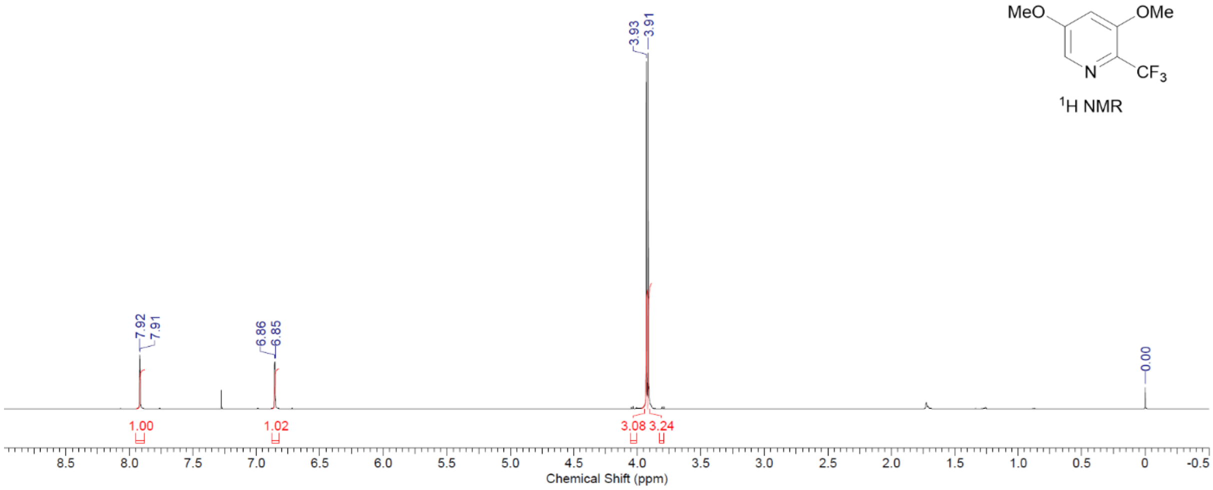
110.14
96.17
56.16
Chemical Shift (ppm)



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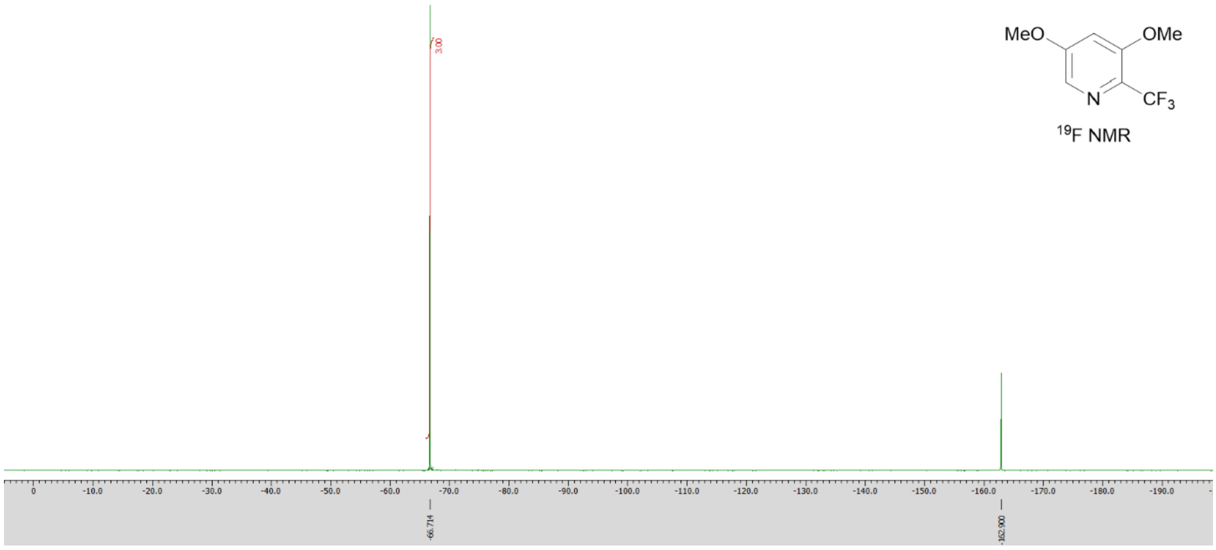
OMe
N
CF3
1H NMR
Chemical Shift (ppm)



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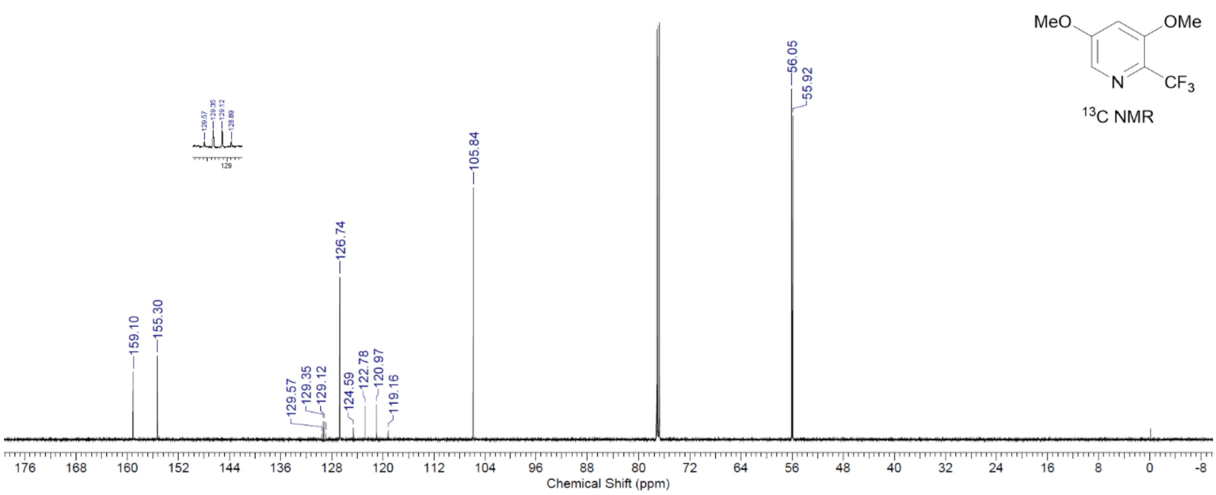

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OMe
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CF3
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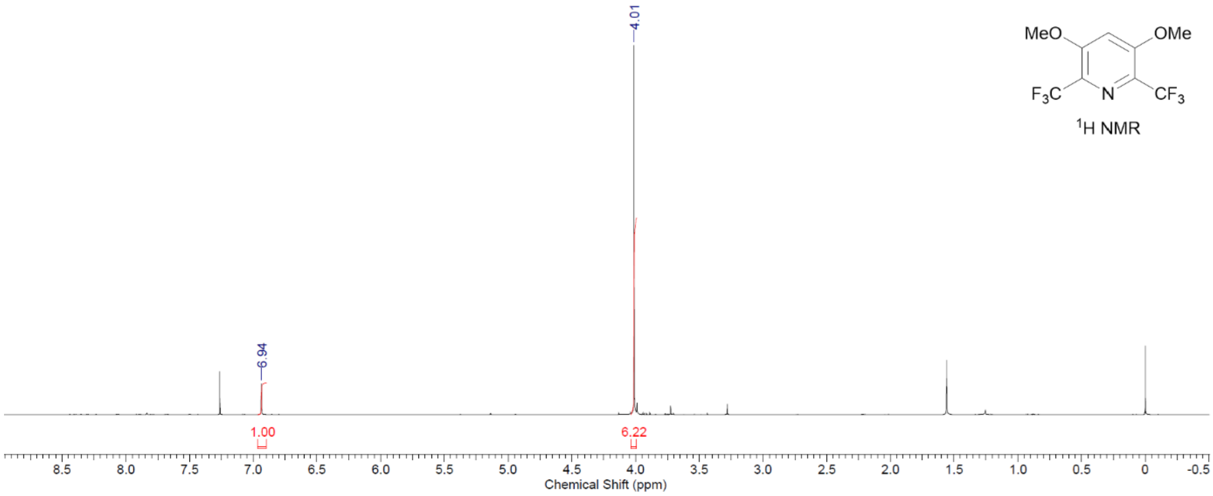
Chemical Shift (ppm)



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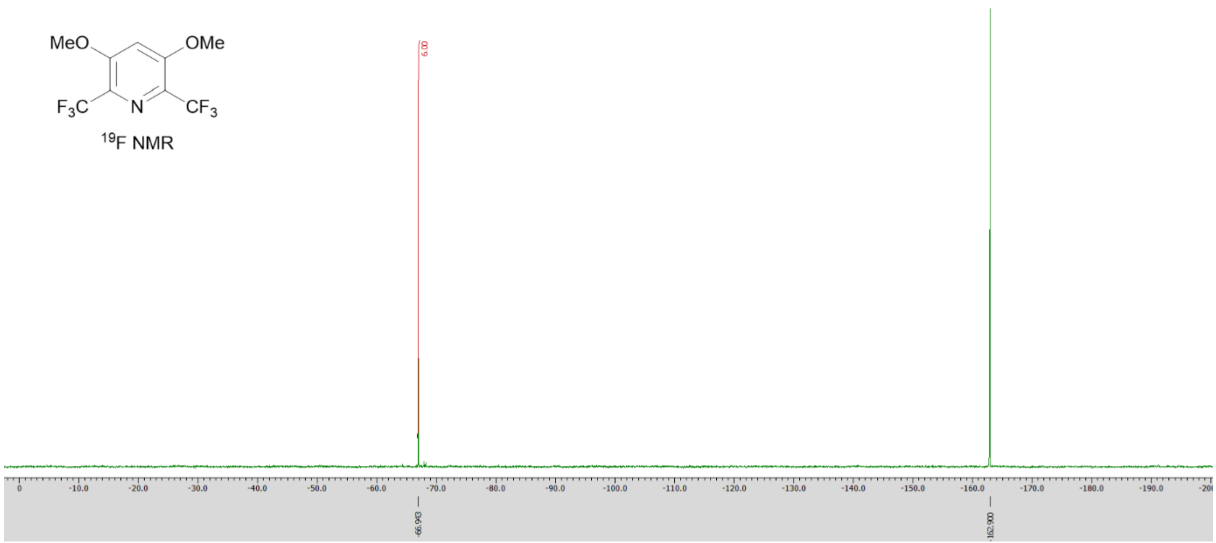
Chemical Shift (ppm)



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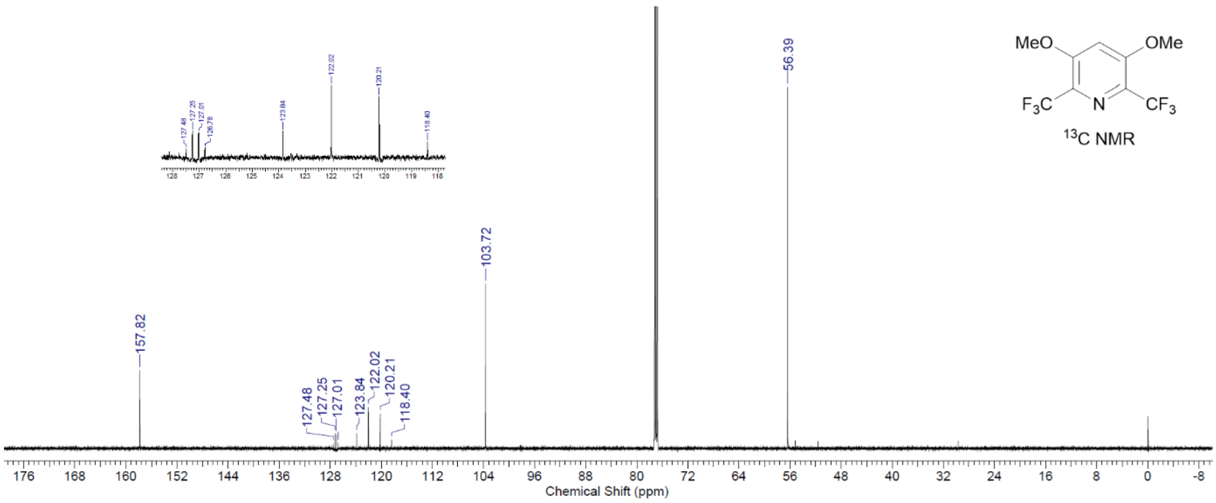

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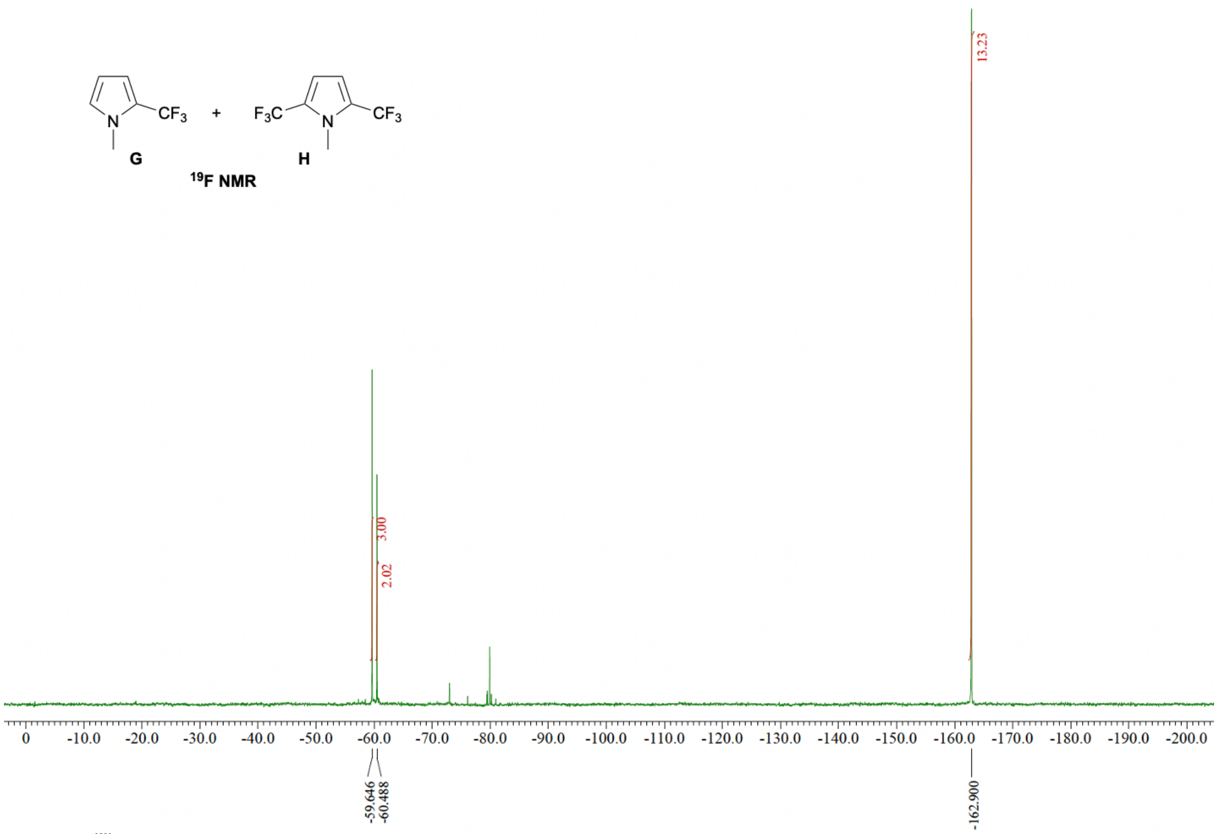
Chemical Shift (ppm)



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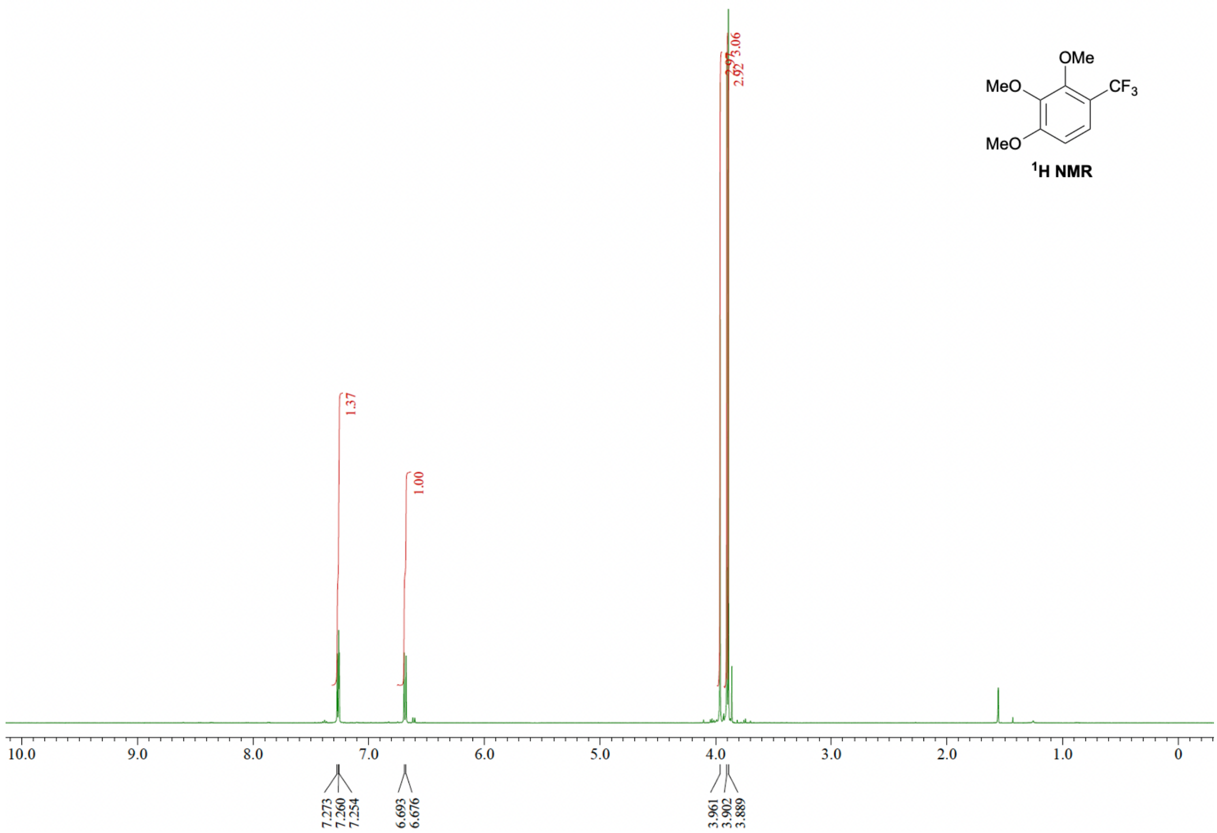

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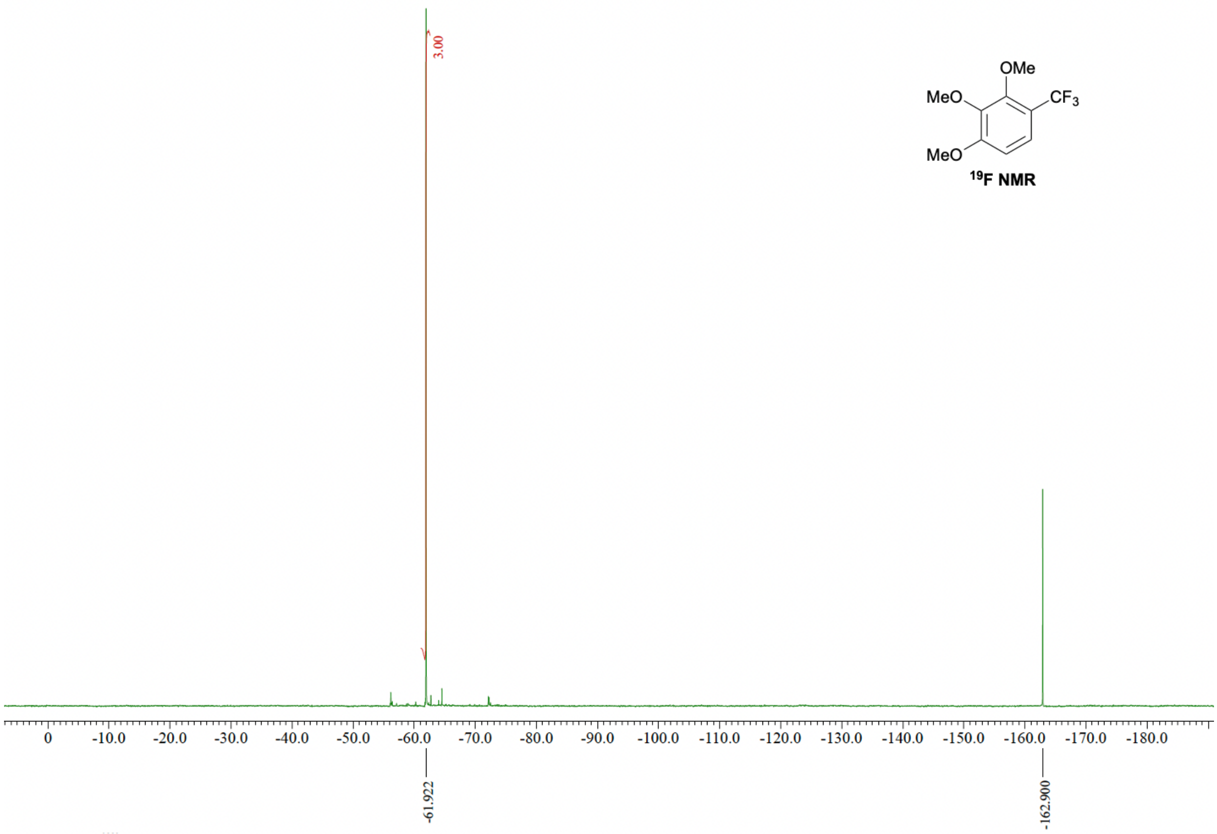
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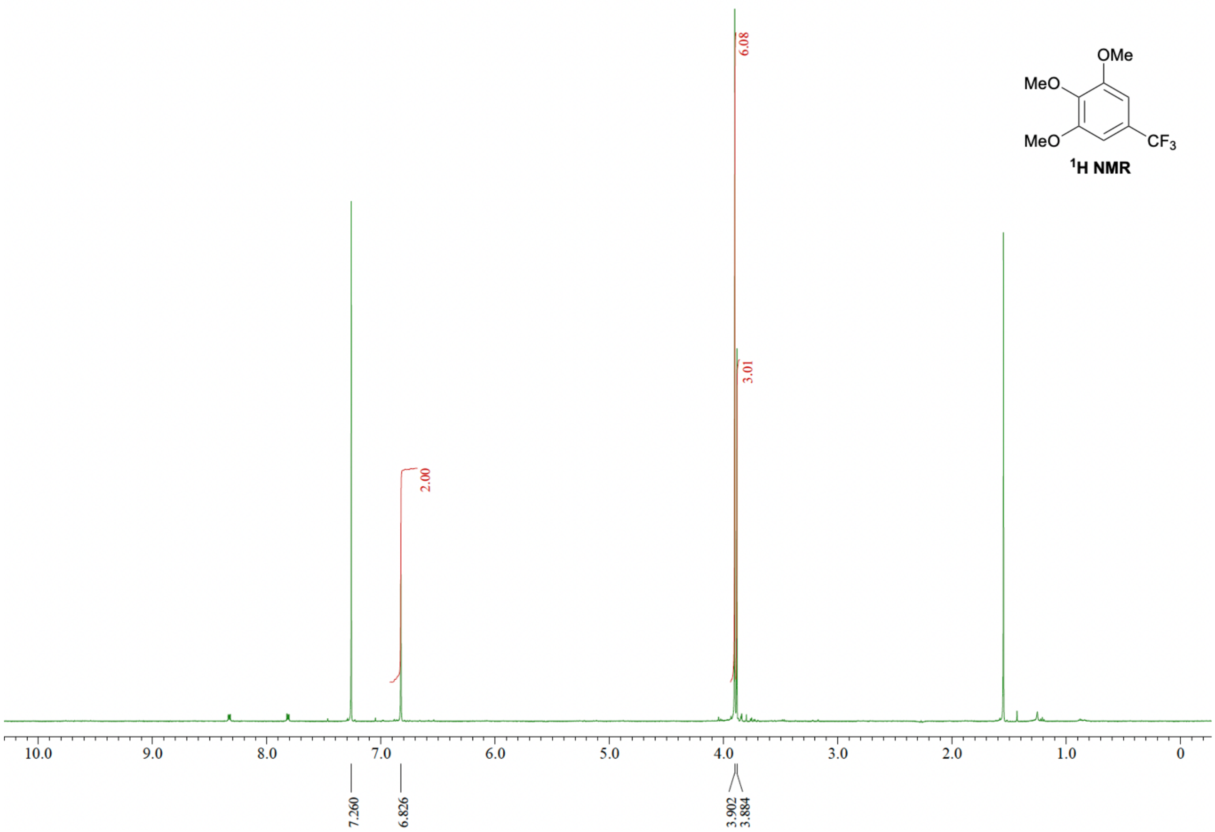
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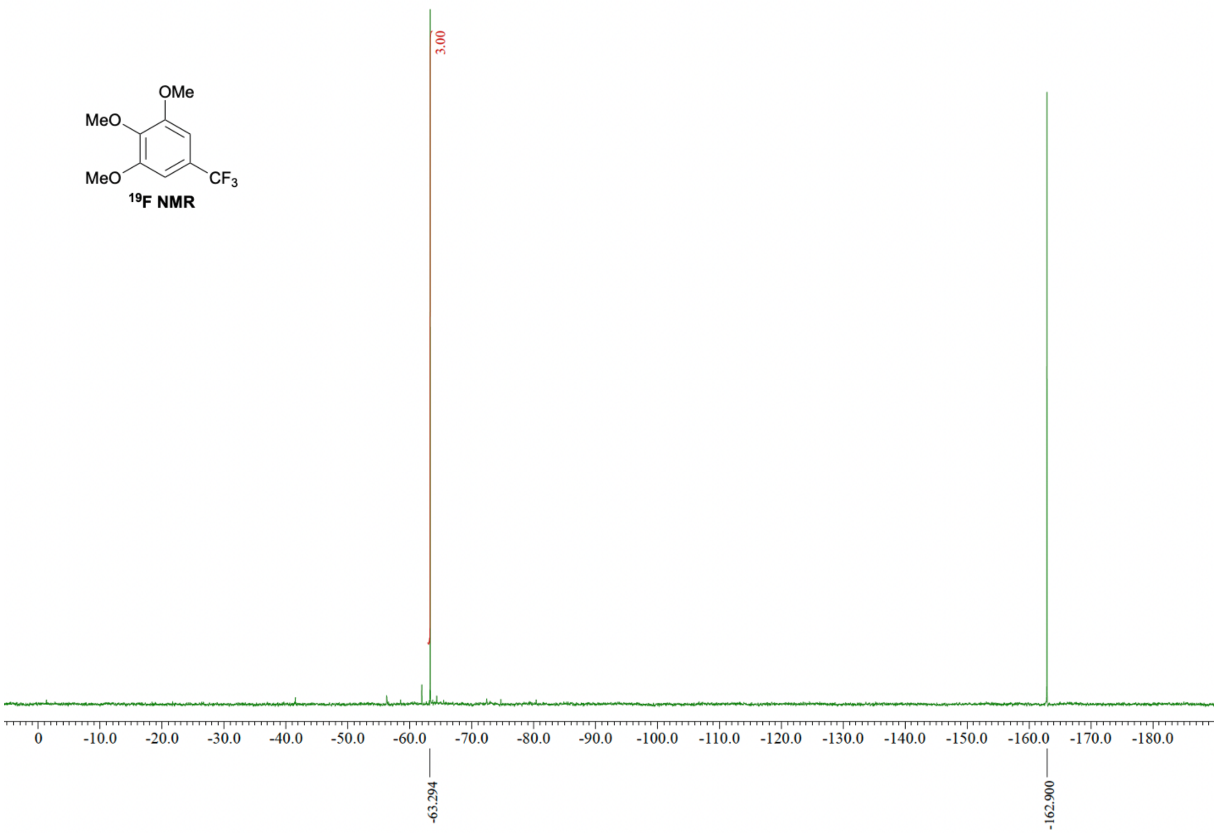
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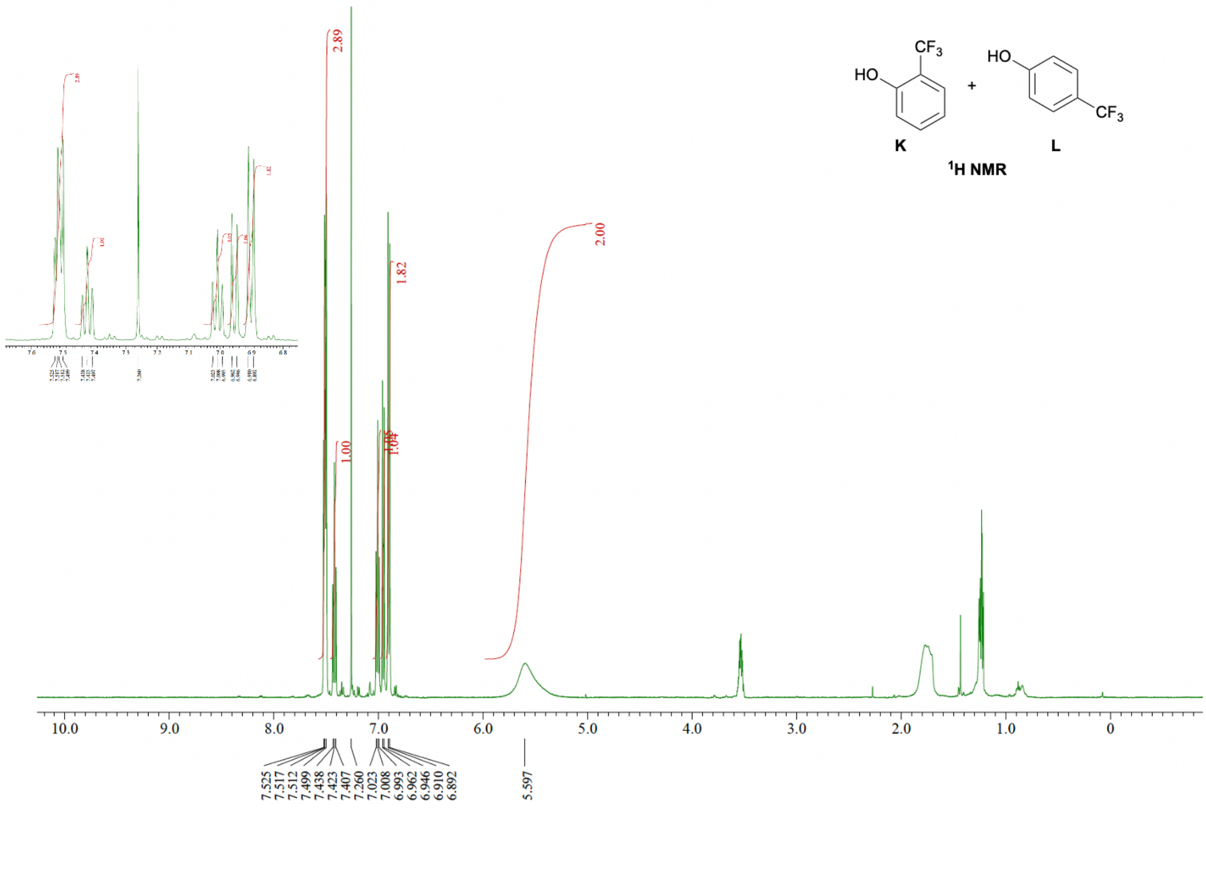
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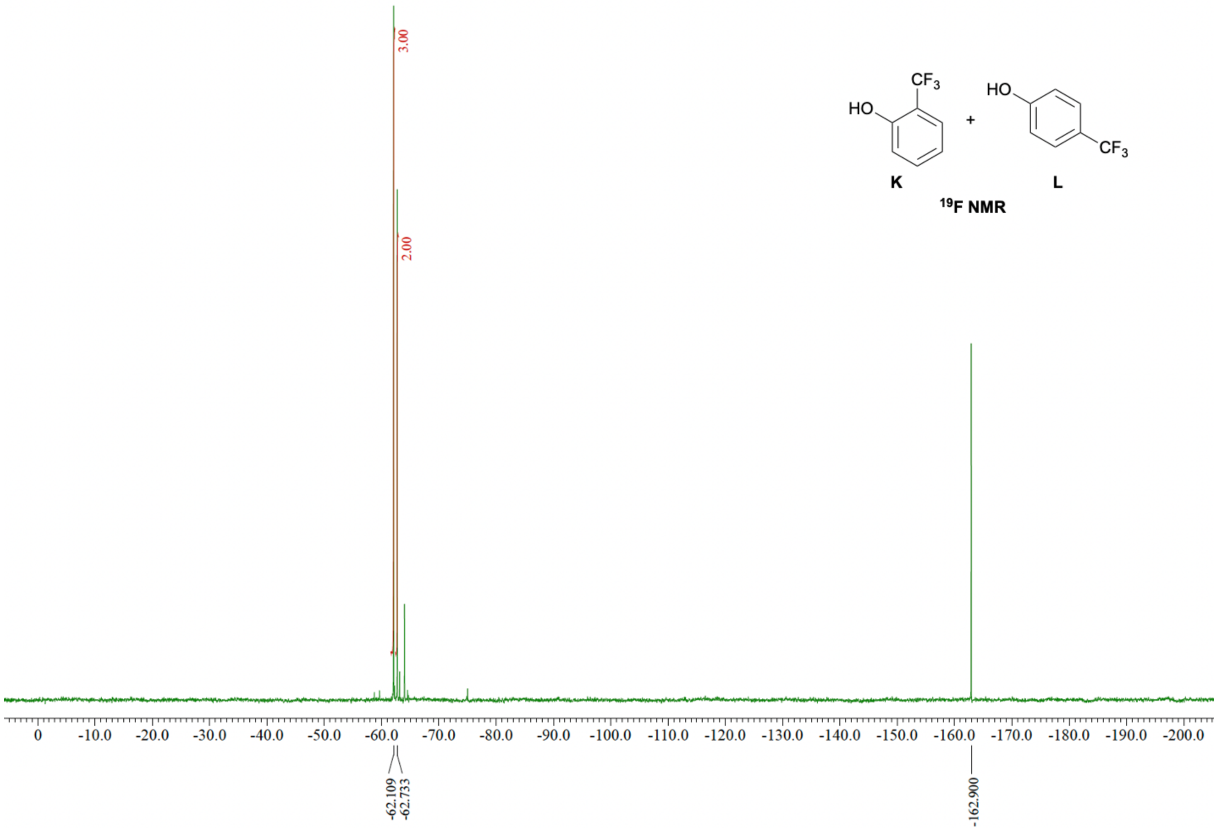

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CF3
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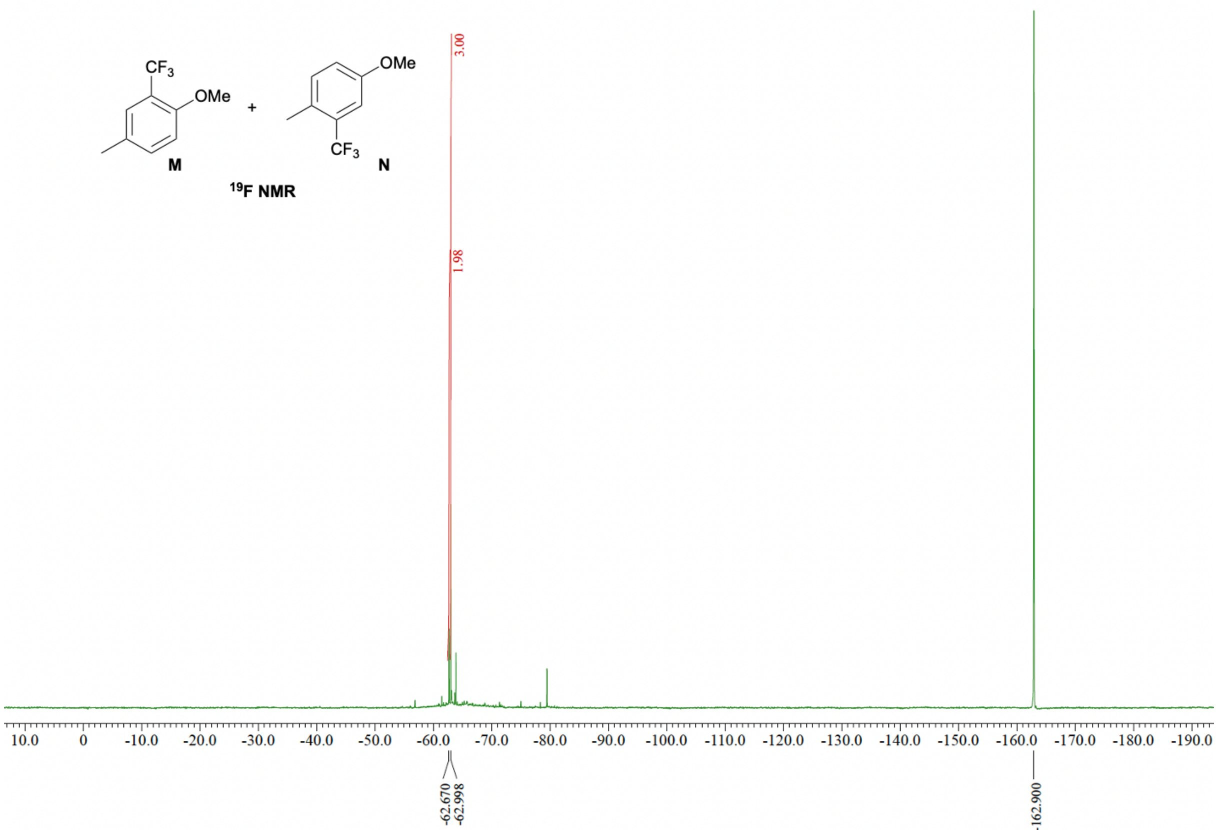

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