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Supporting Information

Electrochemically Driven, Cobalt–Carbon Bond-Mediated Direct Intramolecular Cyclic and Acyclic Perfluoroalkylation of (Hetero)Arenes using $X(CF_2)_4X$

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Experimental Section

Materials and measurements.

All chemical reagents and solvents used in this study were obtained from commercial sources and used as received unless otherwise stated. The vitamin B_{12} model complex, heptamethyl cobyrinate perchlorate [Cob(II)7C_1ester]ClO_4 (**C1**), was prepared according to the literature.[1] ^{1}H NMR and ^{13}C NMR spectra were recorded by using a Bruker Avance 500 NMR spectrometer. The chemical shifts (in ppm) of ^{1}H NMR were referenced relative to tetramethylsilane $(CH_3)_4Si$, with the residual solvent peak of chloroform-*d* ($CDCl_3$) at 7.26 ppm as an internal standard and the chemical shifts (in ppm) of ^{13}C NMR were referenced relative to the residual solvent peak of $CDCl_3$ at 77.2 ppm. ^{19}F NMR spectra were recorded by using a JEOL JNM-ECZ400 NMR spectrometer at the Centre of Advanced Instrumental Analysis in Kyushu University and a Bruker Avance 300 NMR spectrometer. The chemical shifts (in ppm) of ^{19}F NMR were referenced relative to hexafluorobenzene (C_6F_6) at –162.90 ppm in $CDCl_3$. The coupling constants, *J* are reported in Hertz (Hz). Multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Cyclic voltammetry (CV) was carried out using a BAS ALS-630C electrochemical analyzer at a scan rate of 100 mV s^{-1}. The cell was equipped with three electrodes: an Ag/AgCl (3 M NaCl aq.) reference electrode (RE), a glassy carbon working electrode (WE), and a platinum wire counter electrode (CE). The experiments were performed in methanol (CH_3OH) under N_2 atmosphere with tetrabutylammonium perchlorate (TBAP, *n*-Bu_4NClO_4, 0.1 M) as the electrolyte. The concentrations of the analytes were 1×10^{-3} M. The electrolysis was carried out using an ECstat-301WL electrochemical analyzer from EC FRONTIER CO., Ltd. The gas chromatography-mass spectra (GC-MS) were obtained using a Shimadzu GCMS-QP2010SE equipped with an Agilent J&W DB-1 column (length: 30 m; ID: 0.25 mm; film: 0.25 µm) and helium as the carrier gas. For the measurement, the injector and detector temperatures were 250 °C, the oven temperature was initially held at 100 °C for 2 min, then increased to 240 °C at the rate of 10 °C /min. A 200 W tungsten lamp with a 420 nm cut-off filter (Sigma Koki, 42L) and a heat cut-off filter (Sigma Koki, 30H) purchased from TechnoSigma were used as the visible-light irradiation experiment. The ESR spectra were obtained using a Bruker EMX-Plus X-band spectrometer at room temperature. Gel permeation chromatography (GPC) was carried out by a Japan Analytical Industry Co., Ltd., LC-908 apparatus equipped with a UV-3702 attachment using three connected columns (JAIGEL-1H, 2H, and 2.5H) with a chloroform ($CHCl_3$) eluent and a Japan Analytical Industry Co. Ltd., LC-9201 apparatus equipped with a UV-3702 attachment using two connected columns (JAIGEL-GS310) with a CH_3OH eluent. The high-resolution mass spectra (HRMS, EI-MS) were performed with a JEOL JMS-700 instrument. All the products were isolated by silica-gel column chromatography (Kanto Chemicals, 60N) and GPC; and then isolated products were identified by GC-MS, HRMS (EI-MS), ^{1}H, ^{19}F and ^{13}C NMR.

X-ray crystal structure analysis.

The crystals were mounted on a loop. Diffraction data of crystal samples were collected at 93 K or 123 K using a Rigaku XtaLABmini CCD diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Collected data were integrated, corrected, and scaled using CrysAlis(Pro).[2] The structures were refined using SHELXT (Sheldrick, 2015)[3] Intrinsic phasing and SHELXL (Sheldrick, 2015).[4] All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and included in the structure factor calculation but were not refined. The program Olex 2 was used as a graphical interface.[5] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. The data can be obtained free of charge on application to CCDC, 12 Union Road, Canbridge CB21EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). The CCDC numbers for crystal structures of **1a**, **3a**, **5a**, and **7a** are 2004379, 2004380, 2004381, and 2004382, respectively.

General procedure for catalytic reaction under electrochemical conditions.[6]

Controlled-potential electrolysis were carried out in dry CH_3OH at –0.8 V *vs.* Ag/AgCl under N_2 atmosphere in an undivided electrolysis cell. The electrolysis cell was equipped with three electrodes; i.e., a carbon felt cathode, a sacrificial Zn plate anode, and an Ag/AgCl (3.0 M NaCl aq.) as the reference electrode. For a typical reaction, a 5 mL methanol solution of **C1** (5.0×10^{-4} M) (1 mol%), 1,4-dimethoxybenzene (**1**) (5.0×10^{-2} M), TBAP (n-Bu_4NClO_4) (0.1 M) and decafluorobiphenyl ($C_{12}F_{10}$) as the internal standard was degassed by N_2 gas and stirred at room temperature with visible-light irradiation (≥ 420 nm). N_2 gas was passed over the solution during the measurement to remove O_2 from the reaction system. Octafluoro-1,4-diiodobutane (1,4-$C_4F_8I_2$, 6 eq. of substrate) as the fluoroalkylating reagent dissolved in CH_3OH was taken into a 5 mL diameter syringe pump and then it was connected to a reaction cell. A constant flow (0.5 eq. of substrate per 1 h) of this solution was added into the reaction mixture for 12 h. After the catalytic reaction, the reaction mixture was passed through a short silica-gel column to remove the catalyst and TBAP, and then analyzed by GC-MS. All the products were purified by silica-gel column chromatography and GPC. The authentic samples were characterized by NMR and mass spectrometry.

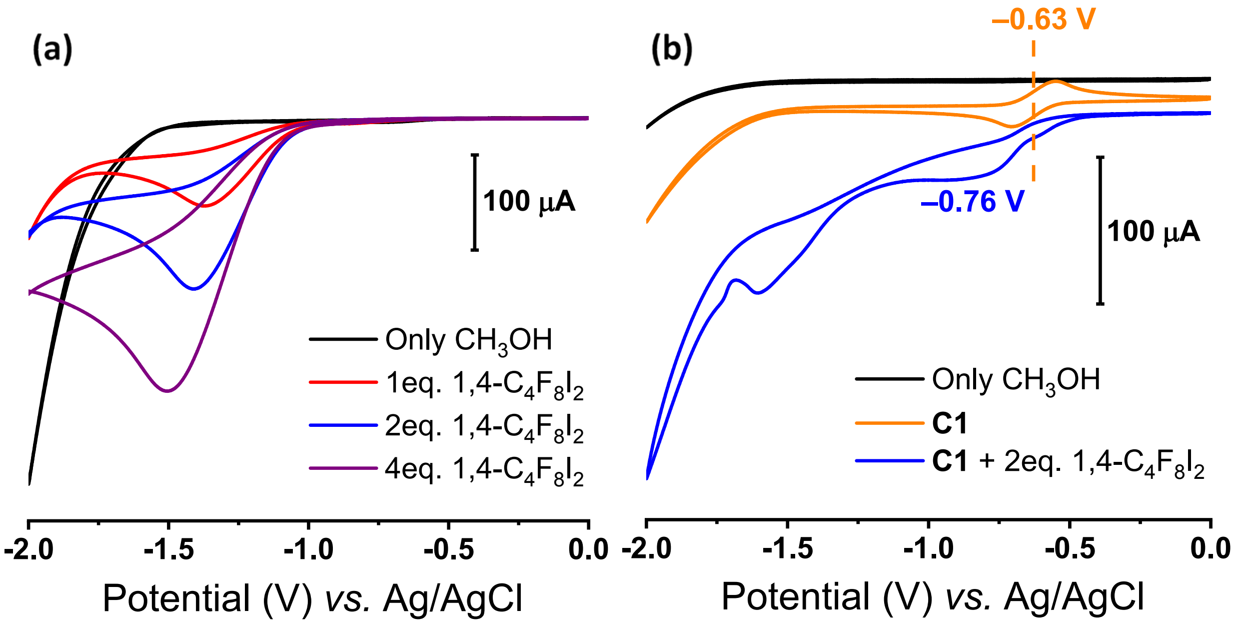


Figure S1. (**a**) CV of octafluoro-1,4-diiodobutane (1,4-$C_4F_8I_2$) and (**b**) [Cob(II)7C_1ester]ClO_4 (**C1**) as the catalyst (1 mM) with/without 1,4-$C_4F_8I_2$ (2 mM) in CH_3OH containing of 100 mM tetrabutylammonium perchlorate (TBAP, *n*-Bu_4NClO_4) under N_2. Reference electrode (RE): Ag/AgCl; Working electrode (WE): glassy carbon; Counter electrode (CE): Pt wire; Scan rate: 100 mV s^{-1}.

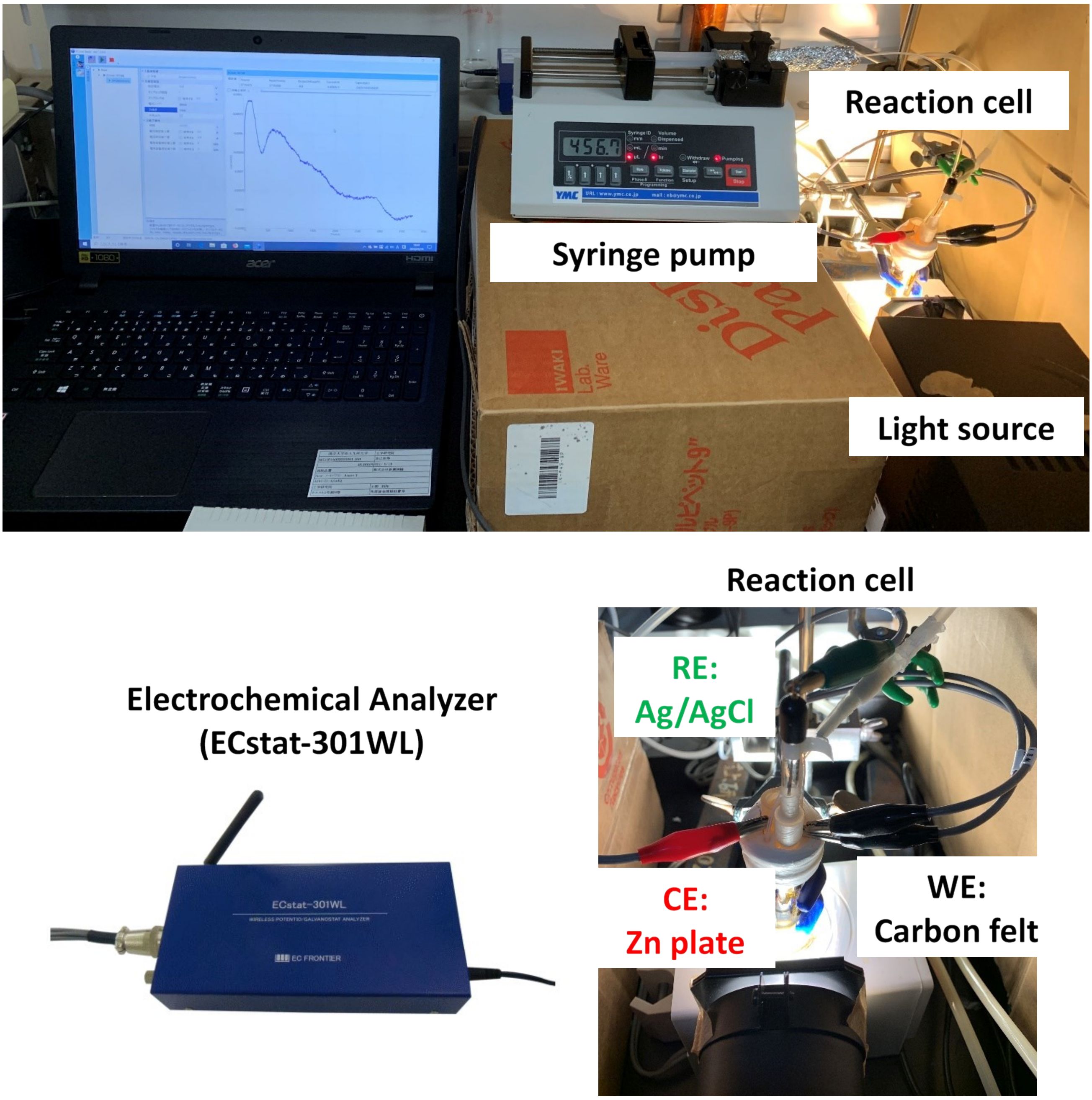
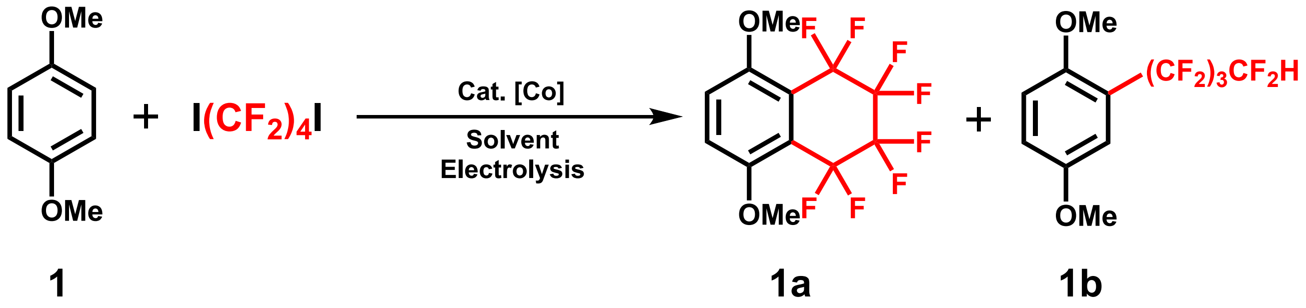


Figure S2. Experimental setup image of controlled-potential electrolysis.

Table S1. Optimization of the reaction conditions for the fluoroalkylation of **1** with 1,4-$C_4F_8I_2$[a]



Entry	Potential (V) *vs.* Ag/AgCl	Solvent[b]	$1,4\text{-}C_4F_8I_2$	Reaction time (h)	Conversion (%)[c]	1a Yield (%)[c]	1b Yield (%)[c]
S1	–0.8 V	CH_3CN	0.5 eq. of substrate per 1 h	6 h	$>$99	*trace*	1
S2	–0.8 V	DMSO	0.5 eq. of substrate per 1 h	6 h	18	*trace*	1
S3	–0.8 V	CH_3OH	0.5 eq. of substrate per 1 h	6 h	58	5	10
S4[d]	–0.8 V	CH_3OH	0.5 eq. of substrate per 1 h	6 h	1	0	*trace*
S5[e]	–0.8 V	CH_3OH	0.5 eq. of substrate per 1 h	6 h	63	*trace*	3
S6[f]	–0.8 V	CH_3OH	0.5 eq. of substrate per 1 h	6 h	52	*trace*	2
S7[f]	–0.8 V	CH_3CN	0.5 eq. of substrate per 1 h	6 h	76	*trace*	*trace*
S8[e, f]	–0.8 V	CH_3CN	0.5 eq. of substrate per 1 h	6 h	0	*0*	*0*
S9	–0.8 V	CH_3OH	1.0 eq. of substrate per 1 h	9 h	$>$99	8	12
S10[g]	–0.8 V	CH_3OH	1.0 eq. of substrate per 1 h	9 h	$>$99	30	23

[a] Reaction conditions: [**C1**] = 5.0×10^{-4} M; [1,4-dimethoxybenzene (**1**)] = 5.0×10^{-2} M; [n-Bu_4NClO_4] = 0.1 M; Decafluorobiphenyl ($C_{12}F_{10}$) as the internal standard; WE: carbon felt; CE: Zn plate; RE: Ag/AgCl (3.0 M NaCl aq.). [b] Abbreviations: CH_3CN, acetonitrile; DMSO, dimethyl sulfoxide; CH_3OH, methanol. [c] The conversions and yields are based on the initial concentration of 1,4-dimethoxybenzene (**1**) and were determined by gas chromatography-mass spectrometry (GC-MS). [d] In the absence of **C1**. [e] WE: Pt mesh. [f] **C2** as the catalyst. [g] With visible light (≥ 420nm).

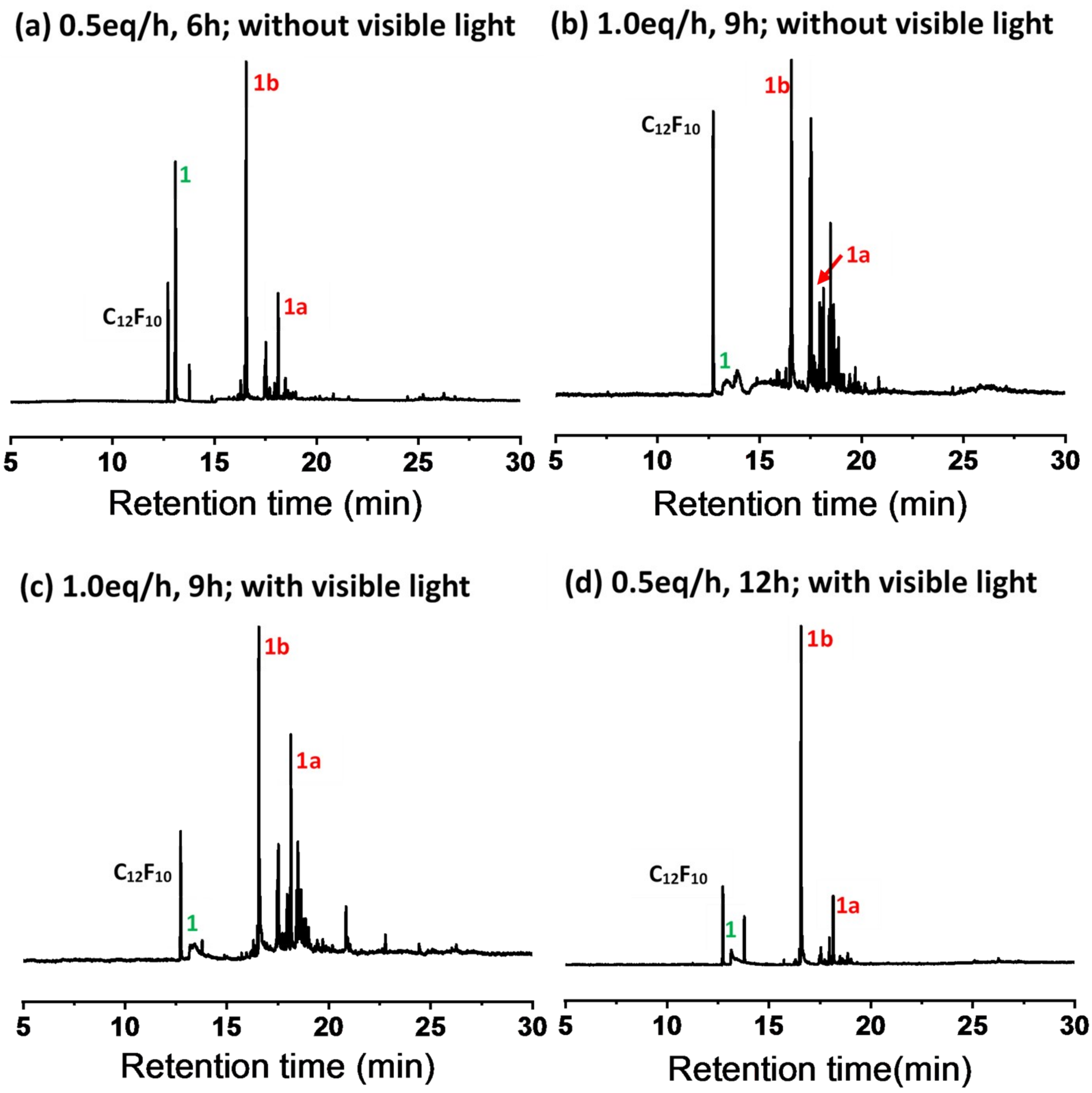
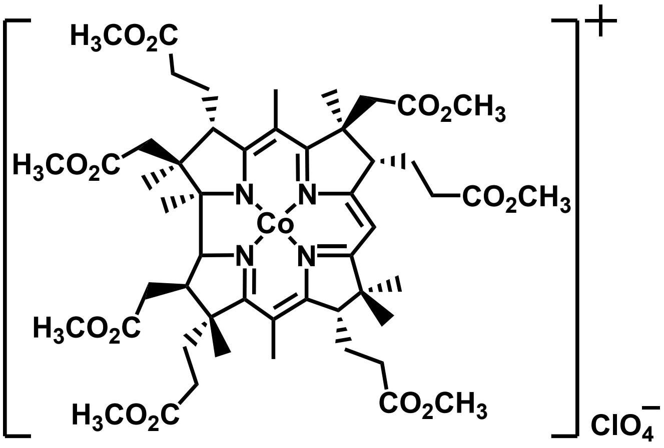
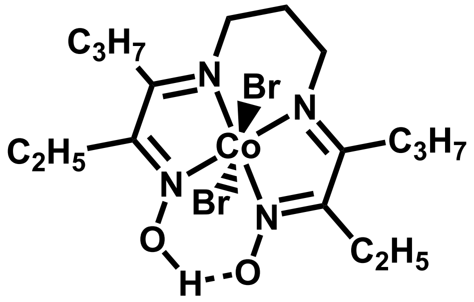


Figure S3. GC-MS spectra for electrochemical perfluoroalkylations of 1,4-dimethoxybenzene (**1**) as the substrate to yield the products **1a** and **1b** (here in red color) with different flow rates of 1,4-$C_4F_8I_2$ in the absence/presence of visible-light irradiation (≥ 420nm). (a) 0.5 eq. of substrate per 1 h for 6 h, without visible light (**Table S1, entry S3**); (b) 1.0 eq. of substrate per 1 h for 9 h, without visible light (**Table S1, entry S9**); (c) 1.0 eq. of substrate per 1 h for 9 h, with visible light (**Table S1, entry S10**) and (d) 0.5 eq. of substrate per 1 h for 12 h, with visible light (**Table 1, entry 2**). Decafluorobiphenyl ($C_{12}F_{10}$) and tetrabutylammonium perchlorate (TBAP, *n*-Bu_4NClO_4) were used as the internal standard and supporting electrolyte, respectively.



$[Cob(II)7C_1ester]ClO_4$
(Vitamin B_{12} derivative, C1)



$[Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2]$
(Imine/oxime-type cobalt complex, C2)

Figure S4. Molecular structures of $[Cob(II)7C_1ester]ClO_4$ (**C1**) and $[Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2]$ (**C2**).

The initial optimized results of the reactions are summarized in **Table S1**. After extensive efforts in different solvents, such as acetonitrile (CH_3CN), dimethyl sulfoxide (DMSO) and methanol (CH_3OH) (**Table S1, entries S1–S3**), CH_3OH was identified as a suitable solvent for this catalytic molecular transformation with the yields of the desired product **1a** to 5% and **1b** to 10% (**Table S1, entry S3; Figure S3(a)**), while other solvents almost failed to yield the desired products. Note that the absence of **C1** resulted in no formation of the desired fluoroalkylated compounds in CH_3OH (**Table S1, entry S4**). Similarly, the Pt mesh cathode also almost failed to afford the desired products (**Table S1, entry S5**). Furthermore, the imine/oxime-type cobalt complex, $[Co(III)\{(C_2C_3)(DO)(DOH)pn\}Br_2]$ (**C2**)[7] (**Figure S4**), was also examined for this molecular transformation under some conditions, such as different solvents and cathodes (**Table S1, entries S6–S8**). To our disappointed, the results were still not so well with almost no products formation. In order to improve the yield of desired products, the flow rate and concentration of 1,4-$C_4F_8I_2$ reagent were also measured to check the reactivity and improve the reaction conversion for better yields (**Table S1, entries S9** and **S10**). We found that increased speed of 1,4-$C_4F_8I_2$ addition led to a slight increase with 8% yield of **1a** and 12% yield of **1b** (**Table S1, entry S9**), associating with relatively lower selectivity (**Figure S3(b)**). In our previous work, visible-light irradiation was essential for the reaction to proceed using **C1** as the catalyst.[6] Herein visible-light promoted molecular transformation was also evaluated. As shown in **entry S10** (**Table S1**), considerable increases in the yields of **1a** and **1b** were observed up to 30% and 23%, respectively, along with a lower selectivity (**Figure S3(c)**). To improve the selectivity and obtain better yields for desired products, further optimizations were shown in **Table 1** based on these findings.

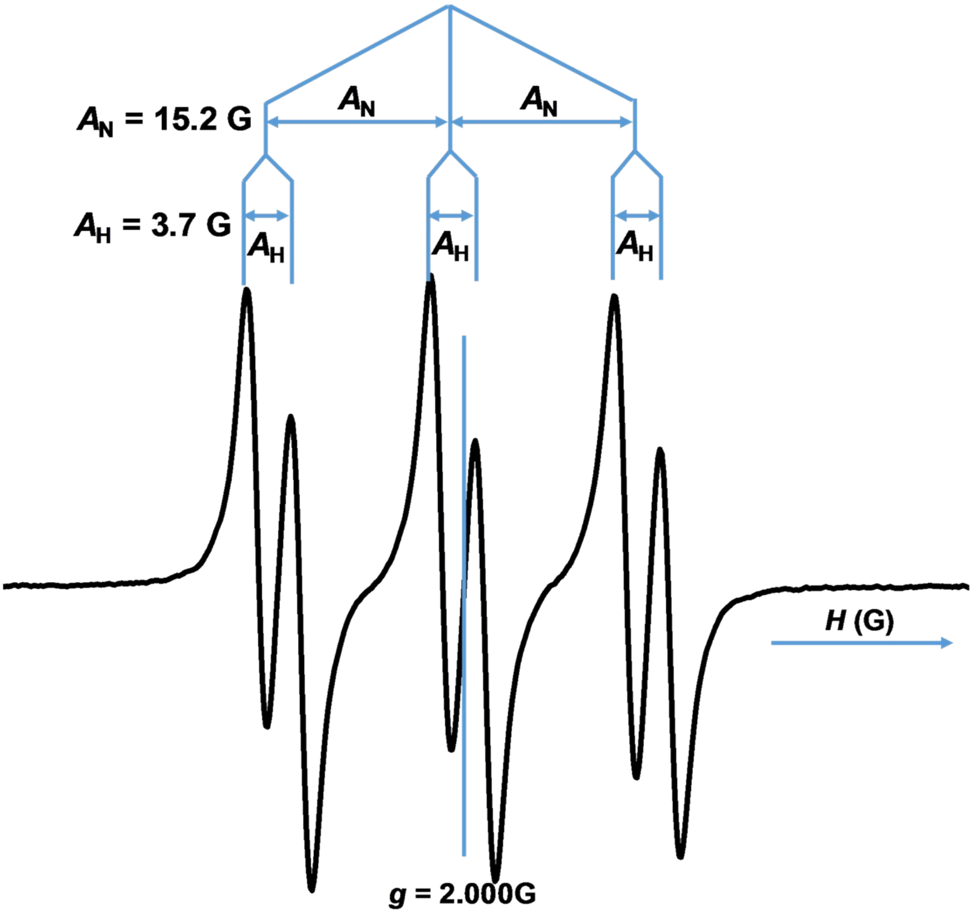


Figure S5. ESR spectrum observed during the electrocatalytic reaction in the presence of 6eq. *N-tert*-butyl-*α*-phenylnitrone (PBN, 3.0×10^{-1} M) to the 1,4-dimethoxybenzene (**1**) (5.0×10^{-2} M) in methanol under nitrogen. The setting parameters for the ESR measurements were a frequency of 9.87 GHz, a power of 1.05 mW, a center field of 3515 G, a sweep width of 150 G, a modulation amplitude of 0.5 G, a time constant of 40.96 ms, and a sweep time of 20.48 s.

Crystal Structures

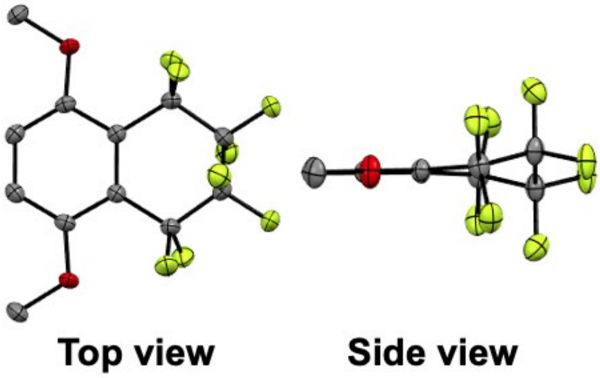


Figure S6. Crystal structure of **1a**. The thermal ellipsoid is drawn at 50% probability. Color code: C, gray; N, light blue; F, light green. Hydrogen atoms are omitted for clarity.

Table S2. Crystallographic data for **1a**.

Compound	**1a**
CCDC No.	2004379
empirical formula	$C_{12}H_8F_8O_2$
formula weight	336.18
temperature [K]	123
wavelength [Å]	0.71073
crystal system	monoclinic
space group	I2/a
a [Å]	6.8488(11)
b [Å]	11.665(2)
c [Å]	15.489(2)
α [°]	90
β [°]	95.319(14)
γ [°]	90
Volume [Å^3]	1232.1(4)
Z	4
Density (calculated) [g/cm^3]	1.812
Absorption coefficient [mm^{-1}]	0.201
F(000)	672.0
ϑ[°]	2.641 to 26.367
Reflections collected	1947
Independent reflections	1947 [$R_{(int)}$ = ?]*
Data / restraints / parameters	1947 / 0 / 102
Goodness-of-fit on F^2	0.840
$R1^a$ [$I>2\sigma(I)$]	0.0526
$wR2^b$ (all data)	0.1383
Largest diff. peak and hole [e.Å^{-3}]	0.38 and -0.34

*The $R_{(int)}$ value is not obtained due for non-merohedral twins.

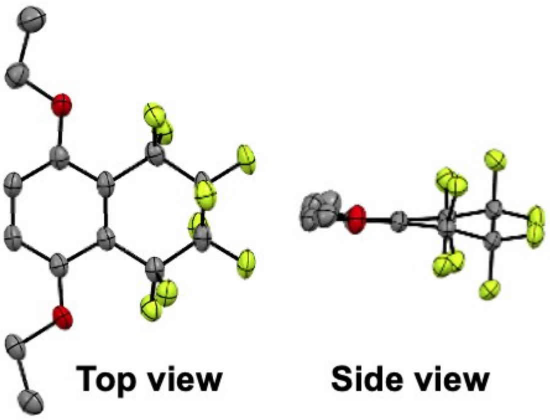


Figure S7. Crystal structure of **3a**. The thermal ellipsoid is drawn at 50% probability. Color code: C, gray; N, light blue; F, light green. Hydrogen atoms are omitted for clarity.

Table S3. Crystallographic data for **3a**.

Compound	**3a**
CCDC No.	2004380
empirical formula	$C_{14}H_{12}F_8O_2$
formula weight	364.24
temperature [K]	123
wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/n$
a [Å]	9.7335(7)
b [Å]	19.260(2)
c [Å]	15.5646(18)
α [°]	90
β [°]	94.317(8)
γ [°]	90
Volume [$Å^3$]	2909.5(5)
Z	8
Density (calculated) [g/cm^3]	1.663
Absorption coefficient [mm^{-1}]	0.177
F(000)	1472.0
θ [°]	2.489 to 26.372
Reflections collected	20021
Independent reflections	5937 [$R_{(int)}$ = 0.0684]
Data / restraints / parameters	5937 / 0 / 437
Goodness-of-fit on F^2	1.041
$R1^a$ [$I>2\sigma(I)$]	0.0611
$wR2^b$ (all data)	0.1851
Largest diff. peak and hole [e.$Å^{-3}$]	0.70 and -0.44

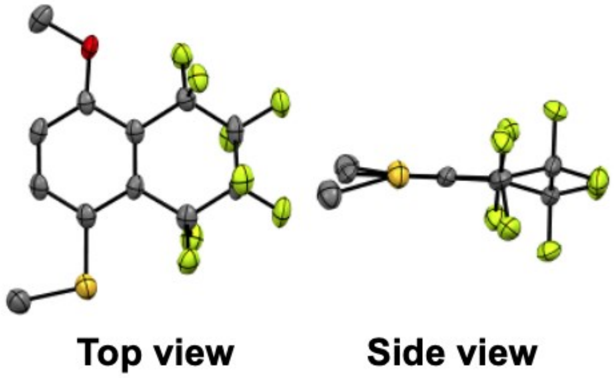


Figure S8. Crystal structure of **5a**. The thermal ellipsoid is drawn at 50% probability. Color code: C, gray; N, light blue; F, light green. Hydrogen atoms are omitted for clarity.

Table S4. Crystallographic data for **5a**.

Compound	**5a**
CCDC No.	2004381
empirical formula	$C_{12}H_8F_8OS$
formula weight	352.24
temperature [K]	123
wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	17.003(3)
b [Å]	7.6340(10)
c [Å]	19.904(3)
α [°]	90
β [°]	98.327(13)
γ [°]	90
Volume [Å^3]	2556.3(6)
Z	8
Density (calculated) [g/cm^3]	1.830
Absorption coefficient [mm^{-1}]	0.350
F(000)	1408.0
θ [°]	2.862 to 26.372
Reflections collected	16792
Independent reflections	5238 [$R_{(int)}$ = 0.1108]
Data / restraints / parameters	5238 / 0 / 401
Goodness-of-fit on F^2	0.951
$R1^a$ [$I>2\sigma(I)$]	0.0748
$wR2^b$ (all data)	0.2440
Largest diff. peak and hole [e.Å^{-3}]	0.85 and -0.63

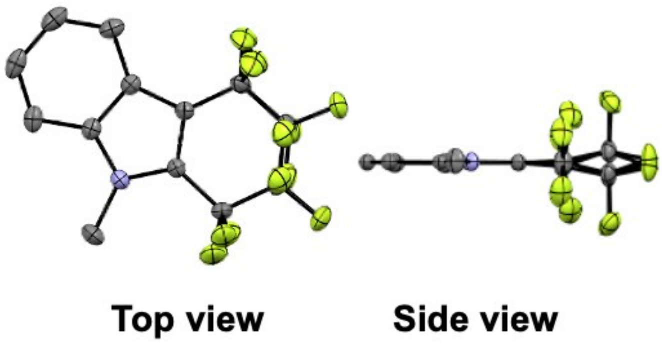


Figure S9. Crystal structure of **7a**. The thermal ellipsoid is drawn at 50% probability. Color code: C, gray; N, light blue; F, light green. Hydrogen atoms are omitted for clarity.

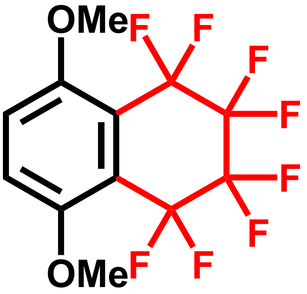
Table S5. Crystallographic data for **7a**.

Compound	**7a**
CCDC No.	2004382
empirical formula	$C_{13}H_7F_8N$
formula weight	329.20
temperature [K]	123
wavelength [Å]	0.71073
crystal system	orthorhombic
space group	Pnma
a [Å]	13.1069(9)
b [Å]	6.8506(6)
c [Å]	13.7875(12)
α [°]	90
β [°]	90
γ [°]	90
Volume [Å^3]	1237.98(17)
Z	4
Density (calculated) [g/cm^3]	1.766
Absorption coefficient [mm^{-1}]	0.189
F(000)	656.0
θ [°]	2.855 to 25.361
Reflections collected	8233
Independent reflections	1376 [$R_{(int)}$ = 0.0266]
Data / restraints / parameters	1376 / 84 / 167
Goodness-of-fit on F^2	1.054
$R1^a$ [$I>2\sigma(I)$]	0.0313
$wR2^b$ (all data)	0.0924
Largest diff. peak and hole [e.Å^{-3}]	0.23 and -0.21

Products data

Note: For the ^{13}C NMR (F coupled), some peaks for the C of perfluoroalkyl chain and C adjacent to perfluoroalkyl chain (in most cases) are too broad to be assigned (not shown in the following data for some compounds).[8]

1,1,2,2,3,3,4,4-octafluoro-5,8-dimethoxy-1,2,3,4-tetrahydronaphthalene (1a)



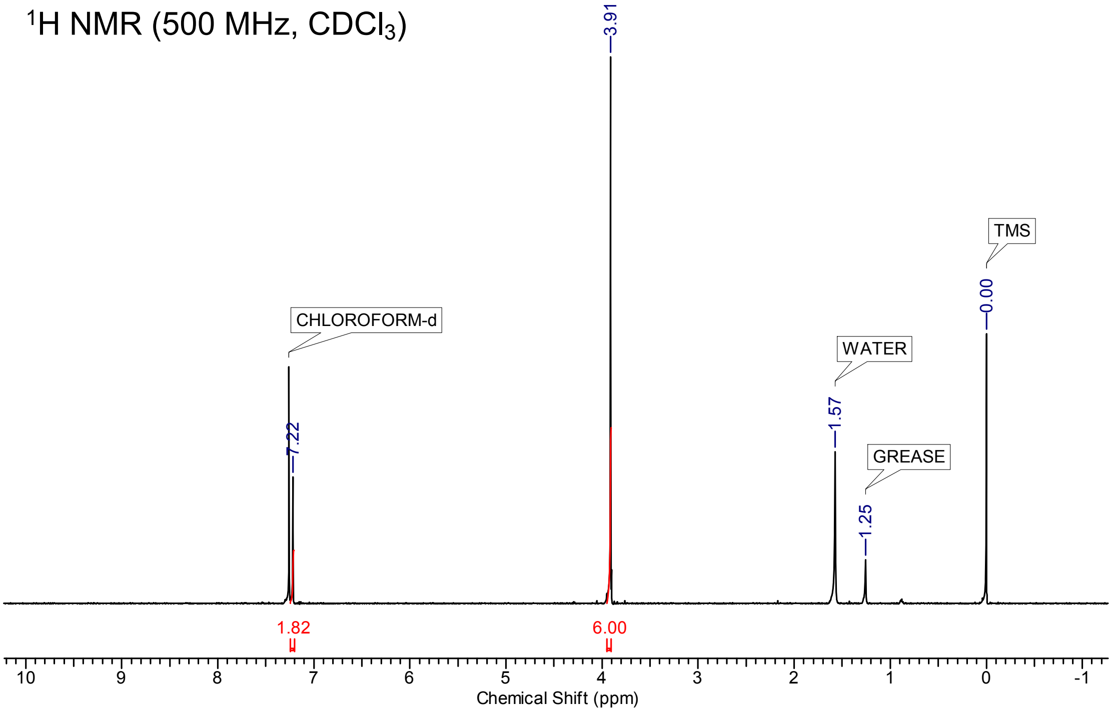
Compound **1a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 24% yield as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.22 (s, 2H), 3.91 (s, 6H);

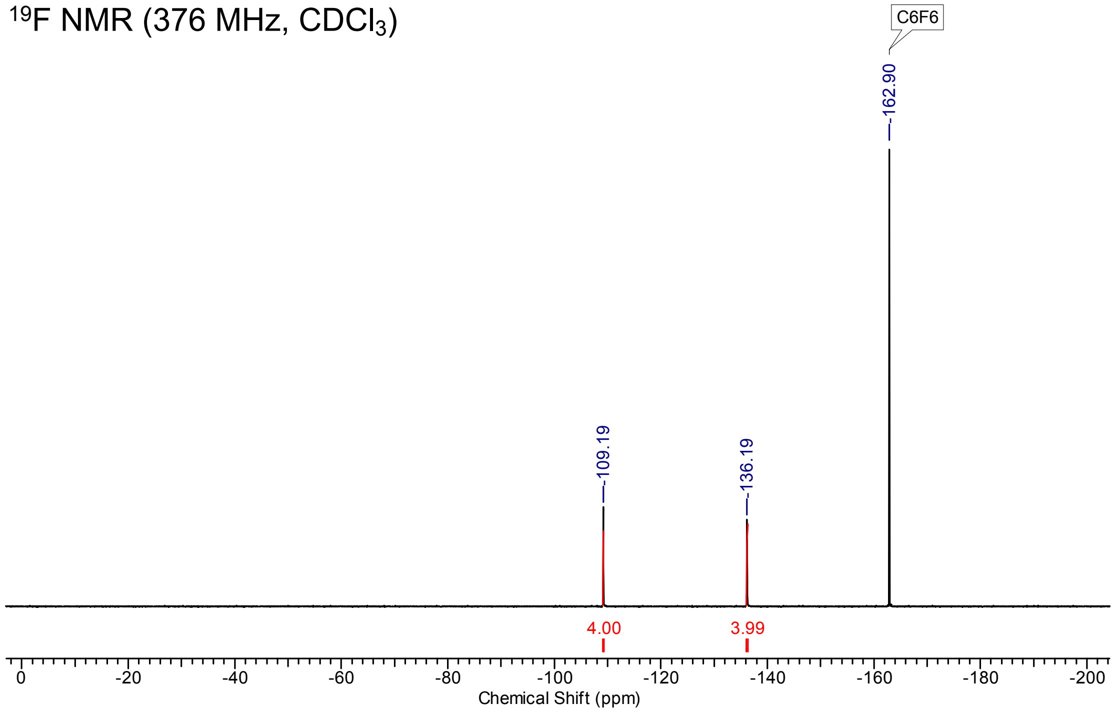
^{19}F NMR (376 MHz, CDCl$_3$): δ –109.19 (s, 4F), –136.19 (s, 4F);

^{13}C NMR (125 MHz, CDCl$_3$): δ 152.8, 117.9, 57.3;

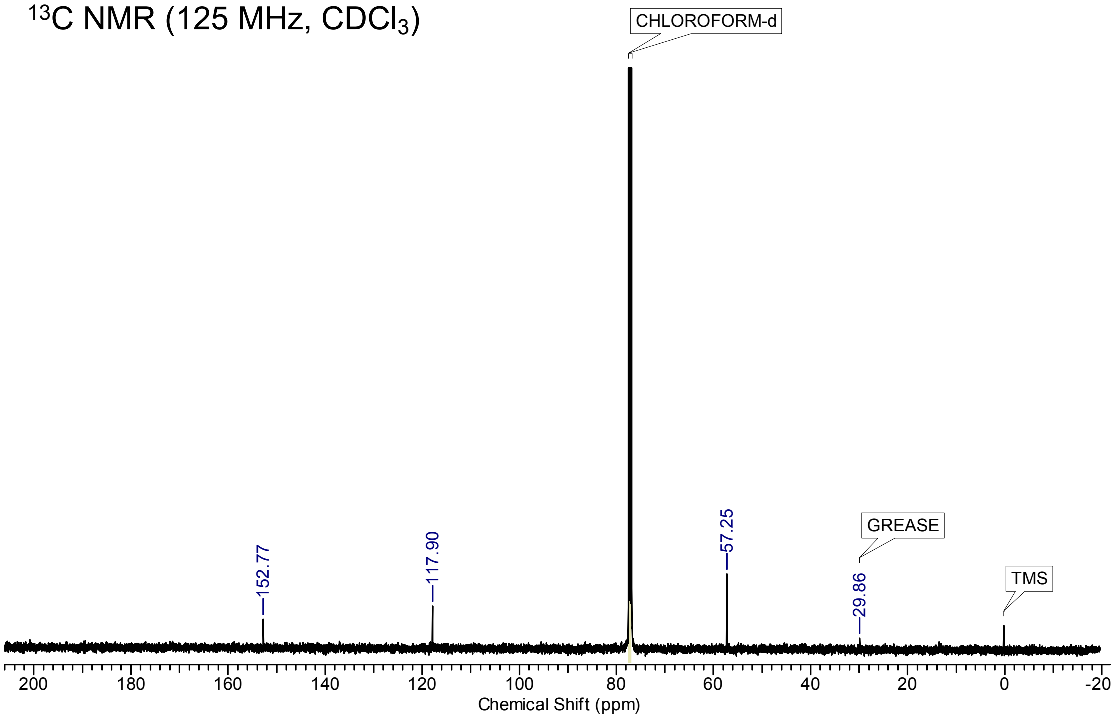
HRMS (EI, *m/z*): Cald. for $C_{12}H_8F_8O_2$ [M]$^+$ 336.0397; found: 336.0395.



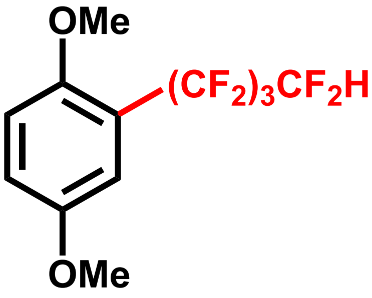
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



1,4-dimethoxy-2-(1,1,2,2,3,3,4,4-octafluorobutyl)benzene (1b)



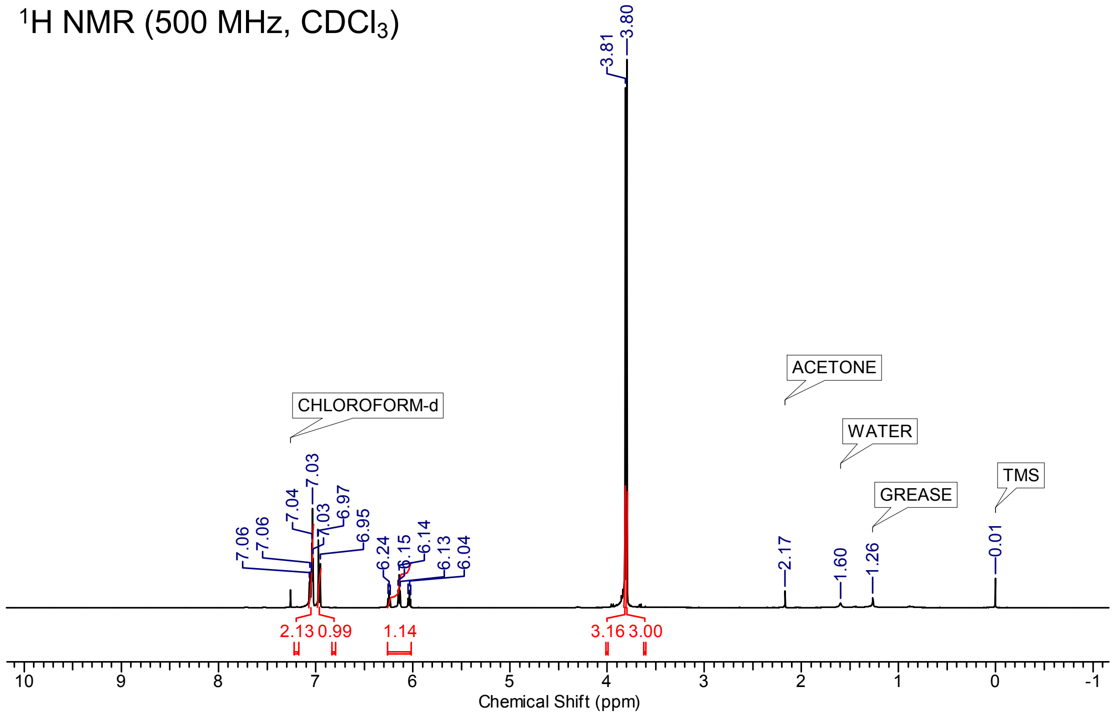
Compound **1b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 41% yield as a yellow oil.

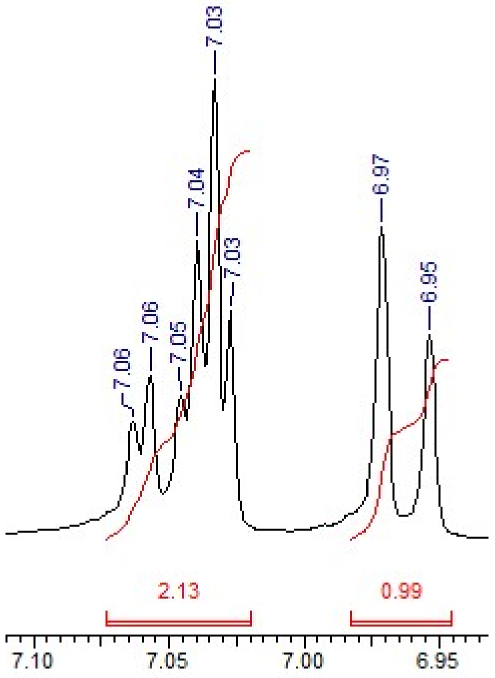
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06-7.03 (m, 2H), 6.96 (d, *J* = 8.83 Hz, 1H), 6.14 (tt, *J* = 52.33 Hz; 5.67 Hz, 1H), 3.81 (s, 3H), 3.80 (s, 3H);

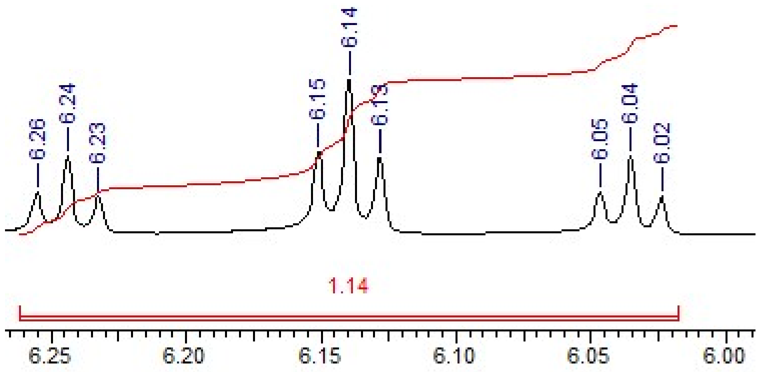
^{19}F NMR (376 MHz, $CDCl_3$): δ –108.80 (s, 2F), –124.65 (s, 2F), –131.59 (s, 2F), –138.47 (d, *J* = 47.69 Hz, 2F);

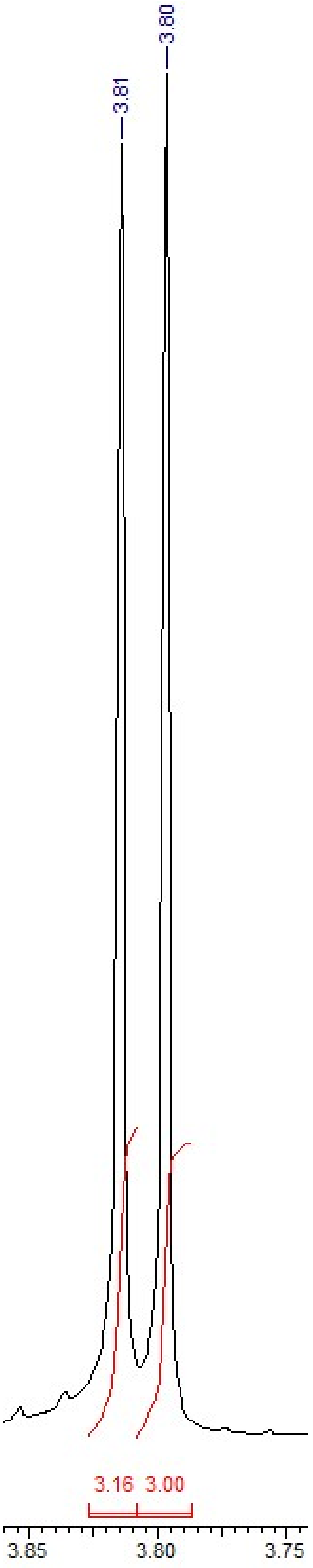
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 152.8, 118.9, 118.0, 116.4, 114.8, 114.5, 108.1, 106.1, 56.9, 56.1;

HRMS (EI, *m/z*): Cald. for $C_{12}H_{10}F_8O_2$ $[M]^+$ 338.0553; found: 338.0547.

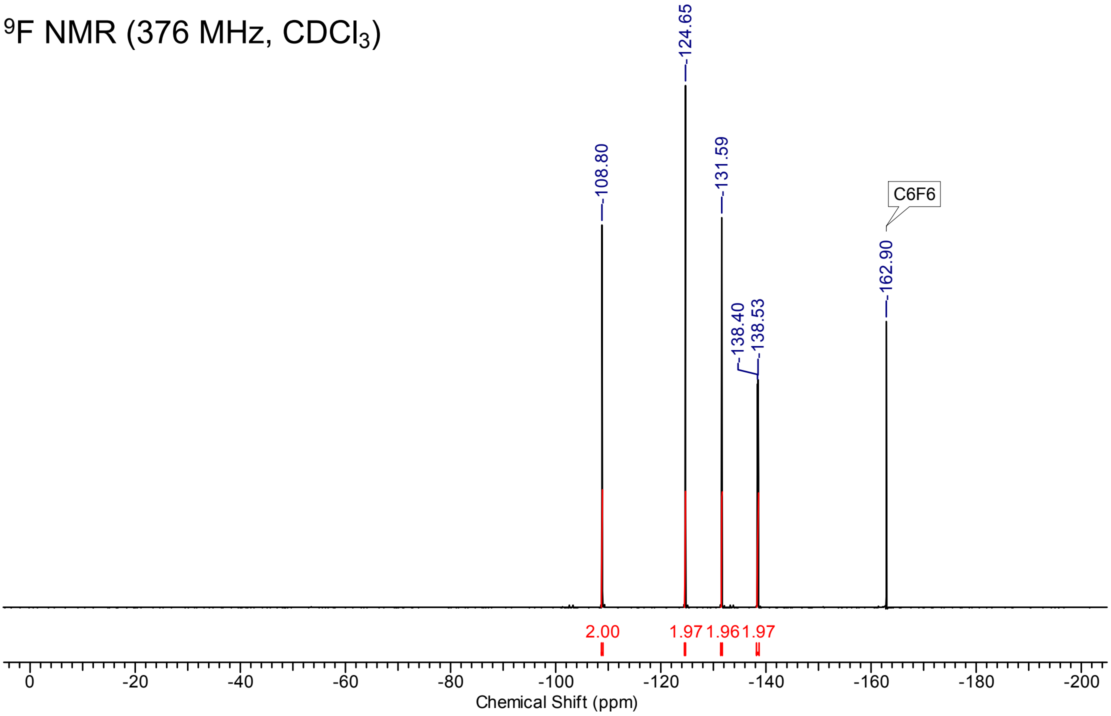



7.06
7.06
7.05
7.04
7.03
7.03
6.97
6.95
2.13
0.99
7.10
7.05
7.00
6.95

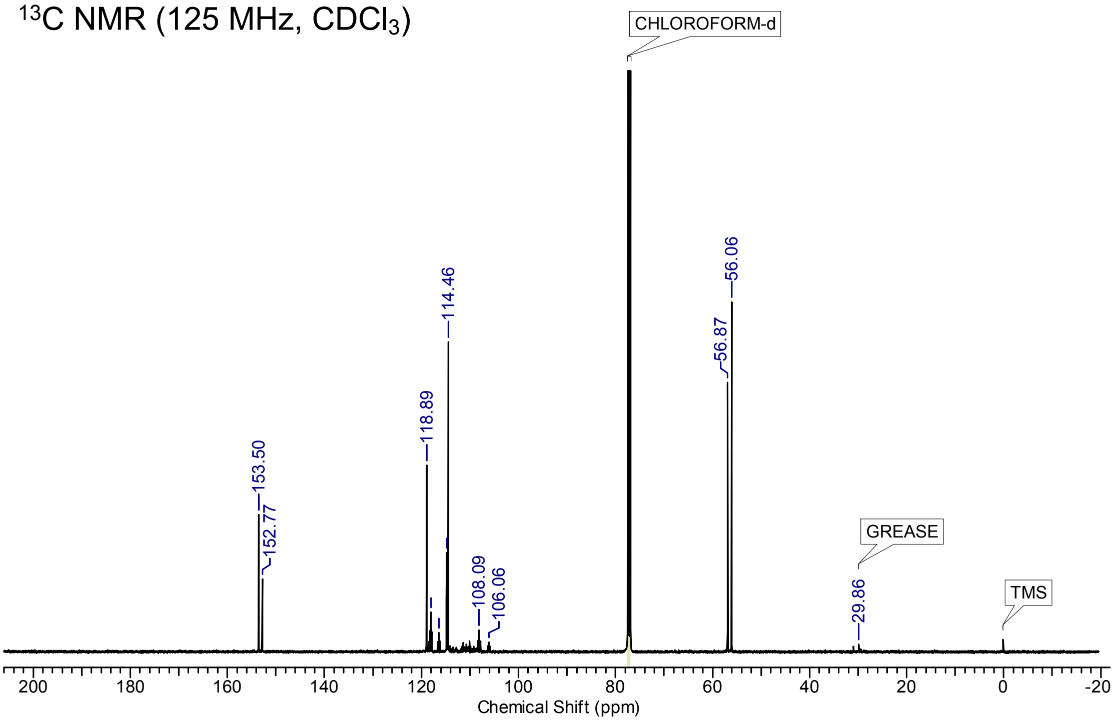

6.26
6.24
6.23
6.15
6.14
6.13
6.05
6.04
6.02
1.14
6.25
6.20
6.15
6.10
6.05
6.00


3.81
3.80
3.16
3.00
3.85
3.80
3.75

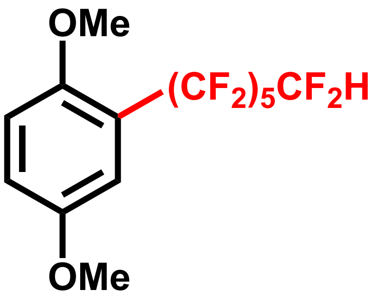
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



2-(1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexyl)-1,4-dimethoxybenzene (1c)



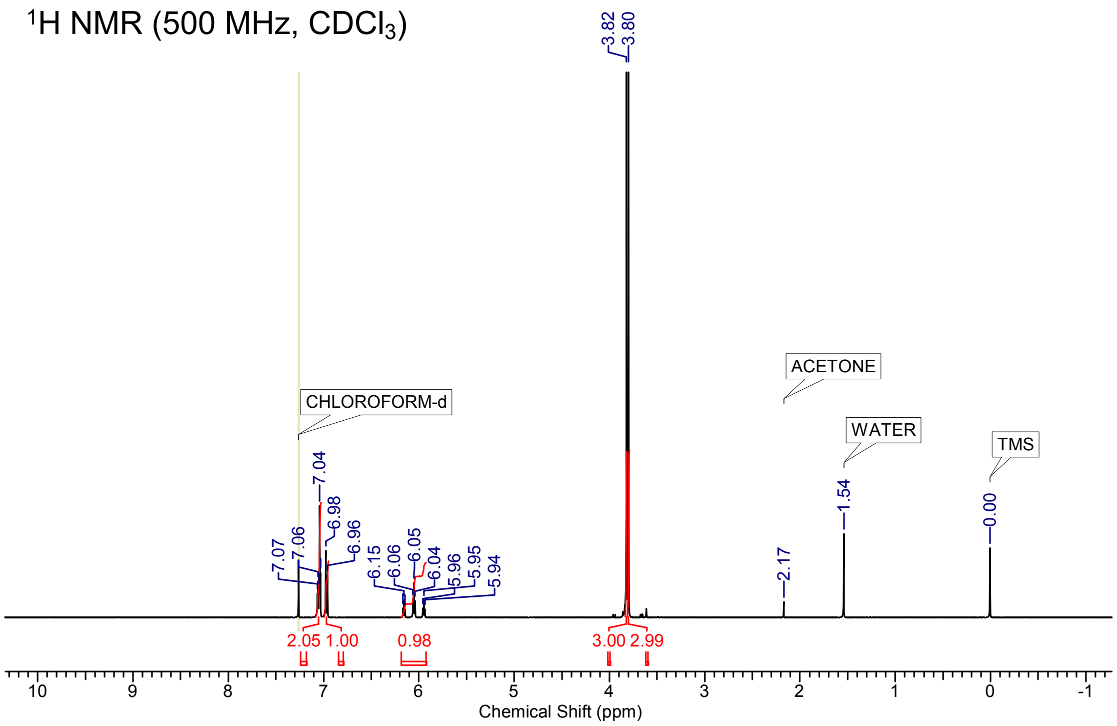
Compound **1c** was prepared according to the general procedure using dodecafluoro-1,6-diiodohexane, 1,6-$C_6F_{12}I_2$ (6 eq., 830.79 mg, 5.0×10^{-2} M) in 51% yield as a colorless oil.

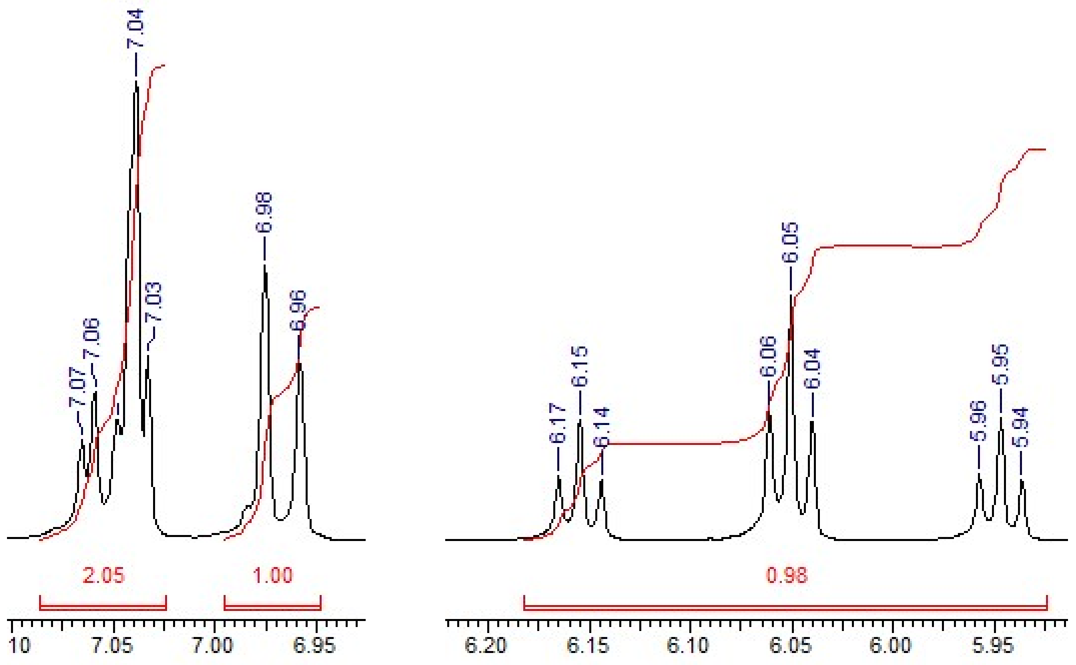
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07-7.03 (m, 2H), 6.97 (d, *J* = 8.51 Hz, 1H), 6.05 (tt, *J* = 52.02 Hz; 5.36 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ −108.84 (s, 2F), −122.30 (s, 2F), −123.03 (s, 2F), −124.59 (s, 2F), −130.89 (s, 2F), −138.20 (d, *J* = 59.60 Hz, 2F);

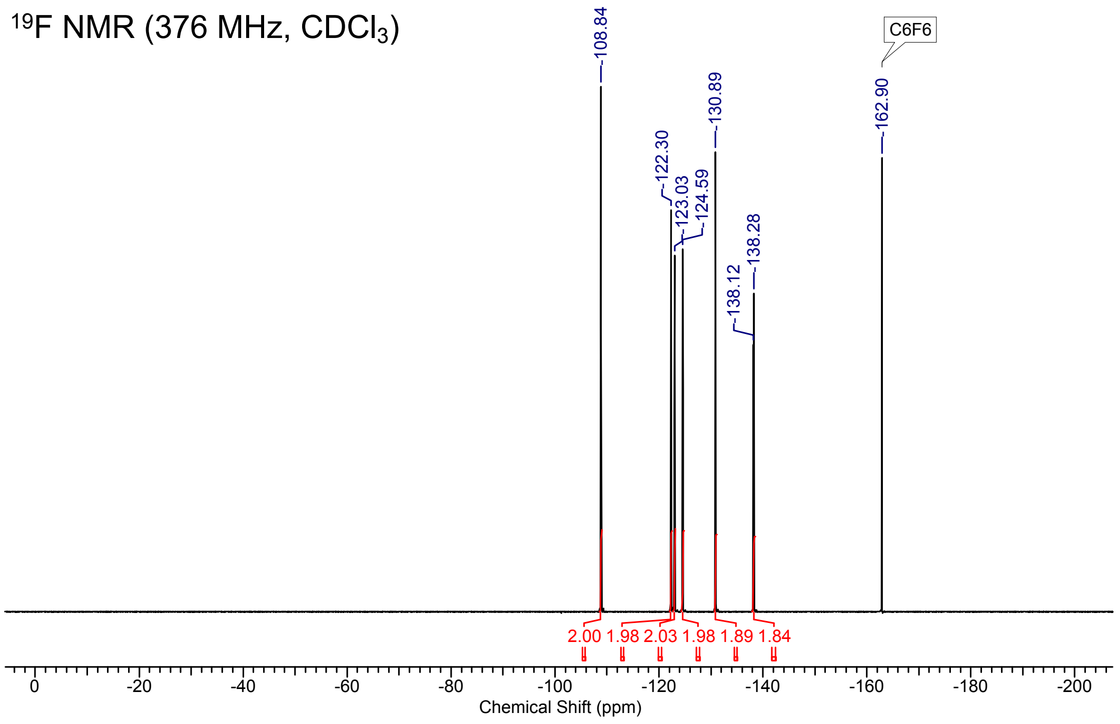
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 152.9, 119.0, 118.2, 116.4, 114.8, 114.5, 109.9, 107.8, 105.8, 57.0, 56.1;

GC-MS (*m/z*): Cald. for $C_{14}H_{10}F_{12}O_2$ $[M]^+$ 438; found: 438.

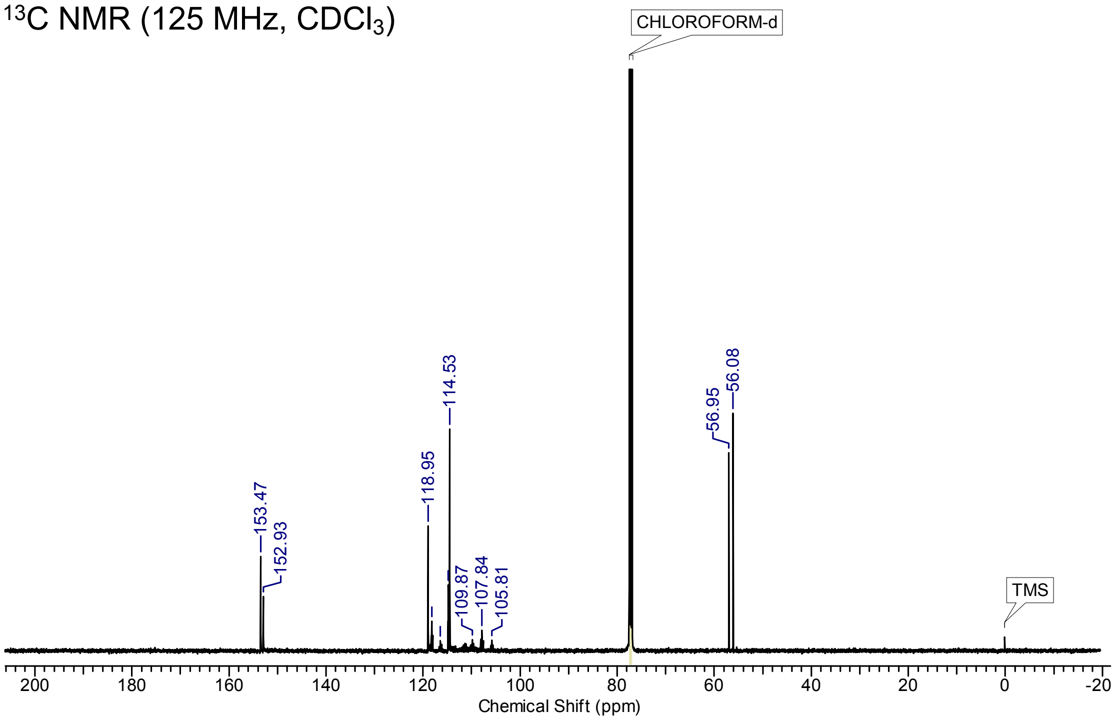




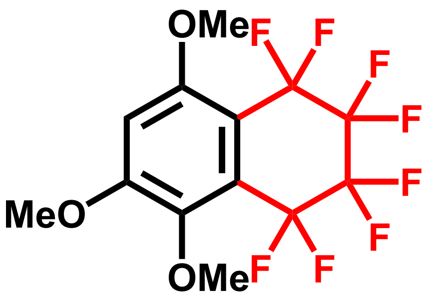
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



1,1,2,2,3,3,4,4-octafluoro-5,6,8-trimethoxy-1,2,3,4-tetrahydronaphthalene (2a)



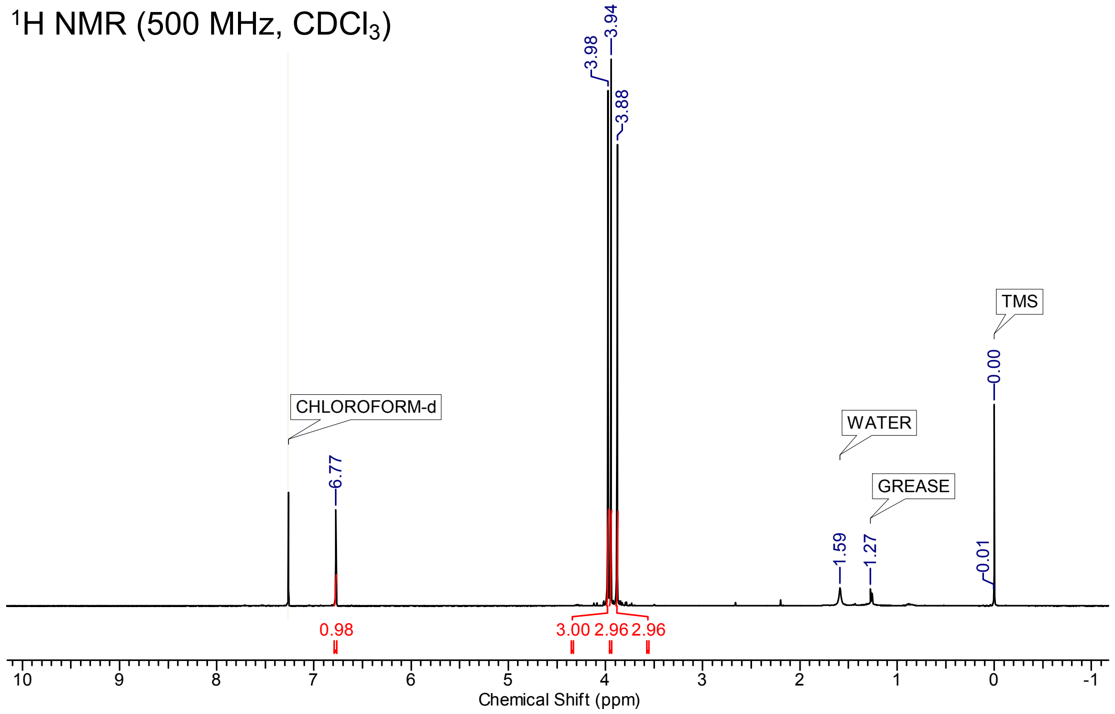
Compound **2a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 11% yield as a white solid.

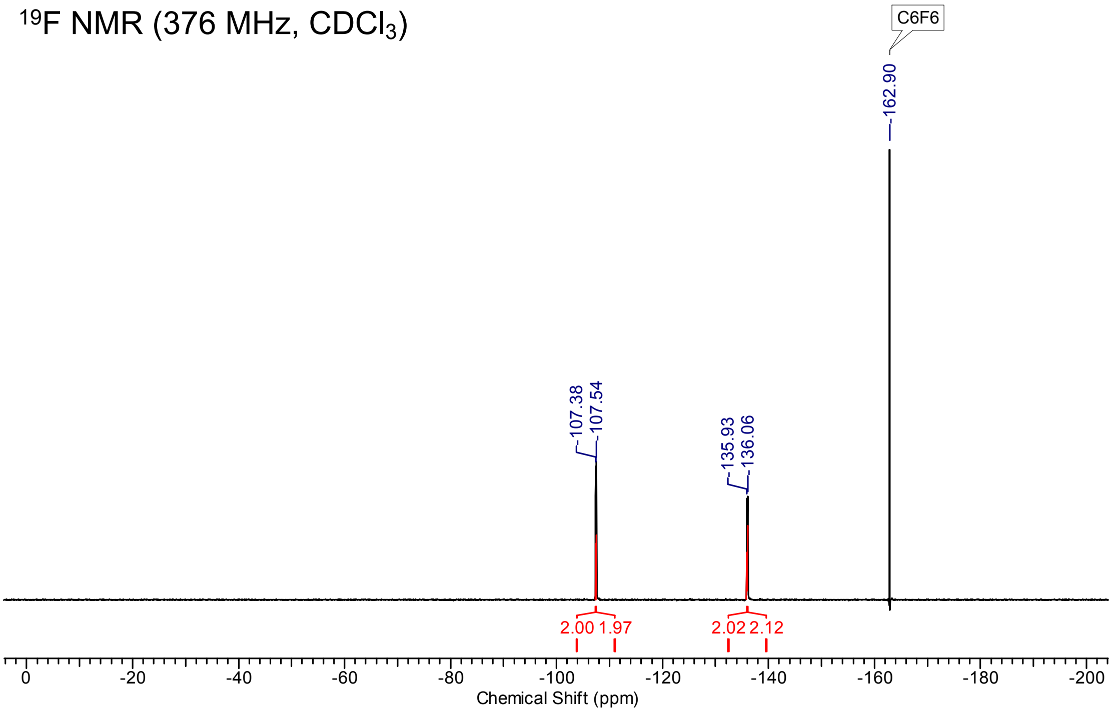
^{1}H NMR (500 MHz, CDCl$_3$): δ 6.77 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.88 (s, 3H);

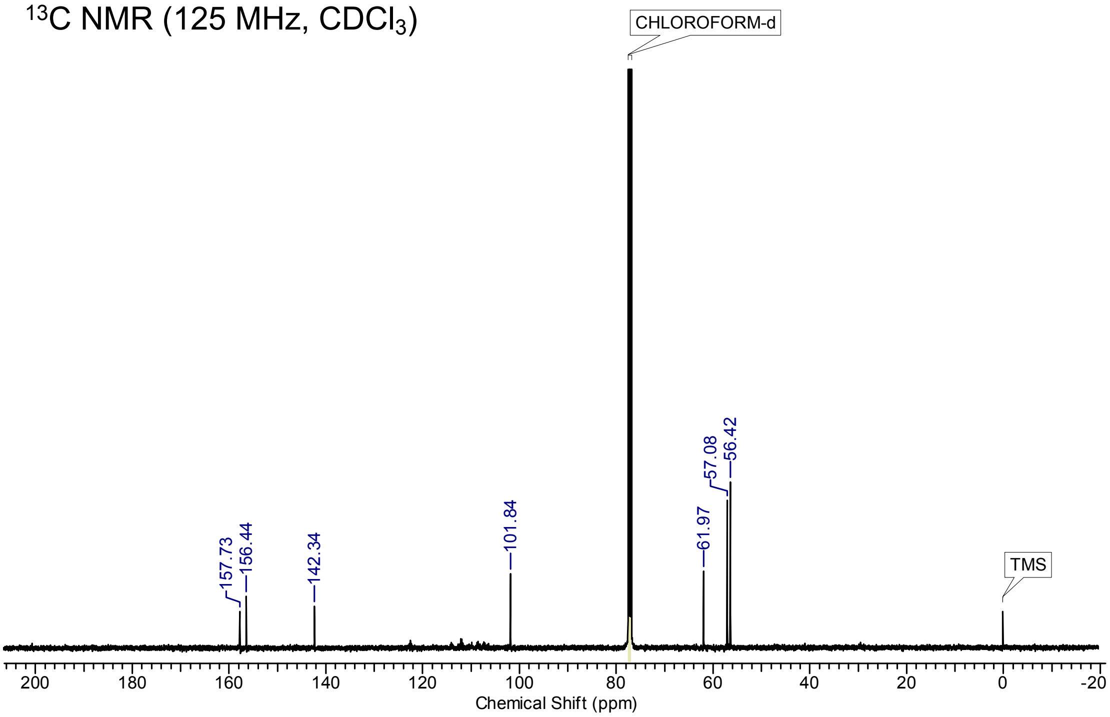
^{19}F NMR (376 MHz, CDCl$_3$): δ –107.38 (s, 2F), –107.54 (s, 2F), –135.93 (s, 2F), –136.06 (s, 2F);

^{13}C NMR (125 MHz, CDCl$_3$): δ 157.7, 156.4, 142.3, 101.8, 62.0, 57.1, 56.4;

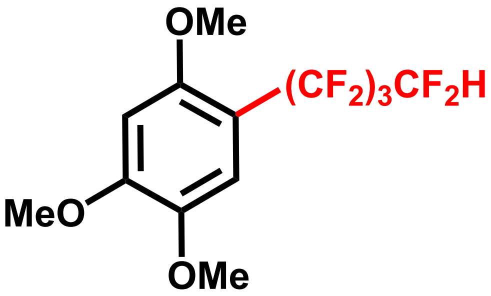
HRMS (EI, *m/z*): Cald. for $C_{13}H_{10}F_8O_3$ [M]$^+$ 366.0502; found: 366.0511.




^{19}F NMR (376 MHz, $CDCl_3$)
C6F6
-162.90
-107.38
-107.54
-135.93
-136.06
2.00
1.97
2.02
2.12
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)


^{13}C NMR (125 MHz, $CDCl_3$)
CHLOROFORM-d
157.73
156.44
142.34
101.84
61.97
57.08
56.42
TMS
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

1,2,5-trimethoxy-3-(1,1,2,2,3,3,4,4-octafluorobutyl)benzene (2b)



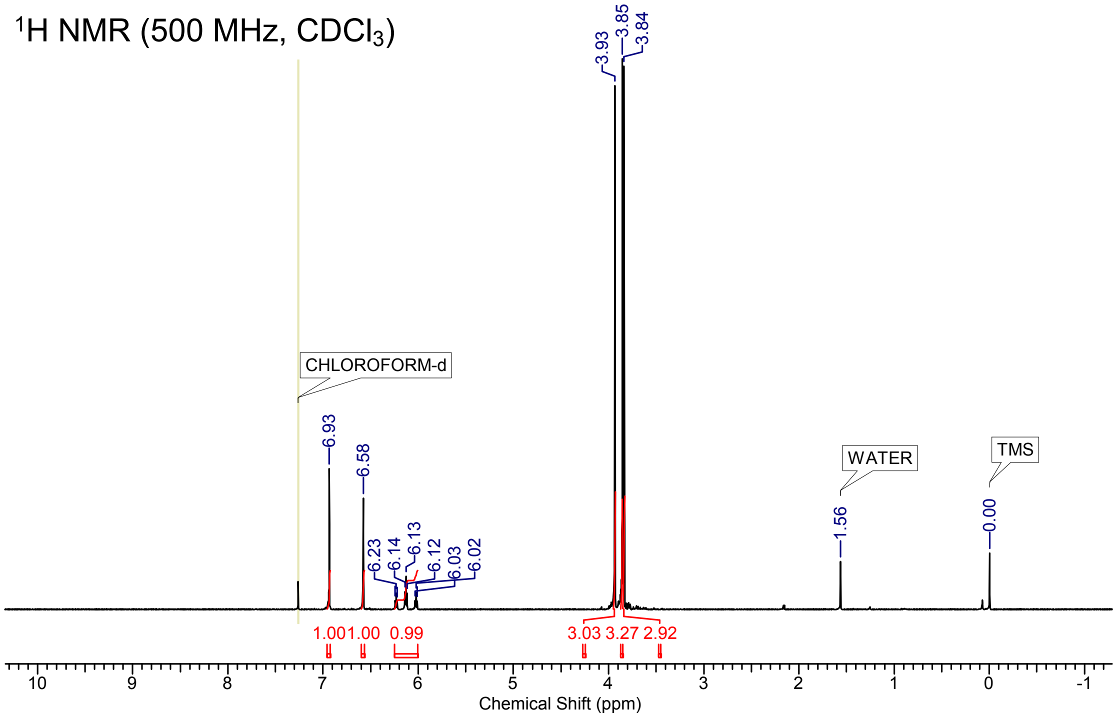
Compound **2b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 29% yield as a yellow oil.

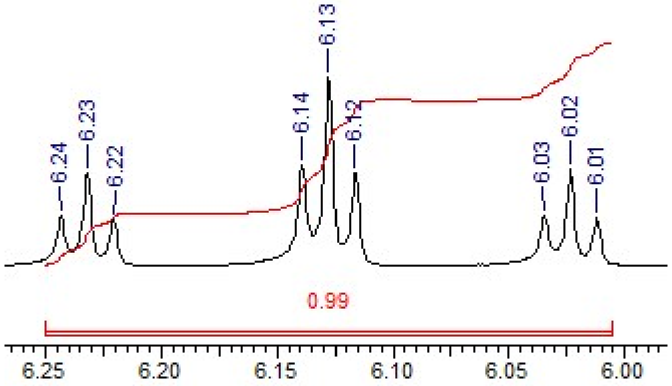
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 1H), 6.58 (s, 1H), 6.13 (tt, *J* = 52.33 Hz; 5.67 Hz, 1H), 3.93 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –107.54 (s, 2F), –124.65 (s, 2F), –131.40 (s, 2F), –138.31 (d, *J* = 47.68 Hz, 2F);

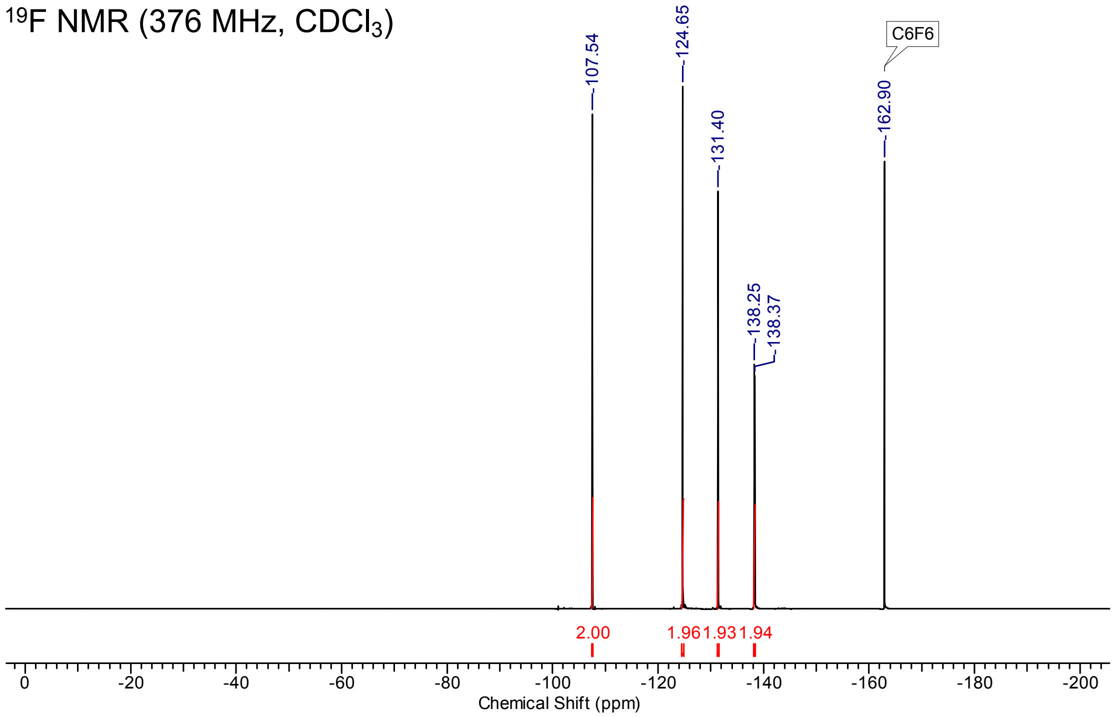
^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 153.3, 143.2, 118.6, 116.6, 114.5, 112.3, 108.3, 106.1, 98.7, 57.1, 56.9, 56.2;

HRMS (EI, *m/z*): Cald. for $C_{13}H_{12}F_8O_3$ $[M]^+$ 368.0659; found: 368.0659.

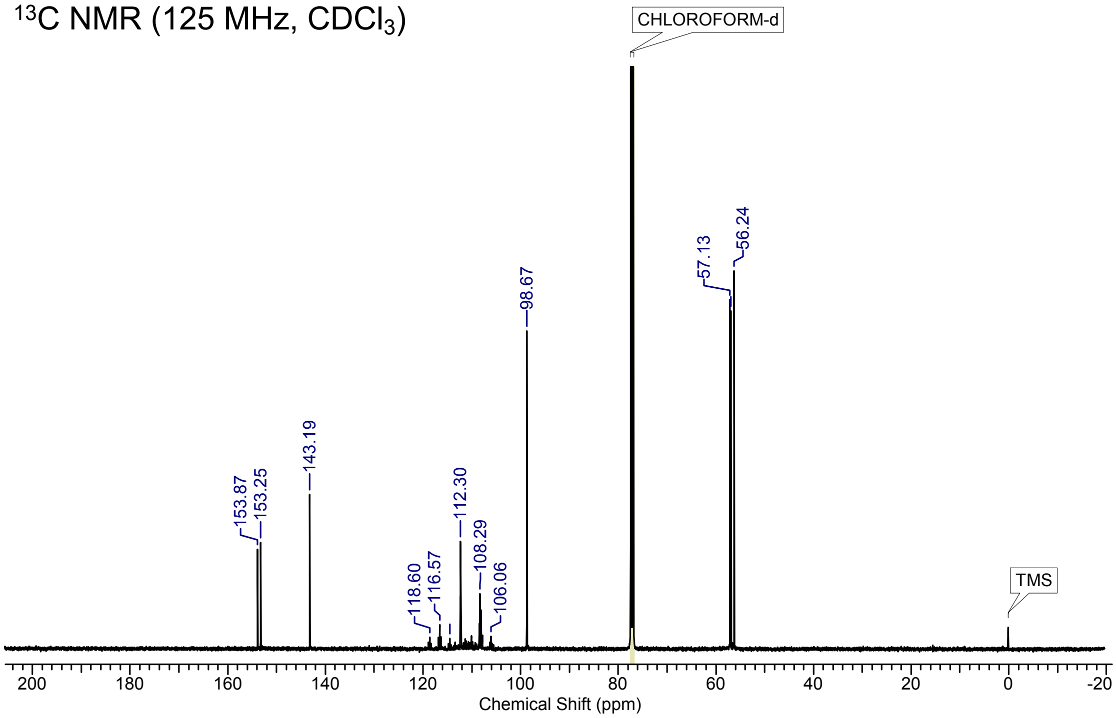




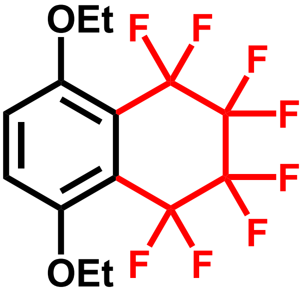
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



5,8-diethoxy-1,1,2,2,3,3,4,4-octafluoro-1,2,3,4-tetrahydronaphthalene (3a)



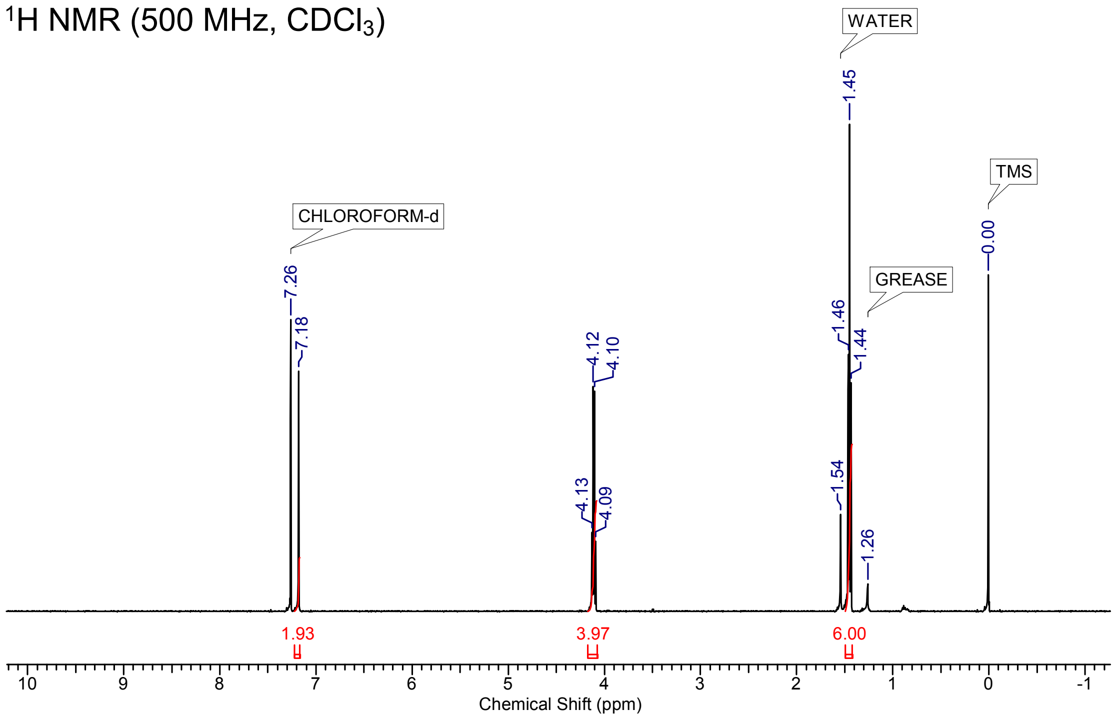
Compound **3a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 9% yield as a white solid.

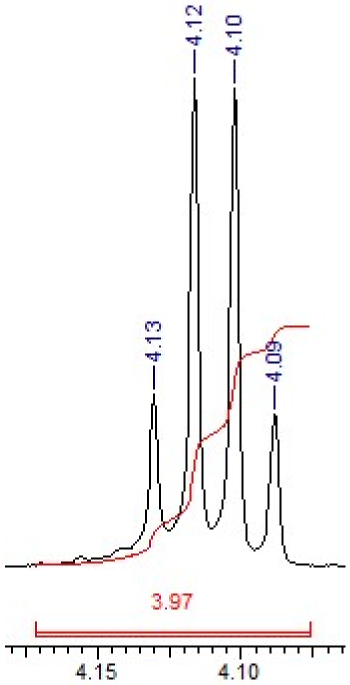
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (s, 2H), 4.11(q, *J* = 6.94 Hz, 4H), 1.45 (t, *J* = 6.94 Hz, 6H);

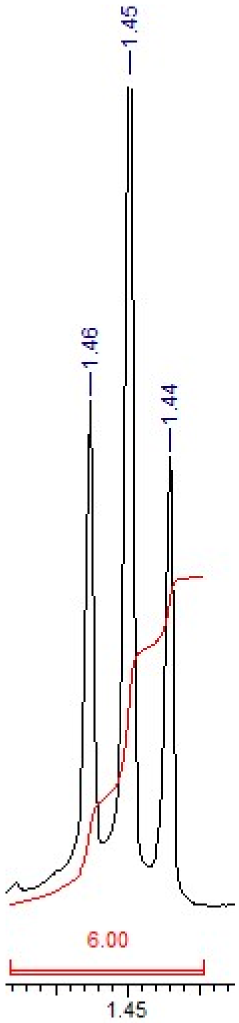
^{19}F NMR (376 MHz, $CDCl_3$): δ –109.06 (s, 4F), –136.28 (s, 4F);

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 119.0, 66.2, 14.8;

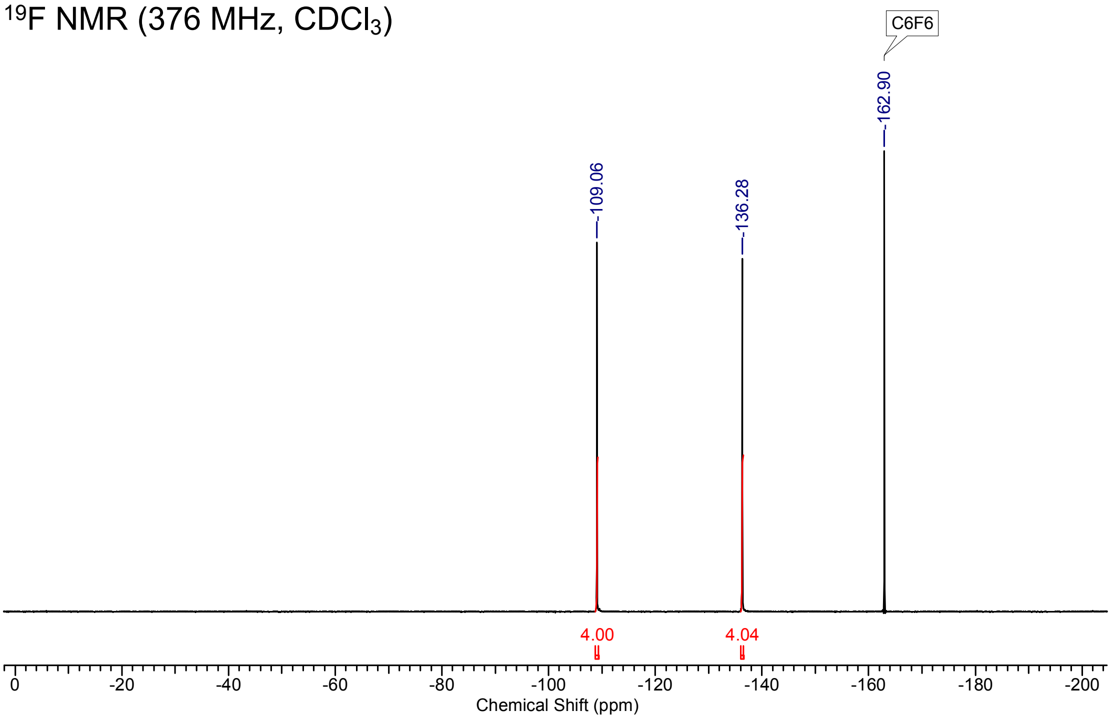
HRMS (EI, *m/z*): Cald. for $C_{14}H_{12}F_8O_2$ $[M]^+$ 364.0710; found: 364.0711.



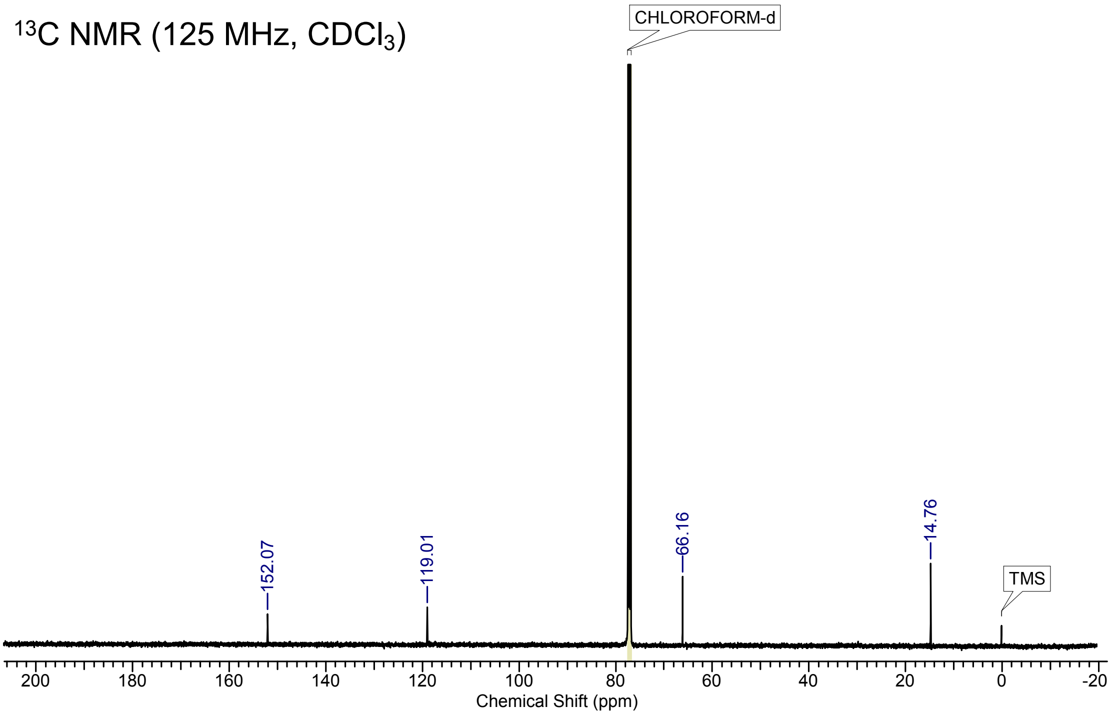

4.13
4.12
4.10
4.09
3.97
4.15
4.10


1.45
1.46
1.44
6.00
1.45

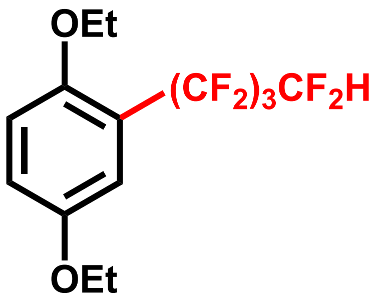
^{19}F NMR (376 MHz, CDCl$_3$)



^{13}C NMR (125 MHz, CDCl$_3$)



1,4-diethoxy-2-(1,1,2,2,3,3,4,4-octafluorobutyl)benzene (3b)



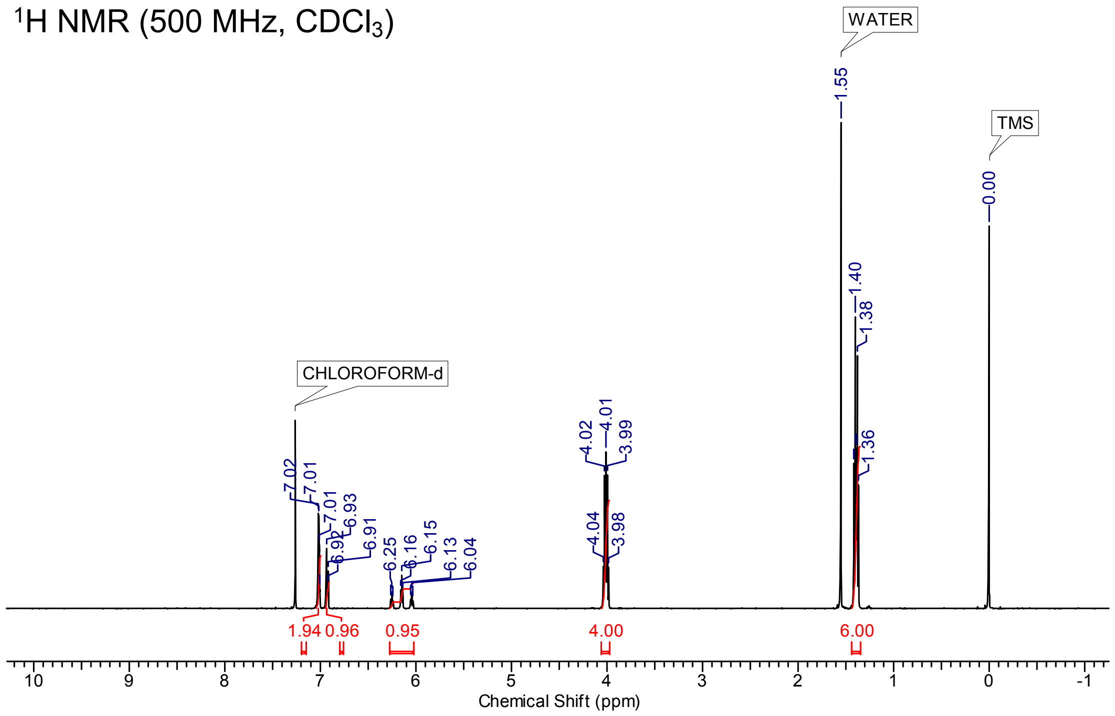
Compound **3b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 14% yield as a yellow oil.

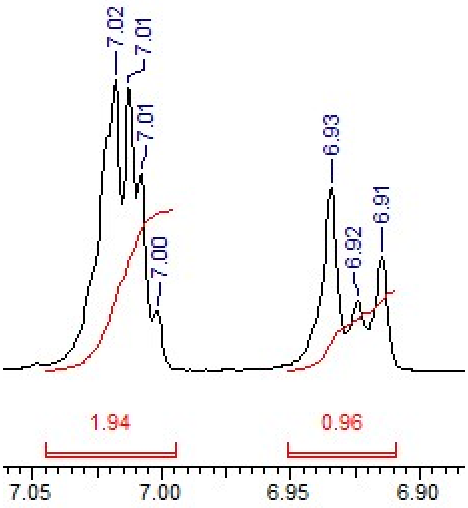
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02-7.00 (m, 2H), 6.93-6.91 (m, 1H), 6.15 (tt, *J* = 52.33 Hz; 5.67 Hz, 1H), 4.04-3.98 (m, 4H), 1.41-1.36 (m, 6H);

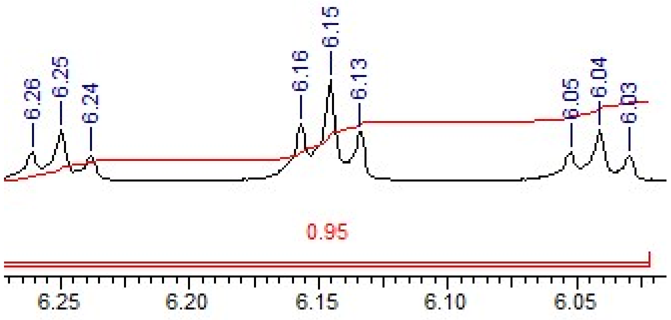
^{19}F NMR (376 MHz, $CDCl_3$): δ –108.61 (s, 2F), –124.46 (s, 2F), –131.72 (s, 2F), –138.50 (d, *J* = 47.69 Hz, 2F);

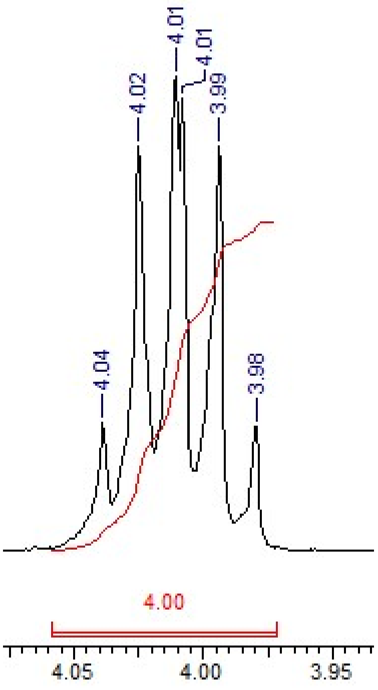
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 152.0, 119.6, 118.1, 116.4, 115.4, 115.3, 115.2, 65.5, 64.5, 14.9, 14.7;

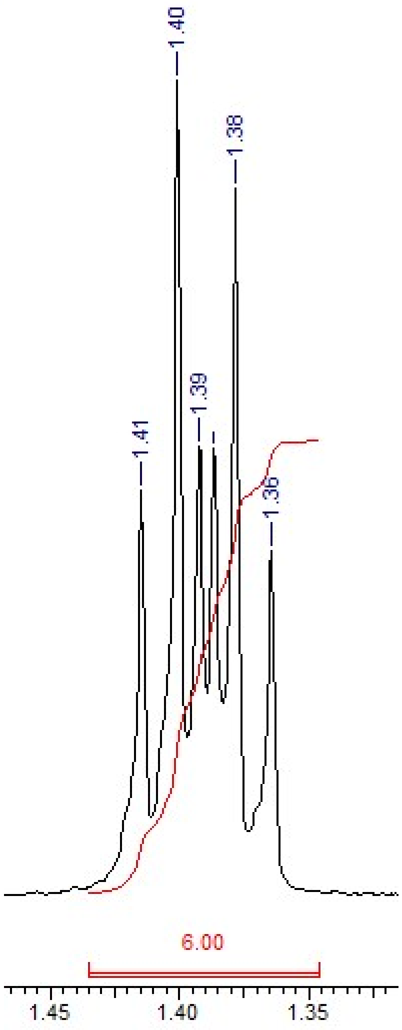
HRMS (EI, *m/z*): Cald. for $C_{14}H_{14}F_8O_2$ $[M]^+$ 366.0866; found: 366.0866.



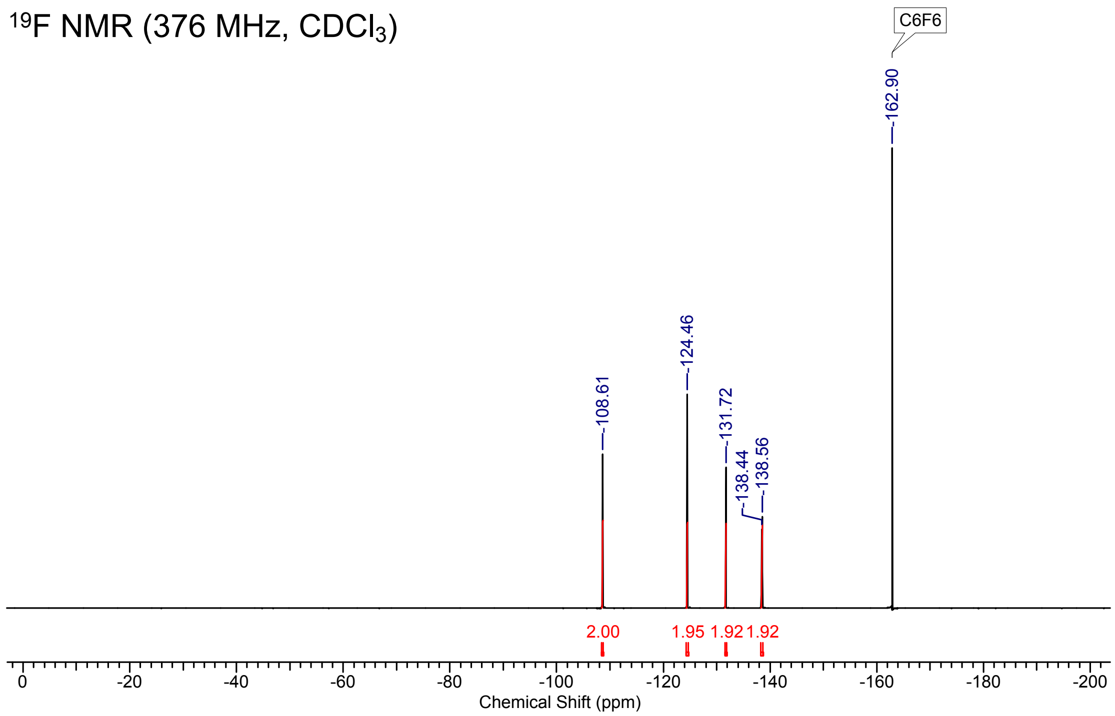

7.02
7.01
7.01
7.00
6.93
6.92
6.91
1.94
0.96
7.05
7.00
6.95
6.90


6.26
6.25
6.24
6.16
6.15
6.13
6.05
6.04
6.03
0.95
6.25
6.20
6.15
6.10
6.05

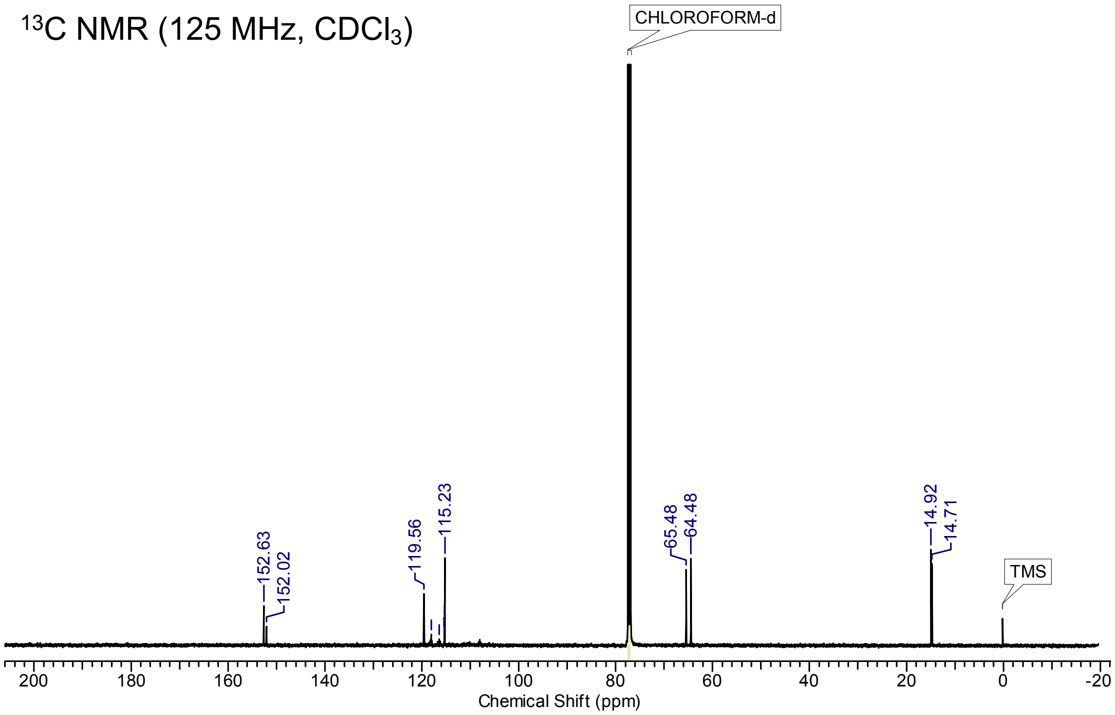

4.04
4.02
4.01
4.01
3.99
3.98
4.00
4.05
4.00
3.95


1.41
1.40
1.39
1.38
1.36
6.00
1.45
1.40
1.35

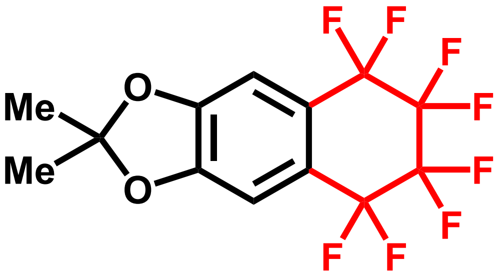
^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



5,5,6,6,7,7,8,8-octafluoro-2,2-dimethyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole (4a)



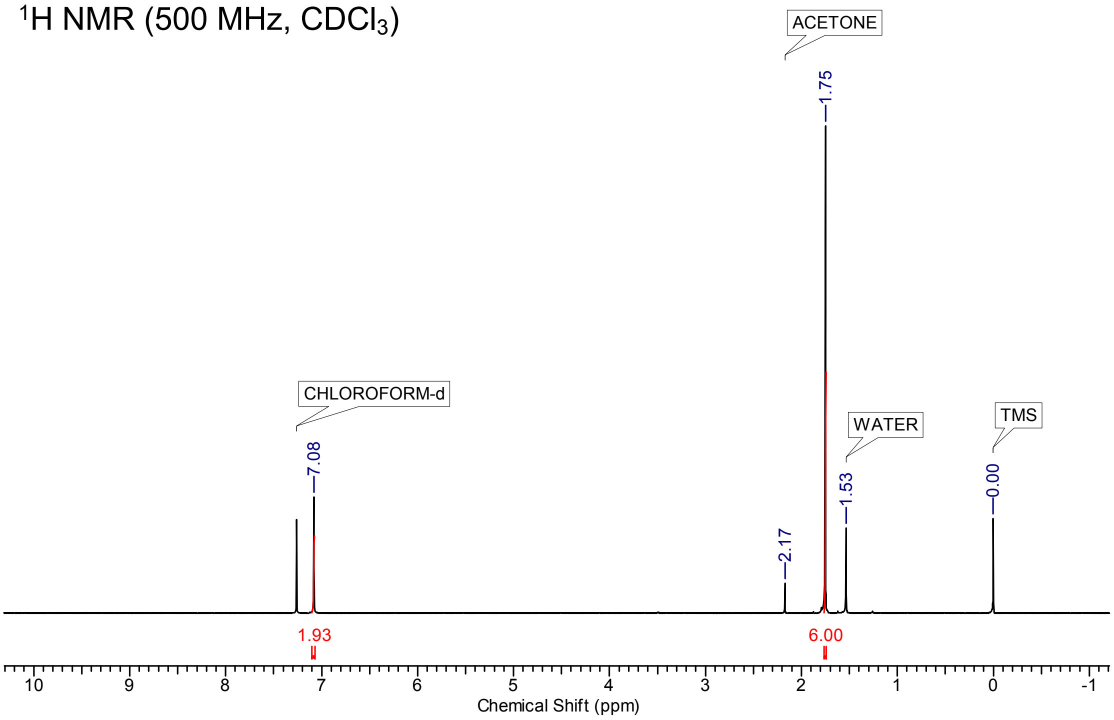
Compound **4a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 7% yield as a white solid.

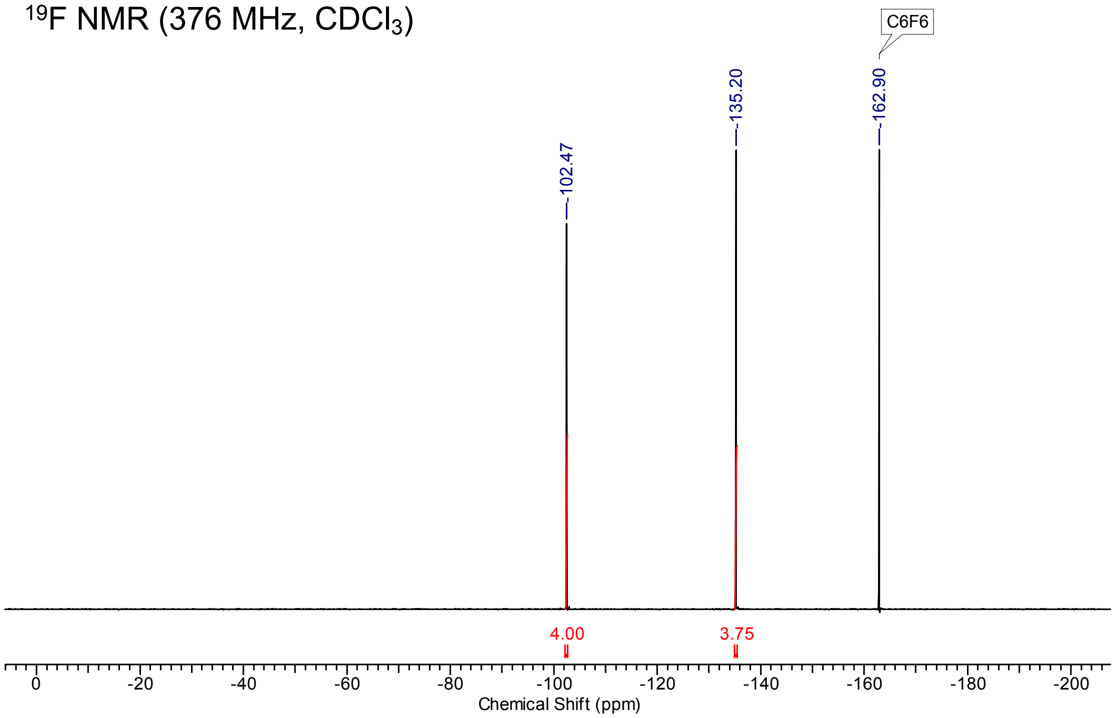
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 2H), 1.75(s, 6H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –102.47 (s, 4F), –135.20 (s, 4F);

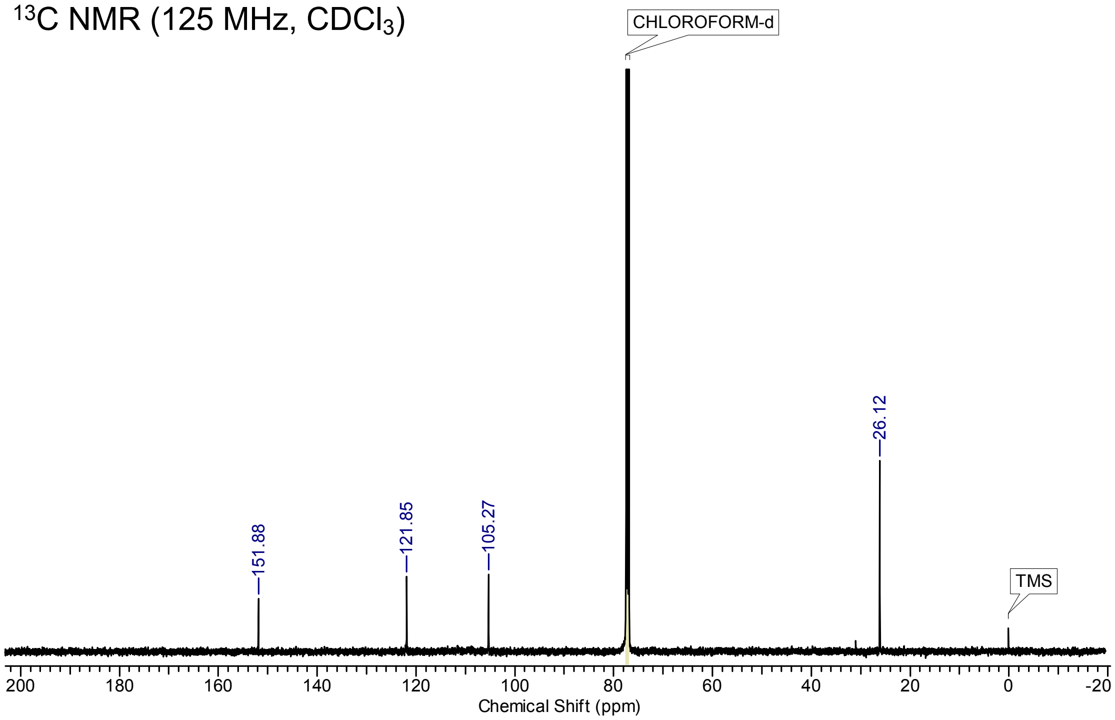
^{13}C NMR (125 MHz, $CDCl_3$): 151.9, 121.9, 105.3, 26.1

HRMS (EI, *m/z*): Cald. for $C_{13}H_8F_8O_2$ $[M]^+$ 348.0397; found: 348.0381



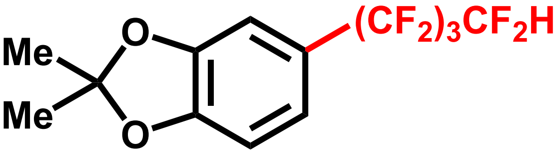


^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

2,2-dimethyl-5-(1,1,2,2,3,3,4,4-octafluorobutyl)benzo[*d*][1,3]dioxole (4b)



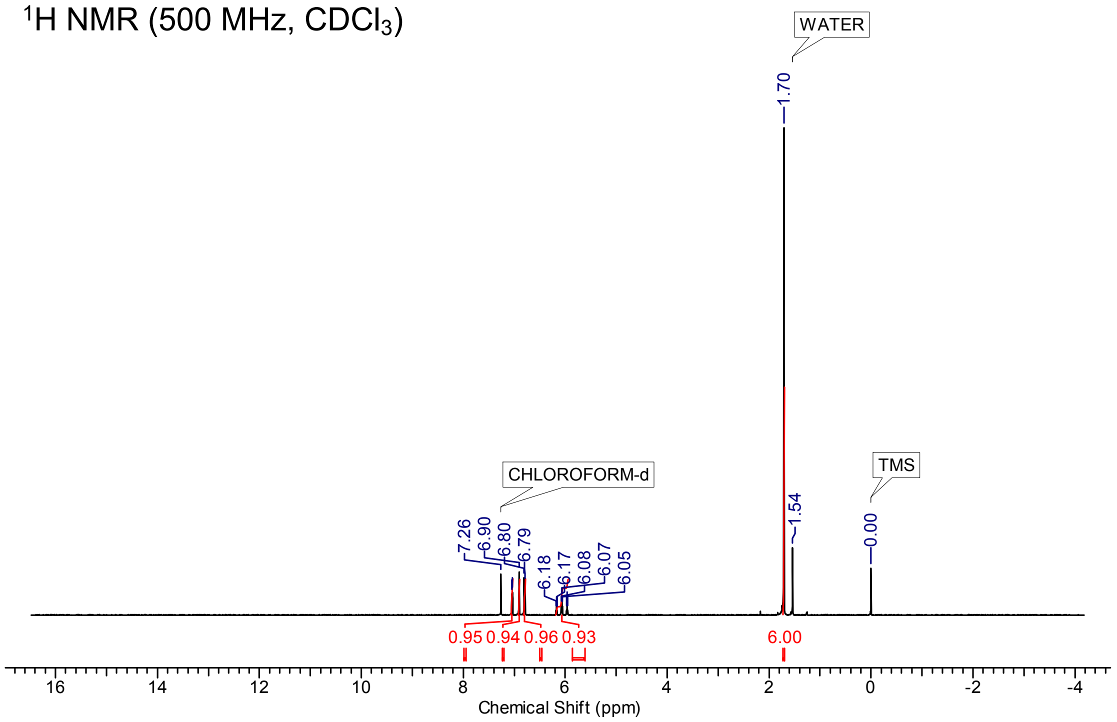
Compound **4b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 16% yield as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.04 (d, *J* = 8.20 Hz, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 8.20 Hz, 1H), 6.07 (tt, *J* = 52.02 Hz; 5.67 Hz, 1H), 1.70 (s, 6H);

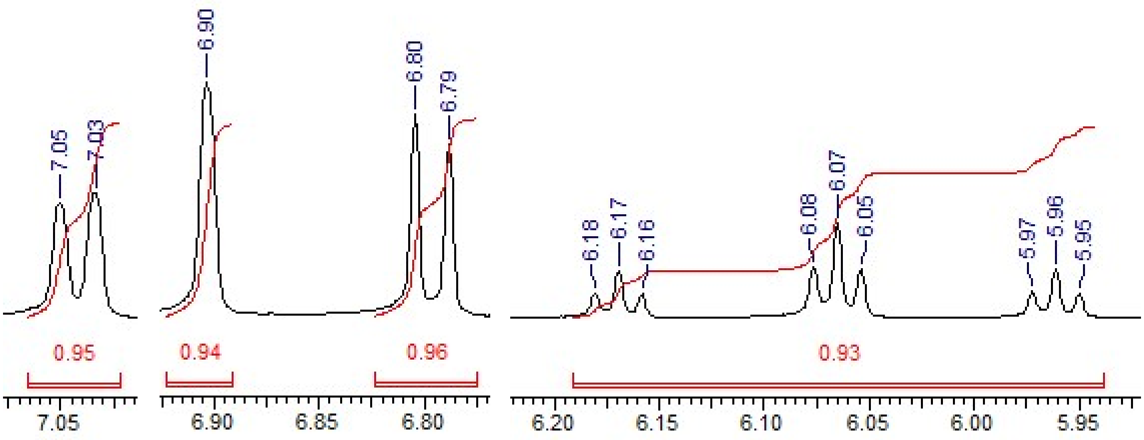
^{19}F NMR (376 MHz, $CDCl_3$): δ –109.95 (s, 2F), –124.83 (s, 2F), –130.73 (s, 2F), –138.29 (d, *J* = 50.66 Hz, 2F);

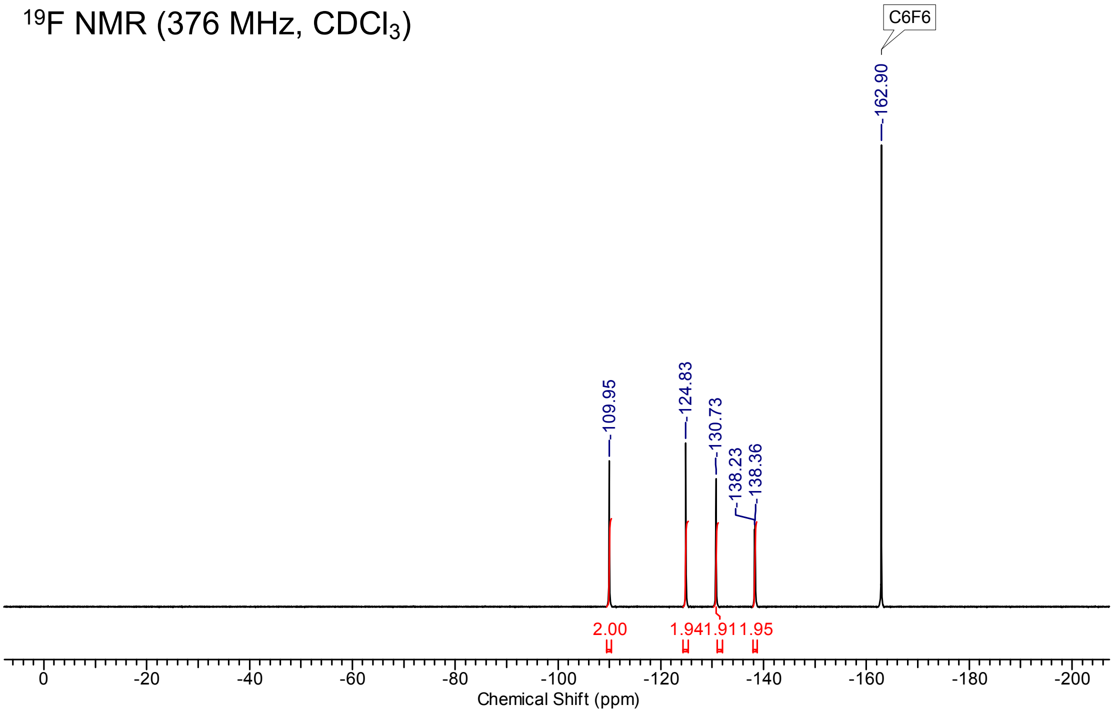
^{13}C NMR (125 MHz, $CDCl_3$): δ 150.5, 147.9, 121.7, 121.0, 119.5, 116.0, 108.1, 107.0, 25.9;

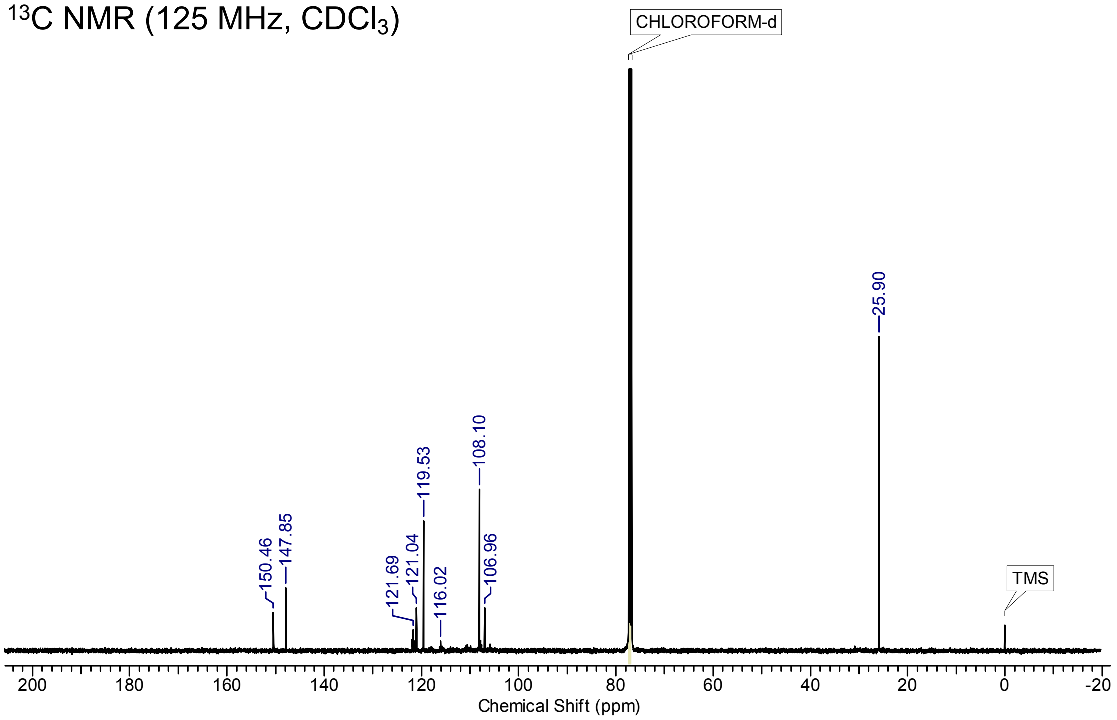
HRMS (EI, *m/z*): Cald. for $C_{13}H_{10}F_8O_2$ $[M]^+$ 350.0553; found: 350.0553



^{1}H NMR (500 MHz, $CDCl_3$)

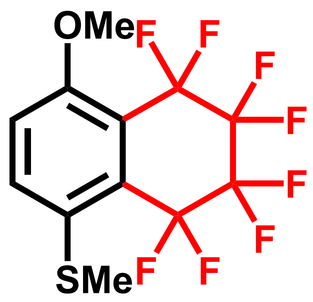



^{19}F NMR (376 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

methyl(5,5,6,6,7,7,8,8-octafluoro-4-methoxy-5,6,7,8-tetrahydronaphthalen-1-yl)sulfane (5a)



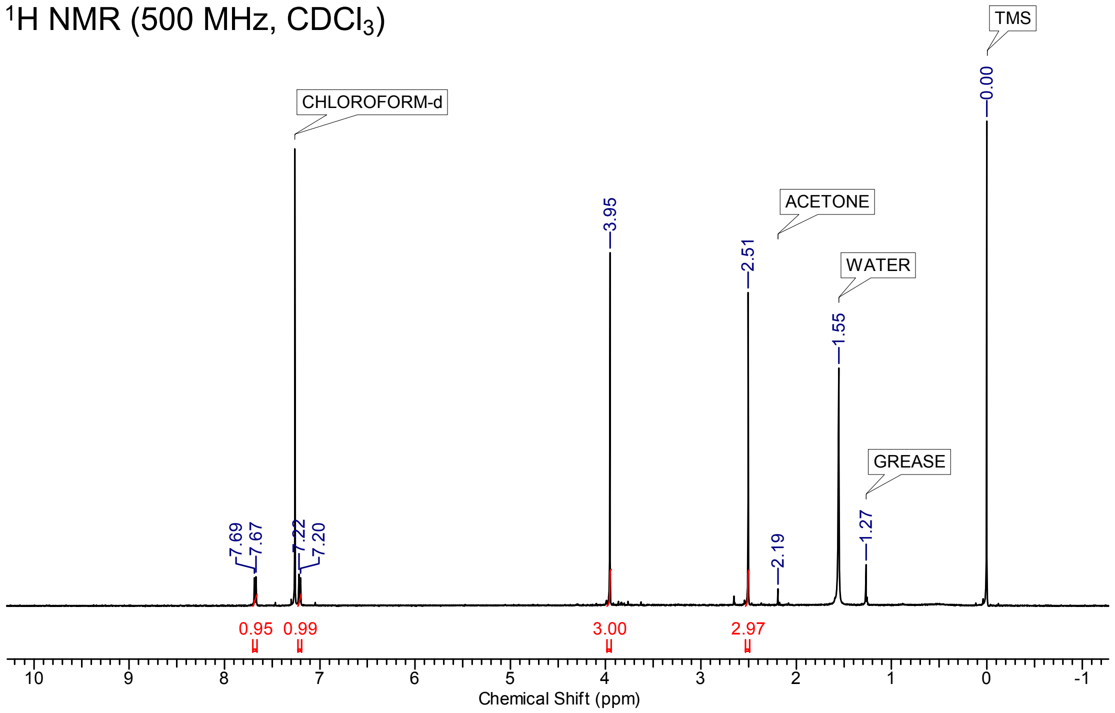
Compound **5a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 2% yield as an earth yellow solid.

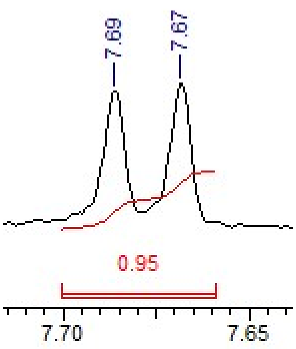
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.83 Hz, 1H), 7.21 (d, *J* = 9.14 Hz, 1H), 3.95 (s, 3H), 2.51 (s, 3H);

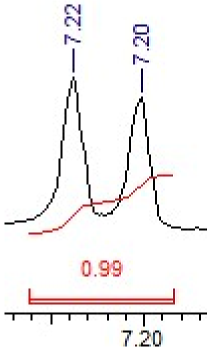
^{19}F NMR (376 MHz, $CDCl_3$): δ –106.21 (s, 2F), –109.12 (s, 2F), –136.15 (s, 4F);

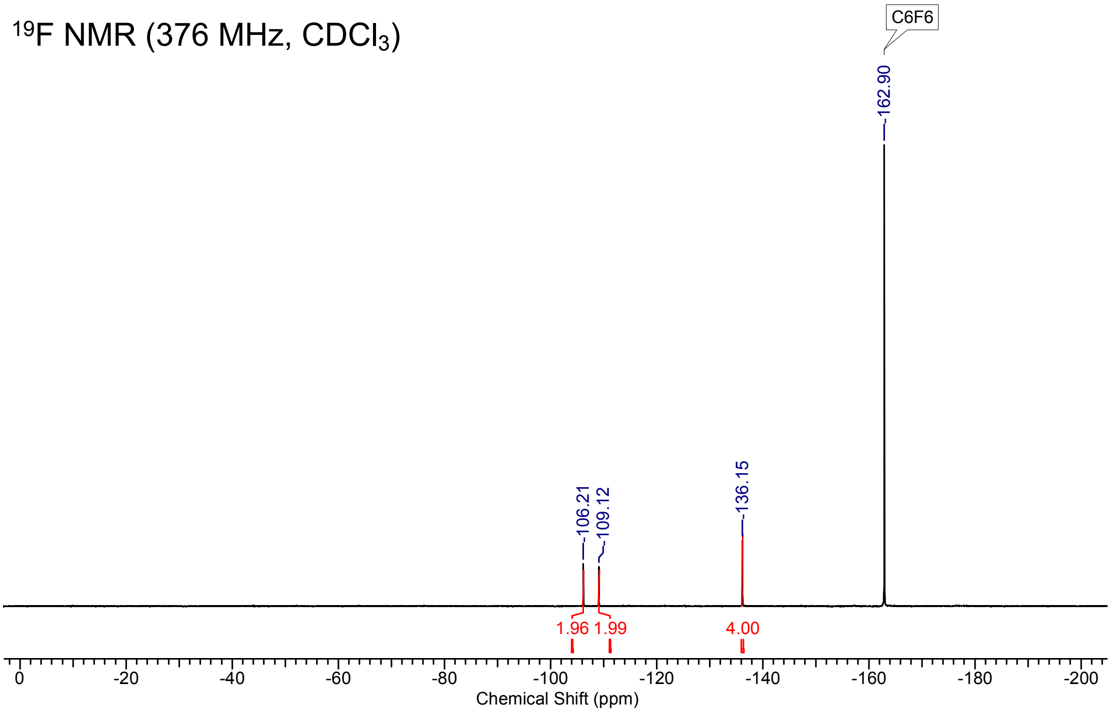
^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 136.5, 131.1, 116.5, 56.9, 18.8;

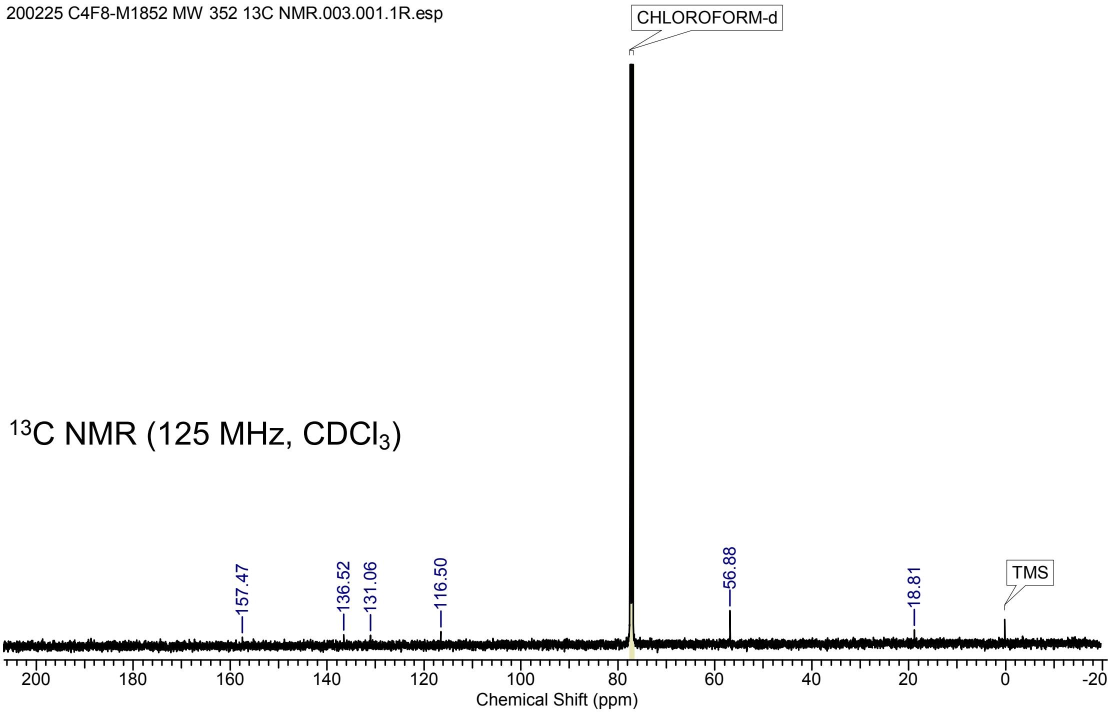
HRMS (EI, *m/z*): Cald. for $C_{12}H_8F_8OS$ $[M]^+$ 352.0168; found: 352.0152.





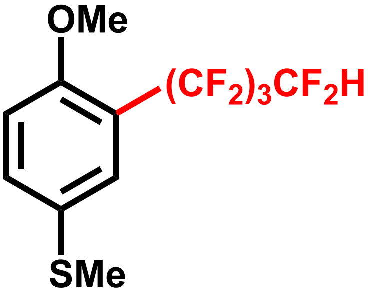



^{19}F NMR (376 MHz, $CDCl_3$)


200225 C4F8-M1852 MW 352 13C NMR.003.001.1R.esp

^{13}C NMR (125 MHz, $CDCl_3$)

(4-methoxy-3-(1,1,2,2,3,3,4,4-octafluorobutyl)phenyl)(methyl)sulfane (5b)



Compound **5b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 11% yield as a yellow oil.

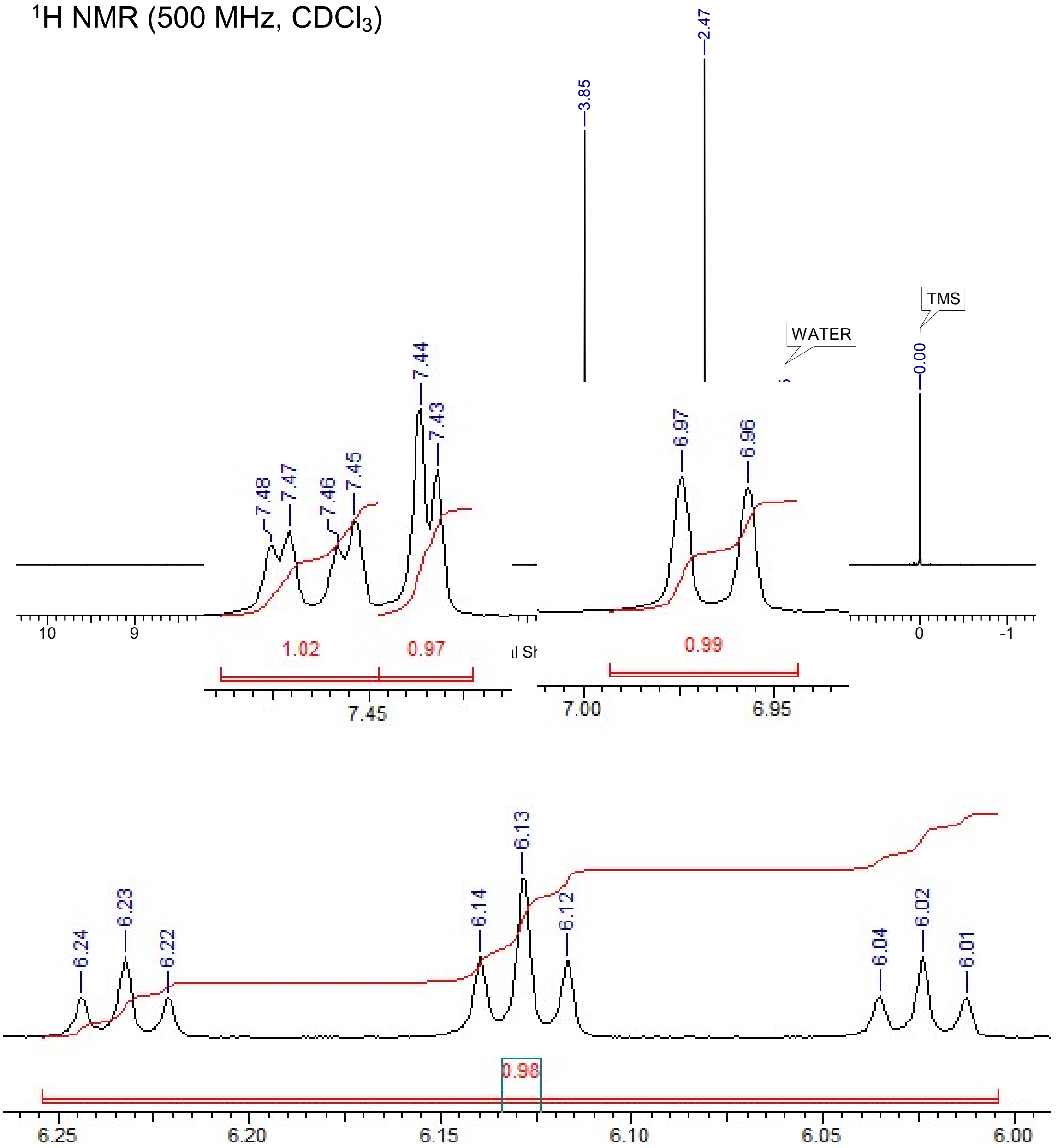
^{1}H NMR (500 MHz, CDCl3): δ 7.47 (dd, *J* = 8.83 Hz; 2.21Hz, 1H), 7.44 (d, *J* = 2.21 Hz, 1H), 6.97 (d, *J* = 8.83 Hz; 1H), 6.13 (tt, *J* = 52.33 Hz; 5.67 Hz, 1H), 3.85 (s, 3H), 2.47 (s, 3H);

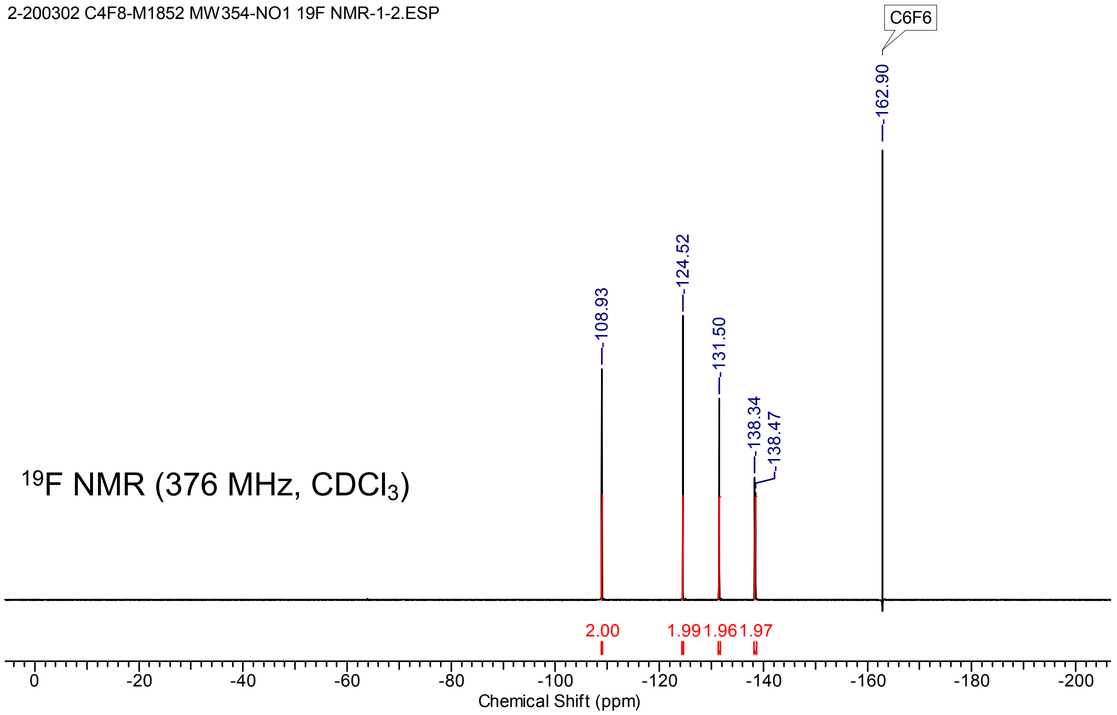
^{19}F NMR (376 MHz, CDCl3): δ –108.93 (s, 2F), –124.52 (s, 2F), –131.50 (s, 2F), –138.40 (d, *J* = 47.69 Hz, 2F);

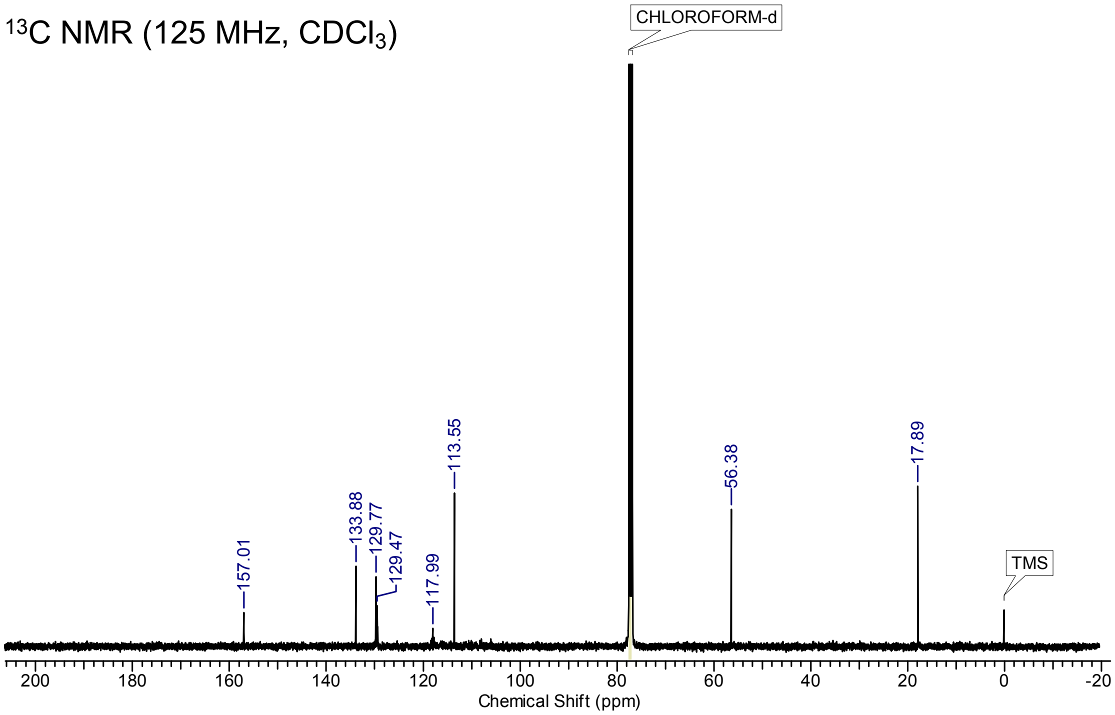
^{13}C NMR (125 MHz, CDCl3): δ 157.0, 133.9, 129.8, 129.5, 118.0, 113.6, 56.4, 17.9;

HRMS (EI, *m/z*): Cald. for $C_{12}H_{10}F_8OS$ $[M]^+$ 354.0325; found: 354.0324.

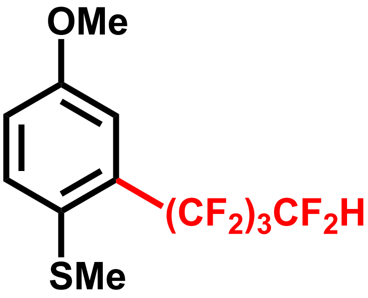
^{1}H NMR (500 MHz, $CDCl_3$)




2-200302 C4F8-M1852 MW354-NO1 19F NMR-1-2.ESP
C6F6
-162.90
-124.52
-108.93
-131.50
-138.34
-138.47
^{19}F NMR (376 MHz, CDCl$_3$)
2.00
1.99
1.96
1.97
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)



(4-methoxy-2-(1,1,2,2,3,3,4,4-octafluorobutyl)phenyl)(methyl)sulfane (5b*)



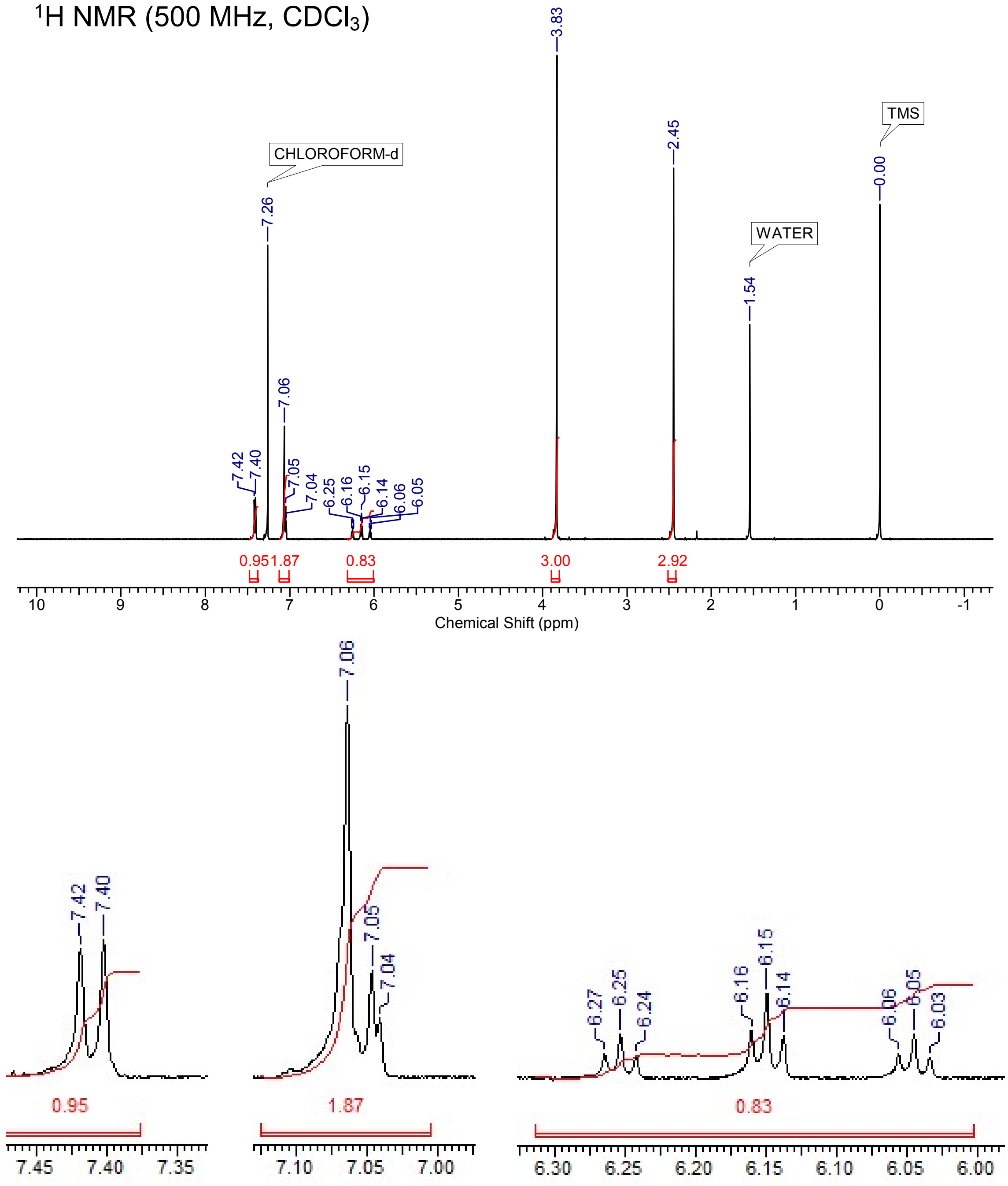
Compound **5b*** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 5% yield as a yellow oil.

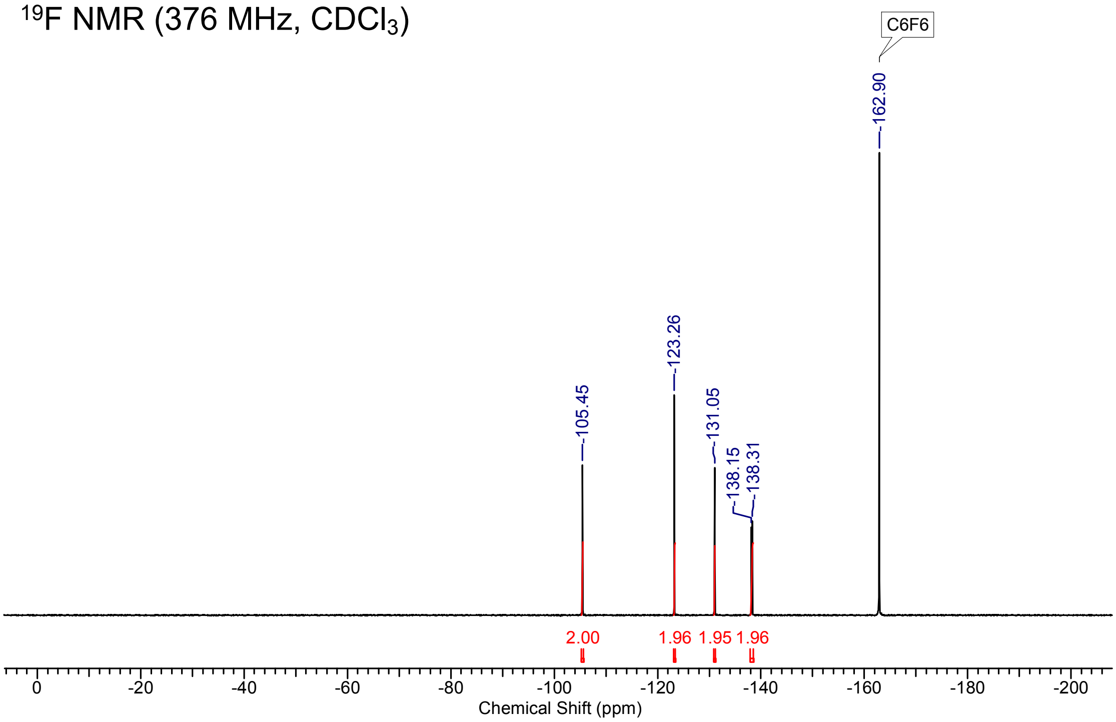
^{1}H NMR (500 MHz, CDCl3): δ 7.41 (d, *J* = 8.51 Hz, 1H), 7.06-7.04 (m, 2H), 6.15 (tt, *J* = 52.33 Hz; 5.67 Hz, 1H), 3.83 (s, 3H), 2.45 (s, 3H);

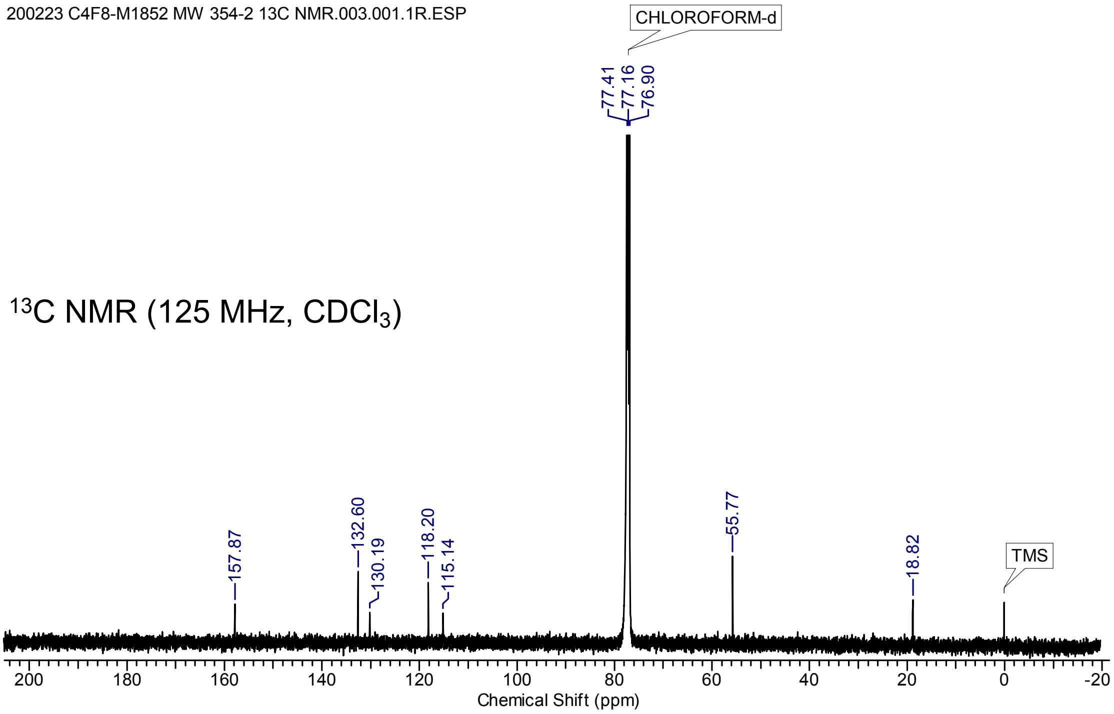
^{19}F NMR (376 MHz, CDCl3): δ –105.45 (s, 2F), –123.26 (s, 2F), –131.05 (s, 2F), –138.23 (d, *J* = 59.60 Hz, 2F);

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 132.6, 130.2, 118.2, 115.1, 55.8, 18.8

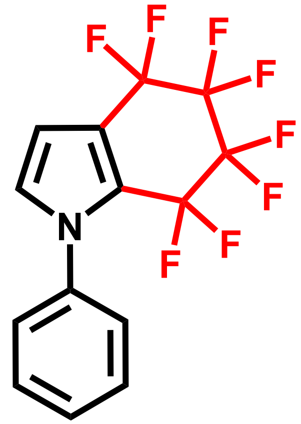
HRMS (EI, *m/z*): Cald. for $C_{12}H_{10}F_8OS$ $[M]^+$ 354.0325; found: 354.0328.


^{1}H NMR (500 MHz, $CDCl_3$)


^{19}F NMR (376 MHz, $CDCl_3$)
C6F6
-105.45
-123.26
-131.05
-138.15
-138.31
-162.90
2.00
1.96
1.95
1.96
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)


200223 C4F8-M1852 MW 354-2 13C NMR.003.001.1R.ESP
CHLOROFORM-d
77.41
77.16
76.90
^{13}C NMR (125 MHz, $CDCl_3$)
157.87
132.60
130.19
118.20
115.14
55.77
18.82
TMS
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

4,4,5,5,6,6,7,7-octafluoro-1-phenyl-4,5,6,7-tetrahydro-1*H*-indole (6a)



Compound **6a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 32% yield as a colorless oil.

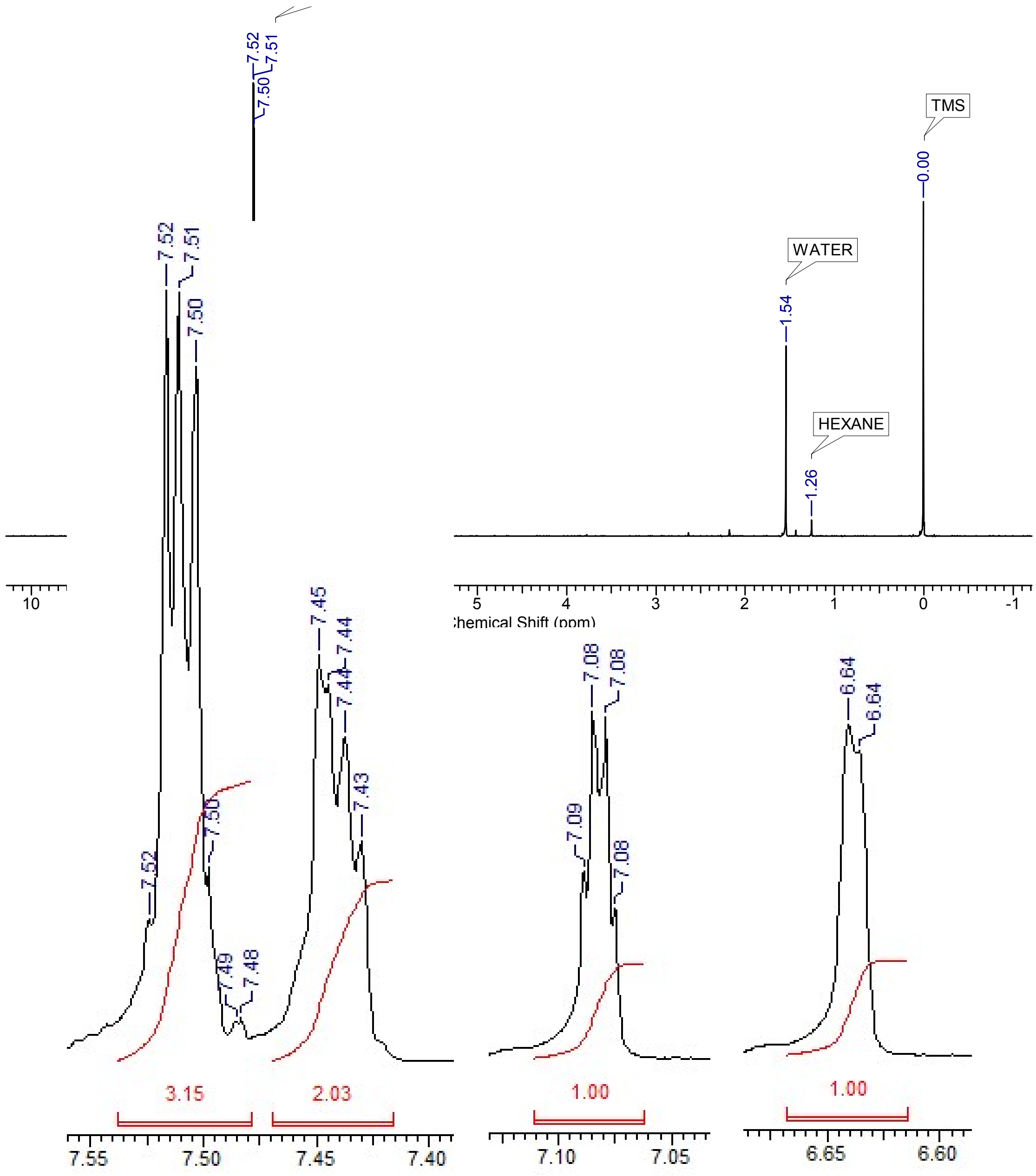
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.48 (m, 3H), 7.45-7.43 (m, 2H), 7.09-7.08 (m, 1H), 6.64 (d, *J* = 2.52 Hz, 1H);

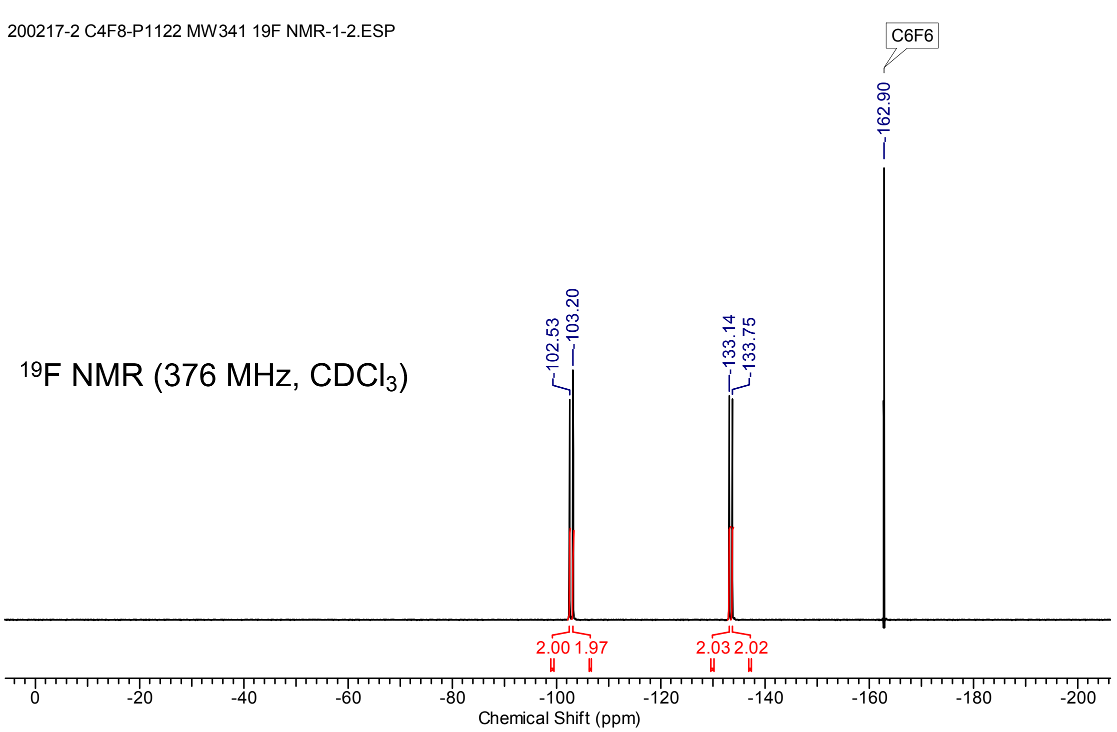
^{19}F NMR (376 MHz, $CDCl_3$): δ –102.53 (s, 2F), –103.20 (s, 2F), –133.14 (s, 2F), –133.75 (s, 2F);

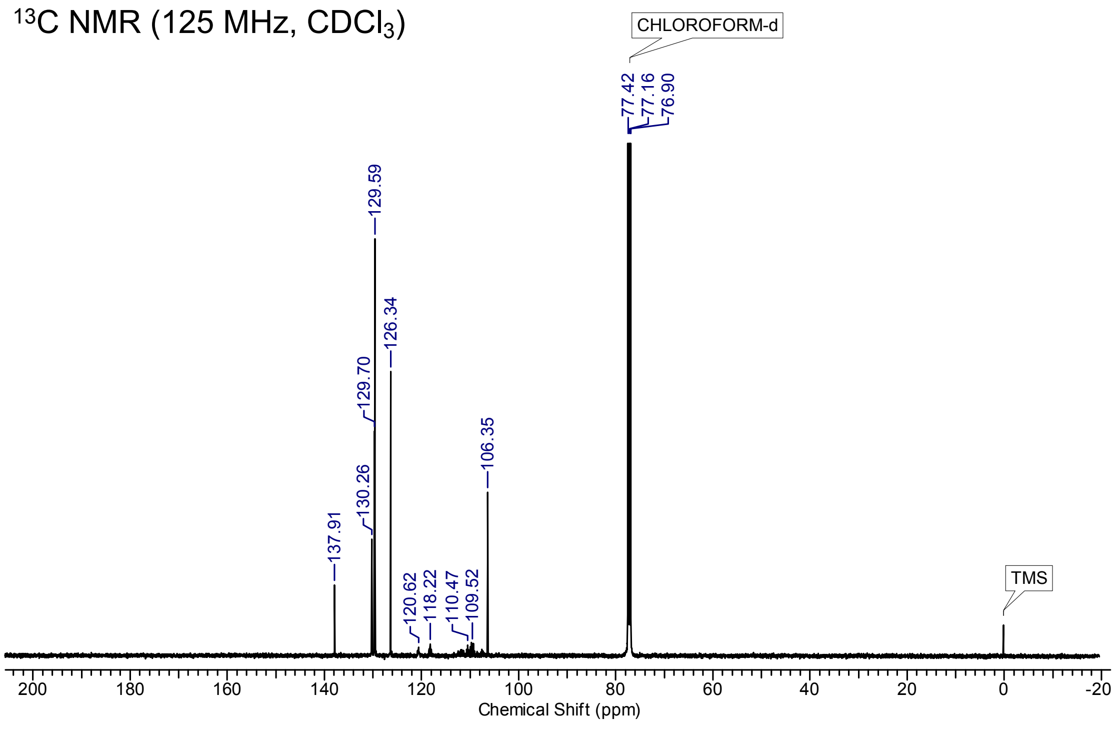
^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 130.3, 129.7, 129.6, 126.3, 120.6, 118.2, 110.5, 109.5, 106.4;

HRMS (EI, *m/z*): Cald. for $C_{14}H_7F_8N$ [M]$^+$ 341.0451; found: 341.0454.

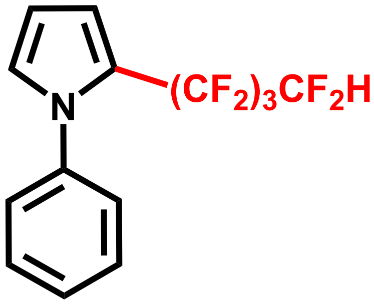
^{1}H NMR (500 MHz, $CDCl_3$)




200217-2 C4F8-P1122 MW341 19F NMR-1-2.ESP
^{19}F NMR (376 MHz, CDCl$_3$)
C6F6
-162.90
-102.53
-103.20
-133.14
-133.75
2.00
1.97
2.03
2.02
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)



2-(1,1,2,2,3,3,4,4-octafluorobutyl)-1-phenyl-1*H*-pyrrole (6b)



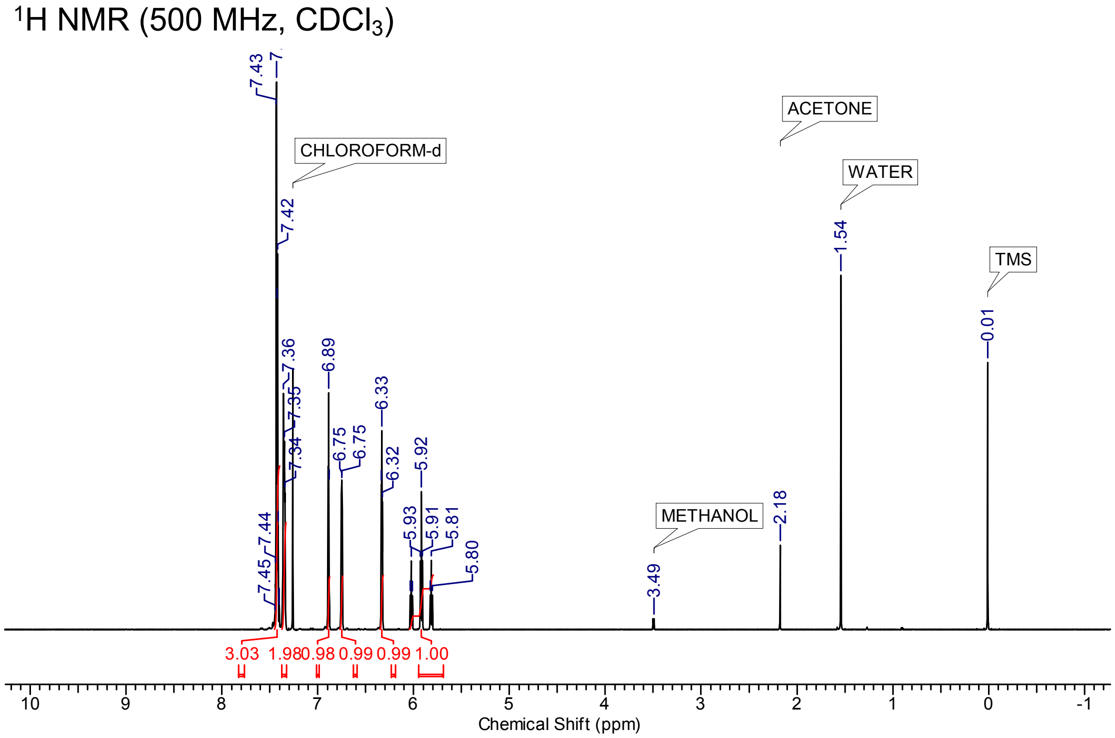
Compound **6b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 19% yield as a colorless oil.

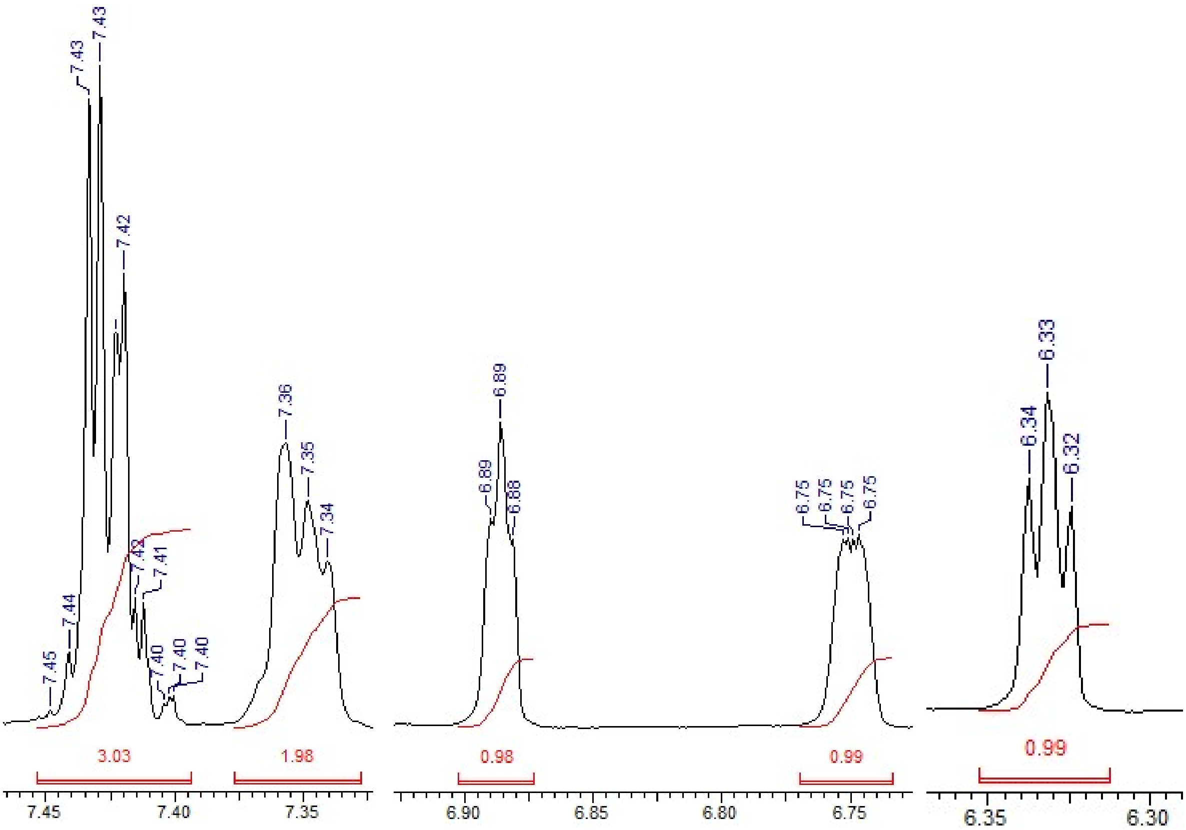
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45-7.40 (m, 3H), 7.36-7.34 (m, 2H), 6.89-6.88 (m, 1H), 6.75 (m, 1H), 6.33 (t, *J* = 3.78 Hz, 1H), 5.92 (tt, *J* = 52.02 Hz; 5.67 Hz, 1H);

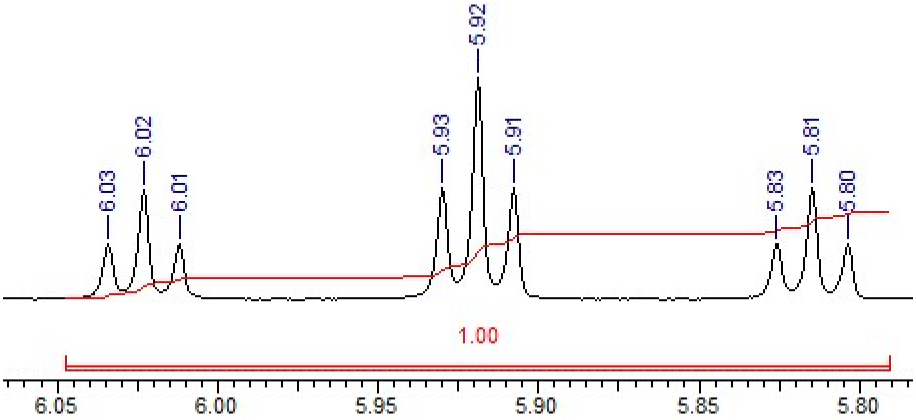
^{19}F NMR (282 MHz, $CDCl_3$): δ (–101.47)-(–101.55) (m, 2F), (–123.45)-(–123.60) (m, 2F), (–131.01)-(–131.15) (m, 2F), (–138.18)-(–138.31) (m, 1F), (–138.37)-(–138.50) (m, 1F);

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 129.2, 128.8, 127.5, 120.3, 115.2, 114.1, 112.1, 110.9, 109.9, 108.9, 107.9, 105.9;

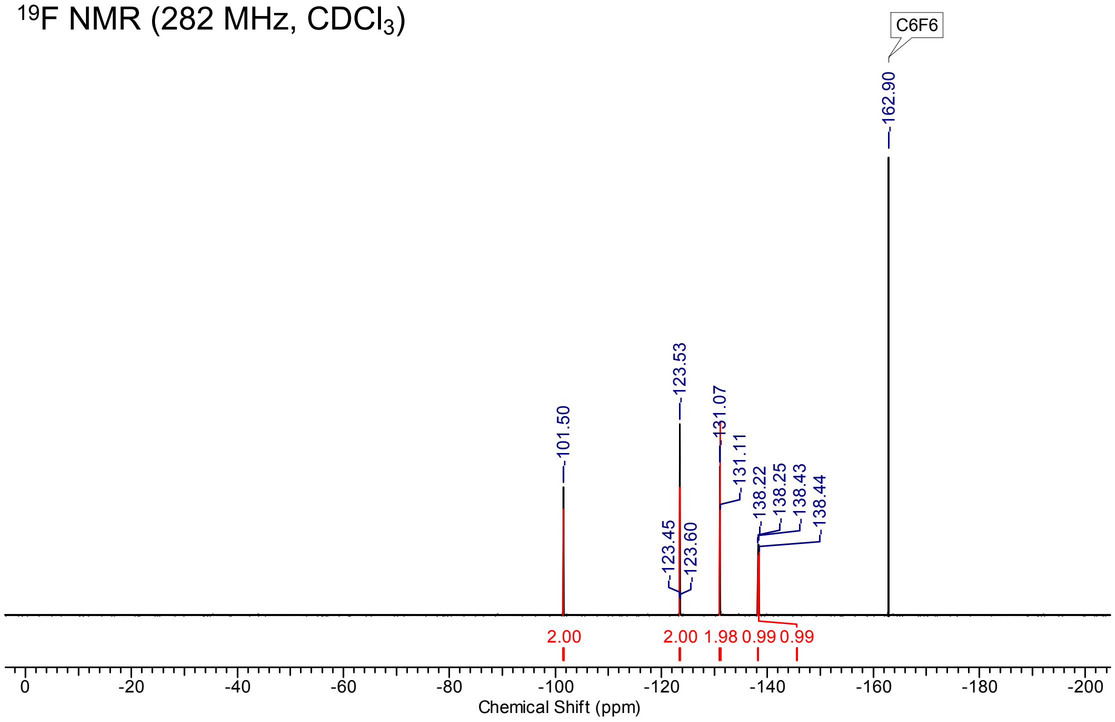
GC-MS (*m/z*): Cald. for $C_{14}H_9F_8N$ $[M]^+$ 343; found: 343.

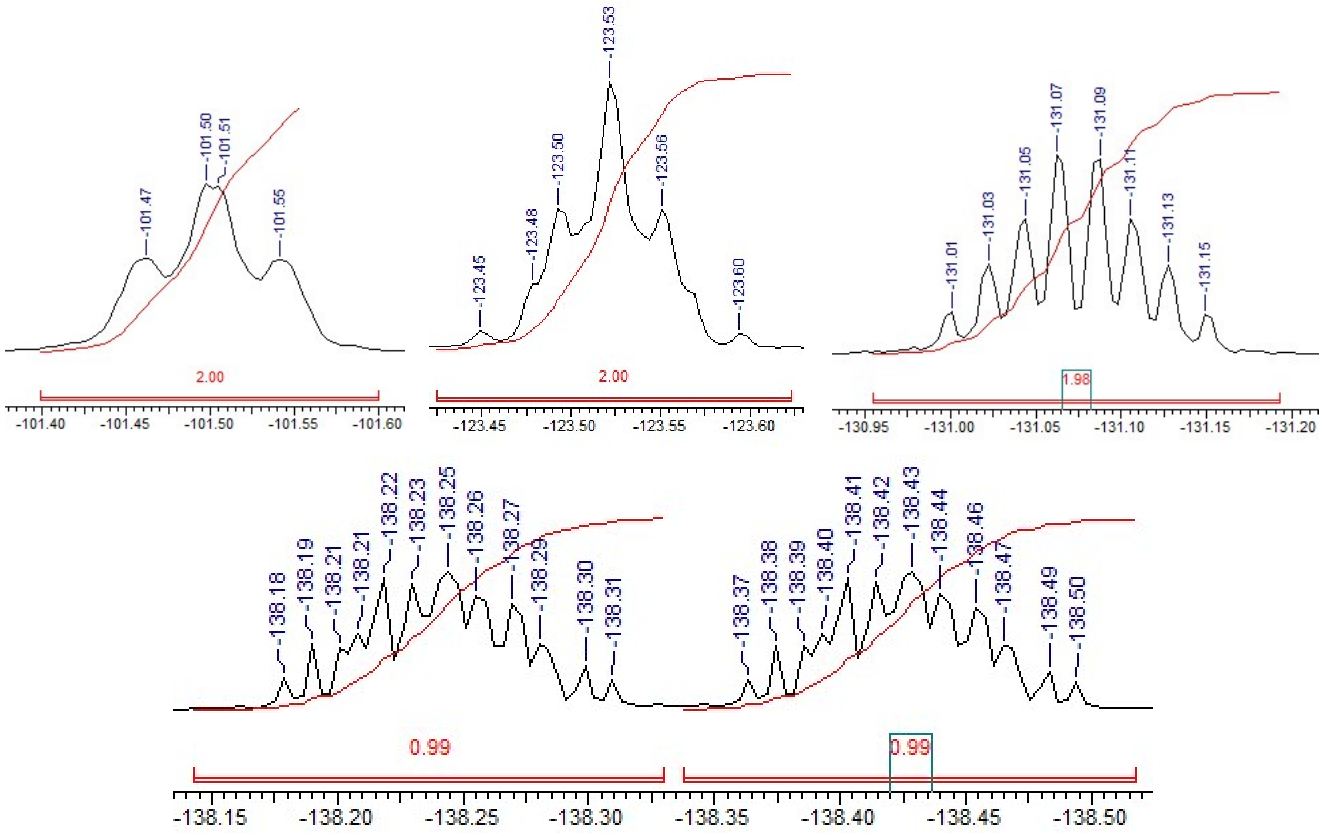



7.45
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.40
7.40
7.36
7.35
7.34
6.89
6.89
6.88
6.75
6.75
6.75
6.75
6.34
6.33
6.32
3.03
1.98
0.98
0.99
0.99
7.45
7.40
7.35
6.90
6.85
6.80
6.75
6.35
6.30

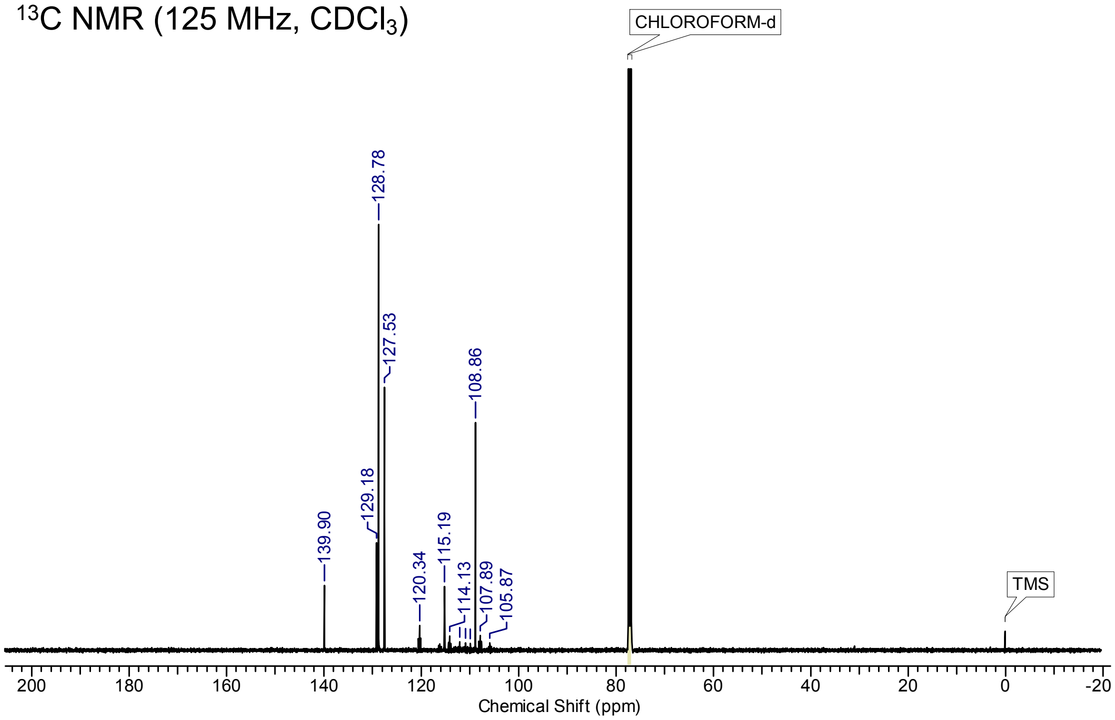

6.03
6.02
6.01
5.93
5.92
5.91
5.83
5.81
5.80
1.00
6.05
6.00
5.95
5.90
5.85
5.80

^{19}F NMR (282 MHz, $CDCl_3$)

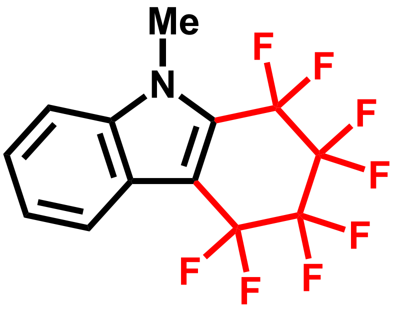




^{13}C NMR (125 MHz, CDCl$_3$)



1,1,2,2,3,3,4,4-octafluoro-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazole (7a)



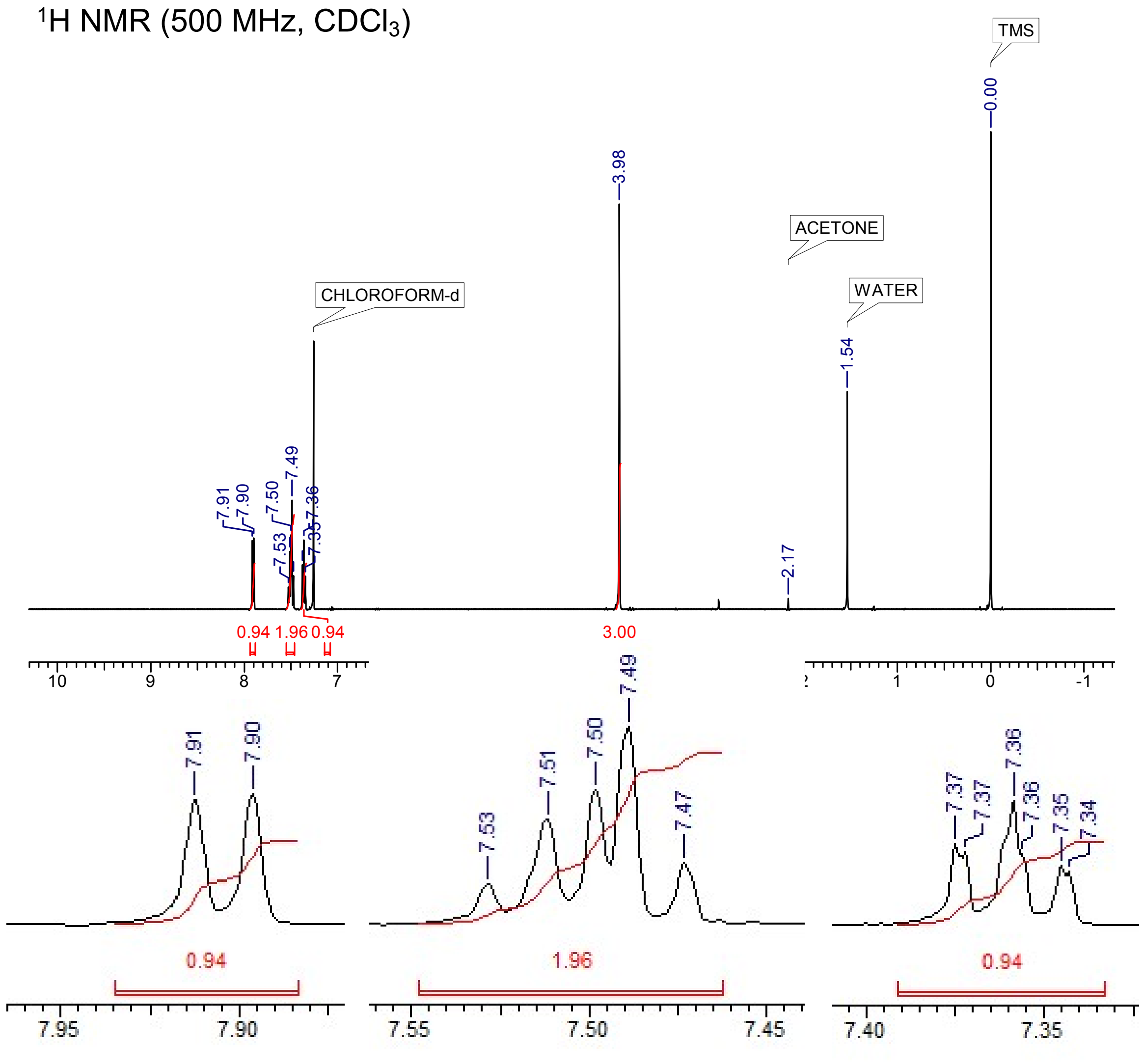
Compound **7a** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 4% yield as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.20 Hz, 1H), 7.53-7.47 (m, 2H), 7.37-7.34 (m, 1H), 3.98 (s, 3H);

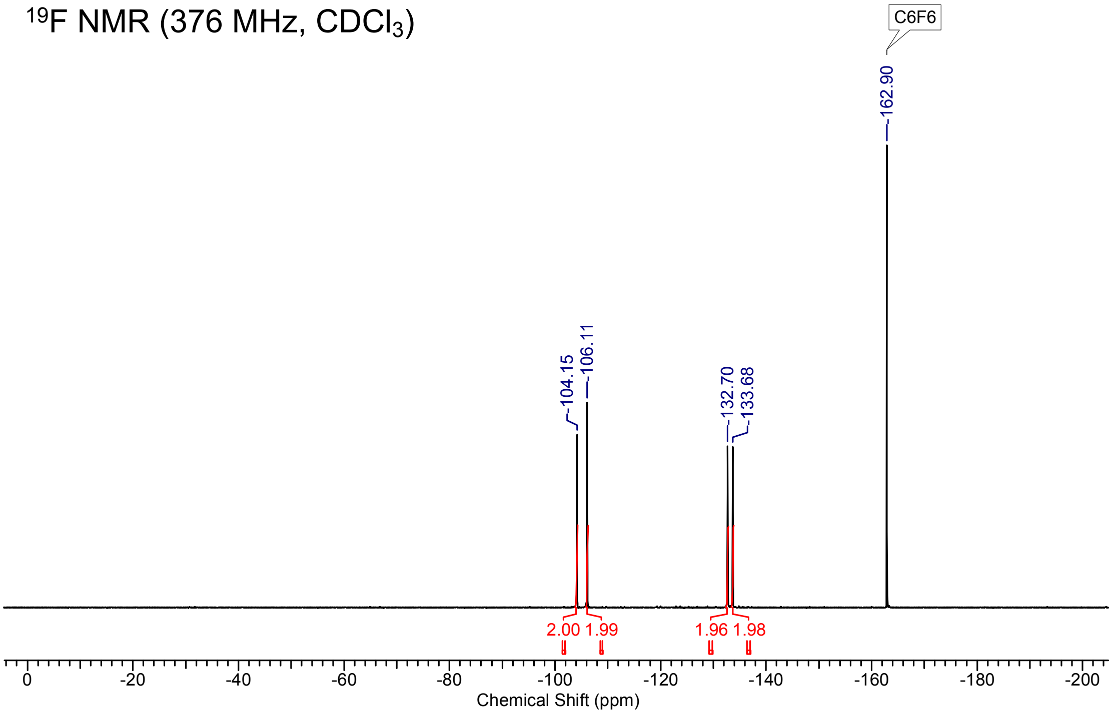
^{19}F NMR (376 MHz, $CDCl_3$): δ –104.15 (s, 2F), –106.11 (s, 2F), –132.70 (s, 2F), –133.68 (s, 2F);

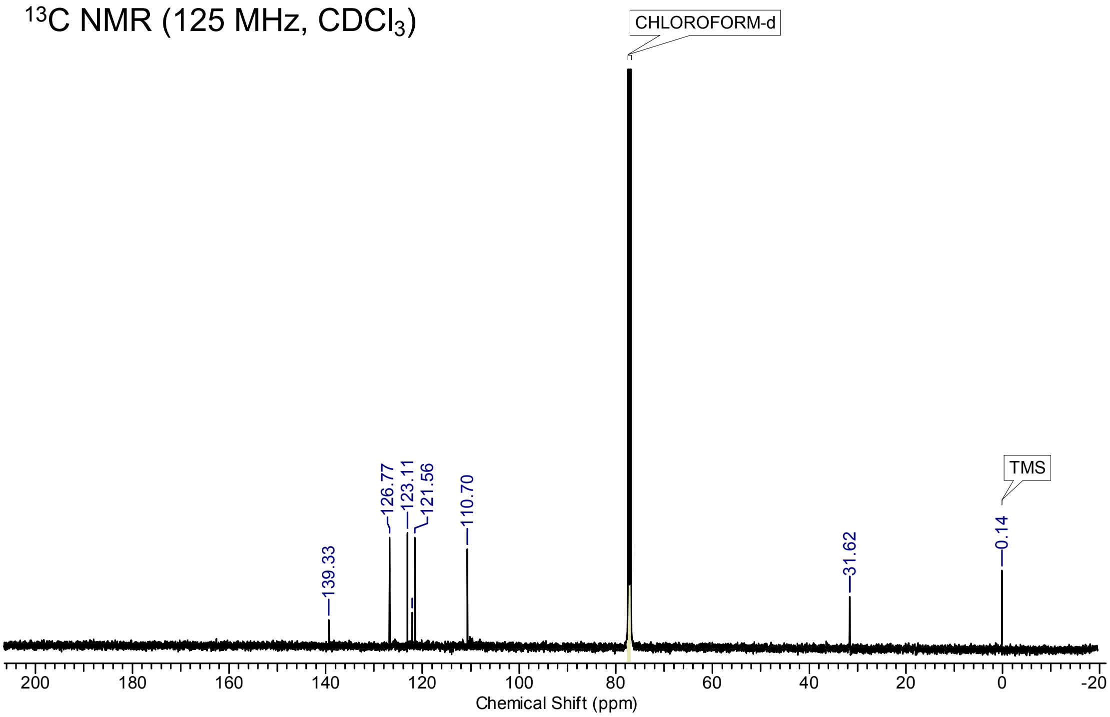
^{13}C NMR (125 MHz, $CDCl_3$): δ 139.3, 126.8, 123.1, 122.2, 121.6, 110.7, 31.6;

HRMS (EI, *m/z*): Cald. for $C_{13}H_7F_8N$ [M]$^+$ 329.0451; found: 329.0448.



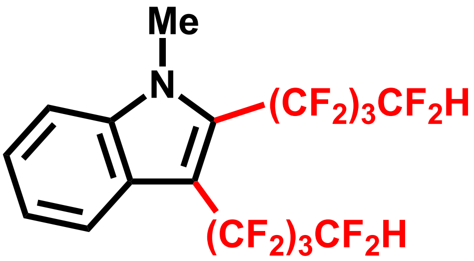
^{19}F NMR (376 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)

1-methyl-2,3-bis(1,1,2,2,3,3,4,4-octafluorobutyl)-1*H*-indole (7b)



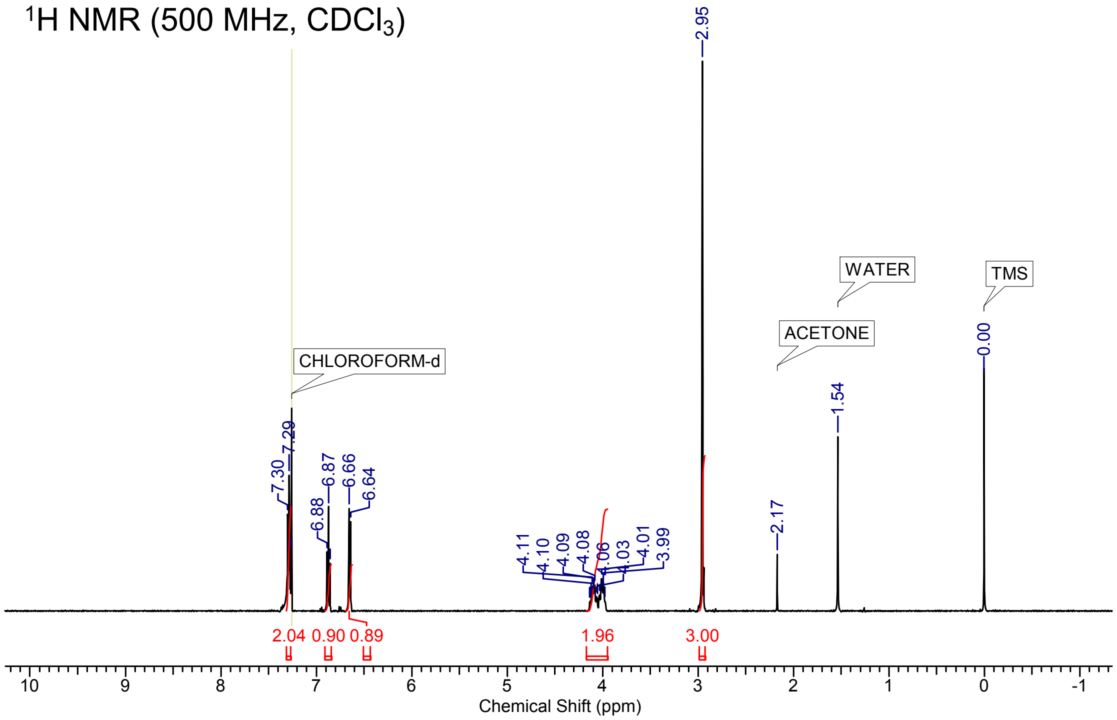
Compound **7b** was prepared according to the general procedure using octafluoro-1,4-diiodobutane, 1,4-$C_4F_8I_2$ (6 eq., 680.76 mg, 5.0 × 10^{-2} M) in 2% yield as a colorless oil.

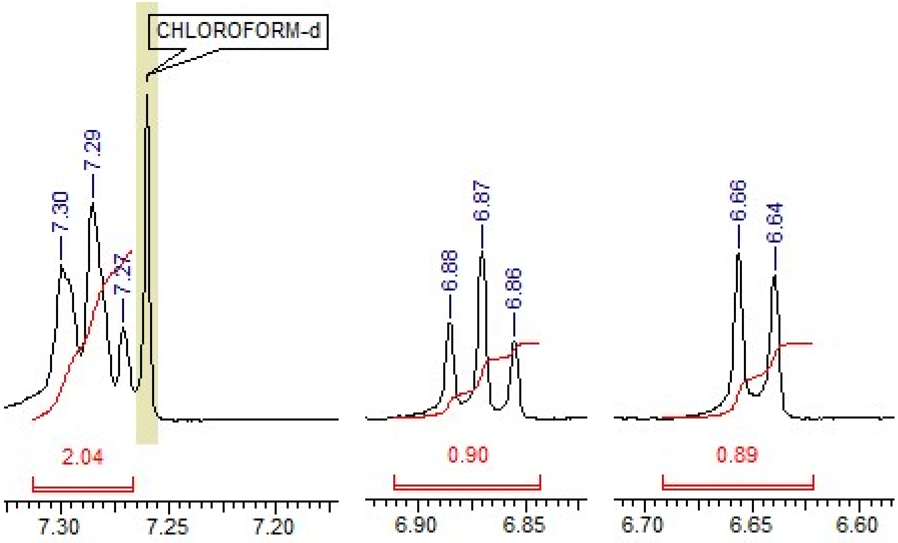
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.27 (m, 2H), 6.87 (t, *J* = 7.25 Hz, 1H), 6.65 (d, *J* = 8.20 Hz, 1H), 4.13-3.98 (m, 2H), 2.95 (s, 3H);

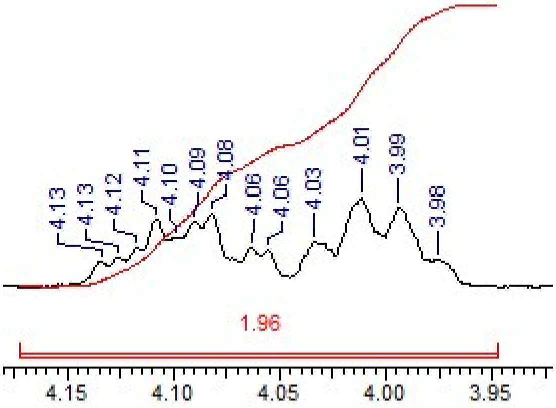
^{19}F NMR (282 MHz, $CDCl_3$): δ (–109.30)-(–109.46) (m, 1F), (–110.30)-(–110.46) (m, 1F), (–111.43)-(–111.47) (m, 1F), (–112.41)-(–112.43) (m, 1F), (–119.32)-(–119.50) (m, 1F), (–120.30)-(–120.47) (m, 1F), (–122.44)-(–122.58) (m, 1F), (–123.44)-(–123.58) (m, 1F), (–132.74)-(–132.93) (m, 1F), (–133.72)-(–133.91) (m, 1F), (–134.16)-(–134.34) (m, 4F), (–135.71)-(–135.81) (m, 1F), (–136.69)-(–136.87) (m, 1F);

^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 130.5, 125.3, 120.3, 120.2, 108.9, (67.5-67.1) (m), (45.9-45.5) (m), 35.9;

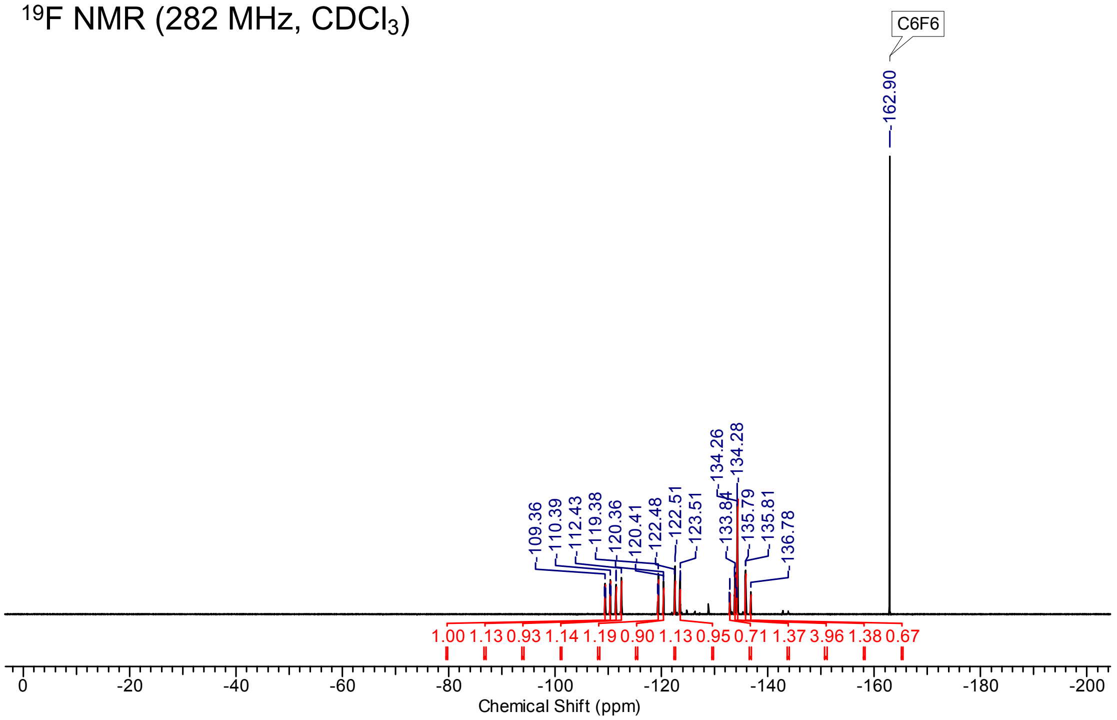
GC-MS (*m/z*): Cald. for $C_{17}H_9F_{16}N$ $[M]^+$ 531; found: $[M–C_4F_8H]^+$ 331.

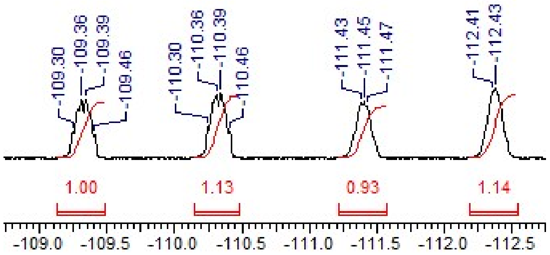


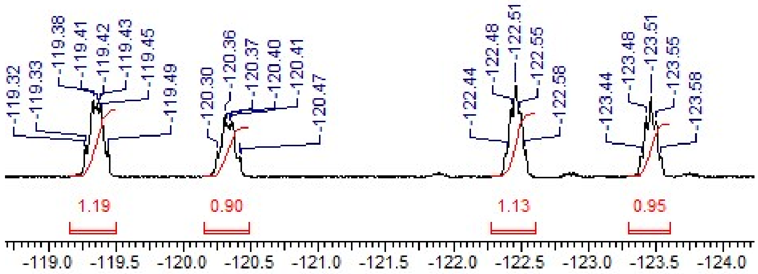

CHLOROFORM-d
7.30
7.29
7.27
6.88
6.87
6.86
6.66
6.64
2.04
0.90
0.89
7.30
7.25
7.20
6.90
6.85
6.70
6.65
6.60

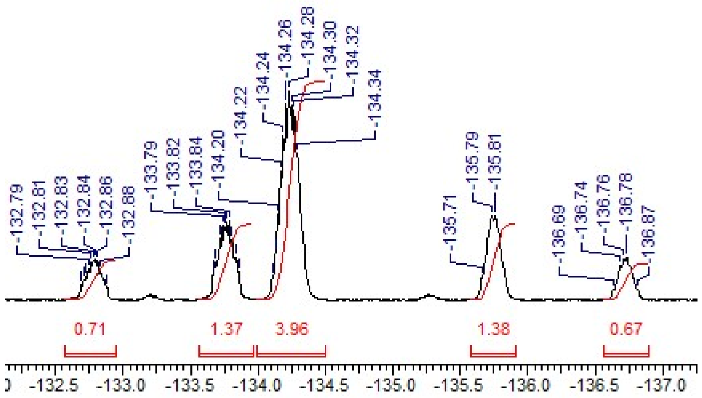

4.13
4.13
4.12
4.11
4.10
4.09
4.08
4.06
4.06
4.03
4.01
3.99
3.98
1.96
4.15
4.10
4.05
4.00
3.95

^{19}F NMR (282 MHz, $CDCl_3$)

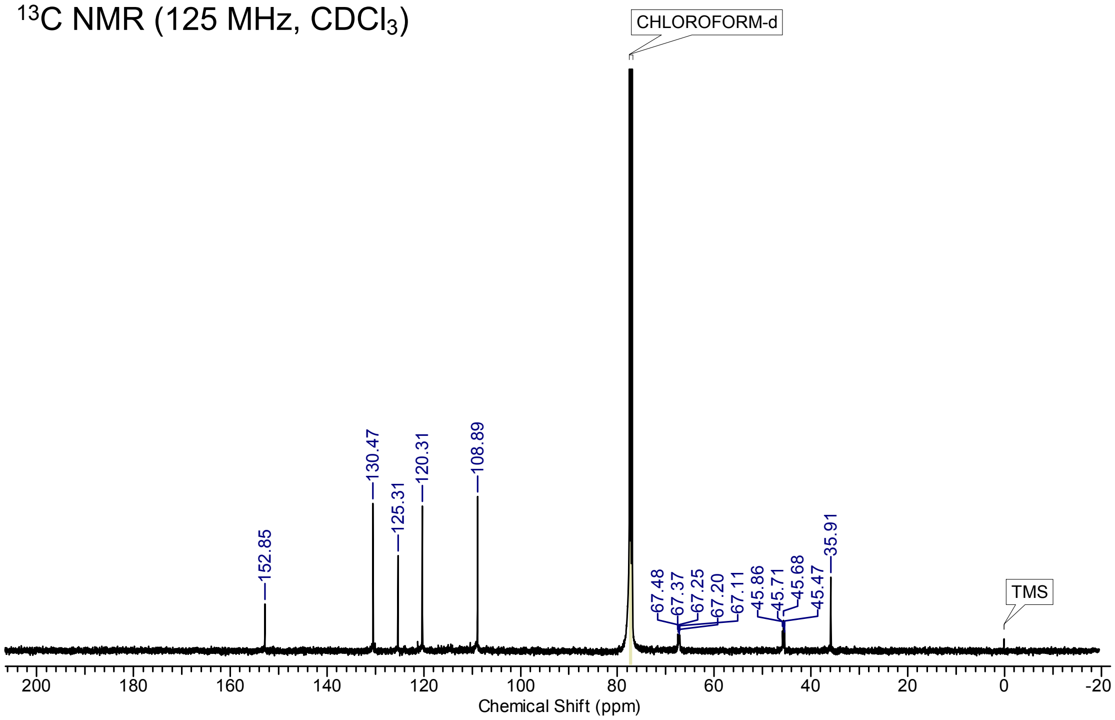


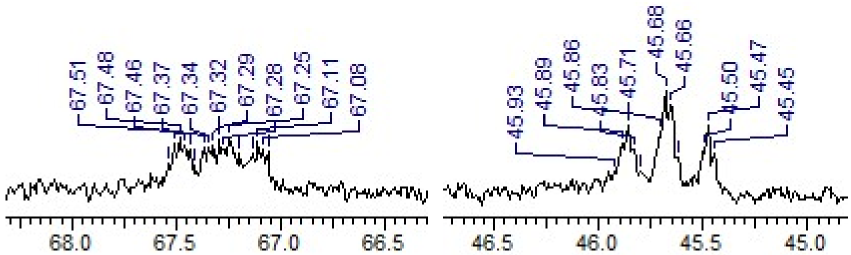






^{13}C NMR (125 MHz, $CDCl_3$)





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2 *Rigaku Oxford Diffraction, CrysAlis(Pro), Rigaku Corporation, Tokyo, Japan*, 2015.

3 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Adv.*, 2015, **71**, 3.

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