Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Electrocatalytic Reactivity of Imine/Oxime-type Cobalt Complex for Direct Perfluoroalkylation of Indole and Aniline Derivatives

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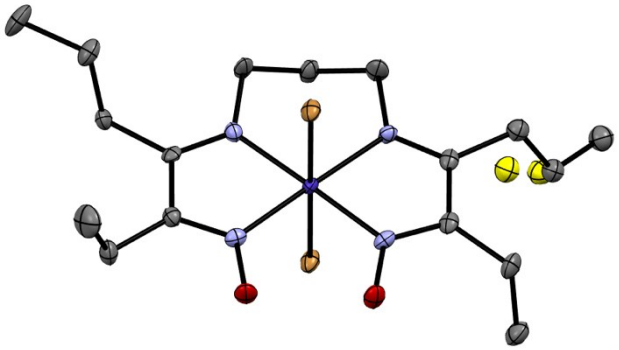


Figure S1. Crystal structure of **C1**. The thermal ellipsoid is drawn at 50% probability. Color code: Co, deep blue; Br, brown; O, red; N, light blue; C, gray; disordered C, yellow. Hydrogen atoms are omitted for clarity.

Table S1. Crystallographic data for **C1**.

Compound	**C1**
CCDC No.	1951624
empirical formula	$C_{17}H_{31}Br_2CoN_4O_2$
formula weight	542.21
temperature [K]	93
wavelength [Å]	0.71073
crystal system	monoclinic
space group	$P2_1/n$
a [Å]	8.0534(6)
b [Å]	15.0332(12)
c [Å]	17.7379(13)
α [°]	90
β [°]	98.892(8)
γ [°]	90
Volume [Å^3]	2121.7(3)
Z	4
Density (calculated) [g/cm^3]	1.697
Absorption coefficient [mm^{-1}]	4.594
F(000)	1096.0
ϑ[°]	2.643 to 26.371
Reflections collected	9584
Independent reflections	4331 [$R_{(int)}$ = 0.0309]
Data / restraints / parameters	4331 / 30 / 263
Goodness-of-fit on F^2	1.173
$R1$[a] [$I>2\sigma(I)$]	0.0463
$wR2$ [b] (all data)	0.1249
Largest diff. peak and hole [e.Å^{-3}]	1.67 and -0.72

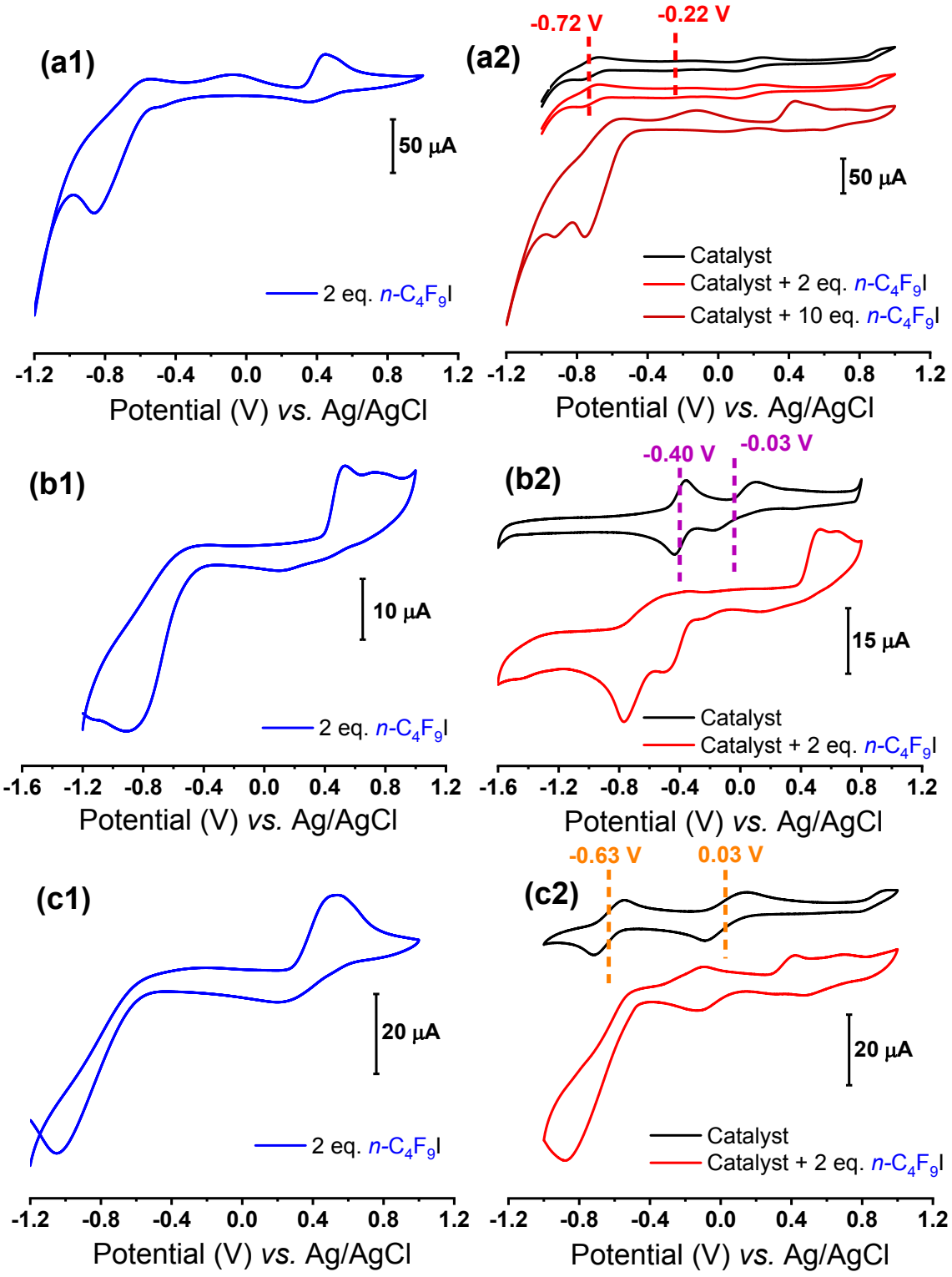


Figure S2. (1) CV of nonafluorobutyl iodide (n-C_4F_9I) (2 mM) and (2) [Co(III){(C_2C_3)(DO)(DOH)pn}Br_2] (**C1**) as the catalyst (1 mM) with/without n-C_4F_9I (2 mM) in different solvents (a) CH_3OH, (b) DMSO and (c) 1-propanol containing of 100 mM tetrabutylammonium perchlorate (TBAP, n-Bu_4NClO_4) under N_2. Reference electrode: Ag/AgCl; Working electrode: Pt; Counter electrode: Pt; Scan rate: 100 mV s^{-1}.

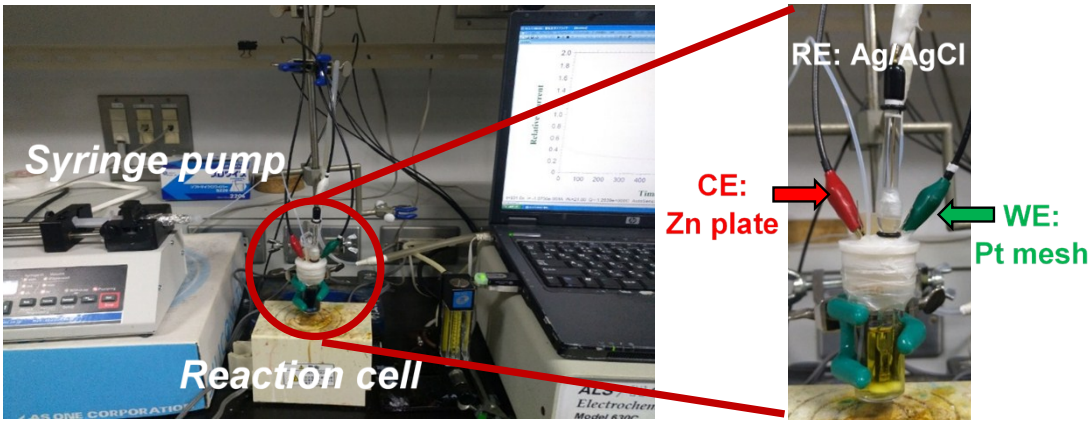


Figure S3. Experimental setup image of controlled-potential electrolysis.

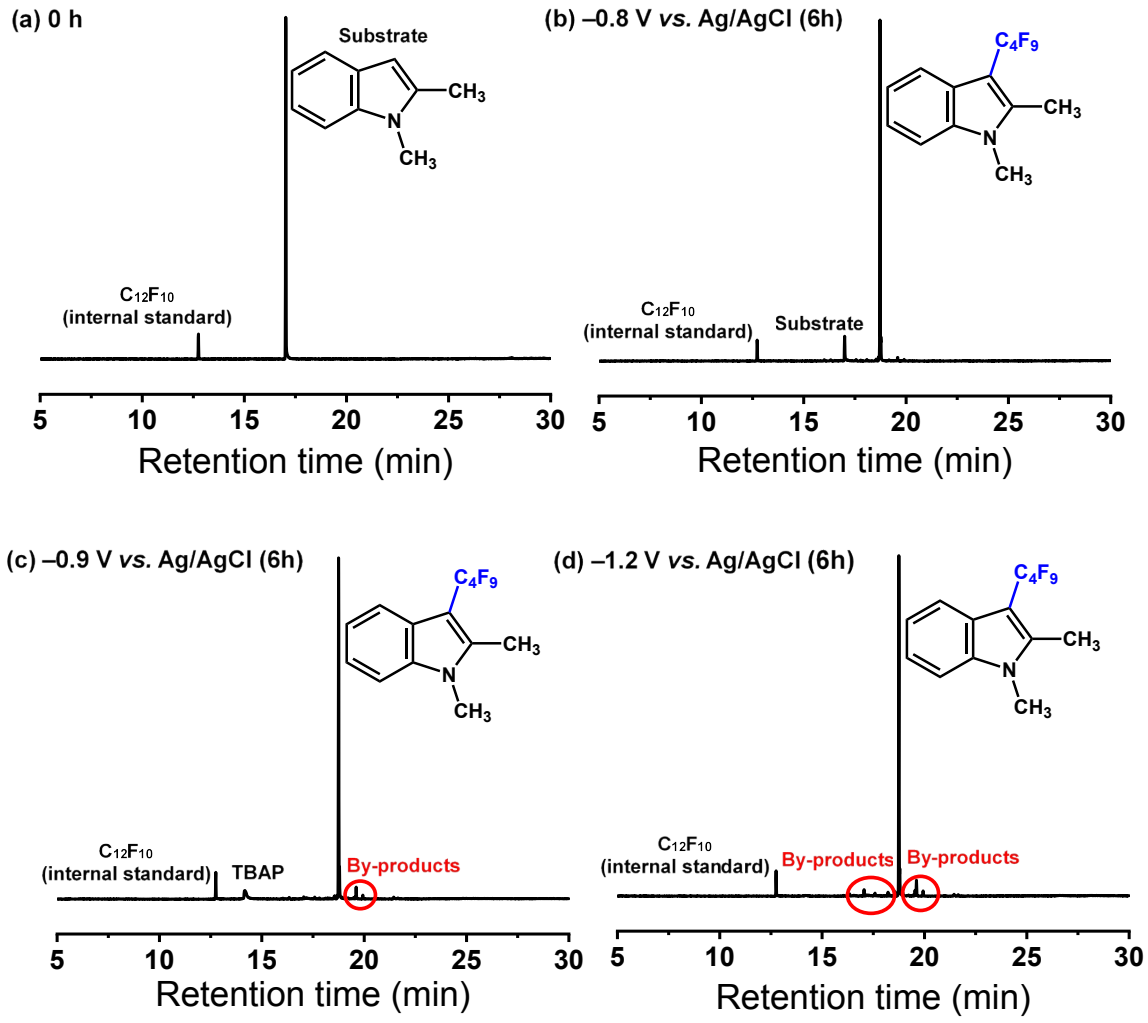


Figure S4. GC-MS spectra for perfluoroalkylation of 1,2-dimethylindole (**1**) as the substrate (a) before and after electrochemical perfluoroalkylation in CH_3CN under (b) –0.8 V *vs.* Ag/AgCl for 6 h (**Table 1, entry 4**), (c) –0.9 V *vs.* Ag/AgCl for 6 h (**Table 1, entry 6**) and (d) –1.2 V *vs.* Ag/AgCl for 6 h (**Table 1, entry 7**). Decafluorobiphenyl ($C_{12}F_{10}$) and tetrabutylammonium perchlorate (TBAP, *n*-Bu_4NClO_4) were used as the internal standard and supporting electrolyte, respectively. The results suggested that –0.8 V *vs.* Ag/AgCl is suitable for performing the catalytic reactions.

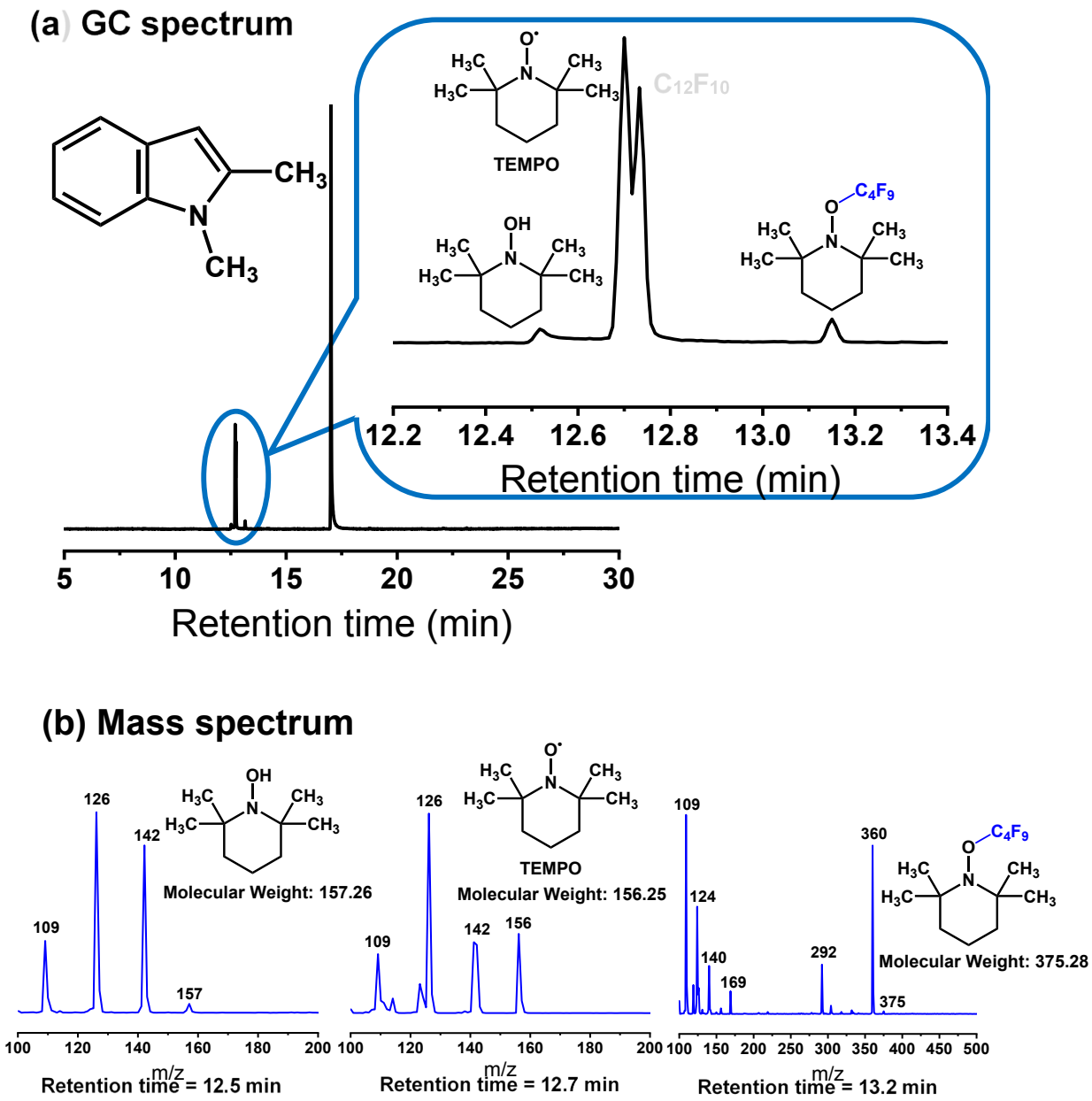


Figure S5. GC-MS spectra for perfluoroalkylation of 1,2-dimethylindole (**1**) (5.0×10^{-2} M) after 6 h electrolysis in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl free radical (TEMPO) (5.0×10^{-2} M) (**Table 1, entry 15**).

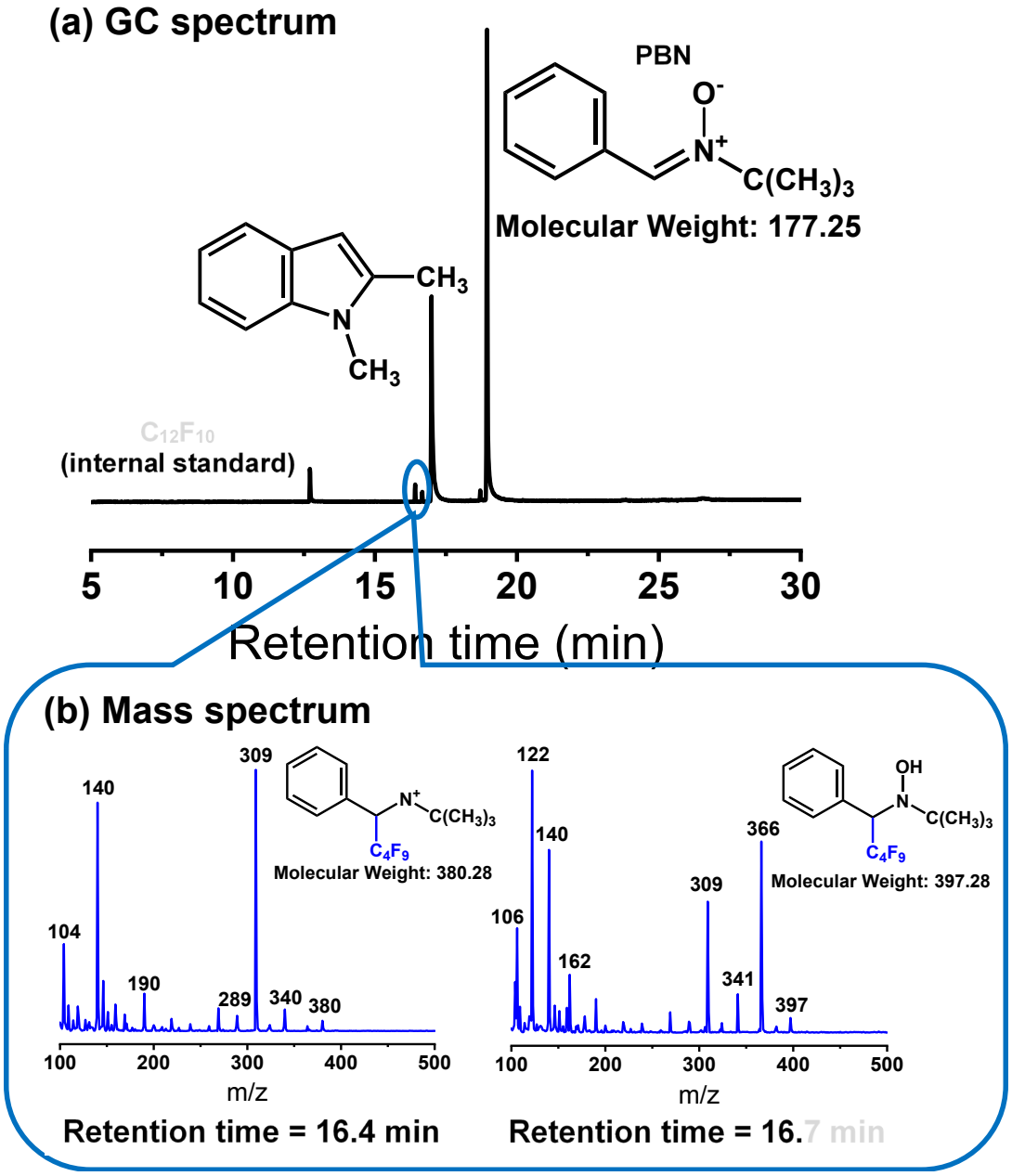


Figure S6. GC-MS spectra for perfluoroalkylation of 1,2-dimethylindole (**1**) (5.0×10^{-2} M) after 6 h electrolysis in the presence of *N*-*tert*-butyl-α-phenylnitrone (PBN) (5.0×10^{-1} M) (**Table 1, entry 16**).

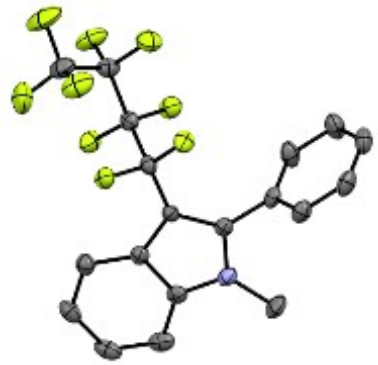
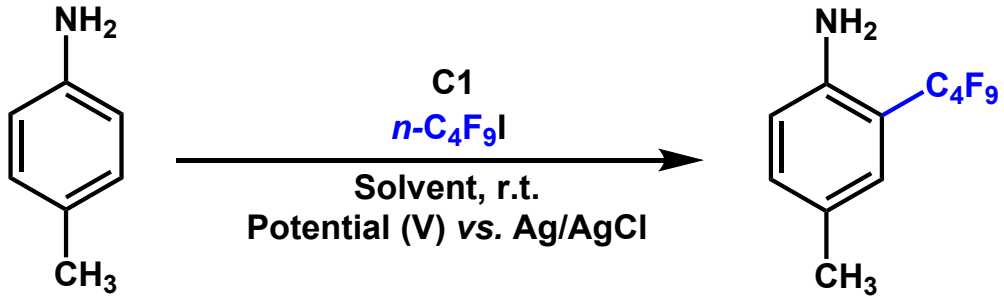


Figure S7. Crystal structure of **3•C_4F_9**. The thermal ellipsoid is drawn at 50% probability. Color code: C, gray; N, light blue; F, light green. Hydrogen atoms are omitted for clarity.

Table S2. Crystallographic data for **3•C_4F_9**.

Compound	**3•C_4F_9**
CCDC No.	1966854
empirical formula	$C_{19}H_{12}F_9N$
formula weight	425.30
temperature [K]	123
wavelength [Å]	0.71073
crystal system	triclinic
space group	P -1
a [Å]	8.7352(10)
b [Å]	9.9728(11)
c [Å]	11.1879(16)
α [°]	89.774(11)
β [°]	74.116(11)
γ [°]	68.544(11)
Volume [Å^3]	867.4(2)
Z	2
Density (calculated) [g/cm^3]	1.628
Absorption coefficient [mm^{-1}]	0.163
F(000)	428.0
□□*ϑ* [°]	2.62 to 25.346
Reflections collected	8448
Independent reflections	3179 [$R_{(int)}$ = 0.0488]
Data / restraints / parameters	3179 / 0 / 263
Goodness-of-fit on F^2	1.072
$R1$[a] [$I>2\sigma(I)$]	0.0432
$wR2$ [b] (all data)	0.1211
Largest diff. peak and hole [e.Å^{-3}]	0.22 and -0.26

Table S3. Optimization of the reaction conditions for the perfluoroalkylation of aniline derivatives[a]



5 **5•C_4F_9**

Entry	Potential (V) *vs.* Ag/AgCl	Solvent[b]	Yield (%)[c]
1	–0.8 V	CH_3CN	17
2[d]	–0.8 V	CH_3CN	1
3[e]	–0.8 V	CH_3CN	2
4[f]	–0.8 V	CH_3CN	20
5	–0.8 V	CH_3OH	10
6	–0.8 V	DMSO	11
7[g]	–0.8 V	DMSO	32
8[h]	–0.8 V	DMSO	30
9[i]	–0.8 V	DMSO	48

[a] Reaction conditions: [**C1**] = 5.0×10^{-4} M (1 mol%); [*p*-toluidine (**5**)] = 5.0×10^{-2} M; [*n*-C_4F_9I] = 0.5 eq. of substrate per 1 h, 3 eq. in total; [*n*-Bu_4NClO_4] = 0.1 M; Internal standard: $C_{12}F_{10}$; Reaction time: 6 h. [b] Abbreviations: CH_3OH, methanol; CH_3CN, acetonitrile; DMSO, dimethyl sulfoxide. [c] The yields are based on the initial concentration of *p*-toluidine (**5**) and were determined by GC-MS. [d] Without **C1** catalyst. [e] In the presence of [PBN] (5.0×10^{-1} M) as the radical trapping reagent. [f] 5 mol% **C1** catalyst in CH_3CN. [g] 5 mol% **C1** catalyst in DMSO. [h] With visible light (≥ 420nm). [i] 3 mol% **C1** catalyst in DMSO with visible light (≥ 420nm).

Initially, we chose the reaction of *p*-toluidine (**5**) in CH_3CN as the model system to screen the most efficient catalytic system (**Table S3**). Regrettably, the above standard conditions led to poor yield of the desired product **5•C_4F_9** (**Table S3, entry 1**) due to the formation of by-products (**Figure S8 (a)**). Moreover, the absence of the **C1** catalyst and the presence of PBN led to nearly no product formation (**Table S3, entries 2** and **3**), demonstrating the vital role of the catalyst and indicating a possible radical pathway in this reaction. To increase the yield, various amounts of the catalyst and different solvents were screened to improve the efficiency. Using 5 mol% **C1** (**Table S3, entry 4**) in CH_3CN did not improve the yield significantly. Similarly, using different solvents still did not increase the yield of **5•C_4F_9** (**Table S3, entries 5** and **6**). Although the yield of **5•C_4F_9** in DMSO was slightly lower than that in CH_3CN due to the lower conversion, we continued to optimize the reaction conditions based on

DMSO solvent because of the excellent reaction selectivity and lower by-product formation in DMSO (**Figure S8 (b)**). Furthermore, we achieved the desired product in a 32% yield using 5 mol% catalyst in DMSO (**Table S3, entry 7**) attributed to the high conversion of **5** in DMSO (**Figure S8 (c)**). In addition, based on our previous work, we assumed that the homolytic cleavage of the Co–C intermediate will be affected by the photolysis.[1] Thus, visible light was optimized for this reaction. As shown in **entry 8** (**Table S3**), the yield for **5•C_4F_9** increased up to 30% using a visible-light source, implying that visible-light irradiation was essential for the reaction to proceed. Furthermore, the optimal reaction conditions were described in **entry 9** (**Table S3**) with 48% yield of **5•C_4F_9** owing to higher conversion than before (**Figure S8 (d)**). Namely, –0.8 V *vs.* Ag/AgCl was chosen as the controlled potential for the electrolysis with the aniline substrates with 3 eq. of *n*-C_4F_9I in the presence of **C1** (3 mol%) in DMSO for 6 h under visible light irradiation.

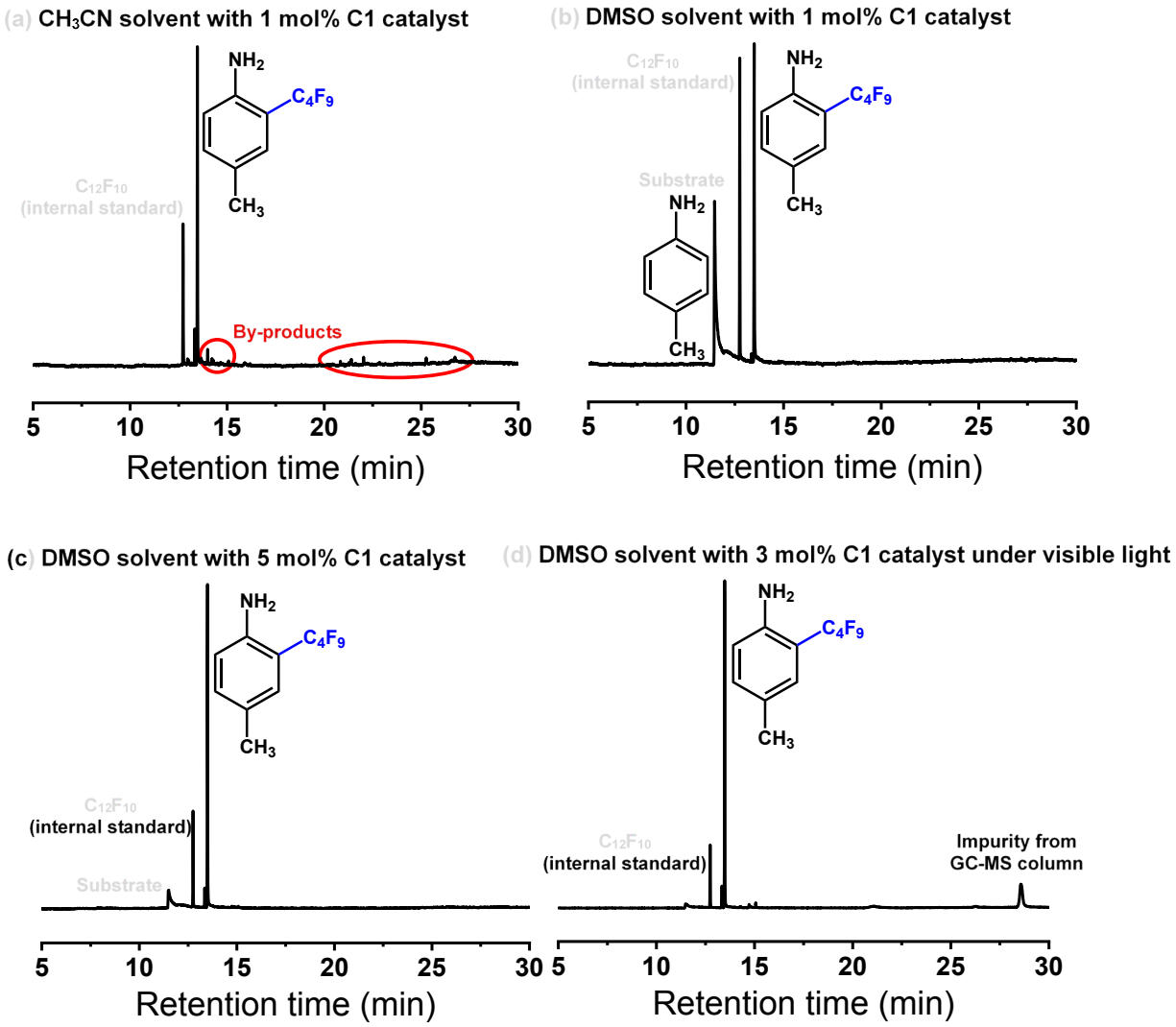


Figure S8. GC-MS spectra for perfluoroalkylation of *p*-toluidine (**5**) as the substrate after 6 h electrolysis in different conditions (a) CH_3CN solvent with 1 mol% **C1** catalyst (**Table S3, entry 1**), (b) DMSO solvent with 1 mol% **C1** catalyst (**Table S3, entry 6**), (c) DMSO solvent with 5 mol% **C1** catalyst (**Table S3, entry 7**), and (d) DMSO solvent with 3 mol% **C1** catalyst under visible light (**Table S3, entry**

9). Decafluorobiphenyl ($C_{12}F_{10}$) was used as the internal standard.

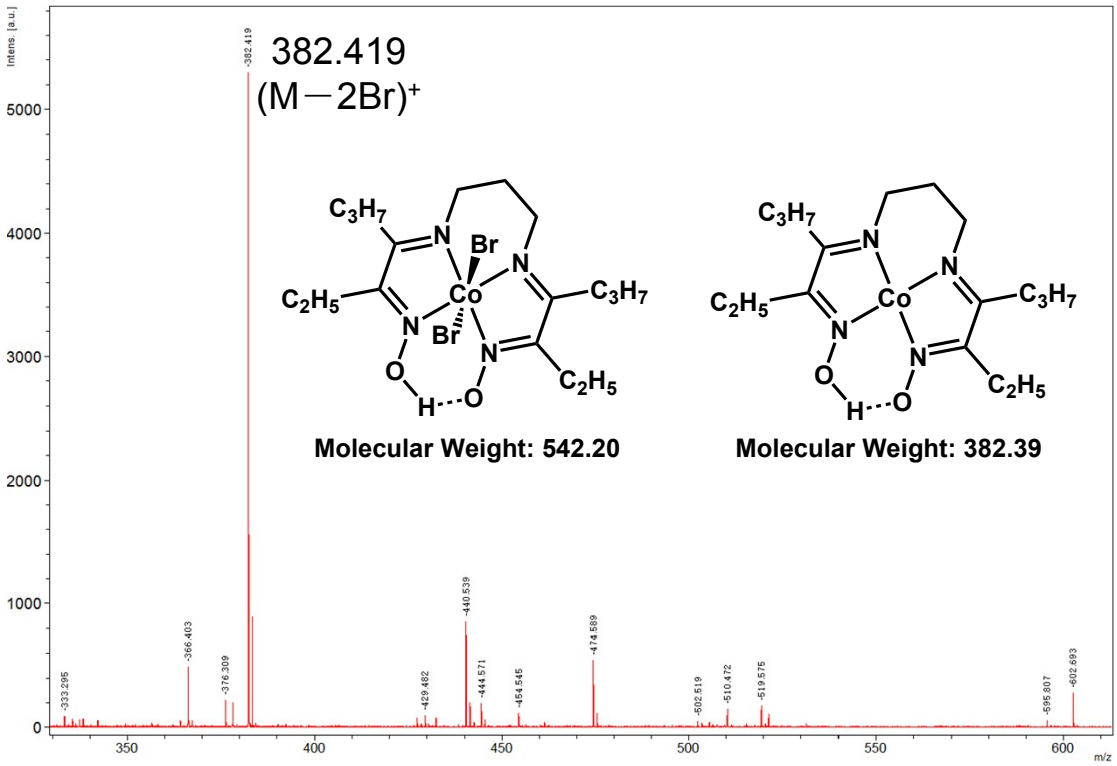
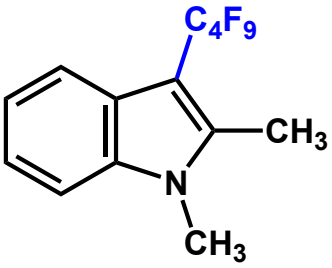


Figure S9. MALDI-TOF-MS result after the catalytic reaction.

Products data

Note: For the ^{13}C NMR (F coupled), peaks for the C of perfluoroalkyl chain and C adjacent to perfluoroalkyl chain (in some cases) are too broad to be assigned (not shown in the following data for some compounds).[2]

1,2-dimethyl-3-(nonafluorobutyl)-1*H*-indole (1•C_4F_9)

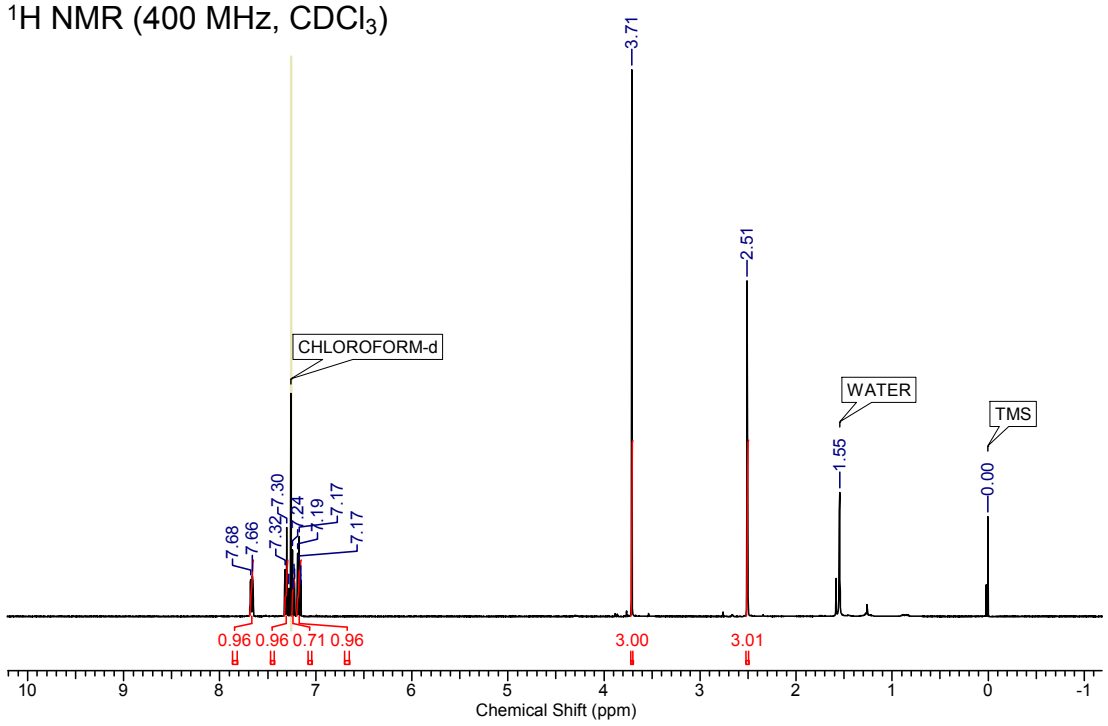


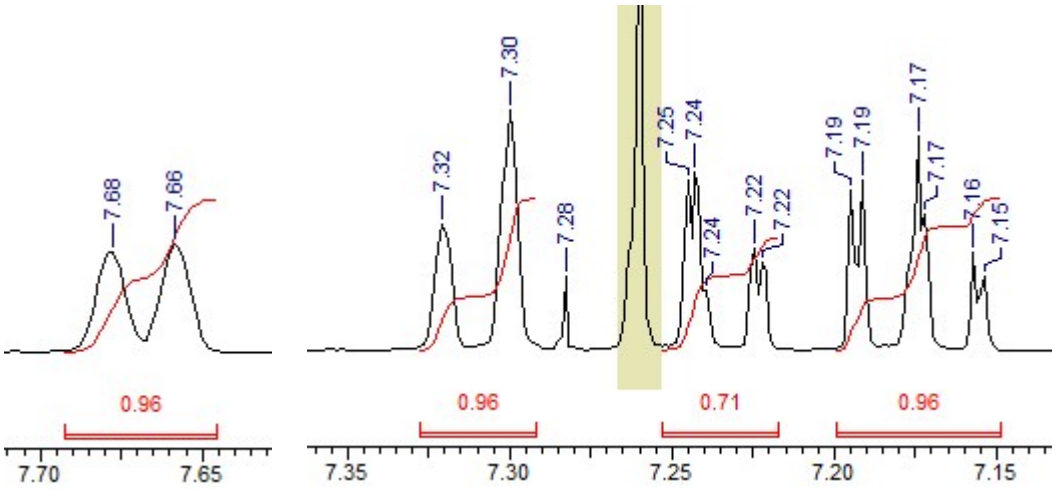
Compound **1•C_4F_9**[1] was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0×10^{-2} M) in 85% yield as a white solid.

^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, *J* = 7.78 Hz, 1H), 7.31 (d, *J* = 8.23 Hz, 1H), 7.25-7.22 (m, 1H), 7.19-7.15 (m, 1H), 3.71 (s, 3H), 2.51 (s, 3H);

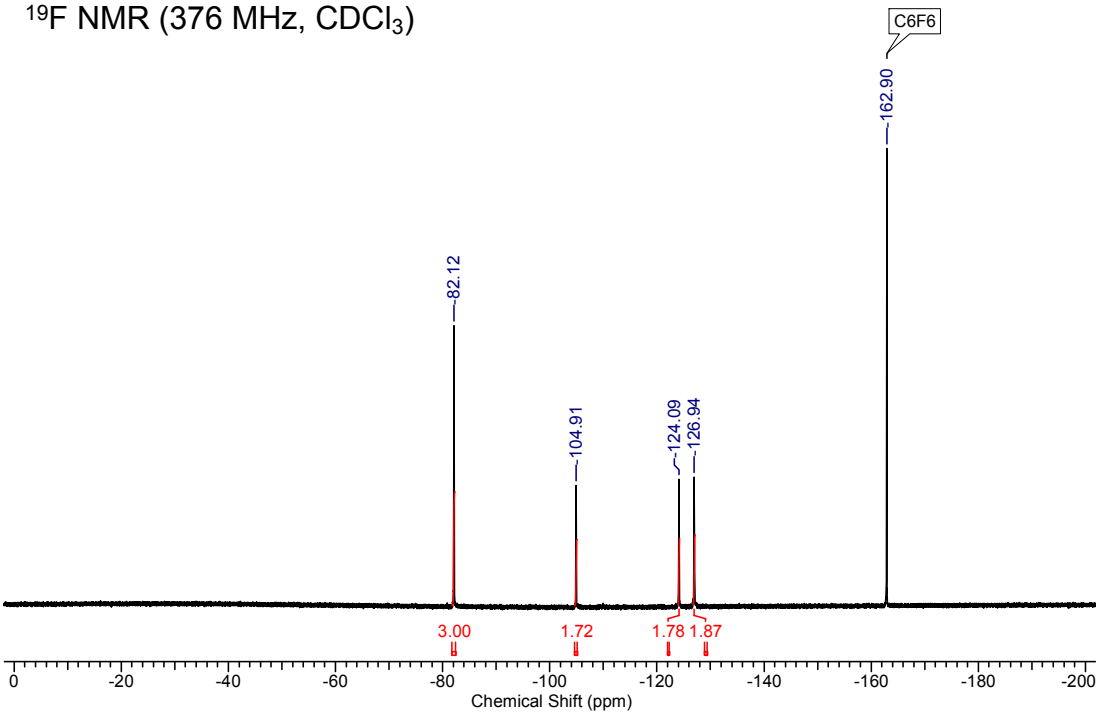
^{19}F NMR (376 MHz, $CDCl_3$): δ –82.12 (3F, $–CF_3$), –104.91 (2F, $–CF_2$), –124.09 (2F, $–CF_2$), –126.94 (2F, $–CF_2$);

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 136.7, 125.8, 122.2, 121.3, 119.9, 119.0, 118.0, 116.8, 116.0, 109.4, 100.4, 29.7, 11.4.

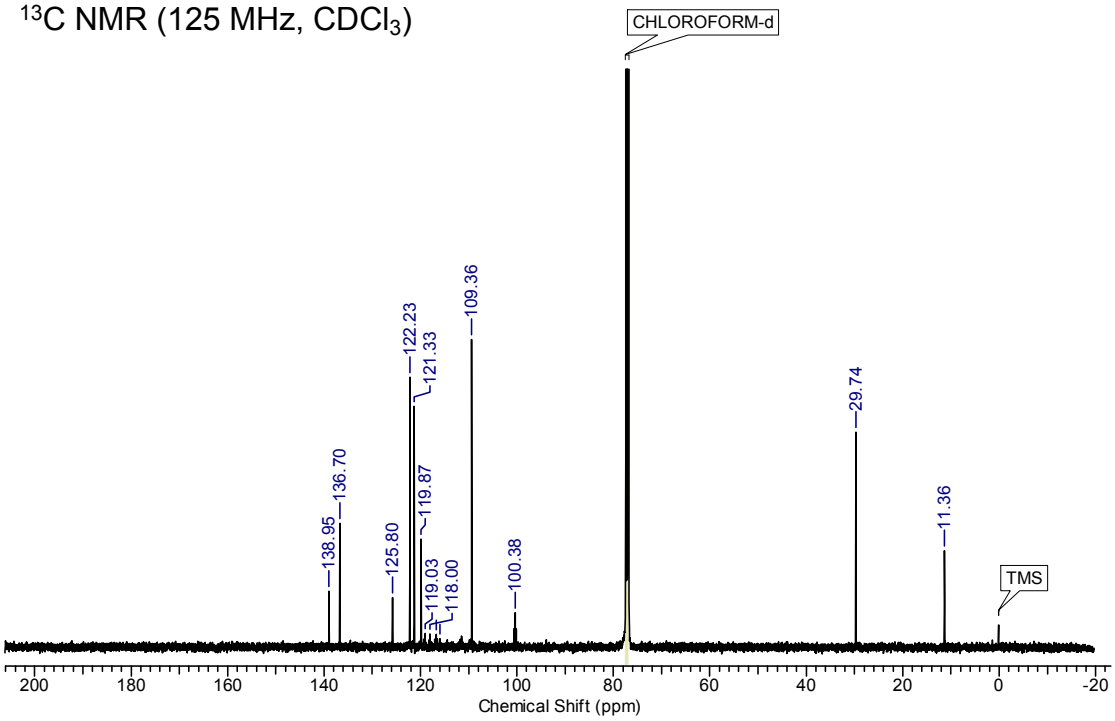




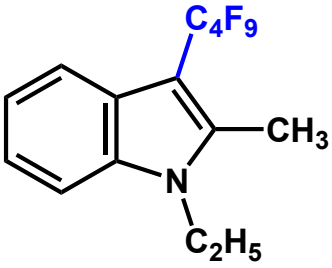
^{19}F NMR (376 MHz, $CDCl_3$)



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



1-ethyl-2-methyl-3-(nonafluorobutyl)-1*H*-indole (2•C_4F_9)



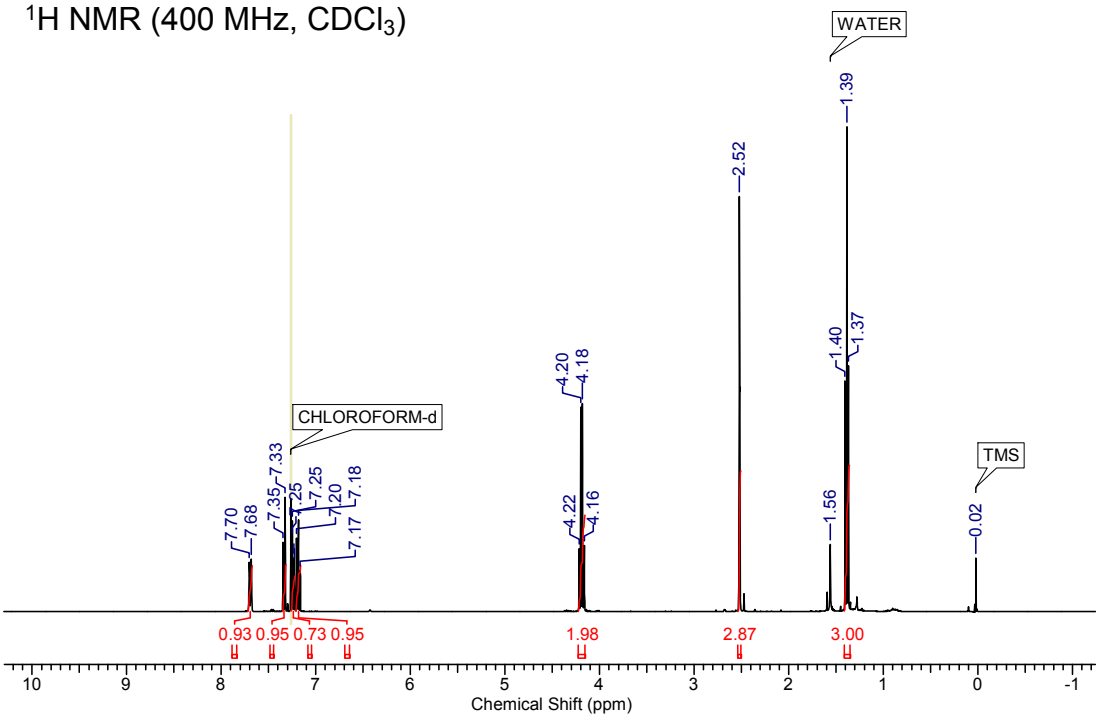
Compound **2•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0×10^{-2} M) in 87% yield as a yellow oil.

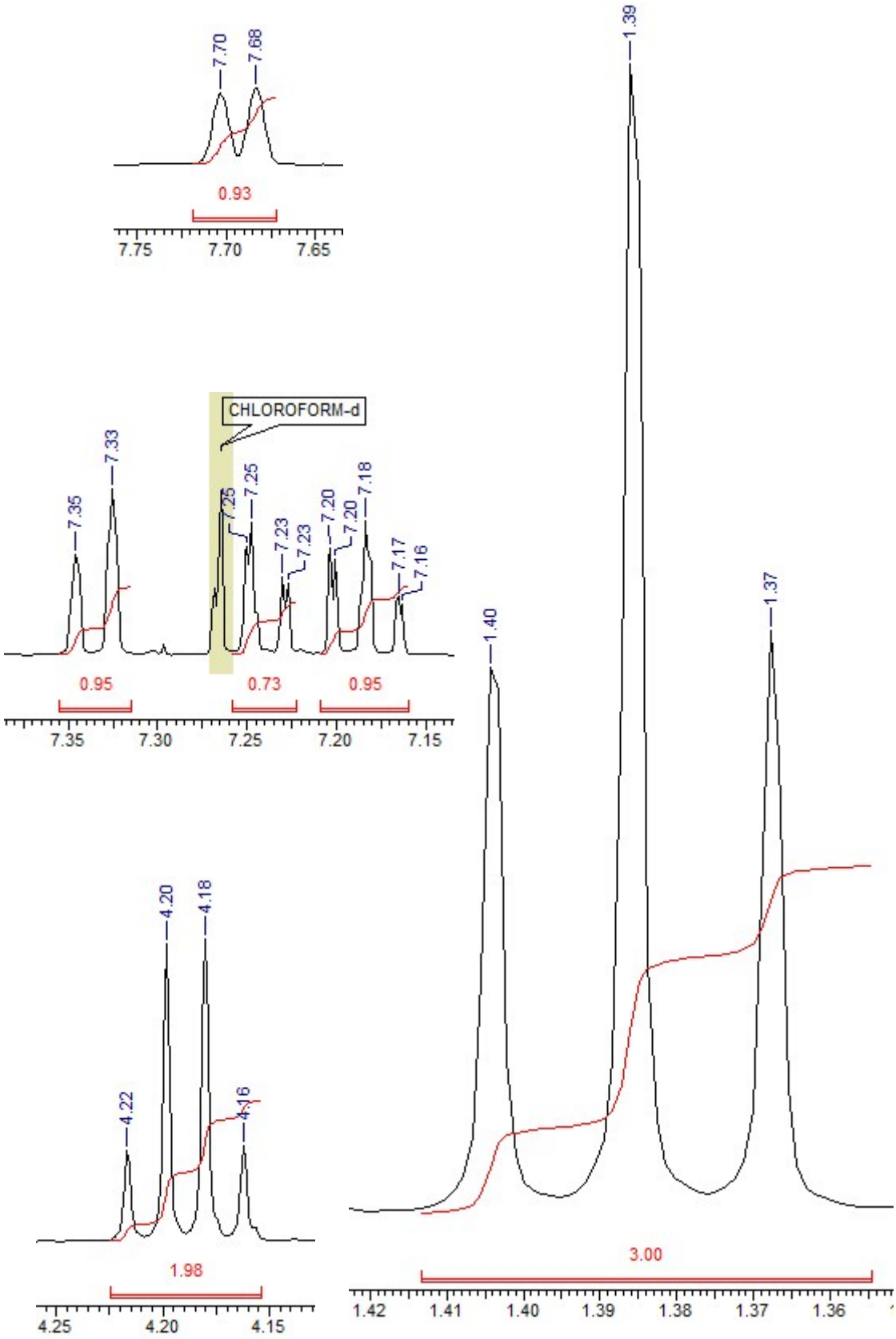
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.78 Hz, 1H), 7.34 (d, *J* = 8.23 Hz, 1H), 7.25-7.23 (m, 1H), 7.20-7.16 (m, 1H), 4.19 (q, *J* = 7.32 Hz, 2H), 2.52 (s, 3H), 1.39 (t, *J* = 7.32 Hz, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –82.09 (3F, $–CF_3$), –104.84 (2F, $–CF_2$), –124.08 (2F, $–CF_2$), –126.96 (2F, $–CF_2$);

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 135.6, 126.0, 122.2, 121.2, 120.0, 119.1, 118.1, 116.8, 116.0, 109.4, 100.4, 38.1, 15.0, 11.0;

HRMS (EI, *m/z*): Cald. for $C_{15}H_{12}F_9N$ $[M]^+$ 377.0826; found: 377.0822.

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1.37
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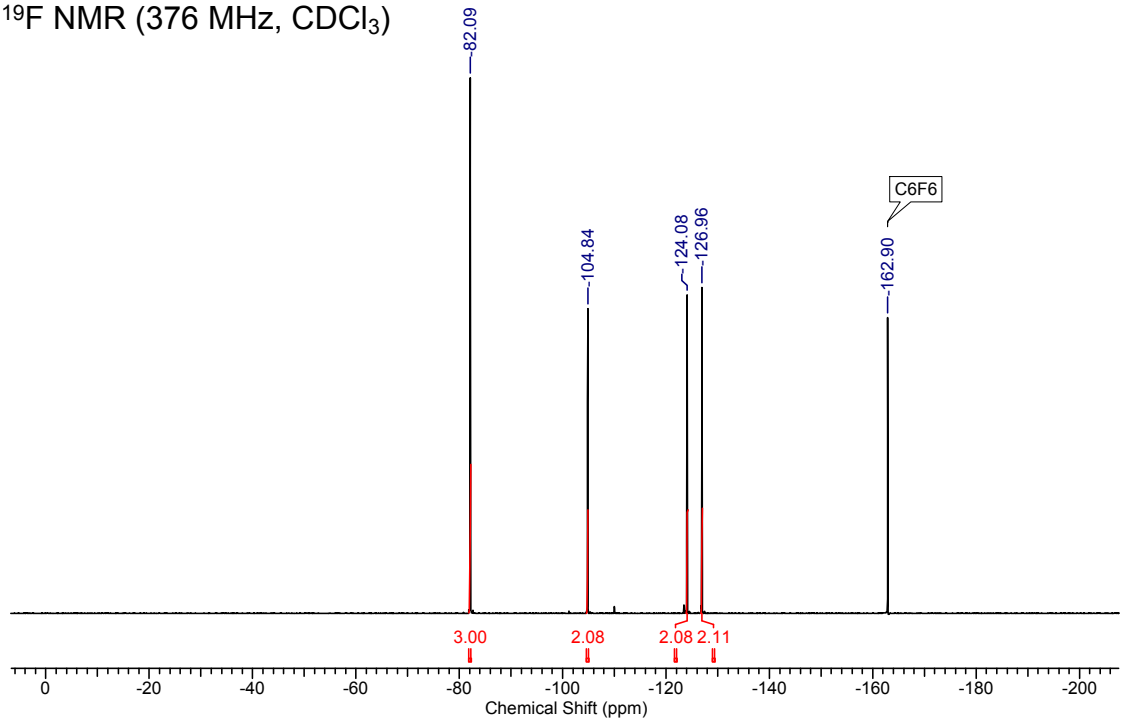
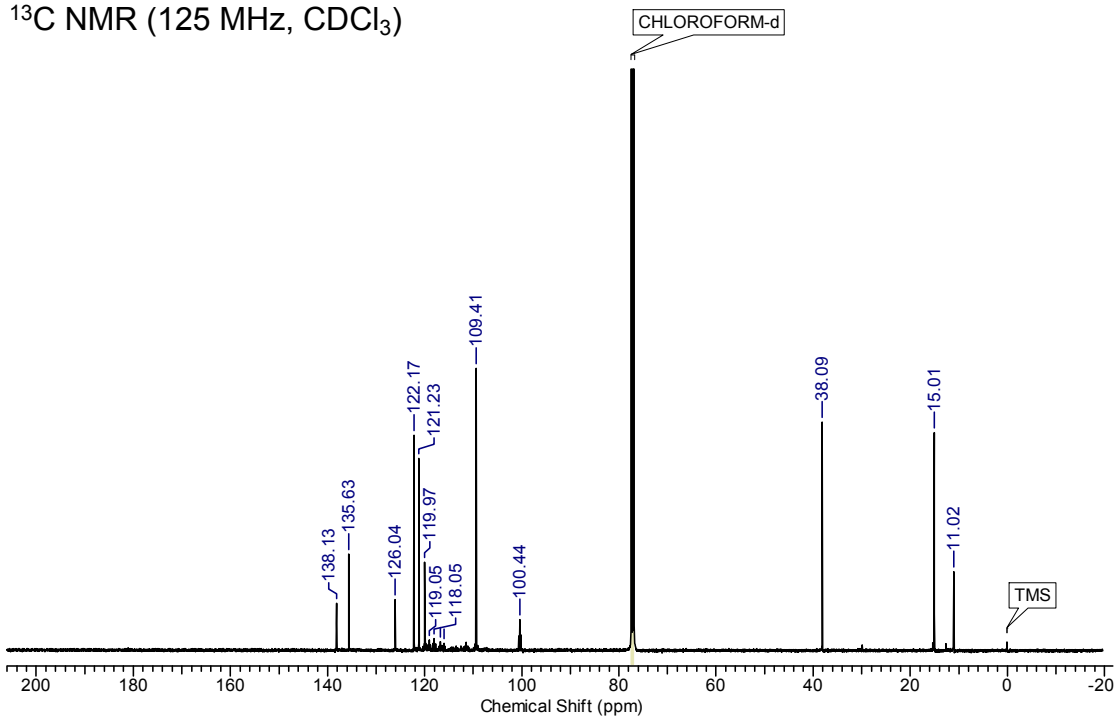
4.15

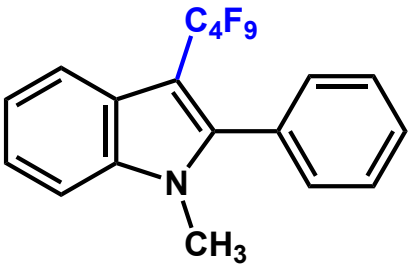
^{19}F NMR (376 MHz, $CDCl_3$)



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



1-methyl-3-(nonafluorobutyl)-2-phenyl-1*H*-indole (3•C_4F_9)



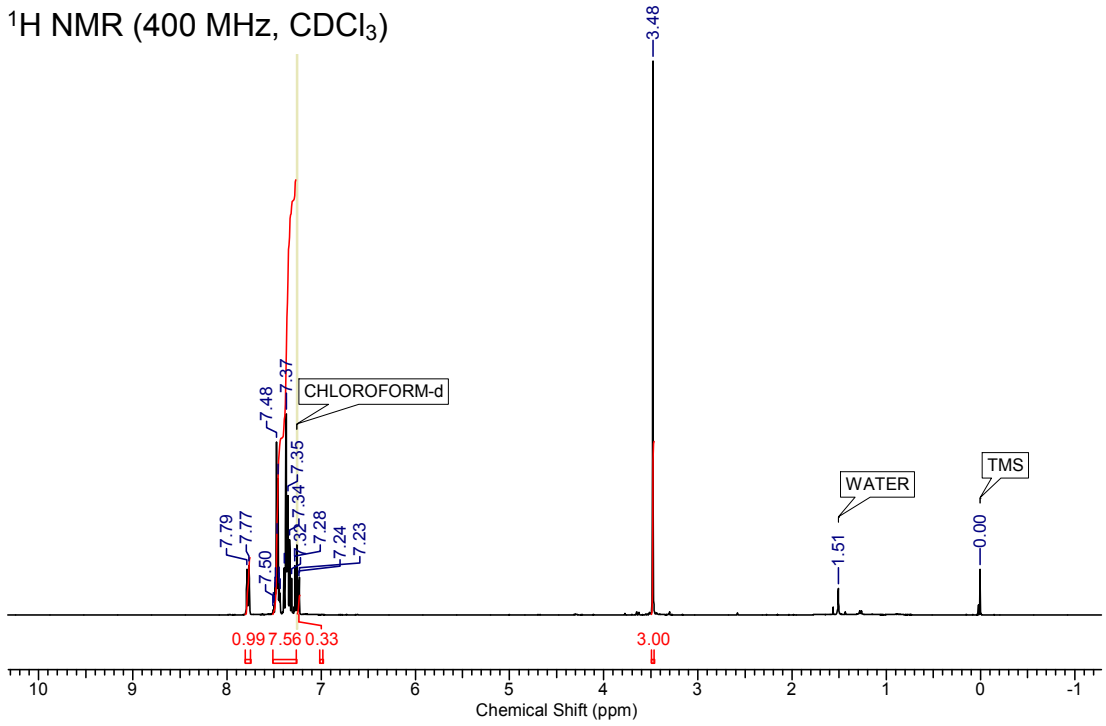
Compound **3•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 64% yield as a white solid.

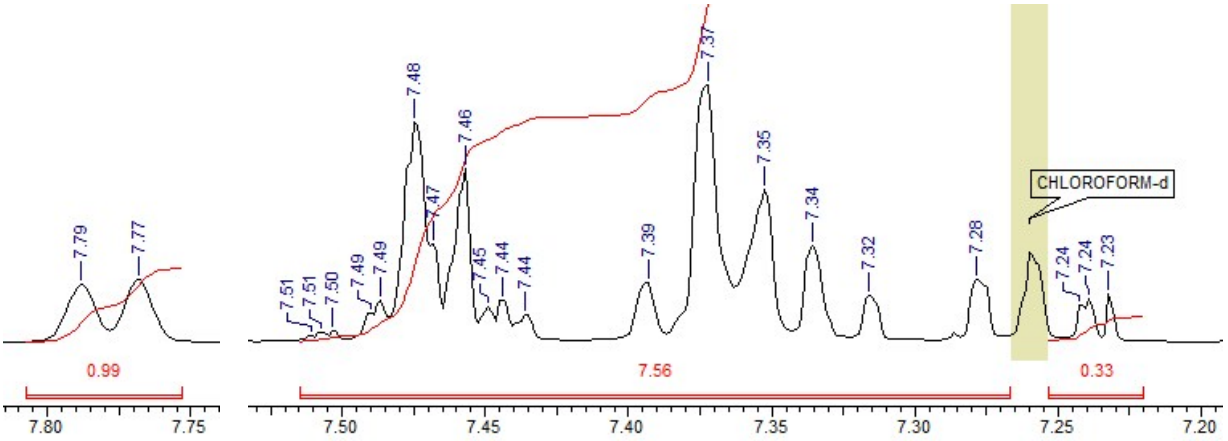
^{1}H NMR (400 MHz, CDCl3): δ 7.78 (d, *J* = 8.23 Hz, 1H), 7.51-7.23 (m, 8H), 3.48 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –82.03 (3F, $–CF_3$), –103.16 (2F, $–CF_2$), –122.81 (2F, $–CF_2$), –126.84 (2F, $–CF_2$);

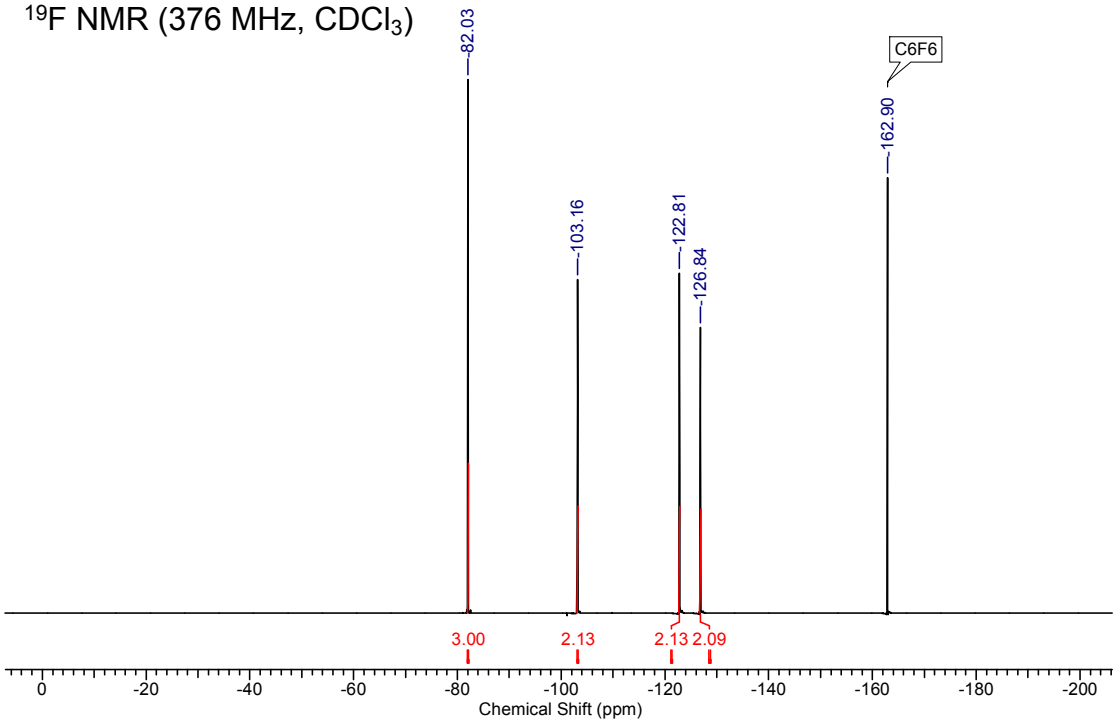
^{13}C NMR (125 MHz, $CDCl_3$): δ 142.5, 136.8, 130.7, 130.6, 129.4, 128.2, 125.6, 123.1, 121.7, 120.7, 119.3, 119.0, 117.3, 116.7, 115.3, 110.0, 101.8, 30.8;

HRMS (EI, *m/z*): Cald. for $C_{19}H_{12}F_9N$ $[M]^+$ 425.0826; found: 425.0824.

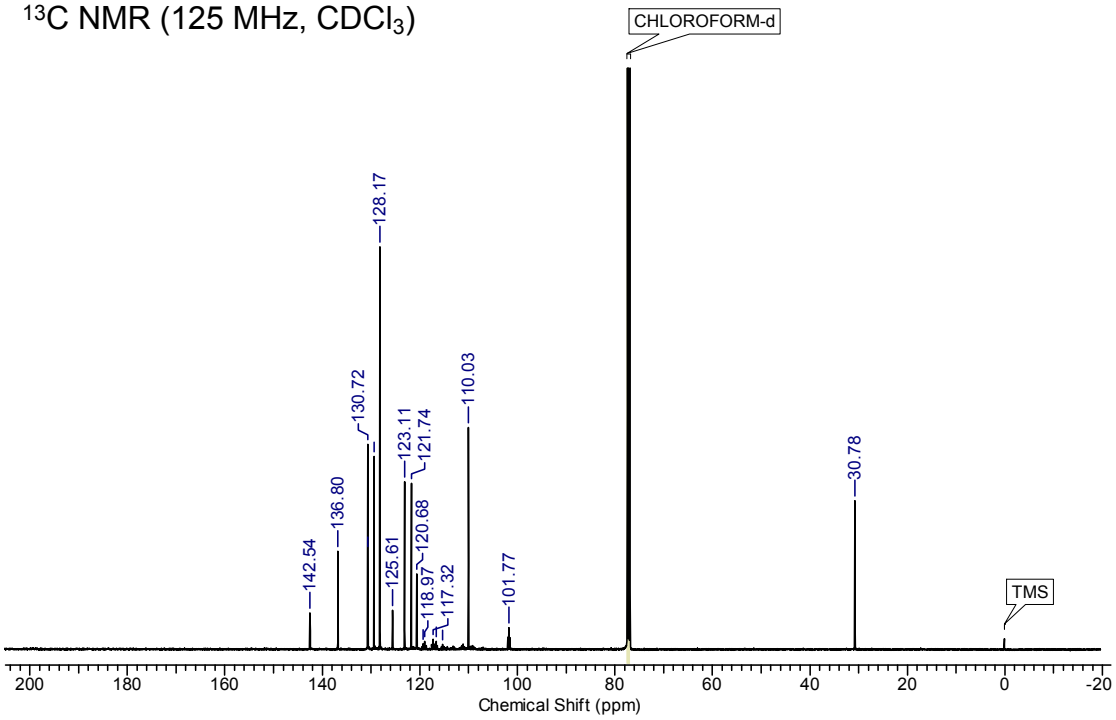




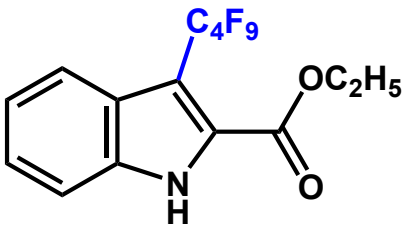
^{19}F NMR (376 MHz, $CDCl_3$)



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



Ethyl 3-(nonafluorobutyl)-1*H*-indole-2-carboxylate (4•C_4F_9)



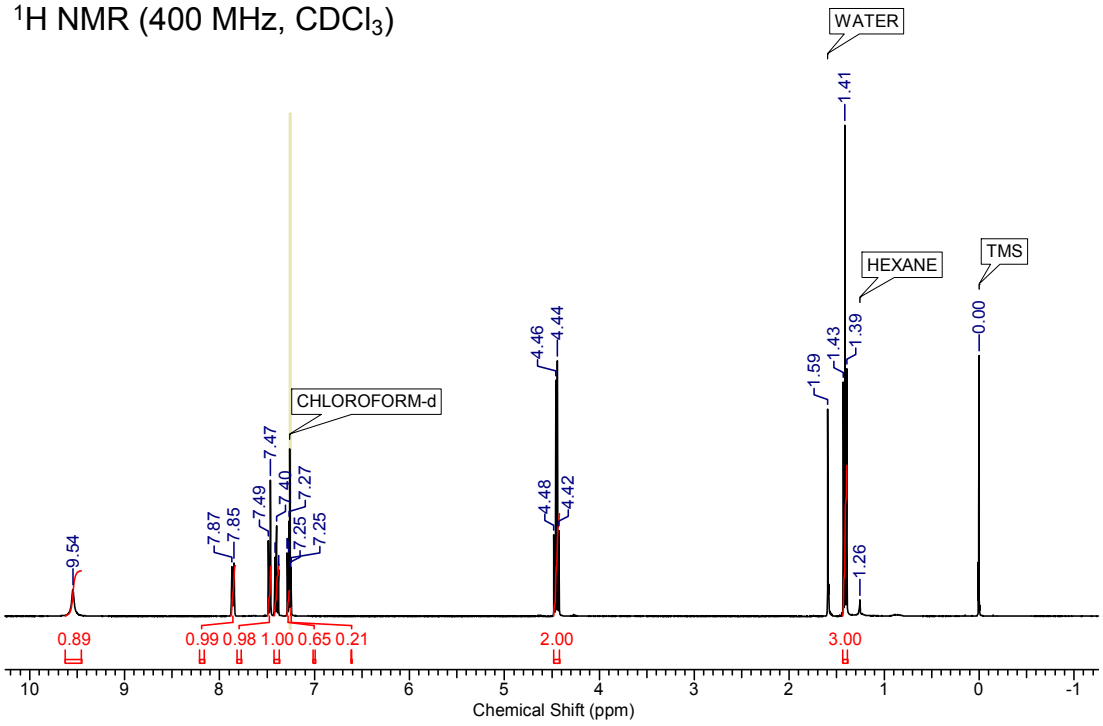
Compound **4•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0×10^{-2} M) in 45% yield as a white solid.

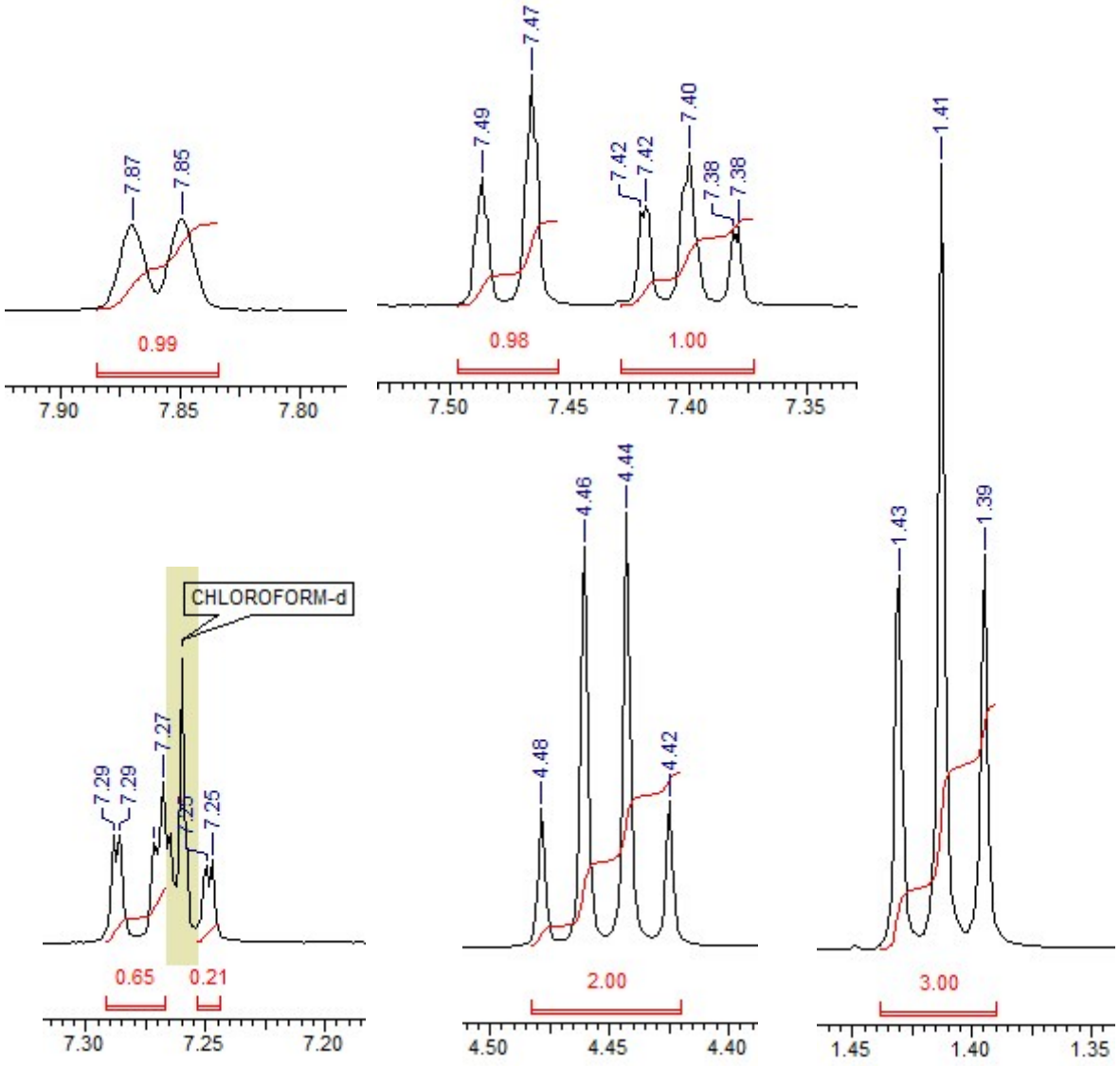
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.54 (brs, 1H), 7.86 (d, *J* = 8.23 Hz, 1H), 7.48 (d, *J* = 8.23 Hz, 1H), 7.42-7.38 (m, 1H), 7.29-7.25 (m, 1H), 4.45 (q, *J* = 7.32 Hz, 2H), 1.41 (t, *J* = 7.32 Hz, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –82.09 (3F, $–CF_3$), –102.66 (2F, $–CF_2$), –122.46 (2F, $–CF_2$), –127.06 (2F, $–CF_2$);

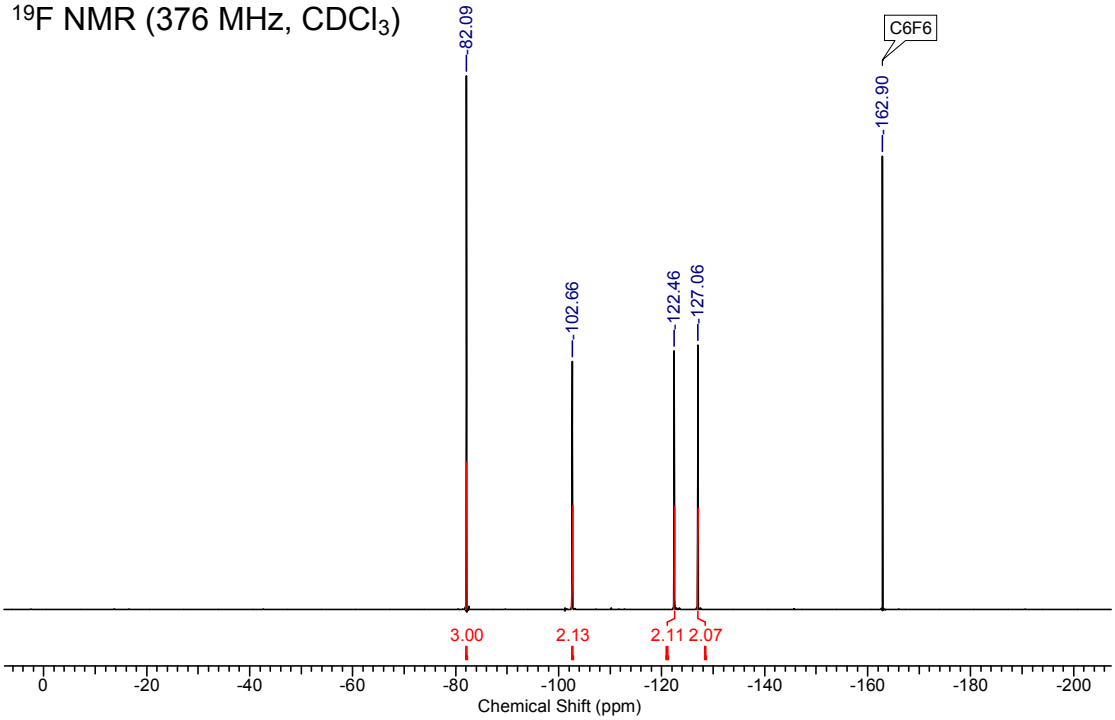
^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 134.8, 127.4, 126.6, 126.3, 122.9, 122.5, 119.0, 116.7, 112.2, 107.5, 62.4, 14.0;

HRMS (EI, *m/z*): Cald. for $C_{15}H_{10}F_9NO_2$ $[M]^+$ 407.0568; found: 407.0556.

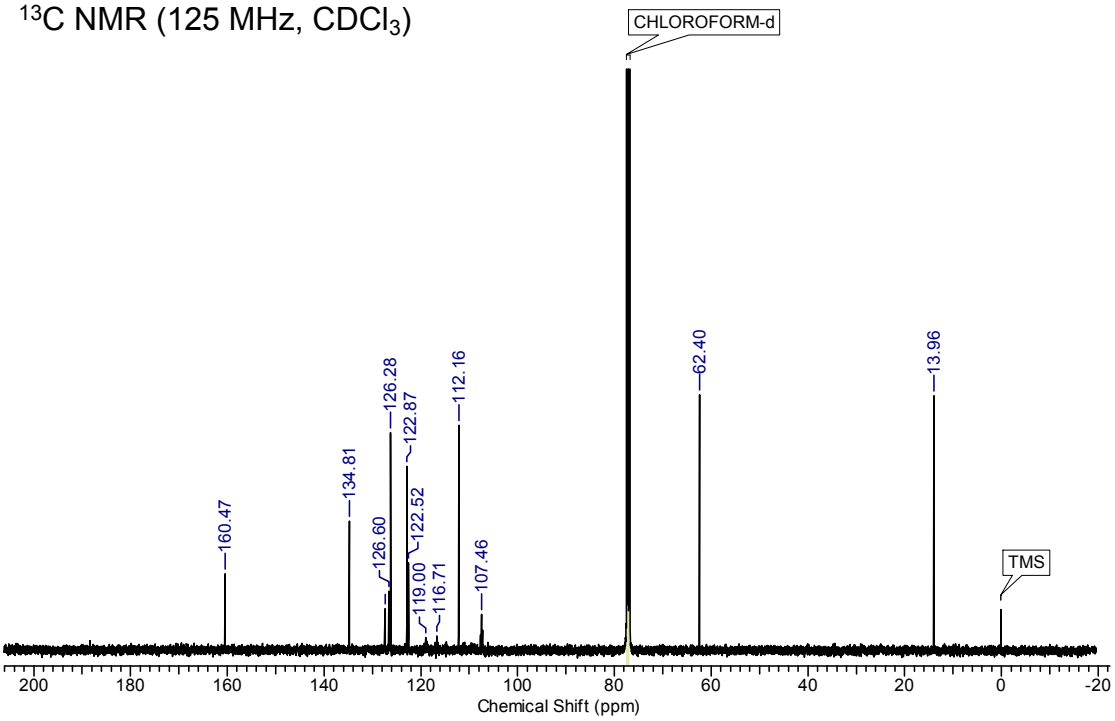



7.87
7.85
0.99
7.90
7.85
7.80
7.49
7.47
7.42
7.42
7.40
7.38
7.38
0.98
1.00
7.50
7.45
7.40
7.35
CHLOROFORM-d
7.29
7.29
7.27
7.25
0.65
0.21
7.30
7.25
7.20
4.48
4.46
4.44
4.42
2.00
4.50
4.45
4.40
1.43
1.41
1.39
3.00
1.45
1.40
1.35

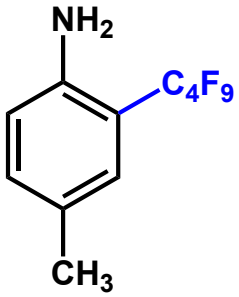
^{19}F NMR (376 MHz, $CDCl_3$)



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



4-methyl-2-(nonafluorobutyl)aniline (5•C_4F_9)

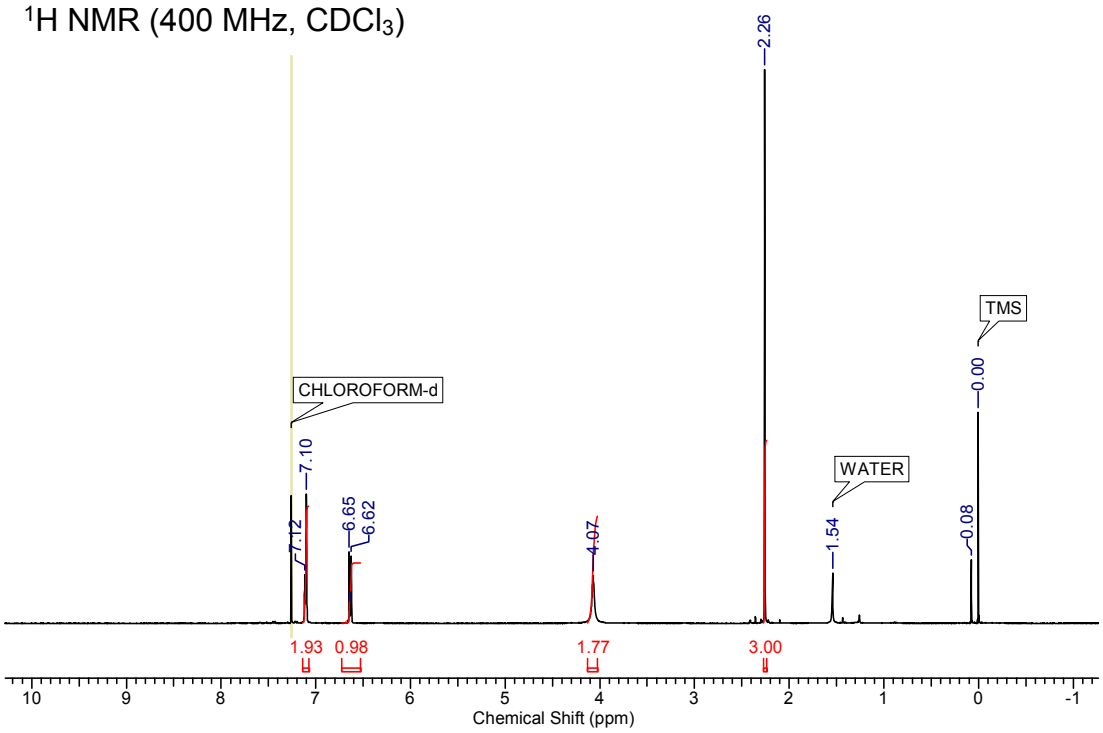


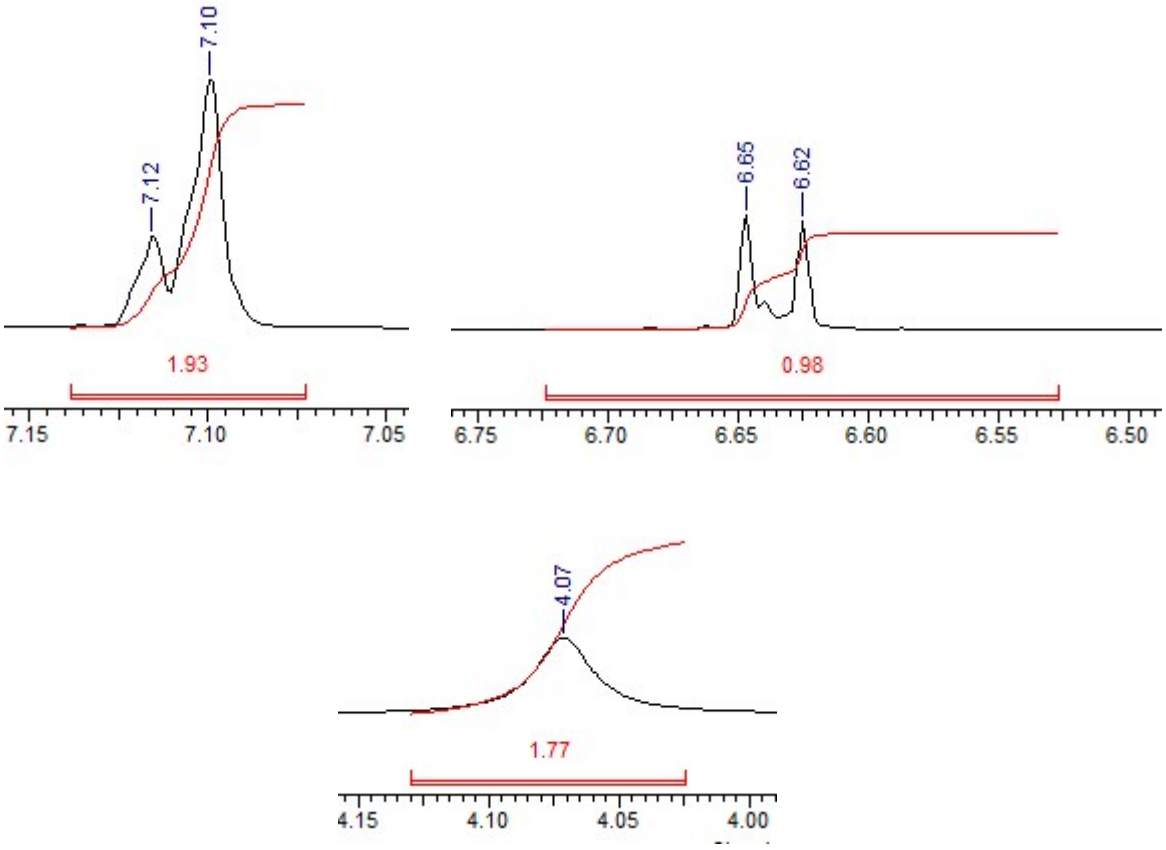
Compound **5•C_4F_9**[3] was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 48% yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.10 (m, 2H), 6.64 (d, *J* = 8.69 Hz, 1H), 4.07 (brs, 2H), 2.26 (s, 3H);

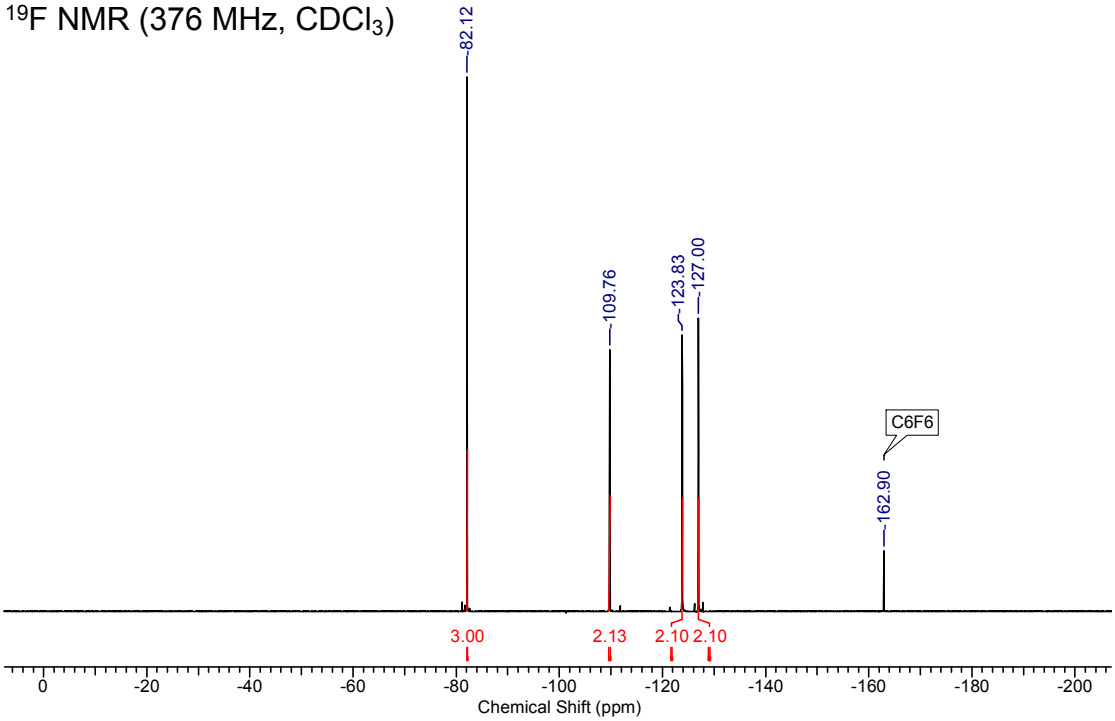
^{19}F NMR (376 MHz, $CDCl_3$): δ –82.12 (3F, $–CF_3$), –109.76 (2F, $–CF_2$), –123.83 (2F, $–CF_2$), –127.00 (2F, $–CF_2$);

^{13}C NMR (125 MHz, $CDCl_3$): δ 143.7, 134.0, 128.9, 127.3, 118.2, 111.3, 20.3.

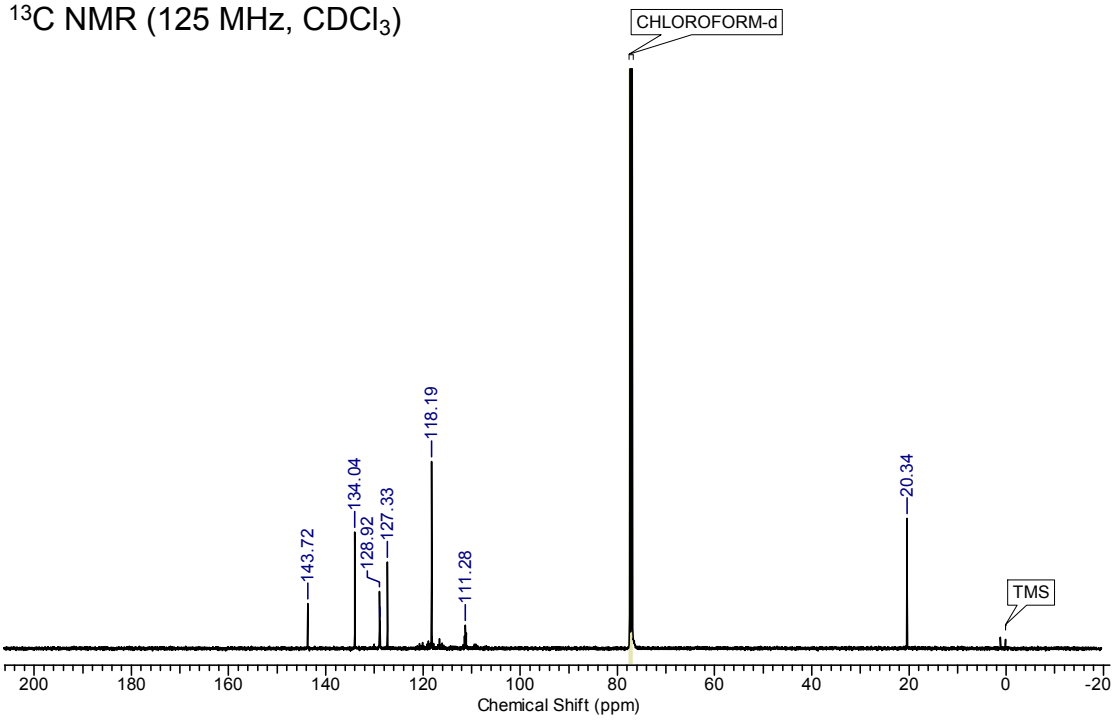



7.10
7.12
1.93
7.15
7.10
7.05
6.65
6.62
0.98
6.75
6.70
6.65
6.60
6.55
6.50
4.07
1.77
4.15
4.10
4.05
4.00

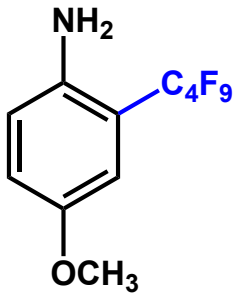
^{19}F NMR (376 MHz, $CDCl_3$)



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



4-methoxy-2-(nonafluorobutyl)aniline (6•C_4F_9)

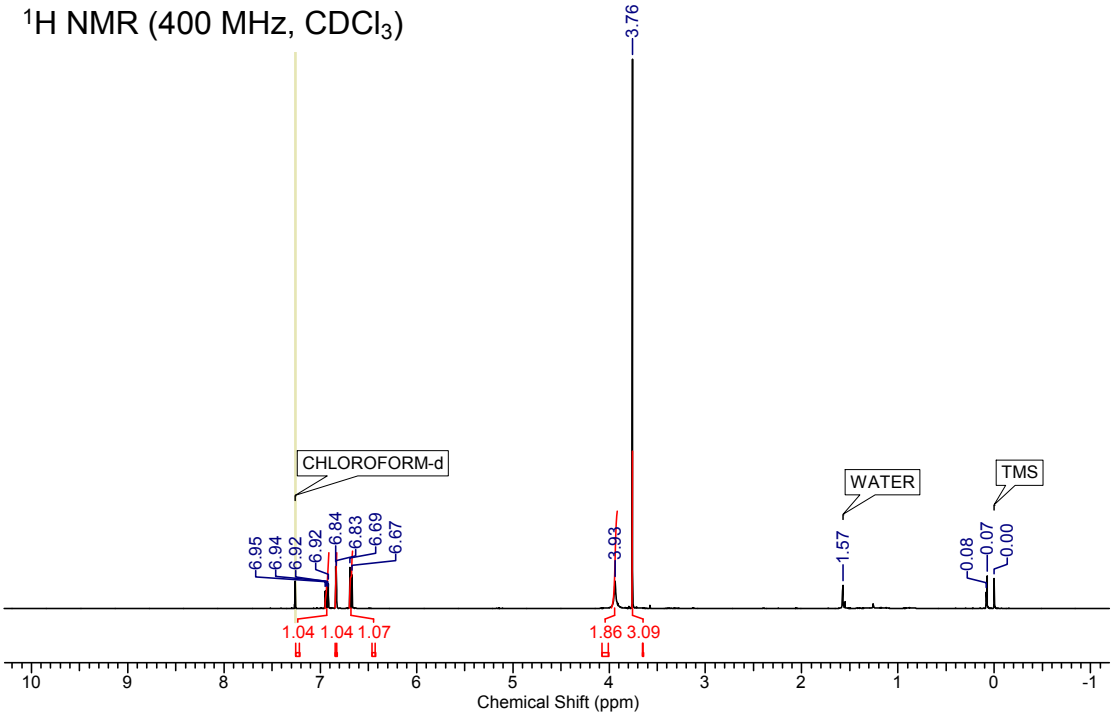


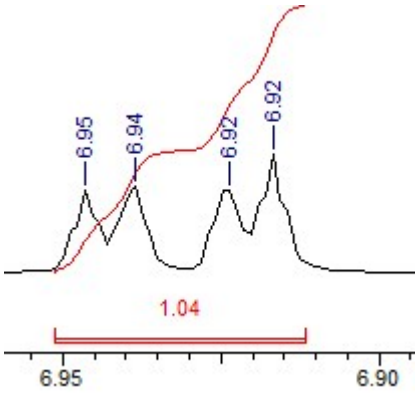
Compound **6•C_4F_9**[3] was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 65% yield as a yellow oil.

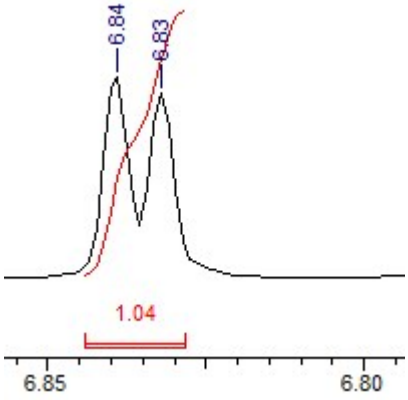
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95-6.92 (m, 1H), 6.84 (d, *J* = 2.74 Hz, 1H), 6.68 (d, *J* = 8.69 Hz, 1H), 3.93 (brs, 2H), 3.76 (s, 3H);

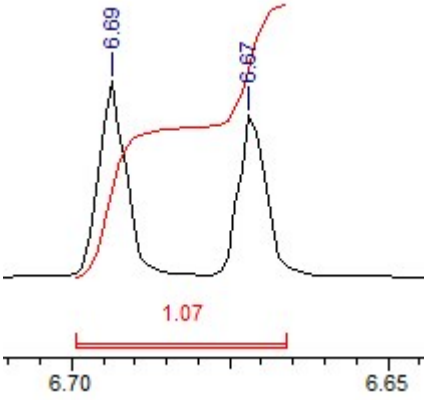
^{19}F NMR (376 MHz, $CDCl_3$): δ –82.15 (3F, –CF_3), –110.04 (2F, –CF_2), –123.86 (2F, –CF_2), –127.06 (2F, –CF_2);

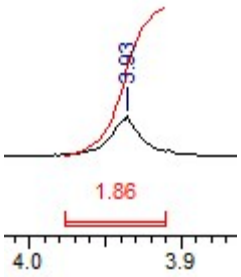
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 140.0, 120.6, 119.7, 118.9, 117.7, 116.6, 115.7, 113.1, 112.0, 56.1.



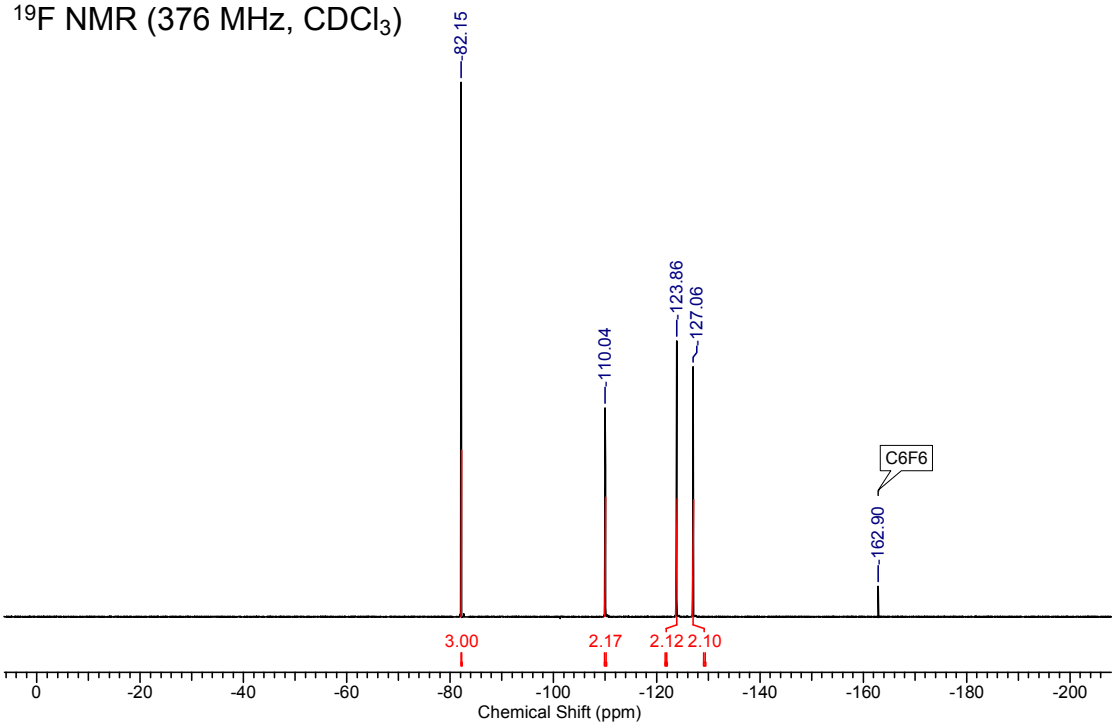

6.95
6.94
6.92
6.92
1.04
6.95
6.90


6.84
6.83
1.04
6.85
6.80

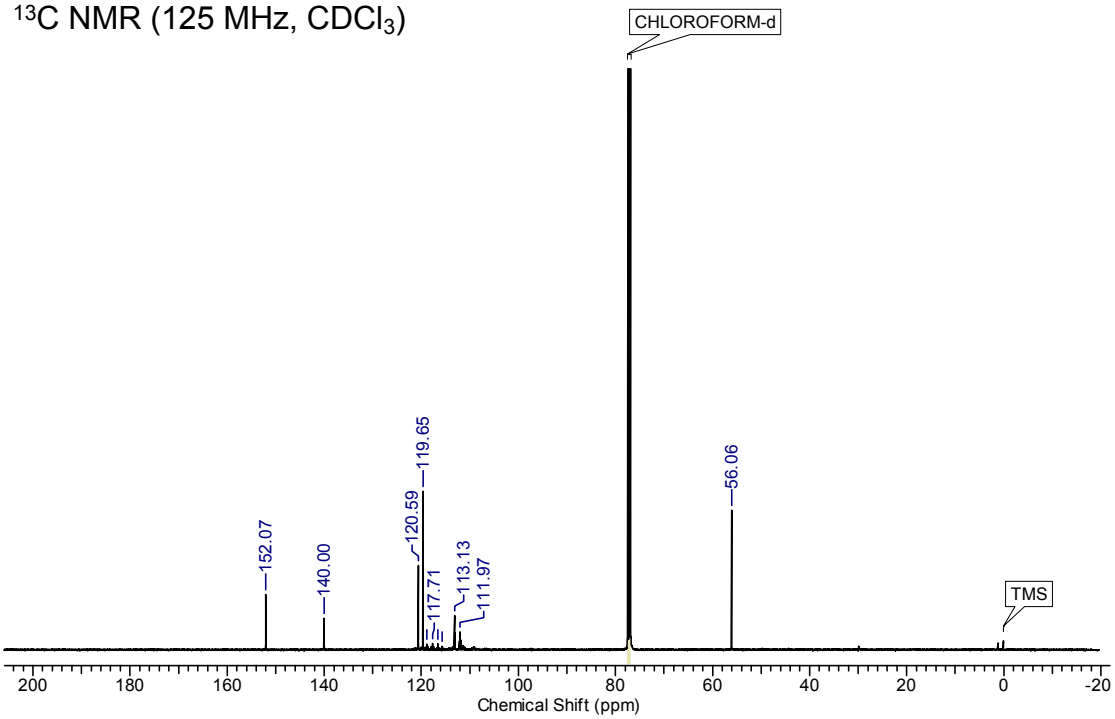

6.69
6.67
1.07
6.70
6.65


3.93
1.86
4.0
3.9

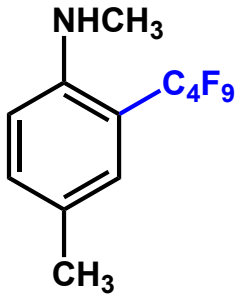
^{19}F NMR (376 MHz, $CDCl_3$)



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



_N_,4-dimethyl-2-(nonafluorobutyl)aniline (7•C_4F_9)



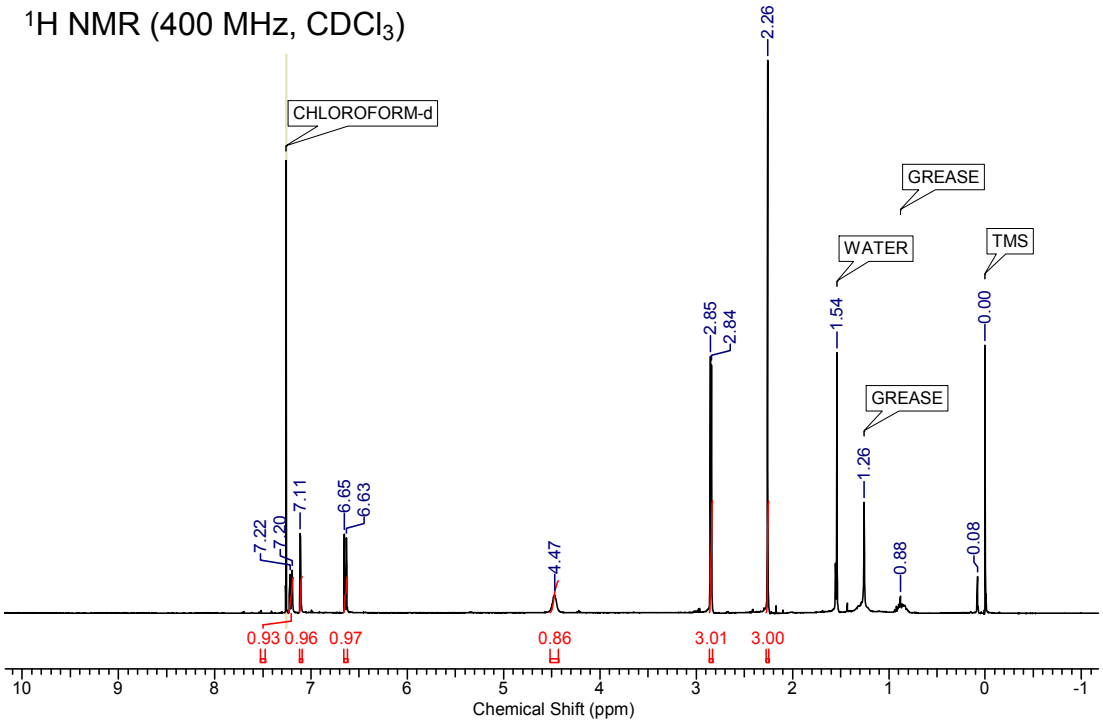
Compound **7•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 34% yield as a yellow oil.

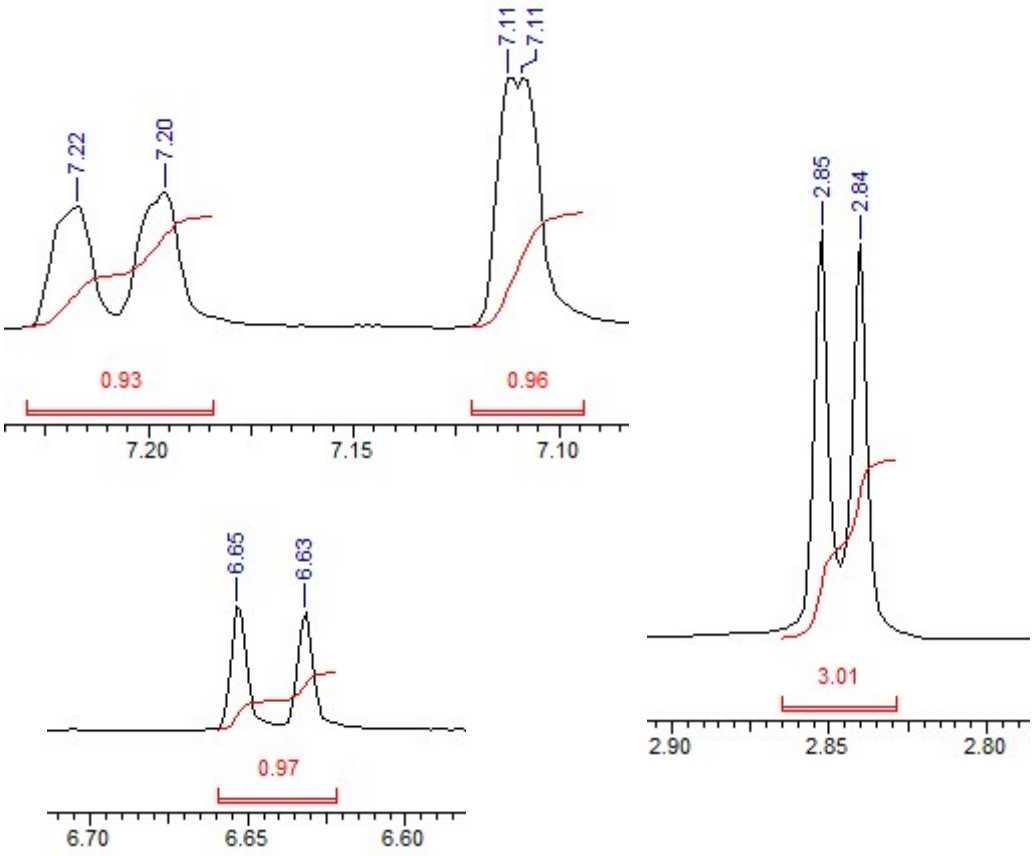
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.69 Hz, 1H), 7.11 (d, *J* = 1.37 Hz, 1H), 6.64 (d, *J* = 8.69 Hz, 1H), 4.47 (brs, 1H), 2.85 (d, *J* = 5.03 Hz, 3H), 2.26 (s, 3H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –82.12 (3F, $–CF_3$), –108.77 (2F, $–CF_2$), –123.79 (2F, $–CF_2$), –127.00 (2F, $–CF_2$);

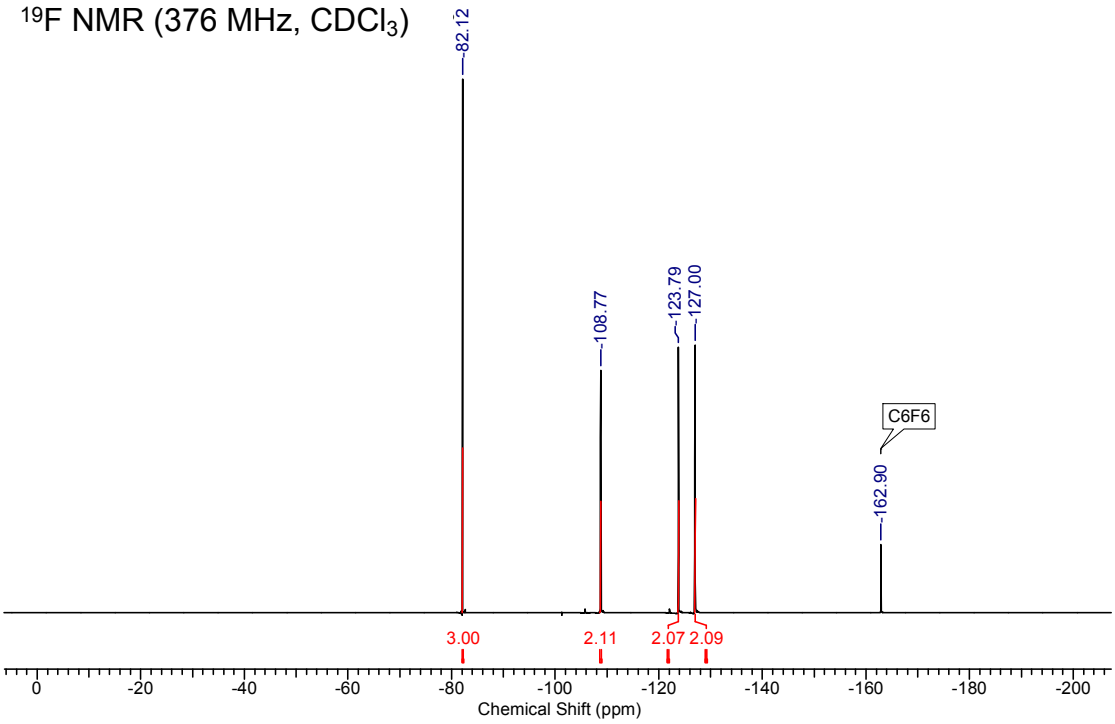
^{13}C NMR (125 MHz, $CDCl_3$): δ 146.1, 134.2, 129.3, 125.3, 112.2, 110.8, 30.9, 20.2;

HRMS (EI, *m/z*): Cald. for $C_{12}H_{10}F_9N$ $[M]^+$ 339.0670; found: 339.0669.

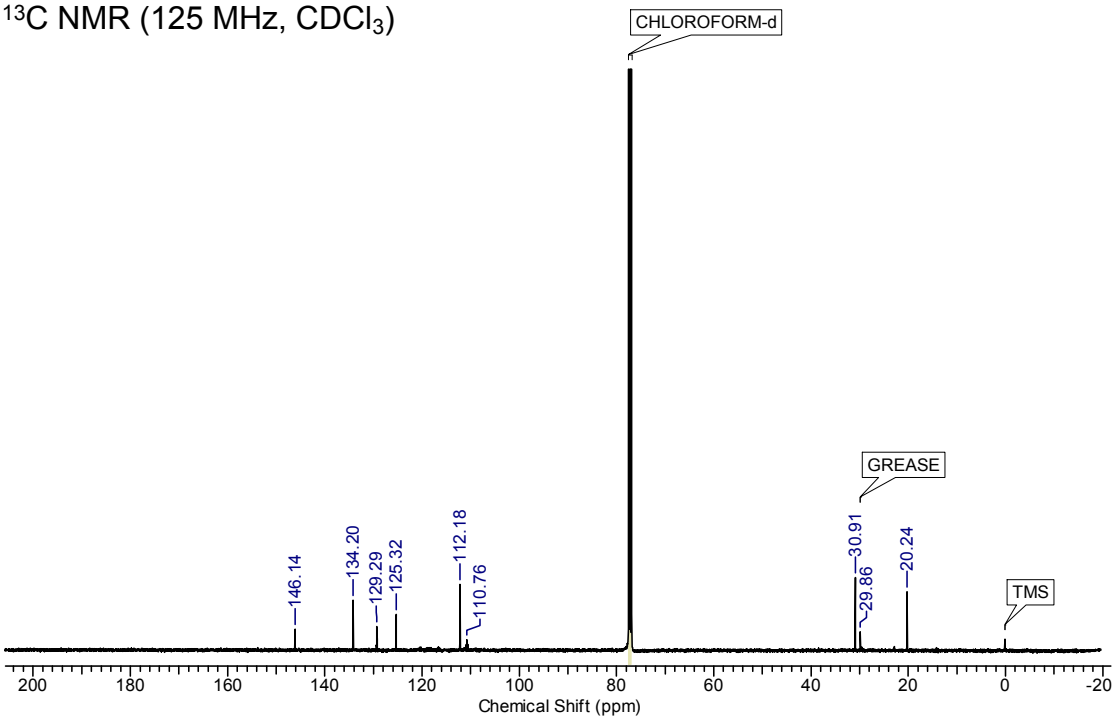




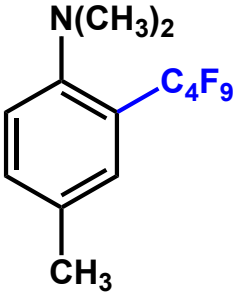
^{19}F NMR (376 MHz, $CDCl_3$)



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



***N,N*,4-trimethyl-2-(nonafluorobutyl)aniline (8•C_4F_9)**



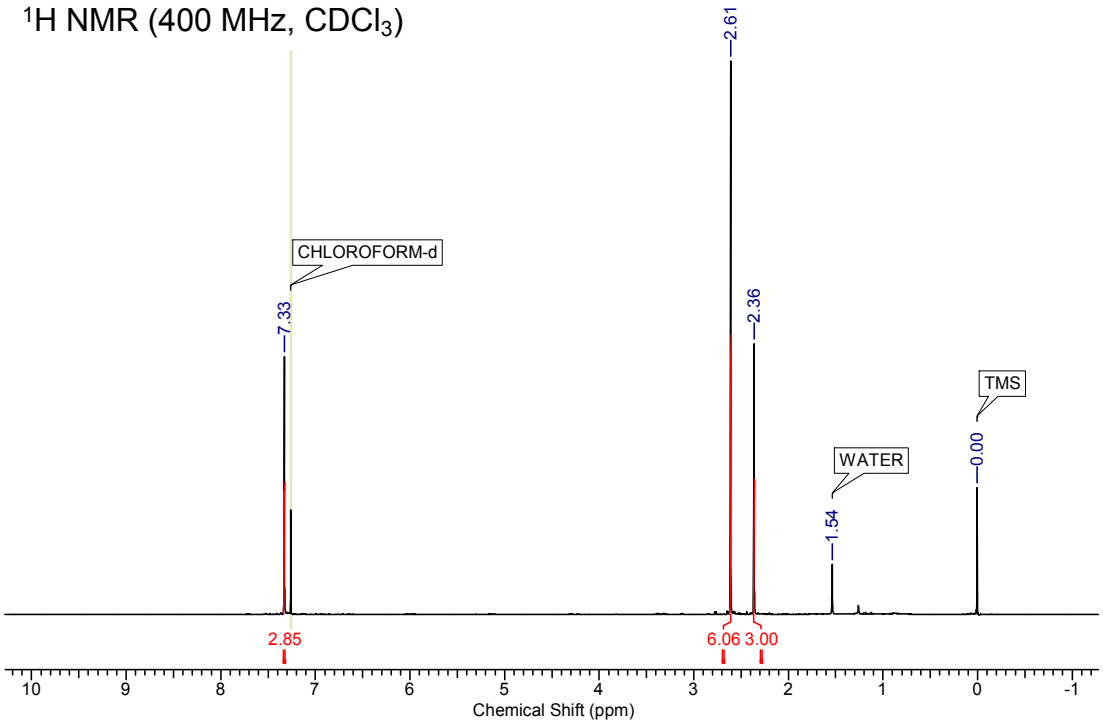
Compound **8•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 10% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, Ar, 3H), 2.61 (s, 6H), 2.36 (s, 3H);

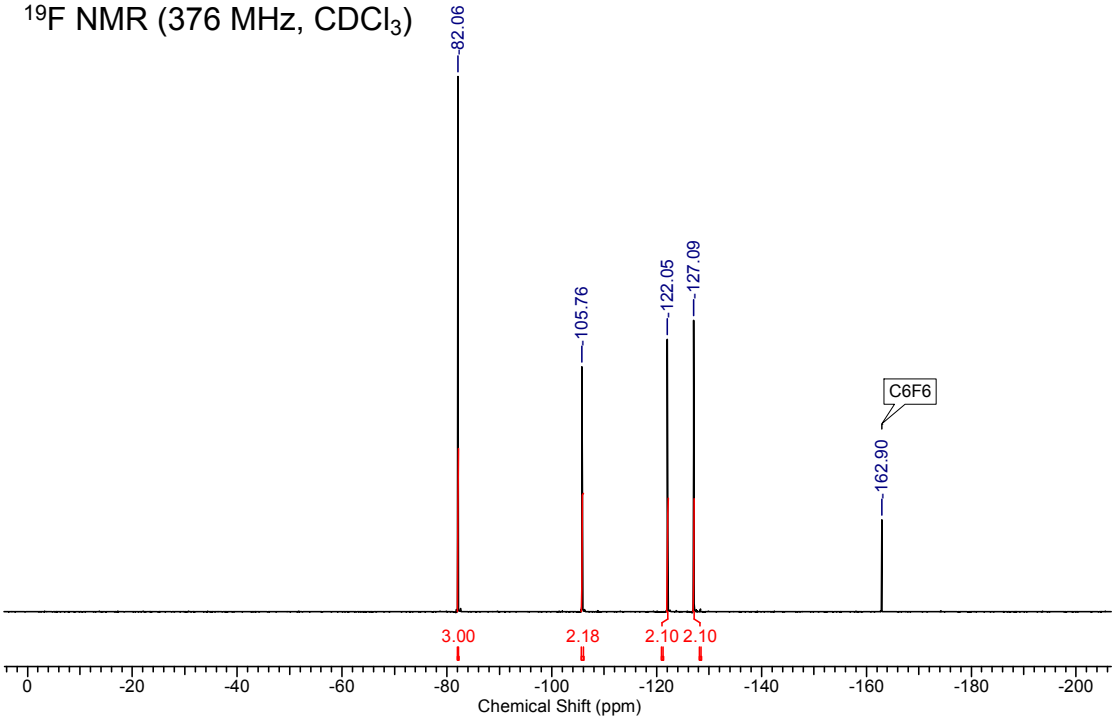
^{19}F NMR (376 MHz, $CDCl_3$): δ –82.06 (3F, –CF_3), –105.76 (2F, –CF_2), –122.05 (2F, –CF_2), –127.09 (2F, –CF_2);

^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 134.8, 133.8, 129.4, 125.6, 124.3, 46.8, 21.0;

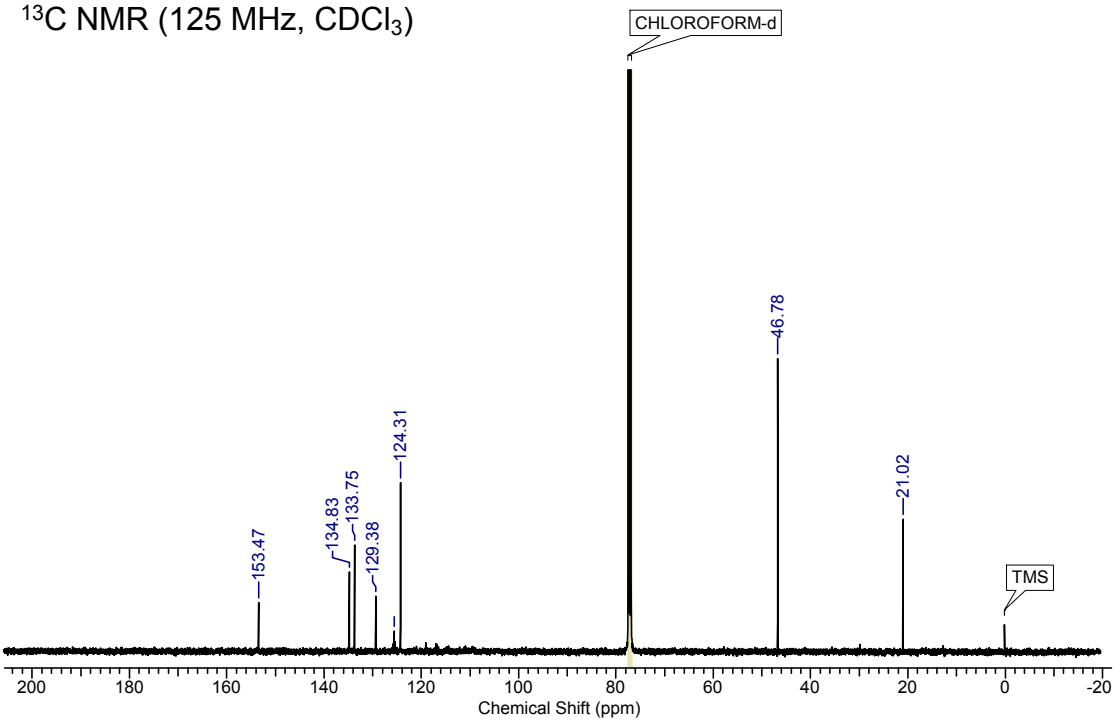
HRMS (EI, *m/z*): Cald. for $C_{13}H_{12}F_9N$ [M-1]$^+$ 352.0748; found: 352.0748.
GC-MS (*m/z*): Cald. for $C_{13}H_{12}F_9N$ [M]$^+$ 353; found: 353.



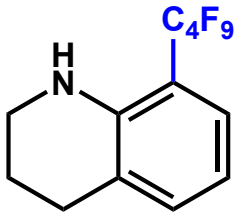
^{19}F NMR (376 MHz, $CDCl_3$)



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



8-(nonafluorobutyl)-1,2,3,4-tetrahydroquinoline (9•C_4F_9)



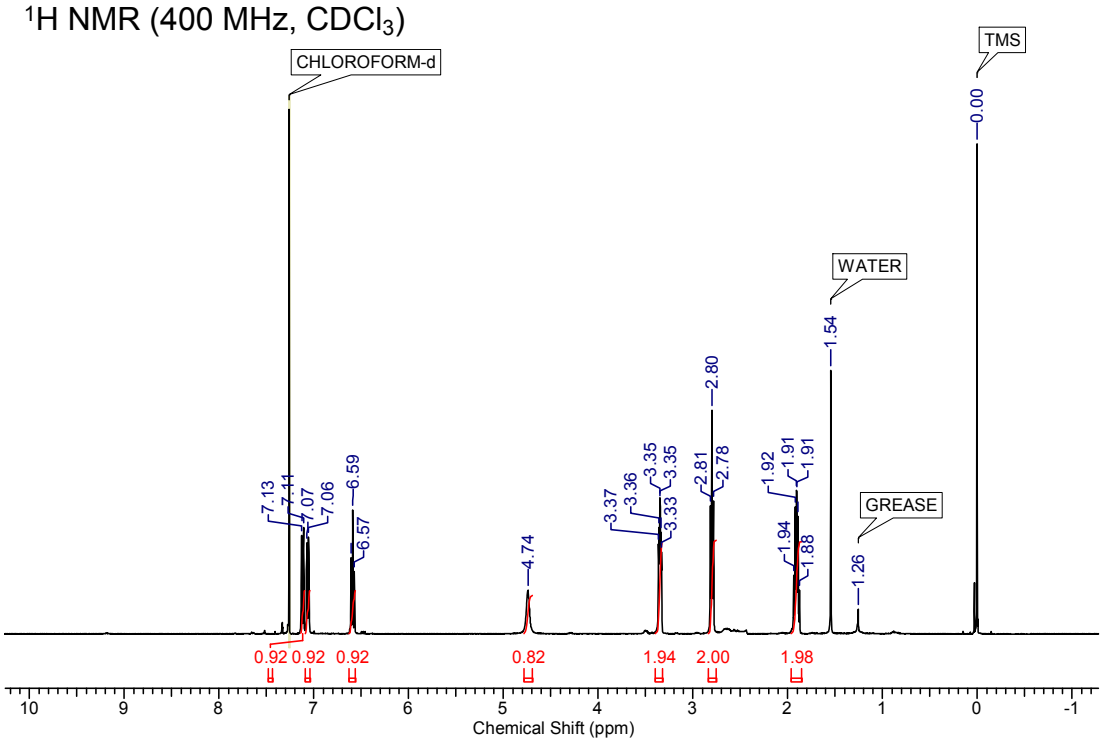
Compound **9•C_4F_9** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 18% yield as a yellow oil.

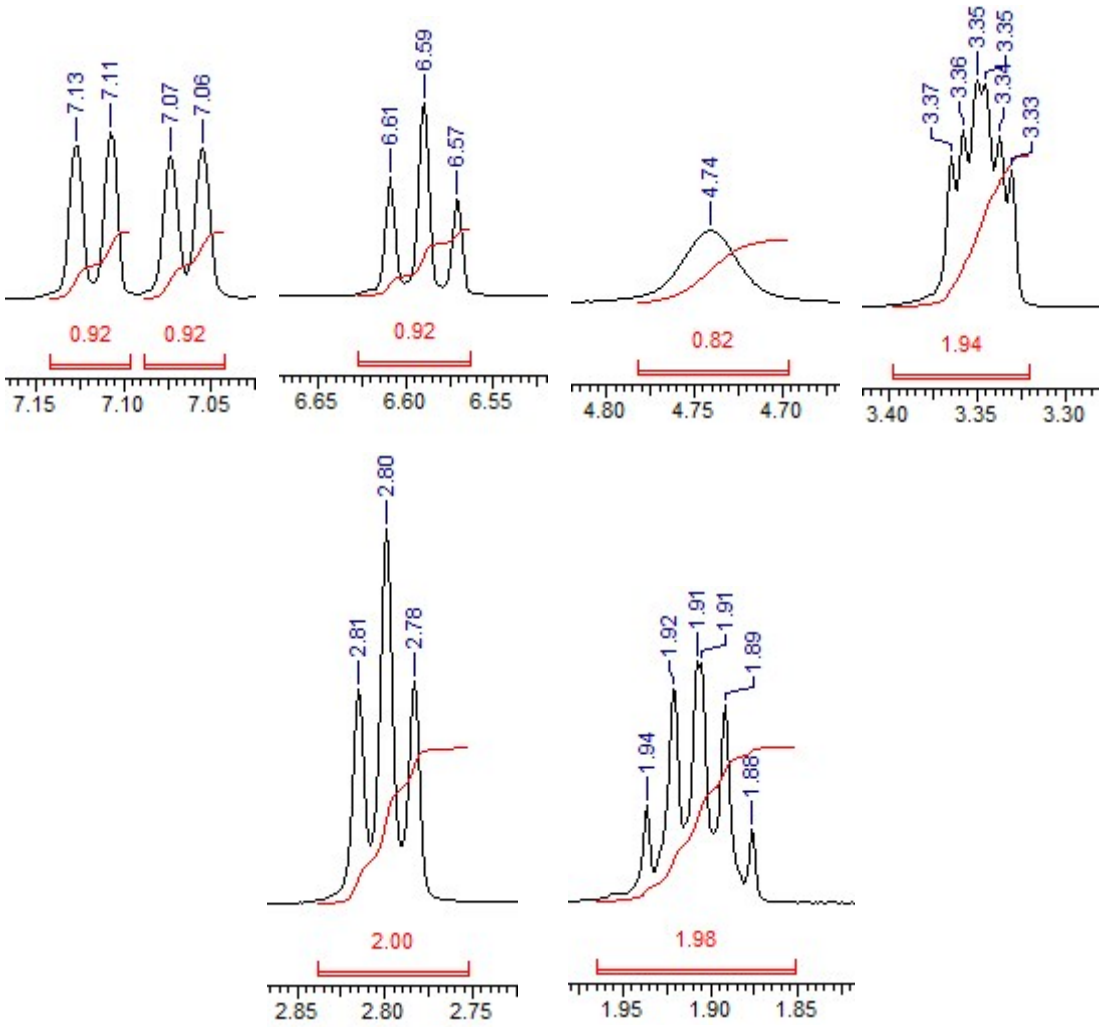
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 7.78 Hz, 1H), 7.07 (d, *J* = 7.32 Hz, 1H), 6.59 (t, *J* = 7.78 Hz, 1H), 4.74 (brs, 1H), 3.37-3.33 (m, 2H), 2.80 (t, *J* = 6.40 Hz, 2H), 1.94-1.88 (m, 2H);

^{19}F NMR (376 MHz, $CDCl_3$): δ –81.99 (3F, $–CF_3$), –108.65 (2F, $–CF_2$), –123.70 (2F, $–CF_2$), –126.90 (2F, $–CF_2$);

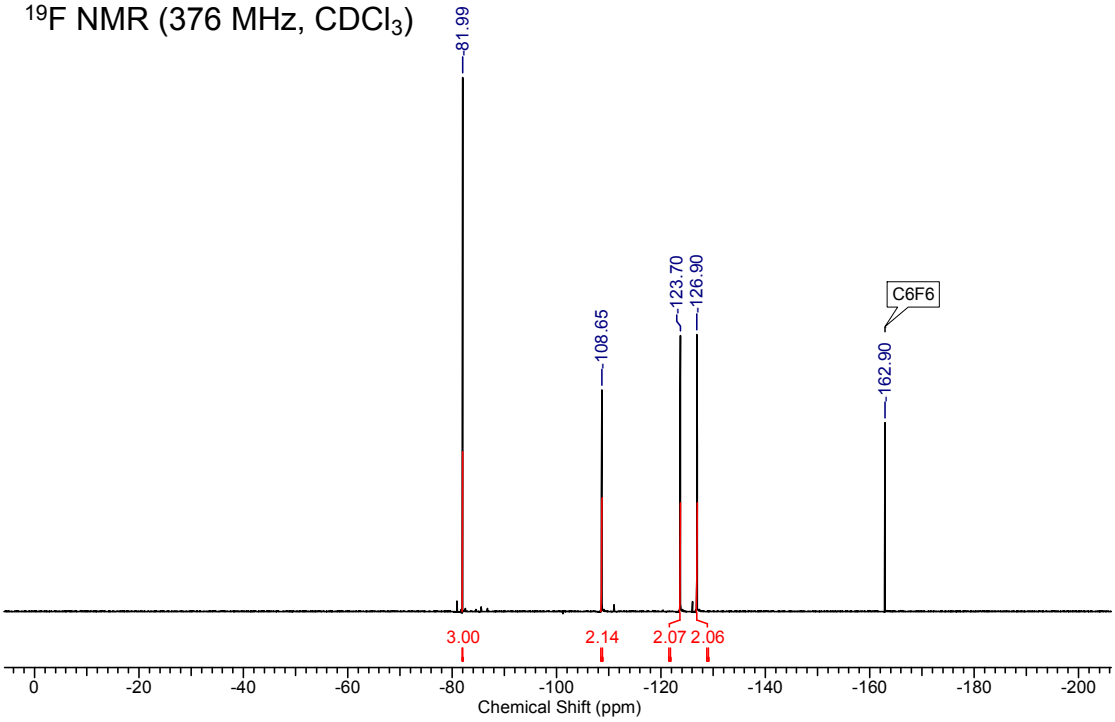
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2, 133.4, 127.2, 123.0, 115.3, 109.7, 42.0, 28.1, 21.2;

HRMS (EI, *m/z*): Cald. for $C_{13}H_{10}F_9N$ $[M]^+$ 351.0670; found: 351.0673.

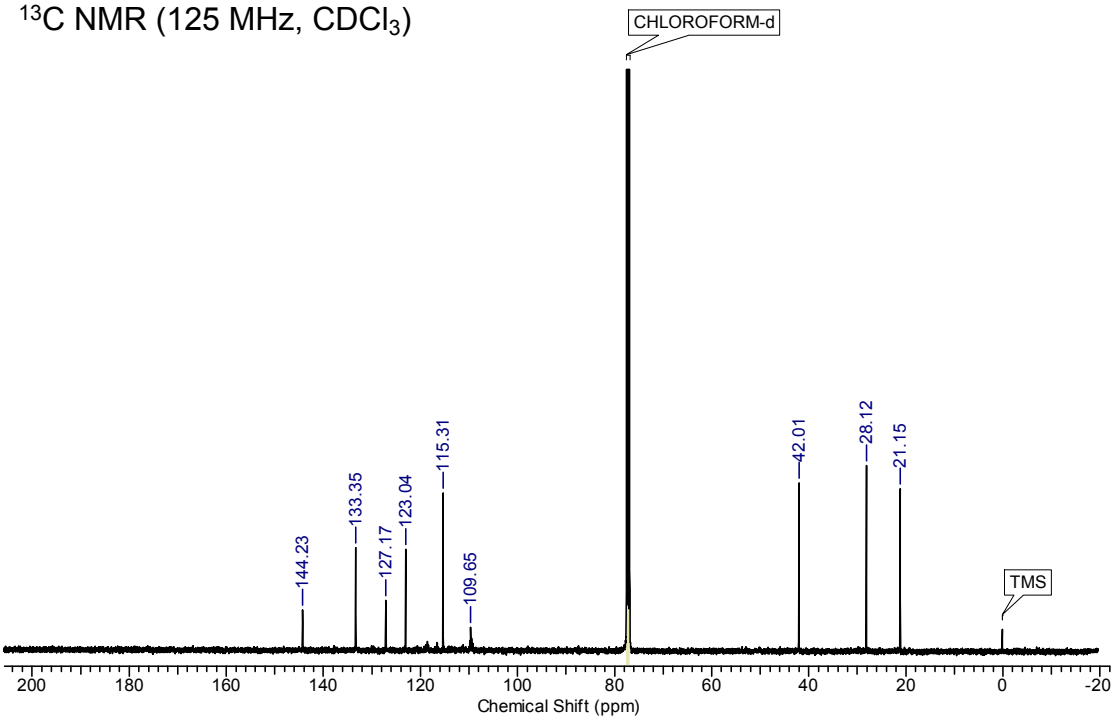



7.13
7.11
7.07
7.06
0.92
0.92
7.15
7.10
7.05
6.61
6.59
6.57
0.92
6.65
6.60
6.55
4.74
0.82
4.80
4.75
4.70
3.37
3.36
3.35
3.35
3.34
3.33
1.94
3.40
3.35
3.30
2.81
2.80
2.78
2.00
2.85
2.80
2.75
1.94
1.92
1.91
1.91
1.89
1.88
1.98
1.95
1.90
1.85

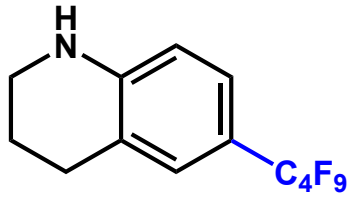
^{19}F NMR (376 MHz, $CDCl_3$)



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



6-(nonafluorobutyl)-1,2,3,4-tetrahydroquinoline (9•C_4F_9*)



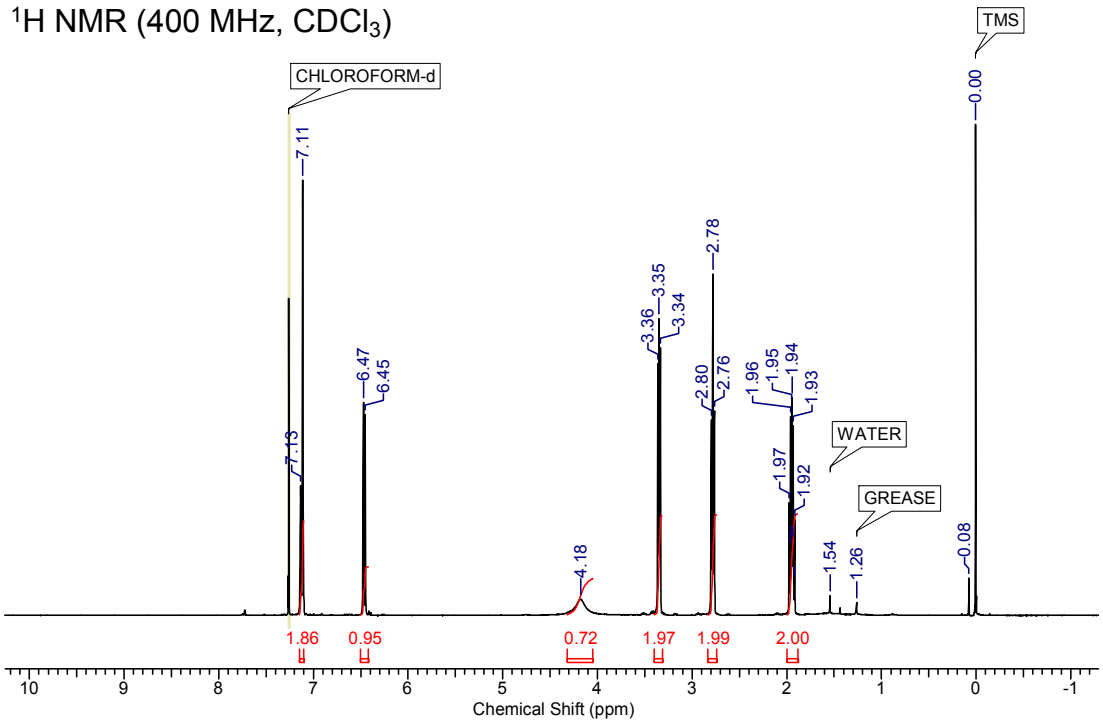
Compound **9•C_4F_9*** was prepared according to the general procedure using nonafluorobutyl iodide, *n*-C_4F_9I (3 eq., 129 µL, 5.0 × 10^{-2} M) in 29% yield as a yellow oil.

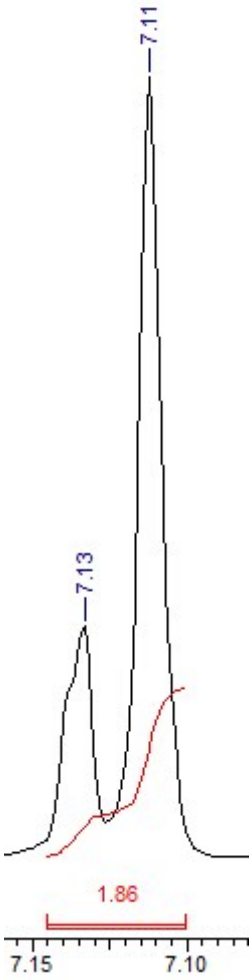
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.11 (m, 2H), 6.46 (d, *J* = 8.23 Hz, 1H), 4.18 (brs, 1H), 3.35 (t, *J* = 5.49 Hz, 2H), 2.78 (t, *J* = 6.40 Hz, 2H), 1.97-1.92 (m, 2H);

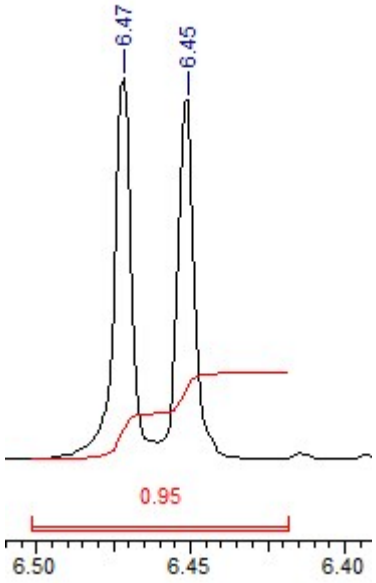
^{19}F NMR (376 MHz, $CDCl_3$): δ –82.07 (3F, $–CF_3$), –110.26 (2F, $–CF_2$), –123.73 (2F, $–CF_2$), –126.63 (2F, $–CF_2$);

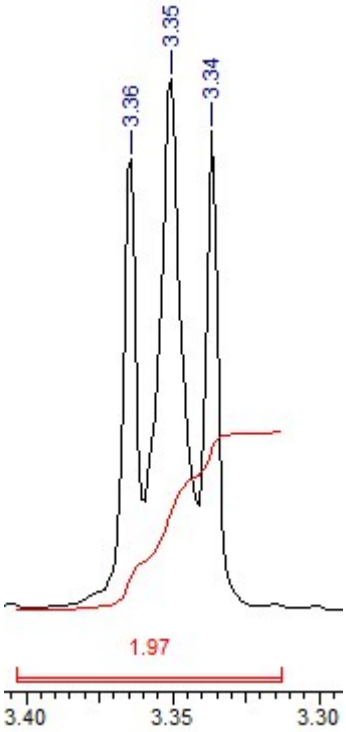
^{13}C NMR (125 MHz, $CDCl_3$): δ 147.7, 128.1, 125.8, 120.7, 119.0, 116.7, 116.6, 116.0, 113.2, 41.9, 27.2, 21.6;

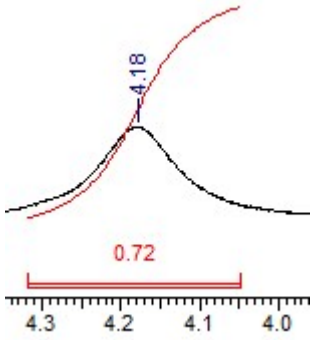
HRMS (EI, *m/z*): Cald. for $C_{13}H_{10}F_9N$ $[M]^+$ 351.0670; found: 351.0661.

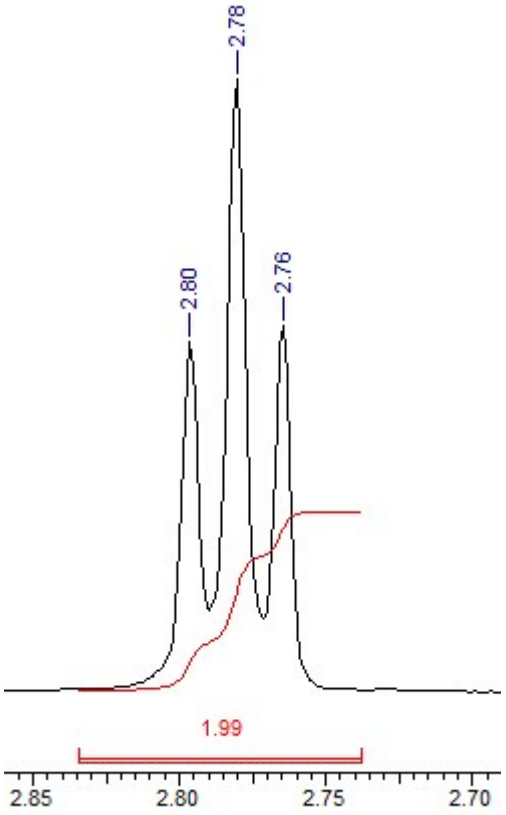


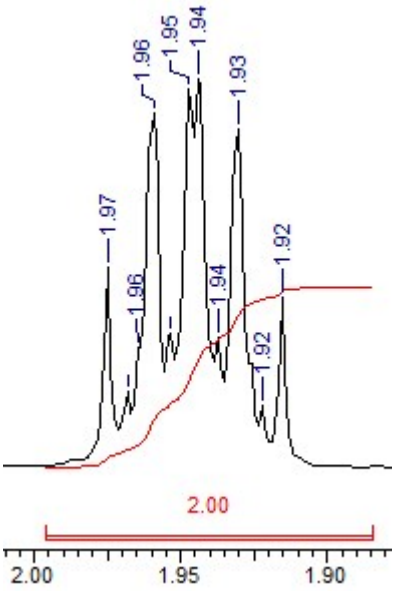

7.11
7.13
1.86
7.15
7.10


6.47
6.45
0.95
6.50
6.45
6.40

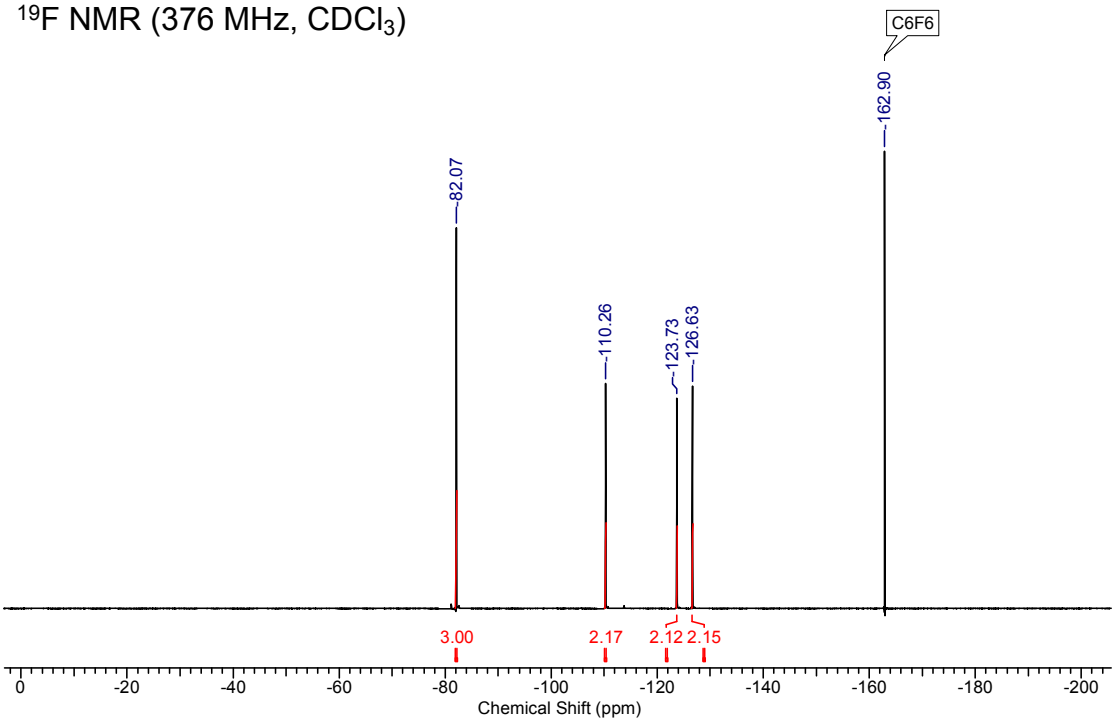

3.36
3.35
3.34
1.97
3.40
3.35
3.30


4.18
0.72
4.3
4.2
4.1
4.0

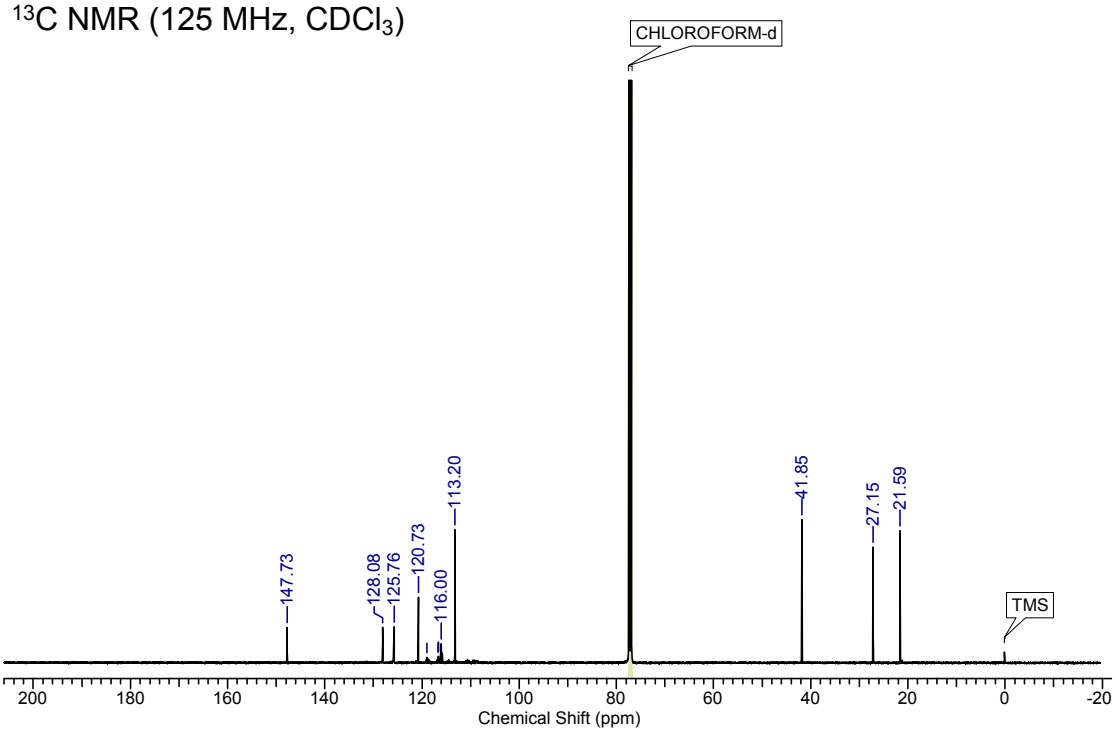

2.78
2.80
2.76
1.99
2.85
2.80
2.75
2.70


1.97
1.96
1.95
1.94
1.93
1.92
2.00
2.00
1.95
1.90

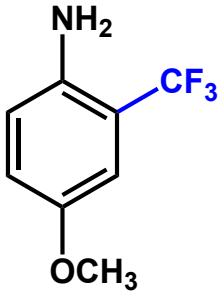
^{19}F NMR (376 MHz, $CDCl_3$)



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



4-methoxy-2-(trifluoromethyl)aniline (6•CF_3)

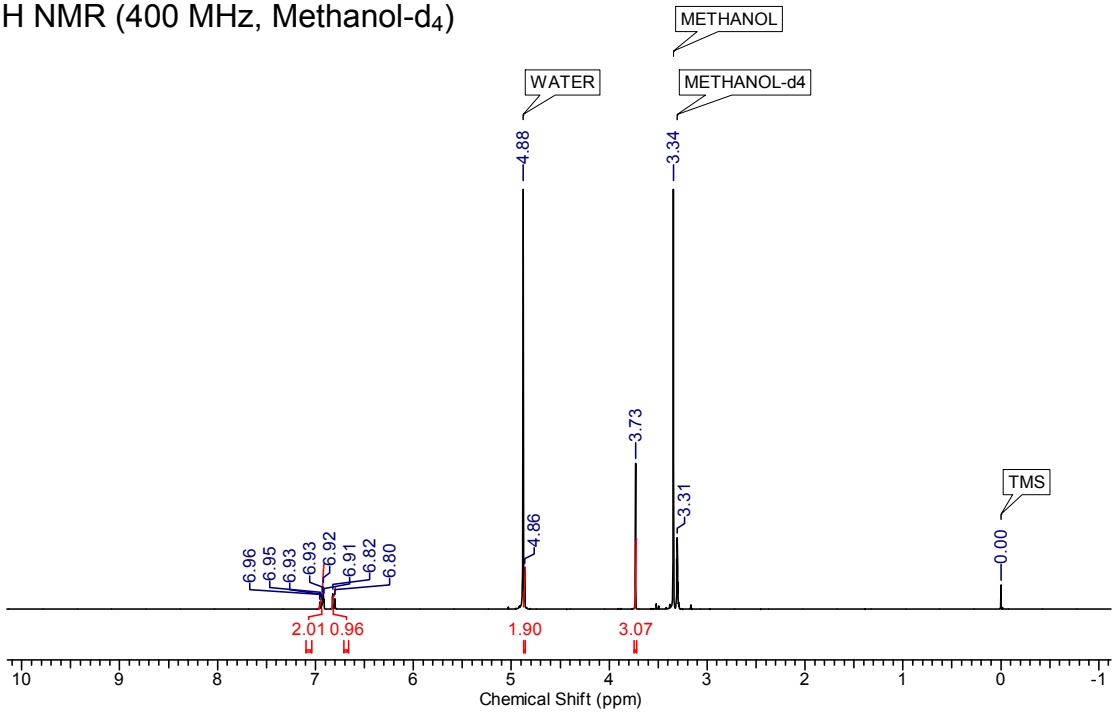


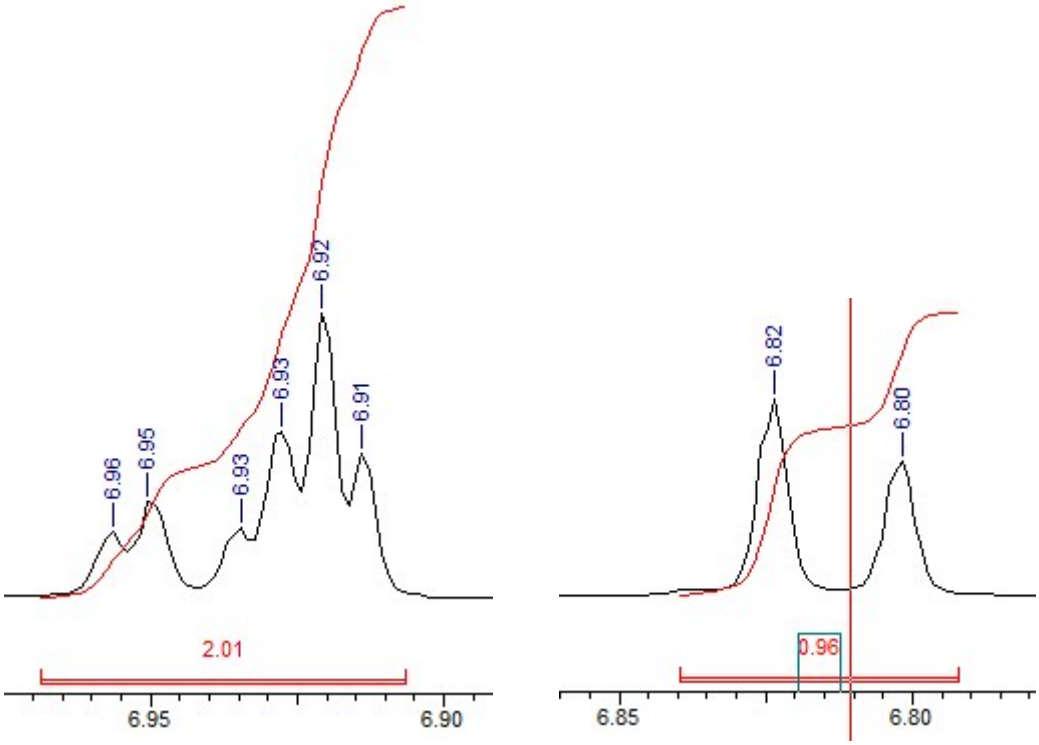
Compound **6•CF_3**[4] was prepared according to the general procedure using 2DMSO•CF_3I (12 eq., 2.5 × 10^{-2} M) in 21% yield as a brown oil.

^{1}H NMR (400 MHz, Methanol-d_4): δ 6.95-6.91 (m, 2H), 6.81 (d, *J* = 8.69 Hz, 1H), 4.86 (s, 2H), 3.73 (s, 3H);

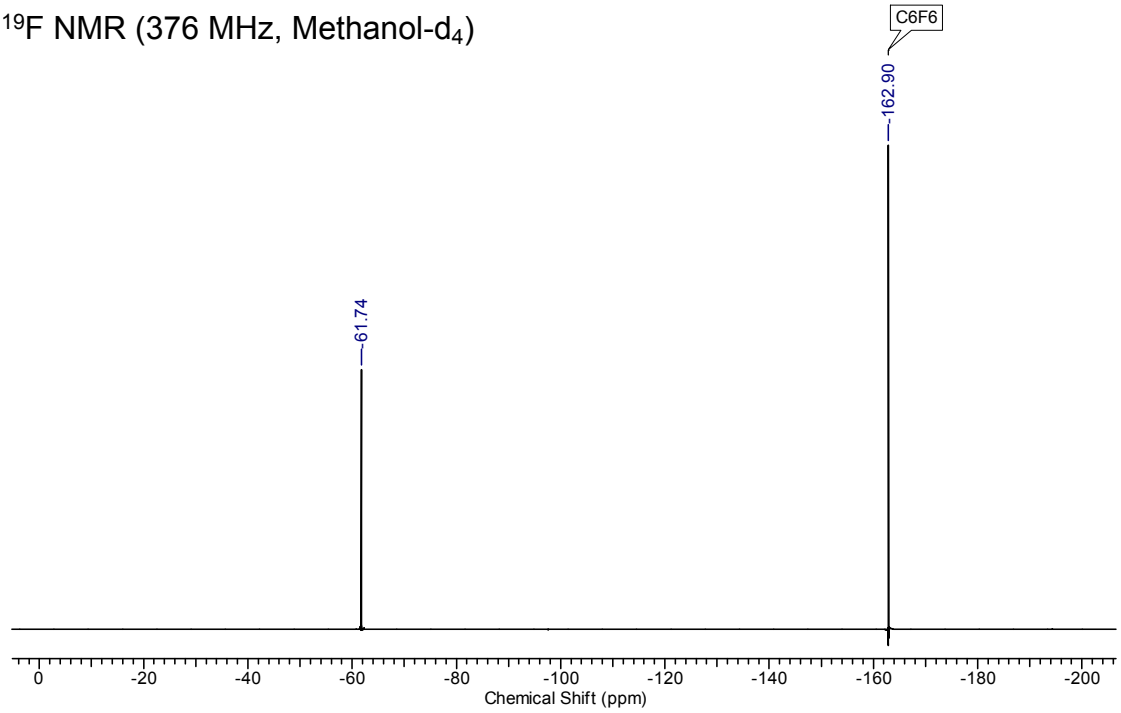
^{19}F NMR (376 MHz, Methanol-d_4): δ –61.74.

^{1}H NMR (400 MHz, Methanol-d_4)





^{19}F NMR (376 MHz, Methanol-d_4)



Computational Chemistry

We used the Becke−Perdew (BP86)[5] method implemented in the Gaussian 09 program.[6] For all atoms, the 6-31G(d) basis set was used. This level of theory BP86/6-31G(d) serves as an appropriate platform for addressing the structural, electronic, and spectroscopic properties of cobalamin cofactors.[7] All calculations were carried out in the gas phase. As truncated models of cobalamin, we used Co(corrin) where all of the peripheral side chains are replaced with hydrogen atoms for the DFT calculations.[8] The BDEs of the Co−C bonds cobalt complexes are defined by the following equation:

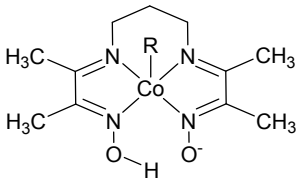
$$\text{BDE} = E\{\text{Co}^{\text{II}}(\text{complex})\} + E(\bullet\text{R}) - E\{\text{Co}^{\text{III}}(\text{R})\ (\text{complex})\}$$

where E(X) is the zero-point energy of the optimized structure of X; and R is a methyl or fluoroalkyl group (CH_3, CF_3 or C_4F_9).

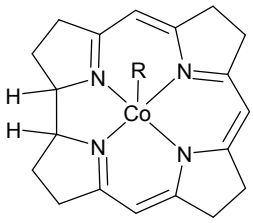
Table S4. DFT-computed bond-dissociation energies (BDEs) of the Co−C bonds in **C2** and corrin in the gas phase[a]

R	BDE (kcal/mol)	
	C2	**Co(corrin)**
CH_3	36.0	42.3[b]
CF_3	46.0	53.1
C_4F_9	40.0	45.8

[a]At the BP86/6-31G(d) level of theory. [b]ref. S8a.



C2



Co(corrin)

Table S5. Cartesian coordinates for the optimized structure of $Co^{III}(CH_3)$(**C2**).

Atom	Coordinates (Å)		
	X	Y	Z
C	1.285399	2.640862	0.207572
C	0.005075	3.101483	-0.499803
C	-1.293267	2.666577	0.190933
N	1.432628	1.180952	0.180998
N	-1.457043	1.207606	0.174282
Co	-0.008834	-0.046809	0.349901
C	2.608775	0.603414	-0.005024
C	2.601018	-0.854637	0.019639
N	1.384399	-1.336756	0.269538
C	3.888705	1.366922	-0.206671
C	3.792069	-1.741953	-0.175522
N	-1.435162	-1.298616	0.249735
C	-2.635032	0.652994	-0.023607
C	-2.637945	-0.819713	-0.005018
C	-3.840758	-1.683061	-0.220559
C	-3.908580	1.423945	-0.231450
O	-1.284317	-2.626001	0.341430
O	1.182887	-2.620504	0.362222
H	2.152957	3.113393	-0.280855
H	1.275404	2.972258	1.263011
H	0.008415	2.753176	-1.549354
H	0.014361	4.205520	-0.526383
H	-2.148298	3.148778	-0.309842
H	-1.291716	2.999133	1.245847
H	4.040541	2.096851	0.607086
H	3.868694	1.929570	-1.158277
H	4.754967	0.691967	-0.229815
H	4.405402	-1.405386	-1.028165
H	4.438659	-1.751548	0.721992
H	3.454833	-2.771864	-0.363374
H	-4.441257	-1.317135	-1.069997
H	-3.530431	-2.718507	-0.420767
H	-4.491076	-1.685413	0.674315
H	-4.047277	2.171708	0.567922
H	-4.782669	0.758795	-0.236164
H	-3.888200	1.966344	-1.195051
H	-0.198575	-2.744176	0.404998
C	0.000046	0.037305	2.235889
H	-1.069708	-0.584621	2.803696
H	1.112995	-0.507496	2.796950
H	-0.044580	1.340944	2.652342

Table S6. Cartesian coordinates for the optimized structure of $Co^{III}(CF_3)$(**C2**).

Atom	Coordinates (Å)		
	X	Y	Z
C	1.285399	2.640862	0.207572
C	0.005075	3.101483	-0.499803
C	-1.293267	2.666577	0.190933
N	1.432628	1.180952	0.180998
N	-1.457043	1.207606	0.174282
Co	-0.008834	-0.046809	0.349901
C	2.608775	0.603414	-0.005024
C	2.601018	-0.854637	0.019639
N	1.384399	-1.336756	0.269538
C	3.888705	1.366922	-0.206671
C	3.792069	-1.741953	-0.175522
N	-1.435162	-1.298616	0.249735
C	-2.635032	0.652994	-0.023607
C	-2.637945	-0.819713	-0.005018
C	-3.840758	-1.683061	-0.220559
C	-3.908580	1.423945	-0.231450
O	-1.284317	-2.626001	0.341430
O	1.182887	-2.620504	0.362222
H	2.152957	3.113393	-0.280855
H	1.275404	2.972258	1.263011
H	0.008415	2.753176	-1.549354
H	0.014361	4.205520	-0.526383
H	-2.148298	3.148778	-0.309842
H	-1.291716	2.999133	1.245847
H	4.040541	2.096851	0.607086
H	3.868694	1.929570	-1.158277
H	4.754967	0.691967	-0.229815
H	4.405402	-1.405386	-1.028165
H	4.438659	-1.751548	0.721992
H	3.454833	-2.771864	-0.363374
H	-4.441257	-1.317135	-1.069997
H	-3.530431	-2.718507	-0.420767
H	-4.491076	-1.685413	0.674315
H	-4.047277	2.171708	0.567922
H	-4.782669	0.758795	-0.236164
H	-3.888200	1.966344	-1.195051
H	-0.198575	-2.744176	0.404998
C	0.000046	0.037305	2.235889
F	-1.069708	-0.584621	2.803696
F	1.112995	-0.507496	2.796950
F	-0.044580	1.340944	2.652342

Table S7. Cartesian coordinates for the optimized structure of $Co^{III}(C_4F_9)$(**C2**).

Atom	Coordinates (Å)		
	X	Y	Z
C	1.316542	2.806661	-0.416218
C	0.028578	3.101696	-1.194727
C	-1.261647	2.893226	-0.389943
N	1.437232	1.387900	-0.060779
N	-1.454619	1.479848	-0.043280
Co	-0.021453	0.283368	0.463120
C	2.594177	0.748056	-0.128138
C	2.565264	-0.646922	0.292102
N	1.347469	-1.020195	0.685235
C	3.875793	1.391158	-0.581519
C	3.740108	-1.575771	0.329828
N	-1.462829	-0.954484	0.584822
C	-2.626571	0.896257	-0.171135
C	-2.641971	-0.540056	0.158513
C	-3.833932	-1.434807	0.030919
C	-3.881411	1.593216	-0.618822
O	-1.330969	-2.251775	0.899790
O	1.128230	-2.224572	1.126230
H	2.181372	3.114134	-1.026101
H	1.338452	3.401018	0.516561
H	-0.002255	2.494075	-2.118410
H	0.059473	4.160976	-1.505546
H	-2.117398	3.258817	-0.979357
H	-1.224134	3.479366	0.546042
H	4.092582	2.293535	0.016322
H	3.810269	1.701273	-1.640630
H	4.724324	0.700773	-0.482218
H	4.314202	-1.535886	-0.611396
H	4.428670	-1.317315	1.156028
H	3.387326	-2.605262	0.487855
H	-4.355108	-1.266337	-0.926327
H	-3.526093	-2.487962	0.091318
H	-4.556934	-1.239817	0.845577
H	-4.048860	2.514004	-0.035002
H	-4.760635	0.945617	-0.499313
H	-3.814461	1.880500	-1.684791
H	-0.266622	-2.344600	1.096291
C	0.094841	0.884576	2.275339
C	-0.922136	0.325436	3.323283
F	1.343051	0.640952	2.792966
F	-0.059029	2.253980	2.264129
C	-0.687605	0.808559	4.801459
F	-2.189735	0.696621	2.959743
F	-0.843149	-1.036956	3.345464
C	-1.874939	0.493745	5.774226
F	0.420662	0.184089	5.289249
F	-0.490810	2.157928	4.832482
F	-1.472636	0.732548	7.041182
F	-2.934947	1.283307	5.499555
F	-2.249428	-0.800498	5.672423

Table S8. Cartesian coordinates for the optimized structure of Co^{II}(**C2**).

Atom	Coordinates (Å)		
	X	Y	Z
C	1.284780	2.624169	-0.112759
C	0.007169	3.080796	-0.822467
C	-1.280967	2.650085	-0.115992
N	1.409453	1.159807	-0.110228
N	-1.432108	1.187382	-0.112681
Co	-0.010155	-0.054999	-0.198152
C	2.618068	0.592942	0.007538
C	2.613410	-0.847081	-0.045144
N	1.355083	-1.323011	-0.171247
C	3.878546	1.393477	0.174797
C	3.765872	-1.796136	0.007681
N	-1.414209	-1.281530	-0.160742
C	-2.644877	0.649073	0.001718
C	-2.655660	-0.805102	-0.049741
C	-3.832259	-1.725060	0.000195
C	-3.897877	1.461342	0.167196
O	-1.299779	-2.615357	-0.223214
O	1.187100	-2.606350	-0.251310
H	2.156501	3.074123	-0.620665
H	1.289524	2.992789	0.934314
H	0.004707	2.710476	-1.864910
H	0.017399	4.184055	-0.875155
H	-2.145157	3.116632	-0.621706
H	-1.278951	3.012649	0.933036
H	3.763922	2.157165	0.963680
H	4.133775	1.925516	-0.762094
H	4.733674	0.755768	0.437708
H	4.731905	-1.280926	0.100890
H	3.647472	-2.494087	0.856890
H	3.783246	-2.421135	-0.903884
H	-4.788051	-1.183869	0.020601
H	-3.821859	-2.396708	-0.877099
H	-3.771403	-2.377954	0.890658
H	-3.769624	2.238468	0.940387
H	-4.754764	0.835493	0.452598
H	-4.160946	1.977340	-0.776724
H	-0.228856	-2.764148	-0.264868

Table S9. Cartesian coordinates for the optimized structure of $Co^{III}(CF_3)$(**corrin**).

Atom	Coordinates (Å)		
	X	Y	Z
C	-0.682200	0.606900	3.305800
C	-1.497600	-2.262500	1.298500
C	-2.221000	-2.734100	2.556800
C	-1.898400	-1.627400	3.584900
C	-1.126700	-0.602800	2.765000
N	-0.944300	-0.976700	1.430300
C	0.027300	1.580100	2.599900
C	0.486200	2.881900	3.245800
C	1.275500	3.569100	2.112800
C	1.046200	2.644200	0.921300
N	0.400200	1.476200	1.293000
C	-1.447900	-2.993000	0.126300
C	1.492800	2.930000	-0.356500
C	0.538800	-1.228300	-2.424000
C	-0.310400	-2.149600	-3.328600
C	-0.713300	-3.282700	-2.357700
C	-0.747200	-2.544100	-1.023100
N	-0.041600	-1.427700	-1.131400
C	1.251200	2.065100	-1.455700
C	1.768100	2.306300	-2.870100
C	1.684800	0.887200	-3.477800
C	0.498500	0.267900	-2.703000
N	0.504000	0.966400	-1.433100
H	-0.902700	0.801900	4.356800
H	-1.860800	-3.724800	2.869400
H	-3.301600	-2.828400	2.367000
H	-2.791100	-1.171300	4.038700
H	-1.272000	-1.994300	4.414000
H	-0.386100	3.476500	3.563900
H	1.081200	2.685500	4.150400
H	2.352800	3.640200	2.332900
H	0.925100	4.589300	1.897900
H	-1.971500	-3.949300	0.087200
H	2.056600	3.849400	-0.519700
H	1.594500	-1.564800	-2.425000
H	0.226300	-2.500100	-4.222100
H	-1.206800	-1.600400	-3.663200
H	-1.670900	-3.766100	-2.598100
H	0.054500	-4.078600	-2.323200
H	2.774300	2.748900	-2.878900
H	1.095900	3.014100	-3.391400
H	1.550500	0.876900	-4.569000
H	2.604000	0.324100	-3.242700
H	-0.454800	0.516000	-3.209800
Co	0.134000	-0.043700	0.104300
C	1.757100	-1.686900	0.774200
F	2.848600	-1.479900	-0.044400
F	1.959300	-1.548500	2.132300
F	1.178300	-2.908400	0.495900

Table S10. Cartesian coordinates for the optimized structure of $Co^{III}(C_4F_9)$(**corrin**).

Atom	Coordinates (Å)		
	X	Y	Z
C	2.897366	-2.823962	-0.621339
C	0.548146	-2.192004	2.030437
C	0.592379	-3.700460	2.220380
C	1.516381	-4.169181	1.075105
C	1.974673	-2.867572	0.443454
N	1.439605	-1.724388	1.048254
C	3.349874	-1.666370	-1.229307
C	4.345869	-1.684448	-2.383435
C	4.474337	-0.195266	-2.760549
C	3.657963	0.500968	-1.683191
N	2.958392	-0.400992	-0.895305
C	-0.232583	-1.333938	2.808388
C	3.567751	1.889964	-1.561167
C	0.153256	2.152446	1.708498
C	-0.350367	2.372526	3.152079
C	-1.067035	1.036991	3.457561
C	-0.274305	0.053525	2.601809
N	0.371061	0.738880	1.659854
C	2.822048	2.513766	-0.549229
C	2.652473	4.022745	-0.403250
C	1.382794	4.116861	0.473710
C	1.463998	2.818362	1.308405
N	2.198898	1.902411	0.461446
H	3.267068	-3.780308	-0.992196
H	-0.416784	-4.132259	2.157065
H	0.991949	-3.955562	3.212169
H	2.375828	-4.764906	1.415179
H	0.982815	-4.778995	0.327714
H	5.305488	-2.113572	-2.048731
H	3.985104	-2.323460	-3.203511
H	4.059519	0.025655	-3.754882
H	5.515422	0.162746	-2.760809
H	-0.832884	-1.778568	3.602787
H	4.104189	2.499006	-2.289581
H	-0.631920	2.441114	0.984196
H	-0.994498	3.256431	3.259685
H	0.516129	2.498689	3.822194
H	-1.071250	0.758575	4.520382
H	-2.120052	1.057049	3.121385
H	2.573714	4.527898	-1.376132
H	3.536337	4.442632	0.111597
H	1.330300	5.029557	1.084988
H	0.483528	4.083320	-0.163714
H	2.074679	2.988303	2.214629
Co	1.330124	0.076758	0.260269
C	-1.078049	-0.474070	-0.879202
F	-1.008205	0.672705	-1.552955
F	-1.019957	-1.475831	-1.757417
C	-2.379458	-0.562530	-0.047253
F	-2.311985	-1.679015	0.678792
F	-2.414769	0.477525	0.779945
C	-3.729165	-0.614899	-0.804628
F	-4.668898	-0.910466	0.098768
F	-3.700802	-1.601037	-1.704018
C	-4.159377	0.692489	-1.501102
F	-5.386378	0.546687	-1.997800
F	-4.201996	1.707888	-0.637872
F	-3.342290	1.023451	-2.499491

Table S11. Cartesian coordinates for the optimized structure of Co^{II}(**corrin**).

Atom	Coordinates (Å)		
	X	Y	Z
C	-0.676758	0.599411	3.301968
C	-1.542129	-2.243947	1.281646
C	-2.302853	-2.676399	2.519661
C	-1.907397	-1.620054	3.567228
C	-1.143881	-0.594554	2.758688
N	-0.940336	-0.995017	1.463470
C	0.044263	1.565010	2.604342
C	0.513196	2.855749	3.238720
C	1.350832	3.514377	2.127753
C	1.088828	2.633004	0.922376
N	0.376899	1.482999	1.276965
C	-1.476548	-2.985075	0.122979
C	1.520185	2.926840	-0.351844
C	0.563286	-1.218278	-2.377363
C	-0.135277	-2.226626	-3.309868
C	-0.628216	-3.317569	-2.326782
C	-0.773600	-2.548960	-1.026831
N	-0.131185	-1.385942	-1.066399
C	1.277269	2.076371	-1.458256
C	1.690009	2.342462	-2.893736
C	1.531467	0.949939	-3.553551
C	0.462866	0.274939	-2.672161
N	0.618061	0.928334	-1.338748
H	-0.892447	0.793457	4.356748
H	-2.040979	-3.705824	2.816394
H	-3.389810	-2.668092	2.316963
H	-2.768621	-1.161539	4.083369
H	-1.251570	-2.035136	4.355689
H	-0.362177	3.469053	3.524490
H	1.078684	2.662693	4.166774
H	2.429749	3.512005	2.369777
H	1.069680	4.562563	1.931313
H	-1.993665	-3.947869	0.088453
H	2.077967	3.853176	-0.514187
H	1.631558	-1.482372	-2.229514
H	0.532113	-2.618352	-4.093270
H	-0.999011	-1.745380	-3.804199
H	-1.570573	-3.800682	-2.635833
H	0.120467	-4.124534	-2.198123
H	2.710579	2.754807	-2.966947
H	1.007108	3.091006	-3.342728
H	1.239988	1.003249	-4.614105
H	2.482174	0.389849	-3.486875
H	-0.560432	0.498571	-3.040463
Co	-0.026761	0.014438	0.121118

Table S12. Cartesian coordinates for the optimized structure of CH_3 radical.

Atom	Coordinates (Å)		
	X	Y	Z
C	-2.133756	0.427111	5.997469
H	-1.490278	0.709019	6.832135
H	-2.748885	1.181212	5.505060
H	-2.158881	-0.608343	5.652737

Table S13. Cartesian coordinates for the optimized structure of CF_3 radical.

Atom	Coordinates (Å)		
	X	Y	Z
C	-1.904701	0.486154	5.801268
F	-1.456920	0.736590	7.039017
F	-2.929738	1.289251	5.486240
F	-2.240441	-0.802995	5.660874

Table S14. Cartesian coordinates for the optimized structure of C_4F_9 radical.

Atom	Coordinates (Å)		
	X	Y	Z
C	0.114748	0.920109	2.378359
C	-0.914027	0.362486	3.353649
F	1.381713	0.580311	2.645852
F	-0.010713	2.221282	2.098475
C	-0.716323	0.805616	4.841910
F	-2.150713	0.777127	2.940335
F	-0.844542	-1.002219	3.308777
C	-1.893271	0.473415	5.811346
F	0.408694	0.197375	5.316700
F	-0.530248	2.161329	4.859413
F	-1.510883	0.733261	7.081473
F	-2.973840	1.227374	5.520103
F	-2.226094	-0.833266	5.715109

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