Supplementary Information

Direct synthesis of *N*-perfluoro-*tert*-butyl secondary amines from *N*-trifluoromethyl secondary amines

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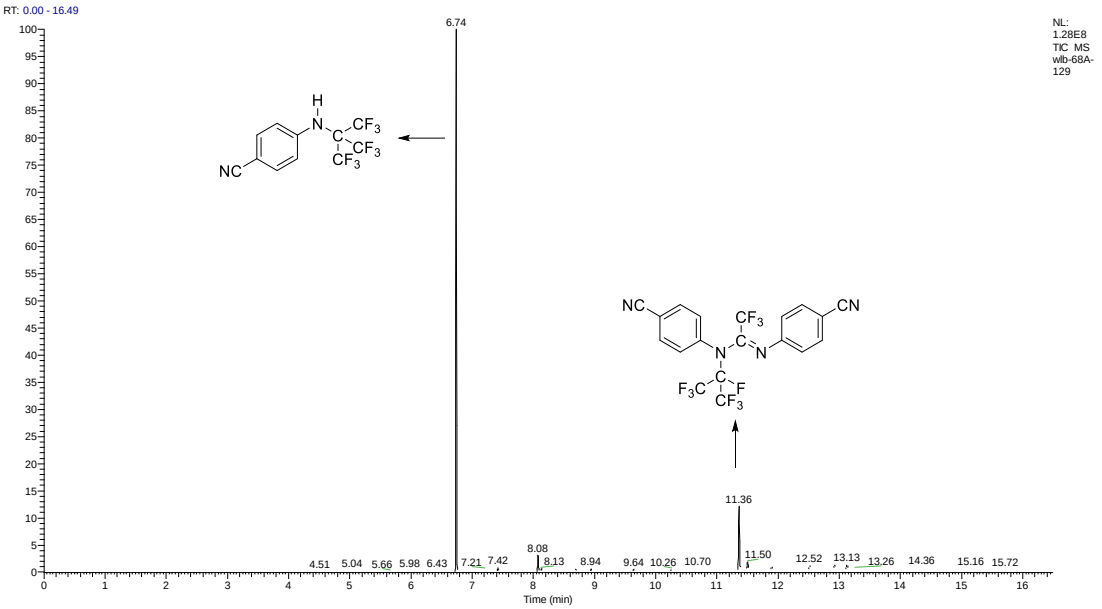
1. General information

Unless otherwise noted, all reactions were conducted in the oven- or flame-dried glassware under an atmosphere of nitrogen, all reagents and starting materials were purchased from commercial sources and used without further purification. All known compounds are identified by appropriate techniques such as ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and compared with previously reported data. All unknown compounds are characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a 500 MHz Bruker DRX 500. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. GC-MS data were recorded on an ISQ LT Single Quadrupole Mass Spectrometer, coupled with a Trace 1300 Gas Chromatograph (Thermo Fisher Scientific). Melting points were measured on a melting point apparatus (HMX-1B) and were uncorrected. High-resolution mass spectral data were acquired on Agilent Technologies 7250 GCQTOF (electro ionization: EI) and JEOL-AccuTOF-GCv4G-GCT MS (FI). The ^{19}F MRI data were recorded on a Bruker 9.4 T BioSpec 94/30 MRI & PET Insert.

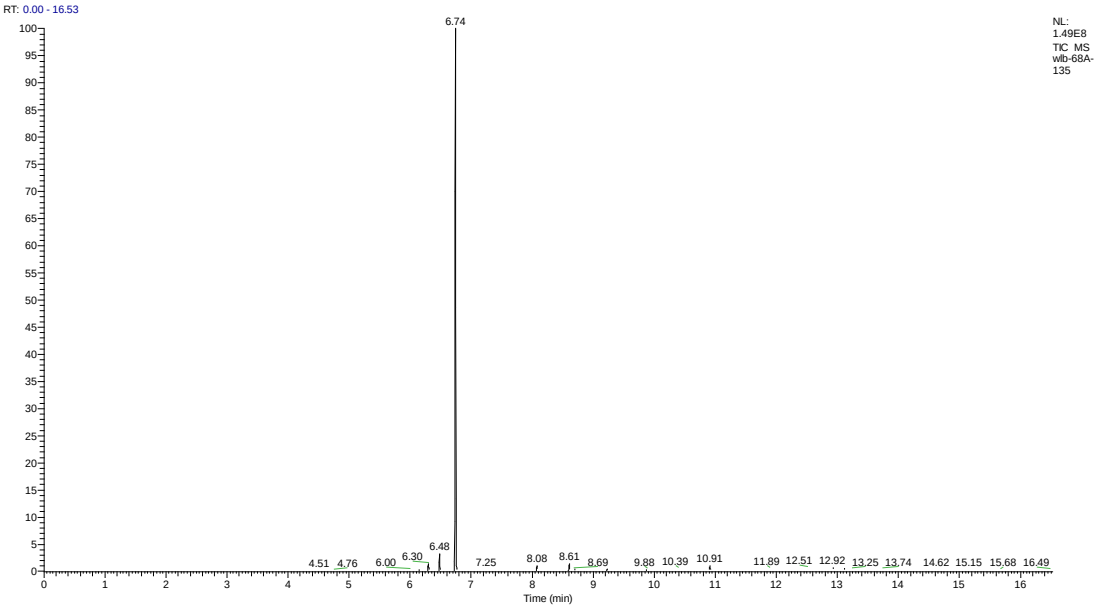
2. Study of condition optimization and reaction path

The variation in CsF dosage resulted in decreased yield, attributed to the formation or increased quantity of by-products. When 0.5 equivalents of CsF was used (entry 13), a dimer was produced during the reaction (Supplementary Figure S1). When 3.0 equivalents of CsF were employed (entry 12), there was a notable increase in by-products compared to the conditions using 1.5 equivalents (entry 11) (Supplementary Figure S2 and S3).

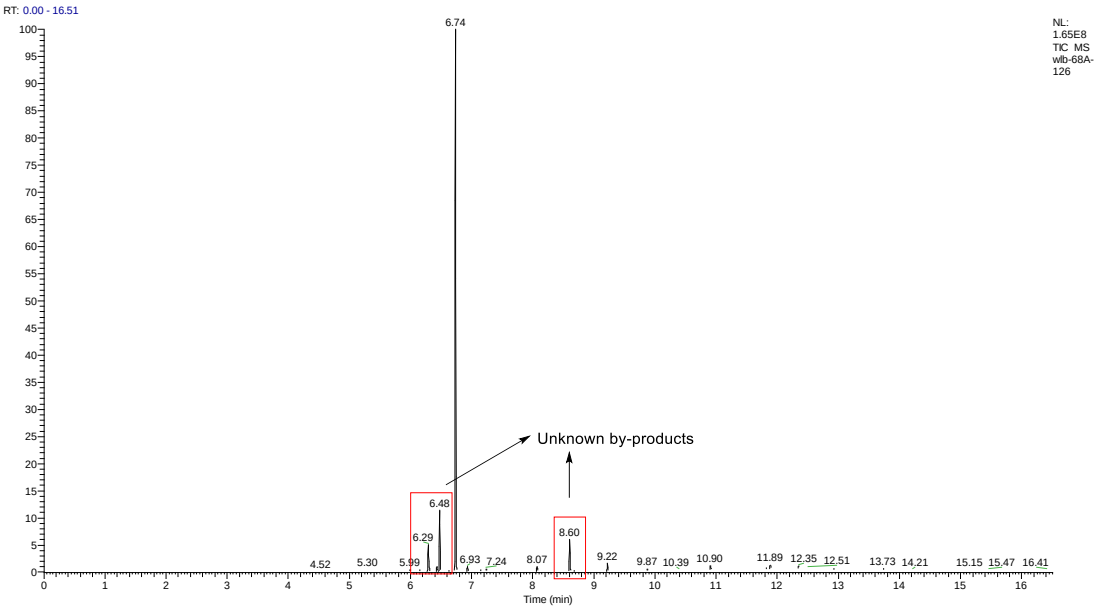
entry	$TMSCF_3$ (equiv)	Additive (equiv)	Solvent	Yield (%)[b]
1	8	KF (1)	THF	33
2	8	KF (3)	THF	38
3	8	KF (5), CuCl (1.0)	THF	54
4	8	KF (3), CuCl (1.0)	THF	47
5	10	KF (5)	THF	43
6	10	KF (3)	THF	42
7	8	\	THF	0
8	8	NaF (3.0)	THF	0
9	8	TBAF (3.0)	THF	0
10	8	CsF (1.0)	THF	65
11	8	CsF (1.5)	THF	73
12	8	CsF (3.0)	THF	67
13	8	CsF (0.5)	THF	60
14	8	CsF (1.5)	DCM	23
15	8	CsF (1.5)	MeCN	41
16	**6**	**CsF (1.5)**	**THF**	**76**
17	10	CsF (3.0)	THF	57



Supplementary Figure S1. Reaction results from GC-MS analysis with the addition of 0.5 equivalents of CsF (entry 13).

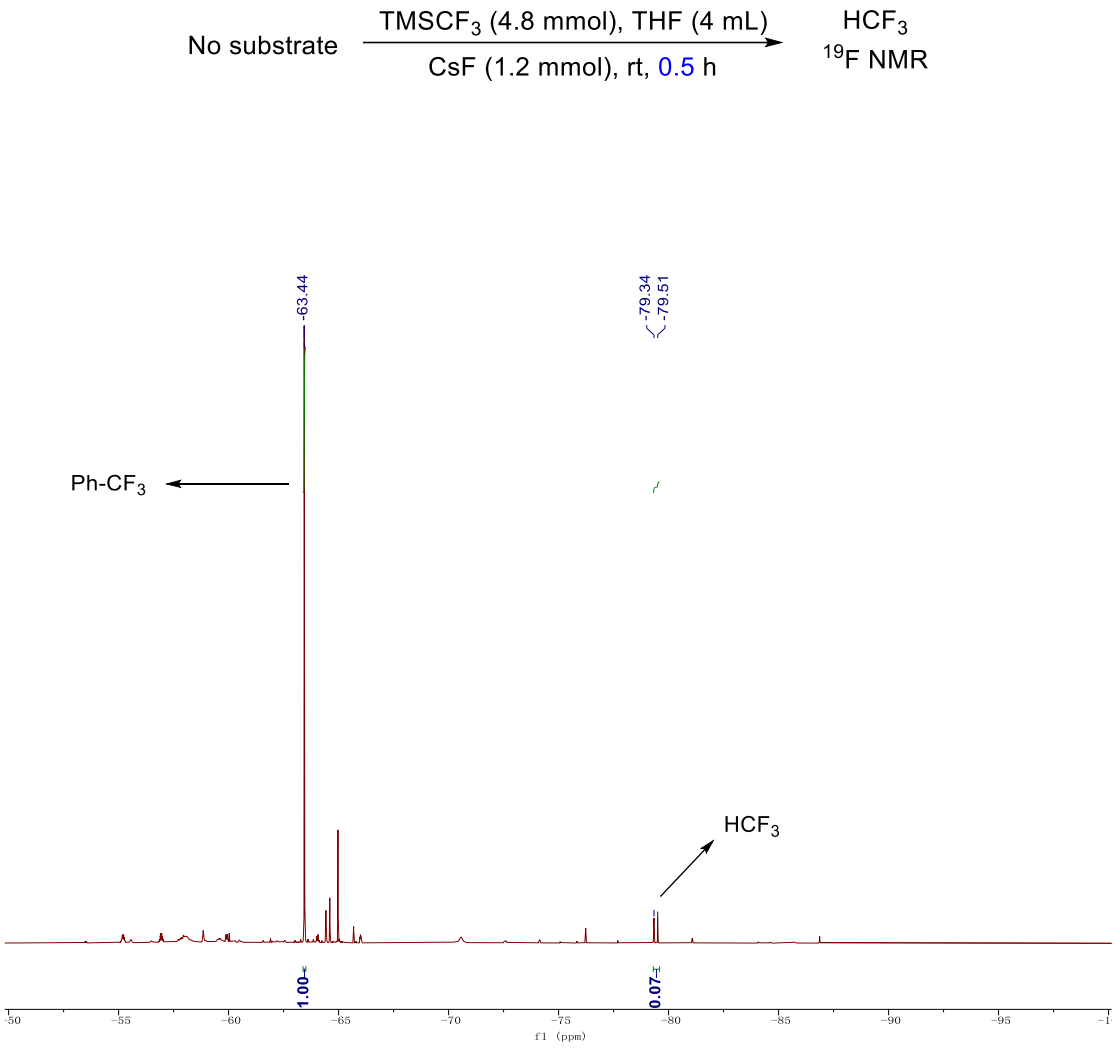


Supplementary Figure S2. Reaction results from GC-MS analysis with the addition of 1.5 equivalents of CsF (entry 11).

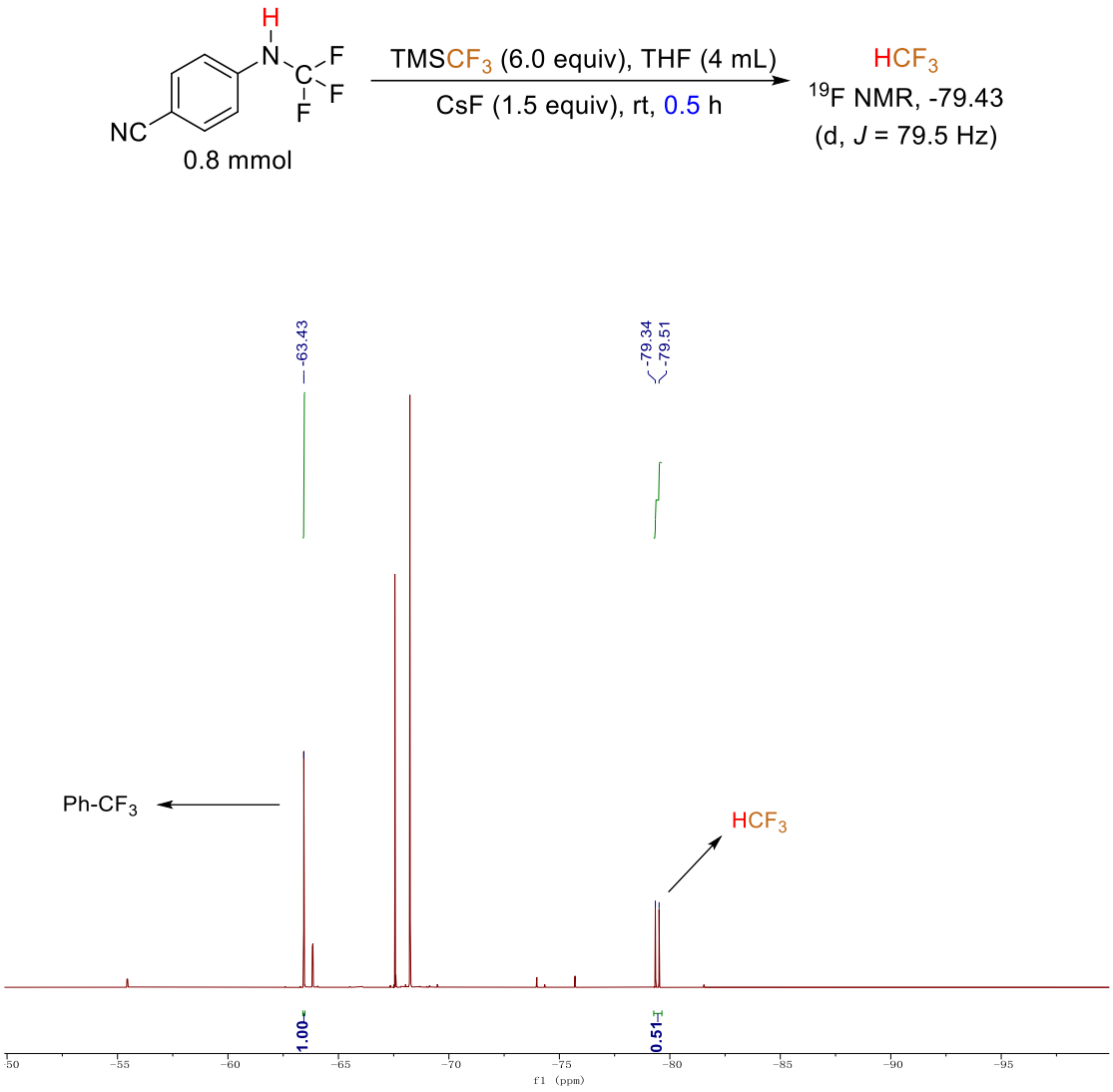


Supplementary Figure S3. Reaction results from GC-MS analysis with the addition of 3.0 equivalents of CsF (entry 12).

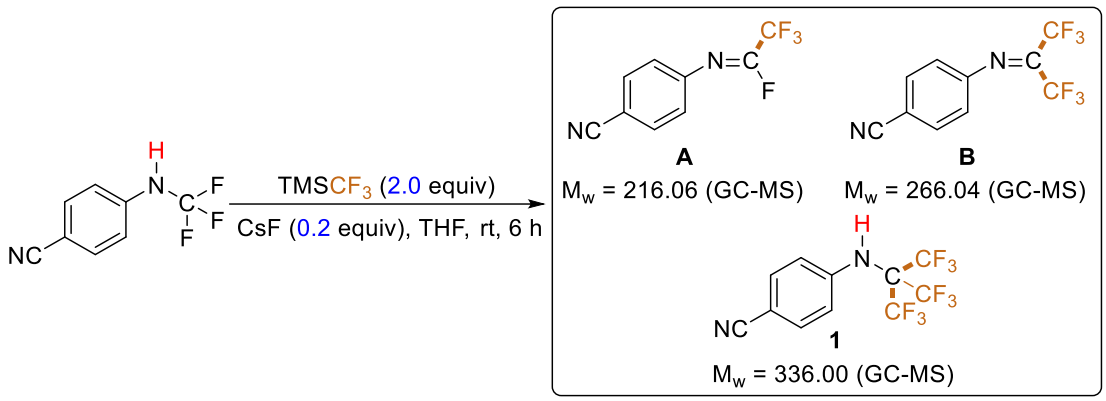
The HCF_3 signal was detected by ^{19}F NMR under reaction conditions without a substrate (4.8 mmol $TMSCF_3$, 1.2 mmol CsF, 4.0 mL dry THF, 0.5 h), using 0.8 mmol of trifluorotoluene as an internal standard. We found that a very small amount of HCF_3 (7%) was generated (Supplementary Figure S4). In contrast, when the substrate (0.8 mmol) was included in the reaction for 0.5 hours, 51% of HCF_3 remained while the final product was formed (Supplementary Figure S5). This indicates that the vast majority of HCF_3 produced during the reaction is sourced from the substrate, with only a minor portion arising from the solvent THF.

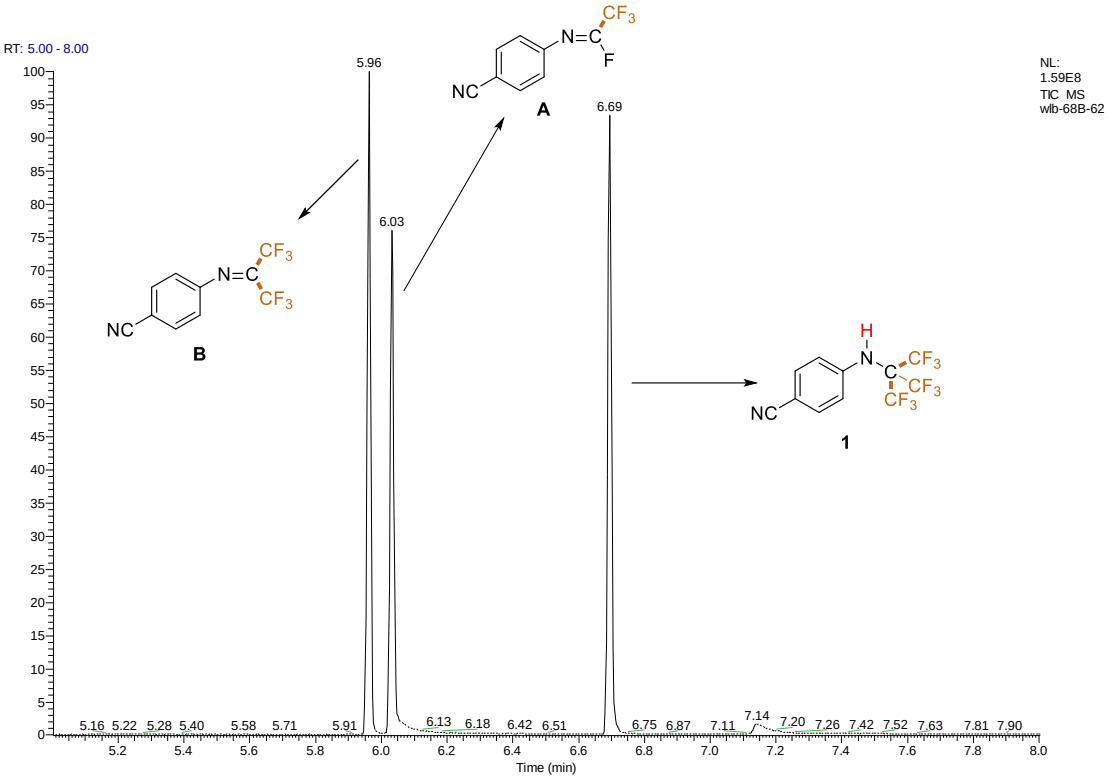


Supplementary Figure S4. ^{19}F NMR detection of HCF_3 in the absence of substrate.

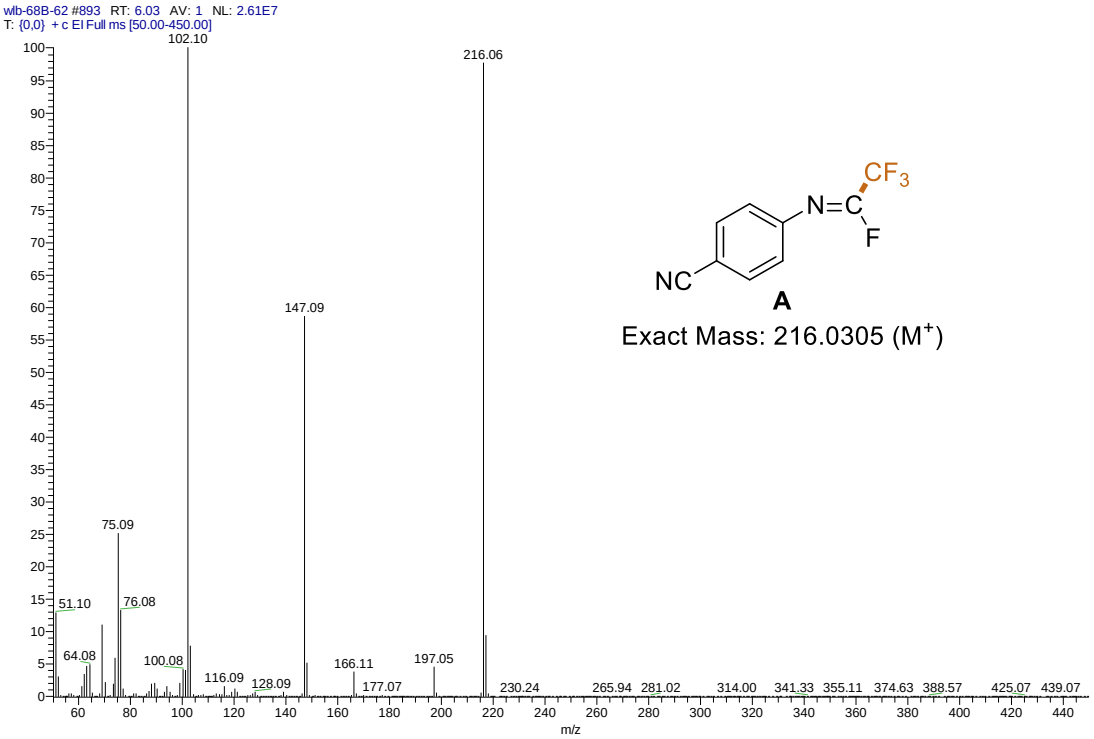


Supplementary Figure S5. ^{19}F NMR detection of HCF_3 in the presence of substrate.

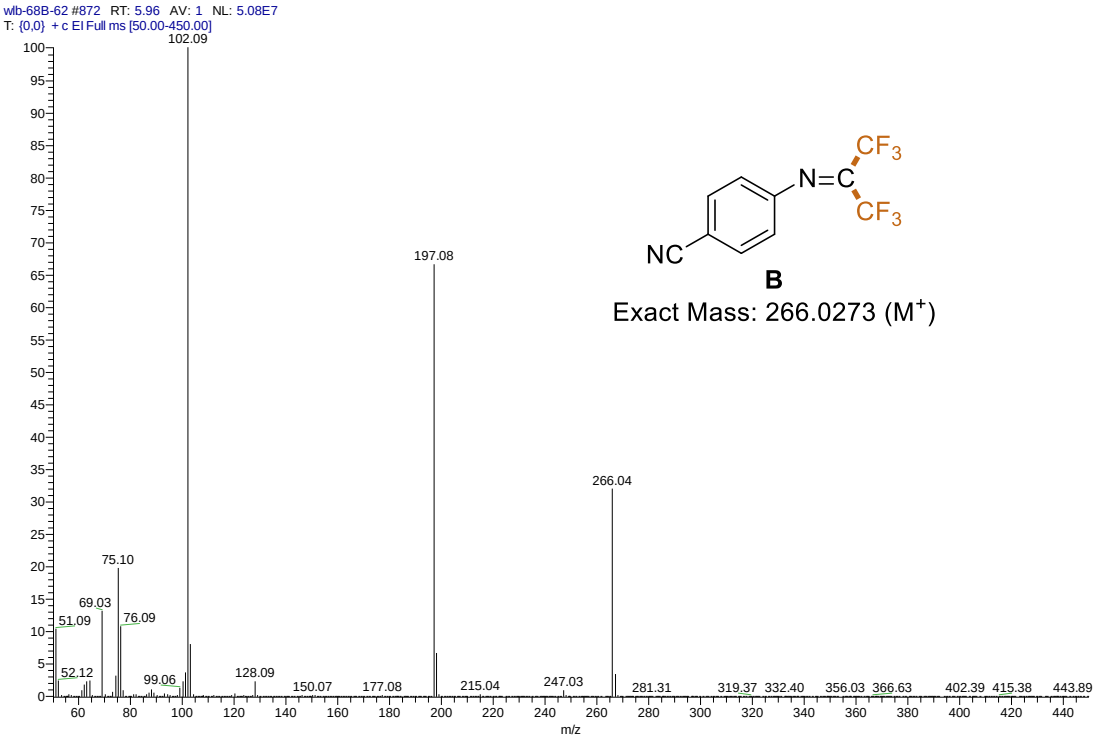




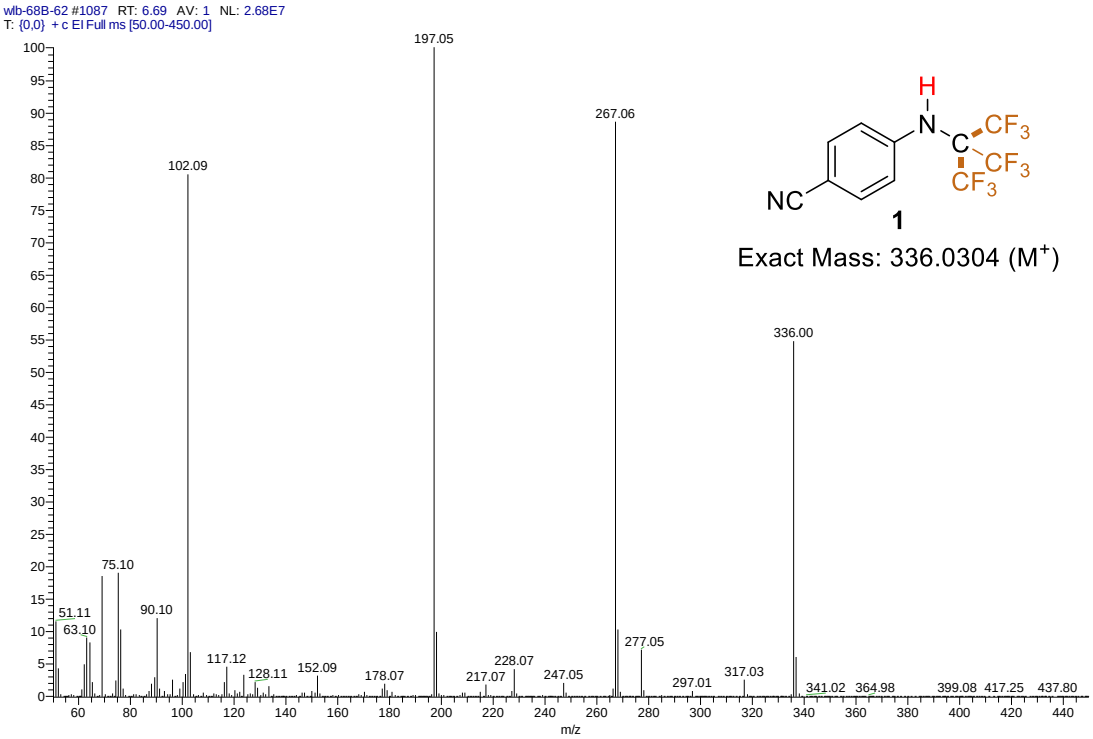
Supplementary Figure S6. The mixed products of mono-, di-, and tri-substituted trifluoromethylation.



Supplementary Figure S7. The mass spectrum of compound A from GC-MS.



Supplementary Figure S8. The mass spectrum of compound B from GC-MS.



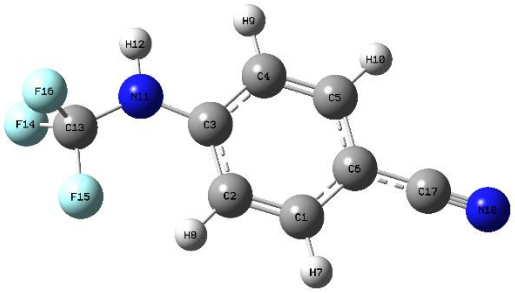
Supplementary Figure S9. The mass spectrum of compound 1 from GC-MS.

3. Density functional theory (DFT) study and calculational details

In the DFT reaction mechanism study, we used Gaussian 16, Revision A.01[1]. Geometry optimizations of all involved compounds were conducted with the PBE0 functional[2] (Integral grid precision is ultrafine) in combination with the D3BJ dispersion correction[3] and the def2-TZVP basis set[4], which is suitable for organic systems of metal K and Cs. The solvation effects of tetrahydrofuran were considered during geometry optimizations using the SMD[5] solvation model. Frequency calculations were carried out at the same theoretical level as for geometry optimization to verify that the stationary points of compound structures on the potential energy surface are either minima (no imaginary frequencies) or first-order saddle points (only one imaginary frequency), as well as to obtain thermal Gibbs free energy corrections. Furthermore, Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the first-order saddle points found were true transition states (TS).

It is determined through TS, QST2, QST3, and relaxed scan that there is no suitable transition state in the reaction process from **IM-1** to the product. This may be due to the large Cs atom causing the bond length to be too long and the small H atom causing the bond length to be too short, resulting in no significant energy barrier change on the potential energy surface. All Gibbs free energy obtained using the implicit solvent model was added with a correction of 1.89 kcal/mol corresponding to the 1M standard state.

4-cyanophenyl *N*-trifluoromethyl secondary amine



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C	2.11115200	1.27472500	-0.00000400
C	2.63023300	-0.02264500	-0.00000400
H	2.14452400	-2.11517900	0.00000500
H	-0.25534500	-1.77933500	0.00002200
H	0.35512300	2.48041600	0.00000200
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N	-1.48214100	0.70810000	0.00002400
H	-1.69418800	1.69604600	0.00004900
C	-2.62516800	-0.07969100	0.00000100
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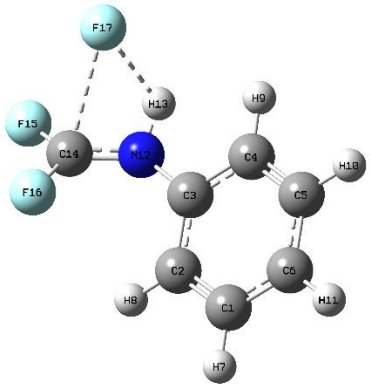
C	4.03481000	-0.23526700	-0.00001200
N	5.17531800	-0.40752200	-0.00001800

TS



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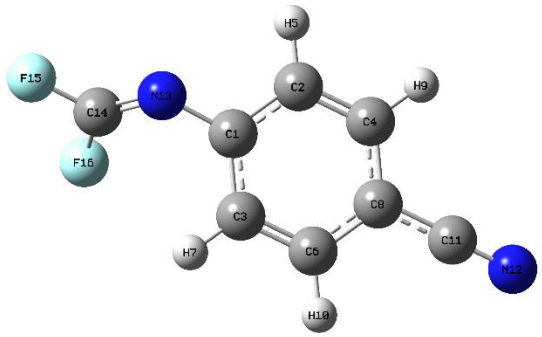
C	0.54406600	1.29801200	-0.26843400
C	1.90949700	1.24812700	-0.07642700
C	2.55267500	0.01210500	-0.01230400
H	2.33817100	-2.12621200	-0.11129100
H	-0.09722500	-2.03996200	-0.47942700
H	0.02585400	2.24867600	-0.30535900
H	2.47889000	2.16270600	0.02877600
N	-1.56008700	0.21037300	-0.61801900
H	-1.97277200	1.15979600	-0.75330100
C	-2.46779500	-0.47361900	-0.01289000
F	-3.68256400	-0.47014200	-0.38034600
F	-2.20426000	-1.38023400	0.84126400
F	-2.92585800	1.69182200	0.64367600
C	3.96274700	-0.04227300	0.18738400
N	5.10217900	-0.08710300	0.34852100

CsF

F	0.00000000	0.00000000	-2.25646600
Cs	0.00000000	0.00000000	0.36924000

IM-1



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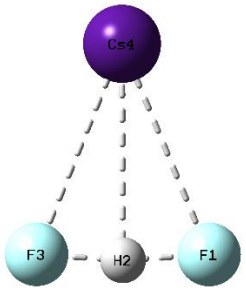
C	1.66947800	1.24883700	-0.22746000
H	-0.13058800	2.41365400	-0.24736500
C	1.40879900	-1.07029100	0.41215700
H	-0.58600000	-1.69734200	0.86585400
C	2.22374400	-0.00904500	0.01647900

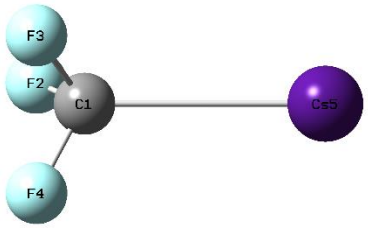
H	2.30718800	2.07121800	-0.52714600
H	1.84482400	-2.04204900	0.60845600
C	3.62538400	-0.20768000	-0.13100300
N	4.76017300	-0.36865400	-0.25163200
N	-1.87031900	0.62780900	0.47877500
C	-2.75595500	-0.04306000	-0.06295200
F	-4.02485100	0.17444600	0.14075800
F	-2.62182900	-1.02975900	-0.91486700

$CsHF_2$



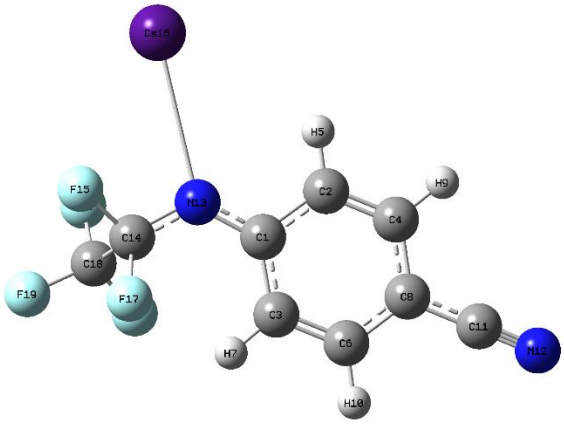
F	1.13095300	-2.04957400	0.00000000
H	0.00011900	-2.12521200	0.00000000
F	-1.13096700	-2.05000600	0.00000000
Cs	0.00000000	0.70948100	0.00000000

$CsCF_3$



C	-1.82666900	0.00029500	-0.00010400
F	-2.47388500	0.28071000	-1.21983500
F	-2.47225600	0.91673600	0.85340300
F	-2.47067500	-1.19821600	0.36715100
Cs	1.41293400	0.00009400	-0.00010600

IM-2



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C	2.33601100	0.90367400	-0.45320700
C	2.98676900	-1.71560200	0.21979600
H	0.89286400	-2.08883600	0.22878800
C	3.65348700	0.53712500	-0.30948900
H	2.11398700	1.92663300	-0.72112100
C	4.00920800	-0.77434900	0.02853800
H	3.24128000	-2.73638200	0.48226300
H	4.43235300	1.27626600	-0.46132200
C	5.36628500	-1.14197500	0.17315700
N	6.47571900	-1.44544200	0.29223300
N	-0.04287200	0.20234700	-0.38699900
C	-0.58141600	1.41247500	-0.62803400
F	-1.89149000	1.25040400	-1.06761800
Cs	-2.49748500	-1.70310600	0.04427400
F	0.00247200	2.18984800	-1.62215500
C	-0.73532800	2.36941500	0.58879000
F	-1.34468100	3.51249400	0.26249700
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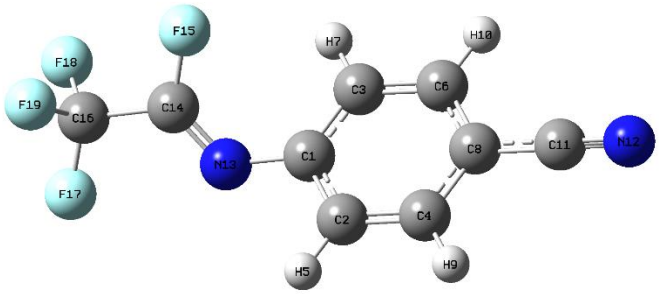
IM-3



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C	-1.36076600	1.41292400	0.12259900
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C	-2.72641400	1.25572200	0.23811100
H	-0.89784900	2.37534600	0.30298500
C	-2.50576200	-1.07014400	-0.39812400
H	-0.51634600	-1.75183000	-0.78623000
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H	-3.35219200	2.09396600	0.51797300
H	-2.96166000	-2.02934100	-0.61002500
C	-4.71361200	-0.15129700	0.08205200
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F	1.49787300	-1.24445800	0.90156500
C	3.17626500	0.08218000	-0.04892500
F	3.39342500	1.14983900	-0.79583200
F	3.75167000	-0.97105000	-0.63273400
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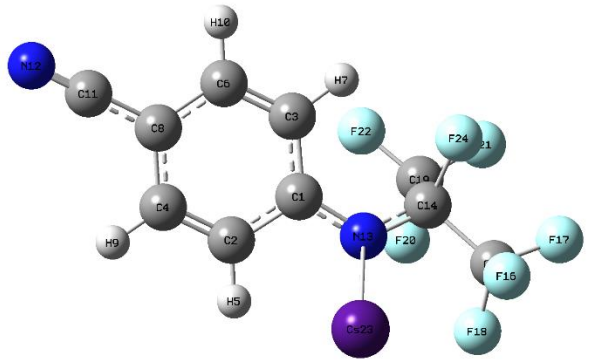
IM-4



C	0.91184900	0.67422100	0.18819900
C	1.84827800	0.16578500	1.12670500
C	1.44601800	1.47205600	-0.85882600
C	3.19535700	0.41414200	1.03089700
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C	2.79418500	1.72135900	-0.95338900
H	0.78583800	1.88931700	-1.60597900
C	3.69651900	1.19580800	-0.01836200
H	3.87612600	0.01489600	1.77445100
H	3.16939100	2.33197100	-1.76729000
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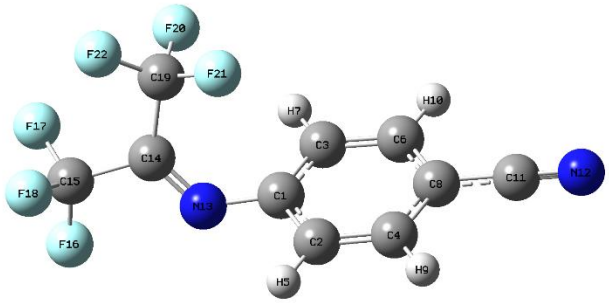
N	6.21764800	1.65250700	-0.22223900
N	-0.37283200	0.28287700	0.33829300
C	-1.43773300	0.90283800	-0.23147700
C	-2.66636500	-0.03722200	-0.10190400
F	-2.43266600	-1.17072600	-0.77968600
F	-3.77974600	0.49348000	-0.60696900
F	-2.91762000	-0.37481900	1.16103300
C	-1.75669100	2.31743100	0.34511300
F	-2.10540200	2.22763400	1.63185400
F	-2.75053000	2.93956300	-0.29539600
F	-0.68757500	3.10890900	0.27351400
Cs	0.28480700	-2.80553400	-0.02133100
F	-1.38898600	1.14018700	-1.64876800

IM-5



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C	3.01864100	-1.01799400	0.90829600
H	1.20477100	-1.92715200	1.60262800
C	2.81071400	0.36960400	-1.06405700
H	0.83517400	0.56236300	-1.86827600
C	3.59754800	-0.19578300	-0.06096500
H	3.63603300	-1.46083800	1.67986500
H	3.26612800	0.99781400	-1.81952500
C	4.99818100	0.05650400	-0.03178700
N	6.13191000	0.26115500	-0.00758800
N	-0.47842000	-1.00674200	-0.15737900
C	-1.44075800	-0.22090200	-0.02291500
C	-2.84953000	-0.79405100	-0.17726100
F	-2.82203100	-1.99874000	-0.72170200
F	-3.59150400	-0.00013200	-0.95497800
F	-3.45712000	-0.88968500	1.00777000
C	-1.36209600	1.27911900	0.29409800
F	-1.27422700	1.99199100	-0.83067100
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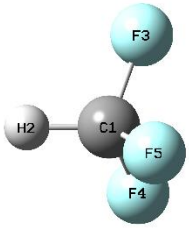
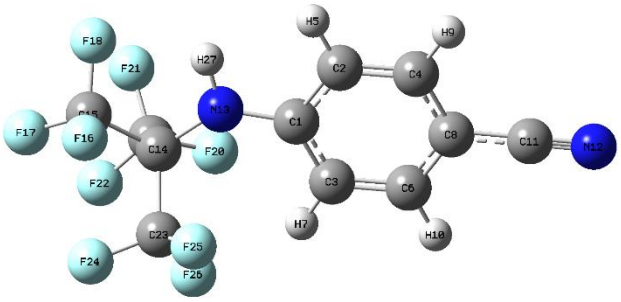
HCF_3



C	0.00002800	-0.00003200	0.34593200
H	0.00010500	-0.00002700	1.43666400
F	-0.31268700	1.20736600	-0.13005800
F	-0.88930800	-0.87444900	-0.13005100
F	1.20196500	-0.33289300	-0.13014200

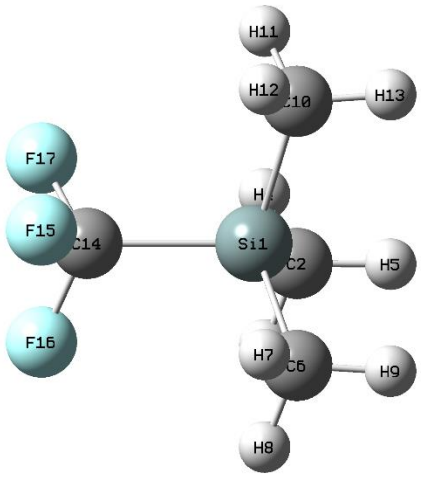
Product



C	1.32267100	0.54248100	-0.00647100
C	2.21435600	1.62646000	0.01482800
C	1.84589500	-0.75157900	-0.03004400
C	3.57349300	1.42941400	0.01956100
H	1.82053900	2.63682900	0.03158700
C	3.21246300	-0.94969500	-0.02035100
H	1.21036300	-1.62022300	-0.07003500
C	4.09111100	0.13093300	0.00545900
H	4.24348500	2.28027500	0.03690600
H	3.60172700	-1.96026500	-0.03940300
C	5.49503100	-0.08240600	0.01320900
N	6.63562600	-0.25357500	0.01976600
N	-0.01970800	0.87854900	0.00806000
C	-1.21451100	0.10463500	-0.00976800
C	-2.36165500	1.10629400	0.36688600
F	-2.31957400	1.38198200	1.66628400
F	-3.55930300	0.62552400	0.07176800

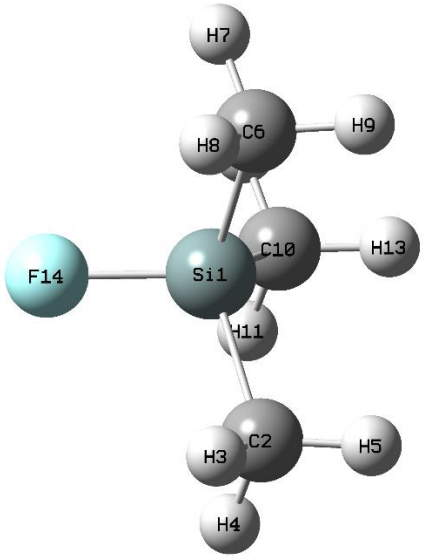
F	-2.21786000	2.25856300	-0.28734100
C	-1.50719300	-0.48672500	-1.42837600
F	-0.43160300	-1.10004100	-1.90856800
F	-1.82238700	0.49107300	-2.27422100
F	-2.50978600	-1.36119100	-1.41214200
C	-1.24135900	-1.05184300	1.05908800
F	-2.48174200	-1.30511600	1.46765100
F	-0.51628300	-0.71790500	2.11443800
F	-0.76297300	-2.19379300	0.56634600
H	-0.17575000	1.86887900	-0.09590300

TMSCF$_3$



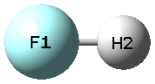
Si	0.86331300	0.00011400	0.00024500
C	1.36512200	-0.23367900	-1.77478700
H	0.99102300	-1.18148200	-2.17125200
H	0.98621000	0.57591400	-2.40444700
H	2.45624600	-0.24168800	-1.85828500
C	1.36453300	-1.42095500	1.08952700
H	0.98697000	-1.29330400	2.10763700
H	0.98835200	-2.37077900	0.69991800
H	2.45559700	-1.48768300	1.14161600
C	1.36542400	1.65411500	0.68525300
H	0.98894000	2.47134600	0.06405600
H	0.98884200	1.79337400	1.70219300
H	2.45658300	1.73152400	0.71744200
C	-1.08081200	0.00013700	-0.00003300
F	-1.61007000	0.15546100	1.23690800
F	-1.60999200	-1.14875900	-0.48405900
F	-1.61002100	0.99368300	-0.75307800

TMSF



Si	-0.00007400	-0.00001000	0.01756200
C	0.79409300	-1.58996800	-0.51768700
H	1.82220900	-1.66275700	-0.15124000
H	0.23733800	-2.45562500	-0.14722100
H	0.82241400	-1.65205600	-1.61019100
C	0.98000200	1.48243200	-0.51806900
H	0.53033800	2.40921600	-0.15002300
H	2.00862300	1.43195200	-0.14929600
H	1.01798900	1.53908000	-1.61059700
C	-1.77399300	0.10723100	-0.51796400
H	-2.35229200	-0.74439100	-0.14790000
H	-2.24388200	1.02442100	-0.15111000
H	-1.84214300	0.10940800	-1.61047600
F	-0.00001900	0.00030200	1.64494500

HF

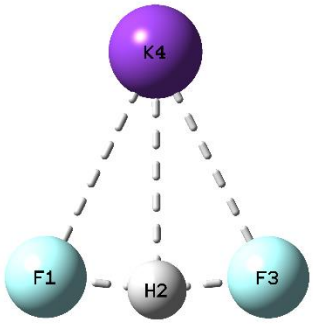


F	0.00000000	0.00000000	0.09260600
H	0.00000000	0.00000000	-0.83345500

KF

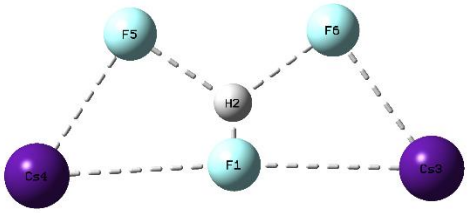
F	0.00000000	0.00000000	-1.56206400
K	0.00000000	0.00000000	0.73992500

KHF_2



F	-1.12771000	-1.14710100	0.00000000
H	-0.00002000	-1.27771300	0.00000000
F	1.12771300	-1.14745100	0.00000000
K	0.00000000	1.15414100	0.00000000

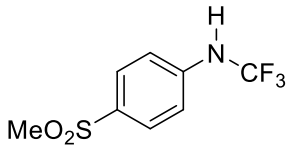
Cs_2HF_3



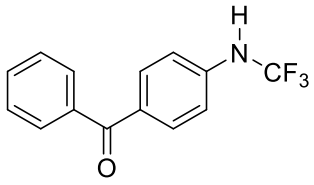
F	0.00000000	0.00000000	-0.18340200
H	0.00000000	0.00000000	0.78198800
Cs	0.00000000	3.07984800	-0.30050400
Cs	0.00000000	-3.07984800	-0.30050400
F	0.00000000	-1.58185300	1.88467000
F	0.00000000	1.58185300	1.88467000

4. General procedure for the synthesis of *N*-CF_3 secondary amines[6]

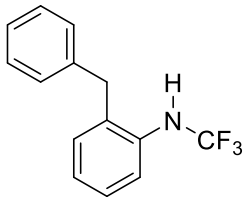
A 25 mL Schlenk flask equipped with a magnetic stir bar was charged with the isothiocyanate (1.0 mmol, 1.0 equiv.) and silver fluoride (5.0 mmol, 5.0 equiv.). The flask was evacuated and refilled with N_2 three times. Triethylsilane (indicated equivalents) was dissolved in acetonitrile (5.0 mL) and the solution was added quickly to the vessel via syringe (if the isothiocyanate was a liquid or an oil, it was added as a solution in the solvent). The reaction mixture was stirred at room temperature for 8 h. The crude mixture was filtered and concentrated under reduced pressure to about 1 mL, subsequently was added to Et_2O (30 mL) and stirred for 10 minutes. The solid was filtered through celite and the solvents were then evaporated. The crude material was dissolved in Et_2O and filtered through a pad of celite again to obtain the corresponding *N*-CF_3 secondary amines.



4-(methylsulfonyl)-*N*-(trifluoromethyl)aniline. The title compound was obtained as a white solid in 92% yield (220 mg) using triethylsilane (1.4 mmol, 1.4 equiv.) following the general procedure for *N*-CF_3 secondary amines. M.p.: 127-129 ºC. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.34 (s, 1H), 7.11 (d, *J* = 8.6 Hz, 2H), 3.01 (s, 3H). **^{19}F NMR** (470 MHz, CD_3CN) δ -56.9 (d, *J* = 13.5 Hz, 3F). **^{13}C NMR** (126 MHz, CD_3CN) δ 143.7, 134.6, 129.7, 121.9 (q, *J* = 255.2 Hz), 116.7, 44.4. **HRMS** (EI): m/z calcd for $C_8H_8F_3NO_2S$: 239.0222 M^+; Found 239.0222.

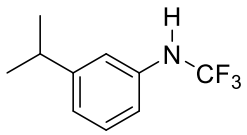


phenyl(4-((trifluoromethyl)amino)phenyl)methanone. The title compound was obtained as a white solid in 95% yield (251 mg) using triethylsilane (1.4 mmol, 1.4 equiv.) following the general procedure for *N*-CF_3 secondary amines. M.p.: 104-106 ºC. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.41 (d, *J* = 5.4 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -54.5 (d, *J* = 5.3 Hz, 3F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 194.8, 143.4, 138.1, 132.4, 132.2, 130.5, 129.7, 128.7, 122.0 (q, *J* = 255.0 Hz), 115.7. **HRMS** (EI): m/z calcd for $C_{14}H_{10}F_3NO$: 265.0709 M^+; Found 265.0705.

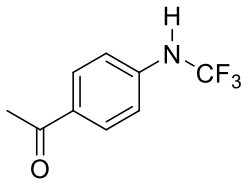


2-benzyl-*N*-(trifluoromethyl)aniline. The title compound was obtained as a colorless oil in 84% yield (211 mg) using triethylsilane (1.3 mmol, 1.3 equiv.) following the general procedure for *N*-CF_3 secondary amines. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.4 Hz, 2H), 7.36 - 7.31 (m, 2H), 7.29 - 7.26 (m, 2H), 7.23 (d, *J* = 7.1 Hz, 2H), 7.17 (td, *J* = 8.1, 1.3 Hz, 1H), 4.94 (s, 1H), 4.06 (s, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -55.1 (d, *J* = 3.9 Hz, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.6, 136.0, 131.3, 130.2, 129.1, 128.5, 127.9, 127.0,

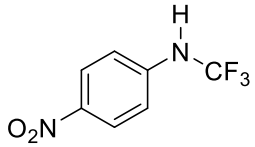
124.0, 121.8 (q, J = 256.2 Hz), 119.6 (q, J = 2.5 Hz), 38.2. **HRMS** (EI): m/z calcd for $C_{14}H_{12}F_3N$: 251.0916 M^+; Found 251.0916.



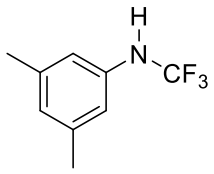
3-isopropyl-*N*-(trifluoromethyl)aniline. The title compound was obtained as a colorless oil in 89% yield (181 mg) using triethylsilane (1.5 mmol, 1.5 equiv.) following the general procedure for *N*-CF_3 secondary amines. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.10 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.8 Hz, 1H), 6.69 (d, J = 10.6 Hz, 2H), 4.97 (s, 1H), 2.80 - 2.71 (m, 1H), 1.13 (d, J = 7.1 Hz, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -55.6 (d, J = 4.6 Hz, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.5, 136.5, 128.3, 120.7 (q, J = 256.1 Hz), 120.4, 115.2, 114.3, 33.1, 22.8. **HRMS** (EI): m/z calcd for $C_{10}H_{12}F_3N$: 203.0916 M^+; Found 203.0915.



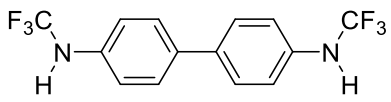
1-(4-((trifluoromethyl)amino)phenyl)ethan-1-one. The title compound was obtained as a white solid in 99% yield (201 mg) using triethylsilane (1.5 mmol, 1.5 equiv.) following the general procedure for *N*-CF_3 secondary amines. M.p.: 103-105 ºC. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.36 (q, J = 5.3 Hz, 1H), 7.83 (d, J = 8.6 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 2.42 (s, 3H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -54.9 (d, J = 5.5 Hz, 3F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 196.5, 143.5, 130.9, 130.5, 121.9 (q, J = 255.0 Hz), 115.7, 26.5. **HRMS** (EI): m/z calcd for $C_9H_8F_3NO$: 203.0552 M^+; Found 203.0551.



4-nitro-*N*-(trifluoromethyl)aniline. The title compound was obtained as a yellow solid in 93% yield (192 mg) using triethylsilane (1.9 mmol, 1.9 equiv.) following the general procedure for *N*-CF_3 secondary amines. M.p.: 102-104 ºC. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 9.93 (s, 1H), 8.22 (d, J = 9.3 Hz, 2H), 7.13 (d, J = 9.2 Hz, 2H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -55.2 (s, 3F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 145.3, 141.7, 125.9, 121.5 (q, J = 255.6 Hz), 115.8. **HRMS** (EI): m/z calcd for $C_7H_5F_3N_2O_2$: 206.0298 M^+; Found 206.0298.

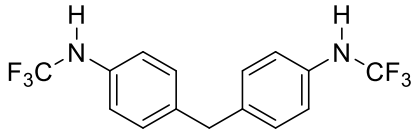


3,5-dimethyl-*N*-(trifluoromethyl)aniline. The title compound was obtained as a colorless oil in 80% yield (151 mg) using triethylsilane (1.4 mmol, 1.4 equiv.) following the general procedure for *N*-CF_3 secondary amines. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.59 (s, 1H), 6.46 (s, 2H), 4.87 (s, 1H), 2.16 (s, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -55.5 (d, J = 5.1 Hz, 3F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.2, 136.4, 123.9, 120.7 (q, J = 256.1 Hz), 114.6, 20.2. **HRMS** (EI): m/z calcd for $C_9H_{10}F_3N$: 189.0760 M^+; Found 189.0760.

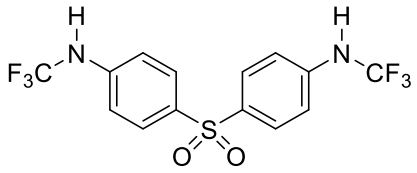


***N*^{4},*N*$^{4'}$-bis(trifluoromethyl)-[1,1'-biphenyl]-4,4'-diamine**. The title compound was obtained as a yellow solid in 90% yield (288 mg) using triethylsilane (3.2 mmol, 3.2 equiv.), silver fluoride (10.0 mmol, 10.0 equiv.), MeCN (10.0 mL) following

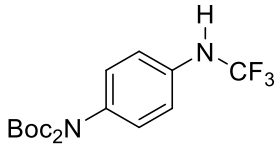
the general procedure for *N*-CF_3 secondary amines. M.p.: 104-106 ºC. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.38 (d, *J* = 8.7 Hz, 4H), 7.06 (q, *J* = 6.0 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 4H). **^{19}F NMR** (470 MHz, CD_3CN) δ -56.0 (d, *J* = 5.7 Hz, 6F). **^{13}C NMR** (126 MHz, CD_3CN) δ 138.3, 135.1, 128.0, 122.8 (q, *J* = 254.0 Hz), 118.4. **HRMS** (EI): m/z calcd for $C_{14}H_{10}F_6N_2$: 320.0743 M^+; Found 320.0743.



4,4'-methylenebis(*N*-(trifluoromethyl)aniline). The title compound was obtained as a white solid in 81% yield (271 mg) using triethylsilane (2.8 mmol, 2.8 equiv.), silver fluoride (10.0 mmol, 10.0 equiv.), MeCN (10.0 mL) following the general procedure for *N*-CF_3 secondary amines. M.p.: 36-37 ºC. **^{1}H NMR** (500 MHz, CD_3CN) δ 6.99 (d, *J* = 8.7 Hz, 4H), 6.83 (d, *J* = 8.3 Hz, 4H), 6.43 (q, *J* = 6.3 Hz, 2H), 3.69 (s, 2H). **^{19}F NMR** (470 MHz, CD_3CN) δ -56.1 (d, *J* = 6.3 Hz, 6F). **^{13}C NMR** (126 MHz, CD_3CN) δ 137.0, 137.0, 130.3, 122.9 (q, *J* = 254.0 Hz), 118.7, 40.4. **HRMS** (EI): m/z calcd for $C_{15}H_{12}F_6N_2$: 334.0899 M^+; Found 334.0899.



4,4'-sulfonylbis(*N*-(trifluoromethyl)aniline). The title compound was obtained as a white solid in 80% yield (307 mg) using triethylsilane (2.8 mmol, 2.8 equiv.), silver fluoride (10.0 mmol, 10.0 equiv.), MeCN (10.0 mL) following the general procedure for *N*-CF_3 secondary amines. M.p.: 167-169 ºC. **^{1}H NMR** (500 MHz, CD_3CN) δ 7.72 (d, *J* = 8.9 Hz, 4H), 7.22 (q, *J* = 5.2 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 4H). **^{19}F NMR** (470 MHz, CD_3CN) δ -57.0 (d, *J* = 5.9 Hz, 6F). **^{13}C NMR** (126 MHz, CD_3CN) δ 143.5, 135.5, 129.7, 121.8 (q, *J* = 255.3 Hz), 116.8. **HRMS** (FI): m/z calcd for $C_{14}H_{10}F_6N_2O_2S$: 384.0362 M^+; Found 384.0364.



***tert*-butyl (*tert*-butoxycarbonyl)(4-((trifluoromethyl)amino)phenyl)carbamate**. The title compound was obtained as a white solid in 97% yield (364 mg) using triethylsilane (1.3 mmol, 1.3 equiv.) following the general procedure for *N*-CF_3 secondary amines. M.p.: 137-139 ºC. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.89 (q, *J* = 5.8 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 1.39 (s, 18H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -54.2 (d, *J* = 5.9 Hz, 3F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 152.1, 138.0, 133.6, 129.2, 122.4 (q, *J* = 253.9 Hz), 117.2, 82.4, 27.9. **HRMS** (EI): m/z calcd for $C_{17}H_{23}F_3N_2O_4$: 376.1604 M^+; Found 376.1609.

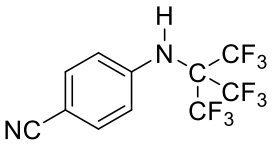
5. General procedure for *N*-perfluoro-*tert*-butyl secondary amines

Under nitrogen atmosphere, a 25 mL Schlenk flask equipped with a magnetic stir bar was charged with the *N*-CF_3 secondary amines (0.8 mmol, 1.0 equiv.), CsF (1.2 mmol, 1.5 equiv.) and dry THF (2.0 mL). The mixture was stirred at room temperature and then $TMSCF_3$ (4.8 mmol, 6.0 equiv.) dissolved in dry THF (2.0 mL) was added dropwise to the reaction mixture. After the addition was completed, the reaction mixture was stirred at room temperature for 6 h. The crude mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using the indicated solvent system to give the corresponding products.

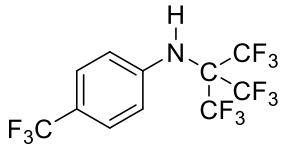
Particular examples

Compounds **27** and **28** were obtained in a one-pot method from isothiocyanates to *N*-PFtB secondary amines. According to general procedure for the synthesis of *N*-CF_3 secondary amines, a mixture of isothiocyanate (0.8 mmol, 1.0 equiv.), silver fluoride (4.0 mmol, 5.0 equiv.), triethylsilane (1.36 mmol, 1.7 equiv.) and replacement of MeCN with THF (4.0 mL) was stirred at room temperature for 12 h. After the reaction was completed, CsF (1.2 mmol, 1.5 equiv.) and $TMSCF_3$ (4.8 mmol, 6.0 equiv.) were added and stirred at room temperature for another 6 h.

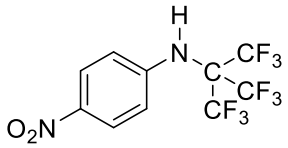
For compounds **29** and **30**, a mixture of isothiocyanate (0.8 mmol, 1.0 equiv.), silver fluoride (4.0 mmol, 5.0 equiv.), triethylsilane (1.2 mmol, 1.5 equiv.) and MeCN (4.0 mL) was stirred at room temperature for 8 h following the general procedure for *N*-CF_3 secondary amines. But THF was used instead of Et_2O to purify the crude mixture, which was then concentrated to about 2 mL and CsF (1.2 mmol, 1.5 equiv.) and $TMSCF_3$ (4.8 mmol, 6.0 equiv.) were added following the general procedure for *N*-perfluoro-*tert*-butyl secondary amines.



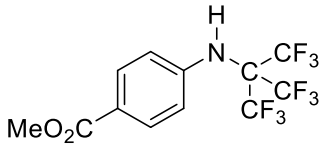
4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-amino)benzonitrile (1). White solid, M.p.: 89-91 ºC, yield 76% (204 mg). Eluent: ethyl acetate/petroleum ether (4:96). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.6 Hz, 2H), 4.71 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 133.3, 121.9, 120.9 (q, *J* = 292.3 Hz), 118.5, 107.2, 69.9 (m). **HRMS** (EI): m/z calcd for $C_{11}H_5F_9N_2$: 336.0304 M^+; Found 336.0307.



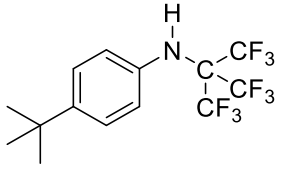
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-4-(trifluoromethyl)aniline**[7] **(2)**. Colorless oil (volatile compound). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 4.23 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.7 (s, 3F), -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.0, 127.1 (q, *J* = 33.3 Hz), 126.4 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.2 Hz), 123.1, 121.0 (q, *J* = 291.7 Hz), 69.9 (m). **HRMS** (EI): m/z calcd for $C_{11}H_5F_{12}N$: 379.0225 M^+; Found 379.0225.



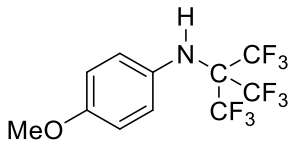
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-4-nitroaniline**[7] **(3)**. White solid, M.p.: 69-70 ºC, yield 85% (242 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 - 8.12 (m, 2H), 7.17 (d, *J* = 9.3 Hz, 2H), 4.91 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.5, 143.4, 125.1, 120.9 (q, *J* = 293.3 Hz), 120.5, 69.9 (m). **HRMS** (EI): m/z calcd for $C_{10}H_5F_9N_2O_2$: 356.0202 M^+; Found 356.0205.



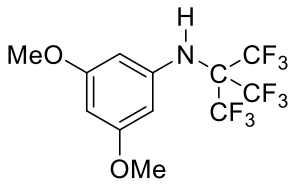
methyl 4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)benzoate (4). White solid, M.p.: 67-68 ºC, yield 80% (236 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 4.51 (s, 1H), 3.86 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 144.3, 130.8, 126.2, 122.0, 121.0 (q, *J* = 293.3 Hz), 70.0 (m), 51.9. **HRMS** (EI): m/z calcd for $C_{12}H_8F_9NO_2$: 369.0406 M^+; Found 369.0413.



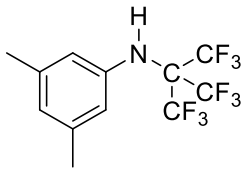
4-(*tert*-butyl)-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline (5). Light yellow oil, yield 31% (91 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 3.89 (s, 1H), 1.31 (s, 9H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.7 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.9, 136.5, 125.9, 125.3, 121.1 (q, *J* = 293.0 Hz), 70.0 (m), 34.4, 31.3. **HRMS** (EI): m/z calcd for $C_{14}H_{14}F_9N$: 367.0977 M^+; Found 367.0980.



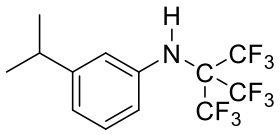
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-4-methoxyaniline**[7] **(6)**. Brown oil, yield 35% (95 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.7 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.1, 131.5, 128.8, 121.1 (q, *J* = 291.8 Hz), 114.0, 70.0 (m), 55.4. **HRMS** (EI): m/z calcd for $C_{11}H_8F_9NO$: 341.0457 M^+; Found 341.0453.



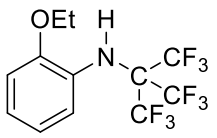
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3,5-dimethoxyaniline (7)**. Light yellow oil, yield 28% (83 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.28 (t, *J* = 4.3 Hz, 1H), 6.27 (d, *J* = 2.2 Hz, 2H), 3.98 (s, 1H), 3.76 (s, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 141.3, 121.0 (q, *J* = 291.9 Hz), 102.9, 97.3, 70.0 (m), 55.3. **HRMS** (EI): m/z calcd for $C_{12}H_{10}F_9NO_2$: 371.0562 M^+; Found 371.0561.



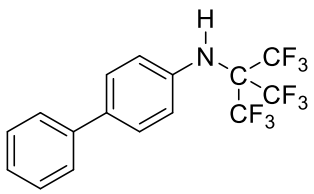
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3,5-dimethylaniline (8)**. Light yellow oil, yield 38% (103 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.79 (s, 2H), 3.91 (s, 1H), 2.32 (s, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 139.3, 138.7, 127.4, 122.9, 121.1 (q, *J* = 293.0 Hz), 70.1 (m), 21.1. **HRMS** (EI): m/z calcd for $C_{12}H_{10}F_9N$: 339.0664 M^+; Found 339.0667.



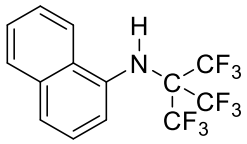
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3-isopropylaniline (9)**. Light yellow oil, yield 39% (110 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 3.98 (s, 1H), 2.95 - 2.87 (m, 1H), 1.27 (d, *J* = 7.1 Hz, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.1, 139.3, 128.9, 123.9, 123.6, 122.7, 121.1 (q, *J* = 293.0 Hz), 70.1 (m), 34.0, 23.7. **HRMS** (EI): m/z calcd for $C_{13}H_{12}F_9N$: 353.0821 M^+; Found 353.0825.



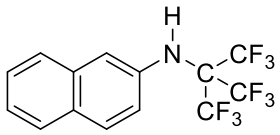
2-ethoxy-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline (10). Colorless oil, yield 61% (173 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 6.87 (t, *J* = 8.7 Hz, 2H), 5.00 (s, 1H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -73.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 150.8, 129.9, 124.6, 121.9, 121.3 (q, *J* = 293.1 Hz), 120.7, 111.3, 70.2 (m), 64.2, 14.5. **HRMS** (EI): m/z calcd for $C_{12}H_{10}F_9NO$: 355.0613 M^+; Found 355.0614.



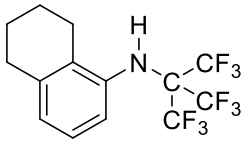
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-[1,1'-biphenyl]-4-amine (11)**. White solid, M.p.: 91-93 ºC, yield 39% (121 mg). Eluent: ethyl acetate/petroleum ether (1:99). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.04 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.6 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.1, 138.7, 138.6, 128.9, 127.7, 127.4, 127.0, 125.7, 121.2 (q, *J* = 292.0 Hz), 70.1 (m). **HRMS** (EI): m/z calcd for $C_{16}H_{10}F_9N$: 387.0664 M^+; Found 387.0671.



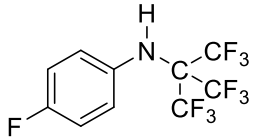
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)naphthalen-1-amine (12)**. White solid, M.p.: 120-122 ºC, yield 38% (110 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.9 Hz, 1H), 4.20 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 134.7, 134.5, 131.0, 128.7, 126.9, 126.7, 126.2, 125.4, 123.3, 121.5, 121.3 (q, *J* = 293.3 Hz), 70.6 (m). **HRMS** (EI): m/z calcd for $C_{14}H_8F_9N$: 361.0508 M^+; Found 361.0510.



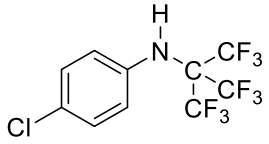
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-naphthalen-2-amine (13)**. White solid, M.p.: 54-55 ºC, yield 54% (156 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 2H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.56 - 7.50 (m, 2H), 7.32 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.22 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 136.9, 133.7, 131.4, 129.0, 127.6, 126.7, 125.8, 124.6, 122.6, 121.3 (q, *J* = 291.7 Hz), 70.2 (m). **HRMS** (EI): m/z calcd for $C_{14}H_8F_9N$: 361.0508 M^+; Found 361.0513.



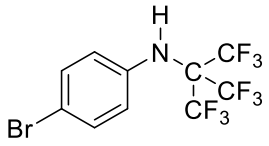
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-5,6,7,8-tetrahydronaphthalen-1-amine (14)**. Colorless oil, yield 30% (88 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.06 - 7.01 (m, 2H), 6.87 (d, *J* = 7.1 Hz, 1H), 3.81 (s, 1H), 2.77 (t, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 6.5 Hz, 2H), 1.88 - 1.83 (m, 2H), 1.78 - 1.73 (m, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.5, 138.0, 130.1, 125.8, 125.7, 121.2 (q, *J* = 293.4 Hz), 119.8 (m), 70.2 (m), 29.9, 24.3, 23.1, 22.4. **HRMS** (EI): m/z calcd for $C_{14}H_{12}F_9N$: 365.0821 M^+; Found 365.0822.



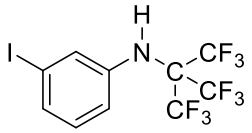
4-fluoro-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline[7] (15). Colorless oil (volatile compound). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 - 7.15 (m, 2H), 7.01 - 6.97 (m, 2H), 3.86 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.4 (s, 9F), -115.8 (s, 1F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0 (d, *J* = 246.5 Hz), 134.8 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 8.7 Hz), 121.0 (q, *J* = 291.6 Hz), 115.8 (d, *J* = 22.6 Hz), 69.9 (m). **HRMS** (EI): m/z calcd for $C_{10}H_5F_{10}N$: 329.0257 M^+; Found 329.0257.



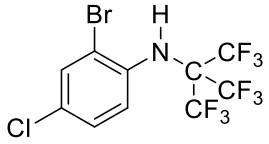
4-chloro-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline (16). Light yellow oil, yield 62% (171 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.8, 131.7, 129.2, 127.1, 121.0 (q, *J* = 293.0 Hz), 69.9 (m). **HRMS** (EI): m/z calcd for $C_{10}H_5ClF_9N$: 344.9961 M^+; Found 344.9965.



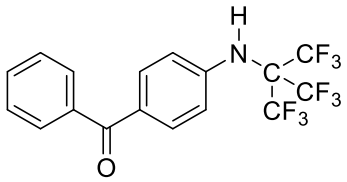
4-bromo-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline[7] **(17)**. Light yellow oil, yield 57% (178 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.7 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.4, 132.2, 127.2, 121.0 (q, *J* = 291.8 Hz), 119.4, 69.9 (m). **HRMS** (EI): m/z calcd for $C_{10}H_5BrF_9N$: 388.9456 M^+; Found 388.9461.



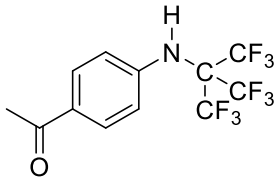
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-3-iodoaniline (18)**. Colorless oil, yield 65% (227 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 1H), 7.50 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.03 (t, *J* = 8.0 Hz, 1H), 3.97 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 140.7, 134.8, 134.1, 130.5, 124.2, 121.0 (q, *J* = 291.9 Hz), 93.8, 69.9 (m). **HRMS** (EI): m/z calcd for $C_{10}H_5F_9IN$: 436.9317 M^+; Found 436.9323.



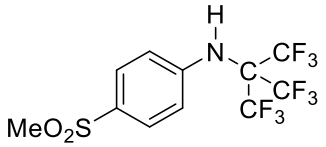
2-bromo-4-chloro-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline (19). Colorless oil, yield 75% (255 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.4 Hz, 1H), 7.23 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 4.83 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 137.0, 132.5, 129.9, 128.5, 122.5 (m), 121.0 (q, *J* = 293.3 Hz), 118.0, 70.1 (m). **HRMS** (EI): m/z calcd for $C_{10}H_4BrClF_9N$: 422.9066 M^+; Found 422.9067.



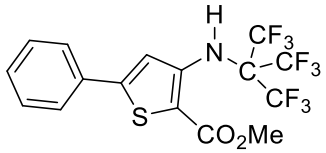
(4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)phenyl)(phenyl)methanone (20). White solid, M.p.: 81-82 ºC, yield 55% (183 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (t, *J* = 6.7 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.46 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -69.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.4, 144.0, 137.7, 133.5, 132.3, 131.6, 129.8, 128.3, 121.6, 121.0 (q, *J* = 293.4 Hz), 70.0 (m). **HRMS** (EI): m/z calcd for $C_{17}H_{10}F_9NO$: 415.0613 M^+; Found 415.0618.



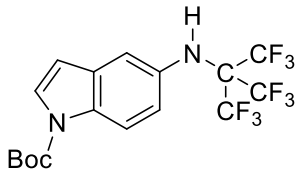
1-(4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)phenyl)ethan-1-one (21). Light yellow solid, M.p.: 66-67 ºC, yield 49% (138 mg). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H), 4.65 (s, 1H), 2.53 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.6 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 196.9, 144.6, 133.0, 129.7, 121.5, 121.0 (q, *J* = 292.1 Hz), 70.0 (m), 26.2. **HRMS** (EI): m/z calcd for $C_{12}H_8F_9NO$: 353.0457 M^+; Found 353.0460.



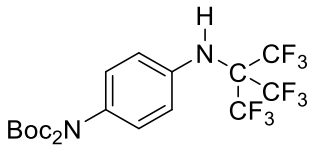
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-4-(methylsulfonyl)aniline (22)**. White solid, M.p.: 111-113 ºC, yield 49% (152 mg). Eluent: ethyl acetate/petroleum ether (25:75). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 4.67 (s, 1H), 3.03 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.3, 135.5, 128.9, 121.6, 120.9 (q, *J* = 293.6 Hz), 69.8 (m), 44.5. **HRMS** (EI): m/z calcd for $C_{11}H_8F_9NO_2S$: 389.0127 M^+; Found 389.0134.



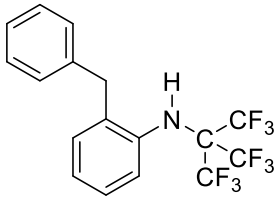
methyl 3-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)-5-phenylthiophene-2-carboxylate (23). Light yellow solid, M.p.: 95-97 ºC, yield 70% (253 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.59 (d, *J* = 6.4 Hz, 2H), 7.44 - 7.39 (m, 3H), 7.10 (s, 1H), 3.91 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 149.8, 148.8, 133.0, 129.5, 129.2, 126.1, 121.1 (q, *J* = 293.6 Hz), 115.4, 107.8, 69.5 (m), 52.0. **HRMS** (EI): m/z calcd for $C_{16}H_{10}F_9NO_2S$: 451.0283 M^+; Found 451.0286.



***tert*-butyl 5-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)-1*H*-indole-1-carboxylate (24)**. Light yellow solid, M.p.: 96-97 ºC, yield 40% (144 mg). Eluent: ethyl acetate/petroleum ether (1:99). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 3.7 Hz, 1H), 7.40 (s, 1H), 7.15 (d, *J* = 9.7 Hz, 1H), 6.53 (d, *J* = 3.7 Hz, 1H), 4.00 (s, 1H), 1.67 (s, 9H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -69.3 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.6, 133.8, 133.5, 131.0, 126.9, 123.7, 121.2 (q, *J* = 292.6 Hz), 119.3, 115.3, 107.1, 83.9, 70.2 (m), 28.1. **HRMS** (EI): m/z calcd for $C_{17}H_{15}F_9N_2O_2$: 450.0984 M^+; Found 450.0987.

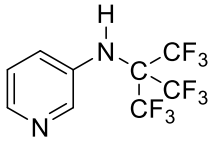


***tert*-butyl (*tert*-butoxycarbonyl)(4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)phenyl)carbamate (25)**. Light yellow oil, yield 54% (277 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.07 (s, 1H), 1.35 (s, 18H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.5, 138.4, 137.2, 128.4, 125.8, 121.0 (q, *J* = 291.7 Hz), 82.7, 70.0 (m), 27.7. **HRMS** (EI): m/z calcd for $C_{20}H_{23}F_9N_2O_4$: 526.1509 M^+; Found 526.1523.

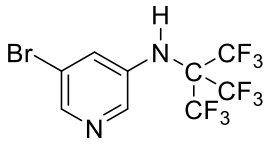


2-benzyl-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline (26). Colorless oil, yield 74% (237 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 - 7.43 (m, 3H), 7.41 - 7.36 (m, 3H), 7.31 - 7.27 (m, 3H), 4.21 (s, 2H), 3.96 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.8 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.6, 138.5, 134.6, 131.6,

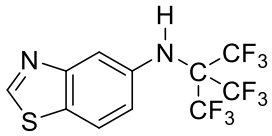
129.0, 128.3, 127.8, 126.9, 125.1, 124.2 (m), 121.3 (q, *J* = 292.0 Hz), 70.3 (m), 38.5. **HRMS** (EI): m/z calcd for $C_{17}H_{12}F_9N$: 401.0821 M^+; Found 401.0825.



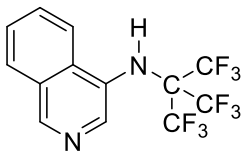
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)pyridin-3-amine (27)**. Violet solid, M.p.: 55-56 ºC, yield 31% (77 mg, 2 steps). Eluent: ethyl acetate/petroleum ether (20:80). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.9 Hz, 1H), 8.37 (d, *J* = 3.3 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.22 (q, *J* = 4.4 Hz, 1H), 4.67 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.6 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.3, 146.7, 136.3, 133.0, 123.5, 120.9 (q, *J* = 293.0 Hz), 69.8 (m). **HRMS** (EI): m/z calcd for $C_9H_5F_9N_2$: 312.0304 M^+; Found 312.0303.



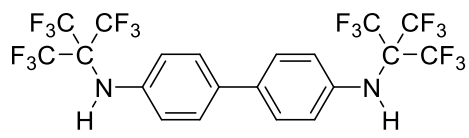
5-bromo-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)pyridin-3-amine (28). White solid, M.p.: 84-85 ºC, yield 35% (109 mg, 2 steps). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.34 (s, 1H), 7.66 (s, 1H), 4.48 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.6 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.7, 144.7, 137.0, 135.0, 120.8 (q, *J* = 293.0 Hz), 120.2, 69.7 (m). **HRMS** (EI): m/z calcd for $C_9H_4BrF_9N_2$: 389.9409 M^+; Found 389.9417.



***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)benzo[*d*]thiazol-5-amine (29)**. Light yellow solid, M.p.: 119-121 ºC, yield 28% (82 mg, 2 steps). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (s, 1H), 7.95 (d, *J* = 2.3 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.27 (dd, *J* = 8.5, 2.3 Hz, 1H), 4.31 (s, 1H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.3 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.4, 153.9, 137.9, 131.3, 124.4, 121.9, 121.1 (q, *J* = 293.0 Hz), 120.6, 70.1 (m). **HRMS** (EI): m/z calcd for $C_{11}H_5F_9N_2S$: 368.0024 M^+; Found 368.0030.

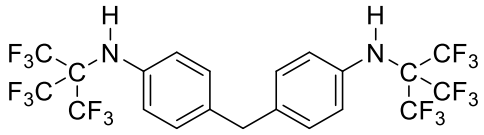


***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)isoquinolin-4-amine (30)**. Light yellow solid, M.p.: 130-132 ºC, yield 25% (72 mg, 2 steps). Eluent: ethyl acetate/petroleum ether (20:80). **^{1}H NMR** (500 MHz, MeOD) δ 9.15 (s, 1H), 8.44 (s, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.89 - 7.85 (m, 1H), 7.74 - 7.71 (m, 1H). **^{19}F NMR** (470 MHz, MeOD) δ -69.9 (s, 9F). **^{13}C NMR** (126 MHz, MeOD) δ 150.7, 141.0 (q, *J* = 2.2 Hz), 135.9, 131.6, 131.1, 129.3, 127.8, 127.7, 122.2, 121.4 (q, *J* = 291.3 Hz), 70.4 (m). **HRMS** (EI): m/z calcd for $C_{13}H_7F_9N_2$: 362.0460 M^+; Found 362.0468.

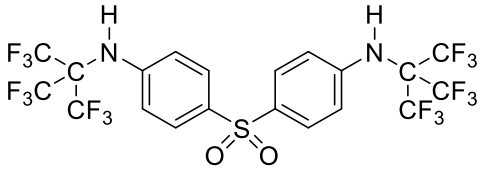


***N*^{4},*N*$^{4'}$-bis(1,1,1,3,3,3-hexafluoro-2-(trifleoroomethyl)propan-2-yl)-[1,1'-biphenyl]-4,4'-diamine (31)**. White solid, M.p.: 95-97 ºC, yield 20% (99 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.6 Hz, 4H),

7.20 (d, J = 8.3 Hz, 4H), 4.02 (s, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -69.2 (s, 18F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.7, 137.5, 127.5, 125.7, 121.1 (q, J = 293.1 Hz), 70.1 (m). **HRMS** (EI): m/z calcd for $C_{20}H_{10}F_{18}N_2$: 620.0551 M^+; Found 620.0558.



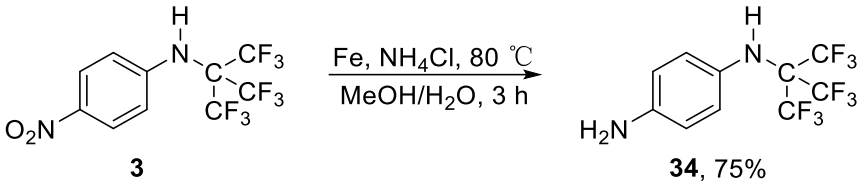
4,4'-methylenebis(*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline) (32). Colorless oil, yield 15% (76 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.07 (s, 8H), 3.93 (s, 2H), 3.90 (s, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.7 (s, 18F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 138.5, 137.4, 129.5, 125.9, 121.1 (q, J = 291.6 Hz), 70.1 (m), 40.5. **HRMS** (EI): m/z calcd for $C_{21}H_{12}F_{18}N_2$: 634.0708 M^+; Found 634.0713.



4,4'-sulfonylbis(*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)aniline) (33). White solid, M.p.: 151-153 ºC, yield 27% (148 mg). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, CD_3CN) δ 7.75 (d, J = 8.9 Hz, 4H), 7.20 (d, J = 8.5 Hz, 4H), 5.48 (s, 2H). **^{19}F NMR** (470 MHz, CD_3CN) δ -69.0 (s, 18F). **^{13}C NMR** (126 MHz, CD_3CN) δ 145.9, 137.2, 129.3, 123.0, 121.7 (q, J = 291.9 Hz), 70.6 (m). **HRMS** (EI): m/z calcd for $C_{20}H_{10}F_{18}N_2O_2S$: 684.0170 M^+; Found 684.0172.

6. Derivative reactions

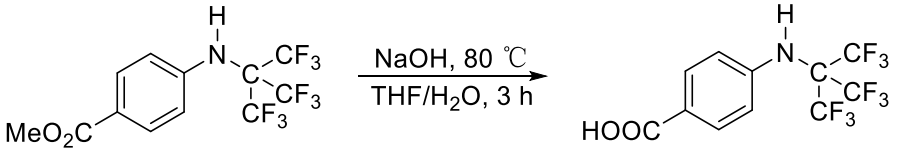
Transformation of 34:



3 **34**, 75%

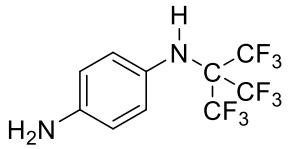
Ferrous powder (7.5 mmol, 5.0 equiv.) was added into the mixture of **3** (1.5 mmol, l.0 equiv.) and ammonium chloride (15.0 mmol, 10.0 equiv.) in 10.0 mL MeOH/H_2O (1: l). The reaction mixture was stirred at 80 ℃ for 3 h, and then cooled to room temperature. The mixture was filtered, the filtrate was collected. After removal of MeOH under reduced pressure, the resulting aqueous fraction was adjusted to pH 4 with 2M HCl and then extracted with ethyl acetate. The organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4. After concentrated under reduced pressure, the crude residue was purified by flash column chromatography on silica gel.

Transformation of 35:



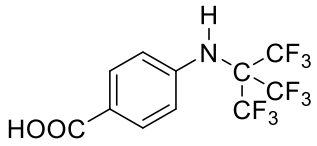
4 **35**, 90%

Compound **4** (1.5 mmol, l.0 equiv.), NaOH (3.0 mmol, 2.0 equiv.) were dissolved in 10.0 mL THF/H_2O (4: l). The reaction mixture was stirred at 80 ℃ for 3 h, and then cooled to room temperature. The reaction mixture diluted with EtOAc (100 mL) and was washed with 0.5M HCl (100 mL). The organic layer was separated, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.



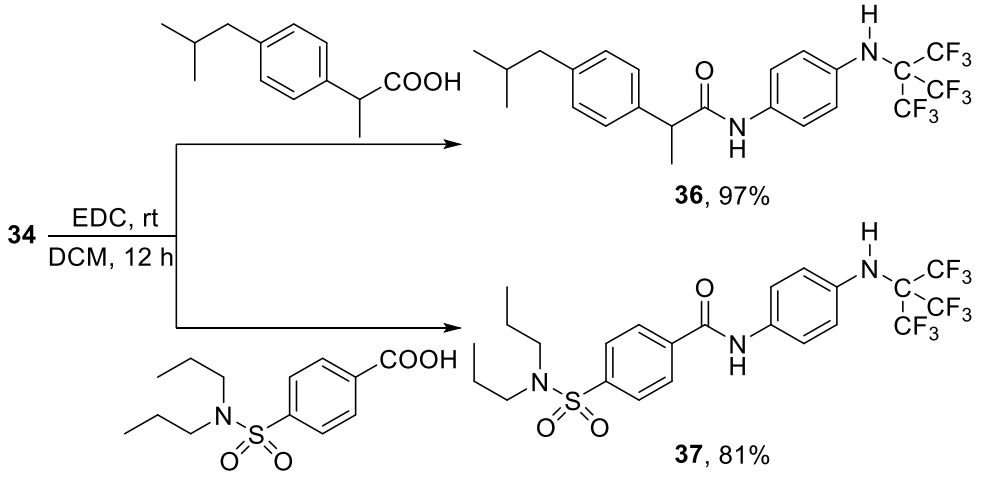
***N*^{1}-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)benzene-1,4-diamine (34)**. White solid, M.p.: 41-42 ºC, yield 75% (367 mg). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 1H), 3.62 (s, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.7 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.1, 129.5, 129.1, 121.2 (q, *J* = 293.1

Hz), 115.1, 70.0 (m). **HRMS** (EI): m/z calcd for $C_{10}H_7F_9N_2$: 326.0460 M^+; Found 326.0462.



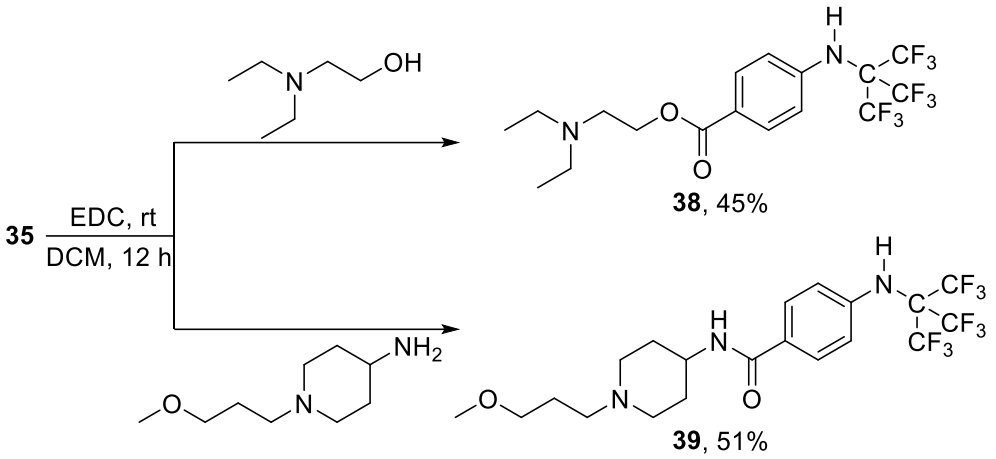
4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)benzoic acid (35). White solid, M.p.: 163-165 ºC, yield 90% (479 mg). Eluent: ethyl acetate/petroleum ether (90:10). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.79 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 1H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -67.3 (s, 9F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 167.3, 145.2, 130.7, 126.7, 123.5, 121.4 (q, *J* = 295.0 Hz), 70.3 (m). **HRMS** (EI): m/z calcd for $C_{11}H_6F_9NO_2$: 355.0249 M^+; Found 355.0244.

Synthesis of 36, 37:

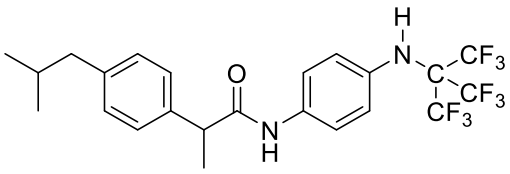


Compound **34** (0.5 mmol, l.0 equiv.) was added into the mixture of acid (1.0 mmol, 2.0 equiv.), EDC (0.75 mmol, l.5 equiv.) and DMAP (0.05 mmol, 0.1 equiv.) in 2.0 mL DCM. The reaction was stirred at room temperature for 12 h. Upon completion, the solution was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.

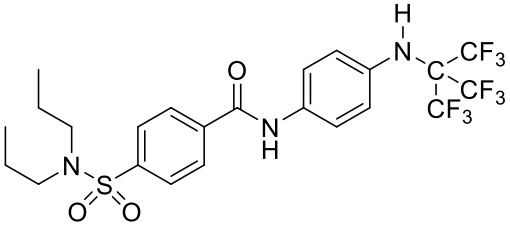
Synthesis of 38, 39:



Alcohol or amine (0.75 mmol, 1.5 equiv.) was added into the mixture of compound **35** (0.5 mmol, l.0 equiv.), EDC (0.75 mmol, l.5 equiv.) and DMAP (0.05 mmol, 0.1 equiv.) in 2.0 mL DCM. The reaction was stirred at room temperature for 12 h. Upon completion, the solution was evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.

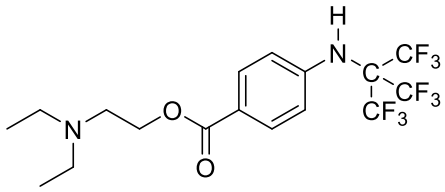


***N*-(4-((1,1,1,3,3,3-hexafluoro-2-(trifluoro-methyl)propan-2-yl)amino)phenyl)-2-(4-isobutylphenyl)propanamide (36)**. Colorless wax, yield 97% (249 mg). Eluent: ethyl acetate/petroleum ether (10:90). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 4.00 (s, 1H), 3.76 (q, *J* = 7.1 Hz, 1H), 2.50 (d, *J* = 7.2 Hz, 2H), 1.94 - 1.85 (m, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.3, 140.0, 137.0, 135.2, 134.0, 128.7, 126.3, 126.0, 120.1 (q, *J* = 291.0 Hz), 119.4, 68.9 (m), 46.4, 44.0, 29.2, 21.3, 17.4. **HRMS** (EI): m/z calcd for $C_{23}H_{23}F_9N_2O$: 514.1661 M^+; Found 514.1665.

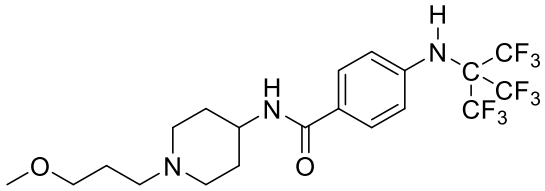


4-(*N*,*N*-dipropylsulfamoyl)-*N*-(4-((1,1,1,3,3,3-hexafluoro-2-(trifleorometh-yl)propan-2-yl)amino)phenyl)benza-mide (37). White solid, M.p.: 222-224 ºC, yield 81% (240 mg). Eluent: ethyl acetate/petroleum ether (20:80). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.50 (s, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 9.0 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.53 (s, 1H), 3.07 (t, *J* = 7.6 Hz, 4H), 1.53 - 1.46 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -67.5 (s, 9F). **^{13}C NMR**

(126 MHz, DMSO-d_6) δ 164.8, 142.4, 138.9, 137.1, 135.7, 129.1, 128.3, 127.3, 121.5 (q, *J* = 293.1 Hz), 121.0, 70.5 (m), 50.2, 22.1, 11.4. **HRMS** (EI): m/z calcd for $C_{23}H_{24}F_9N_3O_3S$: 593.1389 M^+; Found 593.1389.

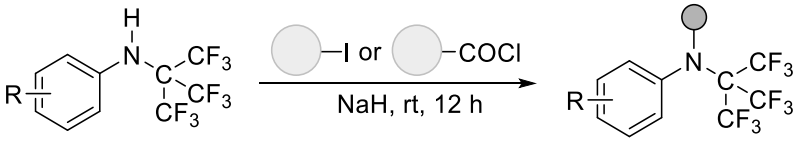


2-(diethylamino)ethyl 4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)benzoate (38). Colorless oil, yield 45% (102 mg). Eluent: ethyl acetate/petroleum ether (30:70). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 8.6 Hz, 2H), 4.40 (s, 1H), 4.34 (t, *J* = 6.3 Hz, 2H), 2.81 (t, *J* = 6.3 Hz, 2H), 2.60 (q, *J* = 7.2 Hz, 4H), 1.04 (t, *J* = 7.2 Hz, 6H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -68.5 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 144.2, 130.9, 126.4, 121.9, 121.0 (q, *J* = 291.9 Hz), 69.9 (m), 63.4, 51.0, 47.8, 12.0. **HRMS** (EI): m/z calcd for $C_{17}H_{19}F_9N_2O_2$: 454.1297 M^+; Found 454.1292.

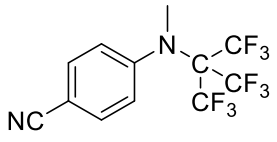


4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)-*N*-(1-(3-methoxypropyl)piperidin-4-yl)benzamilde (39). White solid, M.p.: 158-160 ºC, yield 51% (130 mg). Eluent: methanol/dichloromethane (10:90). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.34 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 3.84 - 3.79 (m, 1H), 3.33 (t, *J* = 6.3 Hz, 2H), 3.21 (s, 3H), 2.99 (d, *J* = 9.1 Hz, 2H), 2.48 (s, 2H), 2.21 (s, 2H), 1.82 - 1.66 (m, 6H). **^{19}F NMR** (470 MHz, DMSO-d_6) δ -67.5 (s, 9F). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.5, 143.3, 131.1, 128.5, 124.4, 121.4 (q, *J* = 294.0 Hz), 70.4, 70.4 (m), 58.2, 54.9, 52.3, 46.8, 31.1, 26.5. **HRMS** (EI): m/z calcd for $C_{20}H_{24}F_9N_3O_2$: 509.1719 M^+; Found 509.1719.

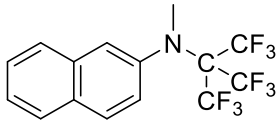
Alkylation and acylation of the N-H bonds in *N*-PFtB secondary amines:



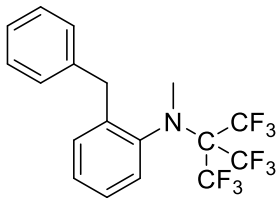
Iodide or acyl chloride (1.5 mmol, 5.0 equiv.) was added into the mixture of *N*-perfluoro-*tert*-butyl secondary amine (0.3 mmol, 1.0 equiv.) and NaH (3.0 mmol, 10.0 equiv.; 40% oil dispersion, washed with Et_2O to remove mineral oil) in 1.5 mL dry THF. The reaction was stirred at room temperature for 12 h. Upon completion, the crude mixture was filtered and evaporated under reduced pressure. The crude residue was purified by column chromatography on silica gel.



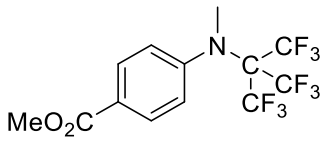
4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-(methyl)amino)benzonitrile (40). White solid, M.p.: 31-32 ºC, yield 89% (93 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 3.04 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.1 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 133.4, 131.3, 121.3 (q, *J* = 296.0 Hz), 118.0, 111.9, 73.6 (m), 42.9 (m). **HRMS** (EI): m/z calcd for $C_{12}H_7F_9N_2$: 350.0460 M^+; Found 350.0462.



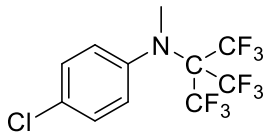
***N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-*N*-methylnaphthalen-2-amine (41)**. Colorless oil, yield 93% (105 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 - 7.81 (m, 4H), 7.53 - 7.49 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 1H), 3.14 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.0 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.9, 133.7, 132.4, 129.1, 128.9, 128.1, 128.0, 127.5, 126.6, 126.3, 121.7 (q, *J* = 296.5 Hz), 74.0 (m), 43.2 (m). **HRMS** (EI): m/z calcd for $C_{15}H_{10}F_9N$: 375.0664 M^+; Found 375.0665.



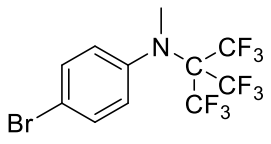
2-benzyl-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-*N*-methylaniline (42). Colorless oil, yield 95% (118 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (t, *J* = 4.5 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 - 7.35 (m, 5H), 7.34 - 7.31 (m, 1H), 4.43 (d, *J* = 15.7 Hz, 1H), 4.16 (d, *J* = 15.7 Hz, 1H), 2.96 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.8, 141.5, 140.6, 131.2, 129.4, 129.4, 128.6, 128.0, 127.4, 126.2, 121.8 (q, *J* = 296.4 Hz), 74.7 (m), 42.6 (m), 36.9. **HRMS** (EI): m/z calcd for $C_{18}H_{14}F_9N$: 415.0977 M^+; Found 415.0973.



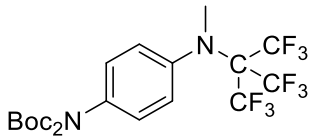
methyl 4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-propan-2-yl)(methyl)amino)benzoate (43). Colorless oil, yield 61% (70 mg). Eluent: ethyl acetate/petroleum ether (1:99). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 3.92 (s, 3H), 3.05 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.1 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 151.7, 130.7, 130.2, 129.5, 121.5 (q, *J* = 295.8 Hz), 73.7 (m), 52.1, 42.9 (m). **HRMS** (EI): m/z calcd for $C_{13}H_{10}F_9NO_2$: 383.0562 M^+; Found 383.0566.



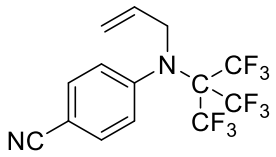
4-chloro-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-*N*-methylaniline (44). Colorless oil, yield 90% (97 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 3.08 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.0, 133.6, 131.6, 129.5, 121.5 (q, *J* = 296.4 Hz), 73.7 (m), 43.1 (m). **HRMS** (EI): m/z calcd for $C_{11}H_7ClF_9N$: 359.0118 M^+; Found 359.0121.



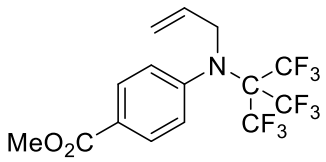
4-bromo-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)-*N*-methylaniline (45). Colorless oil, yield 85% (103 mg). Eluent: petroleum ether. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.03 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.4 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.6, 132.5, 131.9, 121.6, 121.5 (q, *J* = 294.6 Hz), 73.6 (m), 43.1 (m). **HRMS** (EI): m/z calcd for $C_{11}H_7BrF_9N$: 402.9613 M^+; Found 402.9614.



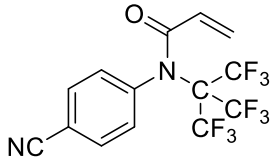
***tert*-butyl (*tert*-butoxycarbonyl)(4-((1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)(methyl)amino)phenyl)carbamate (46)**. White solid, M.p.: 99-100 ºC, yield 66% (107 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 3.03 (s, 3H), 1.38 (s, 18H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.1 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.4, 146.4, 138.9, 130.4, 128.7, 121.5 (q, *J* = 294.4 Hz), 82.8, 73.9 (m), 43.0(m), 27.8. **HRMS** (EI): m/z calcd for $C_{21}H_{25}F_9N_2O_4$: 540.1665 M^+; Found 540.1669.



4-(allyl(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)benzonitrile (47). Colorless oil, yield 50% (57 mg). Eluent: ethyl acetate/petroleum ether (2:98). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 5.67 - 5.59 (m, 1H), 4.92 (d, *J* = 10.1 Hz, 1H), 4.74 (d, *J* = 17.1 Hz, 1H), 3.92 (d, *J* = 6.8 Hz, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.0 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.0, 133.2, 133.0, 132.8, 121.3 (q, *J* = 295.5 Hz), 119.3, 118.1, 112.1, 74.1 (m), 57.0 (m). **HRMS** (EI): m/z calcd for $C_{14}H_9F_9N_2$: 376.0617 M^+; Found 376.0619.



methyl 4-(allyl(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)amino)benzoate (48). Colorless oil, yield 70% (86 mg). Eluent: ethyl acetate/petroleum ether (1:99). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.68 - 5.60 (m, 1H), 4.86 (d, *J* = 10.1 Hz, 1H), 4.72 (d, *J* = 17.6 Hz, 1H), 3.92 (d, *J* = 6.8 Hz, 2H), 3.89 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -65.1 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.3, 148.1, 133.4, 132.1, 130.1, 129.7, 121.4 (q, *J* = 295.7 Hz), 118.6, 74.2 (m), 56.9 (m), 52.06. **HRMS** (EI): m/z calcd for $C_{15}H_{12}F_9NO_2$: 409.0719 M^+; Found 409.0723.

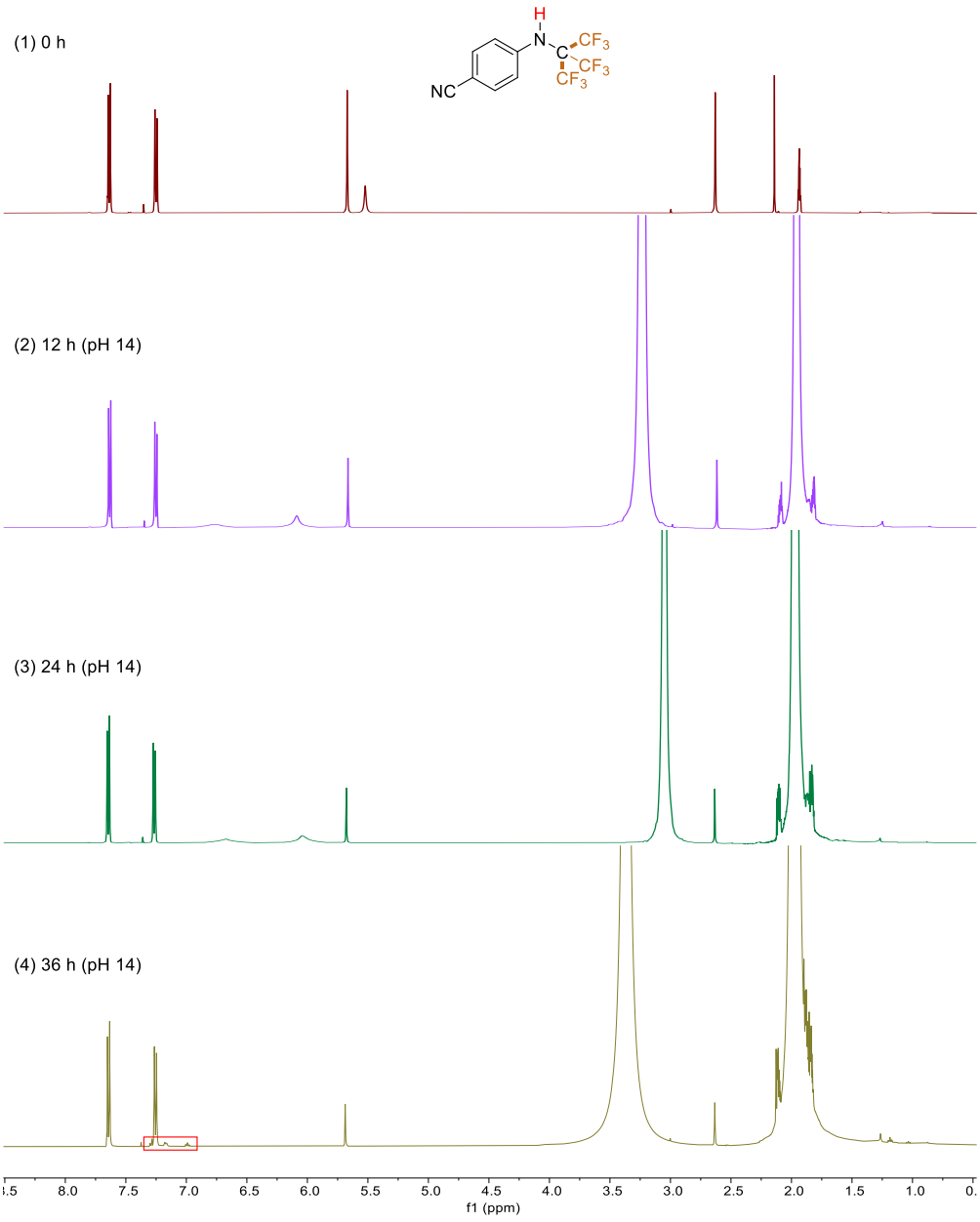


***N*-(4-cyanophenyl)-*N*-(1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)propan-2-yl)acrylamide (49)**. White solid, M.p.: 133-135 ºC, yield 51% (60 mg). Eluent: ethyl acetate/petroleum ether (3:97). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.2 Hz, 2H), 6.40 - 6.33 (m, 1H), 5.57 - 5.50 (m, 2H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -61.9 (s, 9F). **^{13}C NMR** (126 MHz, $CDCl_3$) δ

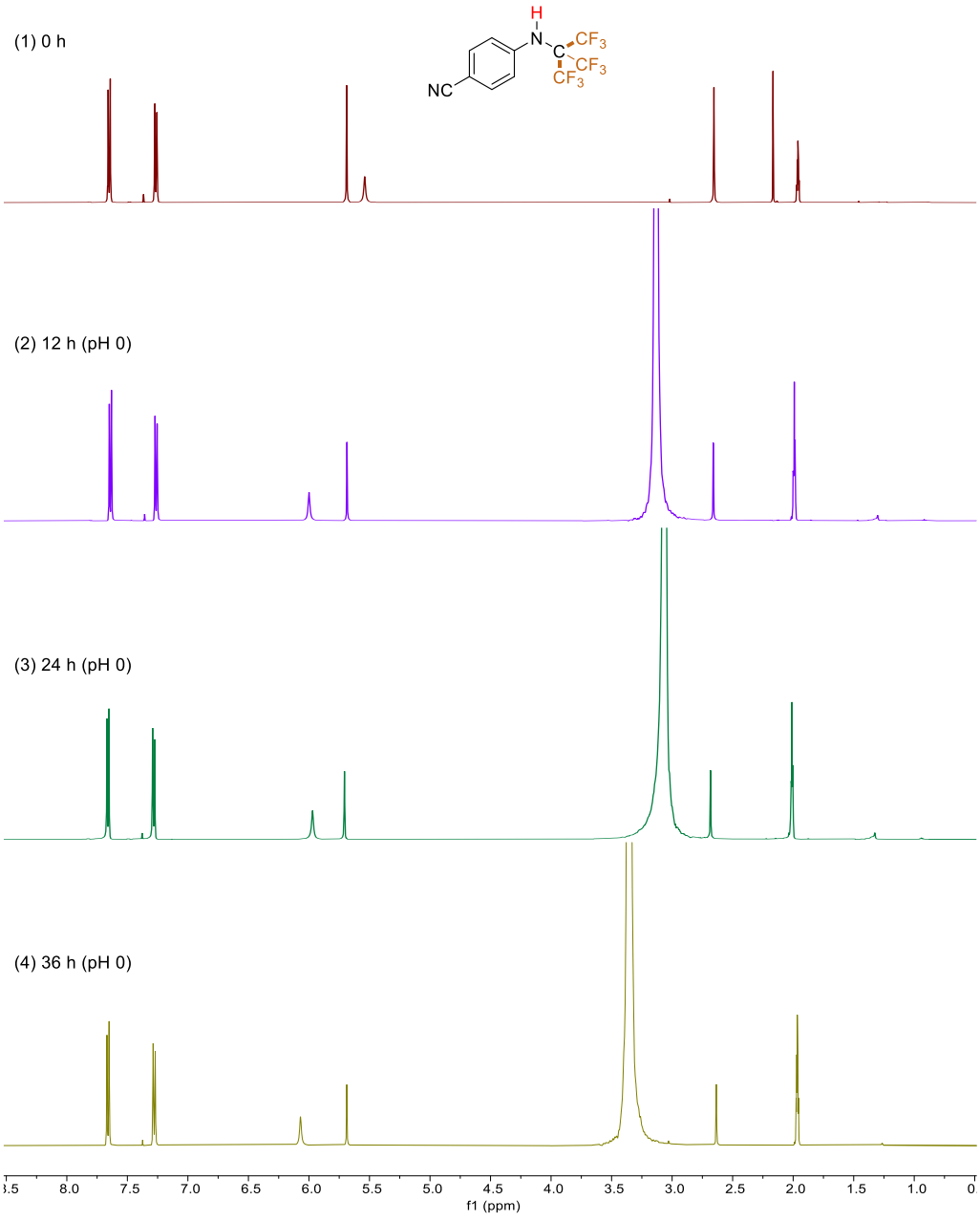
166.2, 142.5, 133.5, 132.9, 131.6, 128.0, 120.7 (q, J = 295.3 Hz), 117.2, 114.7, 74.6 (m). **HRMS** (EI): m/z calcd for $C_{14}H_7F_9N_2O$: 390.0409 M^+; Found 390.0402.

7. Stability study of compound 1

To a solution of the studied compound (0.035 mmol) in MeCN-d_3 (0.75 mL) was added 0.25 mL of either aqueous HCl or NaOH (respective pH 0 and 14). Cyclohexadiene (1~2 µL) was added as an internal standard. The reactions were stirred at room temperature. The solution was filtered through magnesium sulphate. The mixtures were analyzed by ^{1}H NMR.



Supplementary Figure S10. ^{1}H NMR stacked spectra of stability test of compound 1 in aqueous NaOH.



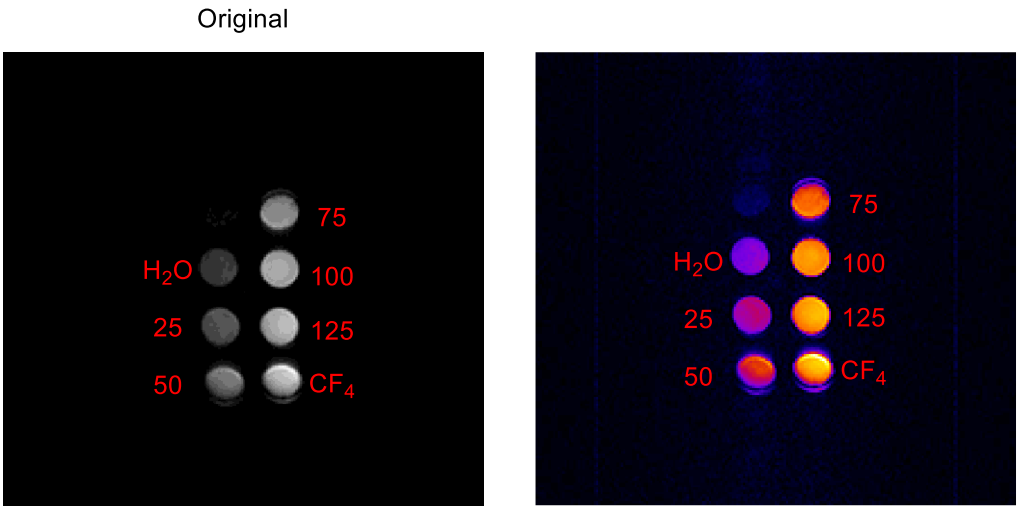
Supplementary Figure S11. ^{1}H NMR stacked spectra of stability test of compound 1 in aqueous HCl.

8. ^{19}F MRI Experiment

Five different concentrations of compound **36** (25, 50, 75, 100, 125 mM in MeCN) were compared with the negative control (H_2O) and the positive control (CF_4, 15mg/mL). The data were recorded on a Bruker 9.4 T BioSpec 94/30 MRI & PET Insert.

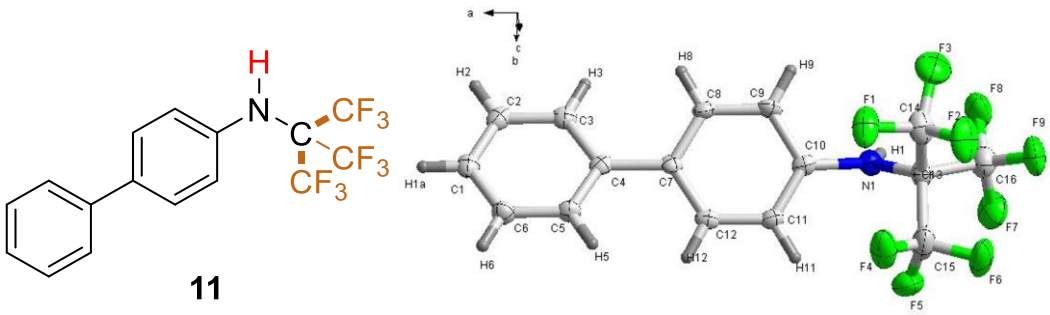
Supplementary Table S1. Experimental data of ^{19}F MRI.

Concentration (mM)	Values		
25	81.3	82.4	76.4
50	57.4	59.2	58.4
75	36.1	36.5	37.4
100	26.0	26.1	27.2
125	11.3	13.5	11.8



Supplementary Figure S12. ^{19}F MR imaging of compound 36.

9. Crystallographic data for compound 11



Compound	**11**
Formula	$C_{32}H_{20}F_{18}N_2$
Formula weight	774.50
Crystal system	$Pca2_1$
space group	Orthorhombic
a (Å)	37.282(2)
b (Å)	7.7234(5)
c (Å)	10.7769(6)
α (º)	90
β (º)	90
γ (º)	90
Volume(Å^3)	3103.1(3)
Z	4
T (K)	193.15
D_{calcd} (g•cm^{-3})	1.658
F(000)	1552
Reflections collected	18441
Unique reflections	5369
Goof	1.088
R_1[a][I> 2σ(I)]	0.0721
wR_2[b][I>2σ(I)]	0.1499
CCDC NO.	2256453

10. References

(1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 16, Revision A.01; Gaussian, Inc.: Wallingford, CT, 2016.

(2) Vetere, V.; Adamo, C.; Maldivi, P. Performance of the 'Parameter Free' PBE0 Functional for the Modeling of Molecular Properties of Heavy Metals. *Chem. Phys. Lett.* **2000**, *325* (1-3), 99-105.

(3) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurateab Initioparametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104.

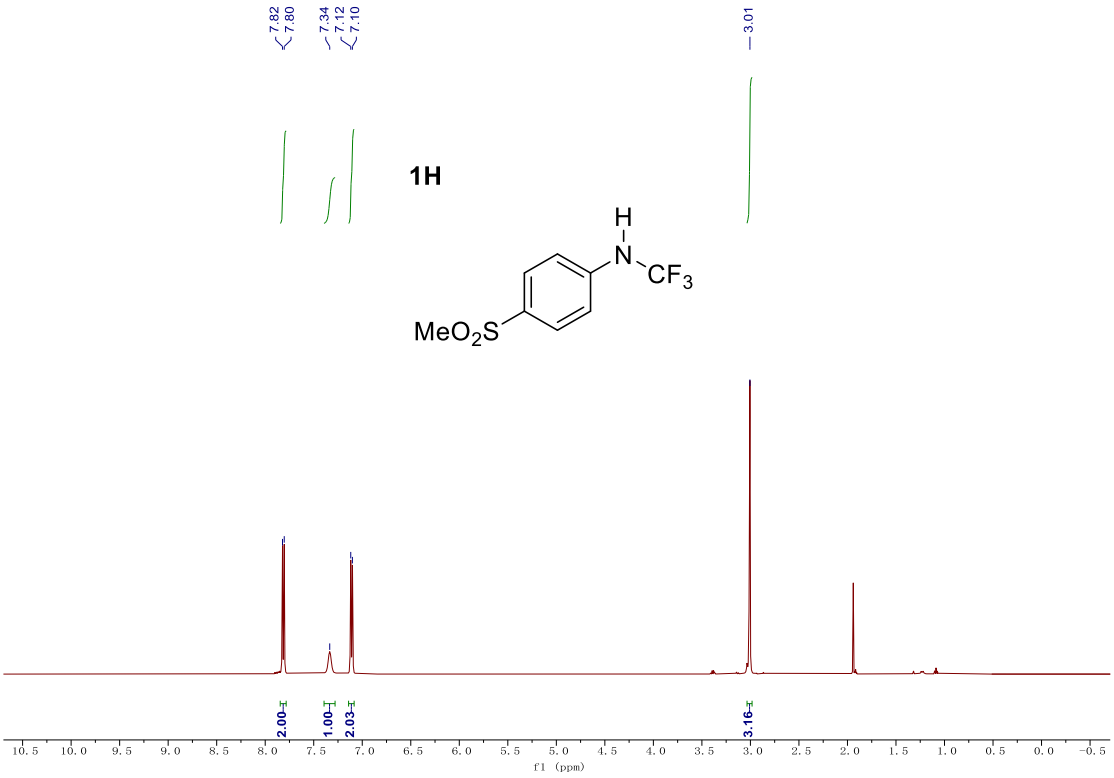
(4) Weigend, F.; Ahlrichs, R. Balanced Basis Sets of Split Valence, Triple Zeta Valence and Quadruple Zeta Valence Quality for H to Rn: Design and Assessment of Accuracy. *Phys Chem Chem Phys.* **2005**, *7* (18), 3297-3305.

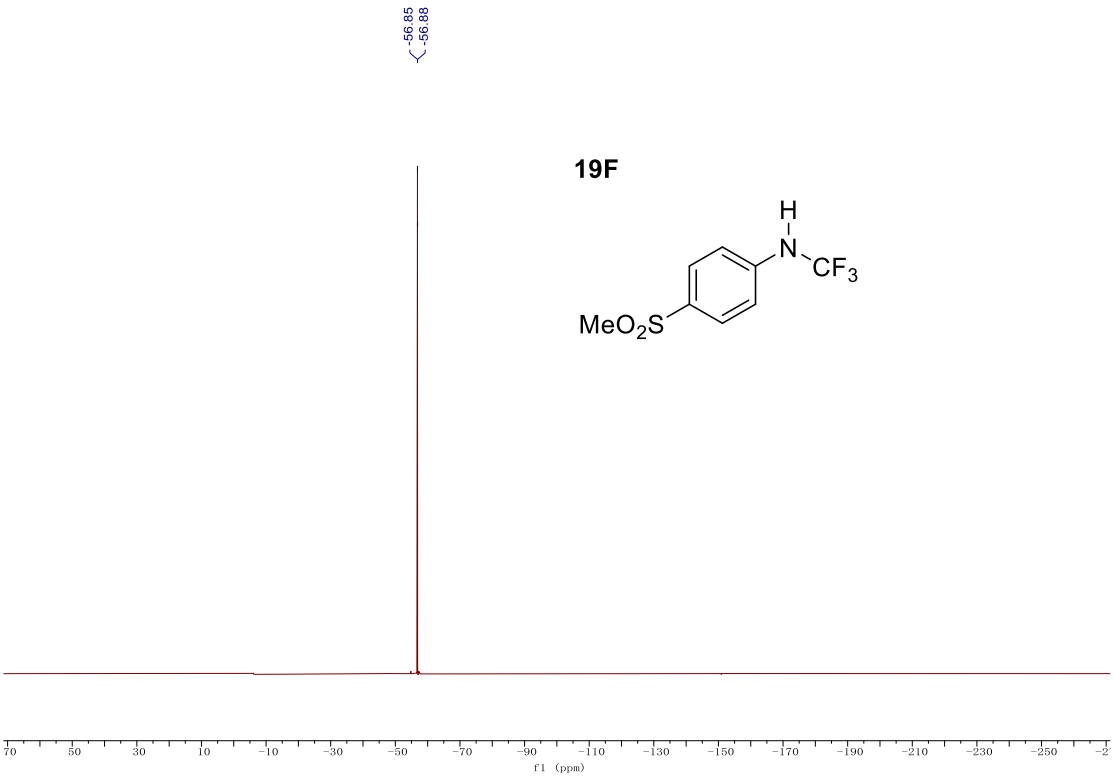
(5) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B.* **2009**, *113* (18), 6378-6396.

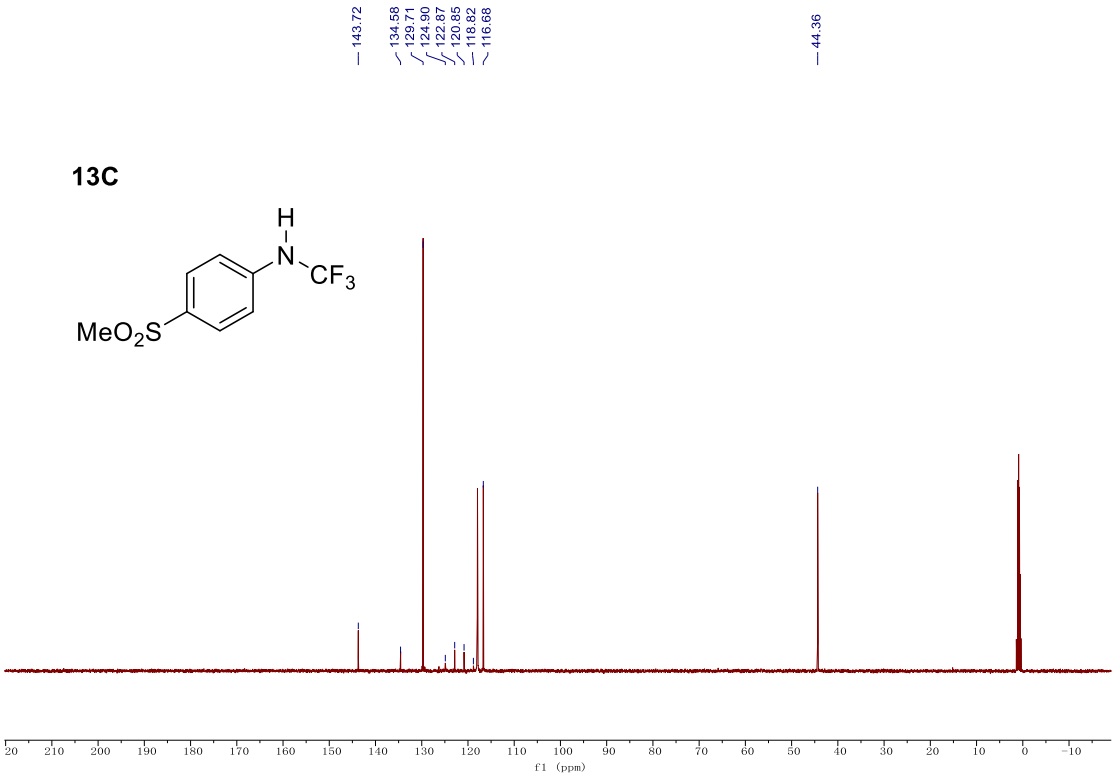
(6) Wang, L.; Wang, J.; Ye, S.; Jiang, B.; Guo, Z.; Mumtaz, Y.; Yi, W. General Access to *N*−CF_3 Secondary Amines and Their Transformation to *N*−CF_3 Sulfonamides. *Angew. Chem., Int. Ed.* **2022**, *61* (49), e202212115.

(7) Petrov, V. A. Reaction of Polyfluorinated Imines with Trifluoromethyltrimethylsilane. Direct Synthesis of *N*-(perfluoro-*t*-butyl)amines. *Tetrahedron Lett.* **2000**, *41* (36), 6959-6963.

11. NMR Spectra



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134.58
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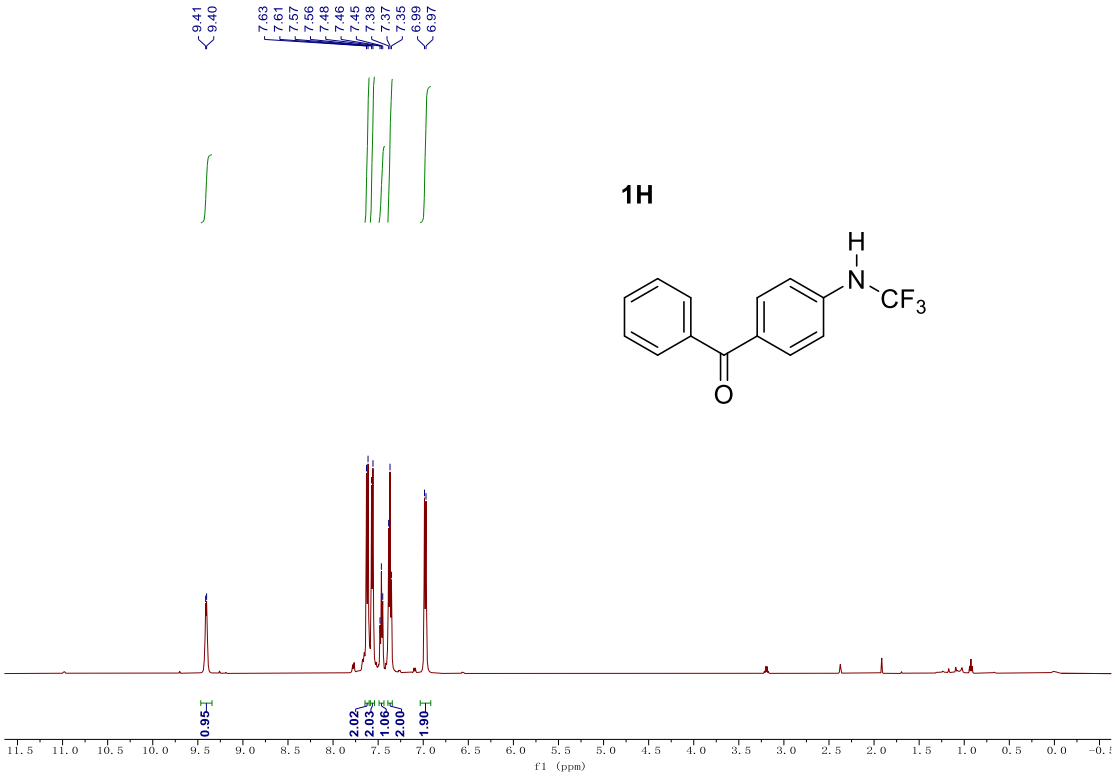
124.90
122.87
120.85
118.82
116.68
44.36
13C
H
N
CF3
MeO2S
f1 (ppm)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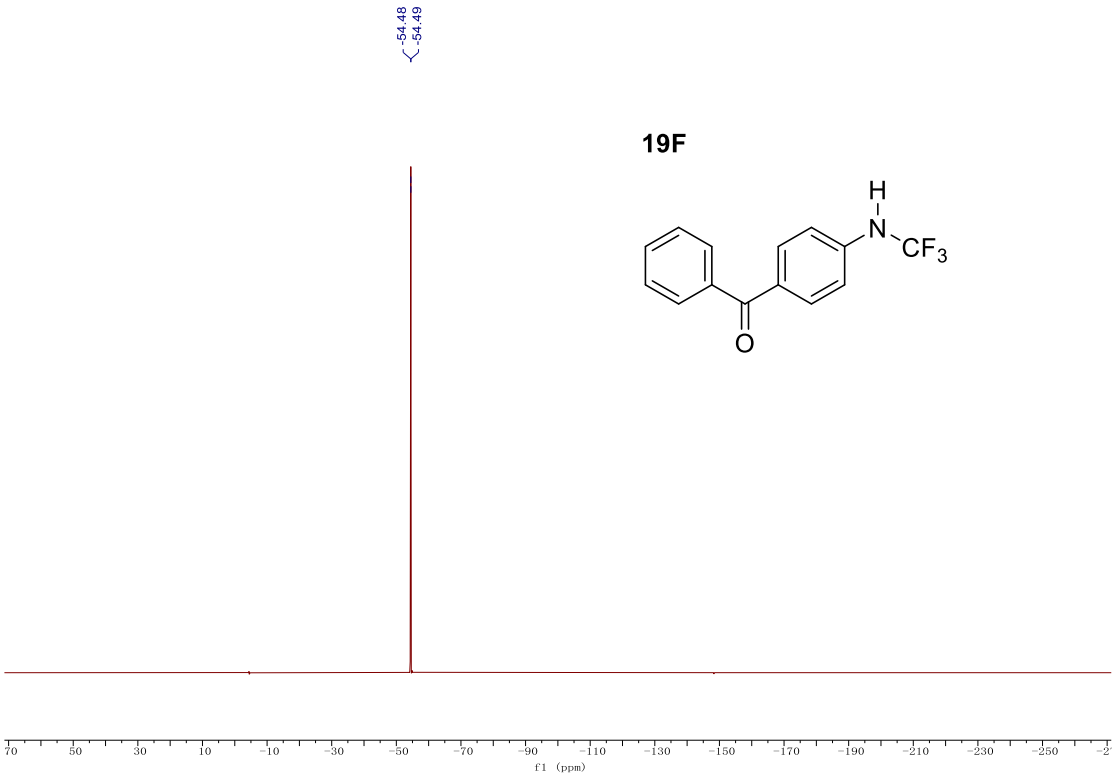
9.40
7.63
7.61
7.57
7.56
7.48
7.46
7.45
7.38
7.37
7.35
6.99
6.97
1H
H
N
CF3
O
0.95
2.02
2.03
1.06
2.00
1.90
f1 (ppm)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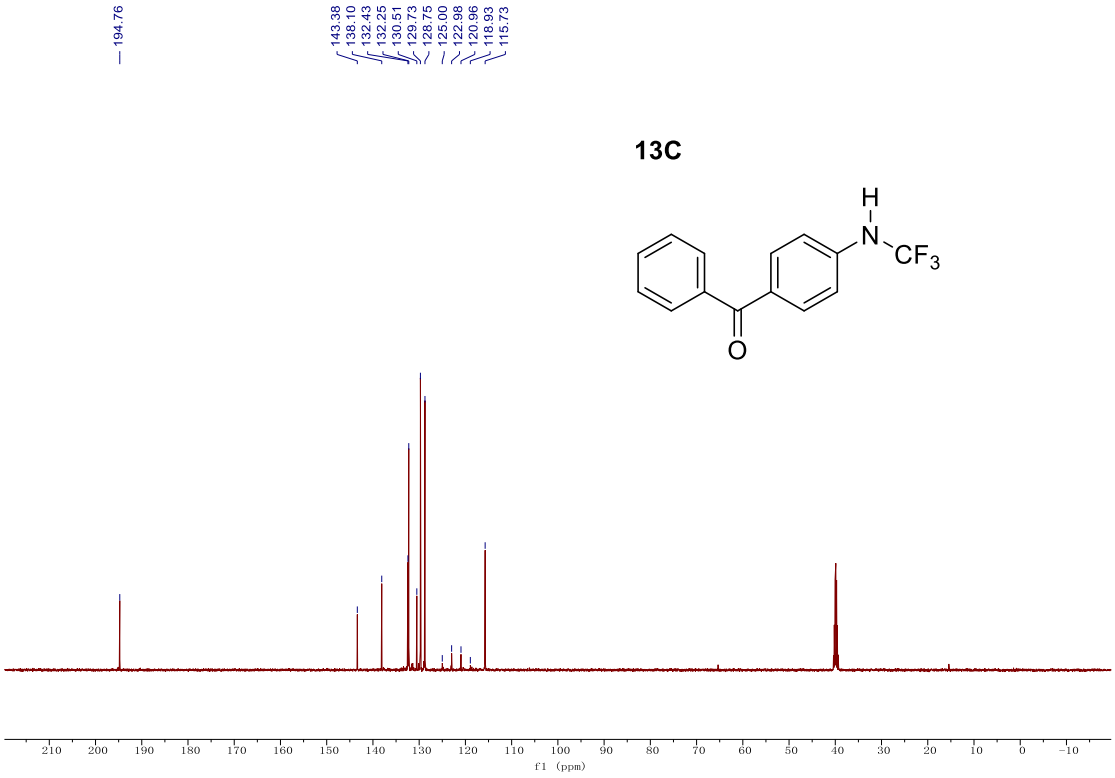
-54.49
19F
H
N
CF3
O
70 50 30 10 −10 −30 −50 −70 −90 −110 −130 −150 −170 −190 −210 −230 −250
f1 (ppm)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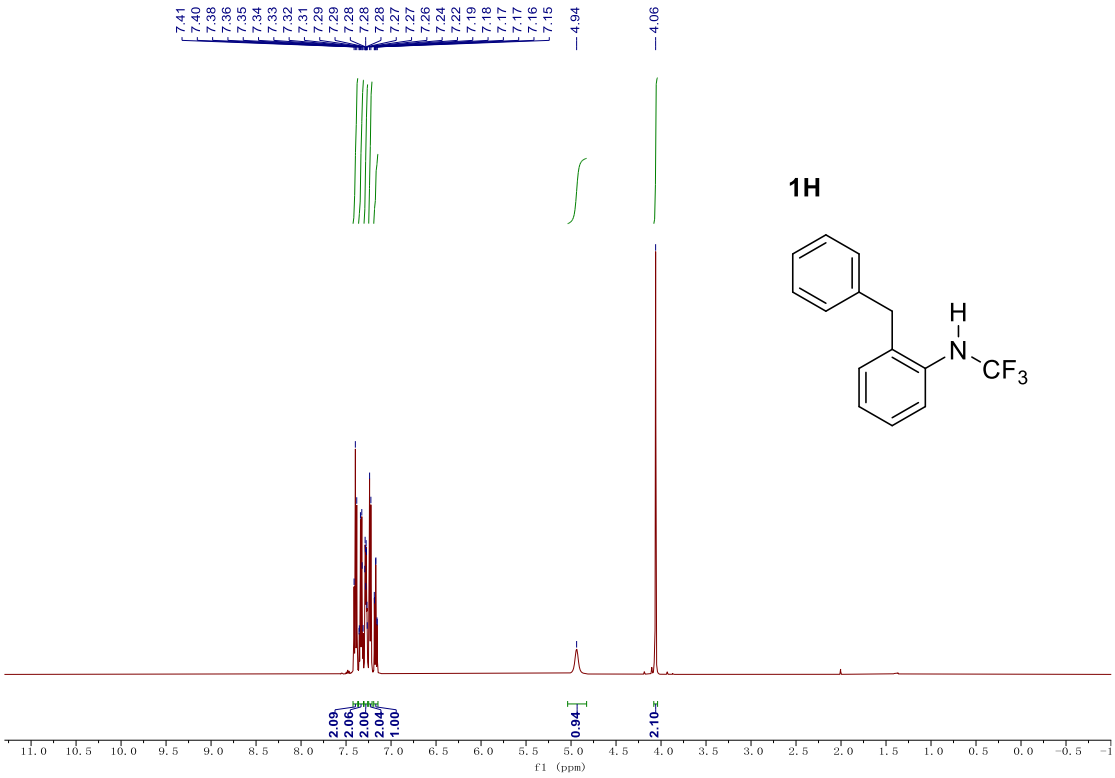
143.38
138.10
132.43
132.25
130.51
129.73
128.75
125.00
122.98
120.96
118.93
115.73
13C
H
N
CF3
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)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7.32
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7.29
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7.28
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7.28
7.27
7.27
7.26
7.24
7.22
7.19
7.18
7.17
7.17
7.16
7.15
4.94
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N
CF3
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2.06
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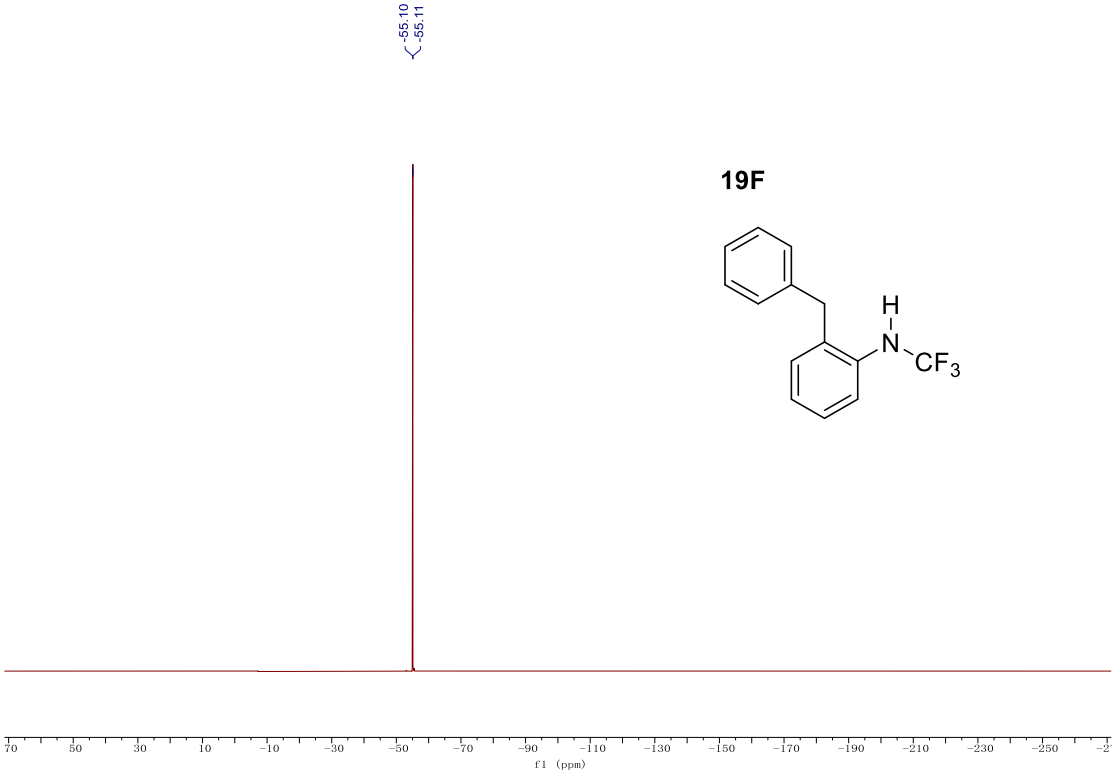
1.00
0.94
2.10
f1 (ppm)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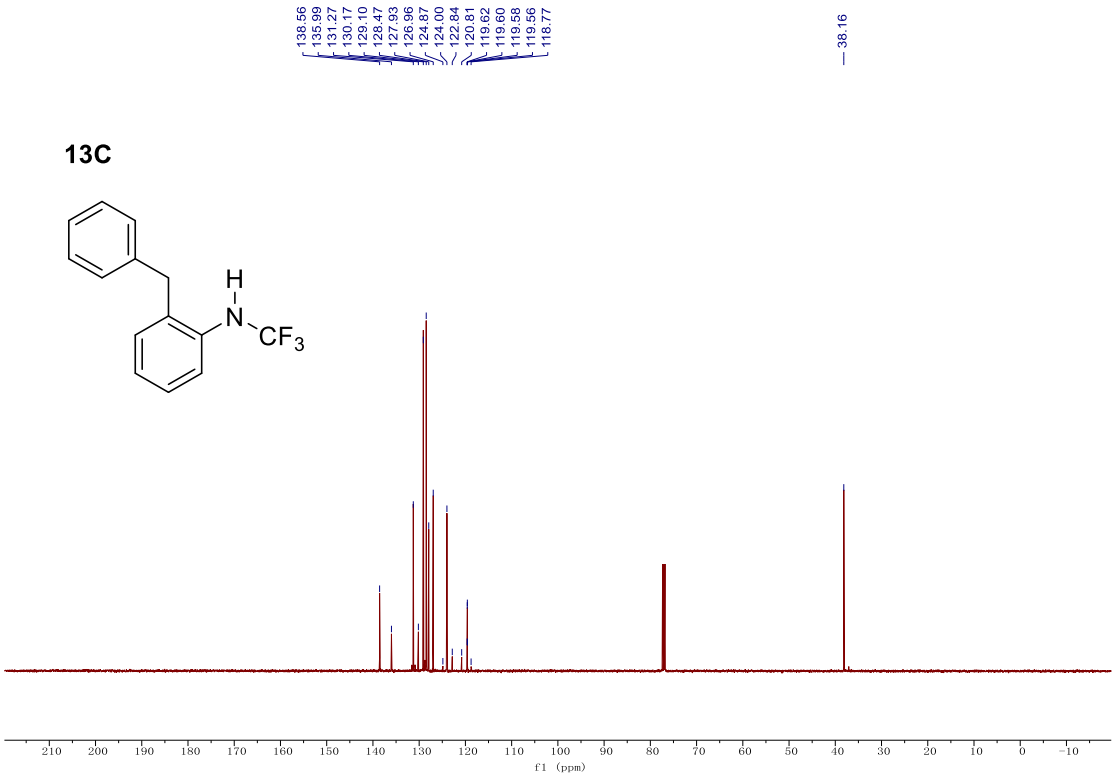
H
N
CF3
f1 (ppm)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126.96
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38.16
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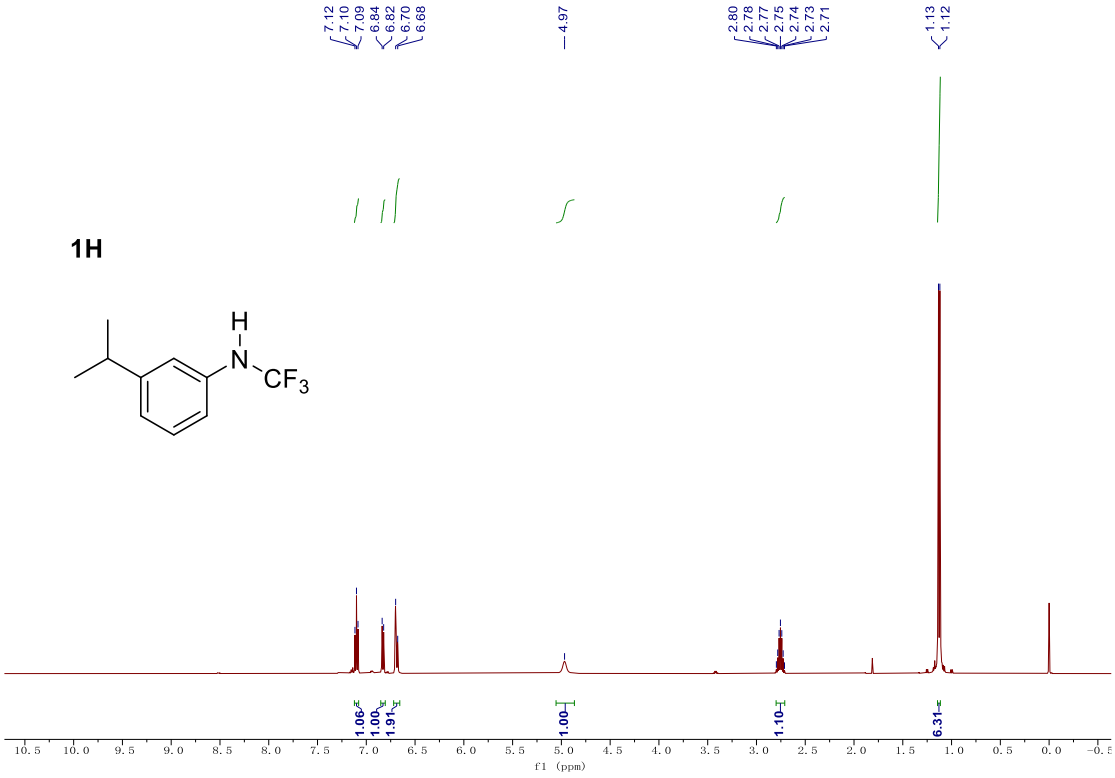
H
N
CF3
f1 (ppm)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2.73
2.71
1.13
1.12
1H
H
N
CF3
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1.00
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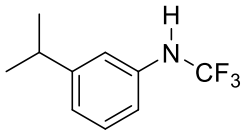
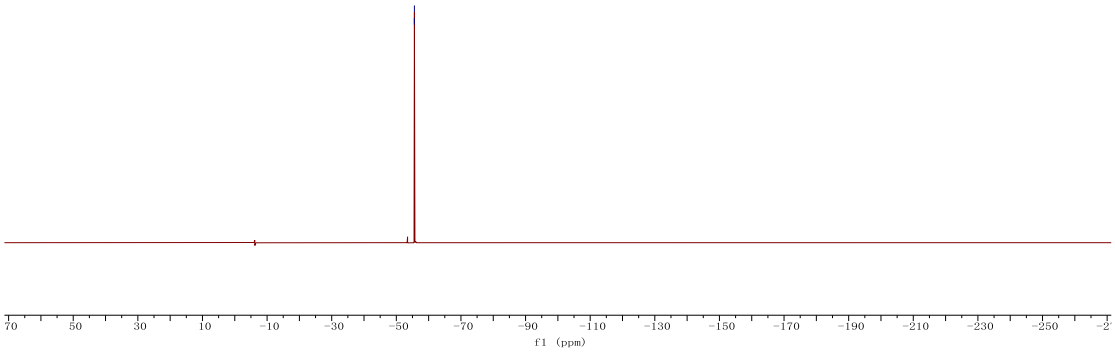
1.00
1.10
6.31
f1 (ppm)

-55.58
-55.59

19F





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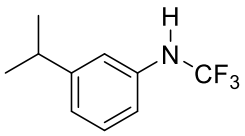
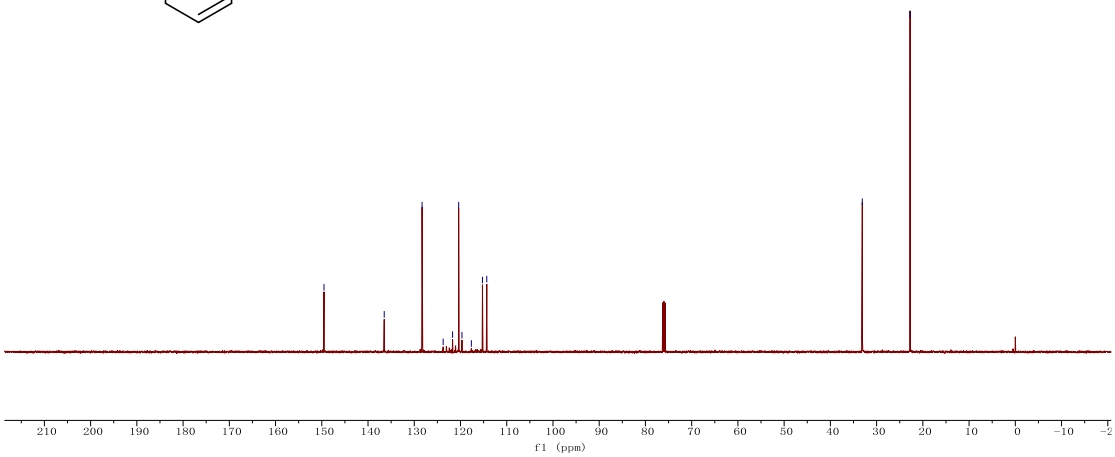
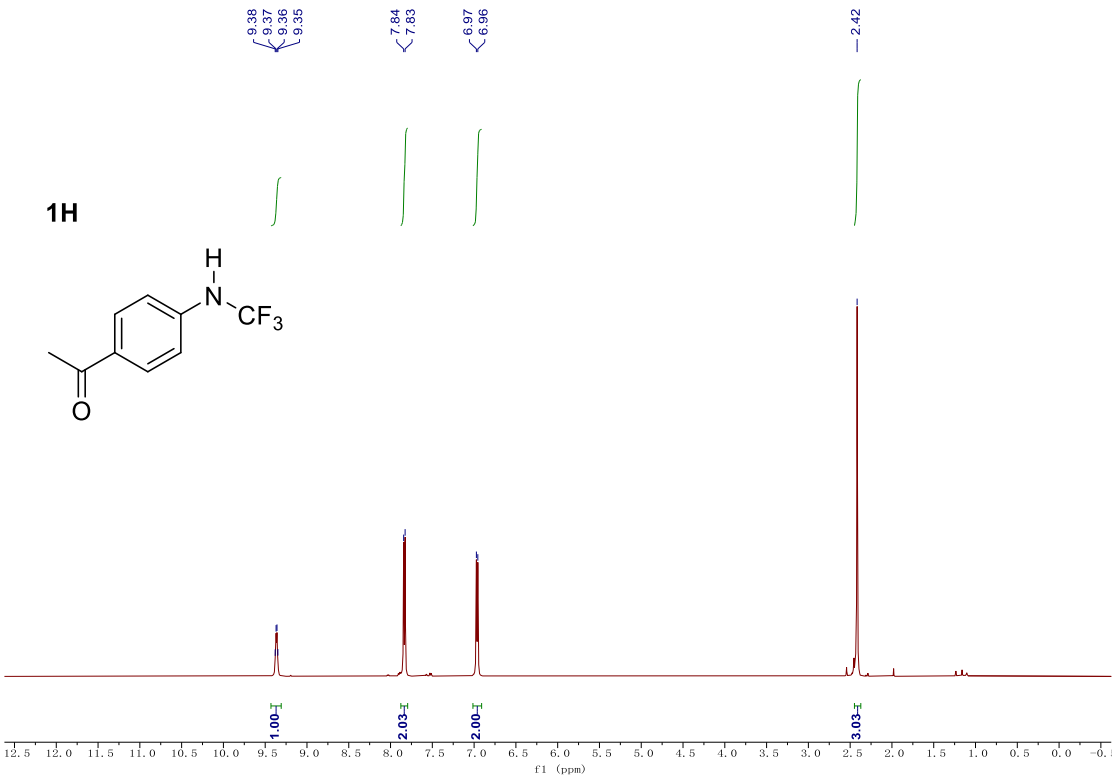
114.32
33.10
22.76

13C



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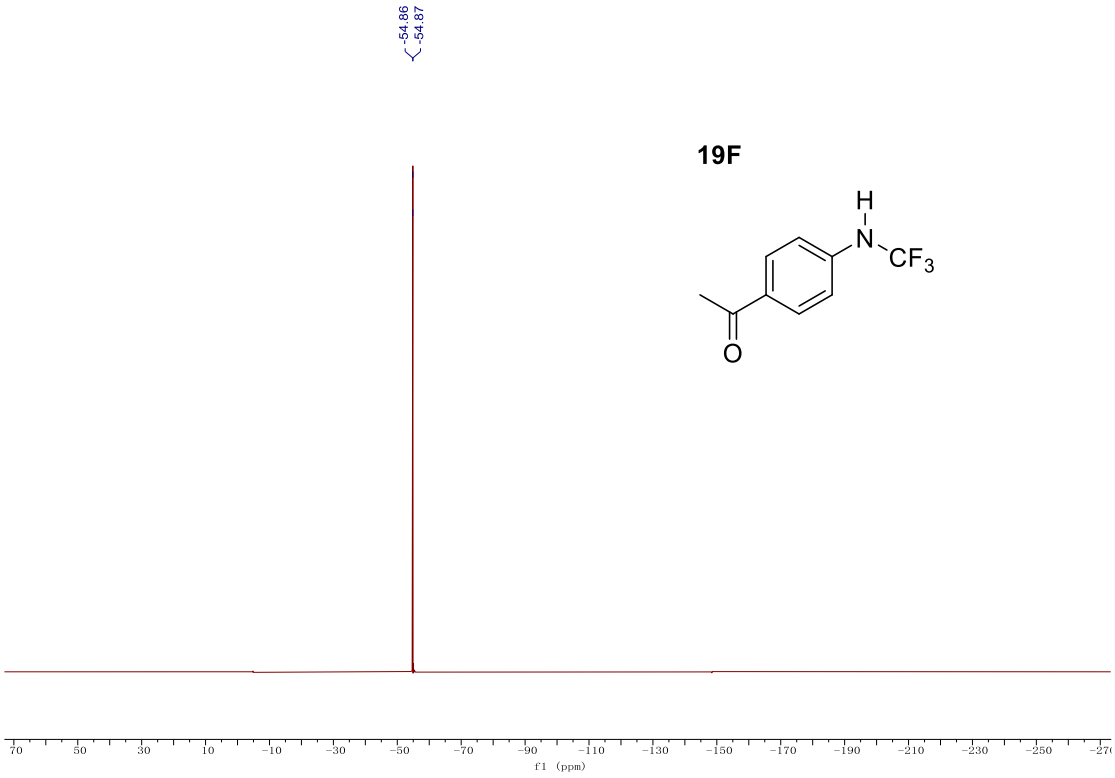
2.00
3.03
f1 (ppm)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N
CF3
O
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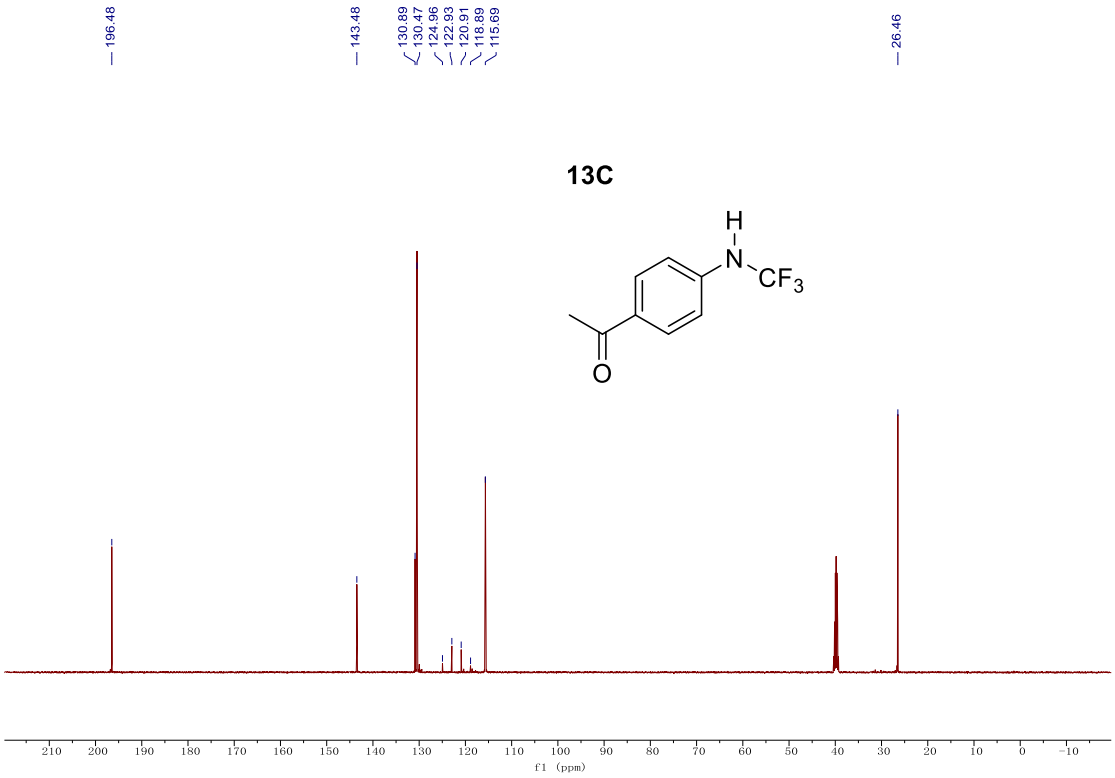
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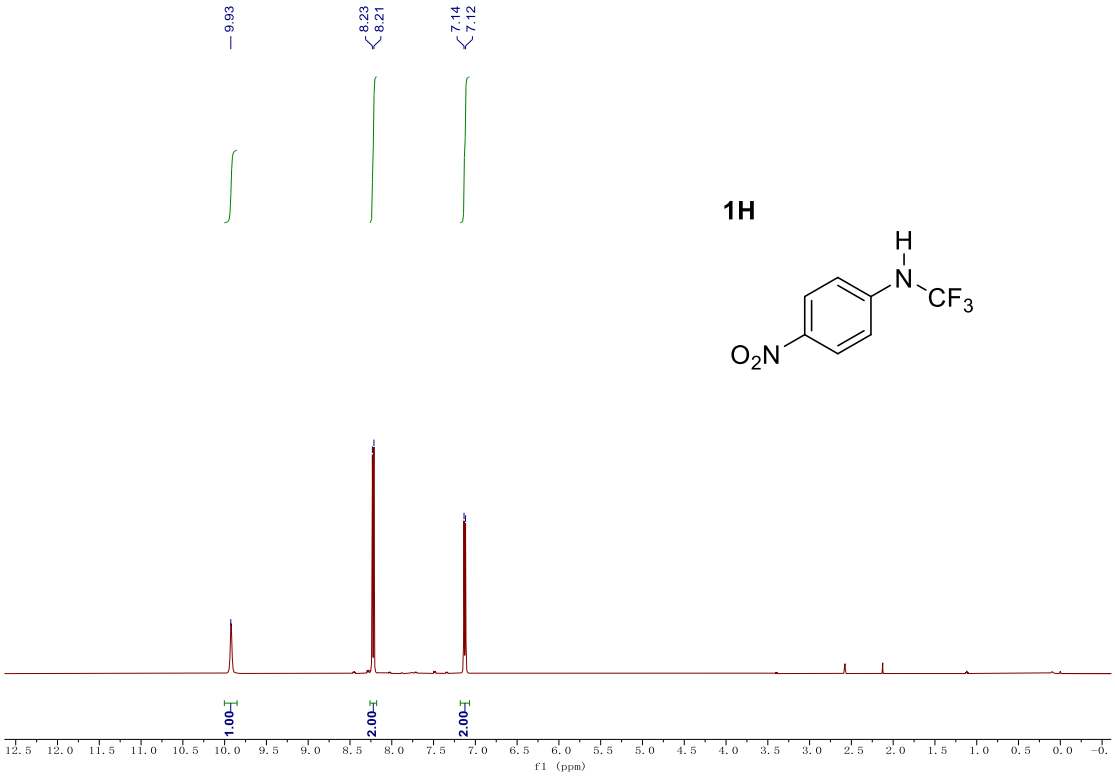
N
CF3
O
f1 (ppm)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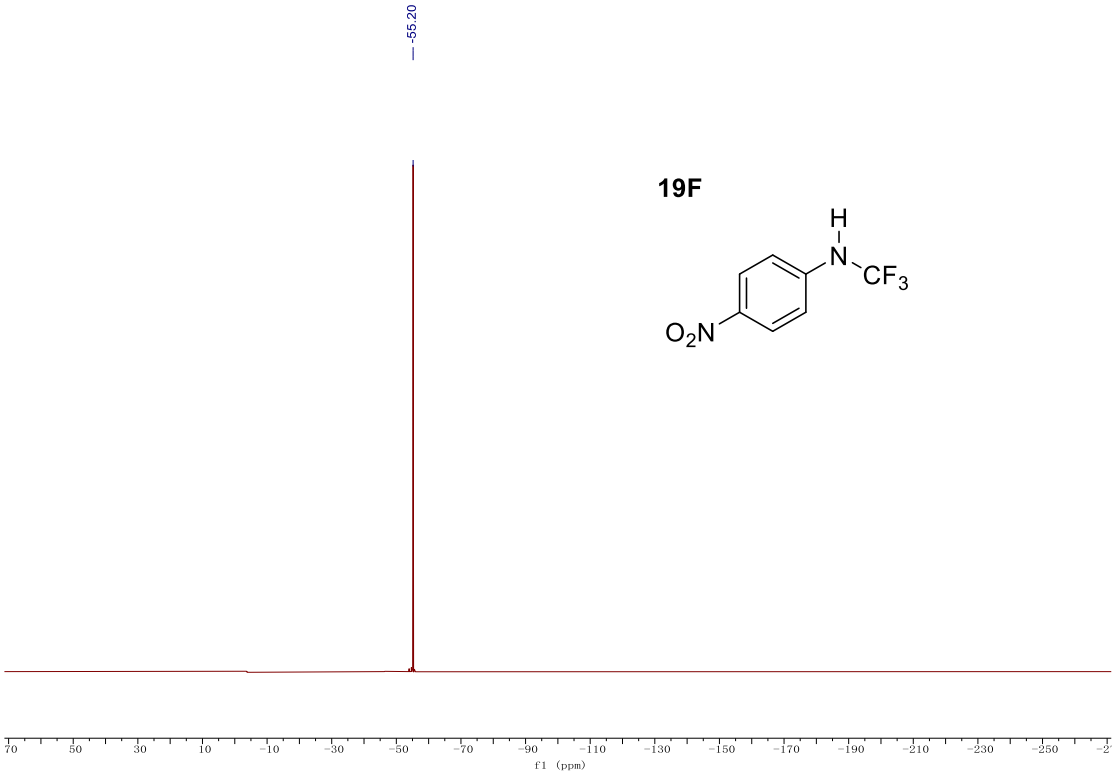
2.00
f1 (ppm)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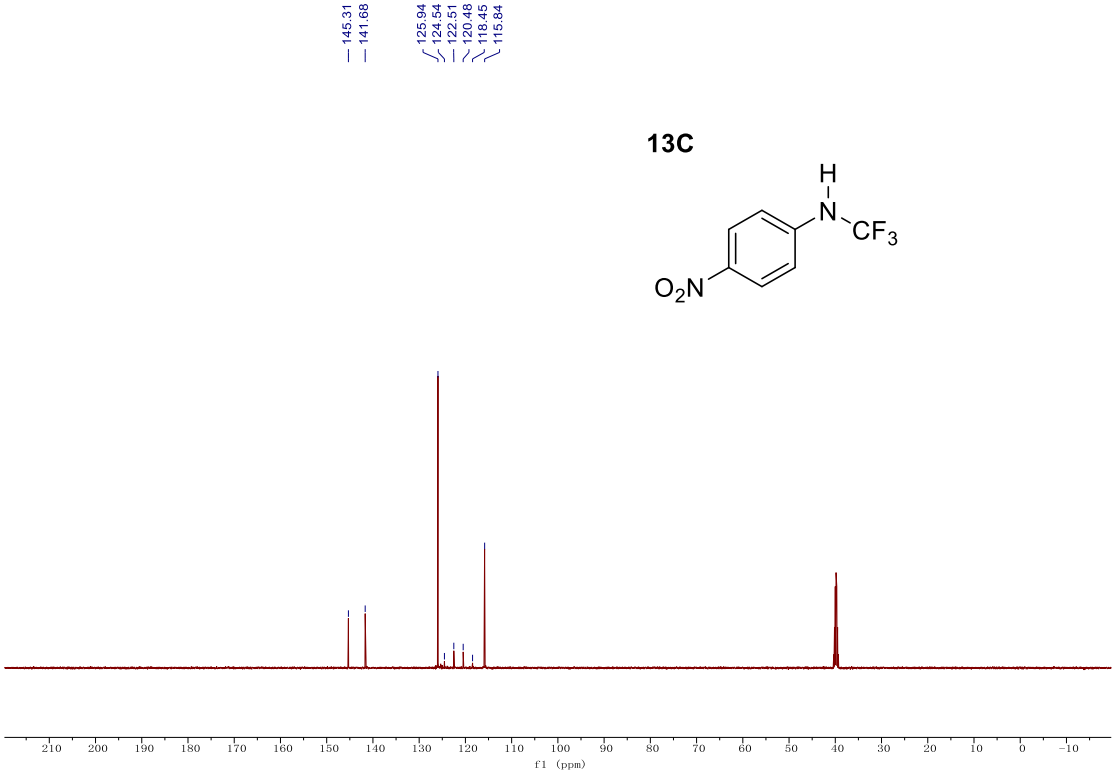
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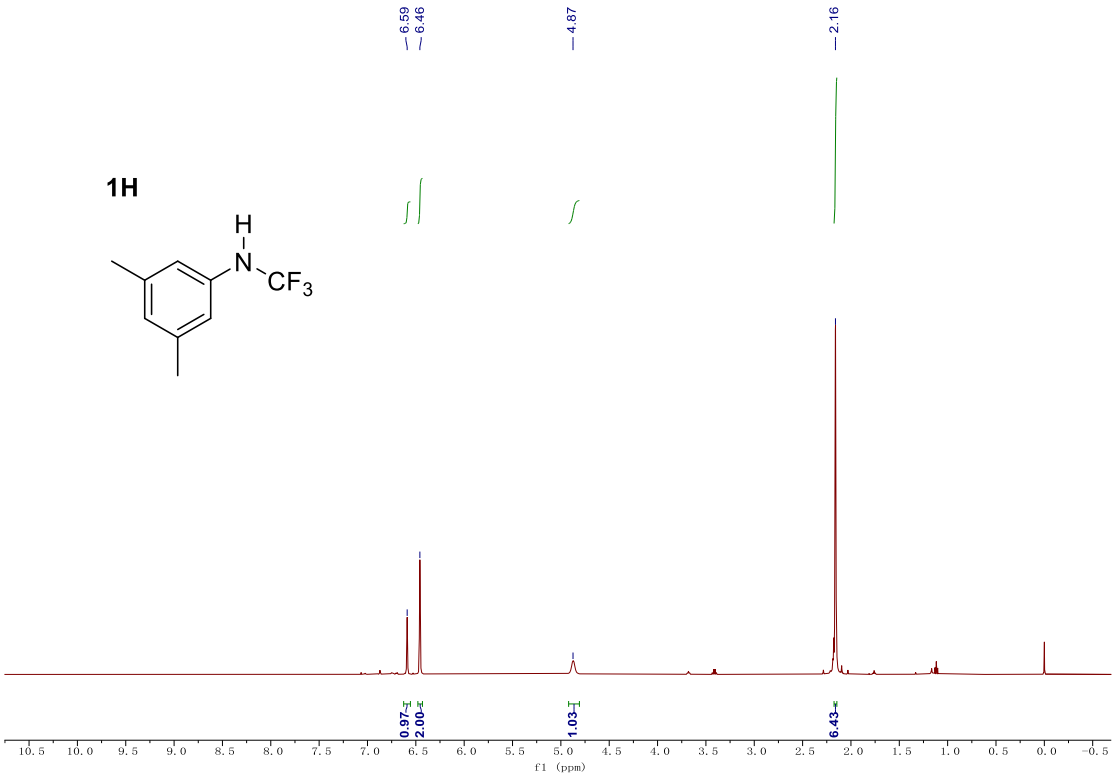
N
CF3
O2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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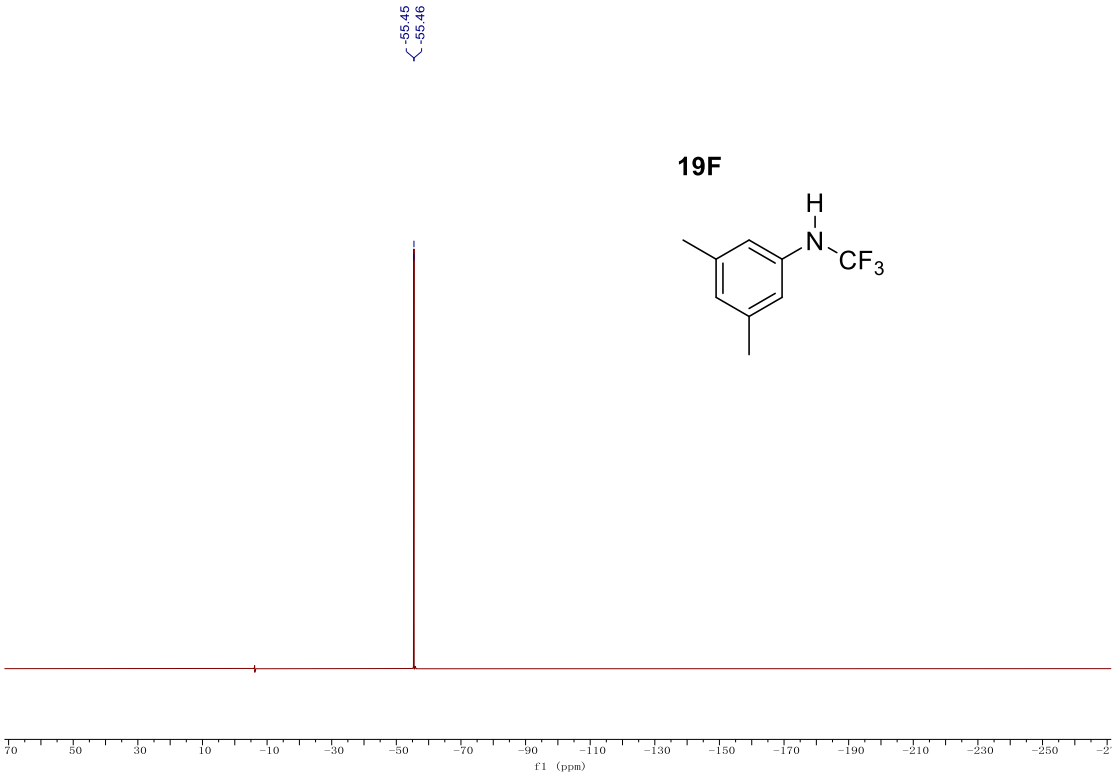
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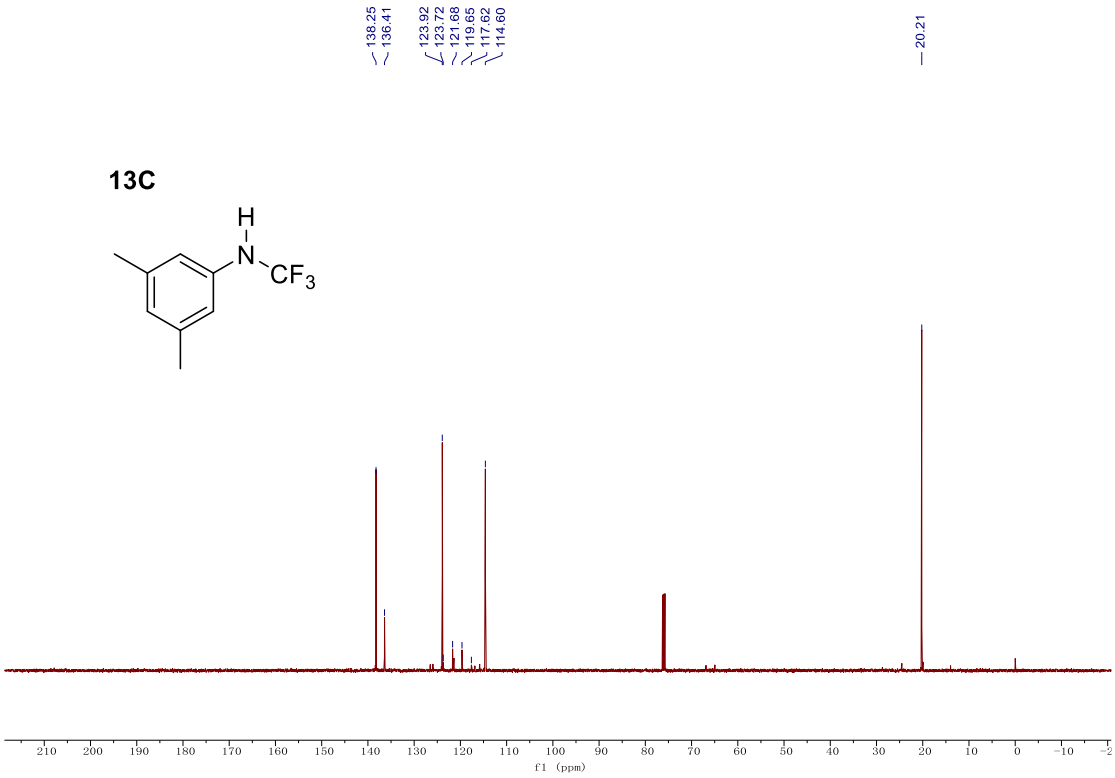
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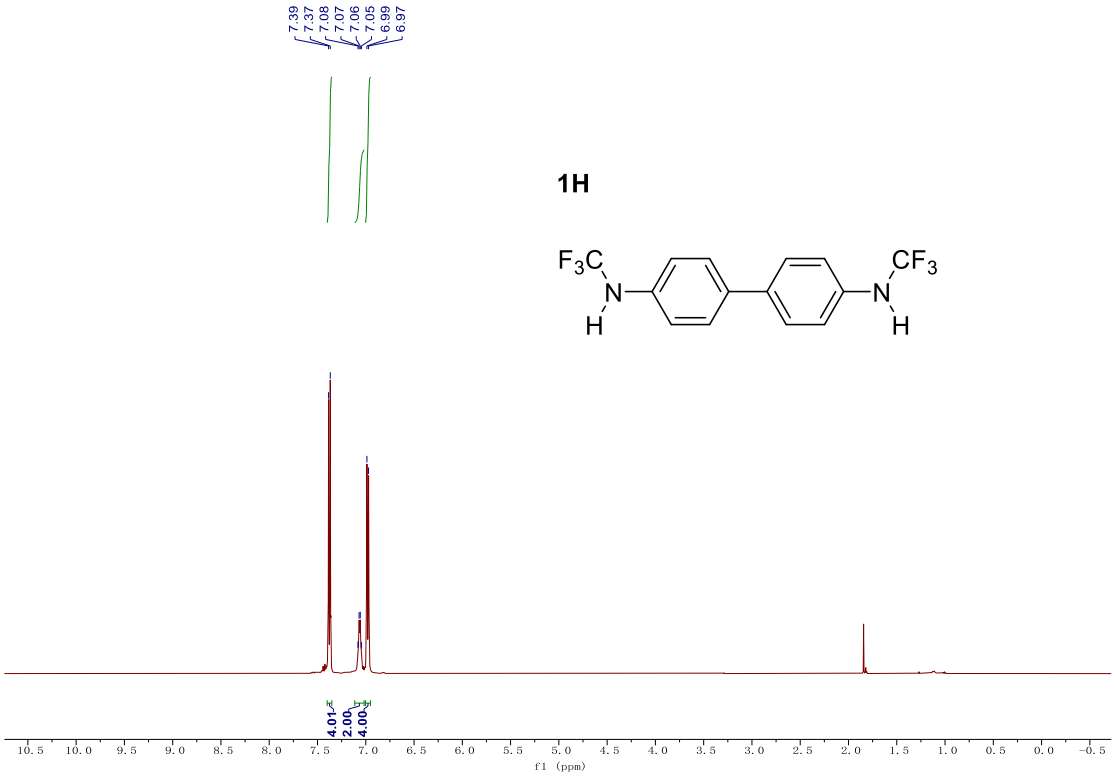
H
N
CF3
f1 (ppm)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H
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H
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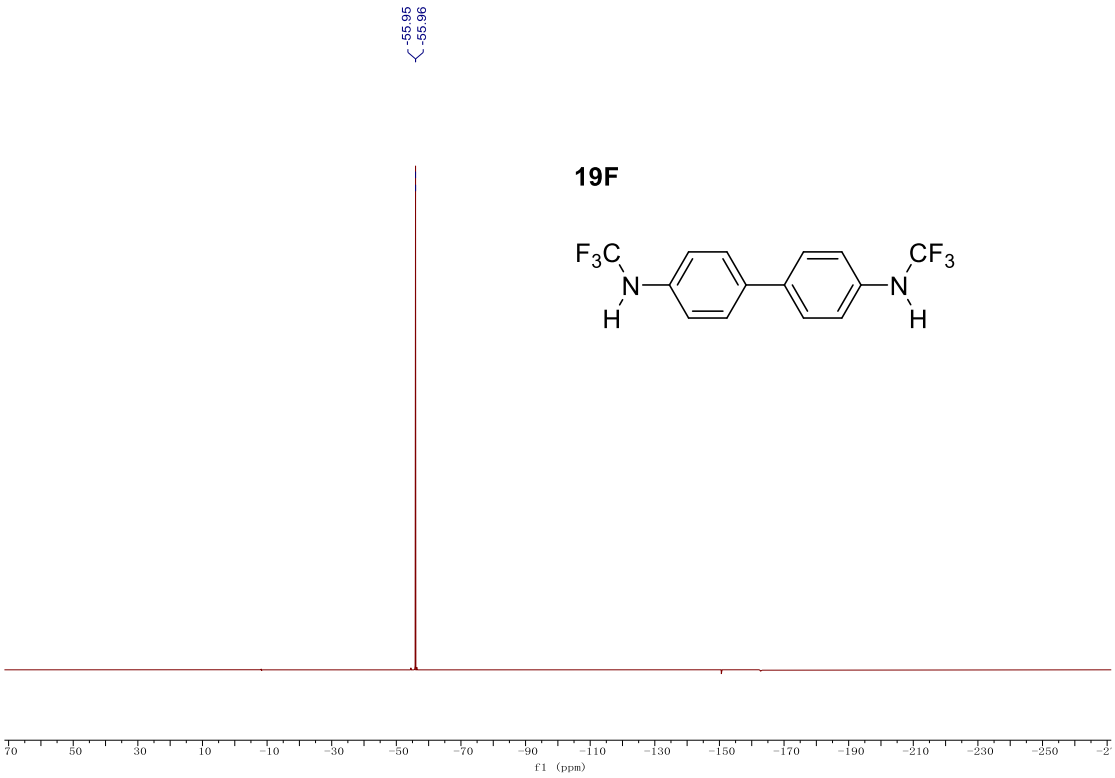
2.00
4.00
f1 (ppm)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N
H
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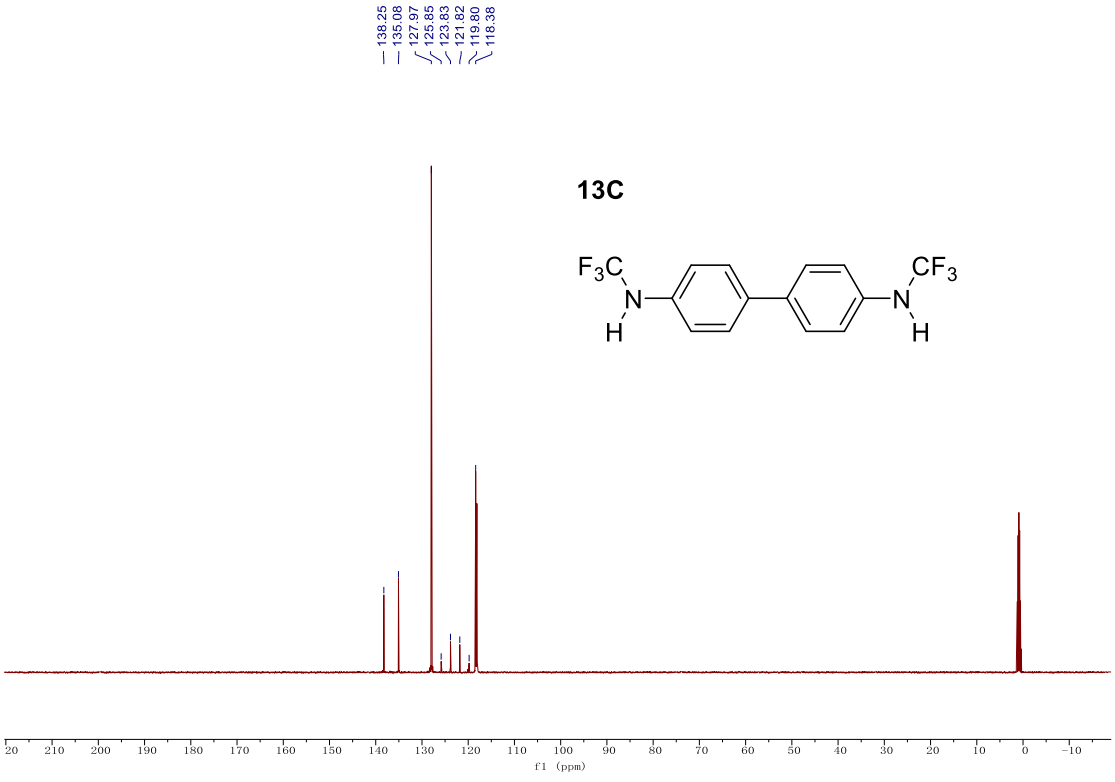
f1 (ppm)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121.82
119.80
118.38
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CF3
N
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H
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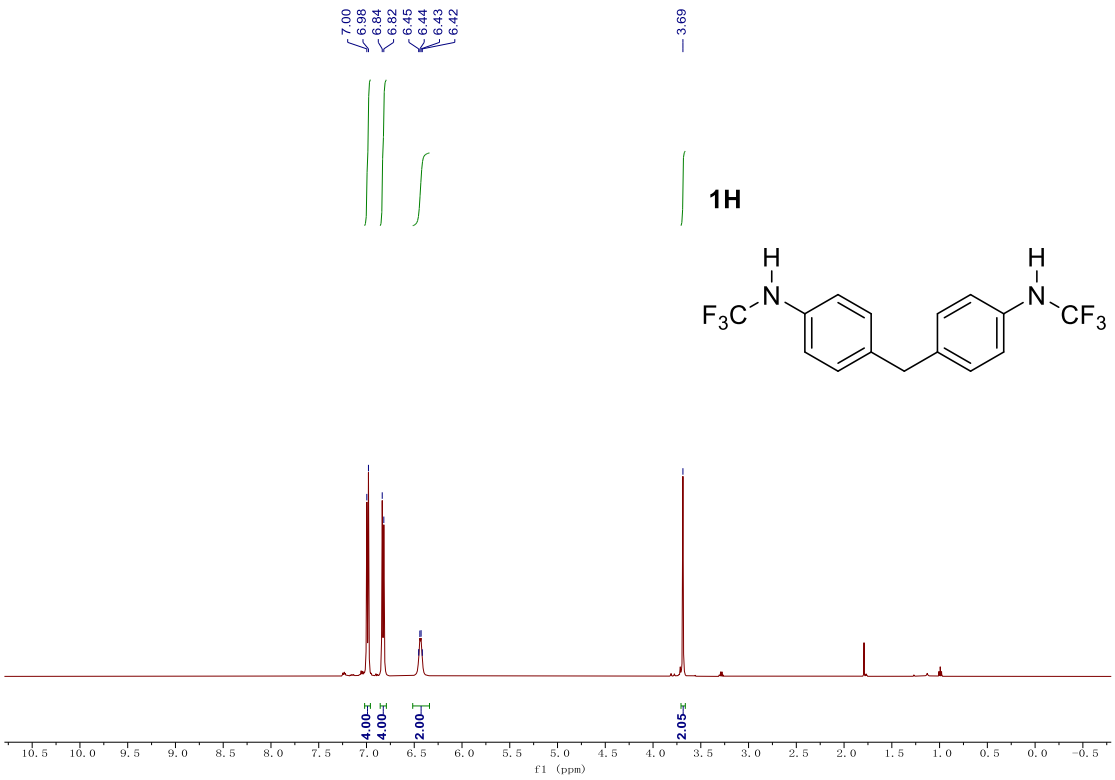
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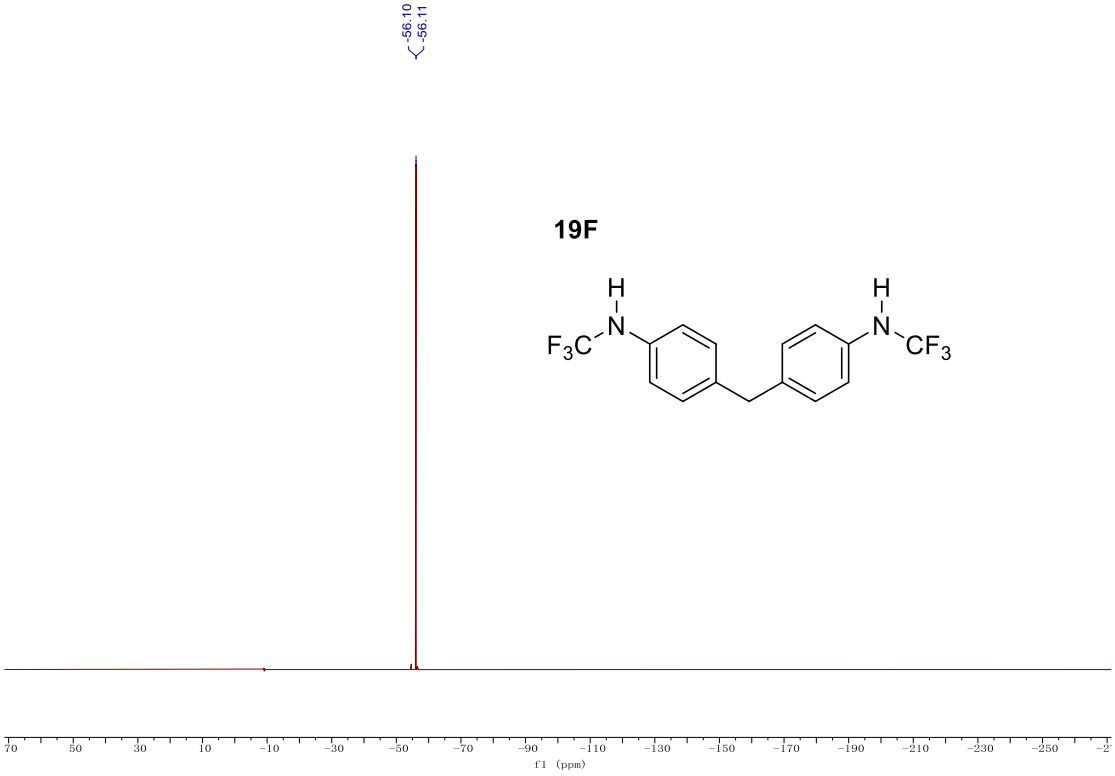
2.05
f1 (ppm)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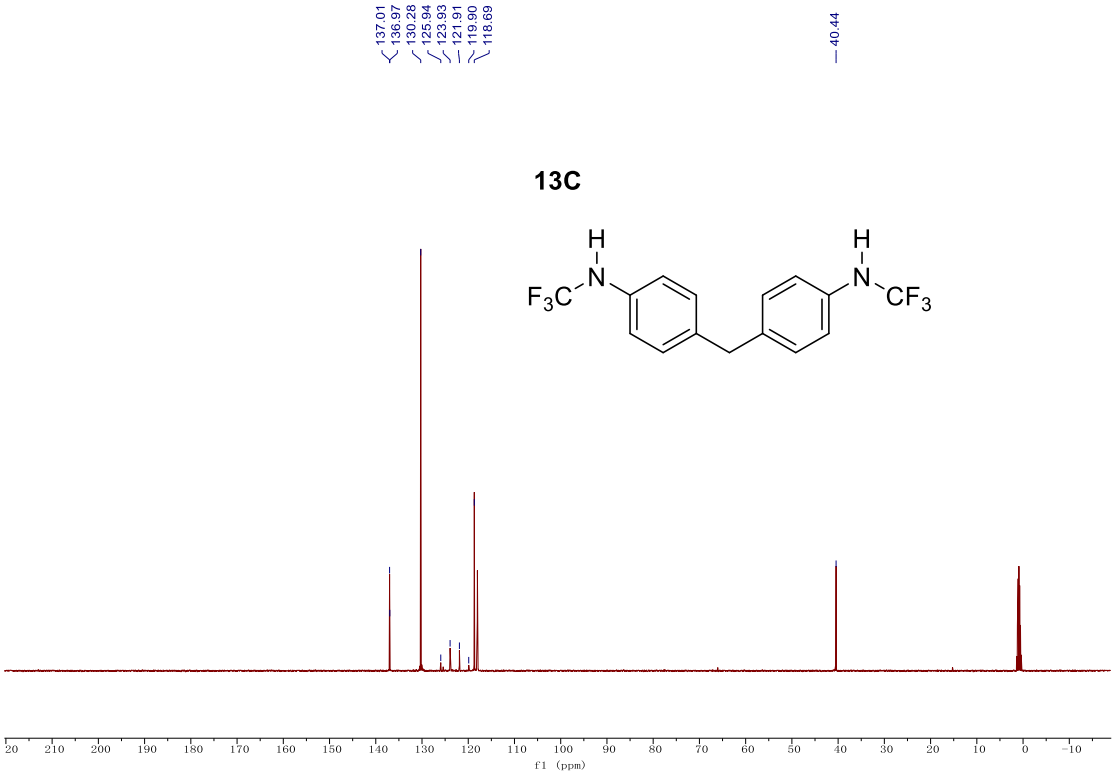
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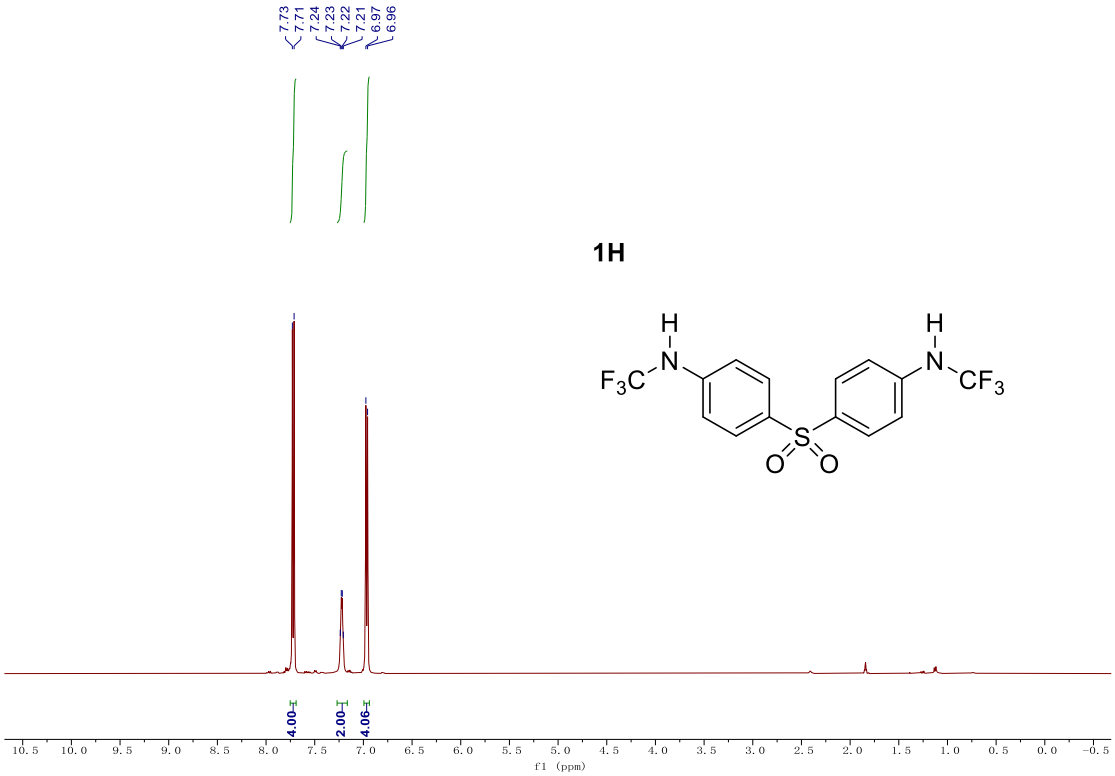
F3C
CF3
f1 (ppm)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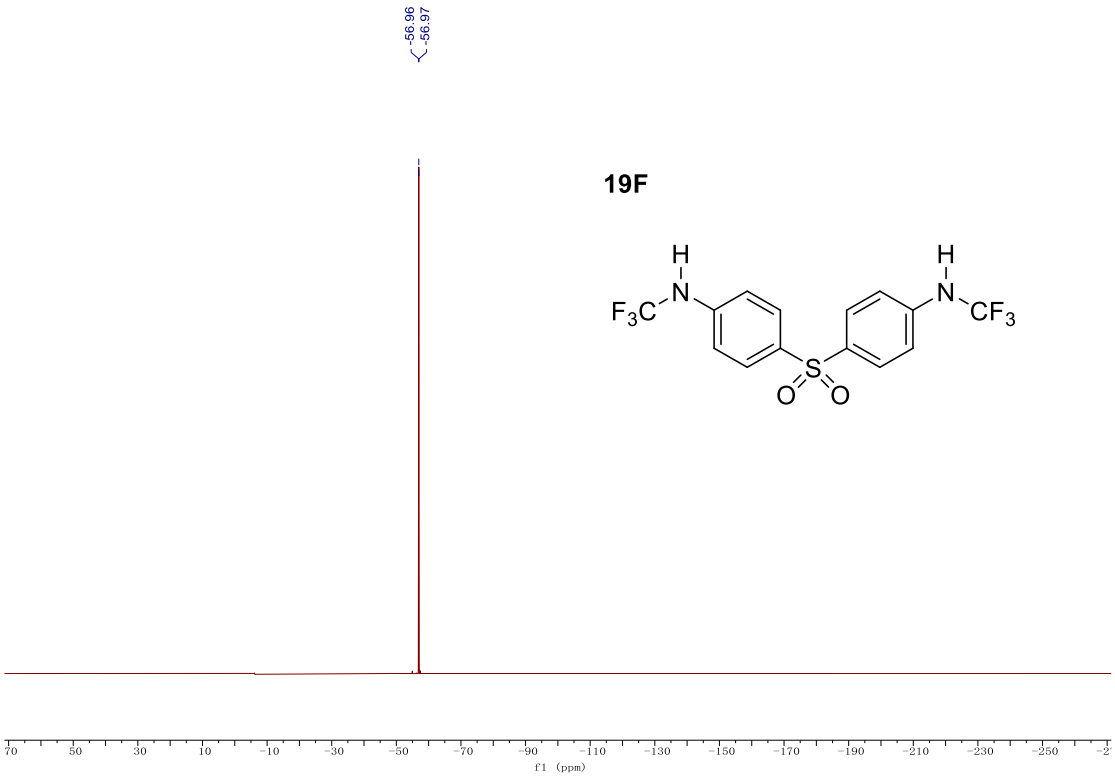
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19F
H
N
F3C
H
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CF3
S
O
O
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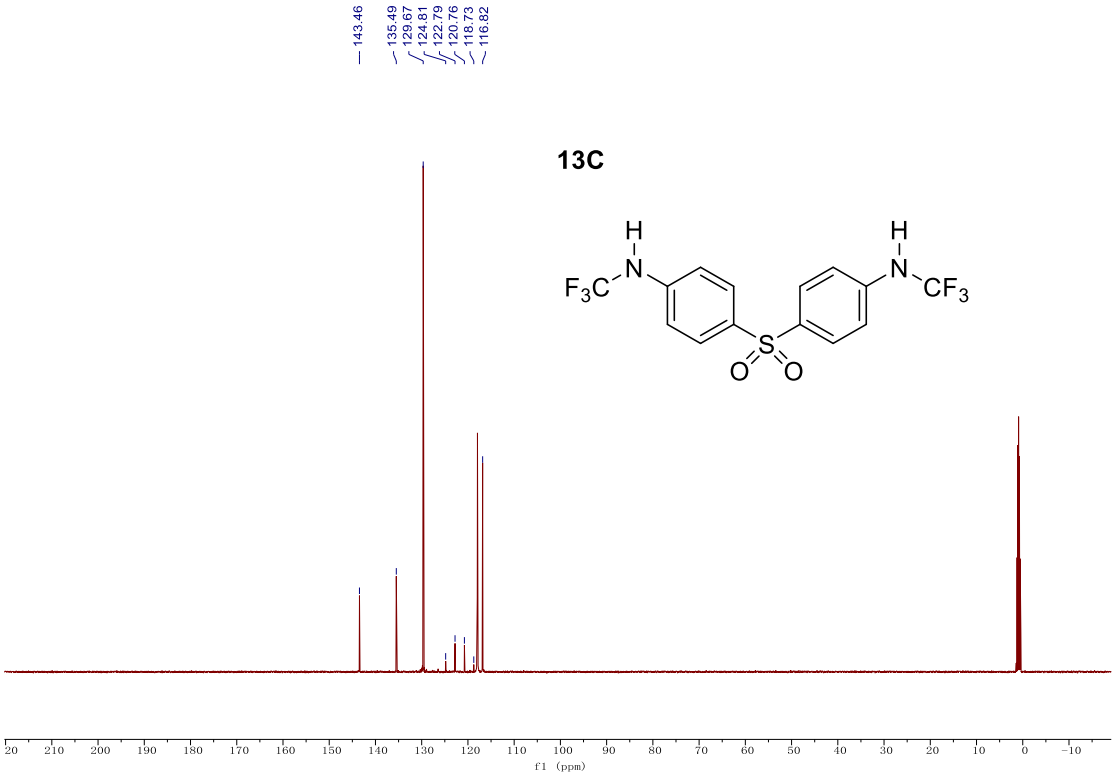
f1 (ppm)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122.79
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H
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F3C
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N
CF3
S
O
O
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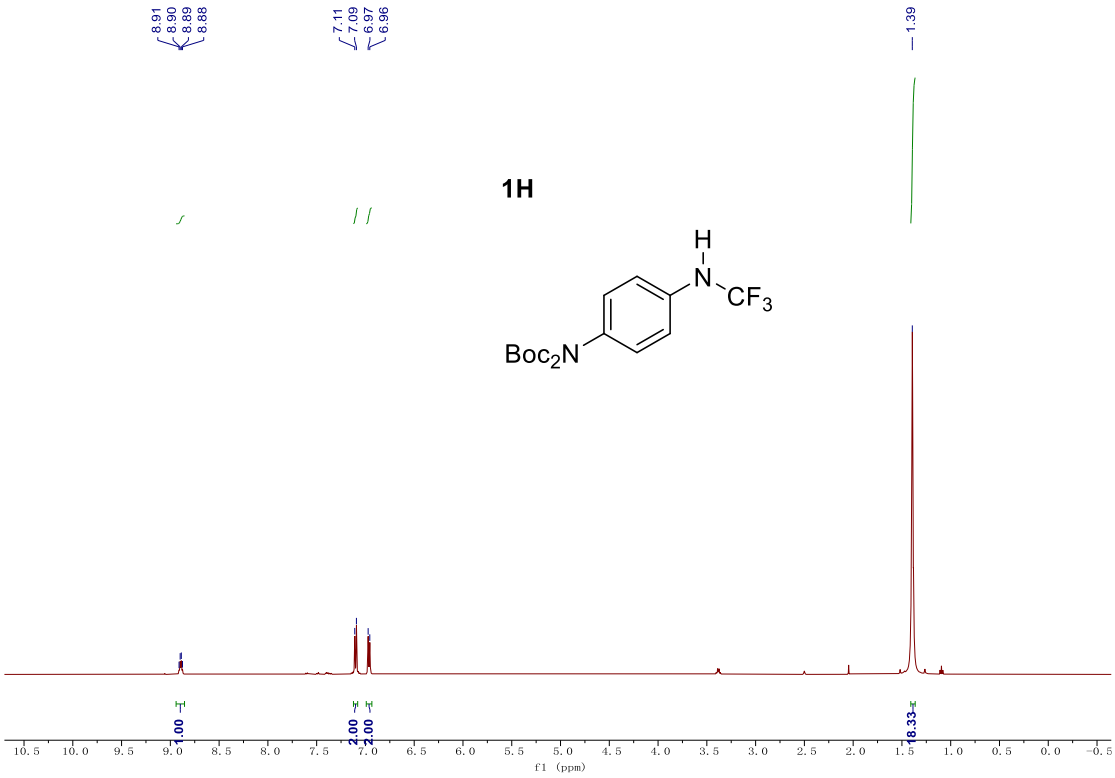
f1 (ppm)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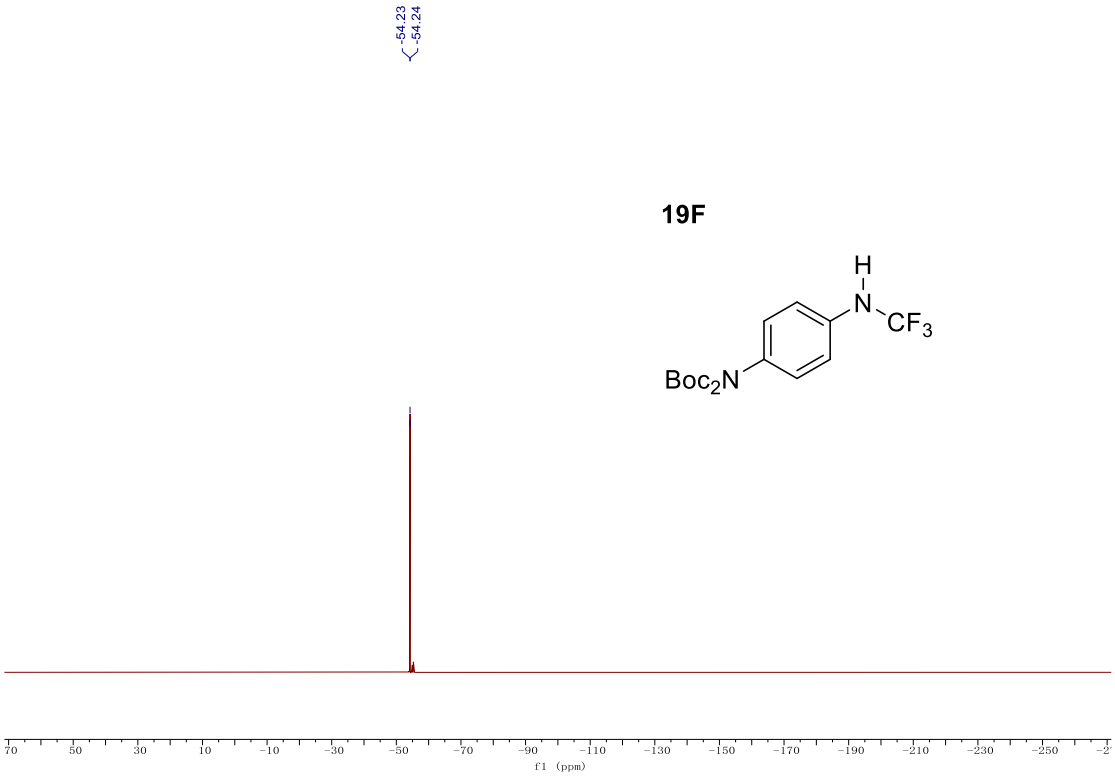
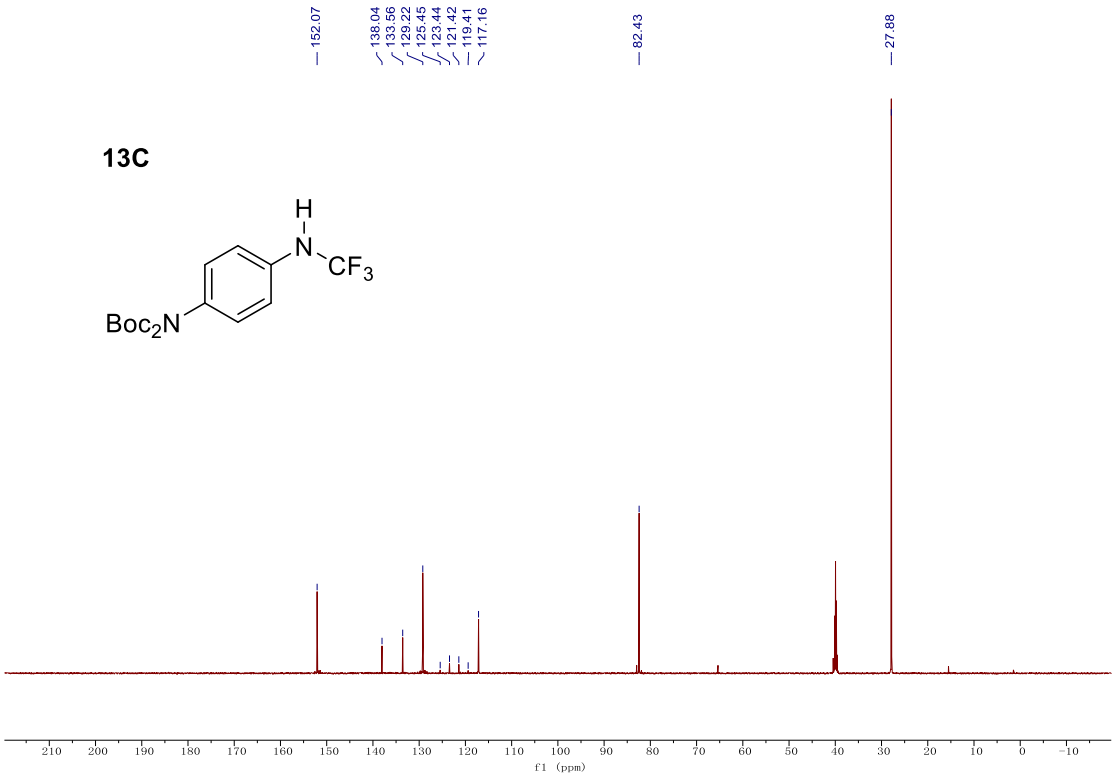
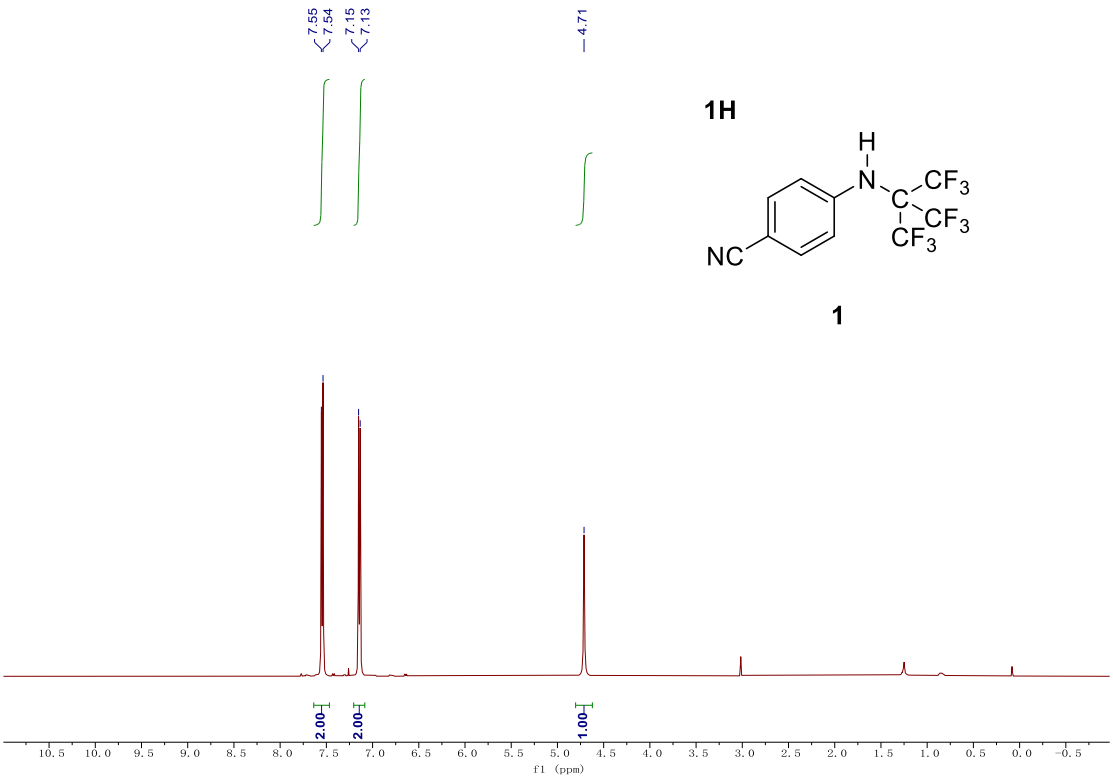
6.97
6.96
1.39
1H
H
N
CF3
Boc2N
1.00
2.00
2.00
18.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-54.23
-54.24
19F
H
N
CF3
Boc2N
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)

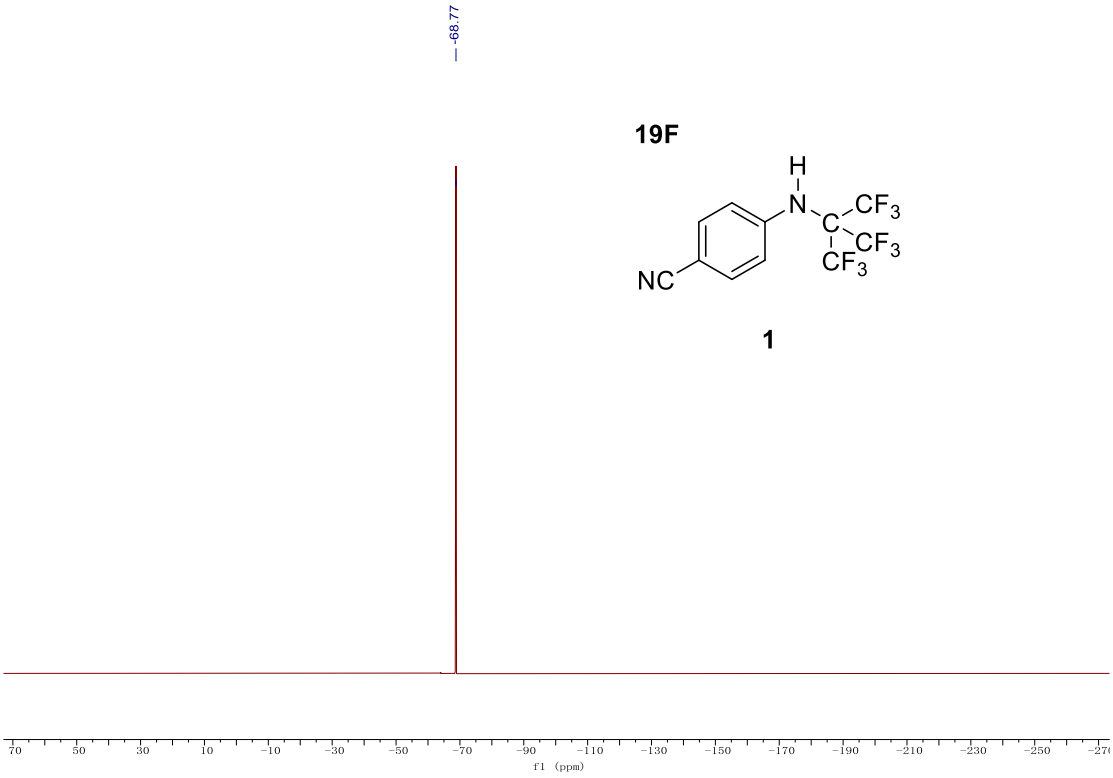

152.07
138.04
133.56
129.22
125.45
123.44
121.42
119.41
117.16
82.43
27.88
13C
H
N
CF3
Boc2N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.55
7.54
7.15
7.13
4.71
2.00
2.00
1.00
f1 (ppm)

1H

H
N
C
CF3
CF3
CF3
NC

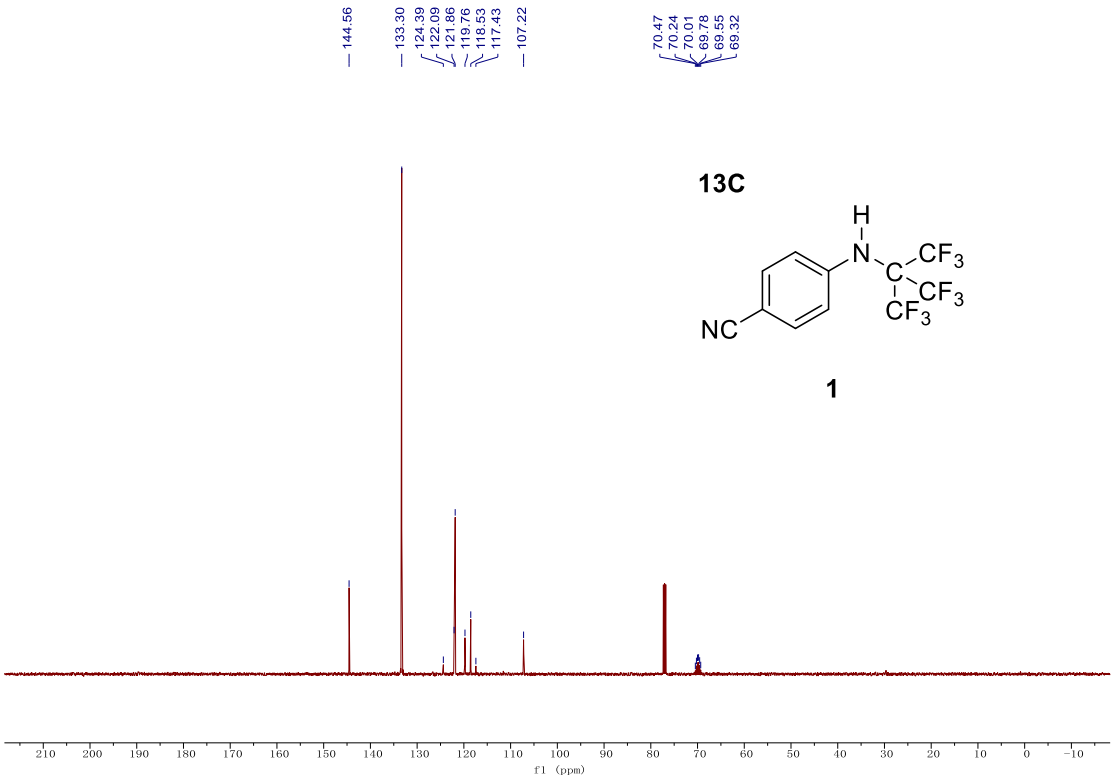
1

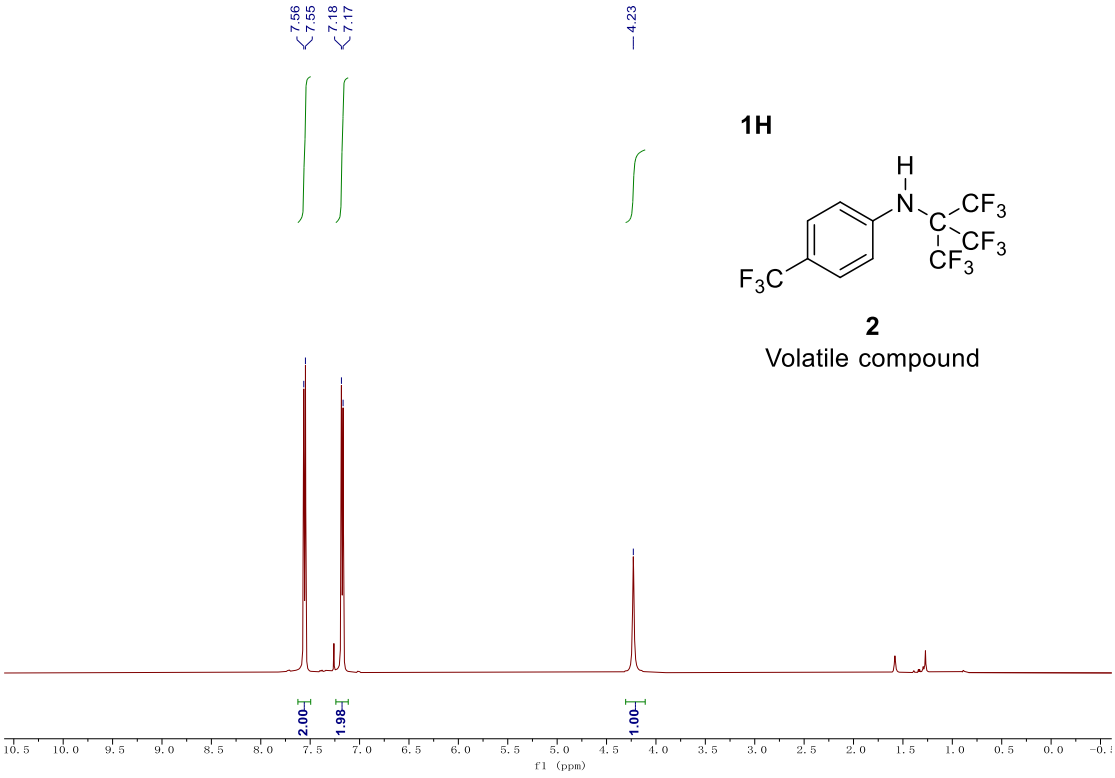

-68.77
f1 (ppm)

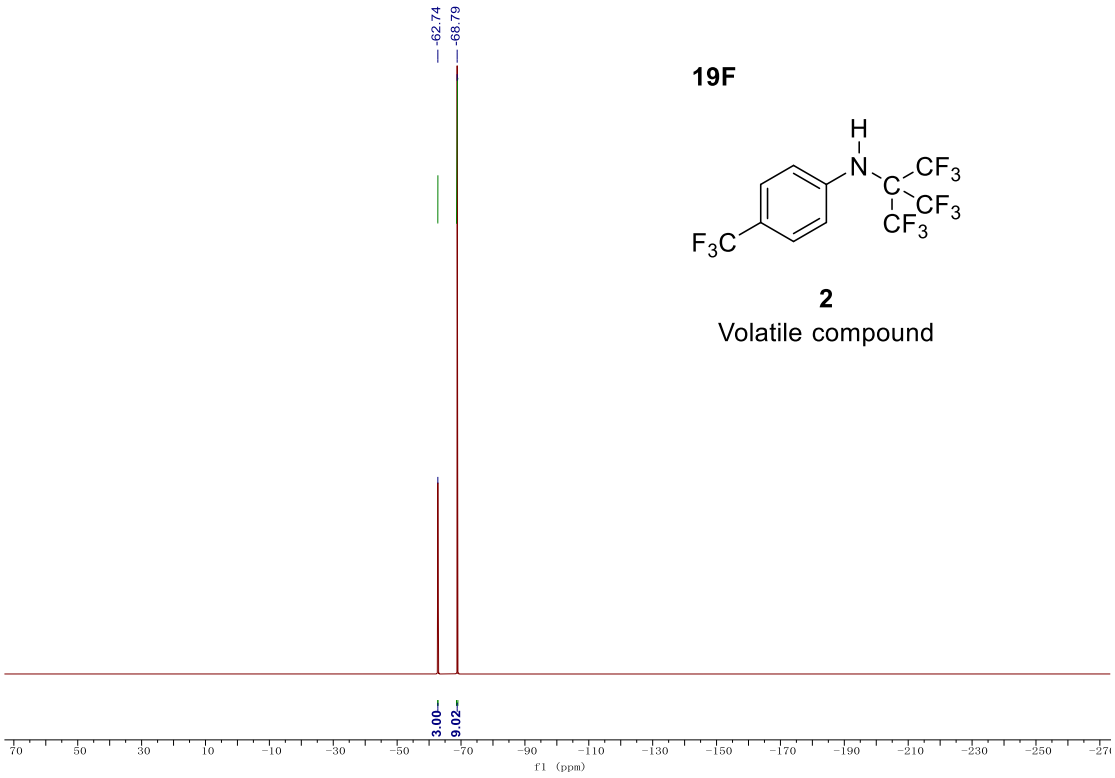
19F

H
N
C
CF3
CF3
CF3
NC

1


144.56
133.30
124.39
122.09
121.86
119.76
118.53
117.43
107.22
70.47
70.24
70.01
69.78
69.55
69.32
13C
H
N
C
CF3
CF3
CF3
NC
1
f1 (ppm)

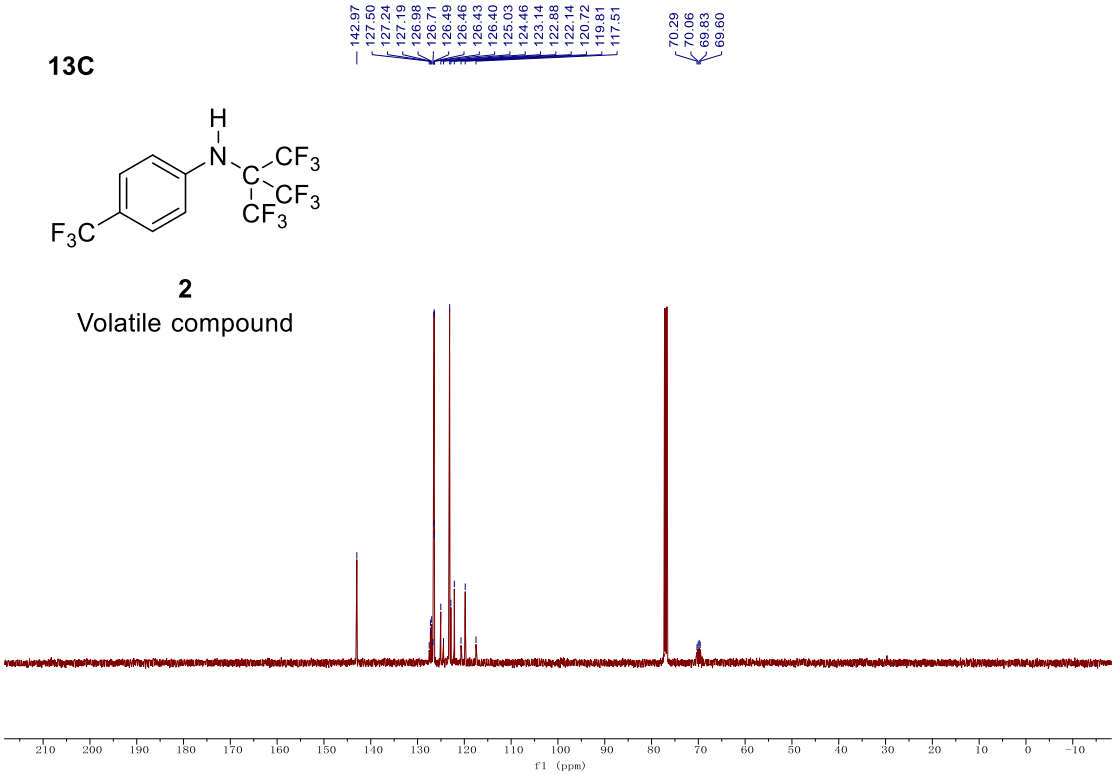

7.56
7.55
7.18
7.17
4.23
1H
H
N
C
CF3
CF3
CF3
F3C
2
Volatile compound
2.00
1.98
1.00
f1 (ppm)



19F

2

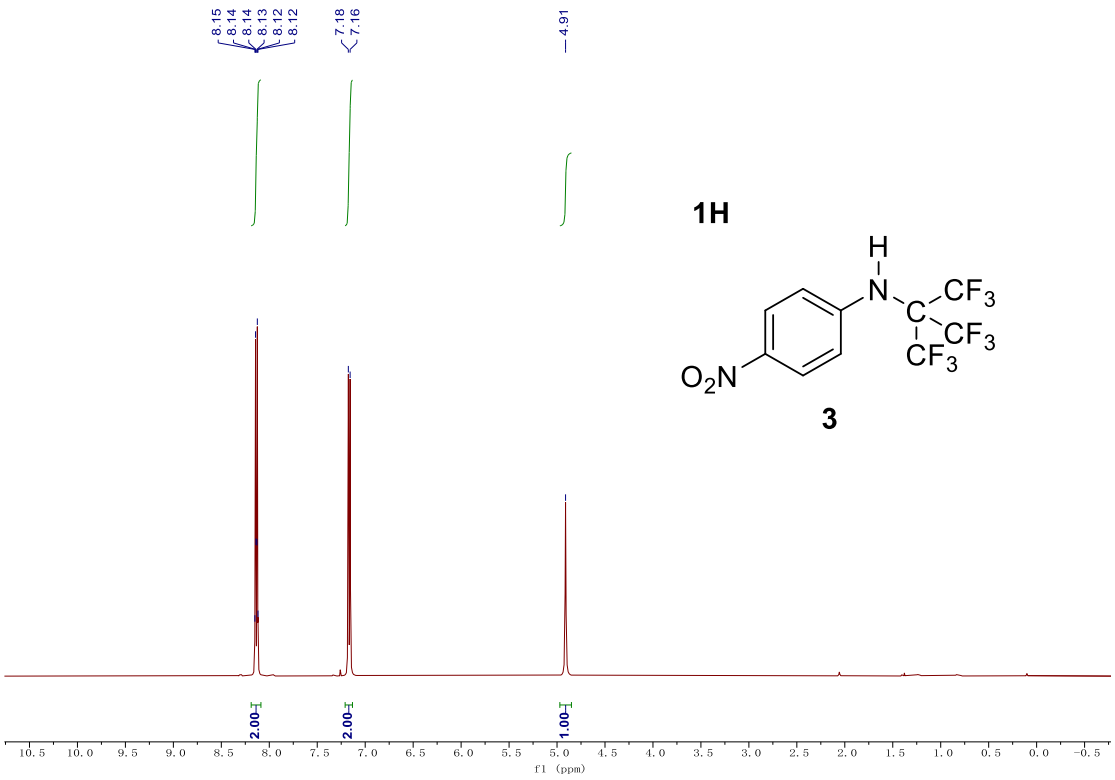
Volatile compound



13C

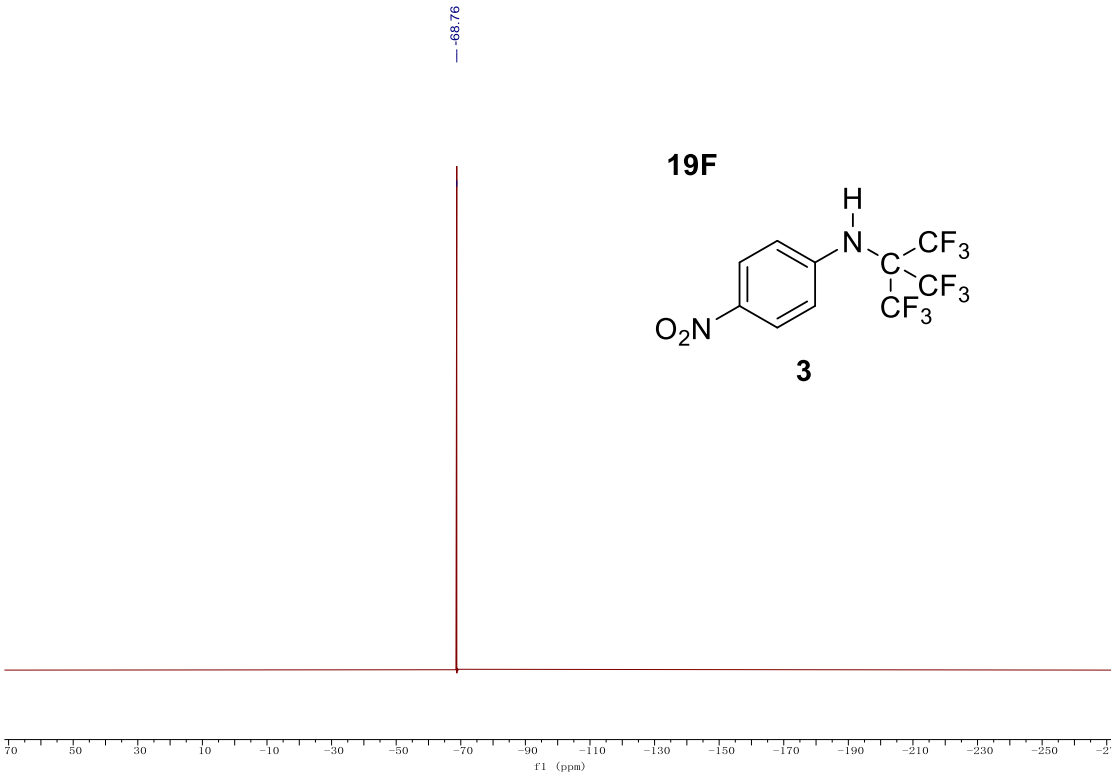
2

Volatile compound


8.15
8.14
8.14
8.13
8.12
8.12
7.18
7.16
4.91
2.00
2.00
1.00
f1 (ppm)

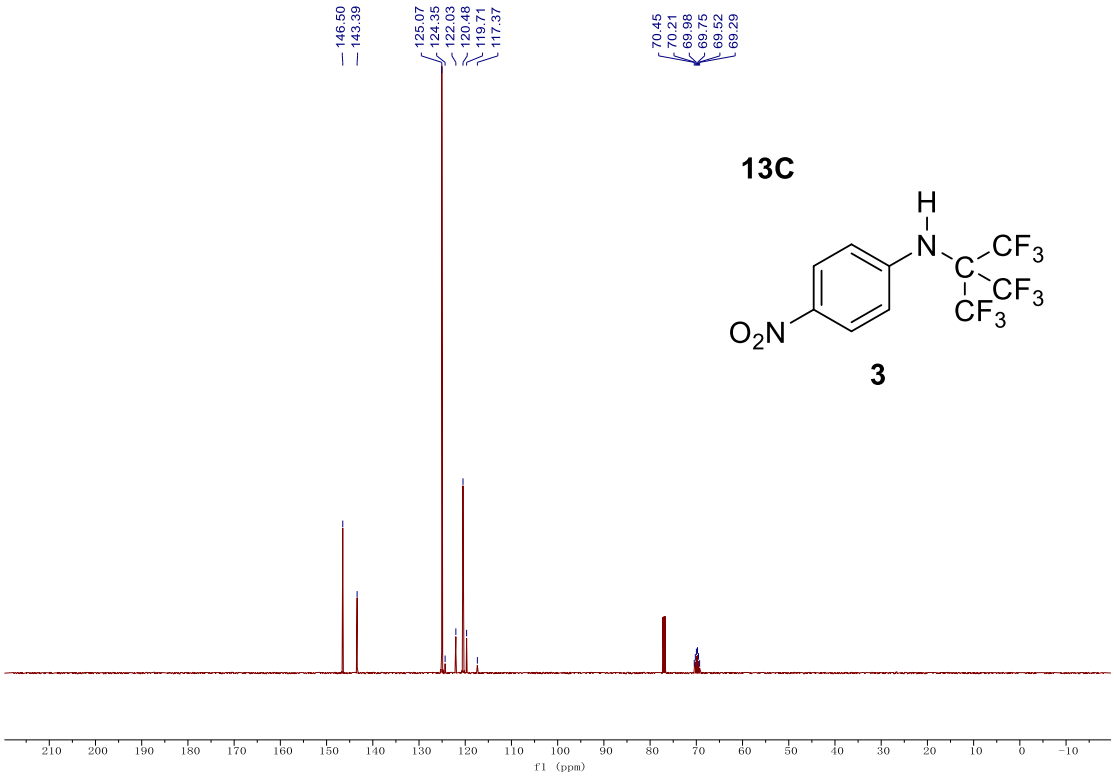
1H

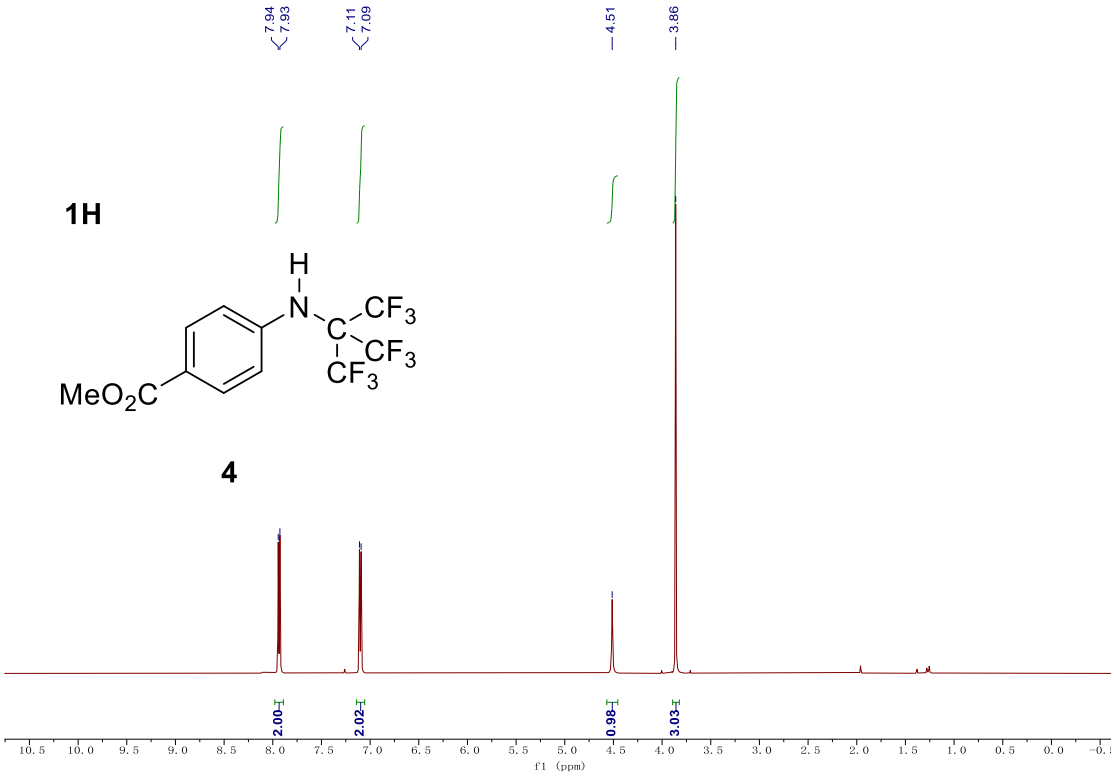
3

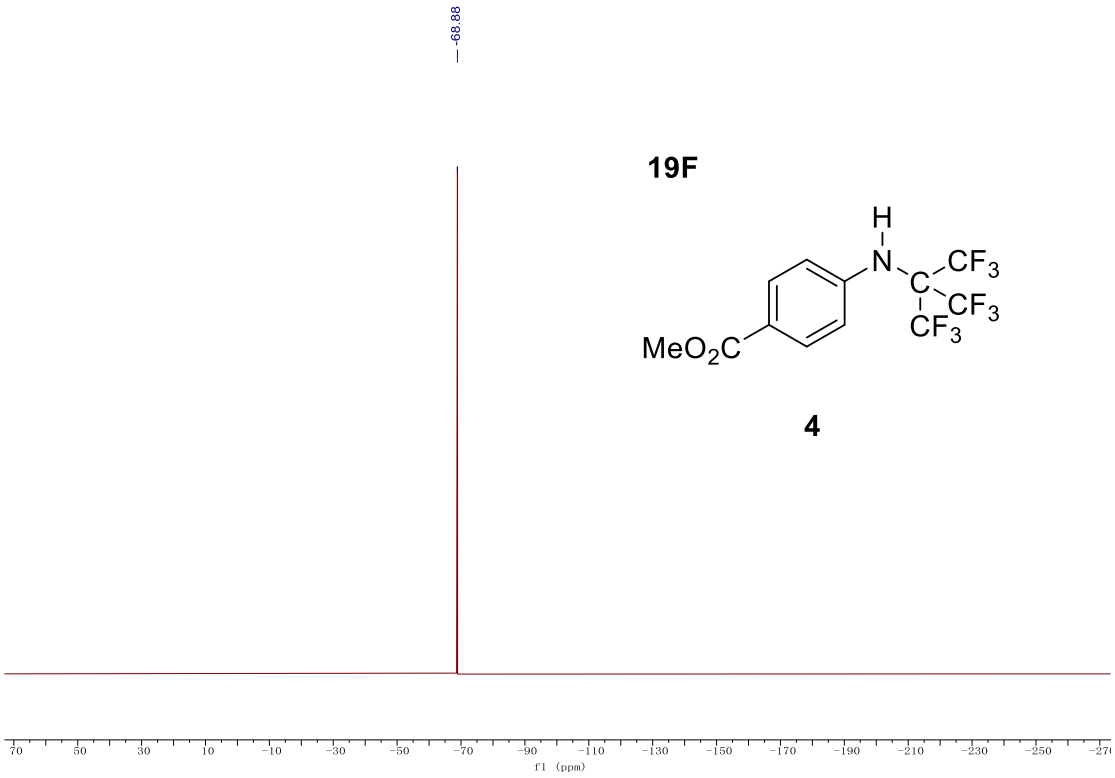

-68.76
f1 (ppm)

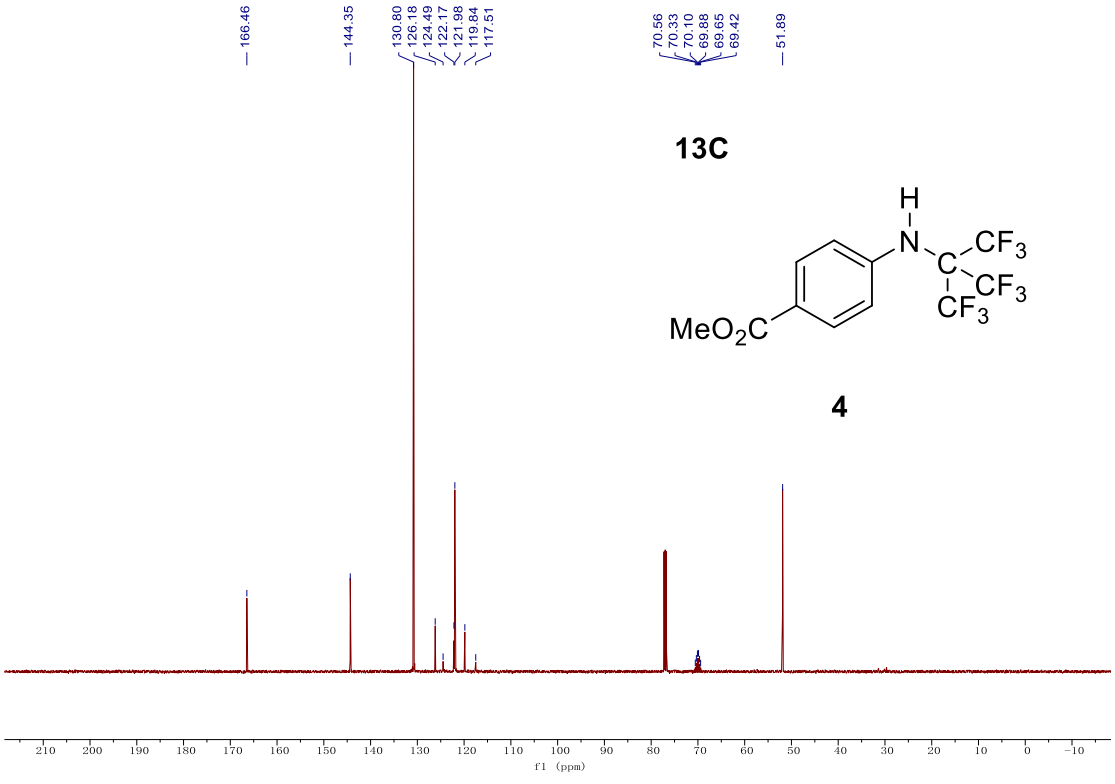
19F

3

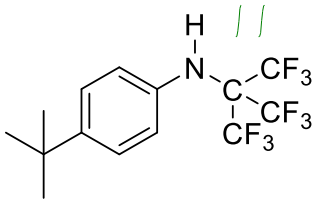

146.50
143.39
125.07
124.35
122.03
120.48
119.71
117.37
70.45
70.21
69.98
69.75
69.52
69.29
13C
H
N
C
CF3
CF3
CF3
O2N
3
f1 (ppm)


7.94
7.93
7.11
7.09
4.51
3.86
1H
H
N
C
CF3
CF3
CF3
MeO2C
4
2.00
2.02
0.98
3.03
f1 (ppm)


-68.88
19F
H
N
C
CF3
CF3
CF3
MeO2C
4
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)


166.46
144.35
130.80
126.18
124.49
122.17
121.98
119.84
117.51
70.56
70.33
70.10
69.88
69.65
69.42
51.89
13C
H
N
C
CF3
CF3
CF3
MeO2C
4
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

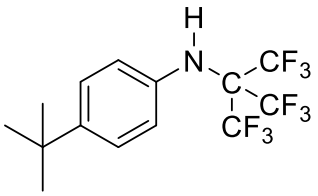
1H


H
N
C
CF3
CF3
CF3

5

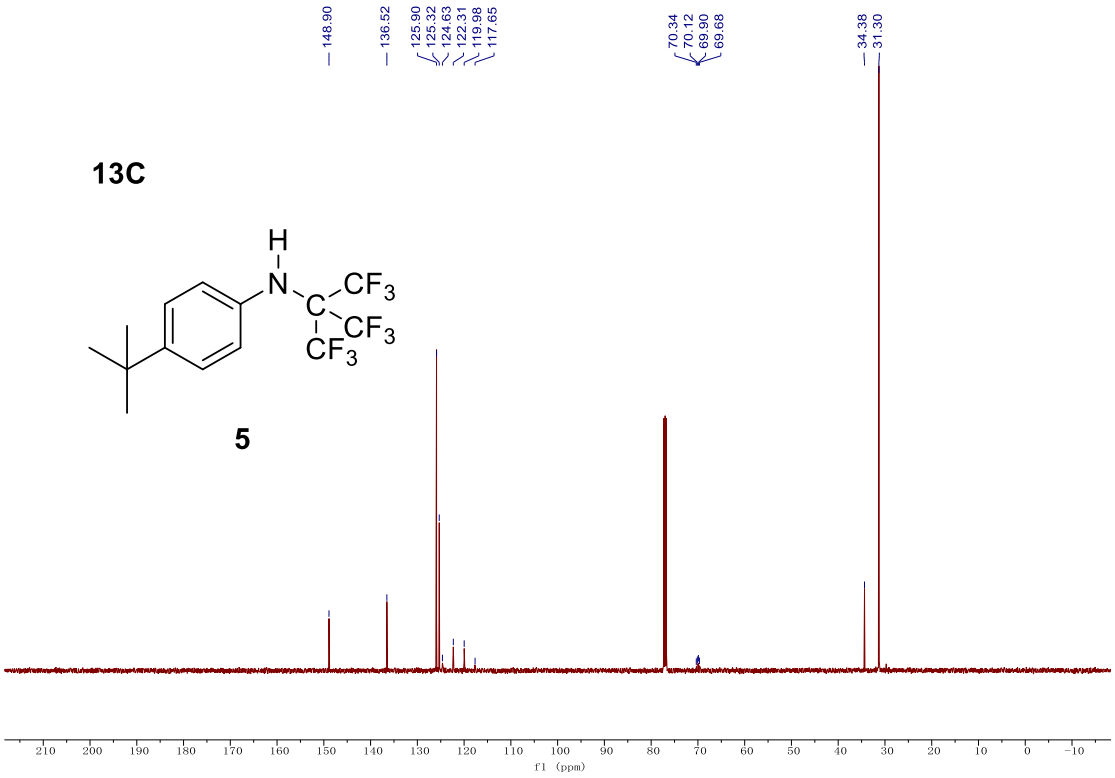
7.31
7.29
7.08
7.07
3.89
1.31
2.00
2.00
0.93
9.24
f1 (ppm)

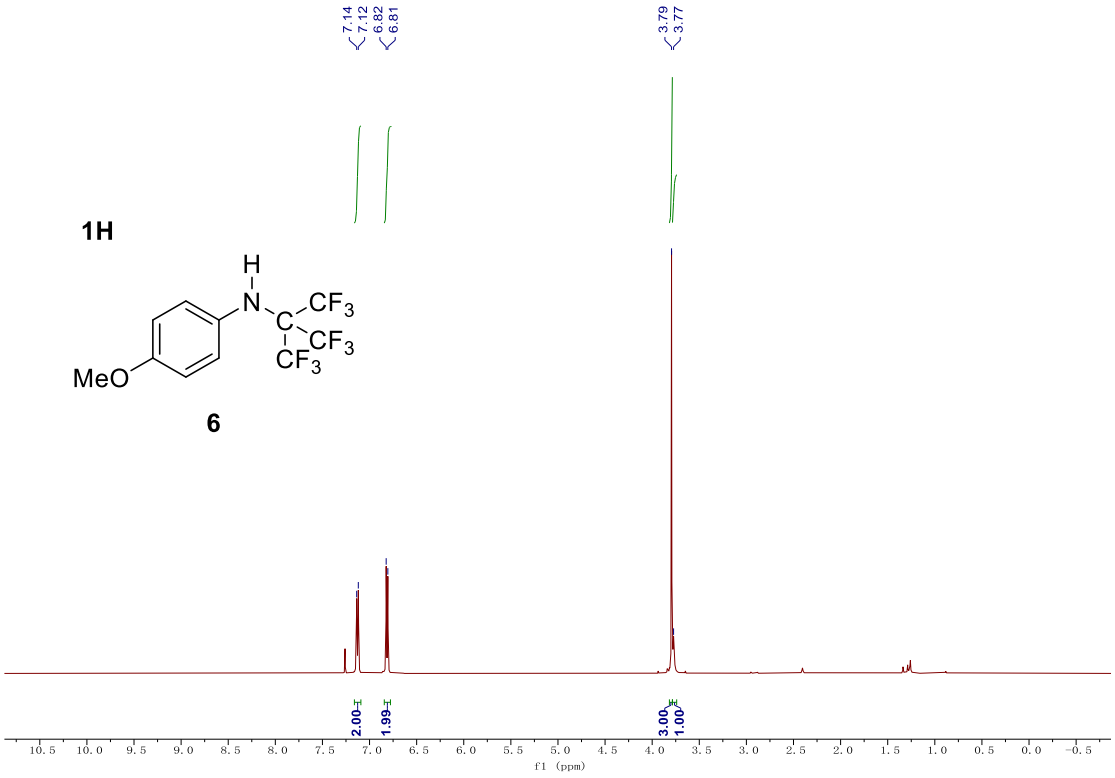
19F

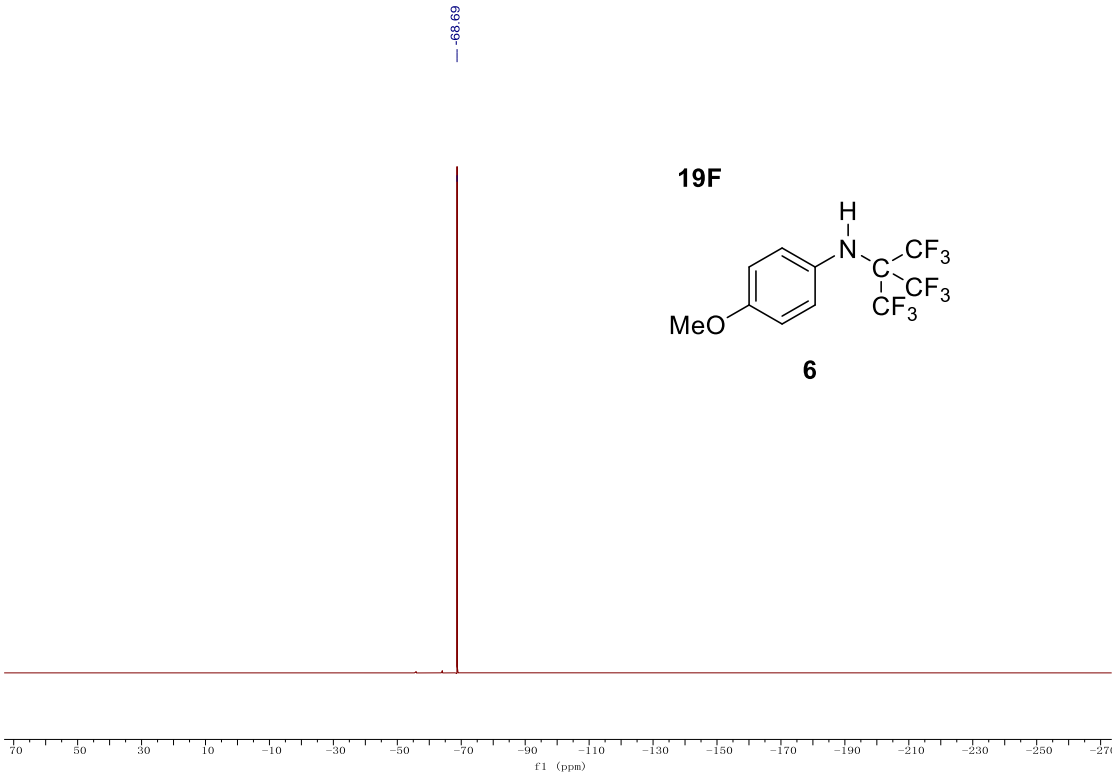

H
N
C
CF3
CF3
CF3

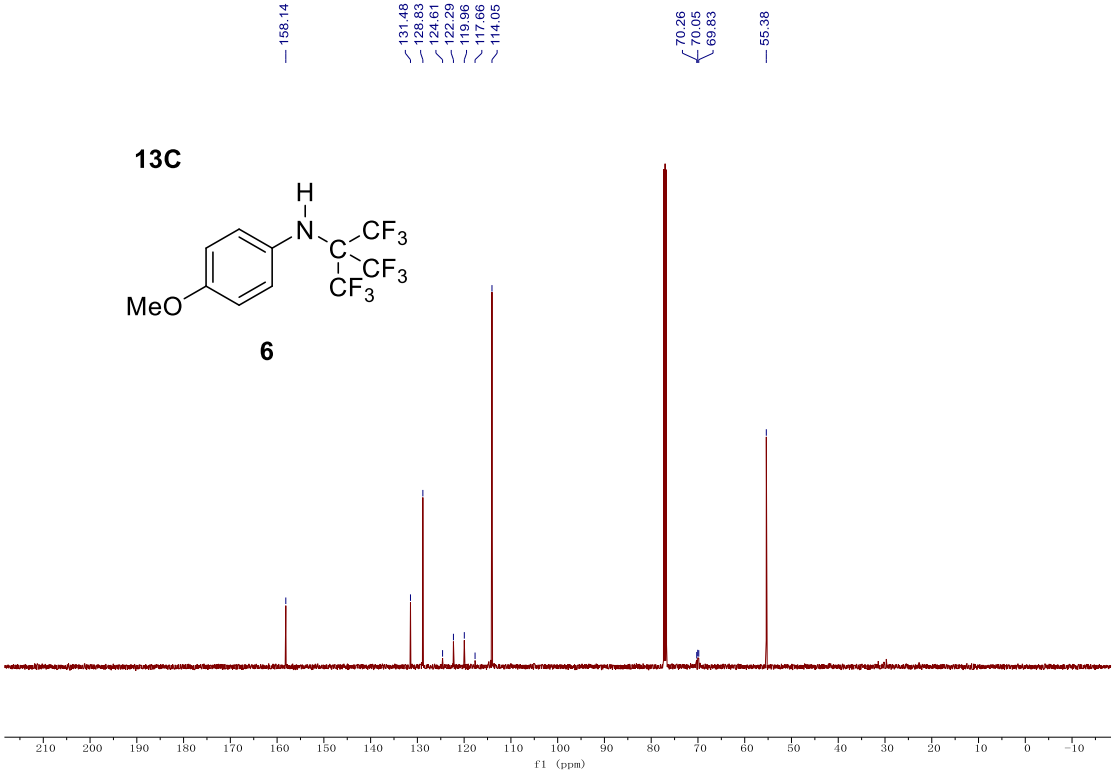
5

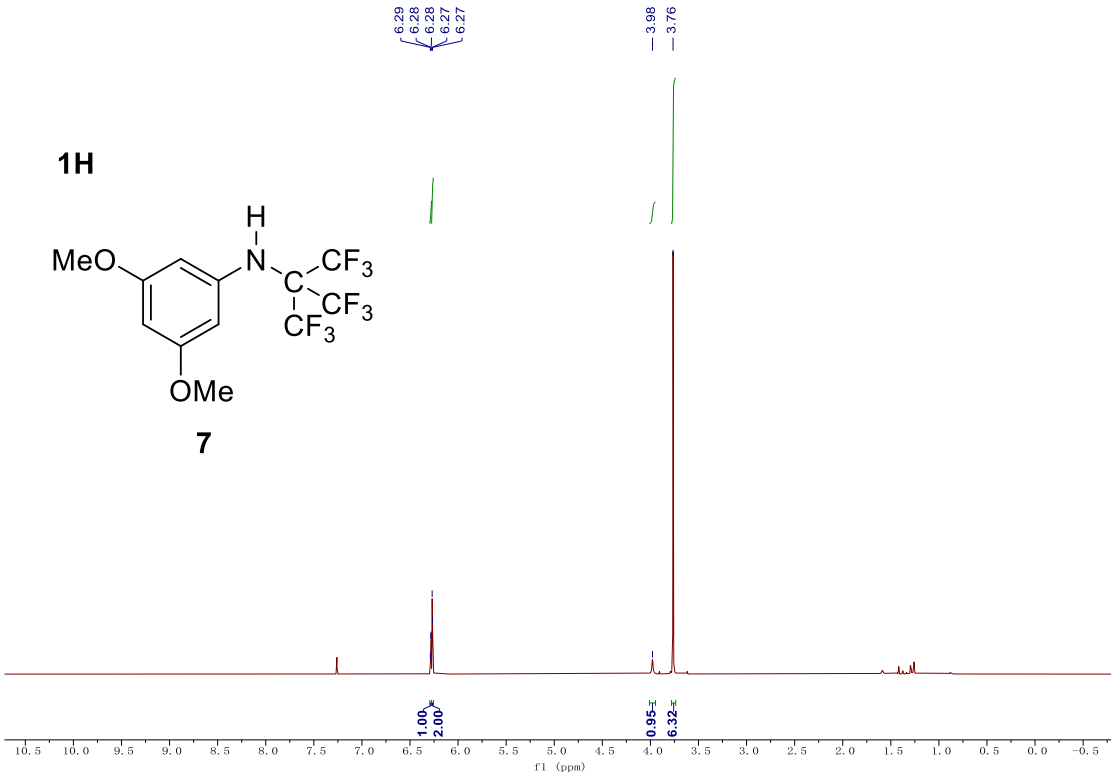
-68.72
f1 (ppm)

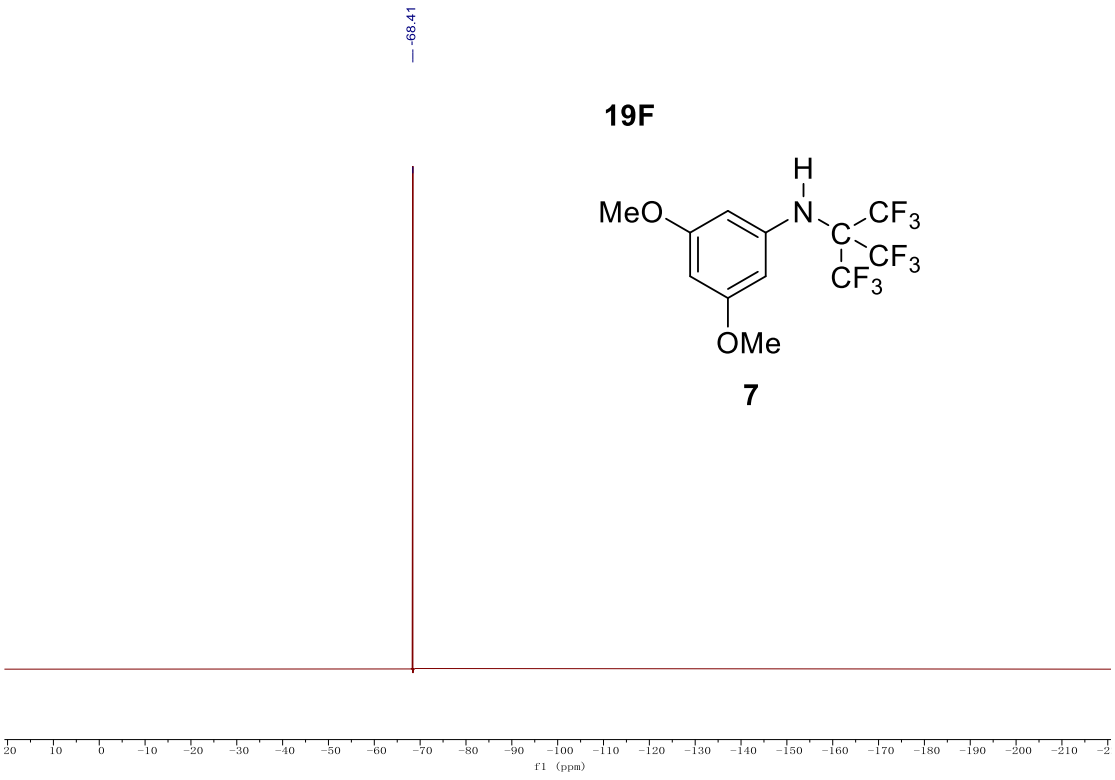

13C
148.90
136.52
125.90
125.32
124.63
122.31
119.98
117.65
70.34
70.12
69.90
69.68
34.38
31.30
H
N
C
CF3
CF3
CF3
5
f1 (ppm)

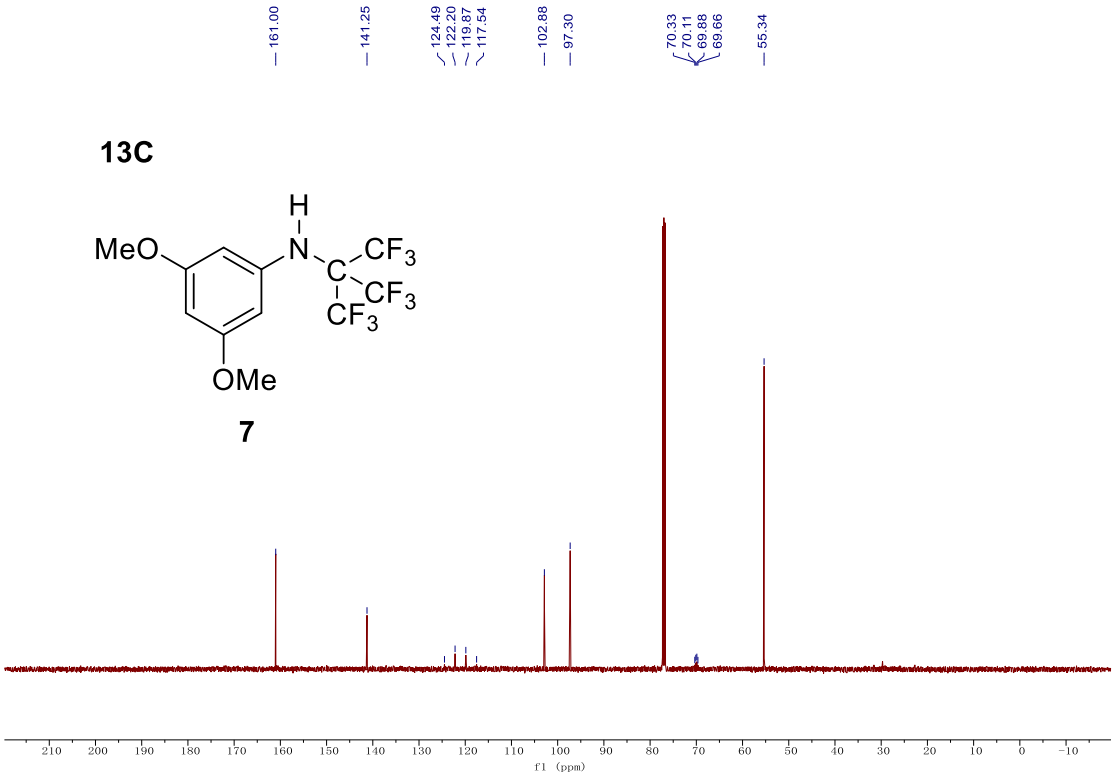

1H
7.14
7.12
6.82
6.81
3.79
3.77
H
N
C
CF3
CF3
CF3
MeO
6
2.00
1.99
3.00
1.00
f1 (ppm)

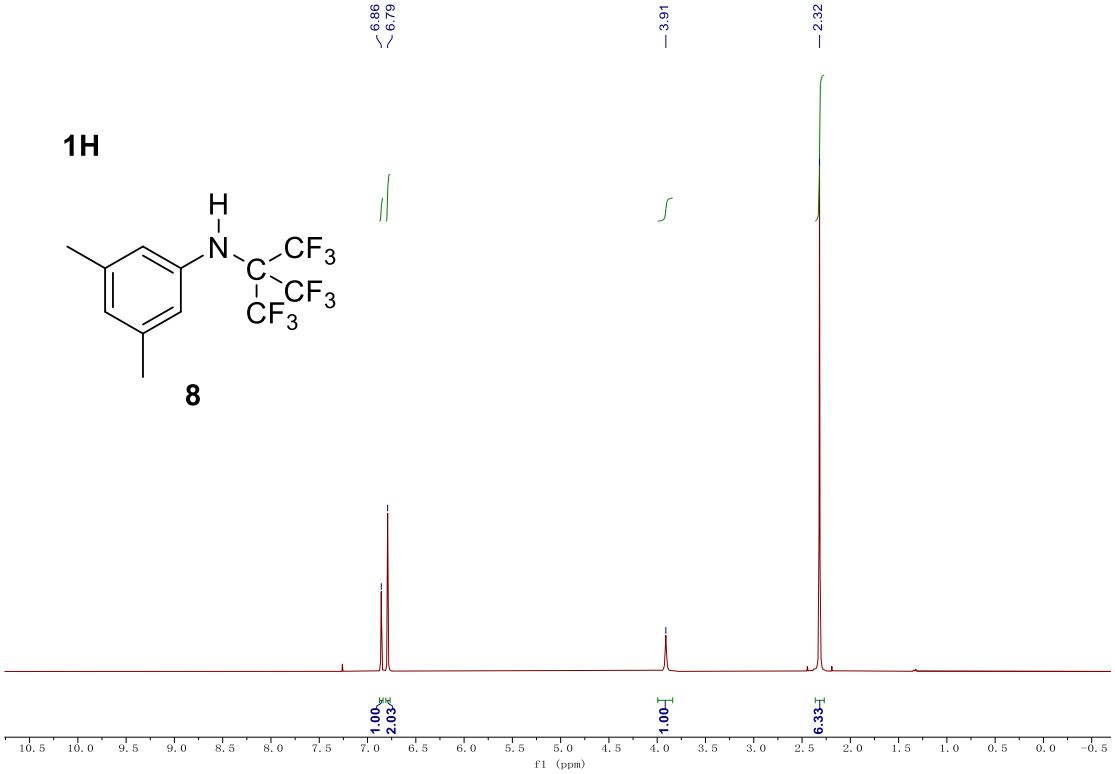

-68.69
19F
H
N
C
CF3
CF3
CF3
MeO
6
f1 (ppm)

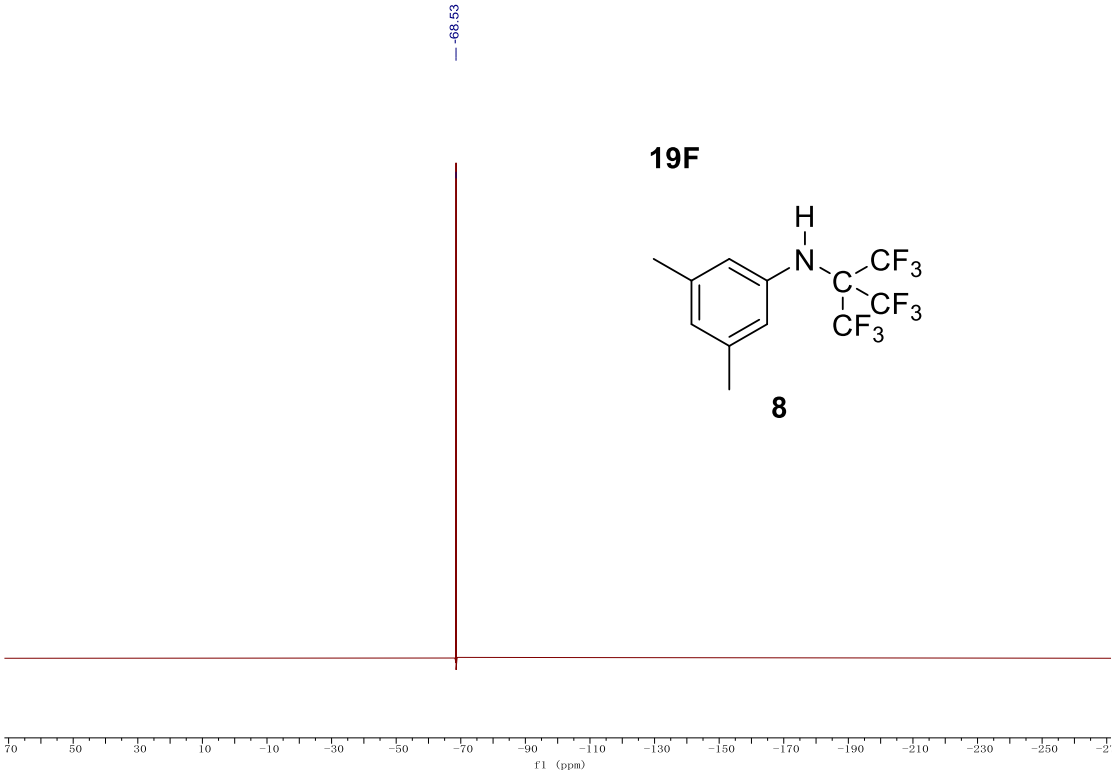

158.14
131.48
128.83
124.61
122.29
119.96
117.66
114.05
70.26
70.05
69.83
55.38
13C
H
N
C
CF3
CF3
CF3
MeO
6
f1 (ppm)

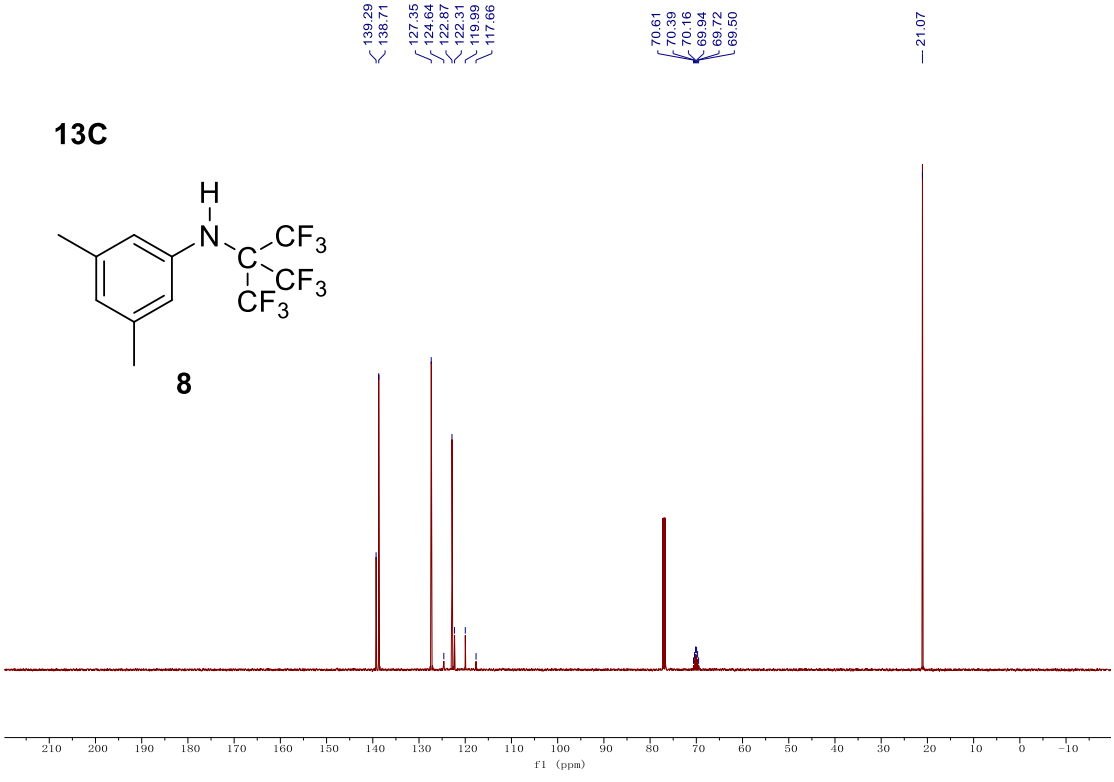

1H
6.29
6.28
6.28
6.27
6.27
3.98
3.76
MeO
H
N
C
CF3
CF3
CF3
OMe
7
1.00
2.00
0.95
6.32
f1 (ppm)

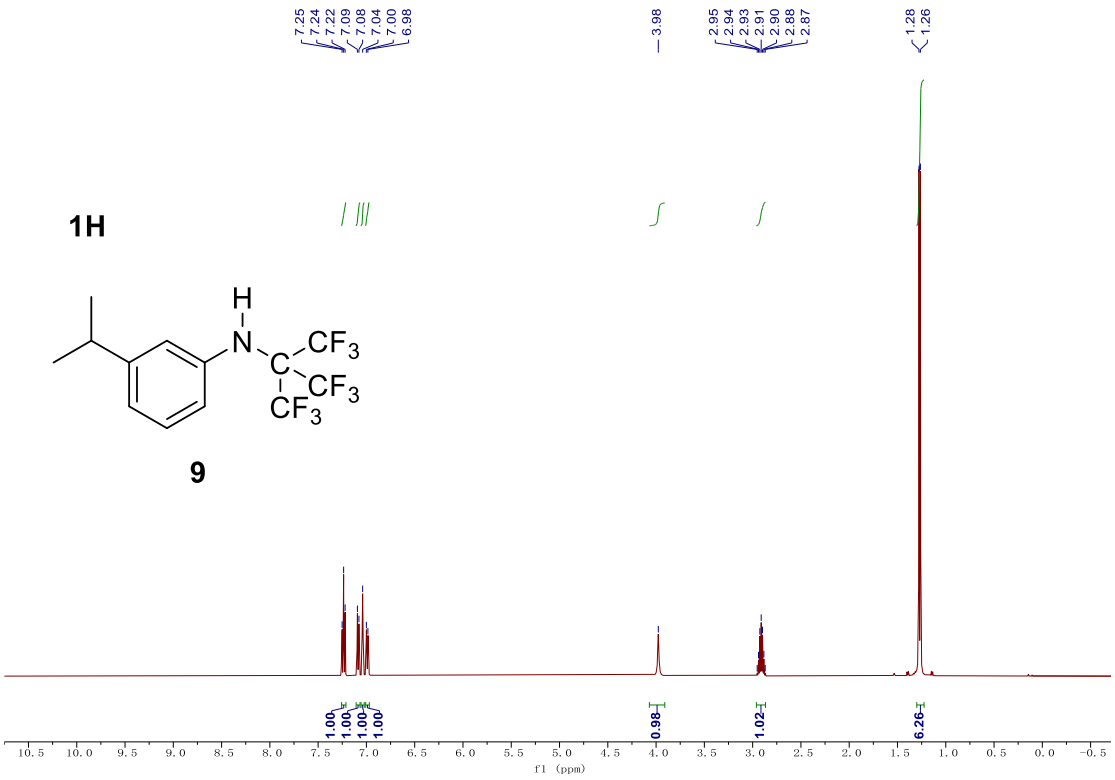

-68.41
19F
MeO
H
N
C
CF3
CF3
CF3
OMe
7
f1 (ppm)

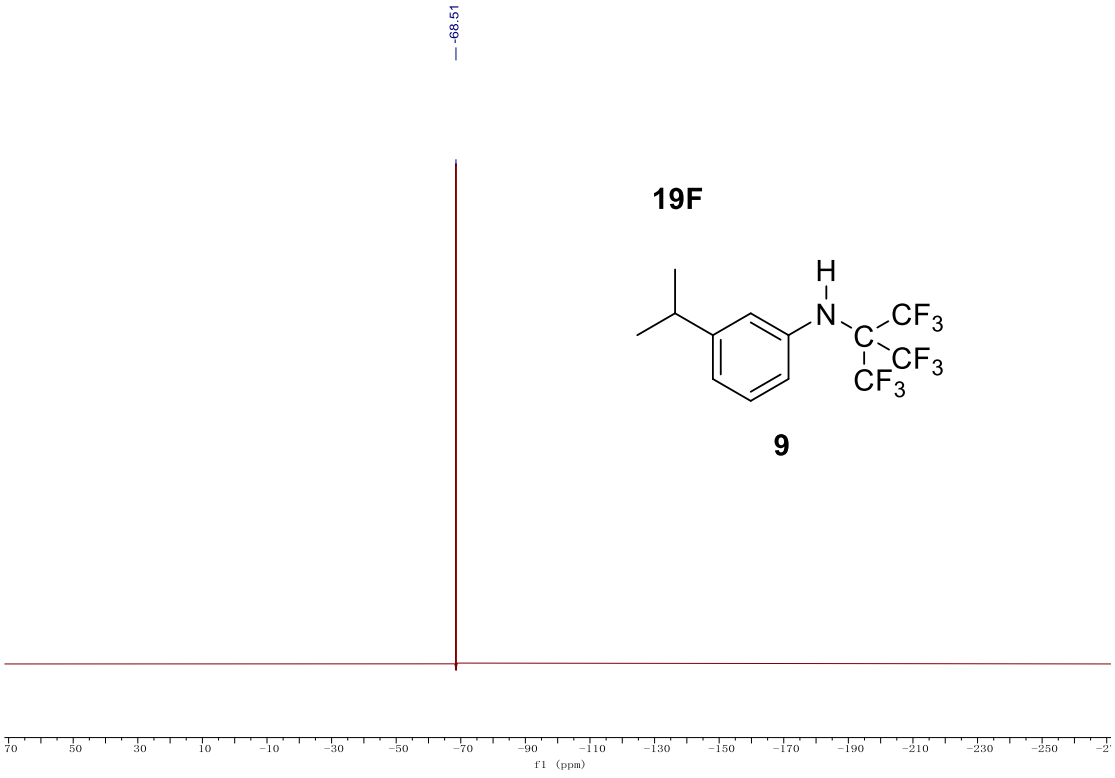

161.00
141.25
124.49
122.20
119.87
117.54
102.88
97.30
70.33
70.11
69.88
69.66
55.34
13C
MeO
OMe
H
N
C
CF3
CF3
CF3
7
f1 (ppm)

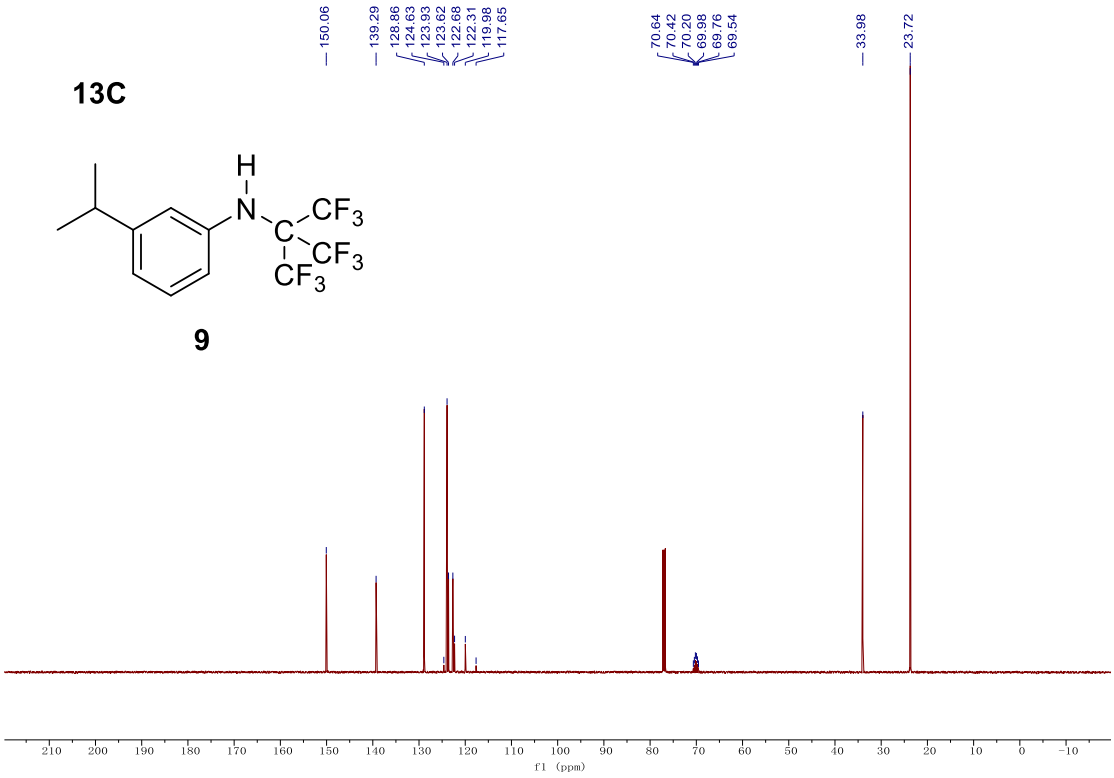

6.86
6.79
3.91
2.32
1H
H
N
C
CF3
CF3
CF3
8
1.00
2.03
1.00
6.33
f1 (ppm)

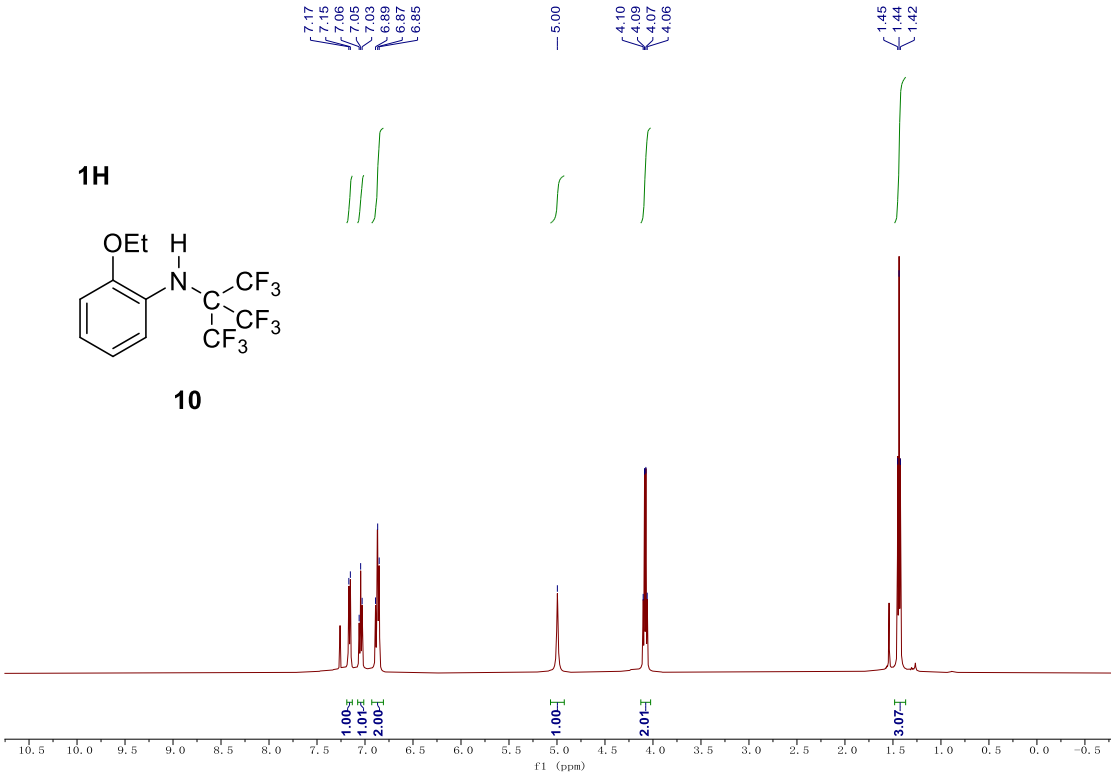

-68.53
19F
H
N
C
CF3
CF3
CF3
8
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)


139.29
138.71
127.35
124.64
122.87
122.31
119.99
117.66
70.61
70.39
70.16
69.94
69.72
69.50
21.07
13C
H
N
C
CF3
CF3
CF3
8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

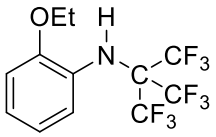

7.25
7.24
7.22
7.09
7.08
7.04
7.00
6.98
3.98
2.95
2.94
2.93
2.91
2.90
2.88
2.87
1.28
1.26
1H
H
N
C
CF3
CF3
CF3
9
1.00
1.00
1.00
1.00
0.98
1.02
6.26
f1 (ppm)


-68.51
19F
H
N
C
CF3
CF3
CF3
9
f1 (ppm)


13C
150.06
139.29
128.86
124.63
123.93
123.62
122.68
122.31
119.98
117.65
70.64
70.42
70.20
69.98
69.76
69.54
33.98
23.72
H
N
C
CF3
CF3
CF3
9
f1 (ppm)


1H
7.17
7.15
7.06
7.05
7.03
6.89
6.87
6.85
5.00
4.10
4.09
4.07
4.06
1.45
1.44
1.42
OEt
H
N
C
CF3
CF3
CF3
10
1.00
1.01
2.00
1.00
2.01
3.07
f1 (ppm)

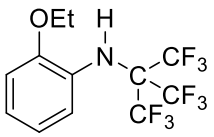
19F


OEt
H
N
C
CF3
CF3
CF3

10

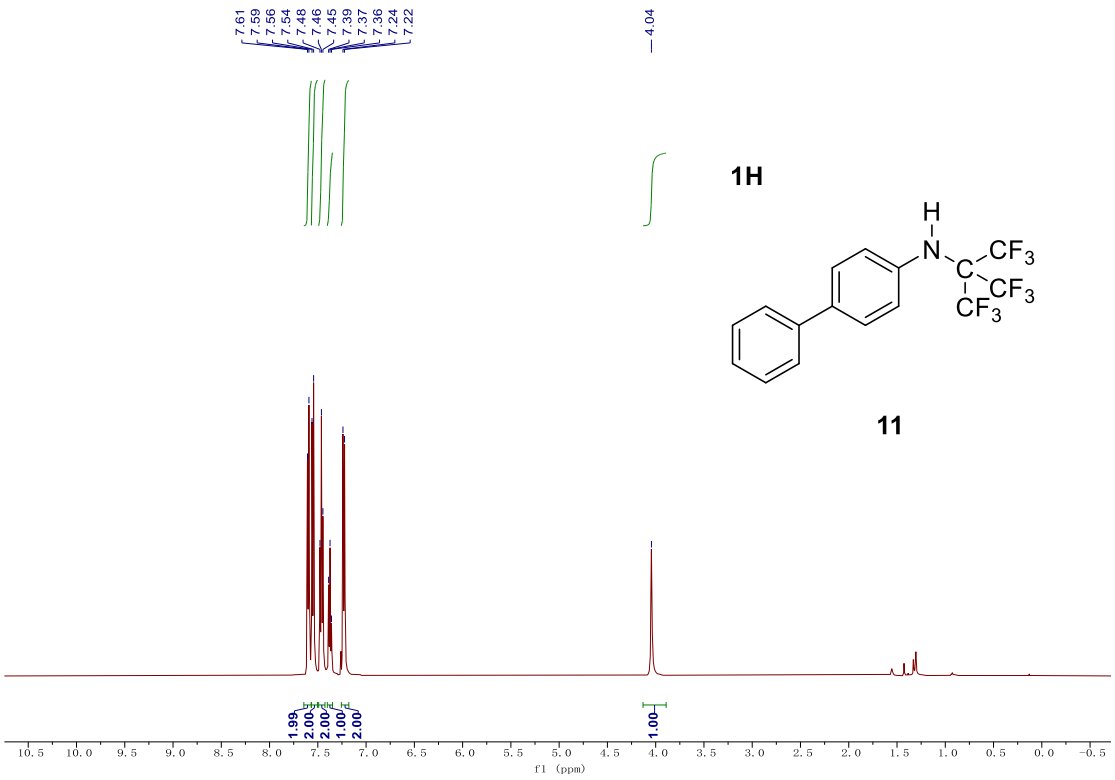
-73.95
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

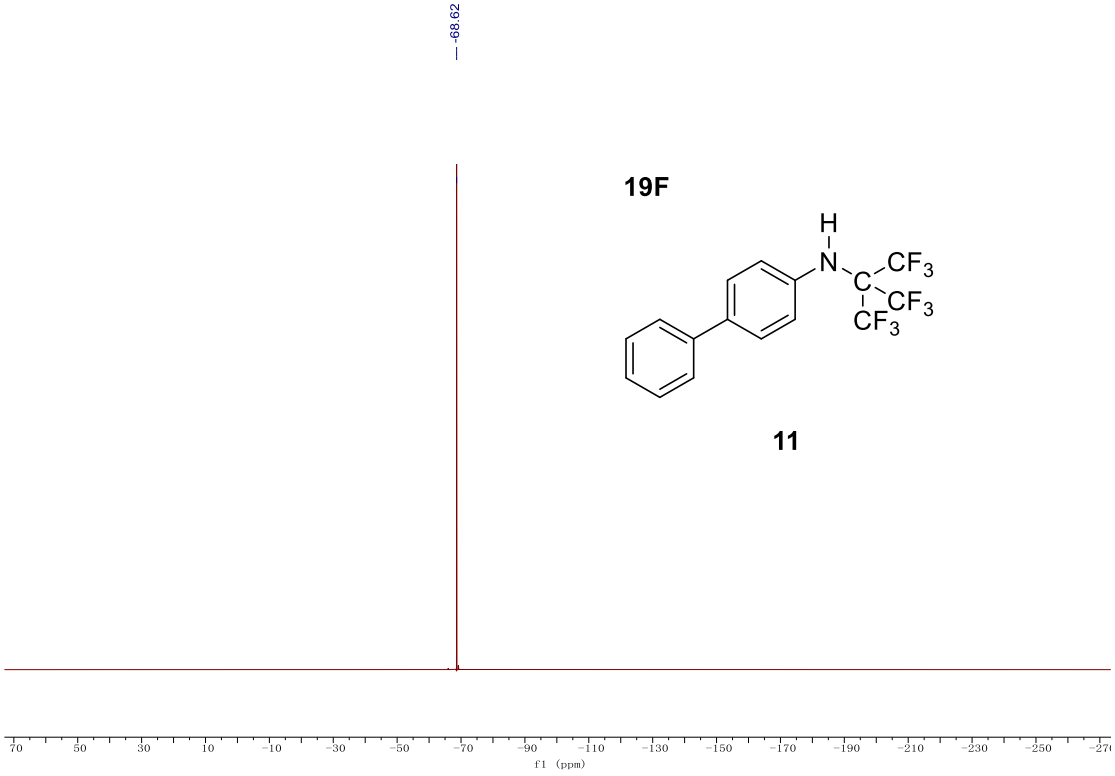
13C

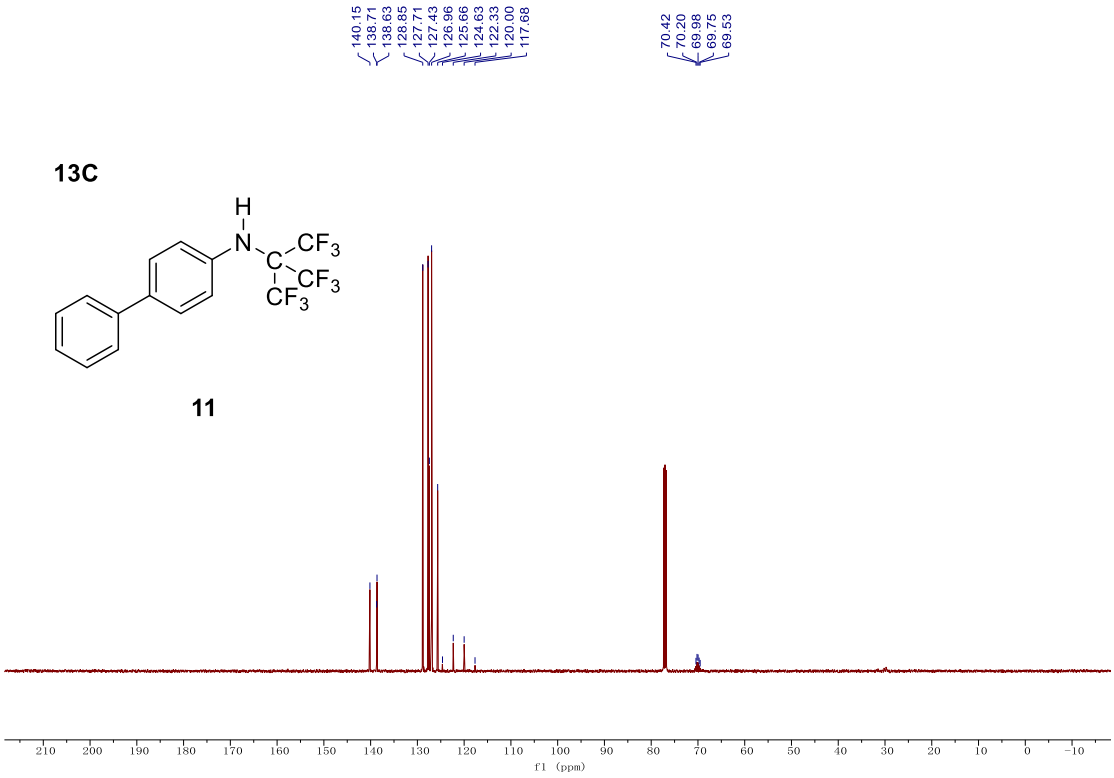

OEt
H
N
C
CF3
CF3
CF3

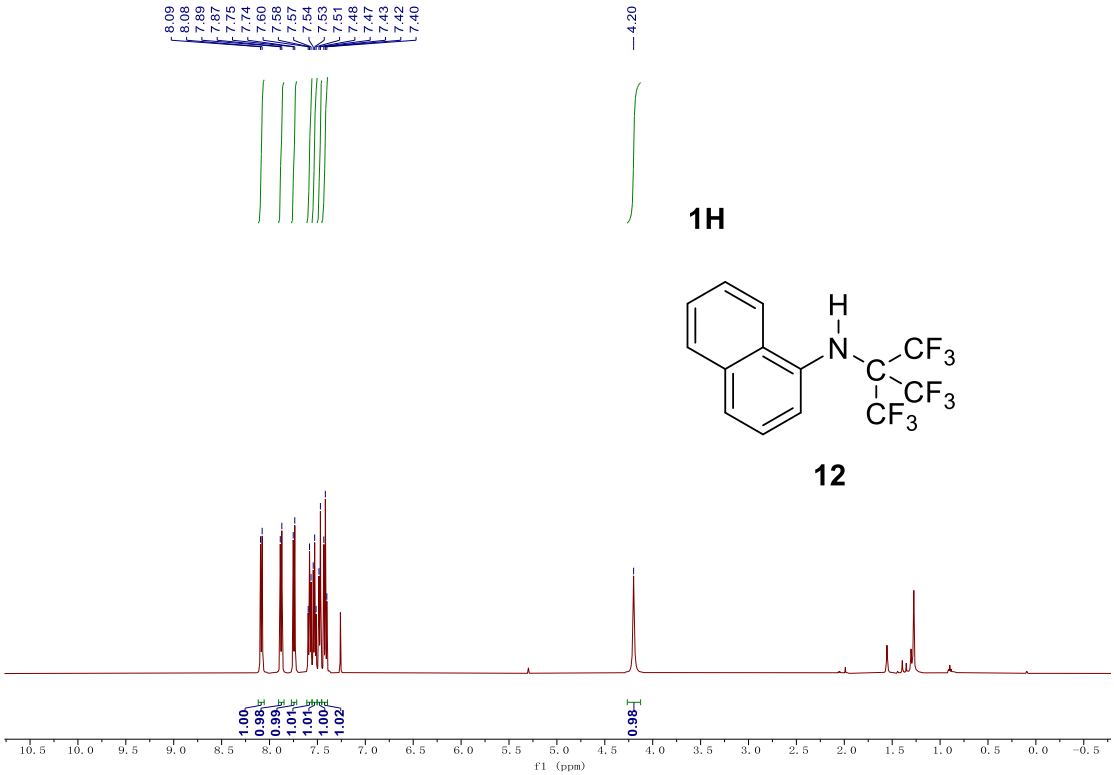
10

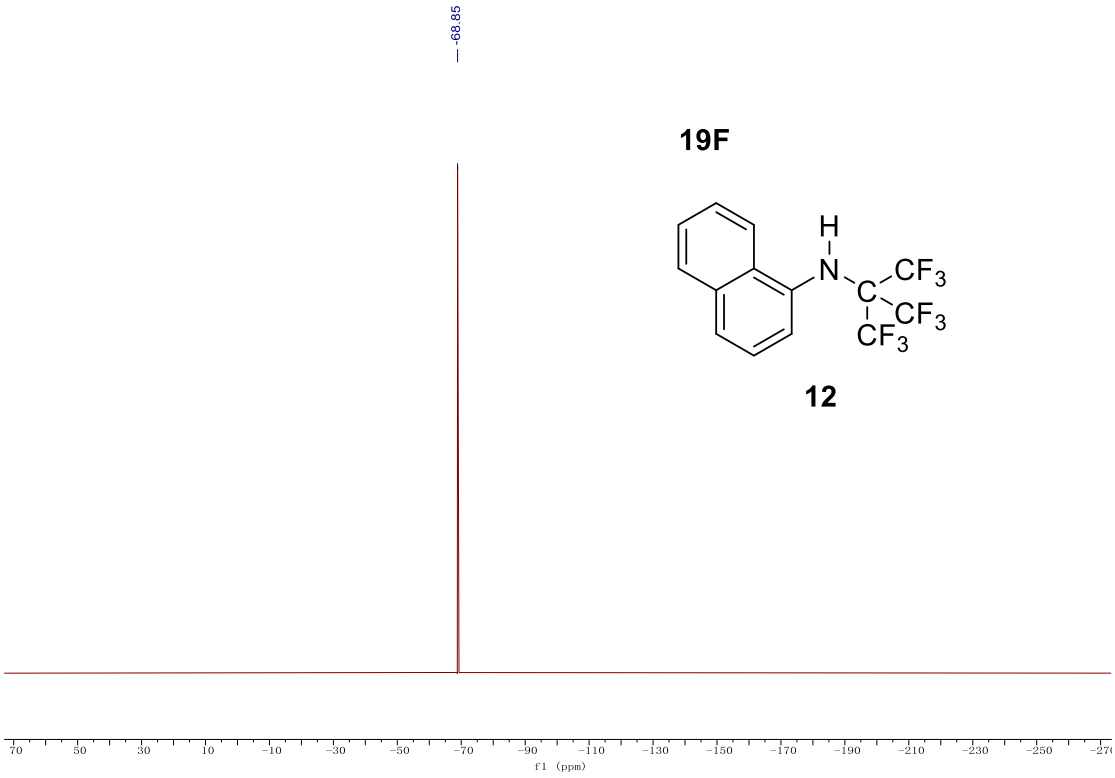
150.79
129.86
124.76
124.56
122.43
121.94
120.65
120.10
117.78
111.30
70.39
70.16
69.94
64.23
14.53
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

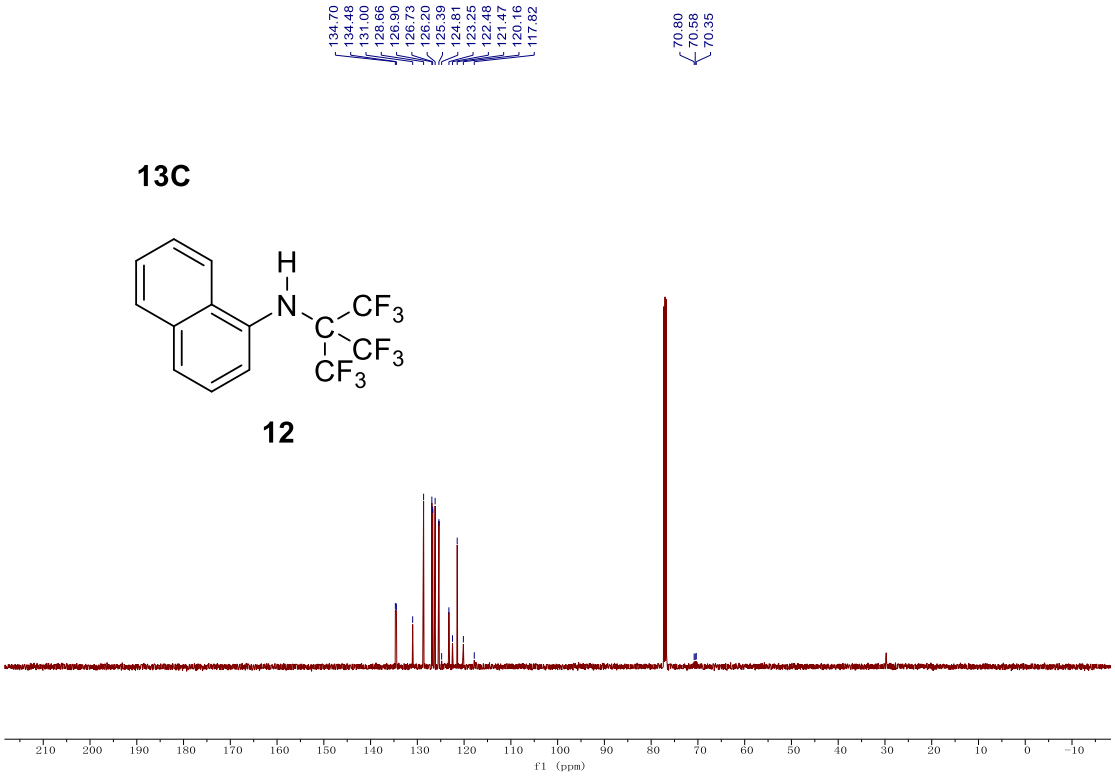

7.61
7.59
7.56
7.54
7.48
7.46
7.45
7.39
7.37
7.36
7.24
7.22
4.04
1H
H
N
C
CF3
CF3
CF3
11
1.99
2.00
2.00
1.00
2.00
1.00
f1 (ppm)

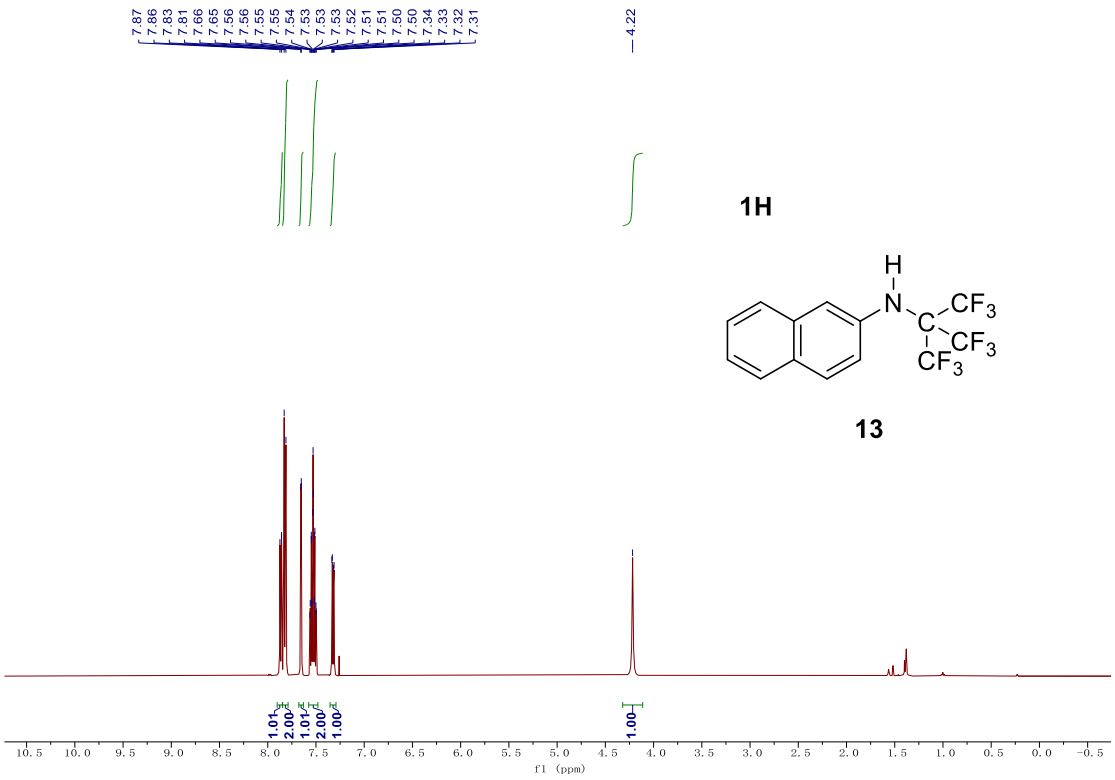

-68.62
19F
H
N
C
CF3
CF3
CF3
11
f1 (ppm)

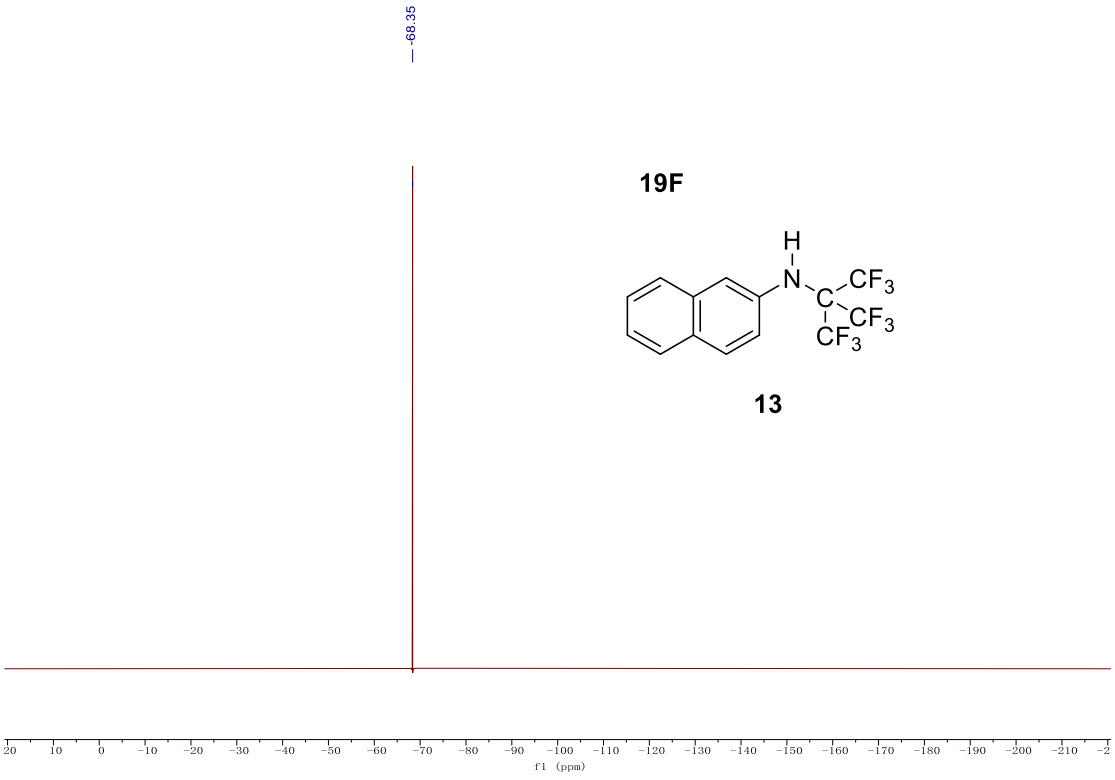

140.15
138.71
138.63
128.85
127.71
127.43
126.96
125.66
124.63
122.33
120.00
117.68
70.42
70.20
69.98
69.75
69.53
13C
H
N
C
CF3
CF3
CF3
11
f1 (ppm)

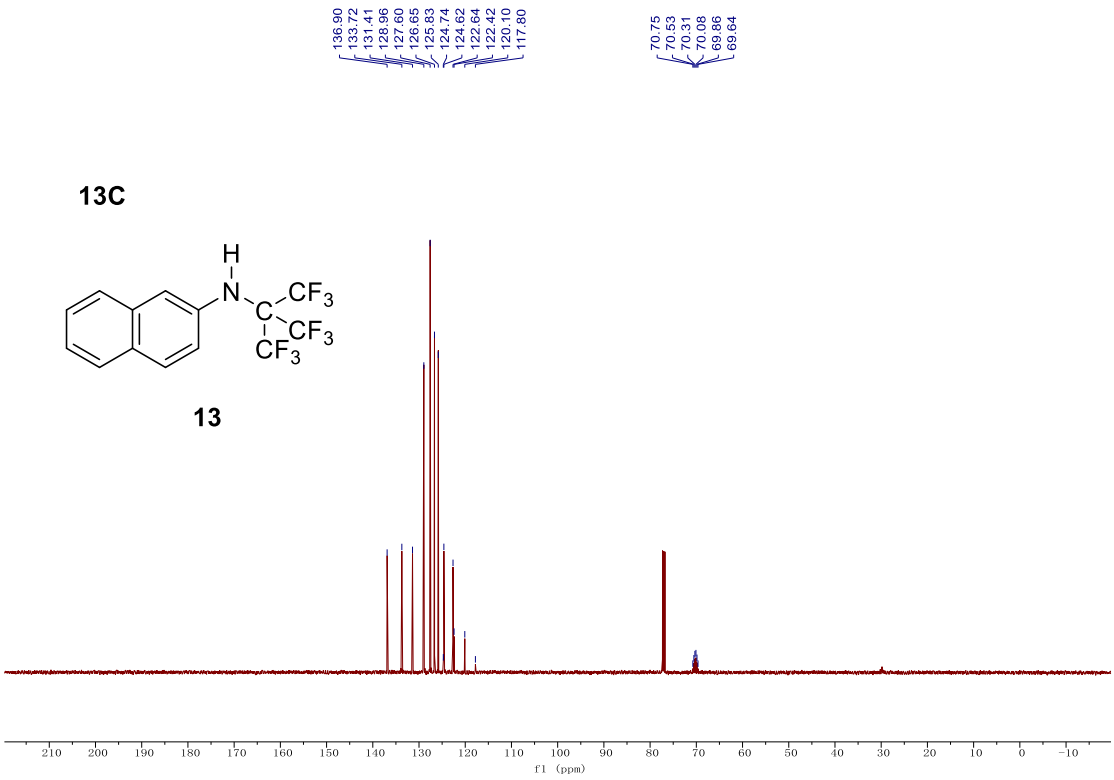

8.09
8.08
7.89
7.87
7.75
7.74
7.60
7.58
7.57
7.54
7.53
7.51
7.48
7.47
7.43
7.42
7.40
4.20
1H
H
N
C
CF3
CF3
CF3
12
1.00
0.98
0.99
1.01
1.01
1.00
1.02
0.98
f1 (ppm)

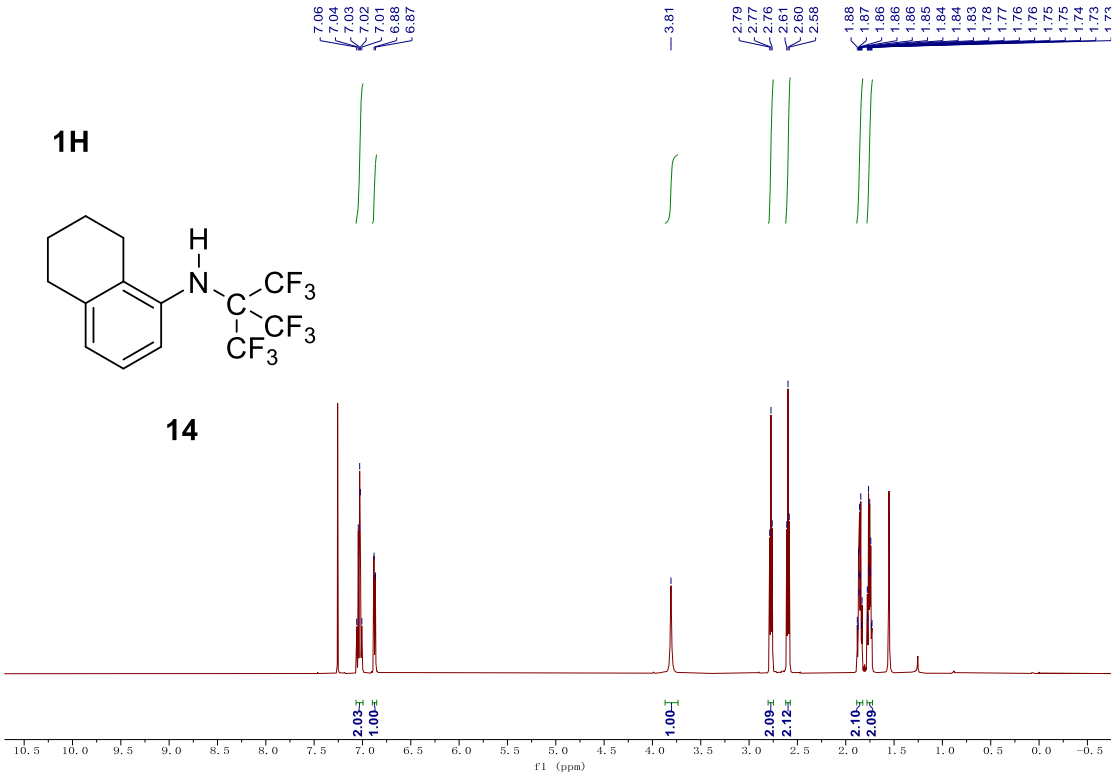

-68.85
19F
H
N
C
CF3
CF3
CF3
12
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

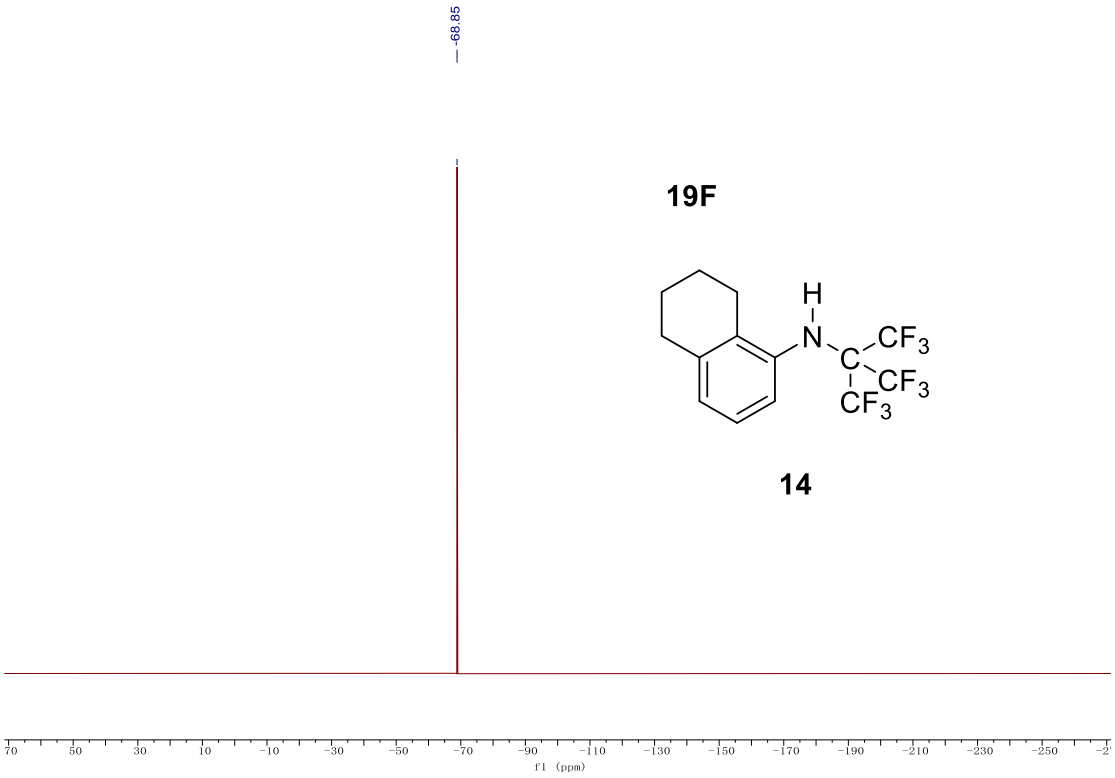

134.70
134.48
131.00
128.66
126.90
126.73
126.20
125.39
124.81
123.25
122.48
121.47
120.16
117.82
70.80
70.58
70.35
13C
H
N
C
CF3
CF3
CF3
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

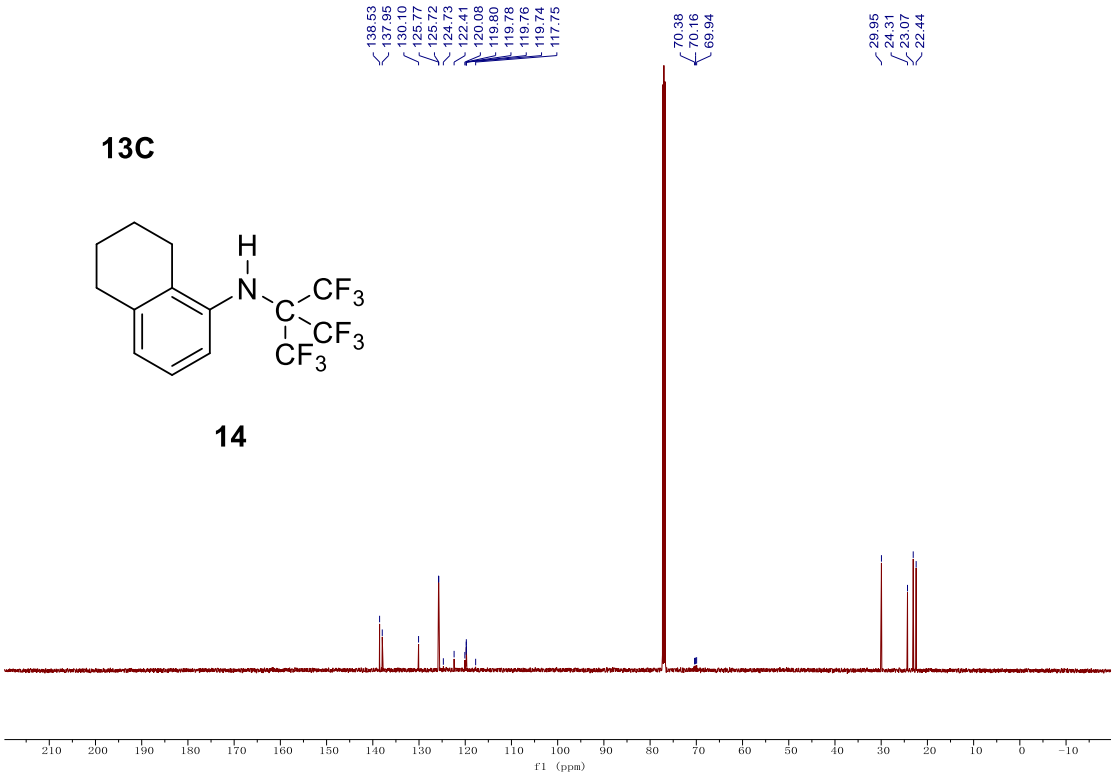

7.87
7.86
7.83
7.81
7.66
7.65
7.56
7.56
7.55
7.55
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.34
7.33
7.32
7.31
4.22
1H
H
N
C
CF3
CF3
CF3
13
1.01
2.00
1.01
2.00
1.00
1.00
f1 (ppm)

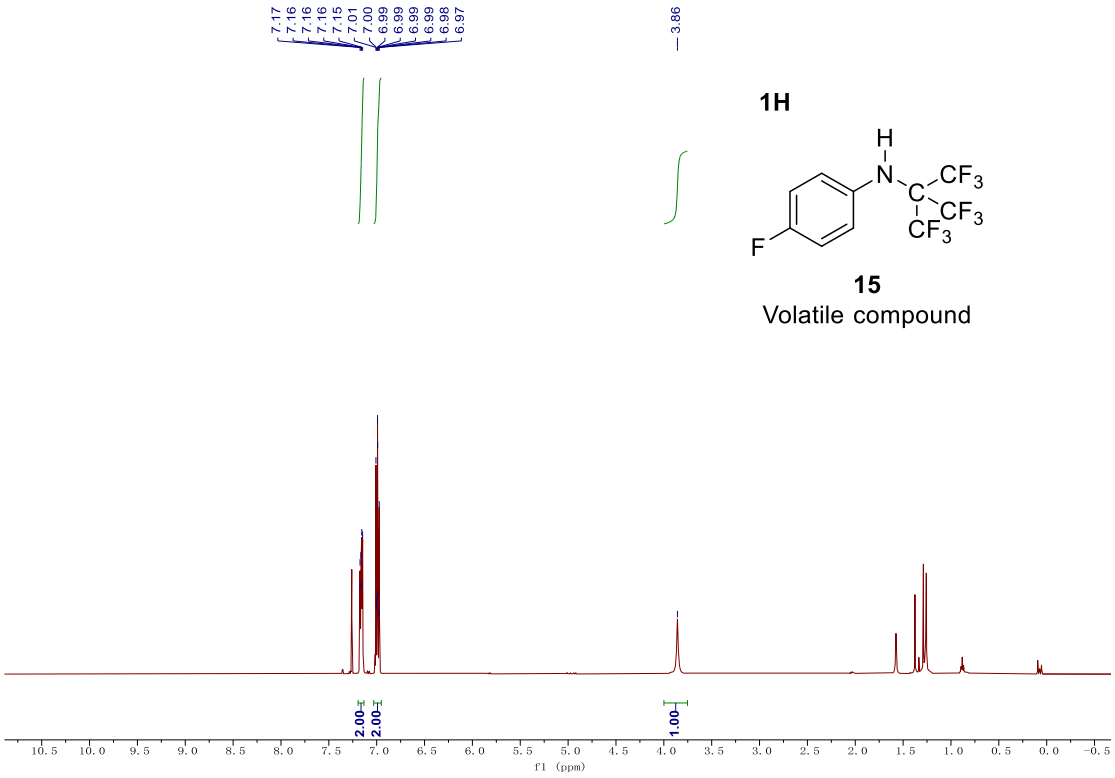

-68.35
19F
H
N
C
CF3
CF3
CF3
13
f1 (ppm)

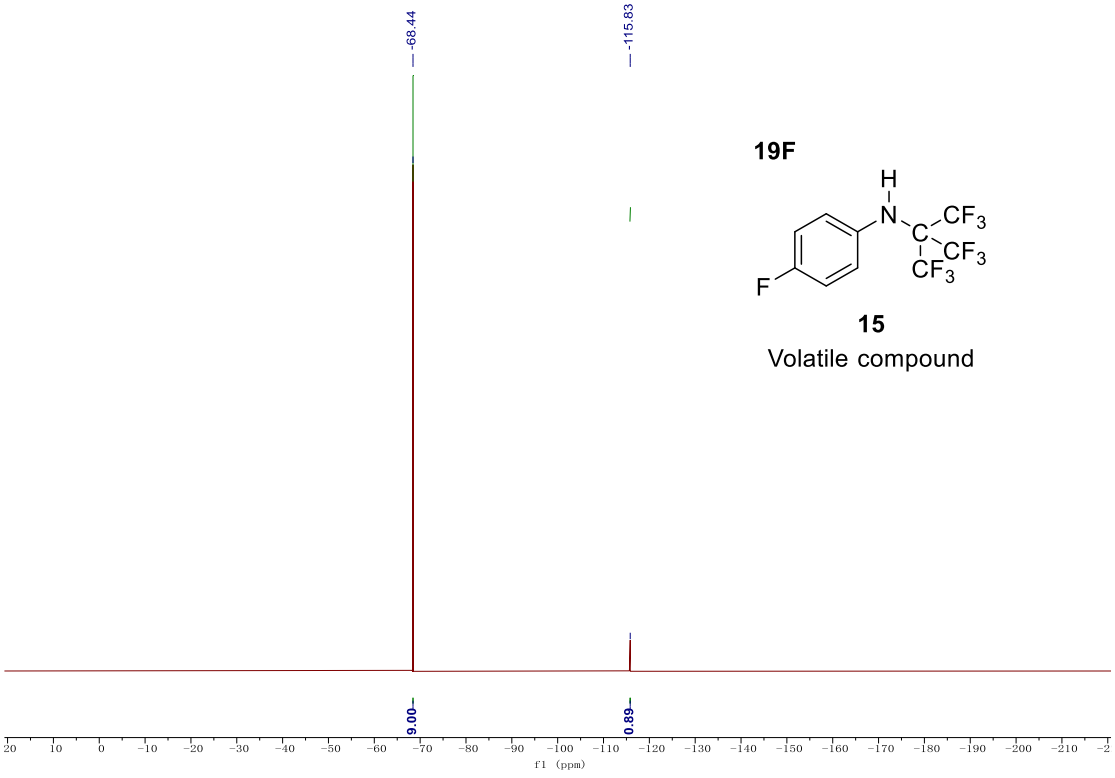

136.90
133.72
131.41
128.96
127.60
126.65
125.83
124.74
124.62
122.64
122.42
120.10
117.80
70.75
70.53
70.31
70.08
69.86
69.64
13C
H
N
C
CF3
CF3
CF3
13
f1 (ppm)

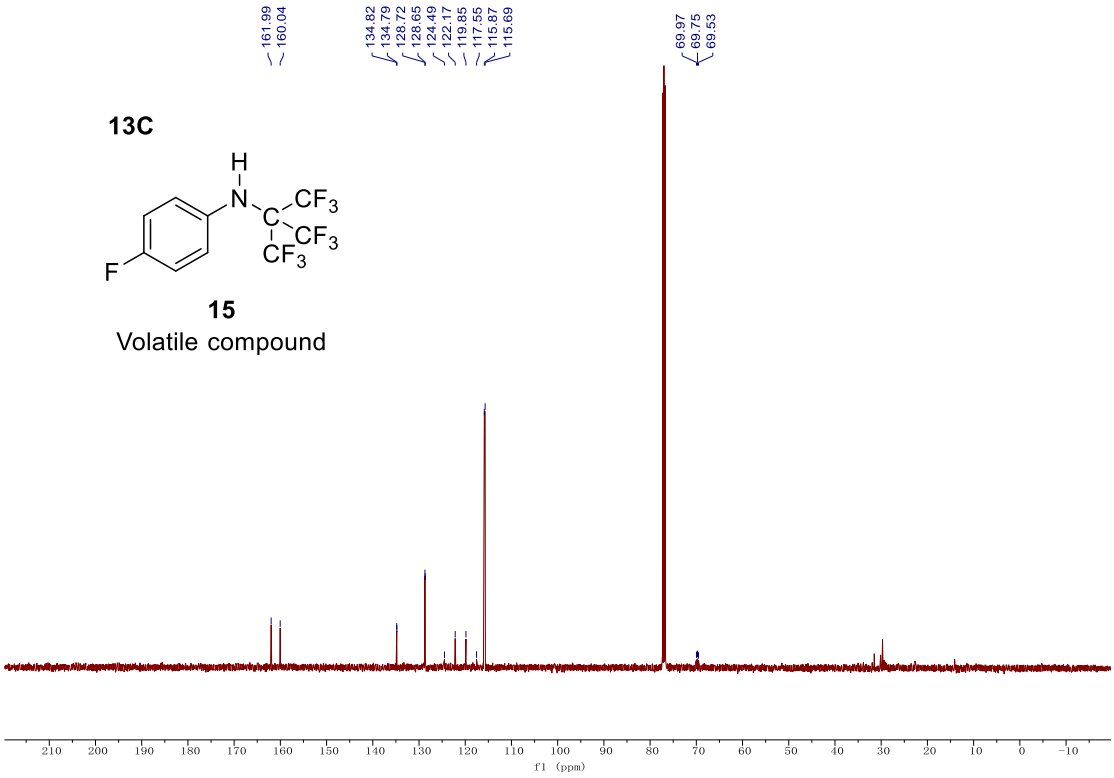

7.06
7.04
7.03
7.02
7.01
6.88
6.87
3.81
2.79
2.77
2.76
2.61
2.60
2.58
1.88
1.87
1.86
1.86
1.86
1.85
1.84
1.84
1.83
1.78
1.77
1.76
1.76
1.75
1.75
1.74
1.73
1H
H
N
C
CF3
CF3
CF3
14
2.03
1.00
1.00
2.09
2.12
2.10
2.09
f1 (ppm)

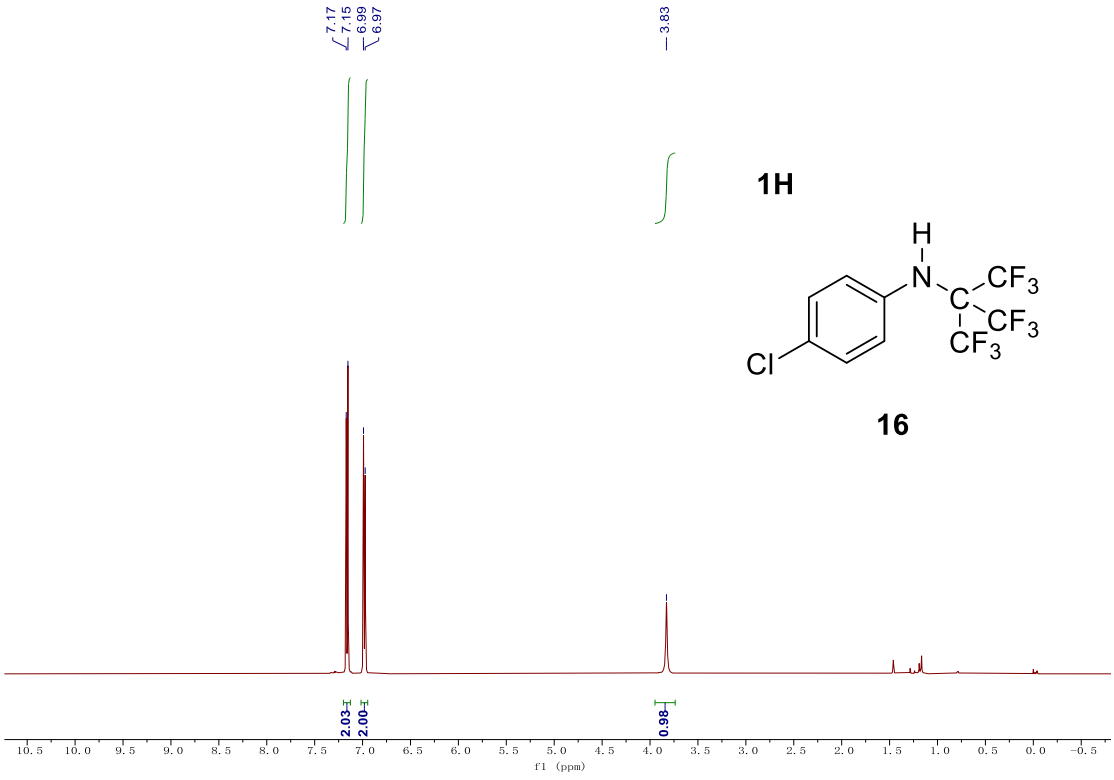

-68.85
19F
H
N
C
CF3
CF3
CF3
14
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)

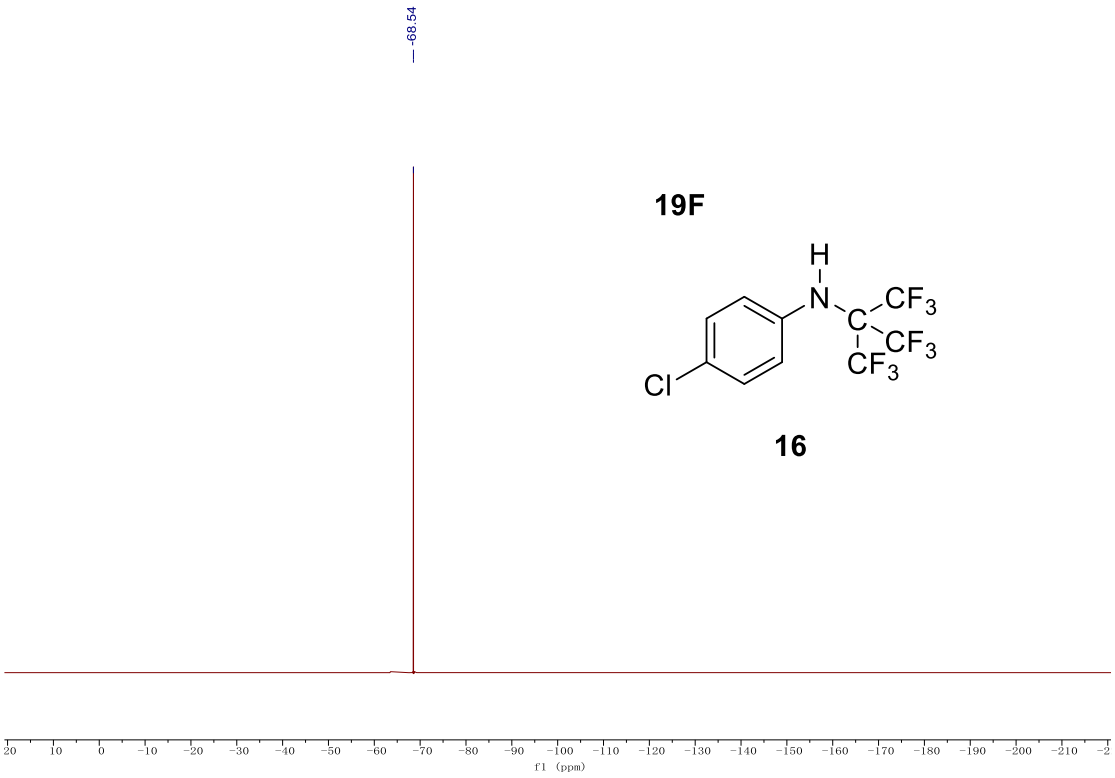

138.53
137.95
130.10
125.77
125.72
124.73
122.41
120.08
119.80
119.78
119.76
119.74
117.75
70.38
70.16
69.94
29.95
24.31
23.07
22.44
13C
H
N
C
CF3
CF3
CF3
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

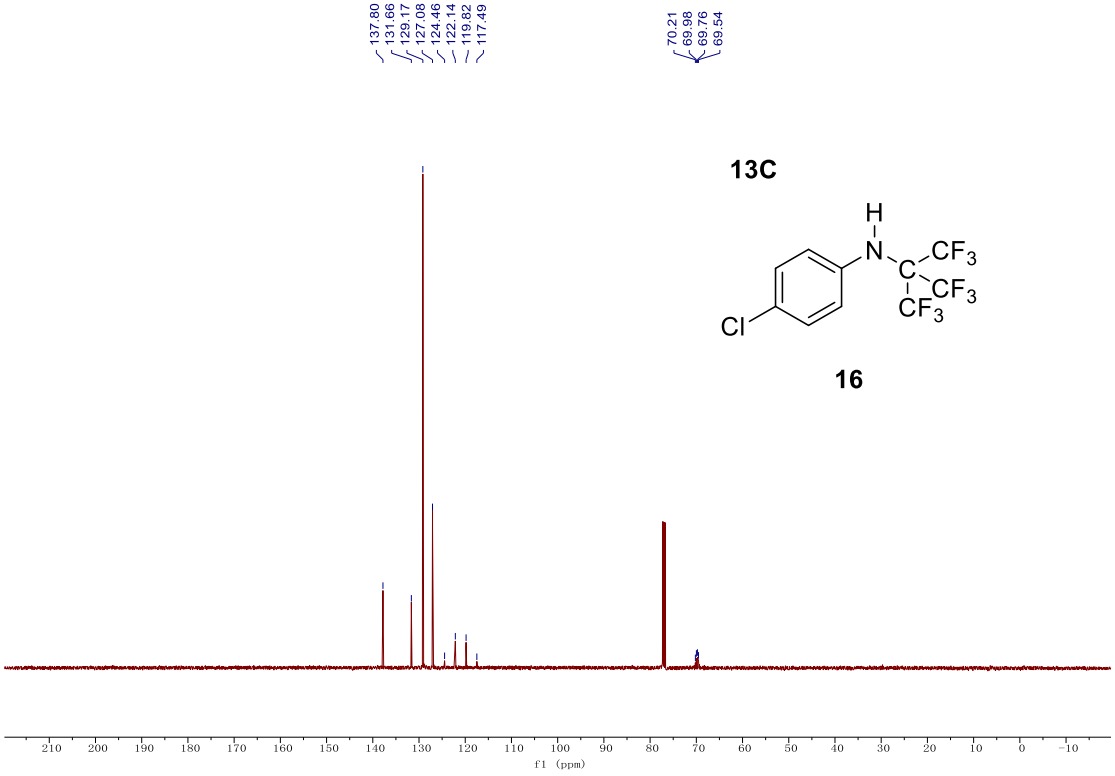

7.17
7.16
7.16
7.16
7.15
7.01
7.00
6.99
6.99
6.99
6.99
6.98
6.97
3.86
1H
H
N
C
CF3
CF3
CF3
F
15
Volatile compound
2.00
2.00
1.00
f1 (ppm)

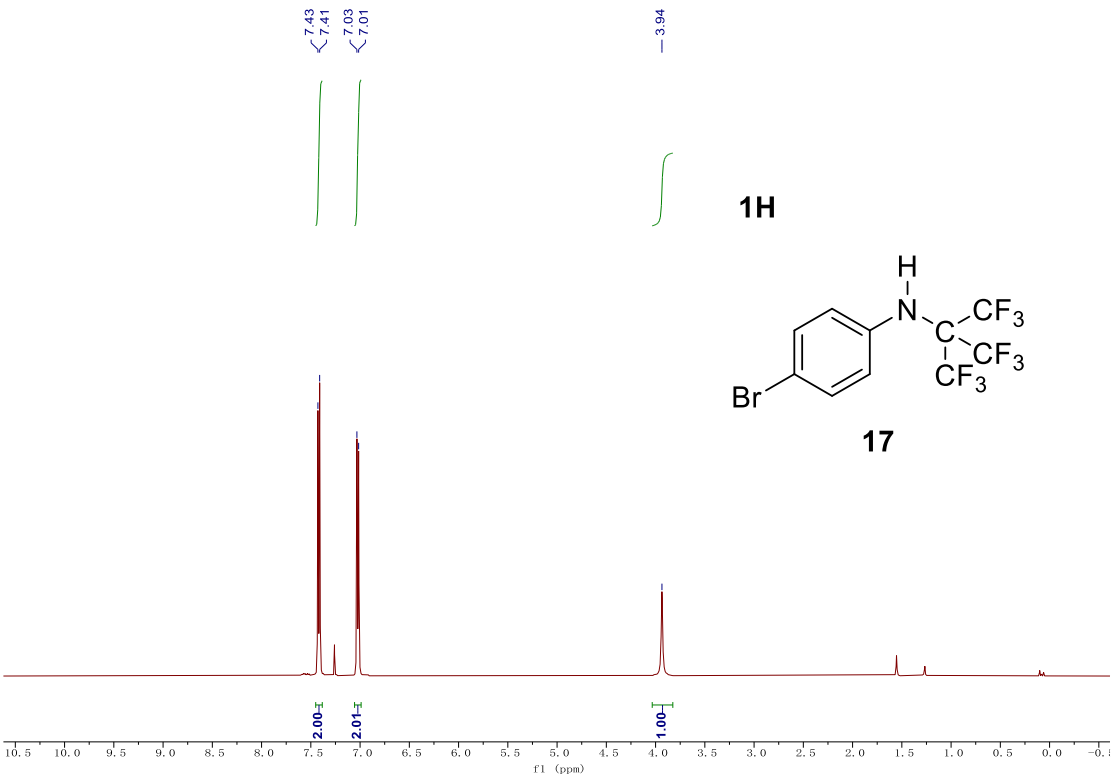

-68.44
-115.83
19F
H
N
C
CF3
CF3
CF3
F
15
Volatile compound
9.00
0.89
f1 (ppm)


161.99
160.04
134.82
134.79
128.72
128.65
124.49
122.17
119.85
117.55
115.87
115.69
69.97
69.75
69.53
13C
H
N
C
CF3
CF3
CF3
F
15
Volatile compound
f1 (ppm)


7.17
7.15
6.99
6.97
3.83
1H
H
N
C
CF3
CF3
CF3
Cl
16
2.03
2.00
0.98
f1 (ppm)


-68.54
19F
H
N
CF3
C
CF3
CF3
Cl
16
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)

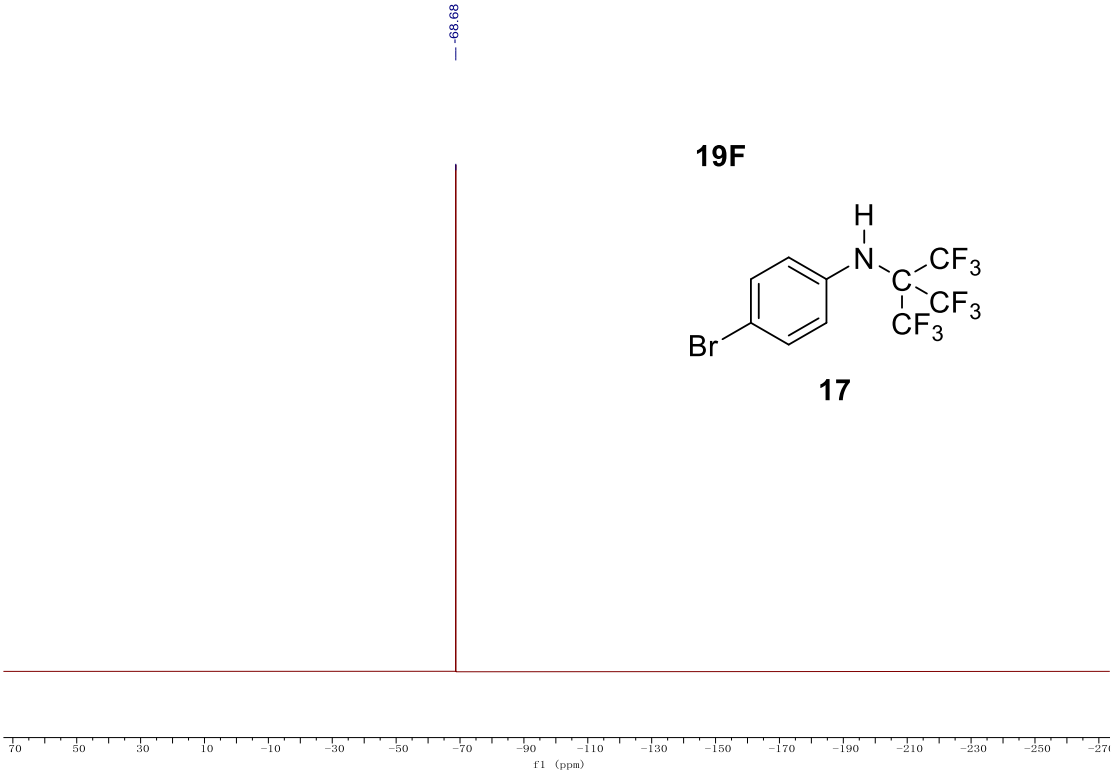

137.80
131.66
129.17
127.08
124.46
122.14
119.82
117.49
70.21
69.98
69.76
69.54
13C
H
N
CF3
C
CF3
CF3
Cl
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.43
7.41
7.03
7.01
3.94
2.00
2.01
1.00
f1 (ppm)

1H

H
N
C
CF3
CF3
CF3
Br

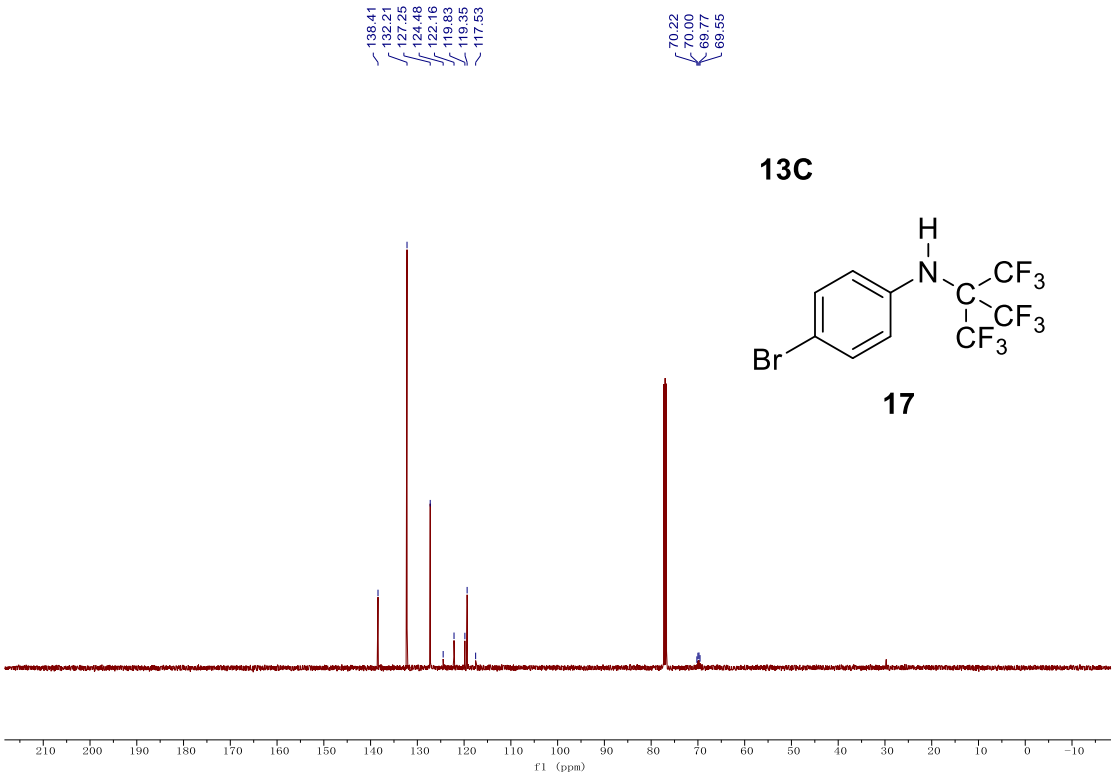
17

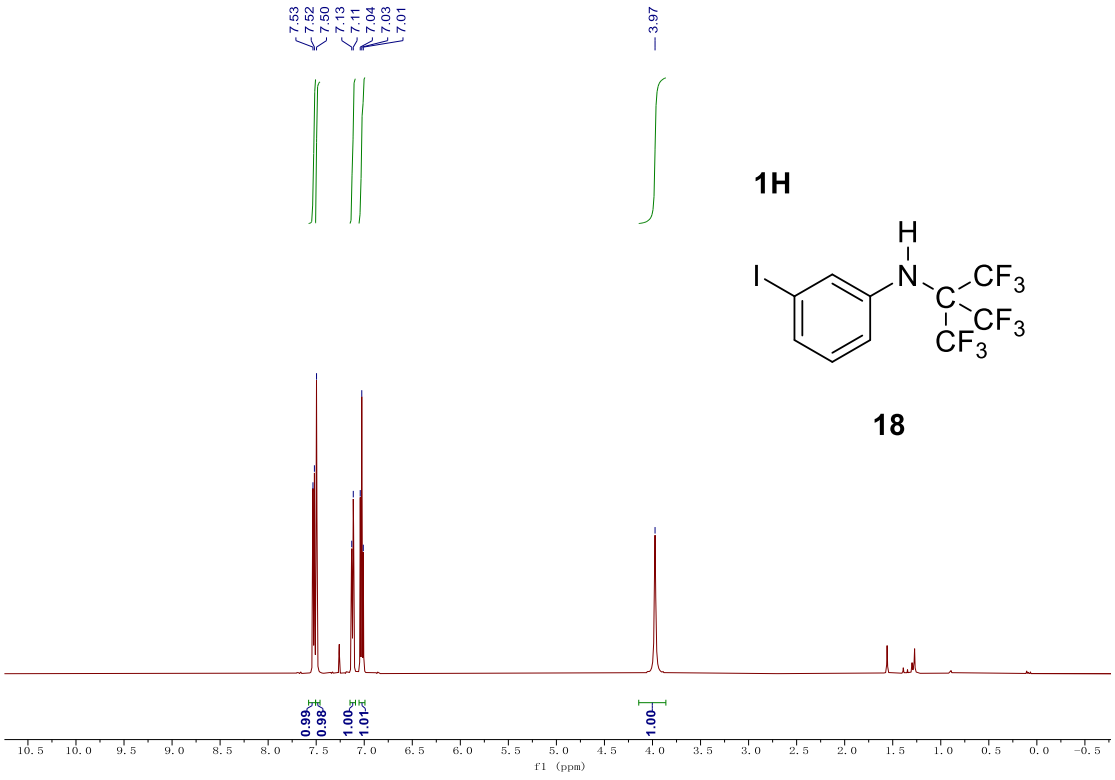

-68.68
f1 (ppm)

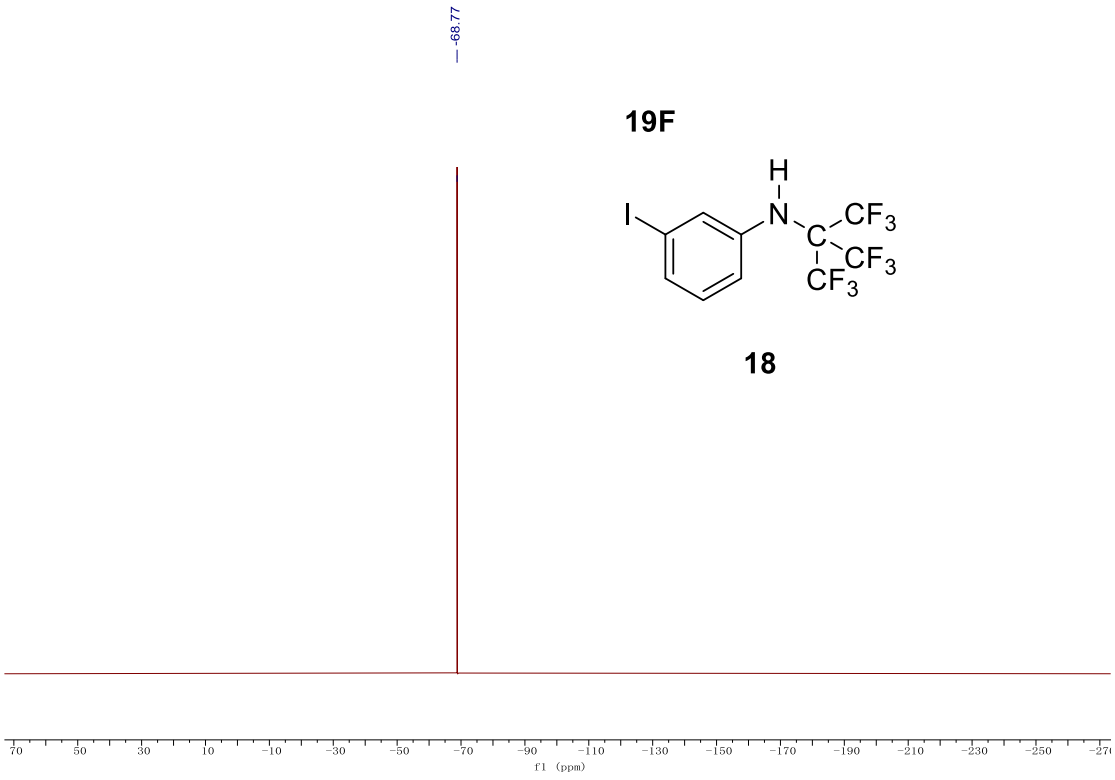
19F

H
N
C
CF3
CF3
CF3
Br

17

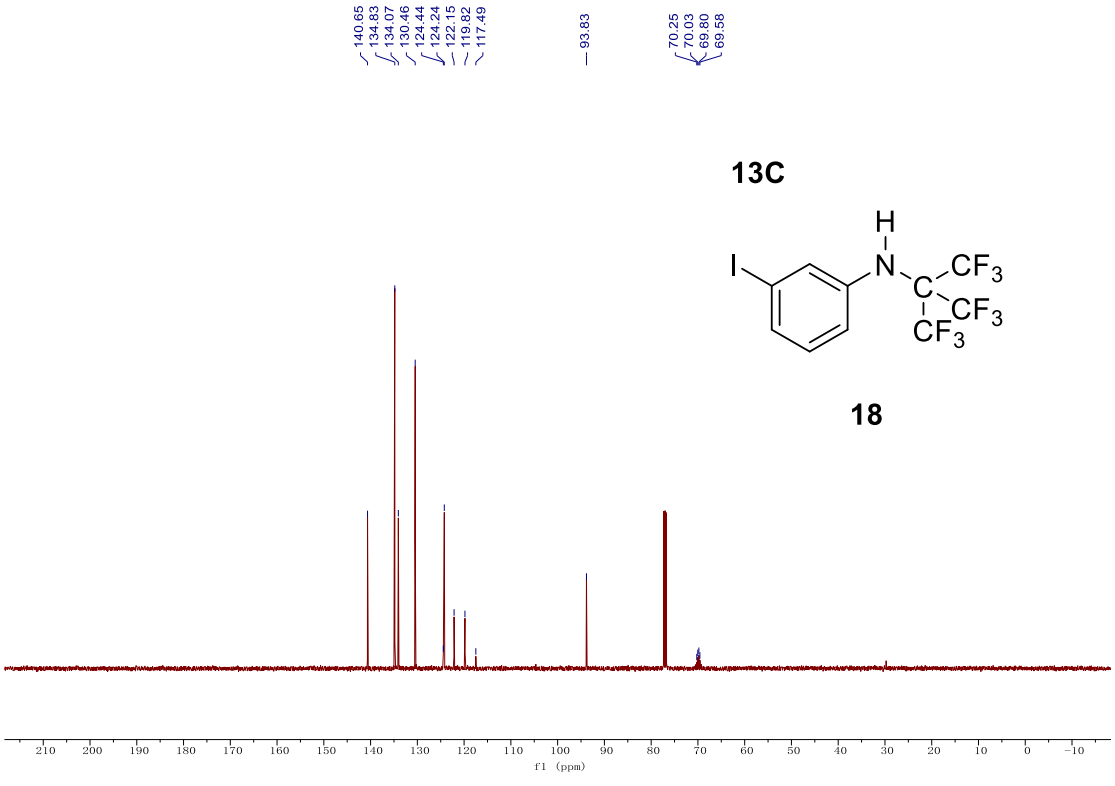

138.41
132.21
127.25
124.48
122.16
119.83
119.35
117.53
70.22
70.00
69.77
69.55
13C
H
N
C
CF3
CF3
CF3
Br
17
f1 (ppm)


7.53
7.52
7.50
7.13
7.11
7.04
7.03
7.01
3.97
1H
H
N
C
CF3
CF3
CF3
I
18
0.99
0.98
1.00
1.01
1.00
f1 (ppm)


-68.77
f1 (ppm)

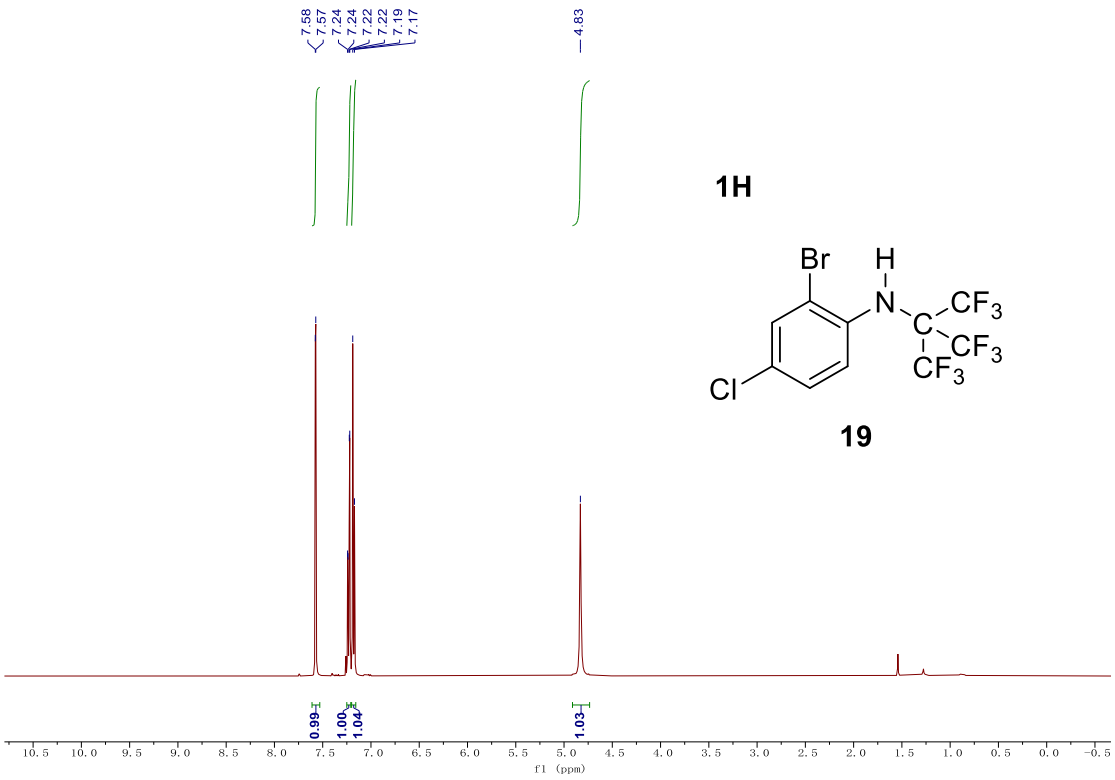
19F

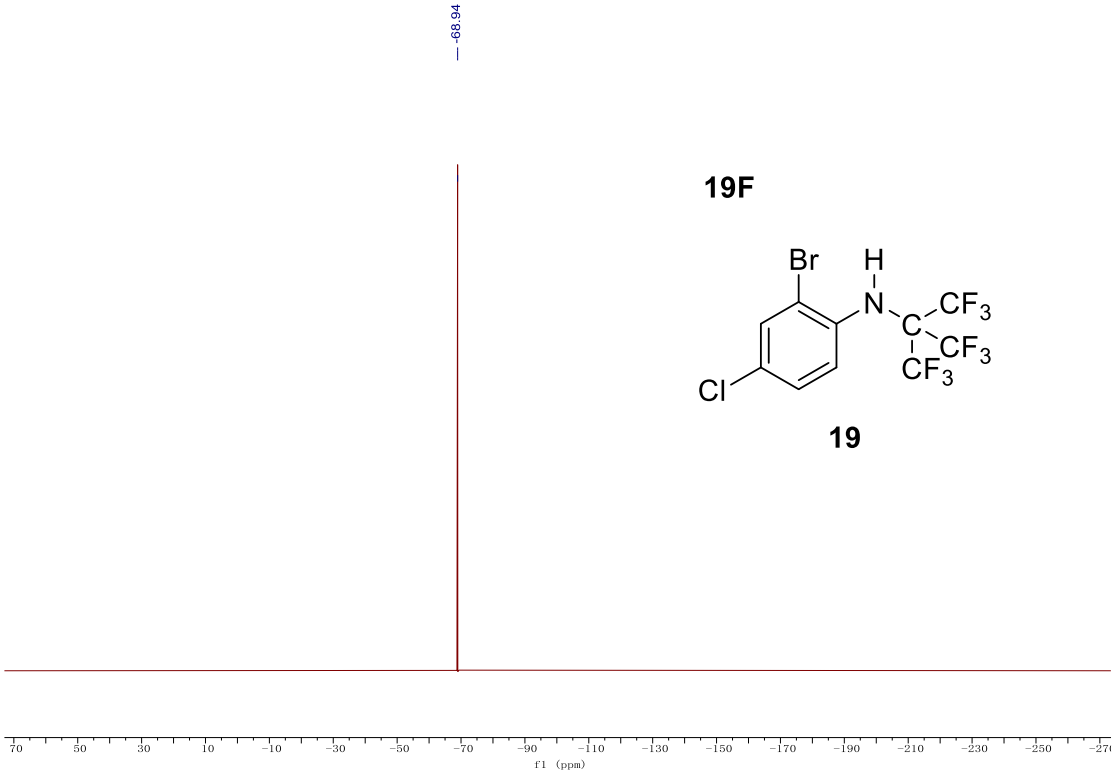
18

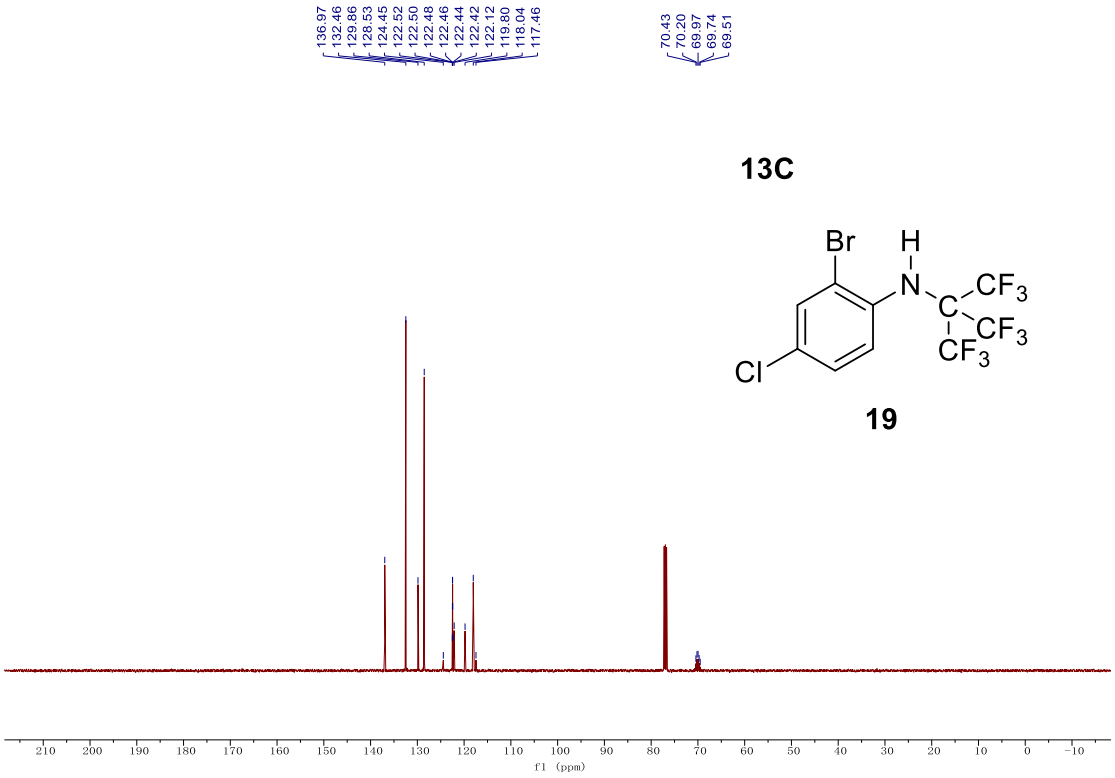

140.65
134.83
134.07
130.46
124.44
124.24
122.15
119.82
117.49
93.83
70.25
70.03
69.80
69.58
f1 (ppm)

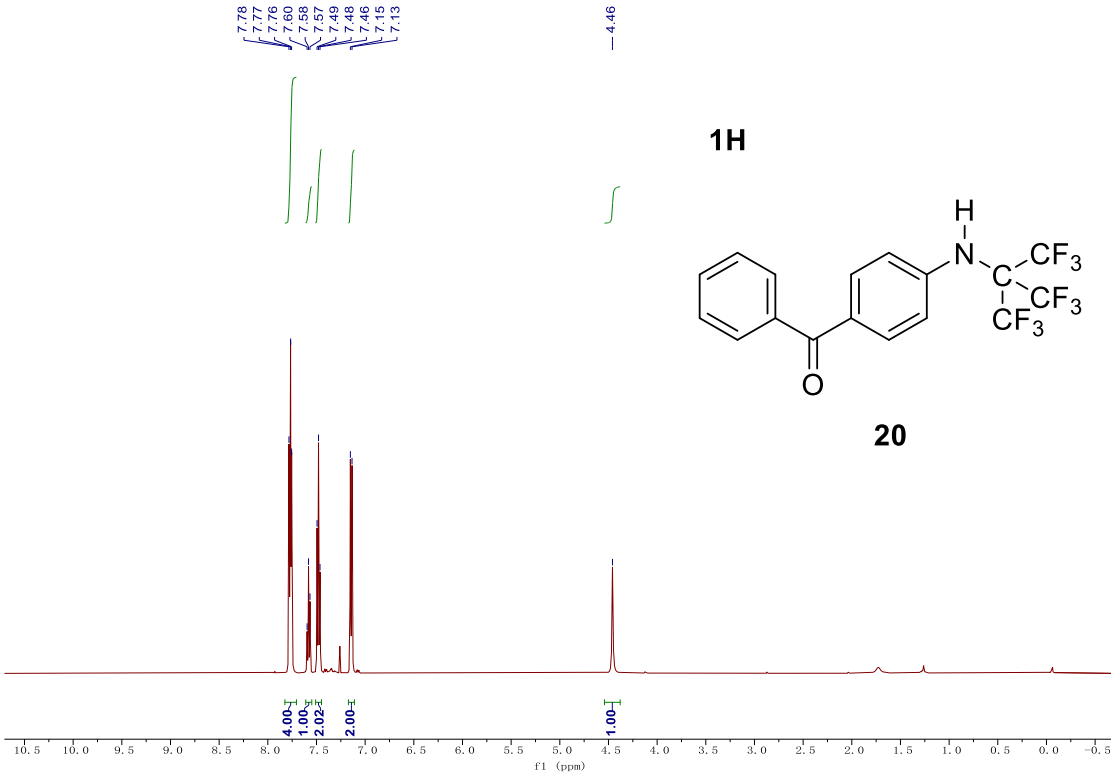
13C

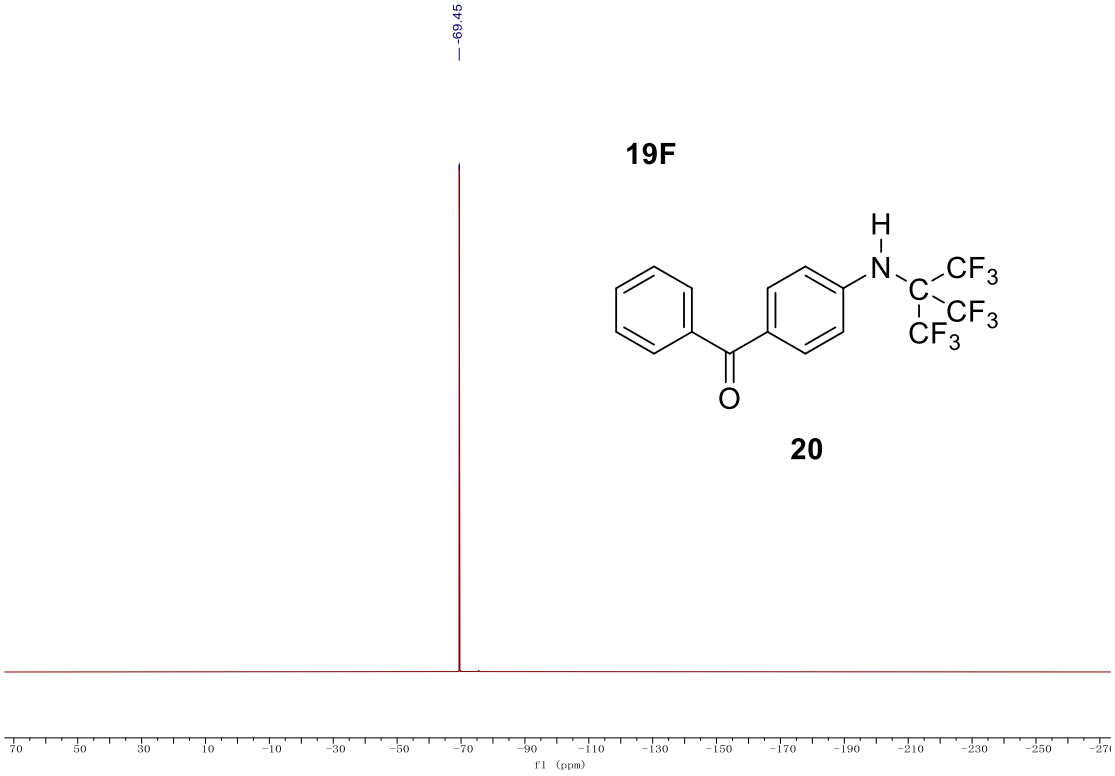
18

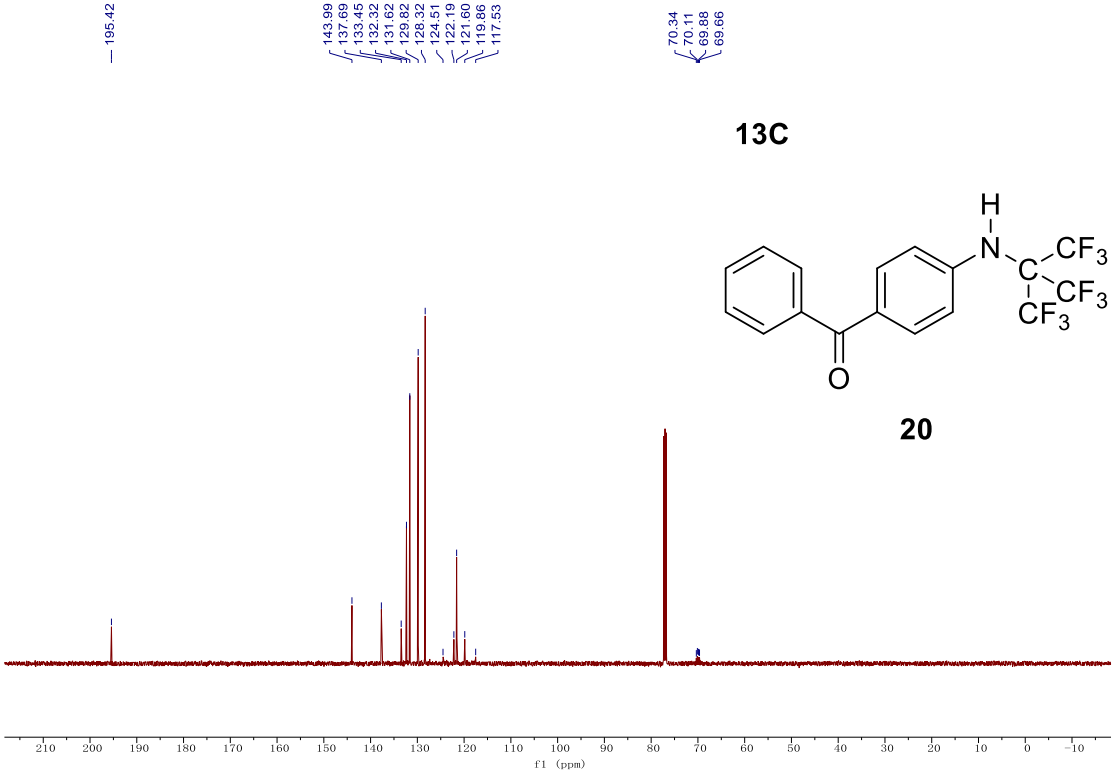

7.58
7.57
7.24
7.24
7.22
7.22
7.19
7.17
4.83
1H
Br
H
N
C
CF3
CF3
CF3
Cl
19
0.99
1.00
1.04
1.03
f1 (ppm)

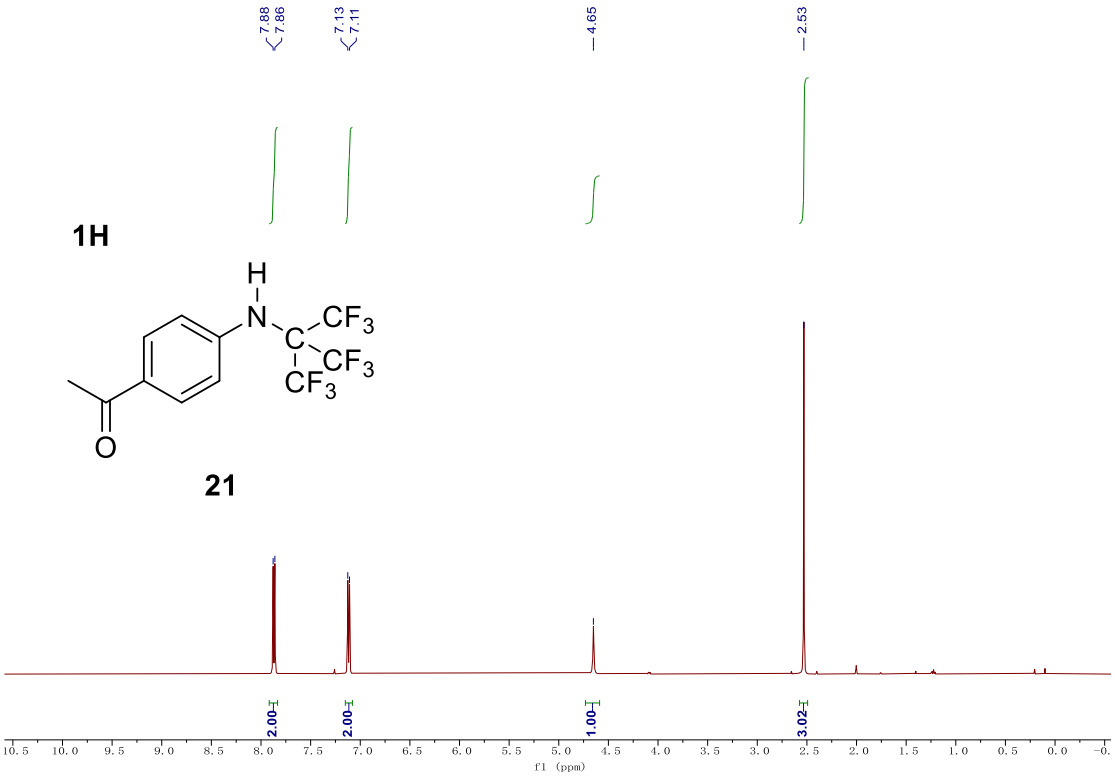

-68.94
19F
Br
H
N
C
CF3
CF3
CF3
Cl
19
f1 (ppm)

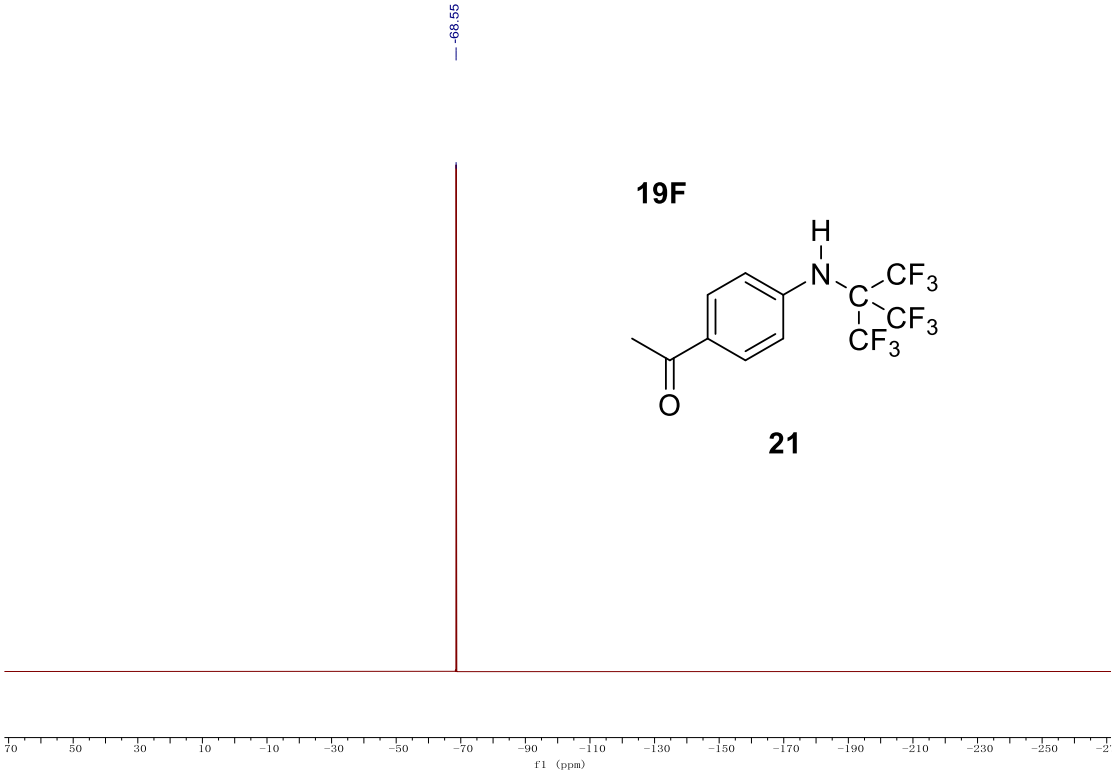

136.97
132.46
129.86
128.53
124.45
122.52
122.50
122.48
122.46
122.44
122.42
122.12
119.80
118.04
117.46
70.43
70.20
69.97
69.74
69.51
13C
Br
H
N
C
CF3
CF3
CF3
Cl
19
f1 (ppm)


7.78
7.77
7.76
7.60
7.58
7.57
7.49
7.48
7.46
7.15
7.13
4.46
1H
H
N
C
CF3
CF3
CF3
O
20
4.00
1.00
2.02
2.00
1.00
f1 (ppm)


-69.45
19F
H
N
C
CF3
CF3
CF3
O
20
f1 (ppm)


195.42
143.99
137.69
133.45
132.32
131.62
129.82
128.32
124.51
122.19
121.60
119.86
117.53
70.34
70.11
69.88
69.66
13C
H
N
C
CF3
CF3
CF3
O
20
f1 (ppm)


7.88
7.86
7.13
7.11
4.65
2.53
1H
H
N
C
CF3
CF3
CF3
O
21
2.00
2.00
1.00
3.02
f1 (ppm)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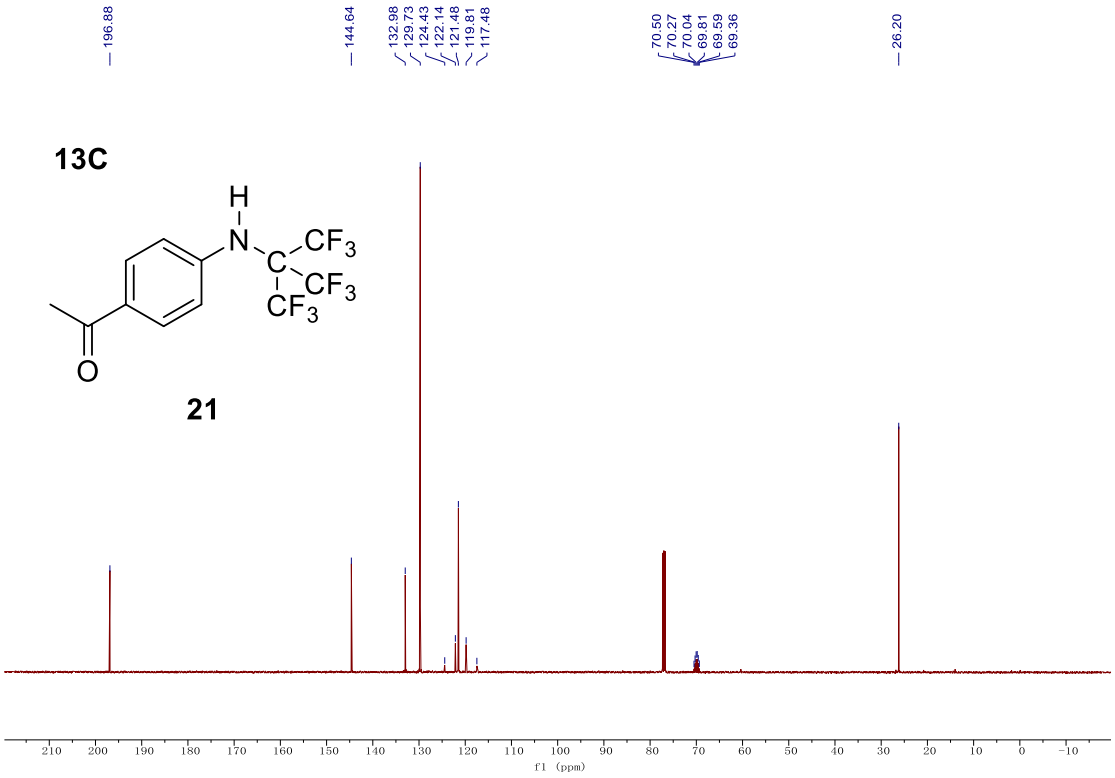
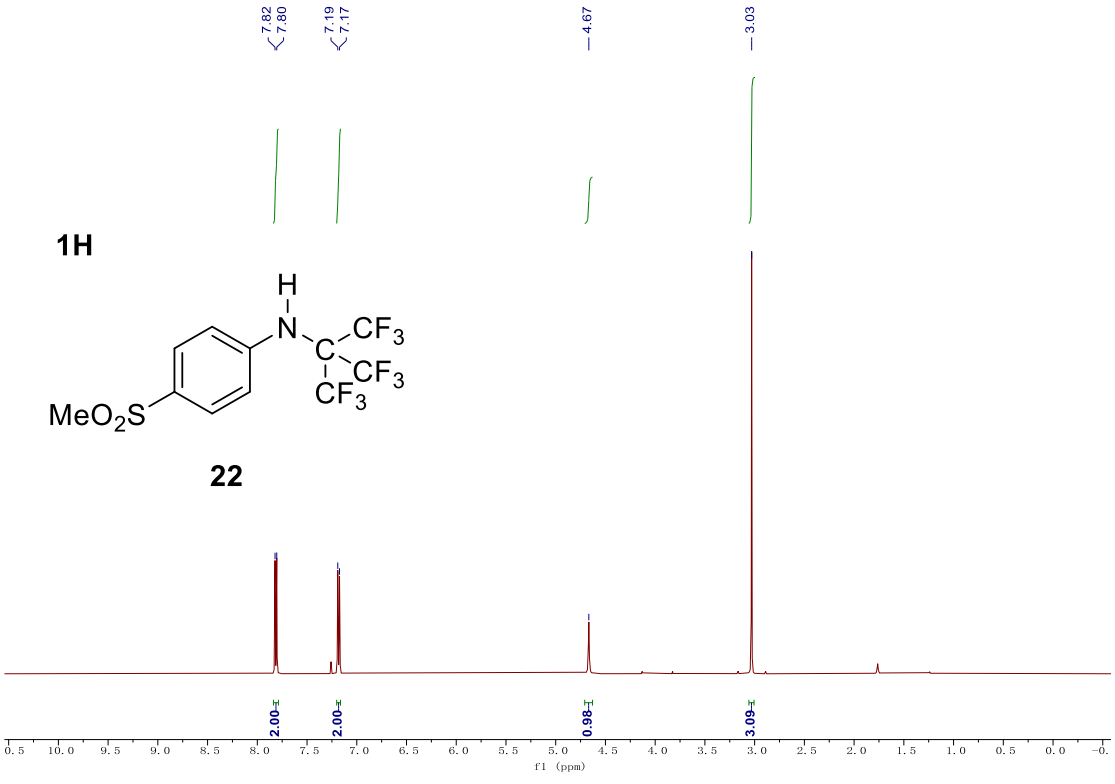
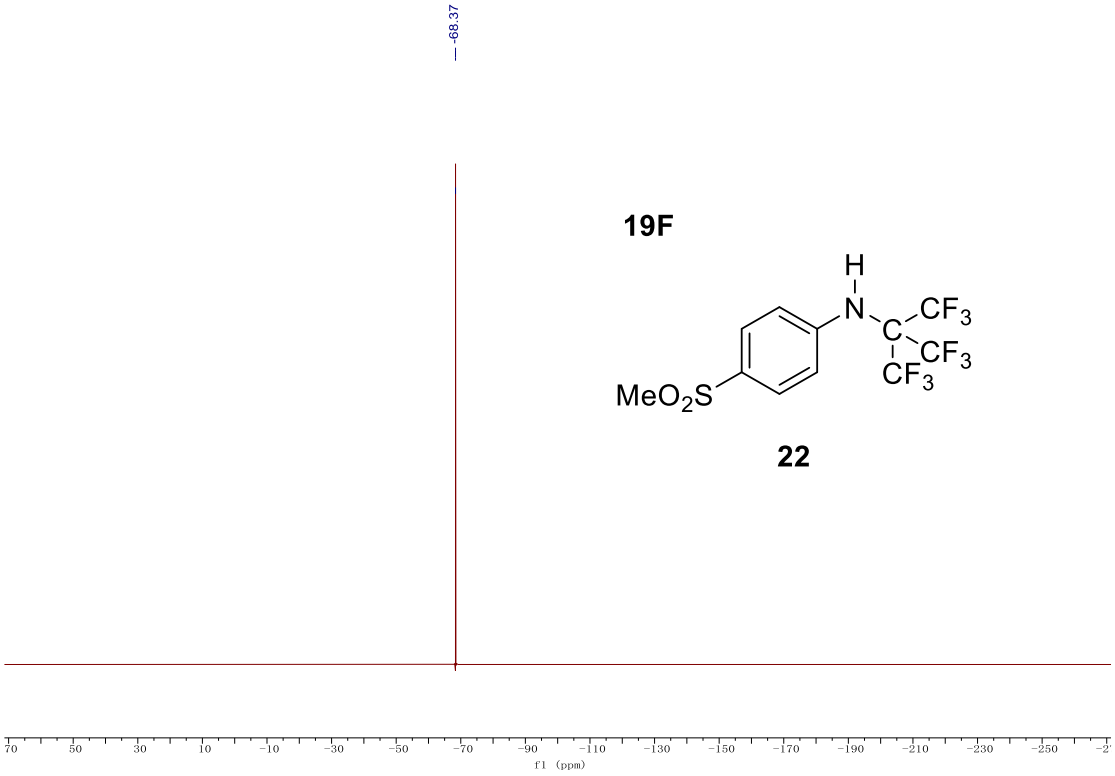
19F
H
N
C
CF3
CF3
CF3
O
21
f1 (ppm)


196.88
144.64
132.98
129.73
124.43
122.14
121.48
119.81
117.48
70.50
70.27
70.04
69.81
69.59
69.36
26.20
13C
H
N
C
CF3
CF3
CF3
O
21
f1 (ppm)


7.82
7.80
7.19
7.17
4.67
3.03
1H
H
N
C
CF3
CF3
CF3
MeO2S
22
2.00
2.00
0.98
3.09
f1 (ppm)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19F
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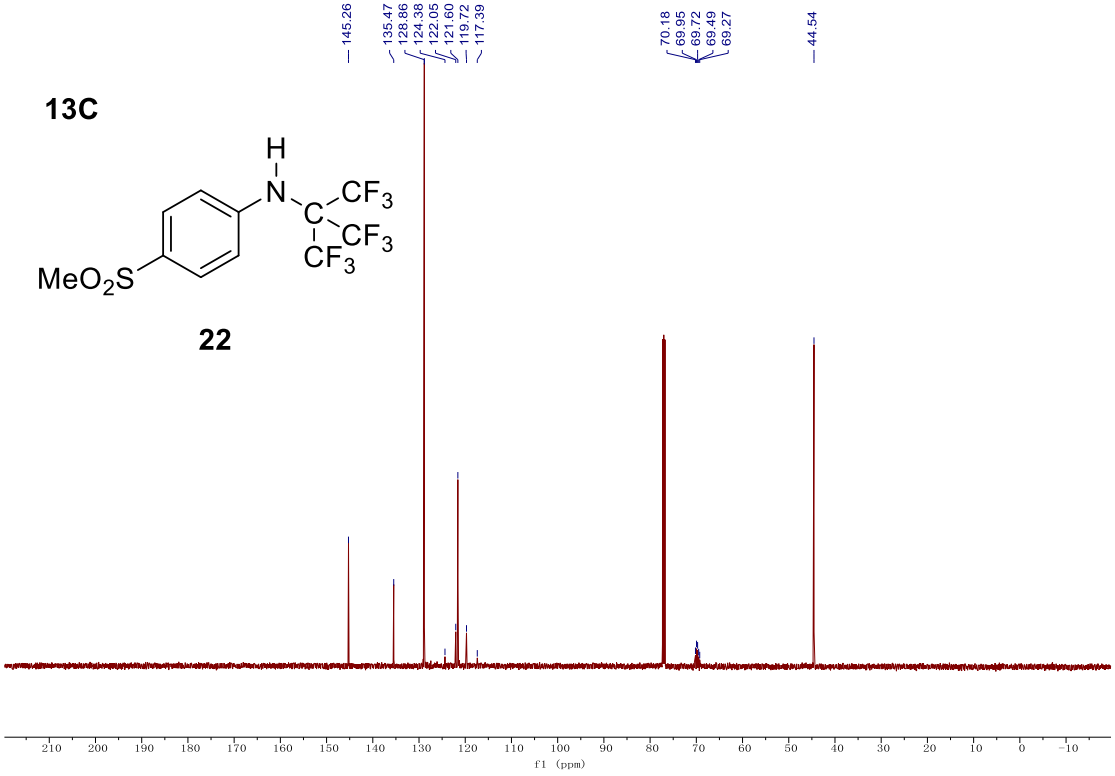
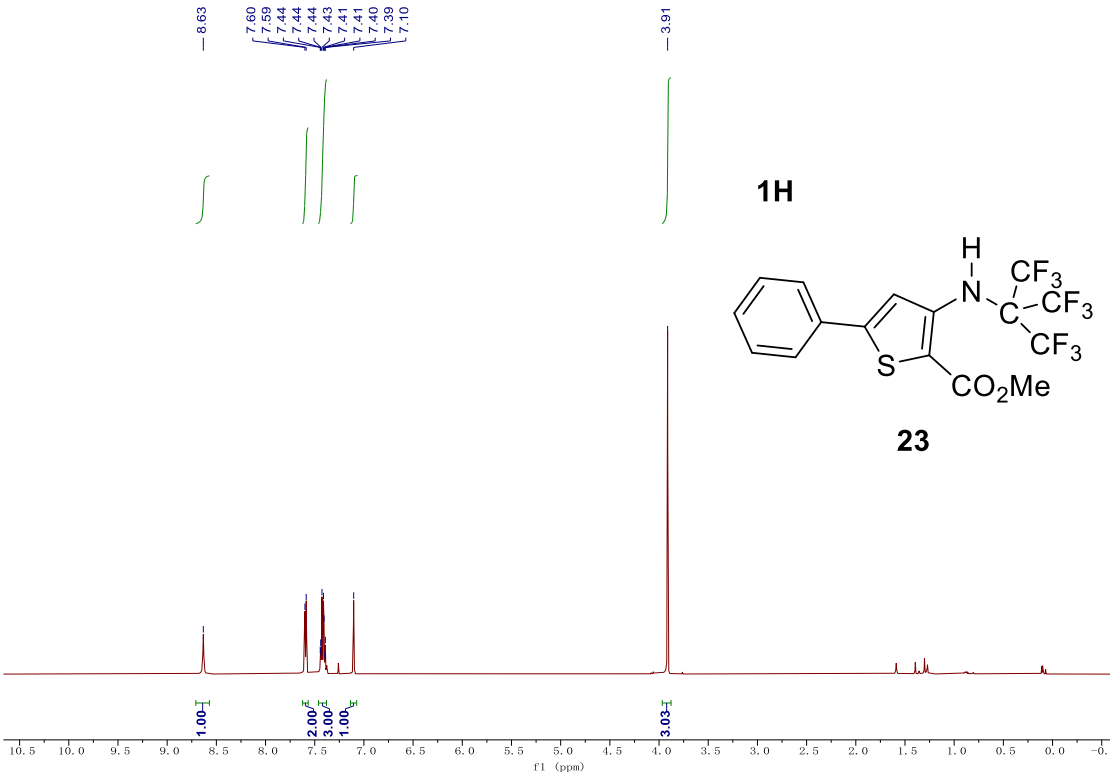
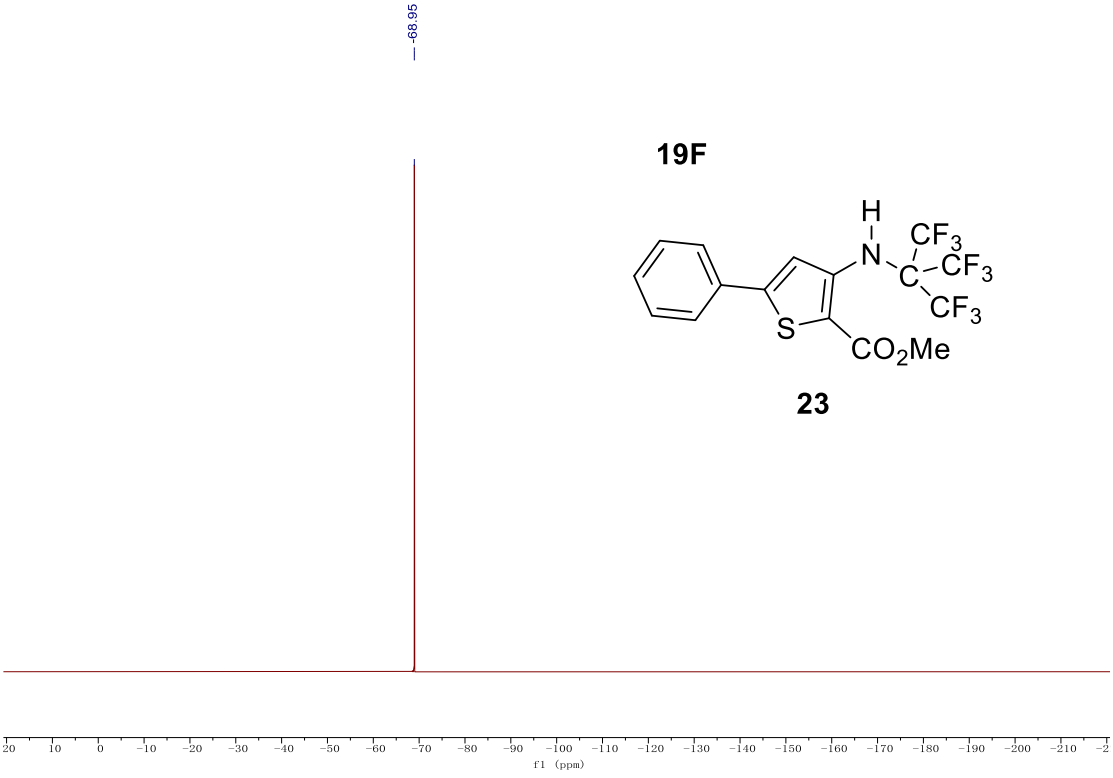
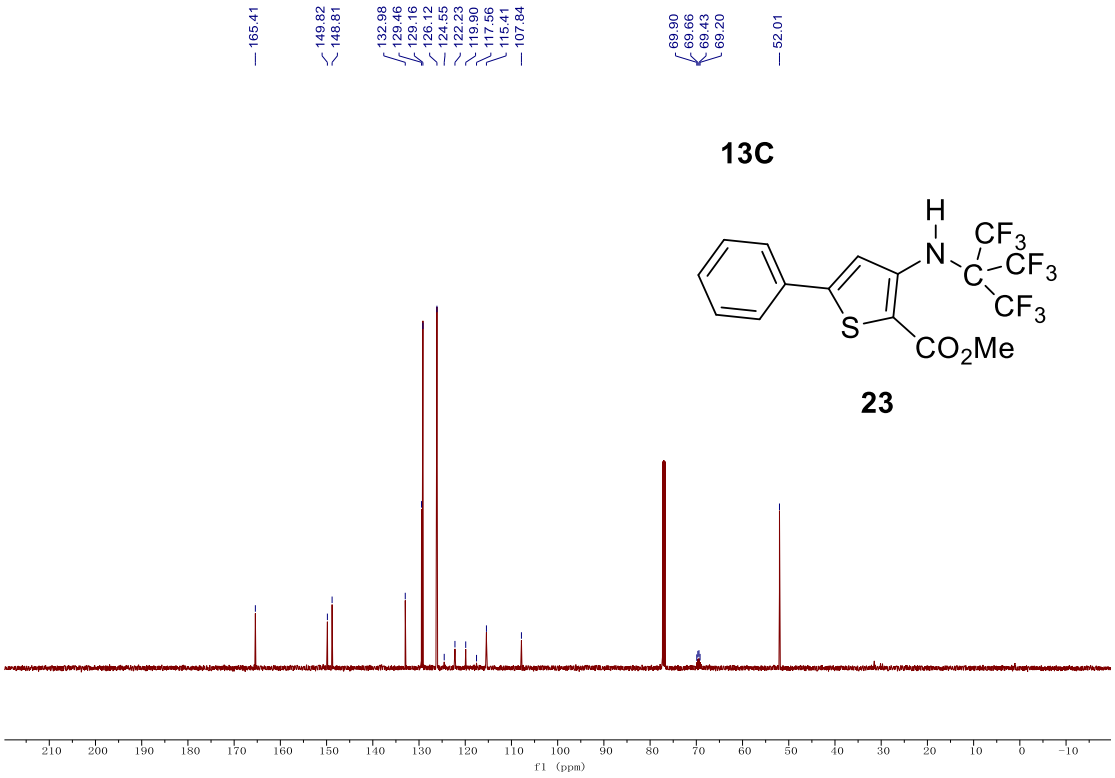
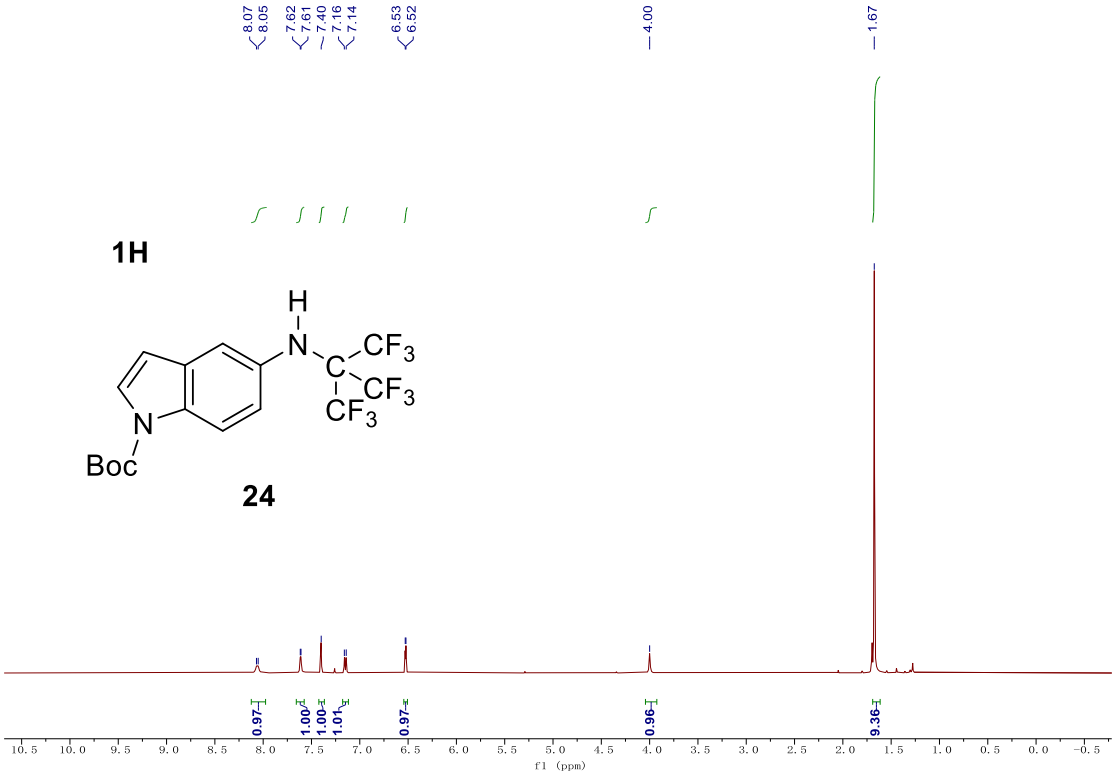
N
C
CF3
CF3
CF3
MeO2S
22
f1 (ppm)


145.26
135.47
128.86
124.38
122.05
121.60
119.72
117.39
70.18
69.95
69.72
69.49
69.27
44.54
13C
H
N
C
CF3
CF3
CF3
MeO2S
22
f1 (ppm)


8.63
7.60
7.59
7.44
7.44
7.44
7.43
7.41
7.41
7.40
7.39
7.10
3.91
1H
H
N
CF3
C
CF3
CF3
S
CO2Me
23
1.00
2.00
3.00
1.00
3.03
f1 (ppm)

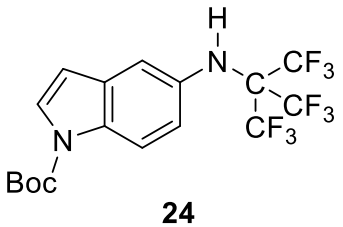

-68.95
19F
H
N
CF3
C
CF3
CF3
S
CO2Me
23
f1 (ppm)


165.41
149.82
148.81
132.98
129.46
129.16
126.12
124.55
122.23
119.90
117.56
115.41
107.84
69.90
69.66
69.43
69.20
52.01
13C
H
N
CF3
C
CF3
CF3
S
CO2Me
23
f1 (ppm)


8.07
8.05
7.62
7.61
7.40
7.16
7.14
6.53
6.52
4.00
1.67
1H
H
N
CF3
C
CF3
CF3
N
Boc
24
0.97
1.00
1.00
1.01
0.97
0.96
9.36
f1 (ppm)

-69.31

19F



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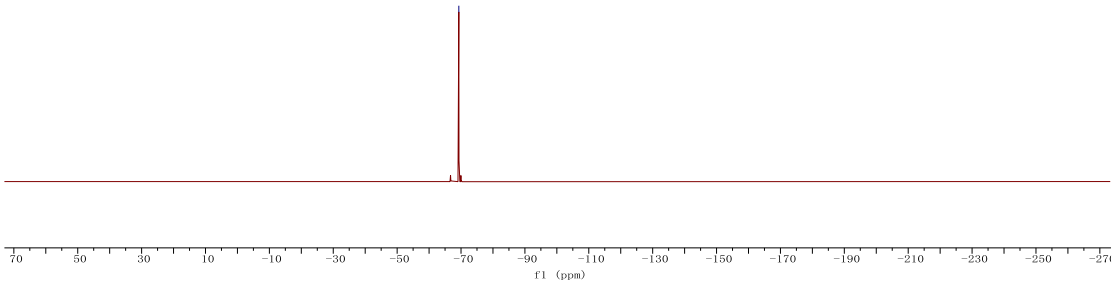
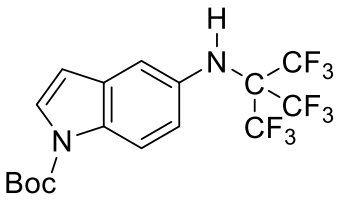
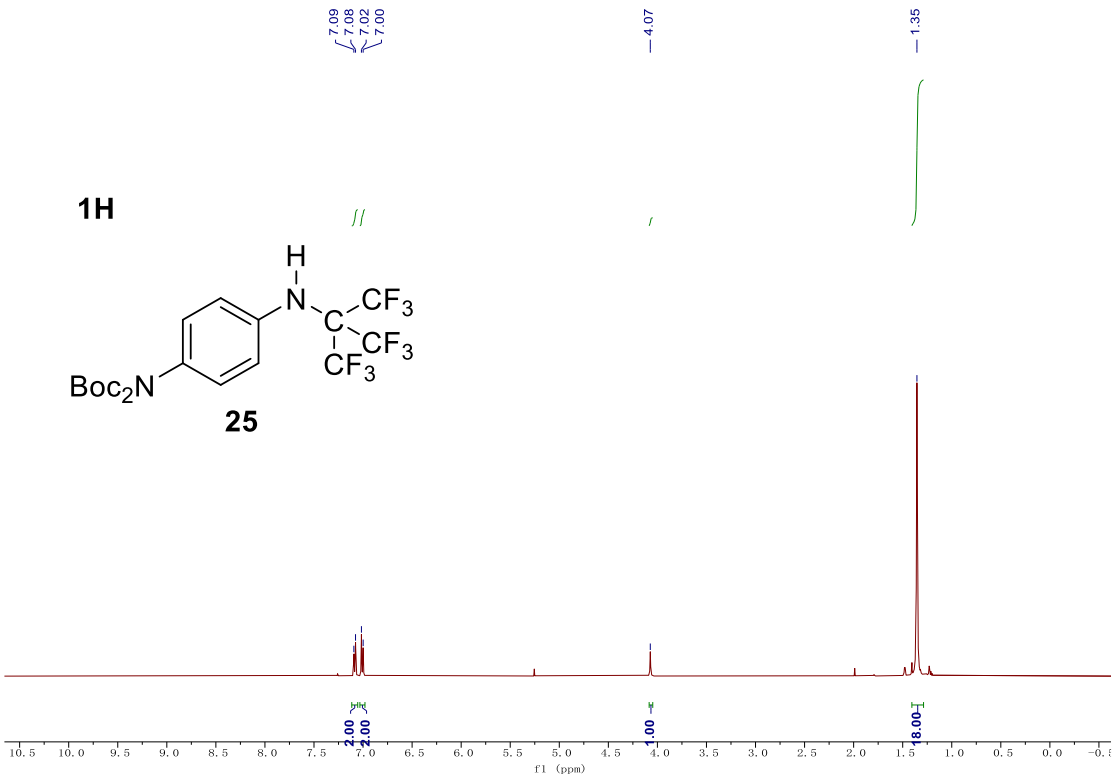


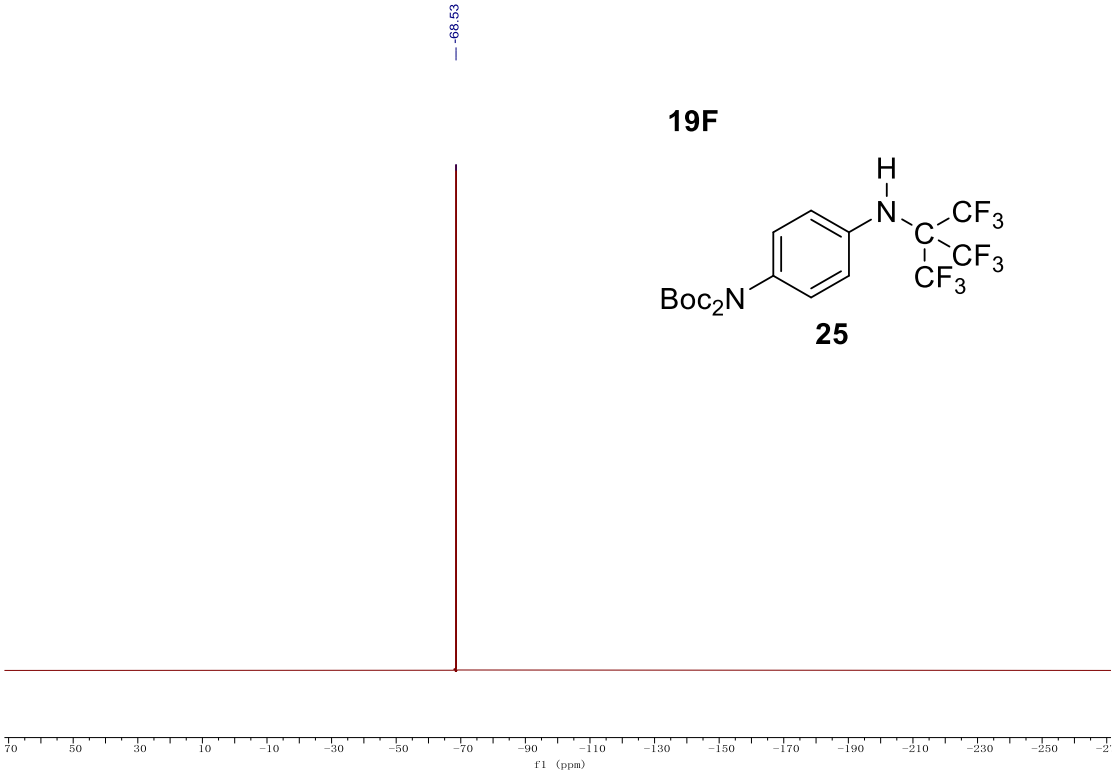
149.58
133.84
133.53
131.01
126.95
124.68
123.72
122.36
120.04
119.25
117.71
115.30
107.07
83.95
70.50
70.28
70.06
69.84
28.14

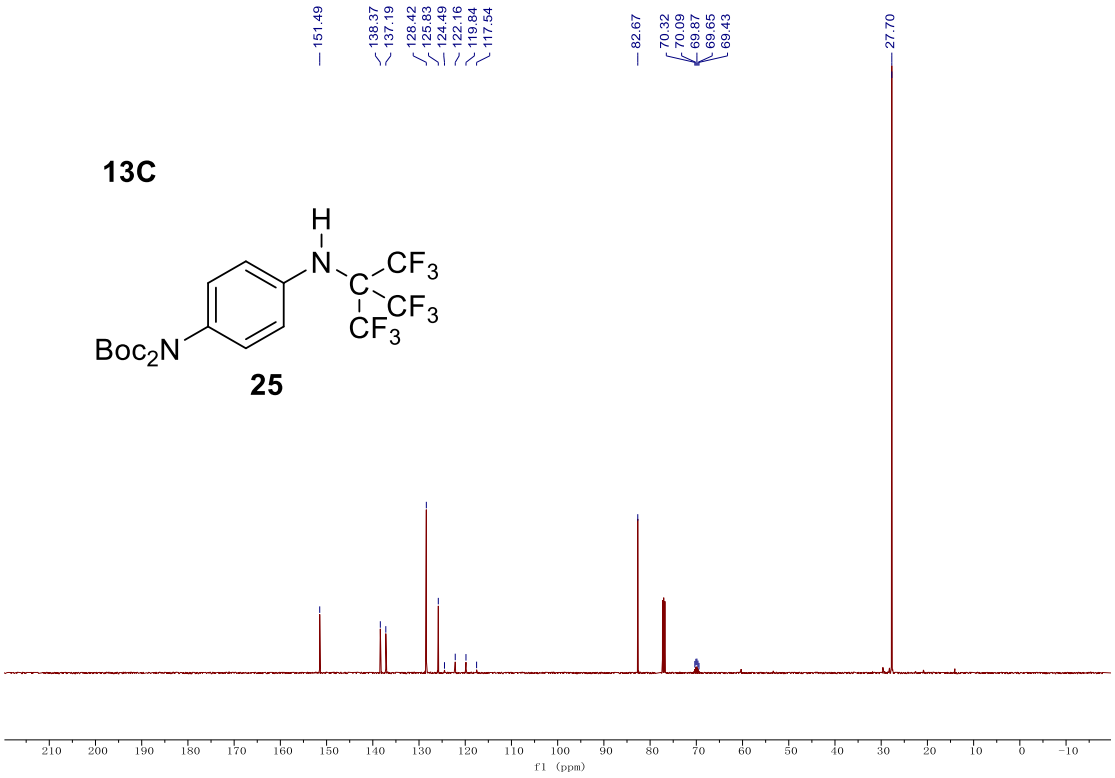
13C

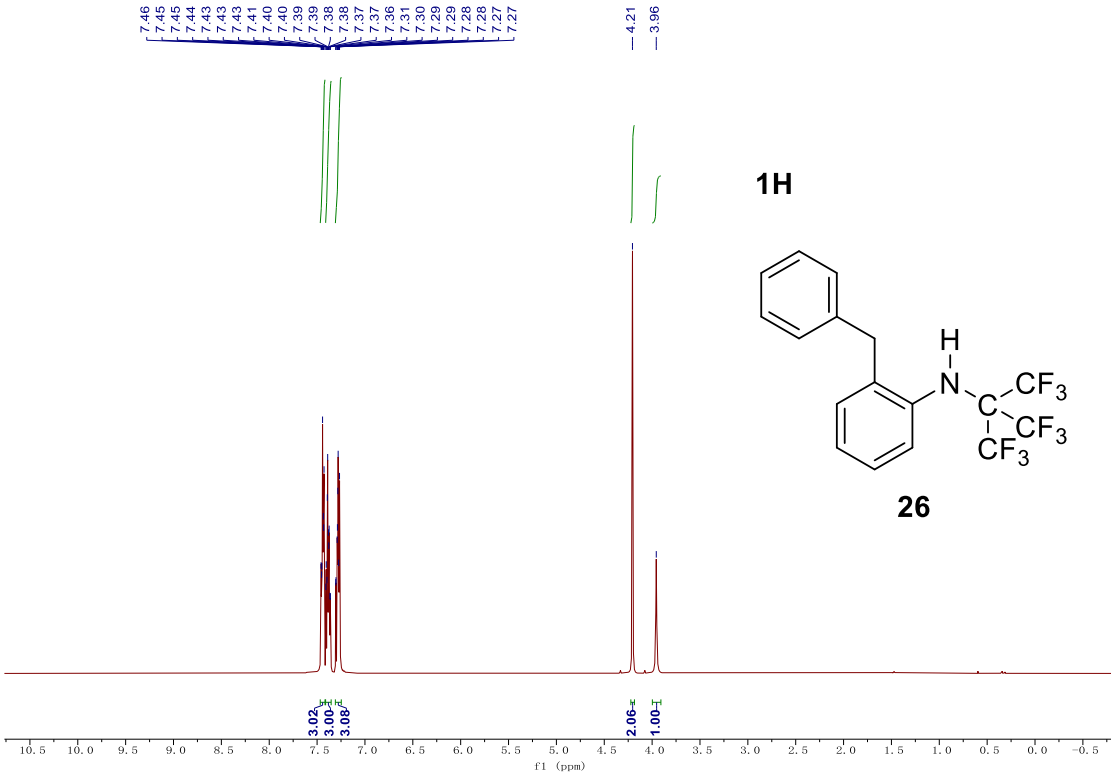


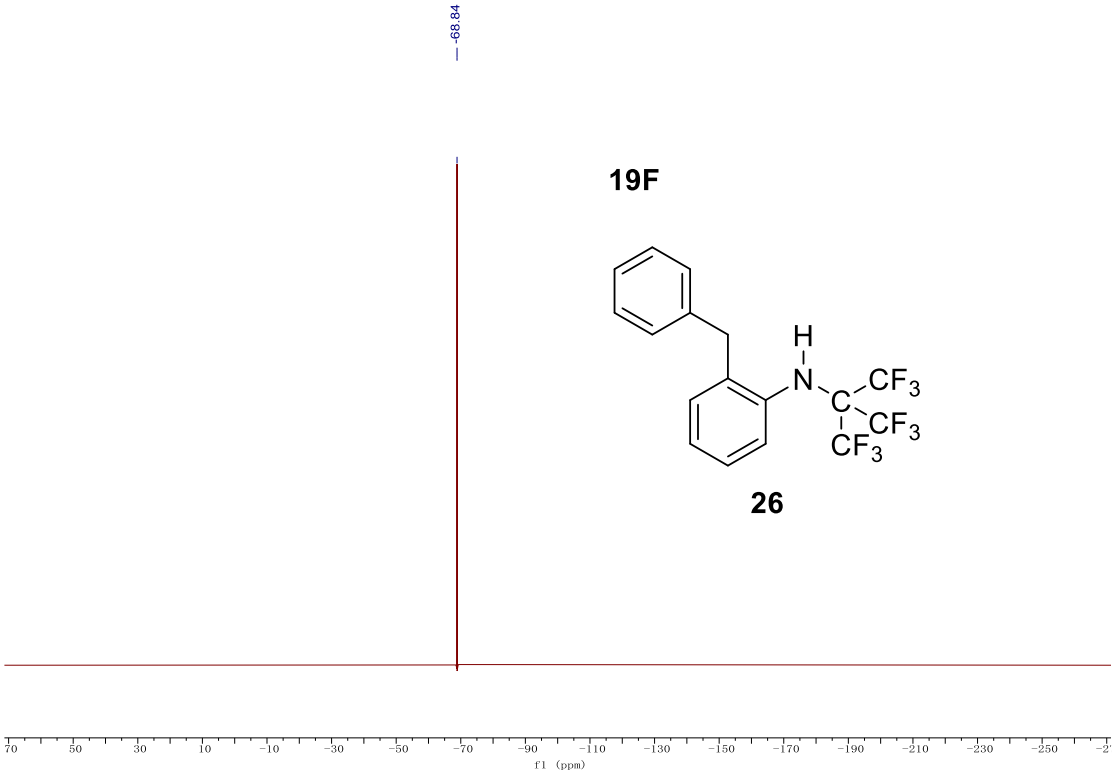
24

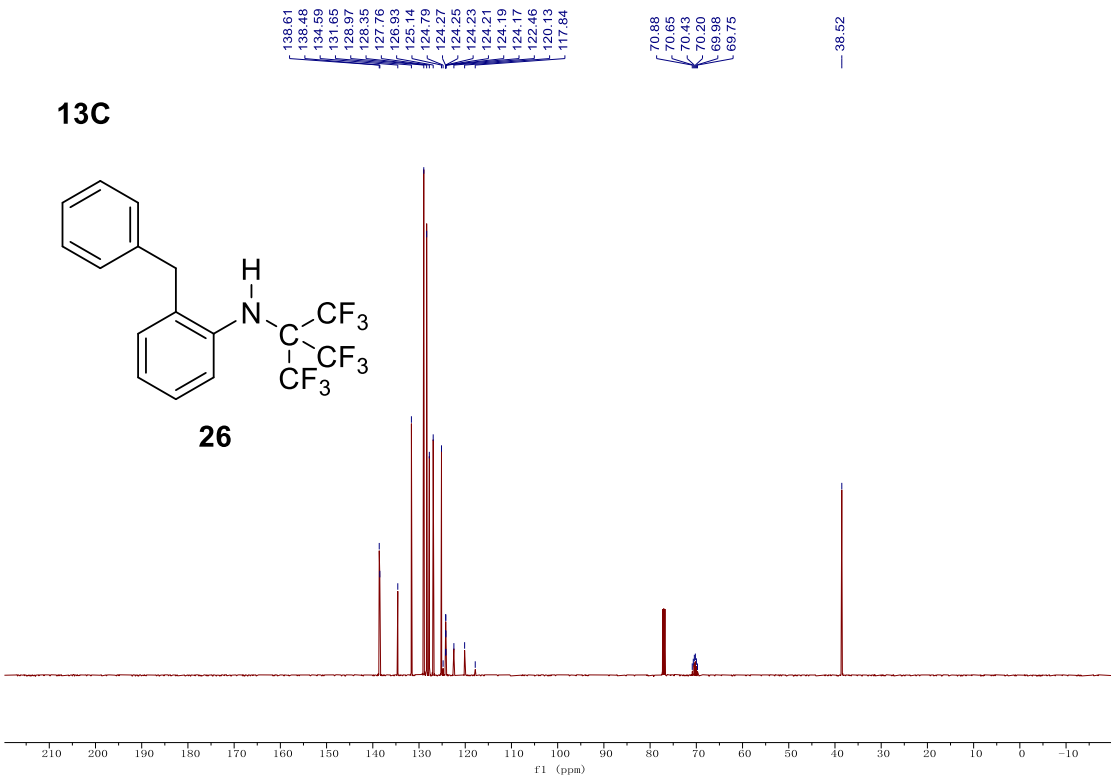

7.09
7.08
7.02
7.00
4.07
1.35
1H
H
N
C
CF3
CF3
CF3
Boc2N
25
2.00
2.00
1.00
18.00
f1 (ppm)

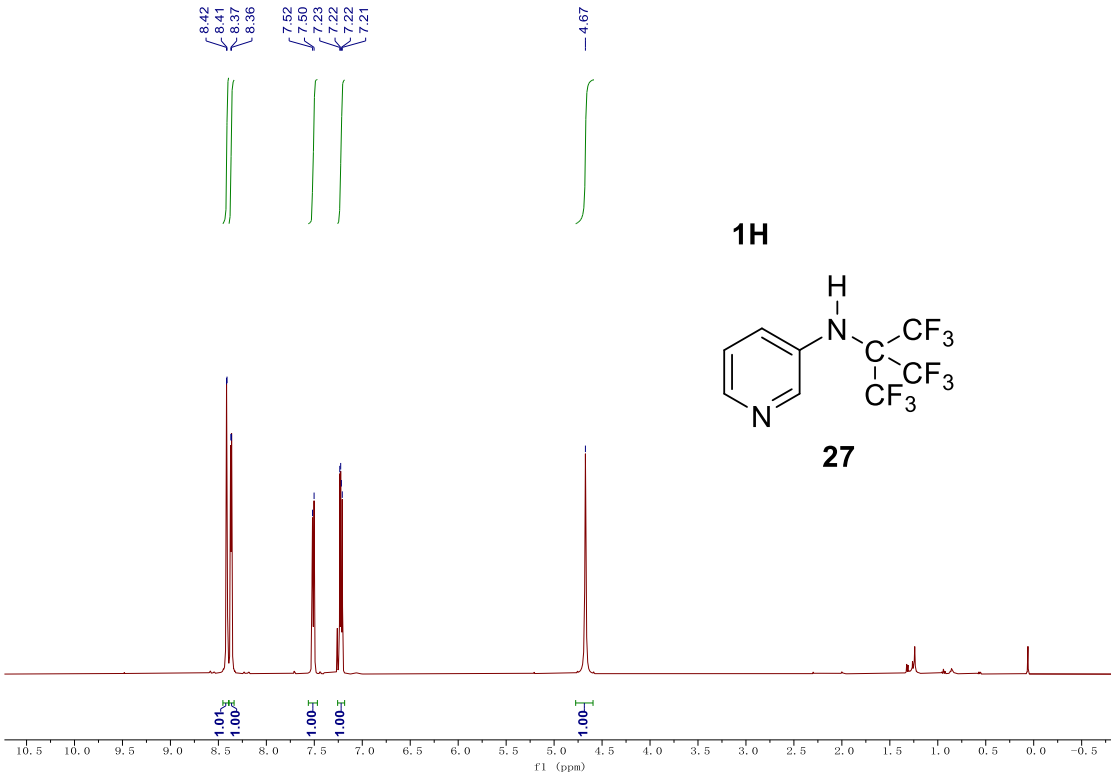

-68.53
19F
H
N
C
CF3
CF3
CF3
Boc2N
25
f1 (ppm)

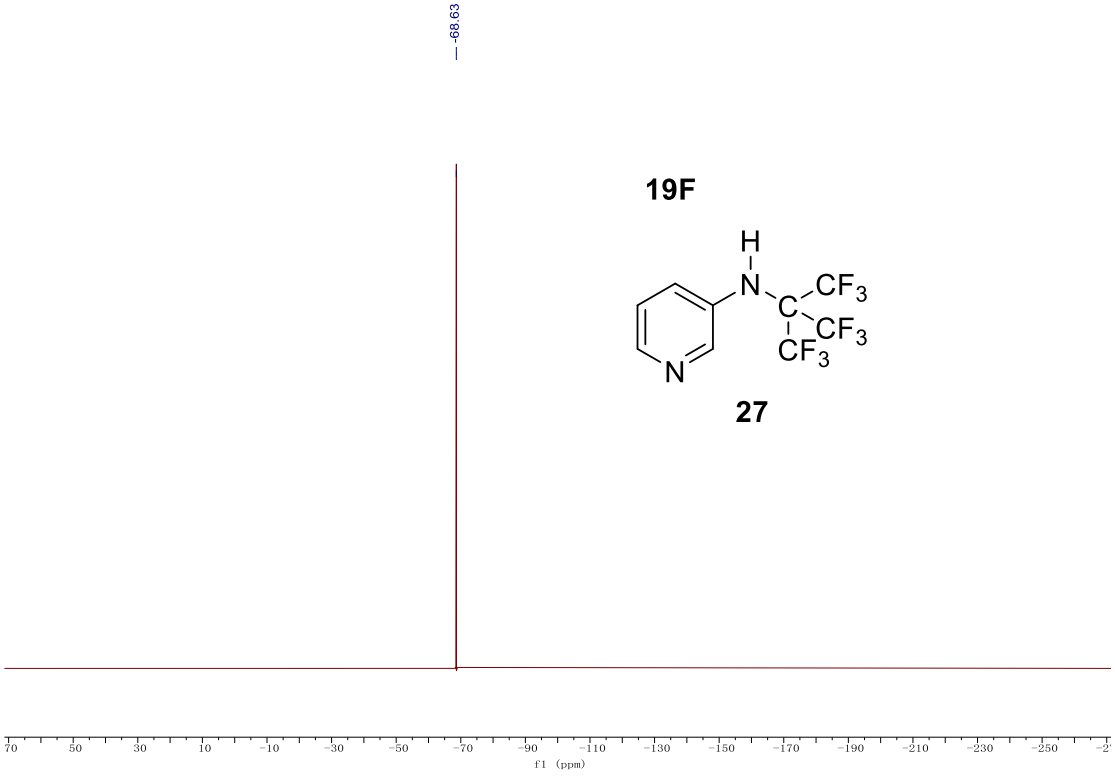

151.49
138.37
137.19
128.42
125.83
124.49
122.16
119.84
117.54
82.67
70.32
70.09
69.87
69.65
69.43
27.70
13C
H
N
C
CF3
CF3
CF3
Boc2N
25
f1 (ppm)

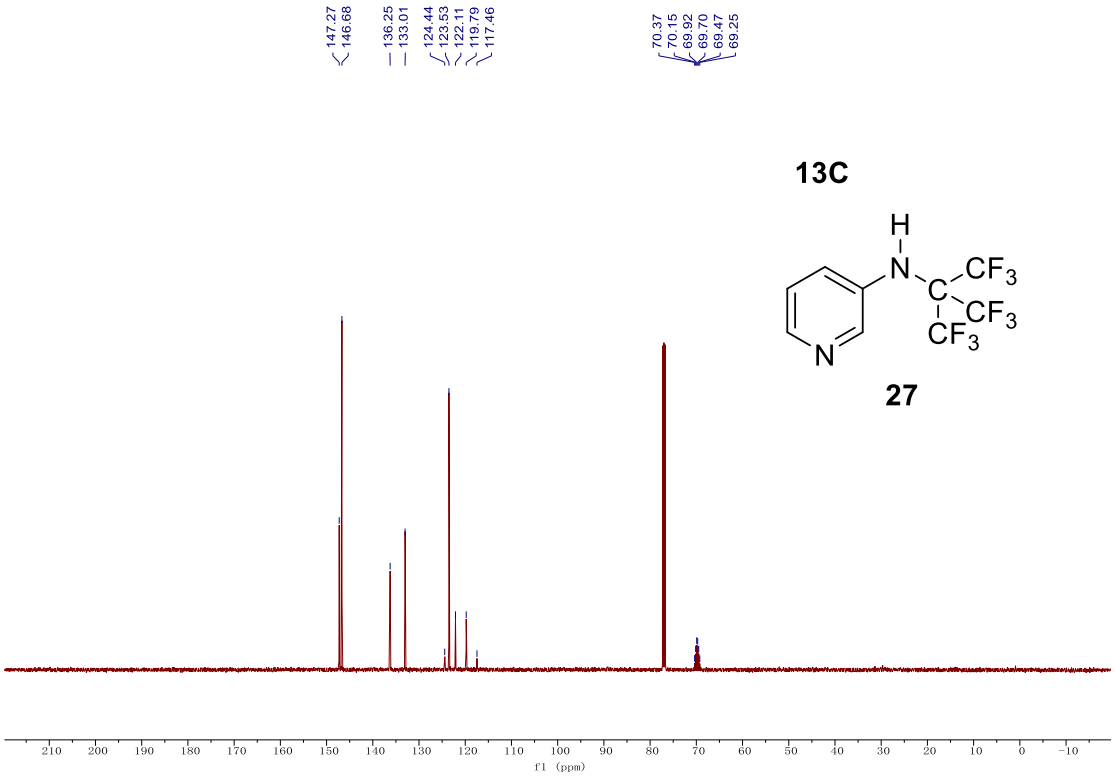

7.46
7.45
7.45
7.44
7.43
7.43
7.43
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.36
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
4.21
3.96
1H
H
N
C
CF3
CF3
CF3
26
3.02
3.00
3.08
2.06
1.00
f1 (ppm)

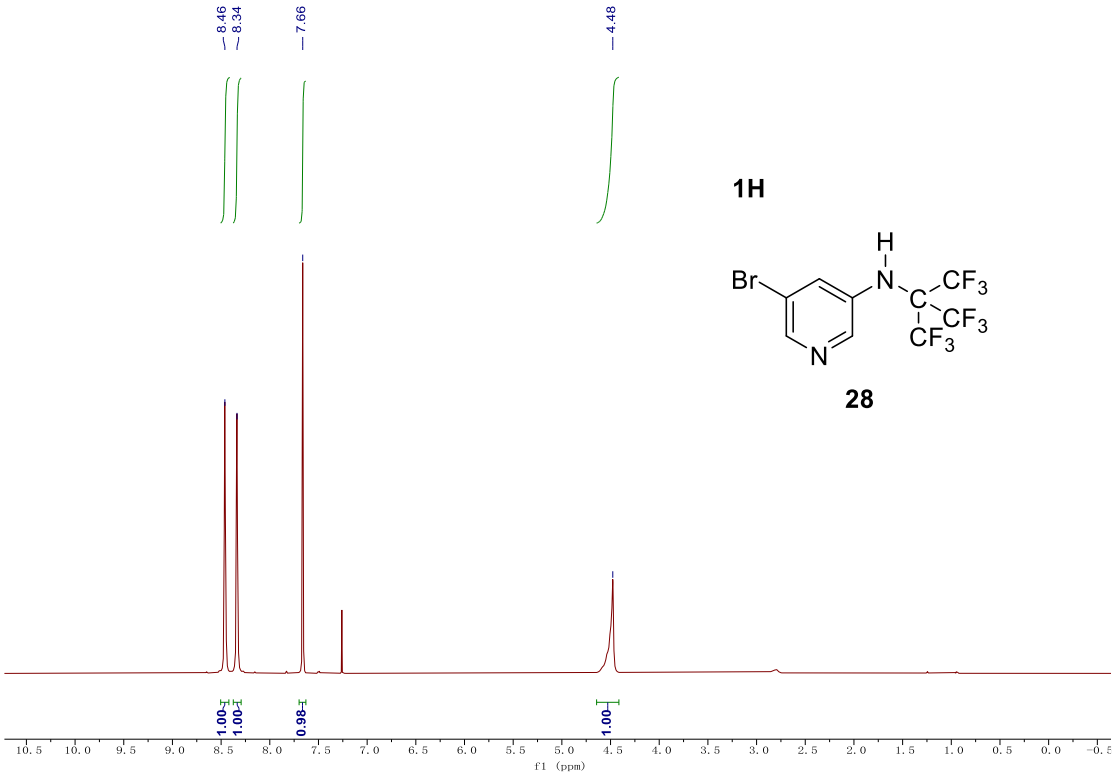

-68.84
19F
H
N
C
CF3
CF3
CF3
26
f1 (ppm)

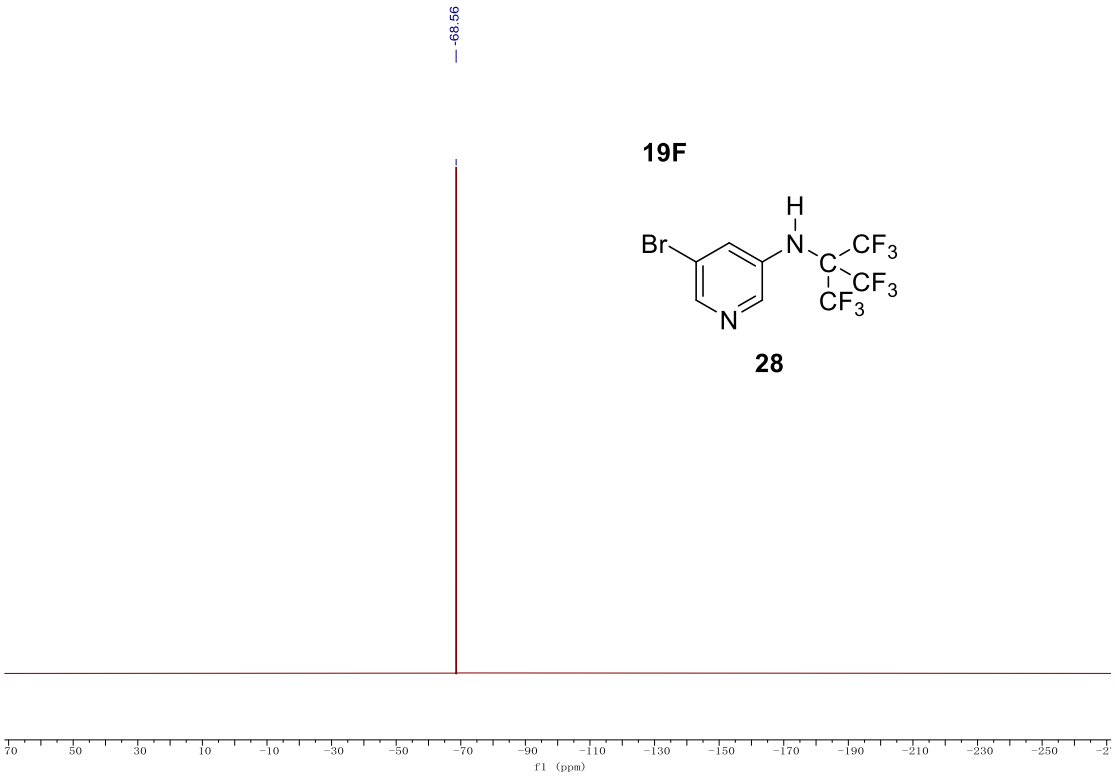

138.61
138.48
134.59
131.65
128.97
128.35
127.76
126.93
125.14
124.79
124.27
124.25
124.23
124.21
124.19
124.17
122.46
120.13
117.84
70.88
70.65
70.43
70.20
69.98
69.75
38.52
13C
H
N
C
CF3
CF3
CF3
26
f1 (ppm)

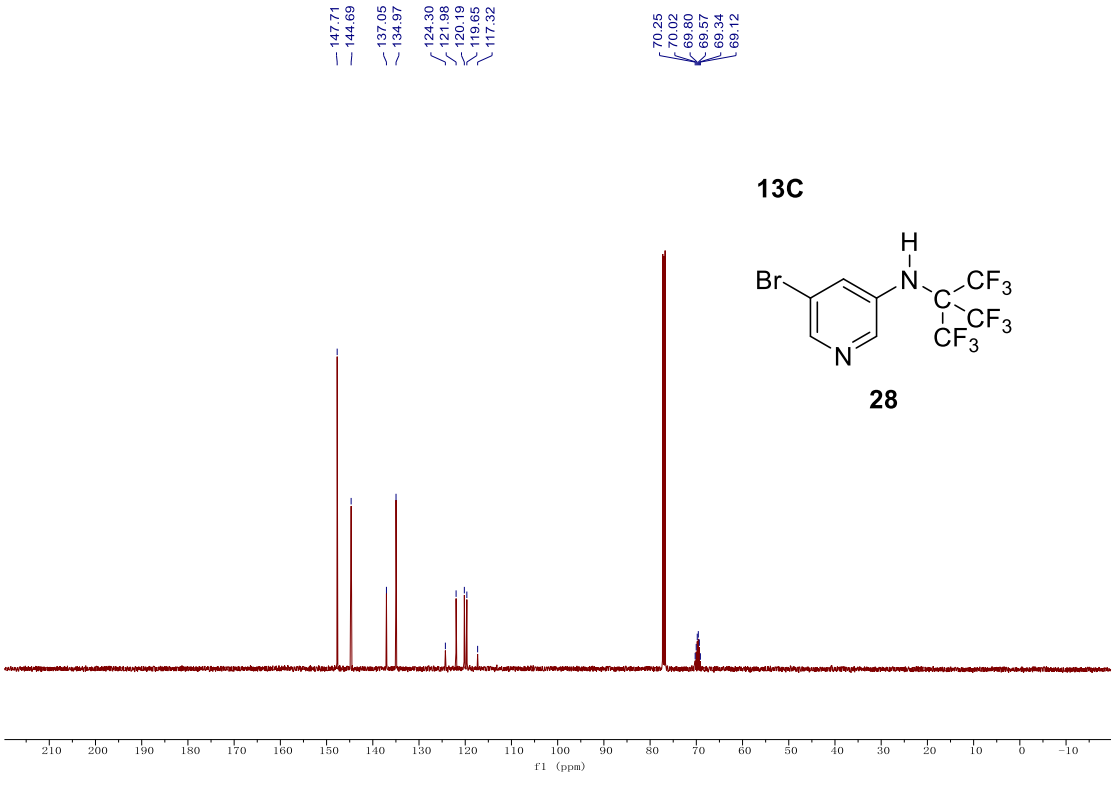

8.42
8.41
8.37
8.36
7.52
7.50
7.23
7.22
7.22
7.21
4.67
1H
H
N
CF3
C
CF3
CF3
N
27
1.01
1.00
1.00
1.00
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

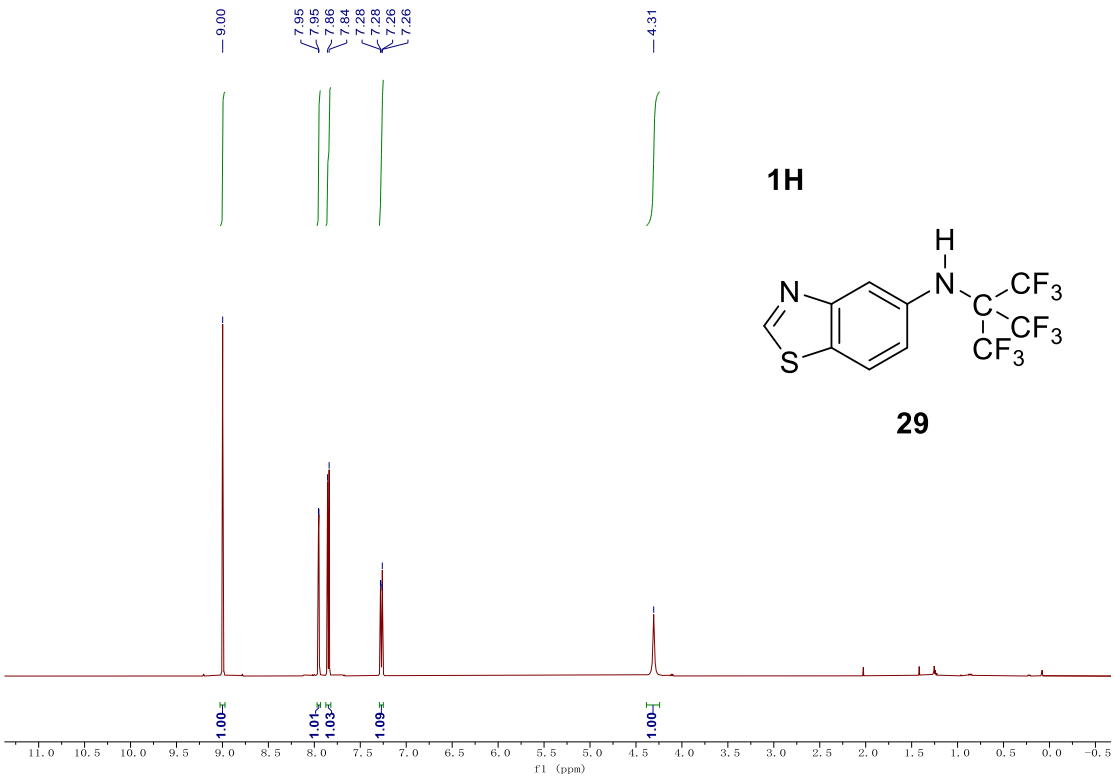

-68.63
19F
H
N
CF3
C
CF3
CF3
N
27
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)


147.27
146.68
136.25
133.01
124.44
123.53
122.11
119.79
117.46
70.37
70.15
69.92
69.70
69.47
69.25
13C
H
N
CF3
C
CF3
CF3
N
27
f1 (ppm)


8.46
8.34
7.66
4.48
1H
H
N
Br
CF3
C
CF3
CF3
N
28
1.00
1.00
0.98
1.00
f1 (ppm)

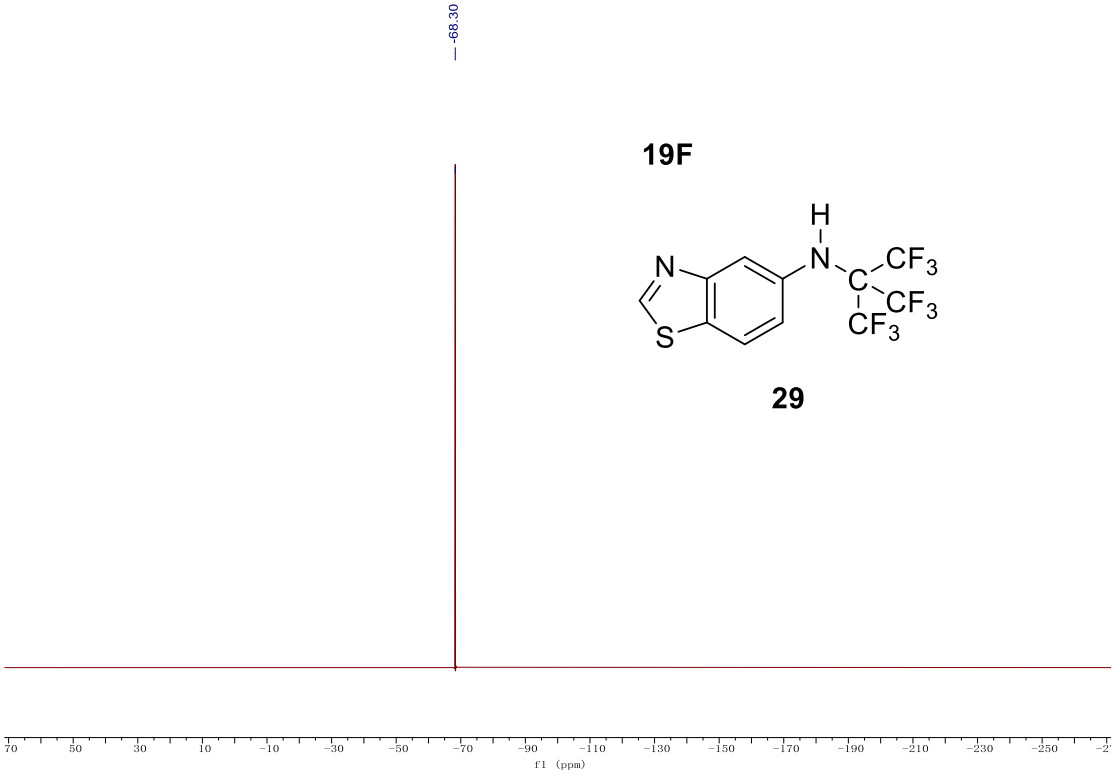

-68.56
19F
Br
H
N
C
CF3
CF3
CF3
N
28
f1 (ppm)


147.71
144.69
137.05
134.97
124.30
121.98
120.19
119.65
117.32
70.25
70.02
69.80
69.57
69.34
69.12
13C
Br
H
N
C
CF3
CF3
CF3
N
28
f1 (ppm)


9.00
7.95
7.95
7.86
7.84
7.28
7.28
7.26
7.26
4.31
1.00
1.01
1.03
1.09
1.00
f1 (ppm)

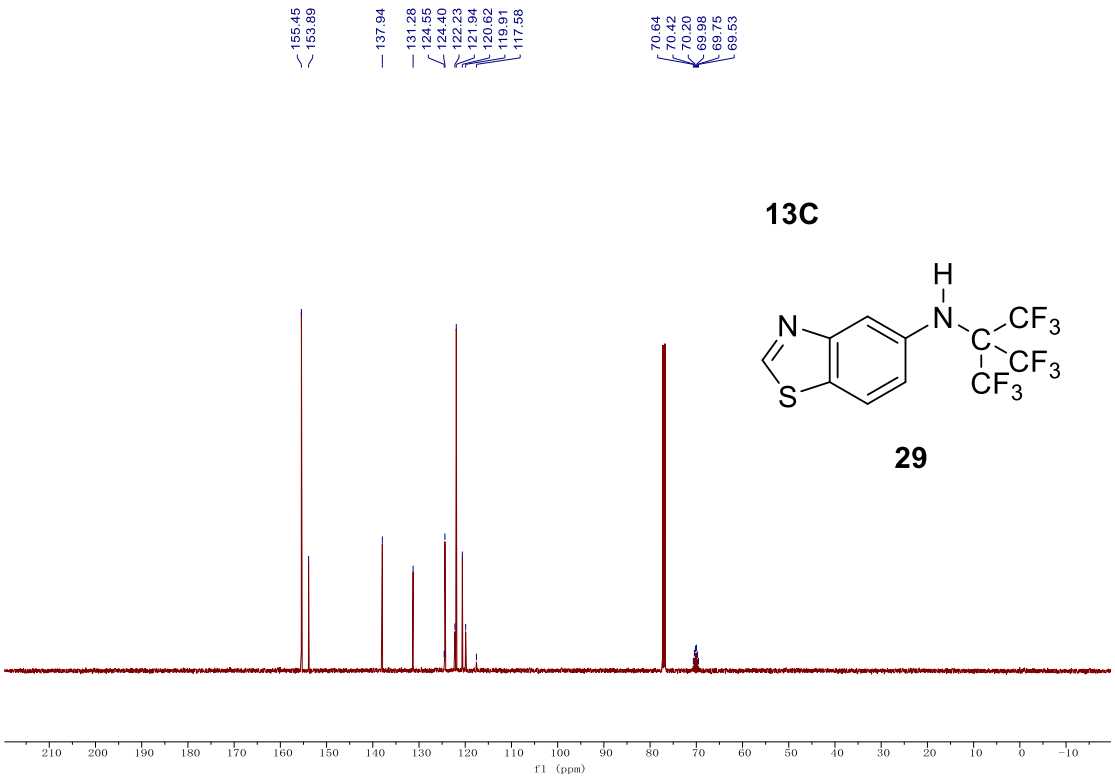
1H

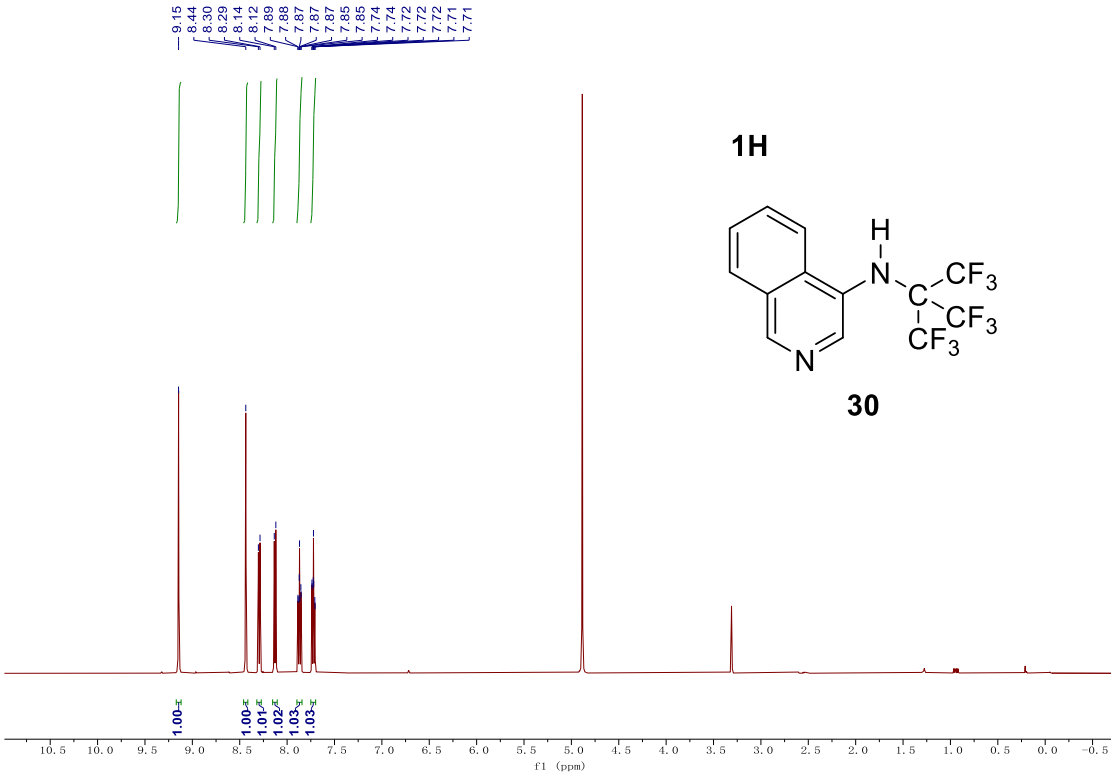
29

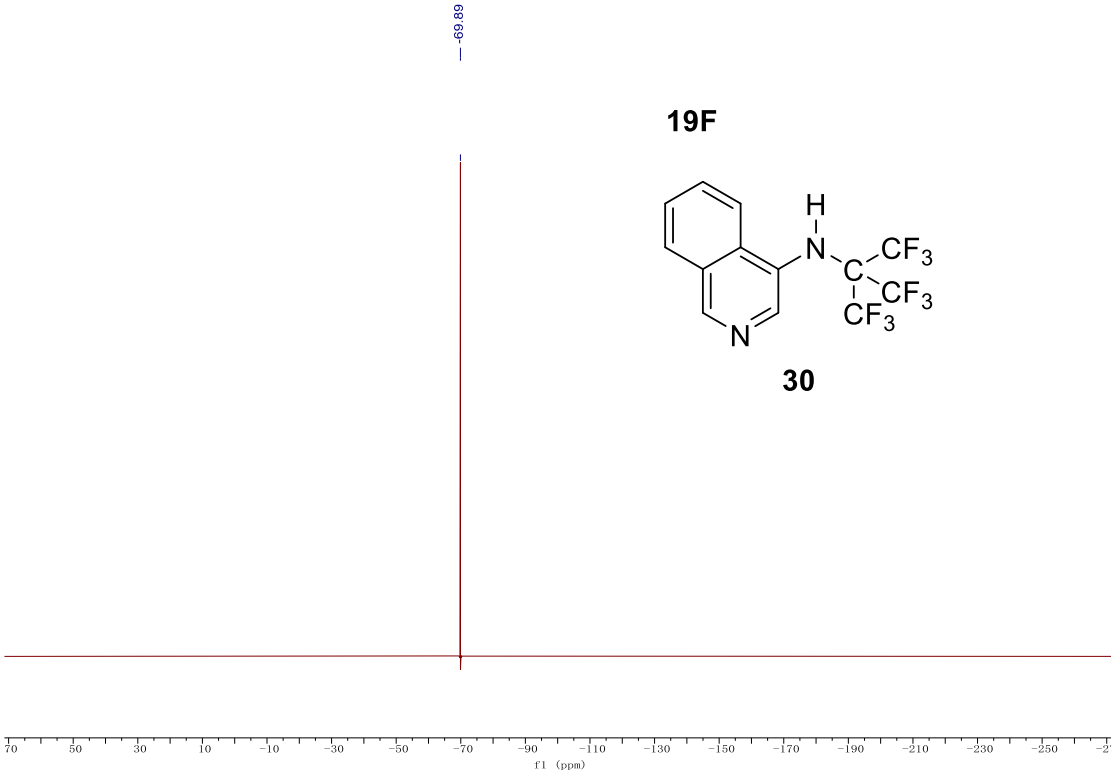

-68.30
f1 (ppm)

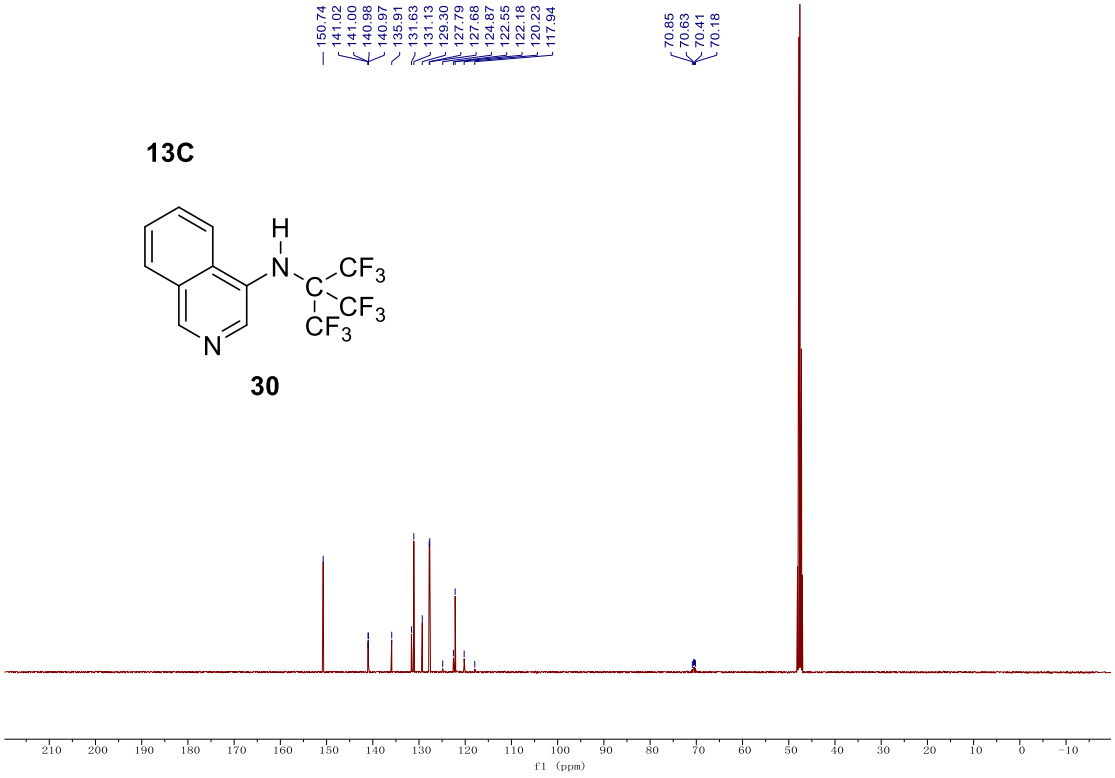
19F

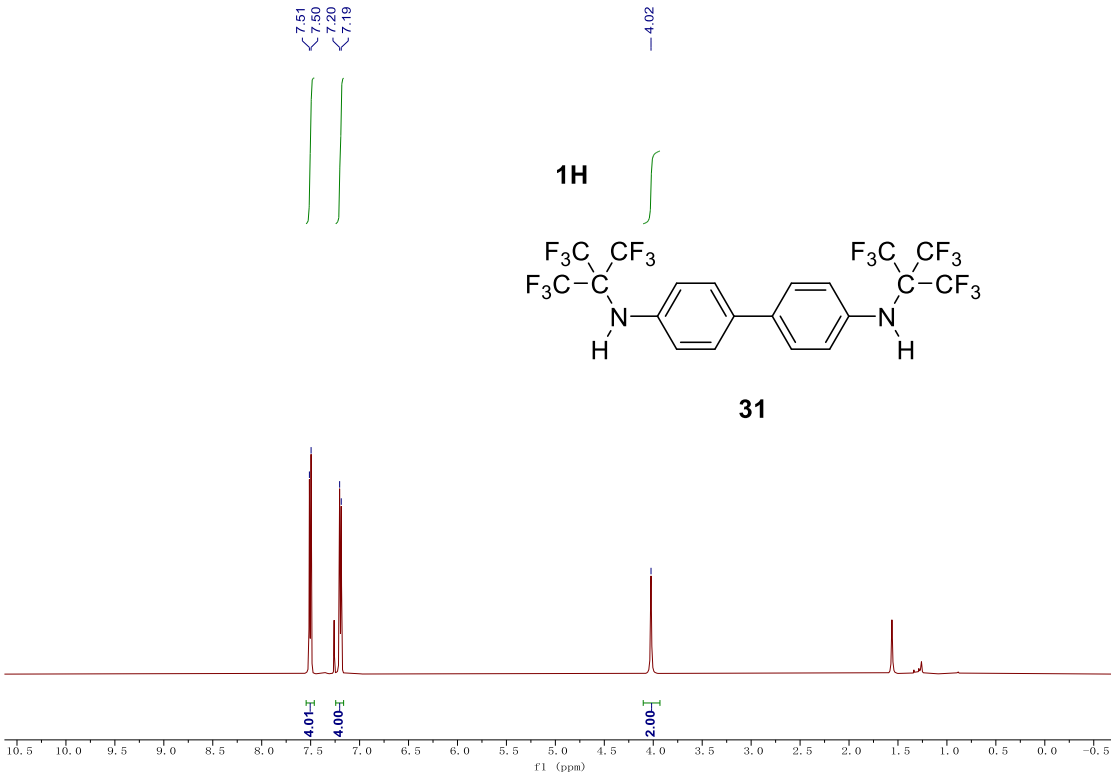
29

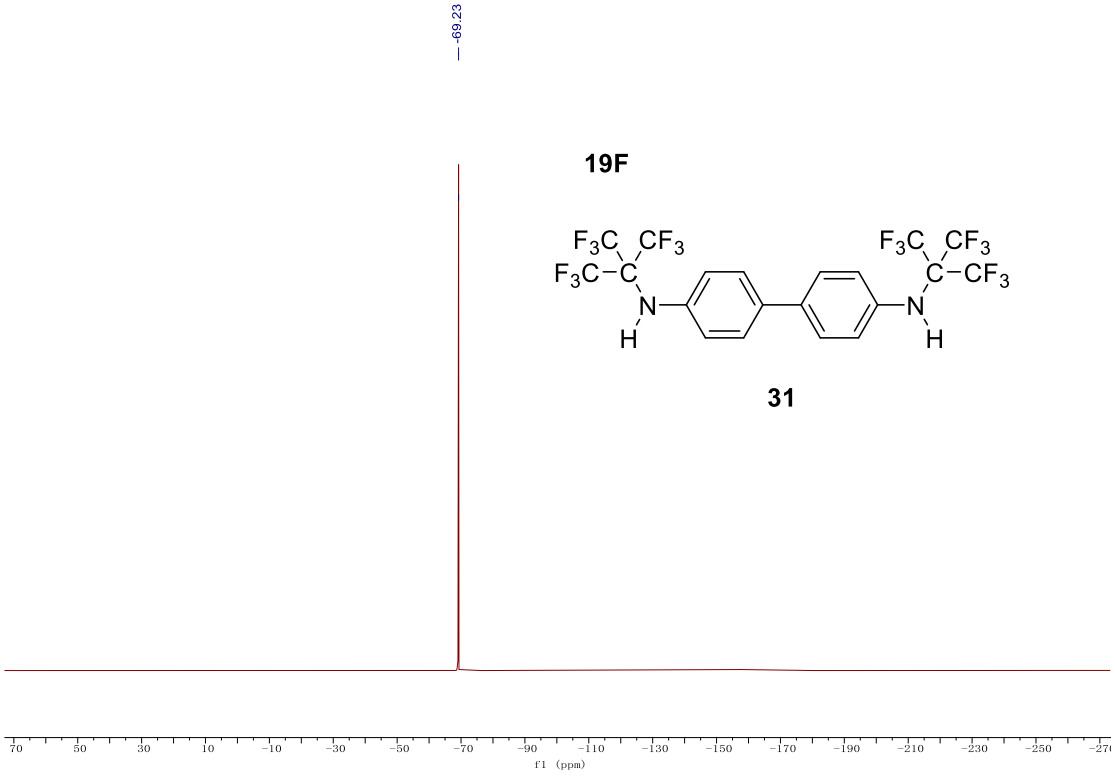

155.45
153.89
137.94
131.28
124.55
124.40
122.23
121.94
120.62
119.91
117.58
70.64
70.42
70.20
69.98
69.75
69.53
13C
H
N
N
C
CF3
CF3
CF3
S
29
f1 (ppm)

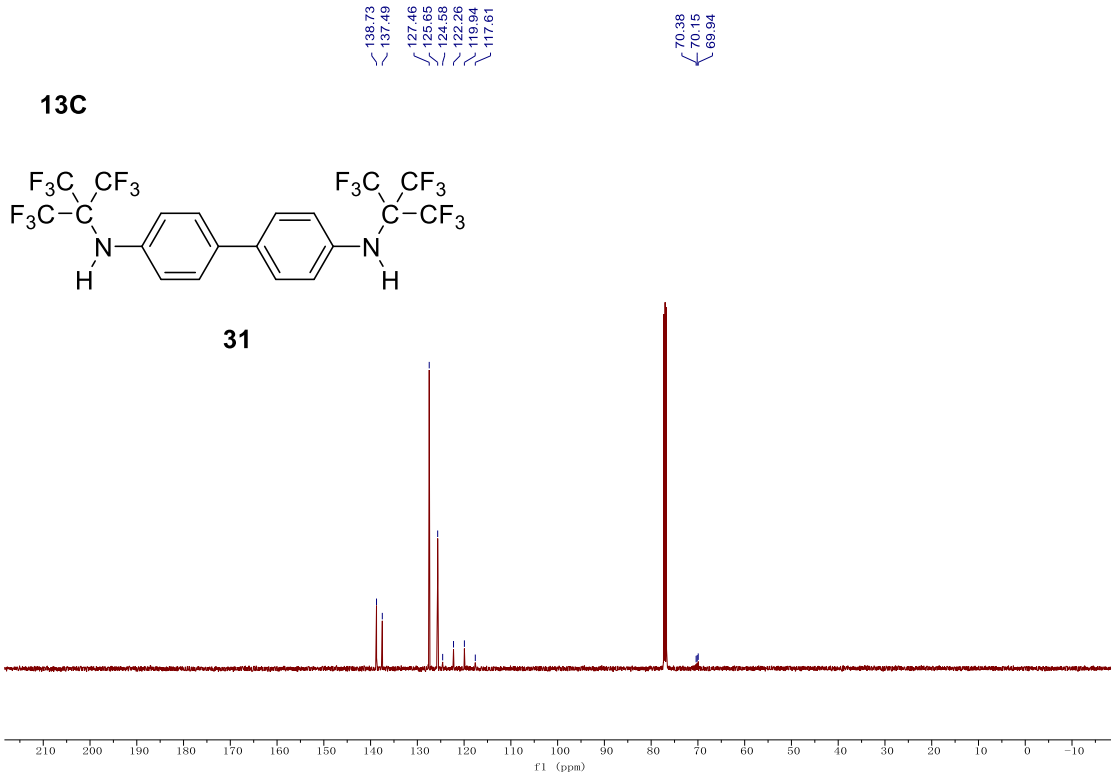

9.15
8.44
8.30
8.29
8.14
8.12
7.89
7.88
7.87
7.87
7.87
7.85
7.85
7.74
7.74
7.72
7.72
7.72
7.71
7.71
1H
H
N
N
C
CF3
CF3
CF3
30
1.00
1.00
1.01
1.02
1.03
1.03
f1 (ppm)

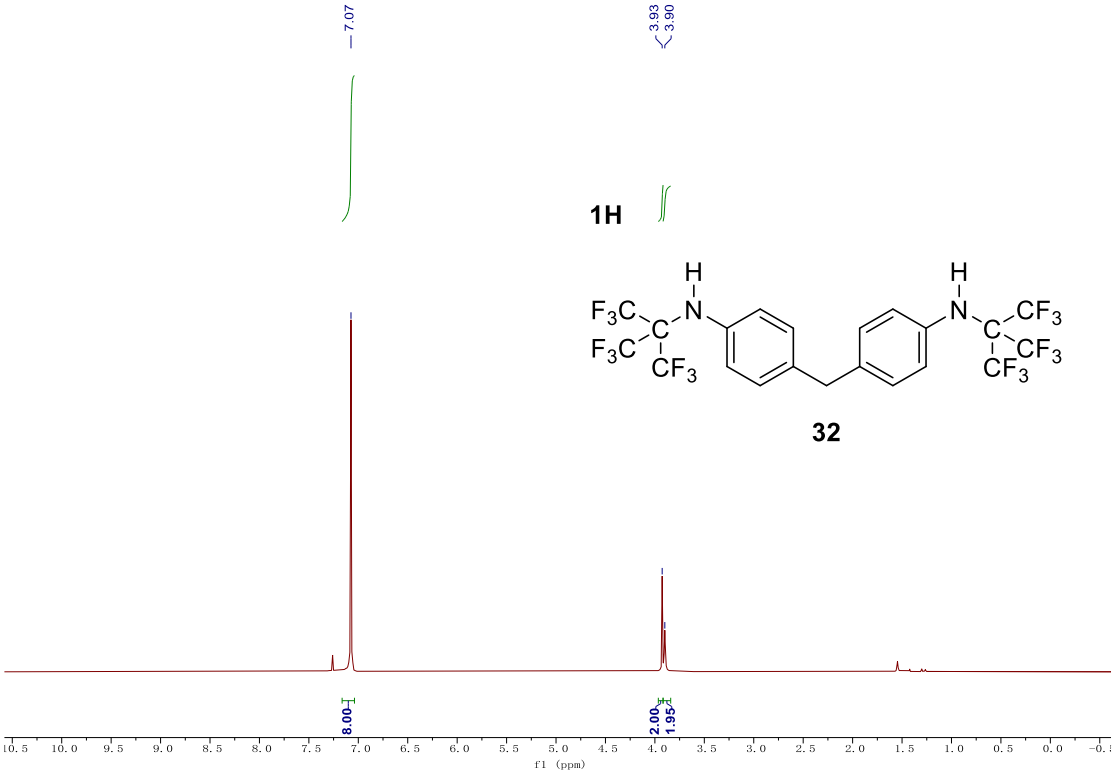

-69.89
19F
H
N
CF3
C
CF3
CF3
N
30
f1 (ppm)

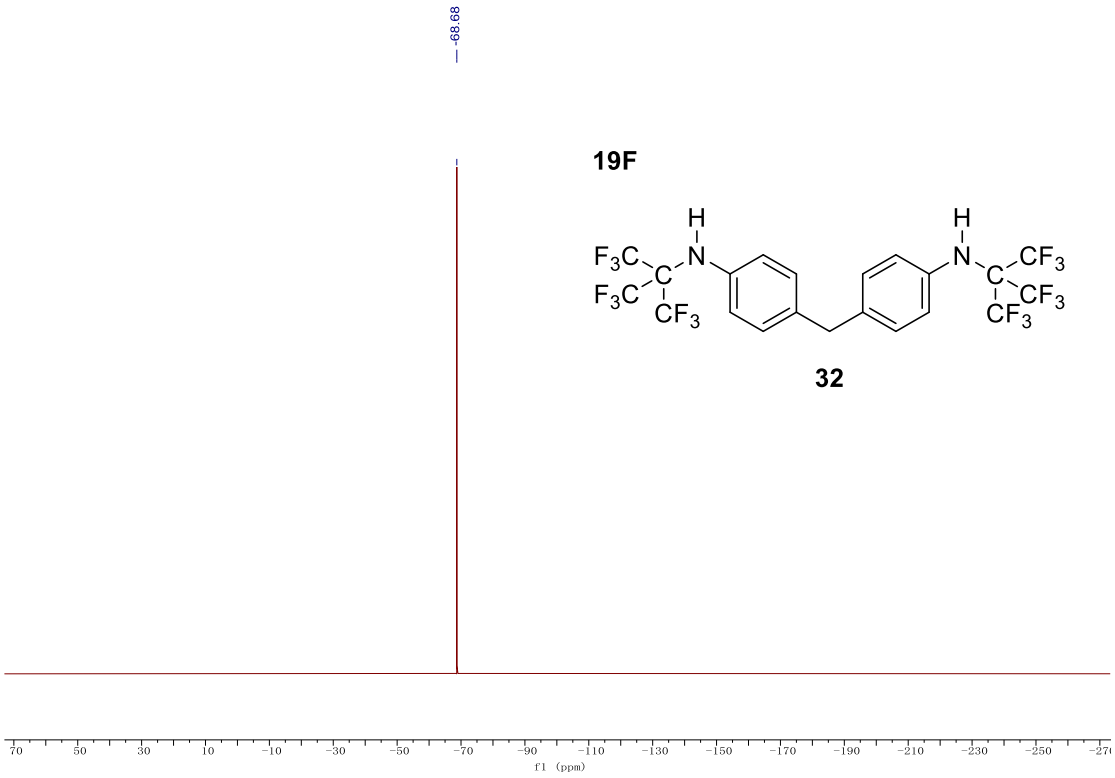

150.74
141.02
141.00
140.98
140.97
135.91
131.63
131.13
129.30
127.79
127.68
124.87
122.55
122.18
120.23
117.94
70.85
70.63
70.41
70.18
13C
H
N
CF3
C
CF3
CF3
N
30
f1 (ppm)


7.51
7.50
7.20
7.19
4.02
1H
F3C CF3
F3C C
N
H
F3C CF3
C CF3
N
H
31
4.01
4.00
2.00
f1 (ppm)

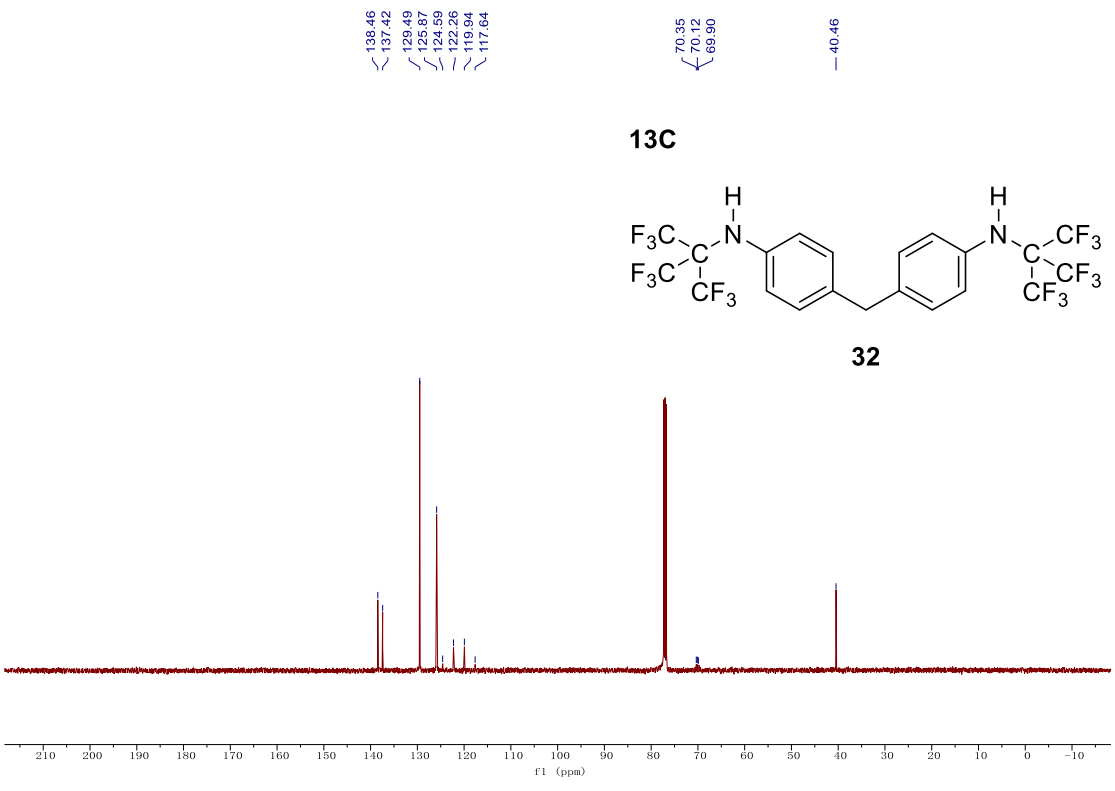

-69.23
19F
F3C CF3
F3C C
N
H
F3C CF3
C CF3
N
H
31
f1 (ppm)


138.73
137.49
127.46
125.65
124.58
122.26
119.94
117.61
70.38
70.15
69.94
13C
31
f1 (ppm)

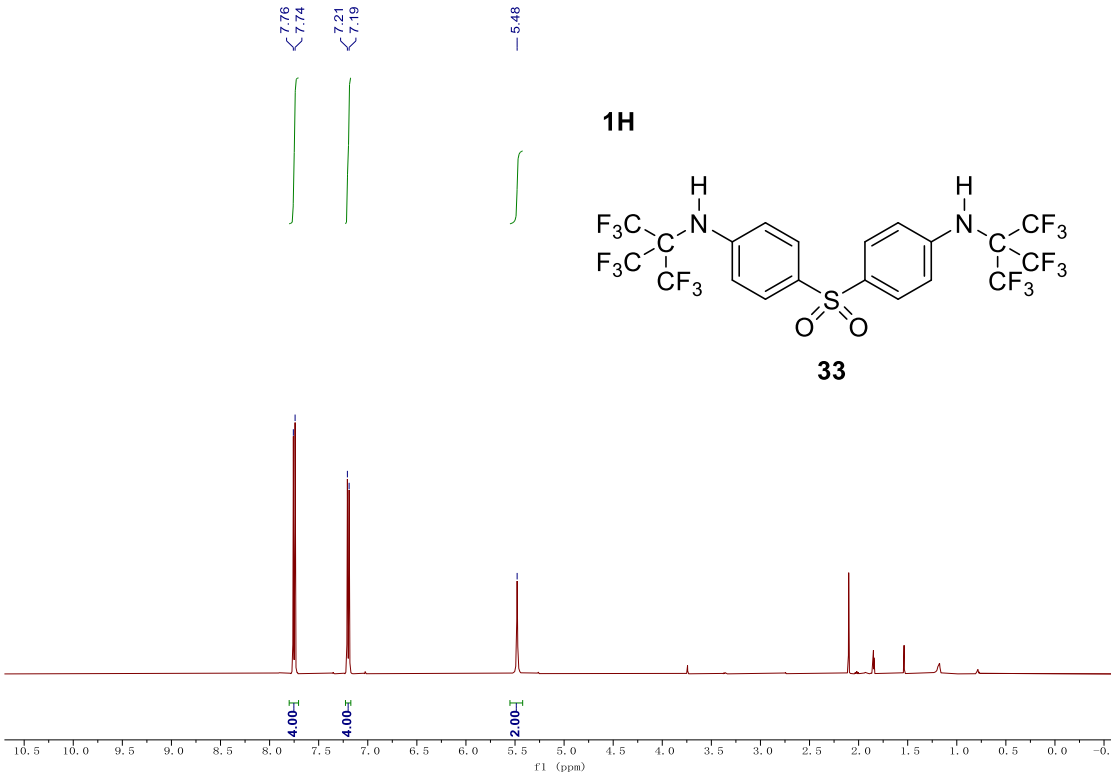

7.07
3.93
3.90
1H
32
8.00
2.00
1.95
f1 (ppm)


-68.68
19F
f1 (ppm)

32

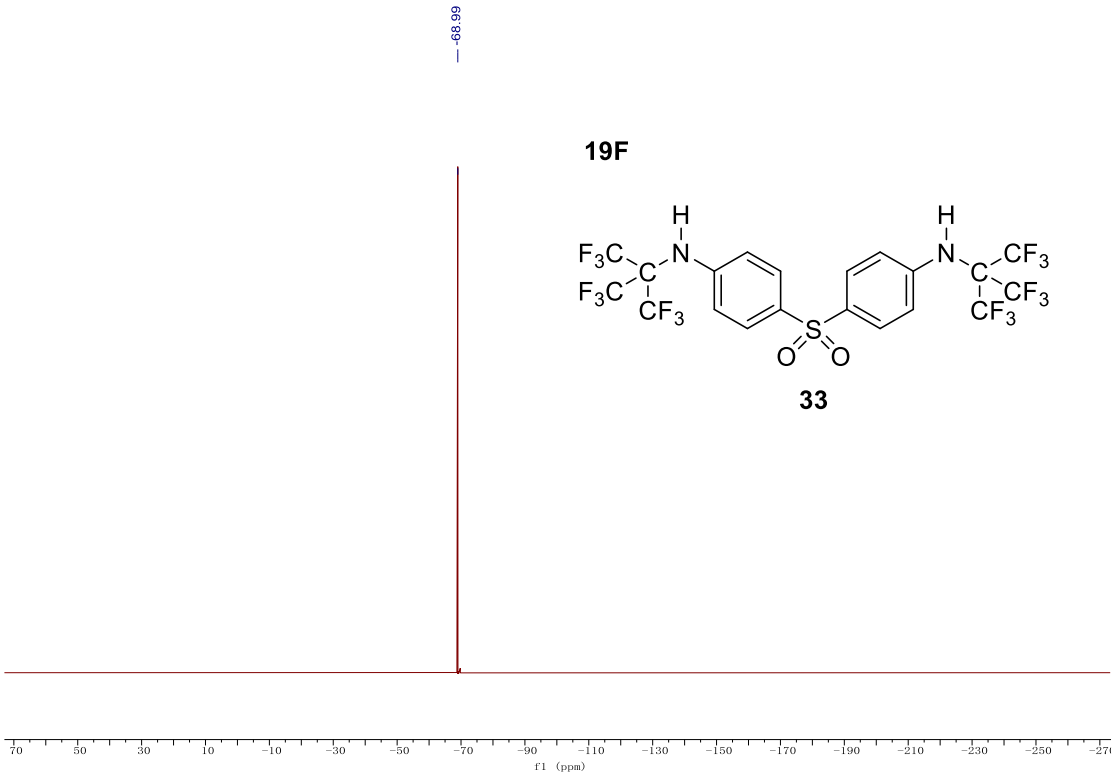

138.46
137.42
129.49
125.87
124.59
122.26
119.94
117.64
70.35
70.12
69.90
40.46
13C
f1 (ppm)

32



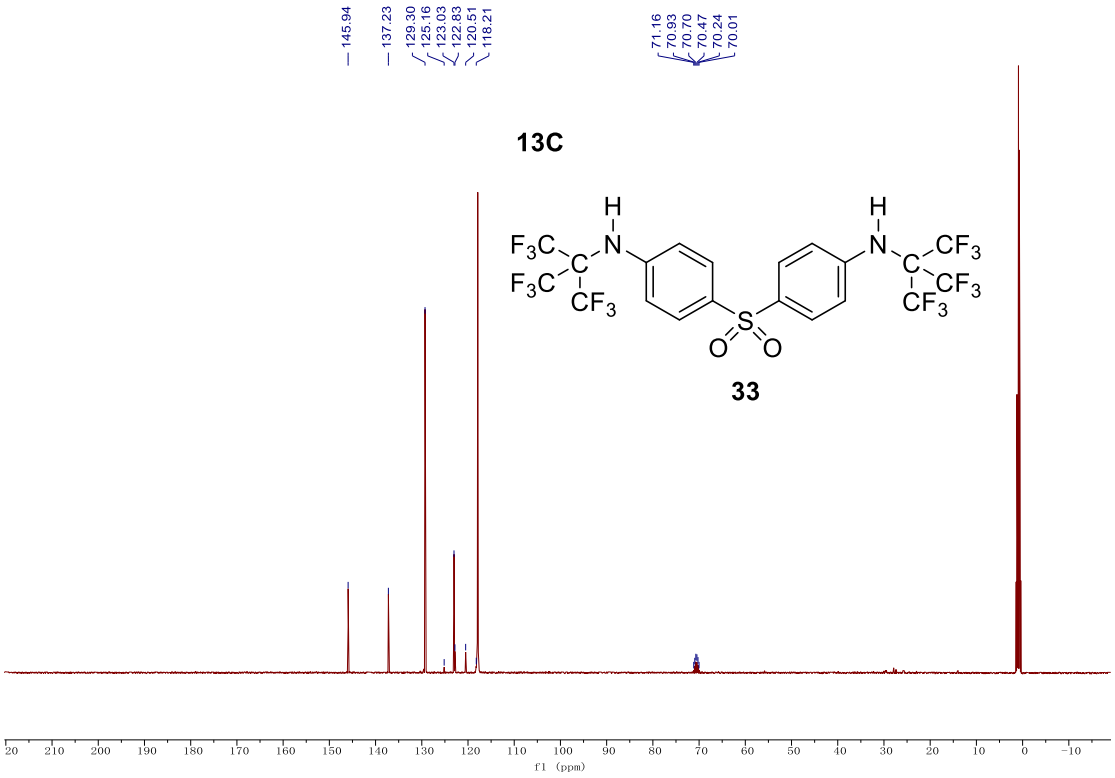
1H

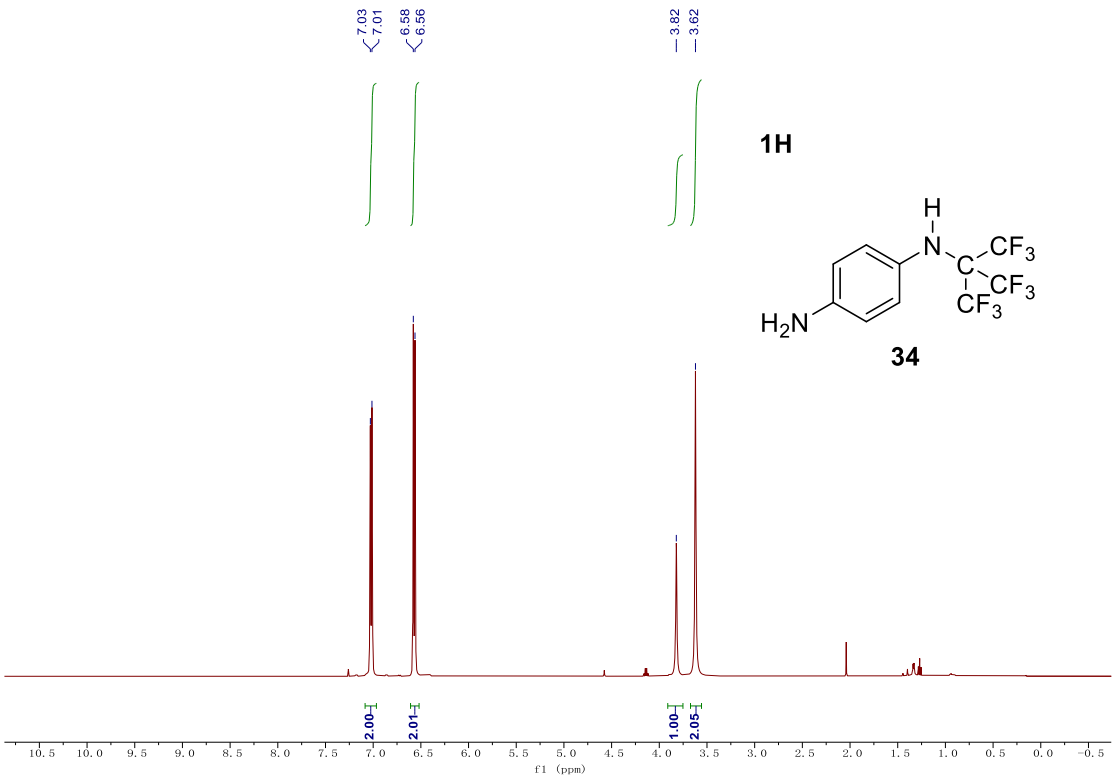
33

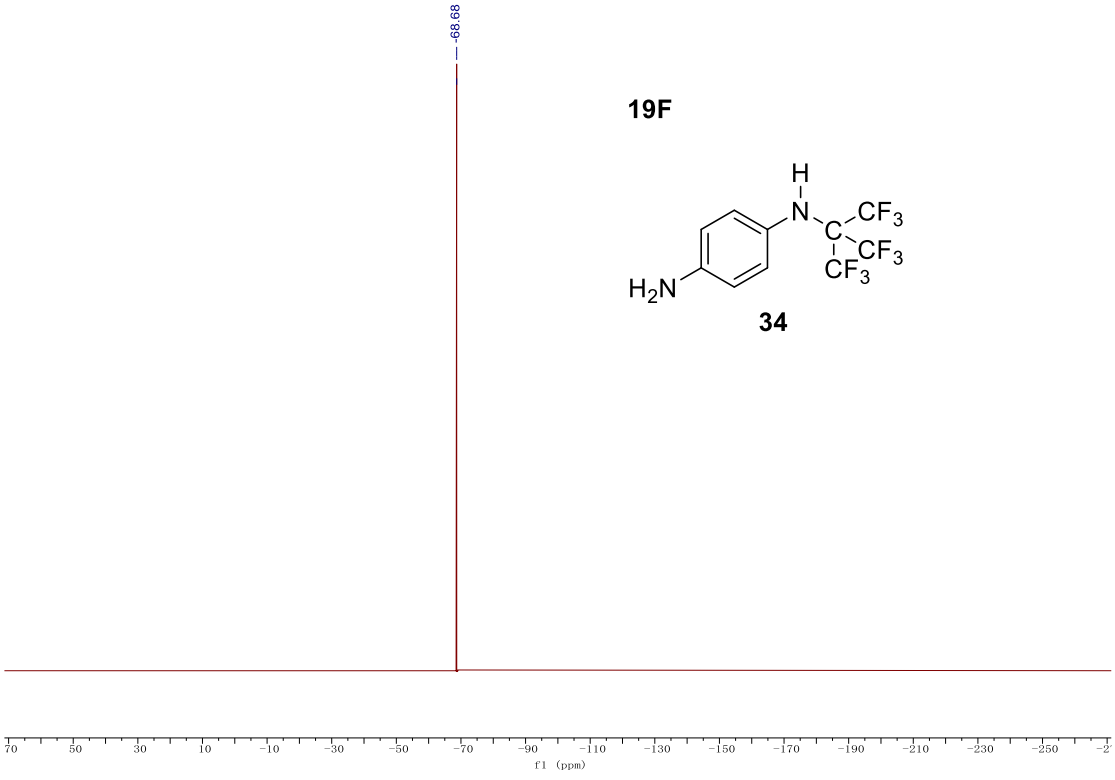


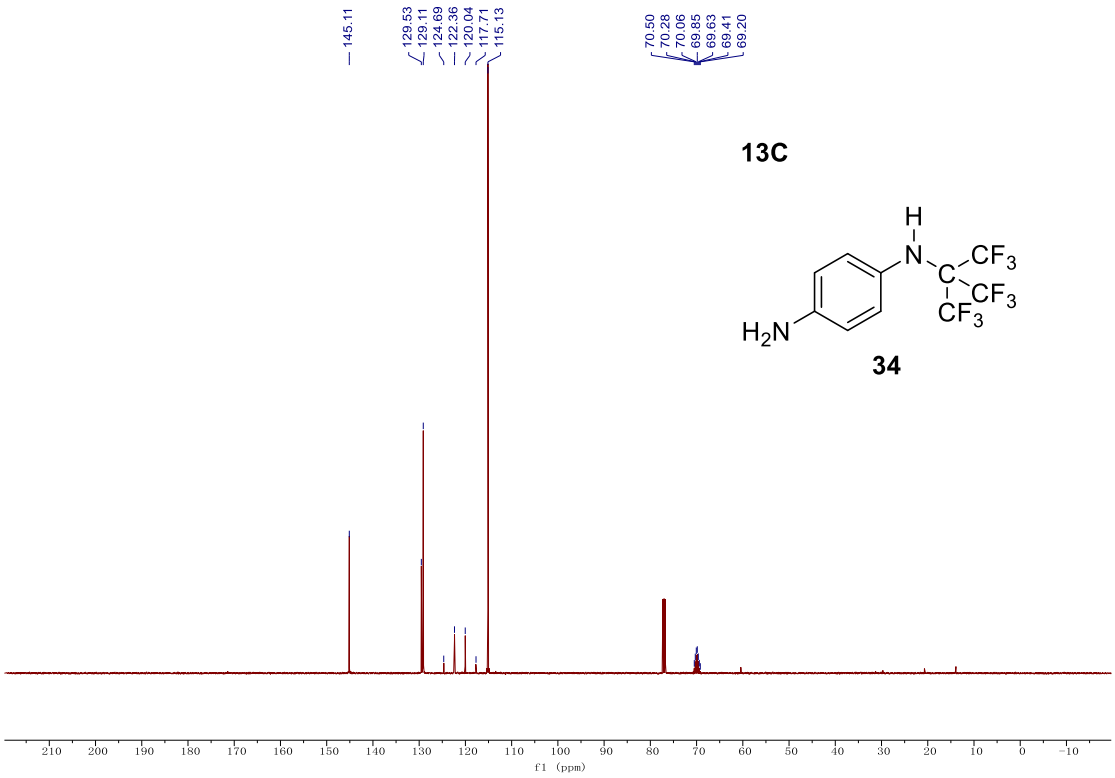
19F

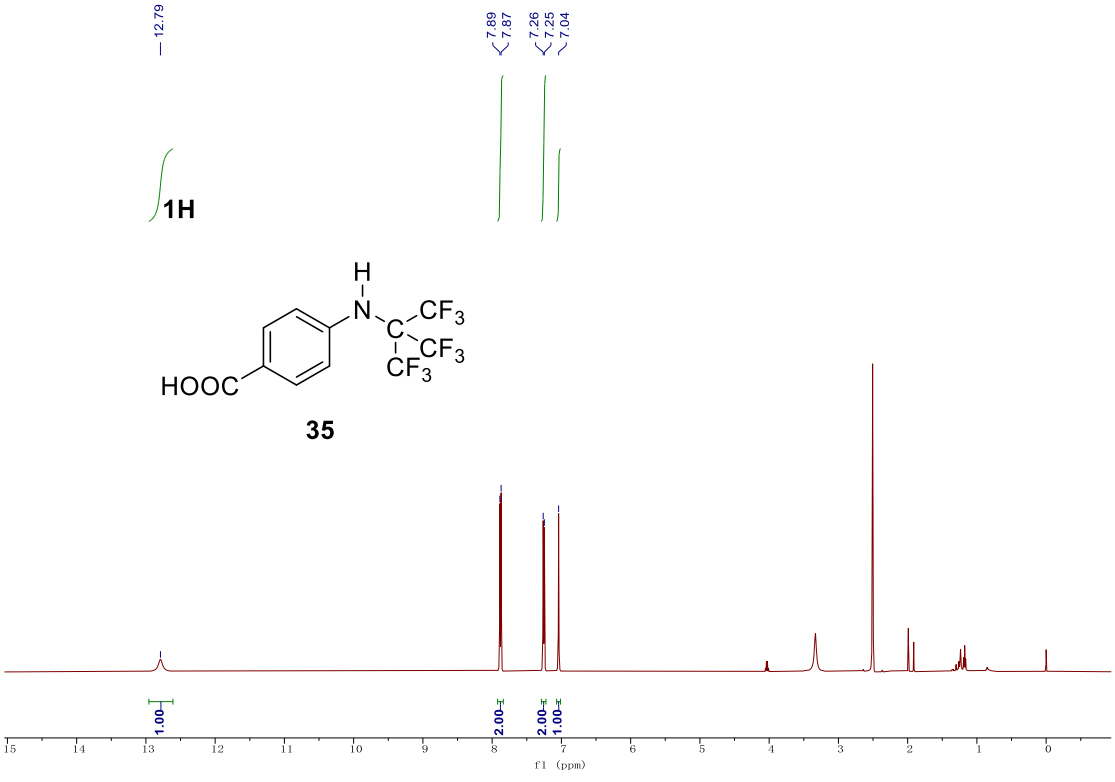
33

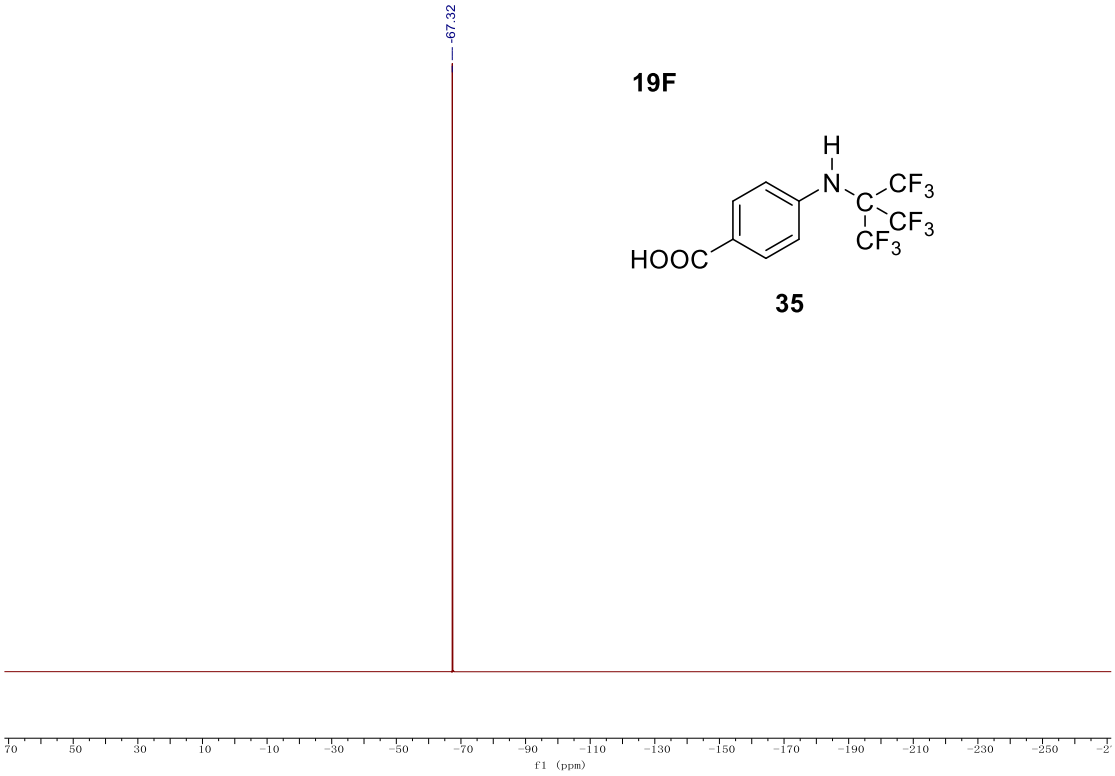

145.94
137.23
129.30
125.16
123.03
122.83
120.51
118.21
71.16
70.93
70.70
70.47
70.24
70.01
13C
33
f1 (ppm)

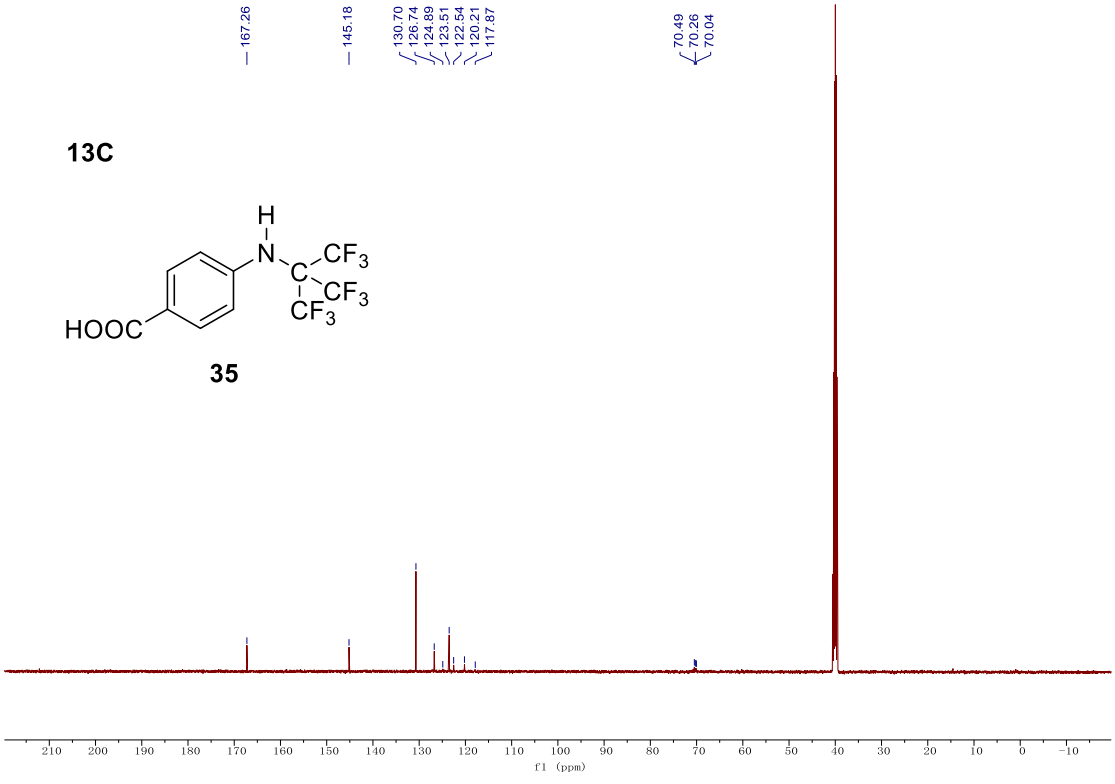

7.03
7.01
6.58
6.56
3.82
3.62
1H
H
N
C
CF3
CF3
CF3
H2N
34
2.00
2.01
1.00
2.05
f1 (ppm)

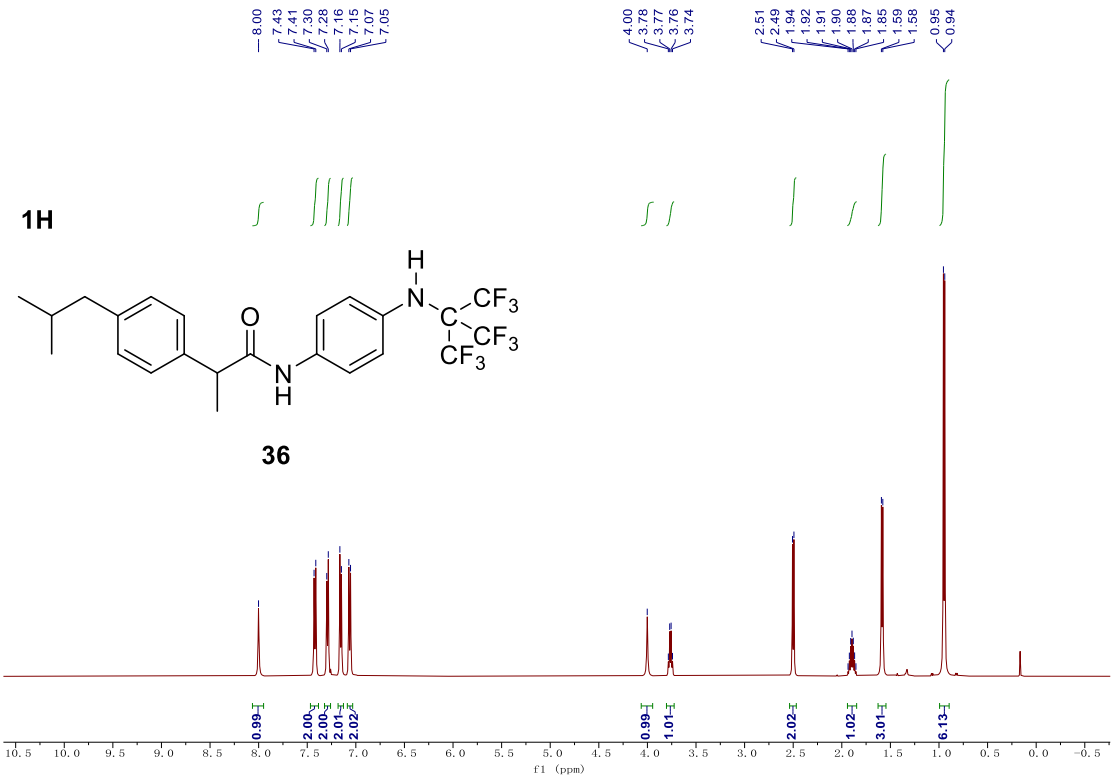

-68.68
19F
H
N
C
CF3
CF3
CF3
H2N
34
f1 (ppm)


145.11
129.53
129.11
124.69
122.36
120.04
117.71
115.13
70.50
70.28
70.06
69.85
69.63
69.41
69.20
13C
H
N
C
CF3
CF3
CF3
H2N
34
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


12.79
7.89
7.87
7.26
7.25
7.04
1H
H
N
C
CF3
CF3
CF3
HOOC
35
1.00
2.00
2.00
1.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


-67.32
19F
H
N
C
CF3
CF3
CF3
HOOC
35
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -2
f1 (ppm)


167.26
145.18
130.70
126.74
124.89
123.51
122.54
120.21
117.87
70.49
70.26
70.04
13C
H
N
C
CF3
CF3
CF3
HOOC
35
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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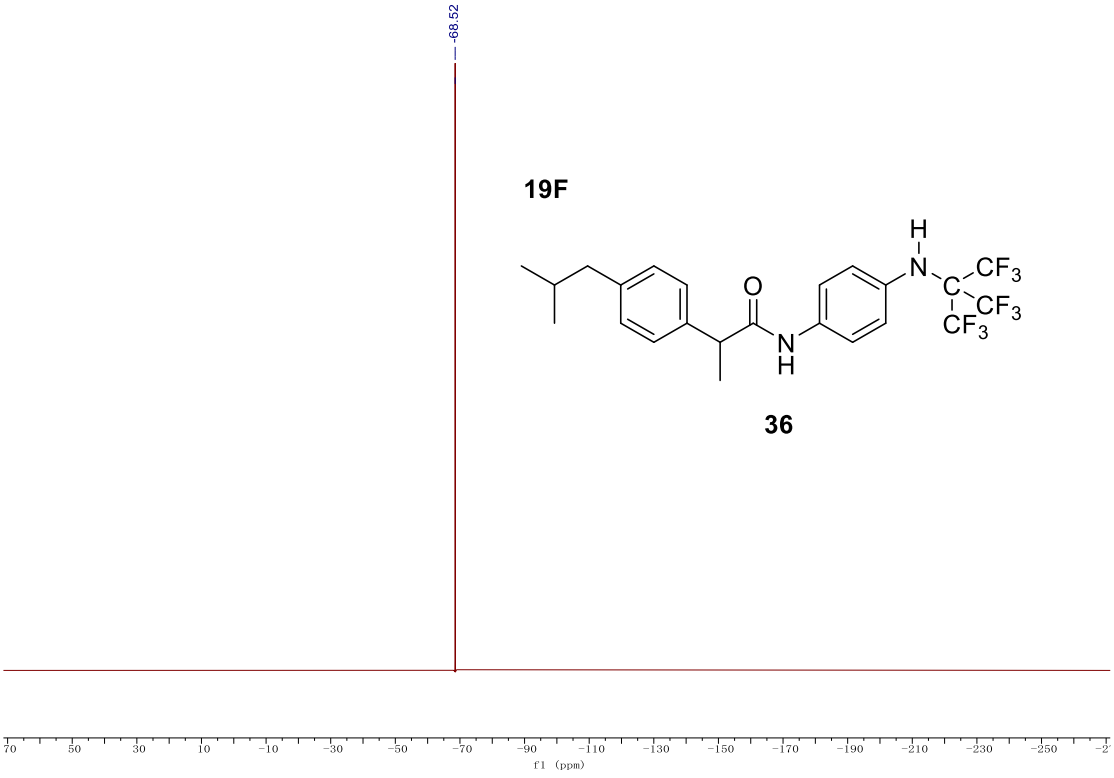
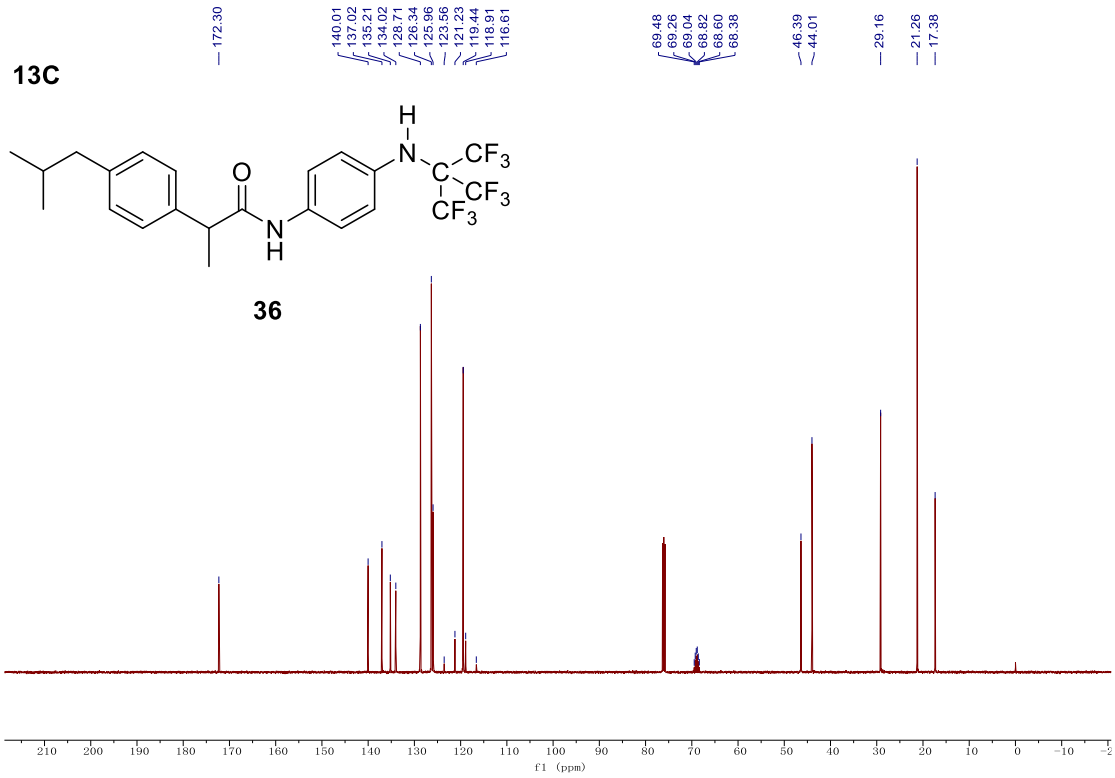
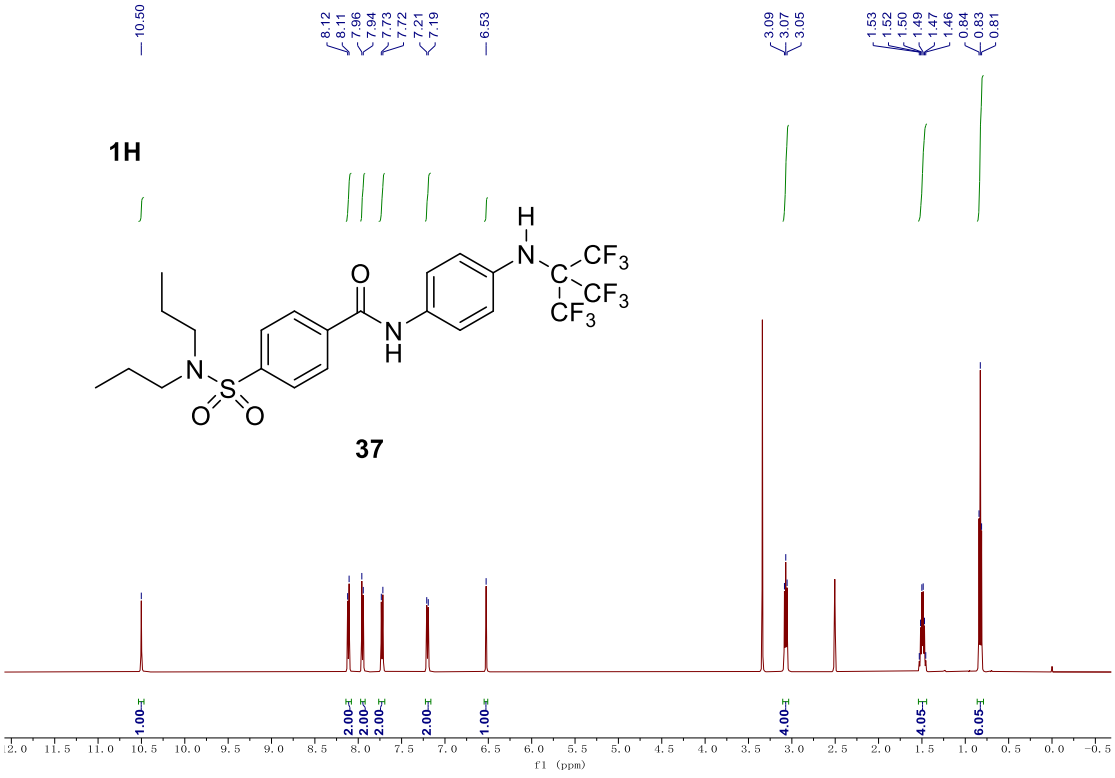
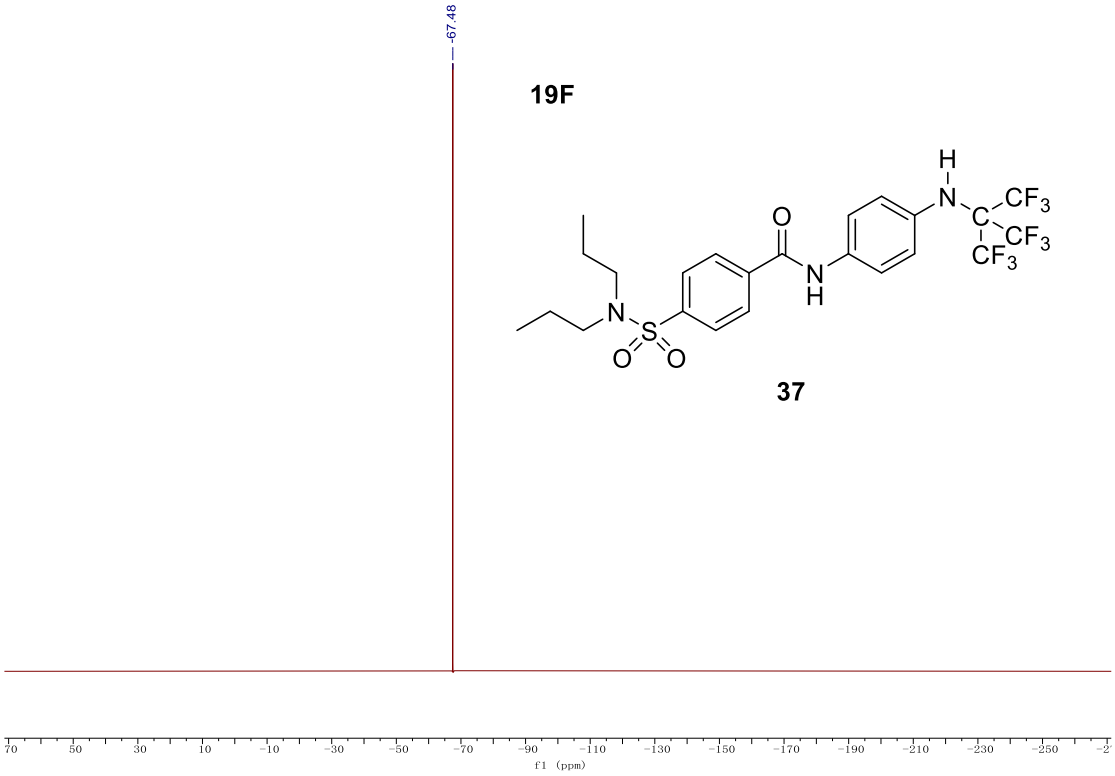
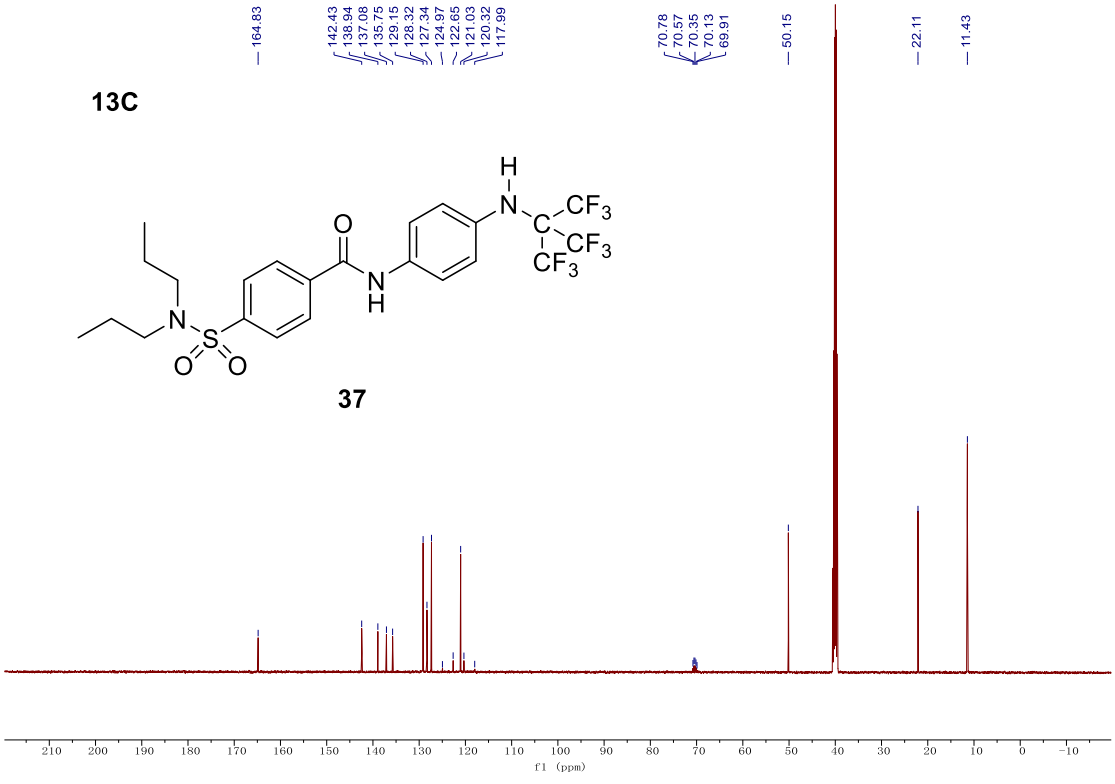
7.43
7.41
7.30
7.28
7.16
7.15
7.07
7.05
4.00
3.78
3.77
3.76
3.74
2.51
2.49
1.94
1.92
1.91
1.90
1.88
1.87
1.85
1.59
1.58
0.95
0.94
1H
H
N
O
N
H
CF3
C
CF3
CF3
36
0.99
2.00
2.00
2.01
2.02
0.99
1.01
2.02
1.02
3.01
6.13
f1 (ppm)

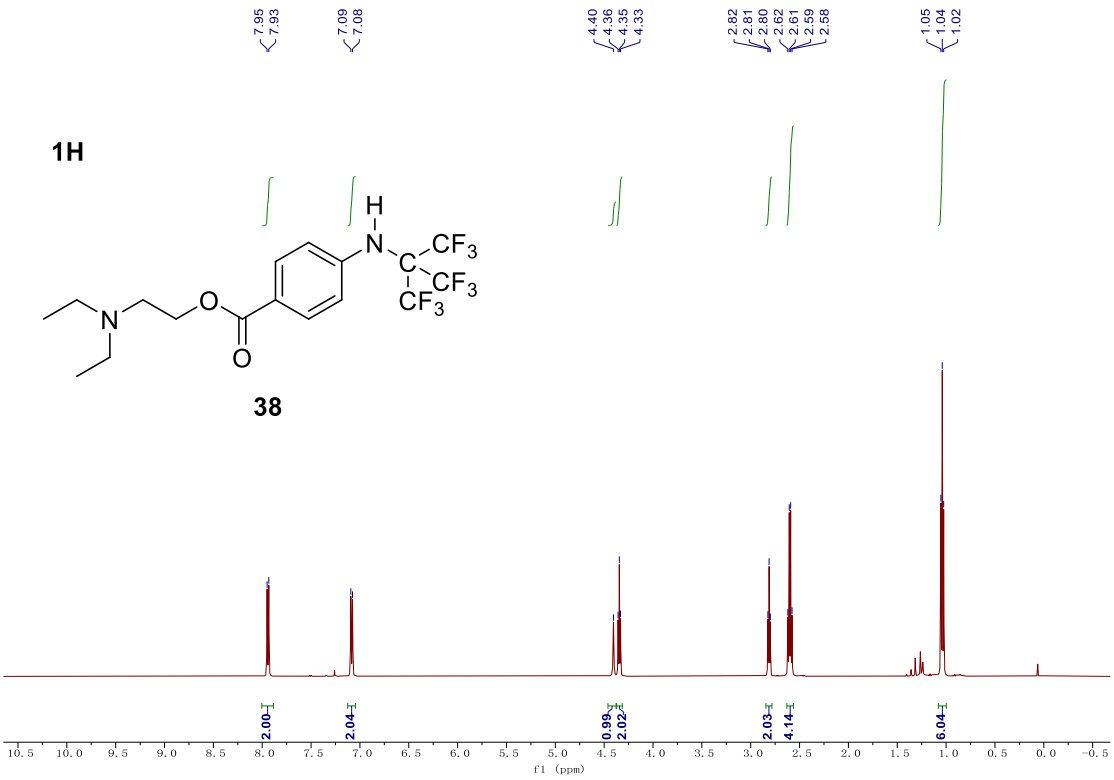

-68.52
19F
H
N
O
N
H
CF3
C
CF3
CF3
36
f1 (ppm)

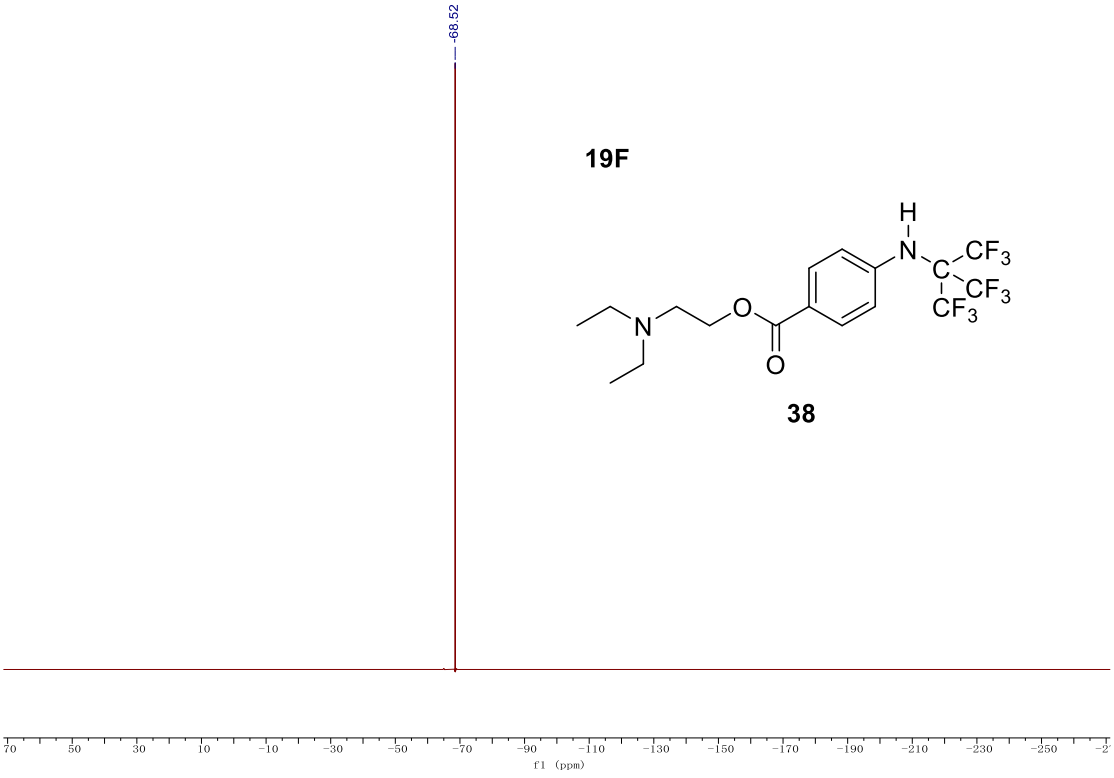

13C
172.30
140.01
137.02
135.21
134.02
128.71
126.34
125.96
123.56
121.23
119.44
118.91
116.61
69.48
69.26
69.04
68.82
68.60
68.38
46.39
44.01
29.16
21.26
17.38
36
f1 (ppm)


1H
10.50
8.12
8.11
7.96
7.94
7.73
7.72
7.21
7.19
6.53
3.09
3.07
3.05
1.53
1.52
1.50
1.49
1.47
1.46
0.84
0.83
0.81
37
1.00
2.00
2.00
2.00
2.00
1.00
4.00
4.05
6.05
f1 (ppm)


-67.48
19F
37
f1 (ppm)


164.83
142.43
138.94
137.08
135.75
129.15
128.32
127.34
124.97
122.65
121.03
120.32
117.99
70.78
70.57
70.35
70.13
69.91
50.15
22.11
11.43
13C
37
f1 (ppm)


1H
7.95
7.93
7.09
7.08
4.40
4.36
4.35
4.33
2.82
2.81
2.80
2.62
2.61
2.59
2.58
1.05
1.04
1.02
H
N
CF3
C
CF3
CF3
O
N
O
O
38
2.00
2.04
0.99
2.02
2.03
4.14
6.04
f1 (ppm)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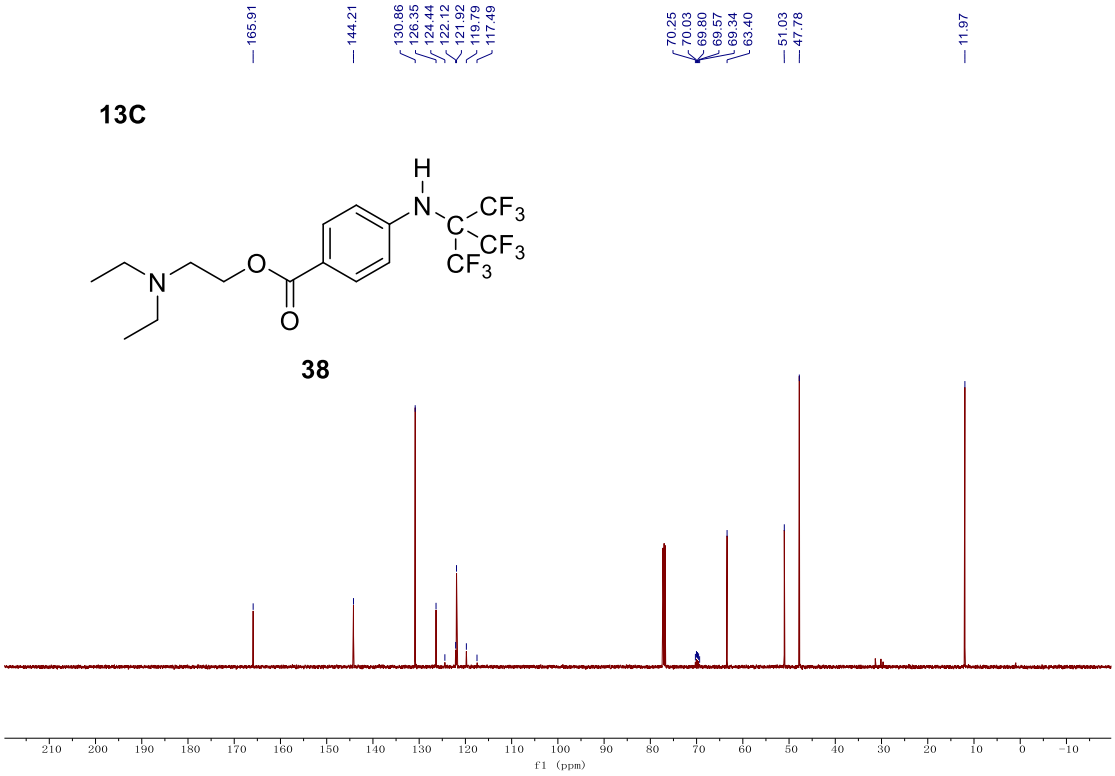
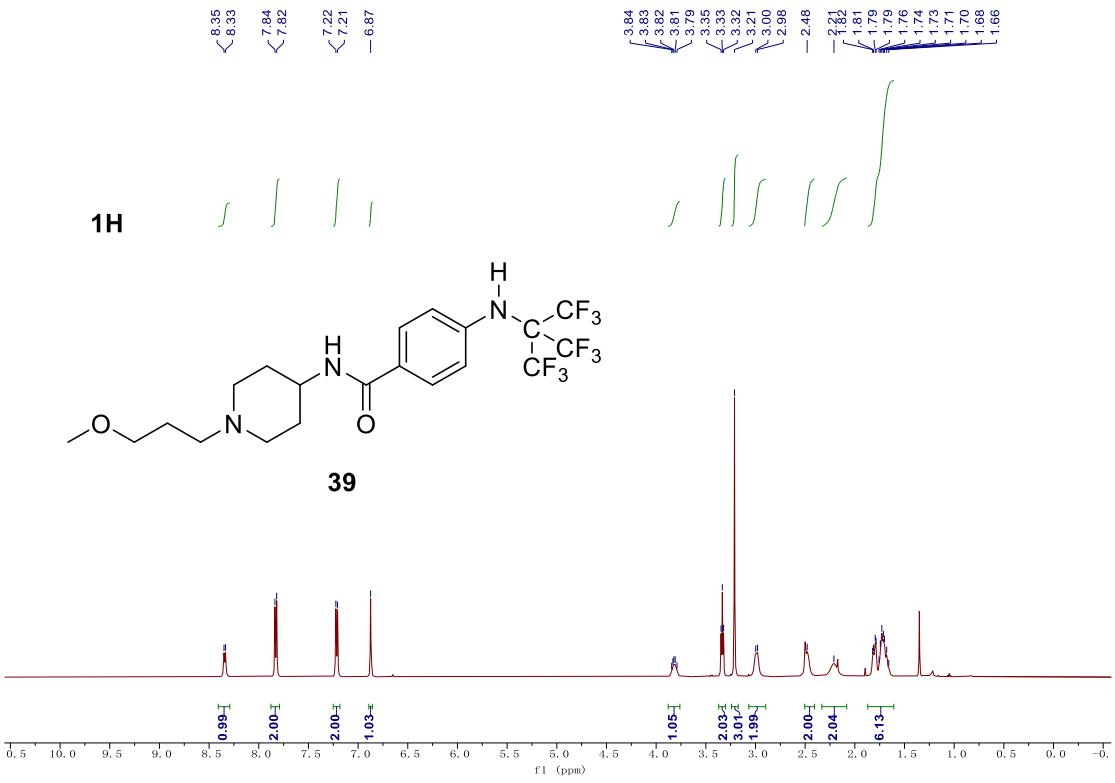
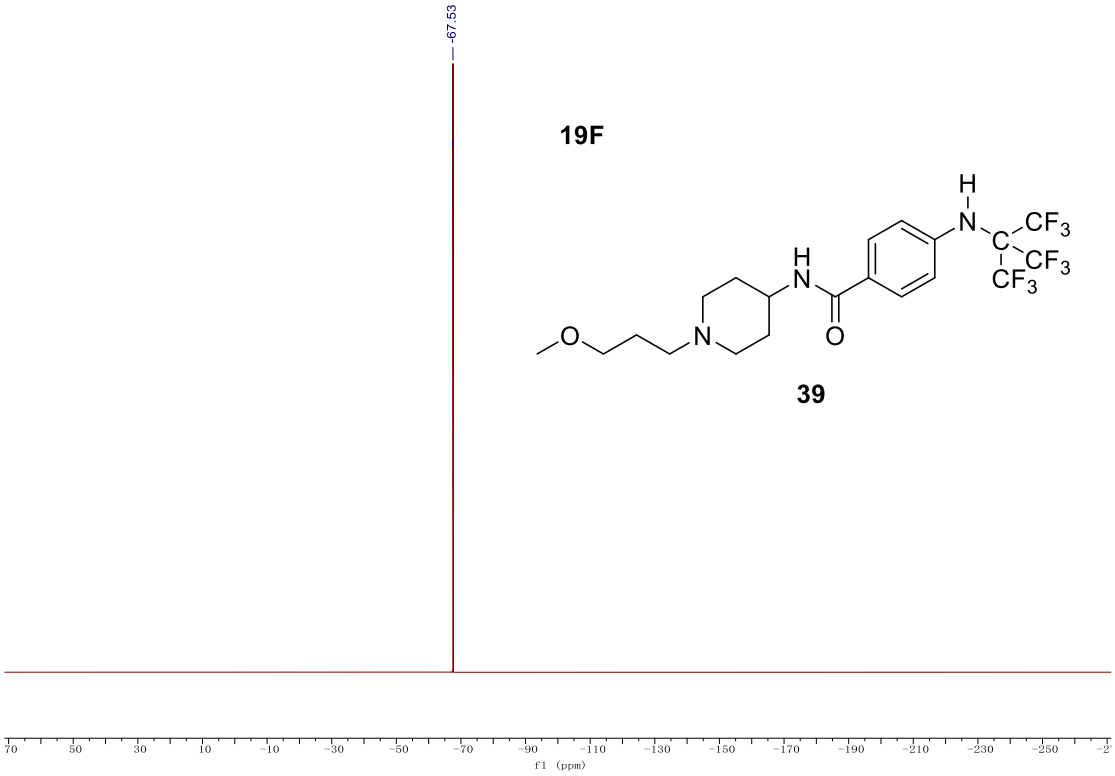
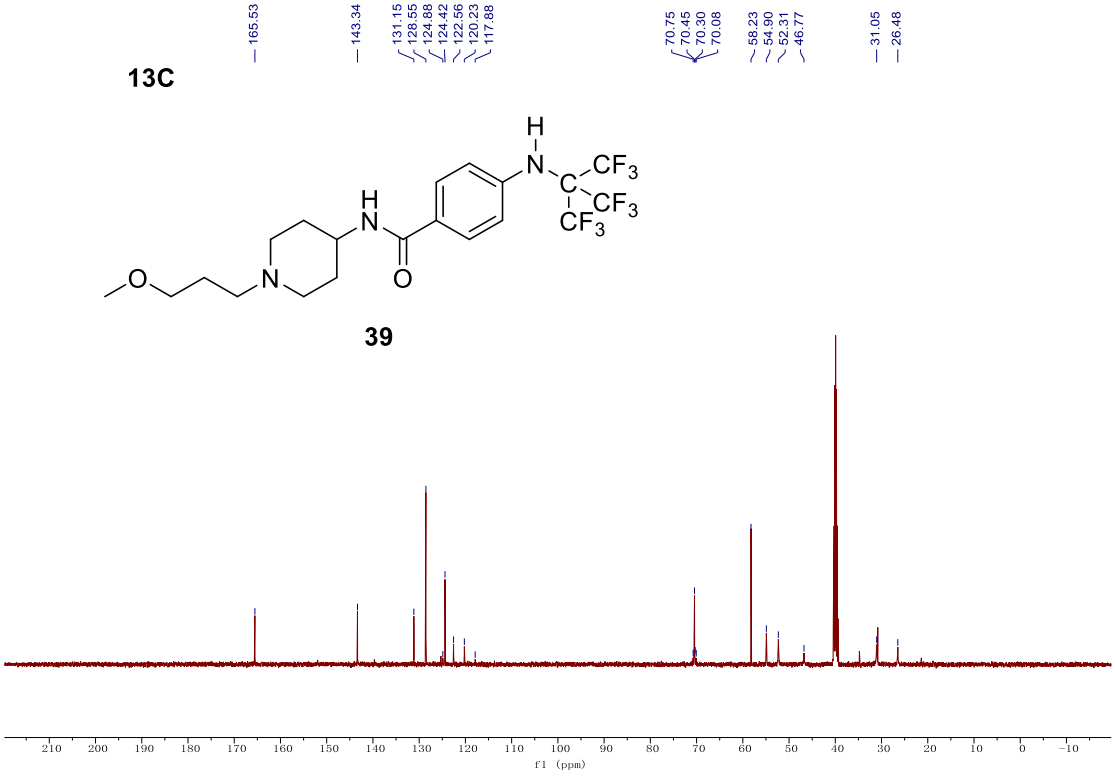
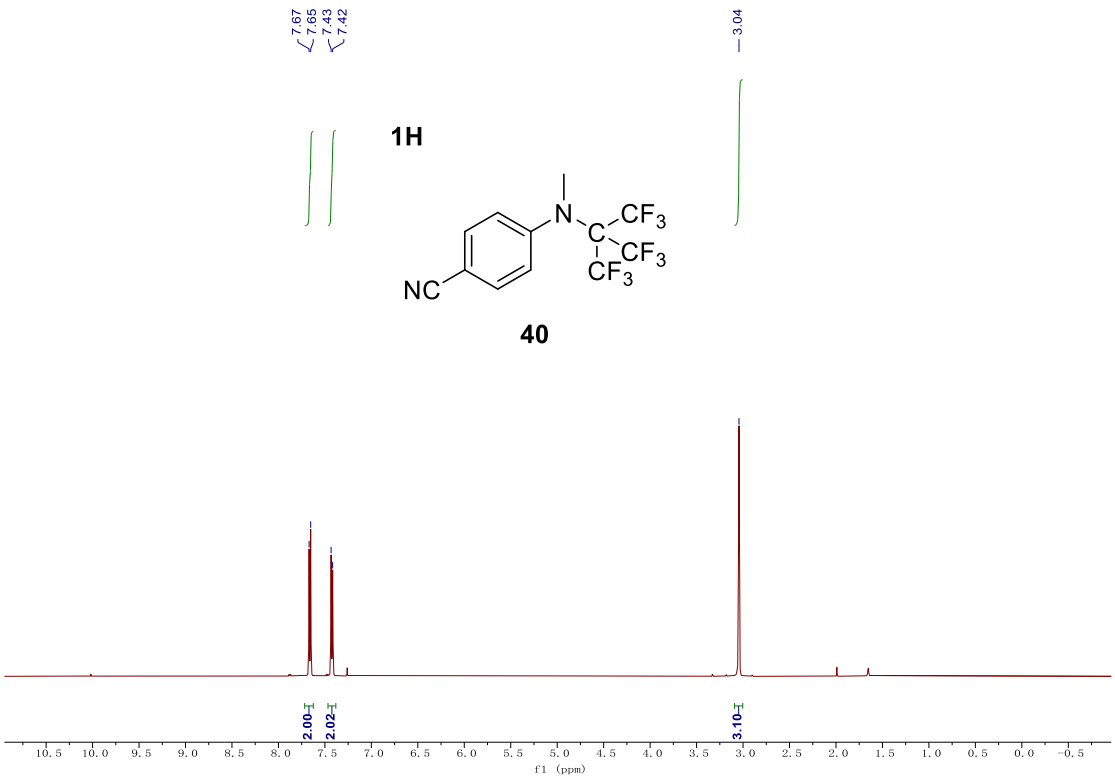
19F
H
N
CF3
C
CF3
CF3
O
N
O
O
38
f1 (ppm)

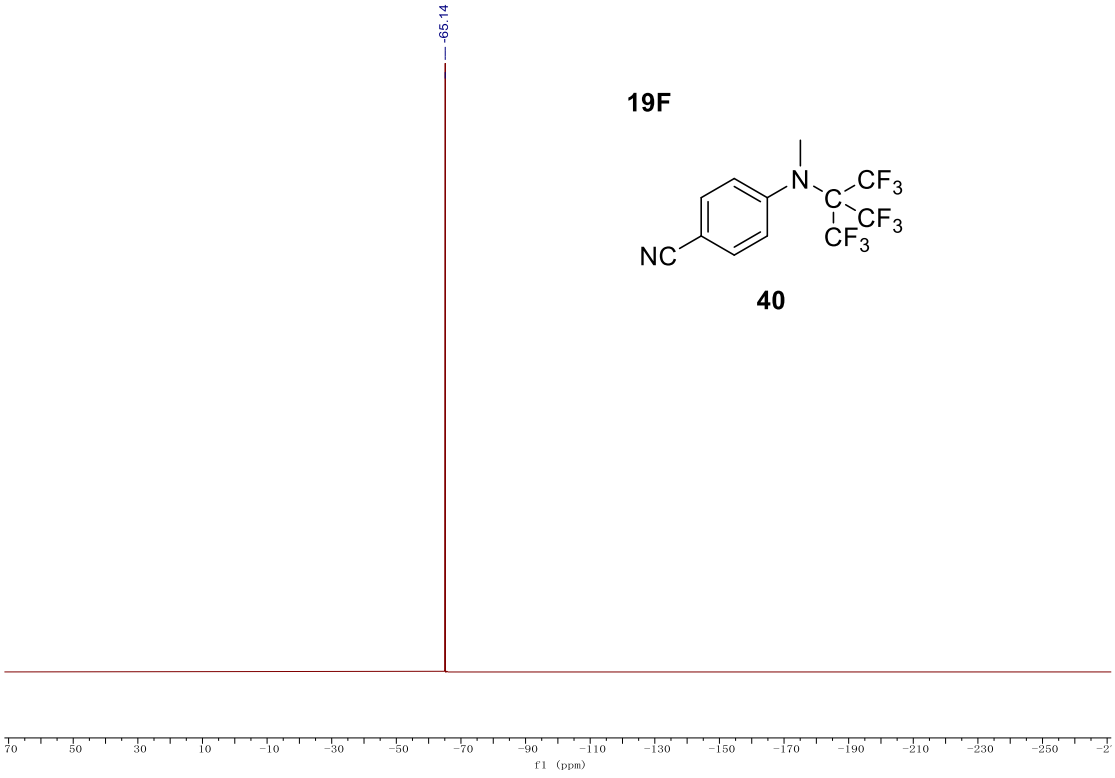

165.91
144.21
130.86
126.35
124.44
122.12
121.92
119.79
117.49
70.25
70.03
69.80
69.57
69.34
63.40
51.03
47.78
11.97
13C
H
N
CF3
C
CF3
CF3
O
N
O
O
38
f1 (ppm)

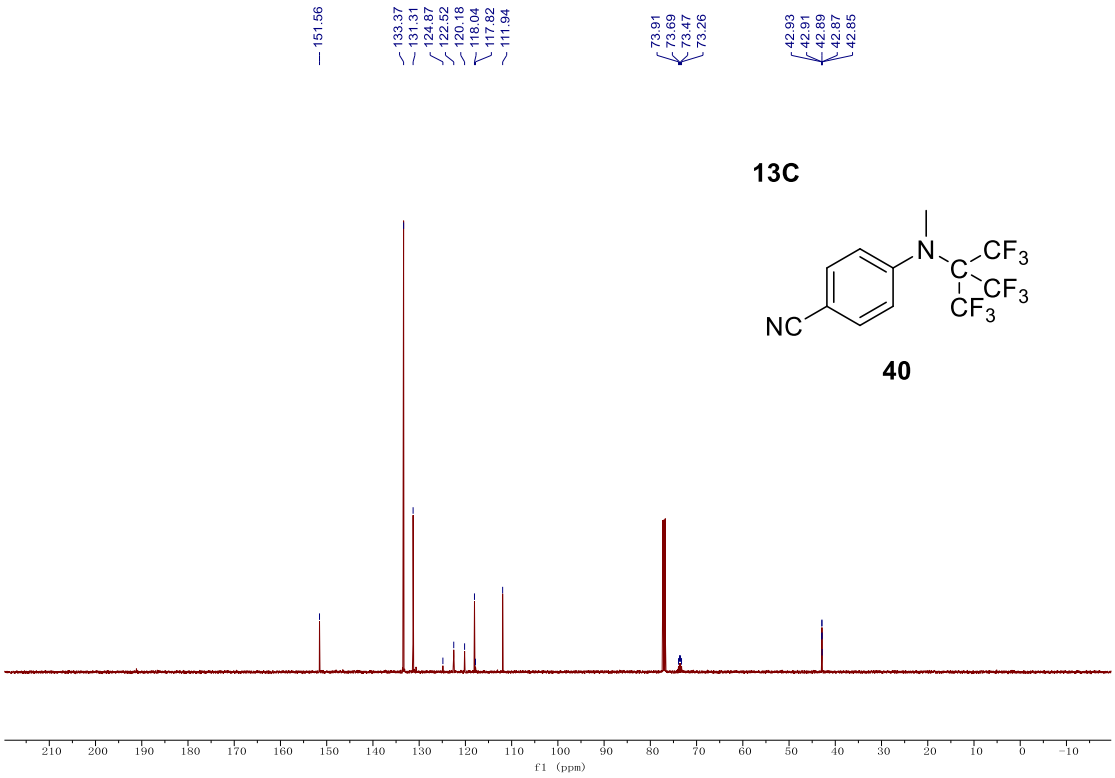

8.35
8.33
7.84
7.82
7.22
7.21
6.87
3.84
3.83
3.82
3.81
3.79
3.35
3.33
3.32
3.21
3.00
2.98
2.48
2.21
1.82
1.81
1.79
1.79
1.76
1.74
1.73
1.71
1.70
1.68
1.66
1H
H
N
CF3
C
CF3
CF3
H
N
O
N
O
39
0.99
2.00
2.00
1.03
1.05
2.03
3.01
1.99
2.00
2.04
6.13
f1 (ppm)

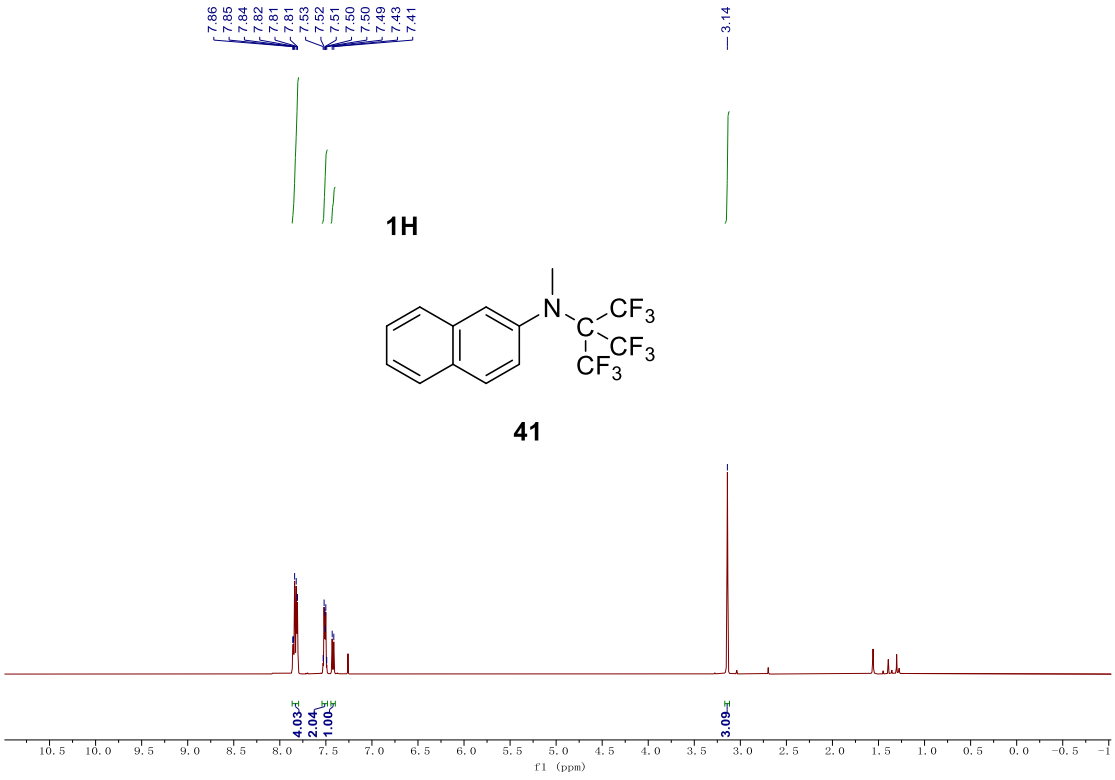

-67.53
19F
H
N
CF3
C
CF3
CF3
H
N
O
O
N
39
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

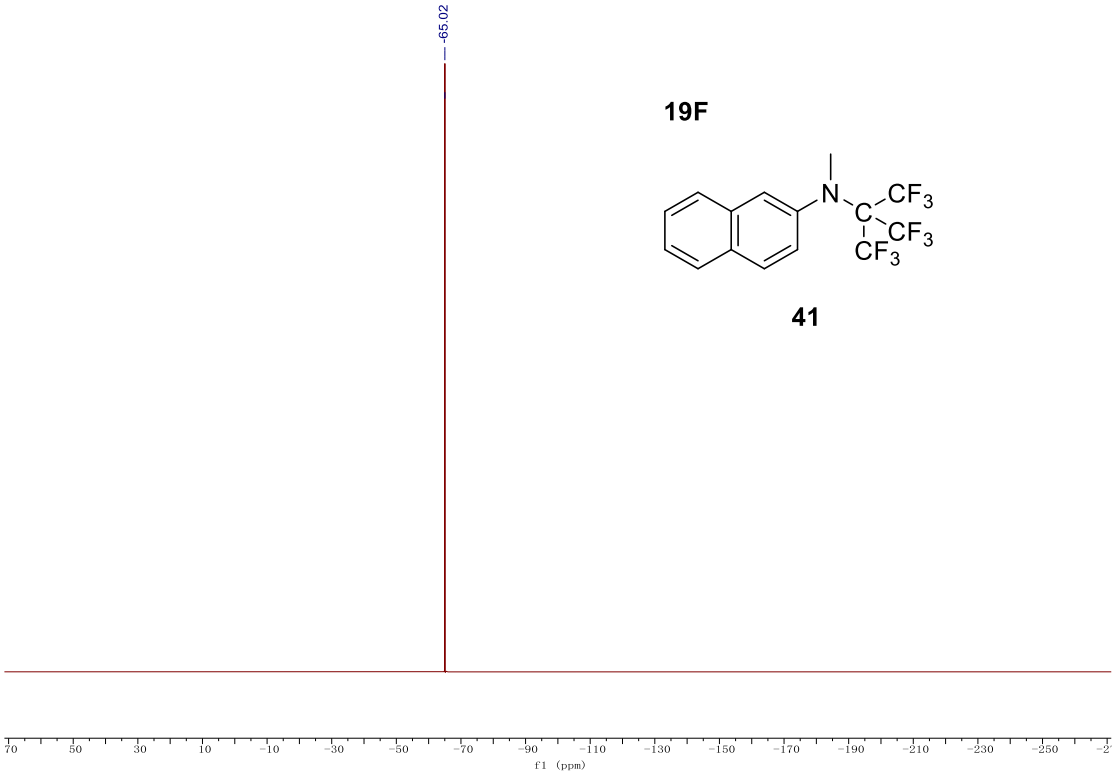

165.53
143.34
131.15
128.55
124.88
124.42
122.56
120.23
117.88
70.75
70.45
70.30
70.08
58.23
54.90
52.31
46.77
31.05
26.48
13C
H
N
CF3
C
CF3
CF3
H
N
O
O
N
39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

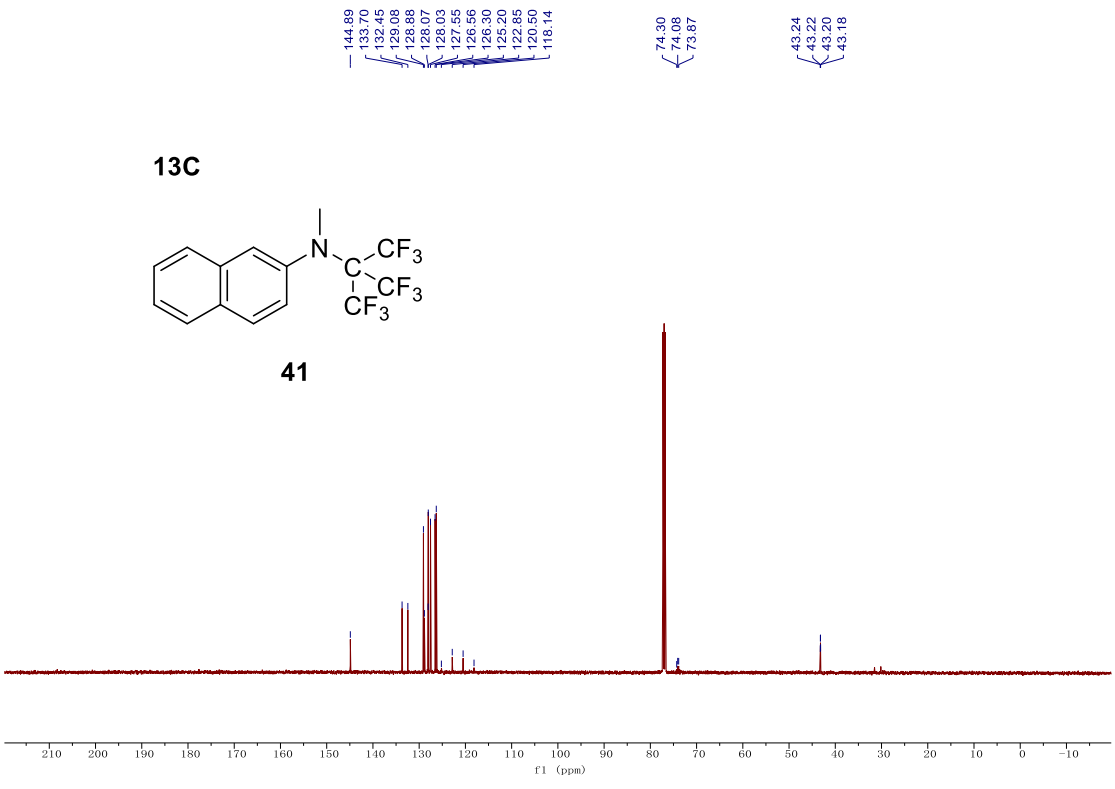

7.67
7.65
7.43
7.42
3.04
1H
N
C
CF3
CF3
CF3
NC
40
2.00
2.02
3.10
f1 (ppm)

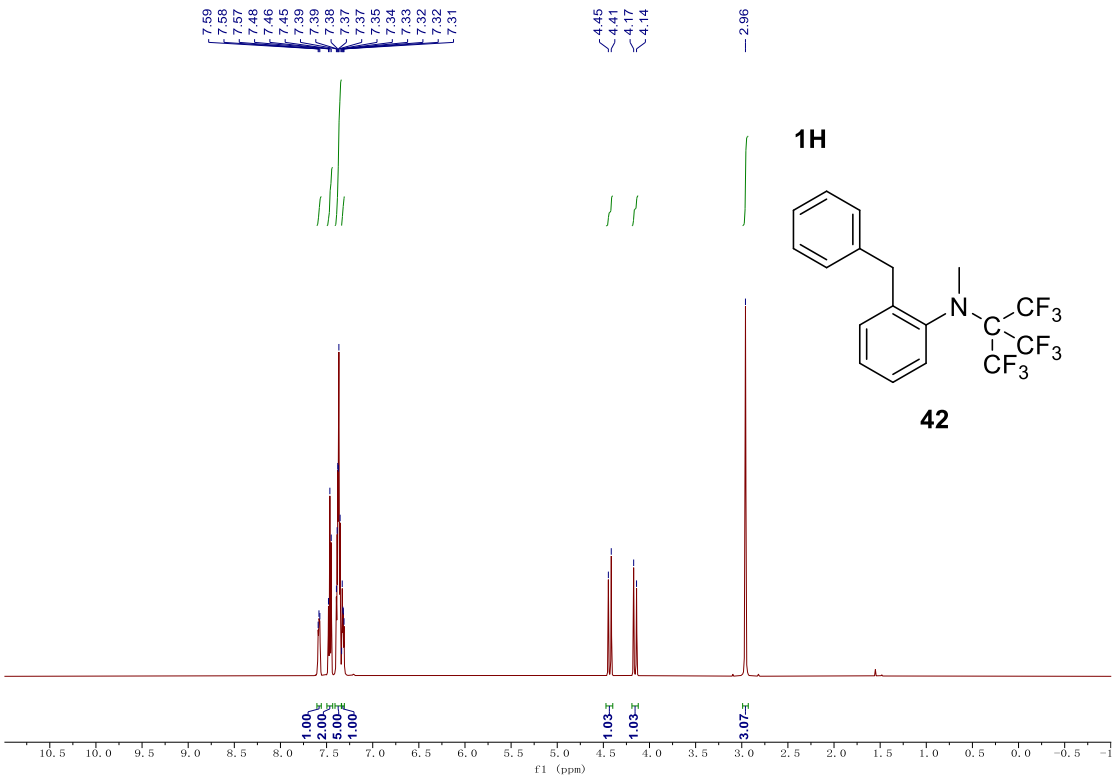

-65.14
19F
N
C
CF3
CF3
CF3
NC
40
f1 (ppm)

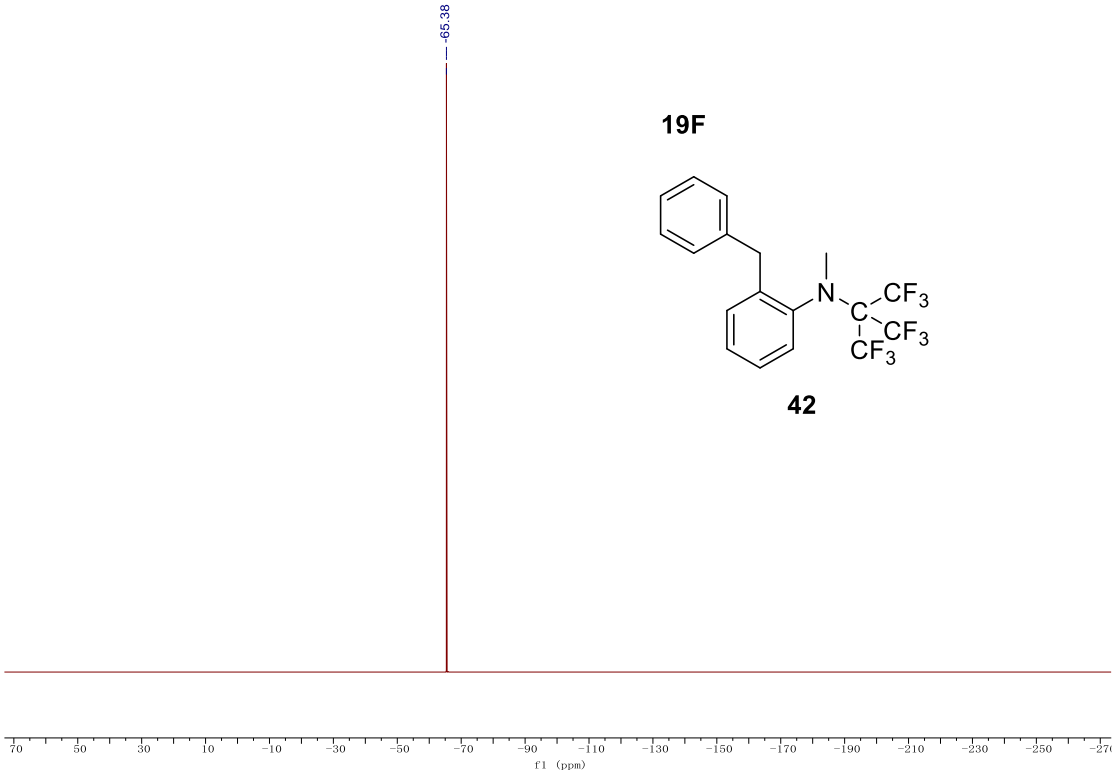

151.56
133.37
131.31
124.87
122.52
120.18
118.04
117.82
111.94
73.91
73.69
73.47
73.26
42.93
42.91
42.89
42.87
42.85
13C
N
C
CF3
CF3
CF3
NC
40
f1 (ppm)


7.86
7.85
7.84
7.82
7.81
7.81
7.53
7.52
7.51
7.50
7.50
7.49
7.43
7.41
3.14
1H
N
C
CF3
CF3
CF3
41
4.03
2.04
1.00
3.09
f1 (ppm)


-65.02
19F
N
C
CF3
CF3
CF3
41
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -2
f1 (ppm)


144.89
133.70
132.45
129.08
128.88
128.07
128.03
127.55
126.56
126.30
125.20
122.85
120.50
118.14
74.30
74.08
73.87
43.24
43.22
43.20
43.18
13C
N
C
CF3
CF3
CF3
41
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.59
7.58
7.57
7.48
7.46
7.45
7.39
7.39
7.38
7.37
7.37
7.35
7.34
7.33
7.32
7.32
7.31
4.45
4.41
4.17
4.14
2.96
1H
N
C
CF3
CF3
CF3
42
1.00
2.00
5.00
1.00
1.03
1.03
3.07
f1 (ppm)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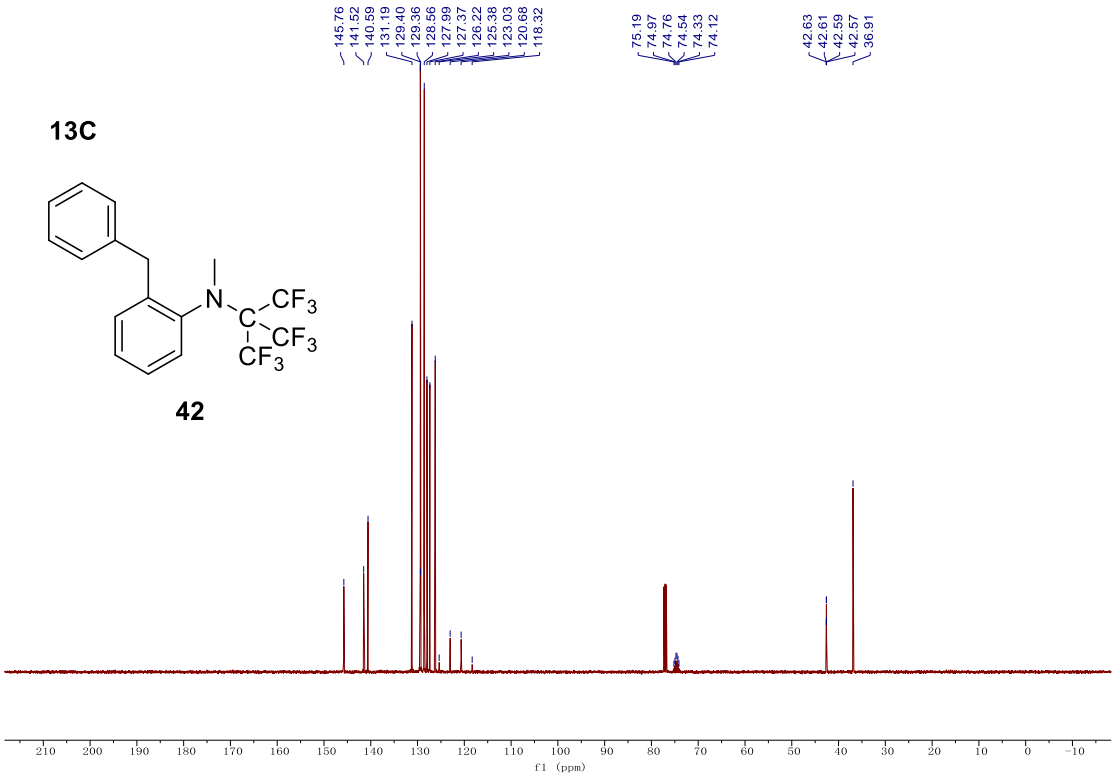
19F
N
C
CF3
CF3
CF3
42
f1 (ppm)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140.59
131.19
129.40
129.36
128.56
127.99
127.37
126.22
125.38
123.03
120.68
118.32
75.19
74.97
74.76
74.54
74.33
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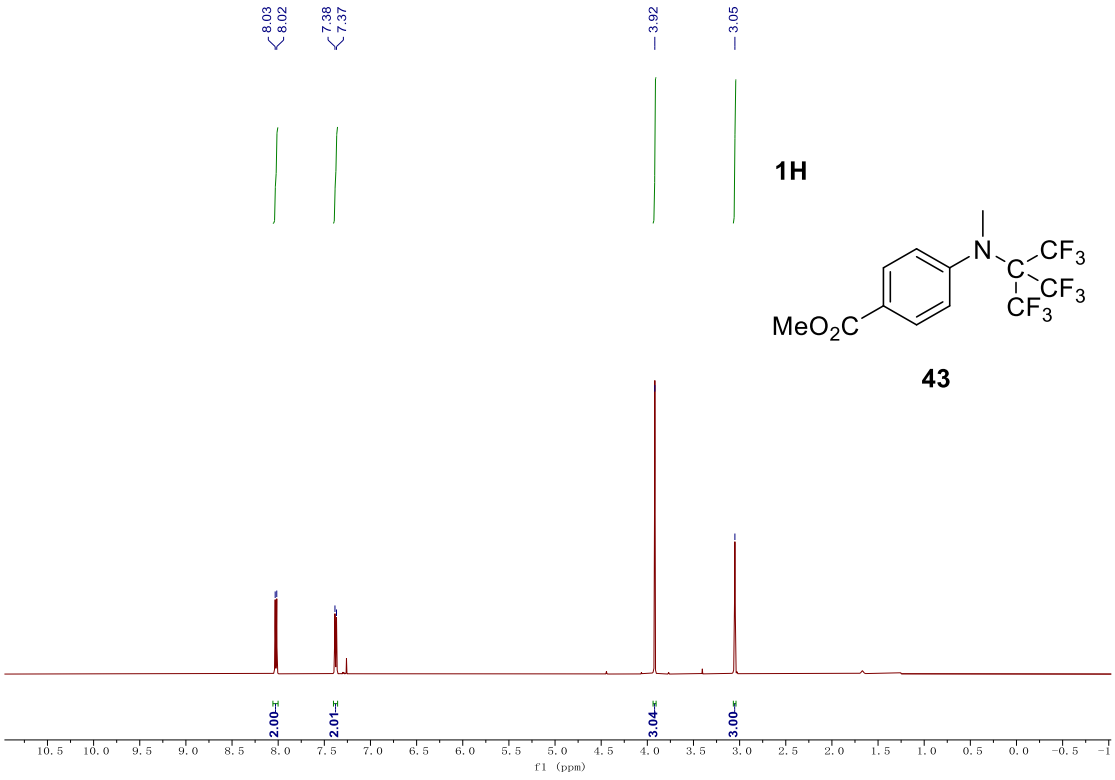
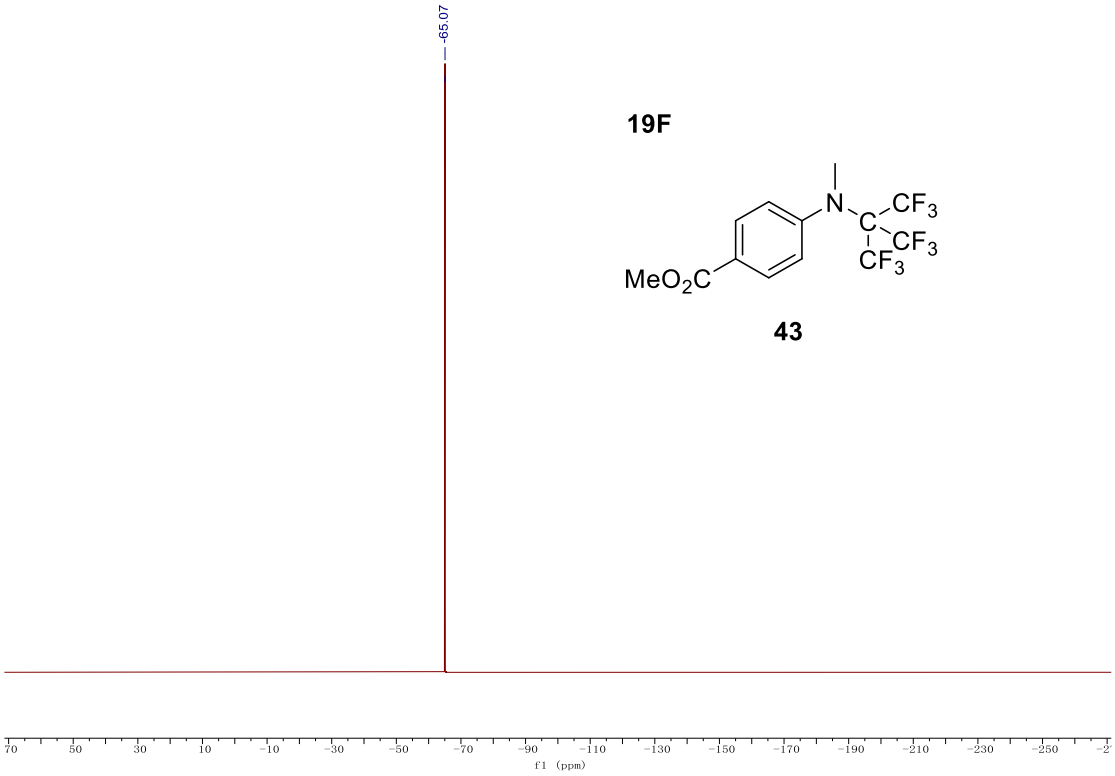
N
C
CF3
CF3
CF3
42
f1 (ppm)


8.03
8.02
7.38
7.37
3.92
3.05
1H
N
C
CF3
CF3
CF3
MeO2C
43
2.00
2.01
3.04
3.00
f1 (ppm)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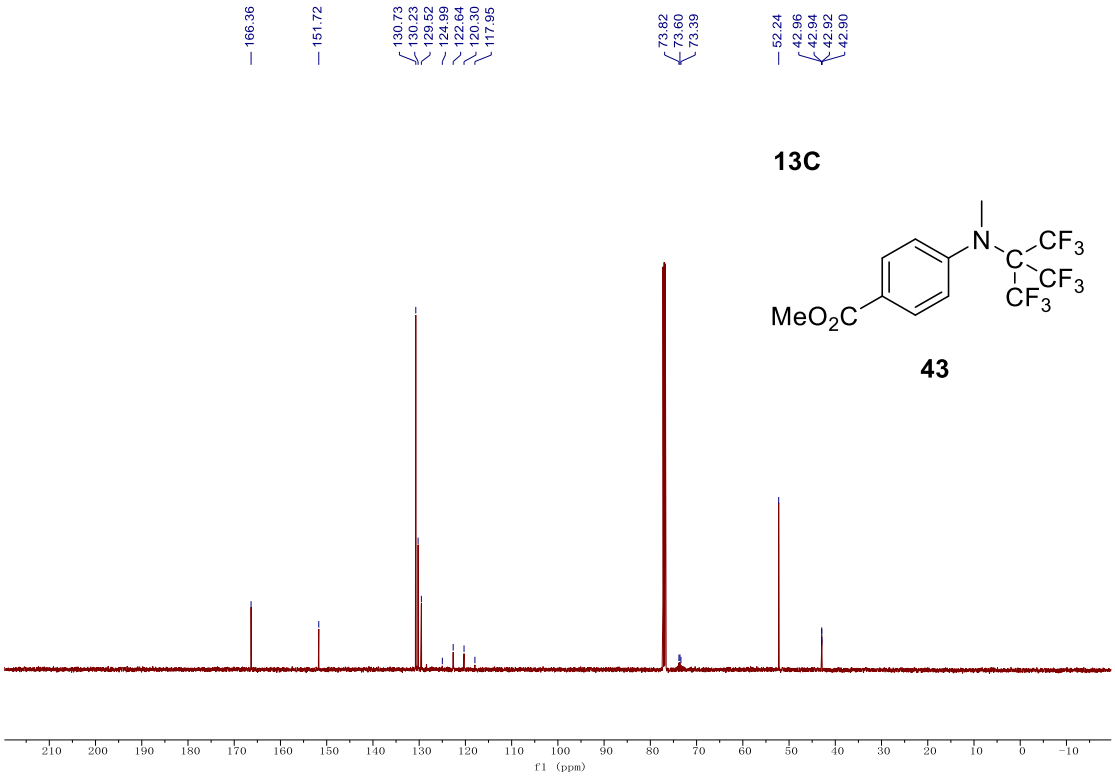
C
CF3
CF3
CF3
MeO2C
43
f1 (ppm)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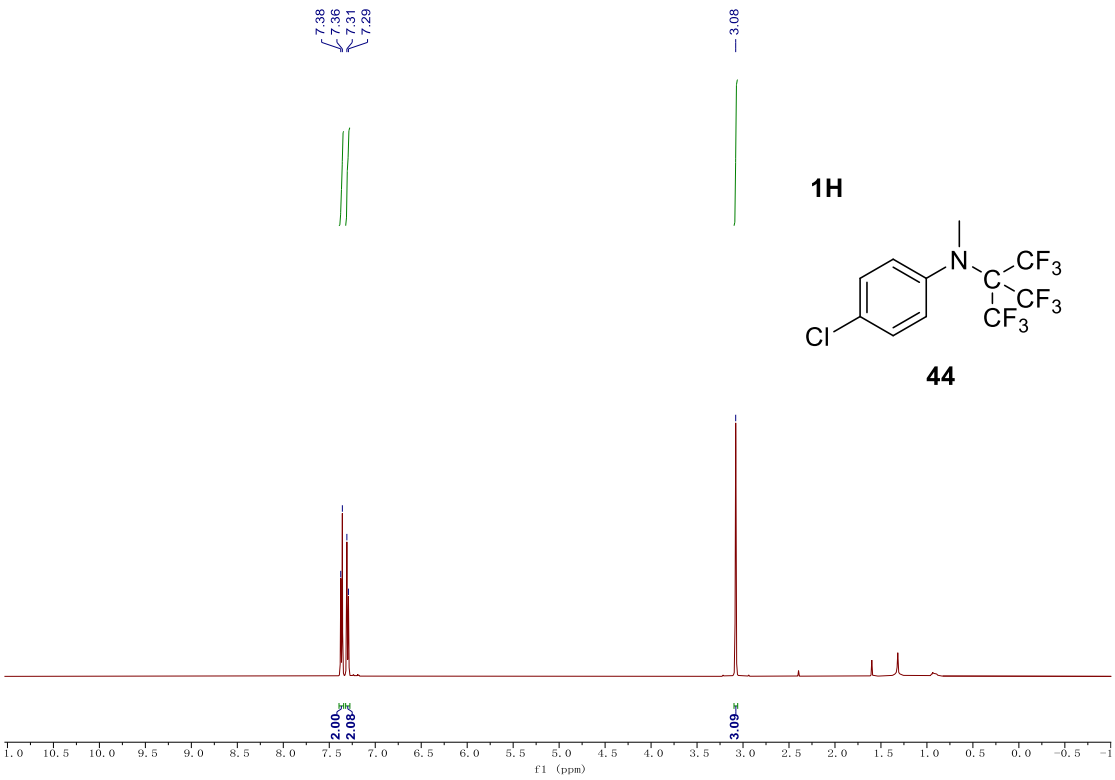
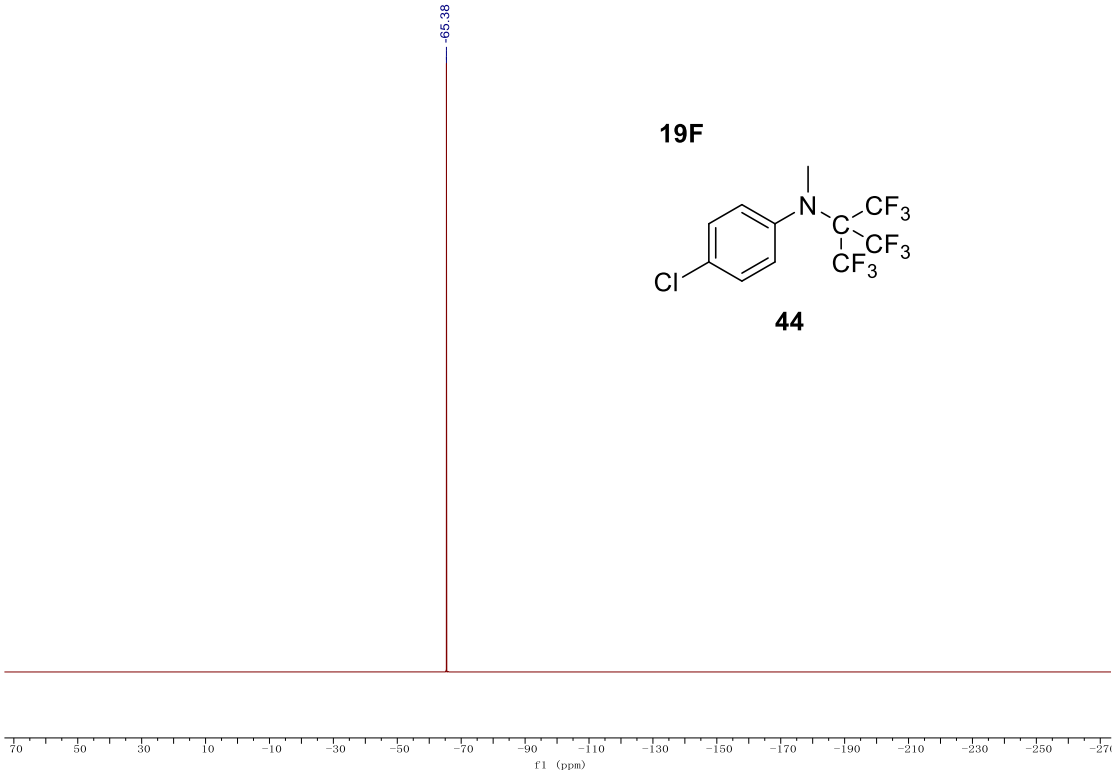
124.99
122.64
120.30
117.95
73.82
73.60
73.39
52.24
42.96
42.94
42.92
42.90
13C
N
C
CF3
CF3
CF3
MeO2C
43
f1 (ppm)


7.38
7.36
7.31
7.29
3.08
1H
N
C
CF3
CF3
CF3
Cl
44
2.00
2.08
3.09
f1 (ppm)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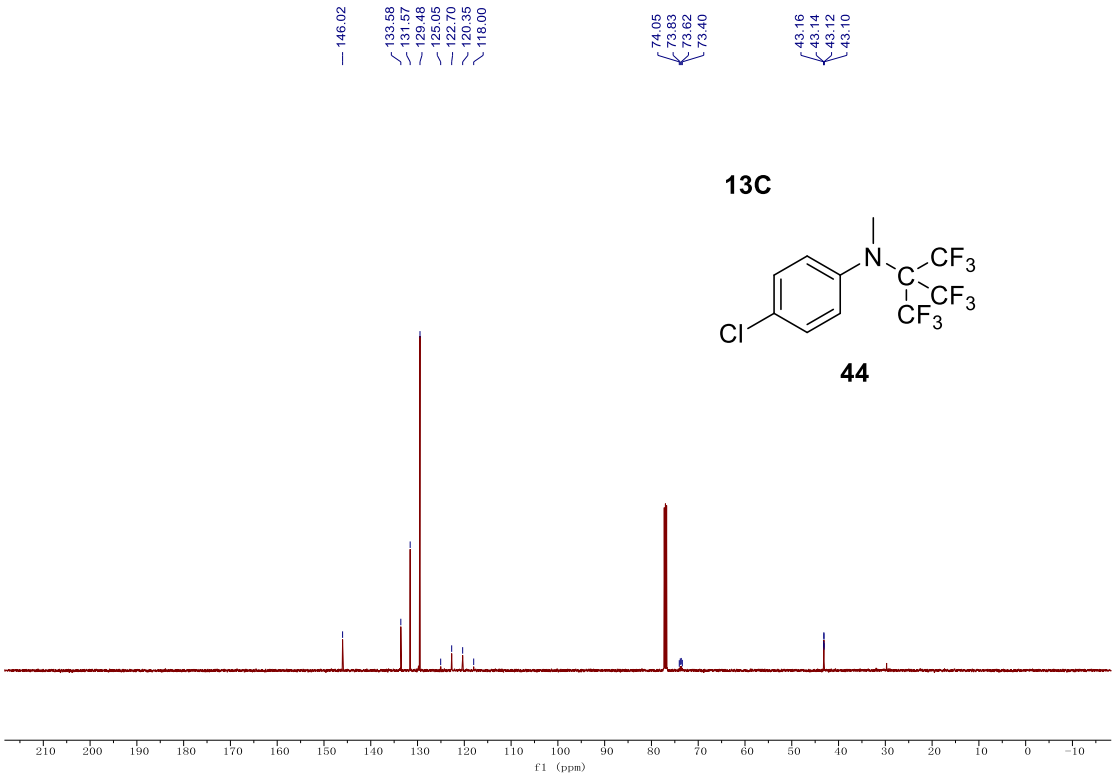
C
CF3
CF3
CF3
Cl
44
f1 (ppm)


146.02
133.58
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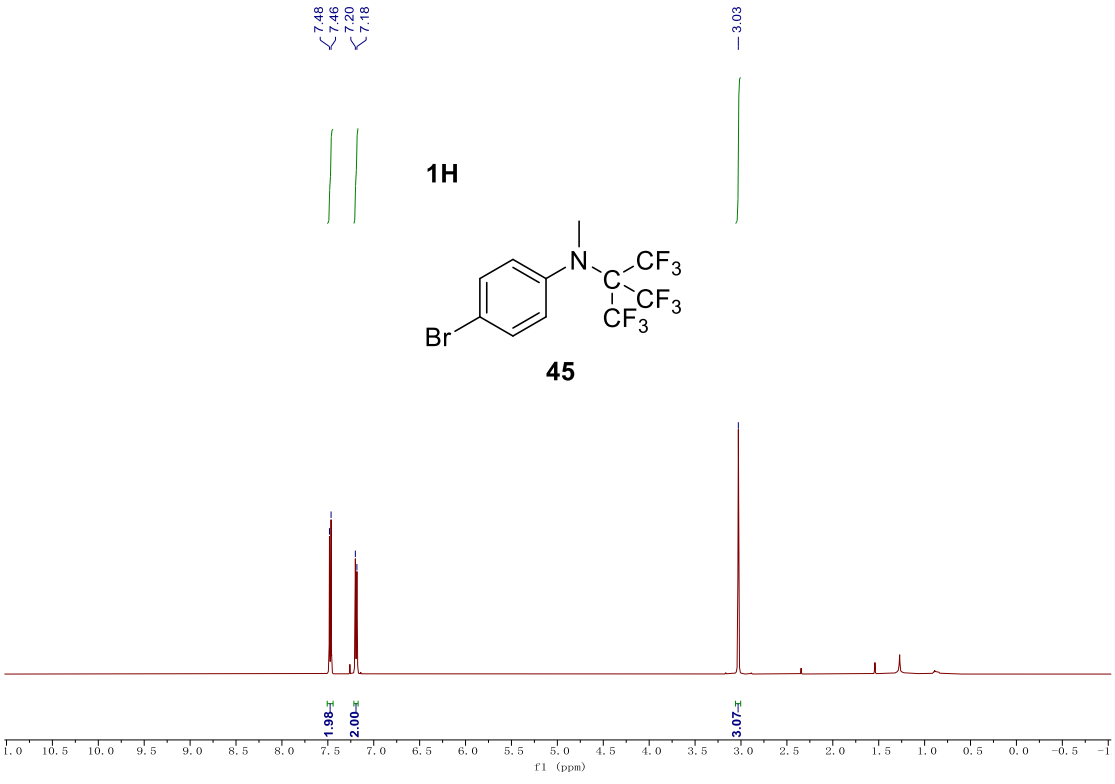
129.48
125.05
122.70
120.35
118.00
74.05
73.83
73.62
73.40
43.16
43.14
43.12
43.10
13C
N
C
CF3
CF3
CF3
Cl
44
f1 (ppm)


7.48
7.46
7.20
7.18
3.03
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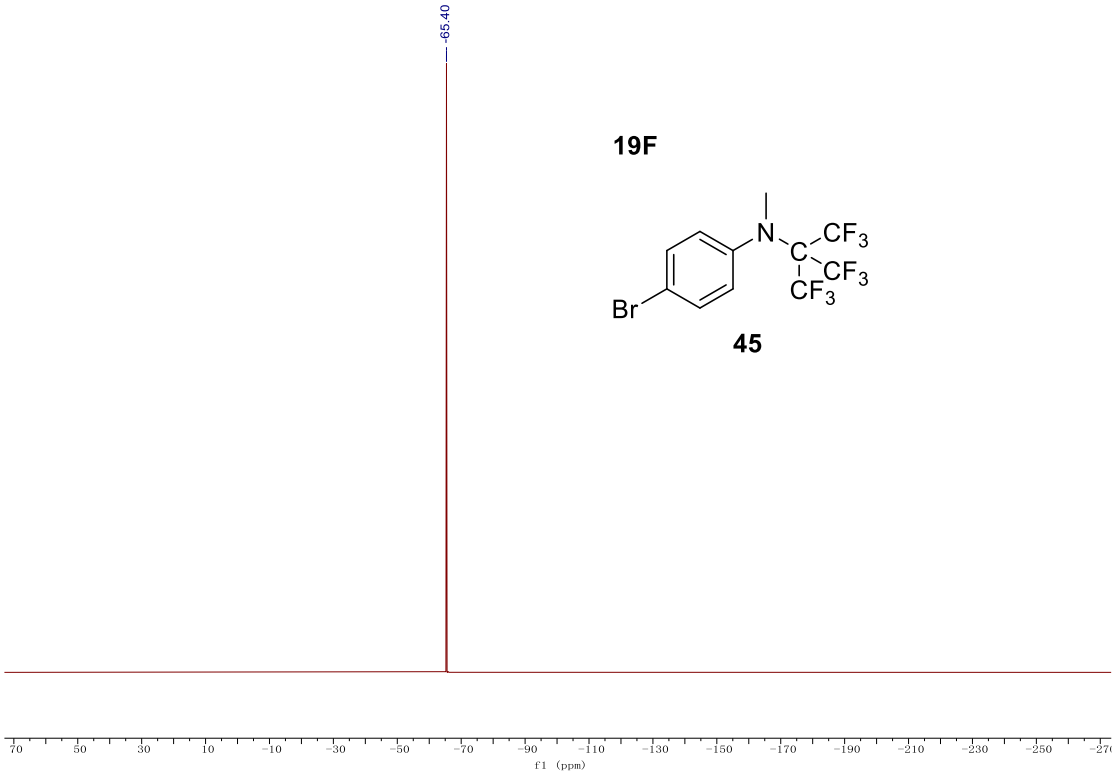
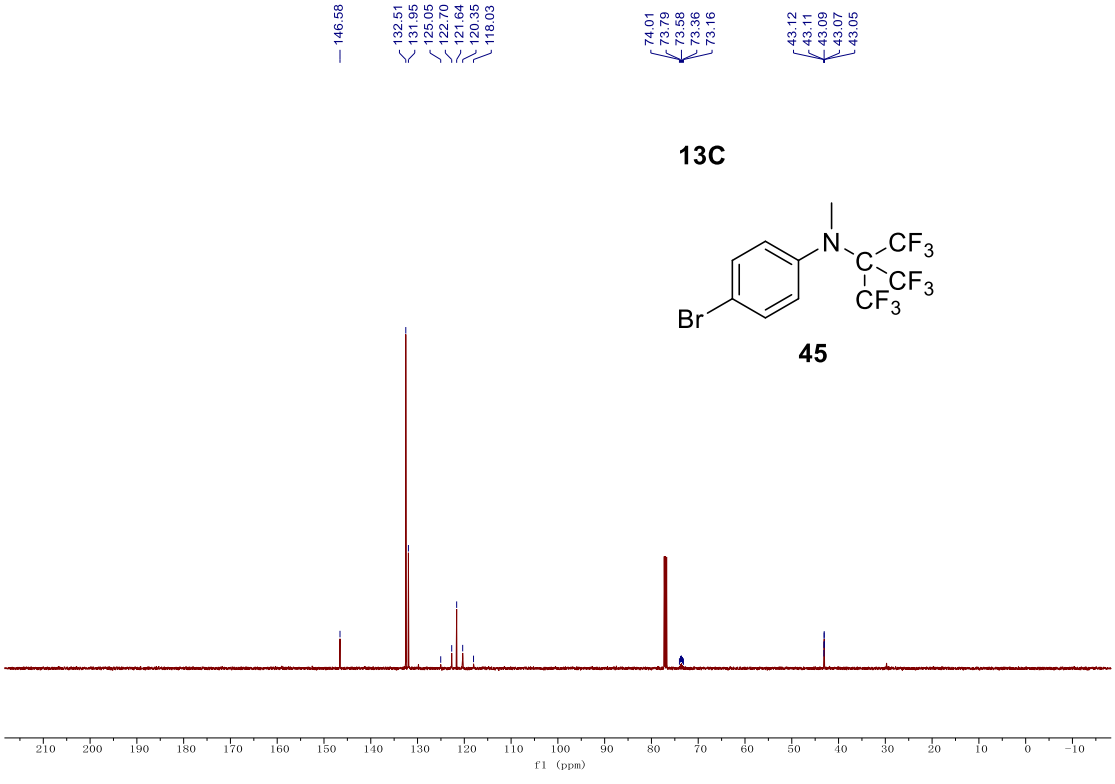
N
C
CF3
CF3
CF3
Br
45
1.98
2.00
3.07
f1 (ppm)


-65.40
70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250
f1 (ppm)

19F

N
C
CF3
CF3
CF3
Br

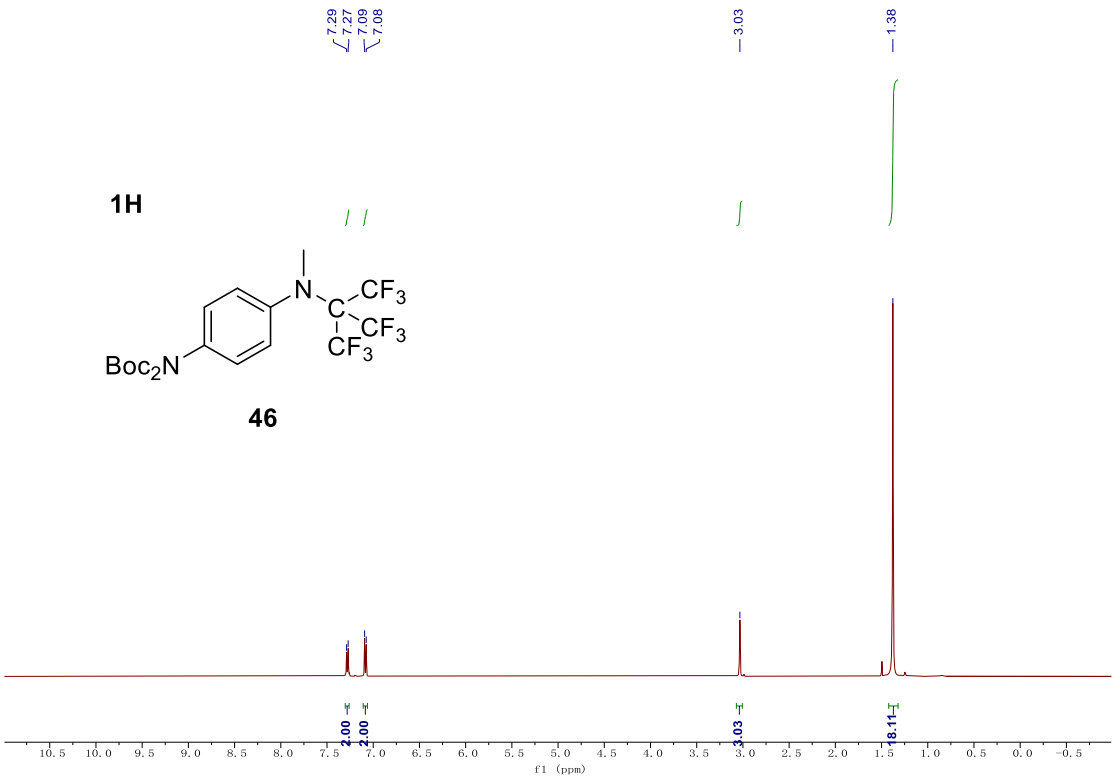
45

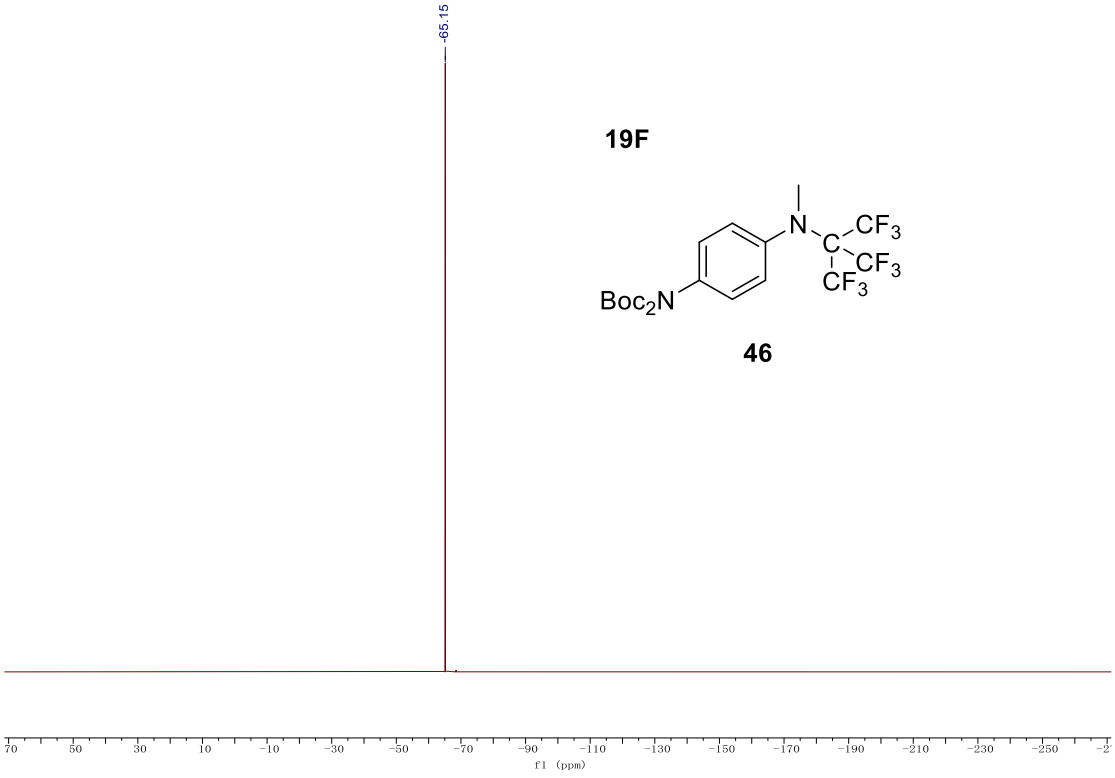

146.58
132.51
131.95
125.05
122.70
121.64
120.35
118.03
74.01
73.79
73.58
73.36
73.16
43.12
43.11
43.09
43.07
43.05
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

13C

N
C
CF3
CF3
CF3
Br

45


7.29
7.27
7.09
7.08
3.03
1.38
1H
N
C
CF3
CF3
CF3
Boc2N
46
2.00
2.00
3.03
18.11
f1 (ppm)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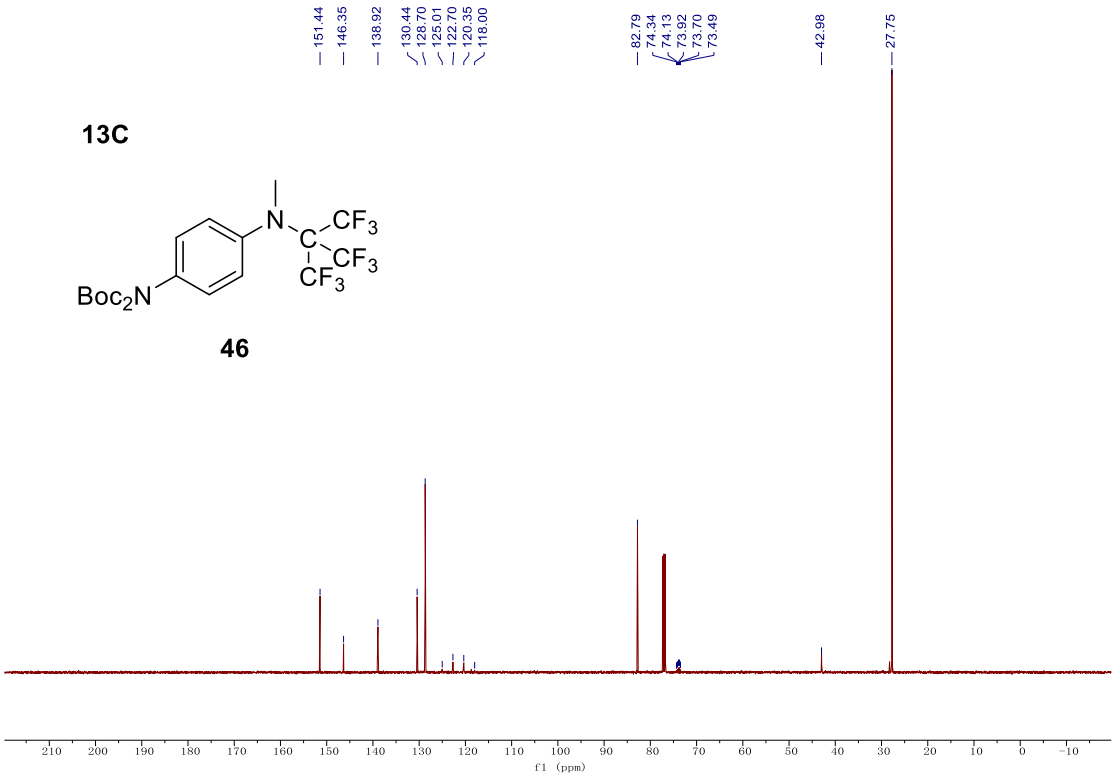
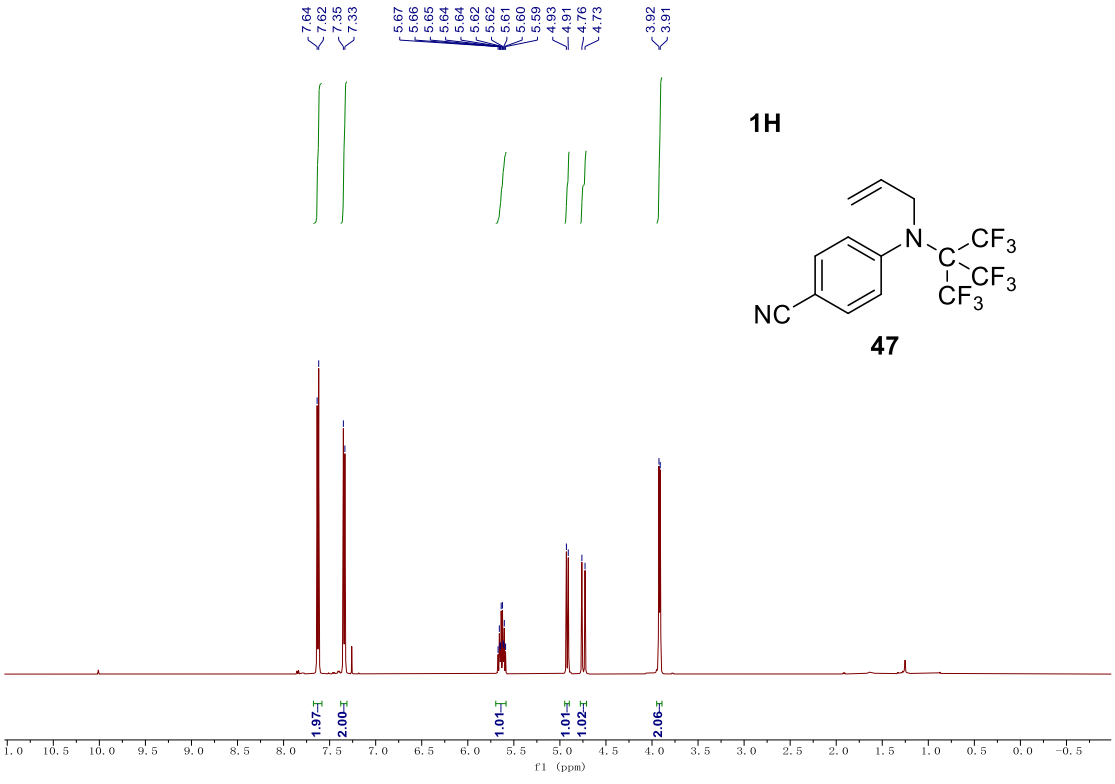
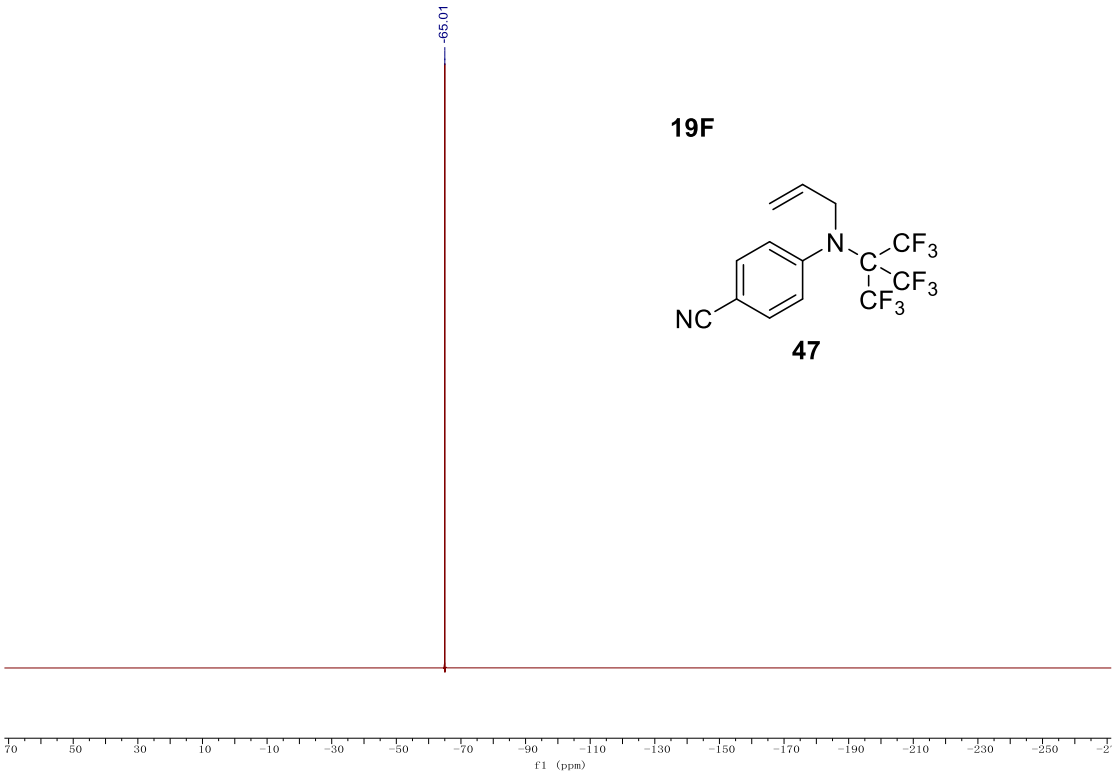
19F
N
C
CF3
CF3
CF3
Boc2N
46
f1 (ppm)

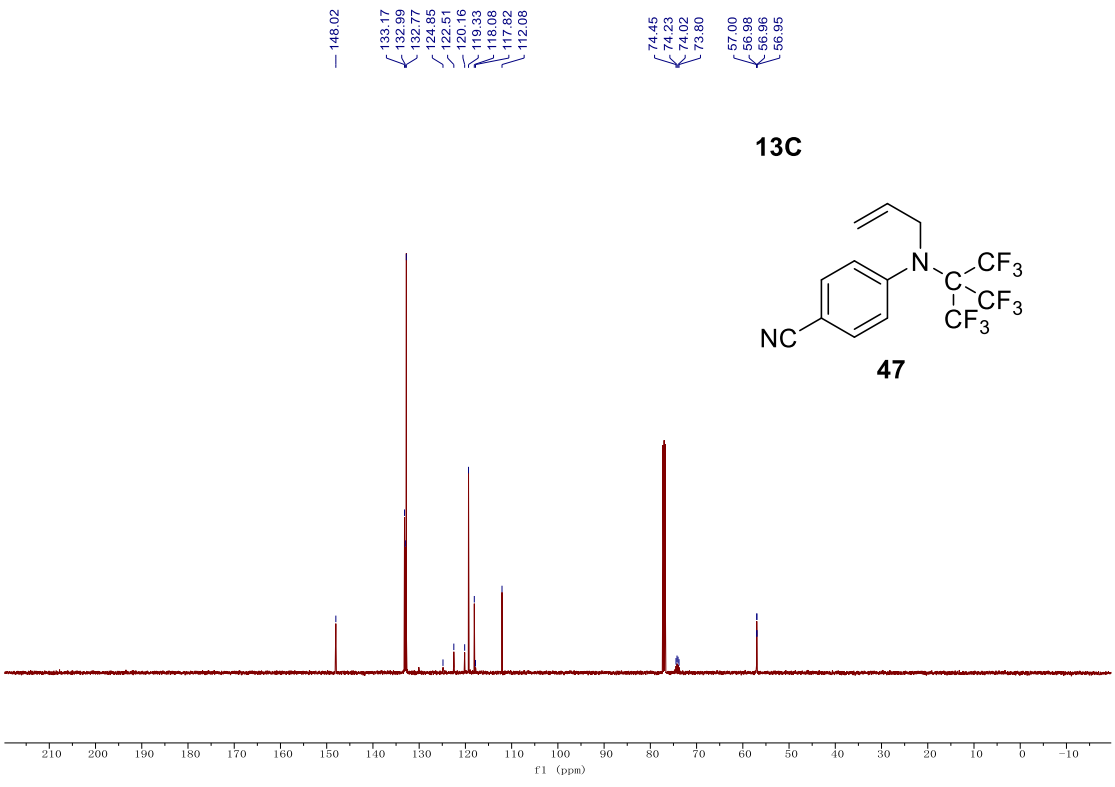

151.44
146.35
138.92
130.44
128.70
125.01
122.70
120.35
118.00
82.79
74.34
74.13
73.92
73.70
73.49
42.98
27.75
13C
N
C
CF3
CF3
CF3
Boc2N
46
f1 (ppm)


7.64
7.62
7.35
7.33
5.67
5.66
5.65
5.64
5.64
5.62
5.62
5.61
5.60
5.59
4.93
4.91
4.76
4.73
3.92
3.91
1H
N
C
CF3
CF3
CF3
NC
47
1.97
2.00
1.01
1.01
1.02
2.06
f1 (ppm)


-65.01
f1 (ppm)

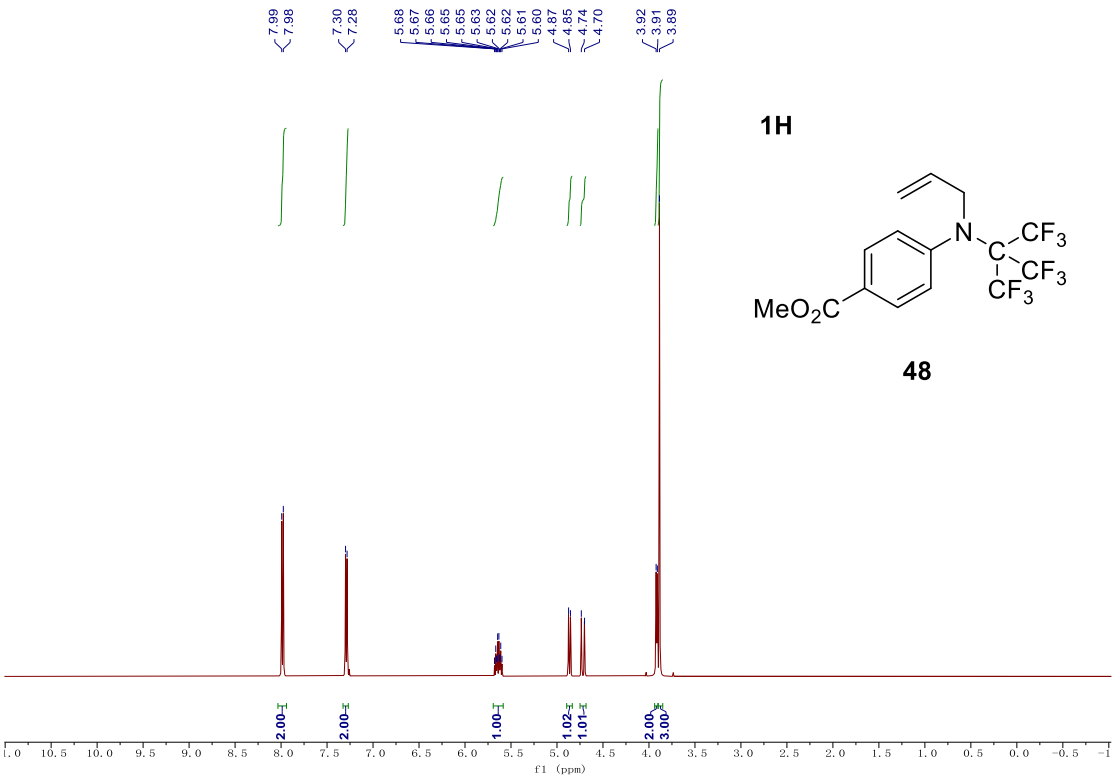
19F

47


148.02
133.17
132.99
132.77
124.85
122.51
120.16
119.33
118.08
117.82
112.08
74.45
74.23
74.02
73.80
57.00
56.98
56.96
56.95
f1 (ppm)

13C

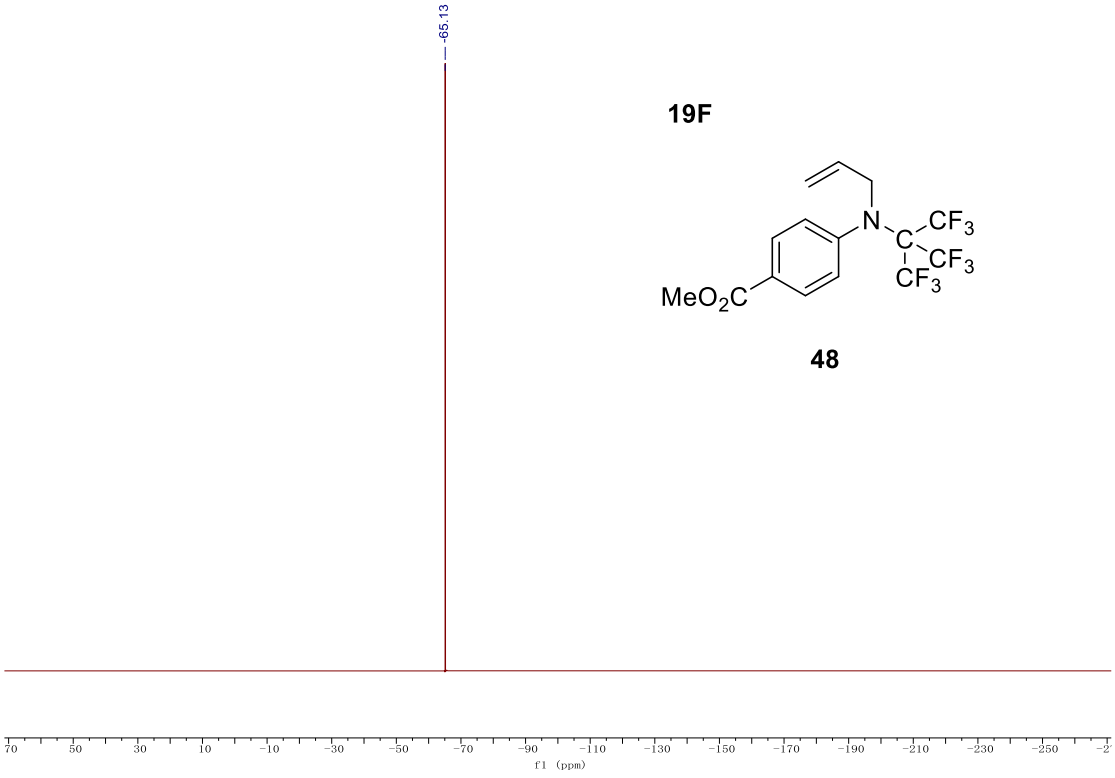
47


7.99
7.98
7.30
7.28
5.68
5.67
5.66
5.65
5.65
5.63
5.62
5.62
5.61
5.60
4.87
4.85
4.74
4.70
3.92
3.91
3.89
2.00
2.00
1.00
1.02
1.01
2.00
3.00
f1 (ppm)

1H

N
C
CF3
CF3
CF3
MeO2C

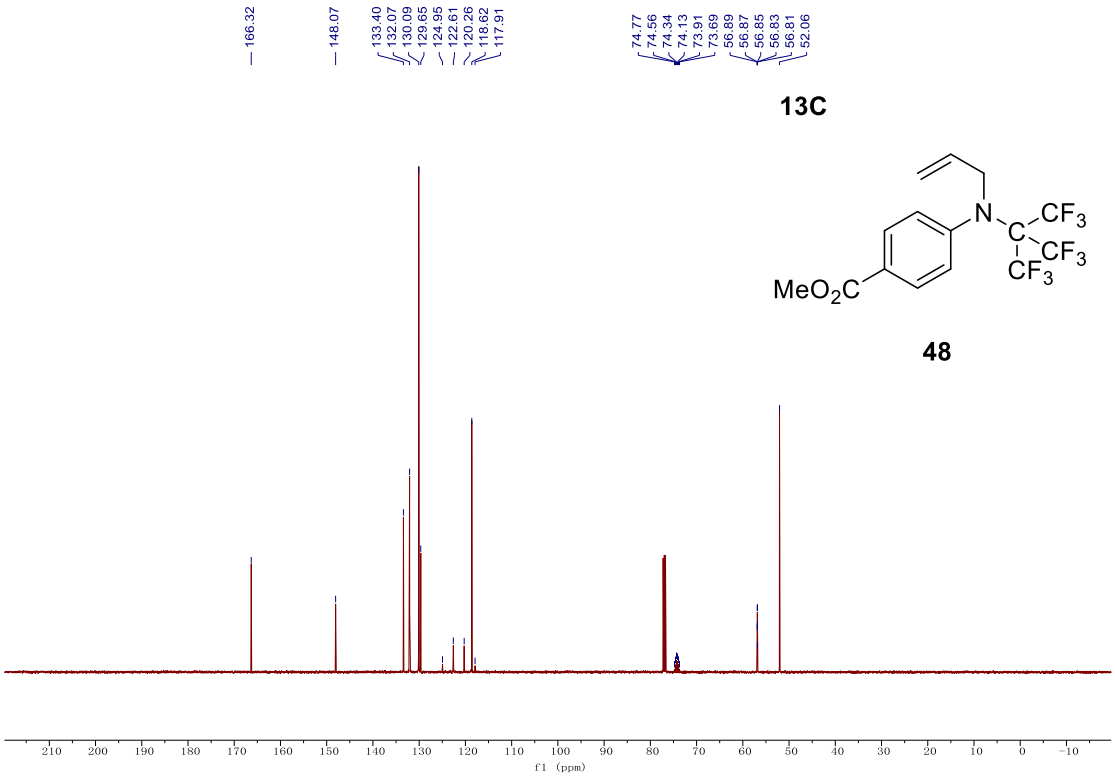
48

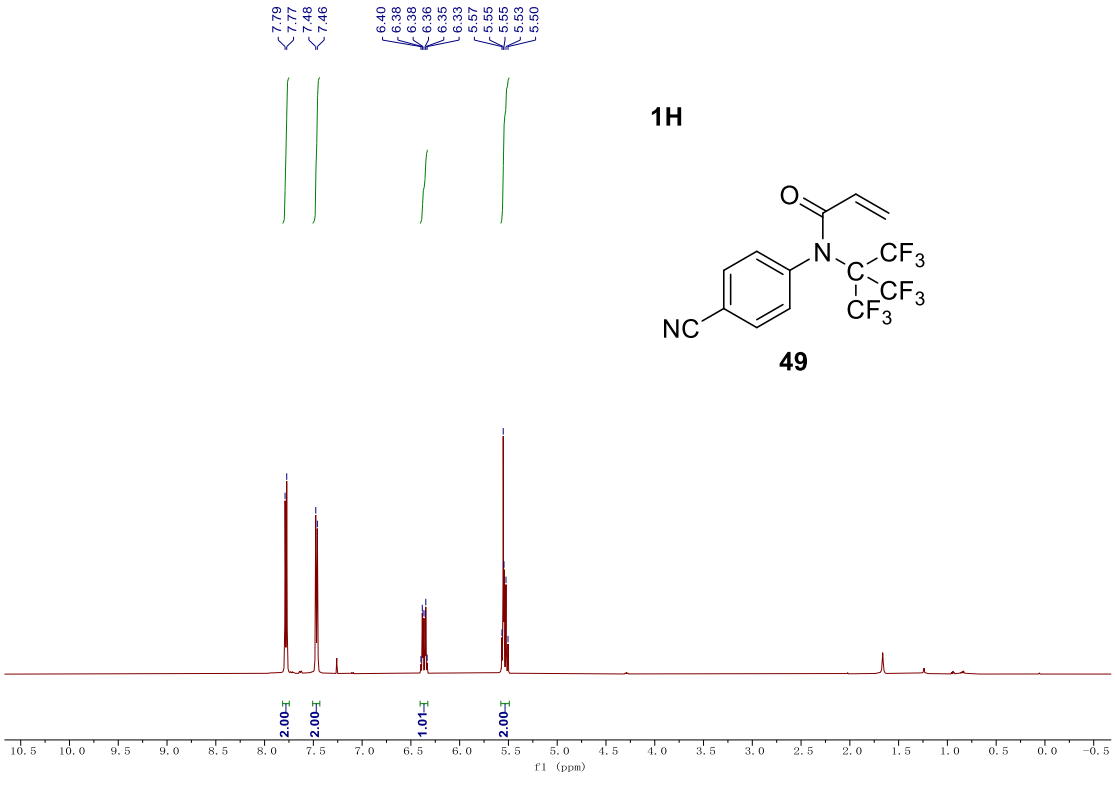

-65.13
f1 (ppm)

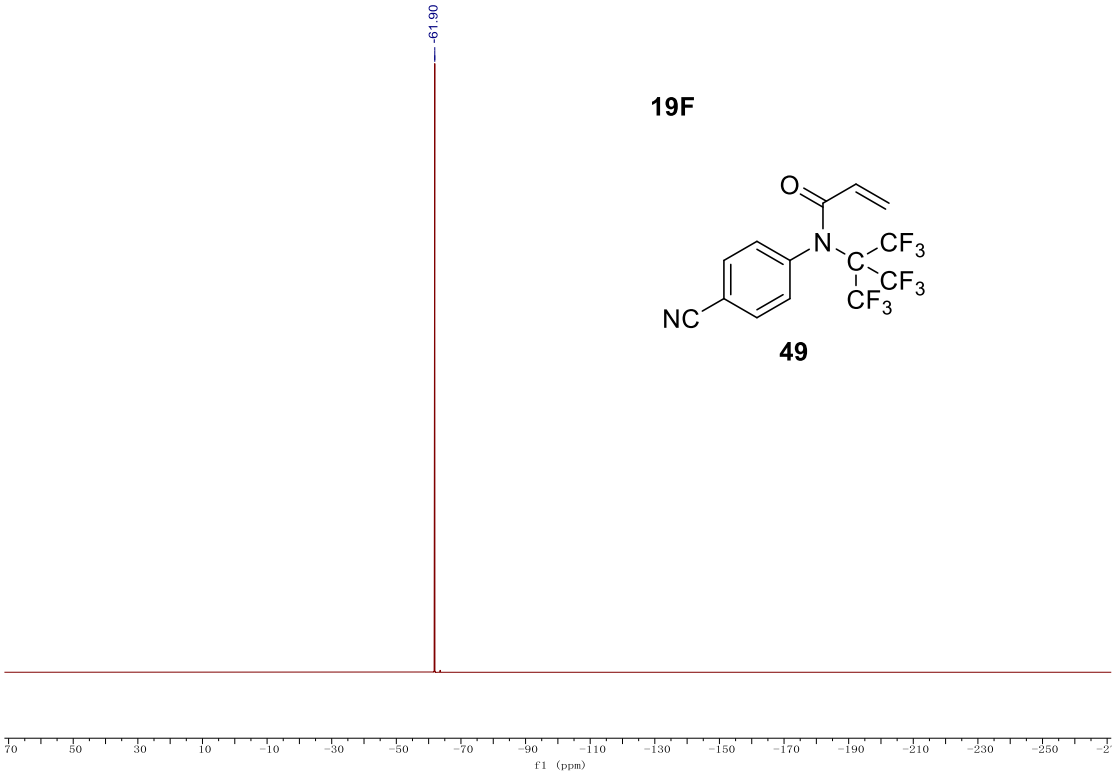
19F

N
C
CF3
CF3
CF3
MeO2C

48

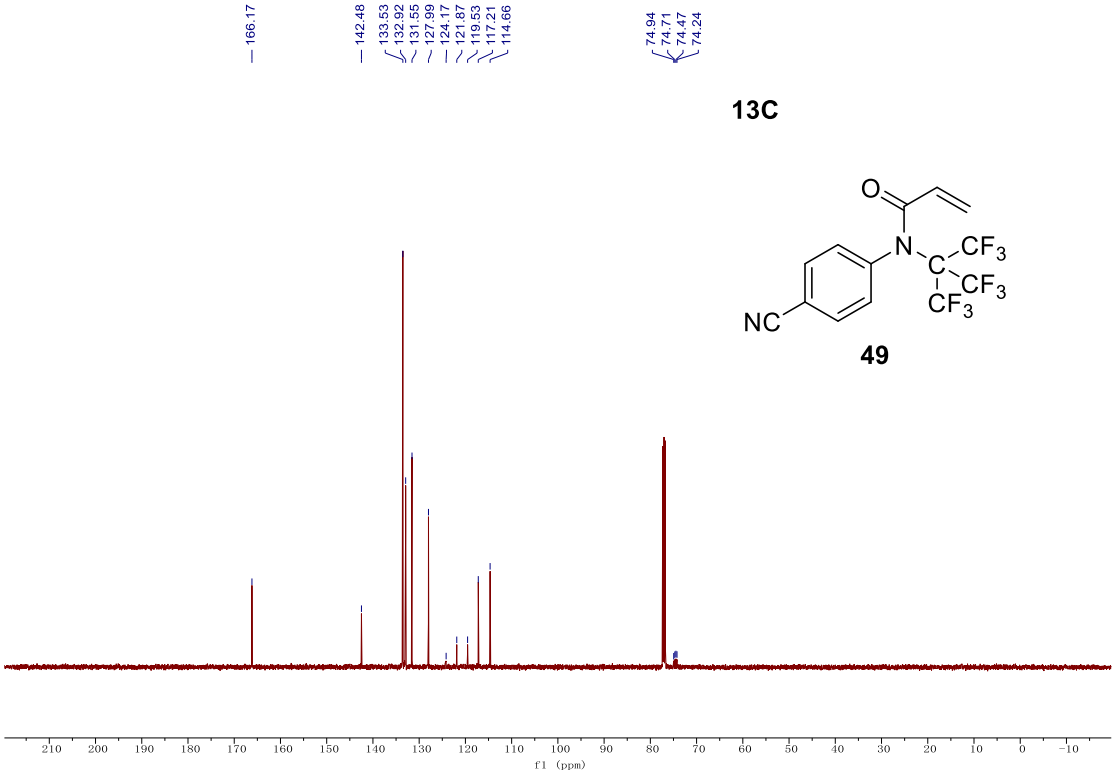

166.32
148.07
133.40
132.07
130.09
129.65
124.95
122.61
120.26
118.62
117.91
74.77
74.56
74.34
74.13
73.91
73.69
56.89
56.87
56.85
56.83
56.81
52.06
13C
N
C
CF3
CF3
CF3
MeO2C
48
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.79
7.77
7.48
7.46
6.40
6.38
6.38
6.36
6.35
6.33
5.57
5.55
5.55
5.53
5.50
1H
O
N
C
CF3
CF3
CF3
NC
49
2.00
2.00
1.01
2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


-61.90
f1 (ppm)

19F

49


166.17
142.48
133.53
132.92
131.55
127.99
124.17
121.87
119.53
117.21
114.66
74.94
74.71
74.47
74.24
f1 (ppm)

13C

49