Supplementary Information

Dual ligand-enabled iron and halogen-containing carboxylate-based photocatalysis for chloro/fluoro-polyhaloalkylation of alkenes

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1. General information

All reagents and catalysts were purchased from commercial sources and used without further purification, and all manipulations were carried out by standard Schlenk techniques. LEDs irradiation was accomplished using the photochemical reactors (Figure **S1**), λ_{max} = 450 nm (Figure **S2**). Thin layer chromatography (TLC) employed glass 0.20 mm-0.25 mm silica gel plates. Purification of products was accomplished using flash chromatography on silica gel. All the new compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ESI-HRMS. The known compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ESI-HRMS. NMR spectra were recorded on a Bruker 400 instrument operating at 400, 101, and 376 MHz for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR respectively. Chemical shifts (δ) were reported in ppm, and coupling constants (*J*) are in Hertz (Hz). Data was reported in ppm using $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.16) or DMSO-d_6 (^{1}H NMR δ 2.50, ^{13}C NMR δ 39.53) as solvent unless otherwise specified. High-resolution mass data was recorded on mass spectrometers in the ESI mode.

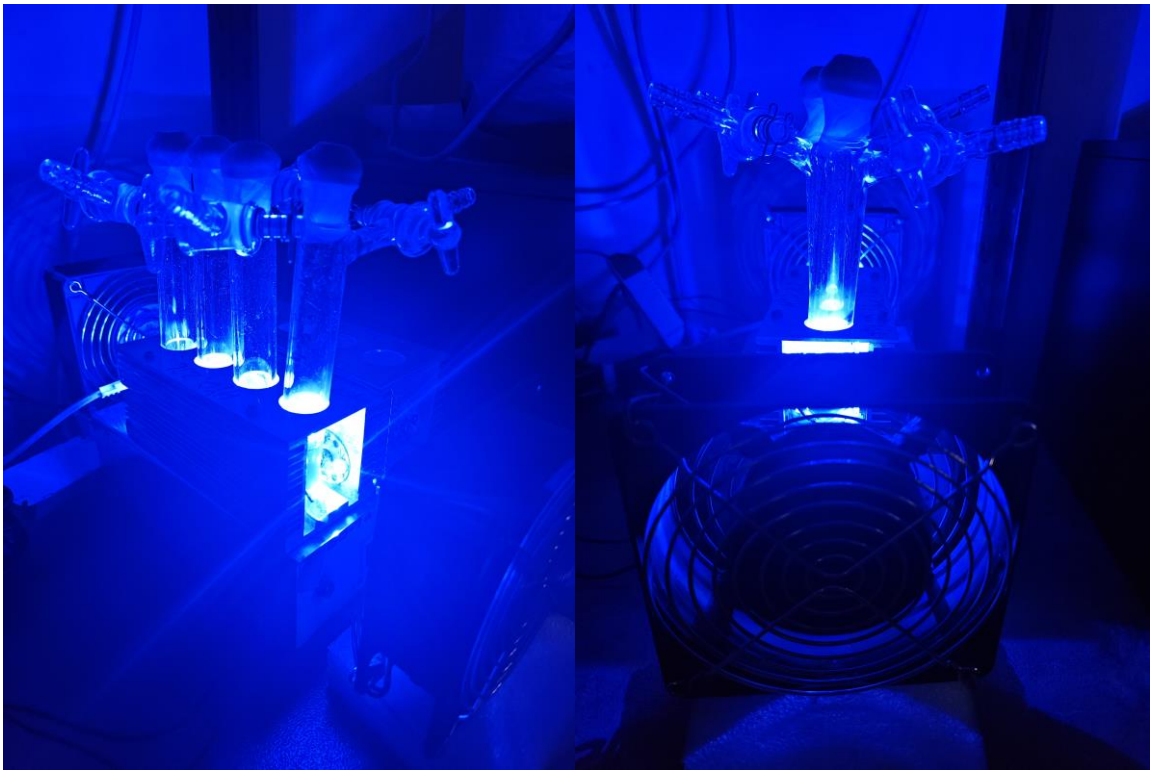


Figure S1. The photochemical reactors.

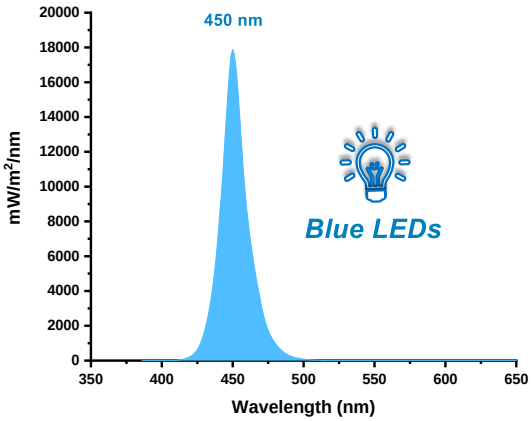


Figure S2. The wavelength spectrum of photochemical reactors.

2. Preparation of substrates

To the solution of the corresponding acid (3.0 mmol) in dry CH_2Cl_2 (28.0 mL) was added dicyclohexylcarbodiimide (3.6 mmol), 4-dimethylaminopyridine (0.45 mmol) and alcohol (3.0 mmol). The reaction mixture was left stirring for 24 h. After full conversion, the precipitate was removed by filtration and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography to afford the products (Figure **S3**).[1]

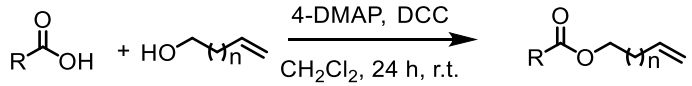


Figure S3. Method A for the synthesis of non-activated alkenes. DCC: Dicyclohexylcarbodiimide, 4-DMAP: 4-Dimethylaminopyridine.

To the solution of the corresponding phenol (0.5 mmol) and K_2CO_3 (1.0 mmol) in acetone (20.0 mL) was added allyl bromide (0.6 mmol). The resulting mixture was then stirred at reflux for 12 h and then filtered through a celite pad and washed with EtOAc. The filtrate was concentrated and the residue was purified by silica gel column chromatography using petroleum ether/EtOAc as the eluent to afford the products (Figure **S4**).[1]

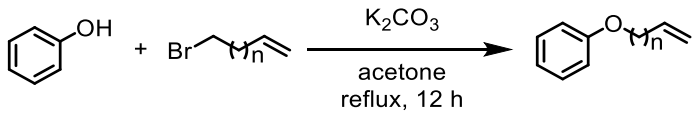


Figure S4. Method B for the synthesis of non-activated alkenes.

To the solution of the heterocycle derivative (5.0 mmol) and K_2CO_3 (10.0 mmol) in acetone (15.0 mL) was added allyl bromide (6.0 mmol). Heat the reaction to 60 ºC and stir for 2 h. After this time, quench the reaction with water. Extract the aqueous solution with ethyl acetone (×3), then wash the combined organic layers with brine and dry over Na_2SO_4, and remove the organic solvent under reduced pressure. Subject the residue to flash column chromatography on silica gel with hexanes/ethyl acetate as the eluent to afford the products (Figure **S5**).[2]

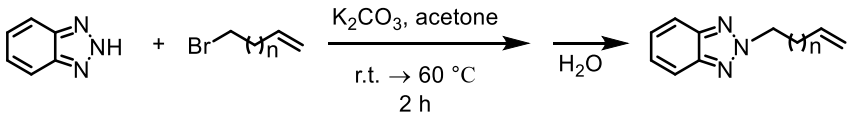


Figure S5. Method C for the synthesis of non-activated alkenes.

To a 50-mL Schlenk tube, iron(III) chloride (5.0 mmol) and silver trifluoroacetate (15.0 mmol) were dissolved in dichloroethane (15.0 mL) and reacted for 3 h at room temperature. The precipitate AgCl was filtered and the residue was washed with acetone. The corresponding filtrate was concentrated under reduced pressure and the resulting product was dried at 80 ºC for 1 h. Iron(III) trifluoroacetate was obtained as red solid (Figure **S6**).[3]

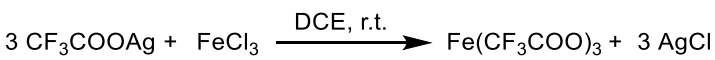
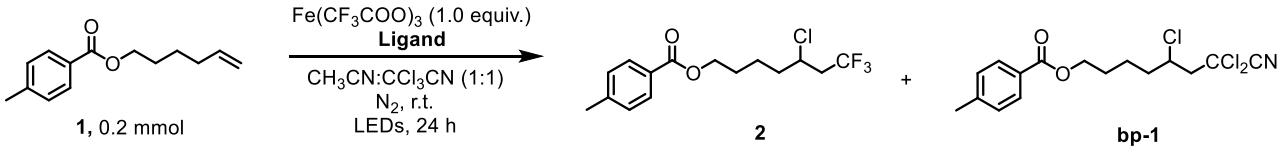


Figure S6. The synthesis of $Fe(CF_3COO)_3$.

3. Experimental procedures for chloro/fluoro-polyhaloalkylation of alkenes

General procedure for stoichiometric experiments: A 25-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(CF_3COO)_3$ (0.2 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), alkene **1** (0.2 mmol), CCl_3CN (1.0 mL). The reaction mixture was stirred under nitrogen atmosphere and irradiated by 365 nm LEDs for 24 h. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the product **2**, and by-product (**bp-1**) (Figure **S7**).



Entry	LEDs	Ligand	Yield of 2 (%)	Yield of bp-1 (%)
1	365 nm	-	28	25
2	390 nm	-	11	15
3	450 nm	-	n.d.	n.d.
4	darkness	-	n.d.	n.d.
5	450 nm	L1	n.d.	n.d.
6	450 nm	L2	24	17
7	450 nm	L3	11	11
8	darkness	L2	n.d.	n.d.

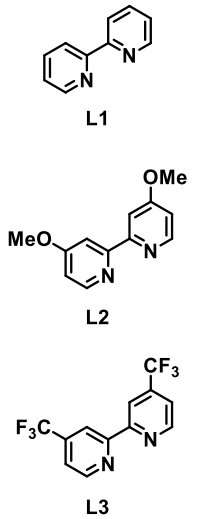
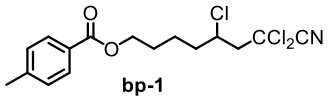
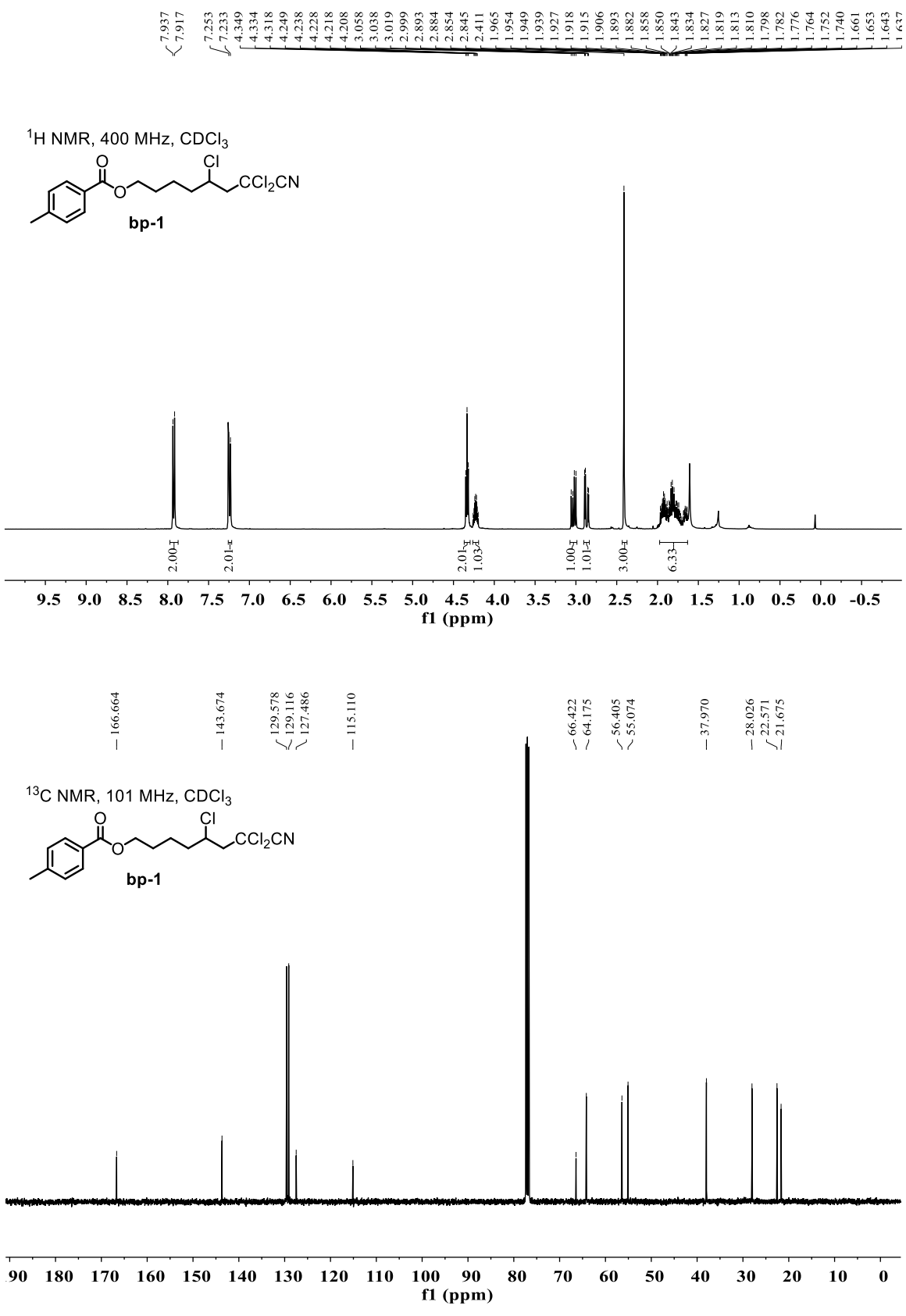


Figure S7. Chloro-trifluoromethylation of alkene **1**.

Data for bp-1:



5,7,7-Trichloro-7-cyanoheptyl 4-methylbenzoate **(bp-1)**: 18.2 mg colorless liquid was isolated, yield: 25%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 6.3 Hz, 2H), 4.26 – 4.19 (m, 1H), 3.08 – 2.98 (m, 1H), 2.92 – 2.82 (m, 1H), 2.41 (s, 3H), 1.99 – 1.63 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.66, 143.67, 129.58, 129.12, 127.49, 115.11, 66.42, 64.18, 56.40, 55.07, 37.97, 28.03, 22.57, 21.68. **ESI-HRMS** exact mass calculated for $[C_{16}H_{18}Cl_3NO_2Na^+]$: 384.0295, found 384.0299.



General procedure for *Standard condition A*: A 25-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol) and C_nF_mCOONa (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), alkene (0.2 mmol) and CCl_3CN (1.0 mL). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 24 h. After

completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the products (Figure **S8**).

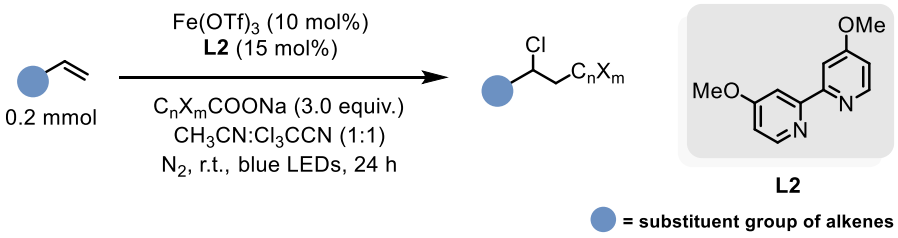


Figure S8. Iron LMCT photocatalysis for radical chloro-polyhaloalkylation of non-activated alkenes.

General procedure for *Standard condition B*: A 25-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(OTf)_3$ (0.02 mmol), **L4** (0.02 mmol), C_nX_mCOONa (0.6 mmol) and Selectfluor (0.3 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (2.0 mL), alkene (0.2 mmol) and anisole (0.08 mmol). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 12 h. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the products (Figure **S9**).

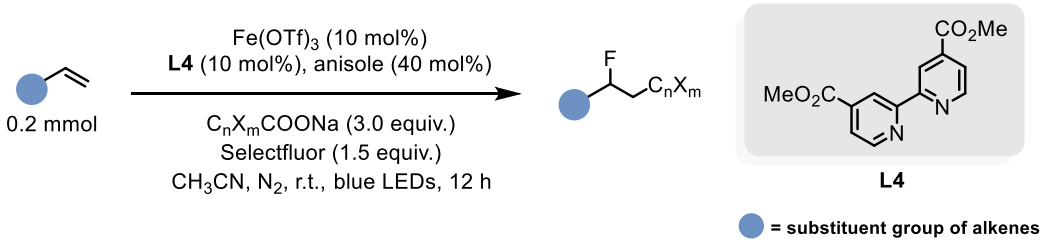


Figure S9. Iron LMCT photocatalysis for radical fluoro-polyhaloalkylation of non-activated alkenes.

General procedure for gram-scale synthesis: A 200-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(OTf)_3$ (1.2 mmol), **L2** (1.8 mmol) and CF_3COONa (36.0 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (60.0 mL), alkene **1** (12.0 mmol), CCl_3CN (60.0 mL). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 7 days. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the product **2** (Figure **S10**).

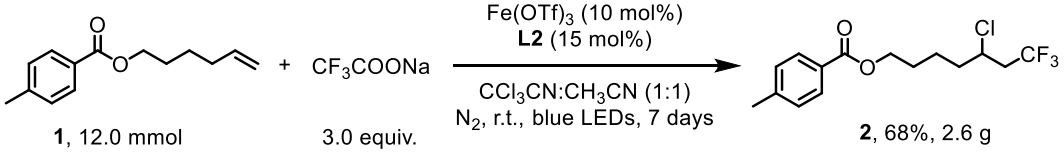


Figure S10. The gram-scale synthesis.

General procedure for TON experiment: A 50-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(OTf)_3$ (0.006 mmol), **L2** (0.009 mmol) and CF_3COONa (6.0 mmol). The flask was evacuated and refilled with N_2

for three times. The vessel was then charged with extra dry CH_3CN (10.0 mL), alkene **1** (2.0 mmol) and CCl_3CN (10.0 mL). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 7 days. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the product **2**(Figure **S11**).

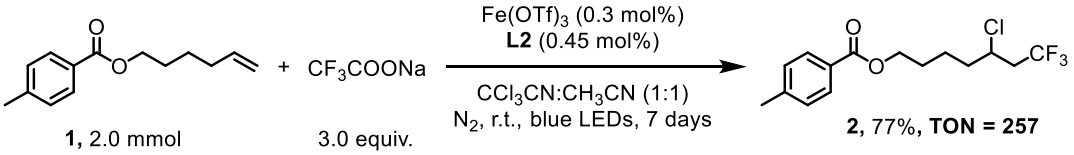


Figure S11. The TON experiment.

General procedure for chloro-trifluoromethylation of conjugated alkene: A 25-mL Schlenk flask equipped with a magnetic bar was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol) and CF_3COONa (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), conjugated alkene (0.2 mmol) and CCl_3CN (1.0 mL). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 24 h. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the products. During the investigations of substrate scope, we found that conjugated alkene are not suitable for this reaction. Only product **44** was observed in a yield of 17% (Figure **S12**).

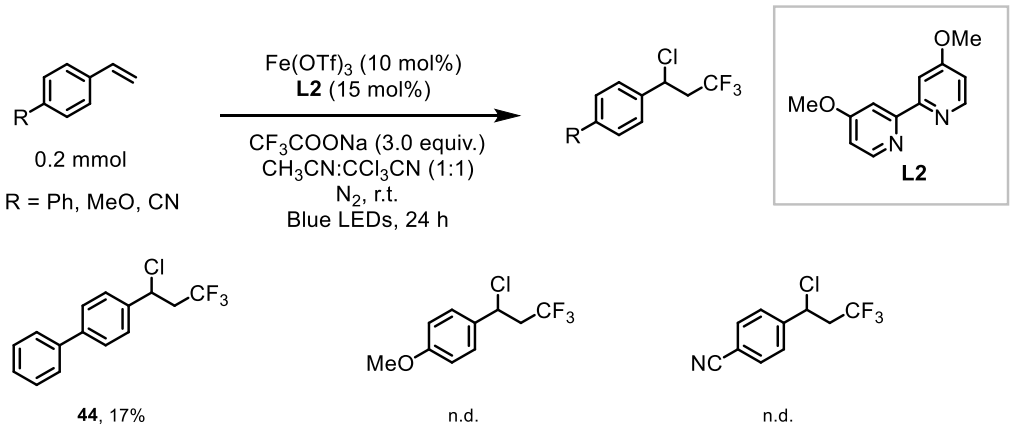


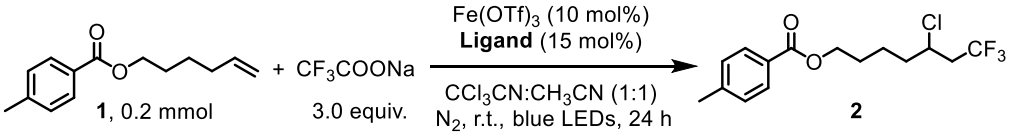
Figure S12. Investigations on the conjugated alkene.

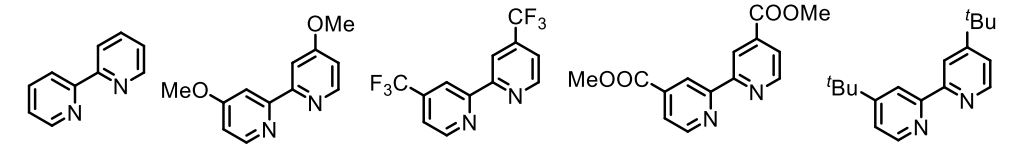
Entry	Deviation from the standard conditions	Conv. (%)	Yield (%)
1	/	100	84
2	no $Fe(OTf)_3$	19	n.d.
3	no **L2**	20	2
4	darkness	0	n.d.
5	purple LEDs	100	44
6	green LEDs	0	n.d.
7	only CCl_3CN as solvent	100	72
8	TFA instead of CF_3COONa	14	5
9	with 4 Å MS	100	82

Figure S13. The results of deviation from ***Standard condition A***. Yields and conversion rates were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard.

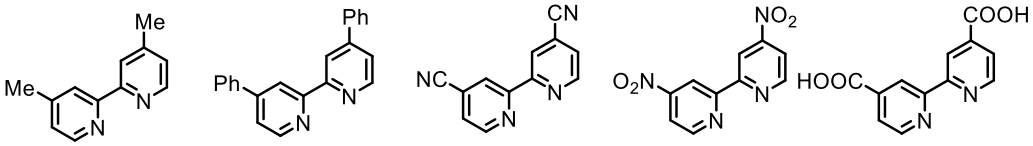
Investigations of ligand：

We investigated the substituent effects of bipyridines (Figure **S14**). For para-substituted bipyridines, it was very interesting that only strong electron-donating/withdrawing functional groups (**L2**, **L3**, **L8**) could efficiently dominate the desired transformation (Figure **S15**-a). However, when installing CN group in the ortho/meta-position of bpy, the yields of **2** dropped dramatically, while moderate electron-deficient substituent group COOMe or COOEt showcased good tuning ability as well (Figure **S15**-b). We have tried our best to understand the interesting substituent effects of bipyridines. However, due to the fact that the substituted bipyridine as the ligand not only influences the performance of in situ generated light-harvesting species but also enables the reducibility of [Fe^{II}/L] species (**III**), the substituent effect of bipyridine is complicated.

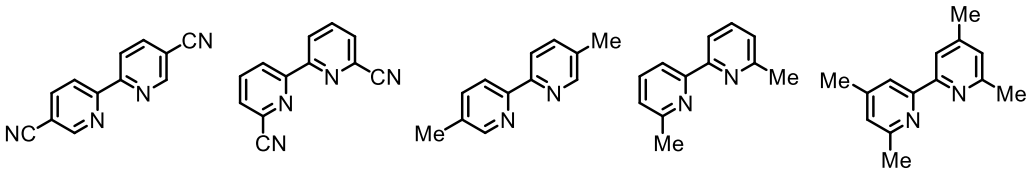




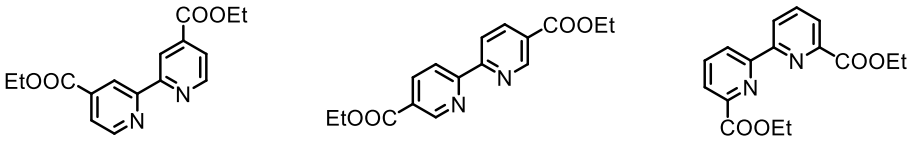
L1, 7% **L2**, 84% **L3**, 83% **L4**, 38% **L5**, 16%



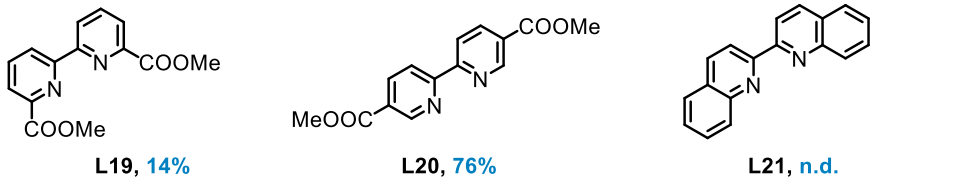
L6, 7% **L7**, 29% **L8**, 79% **L9**, 25% **L10**, n.d.



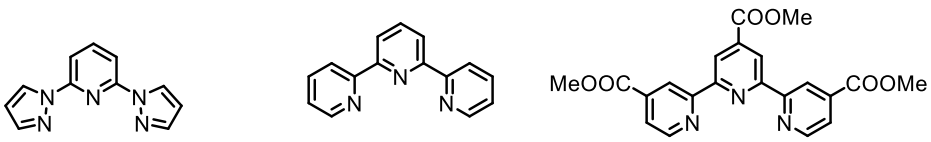
L11, 12% **L12**, n.d. **L13**, n.d. **L14**, 3% **L15**, 1%



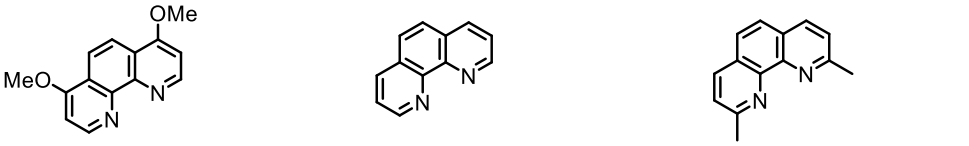
L16, 32% **L17**, 72% **L18**, 3%



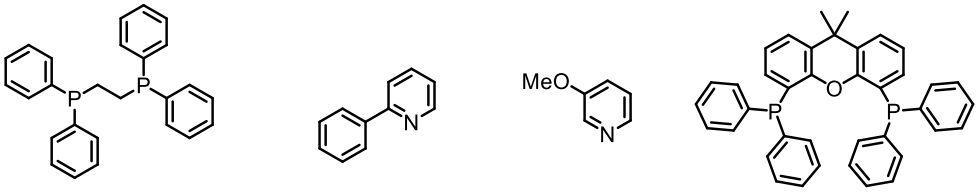
L19, 14% **L20**, 76% **L21**, n.d.



L22, 5% **L23**, 16% **L24**, 8%



L25, n.d. **L26**, 3% **L27**, 6%



L28, 2% **L29**, n.d. **L30**, n.d. **L31**, n.d.

Figure S14. Investigations on the ligand. Yields were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard.

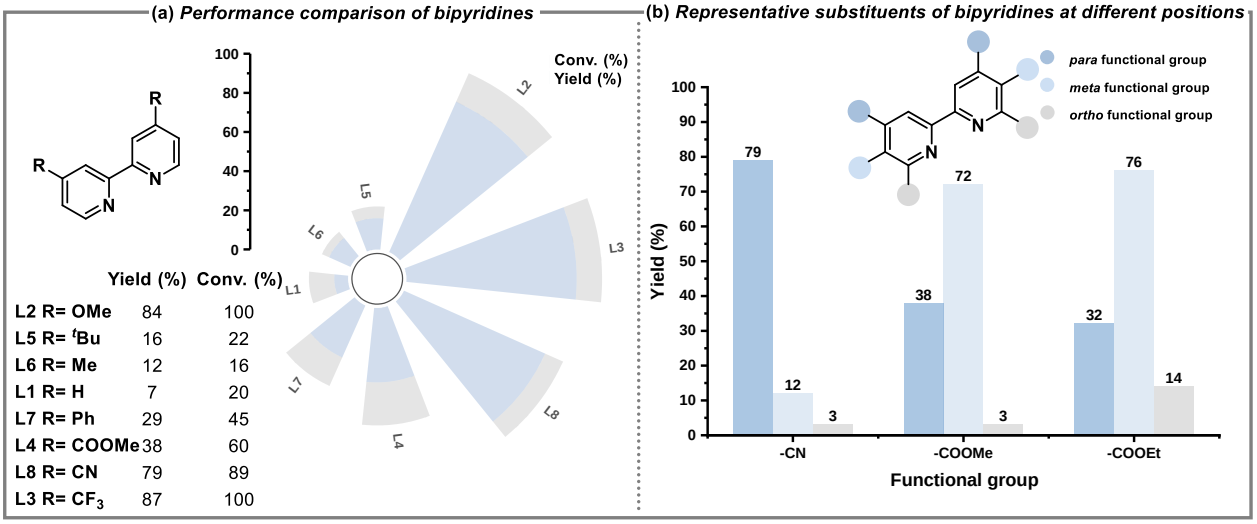
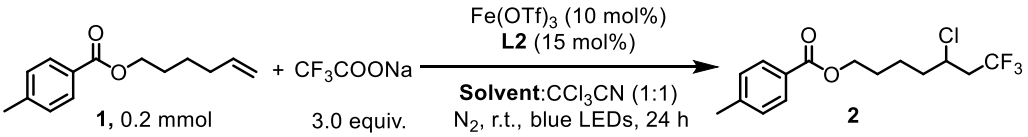


Figure S15. Intriguing ligand effects.

Investigations of solvent:

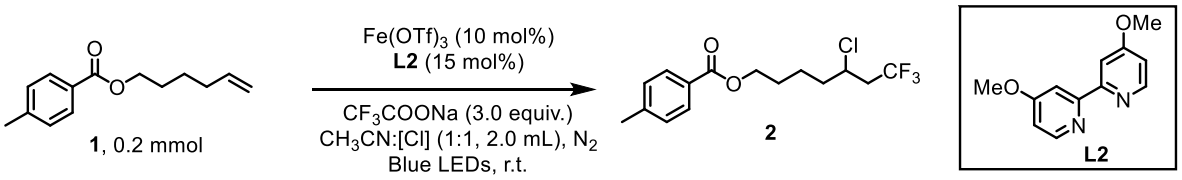


Entry	Solvent	Yield (%)
1	CH_3CN	84
2	CCl_3CN	72
3	benzonitrile	60
4	DCE	80
5	DCM	83
6	DMF	4
7	DMSO	6
8	acetone	80
9	1,4-dioxane	29
10	THF	39
11	EtOAc	58
12	cyclohexane	7
13	toluene	7

Figure S16. Investigations on the solvent. Yields were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard.

Investigations of chlorine source:

The investigations of chlorine source for the determination of ***Standard condition A*** were carried out (Figure **S17**). The results showed that trichloroacetonitrile was competent, while other potential chlorine sources such as trichloromethane, ethyl chloroacetate analogue, NCS (N-chlorosuccinimide), etc. could not yield the desired chloro-trifluoromethylation product. Therefore, the trichloroacetonitrile was chosen as the chlorine source.



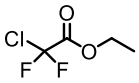
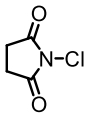
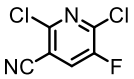
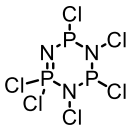
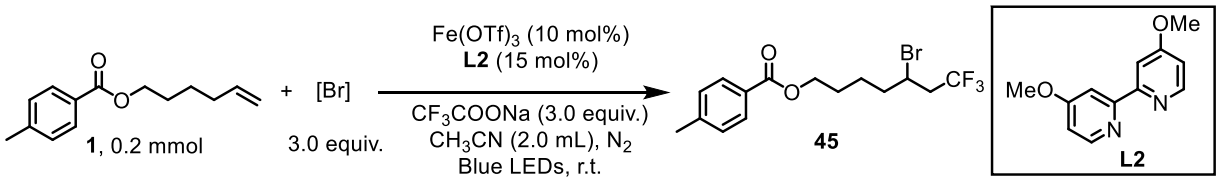
Entry	[Cl]	Yield (%)
1	$CHCl_3$	n.d.
2		n.d.
3	$CHCl_2CN$	n.d.
4[b]		n.d.
5[b]		n.d.
6[b]		n.d.

Figure S17. Investigations on chlorine source. [b]3.0 equiv. [Cl], 2.0 mL CH_3CN.

Investigations of bromine source:

The investigations of bromine sources for the determination of ***Standard condition A*** were carried out (Figure **S18**). It was disappointing that no desired bromo-trifluoromethylation products were detected, while we observed these undesired by-products (**b-1**, **b-2** and **b-3**). It indicated that the bromination reagents were activated preferentially, causing that no CF_3 radical from CF_3COO^- was generated.



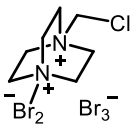
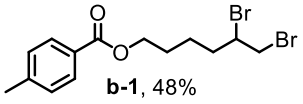
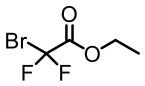
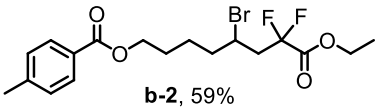
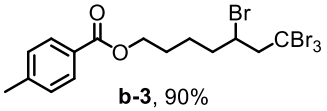
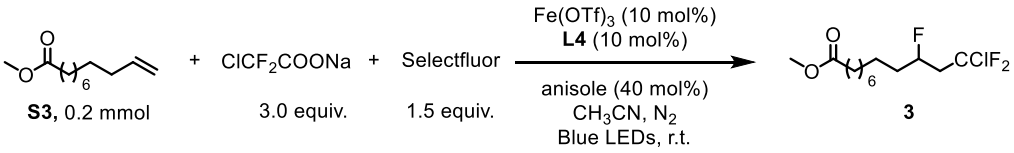
Entry	[Br]	Yield of **45** (%)	Yield of by-product (%)
1		n.d.	 **b-1**, 48%
2		n.d.	 **b-2**, 59%
3	CBr_4	n.d.	 **b-3**, 90%
4	$CHBr_3$	n.d.	/
5	$CHBr_2CN$	n.d.	/

Figure S18. Investigations on bromine source.



Entry	Deviation from the standard conditions	Conv. (%)	Yield (%)
1	/	100	75
2	no $Fe(OTf)_3$	29	n.d.
3	no **L4**	20	n.d.
4	no anisole	100	trace
5	darkness	17	n.d.
6	green LEDs	24	n.d.

Figure S19. The results of deviation from ***Standard condition B***. Yields and conversion rates were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard.

As shown in Figure **S19**, under the standard condition, product **3** could be obtained in 75% yield and 100% conversion rate with anisole (Entry 1). However, there was trace amount of product detected in absence of anisole, but the conversion rate still remained 100% (Entry 4). Based on previous reports,[4] anisole was considered to act as a redox buffer to reduce the reactivity of N radical cation generated from Selectfluor to avoid alkene converting into aminated products (Figure **S20**).

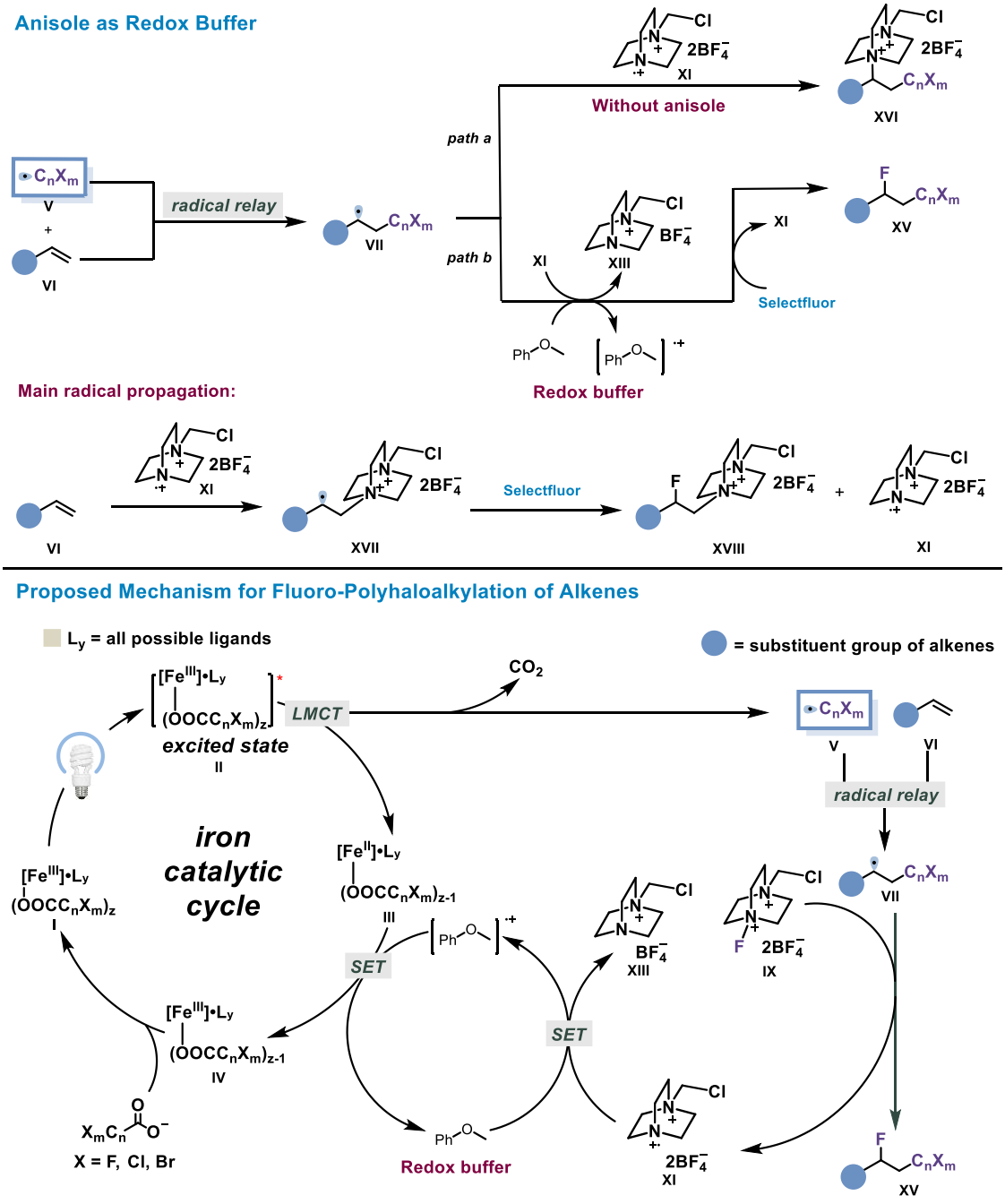


Figure S20. Proposed mechanism for fluoro-polyhaloalkylation of alkenes with anisole as a redox buffer.

4. Mechanistic studies

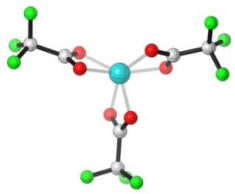
Details of DFT calculations: All the calculations have been performed using the Gaussian Program (Gaussian 16).[5] The geometry optimization was conducted with the B3LYP functional and standard 6-31G(d) basis set. The solvent effect was considered by IEFPCM.[6,7] Harmonic vibrational frequency calculations were performed for all stationary points to confirm whether they are local minima or transition state structures and to derive the thermochemical corrections for the enthalpies and free energies. Furthermore, the entropy in the solution model have been recalculated by the THERMO program[8] which affords a new solution translational entropy.

Free energies of possible light-harvesting species

Species / ΔG （kcal/mol）	Gibbs free energy	Gibbs free energy with the Fang's entropy correction
IntA / 0.0	-2842.263499	-2842.24605
L2	-724.277027	-724.26669
CF_3COO^-	-526.333494	-526.32218
CH_3CN	-132.745397	-132.73426
CCl_3CN	-1511.510476	-1511.49972
IntE / -42.2	-3566.589872	-3566.57998
IntF / -9.9	-3040.216289	-3040.20626
IntG / -16.5	-3172.960958	-3172.95109
IntG1 / -14.7	-3172.958151	-3172.94829
IntB / -20.8	-3305.701959	-3305.69224
IntB1 / -20.9	-3305.702152	-3305.69244
IntB2 / -15.9	-3305.694061	-3305.68434
IntD / -7.8	-4551.712437	-4551.70268
IntD1 / -6.0	-6063.20919	-6063.19964
IntC / -14.8	-3695.4926	-3695.48297
1	-655.279172	-655.26883

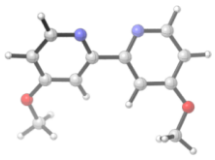
Table S1. Free energies of possible light-harvesting species.

Cartesian coordination of the optimized structures



IntA

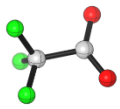
Fe	-0.53682	-0.28552	0.91333
O	-2.27761	-0.20829	-0.30283
C	-2.59755	0.83104	0.33050
O	-1.82692	1.27988	1.23478
O	0.60677	0.59827	-0.54727
C	0.77005	-0.53812	-1.09186
O	0.30095	-1.57113	-0.54475
O	-0.16204	-0.38388	2.94826
C	-0.88894	-1.42008	3.00944
O	-1.42439	-1.87342	1.95968
C	1.46689	-0.63406	-2.45912
C	-1.06988	-2.14651	4.35263
C	-3.93965	1.53461	0.06949
F	-3.78018	2.86353	0.09456
F	-4.44398	1.17618	-1.11415
F	-4.80713	1.18633	1.03496
F	2.38338	0.33031	-2.59413
F	2.05785	-1.82422	-2.60617
F	0.54181	-0.48902	-3.42413
F	-0.11418	-3.08424	4.47047
F	-0.95813	-1.28835	5.37175
F	-2.26597	-2.74121	4.40896



L2

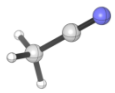
C	-1.26392	-2.66566	-0.55264
C	-2.35527	-3.47760	-0.27746
C	-3.54496	-2.86626	0.14354
C	-3.57067	-1.47211	0.25956
C	-2.41058	-0.74688	-0.05388
N	-1.26531	-1.32738	-0.45043
H	-0.32984	-3.11866	-0.87973
H	-2.30140	-4.55587	-0.37593
H	-4.45431	-0.95489	0.60831
C	-2.41077	0.74713	0.05170
C	-3.57079	1.47212	-0.26250
N	-1.26587	1.32786	0.44900
C	-3.54544	2.86628	-0.14646
H	-4.45410	0.95473	-0.61182
C	-1.26482	2.66614	0.55121
C	-2.35615	3.47786	0.27532
H	-0.33104	3.11933	0.87890
H	-2.30256	4.55614	0.37382
O	-4.58543	3.68643	-0.41917
O	-4.58496	-3.68662	0.41557
C	-5.82189	-3.10615	0.84095

H	-6.22562	-2.43165	0.07860
H	-6.50581	-3.94178	0.98639
H	-5.70176	-2.56440	1.78489
C	-5.82196	3.10571	-0.84538
H	-6.22606	2.43113	-0.08329
H	-6.50595	3.94121	-0.99127
H	-5.70109	2.56399	-1.78924



CF_3COO^-

O	-1.77903	-0.70500	1.32873
C	-1.10276	-0.64742	2.37922
O	0.11612	-0.45547	2.56837
C	-1.95920	-0.88489	3.66978
F	-1.28450	-0.68401	4.82663
F	-3.04838	-0.07207	3.71422
F	-2.43252	-2.16142	3.71687

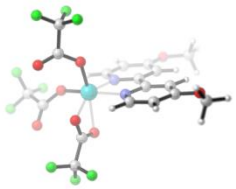


CH_3CN

C	-0.23446	-0.61292	-3.65840
N	-0.38236	-0.62883	-2.50688
C	-0.04884	-0.59288	-5.10516
H	-0.84193	-1.16563	-5.59240
H	-0.07850	0.43608	-5.47229
H	0.91686	-1.03368	-5.36493

CCl_3CN

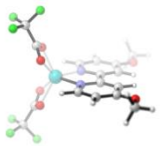
C	-0.24899	-0.61426	-3.55447
N	-0.40111	-0.63123	-2.40471
C	-0.05889	-0.59373	-5.00417
Cl	-1.37998	-1.54372	-5.77409
Cl	-0.11516	1.11054	-5.57186
Cl	1.53490	-1.32546	-5.39077



IntE

C	1.67411	-2.37402	0.02045
C	3.00964	-2.74748	0.02442
C	3.97890	-1.73688	-0.06453
C	3.55329	-0.39840	-0.14966
C	2.19839	-0.11411	-0.14593
N	1.26685	-1.09863	-0.06588
H	0.89101	-3.12141	0.07829
H	3.26833	-3.79495	0.09494
H	4.30530	0.37685	-0.21238
C	1.64202	1.25971	-0.22428
C	2.43365	2.39641	-0.34830
N	0.29074	1.33194	-0.16903
C	1.81242	3.65360	-0.41960
H	3.50900	2.30838	-0.39102
C	-0.30496	2.54210	-0.24658
C	0.40846	3.71530	-0.36985
H	-1.38747	2.54000	-0.21257
H	-0.09592	4.67172	-0.42874

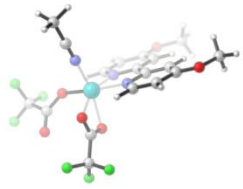
Fe	-0.77867	-0.47491	0.03337
O	-0.83348	-0.80685	1.91757
C	-1.81675	-1.19718	2.67627
O	-2.86777	-1.71647	2.35150
O	-2.46926	0.44504	-0.07792
C	-3.57437	0.27452	-0.73504
O	-3.88489	-0.62822	-1.49241
O	-0.86299	-0.76278	-2.19951
C	-1.29398	-1.90071	-1.91771
O	-1.34918	-2.31894	-0.71619
C	-1.50833	-0.92498	4.17076
C	-4.57481	1.42263	-0.44408
C	-1.72687	-2.86478	-3.03454
F	-2.02436	-2.20240	-4.15991
F	-0.71657	-3.71908	-3.30070
F	-2.79657	-3.58412	-2.66566
F	-5.68128	1.31990	-1.19216
F	-4.00943	2.62463	-0.70099
F	-4.94303	1.41497	0.85350
F	-1.33860	0.39748	4.38362
F	-2.50160	-1.34864	4.96456
F	-0.37457	-1.55036	4.54896
O	2.45748	4.81781	-0.53669
C	3.89450	4.82724	-0.58974
H	4.31978	4.41446	0.32943
H	4.25537	4.26916	-1.45827
H	4.17300	5.87521	-0.68507
O	5.30140	-1.93342	-0.07447
C	5.80702	-3.27707	0.00890
H	5.49979	-3.74991	0.94588
H	5.46781	-3.87278	-0.84325
H	6.89095	-3.18066	-0.01703



IntF

C	0.27918	-2.42935	-0.95270
C	1.48086	-3.07332	-1.18788
C	2.67061	-2.34573	-1.01121
C	2.58943	-0.99729	-0.60813
C	1.34984	-0.42708	-0.39549
N	0.20447	-1.14306	-0.56721
H	-0.66186	-2.95380	-1.07095
H	1.47518	-4.10973	-1.49541
H	3.50739	-0.44088	-0.47205
C	1.13446	0.97491	0.03073
C	2.14743	1.88935	0.24043
N	-0.17307	1.31617	0.20276
C	1.82299	3.20188	0.63915
H	3.18946	1.63114	0.10515
C	-0.48509	2.56742	0.58470
C	0.47032	3.54168	0.81508
H	-1.53964	2.78768	0.70389
H	0.15596	4.53024	1.11964
Fe	-1.57432	-0.16072	-0.18901
O	-2.59675	0.16839	1.61439
C	-2.72839	-1.08383	1.73875
O	-2.27569	-1.85935	0.84980
O	-2.79429	1.23329	-1.21189

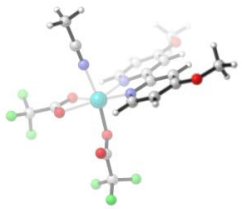
C	-2.93606	0.37838	-2.13020
O	-2.39248	-0.76041	-2.02262
C	-3.38666	-1.65895	3.00401
F	-3.92277	-2.85862	2.75745
F	-2.44917	-1.79252	3.95871
F	-4.34198	-0.83700	3.45302
C	-3.71571	0.73509	-3.40658
F	-2.85435	1.21361	-4.32170
F	-4.31822	-0.34798	-3.90997
F	-4.63722	1.67028	-3.15397
O	2.85280	4.02710	0.81689
O	3.89906	-2.82631	-1.19310
C	4.06635	-4.19839	-1.59909
H	3.59667	-4.37262	-2.57069
H	5.14169	-4.34622	-1.67590
H	3.65065	-4.87533	-0.84818
C	2.60572	5.39005	1.21255
H	3.58921	5.84958	1.28853
H	2.01065	5.90835	0.45599
H	2.10298	5.42494	2.18261



IntG

C	1.82458	-2.33271	0.32981
C	3.15853	-2.64926	0.47230
C	4.11211	-1.61857	0.38727
C	3.66620	-0.30481	0.16238
C	2.30224	-0.07191	0.02984
N	1.39355	-1.07250	0.10981
H	1.05867	-3.09738	0.38288
H	3.47537	-3.66994	0.64619
H	4.36979	0.51164	0.09601
C	1.72041	1.27380	-0.20507
C	2.48269	2.42569	-0.34687
N	0.36532	1.30254	-0.27525
C	1.83085	3.65131	-0.57216
H	3.55985	2.37809	-0.28864
C	-0.26036	2.48200	-0.49533
C	0.42566	3.66624	-0.64621
H	-1.34123	2.44419	-0.55042
H	-0.09941	4.59680	-0.82130
Fe	-0.64218	-0.50174	-0.08651
O	-2.37155	0.28450	-0.23081
C	-3.43078	0.06592	-0.95919
O	-3.65557	-0.87307	-1.69860
O	-0.62362	-0.99865	-2.14846
C	-1.03956	-2.14602	-1.83267
O	-1.14571	-2.48084	-0.61678
C	-4.47232	1.19843	-0.78104
C	-1.37165	-3.16896	-2.93041
F	-1.73426	-2.55578	-4.06285
F	-0.27896	-3.91660	-3.17959
F	-2.36153	-3.98142	-2.54057
F	-3.92107	2.39637	-1.07974
F	-5.53460	1.02021	-1.57422
F	-4.89978	1.25018	0.49563
C	-1.09936	-1.09365	3.07805

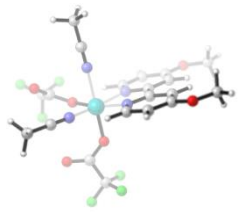
N	-0.92146	-0.88697	1.95397
C	-1.32176	-1.35659	4.48582
H	-0.39080	-1.20196	5.03705
H	-2.08940	-0.67785	4.86582
H	-1.65389	-2.39021	4.61243
O	2.44699	4.82246	-0.72695
O	5.38947	-1.97568	0.53184
C	6.42017	-0.97433	0.45735
H	6.29244	-0.22711	1.24537
H	7.35463	-1.51156	0.60820
H	6.42464	-0.49442	-0.52525
C	3.88444	4.88313	-0.67397
H	4.32622	4.27224	-1.46578
H	4.13397	5.93035	-0.83341
H	4.24912	4.56046	0.30496



IntG1

C	1.94882	-2.53285	-0.13941
C	3.26295	-2.90017	0.05567
C	4.24043	-1.89407	0.16337
C	3.83901	-0.55118	0.06749
C	2.49279	-0.26359	-0.12676
N	1.56205	-1.24182	-0.22613
H	1.17038	-3.27675	-0.25557
H	3.54694	-3.94314	0.11881
H	4.56123	0.24844	0.13722
C	1.96383	1.11537	-0.25372
C	2.75000	2.24834	-0.16045
N	0.62061	1.20084	-0.47464
C	2.15931	3.51929	-0.29798
H	3.81517	2.19427	0.02054
C	0.05897	2.41541	-0.61317
C	0.77802	3.59623	-0.53549
H	-1.00907	2.42938	-0.78746
H	0.26126	4.53828	-0.65533
Fe	-0.42496	-0.61303	-0.51381
O	-2.20354	0.54391	-0.60610
C	-2.89024	-0.51570	-0.51577
O	-2.34064	-1.63764	-0.38471
O	-0.42248	-1.04273	-2.37203
C	-0.37567	-2.23651	-2.89529
O	-0.25029	-3.29991	-2.31485
C	-4.42149	-0.41306	-0.62068
C	-0.49316	-2.18338	-4.43765
F	-1.65070	-1.59771	-4.80321
F	0.51922	-1.46401	-4.96209
F	-0.45644	-3.41027	-4.97238
F	-4.76809	-0.27325	-1.91367
F	-5.01416	-1.51059	-0.13672
F	-4.87049	0.65421	0.05630
C	-0.67817	-0.75691	2.76903
N	-0.60427	-0.68084	1.61723
C	-0.77322	-0.85283	4.21346
H	0.23044	-0.86591	4.64551
H	-1.32542	0.00718	4.60049
H	-1.29816	-1.77287	4.48256

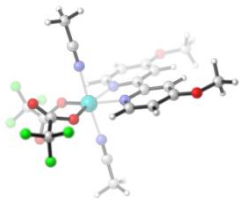
O	2.98259	4.56201	-0.18659
C	2.44781	5.89410	-0.30107
H	2.00396	6.04878	-1.28815
H	1.70786	6.08106	0.48187
H	3.29979	6.55857	-0.17072
O	5.49776	-2.30201	0.34642
C	6.55104	-1.32720	0.45046
H	6.62175	-0.73379	-0.46536
H	6.39237	-0.67559	1.31414
H	7.46433	-1.90325	0.58704



IntB

C	1.79897	-2.28718	1.26455
C	3.09188	-2.75002	1.39314
C	4.14909	-1.92854	0.96514
C	3.84370	-0.66935	0.42441
C	2.51068	-0.28040	0.32994
N	1.50027	-1.07896	0.74623
H	0.96045	-2.89339	1.58485
H	3.29675	-3.72634	1.81429
H	4.63003	-0.01102	0.08677
C	2.08758	1.03147	-0.22414
C	2.98217	1.98433	-0.70017
N	0.75107	1.24612	-0.22919
C	2.48316	3.20101	-1.19396
H	4.04407	1.78969	-0.68946
C	0.27215	2.41802	-0.69890
C	1.09298	3.41294	-1.18534
H	-0.80370	2.53872	-0.66495
H	0.68252	4.34392	-1.55597
Fe	-0.48612	-0.31780	0.44864
O	-2.07003	0.73608	0.25320
C	-3.15890	0.96177	0.92690
O	-3.53402	0.44671	1.96256
O	-0.60891	-1.20441	-1.24943
C	-1.62357	-1.70613	-1.89259
O	-2.75588	-1.90490	-1.49481
C	-4.03353	2.02948	0.22058
C	-1.22912	-2.07271	-3.34652
F	-0.80684	-0.97790	-4.01340
F	-0.22386	-2.97258	-3.35577
F	-2.26229	-2.59664	-4.02016
F	-4.48697	1.56172	-0.96017
F	-5.09027	2.37543	0.96710
F	-3.31615	3.14807	-0.03049
C	-0.22247	0.95198	3.55604
N	-0.27557	0.50059	2.49237
C	-0.15787	1.51827	4.89230
H	0.72757	1.14062	5.40934
H	-0.10149	2.60758	4.82597
H	-1.05294	1.23582	5.45217
O	3.23460	4.19384	-1.67657
O	5.38349	-2.41915	1.10990
C	6.51054	-1.63122	0.68957
H	6.56592	-0.69825	1.25766
H	7.38574	-2.24272	0.90148

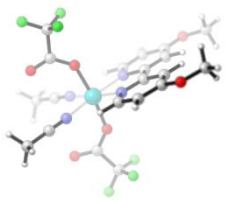
H	6.45860	-1.41980	-0.38216
C	4.66507	4.04778	-1.71052
H	4.95433	3.20452	-2.34378
H	5.03964	4.97517	-2.13991
H	5.06644	3.91954	-0.70129
C	-2.13650	-2.73682	1.87962
N	-1.37906	-1.97580	1.44935
C	-3.08310	-3.69171	2.42197
H	-3.84552	-3.15785	2.99499
H	-3.55853	-4.23771	1.60335
H	-2.56180	-4.39531	3.07579



IntB1

C	-1.14368	-2.65572	0.12719
C	-2.24690	-3.48213	0.17132
C	-3.52789	-2.90279	0.15077
C	-3.63348	-1.50399	0.08256
C	-2.46994	-0.74197	0.03819
N	-1.24268	-1.31117	0.06358
H	-0.13702	-3.05599	0.13950
H	-2.13793	-4.55836	0.22170
H	-4.60180	-1.02668	0.06646
C	-2.47006	0.74222	-0.04057
C	-3.63372	1.50401	-0.08575
N	-1.24289	1.31168	-0.06501
C	-3.52836	2.90283	-0.15376
H	-4.60195	1.02650	-0.07040
C	-1.14411	2.65624	-0.12847
C	-2.24747	3.48243	-0.17338
H	-0.13751	3.05671	-0.13995
H	-2.13868	4.55869	-0.22362
Fe	0.44955	0.00046	0.00035
O	1.63822	1.50212	-0.07663
C	2.76507	1.79209	0.50655
O	3.38305	1.14869	1.33238
O	1.63850	-1.50098	0.07931
C	2.76462	-1.79201	-0.50476
O	3.38192	-1.14984	-1.33204
C	3.30064	3.15929	0.01089
C	3.30010	-3.15895	-0.00826
F	3.58320	-3.10603	1.30945
F	2.37305	-4.12661	-0.18949
F	4.41153	-3.52316	-0.66025
F	2.37376	4.12698	0.19264
F	4.41215	3.52297	0.66303
F	3.58370	3.10700	-1.30687
C	0.39388	-0.14439	-3.29601
N	0.37391	-0.08335	-2.14152
C	0.42022	-0.22169	-4.74512
H	-0.44951	-0.78149	-5.09778
H	0.39843	0.78687	-5.16516
H	1.33358	-0.72896	-5.06568
O	-4.56537	3.74429	-0.20127
O	-4.56476	-3.74446	0.19766
C	-5.90308	-3.21887	0.17690
H	-6.08731	-2.66143	-0.74585

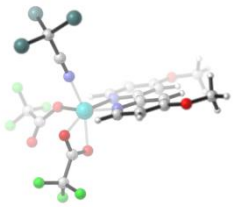
H	-6.55589	-4.08893	0.21714
H	-6.08380	-2.58135	1.04697
C	-5.90359	3.21838	-0.18131
H	-6.08818	2.66080	0.74128
H	-6.55657	4.08829	-0.22183
H	-6.08367	2.58091	-1.05154
C	0.38435	0.14356	3.29689
N	0.37021	0.08396	2.14224
C	0.40287	0.21861	4.74620
H	1.43081	0.35708	5.09020
H	-0.20762	1.06273	5.07631
H	0.00078	-0.70690	5.16566



IntB2

C	-0.80400	0.09856	-2.65922
C	-1.90842	0.14157	-3.48329
C	-3.18741	0.13152	-2.90030
C	-3.28617	0.07693	-1.50073
C	-2.12123	0.03185	-0.74149
N	-0.89431	0.04414	-1.31410
H	0.19569	0.10729	-3.07438
H	-1.80012	0.18394	-4.55981
H	-4.25232	0.07335	-1.01911
C	-2.12125	-0.03130	0.74145
C	-3.28620	-0.07609	1.50068
N	-0.89434	-0.04383	1.31408
C	-3.18747	-0.13057	2.90026
H	-4.25234	-0.07236	1.01904
C	-0.80405	-0.09816	2.65923
C	-1.90850	-0.14085	3.48327
H	0.19562	-0.10708	3.07441
H	-1.80023	-0.18312	4.55980
Fe	0.77165	-0.00016	0.00013
O	0.89802	1.92877	0.05005
C	1.86817	2.79126	0.07667
O	3.06969	2.59229	0.07747
O	0.89719	-1.92912	-0.05026
C	1.86705	-2.79194	-0.07693
O	3.06864	-2.59337	-0.07800
C	1.31839	4.24083	0.11155
C	1.31677	-4.24133	-0.11157
F	0.55028	-4.48613	0.97227
F	0.55163	-4.43386	-1.20694
F	2.30606	-5.14562	-0.13254
F	0.55306	4.43343	1.20678
F	2.30799	5.14477	0.13293
F	0.55223	4.48612	-0.97241
C	3.11475	-0.04261	2.32061
N	2.19328	-0.04051	1.62169
C	4.26439	-0.04457	3.20499
H	4.86524	0.84987	3.02289
H	3.92483	-0.04858	4.24391
H	4.86838	-0.93559	3.01691
O	-4.22670	-0.17499	3.73757
O	-4.22661	0.17631	-3.73762
C	-5.56348	0.16569	-3.20678

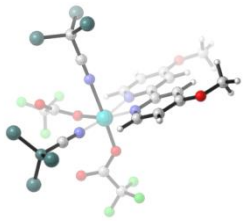
H	-5.73808	1.04263	-2.57714
H	-6.21898	0.20023	-4.07499
H	-5.74862	-0.75119	-2.64022
C	-5.56357	-0.16391	3.20671
H	-5.73848	-1.04079	2.57709
H	-6.21909	-0.19818	4.07492
H	-5.74835	0.75304	2.64012
C	3.11496	0.04184	-2.32039
N	2.19335	0.03972	-1.62167
C	4.26479	0.04374	-3.20454
H	4.86855	0.93496	-3.01666
H	4.86580	-0.85050	-3.02198
H	3.92544	0.04725	-4.24353



IntD

C	1.82878	-2.30730	0.33518
C	3.16016	-2.62300	0.49715
C	4.11609	-1.59410	0.41304
C	3.67411	-0.28171	0.16976
C	2.31291	-0.04834	0.01957
N	1.40110	-1.04810	0.09766
H	1.06218	-3.07124	0.38688
H	3.47363	-3.64221	0.68492
H	4.37958	0.53292	0.10118
C	1.73539	1.29542	-0.23483
C	2.49682	2.44856	-0.36248
N	0.38135	1.32044	-0.33612
C	1.84622	3.67166	-0.60815
H	3.57229	2.40516	-0.27692
C	-0.24374	2.49793	-0.57279
C	0.44243	3.68267	-0.71326
H	-1.32344	2.45784	-0.64637
H	-0.08090	4.61150	-0.90193
Fe	-0.61525	-0.47939	-0.17663
O	-2.35159	0.28414	-0.21691
C	-3.43589	0.05538	-0.90874
O	-3.68112	-0.89620	-1.62366
O	-0.65744	-1.03027	-2.18244
C	-1.05868	-2.18048	-1.83902
O	-1.12850	-2.49338	-0.61813
C	-4.46652	1.19570	-0.72143
C	-1.41377	-3.21437	-2.91920
F	-1.86542	-2.61175	-4.02471
F	-0.30895	-3.91648	-3.23381
F	-2.34634	-4.06373	-2.47389
F	-3.92481	2.37910	-1.08781
F	-5.56305	0.99290	-1.45928
F	-4.83428	1.29389	0.57021
C	-1.10289	-1.12762	3.05150
N	-0.91228	-0.89636	1.93710
C	-1.34811	-1.42989	4.46787
O	2.46198	4.84291	-0.75315
O	5.39020	-1.95068	0.57568
C	6.42421	-0.95165	0.50522
H	6.28807	-0.19797	1.28553
H	7.35534	-1.48986	0.67181

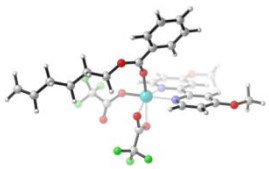
H	6.44114	-0.48050	-0.48133
C	3.89797	4.90966	-0.66460
H	4.36114	4.29701	-1.44256
H	4.14685	5.95720	-0.82244
H	4.23852	4.59267	0.32475
Cl	-2.35669	-0.11669	5.14867
Cl	0.23641	-1.51526	5.29812
Cl	-2.20112	-3.00207	4.55143



IntD1

C	0.92575	-0.43756	2.82260
C	1.78932	-0.39824	3.89616
C	3.17366	-0.43158	3.65226
C	3.61883	-0.50816	2.32217
C	2.68059	-0.54555	1.29688
N	1.34765	-0.50702	1.54254
H	-0.14556	-0.41131	2.97857
H	1.41585	-0.34181	4.91087
H	4.67441	-0.53742	2.09753
C	3.05264	-0.62439	-0.13862
C	4.36554	-0.67571	-0.59051
N	2.00542	-0.63626	-0.99876
C	4.60868	-0.73882	-1.97368
H	5.18590	-0.66729	0.11116
C	2.23853	-0.68826	-2.32925
C	3.51091	-0.74025	-2.85406
H	1.36288	-0.67668	-2.96670
H	3.67215	-0.78151	-3.92394
Fe	0.10085	-0.65224	-0.17088
O	-0.77826	-0.39298	-1.82532
C	-1.68755	0.37282	-2.36111
O	-2.36953	1.21972	-1.82029
O	-0.15814	-2.51926	0.02163
C	-1.16505	-3.29299	-0.28996
O	-2.29966	-2.97048	-0.57813
C	-1.84883	0.06695	-3.87122
C	-0.75043	-4.78495	-0.24372
F	0.25705	-5.02095	-1.10856
F	-0.32337	-5.11966	0.99032
F	-1.77413	-5.58576	-0.56468
F	-2.33669	-1.17664	-4.04814
F	-2.68027	0.93359	-4.46103
F	-0.65506	0.13458	-4.50120
C	0.30010	2.83117	-0.11657
N	0.23948	1.67812	-0.08565
C	0.37430	4.29562	-0.15865
O	5.81842	-0.79448	-2.53113
O	3.97034	-0.38680	4.72147
C	5.39816	-0.40937	4.54317
H	5.72971	0.45588	3.96236
H	5.81456	-0.36011	5.54749
H	5.71362	-1.33680	4.05735
C	6.98894	-0.79463	-1.69333
H	6.98879	-1.66218	-1.02779
H	7.83254	-0.85601	-2.37815
H	7.05007	0.13042	-1.11341

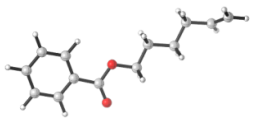
C	-2.81305	-0.08147	1.34271
N	-1.72196	-0.22249	0.99321
C	-4.19983	0.09797	1.79005
Cl	1.02056	4.86993	1.41252
Cl	1.46869	4.75869	-1.50174
Cl	-1.27659	4.93392	-0.43688
Cl	-4.84041	1.58774	1.03202
Cl	-4.18760	0.24511	3.57691
Cl	-5.13944	-1.33603	1.27543



IntC

C	2.49131	-1.96743	0.48780
C	3.85432	-2.15434	0.58019
C	4.70566	-1.06372	0.32713
C	4.13234	0.17440	-0.00749
C	2.74740	0.27682	-0.07988
N	1.93780	-0.78034	0.16282
H	1.80195	-2.78424	0.66661
H	4.26989	-3.11948	0.84154
H	4.75524	1.03415	-0.20351
C	2.03818	1.53705	-0.41794
C	2.69114	2.72348	-0.72749
N	0.68480	1.45078	-0.40365
C	1.92667	3.86353	-1.03088
H	3.77000	2.76554	-0.73627
C	-0.04951	2.54724	-0.69951
C	0.52364	3.76025	-1.01186
H	-1.12470	2.41821	-0.68114
H	-0.08792	4.62327	-1.24327
Fe	-0.15207	-0.40906	0.02286
O	-1.94609	0.20233	-0.27127
C	-2.96226	-0.17713	-0.99022
O	-3.06542	-1.15978	-1.70055
O	-0.04410	-1.10876	-2.02143
C	-0.38823	-2.23334	-1.58352
O	-0.50201	-2.43857	-0.33462
C	-4.16040	0.78875	-0.81213
C	-0.62288	-3.40343	-2.55162
F	-0.93272	-2.96153	-3.77548
F	0.50409	-4.13788	-2.63503
F	-1.61112	-4.19408	-2.11313
F	-3.78645	2.07009	-1.00619
F	-5.15390	0.50882	-1.66152
F	-4.64392	0.69059	0.44913
O	2.43155	5.05737	-1.34327
O	6.01677	-1.29327	0.42799
C	6.94402	-0.22247	0.17550
H	6.79365	0.59635	0.88474
H	7.93170	-0.65659	0.31909
H	6.84581	0.14156	-0.85108
C	3.85898	5.23529	-1.39305
H	4.30288	4.59032	-2.15640
H	4.00946	6.27948	-1.66038
H	4.30871	5.03509	-0.41679
C	2.39826	0.04460	5.13812
C	1.51555	-0.10748	4.07401

C	0.33680	-0.85305	4.24587
C	0.04854	-1.44187	5.49015
C	0.93856	-1.28658	6.54750
C	2.11147	-0.54514	6.37291
H	3.30762	0.62156	5.00761
H	1.72499	0.34955	3.11415
H	-0.86203	-2.01469	5.61782
H	0.71982	-1.74196	7.50755
H	2.80263	-0.42597	7.20144
C	-0.58299	-1.00737	3.11044
O	-0.33764	-0.51081	1.98424
O	-1.67742	-1.67961	3.36133
C	-2.69442	-1.83493	2.31539
C	-3.89857	-2.51070	2.94348
H	-2.25835	-2.43321	1.51208
H	-2.93592	-0.84024	1.93693
C	-5.02093	-2.69860	1.91233
H	-3.59796	-3.48156	3.35413
H	-4.25629	-1.89950	3.78025
C	-6.27666	-3.34898	2.52178
H	-5.28956	-1.72824	1.47737
H	-4.65687	-3.31971	1.08333
H	-5.98588	-4.30820	2.97463
H	-6.66245	-2.72021	3.33353
C	-7.35856	-3.58789	1.50414
C	-8.58461	-3.06435	1.54668
H	-7.08940	-4.23918	0.67100
H	-9.32257	-3.27366	0.77756
H	-8.89631	-2.40838	2.35670



1

C	0.26672	2.10723	1.09541
C	1.63864	1.86713	1.09282
C	2.40242	2.15593	-0.04710
C	1.77964	2.68806	-1.18584
C	0.40621	2.92687	-1.17938
C	-0.35101	2.63746	-0.04100
H	-0.32077	1.88222	1.98011
H	2.13526	1.45635	1.96499
H	2.37070	2.91097	-2.06631
H	-0.07368	3.33862	-2.06179
H	-1.42064	2.82473	-0.03938
C	3.86663	1.87974	0.00275
O	4.44410	1.41439	0.97218
O	4.49454	2.19972	-1.14445
C	5.92361	1.96359	-1.18631
C	6.41991	2.38445	-2.55961
H	6.11099	0.90271	-0.99232
H	6.39926	2.54026	-0.38668
C	7.93139	2.17352	-2.71282
H	5.88382	1.81020	-3.32524
H	6.17177	3.44070	-2.72096
C	8.45107	2.60166	-4.09809
H	8.46585	2.73887	-1.93863
H	8.17369	1.11535	-2.54634

H	7.89242	2.04522	-4.86513	H	10.23836	1.30649	-4.17403
H	8.23662	3.66506	-4.26139	H	11.89385	3.03039	-4.63961
C	9.92303	2.34648	-4.27406	H	10.57538	4.32869	-4.63199
C	10.84257	3.27937	-4.52621				

Table S2. Cartesian coordinates of the optimized structures.

TD-DFT calculations of active species (IntB): The strongest absorption peak in range of experimental blue LEDs.

Excited State 9: 2.7293 eV 454.27 nm f = 0.0269 <S**2> = 8.830

140B ->146B	-0.29224
140B ->147B	-0.13503
141B ->145B	0.47187
141B ->146B	0.24184
141B ->147B	-0.24184
142B ->145B	-0.37854
142B ->146B	-0.44382
142B ->147B	-0.25705
143B ->145B	0.24768
143B ->146B	-0.17240
143B ->147B	0.18416

Table S3. TD-DFT calculations of active species **IntB**.

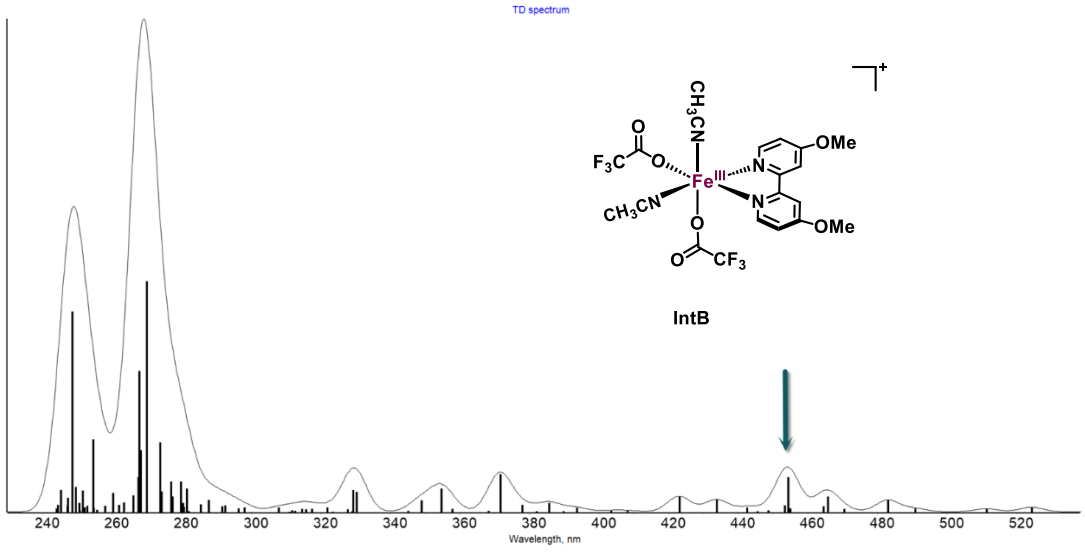


Figure S21. The calculated UV-Vis absorption spectrum of **IntB**.

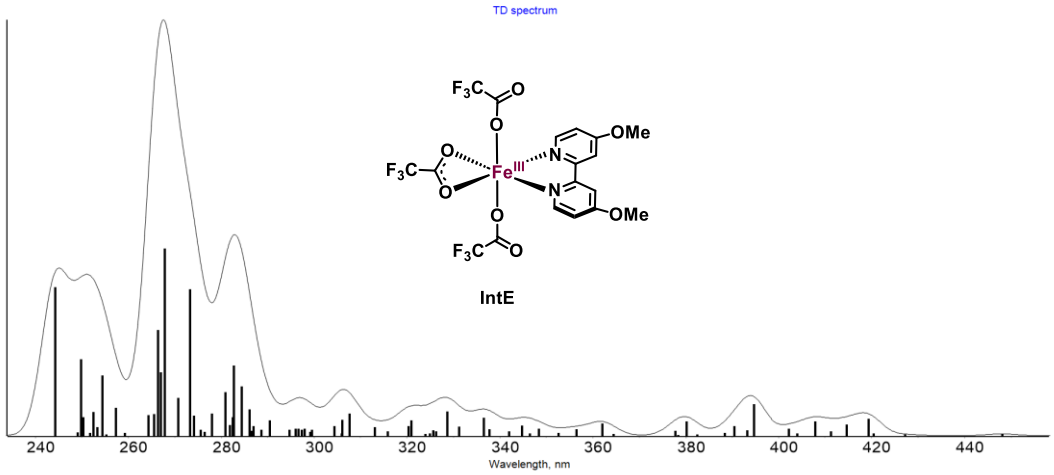


Figure S22. The calculated UV-Vis absorption spectrum of **IntE**.

The neutral species **IntE** did not show obvious blue light absorption (Figure **S22**), and its excited state would not undergo effective LMCT due to the weak oxidizing ability.

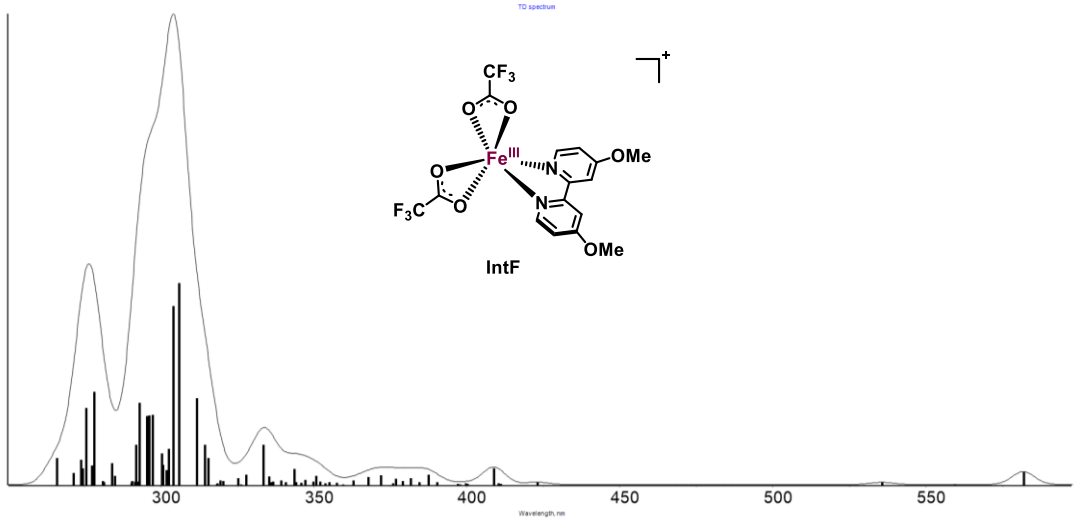


Figure S23. The calculated UV-Vis absorption spectrum of **IntF**.

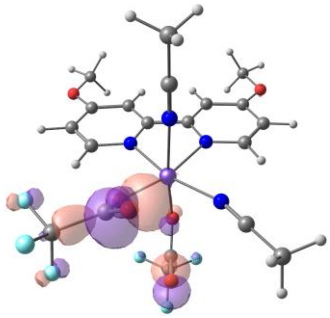
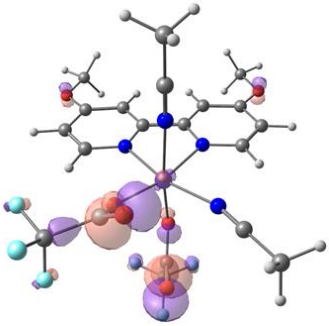
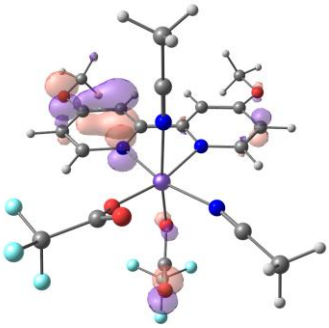
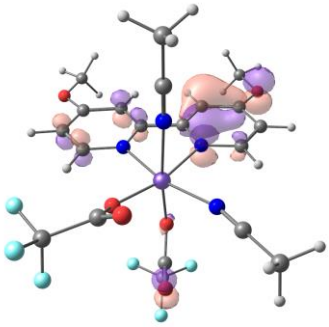
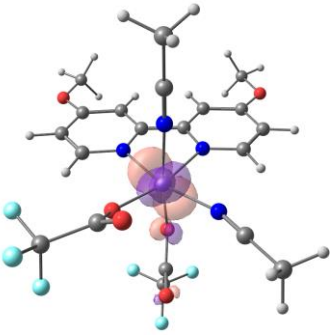
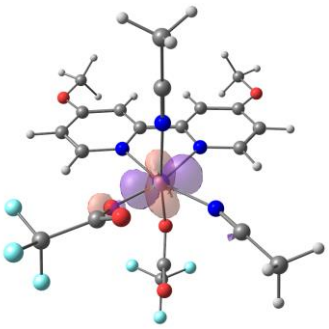
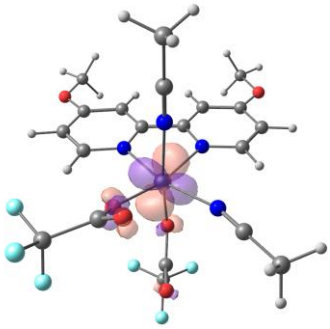
 140-beta	 141-beta
 142-beta	 143-beta
 145-beta	 146-beta
 147-beta	

Figure S24. The key orbitals for the most possible absorption peak.

Free energies of the key species in the calculations

Species	Gibbs free energy	Gibbs free energy with the Fang's entropy correction
IntB	-3305.701959	-3305.69224
TS-B	-2779.530112	-2779.5203
$CF_3^{\cdot}$	-337.56521	-337.55589
CO_2	-188.590143	-188.5811435
Int1	-655.279172	-655.26883
2-ts	-992.83103	-992.82083
Int3	-992.88293	-992.87267
Int4	-1511.51048	-1511.49973
5-ts	-2504.37128	-2504.36133
Int6	-1051.29444	-1051.28358
Product	-1453.13961	-1453.12941
7-ts	-1706.53846	-1706.52833
2b-ts	-1706.53846	-1706.52833
Int2b	-1706.56759	-1706.55746

Table S4. Free energies of the key species in the calculations.

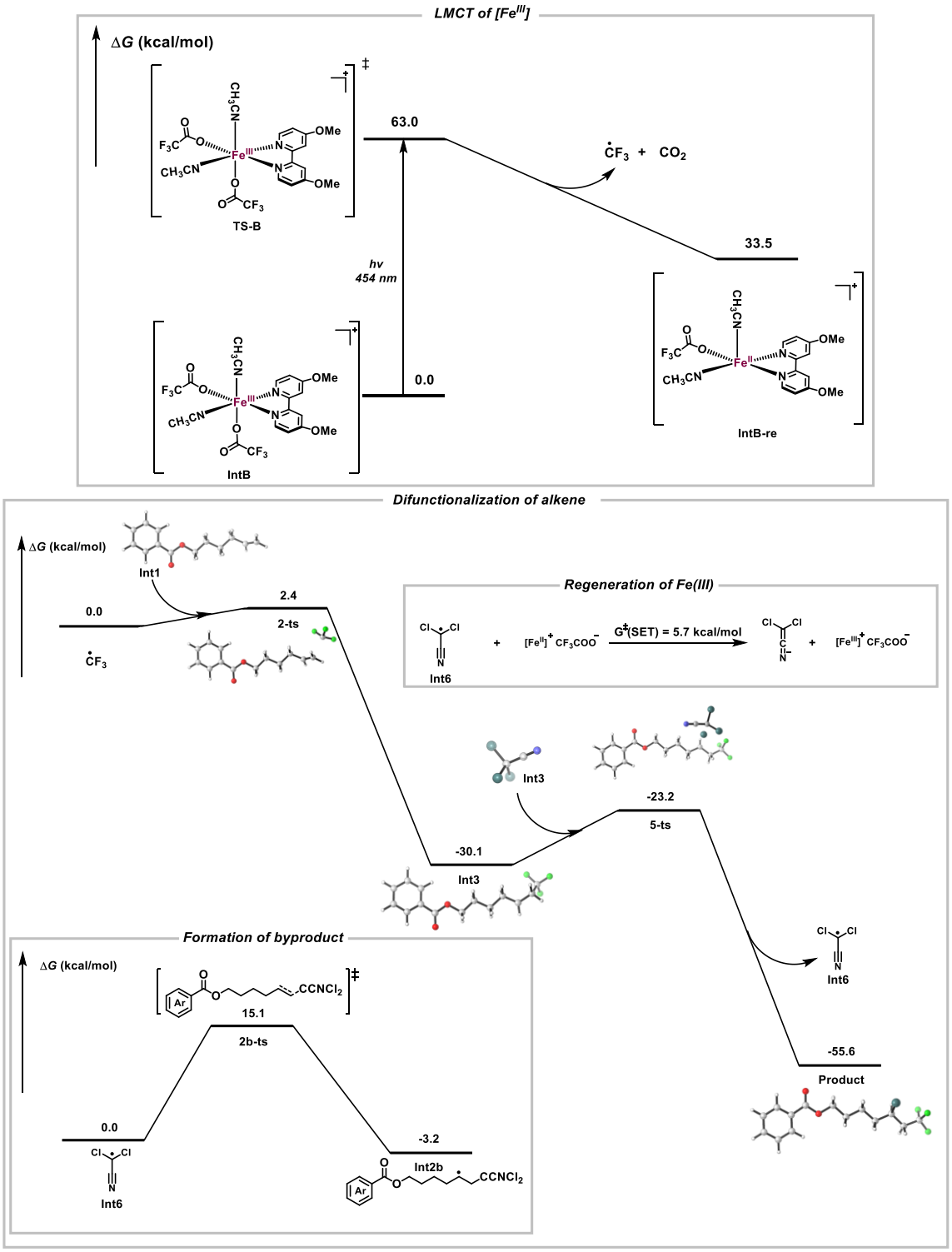


Figure S25. Detailed mechanism description.

Through DFT calculations, we can conclude that the CCl_2CN radical is responsible for the oxidation of iron(II) to regenerate iron(III) under the standard catalytic condition (Figure **S25**). As we can see, the addition of CF_3 radical to alkene **1** (ΔG = 2.4 kcal/mol) and the oxidation of iron(II) to iron(III) by CCl_2CN radical (ΔG = 5.7 kcal/mol) should both occur prior to the radical relay between CCl_2CN radical and **1** (ΔG = 15.1 kcal/mol). Therefore, compared to the stoichiometric reaction, the iron photocatalyzed condition that involves the oxidation of iron(II) to iron(III) by CCl_2CN radical can avoid the formation of CCl_2CN radical addition by-product.

Species	Energy
IntB	-2779.802282
IntB-re	-3306.15977
Int6	-1051.278898
Product	-1051.423348
IntB-ox	-3305.990416

Table S5. Energy for the relevant species.

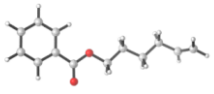
Cartesian coordination of the key species

CF_3·

C	-0.07951	0.96759	-3.78974
F	-0.19969	2.28854	-3.82591
F	1.08347	0.57756	-4.29574
F	-1.09408	0.37638	-4.40765

CO_2

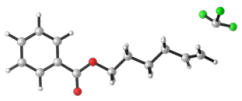
O	-1.35731	0.21979	-2.17243
C	-0.22717	0.40175	-1.93515
O	0.90278	0.58339	-1.69692



Int1

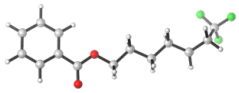
C	0.26672	2.10723	1.09541
C	1.63864	1.86713	1.09282
C	2.40242	2.15593	-0.04710
C	1.77964	2.68806	-1.18584
C	0.40621	2.92687	-1.17938
C	-0.35101	2.63746	-0.04100
H	-0.32077	1.88222	1.98011
H	2.13526	1.45635	1.96499
H	2.37070	2.91097	-2.06631
H	-0.07368	3.33862	-2.06179
H	-1.42064	2.82473	-0.03938
C	3.86663	1.87974	0.00275
O	4.44410	1.41439	0.97218
O	4.49454	2.19972	-1.14445
C	5.92361	1.96359	-1.18631
C	6.41991	2.38445	-2.55961

H	6.11099	0.90271	-0.99232
H	6.39926	2.54026	-0.38668
C	7.93139	2.17352	-2.71282
H	5.88382	1.81020	-3.32524
H	6.17177	3.44070	-2.72096
C	8.45107	2.60166	-4.09809
H	8.46585	2.73887	-1.93863
H	8.17369	1.11535	-2.54634
H	7.89242	2.04522	-4.86513
H	8.23662	3.66506	-4.26139
C	9.92303	2.34648	-4.27406
C	10.84257	3.27937	-4.52621
H	10.23836	1.30649	-4.17403
H	11.89385	3.03039	-4.63961
H	10.57538	4.32869	-4.63199



2-ts

C	7.15945	0.06788	0.34764
C	6.04774	0.90685	0.35295
C	4.75515	0.36409	0.32340
C	4.58535	-1.02794	0.28842
C	5.70057	-1.86433	0.28314
C	6.98692	-1.31891	0.31268
H	8.15833	0.49235	0.37063
H	6.16181	1.98496	0.37987
H	3.58613	-1.44656	0.26568
H	5.56672	-2.94128	0.25600
H	7.85343	-1.97336	0.30850
C	3.59977	1.30625	0.33075
O	3.70605	2.52180	0.36036
O	2.41250	0.67161	0.30119
C	1.23126	1.51045	0.30714
C	0.01782	0.59636	0.26649
H	1.26829	2.17744	-0.55999
H	1.24426	2.13064	1.20902
C	-1.29584	1.38795	0.27260
H	0.07126	-0.03008	-0.63236
H	0.05068	-0.07983	1.12949
C	-2.53484	0.47362	0.23217
H	-1.34427	2.02025	1.16826
H	-1.32011	2.06807	-0.58913
H	-2.46593	-0.16782	-0.65962
H	-2.53186	-0.19651	1.10051
C	-3.82544	1.23678	0.18165
C	-4.85437	1.07201	1.04008
H	-3.93652	1.93978	-0.64446
H	-5.74351	1.69210	0.98217
H	-4.75588	0.44312	1.92115
C	-6.13890	-0.79522	0.05884
F	-7.21620	-0.33746	-0.58584
F	-6.51586	-1.64280	1.02215
F	-5.33111	-1.42093	-0.80101

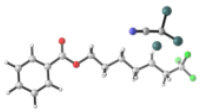


Int3

C	0.14643	2.22592	1.14119
C	1.50800	1.93346	1.16101
C	2.30195	2.19791	0.03583
C	1.71975	2.75829	-1.11081
C	0.35655	3.04945	-1.12677
C	-0.43078	2.78435	-0.00299
H	-0.46451	2.01970	2.01450
H	1.97338	1.49988	2.03940
H	2.33406	2.96211	-1.97989
H	-0.09191	3.48296	-2.01527
H	-1.49233	3.01244	-0.01875
C	3.75348	1.86595	0.10952
O	4.29600	1.37564	1.08677
O	4.41311	2.16567	-1.02539
C	5.83228	1.87392	-1.04321
C	6.36829	2.27607	-2.40709
H	5.97467	0.80638	-0.84769
H	6.31631	2.43083	-0.23461
C	7.87213	2.00460	-2.53390
H	5.82299	1.72440	-3.18275
H	6.16519	3.34153	-2.57093
C	8.43320	2.40495	-3.90788
H	8.41485	2.54879	-1.75049
H	8.06871	0.93779	-2.36296
H	7.85137	1.88479	-4.69060
H	8.25572	3.47539	-4.08627
C	9.88674	2.10148	-4.06667
C	10.74588	2.81624	-5.06092
H	10.28788	1.20654	-3.59760
H	11.80750	2.72504	-4.80960
H	10.50295	3.88477	-5.10244
C	10.59748	2.29538	-6.48209
F	10.91897	0.98457	-6.57966
F	11.39734	2.96542	-7.34553
F	9.32795	2.42477	-6.93980

Int4

C	-0.81019	1.09728	0.00580
N	0.34969	1.09807	0.00495
C	-2.27266	1.09708	0.00531
Cl	-2.85192	-0.60364	-0.05964
Cl	-2.85228	1.89122	1.51068
Cl	-2.85143	2.00354	-1.43526



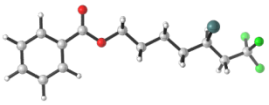
5-ts

C	-7.09199	0.33838	-0.08247
C	-5.87091	1.00740	-0.04883
C	-4.67031	0.28294	-0.05030
C	-4.70312	-1.11901	-0.08561
C	-5.92734	-1.78494	-0.11914

C	-7.12139	-1.05879	-0.11765
H	-8.01912	0.90307	-0.08121
H	-5.82817	2.09068	-0.02114
H	-3.77477	-1.67797	-0.08668
H	-5.95041	-2.86993	-0.14642
H	-8.07323	-1.58077	-0.14385
C	-3.39142	1.04778	-0.01392
O	-3.32066	2.26574	0.01662
O	-2.30770	0.24788	-0.01879
C	-1.01950	0.90836	0.01363
C	0.04989	-0.17134	-0.01609
H	-0.95794	1.51805	0.92064
H	-0.94491	1.57928	-0.84796
C	1.46179	0.42722	0.01044
H	-0.09030	-0.83739	0.84393
H	-0.08299	-0.78103	-0.91810
C	2.54862	-0.65426	-0.01516
H	1.59670	1.09263	-0.85207
H	1.58461	1.04498	0.90665
H	2.45050	-1.32688	0.84708
H	2.39201	-1.29637	-0.90102
C	3.95207	-0.14493	-0.10853
C	5.06416	-1.15237	-0.13518
H	4.10836	0.76681	-0.68130
H	4.82931	-1.91536	-0.89156
H	5.15127	-1.68404	0.81790
C	6.42353	-0.59588	-0.50212
F	6.38257	0.08158	-1.67437
F	7.32289	-1.59470	-0.64666
F	6.91622	0.25219	0.42514
C	4.50988	1.88820	3.80320
C	3.19401	1.92474	4.39752
N	2.12161	1.93758	4.84597
Cl	5.13509	3.52350	3.51753
Cl	4.25558	0.98812	1.99526
Cl	5.62324	0.89247	4.76001

Int6

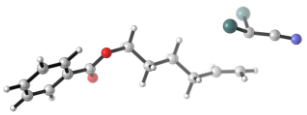
C	-3.64616	2.84247	-0.25751
C	-2.35786	3.26561	-0.56035
N	-1.27062	3.62380	-0.81635
Cl	-4.18799	2.81267	1.36750
Cl	-4.71032	2.34420	-1.50413



Product

C	8.68152	0.49170	0.09723
C	7.43767	0.66702	0.69877
C	6.29677	0.06839	0.14532
C	6.41235	-0.70825	-1.01711
C	7.65911	-0.88131	-1.61623
C	8.79347	-0.28284	-1.06112
H	9.56228	0.95684	0.52892
H	7.33111	1.26424	1.59772

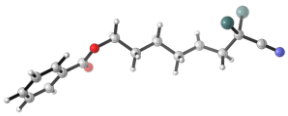
H	5.53001	-1.17032	-1.44399
H	7.74632	-1.48270	-2.51578
H	9.76311	-0.41976	-1.53039
C	4.99024	0.28761	0.82856
O	4.84822	0.95677	1.83928
O	3.96940	-0.33587	0.20955
C	2.65981	-0.17691	0.80711
C	1.66958	-0.95469	-0.04421
H	2.41573	0.88942	0.84421
H	2.69371	-0.54988	1.83569
C	0.24150	-0.85039	0.50704
H	1.70265	-0.57100	-1.07115
H	1.98153	-2.00536	-0.08509
C	-0.76279	-1.63027	-0.34784
H	0.21482	-1.23388	1.53567
H	-0.05692	0.20268	0.55683
H	-0.76428	-1.25141	-1.37698
H	-0.44743	-2.68093	-0.39982
C	-2.19366	-1.63537	0.18927
C	-3.10789	-2.54898	-0.62673
H	-2.20755	-1.93428	1.23889
H	-2.59996	-3.51261	-0.73595
H	-3.27469	-2.14948	-1.63022
C	-4.45499	-2.85980	-0.00733
F	-4.33304	-3.26386	1.28018
F	-5.06057	-3.86308	-0.68502
F	-5.30752	-1.81348	-0.01422
Cl	-2.86558	0.08676	0.20782



2b-ts

C	5.07266	-1.17410	0.98958
C	3.76322	-0.76442	1.22878
C	2.73522	-1.14348	0.35348
C	3.03032	-1.93803	-0.76437
C	4.34220	-2.34619	-1.00016
C	5.36347	-1.96561	-0.12539
H	5.86547	-0.87835	1.66959
H	3.51855	-0.15027	2.08847
H	2.23507	-2.23105	-1.43956
H	4.56830	-2.96098	-1.86583
H	6.38426	-2.28544	-0.31213
C	1.35181	-0.67769	0.65560
O	1.05910	0.01442	1.61725
O	0.45425	-1.10263	-0.25701
C	-0.92778	-0.71240	-0.05843
C	-1.65499	-1.69300	0.85497
H	-1.35790	-0.71193	-1.06255
H	-0.95441	0.30185	0.34640
C	-3.14256	-1.34593	0.99356
H	-1.54277	-2.70587	0.44954
H	-1.17678	-1.68302	1.84103
C	-3.88776	-2.32972	1.91753
H	-3.24956	-0.32844	1.39141
H	-3.61750	-1.34714	0.00510
H	-3.79799	-3.35359	1.53658
H	-3.38902	-2.31825	2.90012

C	-5.32750	-1.98056	2.12294
C	-6.38031	-2.84981	1.97481
H	-5.54451	-0.94429	2.37989
H	-7.36058	-2.56934	2.34687
H	-6.19110	-3.91540	1.87716
C	-7.12324	-2.73246	-0.13101
C	-8.25399	-3.58971	-0.04265
N	-9.16079	-4.30616	0.11921
Cl	-7.52562	-1.04216	-0.42095
Cl	-5.83165	-3.35974	-1.15217



Int2b

C	-7.34997	-0.41334	0.87151
C	-6.11010	-0.93371	0.50866
C	-5.11228	-0.08891	0.00152
C	-5.36689	1.28355	-0.13807
C	-6.60899	1.80062	0.22680
C	-7.60064	0.95473	0.73094
H	-8.11975	-1.07091	1.26326
H	-5.89707	-1.99215	0.61075
H	-4.59481	1.93571	-0.52888
H	-6.80381	2.86302	0.11811
H	-8.56708	1.36098	1.01397
C	-3.80368	-0.69761	-0.37176
O	-3.54641	-1.88527	-0.25798
O	-2.93241	0.21059	-0.85610
C	-1.62085	-0.27041	-1.24454
C	-0.66087	-0.28115	-0.06026
H	-1.29127	0.42928	-2.01606
H	-1.72469	-1.26646	-1.68080
C	0.75417	-0.70092	-0.47607
H	-0.63858	0.71985	0.38774
H	-1.04438	-0.96878	0.70226
C	1.73799	-0.71519	0.70397
H	0.72339	-1.70035	-0.92980
H	1.13119	-0.02011	-1.24995
H	1.78169	0.28163	1.16644
H	1.33448	-1.37743	1.49250
C	3.11285	-1.15730	0.32504
C	4.29804	-0.89305	1.19167
H	3.24369	-1.81130	-0.53267
H	4.76952	-1.82738	1.52904
H	4.01302	-0.33206	2.08790
C	5.43352	-0.08216	0.51402
C	6.54675	0.15128	1.43812
N	7.40613	0.31875	2.19978
Cl	6.10087	-0.98014	-0.92120
Cl	4.82469	1.54331	-0.03005

Table S6. The coordination of the key species involved.

General procedure for UV-Vis experiments: UV-Vis absorption spectra were recorded in CH_3CN (1.0 mL) in 1 cm path quartz cuvettes using an Agilent 8453 spectrophotometer. $Fe(OTf)_3$ (0.01 mmol), **Ligand** (0.01 mmol), CF_3COONa (0.02 mmol) in 1.0 mL CH_3CN. The solution was stirred under darkness or 450 nm blue LEDs illumination and diluted before measurement.

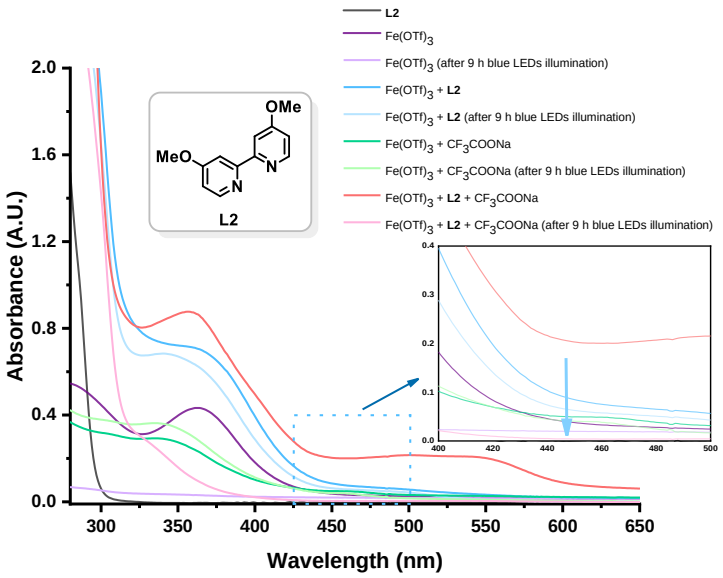


Figure S26. UV-Vis spectra of light-harvesting species.

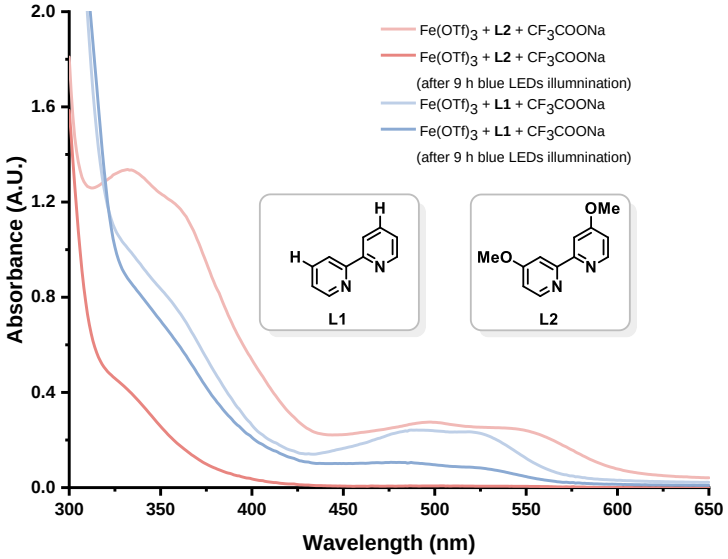


Figure S27. UV-Vis spectra for Fe(III)/ligand (L1/L2)-based species.

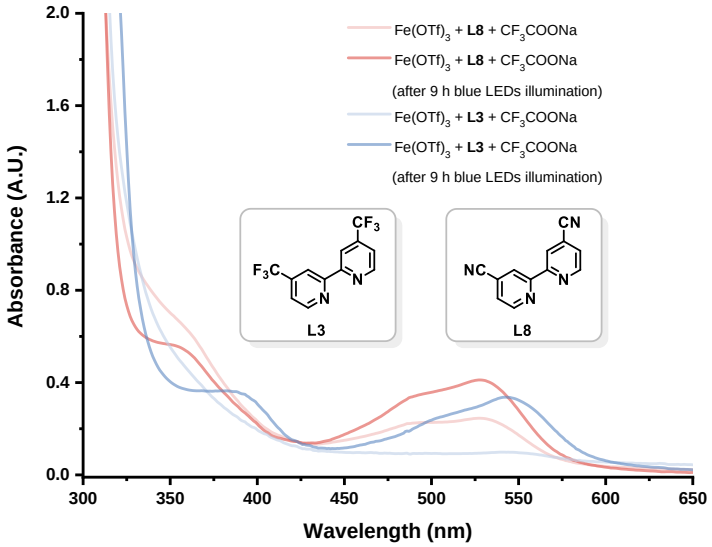


Figure S28. UV-Vis spectra for Fe(III)/ligand (L3/L8)-based species.

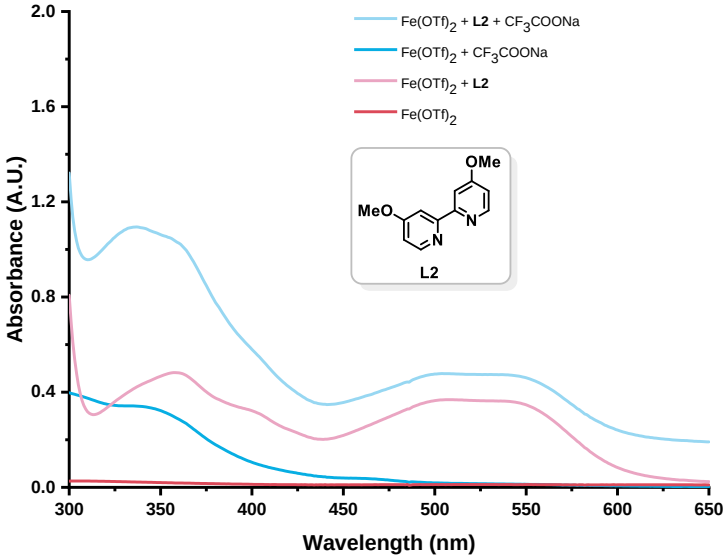


Figure S29. UV-Vis spectra of ligand-Fe(II) species. The solution was stirred under darkness and diluted before measurement.

General procedure for radical trapping experiment: Following general procedure of ***Standard condition A***, a 25-mL Schlenk flask equipped with magneton was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol), CF_3COONa (0.6 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.6 mmol) or butylated hydroxytoluene (BHT) (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), CCl_3CN (1.0 mL) and alkene **1** (0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 24 h. After completion of the reaction, the system was diluted with EtOAc. Yields and conversion rates were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard.

Then crude reaction mixture was used for **ESI-HRMS** detection. **BHT-CF$_3$**: **ESI-HRMS** exact mass calculated for [$C_{16}H_{23}F_3ONa^+$]: 311.1593, found 311.1608 (Figures **S30** and **S31**).

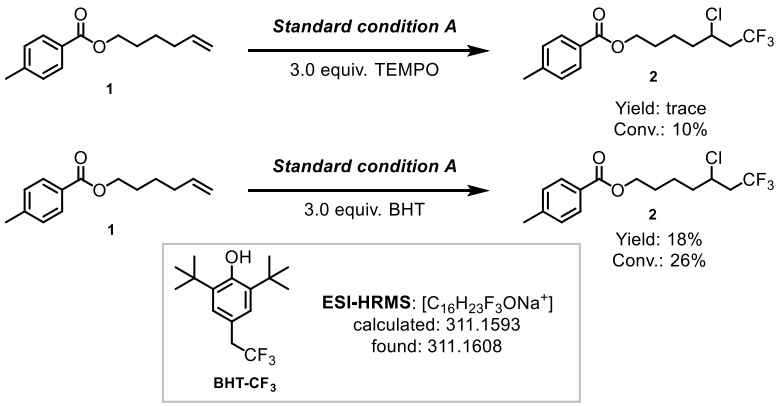


Figure S30. Radical trapping experiment.

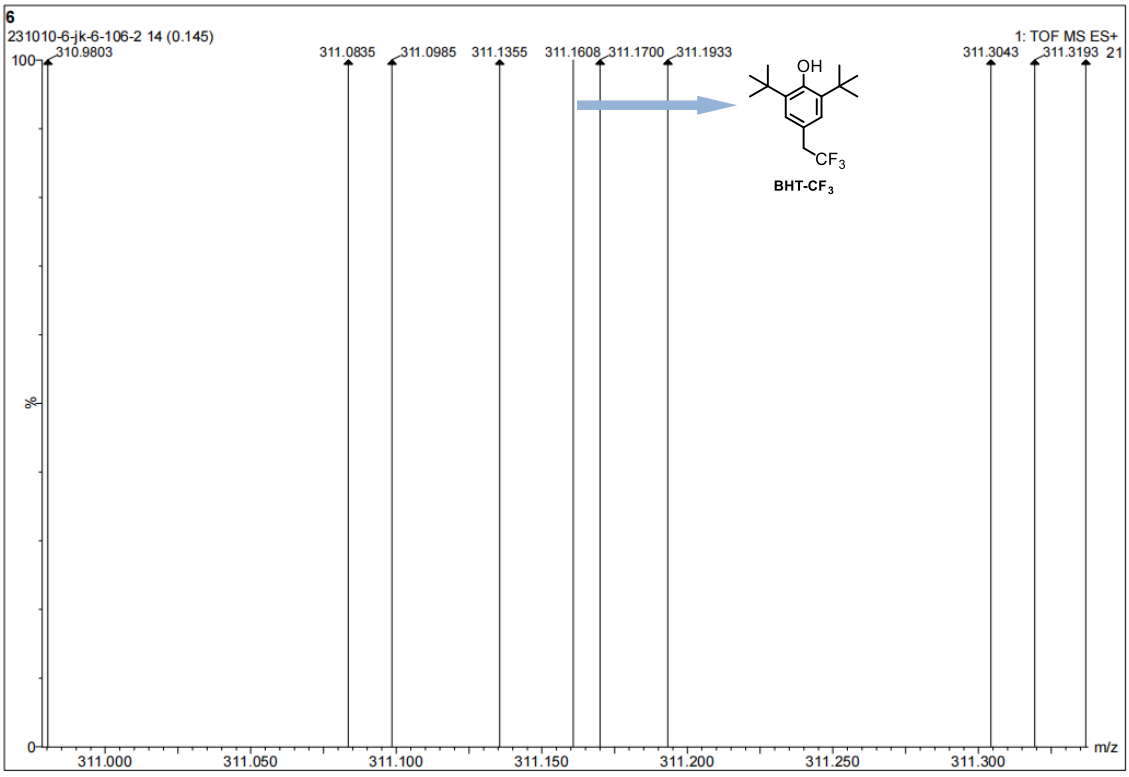


Figure S31. ESI-HRMS detection of **BHT-CF$_3$**.

General procedure for radical clock experiment: Following general procedure of ***Standard condition A***, a 25-mL Schlenk flask equipped with magneton was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol), CF_3COONa (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), CCl_3CN (1.0 mL) and N,N-diallyl-4-methylbenzenesulfonamide **41** (0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 24 h. After completion of the reaction, the system was diluted with EtOAc. After concentrated under vacuum, the resulting residue was purified by silica gel flash column chromatography to give the product **42** in a yield of 63% (**Figure S32**).

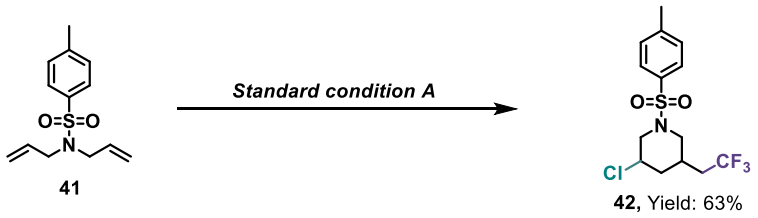


Figure S32. Radical clock experiment.

General procedure for light on/off experiment: Following general procedure of ***Standard condition A***, a 25-mL Schlenk flask equipped with magneton was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol) and CF_3COONa (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), CCl_3CN (1.0 mL) and alkene **1** (0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere. Keep blue LEDs light on in light-on time span and turn off in light-off time span. After completion of the reaction, the system was diluted with EtOAc. Yields were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard. Observed product **2** formation occurred only during periods of light irradiation, which ruled out a radical chain mechanism.

General procedure for kinetic studies of $Fe(OTf)_3$/L2: Following general procedure of ***Standard condition A***, a 25-mL Schlenk flask equipped with magneton was charged with $Fe(OTf)_3$ (n mol%), **L2** (1.5n mol%), and CF_3COONa (82.2 mg, 0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN (1.0 mL), CCl_3CN (1.0 mL) and alkene **1** (0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs for 8 h. After completion of the reaction, the system was diluted with EtOAc. Yields were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard (Table **S7**).

n	**[Fe^{III}]** (mol*L^{-1})	Yield (%)	Initial rate (mol*L^{-1}*h^{-1})
0	0	0	0
1	0.001	7	0.000875
3	0.003	15	0.001875
5	0.005	18	0.00225
6	0.006	20	0.0025
7	0.007	24	0.003
9	0.009	27	0.003375

10	0.01	30	0.00375
12	0.012	34	0.00425

Table S7. The kinetic studies of $Fe(OTf)_3$/**L2**.

Kinetic experiments of alkene 43 in different mixture solvents: Following general procedure of ***Standard condition A***, a 25mL Schlenk flask equipped with magneton was charged with $Fe(OTf)_3$ (0.02 mmol), **L2** (0.03 mmol) and CF_3COONa (0.6 mmol). The flask was evacuated and refilled with N_2 for three times. The vessel was then charged with extra dry CH_3CN or DCM (1.0 mL), CCl_3CN (1.0 mL) and alkene **43** (0.2 mmol). The reaction mixture was stirred under nitrogen atmosphere and irradiated by blue LEDs. After the reaction reached the specified time (10 h, 12 h, 14 h), the system was diluted with EtOAc. Yields were determined by GC analysis of the crude reaction mixture, using biphenyl as an internal standard (Figure **S33**).

(i) CH_3CN and CCl_3CN as solvents;

(ii) DCM and CCl_3CN as solvents.

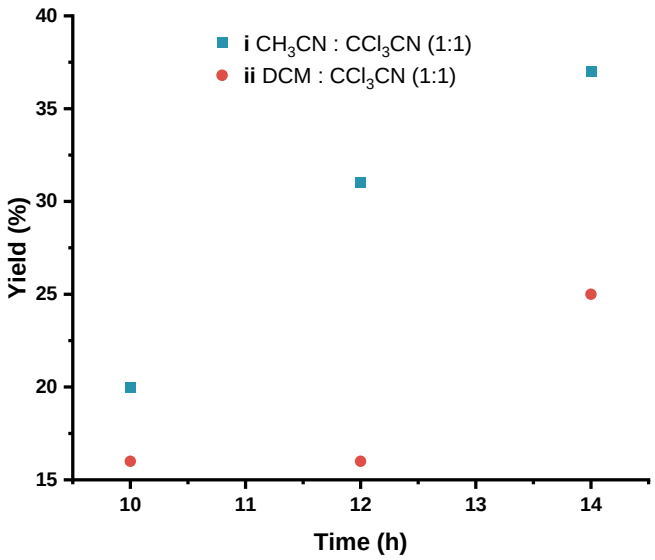


Figure S33. Kinetic experiments in different mixture solvents.

ESI-HRMS detection of IntB: $Fe(OTf)_3$ (0.1 mmol), **L2** (0.1 mmol) and CF_3COONa (0.2 mmol) were diluted in extra dry CH_3CN (2.0 mL). The mixture was stirred in darkness for 8 h. After concentrated under vacuum, crude reaction mixture was used for **ESI-HRMS** detection. The corresponding mass of **IntB** was detected. Exact mass calculated for $[C_{20}H_{18}F_6FeN_4O_6^+]$: 580.0480, found: 580.0475 (Figure **S34**).

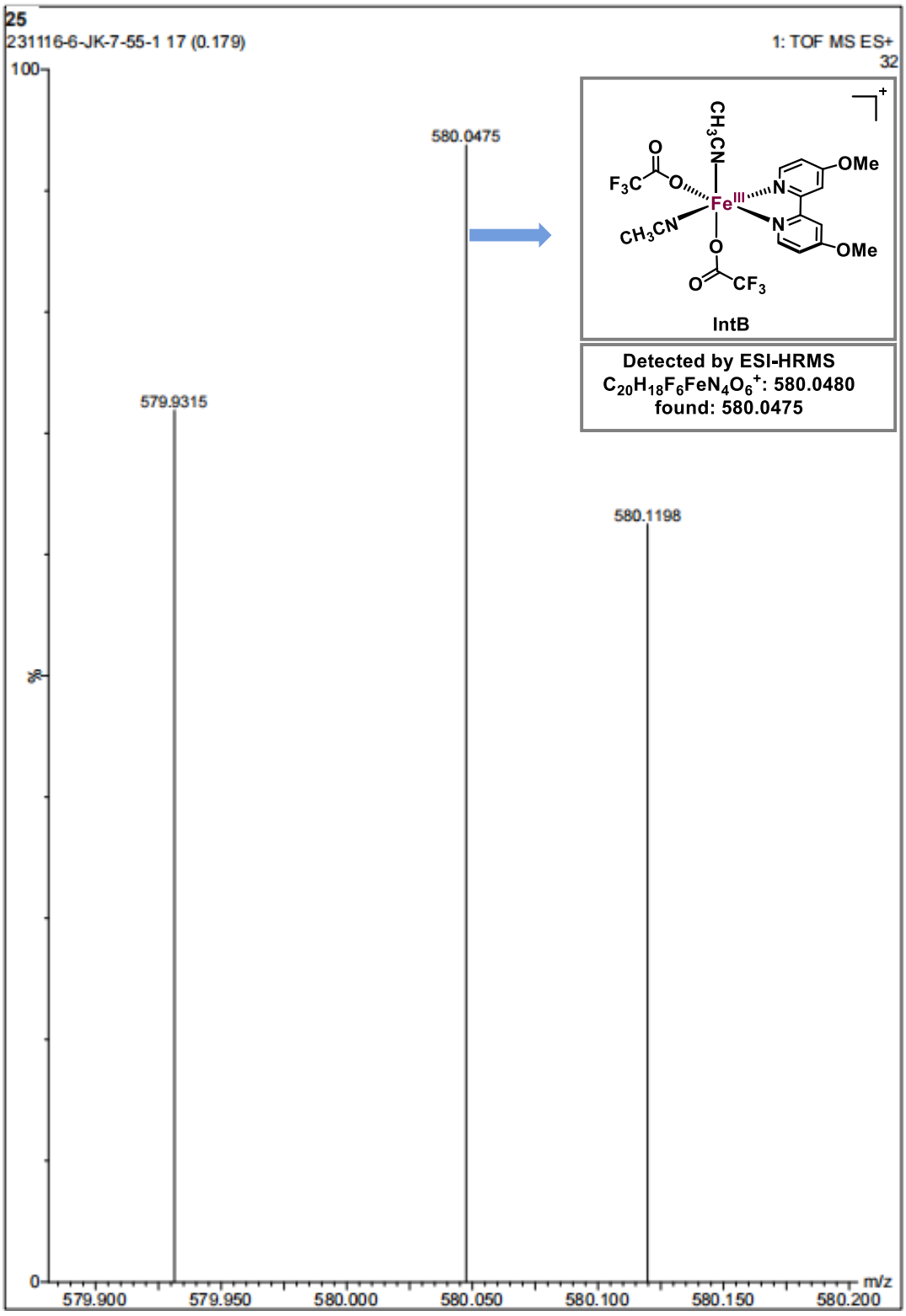
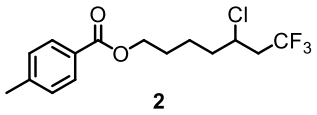


Figure S34. ESI-HRMS detection of **IntB**.

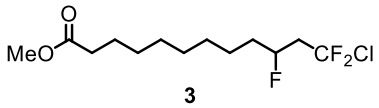
Regarding the roles of the dual ligands, now, we may say that OMe/CF_3-substituted bipyridine is responsible for the visible light absorption of **IntB** rather than UV light (based on the UV-Vis experiments, Figure **4d** and Figures **S26-S29**), and CH_3CN/CCl_3CCN as the second ligand is beneficial to stabilize the whole structure of **IntB**/**IntD** (by comparing the calculation data of **IntB**/**IntD** and **IntF**, Figures **5a** and **5b**, Figures **S21** and **S23**, Tables **S1-S2**).

5. Data for products



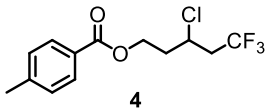
2

***5-Chloro-7,7,7-trifluoroheptyl 4-methylbenzoate* (2)**: 46.4 mg colorless liquid was isolated, yield: 84%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.89 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 4.32 (t, *J* = 6.3 Hz, 2H), 4.19 – 4.08 (m, 1H), 2.71 – 2.45 (m, 2H), 2.41 (s, 3H), 1.97 – 1.87 (m, 1H), 1.86 – 1.72 (m, 4H), 1.64 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.80, 143.75, 129.69, 129.22, 127.66, 125.35 (q, *J* = 277.6 Hz), 64.41, 54.04 (q, *J* = 3.3 Hz), 42.58 (q, *J* = 28.4 Hz), 37.73, 28.18, 22.78, 21.78. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.79 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{15}H_{19}ClF_3O_2^+$]: 323.1020, found 323.1033.



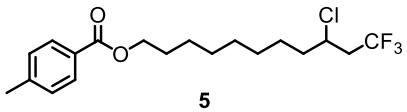
3

***Methyl 12-chloro-10,12,12-trifluorododecanoate* (3)**: 45.3 mg white solid was isolated, yield: 75%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.95 – 4.72 (m, 1H), 3.66 (s, 3H), 2.82 – 2.38 (m, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.66 (m, 1H), 1.65 – 1.57 (m, 3H), 1.47 – 1.23 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.42, 127.96 (td, *J* = 2.6, 292.5, Hz), 88.55 (dt, *J* = 172.6, 3.0 Hz), 51.60, 47.14 (q, *J* = 24.2 Hz), 35.16 (d, *J* = 20.7 Hz), 34.21, 29.33, 29.24, 29.23, 29.20, 25.04, 24.68 (d, *J* = 4.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -48.57 – -50.37 (m, 2F), -181.11 – -181.18 (m, 1F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{22}ClF_3O_2Na^+$]: 325.1153, found 325.1156.



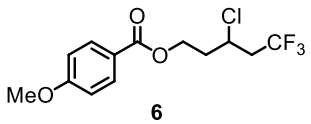
4

***3-Chloro-5,5,5-trifluoropentyl 4-methylbenzoate* (4)**: 49.4 mg colorless liquid was isolated, yield: 84%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 – 7.91 (m, 2H), 6.96 – 6.88 (m, 2H), 4.58 – 4.39 (m, 2H), 4.39 – 4.28 (m, 1H), 3.85 (s, 3H), 2.81 – 2.52 (m, 2H), 2.42 – 2.29 (m, 1H), 2.29 – 2.06 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.44, 144.04, 129.69, 129.29, 127.18, 125.21 (q, *J* = 277.6 Hz), 61.05, 50.83 (q, *J* = 3.2 Hz), 42.57 (q, *J* = 28.7 Hz), 37.10, 21.74. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.98 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{14}ClF_3O_2Na^+$]: 317.0527, found 317.0536.



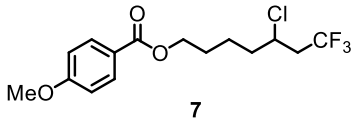
5

***9-Chloro-11,11,11-trifluoroundecyl 4-methylbenzoate* (5)**: 62.1 mg colorless liquid was isolated, yield: 82%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.30 (t, *J* = 6.6 Hz, 2H), 4.15 – 4.04 (m, 1H), 2.69 – 2.51 (m, 2H), 2.40 (s, 3H), 1.88 – 1.63 (m, 4H), 1.53 – 1.22 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.84, 143.54, 129.66, 129.13, 127.89, 125.42 (q, *J* = 277.6 Hz), 64.96, 54.27 (d, *J* = 3.1 Hz), 42.53 (q, *J* = 28.4 Hz), 38.15, 29.37, 29.23, 28.87, 28.82, 26.09, 25.97, 21.72. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.82 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{19}H_{26}ClF_3O_2Na^+$]: 401.1466, found 401.1465.



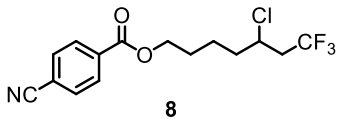
6

***3-Chloro-5,5,5-trifluoropentyl 4-methoxybenzoate* (6)**: 49.0 mg colorless liquid was isolated, yield: 79%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.95 (m, 2H), 6.95 – 6.90 (m, 2H), 4.57 – 4.42 (m, 2H), 4.38 – 4.29 (m, 1H), 3.85 (s, 3H), 2.79 – 2.56 (m, 2H), 2.41 – 2.31 (m, 1H), 2.18 – 2.08 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.06, 163.64, 131.67, 125.21 (q, *J* = 277.6 Hz), 122.27, 113.80, 60.90, 55.48, 50.84 (q, *J* = 3.3 Hz), 42.52 (q, *J* = 28.6 Hz), 37.12. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.65 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{14}ClF_3O_3Na^+$]: 333.0476, found 333.0475.



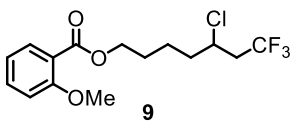
7

***5-Chloro-7,7,7-trifluoroheptyl 4-methoxybenzoate* (7)**: 46.6 mg colorless liquid was isolated, yield: 69%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 – 7.94 (m, 2H), 6.95 – 6.87 (m, 2H), 4.30 (t, *J* = 6.2 Hz, 2H), 4.18 – 4.01 (m, 1H), 3.84 (s, 3H), 2.72 – 2.44 (m, 2H), 1.96 – 1.85 (m, 1H), 1.84 – 1.67 (m, 4H), 1.65 – 1.53 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.37, 163.44, 131.60, 125.33 (q, *J* = 277.6 Hz), 122.75, 113.68, 64.22, 55.44, 54.00 (q, *J* = 3.1 Hz), 42.45 (q, *J* = 28.4 Hz), 37.66, 28.13, 22.70. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.66 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{15}H_{18}ClF_3O_3Na^+$]: 361.0789, found 361.0788.



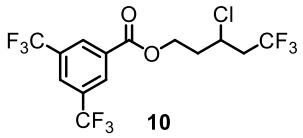
8

***5-Chloro-7,7,7-trifluoroheptyl 4-cyanobenzoate* (8)**: 52.6 mg colorless liquid was isolated, yield: 79%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 – 8.07 (d, 2H), 7.75 – 7.67 (d, 2H), 4.34 (t, *J* = 6.3 Hz, 2H), 4.16 – 4.07 (m, 1H), 2.69 – 2.44 (m, 2H), 1.94 – 1.85 (m, 1H), 1.84 – 1.66 (m, 4H), 1.64 – 1.51 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 164.82, 134.02, 132.17, 129.98, 125.22 (q, *J* = 277.6 Hz), 117.90, 116.29, 65.23, 53.88 (q, *J* = 3.0 Hz), 42.27 (q, *J* = 28.4 Hz), 37.42, 27.83, 22.48. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.75 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{15}H_{16}ClF_3NO_2^+$]: 334.0816, found 334.0828.



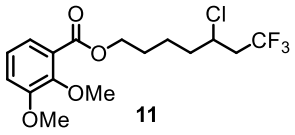
9

***5-Chloro-7,7,7-trifluoroheptyl 2-methoxybenzoate* (9)**: 41.2 mg colorless liquid was isolated, yield: 61%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.77 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.50 – 7.41 (m, 1H), 7.01 – 6.92 (m, 2H), 4.31 (t, *J* = 6.2 Hz, 2H), 4.16 – 4.07 (m, 1H), 3.88 (s, 3H), 2.71 – 2.44 (m, 2H), 1.95 – 1.85 (m, 1H), 1.84 – 1.70 (m, 4H), 1.65 – 1.56 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.34, 159.18, 133.53, 131.55, 125.32 (q, *J* = 277.6 Hz), 120.30, 120.17, 112.09, 64.34, 55.97, 54.03 (q, *J* = 3.1 Hz), 42.45 (q, *J* = 28.4 Hz), 37.66, 28.07, 22.69. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.79 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{15}H_{18}ClF_3O_3Na^+$]: 361.1789, found 361.0799.



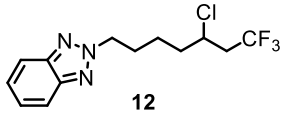
10

***3-Chloro-5,5,5-trifluoropentyl 3,5-bis(trifluoromethyl)benzoate* (10)**: 60.0 mg colorless liquid was isolated, yield: 72%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.46 (s, 2H), 8.07 (s, 1H), 4.70 – 4.55 (m, 2H), 4.36 – 4.27 (m, 1H), 2.83 – 2.56 (m, 2H), 2.51 – 2.36 (m, 1H), 2.27 – 2.14 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.83, 132.49 (q, *J* = 34.1 Hz), 132.17, 129.85 (d, *J* = 2.9 Hz), 126.86 – 126.60 (m), 125.16 (q, *J* = 277.5 Hz), 122.99 (q, *J* = 272.8 Hz), 62.65, 50.63 (q, *J* = 3.2 Hz), 42.63 (q, *J* = 28.8 Hz), 36.83. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.32 (s, 6F), -63.97 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{14}H_{10}ClF_9O_2Na^+$]: 439.0118, found 439.0119.



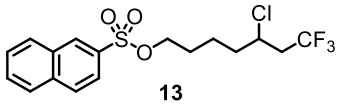
11

***5-Chloro-7,7,7-trifluoroheptyl 3,5-dimethoxybenzoate* (11)**: 61.8 mg colorless liquid was isolated, yield: 84%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.52 (d, *J* = 1.9 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 4.30 (t, *J* = 6.2 Hz, 2H), 4.17 – 4.06 (m, 1H), 3.91 (s, 3H), 3.91 (s, 3H), 2.71 – 2.44 (m, 2H), 1.97 – 1.85 (m, 1H), 1.84 – 1.66 (m, 4H), 1.64 – 1.52 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.41, 153.07, 148.70, 125.29 (q, *J* = 277.6 Hz), 123.57, 122.84, 112.01, 110.32, 64.35, 56.05 (d, *J* = 2.9 Hz), 54.00 (q, *J* = 3.3 Hz), 54.00 (q, *J* = 3.3 Hz), 42.47 (q, *J* = 28.4 Hz), 37.62, 28.14, 22.66. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.79 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{16}H_{20}ClF_3O_4Na^+$]: 391.0894, found 391.0891.



12

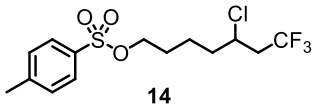
***2-(5-Chloro-7,7,7-trifluoroheptyl)-2H-benzo[d][1,2,3]triazole* (12)**: 45.1 mg colorless liquid was isolated, yield: 74%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.36 (dd, *J* = 6.6, 3.1 Hz, 2H), 4.73 (t, *J* = 7.0 Hz, 2H), 4.11 – 4.00 (m, 1H), 2.67 – 2.38 (m, 2H), 2.25 – 2.04 (m, 2H), 1.89 – 1.70 (m, 2H), 1.69 – 1.57 (m, 1H), 1.55 – 1.42 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.39, 126.37, 125.24 (q, *J* = 277.6 Hz), 118.02, 56.14, 53.72 (q, *J* = 3.1 Hz), 42.40 (q, *J* = 28.5 Hz), 37.35, 29.24, 23.12. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.79 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{16}ClF_3N_3^+$]: 306.0979, found 306.0985.



13

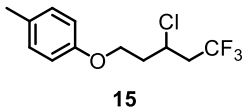
***5-Chloro-7,7,7-trifluoroheptyl naphthalene-2-sulfonate* (13)**: 53.6 mg colorless liquid was isolated, yield: 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.49 (s, 1H), 7.99 (t, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.73 – 7.60 (m, 2H), 4.09 (t, *J* = 6.2 Hz, 2H), 4.01 (m, 1H), 2.66 – 2.33 (m, 2H), 1.87 – 1.51 (m, 5H), 1.53 – 1.37 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.33, 132.82, 131.99, 129.81, 129.73, 129.49, 129.36, 128.07, 127.95, 125.23 (d, *J* = 277.6 Hz), 122.51, 70.39, 53.75 (q, *J* = 3.1 Hz), 42.28 (q, *J* = 28.4 Hz), 37.25, 28.18, 22.08. **^{19}F**

NMR (376 MHz, Chloroform-*d*) δ -63.73 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{17}H_{18}ClF_3O_3SNa^+$]: 417.0509, found 417.0512.



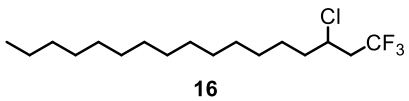
14

***5-Chloro-7,7,7-trifluoroheptyl 4-methylbenzenesulfonate* (14)**: 48.0 mg colorless liquid was isolated, yield: 67%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.09 – 3.98 (m, 3H), 2.63 – 2.44 (m, 2H), 2.42 (s, 3H), 1.80 – 1.70 (m, 1H), 1.70 – 1.50 (m, 4H), 1.49 – 1.38 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.97, 132.99, 129.95, 127.87, 125.25 (q, *J* = 277.6 Hz), 70.09, 53.78 (q, *J* = 3.1 Hz), 42.27 (q, *J* = 28.4 Hz), 37.25, 28.11, 22.05, 21.60. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.79 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{14}H_{18}ClF_3O_3SNa^+$]: 381.0509, found 381.0508.



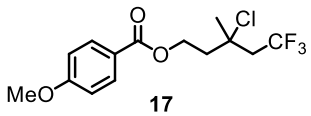
15

***1-((3-Chloro-5,5,5-trifluoropentyl)oxy)-4-methylbenzene* (15)**: 41.5 mg colorless liquid was isolated, yield: 78%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.10 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.50 – 4.41 (m, 1H), 4.21 – 4.10 (m, 2H), 2.75 – 2.62 (m, 2H), 2.40 – 2.33 (m, 1H), 2.30 (s, 3H), 2.18 – 2.08 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.50, 130.54, 130.11, 125.35 (q, *J* = 277.6 Hz), 114.56, 64.11, 51.14 (q, *J* = 3.3 Hz), 42.69 (q, *J* = 28.6 Hz), 37.85, 20.60. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.61 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{12}H_{15}ClF_3O^+$]: 267.1758, found 267.0756.



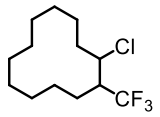
16

***3-Chloro-1,1,1-trifluoroheptadecane* (16)**: 44.0 mg colorless liquid was isolated, yield: 67%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.15 – 4.07 (m, 1H), 2.69 – 2.45 (m, 2H), 1.88 – 1.68 (m, 2H), 1.60 – 1.50 (m, 1H), 1.48 – 1.39 (m, 1H), 1.31 – 1.24 (m, 22H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 125.48 (q, *J* = 277.5 Hz), 54.34 (q, *J* = 3.1 Hz), 42.62 (q, *J* = 28.3 Hz), 38.26, 32.11, 29.87, 29.85, 29.83, 29.82, 29.78, 29.68, 29.57, 29.54, 29.04, 26.08, 22.87, 14.26. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.89 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{17}H_{32}ClF_3Na^+$]: 351.2037, found 351.2039.



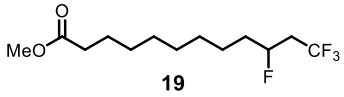
17

***3-Chloro-5,5,5-trifluoro-3-methylpentyl 4-methoxybenzoate* (17)**: 44.1 mg colorless liquid was isolated, yield: 66%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.94 (m, 2H), 6.95 – 6.87 (m, 2H), 4.62 – 4.49 (m, 2H), 3.85 (s, 3H), 2.87 – 2.69 (m, 2H), 2.44 – 2.26 (m, 2H), 1.78 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.15, 163.61, 131.68, 125.02 (q, *J* = 278.7 Hz), 122.39, 113.79, 65.55 (d, *J* = 2.1 Hz), 61.12, 55.50, 47.13 (q, *J* = 27.8 Hz), 42.30, 30.49. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -60.53 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{14}H_{16}ClF_3O_3Na^+$]: 347.0632, found 347.0631.



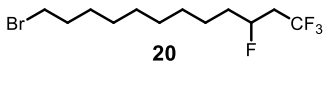
18, d.r. = 4:1

1-Chloro-2-(trifluoromethyl)cyclododecane **(18):** 34.0 mg colorless liquid was isolated, yield: 63%, d.r. = 4:1**.** Characterization data for a mixture of rotamers: **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.28 – 4.12 (m, 1H), 2.64 – 2.51 (m, 1H), 2.20 – 1.95 (m, 1H), 1.84 – 1.59 (m, 4H), 1.55 – 1.22 (m, 15H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 127.71 (q, *J* = 281.6 Hz), 55.23, 44.10 (q, *J* = 24.6 Hz), 34.96, 24.80, 23.52, 22.91, 22.87, 22.82, 22.65, 22.48, 21.72, 21.23. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -64.30 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{22}ClF_3Na^+$]: 293.1254, found 293.1270.



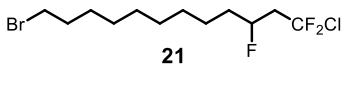
19

Methyl 10,12,12,12-tetrafluorododecanoate **(19)**: 30.9 mg white solid was isolated, yield: 54%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.89 – 4.65 (m, 1H), 3.66 (s, 3H), 2.58 – 2.39 (m, 1H), 2.38 – 2.20 (m, 3H), 1.80 – 1.67 (m, 1H), 1.65 – 1.55 (m, 3H), 1.51 – 1.28 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.41, 125.64 (dq, *J* = 3.3, 276.8 Hz), 87.74 (dq, *J* = 172.0, 3.2 Hz), 51.58, 39.52 (qd, *J* = 28.4, 23.0 Hz), 35.12 (d, *J* = 20.7 Hz), 34.19, 29.32, 29.23, 29.22, 29.19, 25.03, 24.68 (d, *J* = 4.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -64.18 (d, *J* = 7.6 Hz, 3F), -181.82 (q, *J* = 7.6 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{22}F_4O_2Na^+$]: 309.1448, found 309.1456.



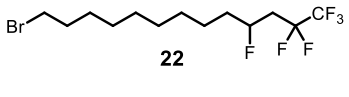
20

12-Bromo-1,1,1,3-tetrafluorododecane **(20)**: 30.1 mg colorless liquid was isolated, yield: 47%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.98 – 4.58 (m, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.83 – 2.56 (m, 2H), 1.87 – 1.73 (m, 2H), 1.70 – 1.50 (m, 2H), 1.46 – 1.23 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 125.64 (qd, *J* = 276.8, 3.2 Hz), 87.73 (dq, *J* = 172.0, 3.2 Hz), 39.52 (qd, *J* = 28.4, 23.0 Hz), 35.13 (d, *J* = 20.8 Hz), 34.11, 32.93, 29.43, 29.41, 29.27, 28.83, 28.26, 24.70 (d, *J* = 4.2 Hz). **^{19}F NMR** (376 MHz, DMSO-d_6) δ -62.45 (d, *J* = 7.8 Hz, 3F), -181.90 (q, *J* = 7.9 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{12}H_{22}BrF_4^+$]: 321.0836, found 321.0823.



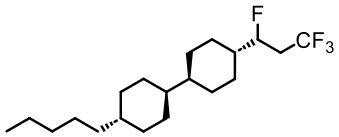
21

12-Bromo-1-chloro-1,1,3-trifluorododecane **(21)**: 34.9 mg colorless liquid was isolated, yield: 52%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.96 – 4.74 (m, 1H), 3.41 (t, *J* = 6.8 Hz, 2H), 2.83 – 2.39 (m, 2H), 1.91 – 1.80 (m, 2H), 1.76 – 1.52 (m, 2H), 1.51 – 1.27 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 127.96 (td, *J* = 292.4, 2.5 Hz), 88.55 (dt, *J* = 172.6, 2.9 Hz), 47.14 (q, *J* = 23.8 Hz), 35.17 (d, *J* = 20.8 Hz), 34.15, 32.93, 29.43, 29.41, 29.28, 28.84, 28.26, 24.69 (d, *J* = 4.3 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -48.48 – -50.41 (m, 2F), -181.10 – -181.18 (m, 1F). **ESI-HRMS** exact mass calculated for [$C_{12}H_{22}BrClF_3^+$]: 337.0540, found 337.0544.



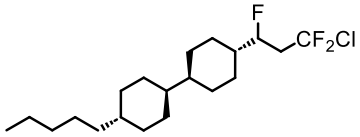
22

13-Bromo-1,1,1,2,2,4-hexafluorotridecane **(22)**: 42.2 mg colorless liquid was isolated, yield: 57%. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 4.99 – 4.78 (m, 1H), 3.52 (t, *J* = 6.7 Hz, 2H), 2.75 – 2.51 (m, 2H), 1.84 – 1.74 (m, 2H), 1.74 – 1.54 (m, 2H), 1.46 – 1.24 (m, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 124.28 – 111.29 (2C, m), 86.95 (dt, *J* = 172.8, 3.2 Hz), 36.80-36.14 (m), 35.75, 35.54, 34.10, 32.94, 29.43, 29.42 (d, *J* = 1.7 Hz), 29.27, 28.84, 28.27, 24.71 (d, *J* = 4.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -80.23 (d, *J* = 3.5 Hz, 3F), -109.70 – -112.17 (m, 2F), -175.64 – -175.75 (m, 1F). **ESI-HRMS** exact mass calculated for [$C_{13}H_{21}BrF_6K^+$]: 409.0362, found 409.0365.



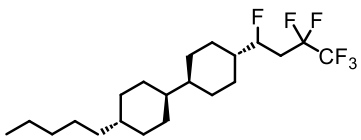
23

(1s,1'S,4S,4'R)-4-Pentyl-4'-((S)-1,3,3,3-tetrafluoropropyl)-1,1'-bi(cyclohexane) **(23)**: 49.7 mg white solid was isolated, yield: 71%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.67 – 4.45 (m, 1H), 2.54 – 2.20 (m, 2H), 1.92 – 1.65 (m, 8H), 1.54 – 1.42 (m, 1H), 1.33 – 1.18 (m, 7H), 1.17 – 1.08 (m, 4H), 1.04 – 0.93 (m, 6H), 0.89 – 0.79 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 126.11 (q, *J* = 276.9 Hz), 91.15 (dq, *J* = 174.2, 2.8 Hz), 43.25 (d, *J* = 27.4 Hz), 42.22 (d, *J* = 19.3 Hz), 38.04, 37.60, 37.23 (qd, *J* = 23.2, 28.3 Hz), 33.73, 32.40, 30.20, 29.36 (d, *J* = 16.7 Hz), 28.56 (d, *J* = 4.3 Hz), 27.24 (d, *J* = 5.7 Hz), 26.83, 22.87, 14.26. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -64.25 (d, *J* = 7.8 Hz, 3F), -187.38 (q, *J* = 7.9 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{20}H_{35}F_4^+$]: 351.2669, found 351.2679.



24

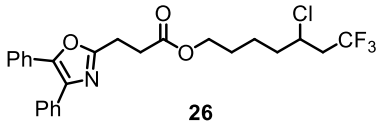
(1S,1's,4R,4'S)-4-((S)-3-Chloro-1,3,3-trifluoropropyl)-4'-pentyl-1,1'-bi(cyclohexane) **(24)**: 46.9 mg white solid was isolated, yield: 64%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.74 – 4.47 (m, 1H), 2.77 – 2.37 (m, 2H), 1.90 – 1.66 (m, 8H), 1.54 – 1.42 (m, 1H), 1.37 – 1.19 (m, 7H), 1.18 – 1.10 (m, 4H), 1.08 – 0.95 (m, 6H), 0.91 – 0.82 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 128.58 (t, *J* = 293.9 Hz), 91.91 (dt, *J* = 175.3, 2.7 Hz), 44.90 (q, *J* = 23.7 Hz), 43.27 (d, *J* = 26.7 Hz), 42.32 (d, *J* = 19.4 Hz), 38.06, 37.62, 33.74, 32.41, 30.20, 29.39 (d, *J* = 15.7 Hz), 28.60 (d, *J* = 4.1 Hz), 27.23 (d, *J* = 5.8 Hz), 26.85, 22.88, 14.27. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -48.27 – -50.66 (m, 2F), -186.67 (t, *J* = 9.3 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{20}H_{34}ClF_3Na^+$]: 389.2193, found 389.2210.



25

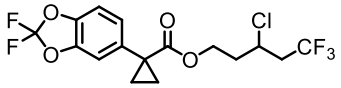
(1S,1's,4R,4'S)-4-((S)-1,3,3,4,4,4-Hexafluorobutyl)-4'-pentyl-1,1'-bi(cyclohexane) **(25)**: 64.8 mg white solid was isolated, yield: 81%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.81 – 4.50 (m, 1H), 2.50 – 2.12 (m, 2H), 1.94 – 1.66 (m, 8H), 1.55 – 1.42 (m, 1H), 1.35 – 1.21 (m, 7H), 1.20 – 1.09 (m, 4H), 1.08 – 0.94 (m, 6H), 0.94 – 0.82 (m, 5H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 125.29 – 111.34 (2C, m), 90.21 (dt, *J* = 175.2, 2.9 Hz), 43.30 (d, *J* = 26.9 Hz), 42.62 (d, *J* = 19.4 Hz), 38.09, 37.65, 34.14 (q, *J* = 22.2 Hz), 33.76, 32.45, 30.23, 29.40 (d, *J* = 16.8 Hz), 28.63 (d, *J* =

4.0 Hz), 27.16 (d, *J* = 5.8 Hz), 26.88, 22.90, 14.24. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -85.86 (d, *J* = 3.2 Hz, 3F), -117.15 – 117.36 (m, 2F), -185.50 – -185.65 (m, 1F). **ESI-HRMS** exact mass calculated for [$C_{21}H_{35}F_6^+$]: 401.2637, found 401.2633.



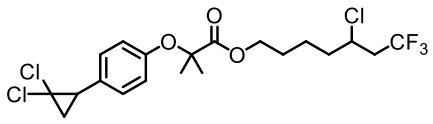
26

***5-Chloro-7,7,7-trifluoroheptyl 3-(4,5-diphenyloxazol-2-yl)propanoate* (26)**: 56.5 mg colorless liquid was isolated, yield: 59%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.60 – 7.55 (m, 2H), 7.40 – 7.28 (m, 6H), 4.15 (t, *J* = 6.3 Hz, 2H), 4.10 – 4.03 (m, 1H), 3.20 (t, *J* = 7.4 Hz, 2H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.69 – 2.40 (m, 2H), 1.88 – 1.75 (m, 1H), 1.75 – 1.59 (m, 4H), 1.55 – 1.42 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 172.07, 161.80, 145.48, 135.19, 132.53, 129.04, 128.72, 128.63, 128.55, 128.15, 127.95, 126.53, 125.29 (q, *J* = 277.5 Hz), 64.39, 53.93 (q, *J* = 3.1 Hz), 42.44 (q, *J* = 28.4 Hz), 37.57, 31.20, 27.97, 23.63, 22.55. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.69 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{25}H_{25}ClF_3NO_3Na^+$]: 502.1367, found 502.1378.



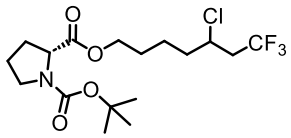
27

***3-Chloro-5,5,5-trifluoropentyl 2-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)cyclopropane-1-carboxylate* (27)**: 66.4 mg colorless liquid was isolated, yield: 83%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.08 – 7.03 (m, 2H), 6.99 – 6.96 (m, 1H), 4.29 – 4.17 (m, 2H), 4.02 – 3.94 (m, 1H), 2.61 – 2.33 (m, 2H), 2.15 – 2.05 (m, 1H), 1.97 – 1.87 (m, 1H), 1.64 – 1.61 (m, 2H), 1.22 – 1.19 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.80, 143.59, 143.02, 135.60, 131.80 (t, *J* = 255.1 Hz), 125.78, 125.09 (q, *J* = 277.6 Hz), 111.96, 109.05, 61.43, 50.60 (q, *J* = 3.3 Hz), 42.35 (q, *J* = 28.6 Hz), 36.72, 29.05, 17.28, 17.13. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -50.08 (s, 2F), -64.21 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{16}H_{14}ClF_5O_4Na^+$]: 432.0393, found 432.0399.



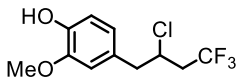
28

***5-Chloro-7,7,7-trifluoroheptyl 2-(3-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate* (28)**: 53.2 mg colorless liquid was isolated, yield: 56%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.14 – 7.06 (m, 2H), 6.83 – 6.75 (m, 2H), 4.16 (t, *J* = 6.3 Hz, 2H), 4.06 – 3.95 (m, 1H), 2.82 (dd, *J* = 10.3, 8.7 Hz, 1H), 2.65 – 2.36 (m, 2H), 1.93 (dd, *J* = 10.7, 7.4 Hz, 1H), 1.80 – 1.73 (m, 2H), 1.72 – 1.62 (m, 3H), 1.60 (s, 6H), 1.55 – 1.45 (m, 1H), 1.42 – 1.32 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.33, 155.11, 129.74, 128.14, 125.31 (q, *J* = 277.5 Hz), 118.40, 79.20, 65.05, 61.00, 53.89 (q, *J* = 2.9 Hz), 42.41 (q, *J* = 28.4 Hz), 37.54, 34.90, 27.81, 25.91, 25.61 – 25.40 (m), 22.47. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.74 (d, *J* = 2.3 Hz, 3F). **ESI-HRMS** exact mass calculated for [$C_{20}H_{24}Cl_3F_3O_3Na^+$]: 497.0635, found 497.0631.



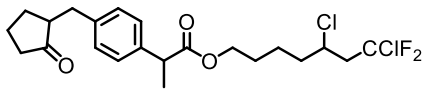
29, d.r. = 1.4:1

1-(Tert-butyl) 2-(5-chloro-7,7,7-trifluoroheptyl) (2R)-pyrrolidine-1,2-dicarboxylate **(29)**: 56.1 mg colorless liquid was isolated, yield: 70%, d.r. = 1.4:1. **^{1}H NMR** (400 MHz, Chloroform-*d*, a mixture of rotamers) δ 4.29-4.17 (m, 1H), 4.15 – 4.03 (m, 3H), 3.56 – 3.31 (m, 2H), 2.71 – 2.40 (m, 2H), 2.25 – 2.09 (m, 1H), 1.97 – 1.79 (m, 4H), 1.77 – 1.58 (m, 4H), 1.55 – 1.46 (m, 1H), [1.42(s, 3.78H), 1.38 (s, 5.22H), 9H]. **^{13}C NMR** (101 MHz, Chloroform-*d*, characterization data for the major isomer) δ 173.30, 153.85, 125.26 (q, *J* = 277.7 Hz), 79.89, 64.42 (d, *J* = 10.4 Hz), 59.23, 53.94, 46.3, 42.50 (q, *J* = 28.8 Hz), 37.56, 31.00, 28.43 (d, *J* = 8.1 Hz), 28.01, 23.68, 22.57. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.85 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{17}H_{27}ClF_3NO_4Na^+$]: 424.1473, found 424.1472.



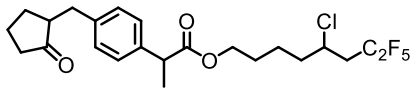
30

4-(2-Chloro-4,4,4-trifluorobutyl)-2-methoxyphenol **(30)**: 23.0 mg colorless liquid was isolated, yield: 43%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.88 (d, *J* = 8.2 Hz, 1H), 6.75 – 6.68 (m, 2H), 5.61 (s, 1H), 4.34 – 4.22 (m, 1H), 3.90 (s, 3H), 3.04 (d, *J* = 6.9 Hz, 2H), 2.64 – 2.47 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.68, 145.03, 128.20, 125.50 (q, *J* = 277.5 Hz), 122.39, 114.62, 111.92, 56.07, 54.41 (q, *J* = 2.9 Hz), 44.28, 41.29 (q, *J* = 28.6 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.55 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{11}H_{12}ClF_3O_2Na^+$]: 291.0370, found 291.0381.



31

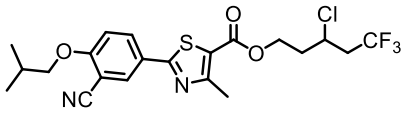
5,7-Dichloro-7,7-difluoroheptyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(31)**: 63.6 mg colorless liquid was isolated, yield: 71%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 4.16 – 3.94 (m, 3H), 3.66 (q, *J* = 7.1 Hz, 1H), 3.08 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.83 – 2.57 (m, 2H), 2.47 (m, *J* = 13.9, 9.5 Hz, 1H), 2.35 – 2.23 (m, 2H), 2.12 – 2.01 (m, 2H), 1.96 – 1.87 (m, 1H), 1.80 – 1.48 (m, 7H), 1.44 (d, *J* = 7.2 Hz, 3H), 1.41 – 1.32 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 219.81, 174.42, 138.80, 138.31 (d, *J* = 2.0 Hz), 129.02, 127.72 (t, *J* = 293.3 Hz), 127.41, 64.02, 54.87 (t, *J* = 2.1 Hz), 50.83, 49.57 (t, *J* = 23.8 Hz), 45.05, 38.04, 37.38, 35.10, 29.15, 27.73, 22.22, 20.45, 18.34 (d, *J* = 1.4 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -48.48 – -49.67 (m, 2F). **ESI-HRMS** exact mass calculated for [$C_{22}H_{28}Cl_2F_2O_3Na^+$]: 471.1276, found 471.1285.



32

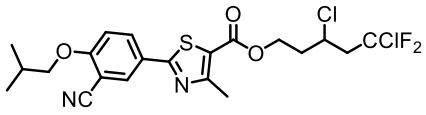
5-Chloro-7,7,8,8,8-pentafluorooctyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate **(32)**: 60.7 mg colorless liquid was isolated, yield: 63%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 4.17 – 4.10 (m, 1H), 4.10 – 4.03 (m, 2H), 3.67 (q, *J* = 7.1 Hz, 1H), 3.08 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.63 – 2.37 (m,

3H), 2.36 – 2.26 (m, 2H), 2.14 – 2.01 (m, 2H), 1.98 – 1.88 (m, 1H), 1.87 – 1.76 (m, 1H), 1.76 – 1.65 (m, 2H), 1.65 – 1.49 (m, 4H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.42 – 1.31 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 219.91, 174.50, 138.86, 138.36 (d, *J* = 2.0 Hz), 129.06, 127.46, 123.91 – 110.97 (2C, m), 64.06, 53.04, 50.90, 45.11, 38.99 (t, *J* = 20.7 Hz), 38.08, 37.95, 35.15, 29.20, 27.77, 22.33, 20.48, 18.35. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -85.93 (d, *J* = 7.2 Hz, 3F), -116.45 – -118.13 (m, 2F). **ESI-HRMS** exact mass calculated for [$C_{23}H_{28}ClF_5O_3Na^+$]: 505.1539, found 505.1550.



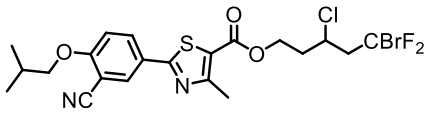
33

***3-Chloro-5,5,5-trifluoropentyl-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate* (33)**: 77.8 mg white solid was isolated, yield: 82%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.2 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 1H), 4.54 – 4.39 (m, 2H), 4.34 – 4.24 (m, 1H), 3.86 (d, *J* = 6.5 Hz, 2H), 2.78 – 2.58 (m, 5H), 2.40 – 2.27 (m, 1H), 2.21 – 2.05 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.44, 162.55, 161.67, 161.58, 132.59, 131.98, 125.78, 125.10 (q, *J* = 277.6 Hz), 121.06, 115.35, 112.66, 102.91, 75.71, 61.50, 50.64 (q, *J* = 3.1 Hz), 42.46 (q, *J* = 28.7 Hz), 36.83, 28.17, 19.03, 17.50. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.58 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{21}H_{23}ClF_3N_2O_3S^+$]: 475.1065, found 475.1068.



34

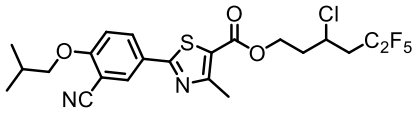
***3,5-Dichloro-5,5-difluoropentyl-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate* (34)**: 76.4 mg white solid was isolated, yield: 78%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 2.2 Hz, 1H), 8.07 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.01 (d, *J* = 8.9 Hz, 1H), 4.58 – 4.44 (m, 2H), 4.42 – 4.34 (m, 1H), 3.89 (d, *J* = 6.5 Hz, 2H), 3.02 – 2.78 (m, 2H), 2.75 (s, 3H), 2.43 – 2.32 (m, 1H), 2.25 – 2.06 (m, 2H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.64, 162.68, 161.82, 161.75, 132.74, 132.21, 127.59 (t, *J* = 293.2 Hz), 125.92, 121.20, 115.48, 112.75, 103.06, 75.81, 61.62, 51.73 (t, *J* = 2.6 Hz), 49.91 (t, *J* = 24.1 Hz), 36.91, 28.25, 19.15, 17.65. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -49.17 (dd, *J* = 18.4, 3.1 Hz, 2F). **ESI-HRMS** exact mass calculated for [$C_{21}H_{23}Cl_2F_2N_2O_3S^+$]: 491.0769, found 491.0766.



35

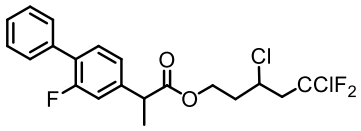
***5-Bromo-3-chloro-5,5-difluoropentyl-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate* (35)**: 70.5 mg yellow solid was isolated, yield: 66%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 – 7.94 (m, 2H), 7.03 – 6.92 (m, 1H), 4.59 – 4.27 (m, 3H), 3.90 – 3.79 (m, 2H), 3.09 – 2.81 (m, 2H), 2.77 – 2.64 (m, 3H), 2.42 – 2.27 (m, 1H), 2.28 – 2.02 (m, 2H), 1.11 – 1.00 (m, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.34, 162.47, 161.54, 161.49, 132.53, 131.88, 125.70, 121.06, 119.98 (t, *J* = 306.7 Hz), 115.29, 112.63, 102.82, 75.65, 61.46, 52.24 (t, *J* = 2.4 Hz), 51.94 (t, *J* = 21.6

Hz), 36.73, 28.11, 19.00, 17.51. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -42.95 (s, 1F), -43.38 (s, 1F). **ESI-HRMS** exact mass calculated for [$C_{21}H_{23}BrClF_2N_2O_3S^+$]: 535.0264, found 535.0270.



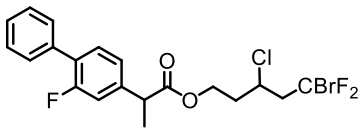
36

3-Chloro-5,5,6,6,6-pentafluorohexyl-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate **(36)**: 83.8 mg yellow solid was isolated, yield: 81%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 2.2 Hz, 1H), 8.00 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.97 (d, *J* = 8.9 Hz, 1H), 4.56 – 4.34 (m, 3H), 3.86 (d, *J* = 6.5 Hz, 2H), 2.70 (s, 3H), 2.67 – 2.49 (m, 2H), 2.44 – 2.31 (m, 1H), 2.26 – 2.06 (m, 2H), 1.05 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.27, 162.45, 161.53, 161.44, 132.46, 131.78, 125.67, 120.98, 123.63 – 111.16 (2C, m), 120.98 115.24, 112.59, 102.78, 75.63, 61.45, 49.85, 39.10 (t, *J* = 20.7 Hz), 37.26, 28.10, 18.90, 17.37. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -85.79 – -85.86 (m, 3F), -116.78 – -117.34 (m, 2F). **ESI-HRMS** exact mass calculated for [$C_{22}H_{23}ClF_5N_2O_3S^+$]: 525.1033, found 525.1041.



37

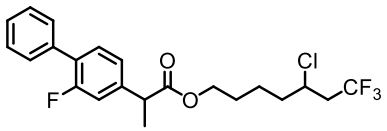
5,7-Dichloro-7,7-difluoroheptyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate **(37)**: 61.9 mg colorless liquid was isolated, yield: 74%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.33 (m, 4H), 7.16 (t, *J* = 9.1 Hz, 2H), 4.45 – 4.26 (m, 2H), 4.26 – 4.13 (m, 1H), 3.85 – 3.74 (m, 1H), 2.93 – 2.60 (m, 2H), 2.31 – 2.14 (m, 1H), 2.04 – 1.91 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.61 (d, *J* = 1.7 Hz), 159.75 (d, *J* = 248.5 Hz), 141.62 (dd, *J* = 7.5, 3.5 Hz), 135.44 , 130.96 (d, *J* = 4.0 Hz), 128.97 (d, *J* = 2.8 Hz), 128.50 , 128.00 (dd, *J* = 1.0, 13.1 Hz), 127.75, 127.57 (td, *J* = 294.9, 3.0 Hz), 123.54, 115.22 (dd, *J* = 23.7, 3.7 Hz), 61.09 (d, *J* = 2.9 Hz), 51.66 – 51.55 (m), 49.64 (t, *J* = 24.0 Hz), 45.00 (dd, *J* = 1.0, 8.1 Hz), 36.78 (d, *J* = 5.0 Hz), 18.19 (d, *J* = 0.9 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -48.45 – -49.79 (m, 2F), -117.32 (d, *J* = 10.3 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{20}H_{19}Cl_2F_3O_2Na^+$]: 441.0606, found 441.0613.



38

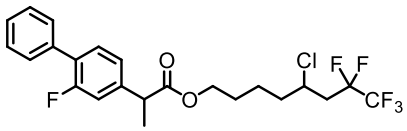
5-Bromo-3-chloro-5,5-difluoropentyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate **(38)**: 62.8 mg colorless liquid was isolated, yield: 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.36 (m, 4H), 7.17 (t, *J* = 8.9 Hz, 2H), 4.44 – 4.27 (m, 2H), 4.26 – 4.15 (m, 1H), 3.85 – 3.75 (m, 1H), 2.99 – 2.70 (m, 2H), 2.28 – 2.14 (m, 1H), 2.04 – 1.92 (m, 1H), 1.58 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.54, 159.71 (d, *J* = 248.5 Hz), 141.61 (dd, *J* = 7.3, 3.8 Hz), 135.39, 130.93 (d, *J* = 3.9 Hz), 128.94 (d, *J* = 2.8 Hz), 128.48, 127.93 (dd, *J* = 14.1, 1.0 Hz), 127.72, 123.53, 120.06 (t, *J* = 306.9 Hz), 115.21 (dd, *J* = 23.6, 2.5 Hz), 61.04 (d, *J* = 3.0 Hz), 52.30 – 52.08 (m), 51.80 (t, *J* = 21.6 Hz), 44.95(dd, *J* = 1.0, 8.0 Hz), 36.67 (d, *J* = 4.0 Hz), 18.19 (d, *J* = 1.1 Hz). **^{19}F NMR** (376 MHz,

Chloroform-*d*) δ -41.90 – -43.50 (m, 2F), -117.24 (d, *J* = 10.4 Hz, 1F). **ESI-HRMS** exact mass calculated for [$C_{20}H_{19}BrClF_3O_2Na^+$]: 485.0101, found 485.0101.



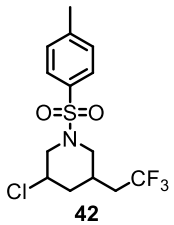
39

***5-Chloro-7,7,7-trifluoroheptyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate* (39)**: 68.0 mg colorless liquid was isolated, yield: 79%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.49 – 7.34 (m, 4H), 7.21 – 7.13 (m, 2H), 4.14 (t, *J* = 6.3 Hz, 2H), 4.11 – 4.04 (m, 1H), 3.78 (q, *J* = 7.2 Hz, 1H), 2.68 – 2.41 (m, 2H), 1.88 – 1.60 (m, 5H), 1.57 (d, *J* = 7.2 Hz, 3H), 1.51 – 1.40 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.98, 159.75 (d, *J* = 248.3 Hz), 141.96 (dd, *J* = 7.7, 1.3 Hz), 135.51, 130.86 (d, *J* = 4.2 Hz), 128.99 (d, *J* = 2.9 Hz), 128.52, 127.88 (d, *J* = 13.5 Hz), 127.75, 125.30 (q, *J* = 277.6 Hz), 123.63 (d, *J* = 3.3 Hz), 115.30 (d, *J* = 23.6 Hz), 64.50, 53.93 (d, *J* = 2.5 Hz), 45.13, 42.38 (q, *J* = 28.3 Hz), 37.50, 27.89, 22.44 (d, *J* = 1.6 Hz), 18.35. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.73 (s, 3F), -117.58 (s, 1F). **ESI-HRMS** exact mass calculated for [$C_{22}H_{23}ClF_4O_2Na^+$]: 453.1215, found 453.1216.



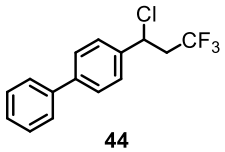
40

***5-Chloro-7,7,8,8,8-pentafluorooctyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate* (40)**: 71.1 mg colorless liquid was isolated, yield: 74%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 – 7.55 (m, 2H), 7.50 – 7.41 (m, 3H), 7.41 – 7.36 (m, 1H), 7.23 – 7.15 (m, 2H), 4.25 – 4.19 (m, 1H), 4.16 (t, *J* = 6.2 Hz, 2H), 3.80 (q, *J* = 7.1 Hz, 1H), 2.70 – 2.38 (m, 2H), 1.94 – 1.61 (m, 5H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.54 – 1.43 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.54, 160.94, 158.47, 141.61 (dd, *J* = 7.3, 3.8 Hz), 135.39, 130.93 (d, *J* = 3.9 Hz), 128.96, 128.93, 128.48, 127.85 (d, *J* = 13.5 Hz), 127.72, 123.11 – 117.01 (2C, C_2F_5), 115.21 (dd, *J* = 23.6, 2.5 Hz), 61.04 (d, *J* = 3.0 Hz), 52.32 – 52.09 (m), 51.80 (t, *J* = 21.6 Hz), 44.96 (dd, *J* = 8.1, 1.0 Hz), 36.69, 36.65, 18.18 (d, *J* = 1.01 Hz).**^{19}F NMR** (376 MHz, Chloroform-*d*) δ -85.90 (s, 3F), -117.09 (s, 1F), -117.35 (s, 1F), -117.60 (s, 1F). **ESI-HRMS** exact mass calculated for [$C_{23}H_{23}ClF_6O_2Na^+$]: 503.1183, found 503.1189.



42

***3-Chloro-1-tosyl-5-(2,2,2-trifluoroethyl)piperidine* (42):** 44.7 mg colorless liquid was isolated, yield: 63%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.48 (dd, *J* = 10.3, 7.0 Hz, 1H), 3.39 (d, *J* = 4.6 Hz, 2H), 3.36 (d, *J* = 5.4 Hz, 1H), 3.20 – 3.02 (m, 2H), 2.57 – 2.45 (m, 2H), 2.43 (s, 3H), 2.28 – 2.11 (m, 1H), 2.05 – 1.86 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 144.05, 133.38, 129.96, 127.51, 126.33 (q, *J* = 278.0 Hz), 51.16 (d, *J* = 1.6 Hz), 50.39, 43.33, 42.13, 35.03 (q, *J* = 2.5 Hz), 31.93 (q, *J* = 29.1 Hz), 21.63. **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.71 (s, 3F). **ESI-HRMS** exact mass calculated for [$C_{14}H_{17}ClF_3O_2S Na^+$]: 377.0560, found 377.0565.



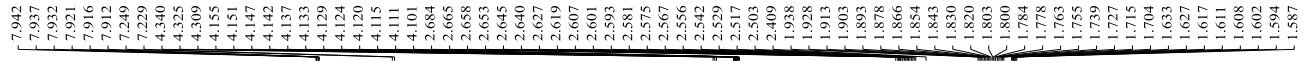
44

***4-(1-Chloro-3,3,3-trifluoropropyl)-1,1'-biphenyl* (44):** 9.7 mg yellow solid was isolated, yield: 17%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.53 (m, 4H), 7.50 – 7.41 (m, 4H), 7.40 – 7.34 (m, 1H), 5.17 (t, *J* = 7.0 Hz, 1H), 3.14 – 2.83 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.18, 140.34, 138.75, 129.01, 127.85, 127.82, 127.38, 127.28, 129.01 – 120.76 (m), 54.91 – 54.52 (m), 43.87 (q, *J* = 28.2 Hz). **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -63.98 (s, 3F) **EI-MS** calculated for [$C_{15}H_{12}ClF_3$]: 284.1, found 284.1.

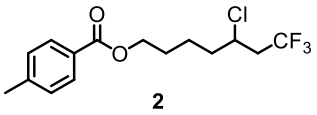
6. Reference

1. Y. Ouyang, X.-H. Xu, F.-L. Qing, *Angew. Chem., Int. Ed.*, 2019, **58**, 18508-18512.
2. Y. Zhang, S. Torker, M. Sigrist, N. Bregović, P. Dydio, *J. Am. Chem. Soc.*, 2020, **142**, 18251-18265.
3. M. S. Jung, W. S. Kim, Y. H. Shin, H. J. Jin, Y. S. Kim, E. J. Kang, *Org. Lett.*, 2012, **14**, 6262-6265.
4. (a) A. S. Pirzer, E. M. Alvarez, H. Friedrich, M. R. Heinrich, *Chem.-Eur. J.*, 2019, **25**, 2786-2792; (b) X. Jiang, Y. Lan, Y. Hao, K. Jiang, J. He, J. Zhu, S. Jia, J. Song, S.-J. Li, L. Niu, *Nat. Commun.*, 2024, **15**, 6115.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel et al., Gaussian16, Gaussian, Inc, Wallingford, CT, 2016.
6. F. Furche and R. Ahlrichs, *J. Chem. Phys.*, 2002, **117**, 7433-7447.
7. G. Scalmani, M. J. Frisch, *J. Chem. Phys.*, 2006, **124**, 094107.
8. D.-C. Fang, THERMO, Beijing Normal University, Beijing, China, 2013.

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



^{1}H NMR, 400 MHz, $CDCl_3$



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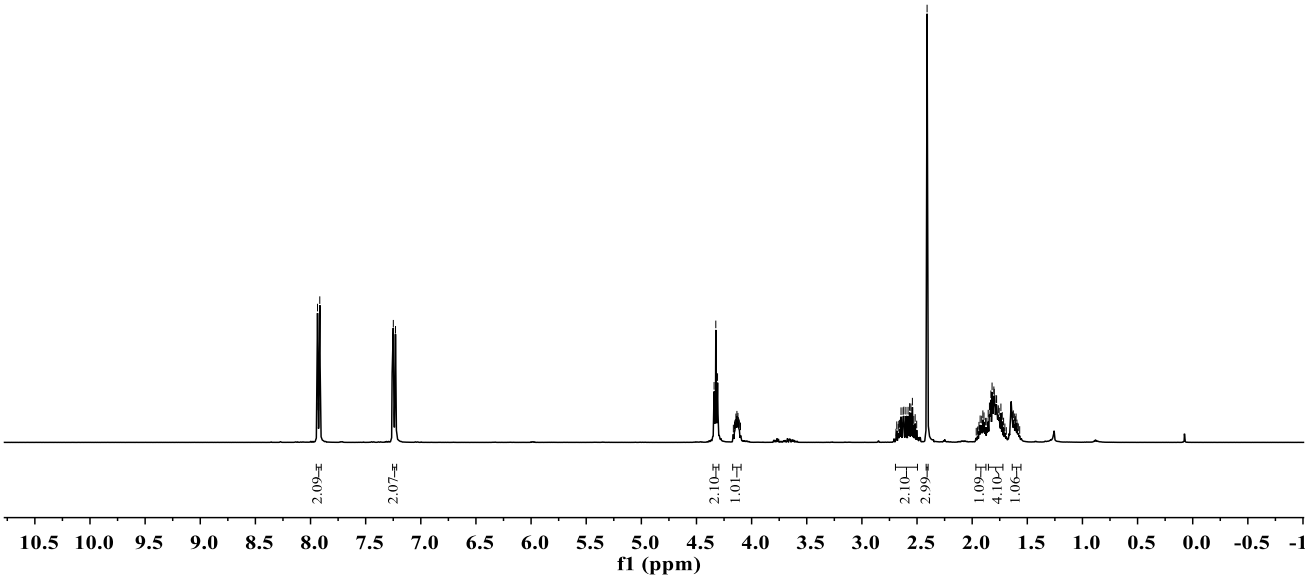
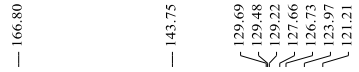
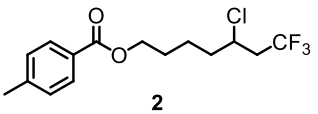


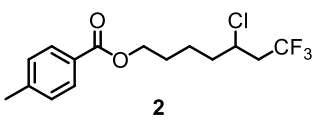


^{13}C NMR, 101 MHz, $CDCl_3$



2

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



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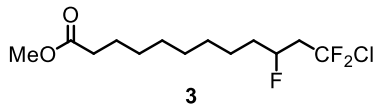
^{1}H NMR, 400 HMz, $CDCl_3$



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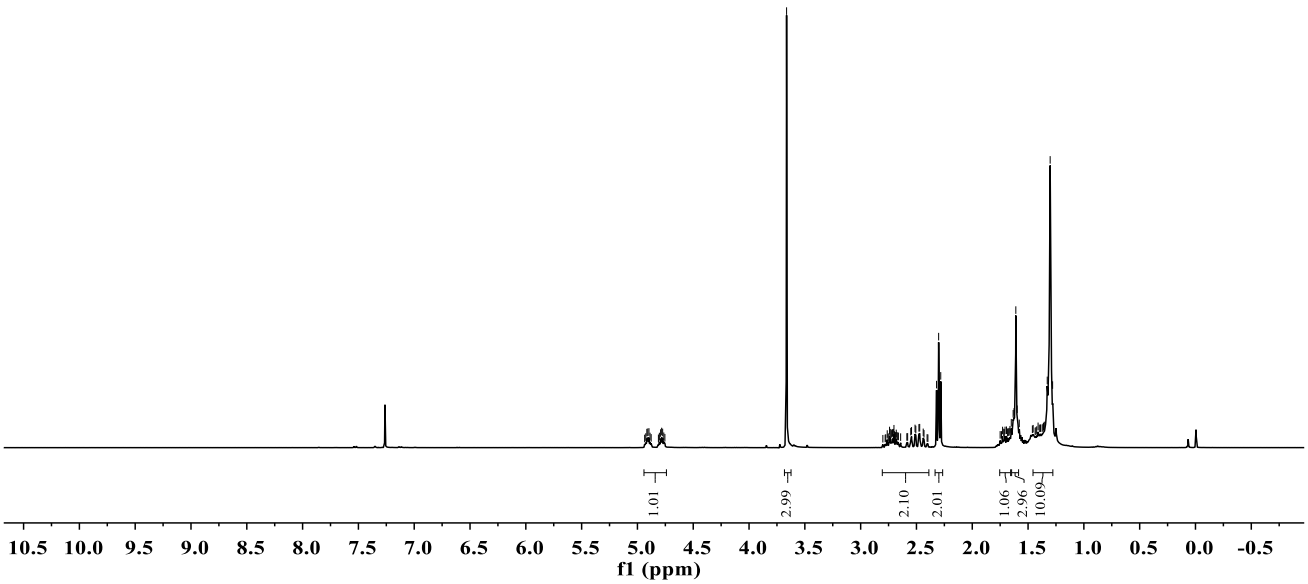

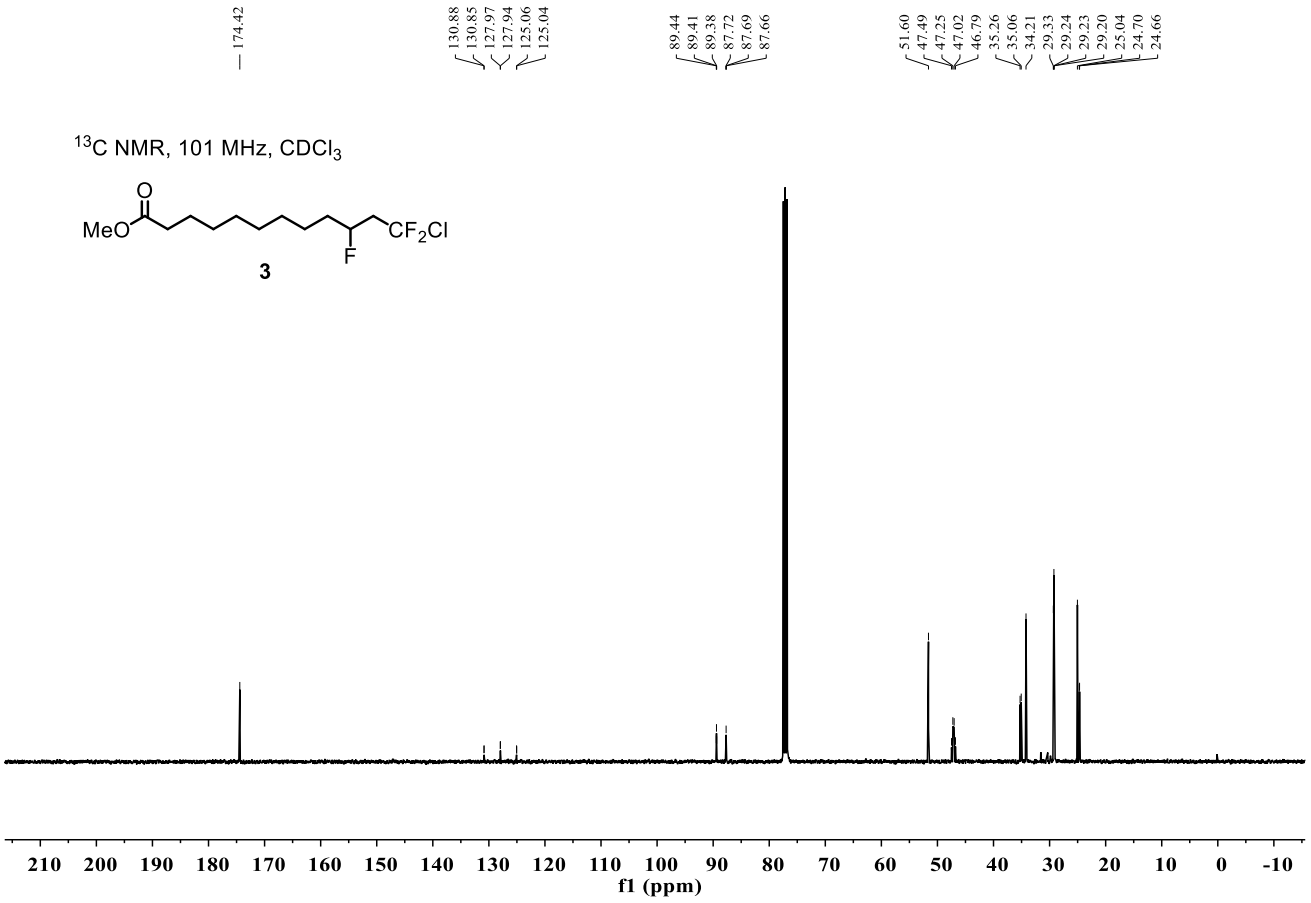
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127.97
127.94
125.06
125.04
89.44
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89.38
87.72
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87.66
51.60
47.49
47.25
47.02
46.79
35.26
35.06
34.21
29.33
29.24
29.23
29.20
25.04
24.70
24.66
13C NMR, 101 MHz, CDCl3
MeO
O
CF2Cl
F
3
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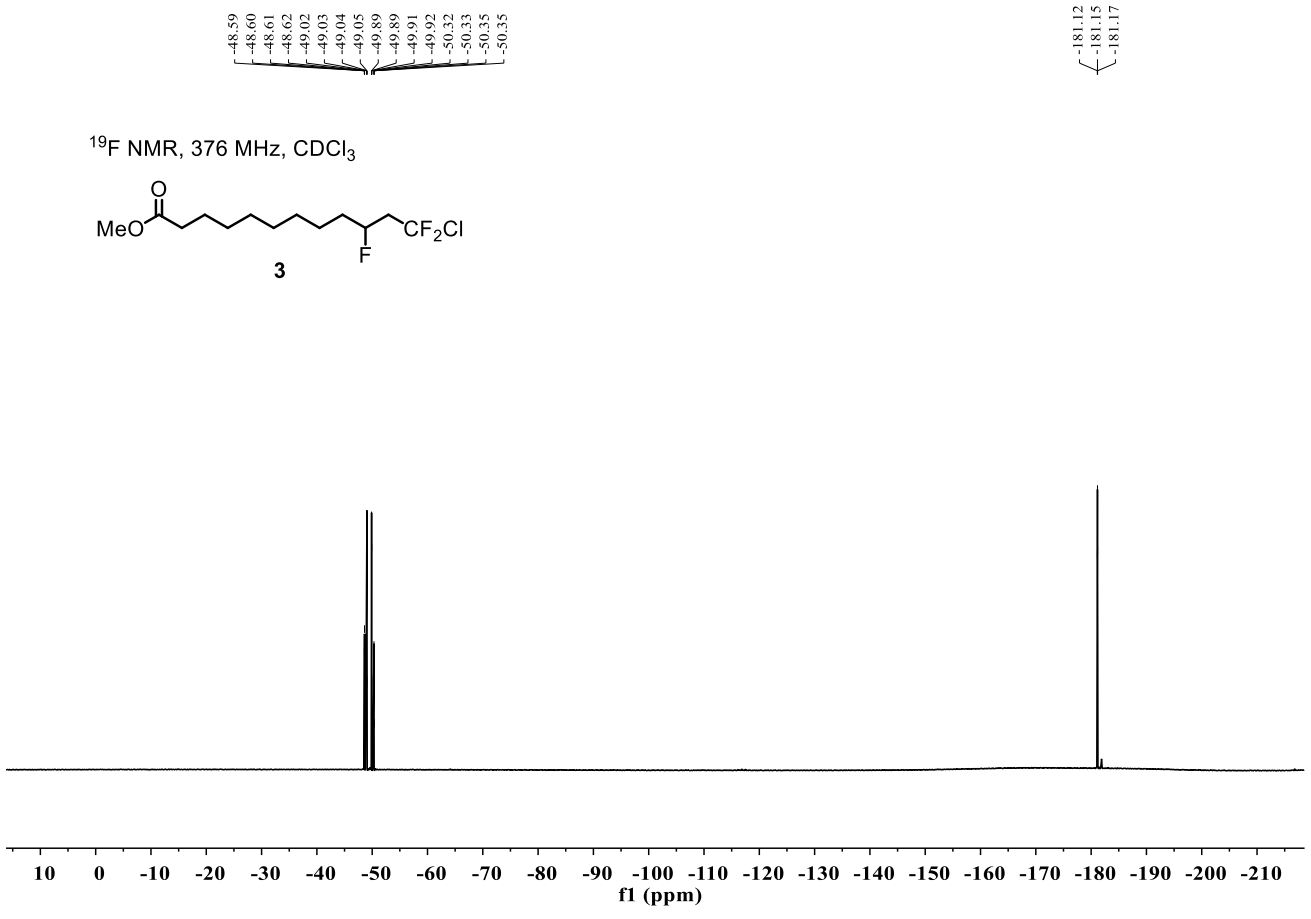
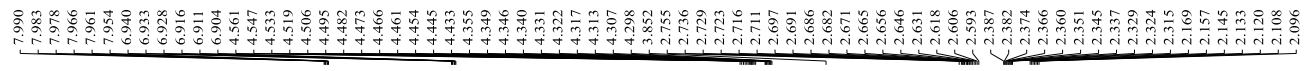
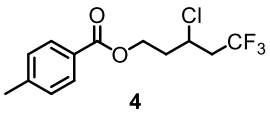
f1 (ppm)


-48.59
-48.60
-48.61
-48.62
-49.02
-49.03
-49.04
-49.05
-49.89
-49.89
-49.91
-49.92
-50.32
-50.33
-50.35
-50.35
-181.12
-181.15
-181.17
19F NMR, 376 MHz, CDCl3
MeO
O
CF2Cl
F
3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



^{1}H NMR, 400MHz, $CDCl_3$



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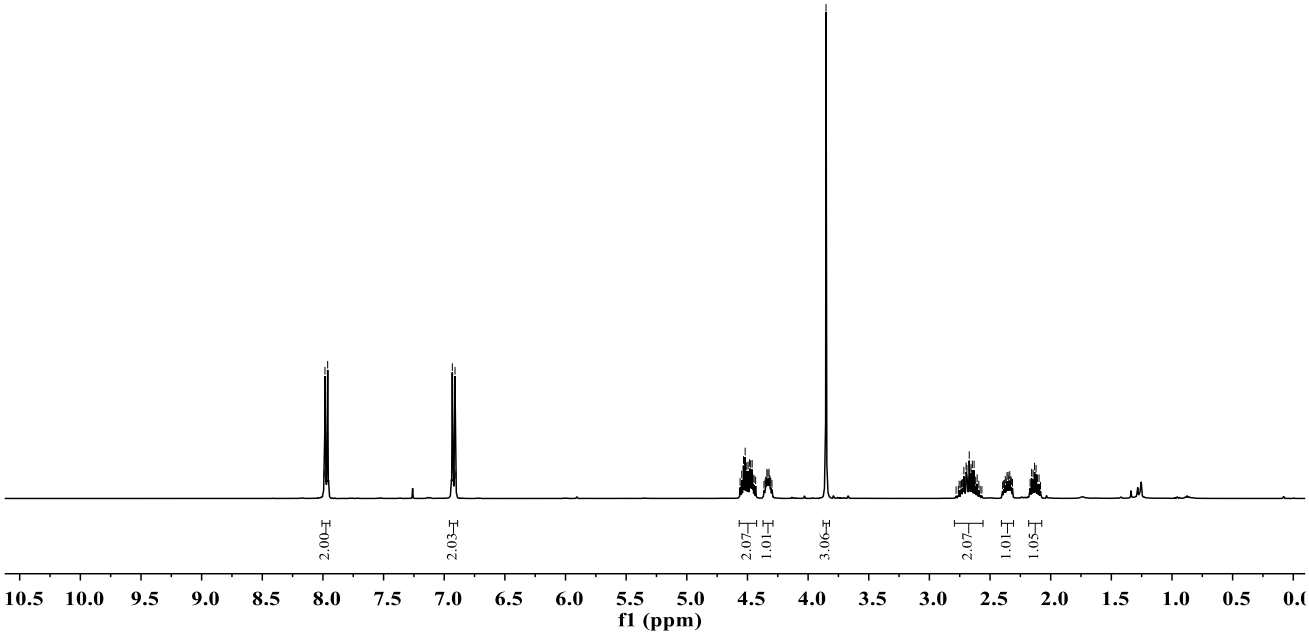
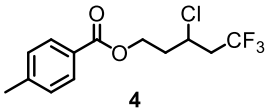


^{13}C NMR, 101 MHz, $CDCl_3$



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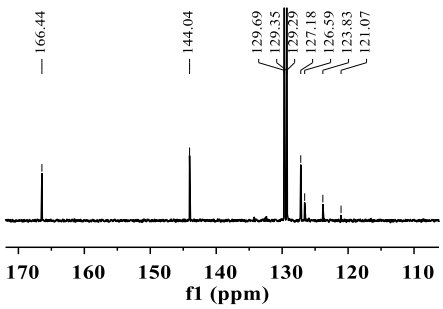
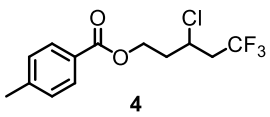
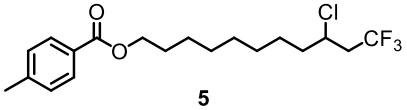


^{19}F NMR, 376 MHz, $CDCl_3$



4

^{1}H NMR, 400 MHz, $CDCl_3$



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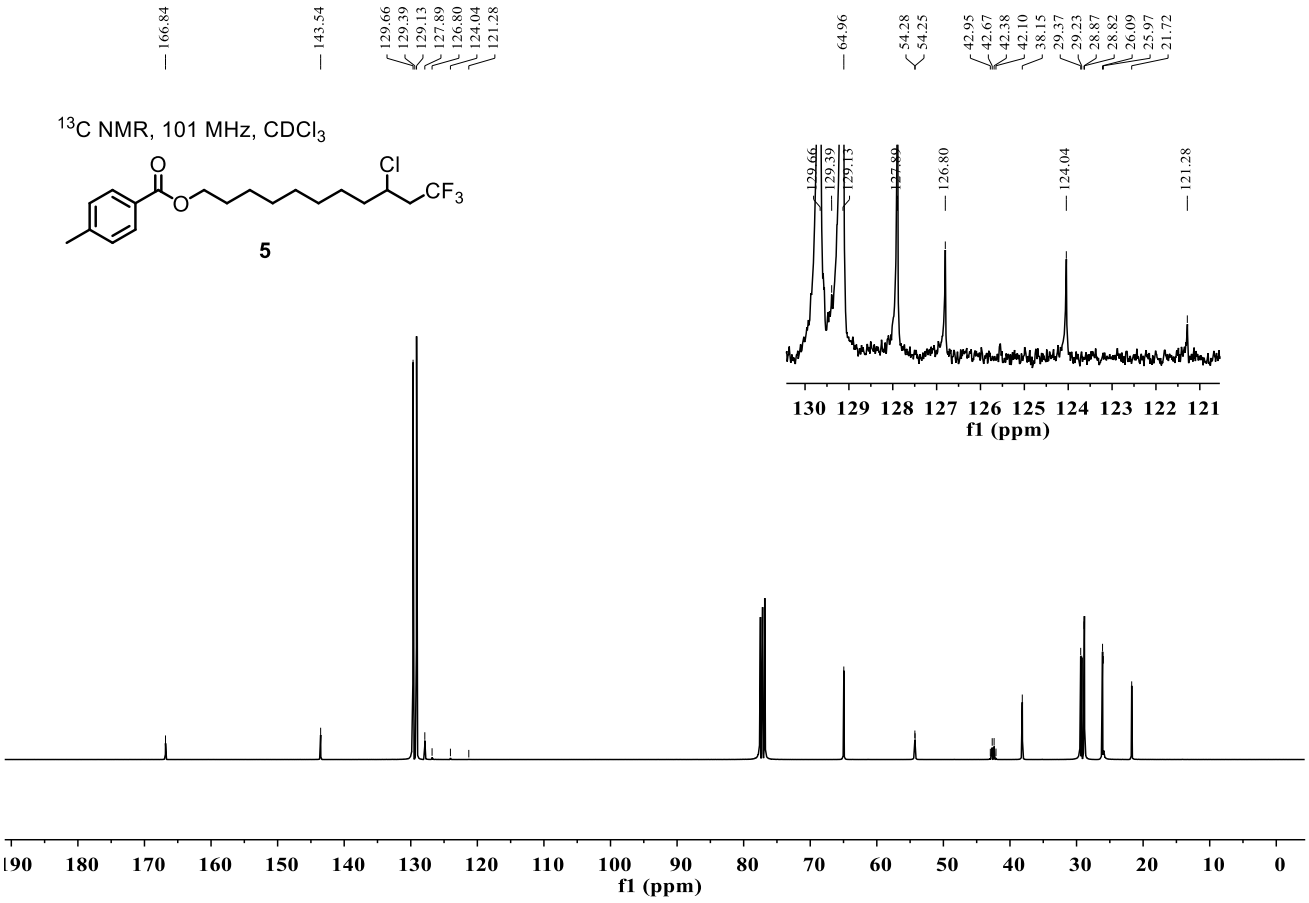
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54.28
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O
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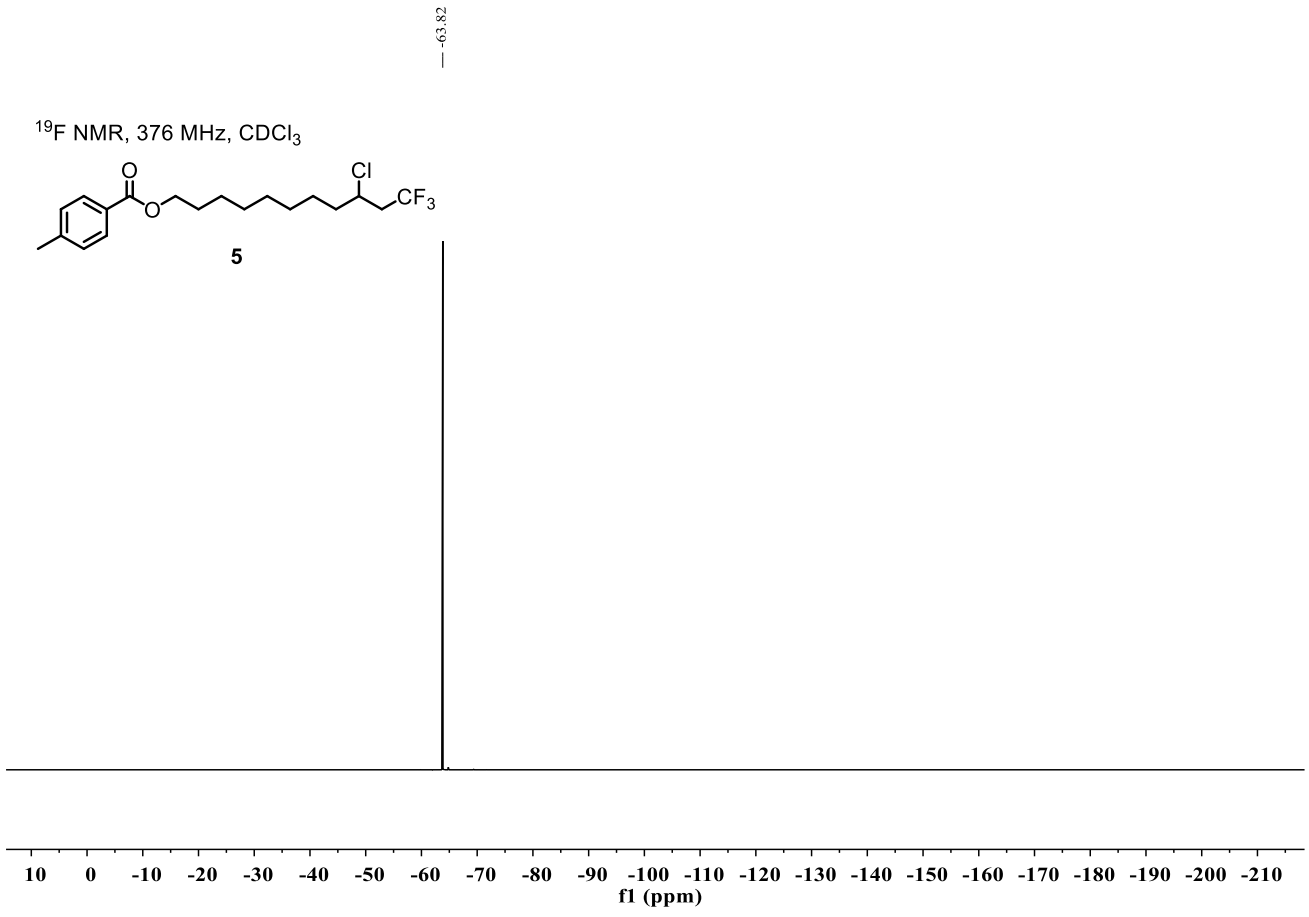
Cl
CF3
5
f1 (ppm)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Cl
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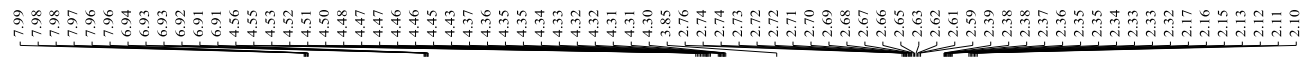
f1 (ppm)



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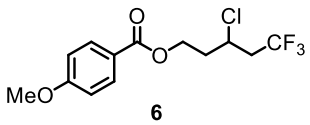

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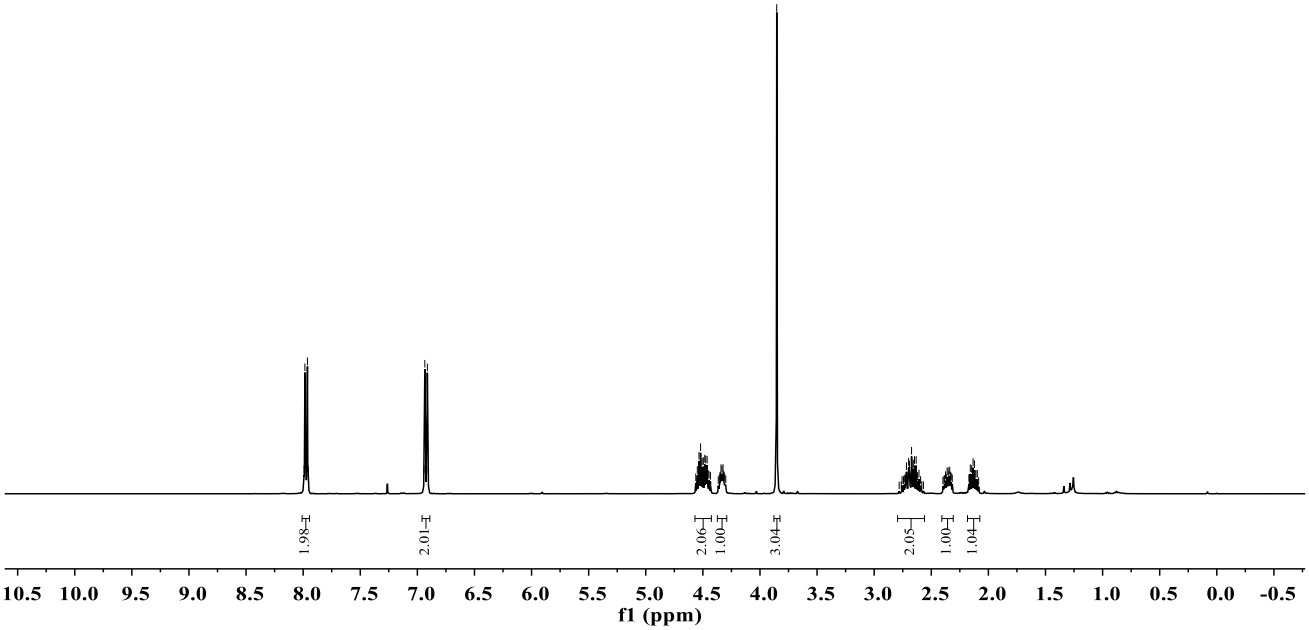
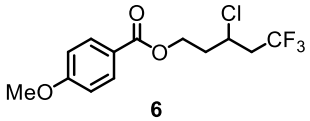


^{13}C NMR, 101 MHz, $CDCl_3$



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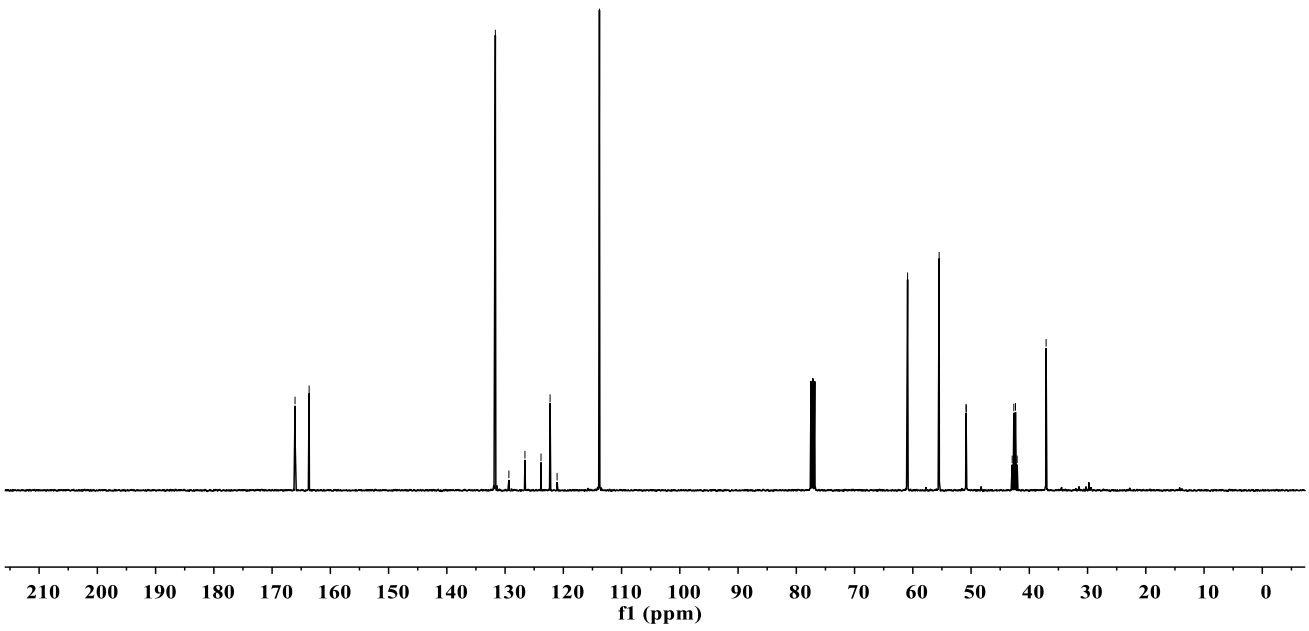
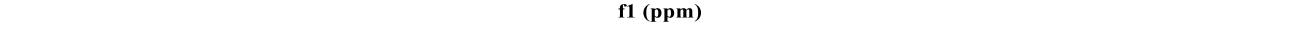
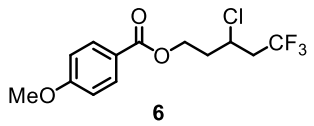




^{19}F NMR, 376 MHz, $CDCl_3$



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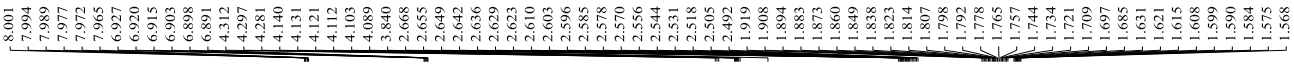

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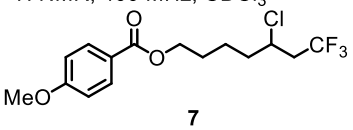

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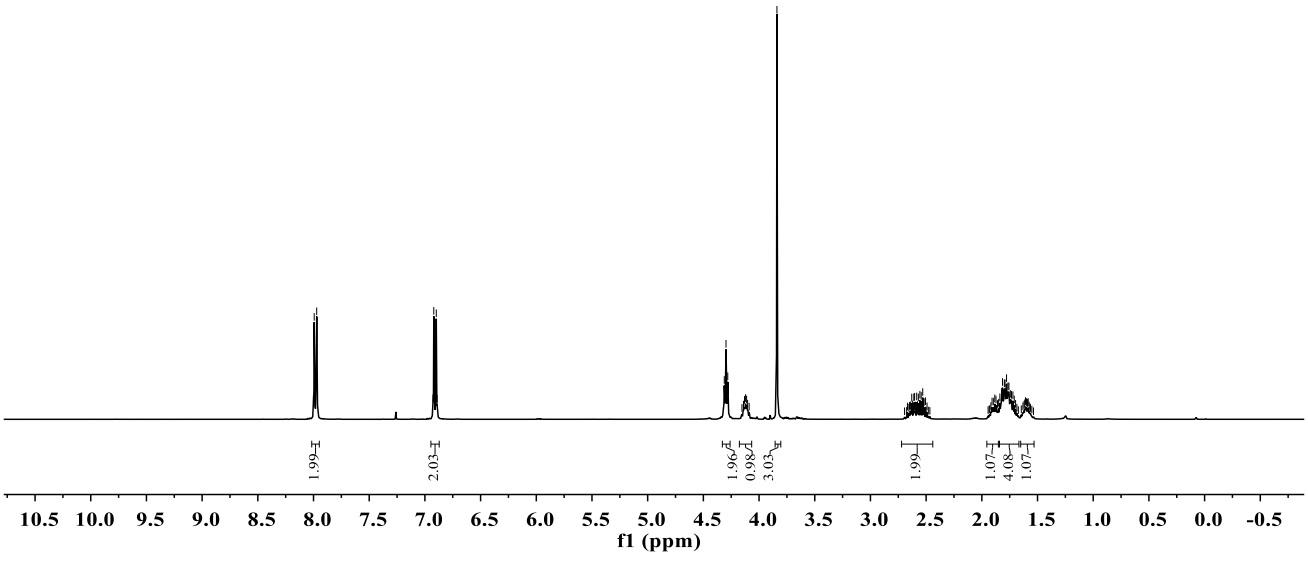

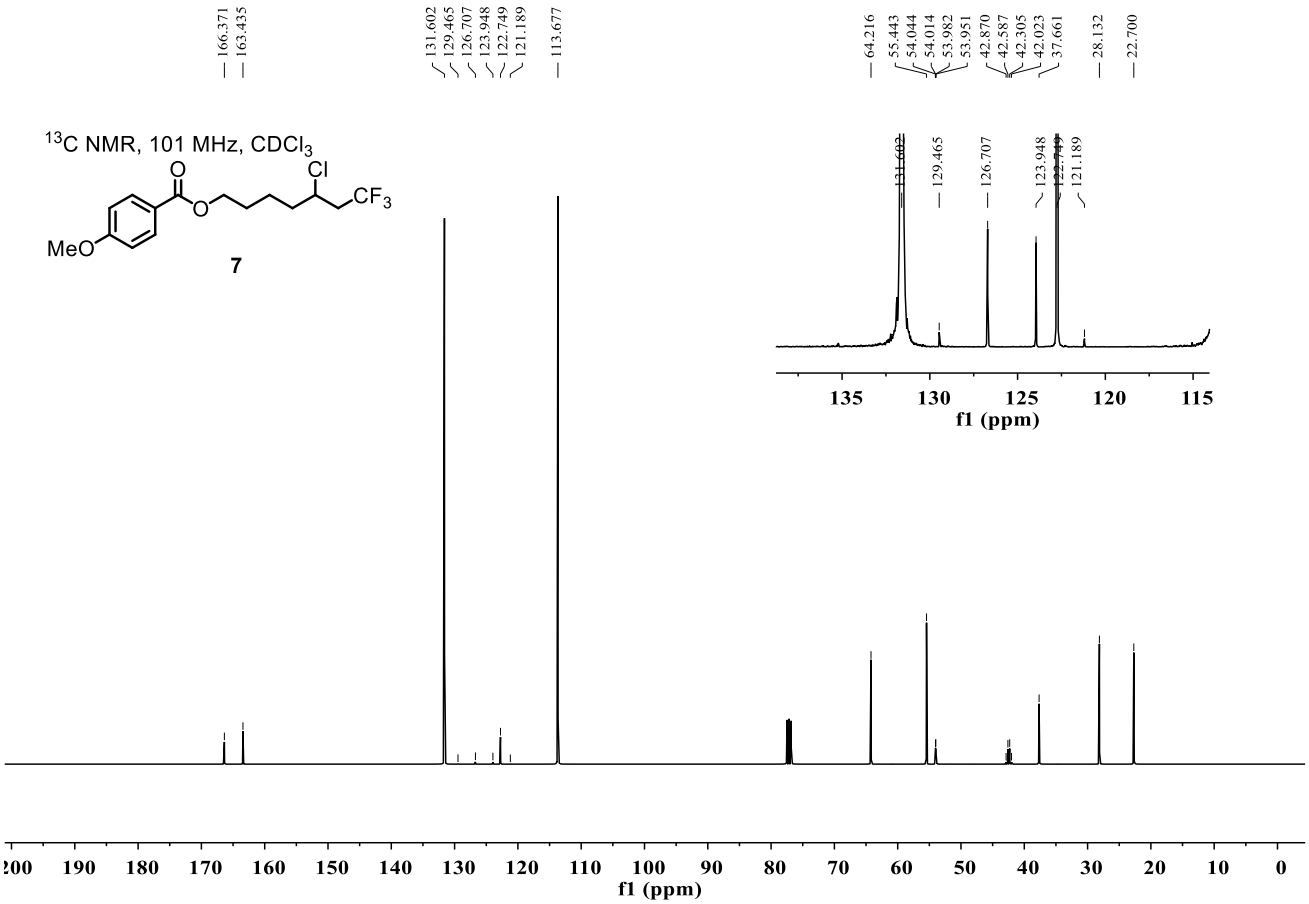
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42.587
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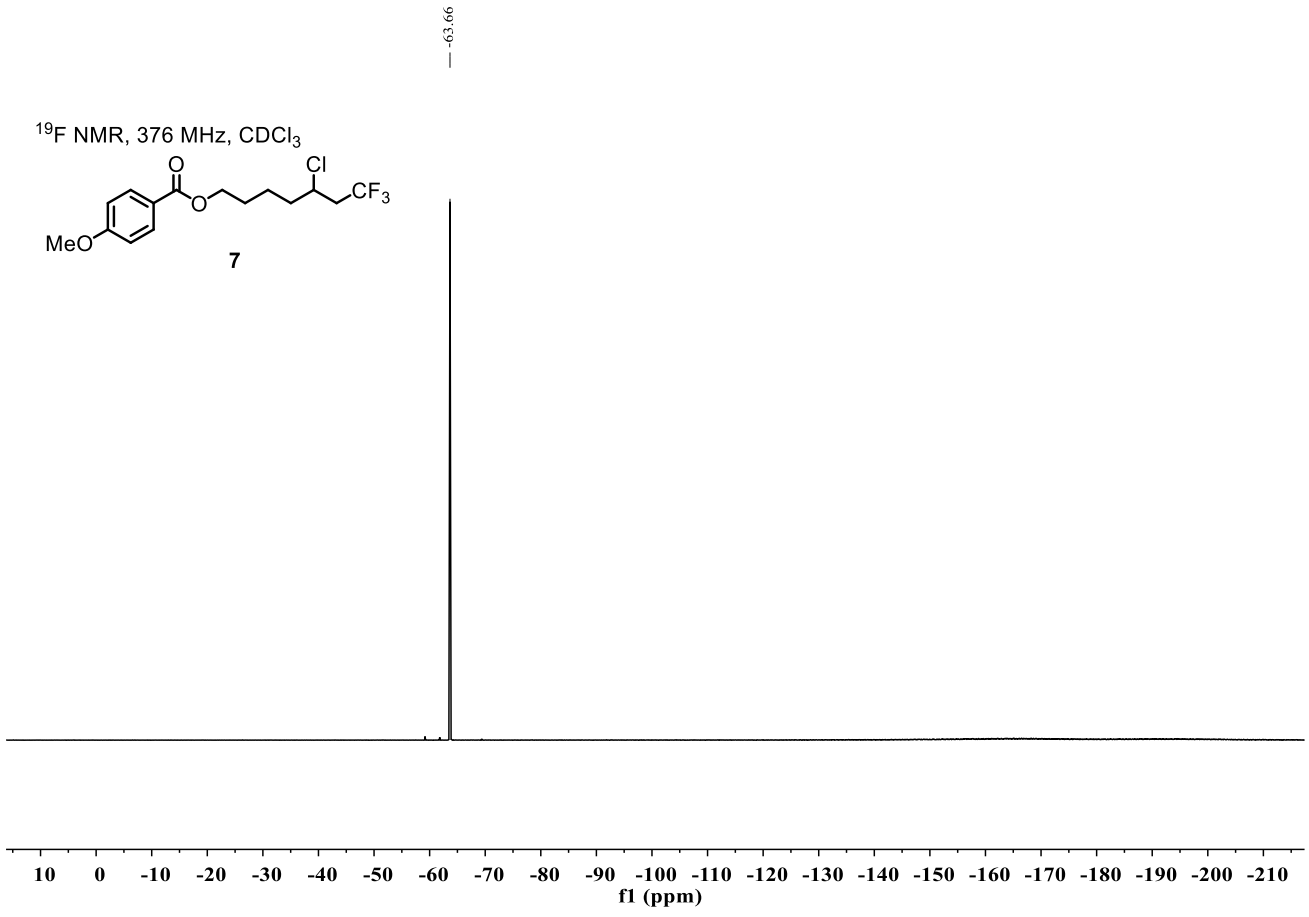
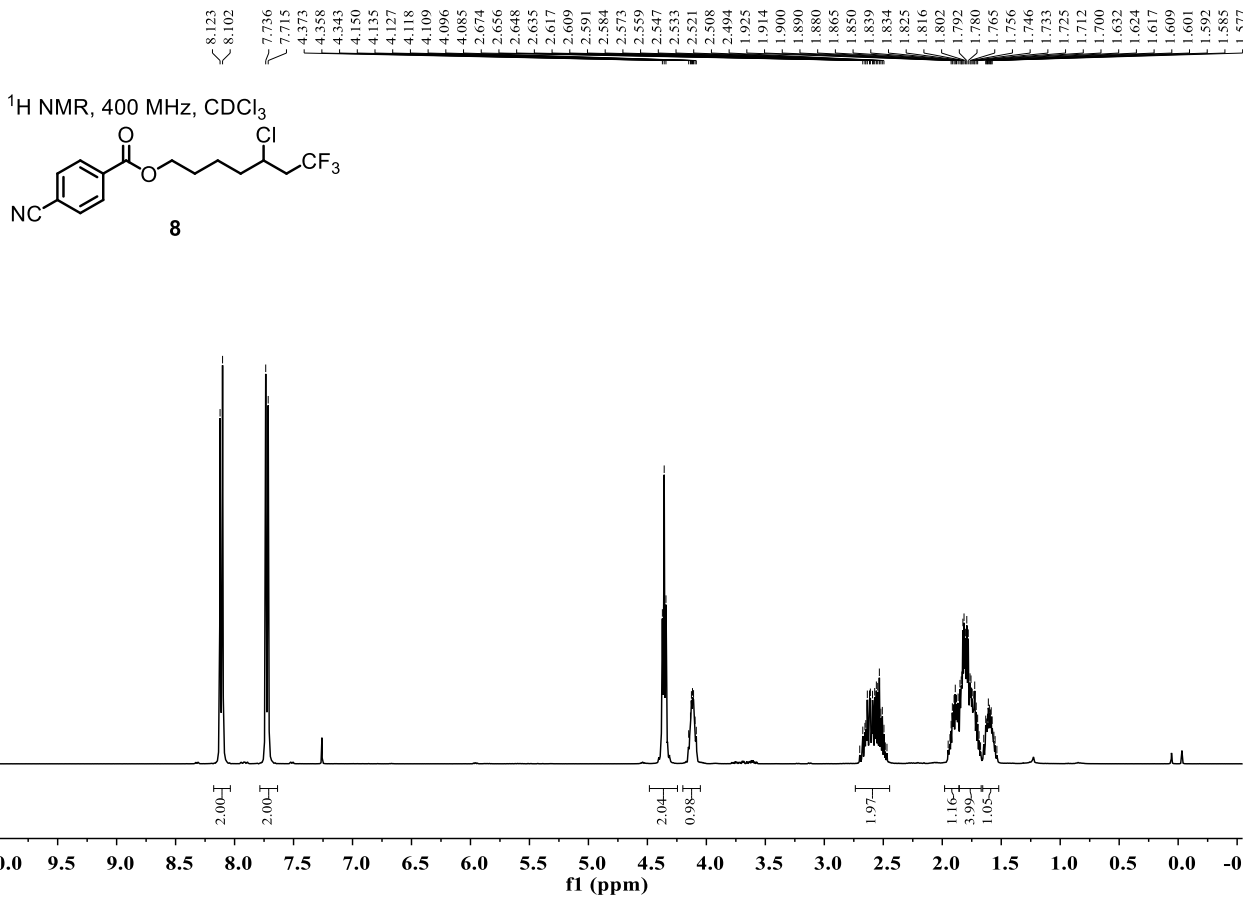
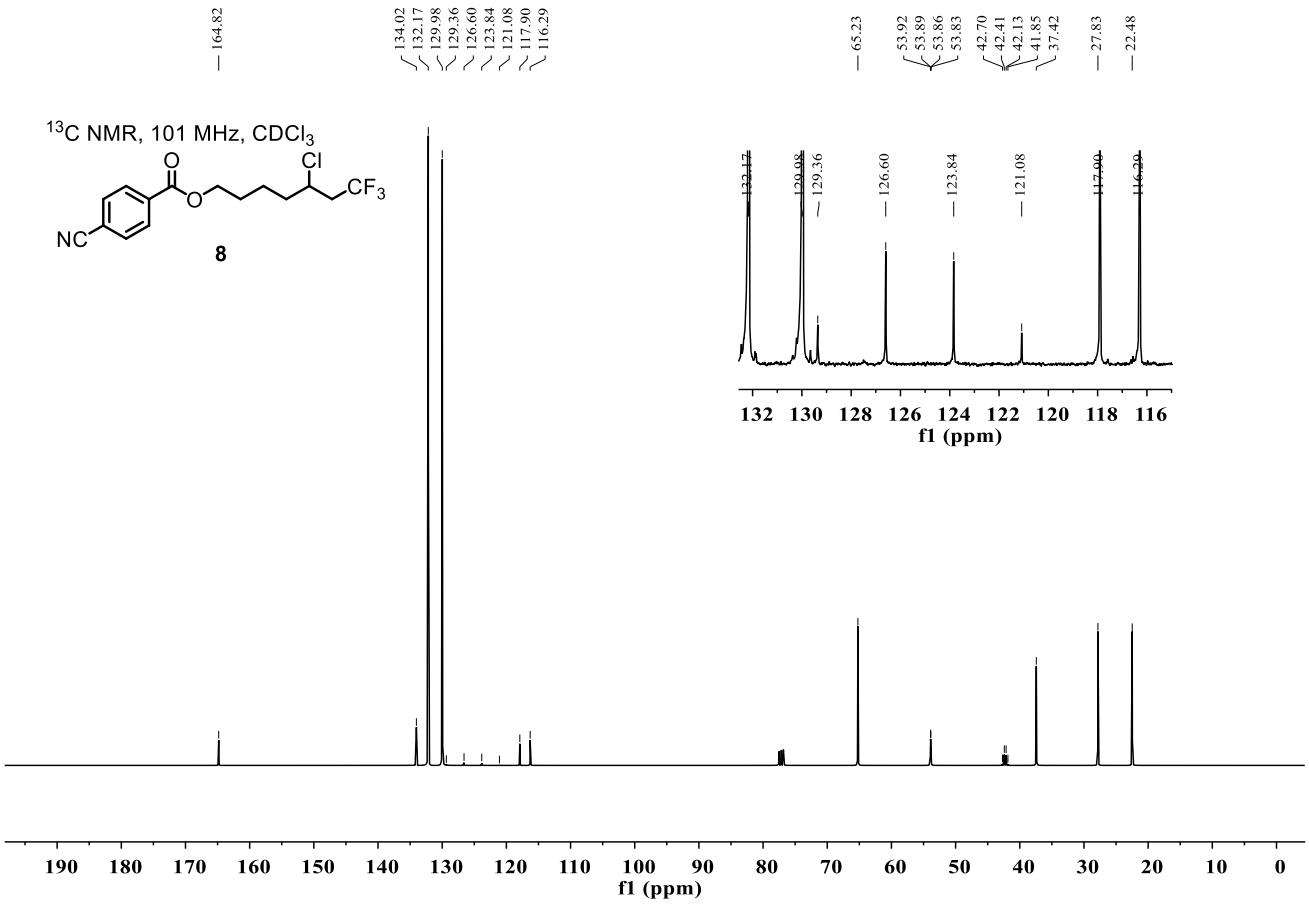
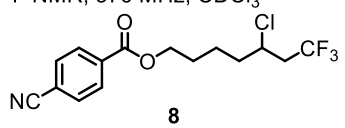
28.132
22.700
13C NMR, 101 MHz, CDCl3
O
Cl
CF3
O
MeO
7
f1 (ppm)


-63.66
19F NMR, 376 MHz, CDCl3
O
Cl
CF3
O
MeO
7
f1 (ppm)


8.123
8.102
7.736
7.715
4.373
4.358
4.343
4.150
4.135
4.127
4.118
4.109
4.096
4.085
2.674
2.656
2.648
2.635
2.617
2.609
2.591
2.584
2.573
2.559
2.547
2.533
2.521
2.508
2.494
1.925
1.914
1.900
1.890
1.880
1.865
1.850
1.839
1.834
1.825
1.816
1.802
1.792
1.780
1.765
1.756
1.746
1.733
1.725
1.712
1.700
1.632
1.624
1.617
1.609
1.601
1.592
1.585
1H NMR, 400 MHz, CDCl3
O
Cl
CF3
O
NC
8
2.00
2.00
2.04
0.98
1.97
1.16
3.99
1.05
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
f1 (ppm)

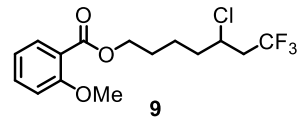

164.82
134.02
132.17
129.98
129.36
126.60
123.84
121.08
117.90
116.29
65.23
53.92
53.89
53.86
53.83
42.70
42.41
42.13
41.85
37.42
27.83
22.48
13C NMR, 101 MHz, CDCl3
O
Cl
CF3
O
NC
8
132.17
129.98
129.36
126.60
123.84
121.08
117.90
116.29
132 130 128 126 124 122 120 118 116
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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

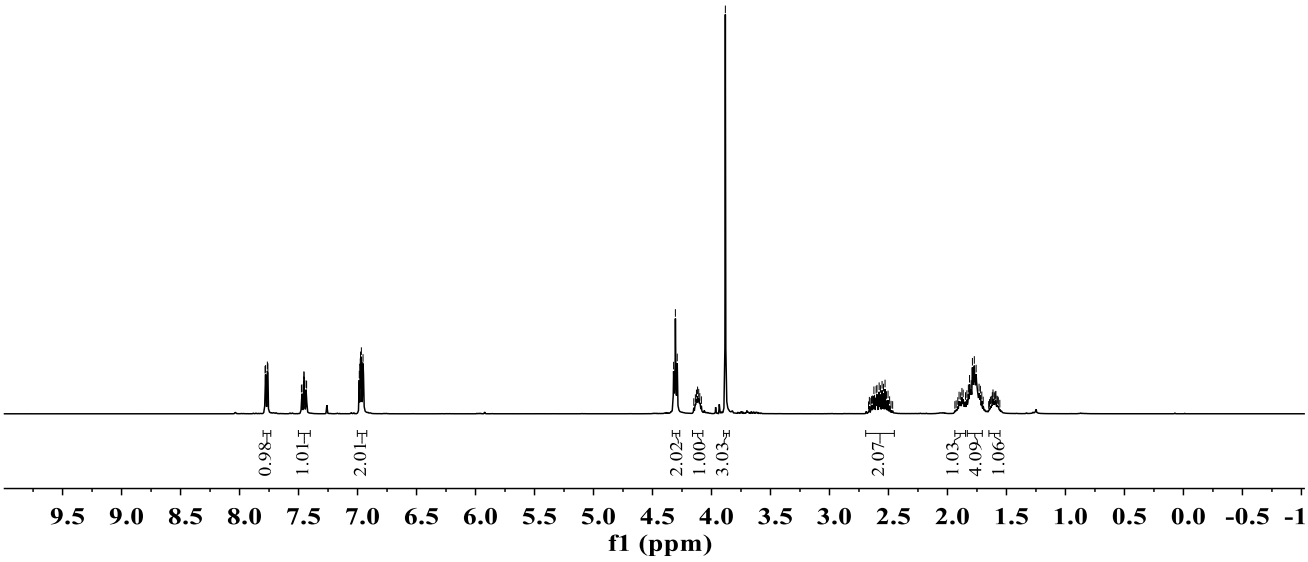


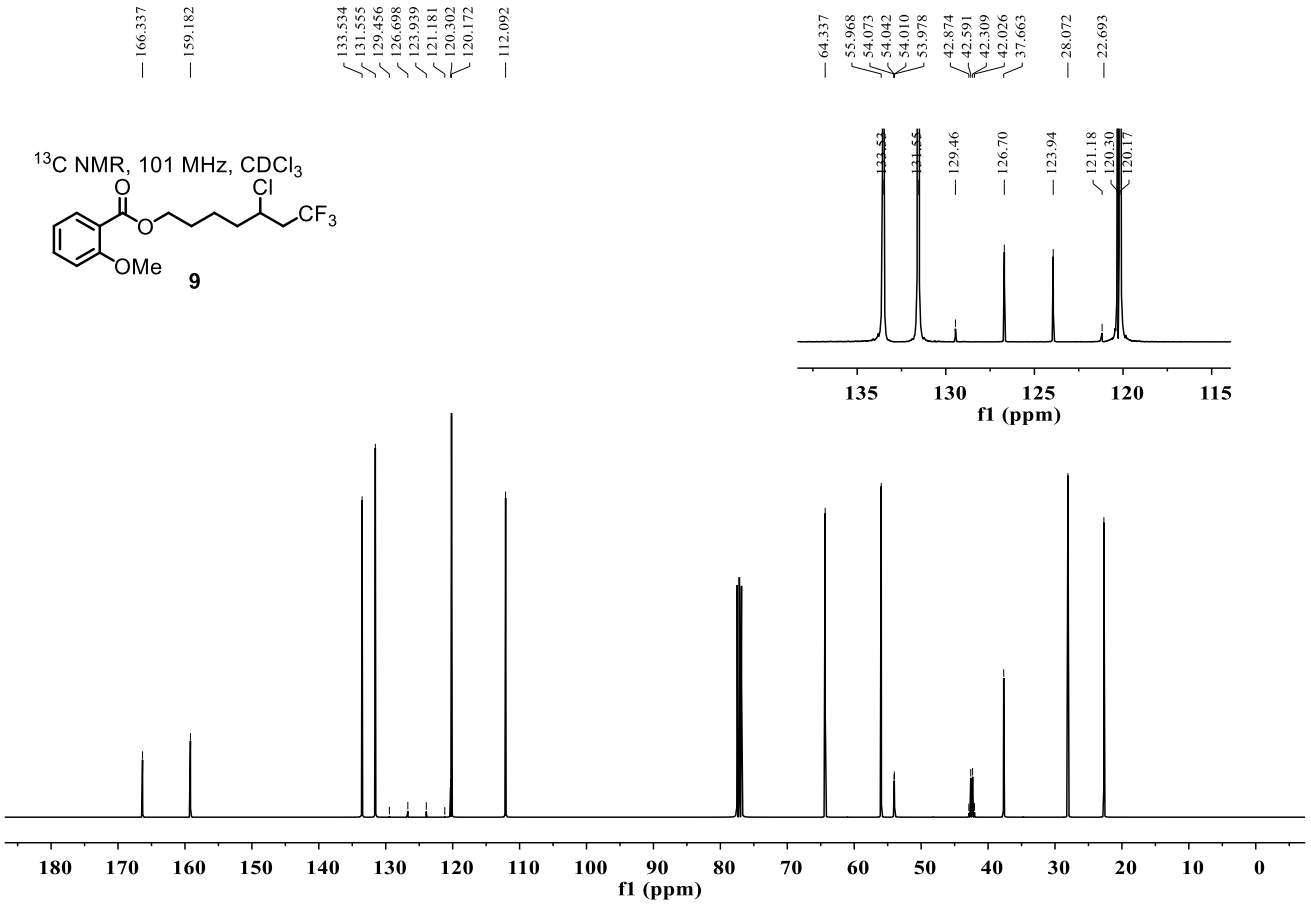
8

^{1}H NMR, 400 MHz, $CDCl_3$



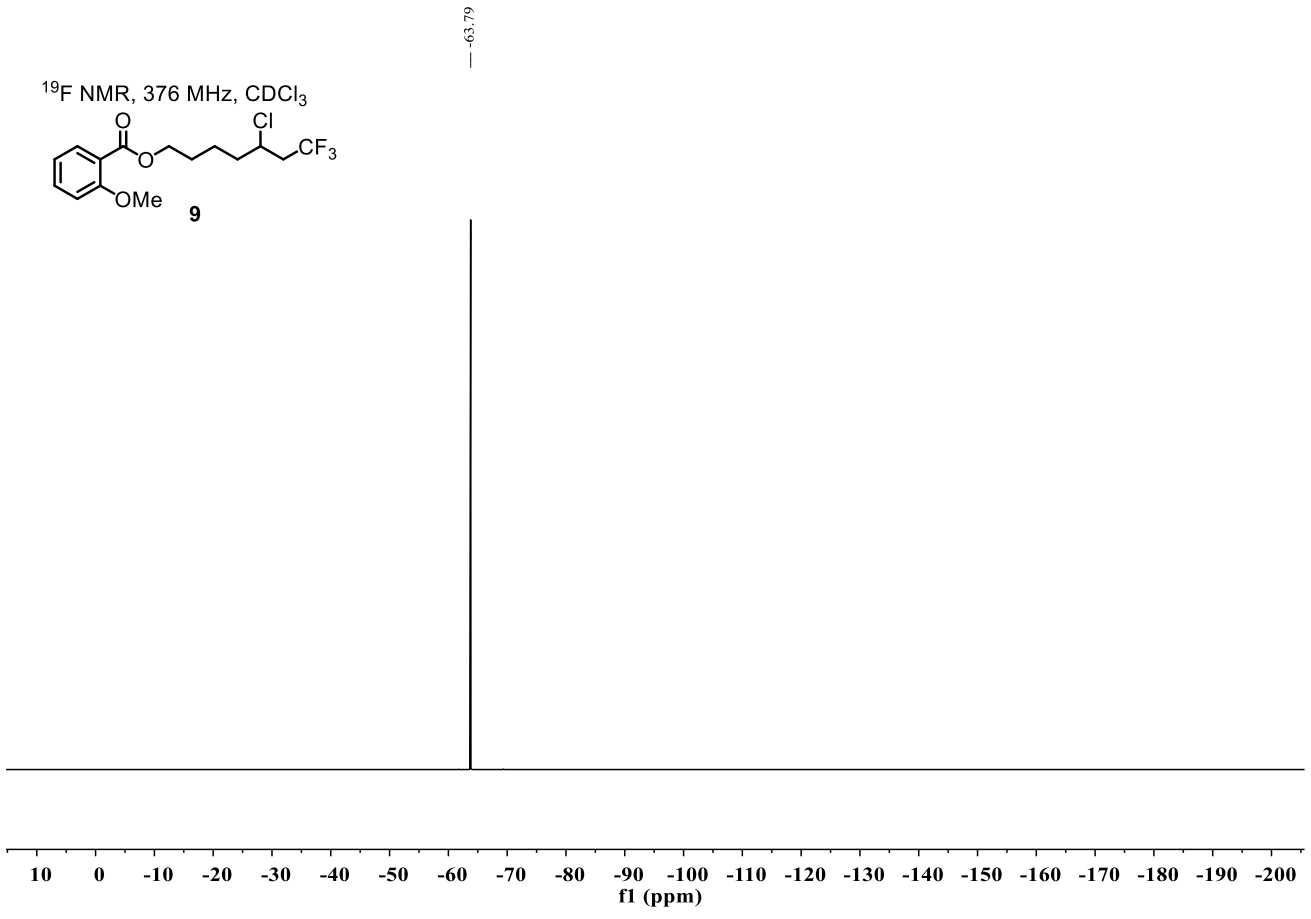
9





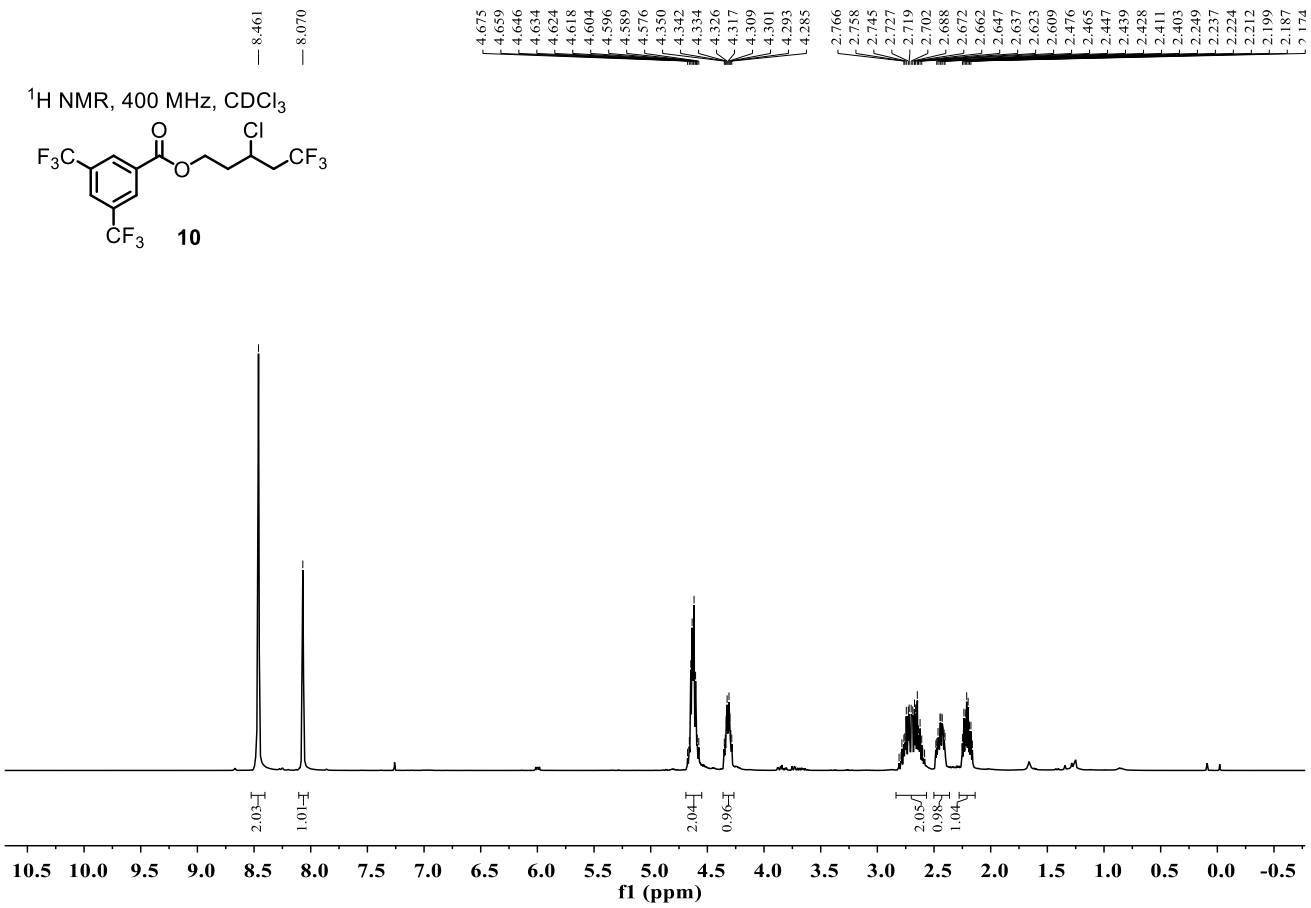
^{13}C NMR, 101 MHz, $CDCl_3$

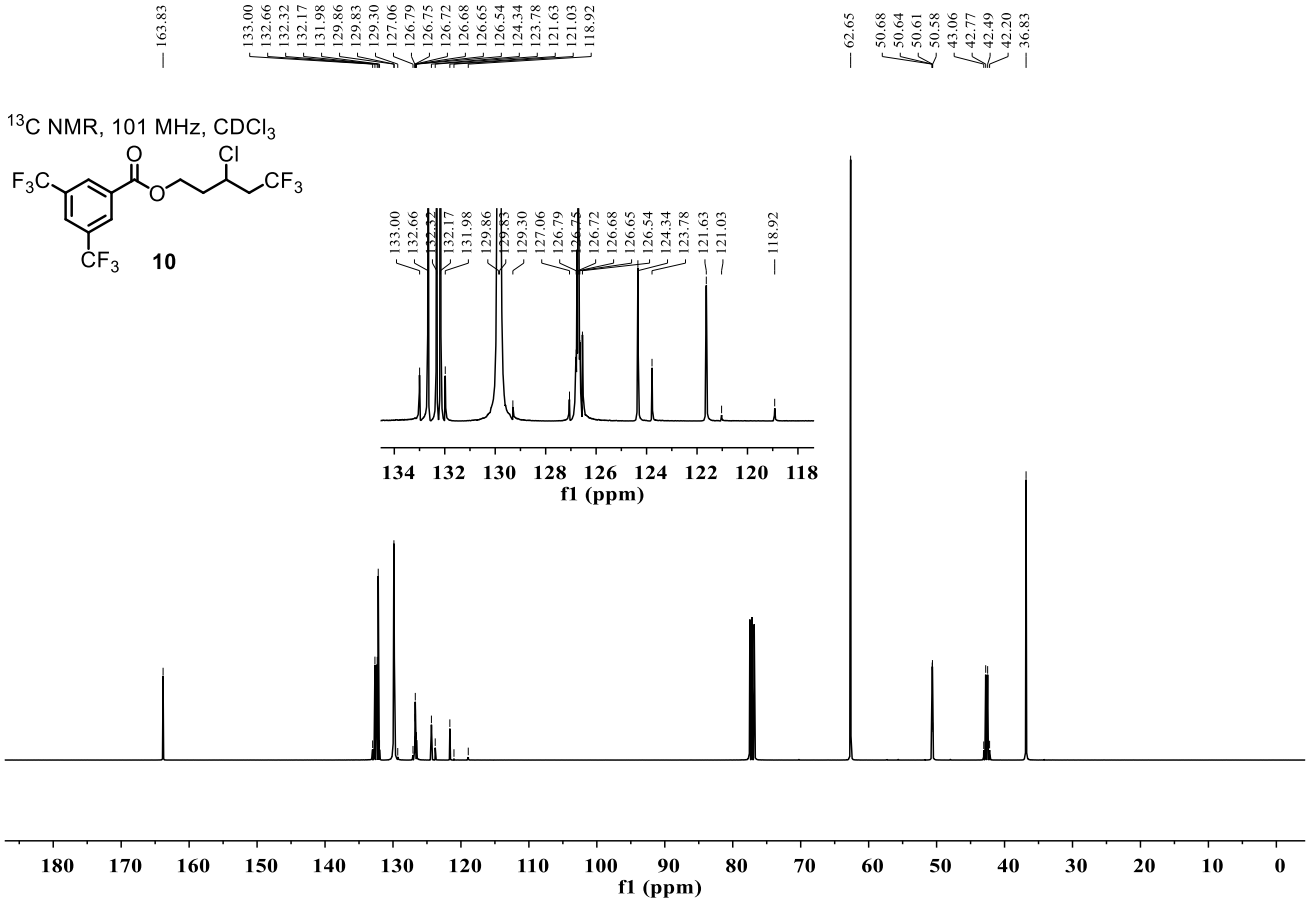
9



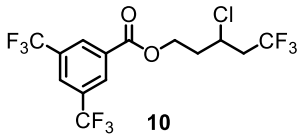
^{19}F NMR, 376 MHz, $CDCl_3$

9

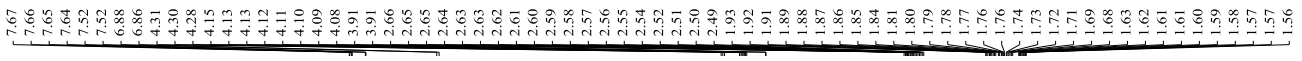

8.461
8.070
4.675
4.659
4.646
4.634
4.624
4.618
4.604
4.596
4.589
4.576
4.350
4.342
4.334
4.326
4.317
4.309
4.301
4.293
4.285
2.766
2.758
2.745
2.727
2.719
2.702
2.688
2.672
2.662
2.647
2.637
2.623
2.609
2.476
2.465
2.447
2.439
2.428
2.411
2.403
2.249
2.237
2.224
2.212
2.199
2.187
2.174
1H NMR, 400 MHz, CDCl3
O
Cl
F3C
O
CF3
CF3
10
2.03
1.01
2.04
0.96
2.05
0.98
1.04
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)


163.83
133.00
132.66
132.32
132.17
131.98
129.86
129.83
129.30
127.06
126.79
126.75
126.72
126.68
126.65
126.54
124.34
123.78
121.63
121.03
118.92
62.65
50.68
50.64
50.61
50.58
43.06
42.77
42.49
42.20
36.83
13C NMR, 101 MHz, CDCl3
O
Cl
F3C
O
CF3
CF3
10
134 132 130 128 126 124 122 120 118
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

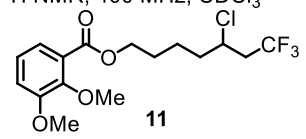
^{19}F NMR, 376 MHz, $CDCl_3$



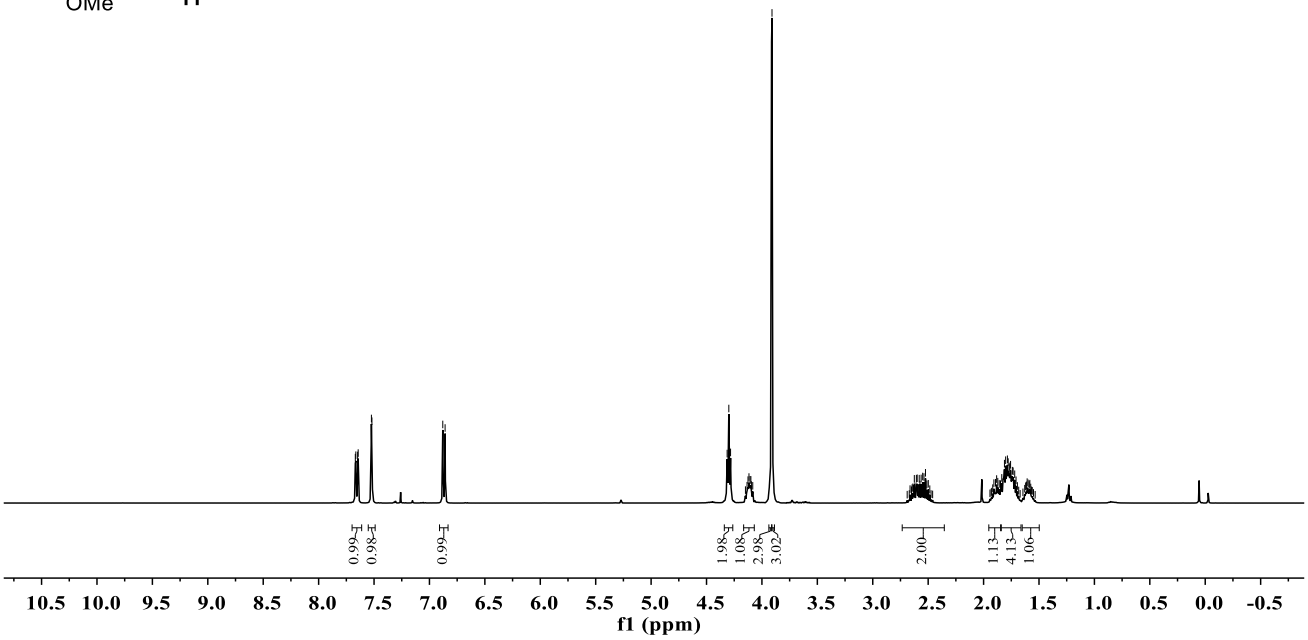
10

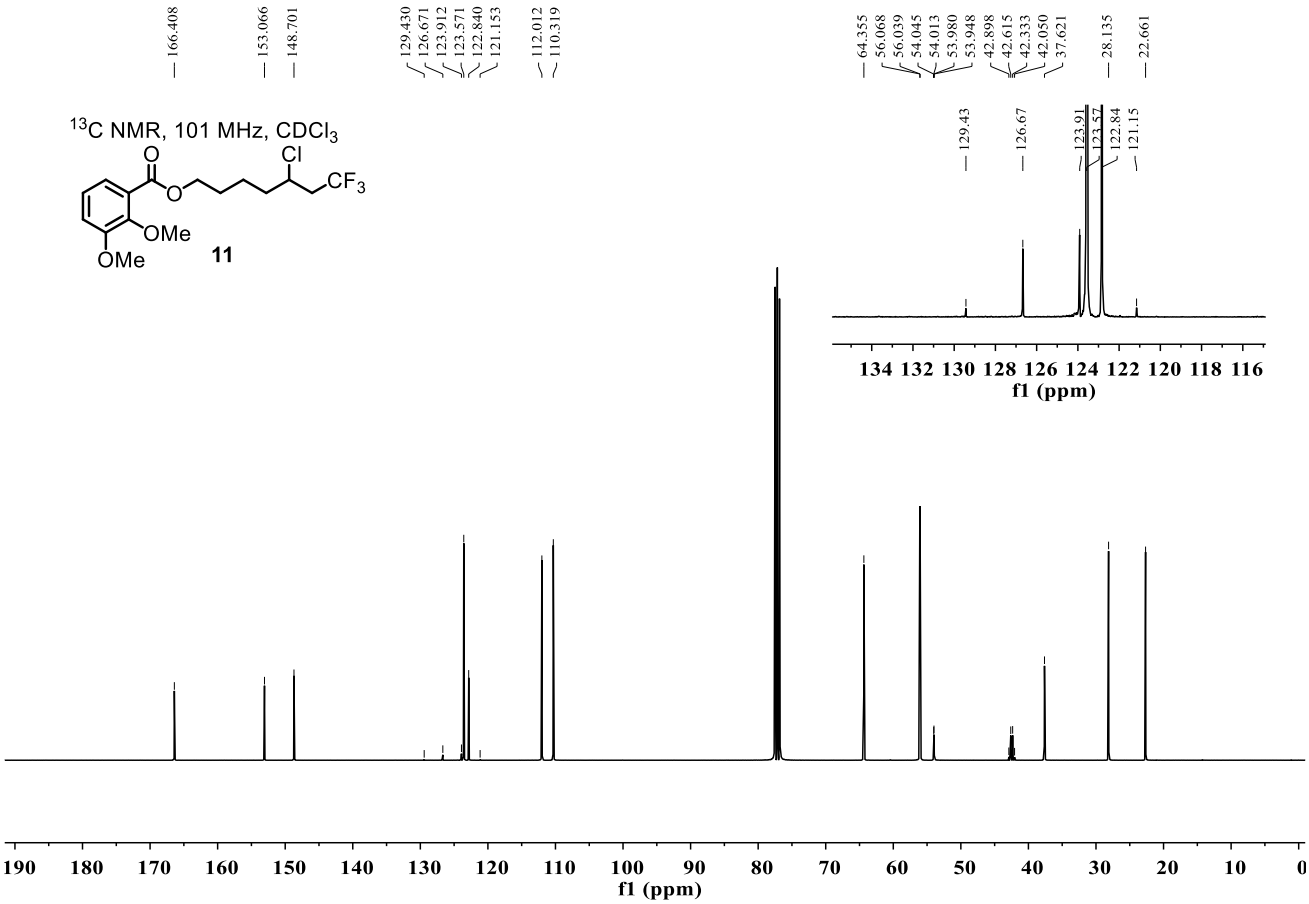


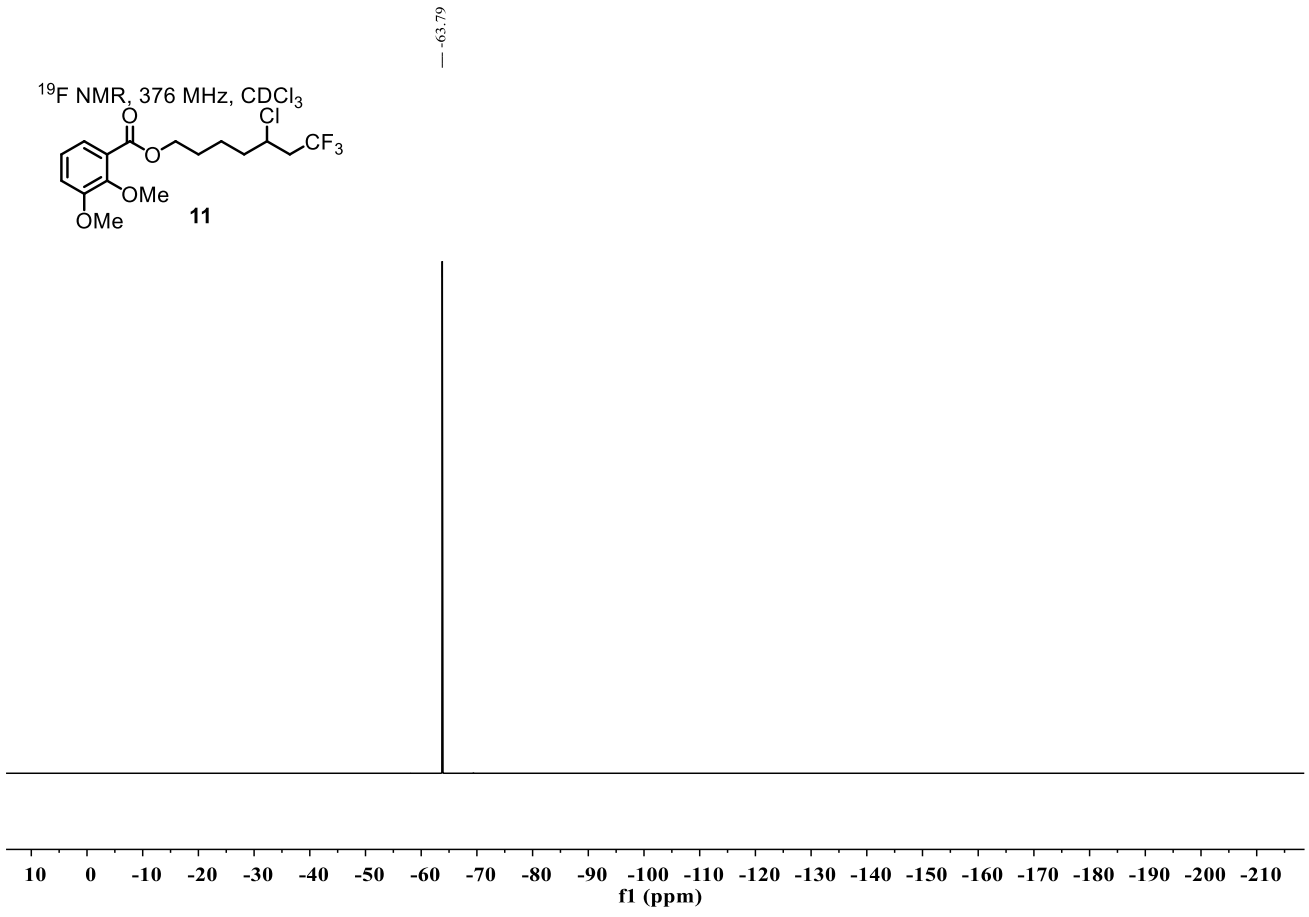
^{1}H NMR, 400 MHz, $CDCl_3$

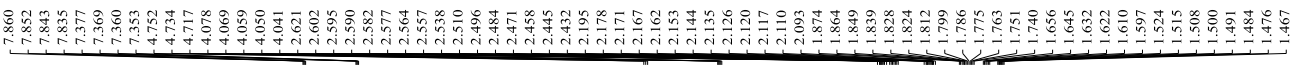


11

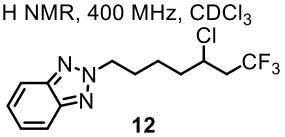



166.408
153.066
148.701
129.430
126.671
123.912
123.571
122.840
121.153
112.012
110.319
64.355
56.068
56.039
54.045
54.013
53.980
53.948
42.898
42.615
42.333
42.050
37.621
28.135
22.661
129.43
126.67
123.91
123.57
122.84
121.15
134 132 130 128 126 124 122 120 118 116
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
13C NMR, 101 MHz, CDCl3
O
Cl
O
CF3
OMe
OMe
11

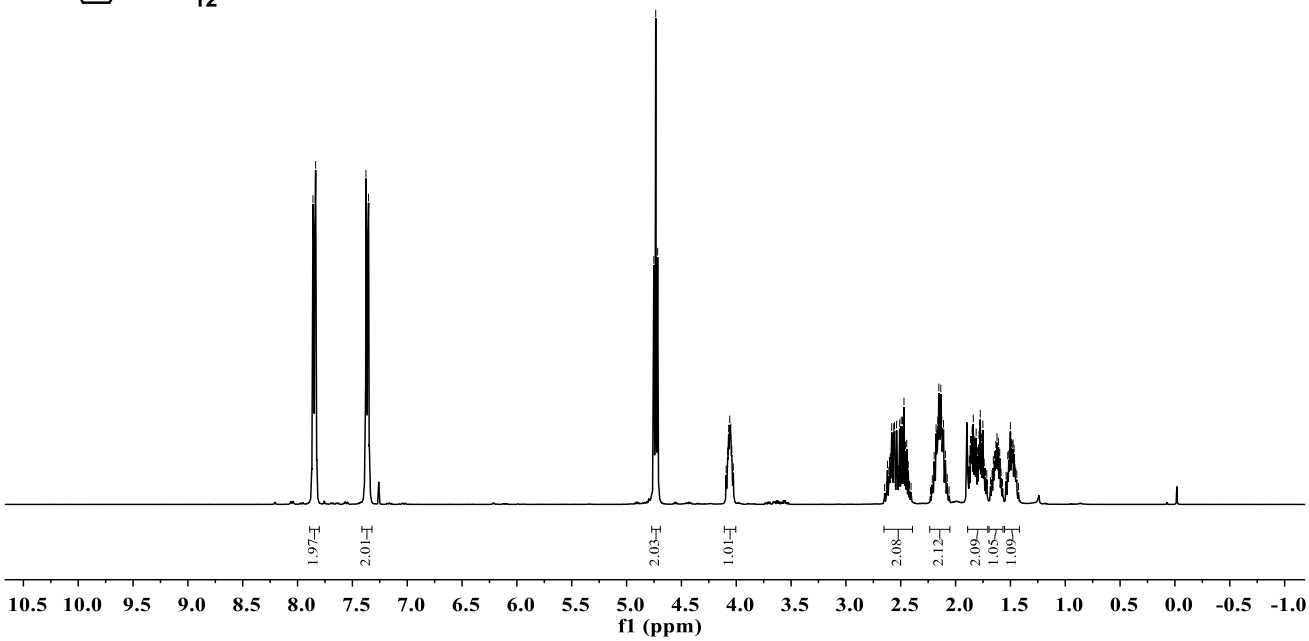

-63.79
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
19F NMR, 376 MHz, CDCl3
O
Cl
O
CF3
OMe
OMe
11

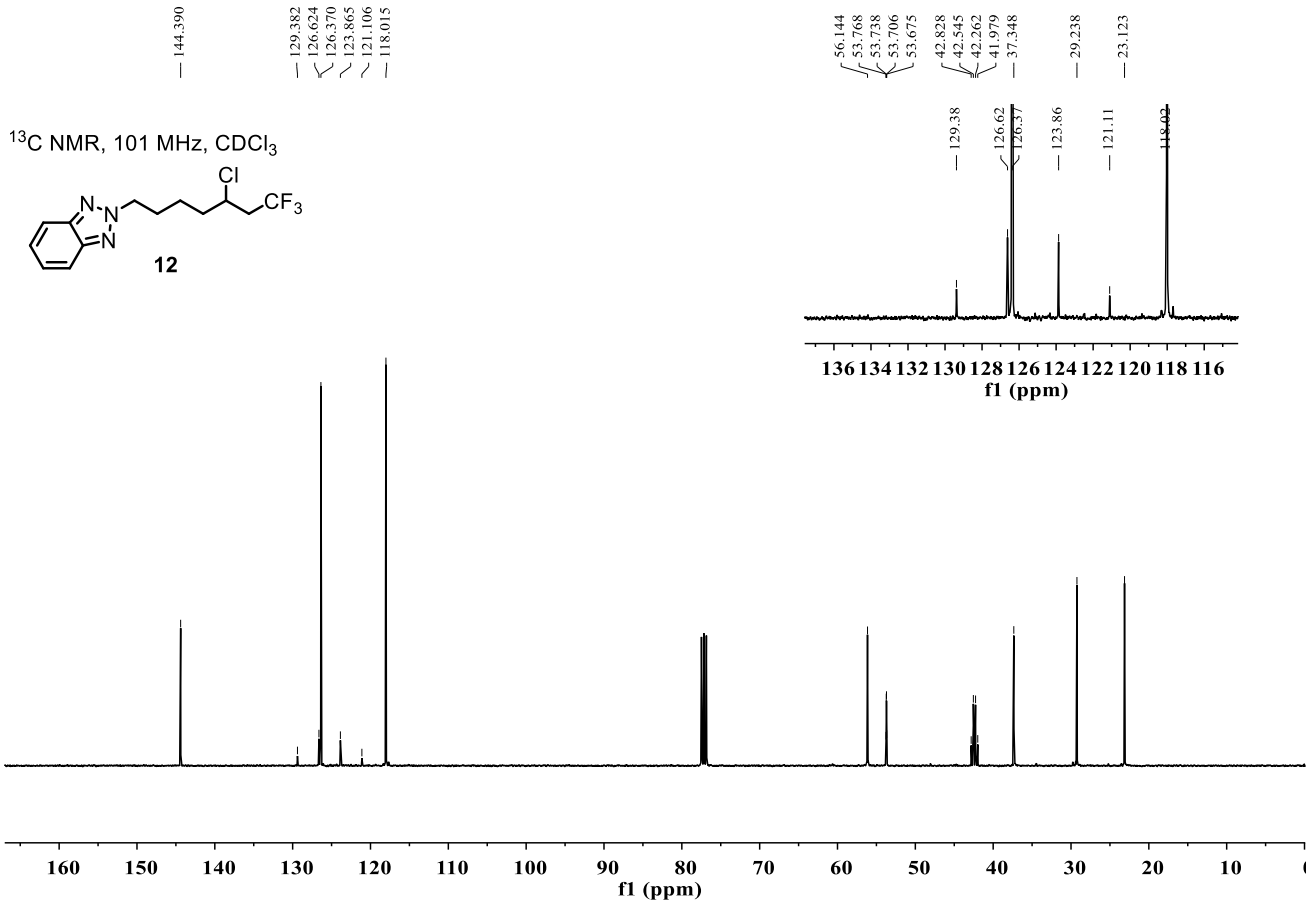


^{1}H NMR, 400 MHz, $CDCl_3$



12

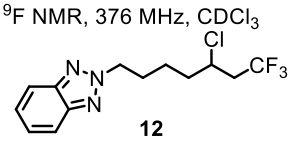




^{13}C NMR, 101 MHz, $CDCl_3$

12

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



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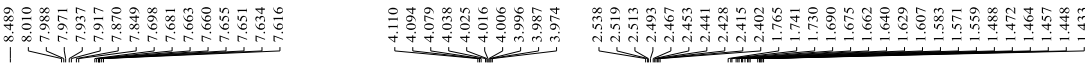
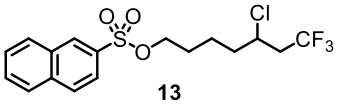
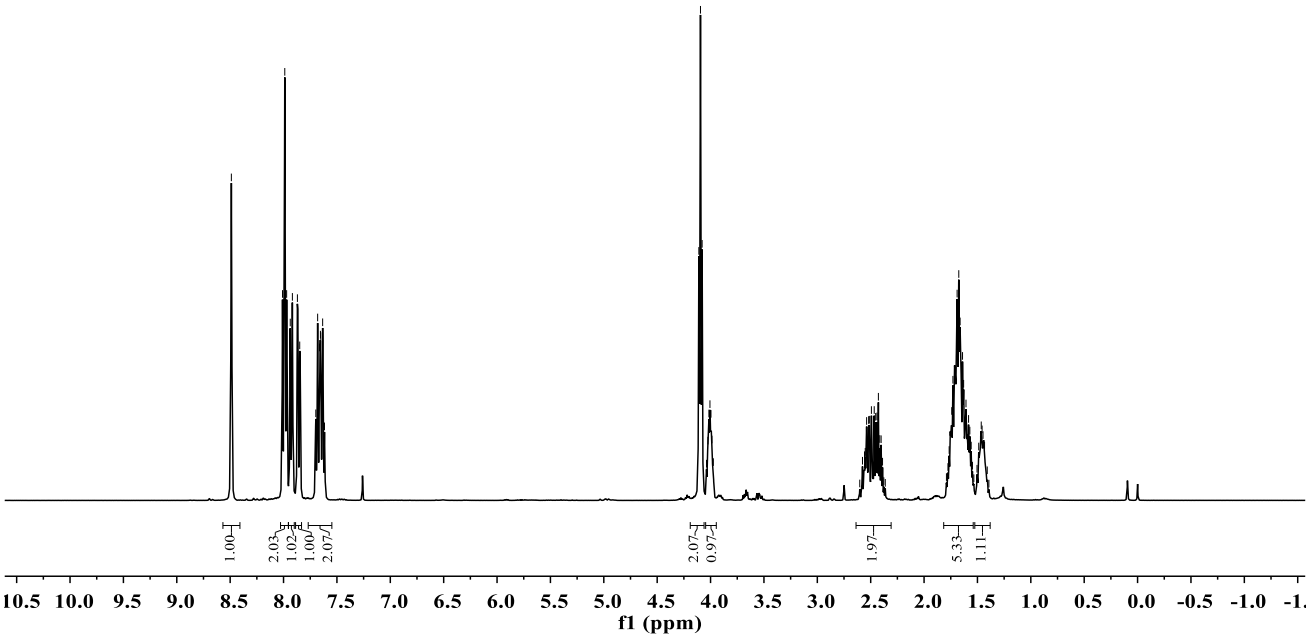
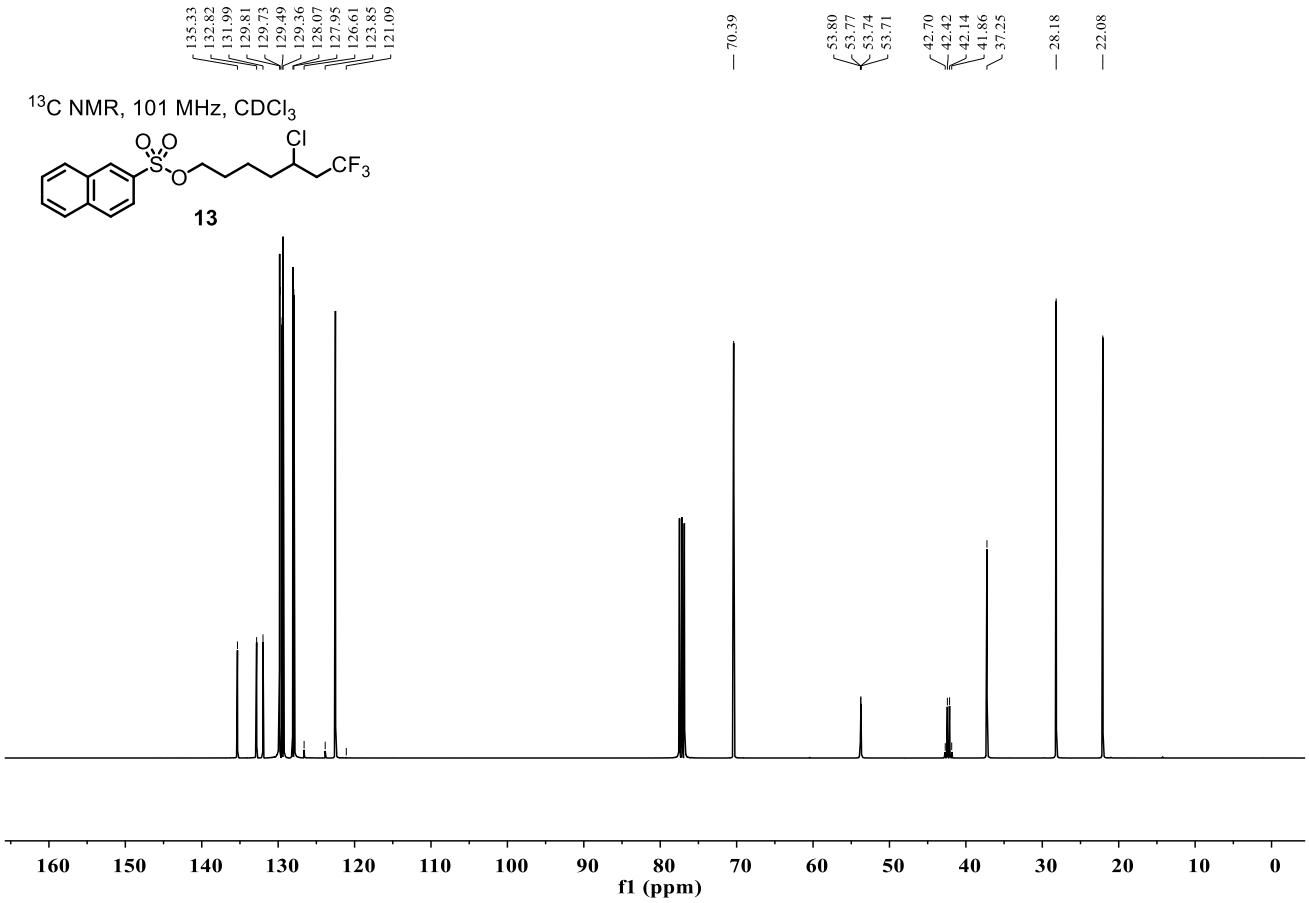


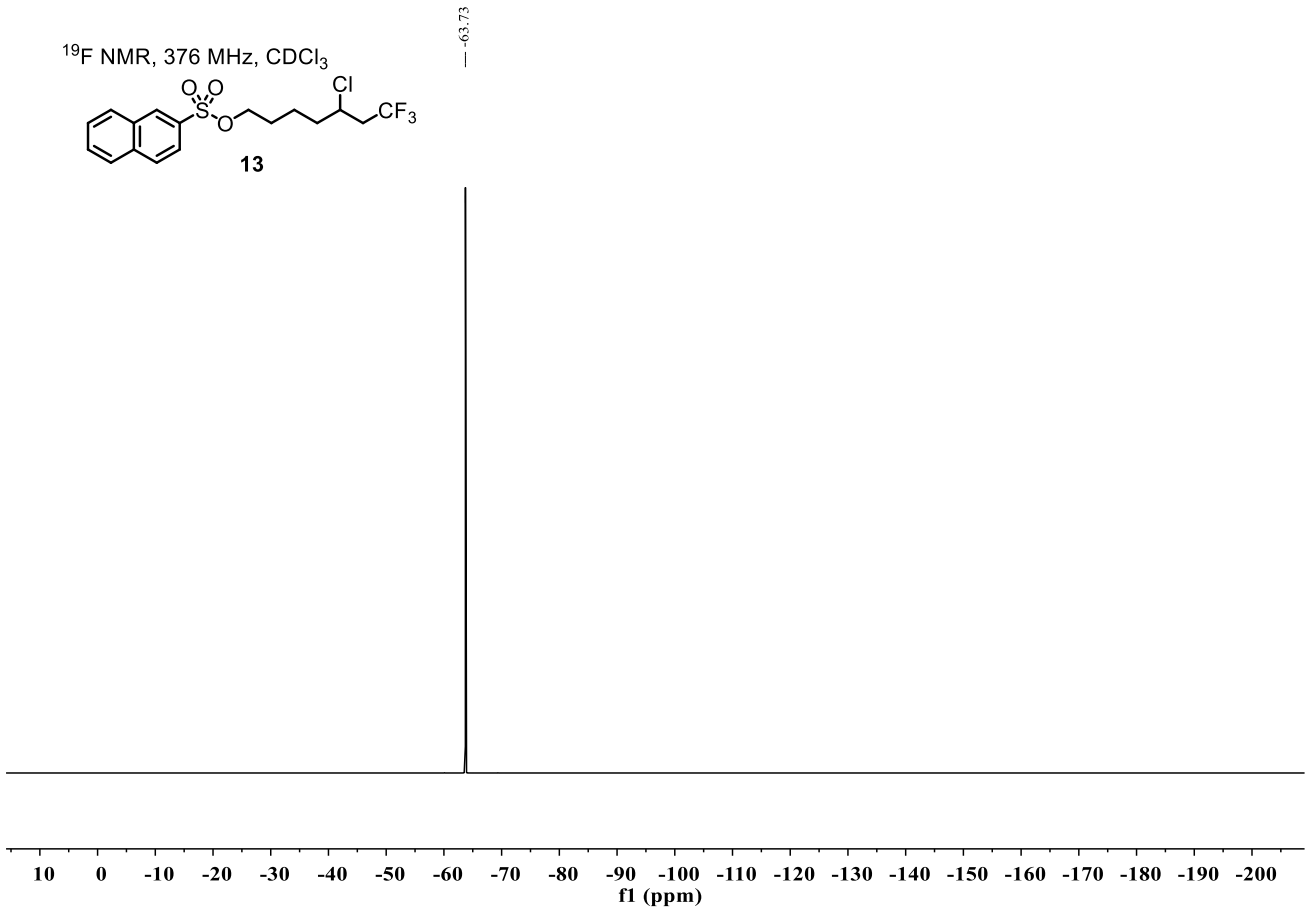
^{1}H NMR, 400 MHz, $CDCl_3$

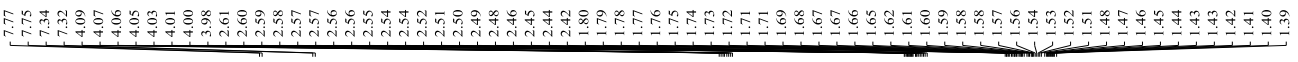


13

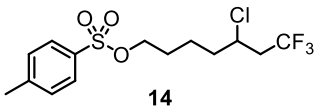



135.33
132.82
131.99
129.81
129.73
129.49
129.36
128.07
127.95
126.61
123.85
121.09
70.39
53.80
53.77
53.74
53.71
42.70
42.42
42.14
41.86
37.25
28.18
22.08
13C NMR, 101 MHz, CDCl3
O
O
S
O
Cl
CF3
13
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

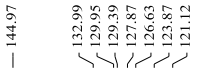

-63.73
19F NMR, 376 MHz, CDCl3
O
O
S
O
Cl
CF3
13
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

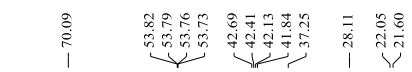


^{1}H NMR, 400 MHz, $CDCl_3$

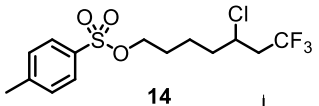


14

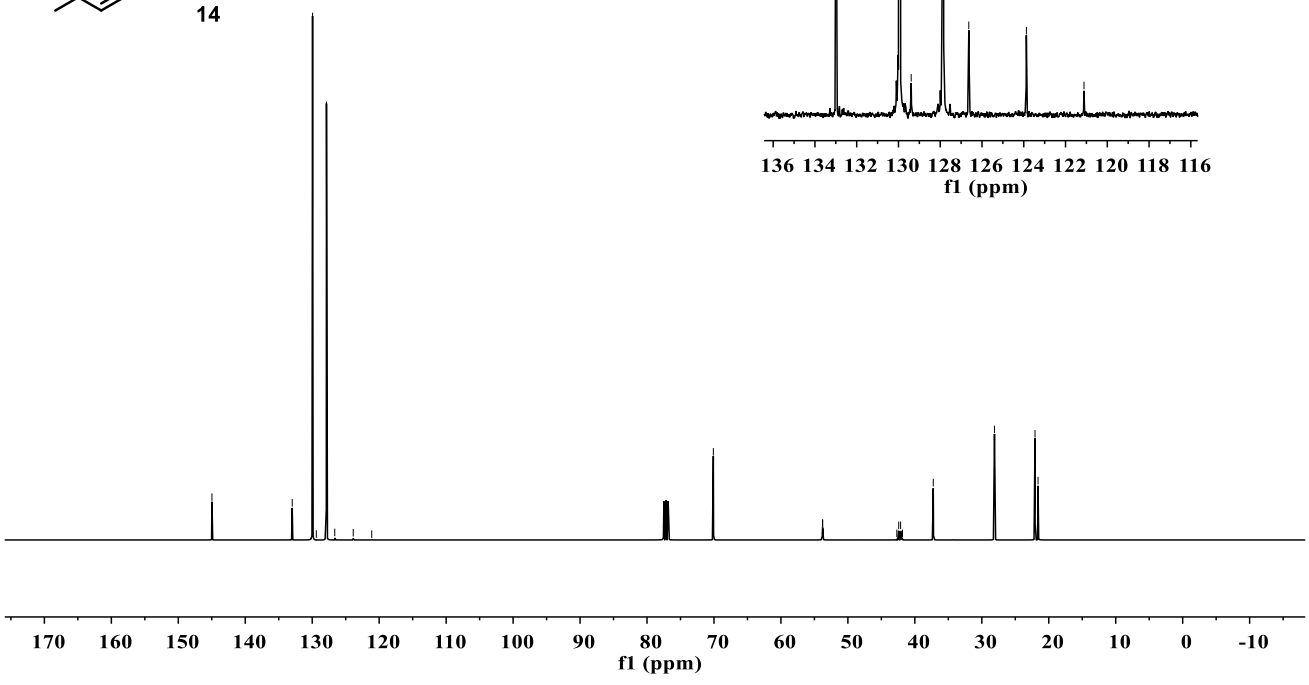




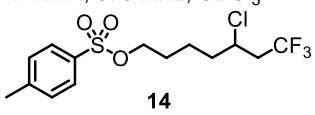
^{13}C NMR, 101 MHz, $CDCl_3$



14

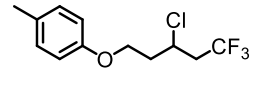


^{19}F NMR, 376 MHz, $CDCl_3$



14

^{1}H NMR, 400 MHz, $CDCl_3$



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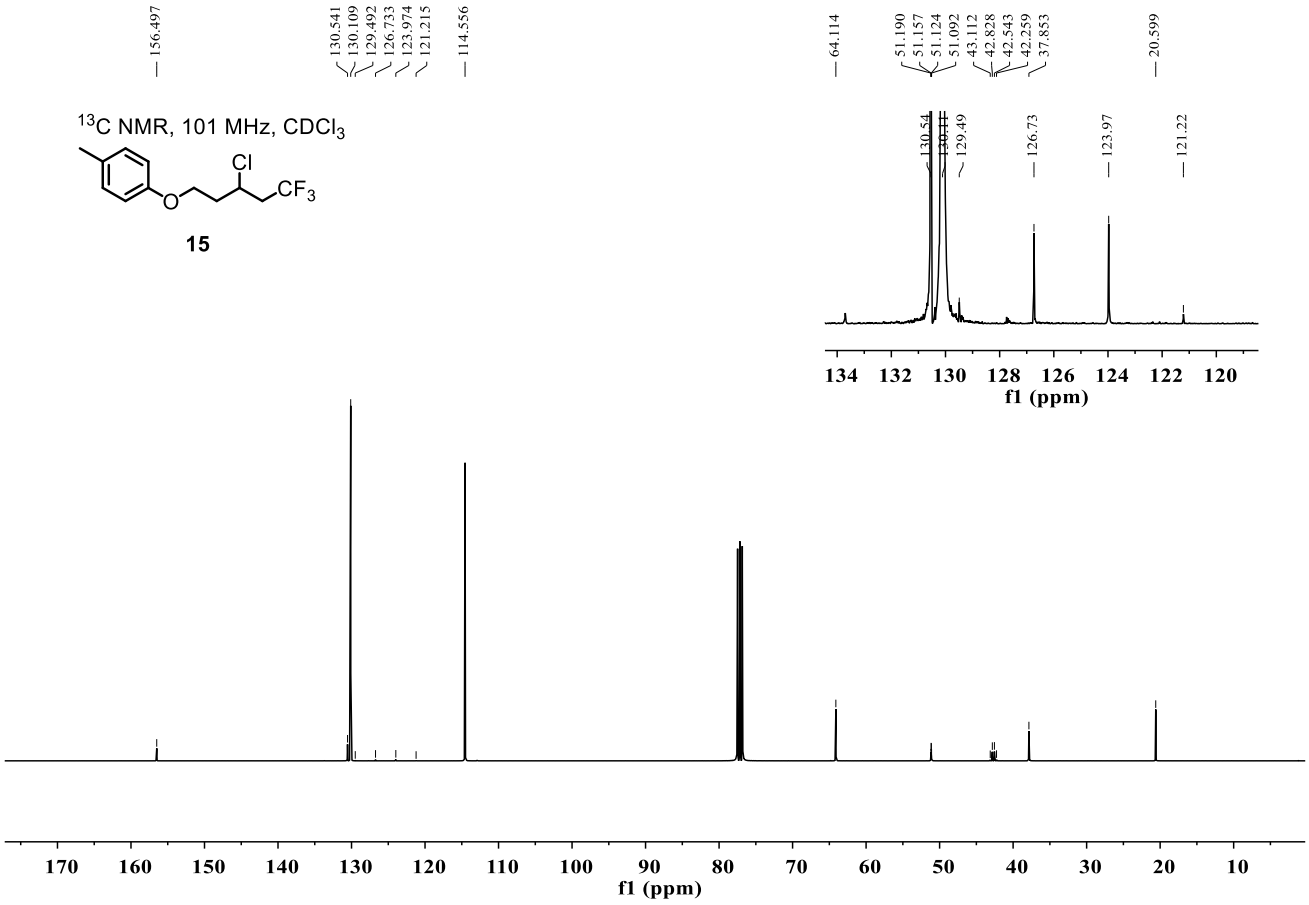
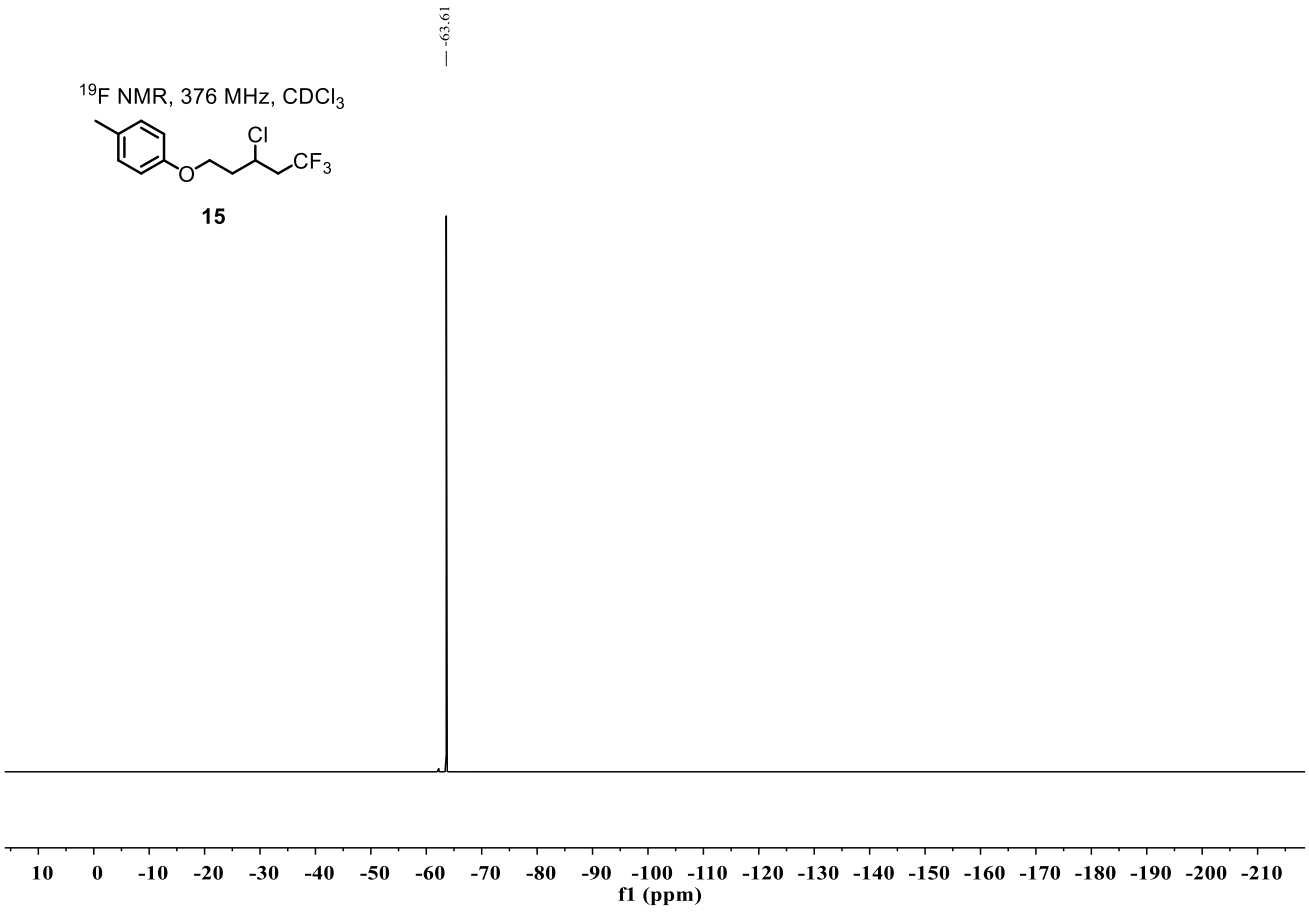
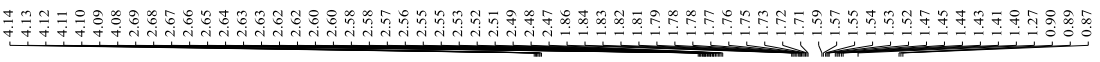
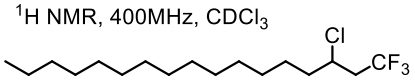

156.497
130.541
130.109
129.492
126.733
123.974
121.215
114.556
64.114
51.190
51.157
51.124
51.092
43.112
42.828
42.543
42.259
37.853
20.599
^{13}C NMR, 101 MHz, $CDCl_3$
Cl
CF_3
O
15
130.54
130.11
129.49
126.73
123.97
121.22
134 132 130 128 126 124 122 120
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-63.61
^{19}F NMR, 376 MHz, $CDCl_3$
Cl
CF_3
O
15
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

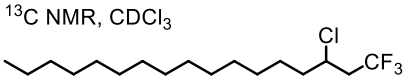


^{1}H NMR, 400MHz, $CDCl_3$

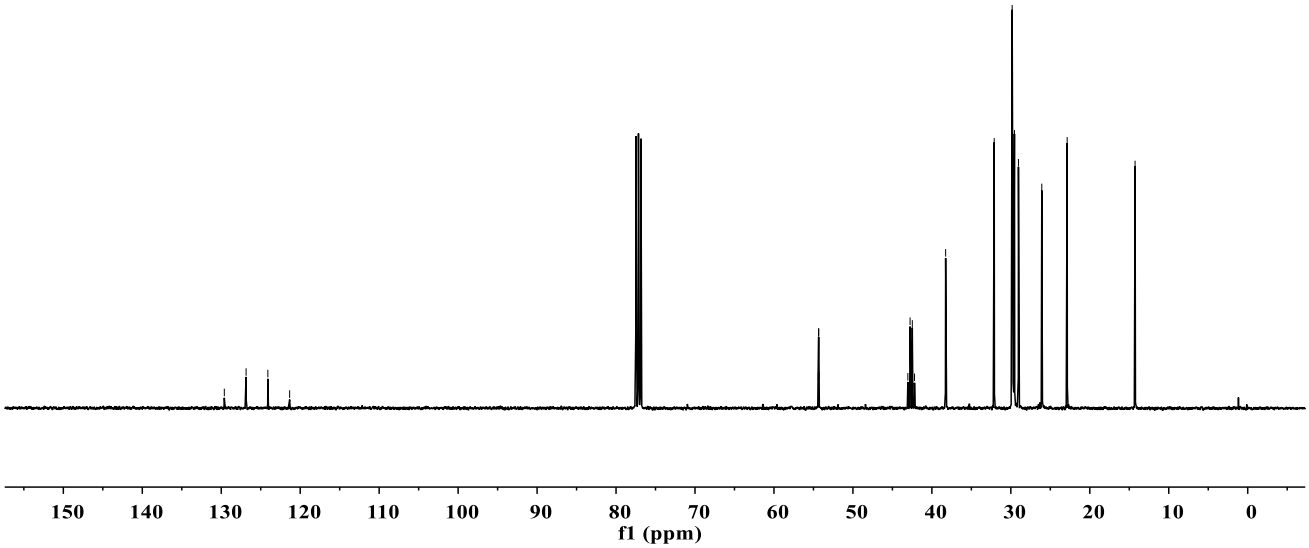


16

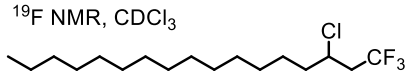
^{13}C NMR, $CDCl_3$



16

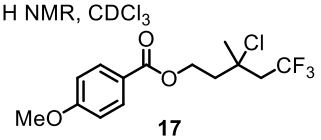


^{19}F NMR, $CDCl_3$

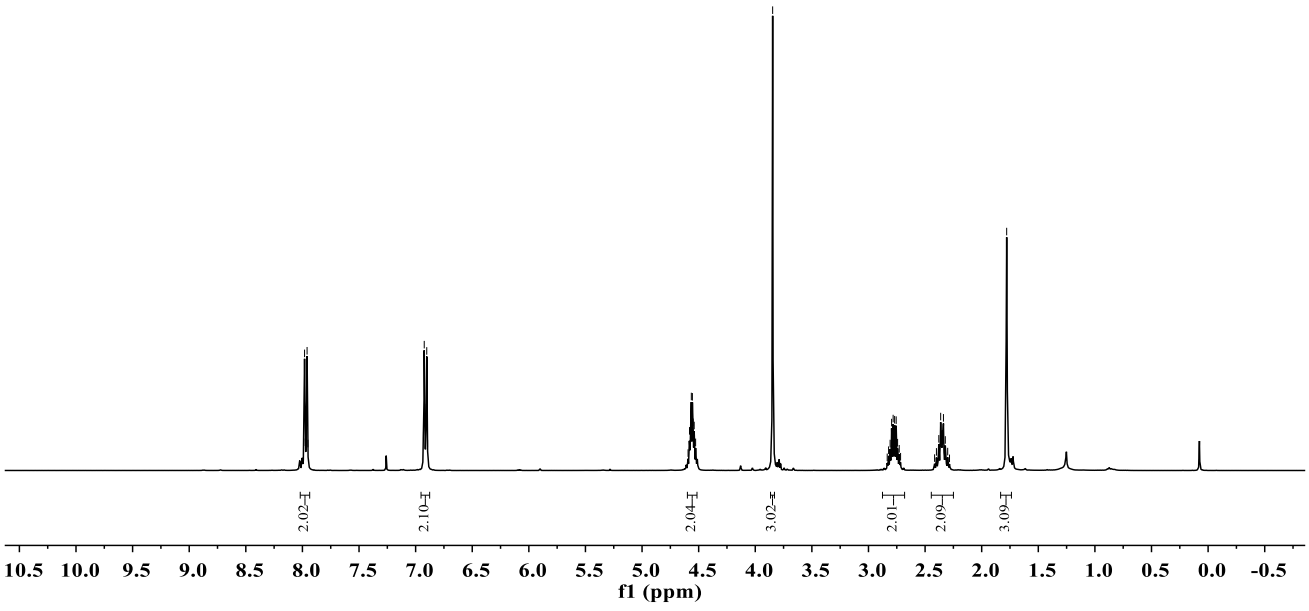


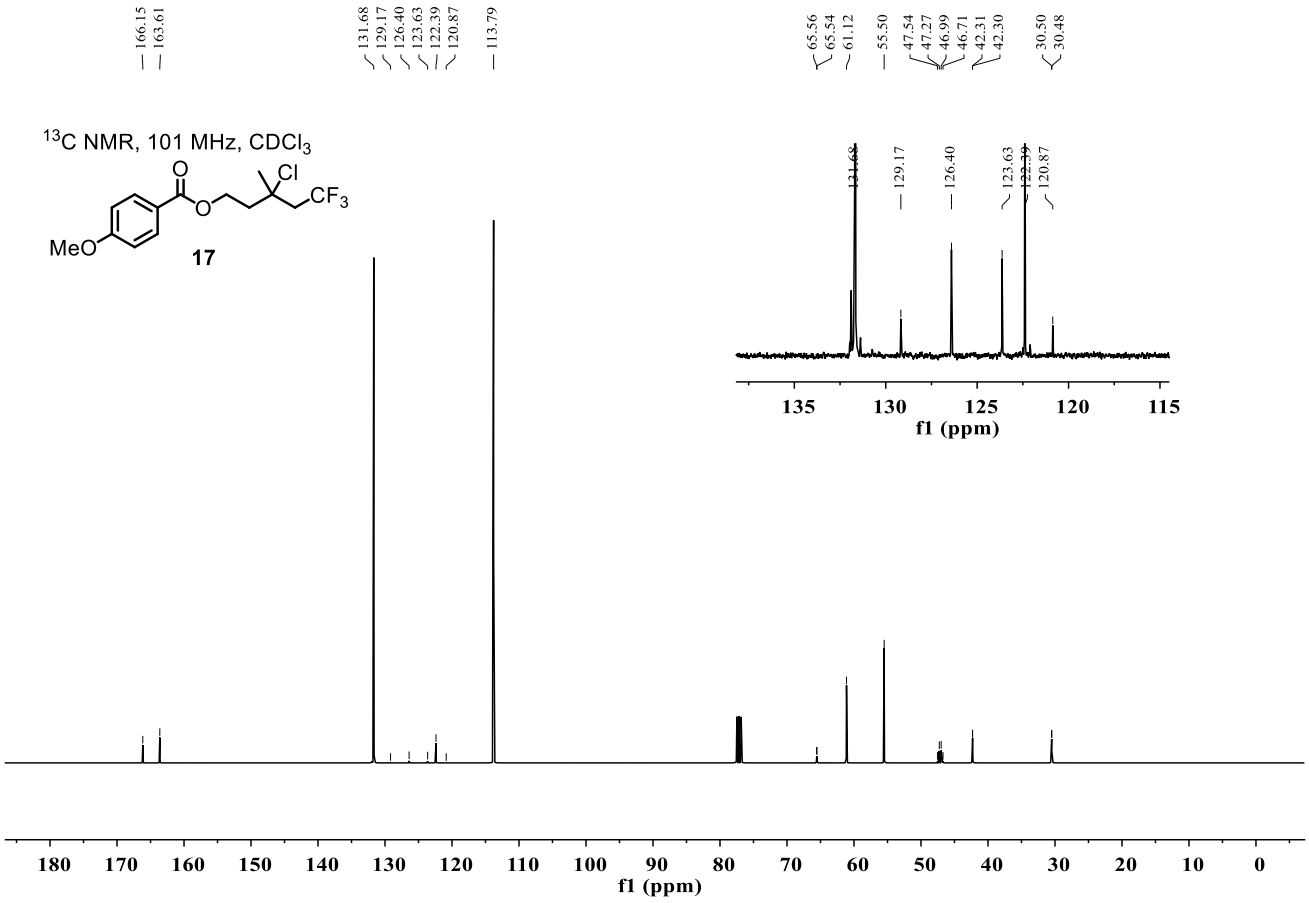
16

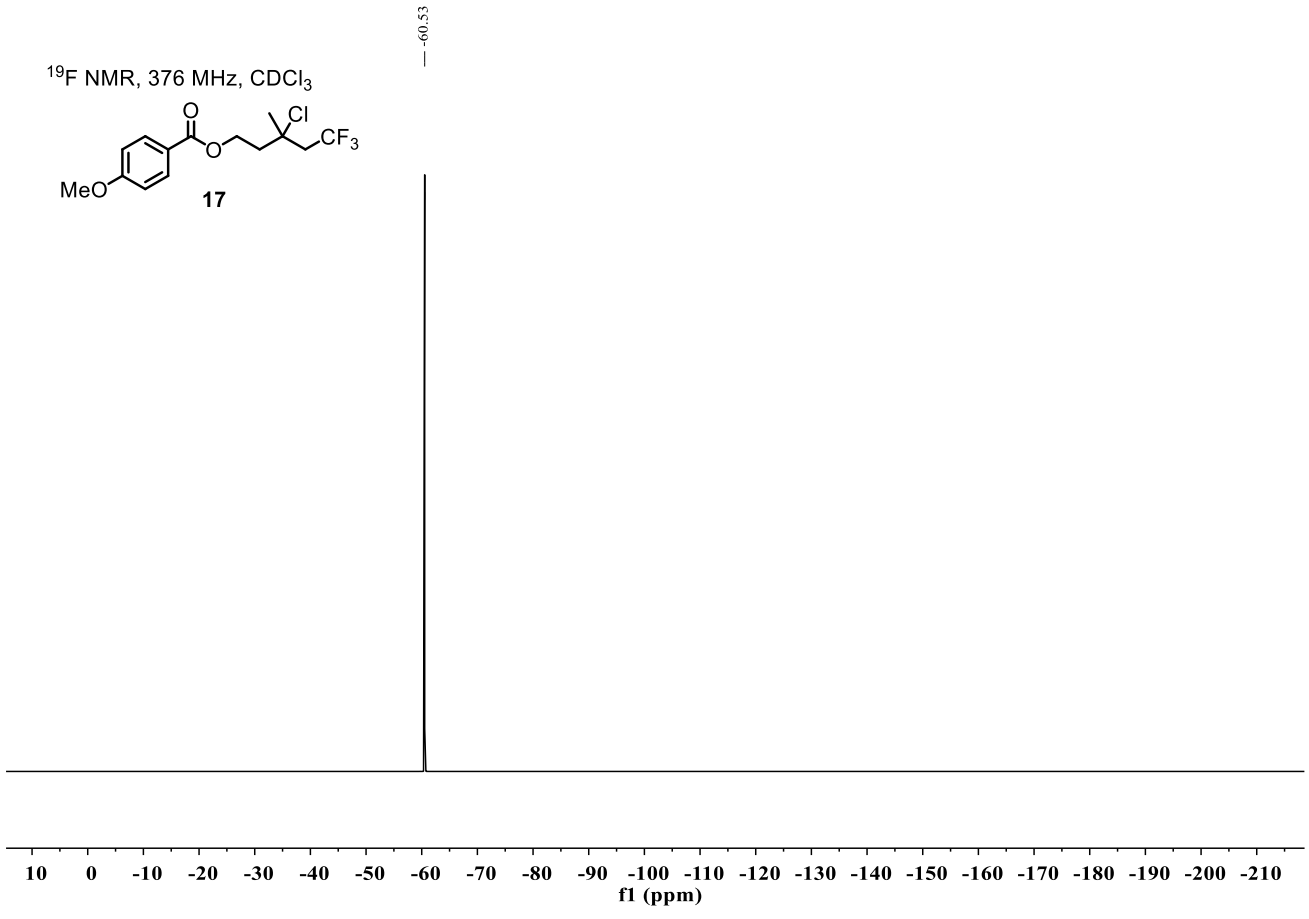
^{1}H NMR, $CDCl_3$



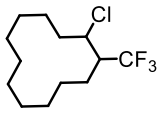
17




166.15
163.61
131.68
129.17
126.40
123.63
122.39
120.87
113.79
65.56
65.54
61.12
55.50
47.54
47.27
46.99
46.71
42.31
42.30
30.50
30.48
13C NMR, 101 MHz, CDCl3
O
Cl
CF3
O
MeO
17
f1 (ppm)

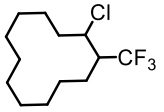

-60.53
19F NMR, 376 MHz, CDCl3
O
Cl
CF3
O
MeO
17
f1 (ppm)

^{1}H NMR, 400 MHz, $CDCl_3$



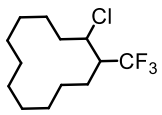
18, d.r. = 4:1

^{13}C NMR, 101 MHz, $CDCl_3$



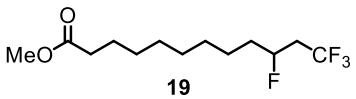
18, d.r. = 4:1

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

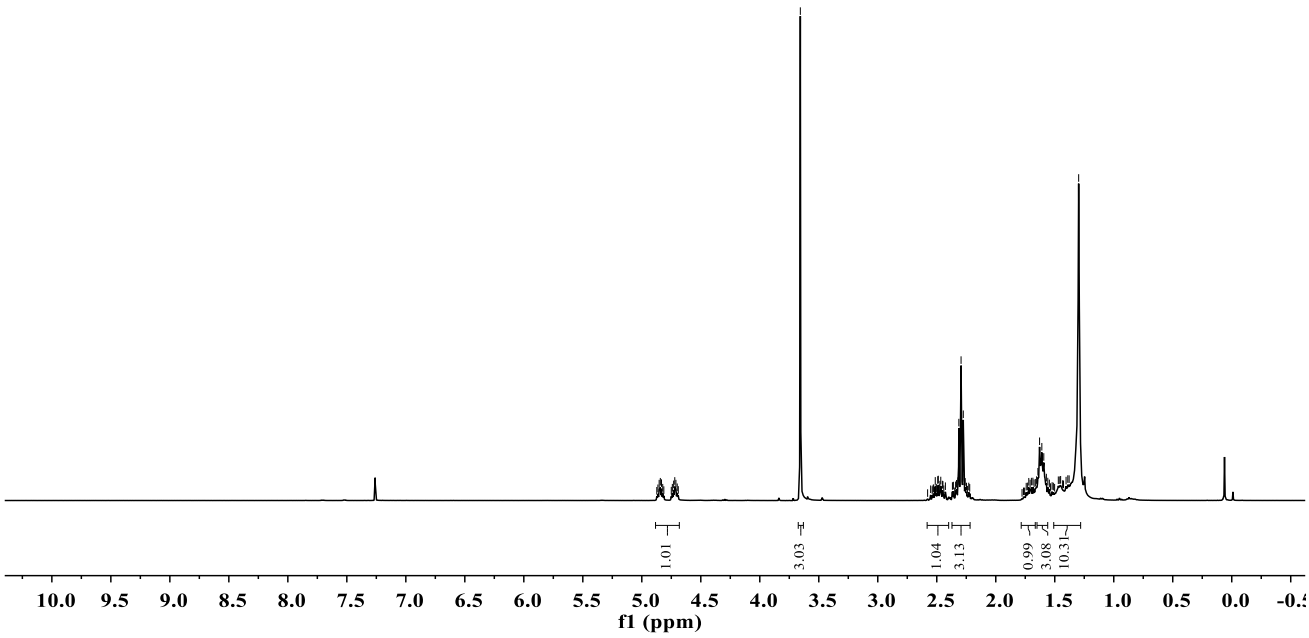


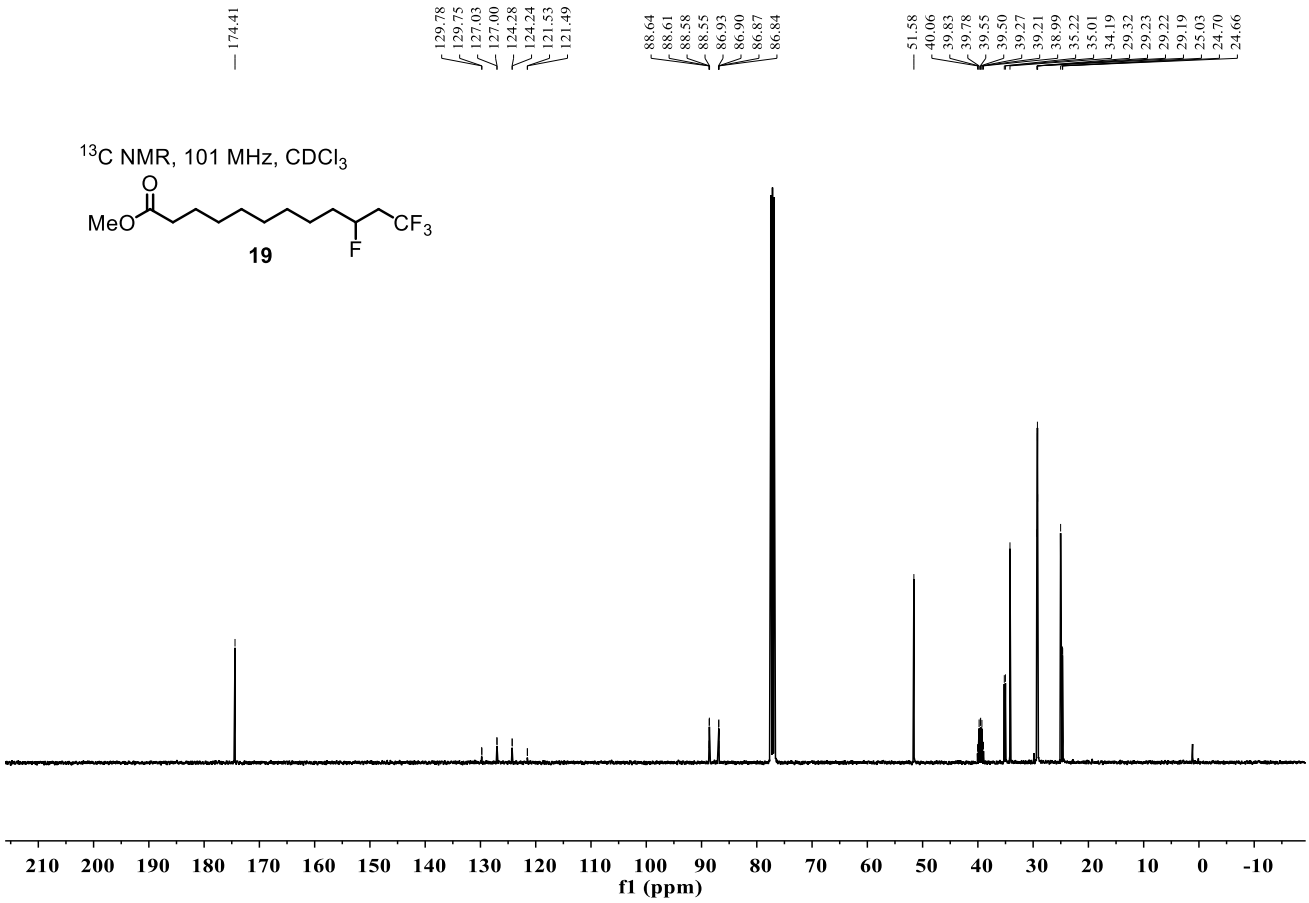
18, d.r. = 4:1

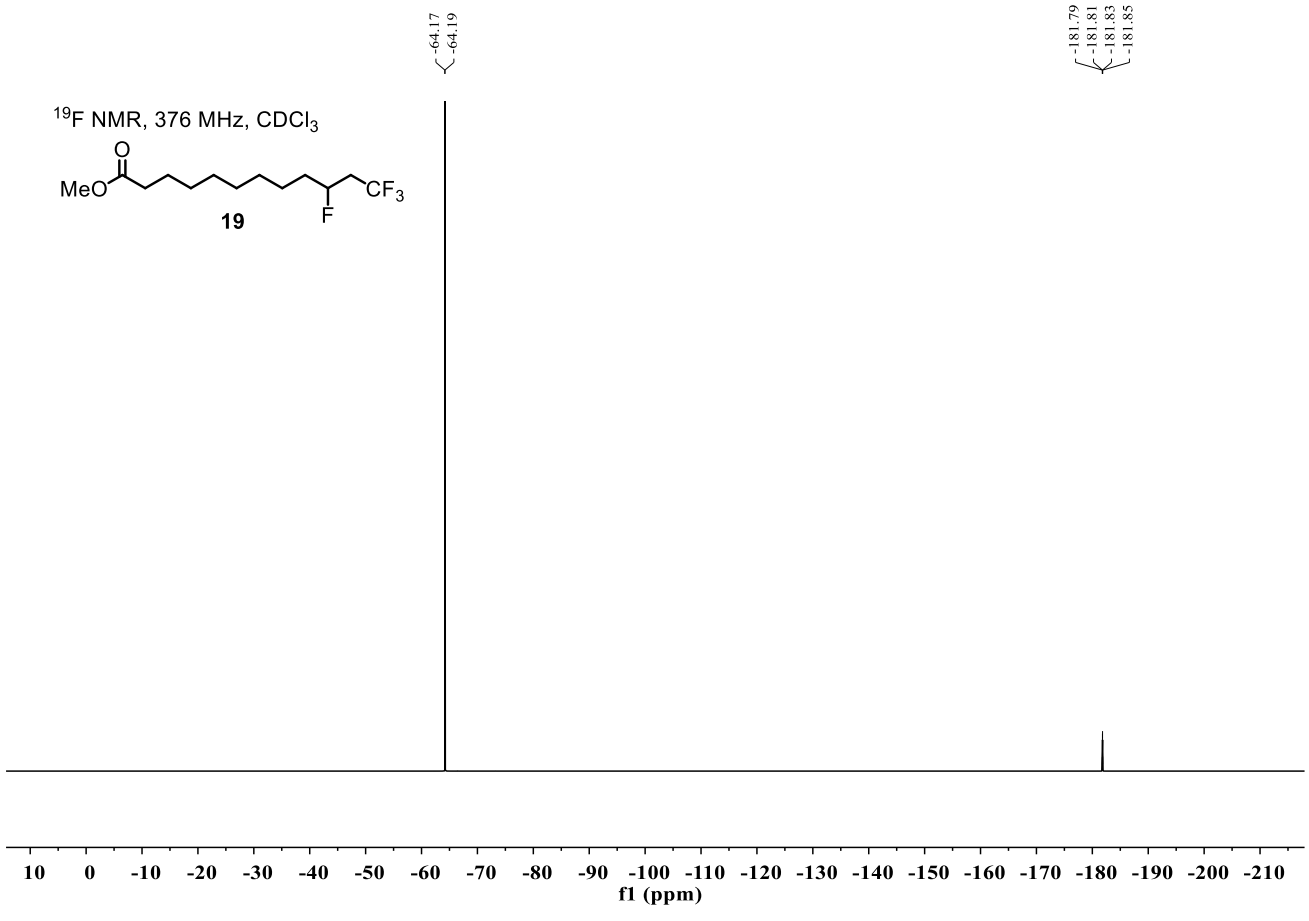
^{1}H NMR, 400 MHz, $CDCl_3$

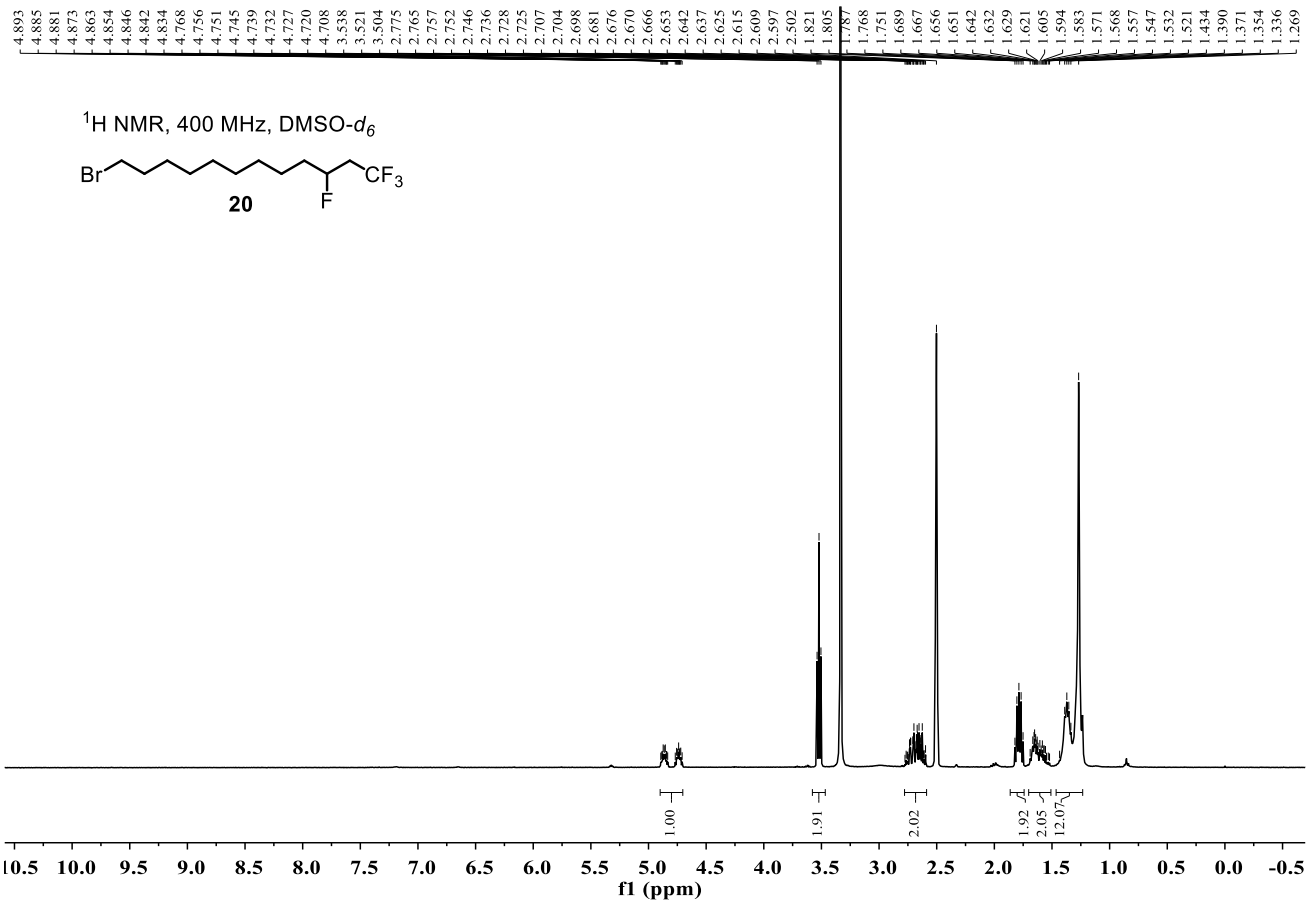


19



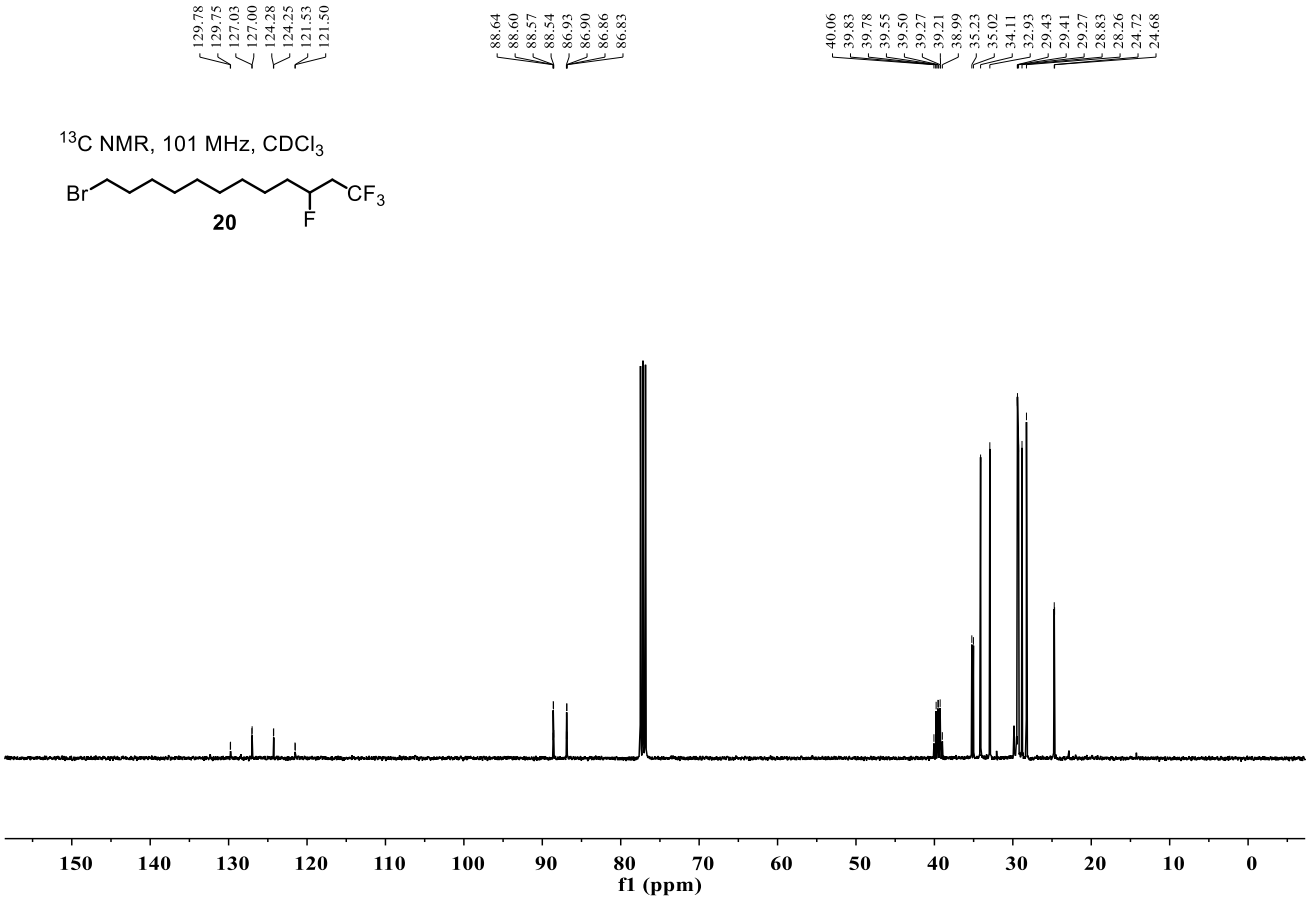

174.41
129.78
129.75
127.03
127.00
124.28
124.24
121.53
121.49
88.64
88.61
88.58
88.55
86.93
86.90
86.87
86.84
51.58
40.06
39.83
39.78
39.55
39.50
39.27
39.21
38.99
35.22
35.01
34.19
29.32
29.23
29.22
29.19
25.03
24.70
24.66
13C NMR, 101 MHz, CDCl3
MeO
O
CF3
F
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-64.17
-64.19
-181.79
-181.81
-181.83
-181.85
19F NMR, 376 MHz, CDCl3
MeO
O
CF3
F
19
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



^{1}H NMR, 400 MHz, DMSO-d_6

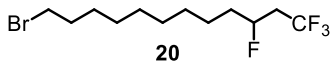
20



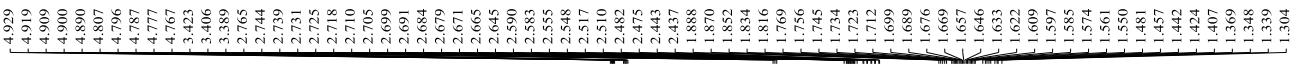
^{13}C NMR, 101 MHz, $CDCl_3$

20

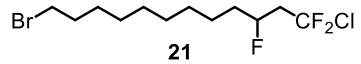
^{19}F NMR, 376 MHz, DMSO-d_6



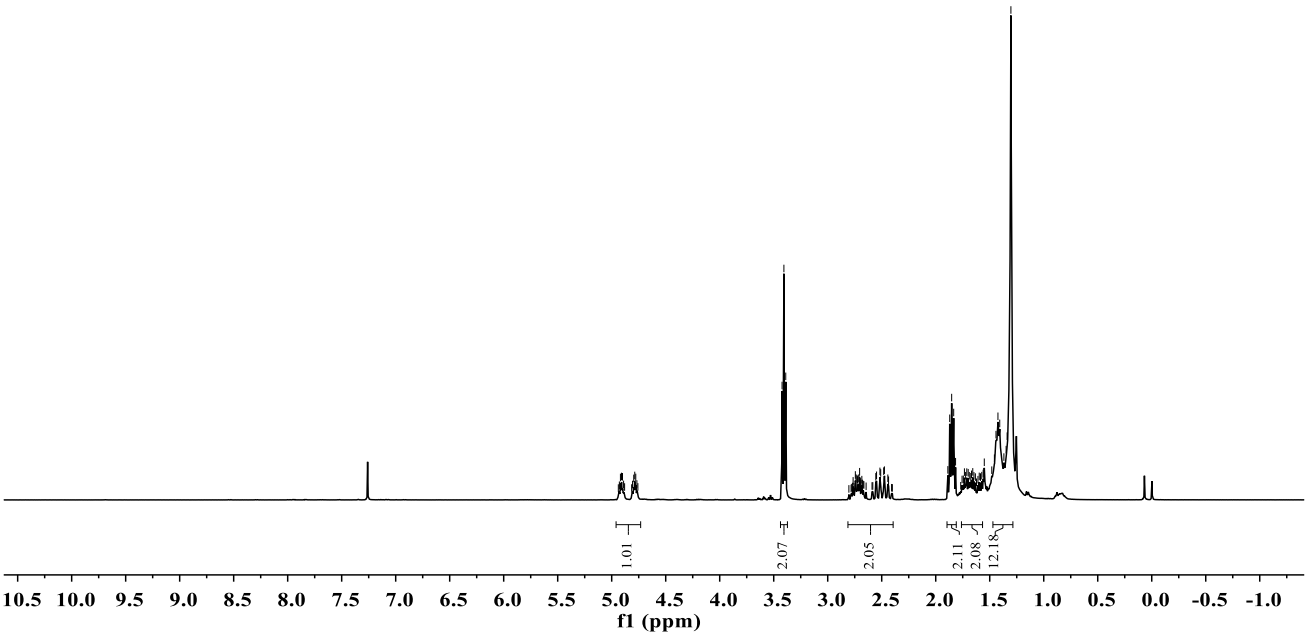
20

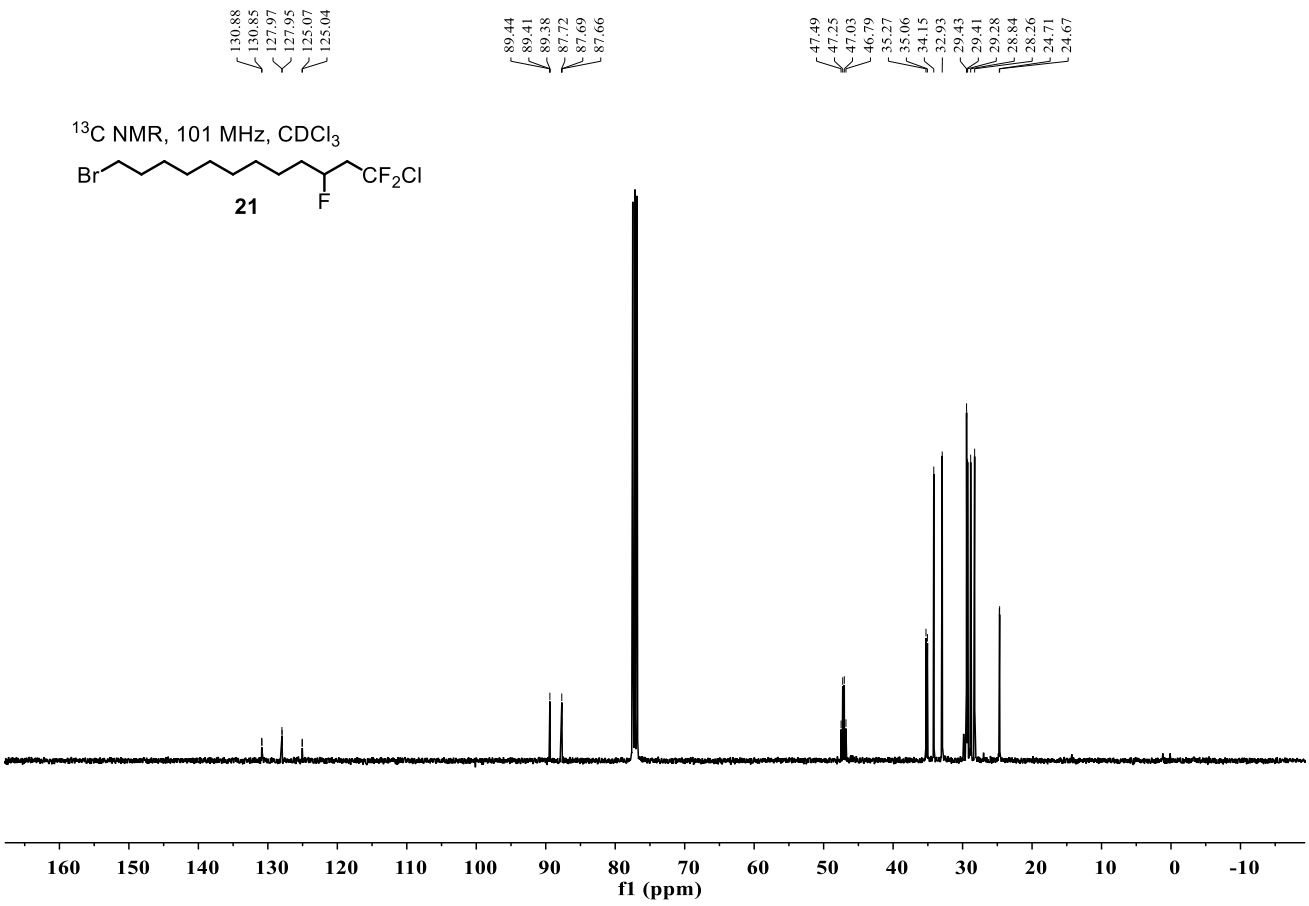


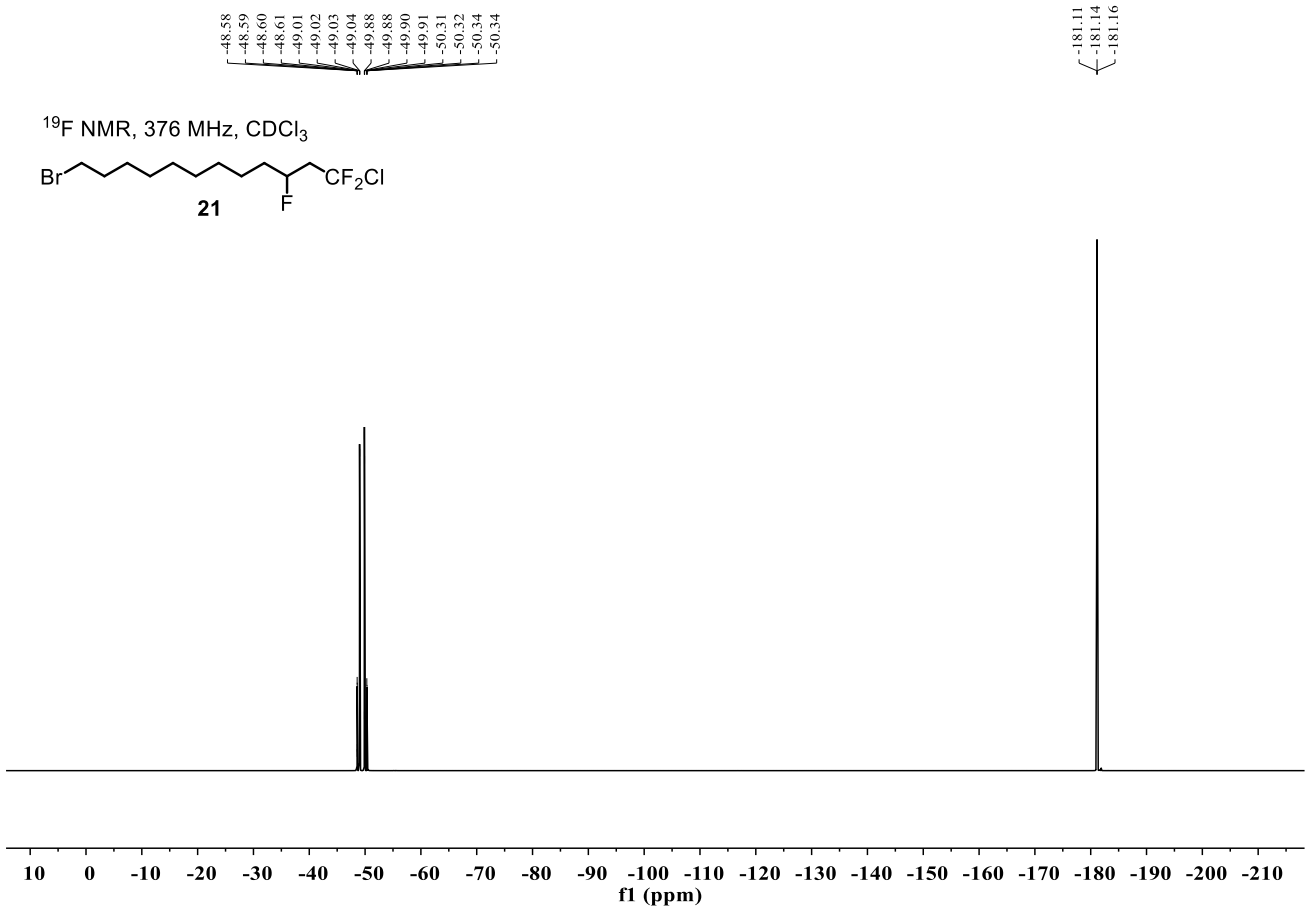
^{1}H NMR, 400 MHz, $CDCl_3$

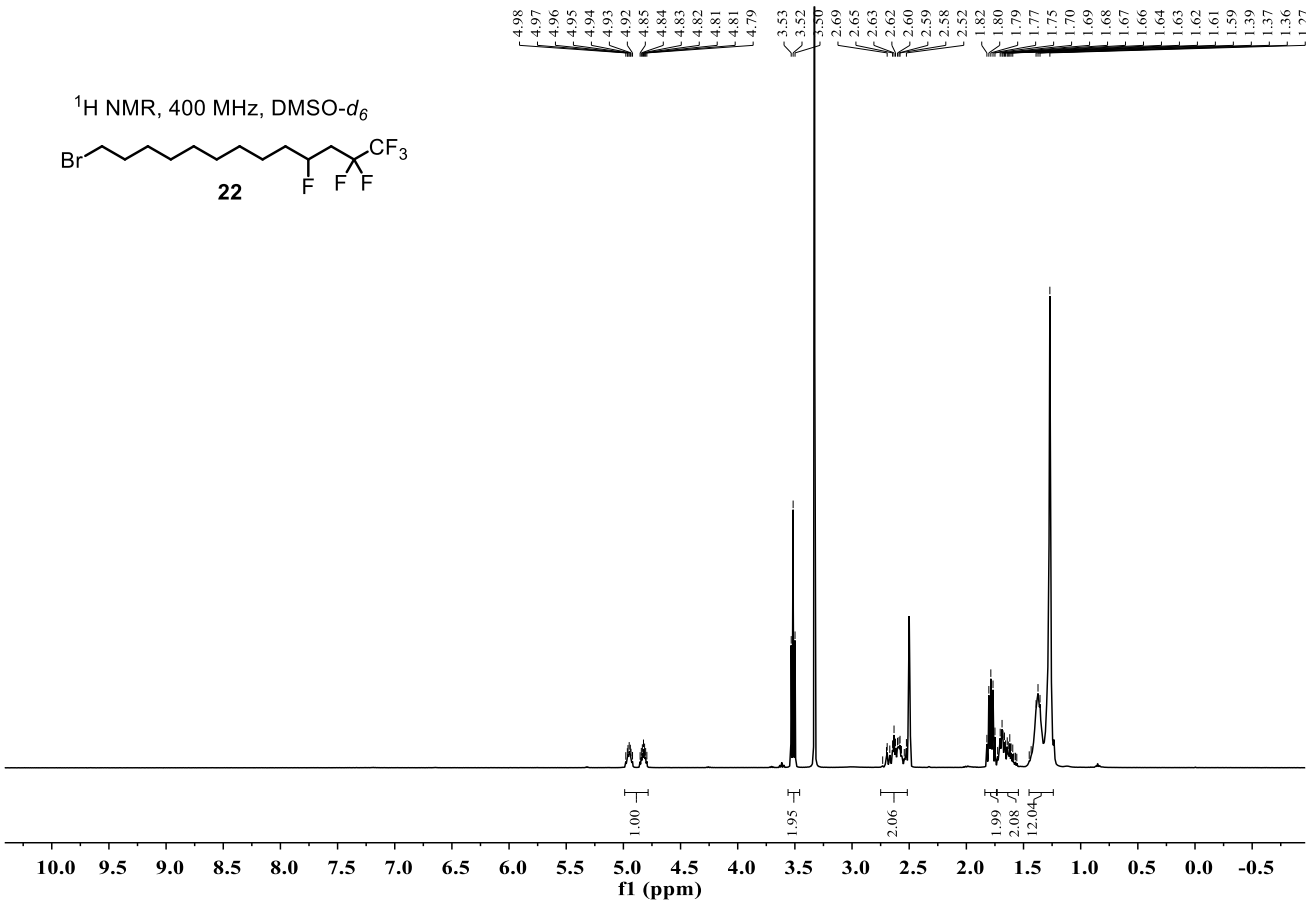


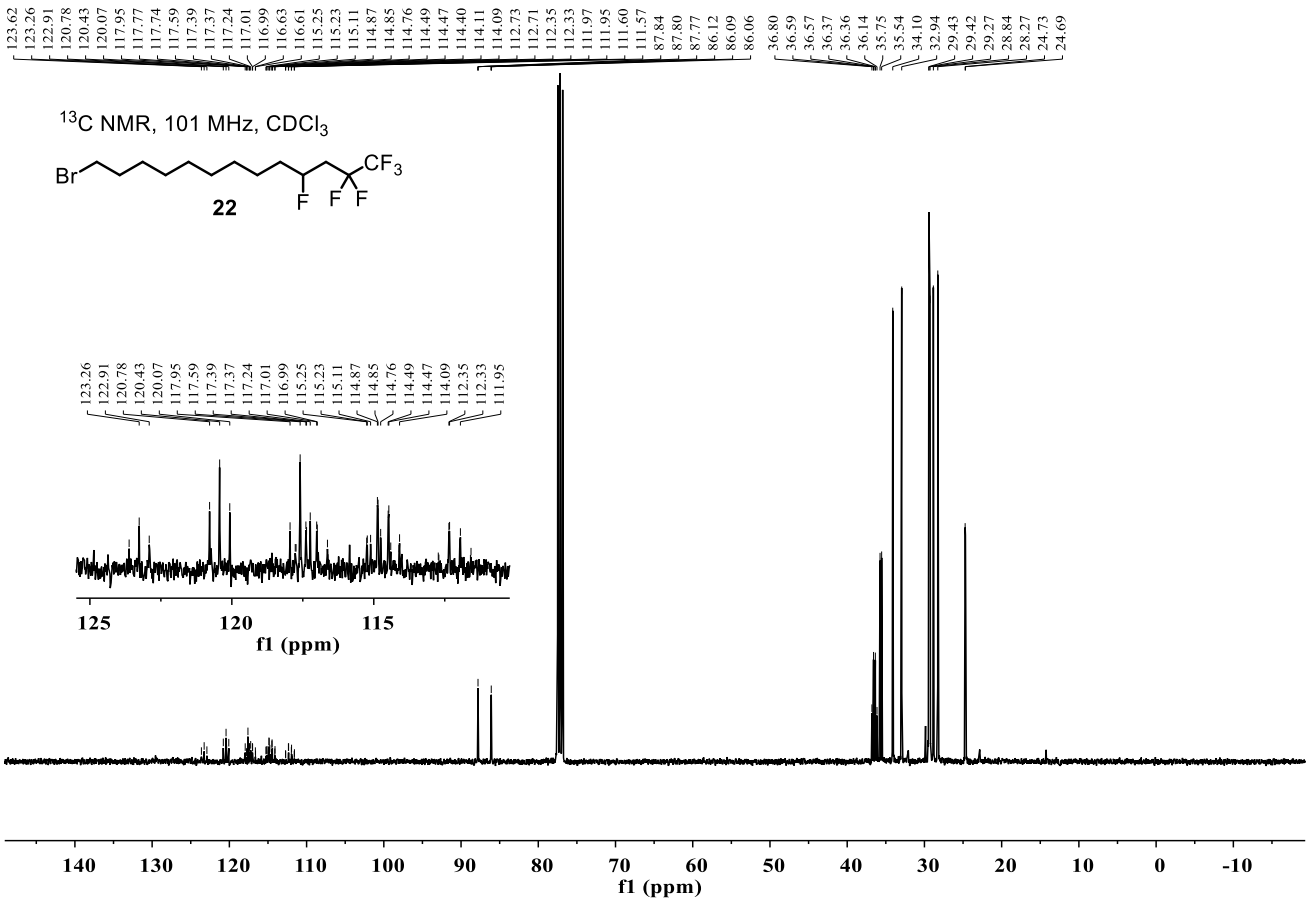
21

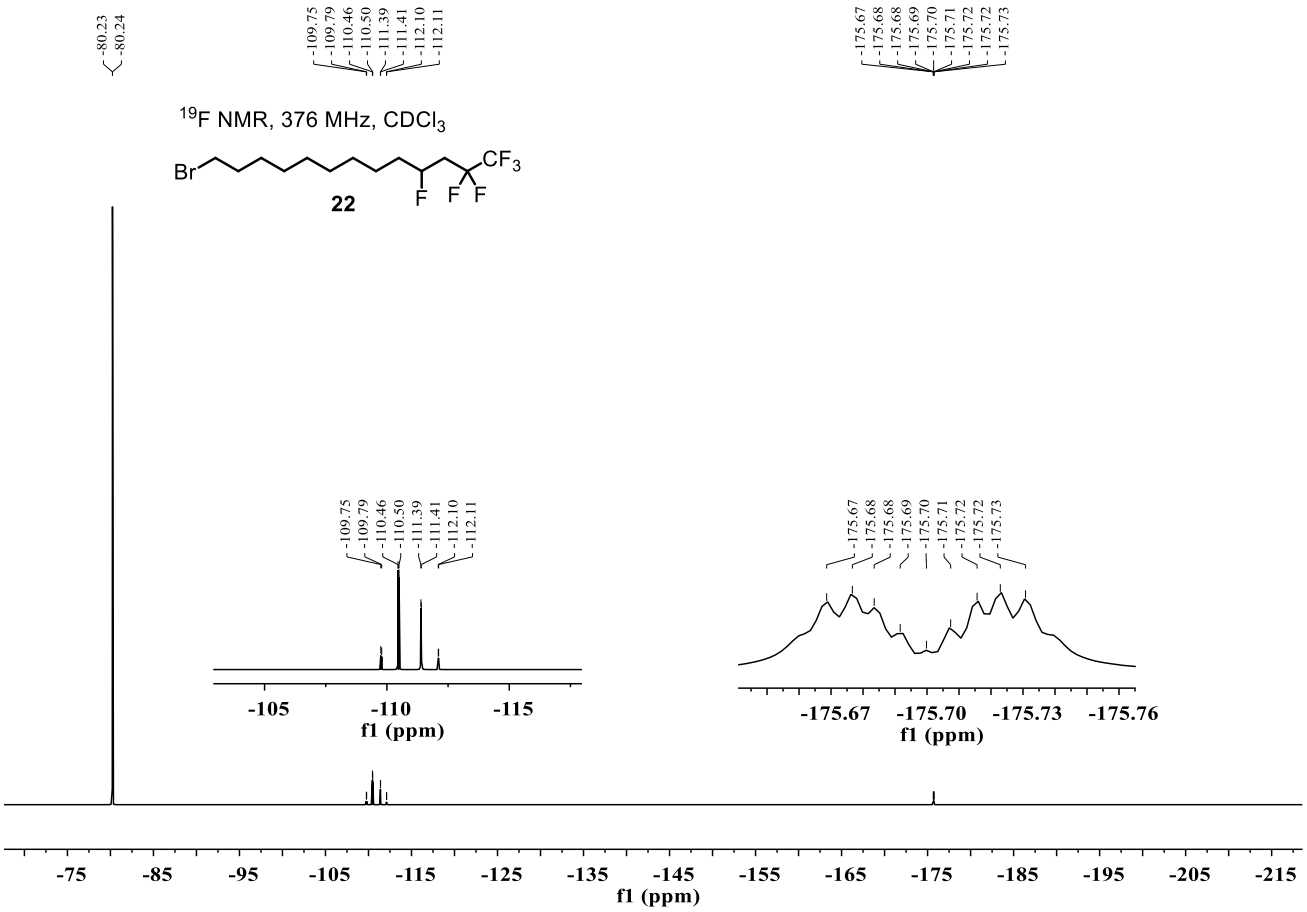


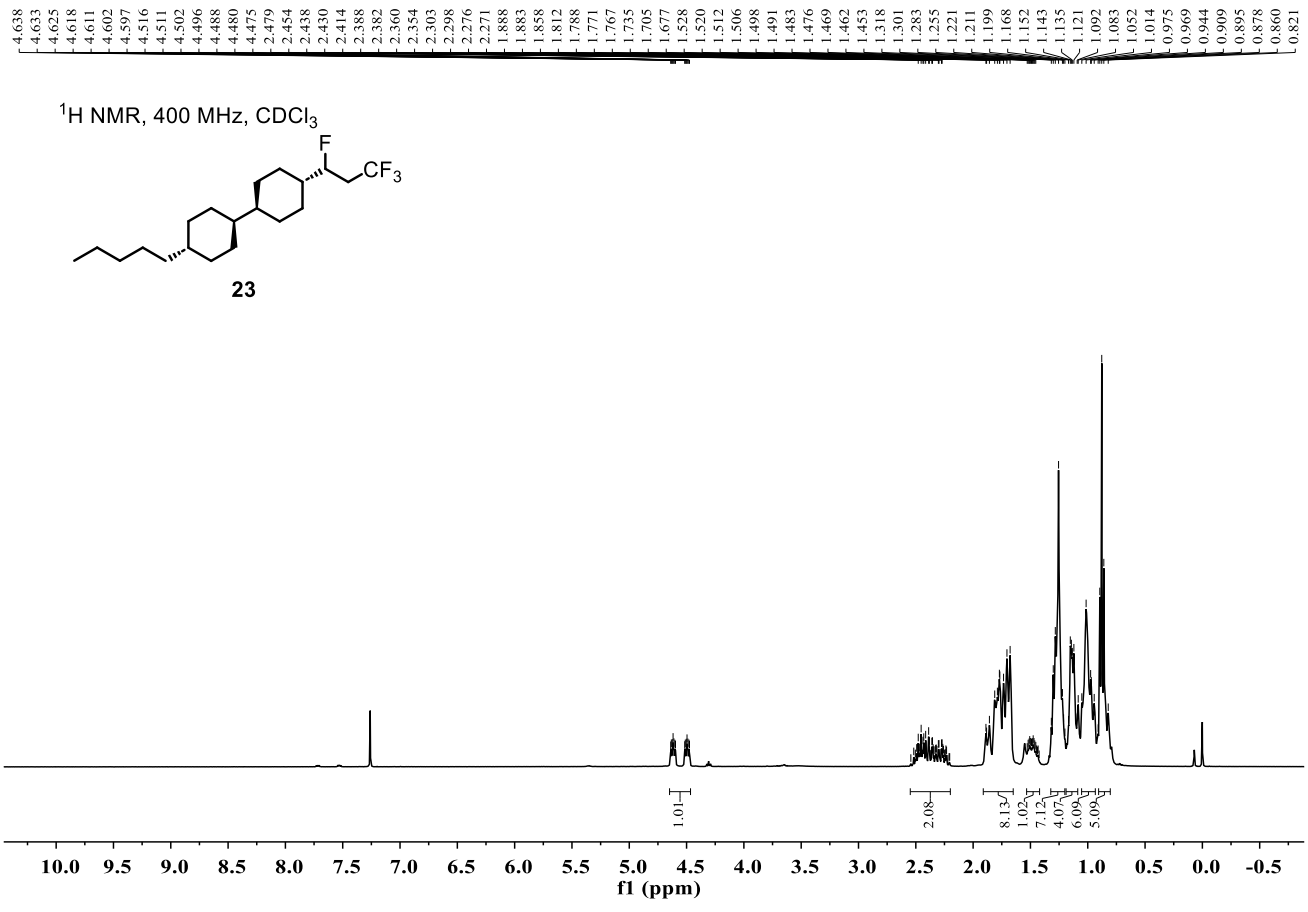

130.88
130.85
127.97
127.95
125.07
125.04
89.44
89.41
89.38
87.72
87.69
87.66
47.49
47.25
47.03
46.79
35.27
35.06
34.15
32.93
29.43
29.41
29.28
28.84
28.26
24.71
24.67
13C NMR, 101 MHz, CDCl3
Br
CF2Cl
F
21
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-48.58
-48.59
-48.60
-48.61
-49.01
-49.02
-49.03
-49.04
-49.88
-49.88
-49.90
-49.91
-50.31
-50.32
-50.34
-50.34
-181.11
-181.14
-181.16
19F NMR, 376 MHz, CDCl3
Br
CF2Cl
F
21
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

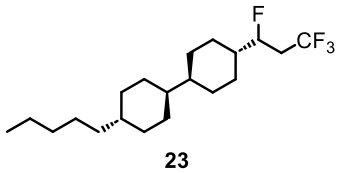

^{1}H NMR, 400 MHz, DMSO-d_6
Br
CF$_3$
F F F
22
4.98 4.97 4.96 4.95 4.94 4.93 4.92 4.85 4.84 4.83 4.82 4.81 4.81 4.79
3.53 3.52 3.50
2.69 2.65 2.63 2.62 2.60 2.59 2.58 2.52
1.82 1.80 1.79 1.77 1.75 1.70 1.69 1.68 1.67 1.66 1.64 1.63 1.62 1.61 1.59 1.39 1.37 1.36
1.00 1.95 2.06 1.99 2.08 12.04
10.0 9.5 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)


^{13}C NMR, 101 MHz, $CDCl_3$
Br
CF$_3$
F F F
22
123.62 123.26 122.91 120.78 120.43 120.07 117.95 117.77 117.74 117.59 117.39 117.37 117.24 117.01 116.99 116.63 116.61 115.25 115.23 115.11 114.87 114.85 114.76 114.49 114.47 114.40 114.11 114.09 112.73 112.71 112.35 112.33 111.97 111.95 111.60 111.57 87.84 87.80 87.77 86.12 86.09 86.06
36.80 36.59 36.57 36.37 36.36 36.14 35.75 35.54 34.10 32.94 29.43 29.42 29.27 28.84 28.27 24.73 24.69
125 120 115
f1 (ppm)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-80.23
-80.24
-109.75
-109.79
-110.46
-110.50
-111.39
-111.41
-112.10
-112.11
-175.67
-175.68
-175.68
-175.69
-175.70
-175.71
-175.72
-175.72
-175.73
19F NMR, 376 MHz, CDCl3
Br
CF3
F
F
F
22
-105
-110
-115
f1 (ppm)
-175.67
-175.70
-175.73
-175.76
f1 (ppm)
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
-175
-185
-195
-205
-215
f1 (ppm)

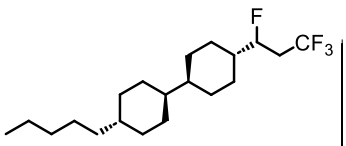

1H NMR, 400 MHz, CDCl3
F
CF3
23
1.01
2.08
8.13
1.02
7.12
4.07
6.09
5.09
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{13}C NMR, 101 MHz, $CDCl_3$

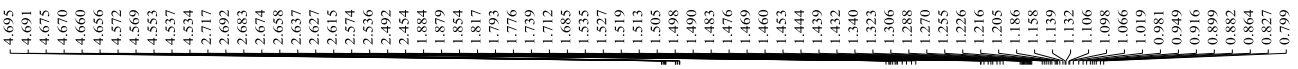


23

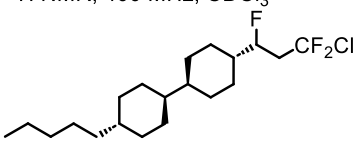
^{19}F NMR, 376 MHz, $CDCl_3$



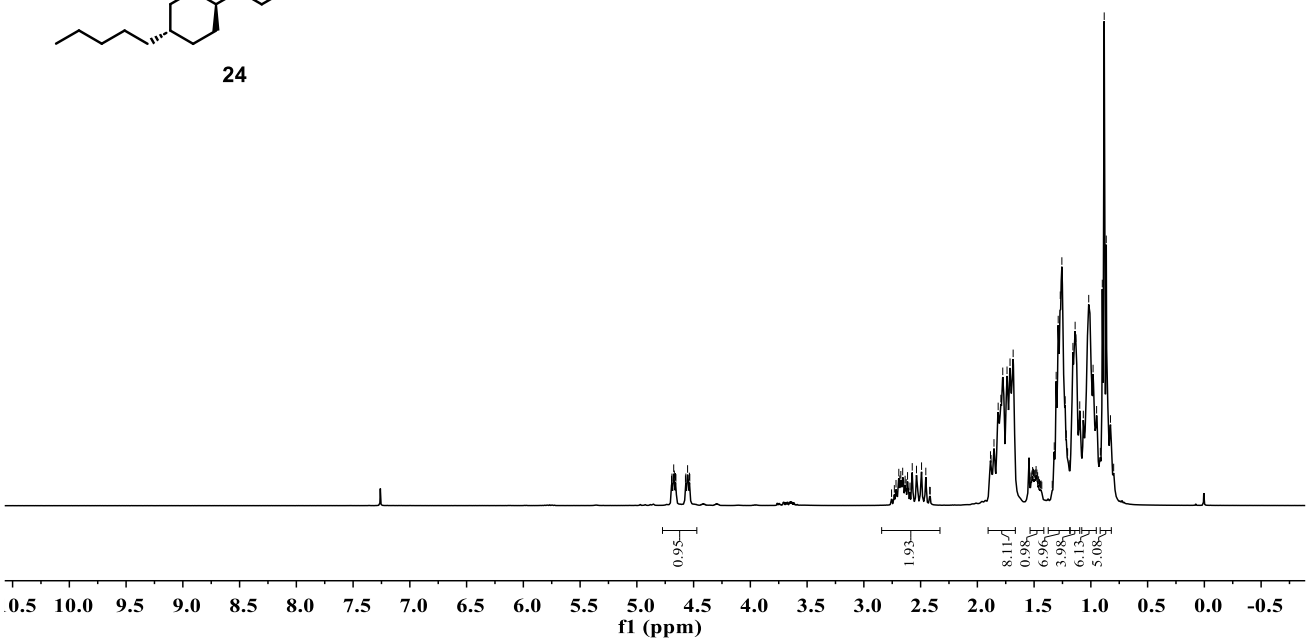
23

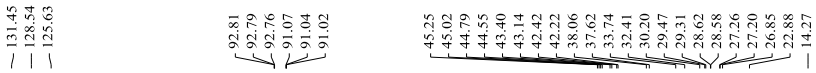


^{1}H NMR, 400 MHz, $CDCl_3$

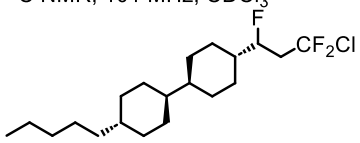


24

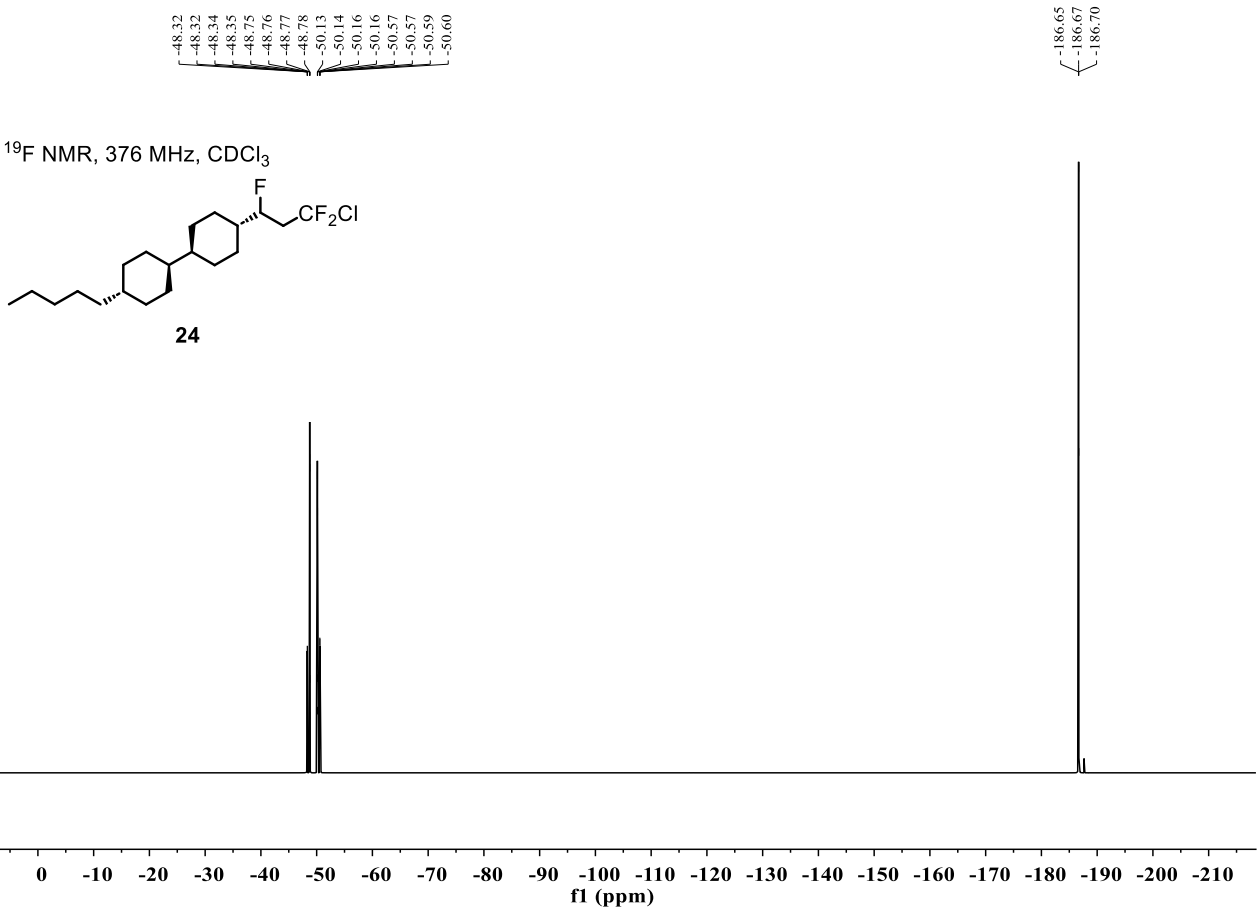


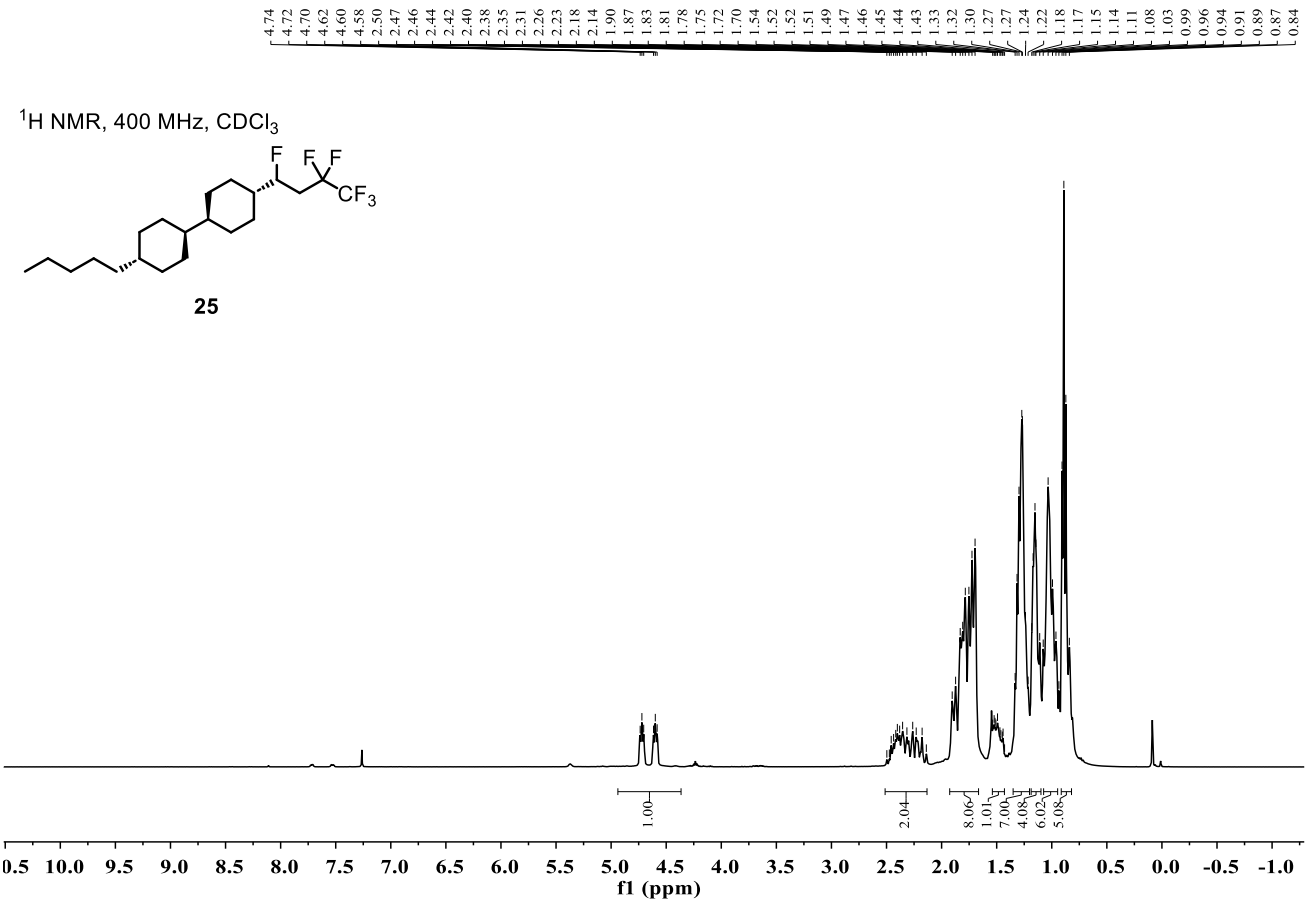


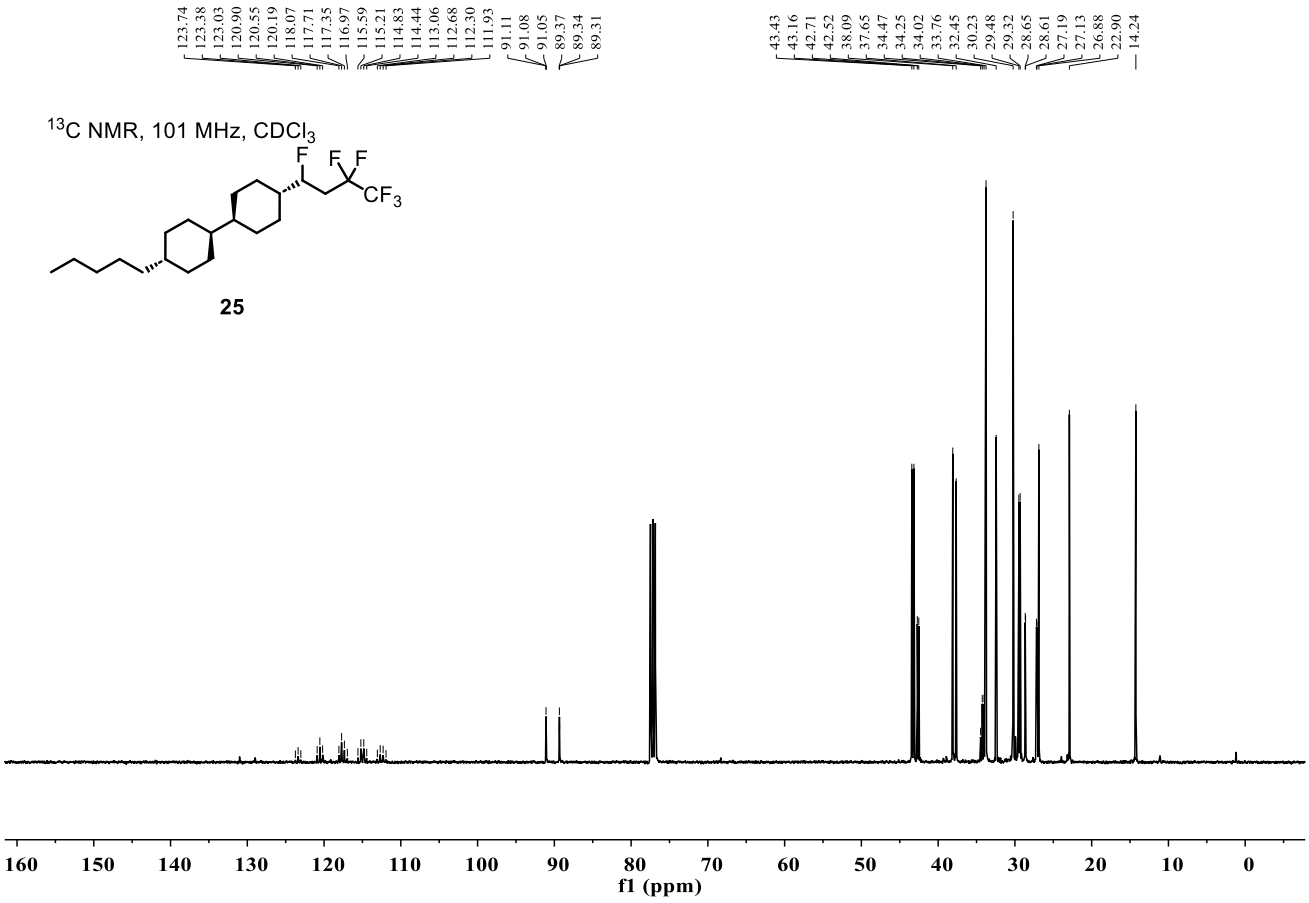
^{13}C NMR, 101 MHz, $CDCl_3$

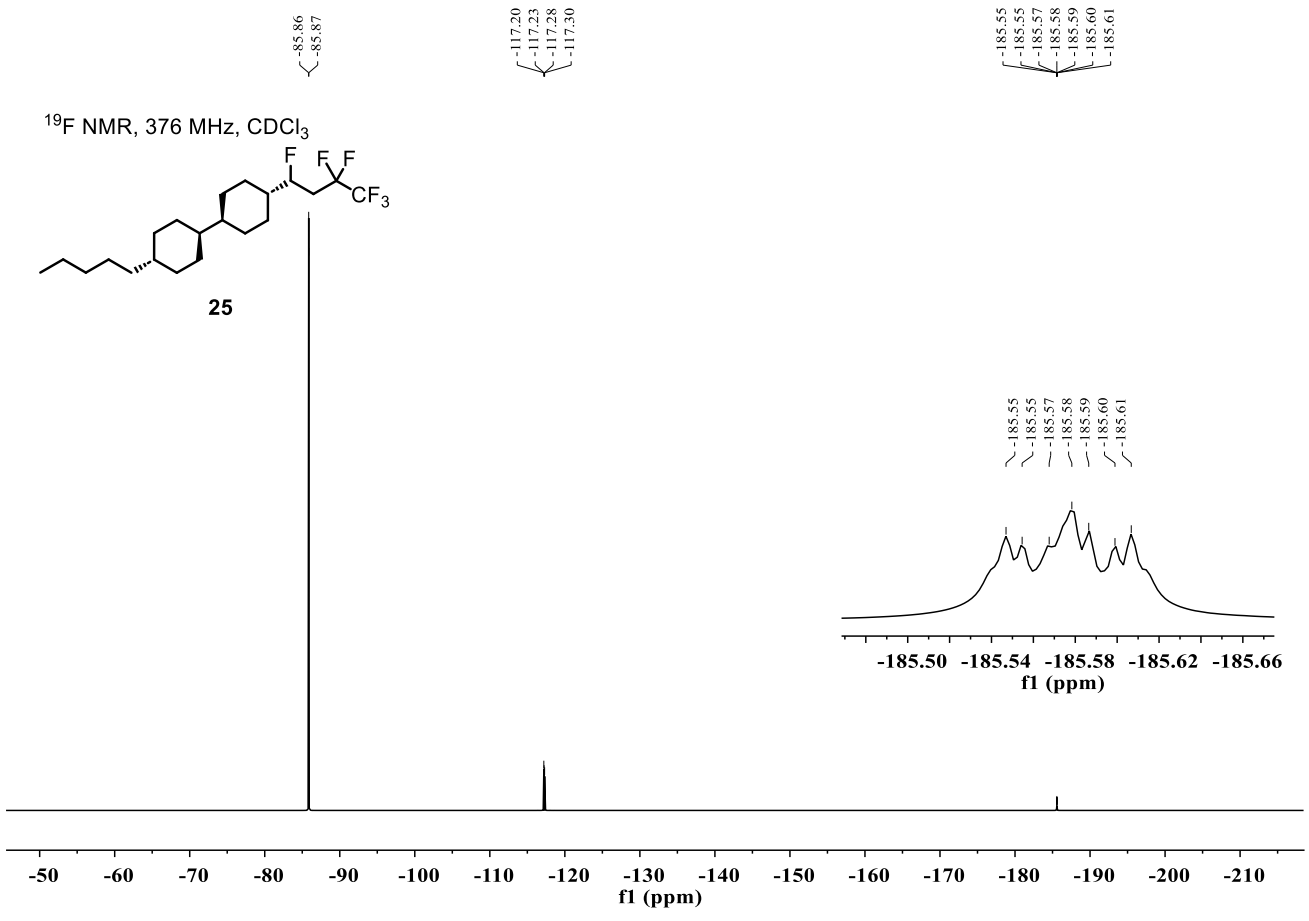


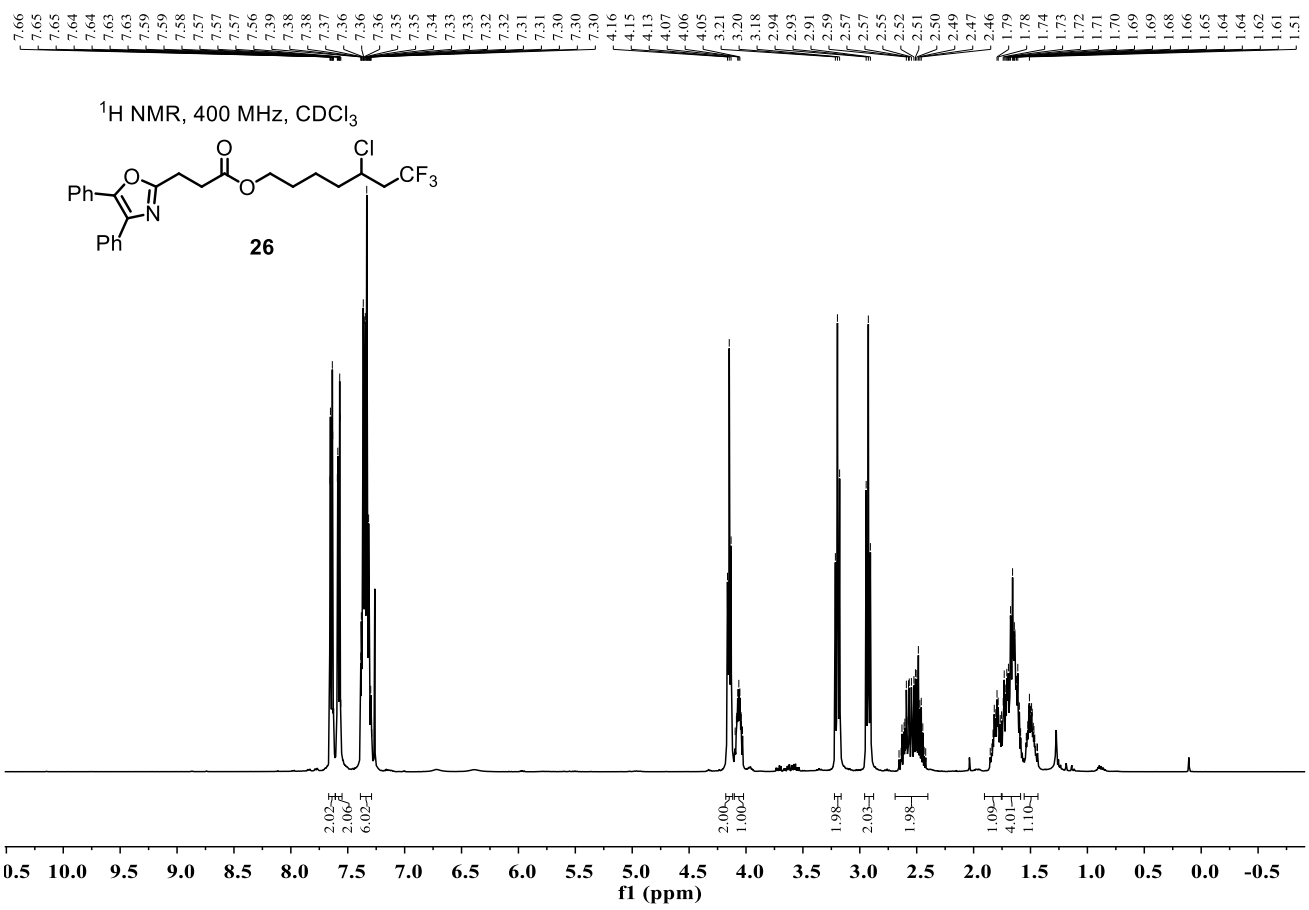
24

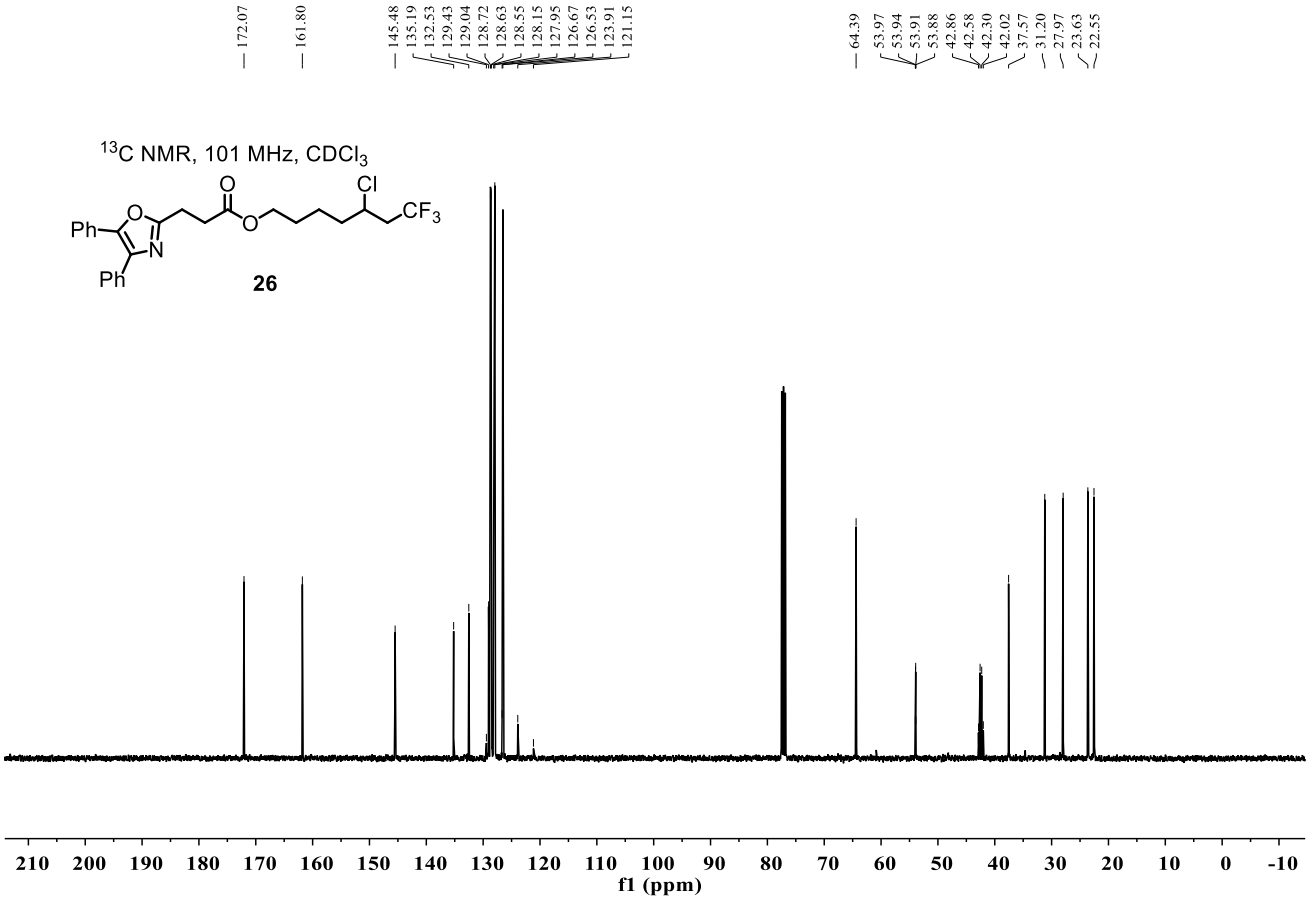

-48.32
-48.32
-48.34
-48.35
-48.75
-48.76
-48.77
-48.78
-50.13
-50.14
-50.16
-50.16
-50.57
-50.57
-50.59
-50.60
-186.65
-186.67
-186.70
19F NMR, 376 MHz, CDCl3
F
CF2Cl
24
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


4.74
4.72
4.70
4.62
4.60
4.58
2.50
2.47
2.46
2.44
2.42
2.40
2.38
2.35
2.31
2.26
2.23
2.18
2.14
1.90
1.87
1.83
1.81
1.78
1.75
1.72
1.70
1.54
1.52
1.52
1.51
1.49
1.47
1.46
1.45
1.44
1.43
1.33
1.32
1.30
1.27
1.27
1.24
1.22
1.18
1.17
1.15
1.14
1.11
1.08
1.03
0.99
0.96
0.94
0.91
0.89
0.87
0.84
1H NMR, 400 MHz, CDCl3
F
F
F
CF3
25
1.00
2.04
8.06
1.01
7.00
4.08
6.02
5.08
0.5 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 -1.0
f1 (ppm)

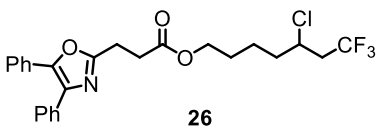

123.74
123.38
123.03
120.90
120.55
120.19
118.07
117.71
117.35
116.97
115.59
115.21
114.83
114.44
113.06
112.68
112.30
111.93
91.11
91.08
91.05
89.37
89.34
89.31
43.43
43.16
42.71
42.52
38.09
37.65
34.47
34.25
34.02
33.76
32.45
30.23
29.48
29.32
28.65
28.61
27.19
27.13
26.88
22.90
14.24
13C NMR, 101 MHz, CDCl3
F
F F
CF3
25
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-85.86
-85.87
-117.20
-117.23
-117.28
-117.30
-185.55
-185.55
-185.57
-185.58
-185.59
-185.60
-185.61
19F NMR, 376 MHz, CDCl3
F
F F
CF3
25
-185.50 -185.54 -185.58 -185.62 -185.66
f1 (ppm)
-50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

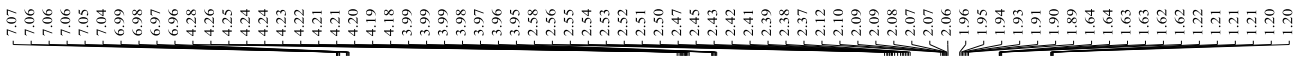

7.66 7.65 7.65 7.64 7.64 7.63 7.63 7.59 7.59 7.58 7.57 7.57 7.57 7.56 7.39 7.38 7.38 7.37 7.36 7.36 7.36 7.35 7.35 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.30
4.16 4.15 4.13 4.07 4.06 4.05 3.21 3.20 3.18 2.94 2.93 2.91 2.59 2.57 2.57 2.55 2.52 2.51 2.50 2.49 2.47 2.46 1.79 1.78 1.74 1.73 1.72 1.71 1.70 1.69 1.69 1.68 1.66 1.65 1.64 1.64 1.62 1.61 1.51
1H NMR, 400 MHz, CDCl3
Ph
O
N
Ph
O
O
Cl
CF3
26
2.02
2.06
6.02
2.00
1.00
1.98
2.03
1.98
1.09
4.01
1.10
0.5 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)


172.07 161.80 145.48 135.19 132.53 129.43 129.04 128.72 128.63 128.55 128.15 127.95 126.67 126.53 123.91 121.15
64.39 53.97 53.94 53.91 53.88 42.86 42.58 42.30 42.02 37.57 31.20 27.97 23.63 22.55
13C NMR, 101 MHz, CDCl3
Ph
O
N
Ph
O
O
Cl
CF3
26
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)

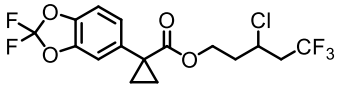
^{19}F NMR, 376 MHz, $CDCl_3$



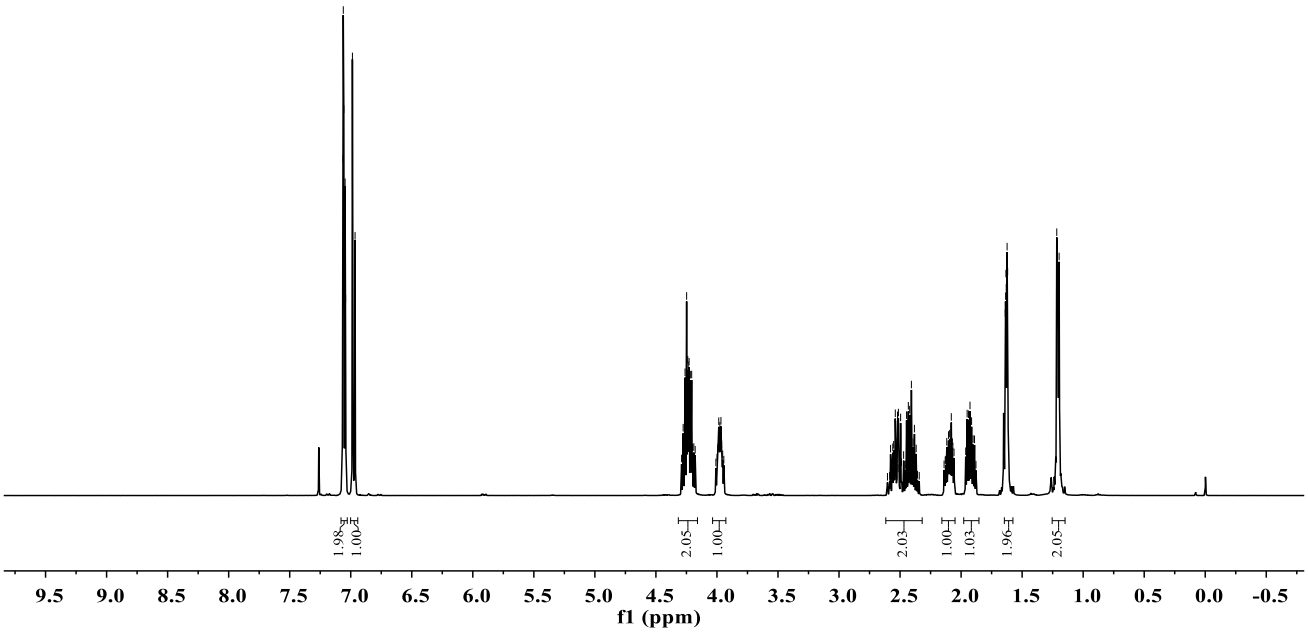
26

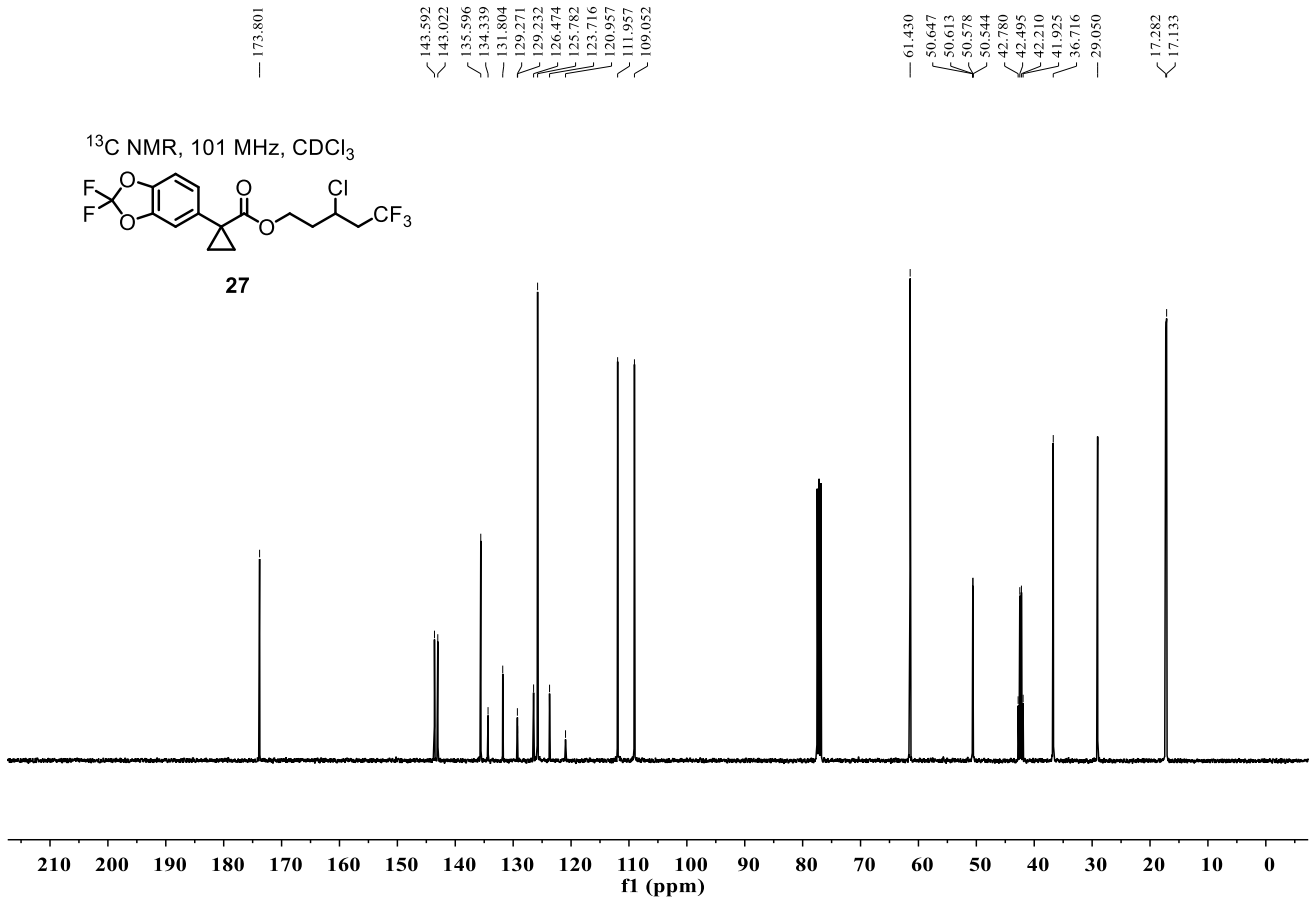


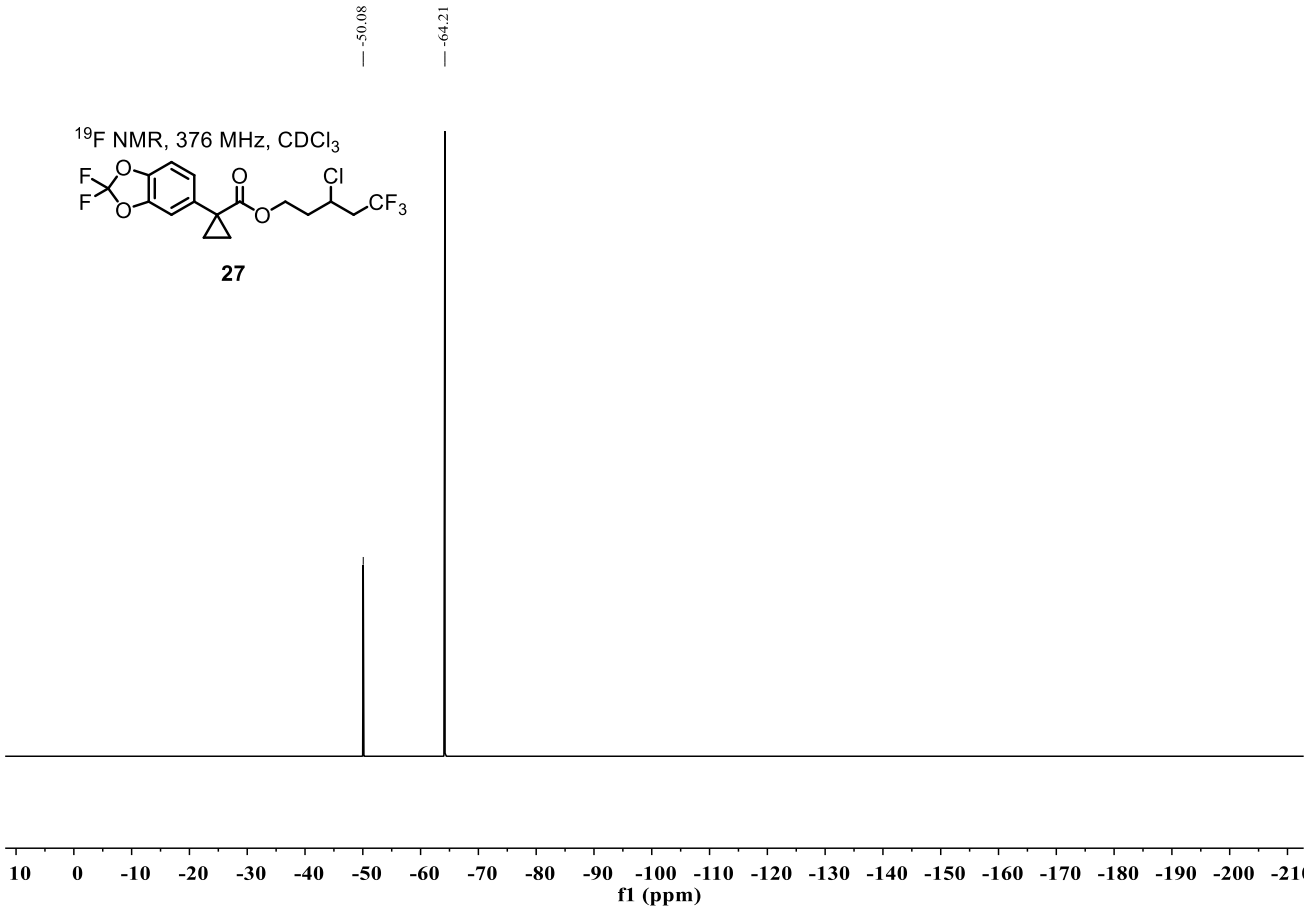
^{1}H NMR, 400 MHz, $CDCl_3$

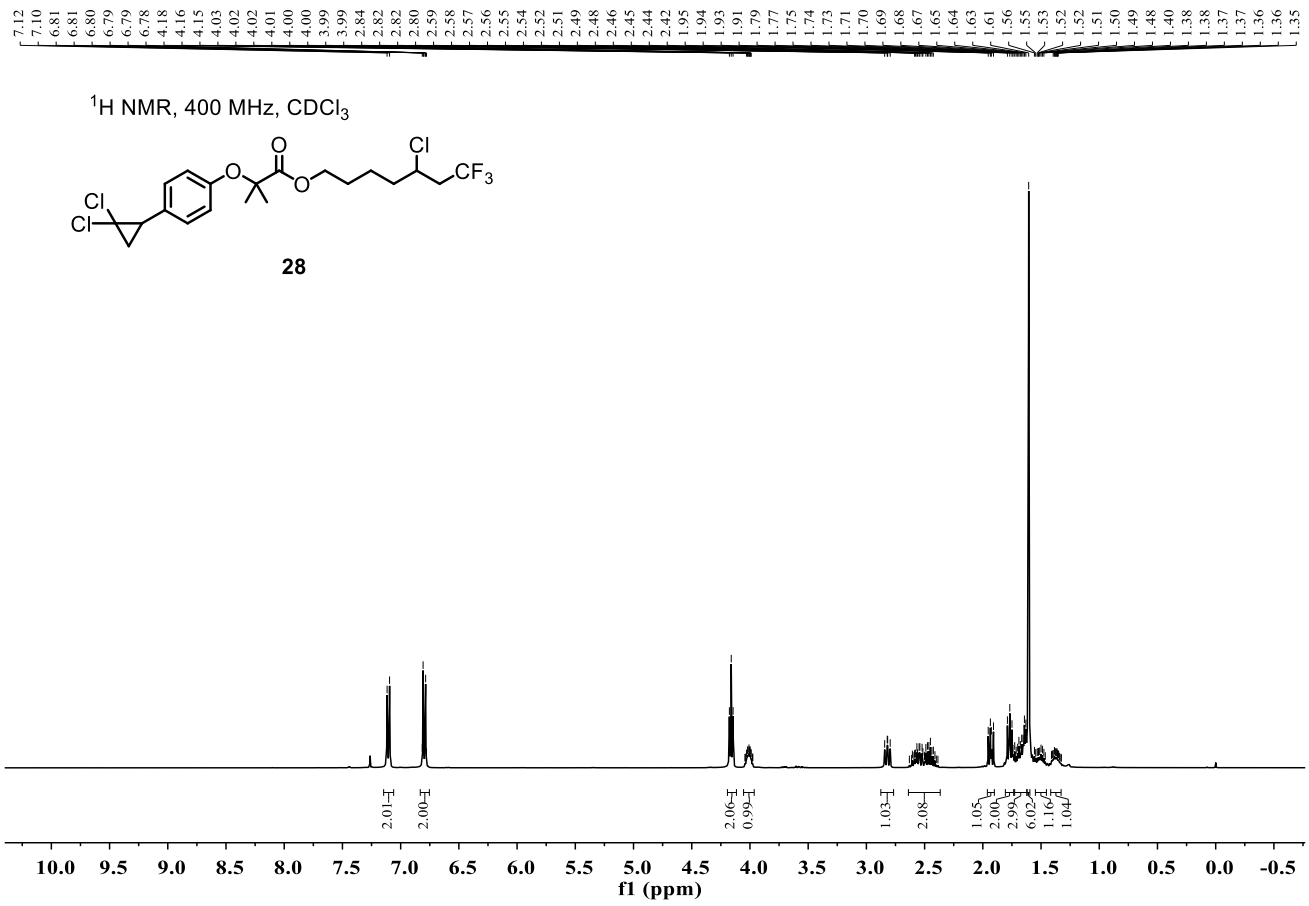


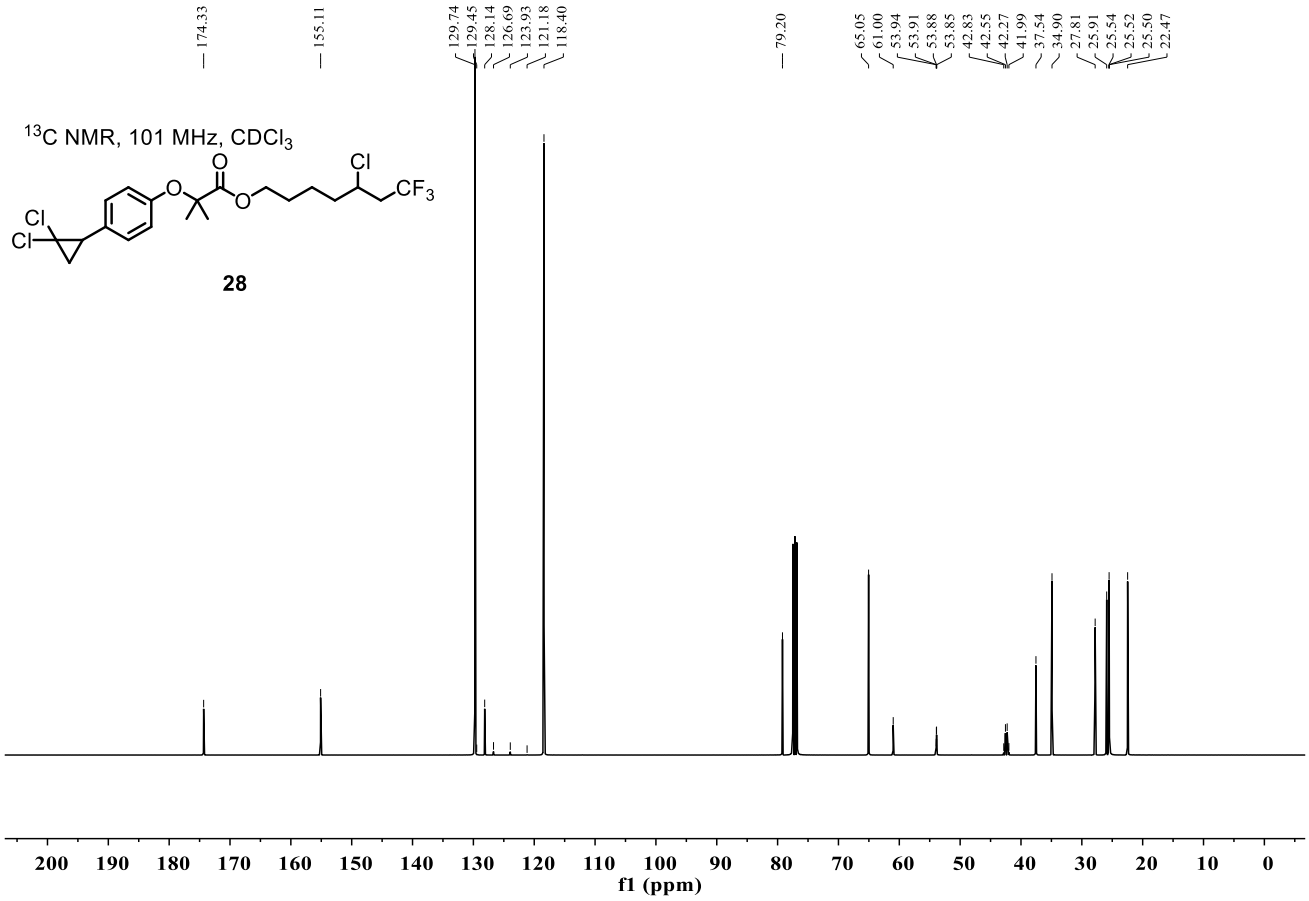
27



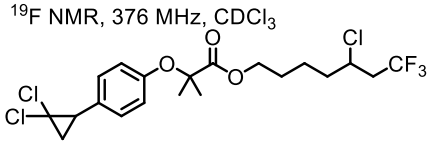

173.801
143.592
143.022
135.596
134.339
131.804
129.271
129.232
126.474
125.782
123.716
120.957
111.957
109.052
61.430
50.647
50.613
50.578
50.544
42.780
42.495
42.210
41.925
36.716
29.050
17.282
17.133
13C NMR, 101 MHz, CDCl3
F
F
O
O
O
O
Cl
CF3
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-50.08
-64.21
19F NMR, 376 MHz, CDCl3
F
F
O
O
O
O
Cl
CF3
27
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -21
f1 (ppm)

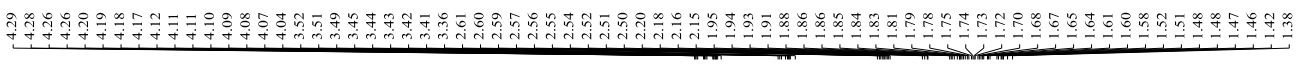

7.12 7.10 6.81 6.81 6.80 6.79 6.79 6.78 4.18 4.16 4.15 4.03 4.02 4.02 4.01 4.00 4.00 3.99 3.99 2.84 2.82 2.82 2.80 2.59 2.58 2.57 2.56 2.55 2.54 2.52 2.51 2.49 2.48 2.46 2.45 2.44 2.42 1.95 1.94 1.93 1.91 1.79 1.77 1.75 1.74 1.73 1.71 1.70 1.69 1.68 1.67 1.65 1.64 1.63 1.61 1.56 1.55 1.53 1.52 1.52 1.51 1.50 1.49 1.48 1.40 1.38 1.38 1.37 1.37 1.36 1.36 1.35
^{1}H NMR, 400 MHz, $CDCl_3$
Cl
Cl
O
O
O
Cl
CF_3
28
2.01 2.00 2.06 0.99 1.03 2.08 1.05 2.00 2.99 6.02 1.16 1.04
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)


174.33 155.11 129.74 129.45 128.14 126.69 123.93 121.18 118.40 79.20 65.05 61.00 53.94 53.91 53.88 53.85 42.83 42.55 42.27 41.99 37.54 34.90 27.81 25.91 25.54 25.52 25.50 22.47
^{13}C NMR, 101 MHz, $CDCl_3$
Cl
Cl
O
O
O
Cl
CF_3
28
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

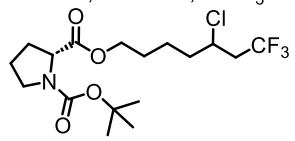
^{19}F NMR, 376 MHz, $CDCl_3$



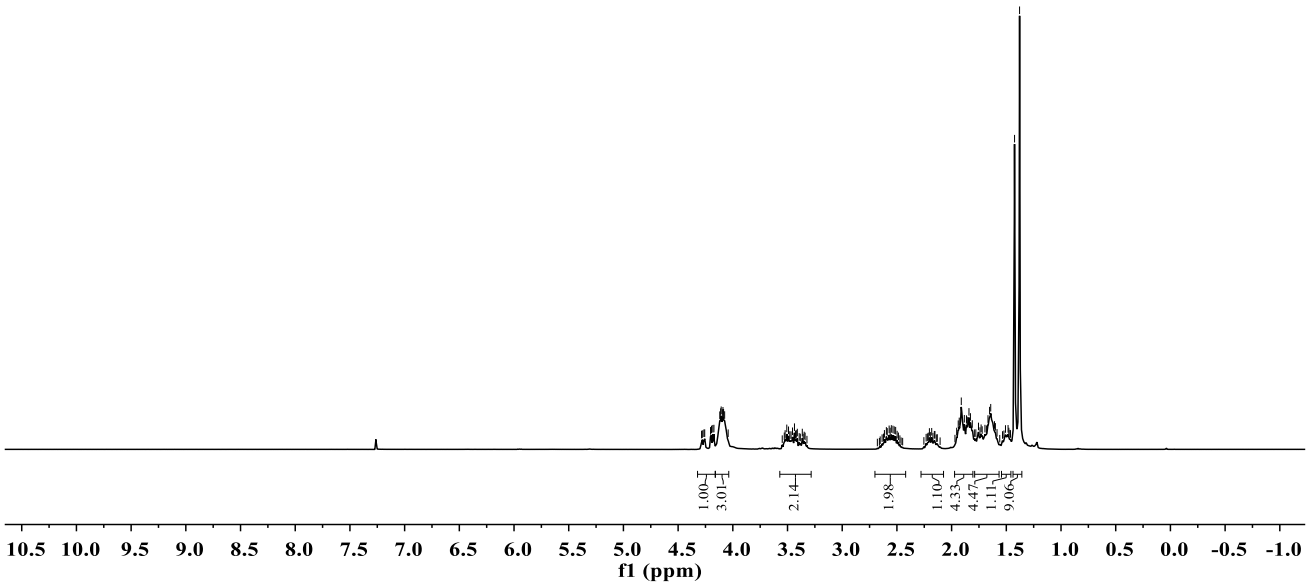
28

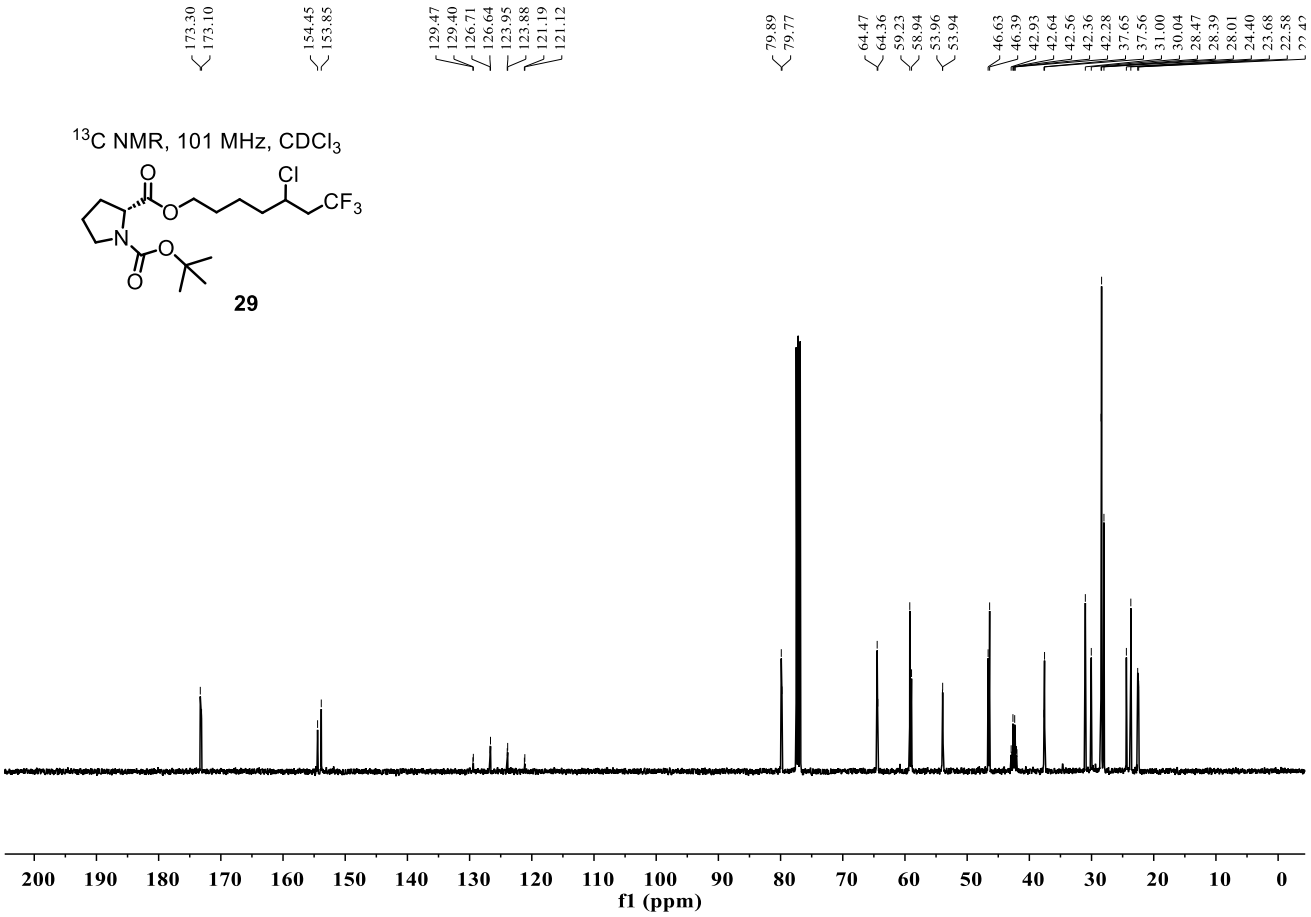


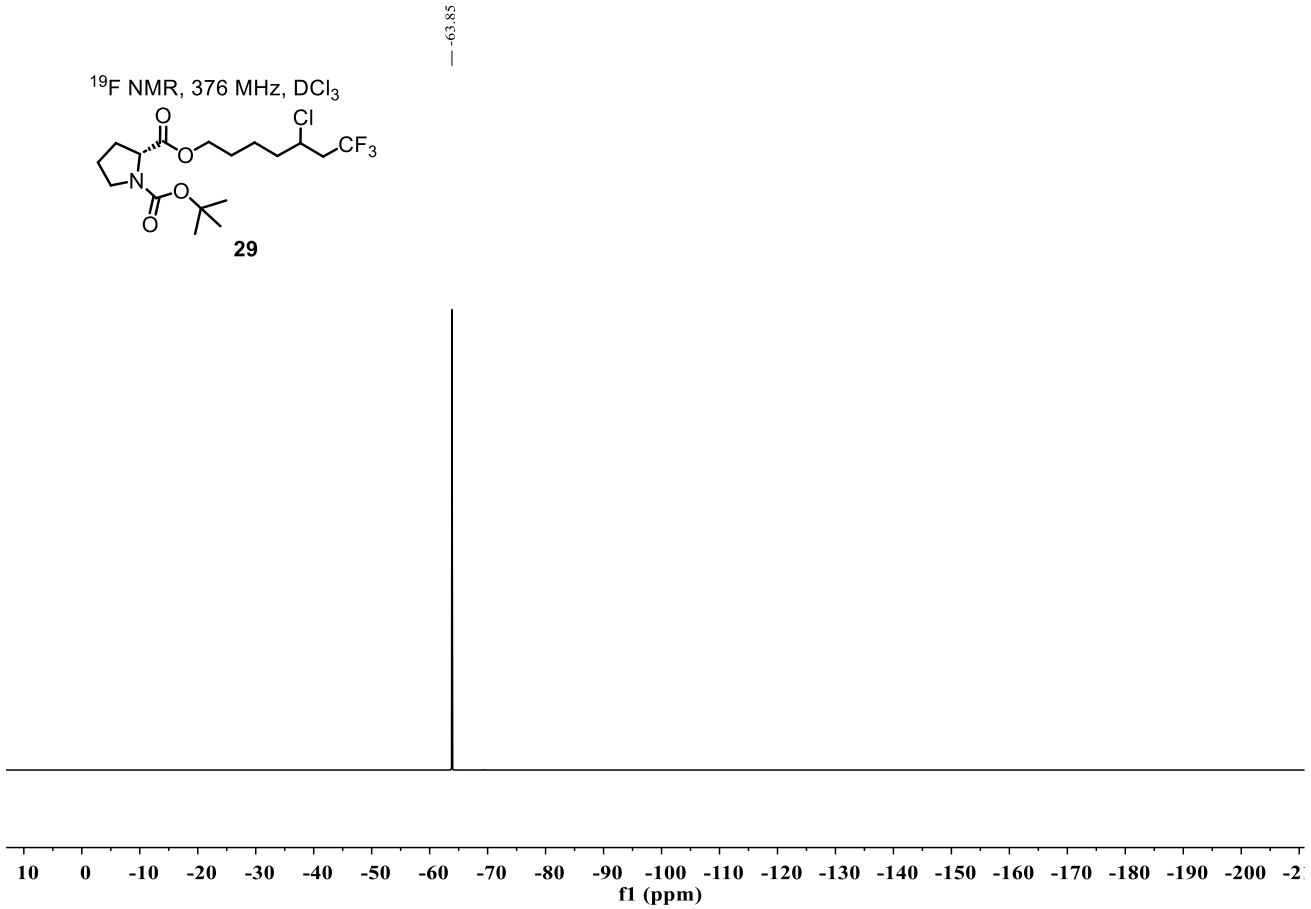
^{1}H NMR, 400 MHz, $CDCl_3$



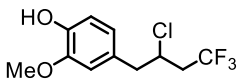
29, d.r. = 1.4:1




173.30
173.10
154.45
153.85
129.47
129.40
126.71
126.64
123.95
123.88
121.19
121.12
79.89
79.77
64.47
64.36
59.23
58.94
53.96
53.94
46.63
46.39
42.93
42.64
42.56
42.36
42.28
37.65
37.56
31.00
30.04
28.47
28.39
28.01
24.40
23.68
22.58
13C NMR, 101 MHz, CDCl3
Cl
CF3
29
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

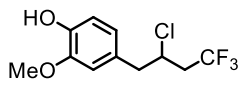

-63.85
19F NMR, 376 MHz, DCl3
Cl
CF3
29
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H NMR, 400 MHz, $CDCl_3$



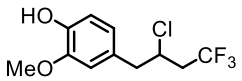
30

^{13}C NMR, 101 MHz, $CDCl_3$

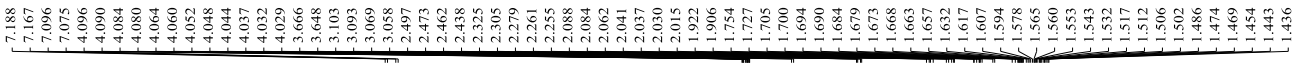


30

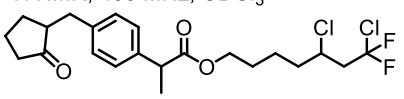
^{19}F NMR, 376 MHz, $CDCl_3$



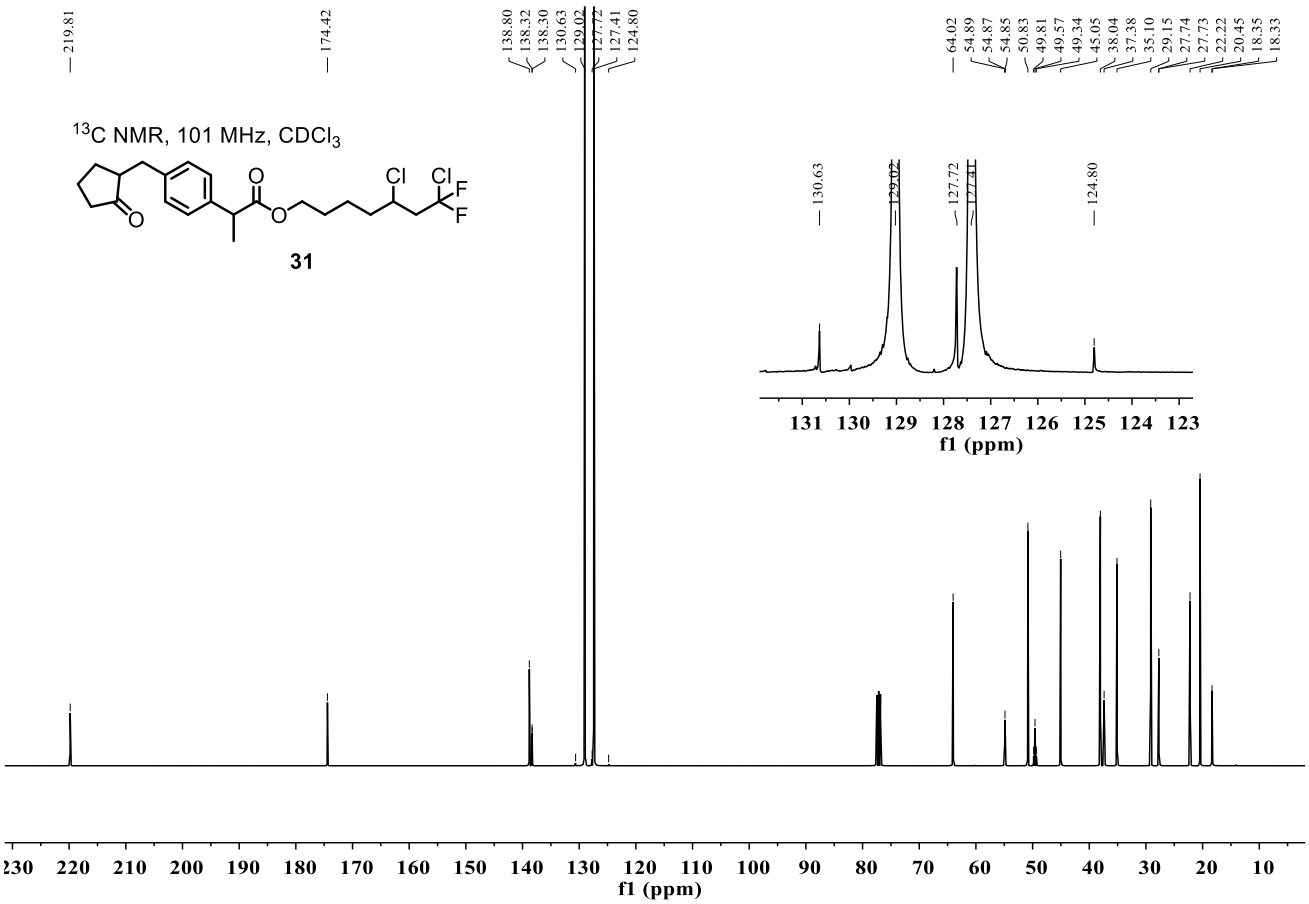
30

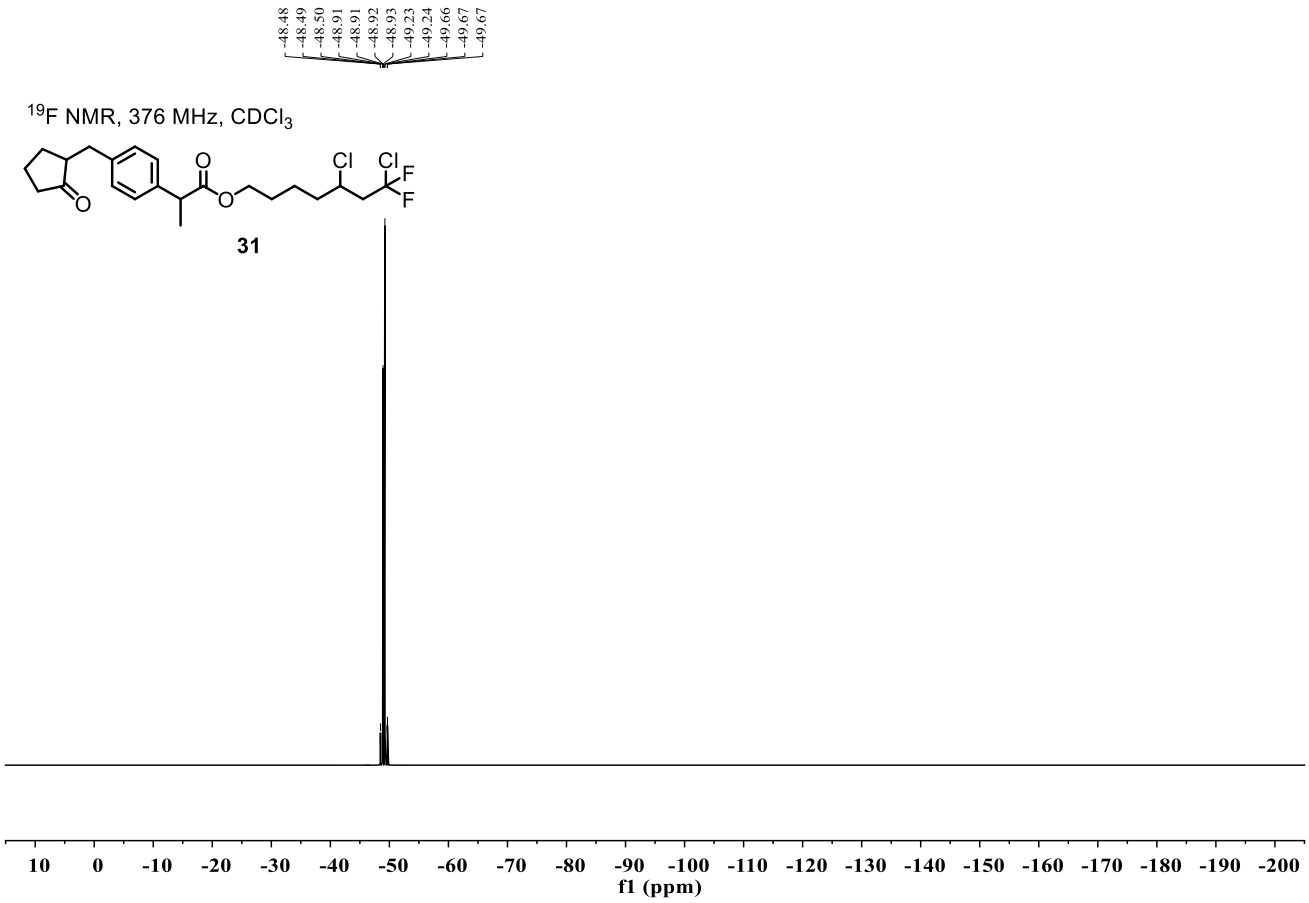


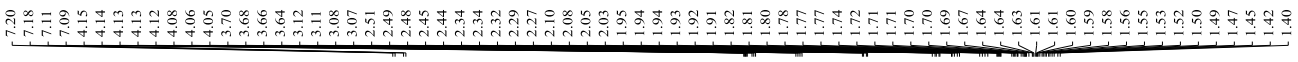
^{1}H NMR, 400 MHz, $CDCl_3$



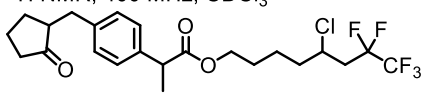
31


219.81
174.42
138.80
138.32
138.30
130.63
129.02
127.72
127.41
124.80
64.02
54.89
54.87
54.85
50.83
49.81
49.57
49.34
45.05
38.04
37.38
35.10
29.15
27.74
27.73
22.22
20.45
18.35
18.33
13C NMR, 101 MHz, CDCl3
O
O
Cl
Cl
F
F
31
130.63
129.02
127.72
127.41
124.80
131 130 129 128 127 126 125 124 123
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

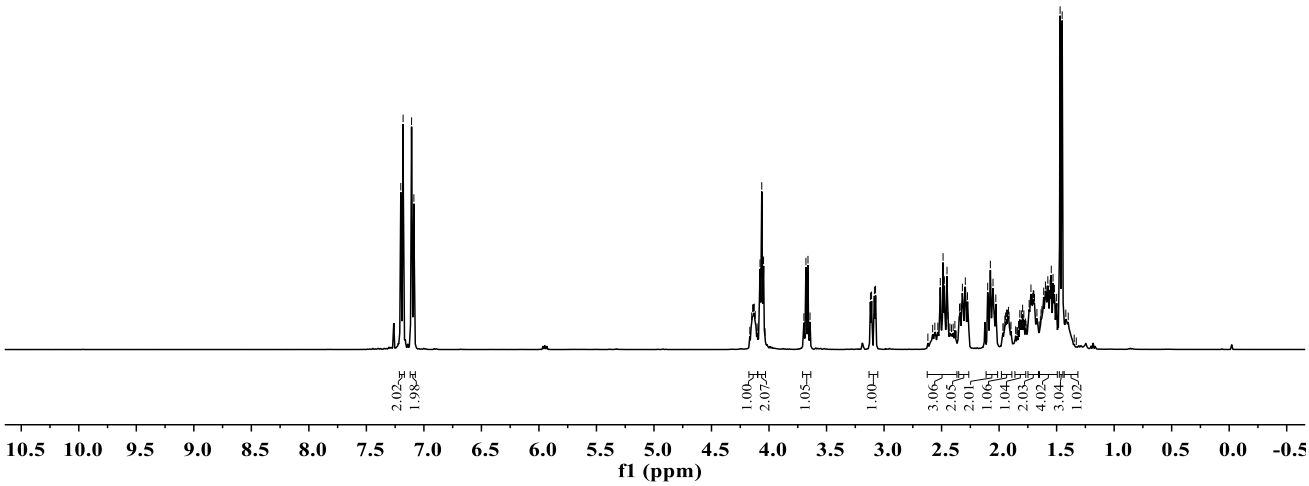

-48.48
-48.49
-48.50
-48.91
-48.91
-48.92
-48.93
-49.23
-49.24
-49.66
-49.67
-49.67
19F NMR, 376 MHz, CDCl3
O
O
Cl
Cl
F
F
31
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

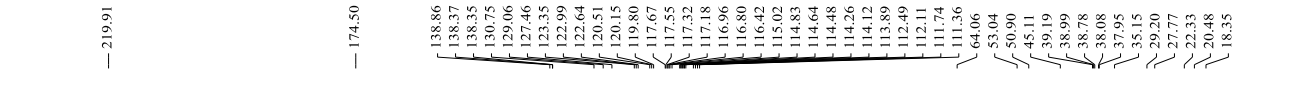


^{1}H NMR, 400 MHz, $CDCl_3$

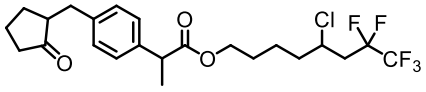


32



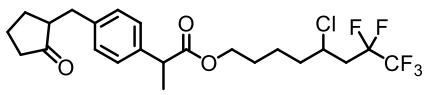


^{13}C NMR, 101 MHz, $CDCl_3$



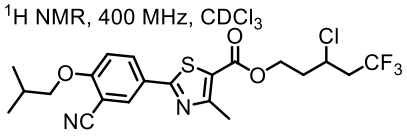
32

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

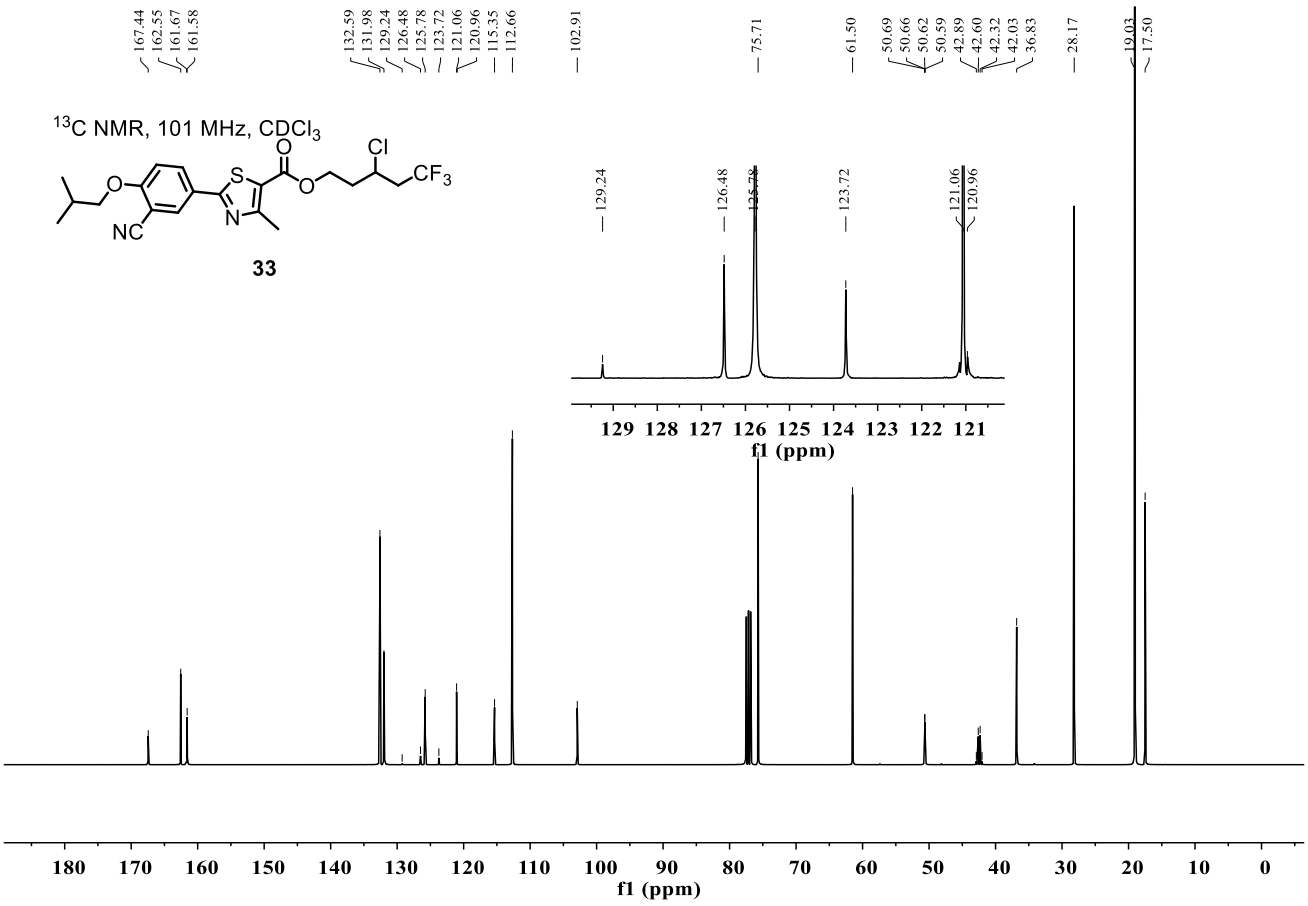


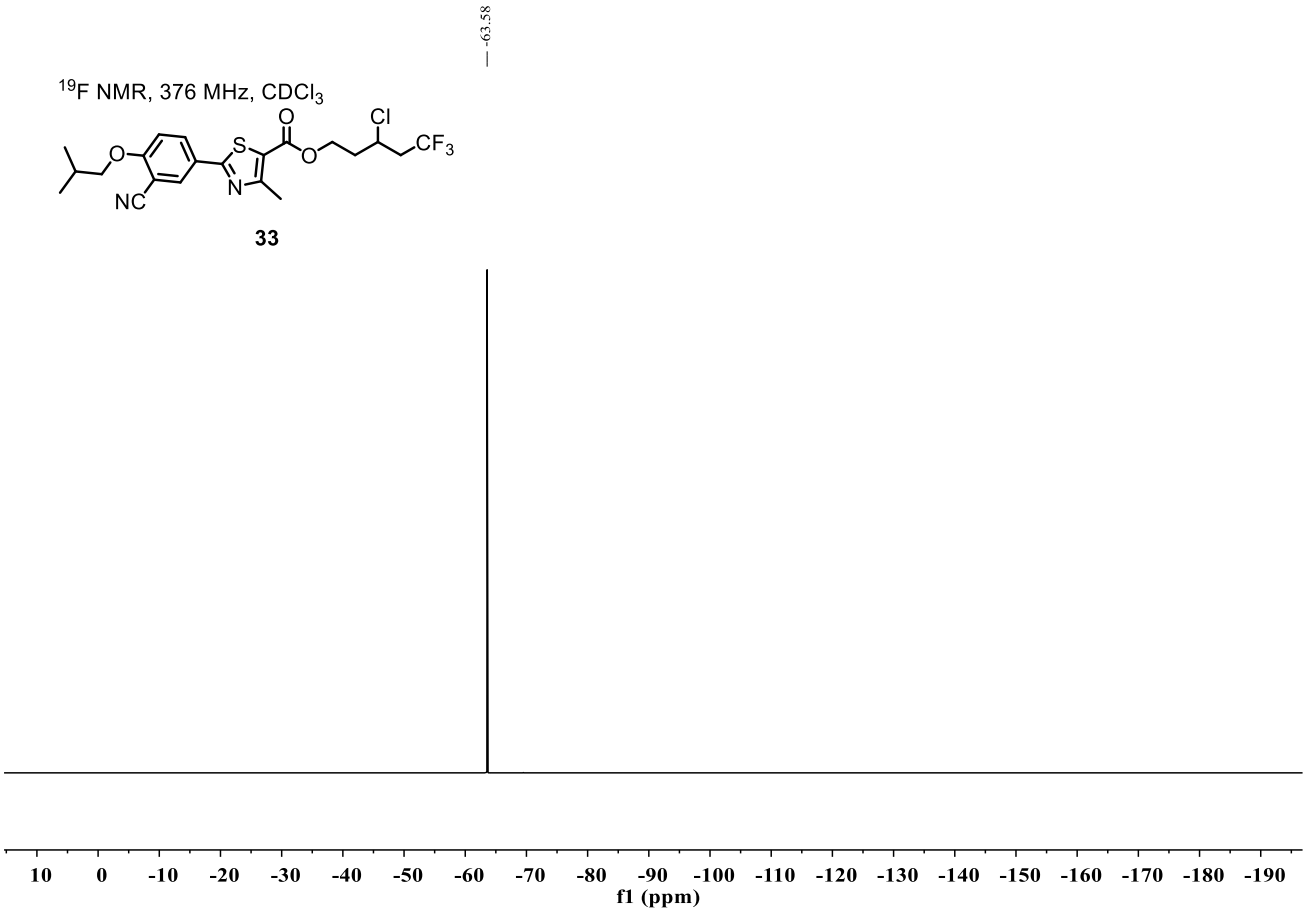
32

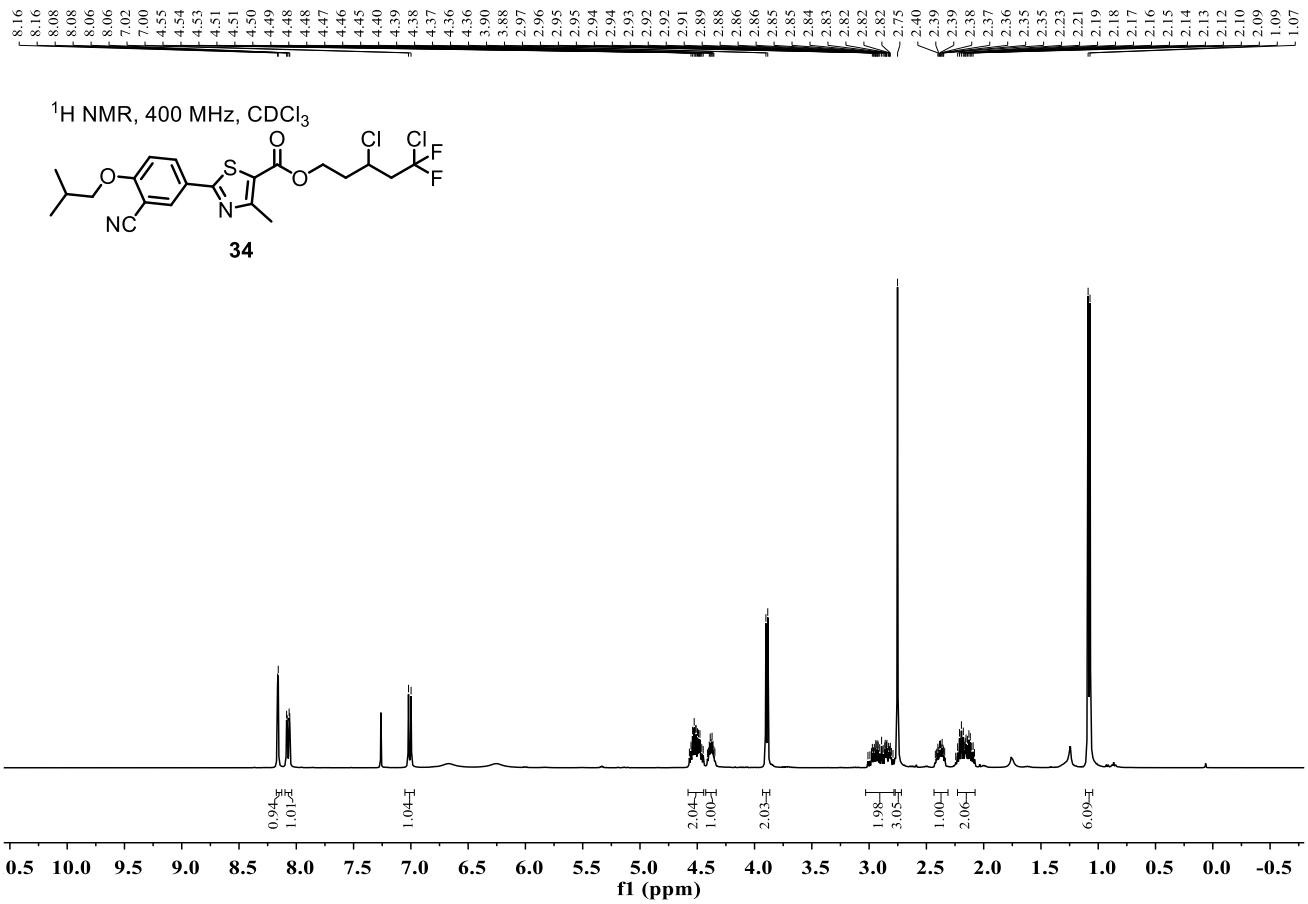
^{1}H NMR, 400 MHz, $CDCl_3$

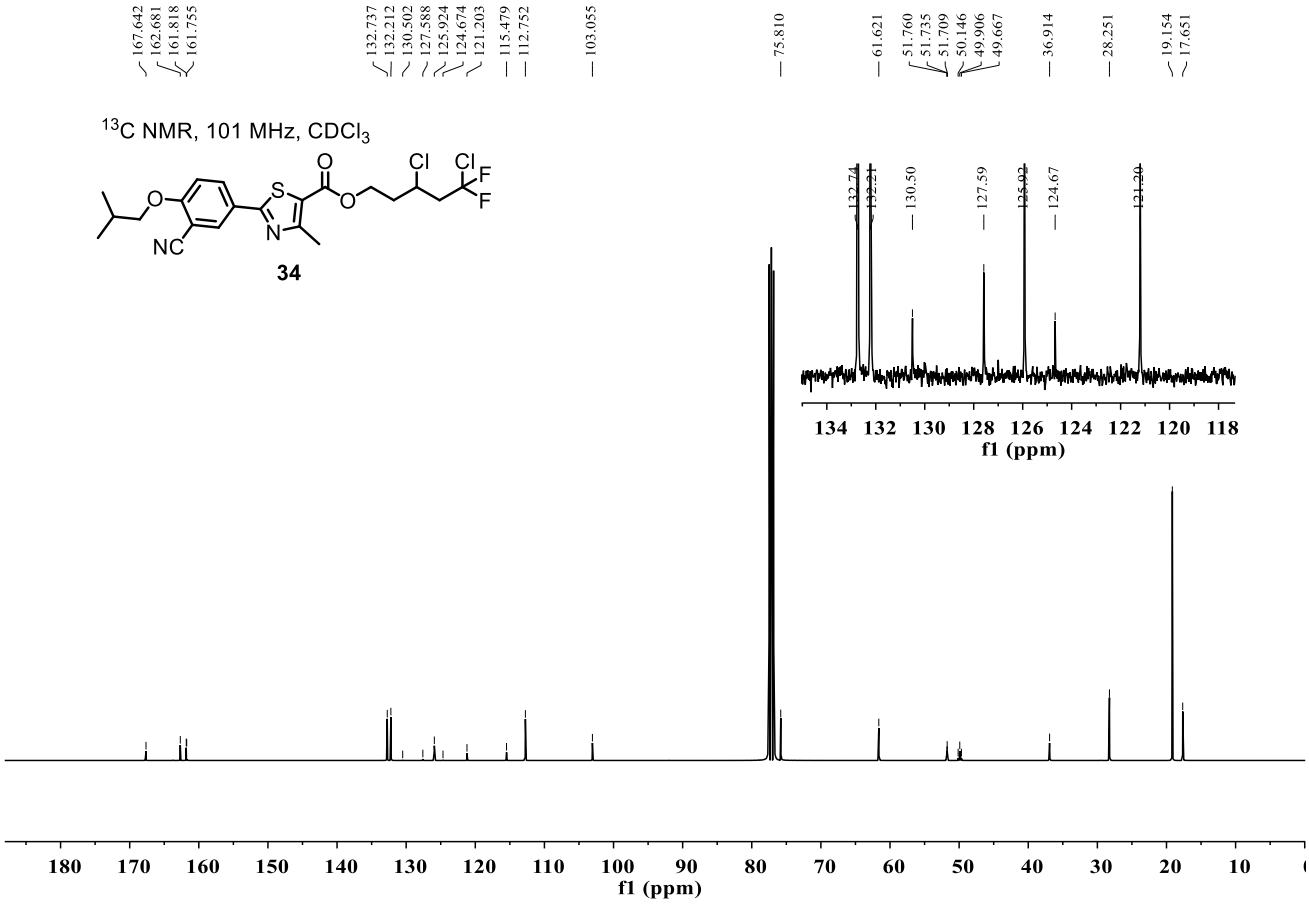


33

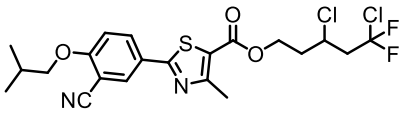

167.44
162.55
161.67
161.58
132.59
131.98
129.24
126.48
125.78
123.72
121.06
120.96
115.35
112.66
102.91
75.71
61.50
50.69
50.66
50.62
50.59
42.89
42.60
42.32
42.03
36.83
28.17
19.03
17.50
13C NMR, 101 MHz, CDCl3
33
129 128 127 126 125 124 123 122 121
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.58
19F NMR, 376 MHz, CDCl3
33
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


8.16 8.16 8.08 8.08 8.06 8.06 7.02 7.00 4.55 4.54 4.53 4.51 4.51 4.50 4.49 4.48 4.48 4.47 4.46 4.45 4.40 4.39 4.38 4.37 4.36 4.36 3.90 3.88 2.97 2.96 2.95 2.95 2.94 2.94 2.93 2.92 2.92 2.91 2.89 2.88 2.86 2.86 2.85 2.85 2.84 2.83 2.82 2.82 2.82 2.75 2.40 2.39 2.39 2.38 2.37 2.36 2.35 2.35 2.23 2.21 2.19 2.18 2.17 2.16 2.15 2.14 2.13 2.12 2.10 2.09 1.09 1.07
1H NMR, 400 MHz, CDCl3
O
S
N
O
O
Cl
Cl
F
F
O
NC
34
0.94 1.01 1.04 2.04 1.00 2.03 1.98 3.05 1.00 2.06 6.09
0.5 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)

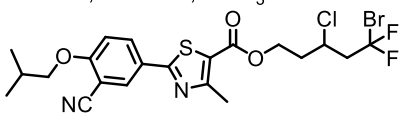

167.642 162.681 161.818 161.755 132.737 132.212 130.502 127.588 125.924 124.674 121.203 115.479 112.752 103.055 75.810 61.621 51.760 51.735 51.709 50.146 49.906 49.667 36.914 28.251 19.154 17.651
13C NMR, 101 MHz, CDCl3
O
S
N
O
O
Cl
Cl
F
F
O
NC
34
132.74 132.21 130.50 127.59 125.92 124.67 121.20
134 132 130 128 126 124 122 120 118
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

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

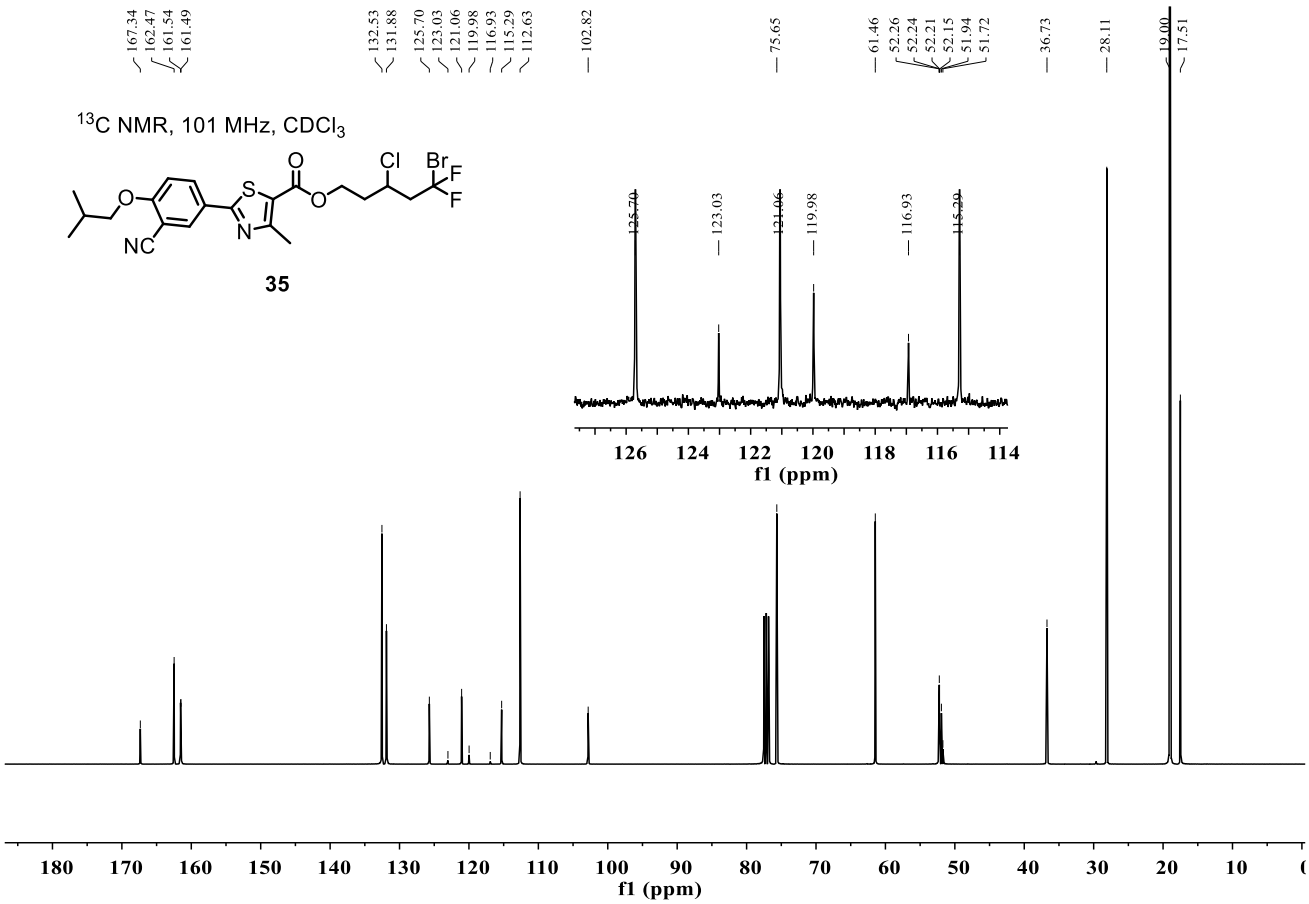


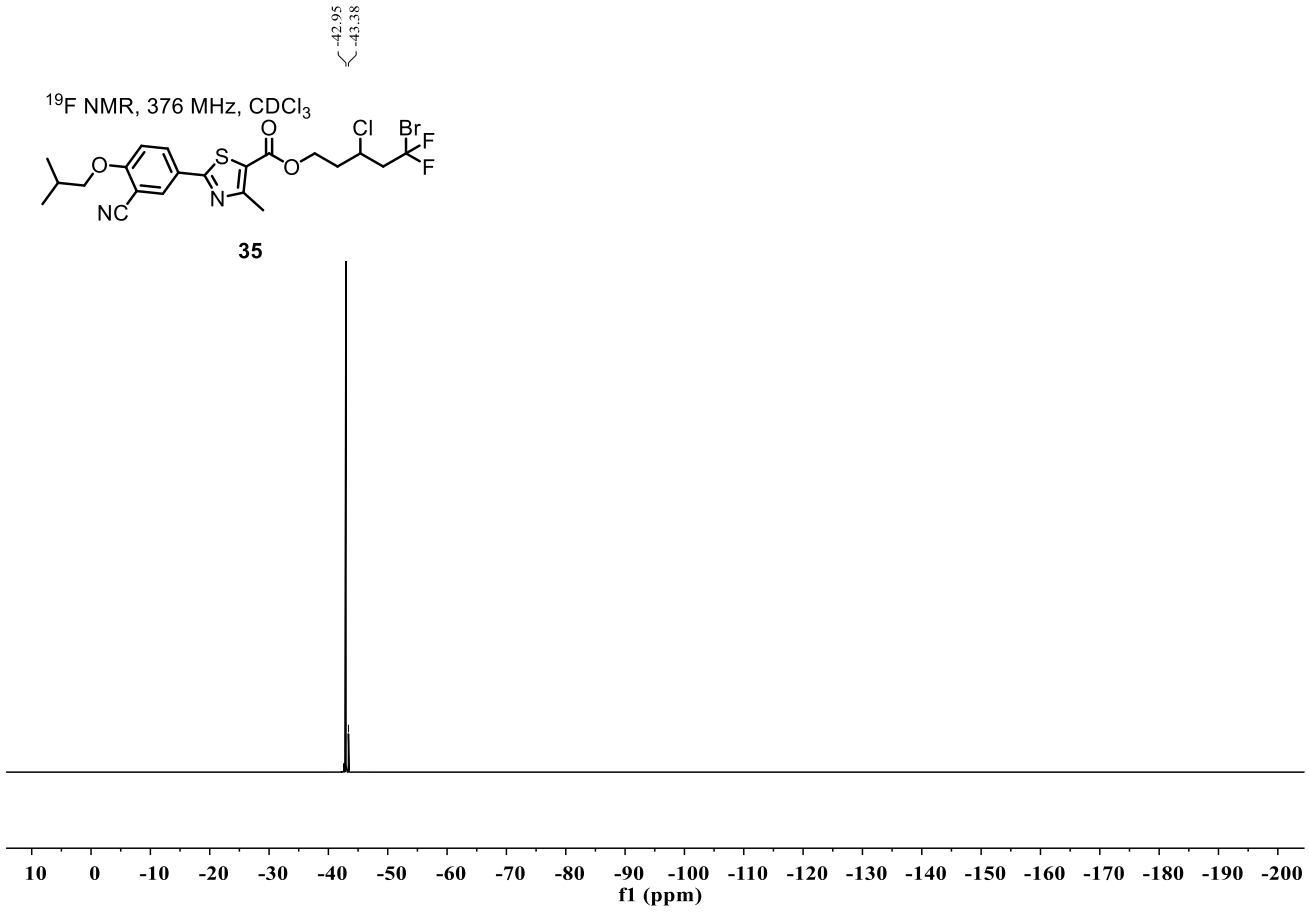
34

^{1}H NMR, 400 MHz, $CDCl_3$

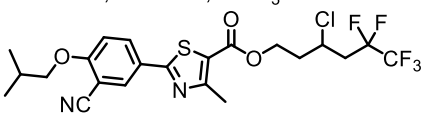


35

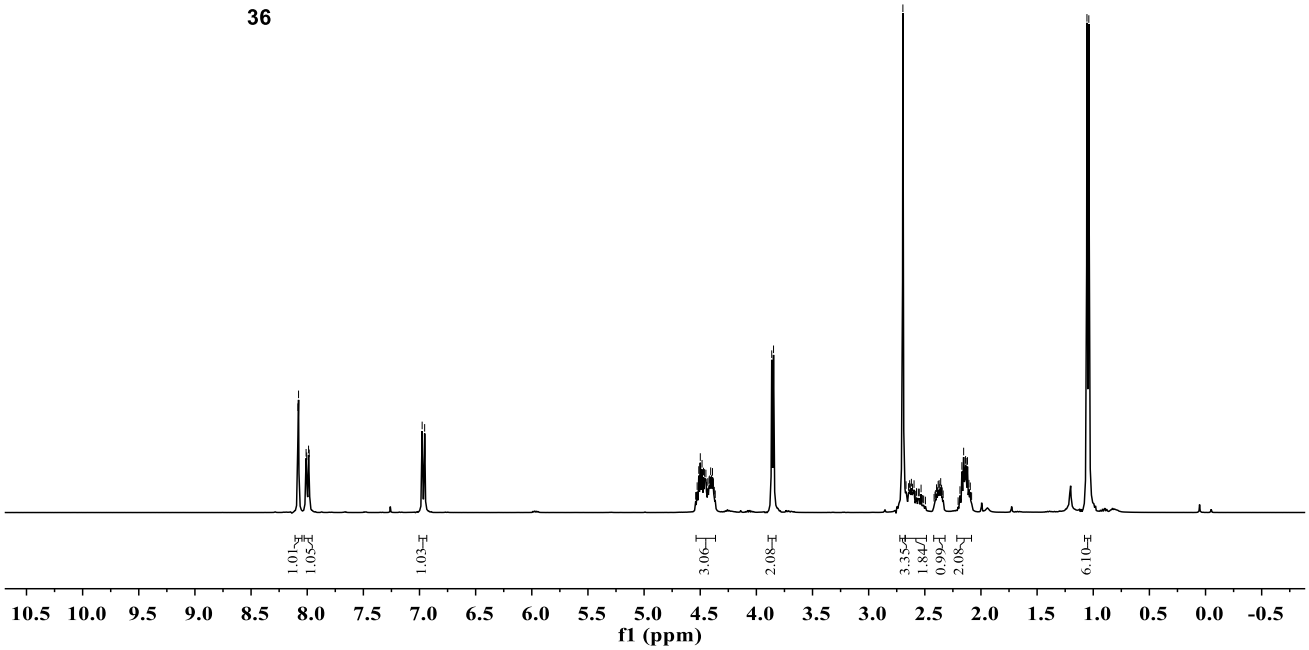

167.34
162.47
161.54
161.49
132.53
131.88
125.70
123.03
121.06
119.98
116.93
115.29
112.63
102.82
75.65
61.46
52.26
52.24
52.21
52.15
51.94
51.72
36.73
28.11
19.00
17.51
13C NMR, 101 MHz, CDCl3
O
Cl
Br
F
F
S
O
O
N
NC
35
125.70
123.03
121.06
119.98
116.93
115.29
126 124 122 120 118 116 114
f1 (ppm)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

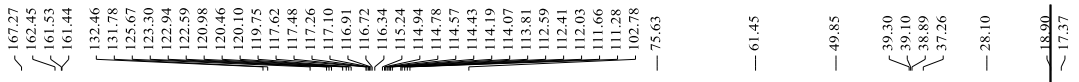

-42.95
-43.38
19F NMR, 376 MHz, CDCl3
O
Cl
Br
F
F
S
O
O
N
NC
35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{1}H NMR, 400 MHz, $CDCl_3$

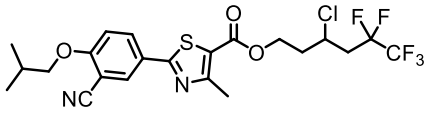


36

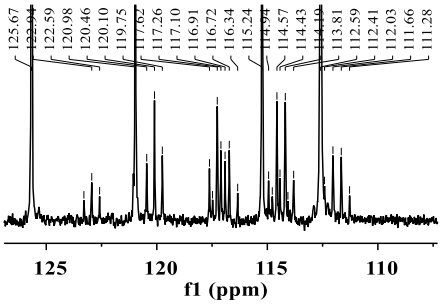


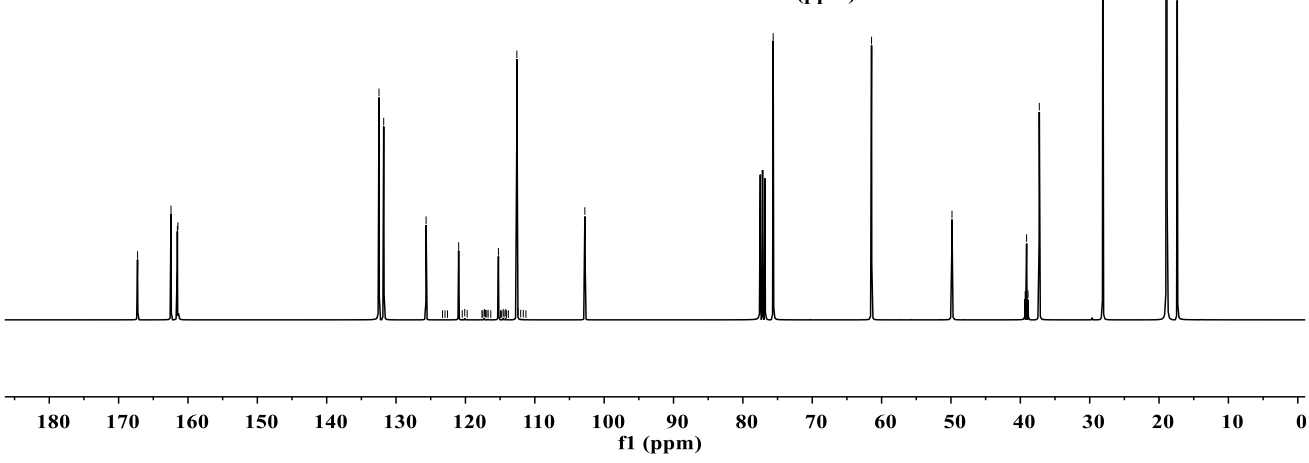


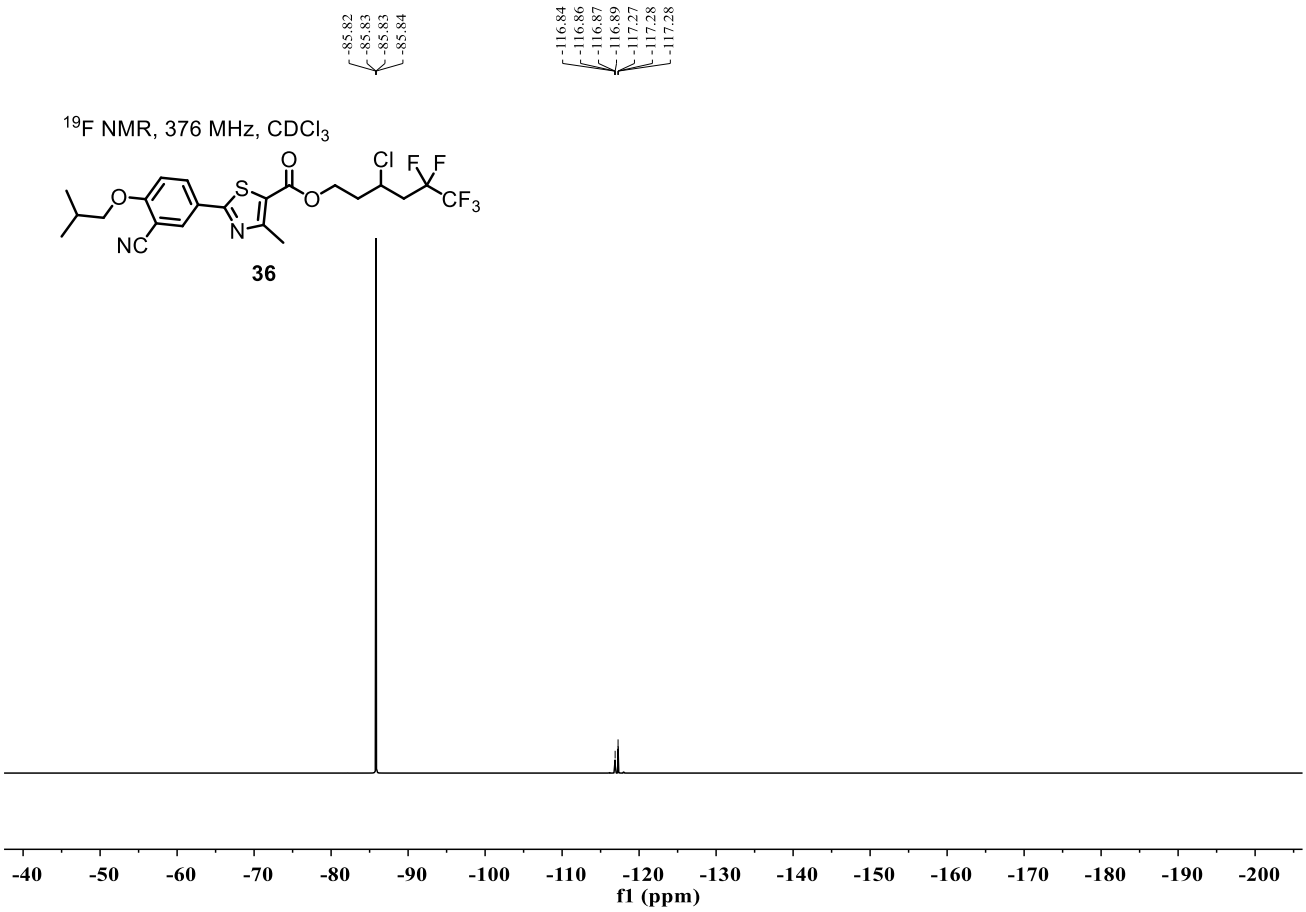
^{13}C NMR, 101 MHz, $CDCl_3$

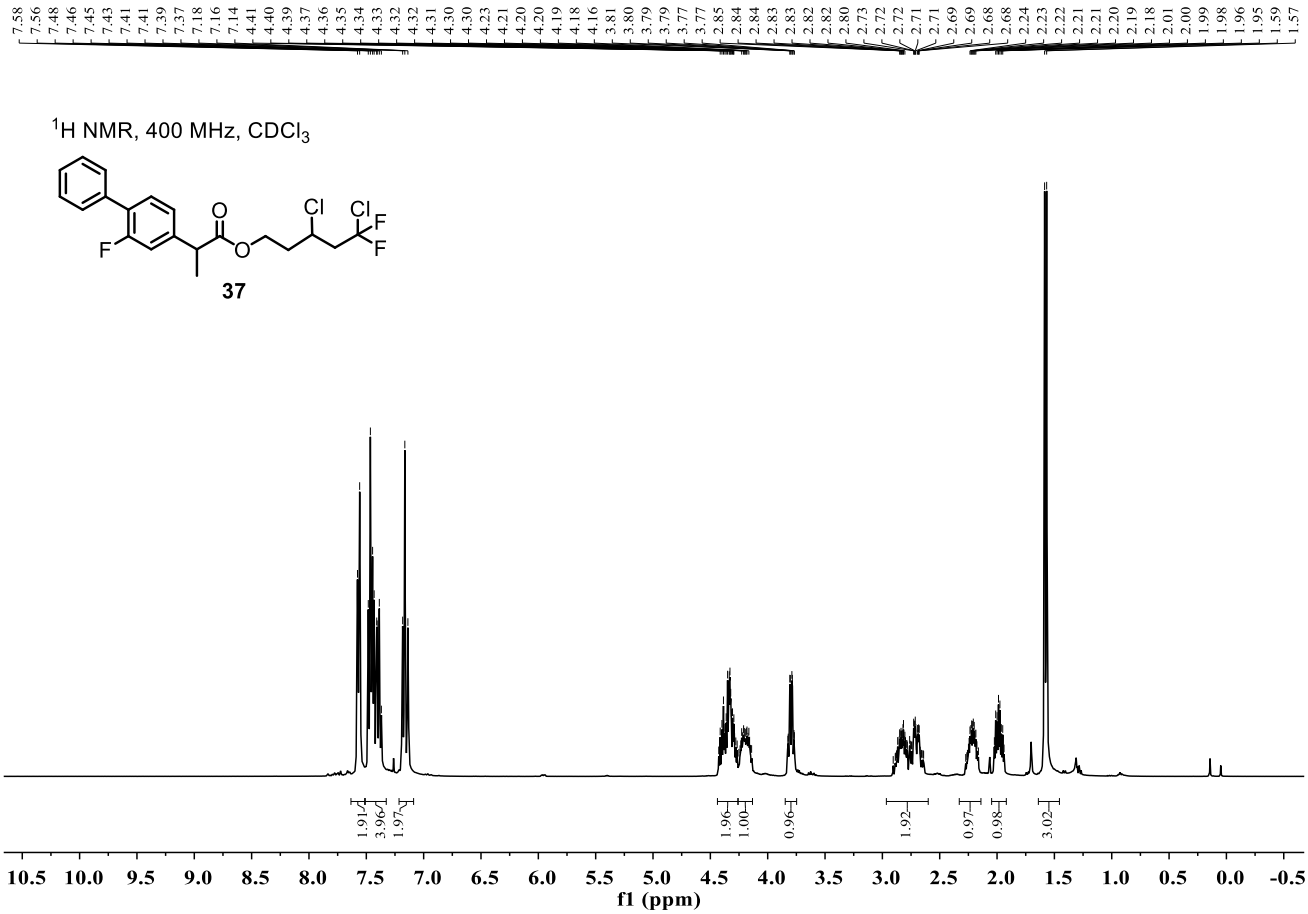


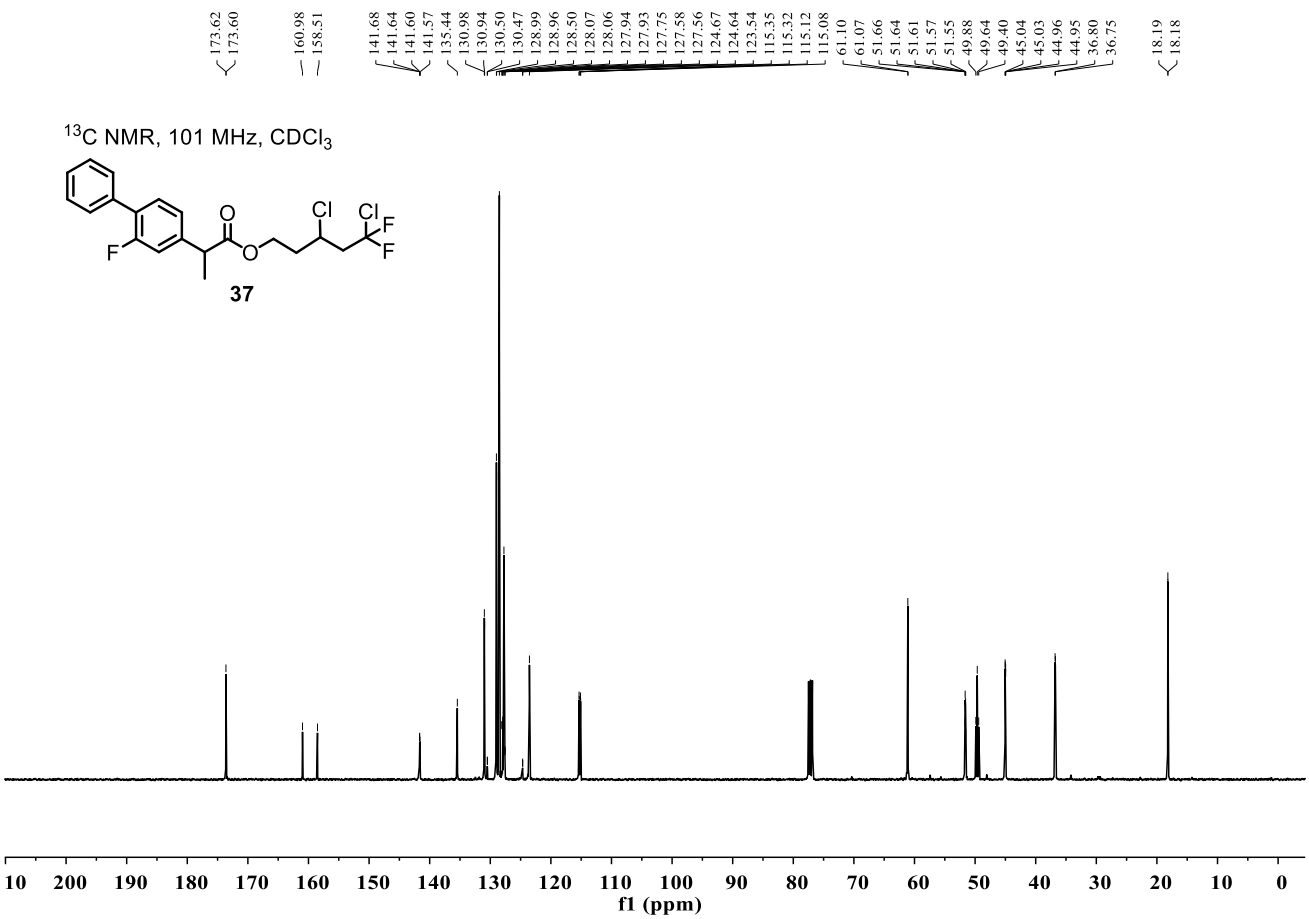
36

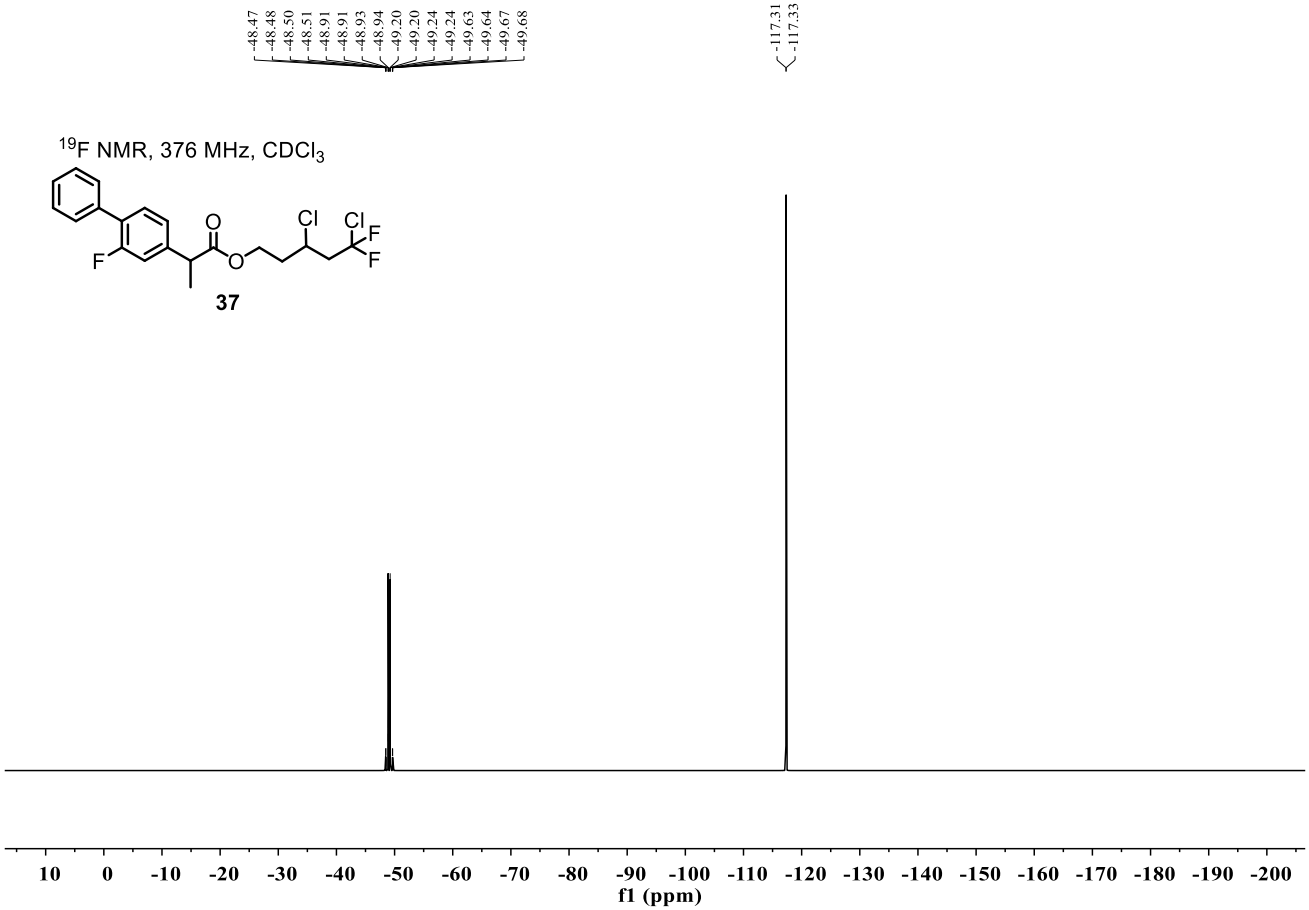


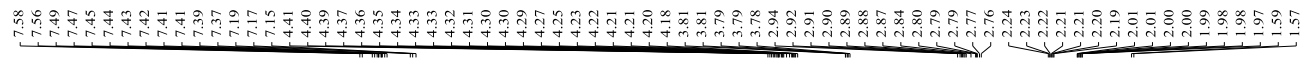



-85.82
-85.83
-85.83
-85.84
-116.84
-116.86
-116.87
-116.89
-117.27
-117.28
-117.28
19F NMR, 376 MHz, CDCl3
O
Cl
F
F
S
O
O
CF3
N
NC
36
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

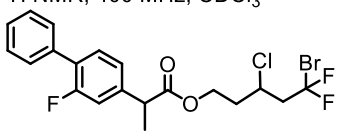

7.58
7.56
7.48
7.46
7.45
7.43
7.41
7.41
7.39
7.37
7.18
7.16
7.14
4.41
4.40
4.39
4.37
4.36
4.35
4.34
4.33
4.32
4.32
4.31
4.30
4.30
4.23
4.21
4.20
4.20
4.19
4.18
4.16
3.81
3.80
3.79
3.79
3.77
3.77
2.85
2.84
2.84
2.83
2.83
2.82
2.82
2.80
2.73
2.72
2.72
2.71
2.71
2.69
2.69
2.68
2.68
2.24
2.23
2.22
2.21
2.21
2.20
2.19
2.18
2.01
2.00
1.99
1.98
1.96
1.95
1.59
1.57
1H NMR, 400 MHz, CDCl3
O
Cl
Cl
F
F
F
O
37
1.91
3.96
1.97
1.96
1.00
0.96
1.92
0.97
0.98
3.02
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)


173.62
173.60
160.98
158.51
141.68
141.64
141.60
141.57
135.44
130.98
130.94
130.50
130.47
128.99
128.96
128.50
128.07
128.06
127.94
127.93
127.75
127.58
127.56
124.67
124.64
123.54
115.35
115.32
115.12
115.08
61.10
61.07
51.66
51.64
51.61
51.57
51.55
49.88
49.64
49.40
45.04
45.03
44.96
44.95
36.80
36.75
18.19
18.18
13C NMR, 101 MHz, CDCl3
O
Cl
Cl
F
F
F
O
37
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

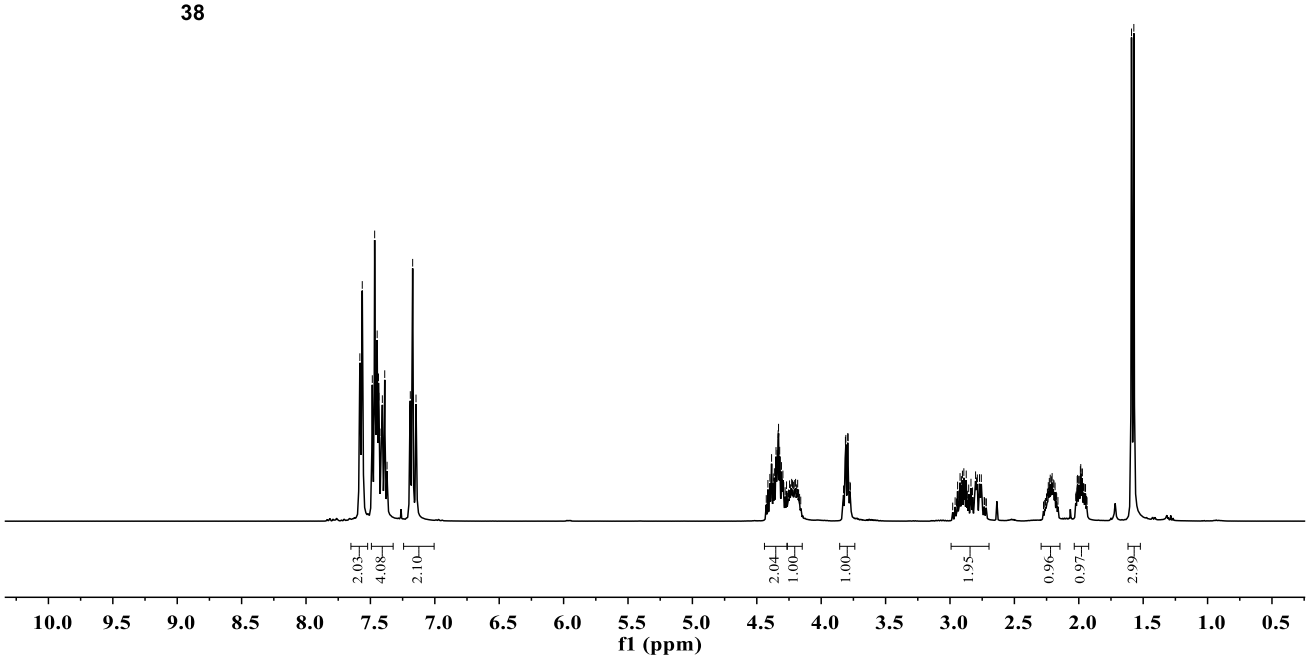

-48.47
-48.48
-48.50
-48.51
-48.91
-48.91
-48.93
-48.94
-49.20
-49.20
-49.24
-49.24
-49.63
-49.64
-49.67
-49.68
-117.31
-117.33
19F NMR, 376 MHz, CDCl3
O
Cl
Cl
F
F
F
O
37
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

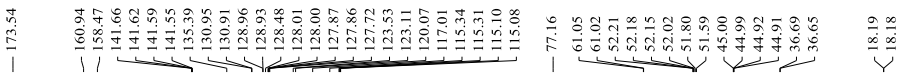


^{1}H NMR, 400 MHz, $CDCl_3$

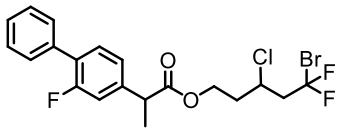


38

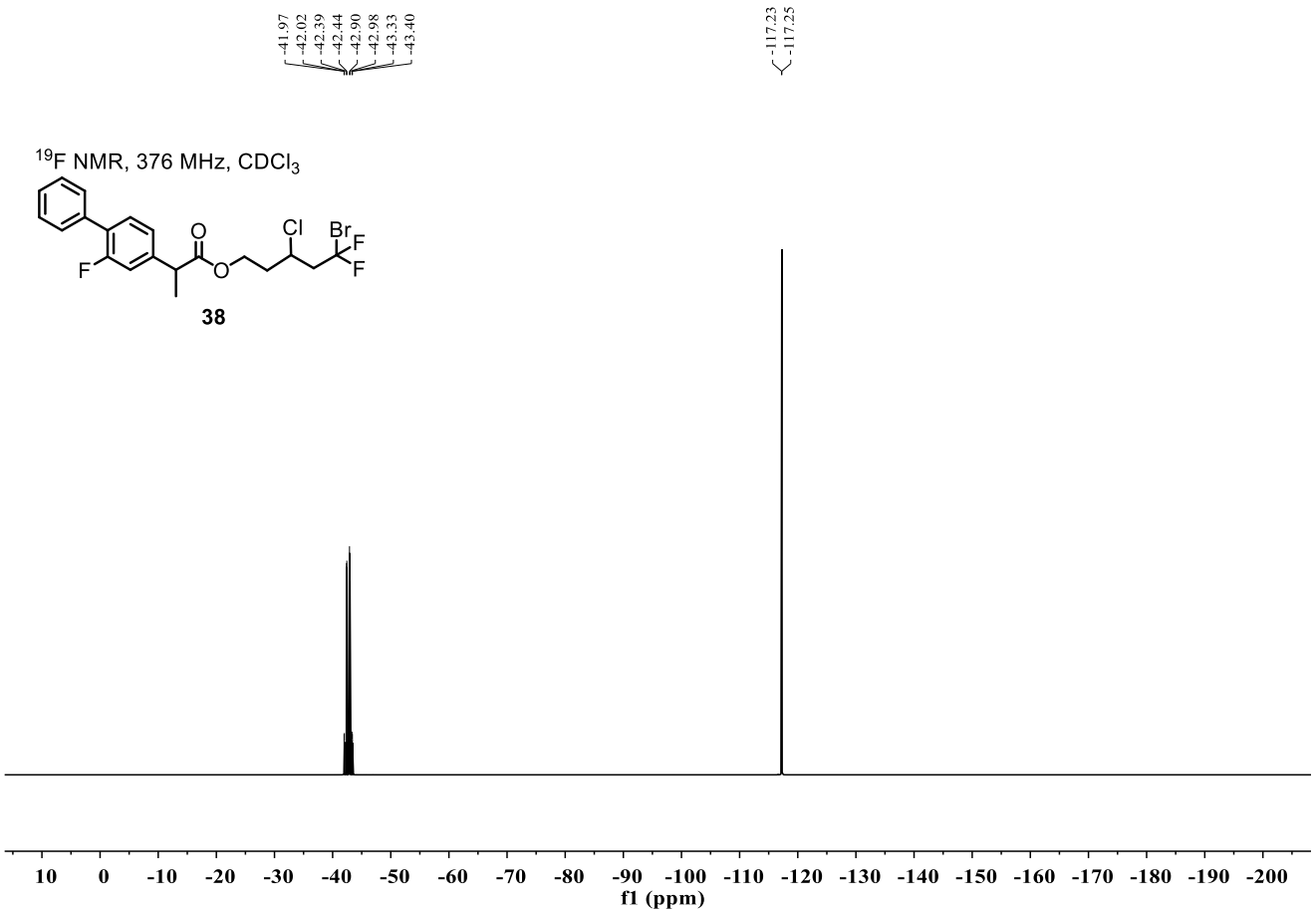


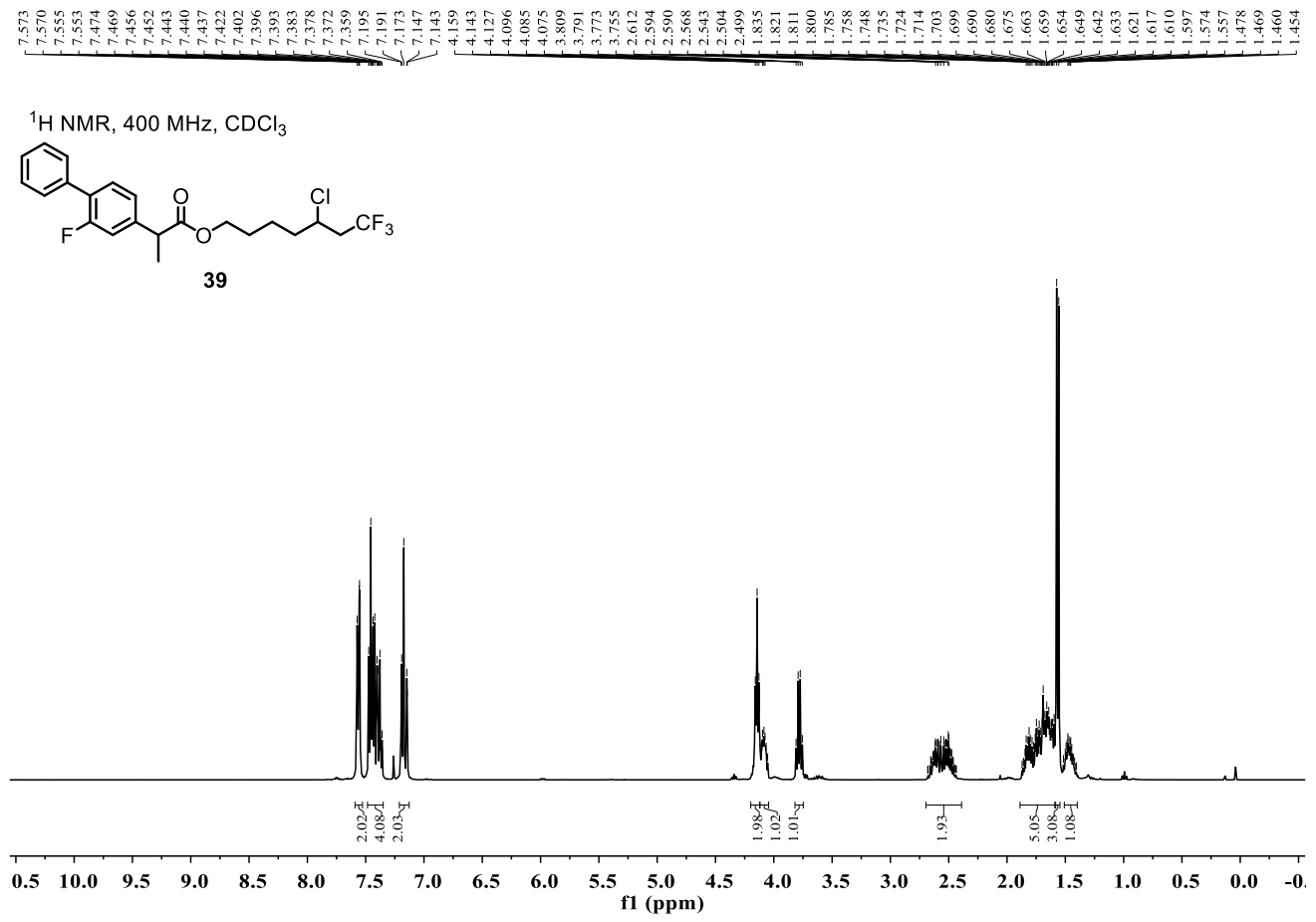


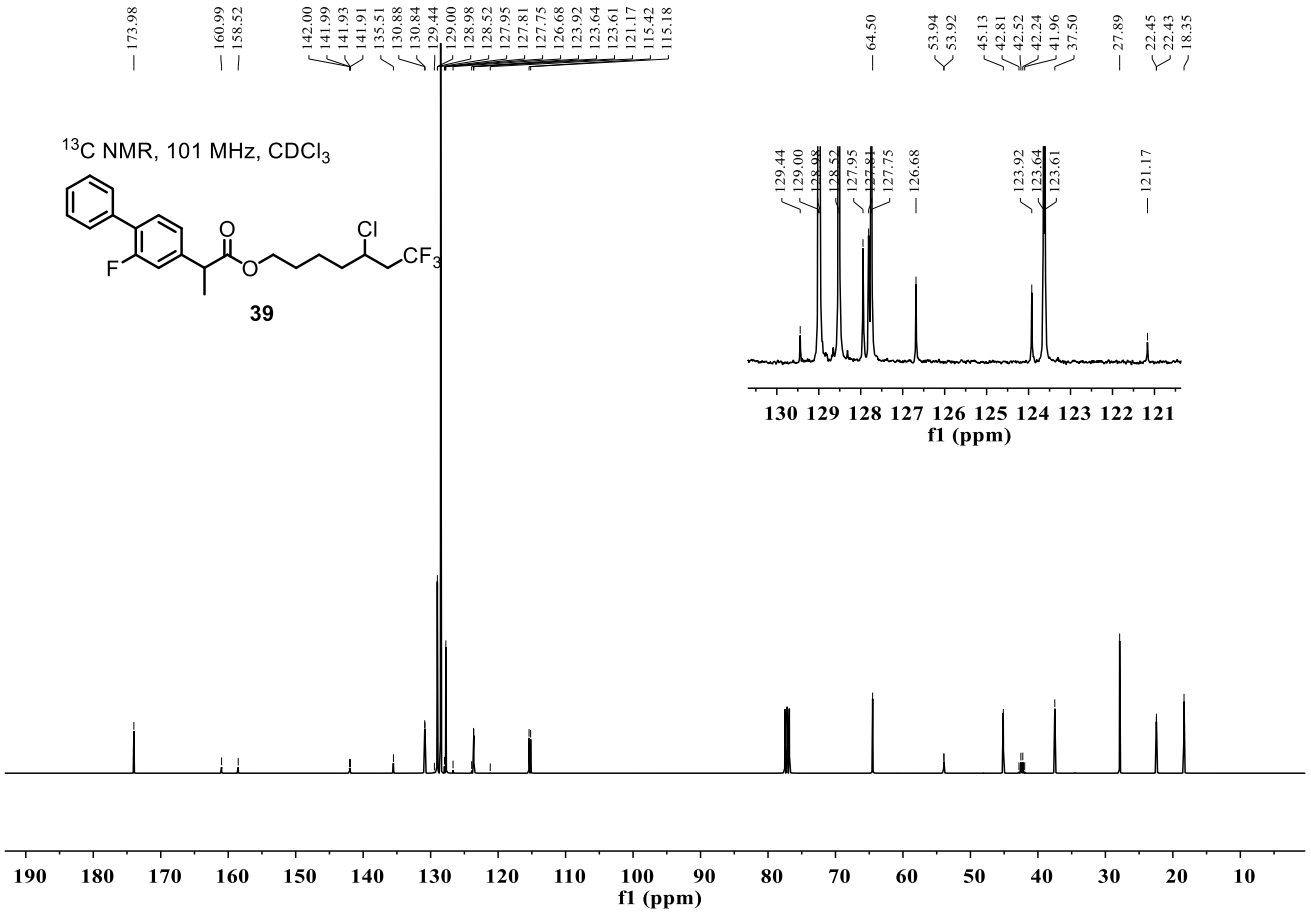
^{13}C NMR, 101 MHz, $CDCl_3$

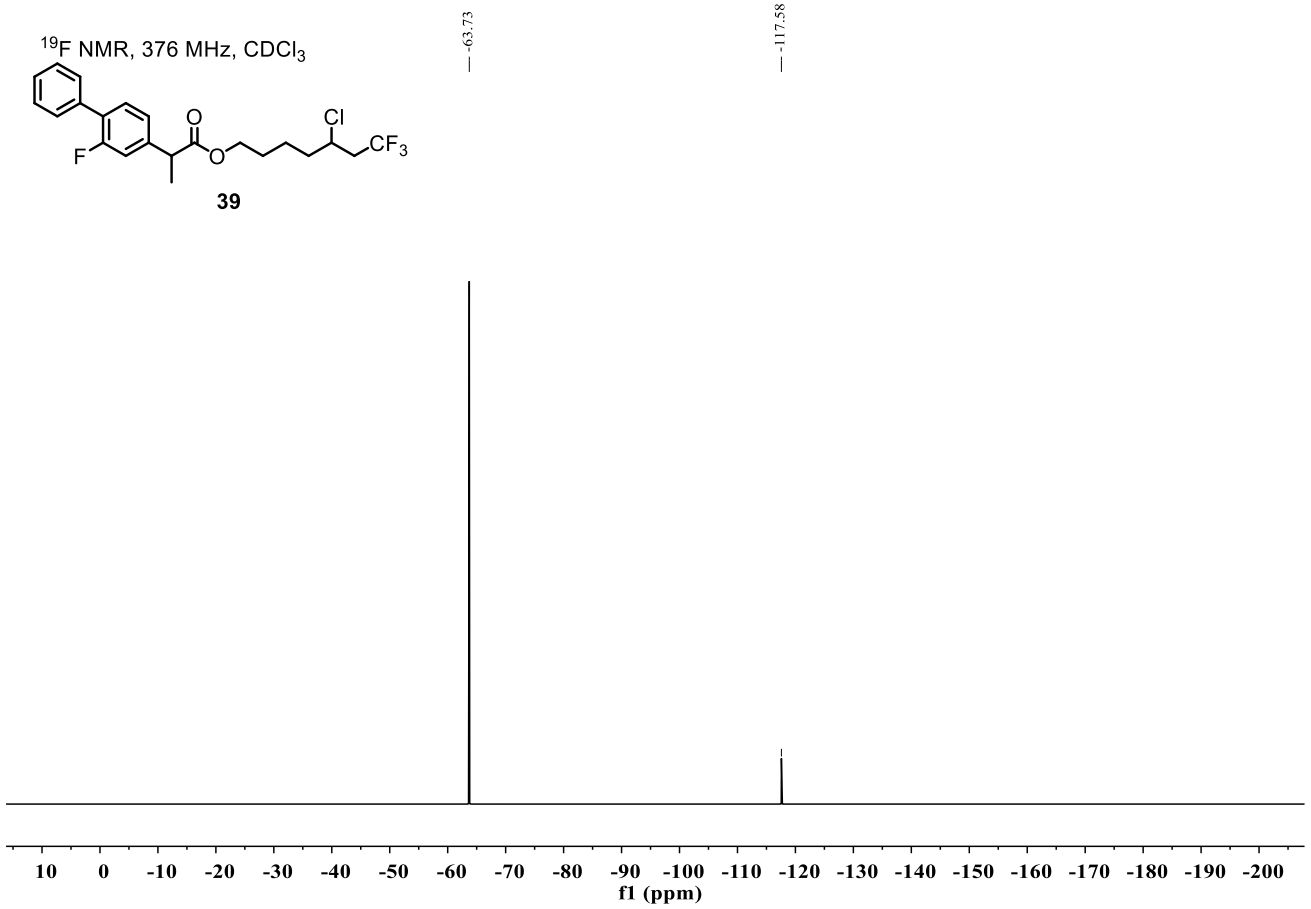


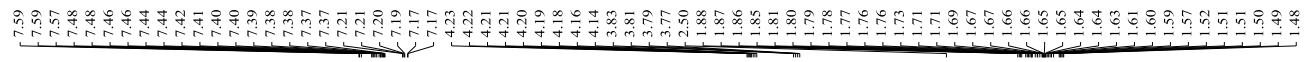
38


-41.97
-42.02
-42.39
-42.44
-42.90
-42.98
-43.33
-43.40
-117.23
-117.25
19F NMR, 376 MHz, CDCl3
F
O
O
Cl
Br
F
F
38
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

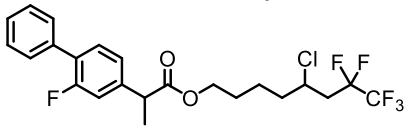

7.573
7.570
7.555
7.553
7.474
7.469
7.456
7.452
7.443
7.440
7.437
7.422
7.402
7.396
7.393
7.383
7.378
7.372
7.359
7.195
7.191
7.173
7.147
7.143
4.159
4.143
4.127
4.096
4.085
4.075
3.809
3.791
3.773
3.755
2.612
2.594
2.590
2.568
2.543
2.504
2.499
1.835
1.821
1.811
1.800
1.785
1.758
1.748
1.735
1.724
1.714
1.703
1.699
1.690
1.680
1.675
1.663
1.659
1.654
1.649
1.642
1.633
1.621
1.617
1.610
1.597
1.574
1.557
1.478
1.469
1.460
1.454
1H NMR, 400 MHz, CDCl3
F
O
O
Cl
CF3
39
2.02
4.08
2.03
1.98
1.02
1.01
1.93
5.05
3.08
1.08
0.5 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
f1 (ppm)


173.98
160.99
158.52
142.00
141.99
141.93
141.91
135.51
130.88
130.84
129.44
129.00
128.98
128.52
127.95
127.81
127.75
126.68
123.92
123.64
123.61
121.17
115.42
115.18
64.50
53.94
53.92
45.13
42.81
42.52
42.24
41.96
37.50
27.89
22.45
22.43
18.35
13C NMR, 101 MHz, CDCl3
O
Cl
F
O
CF3
39
129.44
129.00
128.98
128.52
127.95
127.81
127.75
126.68
123.92
123.64
123.61
121.17
130 129 128 127 126 125 124 123 122 121
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

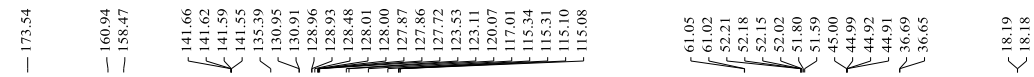

19F NMR, 376 MHz, CDCl3
-63.73
-117.58
O
Cl
F
O
CF3
39
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



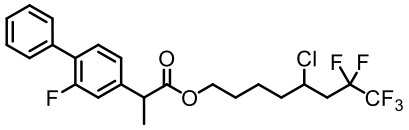
^{1}H NMR, 400 MHz, $CDCl_3$



40

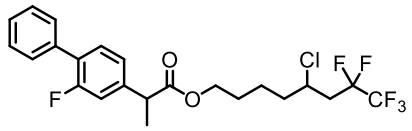


^{13}C NMR, 101 MHz, $CDCl_3$



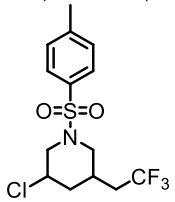
40

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

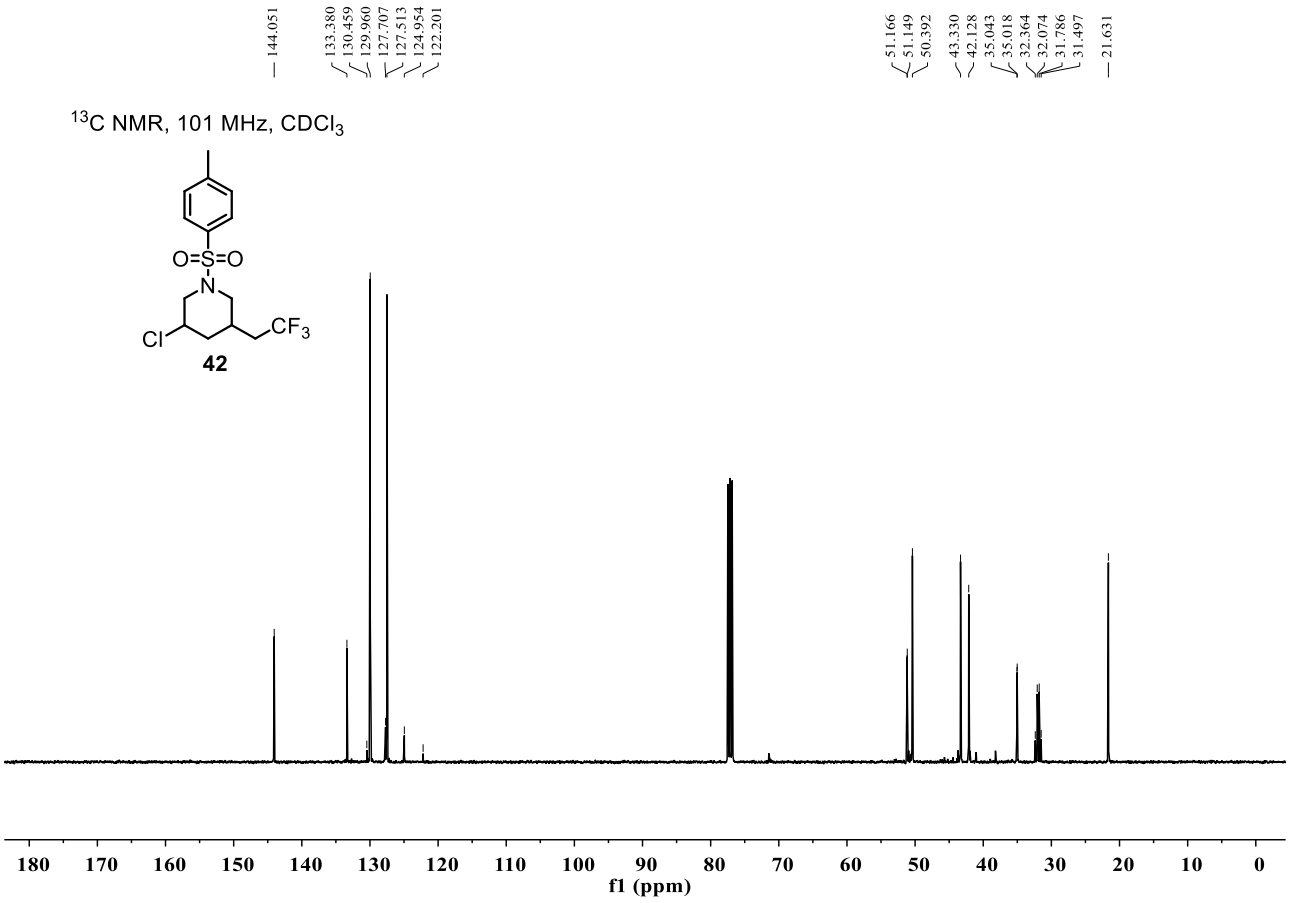


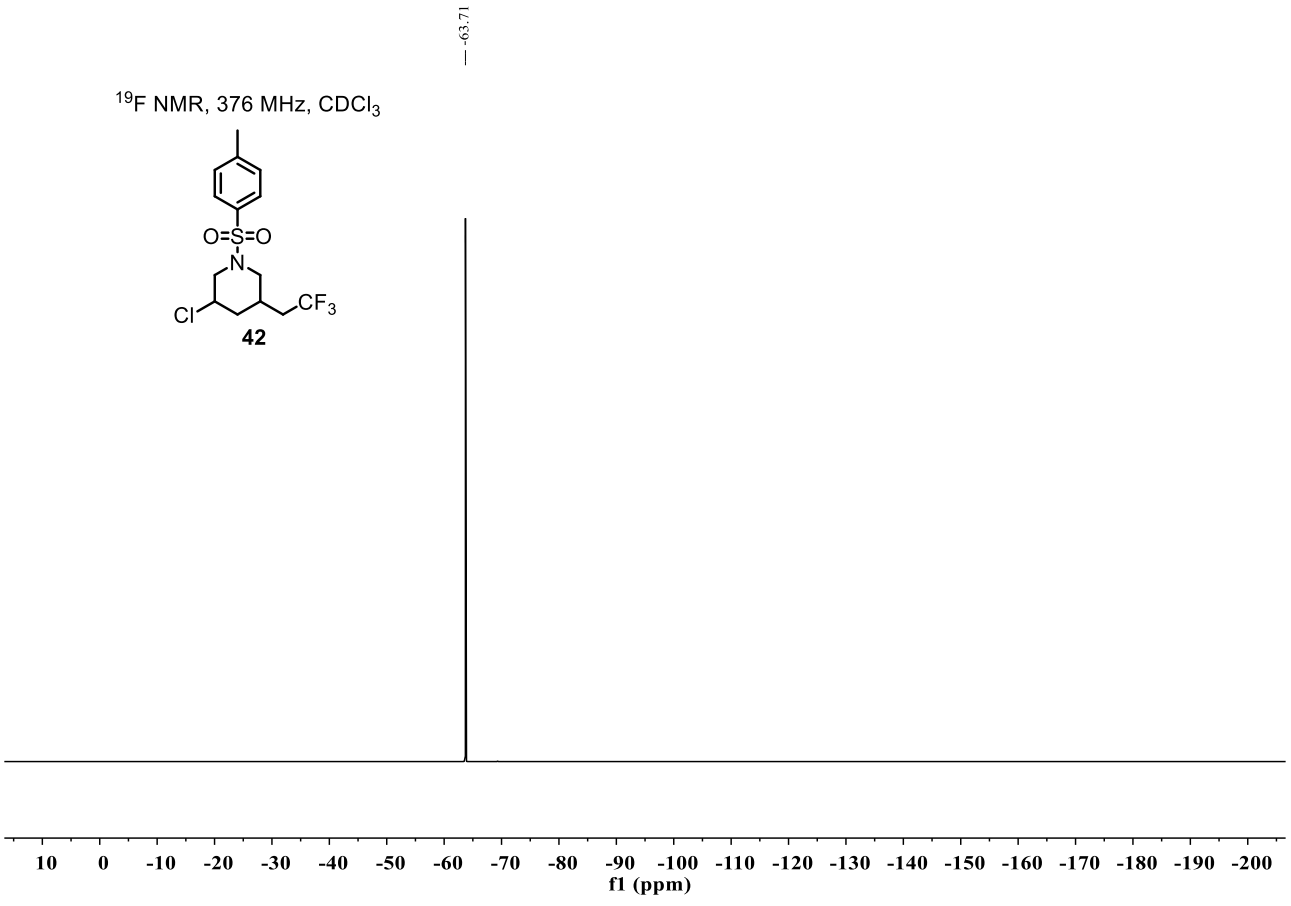
40

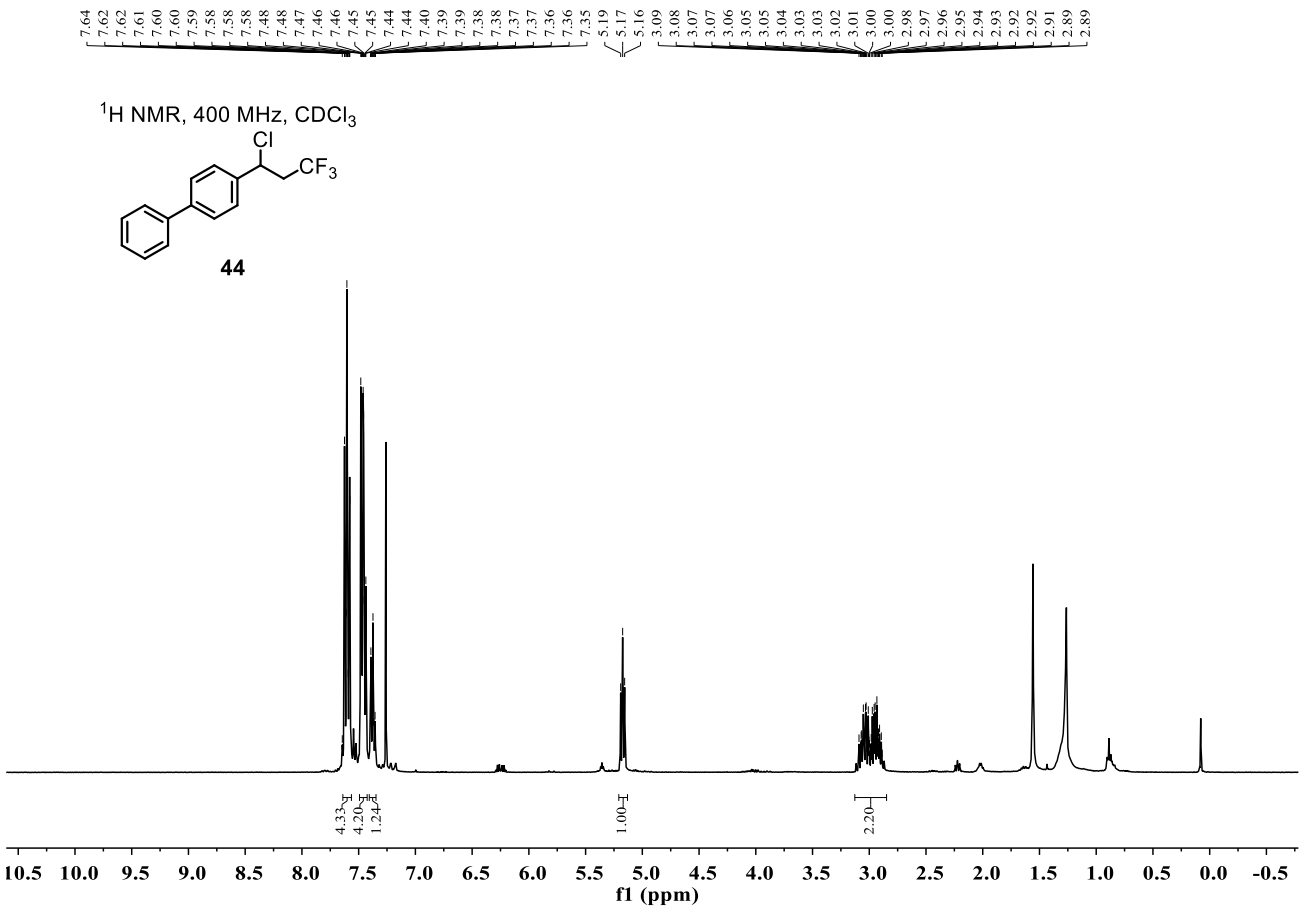
^{1}H NMR, 400 MHz, $CDCl_3$

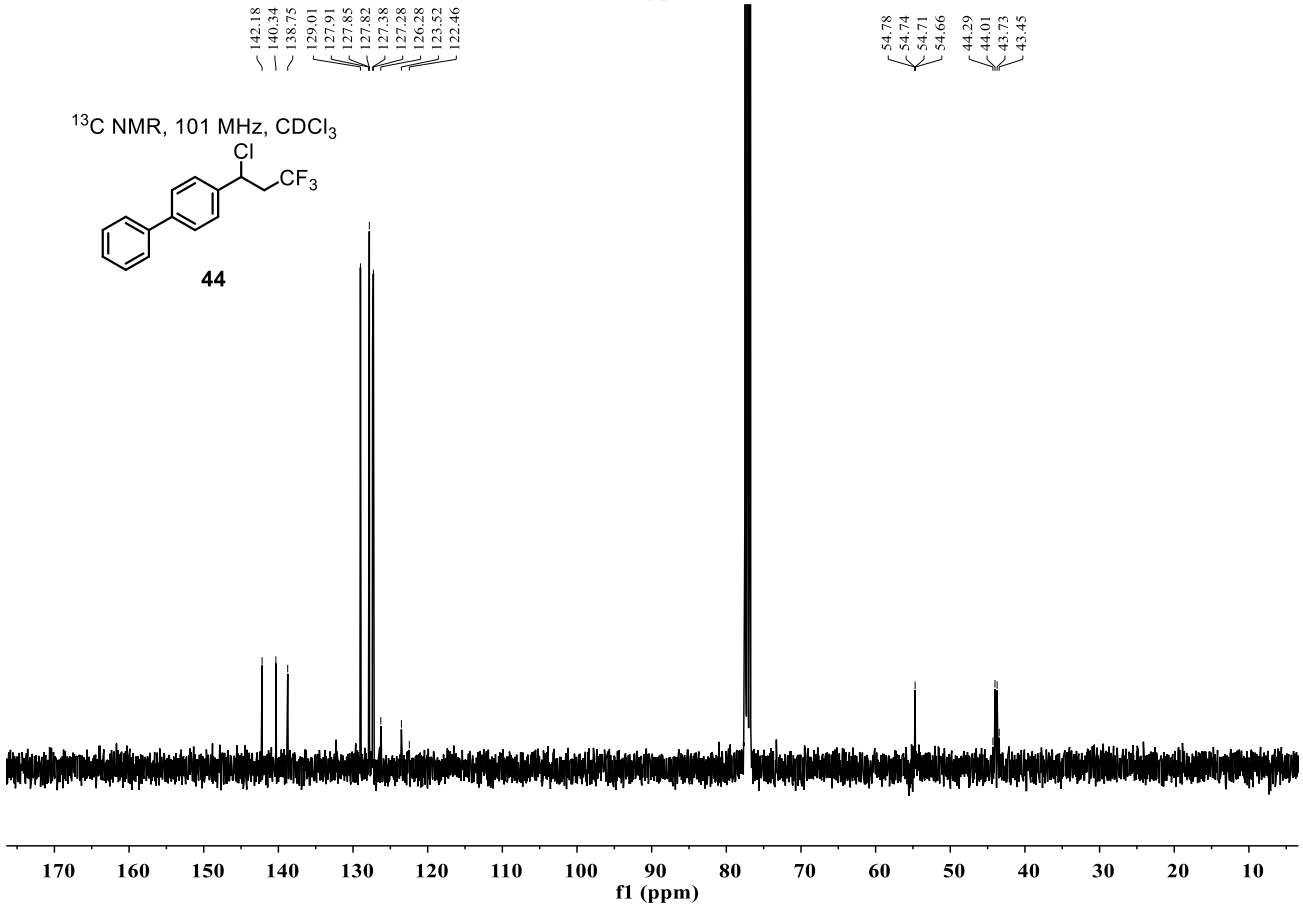


42

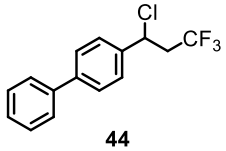

144.051
133.380
130.459
129.960
127.707
127.513
124.954
122.201
51.166
51.149
50.392
43.330
42.128
35.043
35.018
32.364
32.074
31.786
31.497
21.631
13C NMR, 101 MHz, CDCl3
O=S=O
N
Cl
CF3
42
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.71
19F NMR, 376 MHz, CDCl3
O=S=O
N
Cl
CF3
42
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


7.64 7.62 7.62 7.61 7.60 7.60 7.59 7.58 7.58 7.58 7.48 7.48 7.47 7.46 7.46 7.45 7.45 7.44 7.44 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.35
5.19 5.17 5.16
3.09 3.08 3.07 3.07 3.06 3.05 3.05 3.04 3.03 3.03 3.02 3.01 3.00 3.00 2.98 2.97 2.96 2.95 2.94 2.93 2.92 2.92 2.91 2.89 2.89
1H NMR, 400 MHz, CDCl3
Cl
CF3
44
4.33
4.20
1.24
1.00
2.20
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)


142.18 140.34 138.75 129.01 127.91 127.85 127.82 127.38 127.28 126.28 123.52 122.46
54.78 54.74 54.71 54.66 44.29 44.01 43.73 43.45
13C NMR, 101 MHz, CDCl3
Cl
CF3
44
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

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



44