Supporting Information

Water-Promoted Defluorinative Synthesis of Fluoroalkylated 1,5-Diazapentadienes by Using $(NH_4)_2CO_3$ as NH_2 and NH Sources

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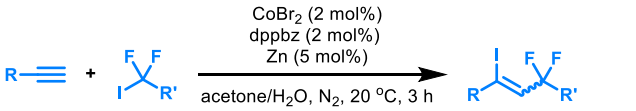
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under N_2 atmosphere using undistilled solvent. Melting points were recorded on an electrothermal digital melting point apparatus. IR spectra were recorded on a FT-IR spectrophotometer using KBr optics. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker Avance or Joel 400 MHz spectrometers. NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), broad (br), doublet of doublets (dd), doublet of triplets (dt), doublet of quartets (dq), triplet of doublets (td), tt (triplet of triplets), quartet of doublets (qd), and quartet of triplets (qt). The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive or negative mode. A suitable crystal was selected and recorded on a XtaLAB AFC12 (RINC): Kappa single diffractometer. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

General procedure for the synthesis of polyfluoroalkylated alkenes 1

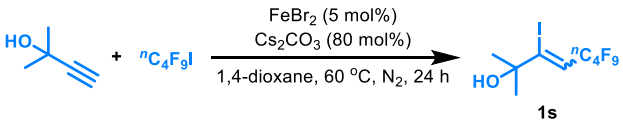
General procedure A (GPA)[1]



1a-l-1a-lV, **1b-1r**, and **1t-x**

According to Jacobi von Wangelin's reported method, a solution of alkyne (511.0 mg, 5 mmol, 1 equiv.), perfluorobutyl iodide (2594.4 mg, 7.5 mmol, 1.5 equiv.), $CoBr_2$ (21.9 mg, 0.1 mmol, 0.02 equiv.), 1,2-bis(diphenylphosphino)benzene (44.6 mg, 0.1 mmol, 0.02 equiv., dppbz), and Zn (16.3 mg, 0.25 mmol, 0.05 equiv.) in acetone/H_2O (10 mL, 30/1) was stirred at 20 °C under N_2 for 3 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~20/1) as eluent to afford the pure product **1**.

General procedure B (GPB)[2]

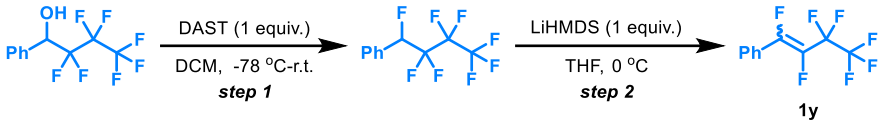


1s

According to Hu's reported method, a solution of 2-methylbut-3-yn-2-ol (420.6 mg, 5 mmol, 1 equiv.), perfluorobutyl iodide (2594.4 mg, 7.5 mmol, 1.5 equiv.), $FeBr_2$ (53.9 mg, 0.25 mmol, 0.05 equiv.), and Cs_2CO_3 (1303.0 mg, 4 mmol, 0.8 equiv.) in anhydrous 1,4-dioxane (20 mL) was stirred at 60 °C under N_2 for 24 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with EtOAc (50 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was

purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1~80/1) as eluent to afford the pure product **1s** (1978.2 mg, 46% yield).

General procedure C (GPC)[3]



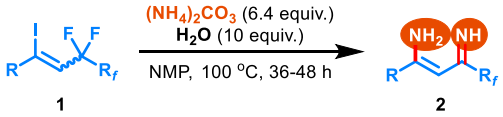
***Step 1*:**

According to Burton's reported method, a solution of 2,2,3,3,4,4,4-heptafluoro-1-phenylbutan-1-ol (1381 mg, 5 mmol, 1 equiv.) in dichloromethane (15 mL) was stirred at -78 °C under N_2. Then, diethylaminosulfur trifluoride (806.0 mg, 5 mmol, 1 equiv., DAST) was added while keeping the temperature around -70 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with Et_2O (50 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~100/1) as eluent to afford (1,2,2,3,3,4,4,4-octafluorobutyl)benzene in 72% yield (1002.5 mg).

***Step 2*:**

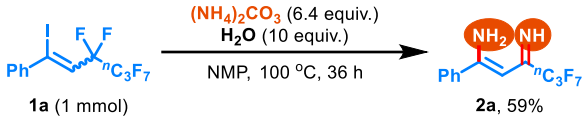
A solution of (1,2,2,3,3,4,4,4-octafluorobutyl)benzene (834.4 mg, 3 mmol, 1 equiv.) in dry THF (6 mL) was stirred at 0 °C under N_2. Then, LiHMDS (2.3 mL, 3 mmol, 1 equiv., 1.3 M in THF) was added while keeping the temperature around 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h. The reaction was then quenched by saturated NH_4Cl solution (50 mL) and extracted with Et_2O (50 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~100/1) as eluent to afford the product **1y** in 43% yield (333.0 mg).

General procedure for the defluorinative synthesis of fluoroalkylated 1,5-diazapentadienes 2



A solution of allylic fluoride **1** (0.3 mmol, 1 equiv.), $(NH_4)_2CO_3$ (184.5 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 36-48 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~2/1) as eluent to afford the pure product **2**.

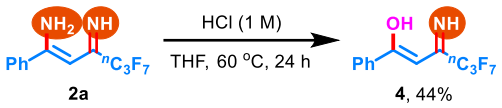
Scale-up synthesis of product 2a



A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (448.1 mg, 1 mmol, 1 equiv., **1a**), $(NH_4)_2CO_3$ (615.0 mg, 6.4 mmol, 6.4 equiv.), and H_2O (180.0 mg, 10 mmol, 10 equiv.) in NMP (10 mL) was stirred at 100 °C (oil bath) under air for 36 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1) as eluent to afford the pure product **2a** (184.2 mg, 59% yield).

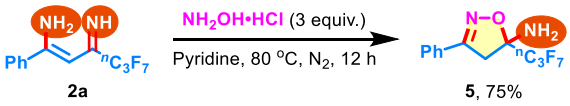
Further transformations of product 2a

a) Hydrolysis of product 2a



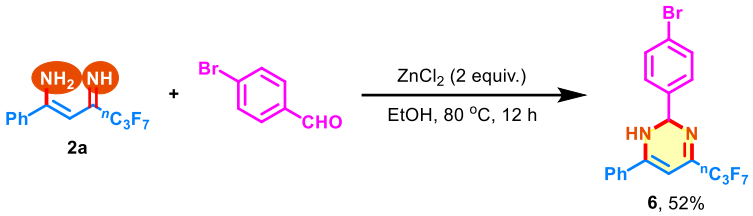
A solution of (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-imino-1-phenylhex-1-en-1-amine (62.8 mg, 0.2 mmol, 1 equiv., **2a**) in HCl (1 M in water, 4 mL, 20 equiv.) and THF (2 mL) was stirred at 60 °C (oil bath) under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~4/1) as eluent to afford the pure product **4** (27.6 mg, 44% yield).

b) The reaction of product 2a with hydroxylamine hydrochloride



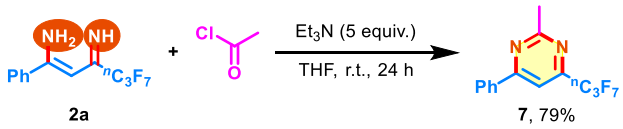
A solution of (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-imino-1-phenylhex-1-en-1-amine (62.8 mg, 0.2 mmol, 1 equiv., **2a**) and hydroxylamine hydrochloride (41.7 mg, 0.6 mmol, 3 equiv., $NH_2OH{\cdot}HCl$) in pyridine (2 mL) was stirred at 80 °C (oil bath) under N_2 for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~4/1) as eluent to afford the pure product **5** (49.4 mg, 75% yield).

c) The reaction of product 2a with 4-bromobenzaldehyde



A solution of (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-imino-1-phenylhex-1-en-1-amine (62.8 mg, 0.2 mmol, 1 equiv., **2a**), 4-bromobenzaldehyde (37.0 mg, 0.2 mmol, 1 equiv.), and $ZnCl_2$ (27.3 mg, 0.2 mmol, 1 equiv.) in EtOH (2 mL) was stirred at 80 °C (oil bath) under air for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~4/1) as eluent to afford the pure product **6** (49.7 mg, 52% yield).

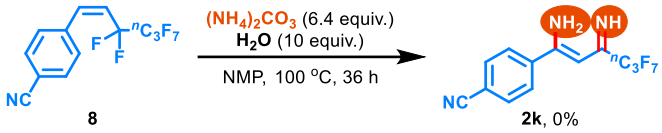
d) The reaction of product 2a with acetyl chloride



A solution of (*Z*)-4,4,5,5,6,6,6-heptafluoro-3-imino-1-phenylhex-1-en-1-amine (62.8 mg, 0.2 mmol, 1 equiv., **2a**), acetyl chloride (69.0 mg, 0.88 mmol, 4.4 equiv.), and Et_3N (101.2 mg, 1 mmol, 5 equiv.) in THF (2 mL) was stirred at room temperature under air for 24 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (100/1~80/1) as eluent to afford the pure product **7** (53.6 mg, 79% yield).

Mechanistic studies

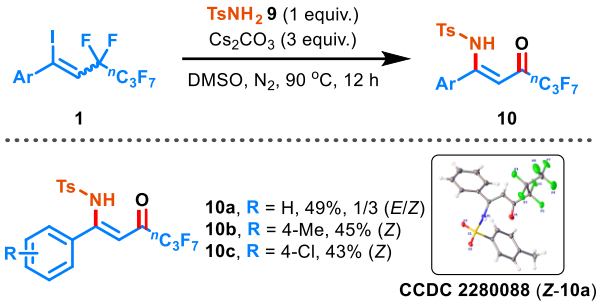
a) The reactivity of perfluoroalkylated alkene 8



A solution of (*Z*)-4-(3,3,4,4,5,5,6,6,6-nonafluorohex-1-en-1-yl)benzonitrile (69.4 mg, 0.2 mmol, 1 equiv., **8**), $(NH_4)_2CO_3$ (123.0 mg, 1.28 mmol, 6.4 equiv.), and H_2O (36.0 mg, 2 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 36 h. No desired product **2k** was detected.

The necessity of an iodine atom at the α-position of the fluoroalkyl alkene demonstrated that the initial reaction might go through a C-I bond displacement.

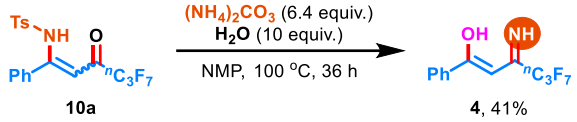
b) The use of $TsNH_2$ (9) as a *N*-source



A solution of allylic fluoride **1** (0.45 mmol, 1.5 equiv.), $TsNH_2$ (51.4 mg, 0.3 mmol, 1 equiv., **9**), and Cs_2CO_3 (293.2 mg, 0.9 mmol, 3 equiv.) in DMSO (2 mL) was stirred at 90 °C (oil bath) under N_2 for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1) as eluent to afford the pure products **10a-c** in 43-49% yields.

These results suggested that 1) deiodinative amination takes place first; 2) H_2O is involved in the C(sp^3)-F bond breaking step as a reagent and/or promoter, not merely for increasing the solubility of $(NH_4)_2CO_3$ in NMP; 3) the further condensation of the resulting enaminoketone with $TsNH_2$ is difficult to occur under basic conditions.

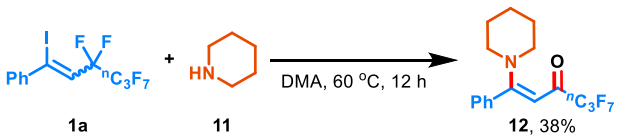
c) The reaction of 10a with $(NH_4)_2CO_3$



A solution of *N*-(4,4,5,5,6,6,6-heptafluoro-3-oxo-1-phenylhex-1-en-1-yl)-4-methylbenzenesulfonamide (93.9 mg, 0.2 mmol, 1 equiv., **10a**), $(NH_4)_2CO_3$ (123.0 mg, 1.28 mmol, 6.4 equiv.), and H_2O (36.1 mg, 2 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 36 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (4/1) as eluent to afford the pure product **4** (26.1 mg, 41% yield).

This result suggested that the further condensation of the enaminoketone 10a with $(NH_4)_2CO_3$ is much easier than $TsNH_2$.

d) The use of piperidine (11) as a *N*-source

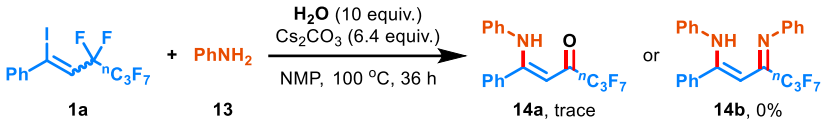


A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**) and piperidine (127.7 mg, 1.5 mmol, 5 equiv., **11**) in DMA (2 mL) was stirred at 60 °C

(oil bath) under air for 12 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (10/1~4/1) as eluent to afford the pure product **12** (43.6 mg, 38% yield).

These results suggested that 1) deiodinative amination takes place first; 2) H_2O is involved in the C(sp^3)-F bond breaking step as a reagent and/or promoter, not merely for increasing the solubility of $(NH_4)_2CO_3$ in NMP; 3) the further condensation of the resulting enaminoketone with the piperidine is difficult to occur under basic conditions.

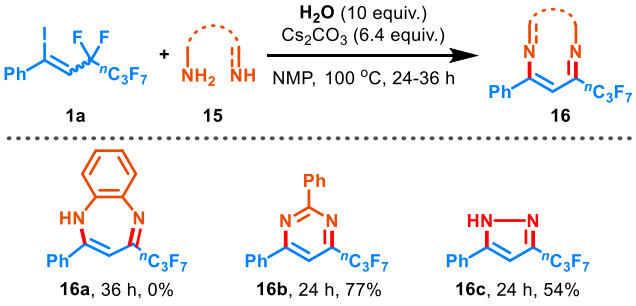
e) The use of aniline (13) as a *N*-source



A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), aniline (178.8 mg, 1.92 mmol, 6.4 equiv., **13**), Cs_2CO_3 (625.6 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 36 h. A trace amount of product **14a** was formed and no desired product **14b** was obtained.

This result suggested that aniline (13) is not a suitable candidate for the present defluoroamination.

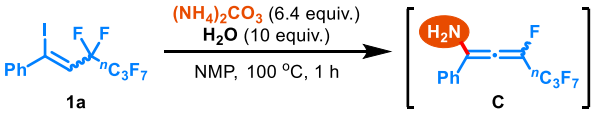
f) The use of diamine compounds 15 as dual *N*-sources



A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (62.8 mg, 0.3 mmol, 1 equiv., **1a**), diamine compound (1.92 mmol, 6.4 equiv., **15a-c**), Cs_2CO_3 (625.6 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 24-36 h. The reaction was then quenched by saturated NH_4Cl solution (20 mL) and extracted with EtOAc (20 mL x 3). The organic layer was washed with saturated brine twice, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash silica gel column chromatography (300-400 mesh) using petroleum ether/ethyl acetate (200/1~2/1) as eluent to afford the pure product **16b** (92.6 mg, 77% yield) or **16c** (50.8 mg, 54% yield). No desired product **16a** was detected.

This result suggested that the nucleophilicity of the N-source is a key factor for the success of the defluorinative transformation.

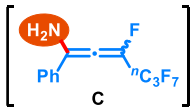
g) Detection of possible intermediate C



A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), $(NH_4)_2CO_3$ (184.5 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 1 h. Then the vial was cooled to room temperature and the reaction mixture was passed through a short pad of Celite followed by rinse with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS.

HRMS analysis of the reaction mixture suggested the involvement of allenylic intermediate C.

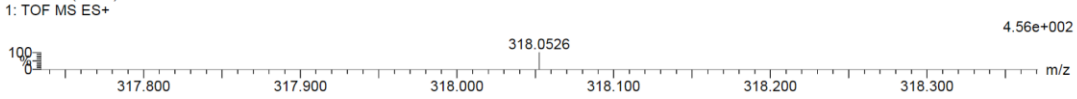
Elemental Composition Report **Page 1**



Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

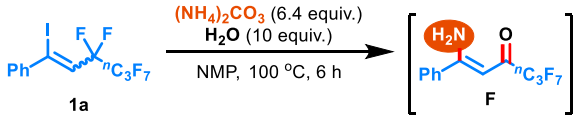
Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 11-13 H: 7-9 N: 0-2 F: 7-9
HW7 228 (1.646)
1: TOF MS ES+

$C_{12}H_8F_8N^+$ $[M+H]^+$
Exact Mass: 318.0524
Found: 318.0526



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
318.0526	318.0529	-0.3	-0.9	5.5	21.0	n/a	n/a	C12 H8 N F8

h) Detection of possible intermediate F

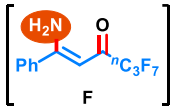


A solution of (3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (134.4 mg, 0.3 mmol, 1 equiv., **1a**), $(NH_4)_2CO_3$ (184.5 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 6 h. Then the vial was cooled to room temperature and the reaction mixture was passed through a short pad of Celite followed by rinse with MeCN. A sample was taken from the filtrate and was directly analyzed by HRMS.

HRMS analysis of the reaction mixture suggested the involvement of aminovinyl ketone F.

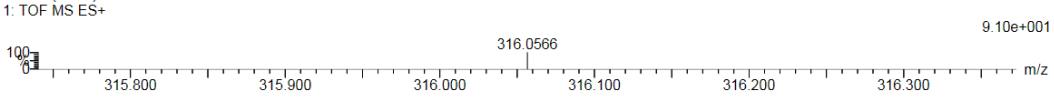
Elemental Composition Report Page 1

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3



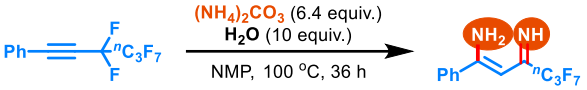
Calcd for $C_{12}H_9F_7NO^+$ $[M+H]^+$
Exact Mass: 316.0567
Found: 316.0566

Monoisotopic Mass, Even Electron Ions
107 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 11-13 H: 8-10 N: 1-3 O: 0-3 F: 7-11 K: 0-1
740 58 (0.433)
1: TOF MS ES+



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
316.0566	316.0572	-0.6	-1.9	5.5	16.3	n/a	n/a	C12 H9 N O F7

i) The reaction of perfluorobutyl alkyne 1a' with $(NH_4)_2CO_3$

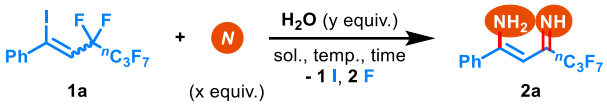


1a' **2a**, 39% NMR yield

A solution of (perfluorohex-1-yn-1-yl)benzene (96.1 mg, 0.3 mmol, 1 equiv., **1a'**), $(NH_4)_2CO_3$ (184.5 mg, 1.92 mmol, 6.4 equiv.), and H_2O (54.0 mg, 3 mmol, 10 equiv.) in NMP (4 mL) was stirred at 100 °C (oil bath) under air for 36 h. The yield of **2a** was determined by ^{19}F NMR analysis with 1-fluoro-4-methoxybenzene (0.1 mmol) as an internal standard.

Optimization of the reaction conditions

Table S1. Optimization of the reaction conditions[a]



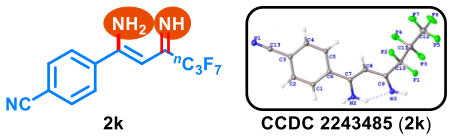
Entry	*N*-source (x equiv)	H_2O (y equiv.)	Solvent	Temp. (°C)	Time (h)	Yield of **1a** (%)[b]	Yield of **2a** (%)[b]
1	$(NH_4)_2CO_3$ (6.4)	5	DMA	70	12	68	11
2	$(NH_4)_2CO_3$ (6.4)	5	DMA	90	12	37	33
3	$(NH_4)_2CO_3$ (6.4)	5	DMA	100	12	38	35
4	$(NH_4)_2CO_3$ (6.4)	5	DMA	100	24	18	48
5	$(NH_4)_2CO_3$ (6.4)	5	DMSO	100	24	0	33
6	$(NH_4)_2CO_3$ (6.4)	5	DMF	100	24	25	8
7	$(NH_4)_2CO_3$ (6.4)	5	NMP	100	24	10	66
6	$(NH_4)_2CO_3$ (6.4)	5	Toluene	100	24	0	0
7	$(NH_4)_2CO_3$ (6.4)	5	1,4-dioxane	100	24	0	0
8	$(NH_4)_2CO_3$ (6.4)	5	MeCN	80	24	0	0
9	$(NH_4)_2CO_3$ (6.4)	5	^{t}BuOH	85	24	0	0
10	$(NH_4)_2CO_3$ (6.4)	5	EtOAc	80	24	0	0
11	$(NH_4)_2CO_3$ (6.4)	0	NMP	100	24	23	44
12	$(NH_4)_2CO_3$ (6.4)	5	NMP	80	24	27	49
13	$(NH_4)_2CO_3$ (6.4)	5	NMP	120	24	0	54
14	$(NH_4)_2CO_3$ (6.4)	8	NMP	100	24	11	67
15	$(NH_4)_2CO_3$ (6.4)	10	NMP	100	24	10	71 (55)[c]
16	$(NH_4)_2CO_3$ (6.4)	15	NMP	100	24	9	62
17	$(NH_4)_2CO_3$ (6.4)	20	NMP	100	24	10	63
18	$(NH_4)_2CO_3$ (4.4)	10	NMP	100	24	5	45
19	$(NH_4)_2CO_3$ (2.4)	10	NMP	100	24	11	34
20	NH_3 (aq. 6.4) + Cs_2CO_3 (6.4)	10	NMP	100	24	trace	trace
21	NH_4OAc (6.4) + Cs_2CO_3 (6.4)	10	NMP	100	24	trace	trace
22	NH_4Cl (6.4) + Cs_2CO_3 (6.4)	10	NMP	100	24	trace	26
23	$(NH_4)_2CO_3$ (6.4)	10	NMP	100	24	17[d,e]	32[d,e]
24	$(NH_4)_2CO_3$ (6.4)	10	NMP	100	24	12[f]	74[f]
25	$(NH_4)_2CO_3$ (6.4)	10	NMP	100	24	13[g]	79[g] (64)[c]
26	**$(NH_4)_2CO_3$ (6.4)**	**10**	**NMP**	**100**	**36**	**7[g]**	**91[g] (82)[c]**
27	--	10	NMP	100	36	83[g]	0

[a] Reaction conditions: **1a** (0.3 mmol), ***N*** source (0.72-1.92 mmol), and H_2O (0-20 mmol) in solvent (1-4 mL) at 70-120 °C under air for 12-36 h. [b] Yields were determined by ^{19}F NMR analysis with 1-fluoro-4-methoxybenzene (0.1 mmol) as an internal standard. [c] Isolated yield. [d] Under N_2. [e] In 1 mL of NMP. [f] In 3 mL of NMP. [g] In 4 mL of NMP.

The X-ray crystal structures of products 2k and *Z*-10a

The single crystals were grown from the mixed solution of EtOAc/EtOH/H_2O by slowly evaporating the above solvents at room temperature.

(*Z*)-4-(1-Amino-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-yl)benzonitrile (2k; displacement ellipsoids are drawn at the 50% probability levels):



CCDC number: 2243485

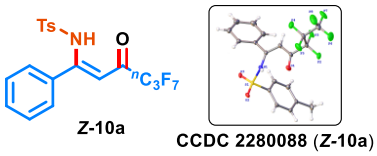
Table S2. Crystal data and structure refinement for **2k**.

Identification code	**2k**
Empirical formula	$C_{13}H_8F_7N_3$
Formula weight	339.22
Temperature/K	199.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.5372(11)
b/Å	11.7335(9)
c/Å	10.3893(9)
α/°	90
β/°	104.132(9)
γ/°	90
Volume/Å^3	1363.9(2)
Z	4
ρ_{calc}g/cm^3	1.652
μ/mm^{-1}	0.168
F(000)	680.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.03 to 49.998
Index ranges	$-13 \le h \le 13$, $-11 \le k \le 13$, $-12 \le l \le 10$
Reflections collected	5493
Independent reflections	2399 [R_{int} = 0.0239, R_{sigma} = 0.0324]
Data/restraints/parameters	2399/0/221
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.0986
Final R indexes [all data]	R_1 = 0.0479, wR_2 = 0.1047
Largest diff. peak/hole / e Å^{-3}	0.19/-0.28

Crystal structure determination of [2k]

Crystal Data for $C_{13}H_8F_7N_3$ (*M* =339.22 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 11.5372(11) Å, *b* = 11.7335(9) Å, *c* = 10.3893(9) Å, *β* = 104.132(9) °, *V* = 1363.9(2) Å^3, *Z* = 4, *T* = 199.99(10) K, μ(Mo Kα) = 0.168 mm^{-1}, *Dcalc* = 1.652 g/cm^3, 5493 reflections measured (5.03° ≤ 2Θ ≤ 49.998°), 2399 unique (R_{int} = 0.0239, R_{sigma} = 0.0324) which were used in all calculations. The final R_1 was 0.0395 (I > 2σ(I)) and wR_2 was 0.1047 (all data).

(*Z*)-*N*-(4,4,5,5,6,6,6-Heptafluoro-3-oxo-1-phenylhex-1-en-1-yl)-4-methylbenzenesulfonamide (*Z*-10a; displacement ellipsoids are drawn at the 50% probability levels):



Z-10a

CCDC 2280088 (*Z*-10a)

CCDC number: 2280088

Table S3. Crystal data and structure refinement for ***Z*-10a**.

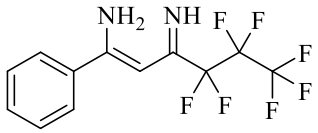
Identification code	***Z*-10a**
Empirical formula	$C_{19}H_{14}F_7NO_3S$
Formula weight	469.37
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	6.2755(10)
b/Å	8.1410(9)
c/Å	19.0094(12)
α/°	81.051(7)
β/°	85.123(9)
γ/°	84.276(11)
Volume/Å^3	952.2(2)
Z	2
ρ_{calc}g/cm^3	1.637
μ/mm^{-1}	2.365
F(000)	476.0
Crystal size/mm^3	0.16 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.718 to 133.198
Index ranges	-7 ≤ h ≤ 7, -9 ≤ k ≤ 9, -22 ≤ l ≤ 14
Reflections collected	5808
Independent reflections	3370 [R_{int} = 0.0882, R_{sigma} = 0.0801]
Data/restraints/parameters	3370/0/281

Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0955, wR_2 = 0.2680
Final R indexes [all data]	R_1 = 0.1060, wR_2 = 0.2865
Largest diff. peak/hole / e $Å^{-3}$	0.91/-1.19

Crystal structure determination of [*Z*-10a]

Crystal Data for $C_{19}H_{14}F_7NO_3S$ (*M* =469.37 g/mol): triclinic, space group P-1 (no. 2), *a* = 6.2755(10) Å, *b* = 8.1410(9) Å, *c* = 19.0094(12) Å, *α* = 81.051(7) °, *β* = 85.123(9) °, *γ* = 84.276(11) °, *V* = 952.2(2) $Å^3$, *Z* = 2, *T* = 150.00(10) K, μ(Cu Kα) = 2.365 mm^{-1}, *Dcalc* = 1.637 g/cm^3, 5808 reflections measured (4.718° ≤ 2Θ ≤ 133.198°), 3370 unique (R_{int} = 0.0882, R_{sigma} = 0.0801) which were used in all calculations. The final R_1 was 0.0955 (I > 2σ(I)) and wR_2 was 0.2865 (all data).

Characterization data for products



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-phenylhex-1-en-1-amine (2a):

Yield = 82% (77.0 mg). Green oil.

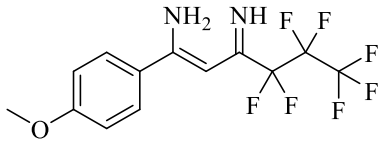
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 9.56 (brs, 2H), 7.61–7.53 (m, 2H), 7.50–7.42 (m, 3H), 5.84 (brs, 1H), 5.33 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): *δ* = -80.32 (t, *J* = 9.4 Hz, 3F), -120.07 (q, *J* = 9.7 Hz, 2F), -126.48 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): *δ* = 160.8, 160.7 (t, J_{C-F} = 22.9 Hz), 138.2, 130.5, 129.1, 126.3, 87.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_{10}F_7N_2$ $[M+H]^+$ 315.0727, found: 315.0721.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(4-methoxyphenyl)hex-1-en-1-amine (2b):

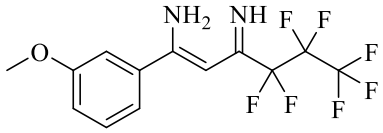
Yield = 69% (71.1 mg). Green oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

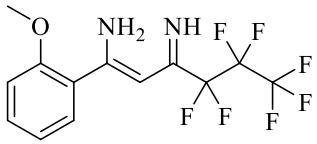
^{1}H NMR (400 MHz, $CDCl_3$): *δ* = 9.51 (brs, 2H), 7.60–7.45 (m, 2H), 7.08–6.87 (m, 2H), 5.81 (brs, 1H), 5.29 (s, 1H), 3.85 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): *δ* = -80.33 (t, *J* = 9.7 Hz, 3F), -120.01 (q, *J* = 8.9 Hz, 2F), -126.49 (s, 2F) ppm.

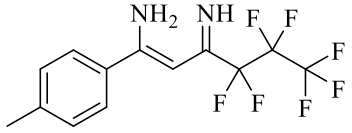
^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 160.7 (t, $J_{C\text{-}F}$ = 23.2 Hz), 160.4, 130.4, 127.7, 114.4, 87.1, 55.5 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{13}H_{12}F_7N_2O$ $[M+H]^+$ 345.0832, found: 345.0825.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(3-methoxyphenyl)hex-1-en-1-amine (2c):
Yield = 69% (71.3 mg). Green oil.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (brs, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.15 (ddd, *J* = 7.7, 1.8, 1.0 Hz, 1H), 7.09–7.07 (m, 1H), 7.00 (ddd, *J* = 8.2, 2.6, 1.0 Hz, 1H), 5.86 (brs, 1H), 5.33 (s, 1H), 3.86 (s, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.34 (t, *J* = 9.7 Hz, 3F), -120.09 (q, *J* = 9.3 Hz, 2F), -126.49 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.7 (t, $J_{C\text{-}F}$ = 24.3 Hz), 160.4, 160.0, 139.7, 130.2, 118.6, 115.6, 112.1, 87.8, 55.5 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{13}H_{12}F_7N_2O$ $[M+H]^+$ 345.0832, found: 345.0831.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(2-methoxyphenyl)hex-1-en-1-amine (2d):
Yield = 27% (27.9 mg, 36 h); 29% (30.2 mg, 48 h). Green oil.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.46 (brs, 2H), 7.50–7.36 (m, 2H), 7.08–6.95 (m, 2H), 6.61 (brs, 1H), 5.24 (s, 1H), 3.88 (s, 3H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.32 (t, *J* = 9.7 Hz, 3F), -119.98 (q, *J* = 10.4 Hz, 2F), -126.50 (s, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.1, 159.9 (t, $J_{C\text{-}F}$ = 22.2 Hz), 156.8, 131.3, 129.6, 126.3, 121.2, 111.7, 89.2, 55.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{13}H_{12}F_7N_2O$ $[M+H]^+$ 345.0832, found: 345.0829.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(*p*-tolyl)hex-1-en-1-amine (2e):

Yield = 34% (33.9 mg, 36 h); 64% (62.7 mg, 48 h). Yellow oil.

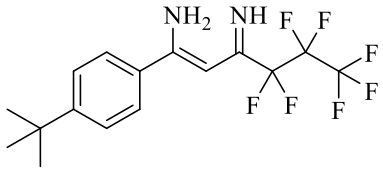
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 (brs, 2H), 7.49–7.44 (m, 2H), 7.28–7.23 (m, 2H), 5.82 (brs, 1H), 5.31 (s, 1H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.31 (t, J = 9.7 Hz, 3F), -120.03 (q, J = 10.4 Hz, 2F), -126.47 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8 (t, $J_{C\text{-}F}$ = 23.2 Hz), 160.7, 140.8, 135.2, 129.8, 126.3, 87.4, 21.5 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{13}H_{12}F_7N_2$ $[M+H]^+$ 329.0883, found: 329.0873.



(*Z*)-1-(4-(*tert*-Butyl)phenyl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (2f):

Yield = 48% (53.5 mg). Yellow oil.

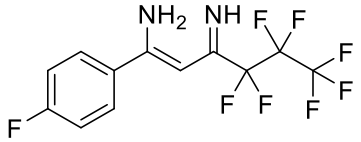
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 200/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.55 (brs, 2H), 7.49 (q, J = 8.4 Hz, 4H), 5.82 (brs, 1H), 5.32 (s, 1H), 1.35 (s, 9H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.36 (s, 3F), -120.00 (s, 2F), -126.47 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8 (t, $J_{C\text{-}F}$ = 23.7 Hz), 160.7, 153.9, 135.2, 126.7 (d, $J_{C\text{-}F}$ = 188.8 Hz), 126.0, 87.5, 35.0, 31.3 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{16}H_{18}F_7N_2$ $[M+H]^+$ 371.1353, found: 371.1348.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-1-(4-fluorophenyl)-3-iminohex-1-en-1-amine (2g):

Yield = 61% (61.2 mg). Yellow oil.

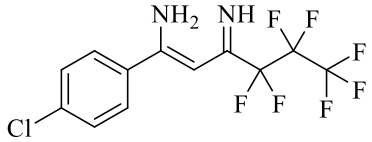
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.79 (brs, 2H), 7.59–7.51 (m, 2H), 7.17–7.09 (m, 2H), 5.79 (brs, 1H), 5.26 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.37 (s, 3F), -110.08 (s, 1F), -120.15 (s, 2F), -126.48 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, $J_{C\text{-}F}$ = 251.5 Hz), 160.6 (t, $J_{C\text{-}F}$ = 23.2 Hz), 159.8, 134.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 128.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 116.1 (d, $J_{C\text{-}F}$ = 22.2 Hz), 87.9 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_{11}F_8N_2$ $[M+H]^+$ 333.0633, found: 333.0626.



(*Z*)-1-(4-Chlorophenyl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (2h):

Yield = 81% (84.6 mg). Green oil.

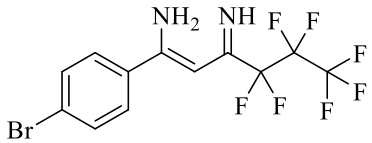
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 40/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (brs, 2H), 7.53–7.46 (m, 2H), 7.45–7.39 (m, 2H), 5.79 (brs, 1H), 5.28 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.31 (t, J = 9.7 Hz, 3F), -120.13 (q, J = 8.9 Hz, 2F), -126.47 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6 (t, $J_{C\text{-}F}$ = 23.7 Hz), 159.6, 136.6, 136.5, 129.3, 127.7, 88.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_9ClF_7N_2$ $[M+H]^+$ 349.0337, found: 349.0331.



(*Z*)-1-(4-Bromophenyl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (2i):

Yield = 83% (98.2 mg). Yellow oil.

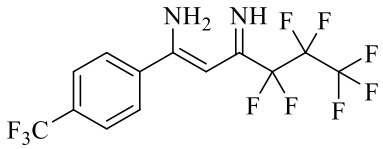
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (brs, 2H), 7.62–7.53 (m, 2H), 7.47–7.39 (m, 2H), 5.79 (brs, 1H), 5.27 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.31 (t, J = 9.7 Hz, 3F), -120.13 (q, J = 8.9 Hz, 2F), -126.46 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6 (t, $J_{C\text{-}F}$ =24.2 Hz), 159.6, 137.1, 132.3, 127.9, 124.7, 88.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_9BrF_7N_2$ $[M+H]^+$ 392.9832, found: 392.9825.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(4-(trifluoromethyl)phenyl)hex-1-en-1-amine (2j):

Yield = 28% (32.1 mg). Yellow oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

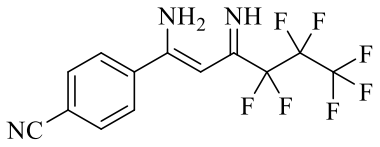
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 2H), 7.69 (q, J = 8.5 Hz, 4H), 5.85 (brs, 1H), 5.31 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -62.74 (s, 3F), -80.31 (t, J = 9.7 Hz, 3F), -120.21 (q, J = 8.9 Hz,

2F), -126.47 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6 (t, $J_{C\text{-}F}$ = 24.2 Hz), 159.3, 141.7, 132.1 (q, $J_{C\text{-}F}$ = 32.3 Hz), 126.8, 126.1 (q, $J_{C\text{-}F}$ = 4.0 Hz), 125.2 (q, $J_{C\text{-}F}$ = 248.5 Hz), 88.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{13}H_9F_{10}N_2$ $[M+H]^+$ 383.0601, found: 383.0608.



(*Z*)-4-(1-Amino-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-yl)benzonitrile (2k):

Yield = 55% (55.9 mg). Yellow solid. M.p. 109.5-110.9 ºC.

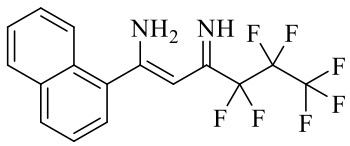
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 2H), 7.78–7.63 (m, 4H), 5.84 (brs, 1H), 5.30 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.25 (t, J = 9.7 Hz, 3F), -120.22 (q, J = 8.9 Hz, 2F), -126.43 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (t, $J_{C\text{-}F}$ = 23.7 Hz), 158.6, 142.4, 132.9, 127.1, 118.3, 113.9, 88.9 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{13}H_9F_7N_3$ $[M+H]^+$ 340.0679, found: 340.0675.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(naphthalen-1-yl)hex-1-en-1-amine (2l):

Yield = 48% (52.9 mg). Yellow oil

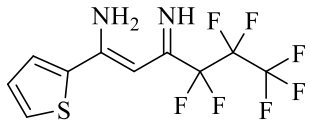
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.74 (brs, 2H), 8.23–8.17 (m, 1H), 7.94–7.88 (m, 2H), 7.58–7.48 (m, 4H), 6.03 (brs, 1H), 5.28 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.31 (s, 3F), -120.08 (s, 2F), -126.44 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 159.9 (t, $J_{C\text{-}F}$ = 23.5 Hz), 136.9, 133.8, 130.3, 129.9, 128.6, 127.0, 126.5, 125.7, 125.3, 125.3, 91.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{16}H_{12}F_7N_2$ $[M+H]^+$ 365.0883, found: 365.0877.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(thiophen-2-yl)hex-1-en-1-amine (2m):

Yield = 50% (48.0 mg). Yellow oil.

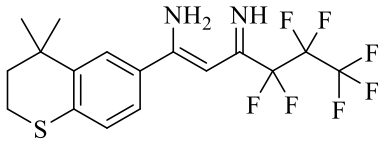
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.11 (brs, 2H), 7.45–7.36 (m, 2H), 7.10 (dd, J = 5.1, 3.7 Hz, 1H), 6.09 (brs, 1H), 5.45 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.29 (t, J = 8.9 Hz, 3F), -120.08 (q, J = 8.9 Hz, 2F), -126.52 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 (t, $J_{C\text{-}F}$ = 23.2 Hz), 154.3, 140.9, 128.2, 127.8, 126.0, 87.9 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{10}H_8F_7N_2S$ $[M+H]^+$ 321.0291, found: 321.0292.



(*Z*)-1-(4,4-Dimethylthiochroman-6-yl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (2n):

Yield = 74% (91.8 mg). Yellow oil.

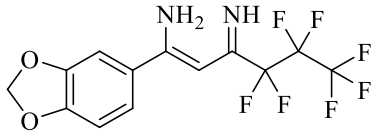
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (brs, 2H), 7.53 (d, J = 2.0 Hz, 1H), 7.22 (dd, J = 8.2, 2.0 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 5.79 (brs, 1H), 5.27 (s, 1H), 3.09–3.03 (m, 2H), 2.00–1.95 (m, 2H), 1.37 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.29 (t, J = 9.7 Hz, 3F), -120.08 (q, J = 9.4 Hz, 2F), -126.47 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 160.6 (t, $J_{C\text{-}F}$ =23.7 Hz), 142.6, 135.5, 133.8, 127.1, 124.1, 123.8, 87.2, 37.2, 33.2, 30.1, 23.2 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{17}H_{18}F_7N_2S$ $[M+H]^+$ 415.1073, found: 415.1071.



(*Z*)-1-(Benzo[*d*][1,3]dioxol-5-yl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (2o):

Yield = 69% (74.1 mg). Green oil.

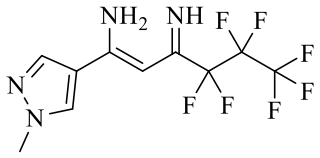
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (brs, 2H), 7.08 (dd, J = 8.1, 1.9 Hz, 1H), 7.02 (d, J = 1.8 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 6.02 (s, 2H), 5.78 (brs, 1H), 5.25 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.38 (s, 3F), -120.02 (s, 2F), -126.50 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (t, $J_{C\text{-}F}$ = 23.2 Hz), 160.3, 149.5, 148.3, 132.3, 120.5, 108.7, 106.8, 101.8, 87.4 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{13}H_{10}F_7N_2O_2$ $[M+H]^+$ 359.0625, found: 359.0621.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(1-methyl-1*H*-pyrazol-4-yl)hex-1-en-1-amine (2p):

Yield = 44% (41.5 mg). Yellow solid. M.p. 71.6-72.7 ºC.

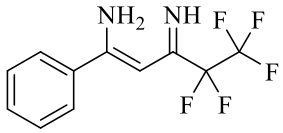
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (brs, 2H), 7.70 (d, J = 0.8 Hz, 1H), 7.63 (d, J = 0.8 Hz, 1H), 5.86 (brs, 1H), 5.23 (s, 1H), 3.93 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.99 – -80.78 (m, 3F), -120.08 (s, 2F), -126.59 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (t, $J_{C\text{-}F}$ = 23.2 Hz), 153.3, 137.0, 128.5, 120.8, 86.4, 39.4 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{10}H_{10}F_7N_4$ $[M+H]^+$ 319.0788, found: 319.0789.



(*Z*)-4,4,5,5,5-Pentafluoro-3-imino-1-phenylpent-1-en-1-amine (2t):

Yield = 42% (33.2 mg). Yellow oil.

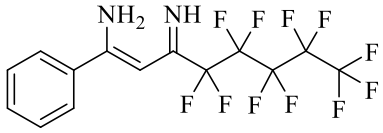
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (brs, 2H), 7.63–7.40 (m, 5H), 5.89 (brs, 1H), 5.33 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -83.29 (s, 3F), -122.92 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 160.7 (t, $J_{C\text{-}F}$ = 22.2 Hz), 138.2, 130.4, 129.1, 126.3, 87.5 ppm, carbons corresponding to the C_2F_5 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{11}H_{10}F_5N_2$ $[M+H]^+$ 265.0759, found: 265.0757.



(*Z*)-4,4,5,5,6,6,7,7,8,8,8-Undecafluoro-3-imino-1-phenyloct-1-en-1-amine (2u):

Yield = 40% (49.0 mg). Yellow oil.

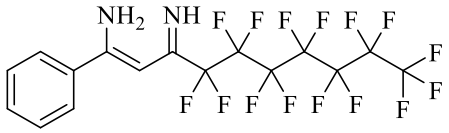
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.41 (brs, 2H), 7.60–7.53 (m, 2H), 7.49–7.41 (m, 3H), 5.82 (brs, 1H), 5.32 (s, 1H) ppm.

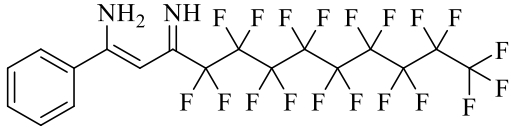
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.66 (t, J = 9.7 Hz, 3F), -119.15 (t, J = 14.2 Hz, 2F), -122.19 (t, J = 16.4 Hz, 2F), -121.82 – -122.42 (m, 2F), -126.03 – -126.23 (m, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (t, $J_{C\text{-}F}$ = 9.1 Hz), 160.6, 138.1, 130.4, 129.1, 126.3, 87.9

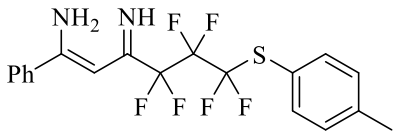
ppm, carbons corresponding to the C_5F_{11} group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{14}H_{10}F_{11}N_2$ $[M+H]^+$ 415.0663, found: 415.0657.



(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-imino-1-phenyldec-1-en-1-amine (2v):
Yield = 49% (76.4 mg). Yellow oil.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.43 (brs, 2H), 7.59–7.41 (m, 5H), 5.82 (brs, 1H), 5.33 (s, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.69 (t, J = 10.1 Hz, 3F), -119.13 (t, J = 14.2 Hz, 2F), -121.32 – -121.61 (m, 2F), -121.96 (s, 4F), -122.67 (dq, J = 21.2, 10.8 Hz, 2F), -125.94 – -126.27 (m, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.9 (t, $J_{C\text{-}F}$ = 24.2 Hz), 160.6, 138.2, 130.4, 129.1, 126.3, 87.9 ppm, carbons corresponding to the C_7F_{15} group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{16}H_{10}F_{15}N_2$ $[M+H]^+$ 515.0599, found: 515.0593.



(*Z*)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Nonadecafluoro-3-imino-1-phenyldodec-1-en-1-amine (2w):
Yield = 33% (59.8 mg). White solid. 79.6-80.8 °C.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 100/1).
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (brs, 2H), 7.74–7.33 (m, 5H), 5.82 (brs, 1H), 5.32 (s, 1H) ppm.
^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.71 (t, J = 9.7 Hz, 3F), -119.15 (t, J = 14.2 Hz, 2F), -121.45 (s, 2F), -121.59 – -122.10 (m, 8F), -122.67 (d, J = 20.1 Hz, 2F), -125.97 – -126.24 (m, 2F) ppm.
^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.63 (t, $J_{C\text{-}F}$ = 23.7 Hz), 160.62, 138.2, 130.4, 129.1, 126.3, 87.9 ppm, carbons corresponding to the C_9F_{19} group cannot be identified due to C-F coupling.
HRMS (m/z): calcd for $C_{18}H_{10}F_{19}N_2$ $[M+H]^+$ 615.0535, found: 615.0543.



(*Z*)-4,4,5,5,6,6-Hexafluoro-3-imino-1-phenyl-6-(*p*-tolylthio)hex-1-en-1-amine (2x)：
Yield = 61% (76.6 mg). Green oil.
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl

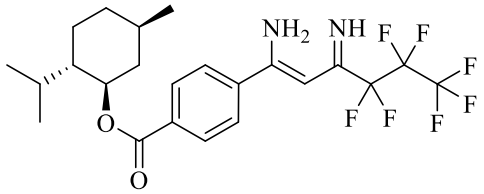
acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (s, 2H), 7.60–7.52 (m, 4H), 7.47–7.41 (m, 3H), 7.24–7.18 (m, 2H), 5.78 (s, 1H), 5.37 (s, 1H), 2.39 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -86.03 (tt, J = 10.8, 4.9 Hz, 2F), -118.06 (t, J = 10.8 Hz, 2F), -119.69 (t, J = 4.9 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9 (t, $J_{C\text{-}F}$ = 23.5 Hz), 160.3, 141.5, 138.4, 137.5, 130.3, 130.2, 129.0, 126.3, 119.8, 88.3, 21.5 ppm, carbons corresponding to the C_3F_6 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{17}F_6N_2S$ $[M+H]^+$ 419.1011, found: 419.1013.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 4-((*Z*)-1-amino-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-yl)benzoate (3a):

Yield = 33% (33.1 mg, 0.2 mmol scale). Yellow oil.

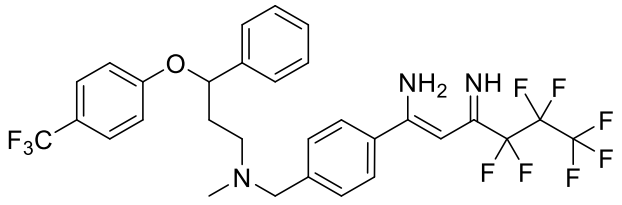
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.47 (brs, 2H), 8.13–8.09 (m, 2H), 7.62 (dd, J = 8.4, 1.7 Hz, 2H), 5.86 (brs, 1H), 5.33 (s, 1H), 4.99–4.90 (m, 1H), 2.17–2.12 (m, 1H), 1.94 (tt, J = 7.1, 3.6 Hz, 1H), 1.76–1.71 (m, 2H), 1.15–1.08 (m, 2H), 0.93 (td, J = 6.7, 1.7 Hz, 9H), 0.79 (dd, J = 6.9, 1.6 Hz, 4H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.34 (s, 3F), -120.13 (s, 2F), -126.44 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 159.6 (t, $J_{C\text{-}F}$ = 22.7 Hz), 142.1, 132.5, 130.3, 126.3, 88.5, 75.4, 47.4, 41.1, 34.4, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{23}H_{28}F_7N_2O_2$ $[M+H]^+$ 497.2034, found: 497.2036.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-(4-((methyl(3-phenyl-3-(4-(trifluoromethyl)phenoxy) propyl)amino)methyl)phenyl)hex-1-en-1-amine (3b):

Yield = 63% (80.7 mg, 0.2 mmol scale). Yellow oil.

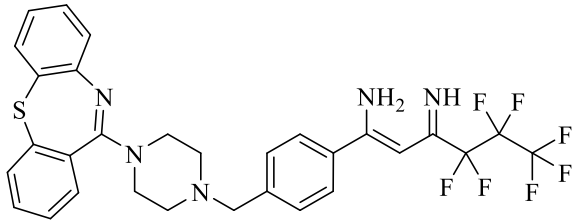
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (brs, 2H), 7.46–7.38 (m, 4H), 7.35–7.27 (m, 7H), 6.92–6.80 (m, 2H), 5.77 (brs, 1H), 5.37 (dd, J = 8.5, 4.5 Hz, 1H), 5.32 (s, 1H), 3.61–3.43 (m, 2H), 2.71–2.62 (m, 1H), 2.45 (ddd, J = 12.3, 7.0, 5.1 Hz, 1H), 2.27 (s, 3H), 2.24–2.15 (m, 1H), 2.03 (dtd, J = 14.4, 7.4, 4.5 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -61.35 (d, J = 18.2 Hz, 3F), -80.29 (s, 3F), -120.02 (s, 2F), -126.45 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 160.7 (t, $J_{C\text{-}F}$ = 23.2 Hz), 160.4, 141.9, 141.4, 136.7, 129.5, 128.9, 127.9, 126.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 126.1, 125.9, 122.8 (q, $J_{C\text{-}F}$ = 32.4 Hz), 121.8 (q, $J_{C\text{-}F}$ = 269.8 Hz), 115.8, 87.5, 78.0, 62.3, 53.2, 42.4, 36.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{28}F_{10}N_3O$ $[M+H]^+$ 636.2067, found: 636.2071.



(*Z*)-1-(4-((4-(Dibenzo[*b*,*f*][1,4]thiazepin-11-yl)piperazin-1-yl)methyl)phenyl)-4,4,5,5,6,6,6-heptafluoro-3-iminohex-1-en-1-amine (3c):

Yield = 72% (134.9 mg). Yellow oil.

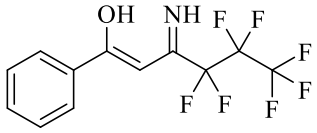
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 2/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.37 (brs, 2H), 7.51 (td, J = 3.7, 1.6 Hz, 5H), 7.41 (s, 3H), 7.41–7.38 (m, 1H), 7.35–7.27 (m, 5H), 7.20–7.15 (m, 1H), 7.07 (dd, J = 8.0, 1.6 Hz, 1H), 6.91–6.86 (m, 1H), 5.87 (brs, 1H), 5.32 (s, 1H), 3.60 (s, 3H), 2.52–2.48 (m, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.29 (t, J = 9.7 Hz, 3F), -119.99 (q, J = 10.4 Hz, 2F), -126.41 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.92, 160.91, 160.7, 160.5, 149.0, 140.5, 140.0, 137.0, 134.2, 132.33, 132.29, 130.9, 129.8, 129.3, 129.1, 128.4, 128.1, 126.3, 125.4, 123.0, 87.7, 62.7, 53.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{30}H_{27}F_7N_5S$ $[M+H]^+$ 622.1870, found: 622.1874.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-3-imino-1-phenylhex-1-en-1-ol (4):

Yield = 44% (28.2 mg, 0.2 mmol scale). White solid. M.p. 69.3-70.7 ^{o}C.

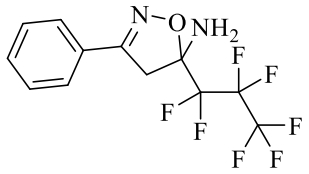
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.31 (brs, 1H), 7.65–7.47 (m, 5H), 6.14 (brs, 1H), 5.85 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.47 (t, J = 8.9 Hz, 3F), -120.96 (q, J = 9.7 Hz, 2F), -126.79 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1 (t, $J_{C\text{-}F}$ = 25.5 Hz), 167.3, 135.4, 132.2, 129.5, 126.6, 89.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_9F_7NO$ $[M+H]^+$ 316.0567, found: 316.0566.



5-(2,2,3,3,4,4,4-Heptafluorobutyl)-3-phenyl-4,5-dihydroisoxazol-5-amine (5):

Yield = 75% (49.4 mg, 0.2 mmol scale). Yellow solid. M.p. 122.6-122.9 ºC.

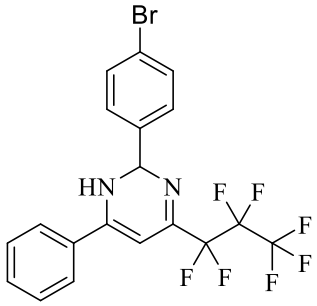
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.62 (m, 2H), 7.48–7.39 (m, 3H), 3.80 (d, *J* = 18.2 Hz, 1H), 3.25 (d, *J* = 18.2 Hz, 1H), 2.46 (brs, 2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.85 (s, 3F), -120.54 (d, *J* = 23.8 Hz, 1F), -122.36 (dd, *J* = 292.0, 17.9 Hz, 1F), -123.32 (d, *J* = 286.1 Hz, 1F), -124.43 – -125.37 (m, 1F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.7, 131.0, 129.1, 128.4, 126.8, 96.5 (t, $J_{C\text{-}F}$ = 25.8 Hz), 43.0 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_{10}F_7N_2O$ $[M+H]^+$ 331.0676, found: 331.0667.



2-(4-Bromophenyl)-4-(perfluoropropyl)-6-phenyl-1,2-dihydropyrimidine (6):

Yield = 52% (49.7 mg, 0.2 mmol scale). Yellow solid. M.p. 83.5-84.9 ºC.

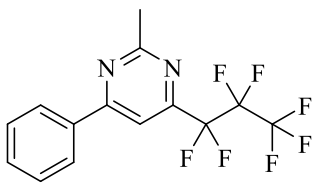
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, *J* = 7.0, 1.7 Hz, 2H), 7.56–7.50 (m, 3H), 7.50–7.43 (m, 4H), 5.95 (s, 1H), 5.79 (s, 1H), 4.36 (brs, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.20 (t, *J* = 14.1 Hz, 3F), -114.64 – -117.86 (m, 2F), -126.45 (d, *J* = 10.4 Hz, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.3 (t, $J_{C\text{-}F}$ = 14.1 Hz), 153.7, 139.1, 132.9, 131.93, 131.90, 129.3, 129.1, 127.4, 122.9, 92.7, 71.5 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{13}BrF_7N_2$ $[M+H]^+$ 481.0145, found: 481.0144.



2-Methyl-4-(perfluoropropyl)-6-phenylpyrimidine (7):

Yield = 79% (53.6 mg, 0.2 mmol scale). Colorless oil.

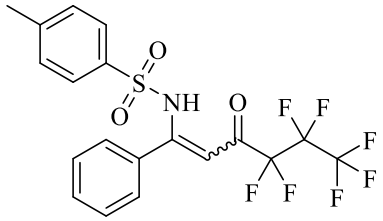
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16–8.12 (m, 2H), 7.83 (s, 1H), 7.58–7.51 (m, 3H), 2.89 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.06 (d, J = 35.8 Hz, 3F), -116.89 (t, J = 23.8 Hz, 2F), -126.09 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5, 166.4, 156.4 (t, $J_{C\text{-}F}$ = 25.3 Hz), 135.9, 132.0, 129.3, 127.6, 111.6, 26.4 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{14}H_{10}F_7N_2$ $[M+H]^+$ 339.0727, found: 339.0727.



***N*-(4,4,5,5,6,6,6-Heptafluoro-3-oxo-1-phenylhex-1-en-1-yl)-4-methylbenzenesulfonamide (10a):**

Yield = 49% (69.0 mg, *E*/*Z* = 1/3). Yellow oil.

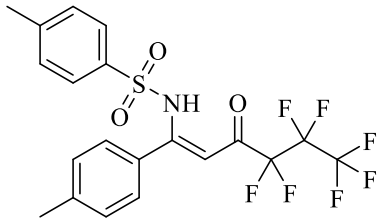
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 11.68 (s, 0.3H), 9.51 (s, 0.7H), 7.67–7.63 (m, 1.5H), 7.54–7.50 (m, 0.4H), 7.47–7.44 (m, 1.9H), 7.43–7.41 (m, 0.4H), 7.40–7.34 (m, 2.6H), 7.28 (s, 0.3H), 7.20–7.18 (m, 1.9H), 5.79 (s, 0.3H), 5.36 (s, 0.7H), 2.41 (s, 0.8H), 2.38 (s, 2.2H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = -80.09 (t, J = 9.7 Hz, 2.1F), -80.46 (t, J = 8.9 Hz, 0.9F), -119.43 (q, J = 10.4 Hz, 1.5F), -121.49 (q, J = 8.9 Hz, 0.5F), -126.44 (s, 1.5F), -126.61 (s, 0.5F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) of *E*- and *Z*-isomers: δ = 182.4, 177.3, 163.4, 147.1 (t, $J_{C\text{-}F}$ = 24.5 Hz), 145.4, 143.3, 139.4, 138.5, 136.0, 132.3, 132.0, 130.6, 129.8, 129.5, 129.3, 128.3, 128.2, 127.7, 127.6, 127.0, 100.7, 97.2, 21.7, 21.6 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{15}F_7NO_3S$ $[M+H]^+$ 470.0655, found: 470.0662.



(*Z*)-*N*-(4,4,5,5,6,6,6-Heptafluoro-3-oxo-1-(*p*-tolyl)hex-1-en-1-yl)-4-methylbenzenesulfonamide

(10b):

Yield = 45% (65.4 mg). Green oil.

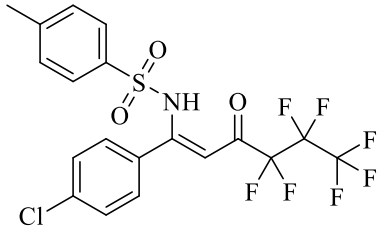
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.74 (s, 1H), 7.40–7.35 (m, 2H), 7.23–7.15 (m, 6H), 5.78 (s, 1H), 2.42 (s, 3H), 2.41 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.46 (t, J = 8.7 Hz, 3F), -121.50 (q, J = 8.7 Hz, 2F), -126.65 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.3 (t, $J_{C\text{-}F}$ = 25.5 Hz), 163.6, 145.3, 143.0, 136.1, 129.8, 129.7, 129.4, 129.0, 127.7, 100.8, 21.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{20}H_{17}F_7NO_3S$ $[M+H]^+$ 484.0812, found: 484.0812.



(*Z*)-*N*-(1-(4-Chlorophenyl)-4,4,5,5,6,6,6-heptafluoro-3-oxohex-1-en-1-yl)-4-methylbenzenesulfonamide (10c):

Yield = 43% (64.8 mg). Green oil.

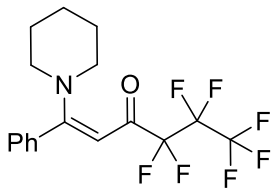
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.68 (s, 1H), 7.41–7.33 (m, 4H), 7.25–7.22 (m, 4H), 5.77 (s, 1H), 2.42 (s, 3H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.42 (t, J = 8.7 Hz, 3F), -121.49 (q, J = 8.7 Hz, 2F), -126.58 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.5 (t, $J_{C\text{-}F}$ = 25.5 Hz), 161.8, 145.5, 138.5, 135.9, 130.8, 130.6, 129.9, 128.6, 127.6, 100.9, 21.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{14}ClF_7NO_3S$ $[M+H]^+$ 504.0266, found: 504.0270.



(*Z*)-4,4,5,5,6,6,6-Heptafluoro-1-phenyl-1-(piperidin-1-yl)hex-1-en-3-one (12):

Yield = 38% (43.6 mg). Yellow oil.

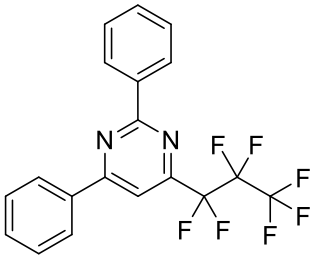
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 4/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (dd, J = 7.4, 2.0 Hz, 2H), 7.53 (dd, J = 8.4, 6.1 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.32 (s, 1H), 3.10 (s, 4H), 1.62 (s, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.27 (s, 3F), -109.37 (s, 2F), -124.83 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ =188.0, 148.8 (t, $J_{C\text{-}F}$ = 21.7 Hz), 139.1, 132.6, 128.7, 128.4, 105.6, 53.3, 26.3, 23.7 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{17}H_{17}F_7NO$ $[M+H]^+$ 384.1193, found: 384.1195.



4-(Perfluoropropyl)-2,6-diphenylpyrimidine (16b):

Yield = 77% (92.6 mg). Colorless oil.

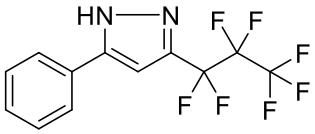
Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 200/1~100/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.69–8.63 (m, 2H), 8.32–8.25 (m, 2H), 7.92 (s, 1H), 7.61–7.53 (m, 6H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -79.95 (t, J = 9.2 Hz, 3F), -116.50 (q, J = 9.8 Hz, 2F), -126.04 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 165.2, 156.9 (t, $J_{C\text{-}F}$ = 26.0 Hz), 136.7, 136.0, 132.0, 131.8, 129.3, 128.9, 128.8, 127.6, 111.7 (t, $J_{C\text{-}F}$ = 4 Hz) ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{19}H_{12}F_7N_2$ $[M+H]^+$ 401.0883, found: 401.0886.



3-(Perfluoropropyl)-5-phenyl-1*H*-pyrazole (16c):

Yield = 54% (50.8 mg). Yellow oil.

Purified by flash silica gel column chromatography through silica gel (petroleum ether/ethyl acetate, 20/1~10/1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 12.46 (s, 1H), 7.63–7.56 (m, 2H), 7.50–7.38 (m, 3H), 6.78 (s, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -80.10 (t, J = 9.8 Hz, 3F), -110.91 (dd, J = 9.2, 8.7 Hz, 2F), -126.93 (s, 2F) ppm.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.5, 142.2 (t, $J_{C\text{-}F}$ = 24.0 Hz), 129.6, 129.4, 128.0, 125.8, 102.8 ppm, carbons corresponding to the C_3F_7 group cannot be identified due to C-F coupling.

HRMS (m/z): calcd for $C_{12}H_8F_7N_2$ $[M+H]^+$ 313.0570, found: 313.0571.

Reference

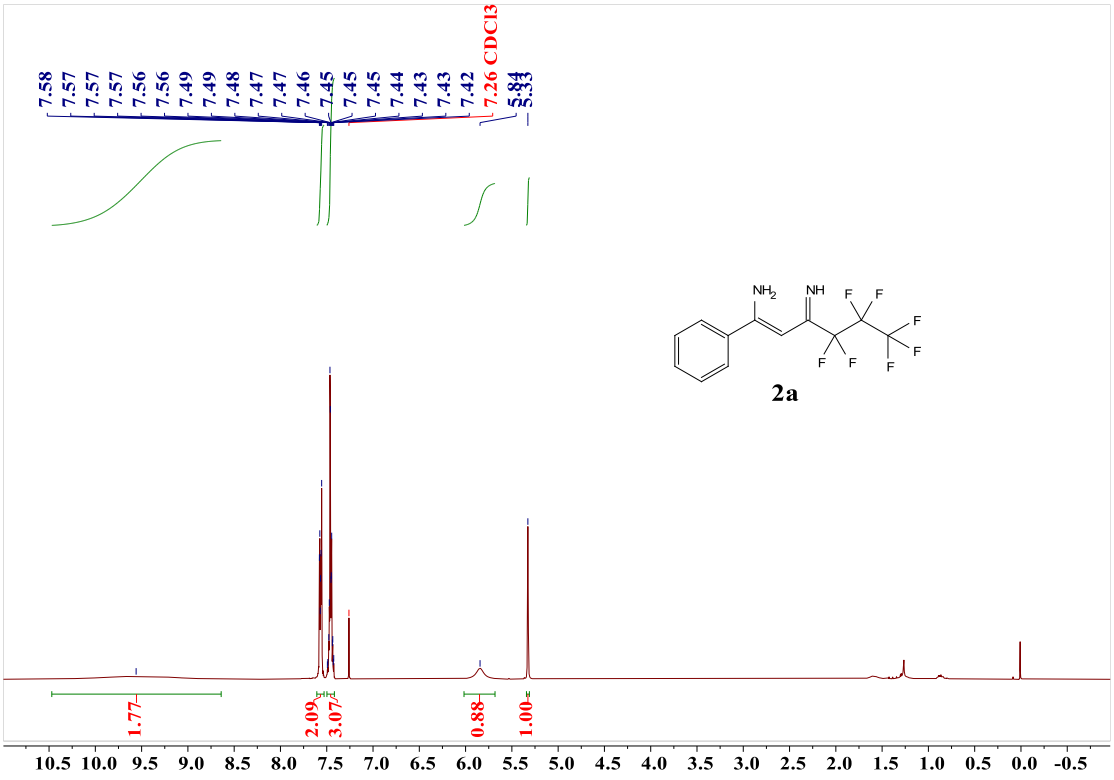
[1] G. Wu, A. Jacobi von Wangelin, *Chem. Sci.* **2018**, *9*, 1795-1802.

[2] T. Xu, C. W. Cheung, X. Hu, *Angew. Chem. Int. Ed.* **2014**, *53*, 4910-4914.

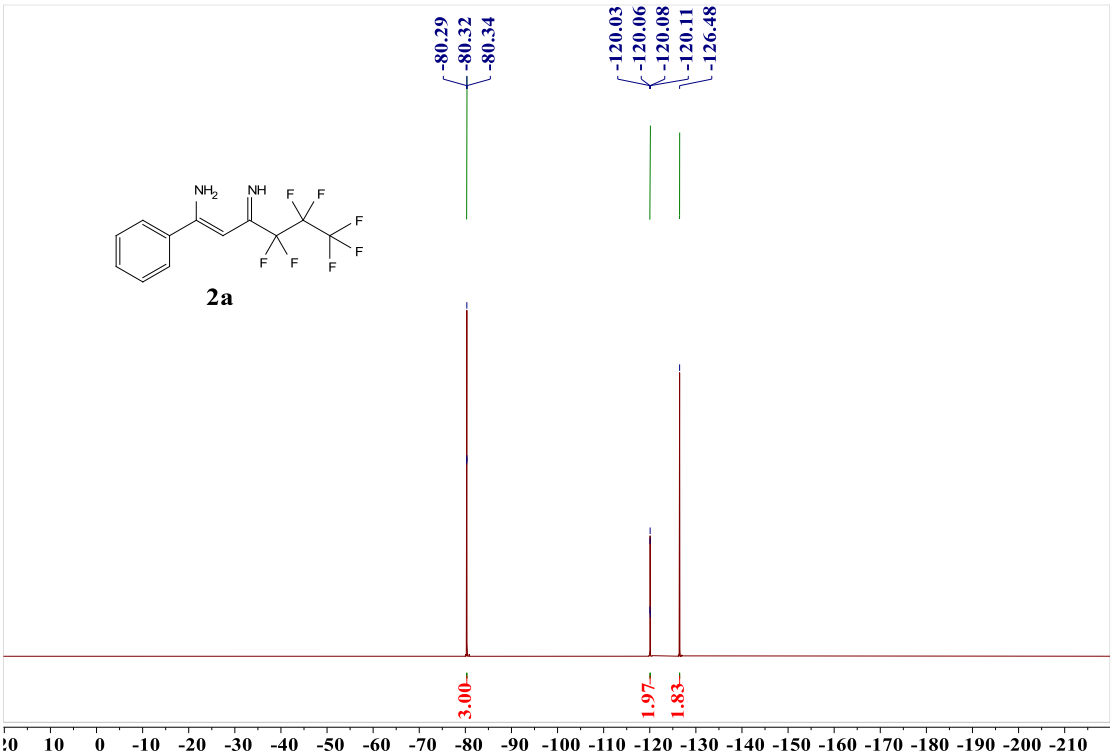
[3] R. Anilkumar, D. J. Burton, *J. Fluorine Chem.* **2005**, *126*, 1174-1184.

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

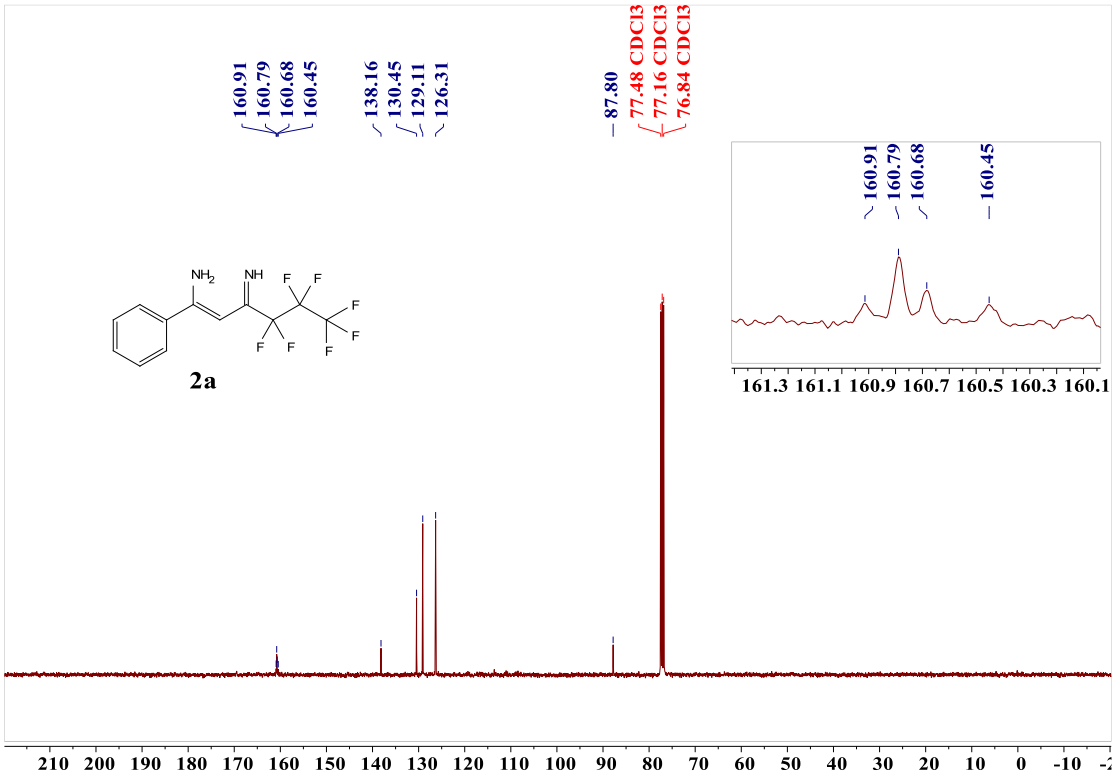
^{1}H NMR spectra of the product **2a** (400 MHz, $CDCl_3$)



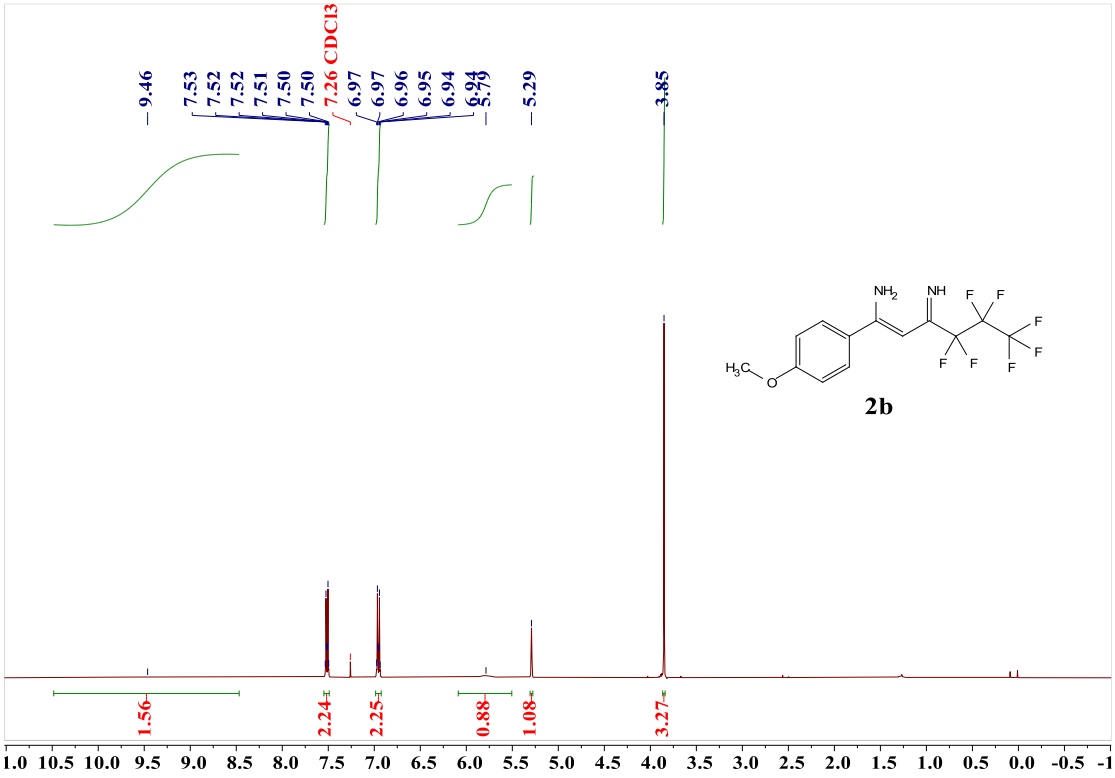
^{19}F NMR spectra of the product **2a** (376 MHz, $CDCl_3$)



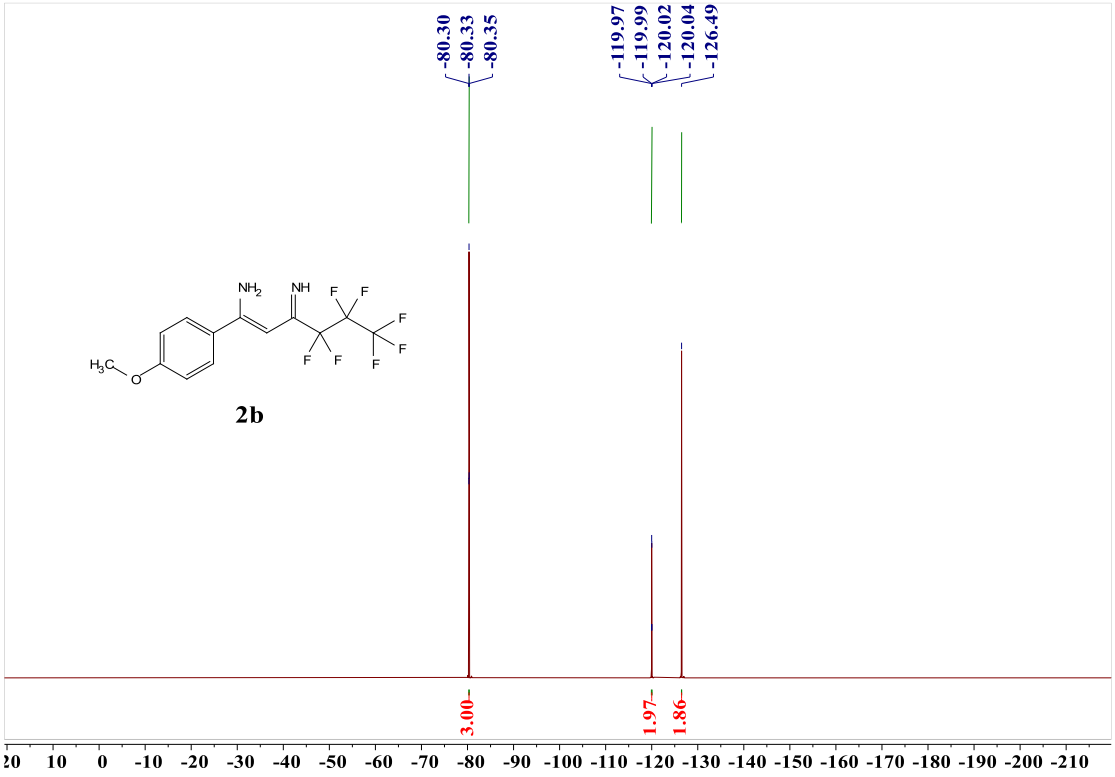
^{13}C NMR spectra of the product **2a** (100 MHz, $CDCl_3$)



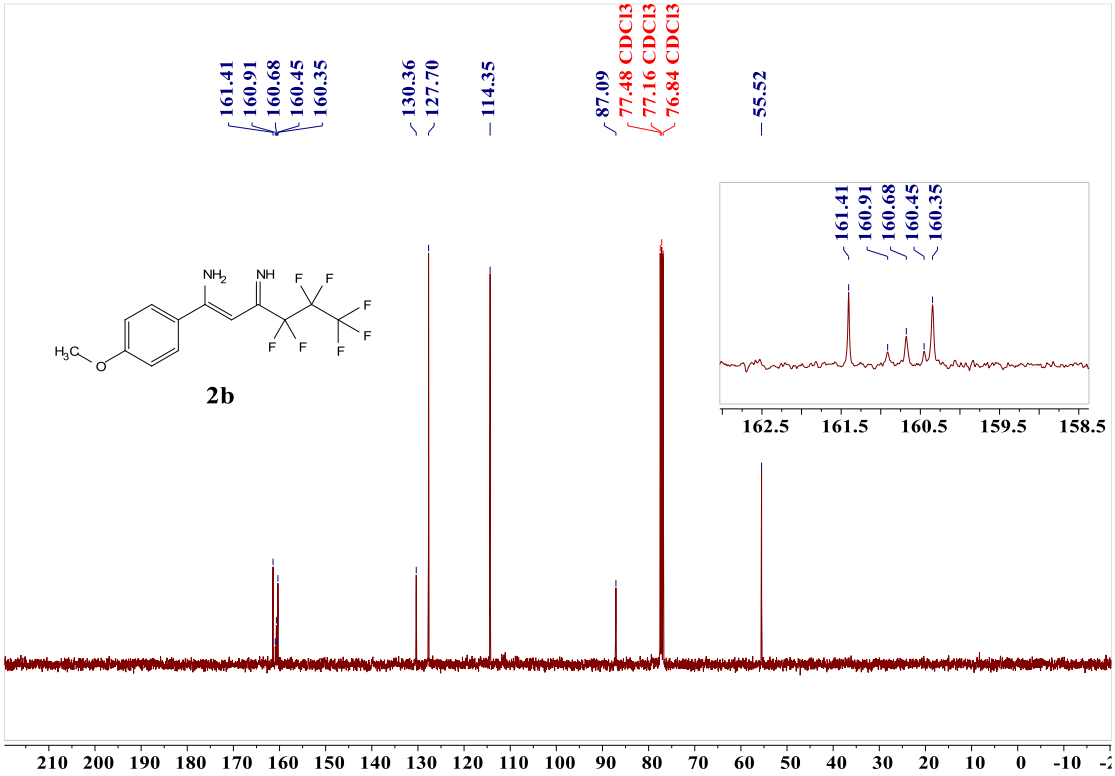
^{1}H NMR spectra of the product **2b** (400 MHz, $CDCl_3$)



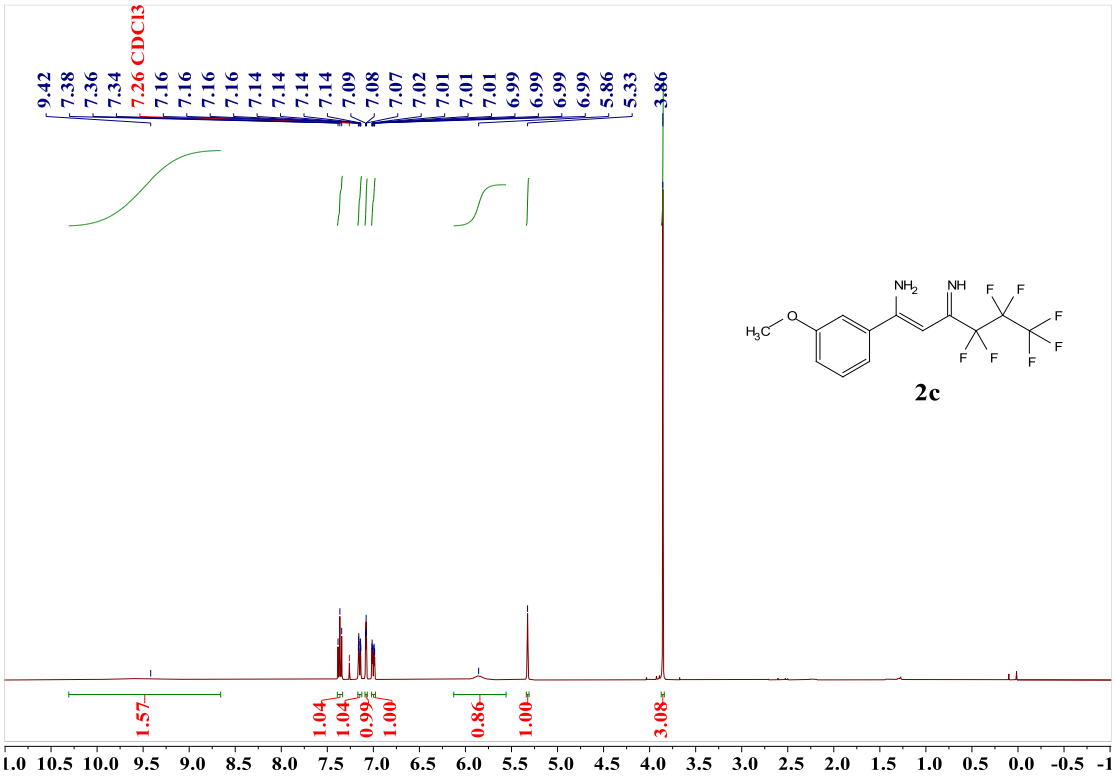
^{19}F NMR spectra of the product **2b** (376 MHz, $CDCl_3$)



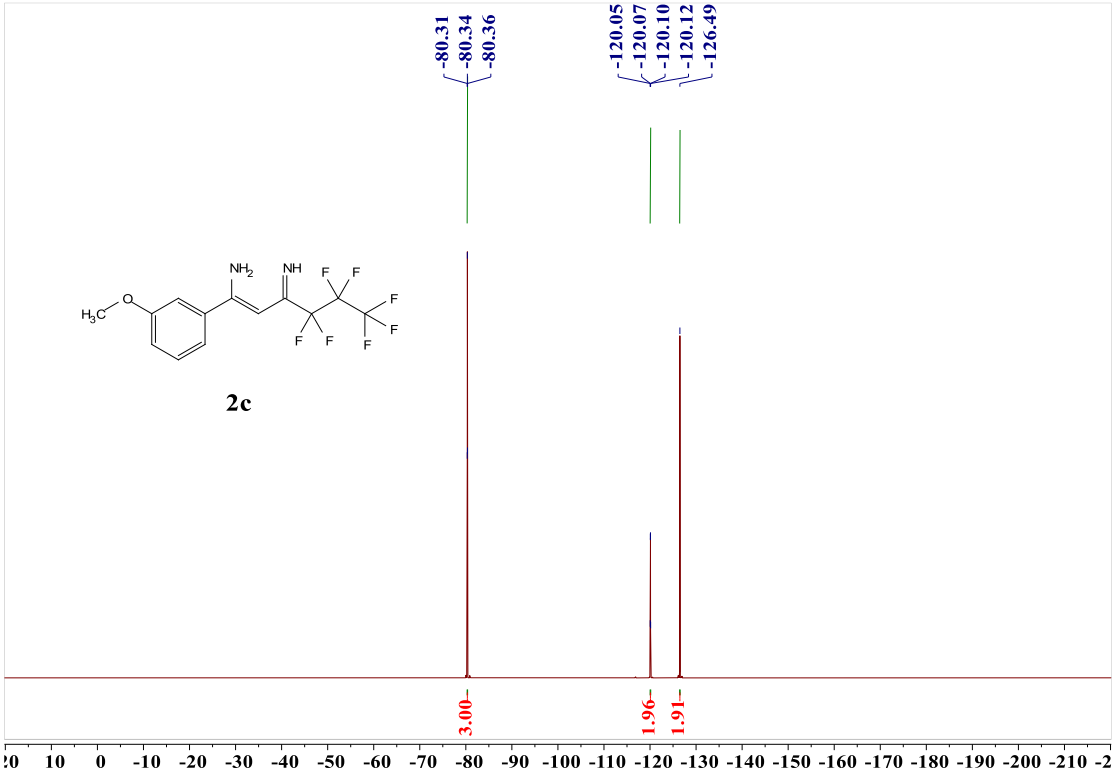
^{13}C NMR spectra of the product **2b** (100 MHz, $CDCl_3$)



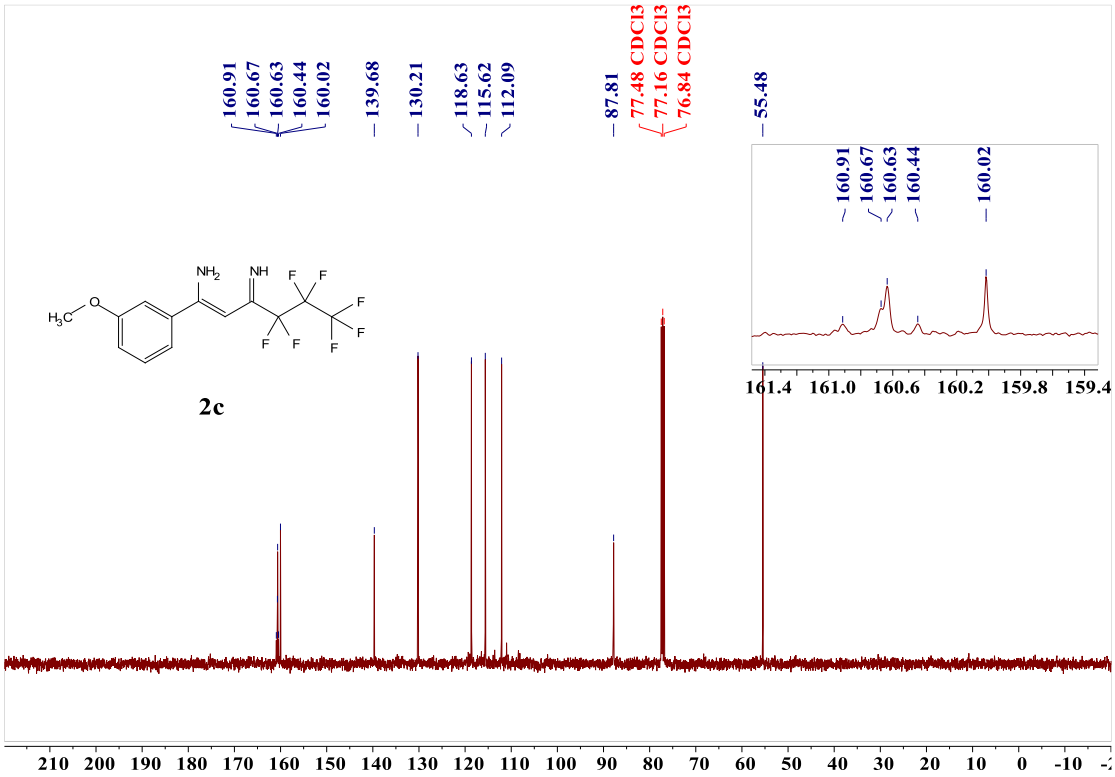
^{1}H NMR spectra of the product **2c** (400 MHz, $CDCl_3$)



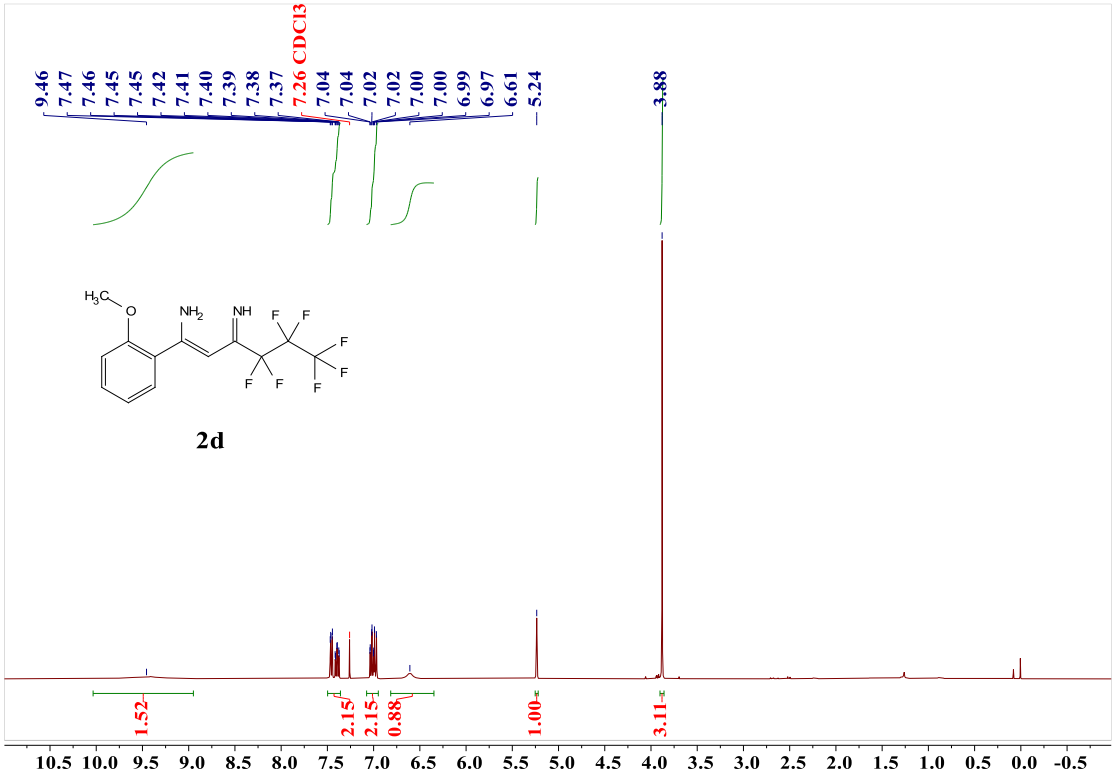
^{19}F NMR spectra of the product **2c** (376 MHz, $CDCl_3$)



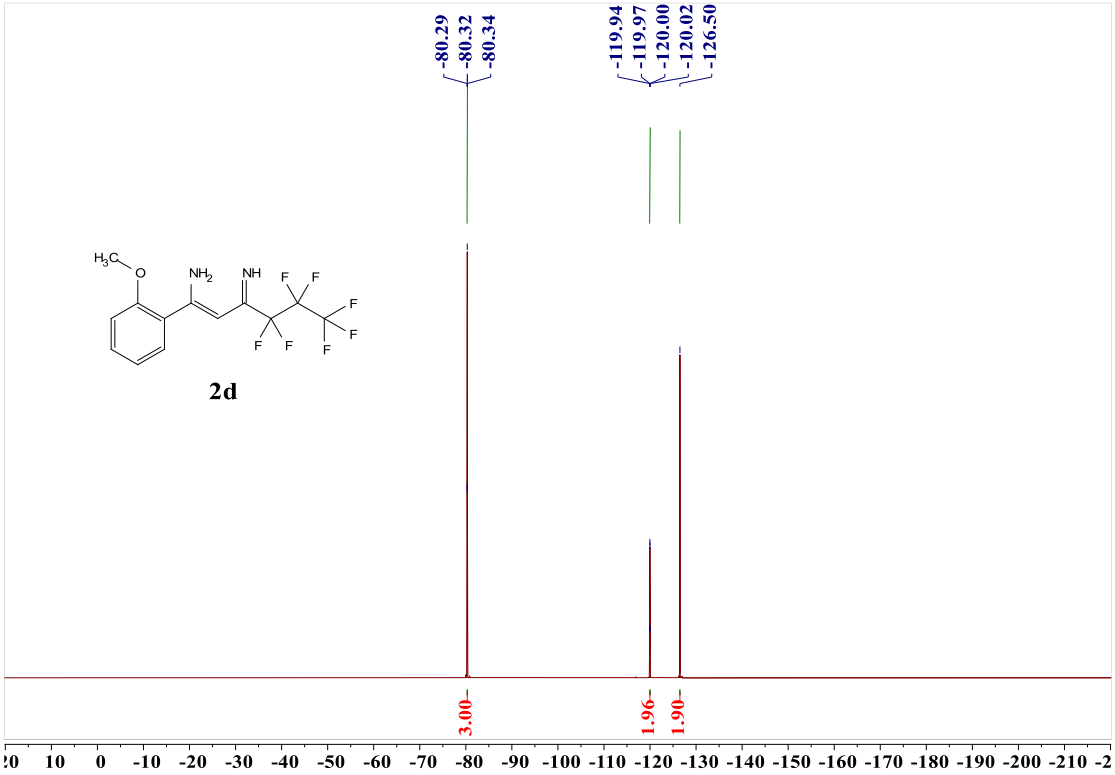
^{13}C NMR spectra of the product **2c** (100 MHz, $CDCl_3$)



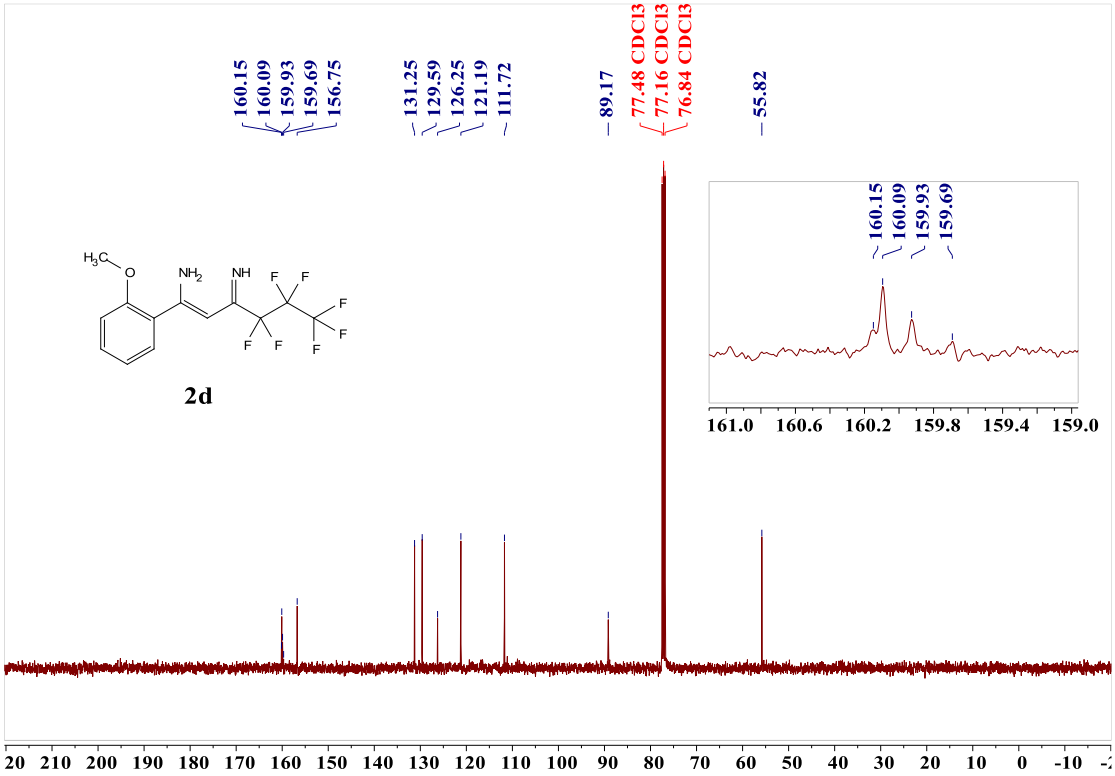
^{1}H NMR spectra of the product **2d** (400 MHz, $CDCl_3$)



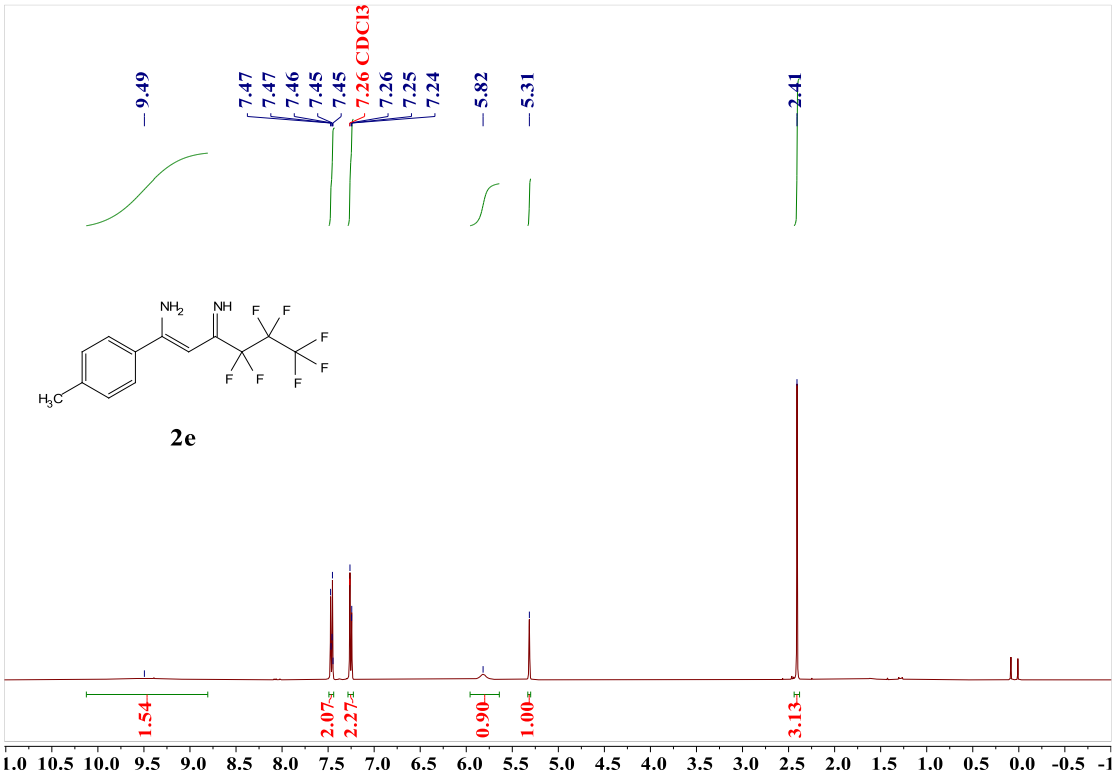
^{19}F NMR spectra of the product **2d** (376 MHz, $CDCl_3$)



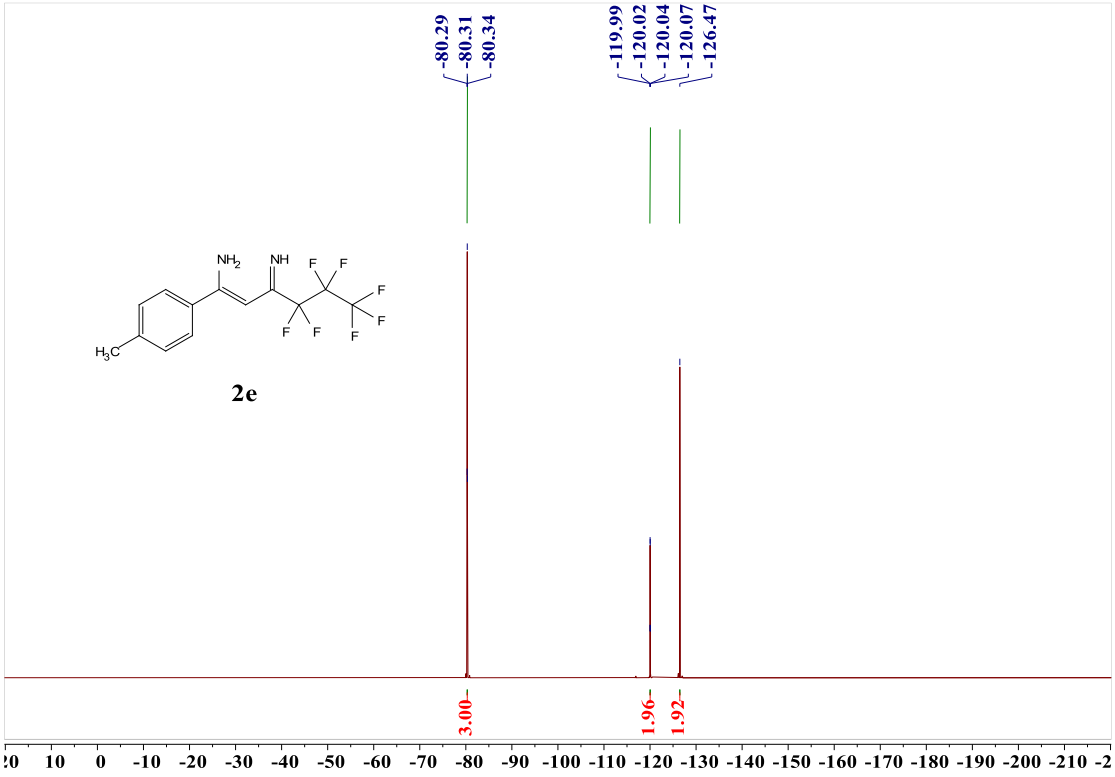
^{13}C NMR spectra of the product **2d** (100 MHz, $CDCl_3$)



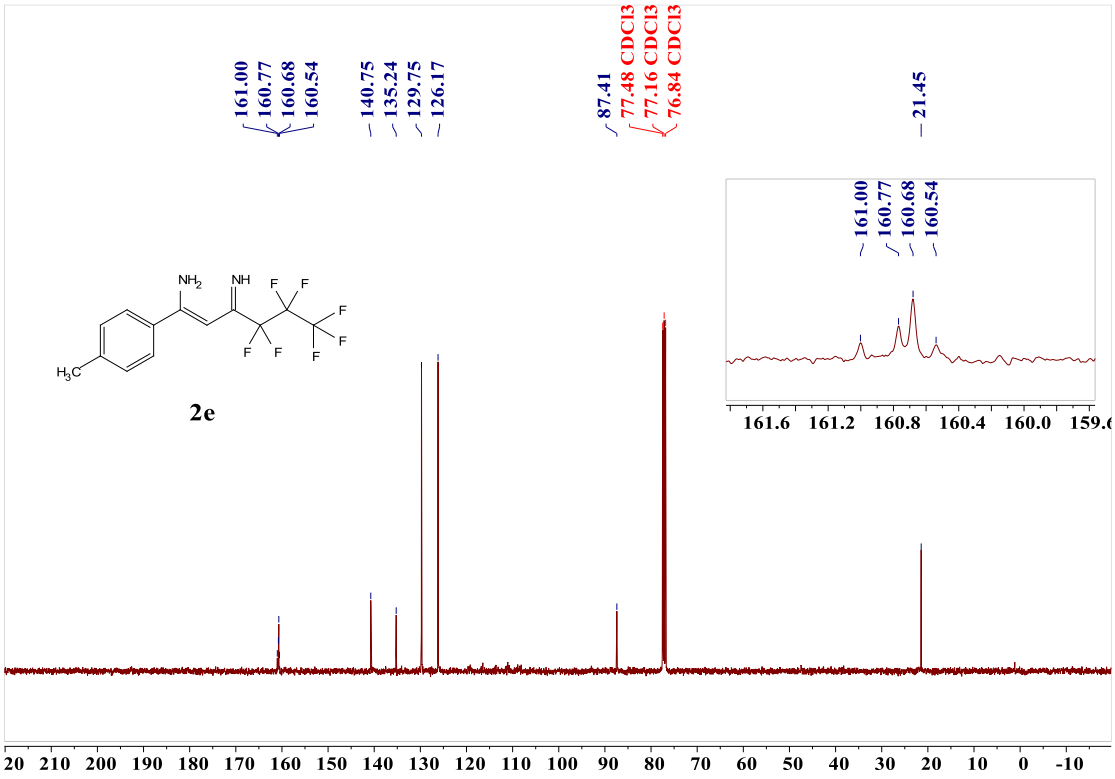
^{1}H NMR spectra of the product **2e** (400 MHz, $CDCl_3$)



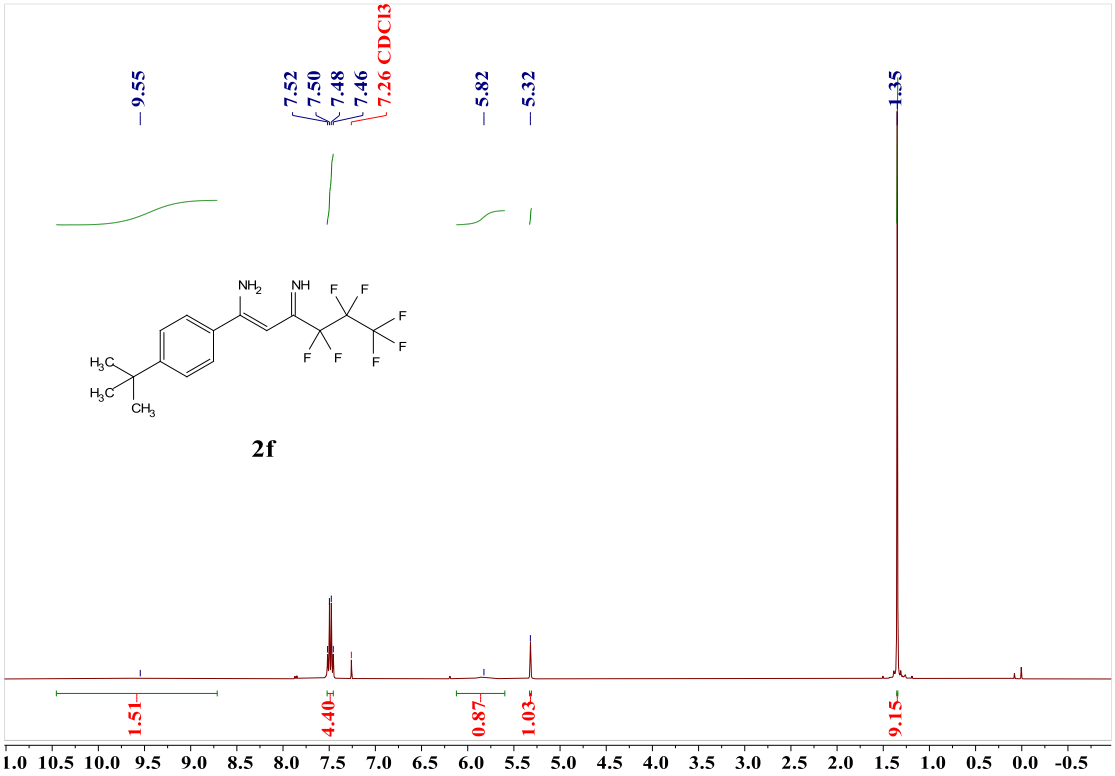
^{19}F NMR spectra of the product **2e** (376 MHz, $CDCl_3$)



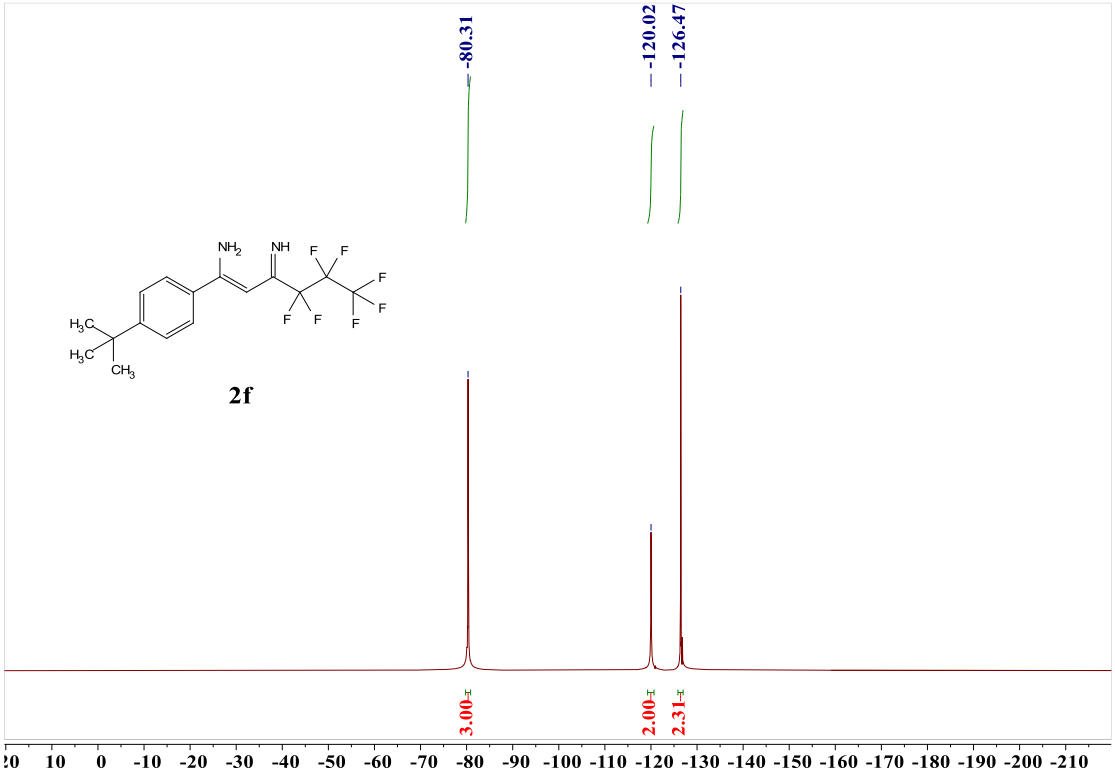
^{13}C NMR spectra of the product **2e** (100 MHz, $CDCl_3$)



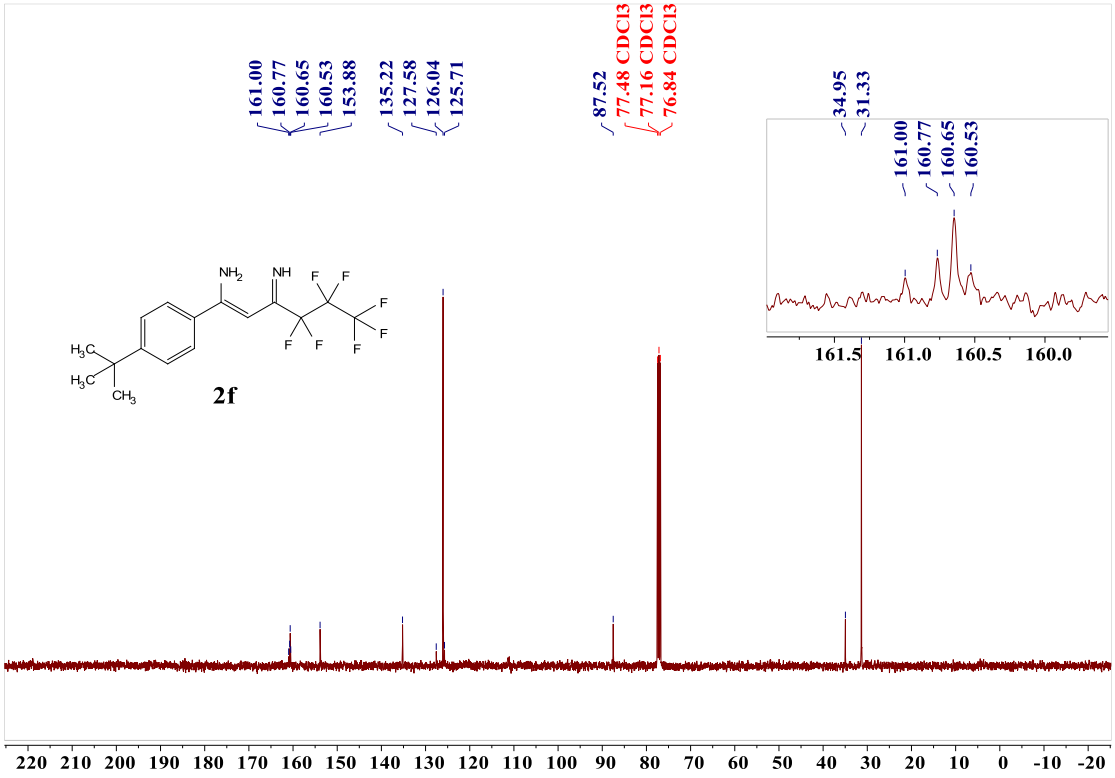
^{1}H NMR spectra of the product **2f** (400 MHz, $CDCl_3$)



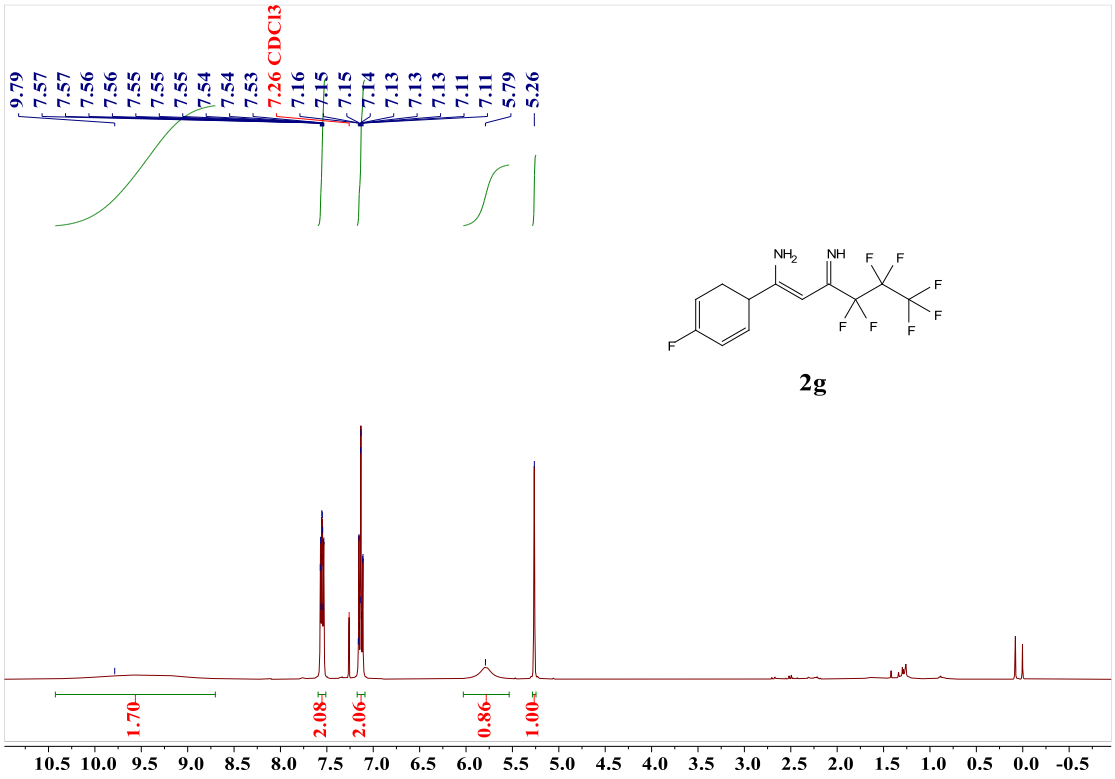
^{19}F NMR spectra of the product **2f** (376 MHz, $CDCl_3$)



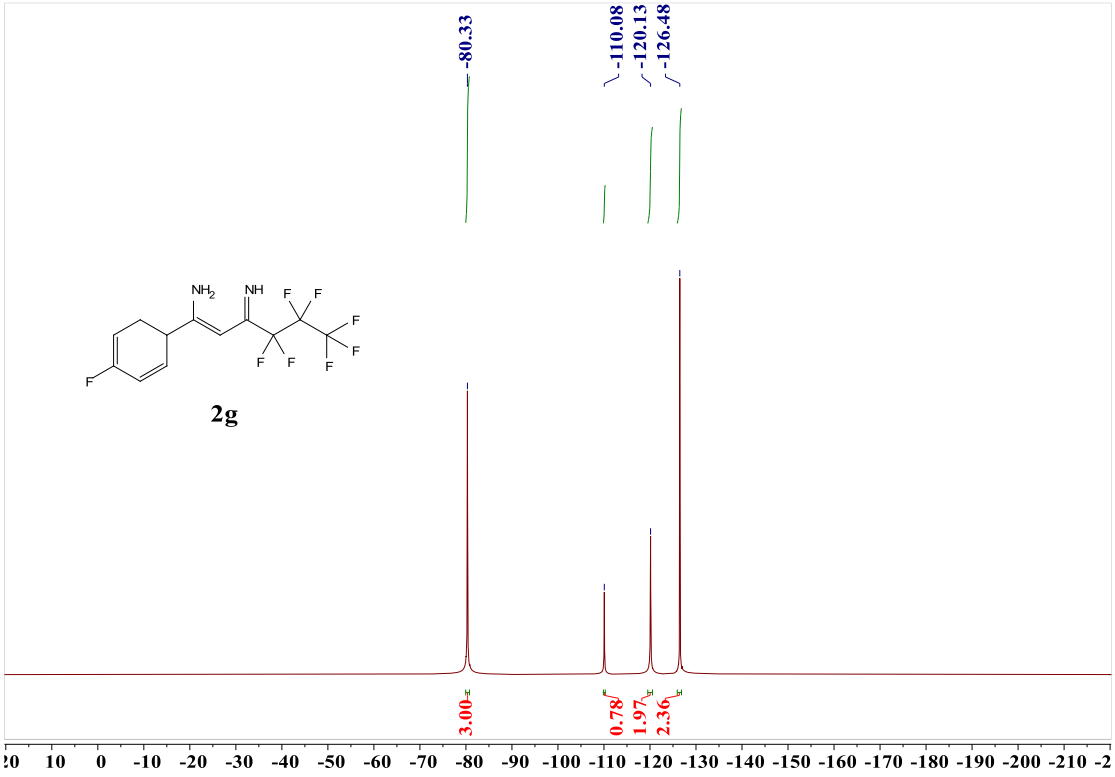
^{13}C NMR spectra of the product **2f** (100 MHz, $CDCl_3$)



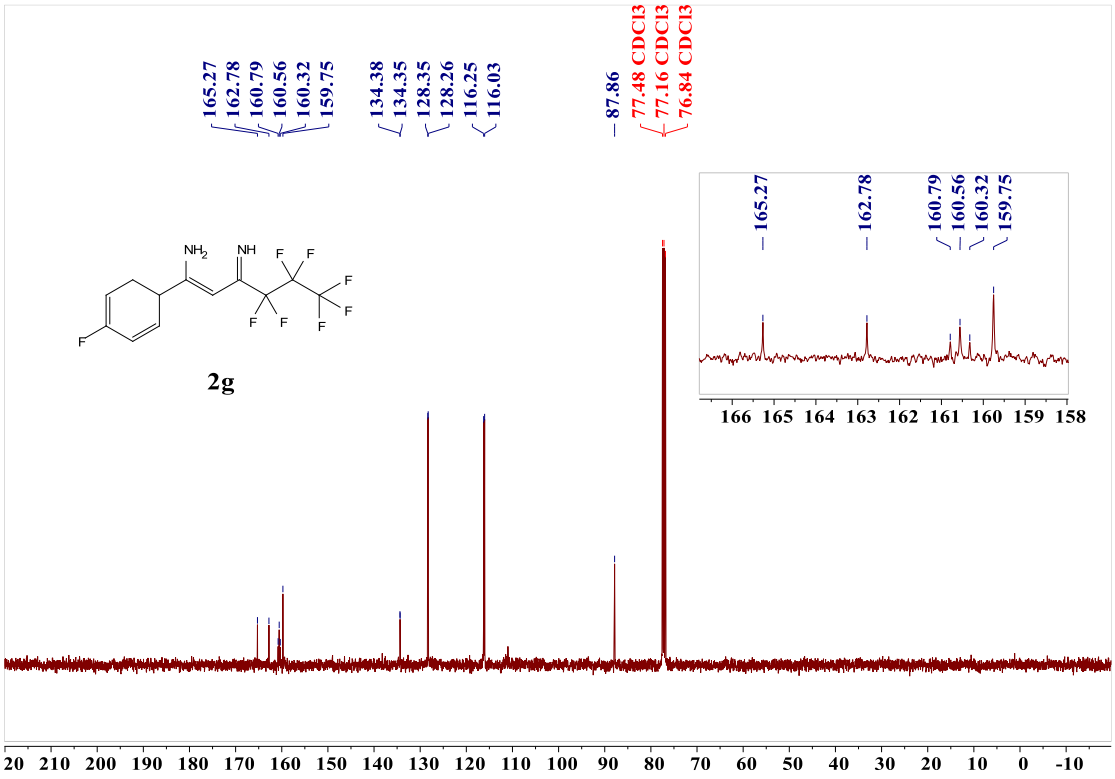
^{1}H NMR spectra of the product **2g** (400 MHz, $CDCl_3$)



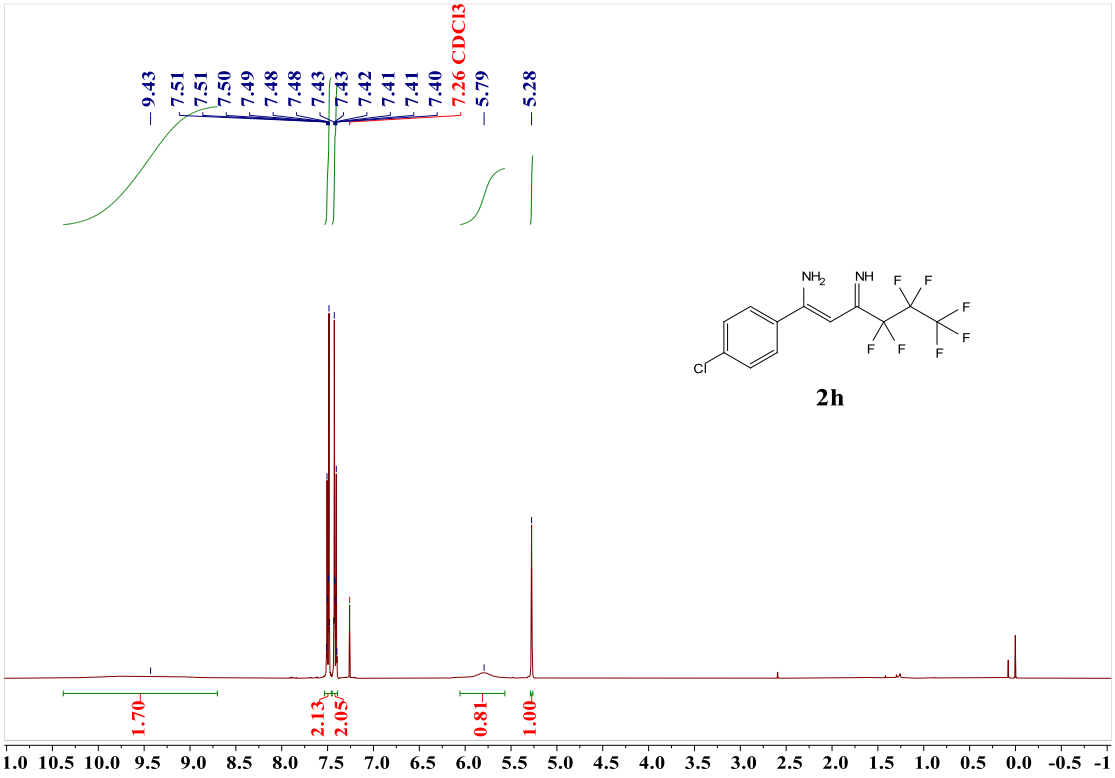
^{19}F NMR spectra of the product **2g** (376 MHz, $CDCl_3$)



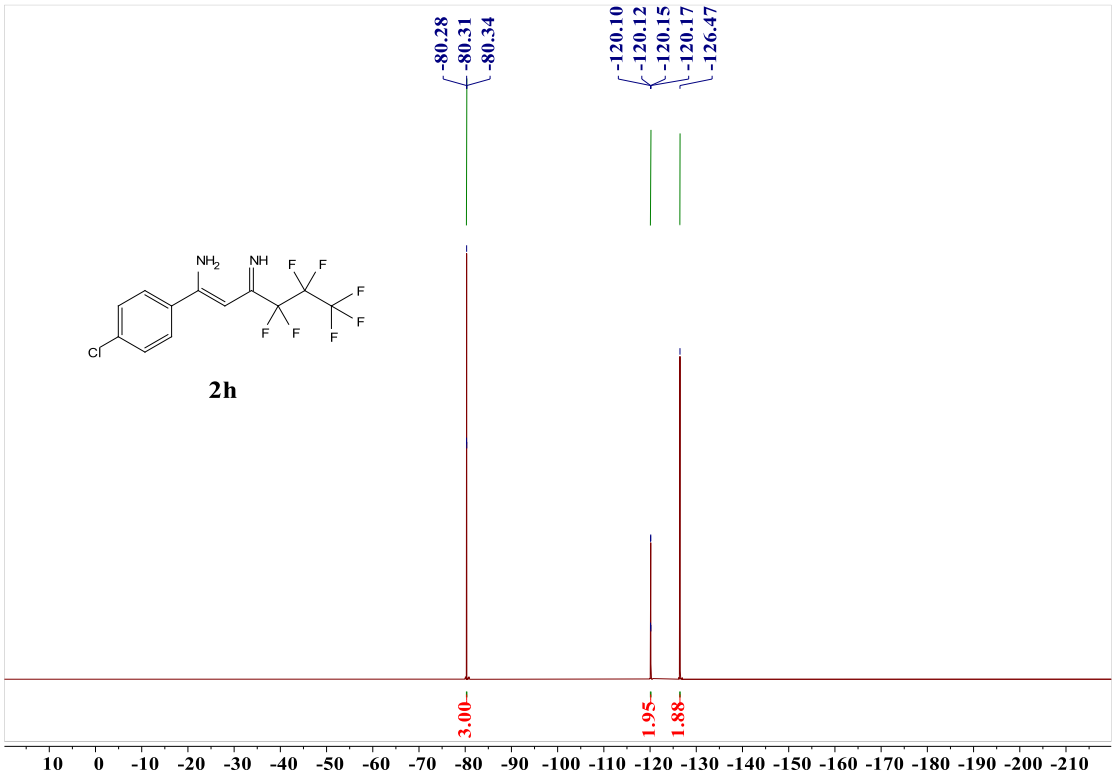
^{13}C NMR spectra of the product **2g** (100 MHz, $CDCl_3$)



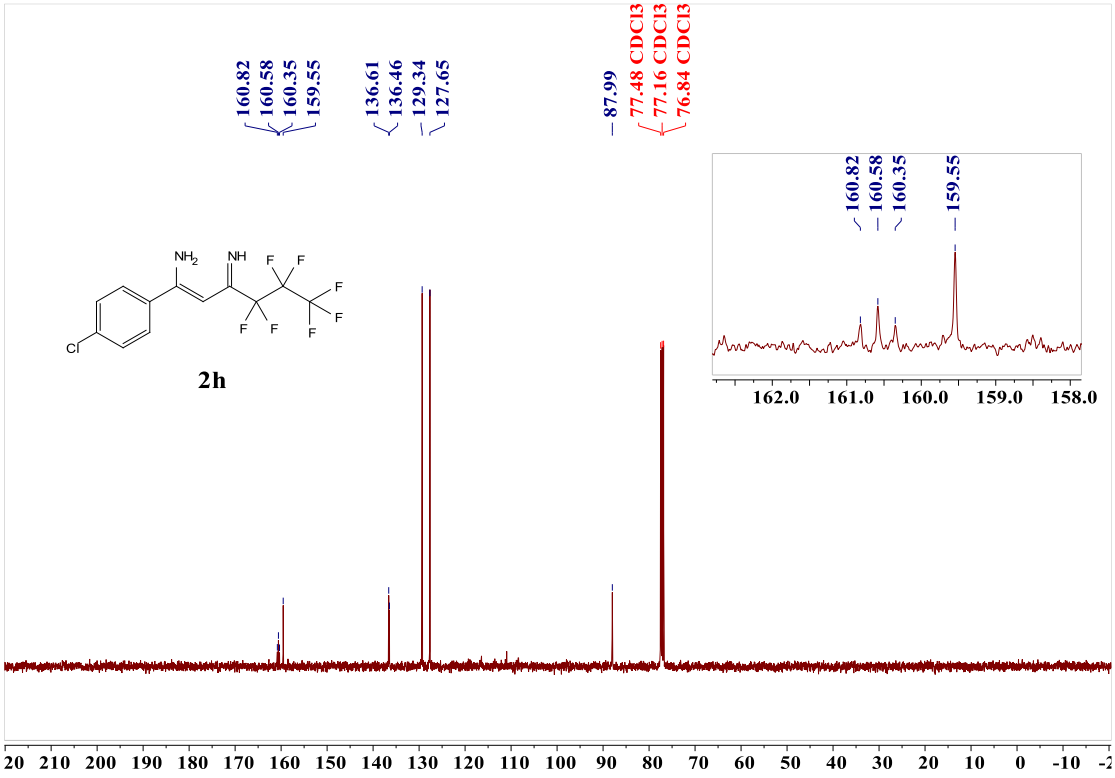
^{1}H NMR spectra of the product **2h** (400 MHz, $CDCl_3$)



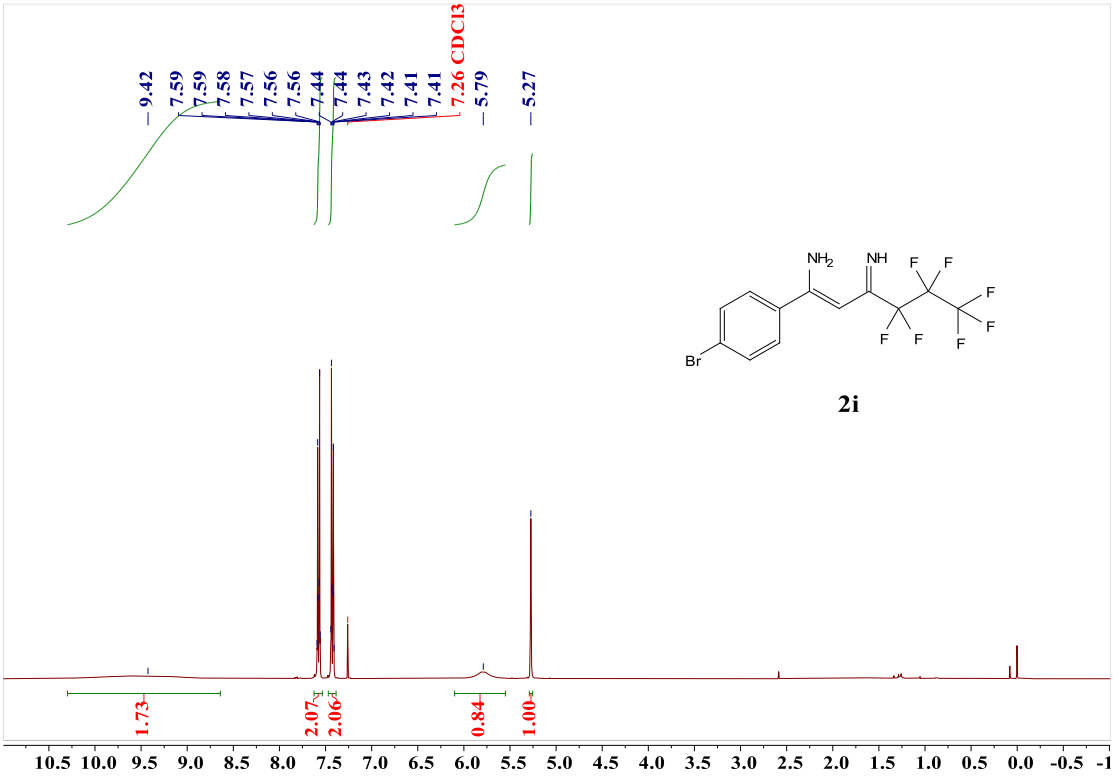
^{19}F NMR spectra of the product **2h** (376 MHz, $CDCl_3$



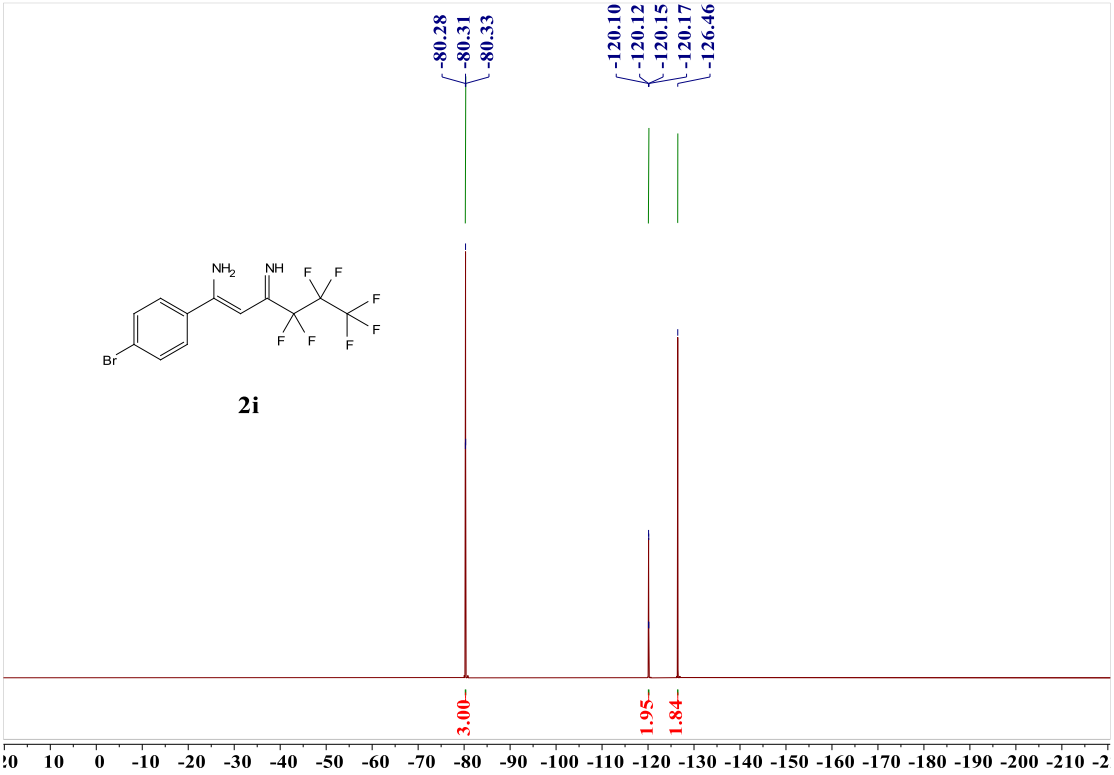
^{13}C NMR spectra of the product **2h** (100 MHz, $CDCl_3$)



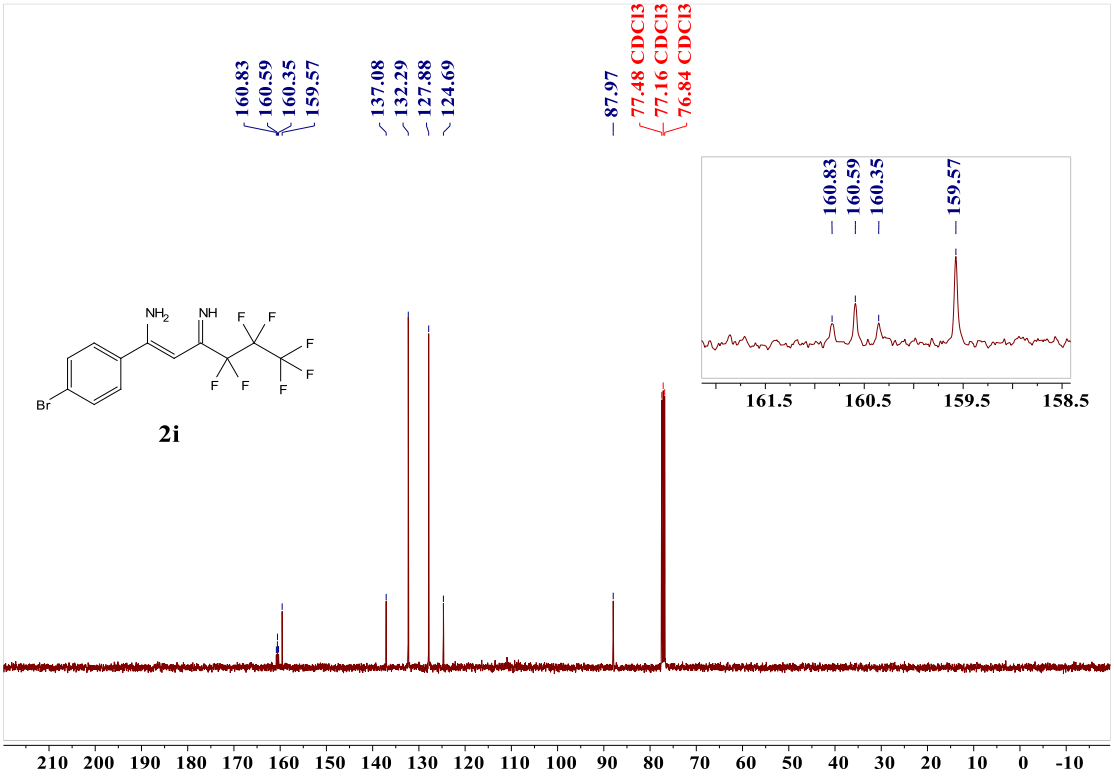
^{1}H NMR spectra of the product **2i** (400 MHz, $CDCl_3$)



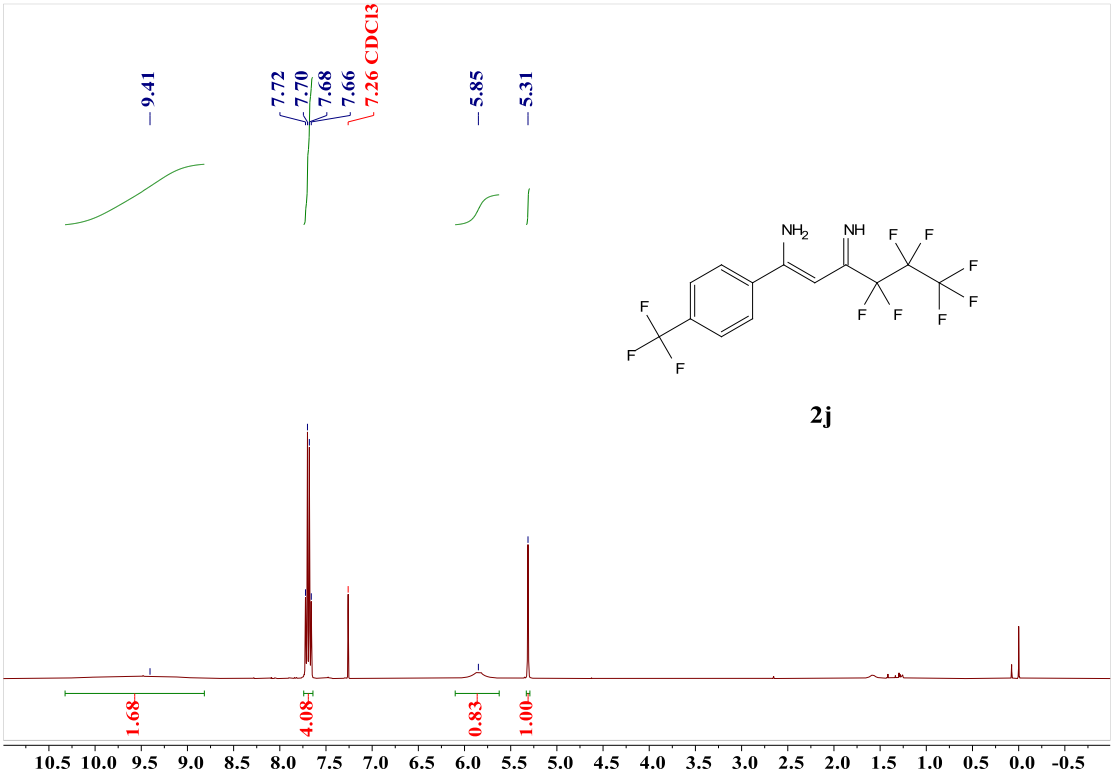
^{19}F NMR spectra of the product **2i** (376 MHz, $CDCl_3$)



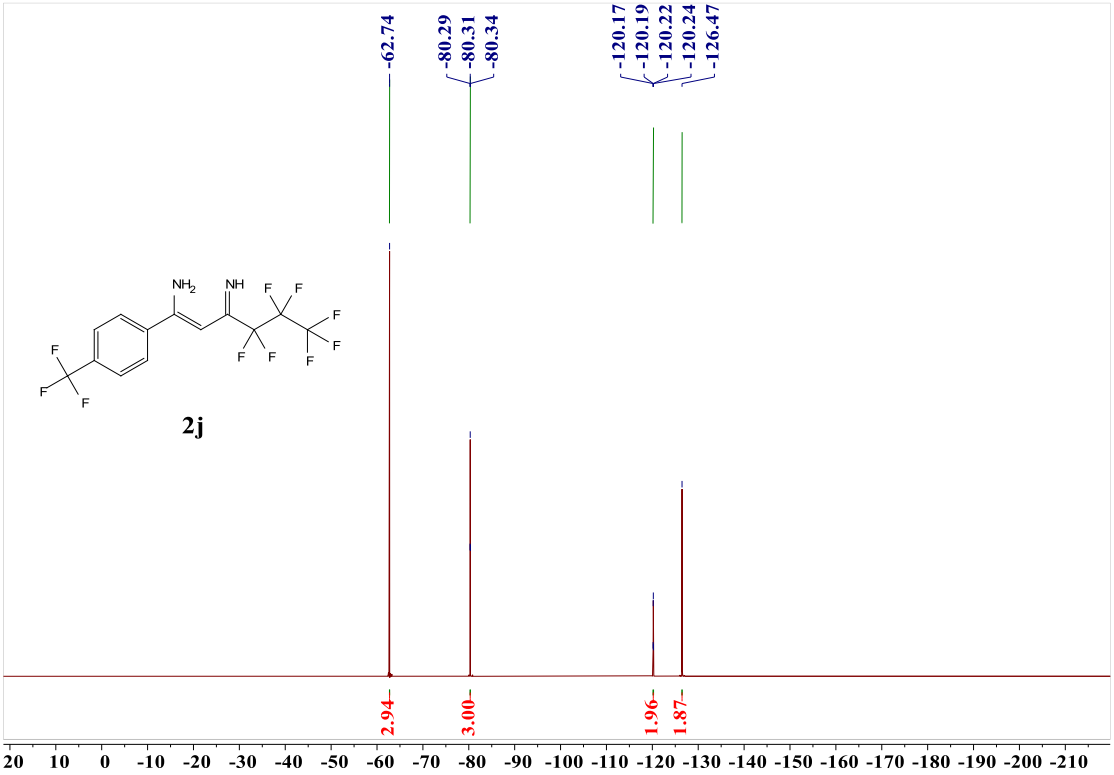
^{13}C NMR spectra of the product **2i** (100 MHz, $CDCl_3$)



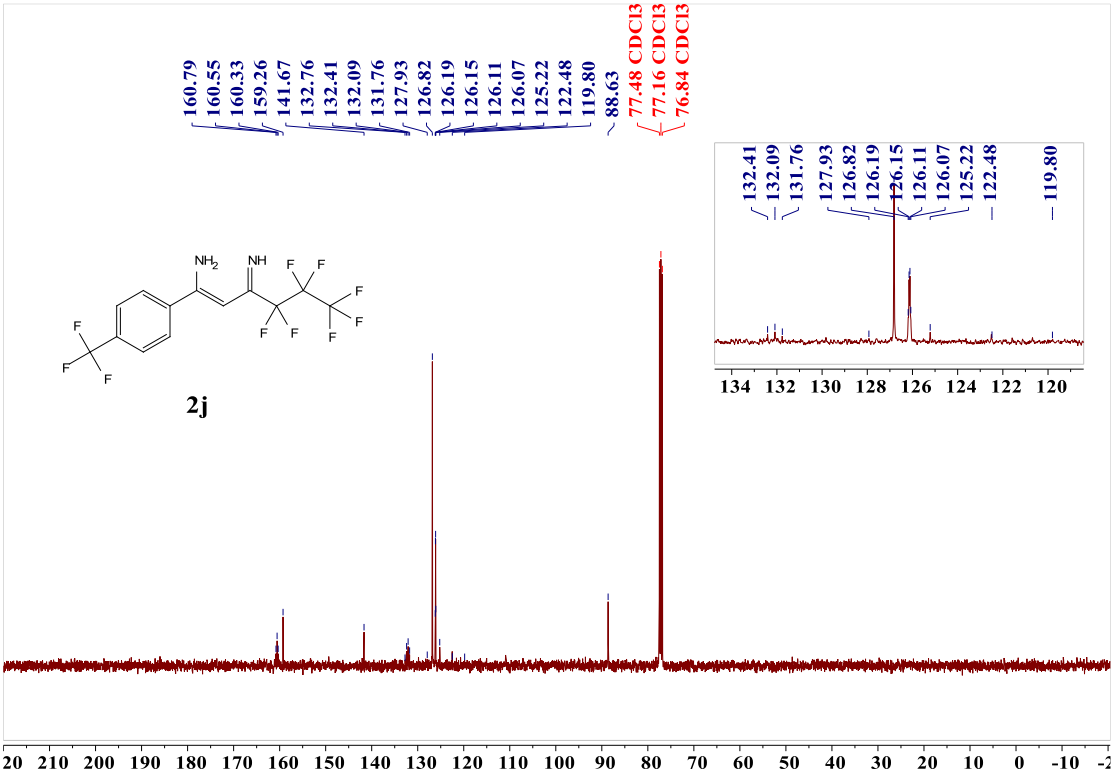
^{1}H NMR spectra of the product **2j** (400 MHz, $CDCl_3$)



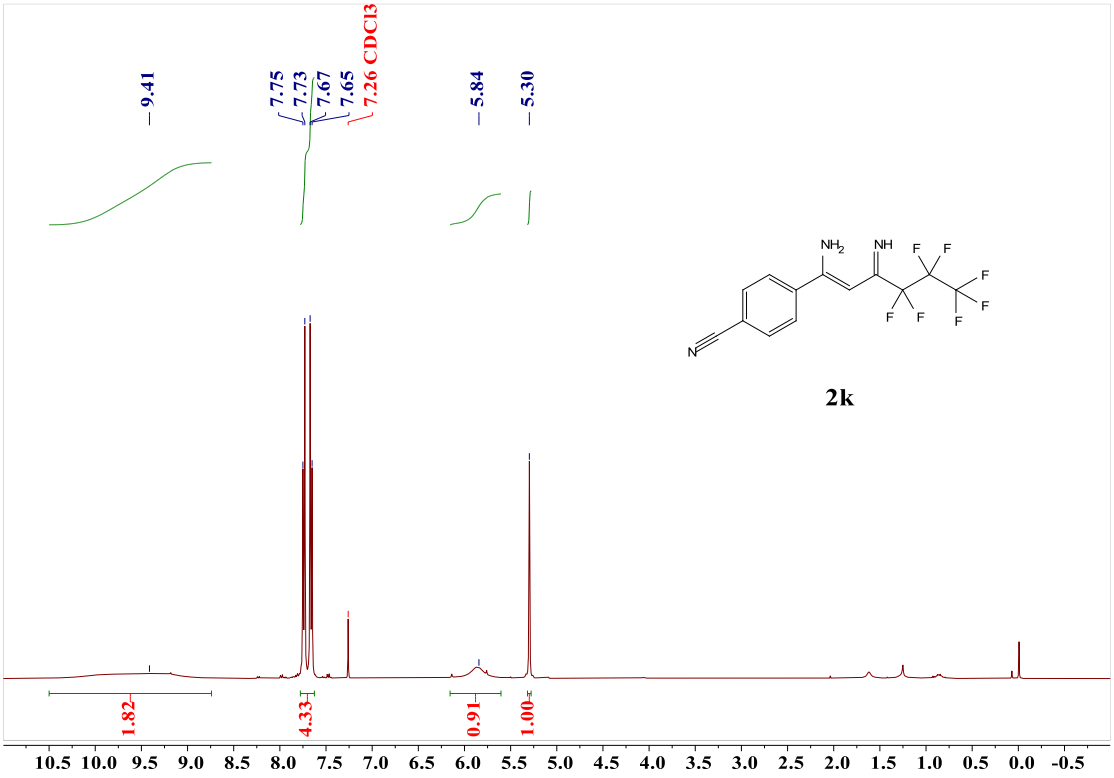
^{19}F NMR spectra of the product **2j** (376 MHz, $CDCl_3$)



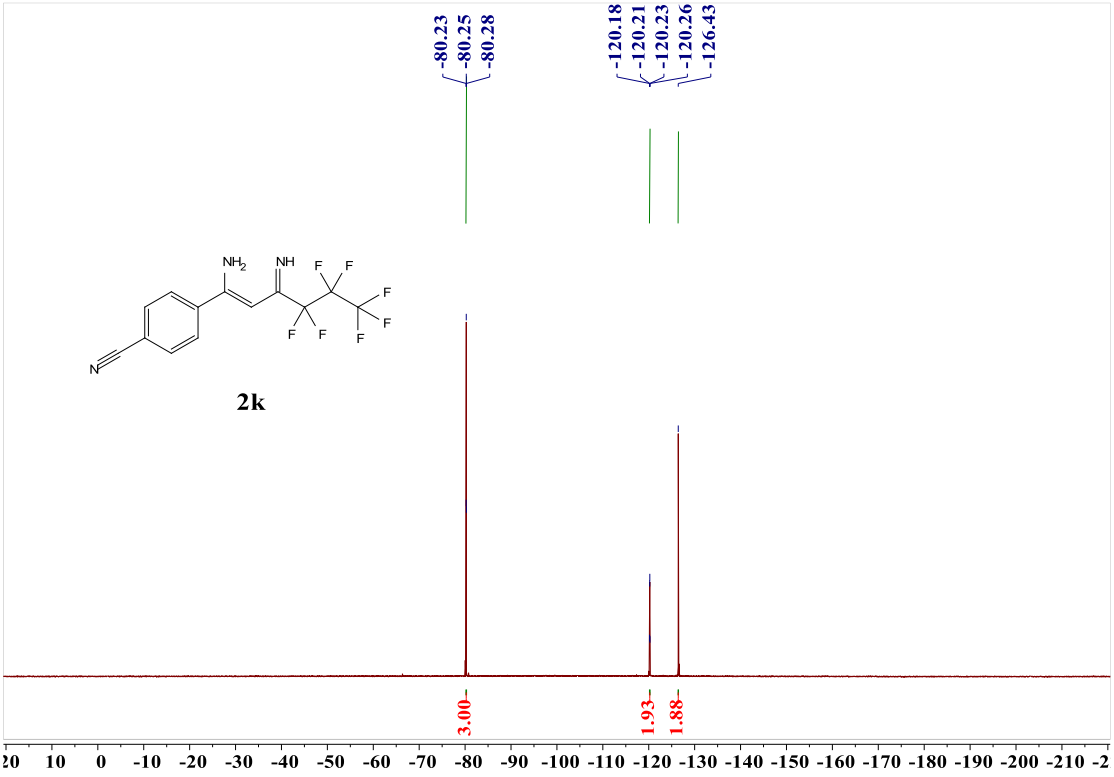
^{13}C NMR spectra of the product **2j** (100 MHz, $CDCl_3$)



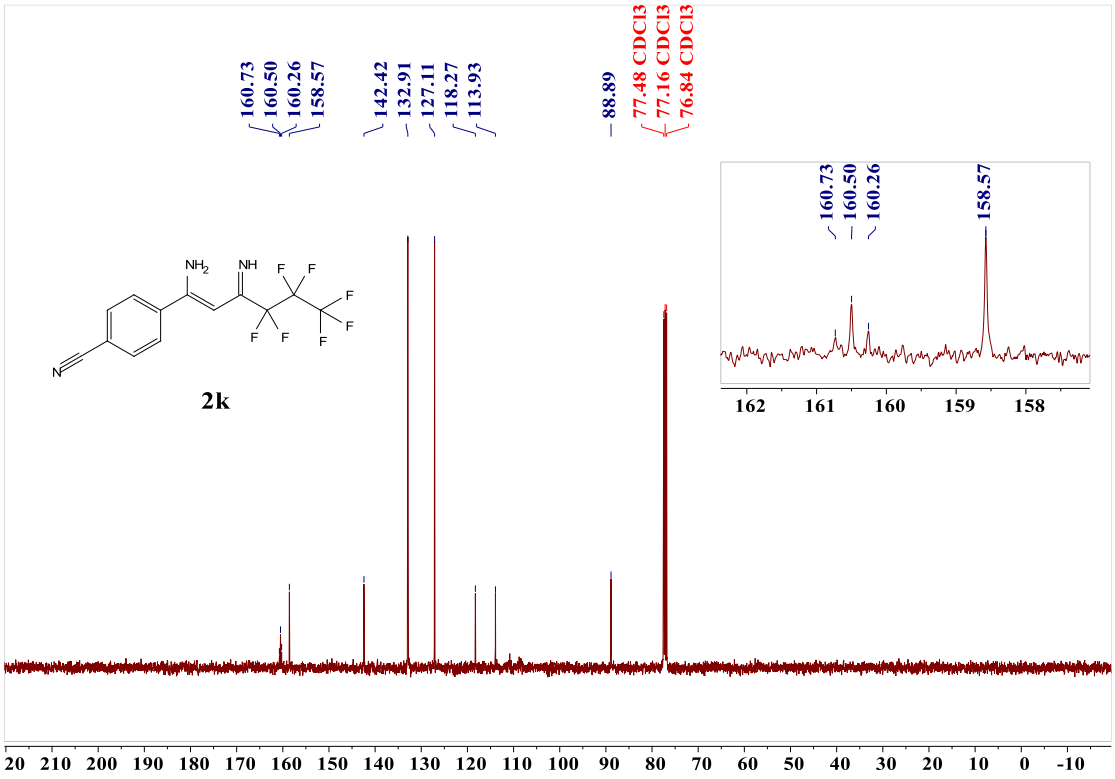
^{1}H NMR spectra of the product **2k** (400 MHz, $CDCl_3$)



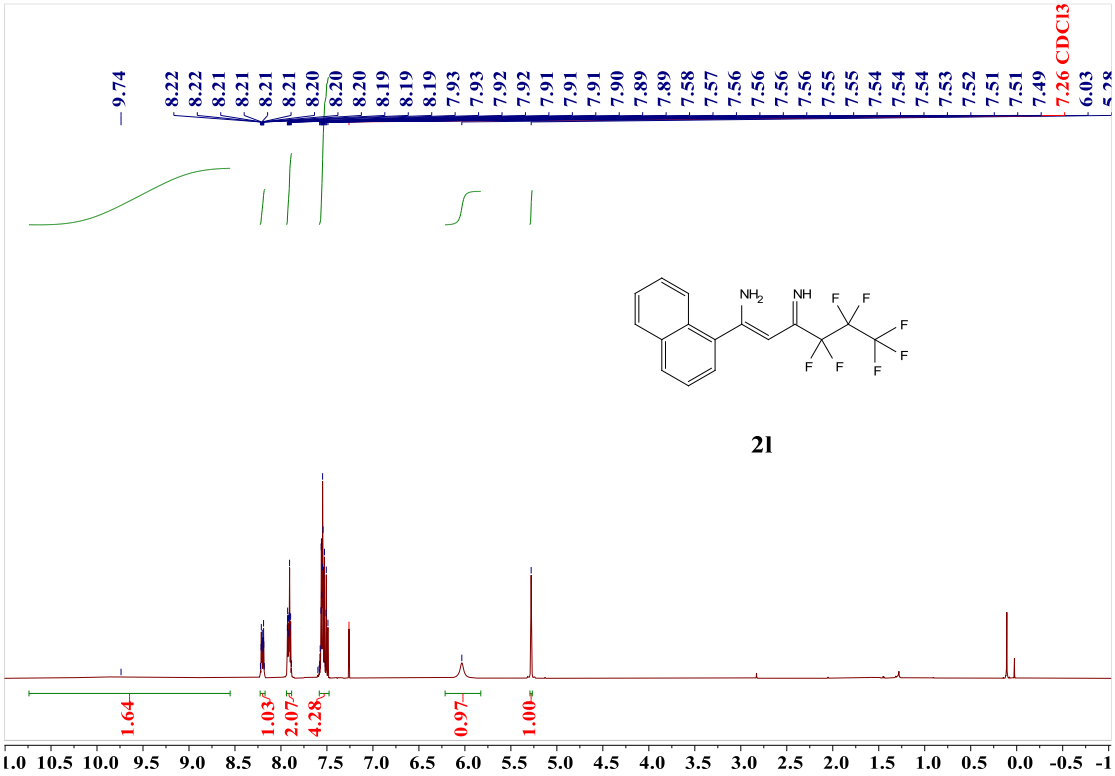
^{19}F NMR spectra of the product **2k** (376 MHz, $CDCl_3$)



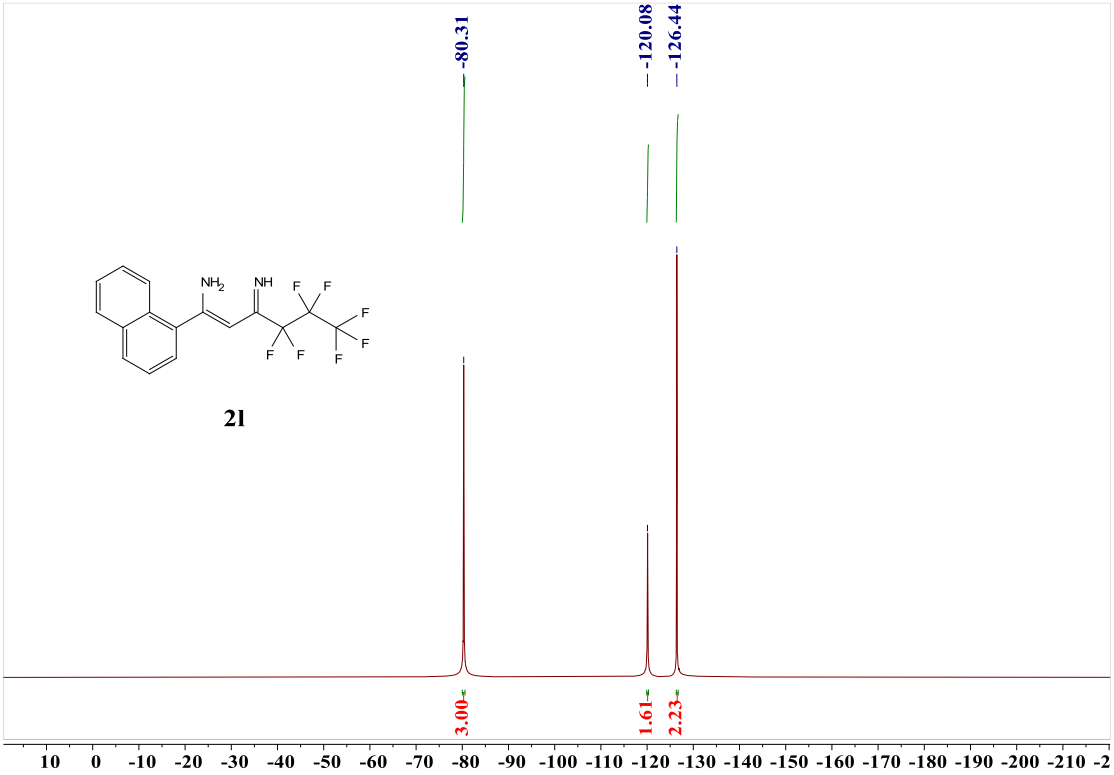
^{13}C NMR spectra of the product **2k** (100 MHz, $CDCl_3$)



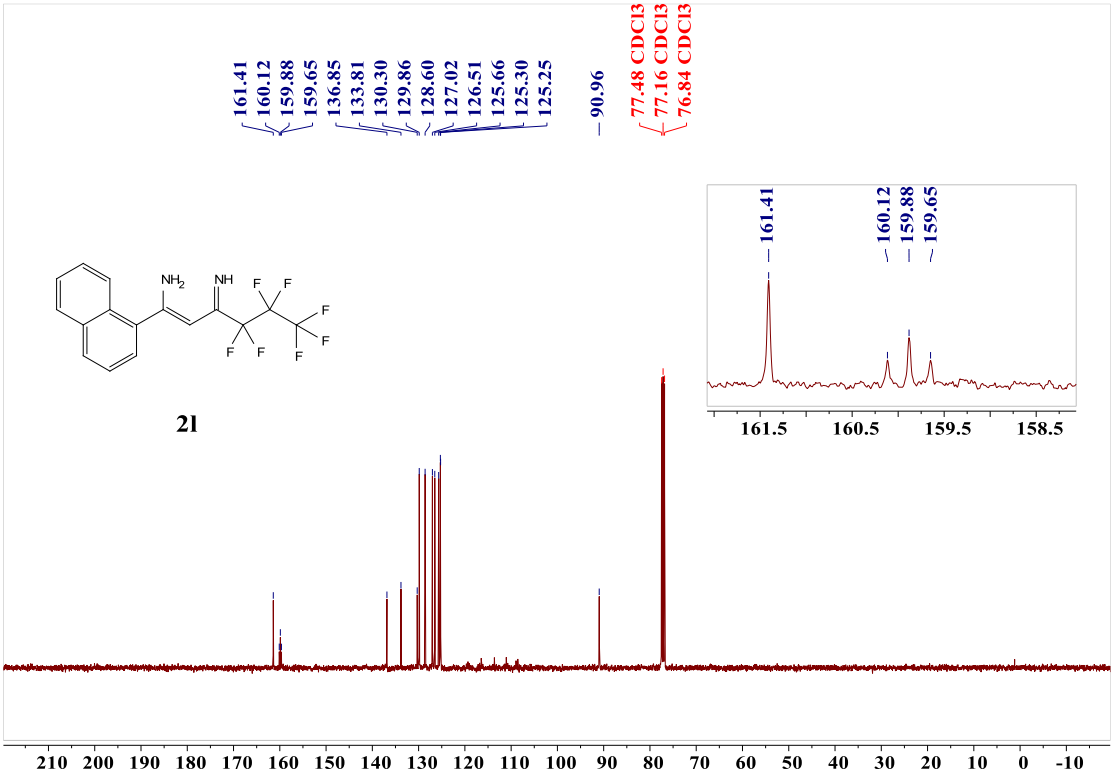
^{1}H NMR spectra of the product **2l** (400 MHz, $CDCl_3$)



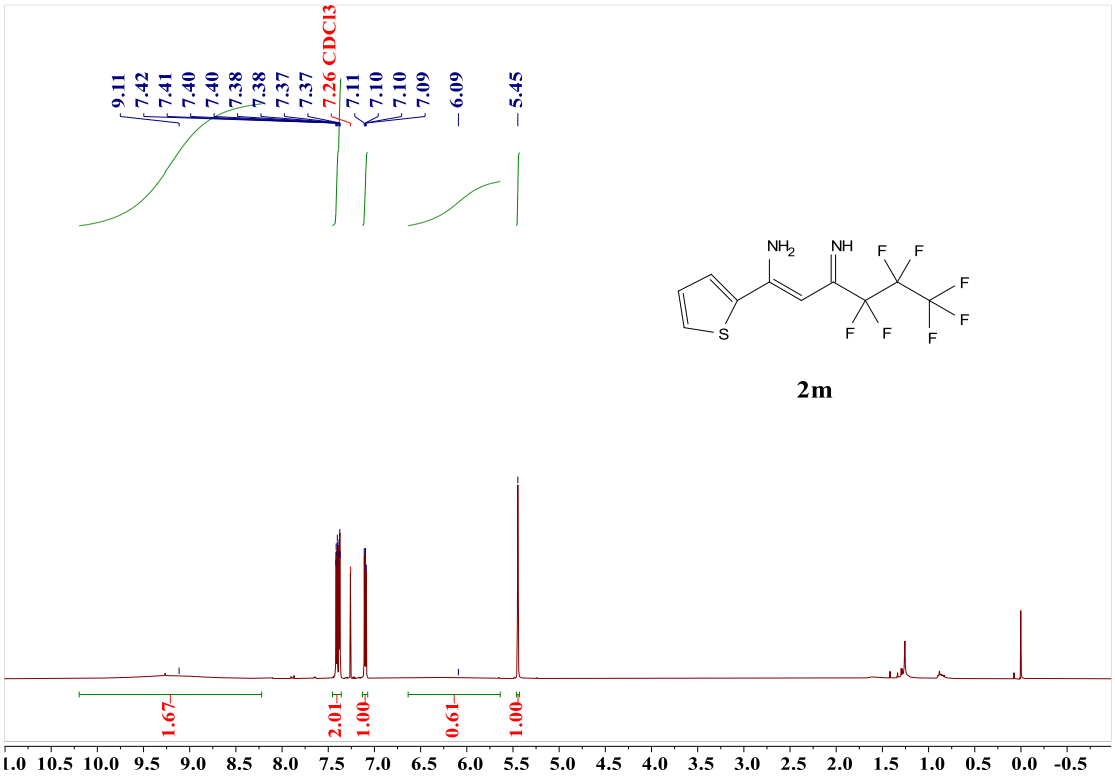
^{19}F NMR spectra of the product **2l** (376 MHz, $CDCl_3$)



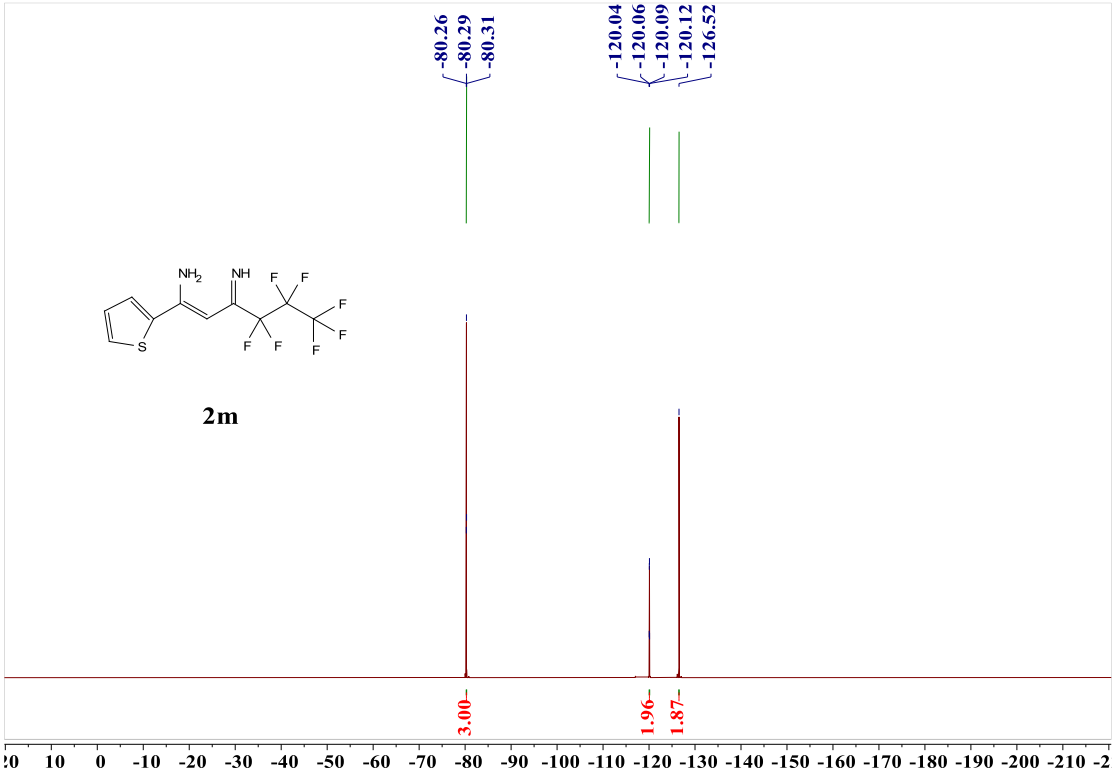
^{13}C NMR spectra of the product **2l** (100 MHz, $CDCl_3$)



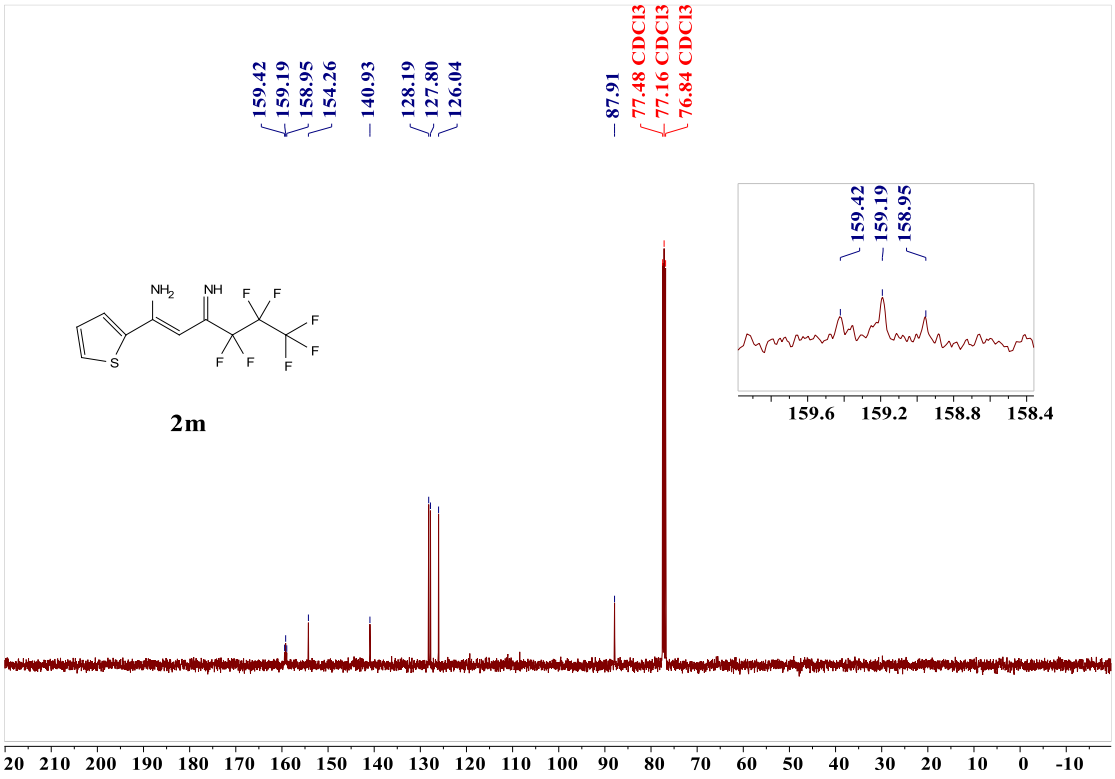
^{1}H NMR spectra of the product **2m** (400 MHz, $CDCl_3$)



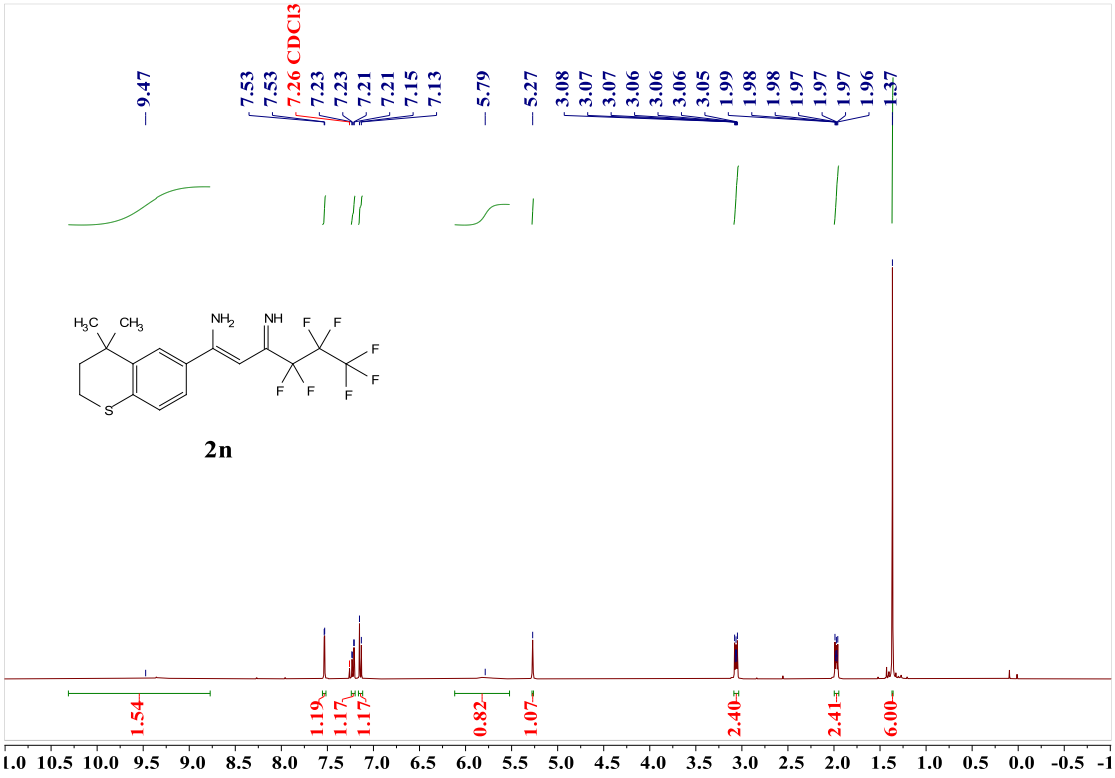
^{19}F NMR spectra of the product **2m** (376 MHz, $CDCl_3$)



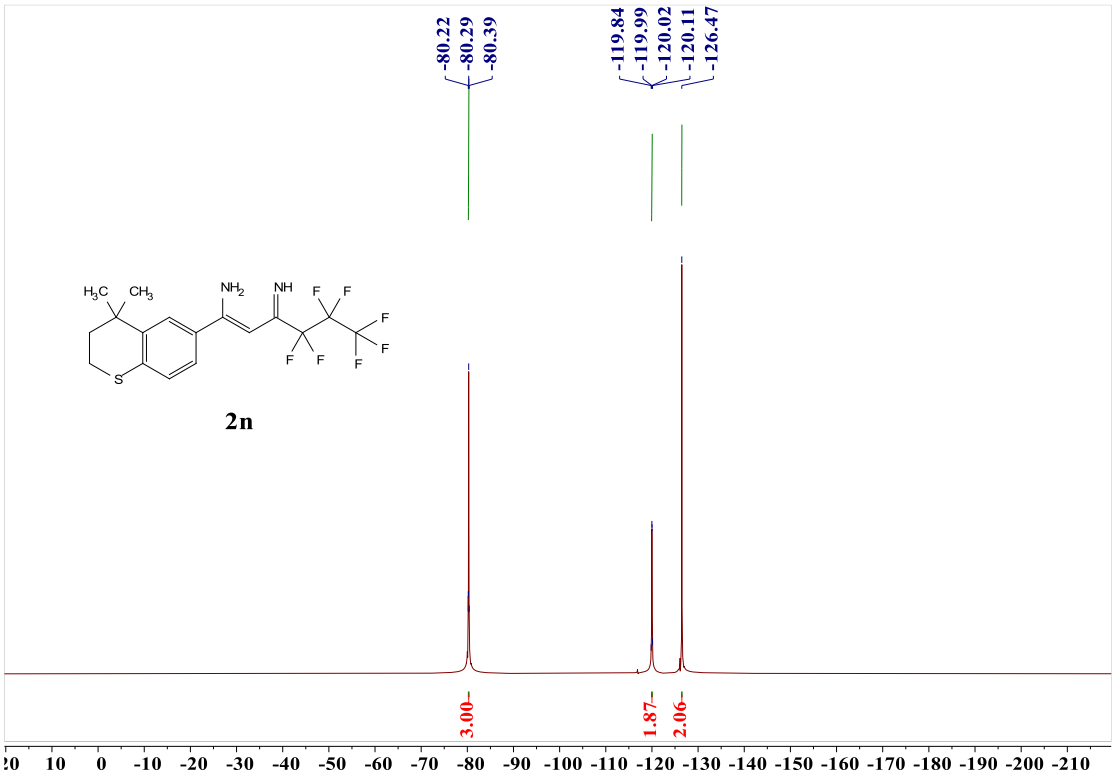
^{13}C NMR spectra of the product **2m** (100 MHz, $CDCl_3$)



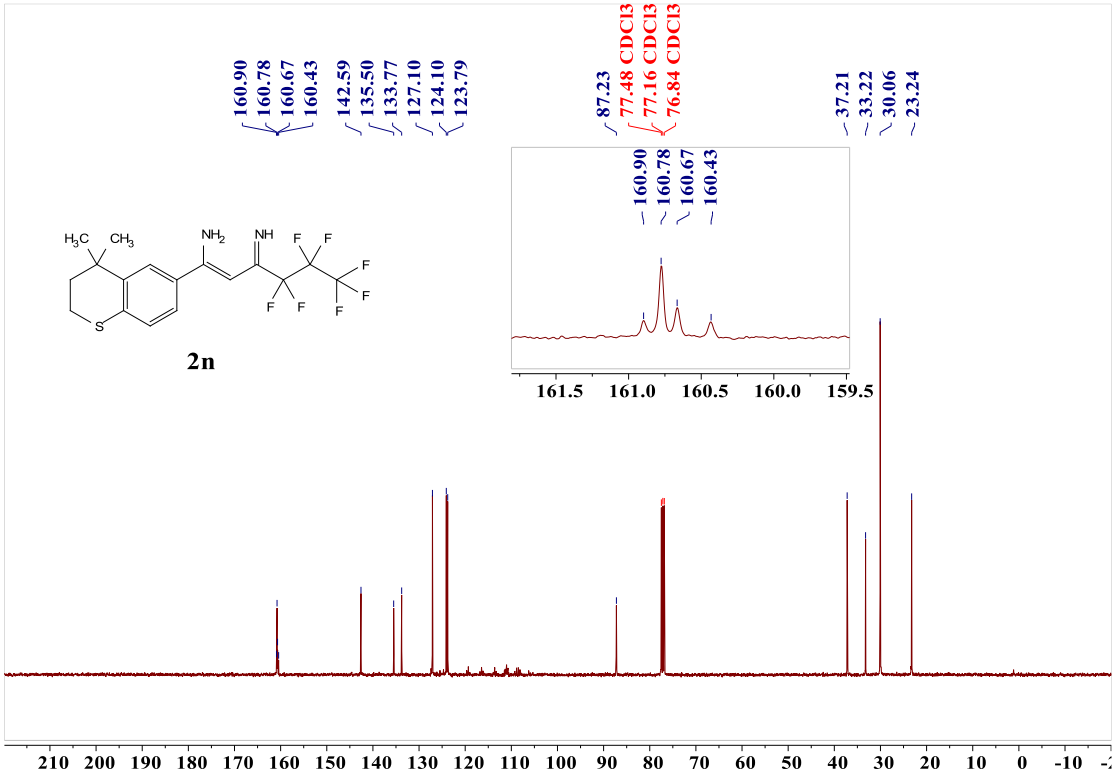
^{1}H NMR spectra of the product **2n** (400 MHz, $CDCl_3$)



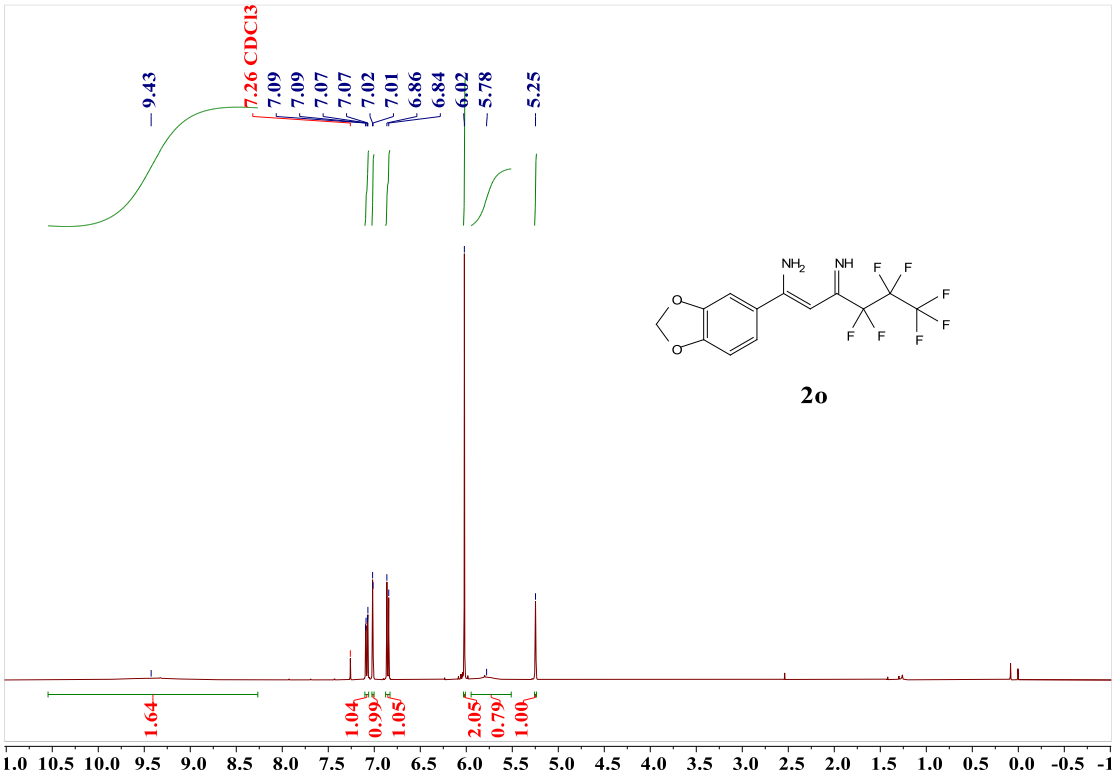
^{19}F NMR spectra of the product **2n** (376 MHz, $CDCl_3$)



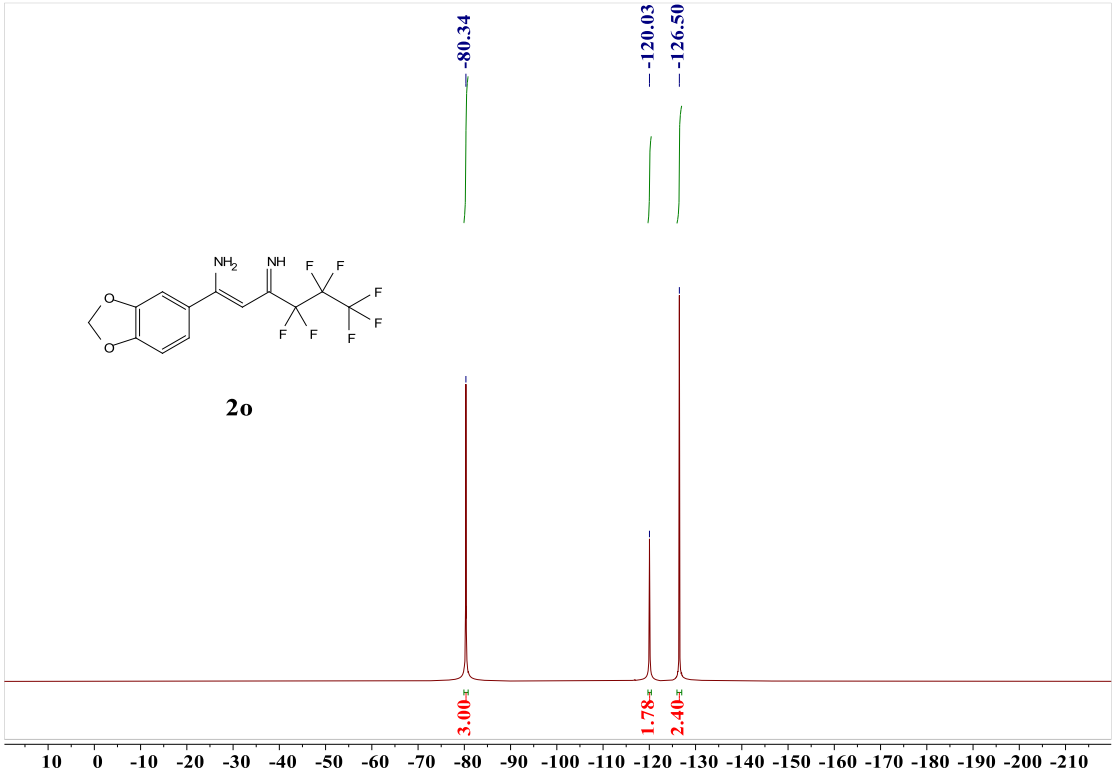
^{13}C NMR spectra of the product **2n** (100 MHz, $CDCl_3$)



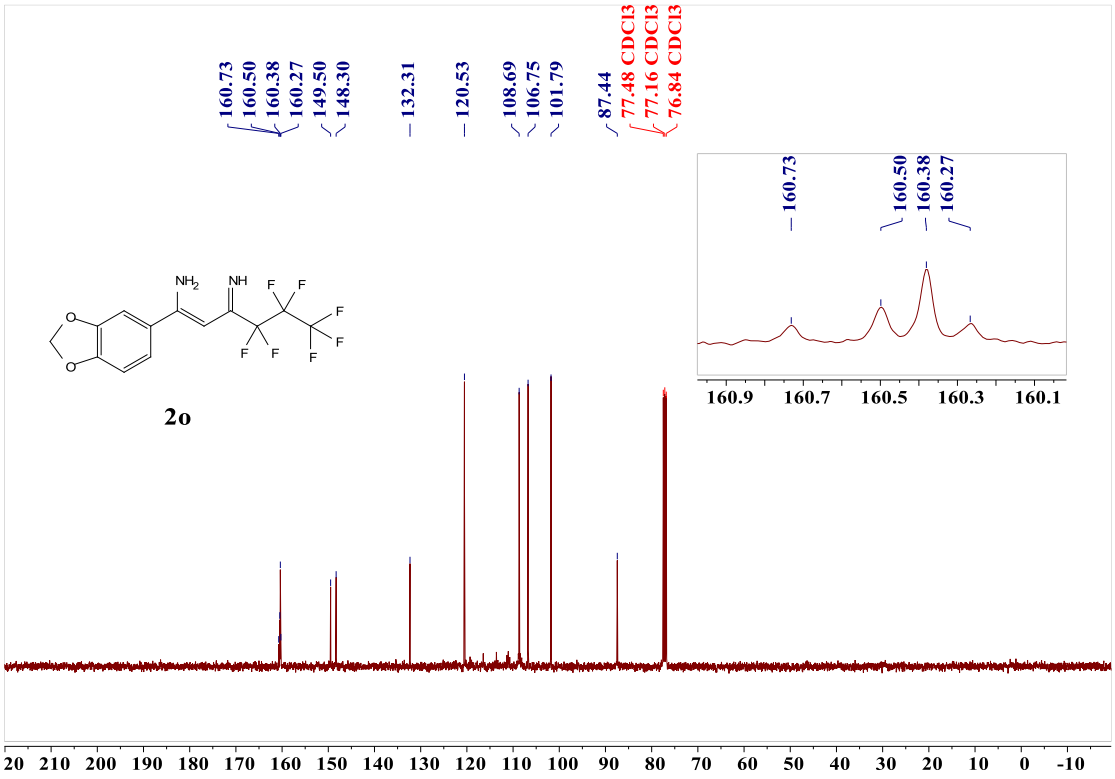
^{1}H NMR spectra of the product **2o** (400 MHz, $CDCl_3$)



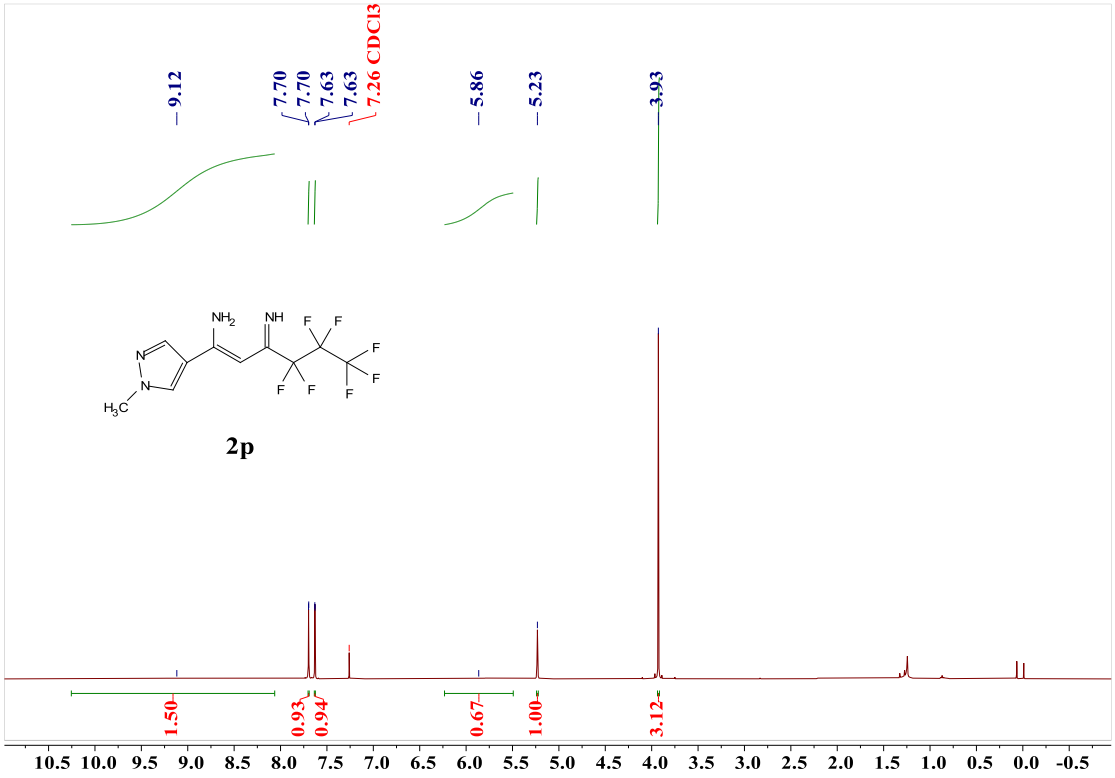
^{19}F NMR spectra of the product **2o** (376 MHz, $CDCl_3$)



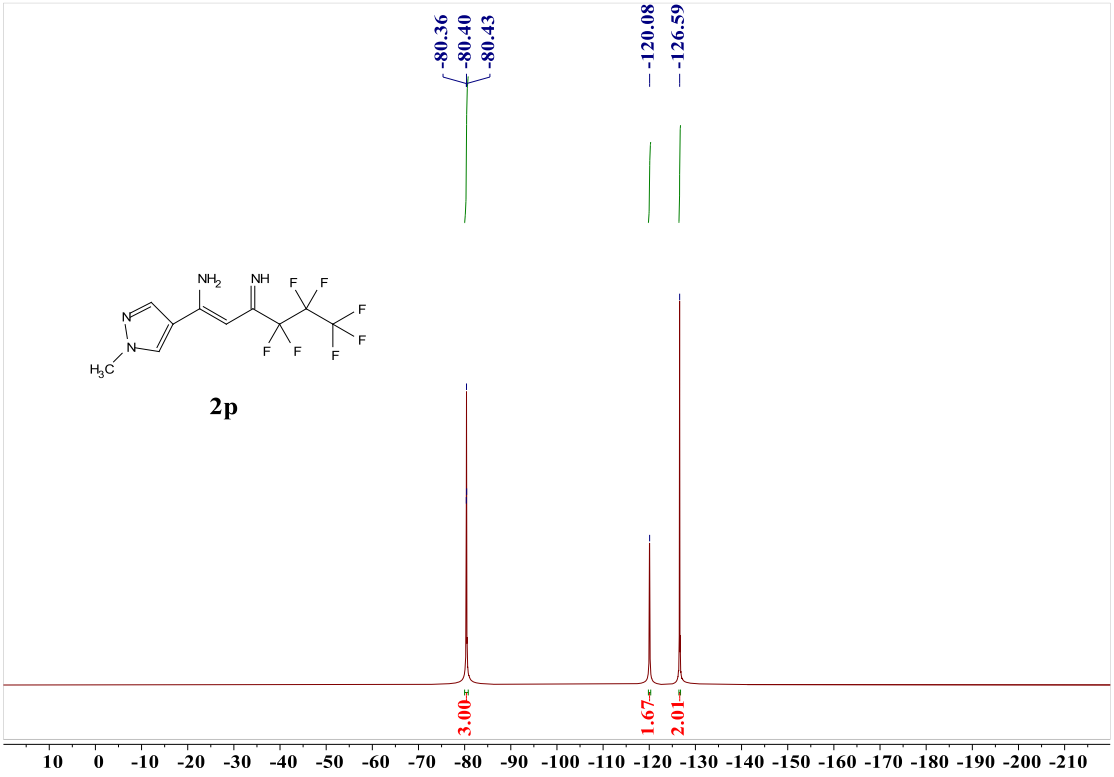
^{13}C NMR spectra of the product **2o** (100 MHz, $CDCl_3$)



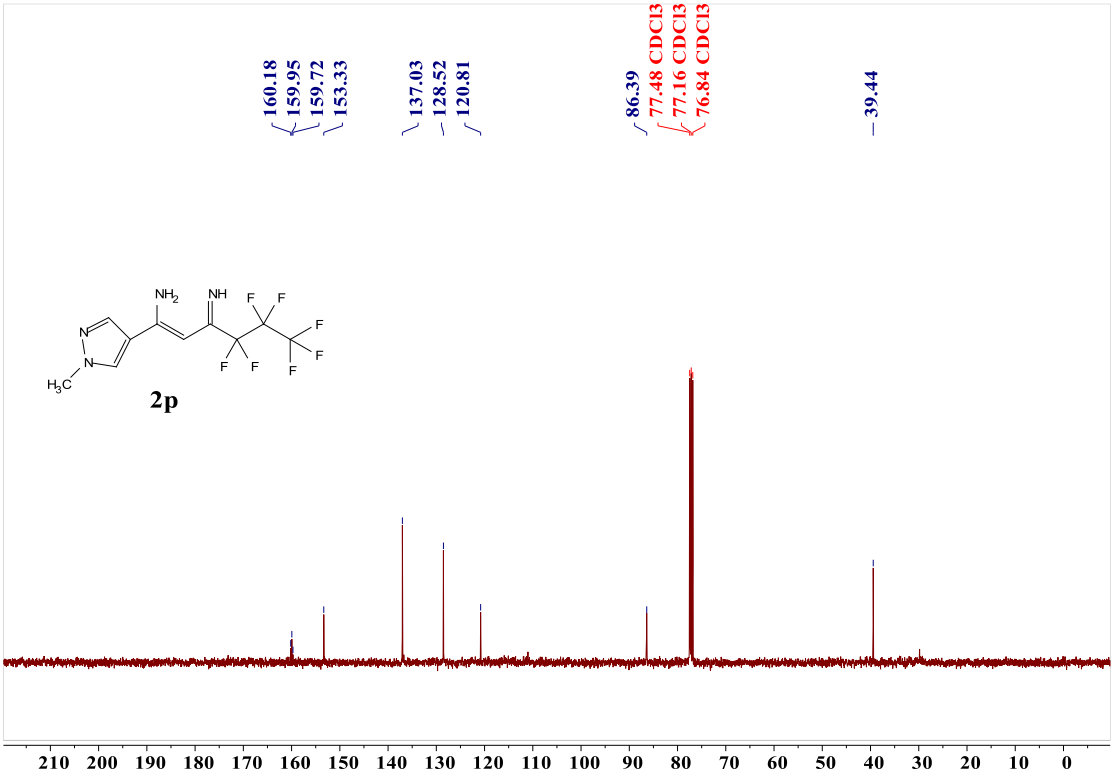
^{1}H NMR spectra of the product **2p** (400 MHz, $CDCl_3$)



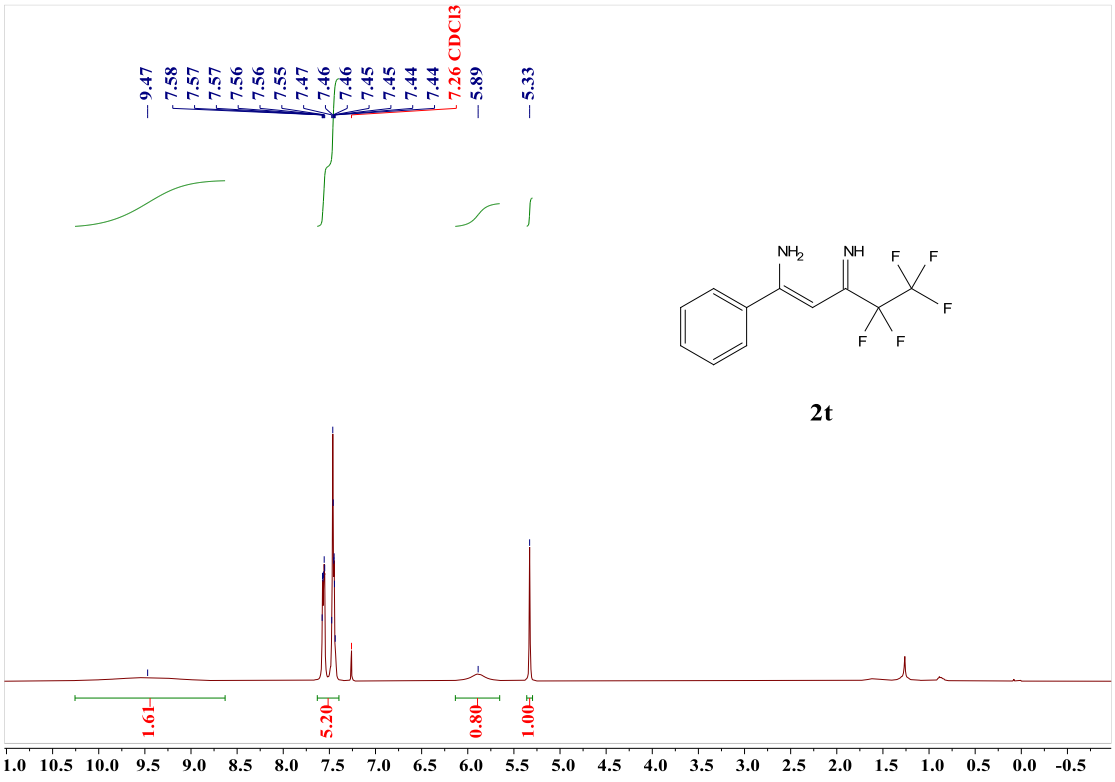
^{19}F NMR spectra of the product **2p** (376 MHz, $CDCl_3$)



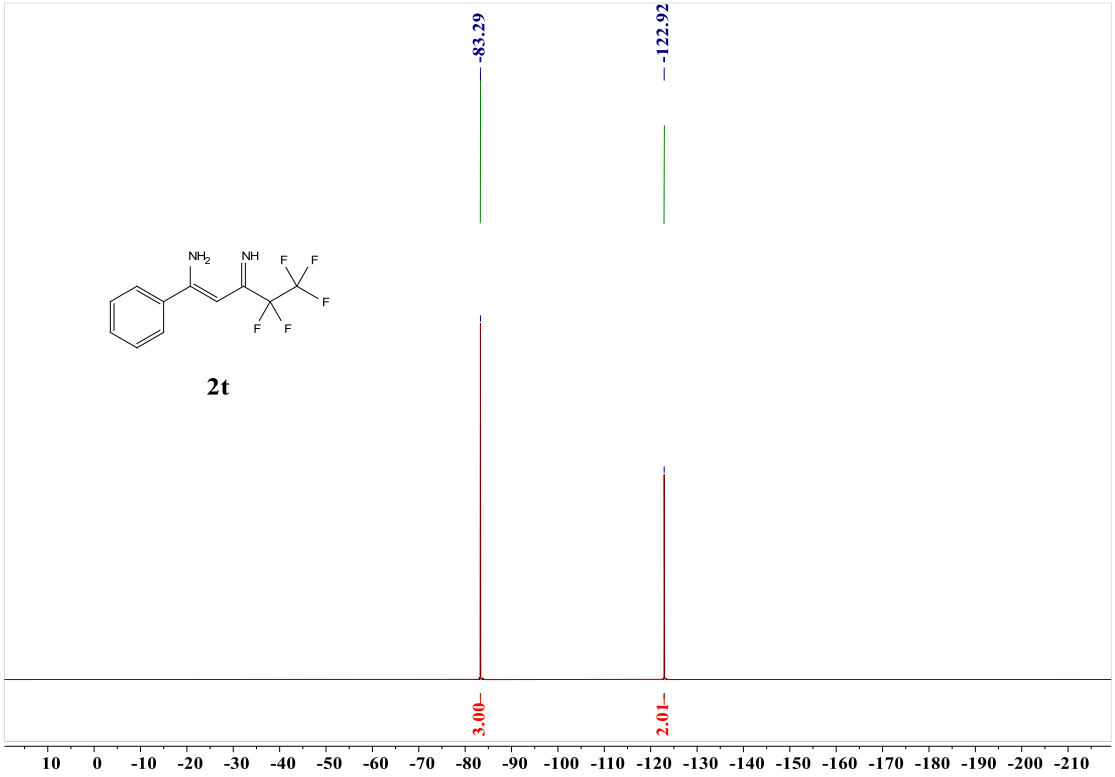
^{13}C NMR spectra of the product **2p** (100 MHz, $CDCl_3$)



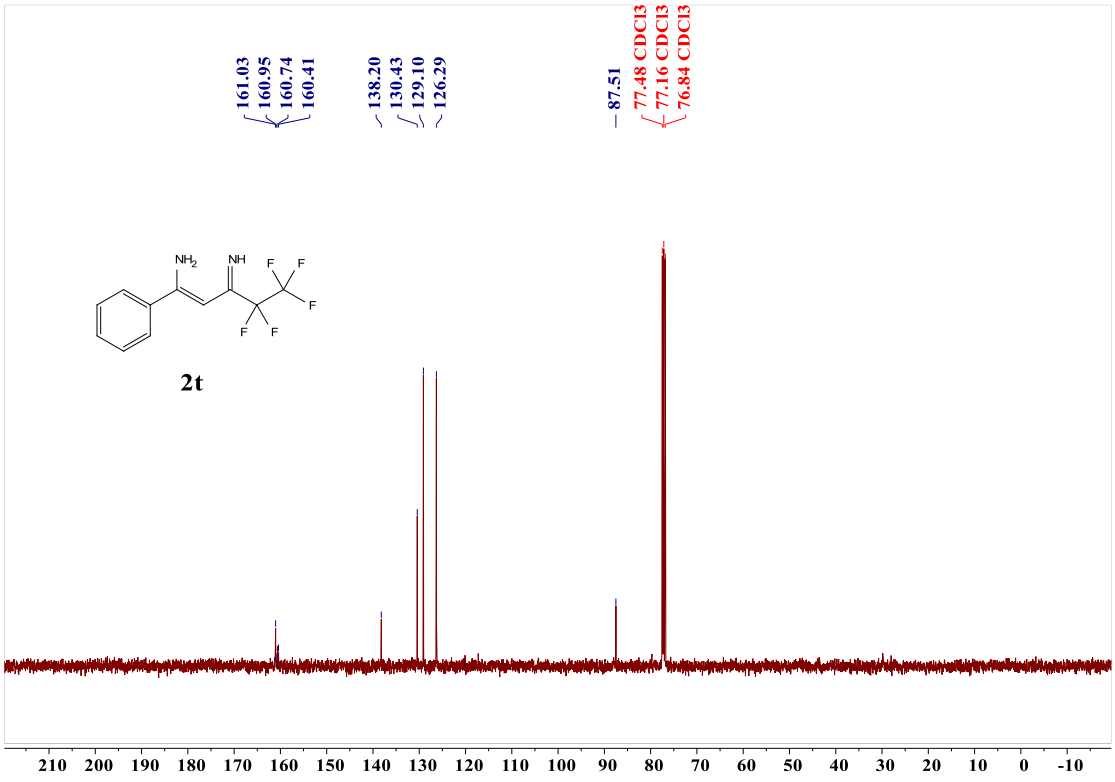
^{1}H NMR spectra of the product **2t** (400 MHz, $CDCl_3$)



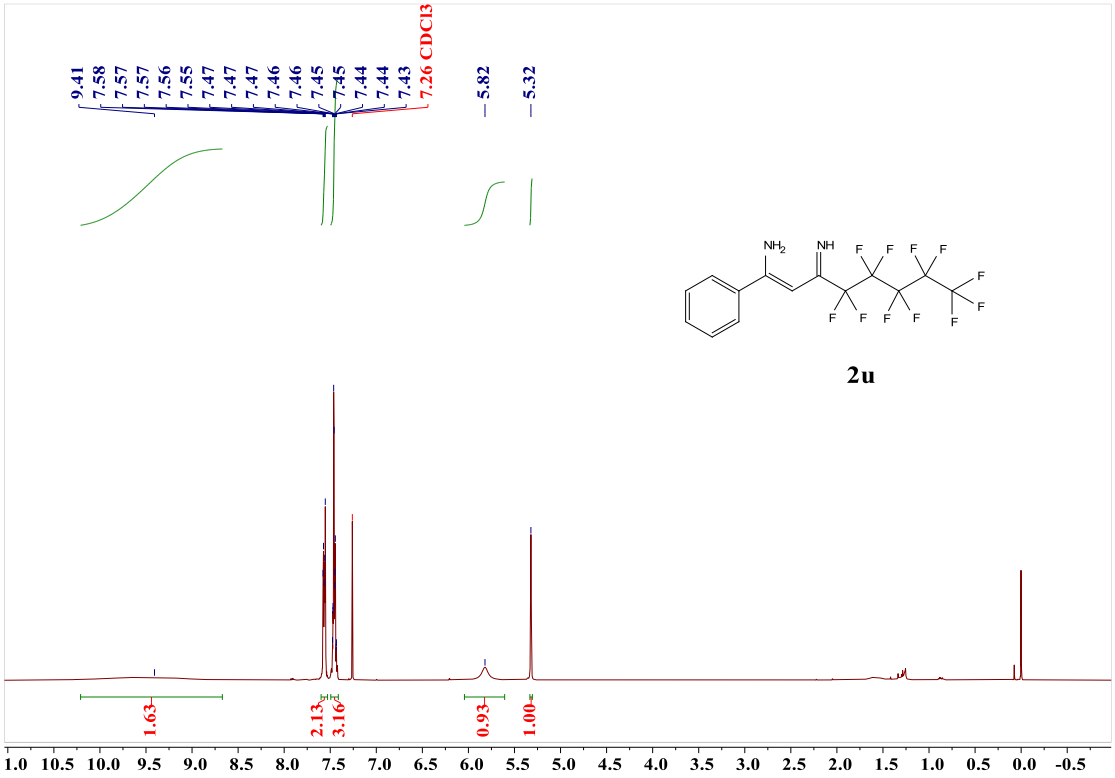
^{19}F NMR spectra of the product **2t** (376 MHz, $CDCl_3$)



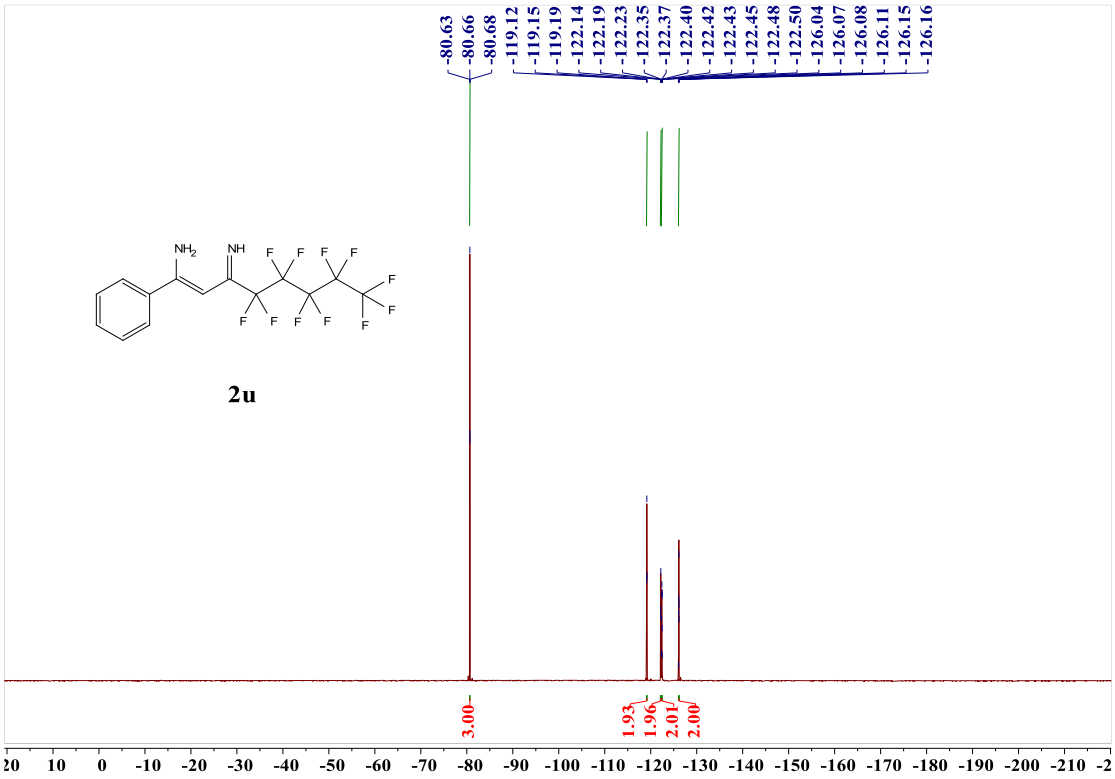
^{13}C NMR spectra of the product **2t** (100 MHz, $CDCl_3$)



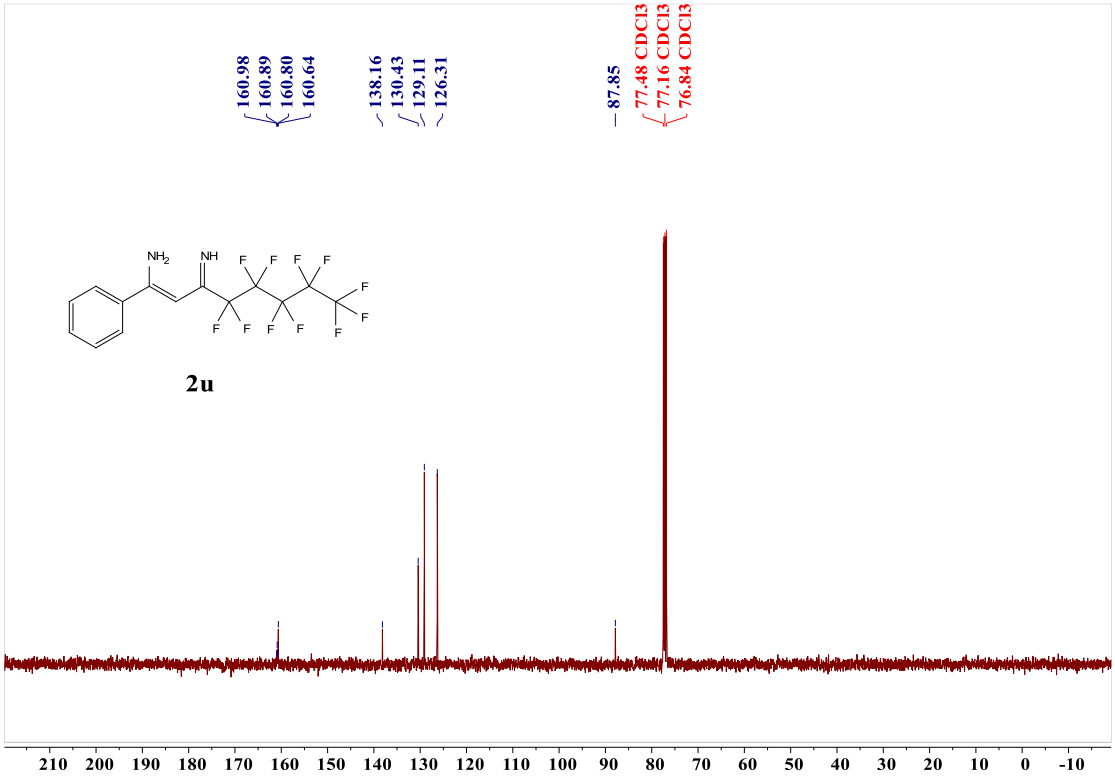
^{1}H NMR spectra of the product **2u** (400 MHz, $CDCl_3$)



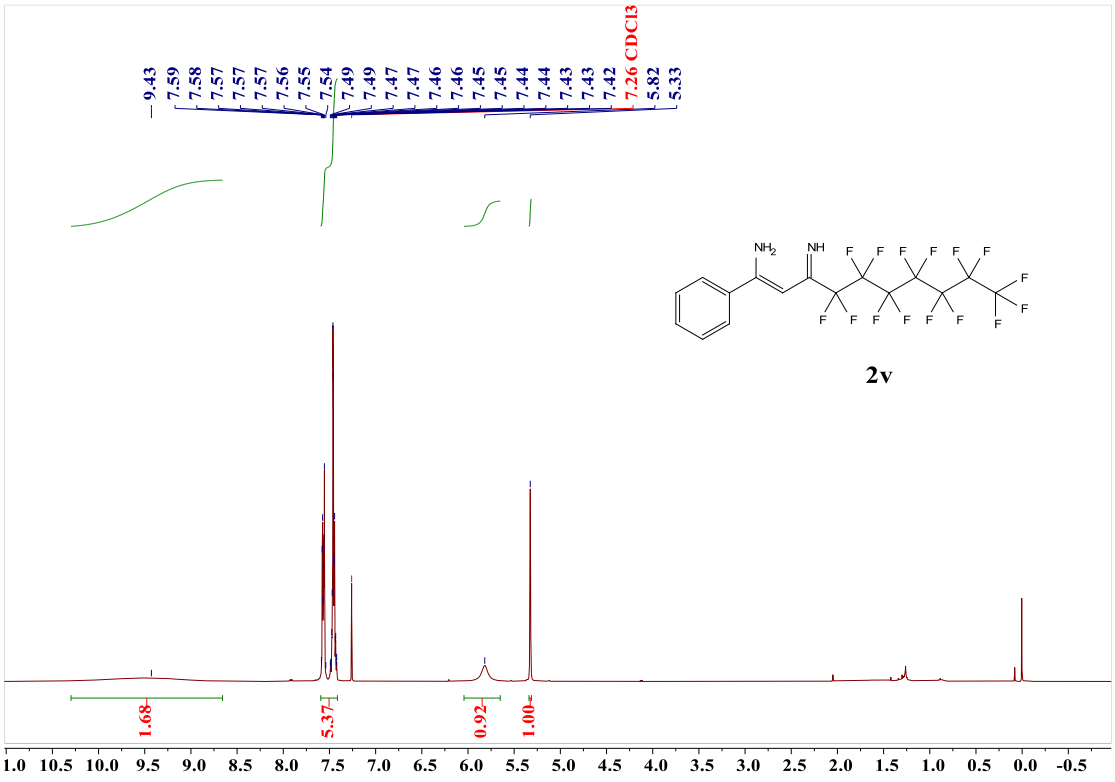
^{19}F NMR spectra of the product **2u** (376 MHz, $CDCl_3$)



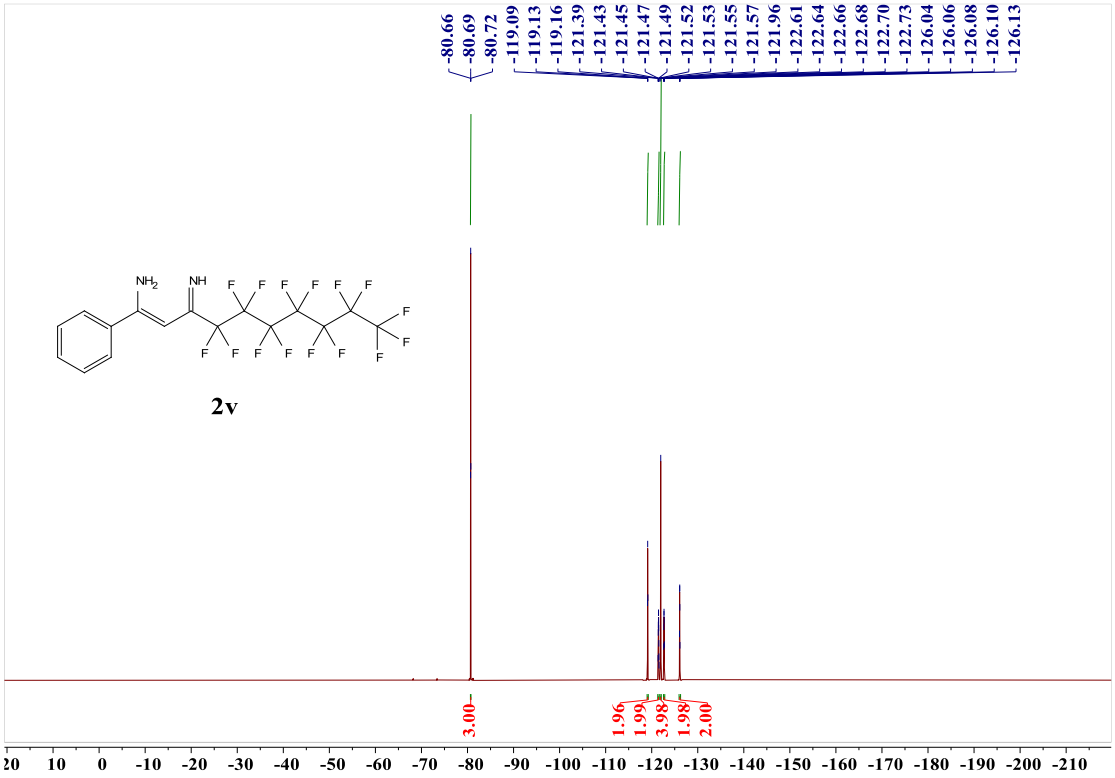
^{13}C NMR spectra of the product **2u** (100 MHz, $CDCl_3$)



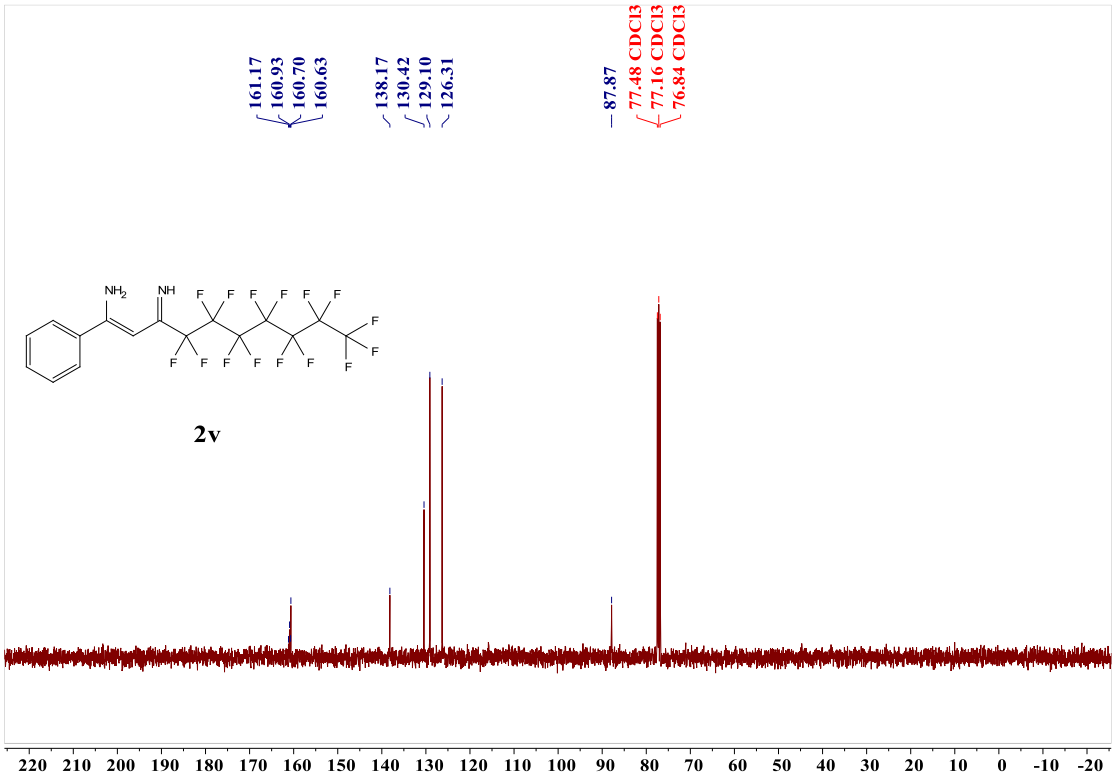
^{1}H NMR spectra of the product **2v** (400 MHz, $CDCl_3$)



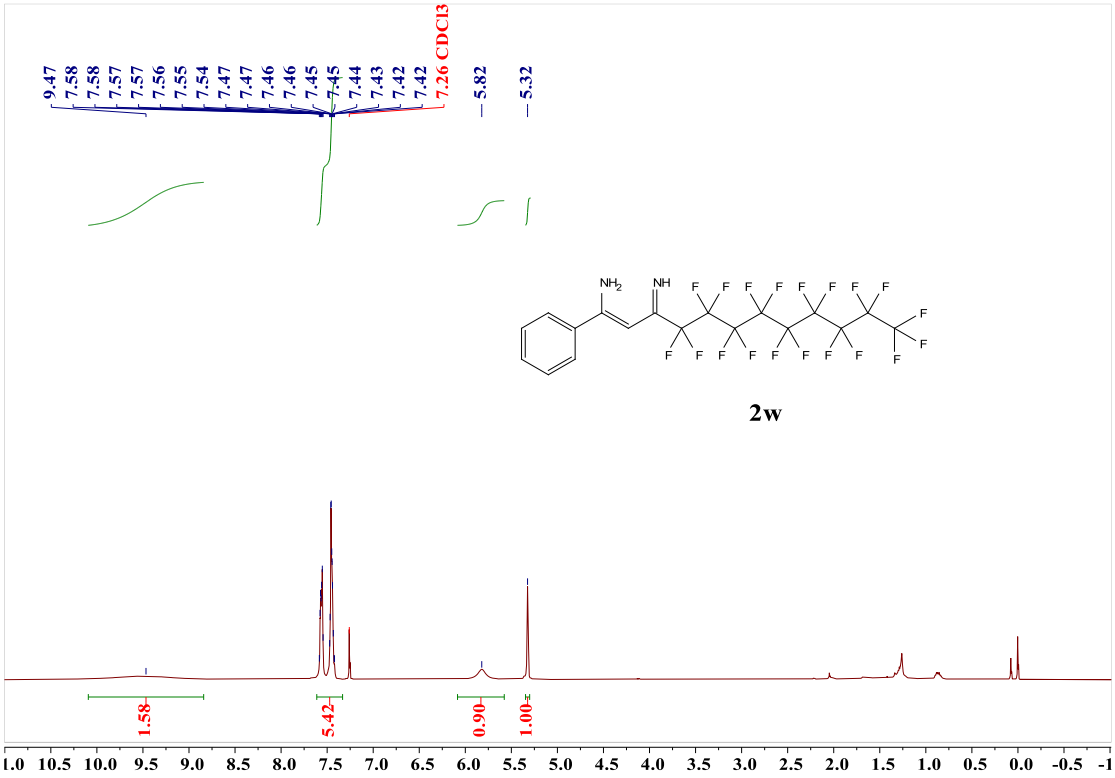
^{19}F NMR spectra of the product **2v** (376 MHz, $CDCl_3$)



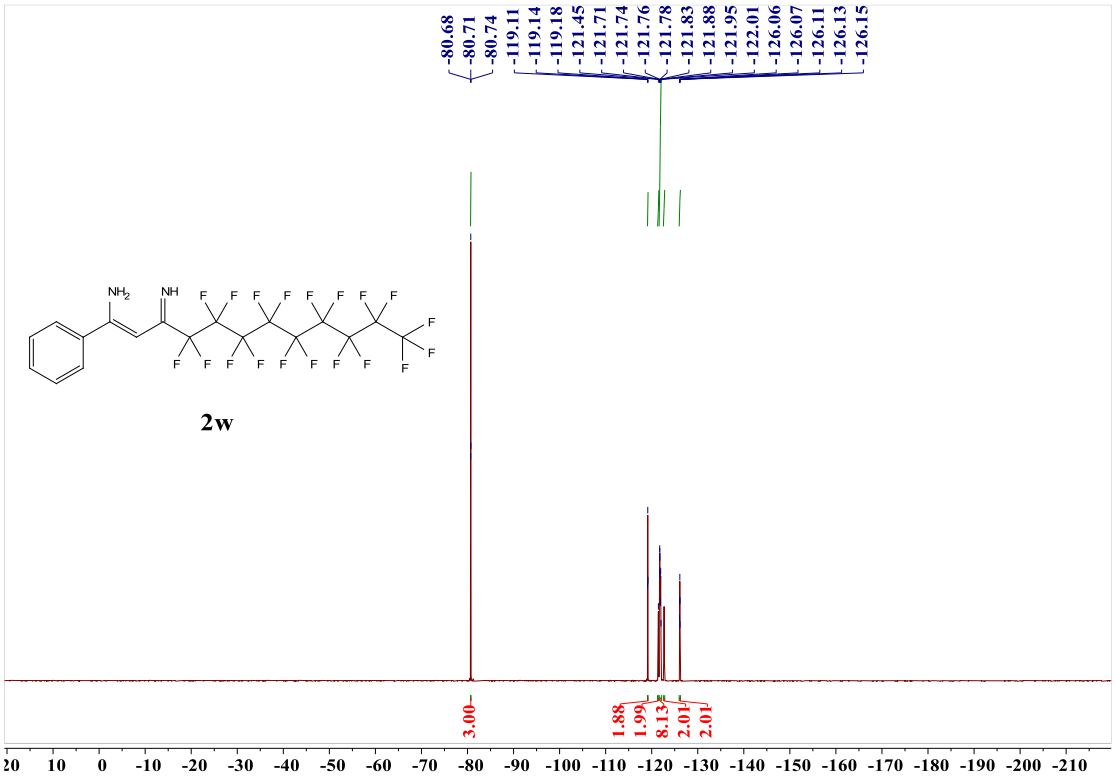
^{13}C NMR spectra of the product **2v** (100 MHz, $CDCl_3$)



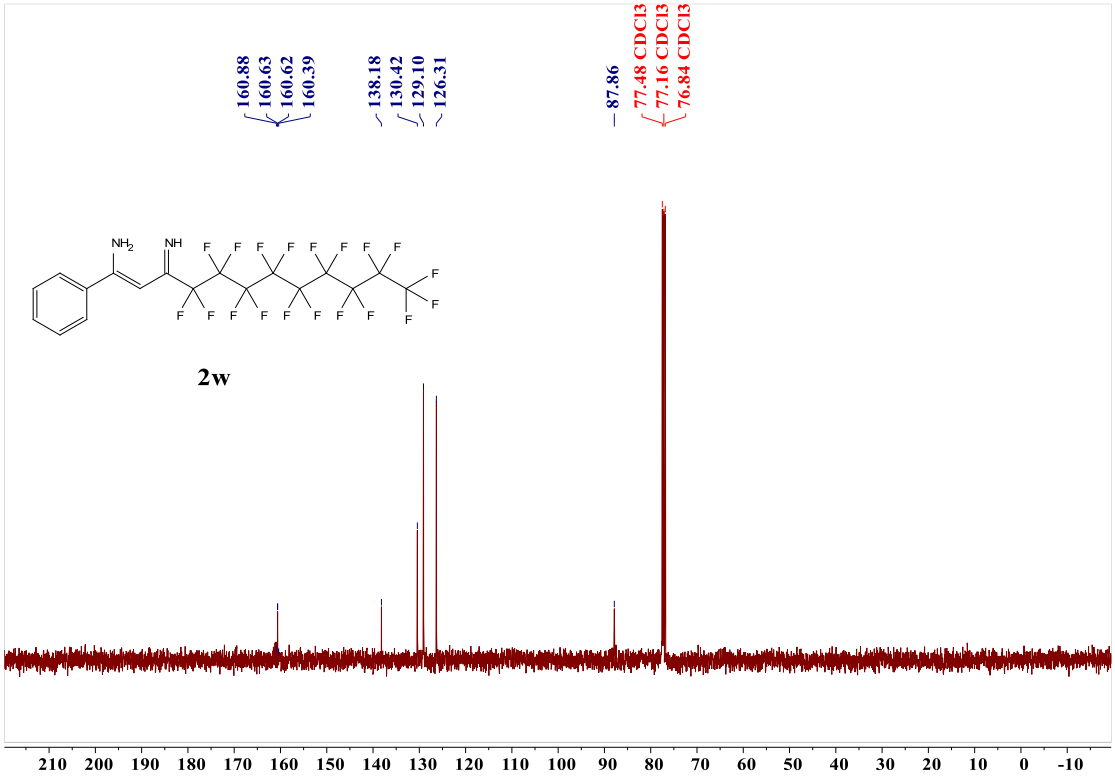
^{1}H NMR spectra of the product **2w** (400 MHz, $CDCl_3$)



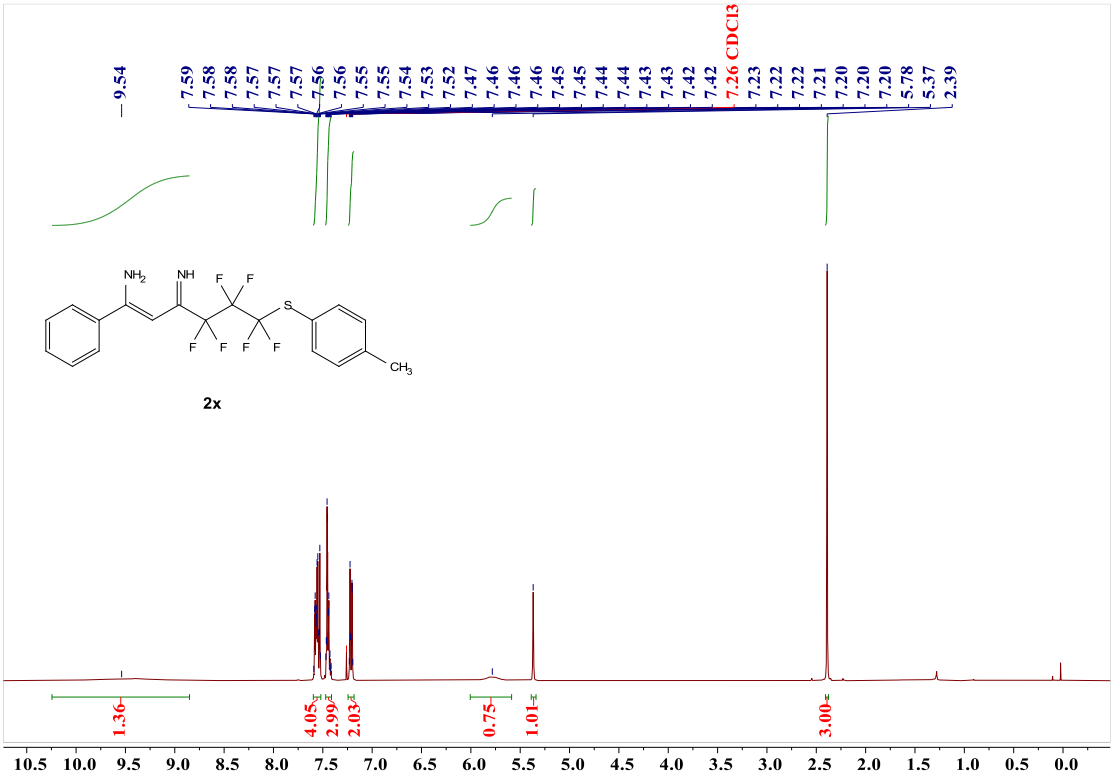
^{19}F NMR spectra of the product **2w** (376 MHz, $CDCl_3$)



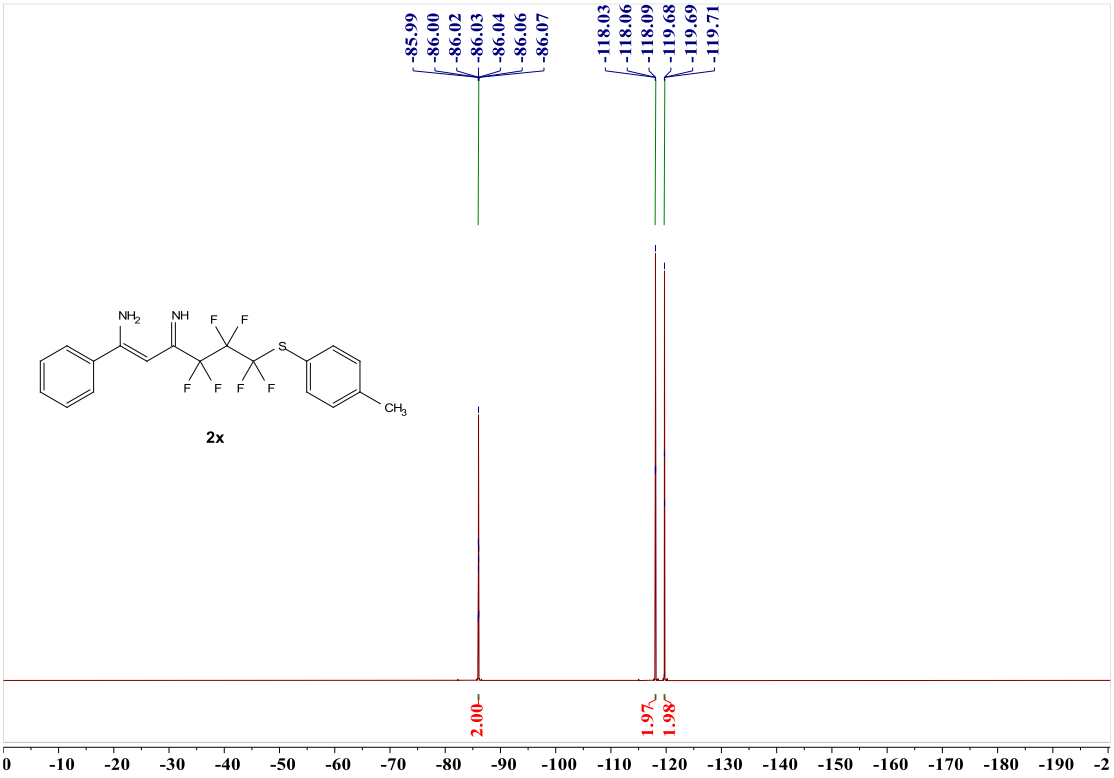
^{13}C NMR spectra of the product **2w** (100 MHz, $CDCl_3$)



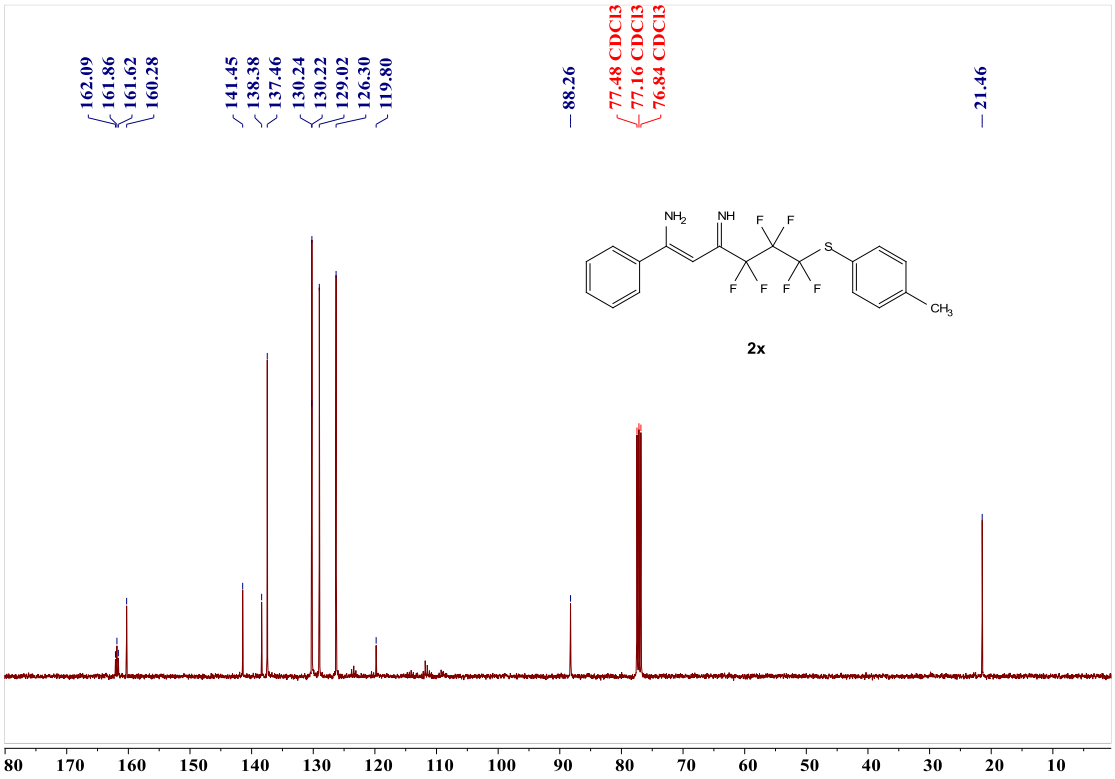
^{1}H NMR spectra of the product **2x** (400 MHz, $CDCl_3$)



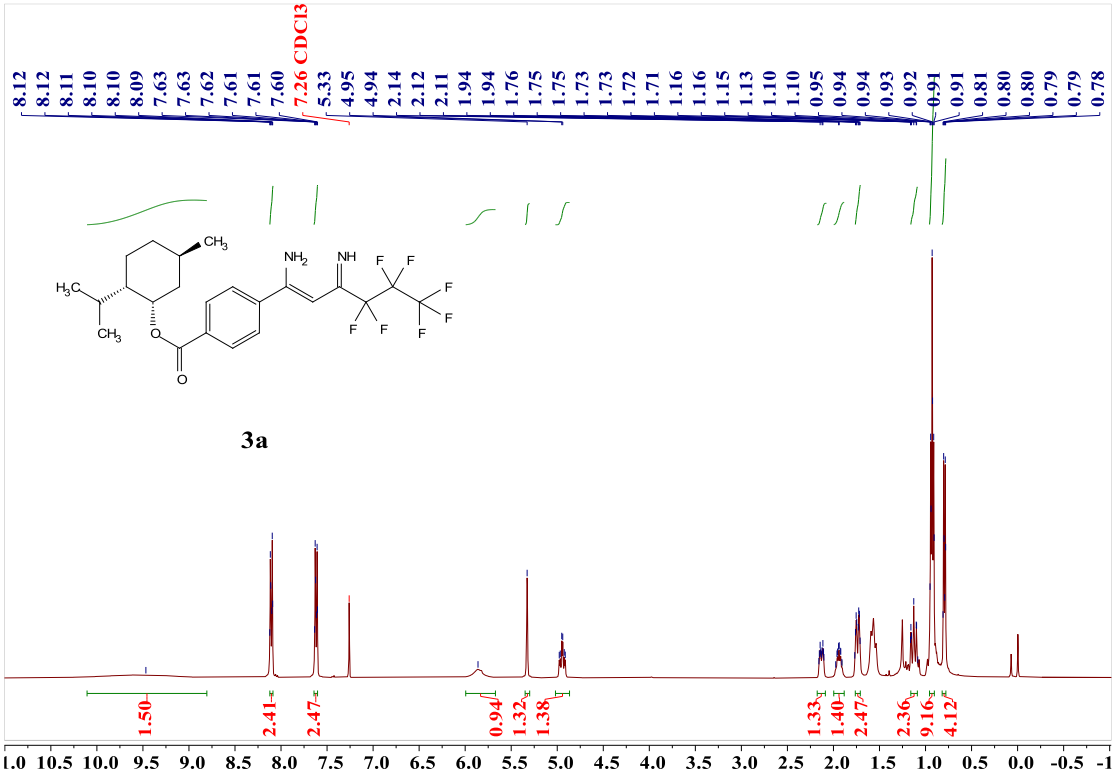
^{19}F NMR spectra of the product **2x** (376 MHz, $CDCl_3$)



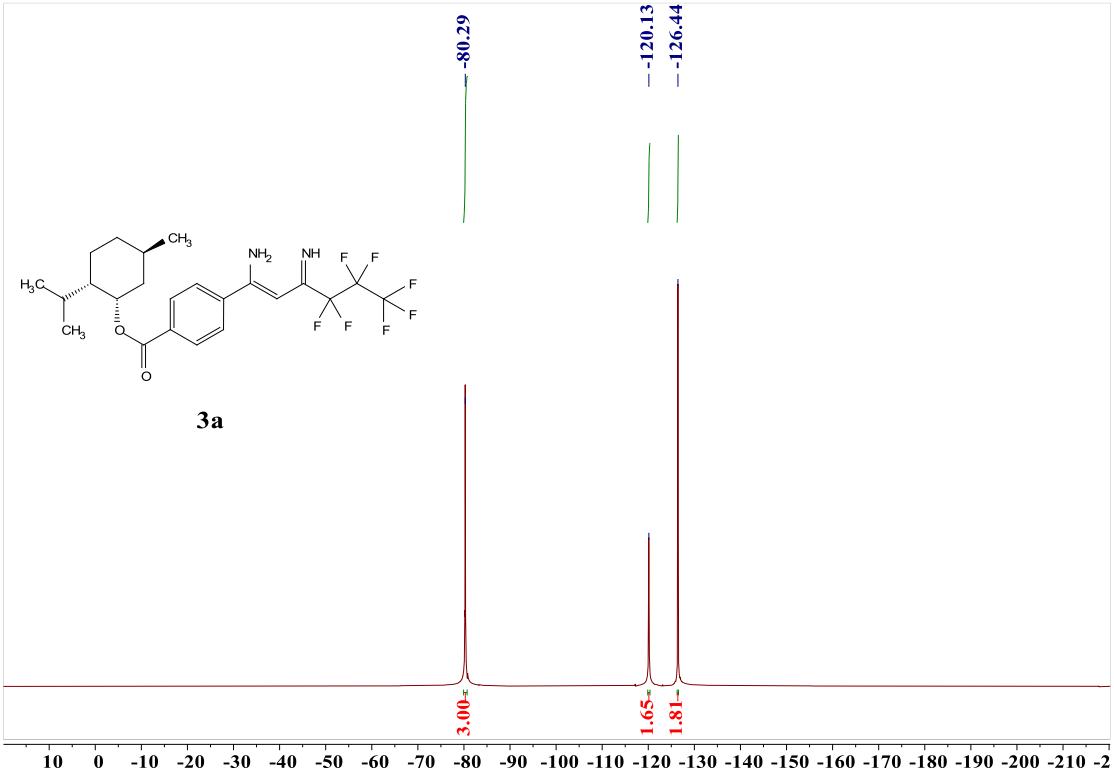
^{13}C NMR spectra of the product **2x** (100 MHz, $CDCl_3$)



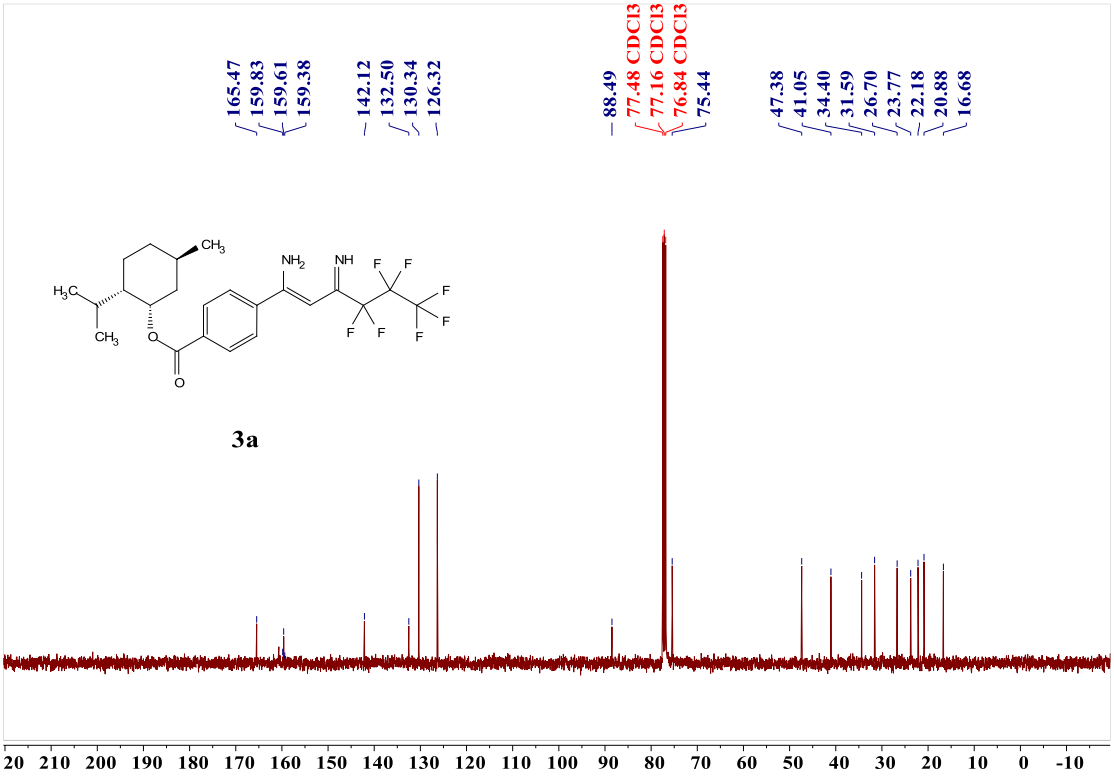
^{1}H NMR spectra of the product **3a** (400 MHz, $CDCl_3$)



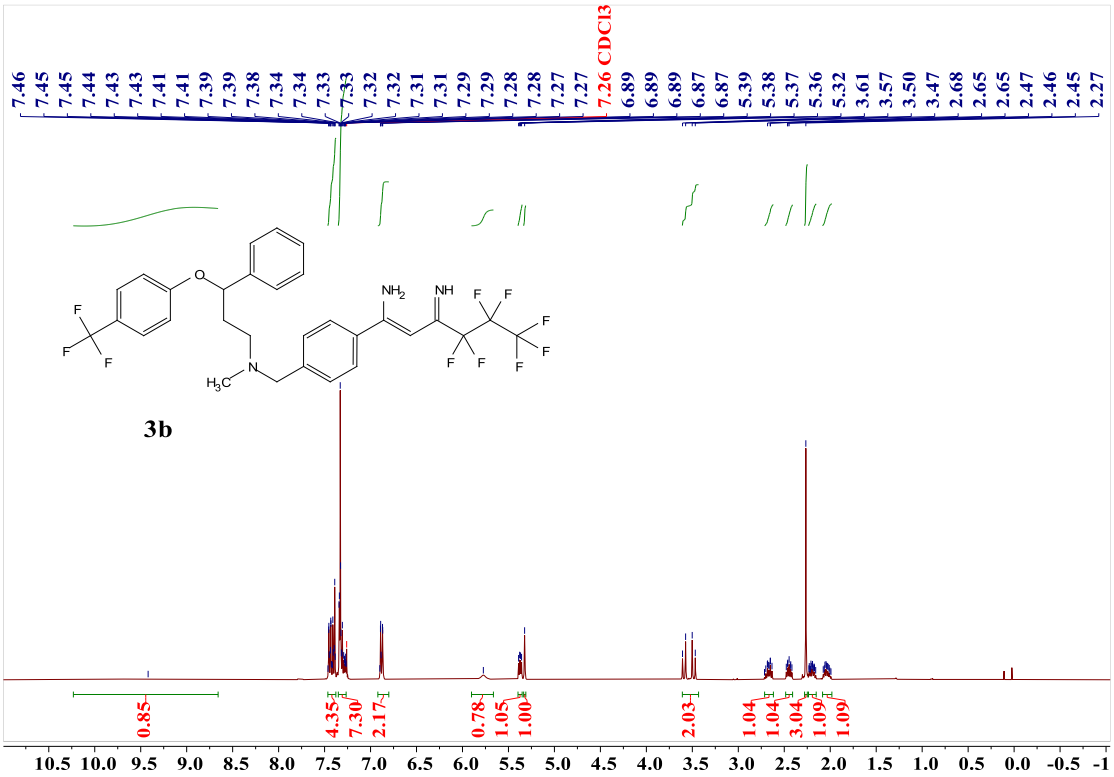
^{19}F NMR spectra of the product **3a** (376 MHz, $CDCl_3$)



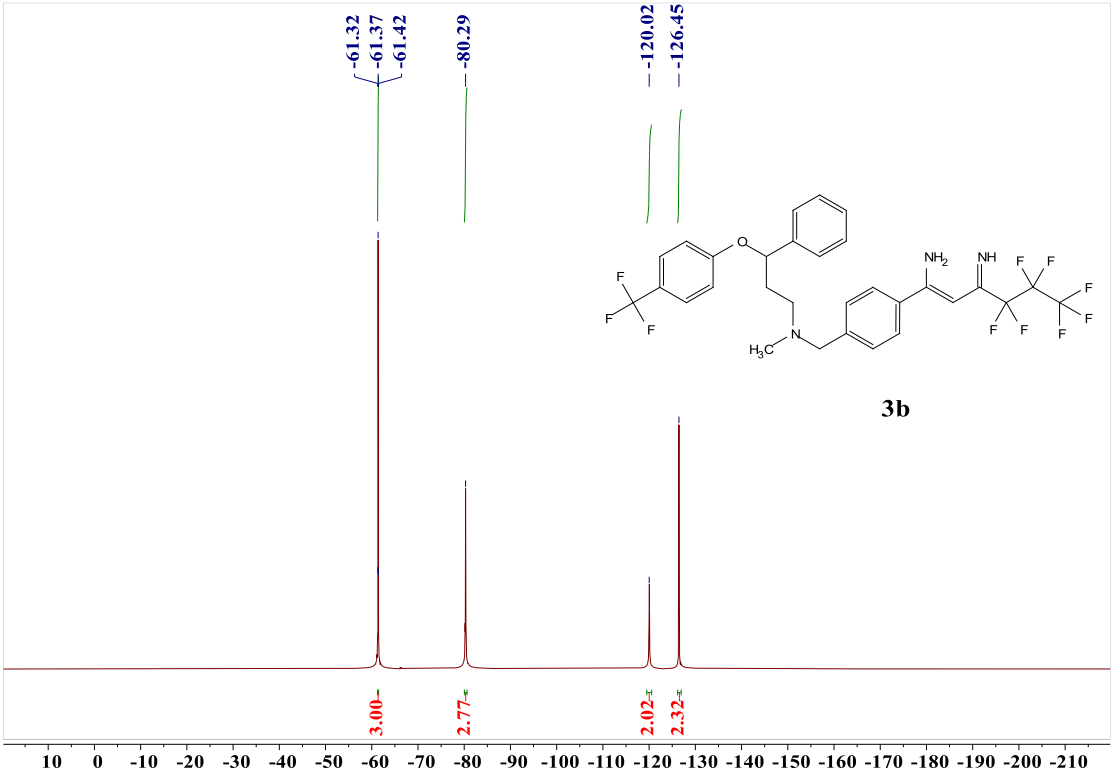
^{13}C NMR spectra of the product **3a** (100 MHz, $CDCl_3$)



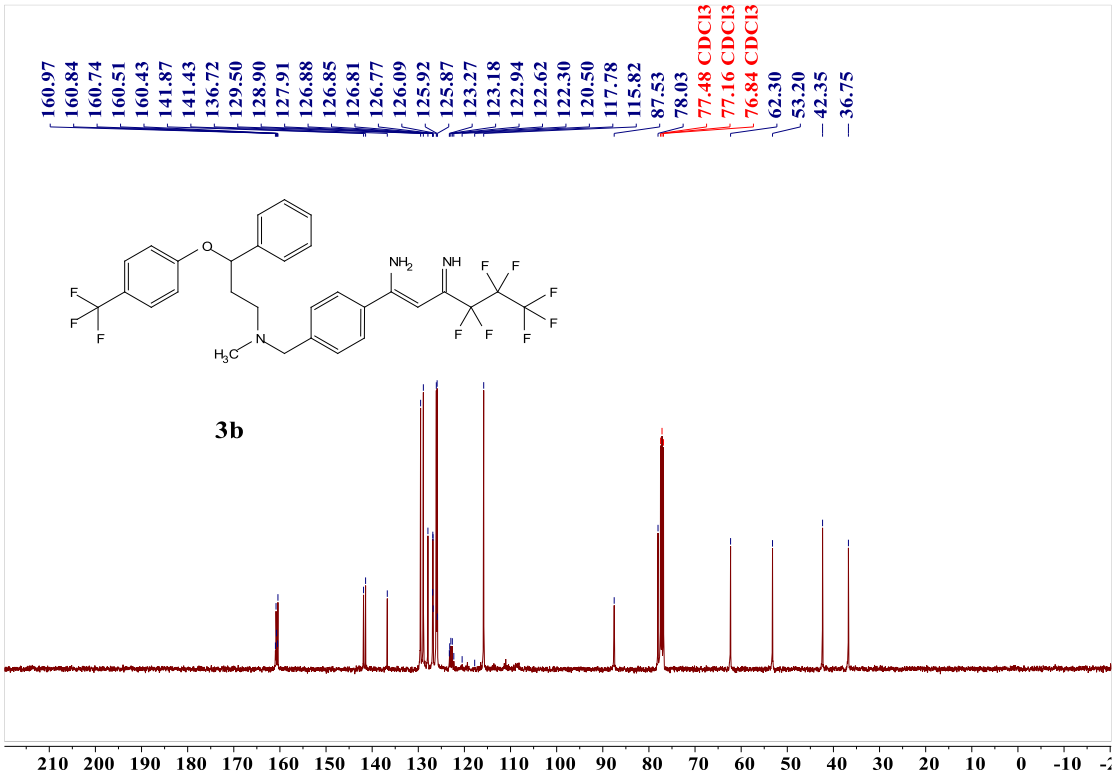
^{1}H NMR spectra of the product **3b** (400 MHz, $CDCl_3$)



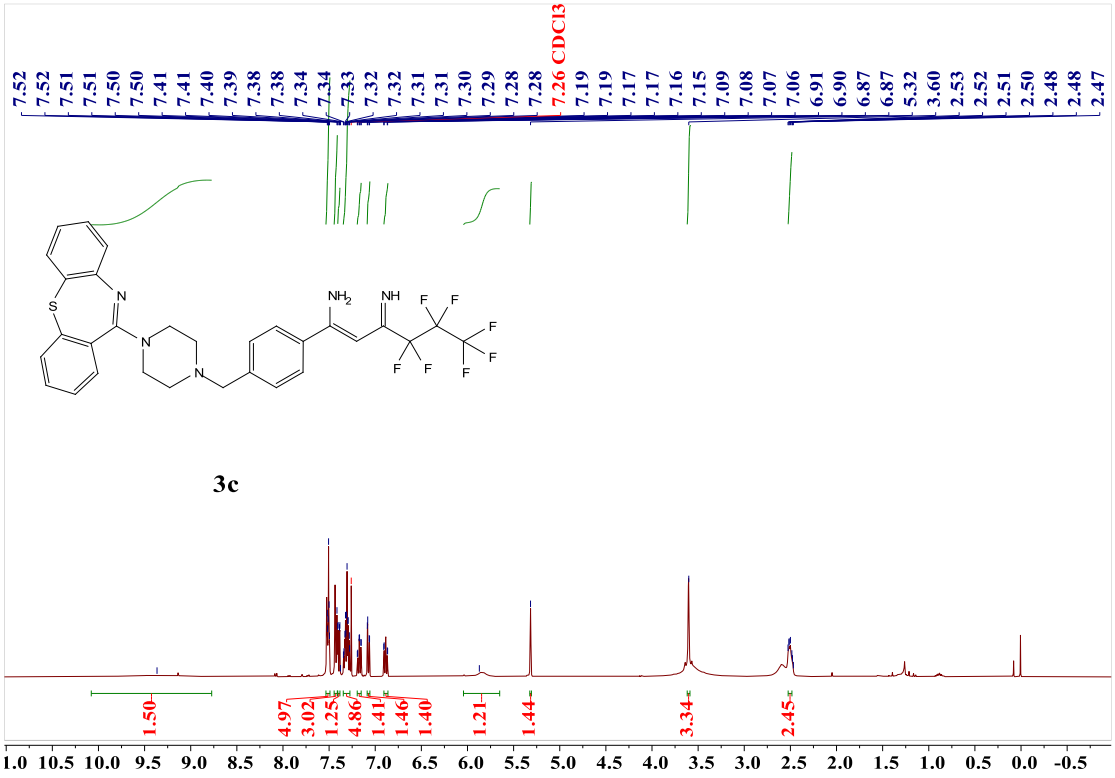
^{19}F NMR spectra of the product **3b** (376 MHz, $CDCl_3$)



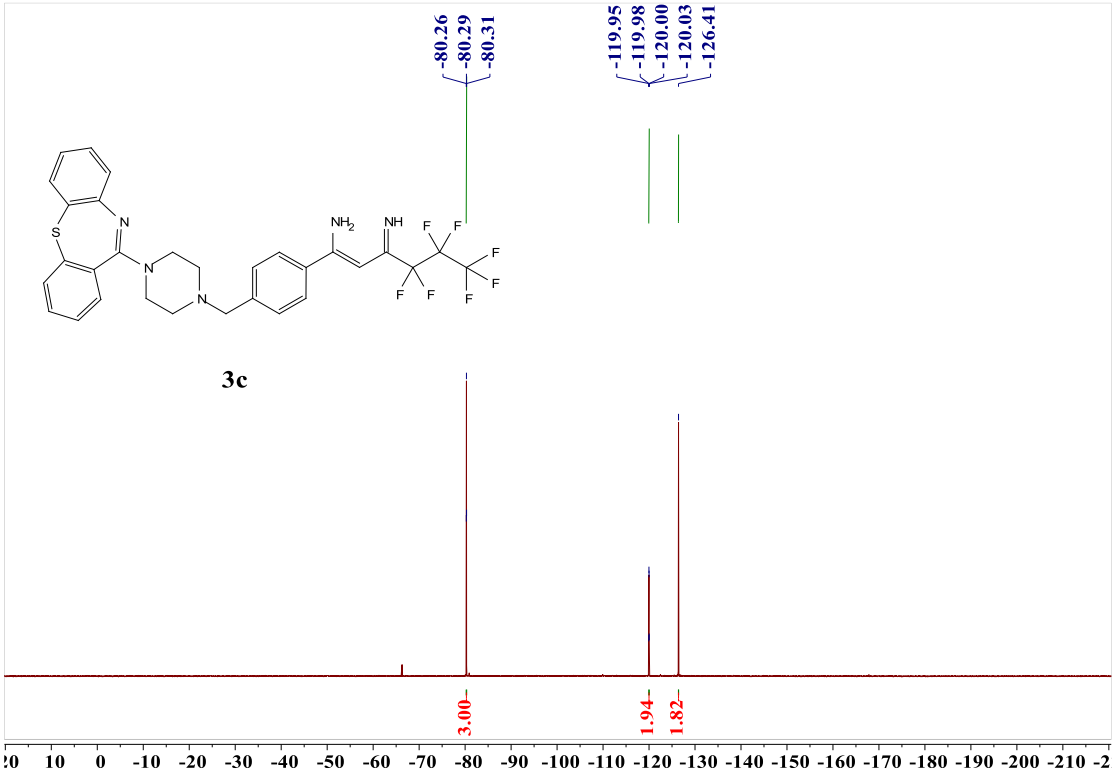
^{13}C NMR spectra of the product **3b** (100 MHz, $CDCl_3$)



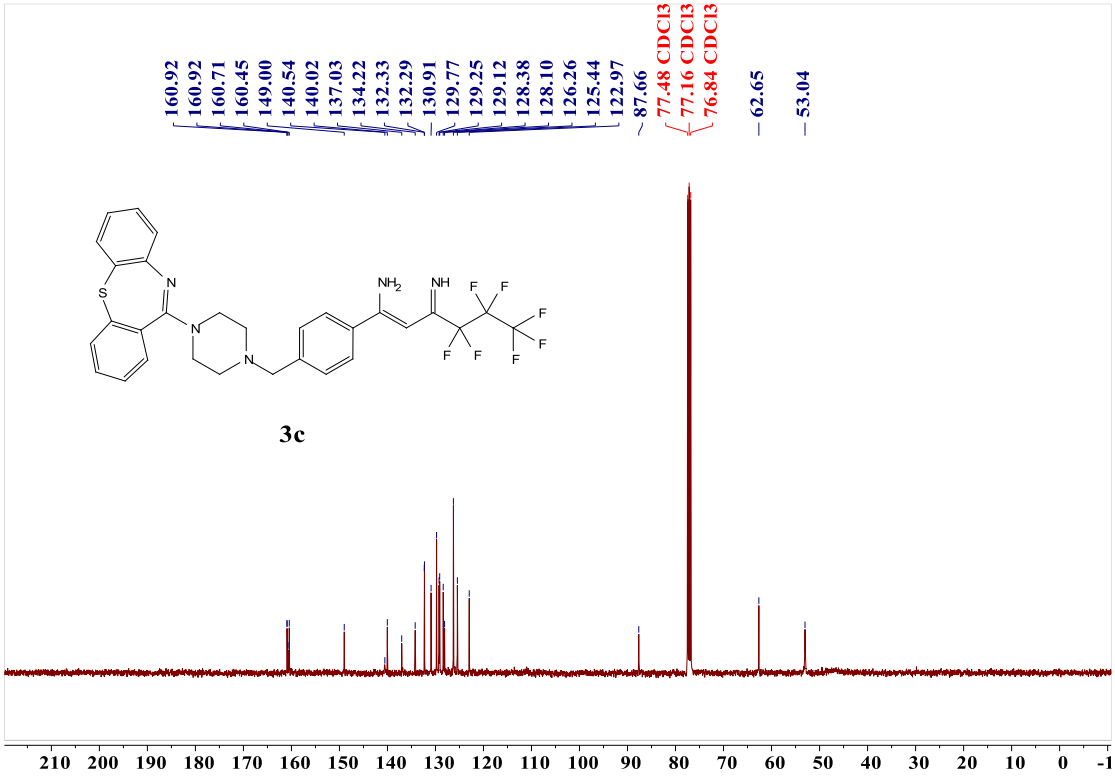
^{1}H NMR spectra of the product **3c** (400 MHz, $CDCl_3$)



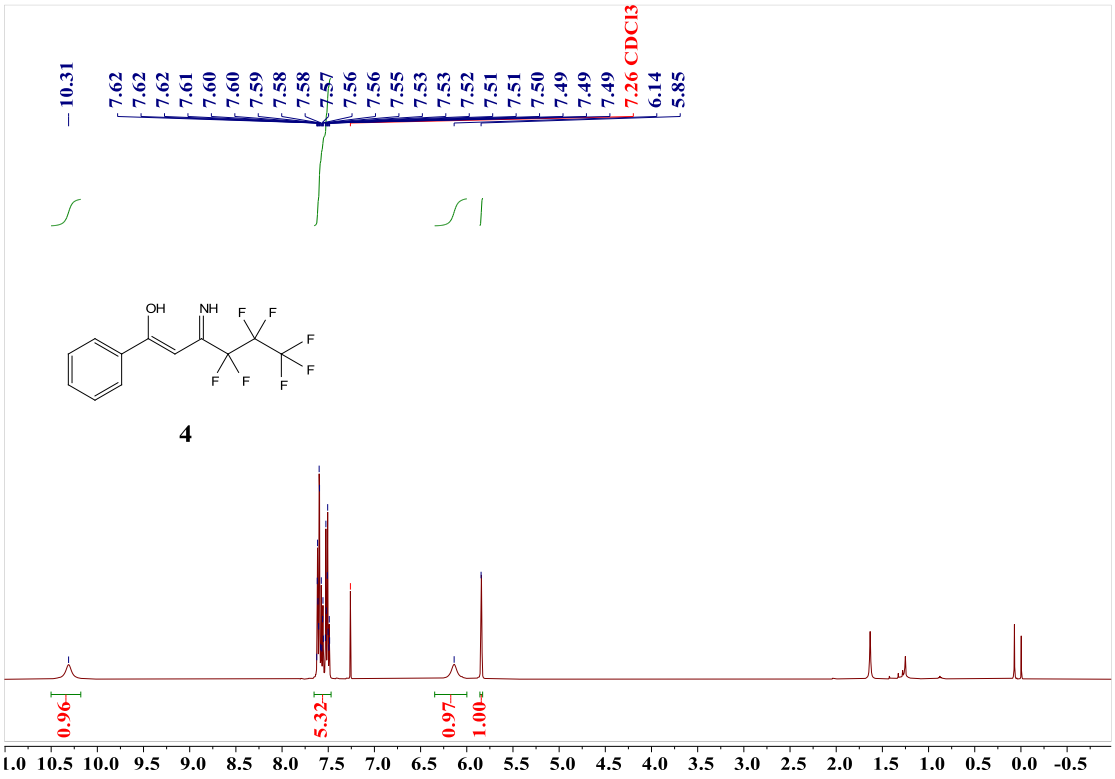
^{19}F NMR spectra of the product **3c** (376 MHz, $CDCl_3$)



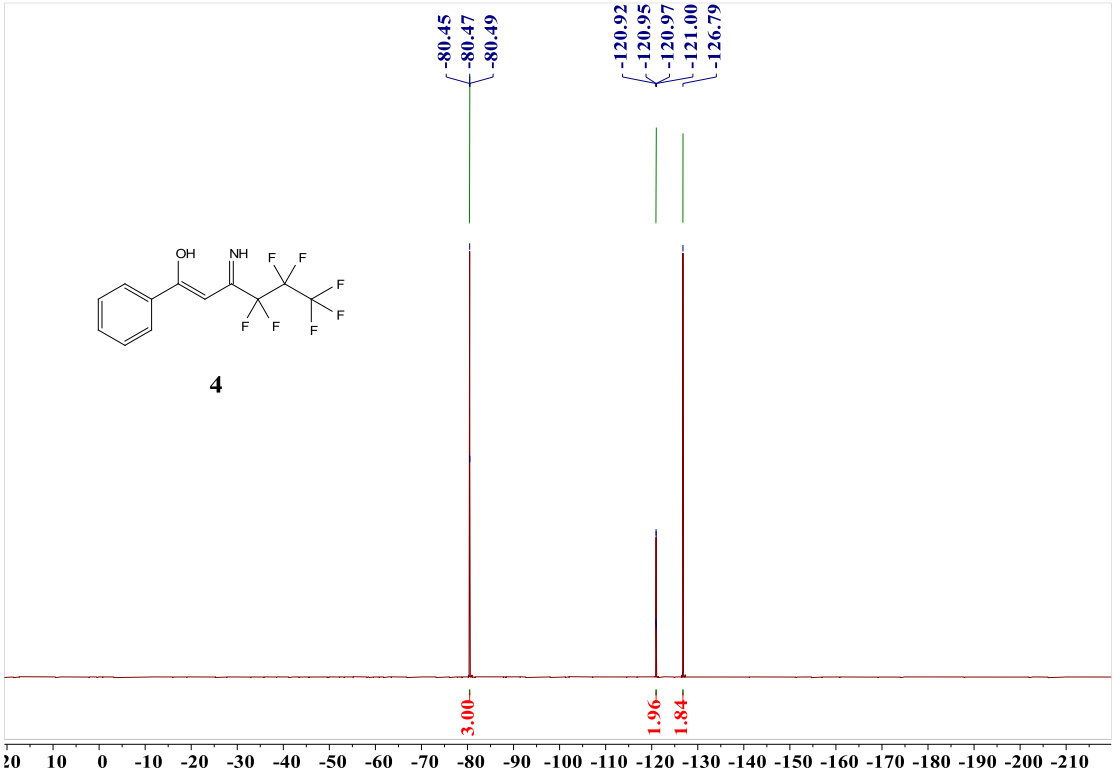
^{13}C NMR spectra of the product **3c** (100 MHz, $CDCl_3$)



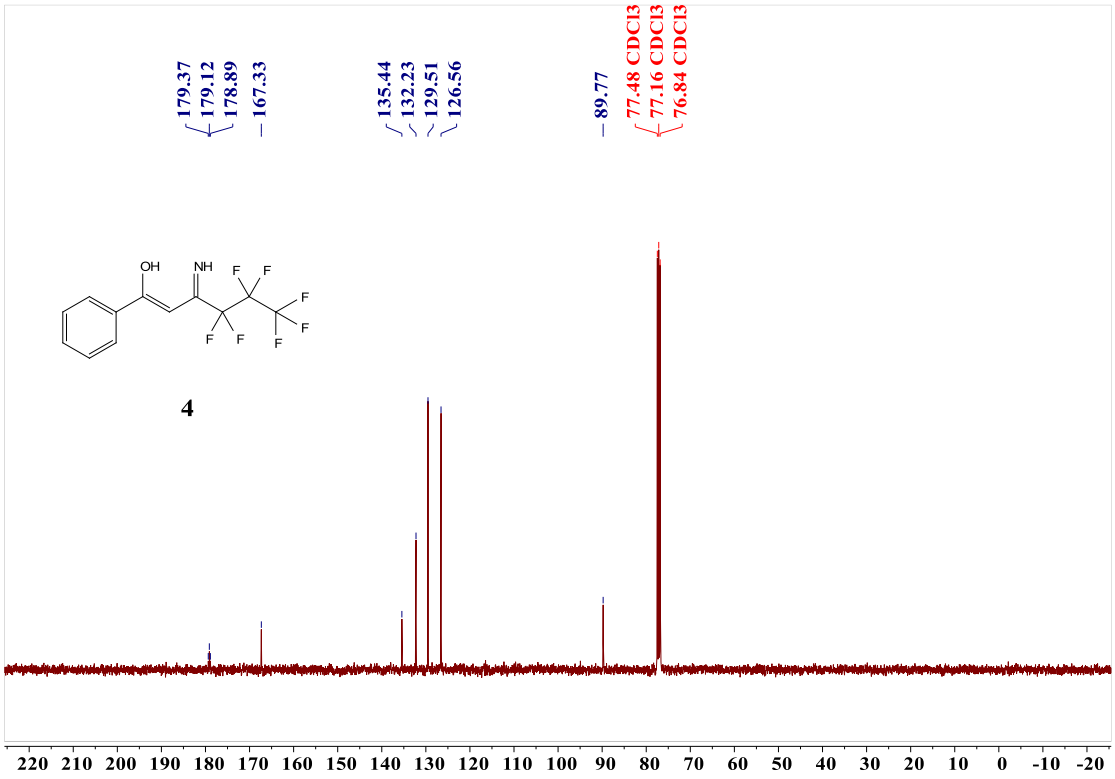
^{1}H NMR spectra of the product **4** (400 MHz, $CDCl_3$)



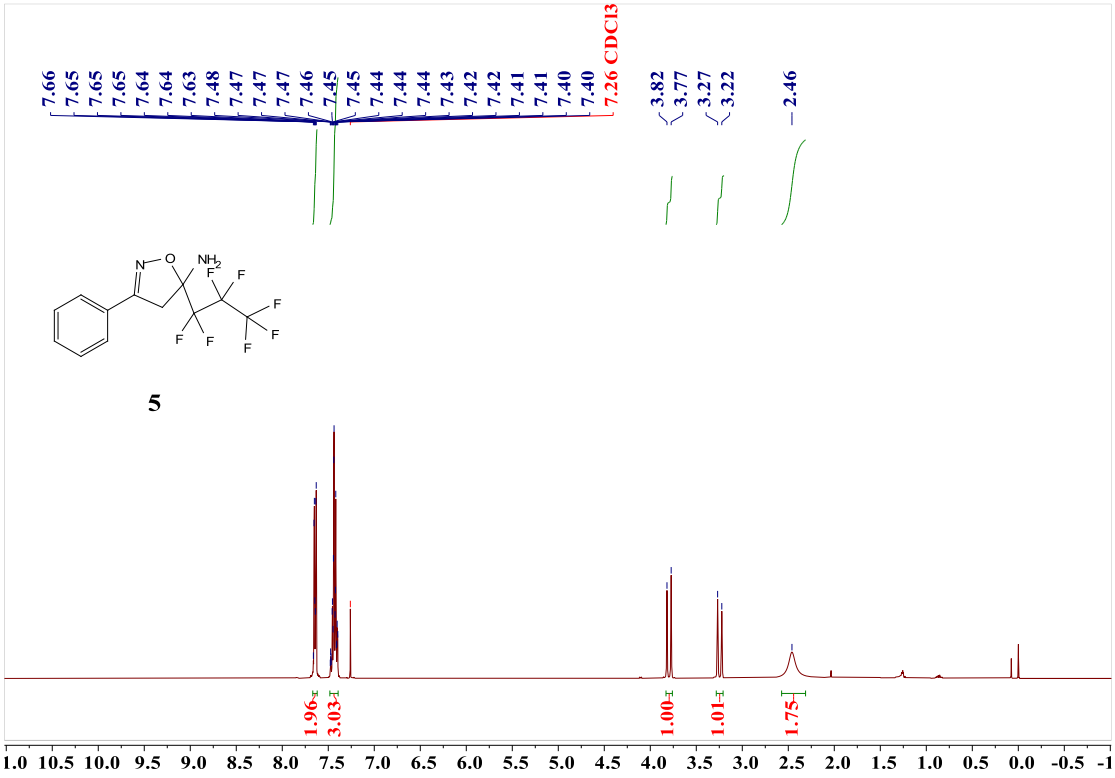
^{19}F NMR spectra of the product **4** (376 MHz, $CDCl_3$)



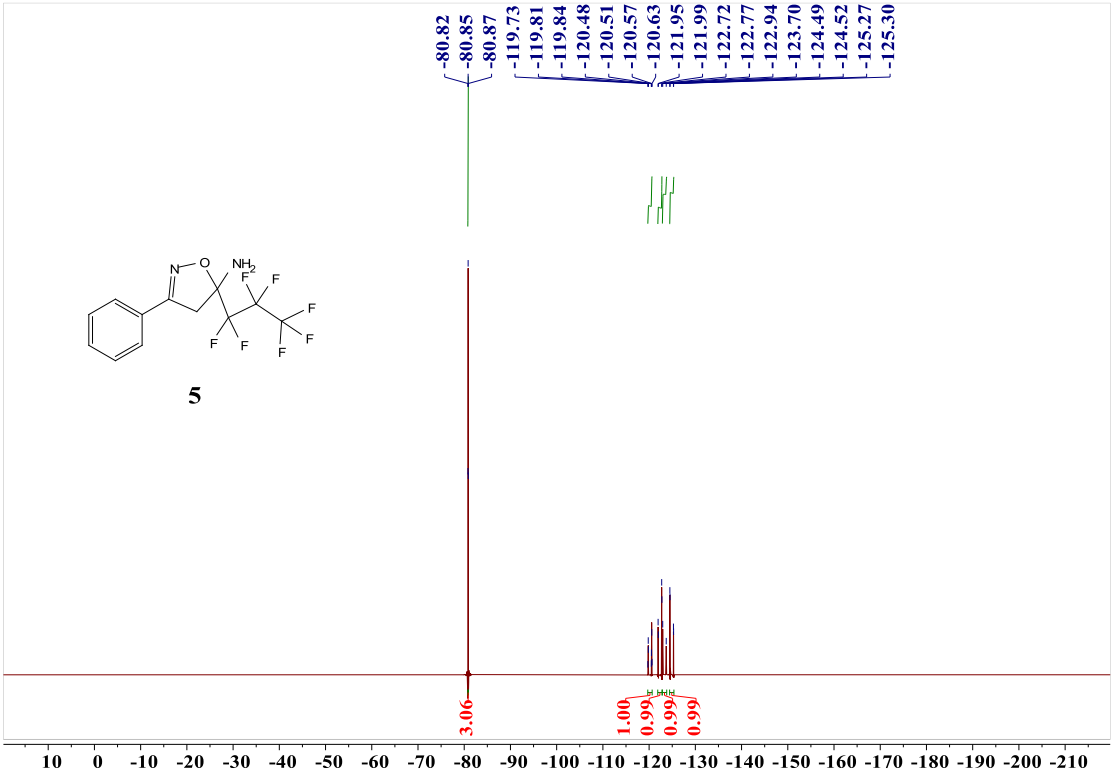
^{13}C NMR spectra of the product **4** (100 MHz, $CDCl_3$)



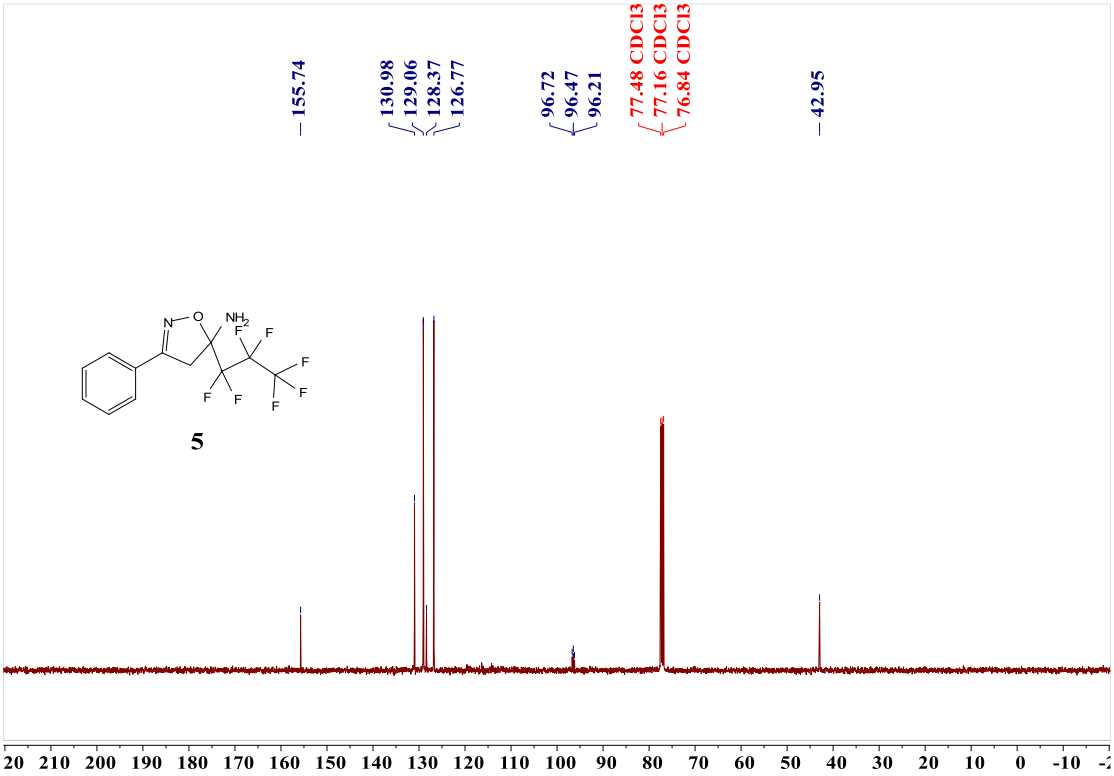
^{1}H NMR spectra of the product **5** (400 MHz, $CDCl_3$)



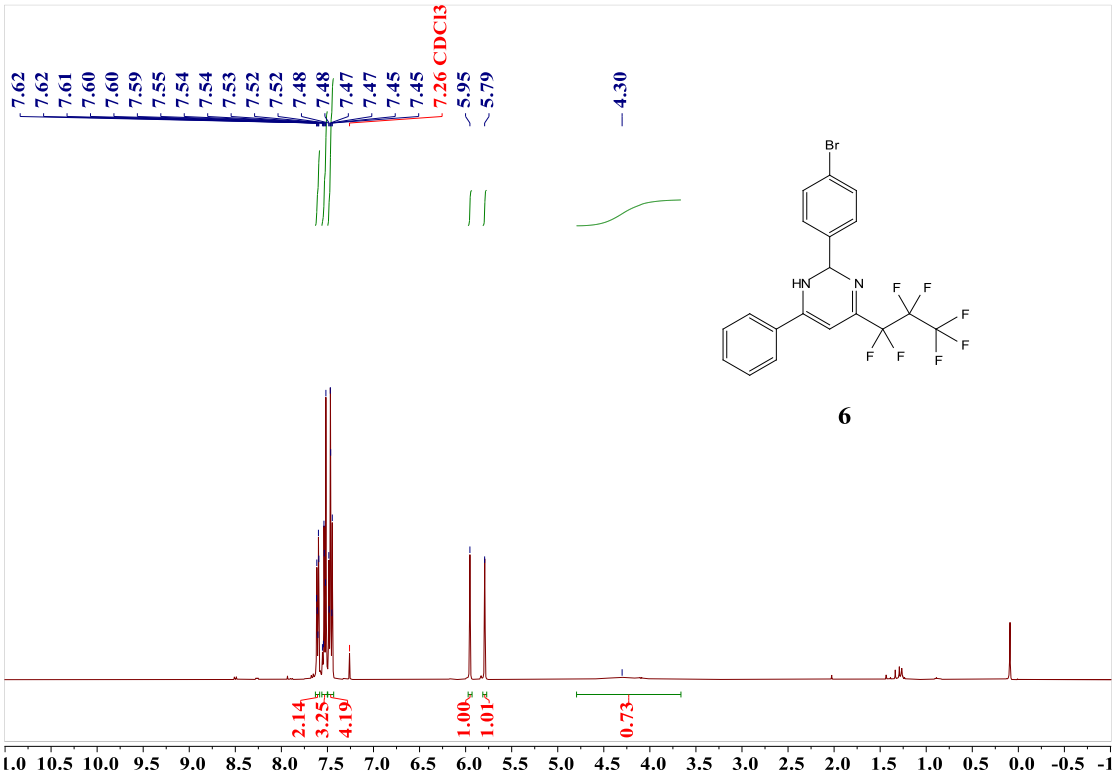
^{19}F NMR spectra of the product **5** (376 MHz, $CDCl_3$)



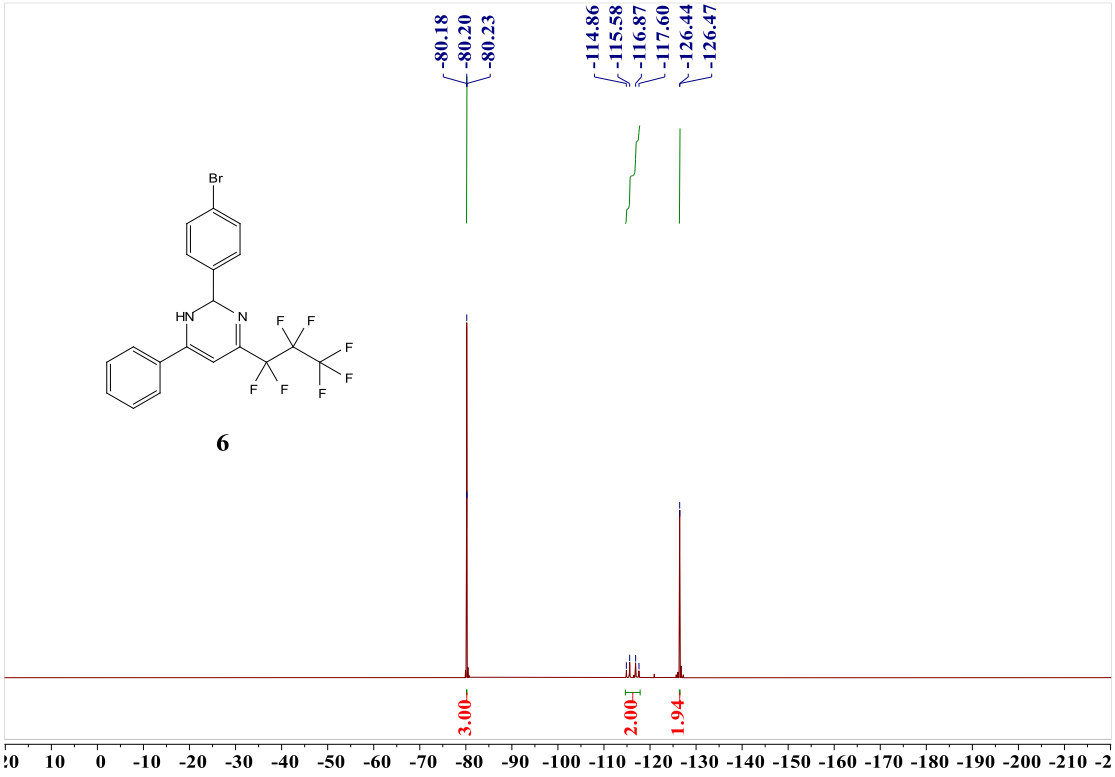
^{13}C NMR spectra of the product **5** (100 MHz, $CDCl_3$)



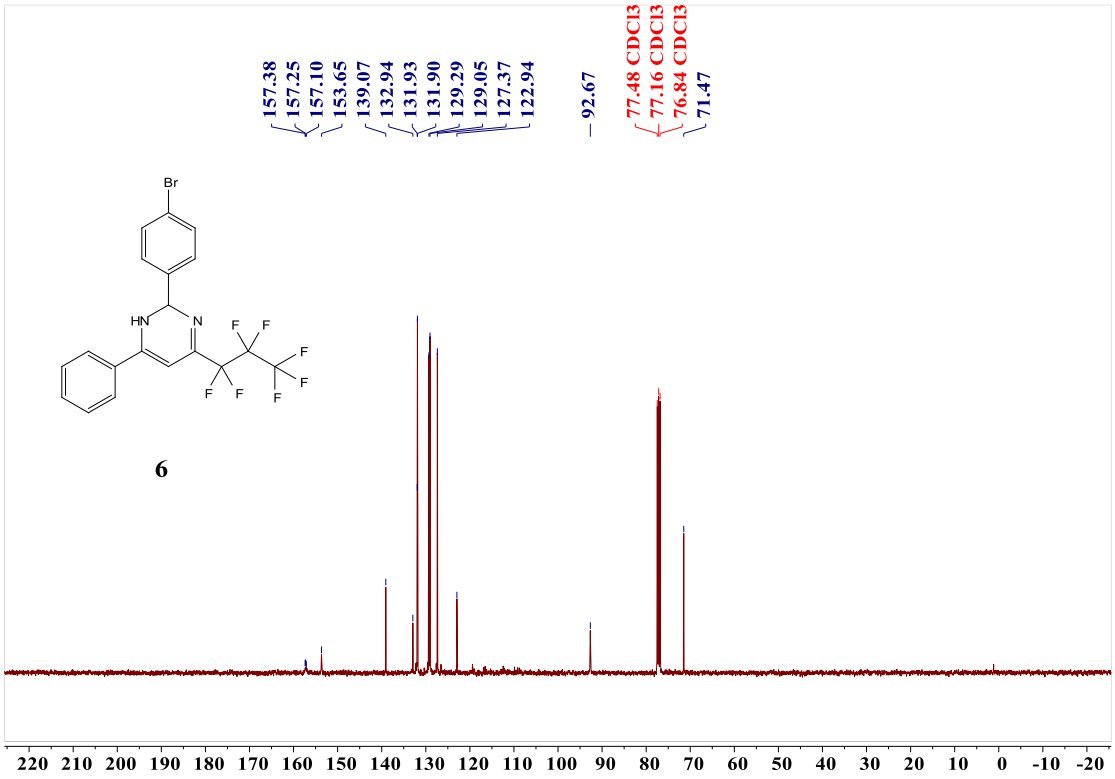
^{1}H NMR spectra of the product **6** (400 MHz, $CDCl_3$)



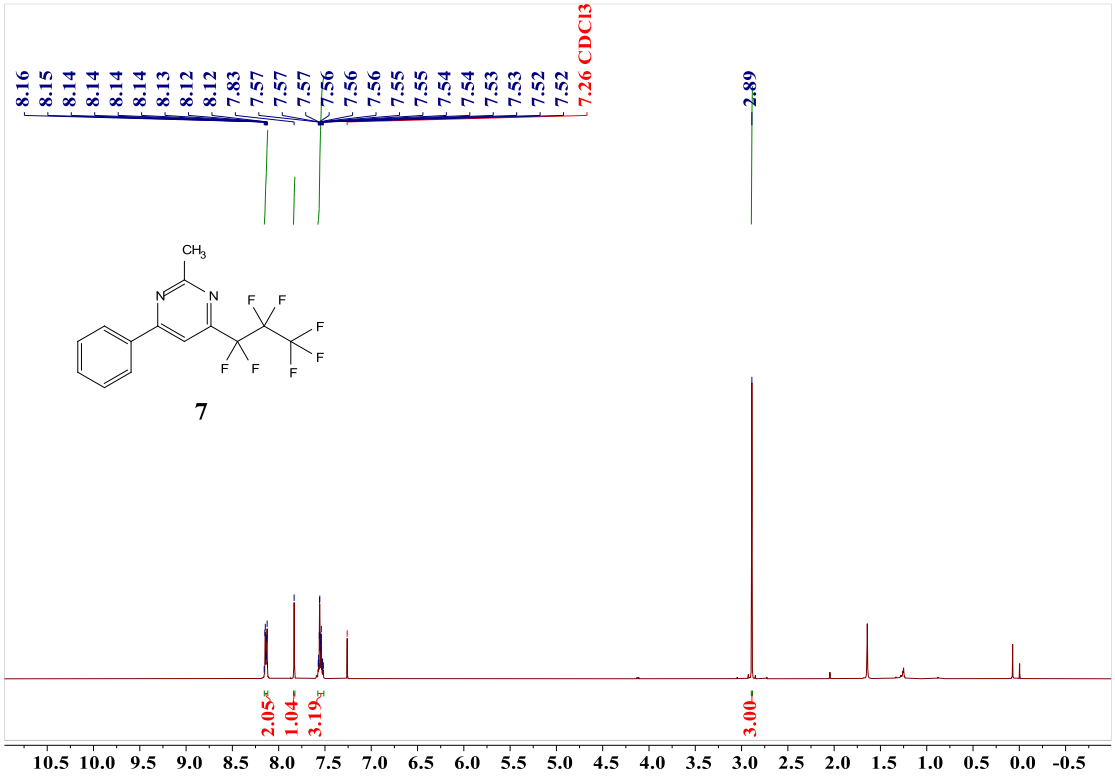
^{19}F NMR spectra of the product **6** (376 MHz, $CDCl_3$)



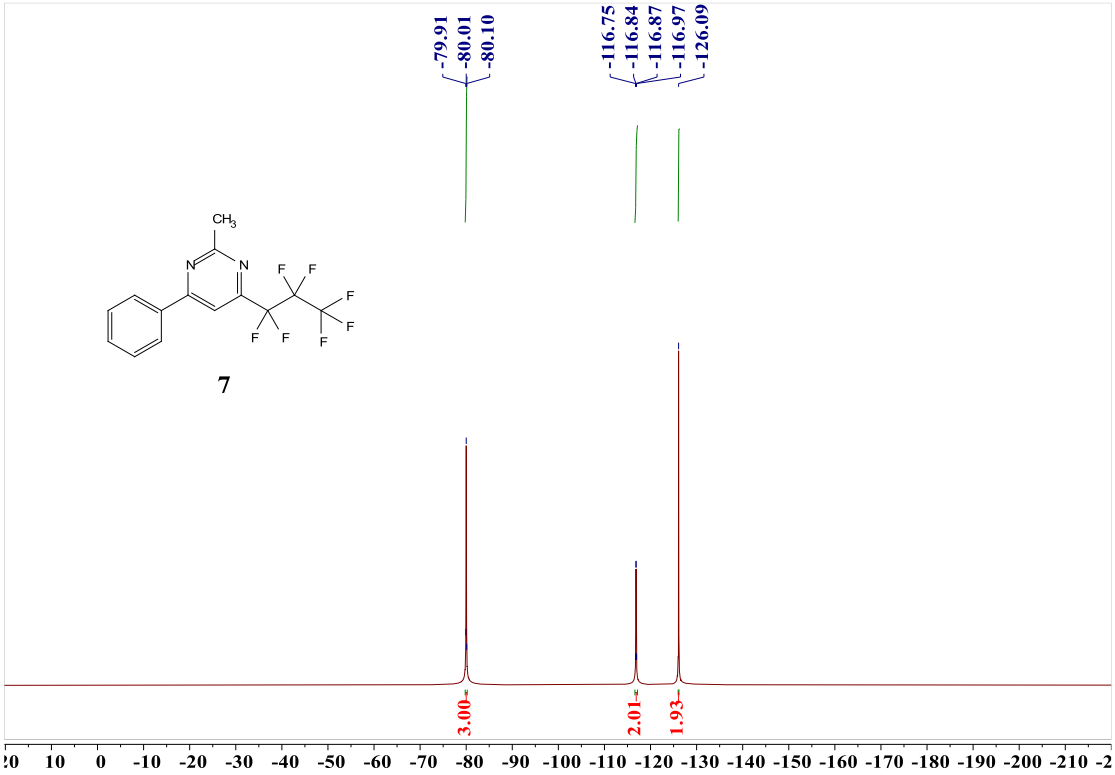
^{13}C NMR spectra of the product **6** (100 MHz, $CDCl_3$)



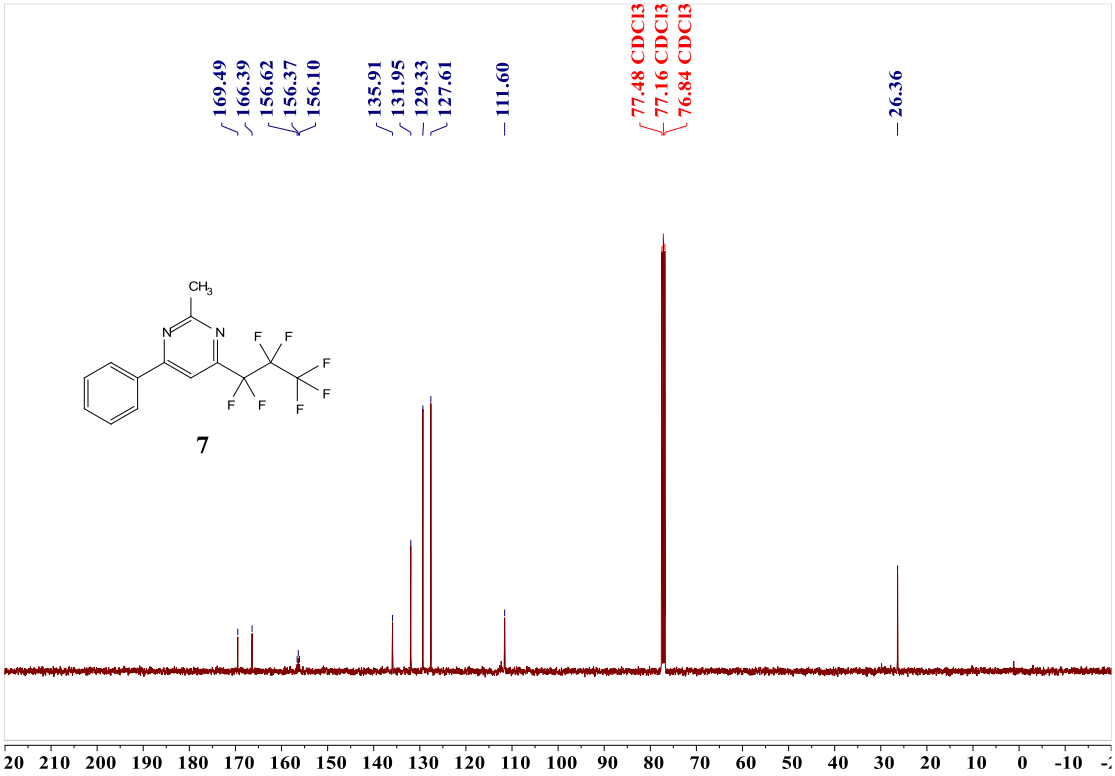
^{1}H NMR spectra of the product **7** (400 MHz, $CDCl_3$)



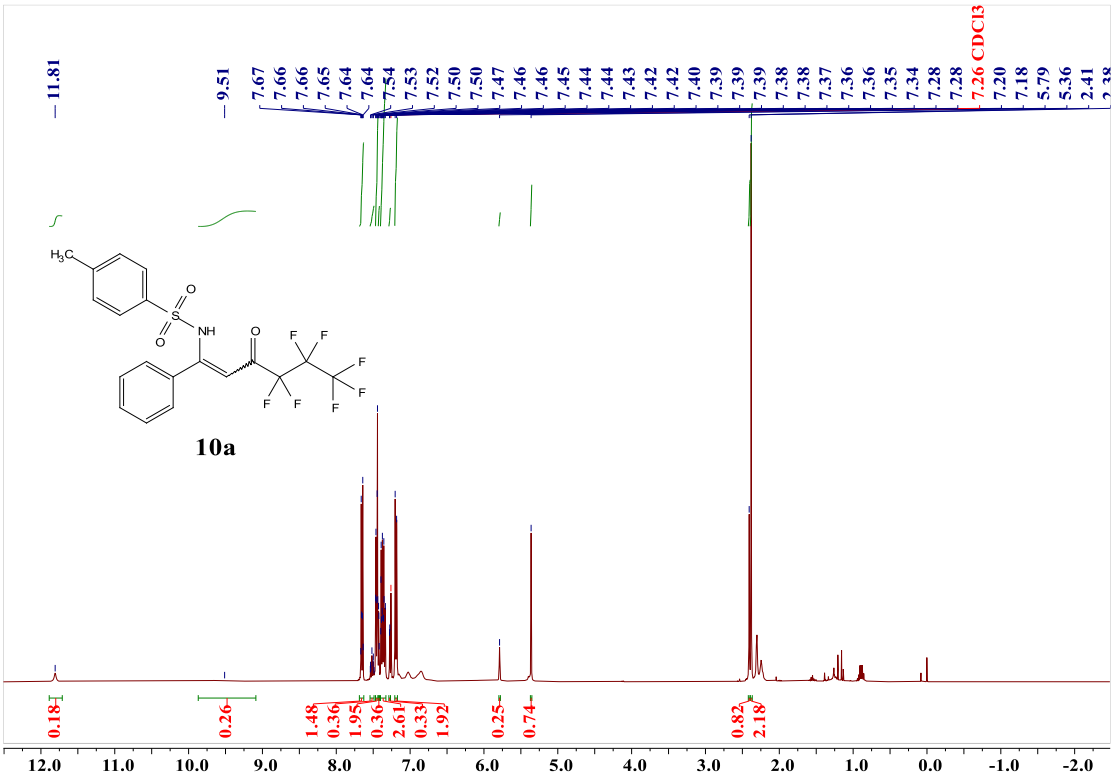
^{19}F NMR spectra of the product **7** (376 MHz, $CDCl_3$)



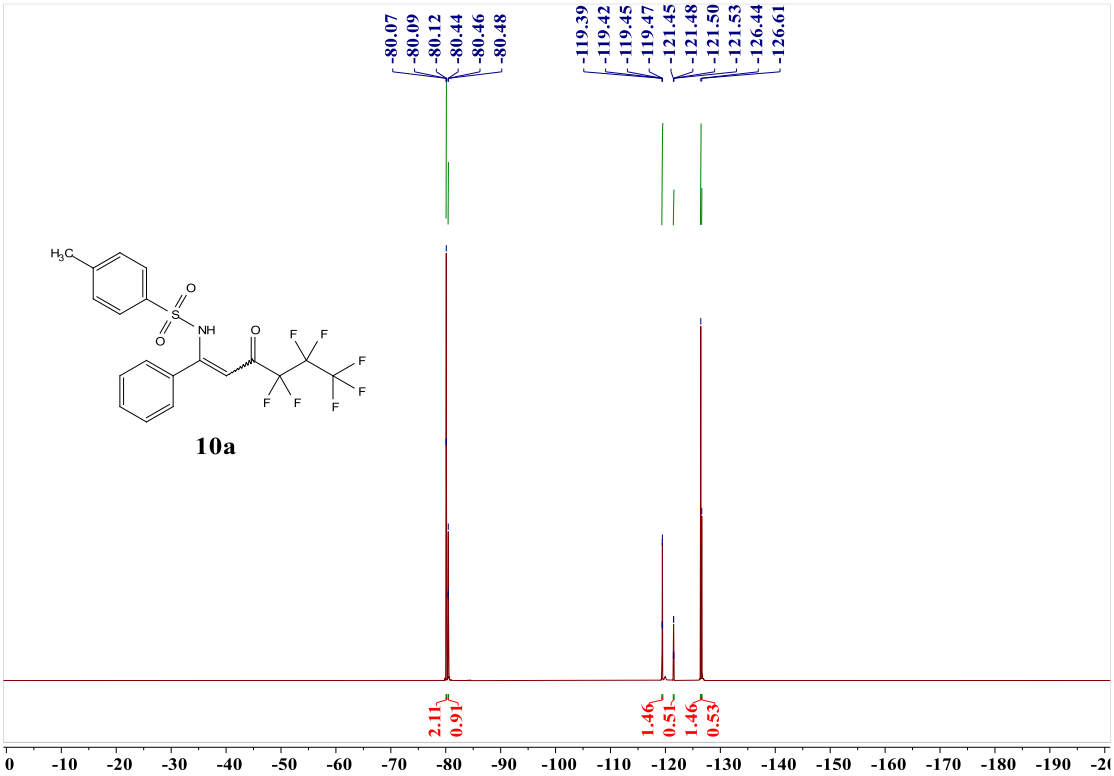
^{13}C NMR spectra of the product **7** (100 MHz, $CDCl_3$)



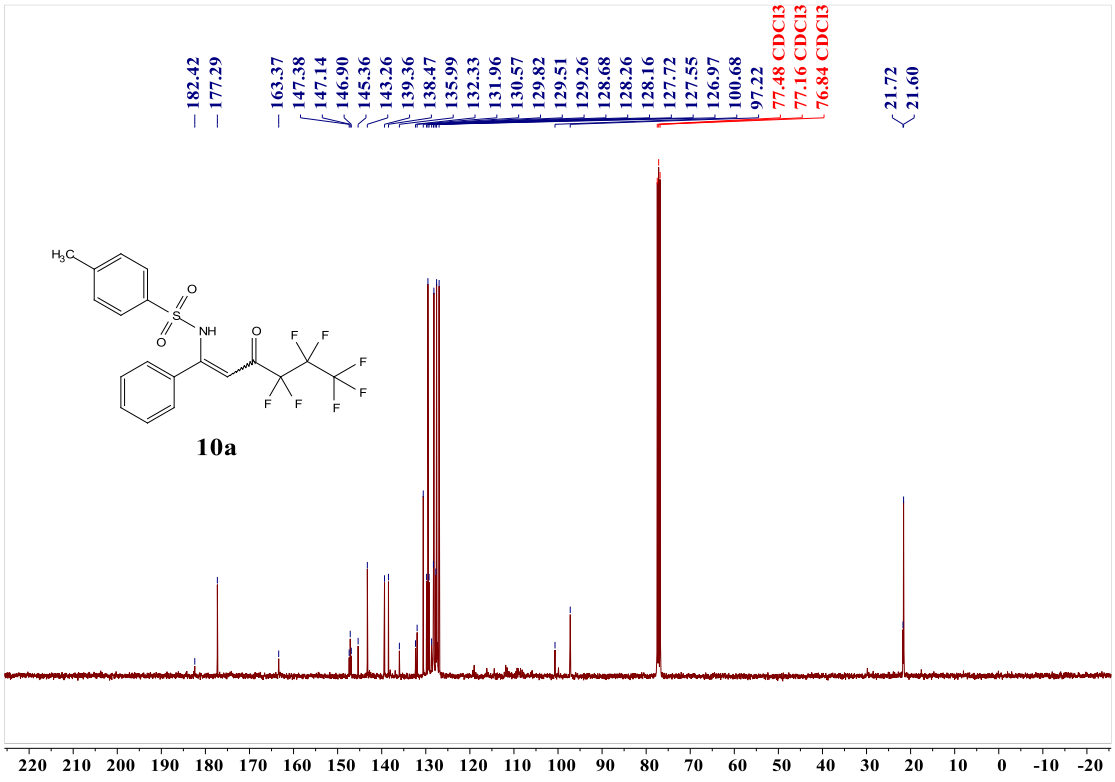
^{1}H NMR spectra of the product **10a** (400 MHz, $CDCl_3$)



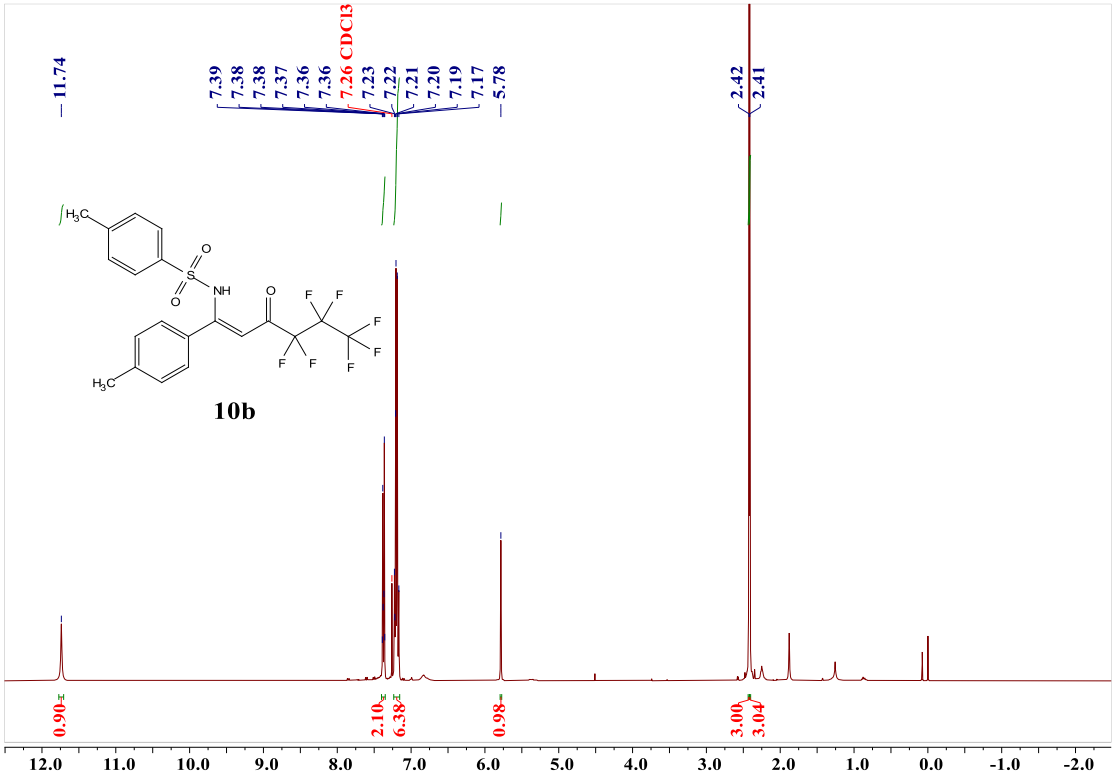
^{19}F NMR spectra of the product **10a** (376 MHz, $CDCl_3$)



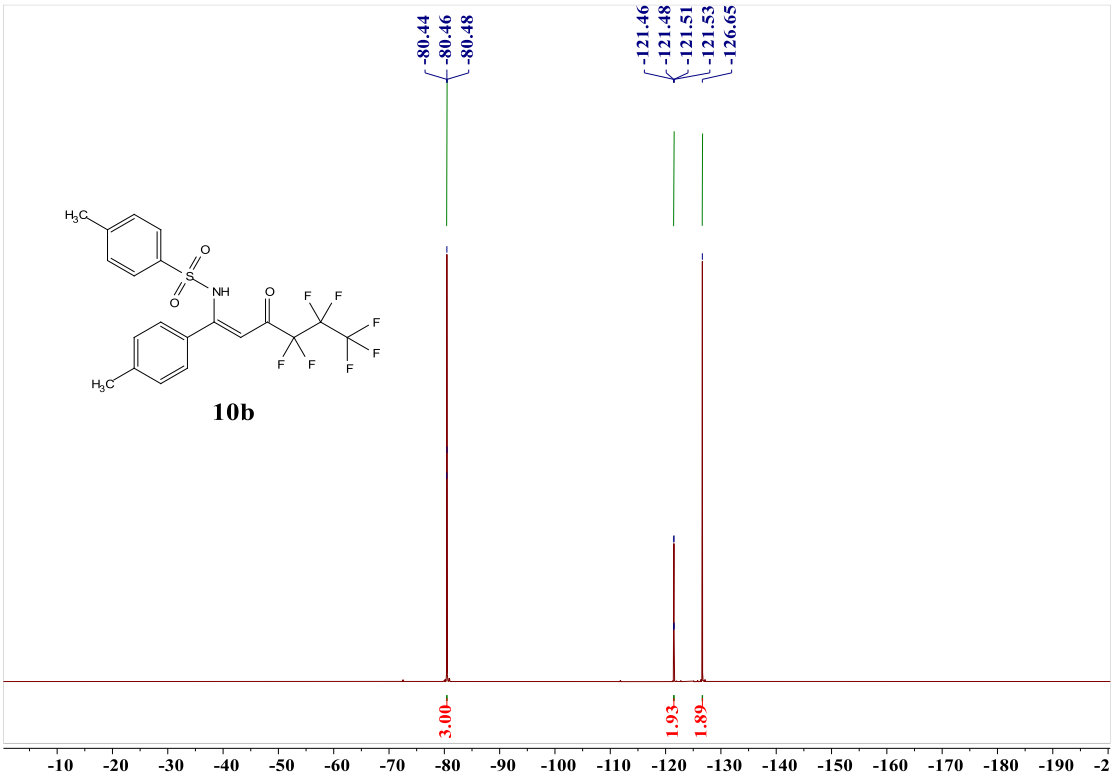
^{13}C NMR spectra of the product **10a** (100 MHz, $CDCl_3$)



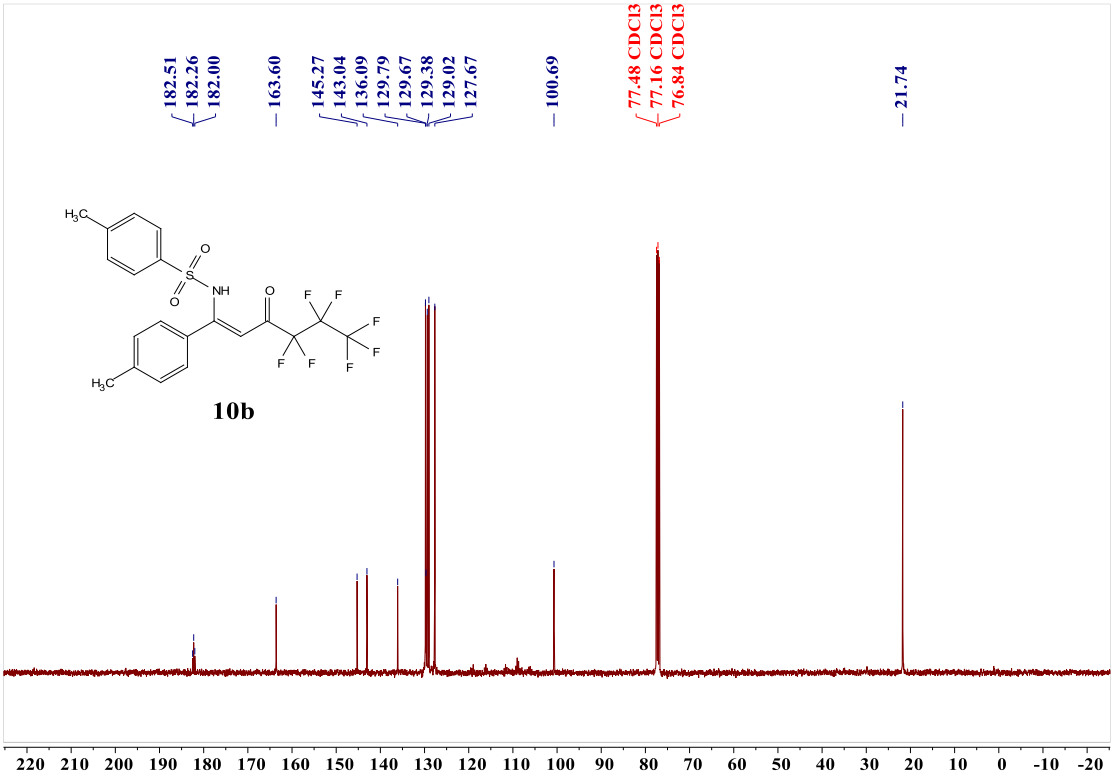
^{1}H NMR spectra of the product **10b** (400 MHz, $CDCl_3$)



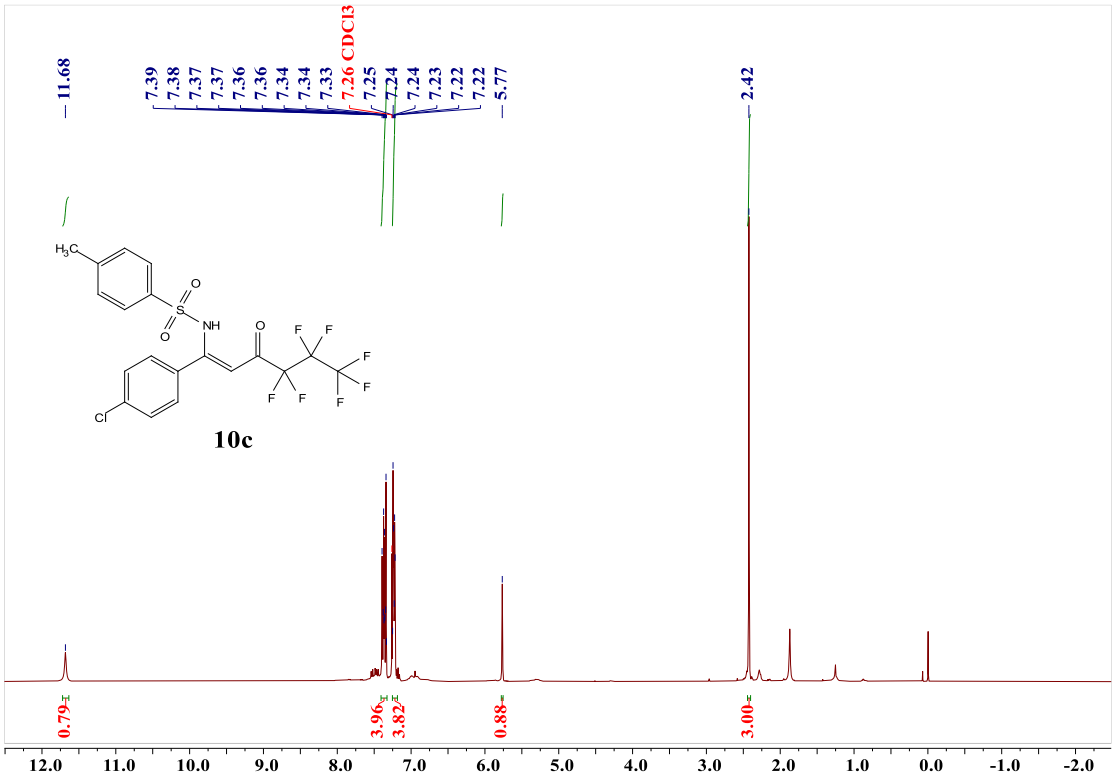
^{19}F NMR spectra of the product **10b** (376 MHz, $CDCl_3$)



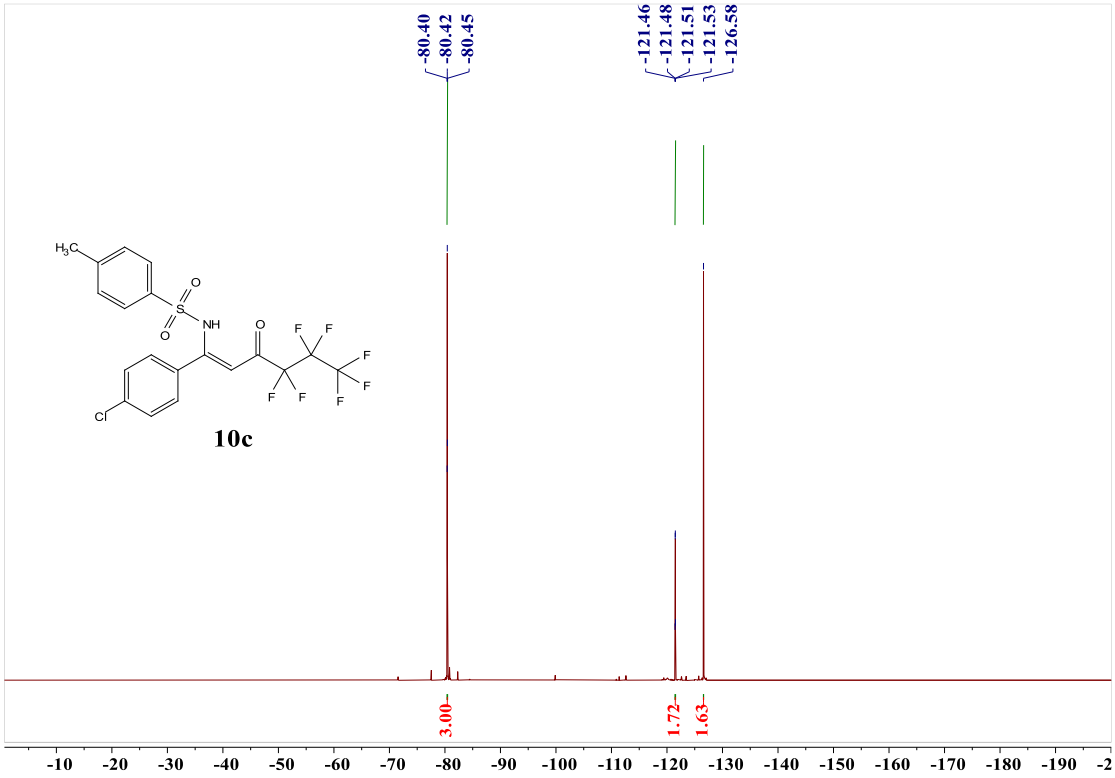
^{13}C NMR spectra of the product **10b** (100 MHz, $CDCl_3$)



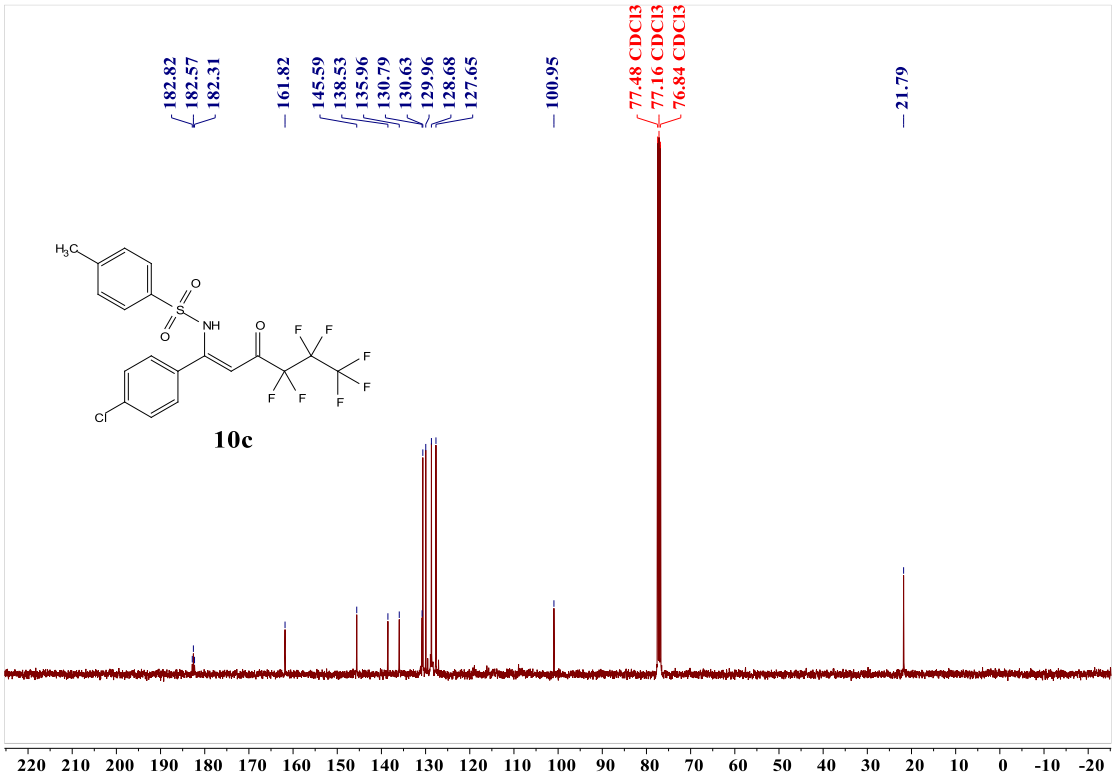
^{1}H NMR spectra of the product **10c** (400 MHz, $CDCl_3$)



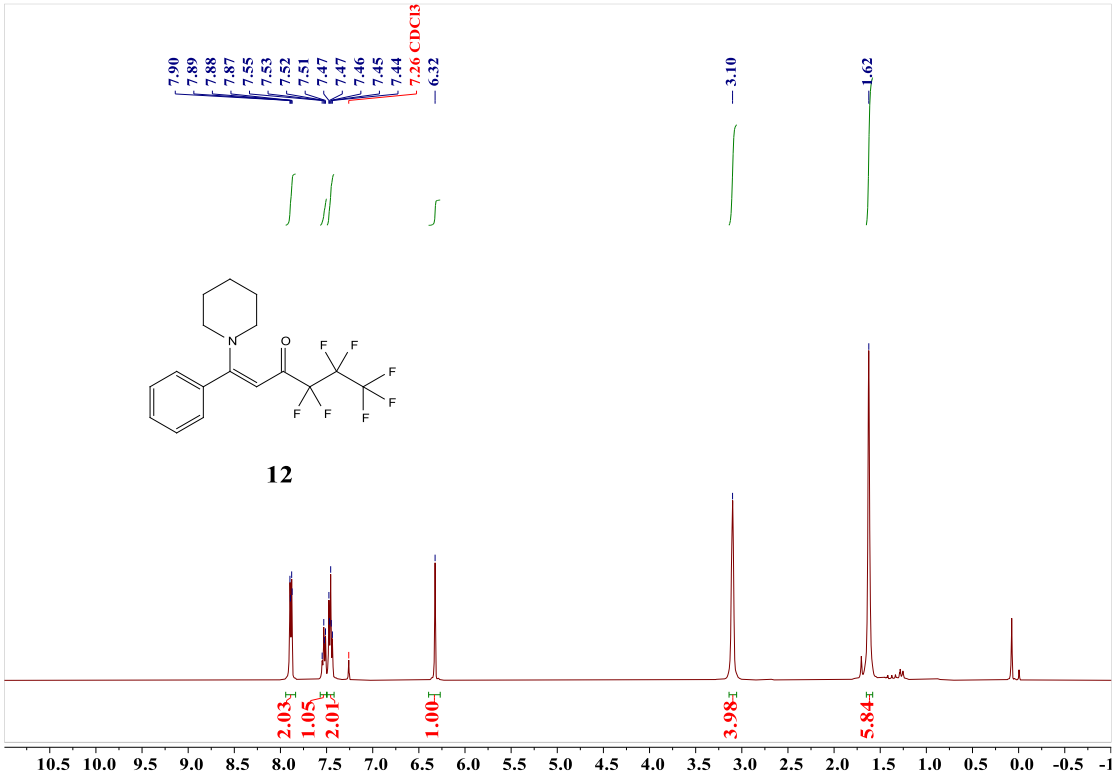
^{19}F NMR spectra of the product **10c** (376 MHz, $CDCl_3$)



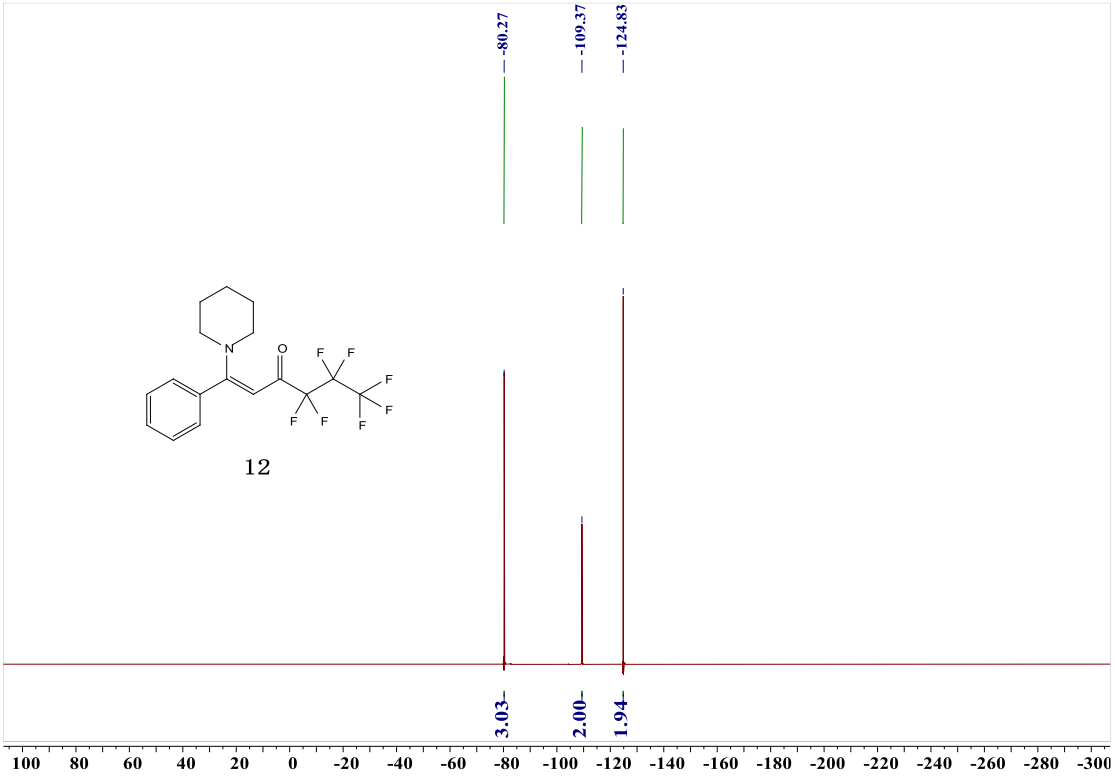
^{13}C NMR spectra of the product **10c** (100 MHz, $CDCl_3$)



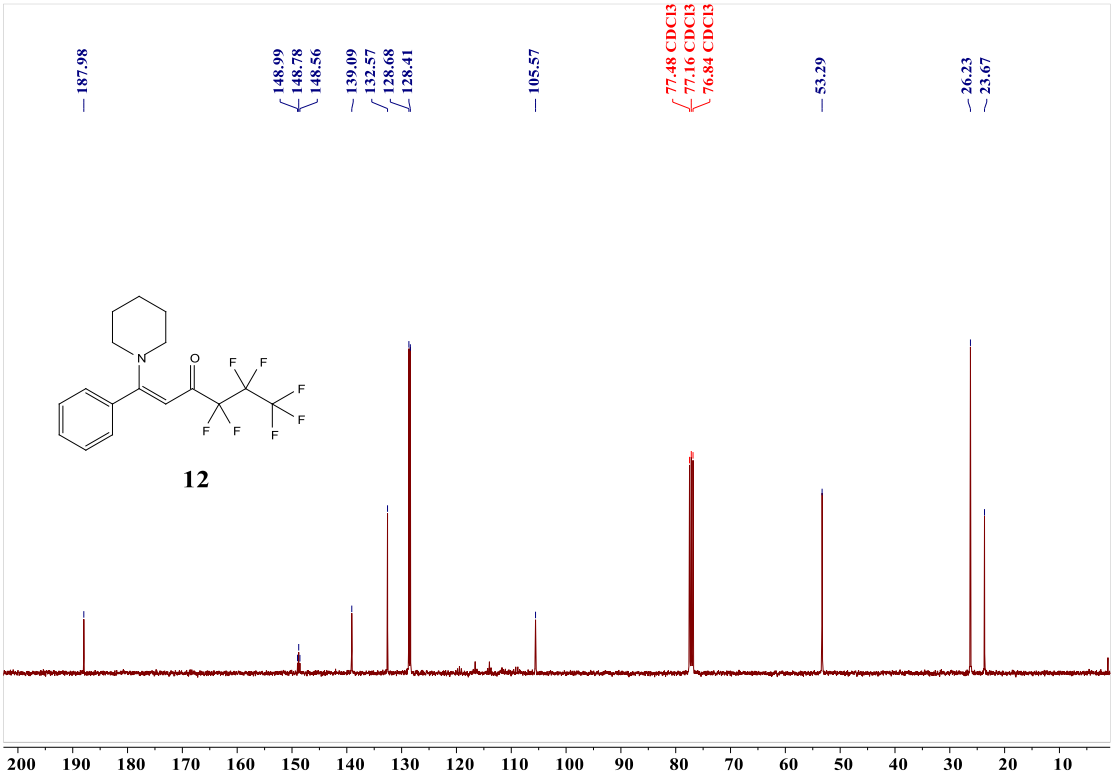
^{1}H NMR spectra of the product **12** (400 MHz, $CDCl_3$)



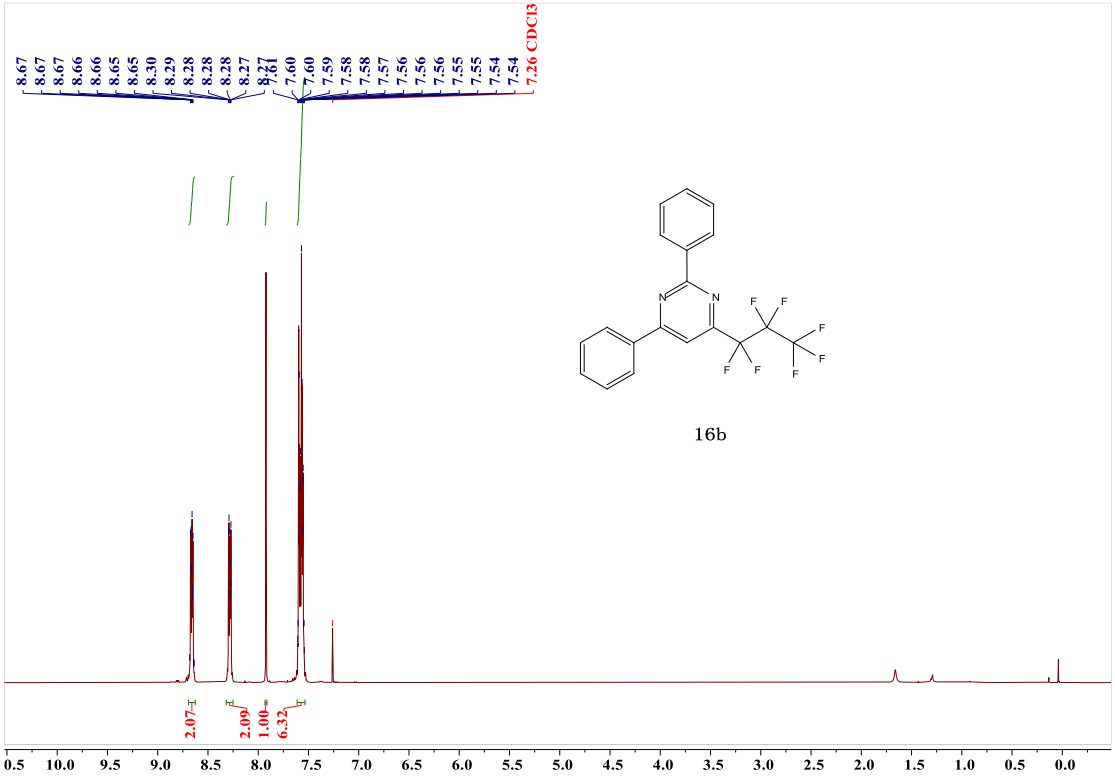
^{19}F NMR spectra of the product **12** (376 MHz, $CDCl_3$)



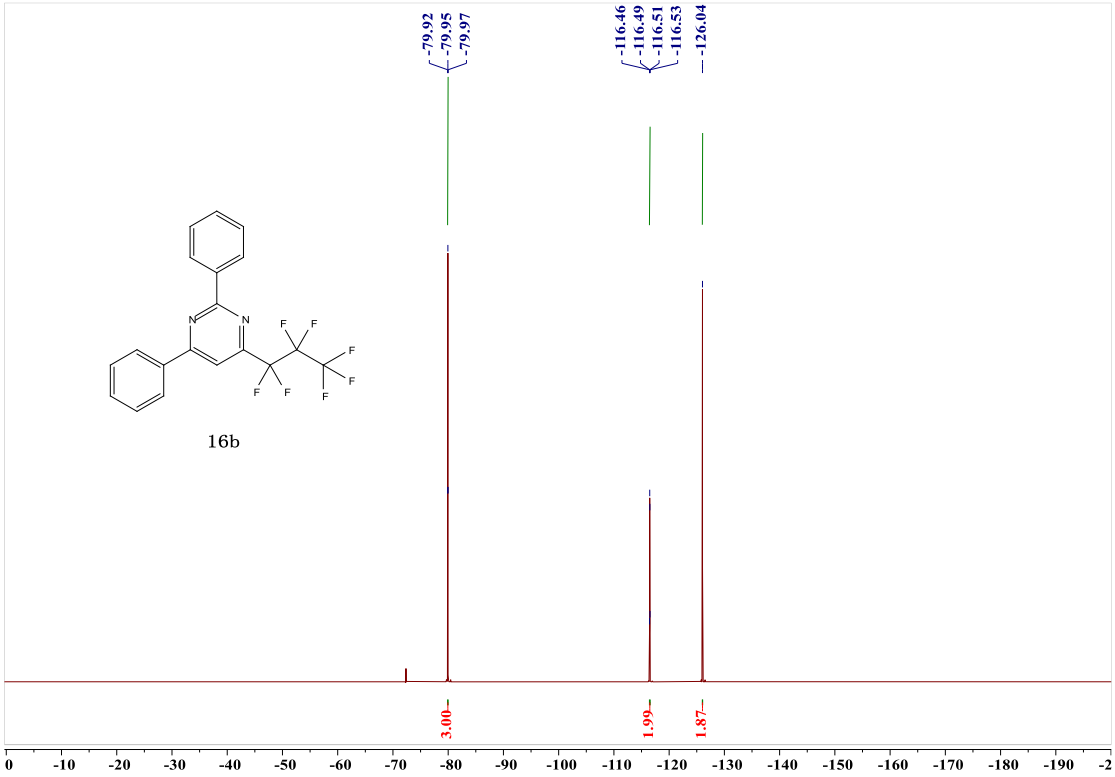
^{13}C NMR spectra of the product **12** (100 MHz, $CDCl_3$)



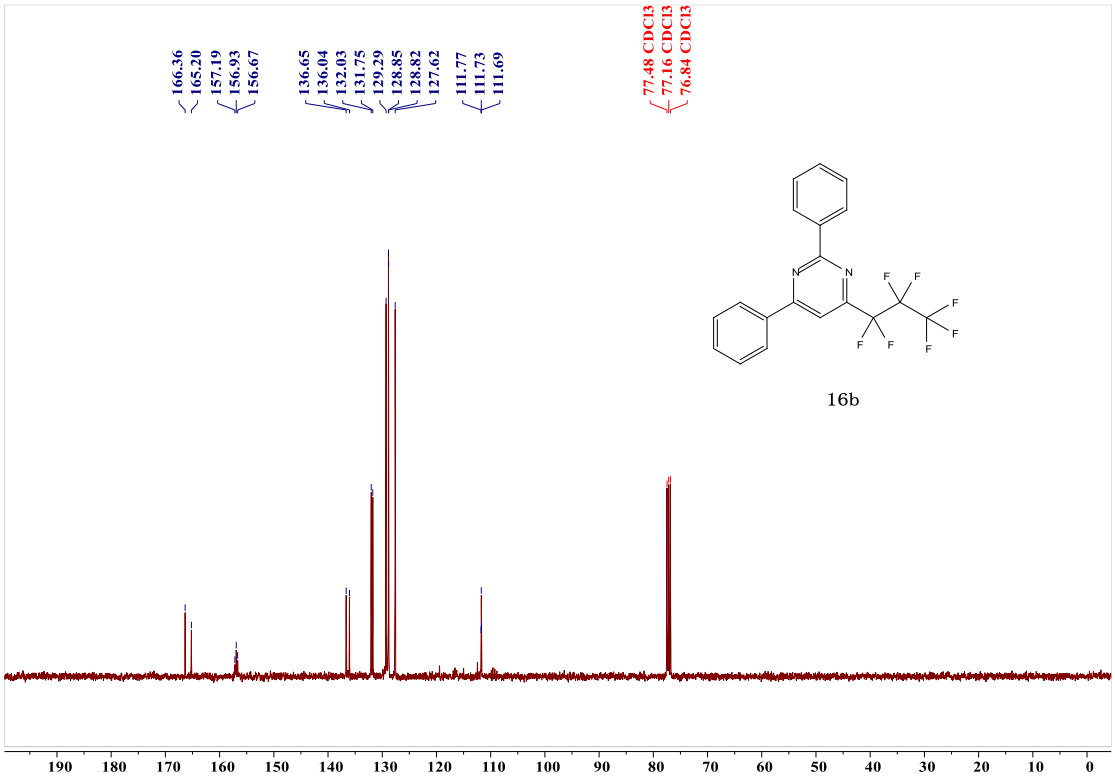
^{1}H NMR spectra of the product **16b** (400 MHz, $CDCl_3$)



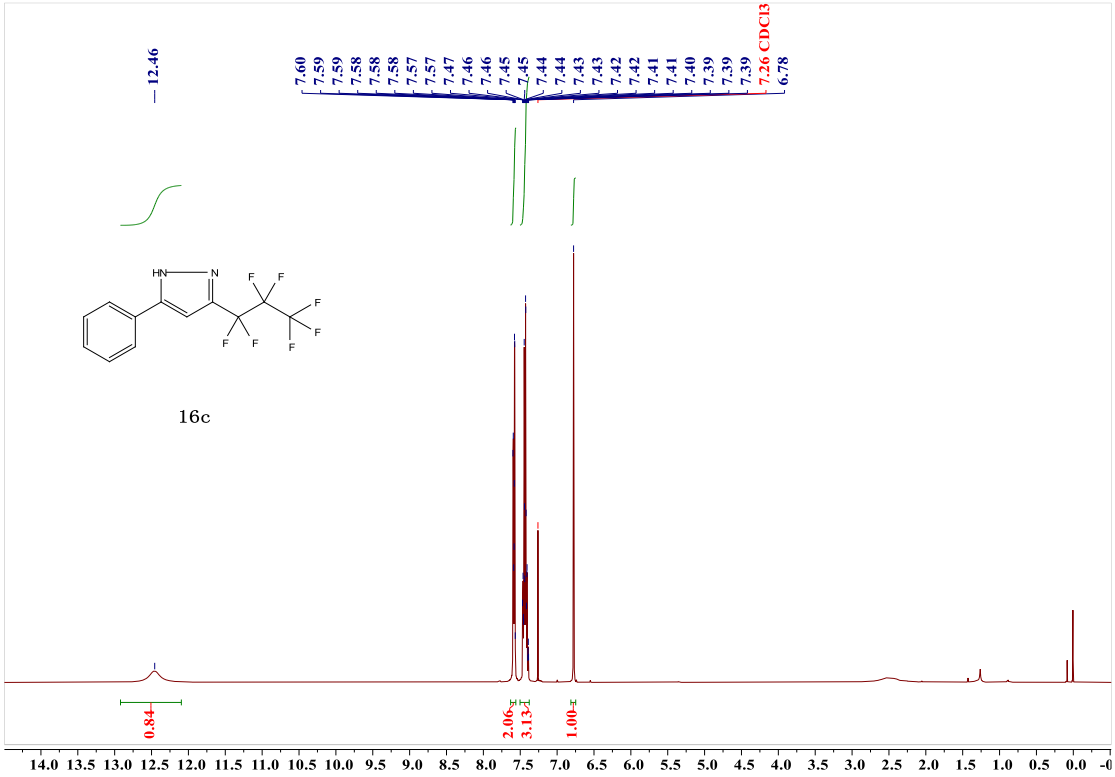
^{19}F NMR spectra of the product **16b** (376 MHz, $CDCl_3$)



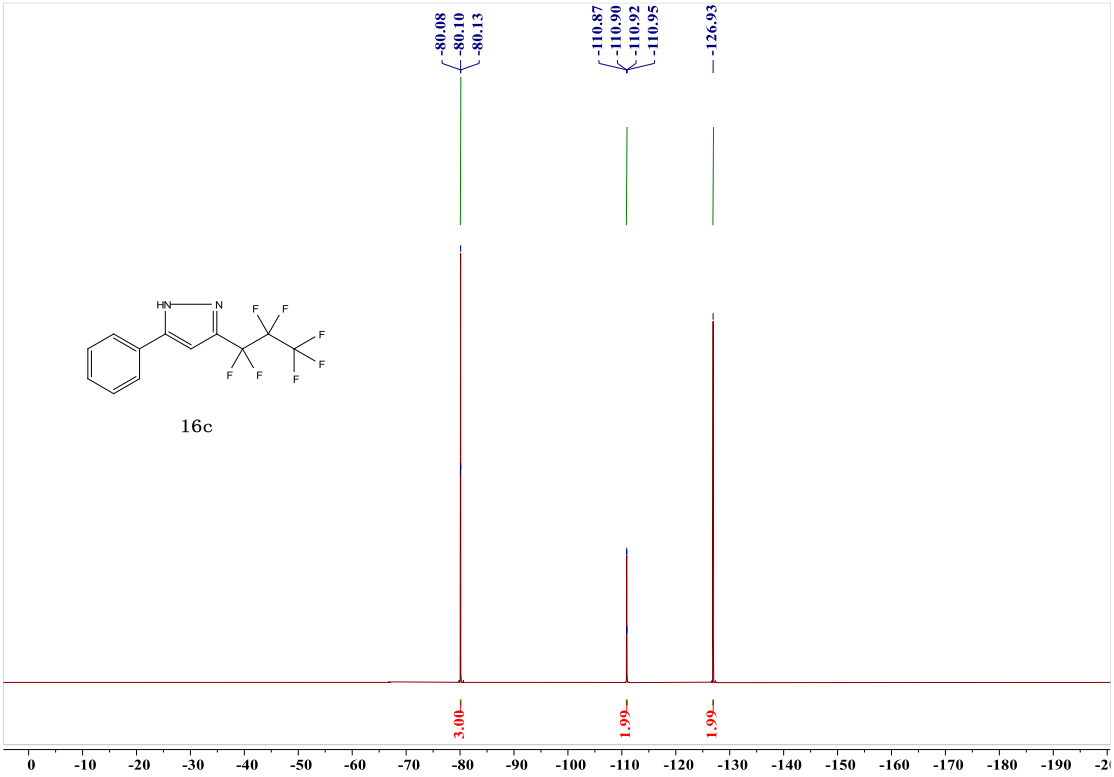
^{13}C NMR spectra of the product **16b** (100 MHz, $CDCl_3$)



^{1}H NMR spectra of the product **16c** (400 MHz, $CDCl_3$)



^{19}F NMR spectra of the product **16c** (376 MHz, $CDCl_3$)



^{13}C NMR spectra of the product **16c** (100 MHz, $CDCl_3$)