Photoinduced, Copper-Catalyzed Three Components Cyanofluoroalkylation of Alkenes with Fluoroalkyl Iodides as Fluoroalkylation Reagents

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Supporting Information

Table of Content:

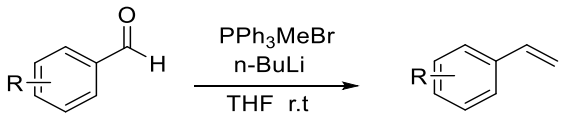
1. General information

Unless stated otherwise, all reactions were carried out under an argon atmosphere. All solvents were purified and dried according to standard methods prior to use. ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra were recorded on a Varian instrument (300 MHz, 75 MHz, 282 MHz, and 121 MHz) spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard unless otherwise noted. Data for **^{1}**H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quartet or unresolved, coupling constant(s) in Hz, integration). Data for ^{13}C NMR, ^{19}F NMR and ^{31}P NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectra (HRMS) were obtained by the ESI or EI ionization sources.

Materials: $Cu(OAc)_2$ was prepared from $Cu(OAc)_2.H_2O$ by refluxing in acetic anhydride and washed with dry Et_2O. All other reagents were commercially available and used as received.

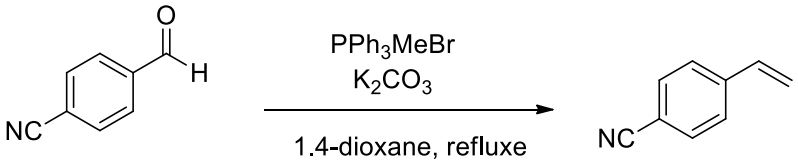
2. General procedure for the synthesis of alkenes

2.1 General procedure for the synthesis of alkenes 2a—2p.[1]



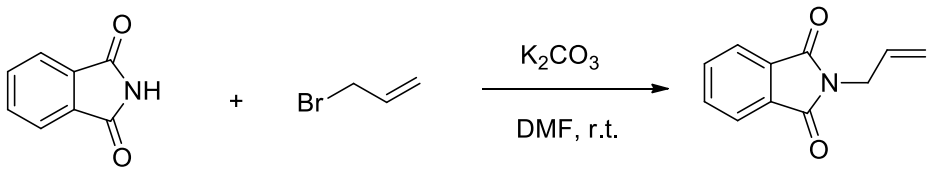
In a 100 mL round bottomed flask equipped with a stir bar, methyltriphenylphosphonium bromide (12 mmol, 1.2 equiv) were dissolved with 50 mL THF under Ar atmosphere，*n*-BuLi (2.5 mol/L, 12mmol, 1.2 equiv) were added dropwise under 0 ℃， the mixture was stirred for 15 minutes. Aldehyde (10.0 mmol) was dissolved with THF, which was added into reaction, and the mixture continues to stir for 1 h under 0 ℃. After the reaction mixture was stirred at room temperature for another 9 h, the mixture was quenched with water and extracted with diethyl ether. The combine organic layer was washed with H_2O and brine ,and dried over by Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed （*n*-hexane）by silica gel column to give alkenes **2a**-**2p**.

2.2 General procedure for the synthesis of alkene 2g.[2]



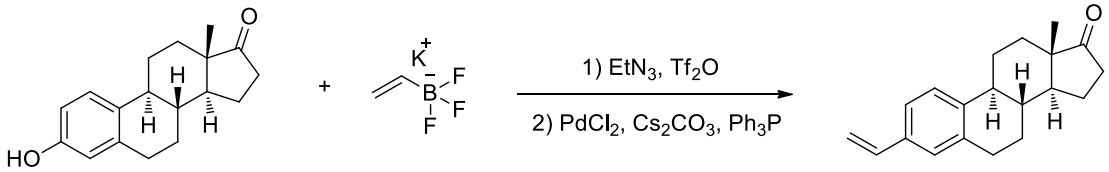
In a 100 mL round bottomed flask equipped with a stir bar, methyltriphenylphosphonium bromide (12 mmol, 1.2 equiv) and K_2CO_3 (20 mmol, 2 equiv) were dissolved with 20 mL 1,4-dioxane, aldehyde (10 mmol) was dissolved with 1,4-dioxane, which was added into the reaction mixture. After the reaction mixture was heated to reflux (110 ℃) overnight, the mixture was cooled to room temperature, quenched with water, and extracted with diethyl ether. The combine organic layer was washed with H_2O and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was chromatographed (*n*-hexane) by silica gel column to give alkene **2g**.

2.3 General procedure for the synthesis of alkene 5e.[3]



In a 50 ml round bottomed flask equipped with a stir bar, isoindoline-1,3-dione (5 mmol) and K_2CO_3 (6.5 mmol, 1.3 equiv) was dissolved with 15 mL DMF. Allyl bromide (6.5 mmol, 1.3 equiv) was added dropwise into the mixture. After the reaction was completed by TLC monitoring, and the reaction mixture was quenched with water and extracted with DCM, washed with brine, and dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was chromatographed by silica gel column to give **5e**.

2.4 General procedure for the synthesis of 5j.[4]



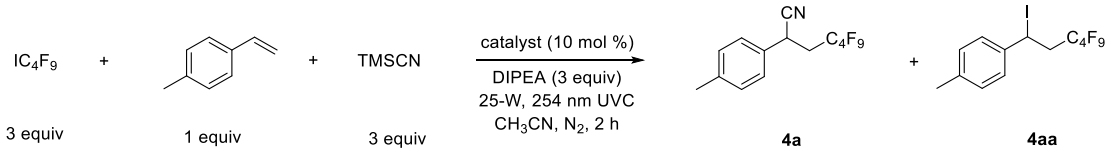
1) A mixture of estrone (5 mmol) dissolved in 30 mL DCM was added Et_3N (10 mmol, 2 equiv). Trifluoromethanesulfonic anhydride (5.5 mmol, 1.1 equiv) was added dropwise no less than 9 minutes into the mixture under 0 ℃. The reaction mixture was stirred at room temperature for 3 h. The resulting mixture was extracted with DCM, washed with sat. NH_4Cl. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was directly used in the next step without further purification.

2) The previous crude product, potassium vinyltrifluoroborate (5 mmol), $PdCl_2$ (0.1 mmol, 0.02 equiv), Ph_3P (0.3 mmol, 0.06 equiv), H_2O (0.6 ml), and $CsCO_3$ (15 mmol, 3 equiv) were combined in an oven-dried sealing tube. The vessel was evacuated and backfilled with N_2 (repeated for 3 times), THF (20 mL) were added *via* syringe. The tube was sealed with a Teflon lined cap and the reaction mixture was placed into a preheated oil bath at 85 ℃ for 19 h. The mixture was then cooled to room temperature, filtered through a plug of silica and washed with EtOAc. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel (PE: EA = 5:1) to give the product **5j**.

3. General procedures for the cyanofluoroalkylation of alkenes.

3.1 Optimization of reaction conditions

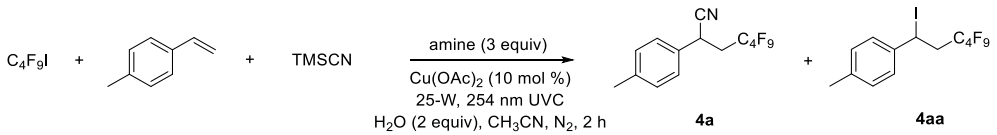
Table S1. Catalysts screening[a]



Entry	Catalyst	Yield (**4a**/**4aa**) (%)[b]	Entry	Catalyst	Yield (**4a**/**4aa**) (%)[b]
1	CuI	31/0	10	CuF_2	65/0
2[c]	CuI	61/0	11	$CuF_2.H_2O$	67/0
3	CuCl	61/0	12	$CuCl_2.H_2O$	63/0
4	CuBr	64/0	13	$Cu(OH)_2$	68/0
5	$Cu(MeCN)_4PF_6$	57/0	14	$CuSO_4$	67/0
6	Cu_2O	65/0	15	$Fe(OTf)_3$	0
7	$Cu(OTf)_2$	59/0	16	$Fe(acac)_3$	0
8	***$Cu(OAc)_2$***	***87/0***	17	$Ni(OTf)_2$	0
9	$Cu(acac)_2$	61/0	18	$Ni(NO_3)_2(H_2O)_6$	11/5

[a]Unless otherwise noted, the reactions were carried out by using **2a** (0.1 mmol), **1a** (3.0 equiv), **3**(3 equiv), amine (3 equiv), solvent (1.0 mL), catalyst (10 mol %), under N_2, and stirred at rt for 2 h under UV light irradiation (25-W UVC (254 nm) compact fluorescent light bulb). [b]Based on ^1H NMR analysis using anisole as an internal standard. [c]2 equiv of H_2O was added here and after.

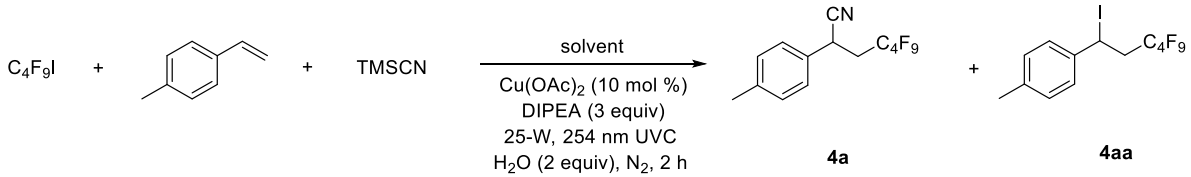
Table S2. Amines screening.[a]



Entry	Amine	Yield (**4a**/**4aa**) (%)[b]	Entry	Amine	Yield (**4a**/**4aa**) (%)[b]
1	Et_3N	61/0	5	TMEDA	30/0
2	DBU	38/0	6	phenylamine	4/30
3	pyridine	9/22	7	DMAP	40/0
4	Et_2NH	66/0	8	DABCO	64/0

[a]0.1 mmol scale. [b]Based on ^{1}H NMR analysis using anisole as an internal standard.

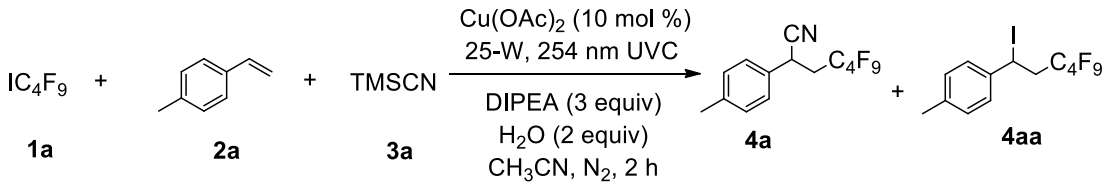
Table S3. Solvents screening[a]



Entry	Solvent	Yield (**4a**/**4aa**) (%)[b]	Entry	Solvent	Yield (**4a**/**5**) (%)[b]
1	DMF	28/0	5	acetone	21/2
2	THF	3/0	6	DCM	28/0
3	DMSO	55/0	7	1,4-dioxane	25/3
4	H_2O	3/0	8	toluene	5/5

[a]0.1 mmol scale. [b]Based on ^{1}H NMR analysis using anisole as an internal standard.

Table S4. Control experiments:

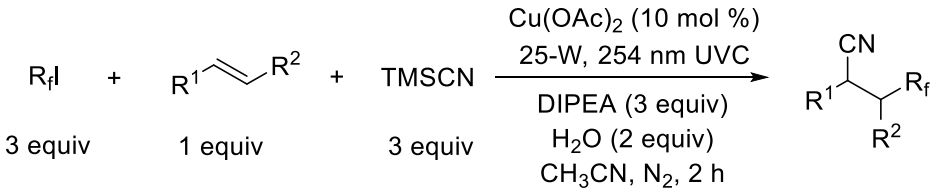


standard conditions[a]

entry	change from the "standard conditions"	yield (**4a**/**4aa**) (%)[b]
1	no change	87/0
2	no hv, 80 ^{o}C, 12 h	0
3	no hv, rt, 24 h	0
4	no DIPEA	0/12
5	no $Cu(OAc)_2$	0
6	**1a** (1.0 equiv)	29/0
7	**1a** (2.0 equiv)	48/0
8	**3a** (1.0 equiv)	24/0
9	**3a** (2.0 equiv)	45/0
10	DIPEA (1.0 equiv)	15/0
11	DIPEA (2.0 equiv)	40/0
12[c]	***DIPEA (4.0 equiv)***	***92(91)/0***
13	5 mol % of $Cu(OAc)_2$	65/0
14	365 nm UVC instead of 254 nm UVC	19/0

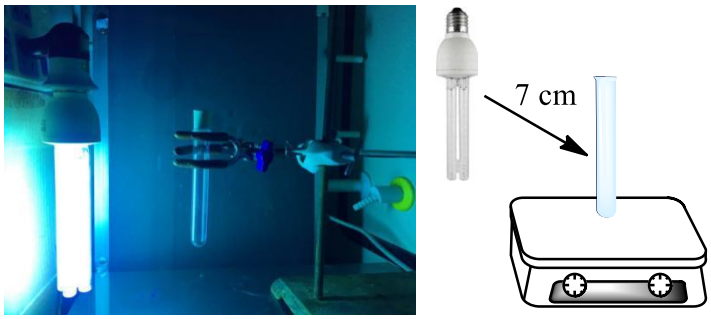
[a]Standard conditions were carried out by using **2a** (0.1 mmol), **1a** (3.0 equiv), $Cu(OAc)_2$ (10 mol %), DIPEA (3.0 equiv), H_2O (2 equiv), CH_3CN (1ml), under Ar, and stirred at rt for 2 h under UV light irradiation. [b]Based on ^{1}H NMR analysis using anisole as an internal standard. [c]Isolated yields in para.

3.2 General procedures of the cyanofluoroalkylation of alkenes



To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added $Cu(OAc)_2$ (0.04 mmol, 10 mol %). Then, air was withdrawn and backfilled with Ar (three times). Perfluoroalkyl iodide (R_fI, 1.2 mmol, 3 equiv), alkene (0.4 mmol) and trimethylsilyl cyanide (TMSCN, 1.2 mmol, 3 equiv), 4 mL of CH_3CN, ethyldiisopropylamine (DIPEA, 1.6 mmol, 4 equiv), H_2O (0.8 mmol, 2 equiv) were added in turn by syringe. Thereafter, the test tube was transferred to a UV photoreactor (25W, see Scheme S1 for details), where it was irradiated at 254 nm for 2 h. Two hours later, the reaction was quenched with water (2 mL), extracted with DCM, dried over anhydrous sodium sulfate, concentrated in *vacuo* and purified by column chromatography (*n*-hexane/dichloromethane 20:1-5:1) to afford the product.

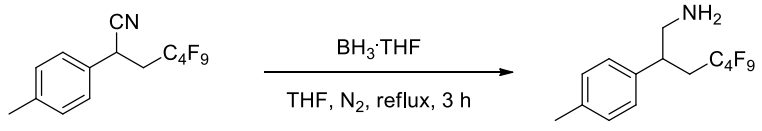
For CF_3I, an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added $Cu(OAc)_2$ (0.04 mmol, 10 mol %), air was withdrawn and backfilled with Ar (three times). The mixture was cooled to -78°C, trifluoromethyl iodide (1.2 mmol, 3 equiv) was condensed and added to the above mixture via a Dewar type condenser fitted with an 18-gauge needle. Then, alkene (0.4 mmol) and trimethylsilyl cyanide (TMSCN, 1.2 mmol, 3 equiv), 4 mL of CH_3CN, ethyldiisopropylamine (DIPEA, 1.6 mmol, 4 equiv), H_2O (0.8 mmol, 2 equiv) were added in turn by syringe. Thereafter, the test tube was transferred to a UV photoreactor (25W, see Scheme S1 for details), where it was irradiated at 254 nm for 2 h. Two hours later, the reaction was quenched with water (2 mL), extracted with DCM, dried over anhydrous sodium sulfate, concentrated in *vacuo* and purified by column chromatography (*n*-hexane/dichloromethane 20:1-5:1) to afford the product.



Scheme S1. Placement of CFL around quartz test tube.

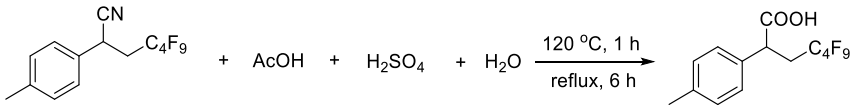
Instructions on placement of CFL: One 25-W UVC compact fluorescent light bulb was placed next to the quartz test tube and the distance was about 7 cm. A cardboard box lined with tin foil was placed over the lamps and stir plate. In one side of the cardboard box, part of the side was cut out, and a high-speed fan was setup for dissipating heat.

4. Synthetic applications.[5]



4a **9**

BH_3.THF (1.8 mmol) was added to a solution of **4a** (0.6 mmol) in dry THF (2 mL) at room temperature under an atmosphere of N_2, and then refluxed for 3 h. The reaction was quenched by the dropwise addition of 6M aqueous HCl (1 mL). After refluxing for a further 2 h, the solution was made basic with 6M aqueous NaOH, then extracted three times with DCM. The combined extracts were dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by flash column chromatography to afford the derivative product **9**.



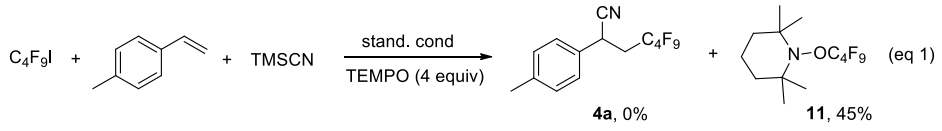
4a **10**

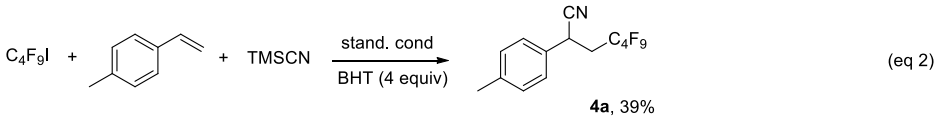
A 10 mL round bottom flask equipped with a stir bar was added **4a**, AcOH (1 mL), H_2O (1 mL), H_2SO_4 (1 mL), and heated to 120℃ for 1 h. Then, refluxed for 6 h. The resulting mixture was cooled to room temperature; sodium hydroxide was used to adjust pH to 14. The suspension was diluted with H_2O until all the solids dissolved. The solution was washed with EtOAc (2×20 ml). The hydrochloric acid was added dropwise until pH = 1. The resulting mixture was extracted with EtOAc (3×20 ml), washed with brine, dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The crude material was purified by flash chromatography on silica gel to afford derivative product **10**.

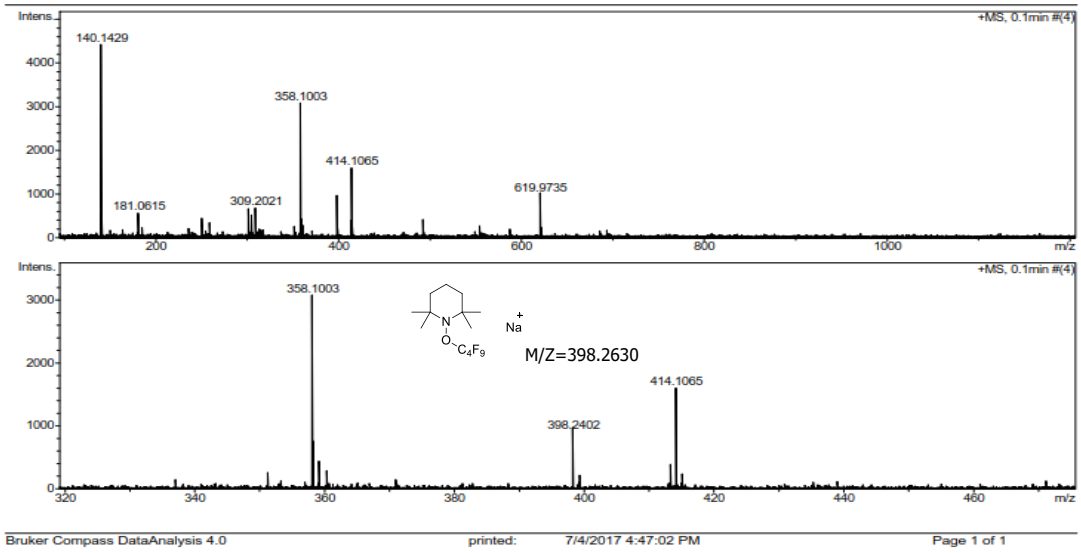
5. The mechanistic study

5.1 Radical inhibition experiments

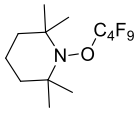
In order to gain some information on the reaction mechanism, radical inhibition experiments were examined. When radical scavenger TEMPO (2,2,6,6-tetromethyl-1-piperidinyloxy, 4.0 equiv) was added under the standard conditions, the reaction was completely suppressed (eq 1). No **4a** was detected and TEMPO-C_4F_9 product **11** was isolated by column chromatography gave 45% yield. Addition of butylated hydroxytoluene (BHT) led to a dramatic decrease of the yield (eq 2). These results indicated that a radical pathway could be involved. Which suggested that a radical pathway was involved in the current reaction.







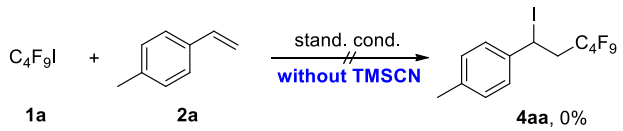
HRMS-ESI



2,2,6,6-tetramethyl-1-(perfluorobutoxy)piperidine (16), Colorless liquid;
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 6H), 1.18 (s, 12H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 61.88, 40.42, 33.43, 20.63, 16.78.
^{19}F NMR (282 MHz, $CDCl_3$) δ -78.84 (t, *J* = 5.4 Hz, 2F), -81.04 (t, *J* = 9.9 Hz, 3F), -124.52—-124.64 (m, 2F), -126.10 (d, *J* = 3.4 Hz, 2F).
HRMS (ESI): $C_{13}H_{18}F_9NO+Na^+$ Calcd: 398.2630, Found: 398.2402.

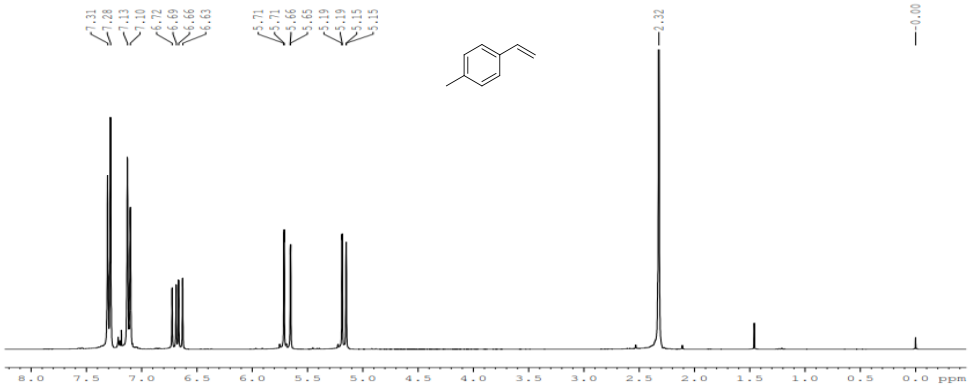
5.2 Control experiments

To further prove the reaction as a multicomponent reaction, control experiment was carried out. Under the standard conditions, in the absence of TMSCN, no iodoperfluorobutylation product could be observed, and the *p*-methylstyrene (**2a**) was mostly consumed, thus questioning vinyl iodides as effective intermediates in these transformations.

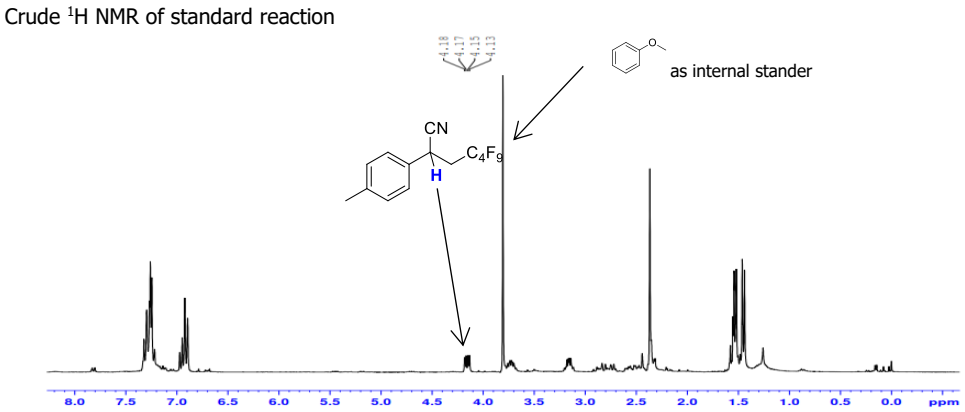


1a **2a**

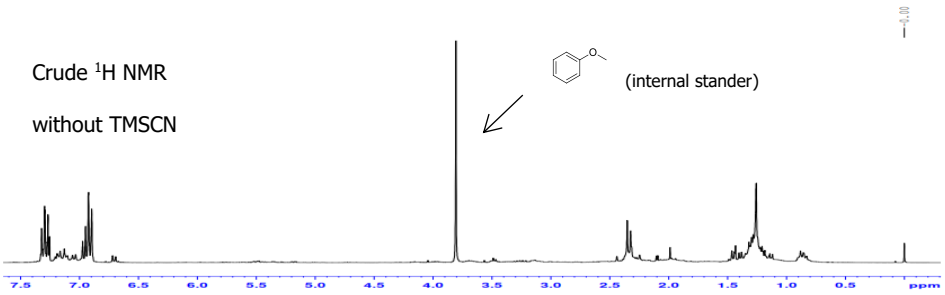
^{1}H NMR of *p*-methylstyrene (2a)



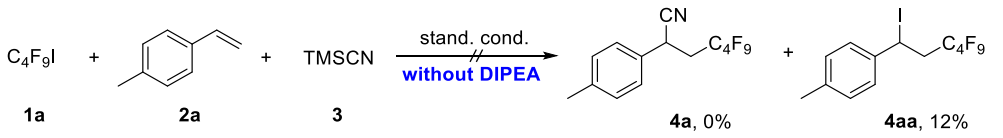
Crude ^{1}H NMR of standard reaction

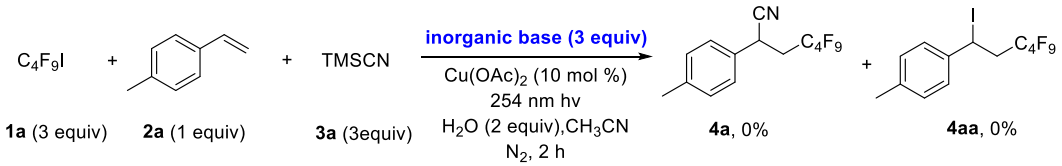


Crude ^{1}H NMR (under the standard conditions, in the absence of TMSCN)



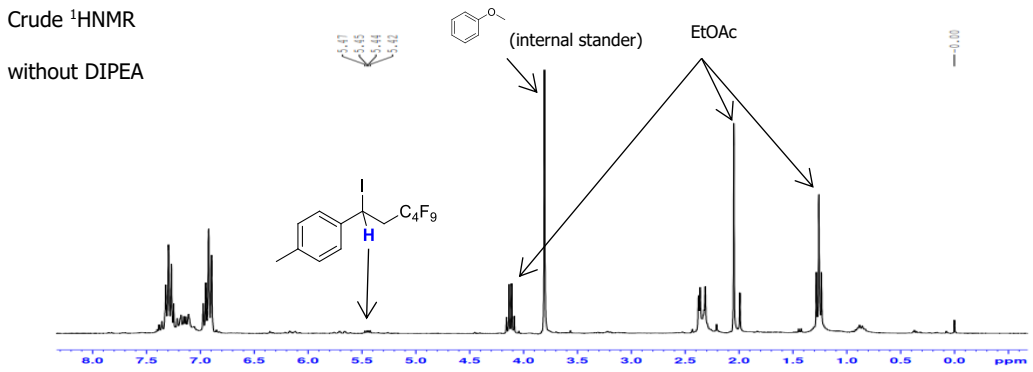
To explore the influence of DIPEA in the reaction, control experiment was carried out. Under the standard conditions, in the absence of DIPEA, no **4a** were observed, whereas the iodoperfluoroalkylation product **4aa** was obtained in 12% yield and *p*-methylstyrene (**2a**) was mostly consumed. Furthermore, to explore the influence of bases, a series of inorganic bases were used instead of DIPEA. However, no **4a** or **4aa** were observed, and *p*-methylstyrene (**2a**) was mostly consumed. The negative results demonstrated the importance of DIPEA in this reaction.



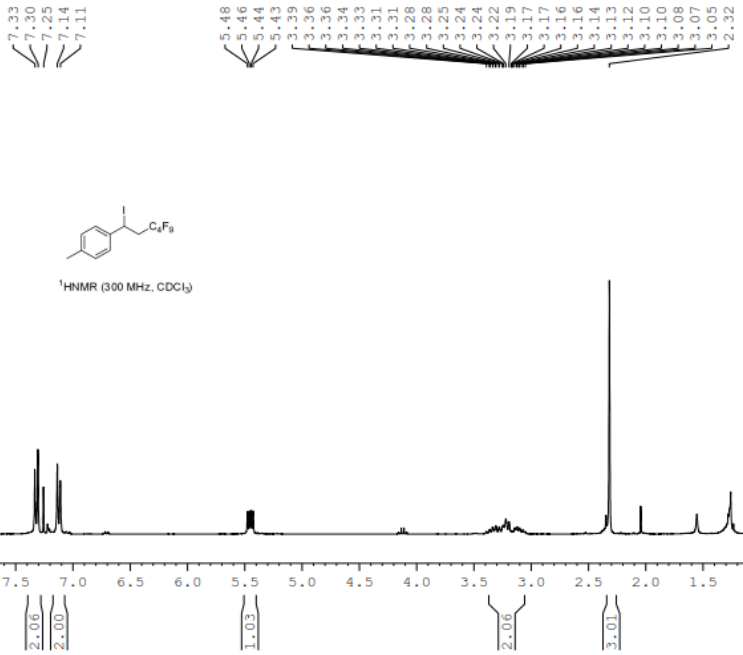


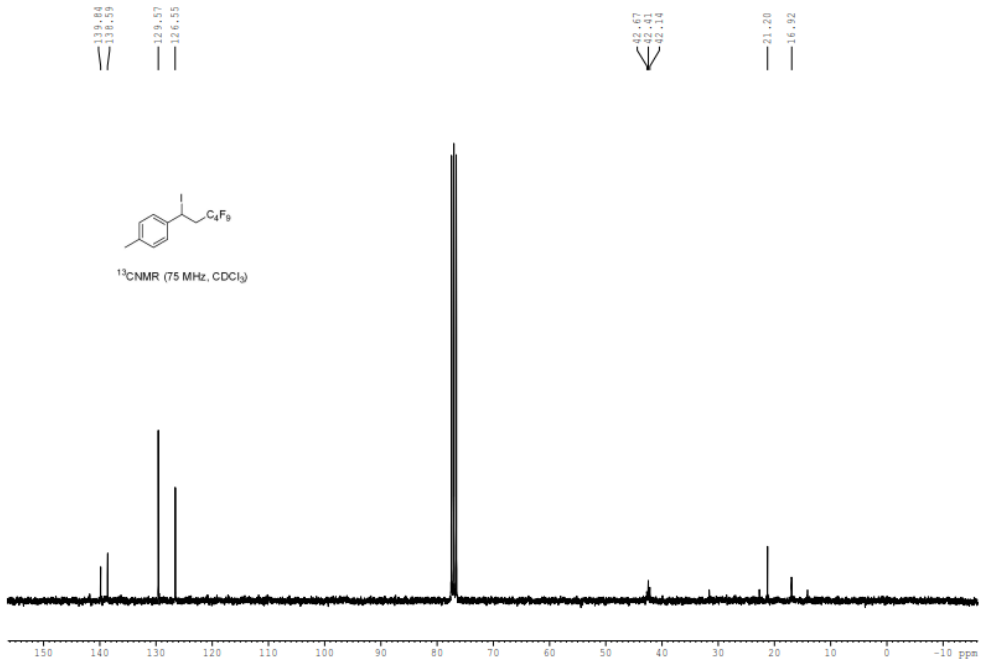
inorganic bases = *t*-BuOK, *t*-BuONa, *t*-BuOLi, Na_2CO_3, Cs_2CO_3, NaOH, and $PhCO_2Na$.

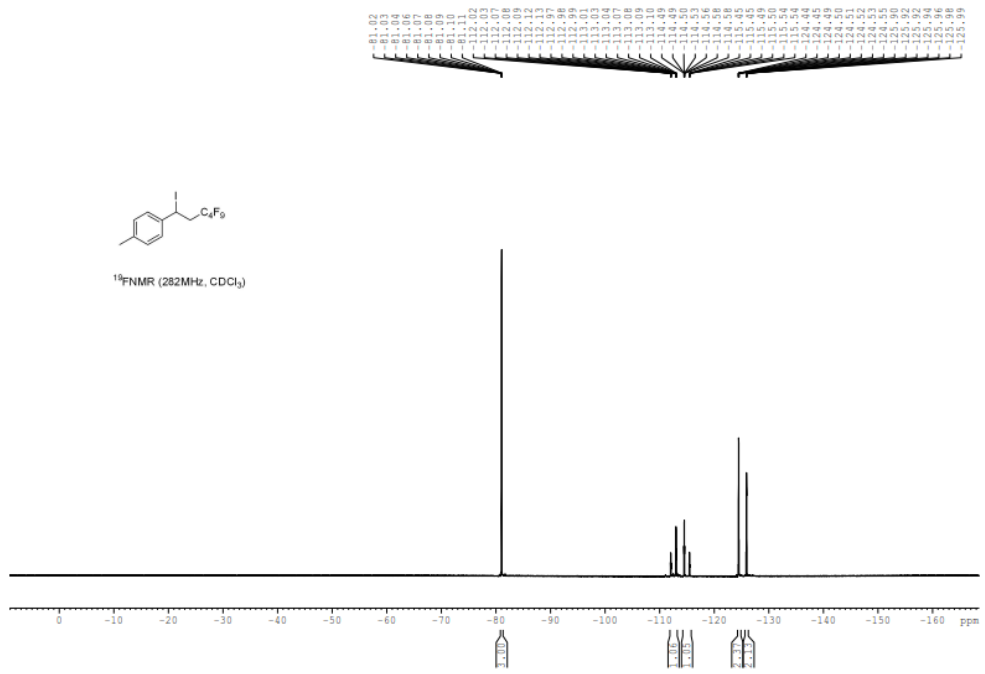
Crude ^{1}H NMR (under the standard conditions, in the absence of DIPEA)

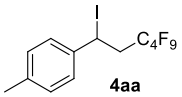


NMR spectra of 4aa





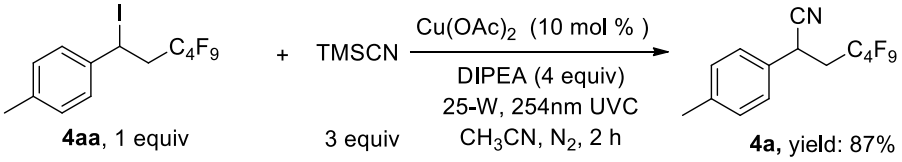




1-methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)benzene (4aa), colorless liquid;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 3.06–3.39 (m, 2H), 2.32 (s, 3H).

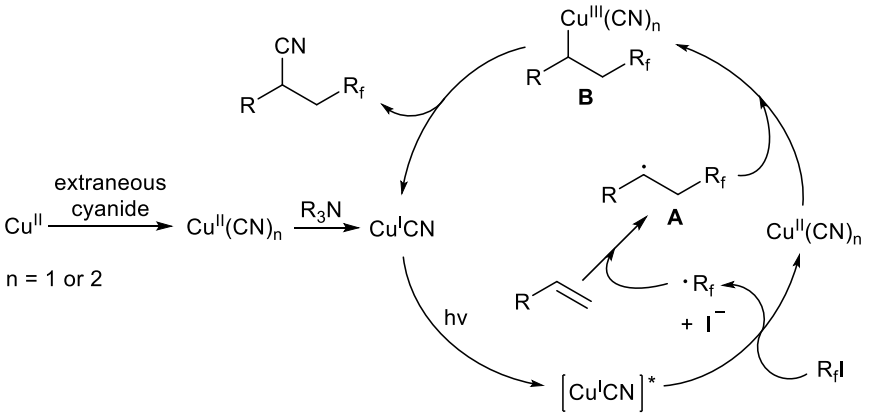
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.84, 138.59, 129.57, 126.55, 42.14 (t, *J* = 20.3 Hz), 21.20, 16.92.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.03 (t, *J* = 8.5 Hz, 3F), -112.10—-115.61 (m, 2F), -124.52 (d, *J* =8.5Hz, 2F), -125.96 (d, *J* =14.1Hz, 2F).

Under standard conditions, **4aa** could react with TMSCN and gave the cross coupling product **4a** in 87% yield.



5.3 Proposed mechanism[6]

Although multiple scenarios can be envisaged, based on these investigations and previous reports, a plausible mechanism was proposed. Firstly, the rapid ligand exchange delivered the Cu^{II} species, which was reduced by the electron rich *tert*-amine and formed an amine radical cation and Cu^{I}. Under UV light irradiation, Cu^{I} was excited to its triplet state $[Cu^{I}]$*. The following oxidative quenching step converted R_fI into $\cdot R_f$ and I^- along with recycling of Cu^{II}. Meanwhile, $\cdot R_f$ attacked alkene to give the radical intermediate **A**. Then, it reacted with $Cu^{II}(CN)_n$ and formed a Cu^{III} spices **B**. The subsequent reductive elimination provided the desired cyanofluoroalkylation product. It should be noted that both Cu^{I} and Cu^{II} salts showed good catalytic activities. These results indicated that the catalytic cycle could be initiated either from Cu^{II} or Cu^{I}. Unstable species TMS^+ and I^- undergo rapid hydrolysis and then neutralized by amine, which promoted a completed conversion.



6. References

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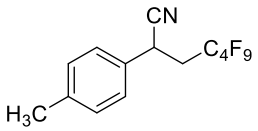
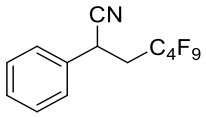
7. Characterization of products



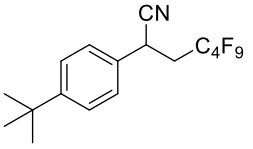
4a

4,4,5,5,6,6,7,7,7-nonafluoro-2-(*p*-tolyl)heptanenitrile (4a), 132.3mg, yield: 91%.
White solid, mp 44-45℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 (q, *J* = 8.4 Hz, 4H), 4.15 (dd, *J* = 4.5, 9.8 Hz, 1H), 2.72-2.82 (m, 1H), 2.42-2.61 (m, 1H), 2.37 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.09, 130.81, 130.26, 127.06, 118.97, 37.02 (t, *J* = 21.0 Hz), 29.32 (d, *J* = 3.8 Hz), 21.04.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.08—-81.12(m, 3F), -112.85—-113.88 (m, 1F), -114.07—-115.09 (m, 1F), -124.37—-124.47 (m, 2F), -125.93—-126.09 (m, 2F).
HRMS (ESI): $C_{14}H_{10}F_9N+Na^+$ Calcd: 386.0562, Found: 386.0566.



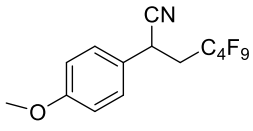
4b

4,4,5,5,6,6,7,7,7-nonafluoro-2-phenylheptanenitrile (4b), 121.5mg, yield: 87%.
Light yellow liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.45 (m, 5H), 4.19 (dd, *J* = 4.5, 9.9 Hz, 1H), 2.75 – 2.95 (m, 1H), 2.33 – 2.64 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 133.78, 129.68, 129.09, 127.22, 118.77, 37.02, 29.73.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.98 (m, 3F), -113.73—-114.03 (m, 2F), -124.36 (dd, *J* = 12.7, 8.7 Hz, 2F), -125.93 (dd, *J* = 12.7, 8.7 Hz, 2F).
HRMS (EI): $C_{13}H_8F_9N$ Calcd: 349.0513, Found: 349.0516.



4c

2-(4-(tert-butyl)phenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (4c), 139.4mg, yield:86%. Light yellow liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.16 (dd, *J* = 10.1, 4.2 Hz, 1H), 2.73 – 2.93 (m, 1H), 2.41 – 2.62 (m, 1H), 1.33 (s, 9H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 152.29, 130.76, 126.89, 126.60, 118.96, 37.03 (t, *J* = 21 Hz), 34.66, 31.16, 29.21.
19F NMR (282 MHz, $CDCl_3$) δ -81.11– -81.04 (m, 3F), -112.78– -113.84 (m, 1F), -114.16– -115.22 (m, 1F), -124.44 (d, *J* = 8.5 Hz, 2F), -125.99 (t, *J* = 14.1 Hz, 2F).
HRMS (ESI): $C_{17}H_{16}F_9N+Na^+$ Calcd: 428.1031, Found: 428.1037.



4d

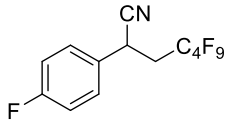
4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-methoxyphenyl)heptanenitrile (4d), 130.4mg, yield: 86%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 4.15 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.82 (s, 3H), 2.71–2.92 (m, 1H), 2.41–2.60 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.99, 128.42, 125.63, 119.07, 114.93, 55.36, 37.04 (t, *J* = 21 Hz), 28.98.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.05– -81.12 (m, 3F), -112.03– -114.05 (m, 1F), -114.35 (dd, *J* =149.2, 136.3 Hz, 1F), -123.17– -125.15 (m, 2F), -126.00 (dd, *J* = 16.0, 7.6 Hz, 2F).

HRMS (ESI): $C_{14}H_{10}F_9NO+Na^+$ Calcd: 402.0511, Found: 402.0523.



4e

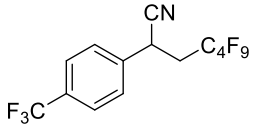
4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-fluorophenyl)heptanenitrile (4e), 130.7mg, yield: 89%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.41 (m, 2H), 7.13 (t, *J* = 8.7 Hz, 2H), 4.21 (dd, *J* = 9.7, 4.6 Hz, 1H), 2.74–2.94 (m, 1H), 2.44–2.62 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.90 (d, *J* = 247.5 Hz), 129.60 (d, *J* = 3.8 Hz), 129.12 (d, *J* = 3.8 Hz), 118.63, 116.69 (d, *J* = 21.8 Hz), 36.88 (t, *J* = 21.0 Hz), 29.09.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.17 (t, J = 9.3 Hz, 3F), -112.10 (d, *J* = 2.1 Hz, 1F), -113.84–114.05 (m, 2F), -114.48(d, *J* = 2.8 Hz, 2F), -126.09 (dd, *J* = 16.0, 7.6 Hz, 2F).

HRMS (ESI): $C_{13}H_7F_{10}N+Na^+$ Calcd: 390.0311, Found: 390.0322.



4f

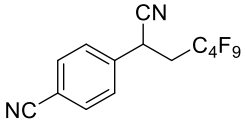
4,4,5,5,6,6,7,7,7-nonafluoro-2-(4-(trifluoromethyl)phenyl)heptanenitrile (4f), 145.1mg, yield: 87%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 4.28 (dd, *J* = 9.4, 4.8Hz, 1H), 2.78–2.98 (m, 1H), 2.47–2.67 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.61, 131.58 (d, *J* = 33 Hz), 127.85, 126.67 (t, *J* = 3.0 Hz), 123.52 (d, *J* = 270 Hz), 118.00, 36.69 (t, *J* = 21.8 Hz), 29.65.

^{19}F NMR (282 MHz, $CDCl_3$) δ -63.04 (s, 3F), -81.06– -81.14 (m, 3F), -111.58– -113.81 (m, 2F), -124.30– -124.43(m, 2F), -125.98 (dd, *J* = 11.7, 9.1 Hz, 2F).

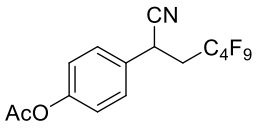
HRMS (ESI): $C_{14}H_7F_{12}N+Na^+$ Calcd: 440.0285, Found: 440.0292.



4g

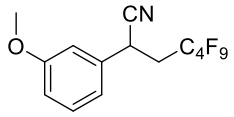
4-(1-cyano-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzonitrile (4g), 113.7mg, yield: 76%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 4.29 (dd, *J* = 9.1, 5.0 Hz, 1H), 2.78–2.99 (m, 1H), 2.48–2.67 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.63, 133.40, 128.29, 117.68, 117.64, 113.48, 36.45 (t, *J* = 21.0 Hz), 29.87.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.99– -81.07 (m, 3F), -112.86– -113.98 (m, 2F), -124.30 (t, *J* = 32.5 Hz, 2F), -125.88– -125.98 (m, 2F).
HRMS (ESI): $C_{14}H_7F_9N_2+Na^+$ Calcd: 397.0363, Found: 397.0361.



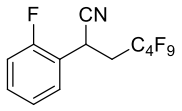
4h

4-(1-cyano-3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl acetate (4h), 127.0mg, yield:78%.
White solid, mp 44-45℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 4.20 (dd, *J* = 9.9, 4.4 Hz, 1H), 2.68–2.94 (m, 1H), 2.45–2.63 (m, 1H), 2.32 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.21, 151.06, 131.20, 128.45, 122.97, 118.54, 37.03, 28.80, (t, *J* = 21.0 Hz), 21.11.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.92– -81.01 (m, 3F), -112.48– -113.89 (m, 1F), -113.97– -115.19 (m, 1F), -124.36(d, *J* = 8.5 Hz, 2F), -125.92 (dd, *J* = 12.8, 8.6 Hz, 2F).
HRMS (ESI): $C_{15}H_{10}F_9NO_2+Na^+$ Calcd: 430.0460, Found: 430.0462.



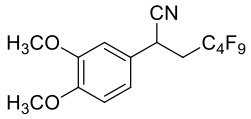
4i

4,4,5,5,6,6,7,7,7-nonafluoro-2-(3-methoxyphenyl)heptanenitrile (4i), 127.4mg, yield:84%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (t, *J* = 11.5, 1H), 6.94 (dd, *J* = 10.8, 7.4 Hz,3H), 4.15 (dd, *J* = 9.9, 4.3 Hz, 1H), 3.84 (s, 3H), 2.74 – 2.94 (m, 1H), 2.44 – 2.64 (m,1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.41, 135.19, 130.77, 119.29, 118.69, 114.28, 113.10, 55.40, 36.99 (t, *J* = 21.0 Hz), 29.68.
^{19}F NMR (282 MHz, $CDCl_3$) δ -79.72– -81.94 (m, 3F), -111.82– -113.88 (m, 1F), -113.79– -115.69 (m, 1F), -124.35(dd, *J* = 12.7, 5.7 Hz, 2F), -125.58– -126.61 (m, 2F).
HRMS (ESI): $C_{14}H_{10}F_9NO+Na^+$ Calcd: 402.0511, Found: 402.0525.



4j

4,4,5,5,6,6,7,7,7-nonafluoro-2-(2-fluorophenyl)heptanenitrile (4j), 126.3mg, yield: 86%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.55 (m, 2H), 7.12–7.27 (m, 2H), 4.48 (dd, *J* = 9.4, 4.7 Hz, 1H), 2.67–2.94 (m, 1H), 2.51–2.66 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 159.63 (d, *J* = 246.8 Hz), 131.25 (d, *J* = 8.3 Hz), 129.03 (d, *J* = 2.6 Hz), 125.27 (d, *J* = 3.7 Hz), 120.94 (d, *J* = 13.6 Hz), 117.80, 116.35 (d, *J* = 21.0 Hz), 35.12 (t, *J* = 21.0 Hz), 24.23.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.00– -81.10 (m, 3F), -112.91– -115.53 (m, 2F), -117.57 (s, 1F), -124.35– -124.46 (m, 2F), -125.91– -126.02 (m, 2F).
HRMS (ESI): $C_{13}H_7F_{10}N+Na^+$ Calcd: 390.0311, Found: 390.0330.



4k

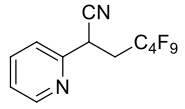
2-(3,4-dimethoxyphenyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (4k), 142.4mg, yield:87%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84–6.95 (m, 3H), 4.13 (dd, *J* = 9.8, 4.5 Hz, 1H), 3.92 (d, 3H), 3.90 (s, 3H), 2.73–2.94 (m, 1H), 2.43–2.63 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.77, 149.55, 126.00, 119.65, 118.99, 111.71, 109.95, 56.07, 56.00, 36.83 (t, *J* = 21.0 Hz), 29.38.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.96– -81.05 (m, 3F), -112.13– -113.99 (m, 1F), -113.99– -115.61 (m, 1F), -122.97– -125.25 (m, 2F), -124.83– -126.45 (m, 2F).

HRMS (ESI): $C_{15}H_{12}F_9NO_2$+Na^+ Calcd: 432.0617, Found: 432.0638.



4l

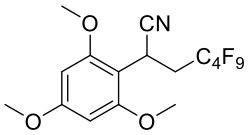
4,4,5,5,6,6,7,7,7-nonafluoro-2-(pyridin-2-yl)heptanenitrile (4l), 119.0mg, yield: 85%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, *J* = 4.5 Hz, 1H), 7.79 (td, *J* = 7.7, 1.6 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.21-7.36 (m, 1H), 4.36 (dd, *J* = 9.2, 4.8 Hz, 1H), 2.7-83.16(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.32, 150.27, 137.79, 123.80, 122.17, 118.16, 34.18 (t, *J* = 21.0 Hz), 31.69

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.99 – -81.07 (m, 3F), -111.09 – -113.50 (m,1F), -113.64 – -116.35 (m,1F), -122.57 – -125.15 (m, 2F), -125.97 (td, *J* = 12.7, 4.2 Hz, 2F).

HRMS (ESI): $C_{12}H_7F_9N_2$+Na^+ Calcd: 373.0363, Found: 373.0365.



4m

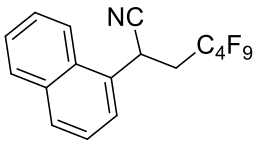
4,4,5,5,6,6,7,7,7-nonafluoro-2-(2,4,6-trimethoxyphenyl)heptanenitrile (4m), 100.1mg, yield:57%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.14 (s, 2H), 4.81 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.88 (s, 6H), 3.82 (s, 3H), 2.90–3.12 (m, 1H), 2.33–2.54 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.90, 158.33, 119.50, 102.70, 90.92, 55.95, 55.41, 33.02, 31.59, 18.02.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.00– -81.10 (m, 3F), -113.64– -114.74 (m, 1F), -115.27– -116.33 (m, 1F), -124.43– -124.52 (m, 2F), -125.95– -126.04 (m, 2F).

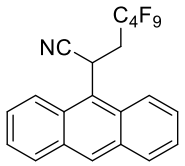
HRMS (ESI): $C_{16}H_{14}F_9NO_3$+Na^+ Calcd: 462.0722, Found: 462.0746.



4n

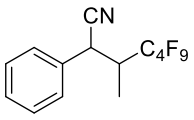
4,4,5,5,6,6,7,7,7-nonafluoro-2-(naphthalen-1-yl)heptanenitrile (4n), 118.1mg, yield: 74%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77–7.97 (m, 4H), 7.51–7.68 (m, 3H), 4.96 (dd, *J* = 10.5, 2.5 Hz, 1H), 2.85–3.02 (m, 1H), 2.59–2.82 (m, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 134.21, 130.10, 129.73, 129.18, 129.09, 127.78, 126.59, 126.08, 125.55, 121.03, 119.05, 36.03 (t, *J* = 21.8 Hz), 26.60.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.97 (dd, *J* = 9.5, 2.8 Hz, 3F), -111.28– -114.04 (m, 1F), -114.76 (dd, *J* = 147.9, 134.8 Hz, 1F), -124.30 (d, *J* = 8.8 Hz, 2F), -125.85 (t, *J* = 11.3 Hz, 2F).
HRMS (ESI): $C_{17}H_{10}F_9N+Na^+$ Calcd: 422.0562, Found: 422.0583.



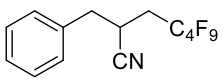
4o

2-(anthracen-9-yl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (4o), 120.4mg, yield: 67%.
Light yellow liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.4 Hz, 1H), 7.54–7.29 (m, 7H), 6.08 (t, *J* = 7.8 Hz, 1H), 4.78 (t, *J* = 16.2 Hz, 1H), 3.68 (dd, *J* = 17.8, 7.8 Hz, 1H), 3.48 (dd, *J* = 17.9, 7.8 Hz, 1H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 140.35, 139.51, 135.25, 130.97, 130.73, 130.08, 128.92, 128.34, 128.03, 127.43, 127.37, 124.58, 117.91, 114.72, 48.94 (t, *J* = 22.5 Hz), 18.48.
^{19}F NMR (282 MHz, $CDCl_3$) δ -79.55– -82.64 (m, 3F), -111.62– -111.83 (m, 2F), -119.37– -119.45 (m, 2F), -125.74– -125.93 (m, 2F).
HRMS (ESI): $C_{21}H_{12}F_9N+Na^+$ Calcd: 472.0718, Found: 472.0715.



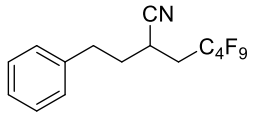
4p

4,4,5,5,6,6,7,7,7-nonafluoro-3-methyl-2-phenylheptanenitrile (4p), 69.7mg, yield: 48%.
Colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.48 (m, 5H), 4.48 (d, *J* = 2.1 Hz, 1H), 2.59–2.72 (m, 1H), 1.27 (d, *J* = 7.0 Hz, 3H）.
^{13}C NMR (75 MHz, $CDCl_3$) δ 132.92, 129.41, 128.81, 127.60, 116.86, 41.99 (t, *J* = 20.3 Hz), 36.06, 8.49.
^{19}F NMR (282 MHz, $CDCl_3$) δ -79.74– -81.79 (m, 3F), -113.10– -115.01 (m, 1F), -117.23– -118.71 (m, 1F), -119.78– -121.26 (m, 1F), -121.26– -122.83 (m, 1F), -124.24– -125.88 (m, 1F), -125.96– -127.70 (m, 1F).
HRMS (ESI): $C_{14}H_{10}F_9N+Na^+$ Calcd: 386.0562, Found: 386.0555.



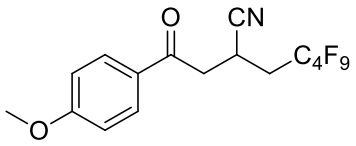
6a

2-benzyl-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (6a), 114.7mg, yield: 79%.
White solid, mp 43℃
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.41 (m, 5H), 3.17–3.27 (m, 1H), 3.28–3.10 (m, 2H), 2.23–2.60 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 134.97, 129.09, 127.99, 119.53, 38.38, 32.61, 25.94.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.96– -81.05 (m, 3F), -112.29– -114.63 (m, 2F), -124.30– -126.02 (m, 4F).
HRMS (ESI): $C_{14}H_{10}F_9N+Na^+$ Calcd: 386.0567, Found: 386.0565.



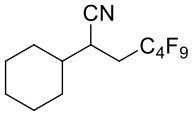
6b

4,4,5,5,6,6,7,7,7-nonafluoro-2-phenethylheptanenitrile (6b), 125.2mg, yield: 83%.
Yellow liquid
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19–7.36 (m, 5H), 2.88–3.01 (m, 2H), 2.71–2.89 (m, 1H), 2.41–2.67(m, 1H), 2.28–2.39 (m, 1H), 1.96–2.19 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.04, 128.85, 128.37, 126.80, 119.65, 34.27, 33.39 (t, *J* = 21.0 Hz), 32.82, 23.52.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.01– -81.10 (m, 3F), -113.58– -113.82 (m, 2F), -124.41– -124.53 (m, 2F), -125.93– -126.04 (m, 2F).
HRMS (ESI): $C_{15}H_{12}F_9N+Na^+$ Calcd: 400.0718, Found: 400.0717.



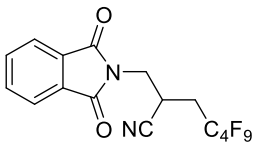
6c

4,4,5,5,6,6,7,7,7-nonafluoro-2-(2-(4-methoxyphenyl)-2-oxoethyl)heptanenitrile. (6c),
116.2mg, yield: 69%. White solid, mp 125-126℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 3.90 (s, 3H), 3.67 (s, 1H), 3.35 – 3.55 (m, 2H), 2.49–2.68 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 192.39, 164.38, 130.44, 128.39, 119.83, 114.13, 55.60, 39.86, 32.56, 19.43.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.98 (t, *J* = 9.0 Hz, 2F), -112.41– -114.81 (m, 2F), -124.34(d, *J* = 7.8 Hz, 2F), -125.90 (t, *J* = 10.4 Hz, 3F).
HRMS (ESI): $C_{16}H_{12}F_9NO_2+Na^+$ Calcd: 4444.0622, Found: 444.0616.



6d

2-cyclohexyl-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (6d), 130.7mg, yield: 92%.
White solid, mp 43-44℃
^{1}H NMR (300 MHz, $CDCl_3$) δ 2. 72–2.98 (m, 1H), 2.40–2.70. (m, 1H), 2.12–2.40 (m, 1H), 1.68–2.00(m, 5H), 1.59 (s, 1H), 1.27–1.36 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 119.13, 39.96, 31.42 (t, *J* = 21.8 Hz), 30.01, 28.47, 25.78, 25.58.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.12 (dd, *J* = 8.0, 4.8 Hz, 3F), -112.14– -116.35 (m, 2F),-123.04– -125.49 (m, 2F), -125.16– -126.96 (m, 2F).
HRMS (ESI): $C_{13}H_{14}F_9N+Na^+$ Calcd: 378.0875, Found: 378.0883.



6e

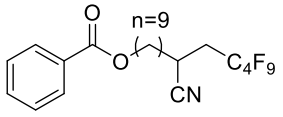
2-((1,3-dioxoisoindolin-2-yl)methyl)-4,4,5,5,6,6,7,7,7-nonafluoroheptanenitrile (6e), 146.9mg, yield:85%. White solid, mp 111-112℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 4.14 (dd, *J* =13.8, 7.9 Hz, 1H), 3.95 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.53–3.63 (m, 1H), 2.38–2.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.58, 134.71, 131.42, 123.94, 117.56, 38.81, 31.55 (t, *J* = 22.5 Hz), 24.15.

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.98– -81.07 (m, 3F), -111.21– -114.98 (m, 2F), -122.97– -125.21 (m, 2F), -124.92– -126.50 (m, 2F).

HRMS (ESI): $C_{16}H_9F_9N_2O_2$+Na^+ Calcd: 455.0413, Found: 455.0401.



6f

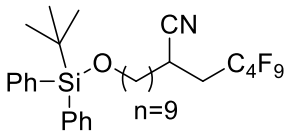
10-cyano-12,12,13,13,14,14,15,15,15-nonafluoropentadecyl benzoate (6f), 149.5mg, yield:72%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (t, *J* = 2.1 Hz, 2H), 7.53–7.59 (m, 1H), 7. 34–7.50 (m, 2H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.87–3.08 (m, 1H), 2. 40–2.66 (m, 1H), 2.11–2.38 (m, 1H), 1.86–1.67 (m, 4H), 1.33–1.85(s, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.68, 132.83, 130.47, 129.51, 128.32, 119.97, 65.04, 33.42 (t, *J* = 21.0 Hz), 32.65, 29.30, 29.15, 28.81, 28.67, 26.71, 25.97, 24.06.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.03– -81.11 (m, 3F), -113.71– -114.00 (m, 2F), -124.42– -124.53 (m, 2F), -125.96– -126.07 (m, 2F).

HRMS (ESI): $C_{23}H_{26}F_9NO_2$+Na^+ Calcd: 542.1712, Found: 542.1704.



6g

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11-((tert-butyldiphenylsilyl)oxy)-2-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)undecanenitrile (6g), 193.4mg, yield: 74%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.69 (m, 4H), 7.35–7.43 (m, 6H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.91–3.01 (m, 1H), 2.17–2.64 (m, 2H), 1.67–1.75 (m, 2H), 1.1.27–1.61 (m, 14H), 1.05 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.58, 134.15, 129.50, 127.58, 120.00, 63.96, 33.47 (t, *J* = 21.0 Hz), 32.70, 32.55, 29.42, 29.28, 29.21, 28.86, 26.86, 26.76, 25.73, 24.09, 19.23.

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.94– -81.04 (m, 3F), -113.70– -113.94 (m, 2F), -124.37– -124.48 (m, 2F), -125.90– -126.01 (m, 2F).

HRMS (ESI): $C_{32}H_{40}F_9NOSi$+Na^+ Calcd: 676.2628, Found: 676.2519.

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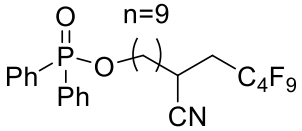
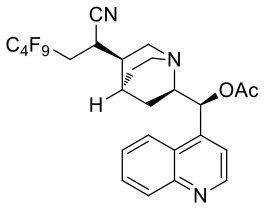


6h

10-cyano-12, 12, 13, 13, 14, 14, 15, 15, 15-nonafluoropentadecyl diphenylphosphinate (6h), 210.52, yield: 85%. Colourless liquid.

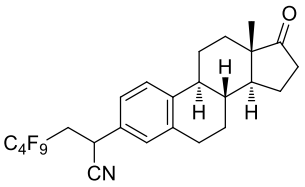
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.83 (m, 4H), 7.42–7.53 (m, 6H), 4.01 (q, *J* = 6.7 Hz, 2H), 2.91–3.01 (m, 1H), 2.43–2.64 (m, 1H), 2.18–2.38 (m, 1H), 1.62–1.78 (m, 4H), 1.35–1.61 (m, 4H), 1.29–1.60 (m, 12H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 132.52, 132.11, 132.08, 131.68, 131.55, 130.70, 128.60, 128.42, 119.97, 64.95 (d, *J* = 6.1 Hz), 33.43 (t, *J* = 21.0 Hz), 32.65, 30.50 (d, *J* = 6.6 Hz), 29.25, 29.13, 29.02, 28.78, 26.71, 25.54, 24.07.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.98– -81.06 (m, 3F), -113.70– -113.96 (m, 2F), -124.39– -124.49 (m, 2F), -125.93– 126.03 (m, 2F).
^{31}P NMR (121 MHz, $CDCl_3$) δ 31.21.
HRMS (ESI): $C_{28}H_{31}F_9NO_2P+Na^+$ Calcd: 638.1841, Found: 638.1912.



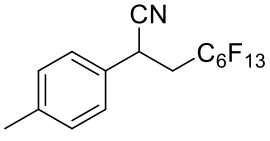
6i

(1S)-((2R,4S,5S)-5-((S)-1-cyano-3,3,4,4,5,5,6,6,6-nonafluorohexyl)quinuclidin-2-yl)(quinolin-4-yl)methyl acetate (6i), 176.8mg, yield:76%, d.r. = 2:1. Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, *J* = 4.3 Hz, 1H), 8.11 (dd, *J* = 17.0, 8.6 Hz, 2H), 7.44–7.87 (m, 2H), 7.34 (d, *J* = 4.4 Hz, 1H), 6.58 (t, *J* = 8.4 Hz, 1H), 2.30–3.27 (m, 8H), 2,15 (s, 3H), 1.53–1.86 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 169.67, 149.97, 148.52, 144.37, 130.59, 129.45, 127.20, 125.39, 122.98, 118.96, 117.83, 73.71, 58.57, 49.70, 48.99, 48.96, 37.45, 31.88, 26.11, 26.42, 25.43, 24.42, 21.71, 21.02.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.89– -80.98 (m, 3F), -111.49– -114.97 (m, 2F), -124.11– -124.18 (m, 2F), -125.80– -125.88 (m, 2F).
HRMS (ESI): $C_{26}H_{24}F_9N_3O_2+H^+$ Calcd: 582.1725, Found: 582.1816.



6j

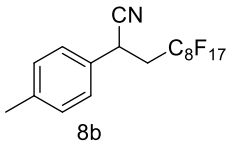
4,4,5,5,6,6,7,7,7-nonafluoro-2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)heptanenitrile (6j), 187.0mg, yield: 89%, d.r. > 20:1. Colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.13 (dd, *J* = 10.1, 4.2 Hz, 1H), 2.94 (dd, *J* = 8.7, 3.9 Hz, 2H), 2.67–2.88 (m, 1H), 2.37–2.67 (m, 3H), 2.30 (t, *J* = 8.4 Hz, 1H), 1.90–2.23 (m, 4H), 1.35–1.78 (m, 6H), 0.91 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 140.87, 138.17, 131.23, 127.67, 126.69, 124.46, 118.93, 50.41, 47.89, 44.24, 37.91, 37.30 (t, *J* = 21.0 Hz), 37.02, 31.50, 29.29, 26.23, 25.64, 21.55, 13.78.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.98– -81.07 (m, 3F), -112.72– -115.14 (m, 2F), -124.37 (t, *J* = 7.6 Hz, 2F), -125.80– -125.98 (m, 2F).
HRMS (ESI): $C_{25}H_{24}F_9NO+Na^+$ Calcd: 548.1612, Found: 548.1615.



8a

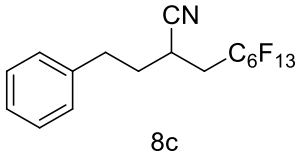
4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-(*p*-tolyl)nonanenitrile (8a), 163.0mg, yield: 88%. Colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.29 (m, 4H), 4.15 (dd, *J* = 9.8, 4.5 Hz, 1H), 2.72–2.93 (m, 1H), 2.46–2.61 (m, 1H), 2.37 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.08, 130.83, 130.26, 127.05, 118.93, 37.15 (t, *J* = 20.3 Hz), 29.38, 21.03.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.83– -80.91 (m, 3F), -113.47– -113.87 (m, 2F), -121.77– -121.86 (m, 2F), -122.84– -122.93 (m, 2F), -123.42– -123.55 (m, 2F), -126.14– -126.27 (m, 2F).
HRMS (ESI): $C_{16}H_{10}F_{13}N+Na^+$ Calcd: 486.0498, Found: 486.0512.



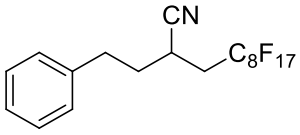
8b

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-(*p*-tolyl)undecanenitrile (8b), 193.7mg, yield: 86%. White solid, mp 65-66℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.29 (m, 4H), 4.16 (dd, *J* = 9.8, 4.5 Hz, 1H), 2.72–2.93 (m, 1H), 2.42–2.61 (m, 1H), 2.37 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.08, 130.82, 130.26, 127.06, 118.95, 37.16, 29.38, 21.06.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.82 (dd, *J* = 9.9 Hz, 3F), -113.48– -113.87 (m, 2F), -121.58– -123.48 (m, 10F), -126.12– -126.27 (m, 2F).
HRMS (ESI): $C_{18}H_{10}F_{17}N+Na^+$ Calcd: 586.0439, Found: 586.0433.



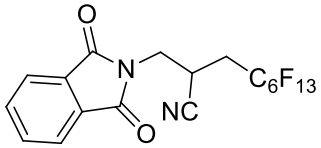
8c

4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-phenethylnonanenitrile (8c), 158.4mg, yield: 83%. White solid, mp 47-48℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.35 (m, 5H), 2.85–3.01 (m, 2H), 2.76–2.84 (m, 1H), 2.44–2.65 (m, 1H), 2.18–2.38 (m, 1H), 1.94–2.15 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.04, 128.83, 128.36, 126.78, 119.63, 34.27, 33.49 (t, *J* = 22.5 Hz), 32.82, 23.55.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.85– -80.94 (m, 3F), -113.34– -113.58 (m, 2F), -121.81– -121.89 (m, 2F),-122.81– -122.94 (m, 2F), -123.47– -123.63 (m, 2F), -126.15– -126.29 (m, 2F).
HRMS (ESI): $C_{18}H_{14}F_{13}N+Na^+$ Calcd: 500.0654, Found: 500.0667.



8d

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-2-phenethylundecanenitrile (8d), 196.2mg, yield: 85%. White solid, mp 75-76℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.36 (m, 5H), 2.87–3.13 (m, 2H), 2.71–2.89 (m, 1H), 2.44–2.69(m, 1H), 2.19–2.33 (m, 1H), 1.94–2.14 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.02, 128.84, 128.36, 126.79, 119.64, 34.28, 33.50, 32.82, 23.55
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.82 (t, *J* = 9.9 Hz, 3F), -113.34– -113.56 (m, 2F), -121.61– -123.48 (m, 10F), -126.12– -126.24 (m, 2F).
HRMS (ESI): $C_{20}H_{14}F_{17}N+Na^+$ Calcd: 600.0590, Found: 600.0627.



8e

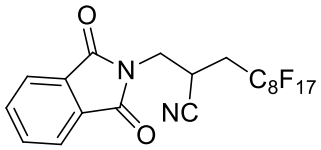
2-((1,3-dioxoisoindolin-2-yl)methyl)-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanenitrile (8e), 168.1mg, yield:79%. White solid, mp 127-128℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.2, 3.1 Hz, 2H), 7.79 (dd, *J* = 5.3, 3.0 Hz, 2H), 4.13 (dd, *J* =13.8, 7.9 Hz, 1H), 3.95 (dd, *J* = 13.8, 6.8 Hz, 1H), 3.49–3.65 (m, 1H), 2.38–2.77 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.57, 134.71, 131.42, 123.95, 117.53, 38.82, 31.82(t, *J* = 20.6 Hz), 24.17.

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.81 (t, *J* = 9.8 Hz, 3F), -112.00– -114.30 (m, 2F), -121.81 (s, 2F), -122.88 (s, 2F), -123.26 (t, *J* = 12.9 Hz, 2F), -126.17 (td, *J* = 15.1, 6.8 Hz, 2F).

HRMS (ESI): $C_{18}H_9F_{13}N_2O_2$+Na^+ Calcd: 555.0354, Found: 555.0360.



8f

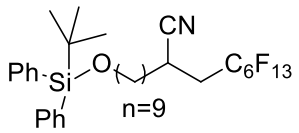
2-((1,3-dioxoisoindolin-2-yl)methyl)-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro undecanenitrile (8f), 207.3mg, yield: 82%. White solid, mp 150-151℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–7.94 (m, 2H), 7.78–7.81 (m, 2H), 4.13 (dd, *J* = 13.8, 7.8Hz, 1H), 3.95 (dd, *J* = 13.8, 6.9 Hz, 1H), 3.68–3.47 (m, 1H), 2.81–2.30 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.56, 134.71, 131.42, 123.97, 117.51, 38.82, 31.70, 24.16

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.78 (t, *J* = 9.9 Hz, 3F), -112.94– -113.31 (m, 2F), -121.56– -123.23 (m, 10F), -126.08– -126.20 (m, 2F).

HRMS (ESI): $C_{20}H_9F_{17}N_2O_2$+Na^+ Calcd: 655.0285, Found: 655.0325.



8g

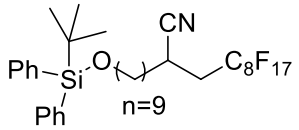
11-((tert-butyldiphenylsilyl)oxy)-2-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)undecane nitrile (8g), 253.1mg, yield: 84%. Colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.68 (m, 4H), 7.34–7.44 (m, 6H), 3.66 (t, *J* = 6.5 Hz, 2H), 2.90–3.00 (m, 1H), 2.43–2.64 (m, 1H), 2.17–2.37 (m, 1H), 1.73 (ddd, *J* = 11.7, 8.9, 5.8 Hz, 2H), 1.67–1.49 (m, 3H), 1.50–1.17 (m, 11H), 1.07 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.58, 134.17, 129.49, 127.57, 119.97, 63.96, 33.58 (t, *J* = 21.8 Hz), 32.71, 32.55, 29.41, 29.27, 29.20, 28.85, 26.85, 26.75, 25.73, 24.12, 19.22.

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.79– -80.88 (m, 3F), -113.44– -113.70 (m, 2F), -121.78– -121.87 (m, 2F), -122.81– 122.90 (m, 2F), -123.42– 123.55 (m, 2F), -125.18– -127.41 (m, 2F).

HRMS (ESI): $C_{34}H_{40}F_{13}NOSi$+Na^+ Calcd: 776.2569, Found: 776.2560.



8h

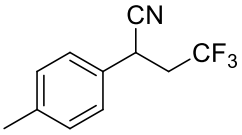
2-(9-((tert-butyldiphenylsilyl)oxy)nonyl)-4,4,5,5,6,6,7,7,8,8,9,10,10,11,11,11-hexadecafluoro-9-methylundecanenitrile (8h), 293.5mg, yield: 86%. Colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65–7.68 (m, 4H), 7.34–7.45 (m, 6H), 3.67 (t, *J* = 6.5 Hz, 2H), 2.90–3.00 (m, 1H), 2.43–2.64 (m, 1H), 2.17–2.37 (m, 1H), 1.62–1.75 (m, 2H), 1.54–1.61 (m, 4H), 1.33 (br, 11H), 1.05 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 135.57, 134.18, 129.48, 127.56, 119.95, 63.96, 33.60 (t, *J* = 21.8 Hz), 32.72, 32.54, 29.40, 29.26, 29.19, 28.85, 26.85, 26.75, 25.72, 24.12, 19.22.

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.82 (t, *J* = 9.9 Hz, 3F), -113.42– -113.65 (m, 2F), -121.59– -122.75(m, 10F), -123.43 (s, 2F), -126.09– -126.21 (m, 2F).

HRMS (ESI): $C_{36}H_{40}F_{17}NOSi+Na^+$ Calcd: 876.2520, Found: 876.2526.



8i

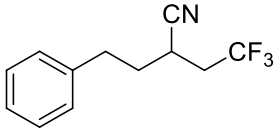
4,4,4-trifluoro-2-(*p*-tolyl)butanenitrile (8i), 64.7mg, yield: 76%, Colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (q, *J* = 8.4 Hz, 4H), 4.05 (dd, *J* = 4.5, 9.8 Hz, 1H), 2.69-2.88 (m, 1H), 2.34-2.64 (m, 1H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.01, 130.50, 130.19, 127.06, 124.74 (q, *J* = 276.0 Hz), 118.82, 39.66 (q, *J* = 27.0 Hz), 30.85 (q, *J* = 3.75 Hz), 21.02.

^{19}F NMR (282 MHz, $CDCl_3$) δ -60.08.

HRMS (ESI): $C_{11}H_{10}F_3N+Na^+$ Calcd: 236.0658, Found: 236.0660.



8j

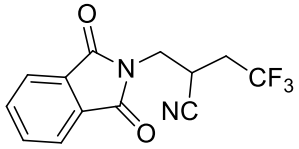
4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-2-phenethylnonanenitrile (8j), 158.4mg, yield: 83%. White solid, mp 47-48℃.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18–7.35 (m, 5H), 2.73–2.99 (m, 3H), 2.24–2.63 (m, 2H), 1.93–2.11(m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.10, 130.56, 128.84, 126.88, 124.99 (q, *J* = 276.8 Hz), 119.45, 36.38 (q, *J* = 29.3 Hz), 33.68, 32.79, 24.94 (d, *J* = 3.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.75.

HRMS (ESI): $C_{12}H_{12}F_3N+Na^+$ Calcd: 250.0820, Found: 250.0823.

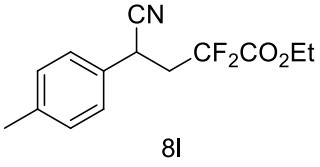


8k

2-((1,3-dioxoisoindolin-2-yl)methyl)-4,4,4-trifluorobutanenitrile (8k), 78.3mg, yield: 73%. Colourless liquid.

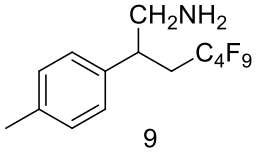
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89–7.93 (m, 2H), 7.77–7.81 (m, 2H), 4.11 (dd, *J* = 13.8, 6.0Hz, 1H), 3.93 (dd, *J* = 13.8, 6.9 Hz, 1H), 3.43–3.53 (m, 1H), 2.40–2.74 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.57, 134.71, 131.42, 124.78 (q, *J* = 274.5 Hz), 123.92, 117.33, 38.45, 34.47 (q, *J* = 30.0 Hz), 25.46 (d, *J* = 2.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -64.80.
HRMS (ESI): $C_{13}H_9F_3N_2O_2$+Na^+ Calcd: 305.0514, Found: 305.0511.



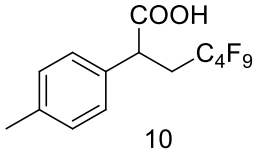
8l

ethyl 4-cyano-2,2-difluoro-4-(*p*-tolyl)butanoate (8l), 61.0mg, yield: 57%.
Colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19–7.26 (m, 4H), 4.27 (qd, *J* = 7.1, 1.3 Hz, 2H), 4.08 (dd, *J*= 9.4, 5.1 Hz, 1H), 2.75–2.92 (m, 1H), 2.48–2.66 (m, 1H), 2.36 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.89 (t, *J* = 31.5 Hz), 138.78, 131.08, 130.06, 127.22, 119.34, 113.86 (t, *J* = 251.3 Hz), 63.50, 40.22 (t, *J* = 23.3 Hz), 30.33 (t, *J* = 4.5 Hz), 21.09, 13.82.
^{19}F NMR (282 MHz, $CDCl_3$) δ -105.28 (d, *J* = 2.3 Hz).
HRMS (ESI): $C_{14}H_{15}F_2NO_2$+Na^+ Calcd: 290.0963, Found: 290.0970.



9

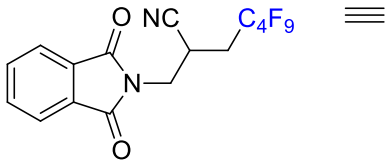
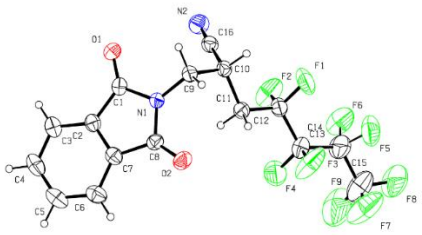
4,4,5,5,6,6,7,7,7-nonafluoro-2-(*p*-tolyl)heptan-1-amine (9), 116.0mg, yield: 79%
Colourless liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.88–3.10 (m, 3H), 2.38–2.53 (m, 2H), 2.34 (s, 3H), 1.64 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.45, 136.83, 129.57, 127.45, 47.72, 41.24, 34.24 (t, *J* = 21.8 Hz), 21.00.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.06– -81.15 (m, 3F), -112.81– -112.92 (m, 2F), -124.41– -124.52(m, 2F), -125.91– -126.03 (m, 2F).
HRMS (ESI): $C_{14}H_{14}F_9N$+H^+ Calcd: 368.1055, Found: 368.1061.



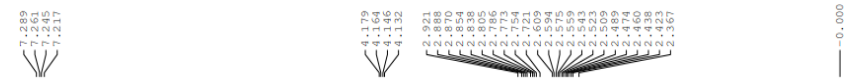
10

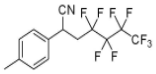
5,5,6,6,7,7,8,8,8-nonafluoro-3-(*p*-tolyl)octanoic acid (10), 129.9mg, yield: 85%.
White solid, mp 77-78℃.
^{1}H NMR (300 MHz, $CDCl_3$) δ 11.08 (br, 1H), 7.14–7.25 (m, 4H), 3.98 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.02–3.23 (m, 1H), 2.35–2.50 (m, 1H), 2.33 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.36, 138.29, 133.54, 129.87, 127.52, 43.26, 33.84 (t, *J* = 21.8 Hz), 21.05.
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.07– -81.15 (m, 3F), -112.62– -115.35 (m, 2F), -124.56– -124.61(m, 2F), -125.91– -126.08 (m, 2F).
HRMS (ESI): $C_{15}H_{13}F_9O_2$+Na^+ Calcd: 405.0508, Found: 405.0484.

8. X-ray structure of 6e

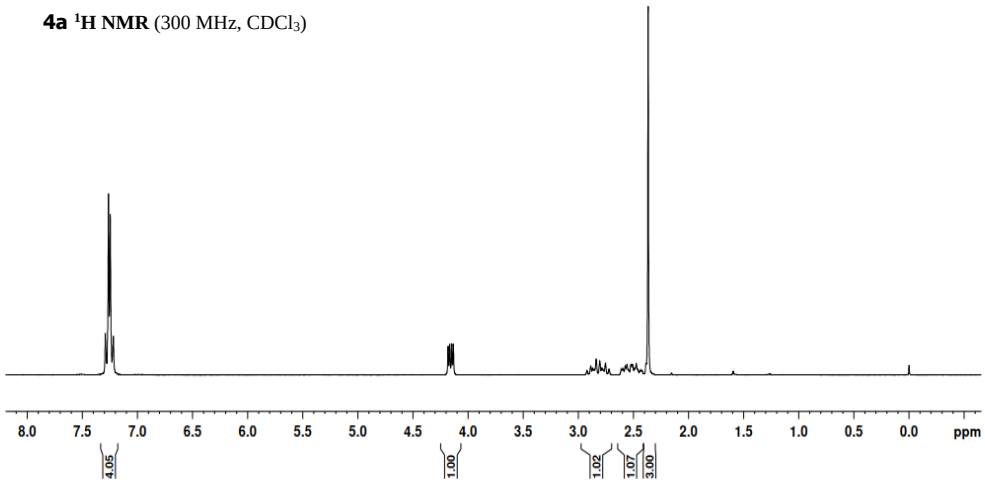
	
Identification code	guoqp_0508
Empirical formula	$C_{16}H_9F_9N_2O_2$
Formula weight	432.25
Temperature/K	291.08(10)
Crystal system	triclinic
Space group	P-1
a/Å	5.7476(7)
b/Å	11.2870(13)
c/Å	14.0380(17)
α/°	76.581(10)
β/°	85.498(10)
γ/°	83.205(10)
Volume/Å^3	878.38(18)
Z	2
ρ_{calc}g/cm^3	1.634
μ/mm^{-1}	0.172
F(000)	432.0
Crystal size/mm^3	0.21 × 0.15 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.14 to 52.04
Index ranges	$-7 \leqslant h \leqslant 7$, $-13 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$
Reflections collected	5554
Independent reflections	3444 [R_{int} = 0.0292, R_{sigma} = 0.0636]
Data/restraints/parameters	3444/42/280
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0905, wR_2 = 0.2296
Final R indexes [all data]	R_1 = 0.1501, wR_2 = 0.2871
Largest diff. peak/hole / e Å^{-3}	0.53/-0.37

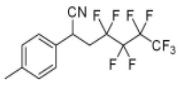
9. NMR spectra of new compounds



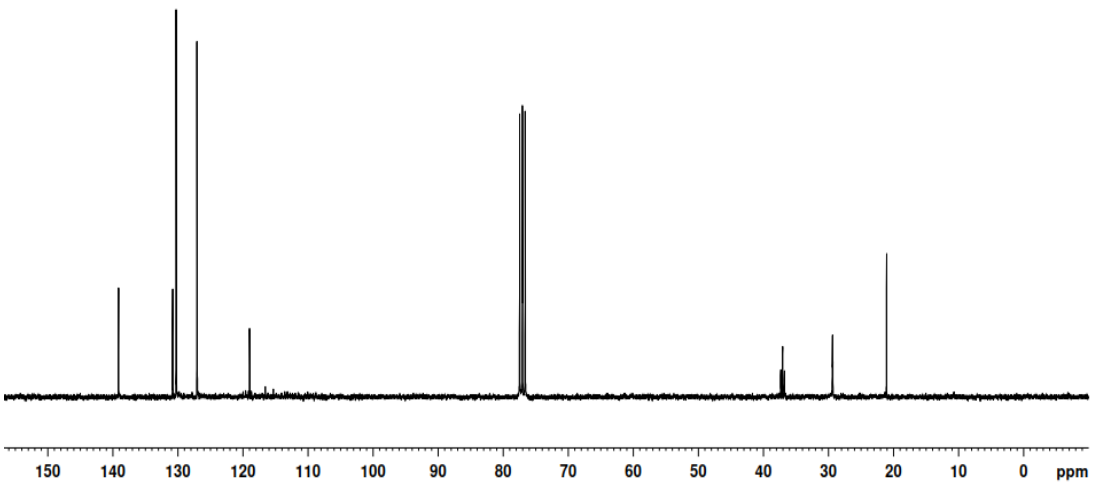


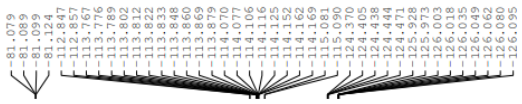
4a **^{1}H NMR** (300 MHz, $CDCl_3$)

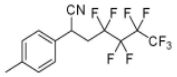




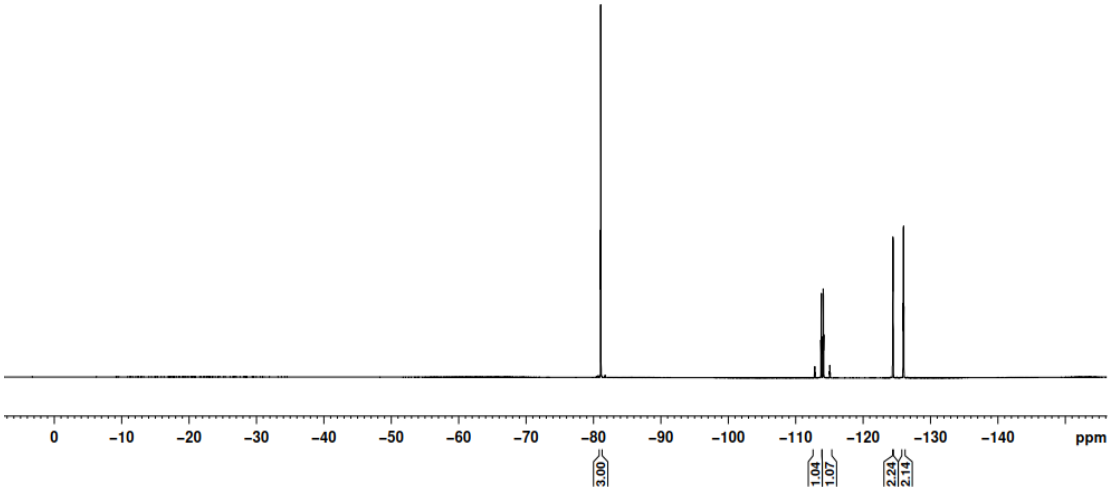
4a **^{13}C NMR** (75 MHz, $CDCl_3$)

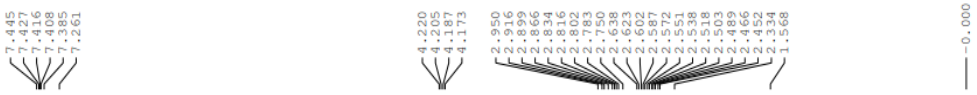


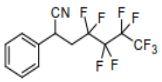




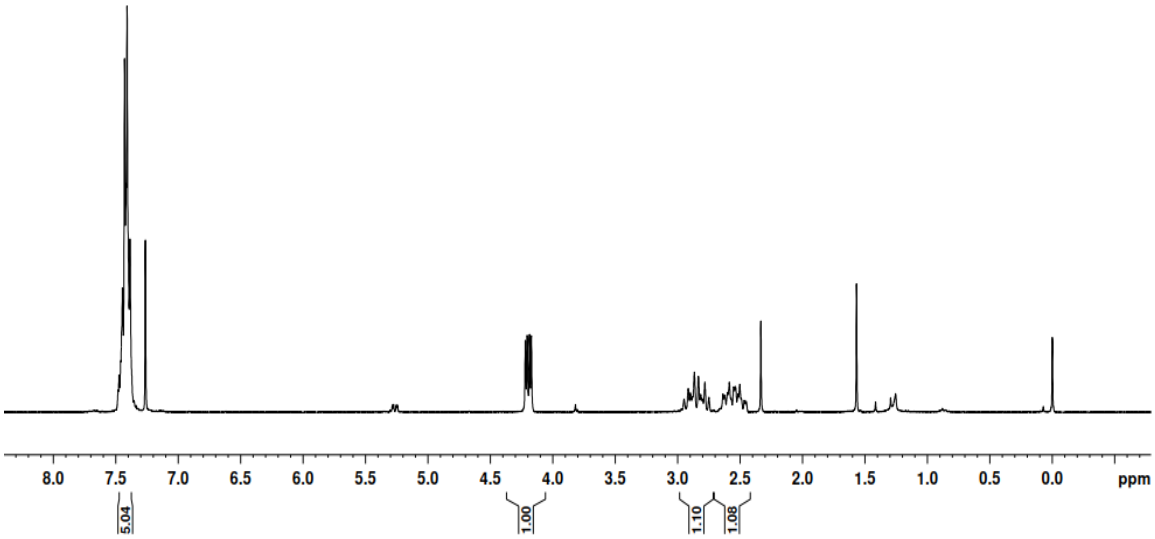
4a ^{19}**F NMR** (282 MHz, $CDCl_3$)

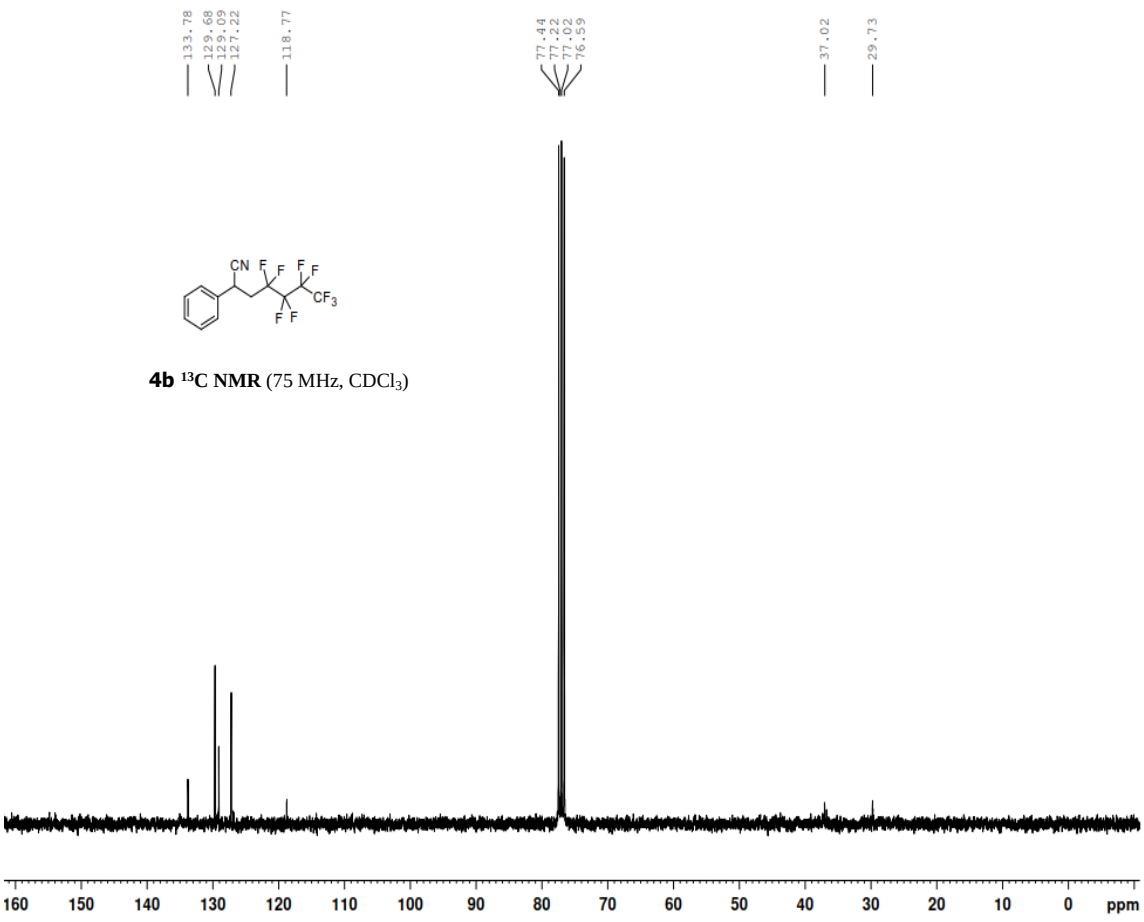




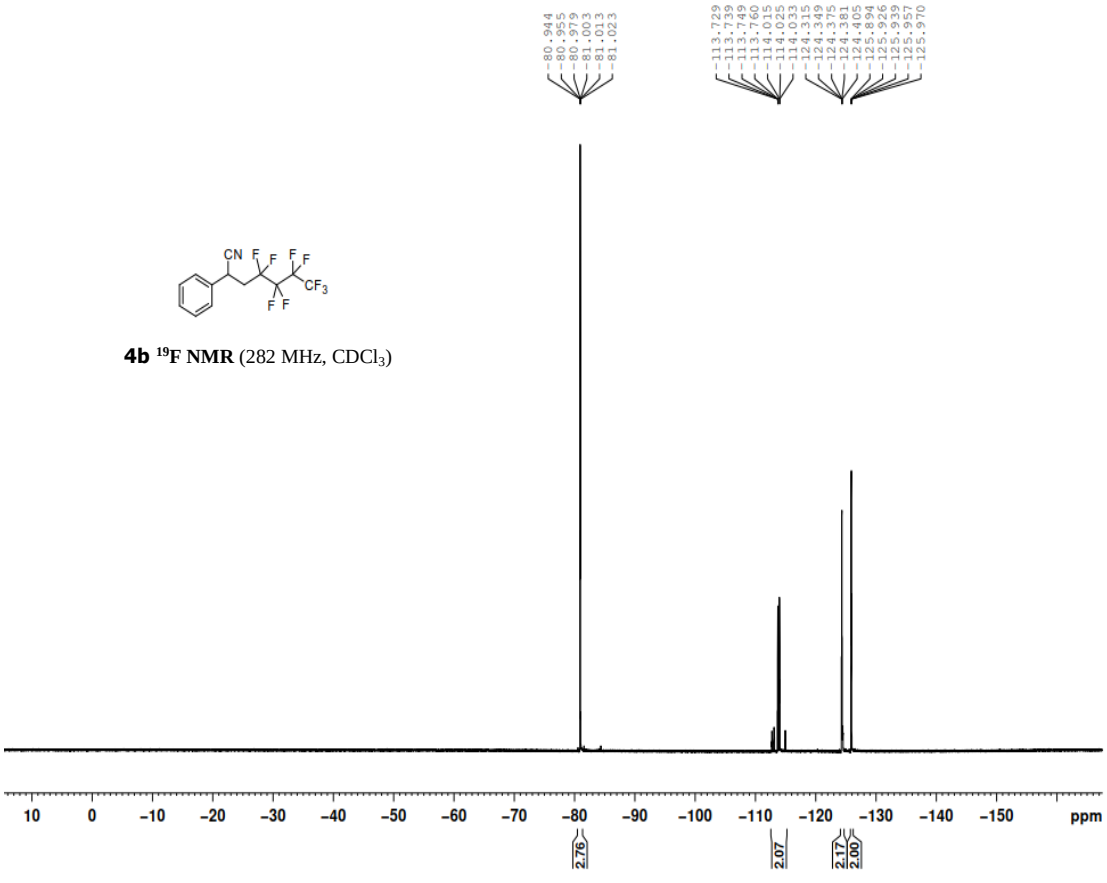


4b ^{1}**H NMR** (300 MHz, $CDCl_3$)

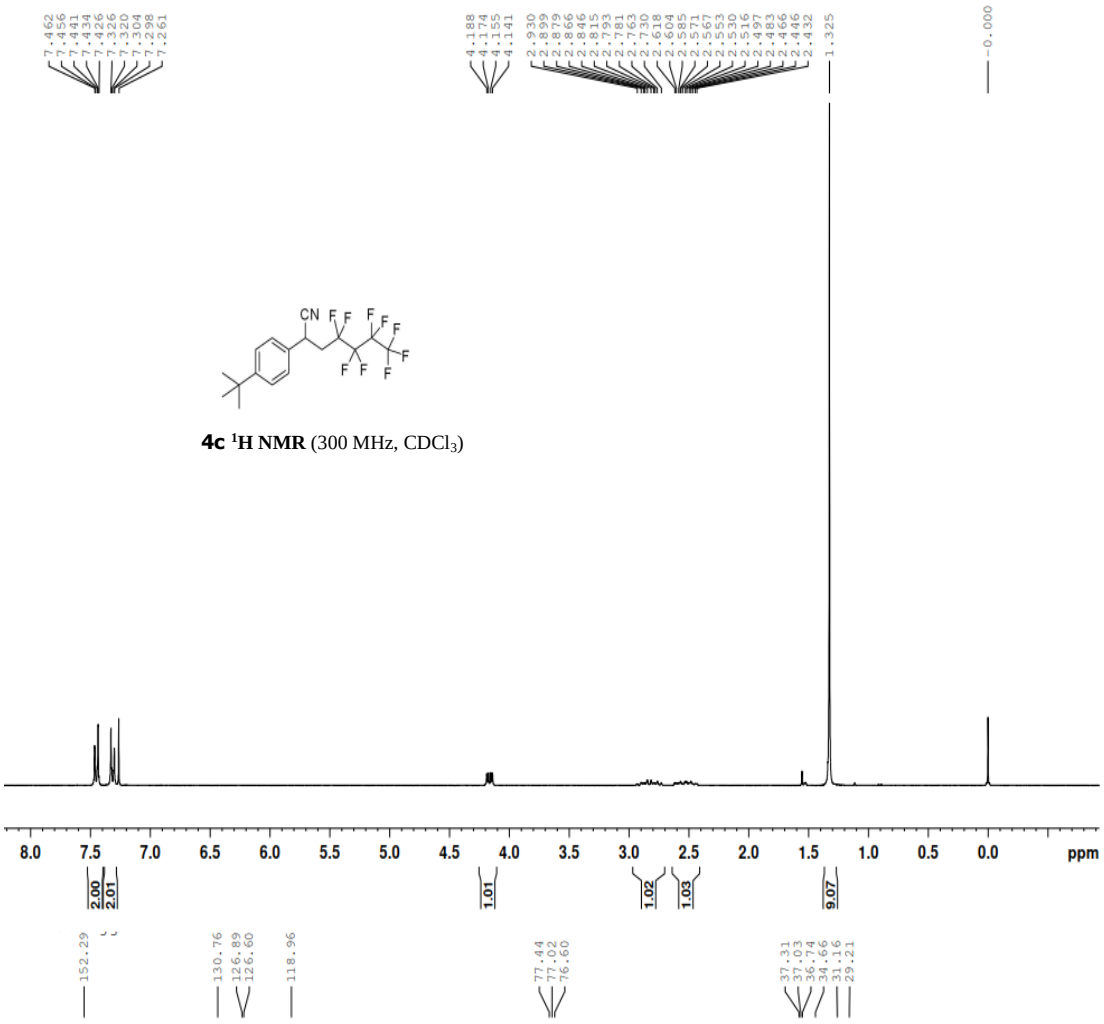




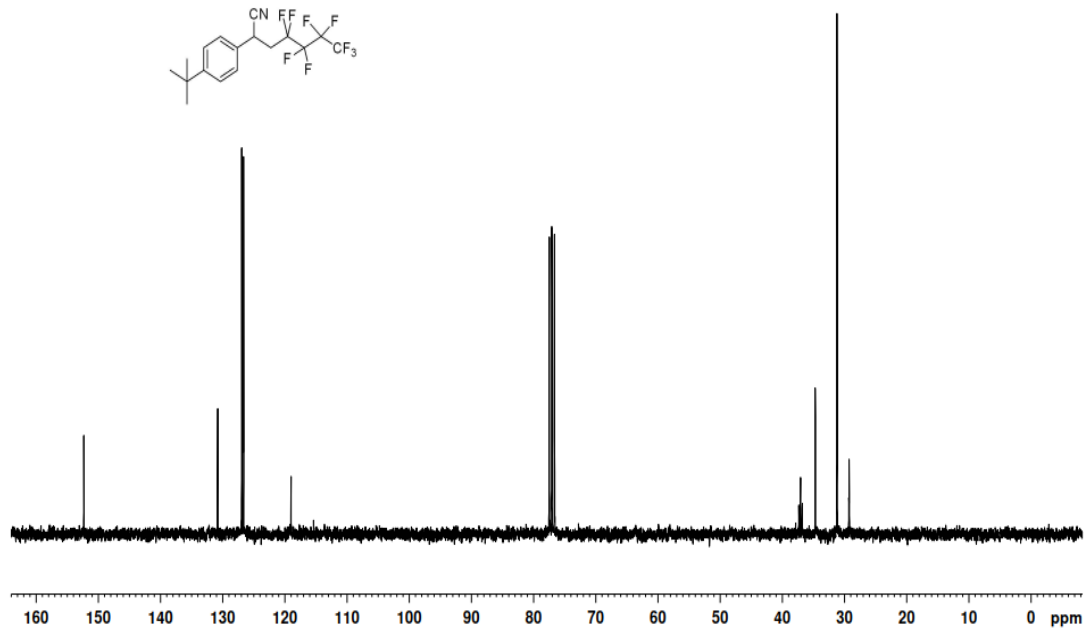
4b ^{13}**C NMR** (75 MHz, $CDCl_3$)



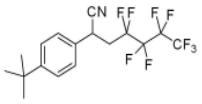
4b ^{19}**F NMR** (282 MHz, $CDCl_3$)



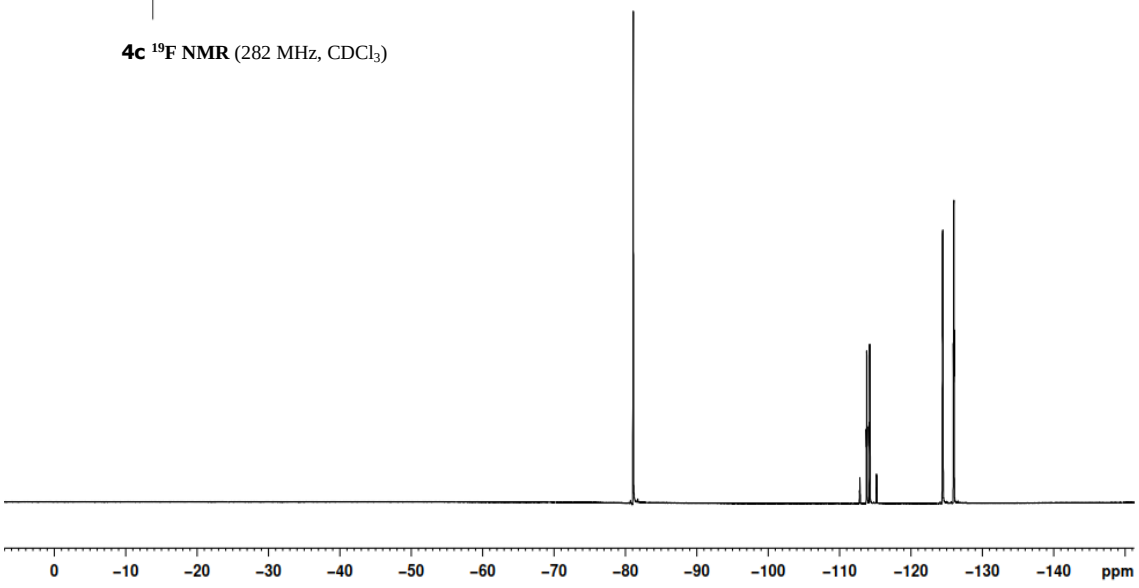
4c ^{1}**H NMR** (300 MHz, $CDCl_3$)

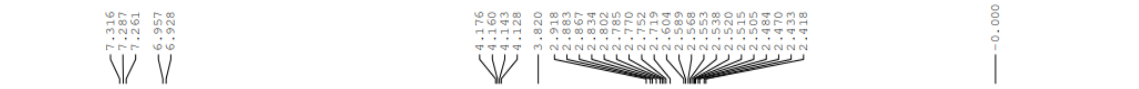


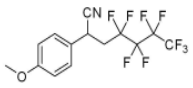
4c ^{13}**C NMR** (75 MHz, $CDCl_3$)



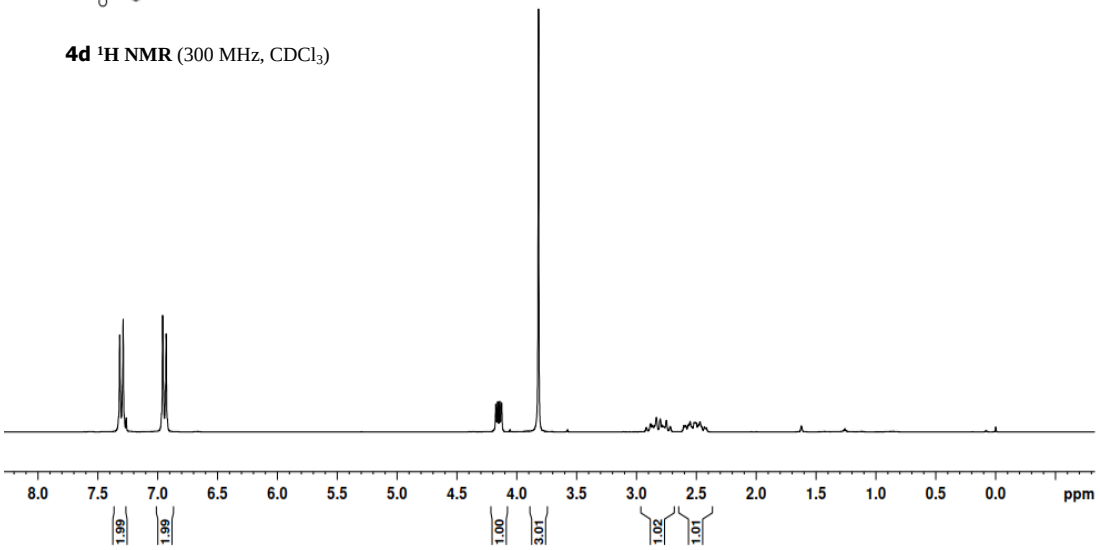
4c ^{19}**F NMR** (282 MHz, $CDCl_3$)

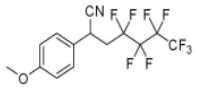




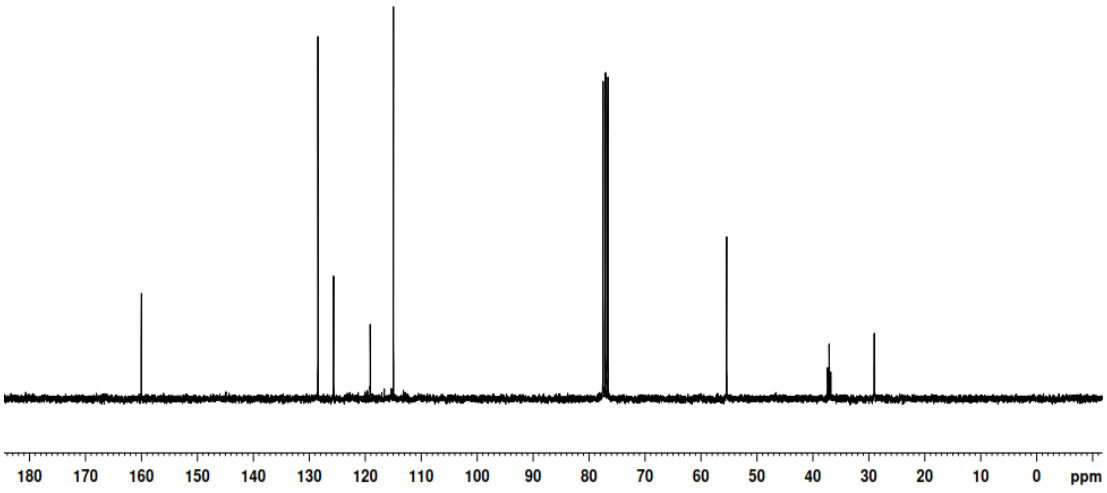


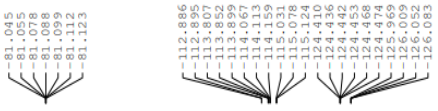
4d ^{1}**H NMR** (300 MHz, $CDCl_3$)

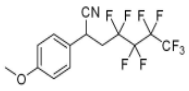




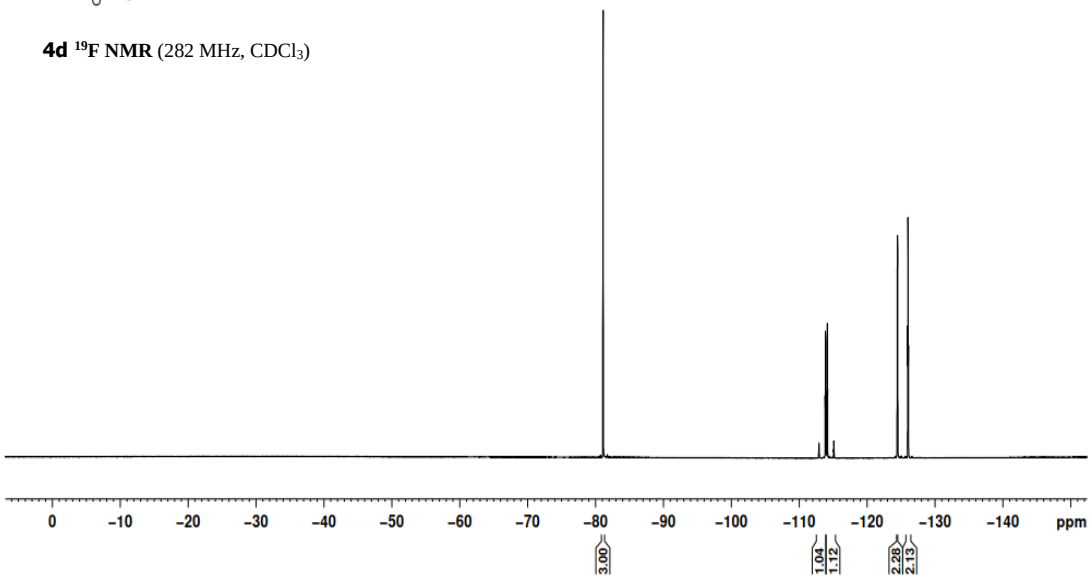
4d ^{13}**C NMR** (75 MHz, $CDCl_3$)

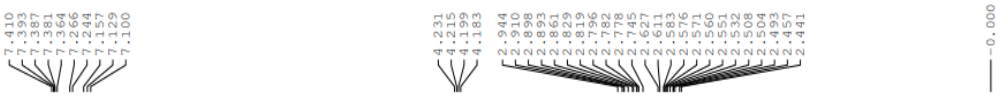


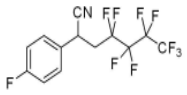




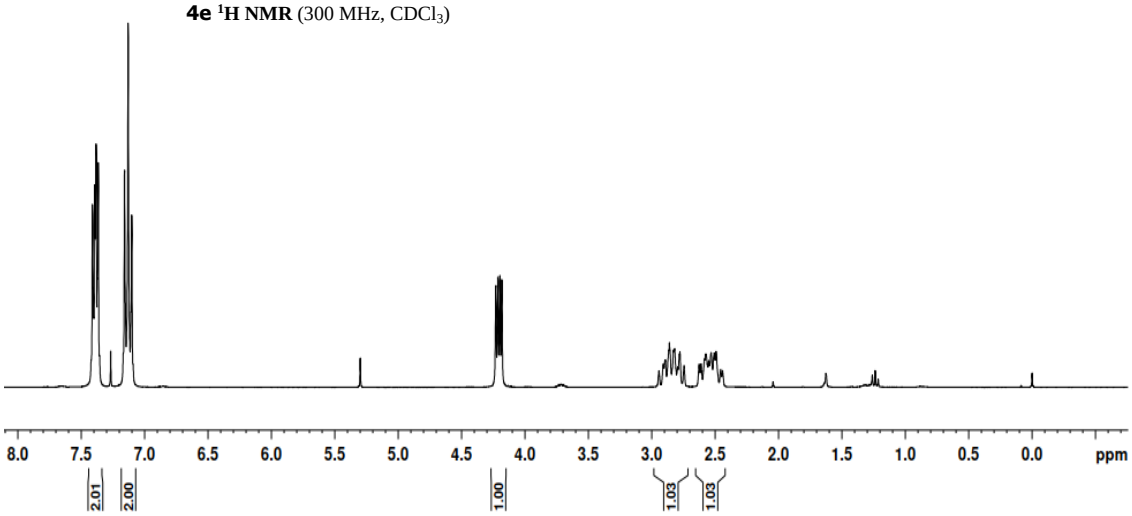
4d ^{19}**F NMR** (282 MHz, $CDCl_3$)

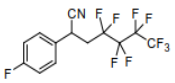




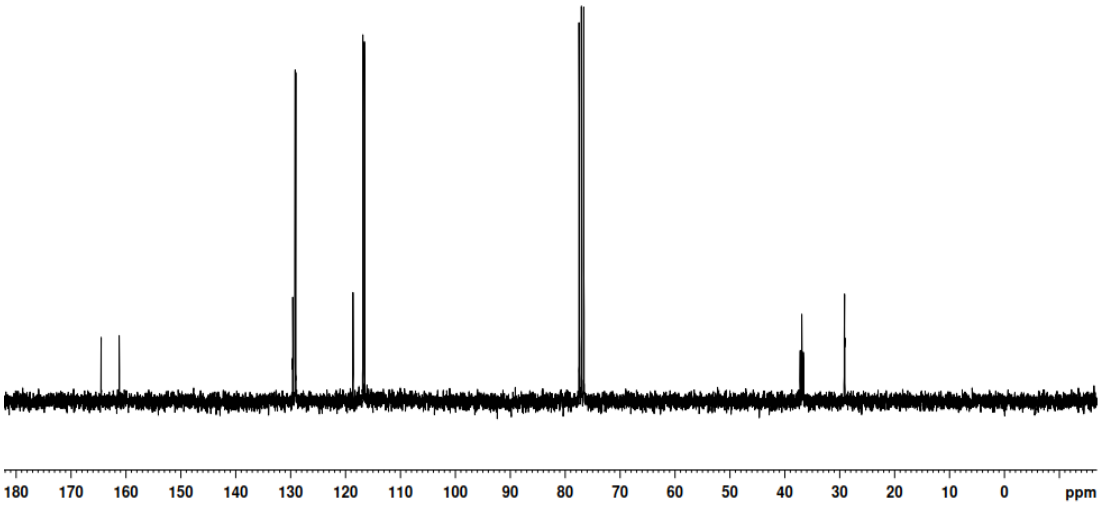


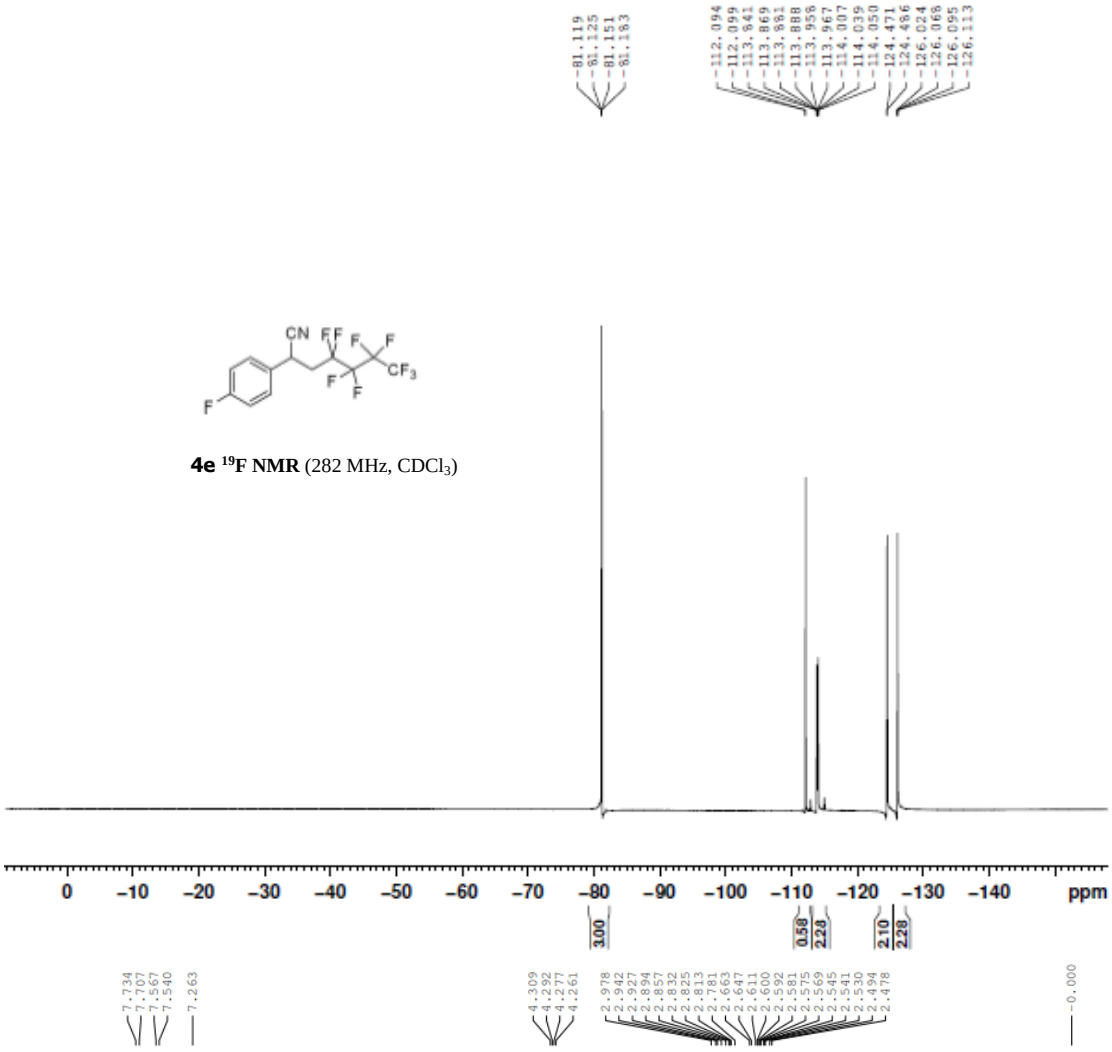
4e **^{1}H NMR** (300 MHz, $CDCl_3$)



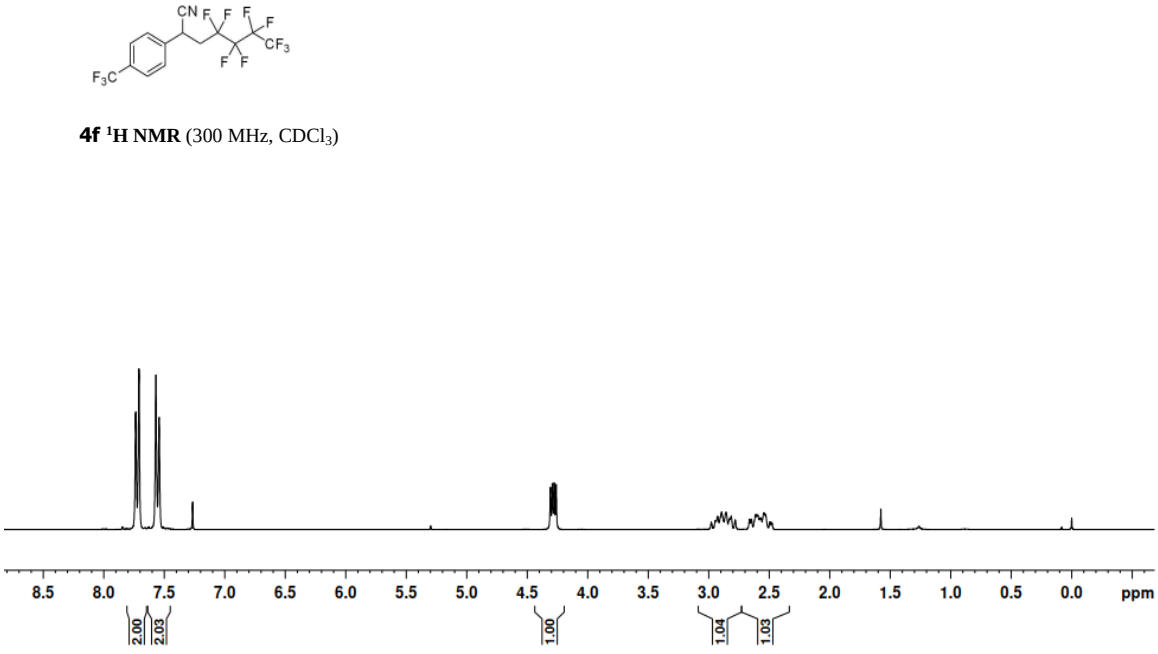


4e **^{13}C NMR** (75 MHz, $CDCl_3$)

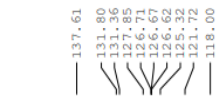


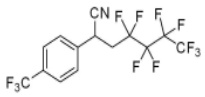


4e **^{19}F NMR** (282 MHz, $CDCl_3$)

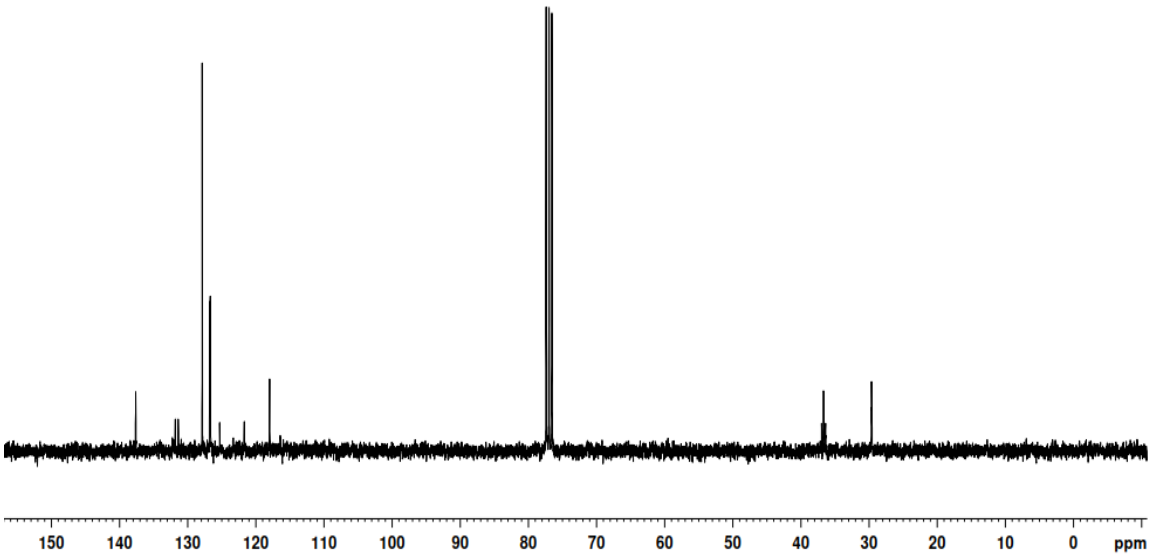


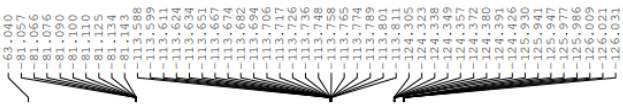
4f **^{1}H NMR** (300 MHz, $CDCl_3$)

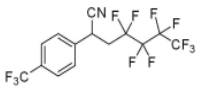




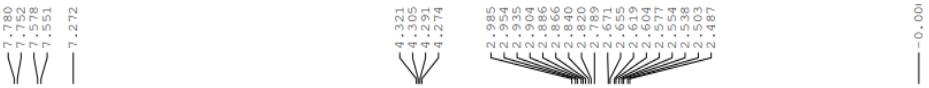
4f ^{13}**C NMR** (75 MHz, $CDCl_3$)

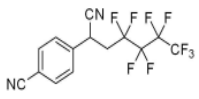




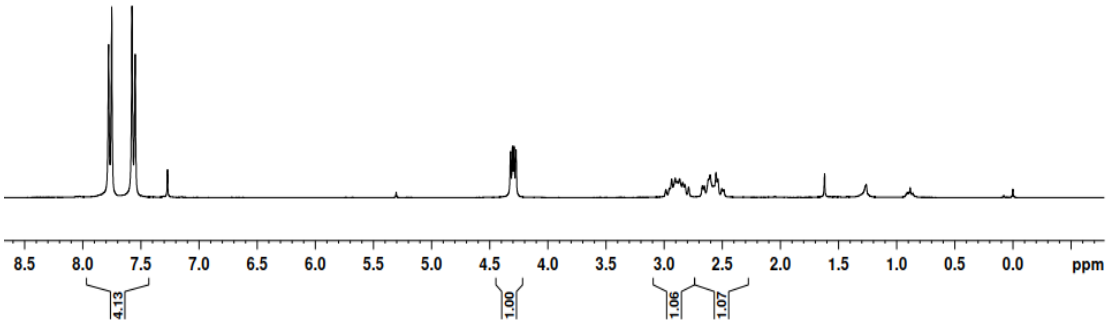


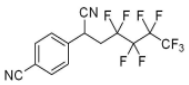
4f ^{19}**F NMR** (282 MHz, $CDCl_3$)



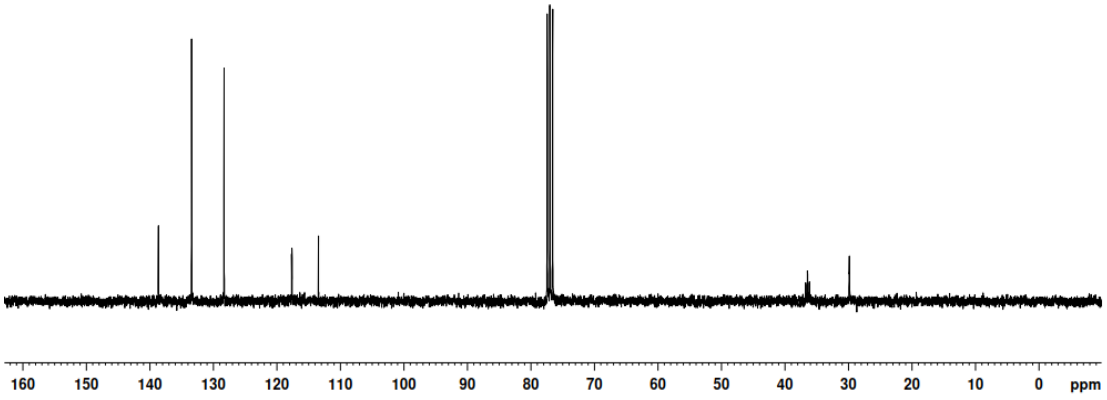


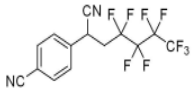
4g **^{1}H NMR** (300 MHz, $CDCl_3$)



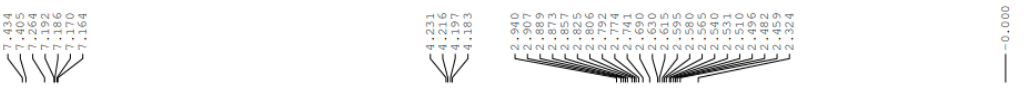


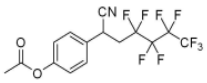
4g **^{13}C NMR** (75 MHz, $CDCl_3$)



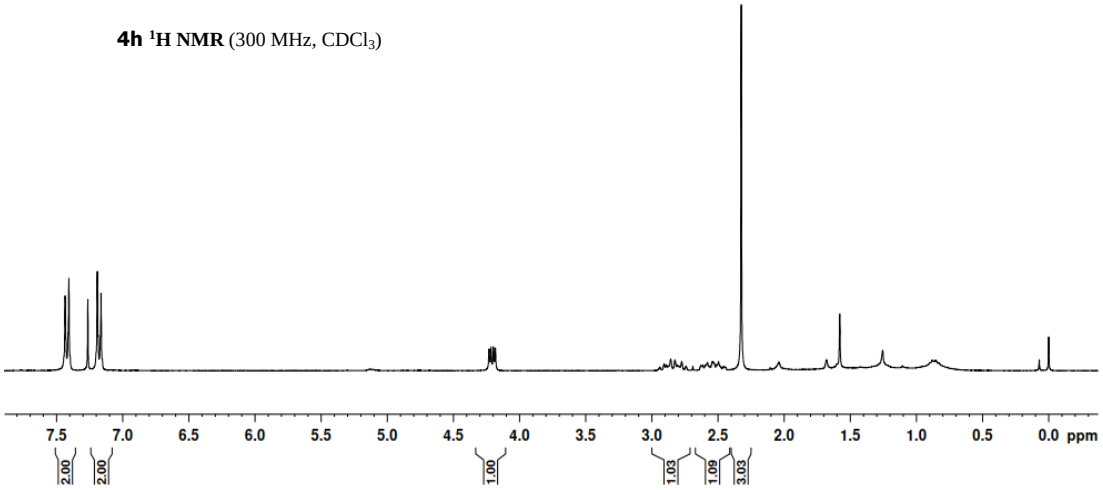


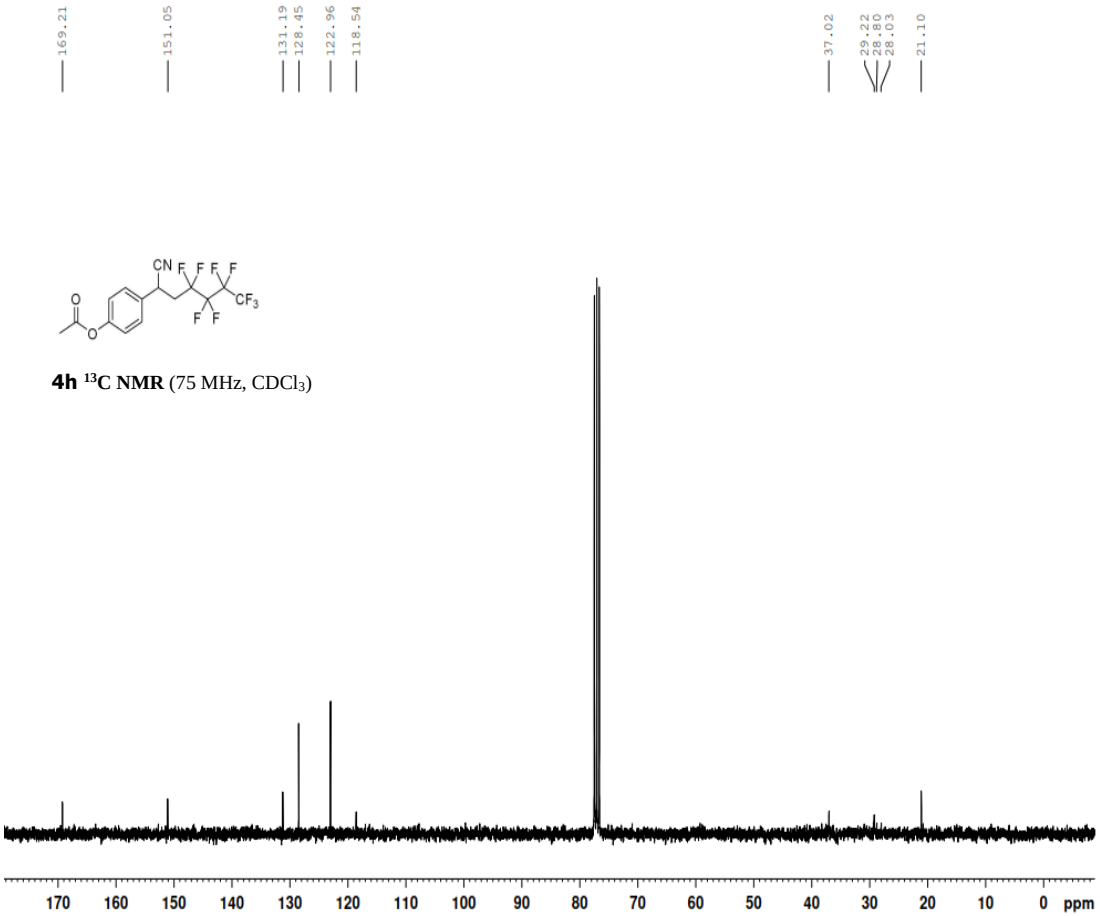
4g ^{19}**F NMR** (282 MHz, $CDCl_3$)



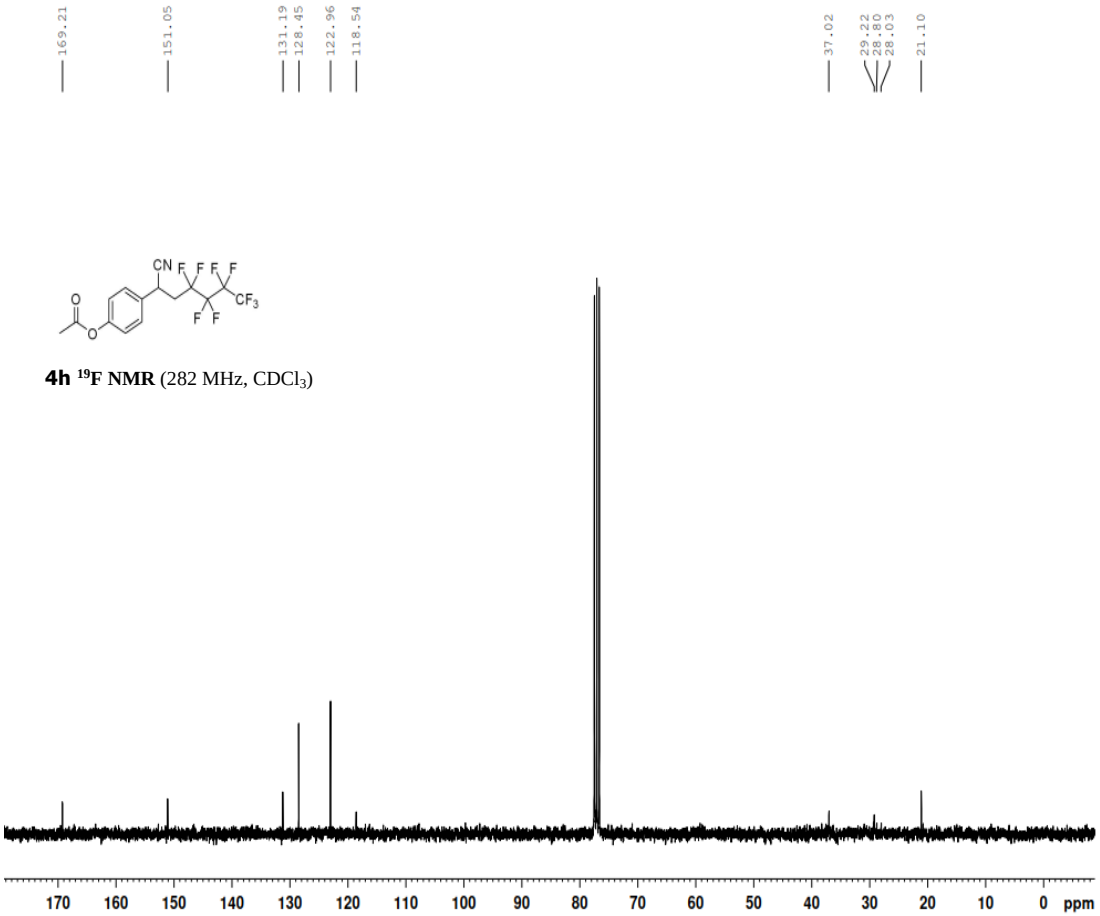


4h ^{1}**H NMR** (300 MHz, $CDCl_3$)

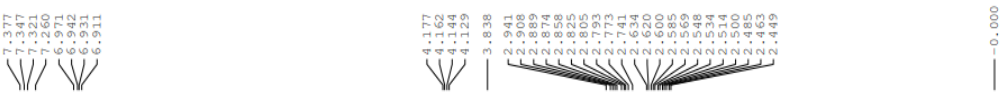


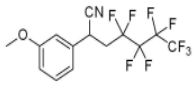


4h ^{13}**C NMR** (75 MHz, $CDCl_3$)

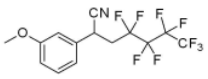


4h ^{19}**F NMR** (282 MHz, $CDCl_3$)

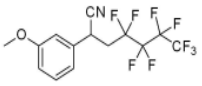




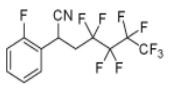
4i **^{1}H NMR** (300 MHz, $CDCl_3$)



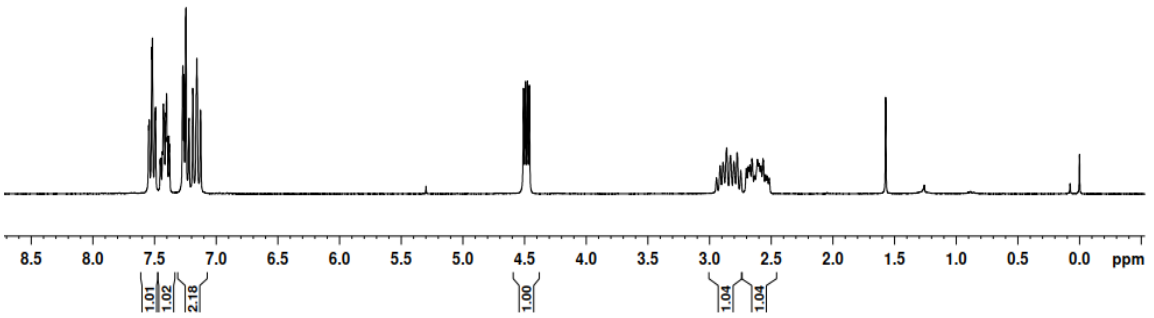
4i **^{13}C NMR** (75 MHz, $CDCl_3$)

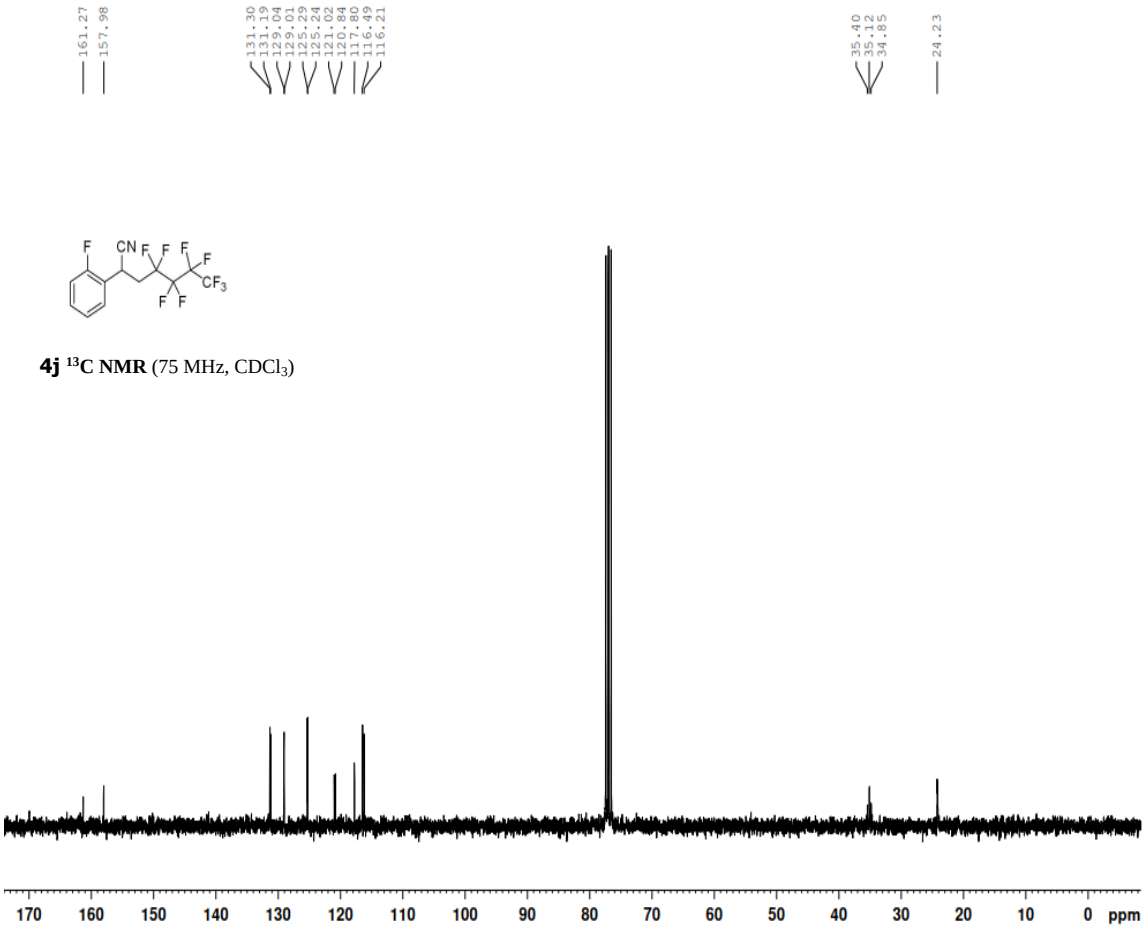


4i **^{19}F NMR** (282 MHz, $CDCl_3$)

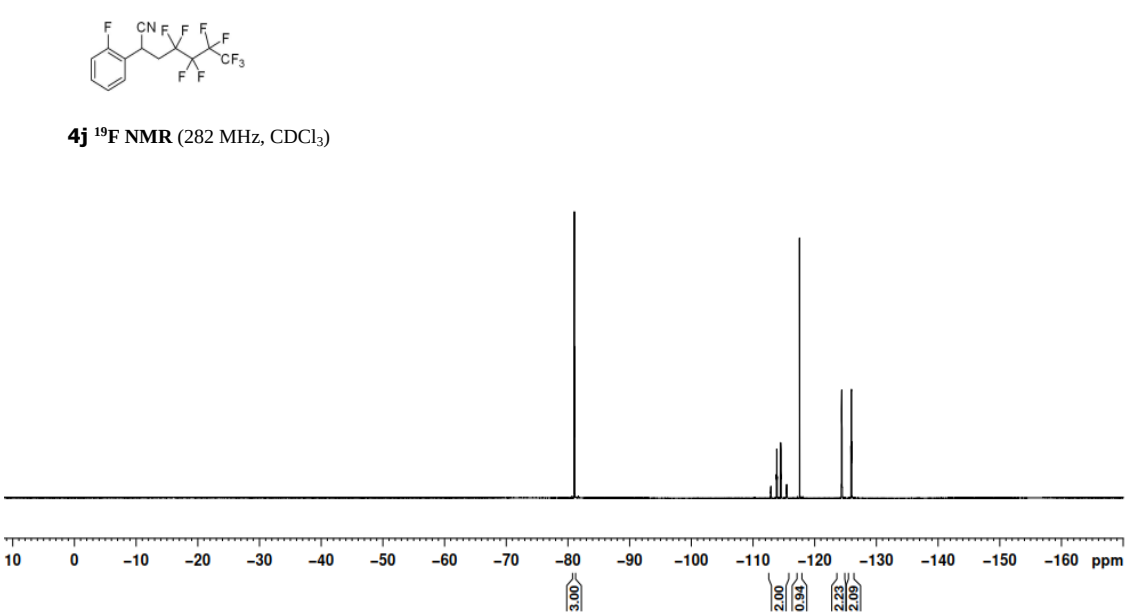


4j **^{1}H NMR** (300 MHz, $CDCl_3$)

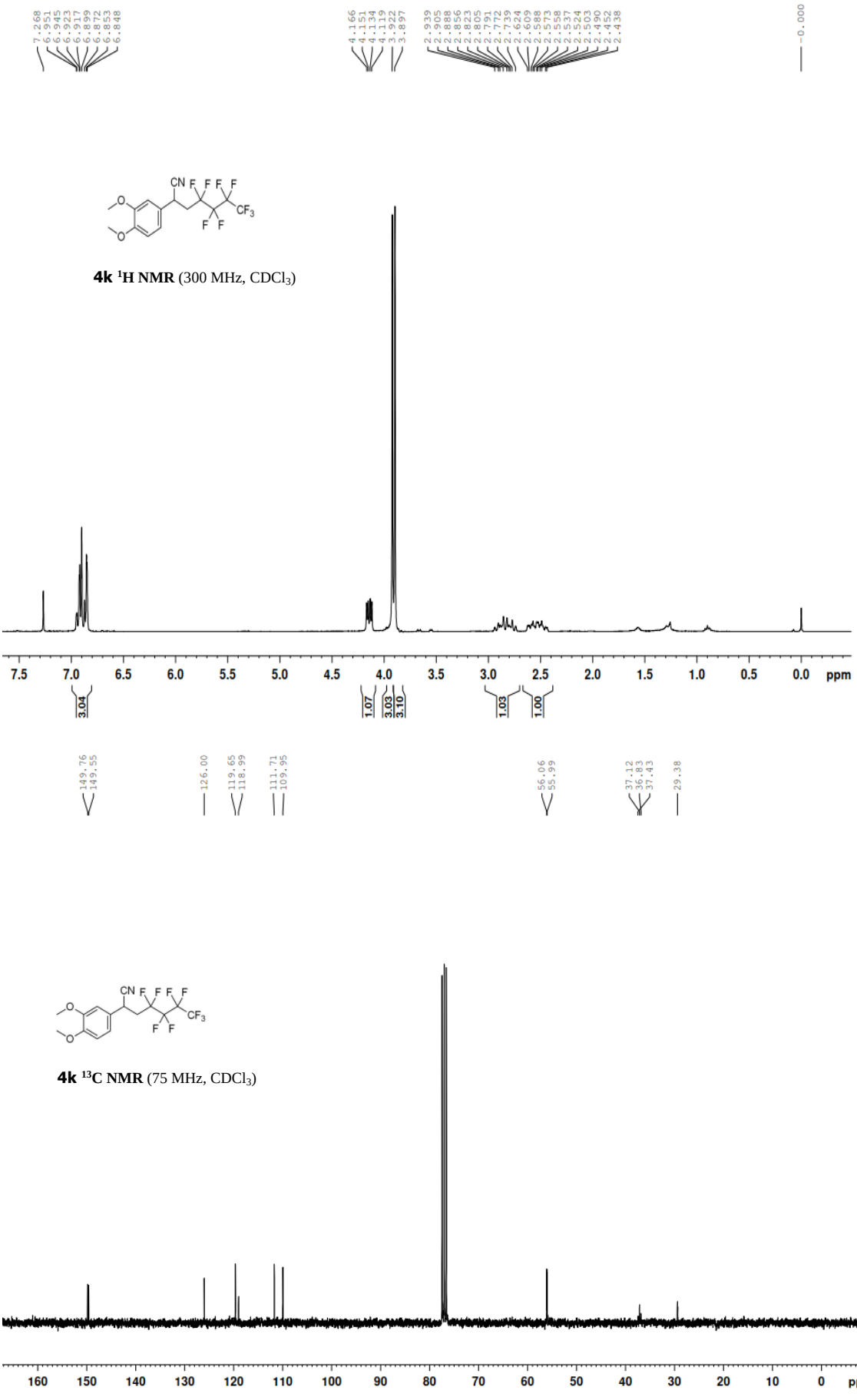




4j ^{13}**C NMR** (75 MHz, $CDCl_3$)

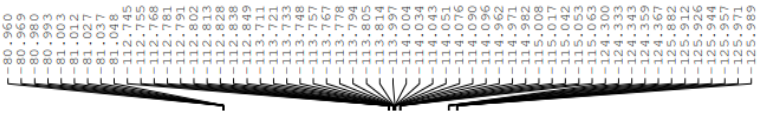


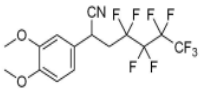
4j ^{19}**F NMR** (282 MHz, $CDCl_3$)



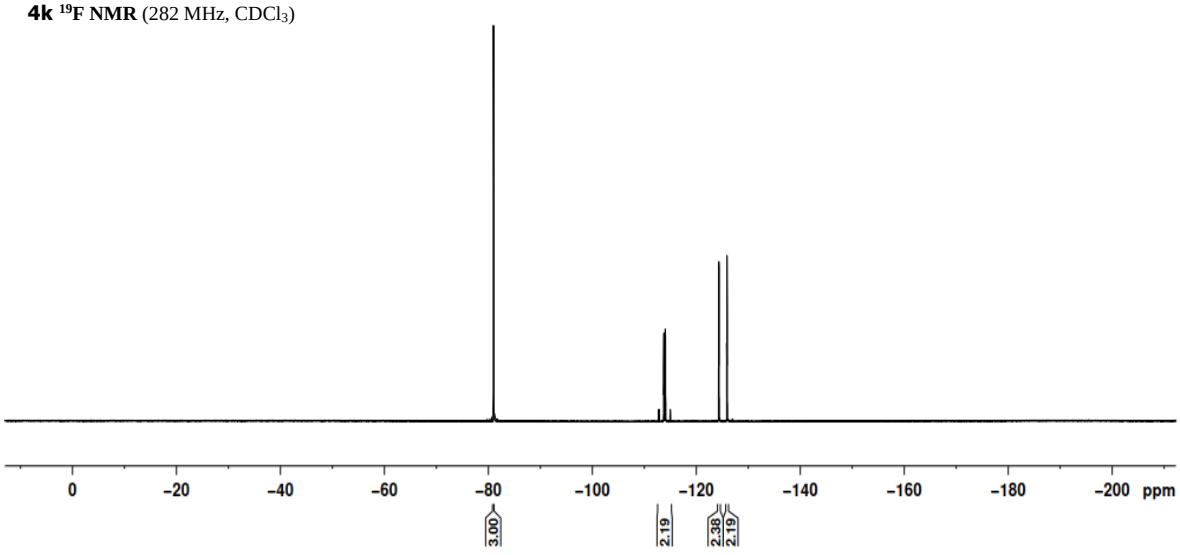
4k ^{1}**H NMR** (300 MHz, $CDCl_3$)

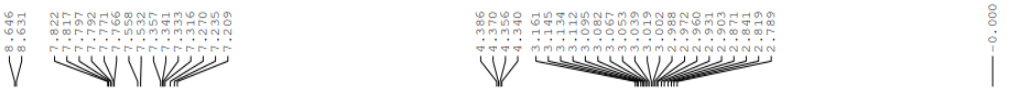
4k ^{13}**C NMR** (75 MHz, $CDCl_3$)

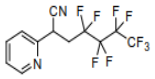




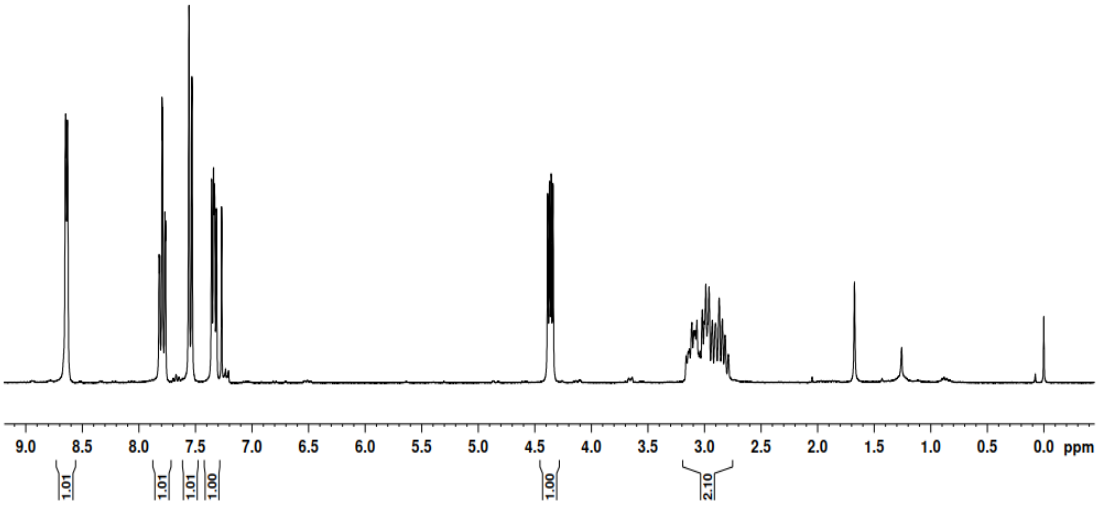
4k ^{19}**F NMR** (282 MHz, $CDCl_3$)

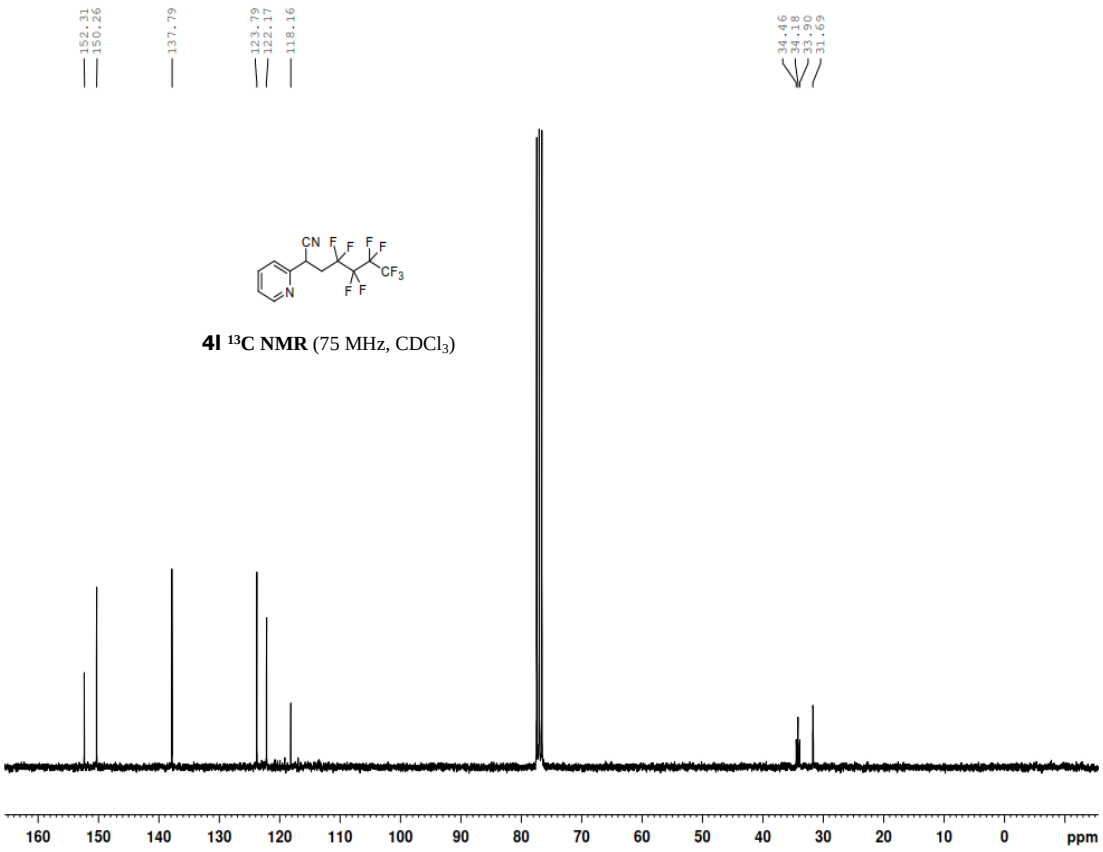




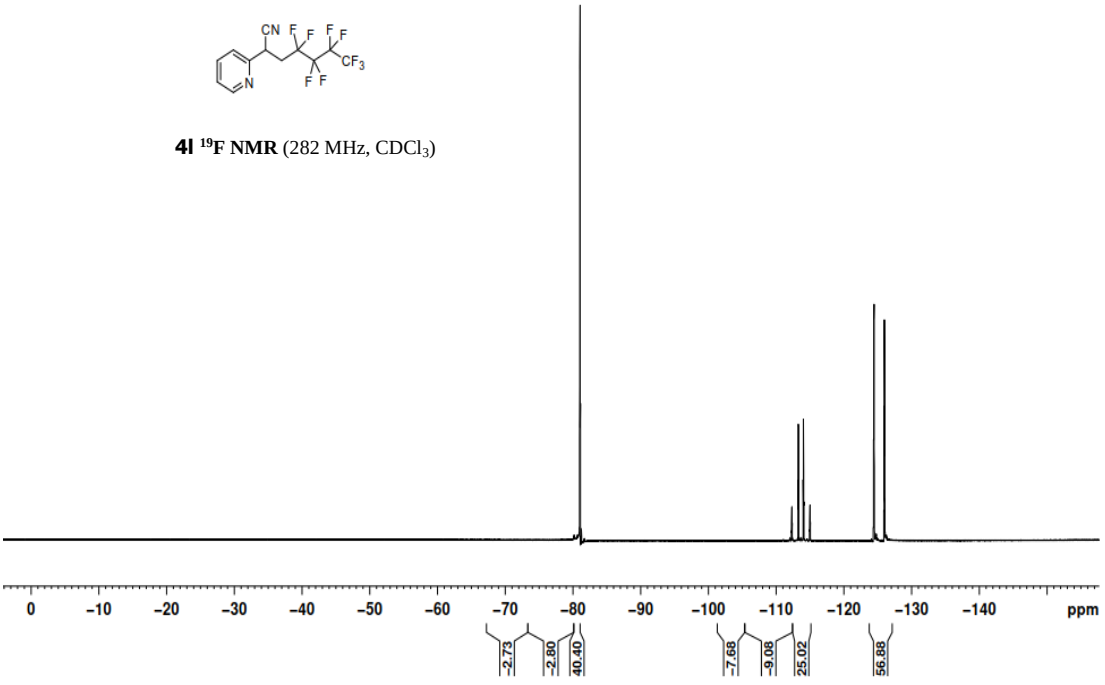


4l ^{1}**H NMR** (300 MHz, $CDCl_3$)

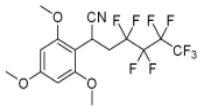




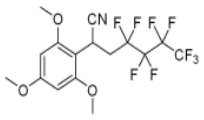
4l **^{13}C NMR** (75 MHz, $CDCl_3$)



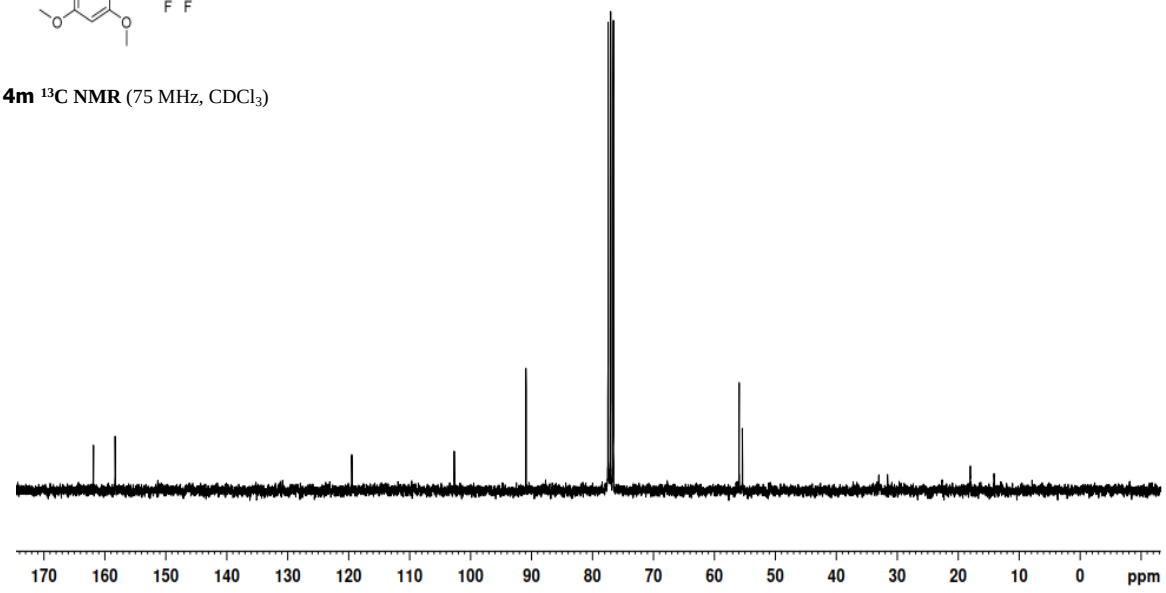
4l **^{19}F NMR** (282 MHz, $CDCl_3$)

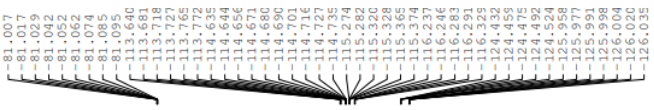


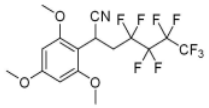
4m **^{1}H NMR** (300 MHz, $CDCl_3$)



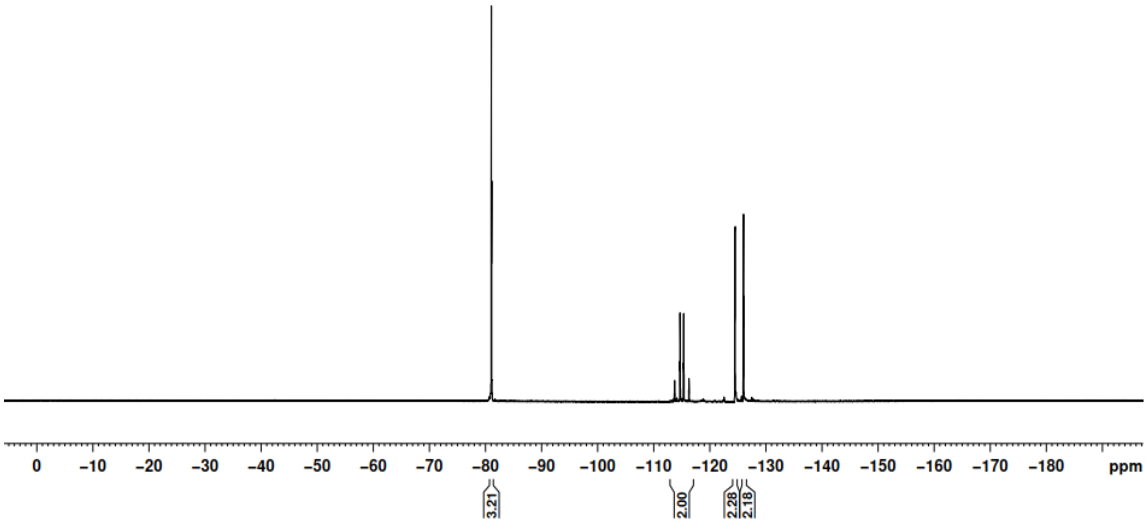
4m **^{13}C NMR** (75 MHz, $CDCl_3$)

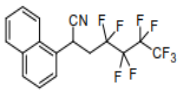




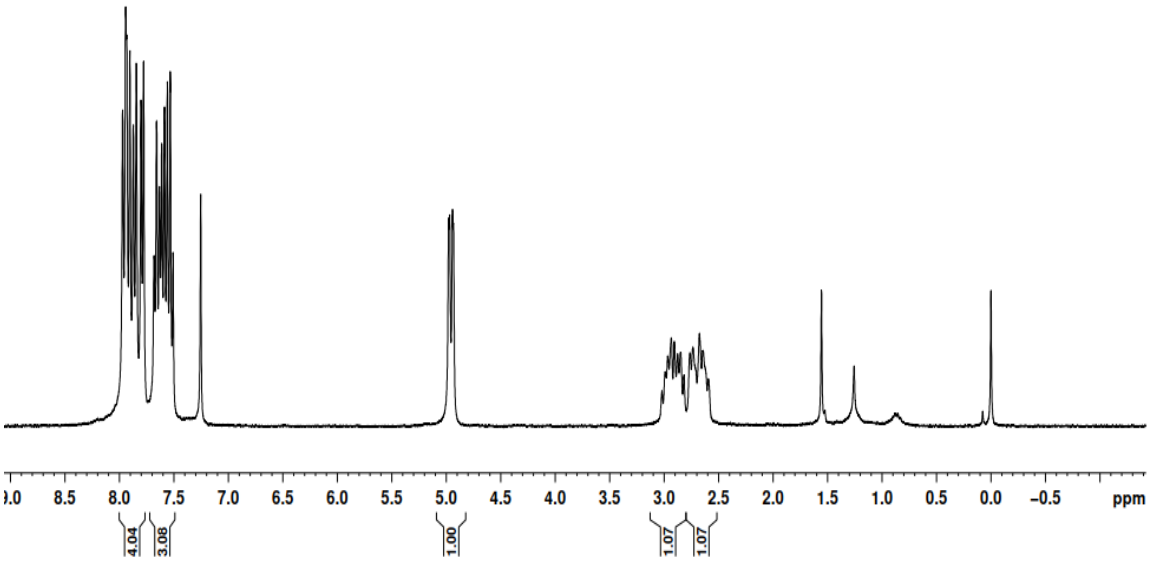


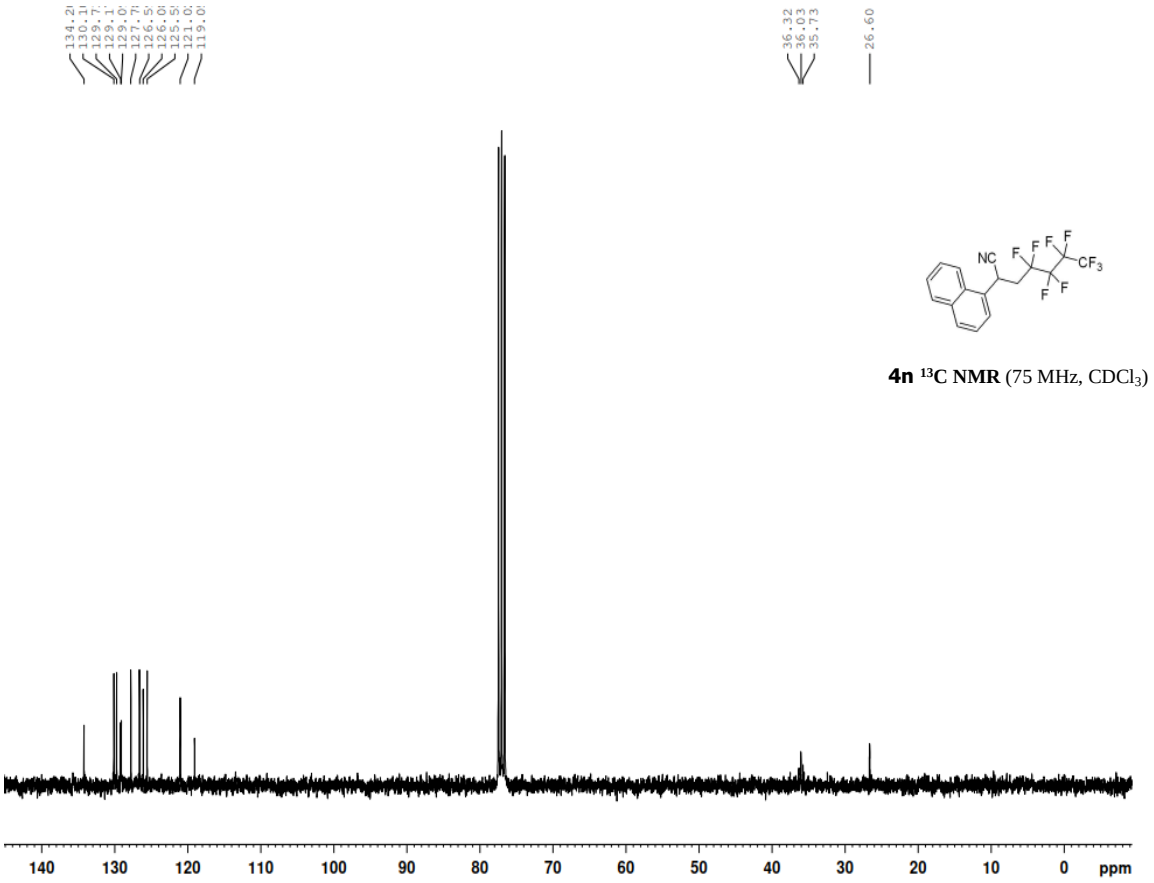
4m ^{19}**F NMR** (282 MHz, $CDCl_3$)



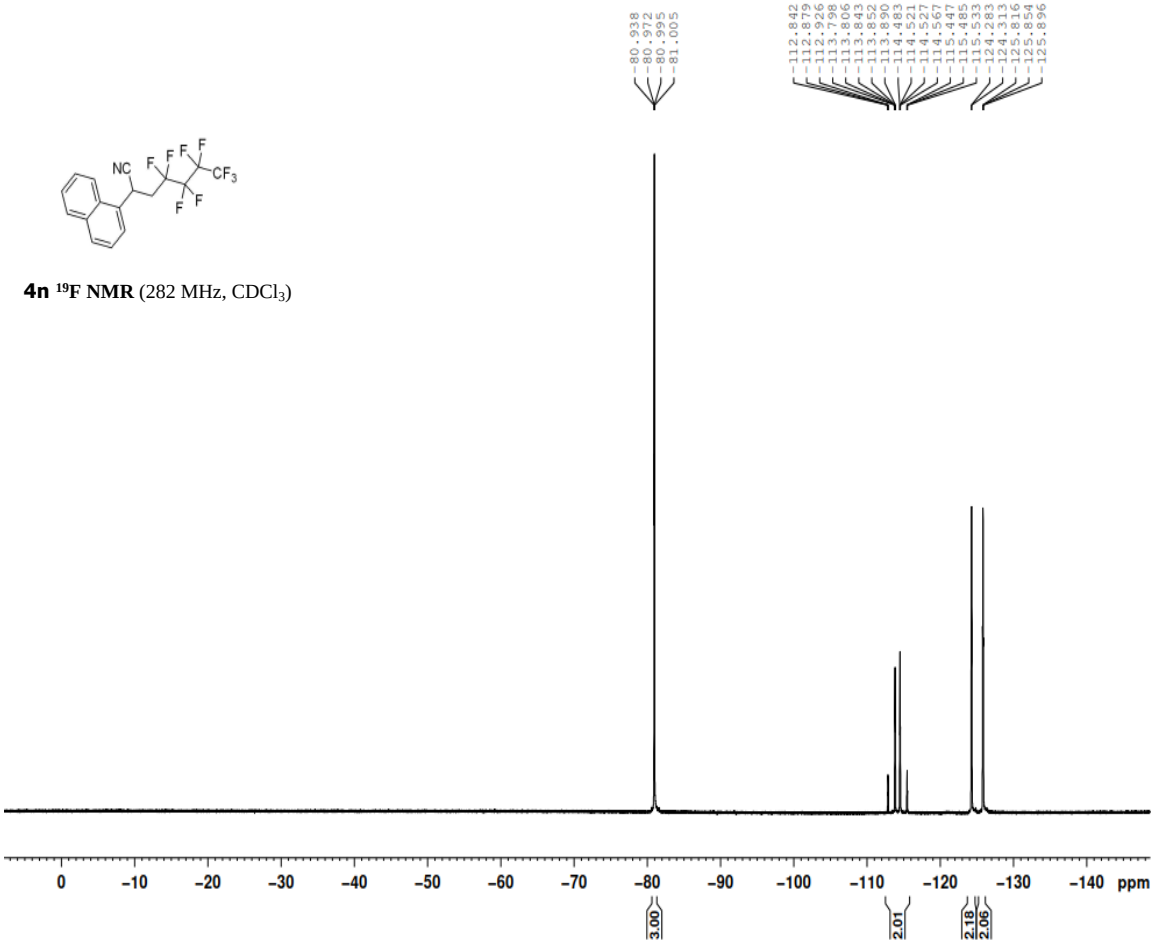


4n ^{1}**H NMR** (300 MHz, $CDCl_3$)

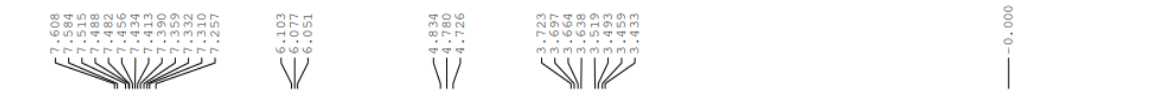


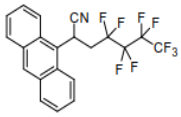


4n ^{13}**C NMR** (75 MHz, $CDCl_3$)

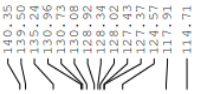


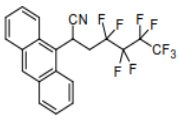
4n ^{19}**F NMR** (282 MHz, $CDCl_3$)



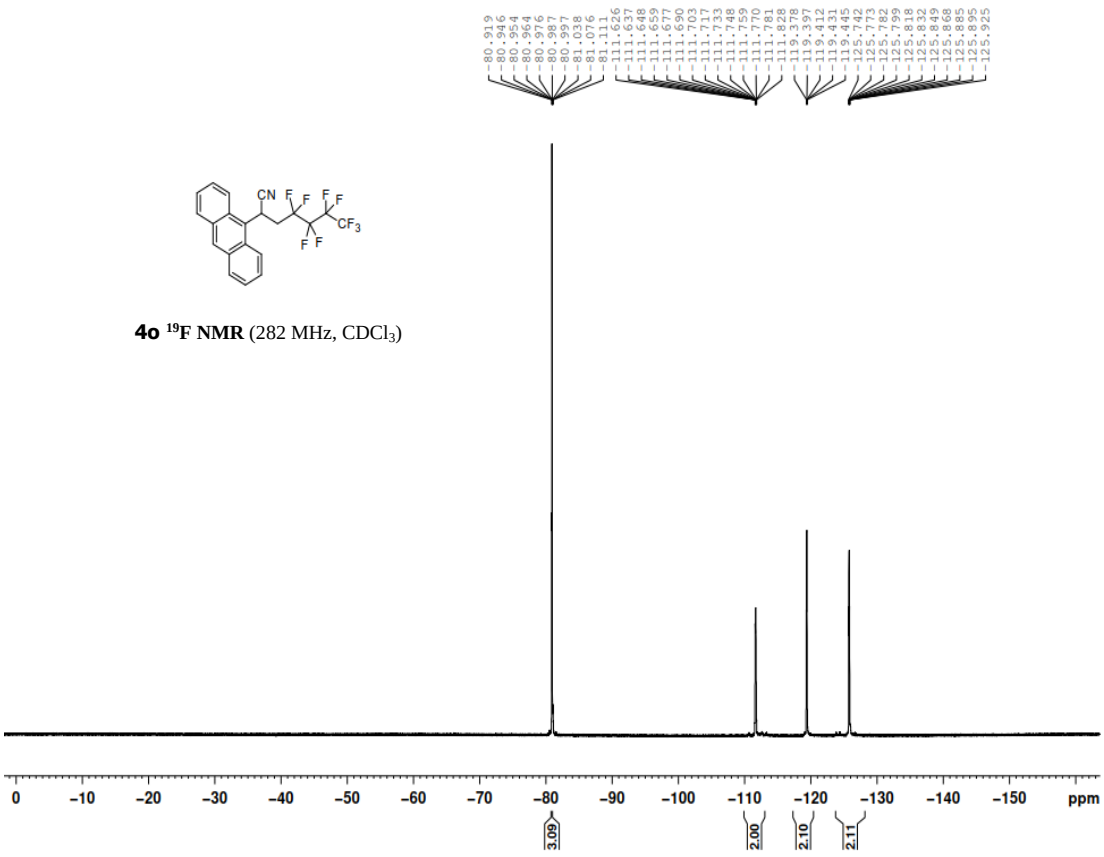


4o ^{1}**H NMR** (300 MHz, $CDCl_3$)

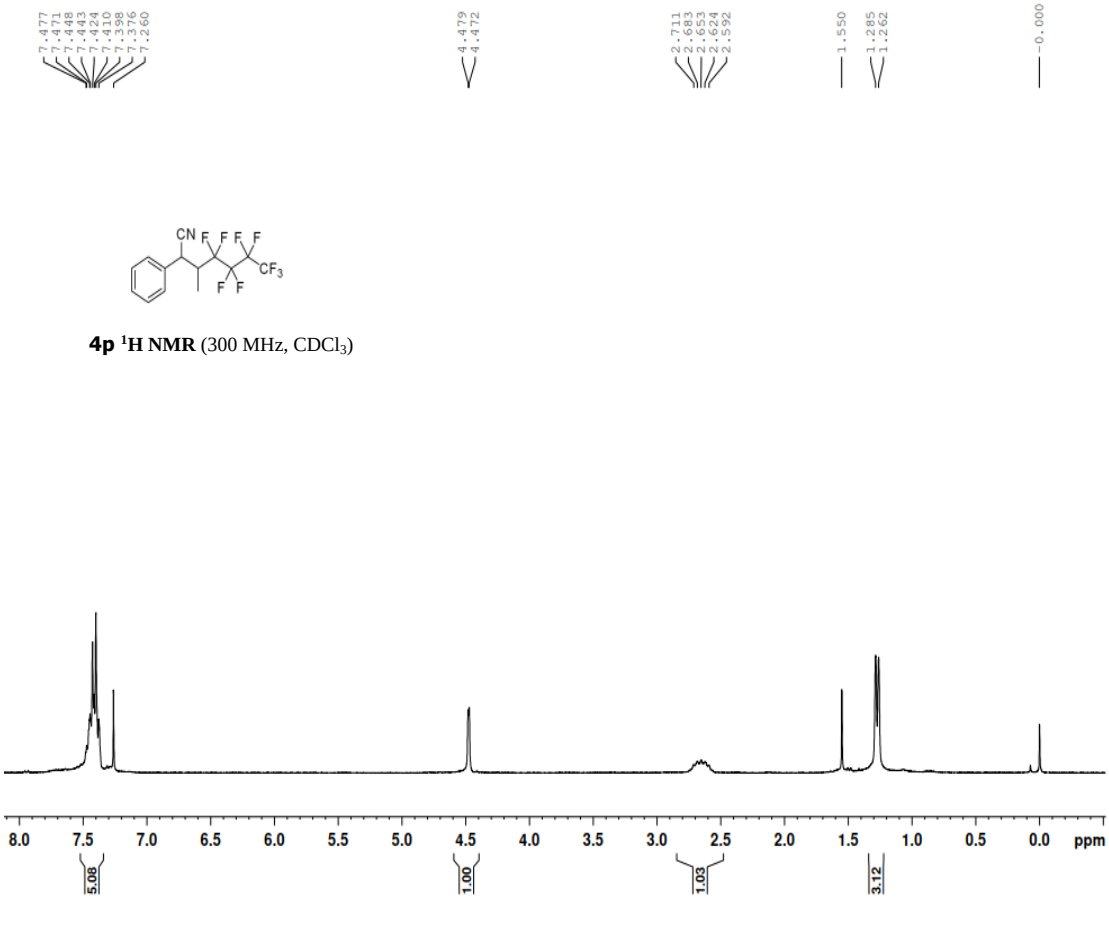




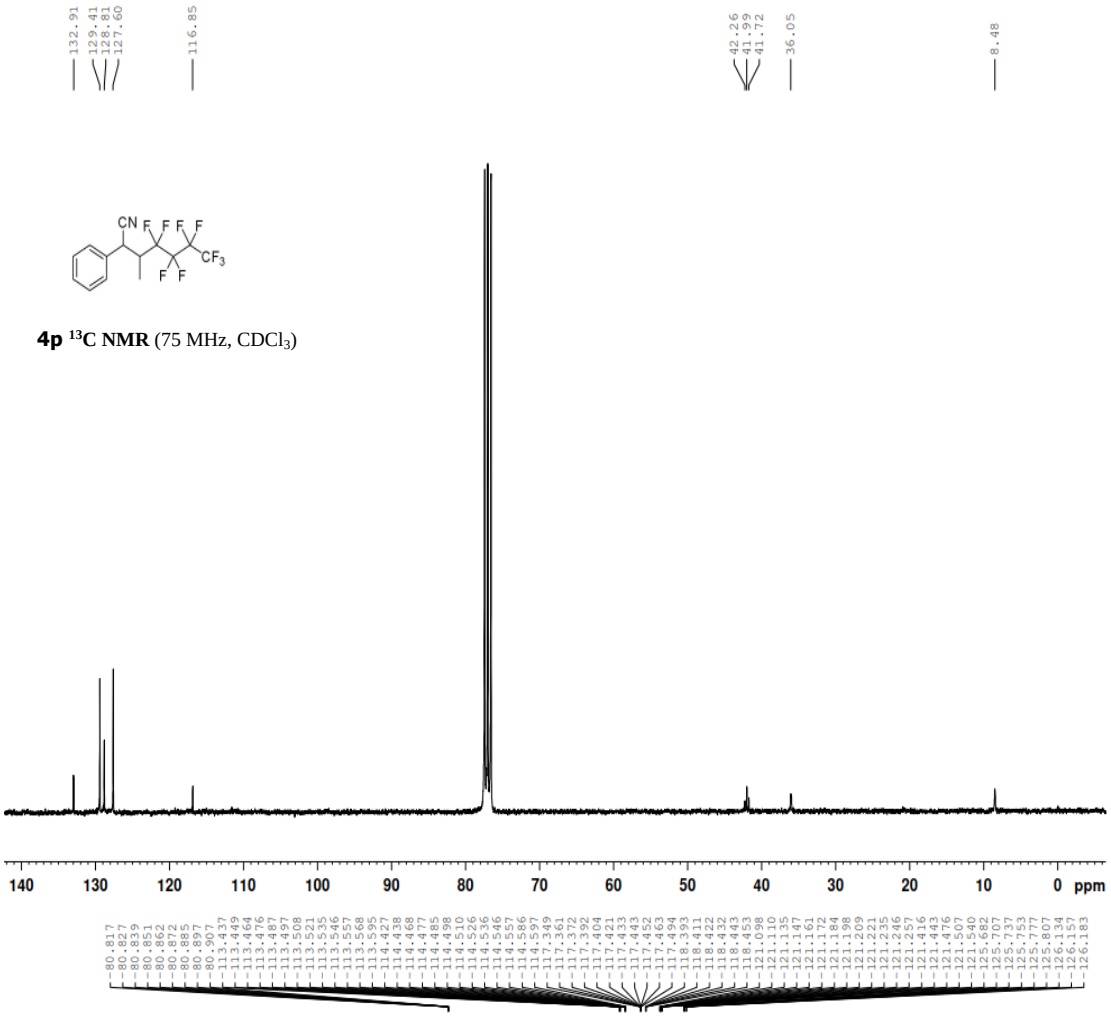
4o ^{13}**C NMR** (75 MHz, $CDCl_3$)



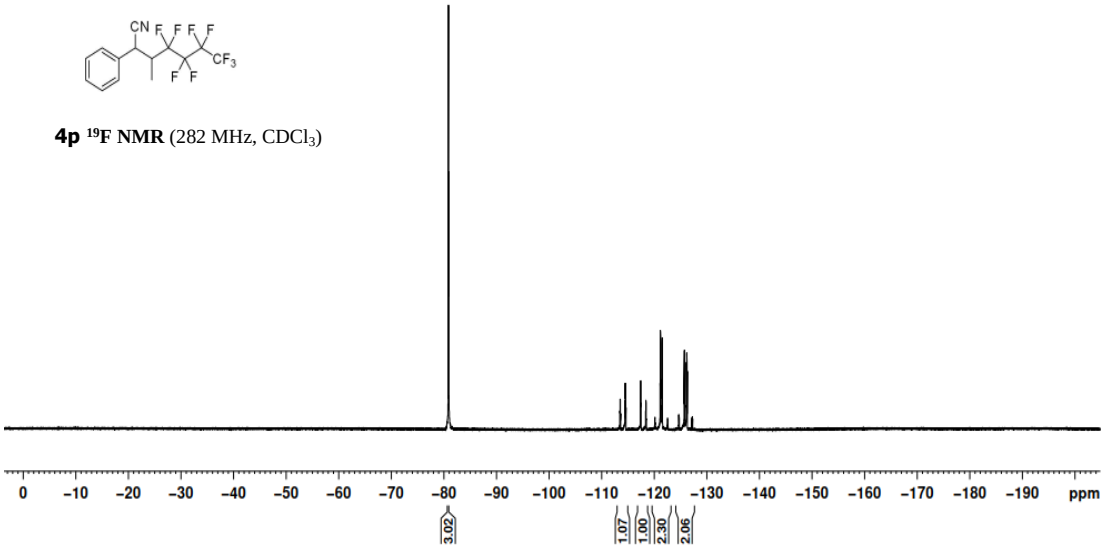
4o **^{19}F NMR** (282 MHz, $CDCl_3$)



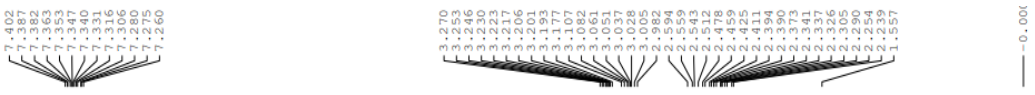
4p **^{1}H NMR** (300 MHz, $CDCl_3$)

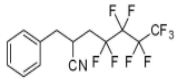


4p **^{13}C NMR** (75 MHz, $CDCl_3$)

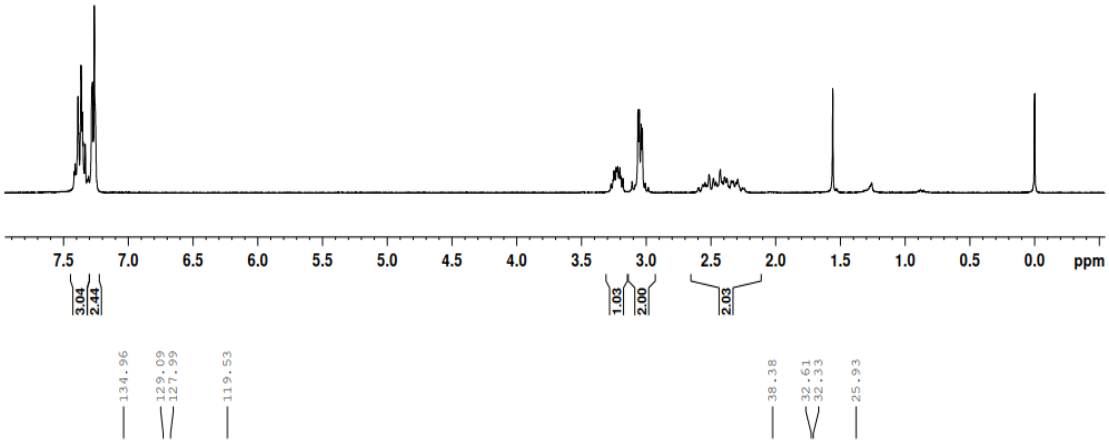


4p **^{19}F NMR** (282 MHz, $CDCl_3$)

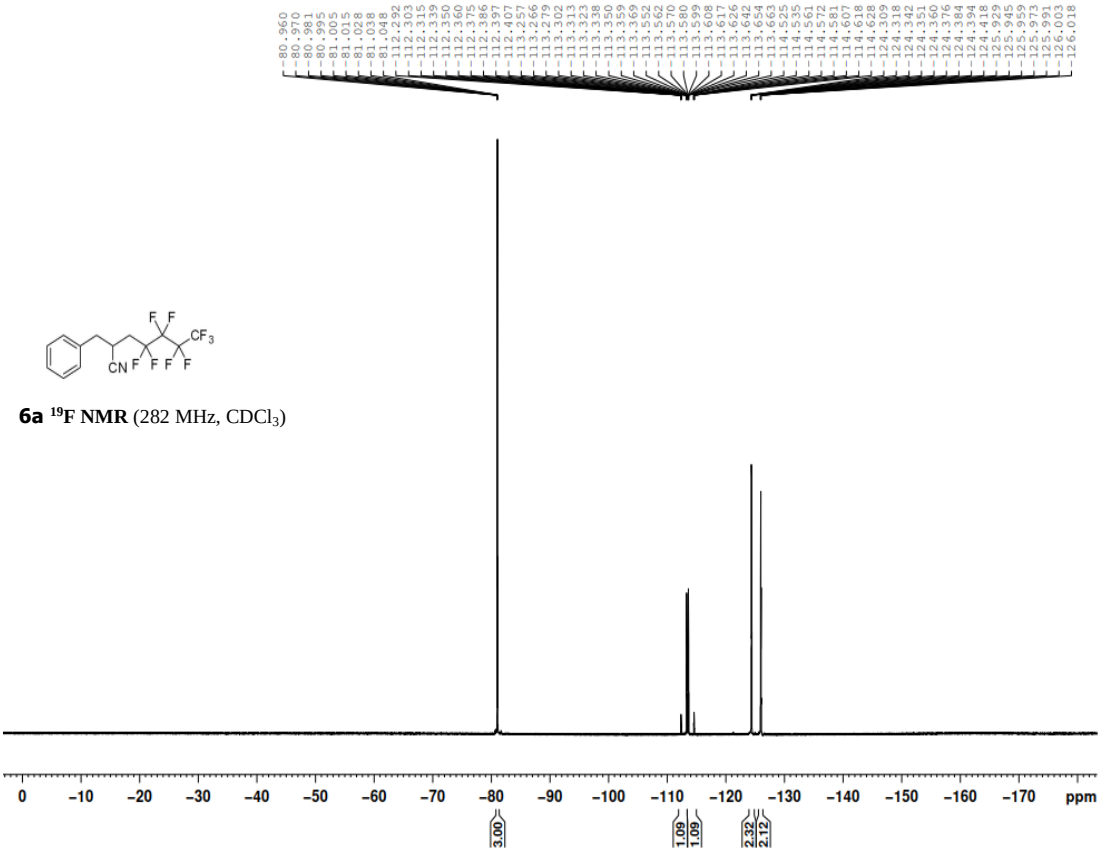




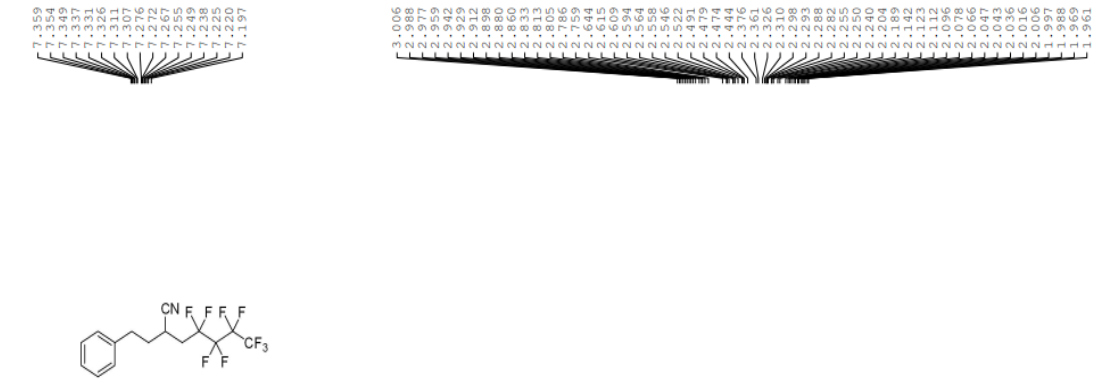
6a **^{1}H NMR** (300 MHz, $CDCl_3$)



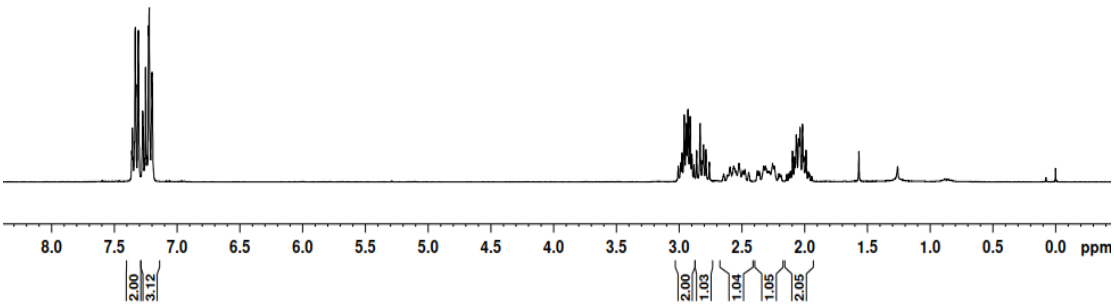
6a **^{13}C NMR** (75 MHz, $CDCl_3$)

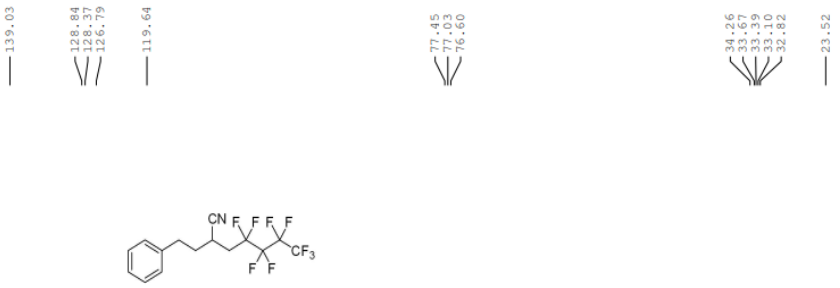


6a **^{19}F NMR** (282 MHz, $CDCl_3$)

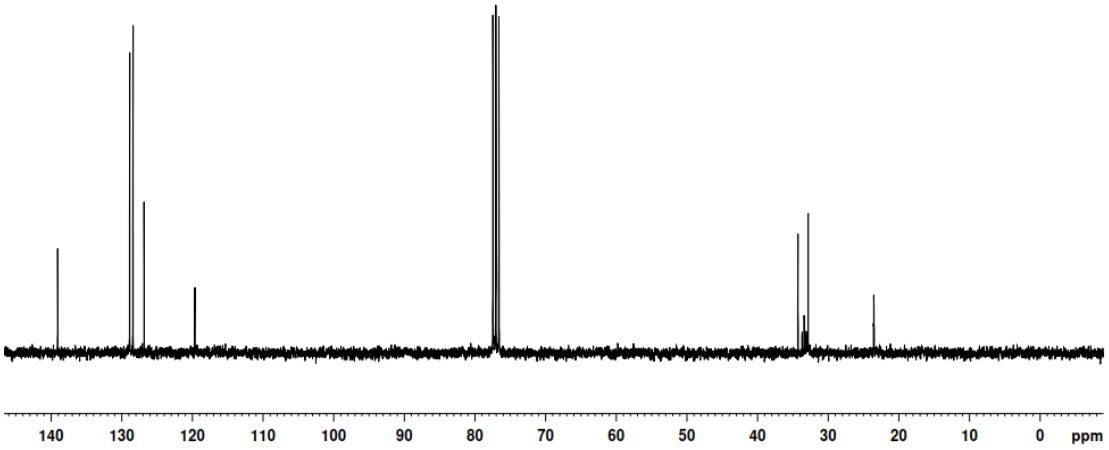


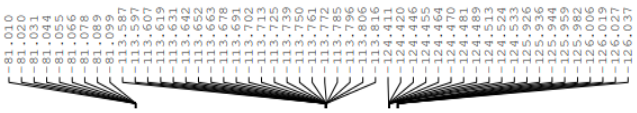
6b **^{1}H NMR** (300 MHz, $CDCl_3$)

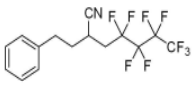




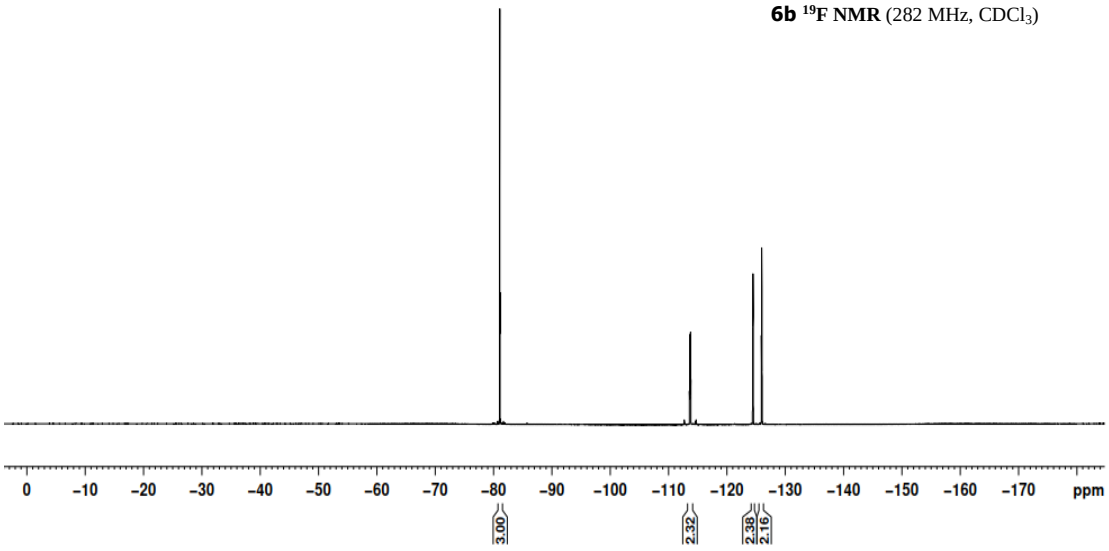
6b ^{13}**C NMR** (75 MHz, $CDCl_3$)

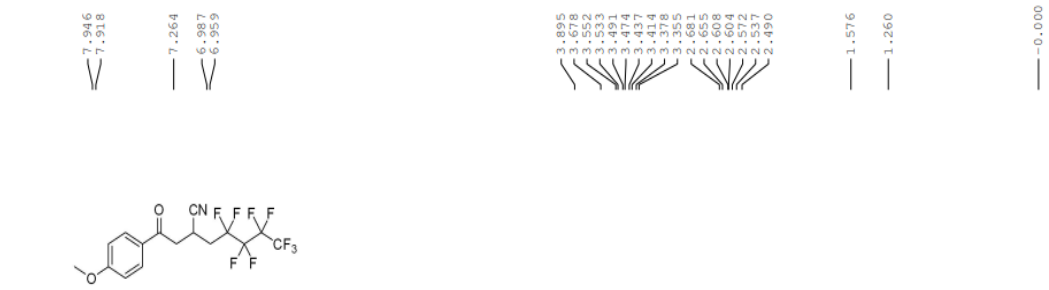




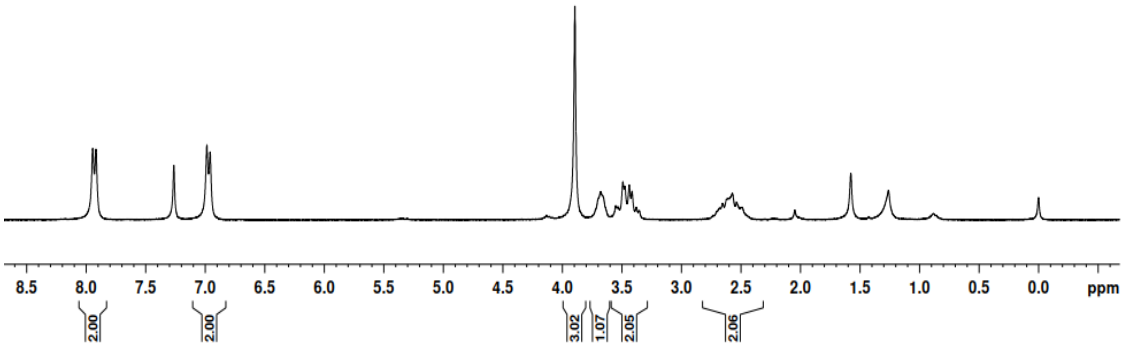


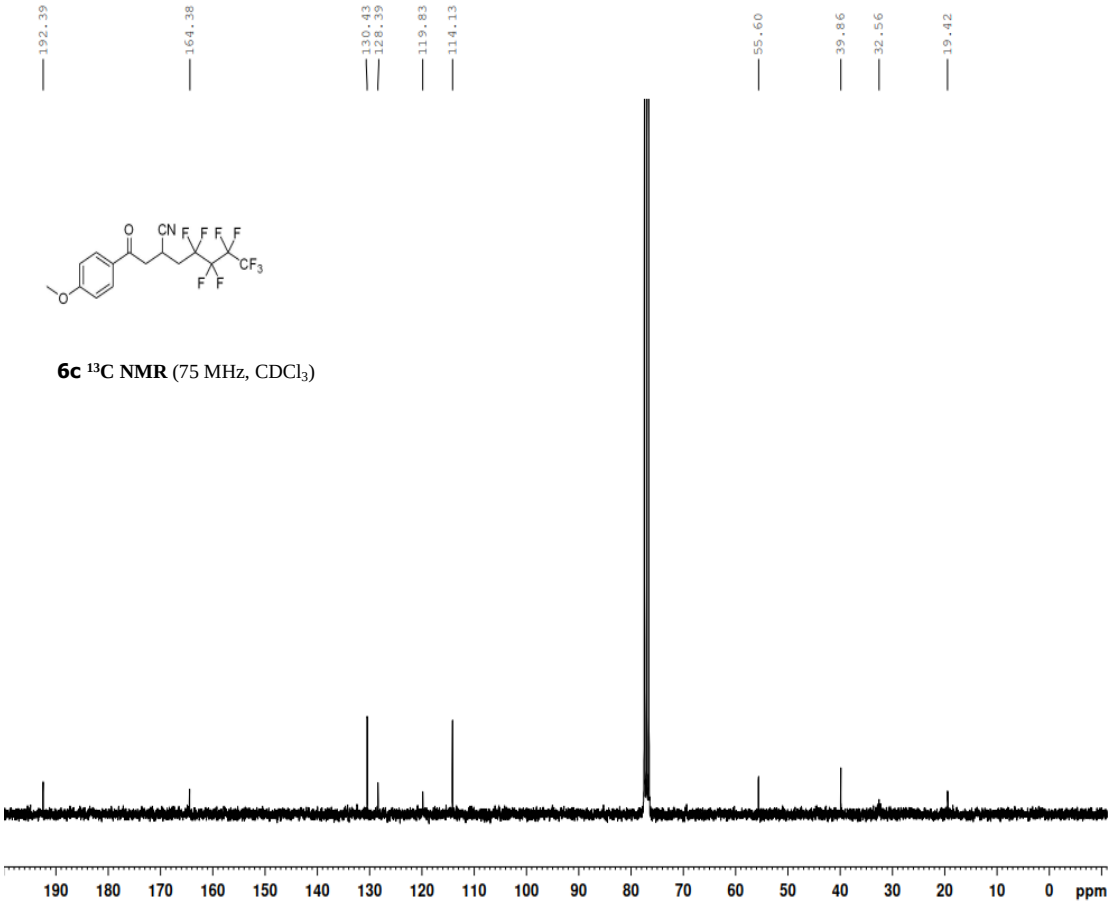
6b ^{19}**F NMR** (282 MHz, $CDCl_3$)



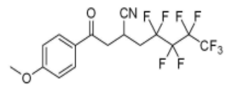


6c **^{1}H NMR** (300 MHz, $CDCl_3$)

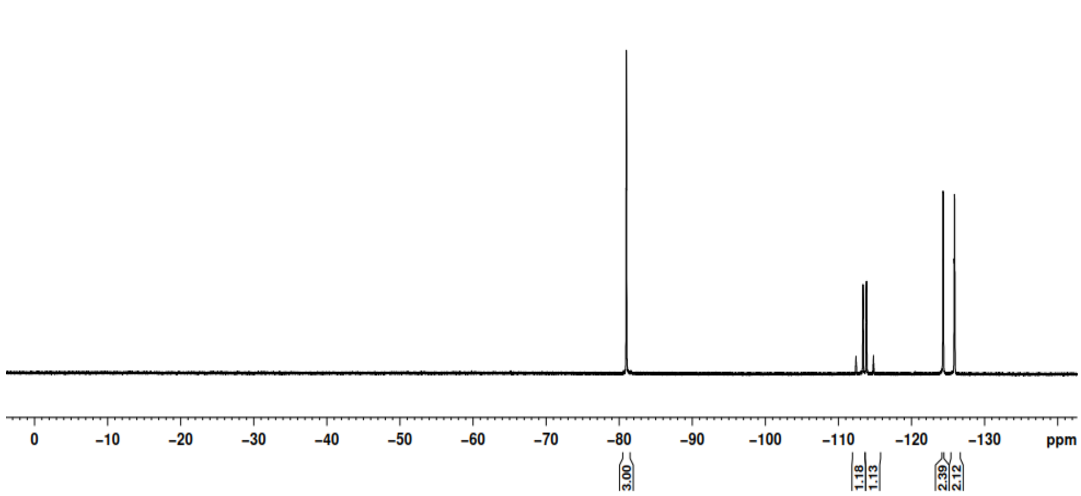


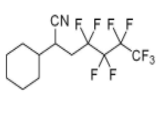


6c **^{13}C NMR** (75 MHz, $CDCl_3$)

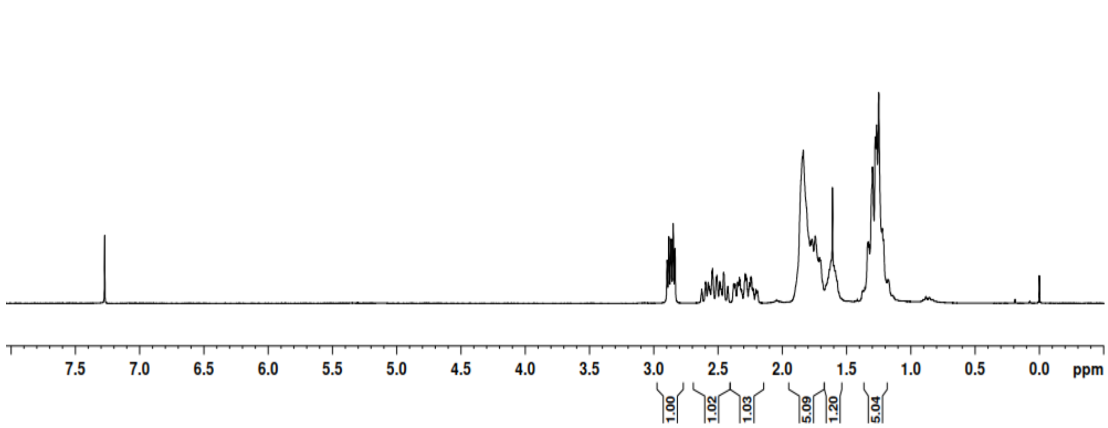


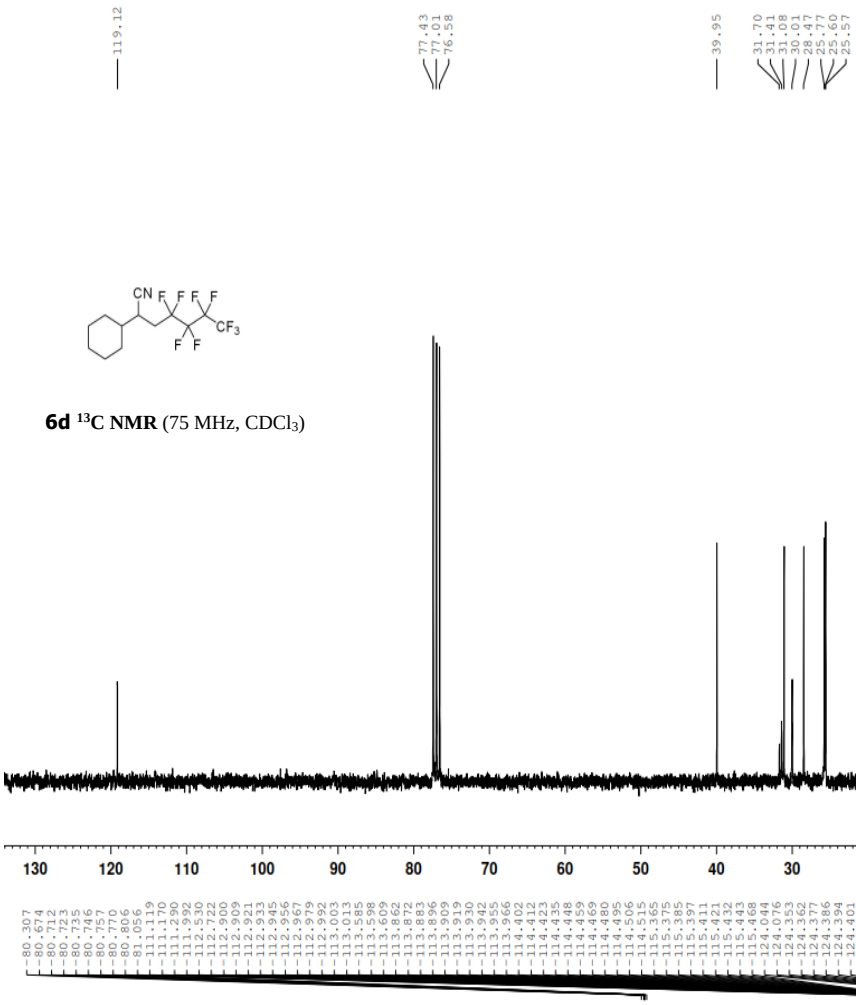
6c ^{19}**F NMR** (282 MHz, $CDCl_3$)



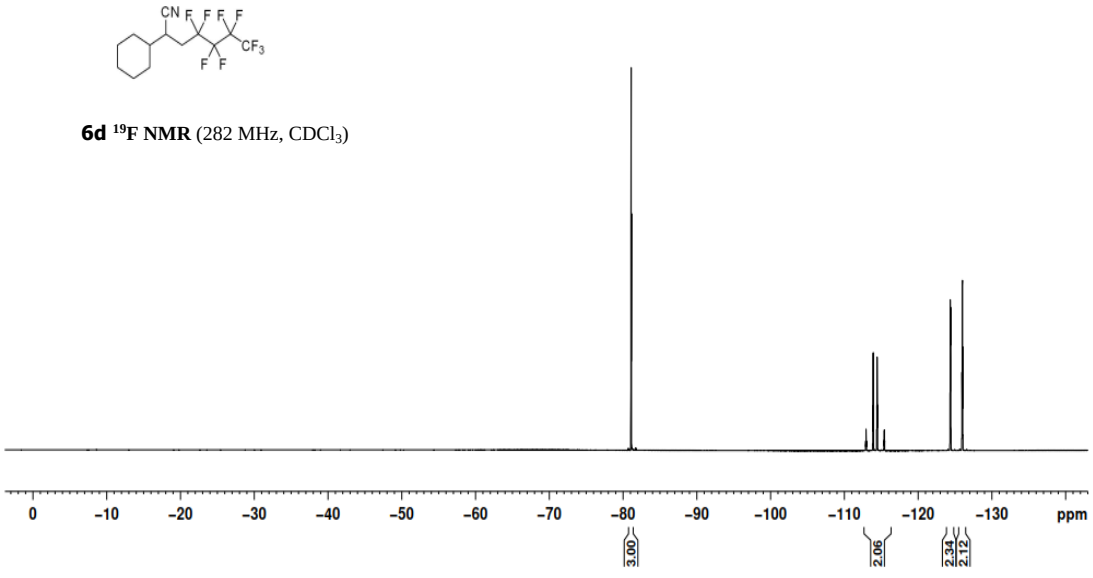


6d ^{1}**H NMR** (300 MHz, $CDCl_3$)

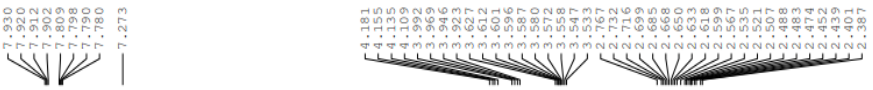


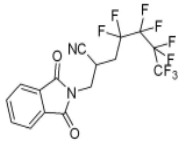


6d ^{13}**C NMR** (75 MHz, $CDCl_3$)

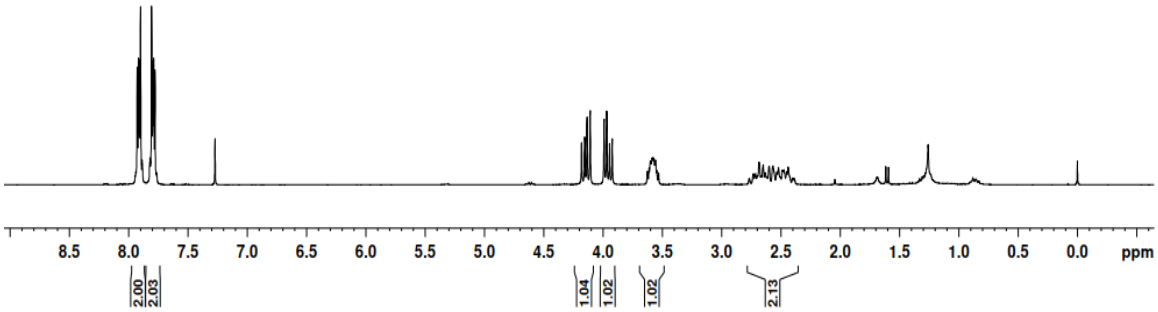


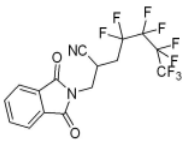
6d ^{19}**F NMR** (282 MHz, $CDCl_3$)



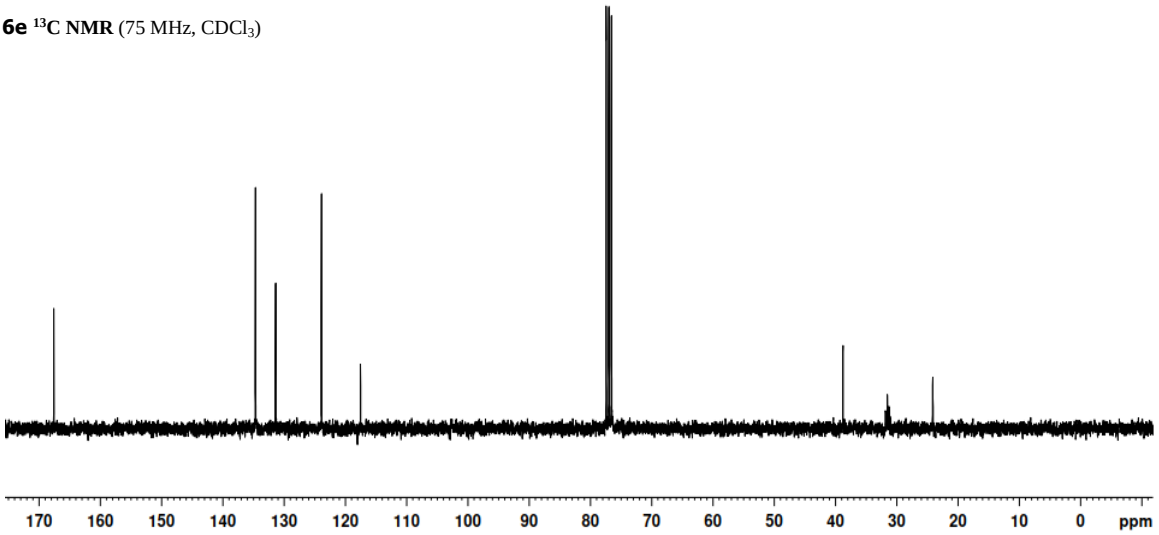


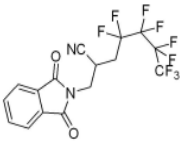
6e **^{1}H NMR** (300 MHz, $CDCl_3$)



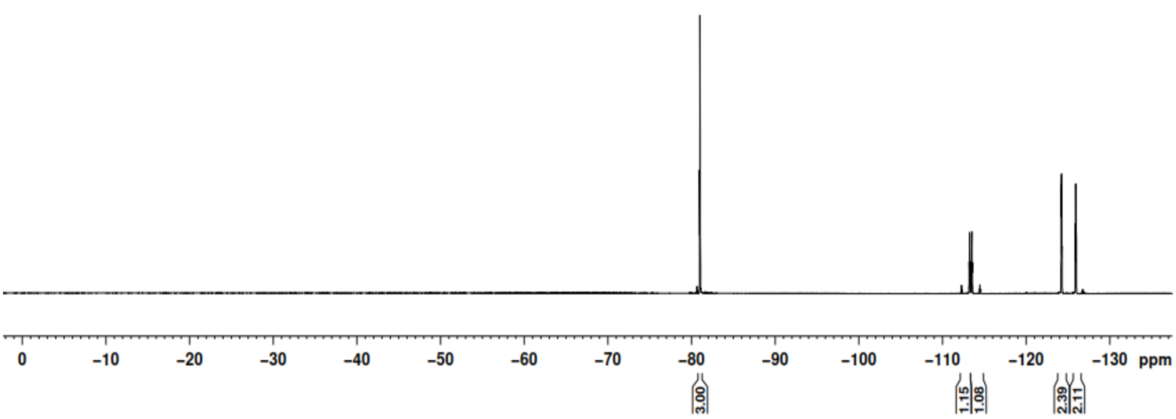


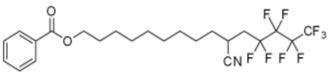
6e **^{13}C NMR** (75 MHz, $CDCl_3$)



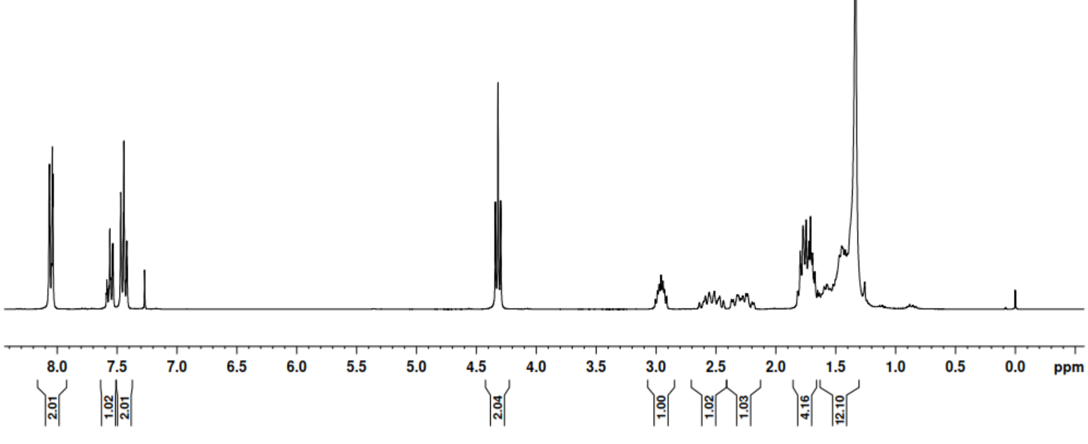


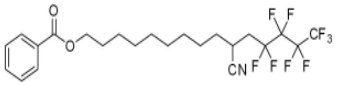
6e **^{19}F NMR** (282 MHz, CDCl$_3$)



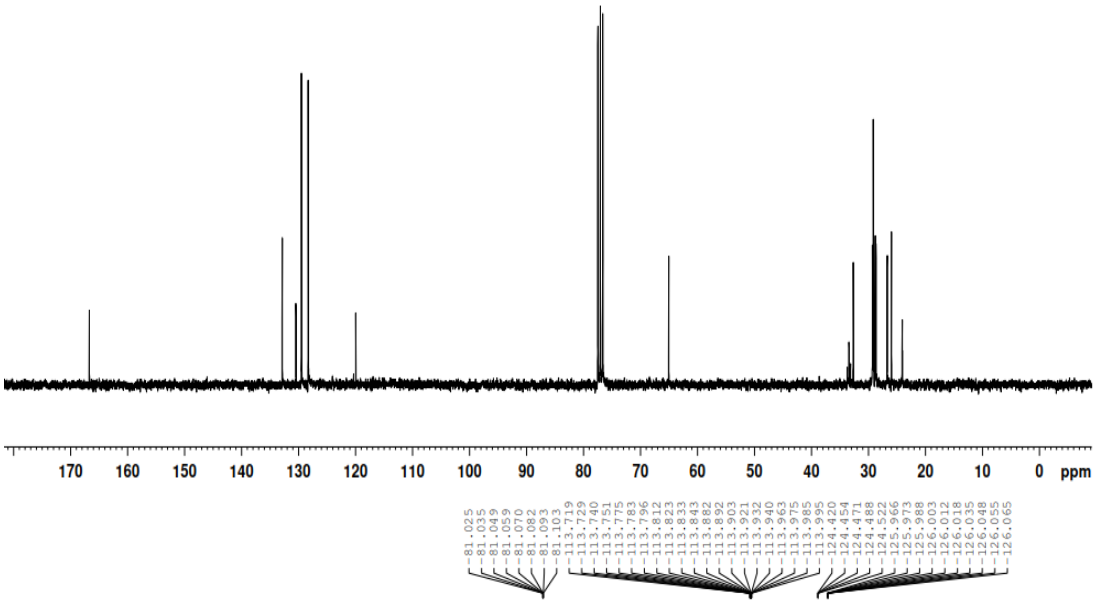


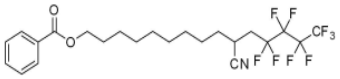
6f **^{1}H NMR** (300 MHz, CDCl$_3$)



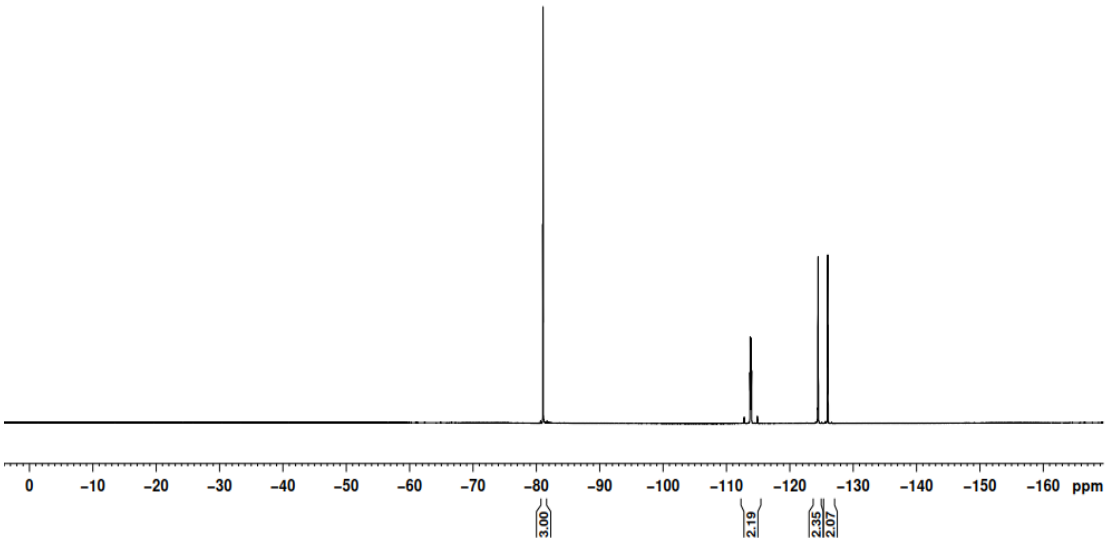


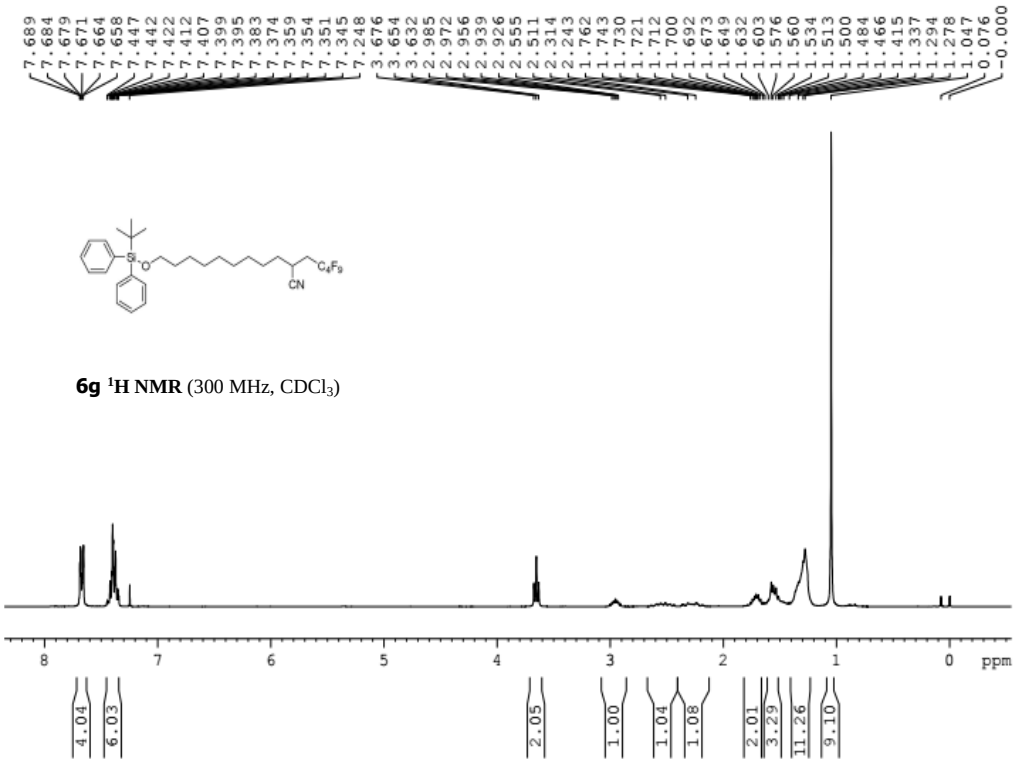
6f ^{13}**C NMR** (75 MHz, $CDCl_3$)



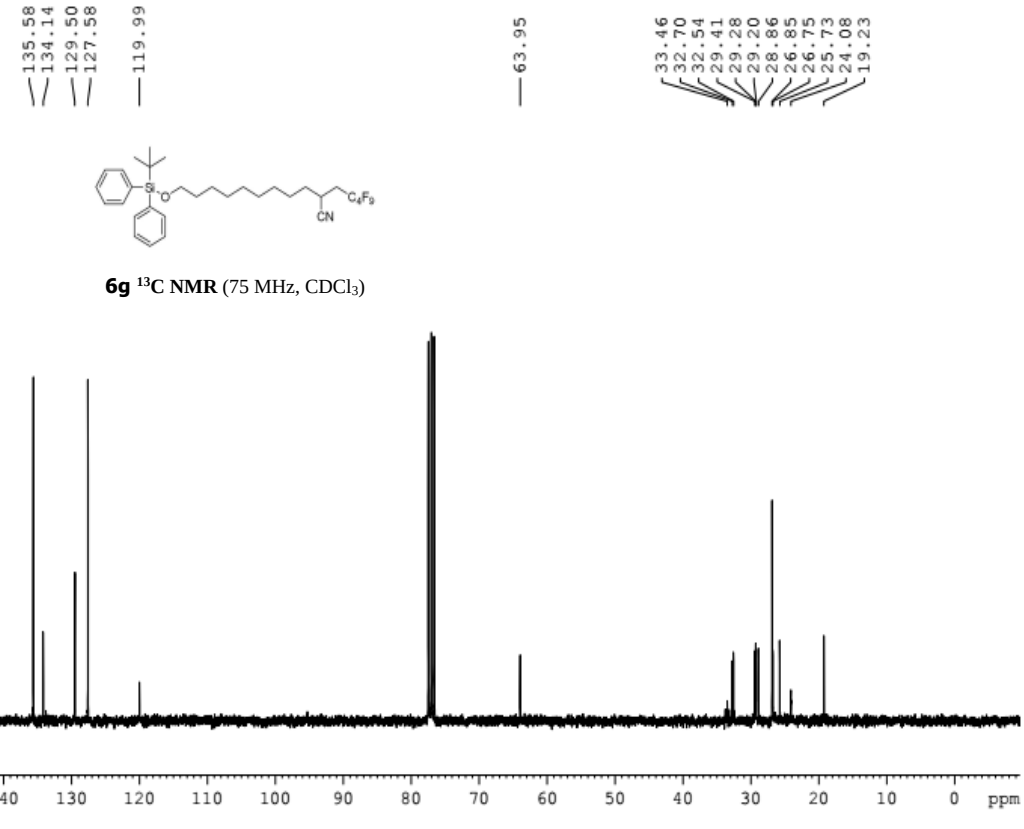


6f ^{19}**F NMR** (282 MHz, $CDCl_3$)

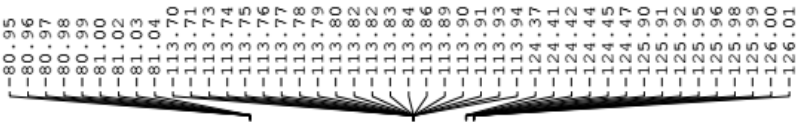


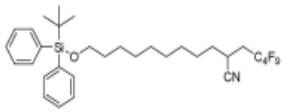


6g **^{1}H NMR** (300 MHz, $CDCl_3$)

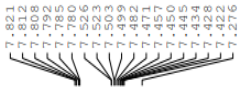


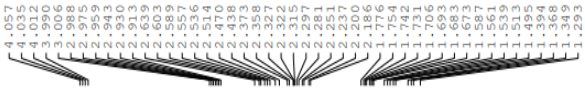
6g **^{13}C NMR** (75 MHz, $CDCl_3$)

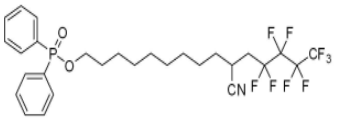




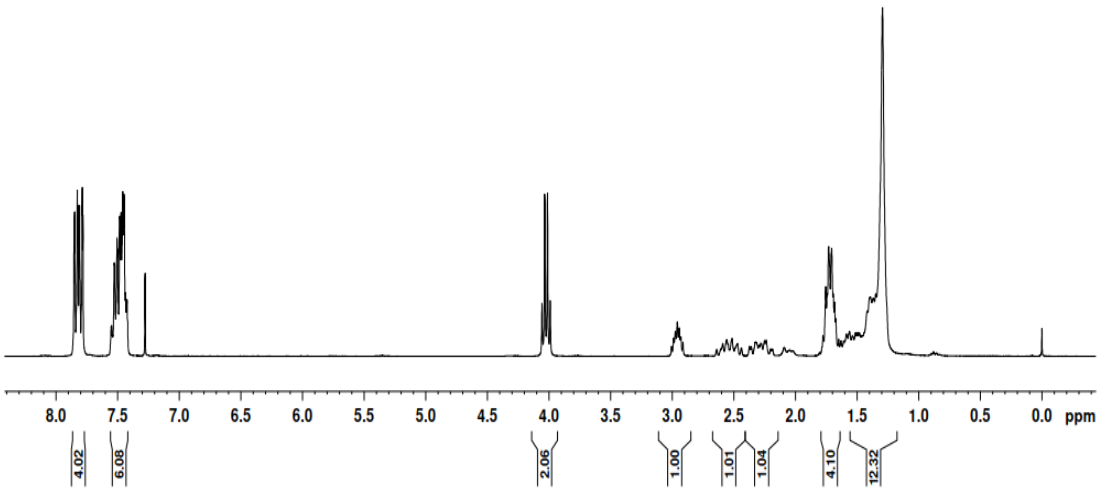
6g **^{19}F NMR** (282 MHz, $CDCl_3$)

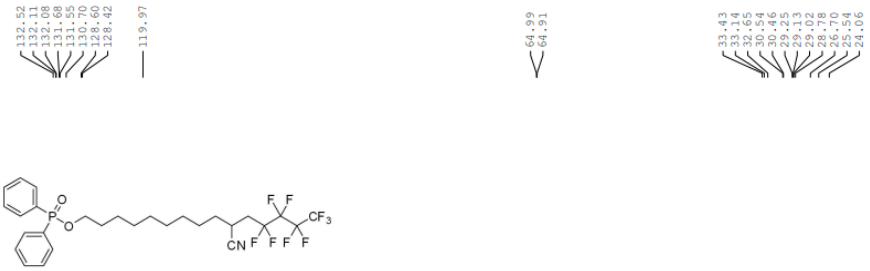




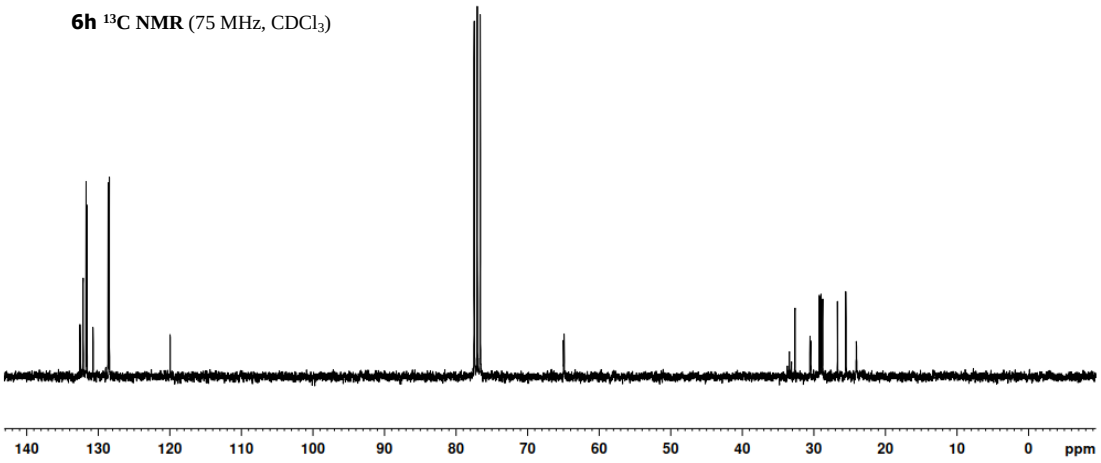


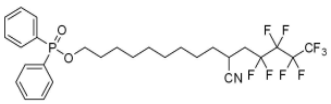
6h **^{1}H NMR** (300 MHz, $CDCl_3$)



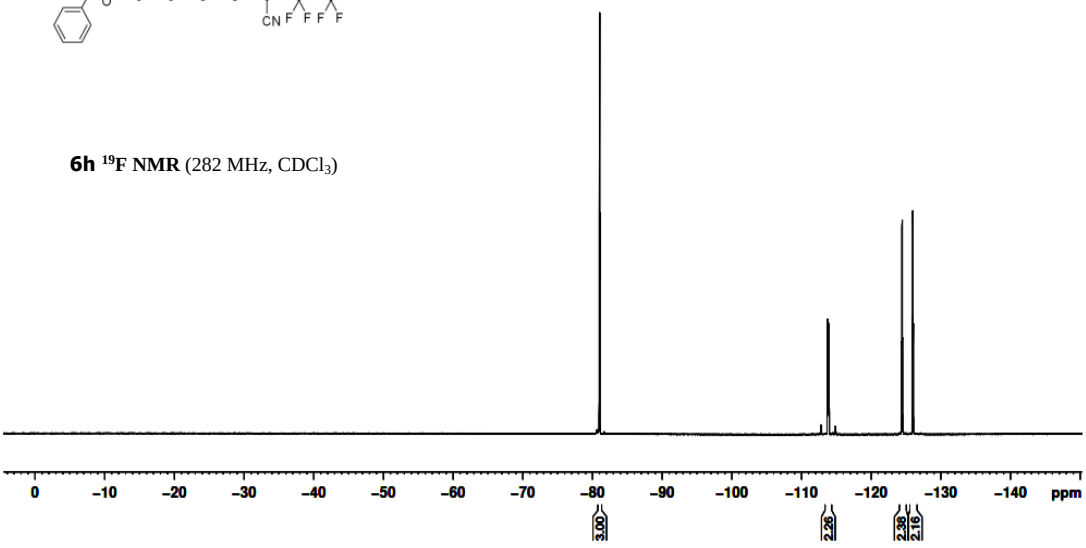


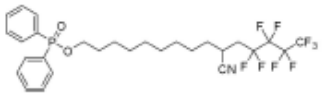
6h ^{13}**C NMR** (75 MHz, $CDCl_3$)



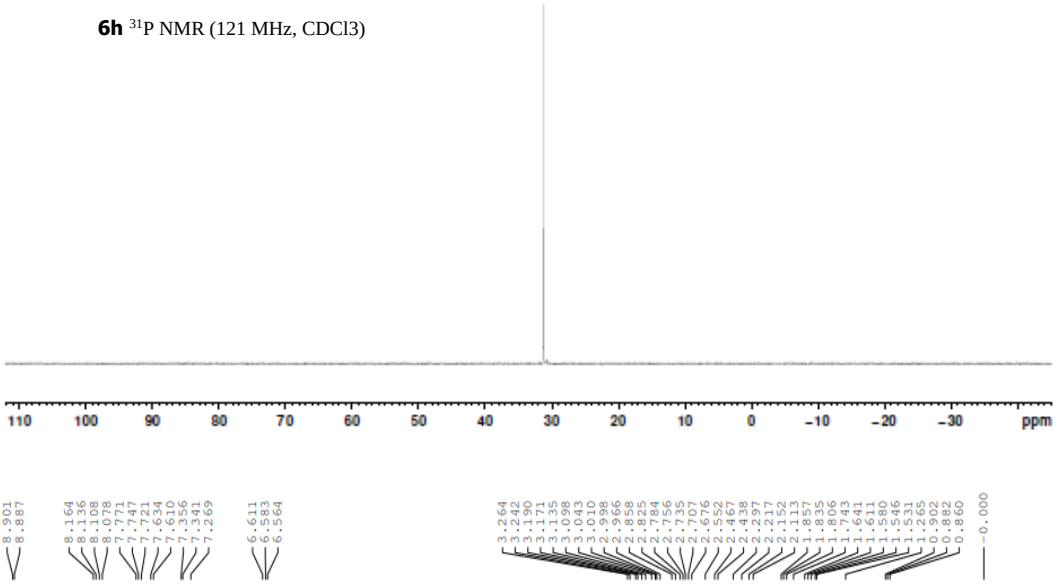


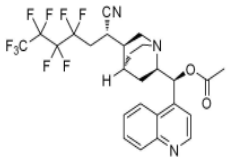
6h ^{19}**F NMR** (282 MHz, $CDCl_3$)



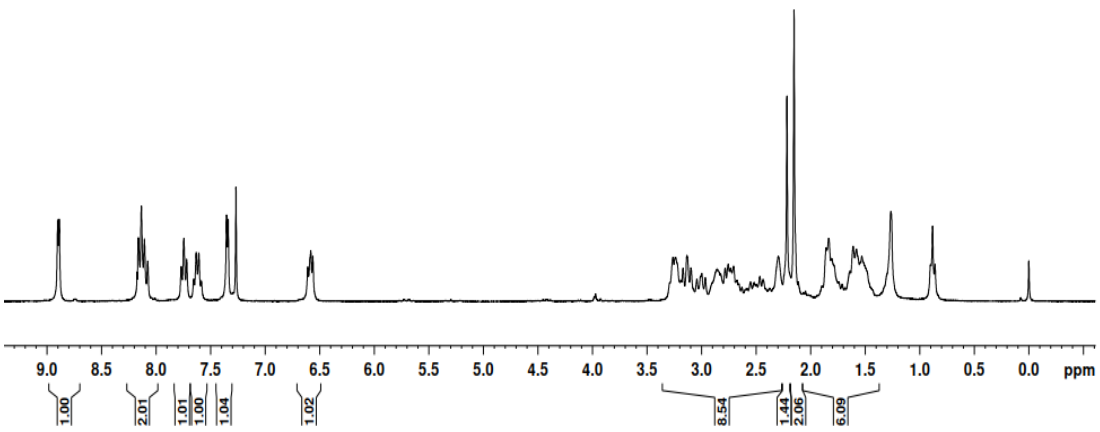


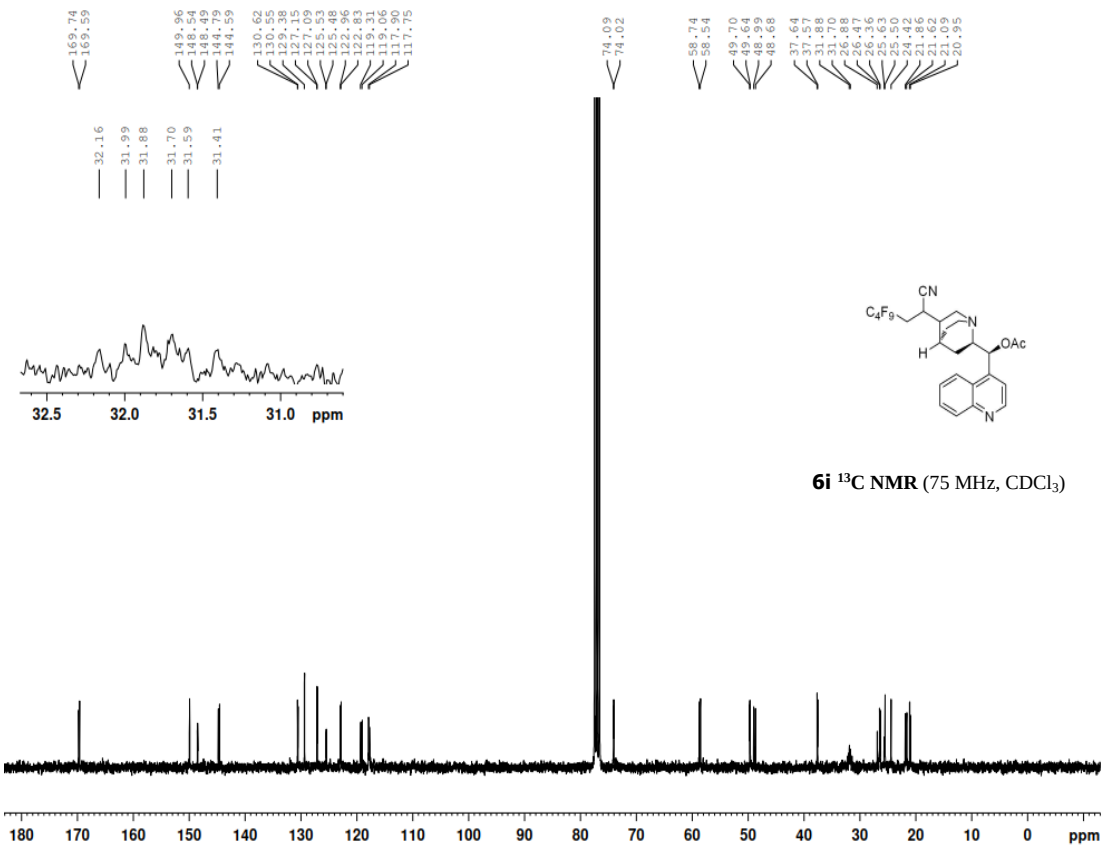
6h ^{31}P NMR (121 MHz, CDCl3)



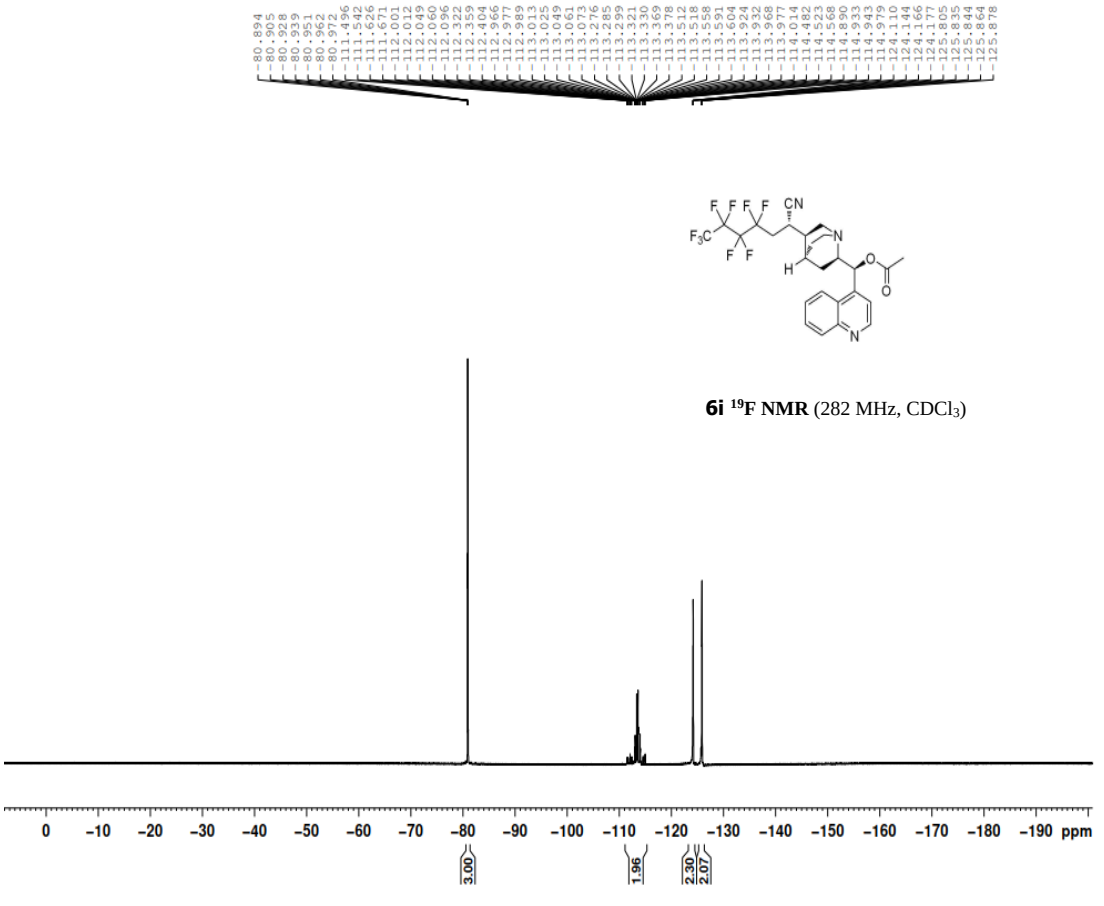


6i **^{1}H NMR** (300 MHz, $CDCl_3$)

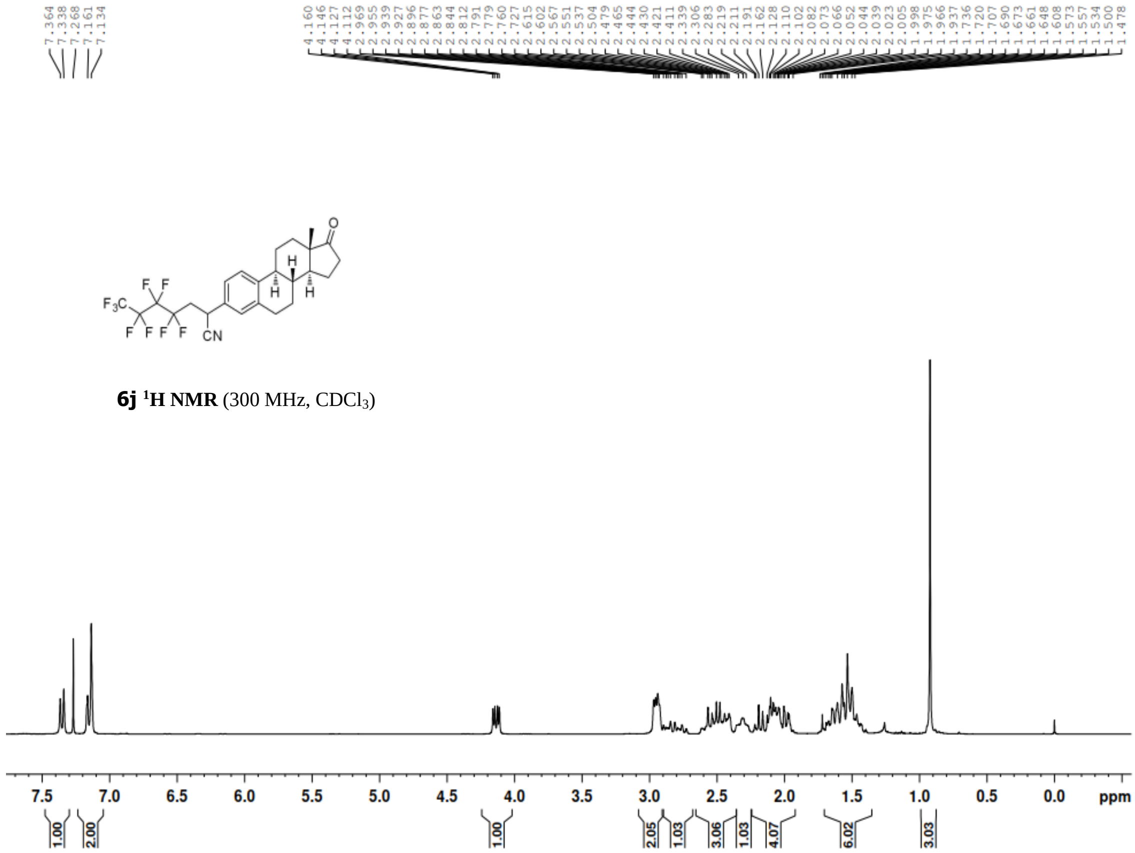




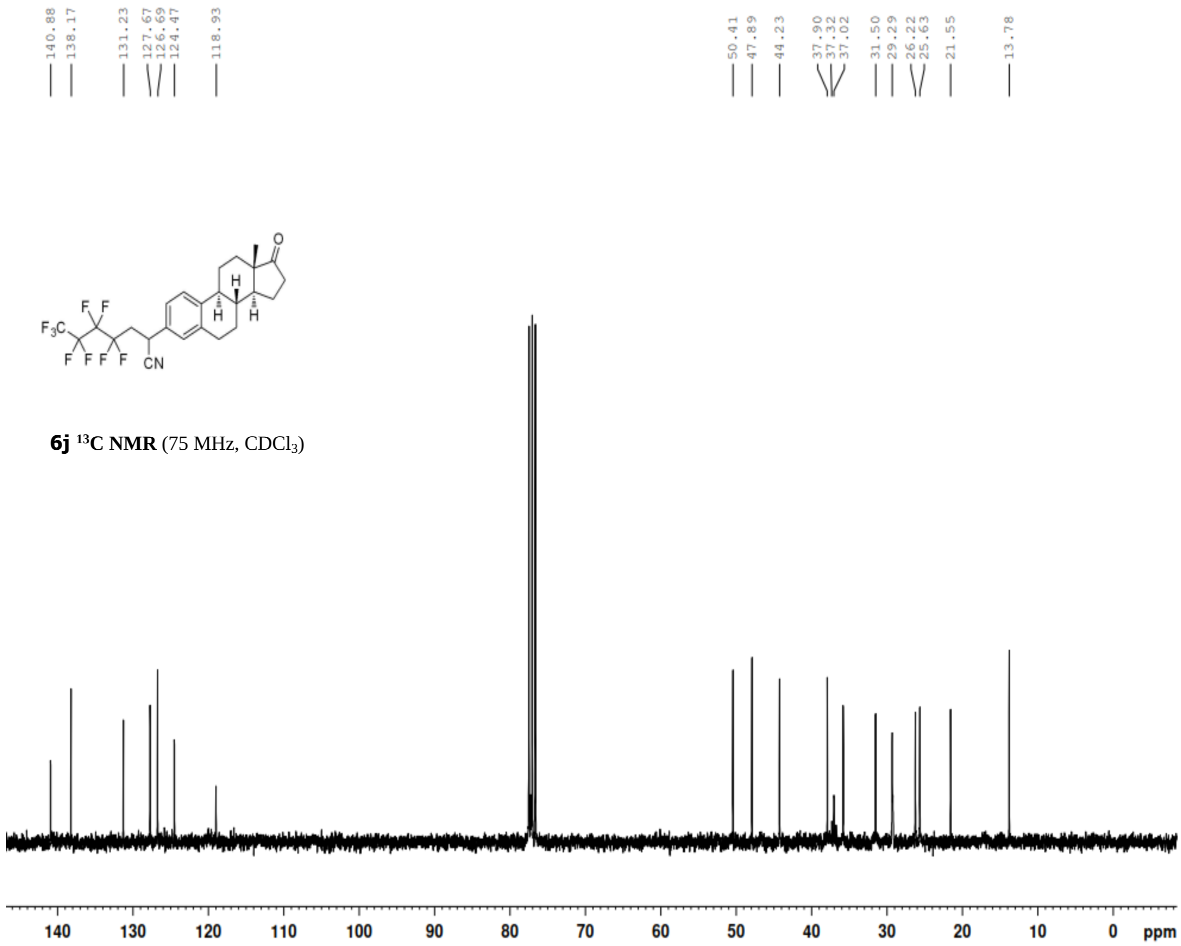
6i ^{13}**C NMR** (75 MHz, $CDCl_3$)



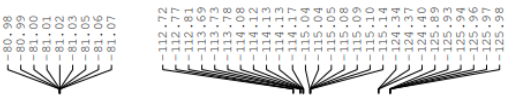
6i ^{19}**F NMR** (282 MHz, $CDCl_3$)

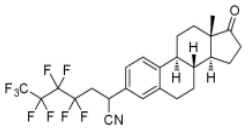


6j **¹H NMR** (300 MHz, $CDCl_3$)

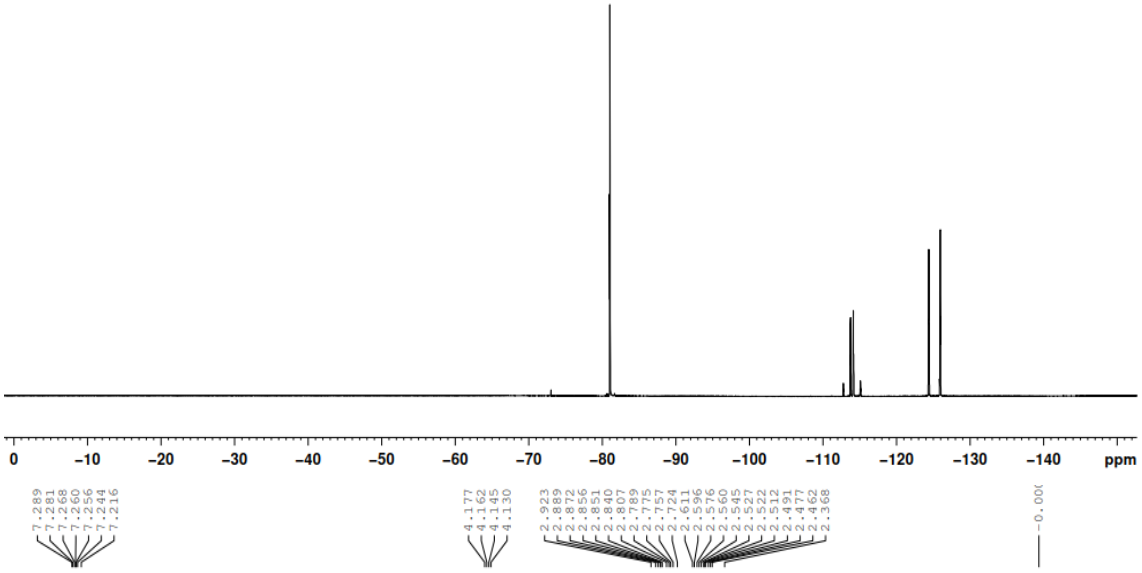


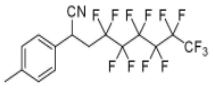
6j **¹³C NMR** (75 MHz, $CDCl_3$)



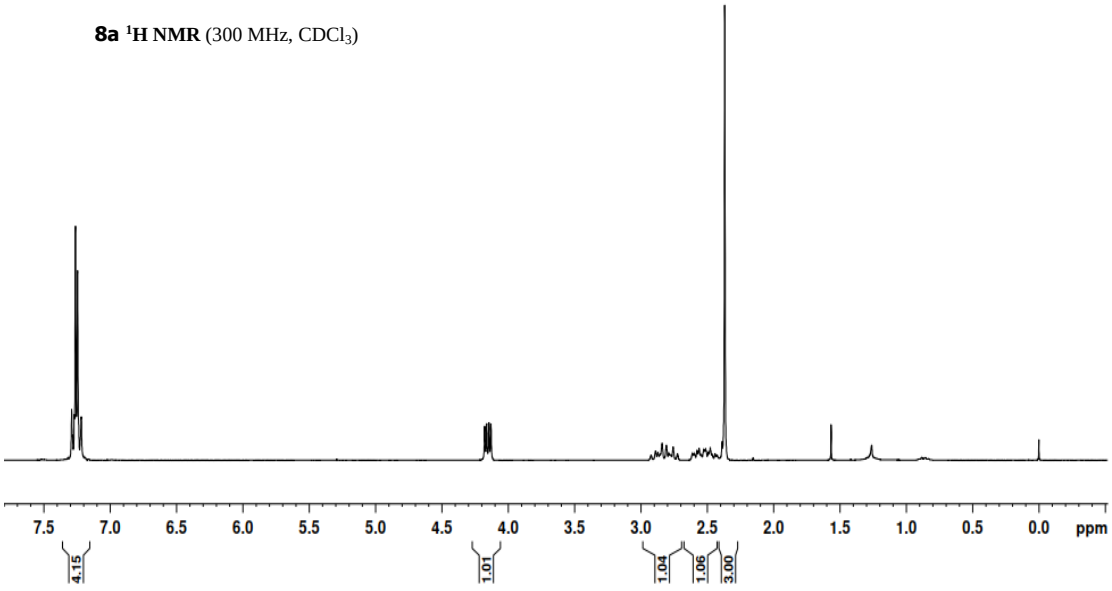


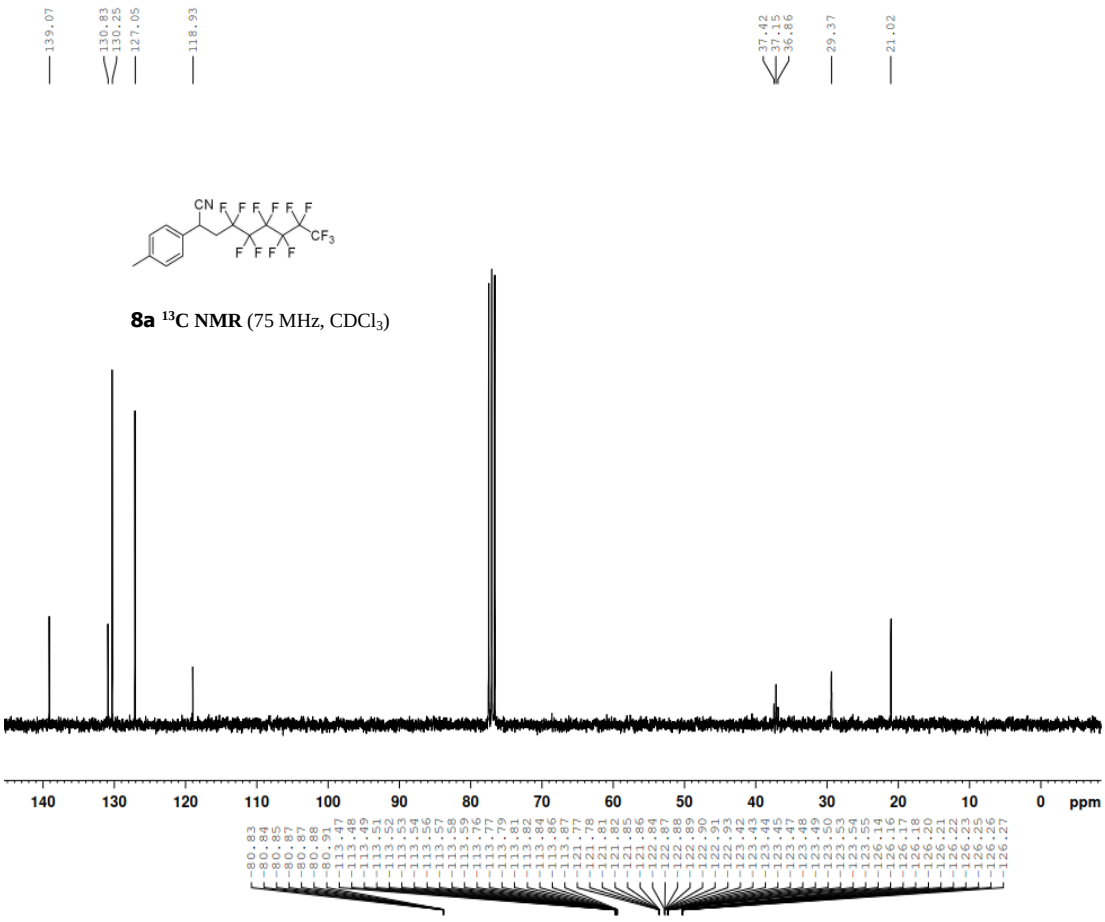
6j ^{19}**F NMR** (282 MHz, $CDCl_3$)



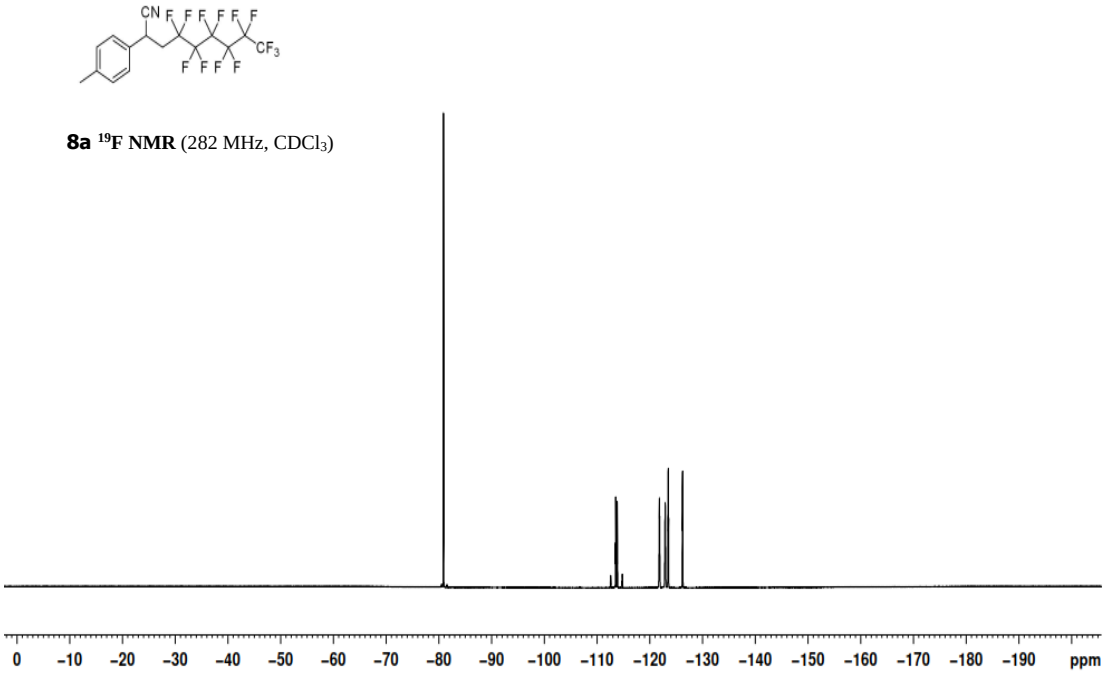


8a ^{1}**H NMR** (300 MHz, $CDCl_3$)

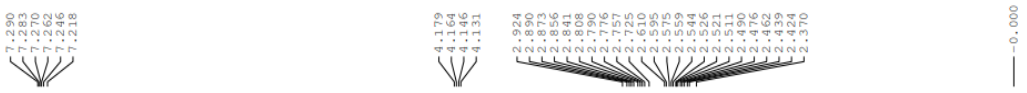




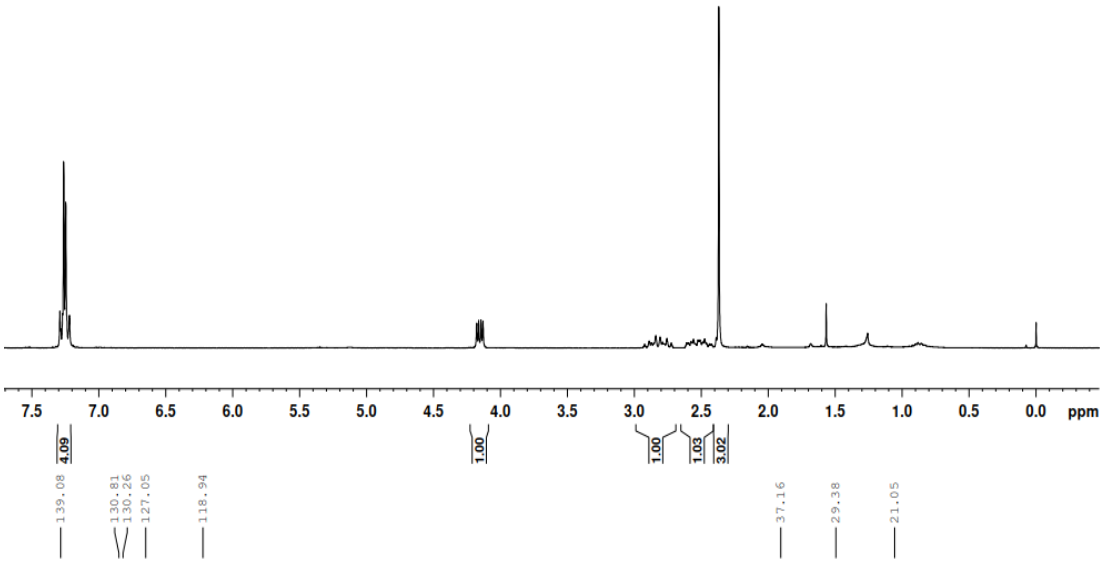
8a **^{13}C NMR** (75 MHz, $CDCl_3$)



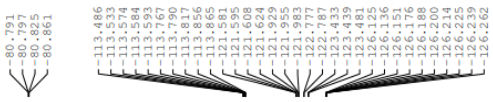
8a **^{19}F NMR** (282 MHz, $CDCl_3$)



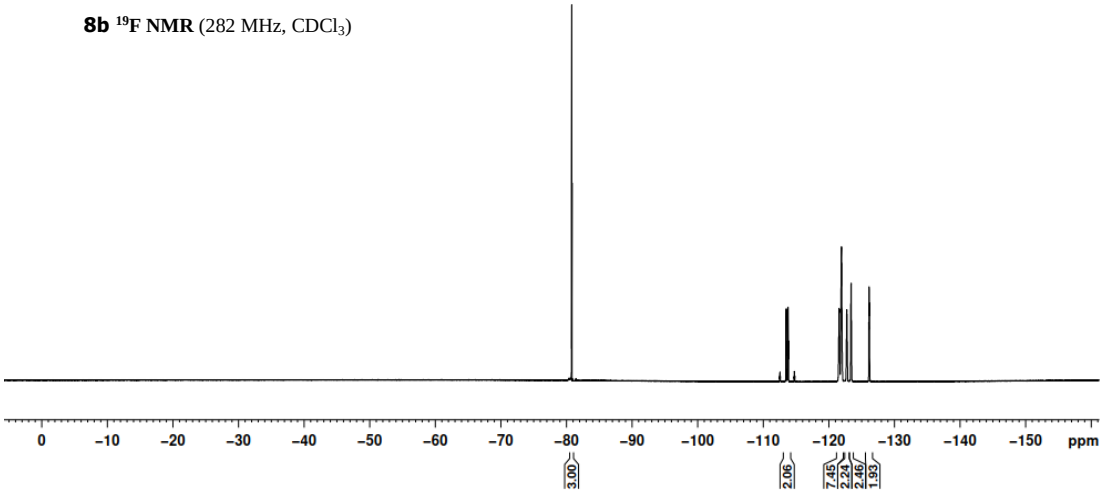
8b **^{1}H NMR** (300 MHz, $CDCl_3$)

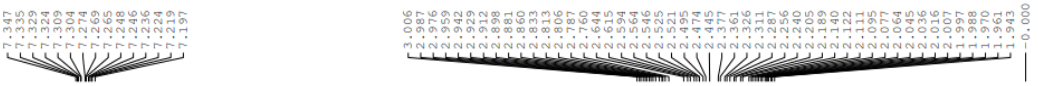


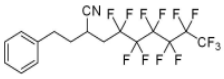
8b **^{13}C NMR** (75 MHz, $CDCl_3$)



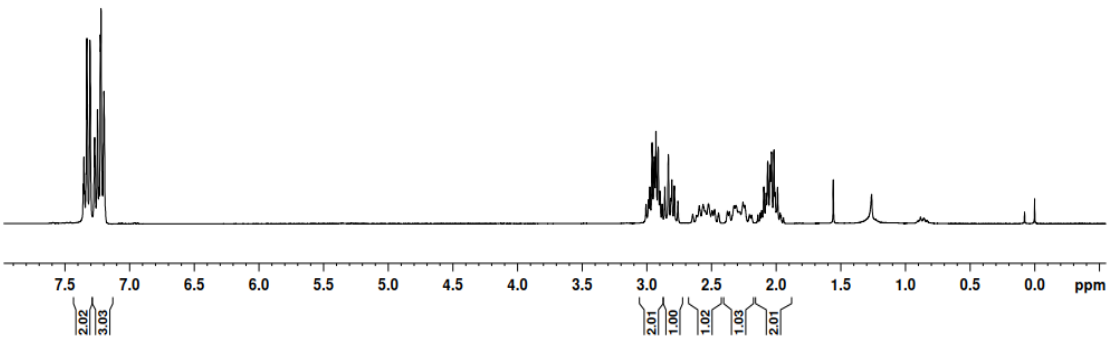
8b ^{19}**F NMR** (282 MHz, $CDCl_3$)

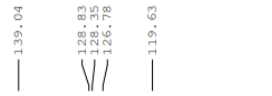


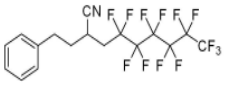




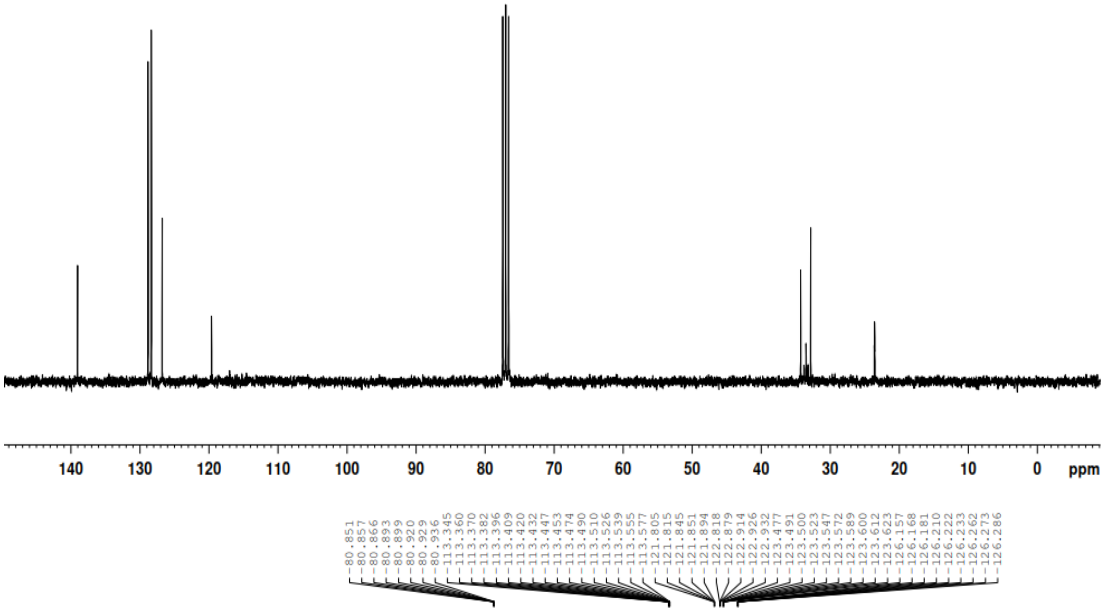
8c ^{1}**H NMR** (300 MHz, $CDCl_3$)

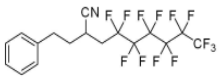




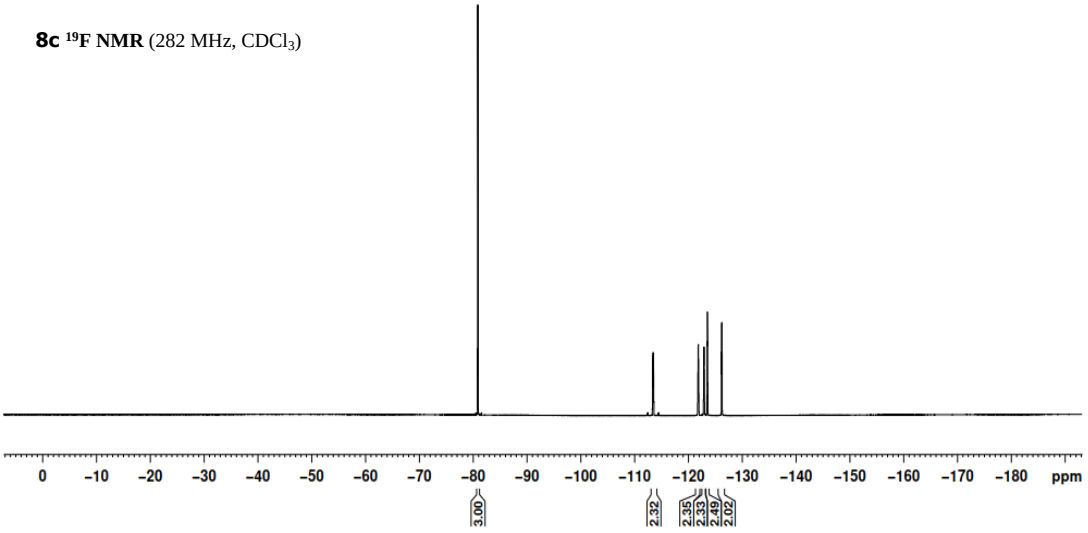


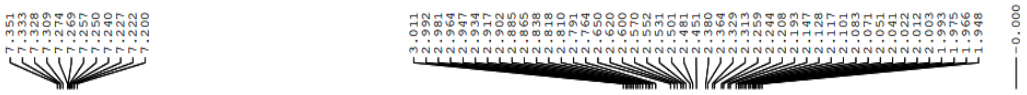
8c ^{13}**C NMR** (75 MHz, $CDCl_3$)

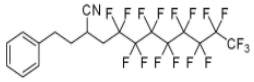




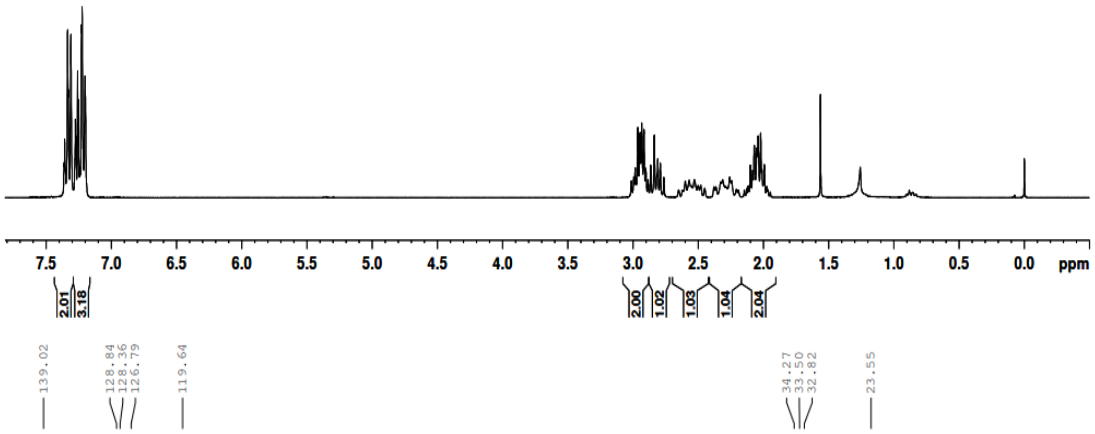
8c ^{19}**F NMR** (282 MHz, $CDCl_3$)

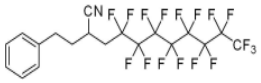




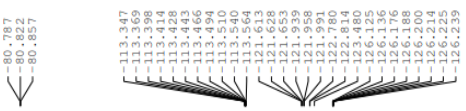


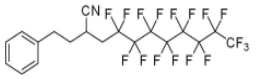
8d **^{1}H NMR** (300 MHz, $CDCl_3$)



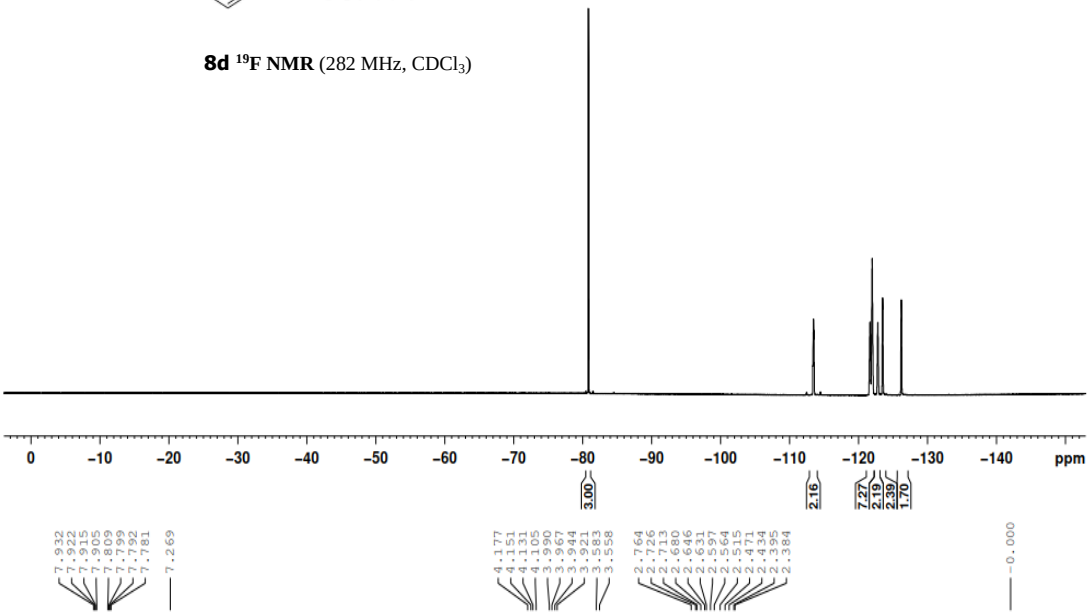


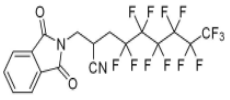
8d **^{13}C NMR** (75 MHz, $CDCl_3$)



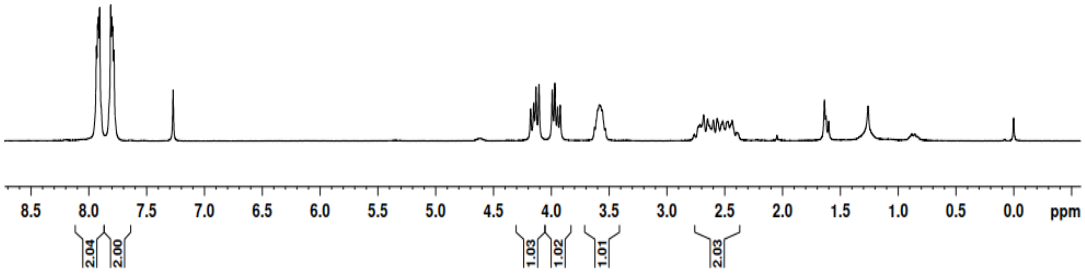


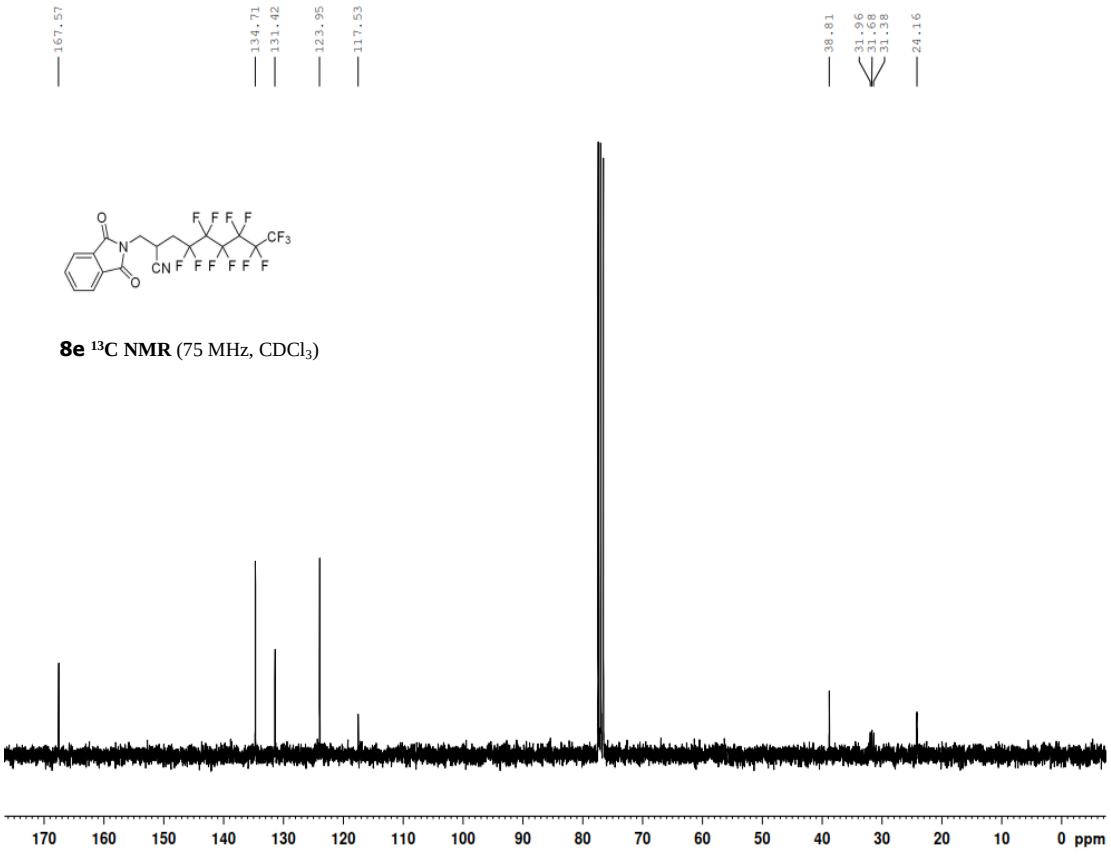
8d **^{19}F NMR** (282 MHz, $CDCl_3$)



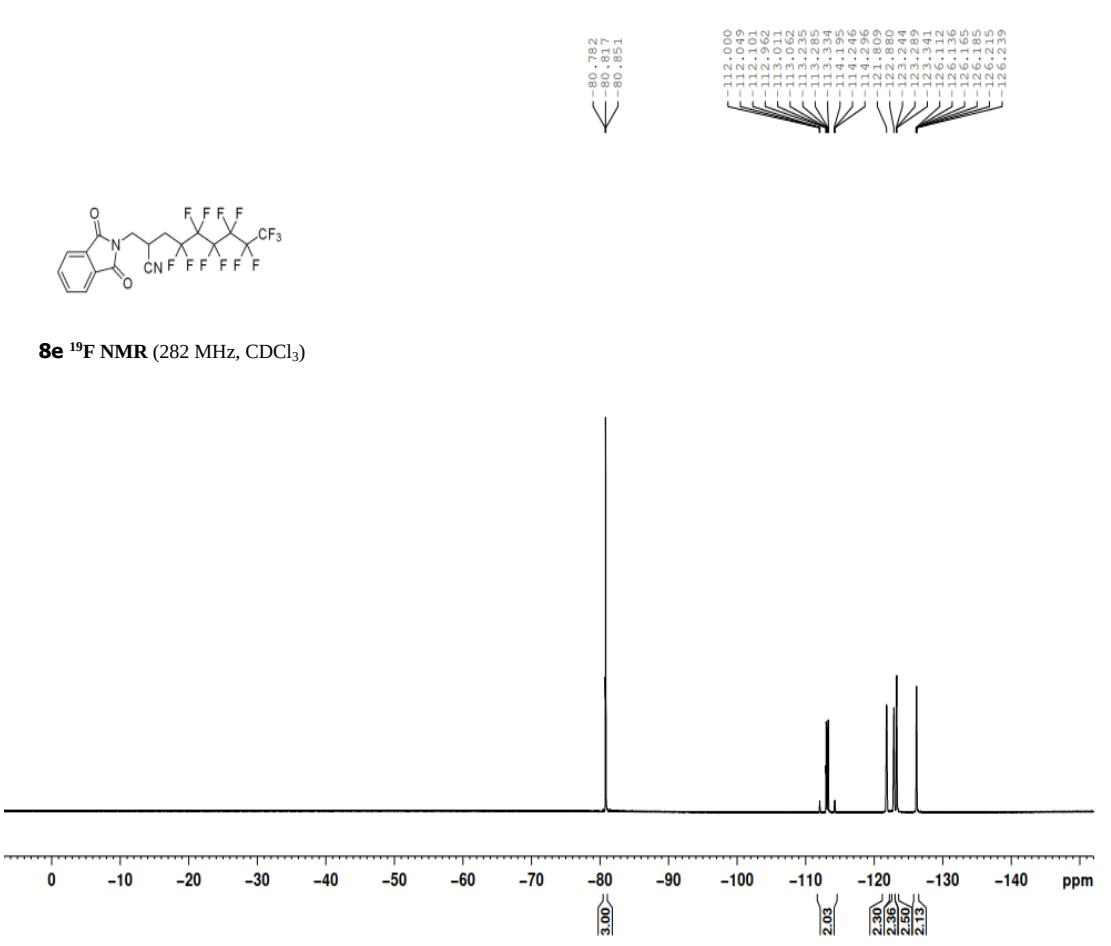


8e **^{1}H NMR** (300 MHz, $CDCl_3$)

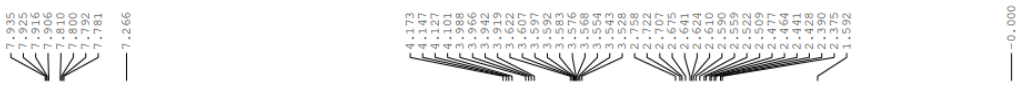


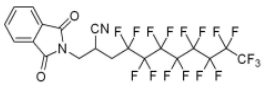


8e ^{13}**C NMR** (75 MHz, $CDCl_3$)

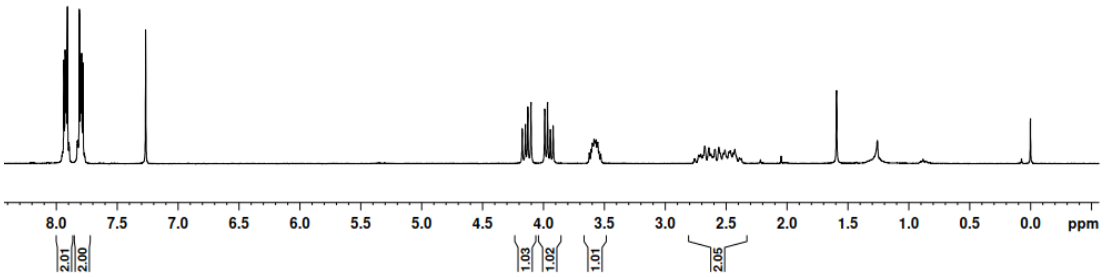


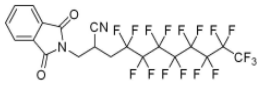
8e ^{19}**F NMR** (282 MHz, $CDCl_3$)



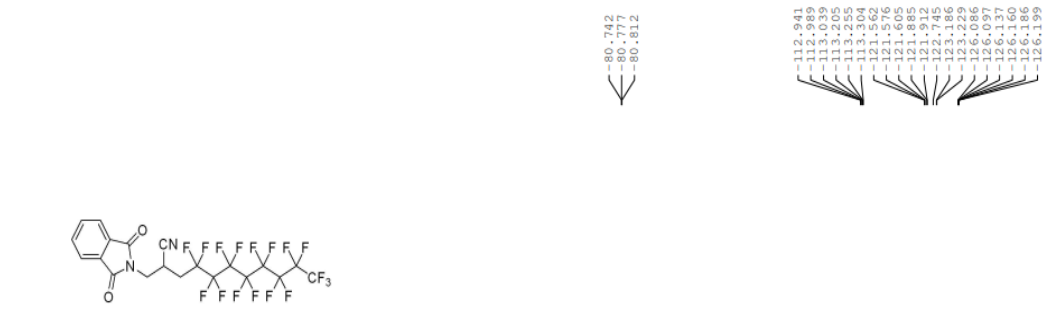


8f **^{1}H NMR** (300 MHz, $CDCl_3$)

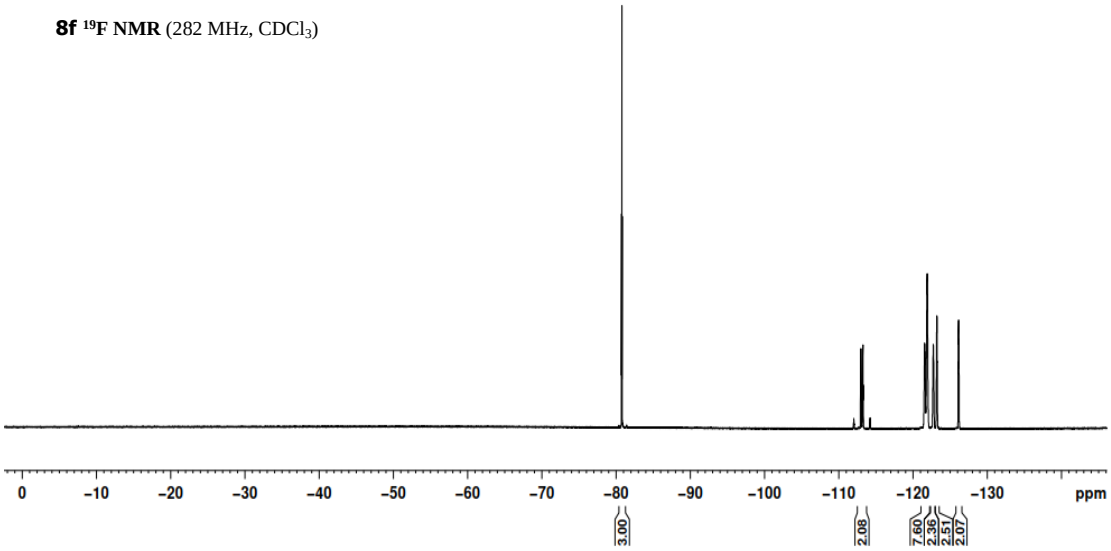


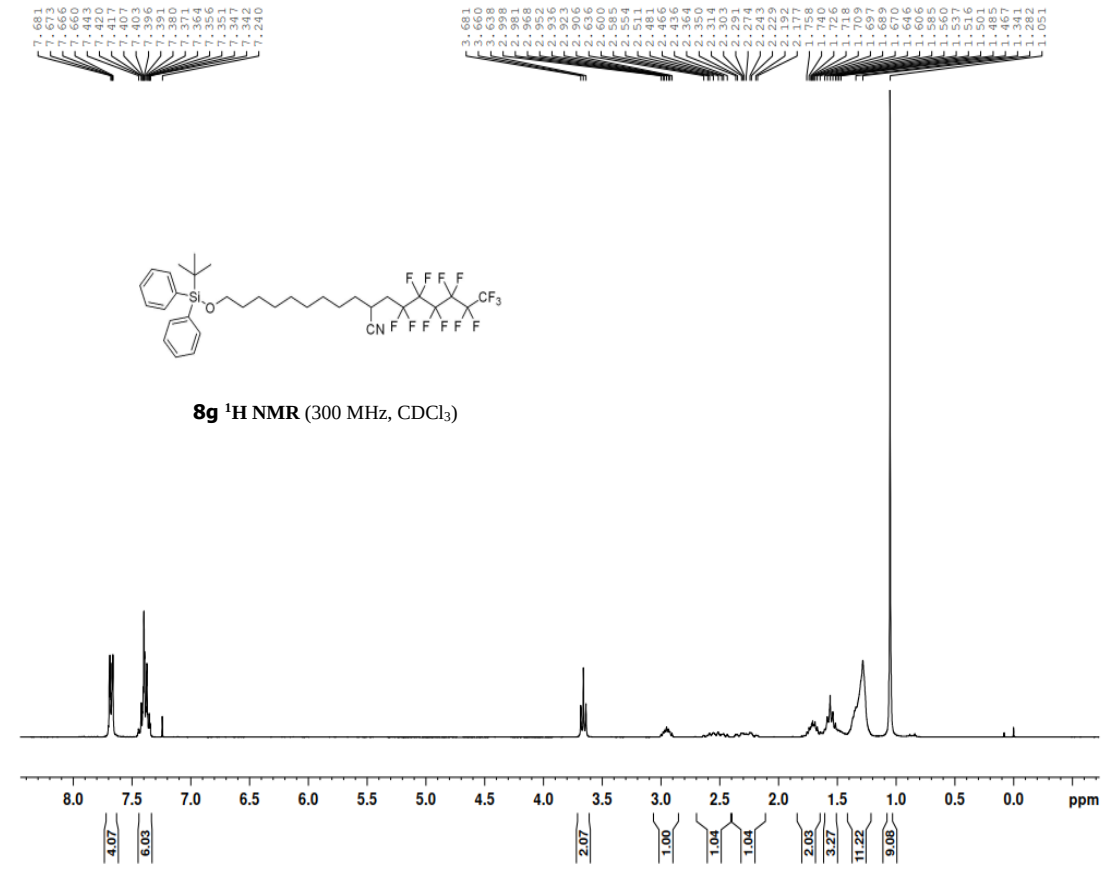


8f **^{13}C NMR** (75 MHz, $CDCl_3$)

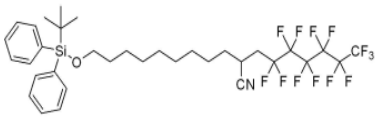


8f ^{19}**F NMR** (282 MHz, $CDCl_3$)

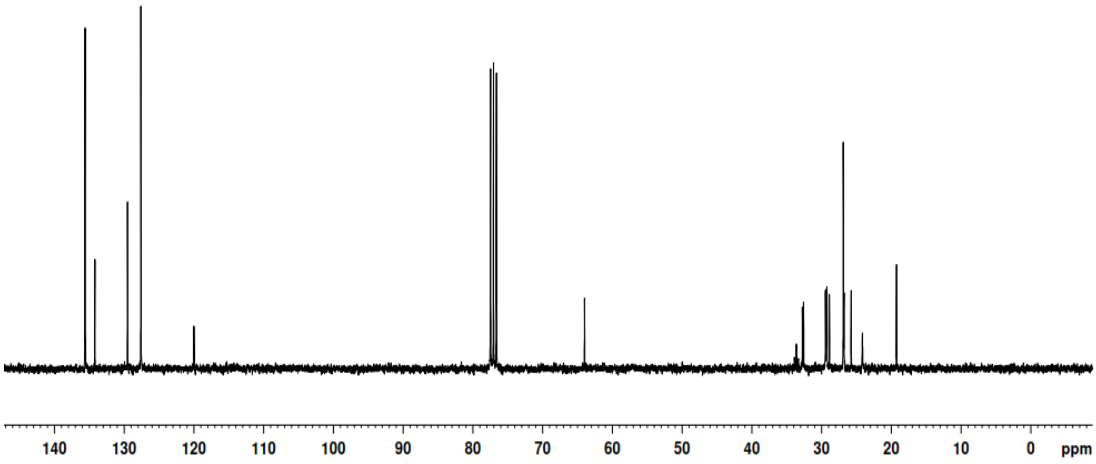


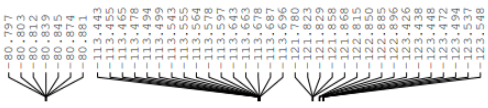


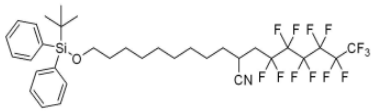
8g ^{1}**H NMR** (300 MHz, $CDCl_3$)



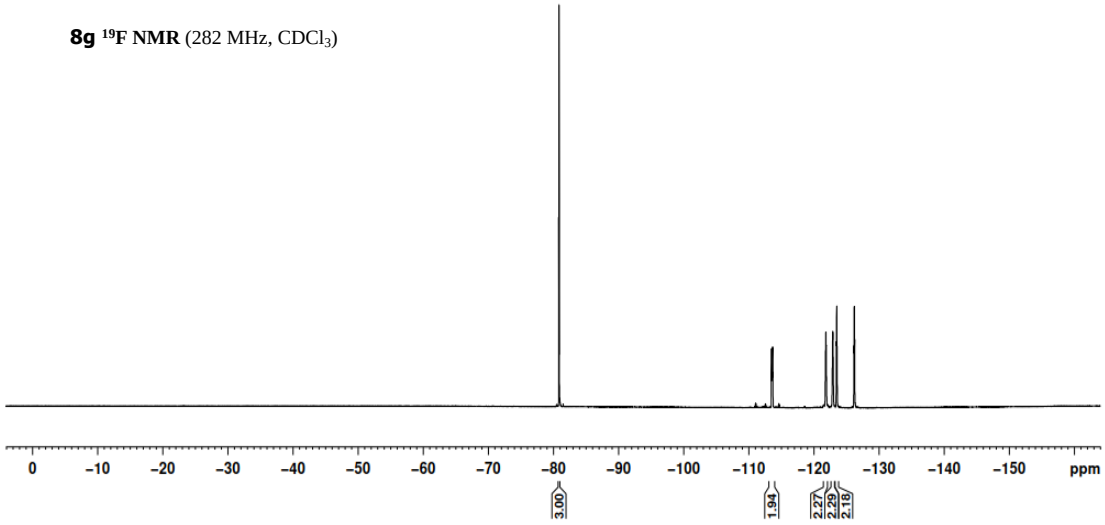
8g **^{13}C NMR** (75 MHz, $CDCl_3$)

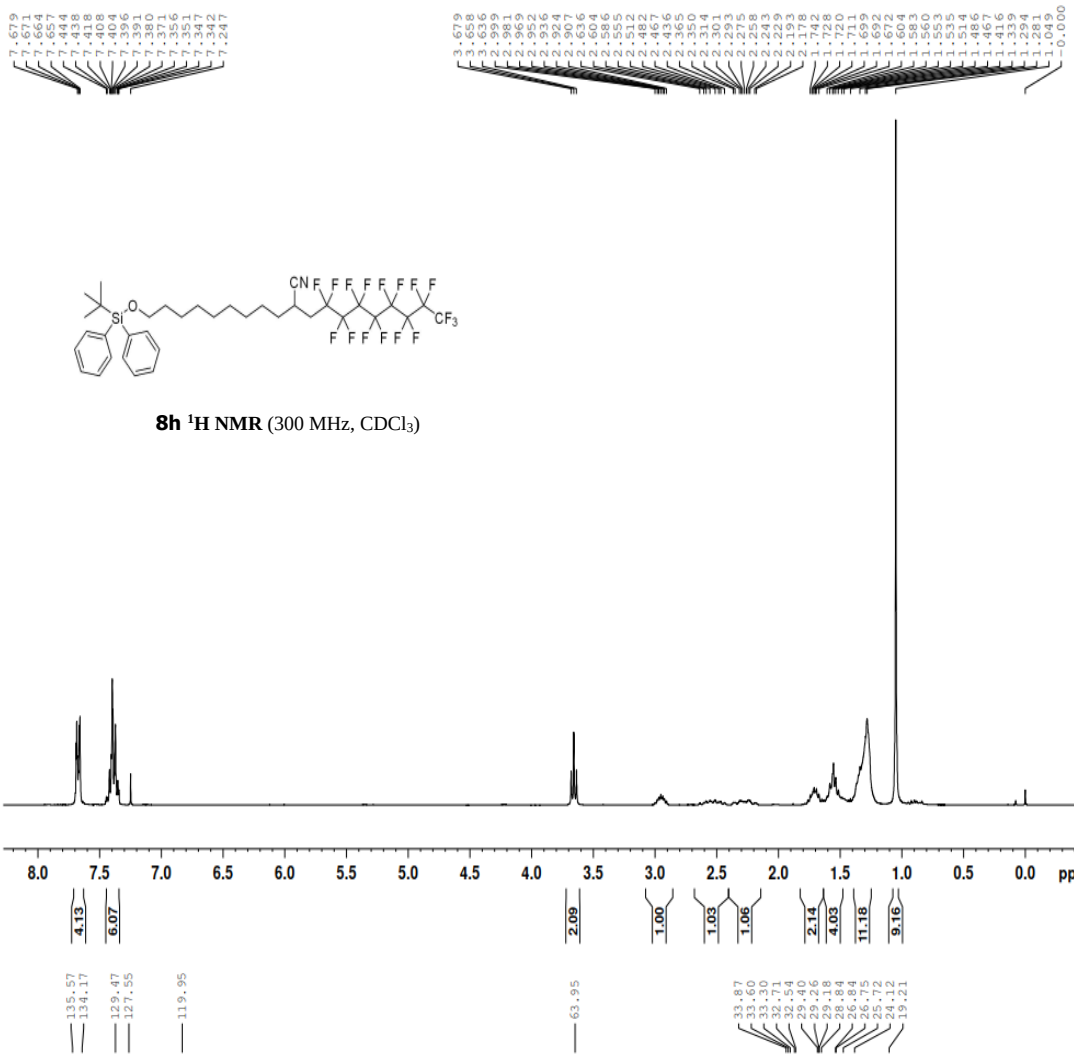




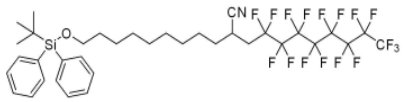


8g **^{19}F NMR** (282 MHz, $CDCl_3$)

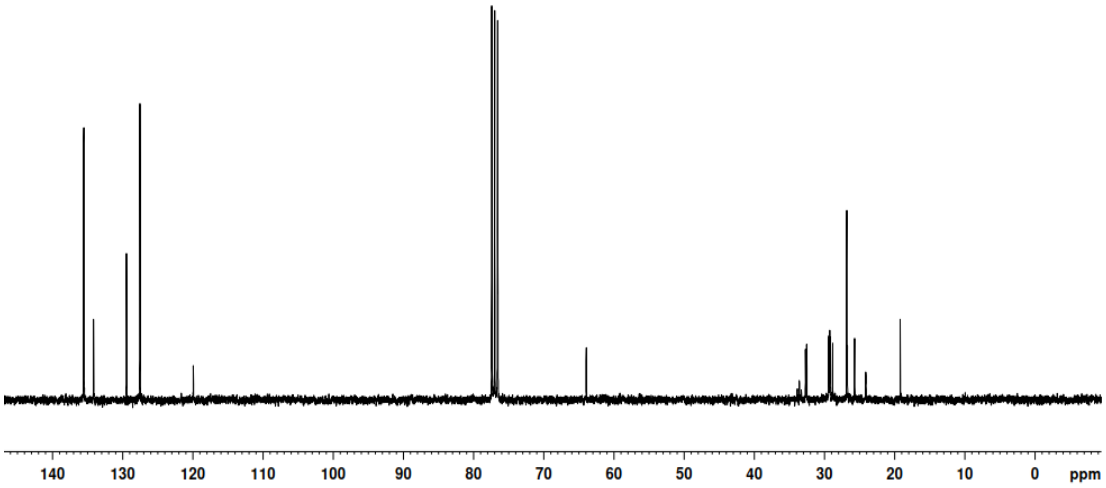


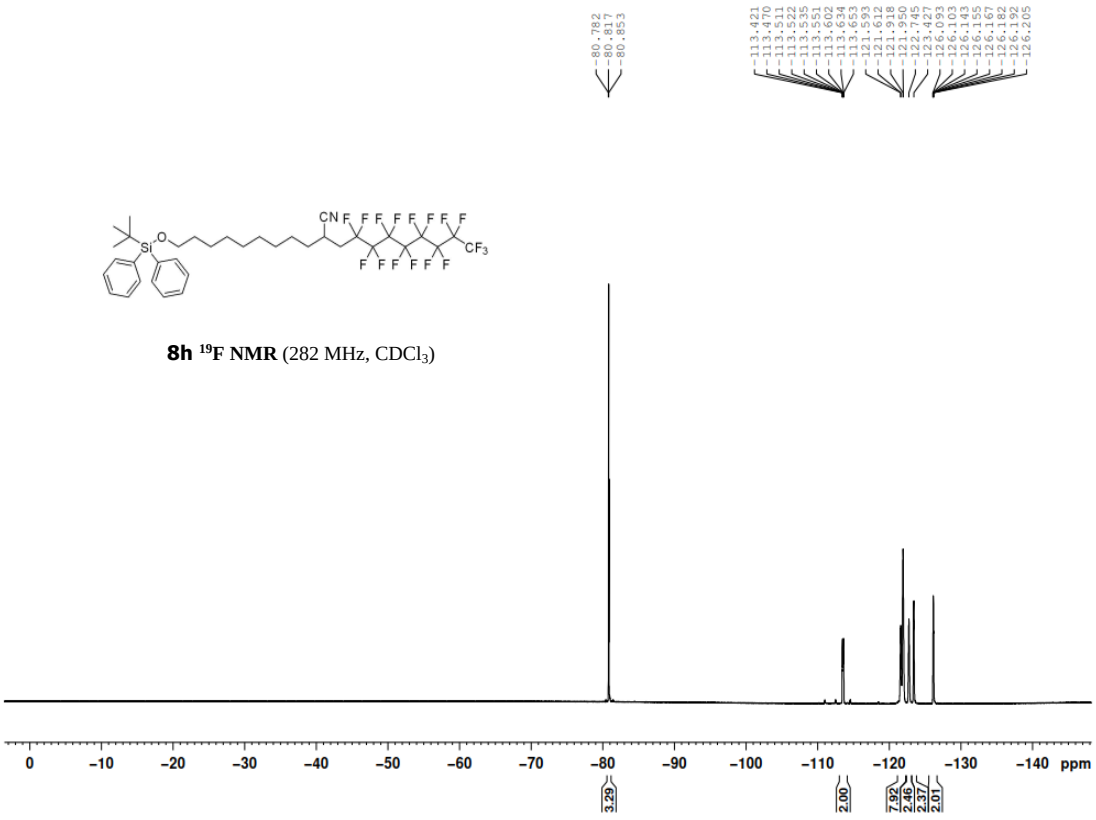


8h ^{1}**H NMR** (300 MHz, $CDCl_3$)

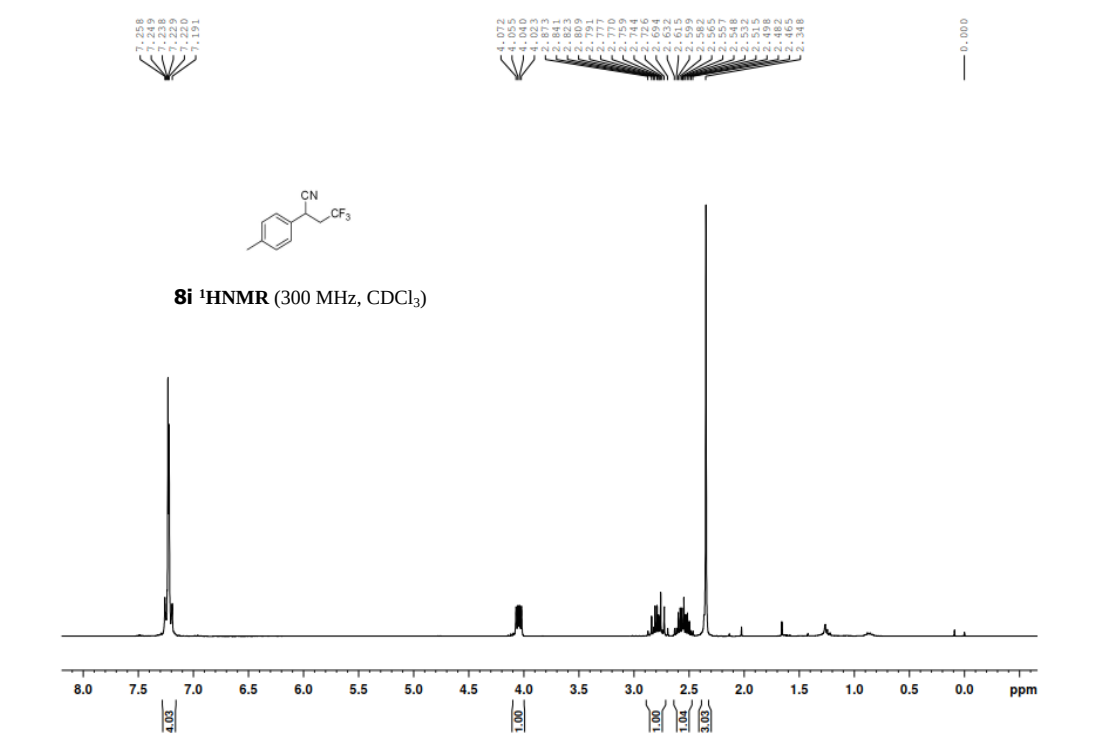


8h ^{13}**C NMR** (75 MHz, $CDCl_3$)

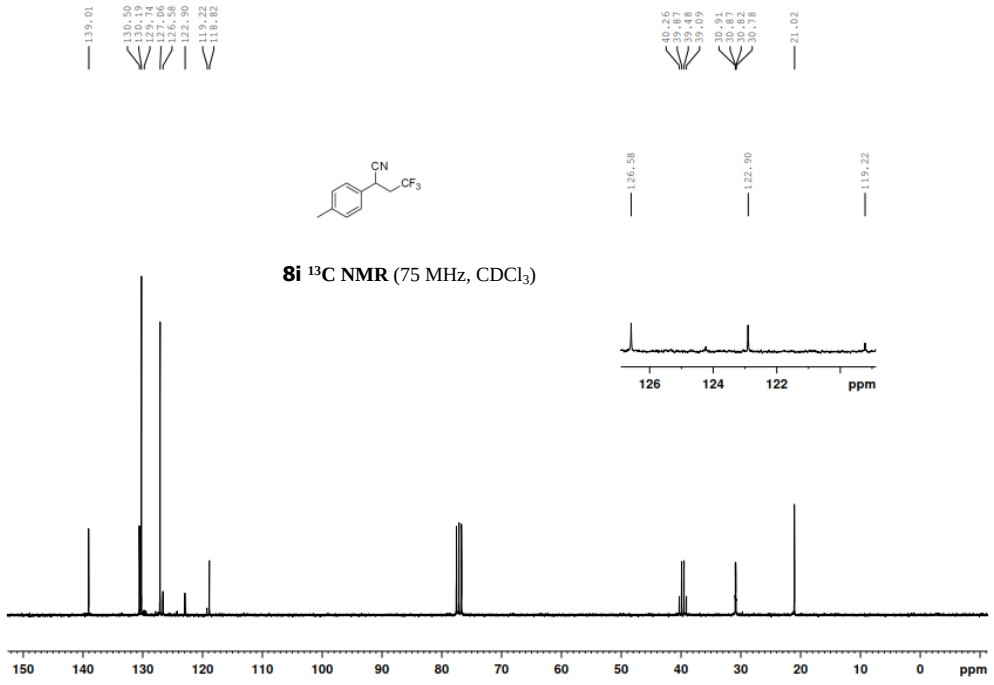




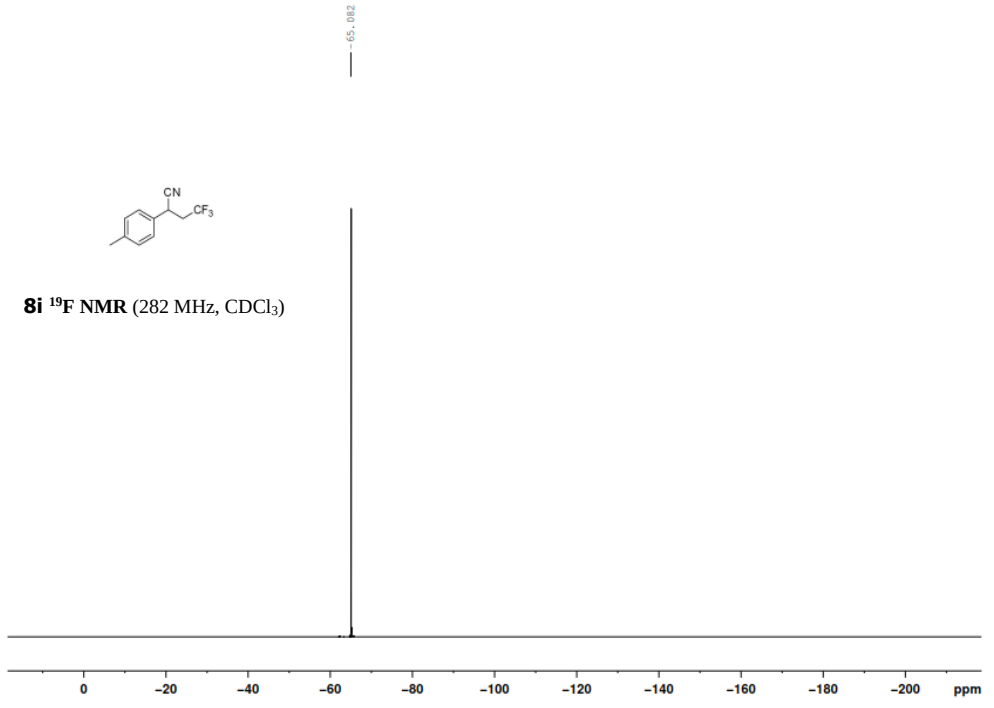
8h **^{19}F NMR** (282 MHz, $CDCl_3$)



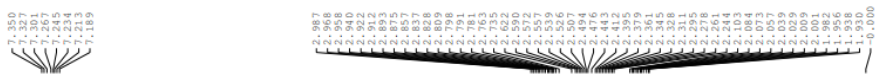
8i **^{1}HNMR** (300 MHz, $CDCl_3$)

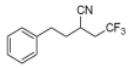


8i ^{13}**C NMR** (75 MHz, $CDCl_3$)

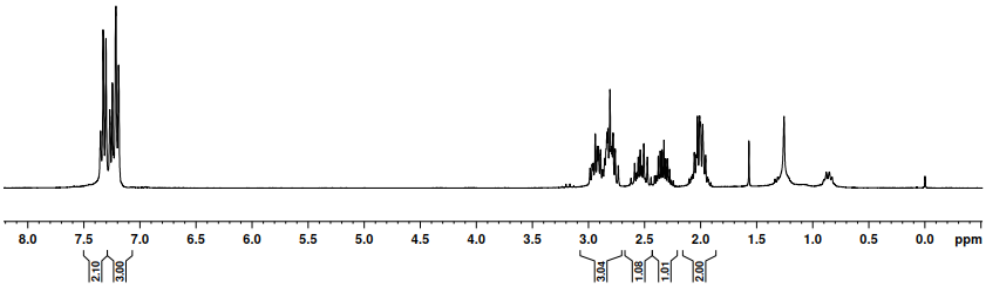


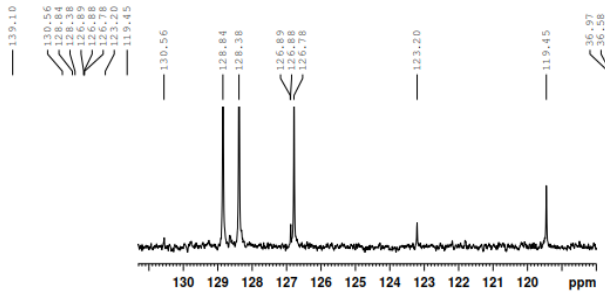
8i ^{19}**F NMR** (282 MHz, $CDCl_3$)

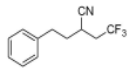




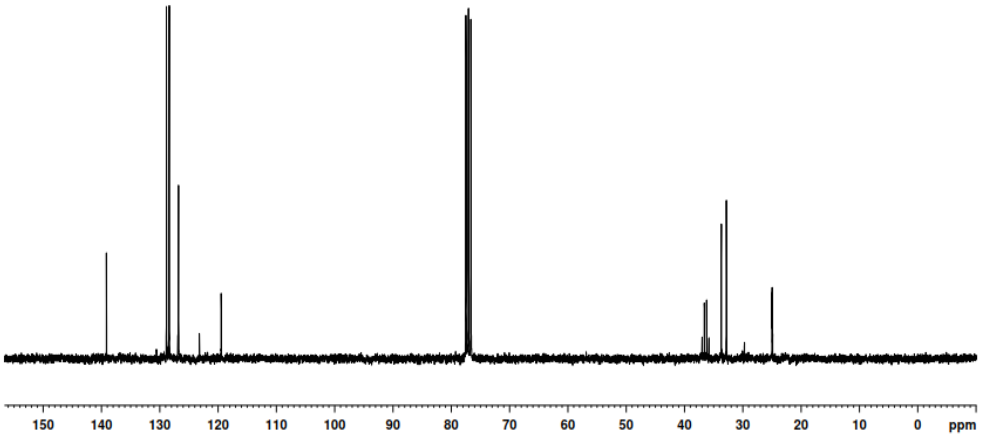
8j ^{1}**H NMR** (300 MHz, $CDCl_3$)

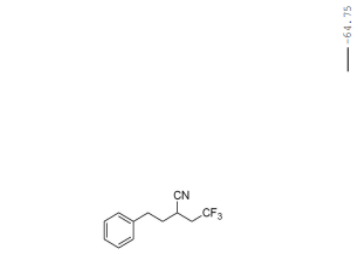




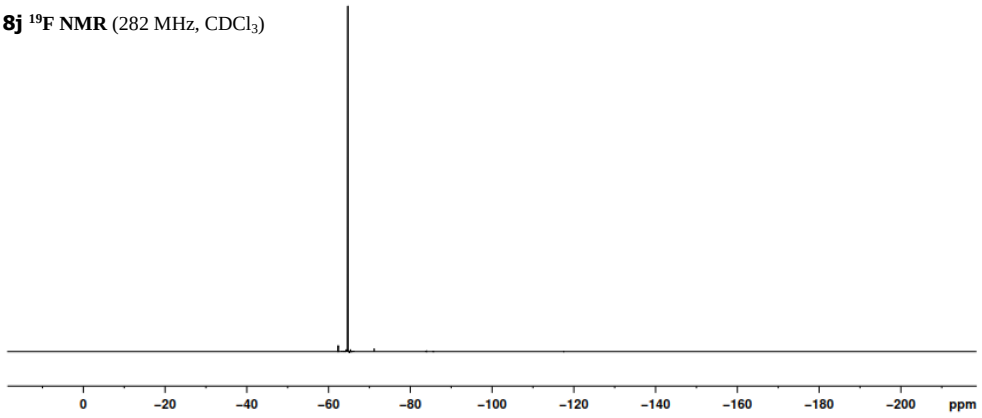


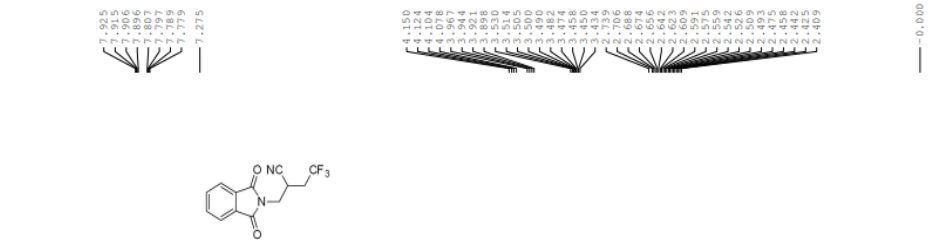
8j ^{13}**C NMR** (75 MHz, $CDCl_3$)



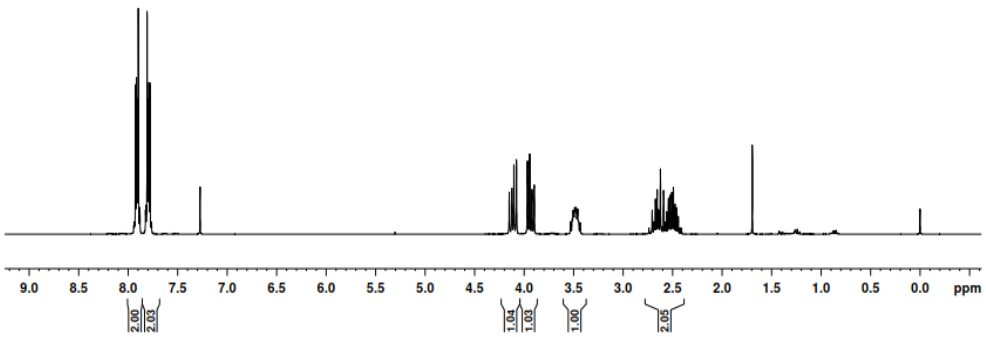


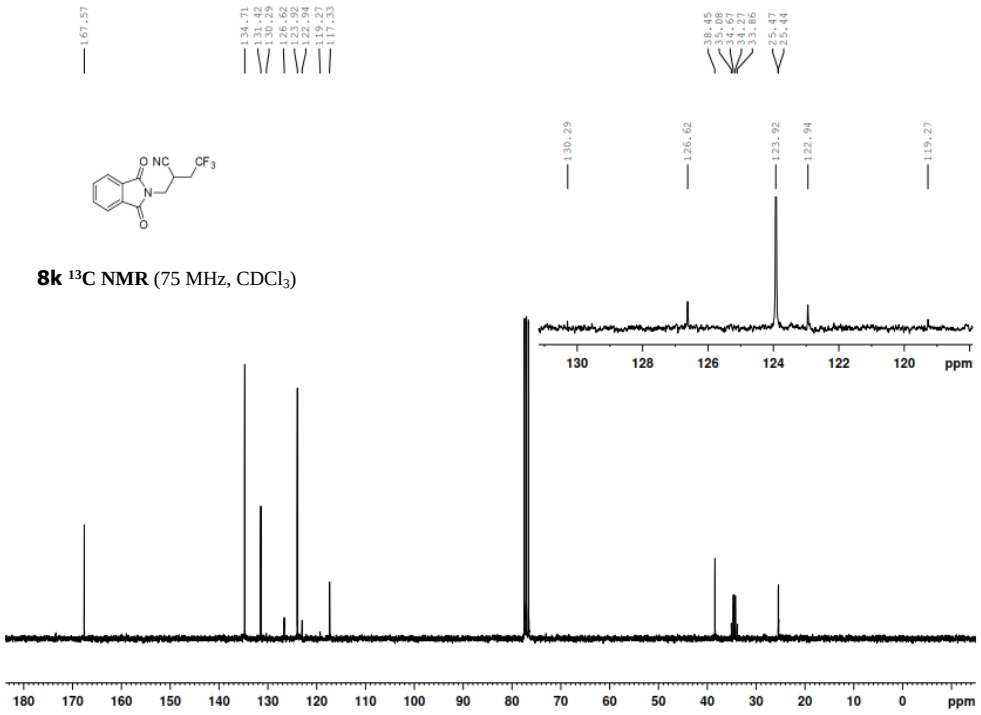
8j ^{19}**F NMR** (282 MHz, $CDCl_3$)



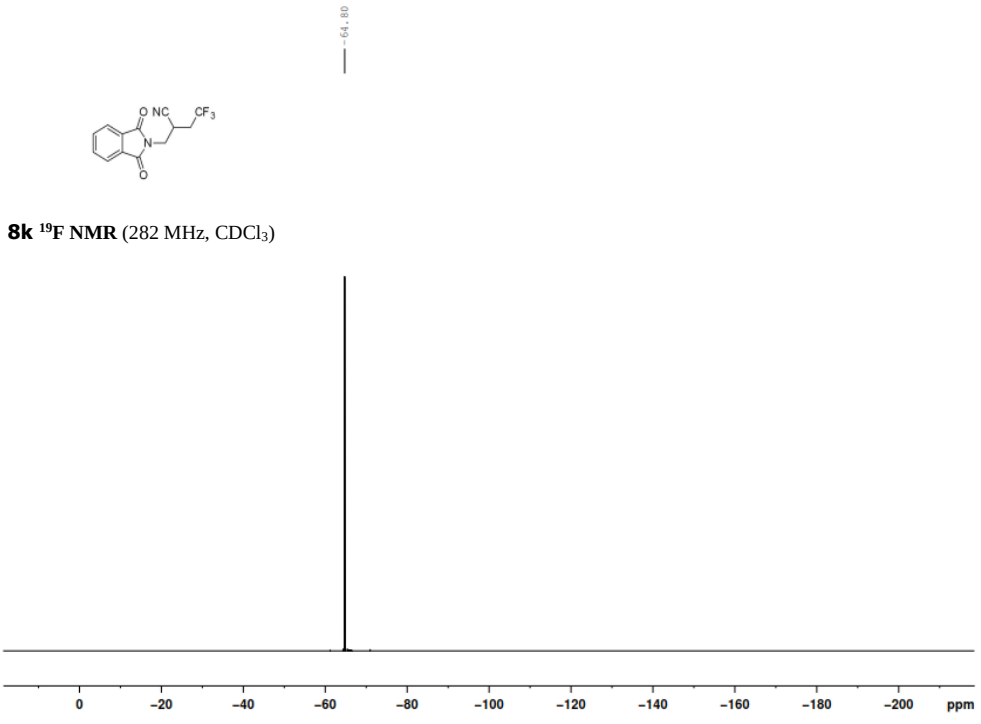


8k ^{1}**H NMR** (300 MHz, $CDCl_3$)

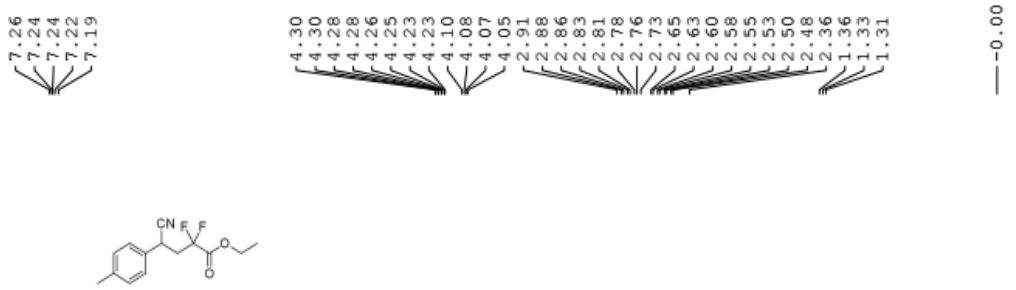




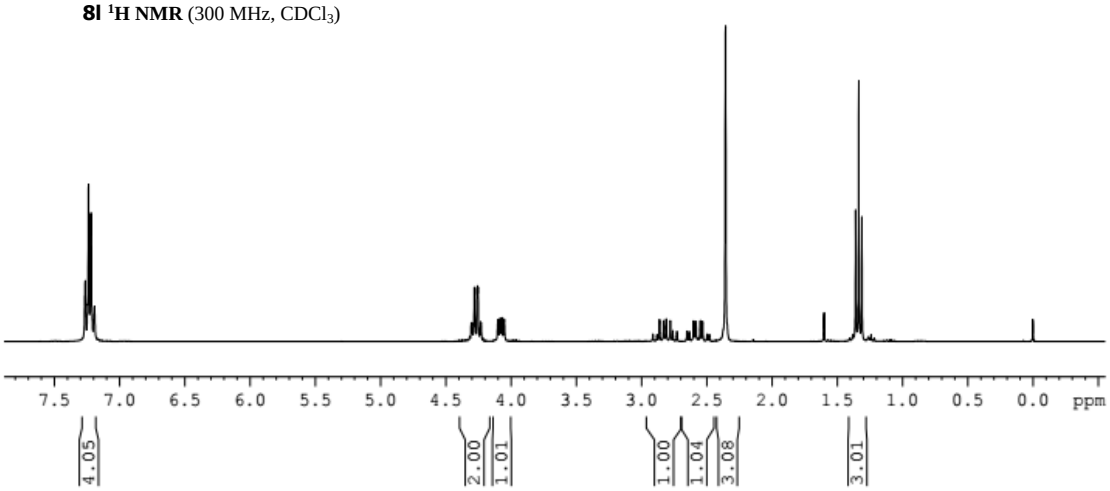
8k **^{13}C NMR** (75 MHz, $CDCl_3$)

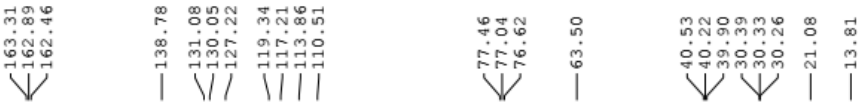


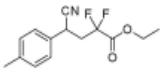
8k **^{19}F NMR** (282 MHz, $CDCl_3$)



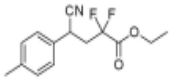
8l **^{1}H NMR** (300 MHz, $CDCl_3$)



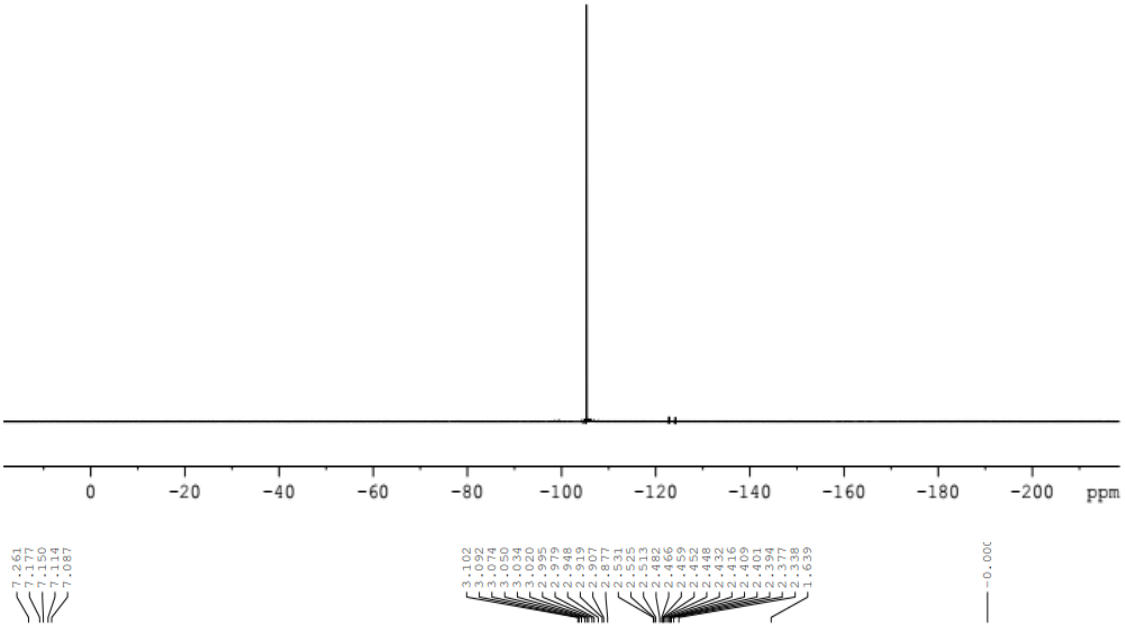


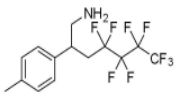


8l **^{13}C NMR** (75 MHz, $CDCl_3$)

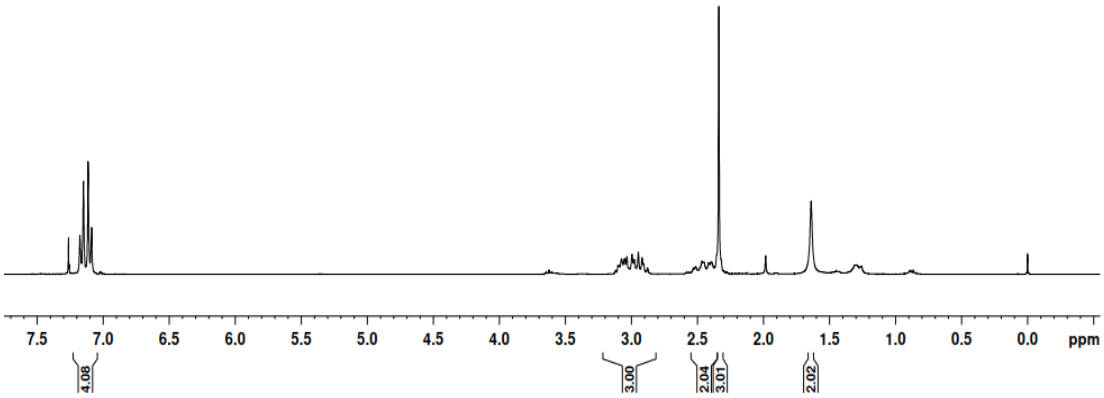


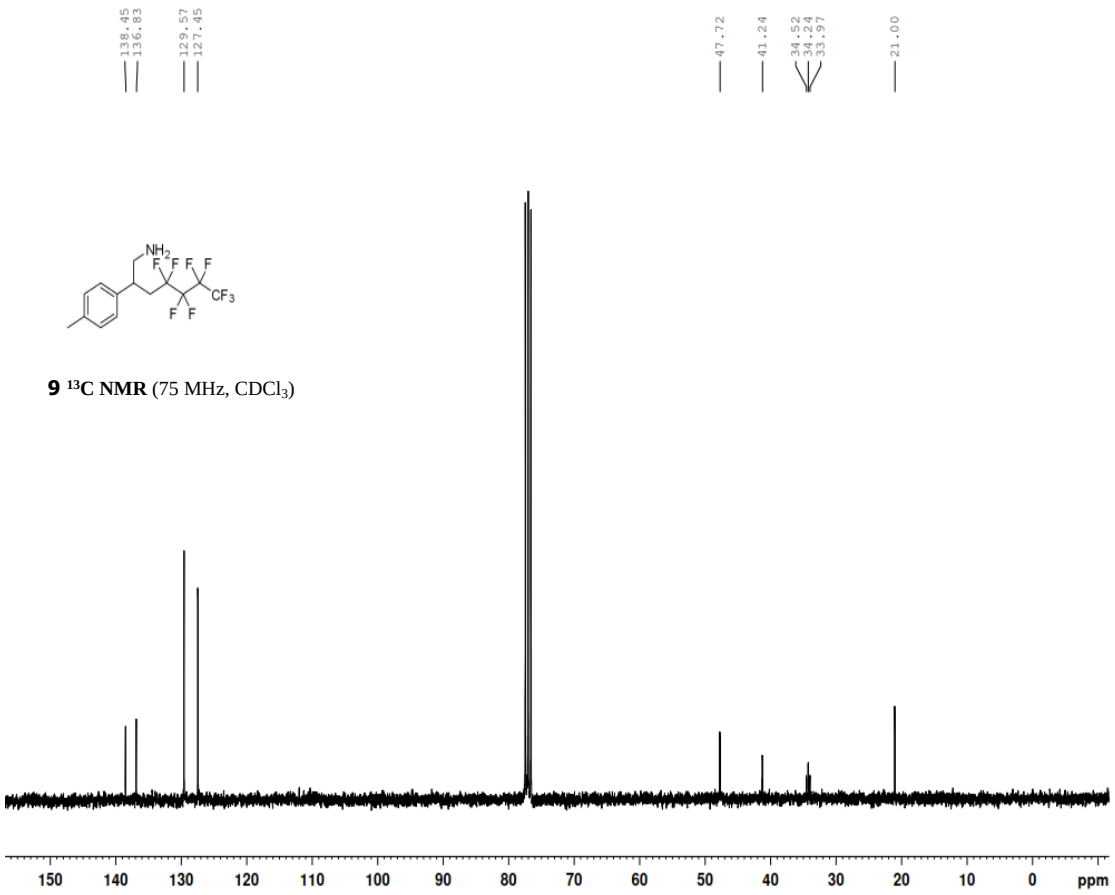
8l **^{19}F NMR** (282 MHz, $CDCl_3$)



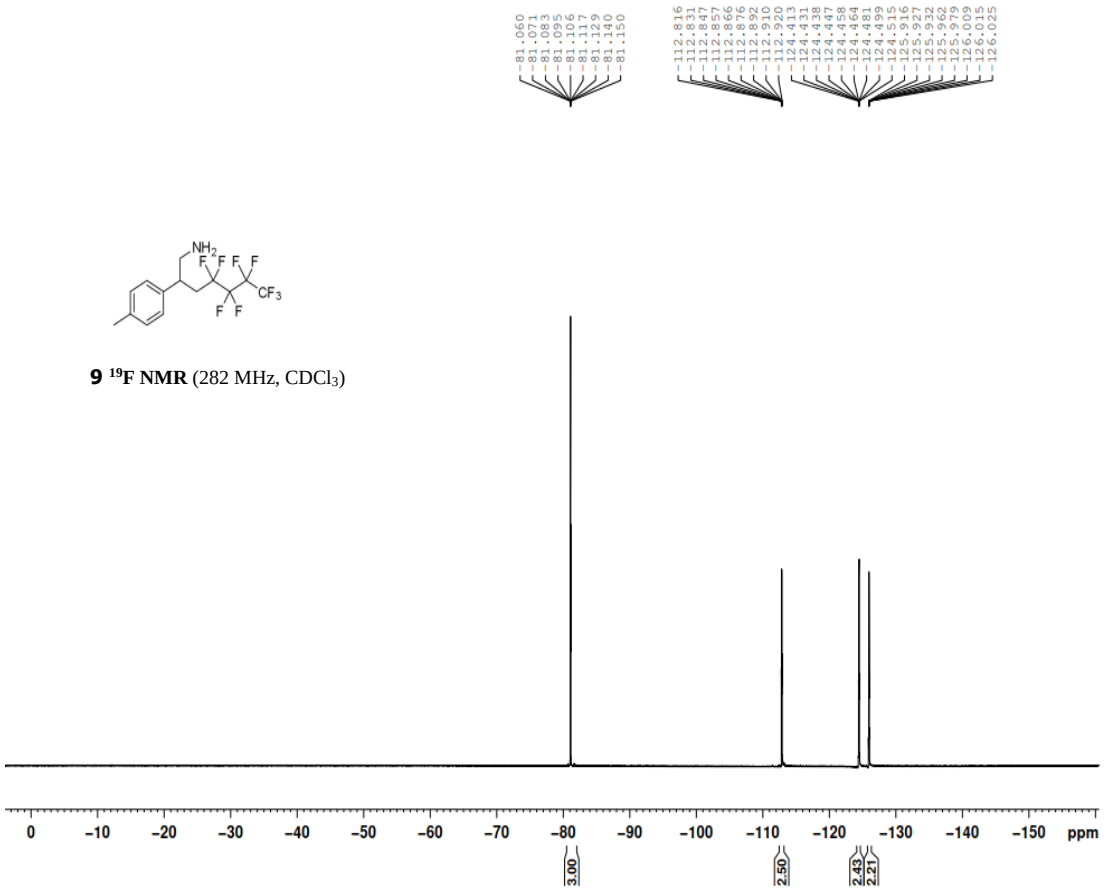


9 **^{1}H NMR** (300 MHz, $CDCl_3$)

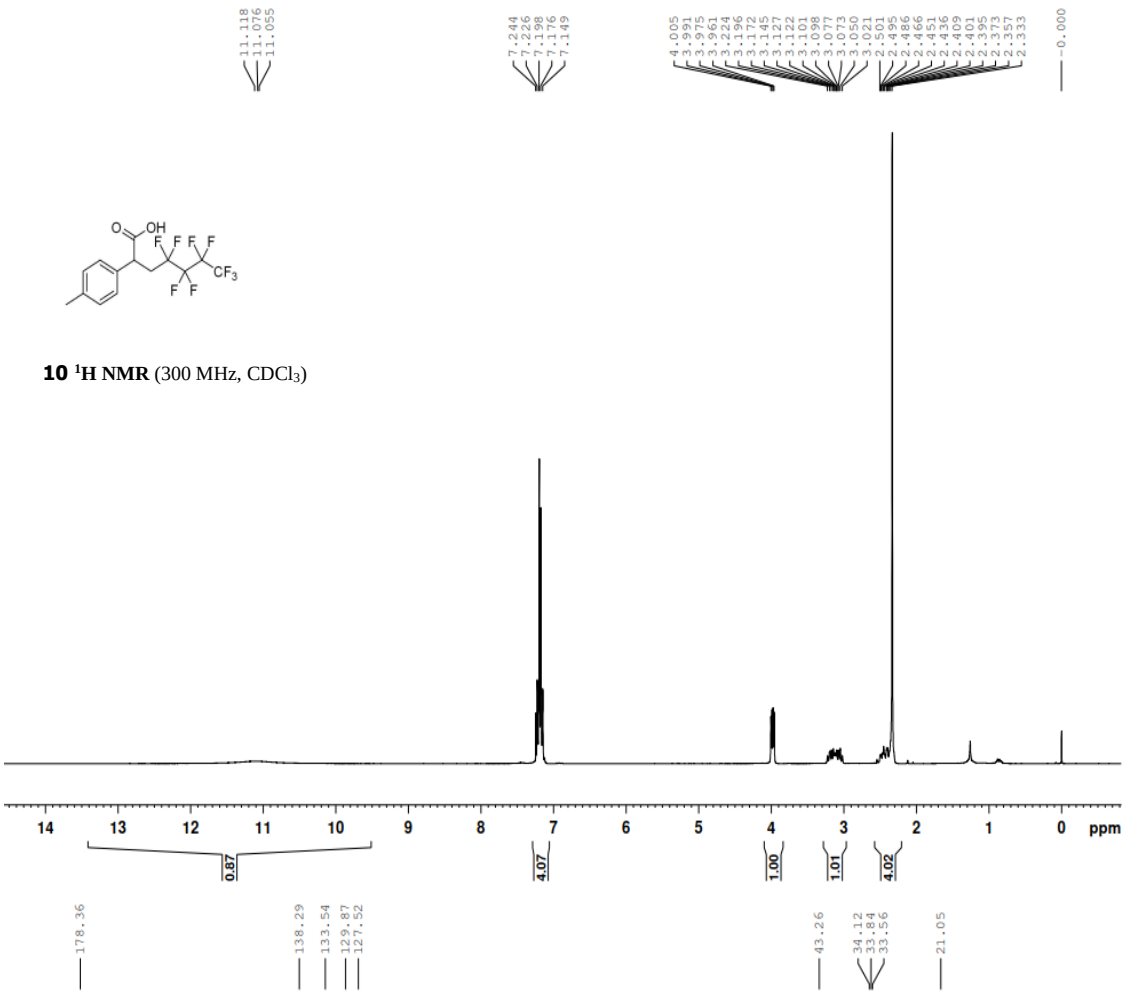




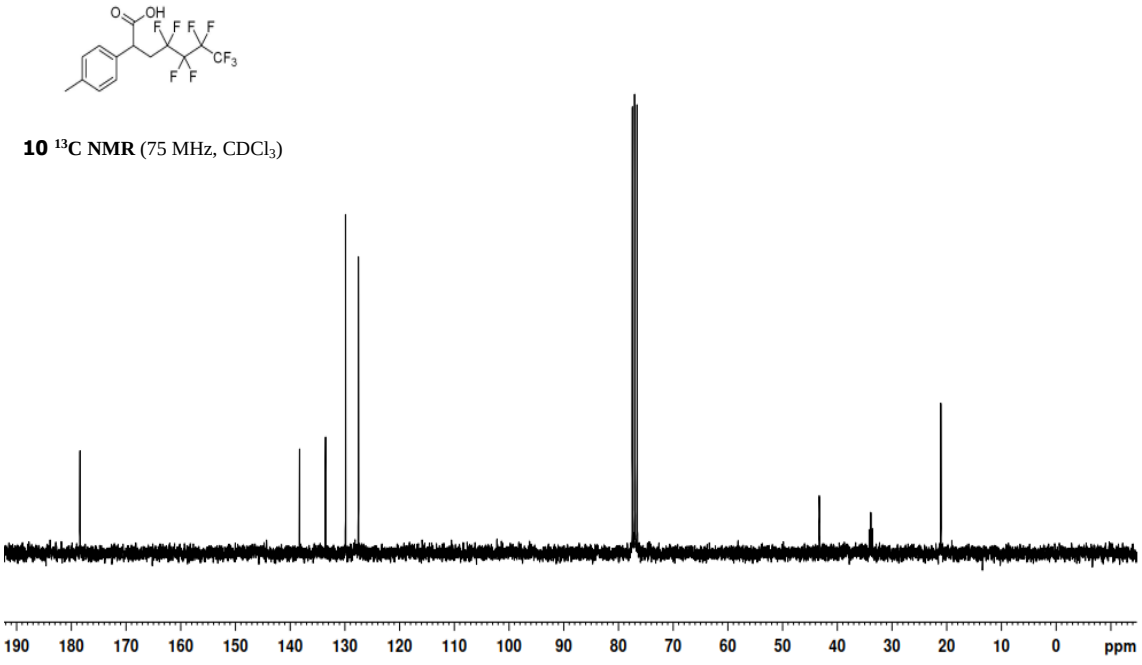
9 **^{13}C NMR** (75 MHz, $CDCl_3$)



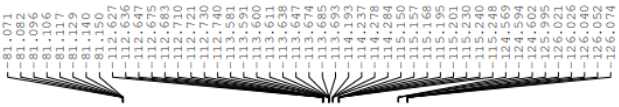
9 **^{19}F NMR** (282 MHz, $CDCl_3$)

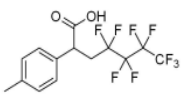


10 **^{1}H NMR** (300 MHz, $CDCl_3$)



10 **^{13}C NMR** (75 MHz, $CDCl_3$)

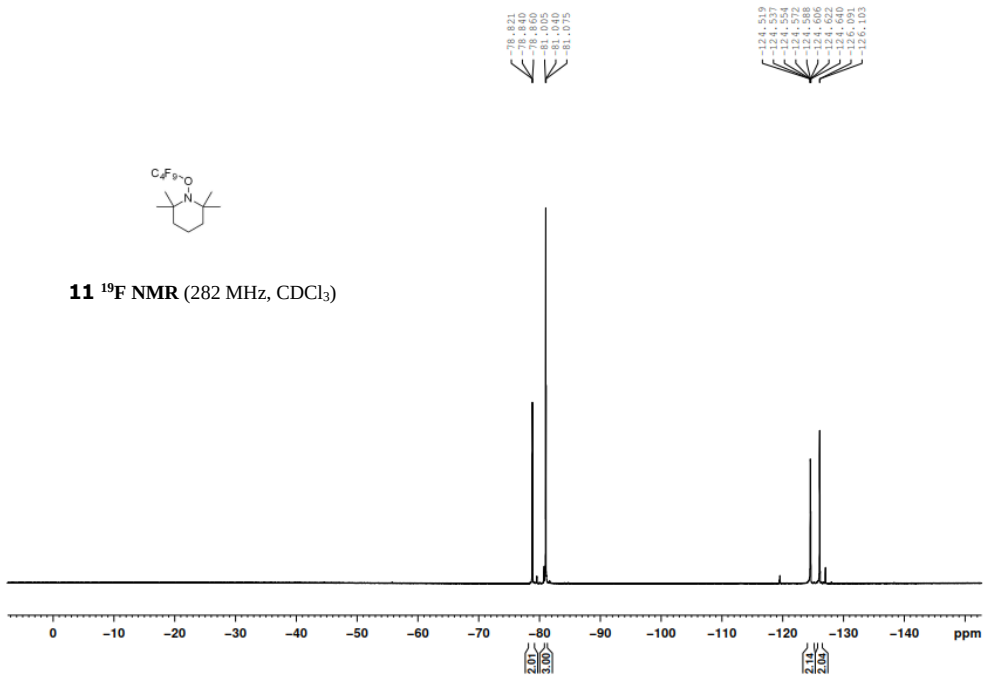




10 **^{19}F NMR** (282 MHz, $CDCl_3$)

11 **^{1}H NMR** (300 MHz, $CDCl_3$)

11 **^{13}C NMR** (75 MHz, $CDCl_3$)



11 **^{19}F NMR** (282 MHz, $CDCl_3$)