Photo-induced, Cu-Catalyzed Three Components Azidofluoroalkylation of Alkenes with CF_3I and R_fI as Fluoroalkylation Reagents

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Supporting Information

Table of Content:

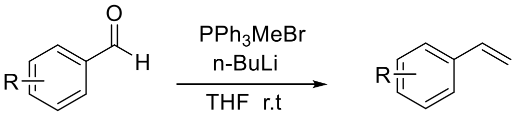
1. General information

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 and^{19}F 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: All other reagents were commercially available andused as received.

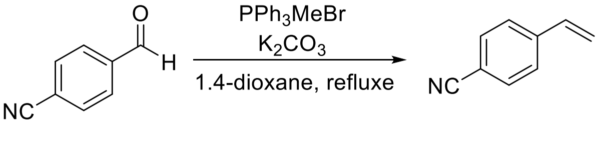
2. General procedure for the synthesis of alkenes

2.1 General procedure for the synthesis of alkenes 2a—2f, 2h-2n.$^{1)}$



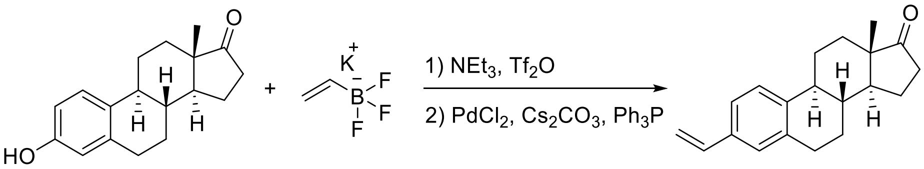
In a 100 mL round bottomed flask equipped with a stir bar, methyltriphenylphosphonium bromide (12 mmol, 1.2 equiv) were dissolved with 50 mL THF under Ar atmosphere，*n*-BuLi (2.5 mol/L, 12mmol, 1.2 equiv) were added dropwise under 0 °C， the mixture was stirred for 15 minutes. Aldehyde (10.0 mmol) was dissolved with THF, which was added into reaction, and the mixture continues to stir for 1 h under 0 °C. 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-2f, 2h-2n**.

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 °C) 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 2o.[3)]



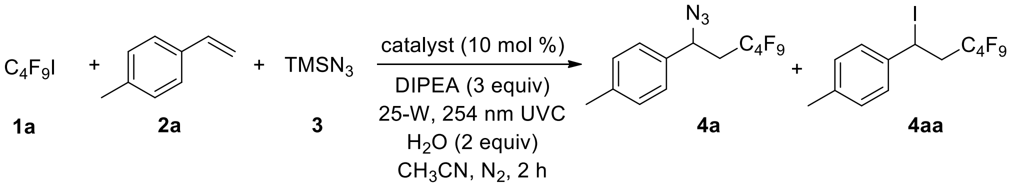
1) A mixture of estrone (5 mmol) dissolved in 30 mL DCM was added Et_3N (10 mmol, 2 equiv). Trifluoromethanesulfonic anhydride (5.5 mmol, 1.1 equiv) was added dropwise no less than 9 minutes into the mixture under 0 °C. The reaction mixture was stirred at room temperature for 3 h. The resulting mixture 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 Cs_2CO_3 (15 mmol, 3 equiv) were combined in an oven-dried sealing tube. The vessel was evacuated andbackfilled 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 °C for 19 h. The mixture was then cooled to room temperature,filtered through a plug of silica and washed with EtOAc. The filtrate was concentratedunder vacuum and purified by flash column chromatography on silica gel(PE: EA = 5:1) to give the product **2o**.

3. General procedures for the azidofluoroalkylation of alkenes.

3.1 Optimization of reaction condition.

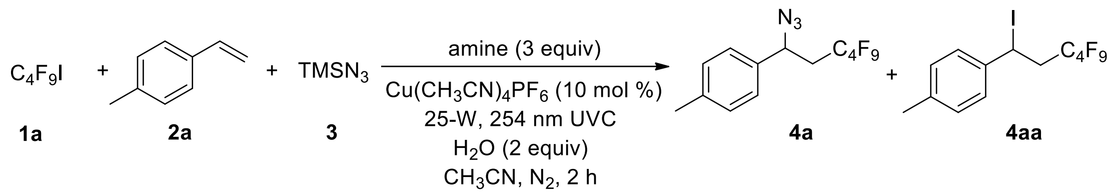
Table S1. Catalysts screening.[a)]



Entry	Catalyst	Yield (**4a**/**4aa**) (%)[b)]	Entry	Catalyst	Yield (**4a**/**4aa**) (%)[b)]
1	CuI	3/4	7	$Cu(OTf)_2$	6/2
2	CuCl	4/3	8	$Cu(OAc)_2$	11/4
3	CuBr	5/5	9	$CuCl_2$	5/1
4	CuTc	7/3	10	CuF_2	5/3
5	***$Cu(MeCN)_4PF_6$***	18/6	11	$Cu(OH)_2$	1/0
6	Cu_2O	1/1	12	$CuSO_4$	6/3

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

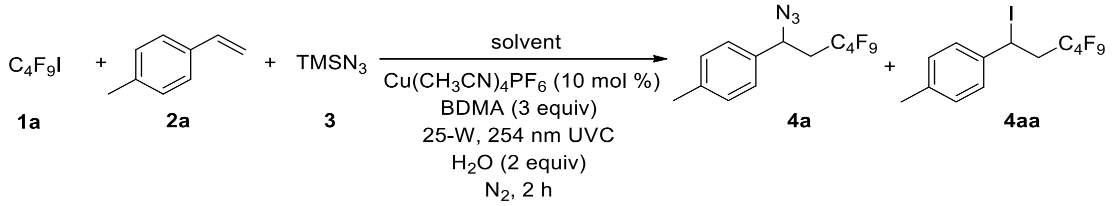
Table S2. Amines screening.[a)]



Entry	Amine	Yield (**4a**/**4aa**) (%)[b)]	Entry	Amine	Yield (**4a**/**4aa**) (%)[b)]
1	Et_3N	12/3	5	TMEDA	15/2
2	DBU	13/0	6	BDMA	30/1
3	DABCO	15/6	7	DMAP	14/6
4	DIPEA	18/6			

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

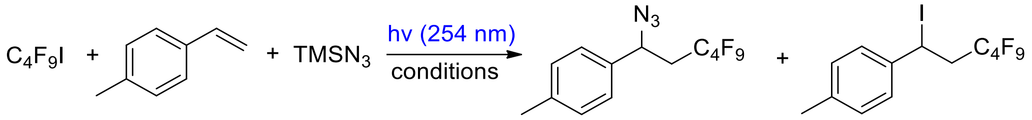
Table S3. Solvents screening.[a)]



Entry	Solvent	Yield (**4a**/**4aa**) (%)[b)]	Entry	Solvent	Yield (**4a**/**4aa**) (%)[b)]
1	DMSO	30/3	4	acetone	31/4
2	THF	22/9	5	DCM	27/2
3	DMAc	44/0	6	CH_3CN	30/1

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

Table S4. Control experiments.$^{a)}$

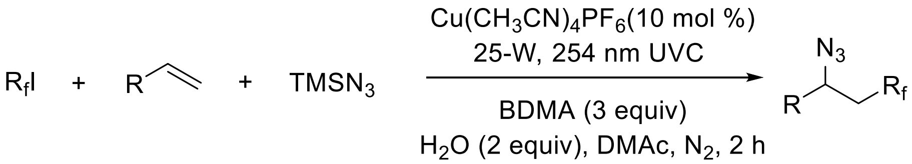


1a **2a** **3** **4a** **4aa**

Entry	Catalyst	Amine	Solvent	Yield (%)$^{b)}$ (**4a**/**4aa**)
1	$Cu(OAc)_2$	DIPEA	CH_3CN	11/4
2	$Cu(CH_3CN)_4PF_6$	DIPEA	CH_3CN	18/6
3	other Cu catalysts instead of $Cu(CH_3CN)_4PF_6$	DIPEA	CH_3CN	1/0 - 11/4
4	$Cu(CH_3CN)_4PF_6$	BDMA	CH_3CN	31/1
5	$Cu(CH_3CN)_4PF_6$	other amines instead of BDMA	CH_3CN	12/3 - 18/6
6	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	44/0
7	$Cu(CH_3CN)_4PF_6$	BDMA	other solvents instead of DMAc	22/9 -31/4
8$^{c)}$	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	25/5
9$^{d)}$	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	60/0
10$^{e)}$	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	75(71)/0
11		BDMA	DMAc	0
12	$Cu(CH_3CN)_4PF_6$		DMAc	0/10
13$^{f)}$	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	0
14$^{g)}$	$Cu(CH_3CN)_4PF_6$	BDMA	DMAc	0

$^{a)}$ Unless otherwise noted, the reactions were carried out by using **2a** (0.1 mmol), **1a** (3.0 equiv), **3** (3 equiv), amine (3 equiv), H_2O (2 equiv), solvent (1.0 mL), catalyst (10 mol %), under N_2, and stirred at room temperature for 2 hours under UV light irradiation (25-W UVC (254 nm) compact fluorescent light bulbs). $^{b)}$ ^1H NMR yields with anisole internal standard. $^{c)}$ 2 equiv **3** used. $^{d)}$ 5 equiv **3** used. $^{e)}$ 0.25 mL DMAc used; isolated yield in parentheses. $^{f)}$ 25-W, 365 nm UVC. $^{g)}$ No light, 24 h at rt or 12 h at 80 °C, respectively.

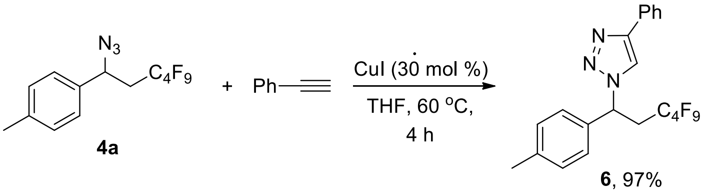
3.2 General procedures of the azidofluoroalkylation of alkenes



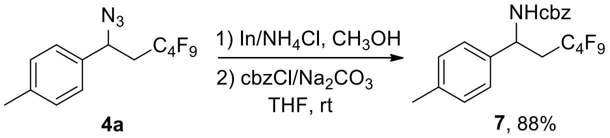
The reactions with R_fI. To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added $Cu(CH_3CN)_4PF_6$ (0.1 mmol, 10 mol %). Then, air was withdrawn and backfilled with Ar (three times). Perfluoroalkyl iodide (R_fI, 3 mmol, 3 equiv), alkene (1 mmol) and azidotrimethylsilane ($TMSN_3$, 5 mmol, 5 equiv), H_2O (2 mmol, 2 equiv), *N*-benzyldimethylamine (BDMA, 3 mmol, 3 equiv), and 2.5 mL of DMAc, were added in turn by syringe. Thereafter, the test tube was transferred to a UV photoreactor (25 W, 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 *n*-hexane, dried over anhydrous sodium sulfate, concentrated in *vacuo* and purified by column chromatography (petroleumether or petroleumether/ethylester 100:1-50:1) to afford the product.

The reaction with CF_3I. To an oven-dried 10 mL quartz test tube with a magnetic stirring bar was added $Cu(CH_3CN)_4PF_6$ (0.1 mmol, 10 mol %), and air was withdrawn and backfilled with Ar. Then, $TMSN_3$ (5 mmol, 5 equiv), H_2O (2 mmol, 2 equiv), and BDMA (3 mmol, 3 equiv) were added in turn by syringe. To another tube, which was cooled to -78℃, CF_3I (3 mmol, 3 equiv) was condensed via a Dewar type condenser fitted with a needle, and then filled with DMAc (2.5mL). The CF_3I solution was transfer to above quartz test tube and move to the UV photoreactor, where it was irradiated at 254 nm. 2 h later, the reaction was quenched with water, extracted with *n*-hexane, dried over anhydrous sodium sulfate, concentrated in *vacuo* and purified by column chromatography to afford the product.

4.Synthetic applications.[4)]

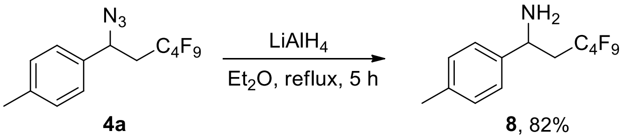


To an oven-dried glass tube, the substrate **4a** (0.2 mmol) was dissolved in THF (l mL), then phenylacetylene (66 μL, 0.6 mmol) and CuI (12.1 mg, 0.06 mmol) were added. After stirred at 60° C for 4 h, the mixture was concentratedunder vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate (10:1 - 4:1) to afford the product**6**.



In a flask, indium powder (48.5 mg, 0.4 mmol) and NH_4Cl (22.6 mg, 0.4 mmol) were added to the above mixture. The mixture was sealed and refluxed for 2 hours. After that, the mixture was diluted with ethyl acetate (5 mL), and filtered through a short pad of celite. The filtrate was concentrated under vacuum. ^{19}F NMR analysis showed that the corresponding amine product was obtained in 95 % yield. Then, benzyl chloroformate (cbzCl, 32 μL, 0.22

mmol)and Na_2CO_3 (26.8 mg, 0.25 mmol) were added to the above amine solution in THF (2 mL). After stirred at room temperature for 2 hours, the mixture was diluted with ethyl acetate (10 mL) and washed with diluted hydrochloric acid (10 mL), saturated $NaHCO_3$ (10 mL), water (10 mL), brine (10 mL) sequentially. The organic layer was concentrated under vacuum. The residue was purified by column chromatography on silica gel with a gradient eluent of petroleum ether and ethyl acetate (20:1 - 8:1) to afford product **7**as a white solid.

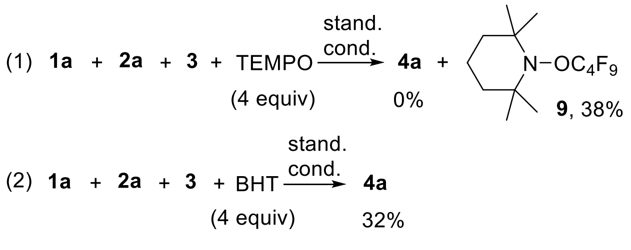


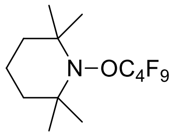
$LiAlH_4$ (0.8 mmol, 4 equiv) was added at room temperature to a solution of **4a** (0.2 mmol) in Et_2O (2 mL). After 5 h reflux, the reaction mixture was carefully quenched with H_2O (36 uL), 15% aq NaOH (108 μL), and H_2O (36 μL). After dilution of the residue with ethyl acetate, the mixture was filtered through celite and anhydrous sodium sulfate. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford product **8**.

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 **16** 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.





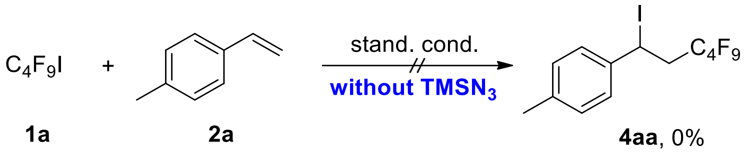
9

2,2,6,6-tetramethyl-1-(perfluorobutoxy)piperidine (9), Colorlessliquid;
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57-1.63 (m, 6H), 1.18 (s, 12H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 61.88, 40.42, 33.43, 20.63, 16.78.

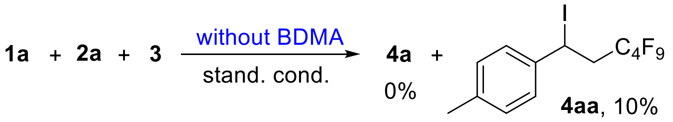
^{19}F NMR (282 MHz, $CDCl_3$) δ -78.81—-78.86 (m, 2F), -81.03 (t, *J* = 9.6 Hz, 3F), -124.51—-124.62 (m, 2F), -126.05—-126.13 (m, *J* = 3.4 Hz, 2F).
HRMS (ESI): $C_{13}H_{18}F_9NO+Na^+$ Calcd: 398.2630, Found: 398.2503.

5.2 Control experiments

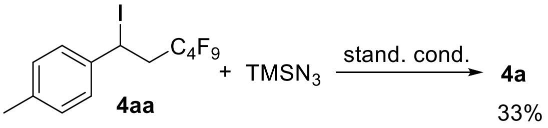
To further prove the reaction as a multicomponent reaction, control experiment was carried out. Under the standard conditions, in the absence of $TMSN_3$, no iodoperfluorobutylation product could be observed, and the *p*-methylstyrene (**2a**) was mostly consumed, thus questioning vinyl iodides as effective intermediates in these transformations.

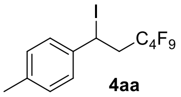


To explore the influence of BDMA in the reaction, control experiment was carried out. Under the standard conditions, in the absence of BDMA, no **4a** were observed, whereas the iodoperfluoroalkylation product **4aa** was obtained in 10% yield and *p*-methylstyrene (**2a**) was mostly consumed. Furthermore, 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 BDMA in this reaction.



Finally, the cross coupling between **4aa** and $TMSN_3$ was proceeded under the standard conditions and gave the azidofluoroalkylation product **4a** in 33% yield.

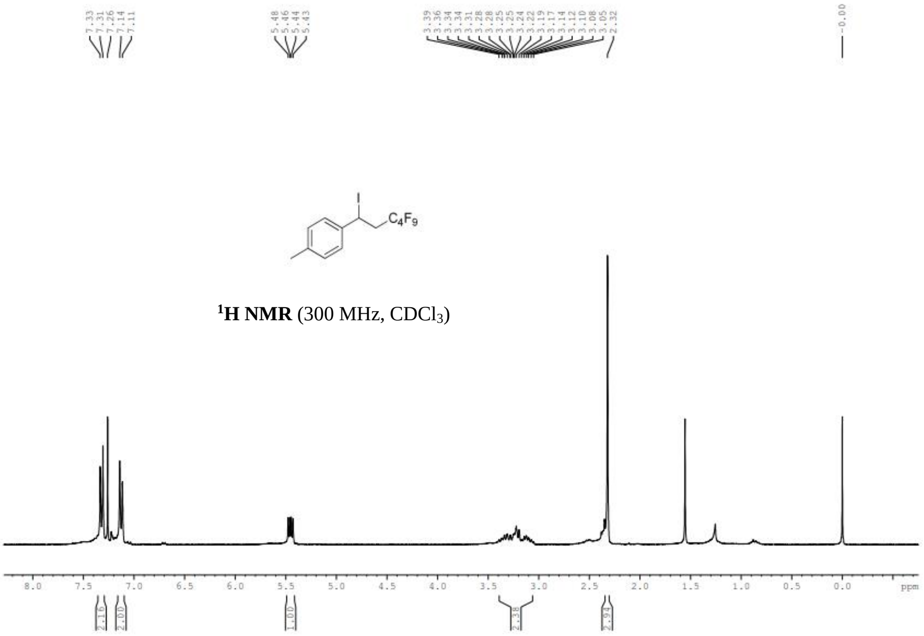




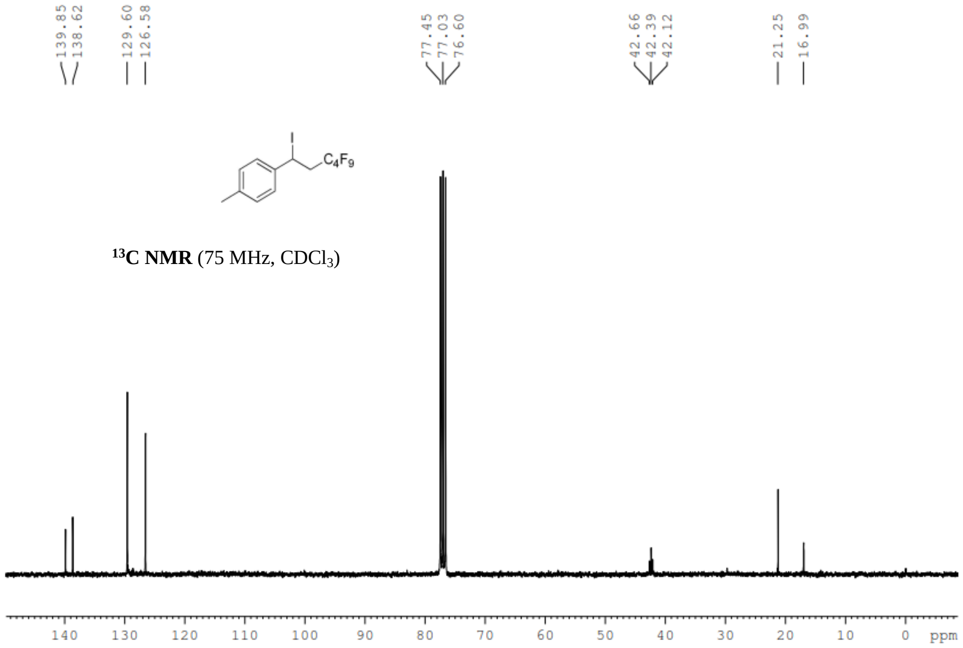
4aa

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), 5.50 (dd, *J* = 5.1,9.6 Hz, 1H), 3.05–3.40 (m, 2H), 2.32 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 139.85, 138.62, 129.60, 126.58, 42.39 (t, *J* = 20.3 Hz), 21.25, 16.99.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.00—-81.08 (m, 3F), -112.05—-115.56 (m, 2F), -124.45—-124.56 (m, 2F), -125.91—- 126.01 (m, 2F).
HRMS (EI): $C_{13}H_{18}F_9NO$ Calcd: 463.9683, Found: 463.9665

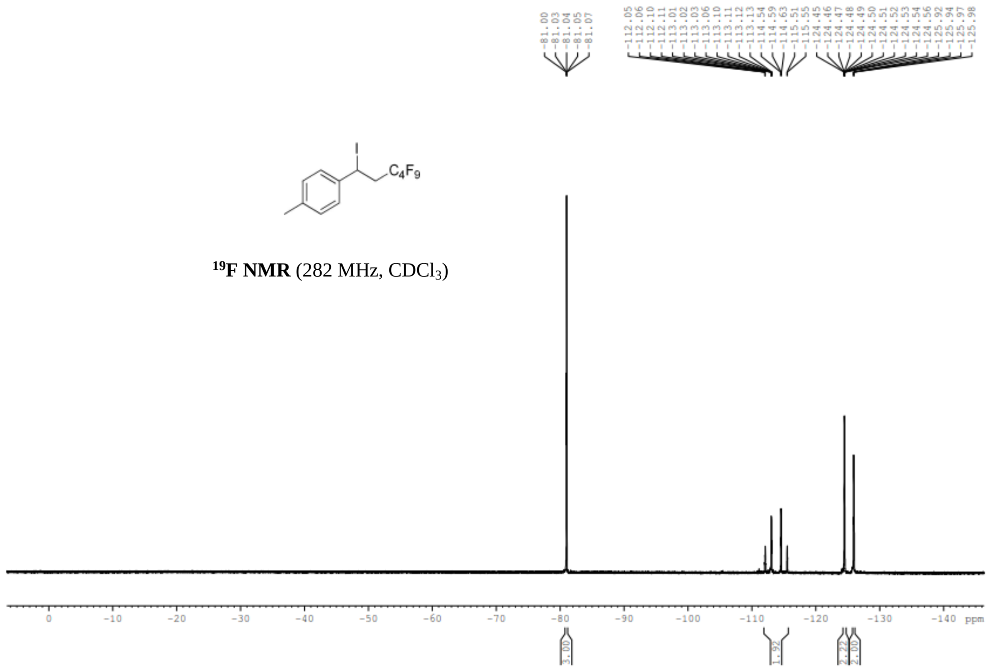
NMR spectra of 4aa



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

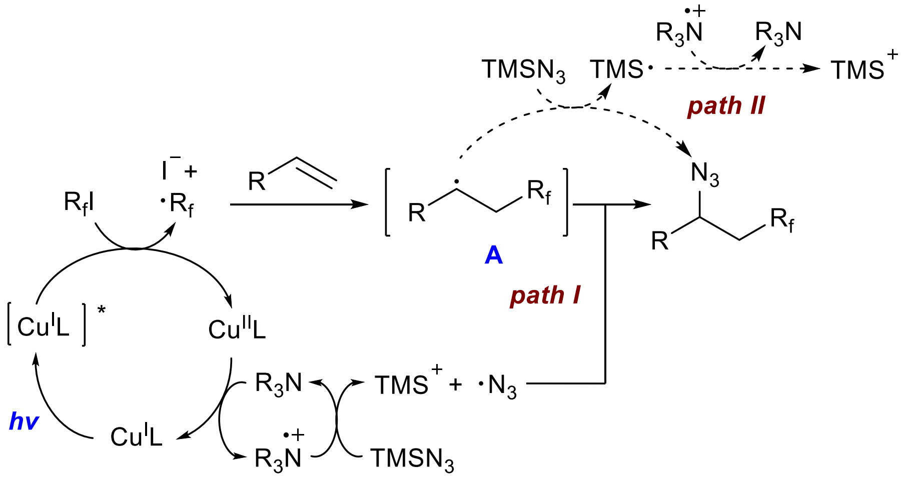


^{13}C NMR (75 MHz, $CDCl_3$)



5.3 Proposed mechanism

Although the mechanism of this transformation is not completely clear yet, on the basis of our mechanistic studies and previous reports, a plausible mechanism was proposed. Firstly, Cu^I was excited to its triplet state $[Cu^I]^*$ under UV light irradiation. R_fI was converted into $\cdot R_f$ and I^- through oxidative quenching of $[Cu^I]^*$ along with Cu^{II}. Cu^{II} was reduced by BDMA and formed an amine radical cation and Cu^I. In the meanwhile, $\cdot R_f$ attacked alkene to give the radical intermediate **A**, which was coupled with $TMSN_3$ with assistance of above *in situ* formed amine radical cation (***path I***). At this stage, the radical propagation pathway of **A** with $TMSN_3$ cannot be completely ruled out at this stage (***path II***). However, the results in the mechanistic studies disfavour this hypothesis. Unstable species TMS^+ and I^-undergo rapid hydrolysis and then neutralized by amine, which promoted a completed conversion. Alternatively, the the oxidation of alkyl radical **A** by Cu(II) forms an alkyl cation, followed by the addition of N_3 anion that results from the coupling of I- with $TMSN_3$ may also account for the reaction.



6. References

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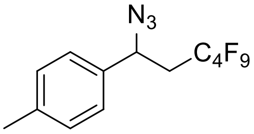
[3] L. Crespin, L. Biancalana, T. Morack, D. C. Blakemore and S. V. Ley, *Org. Lett*. 2017, **19**, 1084.

[4]a) F. Wang, X. Qi, Z. Liang, P. Chen, G. Liu, *Angew. Chem. Int.Ed*. 2014, **53**, 1881.b) K. Kuroda,Y. Hayashi andT. Mukaiyama. *Tetrahedron*, 2007, **63**, 6358.

7.Characterization of products



4a

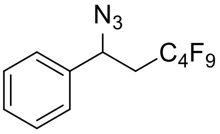
1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-methylbenzene (4a), 269.1mg, yield: 71%. Colourlessliquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.23 (s, 4H), 3.87 (dd, *J* = 4.6, 9.6 Hz, 1H), 2.35–2.65 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 139.04, 135.00, 129.87, 126.57, 58.67, 37.24 (t, *J* = 21.8 Hz), 21.15.

^{19}F NMR (282 MHz, CDCl$_3$) δ -80.02– -81.12 (m, 3F), -113.52– -113.65 (m,2F), -124.45– -124.58(m, 2F), -125.90– -126.01 (m, 2F).

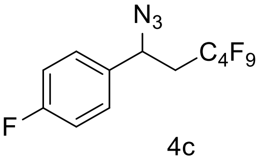
HRMS (EI): $C_{13}H_{10}F_9N_3$Calcd: 379.0731, Found: 379.0737.



4b

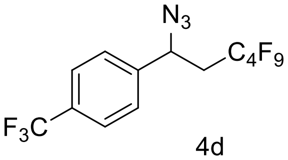
(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzene (4b), 255.5mg, yield: 70%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26–7.44 (m, 5H), 4.89 (dd, *J* =4.8, 8.1Hz, 1H), 2.36 – 2.70 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.16, 129.20, 129.04, 126.61, 58.96, 37.36(t, *J* = 20.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.35 –-81.42 (m, 3F), -113.64 – -113.75 (m, 2F), -124.63 – -124.74 (m, 2F), -126.10 – -126.19 (m, 2F).
HRMS (EI): $C_{12}H_8F_9N_3$Calcd: 365.0573, Found: 365.0569.



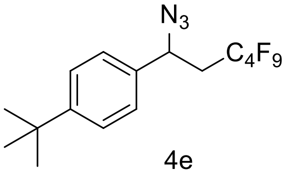
4c

1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-fluorobenzene (4c), 271.9mg, yield: 71%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.36 (m,2H), 7.10(t, *J* =8.7Hz, 2H), 4.89 (dd, *J* =5.4, 8.1Hz, 1H), 2.34 – 2.70 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 162.92 (d, *J* = 246.8 Hz), 133.98 (d, *J* = 3.0 Hz), 136.15 (d, *J* = 21 Hz), 116.15 (d, *J* =21 Hz), 58.30, 37.39 (t, *J* = 20.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.39 – -81.47 (m, 3F), -112.48 (s, 1F), -113.59 – -113.72 (m, 2F), -124.68 – -124.78 (m, 2F), -126.14 – -126.26 (m, 2F).
HRMS (EI): $C_{12}H_7F_{10}N_3$Calcd: 383.0480, Found: 383.0476.



4d

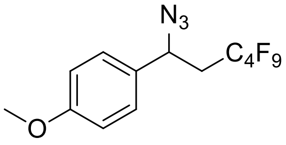
1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-(trifluoromethyl)benzene (4d), 307.4mg, yield: 71%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* =8.1Hz, 2H), 7.49(d, *J* =8.1Hz, 2H), 4.98 (dd, *J* =4.8, 7.8Hz, 1H), 2.36 – 2.72 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 142.08, 131.33 (dd, *J* =4.8, 7.8Hz),127.03, 126.22 (dd, *J* =3.7, 7.4Hz), 123.72 (dd, *J* =270.5, 541.0Hz), 58.49, 37.45(t, *J* = 21.0 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ-63.12 (s, 3F), -81.33 – -81.41(m, 3F), -113.45 – -113.56 (m, 2F), -124.61 – -124.70(m, 2F), -126.10 – -126.22(m, 2F).
HRMS (EI): $C_{13}H_7F_{12}N_3$Calcd: 433.0448, Found: 433.0452.



4e

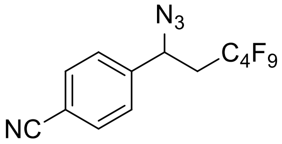
1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-(tert-butyl)benzene (4e), 319.9mg, yield: 76%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, *J* =7.2Hz, 2H), 7.27(t, *J* =8.1Hz, 2H), 4.88 (dd, *J* =4.2, 8.4Hz, 1H), 2.37 – 2.71 (m, 2H), 1.33 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.15, 135.15, 126.27, 126.12, 58.62, 37.33(t, *J* = 21 Hz), 34.65, 31.17.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.15 – -81.18 (m, 3F), -113.68 – -113.78 (m, 2F), -124.55 – -124.58 (m, 2F), -125.99 (s, 2F).
HRMS (EI): $C_{16}H_{17}F_9N_3$Calcd: 421.1201, Found: 421.1205.



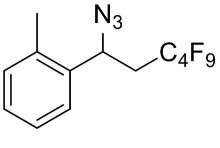
4f

1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-4-methoxybenzene (4f), 284.4mg, yield: 72%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* =8.4Hz, 2H),6.94 (d, *J* =8.4Hz, 2H), 4.86 (dd, *J* =5.4, 7.8Hz, 1H), 3.81 (s, 3H), 2.35 – 2.70 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 160.06, 129.99, 127.96, 114.47, 58.46, 55.19, 37.20 (t, *J* = 21.0 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -80.20 – -81.29 (m, 3F), -113.64 – -113.72 (m, 2F), -124.59 – -124.67 (m, 2F), -126.03 – -126.14 (m, 2F).
HRMS (EI): $C_{13}H_{10}F_9N_3O$Calcd: 395.0680, Found: 395.0676.



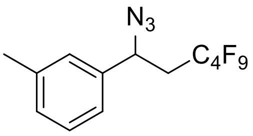
4g

4-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzonitrile (4g),241.8mg, yield: 62%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4Hz, 2H),7.51 (d, *J* = 8.1Hz, 2H), 5.00 (dd, *J* =5.4, 8.1Hz, 1H), 2.36 – 2.73 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 143.19, 133.04, 127.47, 118.05, 113.10, 58.46, 37.37(t, *J* = 20.3 Hz).
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.14 – -81.21(m, 3F), -113.19 – -113.35 (m, 2F), -124.45 – -124.55 (m, 2F), -126.00 – -126.10 (m, 2F).
HRMS (EI): $C_{13}H_7F_9N_4$Calcd: 390.0527, Found: 390.0532.



4h

1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-2-methylbenzene (4h), 269.1mg, yield: 71%.
Light yellow liquid.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.39 (m, 1H), 7.19–7.30 (m, 3H), 5.18 (dd, *J* =4.2, 8.7Hz, 1H), 2.33 – 2.69 (m, 2H), 2.32(s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 136.44, 134.93, 131.21, 128.74, 126.93, 126.16, 55.22, 36.75(t, *J* = 20.3 Hz), 18.88.
^{19}F NMR (282 MHz, $CDCl_3$) δ -81.29 – -81.36 (m, 3F), -114.01 – -114.04 (m, 2F), -124.60 – -124.67 (m, 2F), -126.07– -126.09 (m, 2F).
HRMS (EI): $C_{13}H_{10}F_9N_3$Calcd: 379.0731, Found: 379.0735.



4i

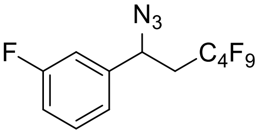
1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-methylbenzene (4i), 246.4 mg, yield: 65%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27–7.33 (m, 1H), 7.11–7.22 (m, 3H), 4.86 (dd, *J* =4.5, 8.4Hz, 1H), 2.40 – 2.70 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.11, 138.09, 129.81, 129.08, 127.25, 123.63, 58.93, 37.36(t, *J* = 20.3 Hz), 21.30.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.21 – -81.28 (m, 3F), -113.66 – -113.71 (m, 2F), -124.55 – -124.65 (m, 2F), -126.00 – -126.10 (m, 2F).

HRMS (EI): $C_{13}H_{10}F_9N_3$Calcd: 379.0731, Found: 379.0736.



4j

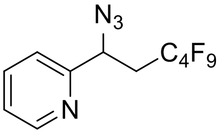
1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-fluorobenzene (4j), 229.8mg, yield: 60%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.44 (m, 1H), 7.05–7.12 (m, 3H), 4.91 (dd, *J* =5.1, 8.1Hz, 1H), 2.35 – 2.69 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.08 (d, *J* =246.8 Hz), 140.58 (d, *J* =6.8 Hz), 130.90 (d, *J* =8.3 Hz), 122.29 (d, *J* =3.0 Hz), 116.08 (d, *J* =21 Hz), 113.69 (d, *J* =22.5 Hz), 58.42, 37.41(t, *J* = 20.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.19 – -81.26 (m, 3F), -111.20 (s, 1F), -113.48 – -113.59 (m, 2F), -124.52 – -124.62 (m, 2F), -126.00 – -126.10 (m, 2F).

HRMS (EI): $C_{12}H_7F_{10}N_3$Calcd: 383.0483, Found: 383.0481.



4k

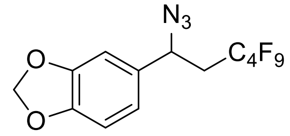
2-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)pyridine (4k), 223.3mg, yield: 61%. Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 – 8.66 (m, 1H),7.73 – 7.80 (m, 1H), 7.40 (d, *J* =8.1Hz, 1H), 7.27 – 7.33 (m, 1H), 4.87 (dd, *J* =4.8, 8.4Hz, 1H), 2.59 – 3.08 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 156.68, 149.90, 137.30, 123.63, 121.75, 59.02, 35.02(t, *J* = 20.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.12 – -81.19 (m, 3F), -112.39 – -114.51 (m, 2F), -124.47 – -124.57 (m, 2F), -125.96 – -126.97 (m, 2F).

HRMS (EI): $C_{11}H_7F_9N_4$Calcd: 366.0527, Found: 366.0521.



4l

5-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)benzo[d][1,3]dioxole (4l),265.9mg, yield: 65%.

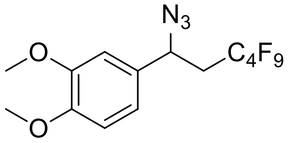
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 3H),6.00 (s, 2H), 4.83 (dd, *J* =5.1, 7.8Hz, 1H), 2.31 – 2.66 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.45, 148.20, 131.78, 120.57, 108.54, 106.71, 101.49, 58.78, 37.32(t, *J* = 21.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.1 – -81.20 (m, 3F), -113.58 – -113.70 (m, 2F), -124.54 – -124.61 (m, 2F), -125.97 – -126.07 (m, 2F).

HRMS (EI): $C_{13}H_8F_9N_3O_2$Calcd: 409.0473, Found: 409.0471.



4m

4-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,2-dimethoxybenzene (4m), 242.3mg, yield: 57%.

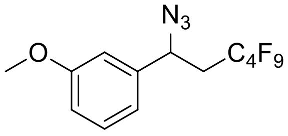
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 2H),6.84 (s, 1H), 4.86 (dd, *J* =4.8, 8.1Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 2.36 – 2.70 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 149.52, 130.44, 119.18, 111.20, 109.30, 58.79, 55.95, 55.89, 37.35(t, *J* = 20.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -80.07 – -81.14 (m, 3F), -113.57 – -113.68 (m, 2F), -124.48 – -124.55 (m, 2F), -125.93 – -126.02(m, 2F).

HRMS (EI): $C_{14}H_{12}F_9N_3O_2$Calcd: 425.0786, Found: 425.0784.



4n

1-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-3-methoxybenzene (4n), 225.2mg, yield: 57%.

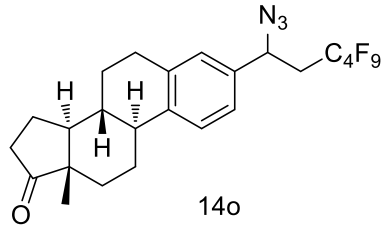
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (t, *J* =8.1Hz, 1H),6.87 – 6.94(m, 3H), 4.87 (dd, *J* =4.8, 8.4Hz, 1H), 3.83 (s, 3H), 2.36 – 2.69 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.17, 139.64, 130.32, 118.74, 114.22, 112.39, 58.83, 55.25, 37.37(t, *J* = 21.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.13 – -81.20 (m, 3F), -113.57 – -113.69 (m, 2F), -124.50 – -124.60 (m, 2F), -125.96 – -126.06(m, 2F).

HRMS (EI): $C_{13}H_{10}F_9N_3O$ Calcd: 395.0680, Found: 395.0677



14o

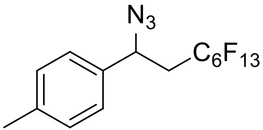
(8R,9S,13S,14S)-3-(1-azido-3,3,4,4,5,5,6,6,6-nonafluorohexyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (4o), 384.3mg, yield: 71%, d.r. > 20:1.Colourlessliquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 2H), 4.85 (dd, *J* = 4.5, 8.4 Hz, 1H), 2.94 (dd, *J* = 3.9, 8.7 Hz, 2H), 2.40–2.57 (m, 4H), 2.31–2.36 (m, 1H), 1.96–2.19(m, 4H), 1.43–1.68 (m, 6H), 0.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 140.78, 137.54, 135.55, 127.15, 126.23, 123.88, 58.62, 50.46, 47.92, 44.34, 37.94, 37.26 (t, *J* = 21.0 Hz), 35.80, 31.54, 29.70, 29.38, 26.32, 25.62, 21.56, 13.79.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.05– -81.12 (m, 3F), -111.17– -113.71 (m, 2F), -124.47– -124.58 (m, 2F), -125.90– -126.00 (m, 2F).

HRMS (EI): $C_{24}H_{24}F_9N_3O$ Calcd: 541.1716, Found: 541.1714.



5a

1-(1-azido-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-4-methylbenzene (5a),263.5mg, yield: 55%.

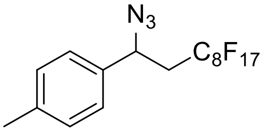
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (s, 4H), 4.87 (dd, *J* =4.8, 8.4Hz, 1H), 2.40 – 2.70 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.03, 135.07, 129.84, 126.55, 58.72, 37.35(t, *J* = 21.0 Hz), 21.03.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.01 – -81.09 (m, 3F), -113.40 – -113.52 (m, 2F), -121.89 – -121.97 (m, 2F), -122.99 – -123.06 (m, 2F), -123.66 – -123.77 (m, 2F), -126.27 – -126.43 (m, 2F).

HRMS (EI): $C_{15}H_{10}F_{13}N_3$Calcd: 479.0667, Found: 479.0662.



5b

1-(1-azido-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-4-methylbenzene (5b), 289.5mg, yield: 50%.

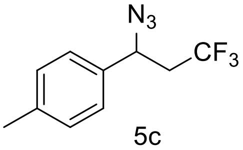
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 4H), 4.86 (dd, *J* =4.8, 8.1Hz, 1H), 2.40 – 2.70 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.01, 135.11, 129.82, 126.53, 58.73, 37.35(t, *J* = 21.0 Hz), 20.95.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.21 – -81.28 (m, 3F), -113.50 – -113.60 (m, 2F), -121.81 – -123.78 (m, 10F), -126.43 – -126.56 (m, 2F).

HRMS (EI): $C_{17}H_{10}F_{17}N_3$Calcd: 579.0603, Found: 579.0608.



5c

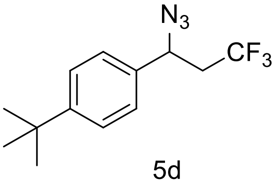
1-(1-azido-3,3,3-trifluoropropyl)-4-methylbenzene (5c),126 mg, yield: 55%.
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 4H),4.73 (dd, *J* =5.4, 8.4 Hz, 1H), 2.40 – 2.67 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.03, 134.63, 129.84, 127.17, 125.33 (q, *J* = 275.3 Hz), 59.71 (d, *J* = 3.8 Hz), 40.29 (dd, *J* = 27.8, 56.3 Hz), 21.12.

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.08.

HRMS (EI):$C_{10}H_{10}F_3N_3$Calcd: 229.0827, Found: 229.0823.



5d

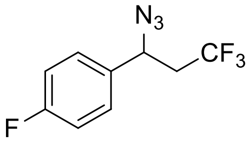
1-(1-azido-3,3,3-trifluoropropyl)-4-(tert-butyl)benzene (5d), 143.6 mg, yield: 53%.
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, *J* =8.1 Hz, 2H),7.24 (d, *J* =8.4 Hz, 2H), 4.75 (dd, *J* =4.2, 8.7 Hz, 1H), 2.42 – 2.68 (m, 2H), 1.32 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.14, 134.73, 126.35, 126.08, 125.36 (q, *J* = 275.3 Hz), 59.63 (d, *J* = 3 Hz), 40.34 (dd, *J* = 27.8, 56.3 Hz), 34.67, 31.22.

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.15.

HRMS (EI):$C_{13}H_{16}F_3N_3$Calcd: 271.1296, Found: 271.1291.



5e

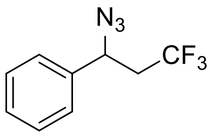
1-(1-azido-3,3,3-trifluoropropyl)-4-fluorobenzene (5e),116.5mg, yield: 50%.
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.34 (m, 2H),7.11 (t, *J* =8.4 Hz, 2H), 4.78 (dd, *J* =5.4, 8.1 Hz, 1H), 2.37 – 2.71 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 162.90 (d, *J* = 246.8 Hz), 133.53 (d, *J* = 3 Hz), 128.55 (d, *J* = 8.3 Hz), 125.12 (q, *J* = 276 Hz), 116.20 (d, *J* = 21.8 Hz), 59.26 (d, *J* = 3 Hz), 40.45 (dd, *J* = 27.8, 55.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.05, -122.2 (d, *J* = 2.0 Hz).

HRMS (EI):$C_9H_7F_4N_3$Calcd: 233.0576, Found: 233.0573.



5f

(1-azido-3,3,3-trifluoropropyl)benzene (5f),96.8mg, yield: 45%.

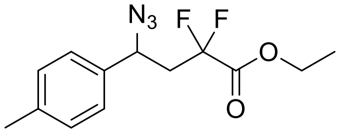
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24-7.46 (m, 5H),4.78 (dd, *J* =3.3, 8.7 Hz, 1H), 2.40 – 2.72 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.67, 129.20, 129.09, 126.69, 125.26 (q, *J* = 276 Hz), 59.91 (d, *J* = 3 Hz), 40.38 (dd, *J* = 28.5, 56.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -64.09.

HRMS (EI):$C_9H_8F_3N_3$Calcd: 215.0670, Found: 215.0675.



5g

ethyl 4-azido-2,2-difluoro-4-(p-tolyl)butanoate (5g), 121mg, yield: 42%.

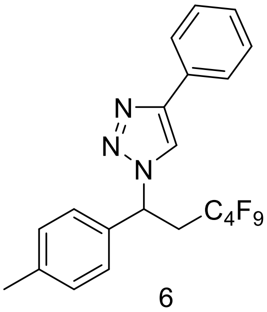
Colourless liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ7.26 (s, 4H), 4.76 (dd, *J* = 9.6, 4.5 Hz, 1H), 4.27-7.35 (m, 2H), 2.63–2.83 (m, 1H), 2.43–2.55 (m, 1H), 2.40 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 163.56 (t, *J* = 32.3 Hz), 138.92, 134.75, 129.74, 126.80, 114.60 (t, *J* = 248.3 Hz), 63.00 (d, *J* = 14.3 Hz), 59.79 (d, *J* = 3.8 Hz), 40.98 (t, *J* = 23.3 Hz), 21.14 (d, *J* = 7.5 Hz), 13.82 (d, *J* = 7.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ -102.00– -107.45 (m).

HRMS (ESI): $C_{13}H_{15}F_2N_3O_2$+Na^+ Calcd: 306.1030, Found: 306.1031.



6

benzyl (3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)carbamate (6), 93.3mg, yield: 97%.

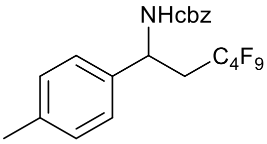
Light yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 1H),7.78 (d, *J* = 8.4Hz, 2H), 7.25 – 7.35 (m, 5H), 7.13 (d, *J* = 7.8Hz, 2H), 6.05 (dd, *J* = 5.4, 7.8Hz, 1H), 3.68 – 3.88 (m, 1H), 2.96 – 3.16 (m, 1H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 148.02, 139.33, 134.83, 130.43, 129.97, 128.79, 128.24, 126.73, 125.74, 119.88, 58.12, 36.05 (t, *J* = 20.3Hz), 20.92.

^{19}F NMR (282 MHz, $CDCl_3$) δ -81.23 – -81.31 (m, 3F), -112.51 – -115.59 (m, 2F), -124.43 – -124.48 (m, 2F), -126.03 – -126.10 (m, 2F).

HRMS (ESI):$C_{21}H_{18}F_9NO_2$+H^+Calcd: 482.1268, Found: 482.1273.



7

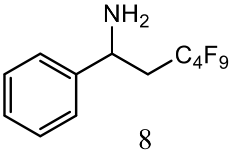
benzyl (3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexyl)carbamate (7), 85.7mg, yield: 88%. Light yellow liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ 7.30 (s, 5H),7.16 (s, 4H), 5.38 (s, 1H), 5.17 (d, *J* = 5.7Hz,1H), 5.07 (s, 2H), 2.43 – 2.72 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 155.27, 138.02, 137.59, 136.13, 129.69, 128.51, 128.20, 128.12, 126.12, 67.06, 49.15, 36.66, 21.05.

^{19}F NMR (282 MHz, CDCl$_3$) δ -81.05 – -81.13 (m, 3F), -113.37 – -113.45 (m, 2F), -124.47 – -124.50 (m, 2F), -125.91 – -125.99 (m, 2F).

HRMS (ESI):$C_{21}H_{18}F_9NO_2+H^+$Calcd: 488.1257, Found: 488.1267.



8

3,3,4,4,5,5,6,6,6-nonafluoro-1-(p-tolyl)hexan-1-amine (8), 57.9mg, yield: 82%.Light yellow liquid.

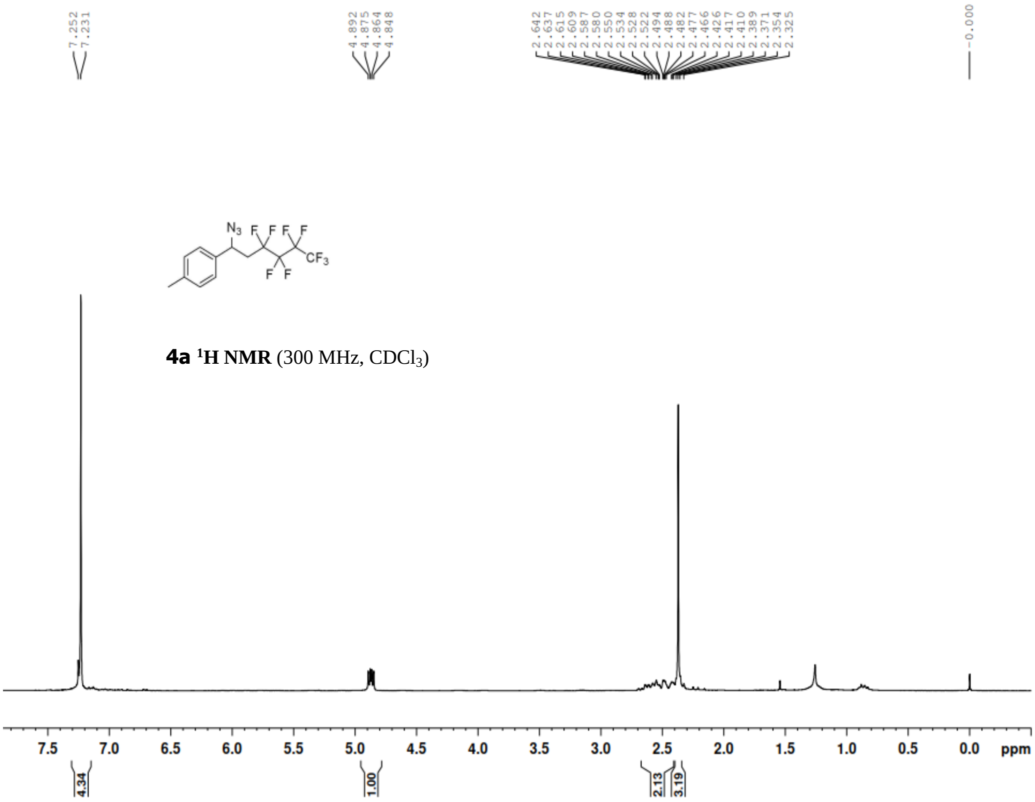
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.27 (d, *J* =8.1Hz, 2H), 7.17 (d, *J* =7.8Hz, 2H), 4.47 (dd, *J* =4.5, 7.8Hz, 1H), 2.41–2.53 (m, 2H), 2.34 (s, 3H), 1.69 (s, 2H).

^{13}C NMR (75 MHz, CDCl$_3$) δ 141.40, 137.57, 129.50, 126.03, 49.39, 40.08 (t, *J* = 21.0Hz), 21.02.

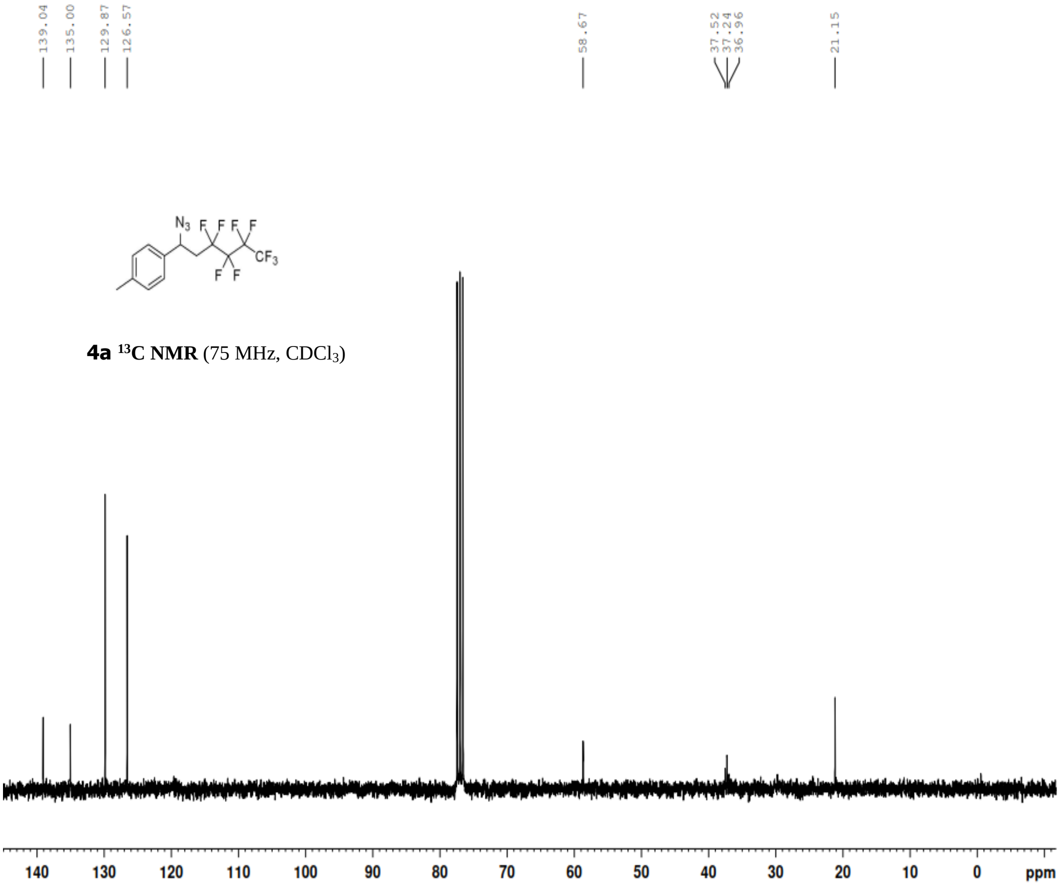
^{19}FNMR (282 MHz, CDCl$_3$) δ -81.10 – -81.17(m, 3F), -112.05 – -114.83 (m, 2F), -124.64 – -124.71 (m, 2F), -125.95 – -126.02 (m, 2F).

HRMS (ESI):$C_{13}H_{12}F_9N+H^+$Calcd: 354.0888, Found: 354.0885.

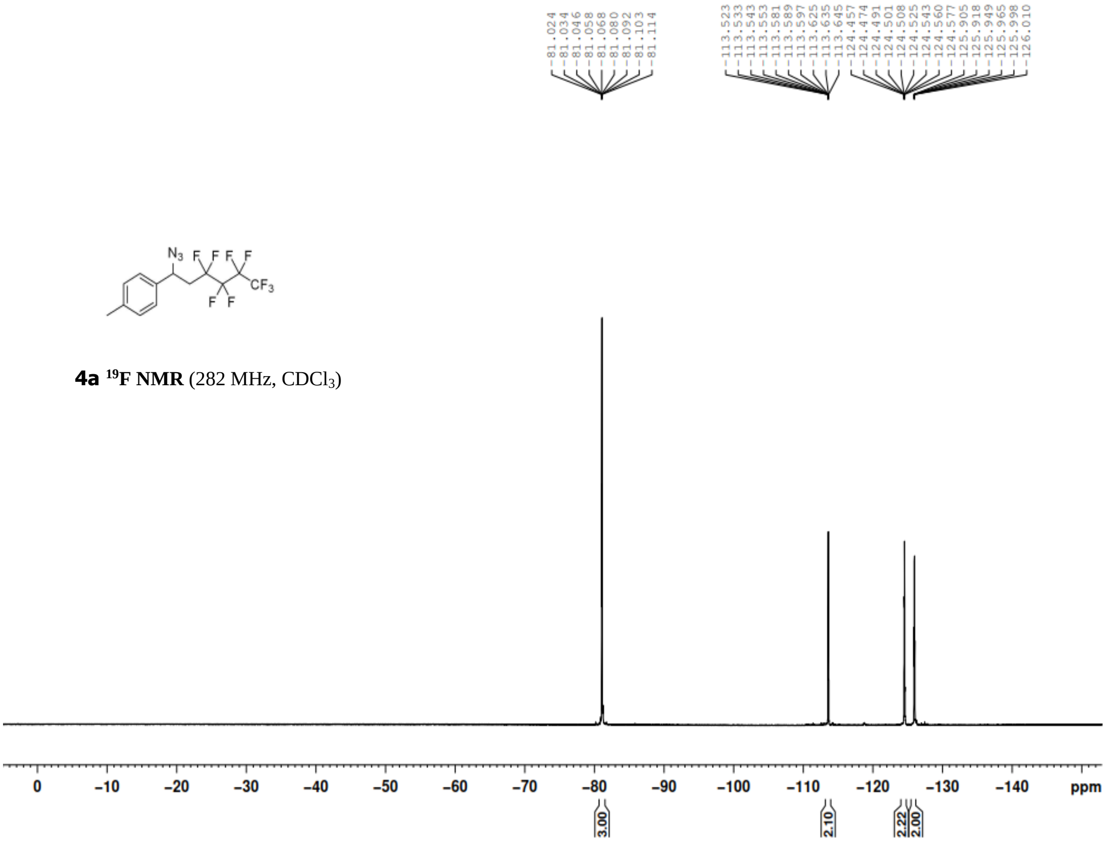
8. NMR spectra of new compounds



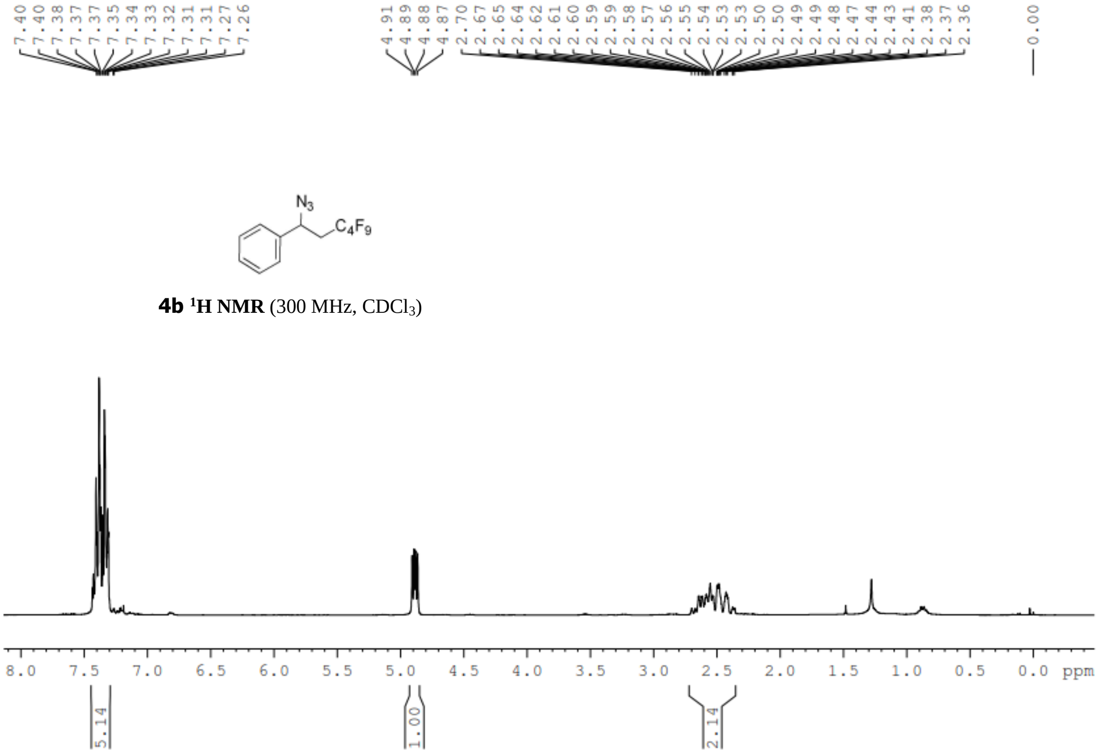
4a **^{1}H NMR** (300 MHz, $CDCl_3$)



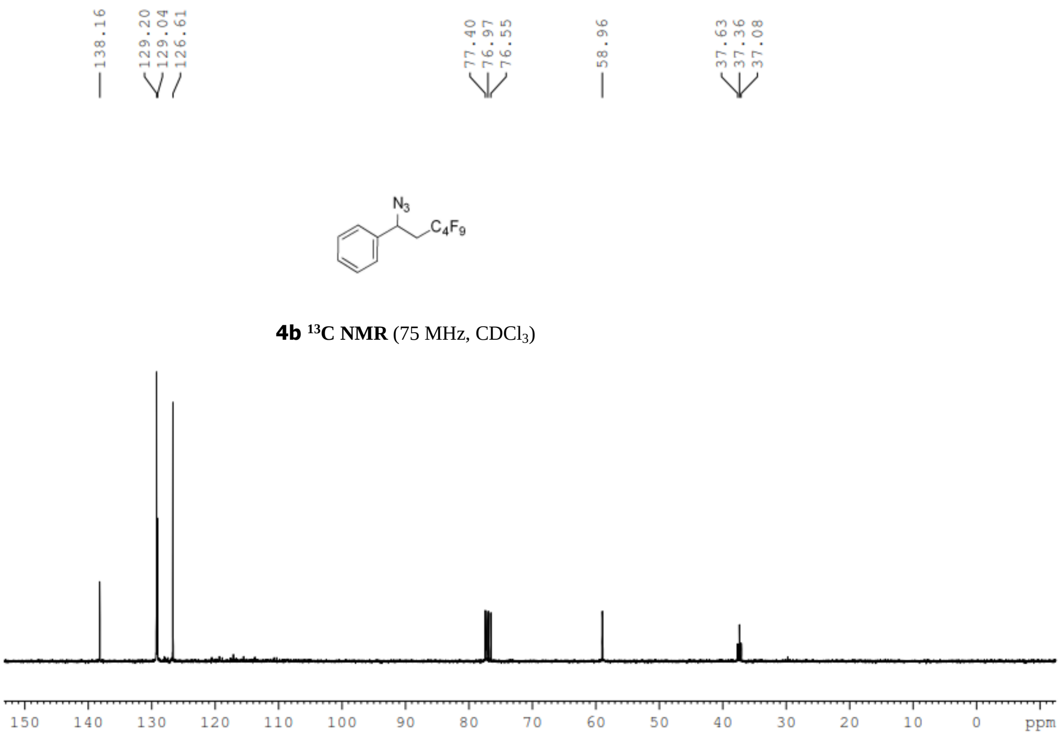
4a **^{13}C NMR** (75 MHz, $CDCl_3$)



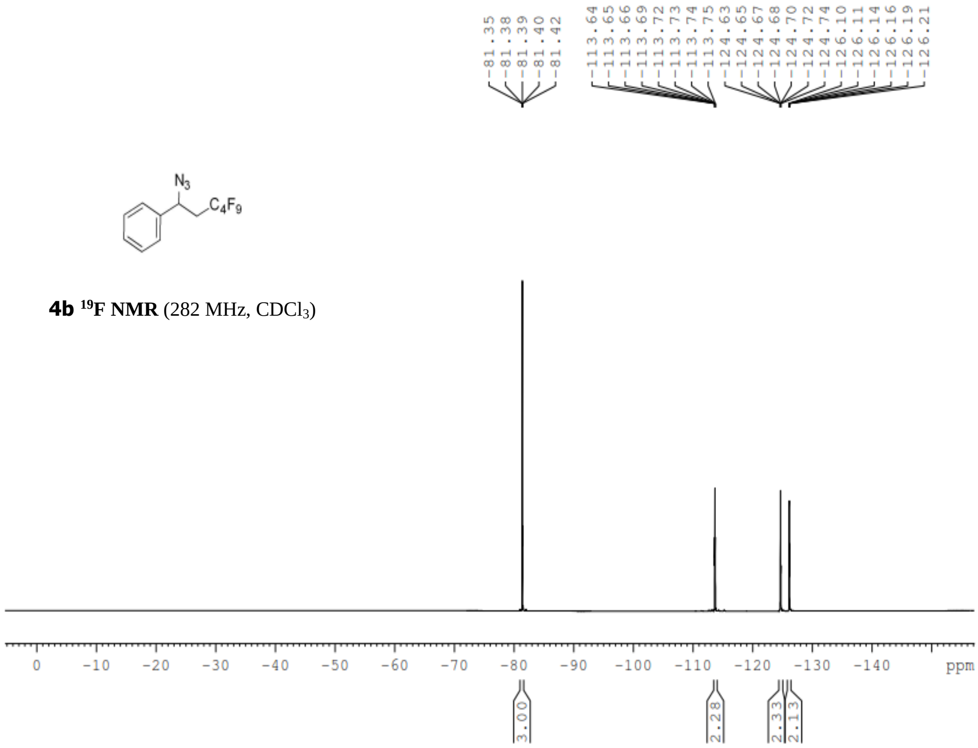
4a ^{19}F NMR (282 MHz, $CDCl_3$)



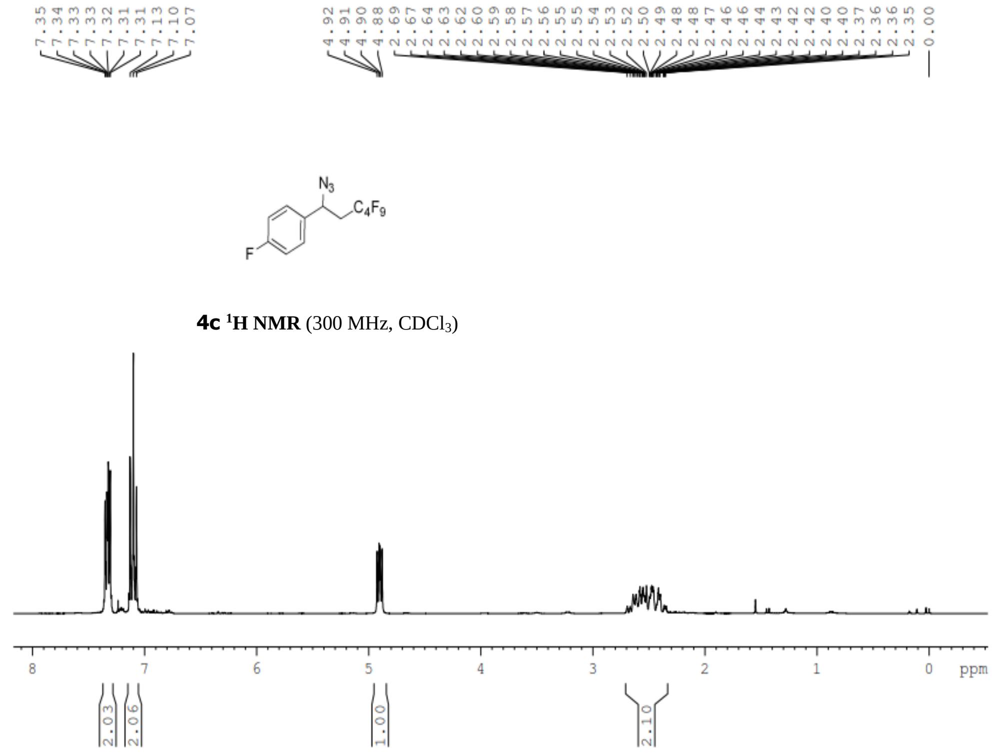
4b ^{1}H NMR (300 MHz, $CDCl_3$)



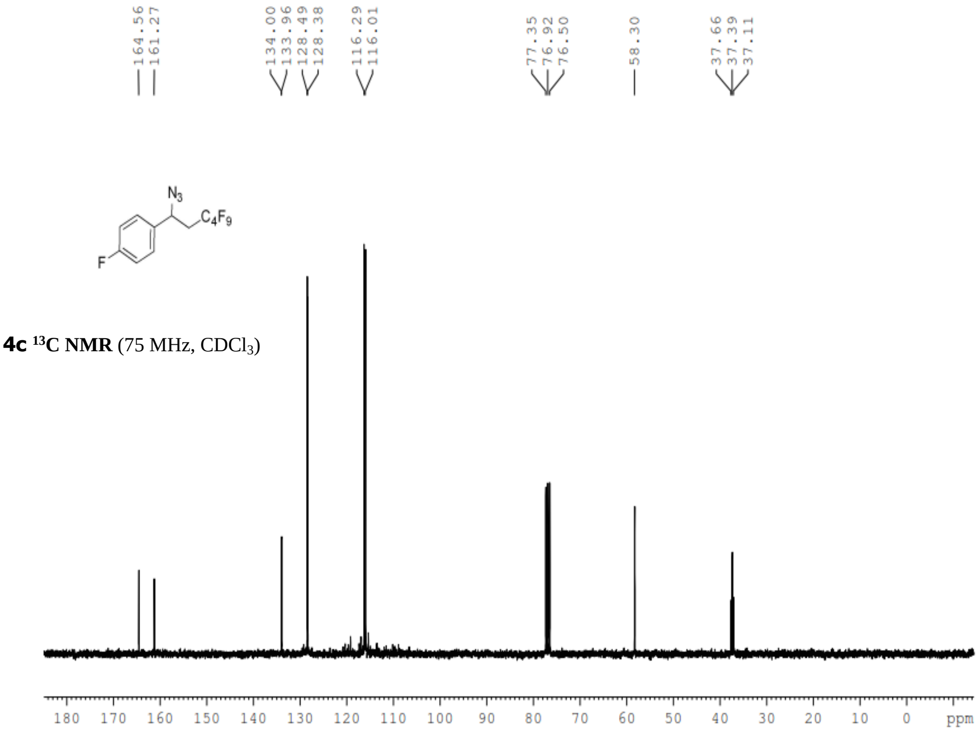
4b **^{13}C NMR** (75 MHz, $CDCl_3$)



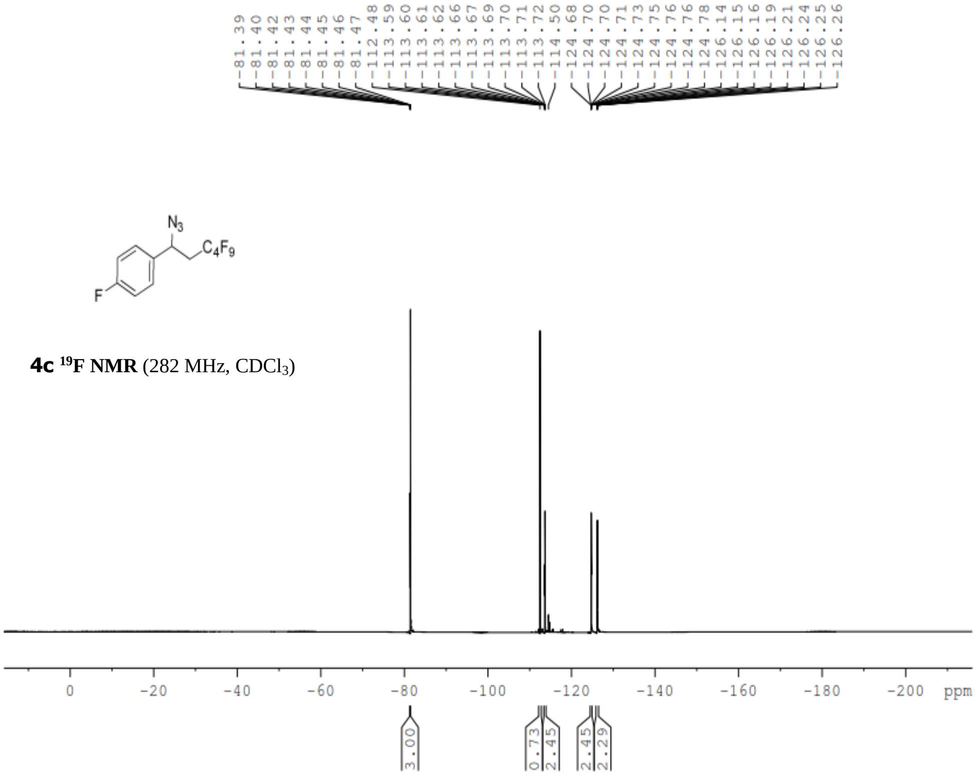
4b **^{19}F NMR** (282 MHz, $CDCl_3$)



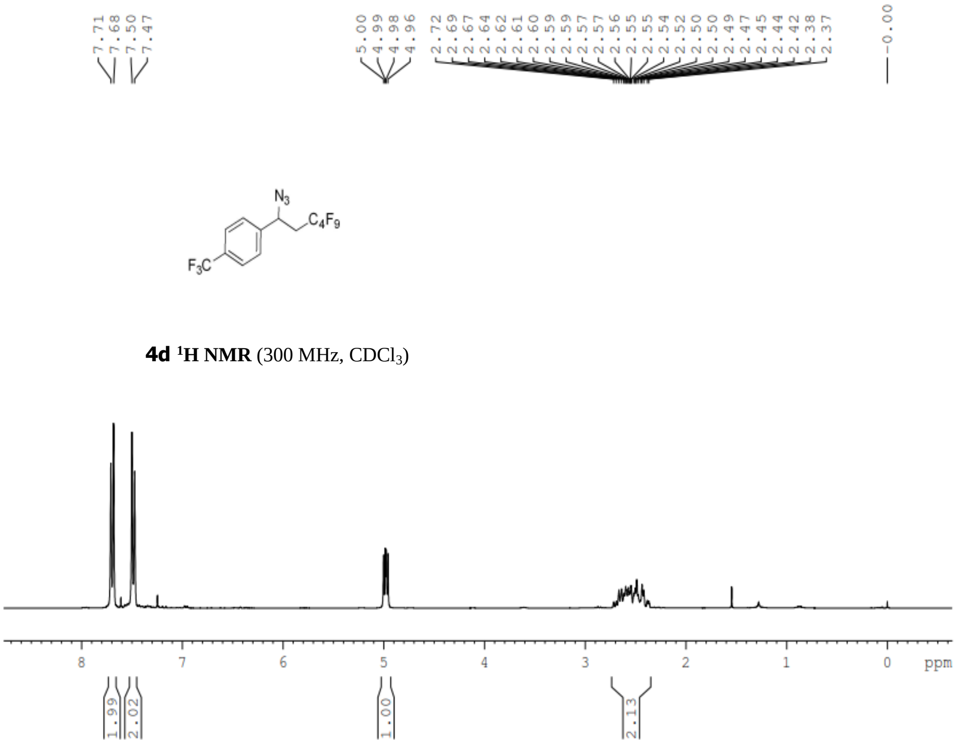
4c ^{1}**H NMR** (300 MHz, $CDCl_3$)



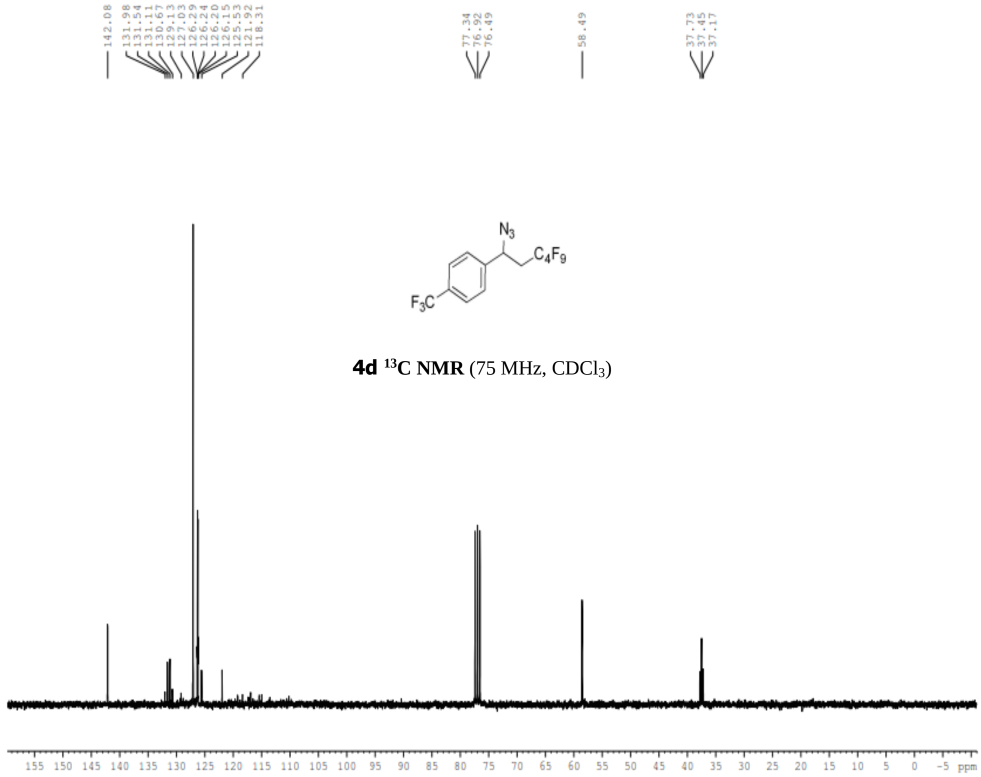
4c ^{13}**C NMR** (75 MHz, $CDCl_3$)



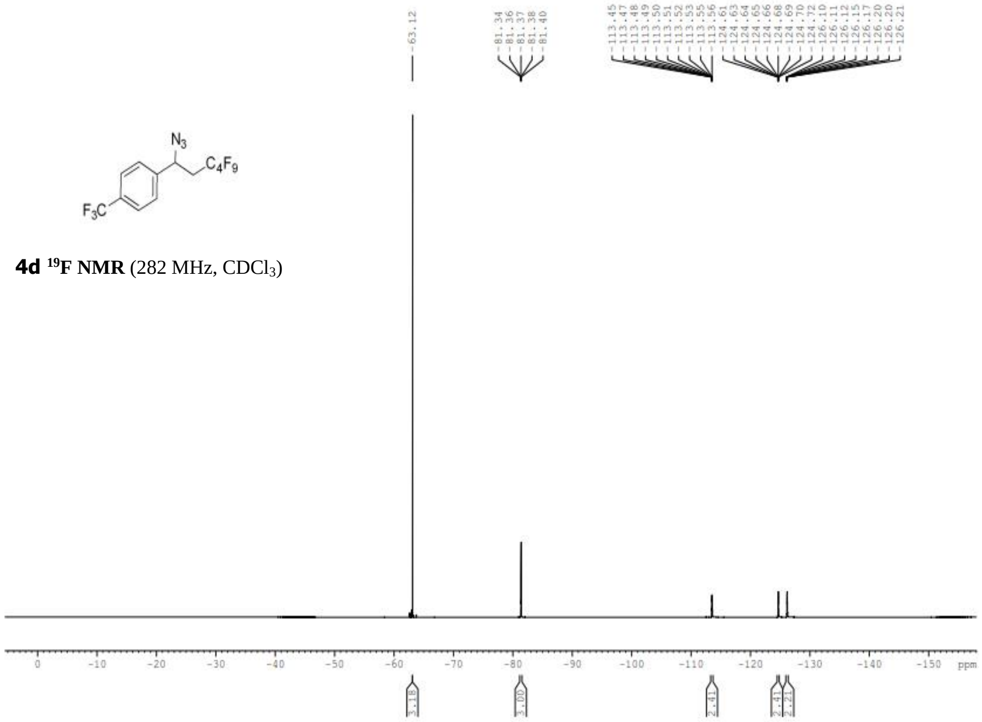
4c **^{19}F NMR** (282 MHz, $CDCl_3$)



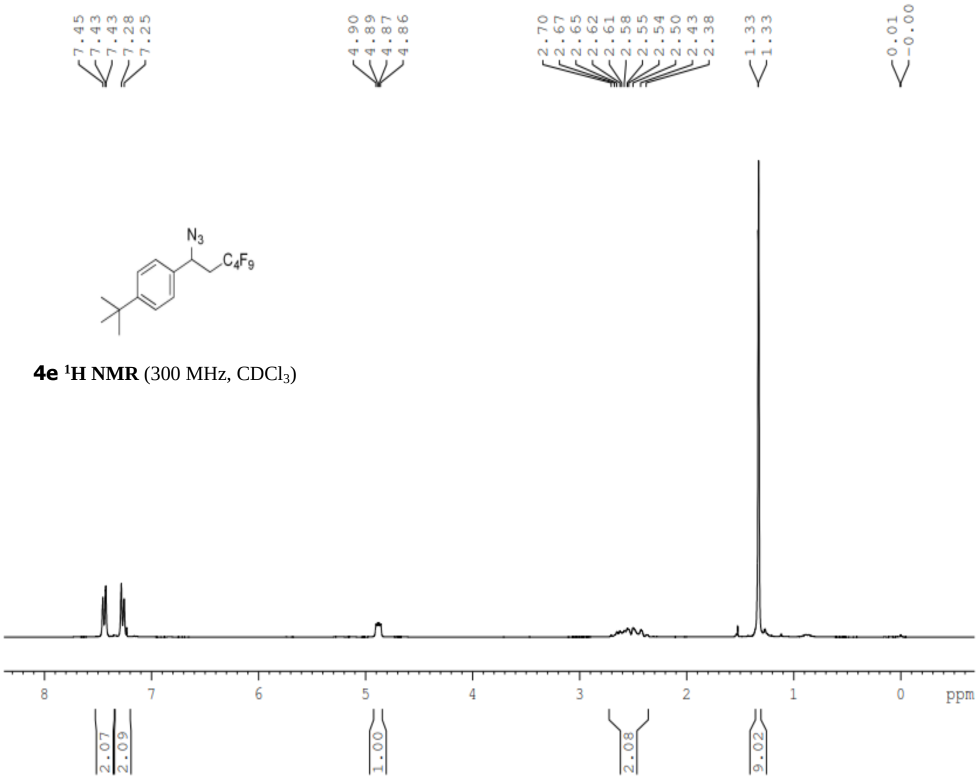
4d **^{1}H NMR** (300 MHz, $CDCl_3$)



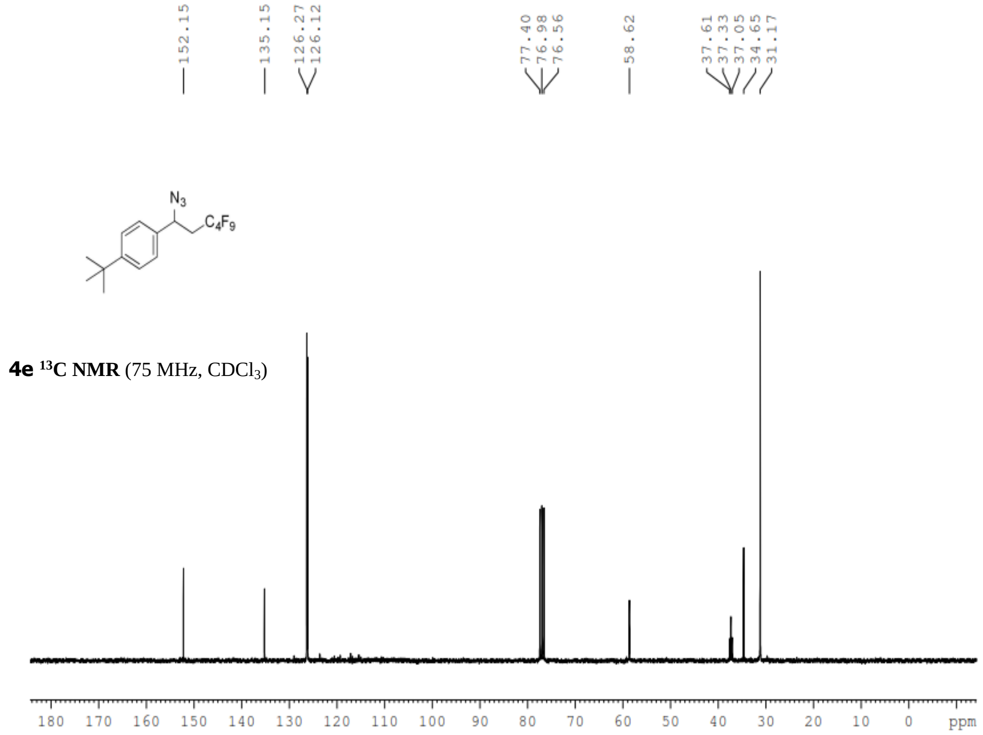
4d ^{13}**C NMR** (75 MHz, $CDCl_3$)



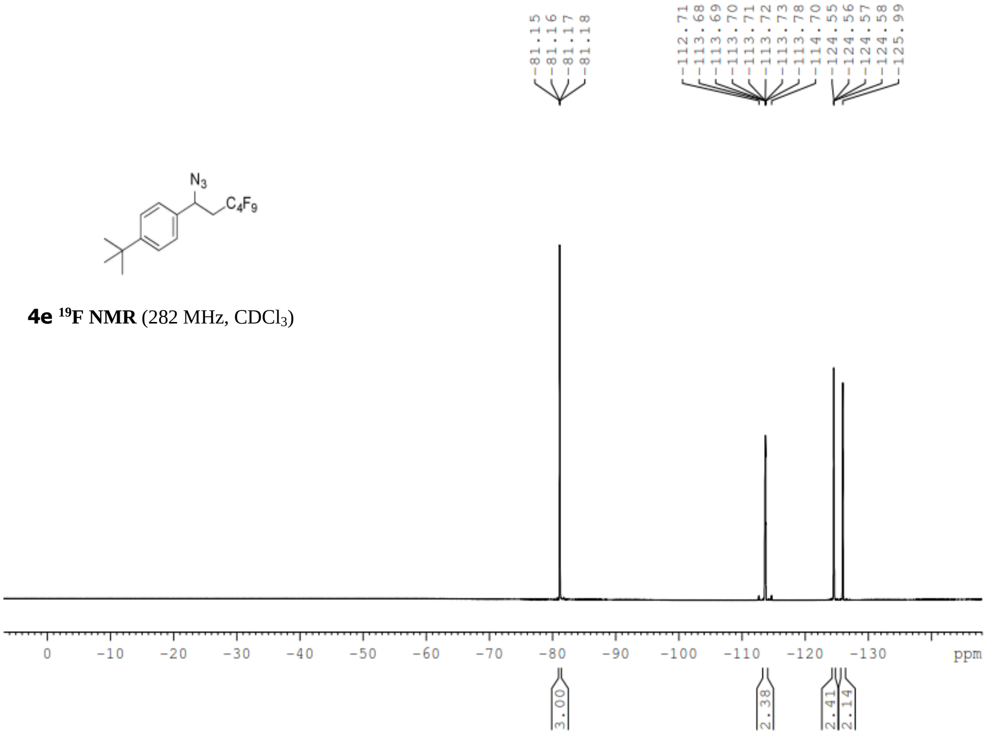
4d ^{19}**F NMR** (282 MHz, $CDCl_3$)



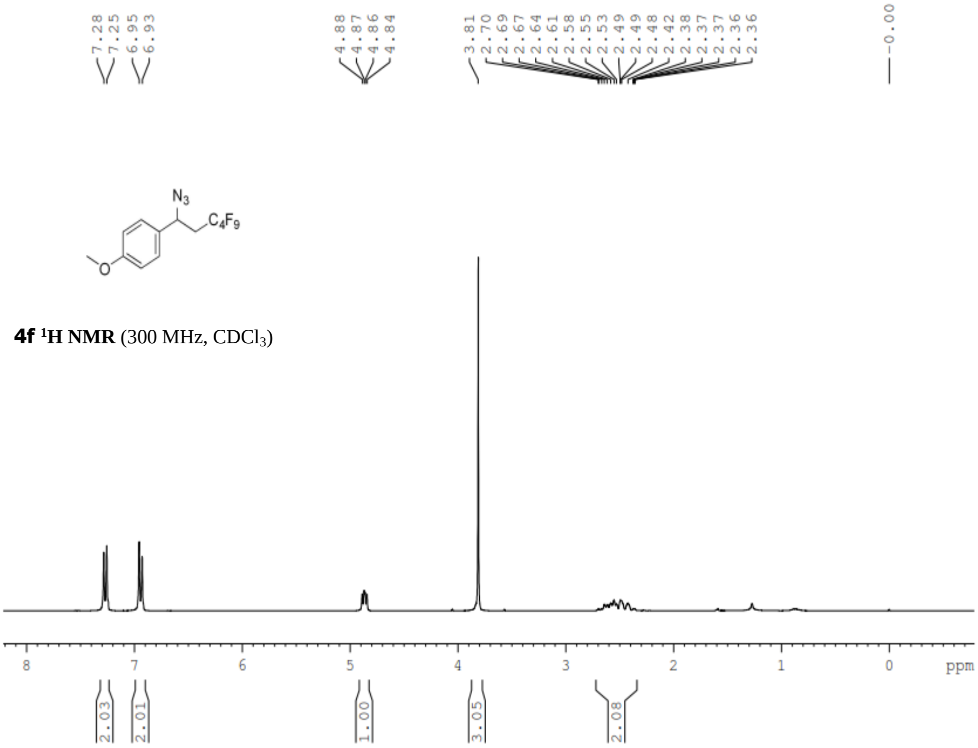
4e ^{1}H NMR (300 MHz, $CDCl_3$)



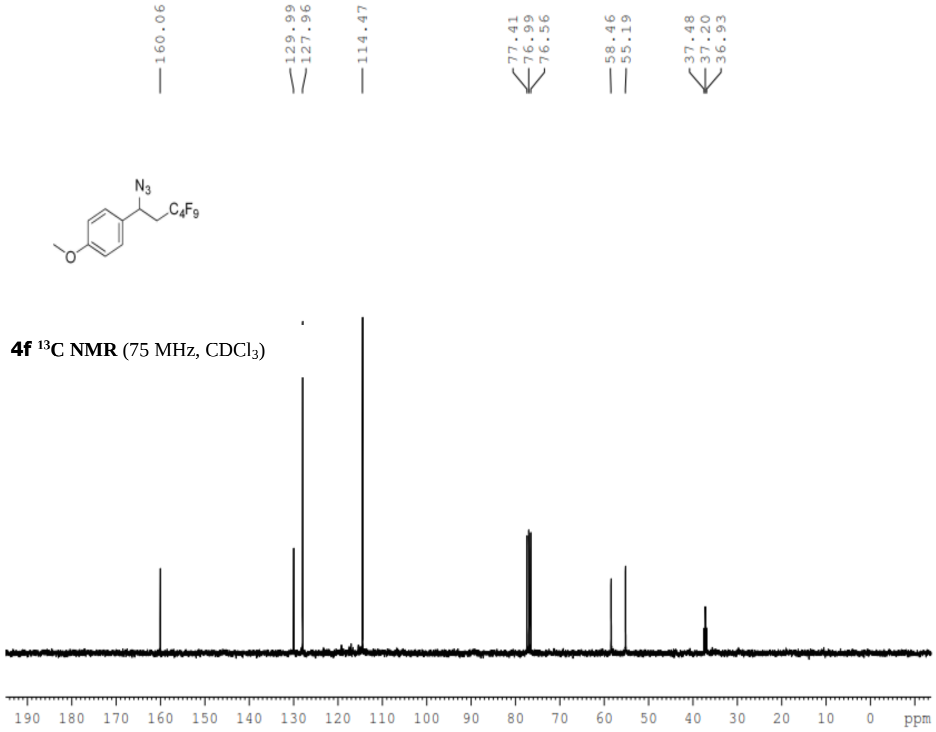
4e ^{13}C NMR (75 MHz, $CDCl_3$)



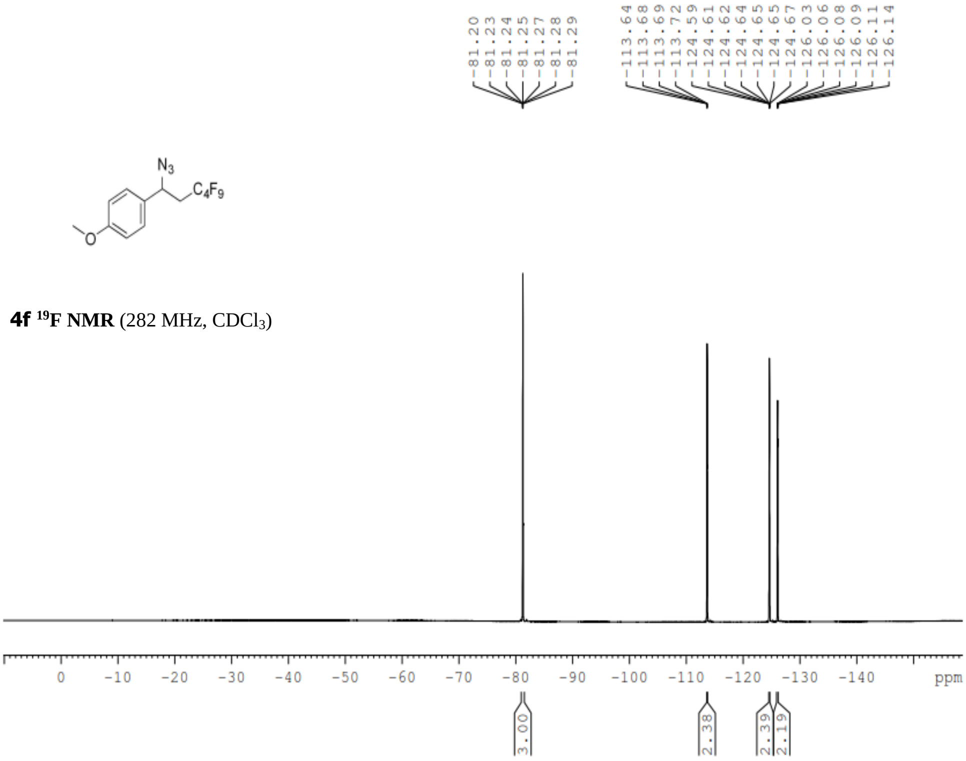
4e ^{19}**F NMR** (282 MHz, $CDCl_3$)



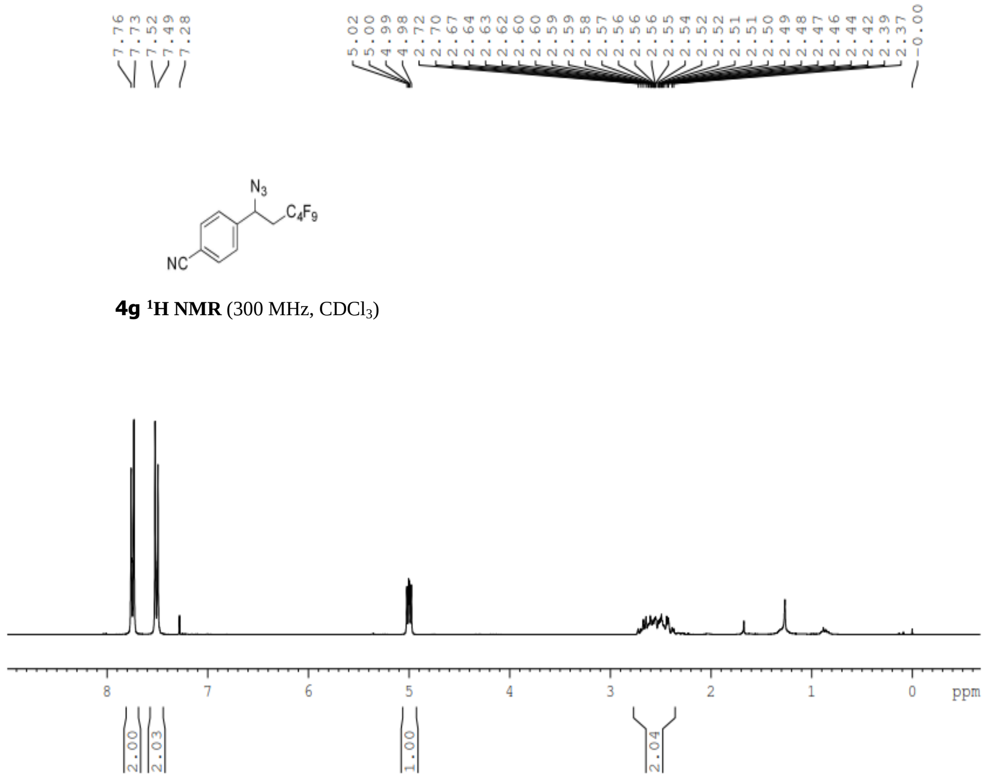
4f ^{1}**H NMR** (300 MHz, $CDCl_3$)



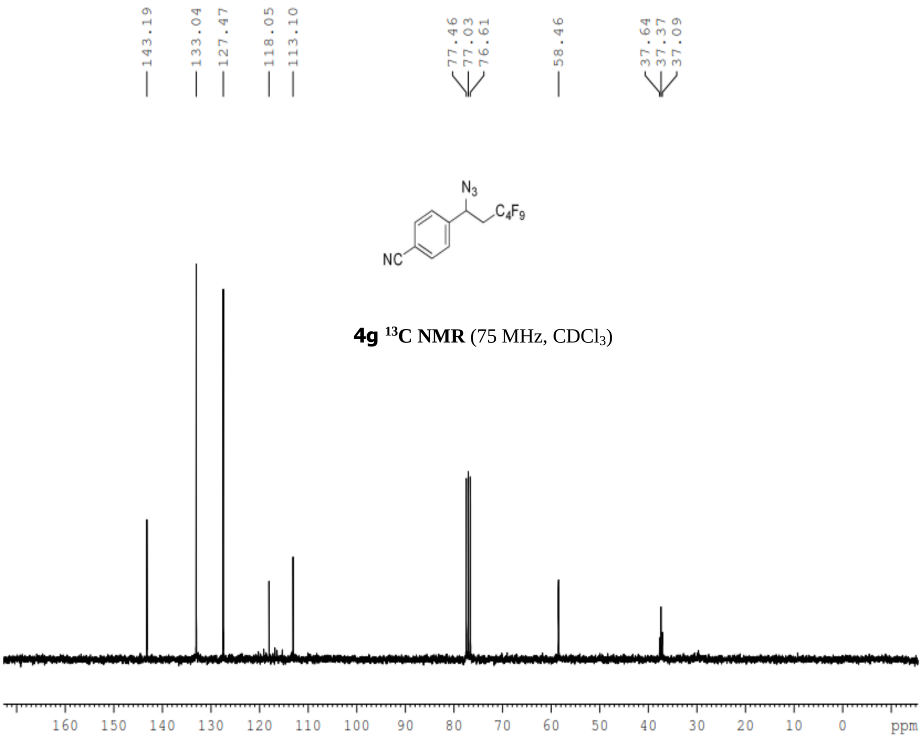
4f ^{13}**C NMR** (75 MHz, $CDCl_3$)



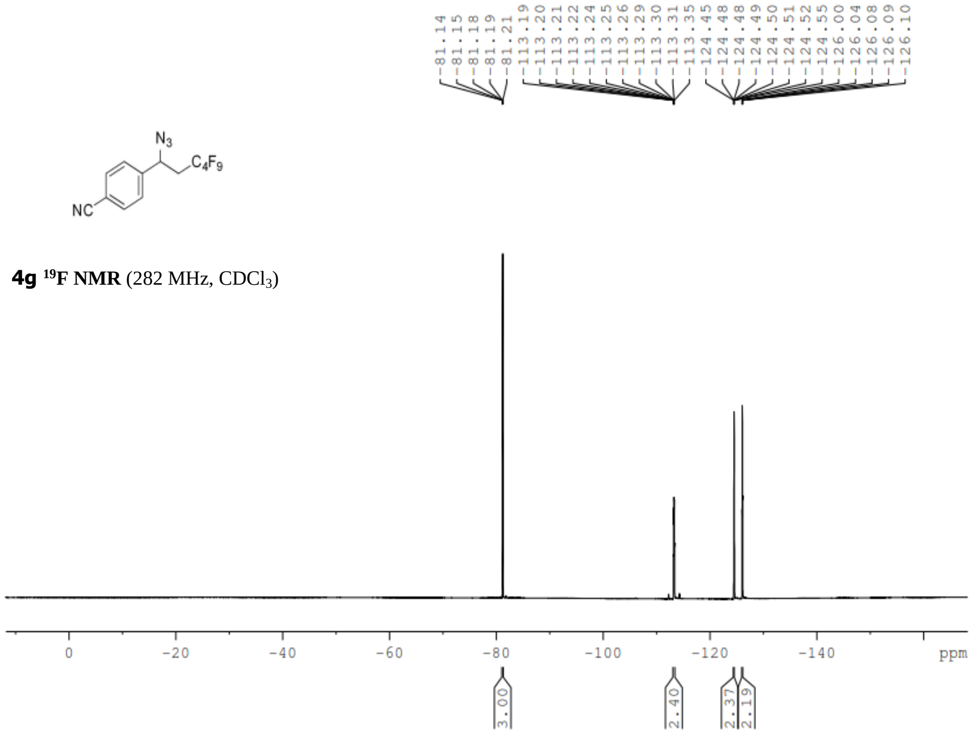
4f ^{19}**F NMR** (282 MHz, $CDCl_3$)



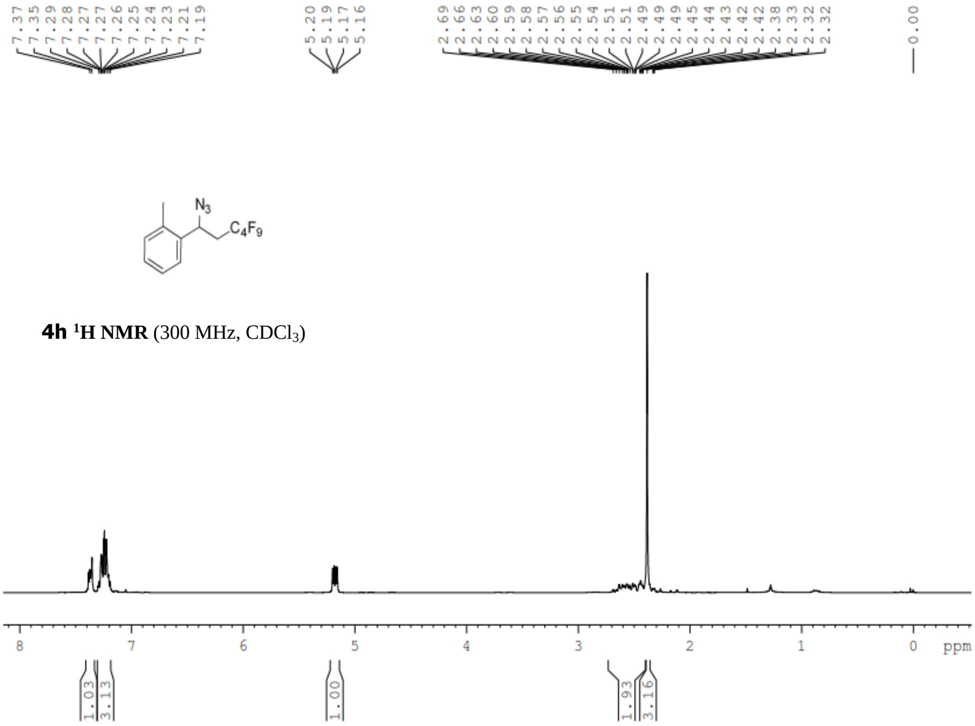
4g **^{1}H NMR** (300 MHz, $CDCl_3$)



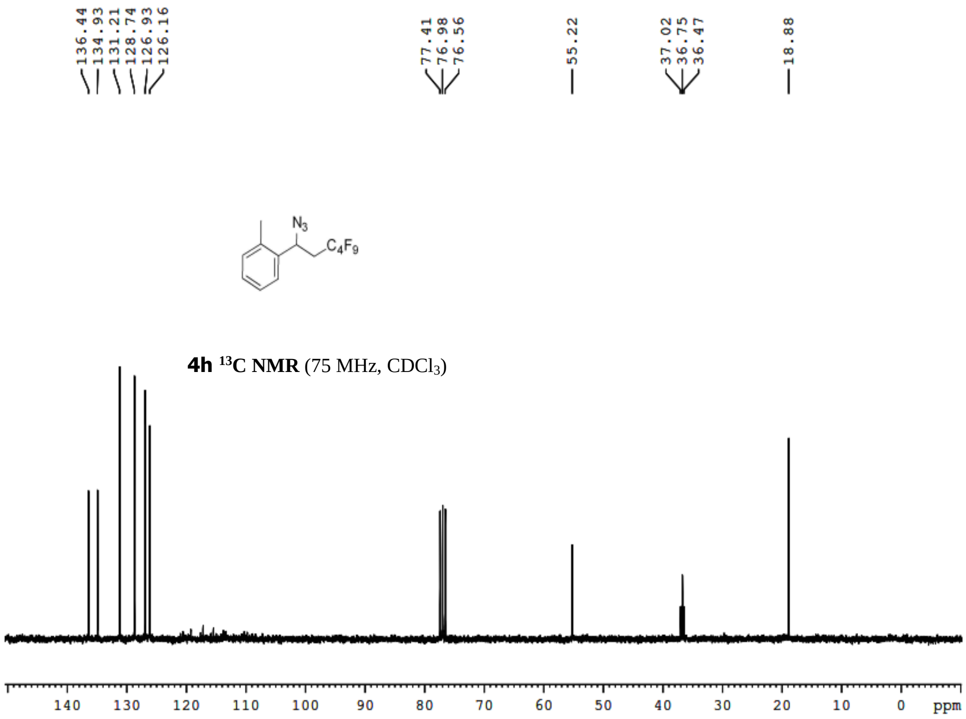
4g **^{13}C NMR** (75 MHz, $CDCl_3$)



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

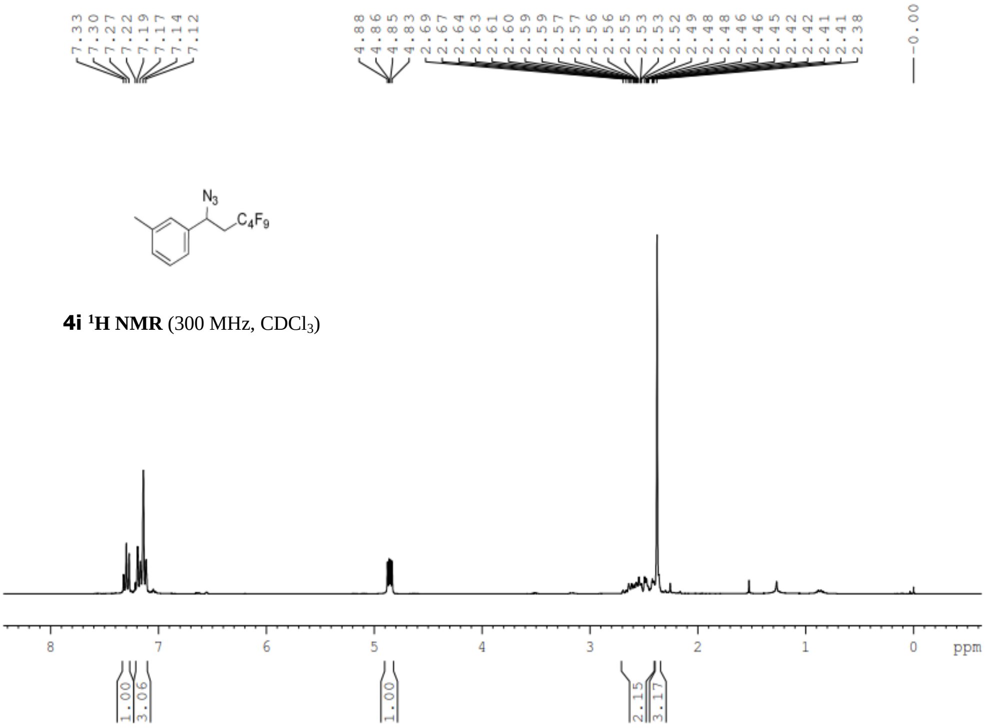


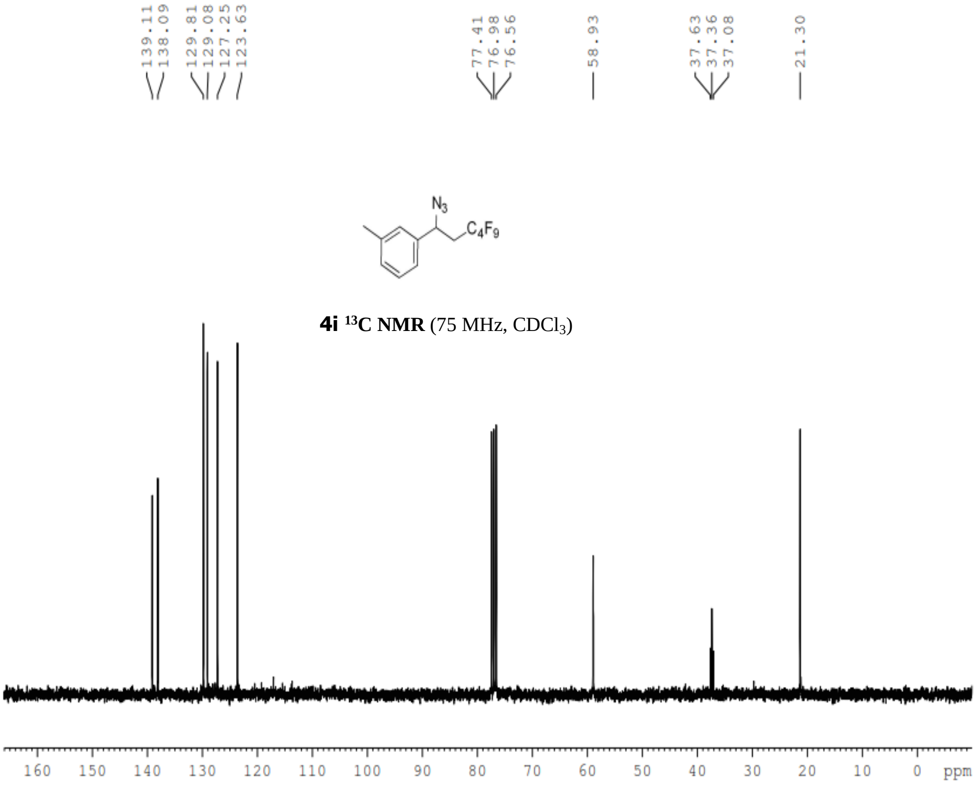
4h **^{1}H NMR** (300 MHz, $CDCl_3$)

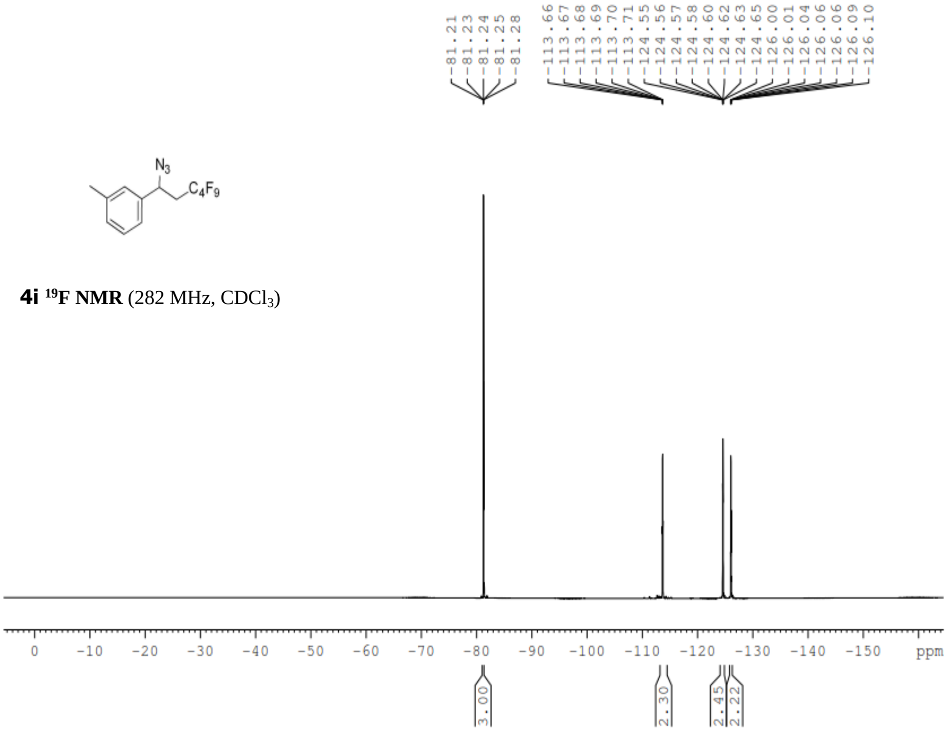


4h **^{13}C NMR** (75 MHz, $CDCl_3$)

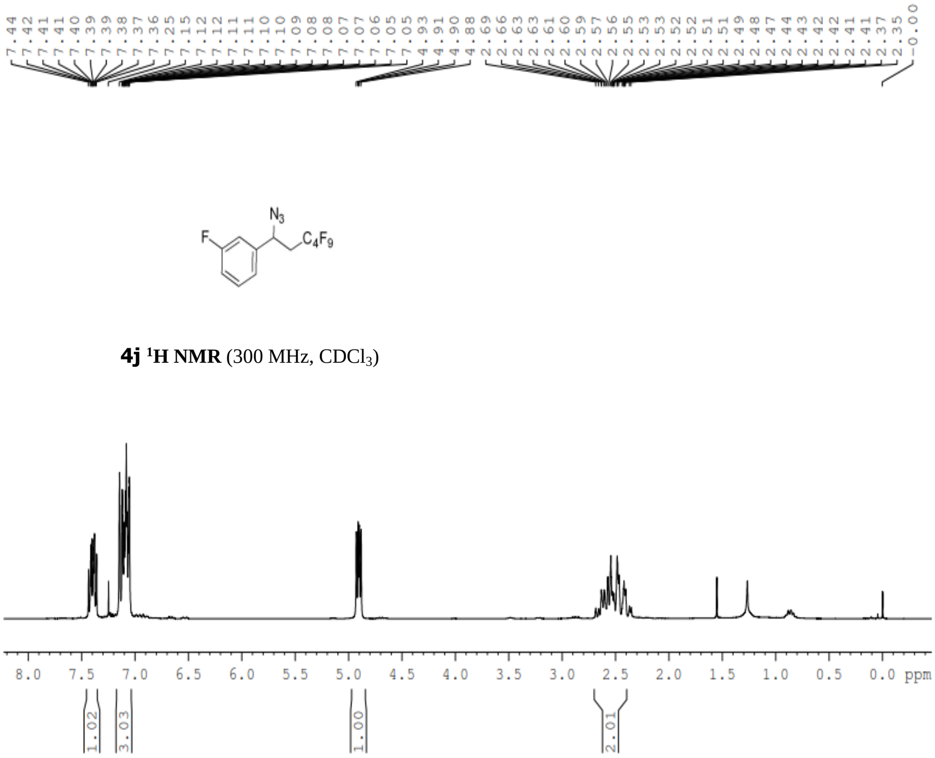
4h **^{19}F NMR** (282 MHz, $CDCl_3$)


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

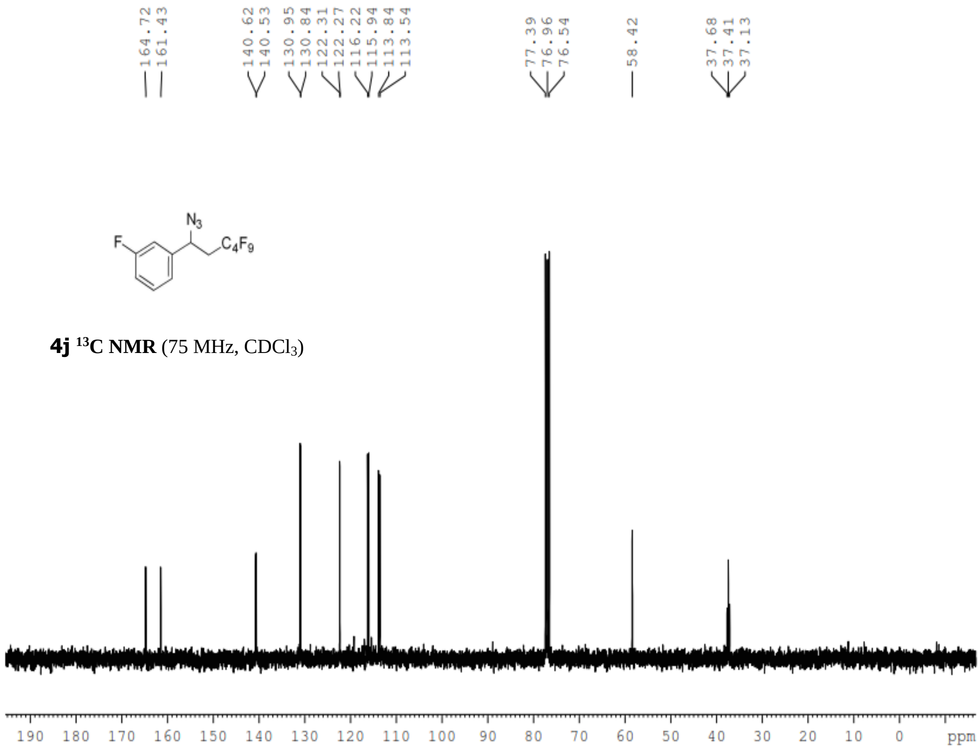

4i **^{13}C NMR** (75 MHz, $CDCl_3$)



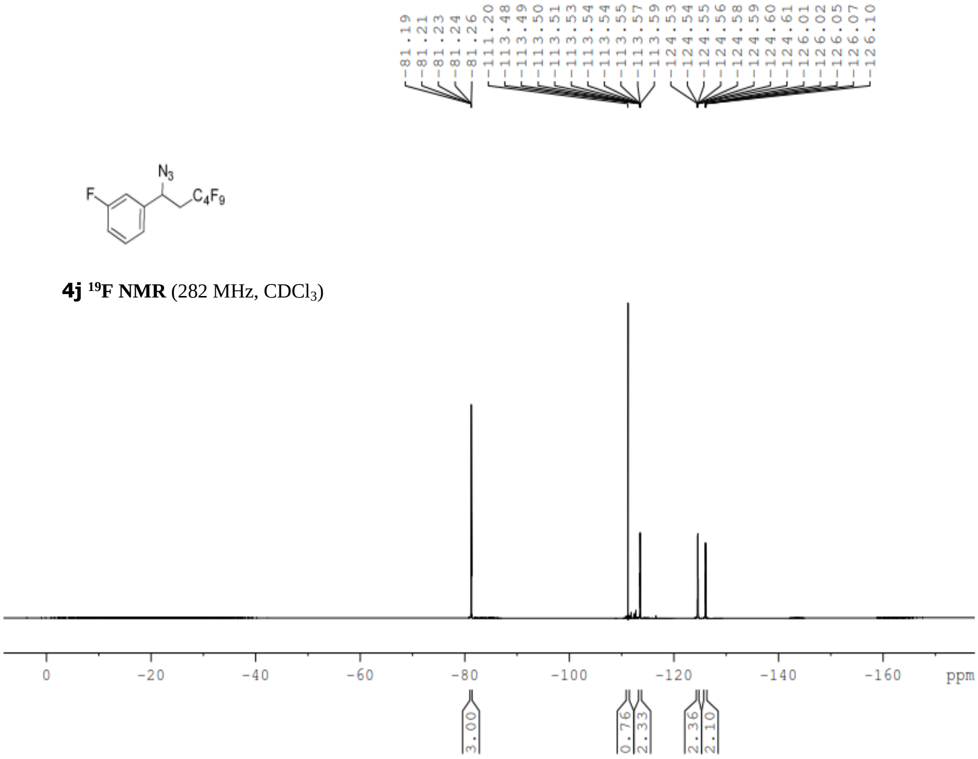
4i **^{19}F NMR** (282 MHz, $CDCl_3$)



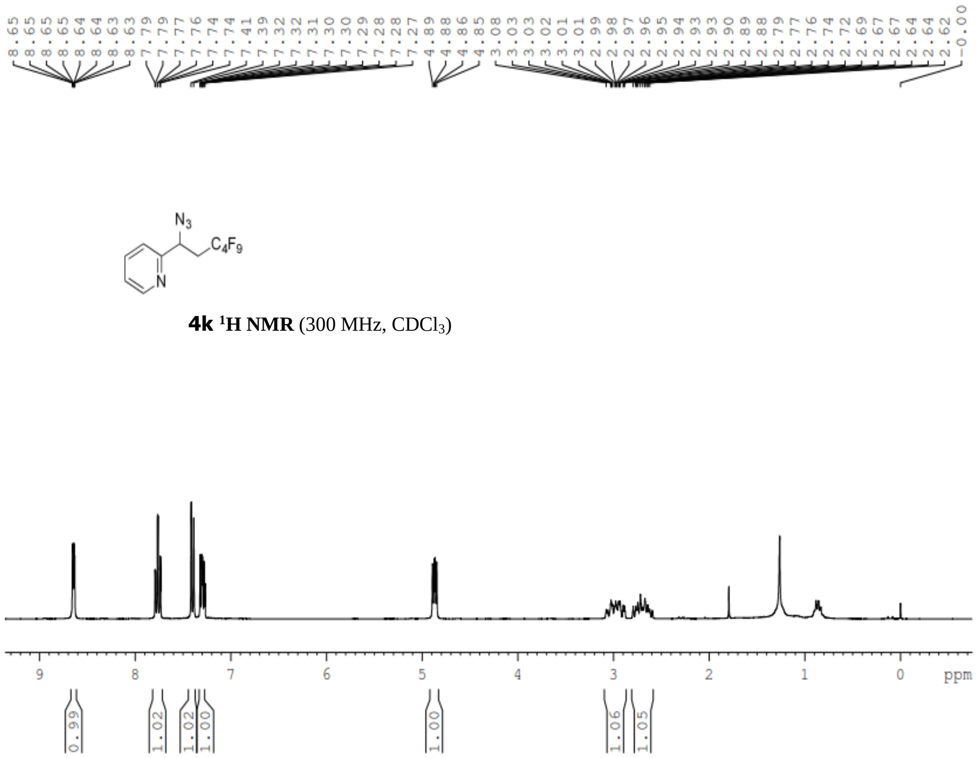
4j **^{1}H NMR** (300 MHz, $CDCl_3$)



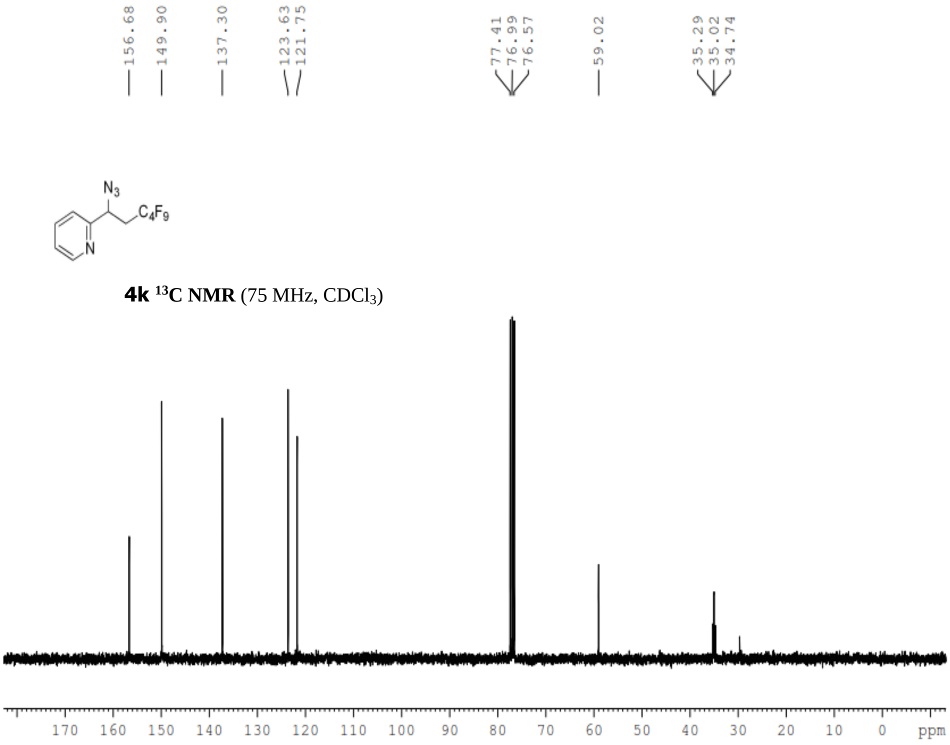
4j **^{13}C NMR** (75 MHz, $CDCl_3$)



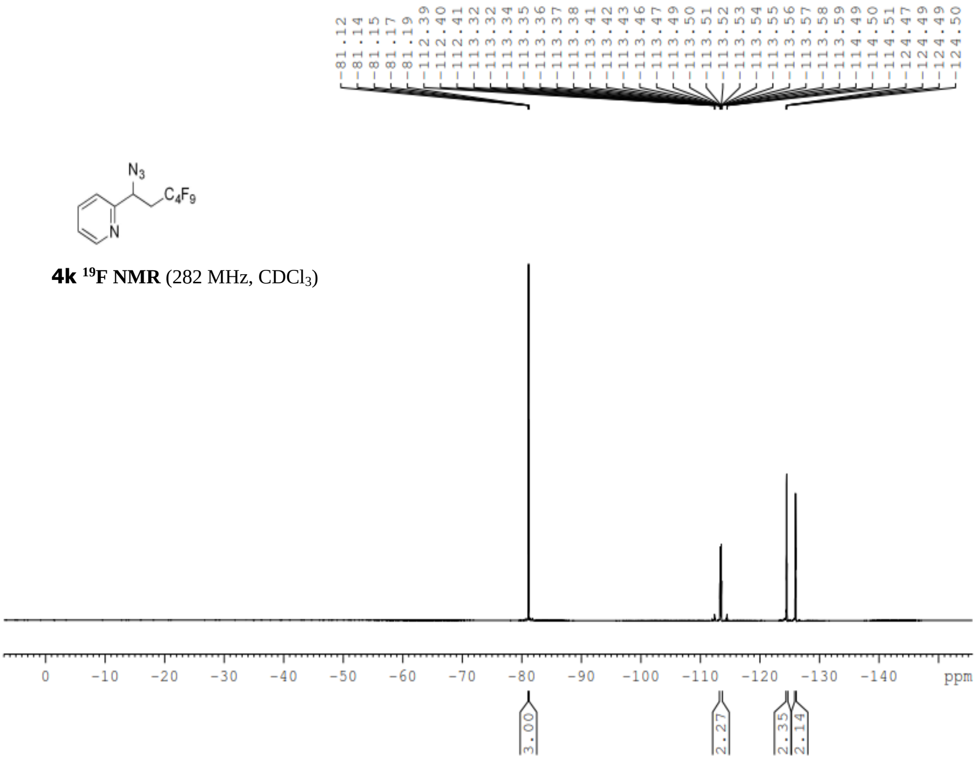
4j **^{19}F NMR** (282 MHz, $CDCl_3$)



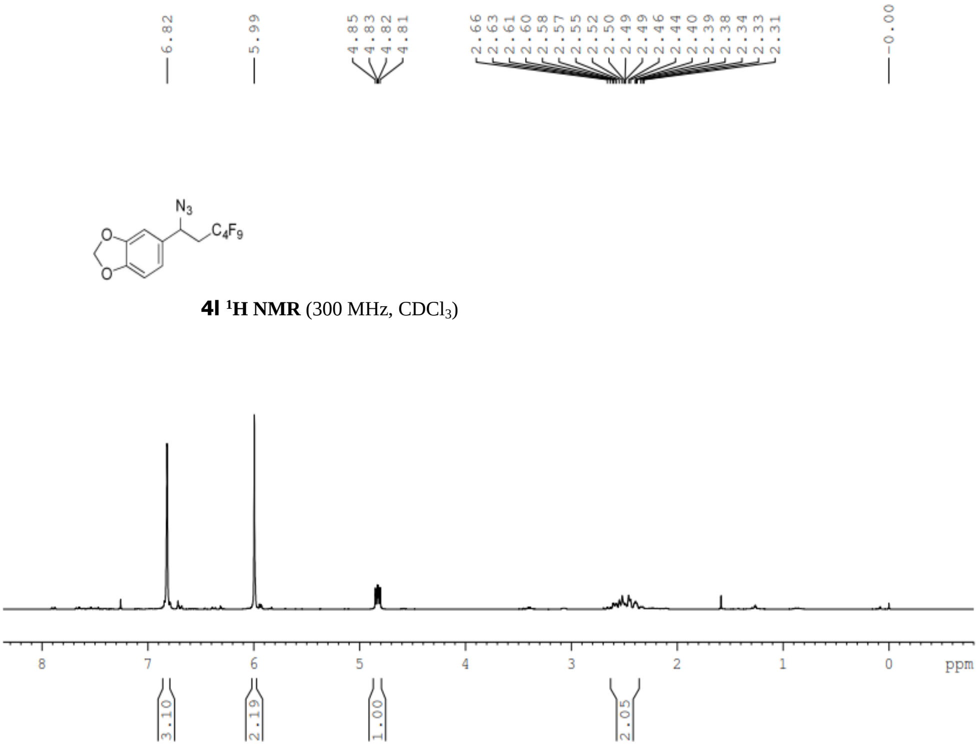
4k **^{1}H NMR** (300 MHz, $CDCl_3$)



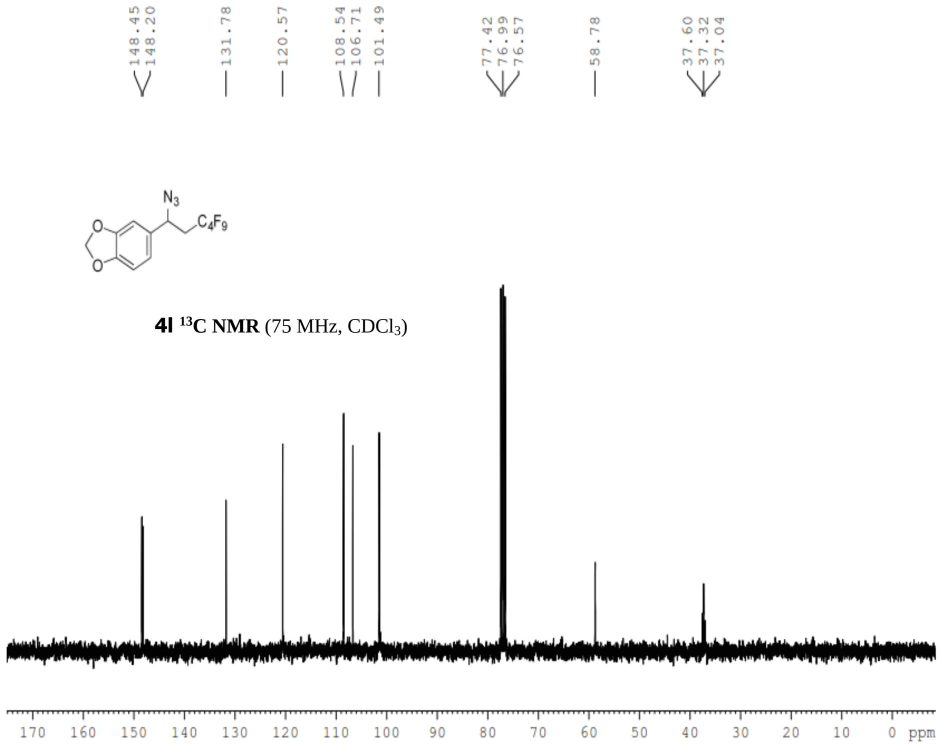
4k **^{13}C NMR** (75 MHz, $CDCl_3$)



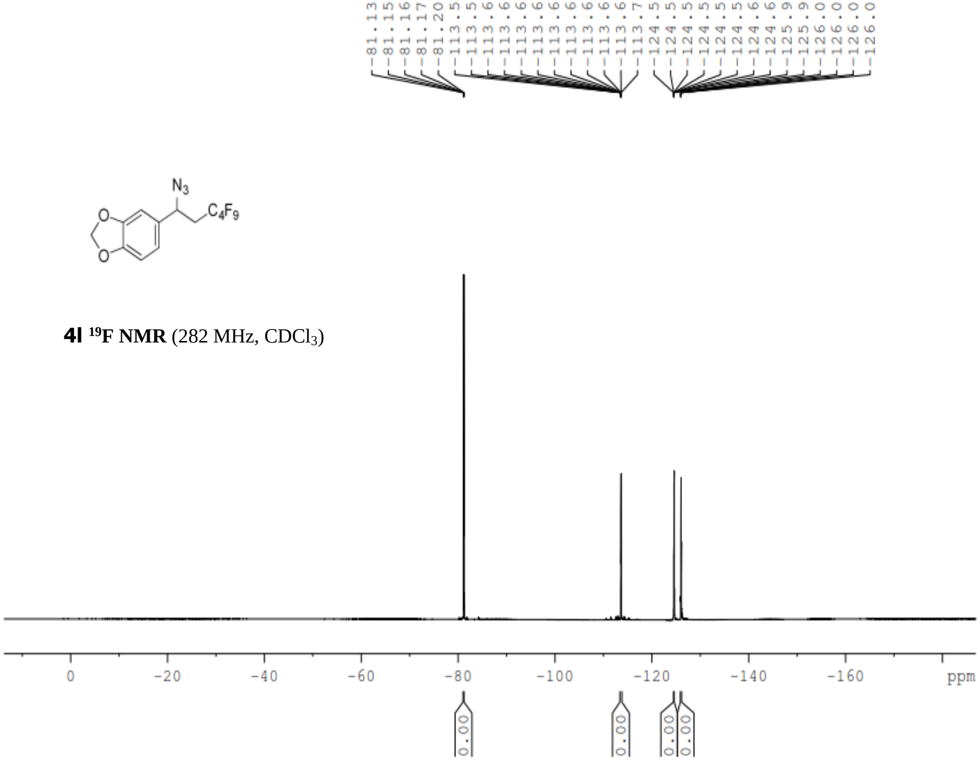
4k ^{19}**F NMR** (282 MHz, CDCl$_3$)



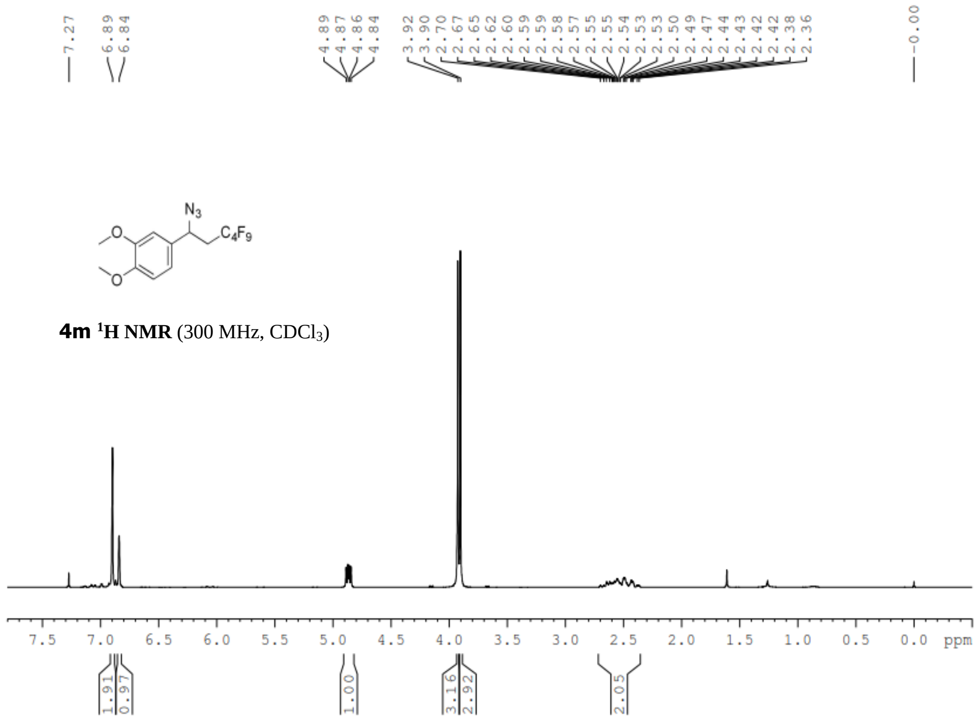
4l ^{1}**H NMR** (300 MHz, CDCl$_3$)



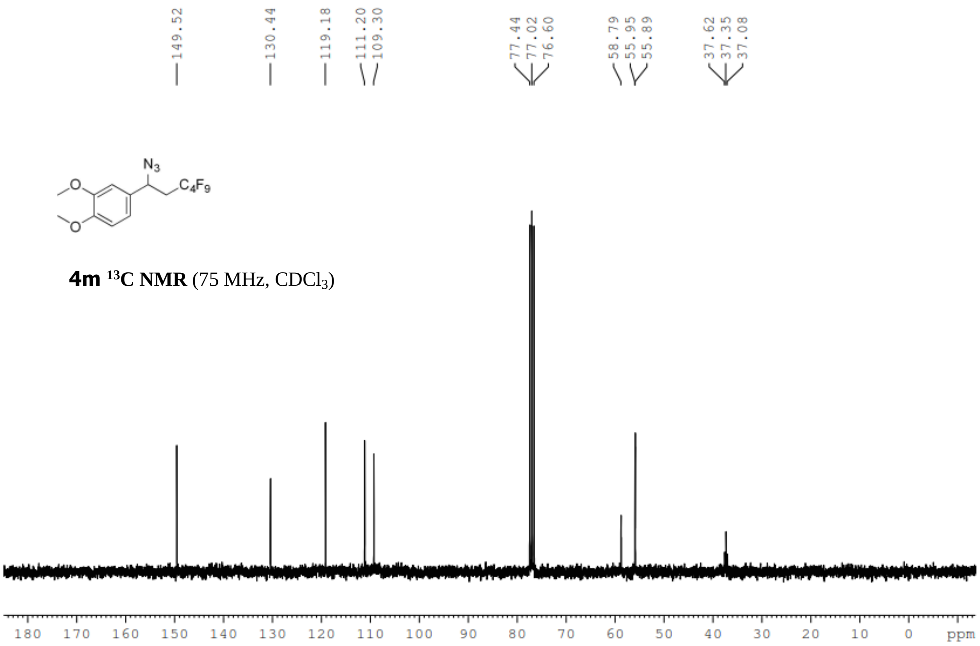
4l ^{13}**C NMR** (75 MHz, CDCl$_3$)



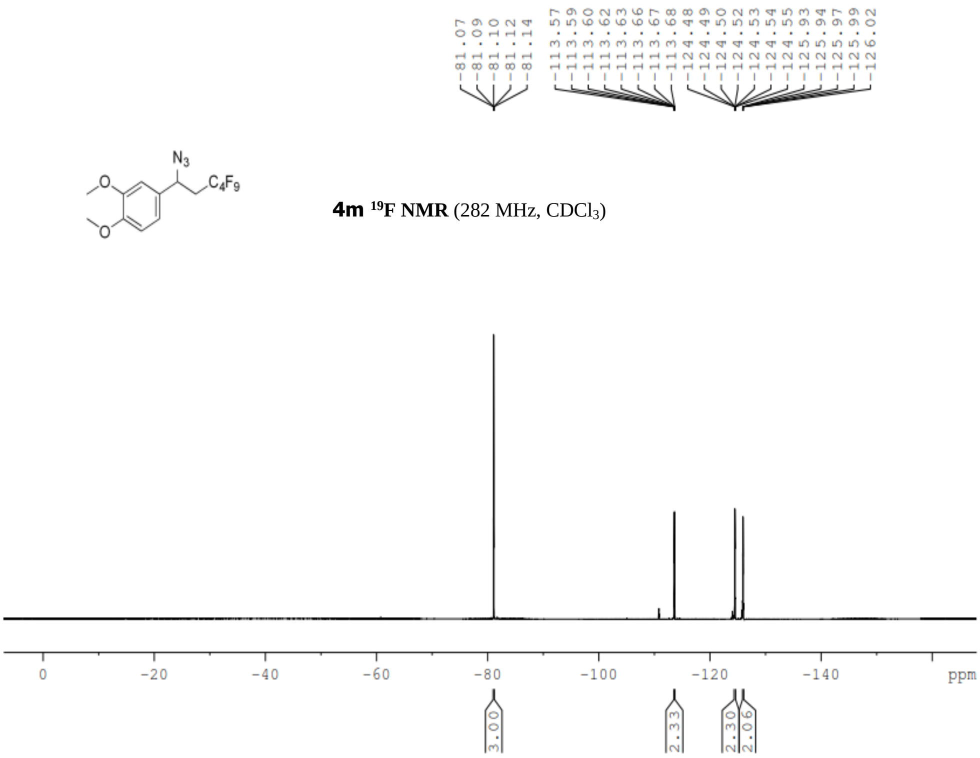
4l ^{19}**F NMR** (282 MHz, CDCl$_3$)



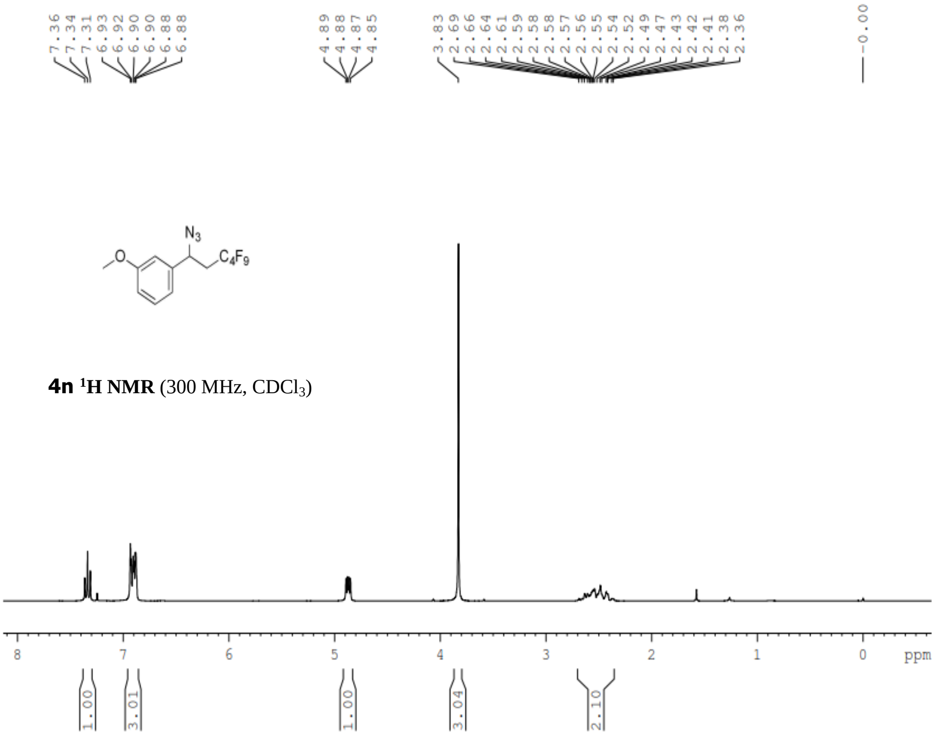
4m ^{1}**H NMR** (300 MHz, $CDCl_3$)



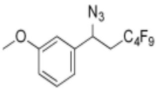
4m ^{13}**C NMR** (75 MHz, $CDCl_3$)



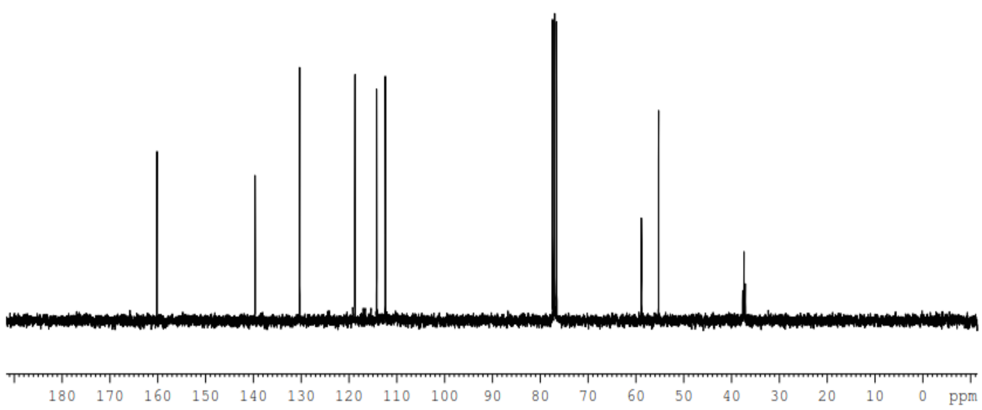
4m ^{19}**F NMR** (282 MHz, $CDCl_3$)

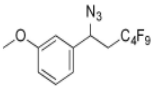


4n ^{1}**H NMR** (300 MHz, $CDCl_3$)

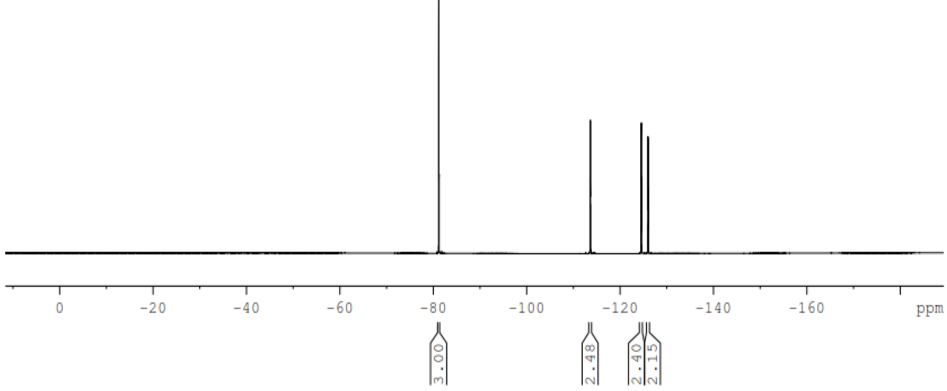


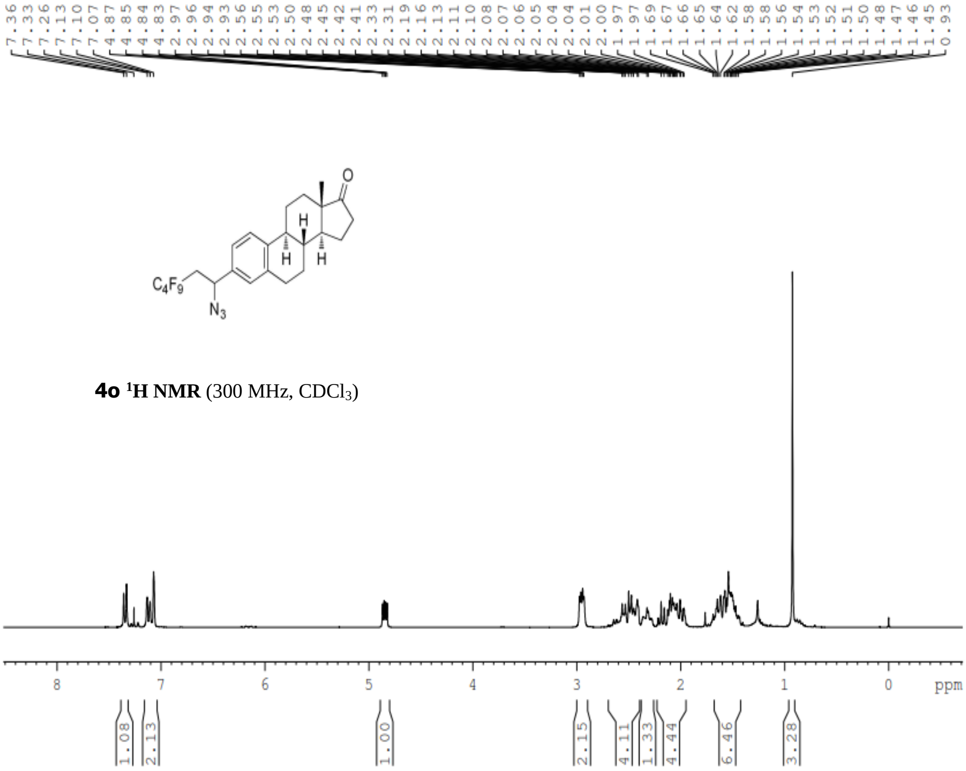
4n **^{13}C NMR** (75 MHz, $CDCl_3$)



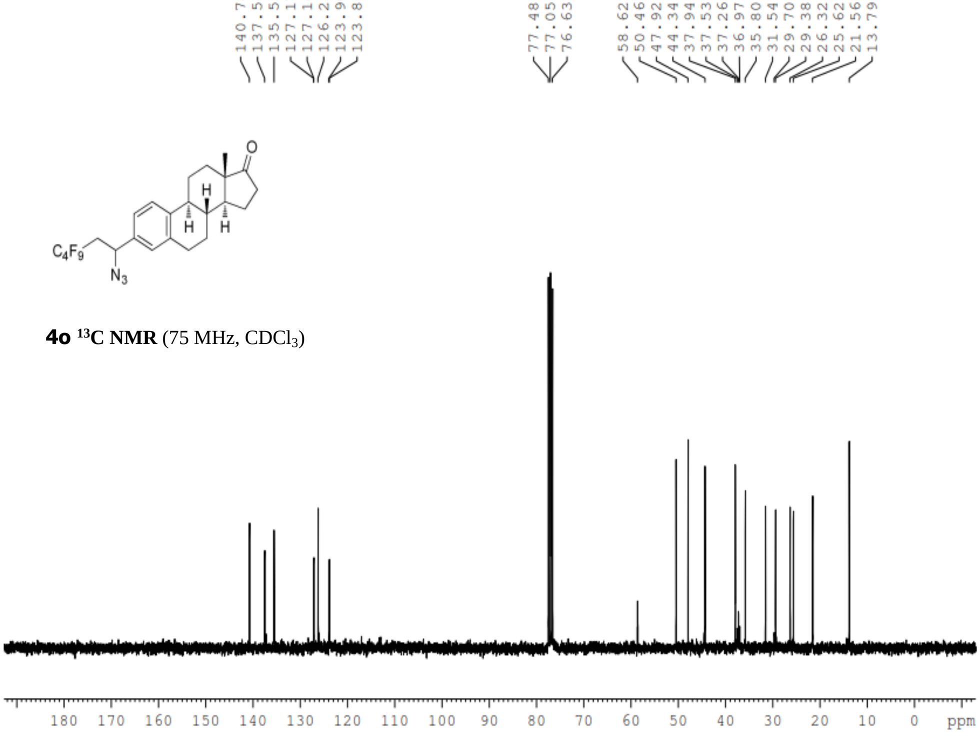


4n **^{19}F NMR** (282 MHz, $CDCl_3$)

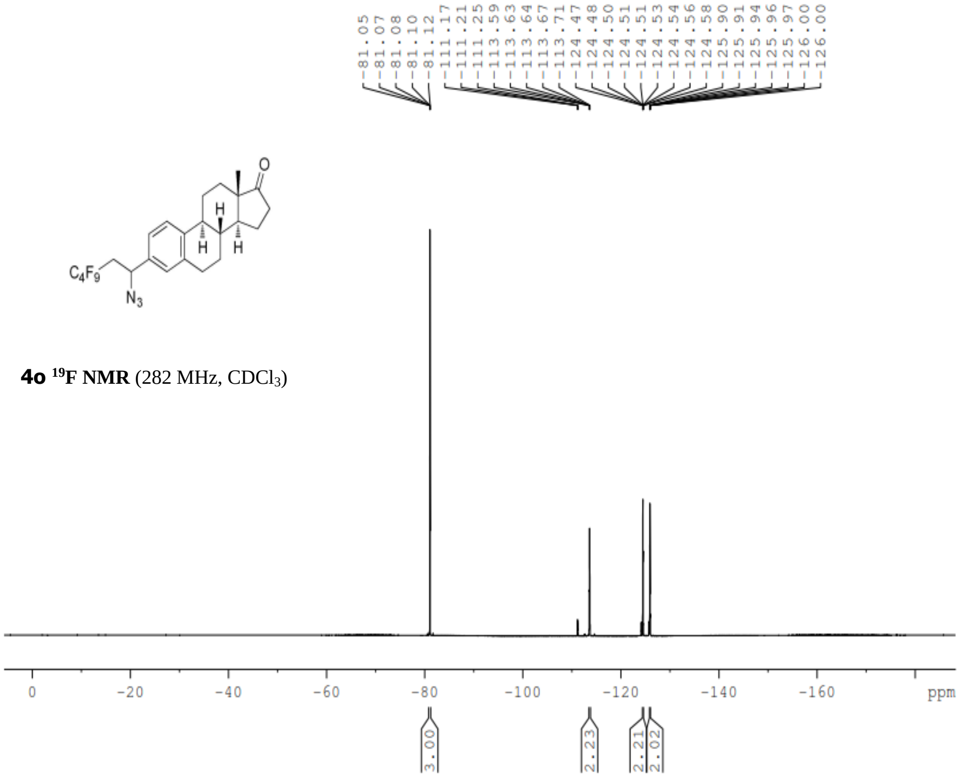




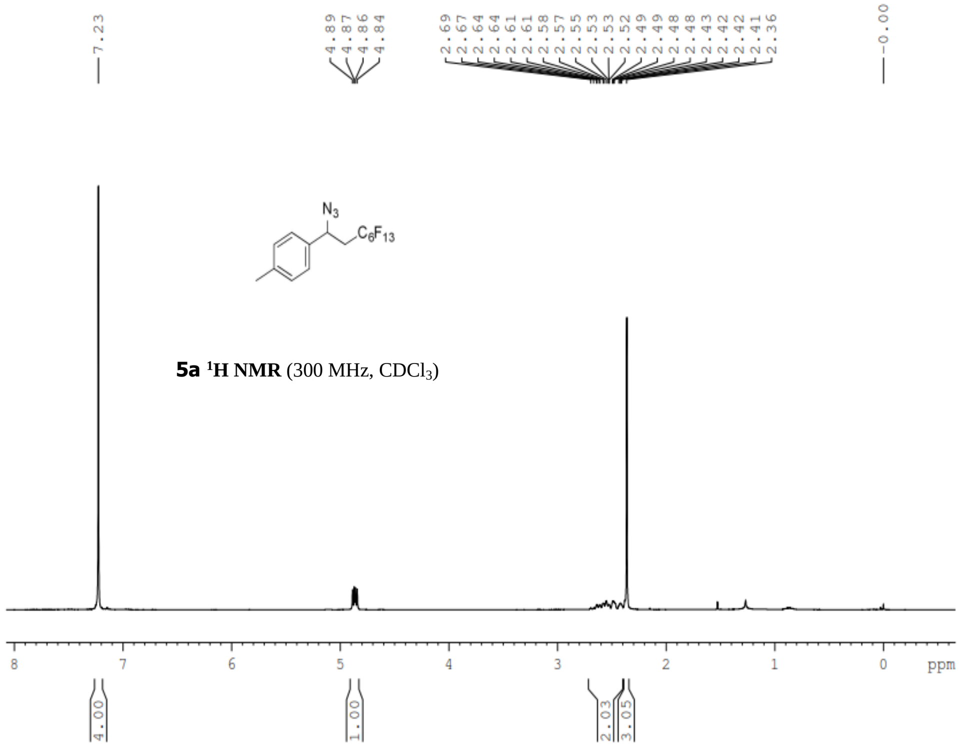
4o **^{1}H NMR** (300 MHz, $CDCl_3$)



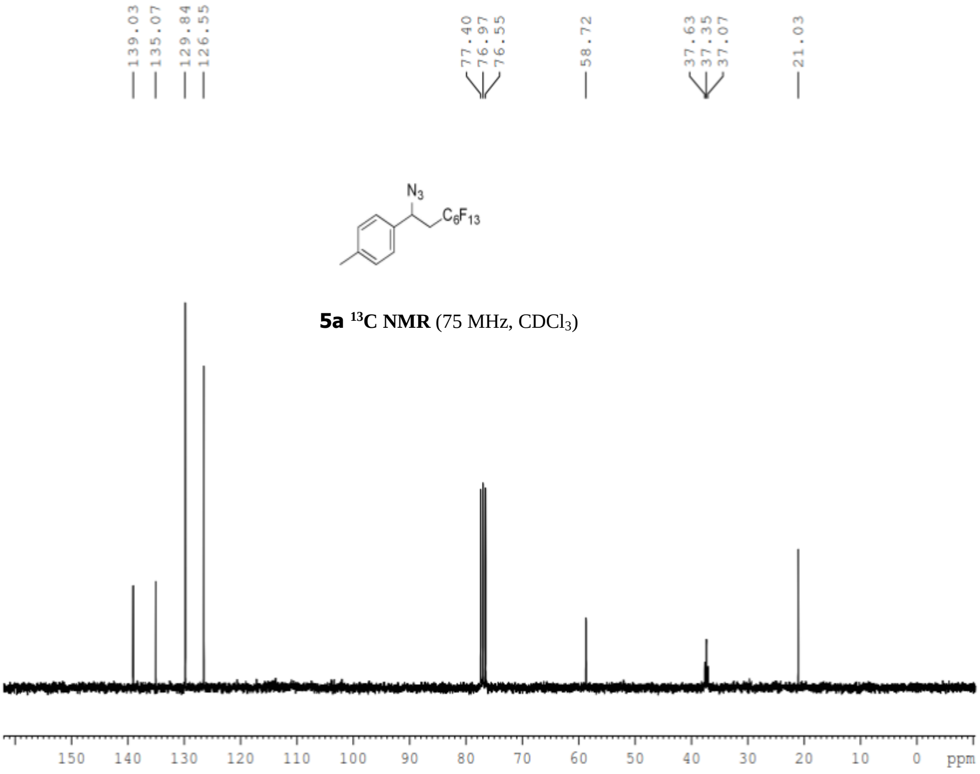
4o **^{13}C NMR** (75 MHz, $CDCl_3$)



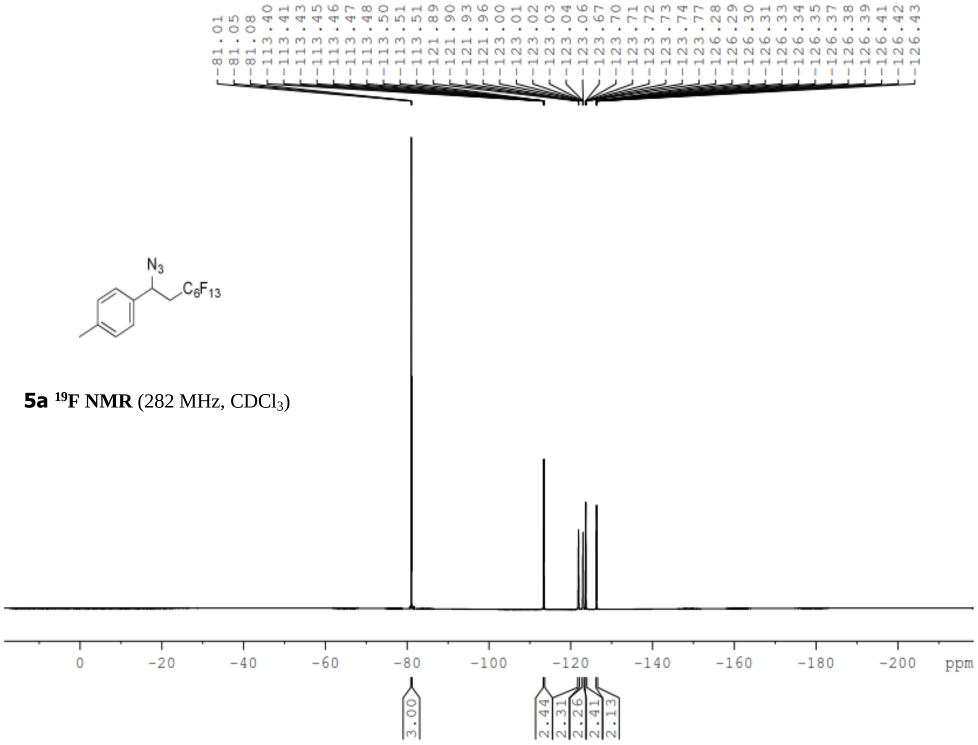
4o ^{19}**F NMR** (282 MHz, $CDCl_3$)



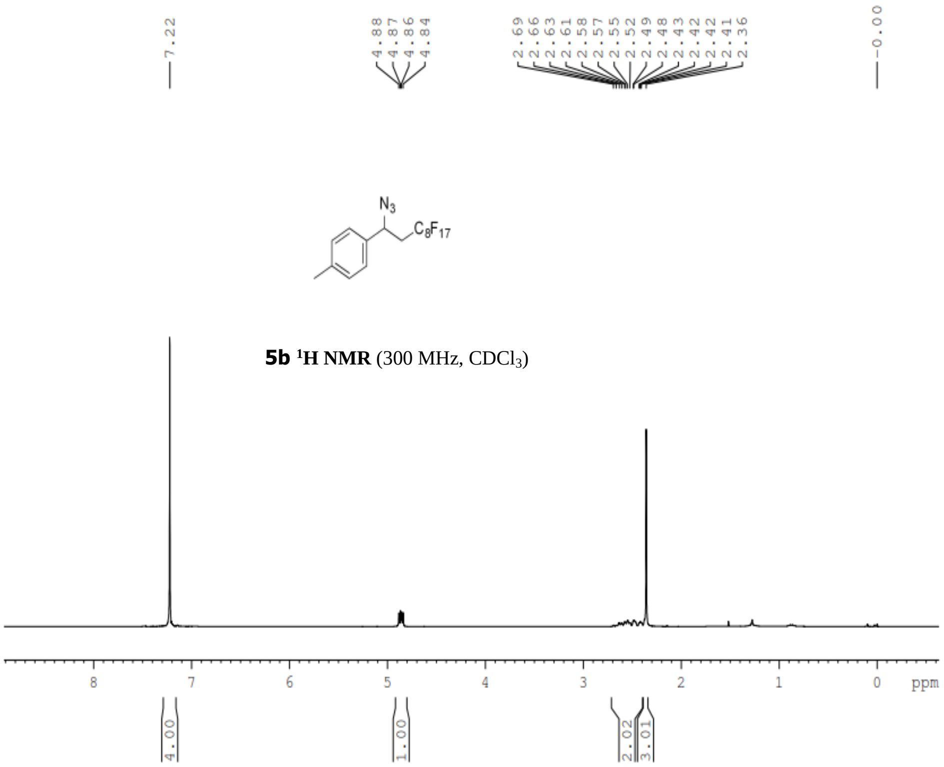
5a ^{1}**H NMR** (300 MHz, $CDCl_3$)



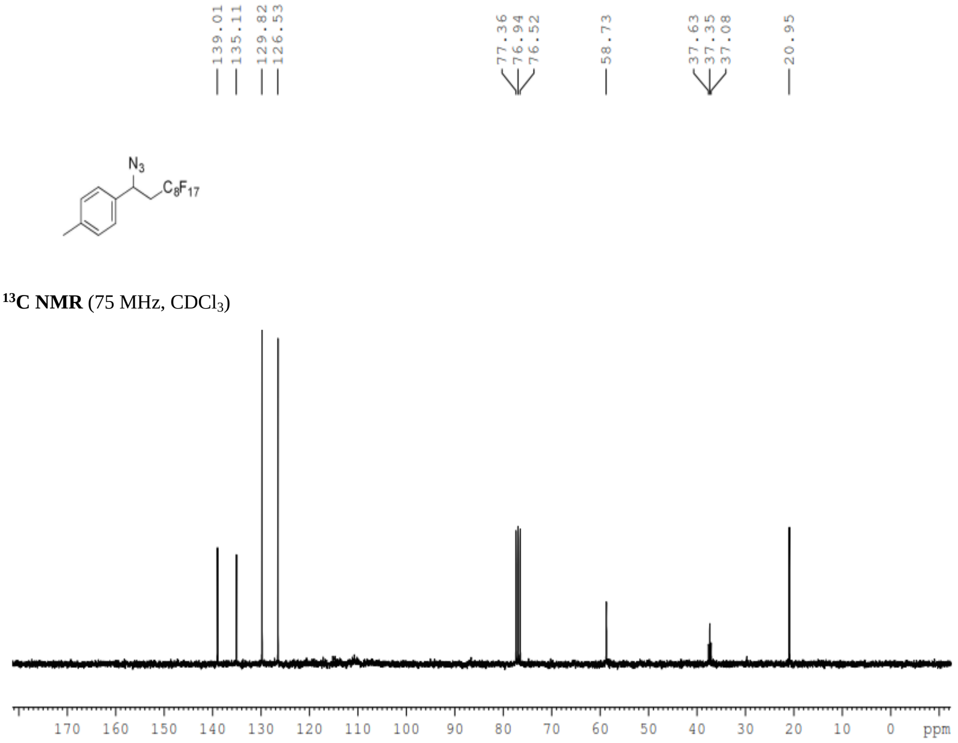
5a **^{13}C NMR** (75 MHz, CDCl$_3$)



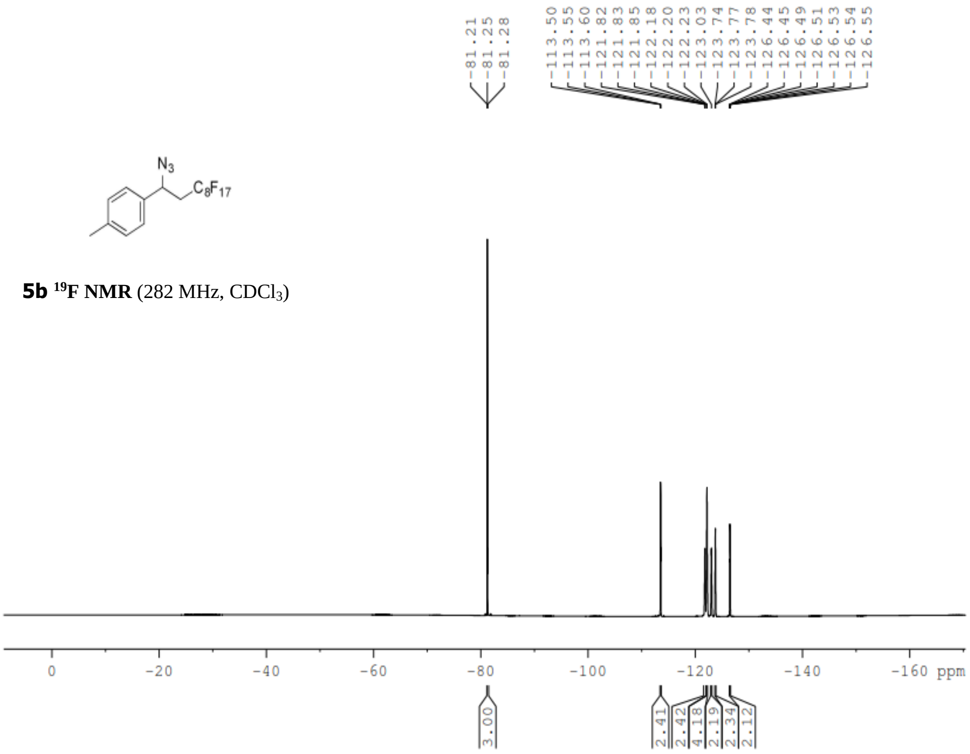
5a **^{19}F NMR** (282 MHz, CDCl$_3$)



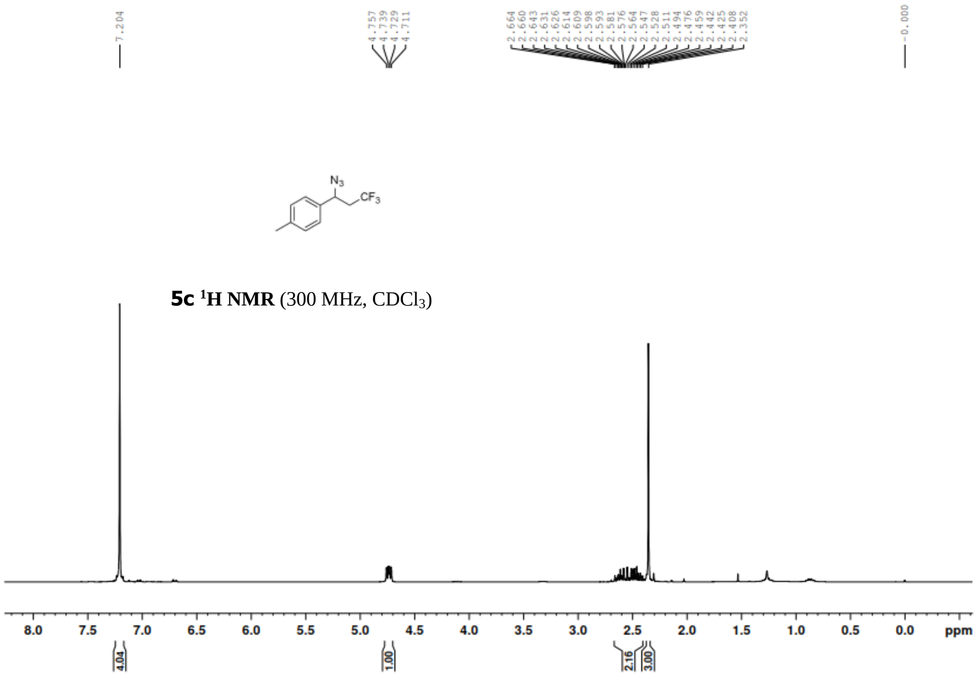
5b ^{1}**H NMR** (300 MHz, $CDCl_3$)



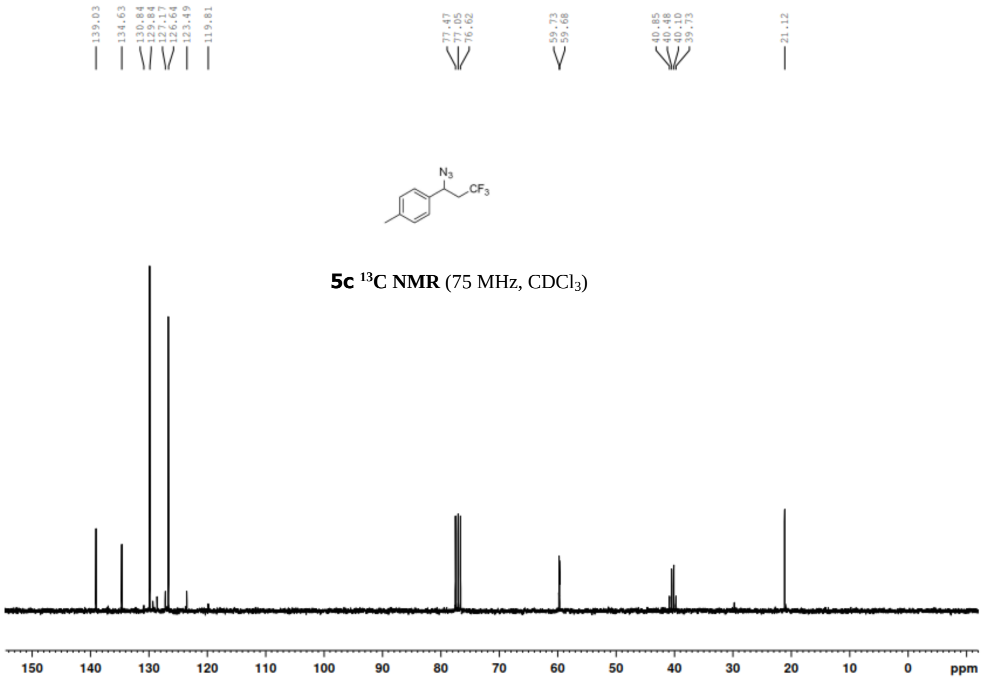
5b ^{13}**C NMR** (75 MHz, $CDCl_3$)



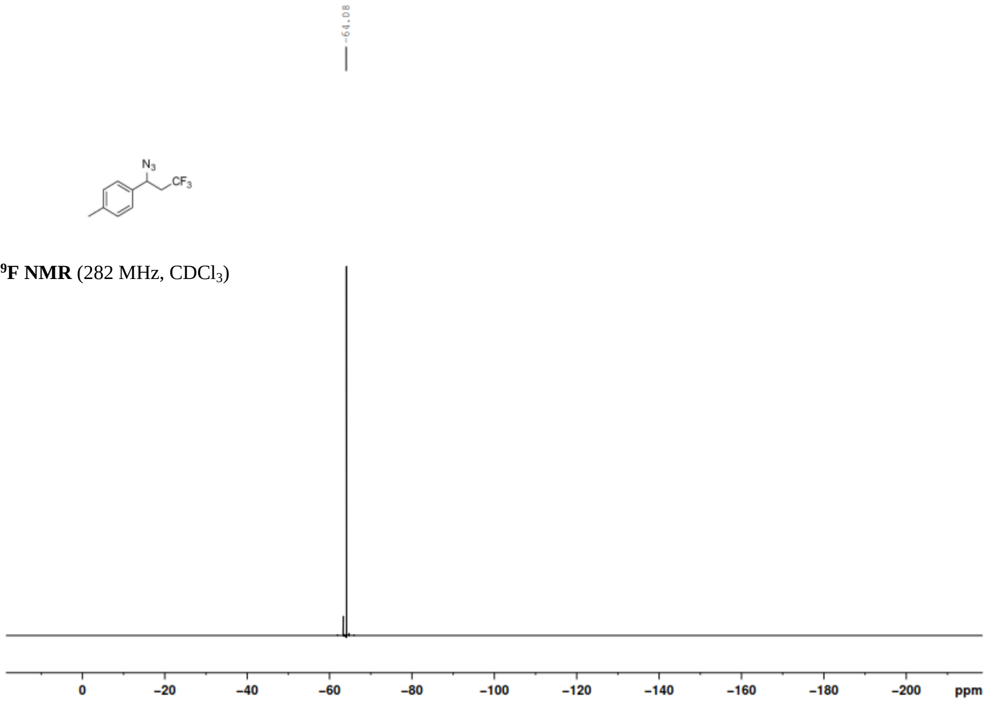
5b **^{19}F NMR** (282 MHz, $CDCl_3$)



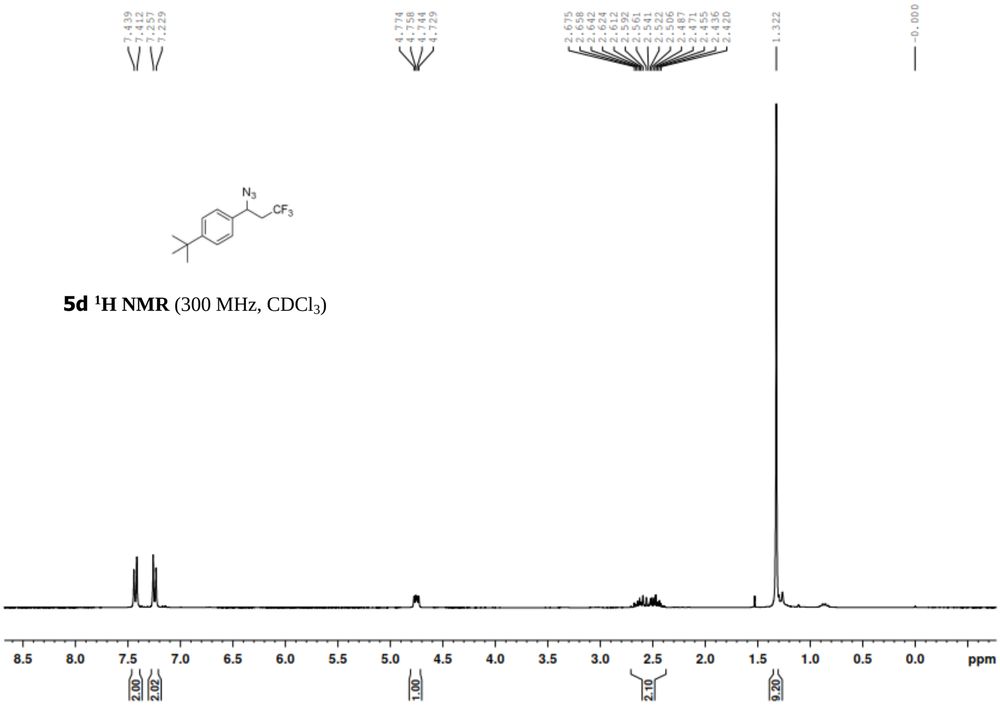
5c **^{1}H NMR** (300 MHz, $CDCl_3$)



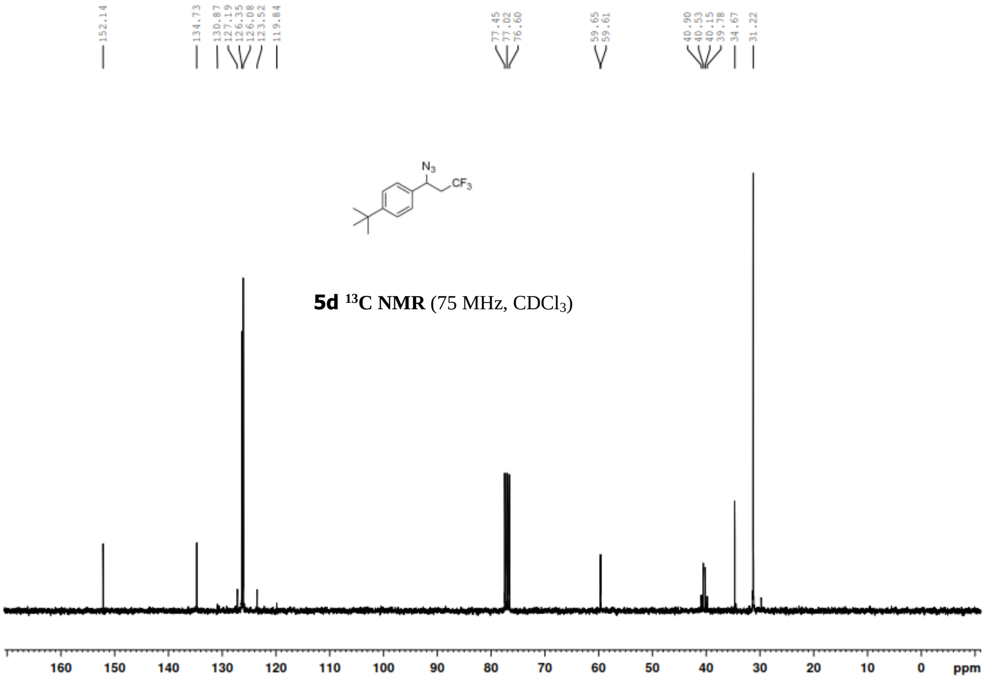
5c ^{13}**C NMR** (75 MHz, $CDCl_3$)



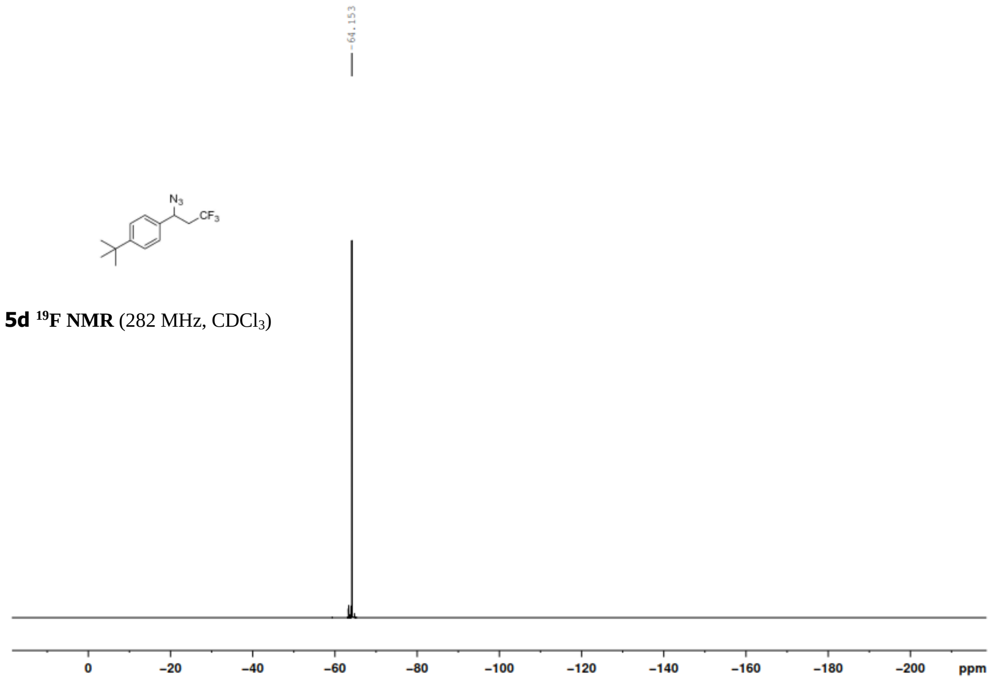
5c ^{19}**F NMR** (282 MHz, $CDCl_3$)



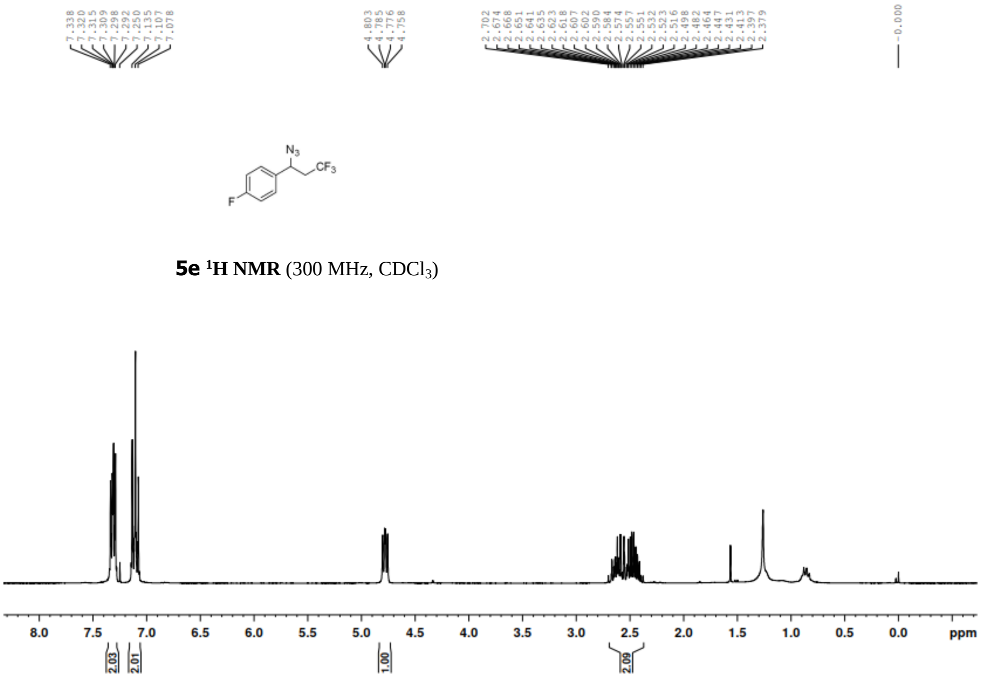
5d **^{1}H NMR** (300 MHz, $CDCl_3$)



5d **^{13}C NMR** (75 MHz, $CDCl_3$)



5d ^{19}**F NMR** (282 MHz, $CDCl_3$)



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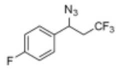
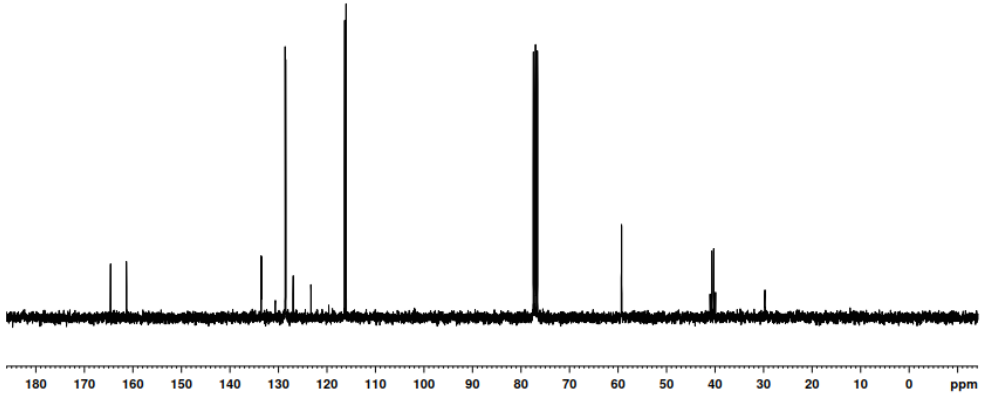
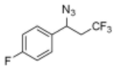
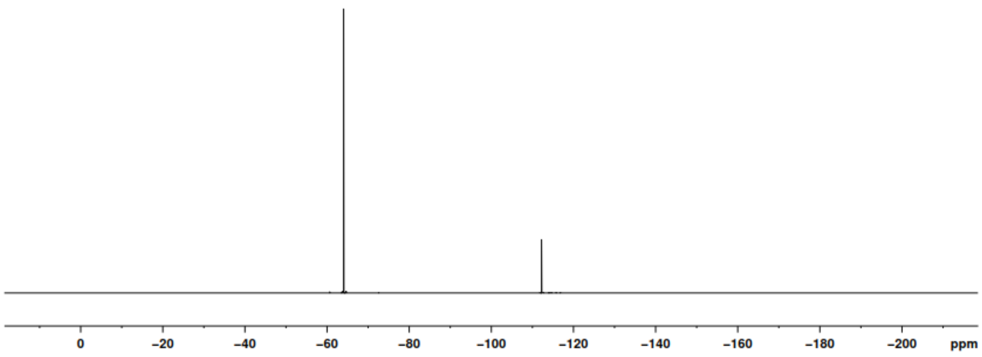


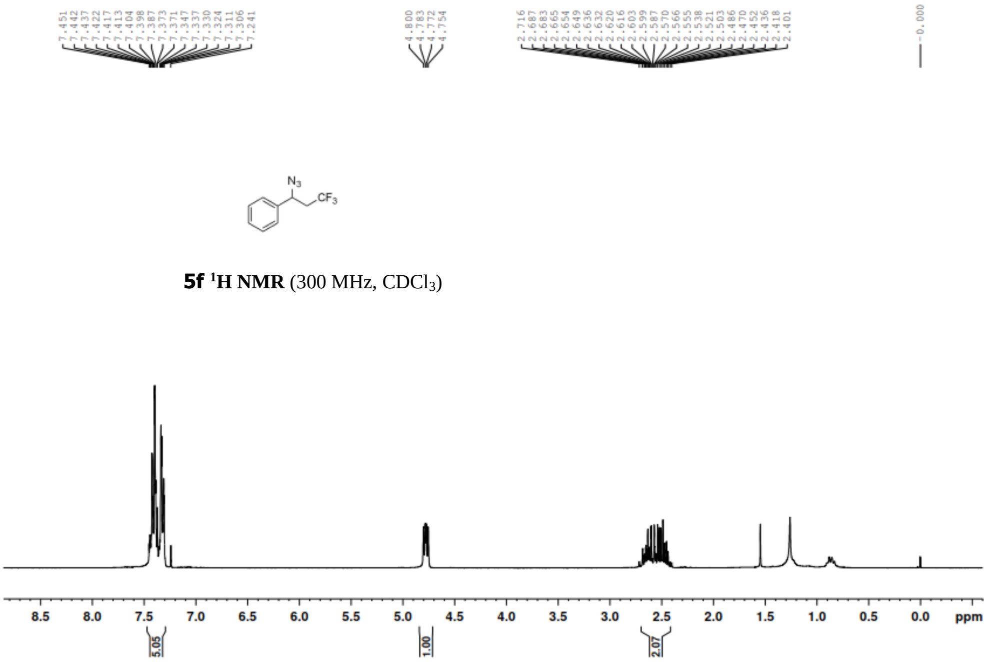
5e ^{13}**C NMR** (75 MHz, $CDCl_3$)



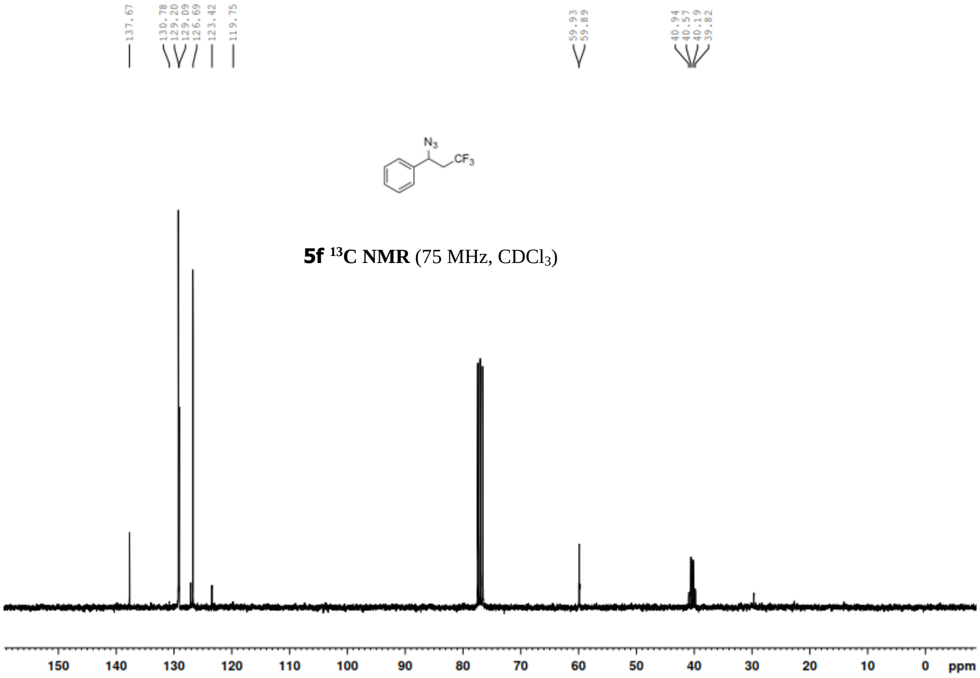


5e ^{19}**F NMR** (282 MHz, $CDCl_3$)

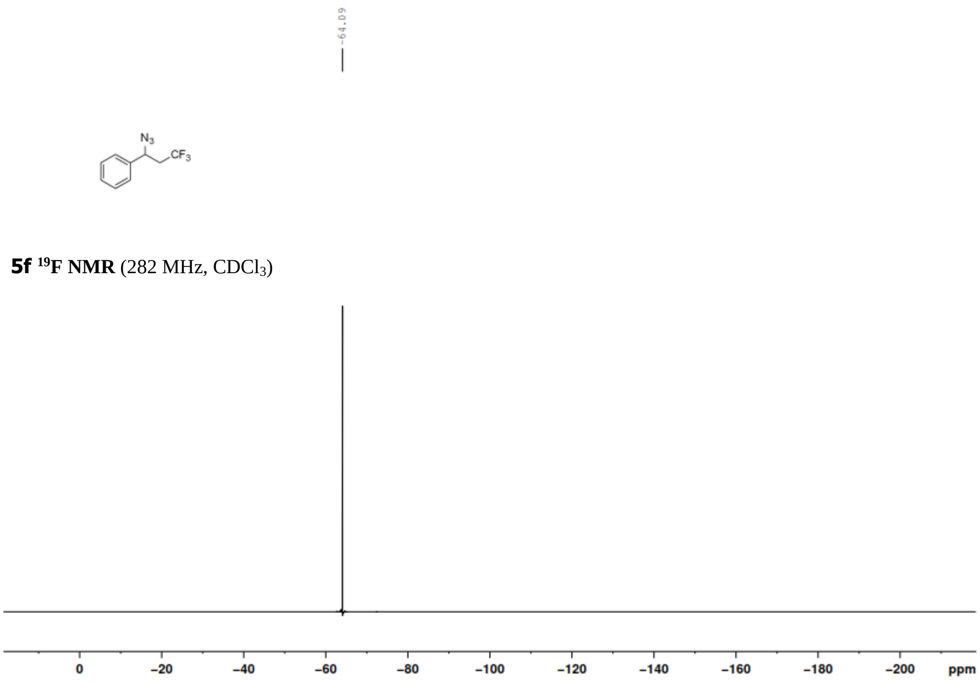




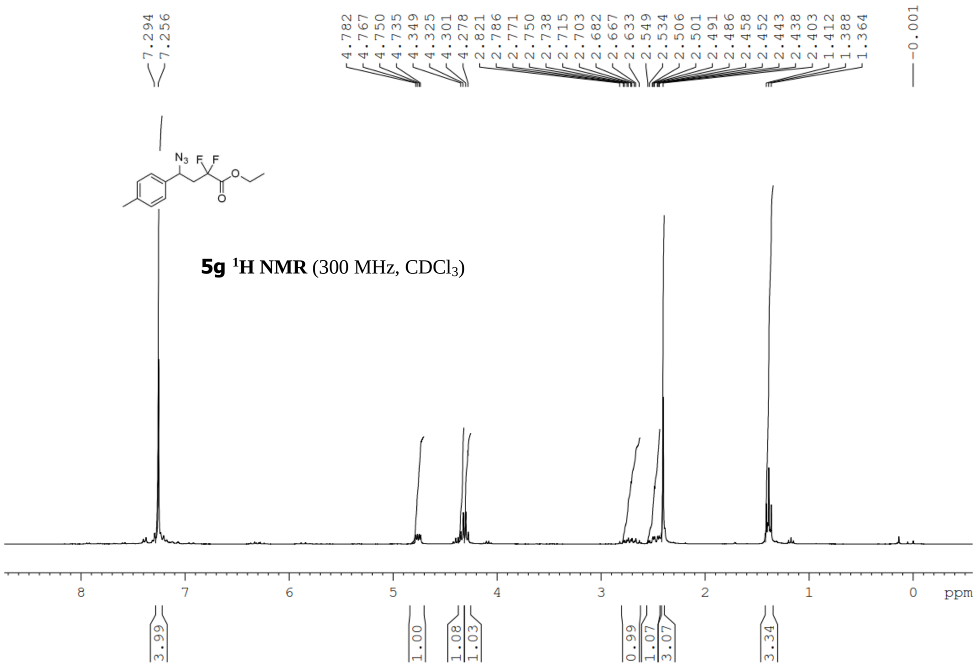
5f ^{1}**H NMR** (300 MHz, $CDCl_3$)



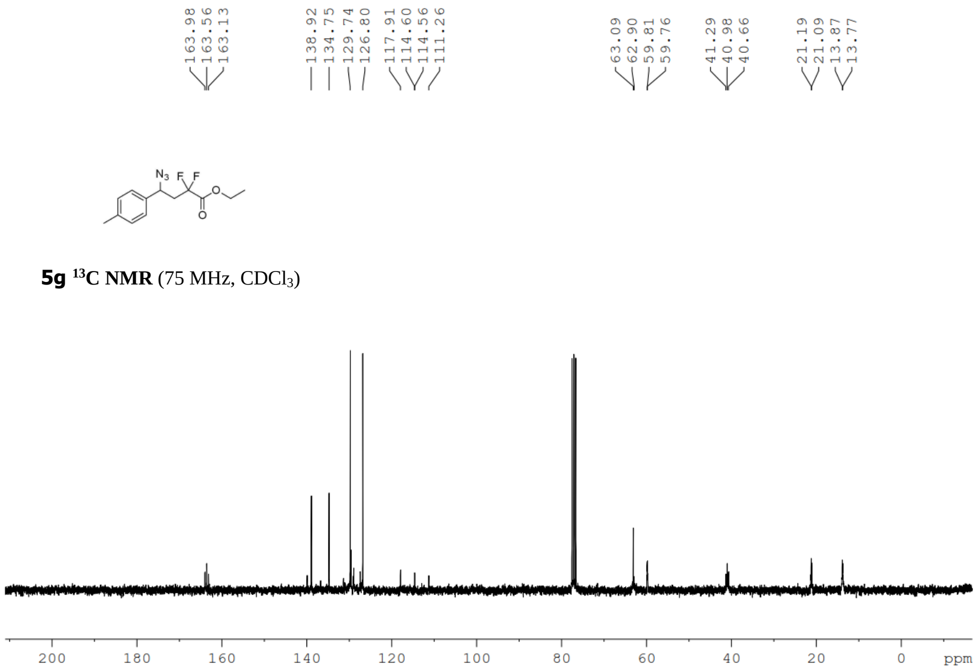
5f ^{13}**C NMR** (75 MHz, $CDCl_3$)



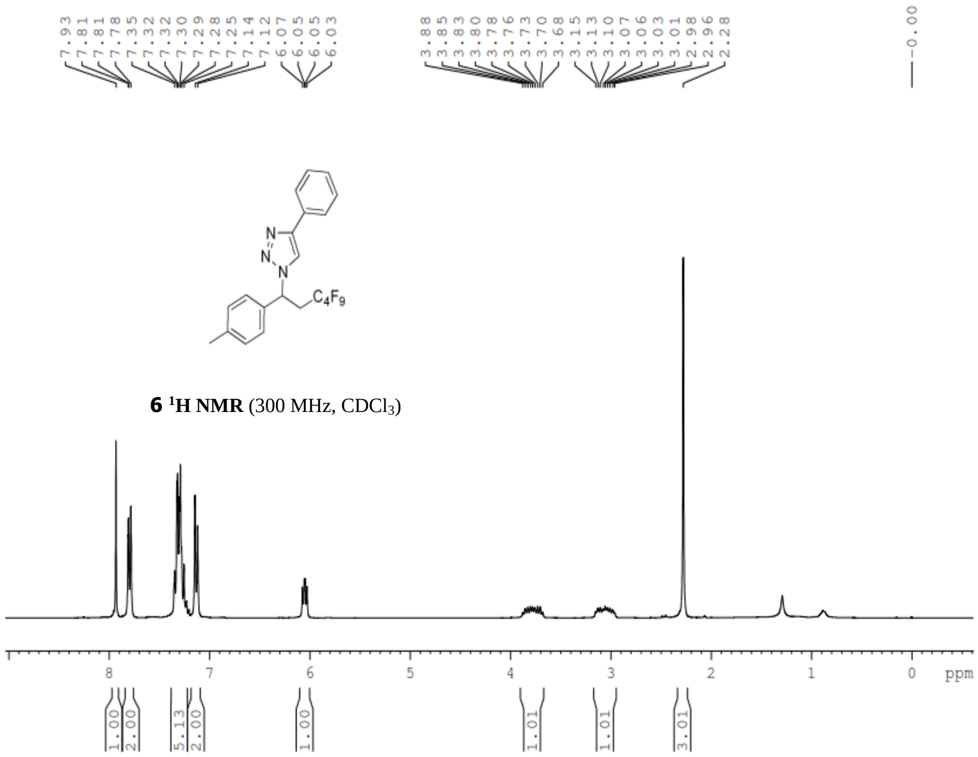
5f ^{19}**F NMR** (282 MHz, $CDCl_3$)



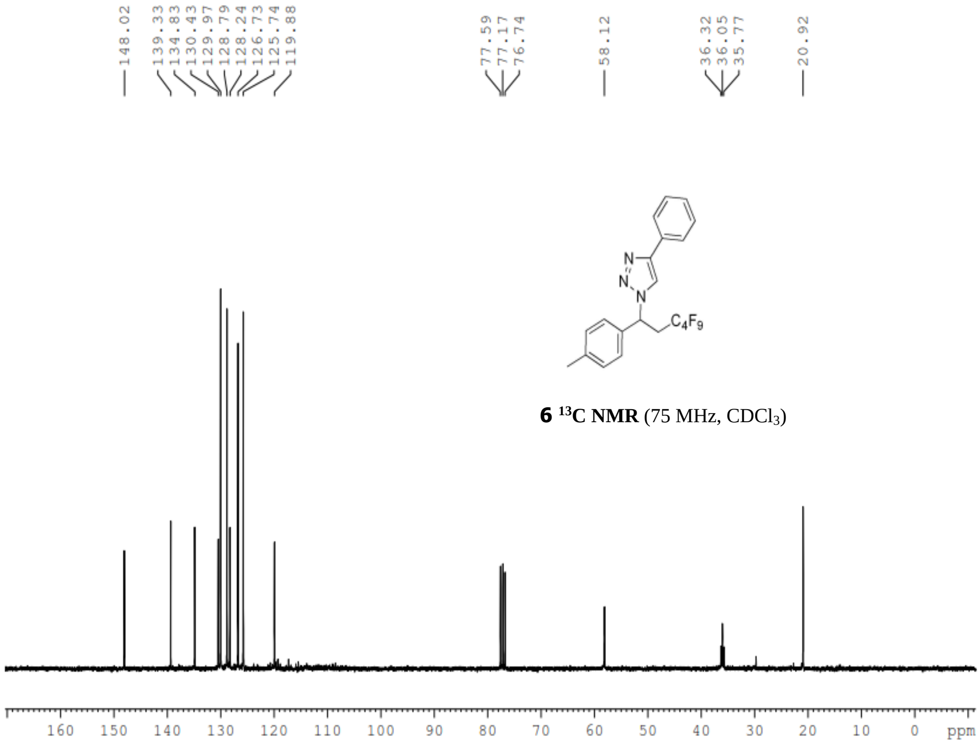
5g ^{1}**H NMR** (300 MHz, $CDCl_3$)



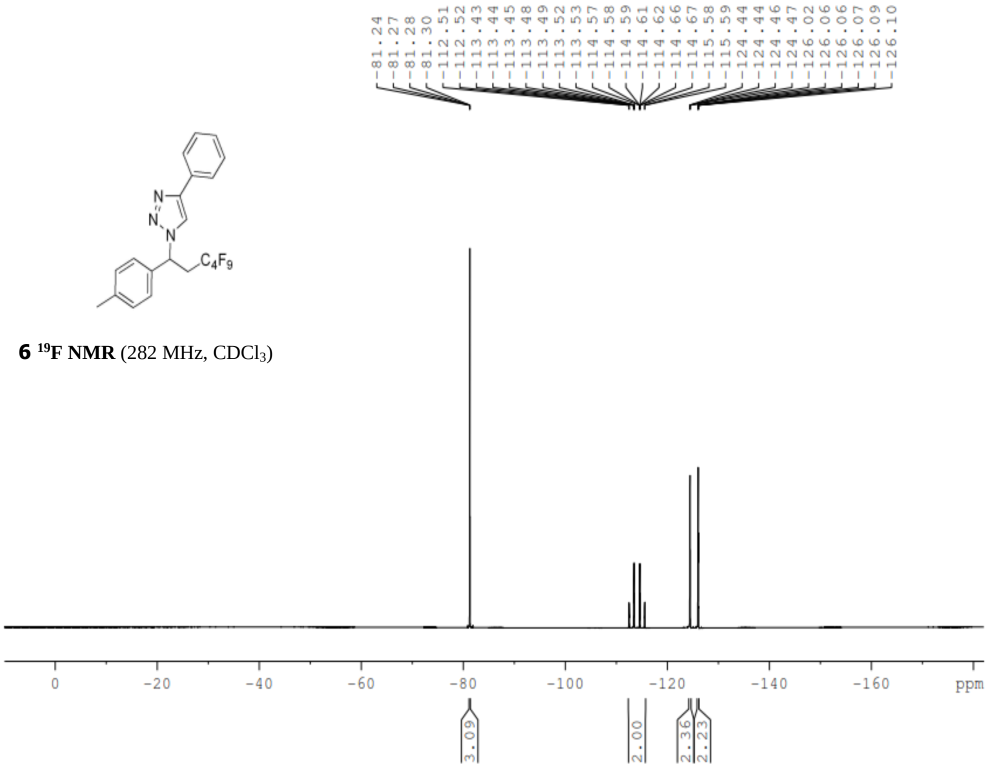
5g **^{13}C NMR** (75 MHz, CDCl$_3$)



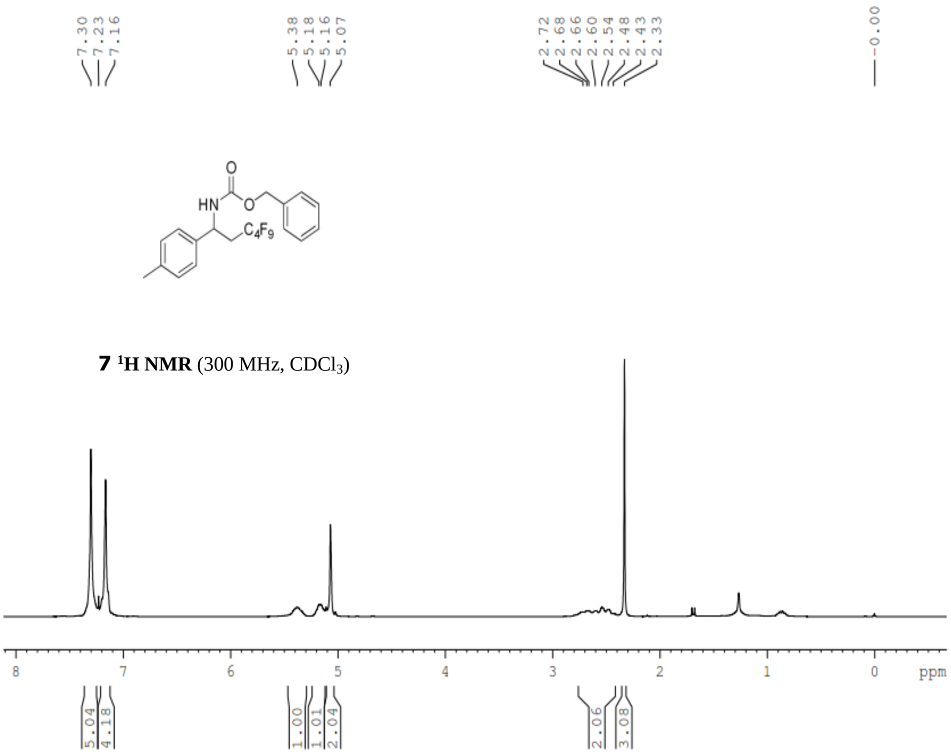
6 **^{1}H NMR** (300 MHz, CDCl$_3$)



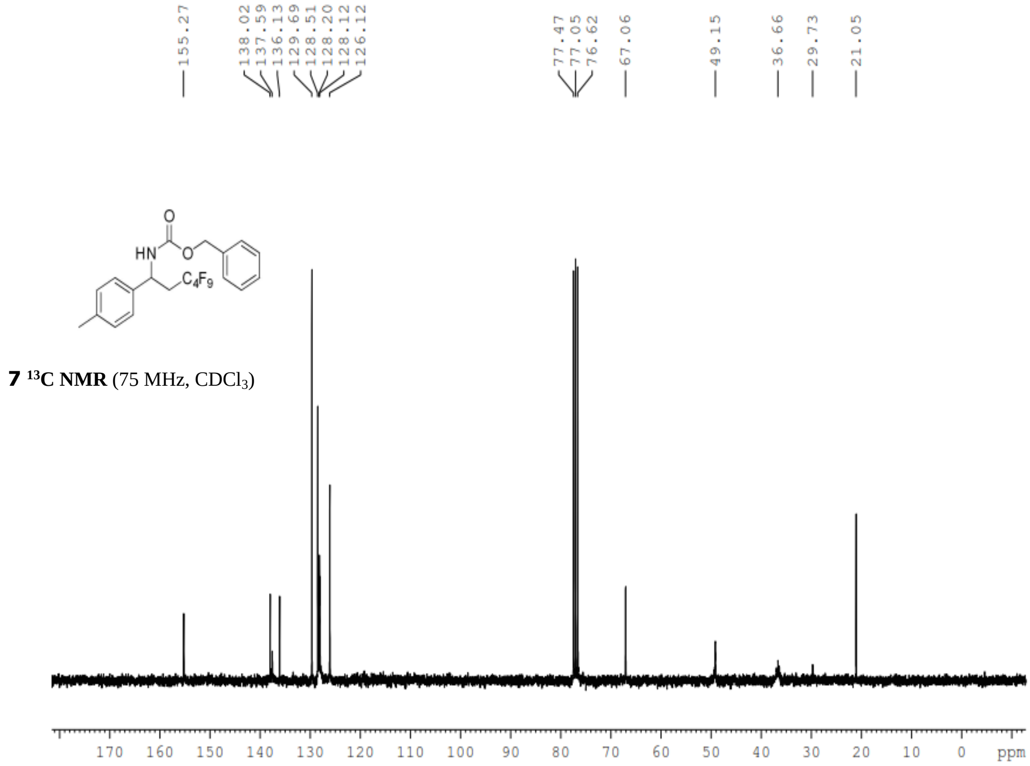
6 **^{13}C NMR** (75 MHz, CDCl$_3$)



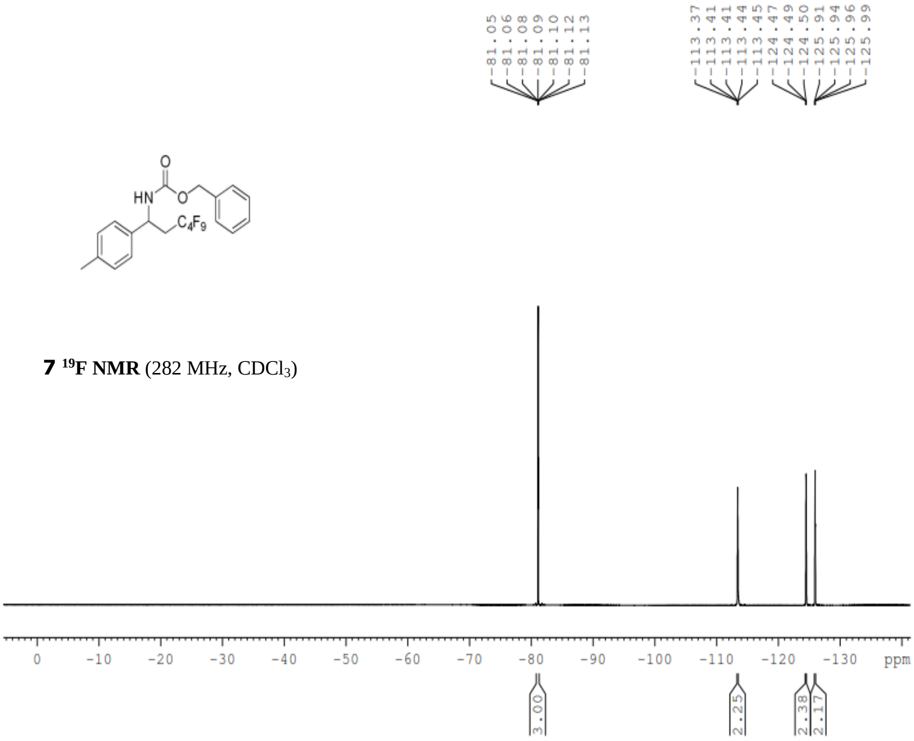
6 **^{19}F NMR** (282 MHz, CDCl$_3$)



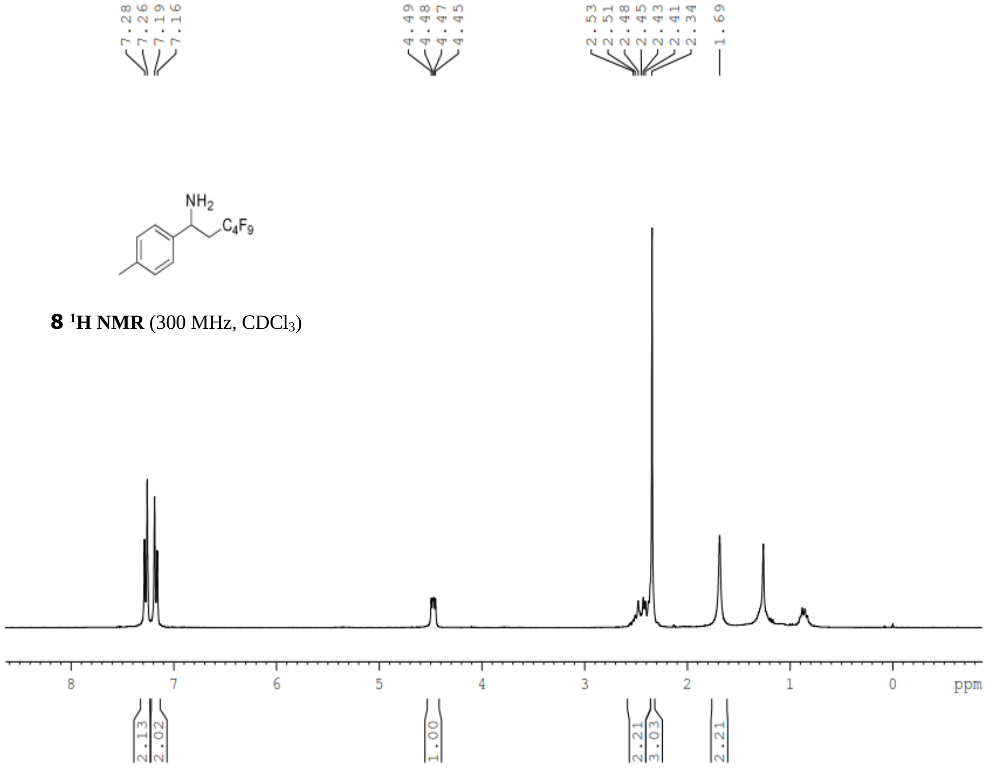
7 **^{1}H NMR** (300 MHz, $CDCl_3$)



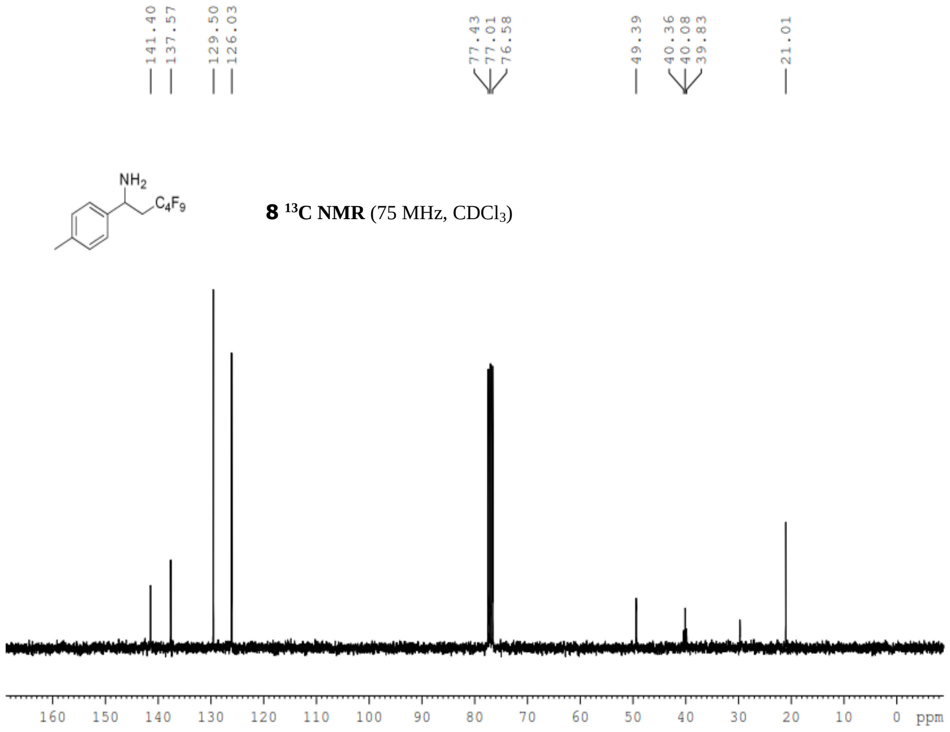
7 **^{13}C NMR** (75 MHz, $CDCl_3$)



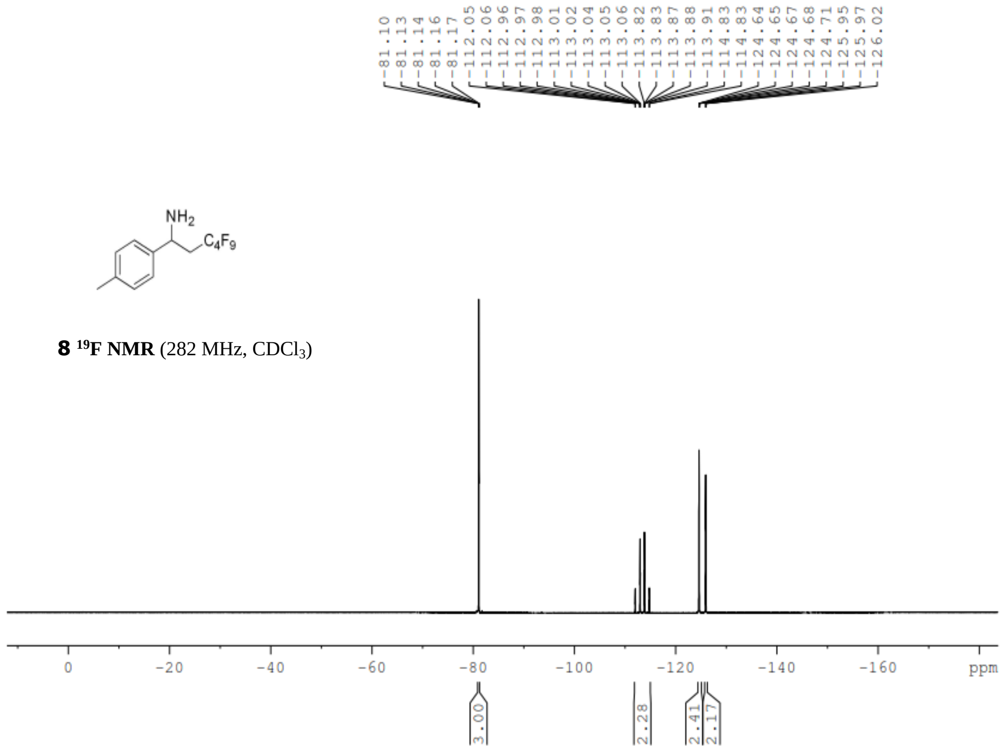
7 **^{19}F NMR** (282 MHz, CDCl$_3$)



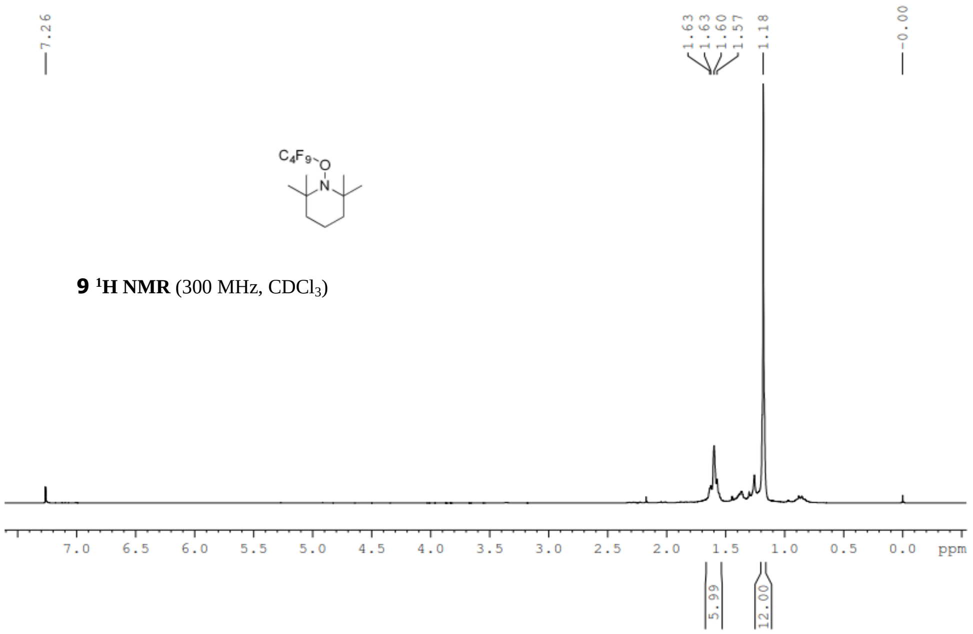
8 **^{1}H NMR** (300 MHz, CDCl$_3$)



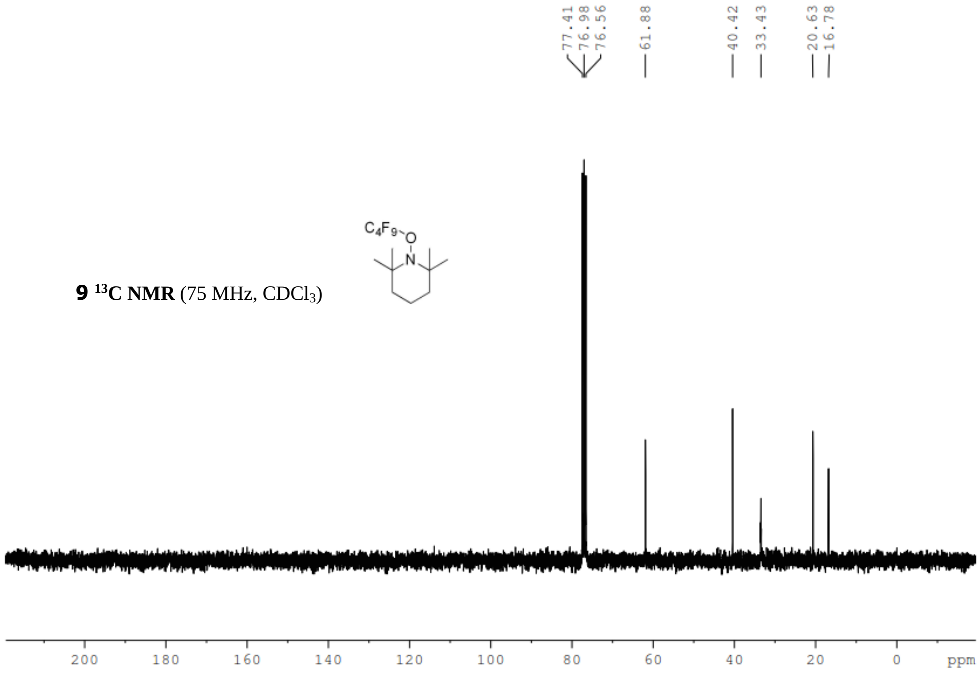
8 **^{13}C NMR** (75 MHz, $CDCl_3$)



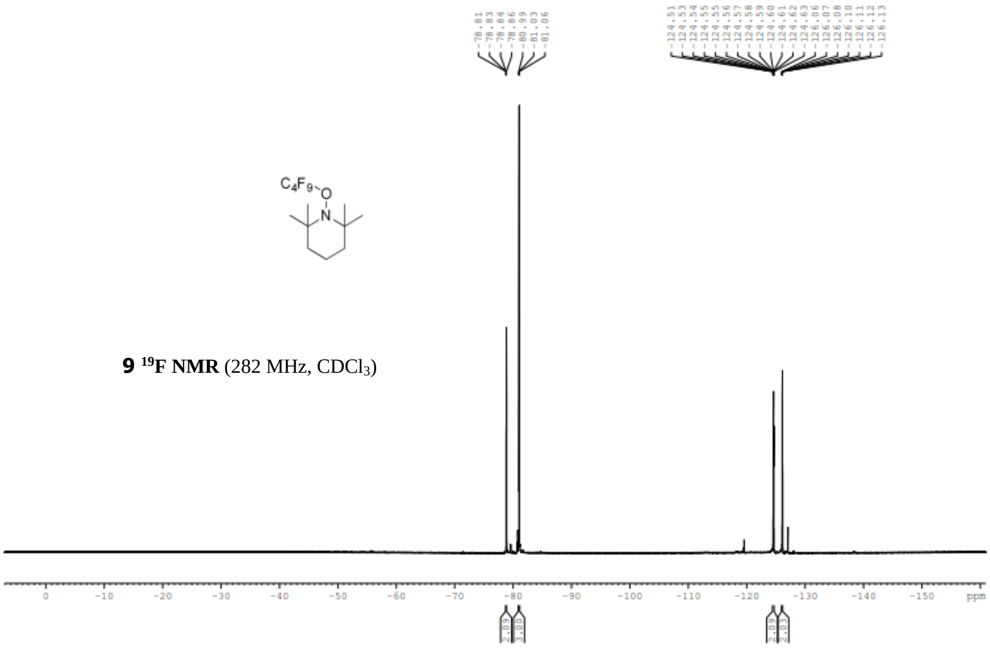
8 **^{19}F NMR** (282 MHz, $CDCl_3$)



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



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



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