Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Aza-Wolff Rearrangement of *N*-Fluoroalkyl Triazoles to Ketenimines

Anna Kubíčková[a,b] Athanasios Markos,[a] Svatava Voltrová,[a] Anežka Marková,[a] Josef Filgas,[b] Blanka Klepetářová,[a] Petr Slavíček[b] and Petr Beier*[a]

[a] A. Kubíčková, Dr. A. Markos, Dr. S. Voltrová, A. Marková, Dr. B. Klepetářová, Dr. P. Beier
The Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences
Flemingovo nam. 2, 16610 Prague 6 (Czech Republic)
E-mail: beier@uochb.cas.cz

[b] A. Kubíčková, J. Filgas, Prof. P. Slavíček
University of Chemistry and Technology,
Technická 5, 166 28 Prague 6 (Czech Republic)

Contents

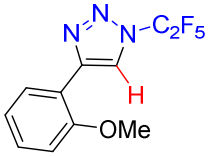
1 General information

All commercially available chemicals were used as received unless stated otherwise, column chromatography was performed using silica gel 60 (0.040–0.063 mm). Automated flash column chromatography was performed on Teledyne ISCO CombiFlash Rf+ Lumen Automated Flash Chromatography System with UV/Vis detection. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured at ambient temperature using 5 mm diameter NMR tubes. ^{13}C NMR spectra were proton decoupled. The chemical shift values (δ) are reported in ppm relative to internal Me_4Si (0 ppm for ^{1}H and ^{13}C NMR) or residual solvents and internal $CFCl_3$ (0 ppm for ^{19}F NMR). Coupling constants (*J*) are reported in Hertz. Structural elucidation was aided by additional acquisition of ^{13}C APT, 1D ^{1}H NOESY and/or various 2D spectra (^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{13}C-^{19}F HMBC, ^{1}H-^{1}H ROESY). High resolution mass spectra (HRMS) were recorded on a Waters Micromass AutoSpec Ultima or Agilent 7890A GC coupled with Waters GCT Premier orthogonal acceleration time-of-flight detector using electron impact (EI) ionization, on an LTQ Orbitrap XL using electrospray ionization (ESI), and on a Bruker solariX 94 ESI/MALDI-FT-ICR using dual ESI/MALDI ionization. Microwave experiments were done on CEM Focused Microwave™ Synthesis System, Model Discover. The method was set-up to 300 W, temperature 140-160 °C, hold time 20-180 min. LRMS spectra were recorded on Agilent 7890A GC (column HP-5MS, 30 m × 0.25 mm × 0.25 μm, 5% phenyl methylpolysiloxane) coupled with 5975C quadrupole mass selective electron impact (EI) detector (70 eV). IR spectra ($CHCl_3$ film) were measured on Bruker IFS 55 Equinox or Bruker Alpha-P spectrometer.

2 Synthesis of starting triazoles **1**

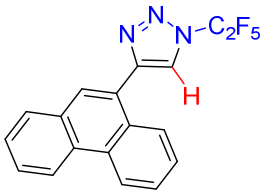
5-Unsubstituted triazoles **1d**, **1i**, **1k**, **1m**, **1q, 1t, 1u, 1v** were prepared according to literature. [1]

*4-(2-Methoxyphenyl)-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1d**):* Yield: 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



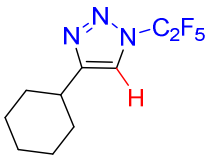
8.41 (s, 1H), 8.39 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.39 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 7.02 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 144.2, 130.3, 128.2, 121.3, 121.0, 117.5, 117.2 (qt, *J* = 287.5, 41.5 Hz), 111.0, 110.4 (tq, *J* = 270.0, 42.9 Hz), 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.3 (s, 3F), -99.1 (s, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_9OF_5N_3$: 294.06603, found 294.06600.

*1-(Pentafluoroethyl)-4-(phenanthren-9-yl)-1H-1,2,3-triazole (**1i**):* Yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



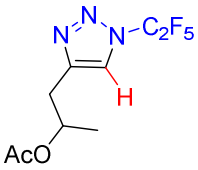
8.79 (d, *J* = 8.3 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.26 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.03 (s, 1H), 7.93 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.79–7.57 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.02, 131.03, 130.92, 130.89, 129.73, 129.58, 129.17, 127.89, 127.37, 127.26, 127.22, 125.71, 124.68, 123.32, 122.78, 121.21, 117.25 (qt, *J* = 287.5, 82.4 Hz), 110.50 (tq, *J* = 270.1, 43.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.19, -98.83; HRMS (APCI$^+$) *m/z* calcd for $C_{18}H_{11}F_5N_3$: 364.08676, found 364.08707.

*4-Cyclohexyl-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1k**):* Yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s,



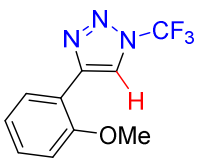
1H), 2.87-2.74 (m, 1H), 2.09-2.05 (m, 2H), 1.83-1.80 (m, 2H), 1.74 (d, *J* = 13.0 Hz, 1H), 1.48-1.36 (m, 4H), 1.32-1.21 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 118.0, 117.2 (qt, *J* = 287.5, 41.6 Hz), 110.3 (tq, *J* = 269.9, 43.0 Hz), 35.1, 32.7, 26.0, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.4 (s, 3F), -98.9 (s, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{13}F_5N_3$: 270.10241, found 270.10248.

*1-(Pentafluoroethyl)-1H-1,2,3-triazol-4-yl)propan-2-yl acetate (**1m**):* Yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$)



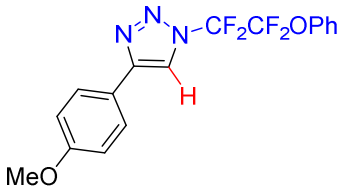
δ 7.75 (s, 1H), 5.18 (h, *J* = 6.3 Hz, 1H), 3.05 (d, *J* = 6.1 Hz, 2H), 1.98 (s, 3H), 1.28 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.40, 145.08, 120.57, 117.08 (qt, *J* = 287.3, 41.4 Hz), 110.22 (tq, *J* = 267.3, 43.1 Hz), 69.34, 31.87, 21.19, 19.65; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.5 (s, 2F), -99.2 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_9H_{11}O_2F_5N_3$: 288.07659, found 288.07686.

*4-(2-Methoxyphenyl)-1-(trifluoromethyl)-1H-1,2,3-triazole (**1q**):* Yield: 77%; ^{1}H NMR (400 MHz, $CDCl_3$)



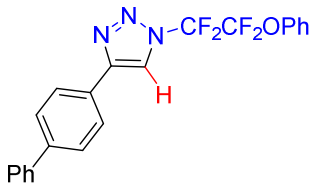
δ 8.41 (d, *J* = 0.5 Hz, 1H), 8.39 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.39 (ddd, *J* = 8.3, 7.4, 1.7 Hz, 1H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 7.02 (dd, *J* = 8.4, 1.0 Hz, 1H), 3.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 144.0, 130.3, 128.3, 121.3, 120.4, 117.9 (q, *J* = 267.4 Hz), 117.6, 111.0, 55.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -59.3 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_8OF_3N_3$: 243.0619, found 243.0623.

*4-(4-Methoxyphenyl)-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-1,2,3-triazole (**1t**):* Yield: 91%; ^{1}H NMR



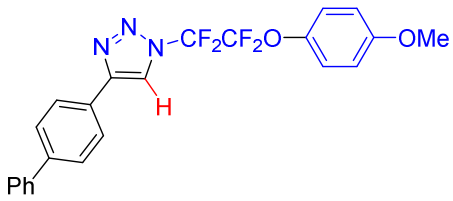
(400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.4, 148.6, 148.3, 129.9, 127.6, 127.2, 121.8, 121.7, 117.5, 115.9 (tt, $^1J_{CF}$ = 273.2 Hz, $^2J_{CF}$ = 36.8 Hz, CF_2), 114.6, 111.6 (tt, $^1J_{CF}$ = 271.1 Hz, $^2J_{CF}$ = 43.5 Hz, CF_2), 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.20 (t, *J* = 3.7 Hz, 2F), -99.31 (t, *J* = 3.6 Hz, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{17}H_{14}F_4N_3O_2$: 368.10167, found 368.10175.

*4-([1,1'-Biphenyl]-4-yl)-1-(1,1,2,2-tetrafluoro-2-phenoxyethyl)-1H-1,2,3-triazole (**1u**):* Yield: 88%; ^{1}H NMR



(400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.02–7.96 (m, 2H), 7.76–7.69 (m, 2H), 7.67–7.63 (m, 2H), 7.51–7.44 (m, 2H), 7.41–7.35 (m, 3H), 7.33–7.27 (m, 1H), 7.18 (ddt, *J* = 8.6, 2.1, 0.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 148.2, 142.1, 140.4, 130.0, 129.0, 128.0, 127.8, 127.2, 127.1, 126.7, 126.6, 121.8, 118.4, 115.9 (tt, *J* = 276.8, 37.8 Hz), 111.6 (tt, *J* = 271.3, 42.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.20 (t, *J* = 3.5 Hz, 2F), -99.31 (t, *J* = 3.6 Hz, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{16}F_4N_3O$: 414.12240, found 414.12236.

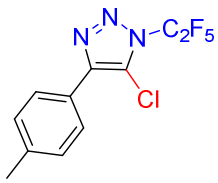
*4-([1,1'-Biphenyl]-4-yl)-1-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)-1H-1,2,3-triazole (**1v**):* Yield:



97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.02–7.98 (m, 2H), 7.76–7.72 (m, 2H), 7.69–7.65 (m, 2H), 7.52–7.47 (m, 2H), 7.43–7.38 (m, 1H), 7.13–7.08 (m, 2H), 6.89 (d, *J* = 9.2 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 148.1, 142.0, 141.8, 140.4, 129.0, 128.0, 127.8, 127.2, 126.7, 126.6, 123.0, 118.4, 115.9 (tt, *J* = 275.0, 37.6 Hz), 114.8, 111.6 (tt, *J* = 270.9, 42.0 Hz), 55.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.51 (t, *J* = 3.7 Hz, 2F), -99.26 (t, *J* = 3.7 Hz, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{23}H_{18}F_4N_3O_2$: 444.13297, found 444.13313.

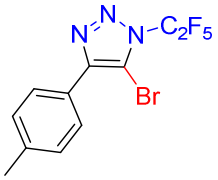
*5-Chlorosubstituted triazole **1y and** 5-bromosubstituted triazoles **1aa**, **1ab**, **1ac** were synthesized according to literature.* [2]

*5-Chloro-1-(pentafluoroethyl)-4-(p-tolyl)-1H-1,2,3-triazole (**1y**):* Yield: 39%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



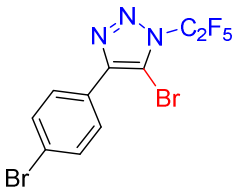
7.84-7.77 (m, 2H), 7.68-7.59 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 139.9, 129.7, 127.0, 124.6, 121.9, 117.1 (qt, *J* = 288.0, 39.0 Hz), 110.9 (tq, *J* = 271.9, 43.3 Hz), 21.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.5 (s, 2F), -97.3 (s, 3F); HRMS (ESI) *m/z* calcd for $C_{11}H_8ClF_5N_3$: 312.03214, found 312.03218.

*5-Bromo-1-(pentafluoroethyl)-4-(p-tolyl)-1H-1,2,3-triazole (**1aa**):* Yield: 13%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



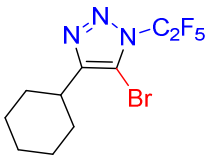
7.89-7.84 (m, 2H), 7.34-7.29 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 139.9, 129.7, 127.6, 124.9, 117.1 (qt, *J* = 288.1, 39.1 Hz), 111.1 (tq, *J* = 271.9, 43.3 Hz), 106.3, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.0 (s, 2F), -95.7 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_8BrF_5N_3$: 355.98163, found 355.98171.

*5-Bromo-4-(4-bromophenyl)-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1ab**):* Yield: 18%; ^{1}H NMR (400 MHz,



$CDCl_3$) δ 7.89-7.85 (m, 2H), 7.66-7.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 132.3, 129.1, 126.8, 124.2, 117.1 (qt, *J* = 288.2, 39.0 Hz), 111.1 (tq, *J* = 272.5, 43.3 Hz), 106.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.0 (s, 2F), -95.8 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_5Br_2F_5N_3$: 419.87649, found 419.87627.

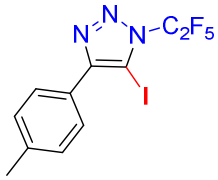
*5-Bromo-4-cyclohexyl-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1ac**):* Yield: 13%; ^{1}H NMR (400 MHz, $CDCl_3$)



δ 2.72 (tt, *J* = 12.0, 3.3 Hz, 1H), 1.90-1.82 (m, 4H), 1.79-1.67 (m, 3H), 1.47-1.25 (m, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 117.1 (qt, *J* = 287.8, 39.4 Hz), 111.0 (tq, *J* = 271.0, 42.6 Hz), 106.9, 34.7, 31.5, 26.3, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -82.3 (s, 2F), -95.9 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{10}H_{12}BrF_5N_3$: 348.01293, found 348.01324.

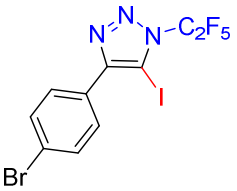
*5-Iodosubstituted triazoles **1ae**, **1af**, **1ag**, **1ah** were prepared according to literature.*[1]

*5-Iodo-1-(pentafluoroethyl)-4-(p-tolyl)-1H-1,2,3-triazole (**1ae**):* Yield: 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



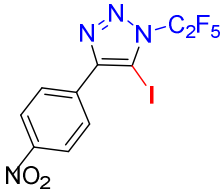
7.82-7.78 (m, 2H), 7.34-7.30 (m, 2H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 139.7, 129.4, 128.3, 125.5, 117.1 (qt, *J* = 288.0, 39.0 Hz), 111.2 (tq, *J* = 270.9, 42.8 Hz), 70.9, 21.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.5 (s, 2F), -93.4 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_8F_5IN_3$: 403.96756, found 403.96776.

*4-(4-Bromophenyl)-5-iodo-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1af**):* Yield: 65%; ^{1}H NMR (400 MHz,



$CDCl_3$) δ 7.84-7.77 (m, 1H), 7.68-7.59 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6, 132.1, 130.0, 127.5, 124.2, 117.1 (qt, *J* = 288.0, 38.8 Hz), 111.3 (tq, *J* = 271.8, 43.1 Hz), 71.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.5 (s, 2F), -93.4 (s, 3F); HRMS (APCI) *m/z* calcd for $C_{10}H_5BrF_5IN_3$: 467.86262, found 467.86310.

*5-Iodo-4-(4-nitrophenyl)-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1ag**):* Yield: 24%; ^{1}H NMR (400 MHz,

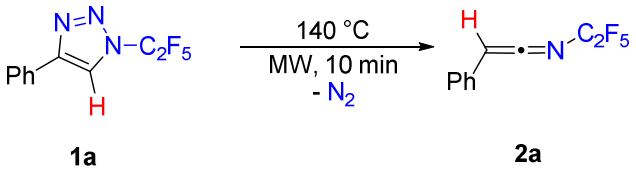


$CDCl_3$) δ 8.39-8.35 (m, 2H), 8.19-8.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 148.4, 134.8, 129.2, 124.1, 117.1 (qt, *J* = 288.2, 38.7 Hz), 111.3 (tq, *J* = 272.7, 43.2 Hz), 72.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.5 (s, 2F), -93.5 (s, 3F); HRMS (APCI) *m/z* calcd for $C_{10}H_5F_5IN_4O_2$: 434.93828, found 434.93875.

*4-([1,1'-Biphenyl]-4-yl)-5-iodo-1-(pentafluoroethyl)-1H-1,2,3-triazole (**1ah**):* Yield: 36%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.99 (m, 2H), 7.77-7.72 (m, 2H), 7.68-7.64 (m, 2H), 7.51-7.45 (m, 2H), 7.42-7.37 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.3, 142.5, 140.3, 129.1, 128.9, 128.0, 127.5, 127.4, 127.3, 117.2 (qt, *J* = 288.0, 39.0 Hz), 111.3 (tq, *J* = 271.8, 42.9 Hz), 71.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -81.4 (s, 2F), -93.3 (s, 3F); HRMS (ESI$^+$) *m/z* calcd for $C_{16}H_{10}F_5IN_3$: 465.98341, found 465.98319.

3 Synthesis of ketenimines **2** – solvent optimization

Thermal decomposition of **1a** can be carried out in wide variety of aprotic solvents with exception of dipolar solvents (Scheme S1). Partial decomposition of THF at higher temperature was observed. The reaction was found to be concentration independent.



1a **2a**

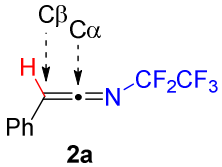
Solvent	^{19}F NMR yield (%)
DCE	80
Toluene	45
Glyme	40
THF	35
Chloroform	34
Acetone	14
Acetonitrile	decomposition
DMF	decomposition
Ethanol	decomposition

Scheme S1 Solvent optimization of the thermal decomposition of triazole **1a**.

4 Characterization of ketenimines **2** – structure and calculations

The ^{13}C NMR spectra of prepared ketenimines **2** support the proposed bent C=C=N-R structure. The resonances of the central carbon (C_α) appear at very low fields at 196-210 ppm, whereas C_β chemical shifts depended strongly on the adjacent atom and were between 31 and 87 ppm.

Table S1 Calculated and experimental NMR and IR data for ketenimine **2a**.



2a

2a	^{13}C NMR		IR
	$\delta_{C\alpha}$ (ppm)	$\delta_{C\beta}$ (ppm)	$\nu_{C=C=N}$ (cm^{-1})
Experimental	204.9	65.0	2026
Calculated	197.6	65.5	2004

Calculated ^{13}C NMR shifts of **2a** (see below for computational details) matched well with experimental values in $CDCl_3$ (Table S1). Calculated IR asymmetric $\nu_{C=C=N}$ frequency also compared well with the experiment (Table S1 and Figure S1, see below for computational details).

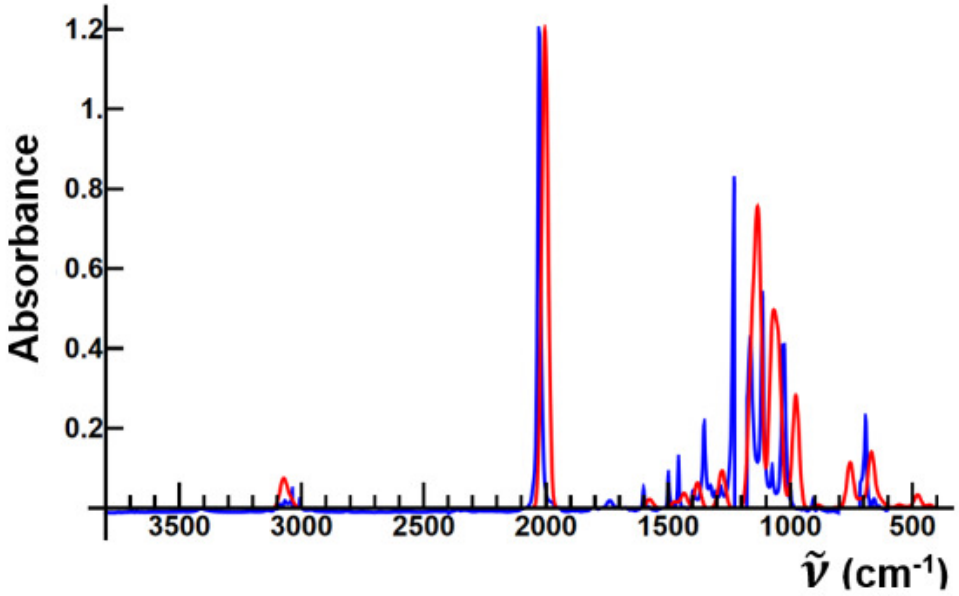


Figure S1 Calculated (red line) and experimental (blue line) IR spectra of **2a** in $CHCl_3$. Absorption signals corresponding to the solvents were removed.

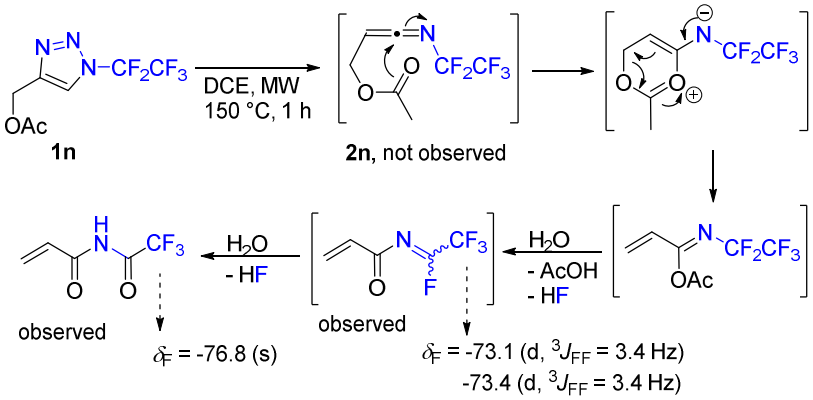
^{13}C NMR calculations: For the ^{13}C NMR calculations was used the geometry optimized at the CASSCF(4,4)/6-31+g* level with $CHCl_3$ as solvent considered at the PCM level. We compared The PBE0, B3LYP and MP2 methods and the basis sets cc-pVDZ, cc-pVTZ and cc-pVQZ and also their augmented versions in order to find the best match for the similar molecules with the NMR characterization available in literature. The selected method for the final calculations was the PBE0/cc-pVDZ with $CHCl_3$ as solvent at the PCM level.

IR spectra calculations: The B3LYP/6-31+g* method for the geometry optimization as well as for the frequency calculation was chosen as the necessary vibrational scaling factors for CASSCF are not available in the NIST database.[3] $CHCl_3$ was used as the solvent (at the PCM level) during the optimization as well as for the frequency calculations. The calculated frequencies are shown in Table S2.

Table S2 Assignments of vibrations to peaks in the IR spectra (Figure S1) of the studied ketenimine. The frequencies were calculated at the B3LYP/6-31+g* level with the geometries optimized at the same level, and the scaling factor from Reference [3] was used. X means the C_β hydrogen atom.

Wavenumber (cm^{-1})	Vibration
666	Benzene
756	Benzene + N + CF_2CF_3
887	Benzene + C(X)
978	$C(F_2)$
1073	$C(F_2)$
1134	Benzene + C(X) + CF_2CF_3
1276	Benzene + CF_2CF_3
1379	C(X) + N
2004	**C=C=N**
3073	Benzene

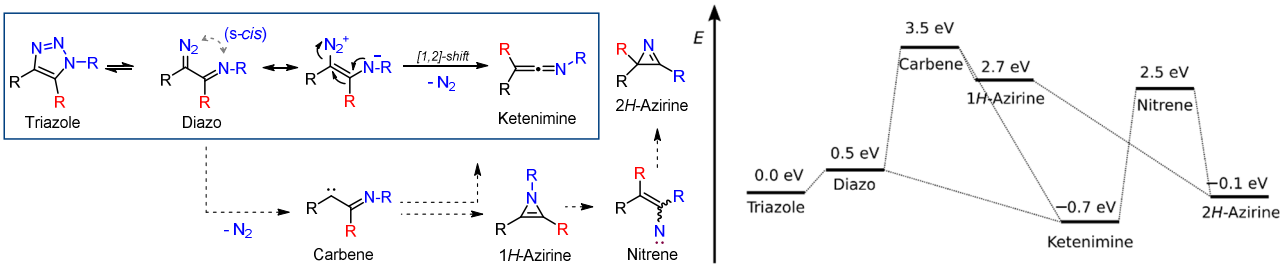
Moreover, inspired by the recent work of Li and co-workers[4], we synthesized triazole **1n** in order to trap the potentially formed ketenimine **2n** via a six-membered intermediate which would lead to decomposition of the ketenimine. Indeed, when triazole **1n** was heated in the microwave reactor, full decomposition of the starting material was observed with no ketenimine formation (Scheme S2). One carbon longer derivative **2m** formed in good yield and displayed standard stability.



Scheme S2 Decomposition of triazole **1n** via a six-membered ring intermediate.

Ab initio energy calculations: We performed optimizations at different levels of electronic structure theory. The structures considered for the calculations are shown in Scheme S3. We were not able to find the singlet minima for carbene and nitrene structure using the MP2, DFT/PBE and DFT/PBE0 methods and 6-31+g* basis. The optimizations in the singlet states converged to ketenimine (for carbene) and to 2*H*-azirine (for nitrene). While the carbene and nitrene structures have a triplet ground state, the triazole is of singlet multiplicity in its ground state and the participation of the triplet intermediates would require a singlet–triplet

transition. That would make such process improbable. We were able to locate the singlet minima for nitrene and carbene with the multireference CASSCF approach (with active spaces (4,4) and (8,8) and the 6-31+g* basis set), but that was achieved only thanks to frequent re-calculations of the Hessian. The perturbatively enhanced multireference method NEVPT2(4,4)/6-31+g* confirmed the CASSCF results. These findings point to a very shallow energetic minima with low energetic barriers leading to a decomposition.



Scheme S3 *Left:* Reactive species considered in the *ab initio* calculations of the reaction mechanism (R = Me, R = H, R = CF_3). *Right:* Calculated energies of the structures (related to the starting triazole) expected in the reaction mechanism. The geometries were optimized at the CASSCF(4,4)/6-31+g* level and the energies were calculated using the CCSD(T)/aug-cc-pVDZ method.

For the optimized structures, we calculated single point energies with the very accurate CCSD(T) method with the aug-cc-pVDZ basis. The results indicate very high energies of carbene and nitrene. It is, therefore, improbable that they would be involved in the mechanism (see Scheme S3). To further check the reliability of the CASSCF geometries, we optimized the ketenimine and 2*H*-azirine molecules also at the CCSD(T)/6-31+g* level. The resulting energy difference is the same as with the CASSCF geometries, i. e. 0.6 eV.

In order to explore the entropic effects, we calculated thermal corrections for temperatures 100, 120, 150, 170 and 200 °C at the BMK/6-31+g* level for the CASSCF geometries. The respective differences were of the order of 10^{-4} eV. We also calculated the energy difference between 2*H*-azirine and ketenimine, assuming DCM as the solvent (at the PCM level) at the CCSD(T)/aug-cc-pVDZ level observing the energy shift of only 0.03 eV.

Optimized structures:

Triazole optimized at the CASSCF(4,4)/6-31+g* level

N	-0.09853724283576	0.00005169176575	0.05200096511915
C	-0.11531222354998	0.00026046314722	1.42497059458876
C	1.19965149048486	0.00012810220409	1.76277726635035
N	1.92577477686718	0.00059548709321	0.58820580847089
N	1.15412977216501	-0.00020367243426	-0.39404091203031

C	1.87542752453746	-0.00012461083357	3.09923678130603
H	-1.01947273712610	0.00029156426119	1.99047630409335
H	2.94806588454204	-0.00003397679622	2.95591647516969
H	1.60948510865035	0.87781020991056	3.67753711357528
H	1.60958848032723	-0.87833855458088	3.67717048627454
C	-1.17128600451418	-0.00007964426302	-0.86744126852347
F	-2.30182248012822	0.00006874747986	-0.19409414884119
F	-1.14709923997707	1.05874933992457	-1.64118222894665
F	-1.14715910944282	-1.05917514687849	-1.64081723660643

Diazo optimized at the CASSCF(4,4)/6-31+g* level

F	0.02082537693694	-0.04861126316311	-0.44252157865449
F	-0.22257812975854	-0.40842112356871	1.64154899060751
F	1.72832555456441	-0.29906720677167	0.80396827598880
N	0.57482316798000	1.60170933300136	1.06399779737077
C	0.52144660110526	0.24835734258260	0.76247153649763
H	-0.22917090599725	2.16449552424754	-0.75308199087830
H	-0.62843898587756	4.50474905225047	-1.39495620785884
H	-1.08117069157376	5.54094642634013	-0.06259707158098
C	-0.26639988571374	4.95551929435194	-0.47867556710785
H	0.53797939675131	5.63376736768735	-0.74815187046128
C	0.16441595258059	2.45668856044016	0.20952330024637
C	0.18533014729020	3.85024233448407	0.43799599109524
N	0.68049243182215	4.20435465377339	1.64575796846002
N	1.08889596988999	4.48880670434447	2.63952242627540

Carbene optimized at the CASSCF(4,4)/6-31+g* level

F	-0.11489120951159	-0.08531193934261	-0.19878354359674
F	-0.12212733501402	-0.18434760878199	1.92383166913836
F	1.72719412697700	-0.18428907243788	0.85586409342488
N	0.60594591918371	1.73218348917181	1.04954316468391
C	0.51570063316458	0.33160399348617	0.89318944170701
H	-0.45004967152510	2.09637395901152	-0.77920129205266
H	0.10712277128107	5.05758231528695	-1.57728472417399
H	-1.41942663535202	5.05747086845574	-0.69629429042046
C	-0.33886230301347	5.05335930579391	-0.58700283813914
H	-0.05054144341196	5.97044272641305	-0.08728770539907

C	0.04112729110338	2.54112354870215	0.07138548715709
C	0.10976485611841	3.87121141424116	0.19024753767081

1*H*-Azirine optimized at the CASSCF(4,4)/6-31+g* level

H	0.16532778254735	5.67113173272894	0.28641862344092
H	0.19714667957601	5.24781321847814	-1.41945302497038
C	-0.26913645952715	5.02725197521870	-0.46615611963506
H	-1.32785457794374	5.24780452547118	-0.53905685184940
C	-0.05480908874344	3.60735115754330	-0.09491641636294
C	-0.11004409759312	2.31292937441889	-0.19058512771002
N	0.56797741549715	2.74277927047341	0.98377638506709
C	1.23109726207027	2.57169181281127	2.13231386335104
F	2.45829991242590	3.12035230287005	2.14928000601395
F	0.63220820713216	3.12035963744055	3.20359219621586
F	1.38066881177641	1.28118150334442	2.39138346290683
H	-0.37635584721780	1.39075648920112	-0.65185199646789

Ketenimine optimized at the CASSCF(4,4)/6-31+g* level

H	-0.45159204808794	5.58932253016240	-0.00998212460848
H	0.74240258915770	5.03677847305563	-1.17195943283104
C	-0.13380028860786	4.74117566454067	-0.60595136054758
H	-0.92535403778272	4.49962889860876	-1.30379468019409
C	0.18836444868053	3.56914232467378	0.29009014564464
C	-0.36804103539183	2.38993583904416	0.19724080274303
N	-0.97025703788174	1.32445689705611	0.19054975603038
C	-0.51520680881539	0.24981609828494	-0.60215401412158
F	0.56315940083551	0.51660136790632	-1.32415700876942
F	-0.22709529042442	-0.78120273304688	0.16468397637497
F	-1.46326113457081	-0.11966925265228	-1.43812603732176
H	0.94459024288898	3.67388289236638	1.04960197760095

Nitrene optimized at the CASSCF(4,4)/6-31+g* level

H	-0.03802265213818	5.97103973266285	-0.01366735088592
H	0.17542871938445	5.04010503884042	-1.48411719105569
C	-0.28495396459421	5.03622158613059	-0.50044150029842
H	-1.36025729822296	5.00776760637031	-0.64552813032651
C	0.19759213422397	3.89066613730885	0.33885784989815

C	0.00900457191727	2.46901481590480	0.02303494347140
N	0.44489577178058	1.54597092170114	0.74245102121685
H	0.74679086611376	4.07812523435341	1.24025793074194
C	-0.76224036681147	2.05091706255065	-1.26077027989731
F	-0.83276388684005	0.74867232397186	-1.38807935413273
F	-1.99409210926031	2.52983294589097	-1.23346782283920
F	-0.16454578555285	2.53867759431414	-2.33423511589254

2H-Azirine optimized at the CASSCF(4,4)/6-31+g* level

F	0.23074234628509	5.38117593688448	-0.64206466669086
C	-0.11500582231045	4.22600069845392	-0.11984173652845
F	-0.14408706629284	4.35662150958692	1.19454095700650
F	-1.33914965910286	3.93806234375823	-0.52265099813889
C	0.83392034468327	3.14512753113792	-0.51530775409442
C	1.23369758118202	1.77237373445002	-0.44431533247842
H	2.47053603944881	1.95160911021295	1.30684842079302
C	1.97492540555400	1.18162940285894	0.72707420331651
H	1.28676423727120	0.65254226862647	1.38024417790266
H	2.72310579720708	0.47381382279926	0.38581118618728
H	0.77168021519755	1.07430018530711	-1.12146912329191
N	1.88038058087712	3.03120045592376	-1.18724433398303

2a ketenimine optimized at the CASSCF(4,4)/6-31+g* level

F	-1.26261286709461	1.67736412721285	2.51153478996074
C	0.06410979426460	1.70458754407484	2.53503784431529
F	0.49733341292530	0.67991339501943	1.79935824442558
F	1.83594231916246	3.05546720562523	1.81789022772939
C	0.51988180924687	2.99411027815370	1.83507698672456
F	0.05689476847154	4.05081601001365	2.45788610408125
F	0.08550067179744	3.01118264616686	0.59607327021535
N	0.50653470030066	1.67400253463284	3.87743841692700
C	1.28377682853374	0.82402844346476	4.27393850087860
C	2.09824931014154	-0.04262960252803	4.79686080715355
H	1.63707899333057	-0.92570641213727	5.20321751440305
C	3.57246915920757	0.08205804524225	4.86421544935037
C	4.30586811779518	-0.94735416824470	5.45504420478282
C	5.69070647789044	-0.86828990960957	5.54548916241143

C	6.36008041300018	0.24119843449709	5.04587189074357
C	5.63598614841416	1.27129829051178	4.45509622678480
C	4.25322228402470	1.19466628339732	4.36311802384735
H	3.79596627867559	-1.81055059511156	5.84545519904596
H	6.24044876111039	-1.67045850057344	6.00411621816343
H	7.43109867290566	0.30382935632429	5.11475366178591
H	6.14583951586970	2.13369948463175	4.06489154660154
H	3.71050343002631	2.00014210923593	3.90123770966842

2a ketenimine optimized at the B3LYP/6-31+g* level

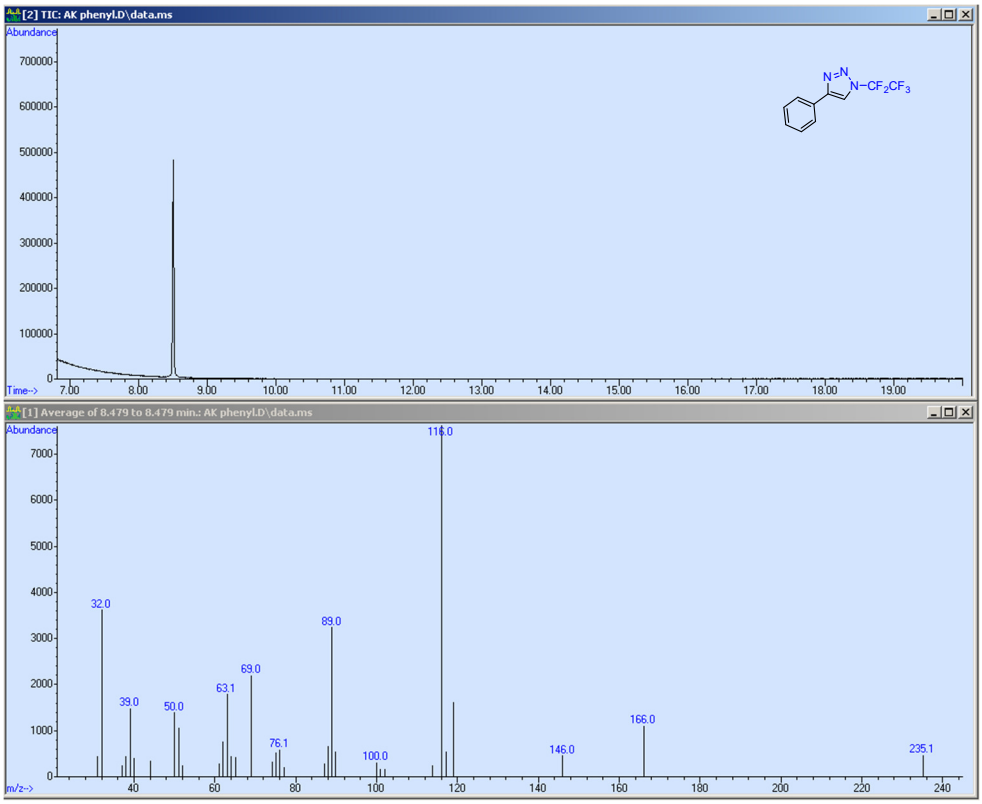
C	4.23142649631423	1.18975098641971	4.41427760583845
C	3.56348430333277	0.03351141572260	4.86318723504627
C	4.31818703849725	-1.00820505881273	5.43333310482145
C	5.70618300279061	-0.89663962716907	5.55371003828239
C	6.36158756128409	0.25578986925164	5.10729471388940
C	5.61678330990760	1.29768471970803	4.53770219465177
C	2.10129544591296	-0.12652730884941	4.76714129919416
C	1.25515929782661	0.73478440702145	4.24753076738019
N	0.44900146444233	1.59975723448631	3.88322017180557
C	-0.00643949673671	1.68732688377391	2.53713474512565
C	0.53087124024751	2.97167257983814	1.83811227779796
F	0.05783245172554	3.05168777907421	0.58380816247760
F	-1.36633853289046	1.75426778267207	2.53586779846851
F	0.34223581442812	0.62380917105321	1.75074247338620
F	1.87549333986405	2.94157393191318	1.78692171515532
F	0.15147960967146	4.07057300399357	2.50935134871475
H	1.66119910166482	-1.04969566163013	5.14405579841645
H	3.81387240665485	-1.90627420508018	5.78266928709235
H	6.27343860240305	-1.71178903939747	5.99646106045286
H	7.44120753118545	0.34324803428551	5.20119295972819
H	6.11676822263479	2.19725560635838	4.18718708523993
H	3.66862478883897	2.00722649536705	3.96958415703442

5 Synthesis of *N*-fluoroalkyl-ketenimines **2** (General procedure)

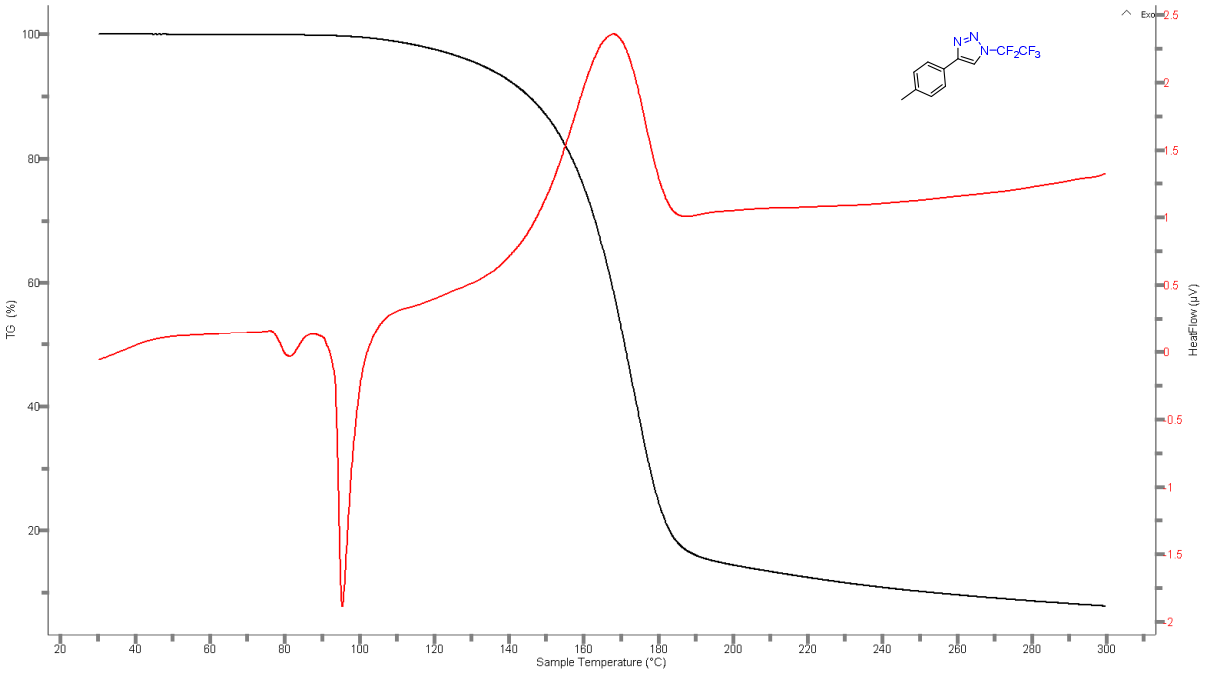
Triazole **1** (0.1-0.5 mmol) in DCE (3 mL) was heated under MW irradiation to 140-160 °C for the time given below (20 min to 3 h). The solvent was then evaporated under reduced pressure.

No	Compd.	R_F	X	R	n (mmol)	T (°C)	Time (min)	Yield (%)
1	**2a**	C_2F_5	H	Ph	0.20	155	60	97
2	**2b**	C_2F_5	H	Tol	0.20	150	40	97
3	**2c**	C_2F_5	H	4-MeO-C_6H_4	0.20	160	40	97
4	**2d**	C_2F_5	H	2-MeO-C_6H_4	0.20	160	60	97
5	**2e**	C_2F_5	H	4-F-C_6H_4	0.20	150	60	97
6	**2f**	C_2F_5	H	4-Br-C_6H_4	0.25	155	60	97
7	**2g**	C_2F_5	H	4-NO_2-C_6H_4	0.25	175	180	97
8	**2h**	C_2F_5	H	naphthalen-1-yl	0.20	160	40	97
9	**2i**	C_2F_5	H	phenanthren-9-yl	0.25	155	30	97
10	**2j**	C_2F_5	H	thiophen-1-yl	0.20	150	60	97
11	**2k**	C_2F_5	H	cyclohexyl	0.30	150	60	67
12	**2l**	C_2F_5	H	dodecan-1-yl	0.53	150	60	95
13	**2m**	C_2F_5	H	(2-AcO)-propyl	0.35	150	60	77
14	**2n**	C_2F_5	H	AcO-CH_2	0.35	150	60	0
15	**2o**	CF_3	H	Ph	0.25	160	180	80
16	**2p**	CF_3	H	4-MeO-C_6H_4	0.20	140	60	97
17	**2q**	CF_3	H	2-MeO-C_6H_4	0.20	160	60	97
18	**2r**	CF_2CF_2Br	H	Ph	0.20	160	60	97
19	**2s**	CF_2CF_2O-Ph	H	Tol	0.34	160	60	97
20	**2t**	CF_2CF_2O-Ph	H	4-MeO-C_6H_4	0.20	160	60	97
21	**2u**	CF_2CF_2O-Ph	H	4-Ph-C_6H_4	0.30	155	120	97
22	**2v**	CF_2CF_2O-4-MeO-Ph	H	4-Ph-C_6H_4	0.25	165	120	96
23	**2w**	CF_2CF_2S-Ph	H	Ph	0.25	165	60	90
24	**2x**	C_2F_5	Cl	Ph	0.33	150	60	87
25	**2y**	C_2F_5	Cl	Tol	0.30	150	60	97
26	**2z**	C_2F_5	Br	Ph	0.49	150	60	97
27	**2aa**	C_2F_5	Br	Tol	0.17	150	60	97
28	**2ab**	C_2F_5	Br	4-Br-C_6H_4	0.15	150	60	93
29	**2ac**	C_2F_5	Br	cyclohexyl	0.14	150	60	92
30	**2ad**	C_2F_5	I	Ph	0.20	130	30	97
31	**2ae**	C_2F_5	I	Tol	0.20	130	40	97
32	**2af**	C_2F_5	I	4-Br-C_6H_4	0.20	130	30	97
33	**2ag**	C_2F_5	I	4-NO_2-C_6H_4	0.16	130	30	96
34	**2ah**	C_2F_5	I	4-Ph-C_6H_4	0.13	130	30	92
35	**2ai**	C_2F_5	I	cyclohexyl	0.20	140	60	89
36	**2aj**	C_2F_5	I	*n*-butyl	0.24	150	40	97
37	**2ak**	CF_2H	I	Tol	0.20	130	45	95
38	**2al**	C_2F_5	*n*-Pr	Ph	0.23	160	75	90
39	**2am**	CF_2H	H	Ph	0.30	165	180	0
40	**2an**	Et	H	Ph	0.30	165	180	0

Gas chromatogram and mass spectrum (GCMS) of triazole **1a** (ketenimine **2a**).

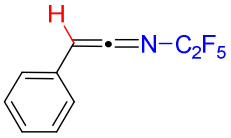


DSC (red line) and TG (black line) analyses of 4-(*p*-tolyl)-1-(perfluoroethyl)-1*H*-1,2,3-triazole **1b** (9.972 mg)

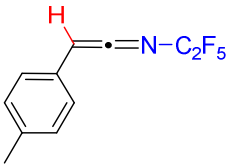


6 Ketenimines 2 – characterization

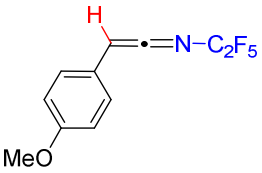
*N-(Pentafluoroethyl)-2-phenylethen-1-imine (**2a**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.28–7.22 (m, 1H), 7.19–7.13 (m, 2H), 5.74–5.64 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9 (t, *J* = 11.2 Hz), 129.4, 127.6, 126.8, 117.7 (qt, *J* = 286.3, 41.3 Hz), 111.6 (tq, *J* = 265.7, 39.7 Hz), 65.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.7, -96.54 to -96.69 (m, 2F); IR ($CHCl_3$) 3065 (w), 3034 (w), 1600 (w) 1498 (m), 1458 (m), 1352 (m), 1287 (m), 1197 (s), 1031 (m), 765 (m), 692 (m) (Ph), 2026 (s) (C=C=N), 1213 (s), 1161 (m, ν(CF_3), ν(CF_2)); HRMS (EI$^+$) *m/z* calcd for $C_{10}H_6F_5N$: 235.0420, found 235.0421.



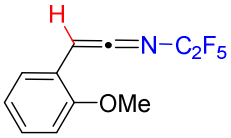
*N-(Pentafluoroethyl)-2-(p-tolyl)ethen-1-imine (**2b**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (dd, 4H), 5.72–5.65 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.0 (t, *J* = 11.4 Hz), 137.6, 130.1, 126.8, 124.4, 117.7 (qt, *J* = 286.4, 41.5 Hz), 111.6 (tq, *J* =265.6, 39.4 Hz), 64.9, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.8, -96.41 to -96.90 (m, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_9F_5N$: 250.0655, found 250.0654.



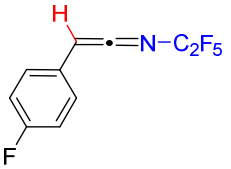
*2-(4-Methoxyphenyl)-N-(pentafluoroethyl)ethen-1-imine (**2c**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.06 (m, 2H), 6.92–6.87 (m, 2H), 5.70–5.66 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.1 (t, *J* = 11.6 Hz), 159.2, 128.0, 119.1, 117.7 (qt, *J* = 286.4, 41.5 Hz), 115.0, 111.6 (tq, *J* = 265.2 Hz, 39.5 Hz), 64.7, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.7 (s, 3F), -96.72 to -96.88 (m, 2F); HRMS (ESI$^+$) *m/z* calcd for $C_{11}H_8OF_5N$: 265.05206, found 265.05172.



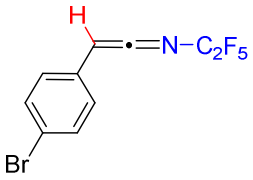
*2-(2-Methoxyphenyl)-N-(pentafluoroethyl)ethen-1-imine (**2d**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 7.07 (dd, *J* = 7.5, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 5.66–5.61 (m, 1H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.2 (t, *J* = 11.3 Hz), 156.6, 128.7, 127.9, 121.2, 117.9 (qt, *J* = 286.3, 42.0 Hz), 117.1, 111.6 (tq, *J* = 264.3, 39.4 Hz), 110.6, 60.6, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –85.6 (s, 3F), -96.69 to -96.89 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{11}H_8OF_5N$: 265.0526, found 265.0525.



*2-(4-Fluorophenyl)-N-(pentafluoroethyl)ethen-1-imine (**2e**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.10 (m, 2H), 7.08–7.02 (m, 2H), 5.71–5.66 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.0 (t, *J* = 10.6 Hz), 162.19 (d, *J* = 247.6 Hz), 128.38 (d, *J* = 8.1 Hz), 123.49 (d, *J* = 3.5 Hz), 116.57 (d, *J* = 22.2 Hz), 119.1 (qt, *J* = 284.1, 41.2 Hz), 111.6 (tq, *J* = 263.8, 38.9 Hz), 64.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.7 (s, 3F), -96.61 to -96.76 (m, 2F), -114.4 (tt, *J* = 8.5, 5.2 Hz, 1F). HRMS (EI$^+$) *m/z* calcd for $C_{10}H_5F_6N$: 253.0326, found 253.0329.

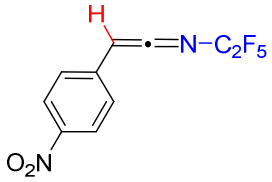


*2-(4-Bromophenyl)-N-(pentafluoroethyl)ethen-1-imine (**2f**):* Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–



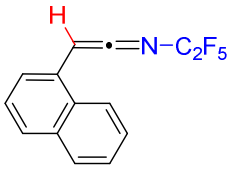
7.42 (m, 2H), 7.05–6.96 (m, 2H), 5.67–5.63 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0 (t, *J* = 11.3 Hz), 132.6, 128.3, 126.9, 121.2, 117.6 (dt, *J* = 286.4, 41.1 Hz), 111.4 (td, *J* = 265.6, 39.8 Hz), 64.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.72, -96.45 to -96.58 (m, 2F). HRMS (EI$^+$) *m/z* calcd for $C_{10}H_5BrF_5N$: 312.9520, found 312.9522.

*2-(4-Nitrophenyl)-N-(pentafluoroethyl)ethen-1-imine (**2g**):* Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–



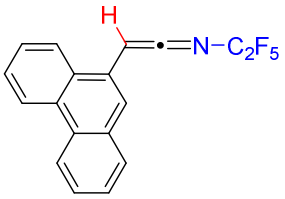
8.15 (m, 2H), 7.33–7.27 (m, 2H), 5.81–5.77 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7 (t, *J* = 10.9 Hz), 146.8, 136.1, 127.2, 124.7, 117.5 (dt, *J* = 286.5, 40.9 Hz), 111.4 (td, *J* = 266.7, 40.2 Hz), 64.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.64 (s, 3F), -95.98 to -96.06 (m, 2F). HRMS (EI$^+$) *m/z* calcd for $C_{10}H_5F_5N_2O_2$: 280.0266, found 280.0264.

*2-(Naphthalen-1-yl)-N-(pentafluoroethyl)ethen-1-imine (**2h**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–



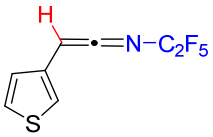
7.37 (m, 7H), 6.37–6.19 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 134.2, 130.7, 129.1, 128.5, 126.8, 126.4, 126.0, 125.9, 124.1, 123.5, 117.7 (qt, *J* = 286.5, 41.3 Hz), 111.7 (tq, J=265.8, 39.8), 61.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.7 (s, 3F), -96.37 to -96.75 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{14}H_8F_5N$: 285.0577, found 285.0578.

*N-(Pentafluoroethyl)-2-(phenanthren-9-yl)ethen-1-imine (**2i**):* White crystals; m.p. 64-66 ℃ ; ^{1}H NMR (400



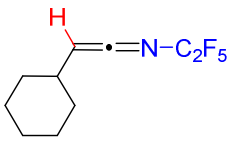
MHz, $CDCl_3$) δ 8.79–8.71 (d, *J* = 8.1 Hz, 1H), 8.66 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 7.8, 1.7 Hz, 1H), 7.84 (d, *J* = 7.8, 1.7 Hz, 1H), 7.77–7.55 (m, 5H), 6.31–6.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4 (t, *J* = 11.4 Hz), 131.5, 131.1, 130.2, 129.6, 128.4, 127.2, 127.2, 127.1, 124.3, 123.5, 122.8, 122.7, 117.8 (qt, *J* = 286.4, 41.6 Hz), 111.8 (tq, *J* = 265.7, 39.6 Hz), 61.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.57 (s, 3F), -96.42 to -96.62 (m, 2F). HRMS (EI$^+$) *m/z* calcd for $C_{18}H_{10}F_5N$: 335.0728, found 335.0727. X-ray analysis - see Section 9 – Crystallographic data.

*N-(Pentafluoroethyl)-2-(thiophen-3-yl)ethen-1-imine (**2j**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd,



J = 5.1, 3.0 Hz, 1H), 7.08 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.88 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.84–5.81 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.9, 127.3, 126.0, 125.9, 121.4, 117.6 (qt, *J* = 286.4, 41.4 Hz), 111.5 (tq, *J* = 265.0, 39.5 Hz), 60.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.6 (s, 3F), -96.69 to -96.94 (m, 2F); HRMS (APCI) *m/z* calcd for $C_8H_4F_5NS$: 240.99791, found 240.99782.

*2-Cyclohexyl-N-(pentafluoroethyl)ethen-1-imine (**2k**):* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56–4.48



(m, 1H), 2.21 (tdd, *J* = 11.0, 6.5, 3.3 Hz, 1H), 1.85–1.70 (m, 3H), 1.70–1.61 (m, 1H), 1.41–1.09 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.3 (t, *J* = 11.9 Hz), 117.8 (qt, *J* = 286.2, 42.3 Hz), 111.7 (tq, *J* = 264.0, 39.1 Hz), 65.0, 33.6, 33.3, 25.9, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.8 (s, 3F), -97.37 to -97.51 (m, 2F); IR ($CHCl_3$) 2928 (m), 2856 (m, ν(C-H)),

1450 (m), 1343 (m, δ(CH_2)), 948 (m), 896 (m, cyclohexane), 2029 (s, C=C=N), 1217 (s), 1157 (m, ν(CF_3), ν(CF_2)); HRMS (APCI) *m/z* calcd for $C_{10}H_{13}F_5N$: 242.09627, found 242.09607.

*2-Dodecyl-N-(pentafluoroethyl)ethen-1-imine (**2l**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.49 (tt, *J* = 7.3, 2.7 Hz, 1H), 2.12 (q, *J* = 7.3 Hz, 2H), 1.44 (q, *J* = 7.1 Hz, 2H), 1.27 (s, 18H), 0.91–0.85 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.4, 129.5, 117.9 (qt, *J* = 286.2, 42.1 Hz), 111.8 (tq, *J* = 263.5, 39.1 Hz), 58.7, 32.1, 29.82, 29.81, 29.77, 29.7, 29.5, 29.4, 29.0, 22.9, 14.3, 1.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.0 (s, 3F), -96.5 (dd, *J* = 5.5, 2.6 Hz, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{16}H_{26}F_5N$: 327.1980, found 327.1979.

*5-((Pentafluoroethyl)imino)pent-4-en-2-yl acetate (**2m**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.92 (dt, *J* = 12.5, 6.3 Hz, 1H), 4.51–4.41 (m, 1H), 2.33 (dt, *J* = 8.2, 6.0 Hz, 2H), 2.00 (s, 3H), 1.24 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8 (t, *J* = 11.6 Hz), 170.5, 117.7 (qt, *J* = 286.1, 41.8 Hz), 111.6 (tq, *J* = 264.3, 39.5 Hz), 69.5, 54.0, 43.6, 21.1, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.0 (s, 3F), -97.34 to -97.71 (m, 2F); HRMS (APCI) *m/z* calcd for $C_9H_{11}F_5NO_2$: 260.07045 found 260.07041.

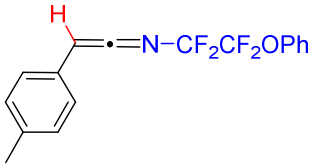
*2-Phenyl-N-(trifluoromethyl)ethen-1-imine (**2o**):* Brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.18 (m, 5H), 5.73–5.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.85 (q, *J* = 8.7 Hz), 129.40, 127.59, 126.87, 120.03 (q, *J* = 265.7 Hz), 65.51; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.74 to -57.95 (m, 3F); HRMS (EI$^+$) m/z calcd for $C_9H_6F_3N$: 185.0447, found 185.0447.

2-(4-Methoxyphenyl)-*N*-(trifluoromethyl)ethen-1-imine (**2p**): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.07 (m, 2H), 6.94–6.85 (m, 2H), 5.67–5.63 (m, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8 (q, *J* = 8.8 Hz), 159.2, 128.1, 120.1 (q, *J* = 265.8 Hz), 119.3, 115.0, 65.2, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.03 to -58.14 (m, 3F); HRMS (EI$^+$) *m/z* calcd for $C_{10}H_8OF_3N$: 215.0558, found 215.0558.

*2-(2-Methoxyphenyl)-N-(trifluoromethyl)ethen-1-imine (**2q**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.19 (m, 1H), 7.08 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 5.63–5.59 (m, 1H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (d, *J* = 9.0 Hz), 156.6, 128.7, 128.0, 121.2, 120.3 (q, *J* = 264.1 Hz), 117.4, 110.6, 61.1, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.40 to -58.47 (m, 3F); HRMS (EI$^+$) *m/z* calcd for $C_{10}H_8OF_3N$: 215.0558, found 215.0556.

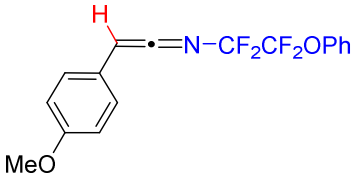
*N-(2-Bromo-1,1,2,2-tetrafluoroethyl)-2-phenylethen-1-imine (**2r**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 2H), 7.27–7.21 (tt, *J* = 7.40, 1.28, 1H), 7.20–7.15 (m, 2H), 5.69–5.65 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2 (t, *J* = 11.1 Hz), 129.0, 127.6, 127.2, 126.6, 114.5 (tt, J=313.8, 43.6), 112.9 (tt, *J*=296.6, 31.1), 64.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.67 (t, *J* = 5.1 Hz, 2F), -92.00 to -93.06 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{10}H_6BrF_4N$: 294.9620, found 294.9622.

*N-(1,1,2,2-Tetrafluoro-2-phenoxyethyl)-2-(p-tolyl)ethen-1-imine (**2s**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$)



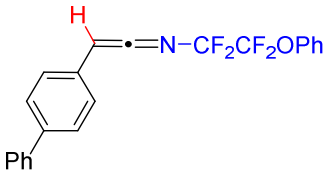
δ 7.42–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.25–7.21 (m, 2H), 7.15–7.08 (m, 4H), 5.64–5.60 (m, 1H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1 (t, *J* = 11.9 Hz), 149.1, 137.1, 130.0, 129.8, 126.7, 126.7, 125.2, 121.8, 116.4 (tt, *J* = 276.2, 37.6 Hz),112.9 (tt, *J* = 263.8, 38.4 Hz), 64.2, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.89 to -87.50 (m, 2F), -95.82 to -95.94 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{17}H_{13}F_4NO$: 323.0933, found 323.0935.

*2-(4-Methoxyphenyl)-N-(1,1,2,2-tetrafluoro-2-phenoxyethyl)ethen-1-imine (**2t**):* Yellow oil; ^{1}H NMR (400



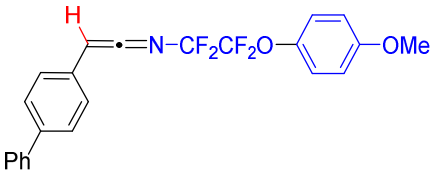
MHz, $CDCl_3$) δ 7.43–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.27–7.20 (m, 2H), 7.15–7.11 (m, 2H), 6.89–6.85 (m, 2H), 5.64–5.61 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.1 (t, *J* = 11.8 Hz), 159.0, 149.1, 129.8, 127.9, 126.7, 121.8, 120.0, 116.4 (tt, *J* = 274.7, 37.2 Hz), 114.9, 112.9 (tt, *J* = 264.3, 37.2 Hz), 63.9, 55.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.80 to -87.51 (m, 2F), -95.58 to -96.43 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{17}H_{13}F_4NO_2$: 339.08769, found 339.08743.

*2-([1,1'-Biphenyl]-4-yl)-N-(1,1,2,2-tetrafluoro-2-phenoxyethyl)ethen-1-imine (**2u**):* Yellow oil; ^{1}H NMR (400



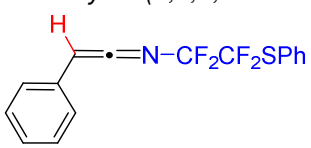
MHz, $CDCl_3$) δ 7.60–7.54 (m, 2H), 7.48–7.21 (m, 12H), 5.69–5.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2 (t, *J* = 11.8 Hz), 149.1, 140.6, 140.1, 130.9, 129.9, 129.0, 128.0, 127.6, 127.2, 127.0, 126.8, 121.8, 116.4 (tt, *J* = 267.7, 38.0 Hz), 112.9 (tt, *J* = 263.7, 38.4 Hz), 64.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.78 to -87.52 (m, 2F), -95.42 to -96.13 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{22}H_{15}F_4NO$: 385.1084, found 385.1099.

*2-([1,1'-Biphenyl]-4-yl)-N-(1,1,2,2-tetrafluoro-2-(4-methoxyphenoxy)ethyl)ethen-1-imine (**2v**):* Yellow oil; ^{1}H



NMR (400 MHz, $CDCl_3$) δ 7.66–7.54 (m, 4H), 7.51–7.45 (m, 2H), 7.40–7.35 (m, 1H), 7.31–7.27 (m, 2H), 7.20–7.16 (m, 2H), 6.96–6.83 (m, 2H), 5.70–5.67 (m, 1H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 11.9 Hz), 158.2, 142.2 (t, *J* = 1.8 Hz), 140.5, 140.1, 129.0, 129.0, 127.9, 127.6, 127.1, 127.0, 123.1, 116.4 (tt, *J* = 275.2, 37.8 Hz), 114.7, 112.9 (tt, *J* = 264.5, 38.6 Hz), 64.0, 55.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.06 to -87.83 (m, 2F), -95.58 to -95.68 (m, 2F); HRMS (EI$^+$) *m/z* calcd for $C_{23}H_{17}F_4NO_2$: 415.1190, found 415.1197.

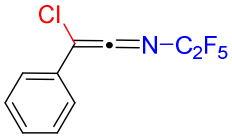
*2-Phenyl-N-(1,1,2,2-tetrafluoro-2-(phenylthio)ethyl)ethen-1-imine (**2w**):* Orange oil; product contains ca 8%



of impurities (starting triazole **1w**), chromatographic separation was not successful; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 2H), 7.56–7.15 (m, 8H), 5.62–5.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.9 (t, *J* = 11.7 Hz), 137.4, 130.9, 129.5, 129.3, 128.6, 127.2, 126.8, 123.7 (t, *J* = 2.6 Hz), 122.7 (tt, *J* = 289.6, 38.8 Hz), 115.2

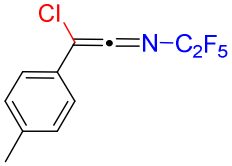
(tt, *J* = 265.6, 32.2 Hz), 64.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.83 to -90.38 (m, 2F), -91.09 to -92.14 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{16}H_{11}F_4NS$: 325.0542, found 325.0543.

*2-Chloro-N-(pentafluoroethyl)-2-phenylethen-1-imine (**2x**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–



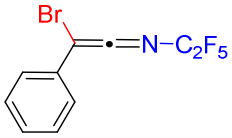
7.42 (m, 2H), 7.40–7.29 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4 (t, *J* = 11.1 Hz), 129.3, 129.0, 127.9, 125.3, 117.6 (qt, *J* = 286.7, 40.5 Hz), 111.5 (tq, *J* = 267.3, 40.0 Hz), 87.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -96.77 to -96.99 (m, 2F); IR ($CHCl_3$) 3075 (w), 1494 (m), 1450 (m), 712 (m, Ph), 2028 (s, C=C=N), 1344 (s), 1140 (s), 1043 (s, ν(CF_3), ν(CF_2)); HRMS (APCI) *m/z* calcd for $C_{10}H_6ClF_5N$ [M+H]: 270.01034, found 270.01088.

*2-Chloro-N-(pentafluoroethyl)-2-(p-tolyl)ethen-1-imine (**2y**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26



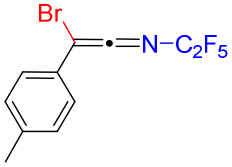
(s, 4H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5 (t, *J* = 11.4 Hz), 139.4, 130.0, 125.3, 124.7, 117.6 (qt, *J* = 286.7, 40.6 Hz), 111.5 (tq, *J* = 267.0, 39.9 Hz), 87.7, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -96.90 to -97.03 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{11}H_8ClF_5N$ [M+H]: 284.02599, found 284.02652.

*2-Bromo-N-(pentafluoroethyl)-2-phenylethen-1-imine (**2z**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–



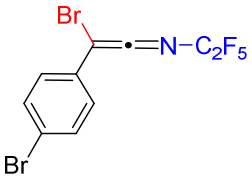
7.38 (m, 4H), 7.36–7.31 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.0 (t, *J* = 11.2 Hz), 129.3, 129.0, 128.9, 126.6, 117.7 (qt, *J* = 286.6, 40.7 Hz), 111.2 (tq, *J* = 266.8, 40.0 Hz), 70.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -96.33 to -96.84 (m, 2F); IR ($CHCl_3$) 3068 (w), 3035 (w), 1597 (m), 1493 (m), 1449 (m, Ph), 2026 (s, C=C=N), 1344 (s), 1173 (s), 1043 (s, ν(CF_3), ν(CF_2)); HRMS (APCI) *m/z* calcd for $C_{10}H_5BrF_5N$: 312.95200, found 312.95186.

*2-Bromo-N-(pentafluoroethyl)-2-(p-tolyl)ethen-1-imine (**2aa**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–



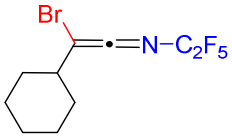
7.25 (m, 2H), 7.24–7.21 (m, 2H), 3.01 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.8 (t, *J* = 11.2 Hz), 139.2, 129.9, 126.4, 124.6, 117.5 (qt, *J* = 286.8, 40.8 Hz), 111.1 (tq, *J* = 266.6, 39.9 Hz), 70.5, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -96.61 to -96.87 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{10}H_5BrF_5N$: 312.95200, found 312.95186.

*2-Bromo-2-(4-bromophenyl)-N-(pentafluoroethyl))ethen-1-imine (**2ab**):* Yellow oil; ^{1}H NMR (400 MHz,



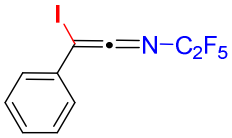
$CDCl_3$) δ 7.56–7.51 (m, 2H), 7.25–7.21 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.1 (t, *J* = 11.2 Hz), 132.5, 128.0, 127.0, 123.0, 117.6 (qt, *J* = 286.9, 40.6 Hz), 111.1 (tq, *J* = 267.2, 40.1 Hz), 69.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -96.16 to -96.79 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{10}H_4Br_2F_5N$: 390.86252, found 390.86190.

*2-Bromo-2-(cyclohexyl)-N-(pentafluoroethyl))ethen-1-imine (**2ac**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ



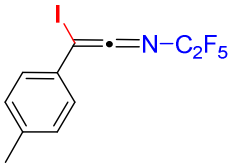
2.24 (tt, *J* = 11.1, 3.5 Hz, 1H), 1.98–1.92 (m, 2H), 1.79 (dt, *J* = 12.4, 3.1 Hz, 2H), 1.71–1.63 (m, 1H), 1.39–1.14 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7 (t, *J* = 11.6 Hz), 117.7 (qt, *J* = 286.7, 41.4 Hz), 111.1 (tq, *J* = 265.4, 39.5 Hz), 74.7, 43.6, 39.82 31.6, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -97.53 to -97.63 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{10}H_{10}BrF_5N$ [M-H]: 317.99113, found 317.99100.

*2-Iodo-N-(pentafluoroethyl)-2-phenylethen-1-imine (**2ad**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–



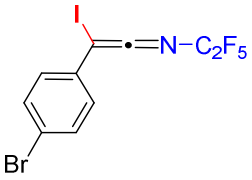
7.34 (m, 4H), 7.31–7.25 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.0 (d, *J* = 11.4 Hz), 129.2, 128.6, 128.3, 128.0, 117.7 (qt, *J* = 286.8, 41.1 Hz), 111.3 (tq, *J* = 266.1, 40.0 Hz), 31.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.3 (s, 3F), -95.49 to -95.99 (m, 2F); IR ($CHCl_3$) 3089 (w), 3066 (w), 3012 (w), 1596 (m), 1579 (w), 1492 (m), 1447 (m, Ph), 2017 (s, C=C=N), 1343 (s), 1132 (s), 1041 (s, ν(CF_3), ν(CF_2)); HRMS (APCI) *m/z* calcd for $C_{10}H_5F_5IN$: 360.93813, found 360.93823.

*2-Iodo-N-(pentafluoroethyl)-2-(p-tolyl)ethen-1-imine (**2ae**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–



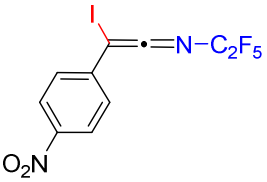
7.25 (m, 2H), 7.21–7.13 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.0, 139.1, 130.0, 128.1, 125.4, 117.9 (qt, *J* = 286.8, 41.3 Hz), 111.5 (tq, *J* = 265.8, 39.8 Hz), 32.0, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.3 (s, 3F), -96.24 to -96.52 (m, 2F). HRMS (APCI) *m/z* calcd for $C_{11}H_7F_5IN$: 374.95378, found 374.95354.

*2-(4-Bromophenyl)-2-iodo-N-(pentafluoroethyl)ethen-1-imine (**2af**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$)



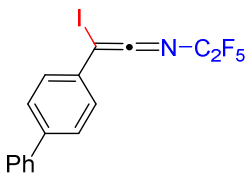
δ 7.50–7.46 (m, 2H), 7.26–7.22 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5 (t, *J* = 11.1 Hz), 132.5, 129.5, 127.7, 122.7, 117.8 (qt, *J* = 286.9, 41.1 Hz), 111.3 (tq, *J* = 266.4, 40.1 Hz), 30.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.72 to -96.53 (m, 2F). HRMS (APCI) *m/z* calcd for $C_{10}H_4BrF_5IN$: 438.84865, found 438.84837.

*2-Iodo-2-(4-nitrophenyl)-N-(pentafluoroethyl)ethen-1-imine (**2ag**):* Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ



8.24–8.19 (m, 2H), 7.56–7.51 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9 (t, *J* = 11.0 Hz), 147.4, 136.0, 128.7, 124.5, 117.7 (qt, *J* = 286.9, 40.7 Hz), 111.3 (tq, *J* = 267.4, 40.5 Hz), 28.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.55 to -95.80 (m, 2F). HRMS (APCI) *m/z* calcd for $C_{10}H_4F_5IN_2O_2$: 405.92321, found 405.92303.

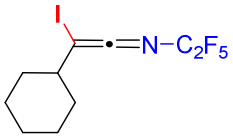
*2-([1,1'-Biphenyl]-4-yl)-2-iodo-N-(pentafluoroethyl)ethen-1-imine (**2ah**):* Yellow amorphous solid; ^{1}H NMR



(400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 4H), 7.50–7.45 (m, 4H), 7.42–7.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6 (t, *J* = 11.2 Hz), 141.7, 140.0, 133.1, 129.1, 128.6, 128.0, 127.9, 127.2, 117.9 (qt, *J* = 286.9, 41.2 Hz), 111.4 (tq, *J* = 266.1, 40.1 Hz),

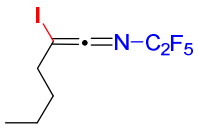
30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.2 (s, 3F), -95.86 to -96.49 (m, 2F). HRMS (APCI) *m/z* calcd for $C_{16}H_9F_5IN$: 436.96943, found 436.96903.

*2-Cyclohexyl-2-iodo-N-(pentafluoroethyl)ethen-1-imine (**2ai**):* Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ



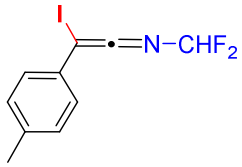
2.02–1.91 (m, 3H), 1.77 (dt, *J* = 12.8, 3.3 Hz, 2H), 1.64 (dt, *J* = 12.7, 3.3 Hz, 1H), 1.39–1.26 (m, 2H), 1.25–1.08 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0 (t, *J* = 11.5 Hz), 118.0 (qt, *J* = 286.7, 41.8 Hz), 111.2 (tq, *J* = 264.7, 39.7 Hz), 40.4, 38.0, 33.0, 32.7, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.4 (s, 3F), -97.14 to -97.24 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{10}H_{12}F_5IN$: 367.99291, found 367.99249.

*2-Butyl-2-iodo-N-(pentafluoroethyl)ethen-1-imine (**2aj**):* Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.30 (t,



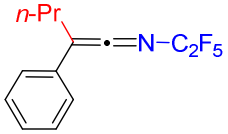
J = 7.2 Hz, 2H), 1.48 (p, *J* = 7.5, 7.0 Hz, 2H), 1.36 (dq, *J* = 14.7, 6.3 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.6 (t, *J* = 11.6 Hz), 117.9 (qt, *J* = 286.7, 41.7 Hz), 111.2 (tq, *J* = 264.9, 39.5 Hz), 36.5, 32.6, 31.0, 21.6, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.5 (s, 3F), -97.27 to -97.42 (m, 2F); HRMS (APCI) *m/z* calcd for $C_8H_{10}F_5IN$: 341.97726, found 341.97664.

*N-(Difluoromethyl)-2-iodo-2-(p-tolyl)ethen-1-imine (**2ak**):* Orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–



7.26 (m, 2H), 7.16–7.13 (m, 2H), 6.60 (t, *J* = 65.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8 (t, *J* = 14.1 Hz), 138.3, 130.0, 129.8, 127.8, 111.5 (t, *J* = 254.4 Hz), 30.4, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -90.37 to -94.68 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{10}H_8F_2IN$: 306.96640, found 306.96686.

*N-(Pentafluoroethyl)-2-phenylpent-1-en-1-imine (**2al**):* Yellowish oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.35



(m, 2H), 7.30–7.21 (m, 3H), 2.58–2.45 (m, 2H), 1.72–1.51 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.0 (t, *J* = 11.4 Hz), 129.2, 128.6, 127.5, 126.0, 117.8 (qt, *J* = 286.1, 41.7 Hz), 111.9 (tq, *J* = 264.8, 39.2 Hz), 77.1, 28.6, 20.8, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.7 (s, 3F), -96.56 to -96.62 (m, 2F); HRMS (APCI) *m/z* calcd for $C_{13}H_{13}F_5N$ [M+H]: 278.09627, found 278.09647.

7 Reactivity of ketenimines **2** - general methods

Preparation of cyclobutenimines from phenylacetylene (General procedure): Triazole **1** (0.25 or 0.5 mmol) in DCE (1.5 or 3 mL) was heated under MW irradiation according to the general procedure for ketenimine preparation. The formation of ketenimine **2** was monitored by ^{19}F NMR. Then, phenylacetylene (2 equiv.) was added and the solution was heated under MW irradiation to 100 °C (for R = H) or 170 °C (for R = *n*-Pr) for 1 h. After the complete conversion of ketenimine the solvent was evaporated under reduced pressure and the residue was chromatographed (silica gel, pentane/DCM or cyclohexane/DCM).

Preparation of cyclobutenimines from diphenylacetylene (General procedure): Triazole **1** (0.25 or 0.5 mmol) and diphenylacetylene (2 equiv.) in DCE (1.5 or 3 mL) were heated under MW irradiation to 165-170 °C for 1-2 h. The formation of the product was monitored by ^{19}F NMR. After the complete conversion of ketenimine the solvent was evaporated under reduced pressure and the residue was chromatographed (silica gel, cyclohexane/DCM).

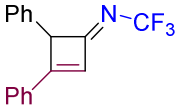
Preparation of cyclobutanimines (General procedure): Triazole **1** (0.25 or 0.5 mmol) in DCE (1.5 or 3 mL) was heated under MW irradiation according to the general procedure for ketenimine preparation. The formation of ketenimine **2** was monitored by ^{19}F NMR. Then 2-ethylbut-1-ene (3 equiv.) was added and the reaction mixture was stirred overnight at 40 °C. After the complete conversion of ketenimine the solvent was evaporated under reduced pressure and the residue was chromatographed (silica gel, cyclohexane/EtOAc) when necessary.

Addition of nucleophiles to ketenimines (General procedure): Triazole **1** (0.25 or 0.5 mmol) in DCE (1.5 or 3 mL) was heated under MW irradiation according to the general procedure for ketenimine preparation. The formation of ketenimine **2** was monitored by ^{19}F NMR. Then the nucleophile amine (1 equiv.) or alcohol (3 equiv.) or thiol (3 equiv.) was added and the reaction mixture was stirred for 30 min at RT. The solvent was evaporated under reduced pressure and the residue was chromatographed (silica gel, cyclohexane/EtOAc) when necessary.

*Preparation of amidine **14f**:* Triazole **1a** (0.5 mmol) in DCE (3 mL) was heated under MW irradiation according to general procedure for ketenimine preparation. The solvent was evaporated under reduced pressure and $CDCl_3$ (0.5 ml) was added. NMR tube was charged with *p*-TolCH_2NH_2 (1 equiv.) and the solution of ketenimine was added under inert atmosphere. The solution of crude amidine was then used for characterization analyses.

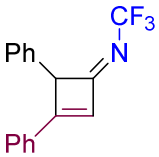
8 Reactivity of ketenimines **2** – product characterization

*(E)-3,4-Diphenyl-N-(trifluoromethyl)cyclobut-2-en-1-imine ((E)-**9a**)*: Yield: 59 %, *E*/*Z* = 75:25, white solid;



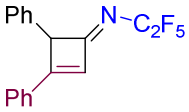
^{1}H NMR (401 MHz, $CDCl_3$) δ 7.59–7.27 (m, 10H), 6.86 (q, *J* = 2.5 Hz, 1H), 4.97 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5 (q, *J* = 9.5 Hz), 169.2, 135.3, 132.5, 130.1, 129.2, 129.1, 129.0, 128.2, 127.8, 127.1, 124.2 (q, *J* = 262.3 Hz), 58.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -56.5 (d, *J* = 2.5 Hz, 3F); HRMS (EI$^+$) *m/z* calcd for $C_{17}H_{12}F_3N$: 287.0916, found 287.0917.

*(Z)-3,4-Diphenyl-N-(trifluoromethyl)cyclobut-2-en-1-imine ((Z)-**9a**)*: ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.61–7.28



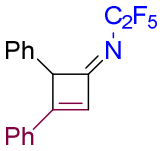
(m, 10H), 6.83 (s, 1H), 5.06 (q, *J* = 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7 (q, *J* = 9.1 Hz), 169.0, 135.6, 132.2, 130.2, 129.2, 129.1, 129.0, 128.9, 128.2, 127.8, 123.5 (q, *J* = 261.9 Hz), 60.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -54.7 (d, *J* = 1.6 Hz, 3F); HRMS (EI$^+$) *m/z* calcd for $C_{17}H_{12}F_3N$: 287.0916, found 287.0917.

*(E)-N-(Perfluoroethyl)-3,4-diphenylcyclobut-2-en-1-imine ((E)-**9b**):* Yield: 72 %, *E*/*Z* = 80:20, white solid; ^{1}H



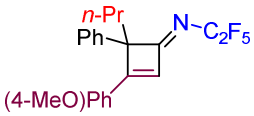
NMR (401 MHz, $CDCl_3$) δ 7.58–7.28 (m, 10H), 6.85 (t, *J* = 3.6 Hz, 1H), 4.99 (s, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0 (t, *J* = 12.7 Hz), 169.8 (t, *J* = 1.9 Hz), 135.4, 132.4, 130.2, 129.4, 129.2, 129.1, 129.0, 128.2, 127.8, 118.6 (qt, *J* = 286.5, 44.4 Hz), 116.0 (tq, *J* = 261.4, 38.7 Hz), 59.5; ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.7 (m, 3F), -95.9 (dm, *J* = 4.0 Hz, 1F), -95.9 (dm, *J* = 4.0 Hz, 1F); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{13}F_5N$: 338.09630, found 338.09627.

*(Z)-N-(Perfluoroethyl)-3,4-diphenylcyclobut-2-en-1-imine ((Z)-**9b**):* ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.61–7.27

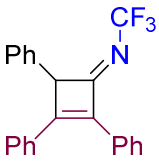


(m, 10H), 6.87 (s, 1H), 5.06 (t, *J* = 1.8 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2 (t, *J* = 10.5 Hz), 169.6 (t, *J* = 1.7 Hz), 135.7, 132.3, 130.2, 129.4, 129.1, 128.9, 128.8, 128.1, 127.7, 118.3 (qt, *J* = 285.7, 44.0 Hz), 115.2 (tq, *J* = 263.0, 39.2 Hz), 61.0.; ^{19}F NMR (377 MHz, $CDCl_3$) δ -86.1 to -86.5 (m, 3F), -94.0 (dt, *J* = 198.2, 1.7 Hz, 1F), -96.2 (dt, *J* = 198.2, 1.8 Hz, 1F); HRMS (ESI$^+$) *m/z* calcd for $C_{18}H_{13}F_5N$: 338.09630, found 338.09627.

*(E)-3-(4-Methoxyphenyl)-N-(perfluoroethyl)-4-phenyl-4-propylcyclobut-2-en-1-imine ((E)-**9c**):* Yield: 81 %,

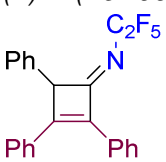


E/*Z* = 96:4, colorless liquid; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.52–7.48 (m, 2H), 7.46–7.42 (m, 2H), 7.35–7.30 (m, 2H), 7.29–7.26 (m, 1H), 6.96–6.90 (m, 2H), 6.64 (t, *J* = 3.6 Hz, 1H), 3.86 (s, 3H), 2.50 (ddd, *J* = 14.1, 12.3, 4.5 Hz, 1H), 2.19 (ddd, *J* = 14.1, 12.5, 4.5 Hz, 1H), 1.48–1.35 (m, 1H), 1.28–1.15 (m, 1H), 0.96 (t, *J* = 7.3 Hz, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.9 (t, *J* = 12.5 Hz), 172.1 (t, *J* = 1.8 Hz), 162.9, 140.0, 131.0, 128.6, 127.5, 126.7, 124.5, 123.3, 118.7 (qt, *J* = 286.8, 45.1 Hz), 116.3 (tq, *J* = 259.2, 38.5 Hz), 114.8, 66.0, 55.6, 34.0, 18.7, 14.7; ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.6 (3F), -94.5 (dd, *J* = 197.6, 3.1 Hz, 1F), -95.7 (dd, *J* = 198.5, 3.9 Hz, 1F); HRMS (ESI$^+$) *m/z* calcd for $C_{22}H_{21}F_5NO$: 410.15378, found 410.15348.



*(E)-2,3,4-Triphenyl-N-(trifluoromethyl)cyclobut-2-en-1-imine (**10a**):* Yield: 74 %, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.88 (m, 2H), 7.69–7.59 (m, 2H), 7.56–7.29 (m, 11H), 5.14 (q, *J* = 1.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5 (q, *J* = 8.9 Hz), 160.4, 141.3, 136.4, 131.7, 131.3, 129.7, 129.6, 129.1, 129.0, 128.9, 128.9, 128.3, 128.1, 128.0, 123.8 (q, *J* = 262.3 Hz), 60.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -54.2 (s, 3F); IR (cm^{-1}, $CHCl_3$) 1695 (s, C=N), 1612 (m, C=C), 3090 (w), 3067 (w), 1599 (w), 1588 (w), 1496 (w), 1486 (w), 1030 (w), 714 (m), 699 (m), 689 (m, Ph), 1364 (w), 1256 (s, CF_3); HRMS (EI) *m/z* calcd for $C_{23}H_{16}F_3N$: 363.1229, found 363.1230.

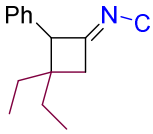
*(E)-N-(Perfluoroethyl)-2,3,4-triphenylcyclobut-2-en-1-imine (**10b**):* Yield: 75 %, white solid, m.p. 106-108



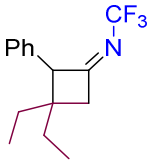
℃; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.96–7.89 (m, 2H), 7.65–7.58 (m, 2H), 7.54–7.27 (m, 11H), 5.10 (t, *J* = 2.4 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6 (t, *J* = 10.2 Hz), 160.8 (t, *J* = 1.5 Hz), 141.8, 136.7, 131.7, 131.4, 129.8, 129.6, 129.1, 129.0, 128.9, 128.9, 128.4, 128.1, 128.0, 118.4 (qt, *J* = 286.1, 44.0 Hz), 115.6 (ddq, *J* = 267.3, 264.3, 39.0 Hz), 61.3; ^{19}F NMR (377 MHz, $CDCl_3$) δ -86.1 (m, 3F), -93.4 (dm, *J* = 197.8 Hz, 2F), -95.8 (dm, *J* = 197.8 Hz, 2F); IR (cm^{-1}, $CHCl_3$) 1696 (m, C=N), 1612 (w, C=C), 3088 (w), 3066 (w), 1599 (w), 1588 (w), 1498 (w), 1485 (w), 1455 (w), 1445

(w), 700 (m), 690 (m, Ph), 1364 (w, CF_3), 1162 (m, C_2F_5); HRMS (APCI$^+$) *m/z* calcd for $C_{24}H_{17}F_5N$: 414.12778, found 414.12757. X-ray analysis: see section 9 Crystallographic data.

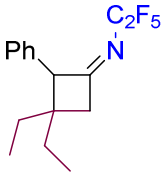
*(E)-3,3-Diethyl-2-phenyl-N-(trifluoromethyl)cyclobutan-1-imine ((E)-**11a**):* Yield: 79 %, *E*/*Z* = 92:8, orange liquid; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.35–7.22 (m, 5H), 4.28 (q, *J* = 2.4 Hz, 1H), 2.88 (m, 2H), 1.78 (q, *J* = 7.4 Hz, 2H), 1.27 (q, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.65 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2 (q, *J* = 9.6 Hz), 134.9, 128.9, 128.5, 127.4, 123.7 (q, *J* = 263.7 Hz), 63.0, 46.9, 42.5 (q, *J* = 1.4 Hz), 31.0, 26.0, 9.0, 8.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.1 (q, *J* = 2.2 Hz, 3F); IR (cm^{-1}, $CHCl_3$) 1708 (m, C=N), 3089 (w), 3065 (w), 3009 (w), 1603 (w), 1579 (w), 1497 (w), 1069 (m), 1032 (w), 698 (m, Ph), 1398 (w), 1245 (s, CF_3), 2968 (w), 2939 (w), 2879 (w), 2862 (w), 1459 (w); HRMS (EI) *m/z* calcd for $C_{15}H_{18}F_3N$: 269.1386, found 269.1384.



*(Z)-3,3-Diethyl-2-phenyl-N-(trifluoromethyl)cyclobutan-1-imine ((Z)-**11a**):* ^{19}F NMR (377 MHz, $CDCl_3$) δ -58.4 (q, *J* = 2.1 Hz, 3F).; HRMS (EI) *m/z* calcd for $C_{15}H_{18}F_3N$: 269.1386, found 269.1384.

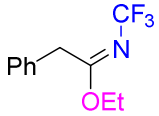


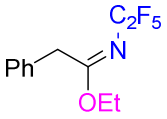
*(E)-3,3-Diethyl-N-(perfluoroethyl)-2-phenylcyclobutan-1-imine ((E)-**11b**):* Yield: 89 %, *E*/*Z* = 93:7, orange liquid; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.35–7.20 (m, 5H), 4.30 (t, *J* = 2.9 Hz, 1H), 2.90 (t, *J* = 3.4 Hz, 2H), 1.78 (q, *J* = 7.4 Hz, 2H), 1.26 (q, *J* = 7.4 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.64 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8 (t, *J* = 12.5 Hz), 135.0, 128.9, 128.5, 127.4, 118.6 (qt, *J* = 286.1, 43.3 Hz), 115.7 (ddq, *J* = 267.5, 258.2, 38.7 Hz), 63.7, 47.9, 42.8 (t, *J* = 1.4 Hz), 30.9, 26.0, 8.9, 8.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -85.9 (s, 3F), -97.0 (dq, *J* = 201.3, 3.4 Hz, 1F), -99.3 (dq, *J* = 201.3, 3.3 Hz, 1F); IR (cm^{-1}, $CHCl_3$) 1710 (m, C=N), 3089 (w), 3065 (w), 3009 (w), 1603 (w), 1582 (w), 1497 (w), 1065 (m), 699 (m, Ph), 1381 (w, CF_3), 1161 (m, C_2F_5), 2968 (w), 2939 (w), 2879 (w), 2862 (w), 1459 (w); HRMS (EI) *m/z* calcd for $C_{16}H_{18}F_5N$: 319.1354, found 319.1356.

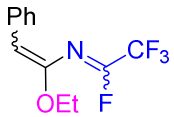


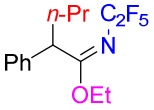
*(Z)-3,3-Diethyl-2-phenyl-N-(trifluoromethyl)cyclobutan-1-imine ((Z)-**11b**):* ^{19}F NMR (377 MHz, $CDCl_3$) δ -86.2 (s, *3F*), -97.9 (dm, *J* = 202.0 Hz, 1F), -100.7 (dt, *J* = 202.0, 3.4 Hz, 1F); HRMS (EI) *m/z* calcd for $C_{16}H_{18}F_5N$: 319.1354, found 319.1356.

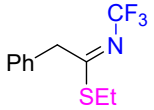
*Ethyl (E)-2-phenyl-N-(trifluoromethyl)acetimidate (**12a**):* Yield: 93%, colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.27 (m, 5H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3 (q, *J* = 6.7 Hz), 134.0, 129.2, 128.7, 127.3, 124.1 (q, *J* = 256.0 Hz), 64.2, 38.9 (q, *J* = 1.9 Hz), 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -50.5 (s, 3F); IR (cm^{-1}, $CHCl_3$) 1653 (s, C=N), 3090 (w), 3067 (w), 3034 (w), 1604 (w), 1586 (w), 700 (m, Ph), 1249 (s), 1150 (w, CF_3), 2986 (w), 2940 (w), 2907 (w), 1477 (w), 1455 (w), 1376 (m), 1150 (s, OEt); HRMS (EI) *m/z* calcd for $C_{11}H_{12}F_3NO$: 231.0866, found 231.0867.

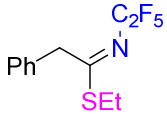


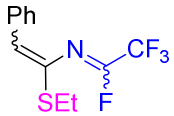
*Ethyl (E)-N-(perfluoroethyl)-2-phenylacetimidate (**12b**):* Yield: 43 %, colorless liquid; ^{1}H NMR (400 MHz, 
$CDCl_3$) δ 7.36–7.24 (m, 5H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 134.1, 129.2, 128.7, 127.3, 118.5 (qt, *J* = 285.0, 45.9 Hz), 114.3 (tq, *J* = 265.3, 38.9 Hz), 64.4, 39.9 (t, *J* = 2.1 Hz), 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.39 (s, 3F), -90.70 (s, 2F); IR (cm^{-1}, $CHCl_3$) 1668 (s), 1646 (m, C=N), 3090 (w), 3067 (w), 3037 (w), 1603 (w), 1586 (w), 1496 (m), 701 (m, Ph), 1353 (w, CF_3), 1168 (m, C_2F_5), 2986 (w), 2941 (w), 2908 (w), 2871 (w), 1477 (w), 1466 (w), 1455 (w), 1445 (w), 1411 (w), 1318 (s), 1188 (s), 951 (m), 939 (m, OEt); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{13}F_5NO$: 282.09118, found 282.09128.

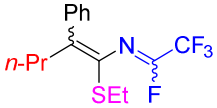
*(Z)-N-((E)-1-(ethylthio)-2-phenylvinyl)-2,2,2-trifluoroacetimidoyl fluoride (**12b'**):* ^{19}F NMR Yield: ca 16 %, ^{19}F 
NMR (376 MHz, $CDCl_3$) δ -41.41 (m, 1F), -72.99 (m, 3F).

*Ethyl (E)-N-(perfluoroethyl)-2-phenylpentanimidate (**12c**):* Yield: 60 %, colorless liquid; ^{1}H NMR (400 MHz, 
$CDCl_3$) δ 7.38–7.24 (m, 5H), 4.32–4.14 (m, 2H), 4.08 (td, *J* = 7.7, 1.0 Hz, 1H), 2.07–1.97 (m, 1H), 1.85 (dddd, *J* = 13.3, 9.8, 7.5, 5.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.28–1.23 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 138.7, 128.63, 128.5, 127.5, 118.5 (qt, *J* = 285.0, 46.0 Hz), 118.5 (tq, *J* = 284.6, 46.0 Hz), 64.2, 49.9, 36.4, 20.8, 13.9, 13.6.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.61 (d, *J* = 1.5 Hz, 3F), -88.88 (d, *J* = 201.0 Hz, 1F), -90.21 (d, *J* = 201.0 Hz, 1F); HRMS (EI$^+$) *m/z* calcd for $C_{15}H_{18}F_5NO$: 323.1203, found 323.1300.

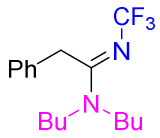
*Ethyl (E)-2-phenyl-N-(trifluoromethyl)ethanimidothioate (**13a**):* Yield: 97 %, colorless liquid; ^{1}H NMR (400 
MHz, $CDCl_3$) δ 7.41–7.26 (m, 5H), 4.00 (s, 2H), 2.96 (q, *J* = 7.4 Hz, 2H), 1.27 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7 (q, *J* = 7.3 Hz), 134.4, 129.8, 128.8, 127.7, 122.6 (q, *J* = 261.0 Hz), 43.3 (q, *J* = 1.6 Hz), 25.9, 13.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -52.7 (s, 3F).; IR (cm^{-1}, $CHCl_3$) 1611 (s, C=N), 3090 (w), 3067 (w), 3033 (w), 1600 (s), 1497 (m), 699 (m, Ph), 1246 (s), 1130 (s, CF_3), 2976 (w), 2933 (w), 2875 (w), 1455 (m), 1408 (w), 1376 (w), 1311 (w, SEt); HRMS (EI$^+$) *m/z* calcd for $C_{11}H_{12}F_3NS$: 247.0637, found 247.0639.

*Ethyl (E)-N-(perfluoroethyl)-2-phenylethanimidothioate (**13b**):* Yield: 59 %, colorless liquid; ^{1}H NMR (400 
MHz, $CDCl_3$) δ 7.39–7.26 (m, 5H), 4.04 (s, 2H), 2.93 (q, *J* = 7.4 Hz, 2H), 1.25 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 134.5, 129.8, 128.8, 127.7, 118.5 (qt, *J* = 285.1, 45.1 Hz), 113.5 (tq, *J* = 271.3, 38.7 Hz), 44.3, 26.3, 13.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -86.9 (s, 3F), -92.9 (s, 2F); IR (cm^{-1}, $CHCl_3$) 1623 (s), 1596 (s, C=N), 3090 (w), 3067 (w), 3009 (m), 1497 (m), 699 (s, Ph), 1345 (w, CF_3), 1179 (s, C_2F_5), 2976 (w), 2934 (w), 2876 (w), 1455 (m), 1412 (w), 1306 (w, SEt); HRMS (ESI$^+$) *m/z* calcd for $C_{12}H_{13}F_5NS$: 298.06834, found 298.06860.

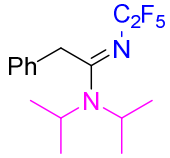
*(Z)-N-((E)-1-(Ethylthio)-2-phenylvinyl)-2,2,2-trifluoroacetimidoyl fluoride (**13b'**):* ^{19}F NMR Yield: ca 16 %, ^{19}F 
NMR (376 MHz, $CDCl_3$) δ -41.51 (m, 1F), -72.88 (m, 3F).

*(Z)-N-((E)-1-(Ethylthio)-2-phenylpent-1-en-1-yl)-2,2,2-trifluoroacetimidoyl fluoride (**13c'**):* Yield: 76 %, 

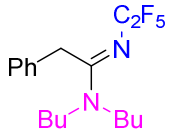
colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.20 (m, 5H), 2.56–2.33 (m, 4H), 1.32–1.24 (m, 2H), 1.14 (t, *J* = 7.3 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.9 (dq, *J* = 364.4, 44.0 Hz), 140.4 (d, *J* = 2.0 Hz), 139.9, 129.7 (d, *J* = 1.8 Hz), 128.9, 128.1, 127.6, 115.4 (qd, *J* = 276.8, 66.8 Hz), 27.2, 21.0, 14.7, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -44.2 (q, *J* = 5.7 Hz, 1F), -72.7 (d, *J* = 5.4 Hz, 3F).; HRMS (APCI$^+$) *m/z* calcd for $C_{15}H_{18}F_4NS$: 320.10906, found 320.10934.

*(E)-N,N-Dibutyl-2-phenyl-N'-(trifluoromethyl)acetimidamide (**14a**):* ^{19}F NMR yield: quantitative; brown liquid; 

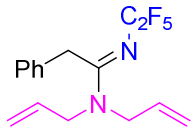
^{19}F NMR (376 MHz, $CDCl_3$) δ -45.43 (s, 3F); LRMS (EI) *m/z* calcd for $C_{17}H_{25}F_3N_2$: 314.2, found 314.2.

*(E)-N,N-Diisopropyl-N'-(perfluoroethyl)-2-phenylacetimidamide (**14b**):* ^{19}F NMR yield: 77%; brown liquid; ^{19}F 

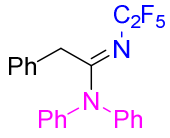
NMR (376 MHz, $CDCl_3$) δ -83.0 to -83.2 (m, 2F), -87.3 to -87.5 (m, 3F).

*(E)-N,N-Dibutyl-N'-(perfluoroethyl)-2-phenylacetimidamide (**14c**):* ^{19}F NMR yield: quantitative; brown liquid; 

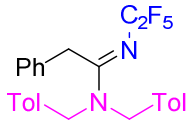
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.31 (m, 2H), 7.29–7.25 (m, 1H), 7.21–7.14 (m, 2H), 4.03 (s, 2H), 3.53–3.42 (m, 2H), 3.12–3.03 (m, 2H), 1.71–1.59 (m, 2H), 1.34 (m, 4H), 1.24–1.10 (m, 2H), 0.98 (t, *J* = 7.4, 3H), 0.84 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.5 (s, 2F), -87.2 to -87.5 (m, 3F).

*(E)-N,N-Diallyl-N'-(perfluoroethyl)-2-phenylacetimidamide (**14d**):* ^{19}F NMR yield: quantitative; brown liquid; 

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.22–7.27 (m, 1H), 7.17–7.12 (m, 2H), 5.87 (ddt, *J* = 16.6, 10.1, 6.2 Hz, 1H), 5.53 (ddt, *J* = 15.7, 10.2, 5.0 Hz, 1H), 5.22–5.06 (m, 4H), 4.14 (d, *J* = 6.2 Hz, 2H), 4.03–3.99 (m, 2H), 3.72 (t, *J* = 6.4 Hz, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.1 (s, 2F), -87.4 (t, *J* = 2.2 Hz, 3F).

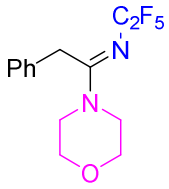
*(E)-N'-(Perfluoroethyl)-N,N,2-triphenylacetimidamide (**14e**):* ^{19}F NMR yield: quantitative; orange oil; ^{1}H NMR 

(400 MHz, $CDCl_3$) δ 7.30–6.84 (m, 15H), 4.05 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -87.1 (m, 2F), -87.4 (m, 3F).

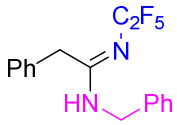
*(E)-N,N-Bis(4-methylbenzyl)-N'-(perfluoroethyl)-2-phenylacetimidamide (**14f**):* Yield: quantitative; brown 

liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.17 (m, 11H), 6.99 (d, *J* = 7.7 Hz, 2H), 4.86 (s, 2H), 4.33 (s, 2H), 4.13 (s, 2H), 2.42 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 137.7, 137.5, 134.9, 134.0, 132.9, 129.9, 129.4, 129.1, 128.9, 127.8, 127.1, 126.3, 118.1 (tq, *J* = 284.3, 48.5 Hz), 115.7 (qt, *J* = 269.4, 38.1 Hz), 50.4, 50.3, 37.3, 21.2, 21.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -84.8 (s, 2F), -87.1 (s, 3F).; HRMS (ESI$^+$) *m/z* calcd for $C_{26}H_{26}F_5N_2$: 461.20121, found 461.20107.

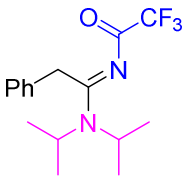
*(E)-1-Morpholino-N-(perfluoroethyl)-2-phenylethan-1-imine (**14g**):* ^{19}F NMR yield: 82%; brown liquid; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.0 (s, 2F), -87.3 to -87.4 (m, 3F).



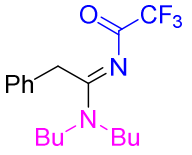
*(E)-N-Benzyl-N'-(perfluoroethyl)-2-phenylacetimidamide (**14h**):* ^{19}F NMR yield: quantitative; brown liquid; decomposed at room temperature on air; ^{19}F NMR (376 MHz, $CDCl_3$) δ -85.93 (s, 2F), -87.17 to -87.34 (m, 3F).



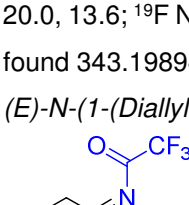
*(E)-N-(1-(Diisopropylamino)-2-phenylethylidene)-2,2,2-trifluoroacetamide (**15b**):* Yield: 66 %, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.28 (m, 2H), 7.27–7.19 (m, 3H), 4.16 (s, 2H), 4.11 (hept, J = 6.7 Hz, 1H), 3.67–3.50 (m, 1H), 1.51 (d, J = 6.9 Hz, 6H), 0.95 (d, J = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.5 (q, J = 35.5 Hz), 135.1, 129.1, 128.0, 127.2, 117.3 (q, J = 287.9 Hz), 51.4, 49.3, 37.8, 19.9, 19.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.5 (s, 3F); HRMS (ESI^+) *m/z* calcd for $C_{16}H_{22}F_3ON_2$: 315.16787, found 315.16769.



*(E)-N-(1-(Dibutylamino)-2-phenylethylidene)-2,2,2-trifluoroacetamide (**15c**):* Yield: 74 %, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.13 (m, 5H), 4.23 (s, 2H), 3.67–3.52 (m, 2H), 3.35–3.21 (m, 2H), 1.69–1.59 (m, 2H), 1.47–1.28 (m, 4H), 1.28–1.17 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 163.8 (q, J = 35.4 Hz), 134.8, 129.0, 128.1, 127.2, 117.1 (q, J = 288.0 Hz), 49.6, 49.5, 36.1, 30.3, 29.0, 20.1, 20.0, 13.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.4 (s, 3F); HRMS (ESI^+) *m/z* calcd for $C_{18}H_{26}F_3ON_2$: 343.19917, found 343.19894.

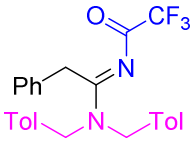


*(E)-N-(1-(Diallylamino)-2-phenylethylidene)-2,2,2-trifluoroacetamide (**15d**):* Yield: 68 %, orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.17 (m, 5H), 5.83 (ddt, J = 16.7, 11.8, 4.0 Hz, 1H), 5.53 (ddt, J = 16.4, 10.4, 5.4 Hz, 1H), 5.29–5.12 (m, 4H), 4.24 (d, J = 6.5 Hz, 2H), 4.21 (s, 2H), 3.91 (d, J = 5.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 164.6 (q, J = 35.7 Hz), 134.4, 130.8, 130.8, 129.2, 128.1, 127.4, 119.6, 119.0, 117.0 (q, J = 288.1 Hz), 51.6, 50.8, 36.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.5 (s, 3F); HRMS (EI) *m/z* calcd for $C_{16}H_{17}F_3ON_2$: 310.1287, found 310.1285.



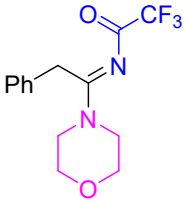
*(E)-N-(1-(Diphenylamino)-2-phenylethylidene)-2,2,2-trifluoroacetamide (**15e**):* Yield: 68 %, off-white solid, m.p. 105-107 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.27 (m, 7H), 7.25–7.03 (m, 5H), 7.03–6.97 (m, 1H), 4.11–4.09 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 164.9 (q, J = 36.6 Hz), 142.9 (bs), 141.6 (bs), 134.6, 129.7 (bs), 129.3 (bs), 128.8 (bs), 128.7, 128.7, 128.0 (bs), 127.6 (bs), 127.1, 126.4 (bs), 116.5 (q, J = 288.1 Hz), 37.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.4 (s, 3F); HRMS (ESI^+) *m/z* calcd for $C_{22}H_{18}F_3ON_2$: 383.13657, found 383.13643.

*(E)-N-(1-(Bis(4-methylbenzyl)amino)-2-phenylethylidene)-2,2,2-trifluoroacetamide (**15f**):* Yield: 70 %, white



solid, m.p. 85-88 °C; ^{1}H NMR (401 MHz, $CDCl_3$) δ 7.35–7.12 (m, 11H), 6.95–6.88 (m, 2H), 4.83 (s, 2H), 4.43 (s, 2H), 4.30 (s, 2H), 2.38 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 164.9 (q, *J* = 35.9 Hz), 138.3, 138.1, 134.4, 132.4, 131.2, 130.0, 129.7, 129.2, 128.8, 128.2, 127.4, 126.7, 117.1 (q, *J* = 288.1 Hz), 51.2, 50.7, 36.2, 21.3, 21.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -76.3 (s, 3F); IR (cm^{-1}, $CHCl_3$) 1665 (m, C=O), 1549 (s, C=N), 3040 (w), 3067 (w), 3026 (w), 1604 (w), 1588 (w), 1496 (m), 1454 (m), 1198 (m), 1029 (w), 1003 (w), 701 (m, Ph), 1359 (m, CF_3); HRMS (ESI$^+$) *m/z* calcd for $C_{26}H_{26}F_3ON_2$: 439.19917, found 439.19910. X-ray analysis: see section 9 Crystallographic data.

*(E)-2,2,2-Trifluoro-N-(1-morpholino-2-phenylethylidene)acetamide (**15g**):* Yield: 52 %, yellow oil; ^{1}H NMR

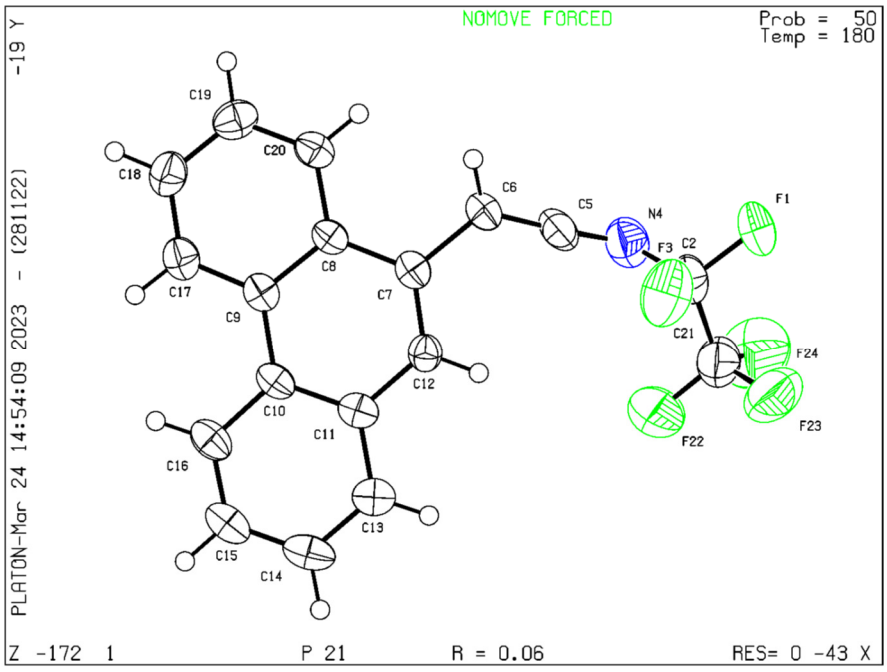


(400 MHz, $CDCl_3$) δ 7.35–7.26 (m, 2H), 7.26–7.18 (m, 3H), 4.21 (s, 2H), 3.93 (dd, *J* = 5.7, 4.2 Hz, 2H), 3.73–3.66 (m, 2H), 3.46 (td, *J* = 4.4, 1.1 Hz, 2H), 3.42–3.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 164.9 (q, *J* = 35.9 Hz), 134.3, 129.2, 127.9, 127.4, 116.9 (q, *J* = 287.9 Hz), 66.2, 66.0, 47.4, 45.9, 35.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.4 (s, 3F); HRMS (EI) *m/z* calcd for $C_{14}H_{15}F_3O_2N_2$: 300.1080, found 300.1087.

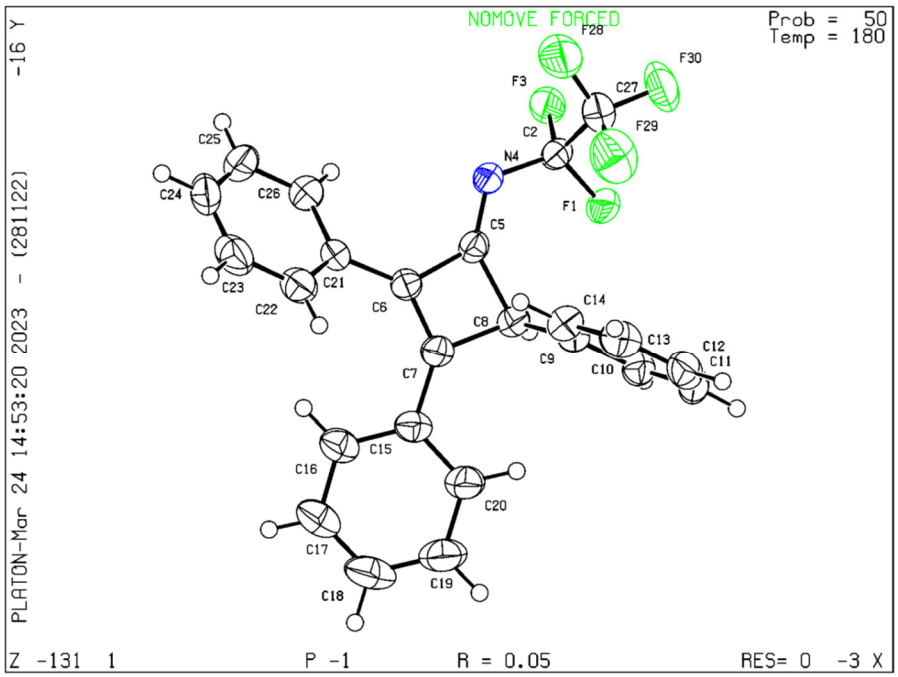
9 Crystallographic data

Single-crystal diffraction data of **2i**, **10b** and **15f** were collected at 180 K using Bruker D8 VENTURE system equipped with a Photon 100 CMOS detector, a multilayer monochromator, and a Cu-Kα (**2i, 15f**) or Mo-Kα (**10b**) Incoatec microfocus sealed tube (λ = 1.54178 Å and 0.71073 Å respectively). The frames were integrated with the with Bruker SAINT[5] software package. The structure was solved by direct methods with SIR92[6] and were refined by full-matrix least-squares on F with CRYSTALS.[7] The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. All hydrogen atoms were located in a difference Fourier map and then they were repositioned geometrically. They were initially refined with soft restraints on the bond lengths and angles to regularise their geometry, then their positions were refined with riding constraints.

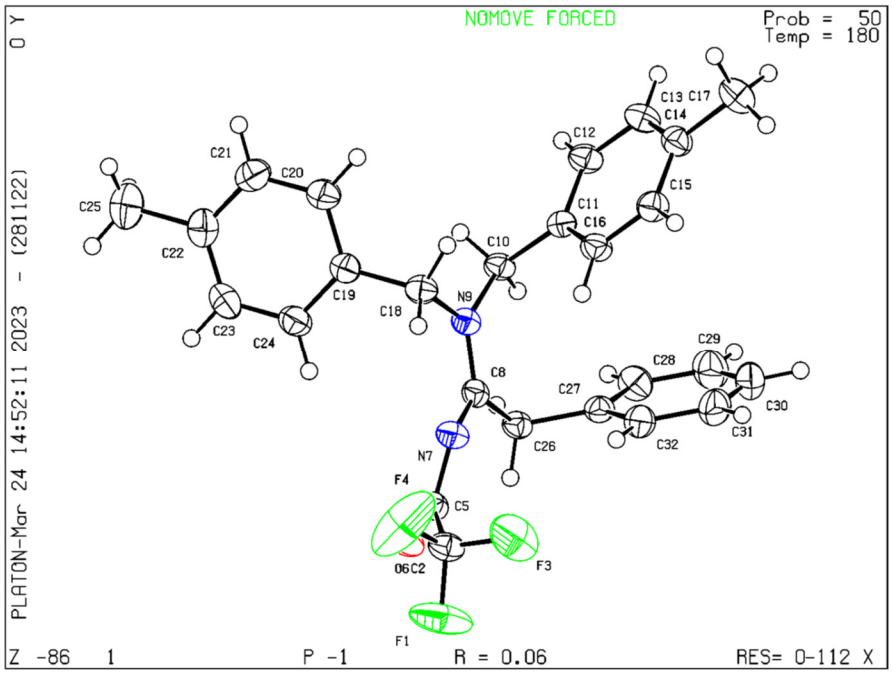
*Crystal data for **2i** (light yellow, 0.047 x 0.053 x 0.956 mm):* $C_{18}H_{10}F_5N_1$, monoclinic, space group $P2_1$, *a* = 11.4557(5) Å, *b* = 5.2006(2) Å, *c* = 13.2348(5) Å, *β* = 109.7150(18)°, *V* = 742.26(5) Å^3, *Z* = 2, *M* = 335.27, 16615 reflections measured, 2691 independent reflections. Final *R* = 0.062, *wR* = 0.069, *GoF* = 1.069 for 2563 reflections with $I > 2\sigma(I)$ and 218 parameters. Flack parameter *x* = 0.2(3). CCDC 2251499.



Crystal data for ***10b*** *(colorless, 0.021 x 0.046 x 0.081 mm):* $C_{24}H_{16}F_5N_1$, triclinic, space group *P*-1, *a* = 9.3435(3) Å, *b* = 10.6287(4) Å, *c* = 11.0605(4)) Å, α = 66.5847(13)°, *β* = 85.0791(13)°, γ = 78.7344(13)°, *V* = 988.49(4) Å^3, *Z* = 2, *M* = 413.39, 73711 reflections measured, 4532 independent reflections. Final *R* = 0.045, *wR* = 0.041, *GoF* = 1.062 for 2835 reflections with $I > 2\sigma(I)$ and 272 parameters. CCDC 2251500.



Crystal data for ***15f*** *(light yellow, 0.136 x 0.378 x 0.552 mm):* $C_{26}H_{25}F_3N_2O_1$, triclinic, space group *P*-1, *a* = 9.2049(3) Å, *b* = 11.1696(4) Å, *c* = 11.5661(4) Å, α = 100.8672(13)°, *β* = 106.0273(12)°, γ = 94.3334(12)°, *V* = 1112.14(7) Å^3, *Z* = 2, *M* = 438.49, 41508 reflections measured, 4048 independent reflections. Final *R* = 0.060, *wR* = 0.064, *GoF* = 1.107 for 3872 reflections with *I* > 2*σ*(*I*) and 290 parameters. CCDC 2251498.



10 References

(1) Blastik, Z. E.; Voltrová, S.; Matoušek, V.; Jurásek, B.; Manley, D. W.; Klepetářová, B.; Beier, P. *Angew. Chem., Int. Ed.* **2017**, *56*, 346.

(2) Markos, A.; Janecký, L.; Chvojka, T.; Martinek, T.; Martinez-Seara, H.; Klepetářová, B.; Beier, P. *Adv. Synth. Catal.* **2021**, *363*, 3258.

(3) https://cccbdb.nist.gov/vibscalejust.asp

(4) Cen, M.; Xiang, Q.; Xu, Y.; Duan, S.; Lv, Y.; Xu, Z.-F.; Li, C.-Y. *Org. Chem. Front.* **2020**, *7*, 596.

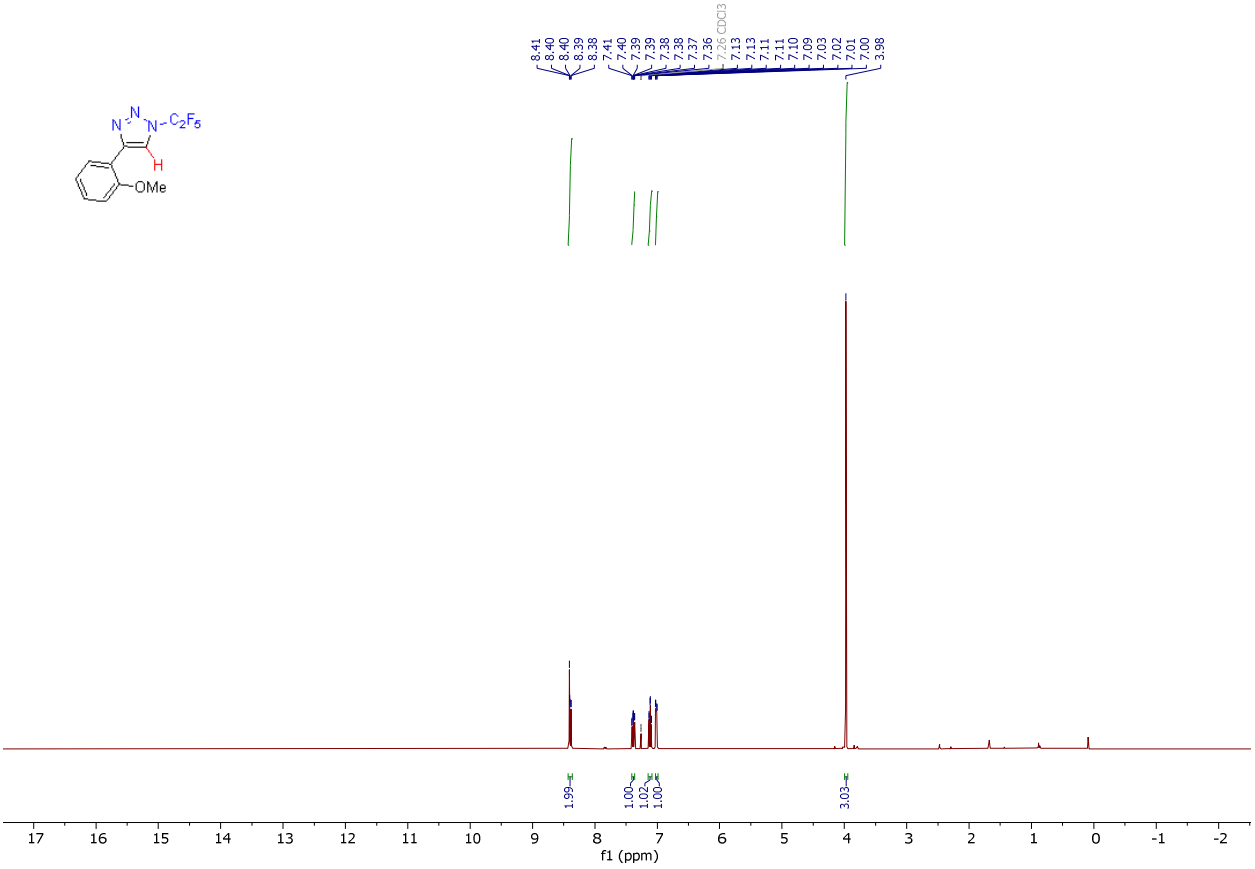
(5) SAINT. Bruker AXS Inc., Madison, Wisconsin, USA, **2015**.

(6) Altomare, A.; Cascarano, G.; Giacovazzo G.; Guagliardi A.; Burla M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994,** *27*, 435.

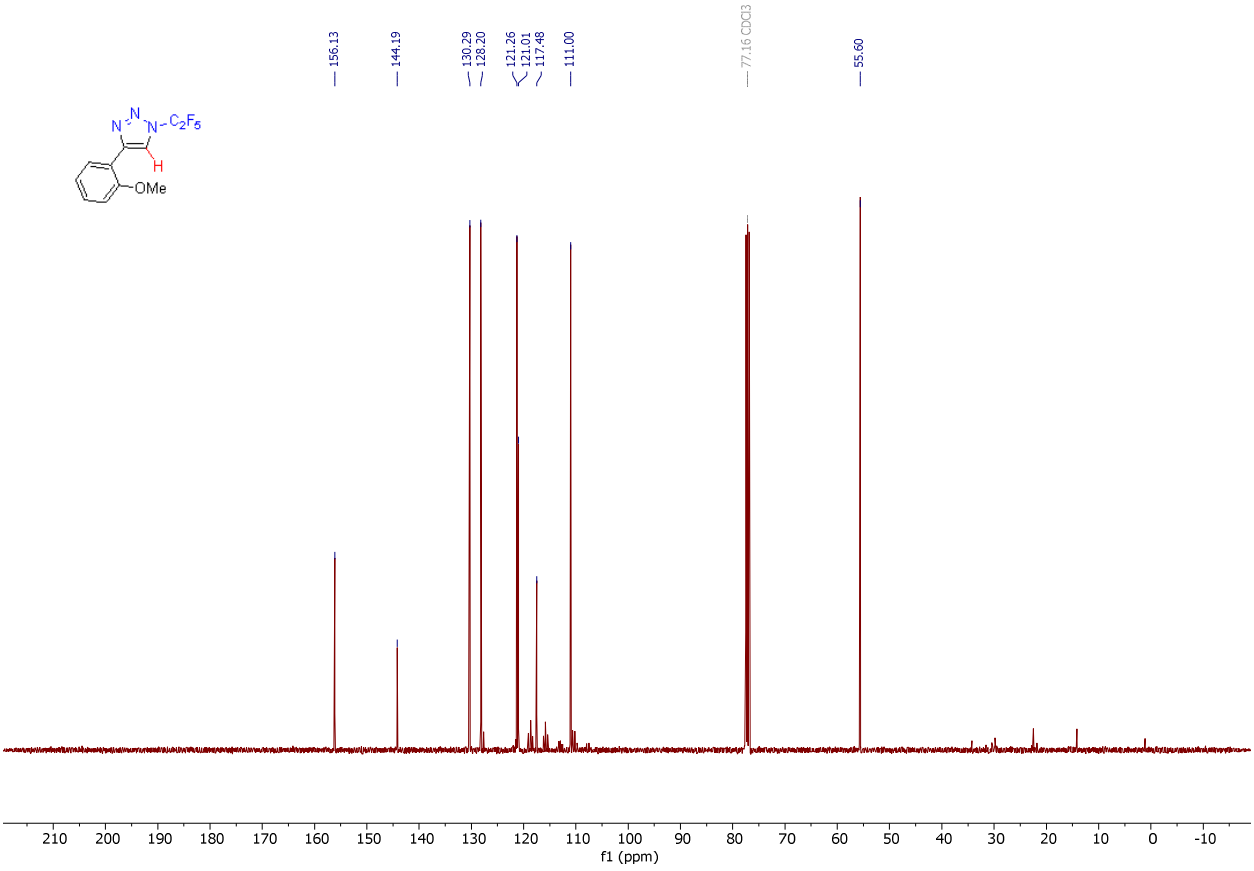
(7) Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Cryst.* **2003**, *36*, 1487.

11 Copies of NMR spectra

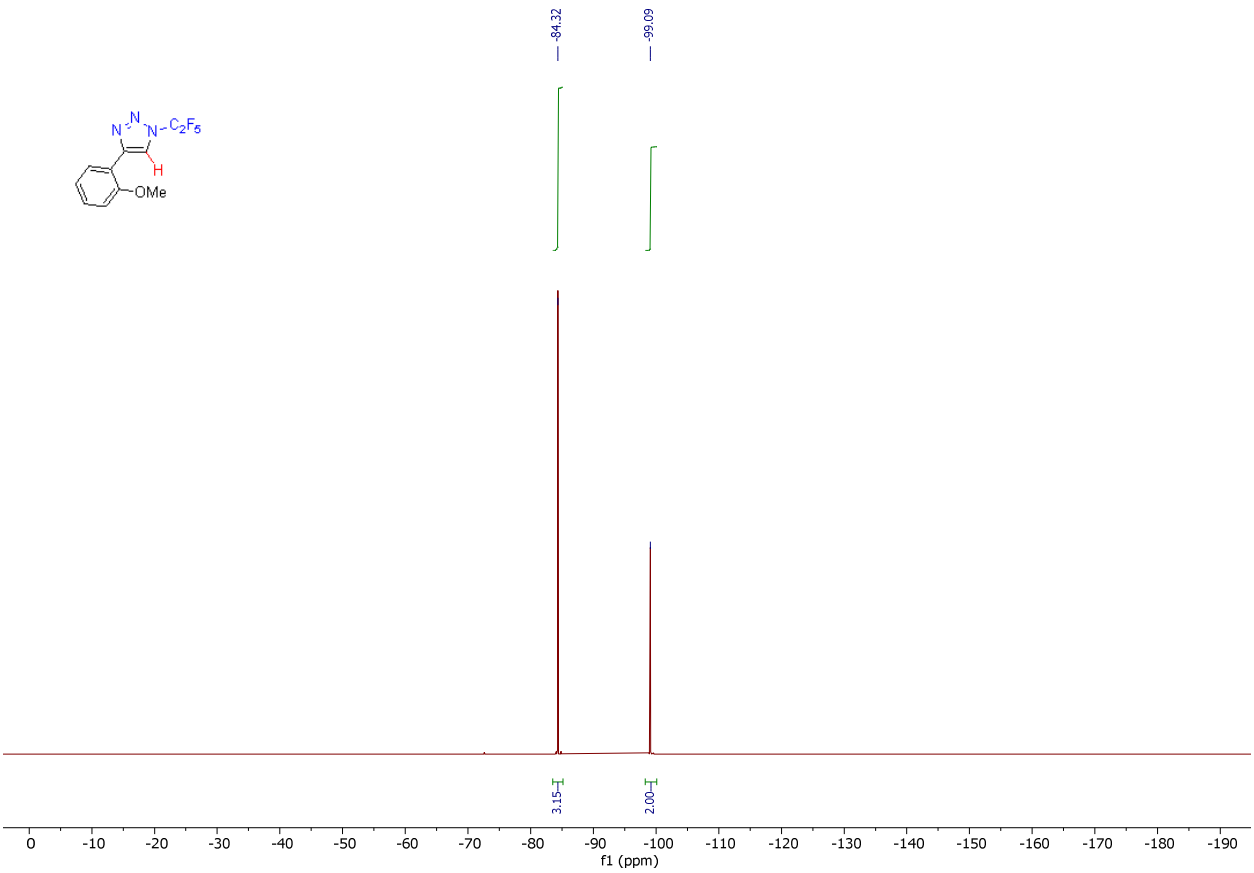
^{1}H NMR spectrum of **1d** ($CDCl_3$, 400 MHz)



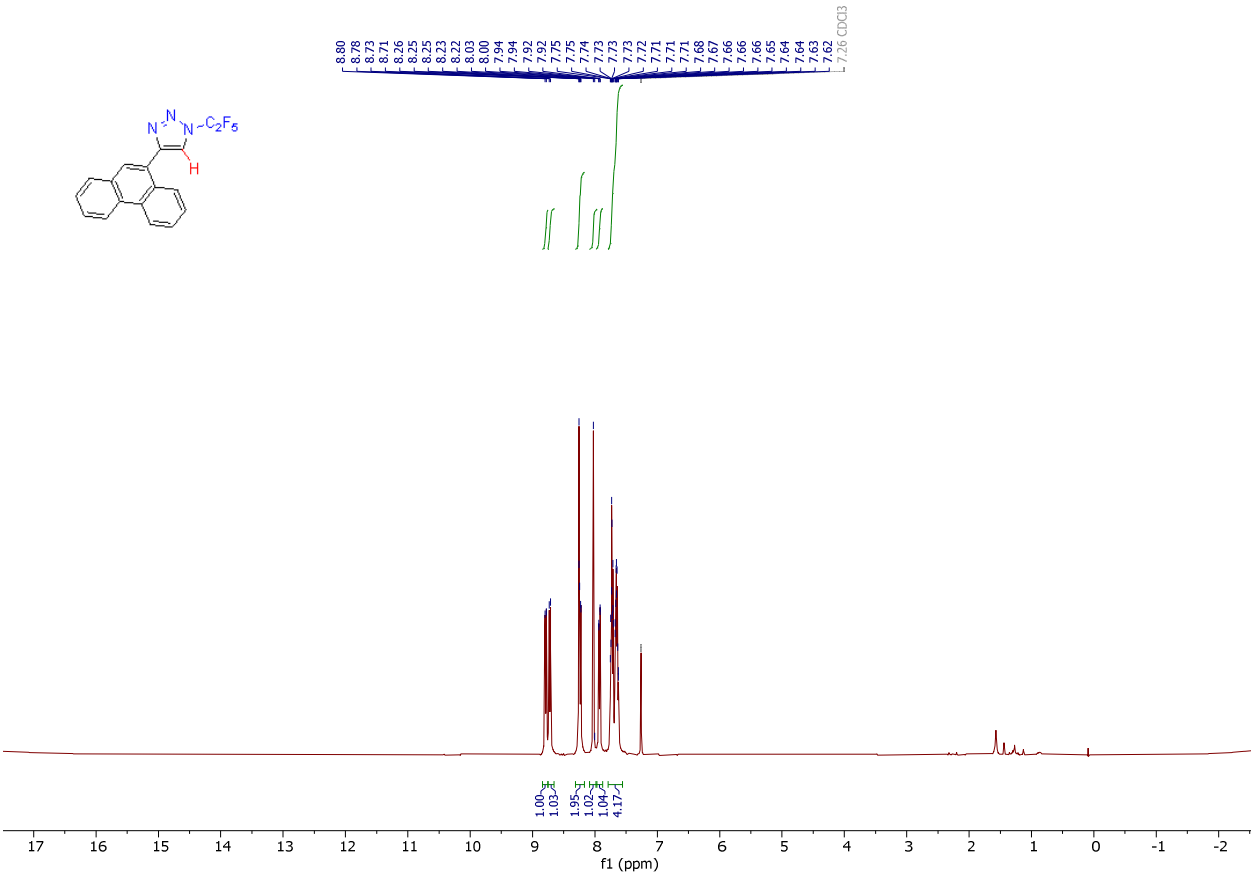
^{13}C NMR spectrum of **1d** ($CDCl_3$, 101 MHz)



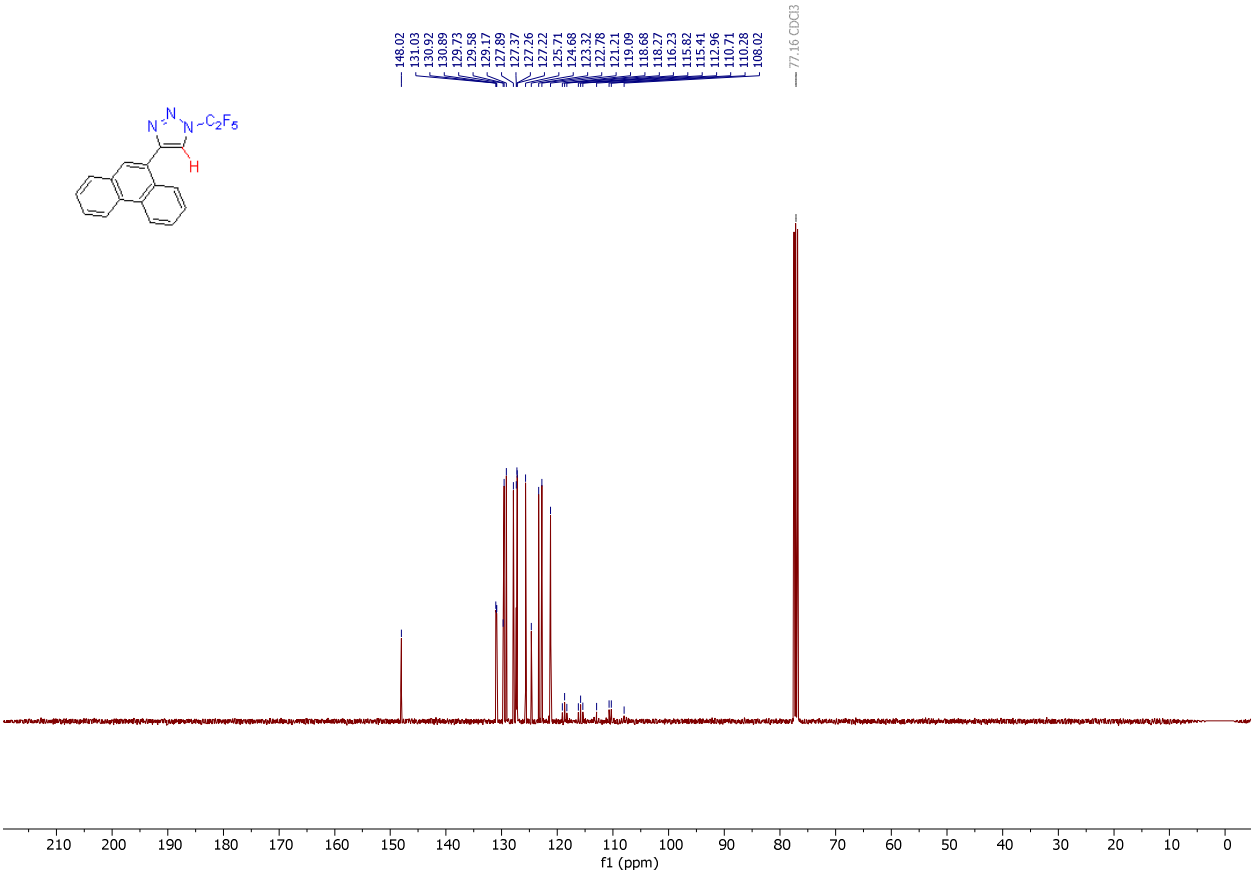
^{19}F NMR spectrum of **1d** ($CDCl_3$, 376 MHz)



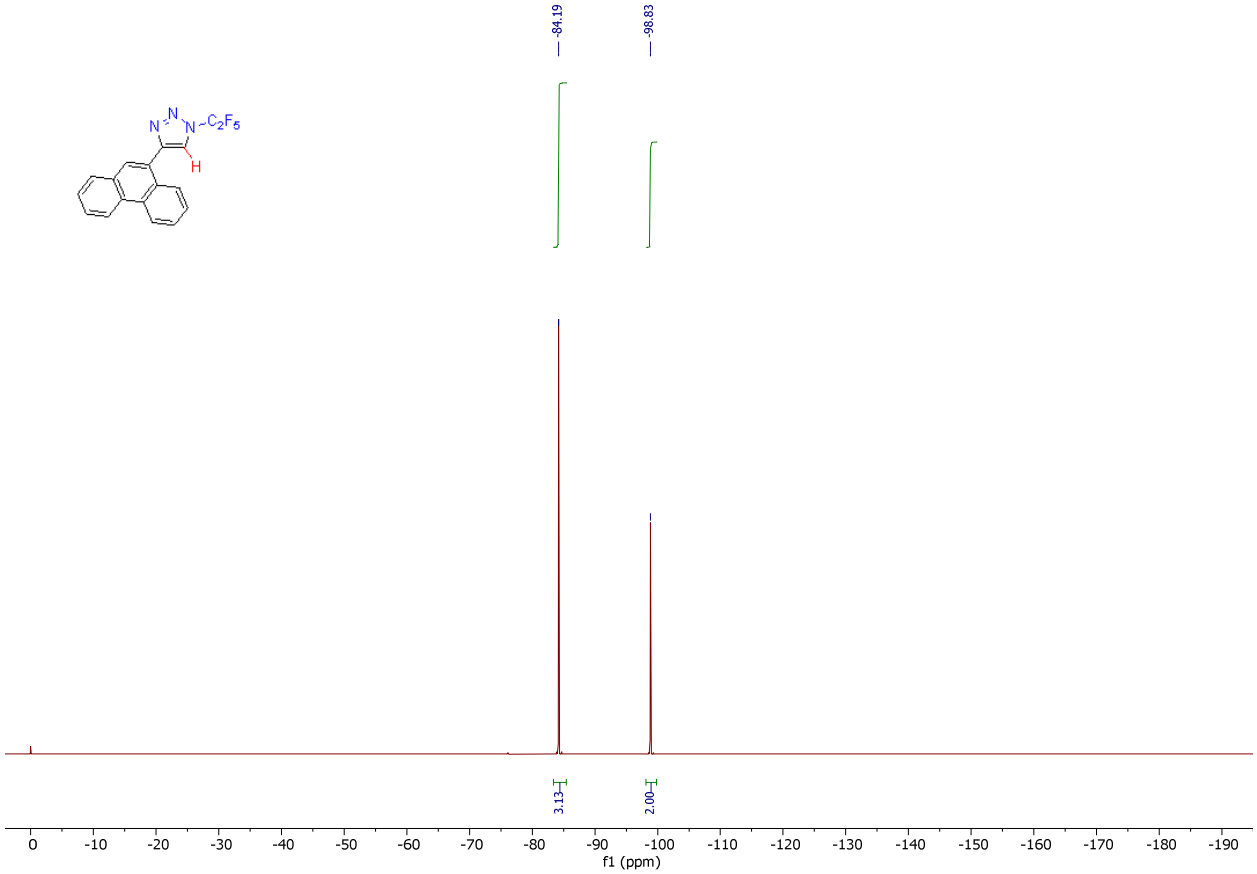
^{1}H NMR spectrum of **1i** ($CDCl_3$, 400 MHz)



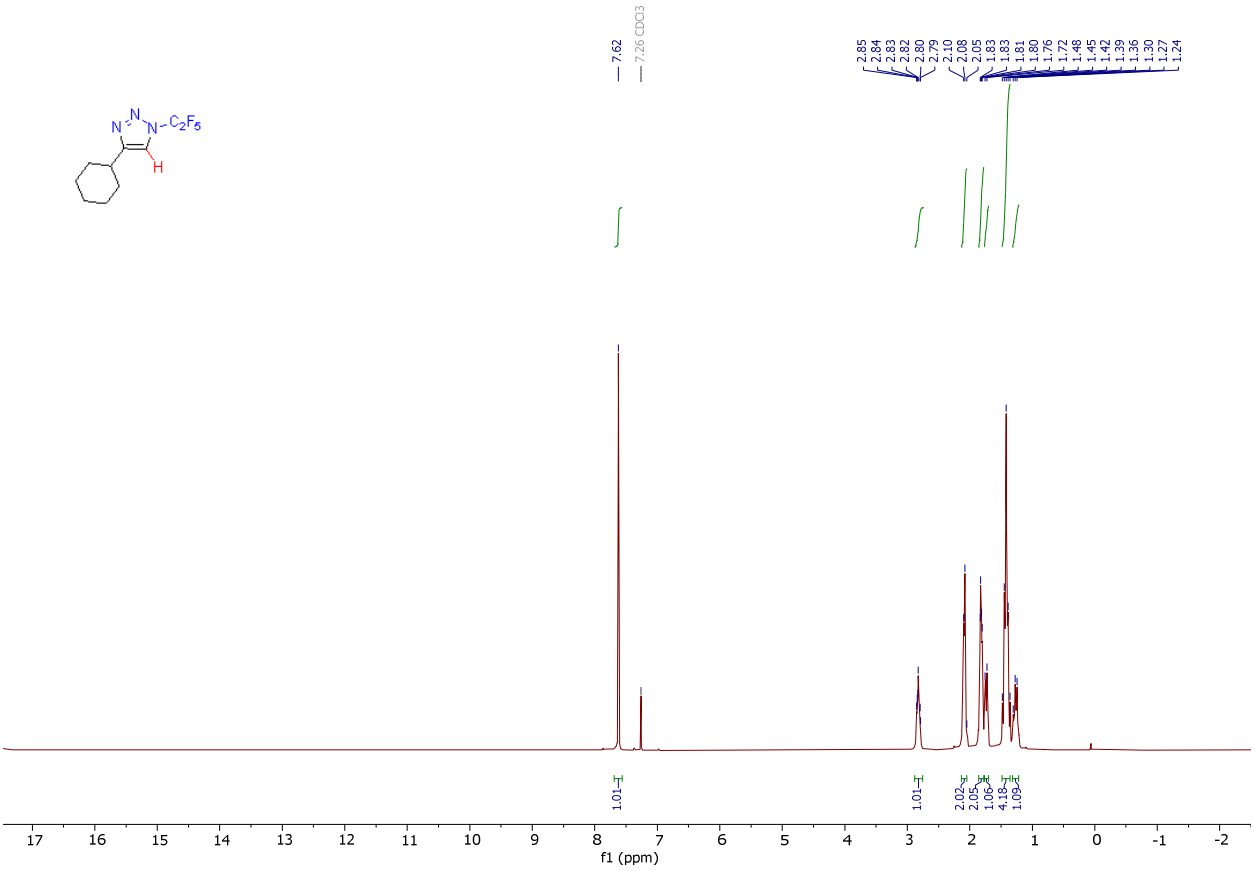
^{13}C NMR spectrum of **1i** ($CDCl_3$, 101 MHz)



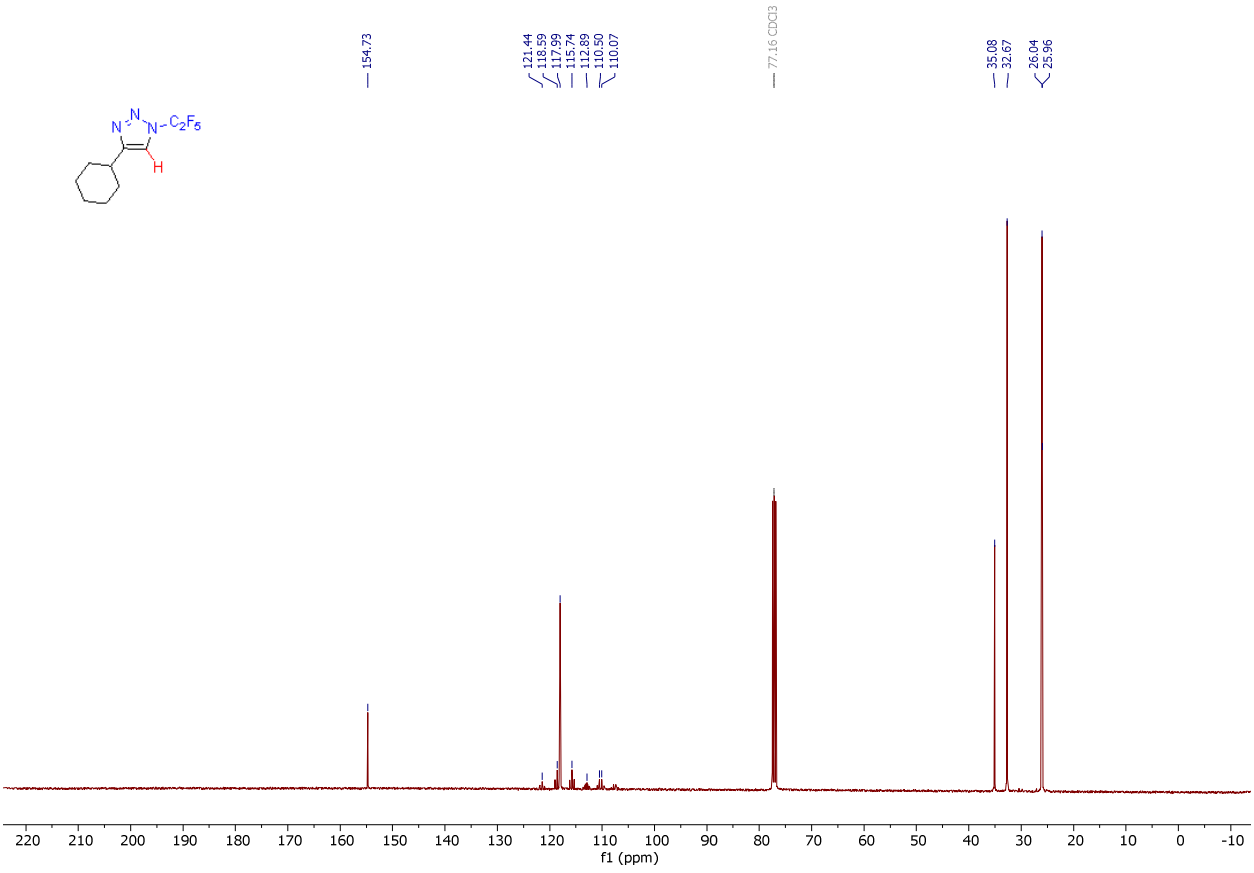
^{19}F NMR spectrum of **1i** ($CDCl_3$, 376 MHz)



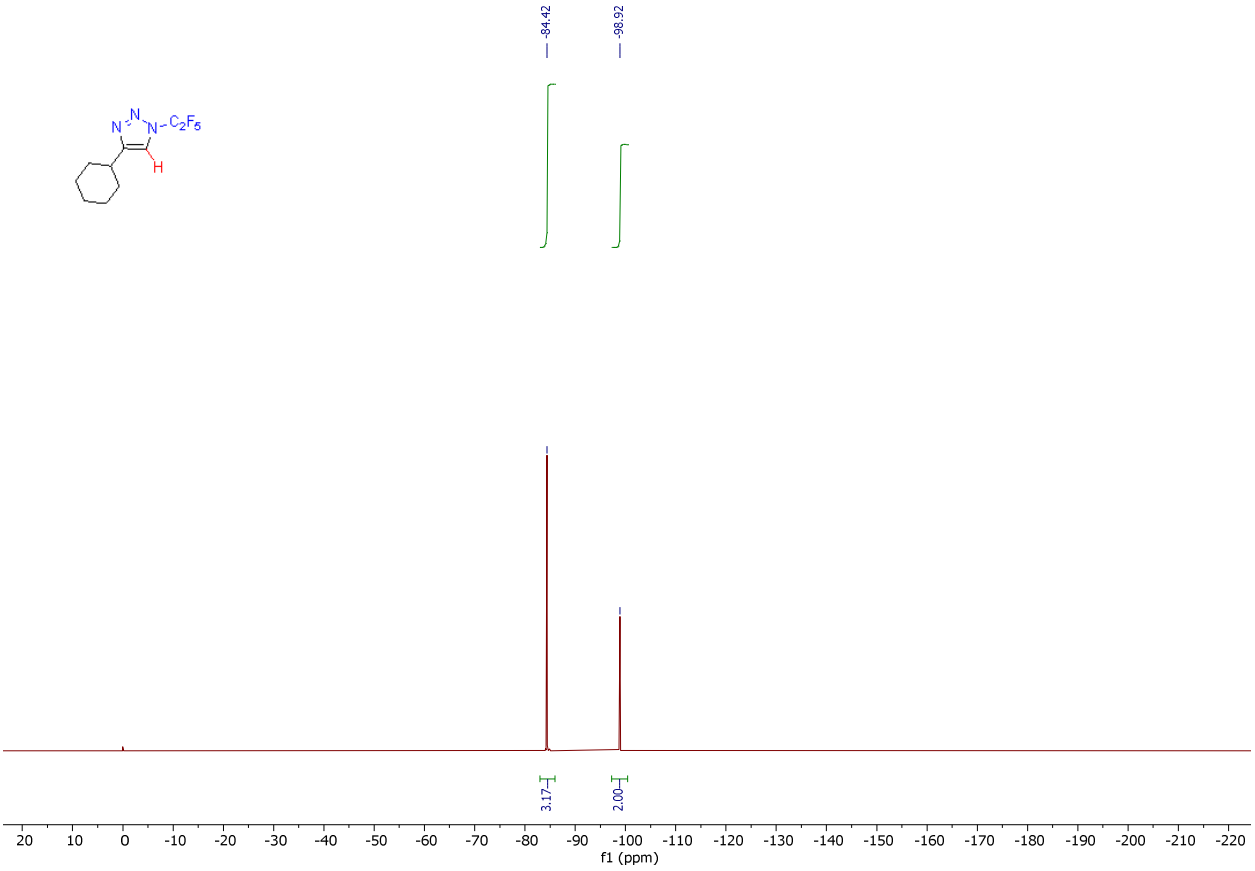
^{1}H NMR spectrum of **1k** ($CDCl_3$, 400 MHz)



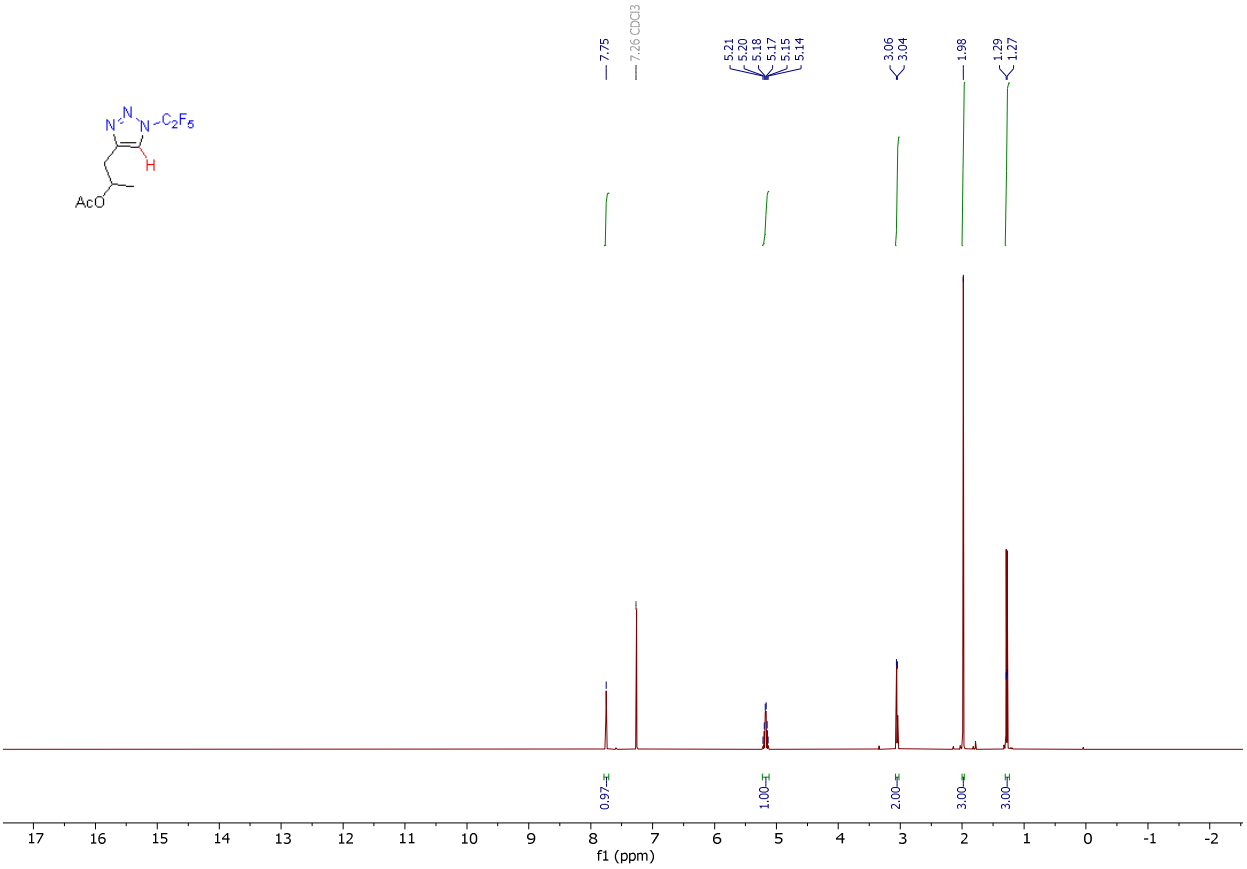
^{13}C NMR spectrum of **1k** ($CDCl_3$, 101 MHz)



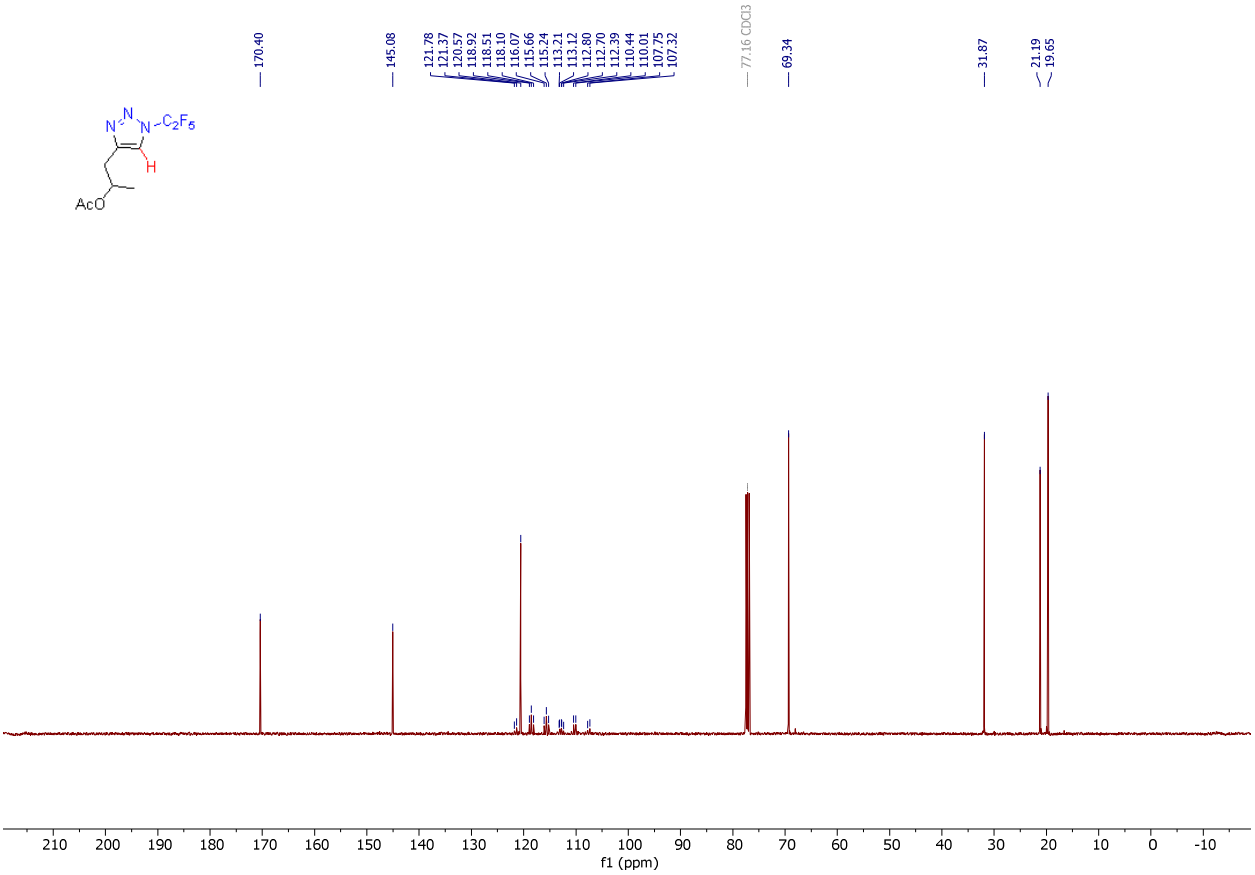
^{19}F NMR spectrum of **1k** ($CDCl_3$, 376 MHz)



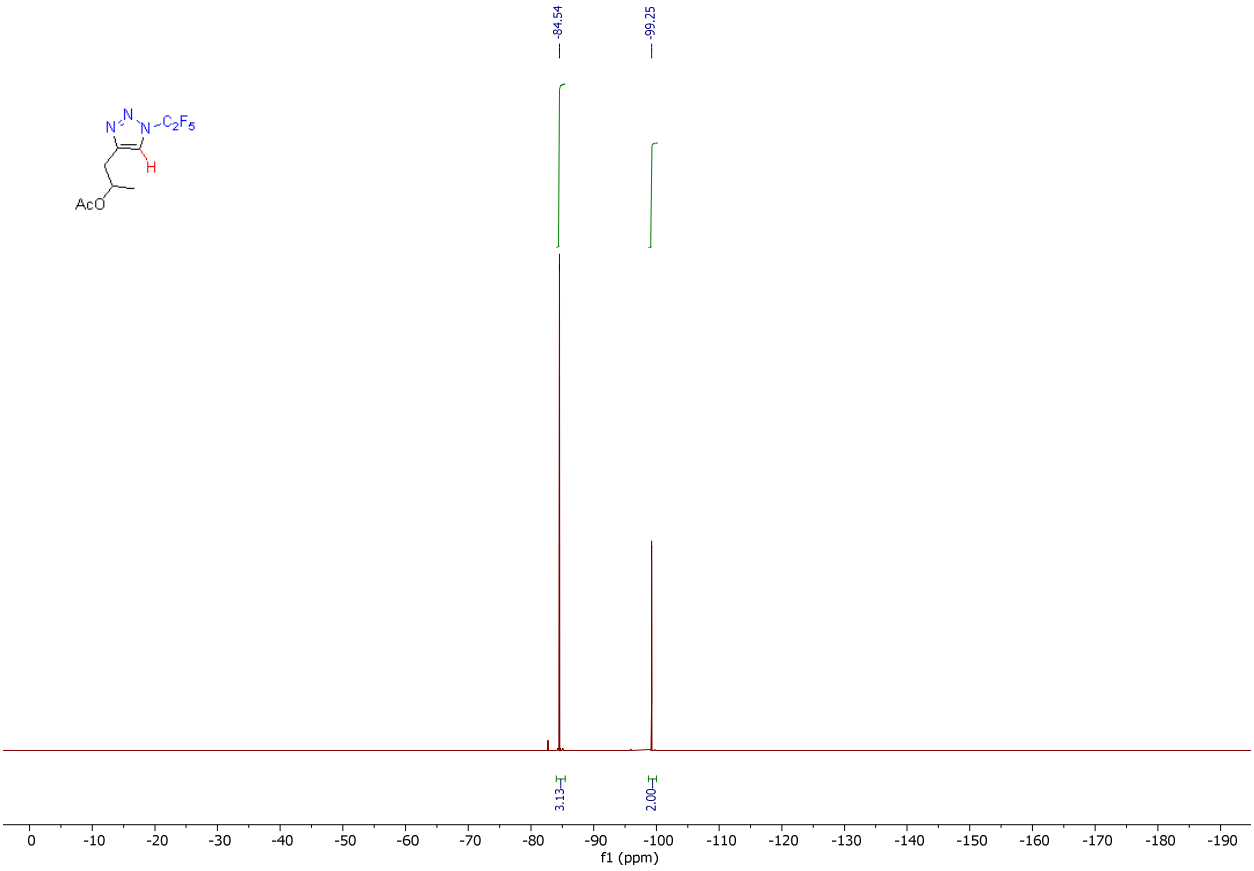
^{1}H NMR spectrum of **1m** ($CDCl_3$, 400 MHz)



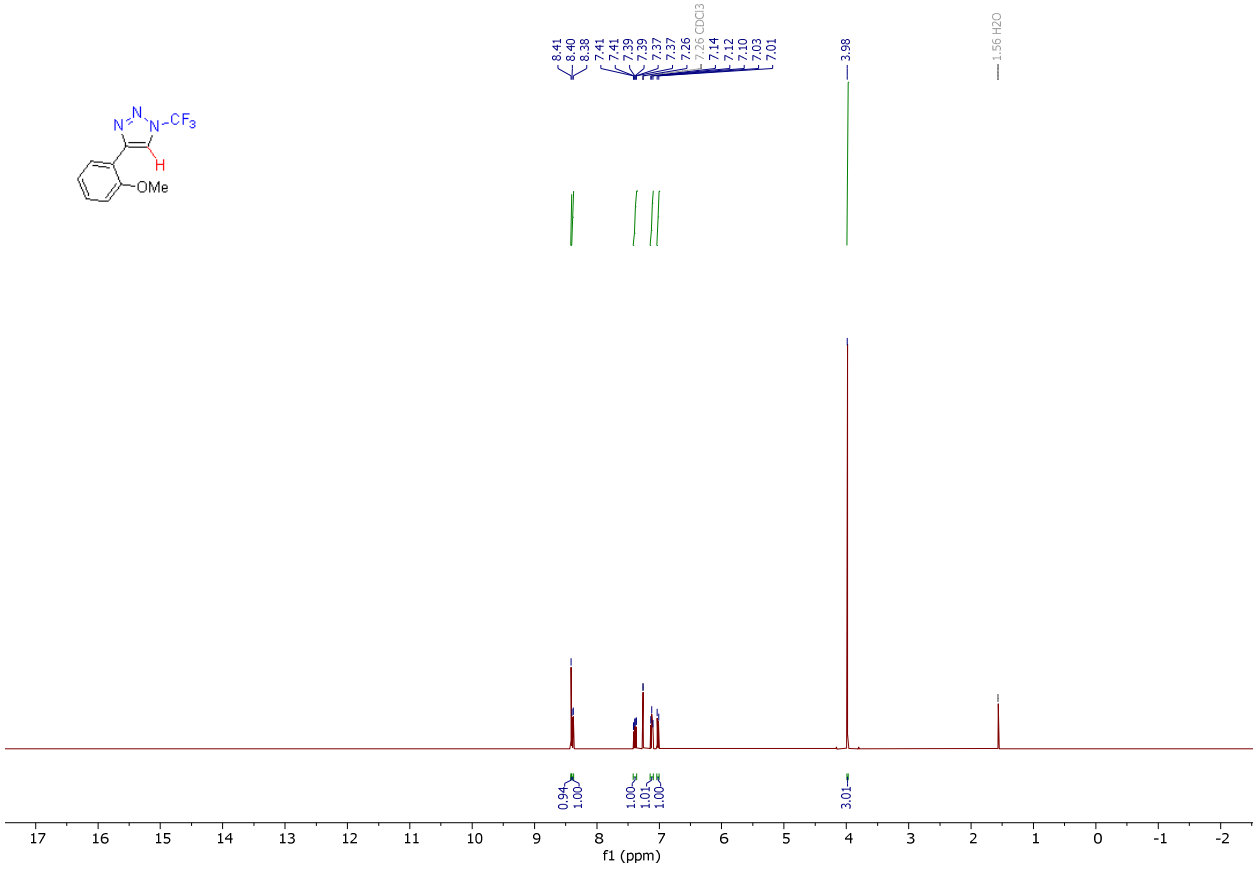
^{13}C NMR spectrum of **1m** ($CDCl_3$, 101 MHz)



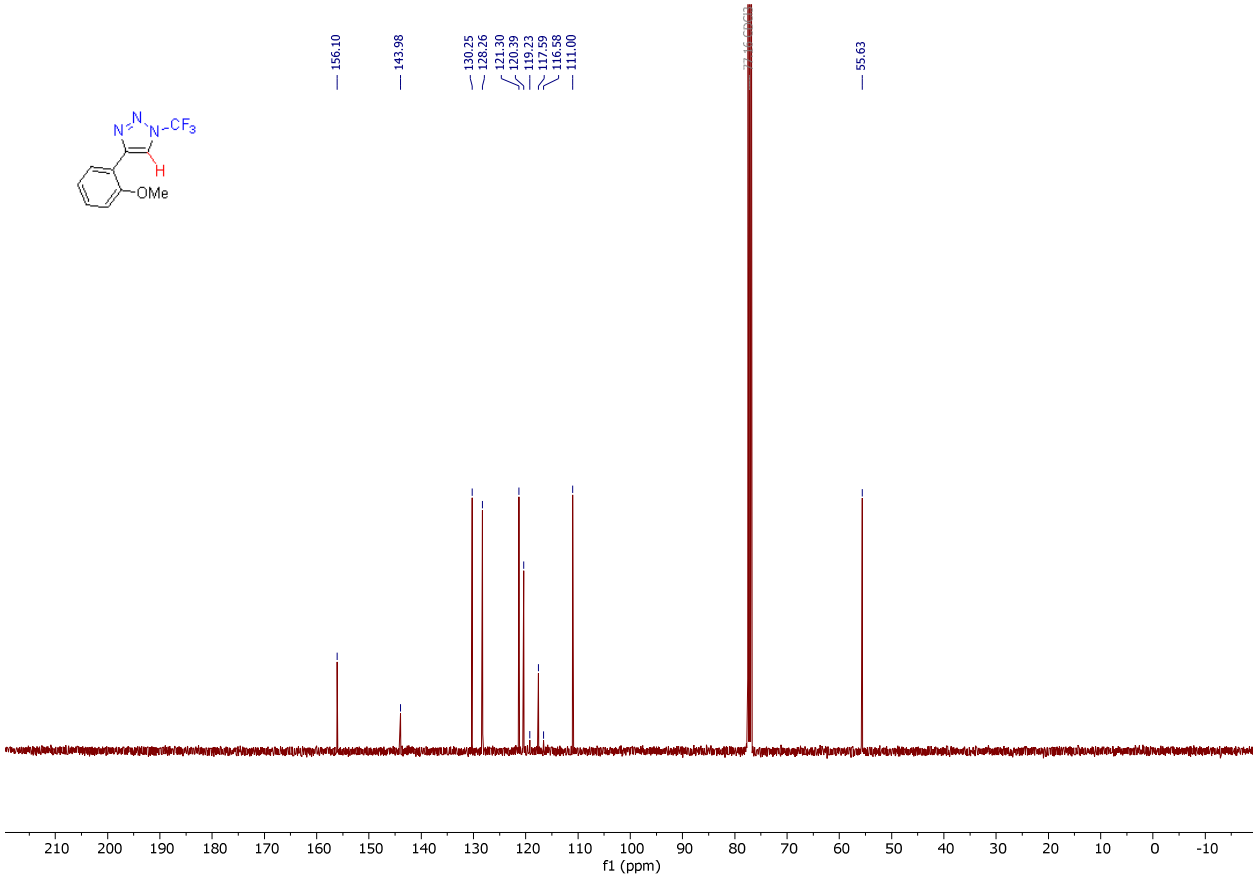
^{19}F NMR spectrum of **1m** ($CDCl_3$, 376 MHz)



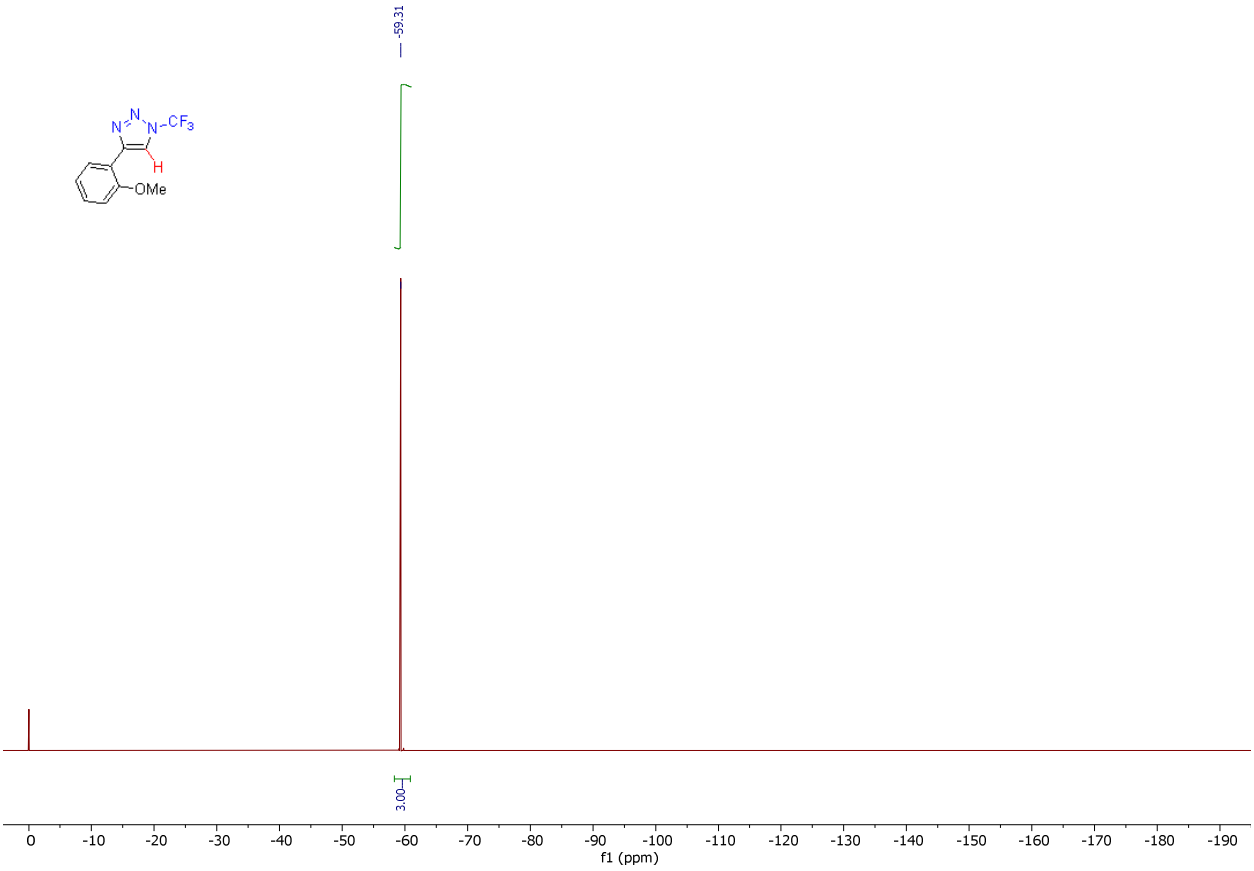
^{1}H NMR spectrum of **1q** ($CDCl_3$, 400 MHz)



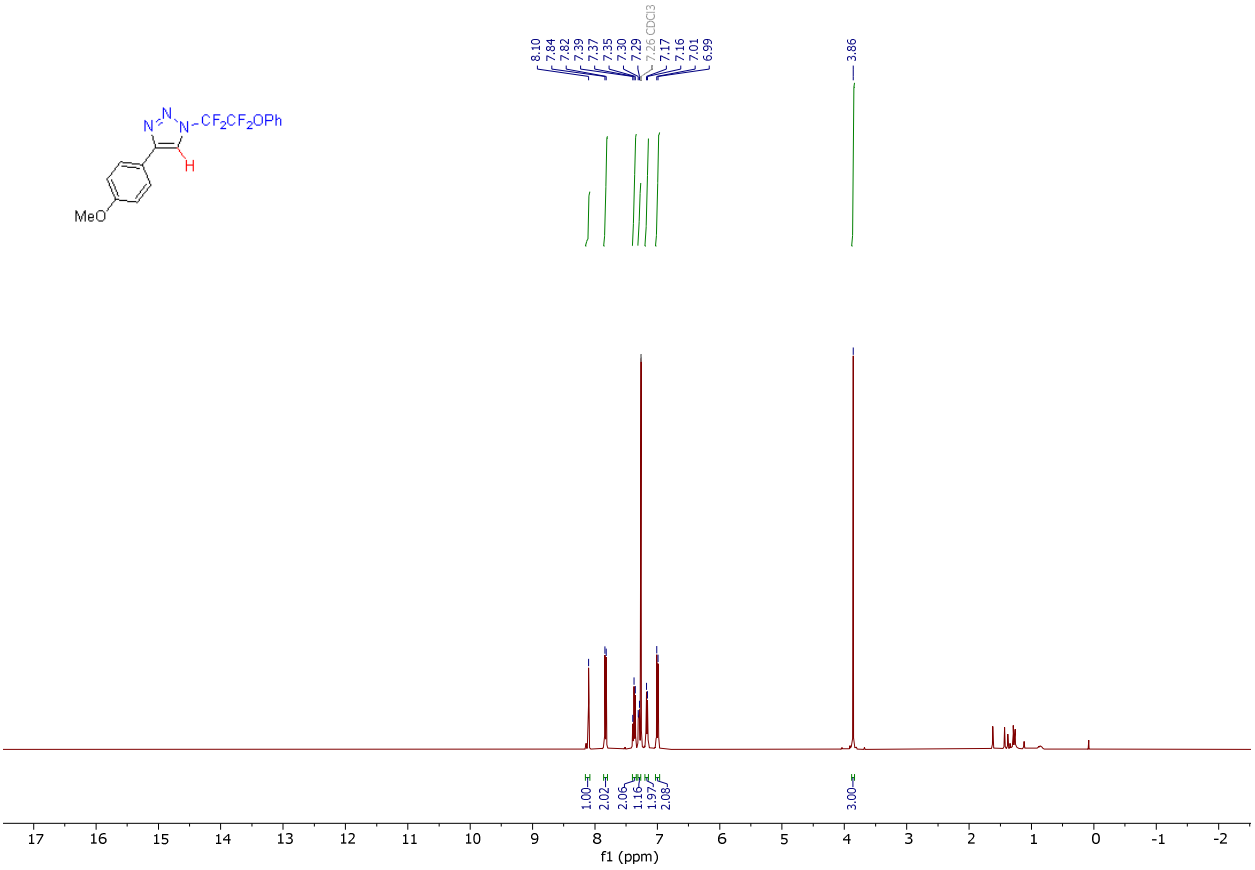
^{13}C NMR spectrum of **1q** ($CDCl_3$, 101 MHz)



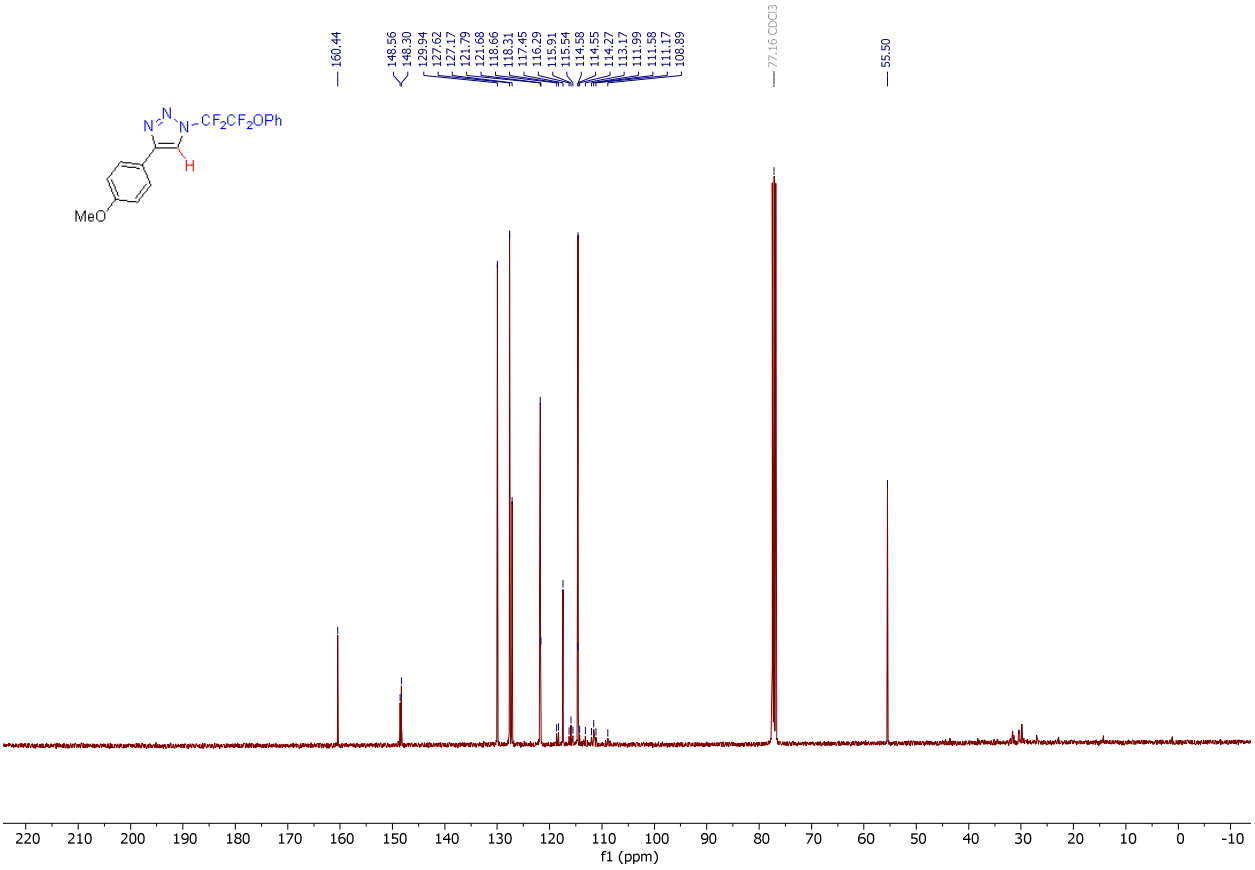
^{19}F NMR spectrum of **1q** ($CDCl_3$, 376 MHz)



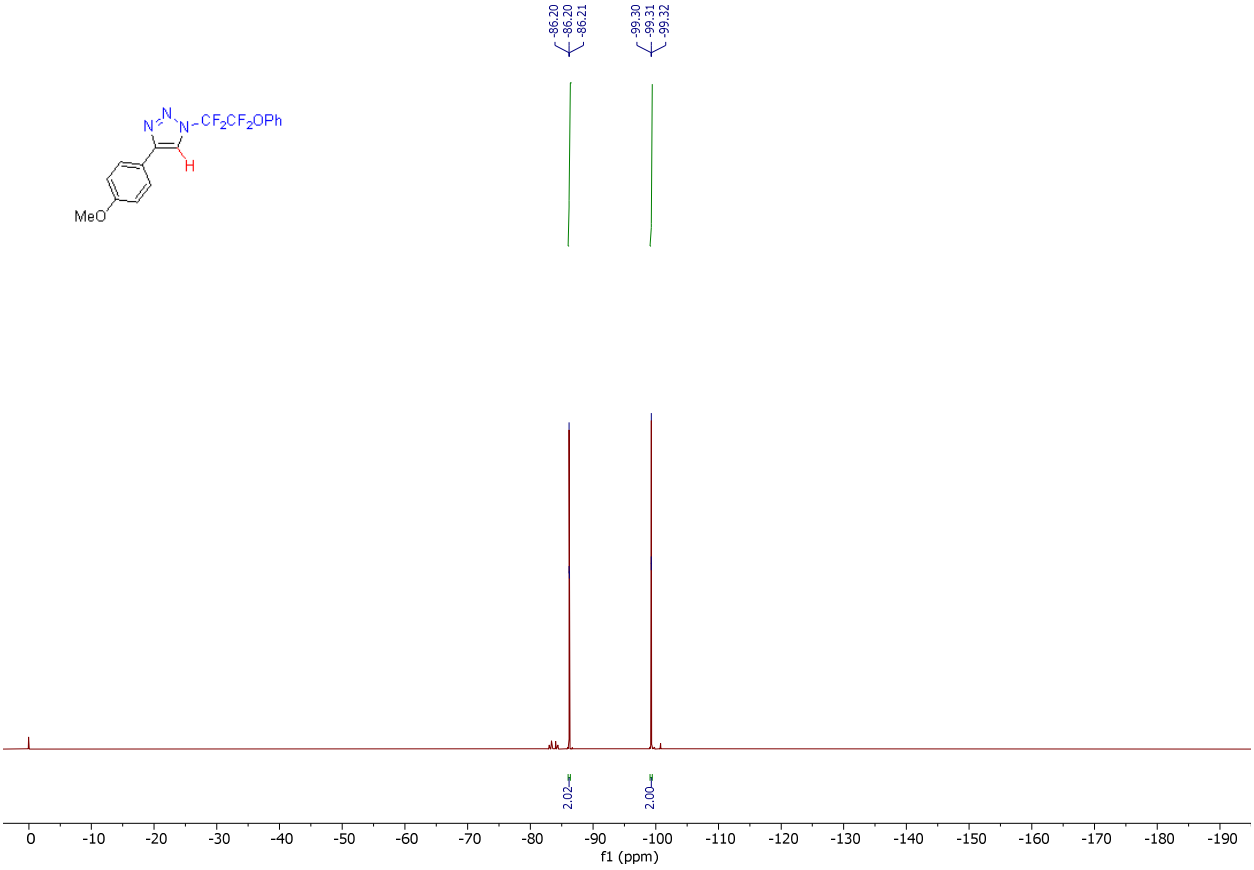
^{1}H NMR spectrum of **1t** ($CDCl_3$, 400 MHz)



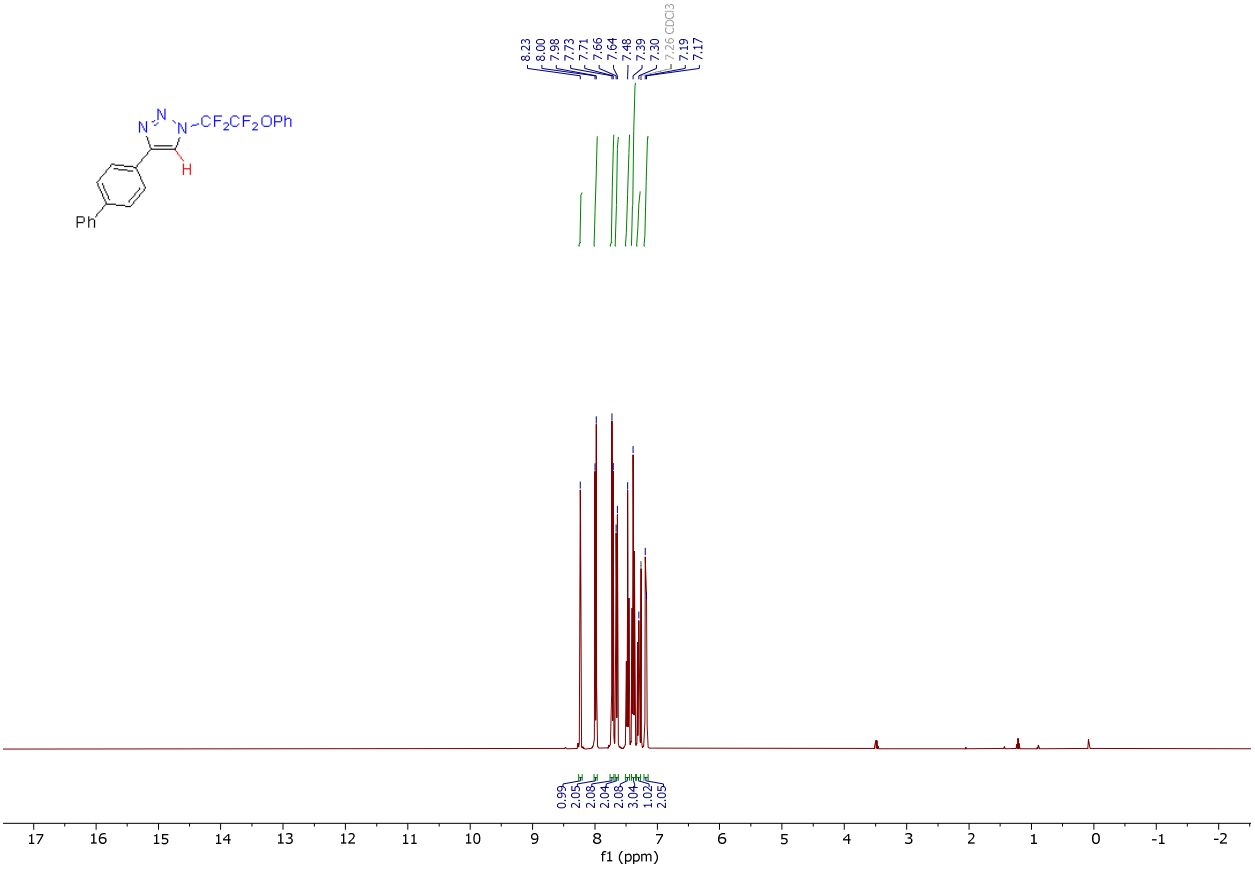
^{13}C NMR spectrum of **1t** ($CDCl_3$, 101 MHz)



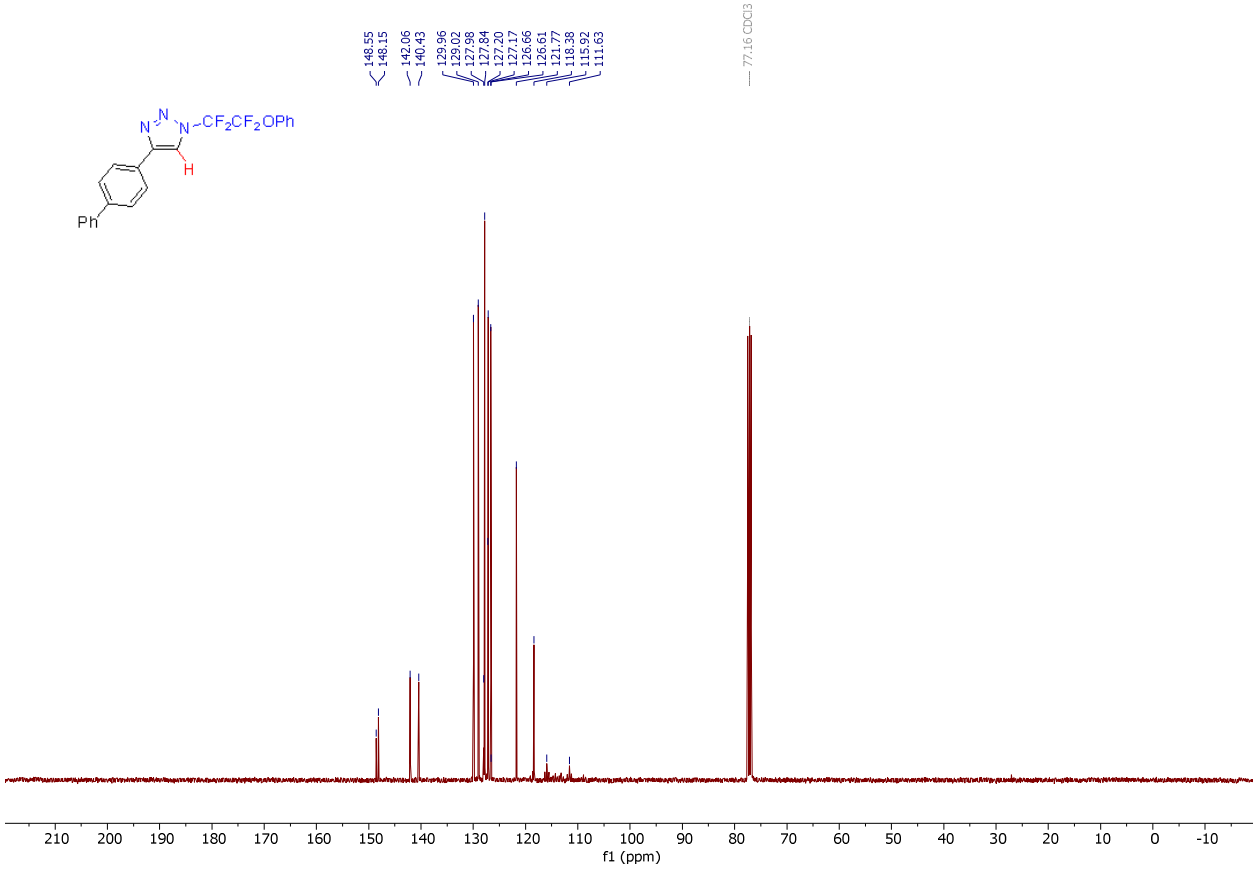
^{19}F NMR spectrum of **1t** ($CDCl_3$, 376 MHz)



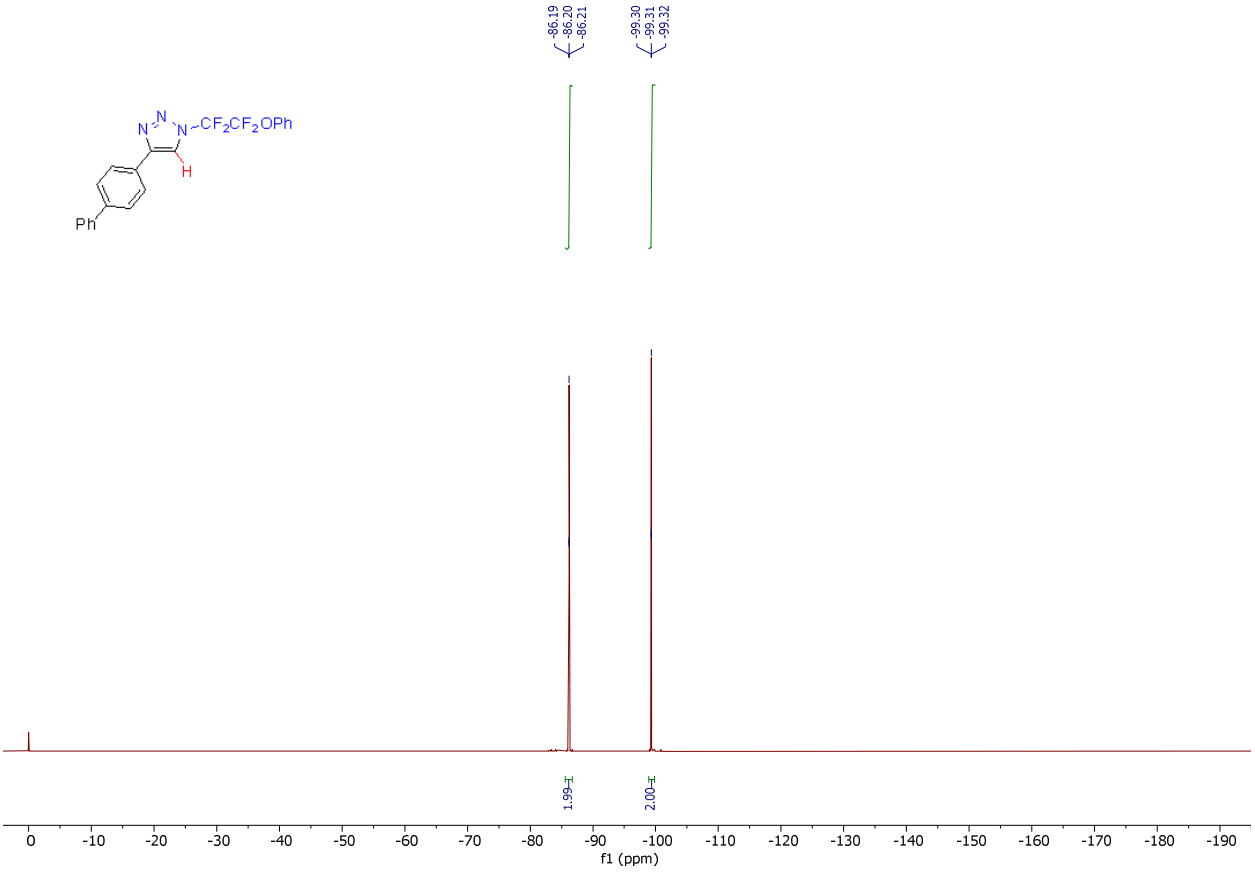
^{1}H NMR spectrum of **1u** ($CDCl_3$, 400 MHz)



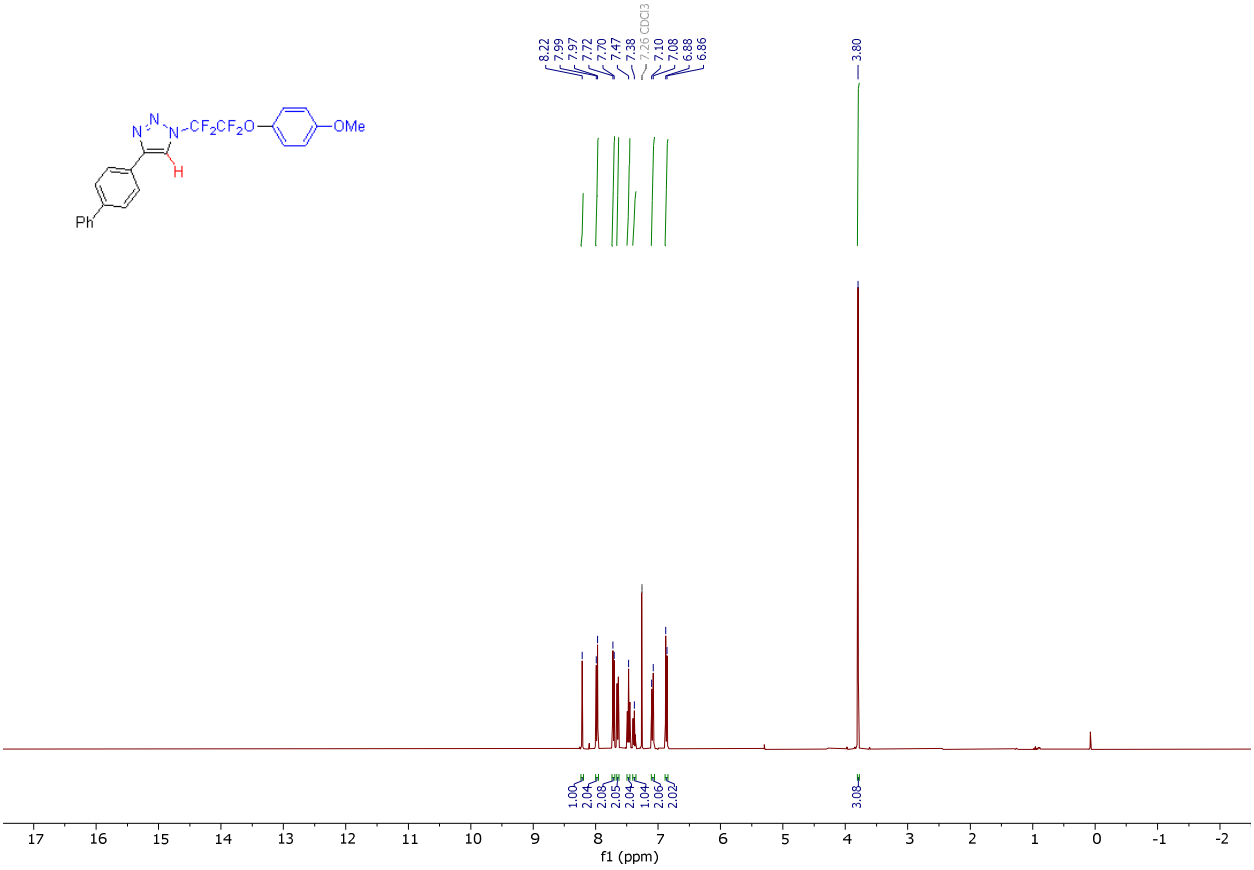
^{13}C NMR spectrum of **1u** ($CDCl_3$, 101 MHz)



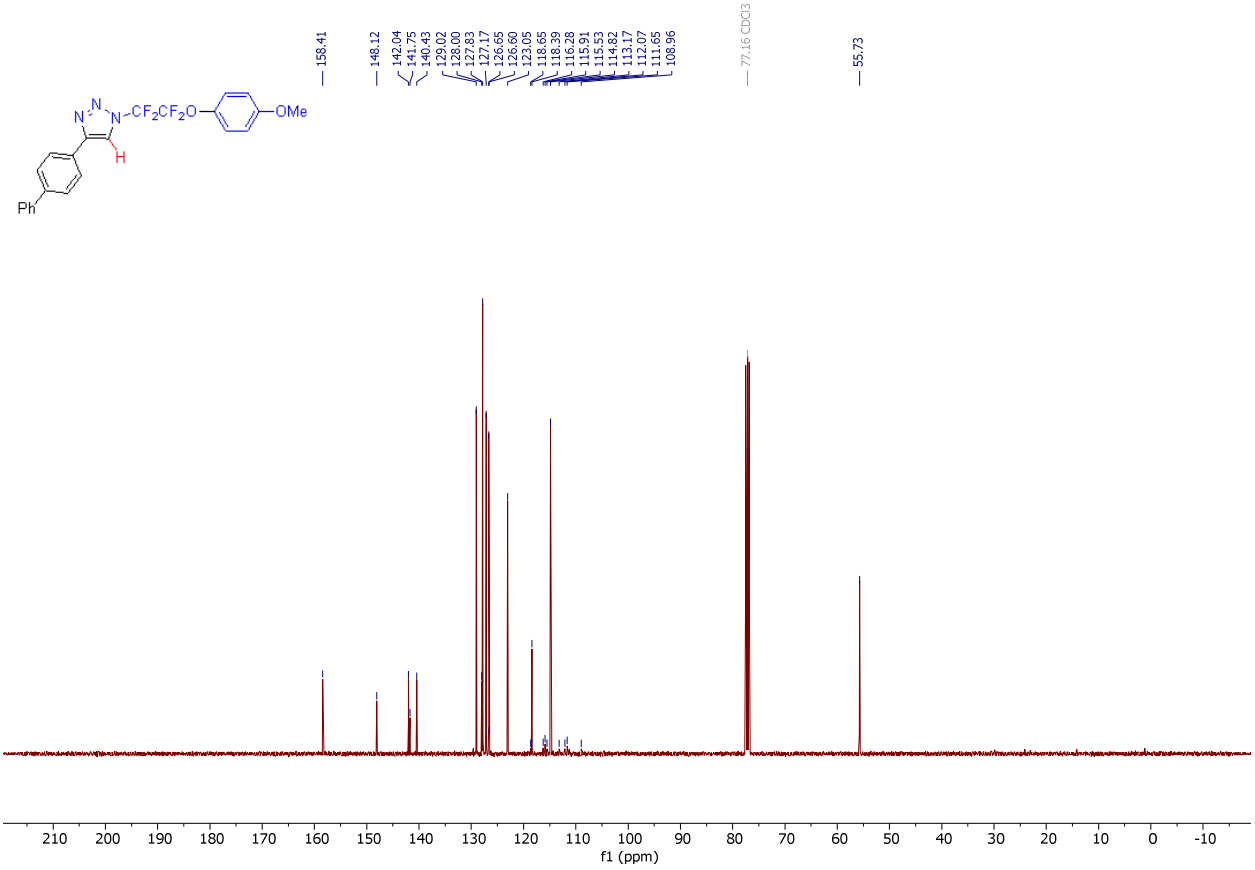
^{19}F NMR spectrum of **1u** ($CDCl_3$, 376 MHz)



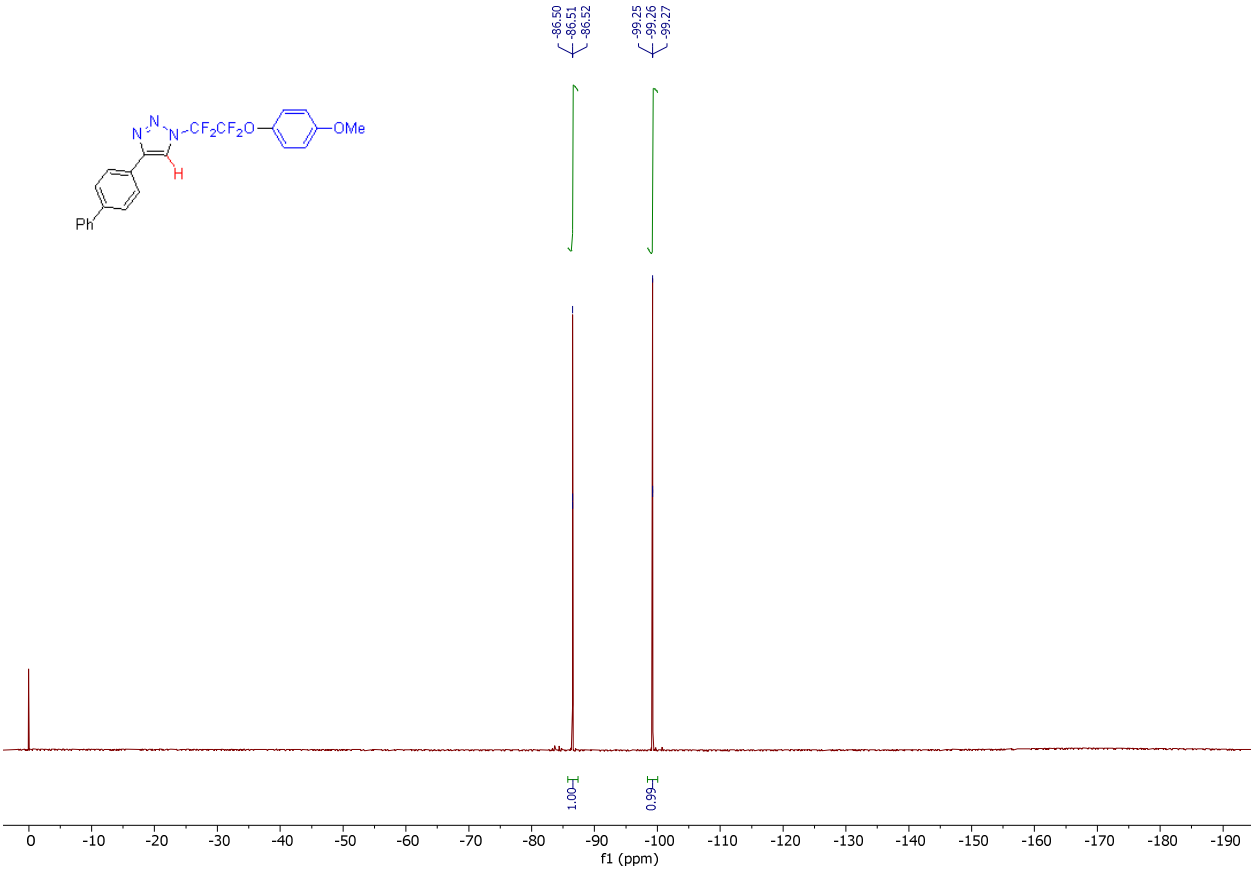
^{1}H NMR spectrum of **1v** ($CDCl_3$, 400 MHz)



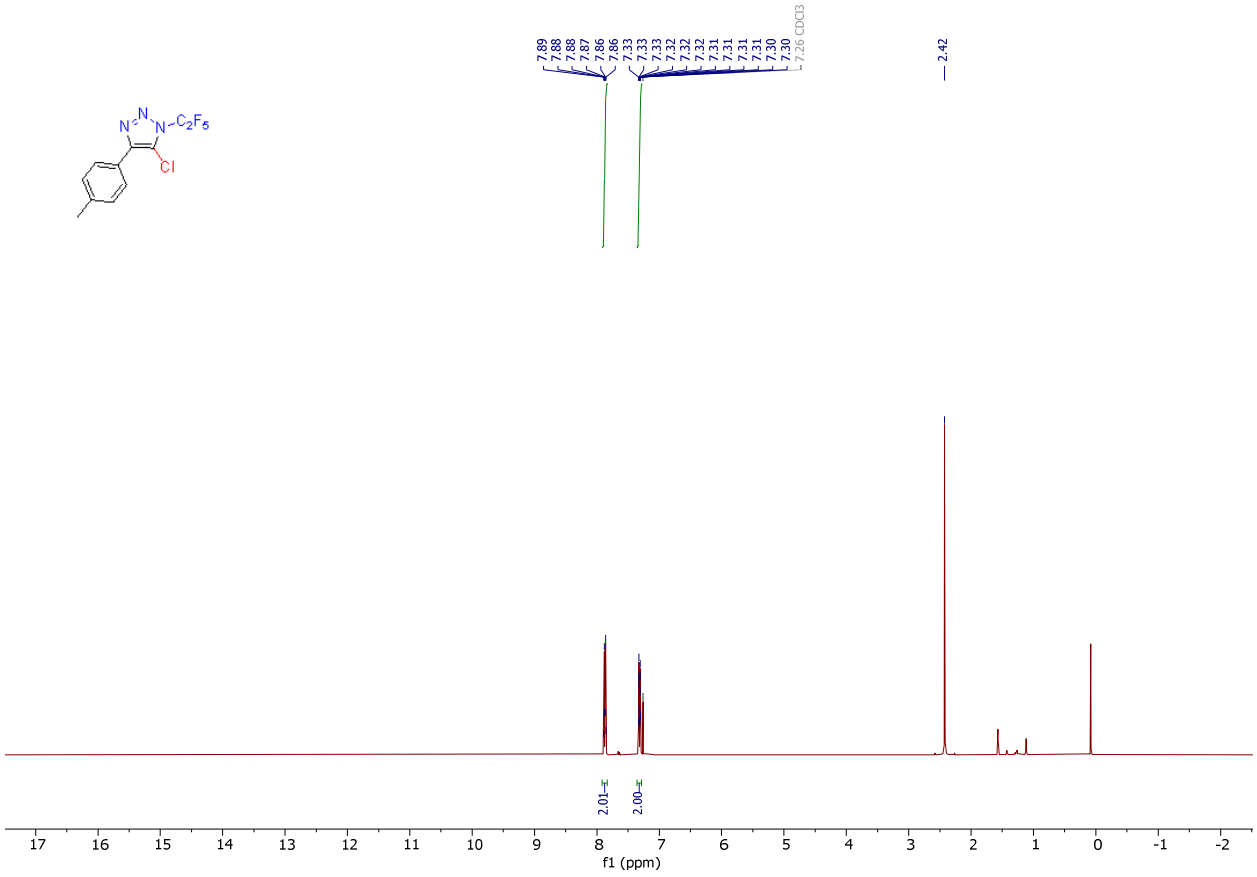
^{13}C NMR spectrum of **1v** ($CDCl_3$, 101 MHz)



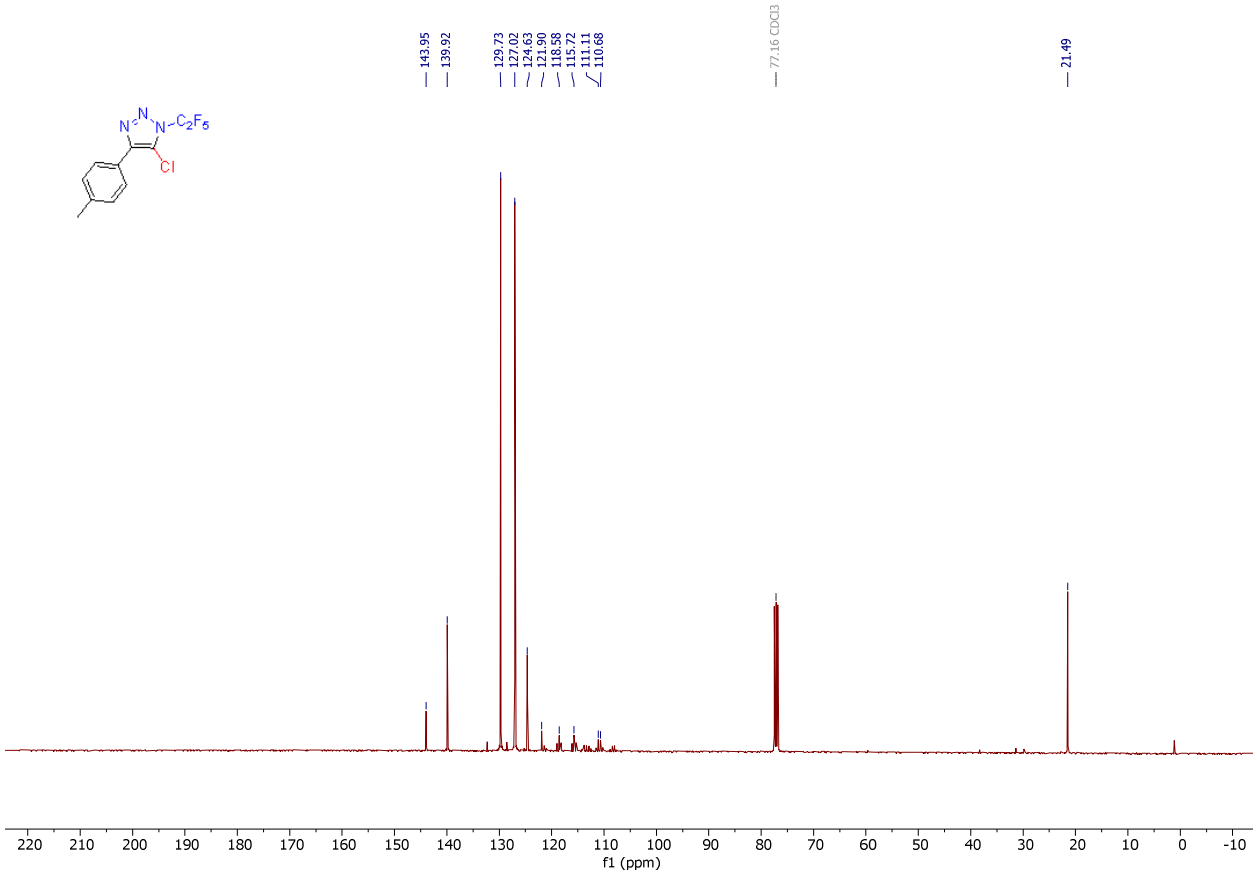
^{19}F NMR spectrum of **1v** ($CDCl_3$, 376 MHz)



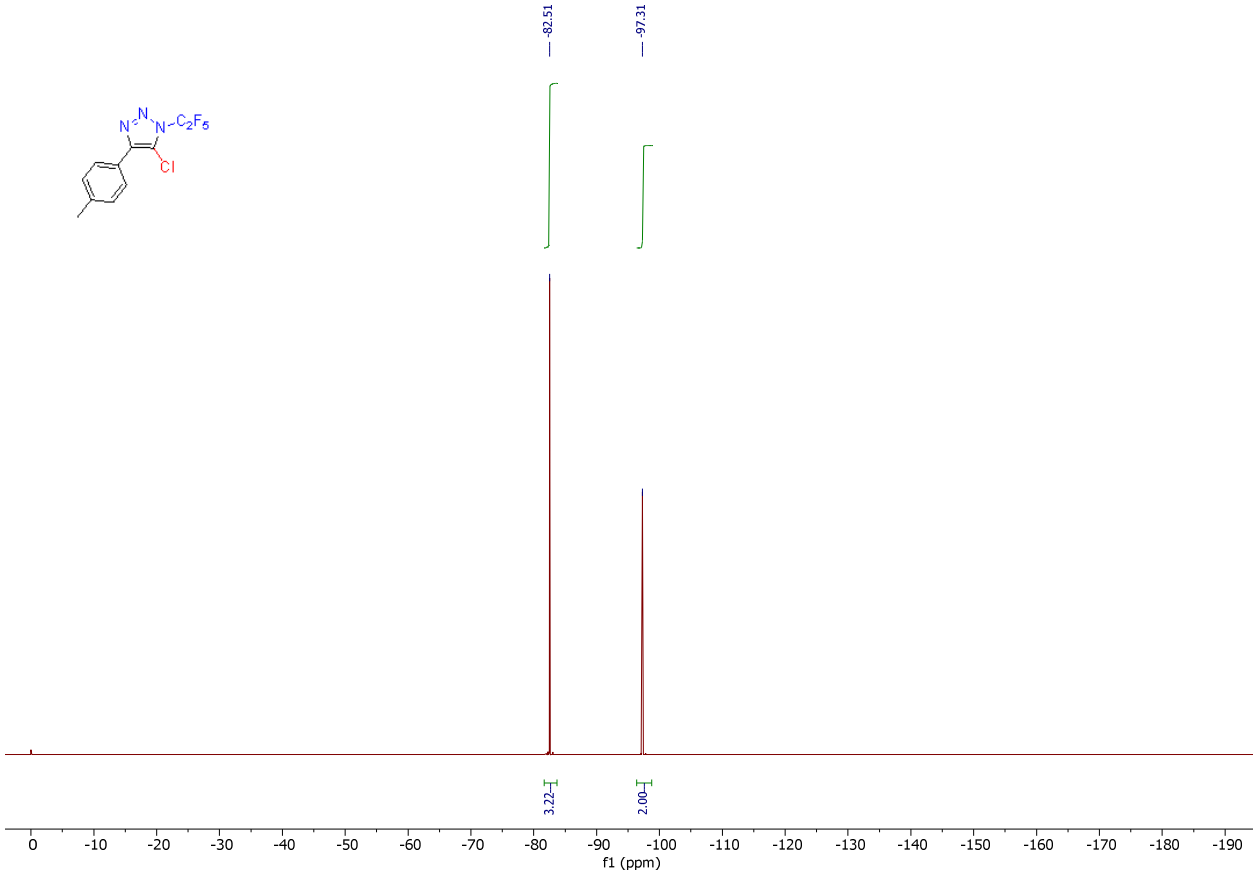
^{1}H NMR spectrum of **1y** ($CDCl_3$, 400 MHz)



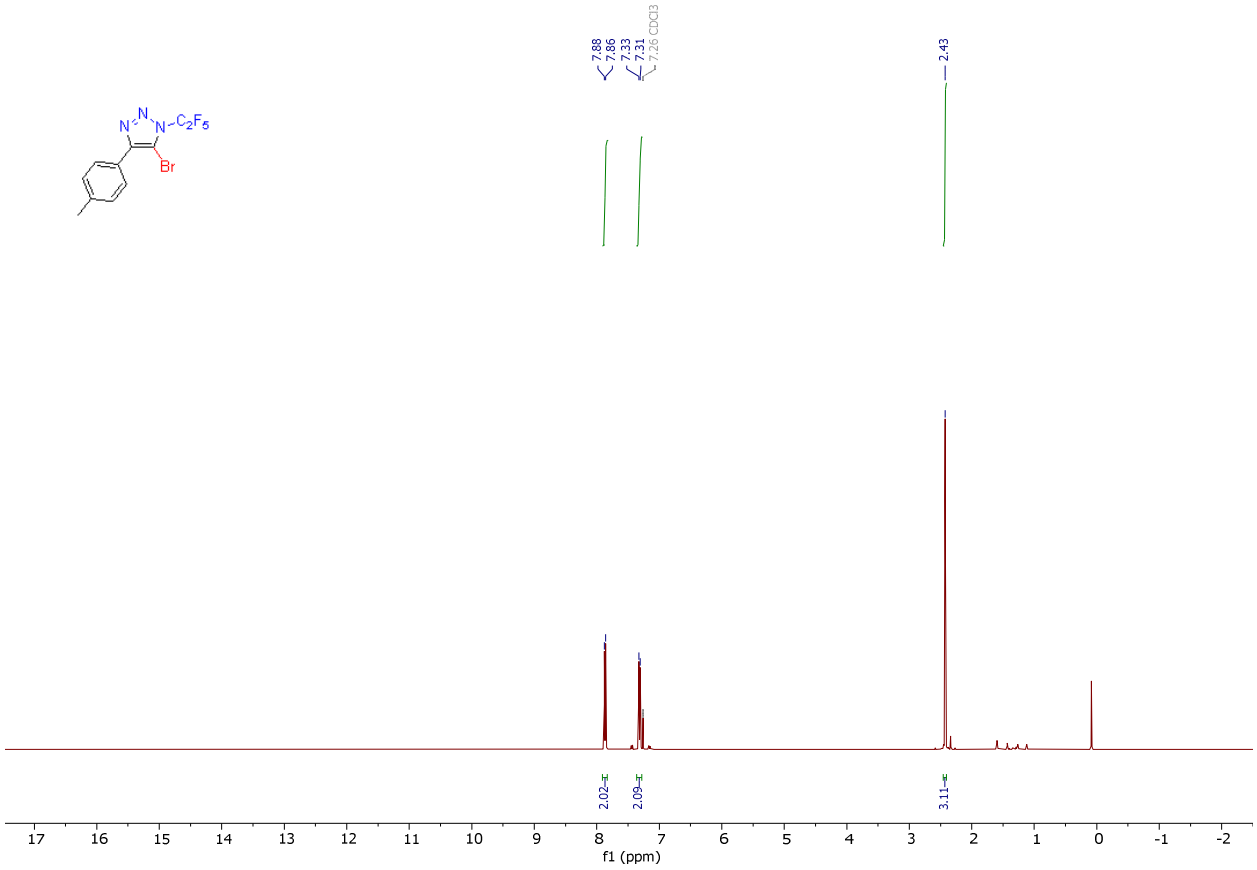
^{13}C NMR spectrum of **1y** ($CDCl_3$, 101 MHz)



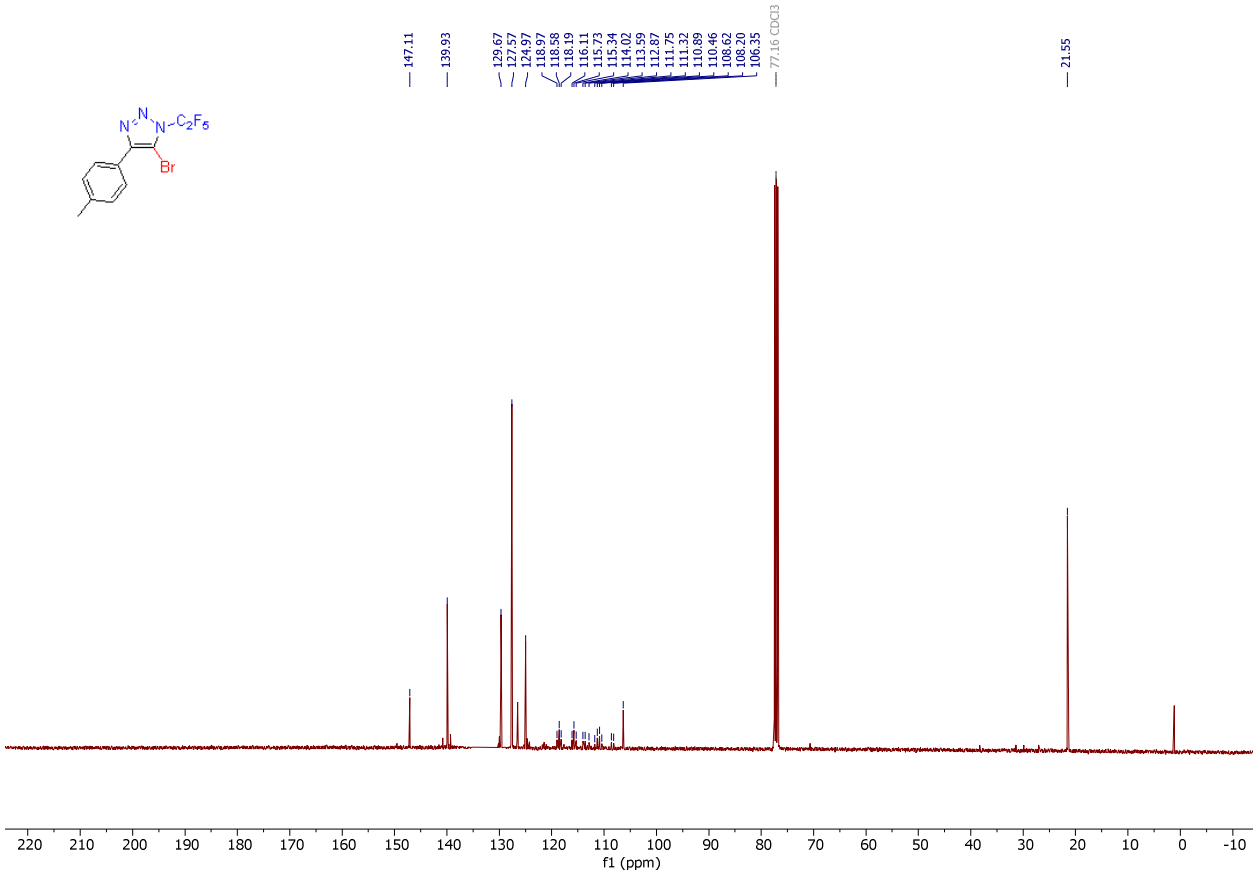
^{19}F NMR spectrum of **1y** ($CDCl_3$, 376 MHz)



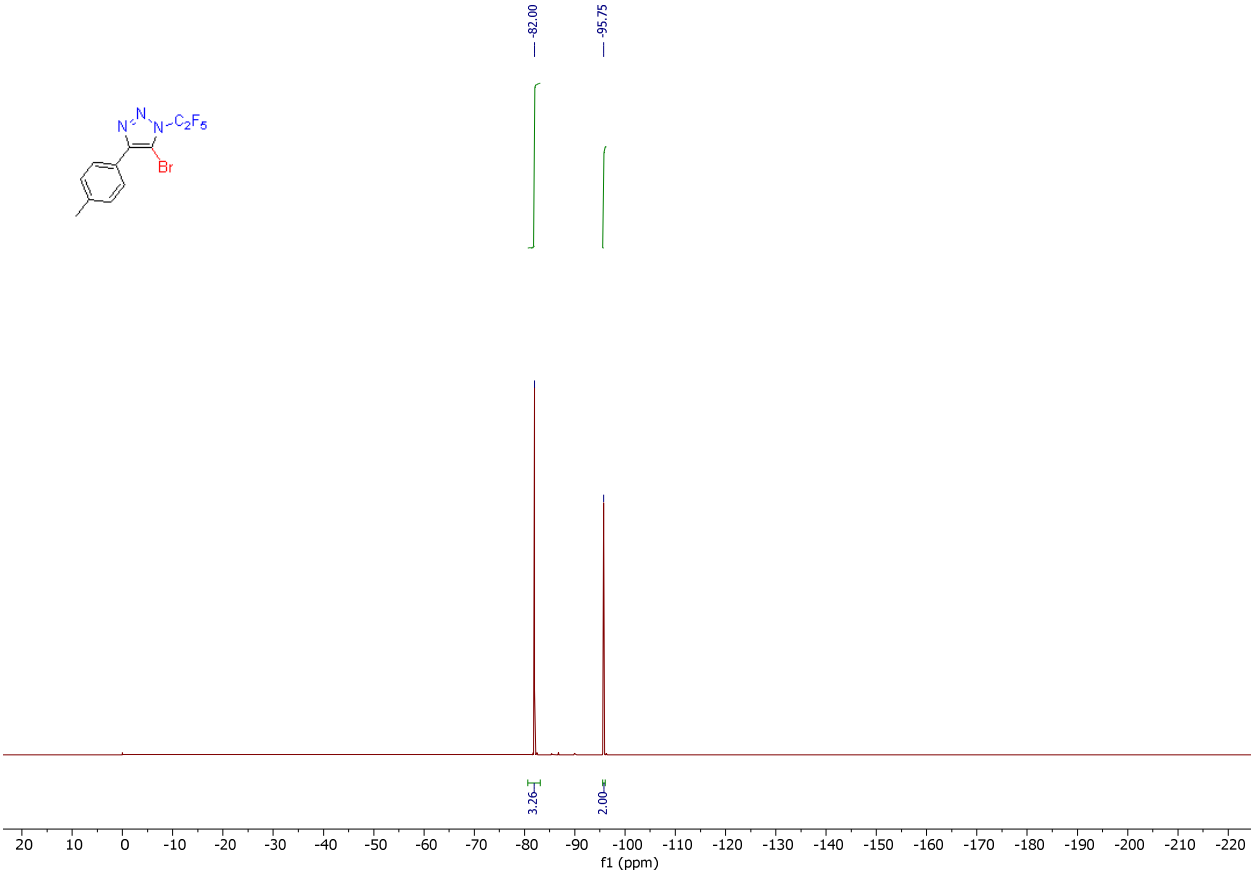
^{1}H NMR spectrum of **1aa** ($CDCl_3$, 400 MHz)



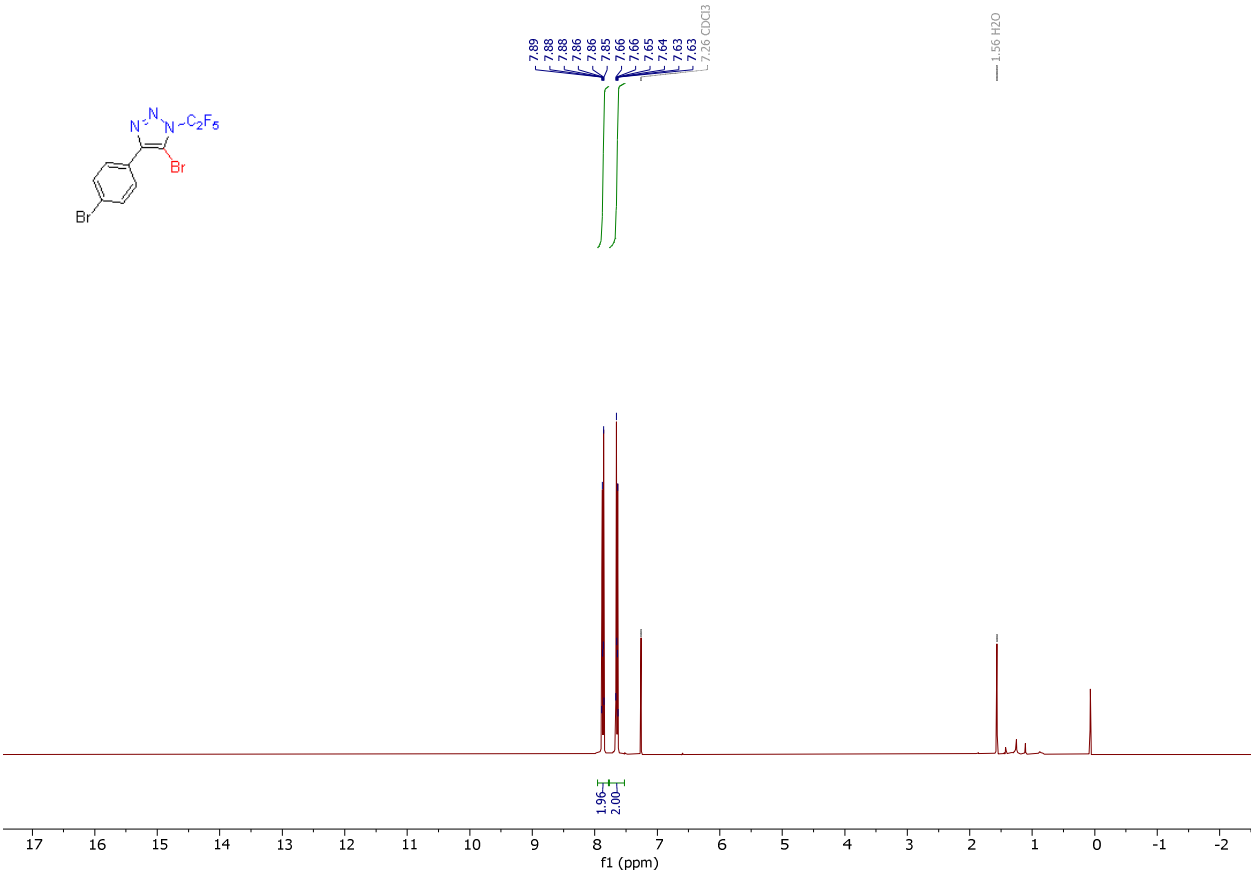
^{13}C NMR spectrum of **1aa** ($CDCl_3$, 101 MHz)



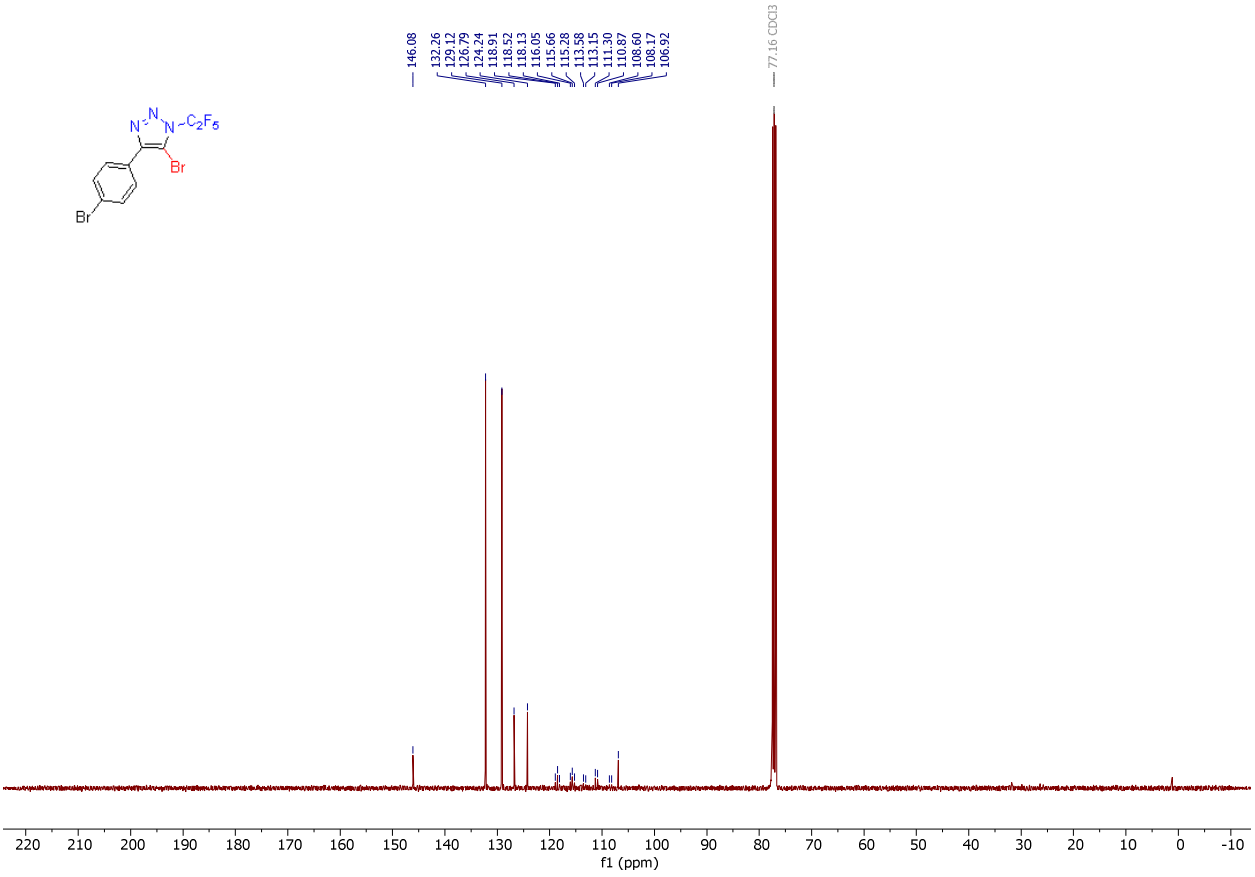
^{19}F NMR spectrum of **1aa** ($CDCl_3$, 376 MHz)



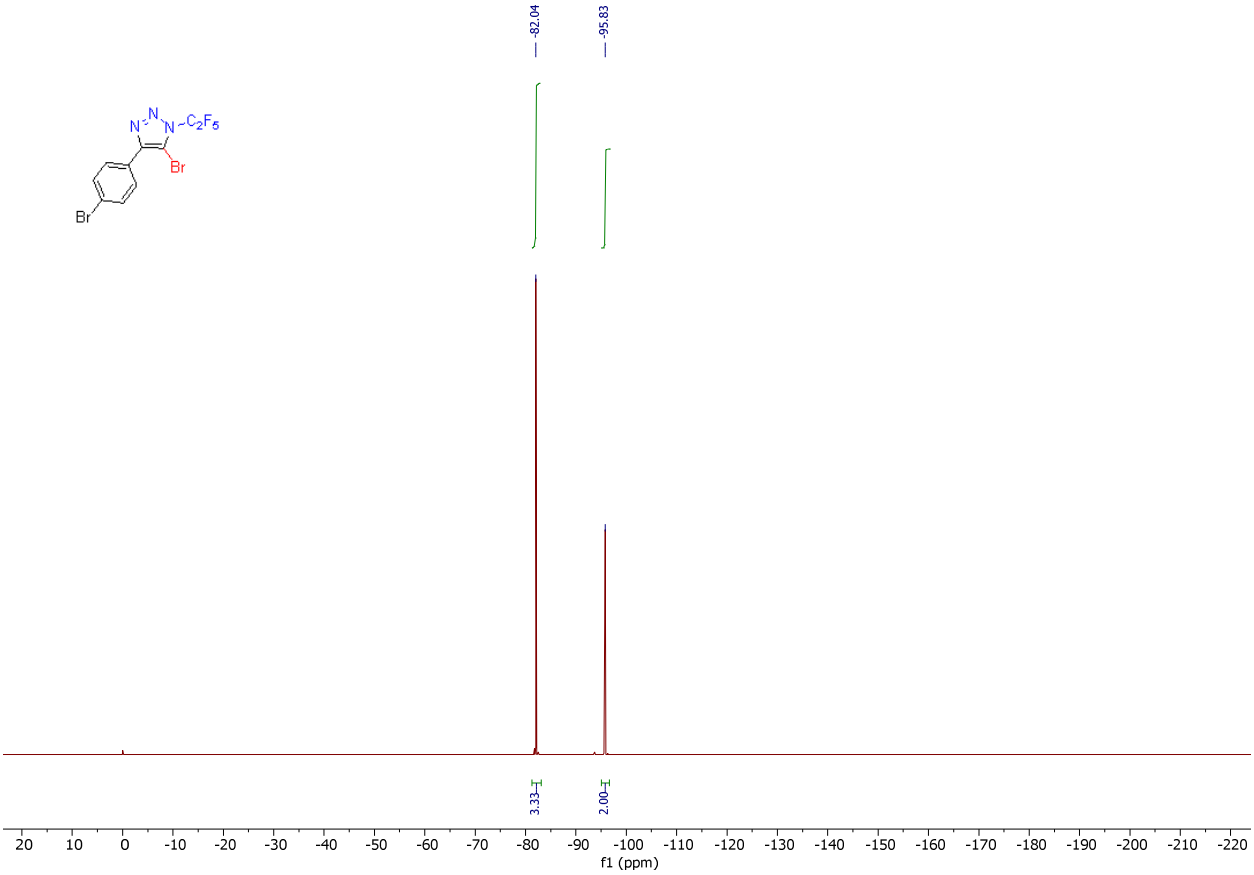
^{1}H NMR spectrum of **1ab** ($CDCl_3$, 400 MHz)



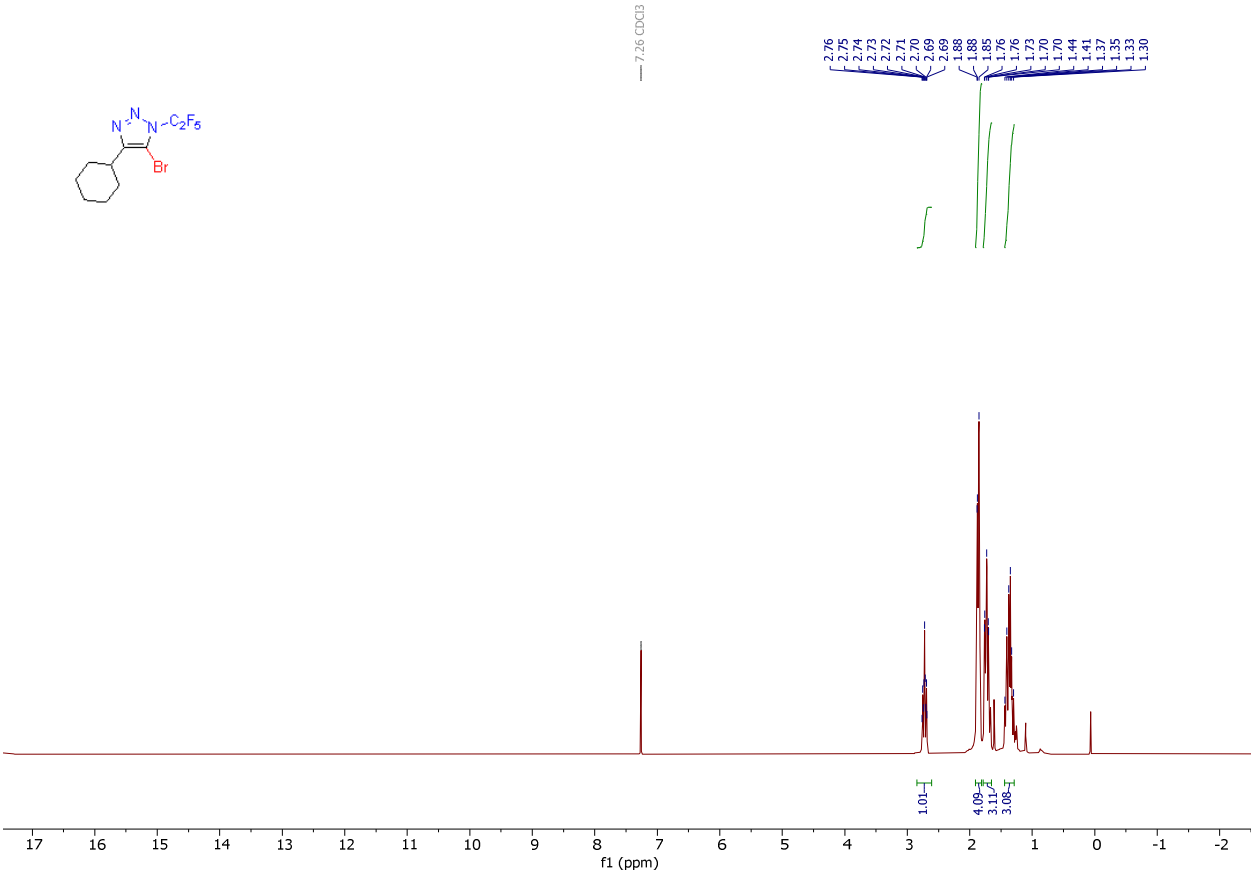
^{13}C NMR spectrum of **1ab** ($CDCl_3$, 101 MHz)



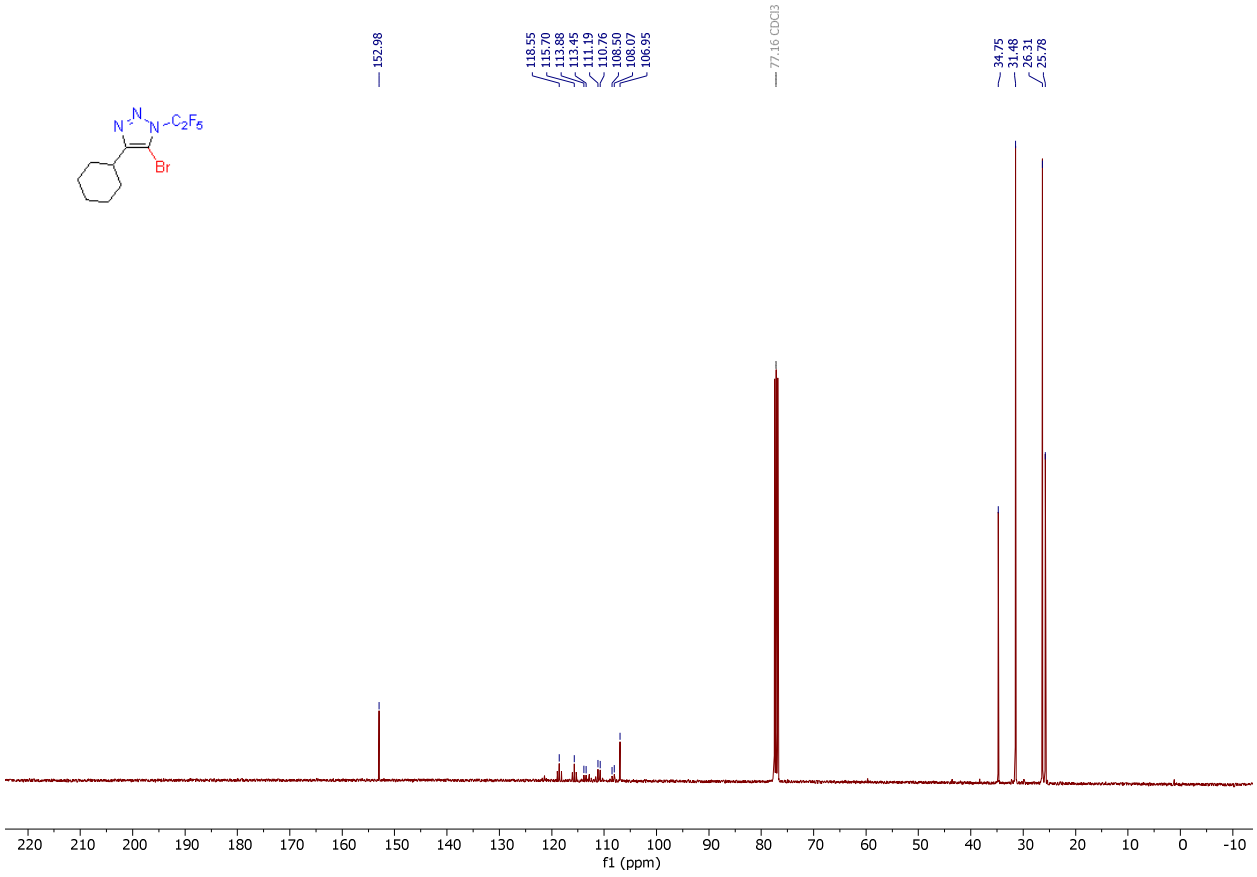
^{19}F NMR spectrum of **1ab** ($CDCl_3$, 376 MHz)



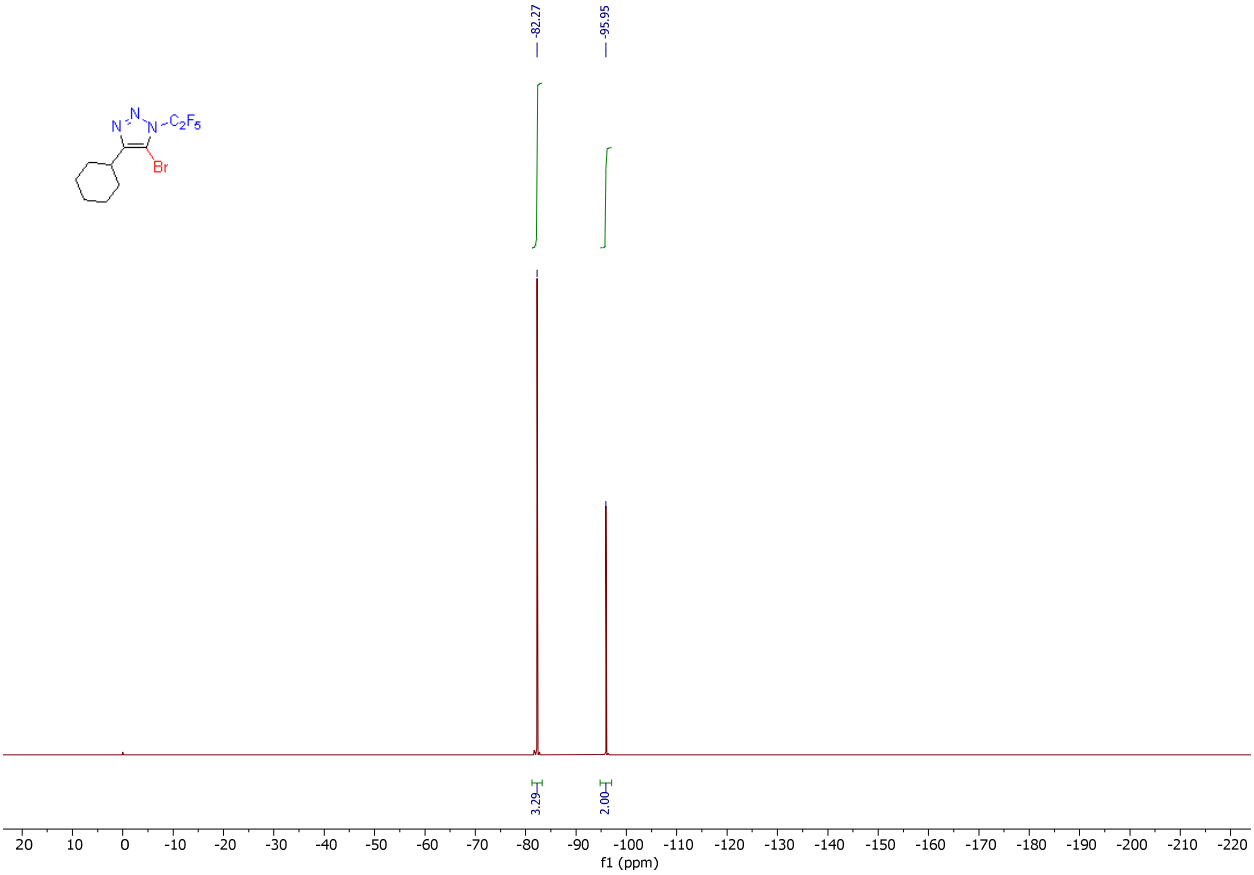
^{1}H NMR spectrum of **1ac** ($CDCl_3$, 400 MHz)



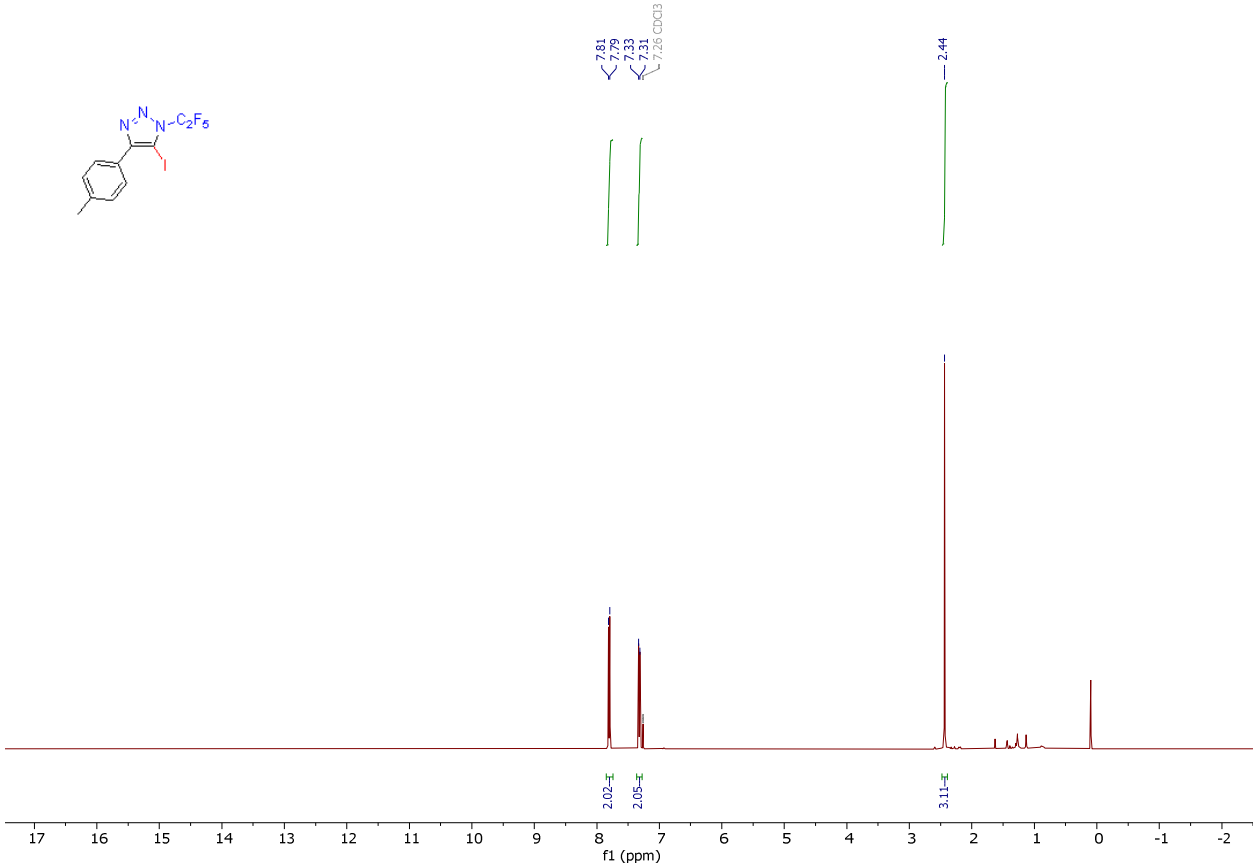
^{13}C NMR spectrum of **1ac** ($CDCl_3$, 101 MHz)



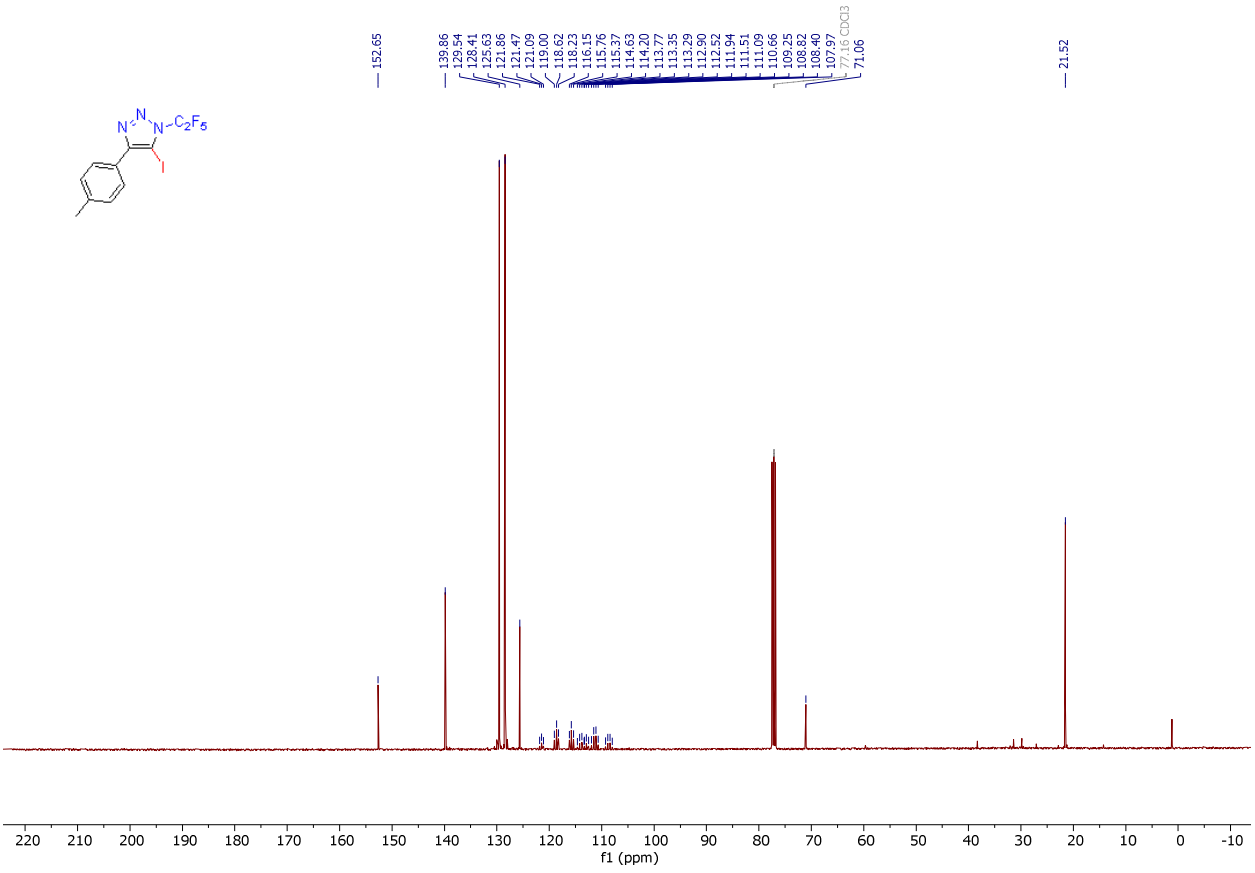
^{19}F NMR spectrum of **1ac** ($CDCl_3$, 376 MHz)



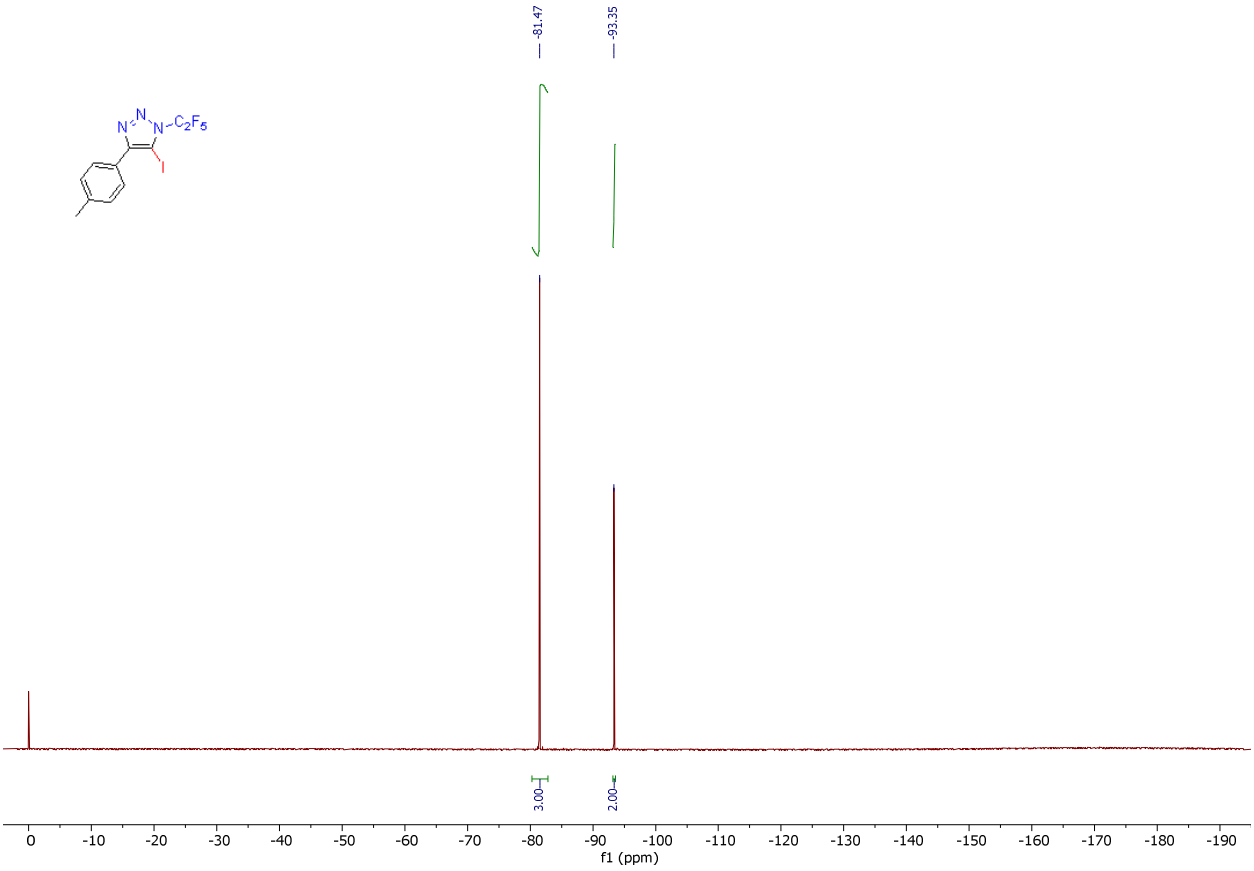
^{1}H NMR spectrum of **1ae** ($CDCl_3$, 400 MHz)



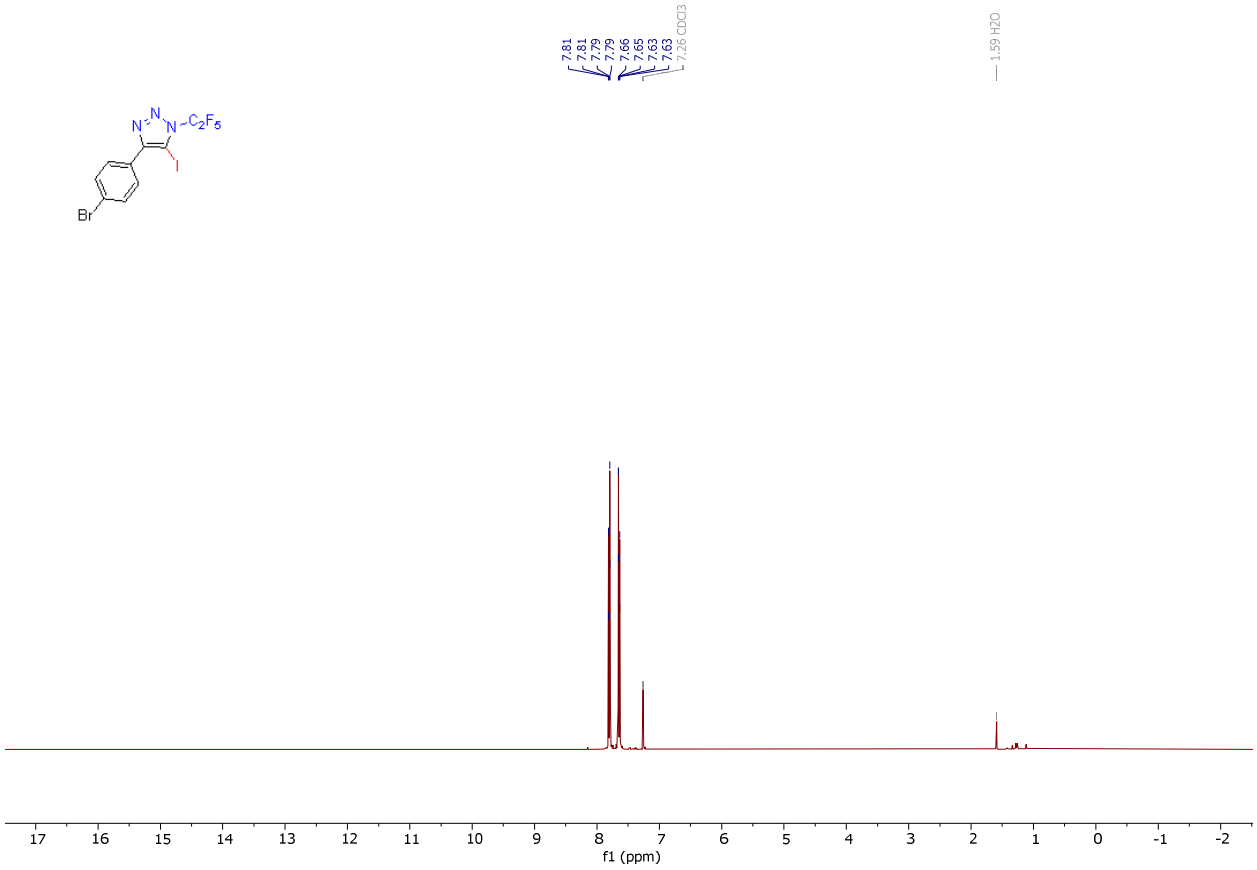
^{13}C NMR spectrum of **1ae** ($CDCl_3$, 101 MHz)



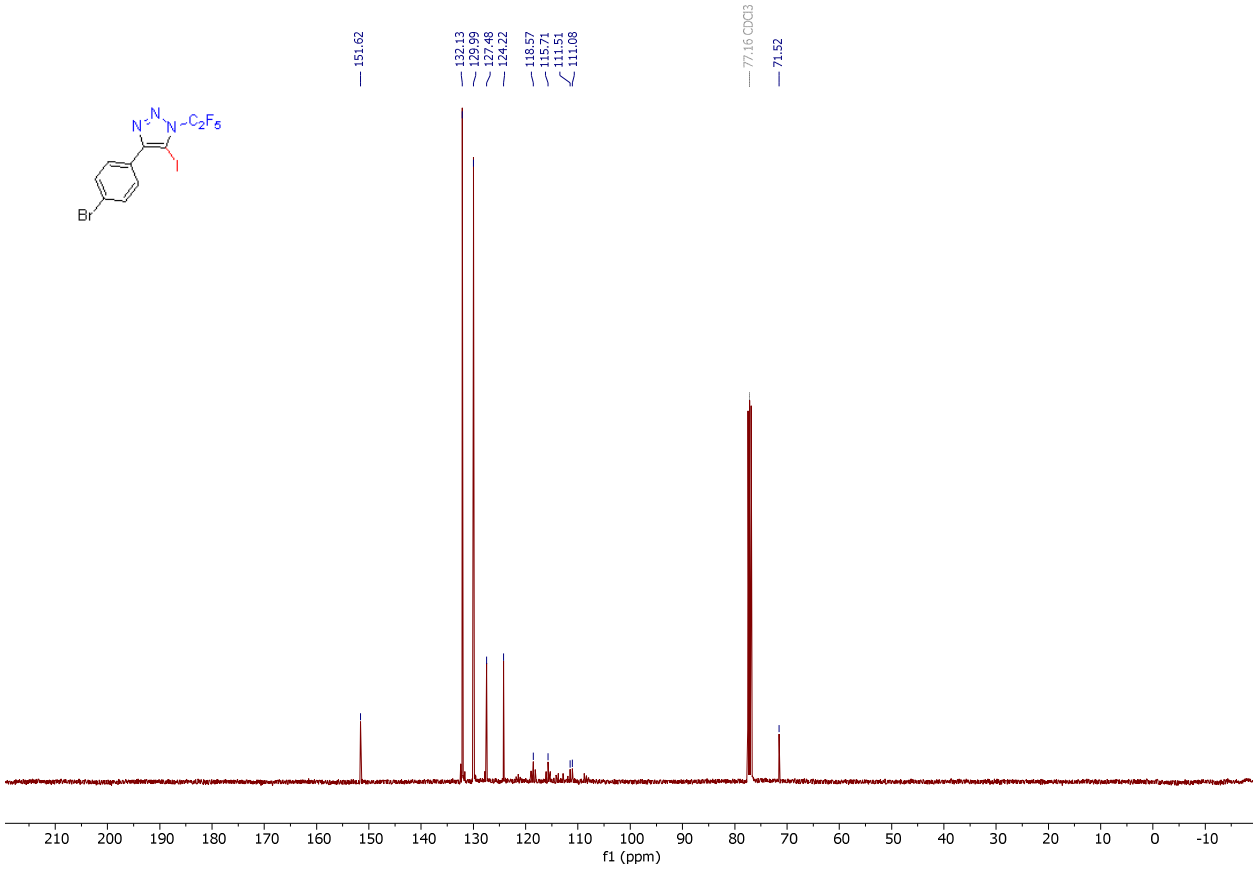
^{19}F NMR spectrum of **1ae** ($CDCl_3$, 376 MHz)



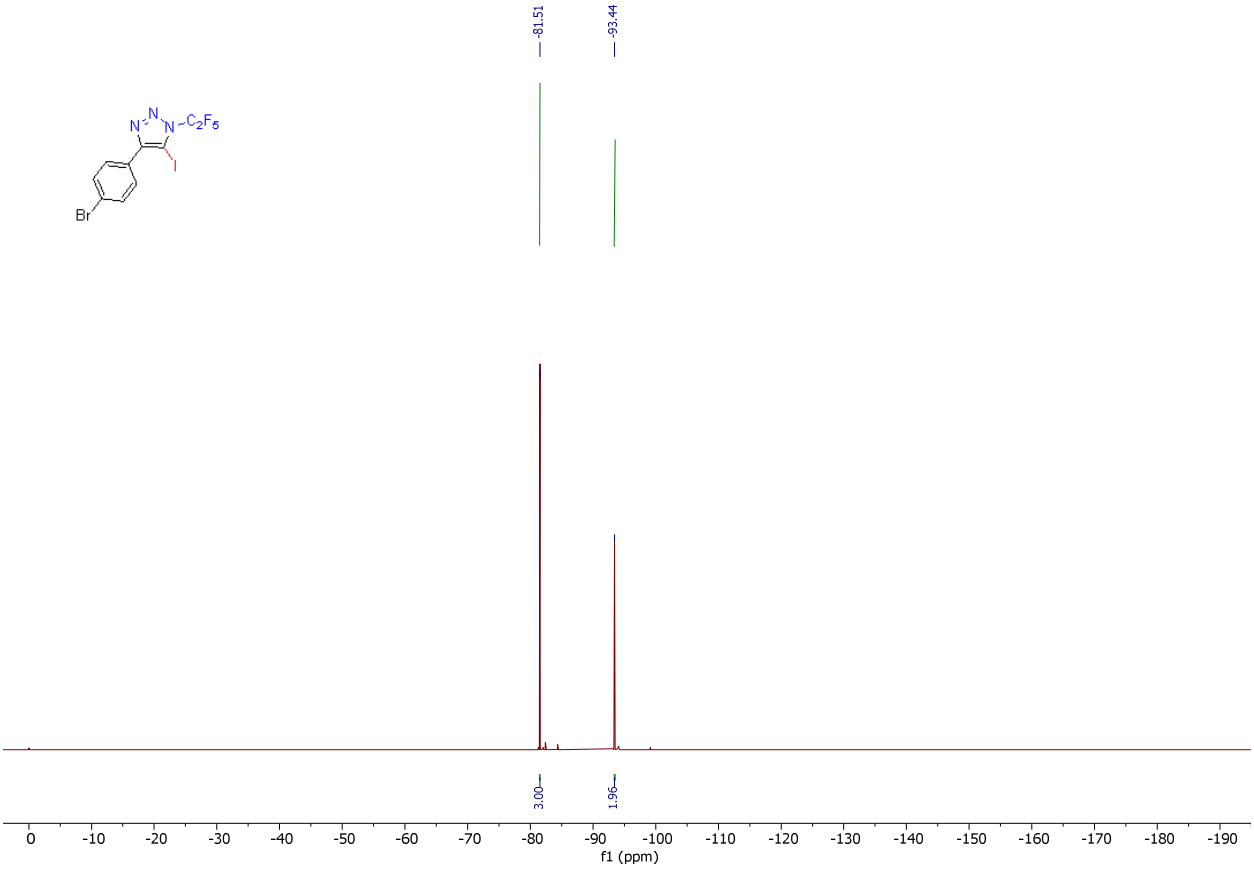
^{1}H NMR spectrum of **1af** ($CDCl_3$, 400 MHz)



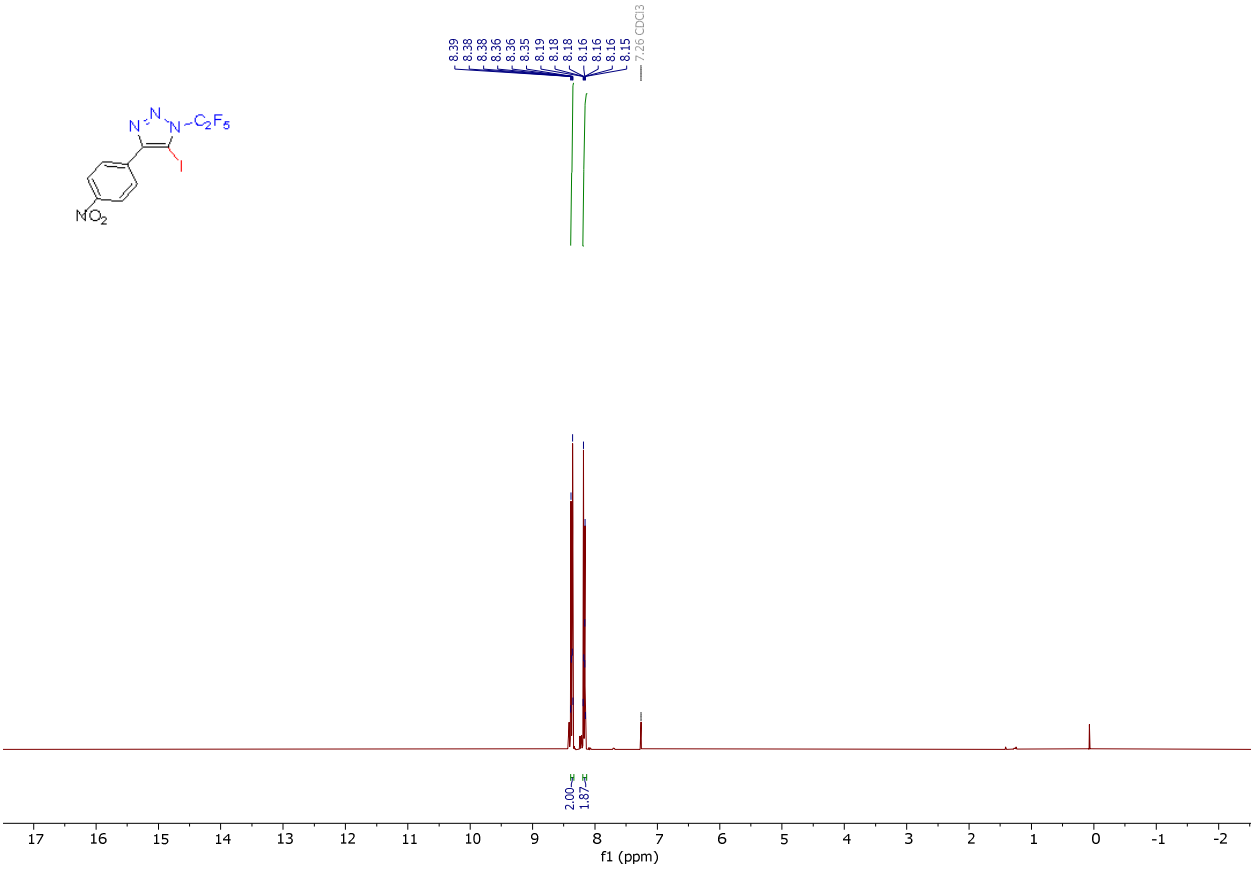
^{13}C NMR spectrum of **1af** ($CDCl_3$, 101 MHz)



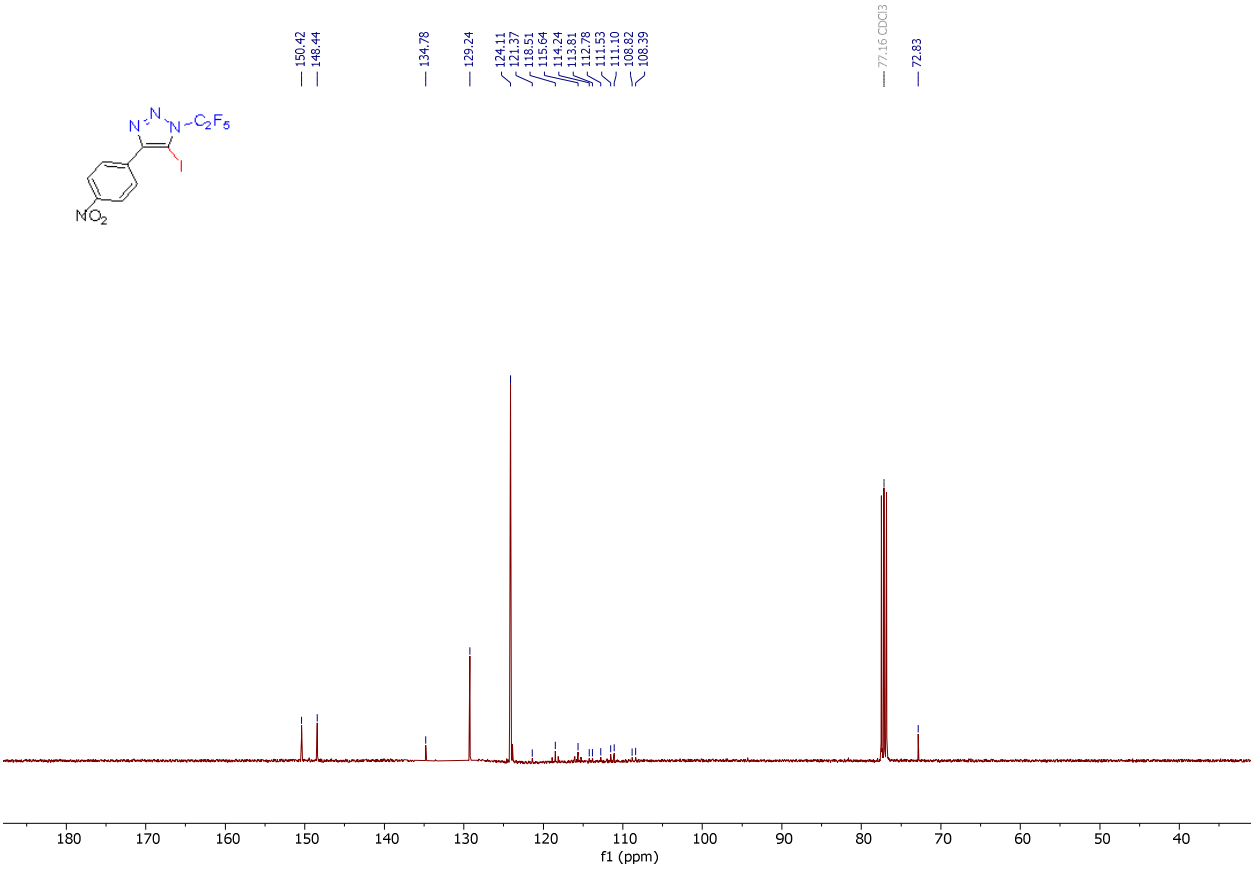
^{19}F NMR spectrum of **1af** ($CDCl_3$, 376 MHz)



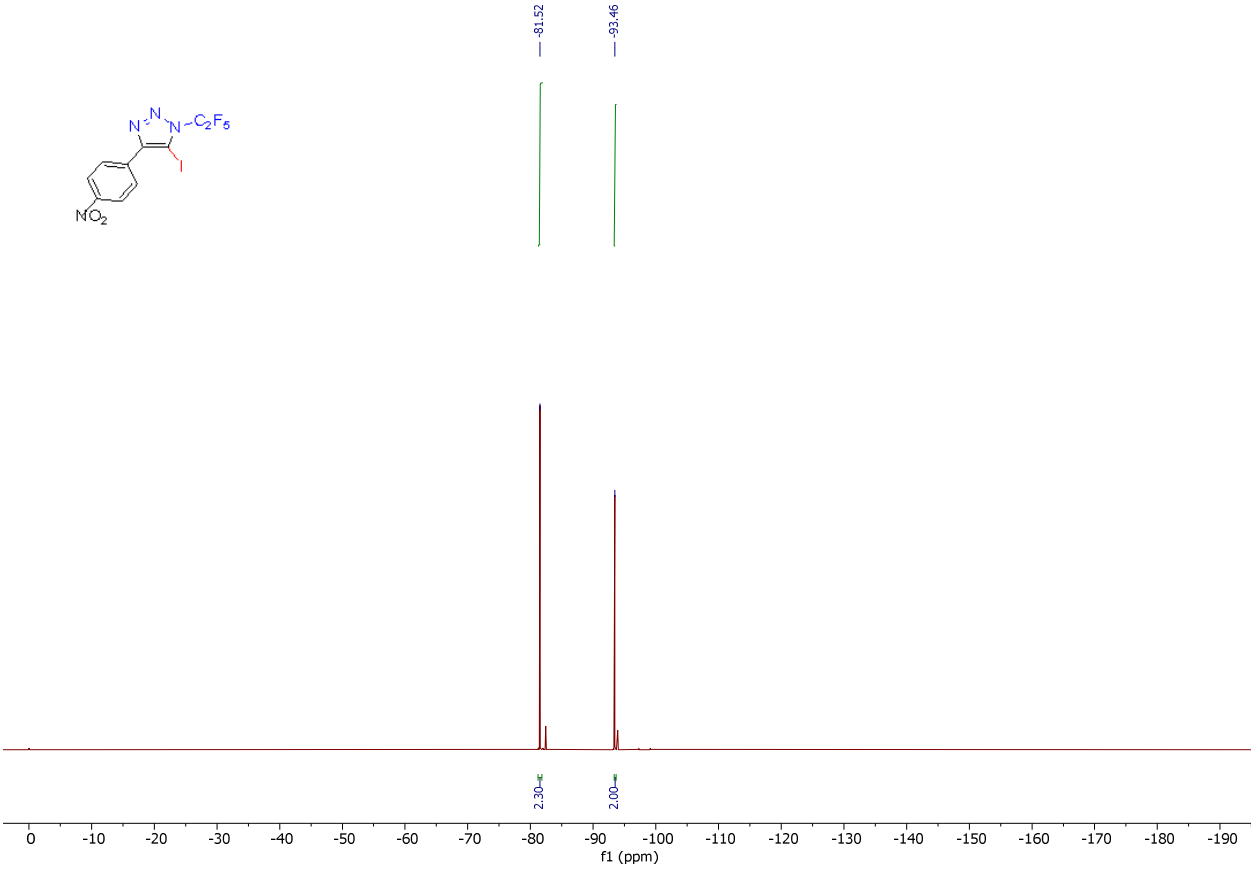
^{1}H NMR spectrum of **1ag** ($CDCl_3$, 400 MHz)



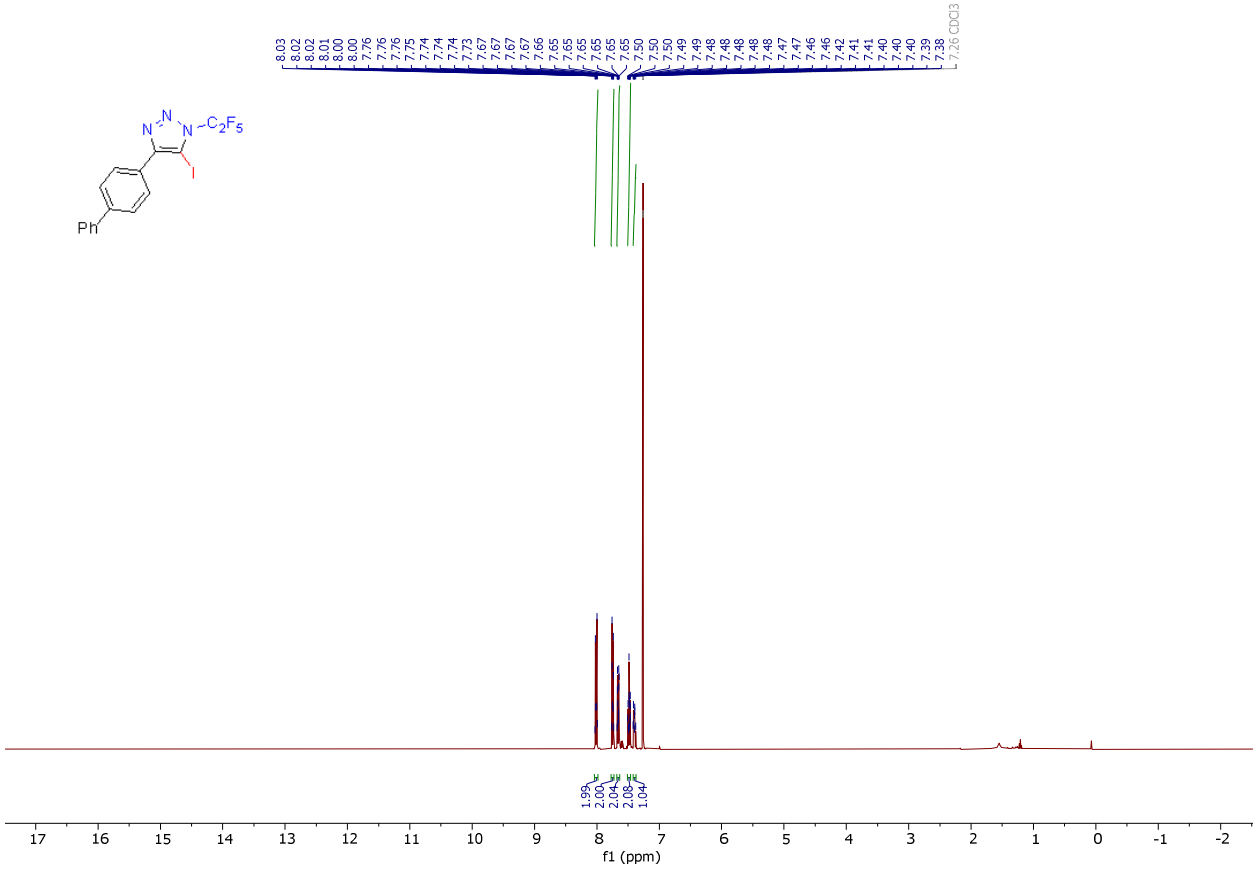
^{13}C NMR spectrum of **1ag** ($CDCl_3$, 101 MHz)



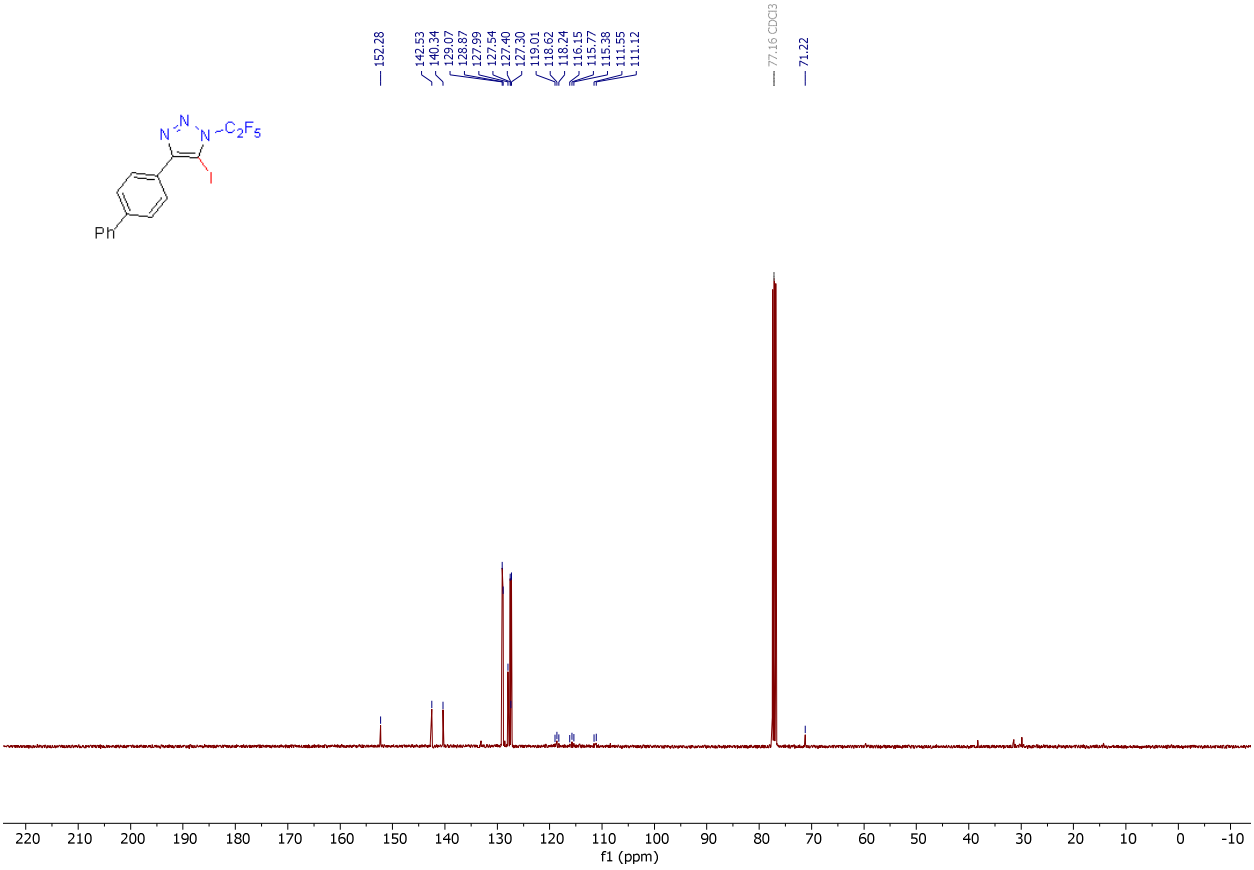
^{19}F NMR spectrum of **1ag** ($CDCl_3$, 376 MHz)



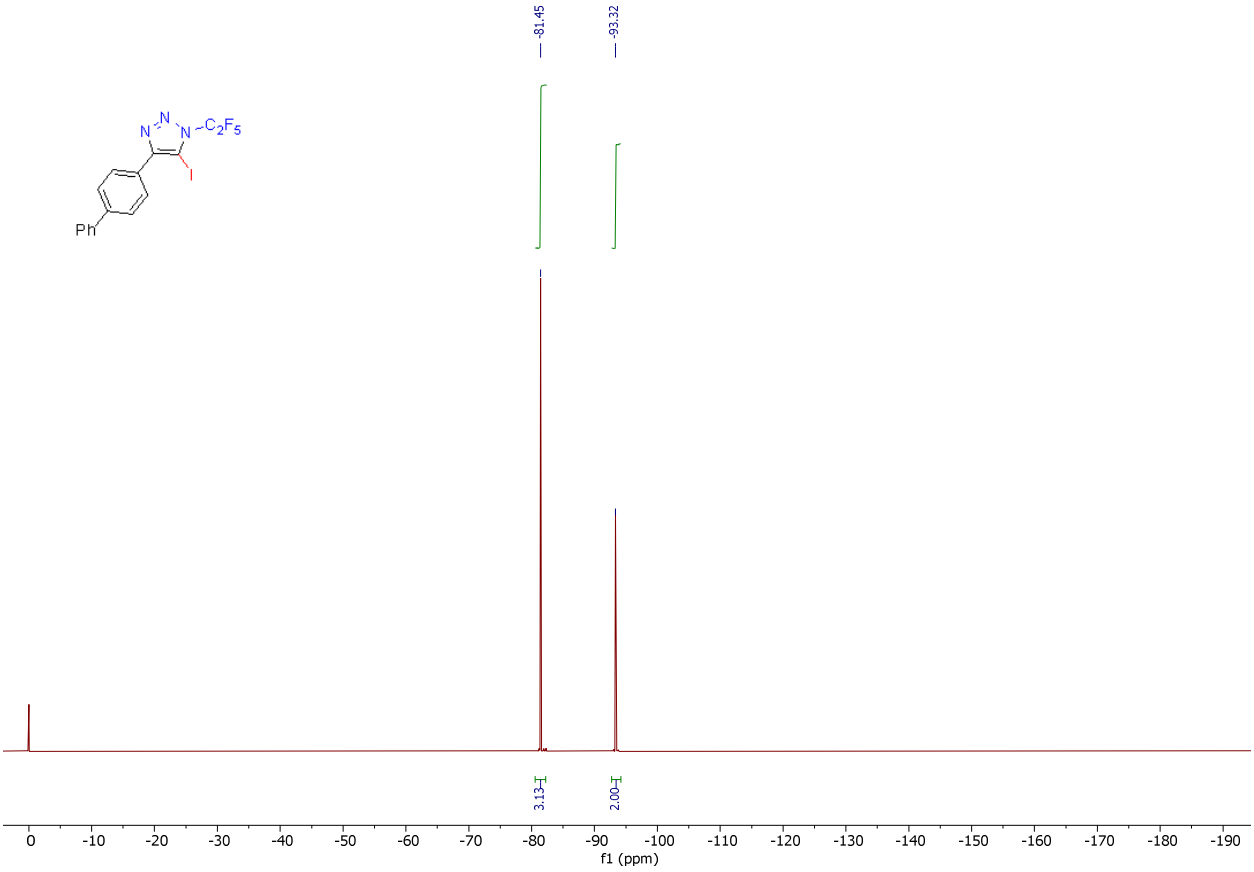
^{1}H NMR spectrum of **1ah** ($CDCl_3$, 400 MHz)



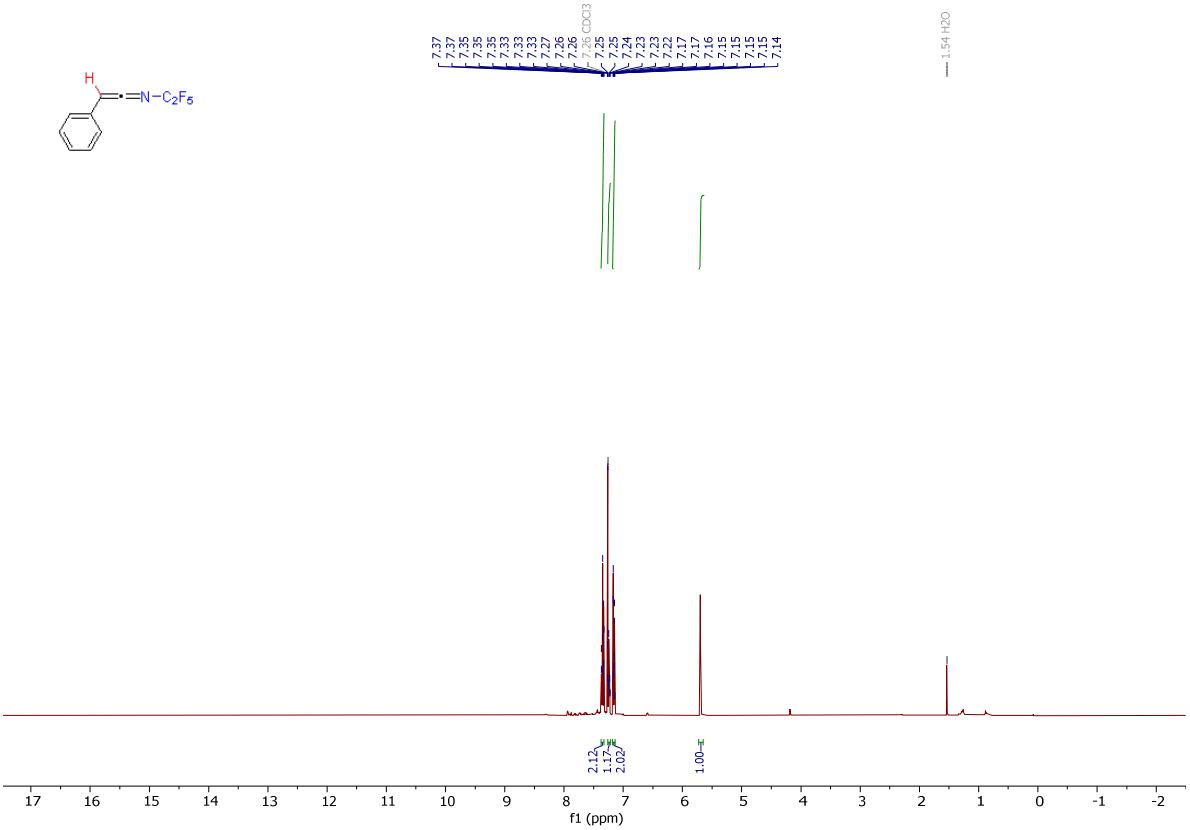
^{13}C NMR spectrum of **1ah** ($CDCl_3$, 101 MHz)



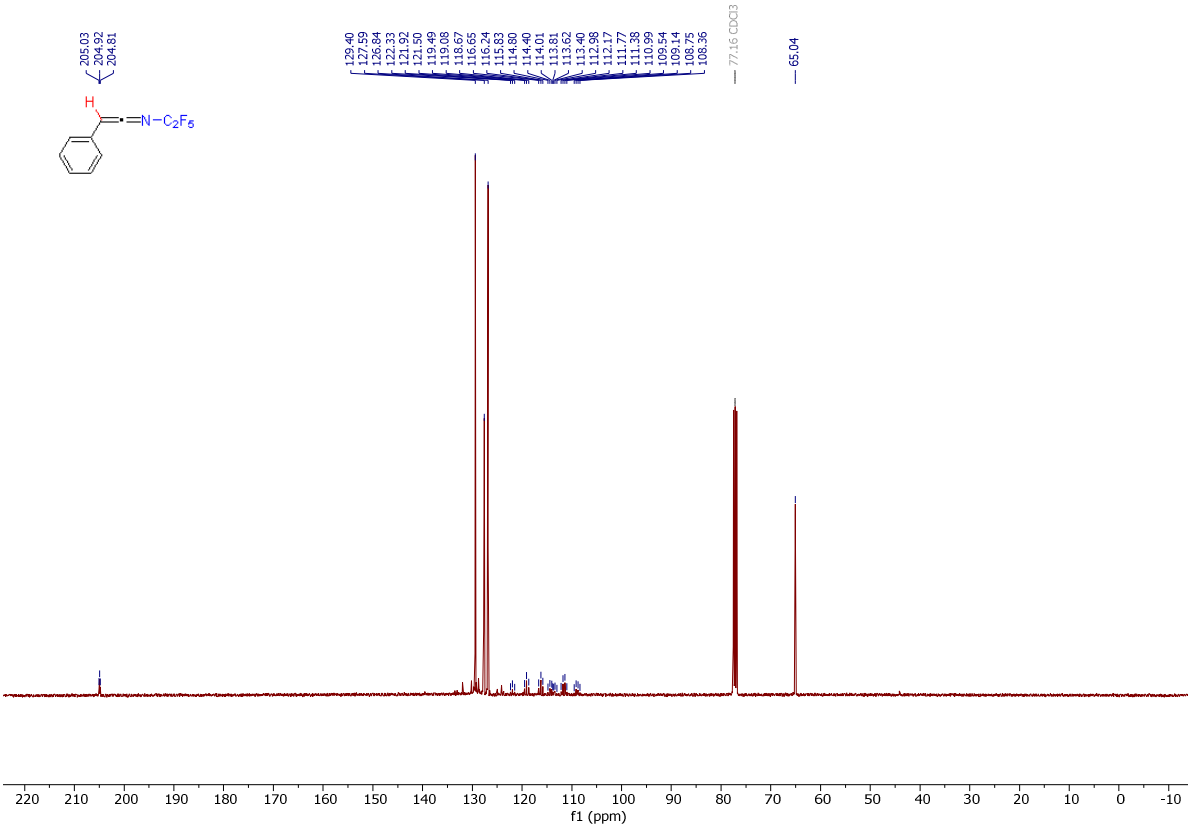
^{19}F NMR spectrum of **1ah** ($CDCl_3$, 376 MHz)



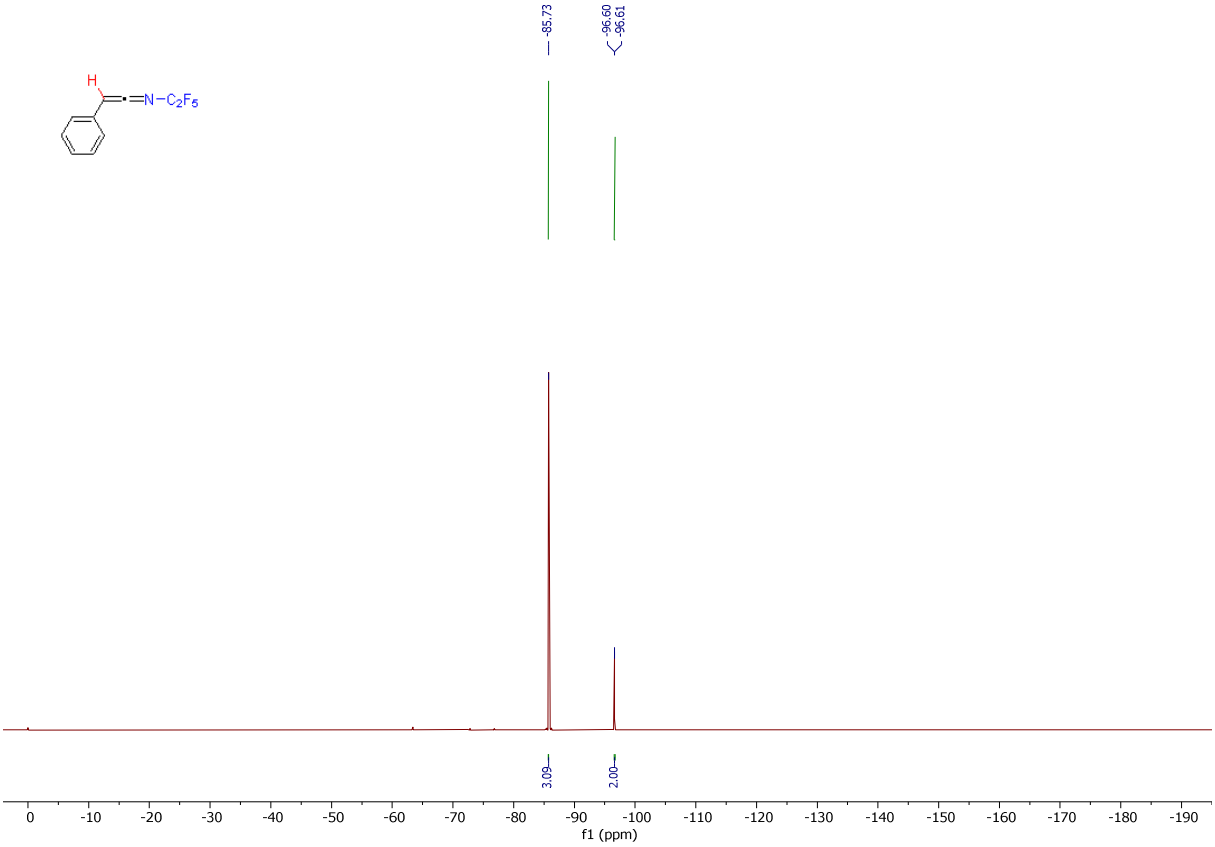
^{1}H NMR spectrum of **2a** ($CDCl_3$, 400 MHz)



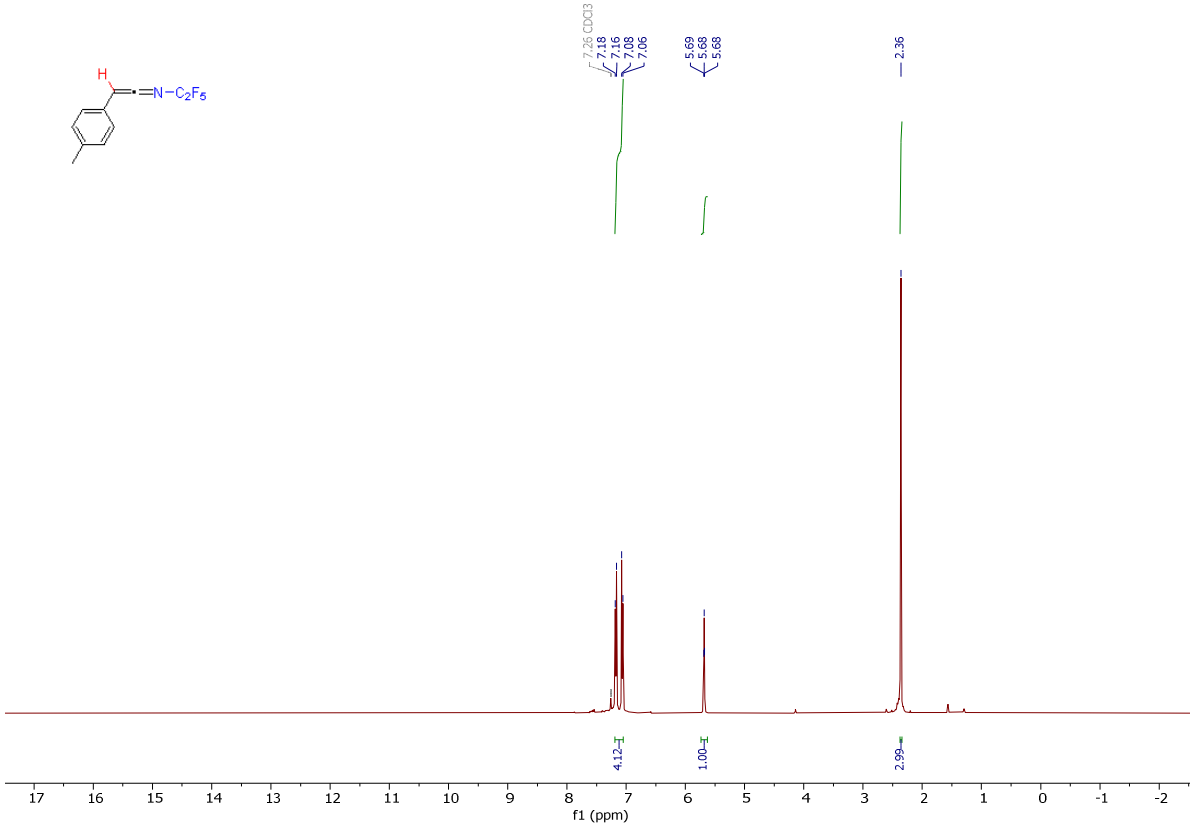
^{13}C NMR spectrum of **2a** ($CDCl_3$, 101 MHz)



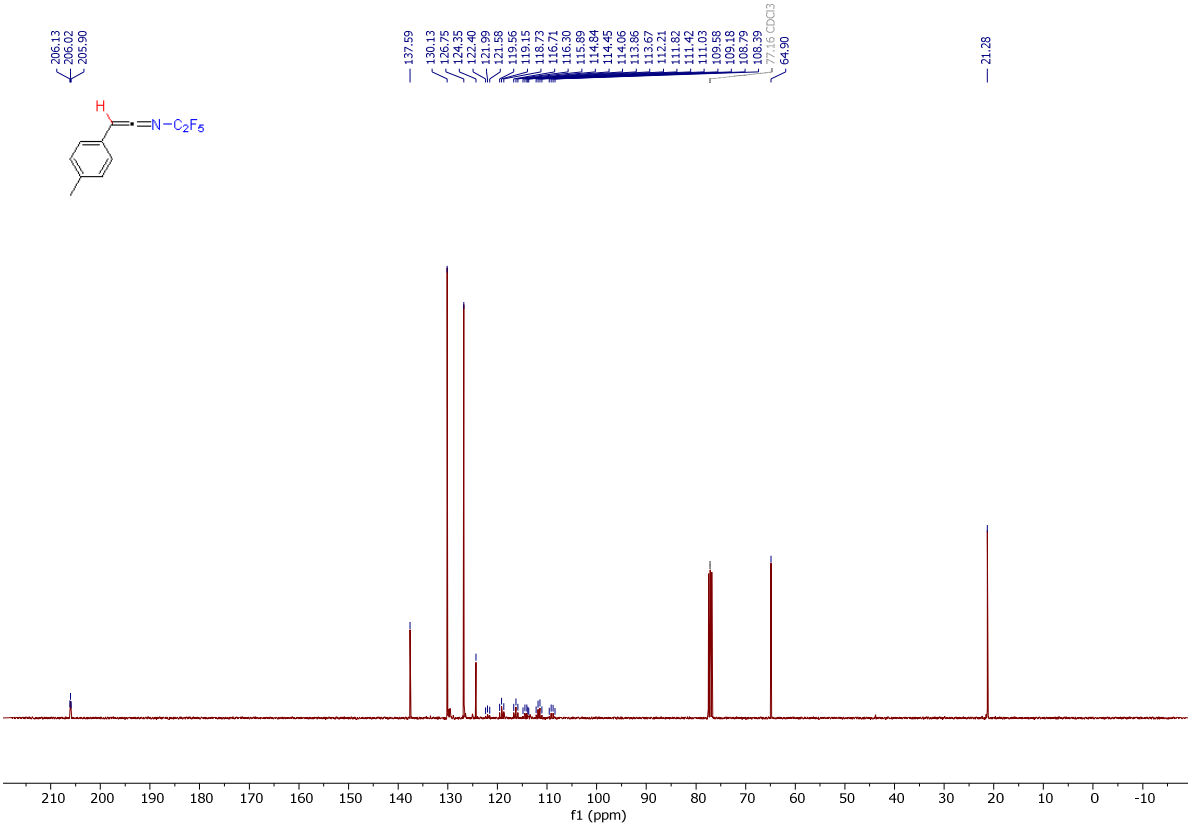
^{19}F NMR spectrum of **2a** ($CDCl_3$, 376 MHz)



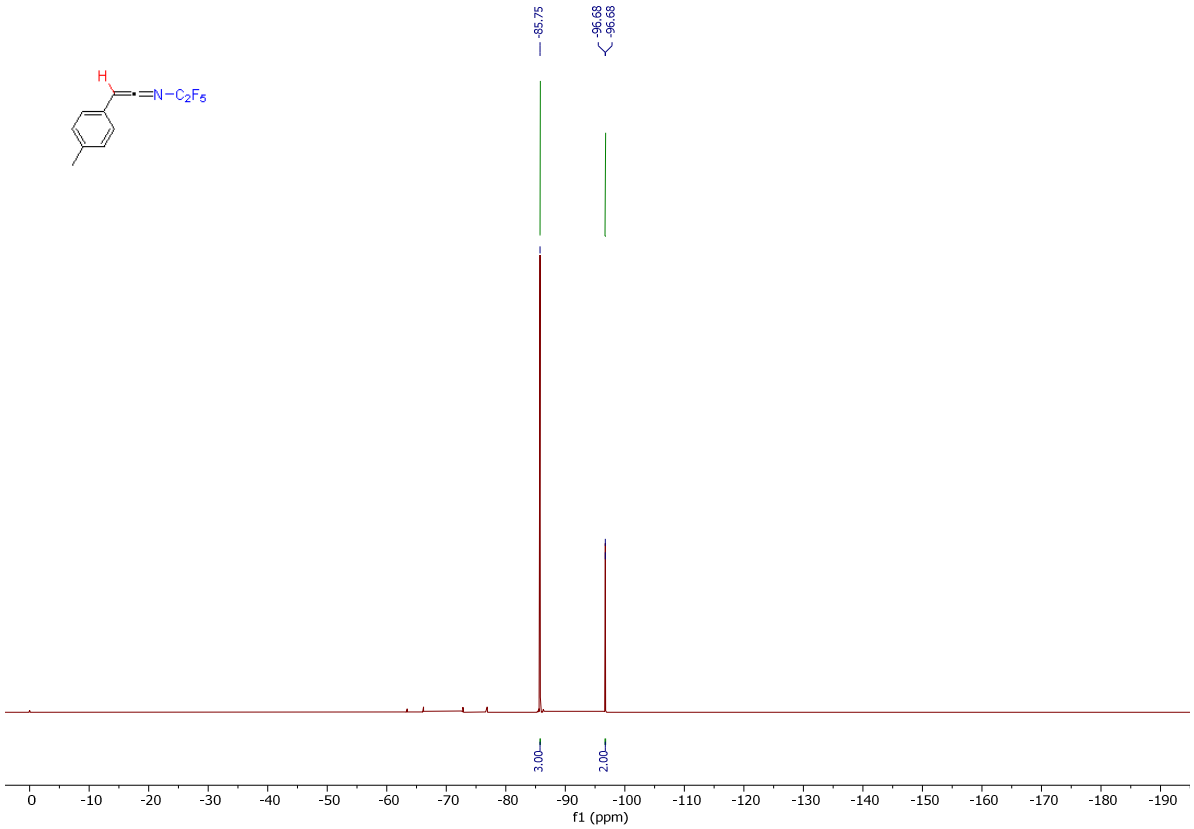
^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz)



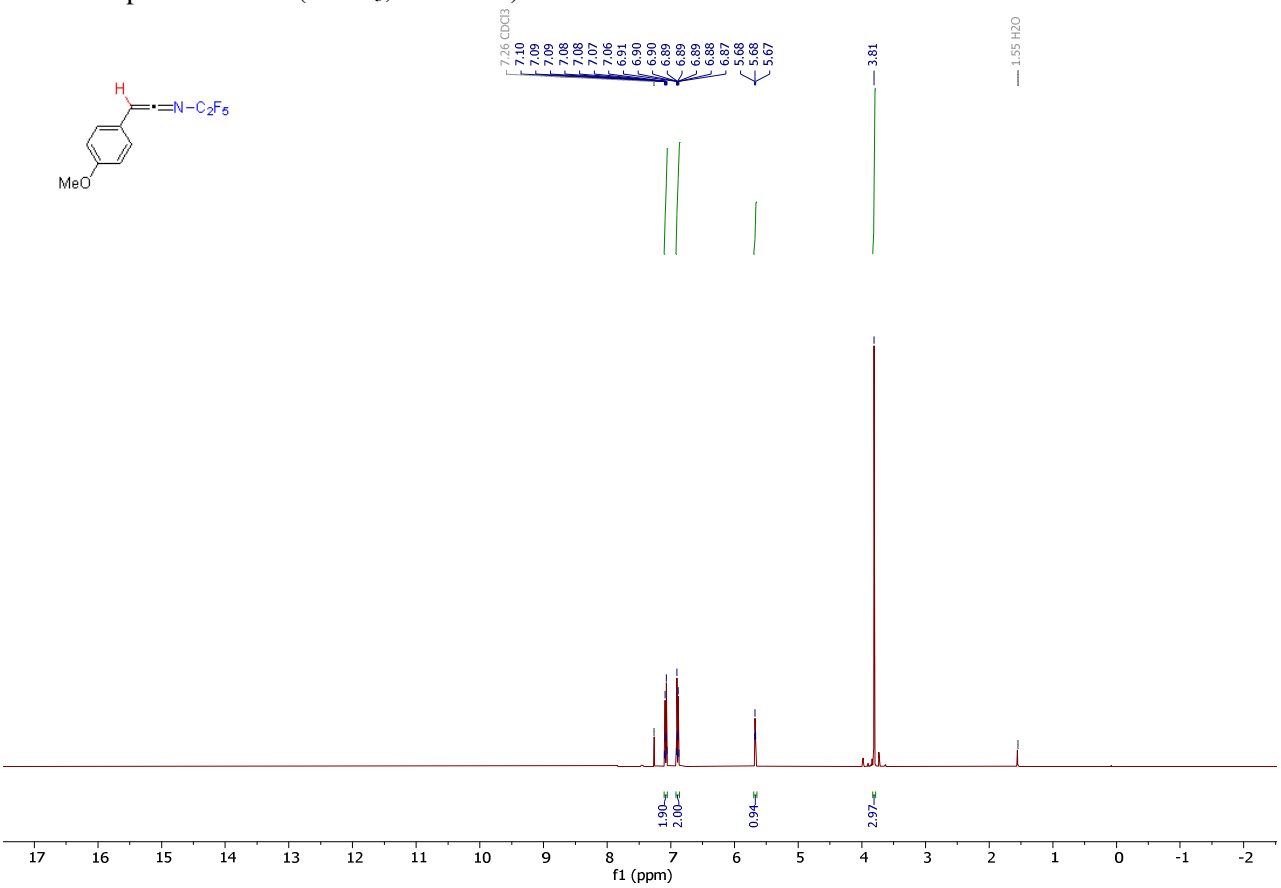
^{13}C NMR spectrum of **2b** ($CDCl_3$, 101 MHz)



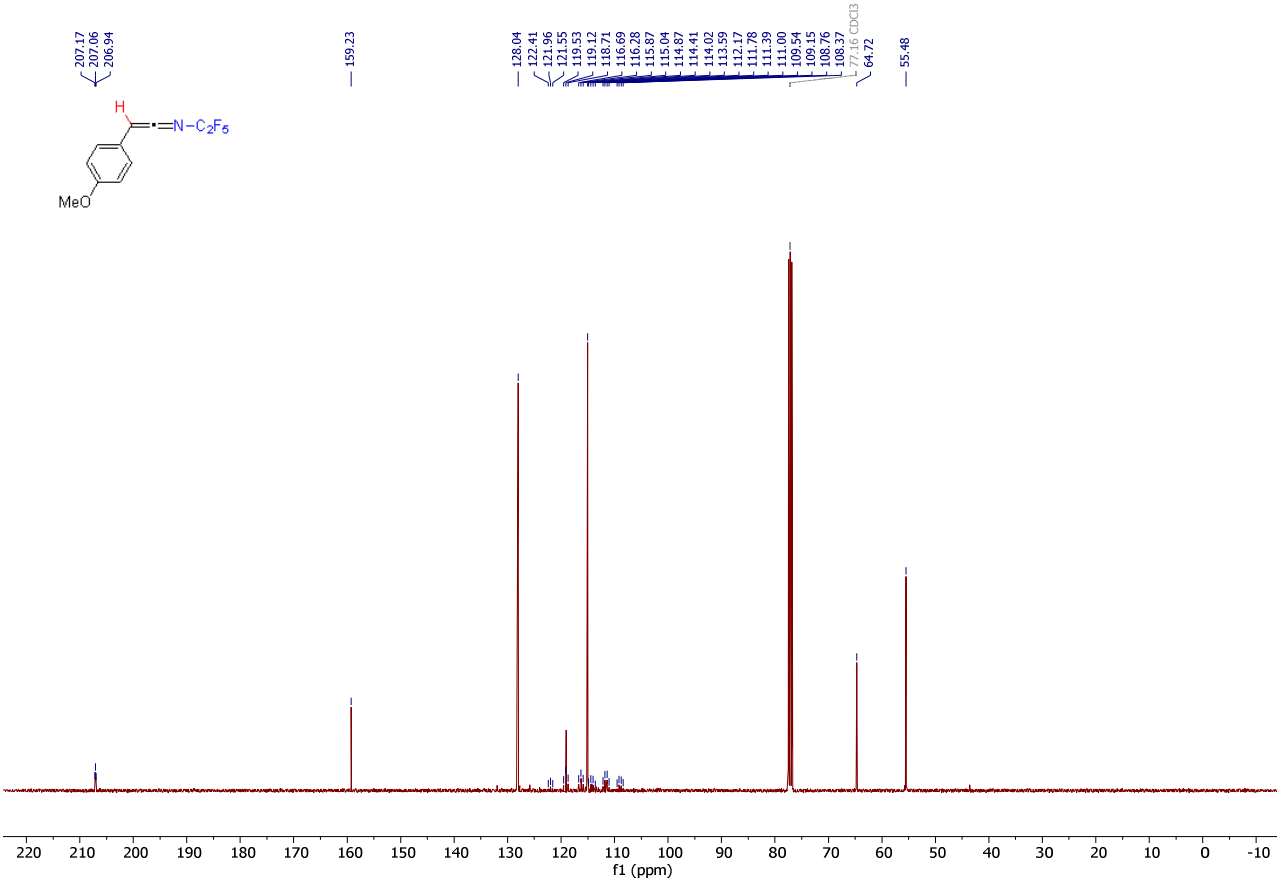
^{19}F NMR spectrum of **2b** ($CDCl_3$, 376 MHz)



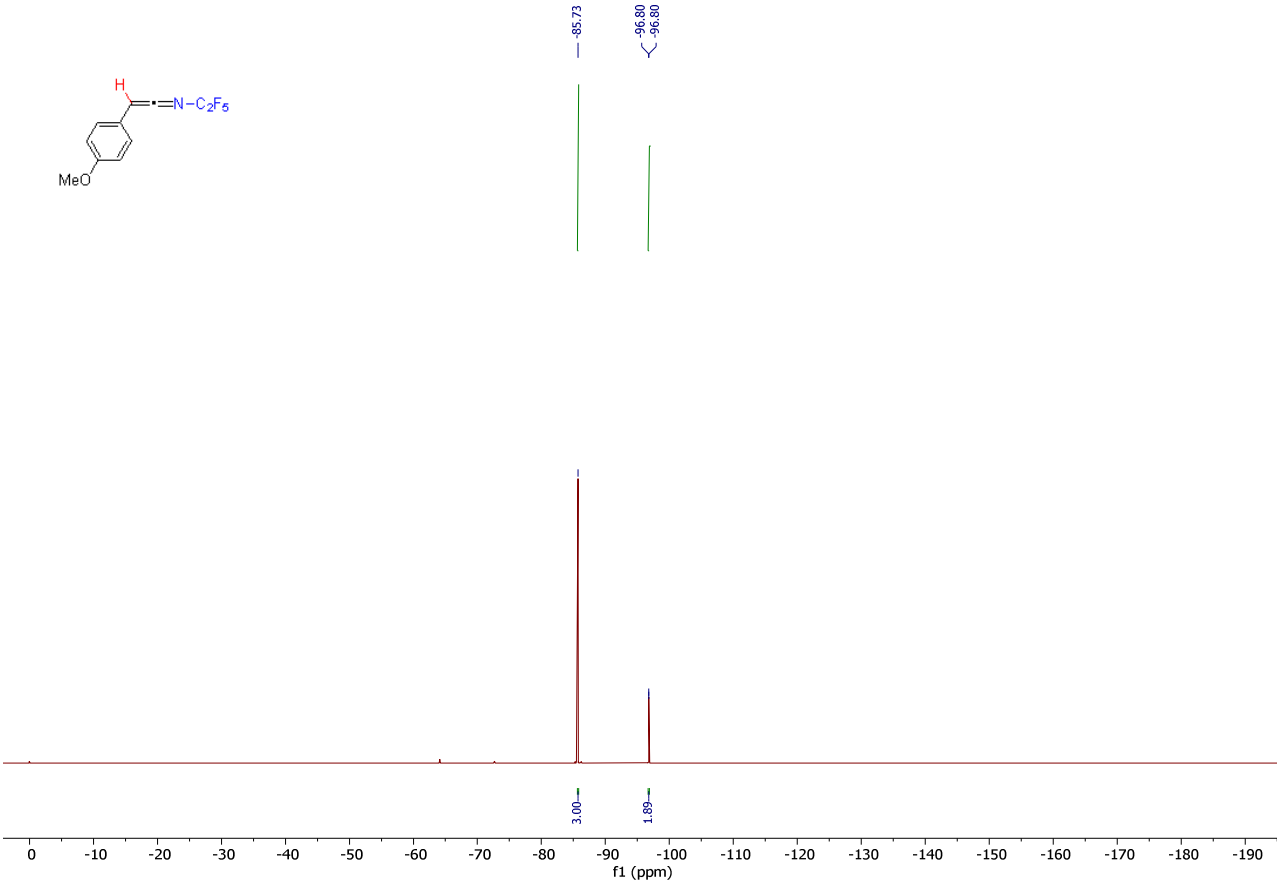
^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz)



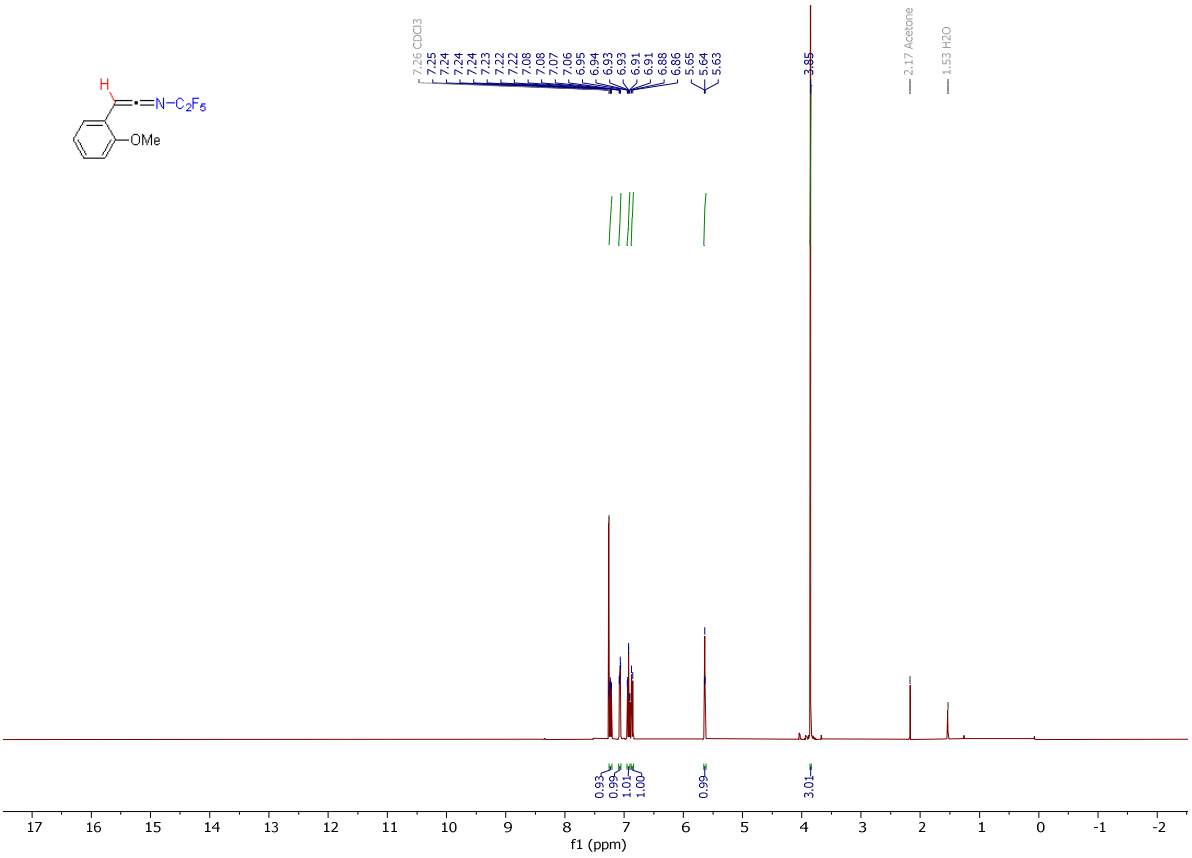
^{13}C NMR spectrum of **2c** ($CDCl_3$, 101 MHz)



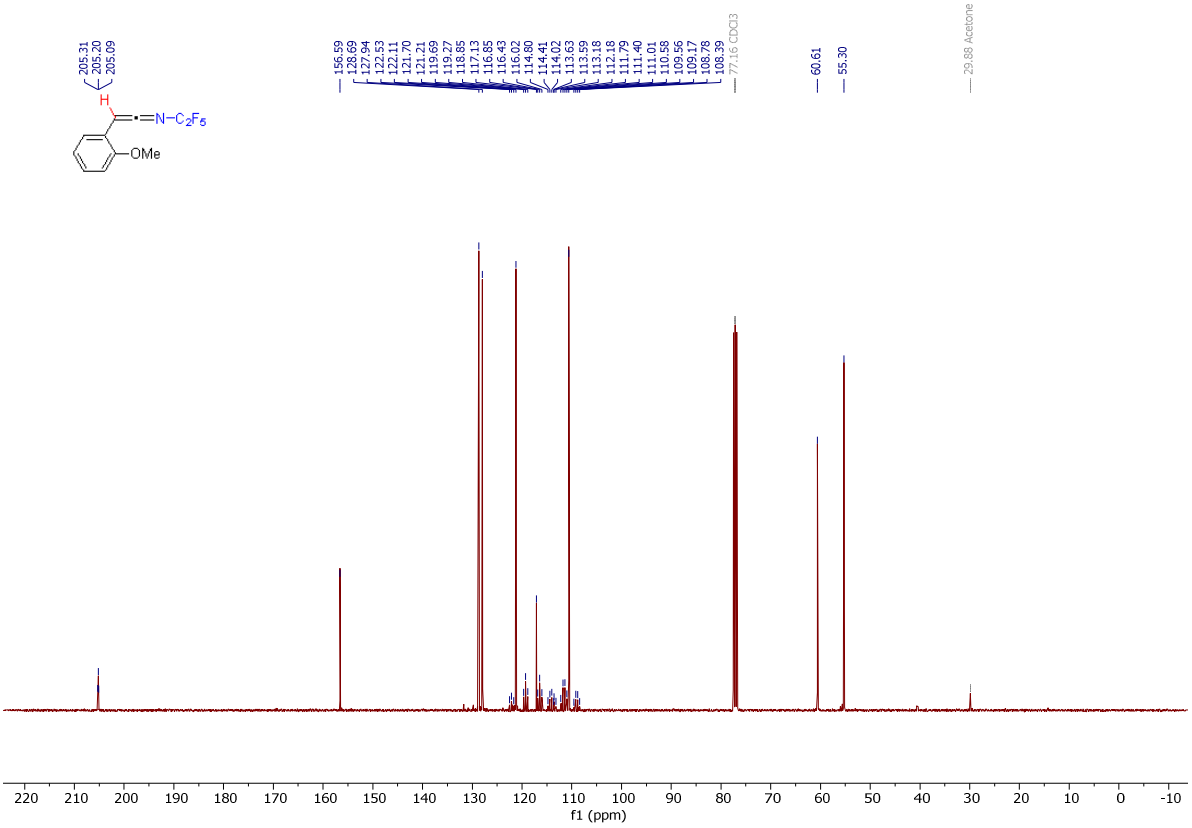
^{19}F NMR spectrum of **2c** ($CDCl_3$, 376 MHz)



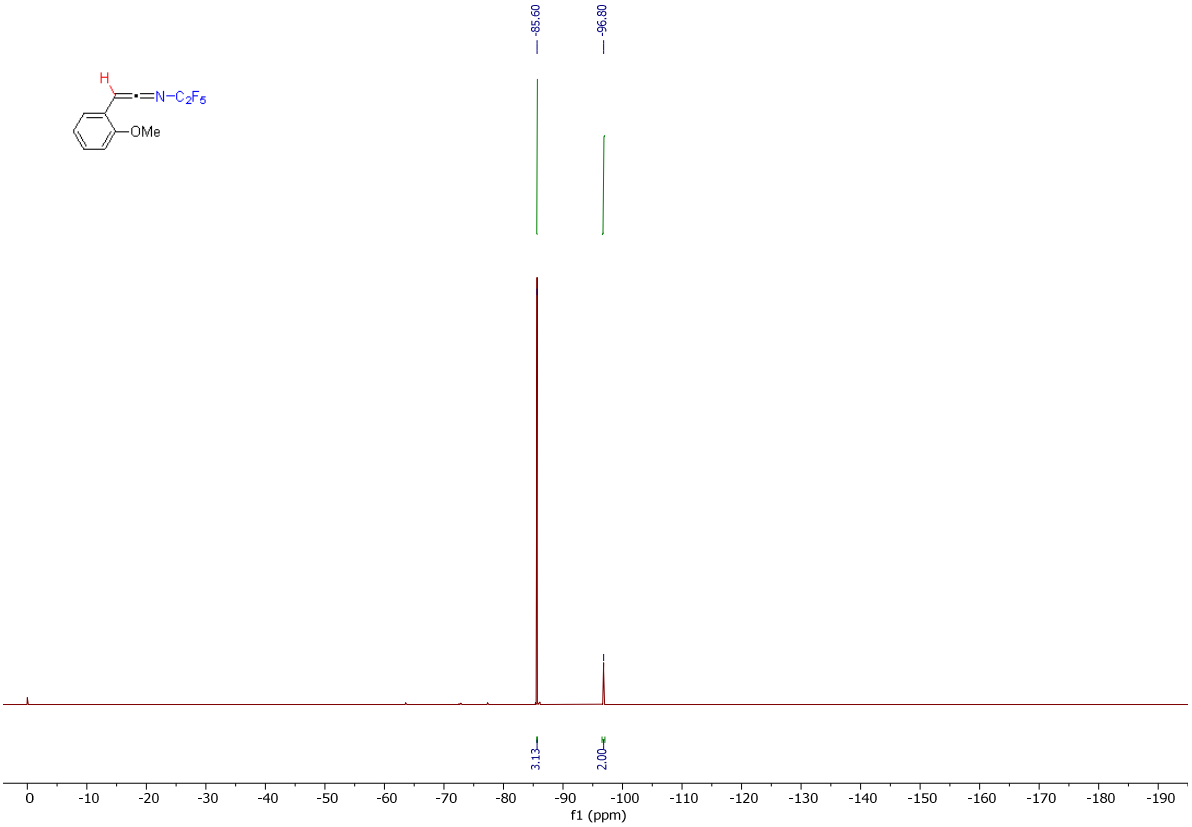
^{1}H NMR spectrum of **2d** ($CDCl_3$, 400 MHz)



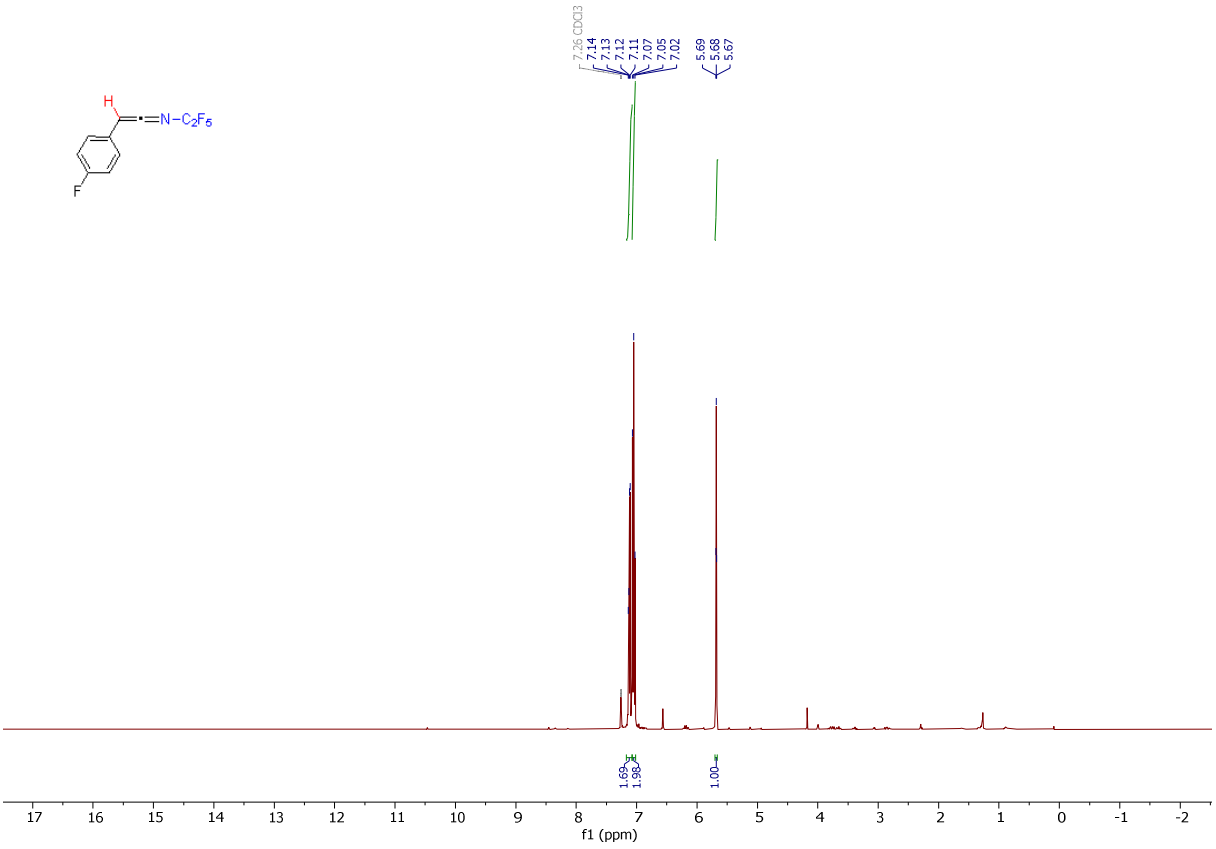
^{13}C NMR spectrum of **2d** ($CDCl_3$, 101 MHz)



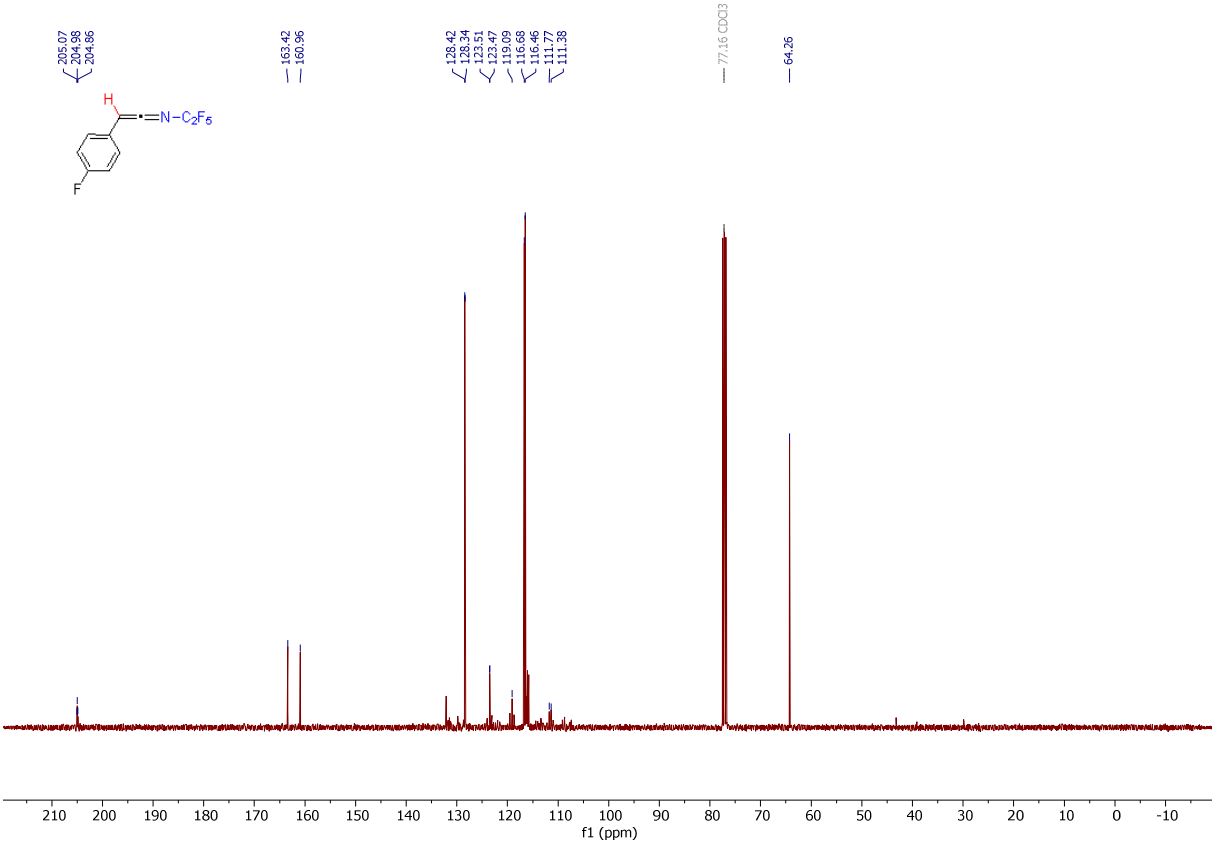
^{19}F NMR spectrum of **2d** ($CDCl_3$, 376 MHz)



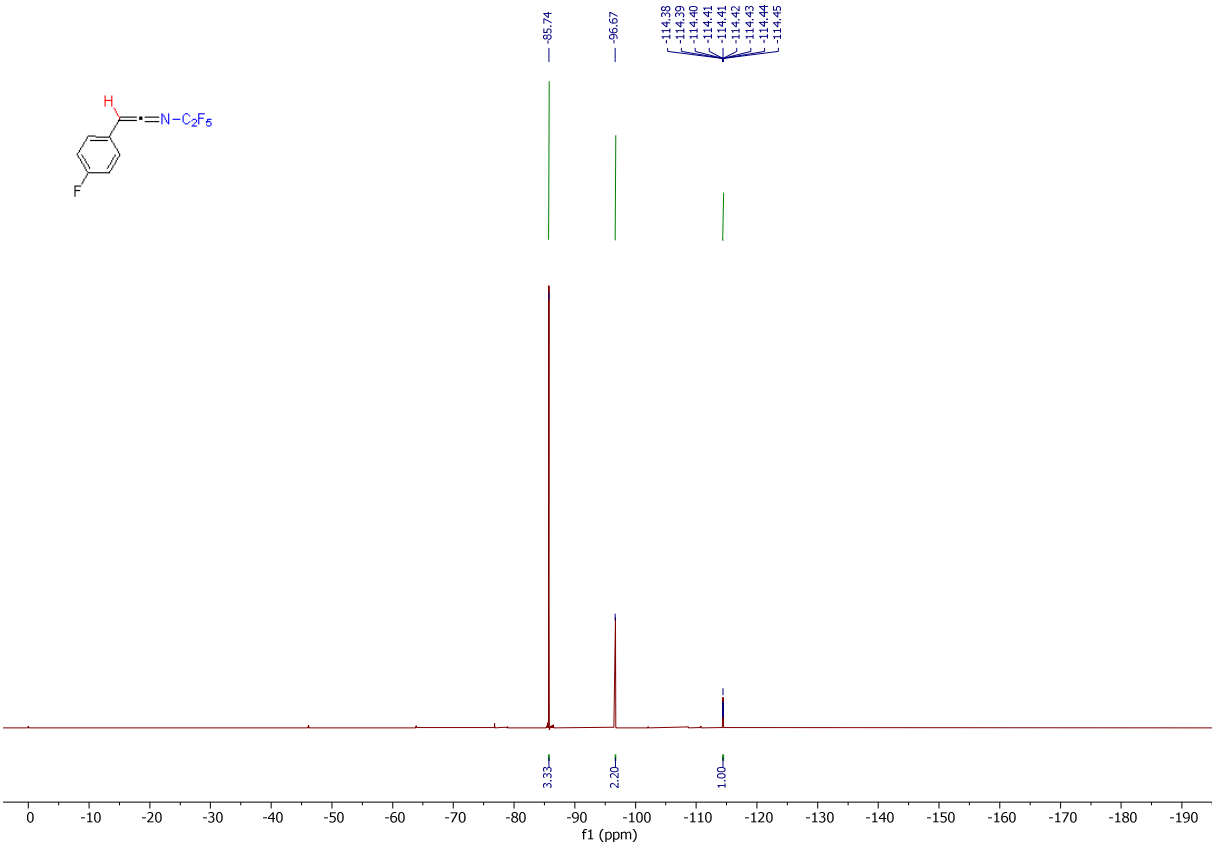
^{1}H NMR spectrum of **2e** ($CDCl_3$, 400 MHz)



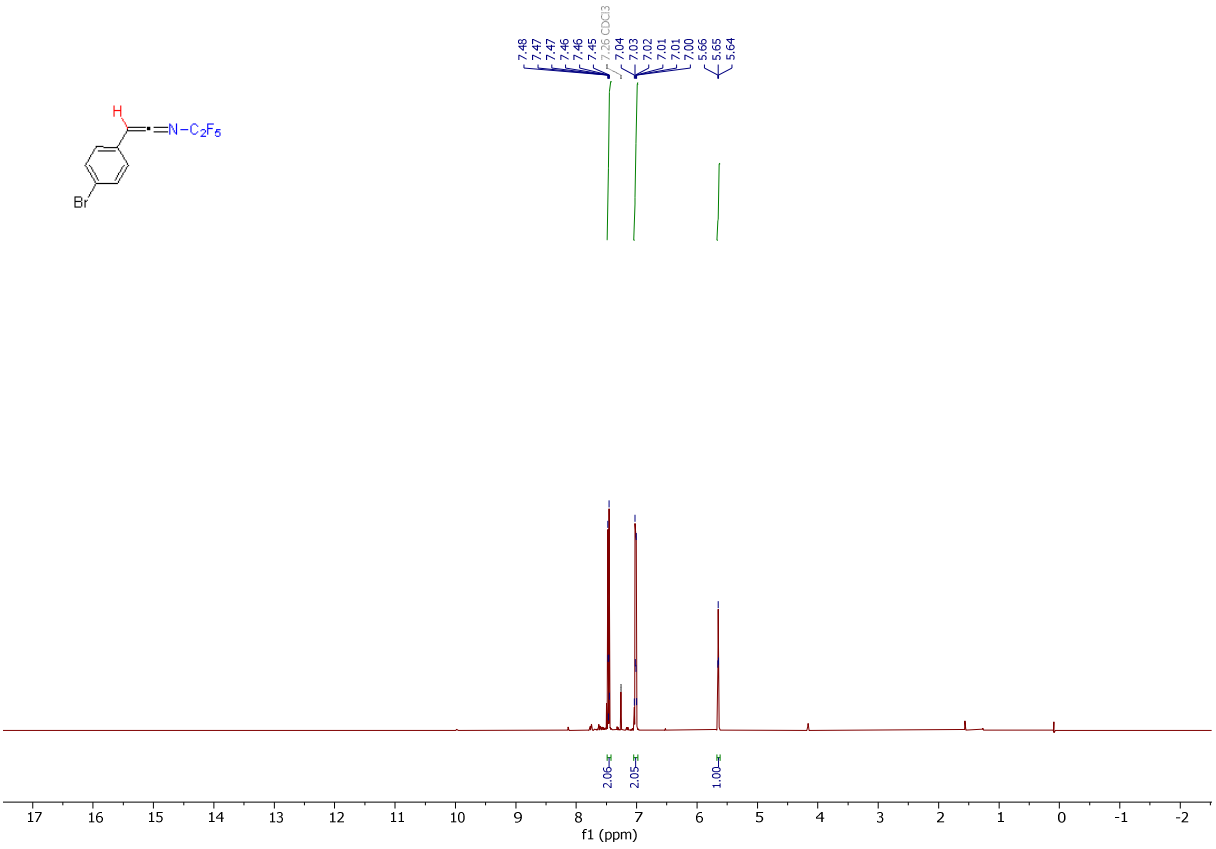
^{13}C NMR spectrum of **2e** ($CDCl_3$, 101 MHz)



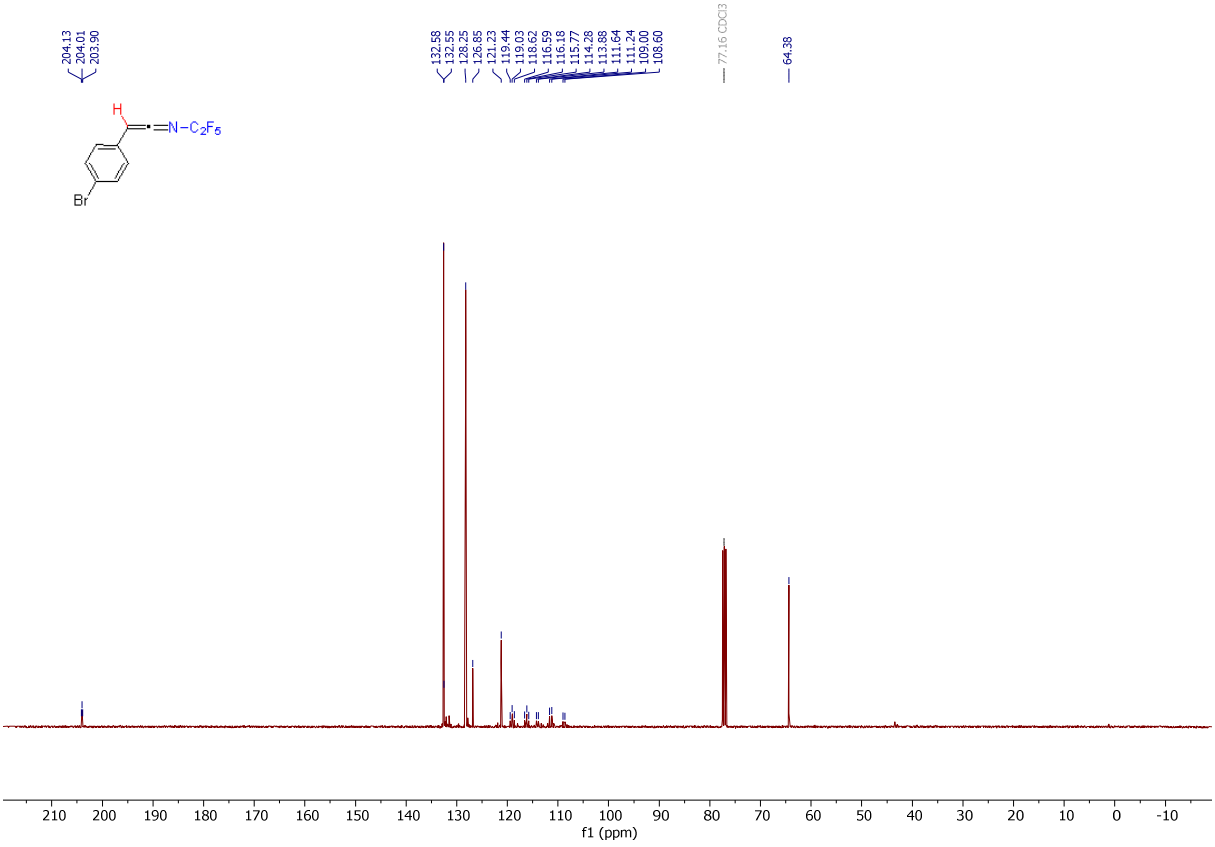
^{19}F NMR spectrum of **2e** ($CDCl_3$, 376 MHz)



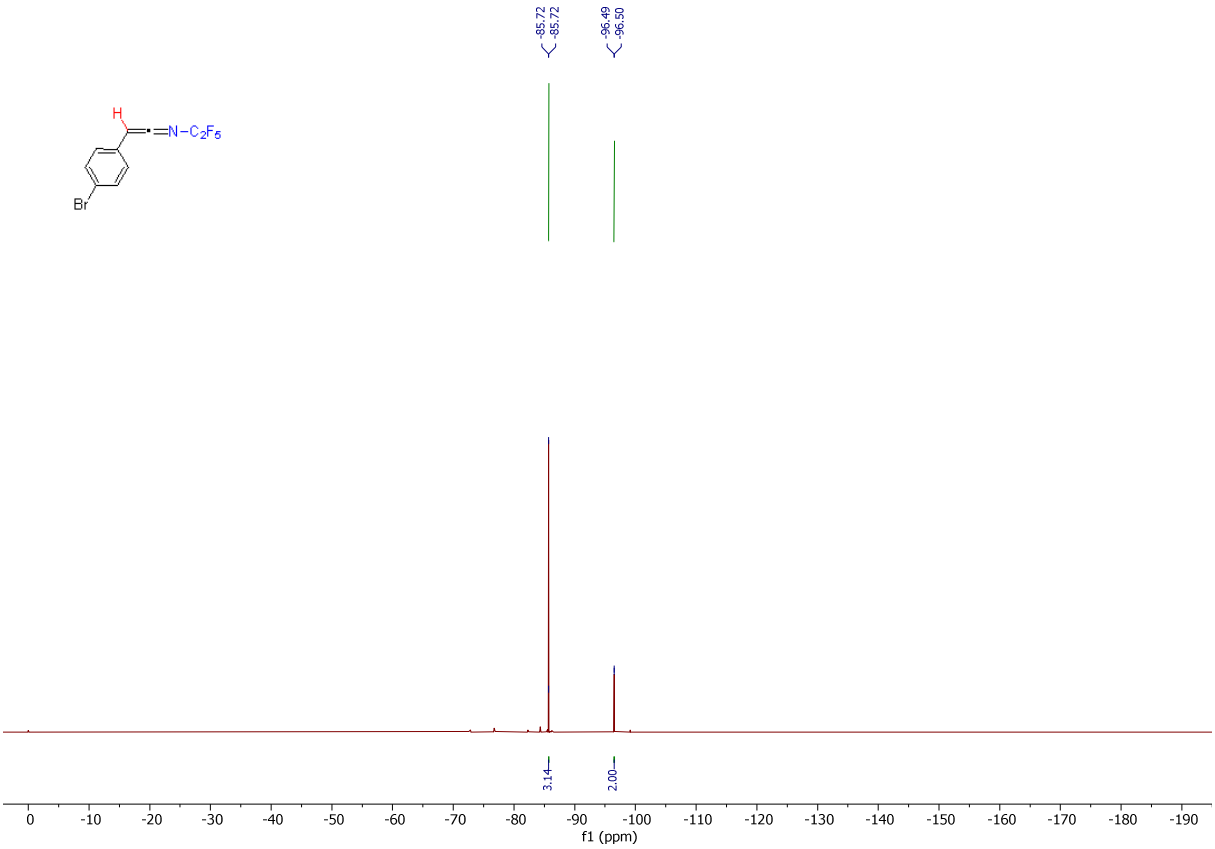
^{1}H NMR spectrum of **2f** ($CDCl_3$, 400 MHz)



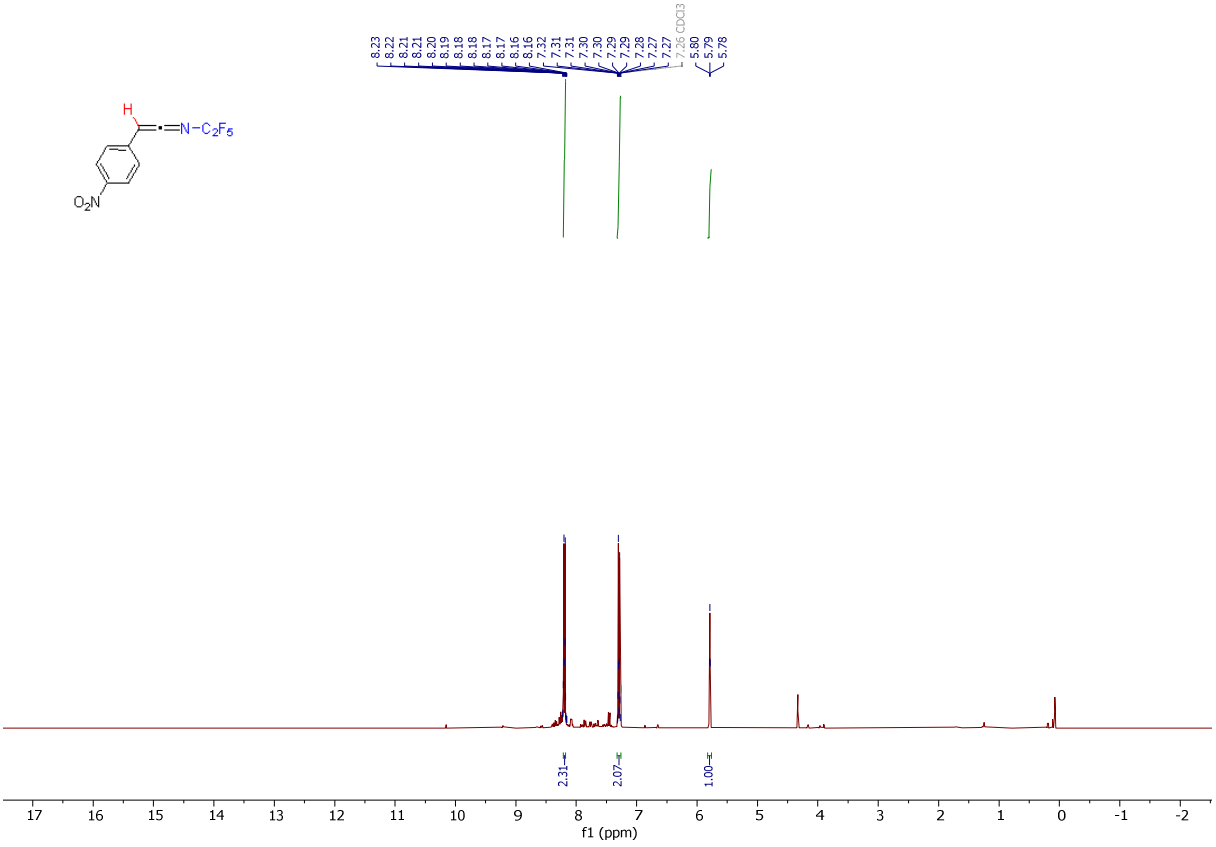
^{13}C NMR spectrum of **2f** ($CDCl_3$, 101 MHz)



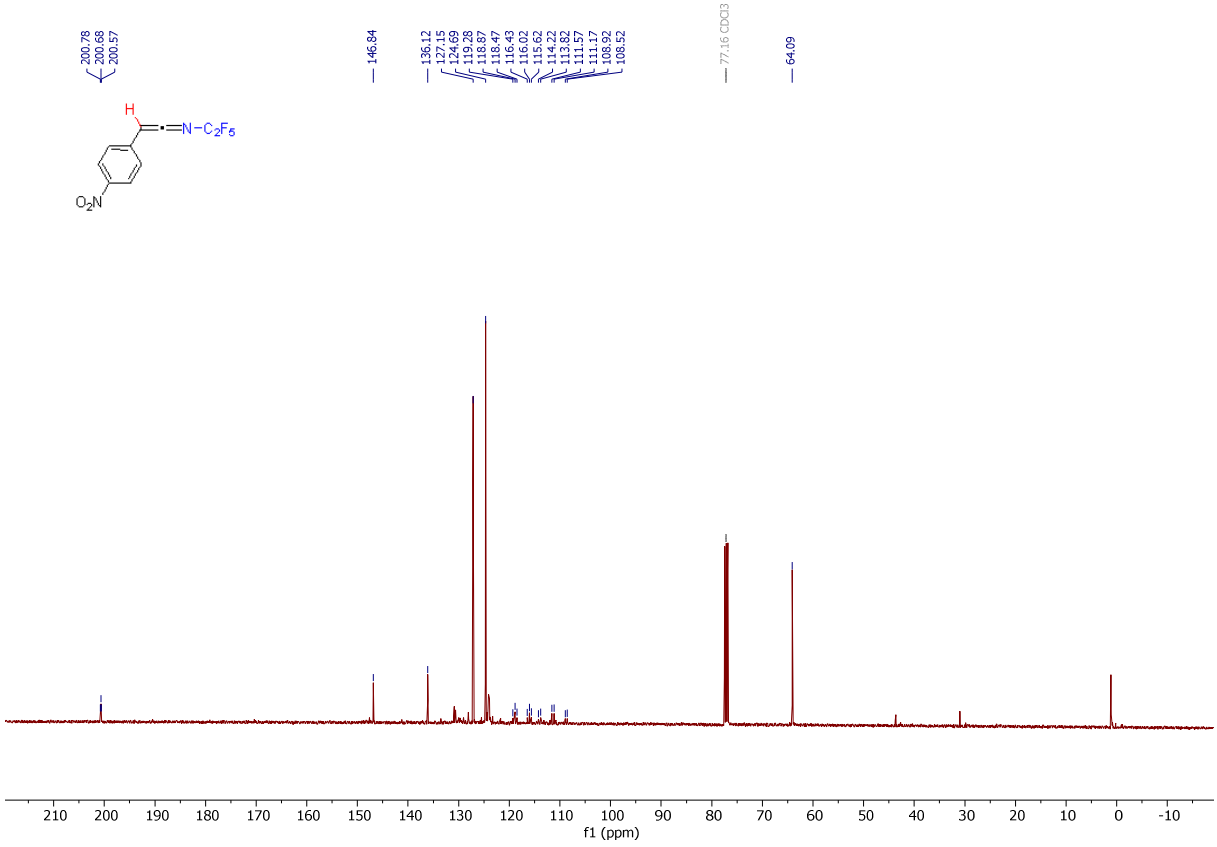
^{19}F NMR spectrum of **2f** ($CDCl_3$, 376 MHz)



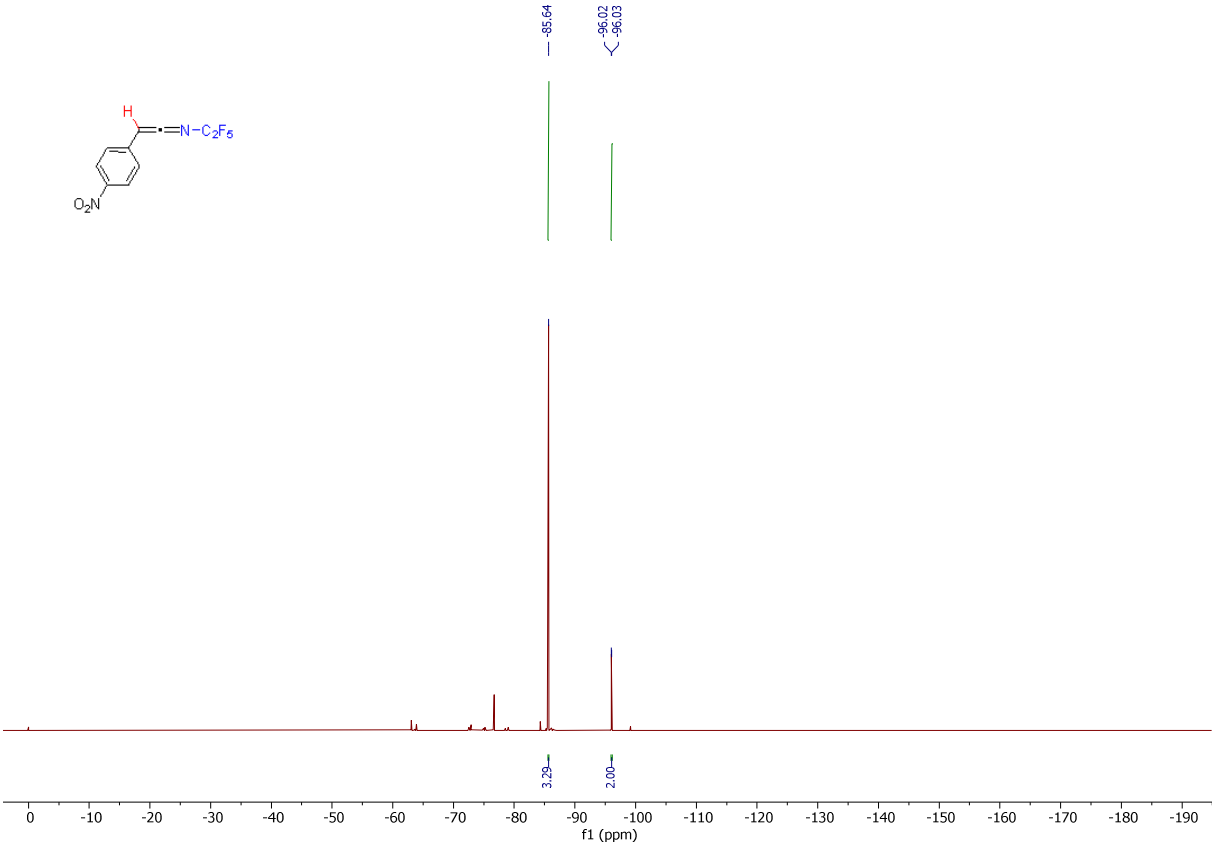
^{1}H NMR spectrum of **2g** ($CDCl_3$, 400 MHz)



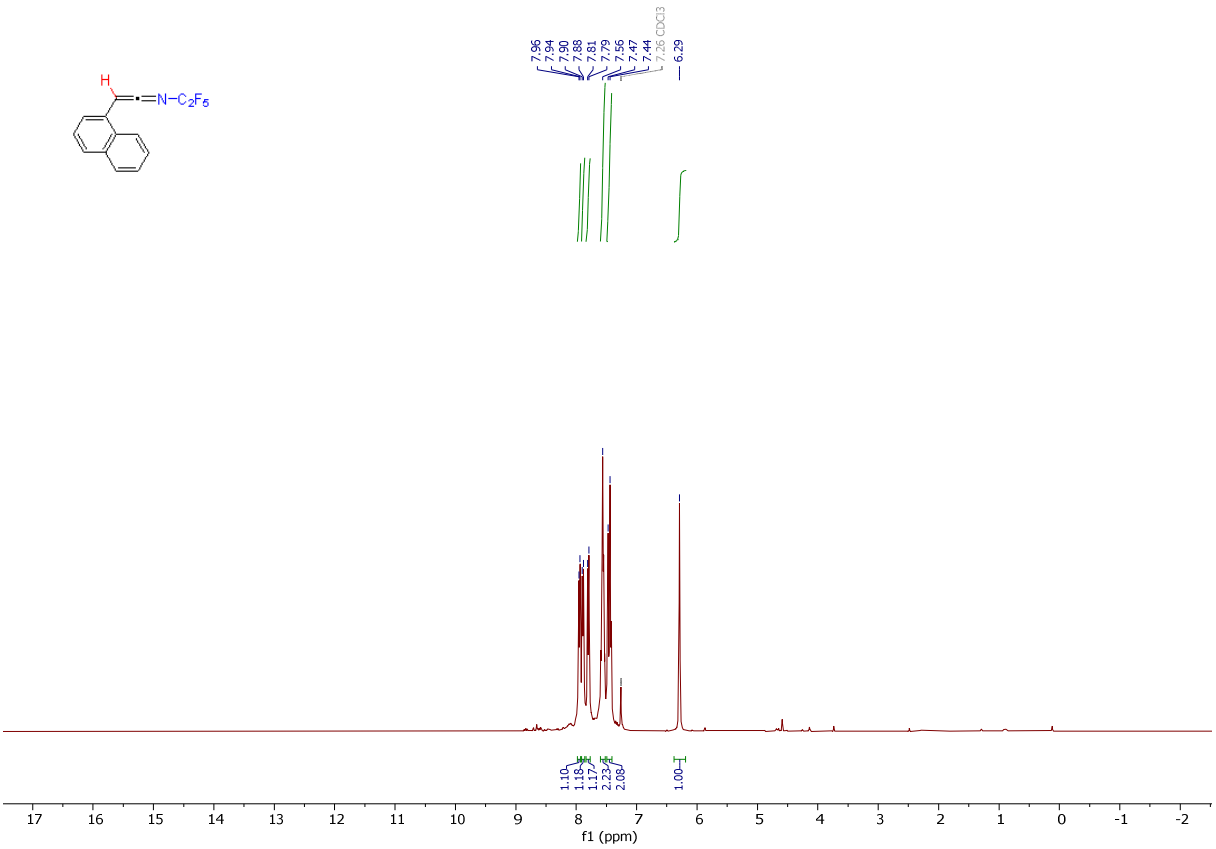
^{13}C NMR spectrum of **2g** ($CDCl_3$, 101 MHz)



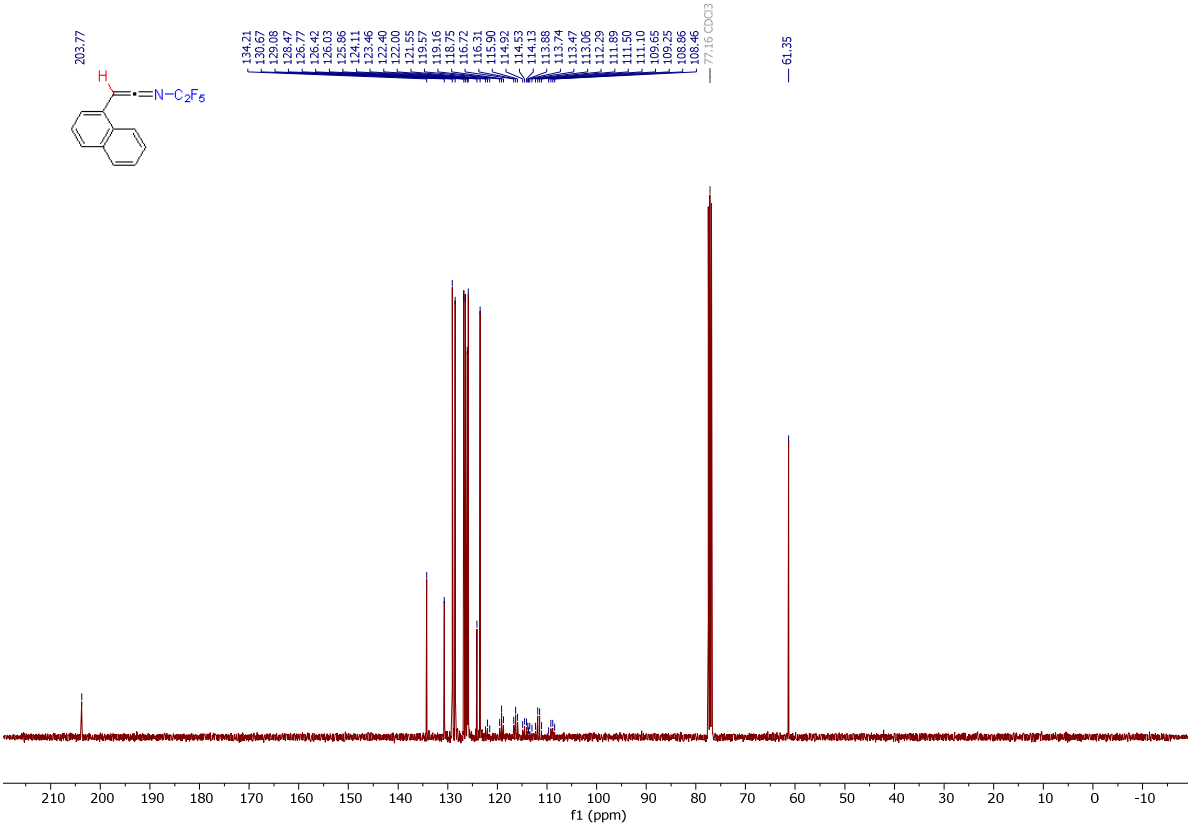
^{19}F NMR spectrum of **2g** ($CDCl_3$, 376 MHz)



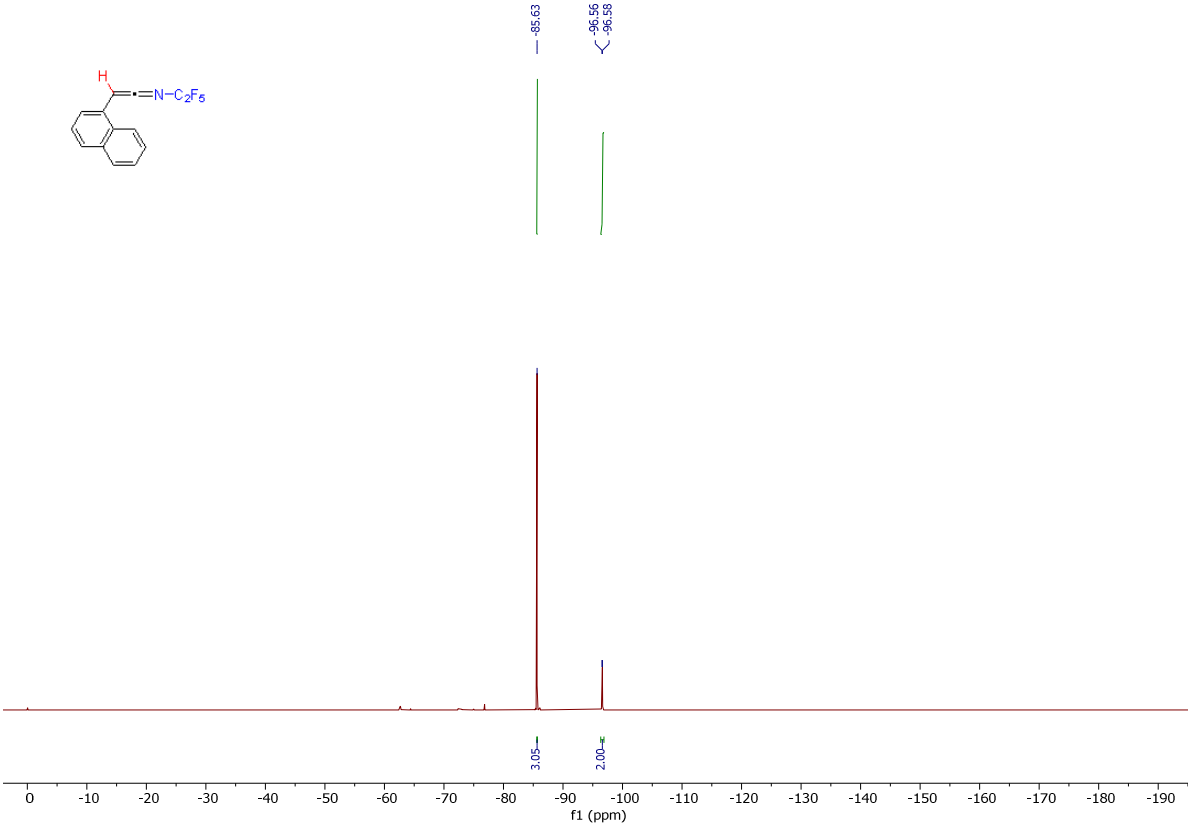
^{1}H NMR spectrum of **2h** ($CDCl_3$, 400 MHz)



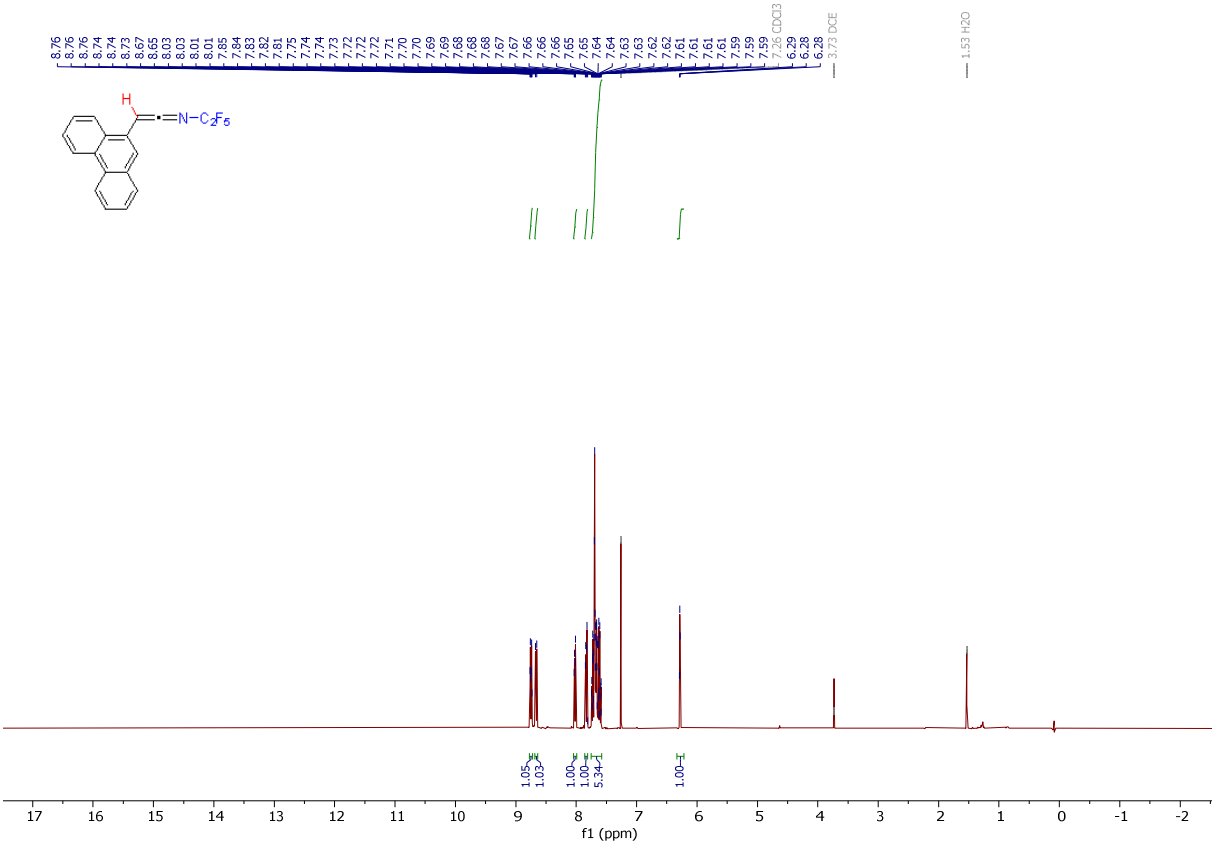
^{13}C NMR spectrum of **2h** ($CDCl_3$, 101 MHz)



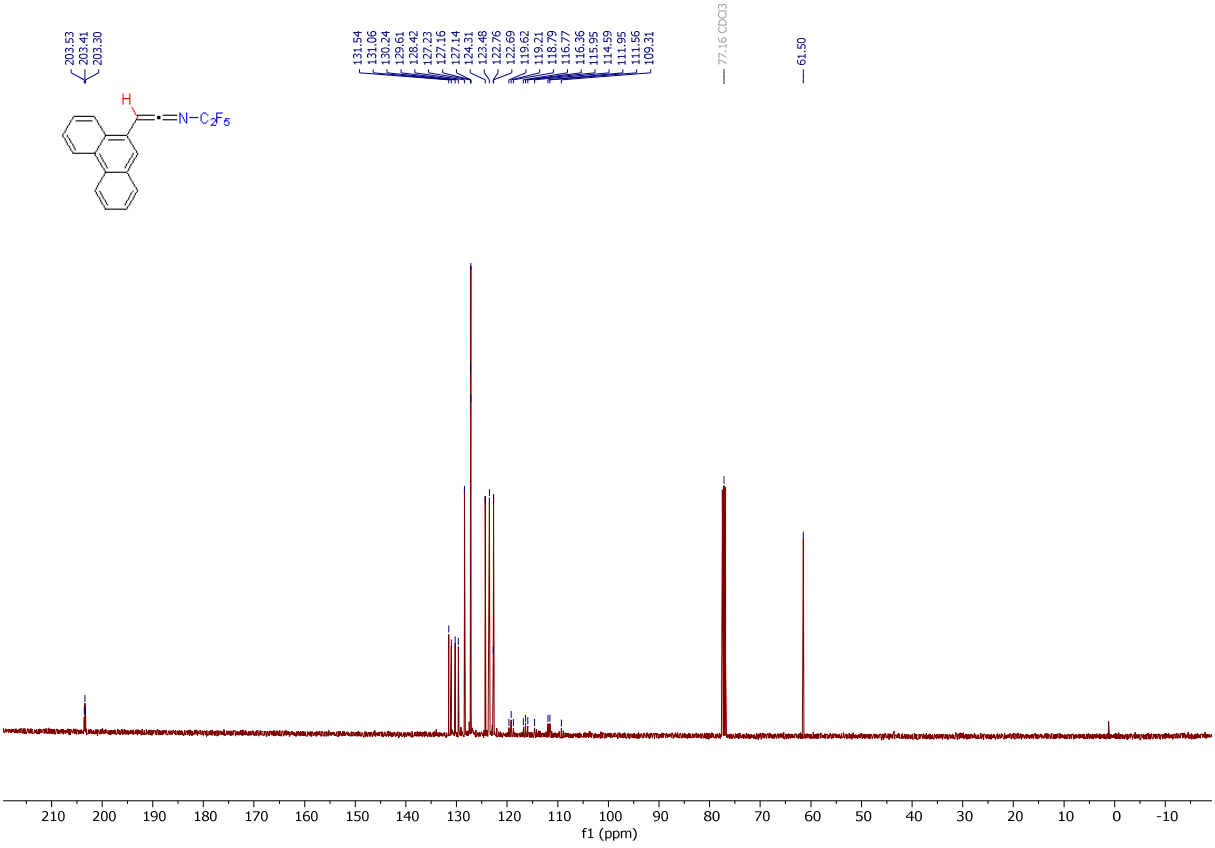
^{19}F NMR spectrum of **2h** ($CDCl_3$, 376 MHz)



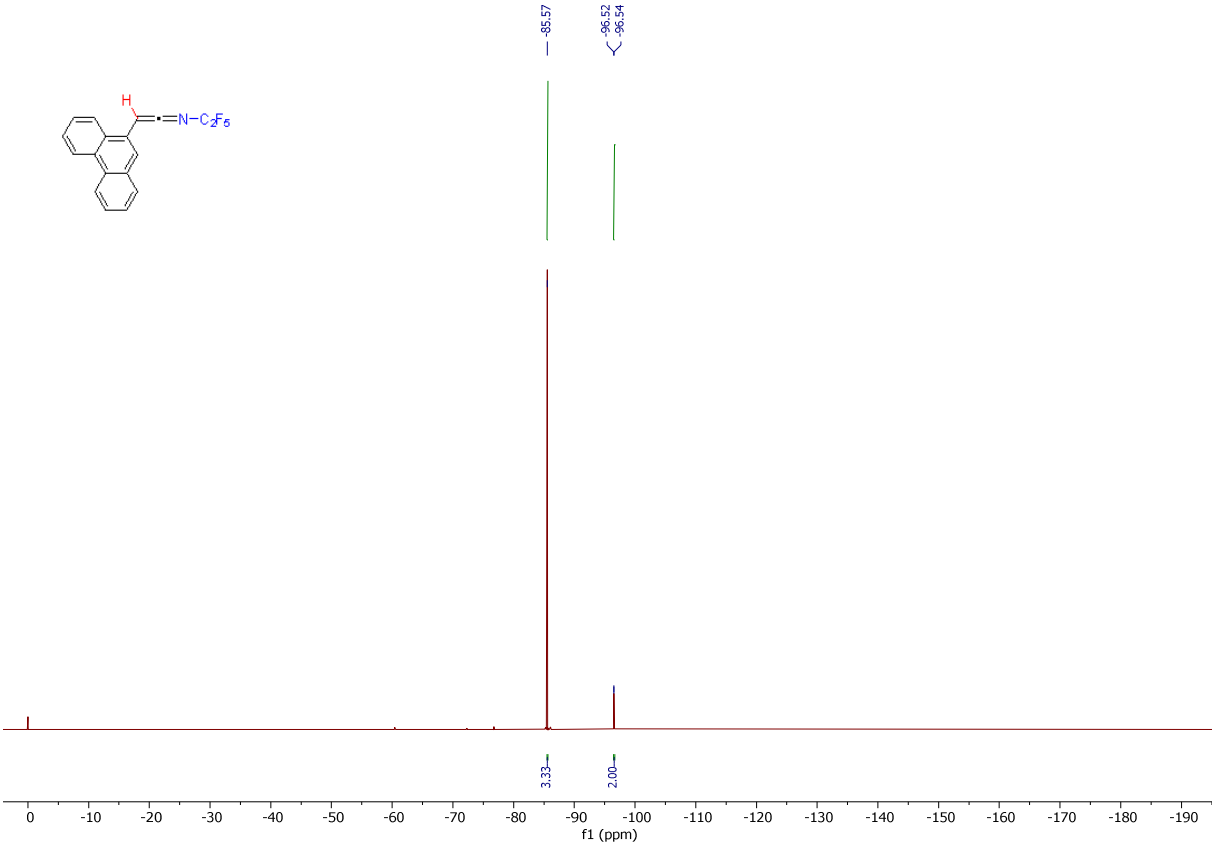
^{1}H NMR spectrum of **2i** ($CDCl_3$, 400 MHz)



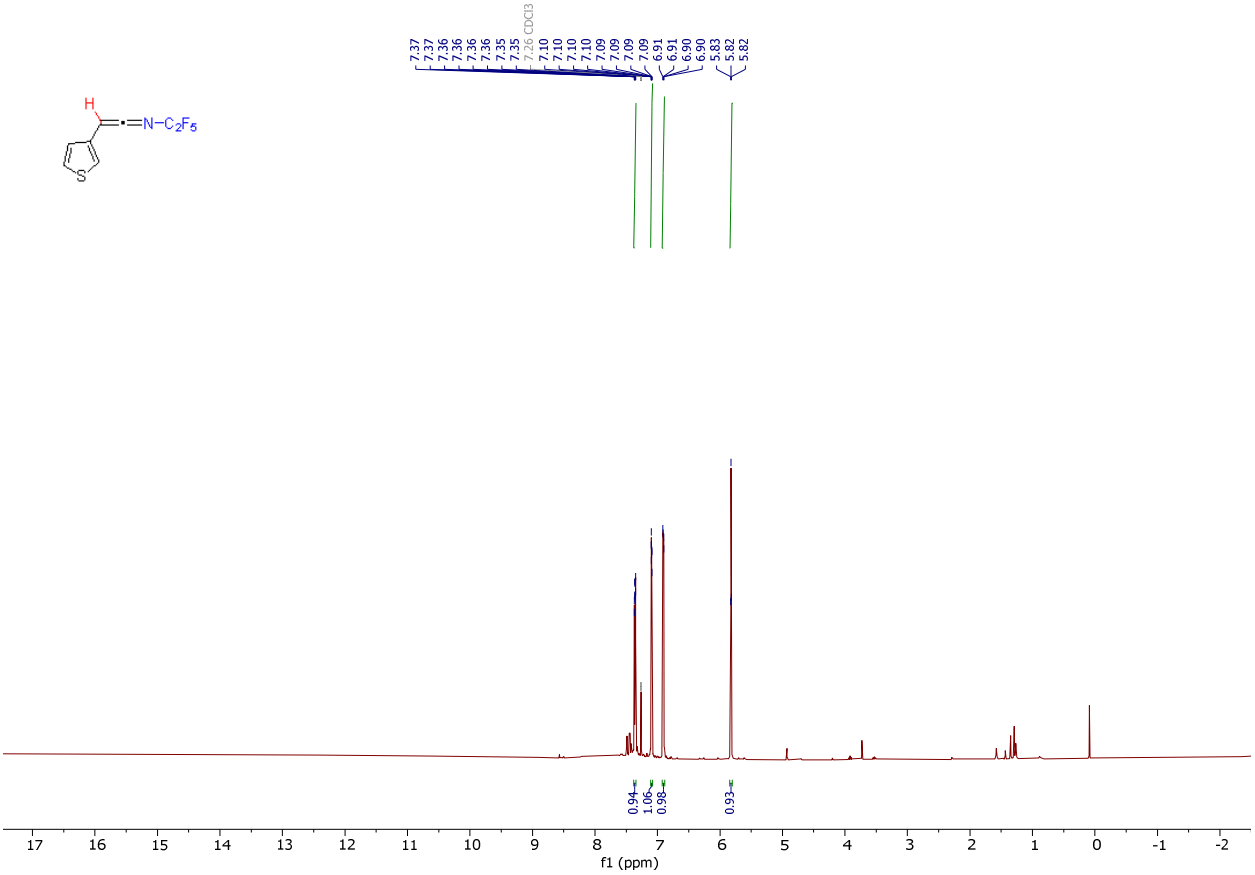
^{13}C NMR spectrum of **2i** ($CDCl_3$, 101 MHz)



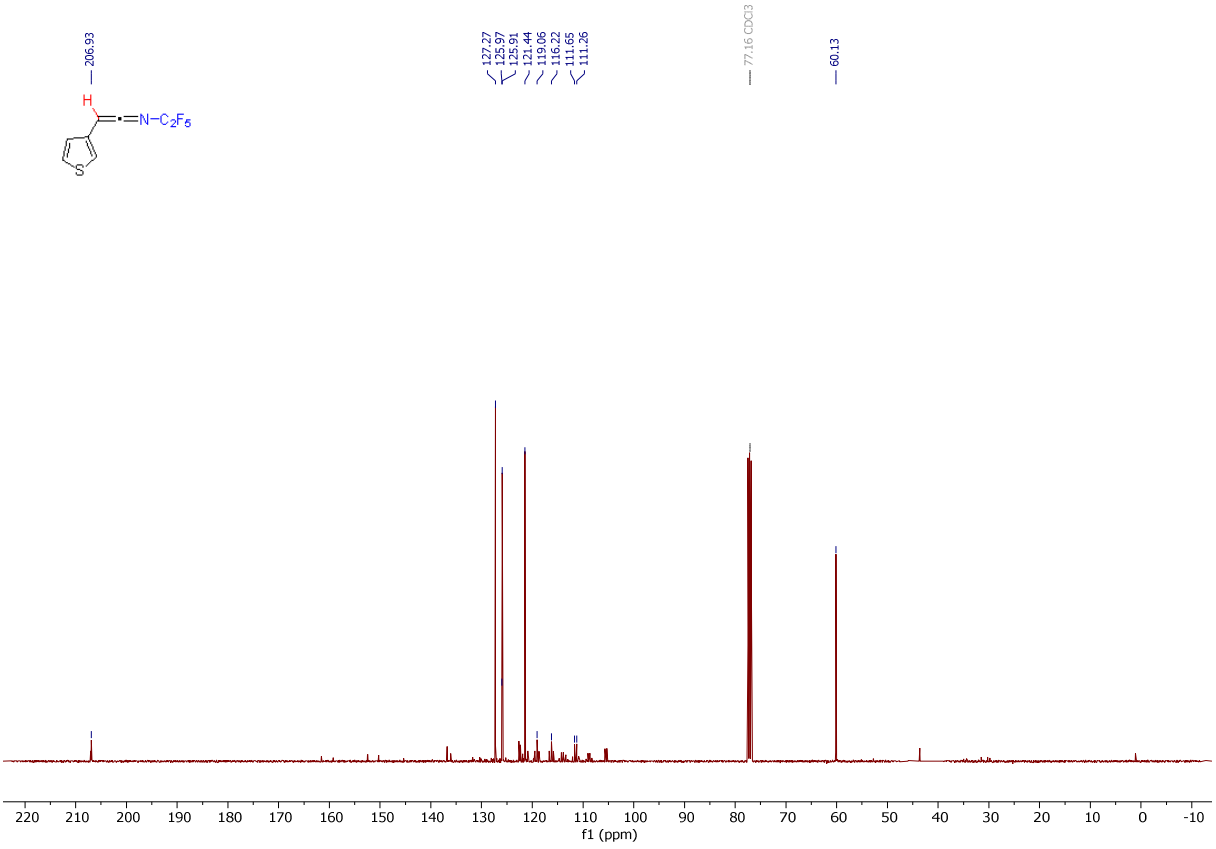
^{19}F NMR spectrum of **2i** ($CDCl_3$, 376 MHz)



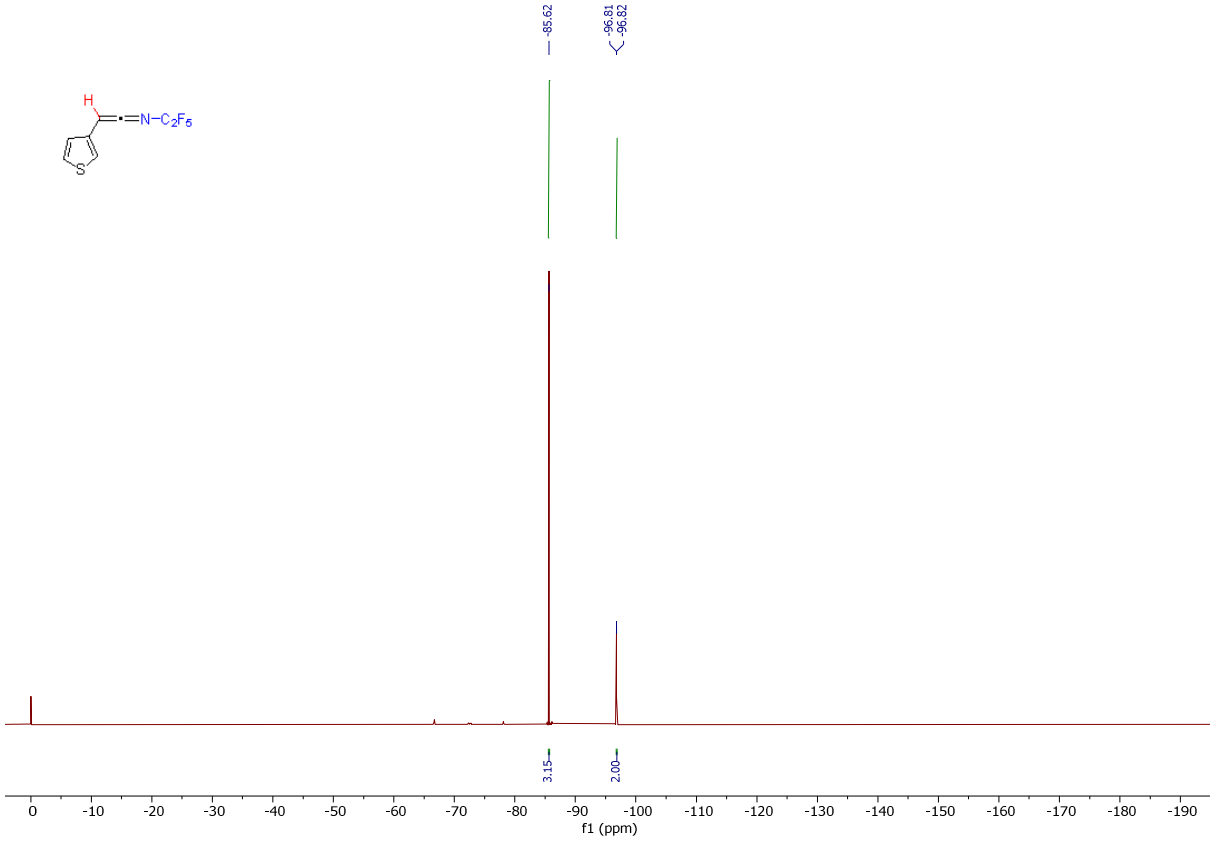
^{1}H NMR spectrum of **2j** ($CDCl_3$, 400 MHz)



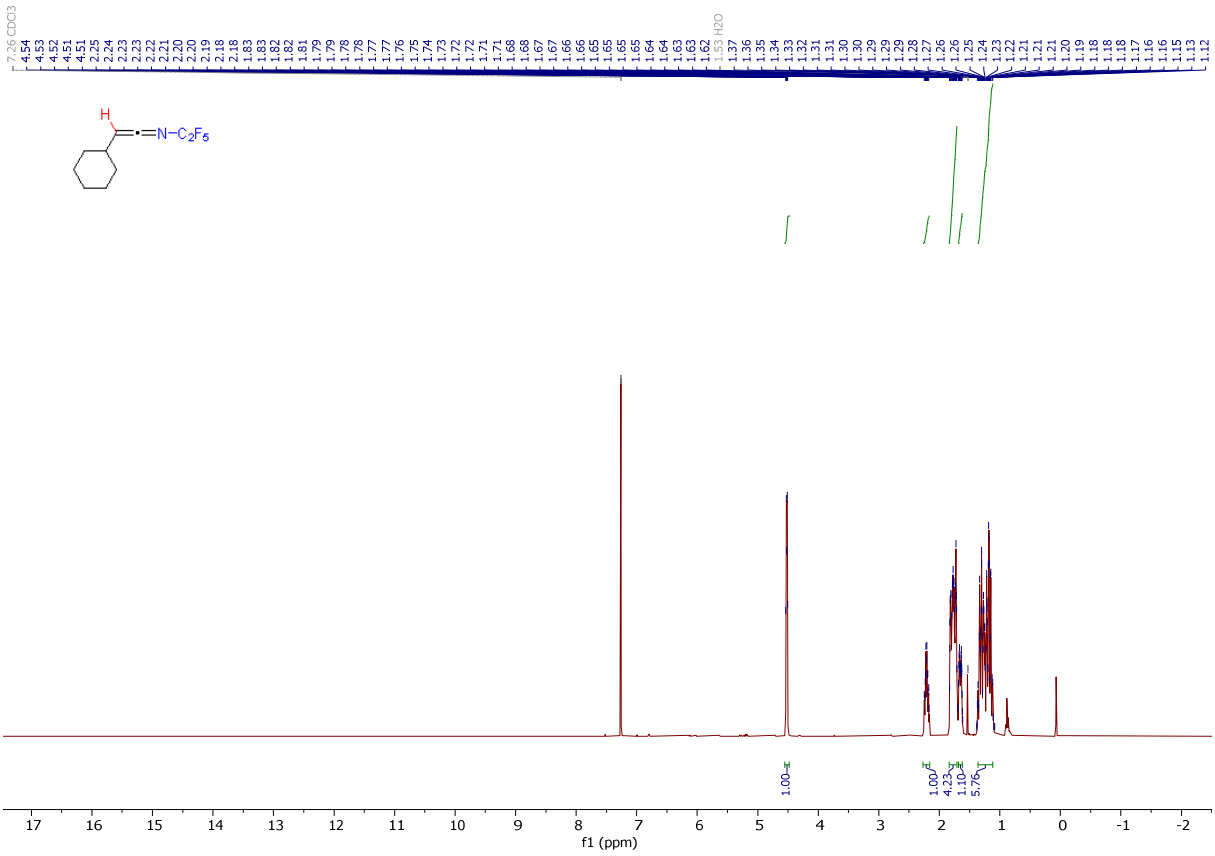
^{13}C NMR spectrum of **2j** ($CDCl_3$, 101 MHz)



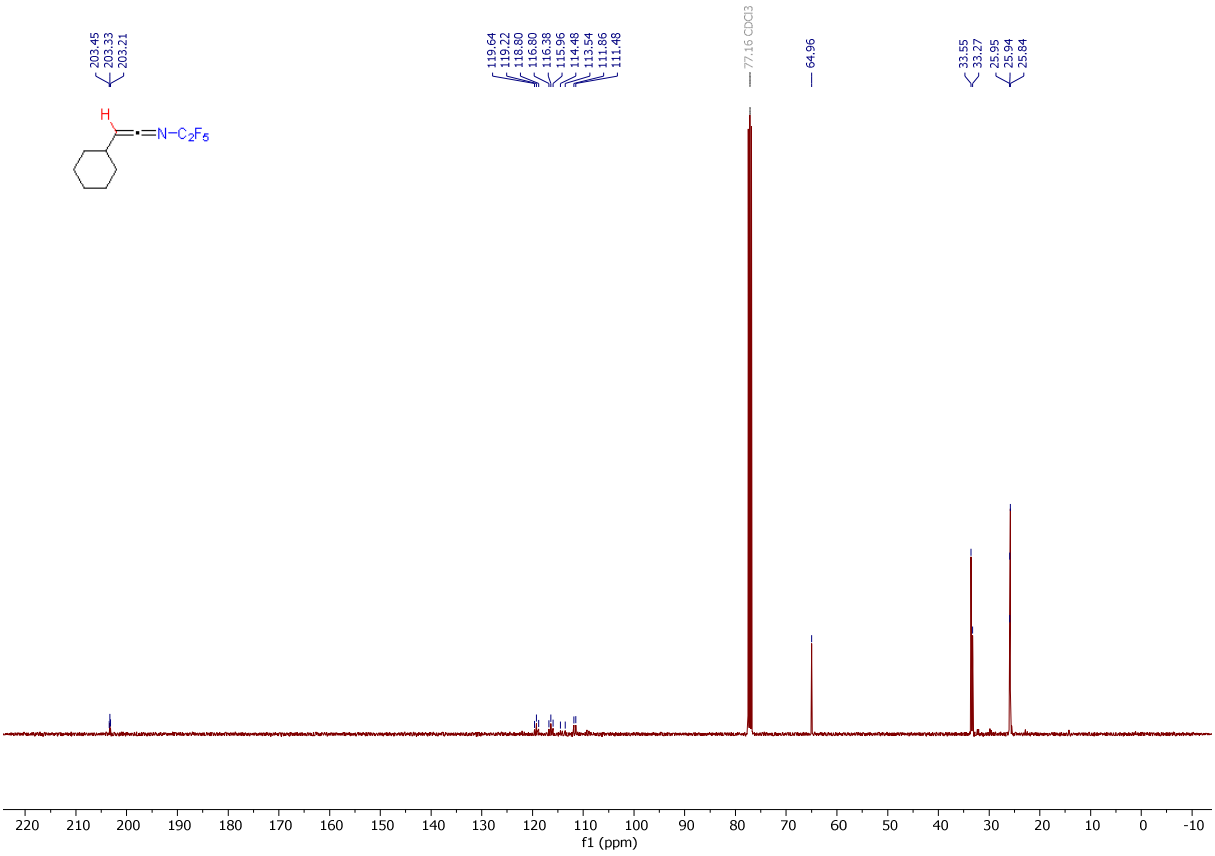
^{19}F NMR spectrum of **2j** ($CDCl_3$, 376 MHz)



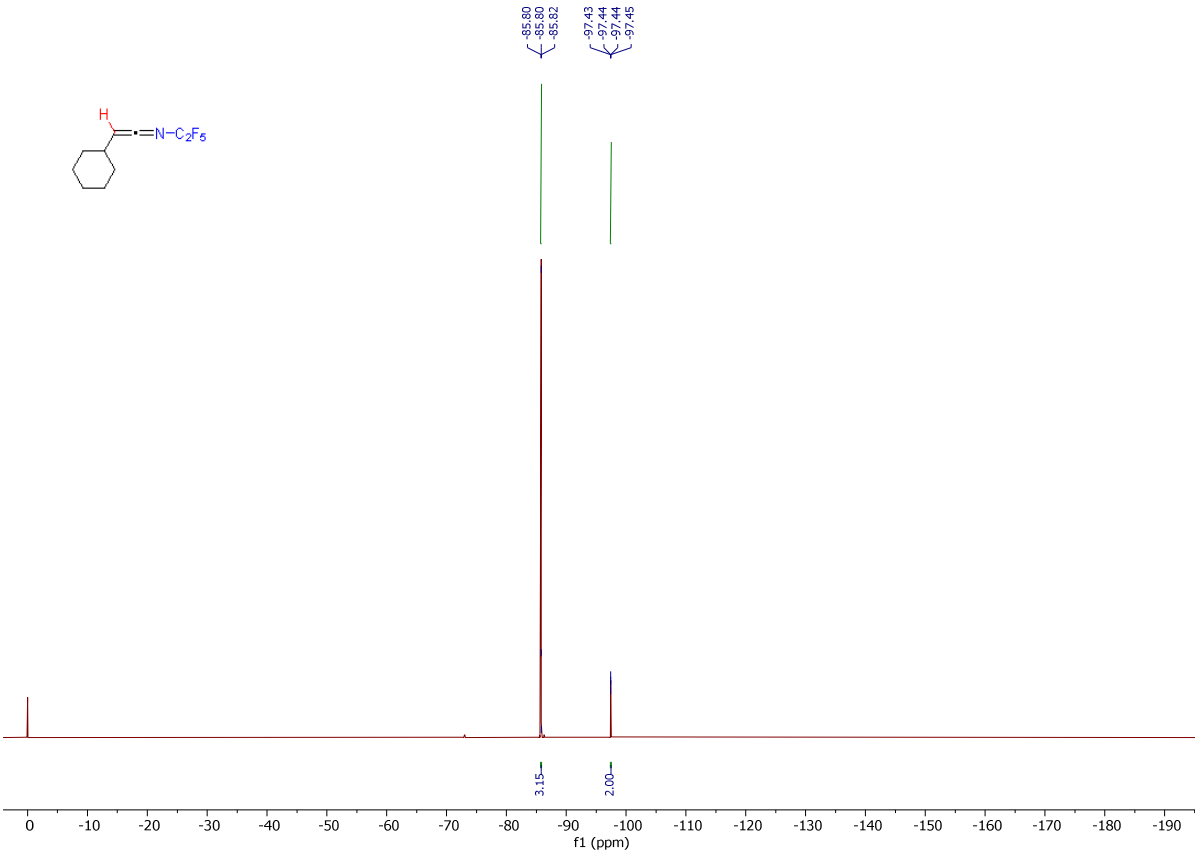
^{1}H NMR spectrum of **2k** ($CDCl_3$, 400 MHz)



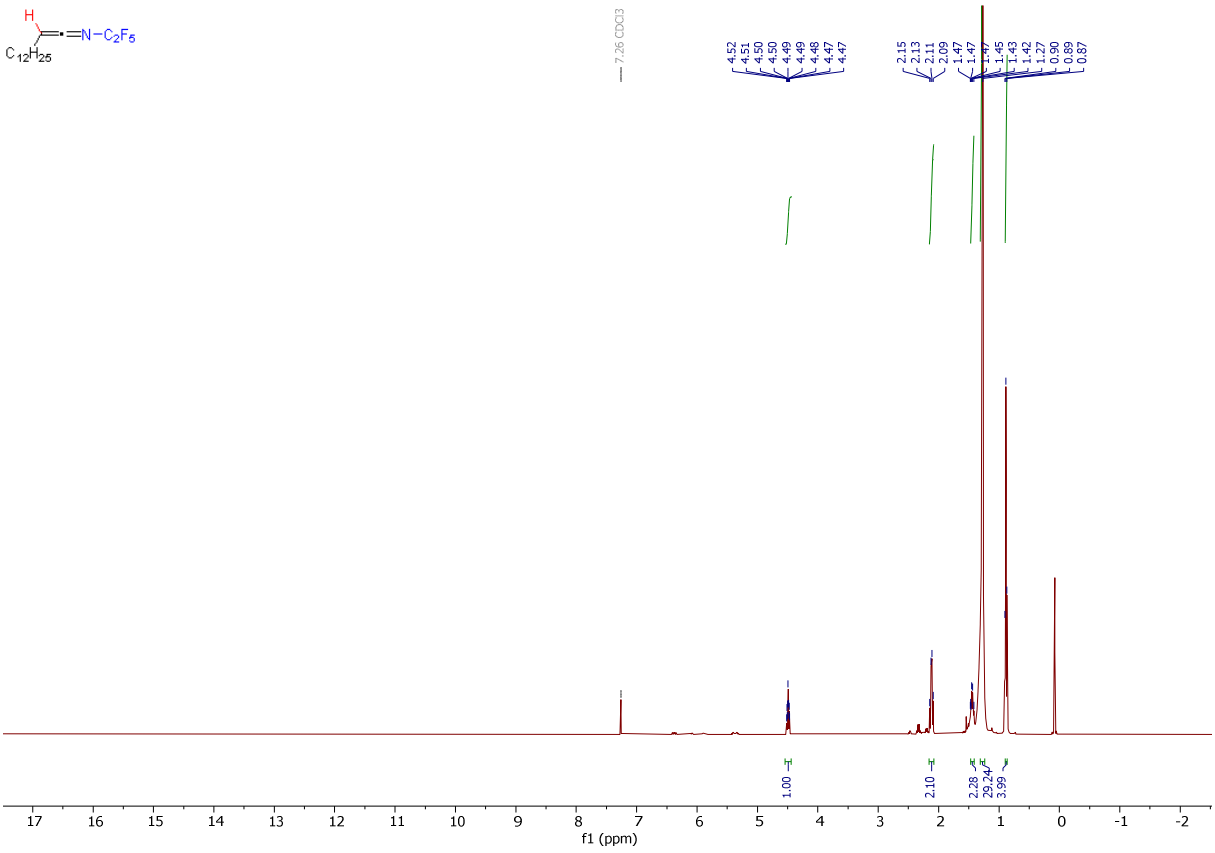
^{13}C NMR spectrum of **2k** ($CDCl_3$, 101 MHz)



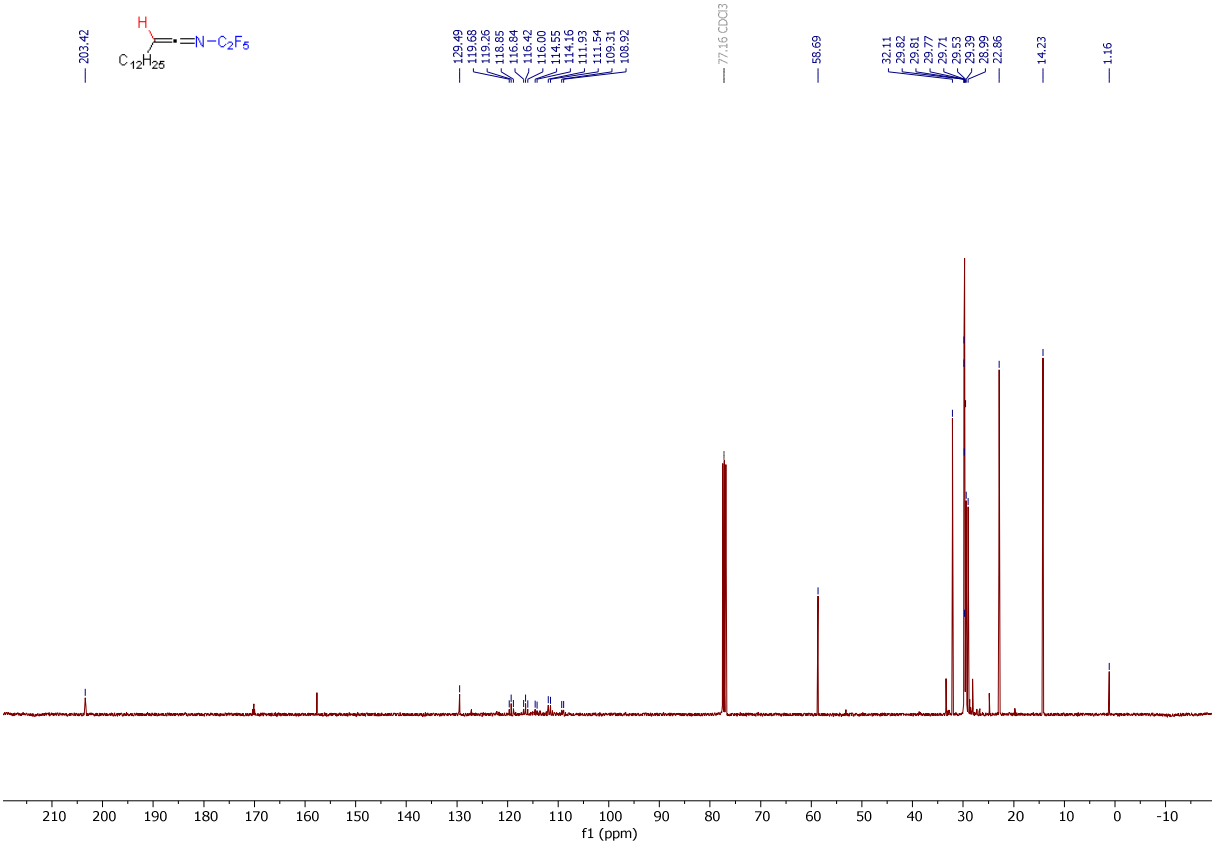
^{19}F NMR spectrum of **2k** ($CDCl_3$, 376 MHz)



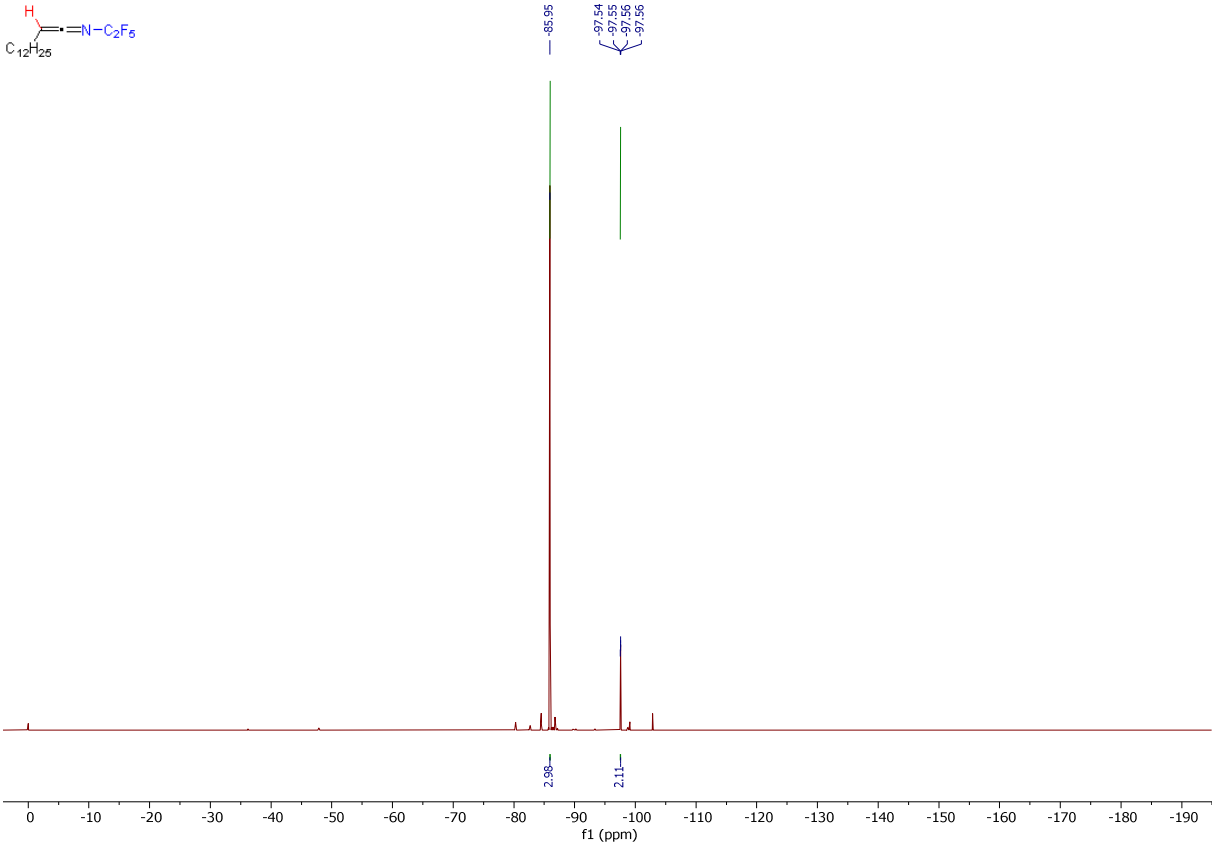
^{1}H NMR spectrum of **2l** ($CDCl_3$, 400 MHz)



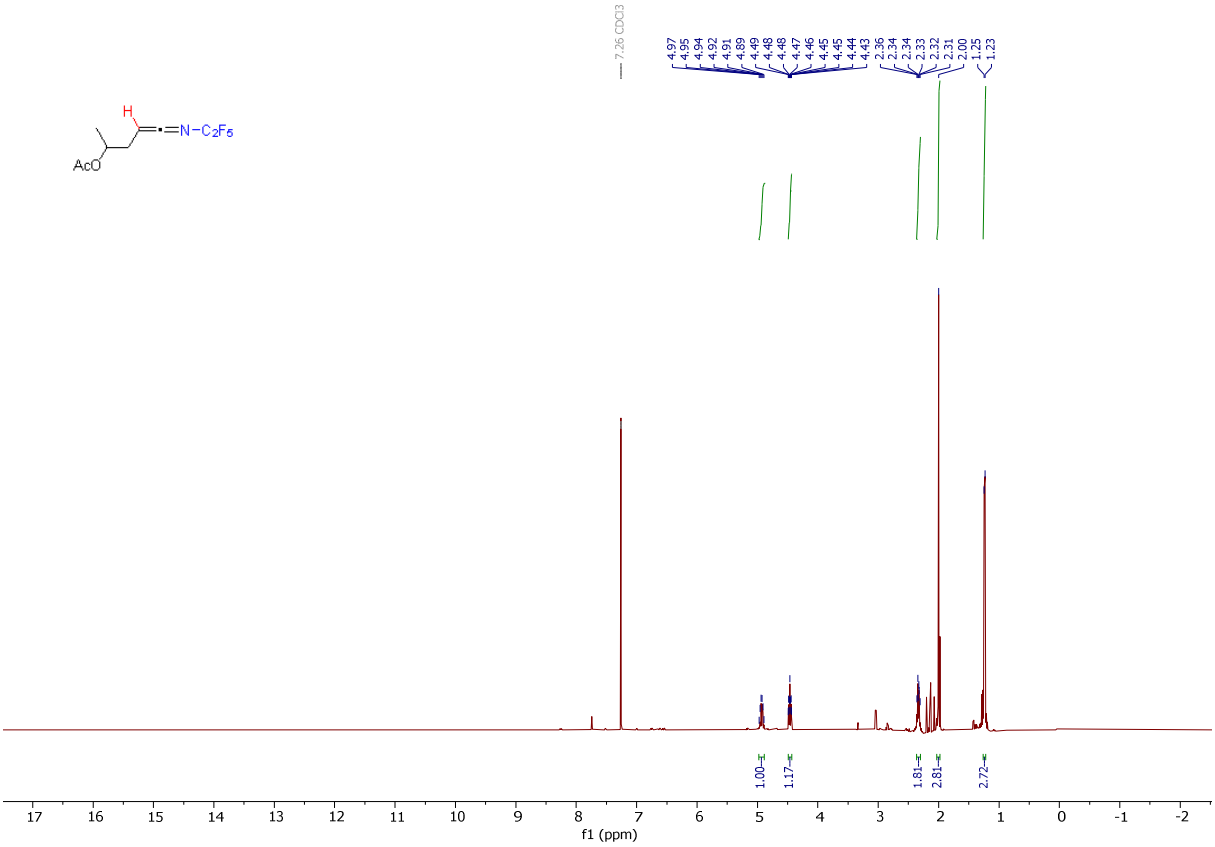
^{13}C NMR spectrum of **2l** ($CDCl_3$, 101 MHz)



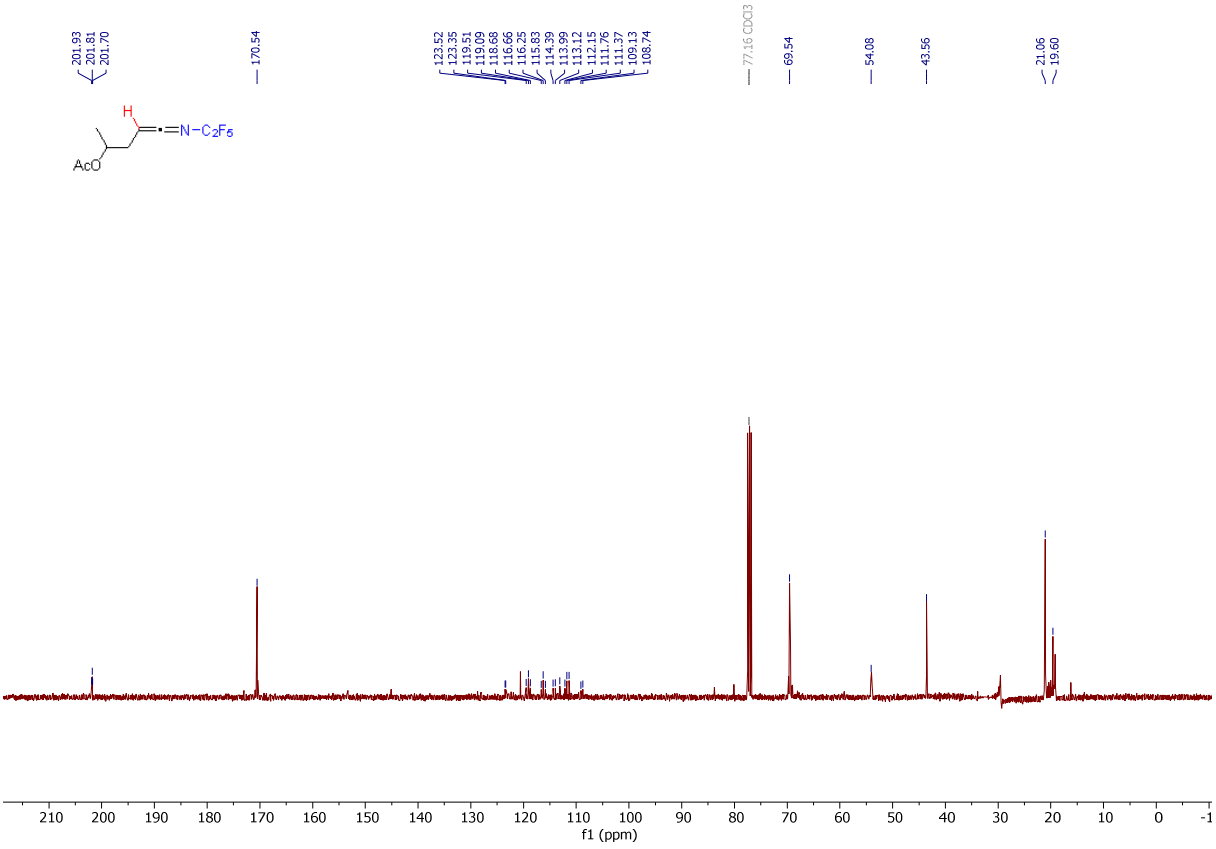
^{19}F NMR spectrum of **2l** ($CDCl_3$, 376 MHz)



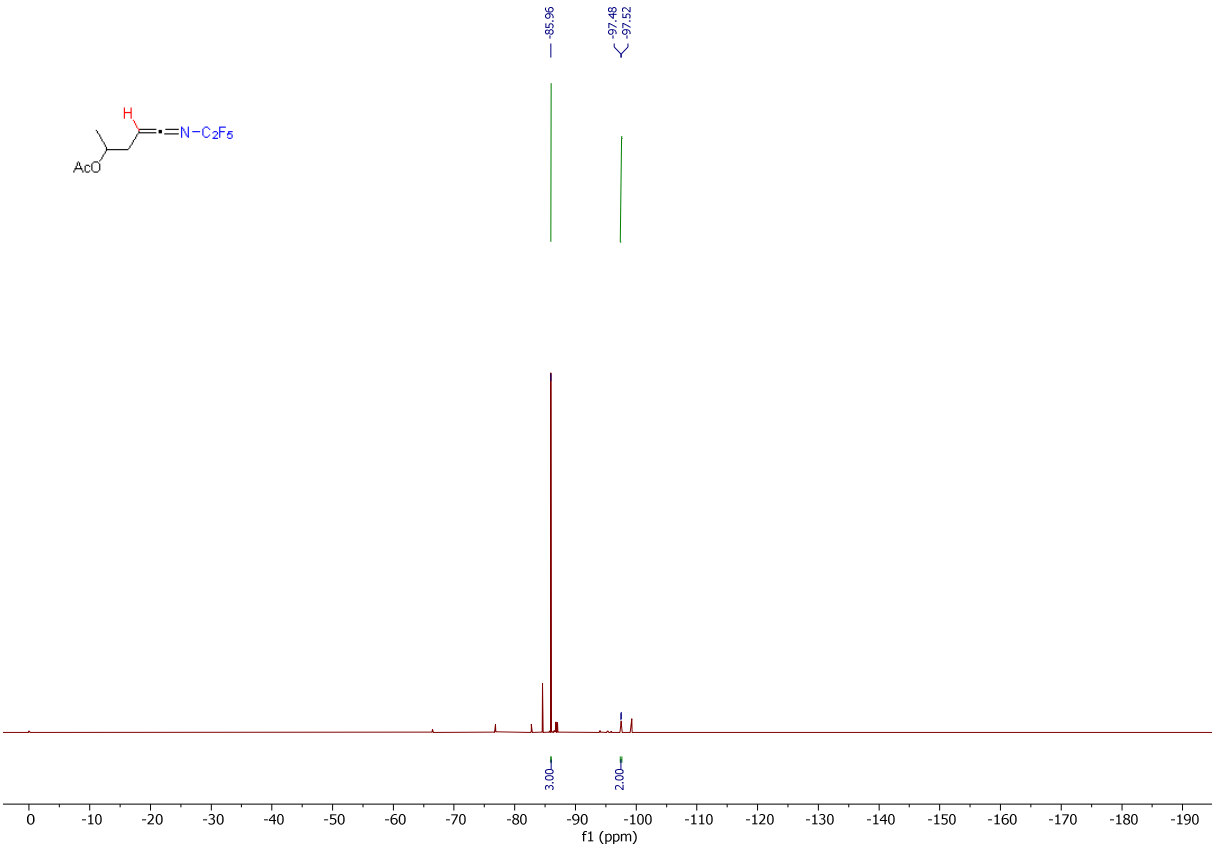
^{1}H NMR spectrum of **2m** ($CDCl_3$, 400 MHz)



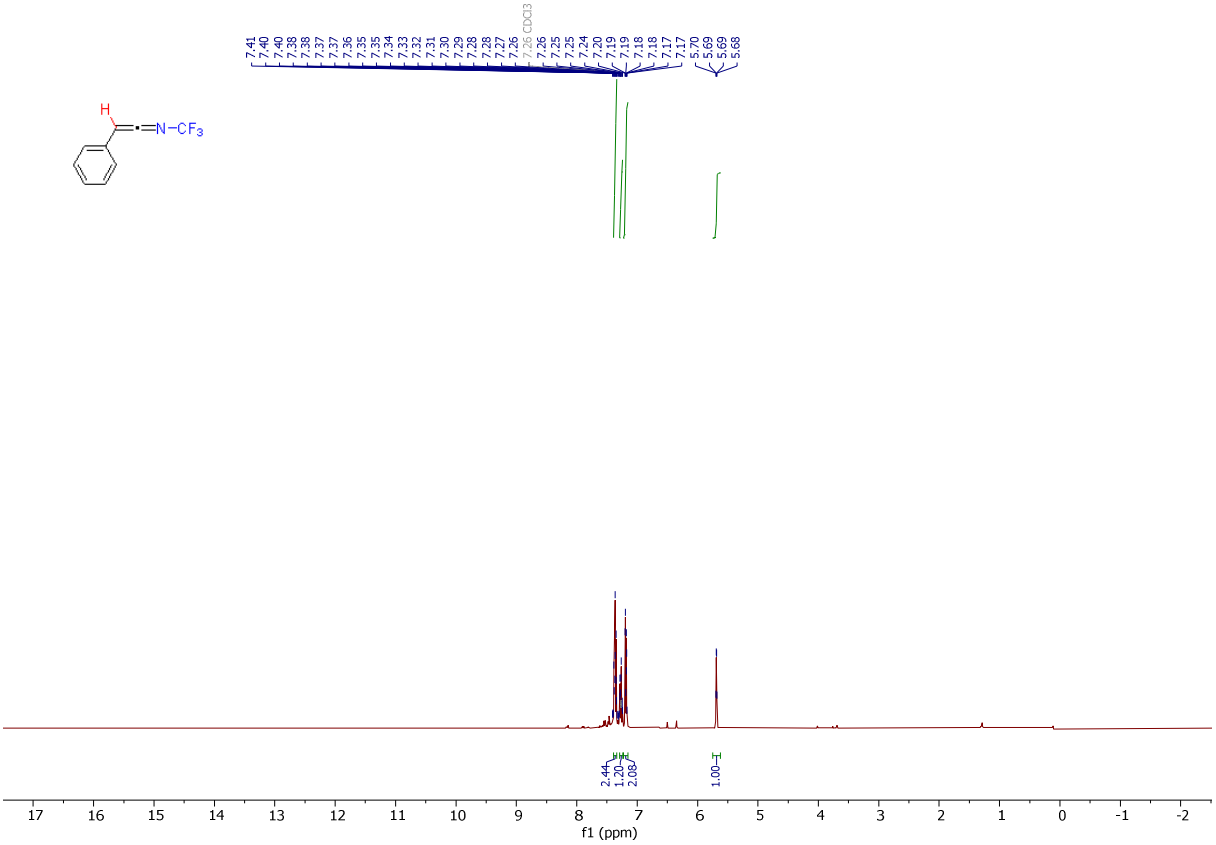
^{13}C NMR spectrum of **2m** ($CDCl_3$, 101 MHz)



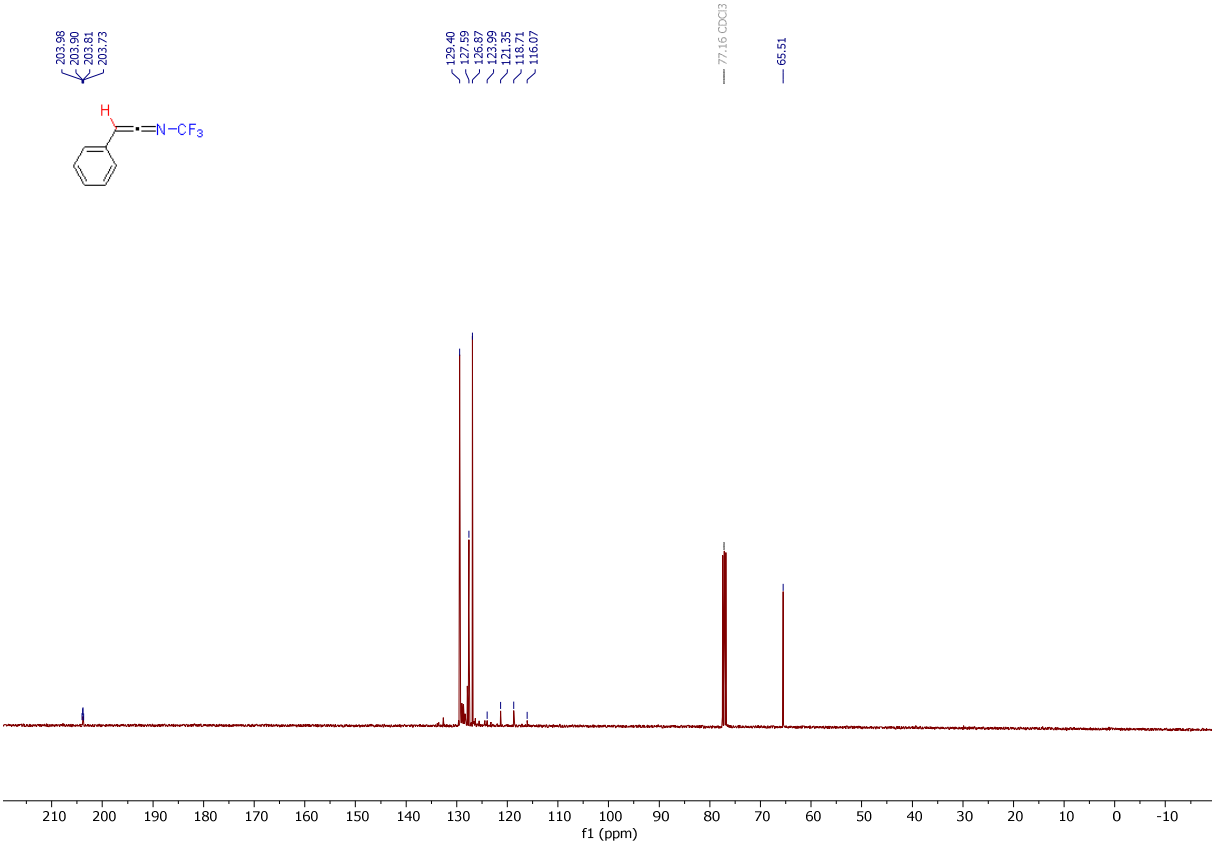
^{19}F NMR spectrum of **2m** ($CDCl_3$, 376 MHz)



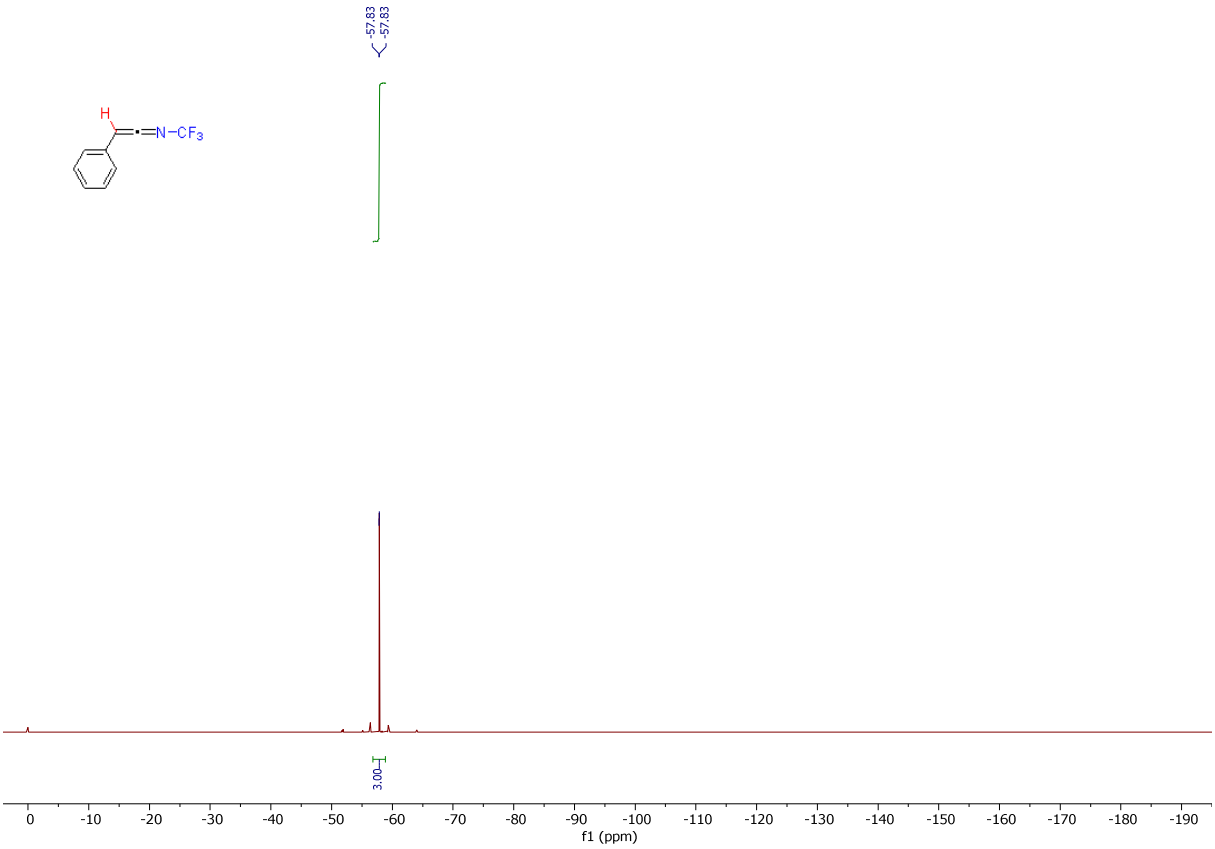
^{1}H NMR spectrum of **2o** ($CDCl_3$, 400 MHz)



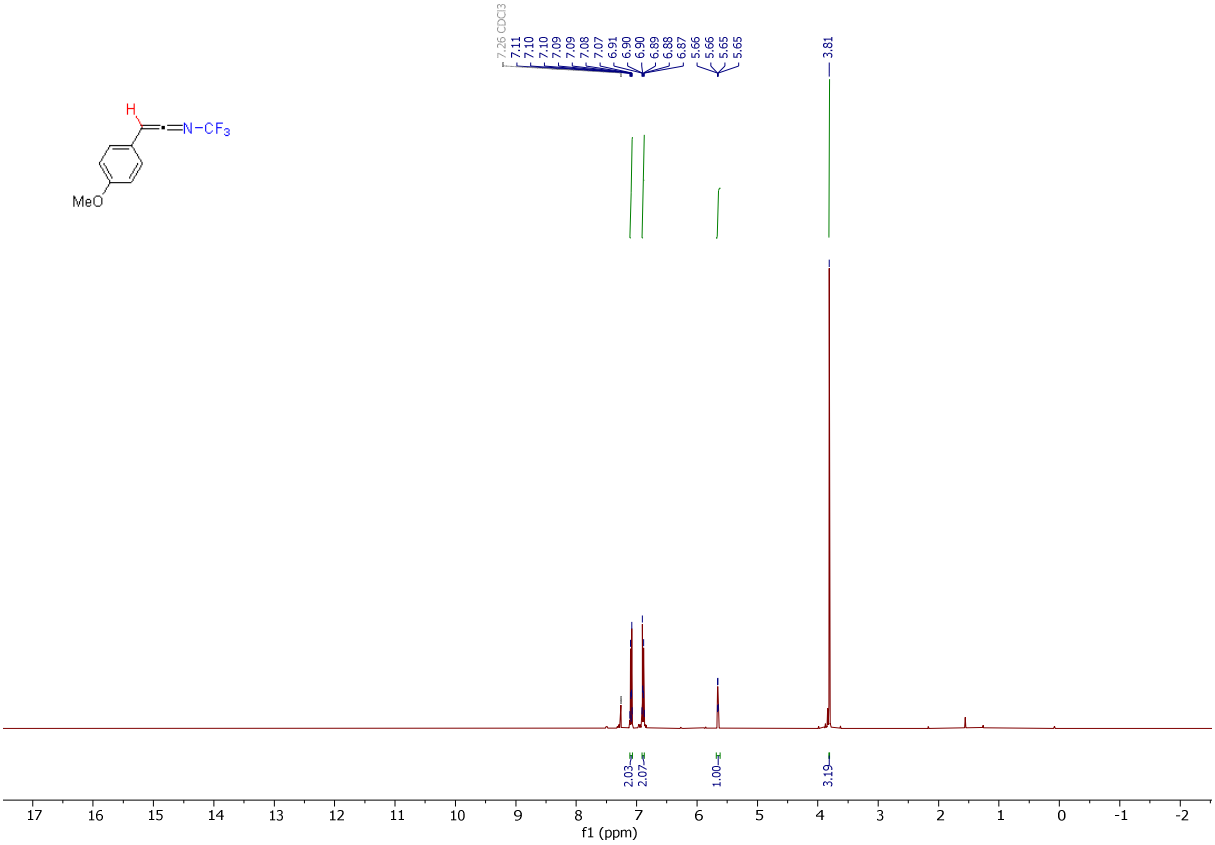
^{13}C NMR spectrum of **2o** ($CDCl_3$, 101 MHz)



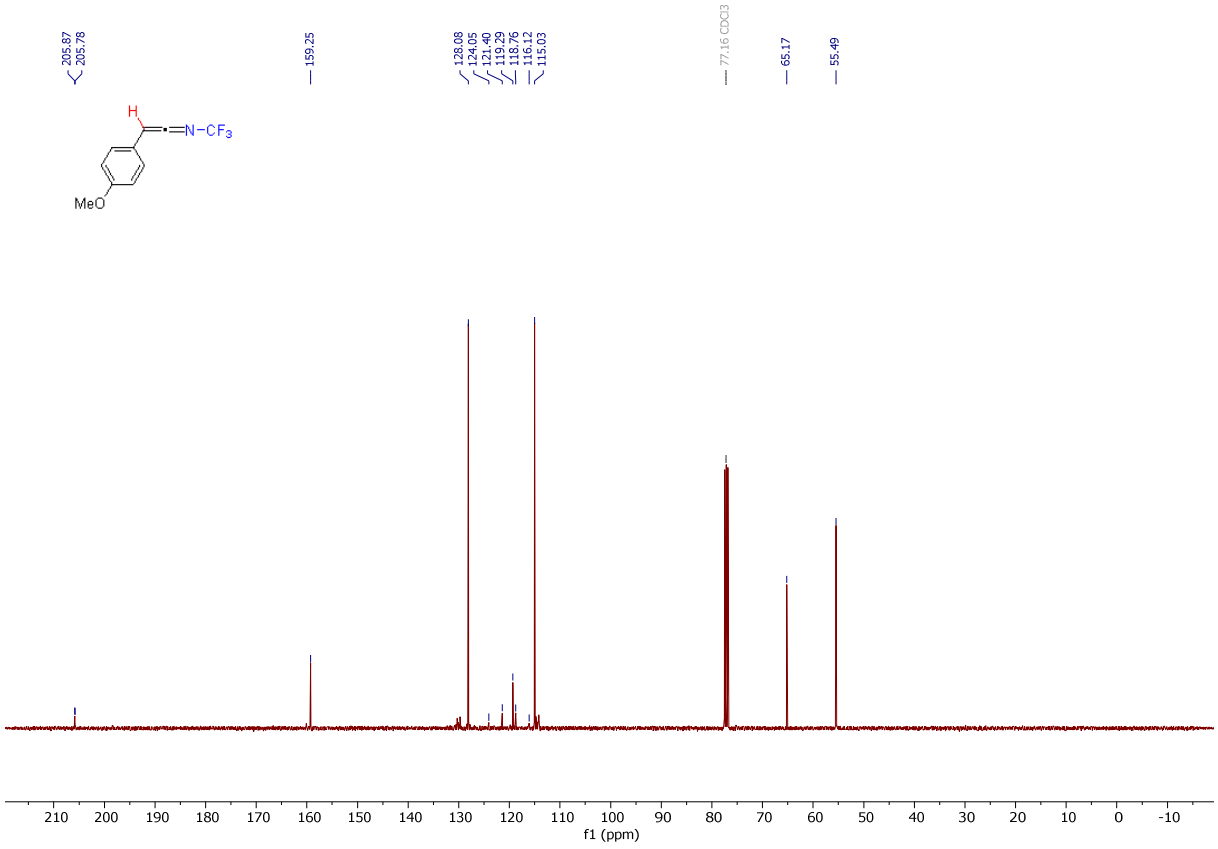
^{19}F NMR spectrum of **2o** ($CDCl_3$, 376 MHz)



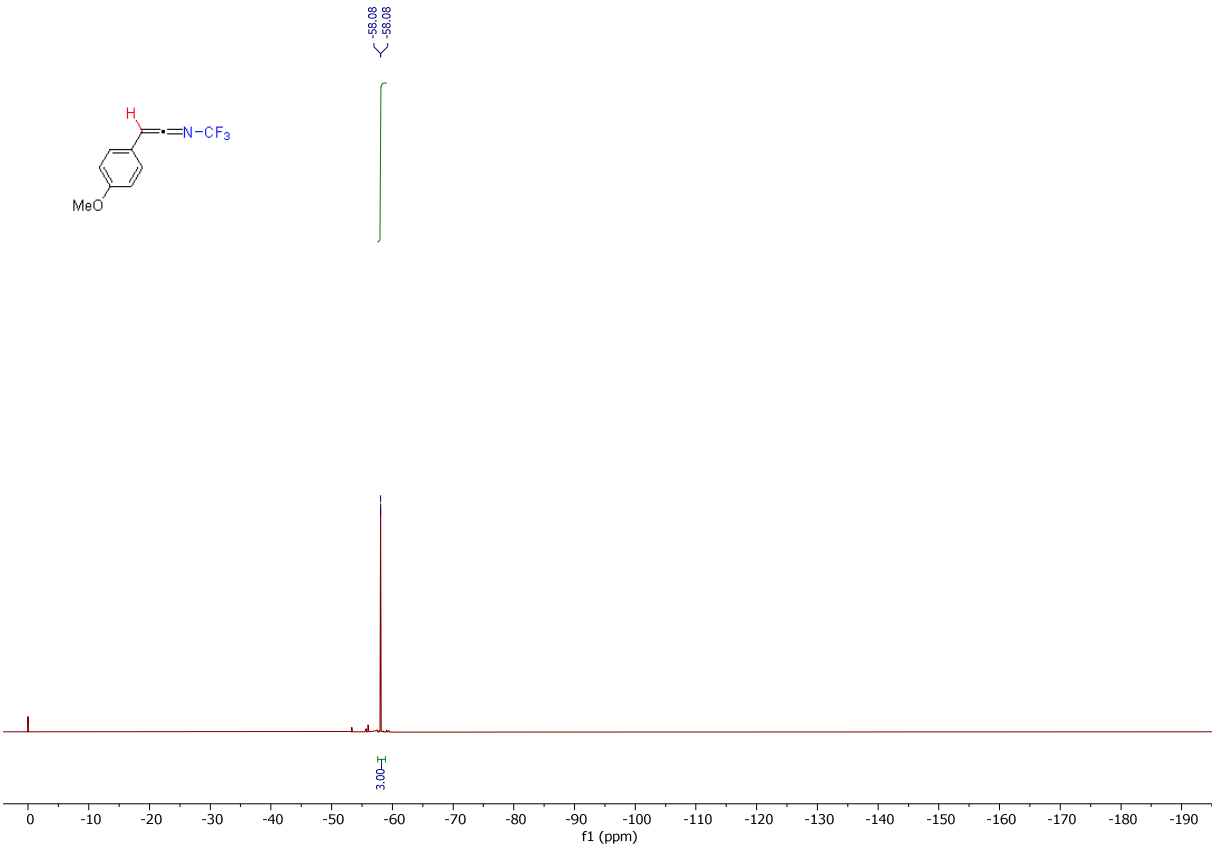
^{1}H NMR spectrum of **2p** ($CDCl_3$, 400 MHz)



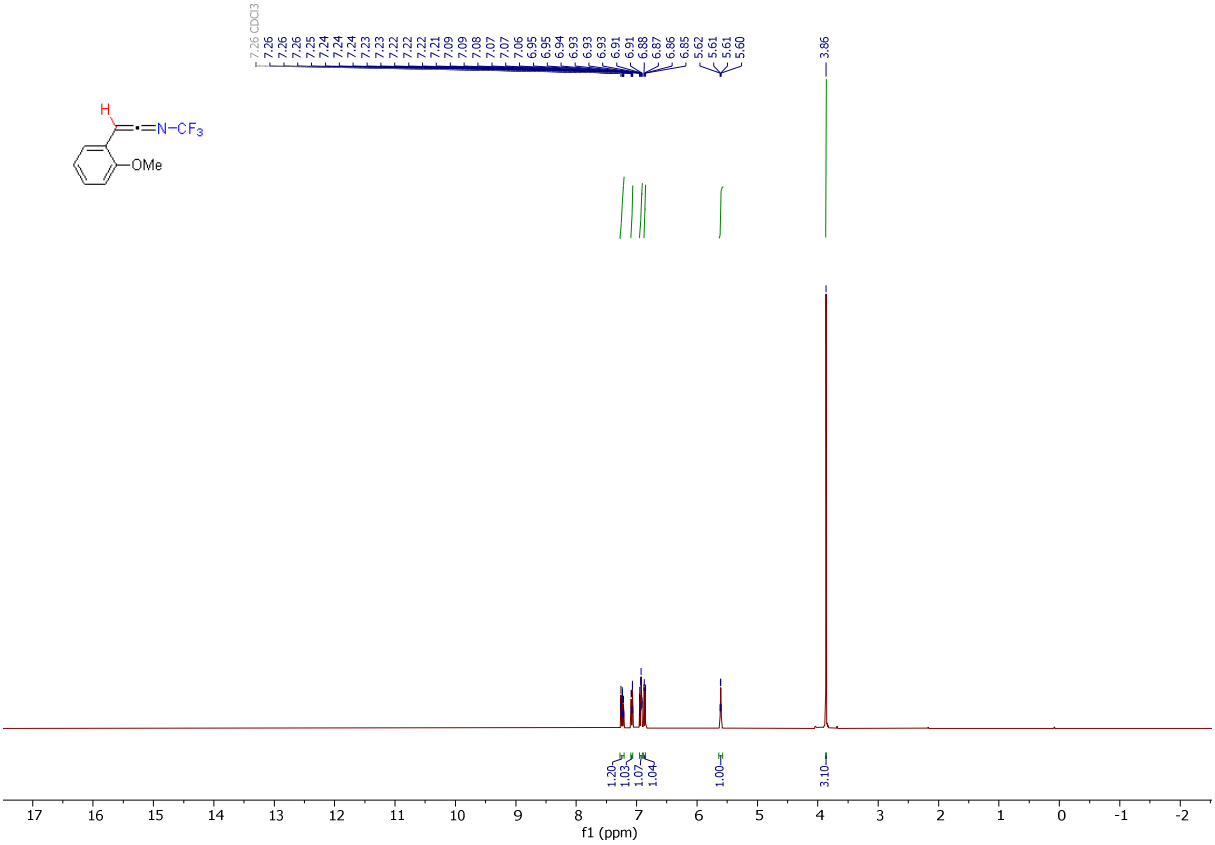
^{13}C NMR spectrum of **2p** ($CDCl_3$, 101 MHz)



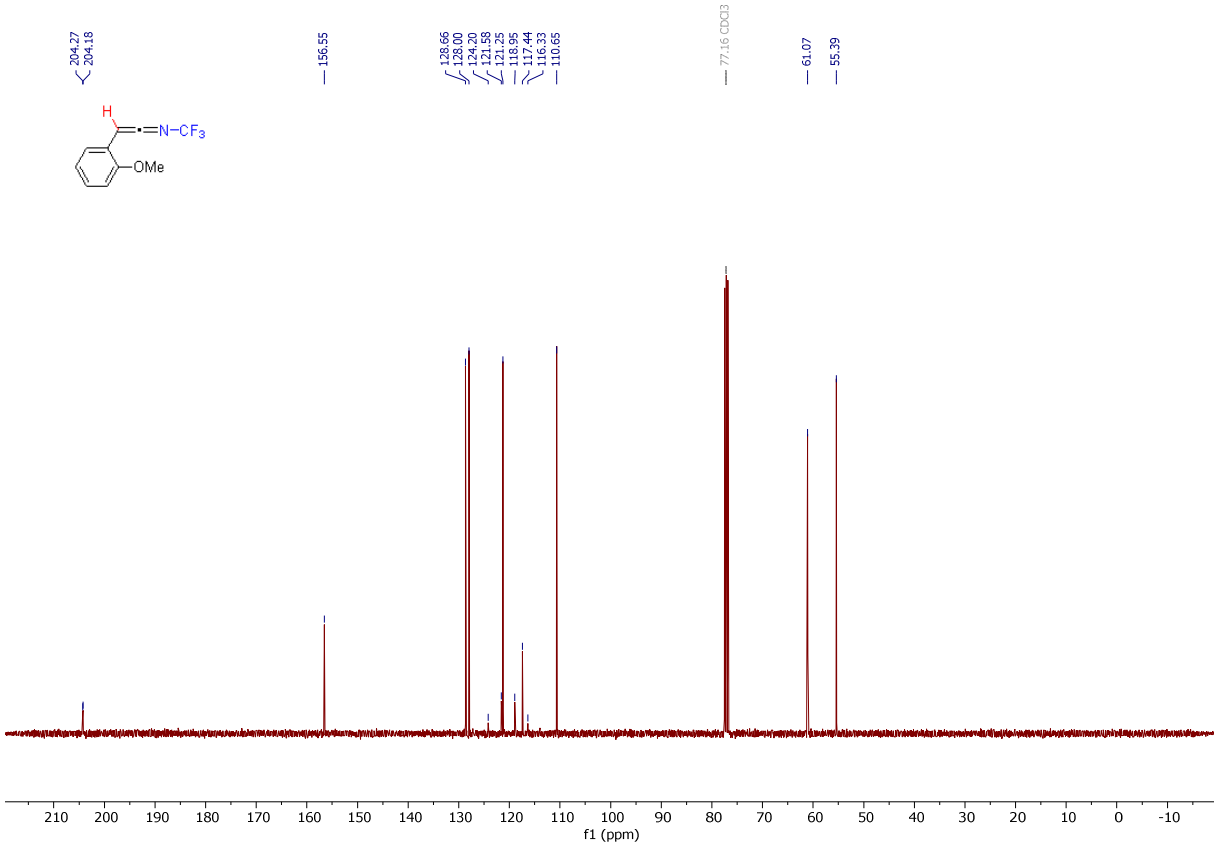
^{19}F NMR spectrum of **2p** ($CDCl_3$, 376 MHz)



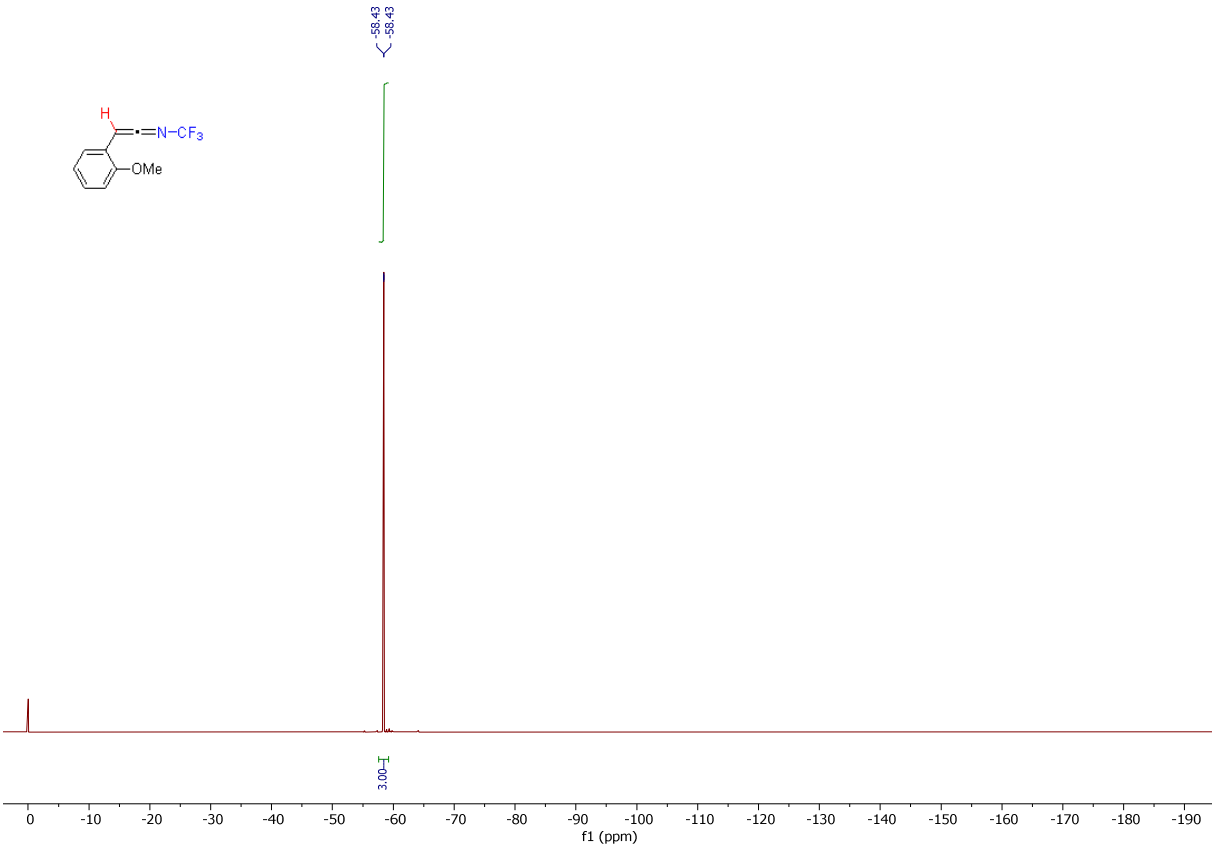
^{1}H NMR spectrum of **2q** ($CDCl_3$, 400 MHz)



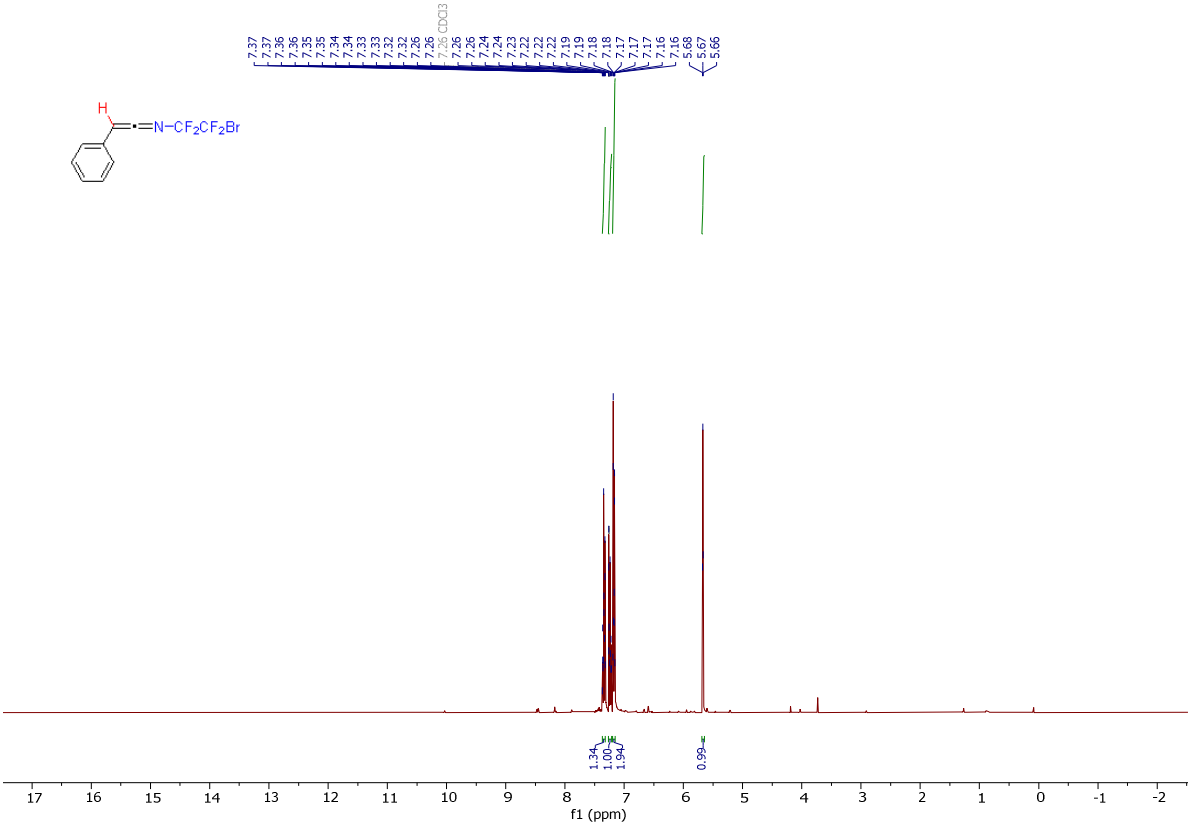
^{13}C NMR spectrum of **2q** ($CDCl_3$, 101 MHz)



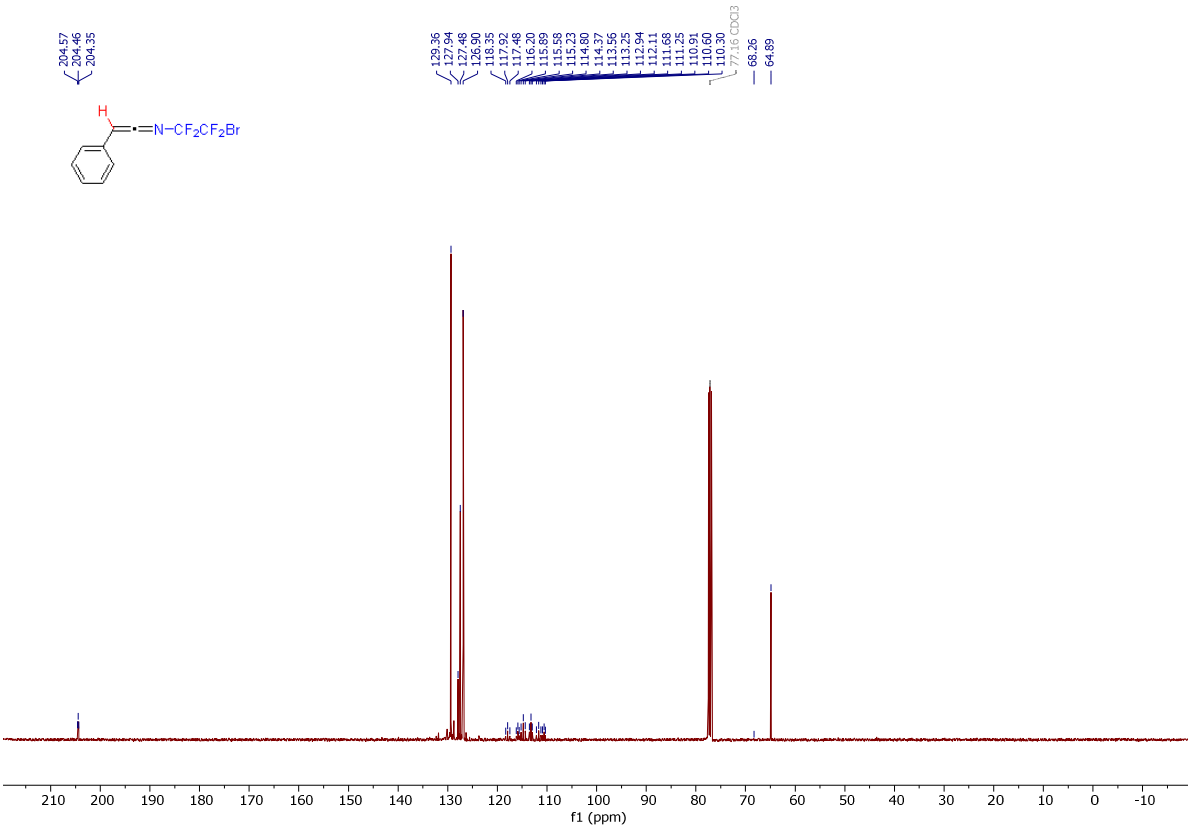
^{19}F NMR spectrum of **2q** ($CDCl_3$, 376 MHz)



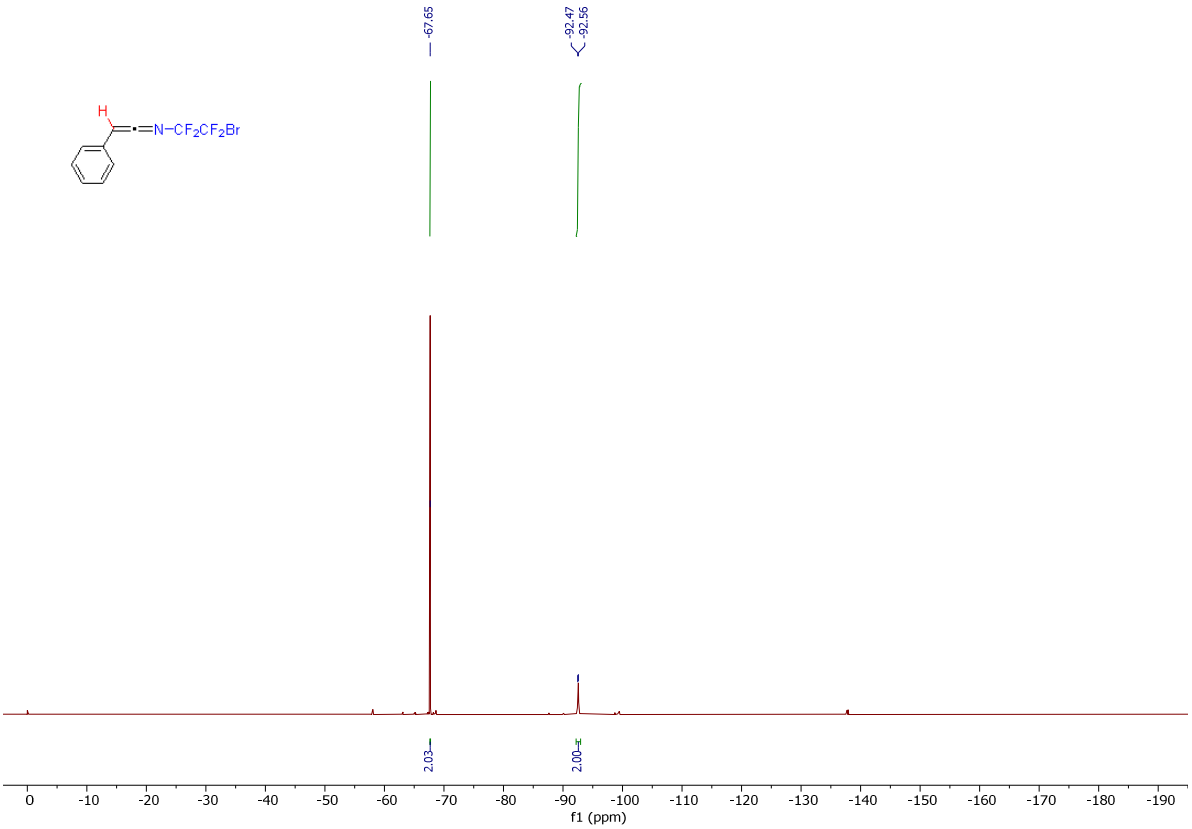
H NMR spectrum of **2r** ($CDCl_3$, 400 MHz)



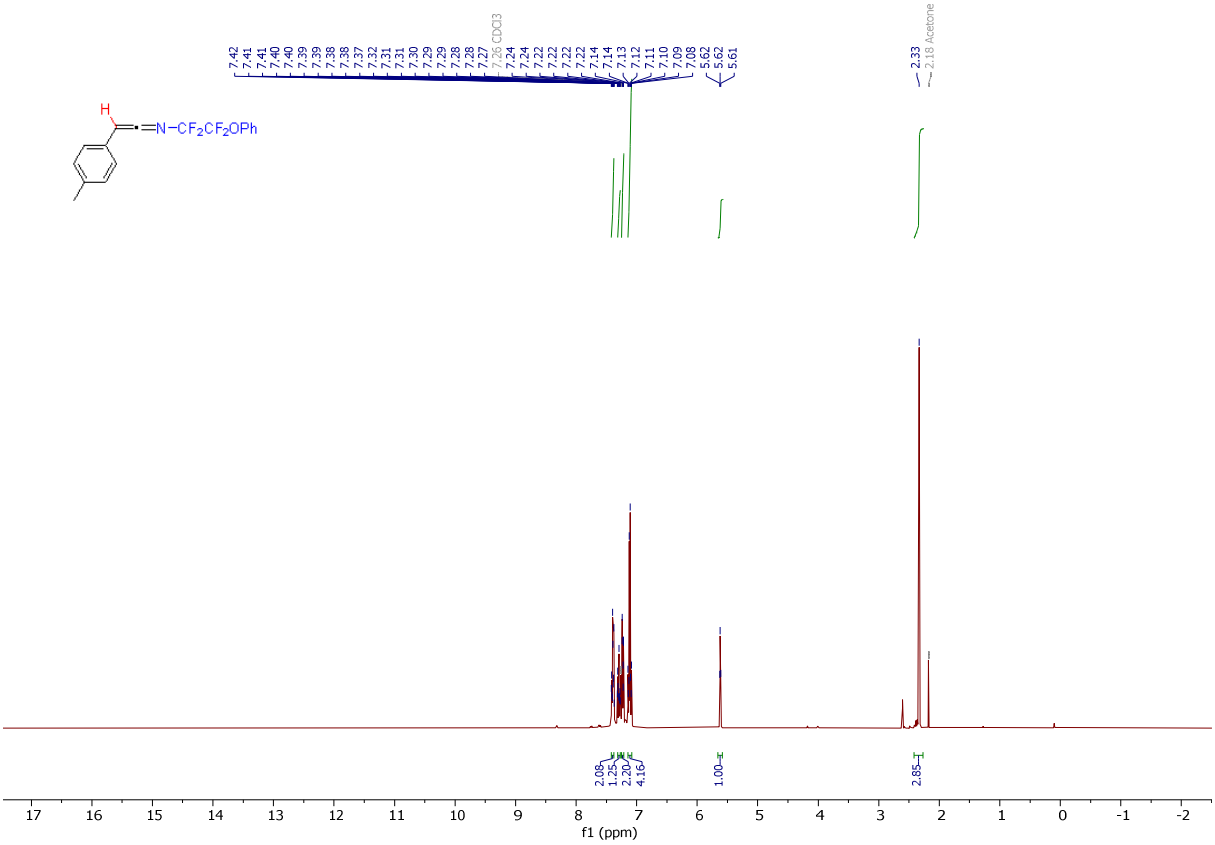
^{13}C NMR spectrum of **2r** ($CDCl_3$, 101 MHz)



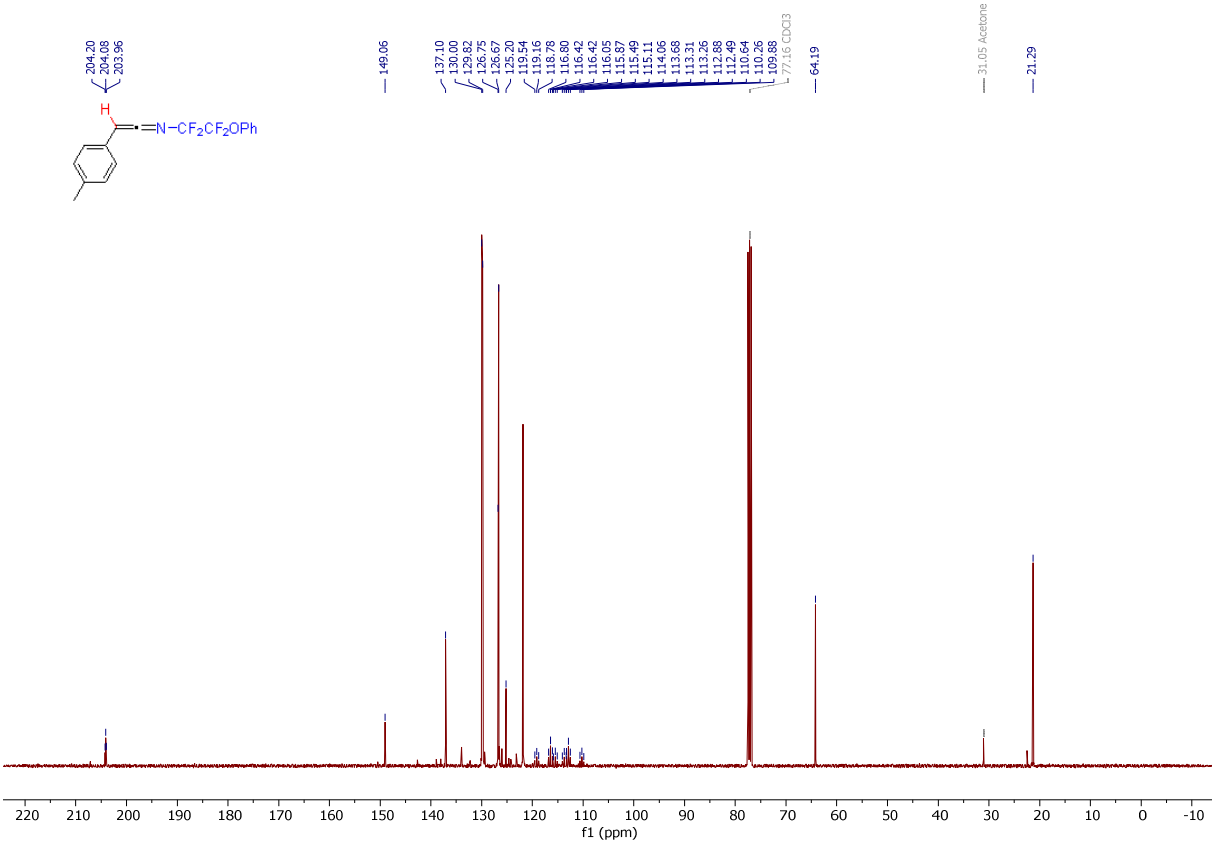
^{19}F NMR spectrum of **2r** ($CDCl_3$, 376 MHz)



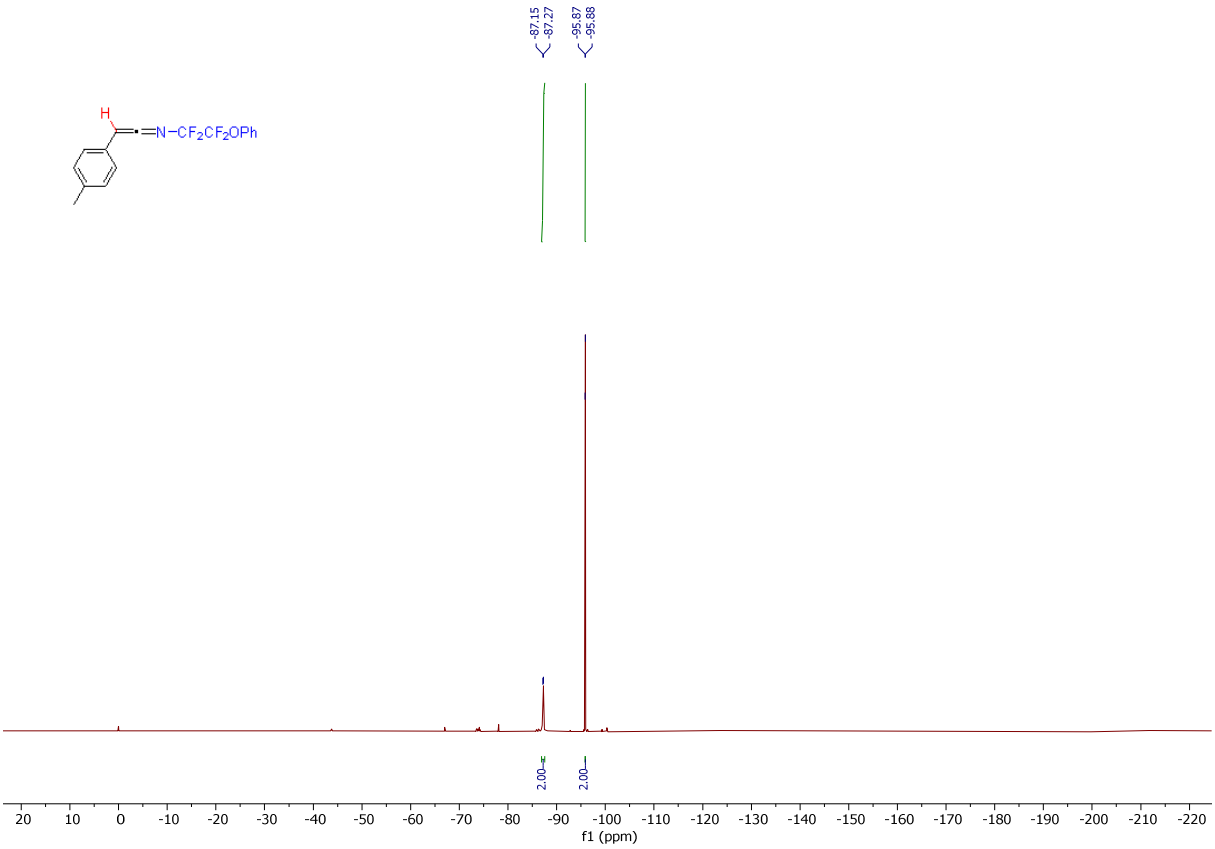
^{1}H NMR spectrum of **2s** ($CDCl_3$, 400 MHz)



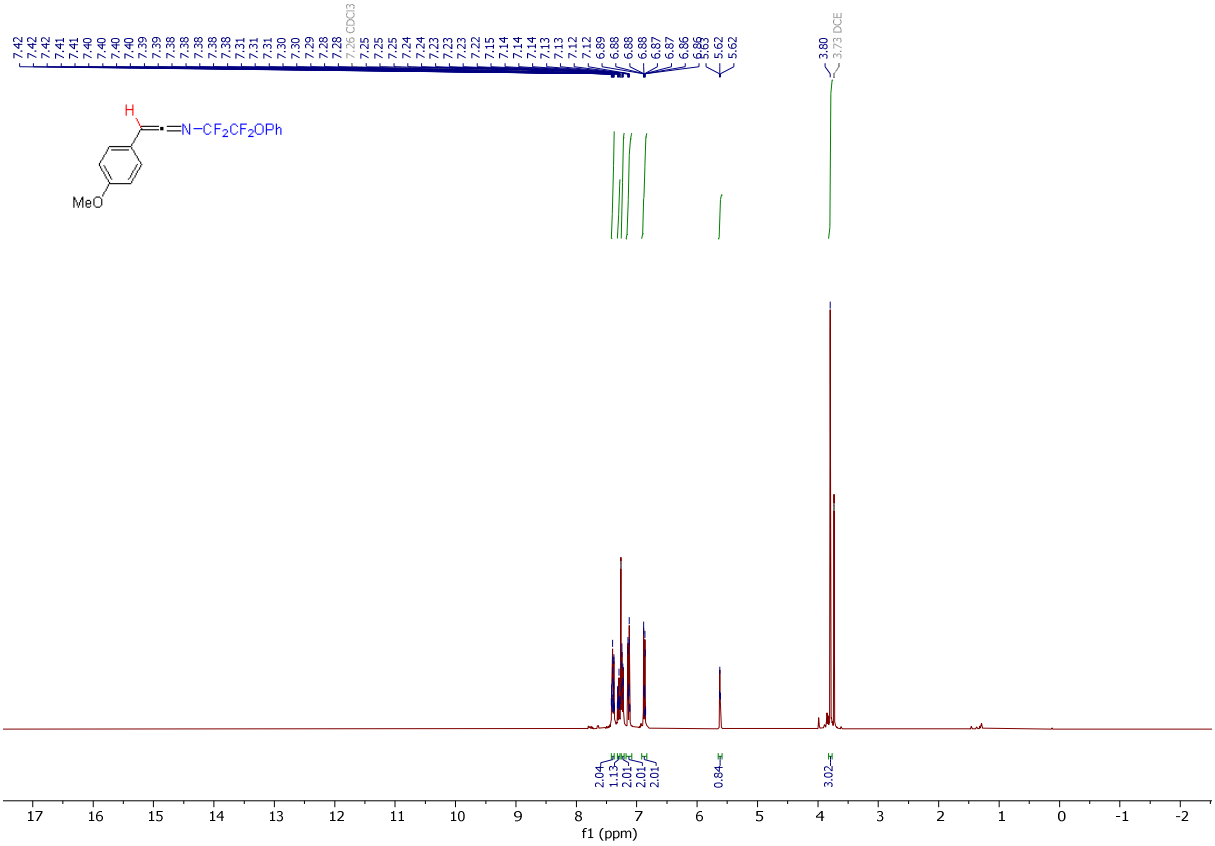
^{13}C NMR spectrum of **2s** ($CDCl_3$, 101 MHz)



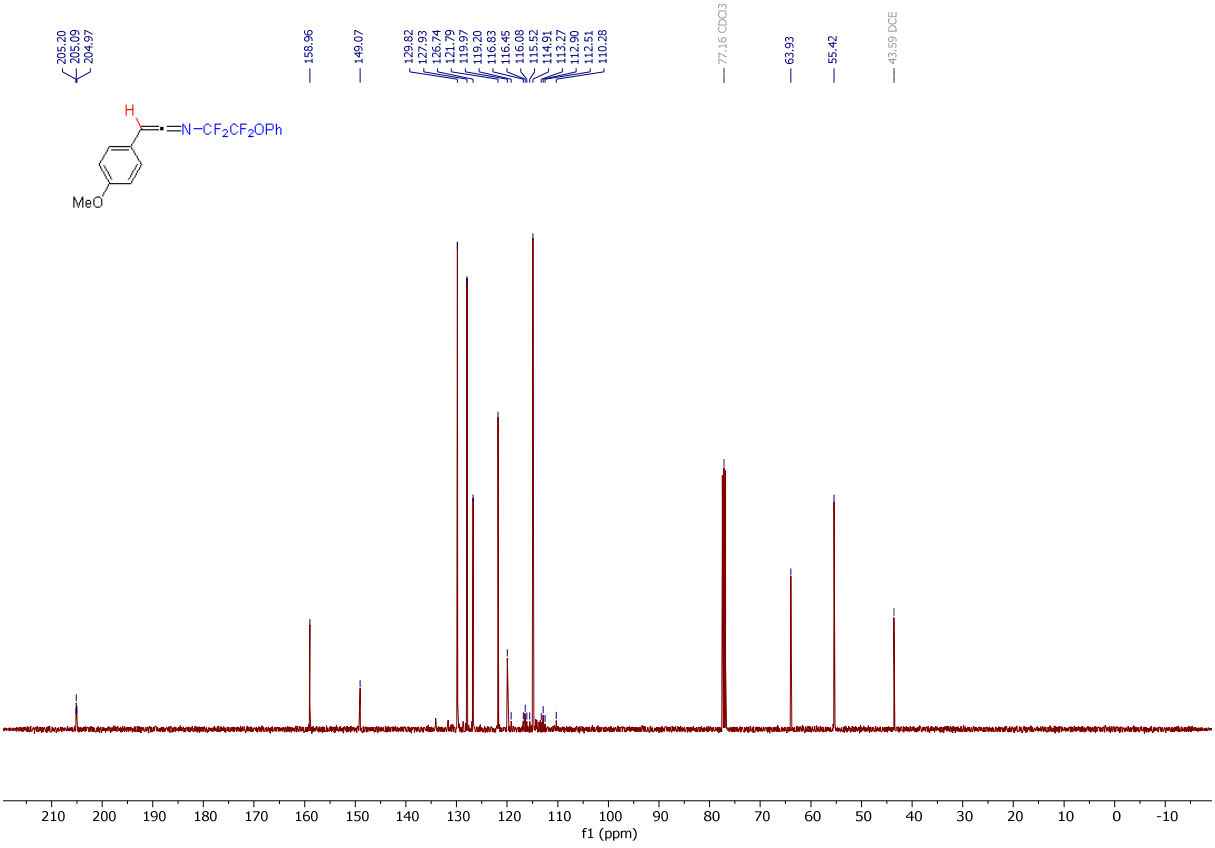
^{19}F NMR spectrum of **2s** ($CDCl_3$, 376 MHz)



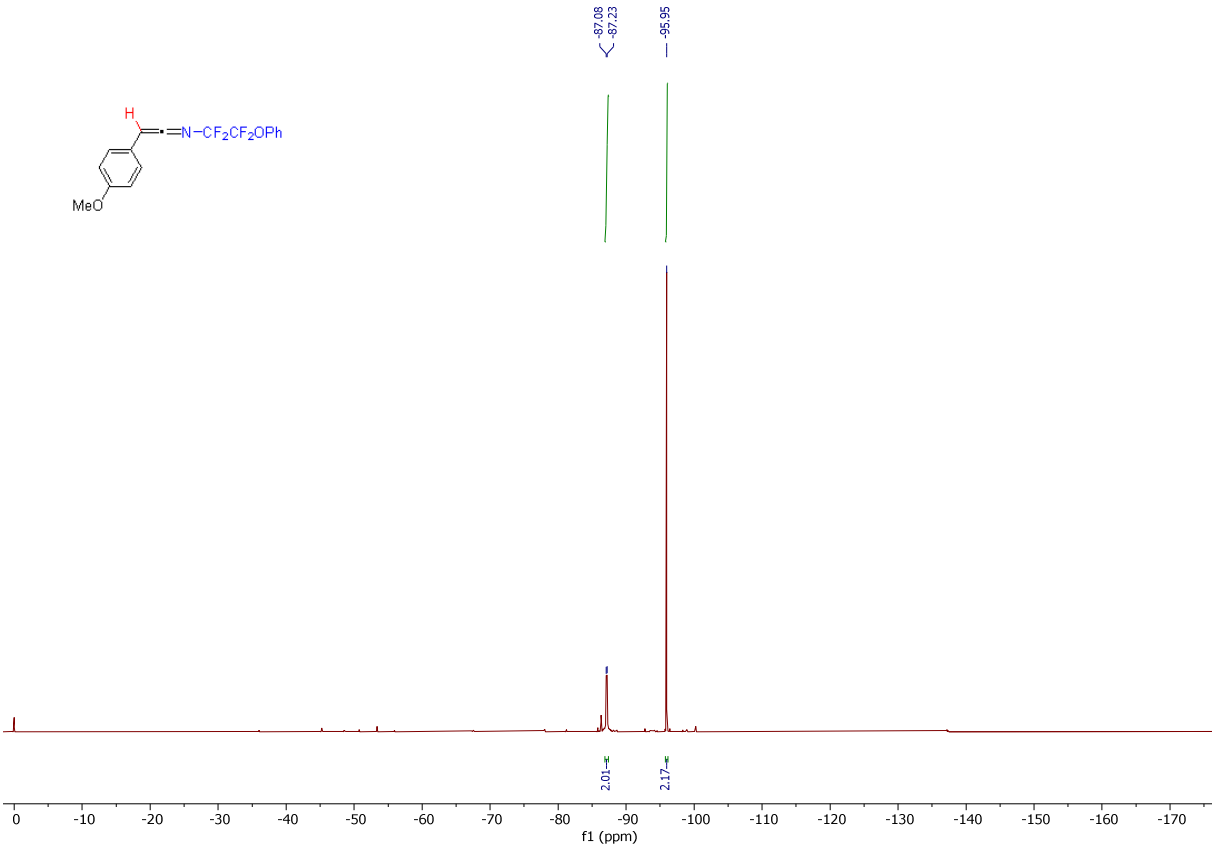
^{1}H NMR spectrum of **2t** ($CDCl_3$, 400 MHz)



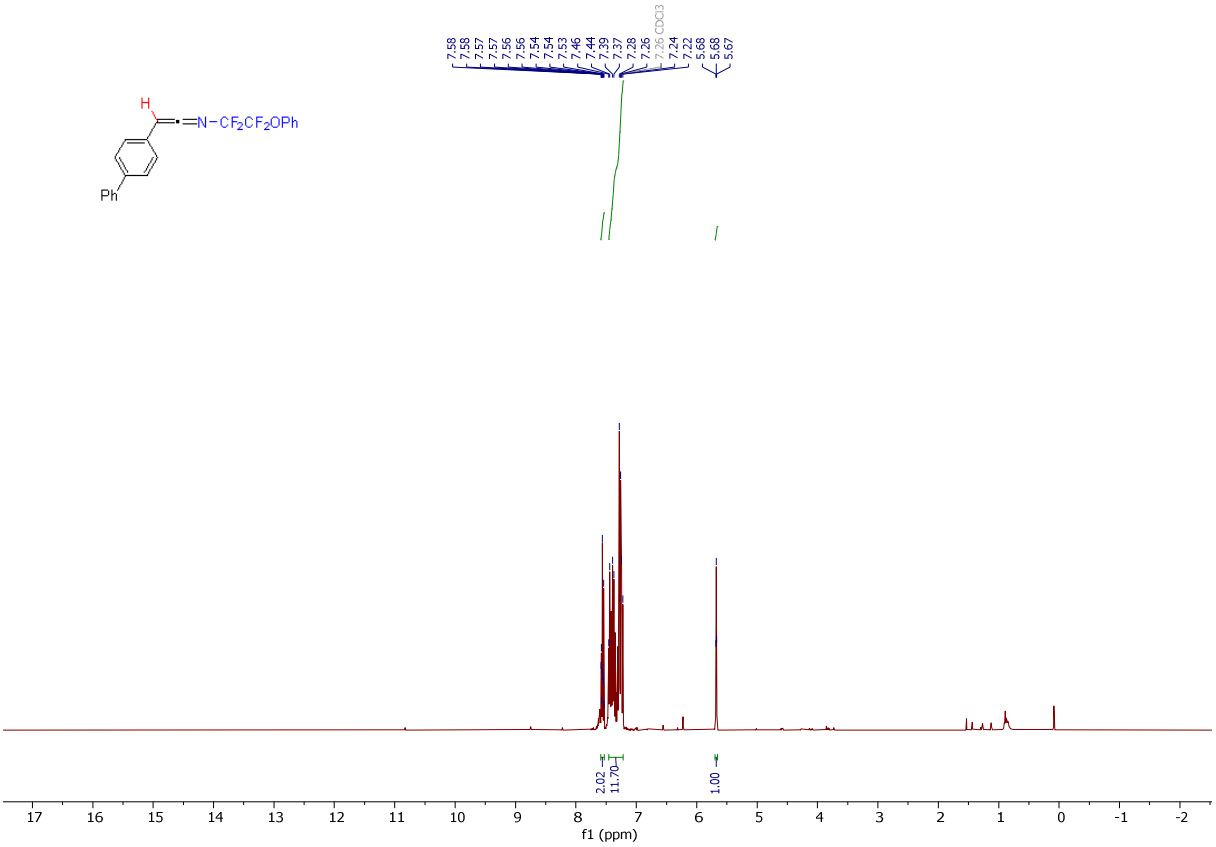
^{13}C NMR spectrum of **2t** ($CDCl_3$, 101 MHz)



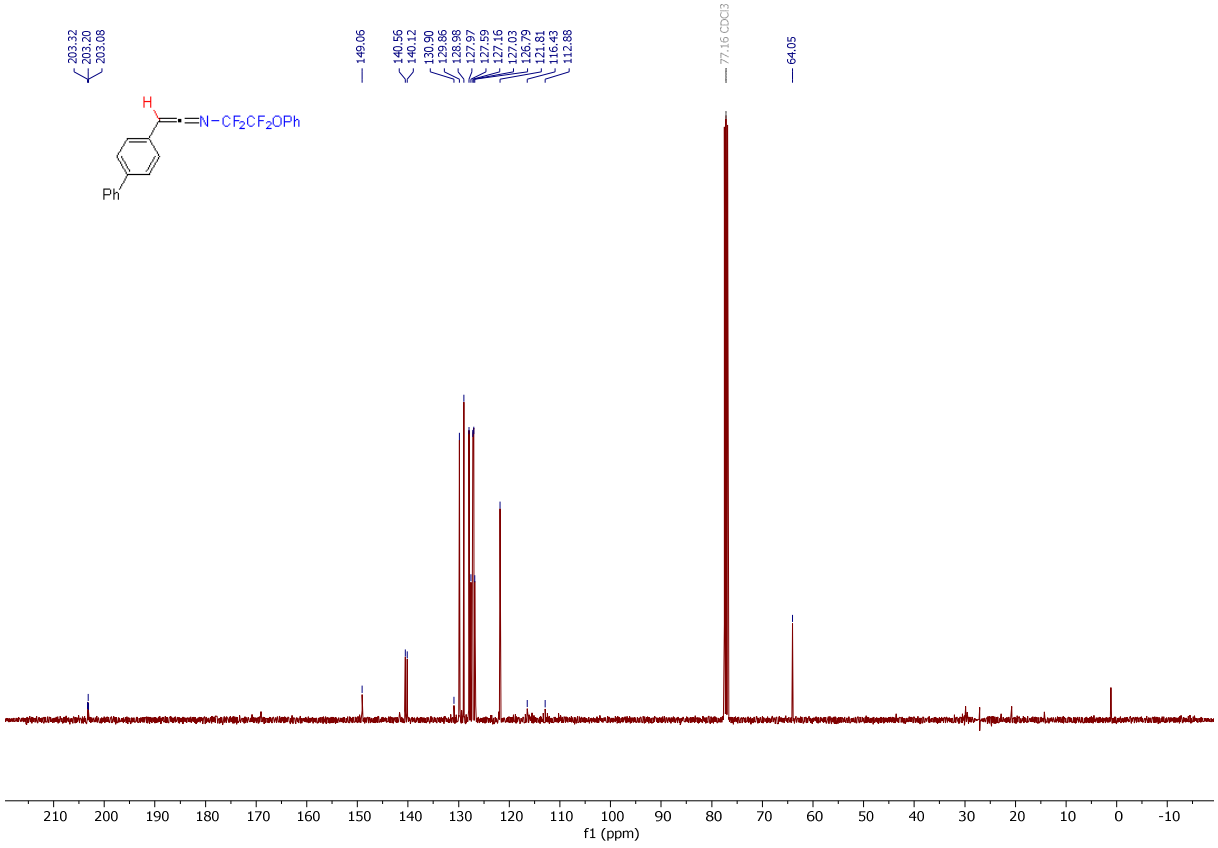
^{19}F NMR spectrum of **2t** ($CDCl_3$, 376 MHz)



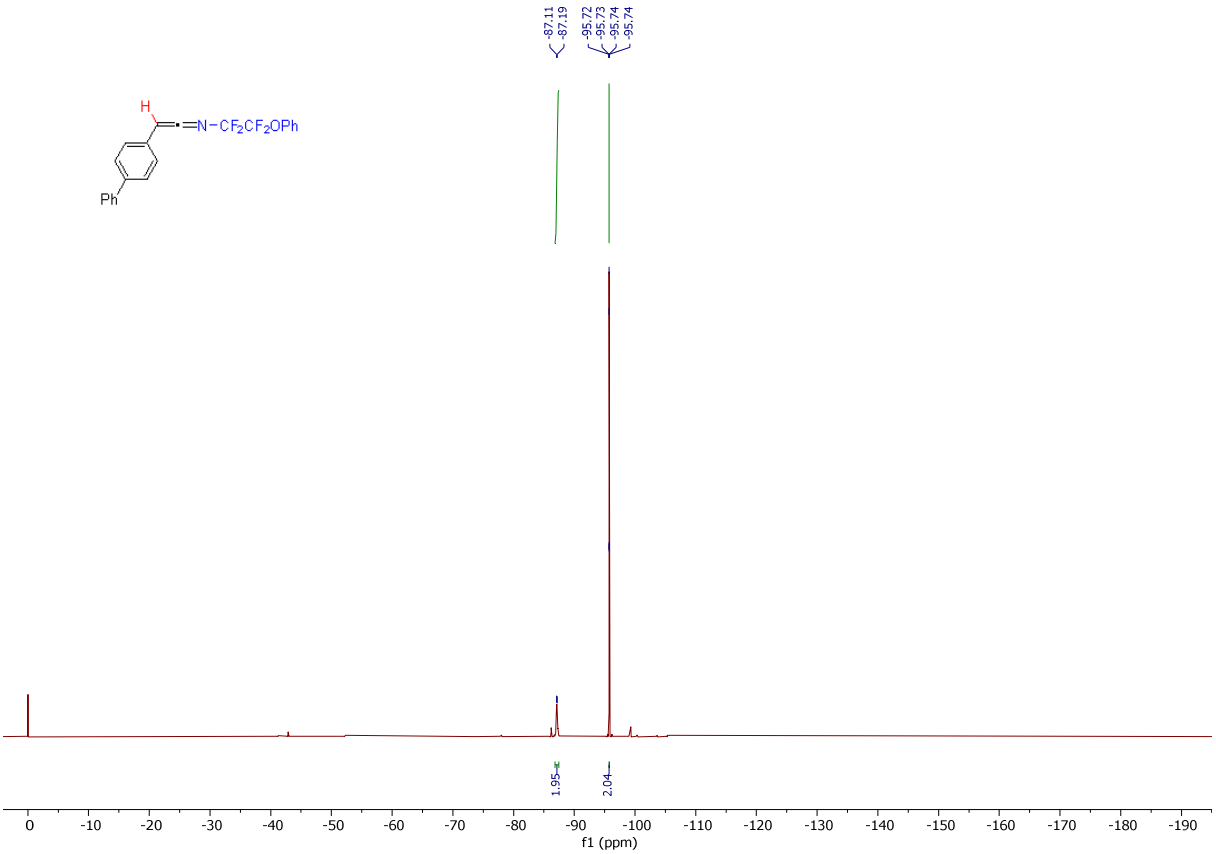
^{1}H NMR spectrum of **2u** ($CDCl_3$, 400 MHz)



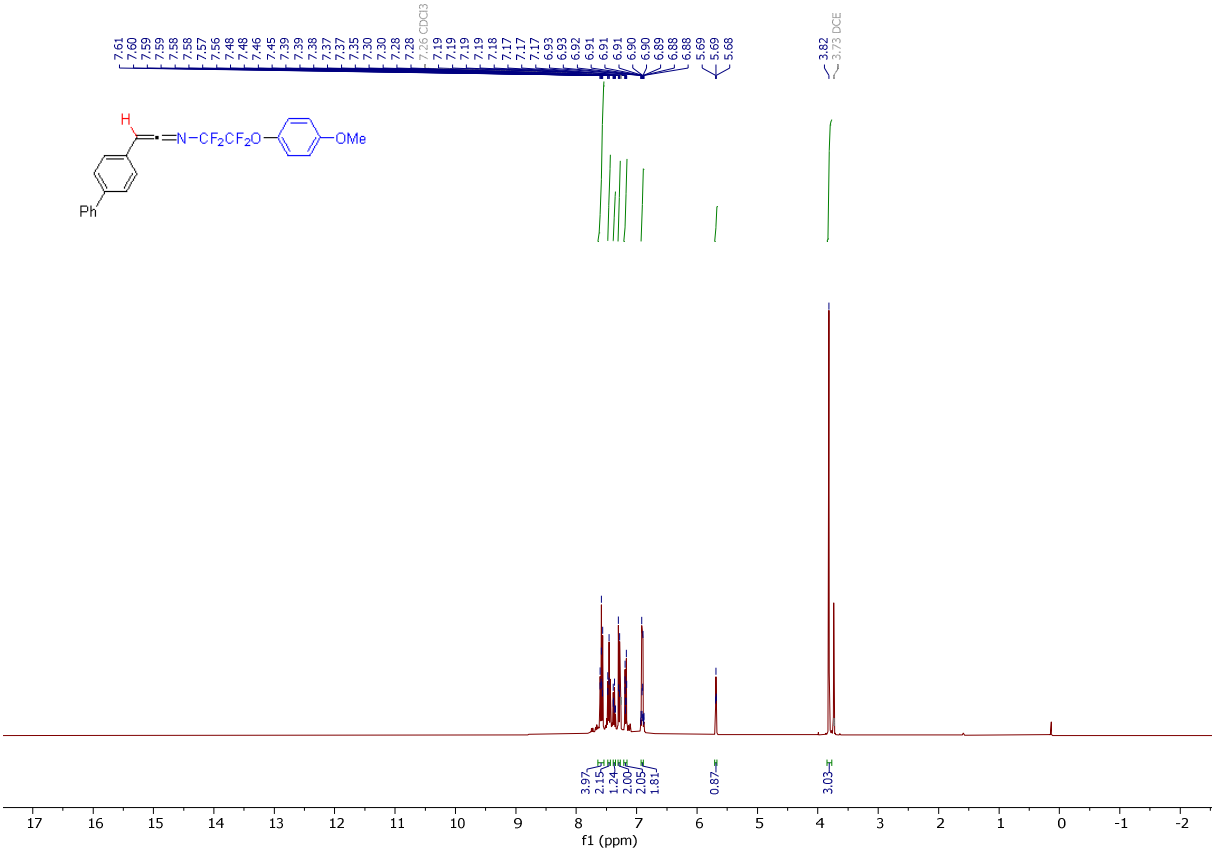
^{13}C NMR spectrum of **2u** ($CDCl_3$, 101 MHz)



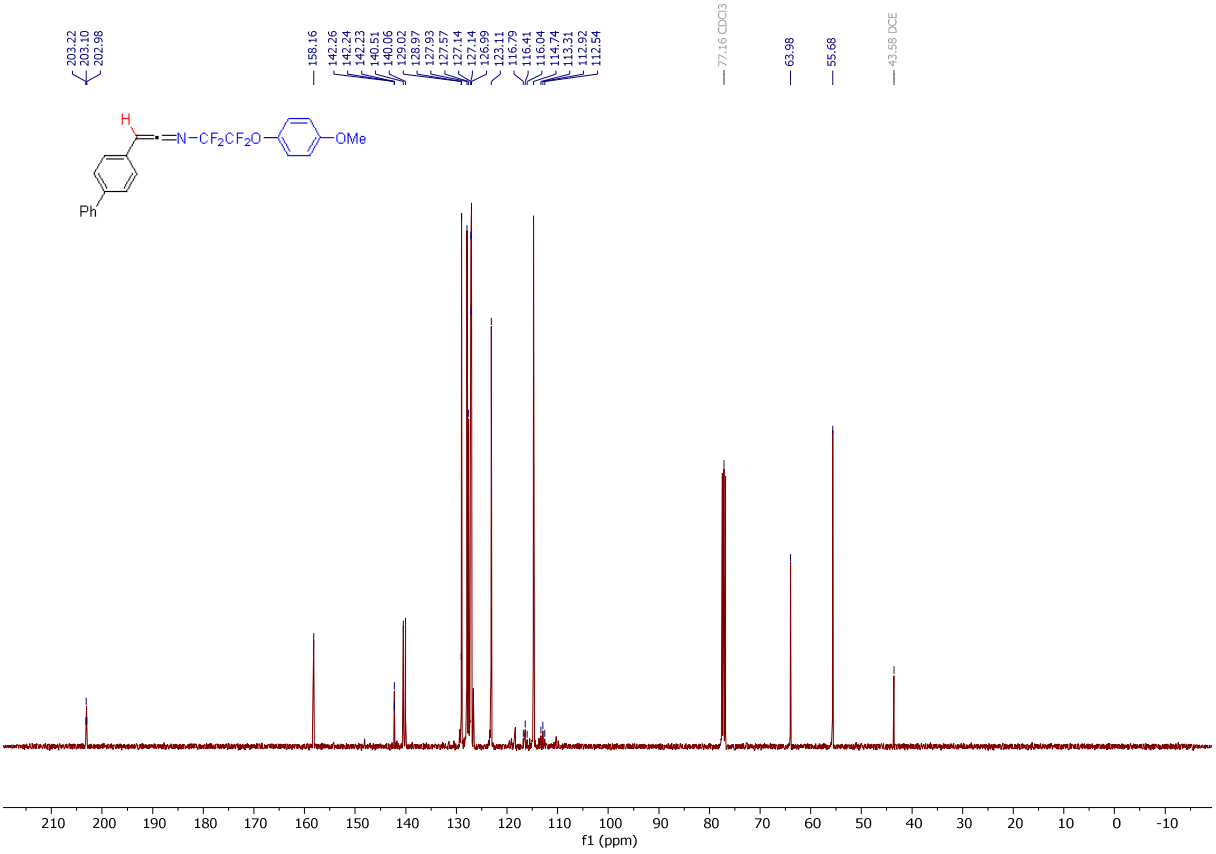
^{19}F NMR spectrum of **2u** ($CDCl_3$, 376 MHz)



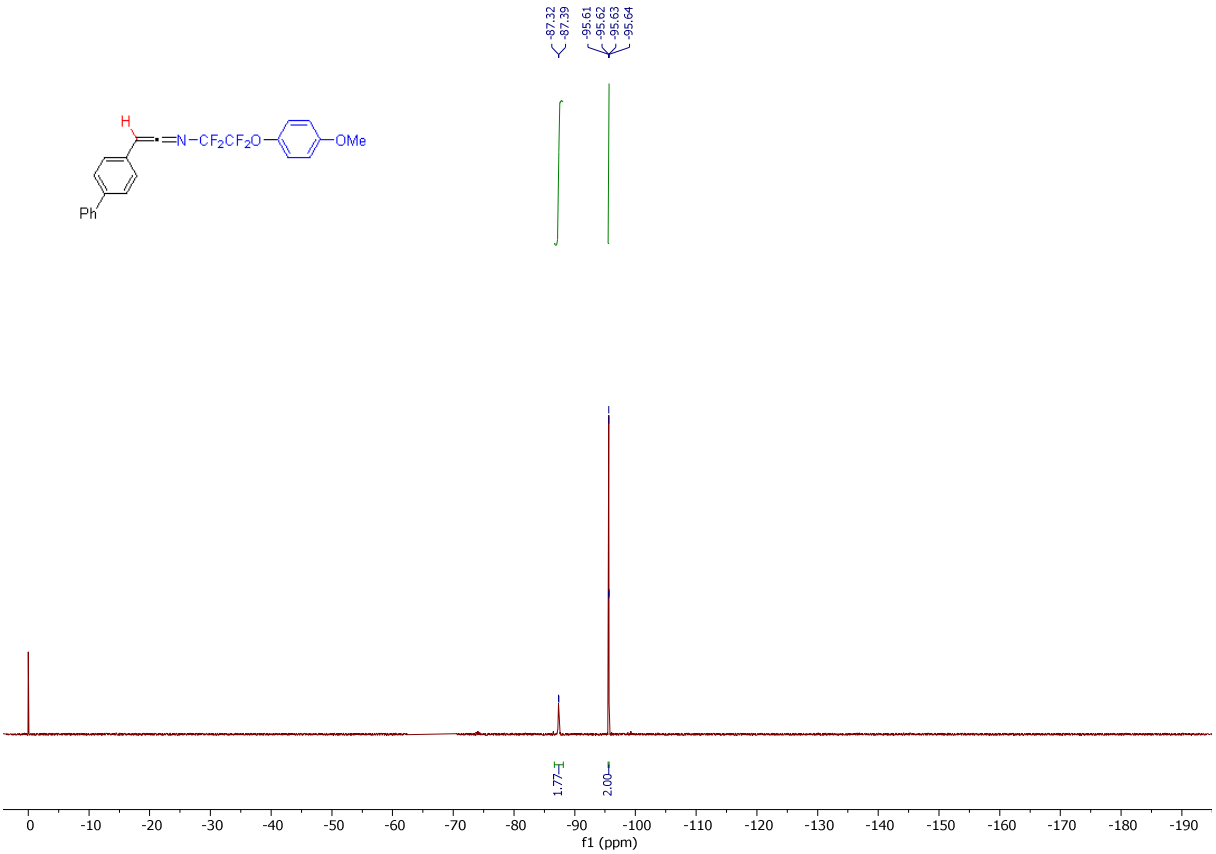
^{1}H NMR spectrum of **2v** ($CDCl_3$, 400 MHz)



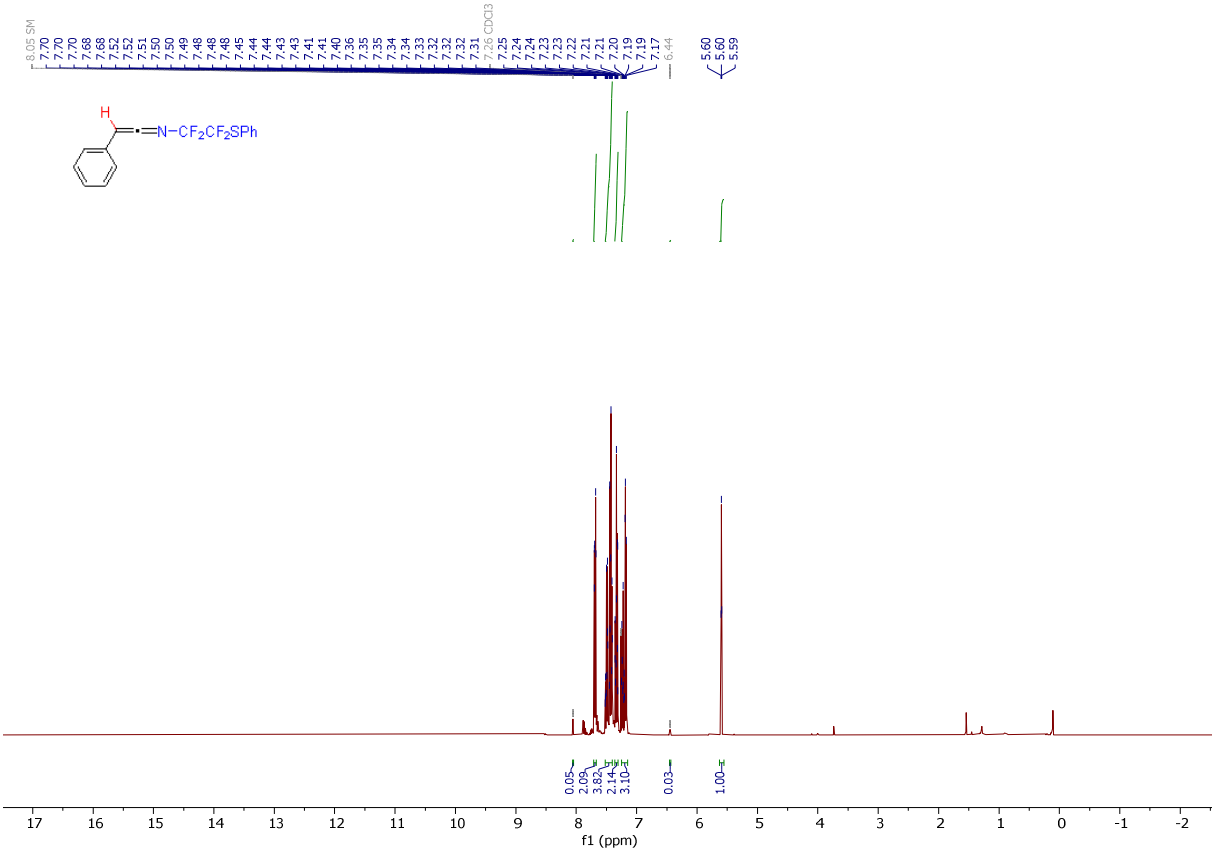
^{13}C NMR spectrum of **2v** ($CDCl_3$, 101 MHz)



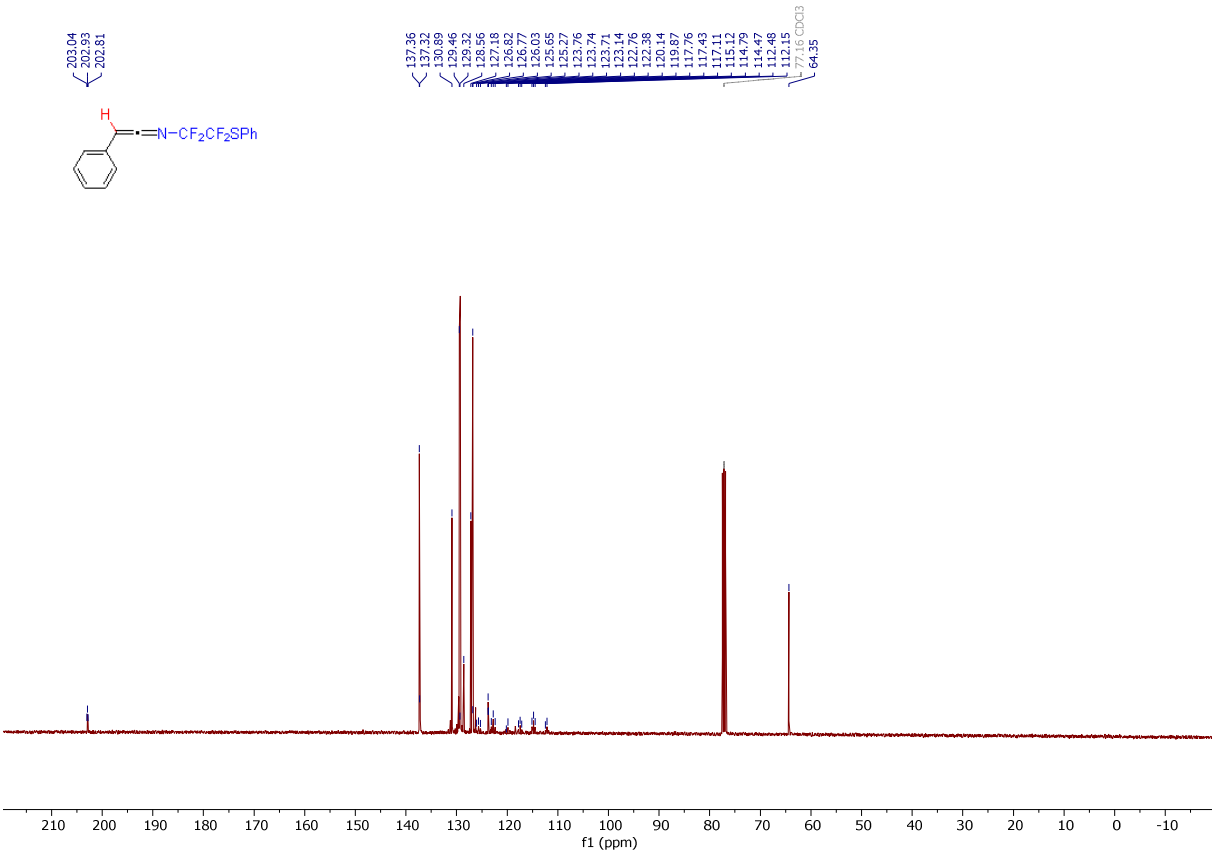
^{19}F NMR spectrum of **2v** ($CDCl_3$, 376 MHz)



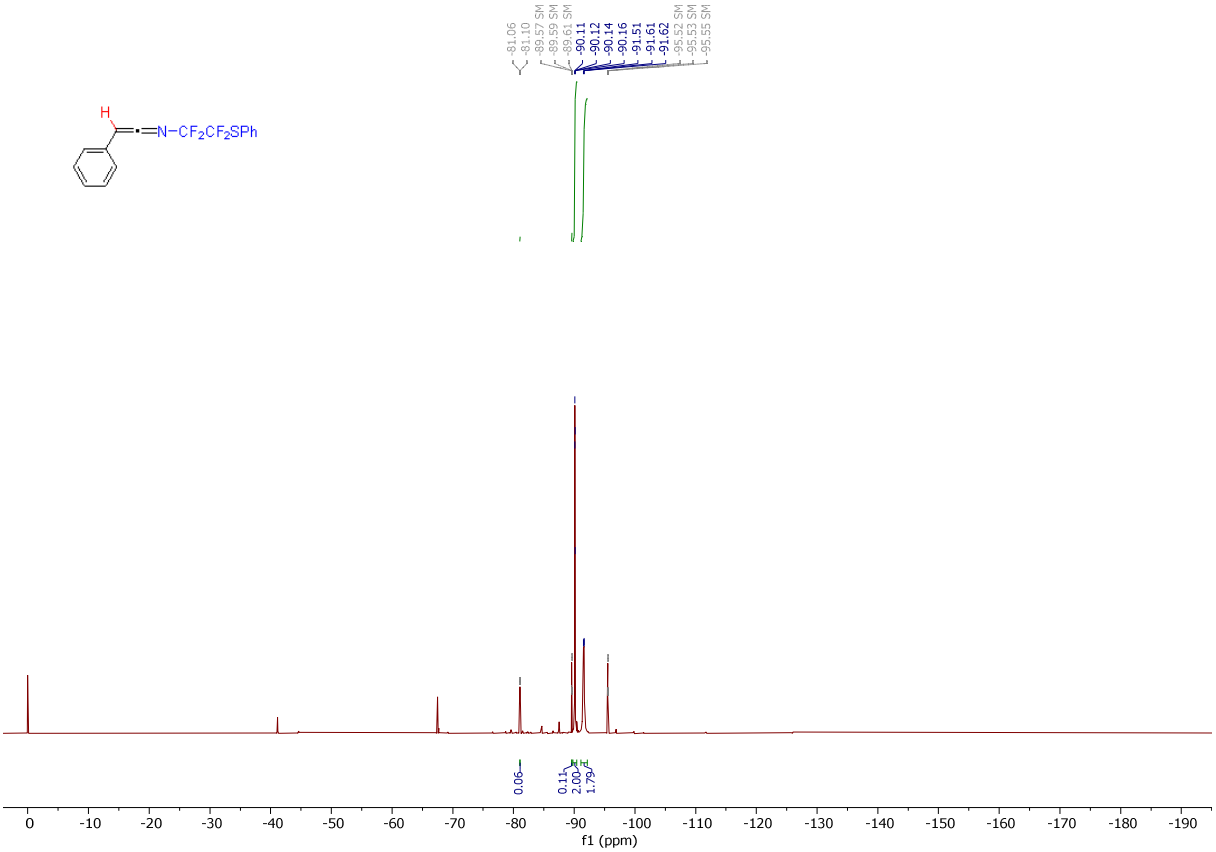
^{1}H NMR spectrum of **2w** ($CDCl_3$, 400 MHz)



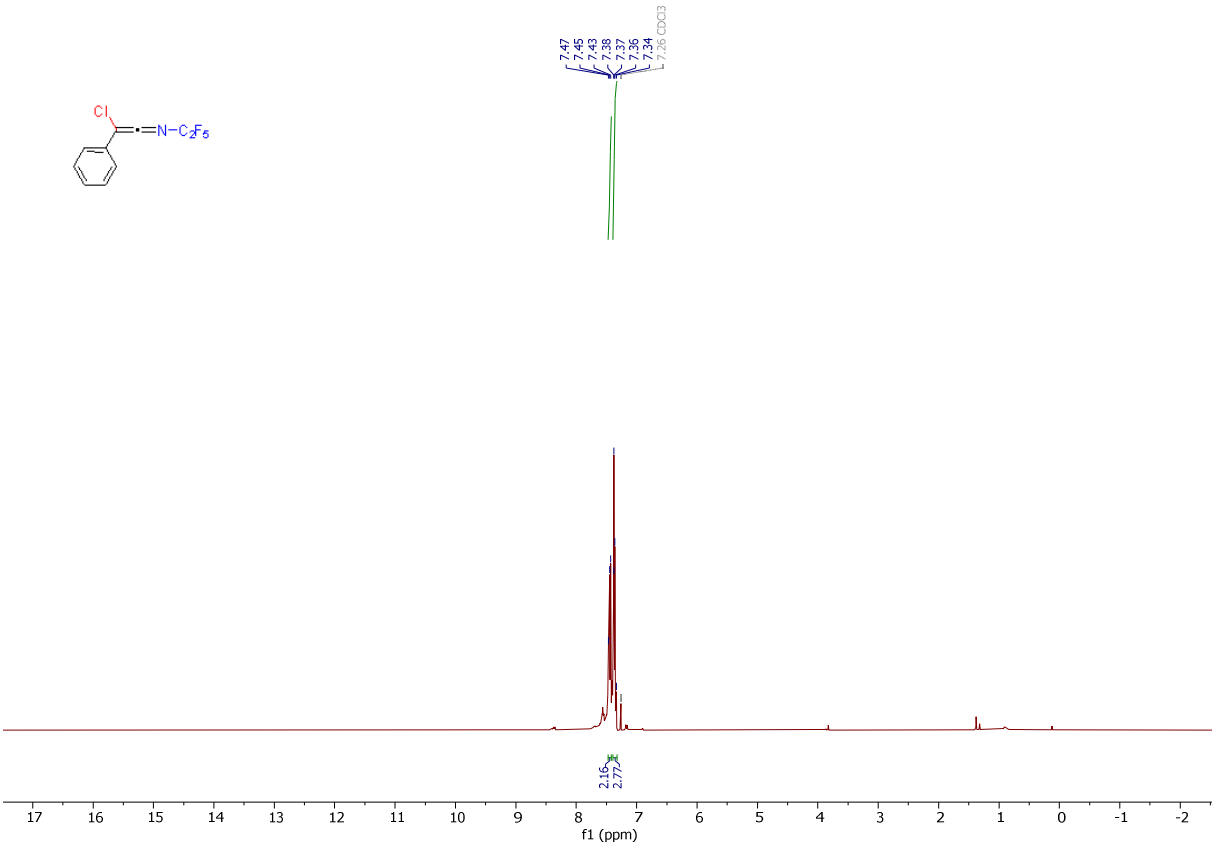
^{13}C NMR spectrum of **2w** ($CDCl_3$, 101 MHz)



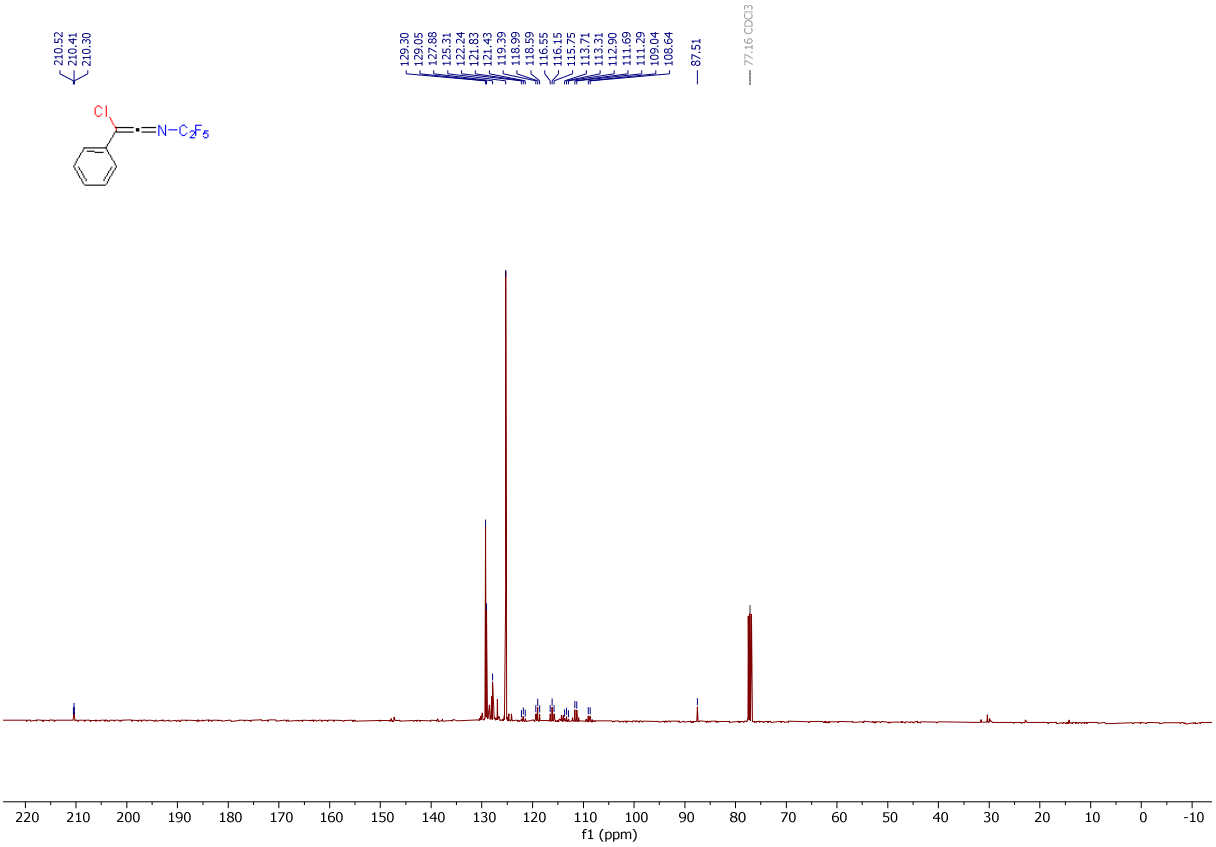
^{19}F NMR spectrum of **2w** ($CDCl_3$, 376 MHz)



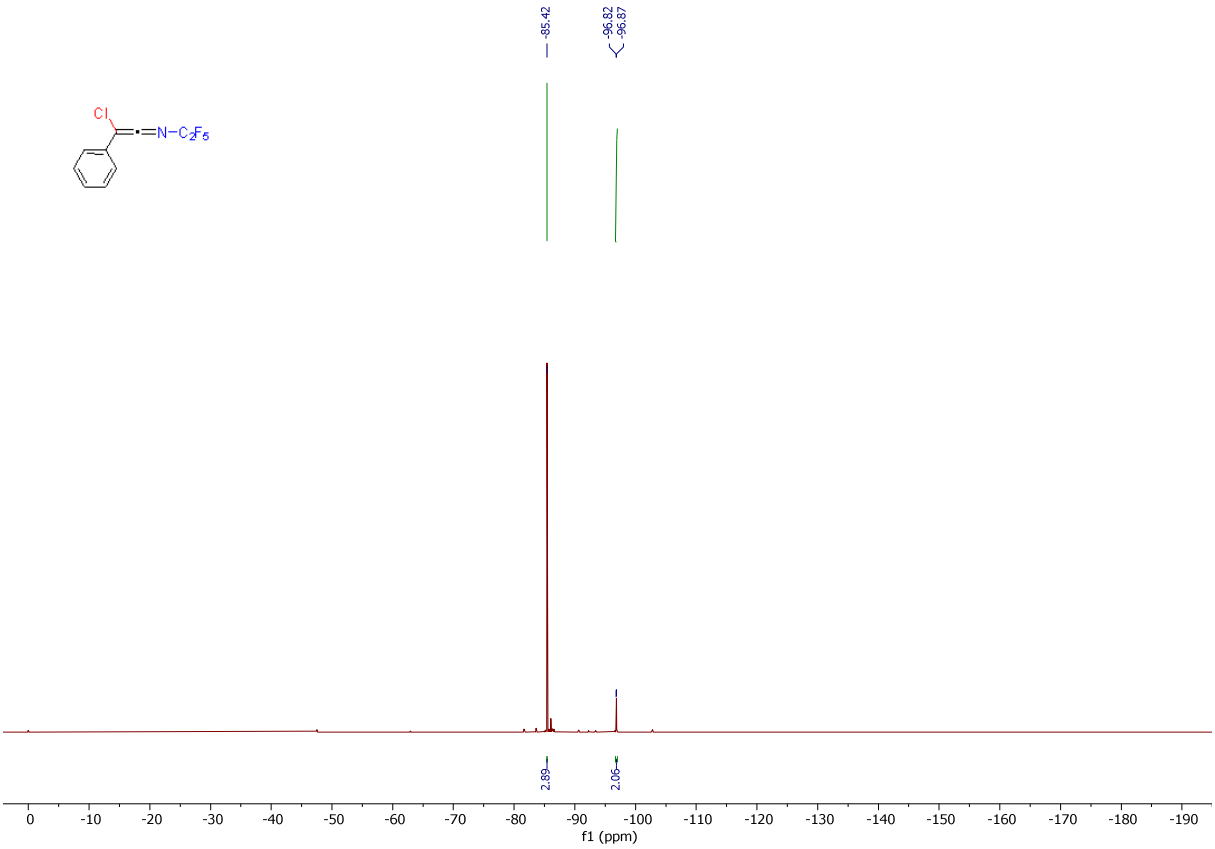
^{1}H NMR spectrum of **2x** ($CDCl_3$, 400 MHz)



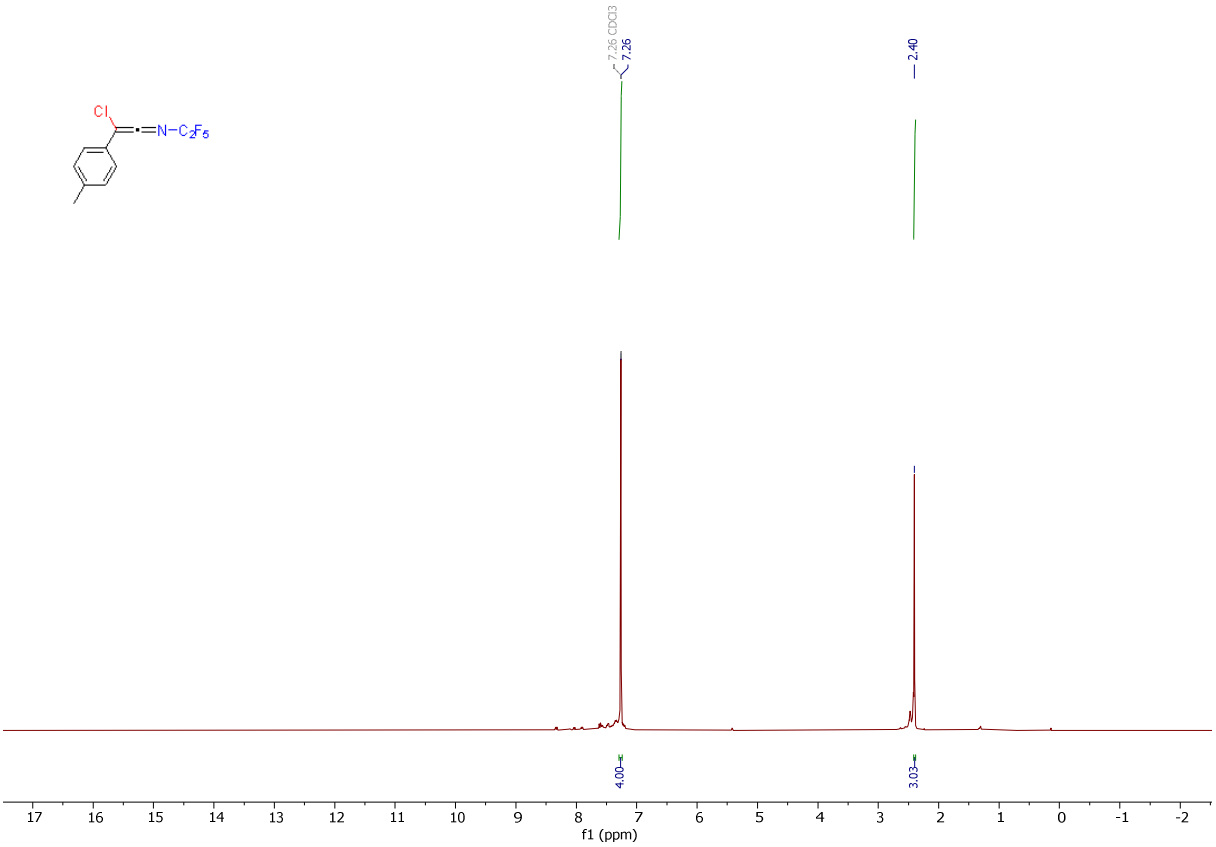
^{13}C NMR spectrum of **2x** ($CDCl_3$, 101 MHz)



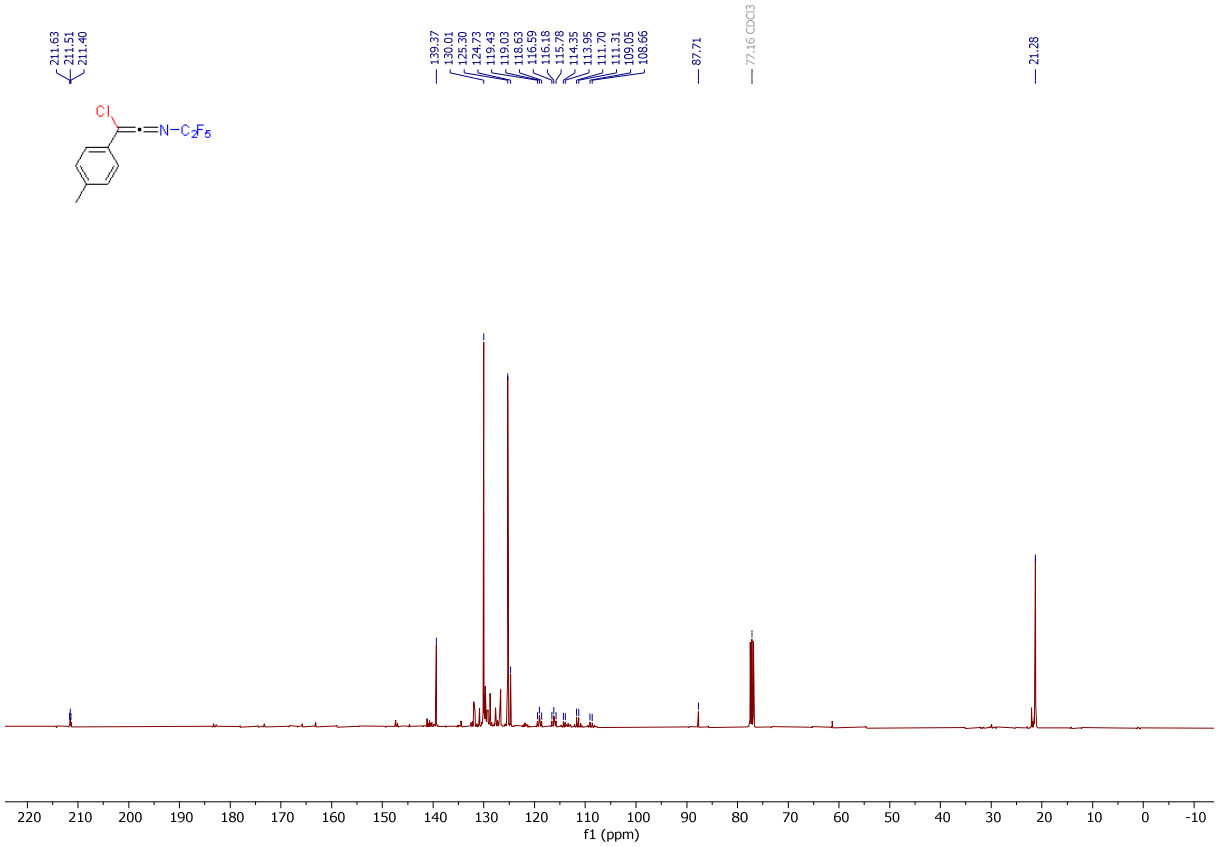
^{19}F NMR spectrum of **2x** ($CDCl_3$, 376 MHz)



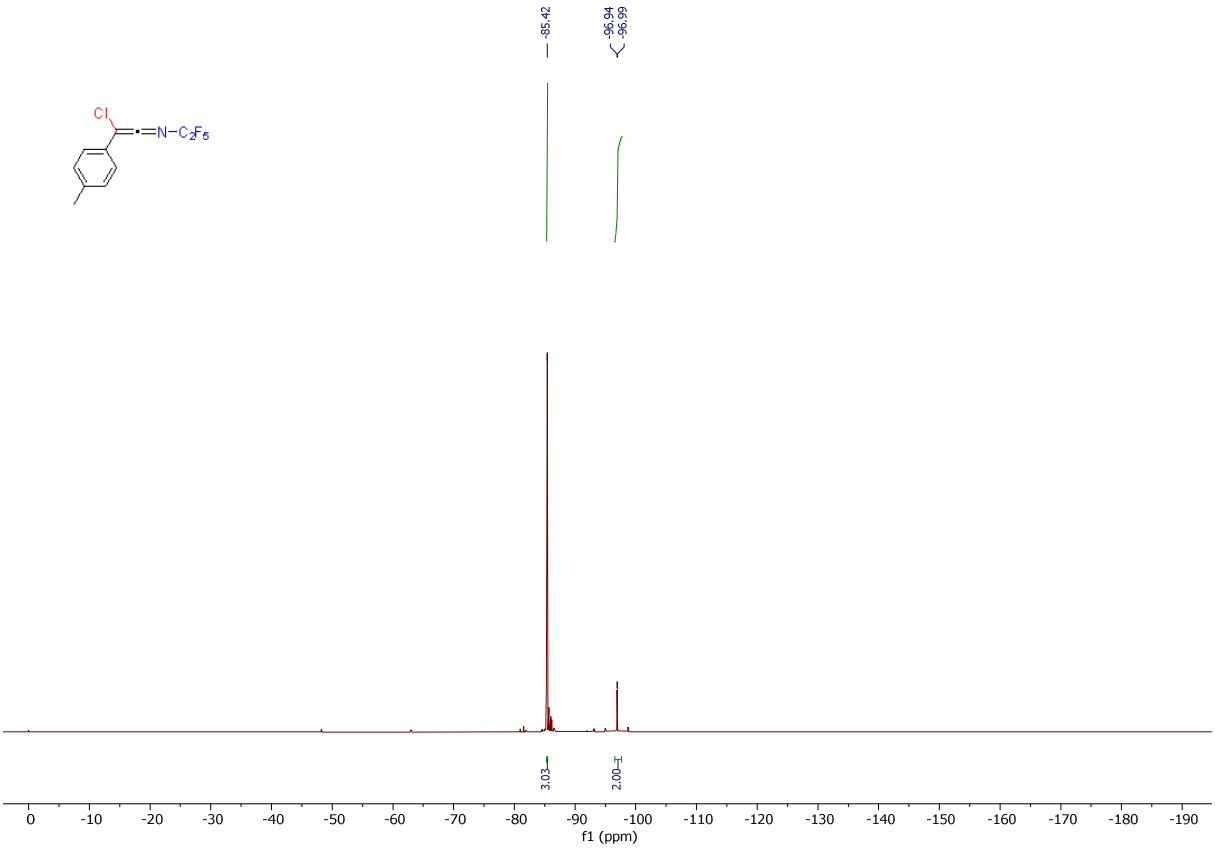
^{1}H NMR spectrum of **2y** ($CDCl_3$, 400 MHz)



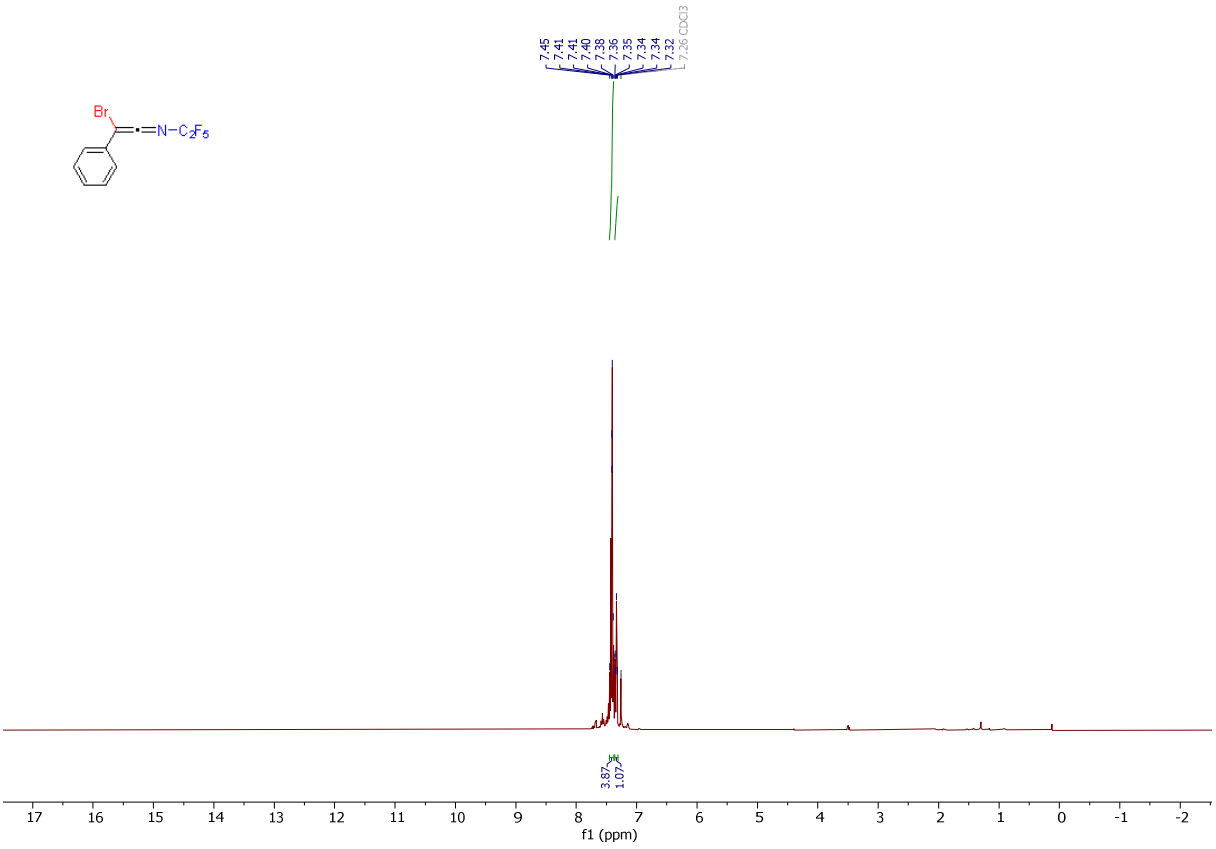
^{13}C NMR spectrum of **2y** ($CDCl_3$, 101 MHz)



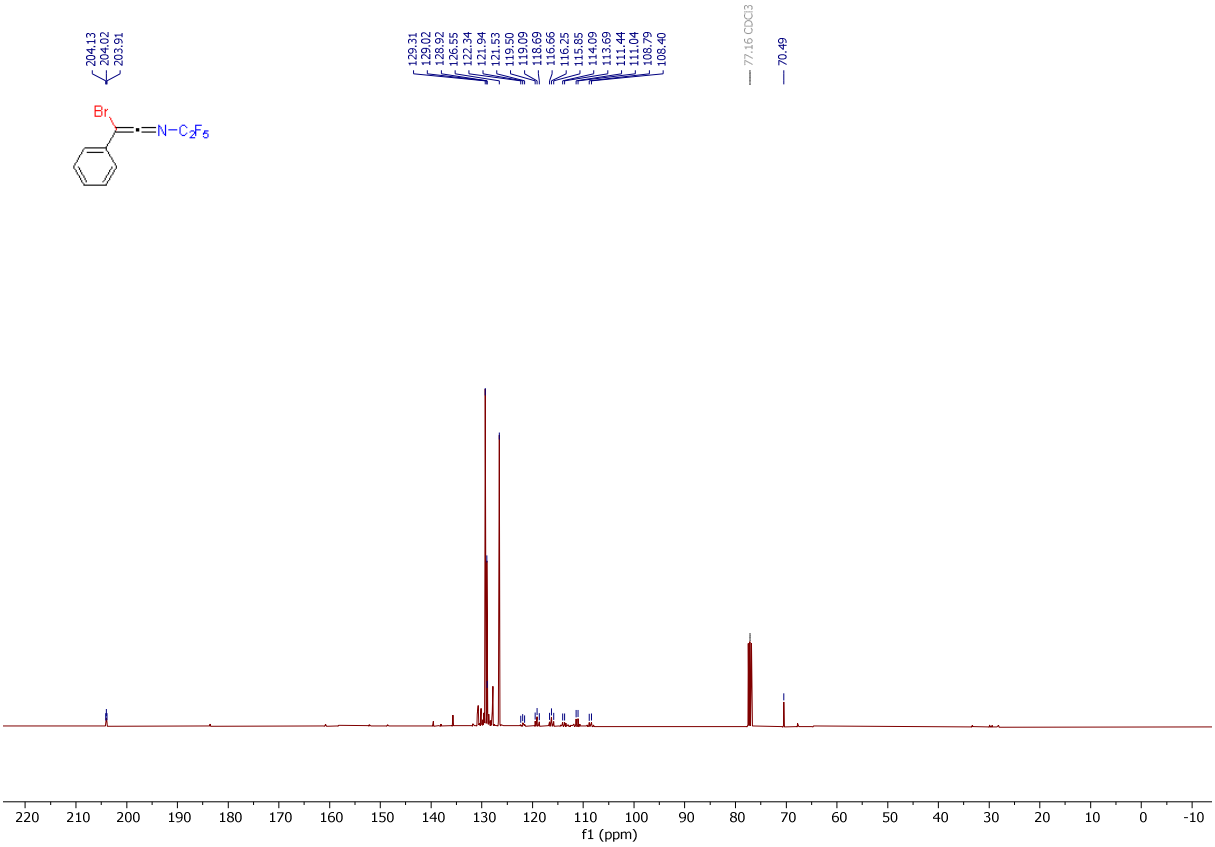
^{19}F NMR spectrum of **2y** ($CDCl_3$, 376 MHz)



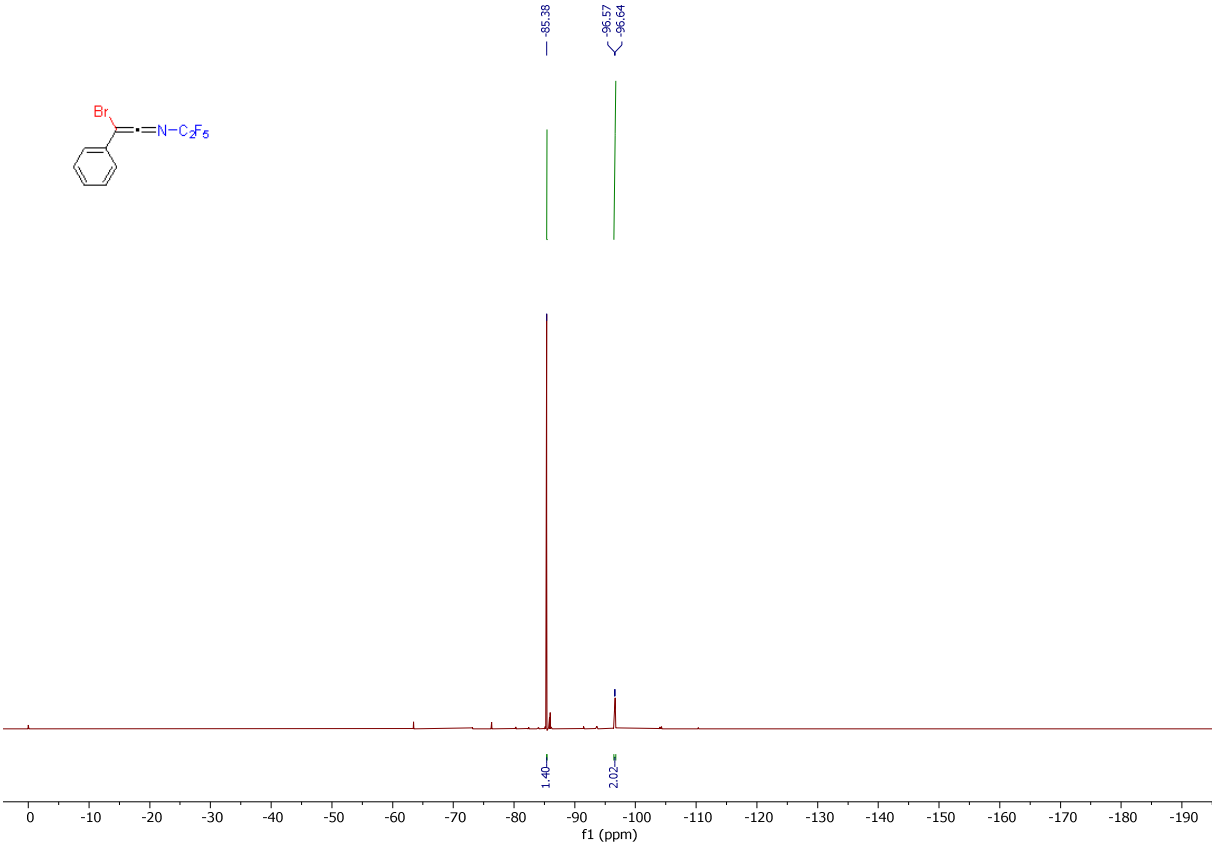
^{1}H NMR spectrum of **2z** ($CDCl_3$, 400 MHz)



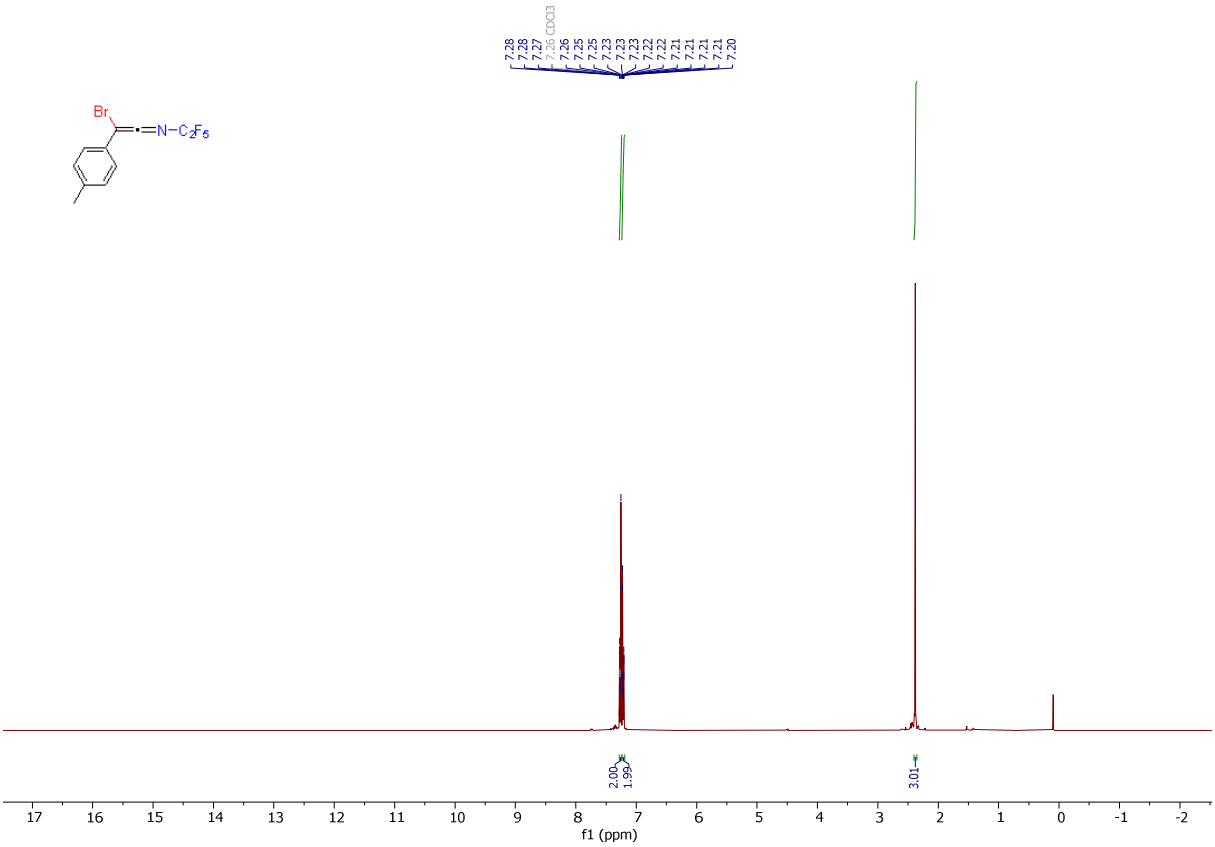
^{13}C NMR spectrum of **2z** ($CDCl_3$, 101 MHz)



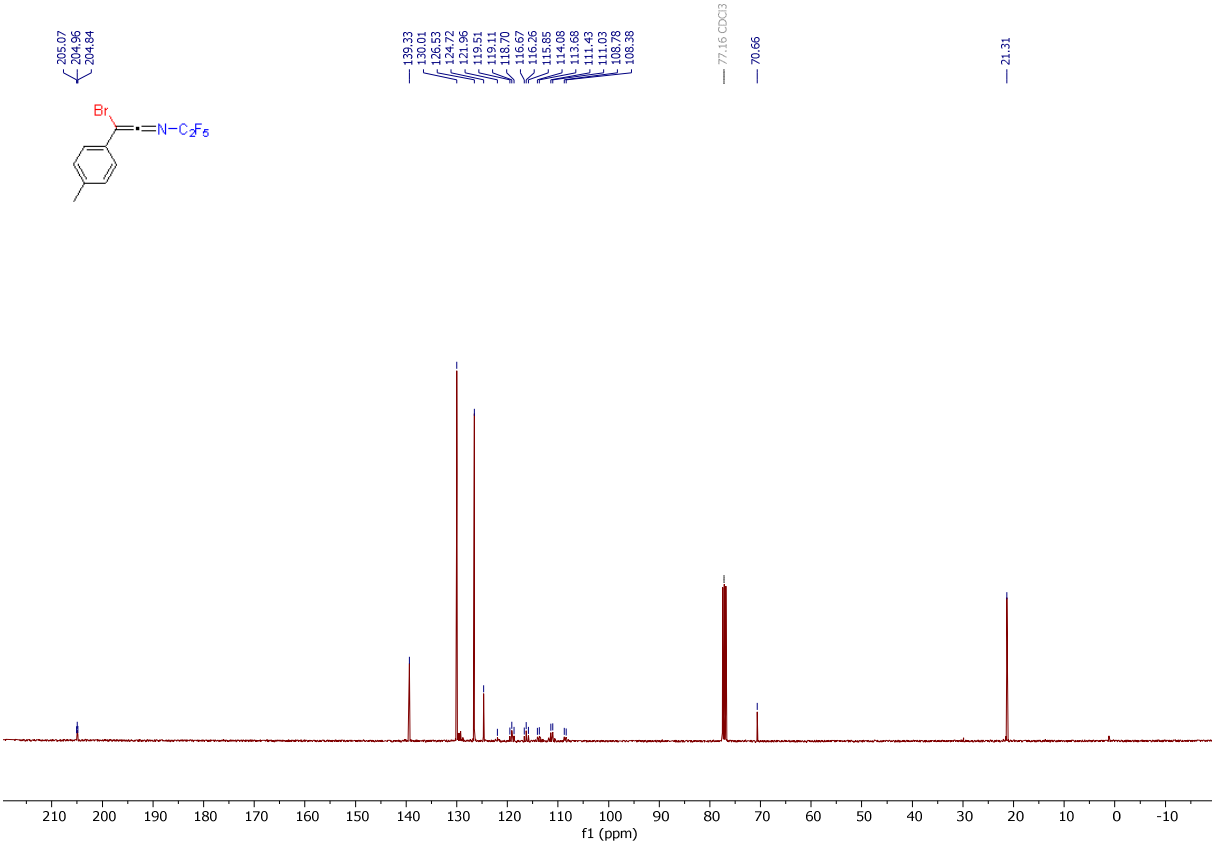
^{19}F NMR spectrum of **2z** ($CDCl_3$, 376 MHz)



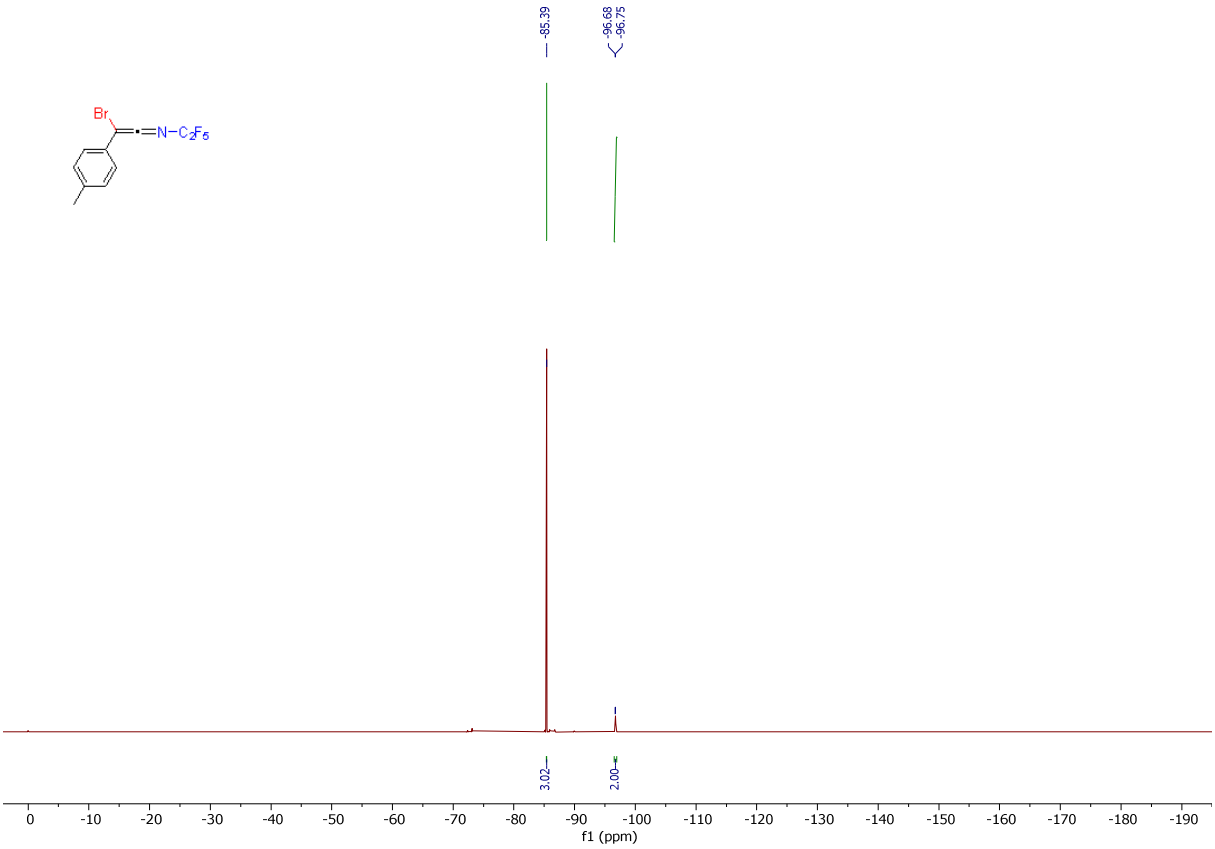
^{1}H NMR spectrum of **2aa** ($CDCl_3$, 400 MHz)



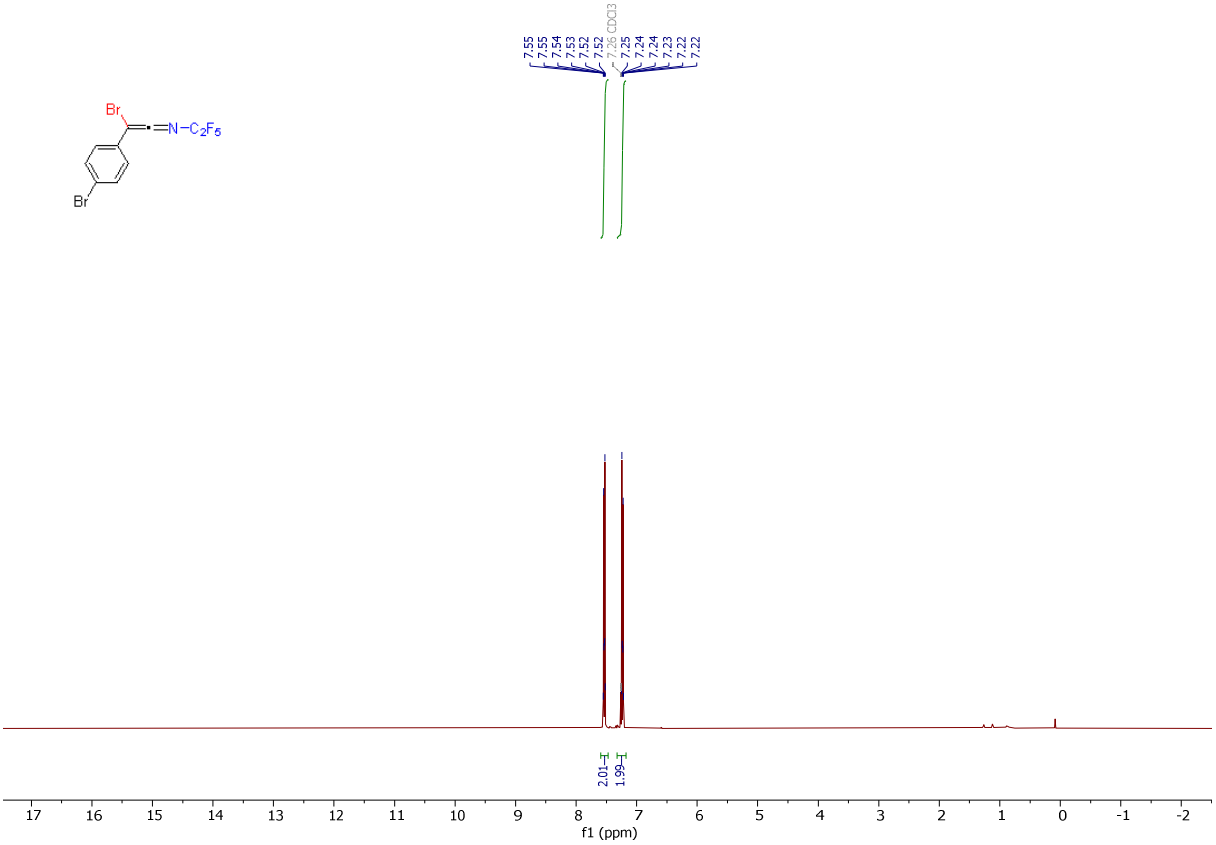
^{13}C NMR spectrum of **2aa** ($CDCl_3$, 101 MHz)



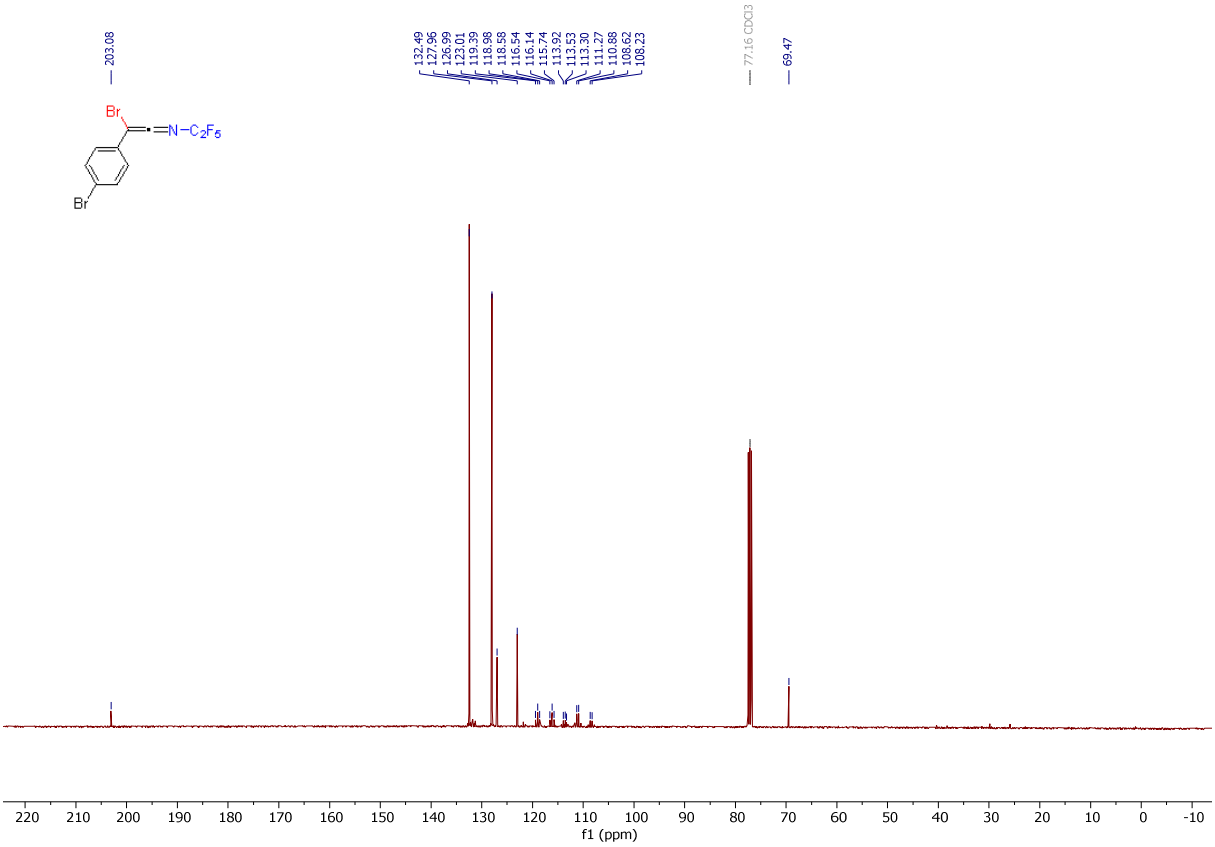
^{19}F NMR spectrum of **2aa** ($CDCl_3$, 376 MHz)



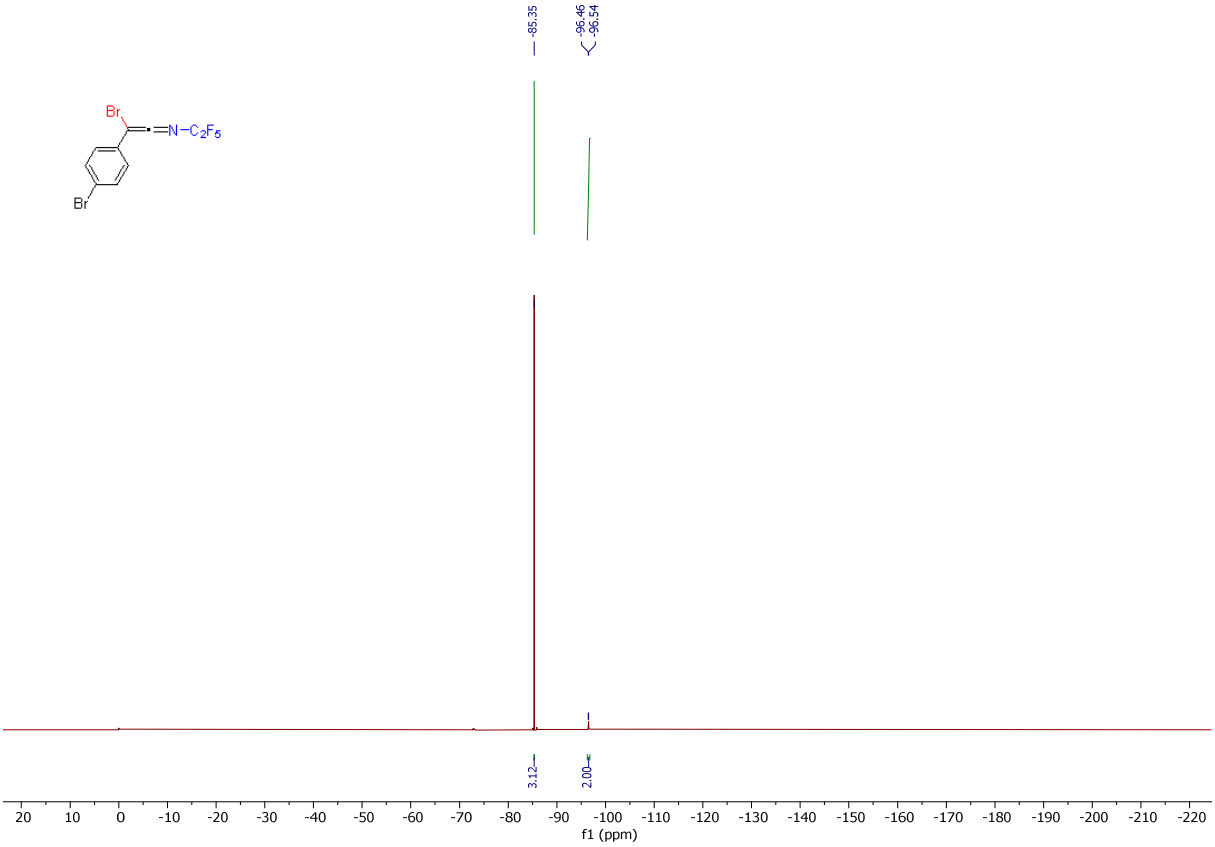
^{1}H NMR spectrum of **2ab** ($CDCl_3$, 400 MHz)



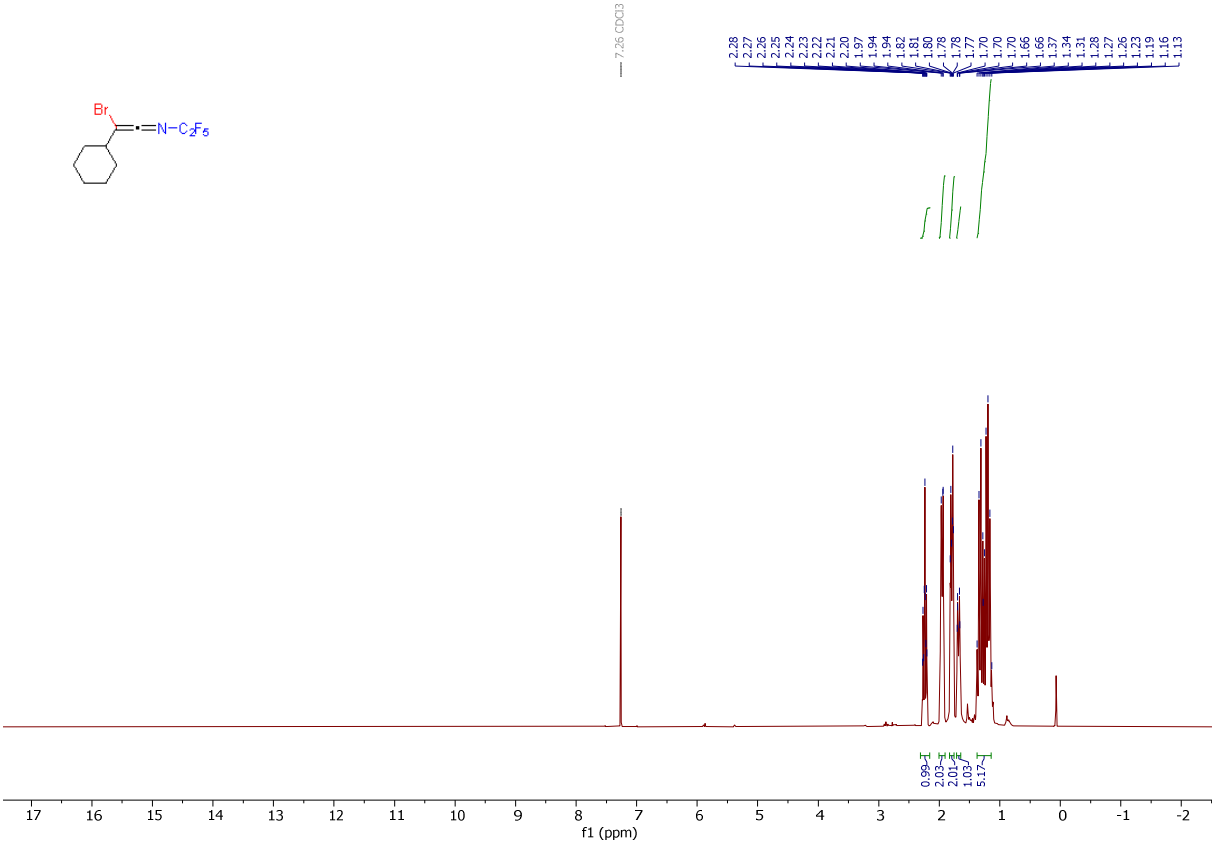
^{13}C NMR spectrum of **2ab** ($CDCl_3$, 101 MHz)



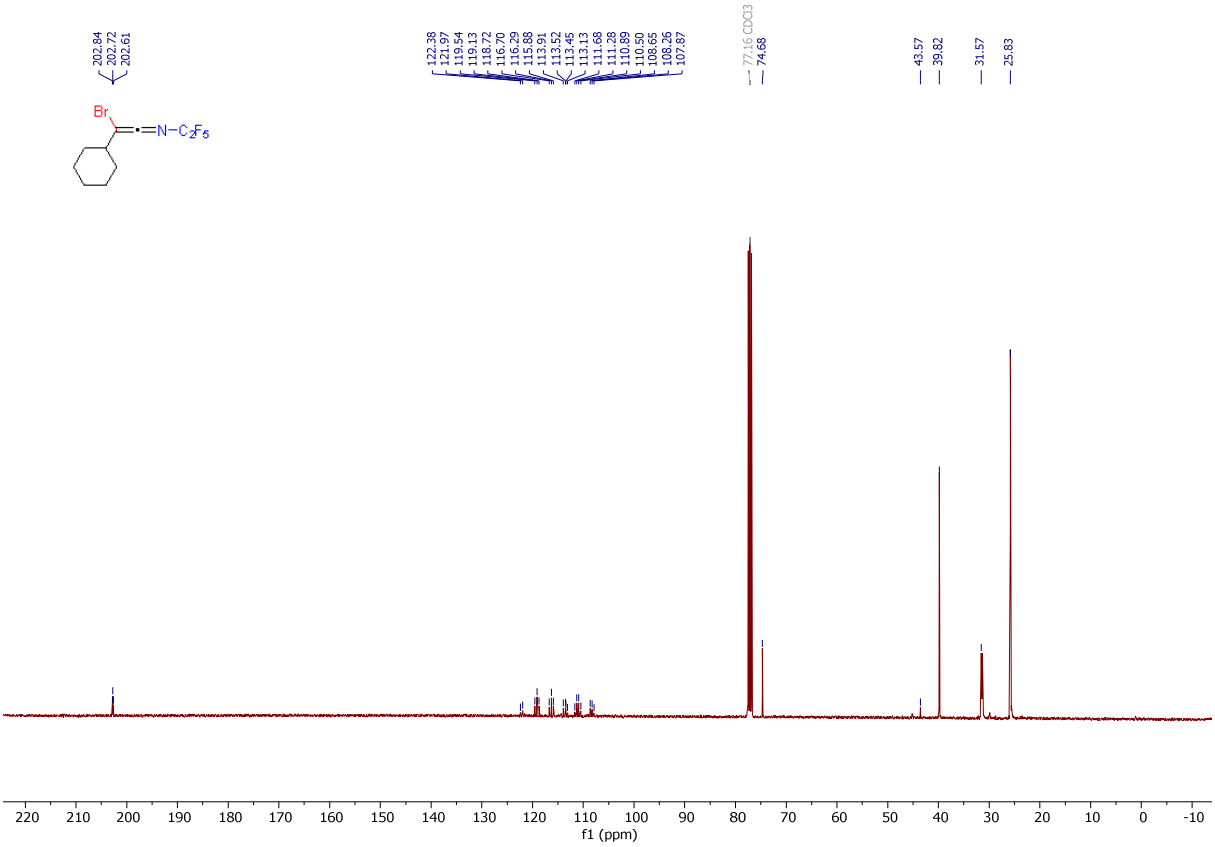
^{19}F NMR spectrum of **2ab** ($CDCl_3$, 376 MHz)



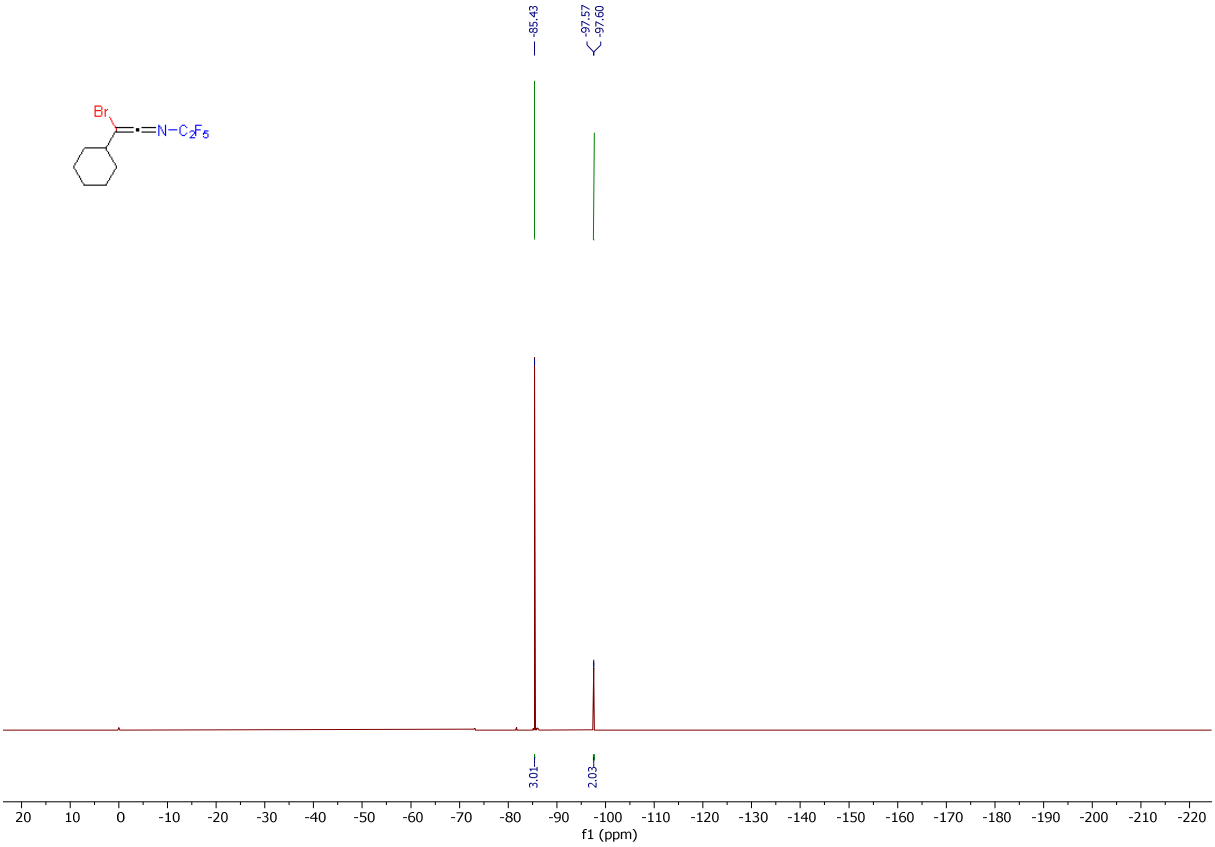
^{1}H NMR spectrum of **2ac** ($CDCl_3$, 400 MHz)



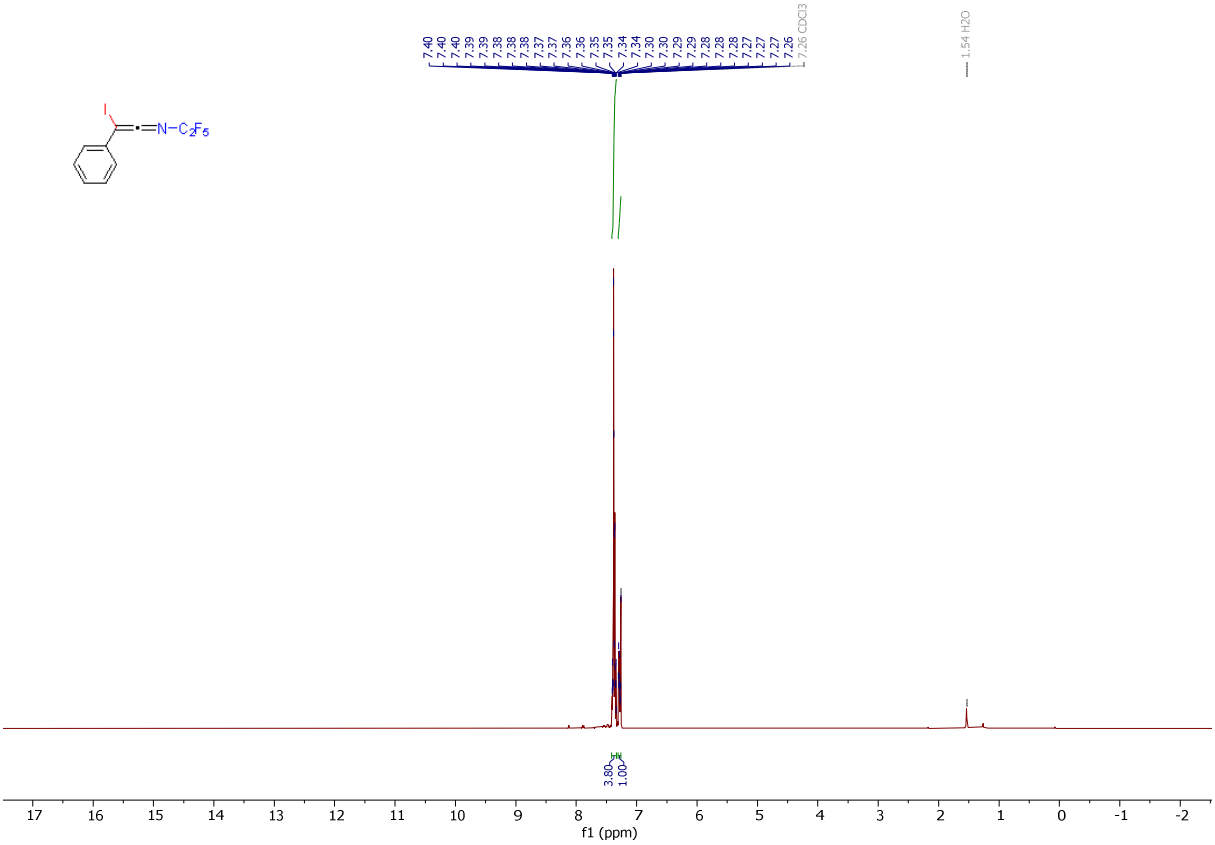
^{13}C NMR spectrum of **2ac** ($CDCl_3$, 101 MHz)



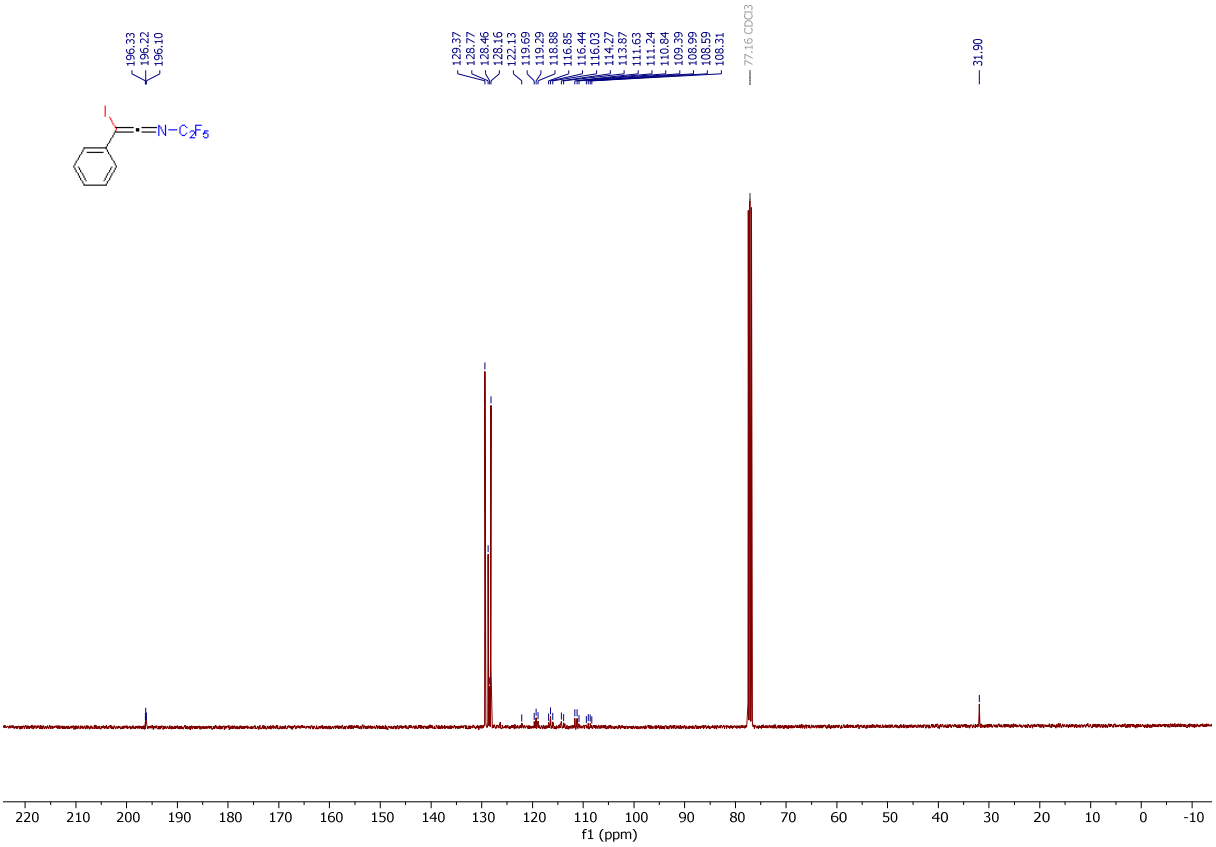
^{19}F NMR spectrum of **2ac** ($CDCl_3$, 376 MHz)



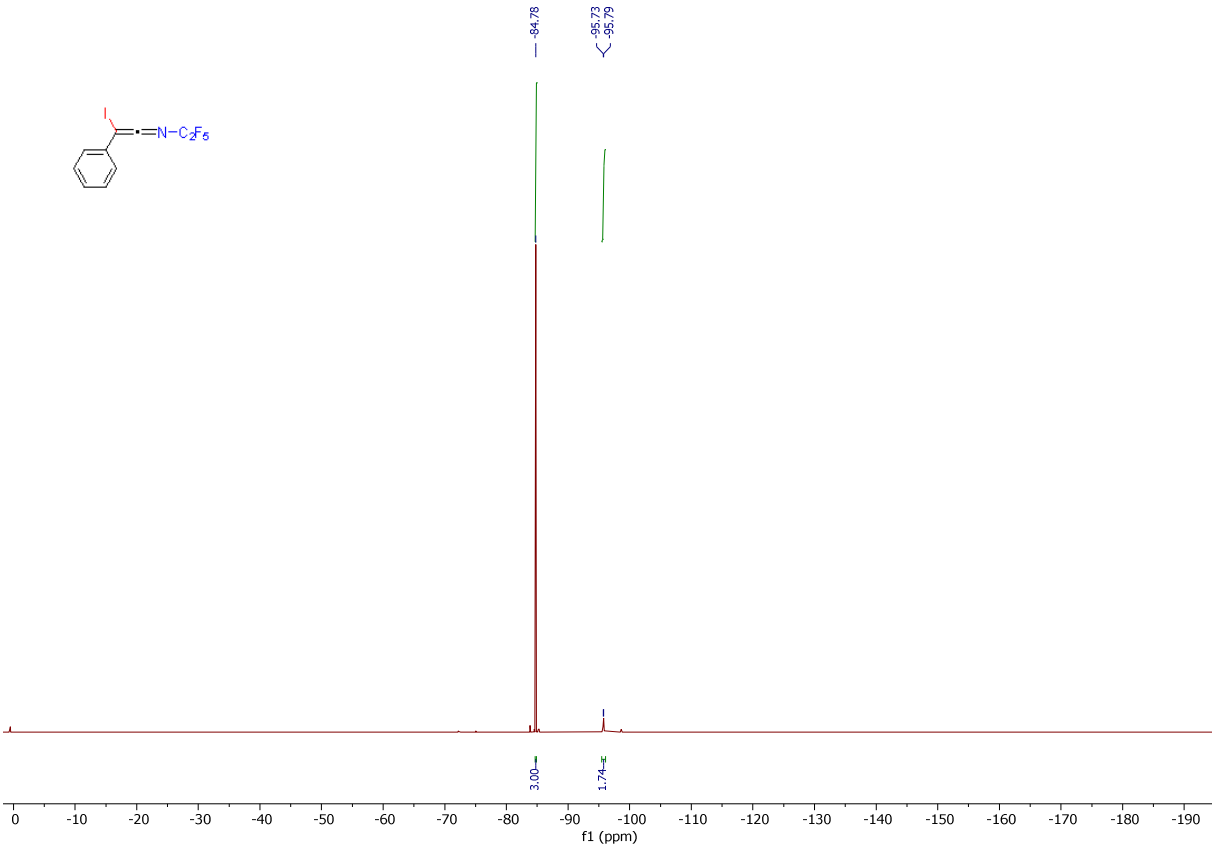
^{1}H NMR spectrum of **2ad** ($CDCl_3$, 400 MHz)



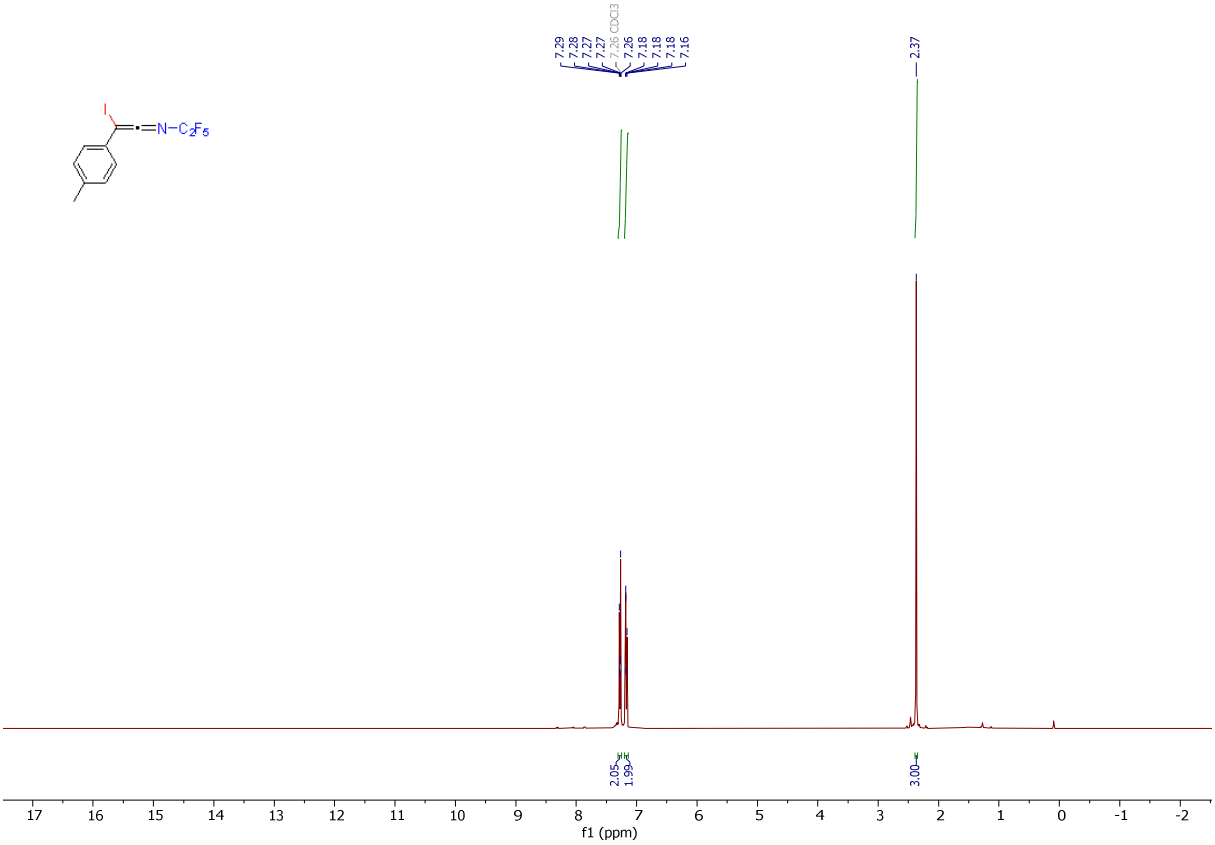
^{13}C NMR spectrum of **2ad** ($CDCl_3$, 101 MHz)



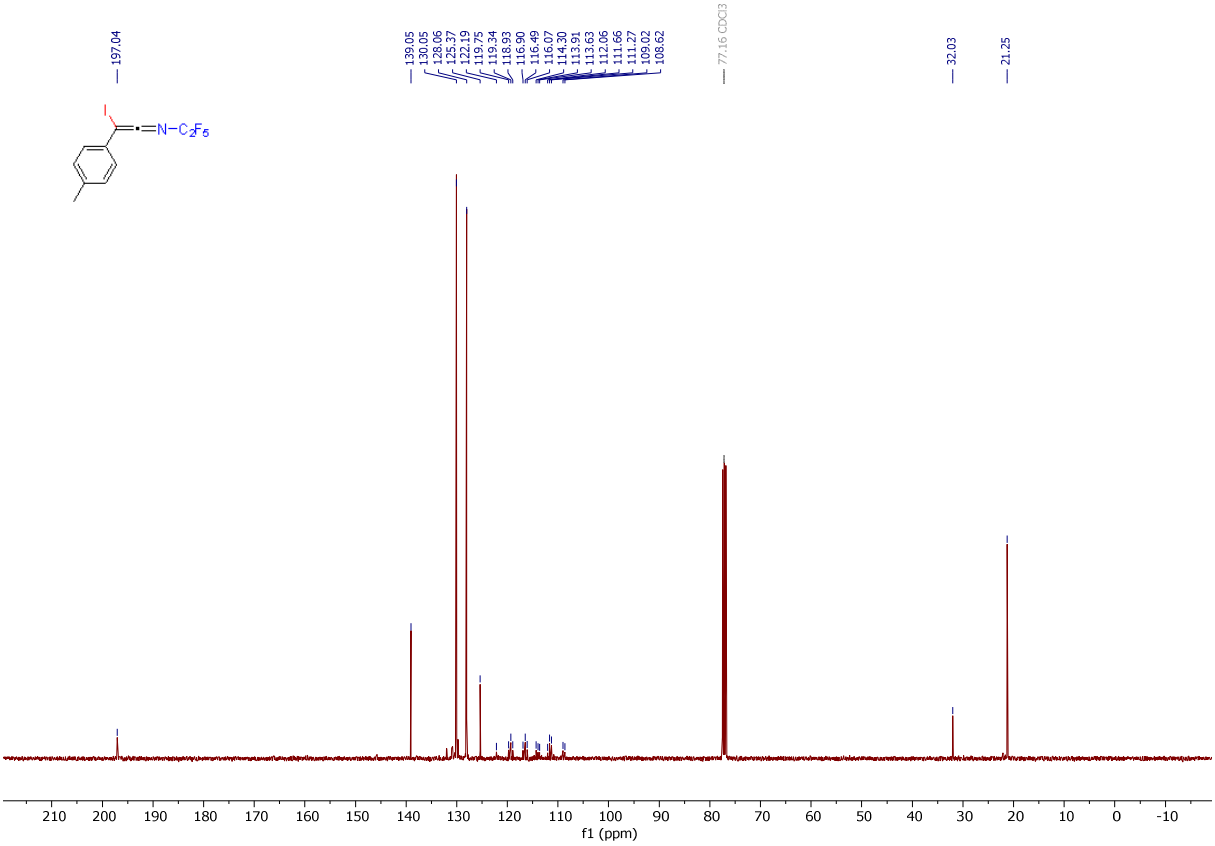
^{19}F NMR spectrum of **2ad** ($CDCl_3$, 376 MHz)



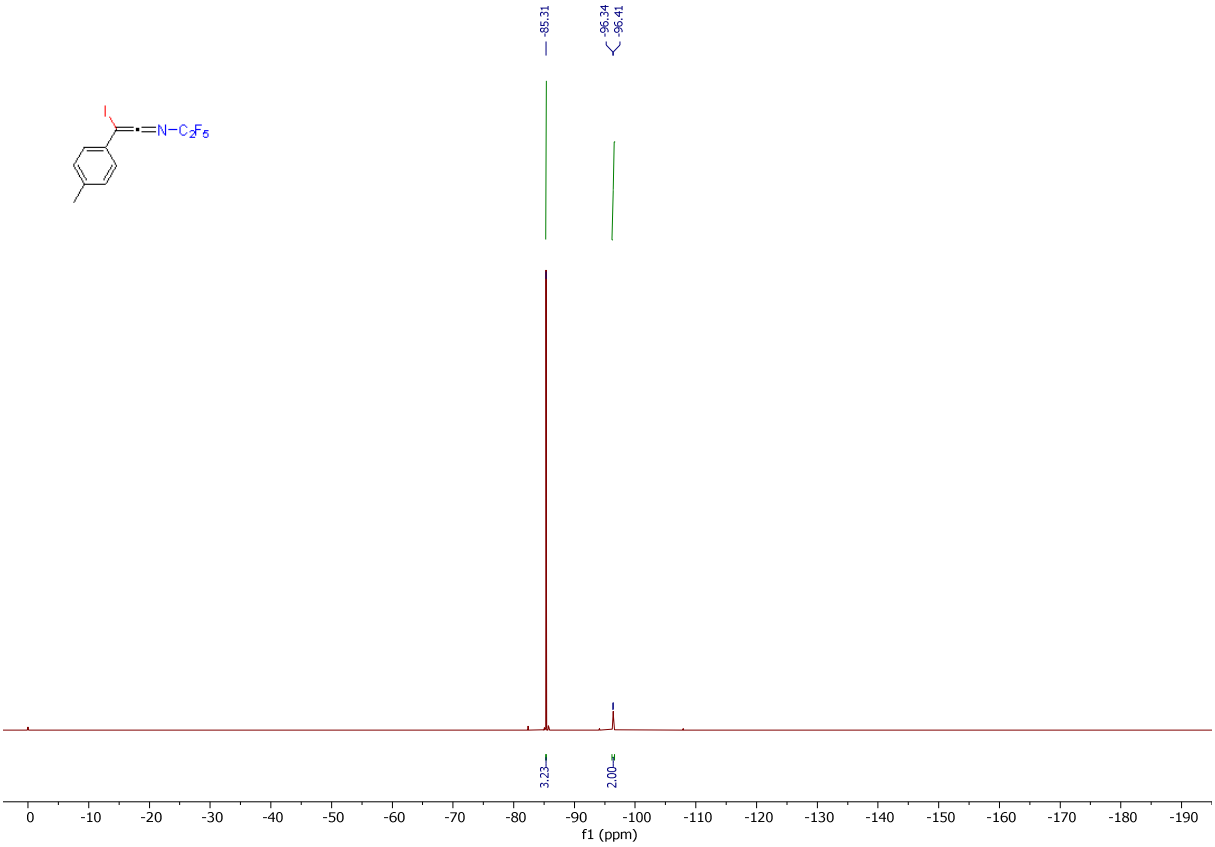
^{1}H NMR spectrum of **2ae** ($CDCl_3$, 400 MHz)



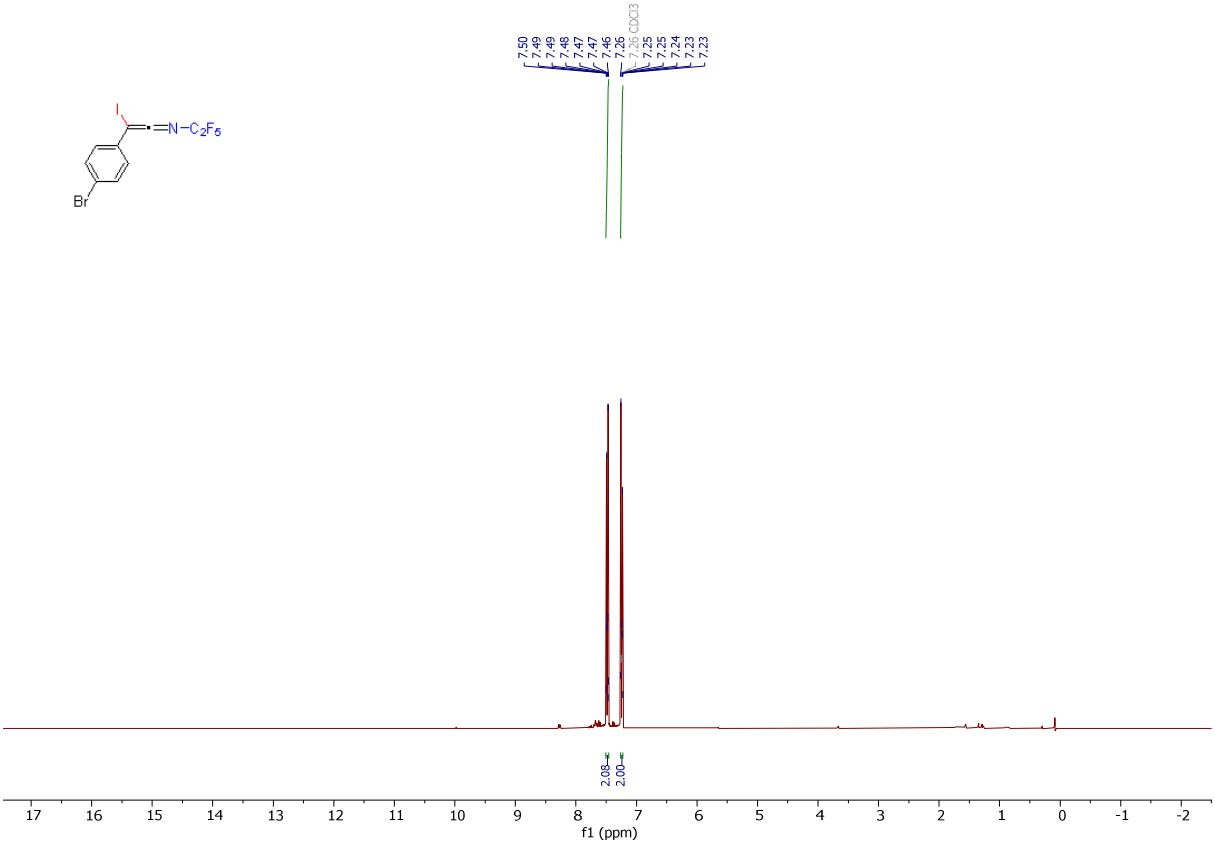
^{13}C NMR spectrum of **2ae** ($CDCl_3$, 101 MHz)



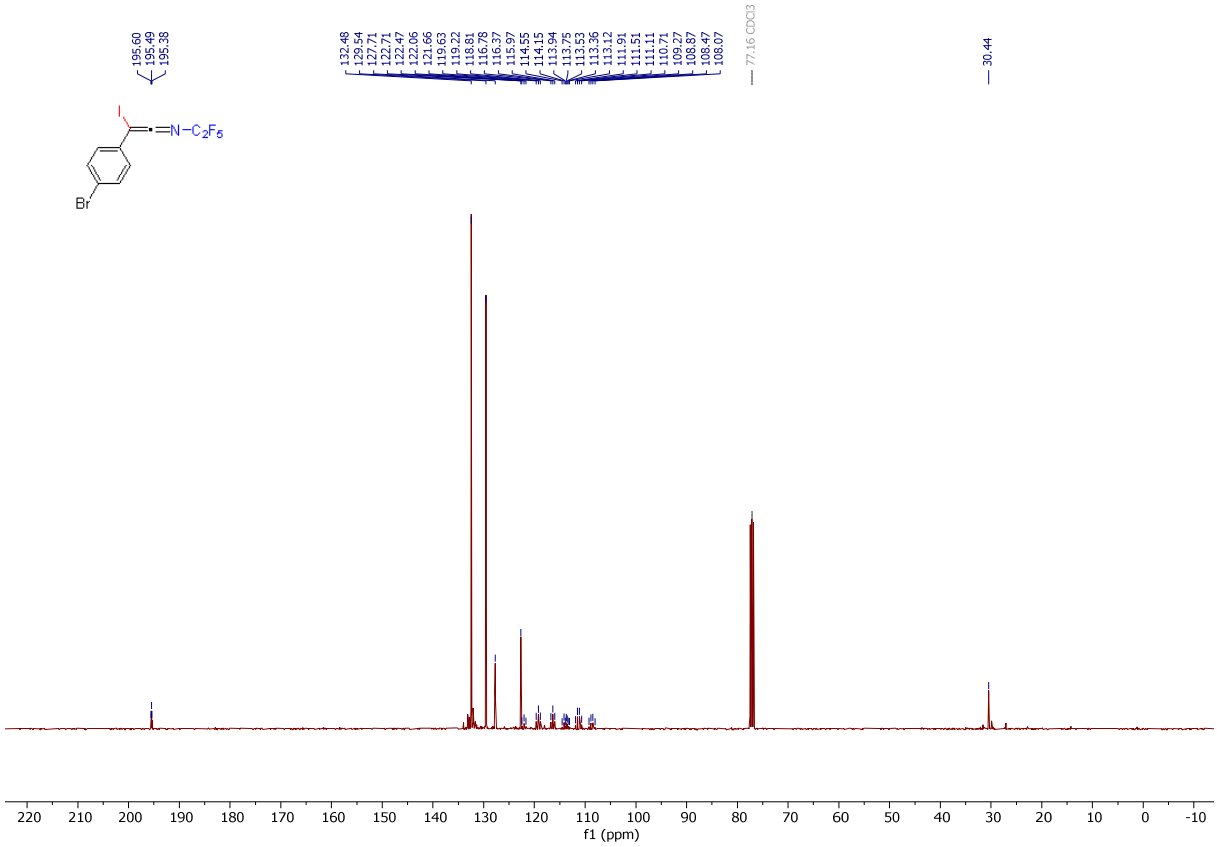
^{19}F NMR spectrum of **2ae** ($CDCl_3$, 376 MHz)



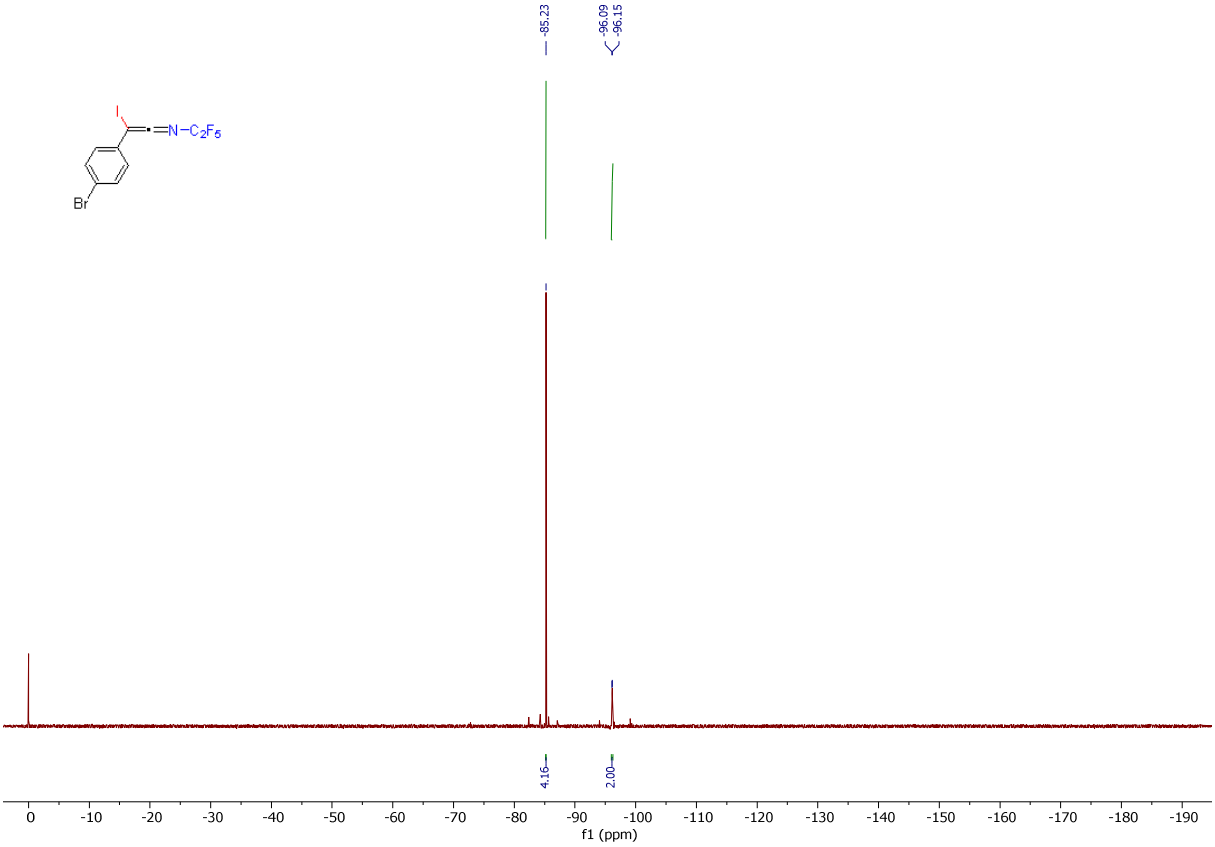
^{1}H NMR spectrum of **2af** ($CDCl_3$, 400 MHz)



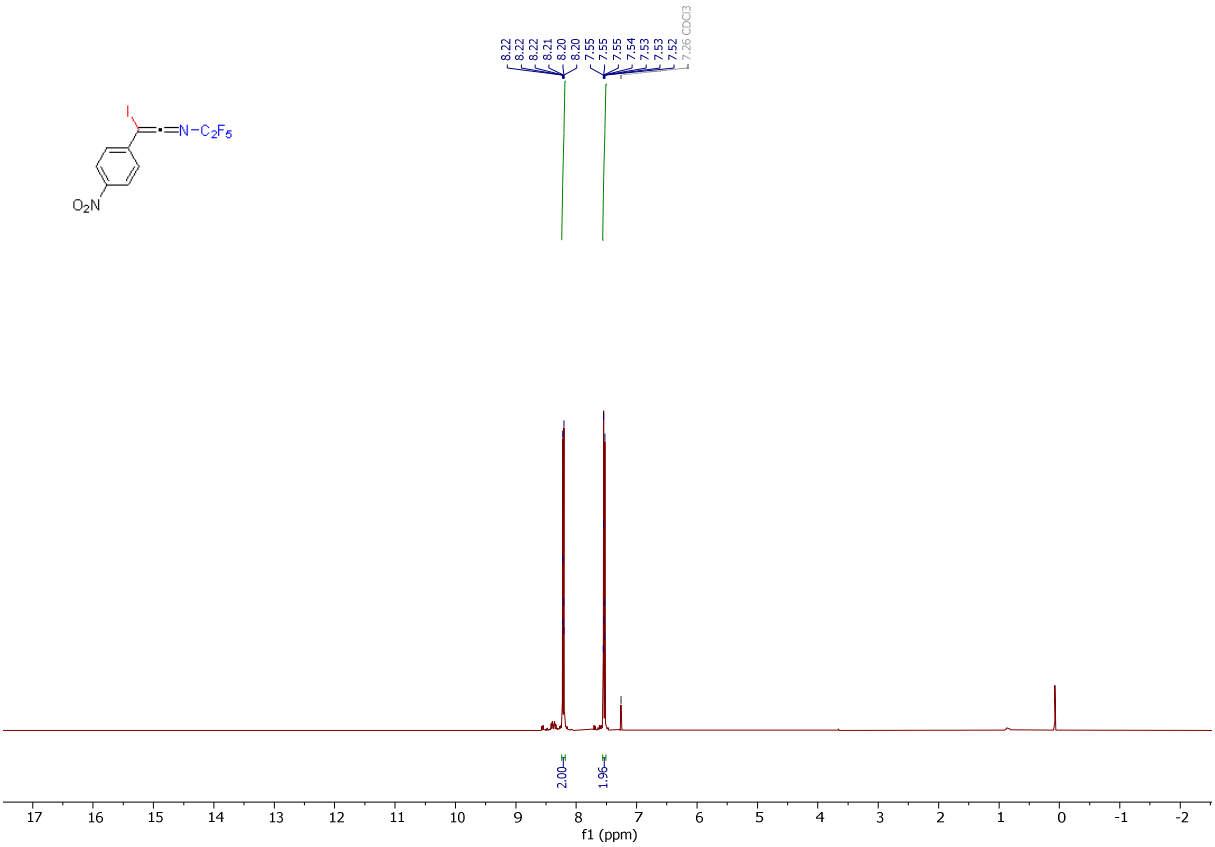
^{13}C NMR spectrum of **2af** ($CDCl_3$, 101 MHz)



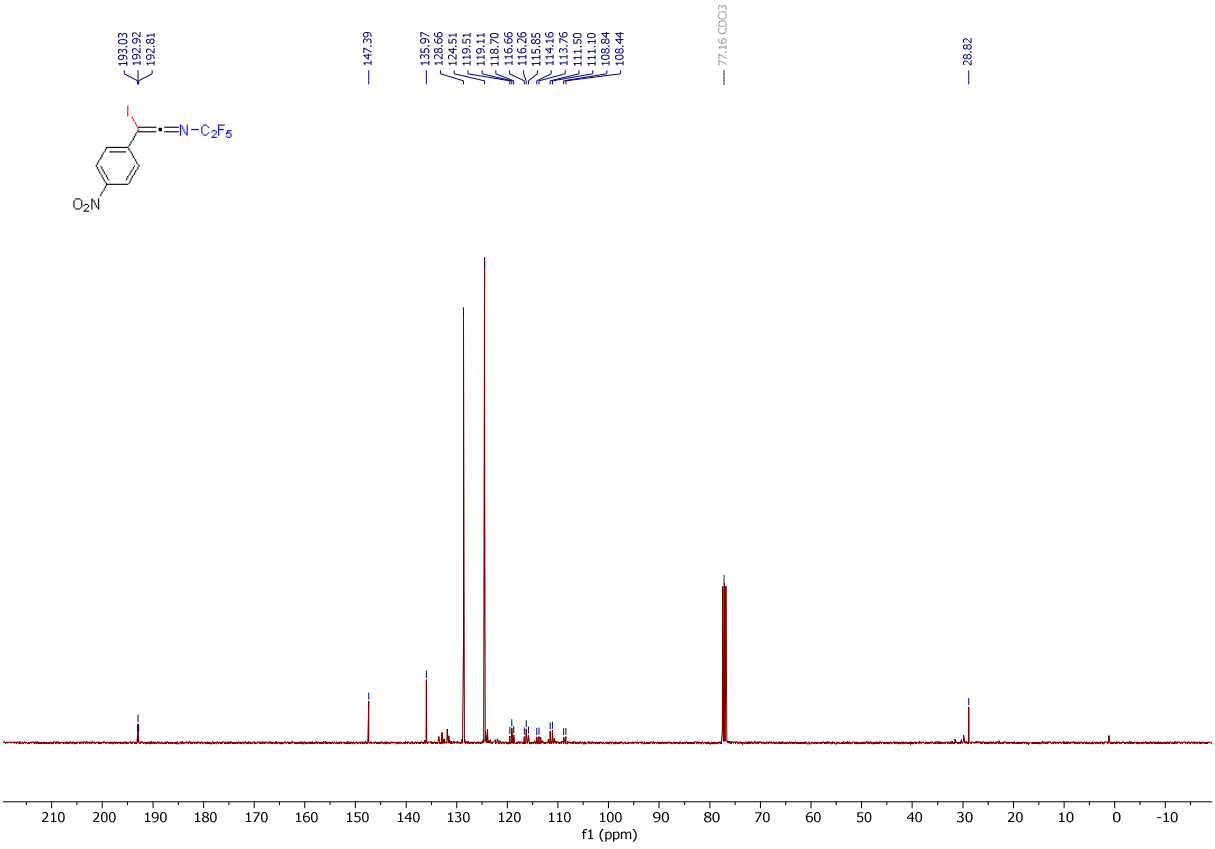
^{19}F NMR spectrum of **2af** ($CDCl_3$, 376 MHz)



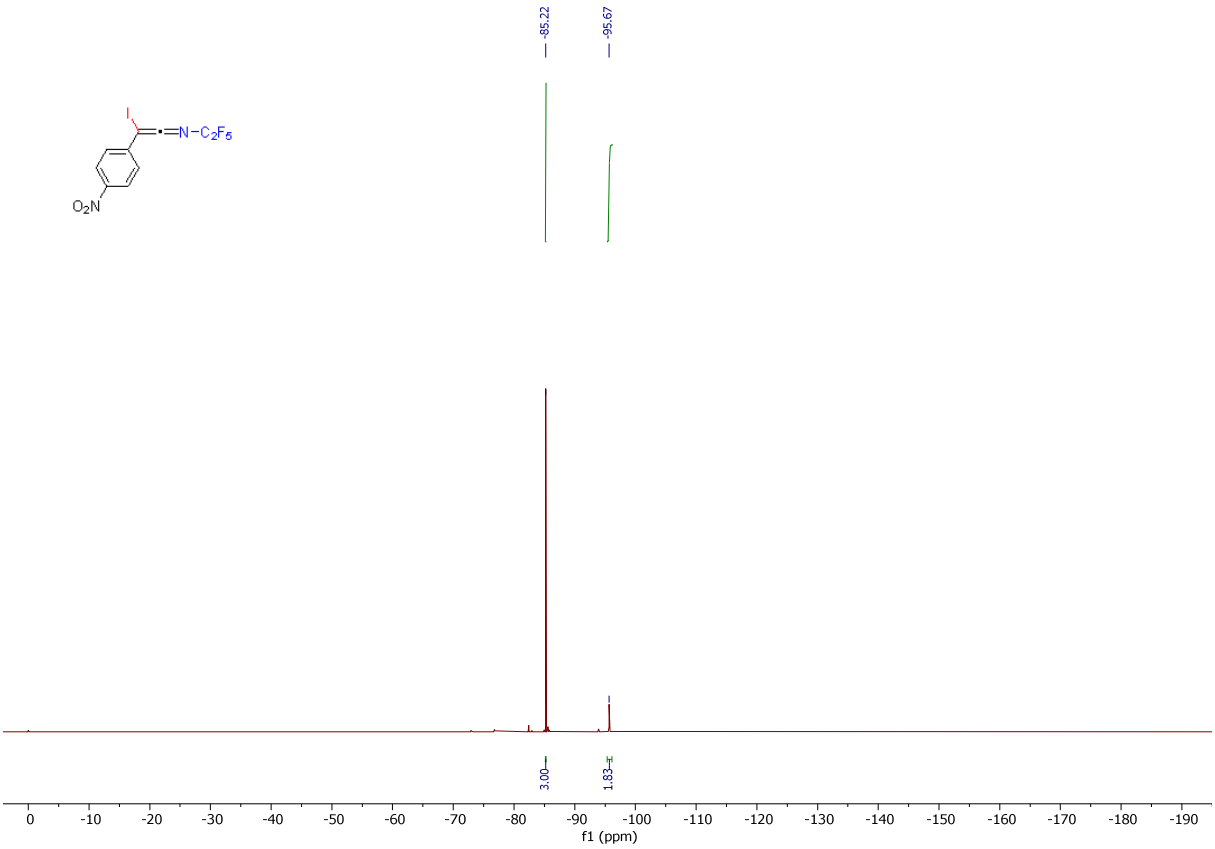
^{1}H NMR spectrum of **2ag** ($CDCl_3$, 400 MHz)



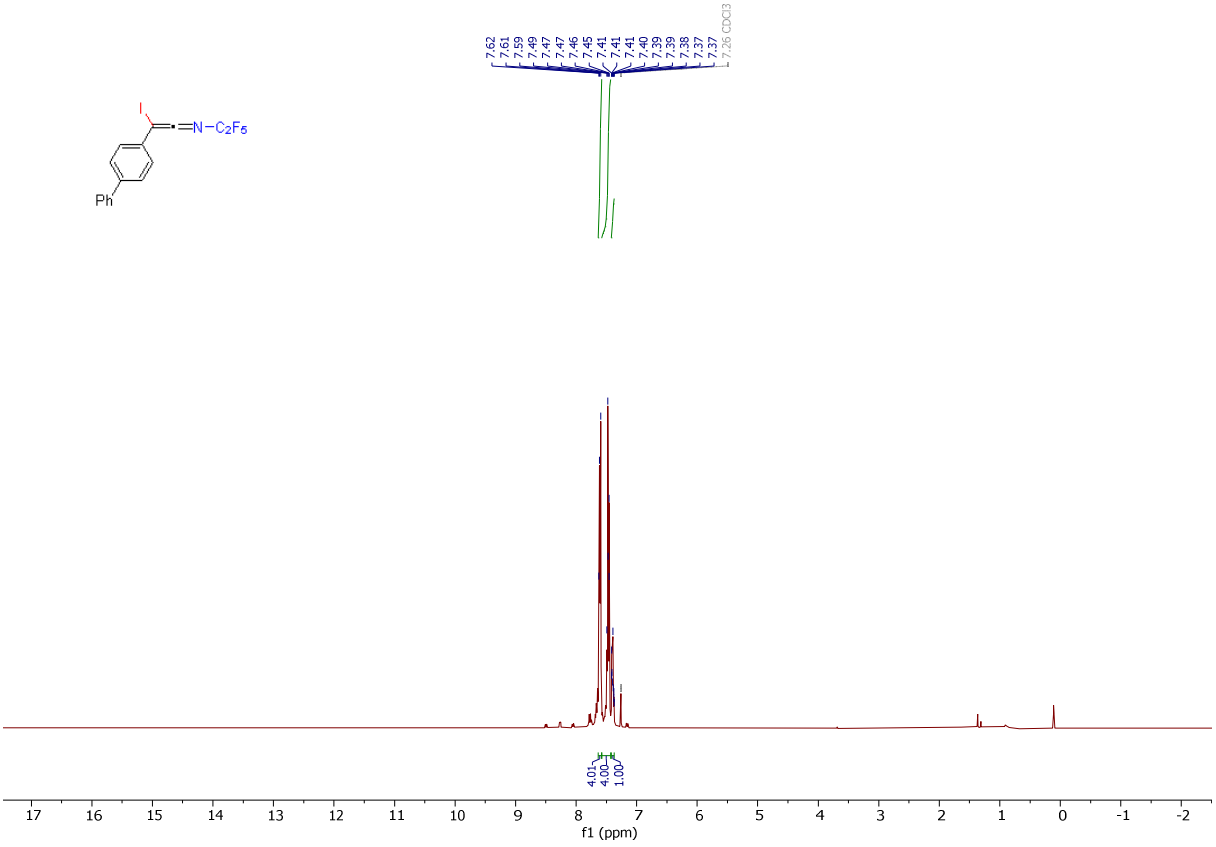
^{13}C NMR spectrum of **2ag** ($CDCl_3$, 101 MHz)



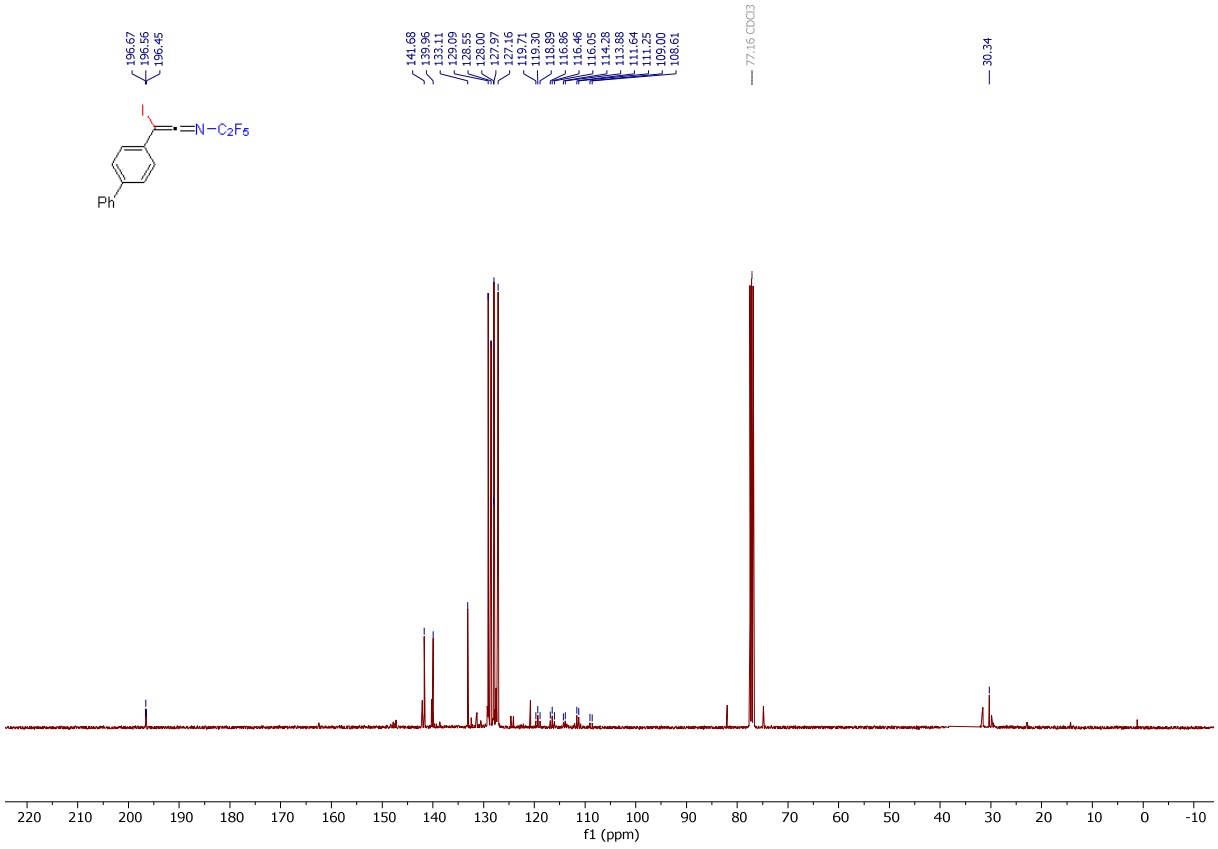
^{19}F NMR spectrum of **2ag** ($CDCl_3$, 376 MHz)



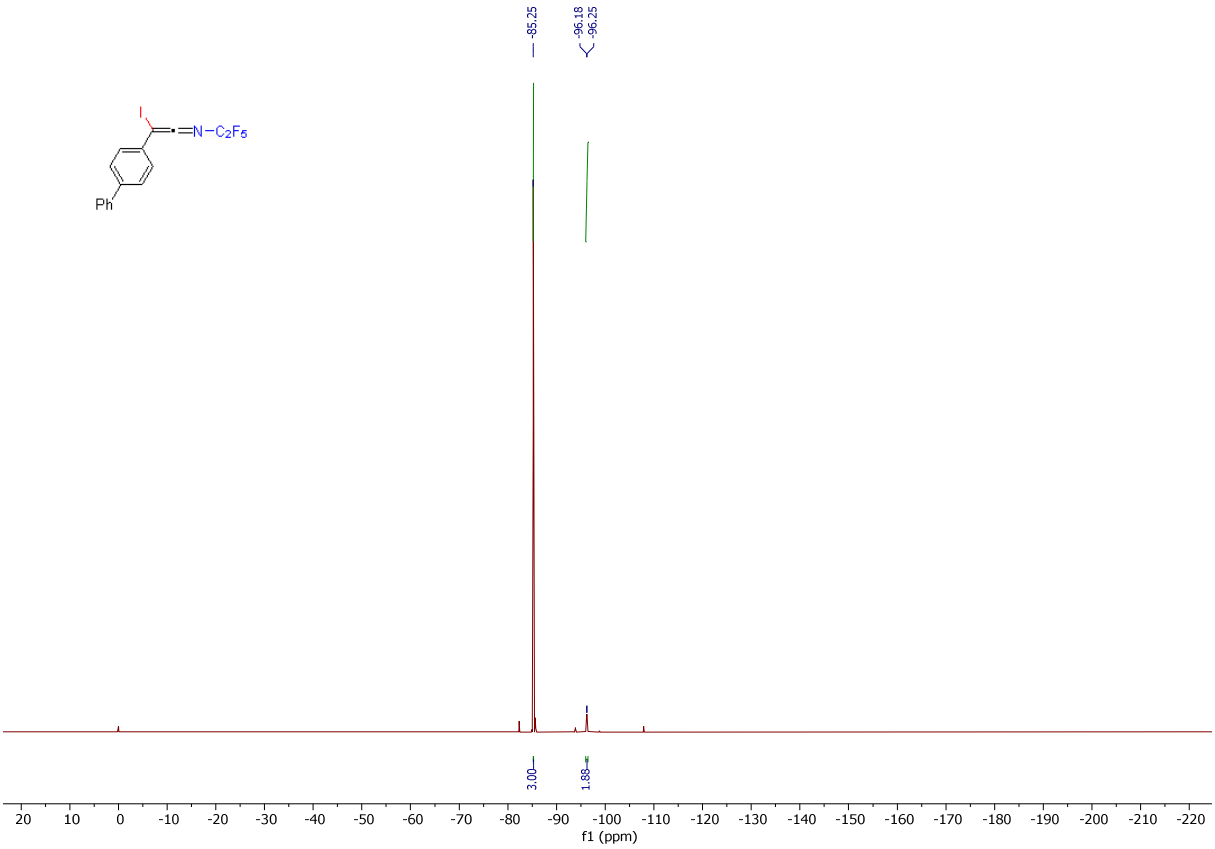
^{1}H NMR spectrum of **2ah** ($CDCl_3$, 400 MHz)



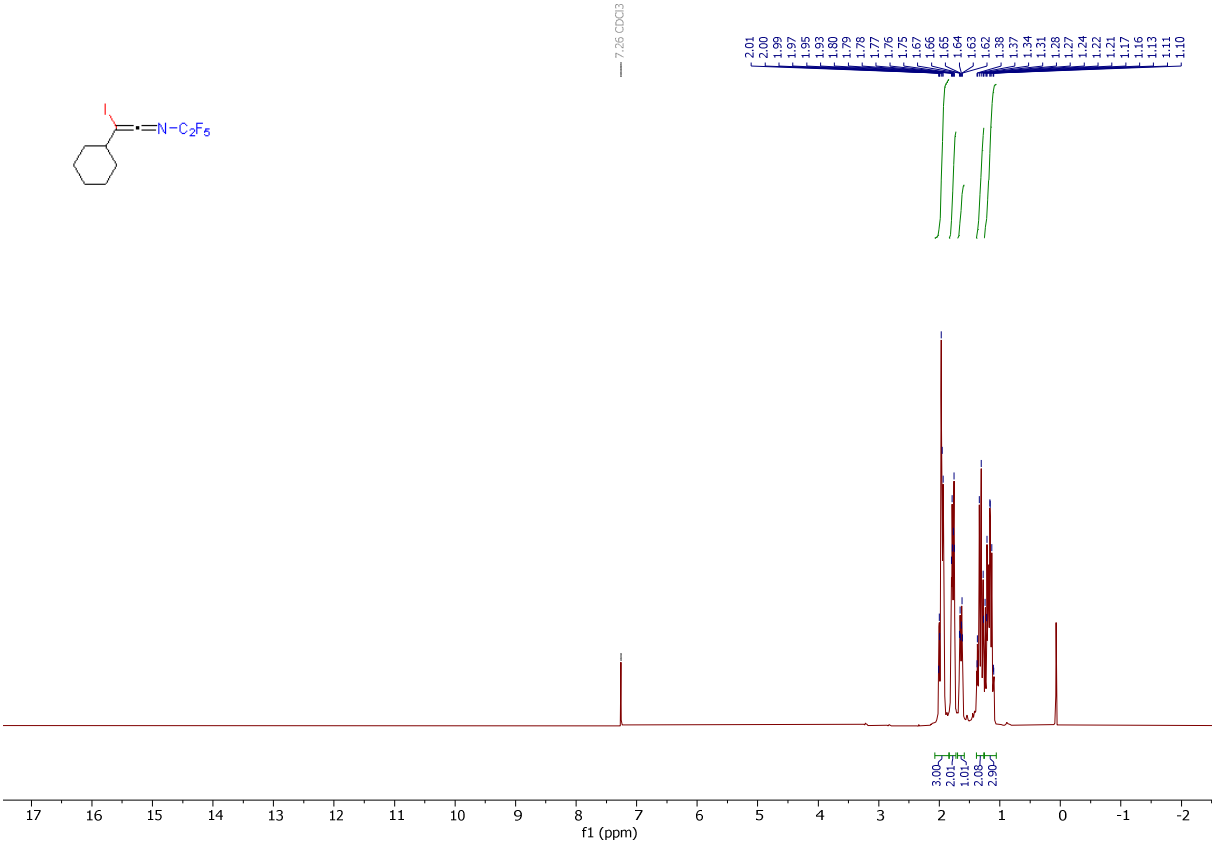
^{13}C NMR spectrum of **2ah** ($CDCl_3$, 101 MHz)



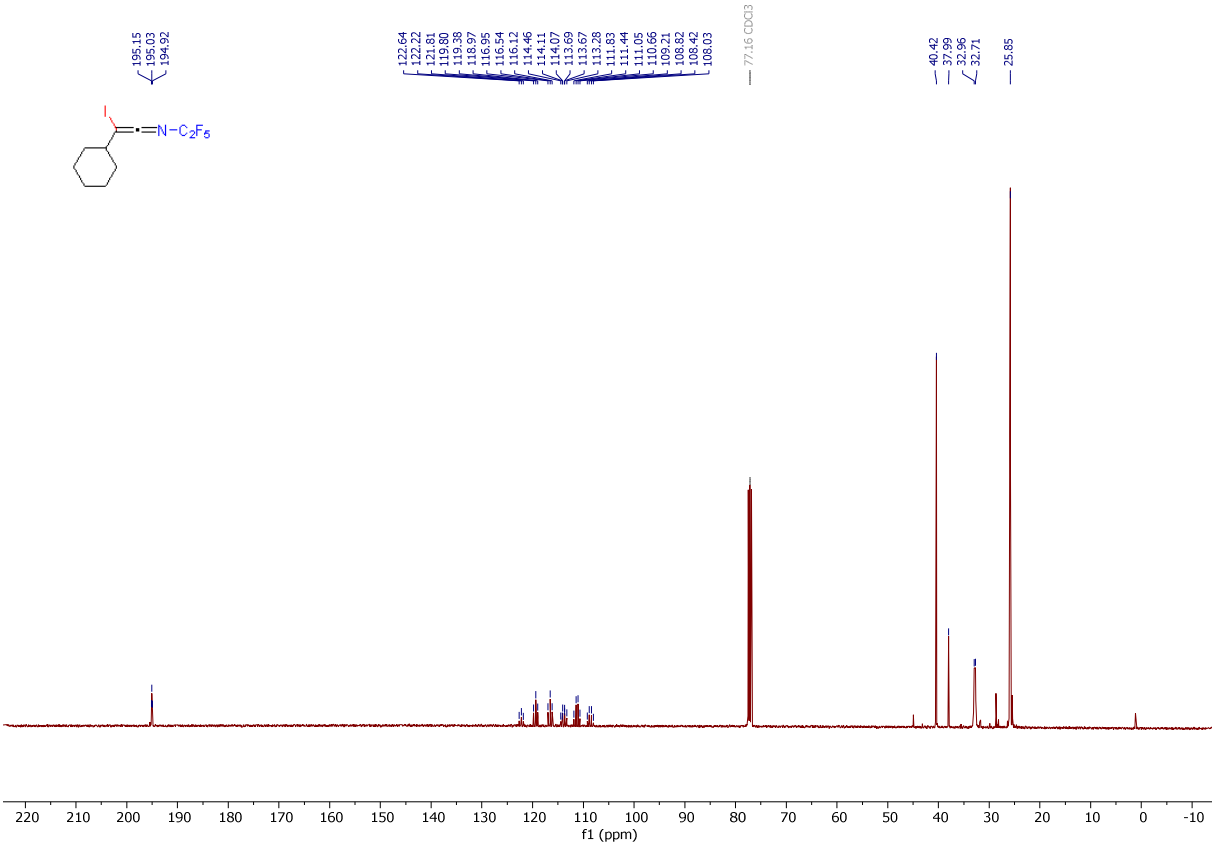
^{19}F NMR spectrum of **2ah** ($CDCl_3$, 376 MHz)



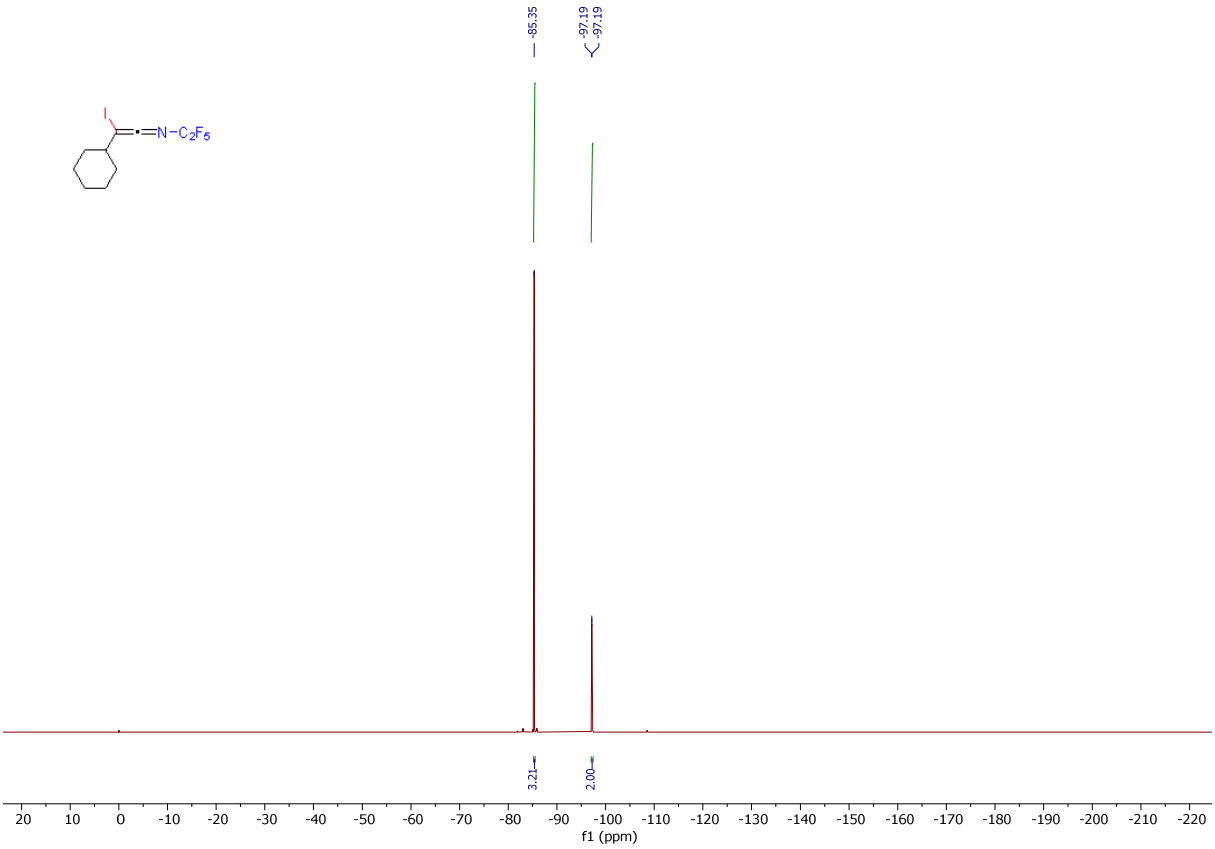
^{1}H NMR spectrum of **2ai** ($CDCl_3$, 400 MHz)



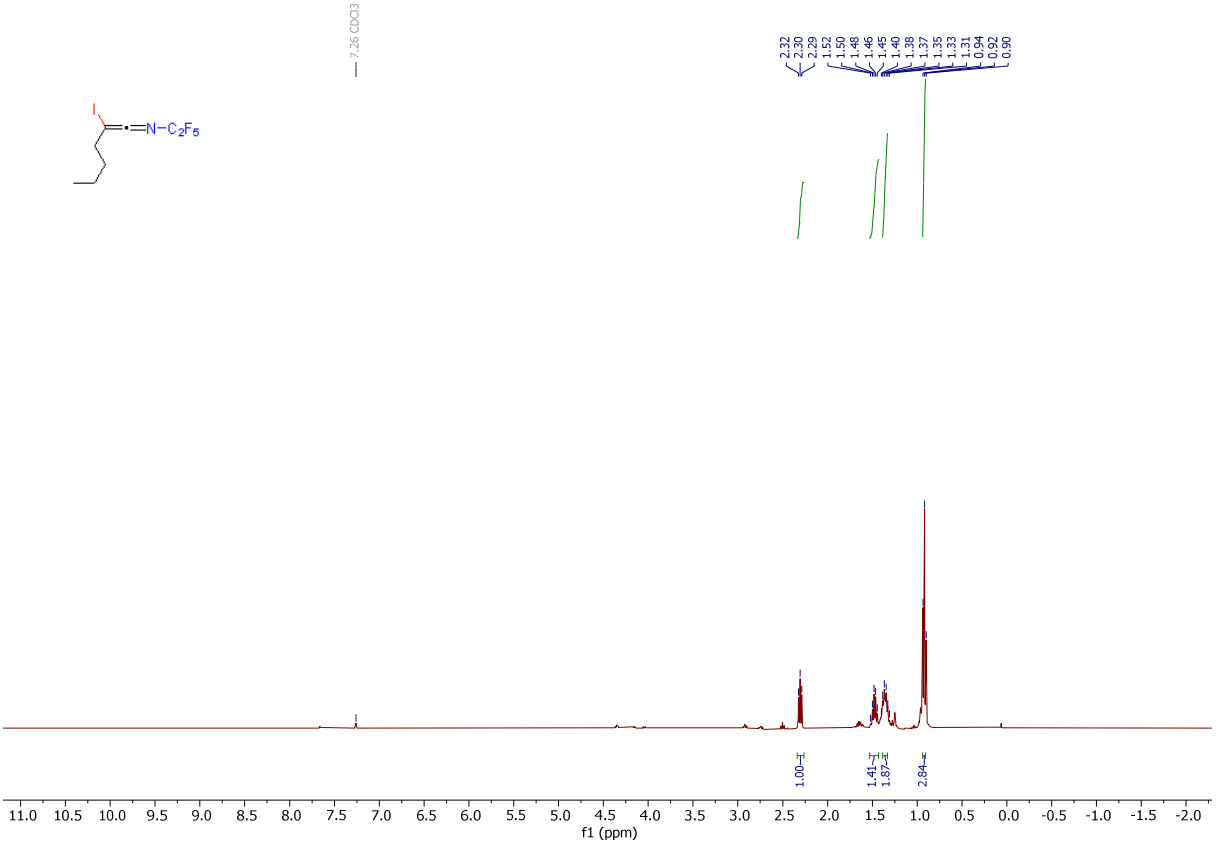
^{13}C NMR spectrum of **2ai** ($CDCl_3$, 101 MHz)



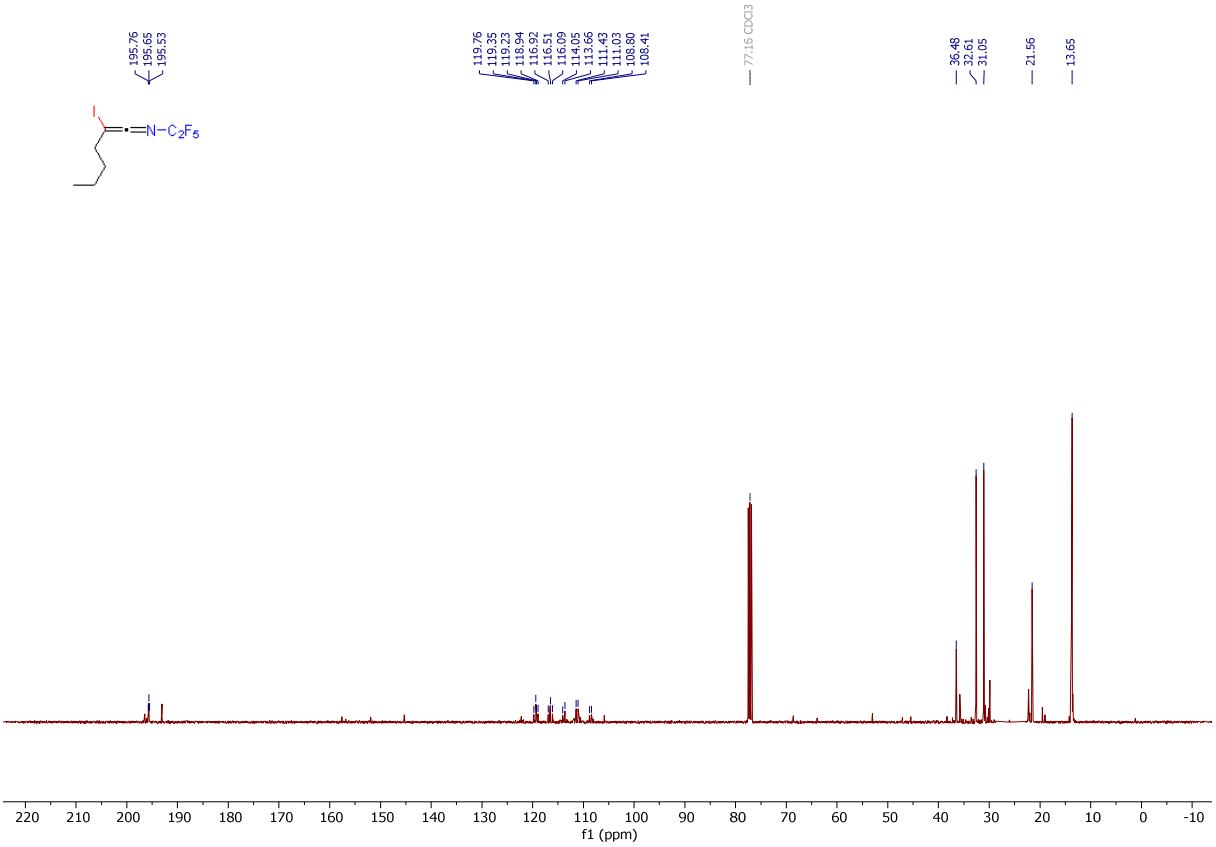
^{19}F NMR spectrum of **2ai** ($CDCl_3$, 376 MHz)



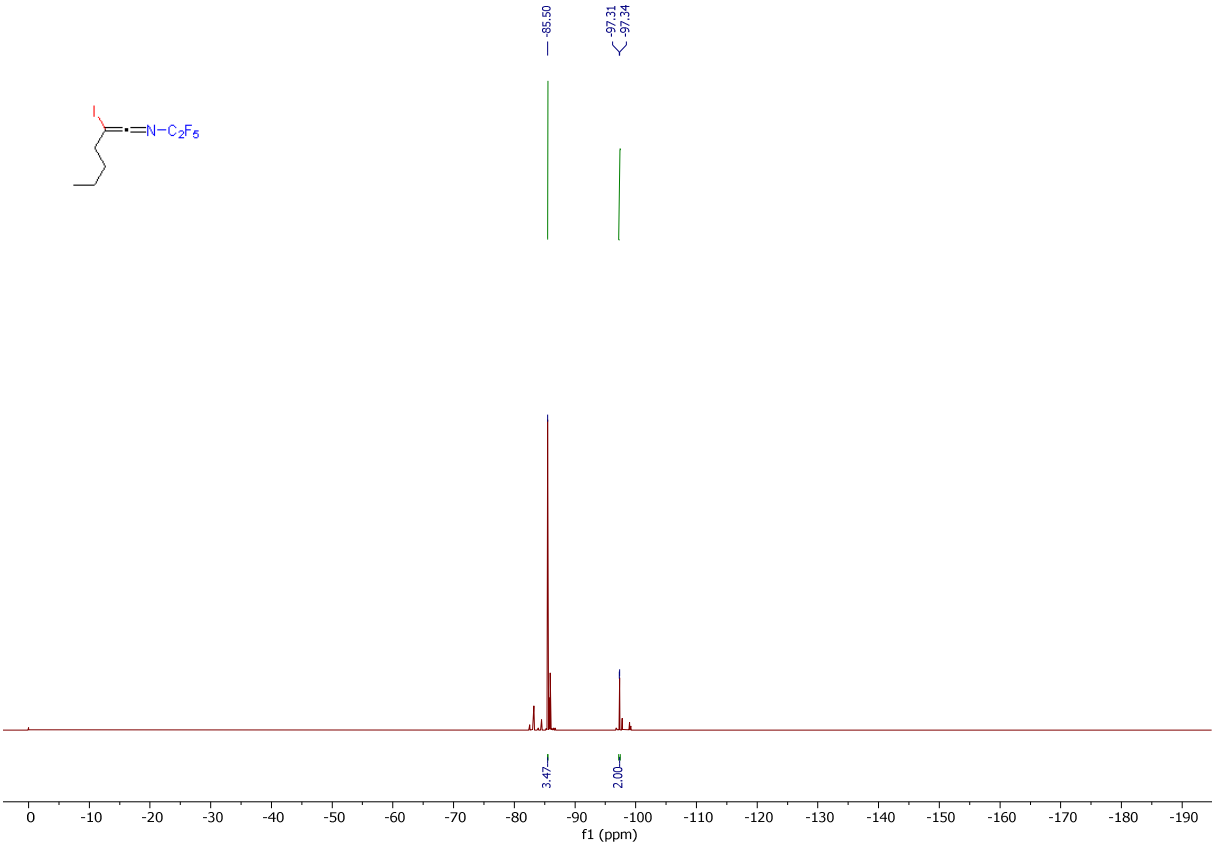
^{1}H NMR spectrum of **2aj** ($CDCl_3$, 400 MHz)



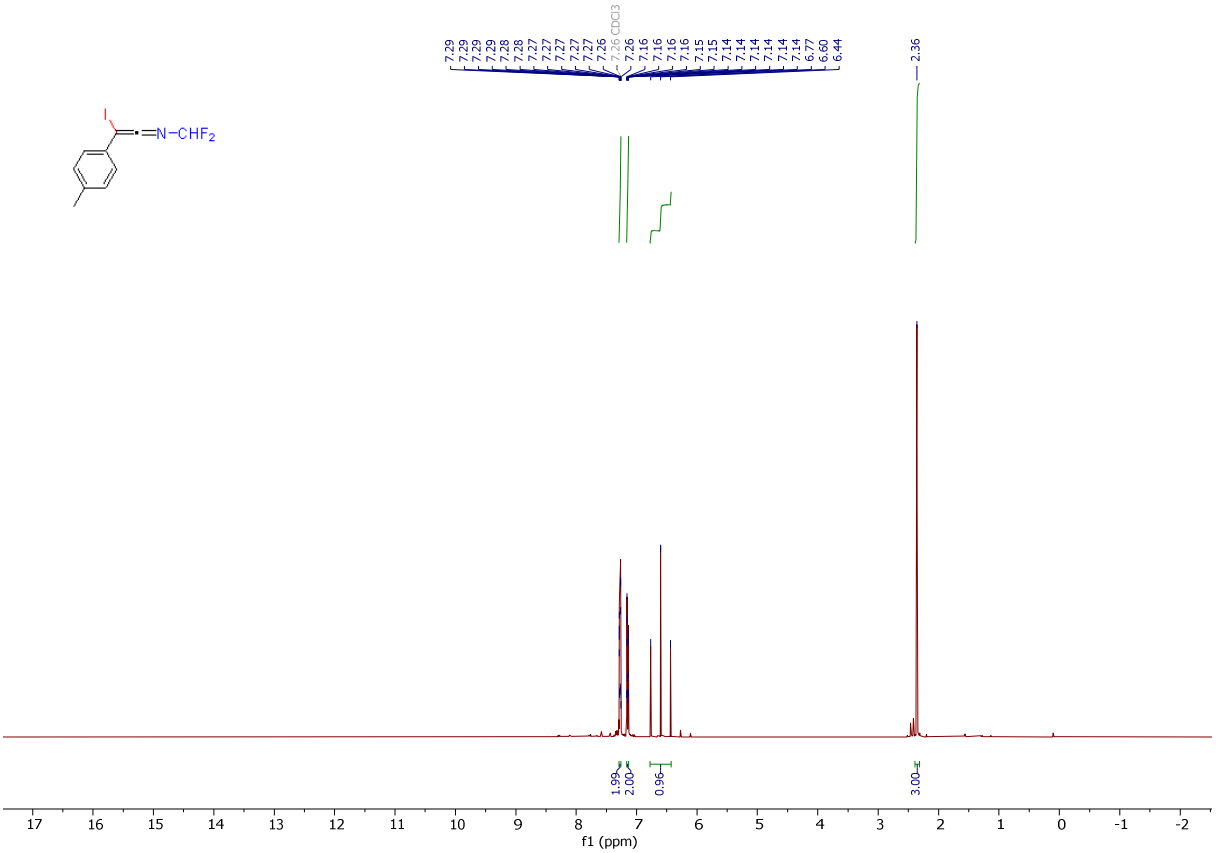
^{13}C NMR spectrum of **2aj** ($CDCl_3$, 101 MHz)



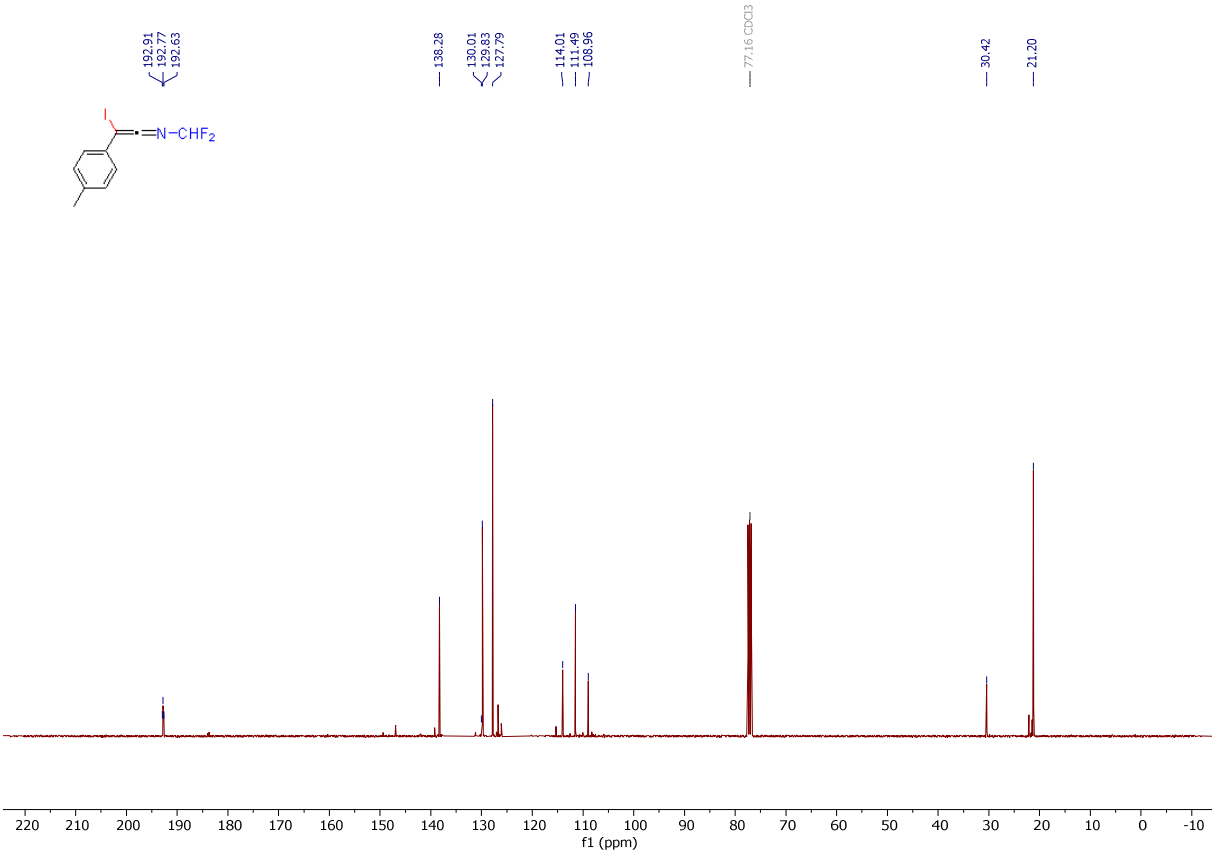
^{19}F NMR spectrum of **2aj** ($CDCl_3$, 376 MHz)



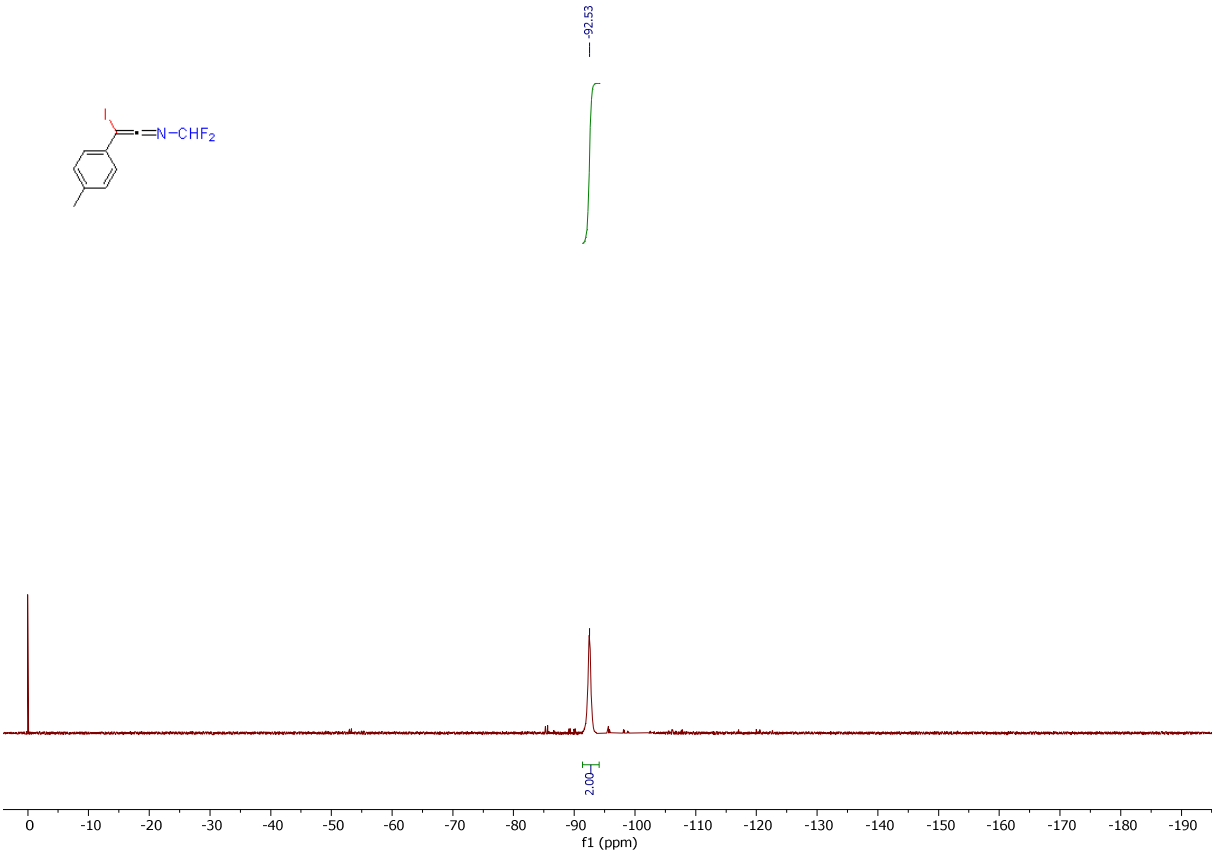
NMR spectrum of **2ak** ($CDCl_3$, 400 MHz)



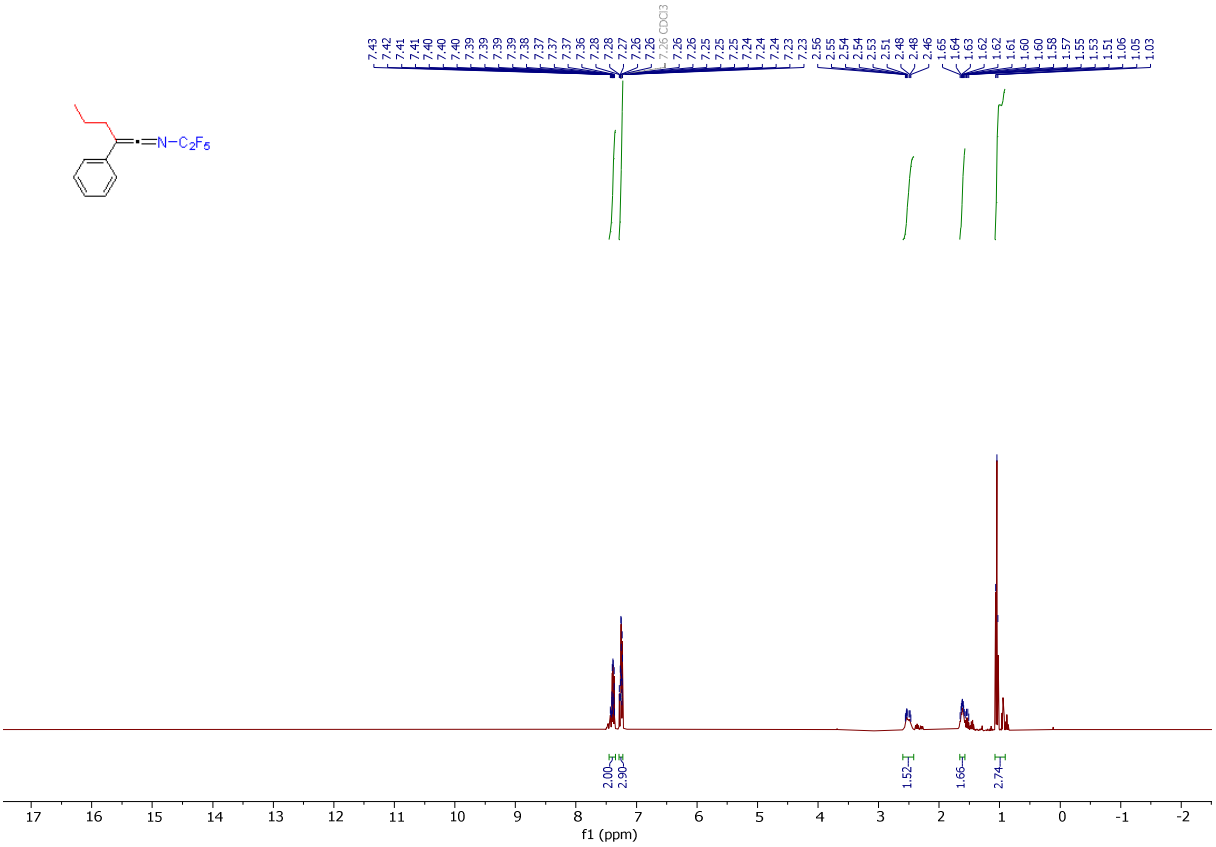
^{13}C NMR spectrum of **2ak** ($CDCl_3$, 101 MHz)



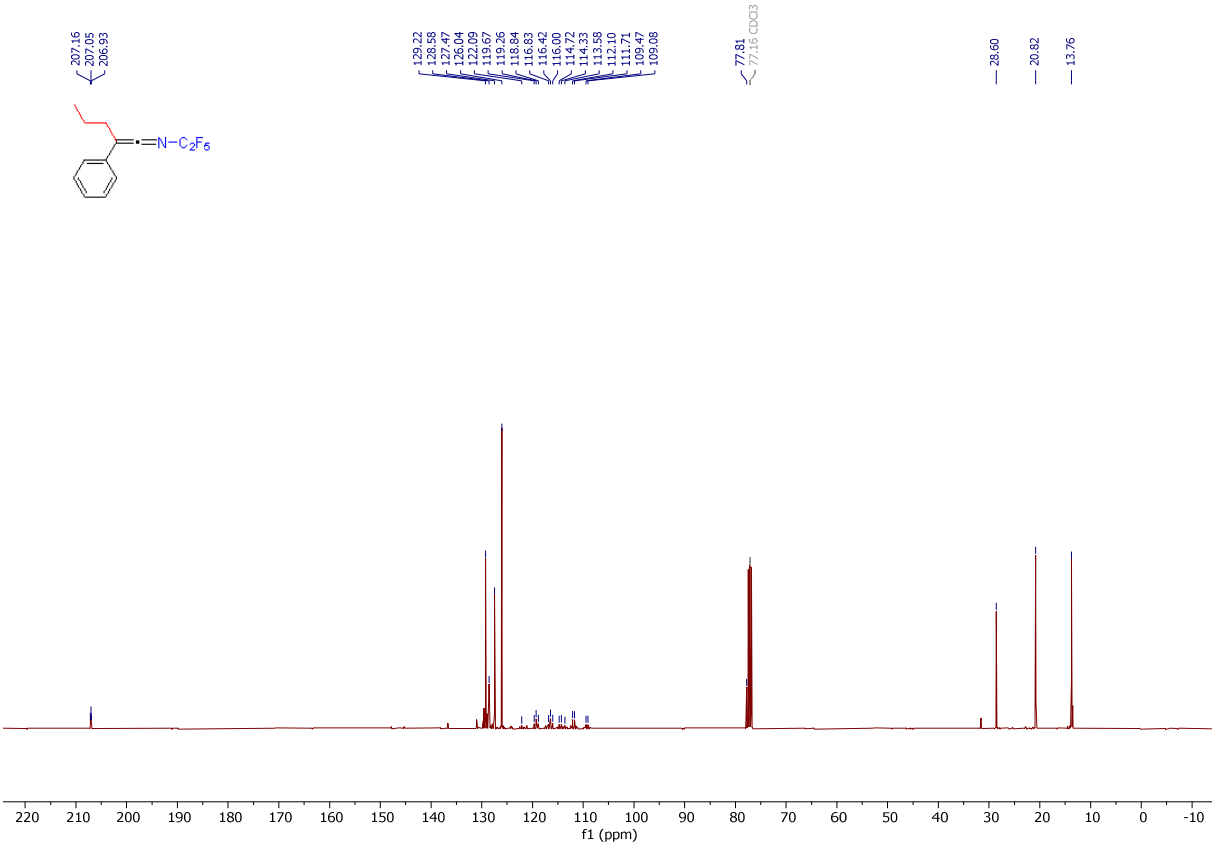
^{19}F NMR spectrum of **2ak** ($CDCl_3$, 376 MHz)



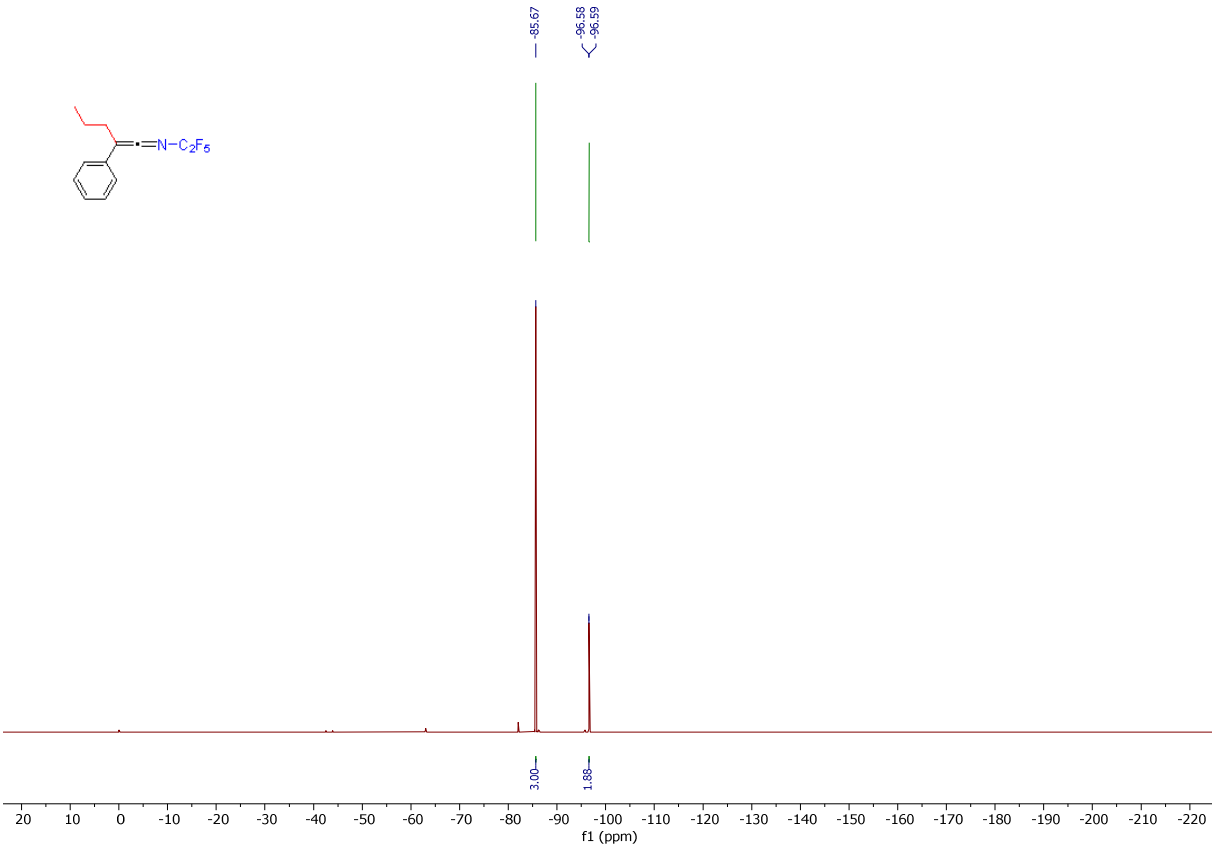
^{1}H NMR spectrum of **2al** ($CDCl_3$, 400 MHz)



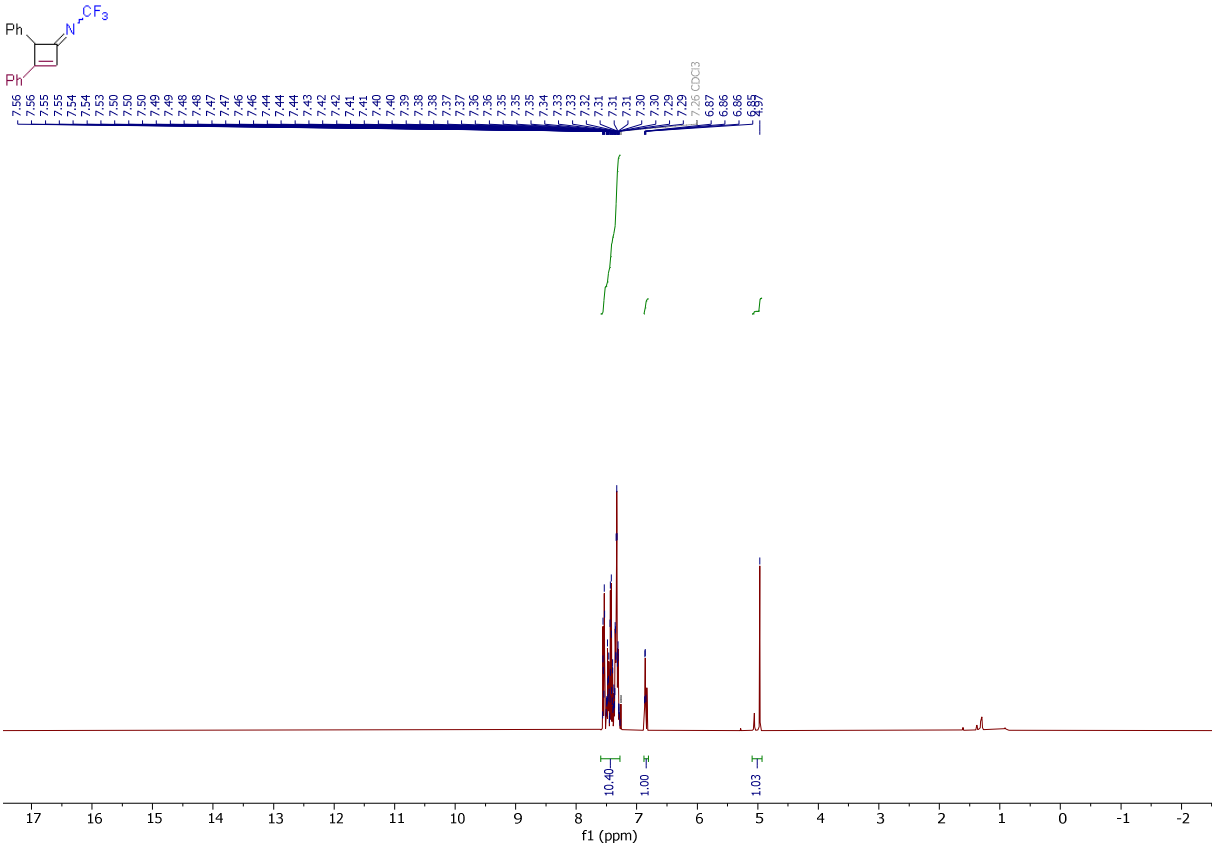
^{13}C NMR spectrum of **2al** ($CDCl_3$, 101 MHz)



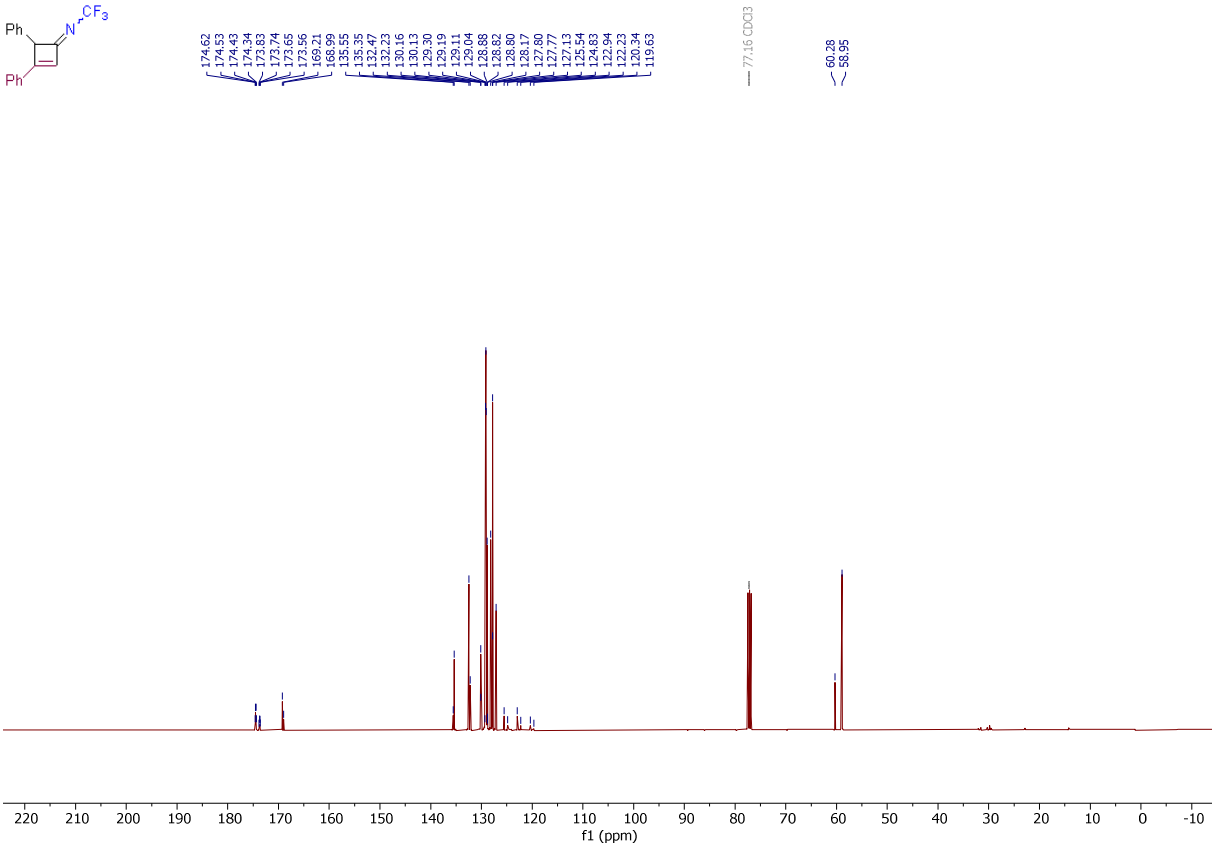
^{19}F NMR spectrum of **2al** ($CDCl_3$, 376 MHz)



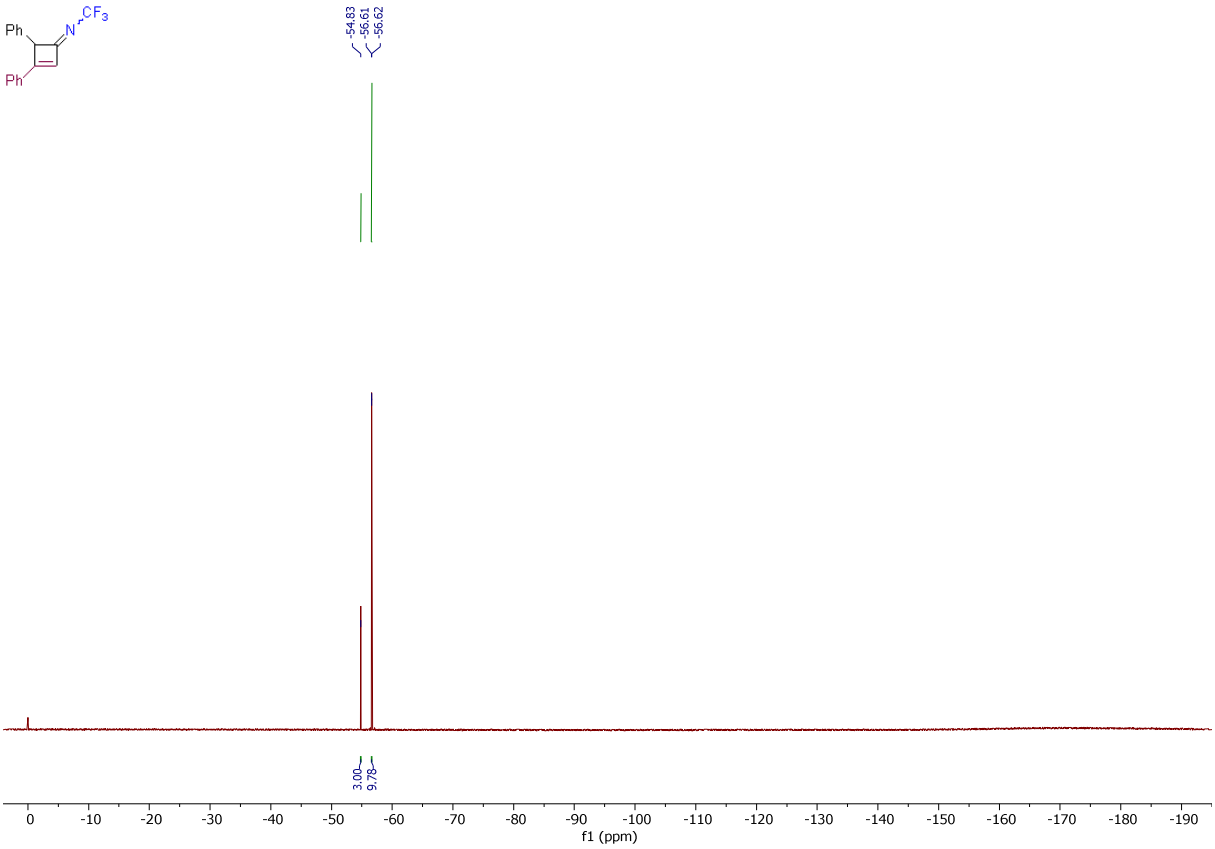
^{1}H NMR spectrum of **9a** ($CDCl_3$, 400 MHz)



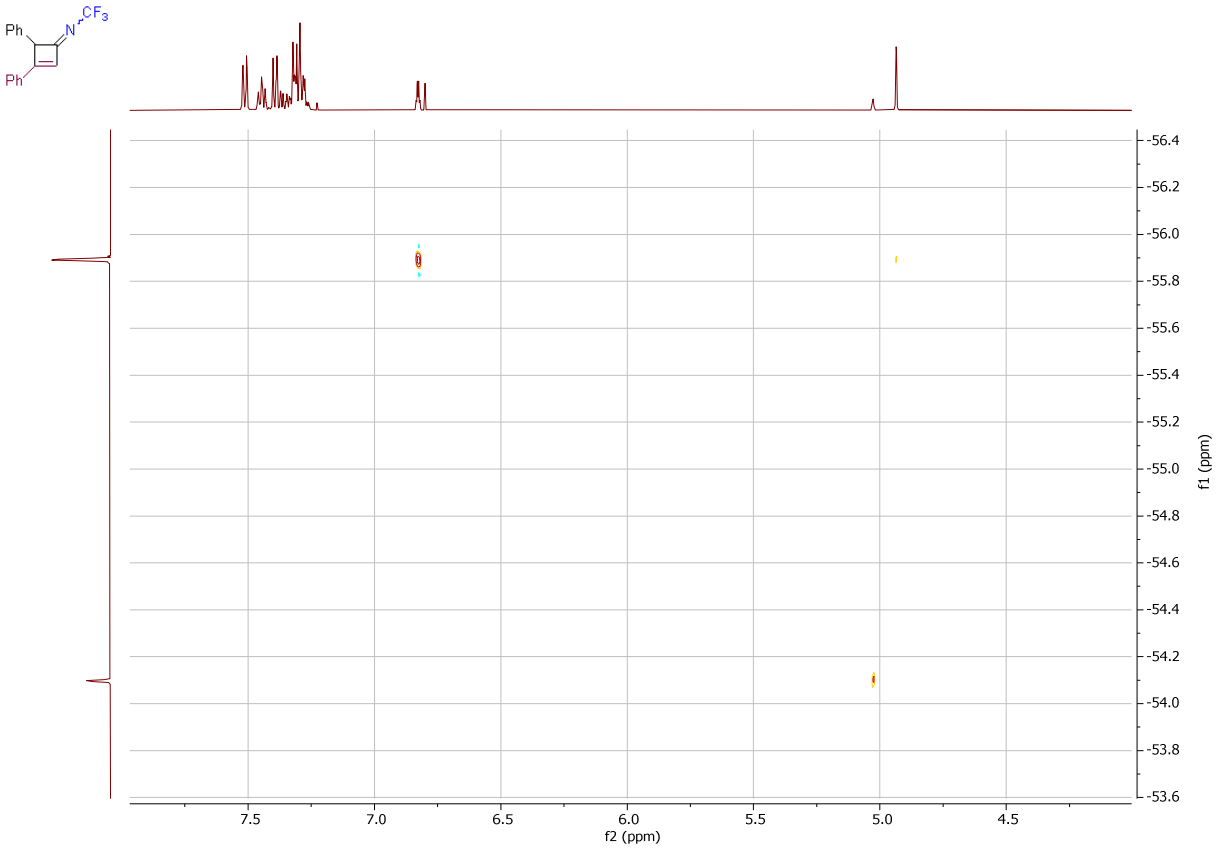
^{13}C NMR spectrum of **9a** ($CDCl_3$, 101 MHz)



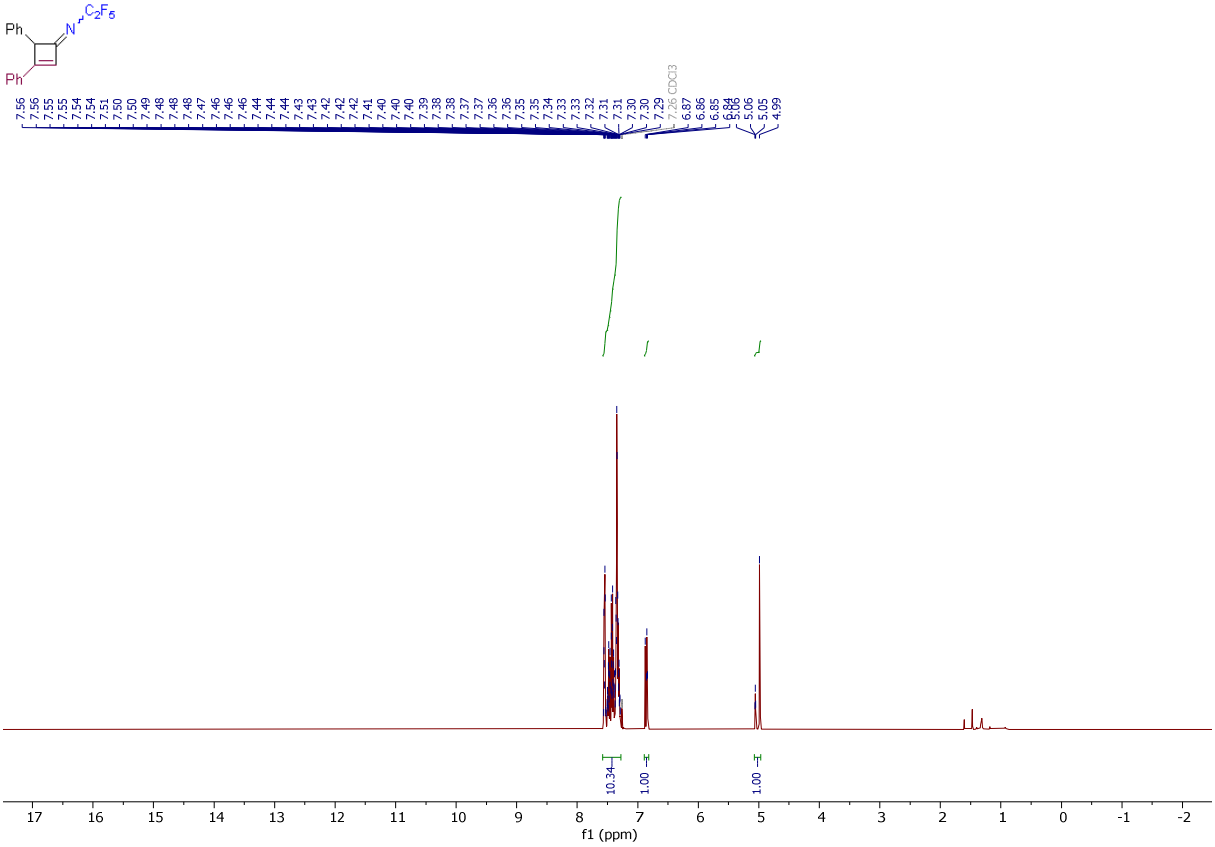
^{19}F NMR spectrum of **9a** ($CDCl_3$, 376 MHz)



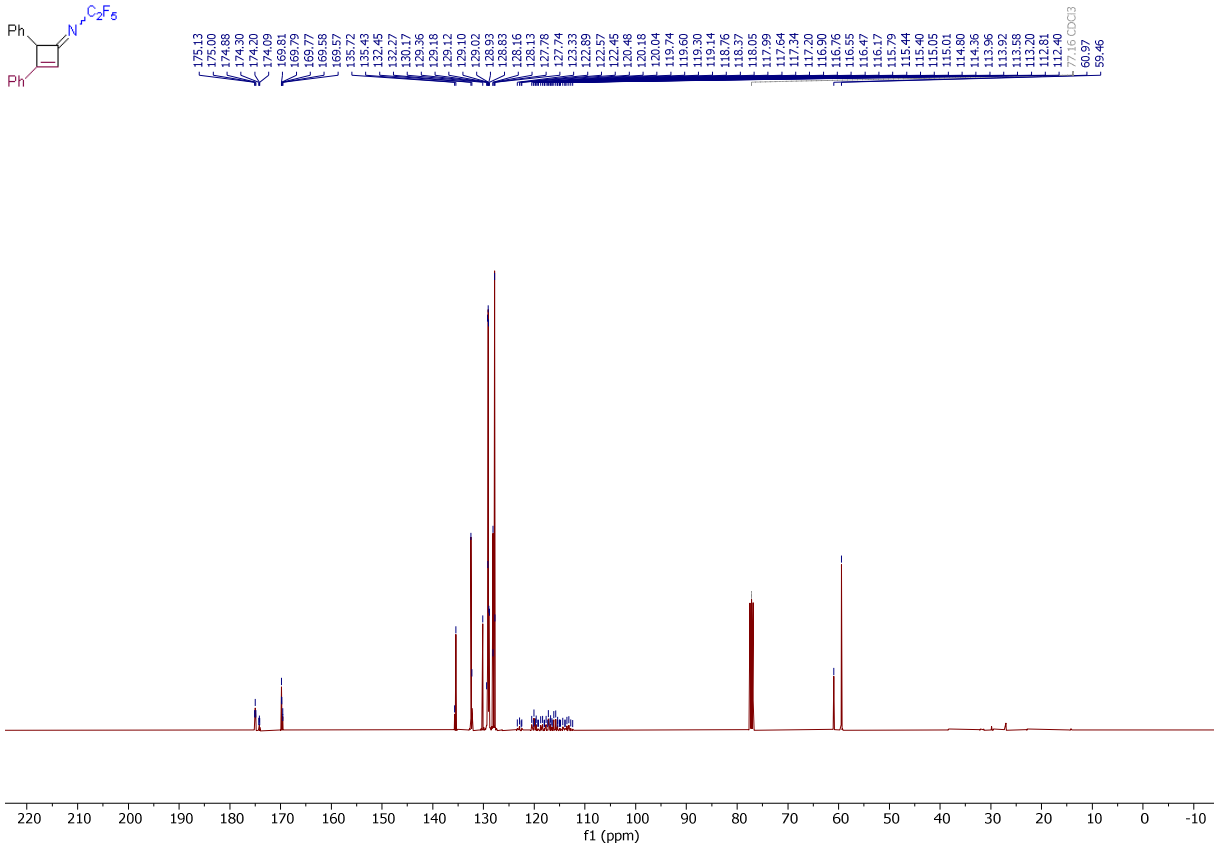
^{1}H-^{19}F HOESY NMR spectrum of **9a** ($CDCl_3$)



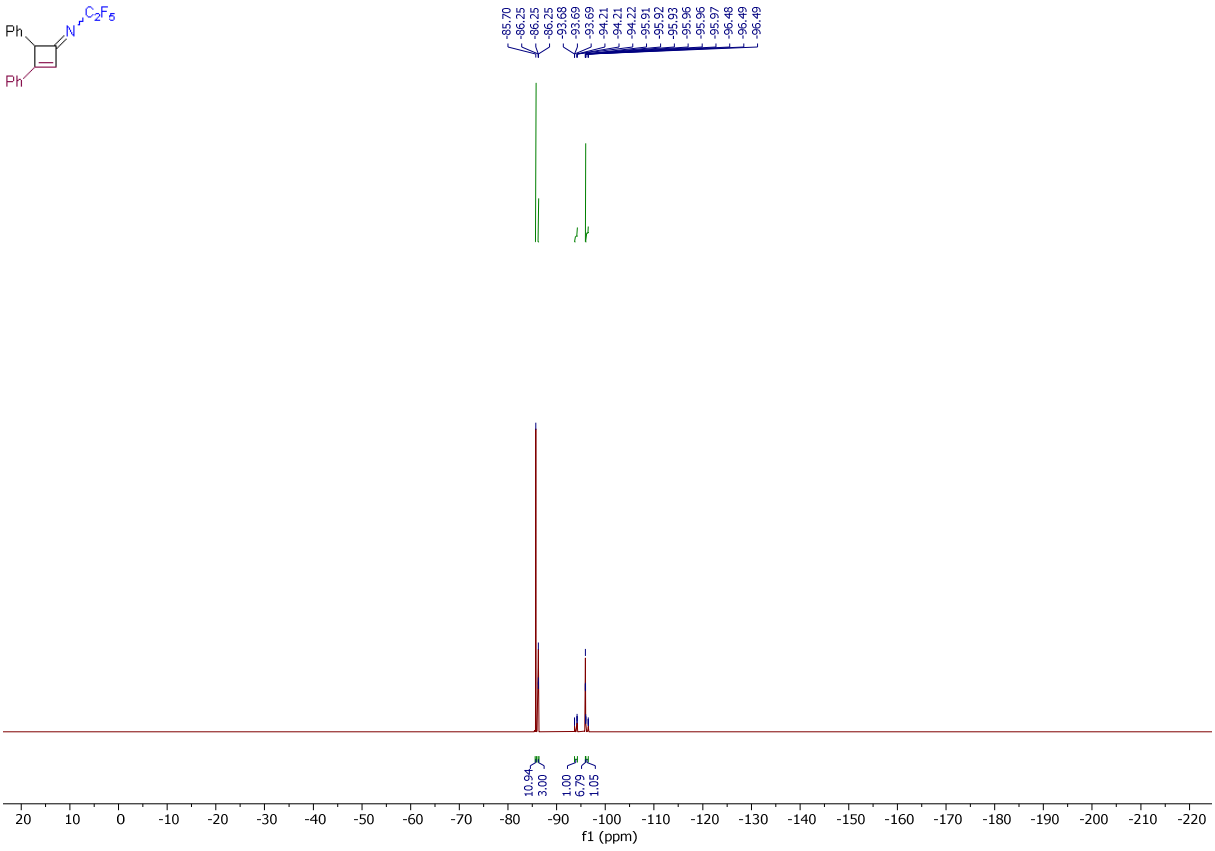
^{1}H NMR spectrum of **9b** ($CDCl_3$, 400 MHz)



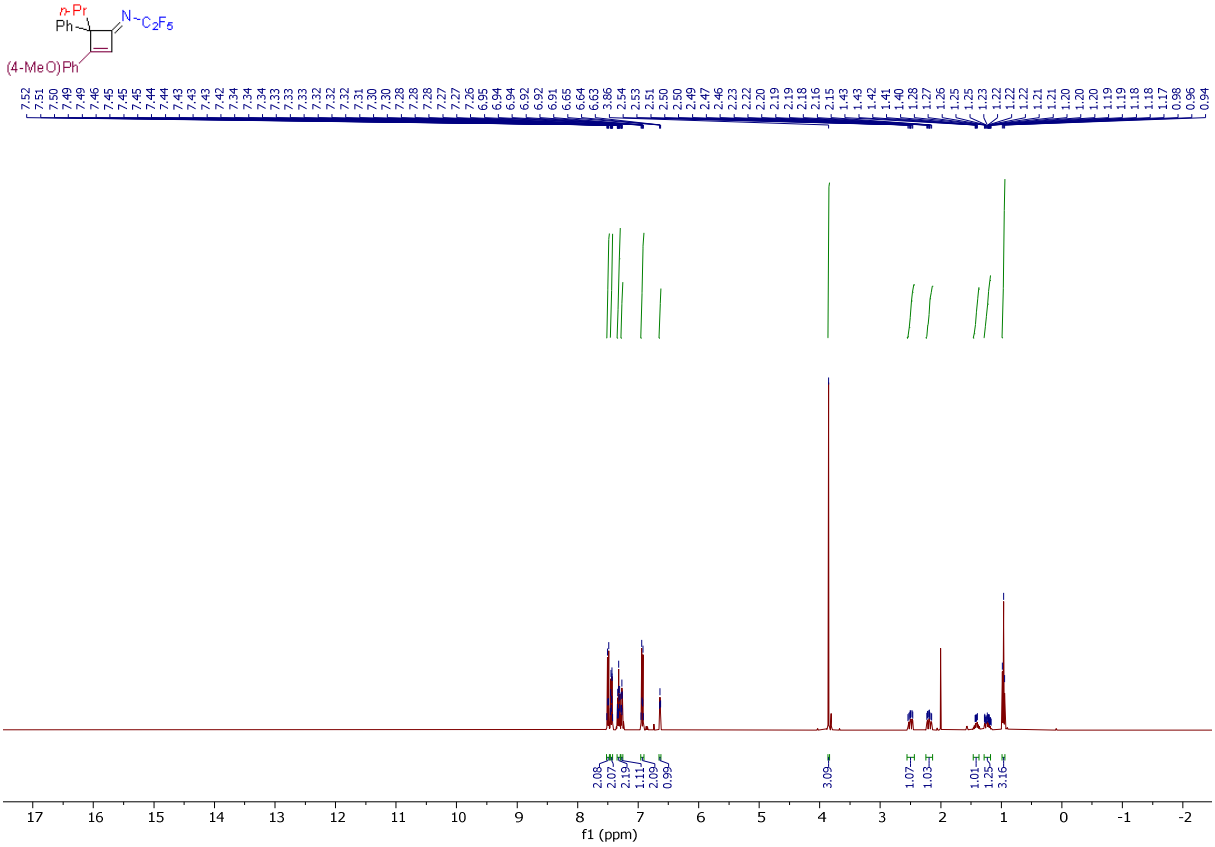
^{13}C NMR spectrum of **9b** ($CDCl_3$, 101 MHz)



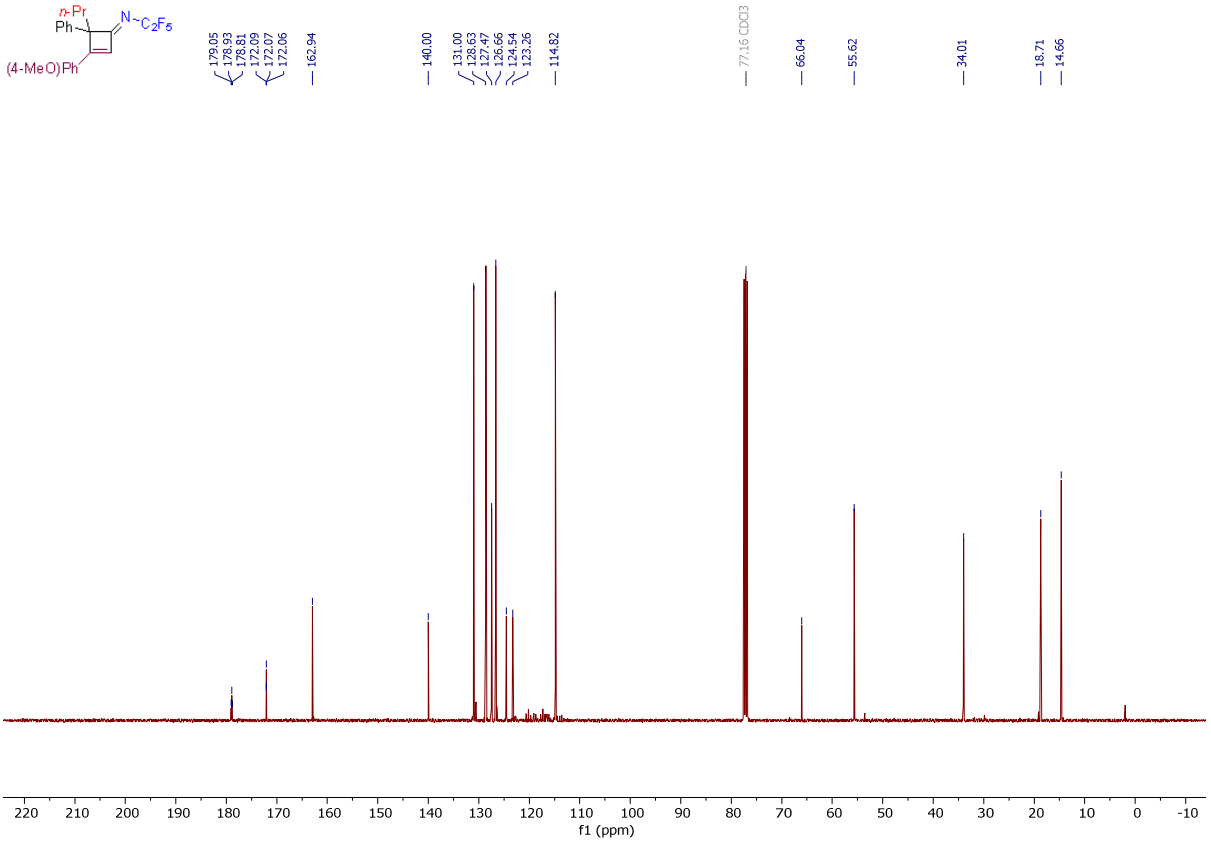
^{19}F NMR spectrum of **9b** ($CDCl_3$, 376 MHz)



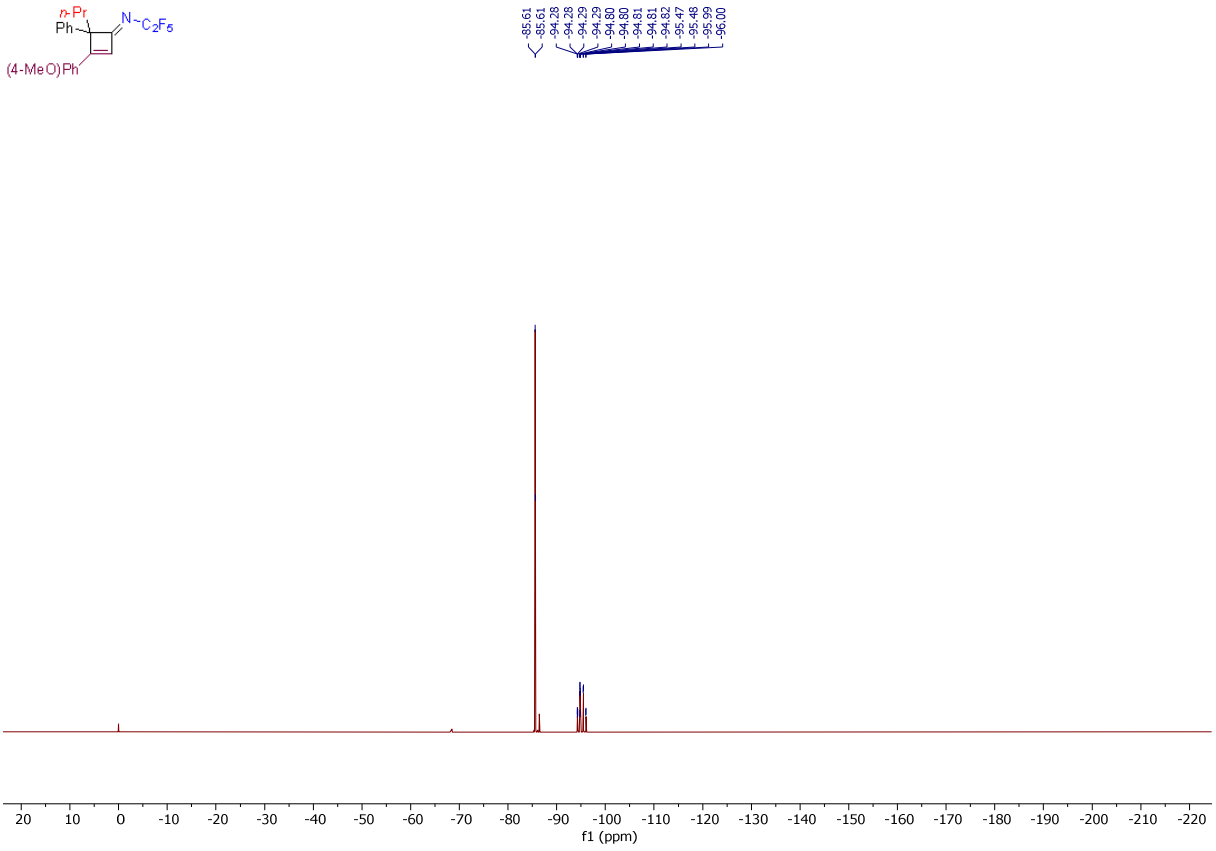
^{1}H NMR spectrum of **9c** ($CDCl_3$, 400 MHz)



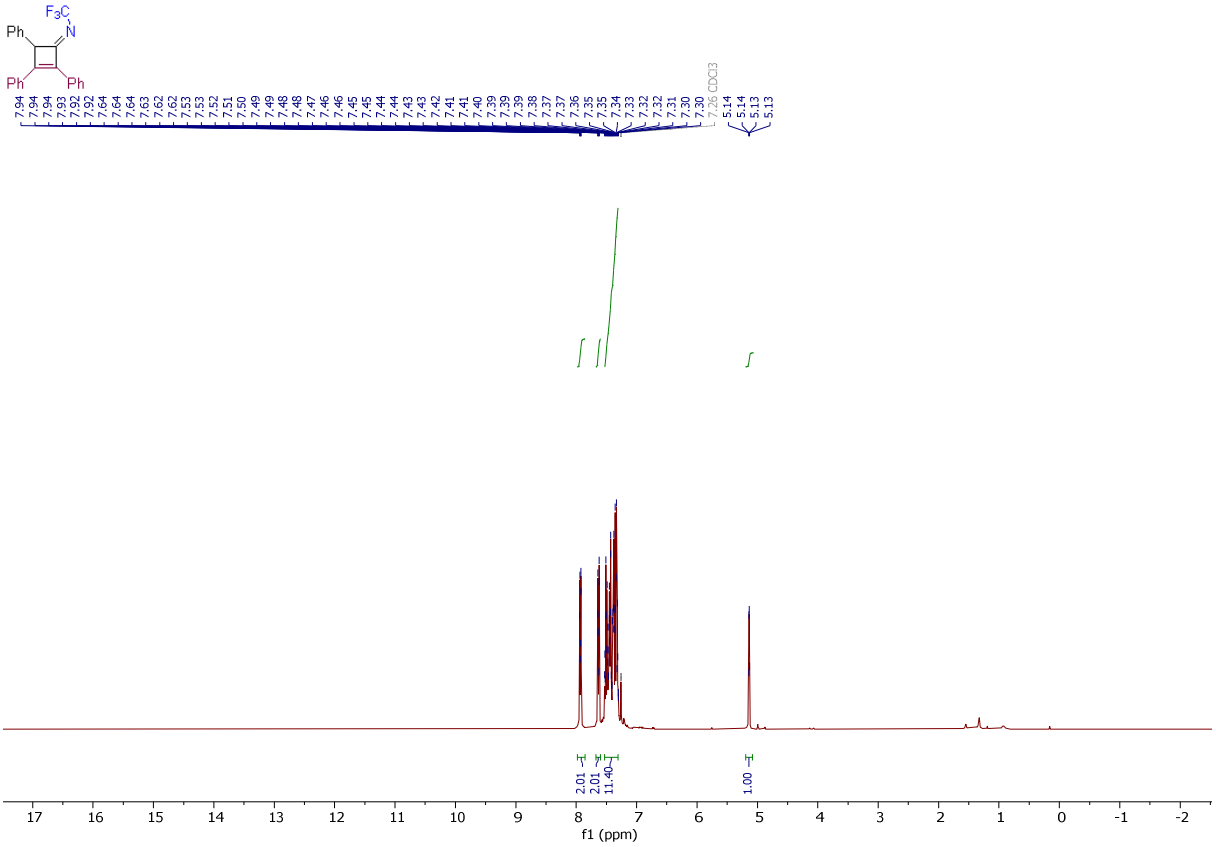
^{13}C NMR spectrum of **9c** ($CDCl_3$, 101 MHz)



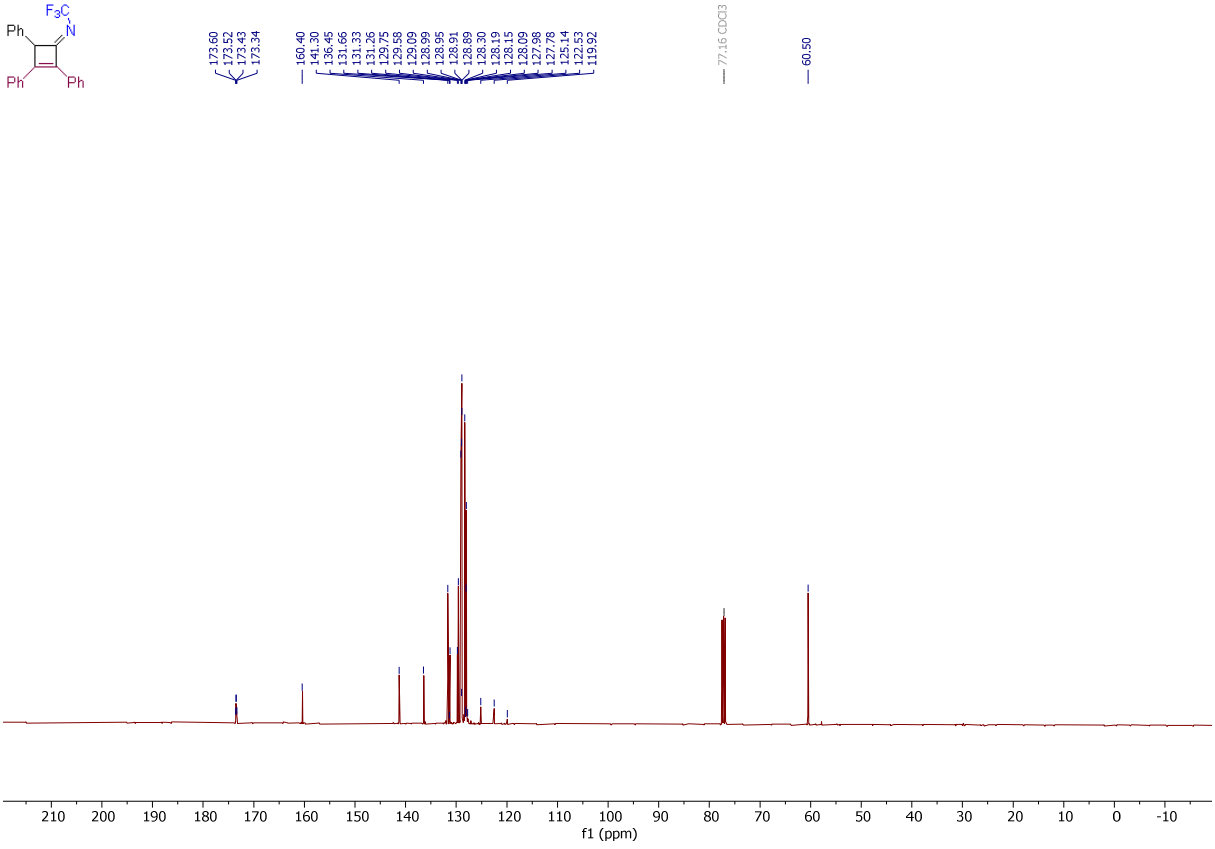
^{19}F NMR spectrum of **9c** ($CDCl_3$, 376 MHz)



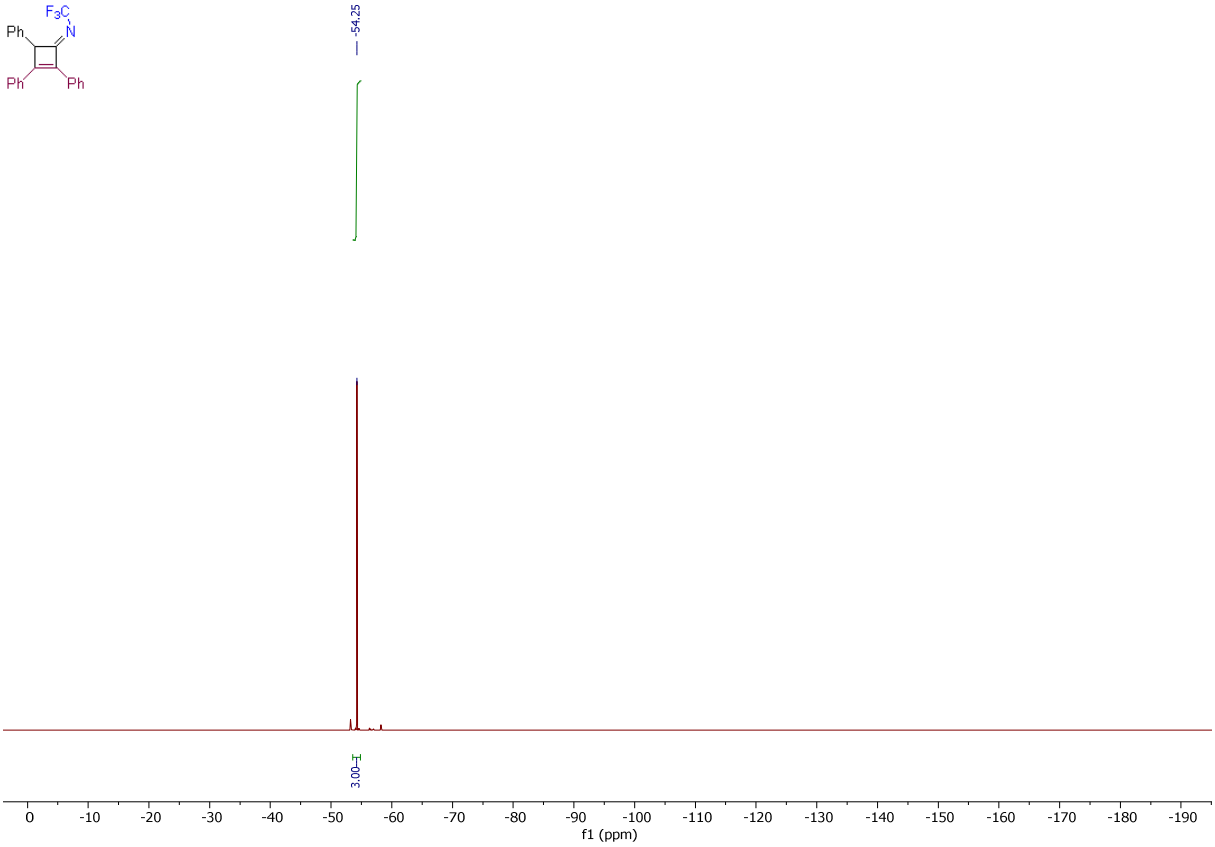
^{1}H NMR spectrum of **10a** ($CDCl_3$, 400 MHz)



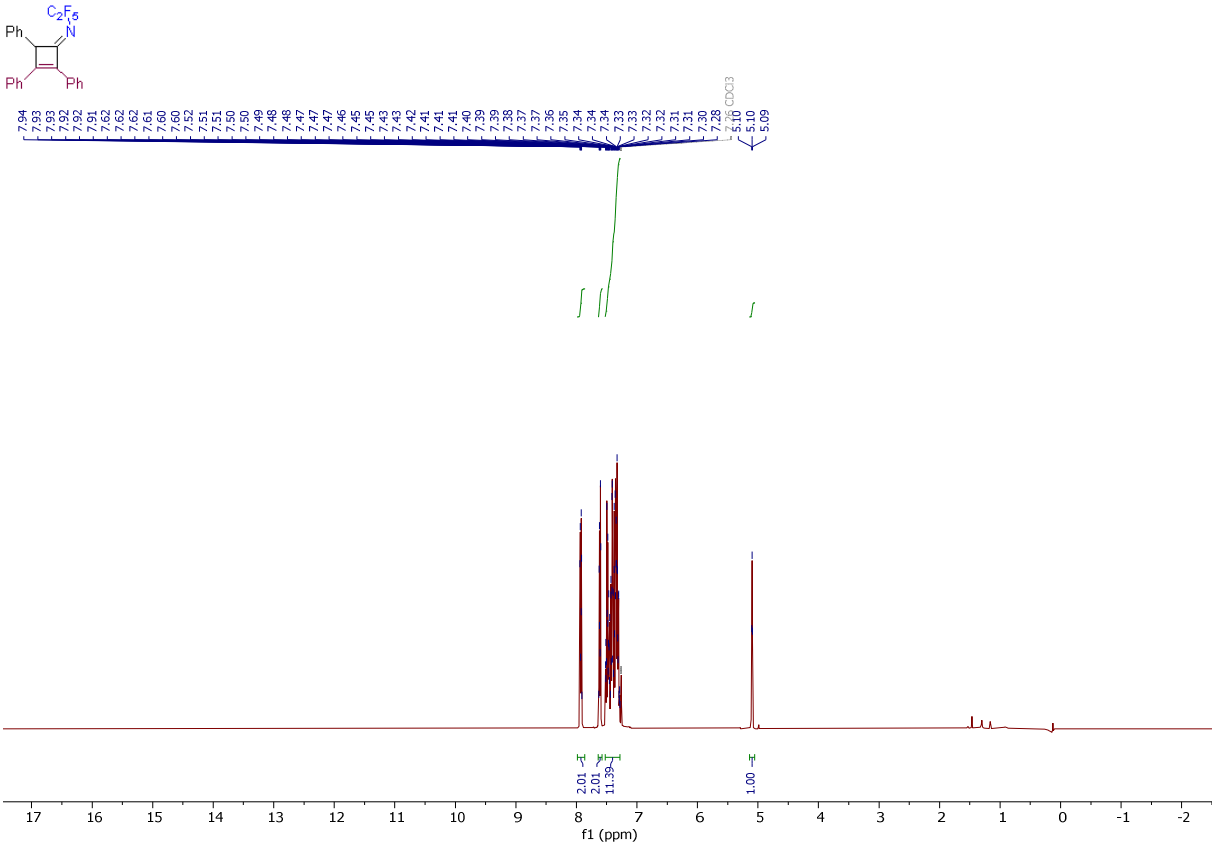
^{13}C NMR spectrum of **10a** ($CDCl_3$, 101 MHz)



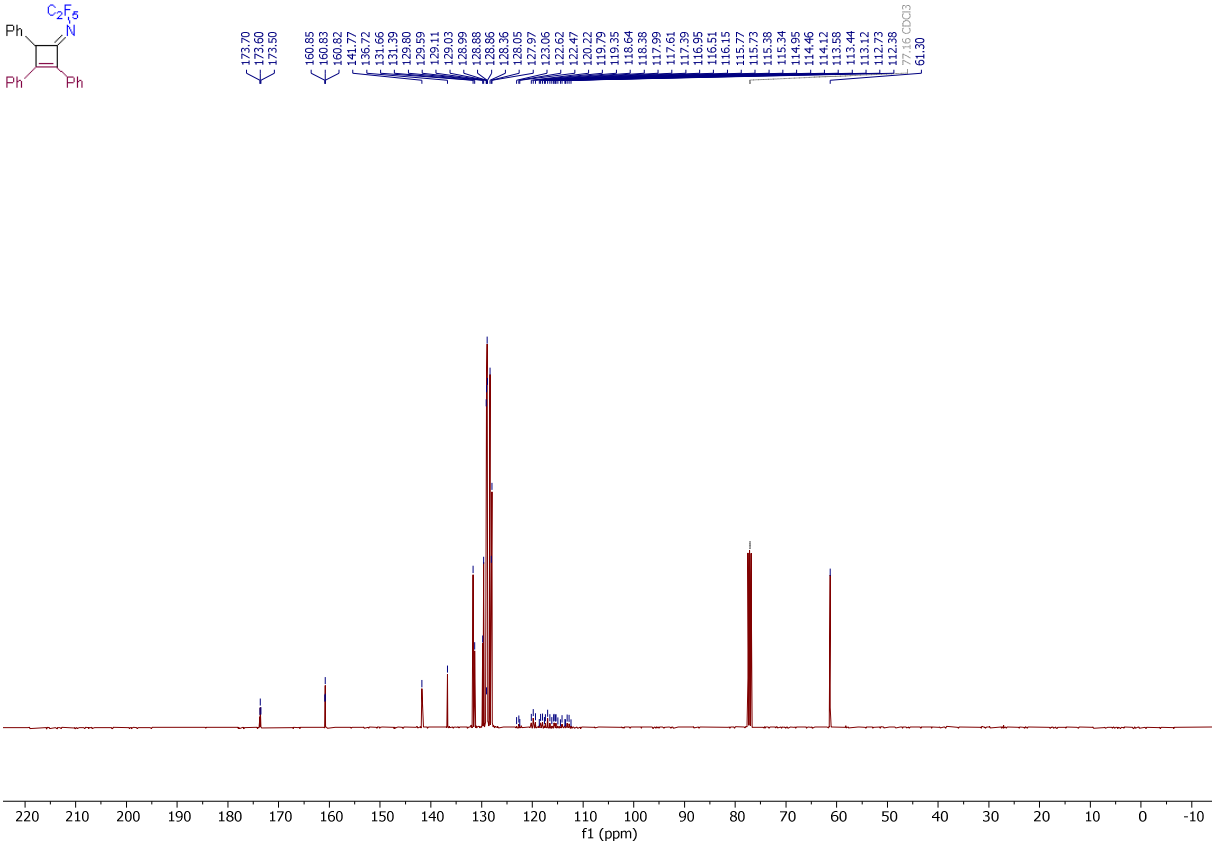
^{19}F NMR spectrum of **10a** ($CDCl_3$, 376 MHz)



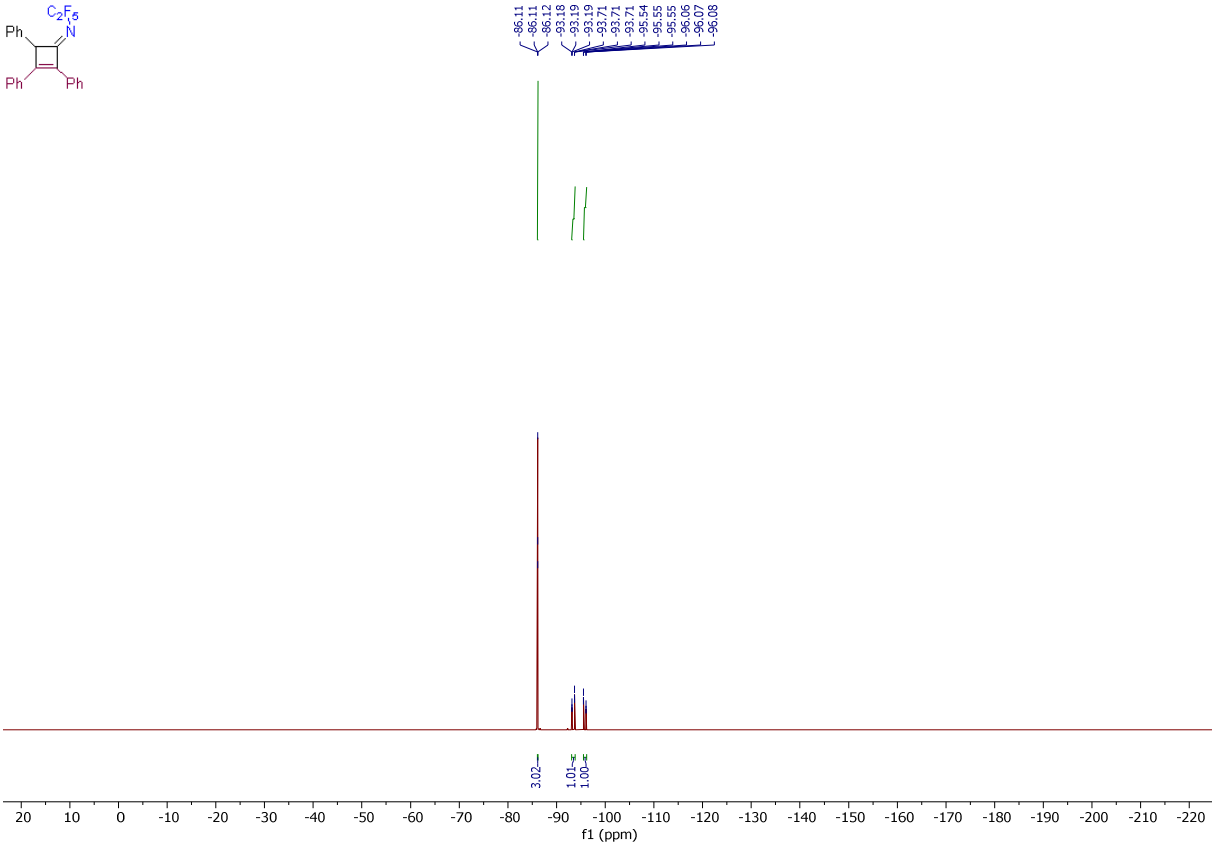
^{1}H NMR spectrum of **10b** ($CDCl_3$, 400 MHz)



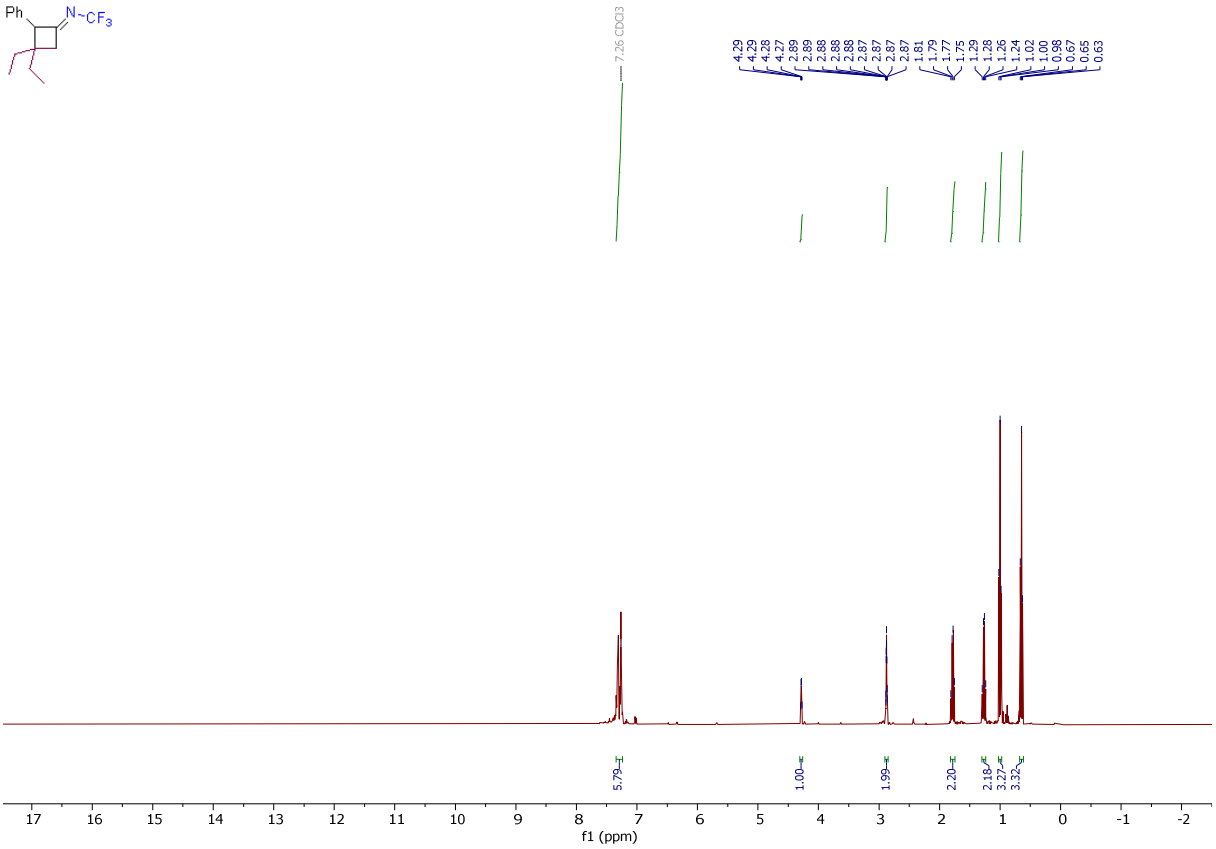
^{13}C NMR spectrum of **10b** ($CDCl_3$, 101 MHz)



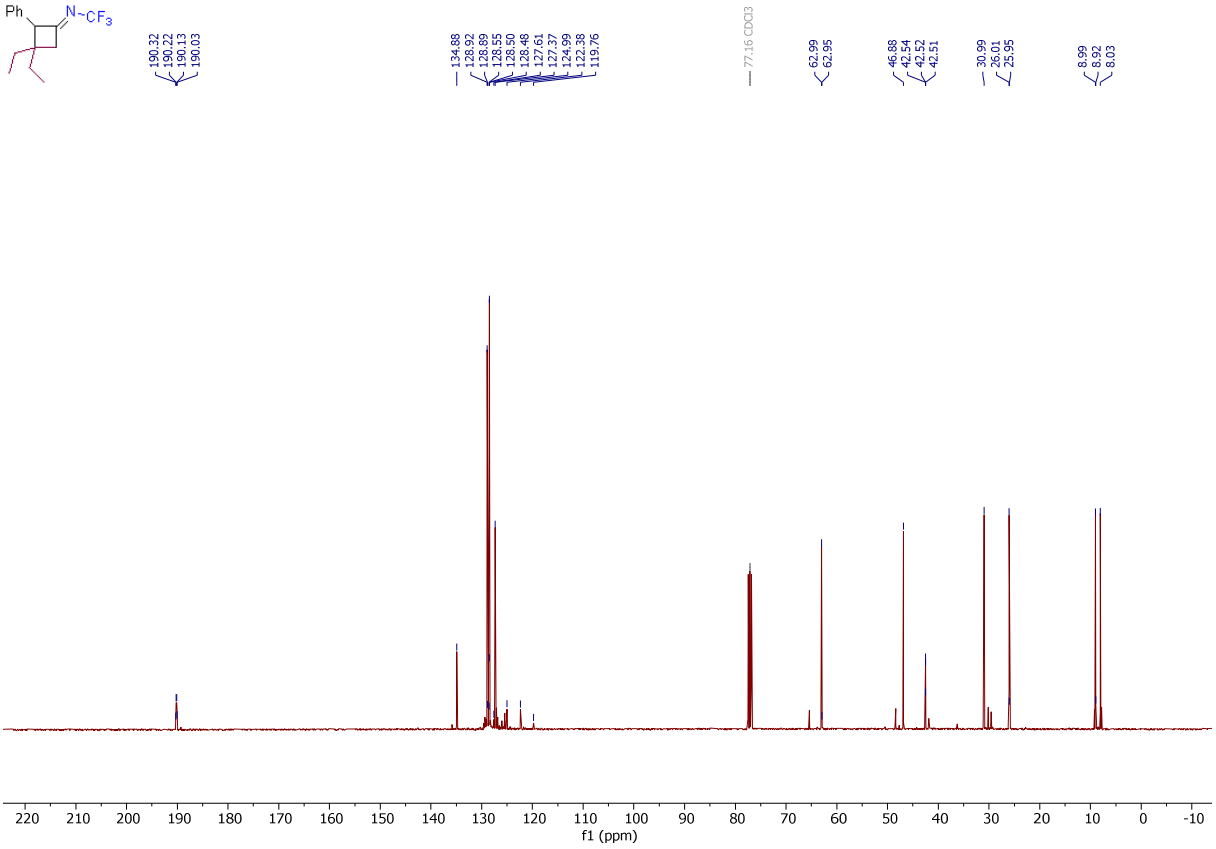
^{19}F NMR spectrum of **10b** ($CDCl_3$, 376 MHz)



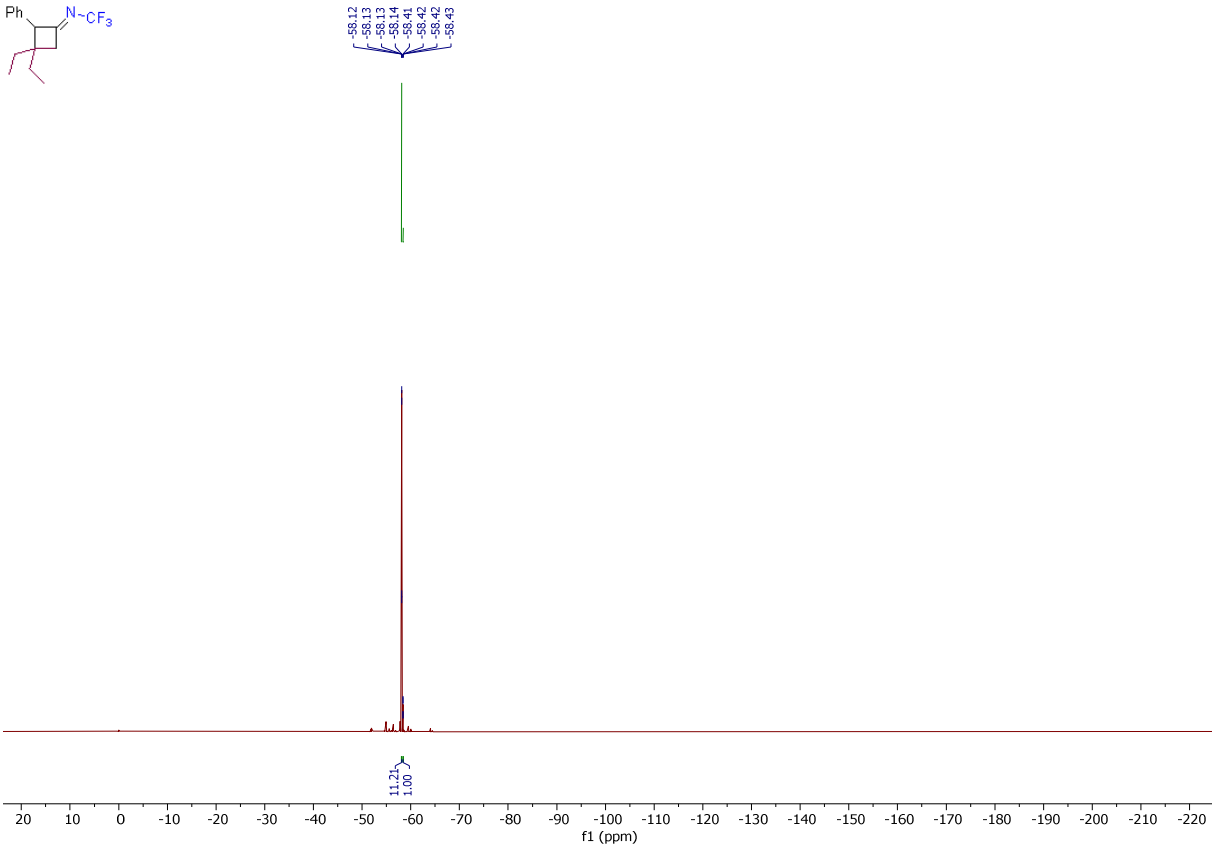
^{1}H NMR spectrum of **11a** ($CDCl_3$, 400 MHz)



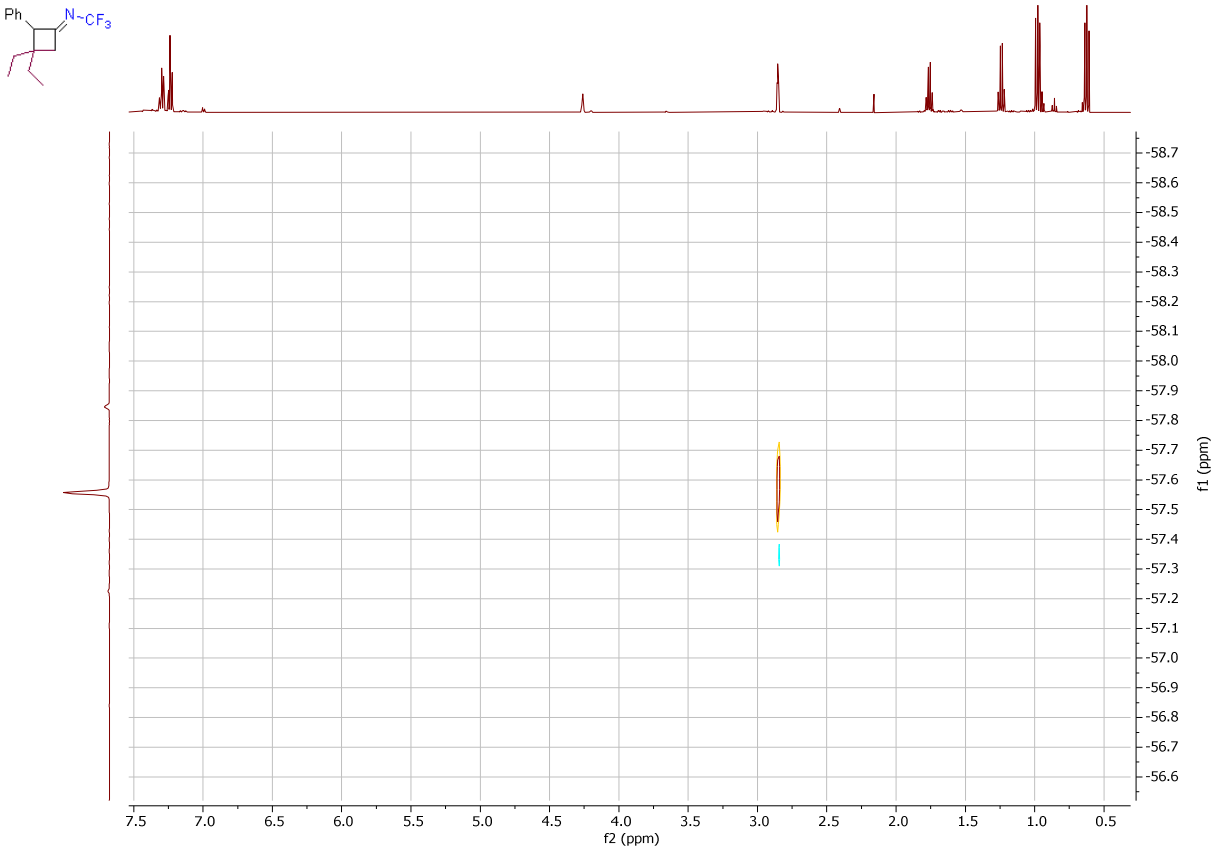
^{13}C NMR spectrum of **11a** ($CDCl_3$, 101 MHz)



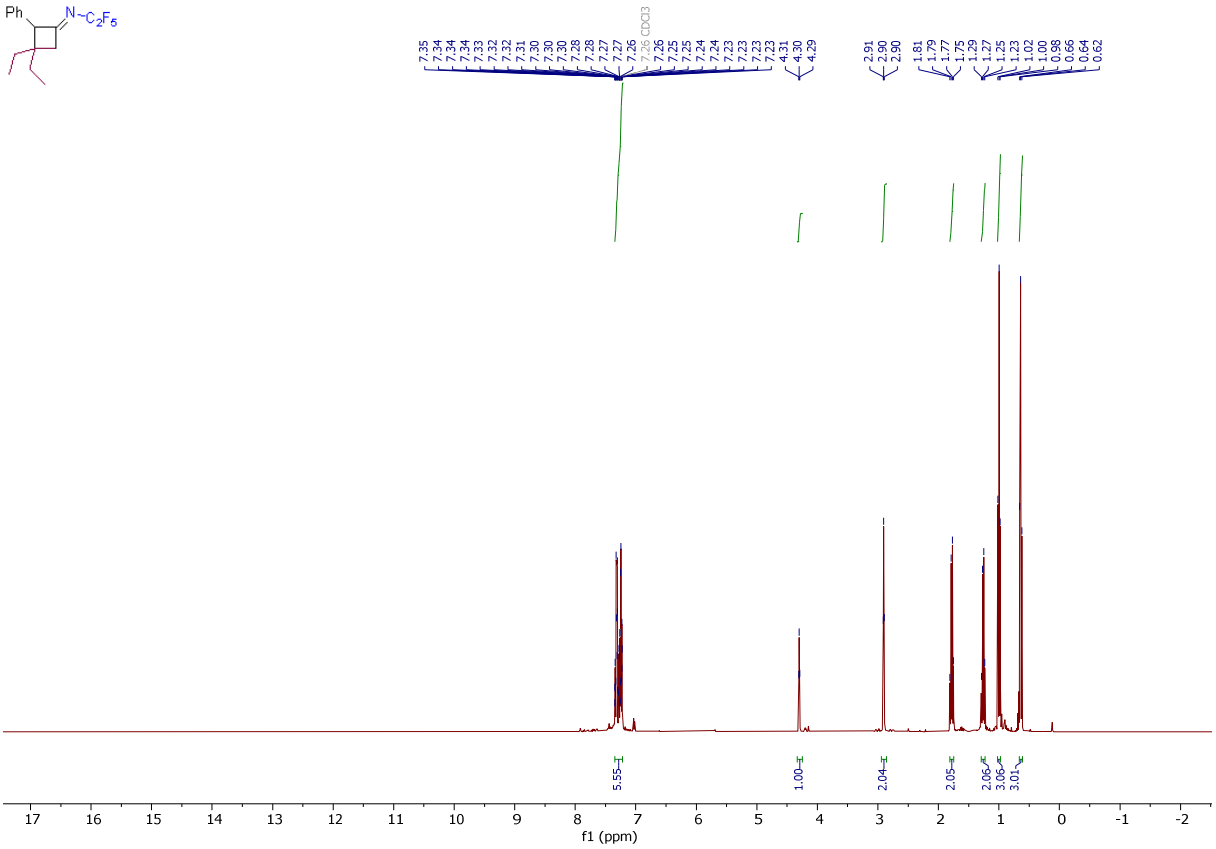
^{19}F NMR spectrum of **11a** ($CDCl_3$, 376 MHz)



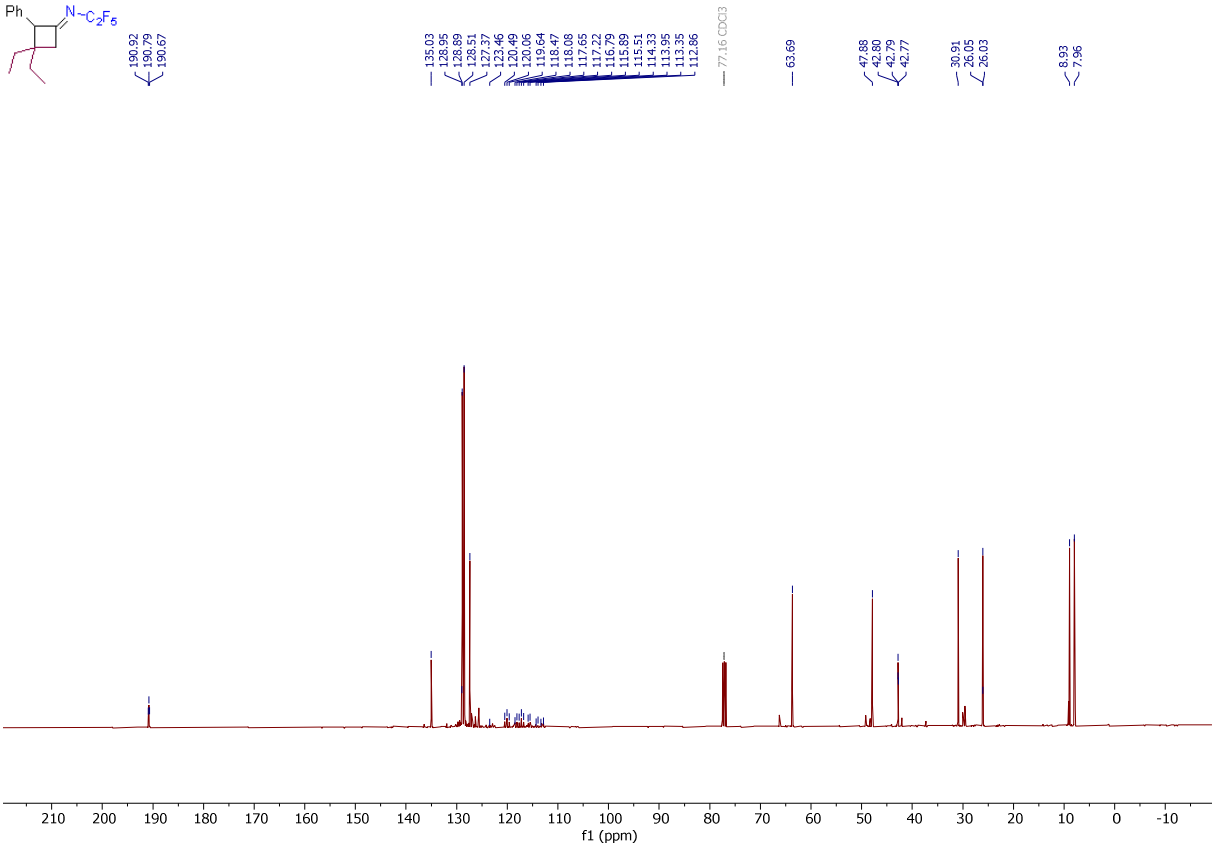
^{1}H-^{19}F HOESY NMR spectrum of **11a** ($CDCl_3$)



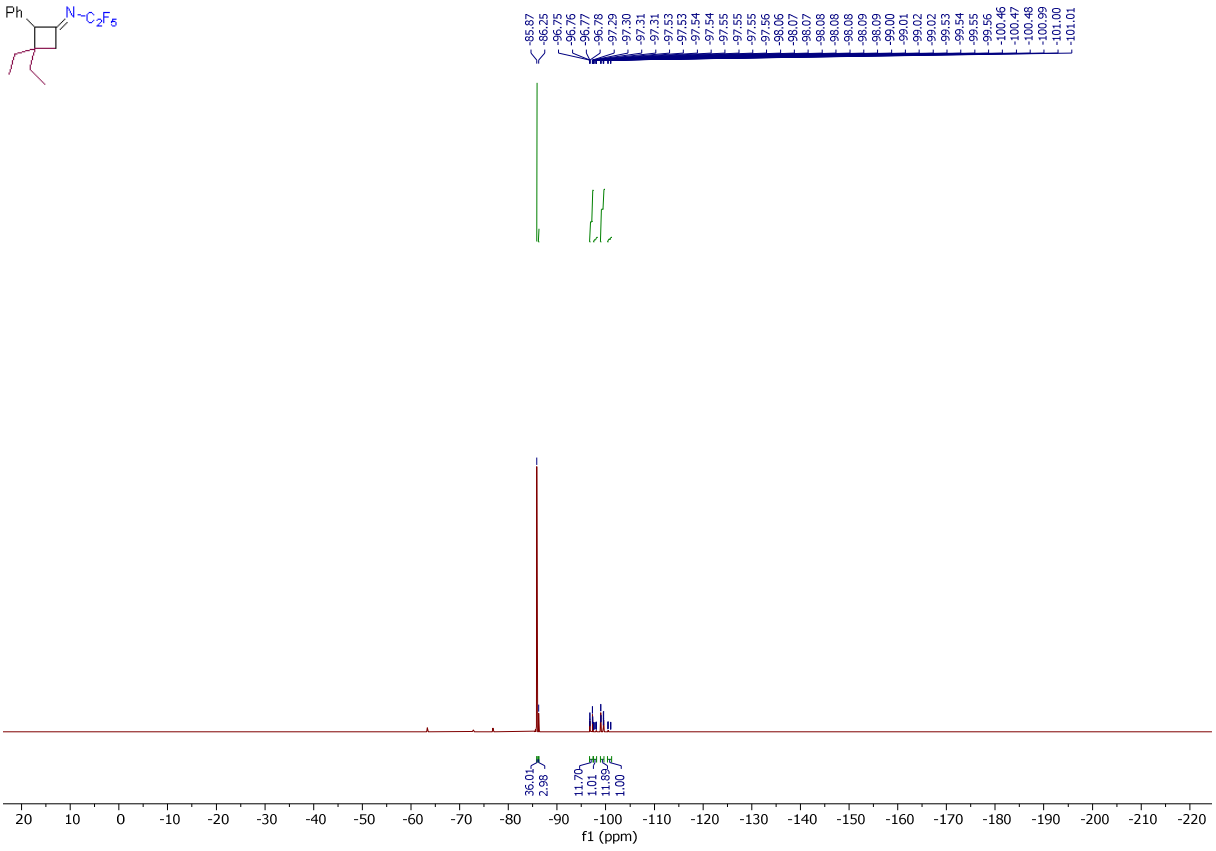
^{1}H NMR spectrum of **11b** ($CDCl_3$, 400 MHz)



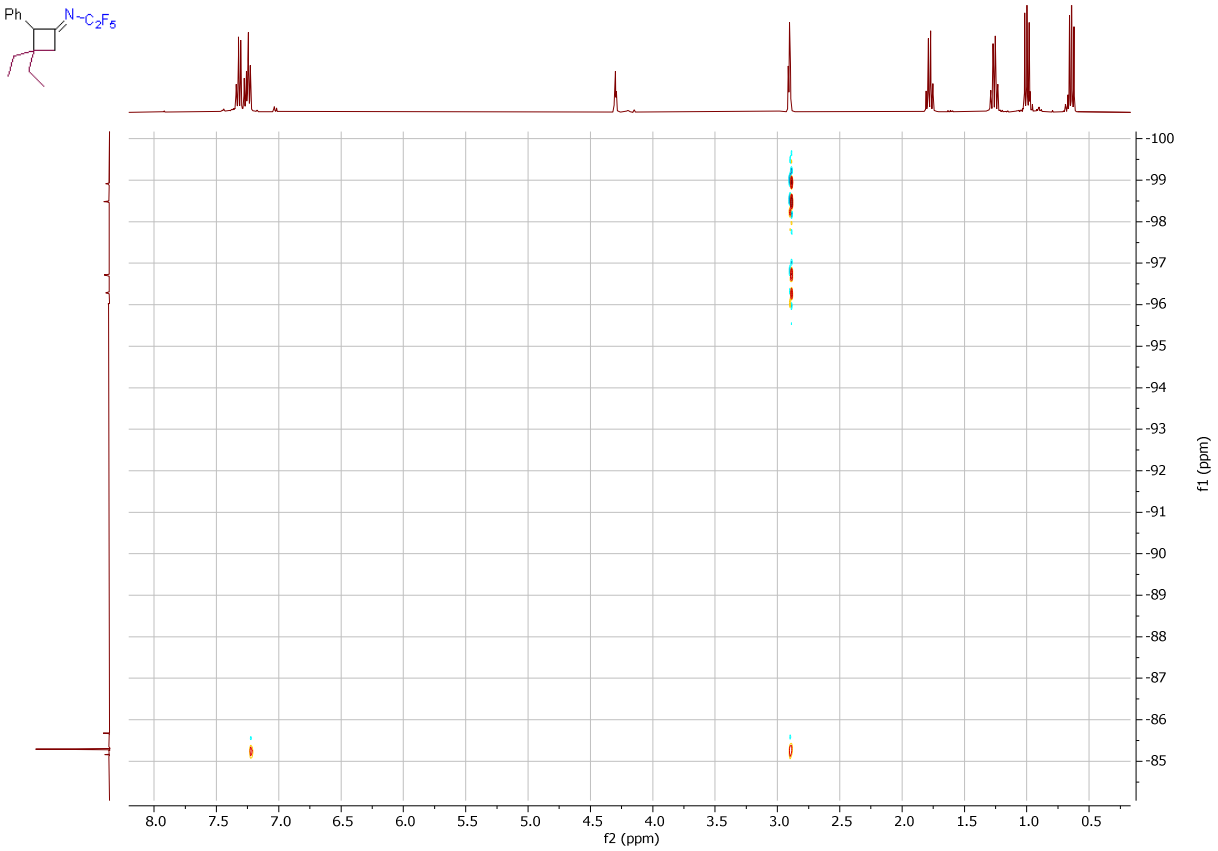
^{13}C NMR spectrum of **11b** ($CDCl_3$, 101 MHz)



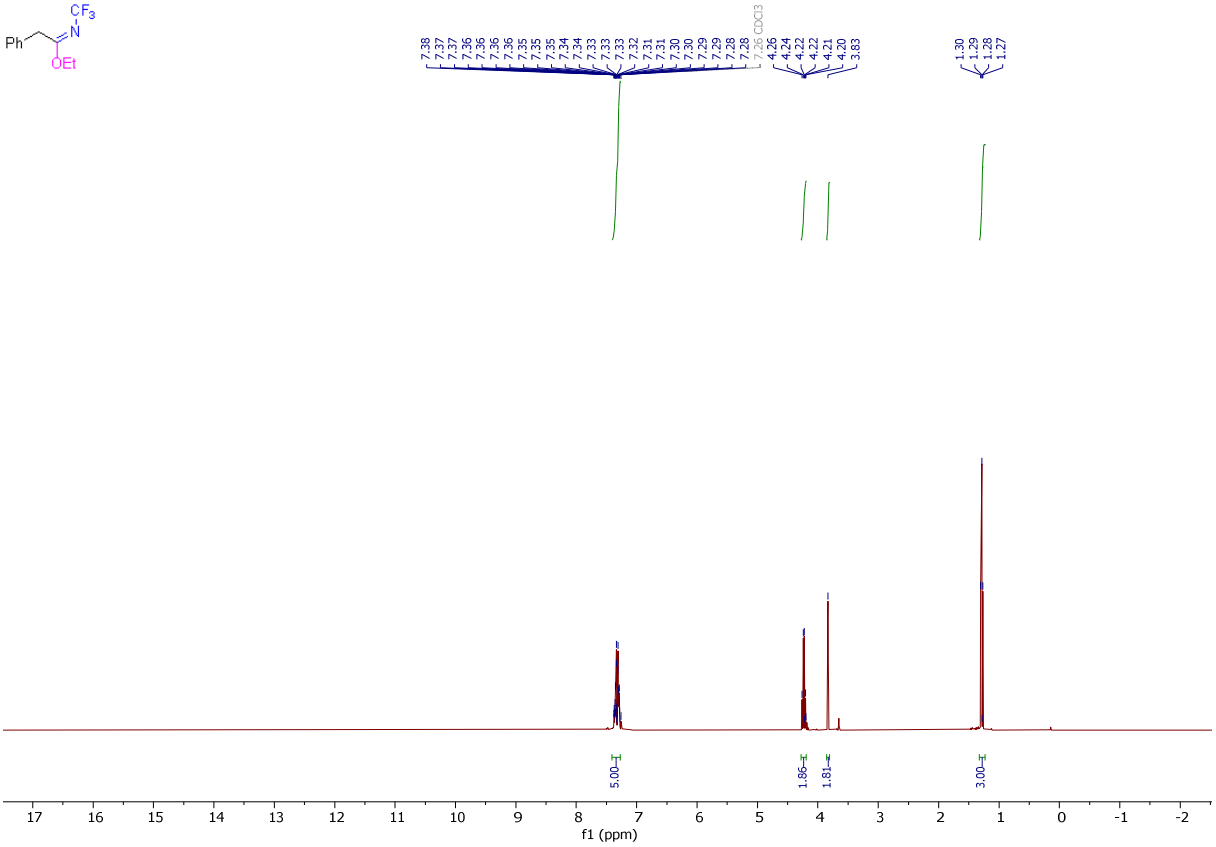
^{19}F NMR spectrum of **11b** ($CDCl_3$, 376 MHz)



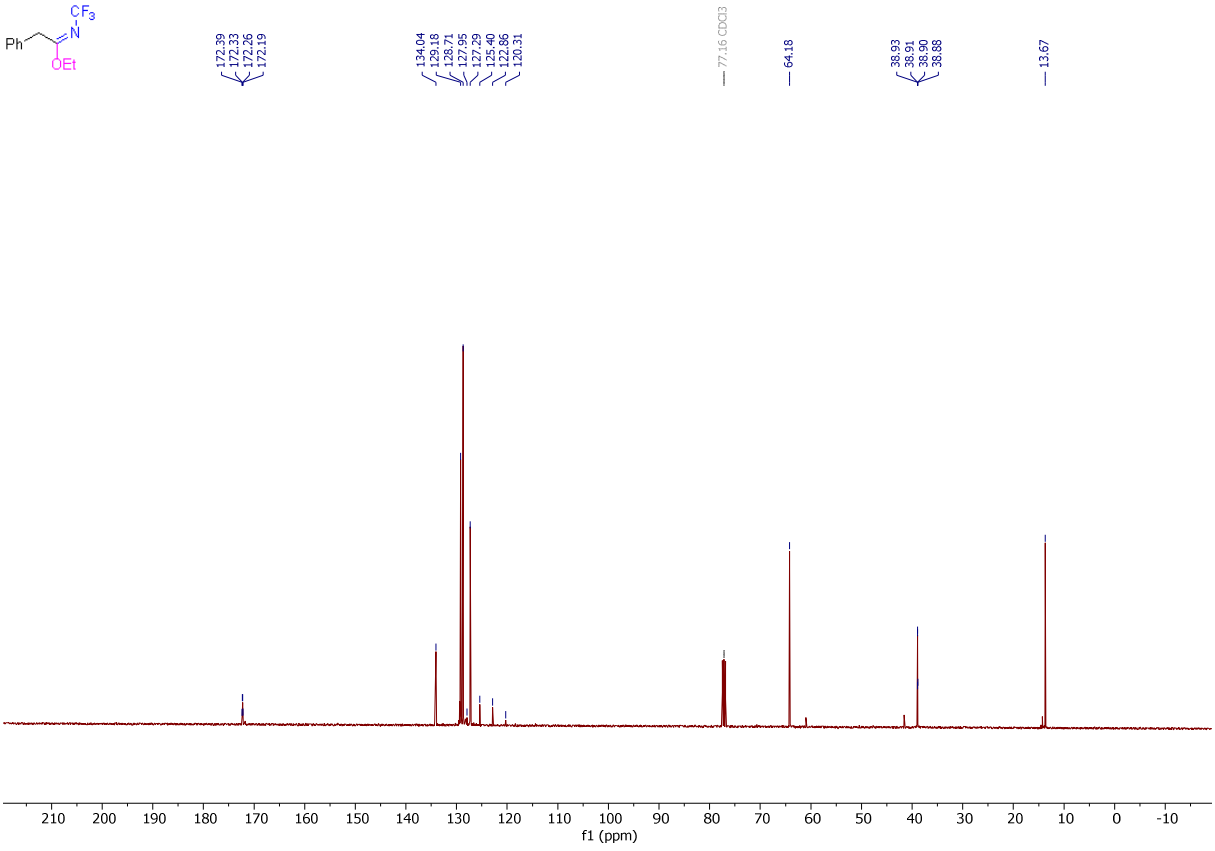
^{1}H-^{19}F HOESY NMR spectrum of **11b** ($CDCl_3$)



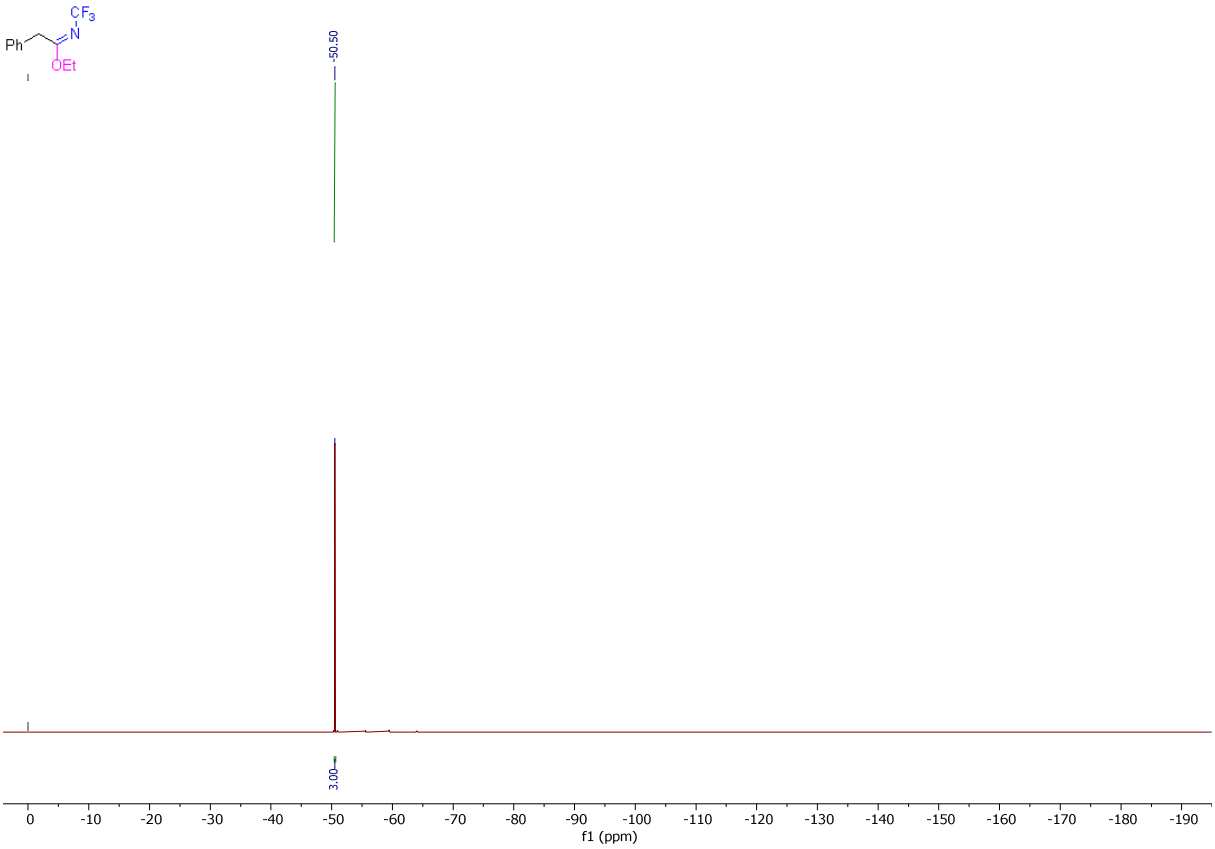
^{1}H NMR spectrum of **12a** ($CDCl_3$, 400 MHz)



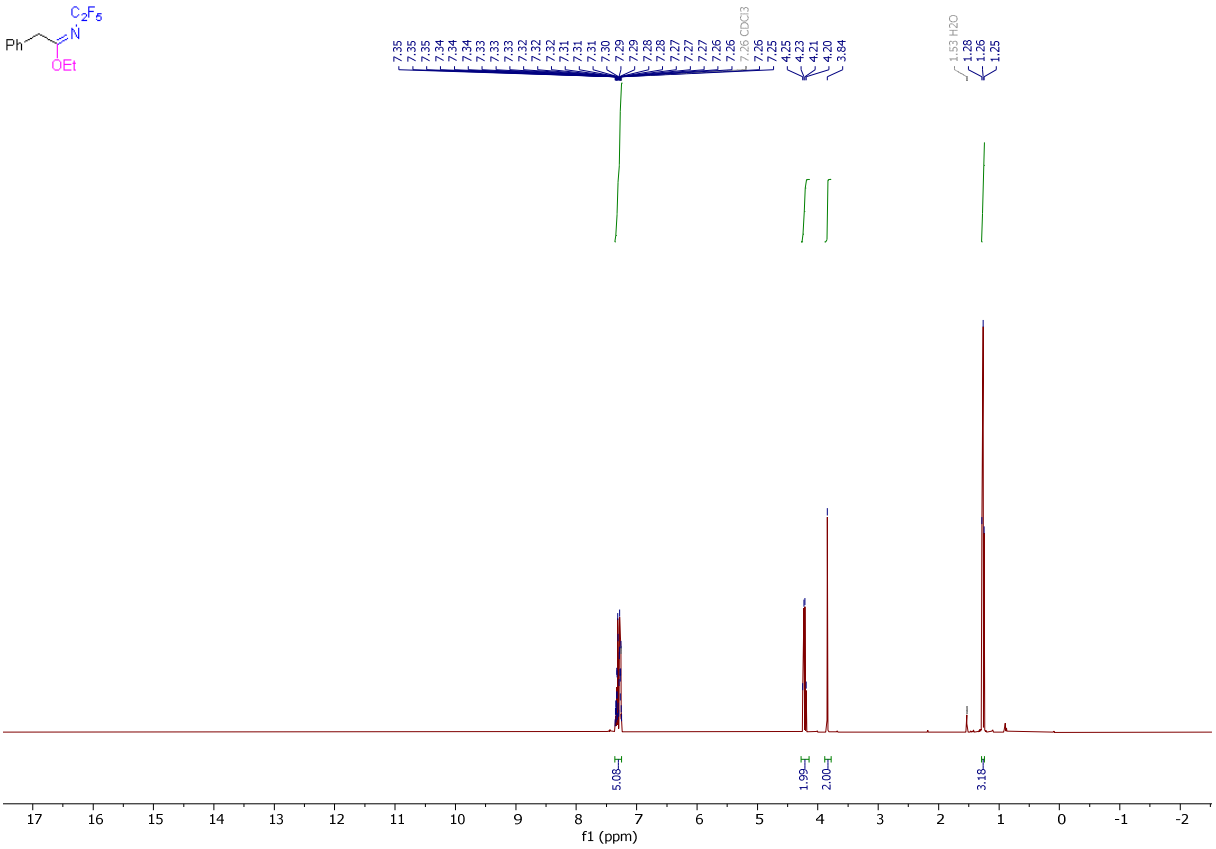
^{13}C NMR spectrum of **12a** ($CDCl_3$, 101 MHz)



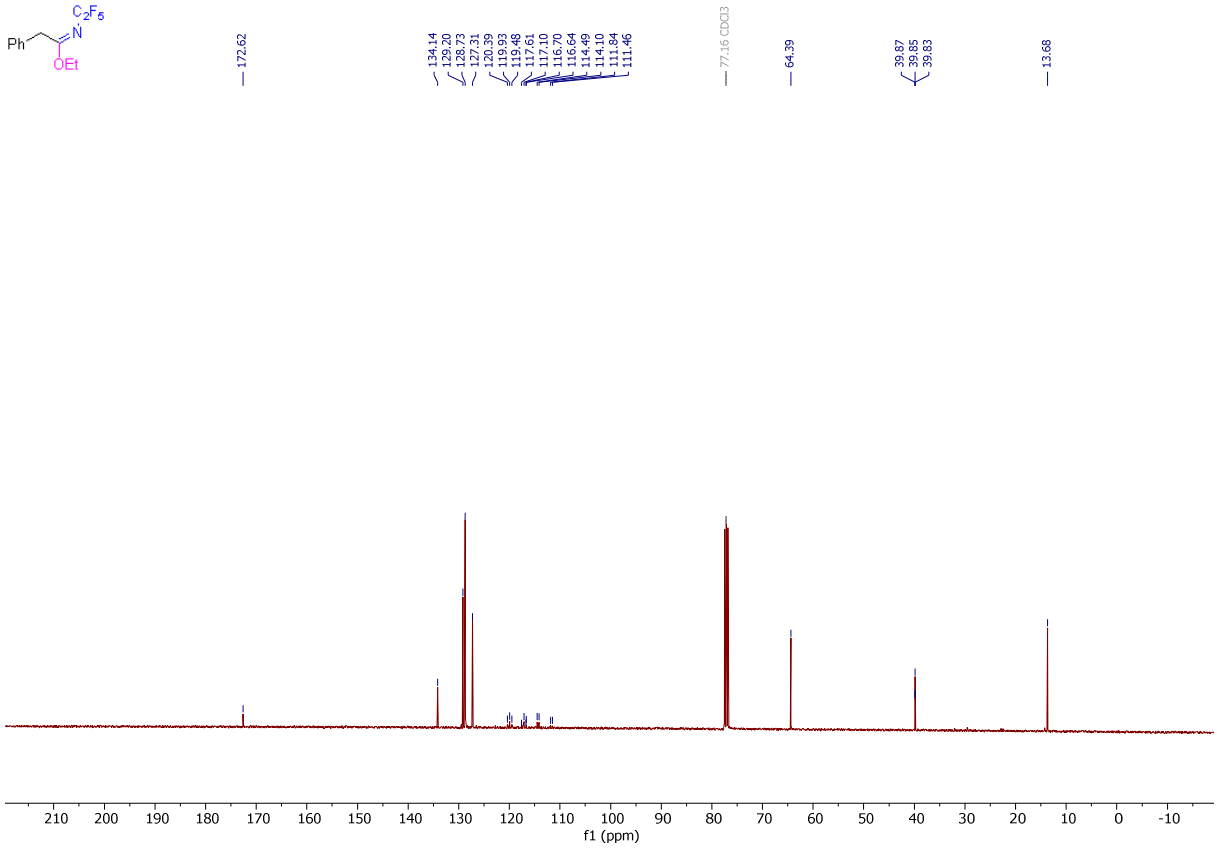
^{19}F NMR spectrum of **12a** ($CDCl_3$, 376 MHz)



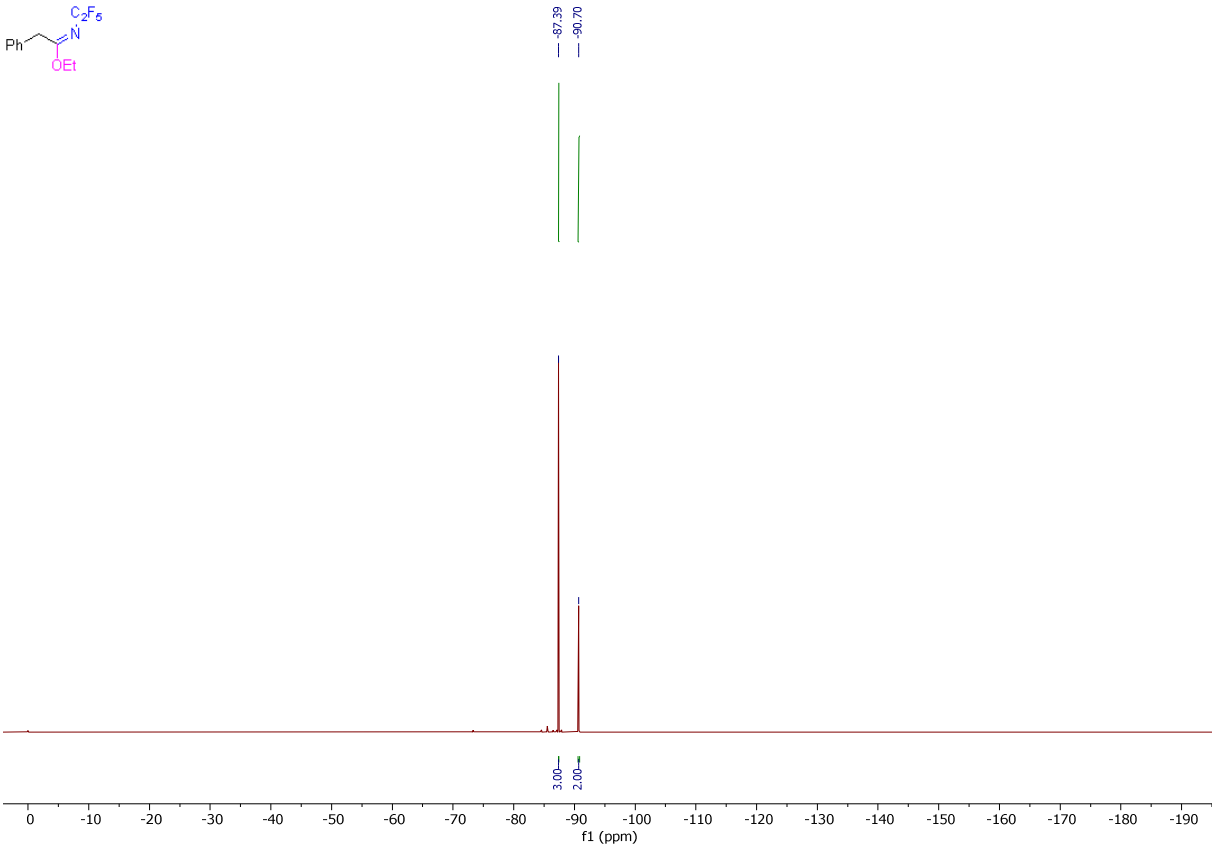
^{1}H NMR spectrum of **12b** ($CDCl_3$, 400 MHz)



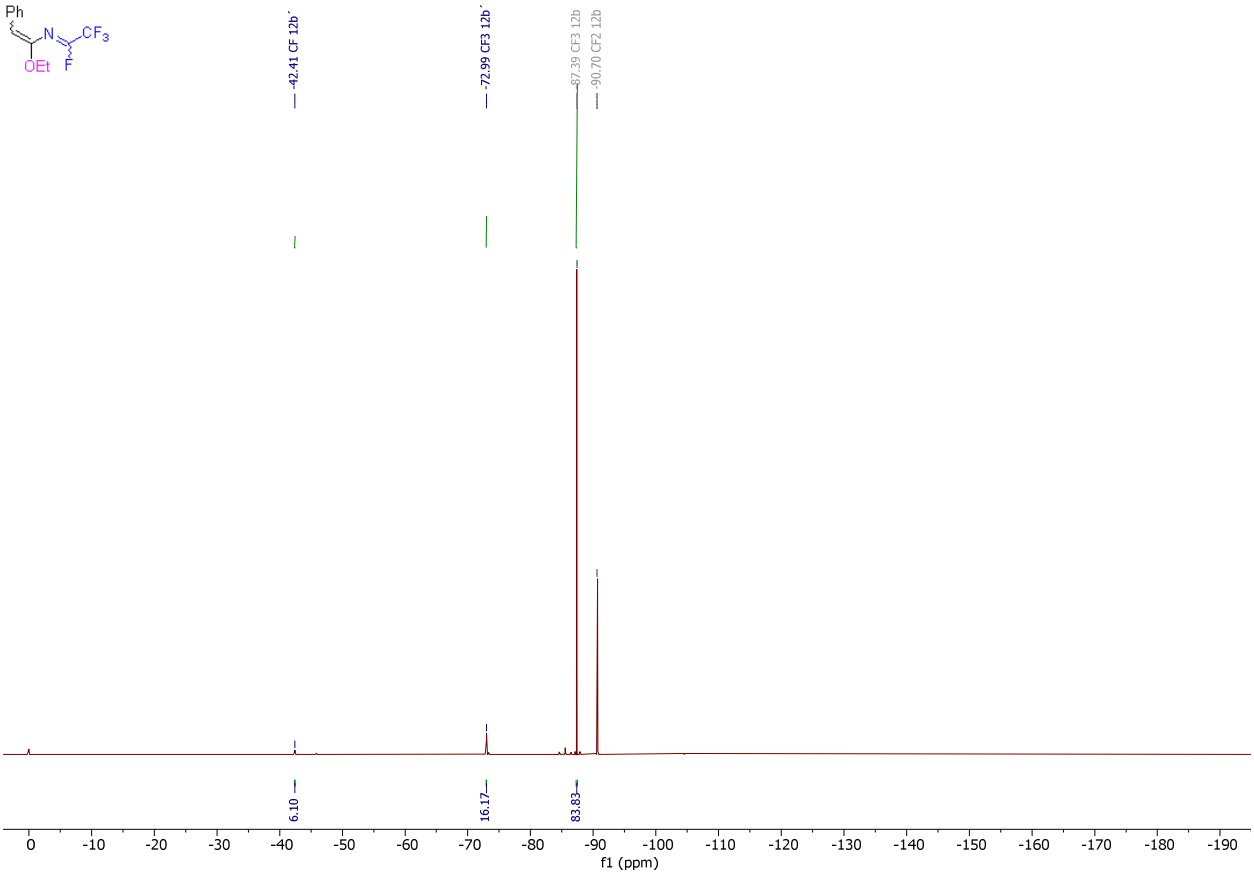
^{13}C NMR spectrum of **12b** ($CDCl_3$, 101 MHz)



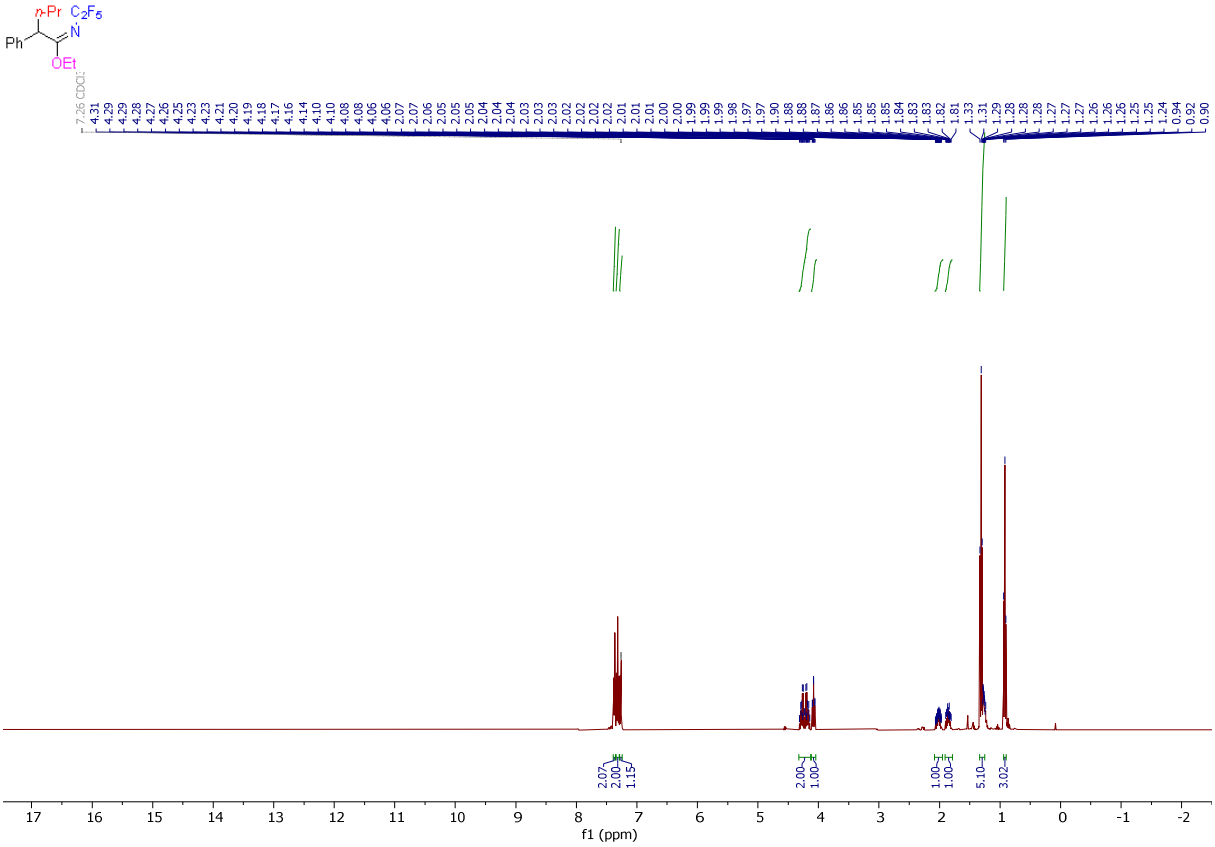
^{19}F NMR spectrum of **12b** ($CDCl_3$, 376 MHz)



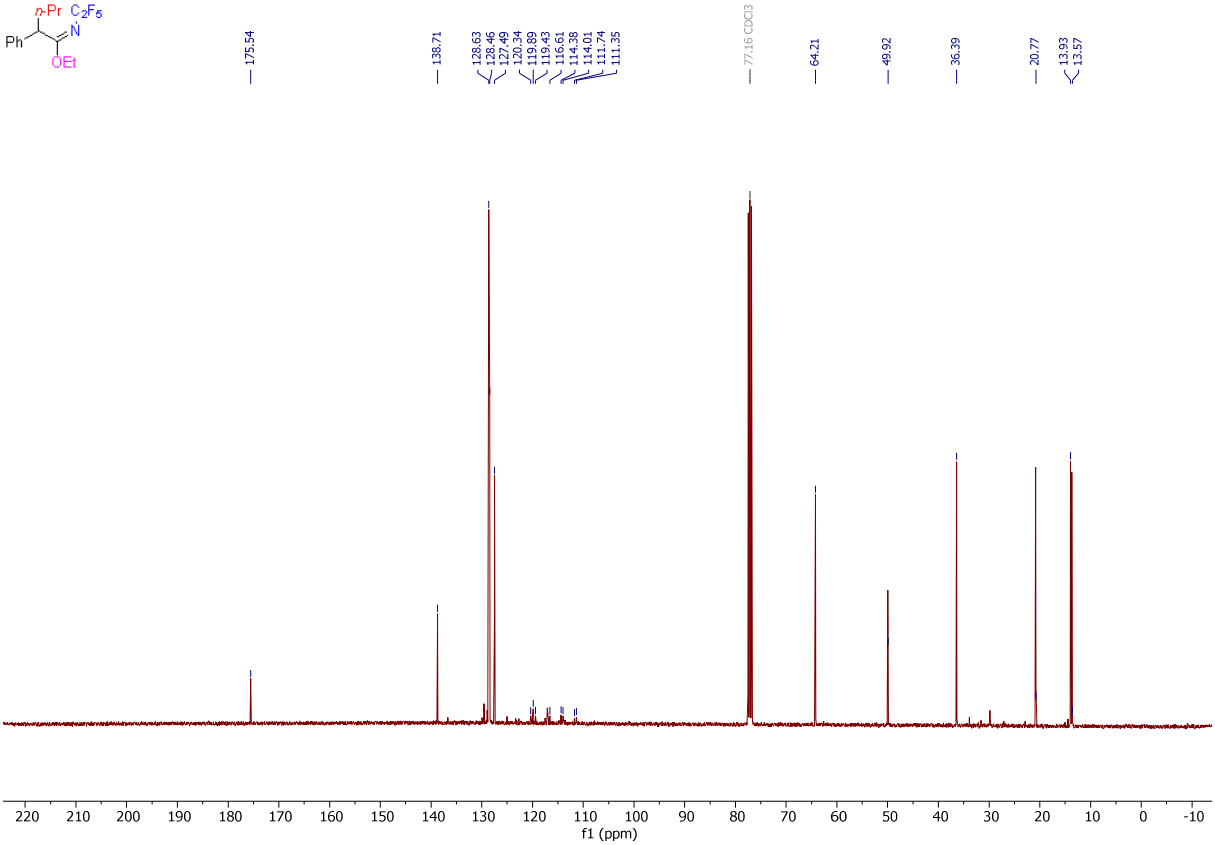
^{19}F NMR spectrum of **12b'** ($CDCl_3$, 376 MHz)



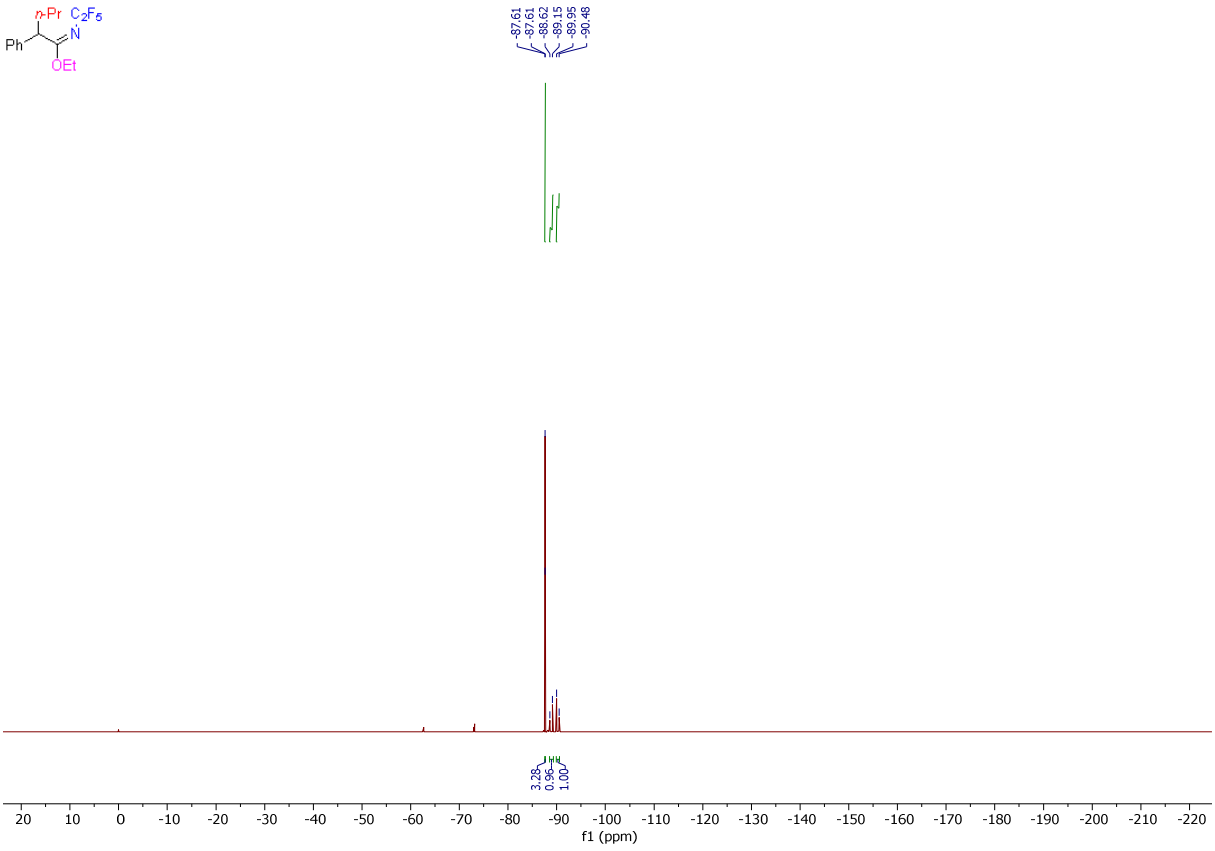
^{1}H NMR spectrum of **12c** ($CDCl_3$, 400 MHz)



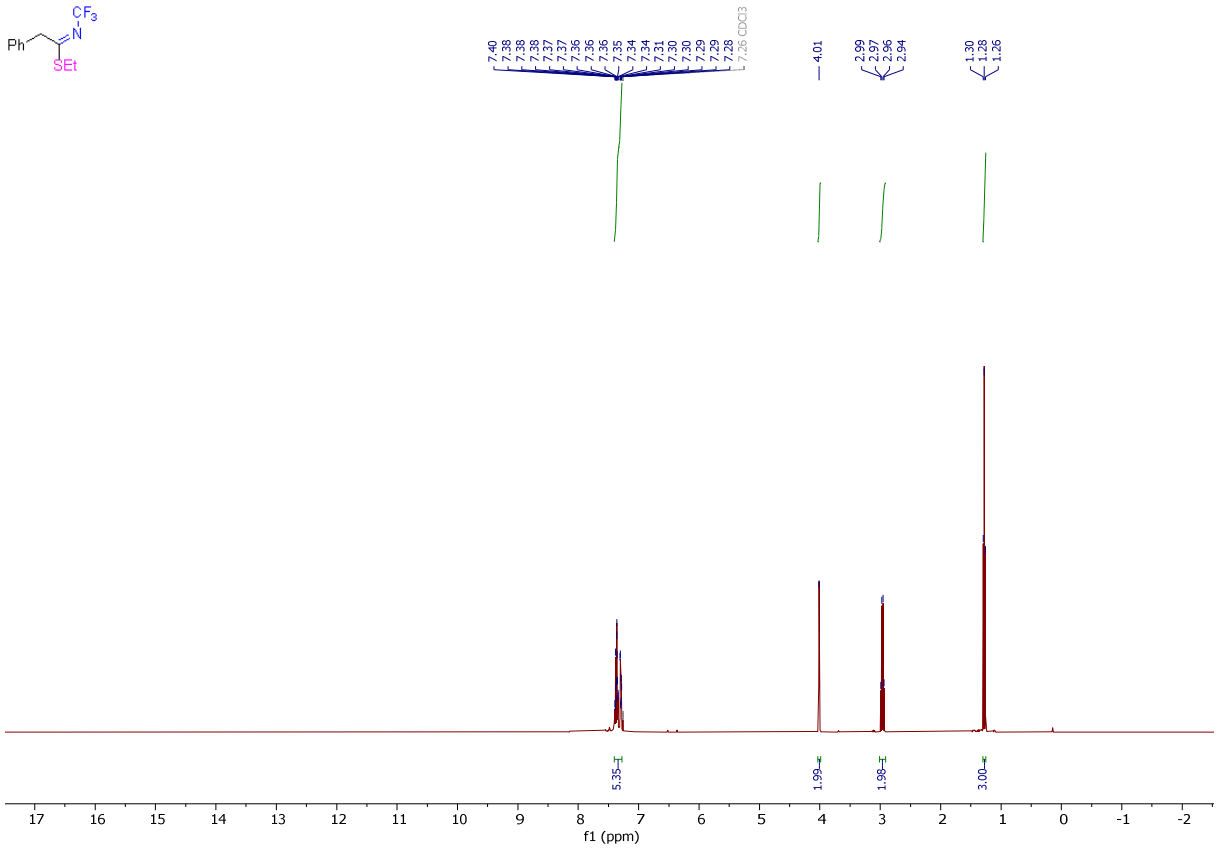
^{13}C NMR spectrum of **12c** ($CDCl_3$, 101 MHz)



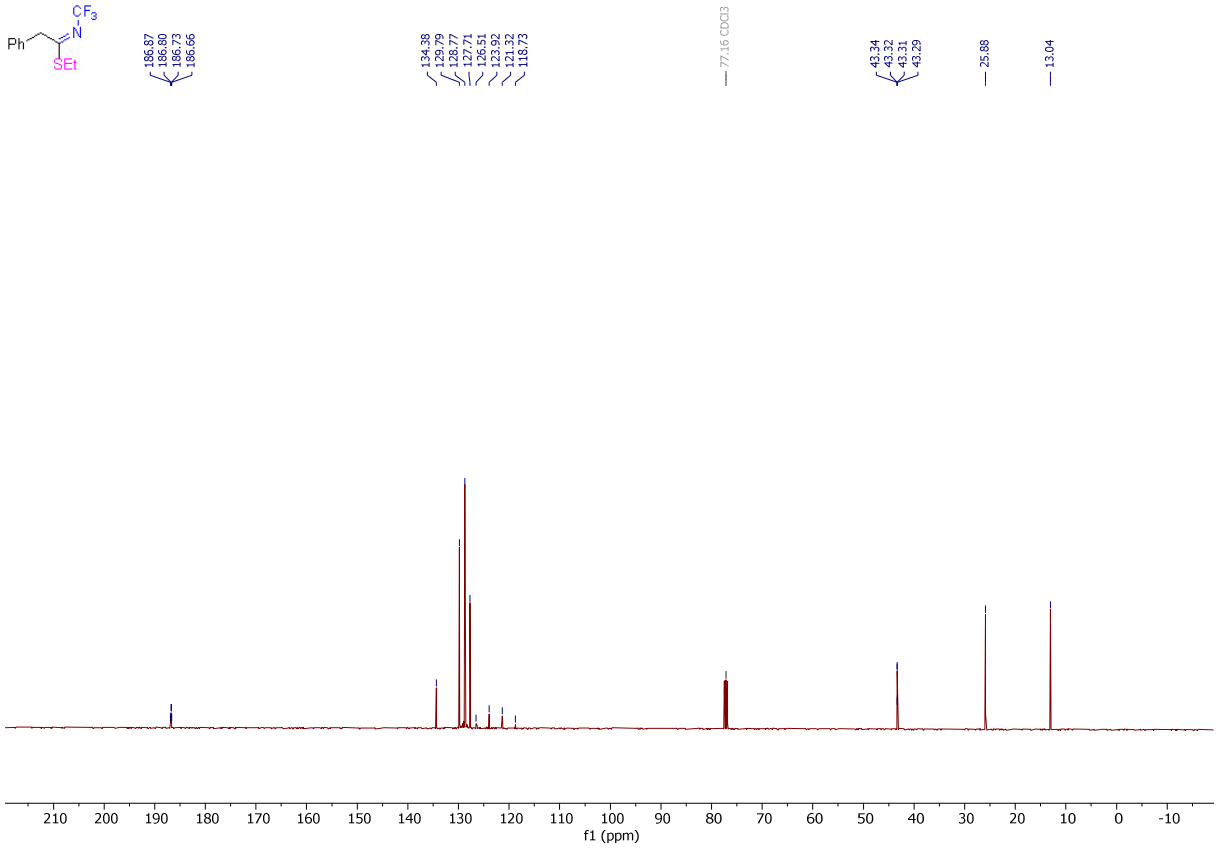
^{19}F NMR spectrum of **12c** ($CDCl_3$, 376 MHz)



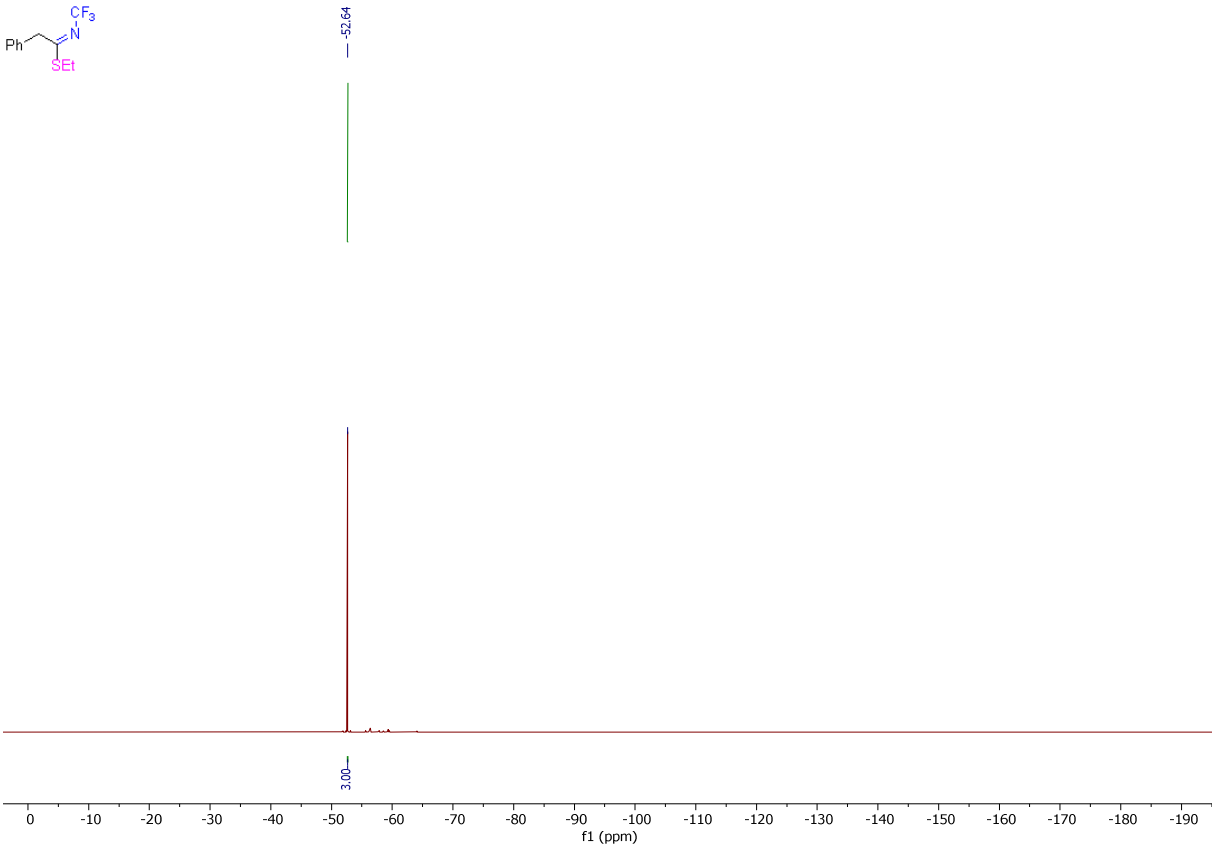
^{1}H NMR spectrum of **13a** ($CDCl_3$, 400 MHz)



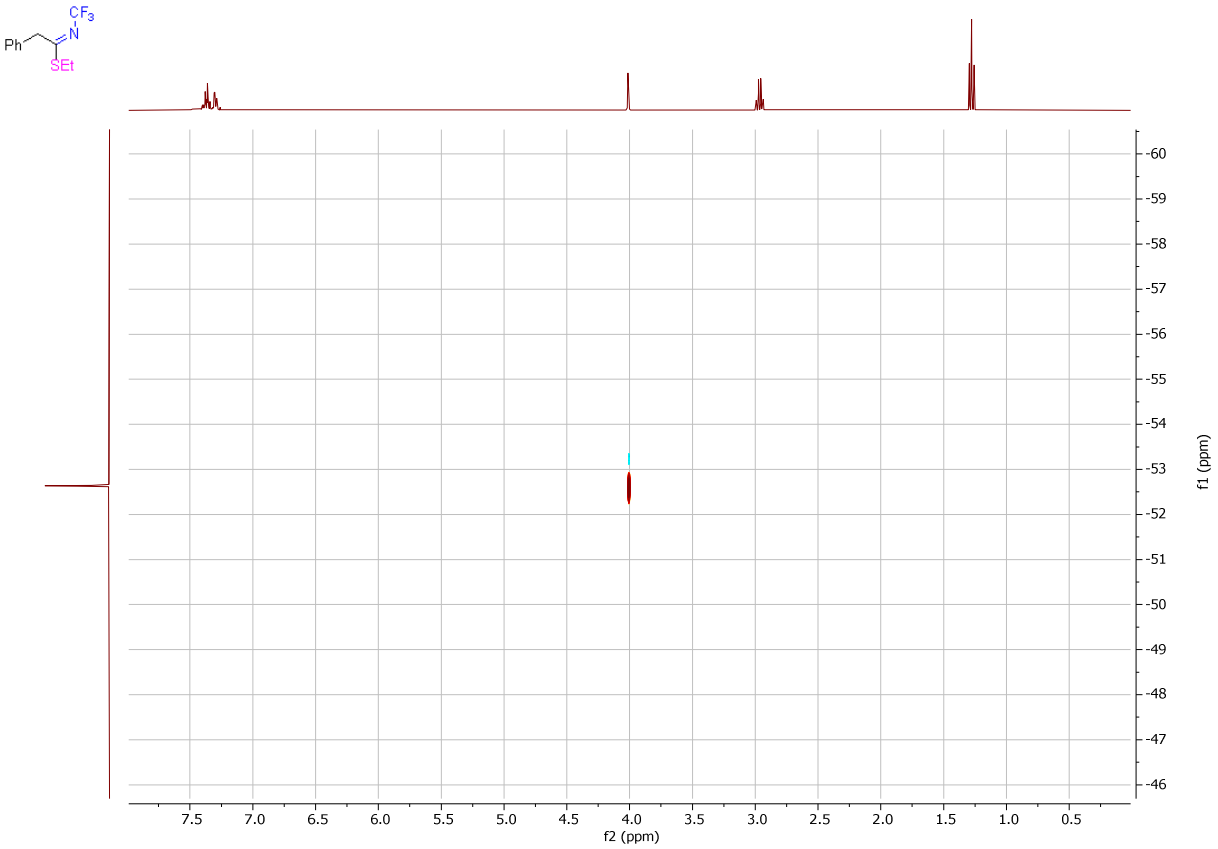
^{13}C NMR spectrum of **13a** ($CDCl_3$, 101 MHz)



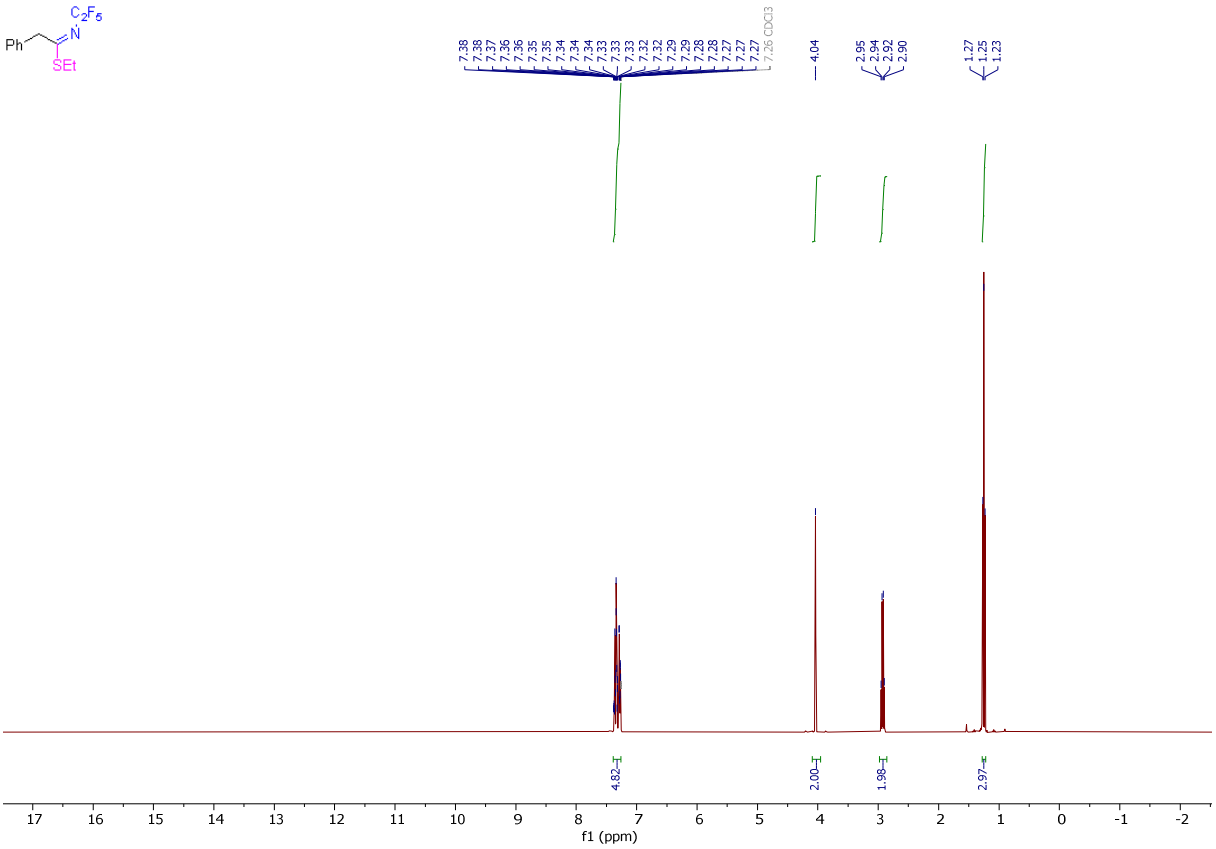
^{19}F NMR spectrum of **13a** ($CDCl_3$, 376 MHz)



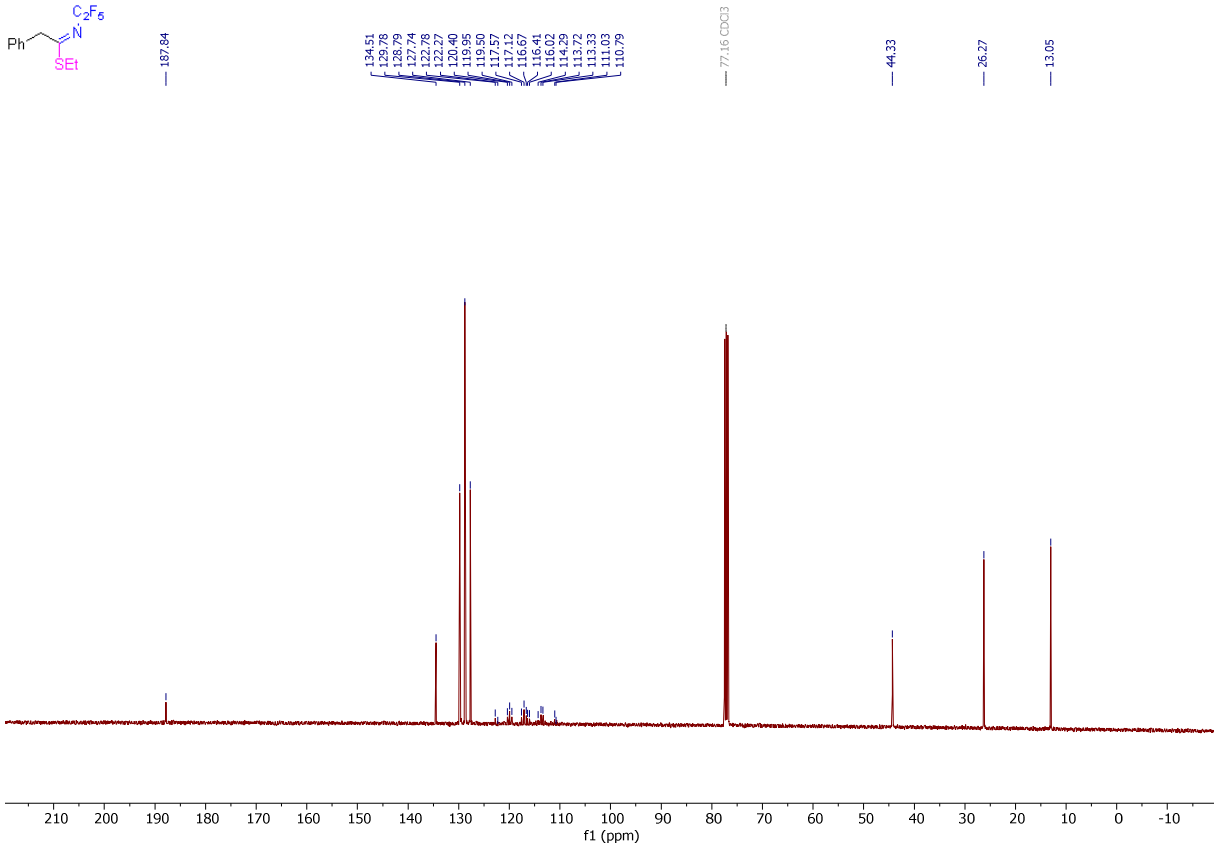
^{1}H-^{19}F HOESY NMR spectrum of **13a** ($CDCl_3$)



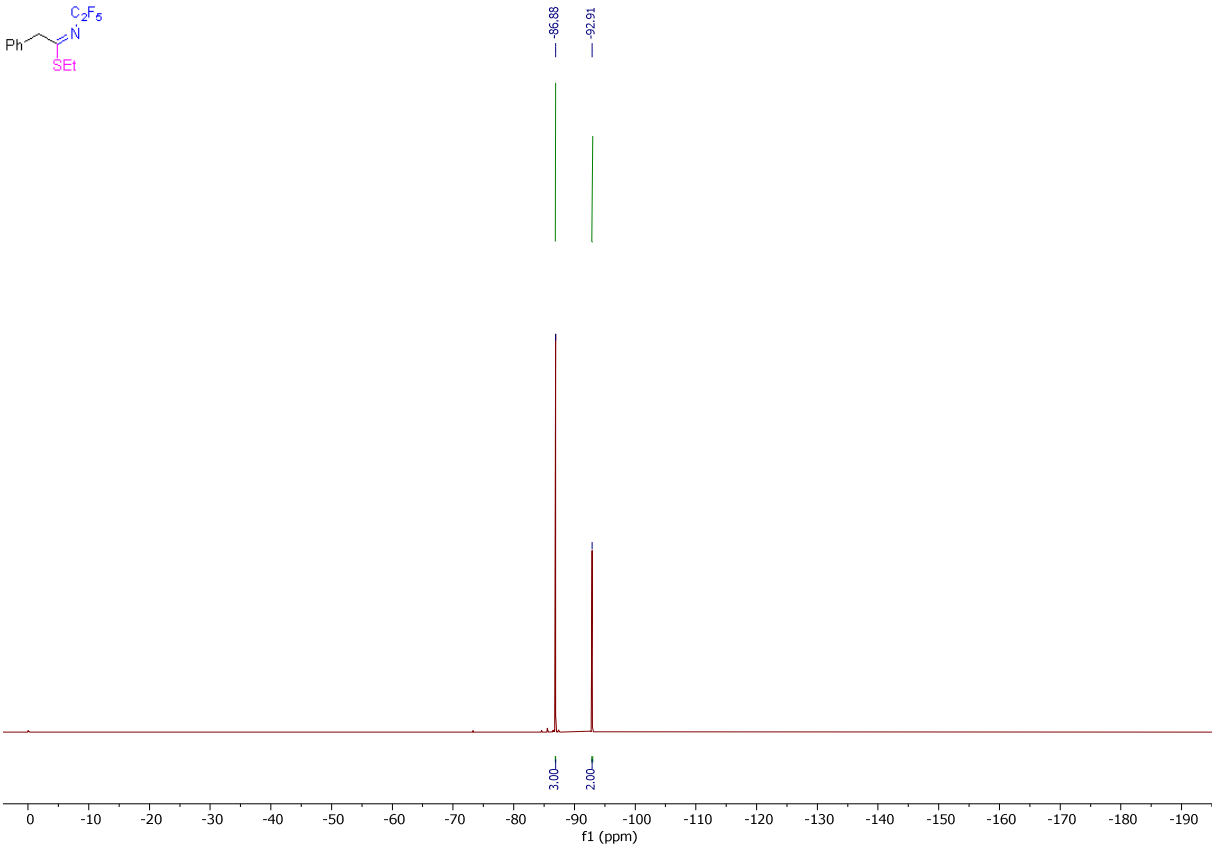
^{1}H NMR spectrum of **13b** ($CDCl_3$, 400 MHz)



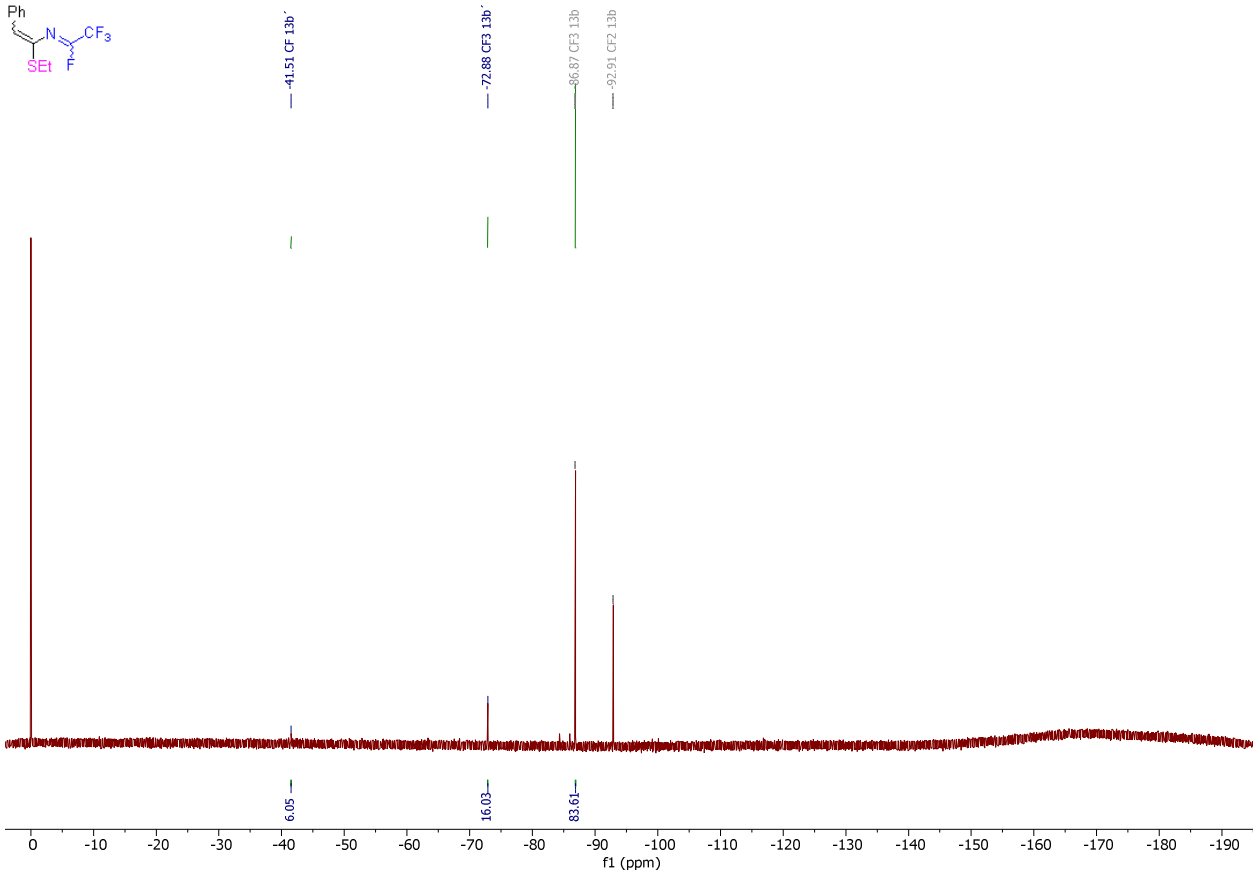
^{13}C NMR spectrum of **13b** ($CDCl_3$, 101 MHz)



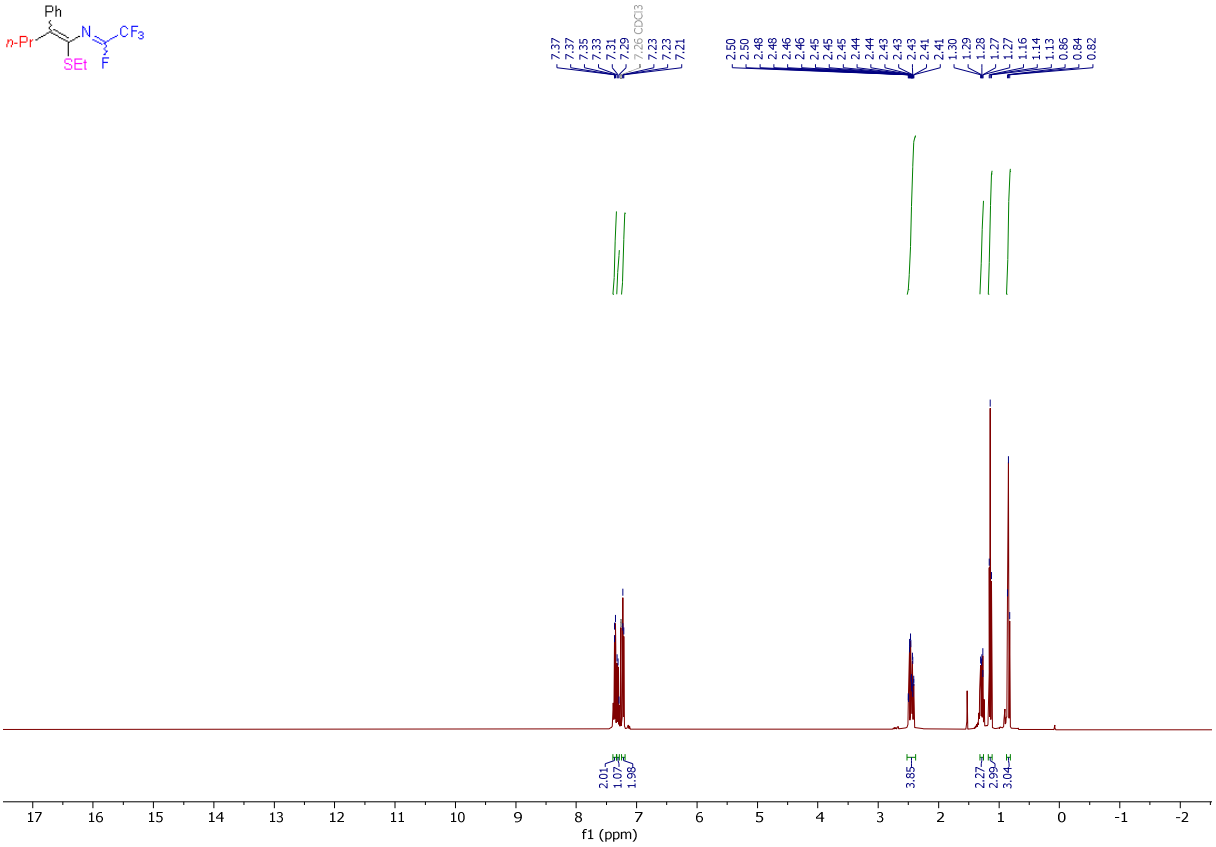
^{19}F NMR spectrum of **13b** ($CDCl_3$, 376 MHz)



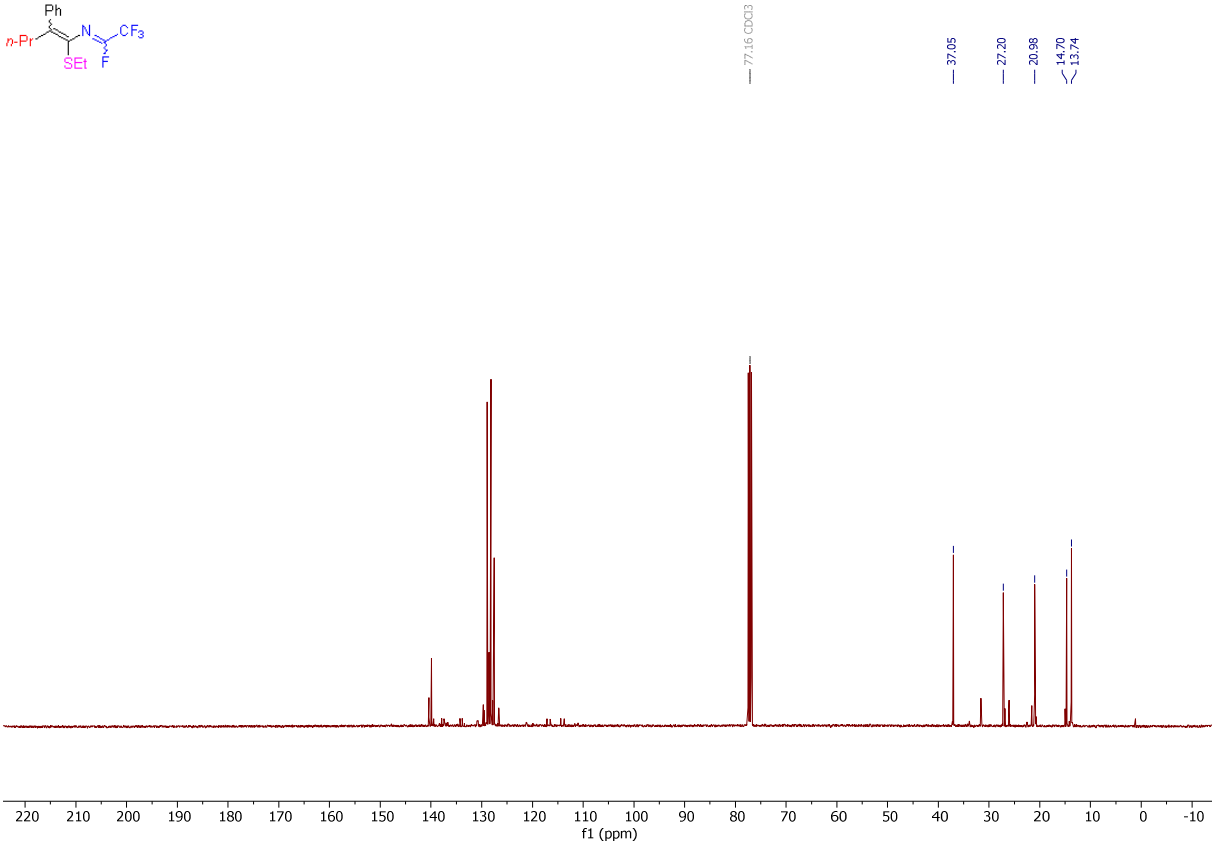
^{19}F NMR spectrum of **13b'** ($CDCl_3$, 376 MHz)



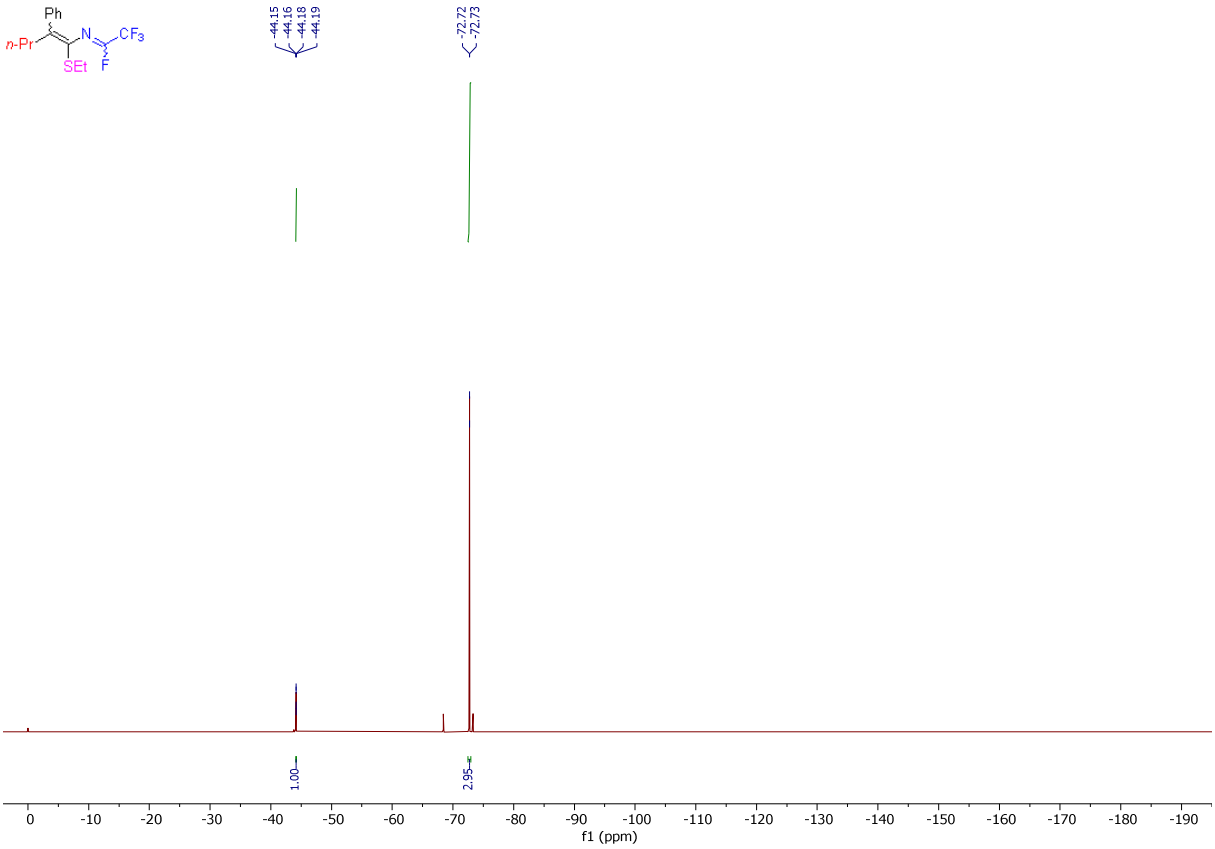
^{1}H NMR spectrum of **13c'** ($CDCl_3$, 400 MHz)



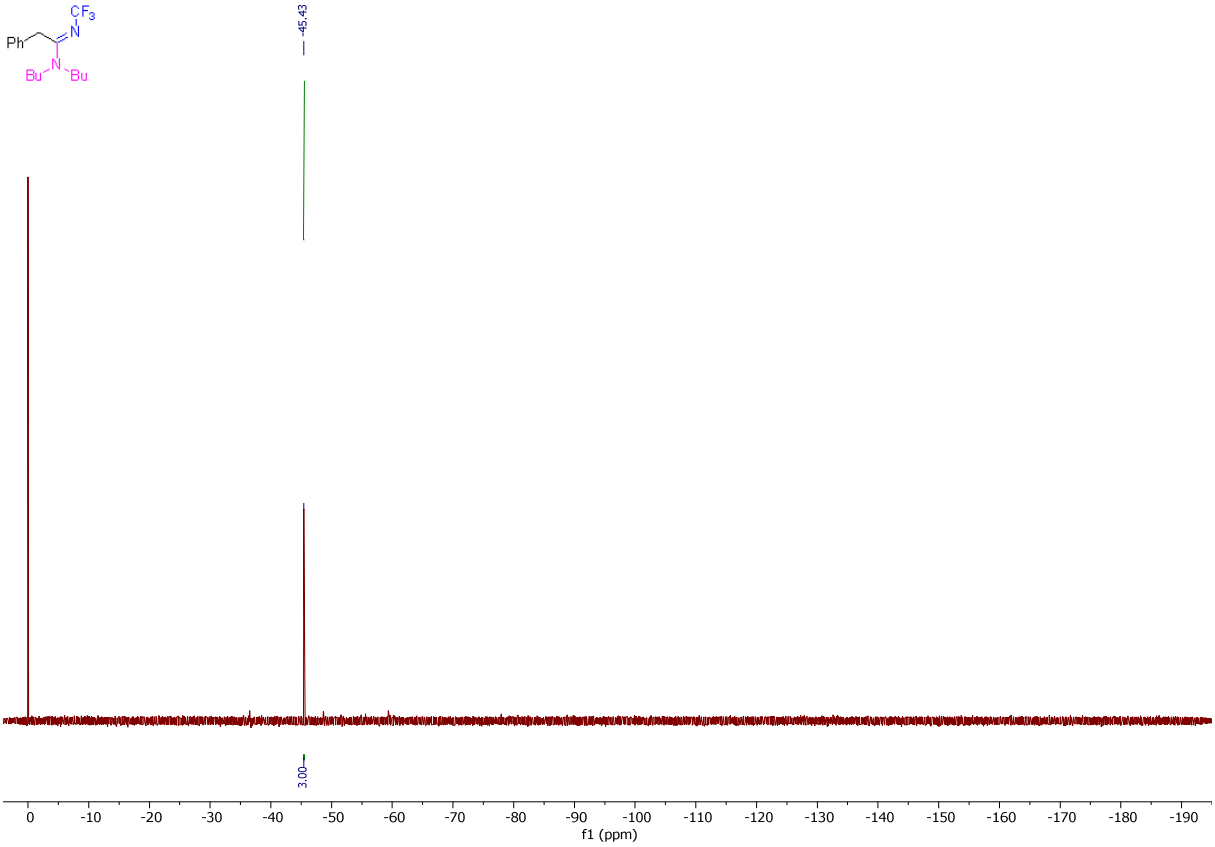
^{13}C NMR spectrum of **13c'** ($CDCl_3$, 101 MHz)



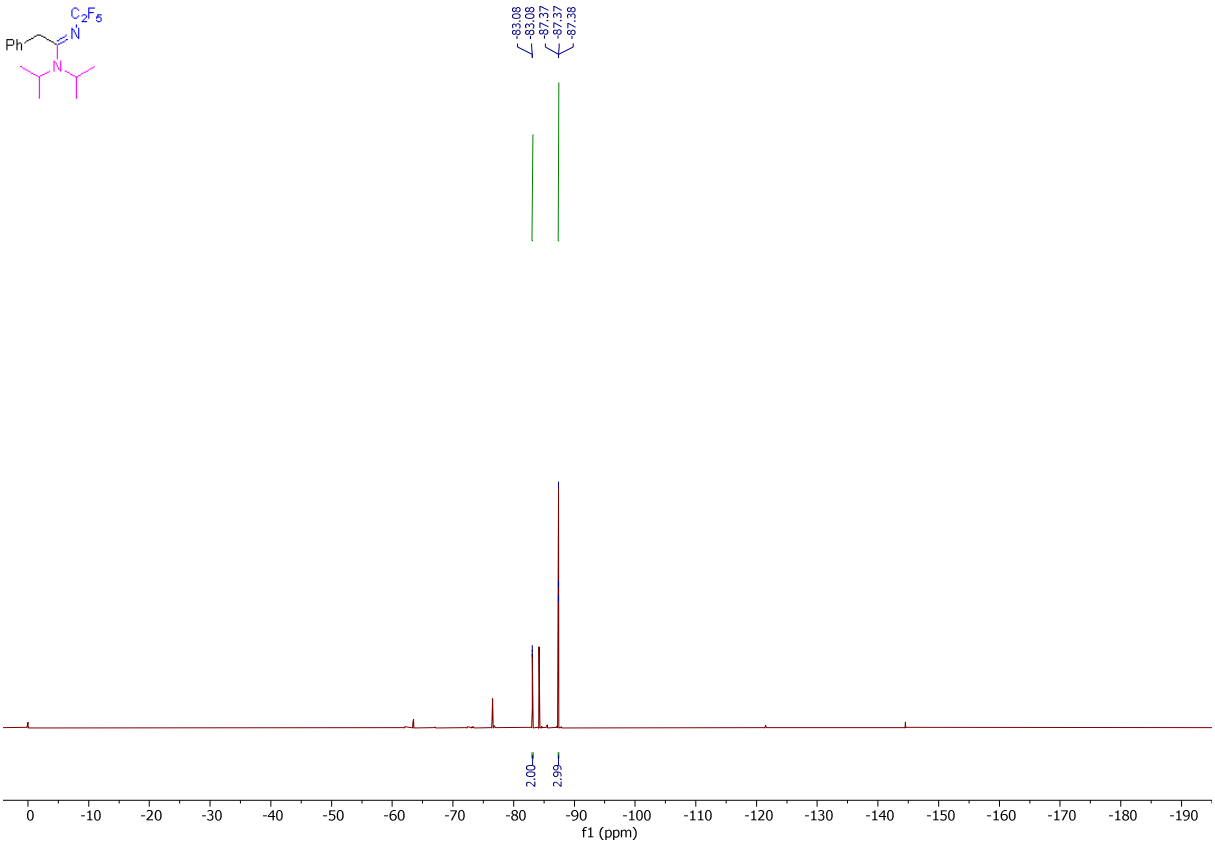
^{19}F NMR spectrum of **13c'** ($CDCl_3$, 376 MHz)



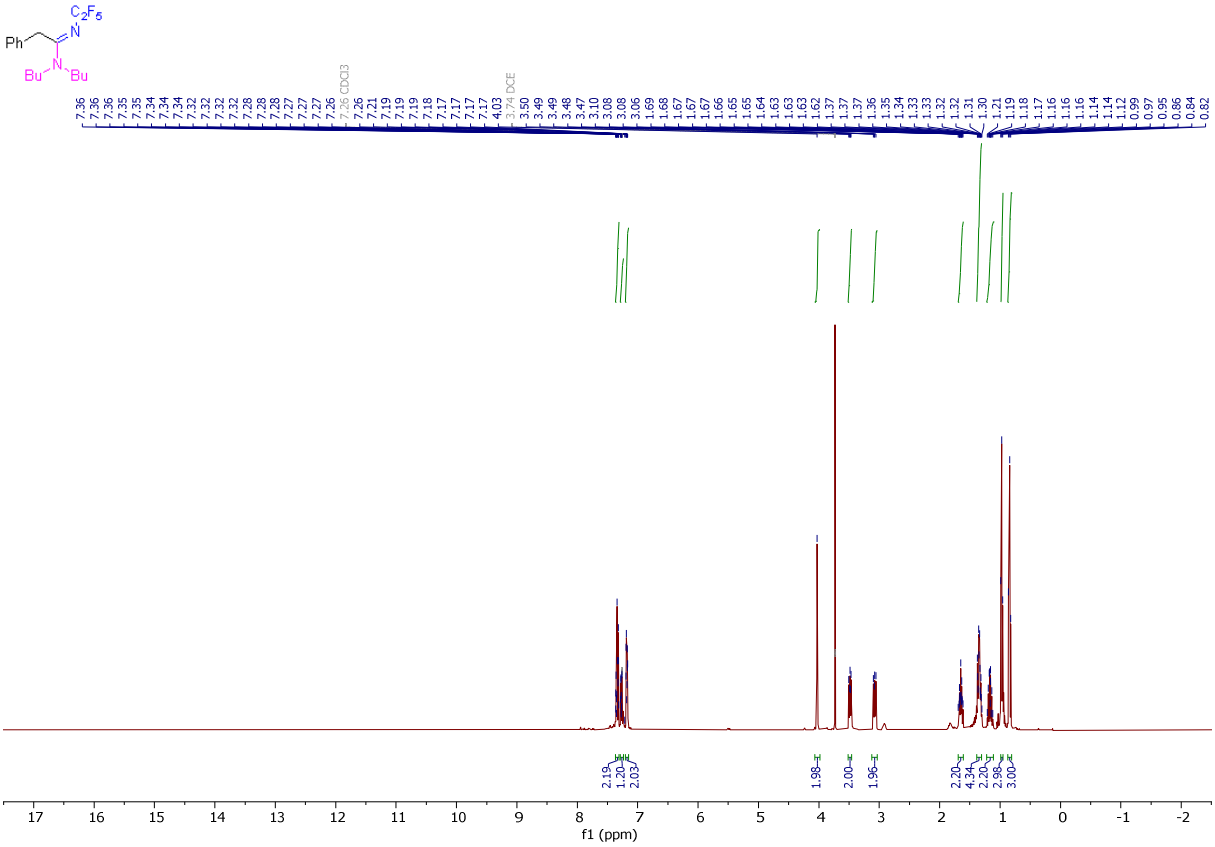
^{19}F NMR spectrum of **14a** ($CDCl_3$, 376 MHz)



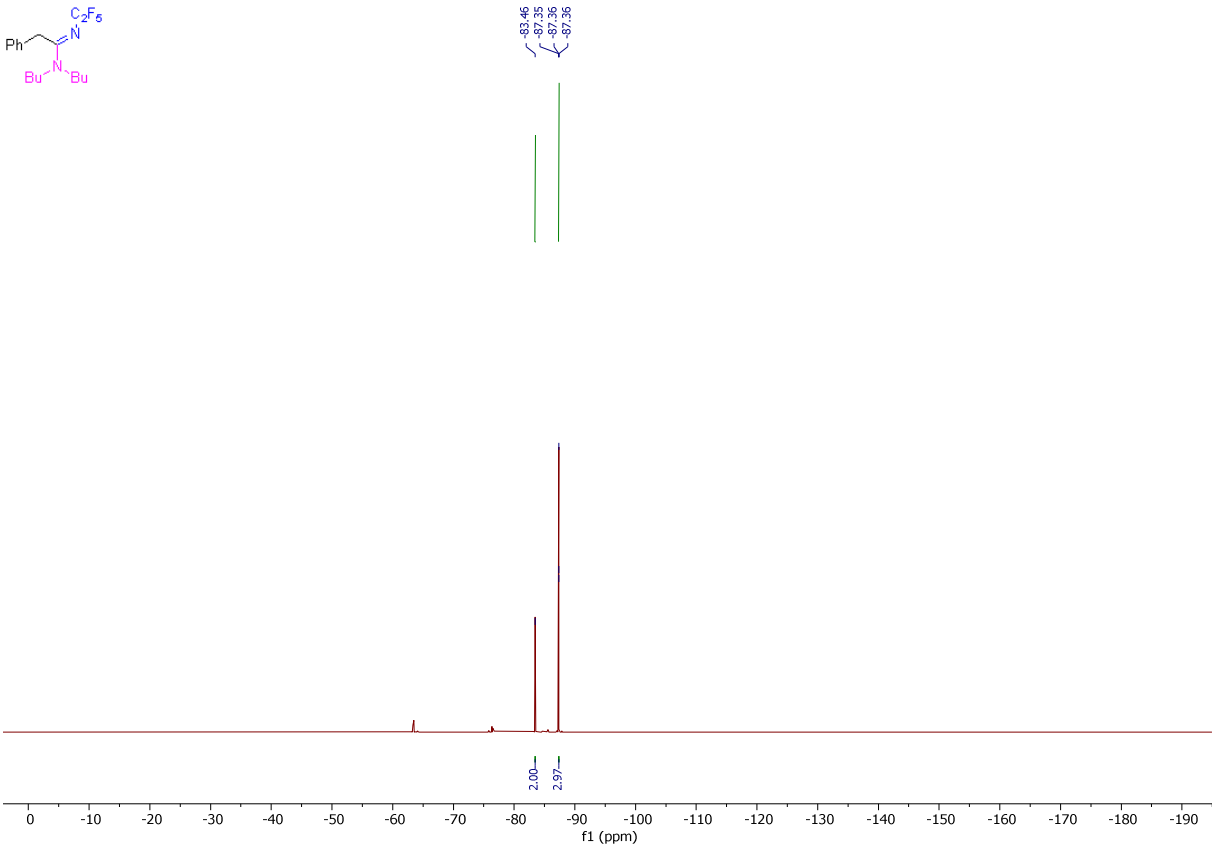
^{19}F NMR spectrum of **14b** ($CDCl_3$, 376 MHz)



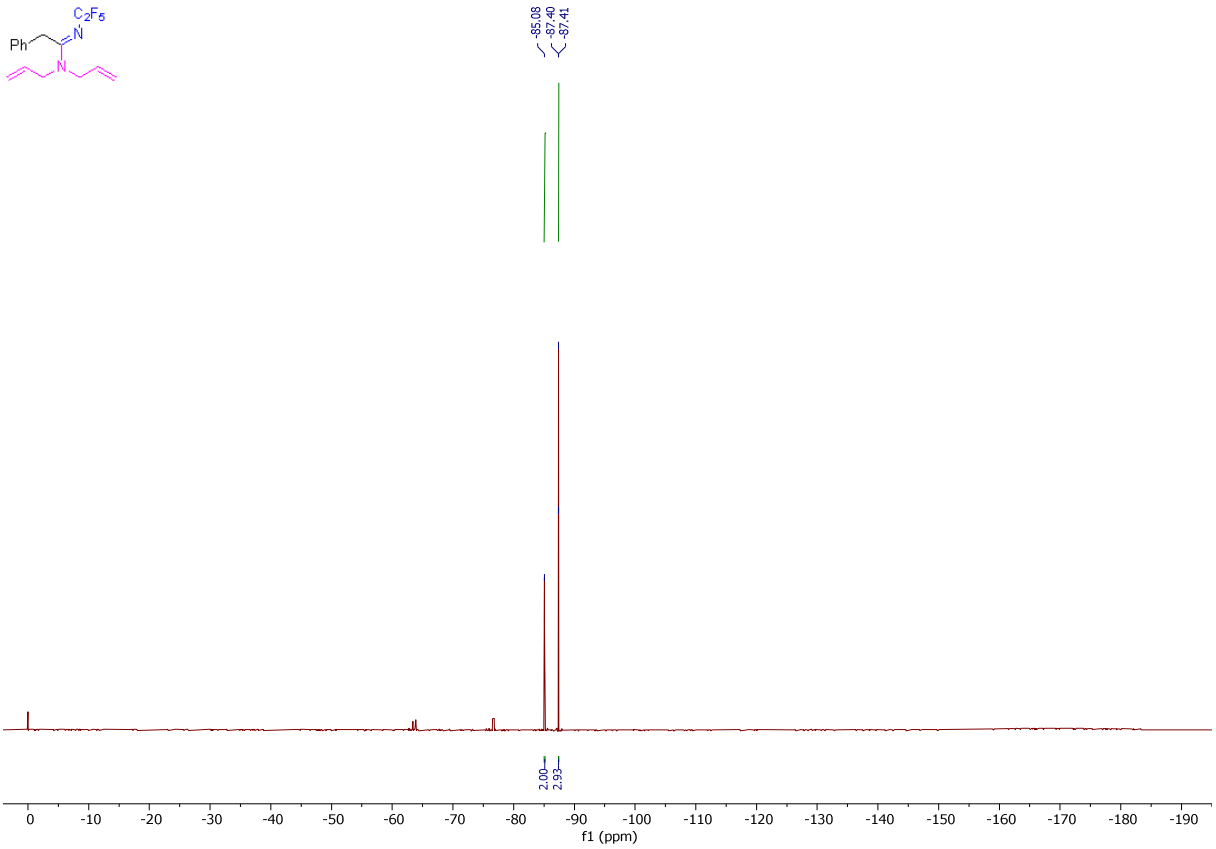
^{1}H NMR spectrum of **14c** ($CDCl_3$, 400 MHz)



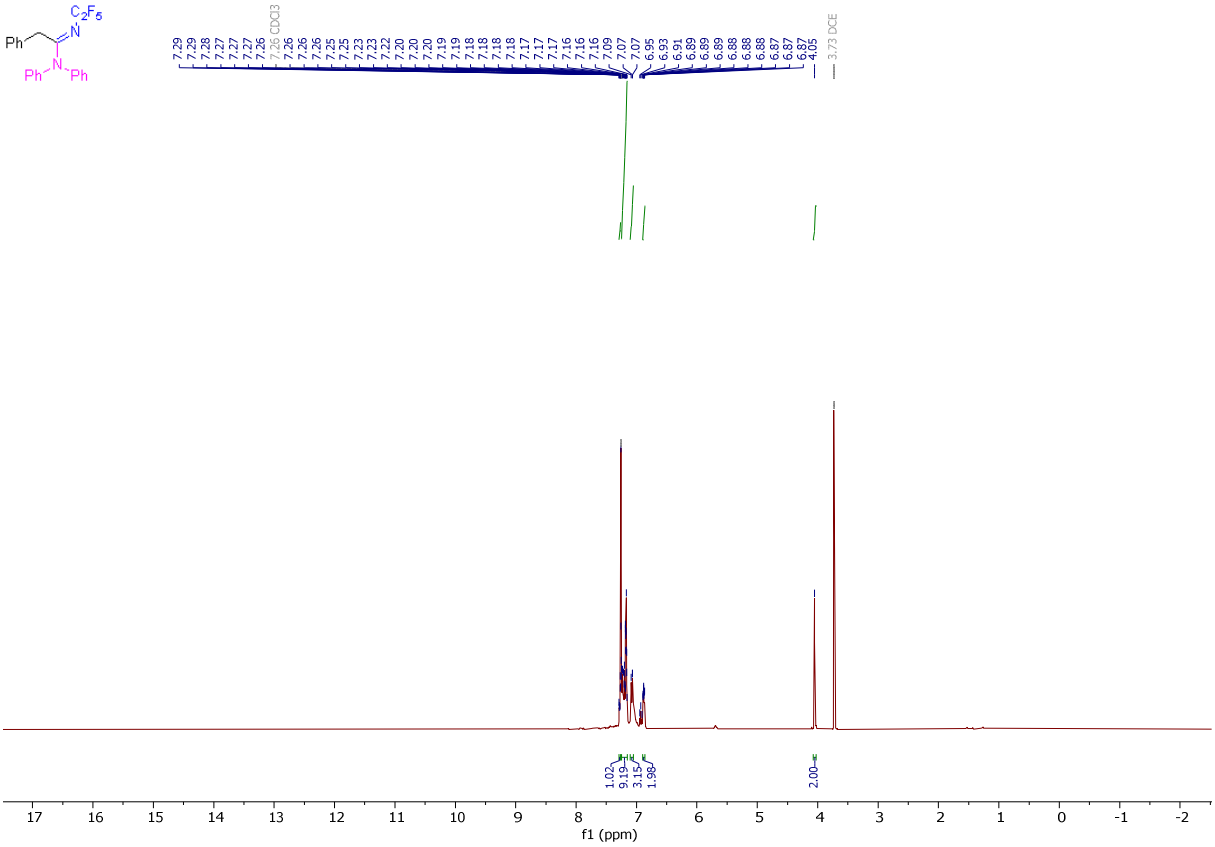
^{19}F NMR spectrum of **14c** ($CDCl_3$, 376 MHz)



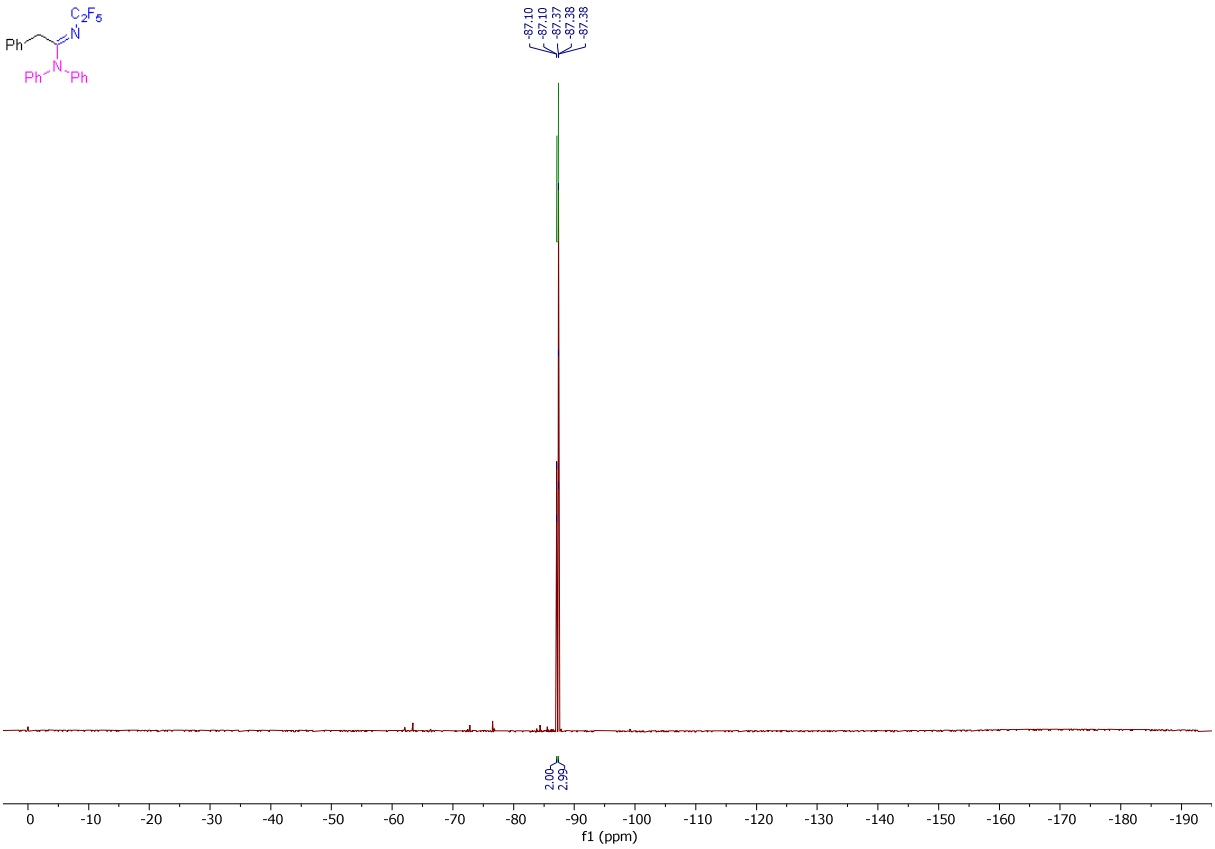
^{19}F NMR spectrum of **14d** ($CDCl_3$, 376 MHz)



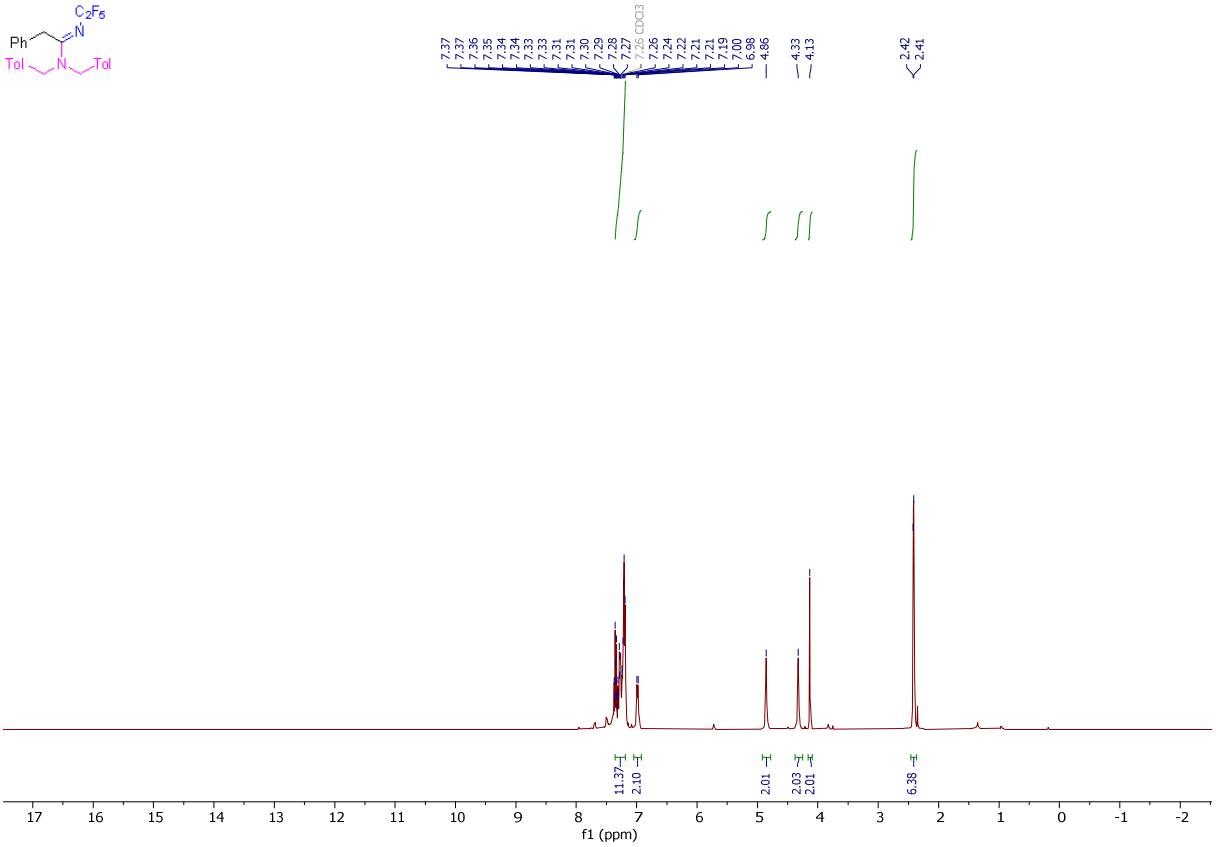
^{1}H NMR spectrum of **14e** ($CDCl_3$, 400 MHz)



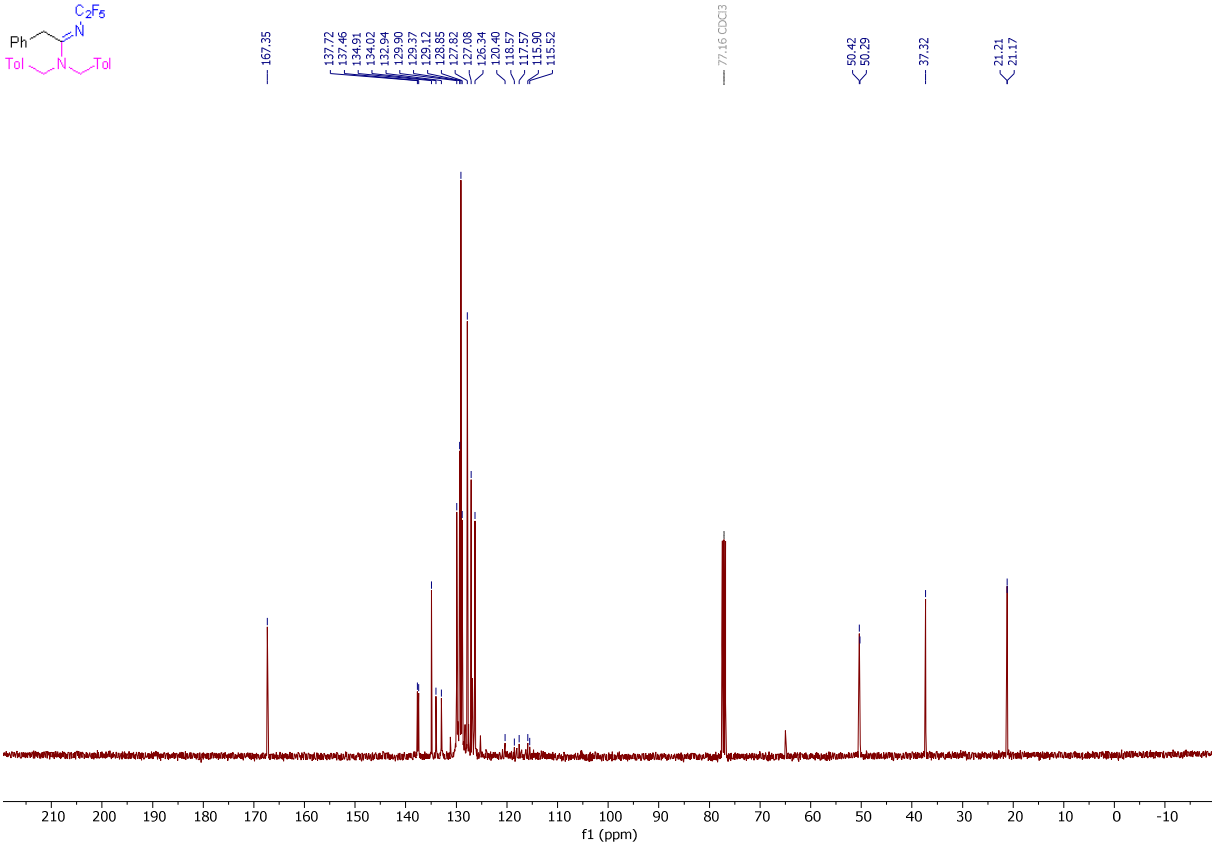
^{19}F NMR spectrum of **14e** ($CDCl_3$, 376 MHz)



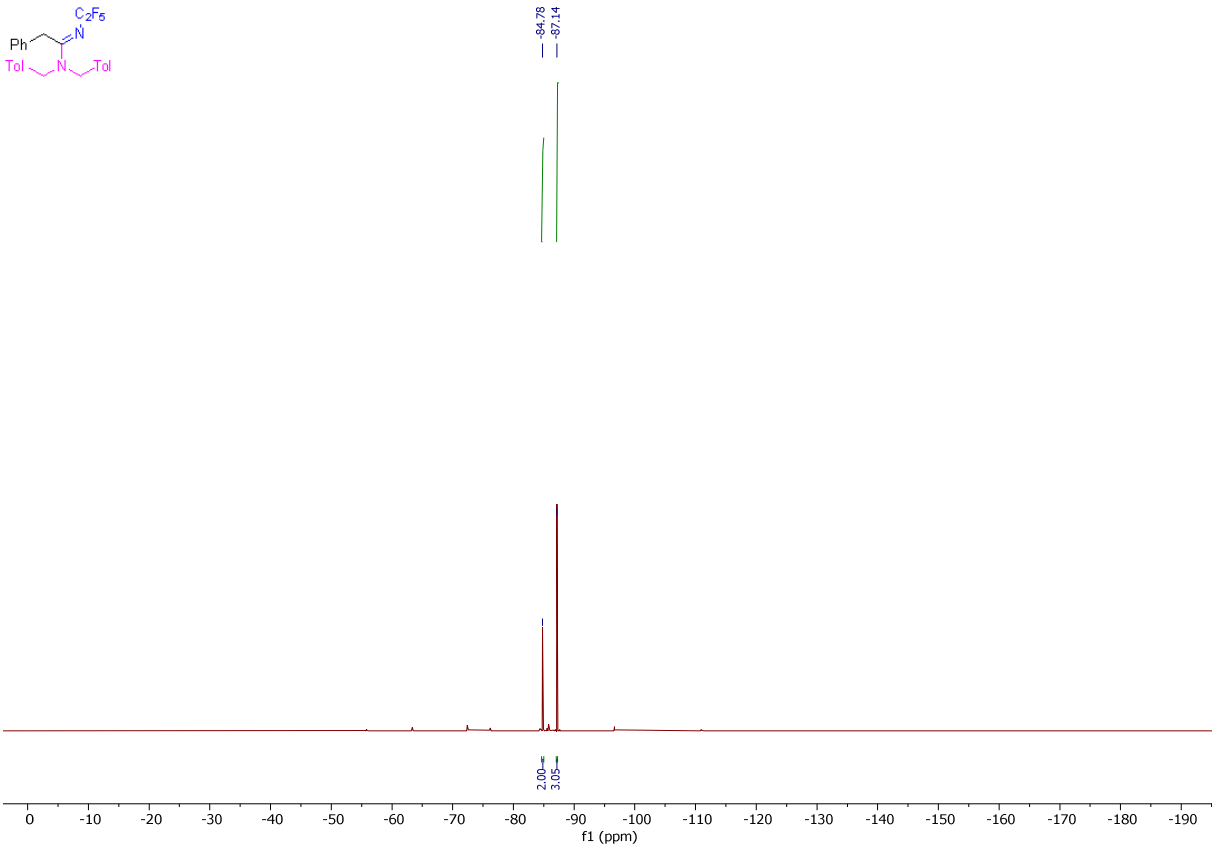
^{1}H NMR spectrum of **14f** ($CDCl_3$, 400 MHz)



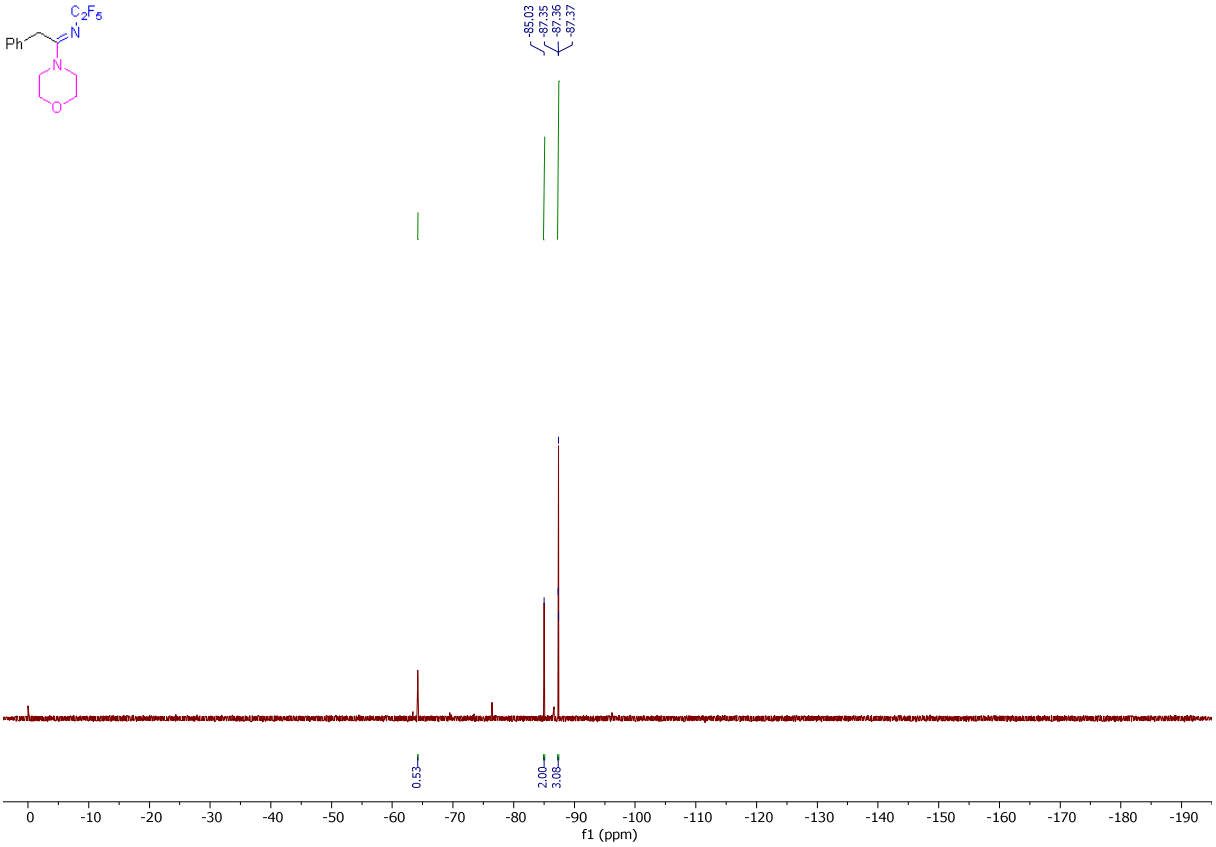
^{13}C NMR spectrum of **14f** ($CDCl_3$, 101 MHz)



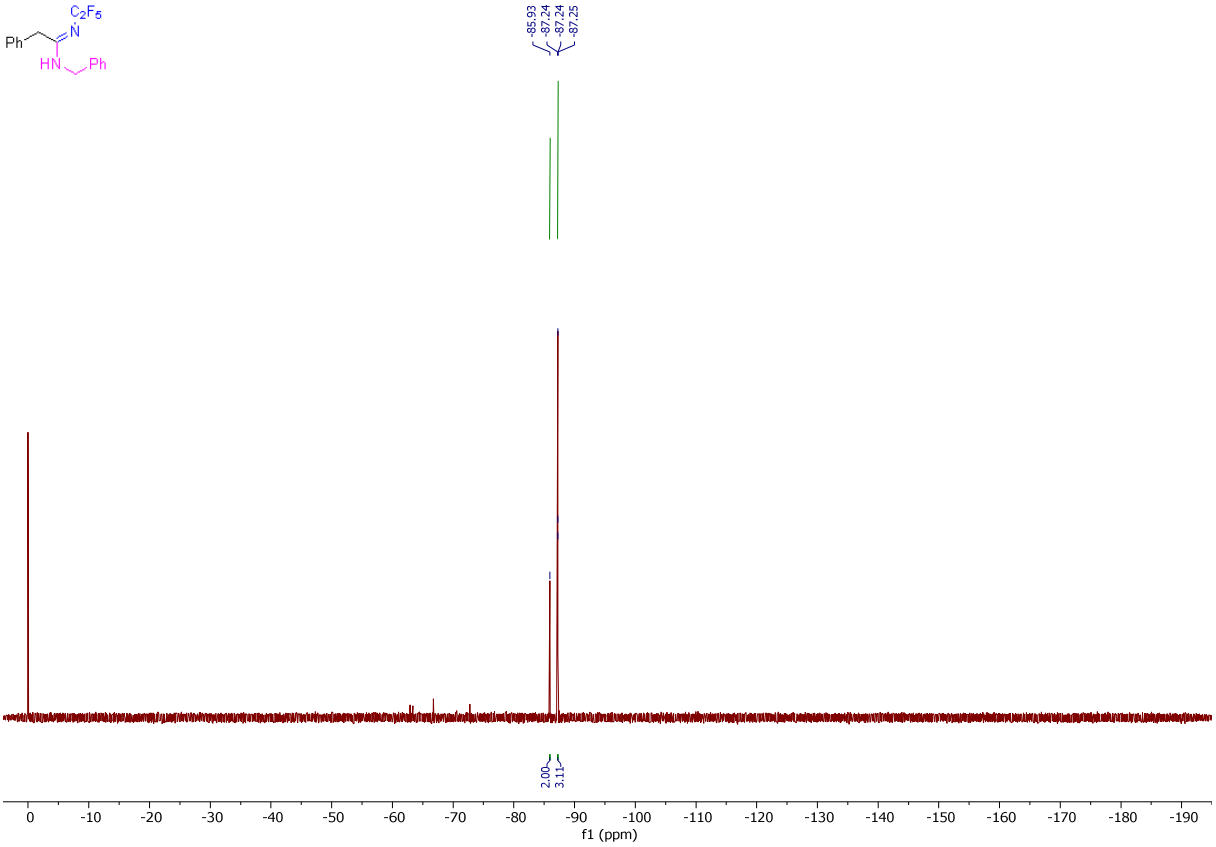
^{19}F NMR spectrum of **14f** ($CDCl_3$, 376 MHz)



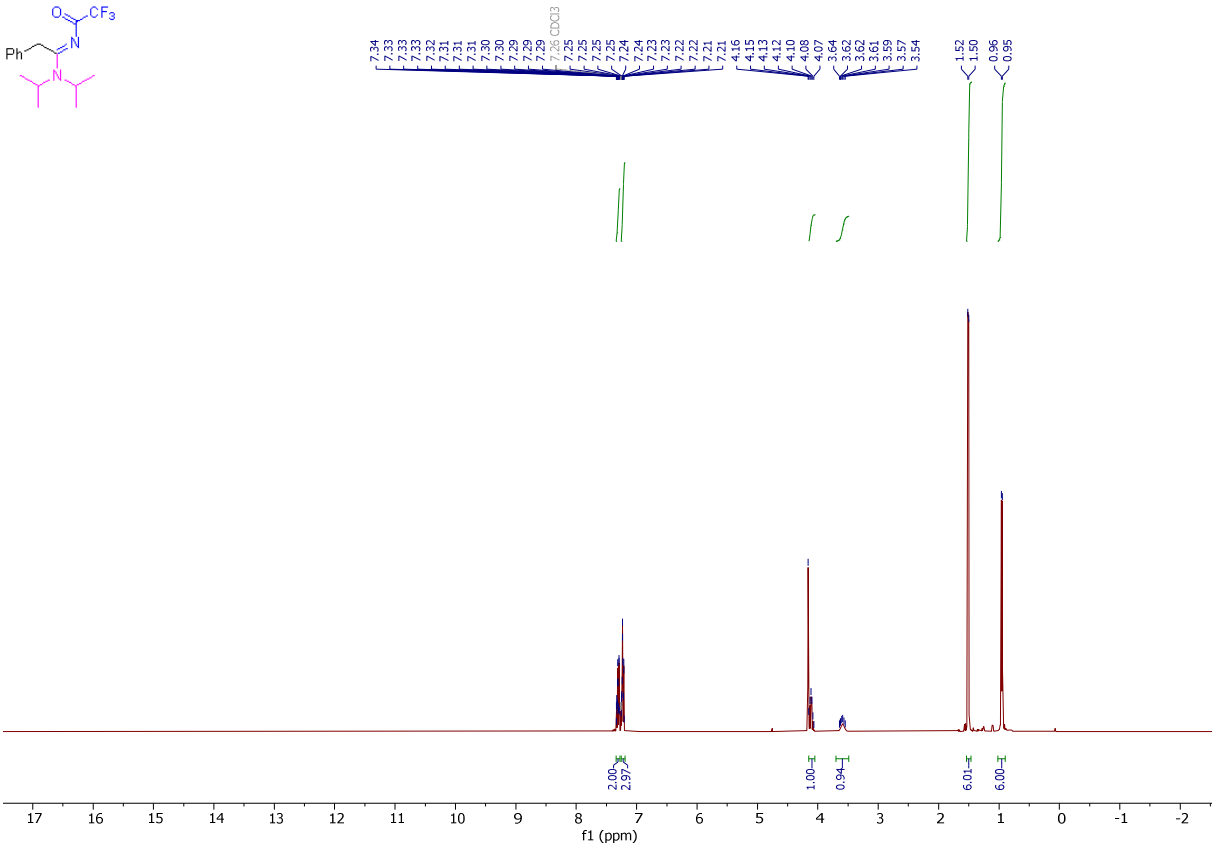
^{19}F NMR spectrum of **14g** ($CDCl_3$, 376 MHz)



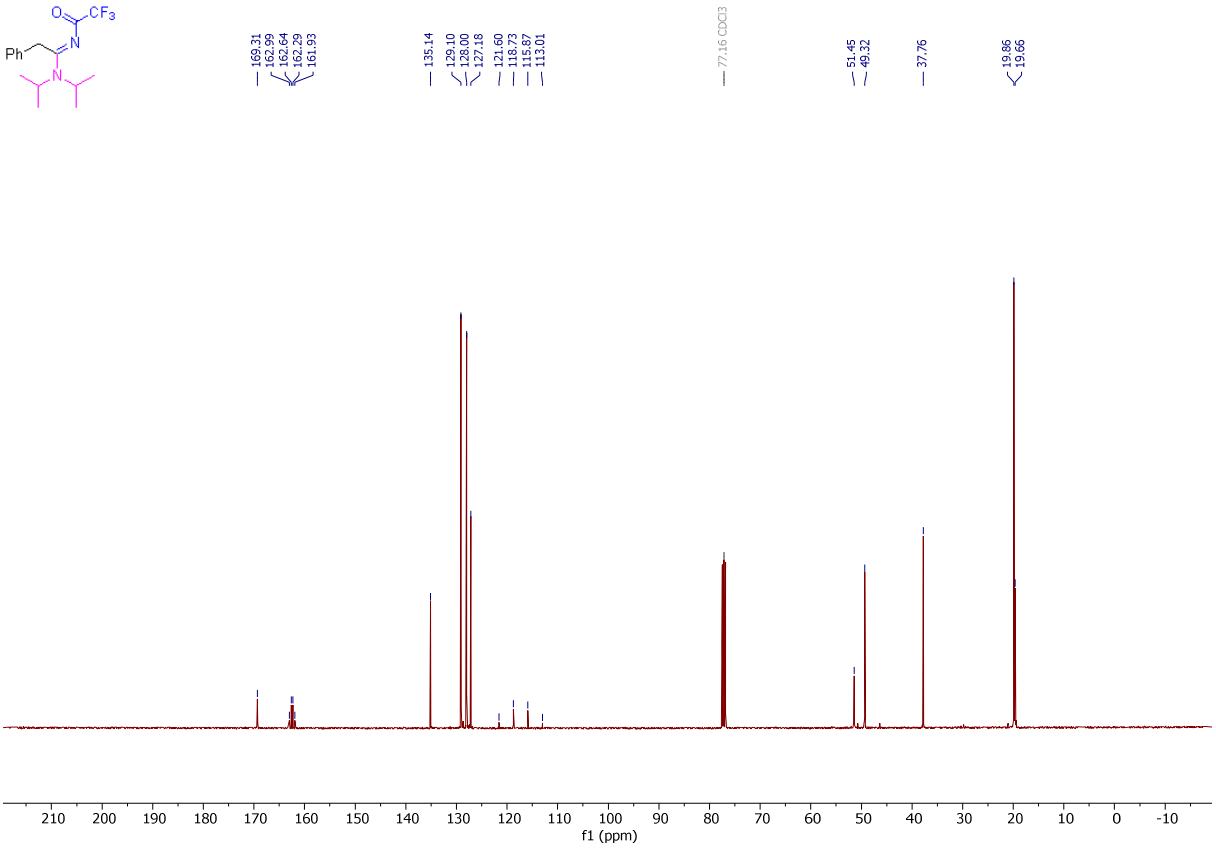
^{19}F NMR spectrum of **14h** ($CDCl_3$, 376 MHz)



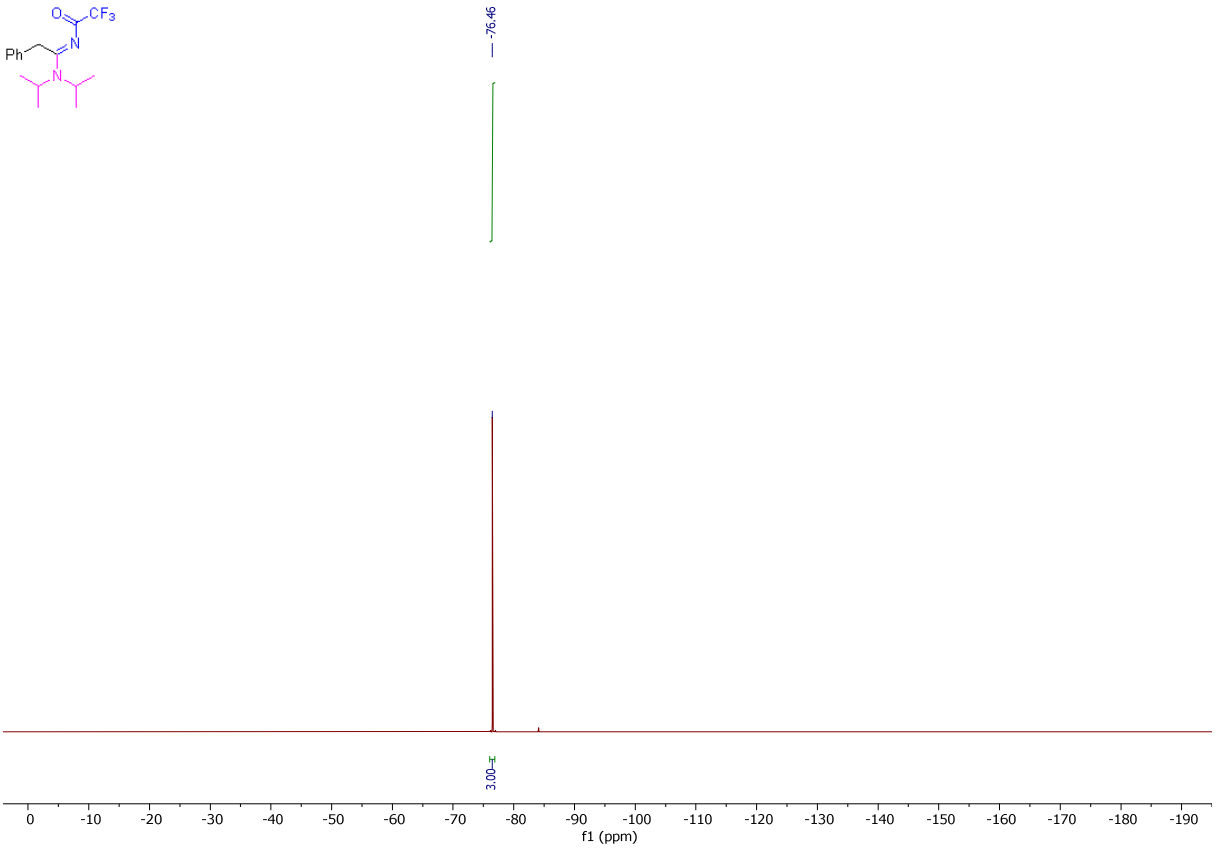
^{1}H NMR spectrum of **15b** ($CDCl_3$, 400 MHz)



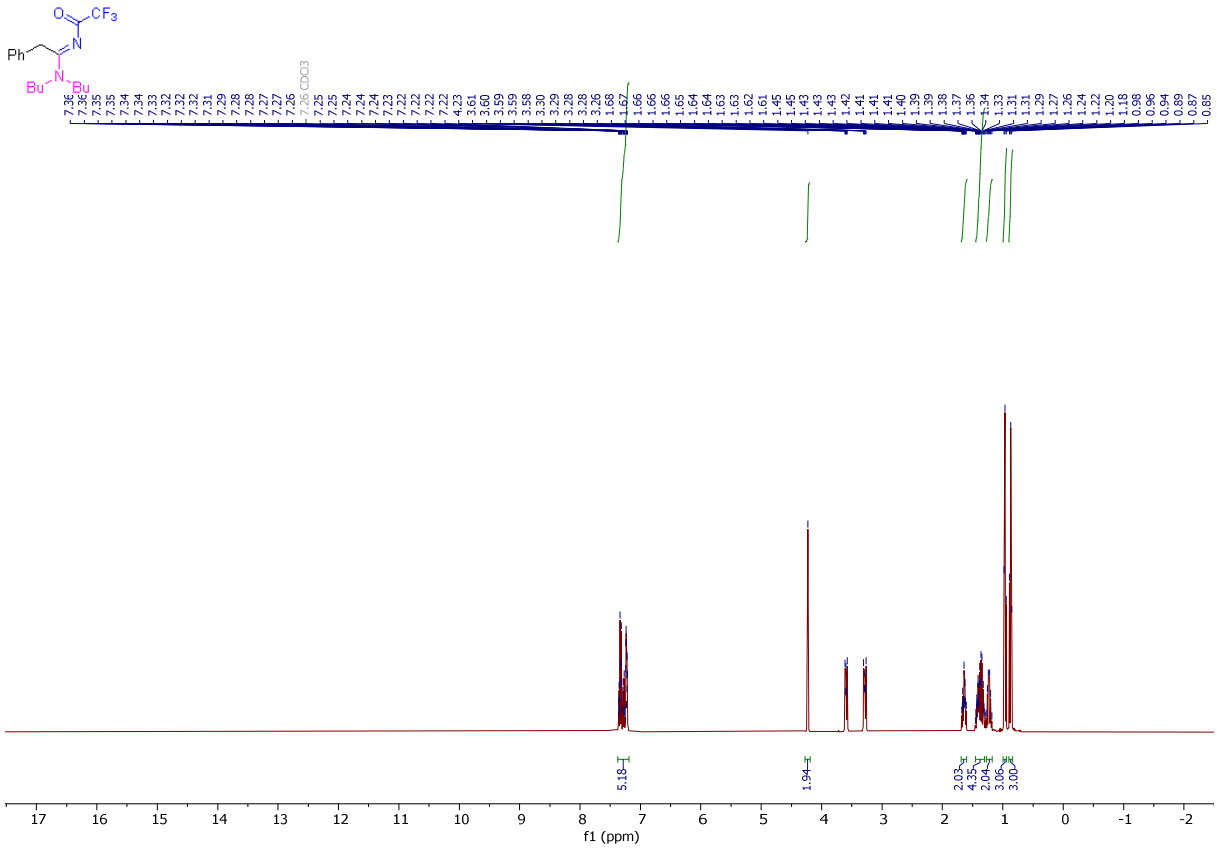
^{13}C NMR spectrum of **15b** ($CDCl_3$, 101 MHz)



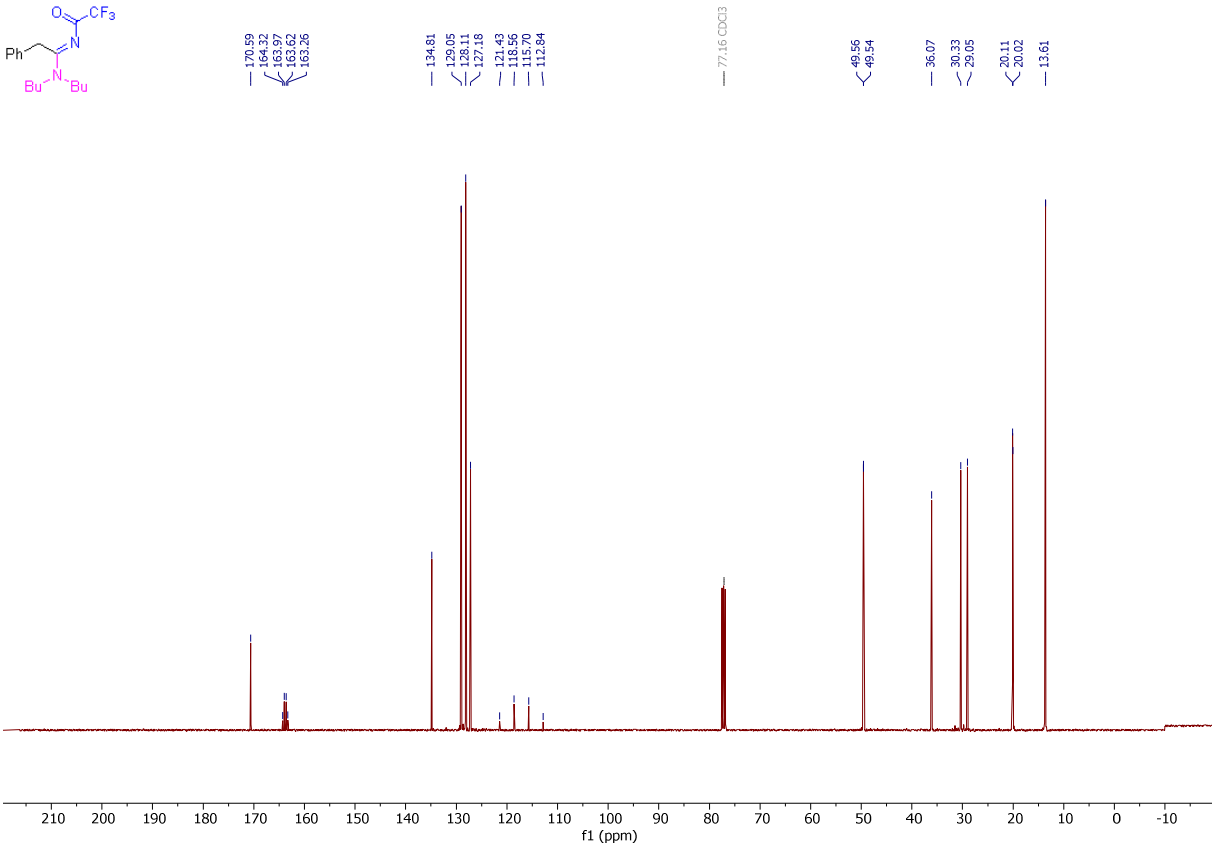
^{19}F NMR spectrum of **15b** ($CDCl_3$, 376 MHz)



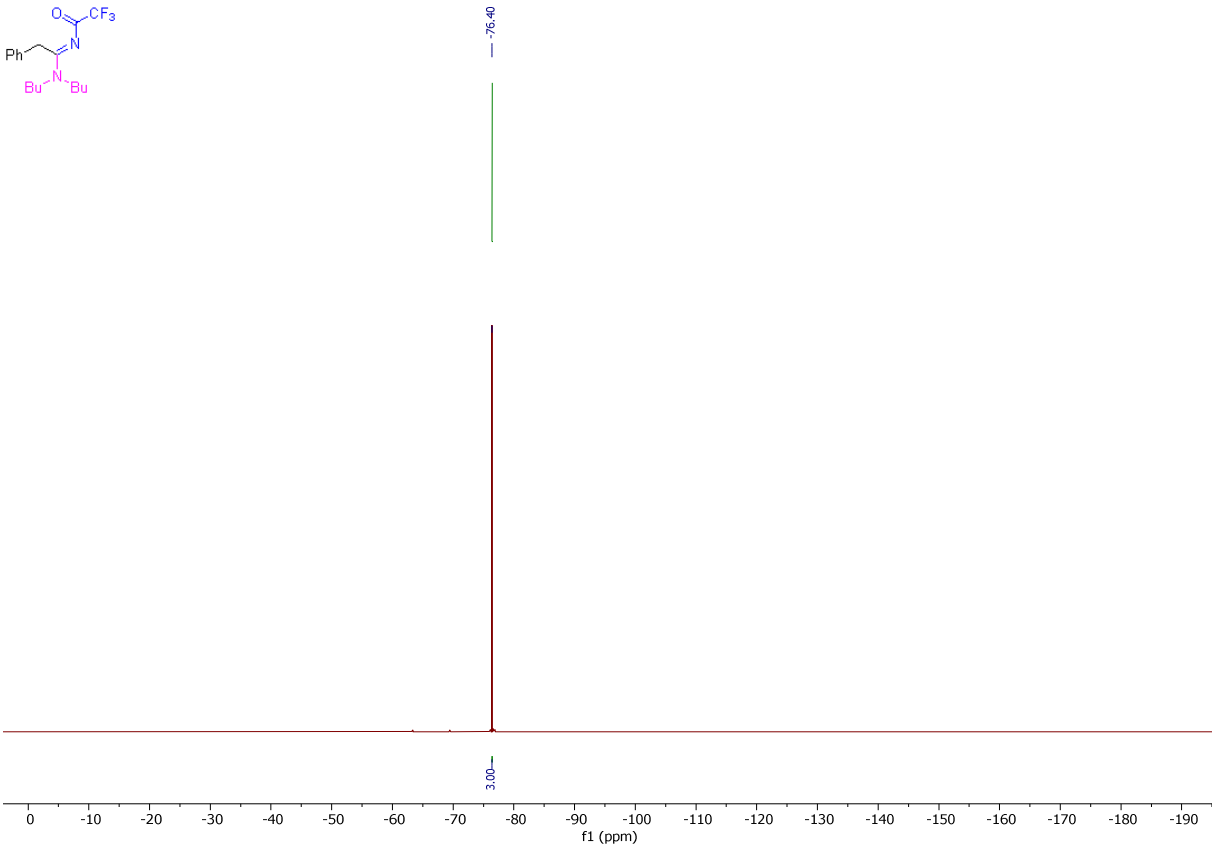
^{1}H NMR spectrum of **15c** ($CDCl_3$, 400 MHz)



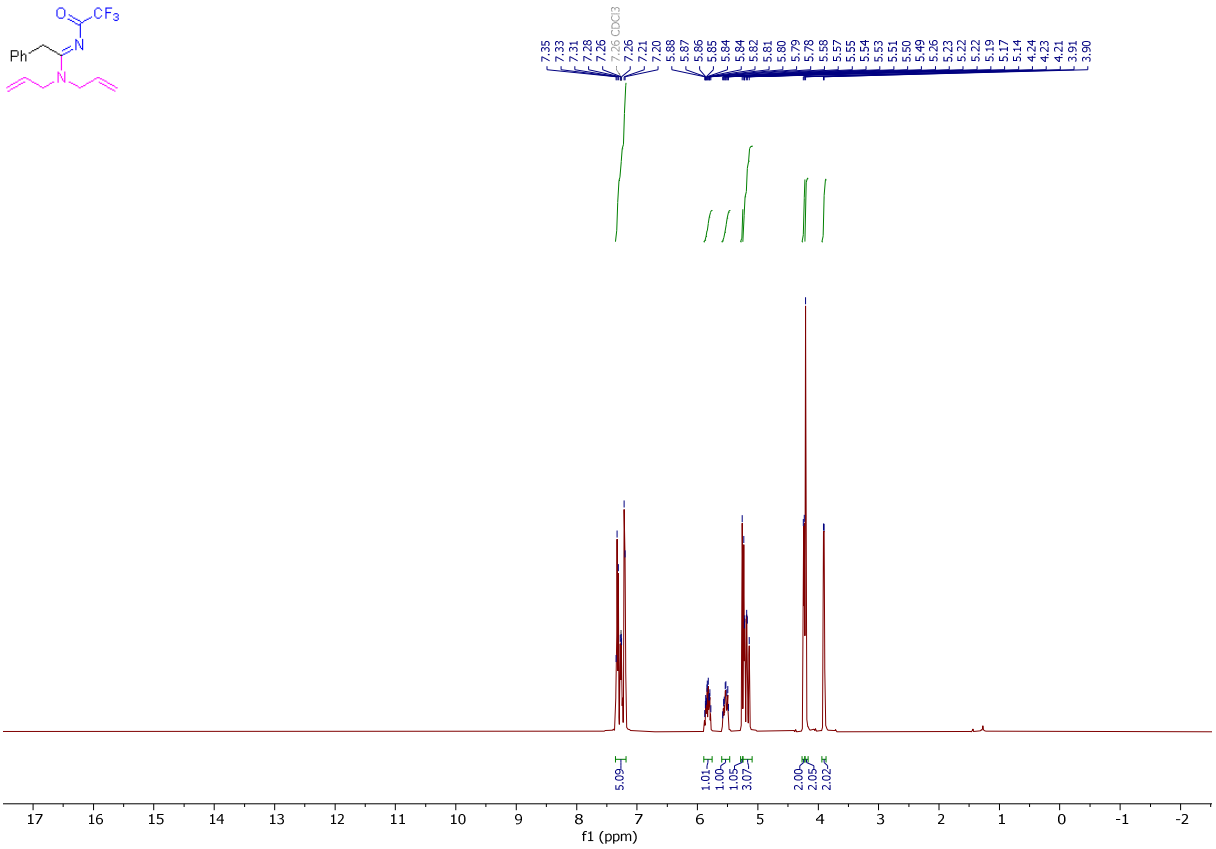
^{13}C NMR spectrum of **15c** ($CDCl_3$, 101 MHz)



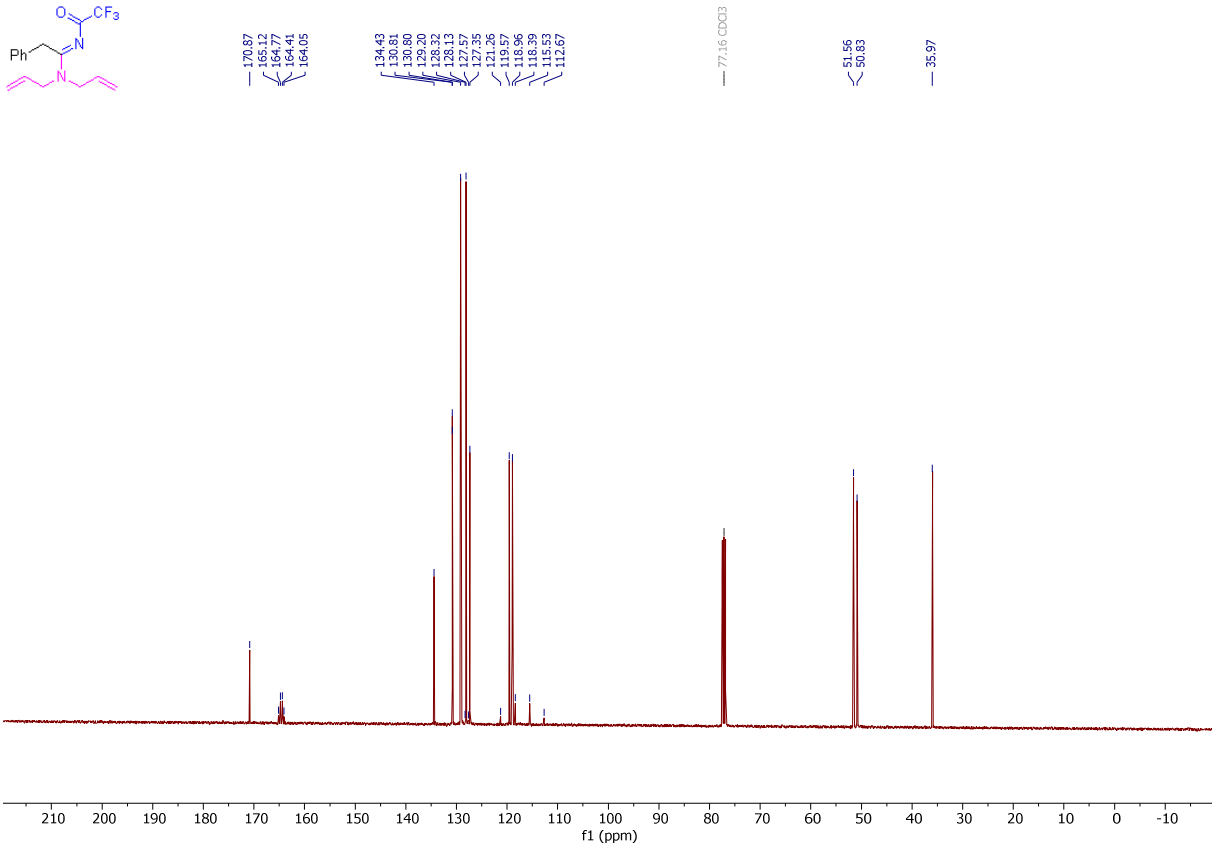
^{19}F NMR spectrum of **15c** ($CDCl_3$, 376 MHz)



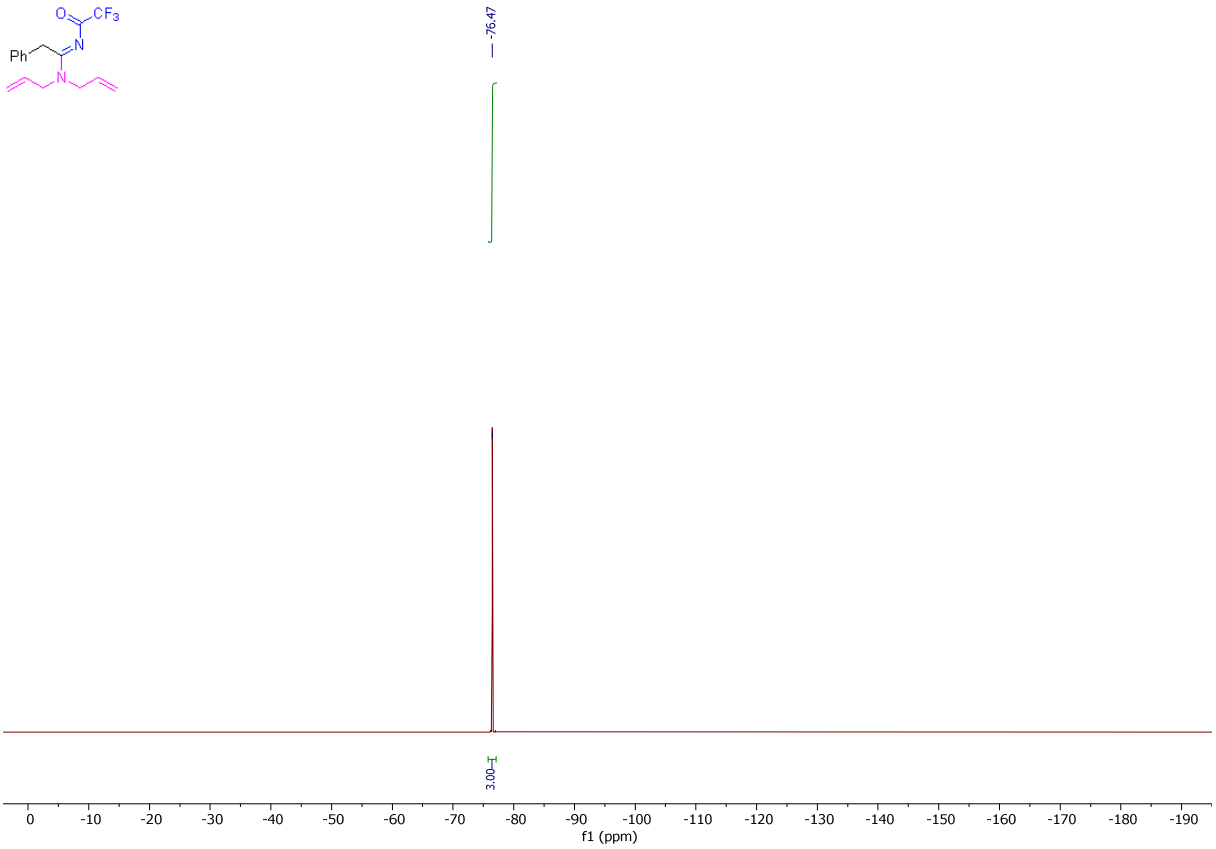
^{1}H NMR spectrum of **15d** ($CDCl_3$, 400 MHz)



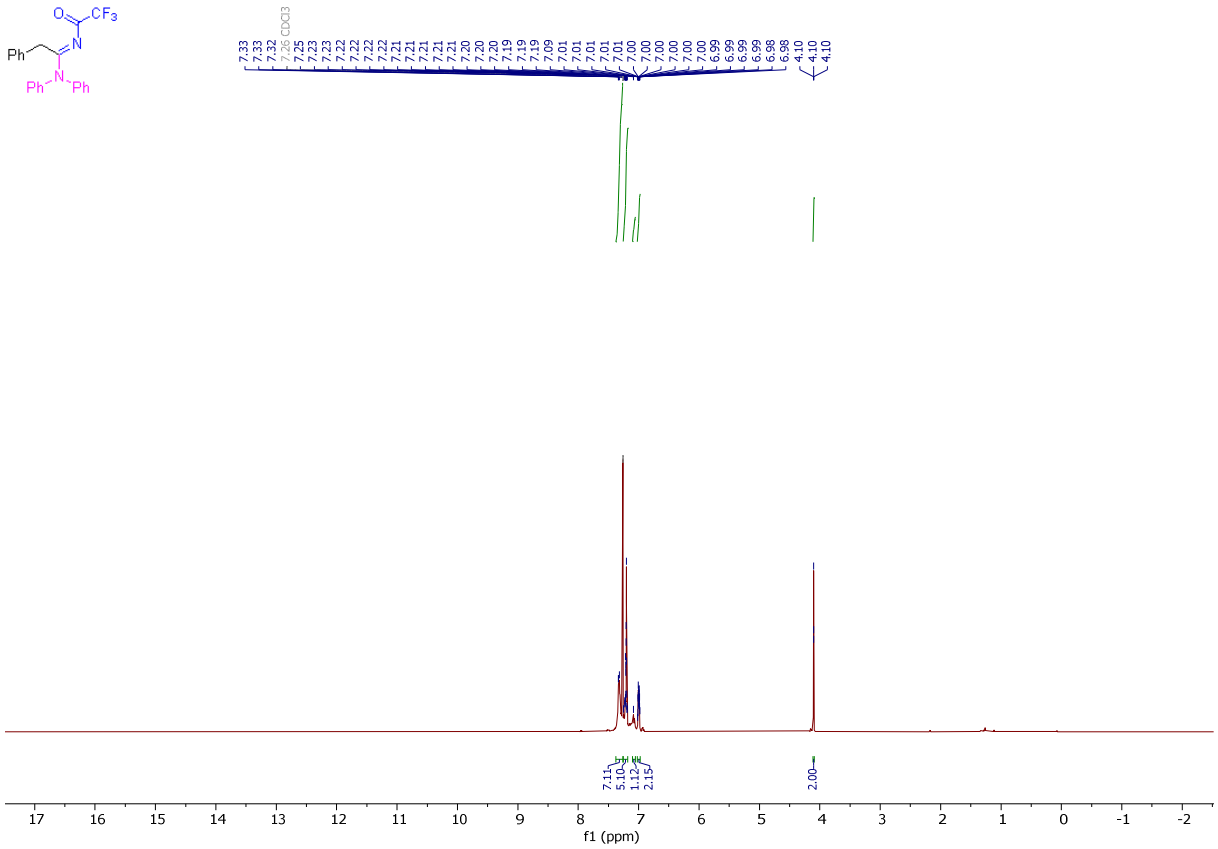
^{13}C NMR spectrum of **15d** ($CDCl_3$, 101 MHz)



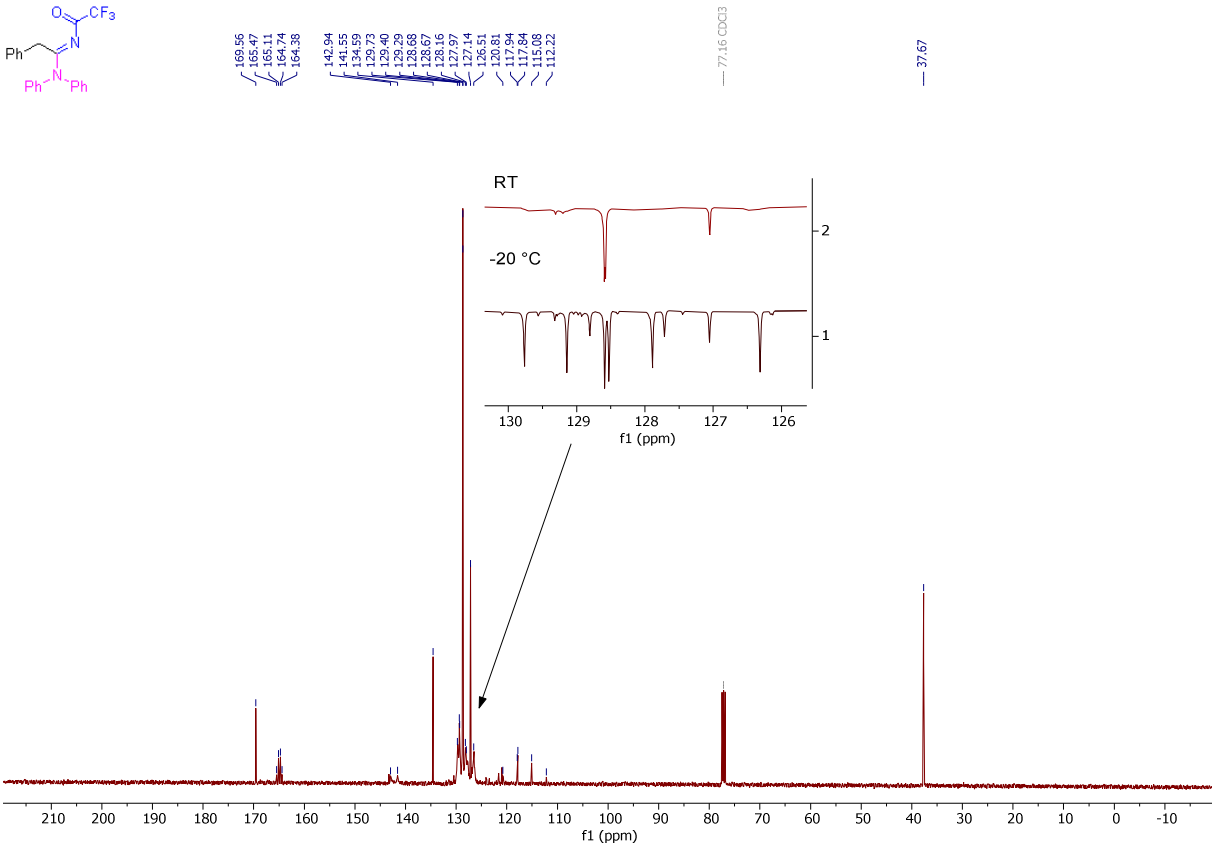
^{19}F NMR spectrum of **15d** ($CDCl_3$, 376 MHz)



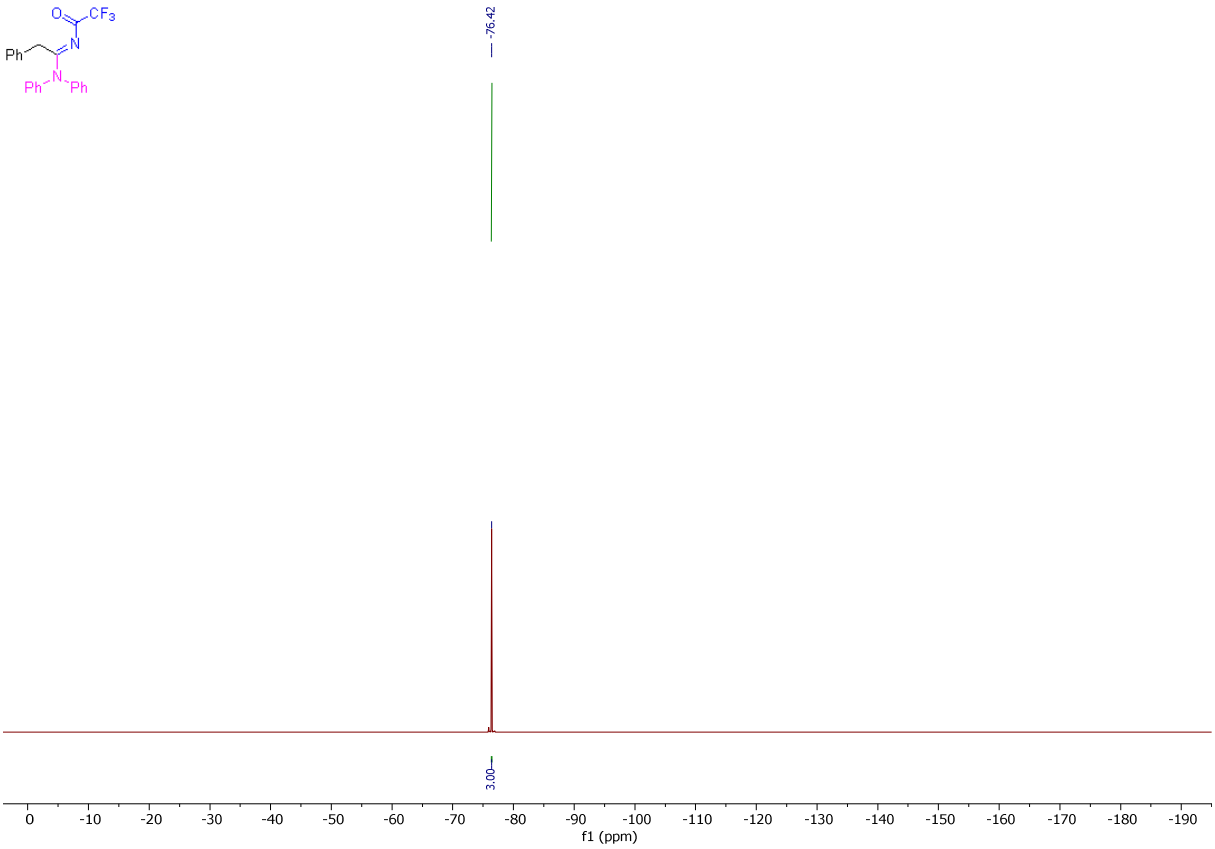
^{1}H NMR spectrum of **15e** ($CDCl_3$, 400 MHz)



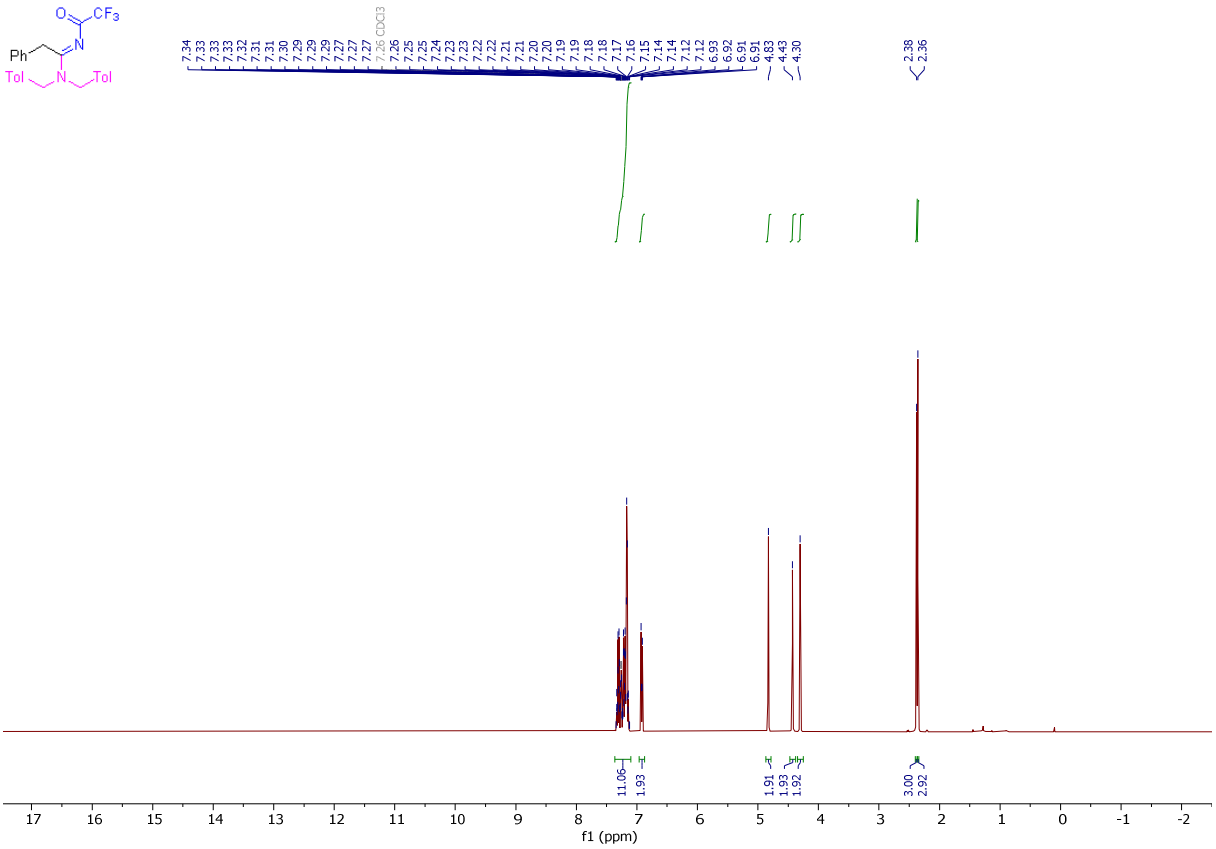
^{13}C NMR spectrum of **15e** ($CDCl_3$, 101 MHz)



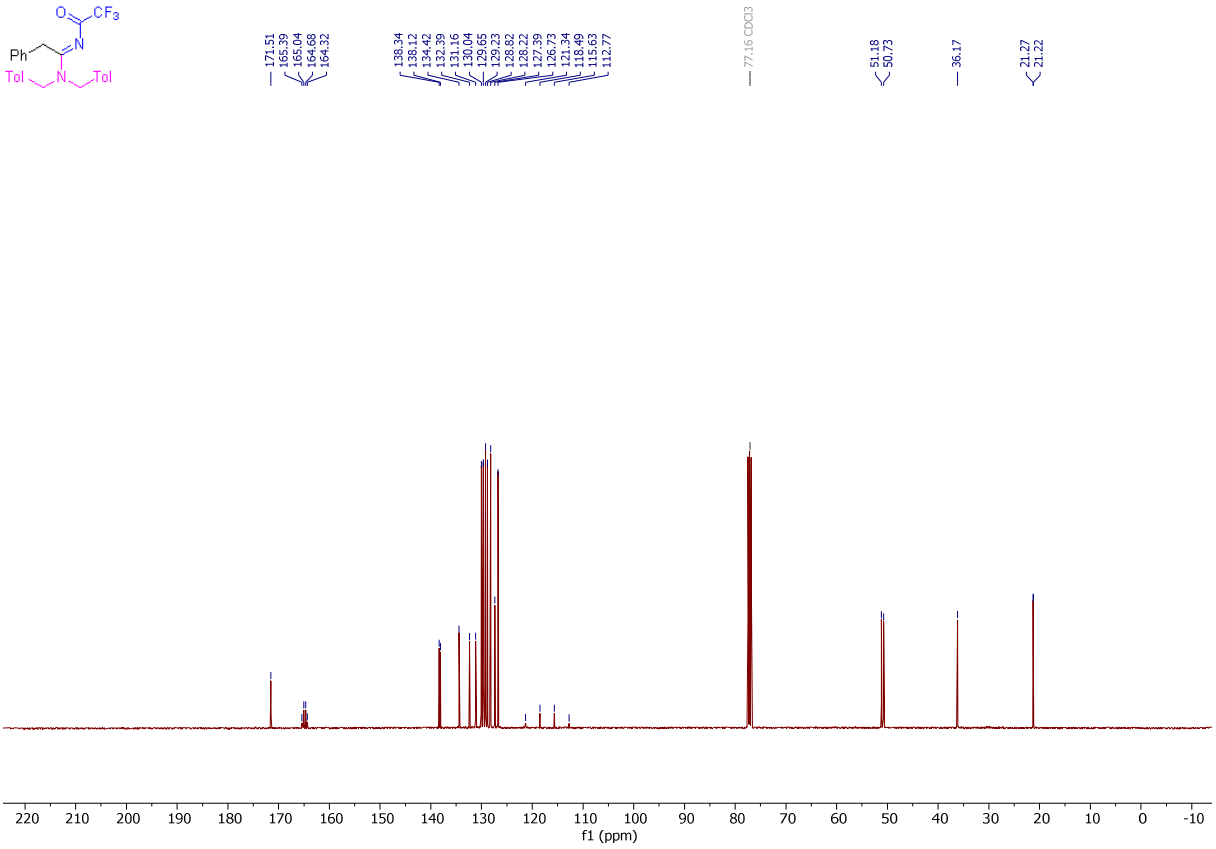
^{19}F NMR spectrum of **15e** ($CDCl_3$, 376 MHz)



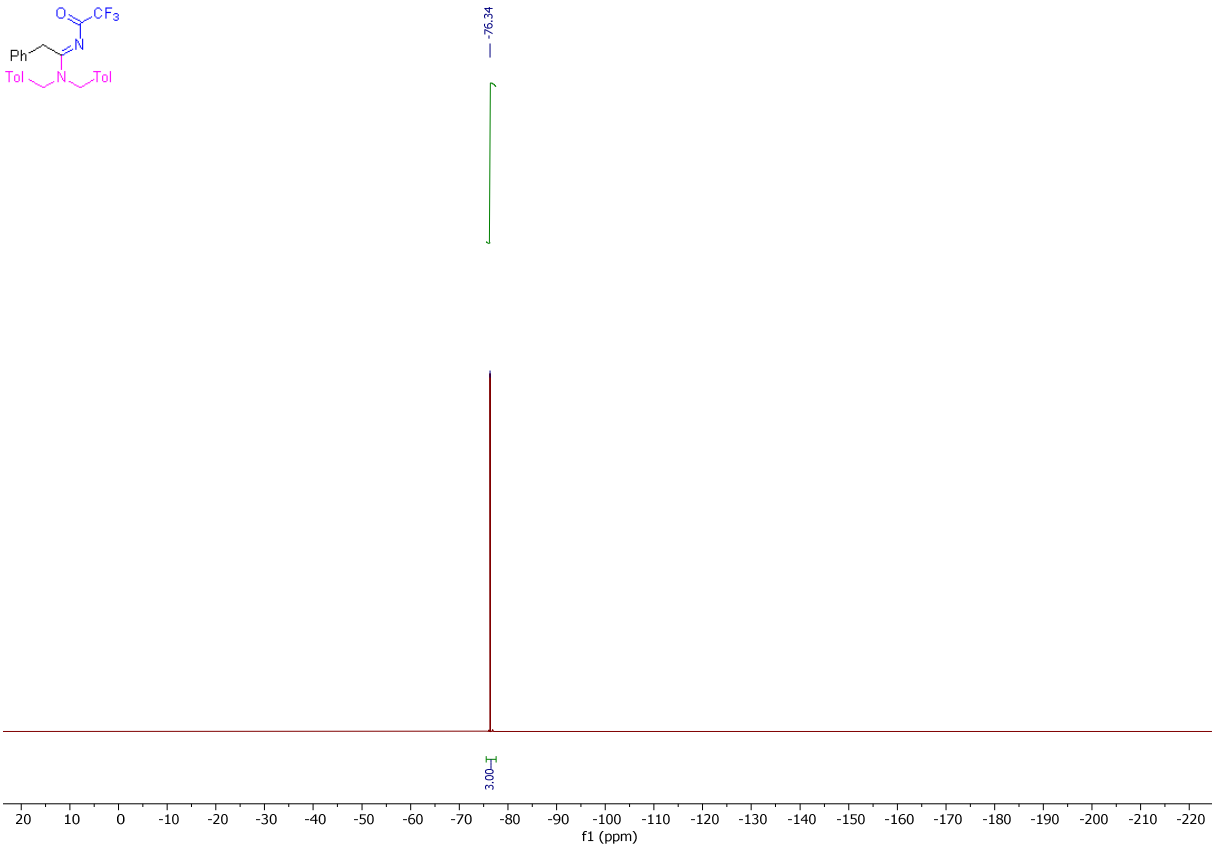
^{1}H NMR spectrum of **15f** ($CDCl_3$, 400 MHz)



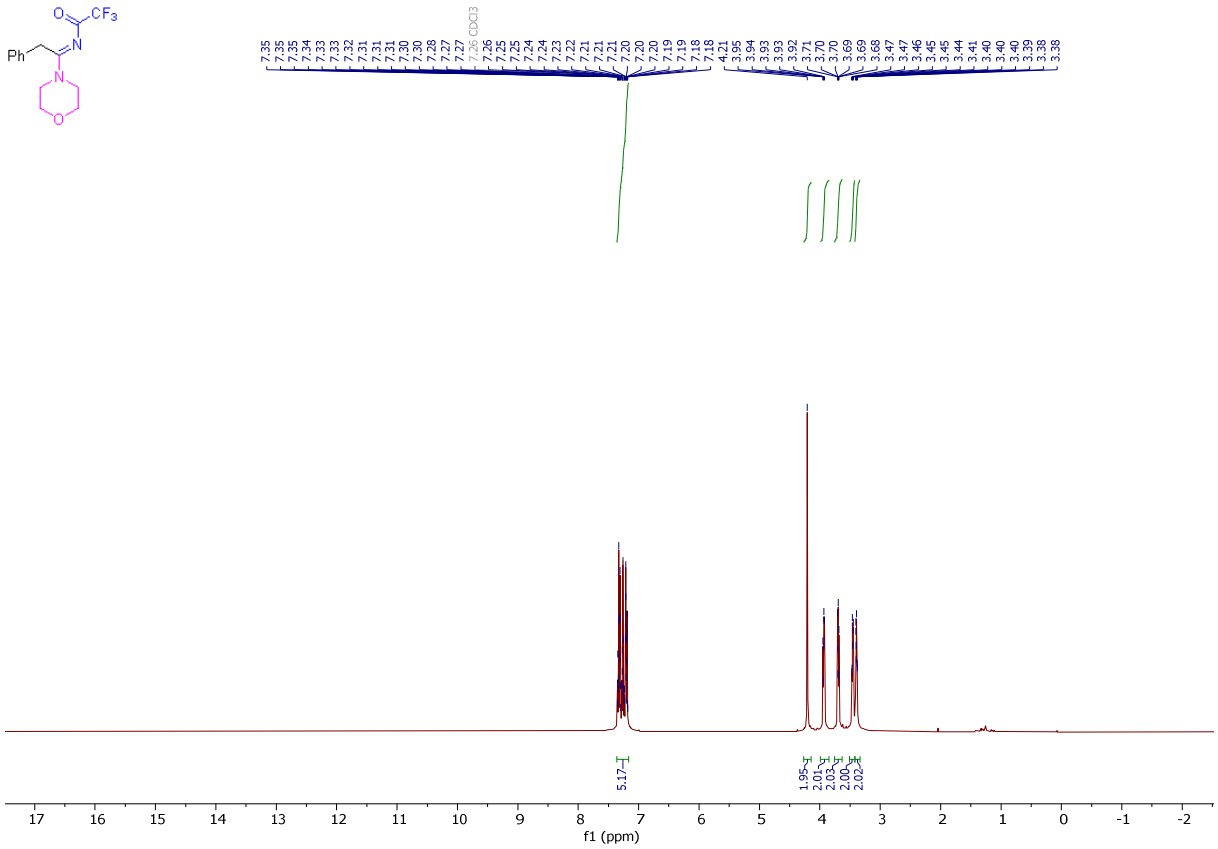
^{13}C NMR spectrum of **15f** ($CDCl_3$, 101 MHz)



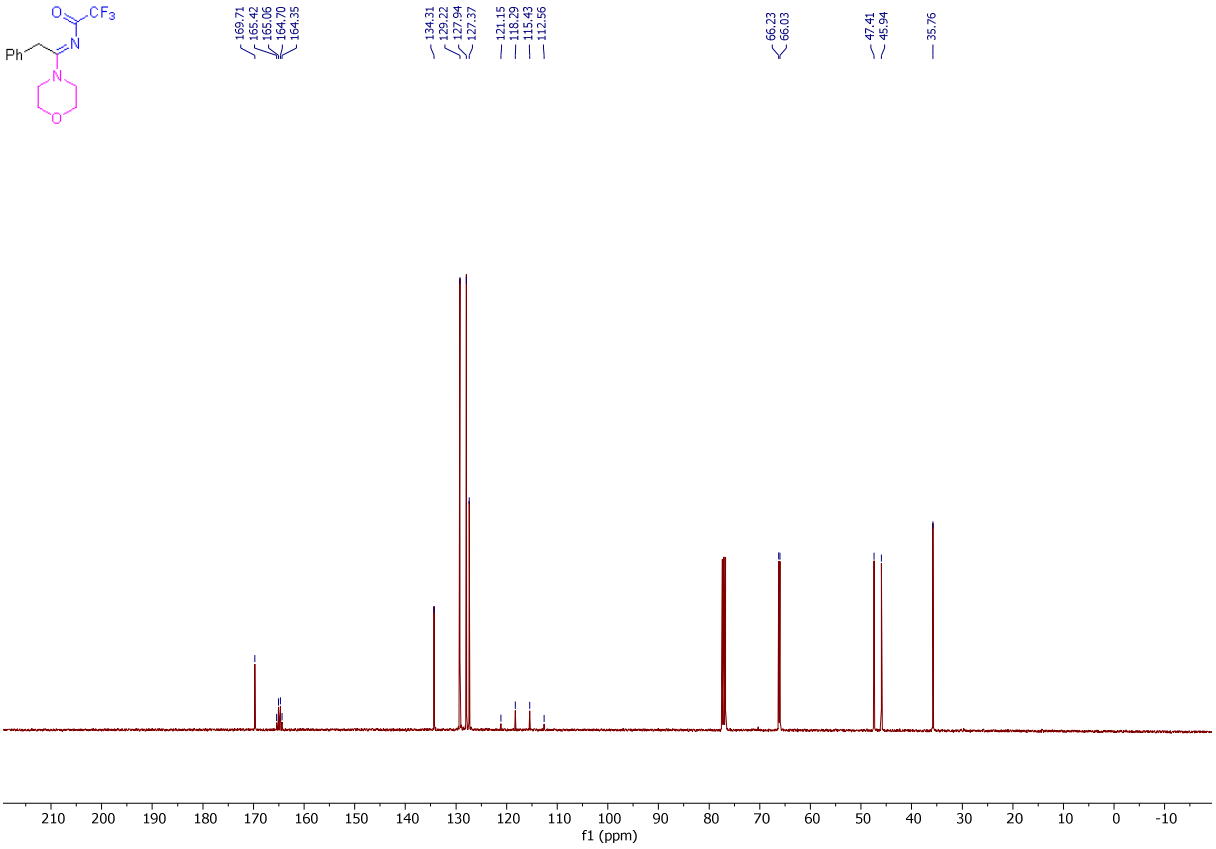
^{19}F NMR spectrum of **15f** ($CDCl_3$, 376 MHz)



^{1}H NMR spectrum of **15g** ($CDCl_3$, 400 MHz)



^{13}C NMR spectrum of **15g** ($CDCl_3$, 101 MHz)



^{19}F NMR spectrum of **15g** ($CDCl_3$, 376 MHz)