Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Photoredox- and Piezo-Catalysed Access to Complex Trifluoromethylated Polycyclic Structures from Ynamides

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1. General information

Reactions were carried out under an argon atmosphere. Glassware for reactions was flame-dried under vacuum prior to use. Liquids and solutions were transferred with syringes.
Acetonitrile (MeCN) was dried over thermally activated 4 Å molecular sieves (MS). Tetrahydrofuran (THF) was dried over sodium/benzophenone and thermally distilled. BaTiO3 (tetragonal powder, <3 µm, 99%, product number: 208108, Sigma-Aldrich). All solid state reactions were performed using grinding vessels in an Anton Paar BM500 (Fig. S1). Both jars and balls were made of stainless steel (Fig. S2). Unless otherwise stated, standard solvents and reagents were obtained from BLD, Doug Discovery, Tokyo Chemical Industry (TCI), Sigma-Aldrich, Alfa Aesar and were used as received. The amides used in ynamide synthesis were prepared according to reported procedures in literature.[1]

Flash column chromatography was performed on Silica 60 M (40–63 µm, Macherey Nagel) silica gel. Technical grade solvents were distilled prior to use. TLC analyses were performed on Merck 60 F254 silica gel pre-coated aluminum-backed plates with a layer thickness of 200 µm. Product spots were visualized under UV light (λmax = 254 nm) and/or by staining with a potassium permanganate solution.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AV300 and AV400 instruments. $CDCl_3$ and DMSO-d_6 were purchased from Eurisotop and used as received. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent signals as the internal standard ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 2.50 ppm for ^{1}H NMR and CDCl3: δ = 77.16 ppm, DMSO-d_6: δ = 39.52 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, hept = heptuplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, tt = triplet of triplets..), coupling constants (Hz) and integration. ^{19}F NMR spectra were calibrated according to the IUPAC recommendation using a unified chemical shift scale based on the proton resonance of Me_4Si as primary reference. Melting points (M.p.) were determined with a Stuart Scientific SMP3 melting point apparatus and are not corrected.

High resolution mass spectrometry (HRMS) analyses were obtained using a S3 mass spectrometer MicroTOF from Bruker with an electron spray ion source (ESI) and a TOF detector at the Institut Parisien de Chimie Moléculaire (Sorbonne Université). Compound names were generated by the computer program ChemDraw according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

Photocatalyzed reactions were irradiated under a blue LED light array homemade apparatus. Reactions were carried out in sealed tubes at a distance of approximately 2 cm from the LEDs and an average temperature of 27°C was maintained by an air cooling system.
All reactions were performed under an atmosphere of argon unless otherwise stated, and monitored by thin layer chromatography (T.L.C.), or by ^{1}H and ^{19}F NMR spectroscopy.

Fig. S1. Anton Paar BM500 used in this study.

Fig. S2. Stainless-steel jar used in this study.

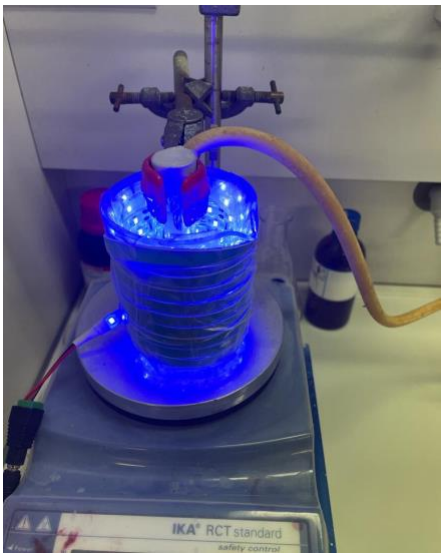
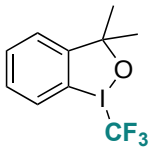


Fig. S3. Homemade Photoreactor used in this study.

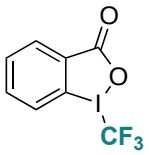
2. Optimization of the reaction parameters

Procedure for optimization and control studies: To a 4 mL reaction vial equipped with a stir bar was added *N*-benzyl-*N*-ethynyl-3-methylbutanamide **1a** (0.1 mmol, 1 equiv.), the CF_3 donor and the appropriate photocatalyst (0.025 equiv.). The vial was sealed with a cap and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with the appropriate anhydrous solvent (1 mL) and was degassed with three freeze-pump-thaw cycles. After this, the cap was sealed with Parafilm® M and the vial was irradiated in the aforementioned LED reactor for indicated time. The temperature of the reaction was maintained at approximately 27 °C via a fan. After this time, an aliquot of the solution was dissolved in deuterated $CDCl_3$, and the reaction mixture was analyzed by ^1H and ^{19}F NMR.

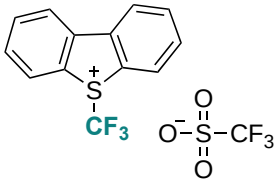
Trifluoromethyl radical source:



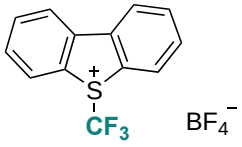
Togni I



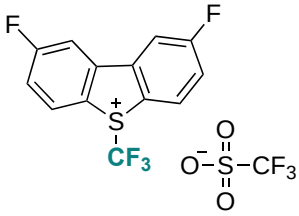
Togni II



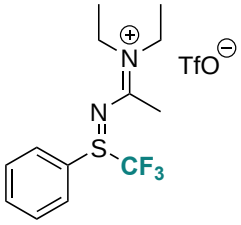
Umemoto



Umemoto.BF_4

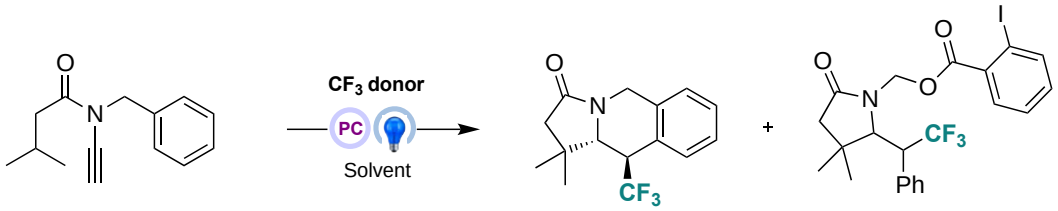


Umemoto.F



Magnier

Table S1: Optimization of the trifluoromethylation cyclization cascade.



1a **2a** **2aa**

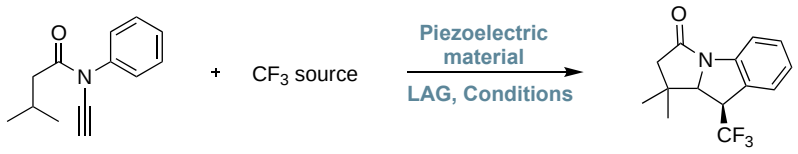
Entry	CF_3 donor	Equiv.	PC (2.5 mol%)	Solvent [a]	t(h)[b]	Yield (%)[c] 2a	Yield (%)[c] 2aa
1	Togni I	1.2	$Ir(ppy)_3$	DMSO	6	42	n.d
2	Togni I	1.2	$Ir(ppy)_3$	DMF	12	29	n.d
3	Togni I	1.2	$Ir(ppy)_3$	MeCN	3	53	n.d
4	Togni I	1.2	$Ir(ppy)_3$	MeOH	16	43	n.d
5	Togni I	1.2	$Ir(ppy)_3$	EtOAc	24	21 +20% SM	n.d
6	Togni I	1.2	$Ir(ppy)_3$	DCM	24	17 +10% SM	n.d
7	Togni I	1.05	$Ir(ppy)_3$	MeCN	4	45	5
8	Togni I	1.5	$Ir(ppy)_3$	MeCN	20	55	n.d
9	Umemoto	1.2	$Ir(ppy)_3$	MeCN	18	22	n.d
10	Umemoto.BF_4	1.2	$Ir(ppy)_3$	MeCN	20	n.d	n.d
11	Magnier	1.2	$Ir(ppy)_3$	MeCN	8	21	n.d
12	Umemoto Na_2HPO_4 (1.2 eq)	1.2	$[Ir(dtbby)(ppy)_2][PF_6]$	MeCN	1	traces	n.d
13	**Togni II**	**1.2**	**$Ir(ppy)_3$**	**MeCN**	**1.5**	**60**	**13**
14	Togni II	1.2	$[Ir(dtbby)(ppy)_2][PF_6]$	MeCN	21	35	n.d
15	Togni II	1.2	$[Ru(bpy)_3]Cl_2.6H_2O$	MeCN	17	40	n.d
16	Togni II	1.2	$Ir(ppy)_3$ (1.5 mol%)	MeCN	17	36	3
17	Togni II	1.2	$Ir(ppy)_3$ (5 mol%)	MeCN	15	41	4
18	Togni II	1.2	$Ir(ppy)_3$	MeCN (0.4 M)	12	30	7
19	Togni II	1.2	$Ir(ppy)_3$	MeCN (0.06M)	18	28	5
20	Togni II	1.2	$Ir(ppy)_3$	MeOH	15	30	n.d
21	Togni II	1.2	$Ir(ppy)_3$ in dark	MeCN	24	n.d	n.d
22	Togni II	1.2	-	MeCN	24	n.d	n.d

Standard conditions: **1a** (0.1 mmol, 1 equiv.), Togni II reagent (1.2 equiv.), $Ir(ppy)_3$ (2.5 mol%), MeCN (0.1 M), r.t, time 1-24h. [a] concentration of the reaction 0.1 M. [b] time until complete conversion of **1a** except for entries 5 and 6. [c] yields determined by ^1H NMR spectroscopy using an internal standard (1,3,5-trimethoxybenzene).

3. Mechanoredox trifluoromethylation cyclization cascade reaction

Ynamide **1g** (20.1 mg, 0.1 mmol), CF_3 source, and $BaTiO_3$ were placed in a stainless-steel milling jar (5.0 mL) with a stainless-steel ball (8 mm diameter) under air. Then LAG (X µL/mg for the solid reactants) was added to the mixture. After the jar was closed in air, the jar was placed in a ball milling apparatus (Anton Paar BM500). After grinding for the indicated time, the reaction mixture was passed through a short silica gel column eluting with ethyl acetate. The crude material was analyzed by ^{19}F and ^1H NMR with 4,4'-Difluorobenzophenone as an internal standard to determine the NMR yield.

Table S2: Optimization of the mechanoredox trifluoromethylation cyclization cascade.

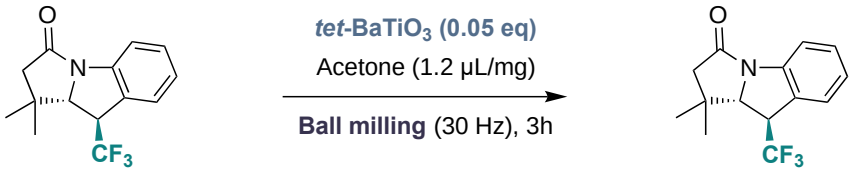


1g **2g**

Entry	CF_3 source	Piezoelectric material	LAG, Hz	Conditions (balls, h)	Yield
1	Togni I (1.2 eq)	$BaTiO_3$ (5 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	4%, degradation
2	Togni I (1.2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	15%, 7% of 1g
3	Togni I (1.2 eq)	$BaTiO_3$ (0.5 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	12%, 13% of 1g
4	Togni II (1.2 eq)	$BaTiO_3$ (0.5 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	9%, messy
5 (2 eq of **1g**)	Togni I (1 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	10%, 57% 1g
6 (2 eq of **1g**)	Togni I (1 eq)	$BaTiO_3$ (5 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	3%, 23% of 1g
7	Togni I (1.2 eq)	$BaTiO_3$ (0.1 eq)	MeCN (0.2µL), 30 Hz	8mm steel ball, 3h	14%, 7% of 1g
8	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	8mm steel ball, 3h	18%, 6% of 1g
9	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	3x3mm balls, 3h	5%, 31% of 1g
10	Togni I (2 eq)	$BaTiO_3$ (0.2 eq)	Acetone (0.2µL), 30 Hz	3x3mm balls, 3h	N.D, degradation
11	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 20 Hz	3h	7%, 33% of 1g
12	Togni I (1.2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	ZrO_2 ball 7mm, 3h	15%, 9% of 1g
13	Togni I (1.2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	in glovebox (Argon), 3h	2%
14	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	6 x ZrO_2 balls 5mm, 3h	18.6%
15	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30 Hz	10 mm steel ball, 3h	18%
16	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3µL), 30 Hz	3h	10%
17	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3µL), 30 Hz	2h	5%, 16% of 1g
18	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (0.3µL), 30 Hz	3h	17%
19	Togni I (2 eq)	$BaTiO_3$ (0.1x2 eq)	Acetone (0.2µL), 30 Hz	2h	2%, 44% of 1g
22	Togni I (0.5x3 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.2µL), 30Hz	add 0.5eq each 1h, 3h	15%
23	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3µL), 30Hz	Sand (2 eq/mg), 3h	15%
24	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3µL), 10 Hz	13h	23%
25	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3µL), 10 Hz	7h	12%, 15% of 1g

Entry	CF_3 source	Piezoelectric material	LAG, Hz	Conditions (balls, h)	Yield
26	Togni I (2 eq)	$BaTiO_3$ (5 eq)	Acetone (0.3μL), 10 Hz	8mm steel ball, 6h	6%
27	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3μL), 20 Hz	8mm steel ball, 2h	2%, 45% of 1g
28	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.3μL), 7 Hz	8mm steel ball, 13h	22%
29	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.67μL), 7 Hz	8mm steel ball, 13h	30%
30	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (0.67μL), 30 Hz	8mm steel ball, 3h	**32%**
31	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.67μL), 30 Hz	8mm steel ball, 3h, Silica (5eq)	30%
32	Togni I (2 eq)	$BaTiO_3$ (0.1 eq)	Acetone (0.67μL), 30 Hz	8mm steel ball, 3h, Alumina (5eq)	N.D
33	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (0.67μL), 30 Hz	8mm steel ball, 3h, 0.2 mmol scale	**33%**
34	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 10 Hz	8mm steel ball, 13h	**38%**
35	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (**1.2μL**), 30 Hz	8mm steel ball, 3h	**38%**
36	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (2μL), 30 Hz	8mm steel ball, 3h	26%, 22% of 1g
37	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.5μL), 30 Hz	8mm steel ball, 3h	24%
38	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (0.87μL), 30 Hz	8mm steel ball, 3h	30%
39	Togni I **(4 eq)**	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	35%
40	Togni I **(4 eq)**	$BaTiO_3$ (0.1 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	32%
41	Togni I **(1.5 eq)**	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	22%
42	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	10mm SS ball, 3h	30%
43	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	6x5mm SS ball, 3h	20%
44	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	6x5mm ZrO_2 ball, 3h	24%
45	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	EtOAc (1.2μL), 30 Hz	8mm steel ball, 3h	37%
46	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Cyclohexane (1.2μL), 30 Hz	8mm steel ball, 3h	15%
47	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	MeOH (1.2μL), 30 Hz	8mm steel ball, 3h	19%
48	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	DMF (1.2μL), 30 Hz	8mm steel ball, 3h	8%
49	Togni I (2 eq)	$LiNbO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	22%, 16% of 1g
50	Togni I (2 eq)	$LiNbO_3$ (0.5 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	21%, 9% of 1g
51	Togni I (2 eq)	$LiNbO_3$ (10 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	6%, 44% of 1g
52	F-umemoto (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	5%, degradation
53	Togni I (2 eq)	$BaTiO_3$ (0.025 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3h	14%, 19% of 1g
54	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 3.5h	13.8%, 29% of 1g
55	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 5h, 0.3 mmol scale	15%, 10% of 1g
56	Togni I (2 eq)	$BaTiO_3$ (0.05 eq)	Acetone (1.2μL), 30 Hz	8mm steel ball, 6x(30 min at 30Hz, and 15 min pause)	24%, 15% of 1g

Degradation of the tricyclic compound **2g** under ball milling conditions (30% degradation).



2g **2g**

70%

reaction performed on 0.1 mmol scale

4. Side reactivity and unsuccessful substrates

It's worth noting some limitation of this cascade. Notably the reaction in presence of cyclopropyl **Y1** leads to the radical clock product **P2** via a 1,4-HAT process. Azetiridine and carbamate ynamides gave mostly degradation products, alongside traces of the product. In the case of ynamides **Y4** and **Y5**, the vinyl radical undergoes a 1,6-HAT instead of a 1,5 resulting in the formation **P4** and **P5** alongside degradation products. We investigated substrates bearing a protected ynamide function (**1y**). Unsurprisingly, when the radical acceptor is protected with a CH_3 or a TMS group no reaction occurs, likely due to the steric hinderance they impose. Ynamide **1z** with a benzamide group was tested as well (Fig. S4). Upon addition of CF_3 radical on **1z** the vinyl radical undergoes a 5-exo-trig cyclization with the arene which is consistent with our previous study[2] that showed that the intermediate vinyl radical undergoes faster cyclization on the benzamide ring than HAT.

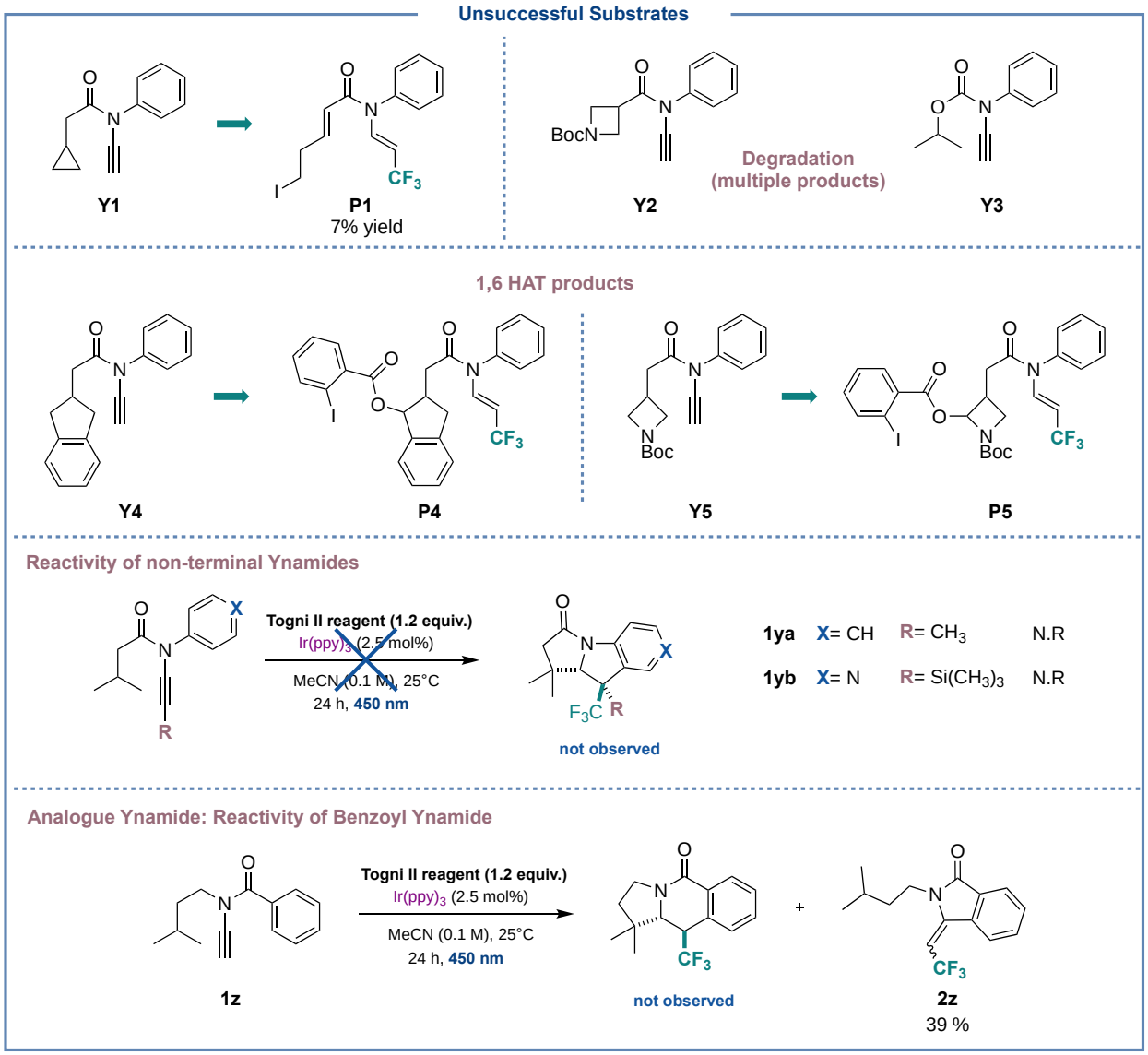


Fig. S4. Reactivity of other ynamides under photoredox conditions.

5. Diastereoselectivity

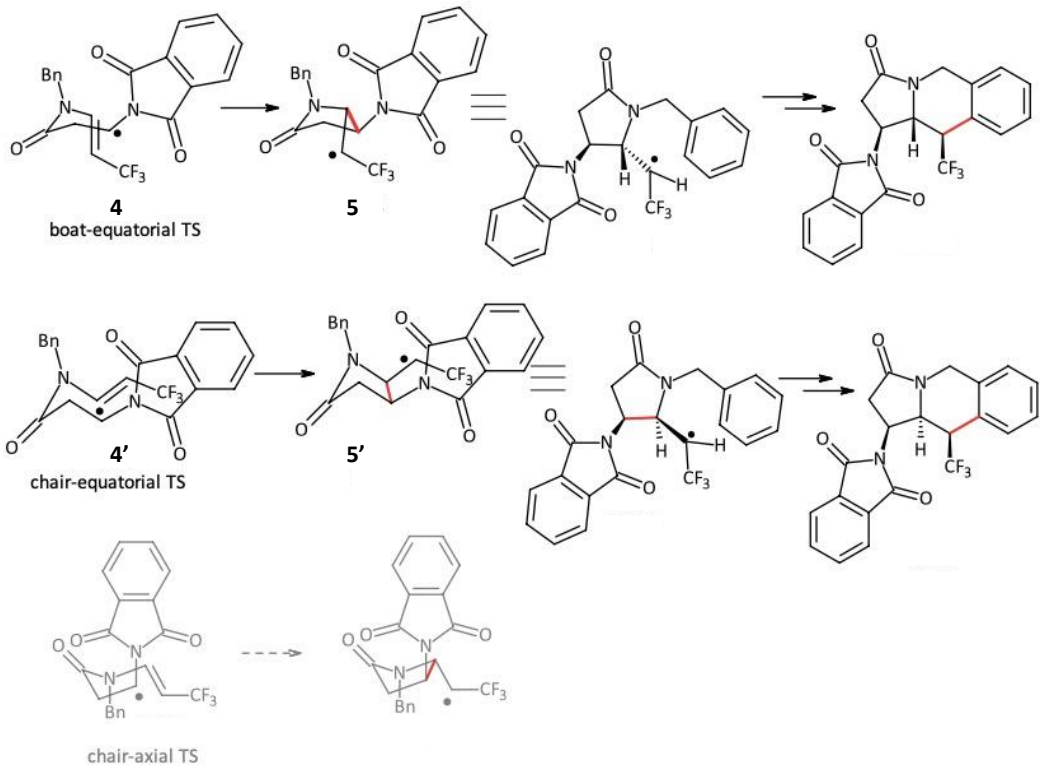


Fig. S5. Beckwith-Houk model for the 5-*exo*-*trig* cyclization of **2e**.

The diastereoselectivity of the third generated stereogenic center could be explained with the Beckwith-Houk. If we take compound **2e** as a case study, the introduction of a polar nitrogen introduces both steric and electronic repulsions between the α-imidoalkyl radical and the trifluoromethylated olefin. In this scenario, the most stable transition state is the boat-equatorial TS **4**, leading to the formation of trans pyrrolidinone **5** after cyclization. Conversely, the other diastereoisomer probably originates from the chair-equatorial **4'**, resulting in the formation of cis pyrrolidinone **5'** through a 5-exo-trig cyclization process. TS **4'** is likely the least stable transition state due to the bulky phtalimide substituent in an axial position.

6. Synthesis of protected Ynamides

6.1 General procedure I-a

In a sealed tube flushed with argon was loaded the amide (1 equiv.), $CuSO_4.5H_2O$ (0.1 equiv.), 1,10- phenanthroline (0.2 equiv.) and K_3PO_4 (2 equiv.). To this mixture was added a solution of 2-bromoethynyl(triisopropyl)silane[3] (1.1 equiv., 1M) in toluene. The reaction mixture was capped and heated at 82 °C for 2.5 days. The reaction mixture was cooled to rt, filtered through a pad of Celite (rinsed with DCM). The filtrate was concentrated under vacuum. The crude product was purified by silica gel column chromatography.

6.2 General procedure I-b

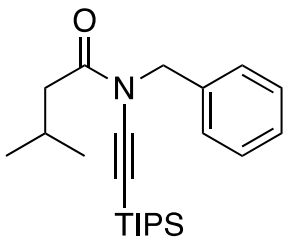
To a solution of the amide (1 equiv.) in toluene (1 M) was added KHMDS (0.5 M in toluene, 1.1 equiv.) at RT. The reaction mixture was stirred at 80°C for 20 min and phenyl(trimethylsilylethynyl)iodonium triflate[4] (1.1 equiv.) was added. The reaction mixture was stirred at 80°C for 1 h, then stirred at rt for 5 h. The reaction mixture was washed with water and extracted twice with EtOAc. The combined organic layers were dried over MgSO4, filtered and concentrated to dryness. The crude was purified by column chromatography.

6.3 General procedure I-c

In a round-bottom flask under argon was dissolved the triazole[5] (1 equiv.) in THF (0.2 M).The solution was cooled down to 0 °C and n-BuLi (2.5M in hexanes, 1.05 eq.) was added dropwise. The mixture was stirred at 0°C for 30 min, then the electrophile (1.05 eq.) was added. The reaction mixture was stirred at rt for 30 min. The solution was quenched with water and extracted with EtOAc. The combined org. layers were dried over MgSO4, filtered and concentrated to dryness. The crude was purified by column chromatography.

6.4 Characterization data of protected ynamides

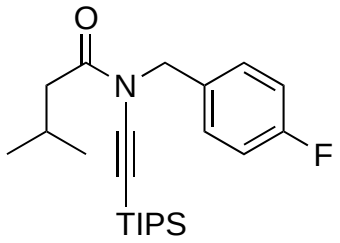
***N*-benzyl-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1a-SiR_3)**



Starting from *N*-benzyl-3-methylbutanamide (0.956 g, 5 mmol), and by following general procedure **I-a**, compound **1a-SiR$_3$** (1.153 g, 62% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE)

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.33 (m, 5H), 4.68 (s, 2H), 2.59 (d, *J* = 7.1 Hz, 2H), 2.21 (sept, *J* = 6.8 Hz, 1H), 1.01 (s, 3H), 1.01 (bs, 18H), 0.96 (d, *J* = 6.8 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174, 136.1, 128.8 (2C), 128.4 (2C), 127.8, 98.4, 72.3, 51.4, 43.4, 25.8, 22.4 (2C), 18.6 (6C), 11.3 (3C).
HRMS (ESI) calcd. for $C_{23}H_{37}NOSiH$ [M+H]+: 372.2717, Found 372.2716.

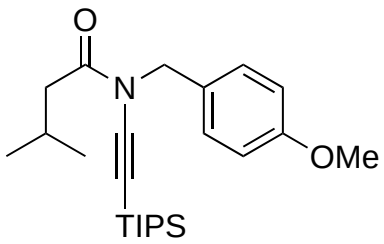
***N*-(4-fluorobenzyl)-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1b-SiR$_3$)**



Starting from *N*-(4-fluorobenzyl)-3-methylbutanamide (1.046 g, 5 mmol), and by following general procedure **I-a**, compound **1b-SiR$_3$** (1.496 g, 76% yield) was obtained as an orange oil by flash chromatography (40% DCM/PE).

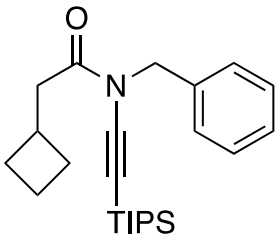
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 (dd, *J* = 8.5, 5.4 Hz, 2H), 6.99 (td, *J* = 8.8, 1.2 Hz, 2H), 4.64 (s, 2H), 2.58 (dd, *J* = 7.1, 1.0 Hz, 2H), 2.19 (dh, *J* = 13.5, 6.7 Hz, 1H), 1.01 (br s, 21H), 0.95 (dd, *J* = 6.6, 1.1 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.0, 163.9 (d, *J* = 245.5 Hz), 132.1 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 8.3 Hz), 115.4 (d, *J* = 21.6 Hz), 98.2, 72.6, 50.7, 43.4, 25.9, 22.5, 18.7, 11.4.
^{19}F NMR (376 MHz, CDCl3) δ ppm -114.52.
HRMS (ESI) calcd. for $C_{23}H_{36}FNOSiH$ [M+H]+: 390.2623. Found 390.2625.

***N*-(4-methoxybenzyl)-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1c-SiR$_3$)**



Starting from N-(4-methoxybenzyl)-3-methylbutanamide (1.106 g, 5 mmol), and by following general procedure **I-a**, compound **1c-SiR$_3$** (1.496 g, 62% yield) was obtained as an orange oil by flash chromatography (30% DCM/PE).
^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.27 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8..7 Hz, 2H), 4.61 (s, 2H), 3.79 (s, 3H), 2.57 (d, *J* = 7.2 Hz, 2H), 2.20 (dp, *J* = 13.6, 6.8 Hz, 1H), 1.02 (s, 21H), 0.95 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.0, 159.4, 130.4, 128.5, 113.9, 98.5, 72.3, 55.4, 50.9, 43.5, 25.9, 22.5, 18.7, 11.5.
HRMS (ESI) calcd. for $C_{24}H_{39}NO2SiH$ [M+H]+: 402.2823. Found 402.2821.

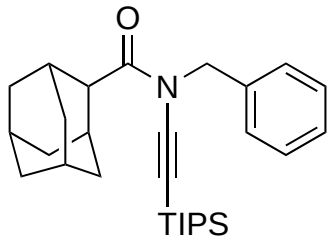
_N_-benzyl-2-cyclobutyl-_N_-((triisopropylsilyl)ethynyl)acetamide (1d-SiR$_3$)



Starting from *N*-benzyl-2-cyclobutylacetamide (1.016 g, 5 mmol), and by following general procedure **I-a**, compound **1d-SiR$_3$** (1.305 g, 68% yield) was obtained as an orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.31 (m, 5H), 4.65 (s, 2H), 2.82 (bs, 2H), 2.79 (m, 1H), 2.13 (m, 2H), 1.87 (m, 2H), 1.74 (m, 2H), 1.02 (bs, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.7, 136.3, 128.9 (2C), 128.6 (2C), 127.9, 98.5, 72.4, 51.3, 41.6, 32.4, 28.3, 18.8 (3C), 18.7 (6C), 11.5 (3C).
HRMS (ESI) Calcd. for $C_{24}H_{37}NOSiH$ [M+H]+: 384.2717. Found 384.272.

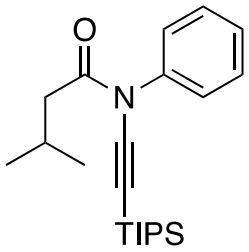
(1_R_,3_S_,5_r_,7_r_)-_N_-benzyl-_N_-((triisopropylsilyl)ethynyl)adamantane-2-carboxamide (1f-SiR$_3$)



Starting from (1*R*,3*S*,5*r*,7*r*)-*N*-benzyladamantane-2-carboxamide (1.347 g, 5 mmol), and by following general procedure **I-a**, compound **1f-SiR$_3$** (0.907 g, 40% yield) was obtained as a pale yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34-7.25 (m, 5H), 4.68 (s, 2H), 3.34 (s, 1H), 2.27 (m, 4H), 1.86 (m, 4H), 1.75 (m, 4H), 1.60 (d, *J* = 12.6 Hz, 2H), 1.02 (br s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.7, 136.6, 128.7 (2C), 128.5 (2C), 127.8, 98.7, 72.0, 51.8, 48.2, 38.8, 37.6, 32.8, 30.1, 28.0, 27.4, 18.7 (6C), 11.5 (3C).
HRMS (ESI) calcd. for $C_{29}H_{43}NOSiH$ [M+H]+: 450.3187. Found 450.3185.

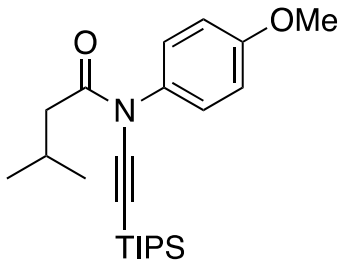
3-methyl-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1g-SiR$_3$)



Starting from 3-methyl-*N*-phenylbutanamide (0.886 g, 5 mmol), and by following general procedure **I-a**, compound **1g-SiR$_3$** (1.348 g, 75% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 2.77 (d, *J* = 7.3 Hz, 2H), 2.3 (sept, *J* = 6.8 Hz, 1H), 1.09 (bs, 21H), 1.04 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.8, 139.2, 128.9 (2C), 127.1, 125.0 (2C), 98.2, 71.8, 44.1, 25.8, 22.6 (2C), 18.8 (6C), 11.5 (3C).
HRMS (ESI) Calcd. for $C_{22}H_{36}NOSi$ [M+H]+: 358.2561, found 358.2565.

***N*-(4-methoxyphenyl)-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1h-SiR$_3$)**

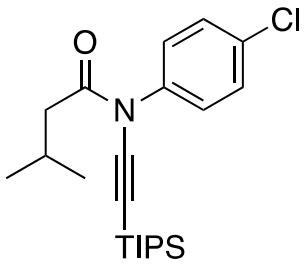


Starting from *N*-(4-methoxyphenyl)-3-methylbutanamide (1.036 g, 5mmol), and by following general procedure **I-a**, compound **1h-SiR$_3$** (1.240 g, 64% yield) was obtained as an off yellow solid by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.34 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 1H), 2.74 (d, *J* = 7.6 Hz, 2H), 2.29 (sept, *J* = 6.9 Hz, 1H), 1.08 (bs, 21H), 1.03 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.9, 158.4, 132.1, 126.4 (2C), 114.2 (2C), 98.6, 71.2, 55.6, 43.9, 25.9, 22.6 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) Calcd for $C_{23}H_{37}NO2SiH$ [M+H]+: 388.2666, Found 388.2657.
M.p.: 49-50°C

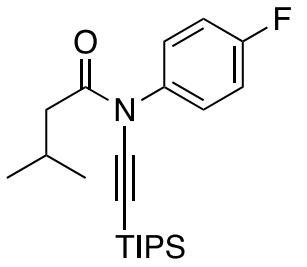
***N*-(4-chlorophenyl)-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1i-SiR$_3$)**



Starting from *N*-(4-chlorophenyl)-3-methylbutanamide (1.058 g, 5 mmol), and by following general procedure **I-a**, compound **1i-SiR$_3$** (1.184 g, 60% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H), 2.76 (d, *J* = 6.7 Hz, 2H), 2.29 (sept, *J* = 6.7 Hz, 1H), 1.09 (bs, 21H), 1.04 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.5, 137.7, 132.5, 129.1 (2C), 126.2 (2C), 97.6, 72.4, 44.1, 25.8, 22.6 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) Calcd. for $C_{22}H_{34}ClNOSiH$ [M+H]+: 392.2171, Found 392.2164.

***N*-(4-fluorophenyl)-3-methyl-*N*-((triisopropylsilyl)ethynyl)butanamide (1j-SiR$_3$)**

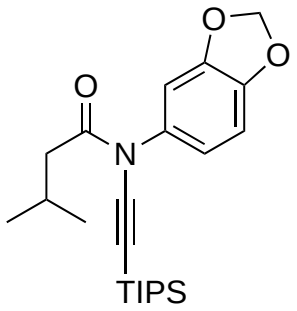


Starting from *N*-(4-fluorophenyl)-3-methylbutanamide (0.976 g, 5 mmol), and by following general procedure **I-a**, compound **1j-SiR$_3$** (1.099 g, 58% yield) was obtained as a yellow oil by flash chromatography (20% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (dd, *J* = 5.0, 7.3 Hz, 2H), 7.07 (t, *J* = 8.0 Hz, 2H), 2.76 (d, *J* = 6.9 Hz, 2H), 2.29 (sept, *J* = 6.8 Hz, 1H), 1.09 (bs, 21H), 1.03 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.7, 162.5 (d, *J* = 247.3 Hz) , 135.2, 126.8 (2C, d, *J* = 8.8 Hz), 115.8 (2C, d, *J* = 23.0 Hz), 98.1, 72.0, 44.0, 25.8, 22.6 (2C), 18.8 (6C), 11.6 (3C).
^{19}F NMR (376 MHz, CDCl3) δ ppm -114.79.
HRMS (ESI) Calcd. for $C_{22}H_{34}FNOSiH$ [M+H]+: 376.2466, Found 376.2467.

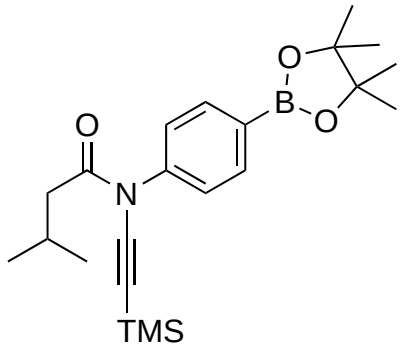
_N_-(benzo[_d_][1,3]dioxol-5-yl)-3-methyl-_N_-((triisopropylsilyl)ethynyl)butanamide (1k-SiR$_3$)



Starting from *N*-(benzo[*d*][1,3]dioxol-5-yl)-3-methylbutanamide (1.106 g, 5 mmol), and by following general procedure **I-a**, compound **1k-SiR$_3$** (1.209 g, 60% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 6.88 (m, 2H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.98 (s, 2H), 2.73 (d, *J* = 7.1 Hz, 2H), 2.28 (m, 1H), 1.08 (s, 21H), 1.03 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 173.9, 147.8, 146.7, 133.1, 118.8, 108.1, 107.0, 101.8, 98.3, 71.4, 43.8, 25.8, 22.6, 18.8 (6C), 11.5 (3C).
HRMS (ESI) calcd. for $C_{23}H_{35}NO_3SiH$ [M+H]+: 402.2459. Found 402.2458.

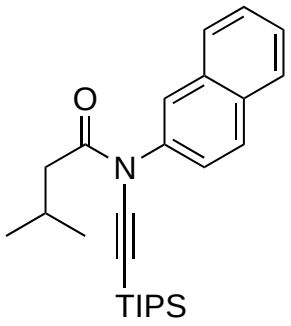
3-methyl-_N_-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-_N_-((trimethylsilyl)-ethynyl)butanamide (1l-SiR$_3$)



Starting from 3-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanamide (1.819 mg, 6 mmol), and by following general procedure **I-b**, compound **1l-SiR$_3$** (0.811 g, 34% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 2.69 (d, *J* = 7.0 Hz, 2H), 2.28 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.34 (s, 12H), 1.04 (d, *J* = 6.7 Hz, 6H), 0.20 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.6, 141.5, 135.6 (2C), 124.3 (2C), 96.7, 84.0 (2C), 75.4, 44.0, 25.9, 24.9 (4C), 22.6 (2C), 0.1 (3C).
HRMS (ESI) calcd. for $C_{22}H_{34}BNO_3SiH$ [M+H]+: 400.2474. Found 400.2476.
M.p.: 92°C

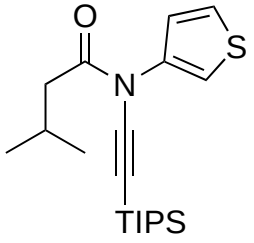
3-methyl-*N*-(naphthalen-2-yl)-*N*-((triisopropylsilyl)ethynyl)butanamide (1m-SiR$_3$)



Starting from 3-methyl-*N*-(naphthalen-2-yl)butanamide (1.136 g, 5 mmol), and by following general procedure **I-a**, compound **1m-SiR$_3$** (1.204 g, 59% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96 (d, *J* = 2.2 Hz, 1H), 7.89 – 7.78 (m, 3H), 7.61 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.49 (m, 2H), 2.84 (d, *J* = 7.1 Hz, 2H), 2.35 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.12 (br s, 21H), 1.09 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.9, 136.7, 133.4, 132.2, 128.7, 128.1, 127.7, 126.6, 126.3, 123.4, 123.2, 98.2, 72.0, 44.2, 25.9, 22.6 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) calcd. for $C_{26}H_{37}NOSiH$ [M+H]+: 408.2717. Found 408.2719.

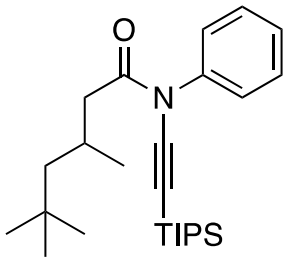
3-methyl-*N*-(thiophen-3-yl)-*N*-((triisopropylsilyl)ethynyl)butanamide (1n-SiR$_3$)



Starting from 3-methyl-*N*-(thiophen-3-yl)butanamide (3.000 g, 16.2 mmol), and by following general procedure **I-a**, compound **1n-SiR$_3$** (2.680 g, 46% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (500 MHz, CDCl3) δ ppm 7.54 (dd, J = 3.3, 1.4 Hz, 1 H), 7.36 (dd, J = 5.3, 1.4 Hz, 1 H), 7.25 (dd, J = 5.3, 3.3 Hz, 1 H), 2.76 (d, J = 7.1 Hz, 2 H), 2.28 (sept, J = 6.7 Hz, 1 H), 1.12 (m, 18 H), 1.11 (m, 3 H), 1.03 (d, J = 6.7 Hz, 6 H).
^{13}C NMR (125 MHz, CDCl3) δ ppm 172.9, 136.7, 124.2, 123.2, 114.7, 97.2, 73.5, 44.4, 25.8, 22.6 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) calcd. for $C_{20}H_{34}NOSSi$ [M+H]+: 364.2125, found 364.2125.

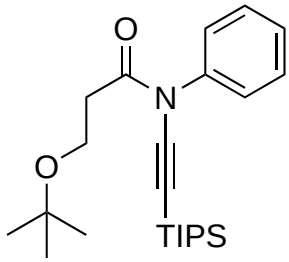
3,5,5-trimethyl-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)hexanamide (1o-SiR$_3$)



Starting from 3,5,5-trimethyl-*N*-phenylhexanamide (1.167 g, 5 mmol), and by following general procedure **I-a**, compound **1o-SiR$_3$** (1.717 g, 83% yield) was obtained as an orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 8.1 Hz, 2H), 7.26 (t, *J* = 8.1 Hz, 1H), 2.80 (qd, *J* = 25.2, 18.5, 7.1 Hz, 2H), 2.27 (m, 1H), 1.39 (dd, *J* = 10.7, 3.6 Hz, 1H), 1.17 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.10 (br s, 22H), 1.08 (m, 3H), 0.94 (br d, *J* = 1.3 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.74, 139.23, 128.93, 127.06, 125.03, 98.24, 71.83, 50.44, 44.54, 31.23, 30.17, 27.17, 23.12, 18.83, 11.58.
HRMS (ESI) Calcd. For $C_{26}H_{43}NOSiH$ [M+H]+: 414.3187. Found 414.3186.

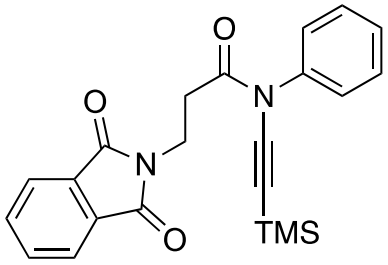
3-(*tert*-butoxy)-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)propenamide (1p-SiR$_3$)



Starting from 3-(*tert*-butoxy)-*N*-phenylpropanamide (1.016 g, 5 mmol), and by following general procedure **I-a**, compound **1p-SiR$_3$** (0.492 g, 24% yield) was obtained as a brown oil by flash chromatography (80% PE/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 8.5 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 3.76 (t, *J* = 6.6 Hz, 2 H), 3.07 (t, *J* = 6.5 Hz, 2 H), 1.21 (s, 2H), 1.08 (s, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.5, 139.2, 128.9 (2C), 127.1, 125.0 (2C), 97.9, 73.3, 71.89, 57.5, 36.8, 27.6 (3C), 18.8 (9C), 11.5 (3C).
HRMS (ESI) Calcd. for $C_{24}H_{39}NO_2SiH$ [M+H]+: 402.2823. Found 402.282.

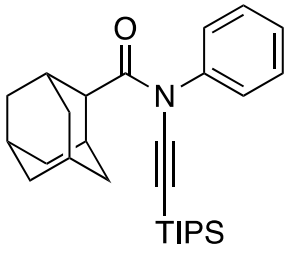
3-(1,3-dioxoisoindolin-2-yl)-*N*-phenyl-*N*-((trimethylsilyl)ethynyl)propenamide (1q-SiR_3)



Starting from 1-phenyl-4-(trimethylsilyl)-1*H*-1,2,3-triazole (0.913 g, 4.2 mmol) and phthalimideporpanoyl chloride (1.000 g, 4.2 mmol), and by following general procedure **I-c**, compound **1q -SiR_3** (0.554 g, 34% yield) was obtained as an orange solid by flash chromatography (20% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.40 (m, 4H), 7.29 (m, 1H), 4.12 (t, *J* = 7.0 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 0.15 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.5, 168.2 (2C), 138.6, 134.1 (2C), 132.2, 129.1 (2C), 127.6, 125.3, 123.5 (2C), 96.0, 75.6, 34.0, 33.8, 0.1.
HRMS (ESI) Calcd. For $C_{22}H_{22}N_2O_3SiH$ [M+H]+: 391.1472. Found 391.1475.
M.p.: 122°C

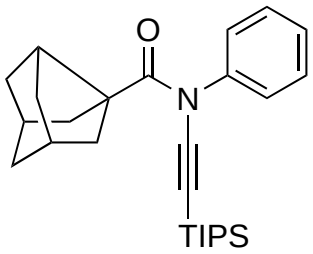
(1*R*,3*S*,5*r*,7*r*)-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)adamantane-2-carboxamide (1r-SiR_3)



Starting from (1*R*,3*S*,5*r*,7*r*)-*N*-phenyladamantane-2-carboxamide (1.276 g, 5 mmol), and by following general procedure **I-a**, compound **1r-SiR_3** (1.587 g, 73% yield) was obtained as an orange solid by flash chromatography (30% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.36 (m, 4 H), 7.25 (t, *J* = 7.2 Hz, 1 H), 3.57 (br s, 1 H), 2.42 (br s, 1 H), 2.30 (br d, *J* = 12.8 Hz, 2 H), 1.96-1.82 (m, 6 H), 1.77 (br s, 2 H), 1.64 (br d, *J* = 12.6 Hz, 2 H), 1.09 (s, 21 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.6, 139.7, 128.8 (2C), 126.9, 125.3 (2C), 98.3, 71.3, 48.6, 38.8, 37.6, 32.8, 30.2, 28.0, 27.5, 18.8 (9C), 11.6 (3C).
HRMS (ESI) Calcd. for $C_{28}H_{41}NOSiH$ [M+H]+: 436.3030. Found 436.3030.
M.p.: 61°C

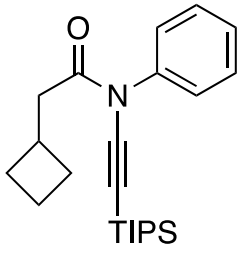
(3a*s*,6a*s*)-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)hexahydro-2,5-methanopentalene-3a(1*H*)-carboxamide (1s-SiR_3)



Starting from (3a*s*,6a*s*)-*N*-phenylhexahydro-2,5-methanopentalene-3a(1*H*)-carboxamide (1.206 g, 5 mmol), and by following general procedure **I-a**, compound **1s-SiR_3** (0.624 g, 30% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 – 7.35 (m, 4H), 7.27 (ddd, *J* = 10.1, 4.9, 3.2 Hz, 1H), 3.18 (t, *J* = 6.7 Hz, 1H), 2.35 (dt, *J* = 11.6, 2.4 Hz, 4H), 2.21 (dd, *J* = 9.9, 2.9 Hz, 2H), 2.05 (m, 2H), 1.71 – 1.58 (m, 4H), 1.06 (m, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.4, 141.5, 128.8, 127.2, 126.1, 99.1, 72.2, 56.9, 47.0, 43.7, 42.6, 37.8, 35.1, 18.7, 11.6.
HRMS (ESI) calcd. for $C_{27}H_{39}NOSiH$ [M+H]+: 422.2874. Found 422.2868.

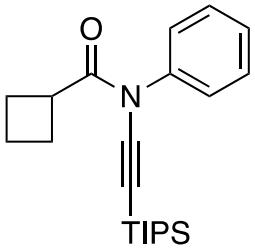
2-cyclobutyl-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)acetamide (1t-SiR_3)



Starting from 2-cyclobutyl-*N*-phenylacetamide (0.946 g, 5 mmol), and by following general procedure **I-a**, compound **1t-SiR_3** (1.037 g, 56% yield) was obtained as a pale orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.4 Hz, 1H), 3.00 (d, *J* = 7.4 Hz, 2H), 2.86 (sept, *J* = 7.7 Hz, 1H), 2.19 (m, 2H),1.91 (m, 2H), 1.79 (m, 2H), 1.10 (bs, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.3, 139.1, 128.9 (2C), 127.0, 124.9 (2C), 98.1, 71.8, 42.8, 32.3, 28.4 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) Calcd. for $C_{23}H_{35}NOSiH$ [M+H]+: 370.2561, Found 370.2555.

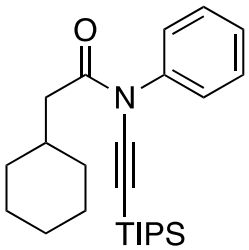
_N_-phenyl-_N_-((triisopropylsilyl)ethynyl)cyclobutanecarboxamide (1u-SiR_3)



Starting from *N*-phenylcyclobutanecarboxamide (0.876 g, 5 mmol), and by following general procedure **I-a**, compound **1u-SiR_3** (1.104 g, 62% yield) was obtained as a pale orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47 (d, *J* = 8.6 Hz, 2 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.3 Hz, 1 H), 3.94 (quint, *J* = 8.5 Hz, 1 H), 2.42 (m, 2H), 2.32 (m, 2H), 1.97 (m, 2H), 1.09 (s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 175.89, 139.35, 128.90 (2C), 126.95, 124.83 (2C), 97.67, 71.08, 39.14, 25.27 (2C), 18.80 (9C), 18.26, 11.60 (3C).
HRMS (ESI) Calcd. for $C_{22}H_{33}NOSiH$ [M+H]+: 356.2404. Found 356.2405.

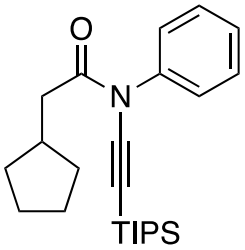
2-cyclohexyl-_N_-phenyl-_N_-((triisopropylsilyl)ethynyl)acetamide (1v-SiR_3)



Starting from 2-cyclohexyl-*N*-phenylacetamide (1.086 g, 5 mmol), and by following general procedure **I-a**, compound **1v-SiR_3** (1.272 g, 64% yield) was obtained as a pale yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.26 (t, 1 H), 2.76 (d, *J* = 7.1 Hz, 2H), 2.01 (m, 1H), 1.82 (m, 2H),1.70 (m, 2H), 1.29 (m, 4H), 1.19 (m, 2H), 1.09 (bs, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.7, 139.2, 128.9 (2C), 127.0, 125.0 (2C), 98.2, 71.7, 42.9, 35.0, 33.3 (2C), 26.4, 26.2 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) Calcd. for $C_{25}H_{39}NOSiH$ [M+H]+: 398.2874, Found 398.2865.

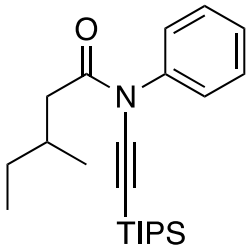
2-cyclopentyl-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)acetamide (1w-SiR$_3$)



Starting from 2-cyclopentyl-*N*-phenylacetamide (1.016 g, 5 mmol), and by following general procedure **I-a**, compound **1w-SiR$_3$** (1.277 g, 66% yield) was obtained as a pale yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 2.90 (d, *J* = 7.2 Hz, 2H), 2.43 (sept, *J* = 7.7 Hz, 1H), 1.90 (m, 2H),1.65/1.53 (m, 4 H), 1.26 (m, 2H), 1.09 (bs, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.0, 139.2, 128.9 (2C), 127.0, 124.9 (2C), 98.2, 71.7, 41.5, 36.5, 32.6 (2C), 25.1 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) Calcd. for $C_{24}H_{37}NOSiNa$ [M+H]+: 406.2537, Found 406.2528**.**

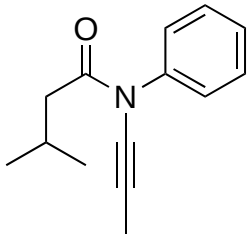
3-methyl-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)pentanamide (1x-SiR$_3$)



Starting from 3-methyl-*N*-phenylpentanamide (0.956 g, 5 mmol), and by following general procedure **I-a**, compound **1x-SiR$_3$** (1.426 g, 76% yield) was obtained as an orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 (d, *J* = 8.5 Hz, 2 H), 7.39 (t, *J* = 8.4, 7.4 Hz, 2 H), 7.26 (t, *J* = 7.3 Hz, 1 H), 2.80 (qd rotamere, *J* = 39.3, 14.8, 6.6 Hz, 2 H), 2.11 (m, 1 H), 1.48 (m, 1 H), 1.30 (m, 1 H), 1.09 (br s, 21 H), 1.03 (d, *J* = 6.7 Hz, 3 H), 0.94 (t, *J* = 7.5 Hz, 3 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.9, 139.2, 128.9, 127.0, 125.0, 98.2, 71.8, 42.2, 31.9, 29.6, 19.3, 18.8, 11.6, 11.4.
HRMS (ESI) Calcd. For $C_{23}H_{37}NOSiH$ [M+H]+: 372.2717. Found 372.2718.

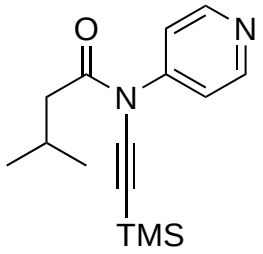
3-methyl-*N*-phenyl-*N*-(prop-1-yn-1-yl)butanamide (1ya)



Starting from 4-methyl-1-phenyl-1*H*-1,2,3-triazole (0.796 g, 5 mmol) and isovaleryl chloride (0.64 mL, 5.25 mmol), and by following general procedure **I-c**, compound **1ya** (0.645 g, 60% yield) was obtained as an orange solid by flash chromatography (20% EtOAc/PE). Note: HRMS could not be obtained for this compound

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.52 (m, 3 H), 7.38 (m, 2 H), 2.60 (s, 3 H), 2.42 (d, J = 6.8 Hz, 2 H), 2.09 (sept, J = 6.8 Hz, 1 H), 0.84 (d, J = 6..8 Hz, 6 H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 191.7, 146.2, 137.4, 133.4, 130.1, 129.4 (2C), 125.6 (2C), 51.6, 24.7, 22.5 (2C), 12.7.
M.p.: 78°C

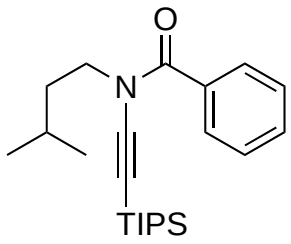
3-methyl-*N*-(pyridin-4-yl)-*N*-((trimethylsilyl)ethynyl)butanamide (1yb)



Starting from 4-(4-(trimethylsilyl)-1*H*-1,2,3-triazol-1-yl)pyridine (1.092 g, 5 mmol), and by following general procedure **I-c**, compound **1yb** (0.960 g, 70% yield) was obtained as an orange oil by flash chromatography (30% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.59 (d, *J* = 6.2 Hz, 2 H), 7.56 (d, *J* = 6.2 Hz, 2 H), 2.74 (d, *J* = 7.0 Hz, 2 H), 2.29 (m, 1 H), 1.04 (d, *J* = 6.3 Hz, 2 H), 0.25 (s, 9 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.38, 150.66 (2C), 146.12, 117.56 (2C), 94.30, 78.39, 44.73, 25.75, 22.58 (2C), 0.01 (3C).
HRMS (ESI) Calcd. for $C_{15}H_{22}N_2OSiH$ [M+H]+: 275.1574. Found 275.1575.

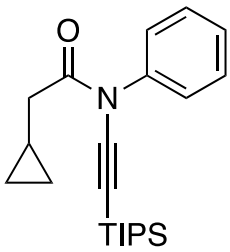
_N_-isopentyl-_N_-((triisopropylsilyl)ethynyl)benzamide (1z-SiR$_3$)



Starting from *N*-isopentylbenzamide (0.956 g, 5 mmol), and by following general procedure **I-a**, compound **1z-SiR$_3$** (1.022 g, 55% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.76 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 3.74 (t, *J* = 7.3 Hz, 2H), 1.71 (m, 3H), 0.98 (d, *J* = 6.3 Hz, 6H), 0.94 (br s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2, 134.3, 131.1, 128.6 (2C), 127.9 (2C), 99.1, 71.3, 47.5, 36.3, 25.8, 22.6, 18.6 (6C), 11.4 (3C).
HRMS (ESI) calcd. for $C_{23}H_{37}NOSiH$ [M+H]+: 372.2717. Found 372.2719.

2-cyclopropyl-_N_-phenyl-_N_-((triisopropylsilyl)ethynyl)acetamide (Y1-SiR$_3$)

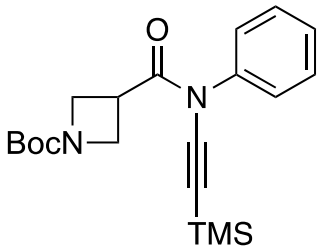


Starting from 2-cyclopropyl-*N*-phenylacetamide (0.876 g, 5 mmol), and by following general procedure **I-a**, compound **Y1-SiR$_3$** (0.347 g, 20% yield) was obtained as a yellow oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 6.9 Hz, 1H), 2.80 (d, *J* = 6.8 Hz, 2H), 1.27 (m, 1H), 1.06 (s, 21H), 0.60 (q, *J* = 7.3 Hz, 2H), 0.26 (q, *J* = 5.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.91, 139.11, 128.94, 127.05, 124.89, 98.07, 77.16, 71.86, 40.56, 18.80, 11.58, 7.10, 4.49.
HRMS (ESI) Calcd. For $C_{22}H_{33}NOSiH$ [M+H]+: 356.2404, found 356.2415.

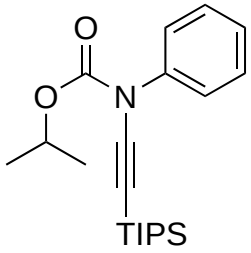
***tert*-butyl 3-(phenyl((trimethylsilyl)ethynyl)carbamoyl)azetidine-1-carboxylate (Y2-SiR$_3$)**



Starting from *tert*-butyl 3-(phenylcarbamoyl)azetidine-1-carboxylate (1.658 g, 6 mmol), and by following general procedure **I-b**, compound **Y2-SiR$_3$** (1.340 g, 60% yield) was obtained as a light brown oil by flash chromatography (20% EtOAct/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (m, 4H), 7.30 (m, 1H), 4.25 (t, *J* = 8.7 Hz, 2H), 4.14 (t, *J* = 8.2 Hz, 2H), 3.99 (m, 1H), 1.45 (s, 10H), 0.21 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.7, 156.2, 138.4, 129.3, 127.6, 124.8, 95.1, 79.9, 75.8, 51.4, 33.6, 28.5, 0.1.
HRMS (ESI) Calcd. For $C_{20}H_{28}N_2O_3SiH$ [M+H]+: 373.1942. Found 373.1947.

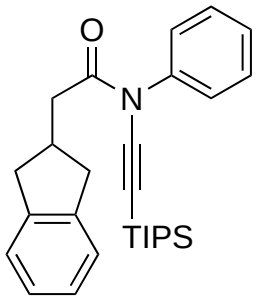
isopropyl phenyl((triisopropylsilyl)ethynyl)carbamate (Y3-SiR$_3$)



Starting from isopropyl phenylcarbamate (0.896 g, 5 mmol), and by following general procedure **I-a**, compound **Y3-SiR$_3$** (1.699 g, 94% yield) was obtained as an orange oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 8.6 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 5.05 (h, *J* = 6.3 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 6H), 1.11 (s, 21H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 154.2, 139.5, 128.8 (2C), 126.4, 124.0 (2C), 96.6, 77.1, 71.73, 69.0, 22.1 (2C), 18.8 (6C), 11.6 (3C).
HRMS (ESI) calcd. for $C_{21}H_{33}NO_2SiH$ [M+H]+: 360.2353. Found 360.2353.

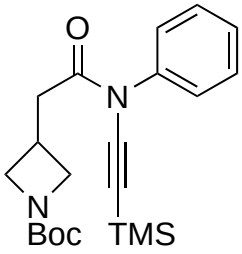
2-(2,3-dihydro-1*H*-inden-2-yl)-*N*-phenyl-*N*-((triisopropylsilyl)ethynyl)acetamide (Y4-SiR_3)



Starting from 2-(2,3-dihydro-1*H*-inden-2-yl)-*N*-phenylacetamide (1.256 g, 5 mmol), and by following general procedure **I-a**, compound **Y4-SiR_3** (1.159 g, 54% yield) was obtained as a pale brown oil by flash chromatography (40% DCM/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.50 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 8.3 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.22 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.18 – 7.12 (m, 2H), 3.24 (dd, *J* = 15.6, 7.0 Hz, 2H), 3.14 – 3.02 (m, 3H), 2.74 (dd, *J* = 15.4, 6.4 Hz, 2H), 1.07 (brs, 21H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 173.5, 142.8, 139.0, 128.9, 127.1, 126.4, 124.8, 124.6, 97.9, 72.2, 41.1, 39.2, 36.0, 18.8, 11.5.
HRMS (ESI) calcd. for $C_{28}H_{37}NOSiH$ [M+H]+: 432.2717. Found 432.2717.

***tert*-butyl 3-(2-oxo-2-(phenyl((trimethylsilyl)ethynyl)amino)ethyl)azetidine-1-carboxylate (Y5-SiR_3)**



Starting from *tert*-butyl 3-(2-oxo-2-(phenylamino)ethyl)azetidine-1-carboxylate (0.580 g, 2 mmol), and by following general procedure **I-b**, compound **Y5-SiR_3** (0.377 g, 48% yield) was obtained as a brown oil by flash chromatography (20% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (m, 4H), 7.29 (m, 1H), 4.14 (t, *J* = 8.5 Hz, 2H), 3.66 (dd, *J* = 8.9, 5.4 Hz, 2H), 3.14 (d, *J* = 7.7 Hz, 2H), 2.98 (ddt, *J* = 10.9, 8.0, 4.0 Hz, 1H), 1.44 (s, 9H), 0.21 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.3, 156.4, 138.4, 129.1 (2C), 127.5, 125.1 (2C), 96.0, 79.5, 76.1, 39.5, 28.5, 25.2, 0.1.
HRMS (ESI) calcd. for $C_{21}H_{30}N_2O_3SiH$ [M+H]+: 387.2098. Found 387.2101.

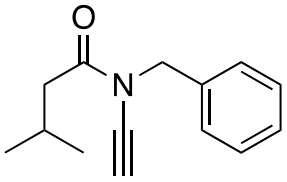
7. Synthesis of Ynamides

7.1 General procedure II

To a solution of the protected ynamide (1 equiv.) in tetrahydrofuran (0.2 M) under argon at 0°C was added tetrabutylammonium fluoride (1M in THF, 1.3 equiv.) dropwise. The reaction mixture was stirred at 0°C for 1 h. After completion of the reaction, a saturated solution of NH_4Cl was added, the aqueous phase was extracted three times with EtOAc. After washing with a saturated solution of NaCl, the organic phases were dried over $MgSO_4$ and concentrated. The crude was purified by column chromatography. The obtained ynamides were stored in the freezer.

7.2 Characterization data of ynamides

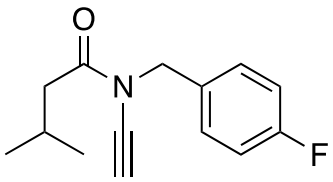
***N*-benzyl-*N*-ethynyl-3-methylbutanamide (1a)**



Starting from the corresponding ynamide **1a-SiR$_3$** (0.584 g, 1.57 mmol), and by following the general procedure **II**, compound **1a** (0.181 g, 54% yield) was obtained as a yellow-white solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36 – 7.30 (m, 5H), 4.69 (s, 2H), 2.98 (s, 1H), 2.57 (d, *J* = 7.0 Hz, 2H), 2.21 (dq, *J* = 13.5, 6.8 Hz, 1H), 0.97 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.1, 136.2, 128.6 (3C), 128.0 (2C), 78.1, 62.2, 51.2, 43.1, 25.7, 22.6.
HRMS (ESI) Calcd. for $C_{14}H_{17}NOH$ [M+H]+: 216.1383, Found 216.1378.
M.p.: 36°C

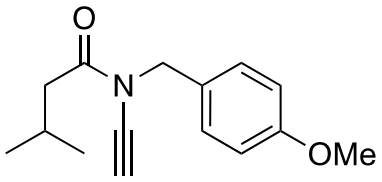
***N*-ethynyl-*N*-(4-fluorobenzyl)-3-methylbutanamide (1b)**



Starting from the corresponding ynamide **1b-SiR$_3$** (0.975 g, 2.5 mmol), and by following the general procedure **II**, compound **1b** (0.497 g, 85% yield) was obtained as a yellow yellow by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.32 (dd, *J* = 8.5, 5.5 Hz, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 4.64 (s, 2H), 2.99 (s, 1H), 2.55 (d, *J* = 7.0 Hz, 2H), 2.19 (non, *J* = 6.7 Hz, 1H), 0.96 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 174.1, 163.9, 161.4, 132.1 (d, *J* = 3.4 Hz), 130.5 (d, *J* = 8.3 Hz, 2C), 115.5 (d, *J* = 21.5 Hz, 2C), 77.9, 62.3, 50.5, 43.1, 25.7, 22.5 (2C).
^{19}F NMR (376 MHz, CDCl3) δ ppm -114.26.
HRMS (ESI) calcd. for $C_{14}H_{16}FNOH$ [M+H]+: 234.1289. Found 234.129.

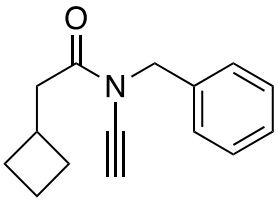
***N*-ethynyl-*N*-(4-methoxybenzyl)-3-methylbutanamide (1c)**



Starting from the corresponding ynamide **1c-SiR$_3$** (0.767 g, 1.9 mmol), and by following the general procedure **II**, compound **1c** (0.273 g, 58% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.28 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 6.9 Hz, 2H), 4.61 (s, 2H), 3.79 (s, 3H), 2.97 (s, 1H), 2.54 (d, *J* = 7.0 Hz, 2H), 2.20 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 174.1, 159.5, 130.2 (2C), 128.4, 114.0 (2C), 78.1, 62.2, 55.3, 50.7, 43.1, 25.7, 22.5 (2C).
HRMS (ESI) calcd. for $C_{15}H_{19}NO_2H$ [M+H]+: 246.1489. Found 246.1489.

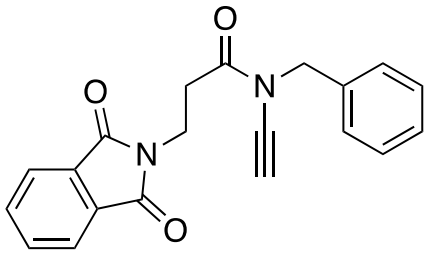
***N*-benzyl-2-cyclobutyl-*N*-ethynylacetamide (1d)**



Starting from the corresponding ynamide **1d-SiR$_3$** (0.713 g, 1.85 mmol), and by following the general procedure **II**, compound **1d** (0.368 g, 89% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.32 (m, 5H), 4.66 (s, 2H), 2.97 (s, 1H), 2.80 (m, 3H), 2.15 (m, 2H), 1.88 (m, 2H), 1.74 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm δ 173.83, 136.22, 128.65 (3C), 128.05 (2C), 78.10, 62.15, 51.13, 41.12, 32.26, 28.41, 18.85.
HRMS (ESI) Calcd. for $C_{15}H_{17}NOH$ [M+H]+: 228.1383. Found 228.1376.

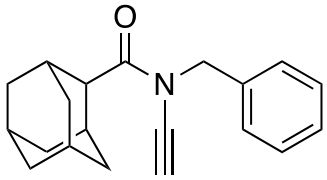
***N*-benzyl-3-(1,3-dioxoisoindolin-2-yl)-*N*-ethynylpropanamide (1e)**



Compound was received from Servier as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.84 (m, 2 H), 7.71 (m, 2H), 7.33 (br m, 4H), 7.26 (m, 1H), 4.66 (s, 2 H), 4.06 (t, *J* = 7.4 Hz, 2 H), 3.11 (t, *J* = 7.4 Hz, 2 H), 2.93 (s, 1 H).
^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 171.82, 168.13, 135.67, 134.10, 132.20, 128.79, 128.67, 128.17, 123.43, 62.90, 51.23, 33.79, 33.10.
HRMS (ESI) Calcd. for $C_{20}H_{16}N_2O_3Na$ $[M+Na]^+$: 355.1053, Found 355.1044.
M.p.: 138°C

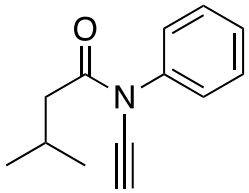
(1*R*,3*S*,5*r*,7*r*)-*N*-benzyl-*N*-ethynyladamantane-2-carboxamide (1f)



Starting from the corresponding ynamide **1f-SiR$_3$** (0.706 g, 1.57 mmol), and by following the general procedure **II**, compound **1f** (0.281 g, 61% yield) was obtained as a transparent oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.34-7.28 (m, 5H), 4.68 (s, 2H), 3.31 (br s, 1H), 3.00 (s, 1H), 2.26 (m, 4H), 1.92-1.74 (m, 8H), 1.61 (d, *J* = 12.4 Hz, 2H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 176.8, 136.6, 128.6 (2C), 128.4 (2C), 127.9, 78.3, 61.9, 51.3, 48.0, 38.6 (2C), 37.6, 32.7 (2C), 30.0 (2C), 27.9, 27.4.
HRMS (ESI) calcd. for $C_{20}H_{23}NOH$ [M+H]+: 294.1852. Found 294.1853.

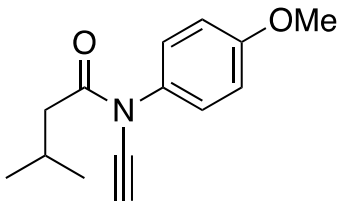
***N*-ethynyl-3-methyl-*N*-phenylbutanamide (1g)**



Starting from the corresponding ynamide **1g-SiR$_3$** (0.502 g, 1.4 mmol), and by following the general procedure **II**, compound **1g** (0.161 g, 57% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 (m, 2 H), 7.41 (m, 2 H), 7.31 (dt, *J* = 8.8, 4.3 Hz, 1 H), 3.06 (s, 1 H), 2.68 (br d, *J* = 7.0 Hz, 2 H), 2.28 (dq, *J* = 13.5, 6.6 Hz, 1H), 1.04 (m, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.8, 138.9, 129.2 (2C), 127.6, 125.6 (2C), 77.5, 61.2, 43.5, 25.8, 22.6, 22.5.
HRMS (ESI) Calcd. for $C_{13}H_{15}NOH$ [M+H]+: 202.1226, Found 202.1222.
M.p.: 55°C

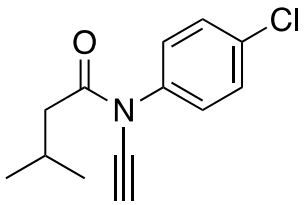
***N*-ethynyl-*N*-(4-methoxyphenyl)-3-methylbutanamide (1h)**



Starting from the corresponding ynamide **1h-SiR$_3$** (0.530 g, 1.367 mmol), and by following the general procedure **II**, compound **1h** (0.137 g, 44% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.29 (d, *J* = 8.2 Hz, 2 H), 6.92 (d, *J* = 8.4 Hz, 2 H), 3.81 (s, 3 H), 3.03 (s, 1 H), 2.64 (bs, 2 H), 2.26 (dq, *J* = 13.6, 6.7 Hz, 1H), 1.02 (d, *J* = 6.3 Hz, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.1, 158.9, 131.8, 127.0 (2C), 114.5 (2C), 78.2, 60.8, 55.6, 43.3, 25.8, 22.4 (2C).
HRMS (ESI) Calcd. for $C_{14}H_{17}NO_2H$ [M+H]+: 232.1332, Found 232.1333.
M.p.: 49-50°C

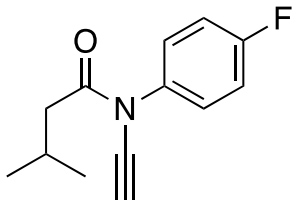
***N*-(4-chlorophenyl)-*N*-ethynyl-3-methylbutanamide (1i)**



Starting from the corresponding ynamide **1i-SiR$_3$** (0.551 g, 1.405 mmol), and by following the general procedure **II**, compound **1i** (90 mg, 27% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.37 (m, 4 H), 3.09 (s, 3 H), 2.69 (d, *J* = 6.9 Hz, 2 H), 2.26 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.03 (d, *J* = 6.7 Hz, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.67, 137.38, 133.08, 129.27 (2C), 126.68 (2C), 61.77, 43.55, 25.74, 22.62 (2C).
HRMS (ESI) Calcd. for $C_{13}H_{14}ClNOH$ [M+H]+: 236.0837, Found 236.0837.

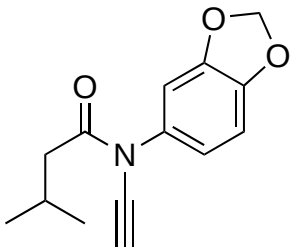
***N*-ethynyl-*N*-(4-fluorophenyl)-3-methylbutanamide (1j)**



Starting from the corresponding ynamide **1j-SiR$_3$** (0.492 g, 1.30 mmol), and by following the general procedure **II**, compound **1j** (58 mg, 19% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.38 (m, 2 H), 7.09 (t, *J* = 8.5 Hz, 2 H), 3.07 (s, 3 H), 2.68 (d, *J* = 6.9 Hz, 2 H), 2.27 (sept, *J* = 6.7 Hz, 1 H), 1.03 (d, *J* = 6.8 Hz, 6 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm173.8, 162.8 (d, *J* = 247.5 Hz), 134.8 (d, *J* = 3.2 Hz), 127.4 (d, *J* = 7.3 Hz), 116.0 (d, *J* = 22.7 Hz), 77.7, 61.4, 43.4, 25.7, 22.6.
^{19}F NMR (376 MHz, CDCl3) δ ppm -114.11.
HRMS (ESI) Calcd. for $C_{13}H_{14}FNOH$ [M+H]+: 220.1132, Found 220.1133.
M.p.: 68°C

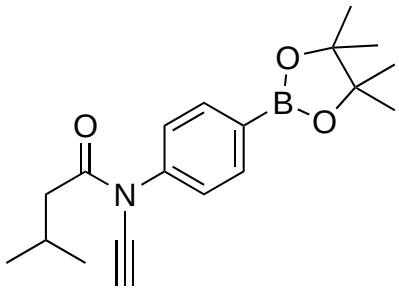
***N*-(benzo[*d*][1,3]dioxol-5-yl)-*N*-ethynyl-3-methylbutanamide (1k)**



Starting from the corresponding ynamide **1k-SiR$_3$** (0.665 g, 1.65 mmol), and by following the general procedure **II**, compound **1k** (0.178 g, 44% yield) was obtained as a brown solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 6.87 – 6.80 (m, 3H), 6.00 (s, 2H), 3.04 (s, 1H), 2.63 (m, 2H), 2.26 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 7H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 174.0, 148.1, 147.2, 132.8, 119.4, 108.3, 107.4, 101.9, 78.0, 61.0, 43.3, 25.8, 22.6, 22.5.
HRMS (ESI) calcd. for $C_{14}H_{15}NO_3H$ [M+H]+: 246.1125. Found 246.1126.
M.p.: 43°C

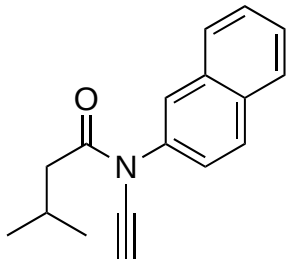
***N*-ethynyl-3-methyl-*N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanamide (1l)**



Starting from the corresponding ynamide **1l-SiR$_3$** (0.720 g, 1.8 mmol), and by following the general procedure **II**, compound **1l** (0.344 g, 58% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.86 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 3.09 (s, 1H), 2.70 (d, *J* = 7.0 Hz, 2H), 2.30 (m, 1H), 1.37 (s, 12H), 1.05 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 173.6, 141.4, 135.7 (2C), 124.5 (2C), 84.1, 77.6, 61.6, 43.6, 25.7, 25.01, 25.0, 22.6 (4C), 22.5 (2C).
HRMS (ESI) calcd. for $C_{19}H_{26}BNO_3H$ [M+H]+: 328.2079. Found 328.2073.
M.p.: 80°C

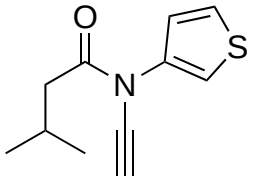
***N*-ethynyl-3-methyl-*N*-(naphthalen-2-yl)butanamide (1m)**



Starting from the corresponding ynamide **1m-SiR$_3$** (0.746 g, 1.83 mmol), and by following the general procedure **II**, compound **1m** (0.280 g, 60% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.94 – 7.81 (m, 4H), 7.56 – 7.47 (m, 3H), 3.12 (s, 1H), 2.74 (d, *J* = 7.0 Hz, 2H), 2.33 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.07 (d, *J* = 6.7 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 174.0, 136.4, 133.5, 132.4, 129.0, 128.1, 127.8, 126.7, 126.6, 123.9, 123.8, 77.9, 61.4, 43.5, 25.8, 22.6 (2C).
HRMS (ESI) calcd. for $C_{17}H_{17}NOH$ [M+H]+: 252.1383. Found 252.1383.

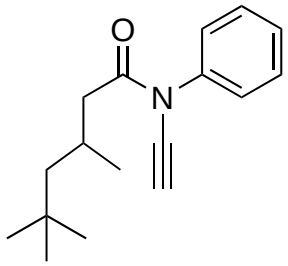
***N*-ethynyl-3-methyl-*N*-(thiophen-3-yl)butanamide (1n)**



Starting from the corresponding ynamide **1n-SiR$_3$** (2.680 g, 7.37 mmol), and by following the general procedure **II**, compound **1n** (0.928 g, 61% yield) was obtained as an orange oil by flash chromatography (20% EtOAc/PE).

^{1}H NMR (500 MHz, CDCl3) δ ppm 7.5 (dd, *J* = 3.2, 1.5 Hz, 1H), 7.31 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.27 (dd, *J* = 5.3, 3.2 Hz, 1H), 3.20 (s, 1 H), 2.70 (br d, J = 6.6 Hz, 2 H), 2.27 (sept, J = 6.8 Hz, 1 H), 1.03 (d, J = 6.7 Hz, 6 H).
^{13}C NMR (125 MHz, CDCl3) δ ppm 173.1, 136.5, 124.6 (2C), 123.4 (2C), 115.3, 77.6, 62.6, 43.8, 25.7, 22.6 (2C).
HRMS (ESI) calcd. for $C_{11}H_{14}NOS$ [M+H]+: 208.0791, found 208.0791.

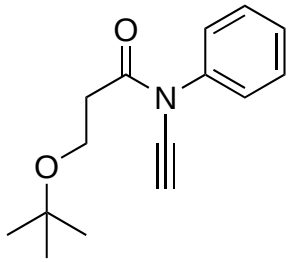
***N*-ethynyl-3,5,5-trimethyl-*N*-phenylhexanamide (1o)**



Starting from the corresponding ynamide **1o-SiR$_3$** (0.618 g, 1.49 mmol), and by following the general procedure **II**, compound **1o** (0.201 g, 52% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.41 (m, 4H), 7.30 (m, 1H), 3.07 (s, 1H), 2.71 (qd, *J* = 45.3, 8.0, 6.0 Hz, 2H), 2.25 (m, 2H), 1.27 (qd, *J* = 50.6, 6.6, 4.1 Hz, 2H), 1.06 (d, *J* = 6.6 Hz, 3H), 0.93 (s, 9H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 173.87, 138.97, 129.22 (2C), 127.62, 125.58 (2C), 78.03, 61.21, 50.90, 44.24, 31.30, 30.17, 30.08, 27.07, 22.85.
HRMS (ESI) calcd. for $C_{17}H_{23}NOH$ $[M+Na]^+$: 258.1852. Found 258.1855.

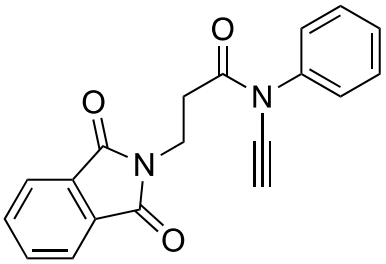
3-(*tert*-butoxy)-*N*-ethynyl-*N*-phenylpropanamide (1p)



Starting from the corresponding ynamide **1p-SiR$_3$** (0.486 g, 1.21 mmol), and by following the general procedure **II**, compound **1p** (0.230 g, 77% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.41 (m, 4 H), 7.30 (m, 1 H), 3.74 (t, *J* = 6.8 Hz, 2 H), 3.05 (s, 1 H), 3.01 (br s, 2 H), 1.22 (s, 9 H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 172.6, 138.8, 129.2 (2C), 127.7, 125.6 (2C), 77.5, 73.4, 61.4, 57.4, 36.2, 27.6 (3C).
HRMS (ESI) calcd. for $C_{15}H_{19}NO_2H$ [M+H]+: 246.1489. Found 246.1490.

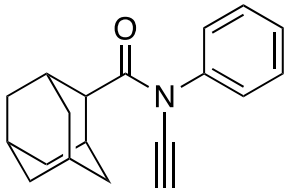
3-(1,3-dioxoisoindolin-2-yl)-*N*-ethynyl-*N*-phenylpropanamide (1q)



Starting from the corresponding ynamide **1q-SiR$_3$** (0.514 g, 1.31 mmol), and by following the general procedure **II**, compound **1q** (0.261 g, 63% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.85 (dd, *J* = 5.2, 3.2 Hz, 2H), 7.71 (dd, *J* = 5.5, 2.9 Hz, 2H), 7.40 (m, 4H), 7.30 (m, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 3.23 (br t, *J* = 6.8 Hz, 2H), 3.02 (s, 1H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 171.56, 168.20, 138.37, 134.16, 132.23, 129.29, 127.86, 125.48, 123.48, 77.36, 61.75, 33.85, 33.68.
HRMS (ESI) calcd. for $C_{19}H_{14}N_2O_3H$ [M+H]+: 319.1077. Found 319.1079.
M.p.: 143°C

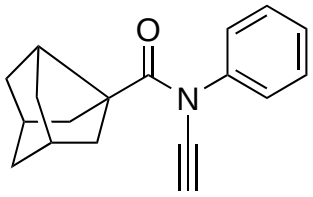
(1*R*,3*S*,5*r*,7*r*)-*N*-ethynyl-*N*-phenyladamantane-2-carboxamide (1r)



Starting from the corresponding ynamide **1r-SiR$_3$** (0.936 g, 2.12 mmol), and by following the general procedure **II**, compound **1r** (0.451 g, 76% yield) was obtained as a white solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39 (m, 4 H), 7.28 (m, 1 H), 3.48 (br s, 1 H), 3.08 (s, 1 H), 2.39 (br s, 2 H), 2.28 (d, *J* = 12.9 Hz, 2 H), 1.96-1.82 (m, 6 H), 1.77 (br s, 2 H), 1.65 (d, *J* = 12.9 Hz, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.7, 139.3, 129.1 (2C), 127.4, 125.7 (2C), 78.1, 60.9, 48.3, 38.7, 37.6, 32.7, 30.1, 27.9, 27.4.
HRMS (ESI) Calcd. for $C_{19}H_{21}NOH$ [M+H]+: 280.1696. Found 280.1697.
M.p.: 110°C

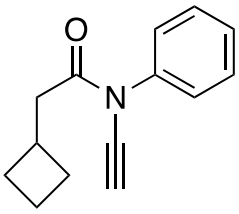
(3a*s*,6a*s*)-*N*-ethynyl-*N*-phenylhexahydro-2,5-methanopentalene-3a(1*H*)-carboxamide (1s)



Starting from the corresponding ynamide **1s-SiR$_3$** (0.510 g, 1.2 mmol), and by following the general procedure **II**, compound **1s** (0.302 g, 94% yield) was obtained as a white solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.45 – 7.33 (m, 4H), 7.35 – 7.27 (m, 1H), 3.14 (t, *J* = 6.9 Hz, 1H), 3.05 (s, 1H), 2.37 (dd, *J* = 7.8, 2.1 Hz, 4H), 2.04 (dp, *J* = 8.0, 2.3 Hz, 4H), 1.72 – 1.52 (m, 4H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 177.9, 140.9, 129.1, 127.6, 126.2, 78.7, 61.8, 56.7, 47.1, 43.7, 42.8, 37.7, 35.2.
HRMS (ESI) calcd. for $C_{18}H_{19}NOH$ [M+H]+: 266.1539. Found 266.154.
M.p.: 135°C

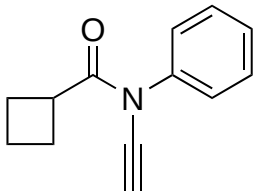
2-cyclobutyl-*N*-ethynyl-*N*-phenylacetamide (1t)



Starting from the corresponding ynamide **1t-SiR$_3$** (0.700 g, 1.89 mmol), and by following the general procedure **II**, compound **1t** (0.200 g, 49% yield) was obtained as a pale yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (m, 4 H), 7.30 (m, 1 H), 3.06 (s, 1 H), 2.91 (br d, *J* = 7.5 Hz, 2 H), 2.83 (sept, *J* = 7.7 Hz, 1 H), 2.19 (m, 2 H), 1.97/1.75 (m, 4 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.5, 138.8, 129.2 (2C), 127.6, 125.5 (2C), 77.9, 61.2, 41.6, 32.2, 28.5 (2C), 18.9.
HRMS (ESI) Calcd. for $C_{14}H_{15}NOH$ [M+H]+: 214.1226, Found 214.1222**.**

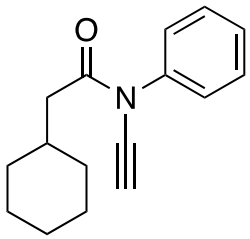
***N*-ethynyl-*N*-phenylcyclobutanecarboxamide (1u)**



Starting from the corresponding ynamide **1u-SiR$_3$** (0.747 g, 2.1 mmol), and by following the general procedure **II**, compound **1u** (0.273 g, 65% yield) was obtained as a pale yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.41 (m, 4 H), 7.30 (m, 1 H), 3.82 (br s, 1 H), 3.01 (s, 1 H), 2.48-2.38 (m, 2 H), 2.27 (br s, 2 H), 2.05-1.90 (m, 2 H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 176.1, 138.9, 129.1 (2C), 127.5, 125.3 (2C), 77.3, 60.5, 38.7, 25.2 (2C), 18.1.
HRMS (ESI) calcd. for $C_{13}H_{13}NOH$ [M+H]+:200.1070. Found 200.1071.
M.p.: 49°C

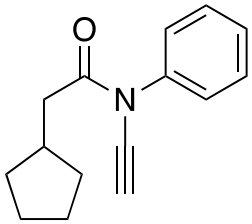
2-cyclohexyl-*N*-ethynyl-*N*-phenylacetamide (1v)



Starting from the corresponding ynamide **1v-SiR$_3$** (0.725 g, 1.825 mmol), and by following the general procedure **II**, compound **1v** (0.140 g, 32% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (d, *J* = 4.6 Hz, 4 H), 7.30 (m, *J* = 4.5 Hz, 1 H), 3.06 (s, 1 H), 2.67 (d, *J* = 6.6 Hz, 2 H), 1.96 (m, 1 H), 1.86/1.62 (m, 5 H), 1.29 (q, *J* = 12.8 Hz, 2 H), 1.18 (br t, *J* = 12.3 Hz, 1 H), 1.05 (q, *J* = 12.3 Hz, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.8, 138.9, 129.2 (2C), 127.6, 125.6 (2C), 77.9, 61.2, 42.2, 35.1, 33.2 (2C), 26.3, 26.23 (2C).
HRMS (ESI) Calcd. for $C_{16}H_{19}NOH$ [M+H]+: 242.1539, Found 242.1539.
M.p.: 68-70°C

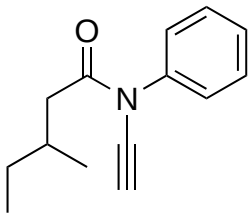
2-cyclopentyl-*N*-ethynyl-*N*-phenylacetamide (1w)



Starting from the corresponding ynamide **1w-SiR$_3$** (0.948 g, 2.471 mmol), and by following the general procedure **II**, compound **1w** (90 mg, 16% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (m, 2 H), 7.40 (m, 2 H), 7.30 (m, 1 H), 3.06 (s, 1 H), 2.82 (br d, *J* = 7.3 Hz, 2 H), 2.39 (sept, *J* = 7.6 Hz, 1 H), 1.91 (m, 2 H), 1.61 (m, 4 H), 1.25 (m, 2 H).
^{13}C NMR (101MHz, $CDCl_3$) δ ppm 174.1, 138.9, 129.2 (2C), 127.6, 125.5 (2C), 77.9, 61.2, 40.8, 36.5, 32.6 (2C), 25.2 (2C).
HRMS (ESI) Calcd. for $C_{15}H_{17}NOH$ [M+H]+: 228.1383, Found 228.1376.

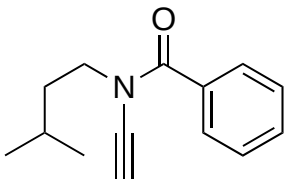
***N*-ethynyl-3-methyl-*N*-phenylpentanamide (1x)**



Starting from the corresponding ynamide **1x-SiR$_3$** (0.824 g, 2.21 mmol), and by following the general procedure **II**, compound **1x** (0.224 g, 47% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46 – 7.37 (m, 4H), 7.30 (m, 1H), 3.06 (s, 1H), 2.70 (ddd, *J* = 80.2, 15.3, 6.9 Hz, 2H), 2.07 (d, *J* = 6.7 Hz, 1H), 1.52 – 1.24 (m, 3H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101MHz, $CDCl_3$) δ ppm 174.0, 138.9, 129.2, 127.6, 125.6, 77.9, 61.2, 41.6, 32.0, 29.6, 19.4, 17.8, (12.4, 11.5, silanol).
HRMS (ESI) Calcd. for $C_{14}H_{17}NOH$ [M+H]+: 216.1383. Found 216.1376.

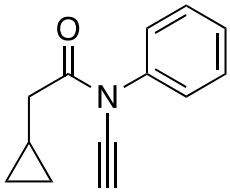
_N_-ethynyl-_N_-isopentylbenzamide (1z)



Starting from the corresponding ynamide **1z-SiR$_3$** (0.702 g, 1.89 mmol), and by following the general procedure **II**, compound **1z** (0.311 g, 74% yield) was obtained as a yellow oil by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.76 (d, *J* = 7.9 Hz, 2H), 7.47 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 3.73 (dd, *J* = 8.1, 5.2 Hz, 2H), 2.77 (s, 1H), 1.77 – 1.62 (m, 3H), 0.98 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 171.1, 133.9, 131.4, 128.7 (2C), 127.9 (2C), 78.8, 61.0, 47.6, 36.2, 25.8, 22.6 (2C).
HRMS (ESI) calcd. for $C_{14}H_{17}NOH$ [M+H]+: 216.1383. Found 216.1382.

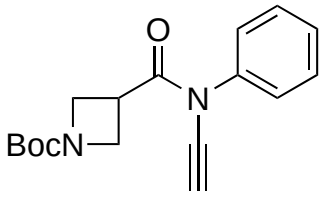
2-cyclopropyl-_N_-ethynyl-_N_-phenylacetamide (Y1)



Starting from the corresponding ynamide **Y1-SiR$_3$** (0.347 g, 0.97 mmol), and by following the general procedure **II**, compound **Y1** (0.108 mg, 55% yield) was obtained as a yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42 (m, 4 H), 7.30 (t, *J* = 7.1 Hz, 1 H), 3.05 (s, 1 H), 2.72 (d, *J* = 7.0 Hz, 2 H), 1.20 (m, 1 H), 0.61 (dt, *J* = 8.1, 5.7 Hz, 2 H), 0.25 (q, *J* = 5.3 Hz, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.0, 138.8, 129.2 (2C), 127.6, 125.4 (2C), 77.8, 61.2, 40.0, 17.8, 6.9, 4.5.
HRMS (ESI) Calcd. for $C_{13}H_{13}NOH$ [M+H]+: 200.1070, Found 200.1065.
M.p.: 81°C

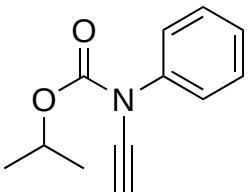
***tert*-butyl 3-(ethynyl(phenyl)carbamoyl)azetidine-1-carboxylate (Y2)**



Starting from the corresponding ynamide **Y2-SiR$_3$** (0.755 g, 2.02 mmol), and by following the general procedure **II**, compound **Y2** (85 mg, 14% yield) was obtained as a yellow oil by flash chromatography (50% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (m, 4H), 7.33 (m, *J* = 4.4 Hz, 1H), 4.30 – 4.22 (m, 2H), 4.13 (t, *J* = 7.2 Hz, 2H), 3.99 (br s, 1H), 3.07 (s, 1H), 1.45 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 72.9, 156.2, 138.2, 129.3, 127.9, 125.0, 80.0, 77.3, 76.4, 61.6, 51.4, 33.4, 28.5, 28.5.
HRMS (ESI) Calcd. for $C_{17}H_{20}N_2O_3H$ [M+H]+: 301.1547. Found 301.1552.

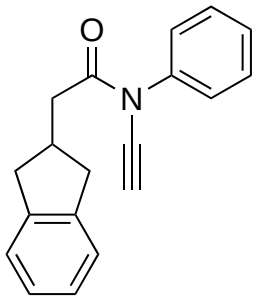
isopropyl ethynyl(phenyl)carbamate (Y3)



Starting from the corresponding ynamide **Y3-SiR$_3$** (0.950 g, 2.64 mmol), and by following the general procedure **II**, compound **Y3** (0.528 g, 98% yield) was obtained as an off yellow solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.47 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 8.4 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 5.06 (hept, *J* = 6.3 Hz, 1H), 2.89 (s, 1H), 1.34 (d, *J* = 6.3 Hz, 6H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 154.1, 139.2, 129.0 (2C), 127.1, 124.8 (2C), 76.6, 72.1, 58.5, 21.9 (2C).
HRMS (ESI) calcd. for $C_{12}H_{13}NO_2NH_4$ [M+NH_4]+: 221.1285. Found 221.1286.
M.p.: 92°C

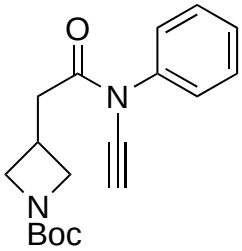
2-(2,3-dihydro-1*H*-inden-2-yl)-*N*-ethynyl-*N*-phenylacetamide (Y4)



Starting from the corresponding ynamide **Y4-SiR$_3$** (0.691 g, 1.6 mmol), and by following the general procedure **II**, compound **Y4** (0.351 g, 80% yield) was obtained as a white solid by flash chromatography (10% EtOAc/PE).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.48 – 7.40 (m, 4H), 7.34 – 7.29 (m, 1H), 7.22 (dd, *J* = 5.4, 3.4 Hz, 2H), 7.16 (m, 2H), 3.23 (dd, *J* = 15.6, 7.3 Hz, 2H), 3.07 (s, 1 H), 3.02 (m, 3H), 2.75 (m, *J* = 15.8, 6.8 Hz, 2H).
^{13}C NMR (101 MHz, CDCl3) δ ppm 173.6, 142.8 (2C), 138.8, 129.2 (2C), 127.7, 126.4 (2C), 125.5 (2C), 124.6 (2C), 77.7 (2C), 77.1, 61.6, 40.5, 39.1 (2C), 36.0.
HRMS (ESI) calcd. for $C_{19}H_{17}NOH$ [M+H]+: 276.1383. Found 276.1383.
M.p.: 91°C

***tert*-butyl 3-(2-(ethynyl(phenyl)amino)-2-oxoethyl)azetidine-1-carboxylate (Y5)**



Starting from the corresponding ynamide **Y5-SiR$_3$** (0.485 g, 1.25 mmol), and by following the general procedure **II**, compound **Y5** (0.160 g, 41% yield) was obtained as an orange oil by flash chromatography (20% EtOAc/PE).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (m, 4H), 7.31 (m, 1H), 4.14 (t, *J* = 8.5 Hz, 2H), 3.66 (m, 2H), 3.13 (br s, 2H), 3.11 (s, 1H), 2.98 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.4, 156.4, 138.4, 129.3 (2C), 127.8, 125.3 (2C), 79.5, 77.3, 61.9, 39.4, 28.5 (3C), 25.2.
HRMS (ESI) Calcd. for $C_{18}H_{22}N_2O_3H$ [M+H]+: 315.1703. Found 315.1705.

8. Trifluoromethylated products

8.1 General procedure: photoredox

To a capped vial equipped with a stirring bar was added fac-Ir(ppy)$_3$ (0.025 equiv.), ynamide **1** (1.0 equiv.), and the Togni reagent (1.2 equiv.). The reaction vial was evacuated and back-filled with nitrogen three times. Degassed MeCN (0.1 M) was added. The reaction mixture was freeze pumped twice to deoxygenate the solvent. The vial was sealed. The stirred mixture was irradiated with blue LEDs for the specified time. The reaction mixture was concentrated, washed with an aqueous solution of $NaHCO_3$ and extracted with EtOAc. The residue was purified twice by a column chromatography, first with PE/EtOAc 80:20, and then a second column with Toluene/EtOAc 90:10.

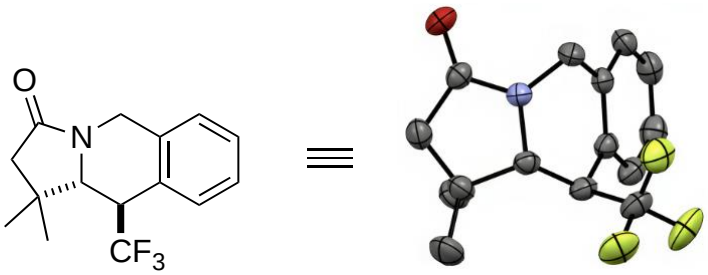
8.2 Procedure for mechanoredox trifluoromethylation cyclization cascade reaction

Ynamide (0.1 mmol, 1 equiv.), Togni I reagent (66.01 mg, 0.2 mmol, 2 equiv.), and tet-$BaTiO_3$ (1.16 mg, 0.005 mmol, 0.05 equiv.) were placed in a stainless-steel milling jar (5.0 mL) with a stainless-steel ball (8 mm, diameter) in air. Then Acetone (1.2 µL/mg for the solid reactants) was added to the mixture. After the jar was closed in air, the jar was placed in a ball mill (Anton Paar BM500). After grinding for the 3h at 30 Hz, the reaction mixture was passed through a short silica gel column eluting with ethyl acetate. The crude material was purified by silica gel column chromatography.

8.3 Characterization data of Trifluoromethylated products

All products were obtained in a racemic mixture of (R,R) and (S,S).

1,1-dimethyl-10-(trifluoromethyl)-1,5,10,10a-tetrahydropyrrolo[1,2-*b*]isoquinolin-3(2*H*)-one (2a)



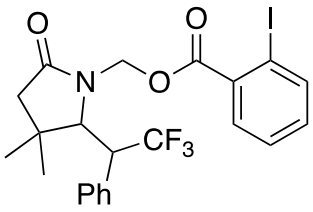
X-ray structure
CCDC 2295986

Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1a** (43 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using Ir(ppy)$_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1h 15 min. The

compound **2a** (29.4 mg, 52% yield) was obtained as white solid by flash chromatography (PE/EtOAc 50:50).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.30 (m, 3H), 7.22 (d, *J* = 8.1 Hz, 1H), 4.98 (d, *J* = 15.4 Hz, 1H), 4.05 (d, *J* = 2.3 Hz, 1H), 3.98 (d, *J* = 15.4 Hz, 1H), 3.56 (p, *J* = 10.6 Hz, 1H), 2.45 (d, *J* = 15.8 Hz, 1H), 2.13 (d, *J* = 15.8 Hz, 1H), 1.26 (s, 3H), 0.75 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.1, 136.2, 131.4, 128.9, 128.0, 127.9 (q, *J* = 279.3 Hz), 127.5 (q, *J* = 1.9 Hz), 127.1, 62.0 (q, *J* = 2.2 Hz), 47.2, 43.1 (q, *J* = 27.1 Hz), 40.6, 39.4, 24.6, 21.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -70.30.
HRMS (ESI): calcd. for $C_{15}H_{16}F_3NOH$ $[M+H]^+$: 284.1257. Found 284.1256.
M.p.: 140.6-142.4°C

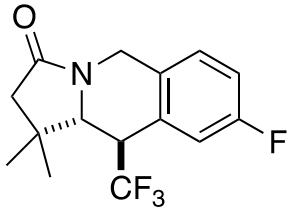
(3,3-dimethyl-5-oxo-2-(2,2,2-trifluoro-1-phenylethyl)pyrrolidin-1-yl)methyl 2-iodobenzoate (2aa)



The compound **2aa** (13.8 mg, 13% yield) was obtained as a colorless oil by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.01 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.82 (dd, *J* = 7.9, 1.7 Hz, 1 H), 7.38 (m, 4 H), 7.31 (m, 2 H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1 H), 6.02 (d, *J* = 10.6 Hz, 1 H), 5.62 (d, *J* = 10.6 Hz, 1 H), 4.12 (m, 1 H), 3.68 (dq, *J* = 11.2, 8.2 Hz, 1 H), 1.70 (d, *J* = 16.5 Hz, 1 H), 1.41 (d, *J* = 16.6 Hz, 1 H), 1.26 (s, 3 H), 1.14 (s, 3 H).
^{19}F NMR (101 MHz, $CDCl_3$) δ ppm -65.74.
^{13}C NMR (376 MHz, $CDCl_3$) δ ppm 176.9, 166.3, 141.6, 134.4, 133, 131, 130.6 (2C), 130.4, 128.8 (3C), 128, 126.5, 94.3, 67.6, 65.2, 51.1, 43.9, 38.9, 30.4, 22.6.
HRMS (ESI): calcd. for $C_{22}H_{22}F_3INO_3$ $[M+H]^+$: 532.0591, found 532.0602.

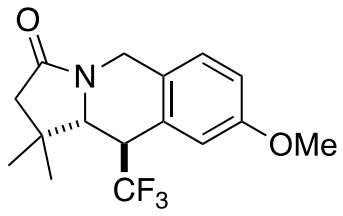
8-fluoro-1,1-dimethyl-10-(trifluoromethyl)-1,5,10,10a-tetrahydropyrrolo[1,2-*b*]isoquinolin-3(2*H*)-one (2b)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1b** (46.6 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. The compound **2b** (36.1 mg, 60% yield) was obtained as a yellow solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.20 (dd, *J* = 8.2, 5.5 Hz, 1H), 7.03 (ddd, *J* = 10.1, 8.0, 2.2 Hz, 2H), 4.97 (d, *J* = 15.3 Hz, 1H), 4.03 (d, *J* = 2.2 Hz, 1H), 3.91 (d, *J* = 15.3 Hz, 1H), 3.53 (qd, *J* = 10.3, 2.2 Hz, 1H), 2.44 (d, *J* = 15.9 Hz, 1H), 2.15 (d, *J* = 15.9 Hz, 1H), 1.25 (s, 3H), 0.75 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.0, 163.0, 160.5, 132.1 (d, *J* = 3.1 Hz), 129.4 (dd, *J* = 8.2, 2.2 Hz), 128.6 (d, *J* = 7.9 Hz), 126.3 (q, *J* = 279.3 Hz), 118.2 (d, *J* = 21.2 Hz), 116.1 (d, *J* = 21.2 Hz), 61.7 (q, *J* = 2.2 Hz), 47.1, 43.1 (qd, *J* = 26.6, 1.3 Hz), 40.0 (brq, *J* = 1.3 Hz), 39.4, 24.6, 21.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -70.17, -113.76.
HRMS (ESI): calcd. for $C_{15}H_{15}F_4NOH$ [M+H]+:302.1163. Found 302.1164.
M.p.: 132°C

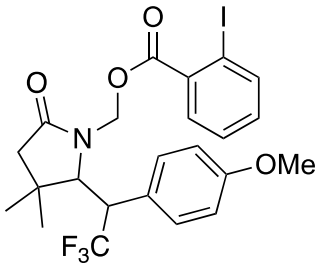
8-methoxy-1,1-dimethyl-10-(trifluoromethyl)-1,5,10,10a-tetrahydropyrrolo[1,2-*b*]isoquinolin-3(2*H*)-one (2c)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1c** (49.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. The compound **2c** (19 mg, 30% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.14 (d, *J* = 8.3 Hz, 1H), 6.84 (m, 2H), 4.92 (d, *J* = 15.2 Hz, 1H), 4.02 (d, *J* = 2.1 Hz, 1H), 3.90 (d, *J* = 15.1 Hz, 1H), 3.80 (s, 3H), 3.50 (qd, *J* = 10.5, 2.1 Hz, 1H), 2.44 (d, *J* = 15.8 Hz, 1H), 2.13 (d, *J* = 15.8 Hz, 1H), 1.24 (s, 3H), 0.75 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.0, 158.9, 128.5 (q, *J* = 2.0 Hz), 128.3, 128.0, 126.3 (q, *J* = 280.1 Hz), 117.1, 114.0, 61.9 (q, *J* = 2.1 Hz), 55.5, 47.2, 43.3 (q, *J* = 26.3 Hz), 40.1, 39.5, 24.6, 21.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -70.16.
HRMS (ESI): calcd. for $C_{16}H_{18}F_3NO_2H$ [M+H]+:314.1362. Found 314.1362.
M.p.: 136°C

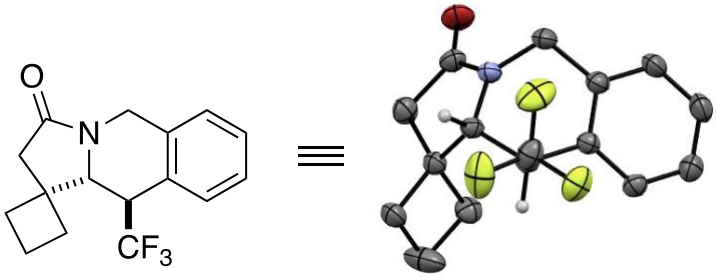
(3,3-dimethyl-5-oxo-2-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)pyrrolidin-1-yl)methyl 2-iodobenzoate (2ca)



The compound **2ca** (29 mg, 26% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 90:10).

^{1}H NMR (400 MHz, CDCl3) δ ppm 8.00 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.81 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.39 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.16 (td, *J* = 7.7, 1.7 Hz, 1H), 6.89 (m, 2H), 6.02 (d, *J* = 10.6 Hz, 1H), 5.61 (d, *J* = 10.5 Hz, 1H), 4.17 (d, *J* = 1.4 Hz, 1H), 3.80 (s, 3H), 3.63 (m, 1H), 1.70 (d, *J* = 16.6 Hz, 1H), 1.44 (d, *J* = 16.6 Hz, 1H), 1.25 (s, 3H), 1.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 177.1, 166.2, 160.1, 141.6, 134.4, 133.1, 131.9, 131.3, 128.1, 126.6 (q, *J* = 280.9 Hz), 122.2 (q, *J* = 1.4 Hz), 114.5, 94.3, 67.8 (q, *J* = 4.1 Hz), 65.1 (d, *J* = 2.1 Hz), 55.3, 50.1 (q, *J* = 26.2 Hz), 43.9, 39.0, 30.4, 22.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -66.04.
HRMS (ESI): calcd. for $C_{23}H_{23}F_3INO_4Na$ [M+Na]+: 584.0516. Found 584.0515.

10'-(trifluoromethyl)-10',10a'-dihydro-5'*H*-spiro[cyclobutane-1,1'-pyrrolo[1,2-*b*]isoquinolin]-3'(2'*H*)-one (2d)

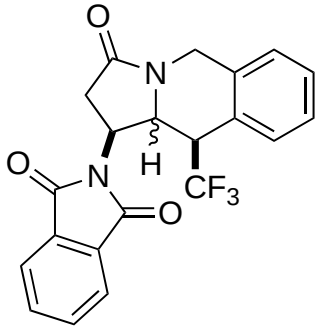


X-ray structure
CCDC 2295985

Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1d** (45.5 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 15 h. The compound **2d** (20 mg, 34% yield) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

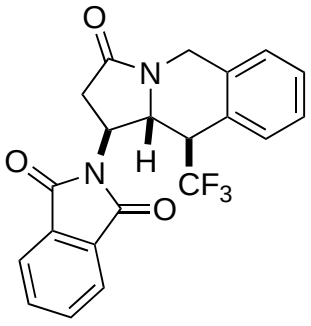
^{1}H NMR (400 MHz, CDCl3) δ ppm 7.37 – 7.33 (m, 1H), 7.32 – 7.27 (m, 2H), 7.22 (dd, *J* = 6.6, 2.4 Hz, 1H), 4.92 (d, *J* = 15.4 Hz, 1H), 4.04 (d, *J* = 2.7 Hz, 1H), 3.95 (d, *J* = 15.4 Hz, 1H), 3.84 (qd, *J* = 10.3, 2.8 Hz, 1H), 2.61 – 2.55 (m, 2H), 2.27 – 2.16 (m, 1H), 2.10 – 1.83 (m, 4H), 1.60 (dddd, *J* = 14.3, 11.3, 5.2, 2.4 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.0, 137.2, 131.5, 128.8, 127.9, 127.1 (q, *J* = 2.3 Hz), 127.0, 126.5 (q, *J* = 279.9 Hz), 60.6 (q, *J* = 2.2 Hz), 45.8, 44.8, 43.9 (q, *J* = 26.5 Hz), 40.8, 28.6 (d, *J* = 3.8 Hz), 15.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -69.87.
HRMS (ESI): calcd. for $C_{16}H_{16}F_3NOH$ [M+H]+: 296.1257. Found 296.1258.
M.p.: 115°C

2-((1*S*,10*R*)-3-oxo-10-(trifluoromethyl)-1,2,3,5,10,10a-hexahydropyrrolo[1,2-*b*]isoquinolin-1-yl)isoindoline-1,3-dione (2e)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1e** (43.1 mg, 0.2 mmol), Togni II reagent (142.2 mg, 0.18 mmol) using $Ir(ppy)_3$ (2.5 mg, 0.0037 mmol) as photocatalyst, and irradiating the mixture for 3 h. A mixture of two diastereoisomers were obtained.

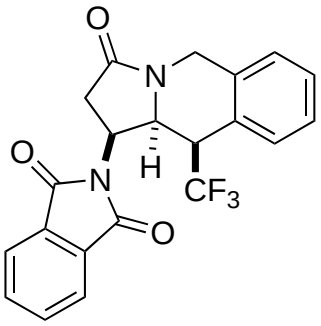
2-((1*S*,10*R*,10a*R*)-3-oxo-10-(trifluoromethyl)-1,2,3,5,10,10a-hexahydropyrrolo[1,2-*b*]isoquinolin-1-yl)isoindoline-1,3-dione (2e)



The compound **2e** (31.3 mg, 39% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 20:80).

^{1}H NMR (400 MHz, DMSO-*d6*) δ ppm 7.75 (br m, 4H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (td, *J* = 7.4, 1.4 Hz, 1H), 7.23 (d, *J* = 7.7 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 5.20 (t, *J* = 9.1 Hz, 1H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.66 (dd, *J* = 7.0, 5.2 Hz, 1H), 4.00 (m, 2H), 2.96 (ddd, *J* = 17.3, 9.3, 1.4 Hz, 1H), 2.62 (dd, *J* = 17.3, 1.5 Hz, 1H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ ppm 170.8 (2C), 167.6, 135.1 (4C), 134.3, 131.5, 130.5, 128.1, 126.9, 126.7 (q, *J* = 280.5 Hz), 126.7 (2C), 123.1, 55.1 (q, *J* = 2.7 Hz), 46.5, 41.1 (q, *J* = 25.0 Hz), 40.4, 35.4.
^{19}F NMR (376 MHz, DMSO-*d6*) δ ppm -69.14.
HRMS (ESI): calcd. for $C_{21}H_{15}F_3N_2O_3Na$ [M+Na]+ : 423.0927. Found 423.0925.

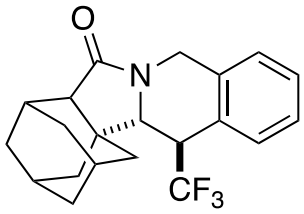
2-((1*S*,10*R*,10a*S*)-3-oxo-10-(trifluoromethyl)-1,2,3,5,10,10a-hexahydropyrrolo[1,2-*b*]isoquinolin-1-yl)isoindoline-1,3-dione (2e')



The compound **2e'** (5 mg, 6% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 20:80).

^{1}H NMR (400 MHz, DMSO-*d6*) δ ppm 7.95 (m, 2H), 7.91 (m, 2H), 7.46 (br d, *J* = 6.9 Hz, 1H), 7.39 (m, 3H), 5.01 (m, 1H), 4.98 (d, *J* = 16.4 Hz, 1H), 4.43 (m, 1H), 4.42 (m, 1H), 4.13 (d, *J* = 16.3 Hz, 1H), 2.84 (m, 2H).
^{13}C NMR (101 MHz, DMSO-*d6*) δ ppm 169.4, 167.3 (2C), 134.9, 134.8, 131.3, 129.7, 127.38 (q, *J* = 280.7 Hz), 123.3, 56.7 (q, *J* = 2.9 Hz), 48.8, 46.1, 45.9 (q, *J* = 24.7 Hz), 40.3, 34.2.
^{19}F NMR (376 MHz, DMSO-*d6*) δ ppm -69.79 (d, *J* = 10.8 Hz).
HRMS (ESI): calcd. for $C_{21}H_{15}F_3N_2O_3H$ [M+H]+ : 401.1108. found 401.1108.

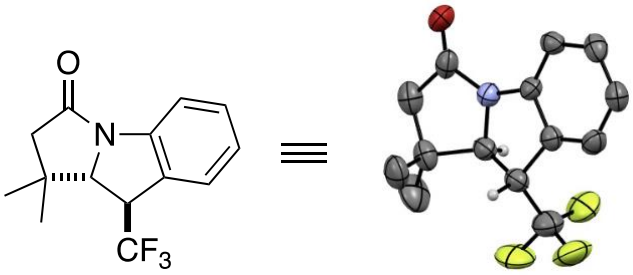
(7a*R*,8*S*,10*R*,12*S*,13a*S*)-14-(trifluoromethyl)-8,9,10,11,12,13,13b,14-octahydro-5*H*-8,12:10,13a-dimethanocycloocta[3,4]pyrrolo[1,2-*b*]isoquinolin-7(7a*H*)-one (2f)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1f** (58.7 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. The compound **2f** (30 mg, 40% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.36 – 7.22 (m, 4H), 5.02 (d, *J* = 15.5 Hz, 1H), 3.97 (d, *J* = 15.5 Hz, 1H), 3.85 (d, *J* = 1.9 Hz, 1H), 3.53 (qd, *J* = 10.7, 1.9 Hz, 1H), 2.38 (m, 2H), 2.13 (p, *J* = 3.2 Hz, 1H), 1.93 (dt, *J* = 12.9, 1.9 Hz, 1H), 1.89 – 1.54 (m, 8H), 1.25 – 1.17 (m, 1H), 1.03 (dq, *J* = 12.6, 2.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 173.1, 136.2, 131.2, 128.9, 127.8, 127.6 (d, *J* = 2.3 Hz), 127.2, 126.6 (q, *J* = 280.3 Hz), 61.2 (q, *J* = 2.3 Hz), 54.5, 42.4 (q, *J* = 26.2 Hz), 42.3, 40.2, 38.7, 37.7, 37.1, 32.6, 32.1, 28.6, 27.1, 26.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -70.33.
HRMS (ESI): calcd. for $C_{21}H_{22}F_3NOH$ [M+H]+:362.1726. Found 362.1727.

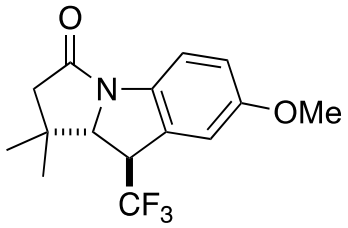
1,1-dimethyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2g)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1g** (40 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1 h. The compound **2g** (38.5 mg, 72% yield) was obtained as white solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (d, *J* = 7.9 Hz, 1H), 7.36 (q, *J* = 8.0, 7.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 8.5 Hz, 1H), 4.13 (p, *J* = 8.5 Hz, 1 H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.33 (d, *J* = 16.1 Hz, 1H), 1.30 (s, 3H), 1.06 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.4, 140.4, 130.0, 127.5/124.8 (q, *J* = 277.1 Hz), 125.8, 124.5, 114.9, 71.0 (q, *J* = 3.0 Hz), 51.0, 46.0 (q, *J* = 29.2 Hz), 39.86, 25.10, 22.60.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.57.
HRMS (ESI): calcd. for $C_{14}H_{15}F_3NO$ [M+H]+: 270.1100, found 270.1102.
M.p.: 75.5-77°C

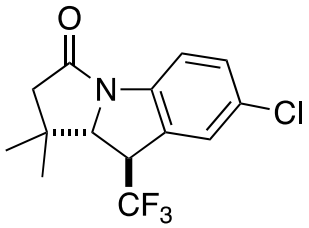
7-methoxy-1,1-dimethyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2h)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1h** (46.2 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1.5 h. The compound **2h** (34.7 mg, 58% yield) was obtained in a mixture of diastereoisomers (95:5) as a pale yellow solid by flash chromatography (PE/EtOAc 80:20), and was purified a second time with column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.57 (d, *J* = 8.7 Hz, 1H), 6.92 (dt, *J* = 2.6, 1.4 Hz, 1H), 6.87 (ddd, *J* = 8.7, 2.5, 0.8 Hz, 1H), 4.45 (d, *J* = 8.5 Hz, 1H), 4.10 (p, *J* = 8.4 Hz, 1H), 3.79 (s, 3H), 2.78 (d, *J* = 15.9 Hz, 1H), 2.29 (d, *J* = 15.9 Hz, 1H), 1.29 (s, 3H), 1.05 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.8, 157.0, 134.1, 128.0 (q, *J* = 2.4 Hz), 126.1 (q, *J* = 277.4 Hz), 115.5, 114.8, 112.1, 71.4 (q, *J* = 2.9 Hz), 55.9, 50.9, 46.1 (q, *J* = 28.9 Hz), 39.7, 29.8, 25.2, 22.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.51.
HRMS (ESI): calcd. for $C_{15}H_{16}F_3NO_2H$ [M+H]+: 300.1206. Found 300.1207.
M.p.: 108°C

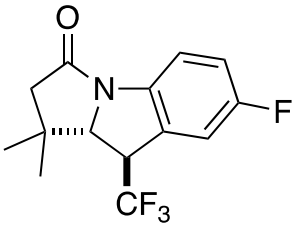
7-chloro-1,1-dimethyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2i)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1i** (36.5 mg, 0.154 mmol), Togni II reagent (146.8 mg, 0.185 mmol) using $Ir(ppy)_3$ (2.5 mg, 0.0038 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. The compound **2i** (36.3 mg, 77% yield) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.60 (d, *J* = 8.48 Hz, 1H), 7.35 (s, 1H), 7.32 (d, *J* = 8.48 Hz, 1H), 4.47 (d, *J* = 8.25 Hz, 1H), 4.10 (p, *J* = 8.48 Hz, 1H), 2.78 (d, *J* = 16.20 Hz, 1H), 2.32 (d, *J* = 16.20 Hz, 1H), 1.30 (s, 3H), 1.05 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.4, 139.1, 130.2, 129.6, 128.2 (q, *J* = 2.5 Hz), 126.2, 125.7 (q, *J* = 276.2 Hz), 115.8, 71.2 (q, *J* = 2.6 Hz), 50.7, 46.0 (q, *J* = 29.5 Hz), 39.9, 25.0, 22.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.60.
HRMS (ESI): calcd. For $C_{14}H_{13}ClF_3NOH$ 304.0711. Found 304.0709.
M.p.: 72°C

7-fluoro-1,1-dimethyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2j)

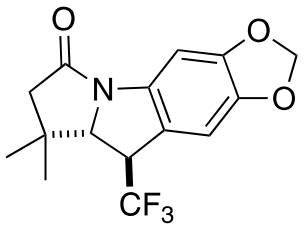


Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1j** (43.1 mg, 0.15 mmol), Togni II reagent (142.2 mg, 0.18 mmol) using $Ir(ppy)_3$ (2.5 mg, 0.0037 mmol) as photocatalyst, and irradiating the mixture for 1 h. The compound **2j** (27.1 mg, 63% yield) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.62 (dd, *J* = 8.7, 4.7 Hz, 1H), 7.09 (d, *J* = 8.43 Hz, 1H), 7.04 (t, *J* = 8.72 Hz, 1H), 4.49 (d, *J* = 8.52 Hz, 1H), 4.12 (p, *J* = 8.43 Hz, 1H), 2.79 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.0 Hz, 1H), 1.30 (s, 3H), 1.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2, 159.6 (d, *J* = 246.5 Hz), 136.7, 128.23 (dd, *J* = 8.6 Hz), 125.9 (q, *J* = 277.5 Hz), 116.8 (d, *J* = 23.5 Hz), 115.8 (d, *J* = 8.2 Hz), 113.5 (d, *J* = 25.2 Hz), 71.4 (q, *J* = 2.6 Hz), 50.8, 46.2 (q, *J* = 29.5 Hz), 39.8, 25.1, 22.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.68, -117.22.
HRMS (ESI): calcd. for $C_{14}H_{13}F_4NOH$ 288.1006. Found 288.1007.
M.p.: 80°C

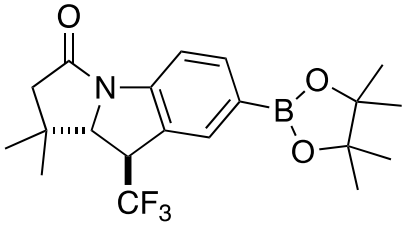
8,8-dimethyl-9-(trifluoromethyl)-7,8,8a,9-tetrahydro-6*H*-[1,3]dioxolo[4,5-*f*]pyrrolo[1,2-*a*]indol-6-one (2k)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1k** (49 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. The compound **2k** (21 mg, 34% yield, d.r 95:5) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.23 (s, 1H), 6.81 (m, 1H), 5.97 (s, 2H), 4.43 (d, *J* = 8.3 Hz, 1H), 4.03 (p, *J* = 8.3 Hz, 1H), 2.76 (d, *J* = 15.9 Hz, 1H), 2.28 (d, *J* = 16.0 Hz, 1H), 1.28 (s, 3H), 1.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.0, 149.0, 144.8, 135.3, 126.1 (q, *J* = 275.7 Hz), 118.2 (q, *J* = 2.6 Hz), 106.0, 101.9, 97.6, 71.7 (q, *J* = 2.8 Hz), 50.8, 46.0 (q, *J* = 29.5 Hz), 39.8, 25.0, 22.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.17, -69.13 (major).
HRMS (ESI): calcd. for $C_{15}H_{14}F_3NO_3H$ [M+H]+: 314.0999. Found 314.0999.
M.p.: 161°C

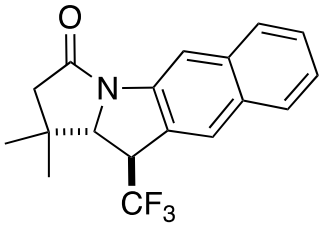
1,1-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2l)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1l** (65.4 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. The compound **2l** (45.2 mg, 57% yield) was obtained as a yellow solid by flash chromatography (PE/EtOAc 60:40).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.81 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 1H), 4.44 (d, *J* = 8.2 Hz, 1H), 4.08 (p, *J* = 8.4 Hz, 1H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.32 (d, *J* = 16.0 Hz, 1H), 1.33 (d, *J* = 3.3 Hz, 12H), 1.29 (s, 3H), 1.02 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.6, 142.8, 137.2, 132.2, 126.0 (q, *J* = 277.9 Hz), 125.9 (q, *J* = 2.2 Hz), 114.1, 84.0, 71.0 (q, *J* = 2.8 Hz), 51.0, 45.8 (q, *J* = 29.4 Hz), 40.0, 25.0, 24.9, 24.9, 22.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.45.
HRMS (ESI): calcd. for $C_{20}H_{25}BF_3NO_3H$ [M+H]+:396.1952. Found 396.1953.
M.p.: 210°C

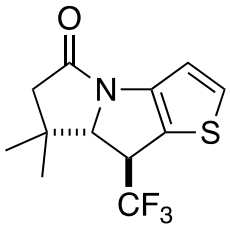
1,1-dimethyl-11-(trifluoromethyl)-1,2,11,11a-tetrahydro-3*H*-benzo[*f*]pyrrolo[1,2-*a*]indol-3-one (2m)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1m** (50.3 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. The compound **2m** (34 mg, 53% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 8.00 (d, *J* = 8.7 Hz, 1H), 7.96 – 7.84 (m, 3H), 7.54 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.42 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 4.54 (m, 2H), 2.80 (d, *J* = 15.7 Hz, 1H), 2.27 (d, *J* = 15.7 Hz, 1H), 1.34 (s, 3H), 0.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.2, 142.1, 131.8, 131.5, 130.8, 129.2, 127.5, 126.7 (q, *J* = 279.7 Hz), 124.6, 123.4 (q, *J* = 4.5 Hz), 117.5 (q, *J* = 2.3 Hz), 114.7, 71.4 (q, *J* = 3.3 Hz), 50.0, 46.1 (q, *J* = 29.1 Hz), 41.6, 24.2, 21.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -67.60.
HRMS (ESI): calcd. for $C_{18}H_{16}F_3NOH$ [M+H]+:320.1257. Found 320.1257.

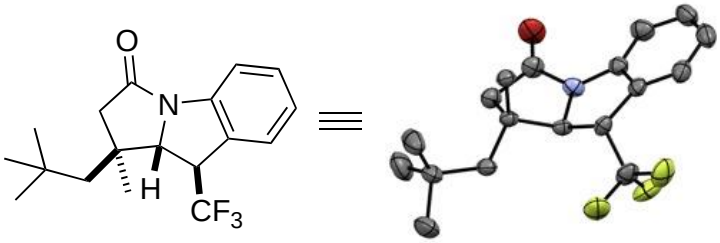
7,7-dimethyl-8-(trifluoromethyl)-6,7,7a,8-tetrahydro-5*H*-thieno[2,3-*b*]pyrrolizin-5-one (2n)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1n** (83 mg, 0.4 mmol), Togni II reagent (379.2 mg, 0.48 mmol) using $Ir(ppy)_3$ (6.6 mg, 0.01 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. The compound **2n** (68 mg, 60% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (500 MHz, CDCl3) δ ppm 7.31 (dd, J = 5.2, 1.1 Hz, 1 H), 7.17 (d, J = 5.2 Hz, 1 H), 4.81 (d, J = 7.8 Hz, 1 H), 4.25 (quint, J = 7.7 Hz, 1 H), 2.76 (dd, J = 15.8, 0.6 Hz, 1 H), 2.27 (d, J = 15.8 Hz, 1 H), 1.29 (s, 3 H), 1.08 (s, 3 H).
^{13}C NMR (125 MHz, CDCl3) δ ppm 170.3, 145.1, 131.7, 125.5 (q, J = 278.2 Hz), 120.1 (bq, J = 3.3 Hz), 115.0, 77.2 (bq, J = 2.4 Hz), 50.1, 46.2 (q, J = 30.9 Hz), 40.4, 25.0, 22.9.
^{19}F NMR (376 MHz, CDCl3) δ ppm -70.67.
HRMS (ESI): calcd. for $C_{12}H_{13}F_3NOS$ [M+H]+: 276.0664, found 276.0664.

(1*R*,9*R*,9a*R*)-1-methyl-1-neopentyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2o)



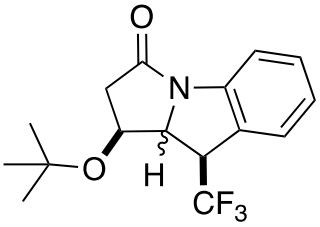
X-ray structure
CCDC 2301768

Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1o** (51.5 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. the compound **2o** (20.2 mg, 31% yield, d.r. 96:4) was isolated as yellow solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.68 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 4.36 (d, *J* = 7.5 Hz, 1H), 4.11 (p, *J* = 8.2 Hz, 1H), 2.87 (d, *J* = 15.9 Hz, 1H), 2.49 (d, *J* = 15.8 Hz, 1H), 1.71 (d, *J* = 14.5 Hz, 1H), 1.57 (m, 1H), 1.08 (s, 3H), 1.03 (s, 9H).

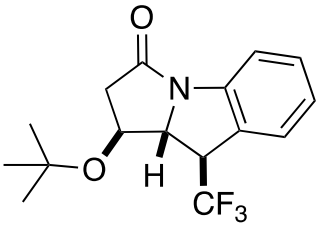
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.6, 141.0, 130.1, 126.2 (q, *J* = 2.4 Hz), 126.0, 125.9 (q, *J* = 277.4 Hz), 124.4, 114.9, 72.7 (q, *J* = 2.7 Hz), 51.8, 50.2, 45.9 (q, *J* = 28.9 Hz), 45.0, 32.1, 31.7, 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.44, -68.65 mixture 96:4.
HRMS (ESI): calcd. for $C_{18}H_{22}F_3NOH$ [M+H]+: 326.1726. Found 326.1727.
M.p.: 118°C

(1*S*,9*R*)-1-(*tert*-butoxy)-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2p)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1p** (49.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 16 h. Two diastereoisomers were isolated as white oils by flash chromatography (PE/EtOAc 70:30).

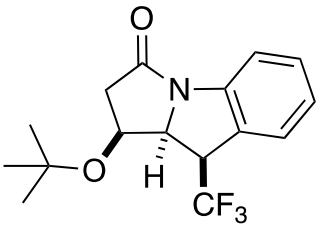
(1*S*,9*R*,9a*R*)-1-(*tert*-butoxy)-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2p)



The compound **2p** (7.7 mg, 12% yield) was obtained as a white oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.64 (d, *J* = 8.0 Hz, 1H), 7.36 (m, 2H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 4.49 (t, *J* = 8.0 Hz, 1H), 4.31 (dt, *J* = 9.2, 7.6 Hz, 1H), 4.04 (p, *J* = 8.2 Hz, 1H), 2.83 (m, 2H), 1.24 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.8, 140.2, 130.1, 126.6 (q, *J* = 2.4 Hz), 125.9 (q, *J* = 277.7 Hz), 125.8 (brd, *J* = 1.6 Hz), 124.9, 115.7, 74.7, 73.9, 67.5 (q, *J* = 2.6 Hz), 51.3 (q, *J* = 29.5 Hz), 44.8, 29.8, 28.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.47.
HRMS (ESI): calcd. for $C_{16}H_{18}F_3NO_2H$ [M+H]+:314.1362. Found 314.1363.

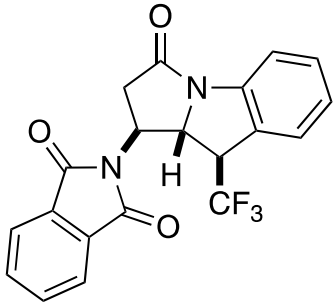
(1*S*,9*R*,9a*S*)-1-(*tert*-butoxy)-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2p')



The compound **2p'** (9.5 mg, 15% yield) was obtained as a white oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.64 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 4.79 (dd, *J* = 9.0, 4.5 Hz, 1H), 4.62 (p, *J* = 8.9 Hz, 1H), 4.42 (t, *J* = 4.5 Hz, 1H), 3.06 (dd, *J* = 16.7, 4.5 Hz, 1H), 2.56 (d, *J* = 16.7 Hz, 1H), 1.21 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.8, 139.9, 129.7, 127.7 (q, *J* = 2.6 Hz), 126.4 (q, *J* = 277.1 Hz), 125.6, 124.6, 115.2, 75.6, 67.5 (q, *J* = 3.2 Hz), 67.2, 45.9, 45.2 (q, *J* = 29.1 Hz), 28.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.03.
HRMS (ESI): calcd. for $C_{16}H_{18}F_3NO_2H$ [M+H]+:314.1362. Found 314.1362.

2-(3-oxo-9-(trifluoromethyl)-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-1-yl)isoindoline-1,3-dione (2q)

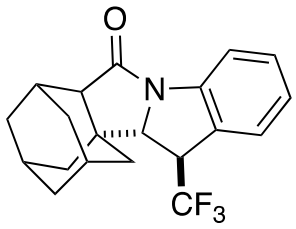


Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1q** (63.6 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 1 h 30 min. The compound **2q** (29.5 mg, 38% yield) was obtained as a pale orange solid by flash chromatography (PE/EtOAc 50:50), and with a second column with Toluene/EtOAc 70:30.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.88 – 7.74 (m, 4H), 7.40 (tt, *J* = 7.7, 1.1 Hz, 1H), 7.28 (m, 2H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 5.35 (ddd, *J* = 8.6, 6.8, 0.9 Hz, 1H), 5.09 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.88 (p, *J* = 8.3 Hz, 1H), 3.41 (dd, *J* = 17.6, 8.6 Hz, 1H), 2.78 (dd, *J* = 17.6, 0.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.1, 140.0, 134.8, 131.3, 130.4, 126.1 (q, *J* = 2.5 Hz), 125.6 (q, *J* = 277.8 Hz), 125.4, 124.8, 124.2, 115.7, 65.1 (q, *J* = 3.2 Hz), 47.4 (q, *J* = 29.6 Hz), 46.8, 41.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.67.

HRMS (ESI): calcd. for $C_{20}H_{13}F_3N_2O_3H$ [M+H]+:387.0951. Found 387.0952.
M.p.: 180°C

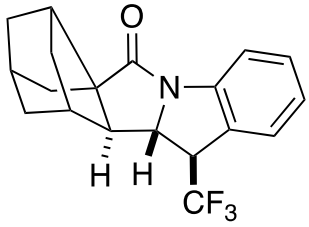
9'-(t(6a*R*,7*S*,9*R*,11*S*,12a*S*)-13-(trifluoromethyl)-7,8,9,10,11,12,12b,13-octahydro-7,11:9,12a-dimethanocycloocta[3,4]pyrrolo[1,2-*a*]indol-6(6a*H*)-one (2r)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1r** (55.9 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 2 h 30 min. The compound **2r** (49 mg, 70% yield) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.67 (d, *J* = 7.9 Hz, 1H), 7.34 (m, 2H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H), 4.21 (d, *J* = 7.9 Hz, 1H), 4.11 (p, *J* = 8.4 Hz, 1H), 2.73 (q, *J* = 1.9 Hz, 1H), 2.42 (h, *J* = 3.4 Hz, 1H), 2.12 (hept, *J* = 3.3 Hz, 1H), 1.98 (m, 2H), 1.87 (m, 2H), 1.79 – 1.61 (m, 5H), 1.54 (dq, *J* = 12.3, 3.6 Hz, 1H), 1.36 (dq, *J* = 12.4, 2.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.8, 141.3, 129.9, 126.3 (q, *J* = 276.7 Hz), 126.1 (q, *J* = 2.4 Hz), 125.9, 124.0, 115.0, 69.9 (q, *J* = 3.0 Hz), 57.3, 44.3 (q, *J* = 29.3 Hz), 42.4, 39.3, 37.5, 36.8, 33.4, 31.9, 28.3, 27.3, 26.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -69.00.
HRMS (ESI): calcd. for $C_{20}H_{20}F_3NOH$ [M+H]+:348.1570. Found 348.157.
M.p.: 130°C

(2*S*,5*R*,5a*S*,5b*S*,6*R*,12a*R*)-6-(trifluoromethyl)-2,3,3a,4,5,5a,5b,6-octahydro-1*H*,12*H*-2,5-methanopentaleno[1',6a':3,4]pyrrolo[1,2-*a*]indol-12-one (2s)

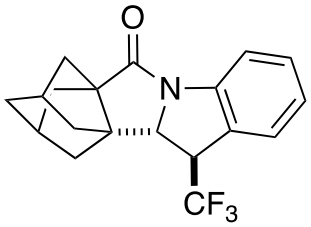


Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1s** (53.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using

$Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. Two compounds were isolated as white solids by flash chromatography (PE/EtOAc 80:20), compound **2s** (23 mg, 36% yield).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.66 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.35 (m, 2H), 7.11 (td, *J* = 7.6, 1.1 Hz, 1H), 4.33 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.96 (p, *J* = 8.6 Hz, 1H), 2.70 (t, *J* = 6.9 Hz, 1H), 2.50 (d, *J* = 6.6 Hz, 2H), 2.37 (m, 1H), 2.20 (dddd, *J* = 13.5, 11.0, 4.6, 2.1 Hz, 2H), 1.92 – 1.72 (m, 4H), 1.69 – 1.58 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 175.6, 140.4, 129.9, 127.6 (q, *J* = 2.5 Hz), 126.2 (q, *J* = 277.1 Hz), 125.2, 124.7, 115.8, 63.5 (q, *J* = 3.3 Hz), 63.1, 60.4, 53.2 (q, *J* = 29.1 Hz), 44.8, 44.6, 44.3, 40.6, 39.2, 37.3, 35.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.37.
HRMS (ESI): calcd. for $C_{19}H_{18}F_3NOH$ [M+H]+:334.1413. Found 334.1413.
M.p.: 158°C

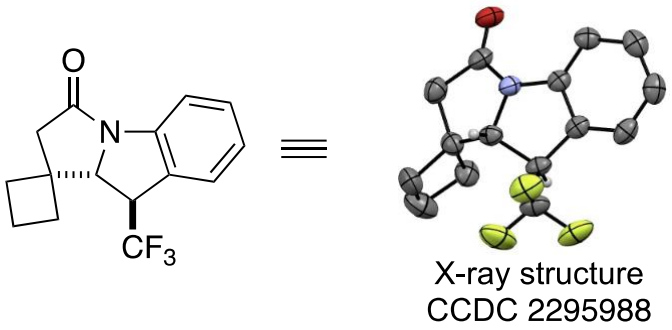
(6a*S*,8*R*,10*S*,11a*S*,11b*R*,12*R*)-12-(trifluoromethyl)-8,9,10,11,11b,12-hexahydro-6*H*,7*H*-6a,10:8,11a-dimethanocyclohepta[3,4]pyrrolo[1,2-*a*]indol-6-one (2sa)



The compound **2sa** (5 mg, 8% yield) was obtained as a white solid by flash chromatography (PE/EtOAc 80:20).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.64 (d, *J* = 7.9 Hz, 1H), 7.35 (qt, *J* = 7.8, 1.5 Hz, 2H), 7.12 (td, *J* = 7.6, 1.1 Hz, 1H), 4.49 (d, *J* = 11.1 Hz, 1H), 4.14 (m, 1H), 2.59 (m, 2H), 2.17 – 1.98 (m, 5H), 1.95 – 1.81 (m, 4H), 1.69 (tt, *J* = 3.0, 1.4 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.4, 140.2, 129.8, 129.5, 128.1 (q, *J* = 2.3 Hz), 125.3, 124.9, 115.9, 69.8 (q, *J* = 3.2 Hz), 65.0, 52.4, 51.5, 48.0 (q, *J* = 29.1 Hz), 47.2, 45.5, 45.4, 41.1, 39.7, 34.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -63.66 (impurity), -67.91.
HRMS (ESI): calcd. for $C_{19}H_{18}F_3NOH$ [M+H]+:334.1413. Found 334.1413.
M.p.: 155°C

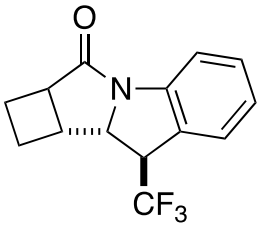
9'-(trifluoromethyl)-9',9a'-dihydrospiro[cyclobutane-1,1'-pyrrolo[1,2-*a*]indol]-3'(2'*H*)-one (2t)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1t** (46 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 20 h. The compound **2t** (25 mg, 44% yield) was obtained as a pale yellow solid by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.64 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 4.50 (d, *J* = 8.6 Hz, 1H), 4.30 (p, *J* = 8.4 Hz, 1H), 2.93 (d, *J* = 16.2 Hz, 1H), 2.77 (d, *J* = 16.2 Hz, 1H), 2.31 – 2.07 (m, 3H), 2.04 – 1.82 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.8, 139.9, 130.1, 126.7 (q, *J* = 2.4 Hz), 125.8, 125.7 (q, *J* = 278.2 Hz), 124.6, 115.0, 69.2 (q, *J* = 2.8 Hz), 49.5, 47.4 (q, *J* = 28.5 Hz), 45.7, 29.2, 28.4, 15.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.31.
HRMS (ESI): calcd. for $C_{15}H_{14}F_3NOH$ [M+H]+: 282.1100. Found 282.1101.
M.p.: 94°C

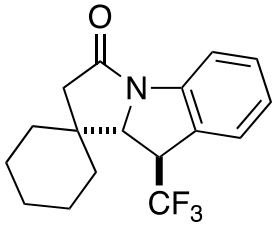
9-(trifluoromethyl)-1,2,2a,9,9a,9b-hexahydro-3*H*-cyclobuta[3,4]pyrrolo[1,2-*a*]indol-3-one (2u)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1u** (40 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 20 h. The compound **2u** (13.6 mg, 25% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.74 (d, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.14 (td, *J* = 7.6, 1.2 Hz, 1H), 4.78 (dd, *J* = 9.9, 5.6 Hz, 1H), 4.07 (p, *J* = 8.5 Hz, 1H), 3.37 (m, 2H), 2.46 (m, 1H), 2.26 – 2.00 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 174.7, 140.4, 130.0, 128.2 (q, *J* = 2.4 Hz), 126.4 (q, *J* = 277.4 Hz), 125.6, 124.9, 115.6, 64.3 (q, *J* = 3.4 Hz), 46.9, 46.7 (q, *J* = 27.5 Hz), 36.1, 22.9, 20.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.33.
HRMS (ESI): calcd. for $C_{14}H_{12}F_3NOH$ [M+H]+:268.0944. Found 268.0944.

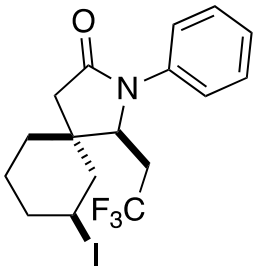
(9'*R*,9a'*R*)-9'-(trifluoromethyl)-9',9a'-dihydrospiro[cyclohexane-1,1'-pyrrolo[1,2-*a*]indol]-3'(2'*H*)-one (2v)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1v** (49.6 mg, 0.205 mmol), Togni II reagent (194 mg, 0.246 mmol) using $Ir(ppy)_3$ (3.4 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 21 h. The compound **2v** (13.4 mg, 21% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.67 (d, *J* = 7.9 Hz, 1H), 7.35 (m, 2H), 7.13 – 7.09 (td, *J* = 7.6, 1.1 Hz, 1H), 4.41 (d, *J* = 8.5 Hz, 1H), 4.24 (p, *J* = 8.4 Hz, 1H), 2.78 (d, *J* = 16.3 Hz, 1H), 2.59 (dd, *J* = 16.4, 1.9 Hz, 1H), 1.76 – 1.58 (m, 5H), 1.45 – 1.26 (m, 5H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.2, 140.3, 130.0, 126.6 (q, *J* = 2.1 Hz), 125.9, 124.9 (q, *J* = 277.7 Hz), 124.5, 114.9, 71.8 (q, *J* = 2.7 Hz), 45.6 (q, *J* = 28.5 Hz), 45.5, 43.4, 35.5, 29.7, 25.9, 23.5, 21.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.23.
HRMS (ESI): calcd. for $C_{17}H_{18}F_3NOH$ [M+H]+: 310.1413. Found 310.1413.

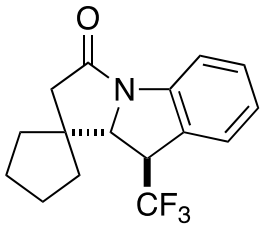
7-iodo-2-phenyl-1-(2,2,2-trifluoroethyl)-2-azaspiro[4.5]decan-3-one (2va)



The compound **2va** (17.5 mg, 20% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 4.16 (tt, *J* = 12.9, 4.1 Hz, 1H), 4.07 (dd, *J* = 7.0, 4.1 Hz, 1H), 2.55 (d, *J* = 5.1 Hz, 1H), 2.46 (m, 1H), 2.40 (dt, *J* = 12.7, 2.2 Hz, 1H), 2.27 (m, 1H), 2.19 – 2.08 (m, 1H), 1.97 (dt, *J* = 12.3, 6.8 Hz, 2H), 1.68 – 1.53 (m, 4H), 0.88 (tdd, *J* = 11.6, 7.9, 4.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.7, 136.6, 129.4, 126.9, 124.6, 64.6 (br q, *J* = 2.8 Hz), 45.7, 43.1, 40.3, 39.8, 34.8, 33.4 (q, *J* = 29.8 Hz), 29.8, 24.6, 23.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.30.
HRMS (ESI): calcd. for $C_{17}H_{19}F_3INOH$ [M+H]+: 438.0536 . Found 438.0537.

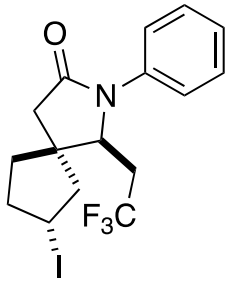
9'-(trifluoromethyl)-9',9a'-dihydrospiro[cyclopentane-1,1'-pyrrolo[1,2-*a*]indol]-3'(2'*H*)-one (2w)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1w** (45.4 mg, 0.20 mmol), Togni II reagent (194 mg, 0.246 mmol) using $Ir(ppy)_3$ (3.4 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 22 h. The compound **2w** (12.4 mg, 21% yield) was obtained as an off white oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, DMSO-*d6*) δ ppm 7.54 (d, *J* = 7.8 Hz, 1H), 7.41 (m, 2H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 4.75 (d, *J* = 7.7 Hz, 1H), 4.66 (p, *J* = 8.6 Hz, 1H), 2.92 (d, *J* = 15.6 Hz, 1H), 2.35 (d, *J* = 15.6 Hz, 1H), 1.83 – 1.56 (m, 7H), 1.27 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.4, 135.3, 125.1, 121.5 (br q, *J* = 2.2 Hz), 121.2 (q, *J* = 278.2 Hz), 120.9, 119.5, 110.0, 64.1 (br q, *J* = 2.7 Hz), 46.2, 44.9, 41.7 (q, *J* = 28.1 Hz), 29.9, 27.7, 19.3, 19.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.42.
HRMS (ESI): calcd. for $C_{16}H_{17}F_3NO$ [M+H]+: 296.1257, found 296.1257.

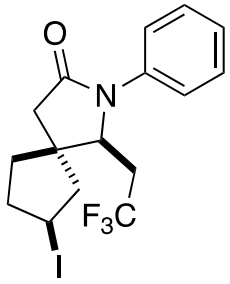
7-iodo-2-phenyl-1-(2,2,2-trifluoroethyl)-2-azaspiro[4.4]nonan-3-one (2wa)



The compound **2wa** (6 mg, 7% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40 (m, 4H), 7.25 (m, 1H), 4.38 (m, 1H), 4.15 (dd, *J* = 6.2, 3.5 Hz, 1H), 2.8 (d, J = 16.7 Hz, 1 H), 2.75 (d, J = 16.6 Hz, 1 H), 2.62 (dd, *J* = 14.9, 7.5 Hz, 1H), 2.57/2.46 (m, 1H), 2.44/2.22 (m, 4H), 2.11/2.05 (m, 1H), 1.92 (dt, *J* = 13.2, 7.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 172.1, 136.8, 129.4, 126.6, 125.7 (q, *J* = 277.6 Hz), 123.8, 64.3 (bq, *J* = 2.5 Hz), 48.3, 46.1, 45.3, 40.6, 38.8, 35.2 (q, *J* = 28.4 Hz), 20.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.75.
HRMS (ESI): calcd. for $C_{16}H_{18}F_3INO$ [M+H]+: 424.0380, found 424.0376.

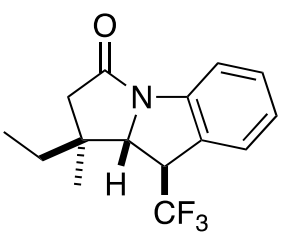
(1*S*,5*S*,7*S*)-7-iodo-2-phenyl-1-(2,2,2-trifluoroethyl)-2-azaspiro[4.4]nonan-3-one (2wa')



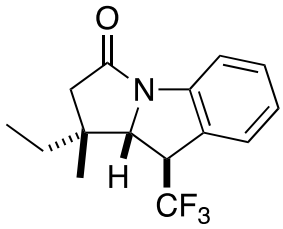
The compound **2wa'** (7 mg, 8% yield) was obtained as a yellow oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.42 (m, 4 H), 7.27 (tt, *J* = 6.9, 1.6 Hz, 1H), 4.38 (bt, J = 5.0 Hz, 1 H), 4.29 (p, J = 7.3 Hz, 1 H), 2.63/2.52 (m, 2 H), 2.48/2.34 (m, 5 H), 2.28 (dddd, *J* = 14.3, 9.3, 6.9, 5.1 Hz, 1H), 2.14/1.95 (m, 2 H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.6, 136.8, 129.4, 126.7, 125.5 (q, J = 277.1 Hz), 124.1, 64.1 (bq, J = 2.4 Hz), 48.2, 46.8, 44.8, 40.0, 37.9, 35.3 (q, J = 28.5 Hz), 19.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.17.
HRMS (ESI): calcd. for $C_{16}H_{18}F_3INO$ [M+H]+: 424.0380, found 424.0376.

(1*S*,9*R*,9a*S*)-1-ethyl-1-methyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one, (1*R*,9*R*,9a*R*)-1-ethyl-1-methyl-9-(trifluoromethyl)-1,2,9,9a-tetrahydro-3*H*-pyrrolo[1,2-*a*]indol-3-one (2x)



major product (80%)

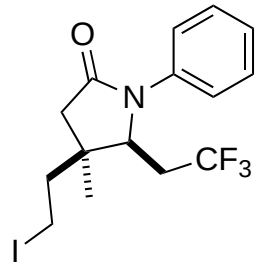


minor product (20%)

Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1x** (43.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 16 h. The compound **2x** (19 mg, 33% yield, d.r 80:20) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.68 (m, 1H), 7.33 (m, 2H), 7.10 (td, *J* = 7.6, 1.1 Hz, 1H), 4.48 (d, *J* = 8.2 Hz, 1H), 4.13 (p, *J* = 8.3 Hz, 1H), 2.79 (dd, *J* = 16.0, 0.9 Hz, 1H), 2.26 (d, *J* = 16.0 Hz, 1H), 1.63 (dt, *J* = 14.1, 7.2 Hz, 2H), 1.25 (s, 1H), 1.02 (m, 6H), 0.88 (t, *J* = 7.4 Hz, 1H).
Second diastereoisomer: ^{1}H NMR (400 MHz, CDCl3) δ ppm 7.63 (m, 1H), 7.33 (s, 2H), 7.10 (m, 1H), 4.51 (d, *J* = 8.6 Hz, 1H), 4.23 (m, 1H), 2.66 (d, *J* = 16.4 Hz, 1H), 2.56 (d, *J* = 16.3 Hz, 1H), 1.65 (m, 1H), 1.25 (s, 3H), 0.88 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.6, 171.3, 140.6, 140.2, 130.0, 126.6 (q, *J* = 2.6 Hz), 126.5 (q, *J* = 2.6 Hz), 126.2 (q, *J* = 277.3 Hz), 125.9, 124.5, 115.0, 71.9 (q, *J* = 2.8 Hz), 70.1 (q, *J* = 2.8 Hz), 53.5, 47.8, 46.7, 46.2 (q, *J* = 22.3 Hz), 45.9 (q, *J* = 30.0 Hz),, 43.8, 42.5, 41.5, 36.2, 33.8, 31.1, 29.8, 29.2, 29.0, 27.8, 27.7, 23.2, 22.7, 20.5, 20.1, 19.5, 19.0, 18.9, 14.4, 11.5, 9.1, 8.3.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -68.53, -68.59.
HRMS (ESI): calcd. for $C_{15}H_{16}F_3NOH$ [M+H]+: 284.1257. Found 284.1257.
M.p.: 101°C

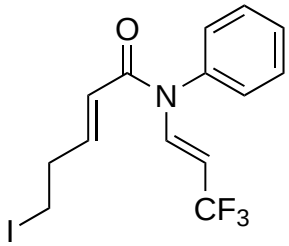
4-(2-iodoethyl)-4-methyl-1-phenyl-5-(2,2,2-trifluoroethyl)pyrrolidin-2-one (2xa)



The compound **2xa** (10 mg, 12% yield) was obtained as a pale yellow oil by flash chromatography (PE/EtOAc 70:30).

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.41 (t, *J* = 7.7 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 4.13 (dd, *J* = 6.9, 4.2 Hz, 1H), 3.24 (ddd, *J* = 10.9, 9.6, 5.9 Hz, 1H), 3.12 (ddd, *J* = 11.6, 9.6, 5.9 Hz, 1H), 2.57 (d, *J* = 16.6 Hz, 1H), 2.53 – 2.42 (m, 1H), 2.36 (d, *J* = 16.2 Hz, 1H), 2.35 – 2.14 (m, 3H), 1.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 171.9, 136.7, 129.4, 126.9, 124.6, 64.0 (q, *J* = 2.8 Hz), 43.1, 41.7, 41.5, 33.6 (q, *J* = 28.3 Hz), 29.8, 24.7, -2.4.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.36.
HRMS (ESI): calcd. for $C_{15}H_{17}F_3INOH$ [M+H]+: 412.0380. Found 412.0379.

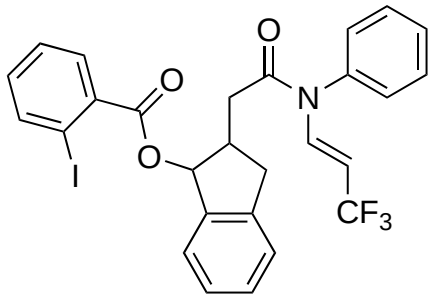
(*E*)-5-iodo-*N*-phenyl-*N*-((*E*)-3,3,3-trifluoroprop-1-en-1-yl)pent-2-enamide (A1)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **Y1** (39.8 mg, 0.20 mmol), Togni II reagent (194 mg, 0.246 mmol) using $Ir(ppy)_3$ (3.4 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 22 h. The compound **A1** (5.5 mg, 7% yield) was obtained as an off white oil by flash chromatography (PE/EtOAc 80:20), and with a second column with Toluene/EtOAc 90:10.

^{1}H NMR (400 MHz, CDCl3) δ ppm δ 8.30 (dq, *J* = 14.4, 2.0 Hz, 1H), 7.53 (m, 3H), 7.21 (m, 2H), 6.94 (dt, *J* = 15.2, 7.0 Hz, 1H), 5.66 (dt, *J* = 15.1, 1.5 Hz, 1H), 4.56 (dq, *J* = 14.4, 6.5 Hz, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.66 (qd, *J* = 7.0, 1.5 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 164.1, 147.2, 137.4, 136.1 (q, *J* = 7.5 Hz), 130.7, 129.8, 129.0, 125.9, 122.3, 101.0 (q, *J* = 34.7 Hz), 36.1, 1.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -60.31.
HRMS (ESI): calcd. for $C_{14}H_{13}F_3INOH$ [M+H]+: 396.0067. Found 396.0066.

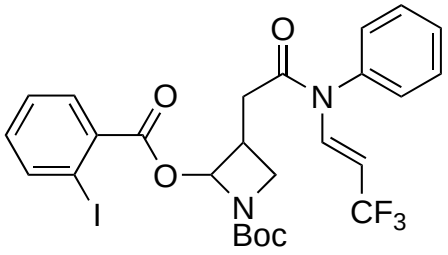
(*E*)-2-(2-oxo-2-(phenyl(3,3,3-trifluoroprop-1-en-1-yl)amino)ethyl)-2,3-dihydro-1*H*-inden-1-yl 2-iodobenzoate (A4)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **Y4** (55.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 16 h. The compound **A4** (20 mg, 17% yield) was obtained as an yellow oil by flash chromatography (PE/EtOAc 90:10).

^{1}H NMR (400 MHz, CDCl3) δ ppm 8.27 (d, *J* = 14.4 Hz, 1H), 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.55 – 7.44 (m, 3H), 7.41 – 7.35 (m, 2H), 7.29 (m, 1H), 7.25 – 7.13 (m, 5H), 6.14 (d, *J* = 5.4 Hz, 1H), 4.54 (m, 1H), 3.42 (dd, *J* = 16.1, 8.2 Hz, 1H), 3.10 (tdd, *J* = 13.9, 6.9, 3.5 Hz, 1H), 2.63 (dd, *J* = 16.1, 6.6 Hz, 2H), 2.33 (dd, *J* = 16.7, 8.9 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 170.6, 166.8, 142.5, 141.4, 139.8, 137.5, 135.8 (q, *J* = 7.3 Hz), 135.0, 132.8, 131.2, 130.8 (br s), 129.8, 129.3, 128.8 (br s), 128.1, 127.1, 125.6, 125.0, 100.4 (q, *J* = 34.8 Hz), 94.2, 83.3, 42.4, 38.7, 36.9, 29.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -60.27.
HRMS (ESI): calcd. for $C_{27}H_{21}F_3INO_3Na$ [M+Na]+: 614.0410. Found 614.041.

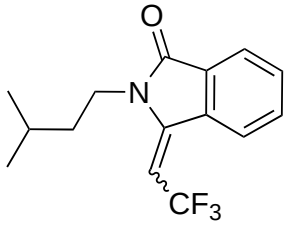
***tert*-butyl (*E*)-2-((2-iodobenzoyl)oxy)-3-(2-oxo-2-(phenyl(3,3,3-trifluoroprop-1-en-1-yl)amino)ethyl)azetidine-1-carboxylate (A5)**



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **Y5** (62.8 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 3 h. the compound **A5** (18.8 mg, 15% yield) was isolated as yellow oil by flash chromatography (PE/EtOAc 75:25).

^{1}H NMR (400 MHz, CDCl3) δ ppm 8.22 (d, *J* = 14.5 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.57 (dq, *J* = 14.0, 7.3 Hz, 3H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.20 (m, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.09 (s, 1H), 4.48 (dq, *J* = 13.6, 6.6 Hz, 1H), 3.67 (d, *J* = 1.7 Hz, 2H), 3.04 – 2.93 (m, 1H), 2.72 (d, *J* = 17.9 Hz, 1H), 2.63 (dd, *J* = 7.9, 1.6 Hz, 1H), 2.45 (d, *J* = 11.7 Hz, 1H), 1.41 (m, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 169.6, 165.3, 154.8, 141.6, 137.2, 135.4 (q, *J* = 7.8 Hz), 134.0, 133.2, 131.5, 130.1, 128.1, 100.8 (q, *J* = 34.5 Hz), 94.3, 88.2, 81.1, 79.5, 51.8, 38.4, 36.7, 35.0, 28.4, 25.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -60.41.
HRMS (ESI): calcd. for $C_{26}H_{26}F_3IN_2O_5Na$ [M+Na]+:653.0731. Found 653.073.

2-isopentyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one (2z)



Following the general procedure for the preparation of fluorinated tricycles: starting from the corresponding ynamide **1z** (43.1 mg, 0.2 mmol), Togni II reagent (189.6 mg, 0.24 mmol) using $Ir(ppy)_3$ (3.3 mg, 0.005 mmol) as photocatalyst, and irradiating the mixture for 2 h. The compound **2z** (22 mg, 39% yield) was obtained as mixture of E/Z isomers (E/Z ratio 63:37), as a pale yellow oil by flash chromatography (PE/EtOAc 90:10).

(*E*)-2-isopentyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one

^{1}H NMR (400 MHz, CDCl3) δ ppm 7.85 (m, 1H), 7.66 – 7.53 (m, 3H), 5.42 (q, *J* = 8.9 Hz, 1H), 3.75 (dd, *J* = 7.8, 6.2 Hz, 2H) 1.52 (dt, *J* = 8.8, 6.7 Hz, 3H), 0.99 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 166.7, 144.7 (q, *J* = 5.9 Hz), 137.3, 132.9, 131.3, 124.9 (q, *J* = 5.6 Hz), 123.6, 122.9, 119.8, 94.9 (q, *J* = 39.7 Hz), 38.1, 37.0 (q, *J* = 2.0 Hz), 36.5, 26.3, 22.5.
^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -52.92.
HRMS (ESI): calcd. for $C_{15}H_{16}F_3NOH$ [M+H]+:284.1257. Found 284.1257.

(*Z*)-2-isopentyl-3-(2,2,2-trifluoroethylidene)isoindolin-1-one

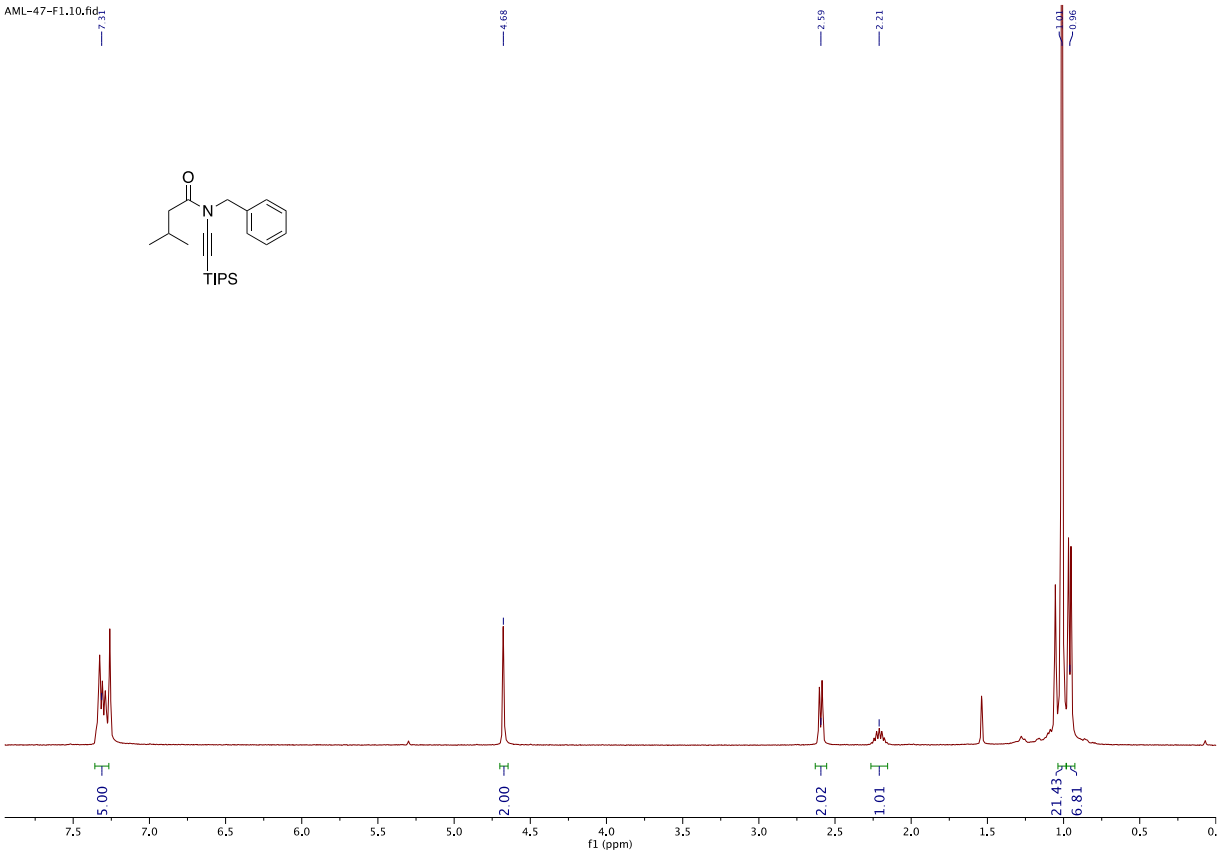
^{1}H NMR (400 MHz, CDCl3) δ ppm 8.01 (d, *J* = 7.7 Hz, 1H), 7.85 (m, 1H), 7.66 – 7.53 (m, 2H), 5.62 (q, *J* = 9.6 Hz, 1H), 3.91 (dd, *J* = 8.2, 5.7 Hz, 2H), 1.66 (ddq, *J* = 13.2, 8.8, 6.7 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 168.6, 141.7 (q, *J* = 7.0 Hz), 132.7, 132.6, 131.0, 130.2, 128.3, 127.6, 125.6, 124.7, 123.7, 122.0, 90.9 (q, *J* = 39.4 Hz), 40.6 (q, *J* = 4.2 Hz), 26.5, 22.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -50.23.
HRMS (ESI): calcd. for $C_{15}H_{16}F_3NOH$ [M+H]+:284.1257. Found 284.1257.

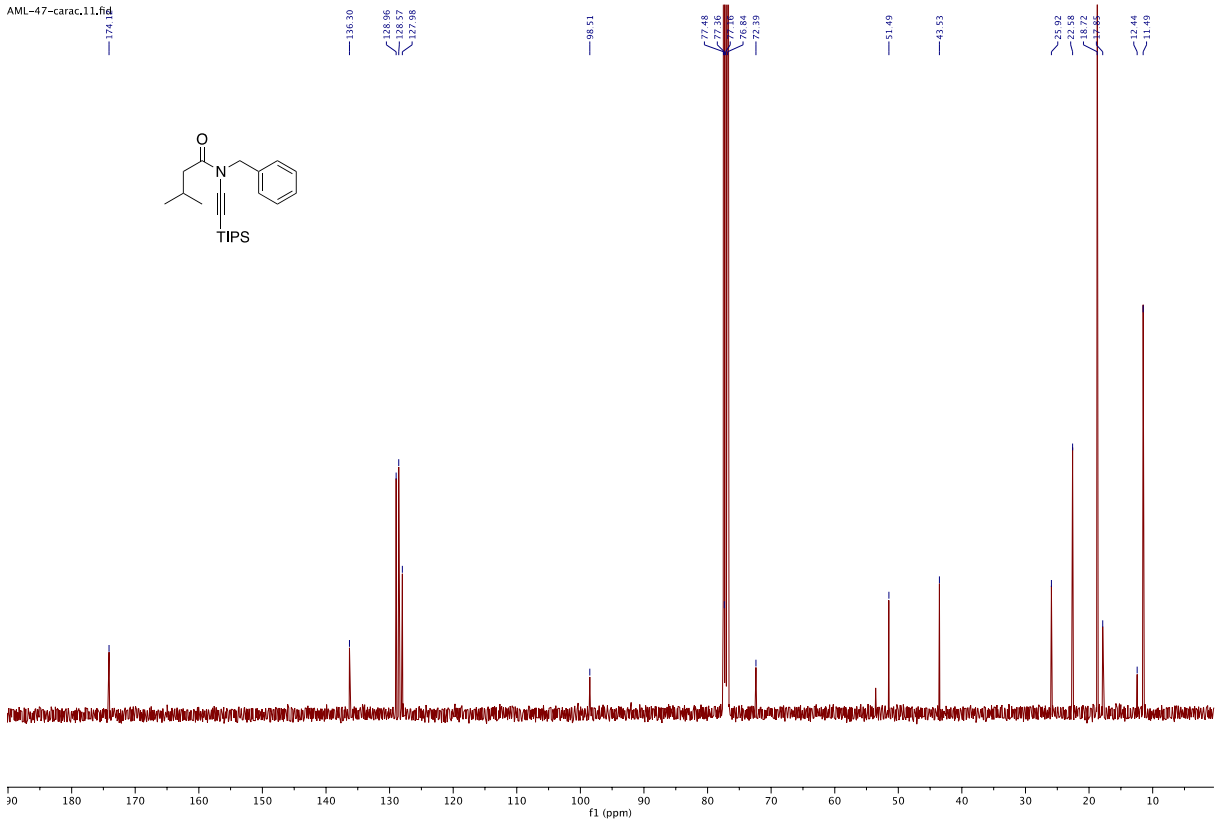
9. NMR Spectra

9.1 Protected Ynamides

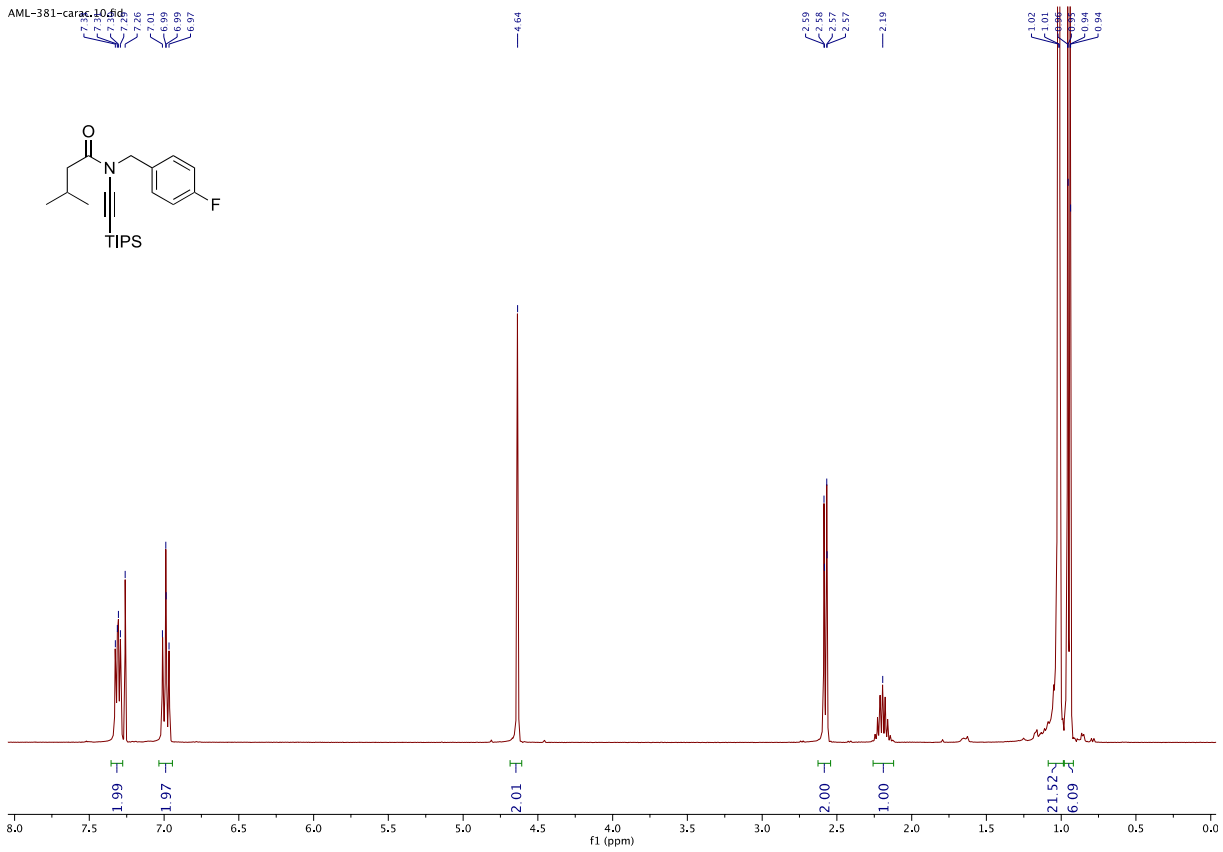
^{1}H NMR of **1a-SiR$_3$**



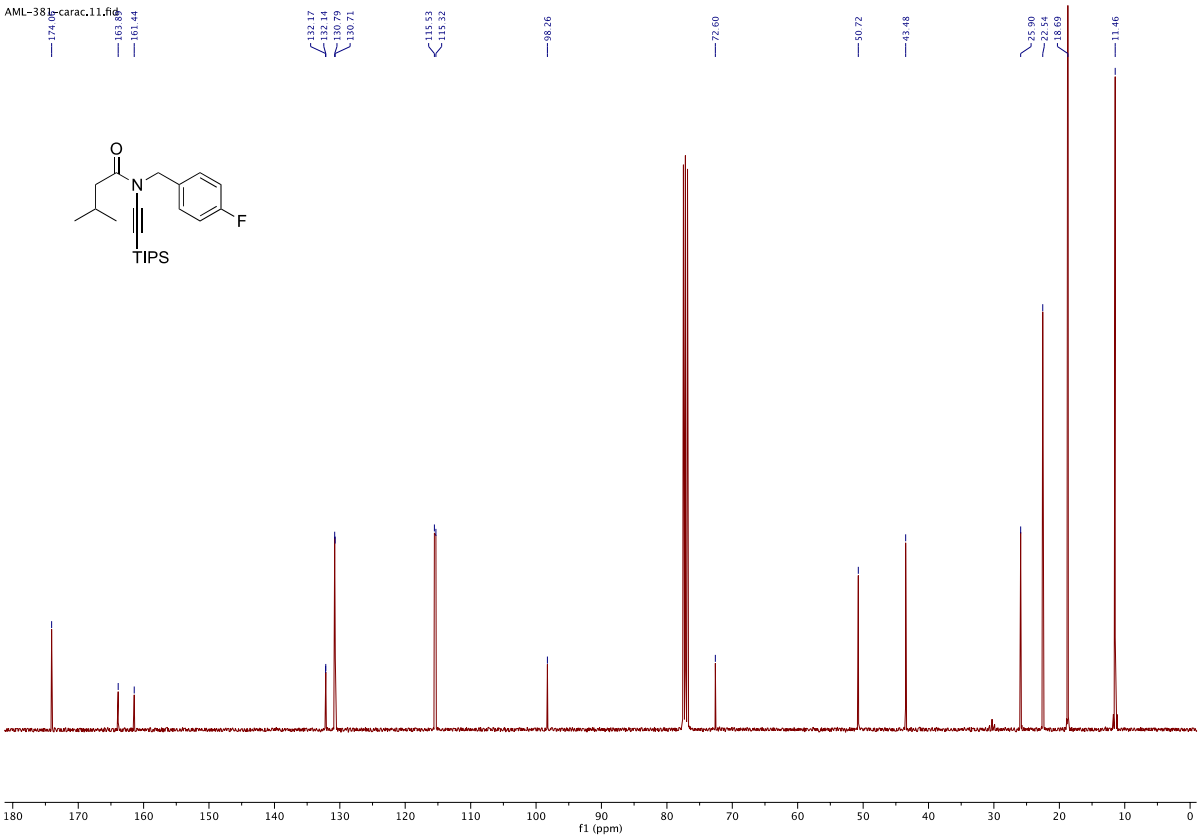
^{13}C NMR of **1a-SiR$_3$**



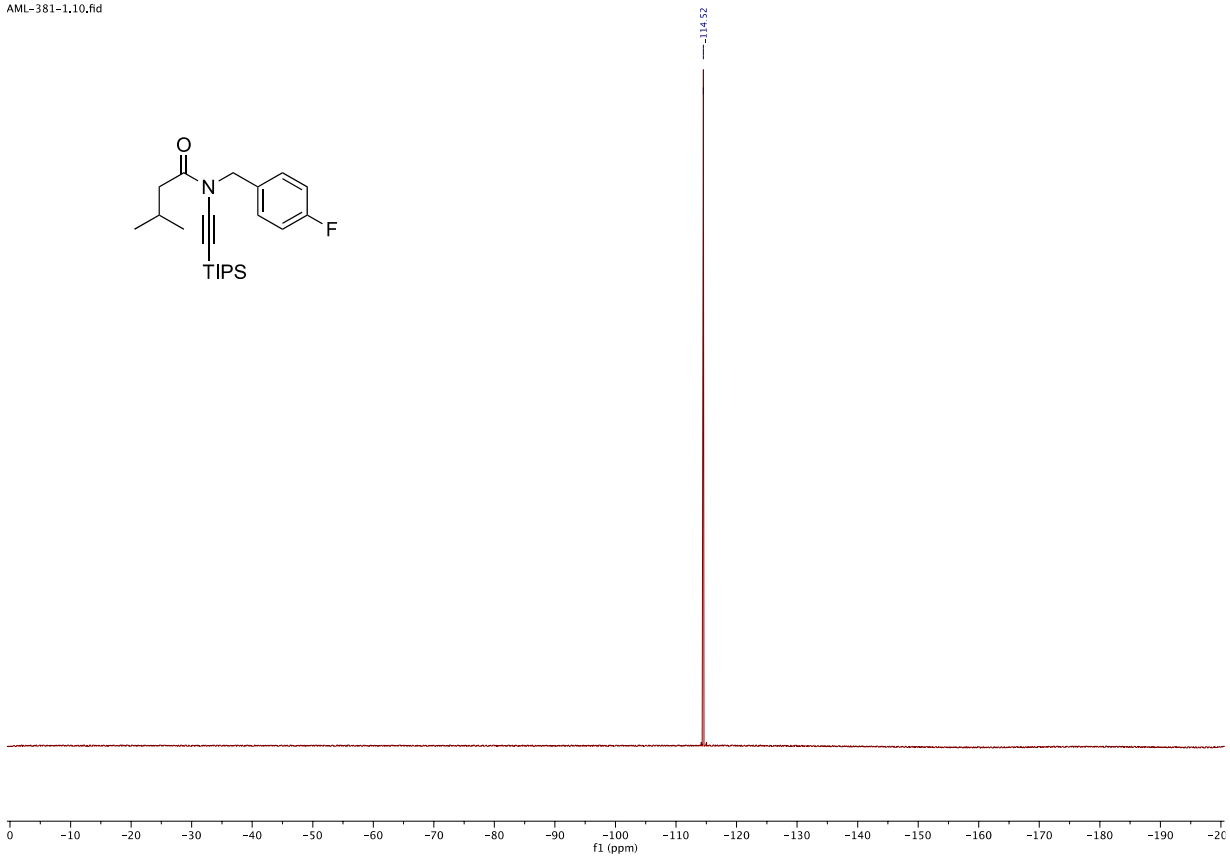
^{1}H NMR of **1b-SiR$_3$**



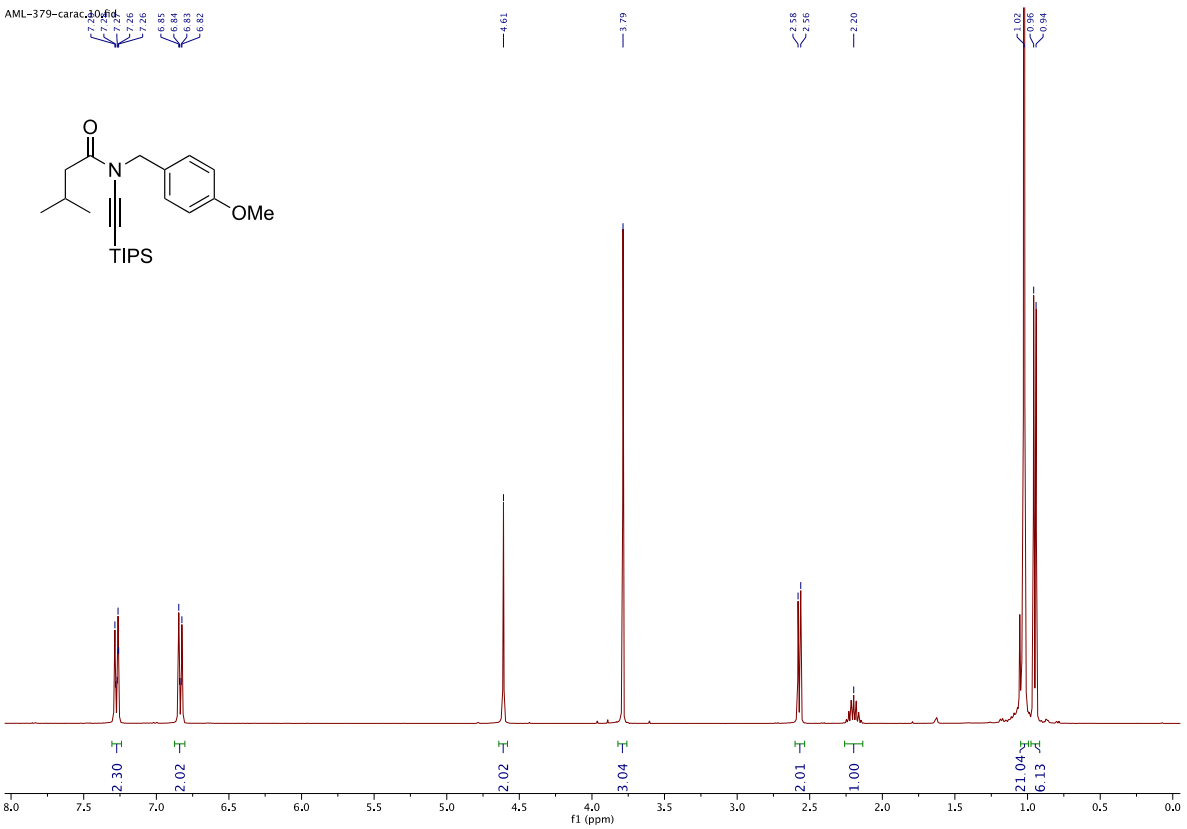
^{13}C NMR of **1b-SiR$_3$**



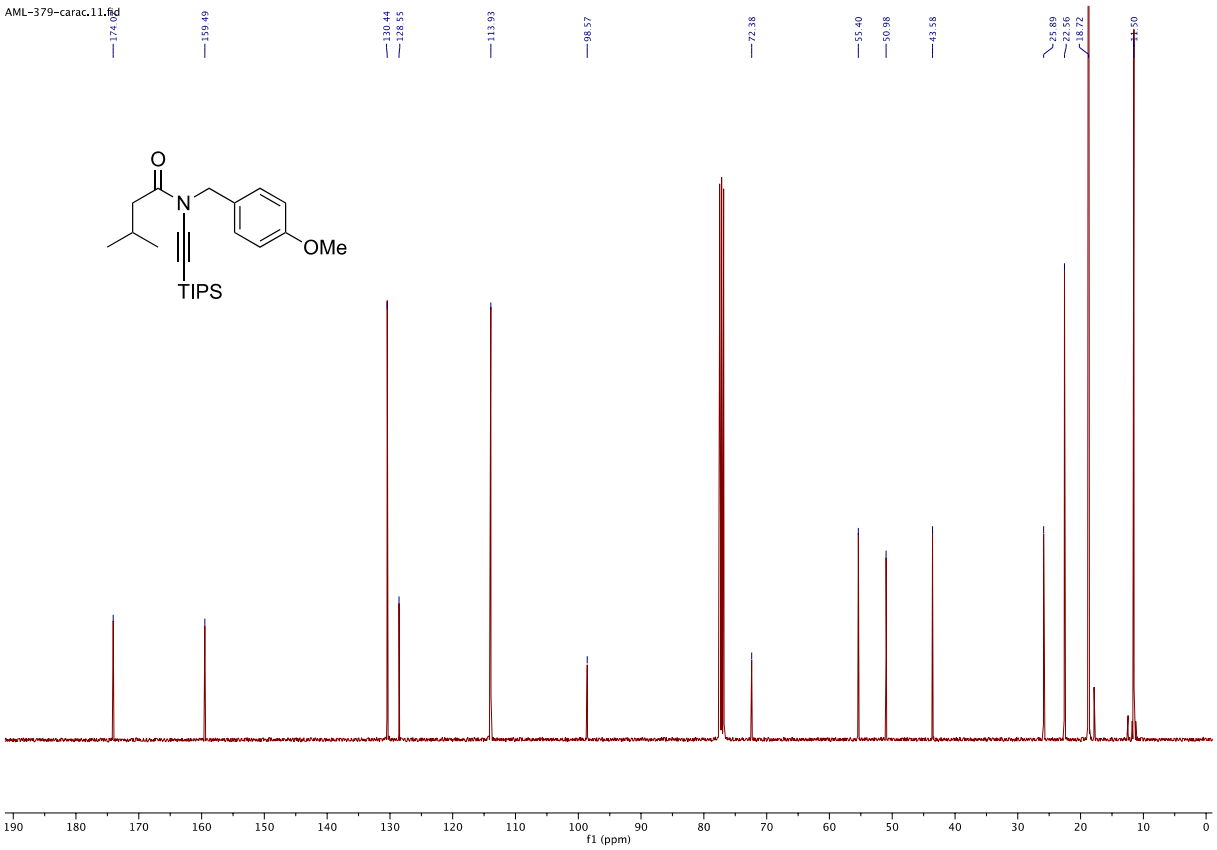
^{19}F NMR of **1b-SiR$_3$**



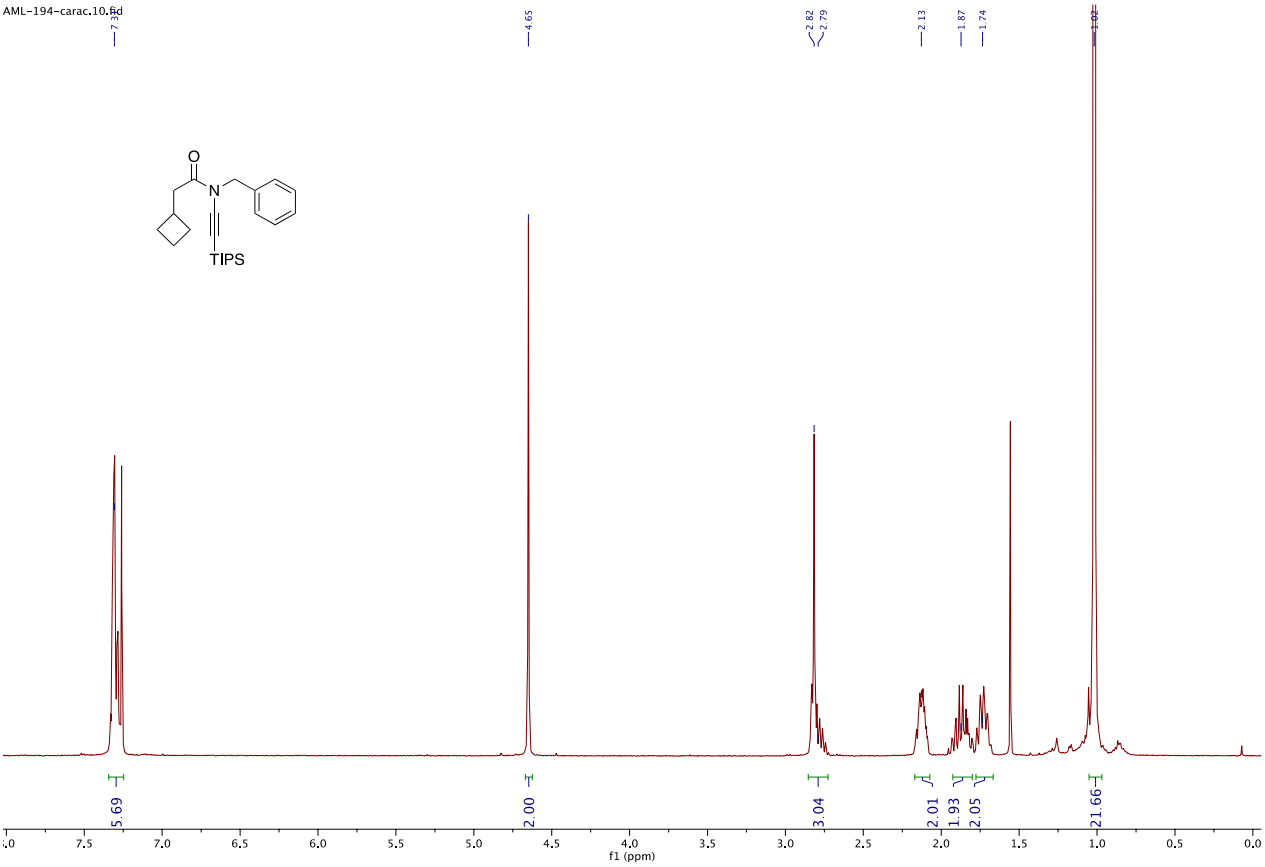
^{1}H NMR of **1c-SiR$_3$**



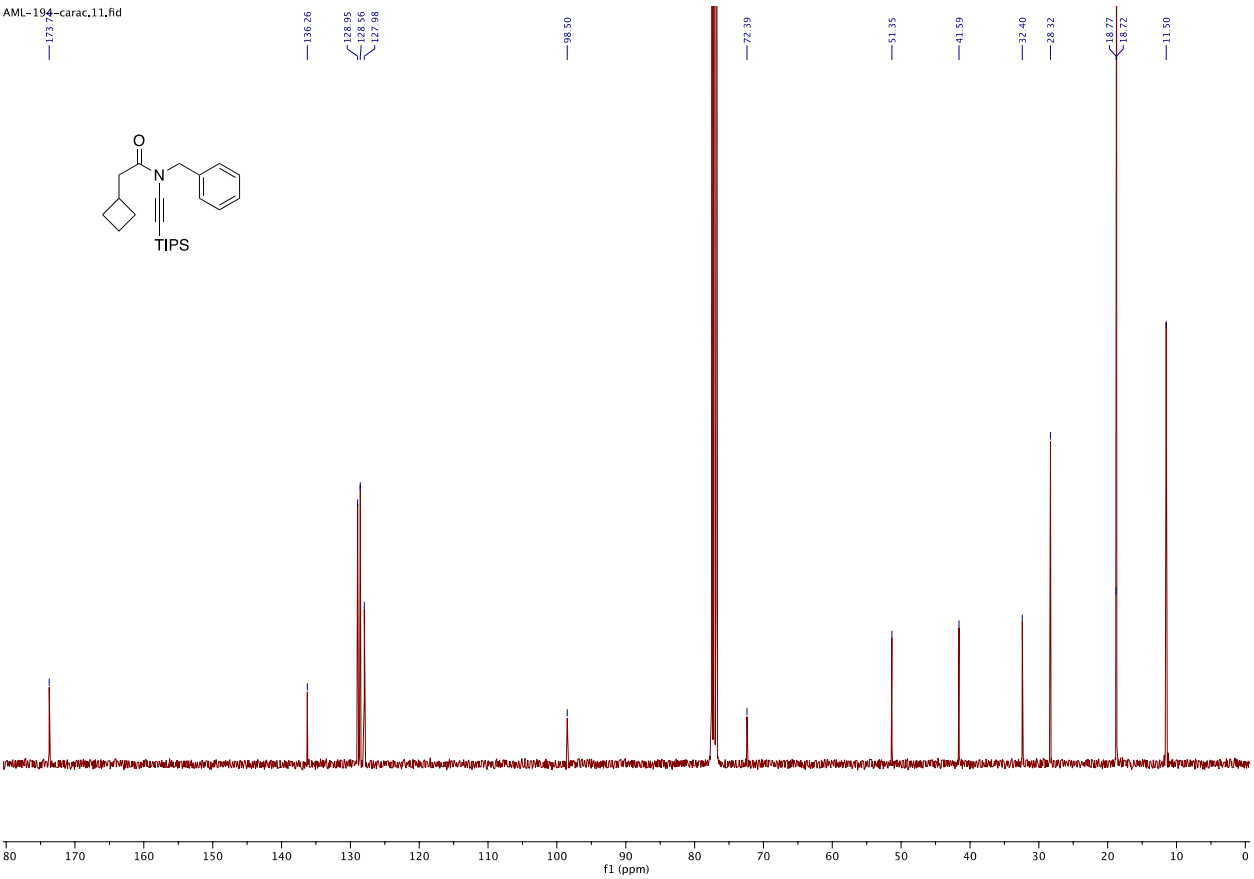
^{13}C NMR of **1c-SiR$_3$**



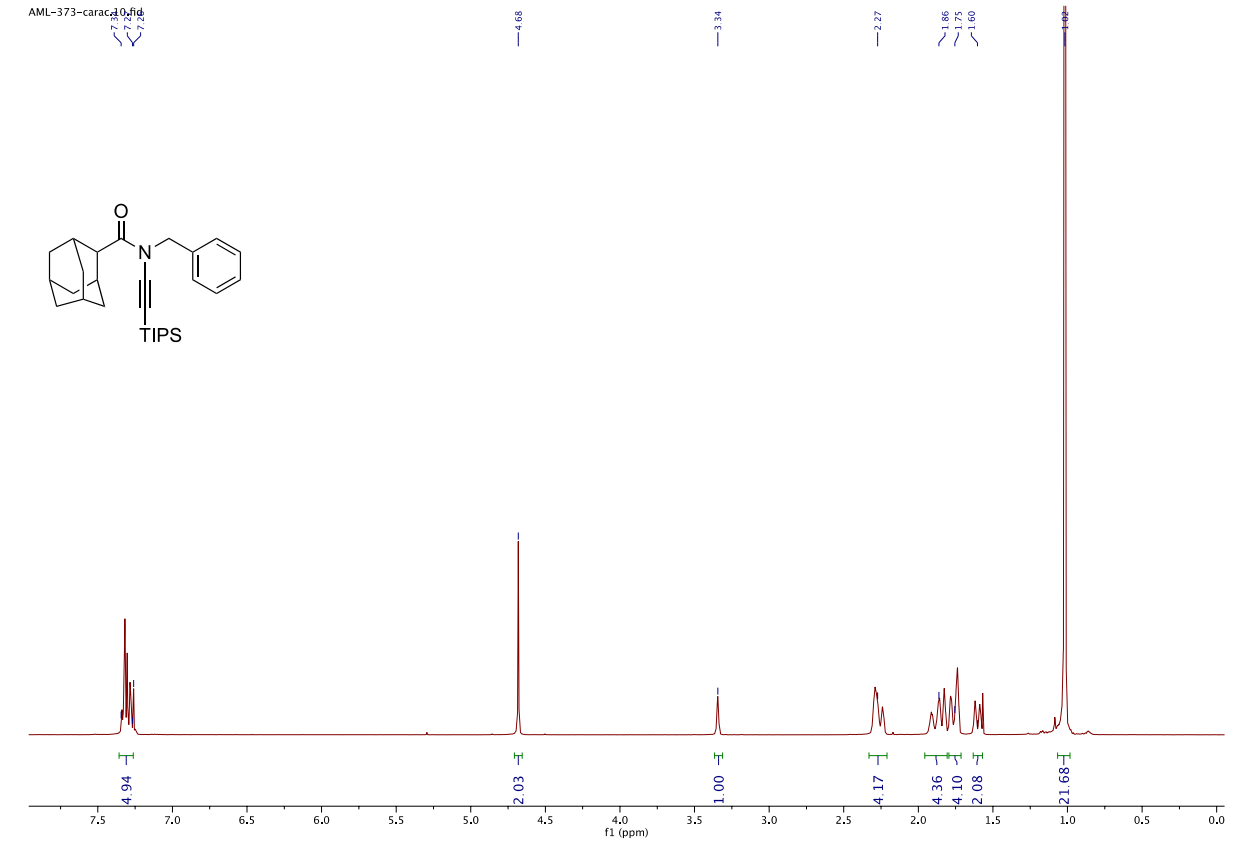
^{1}H NMR of **1d-SiR$_3$**



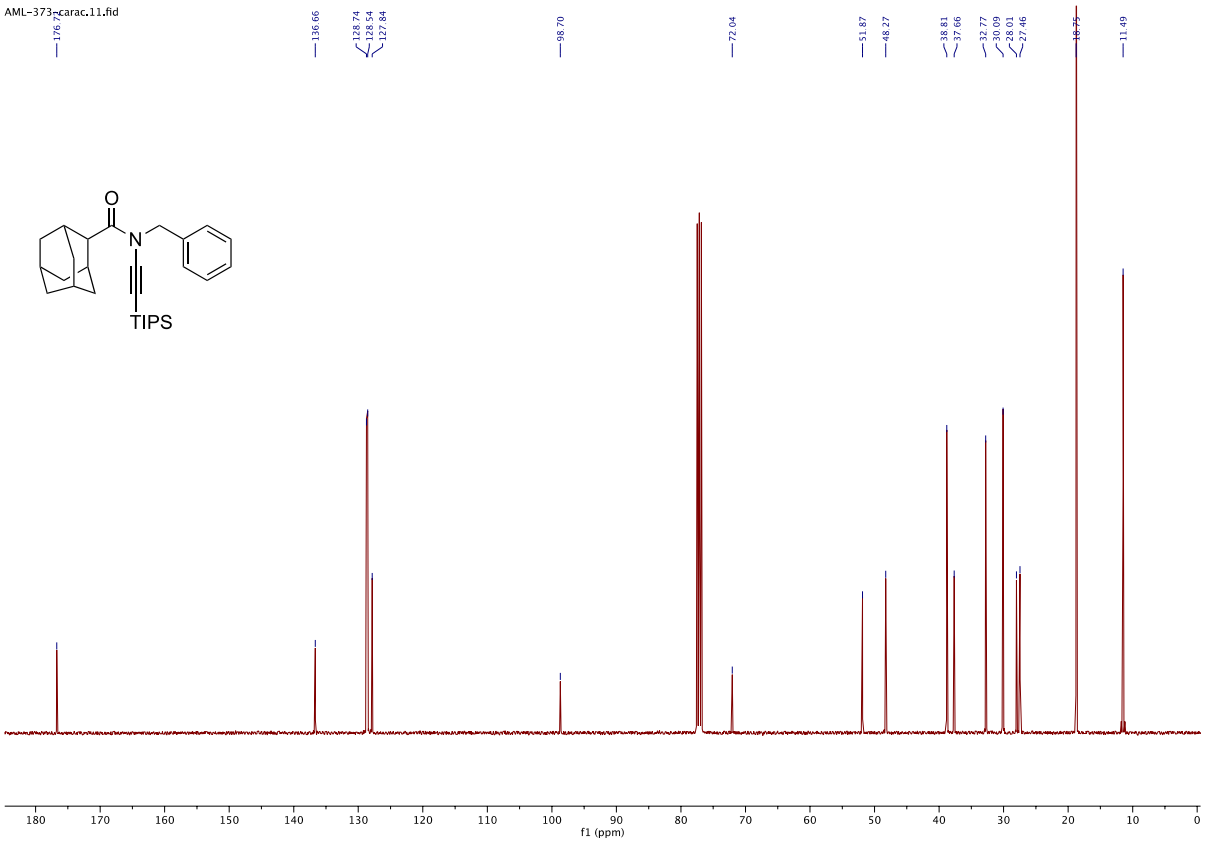
^{13}C NMR of **1d-SiR$_3$**



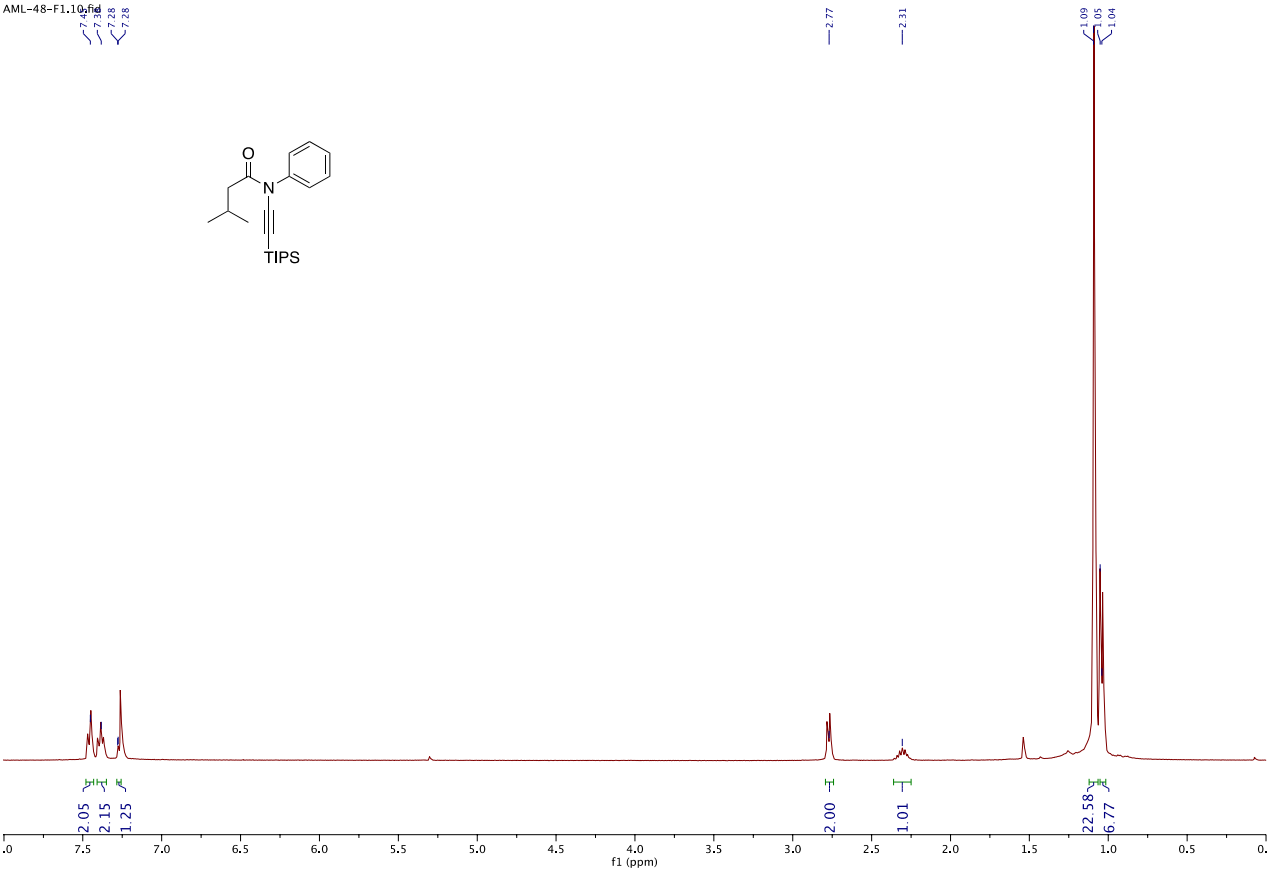
^{1}H NMR of **1f-SiR$_3$**



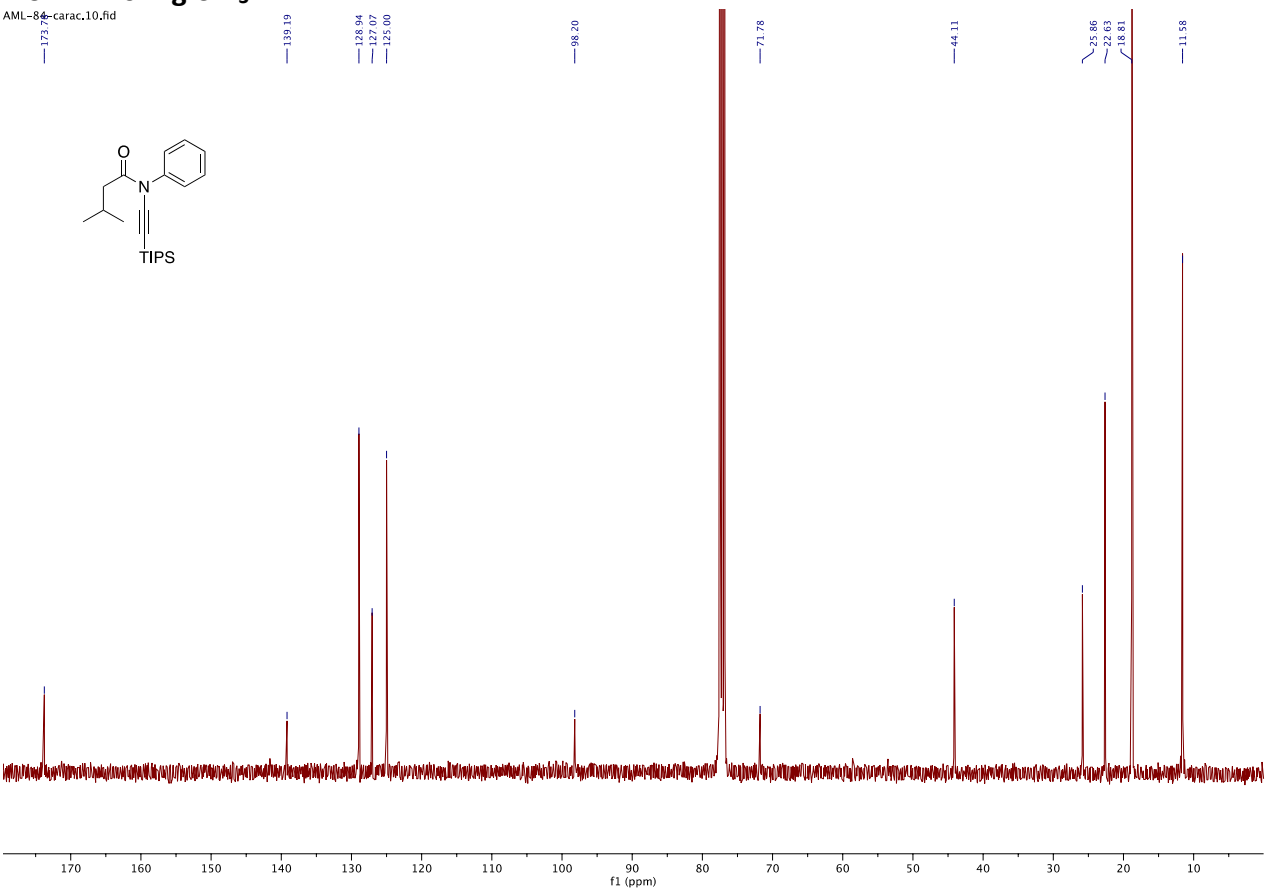
^{13}C NMR of **1f-SiR$_3$**



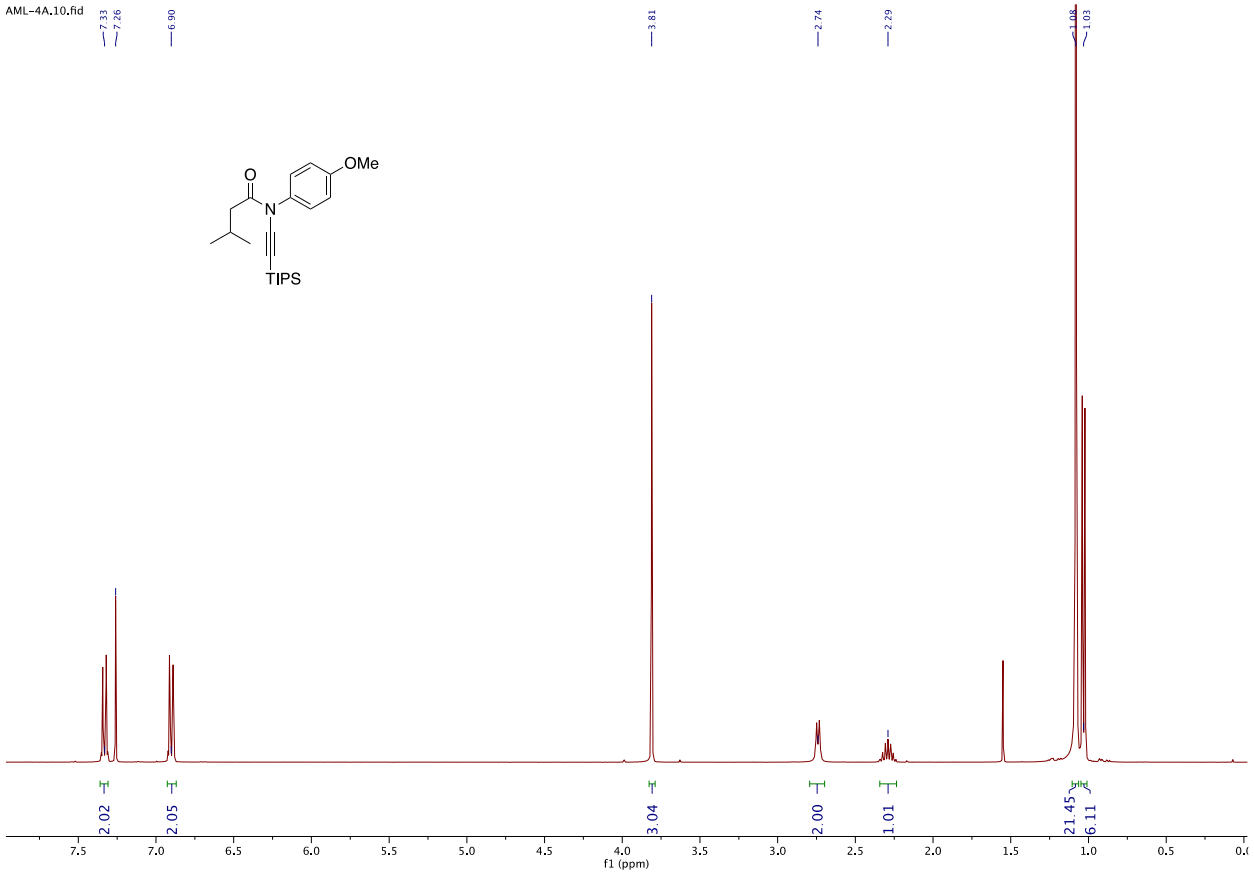
^{1}H NMR of **1g-SiR$_3$**



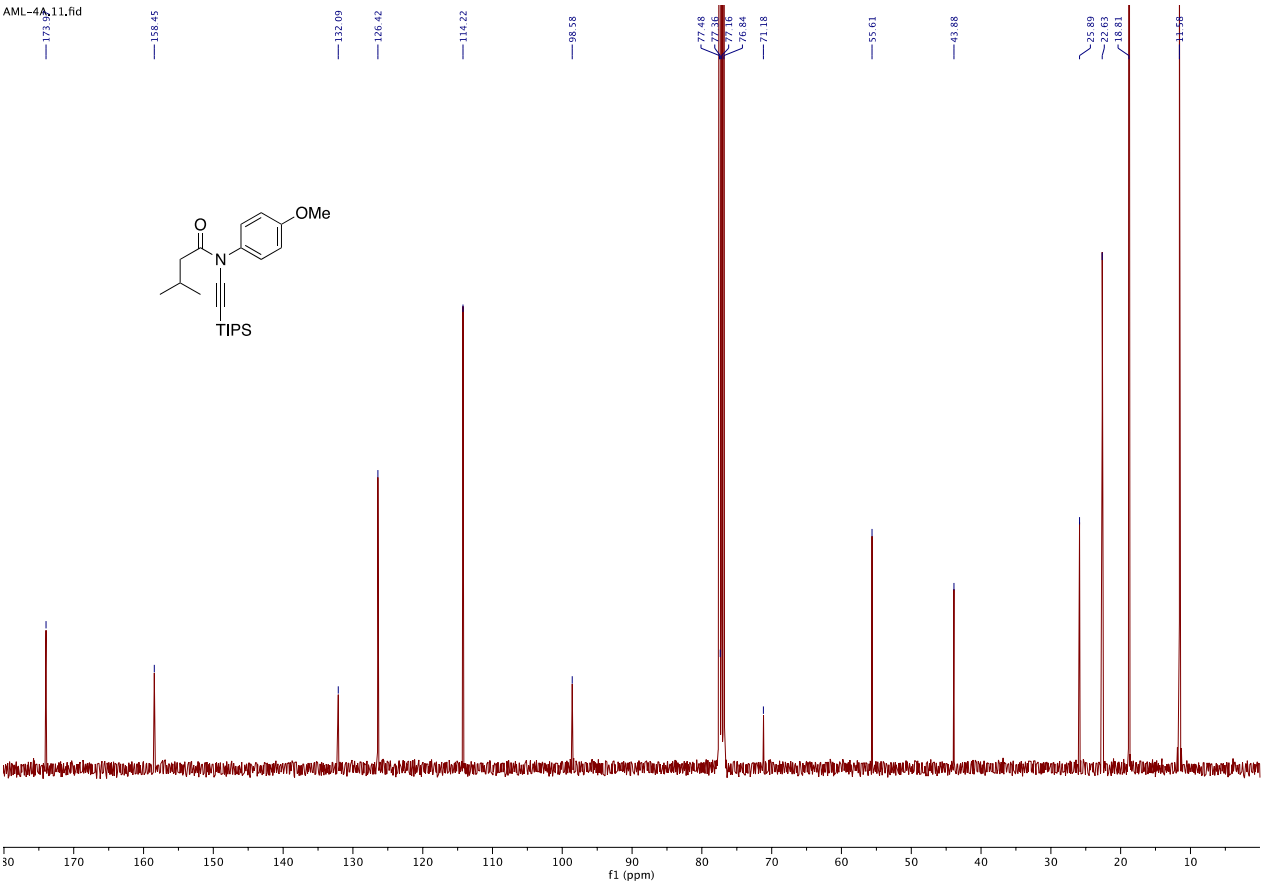
^{13}C NMR of **1g-SiR$_3$**



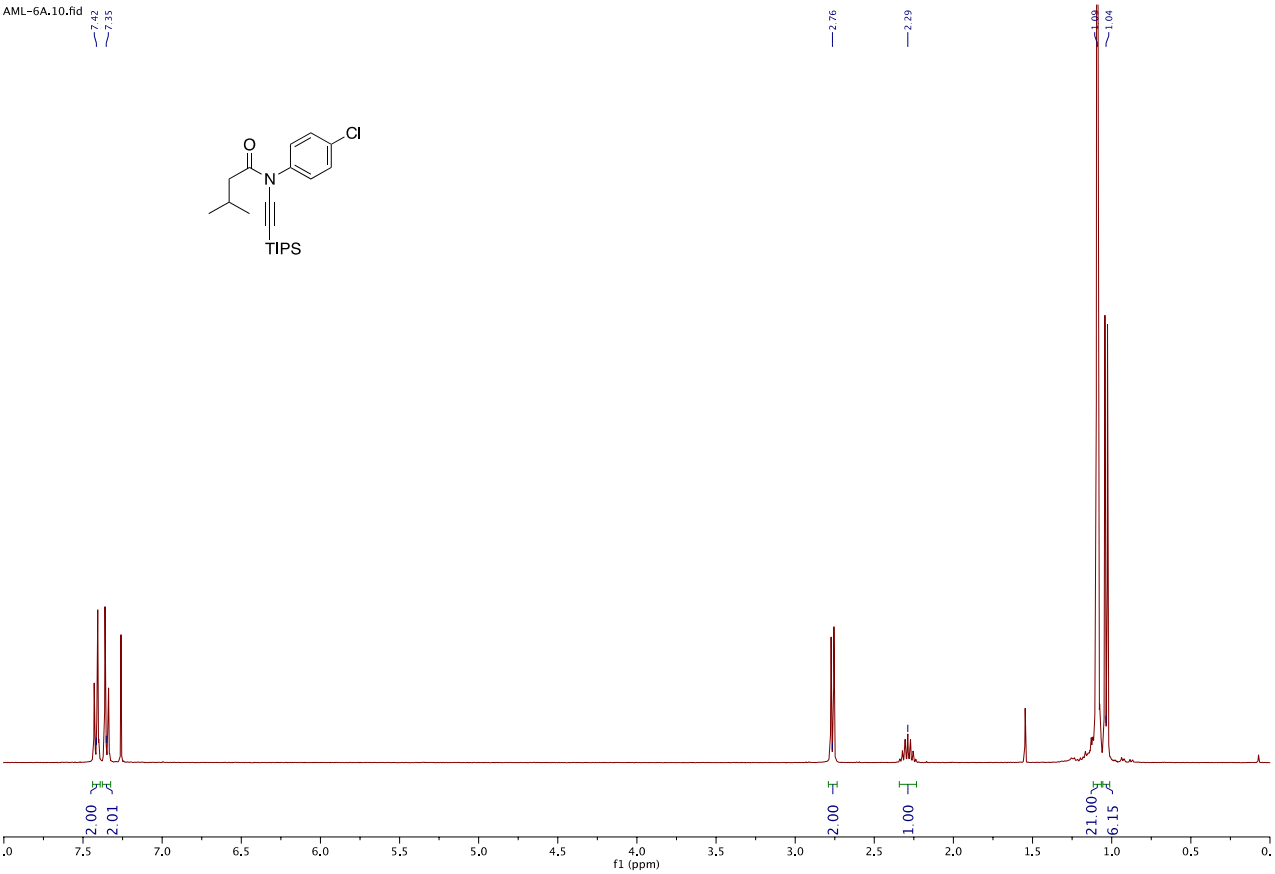
^{1}H NMR of **1h-SiR$_3$**



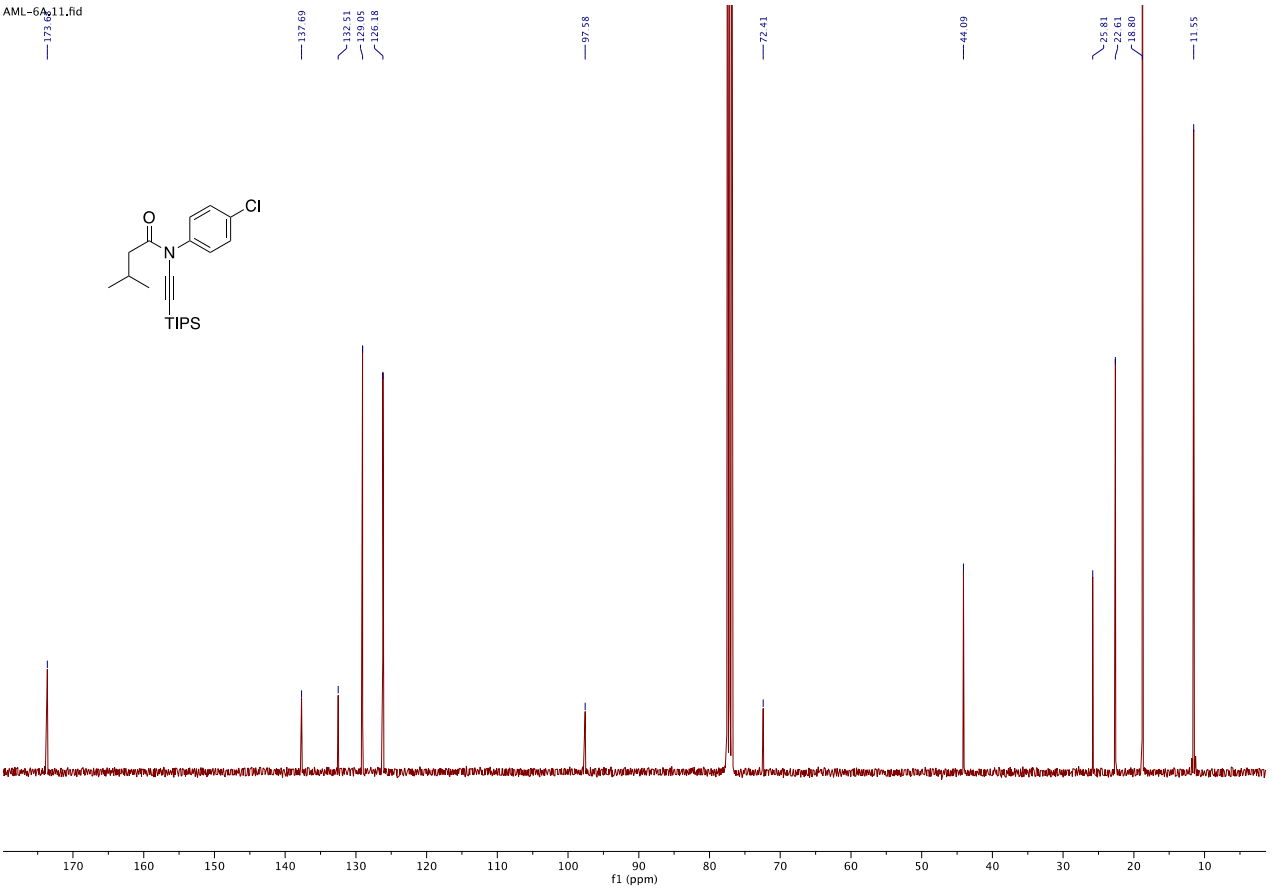
^{13}C NMR of **1h-SiR$_3$**



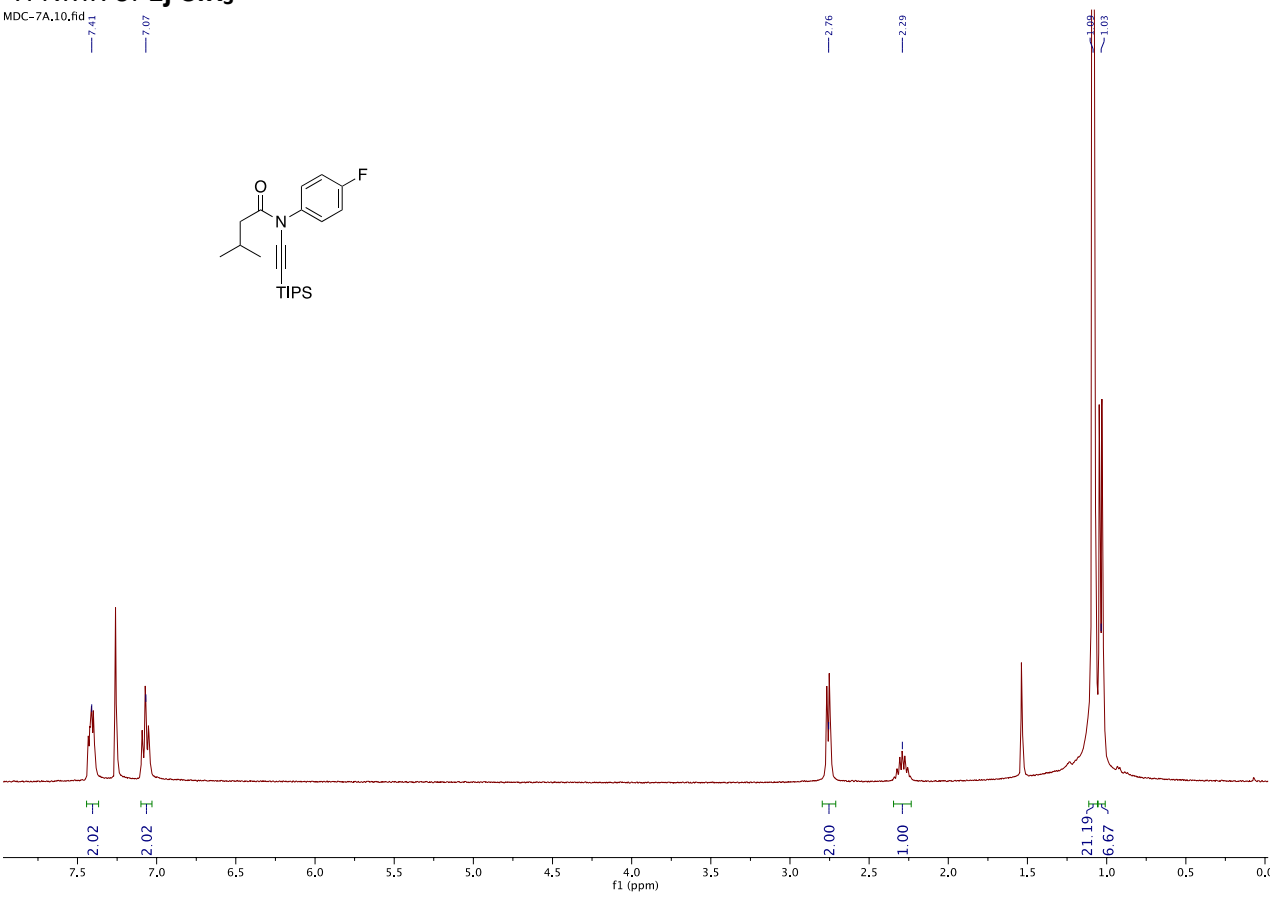
^{1}H NMR of **1i-SiR$_3$**



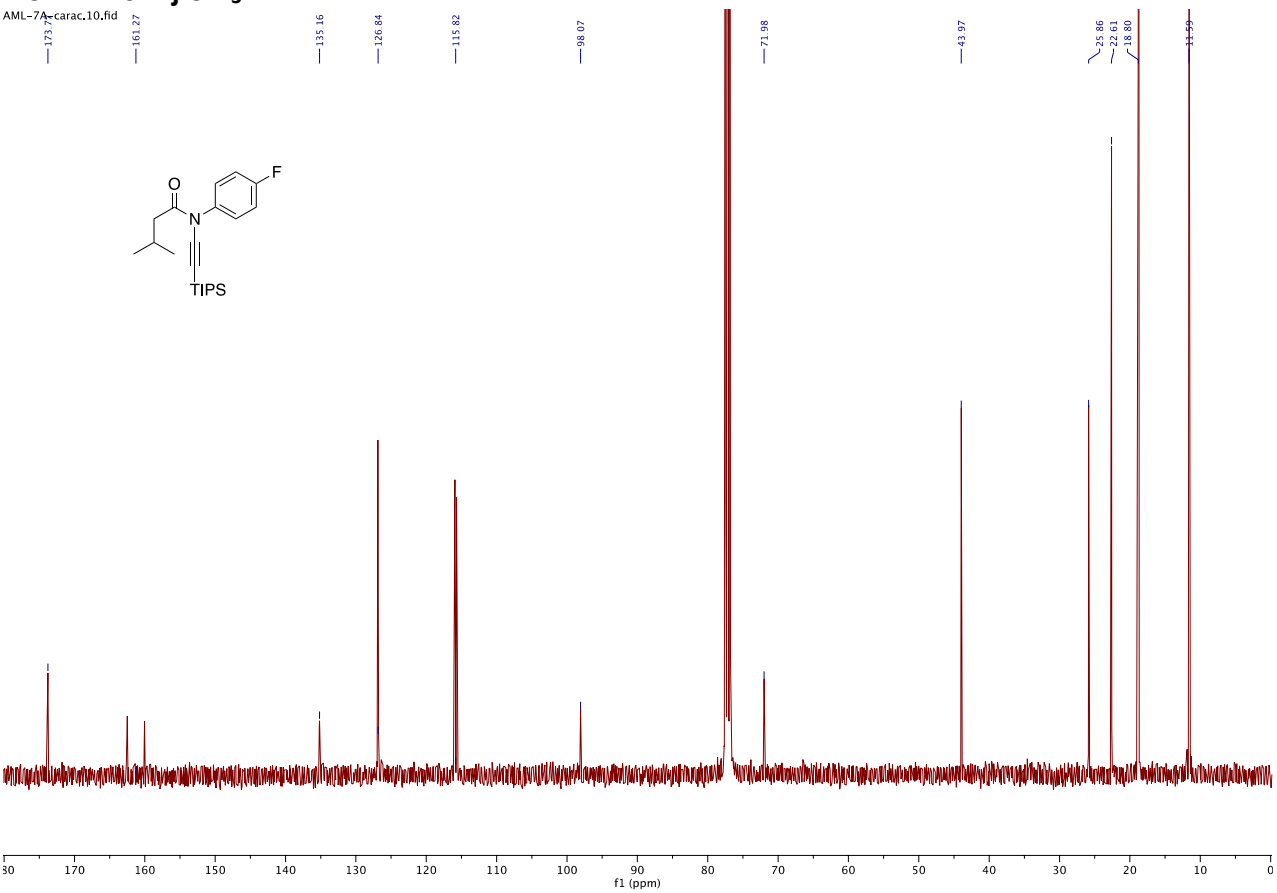
^{13}C NMR of **1i-SiR$_3$**



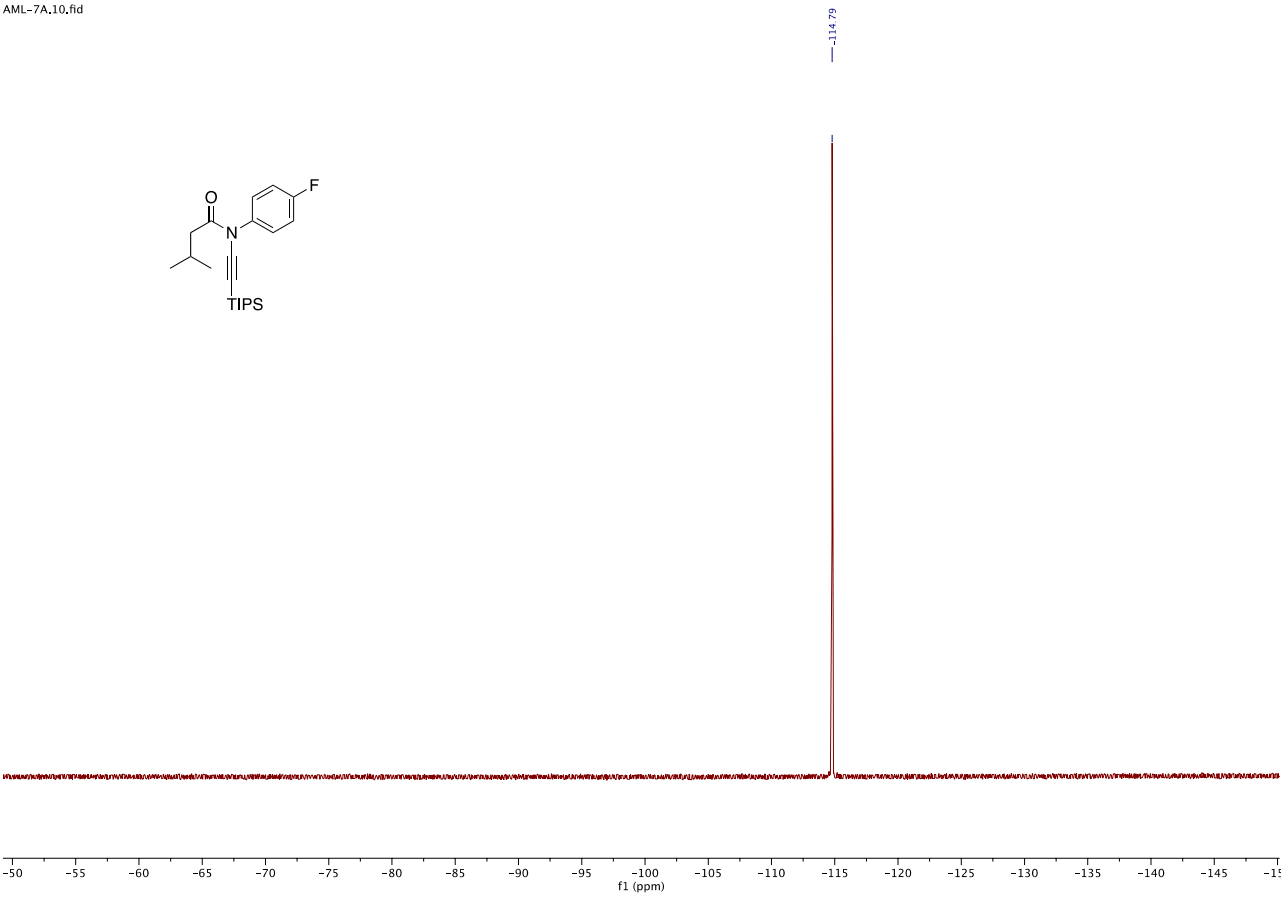
^{1}H NMR of **1j-SiR$_3$**



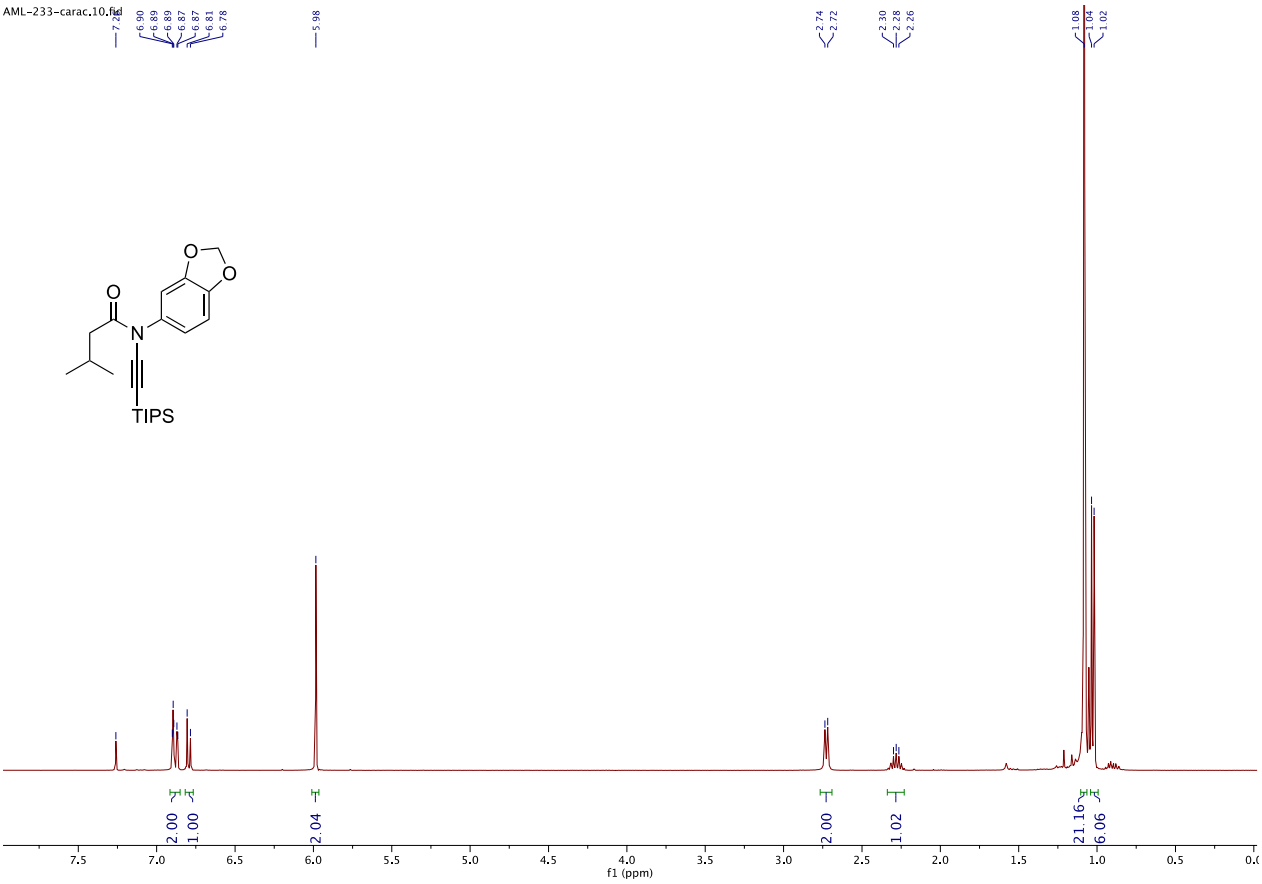
^{13}C NMR of **1j-SiR$_3$**



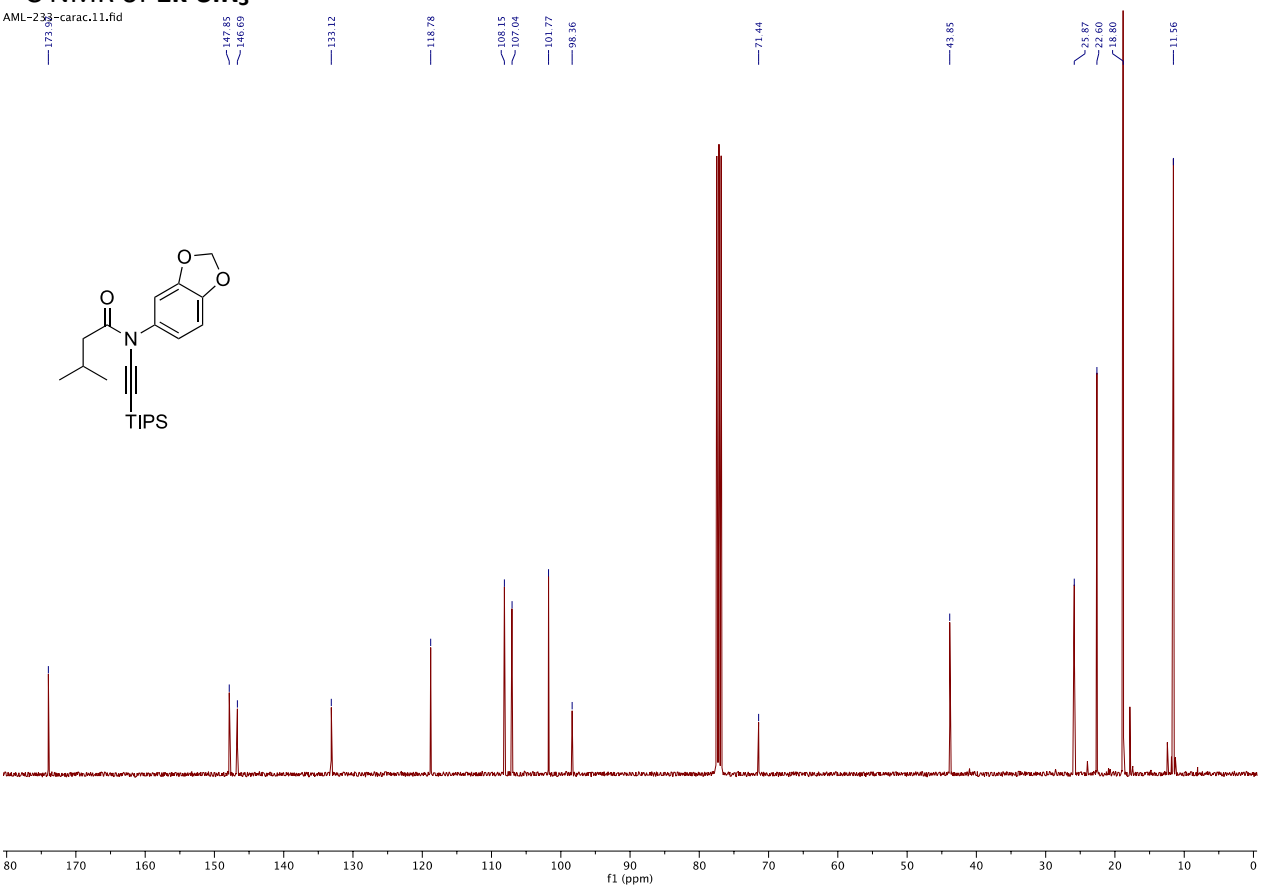
^{19}F NMR of **1j-SiR$_3$**



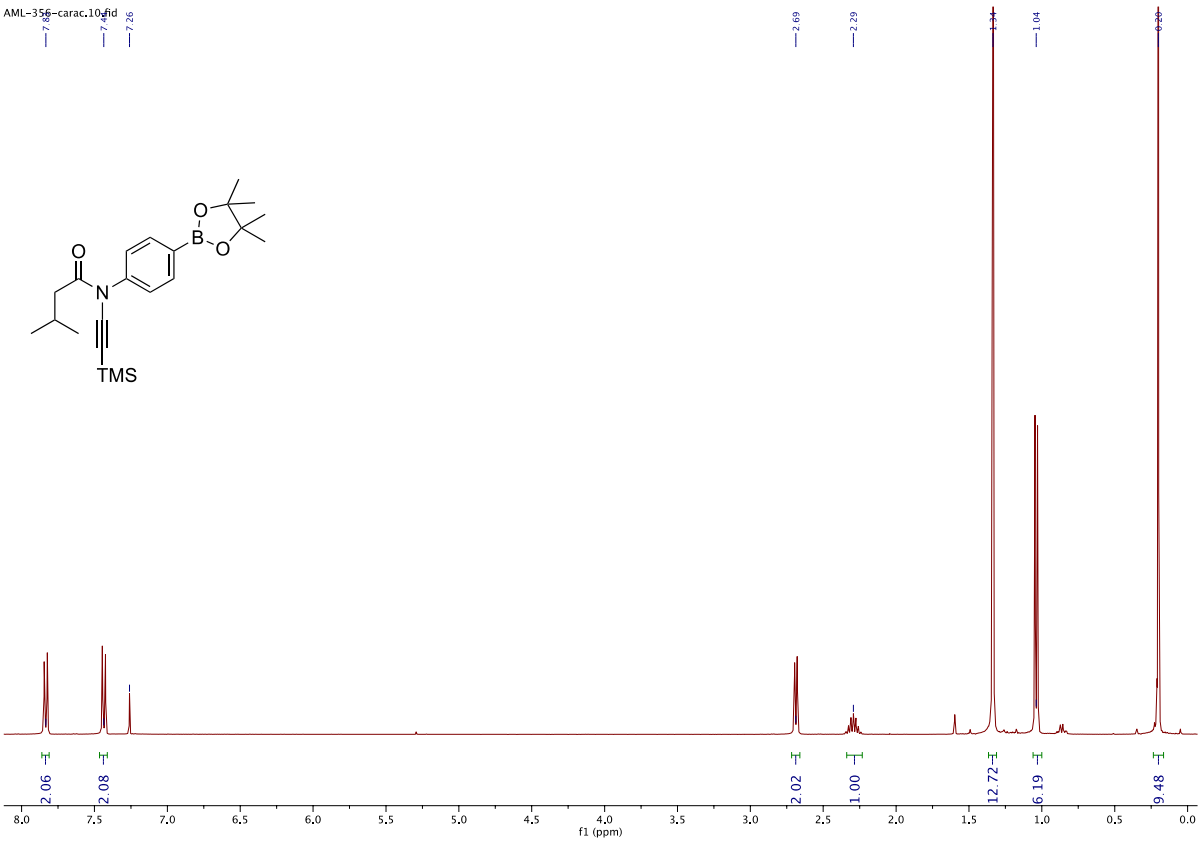
^{1}H NMR of **1k-SiR$_3$**



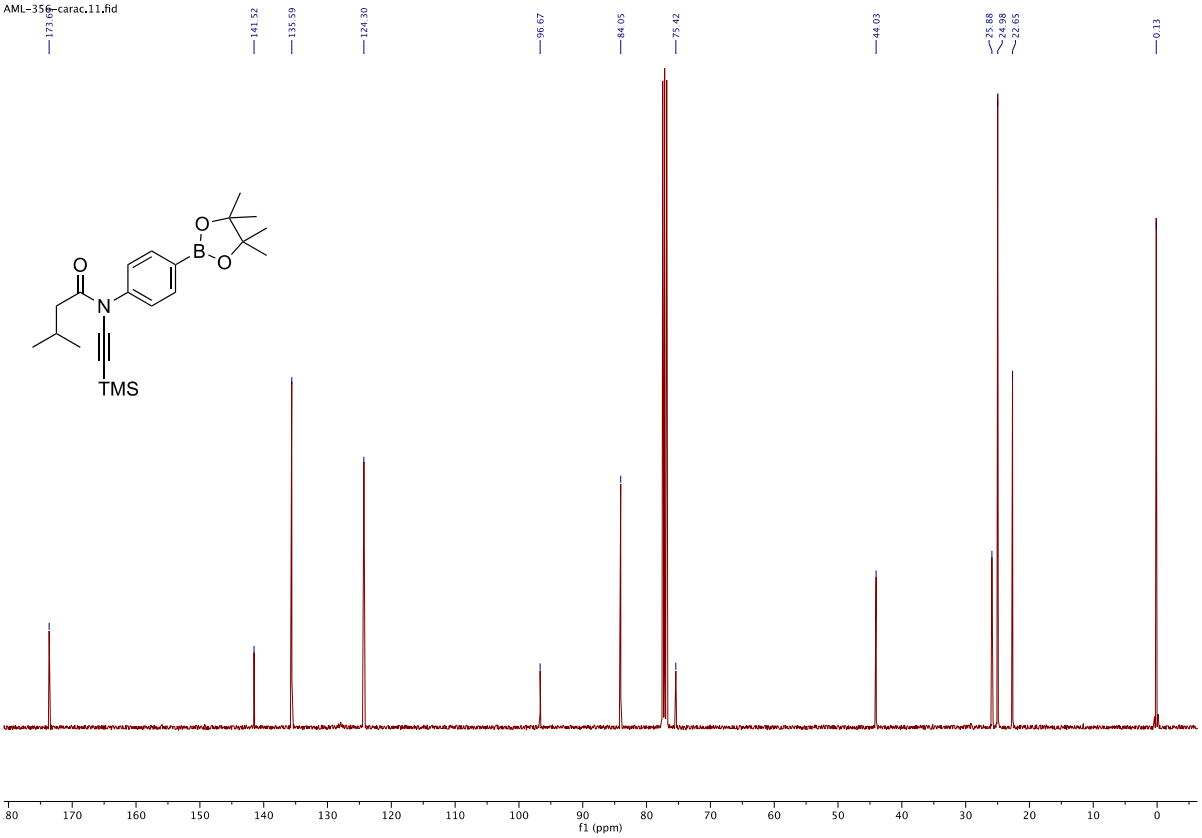
^{13}C NMR of **1k-SiR$_3$**



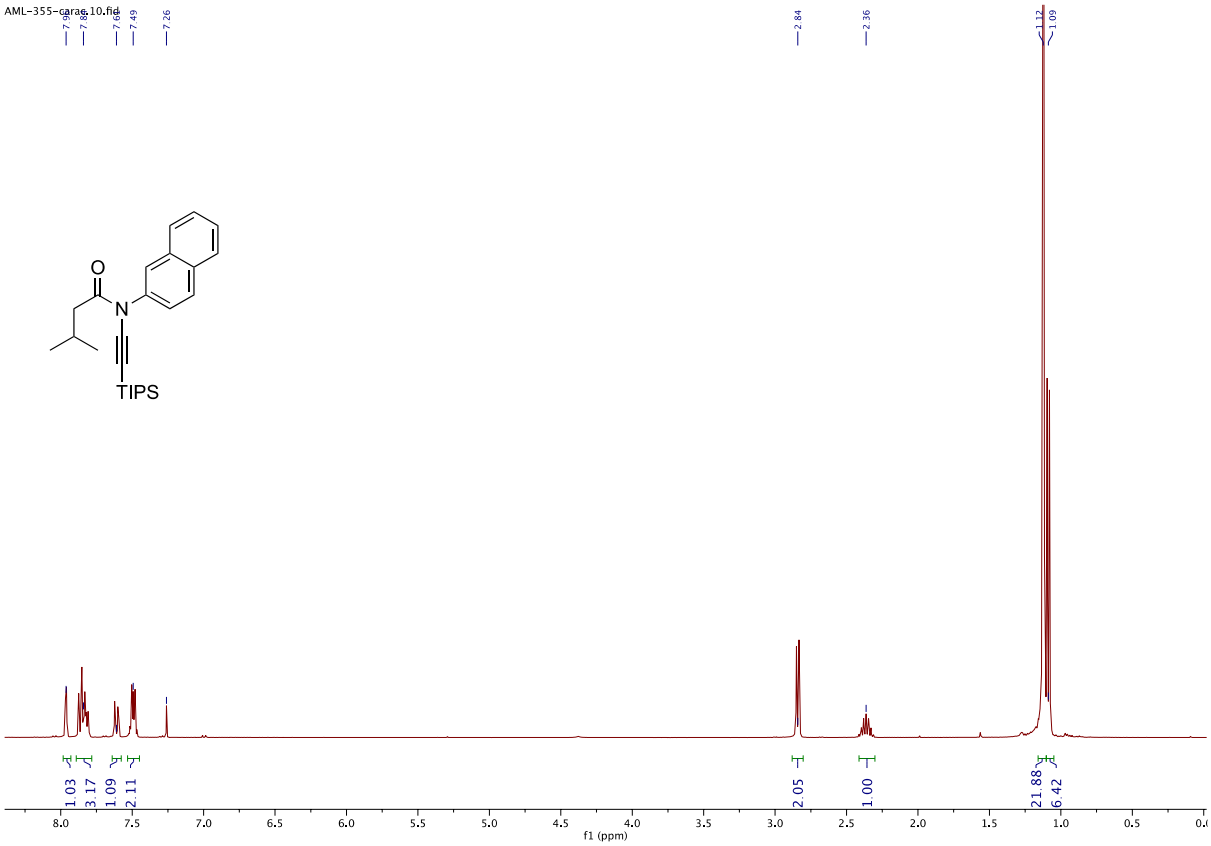
^{1}H NMR of **1l-SiR$_3$**



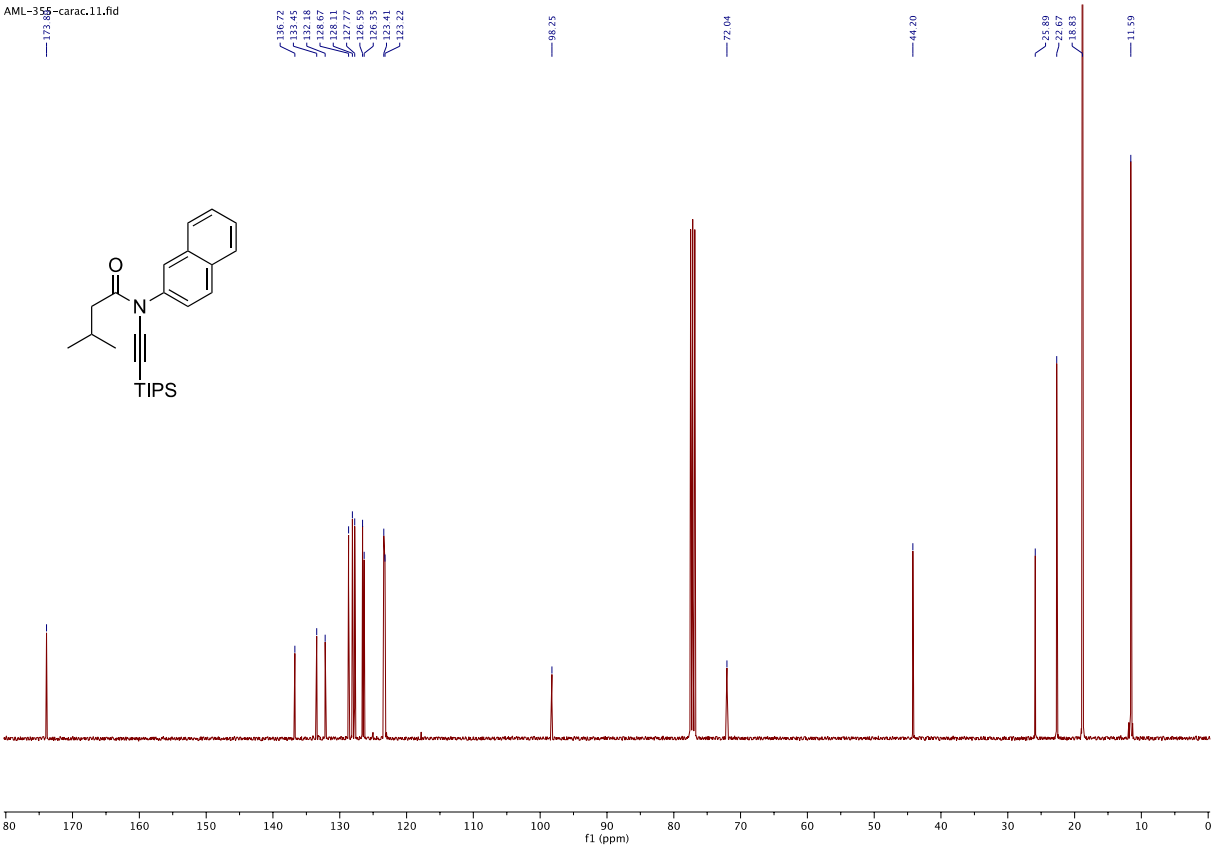
^{13}C NMR of **1l-SiR$_3$**



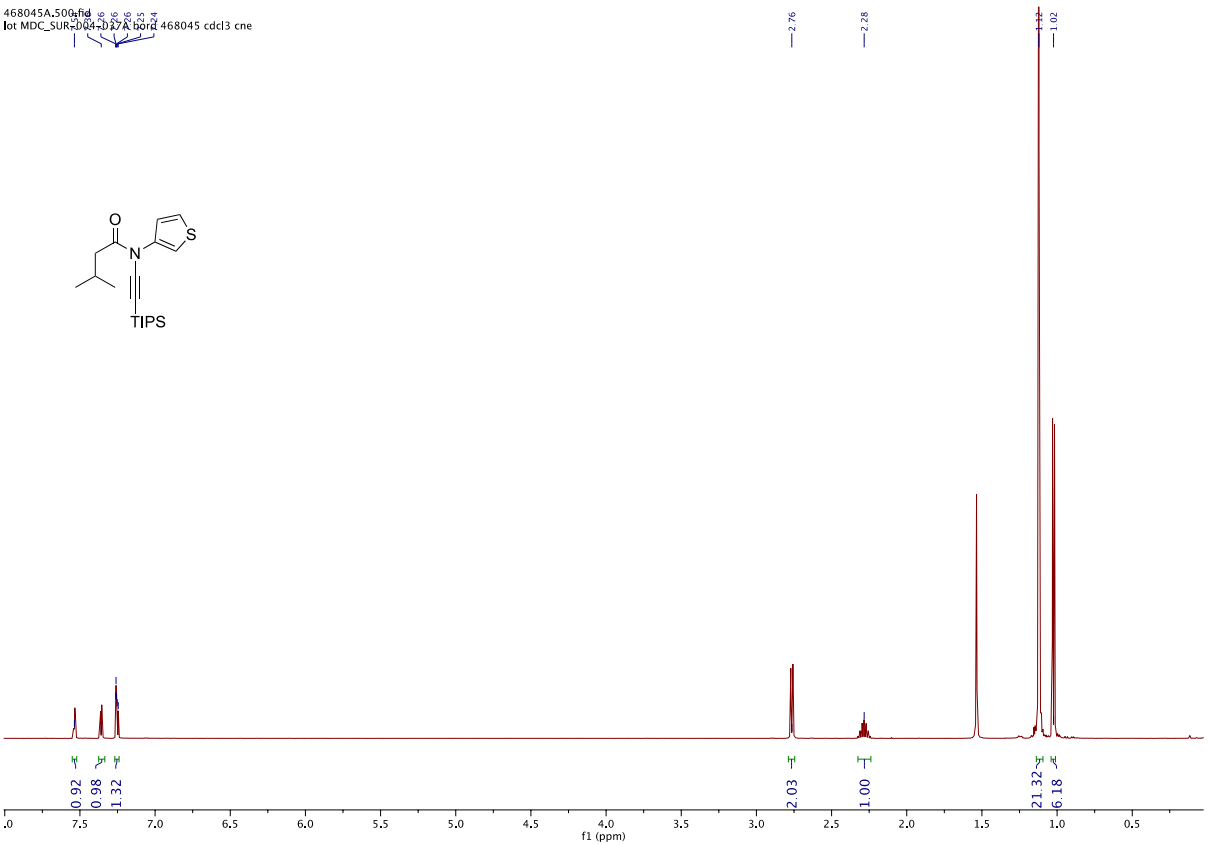
^{1}H NMR of **1m-SiR$_3$**



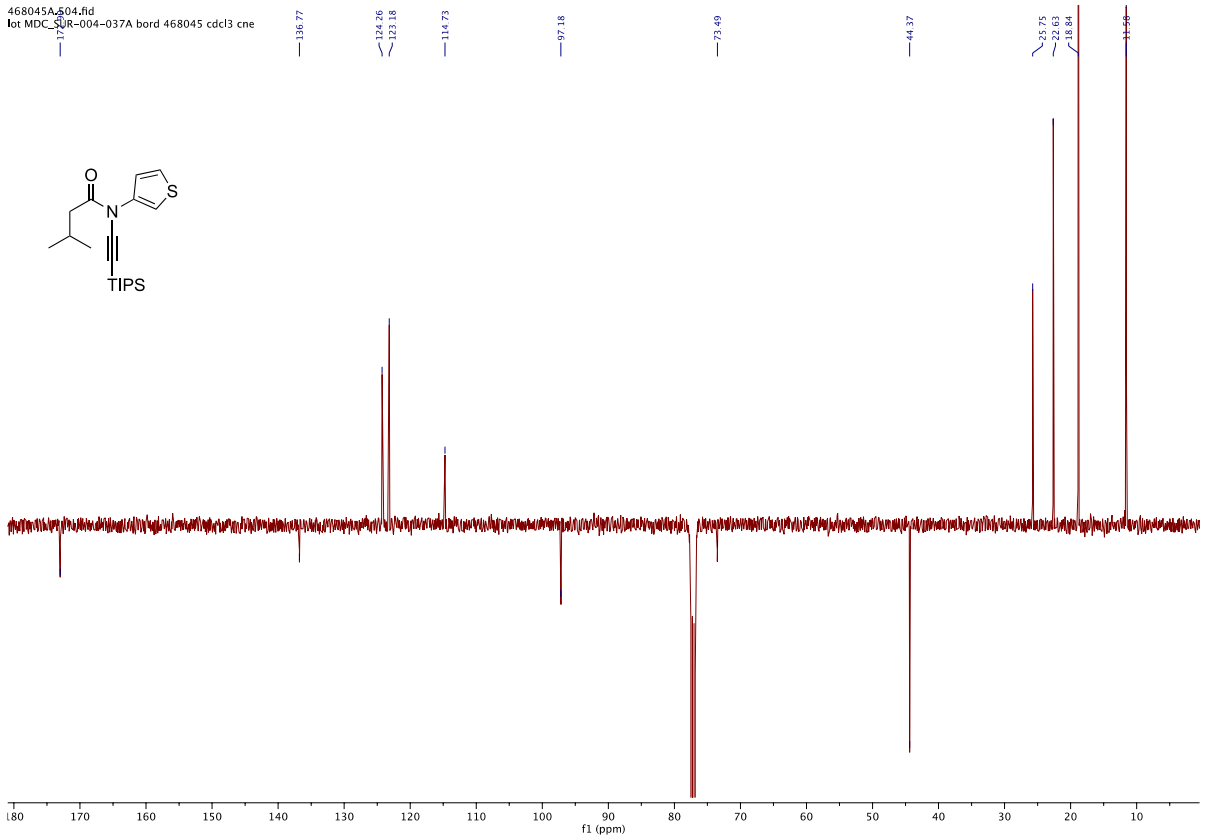
^{13}C NMR of **1m-SiR$_3$**



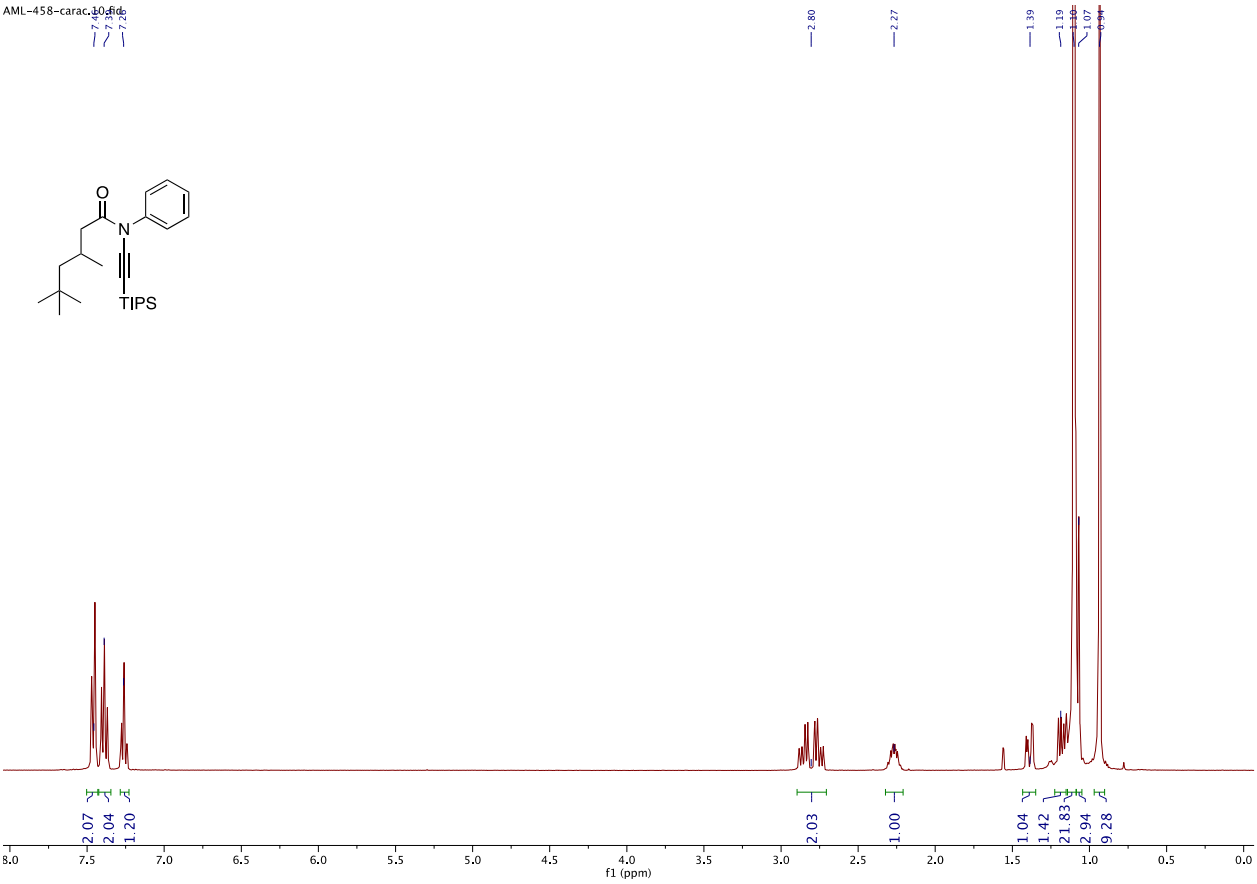
^{1}H NMR of **1n-SiR$_3$**



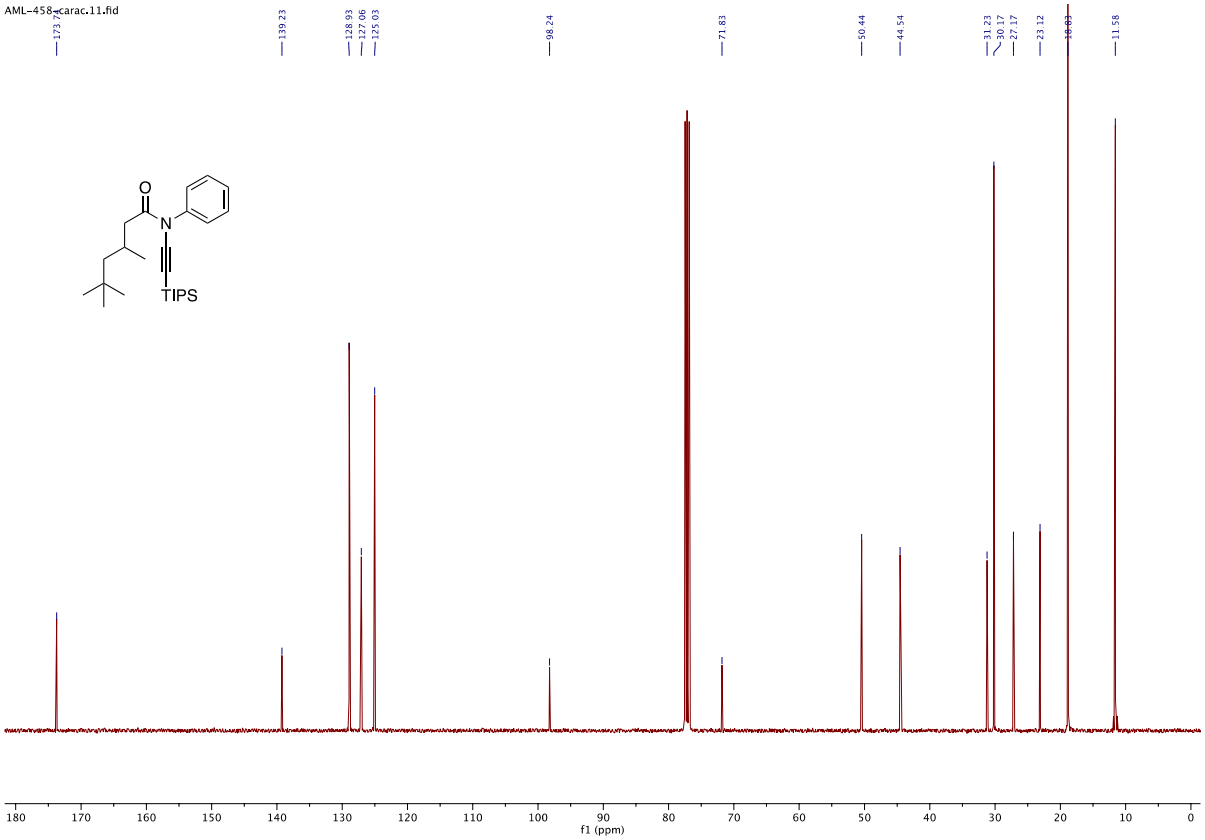
^{13}C NMR of **1n-SiR$_3$**



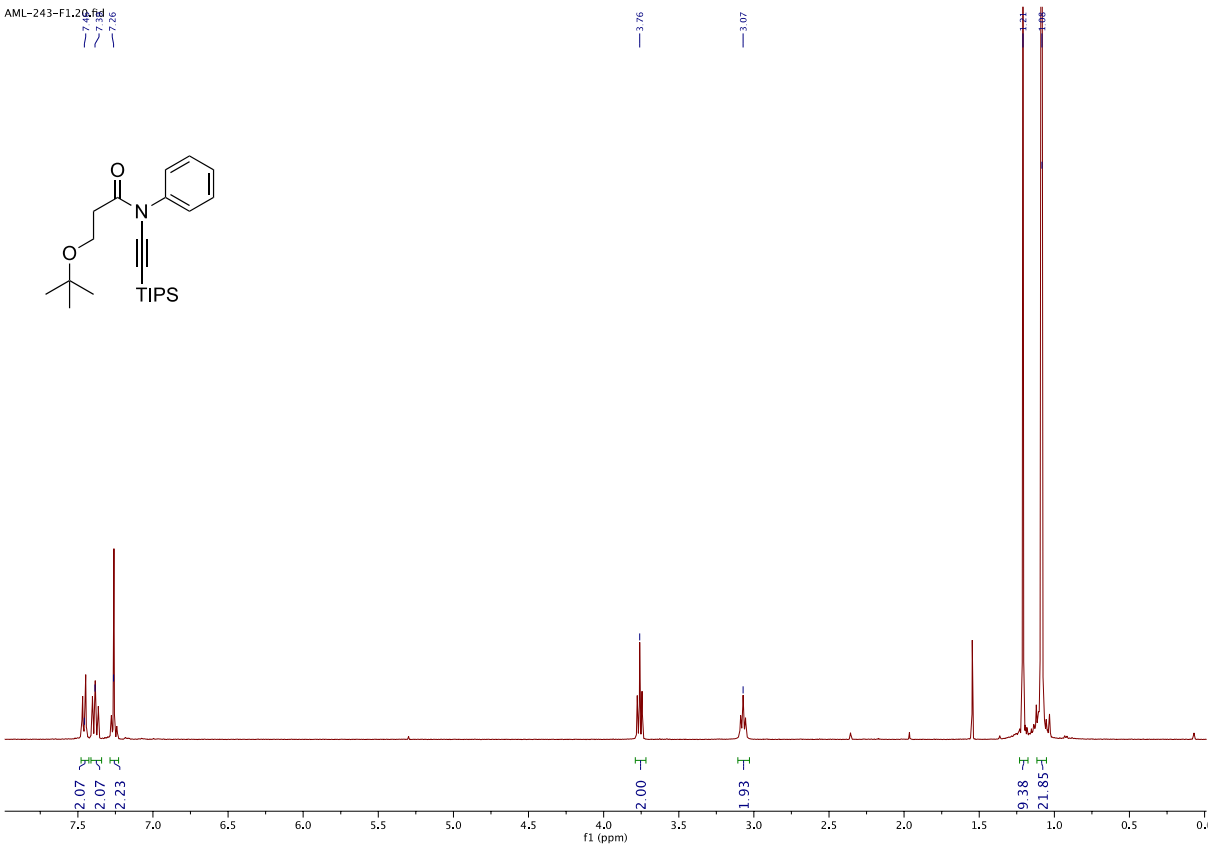
^{1}H NMR of **1o-SiR$_3$**



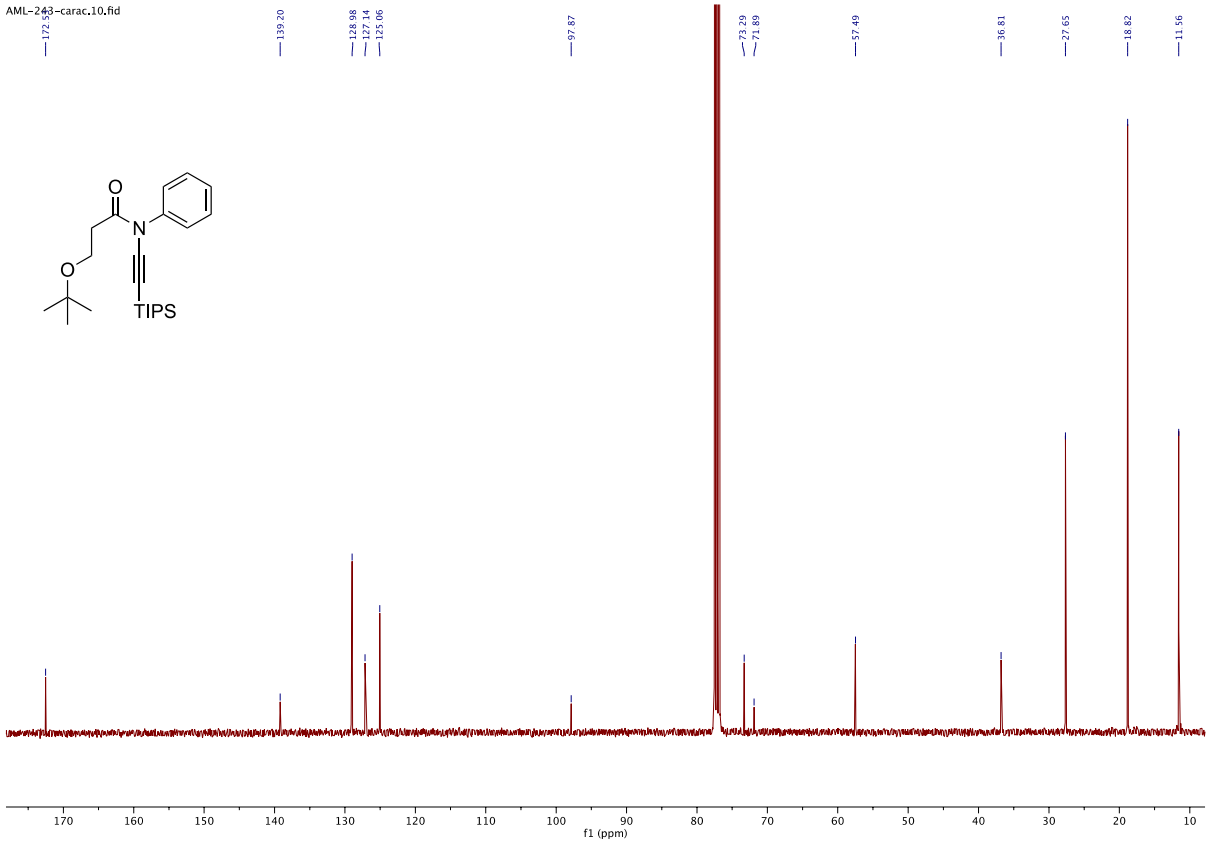
^{13}C NMR of **1o-SiR$_3$**



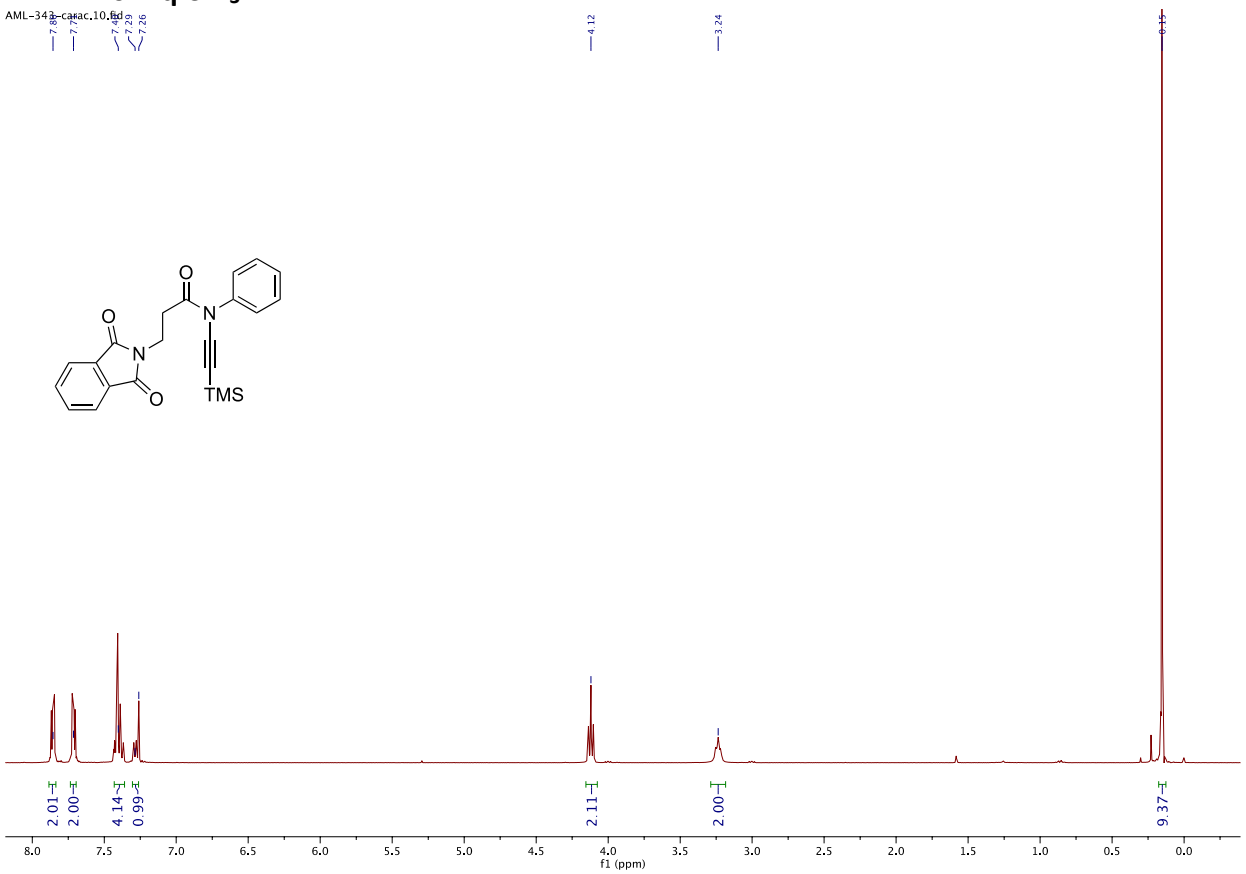
^{1}H NMR of **1p-SiR$_3$**



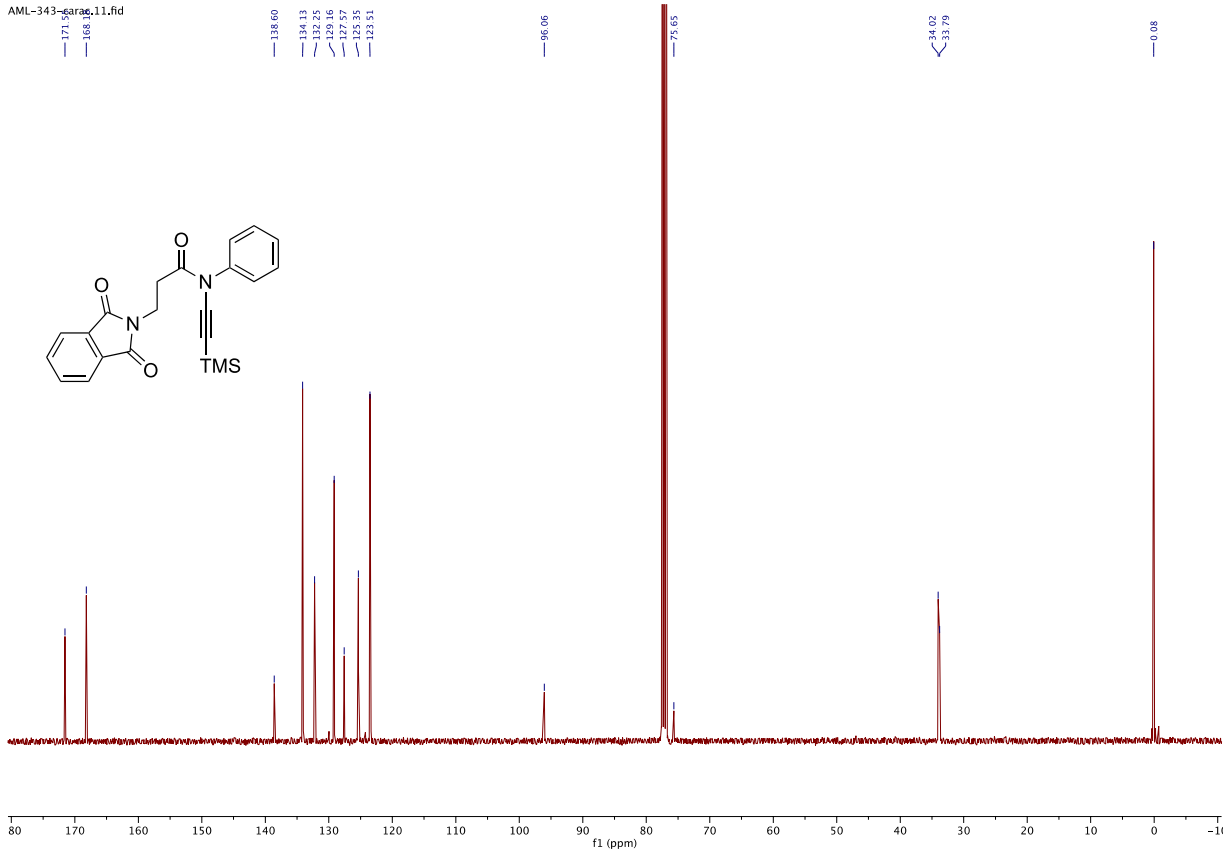
^{13}C NMR of **1p-SiR$_3$**



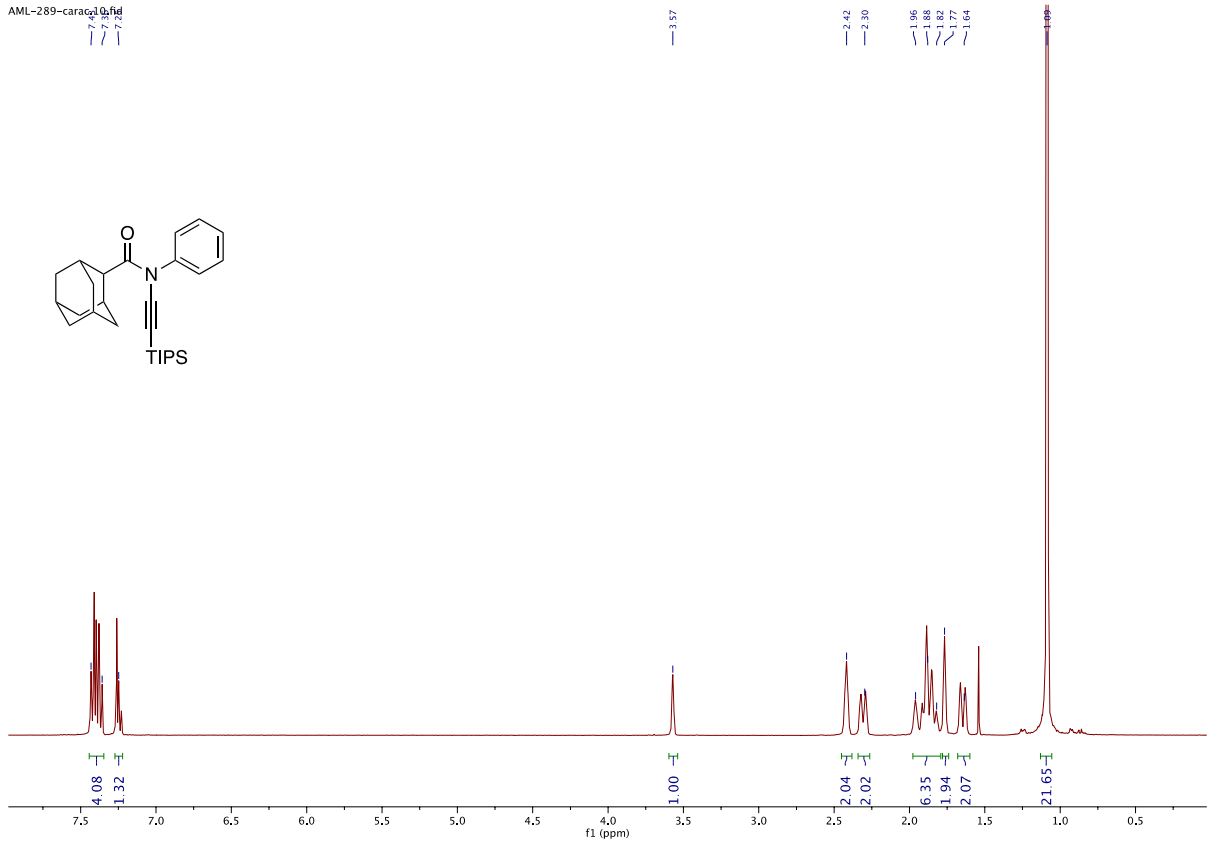
^{1}H NMR of **1q-SiR$_3$**



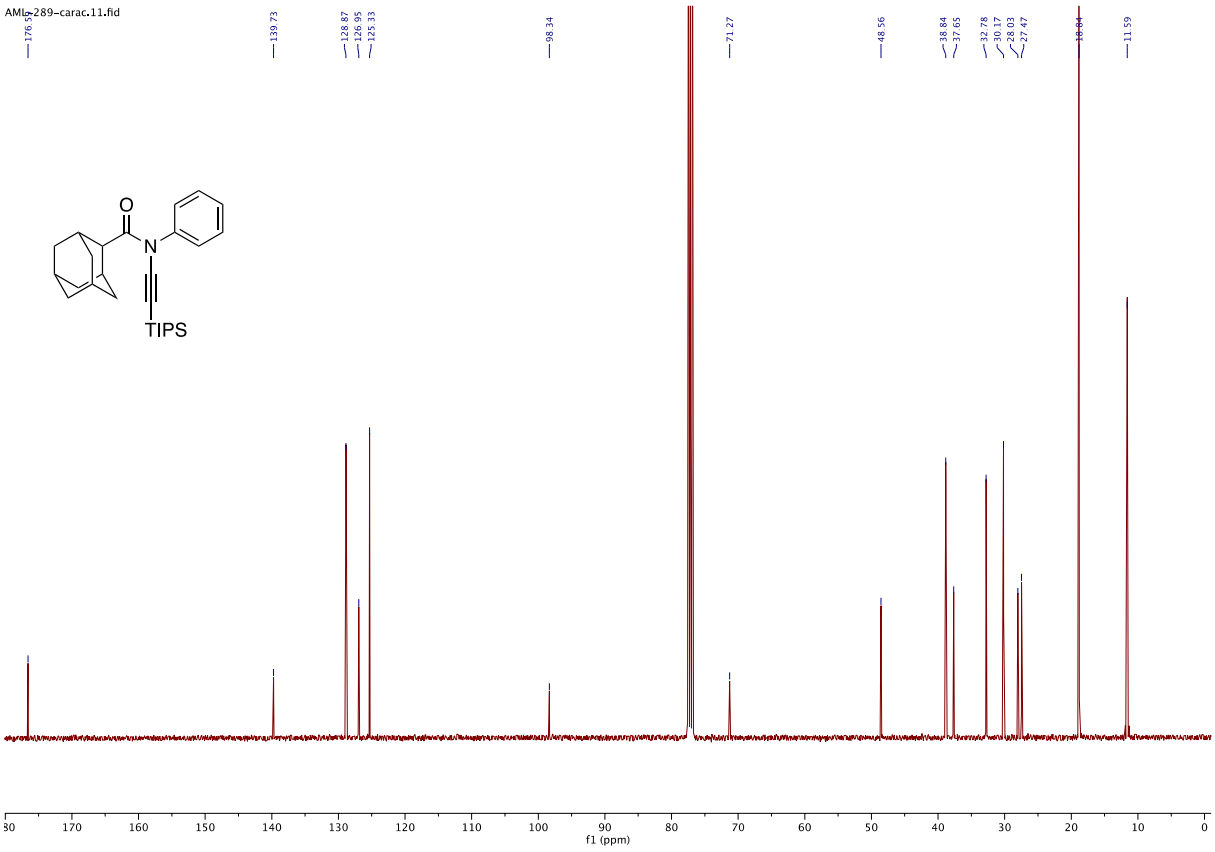
^{13}C NMR of **1q-SiR$_3$**



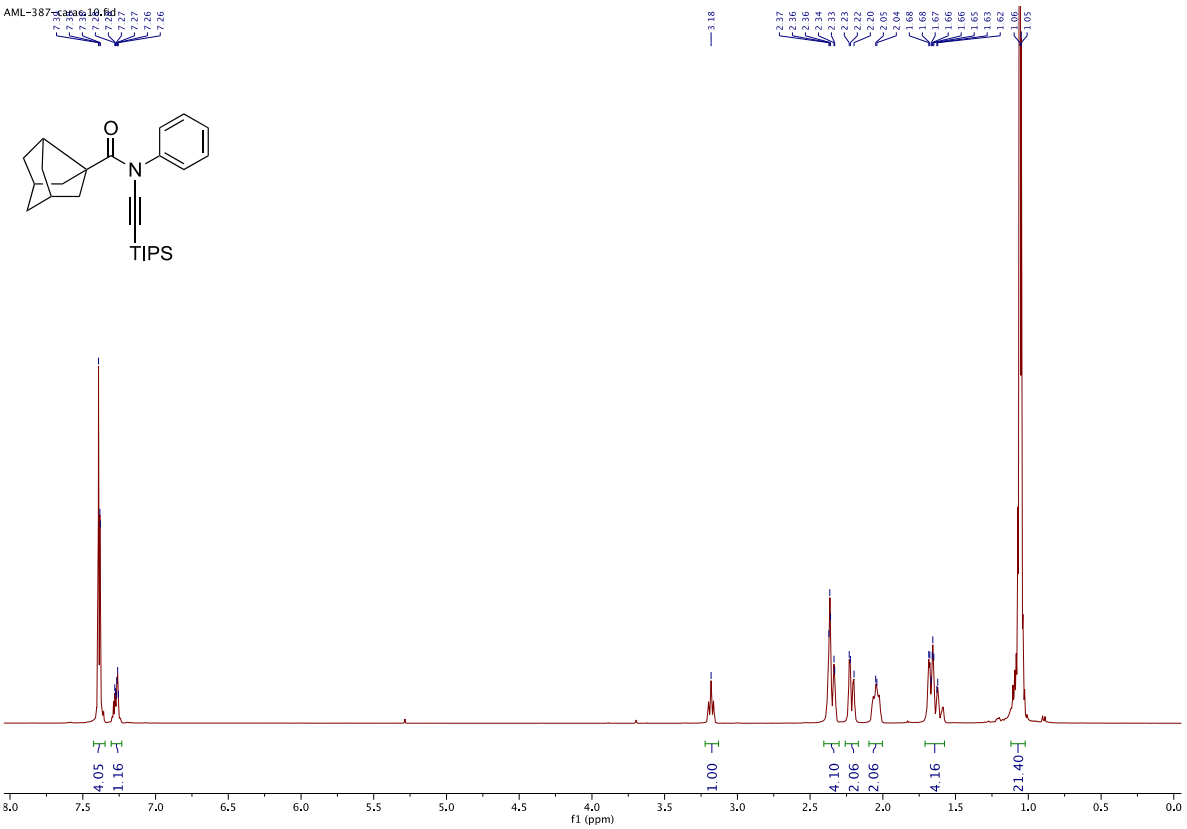
^{1}H NMR of **1r-SiR$_3$**



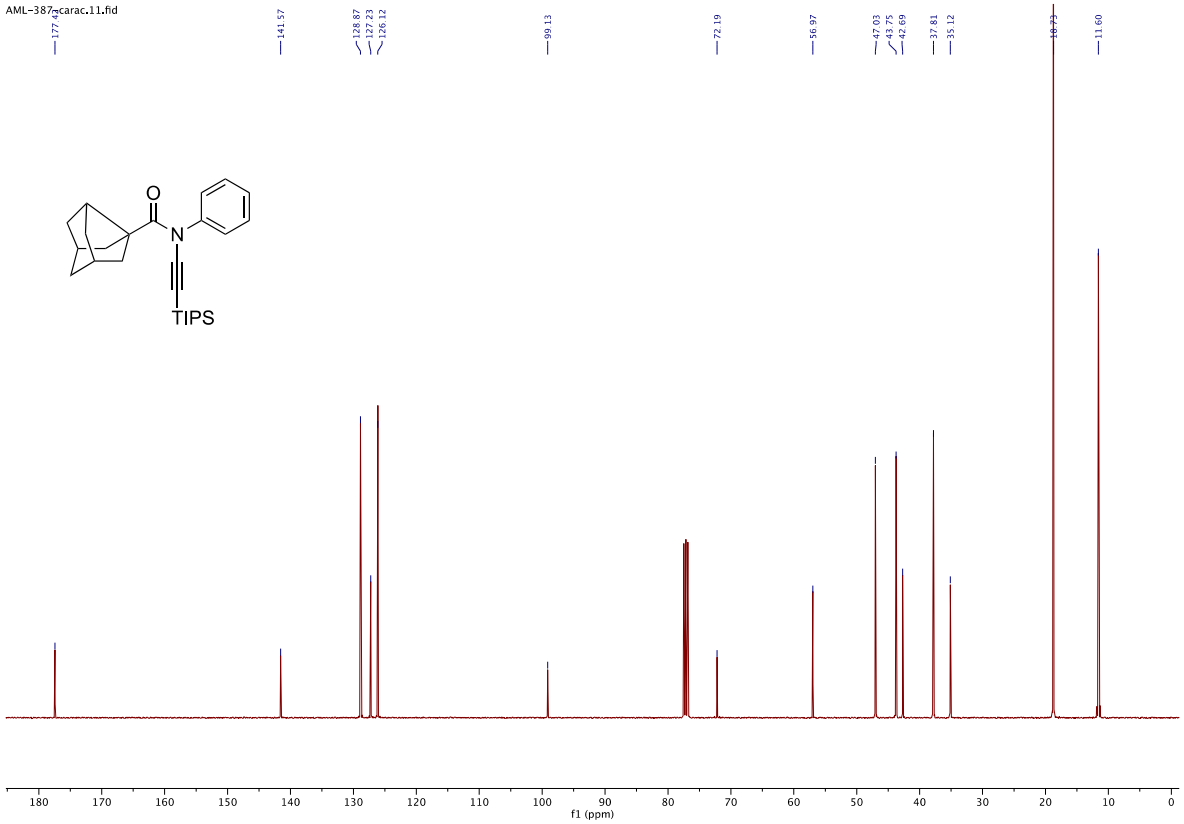
^{13}C NMR of **1r-SiR$_3$**



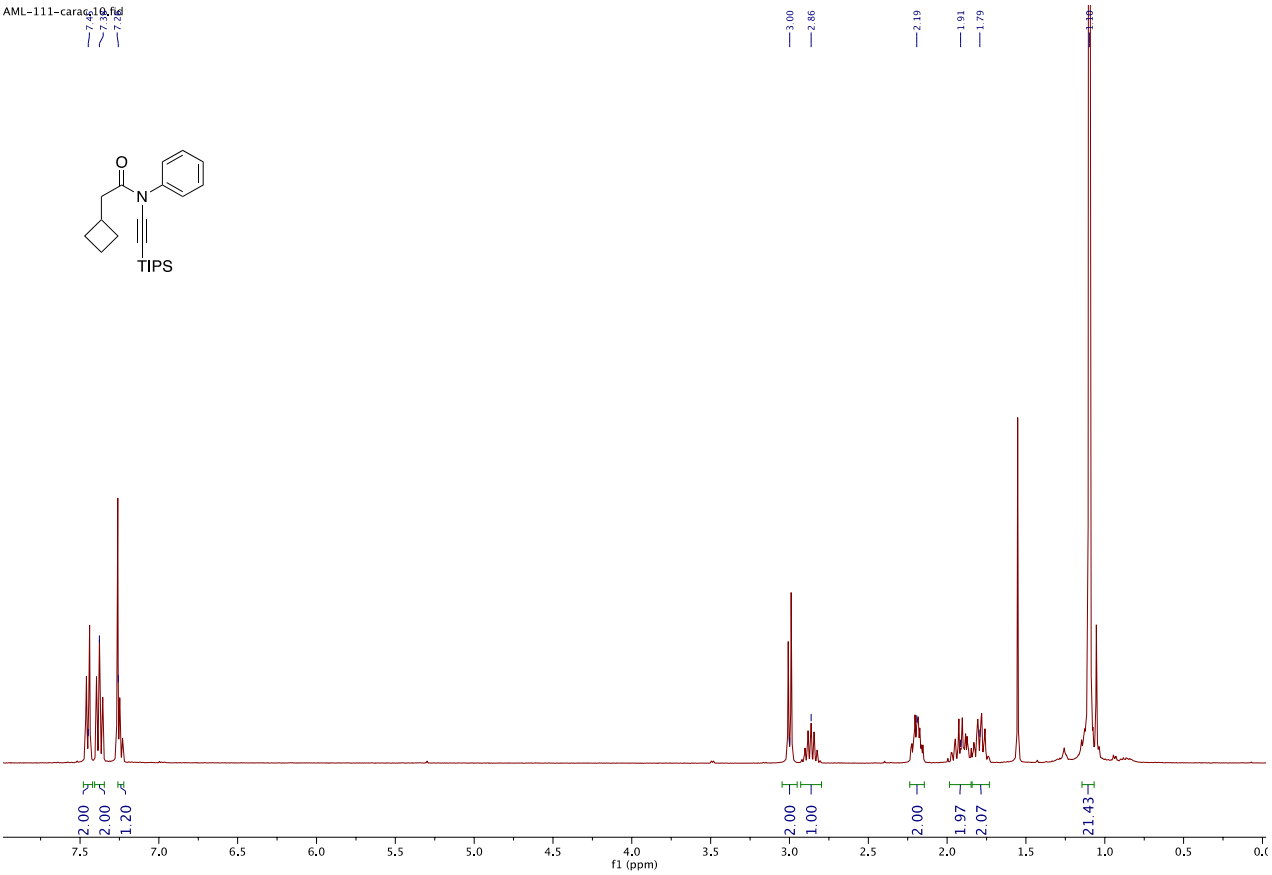
^{1}H NMR of **1s-SiR$_3$**



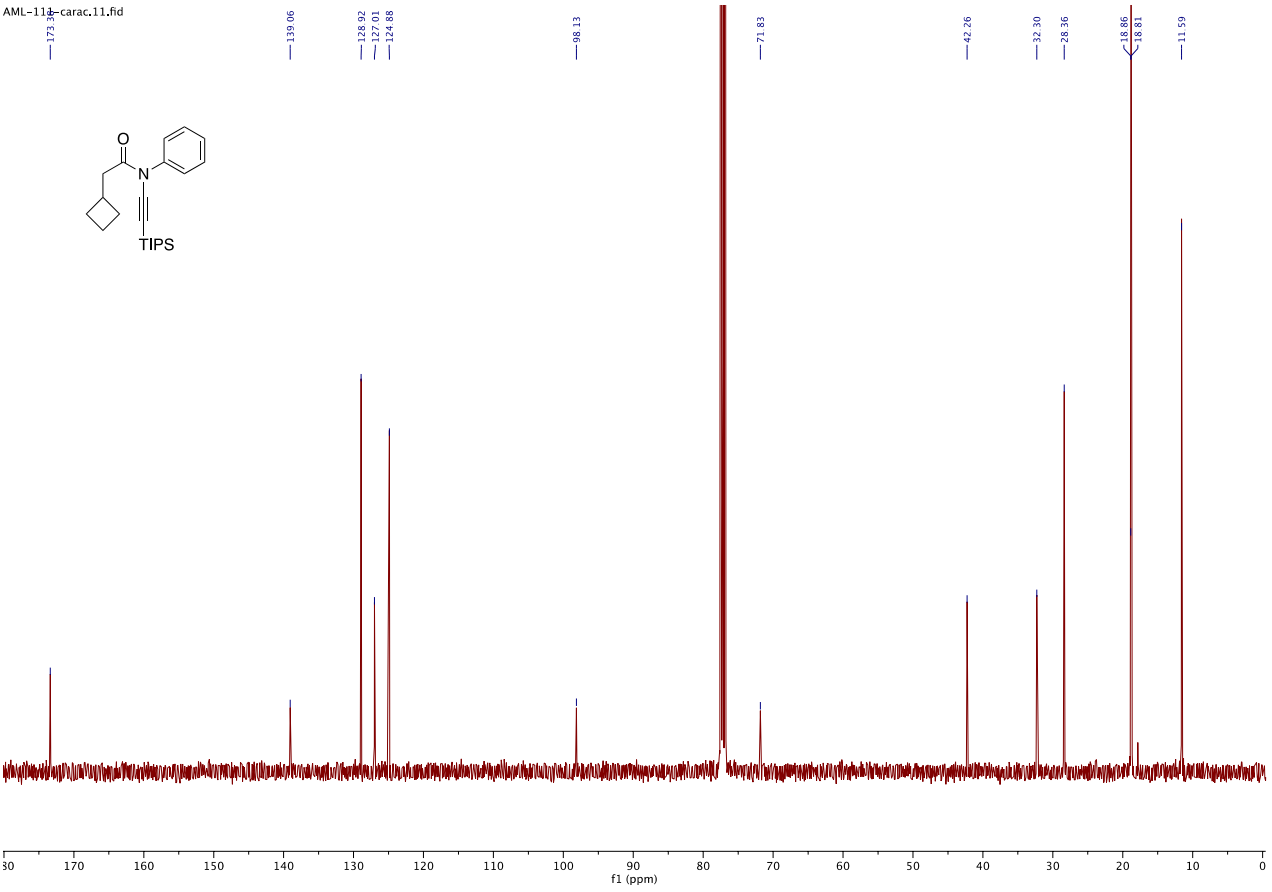
^{13}C NMR of **1s-SiR$_3$**



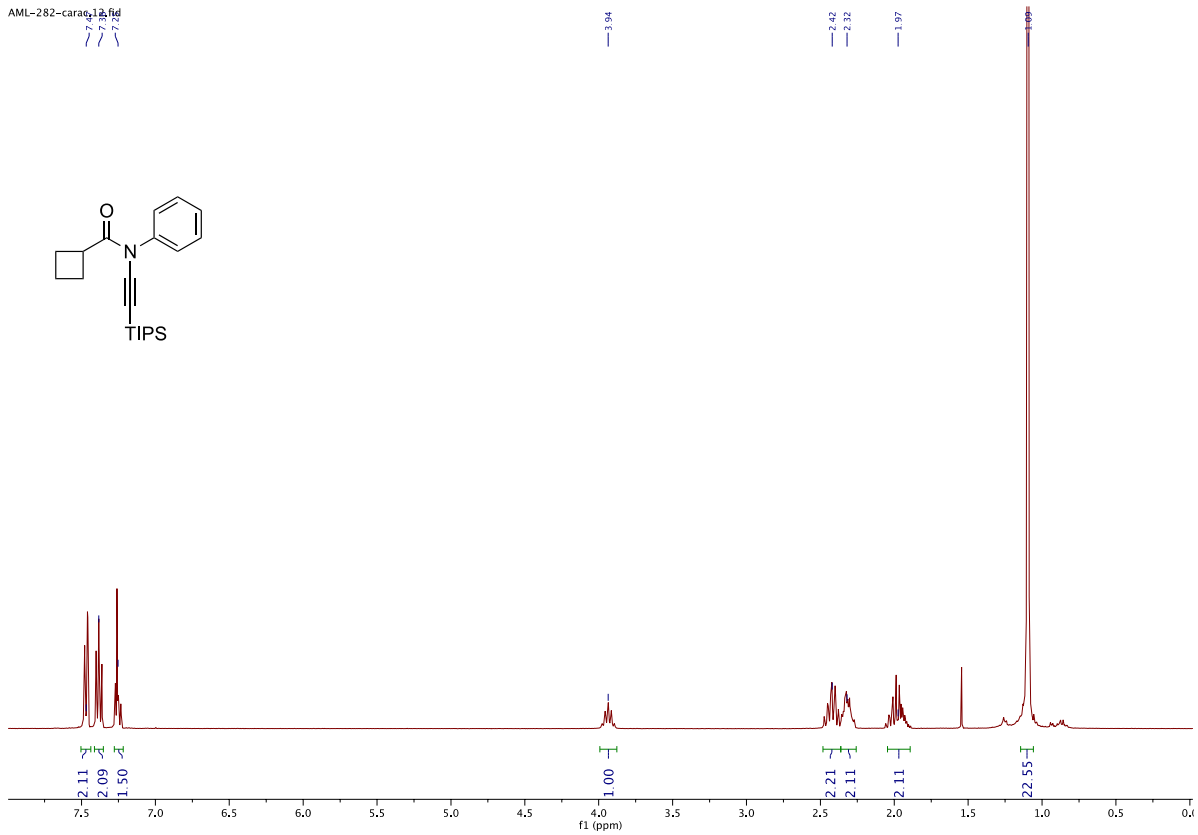
^{1}H NMR of **1t-SiR$_3$**



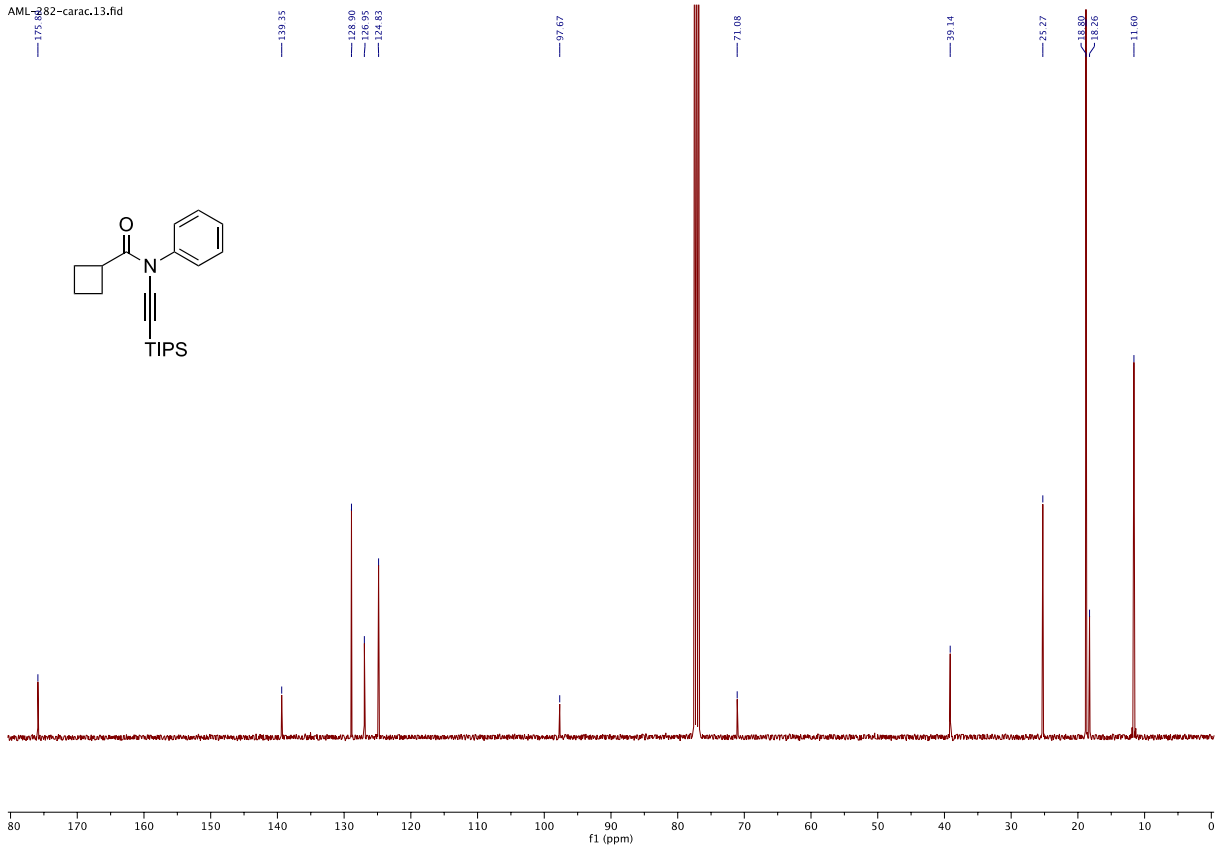
^{13}C NMR of **1t-SiR$_3$**



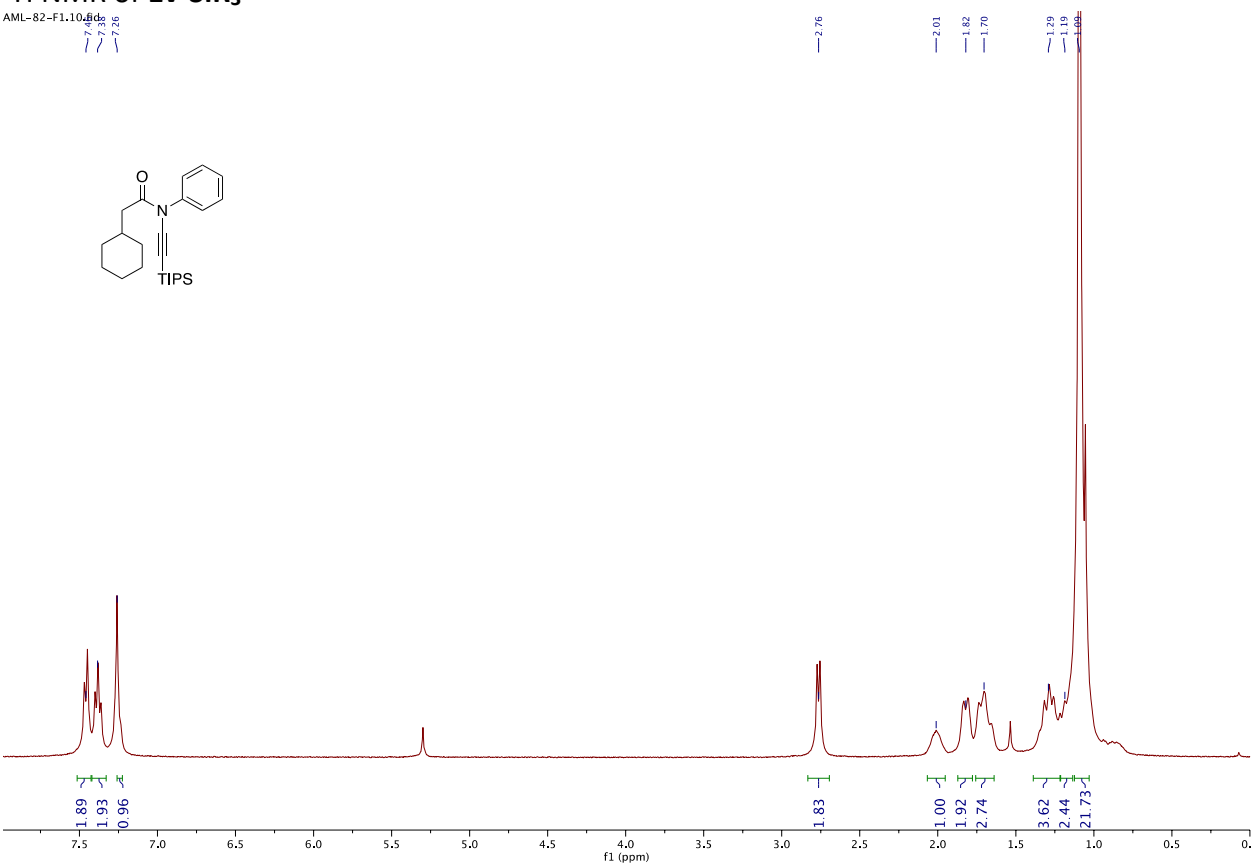
^{1}H NMR of **1u-SiR$_3$**



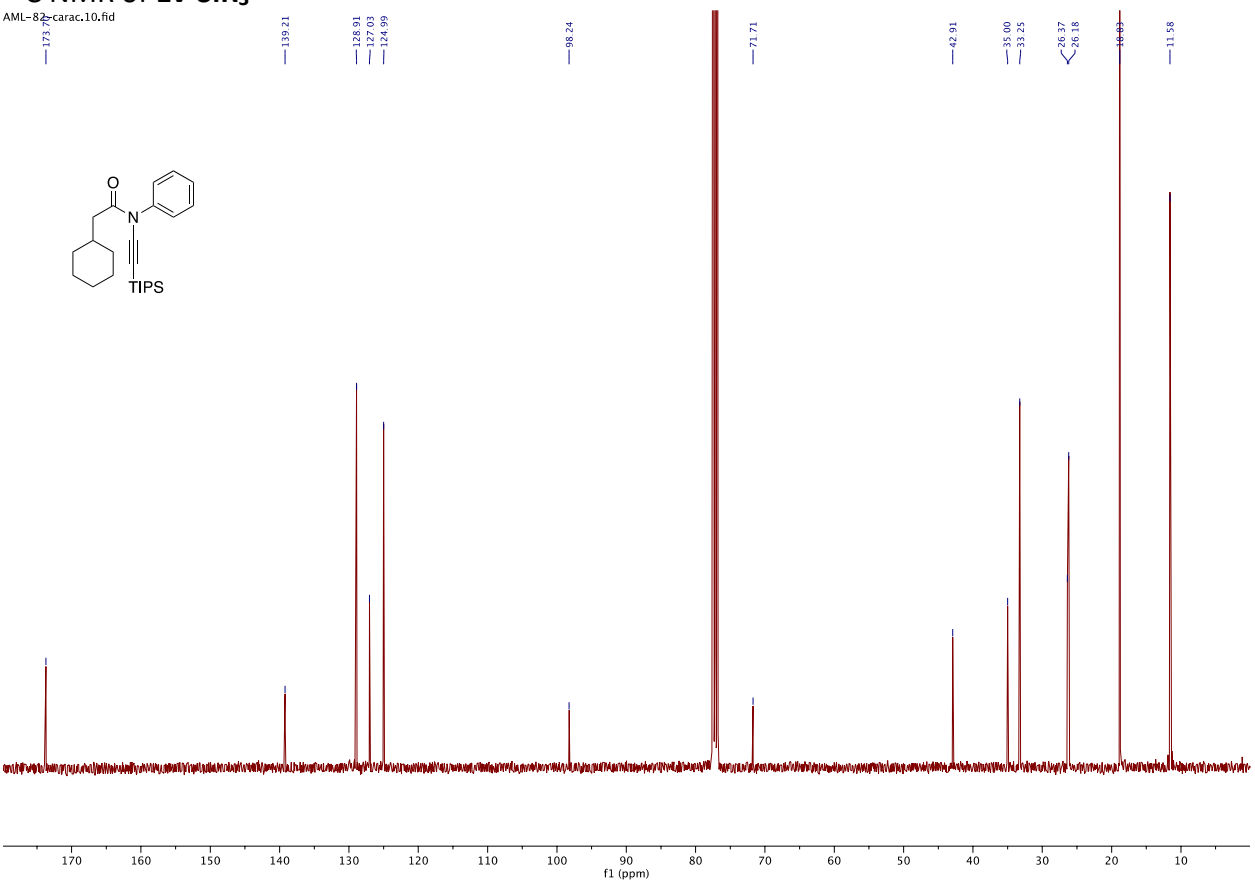
^{13}C NMR of **1u-SiR$_3$**



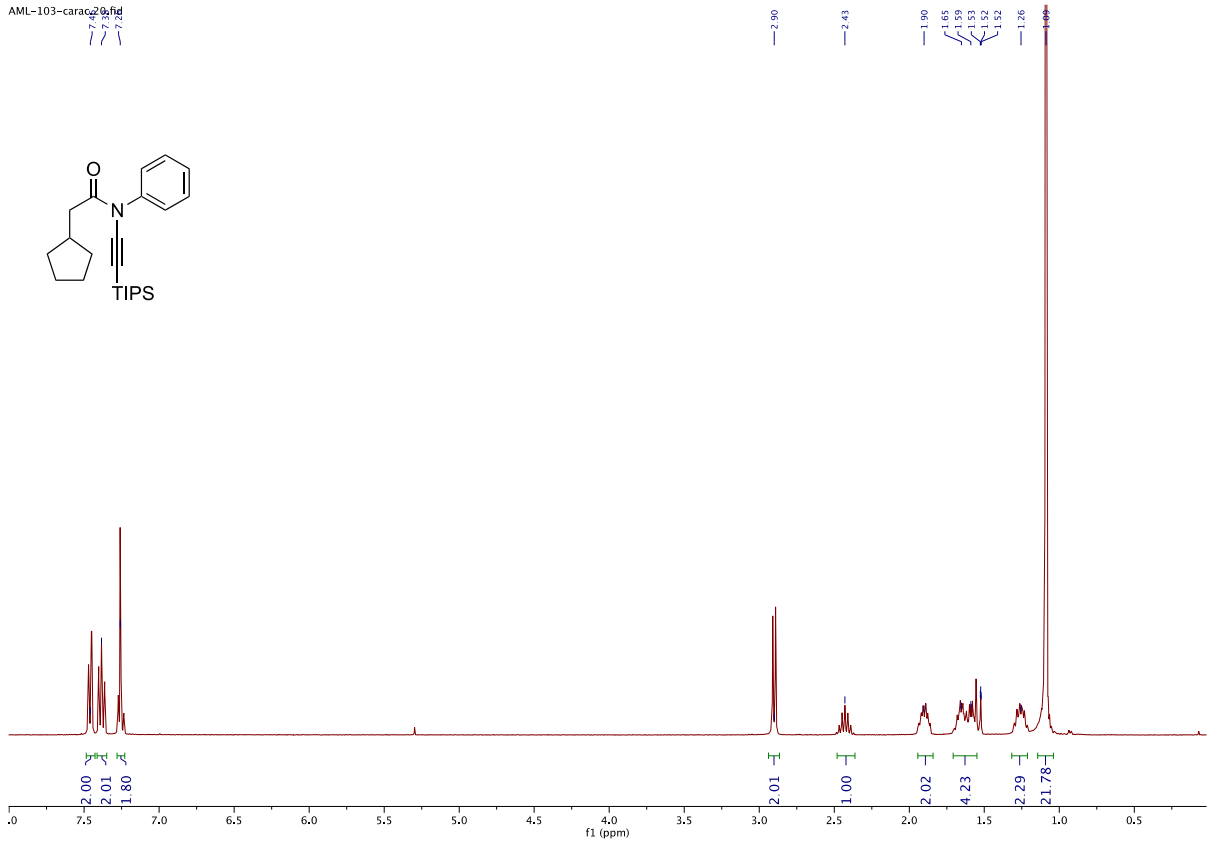
^{1}H NMR of **1v-SiR$_3$**



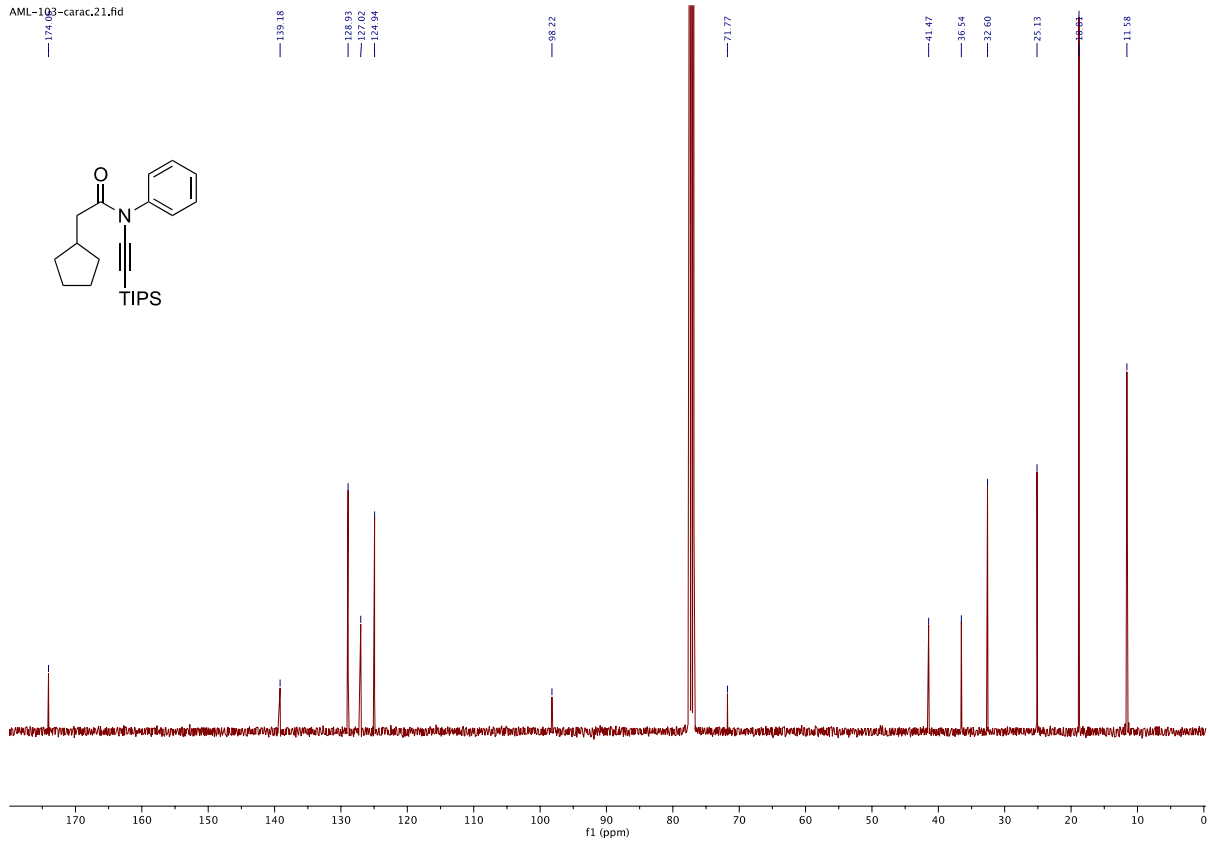
^{13}C NMR of **1v-SiR$_3$**



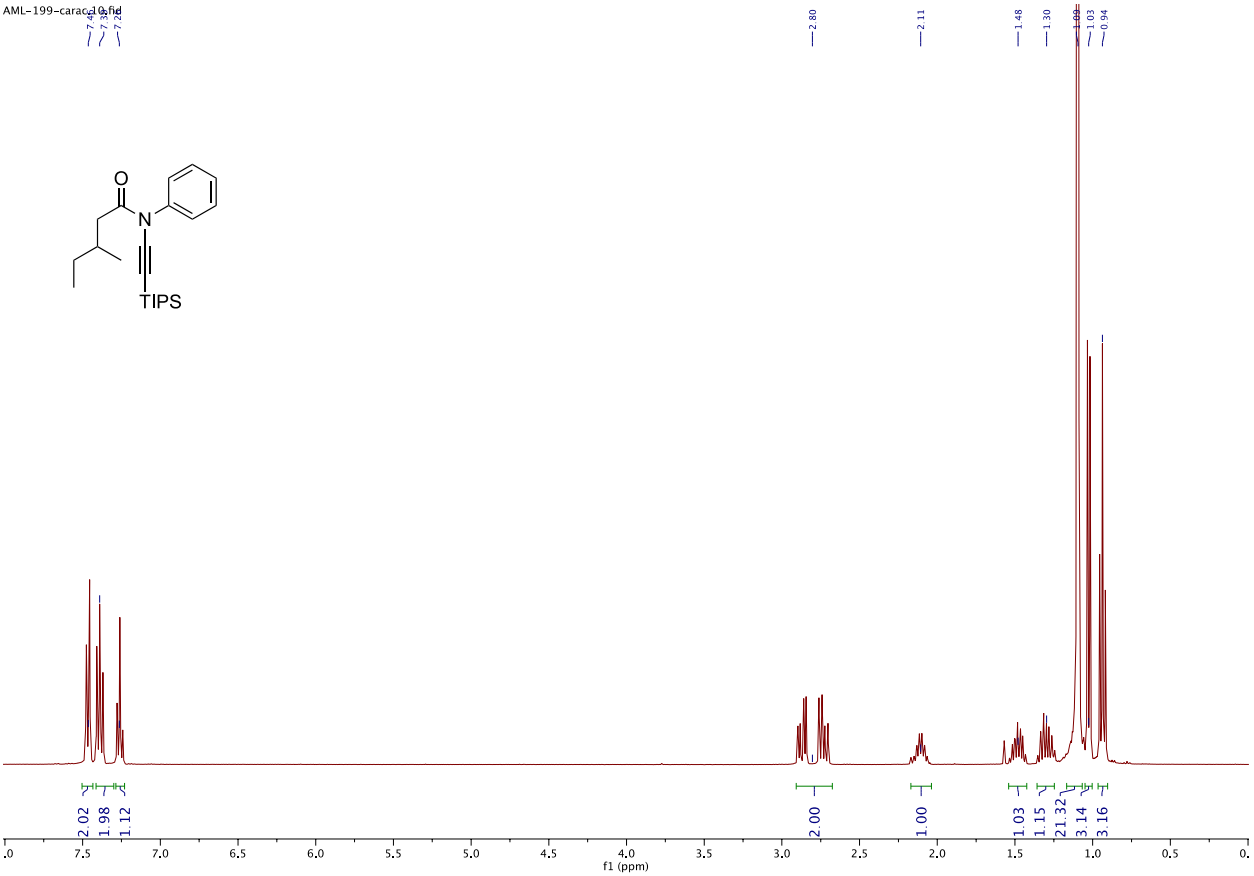
^{1}H NMR of **1w-SiR$_3$**



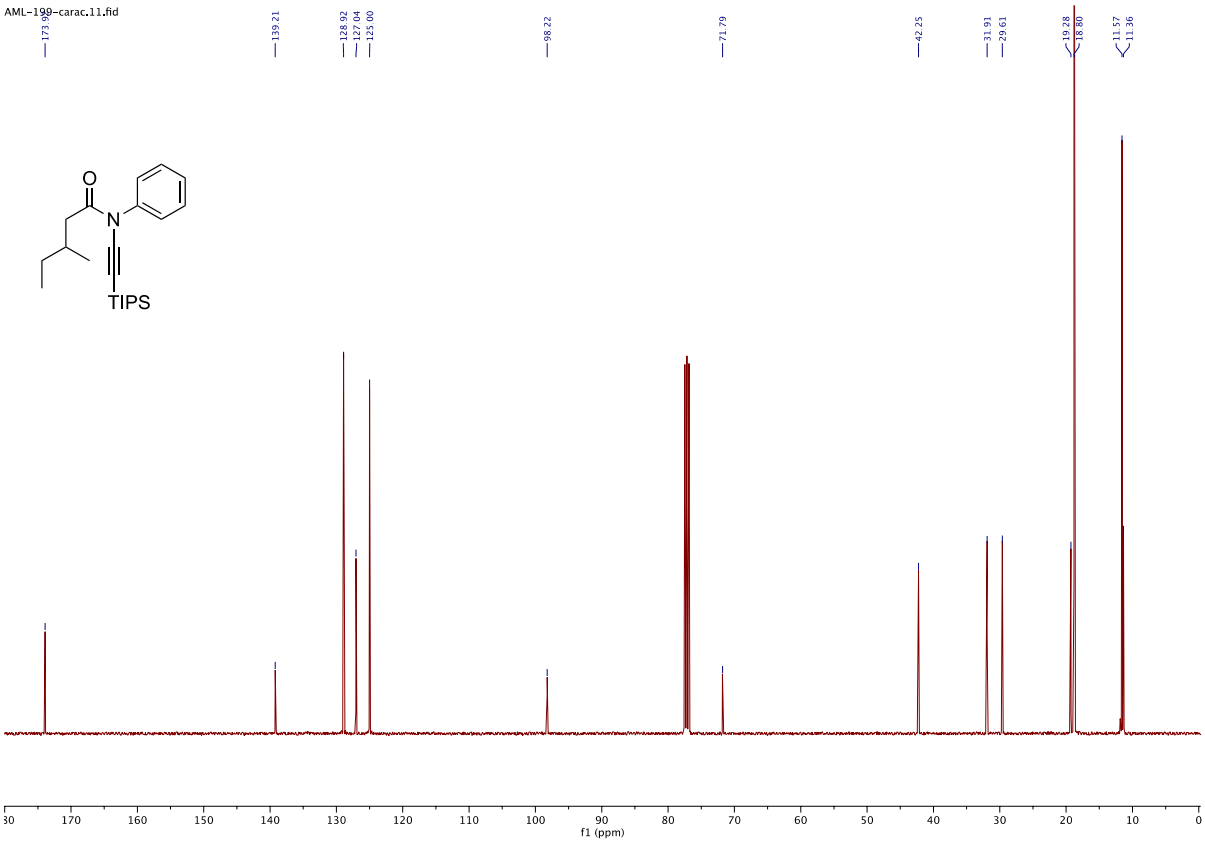
^{13}C NMR of **1w-SiR$_3$**



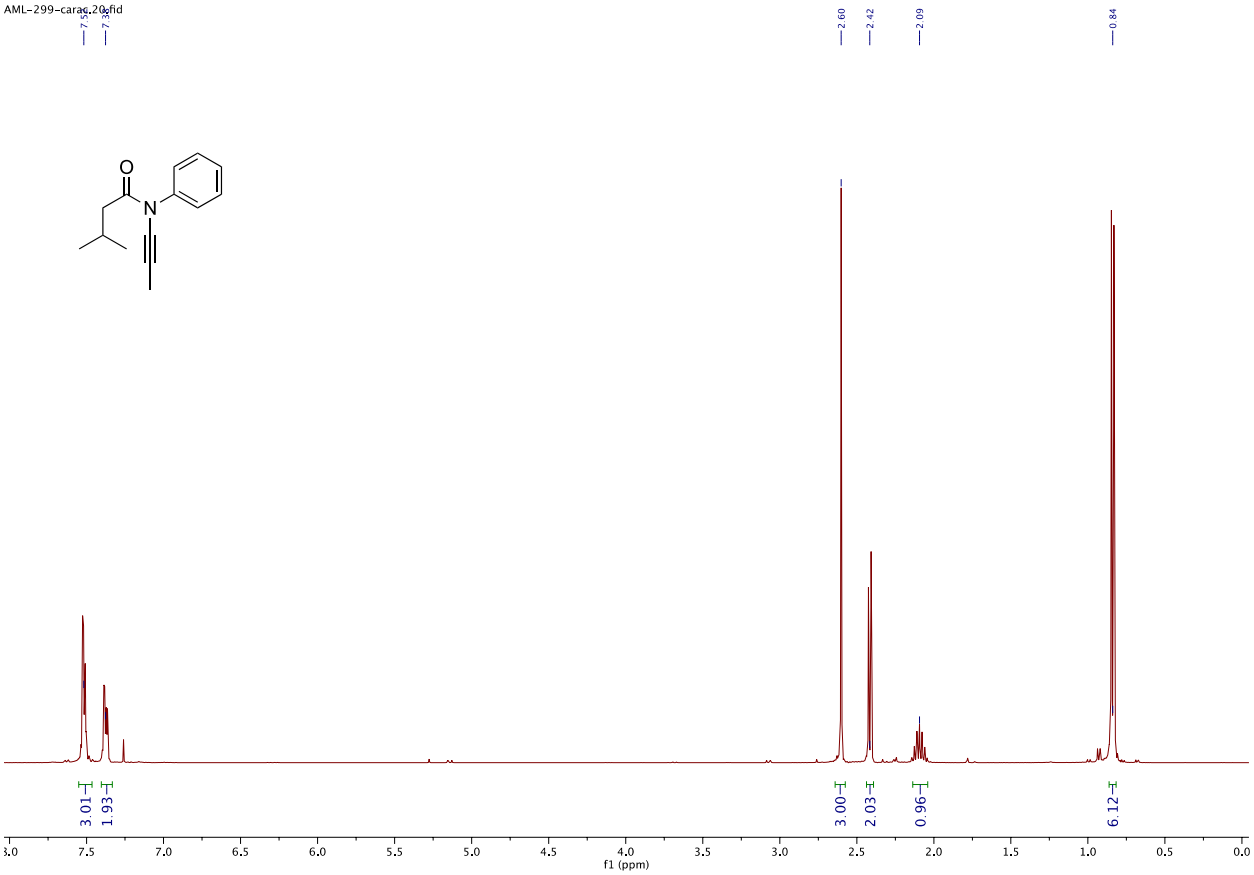
^{1}H NMR of **1x-SiR$_3$**



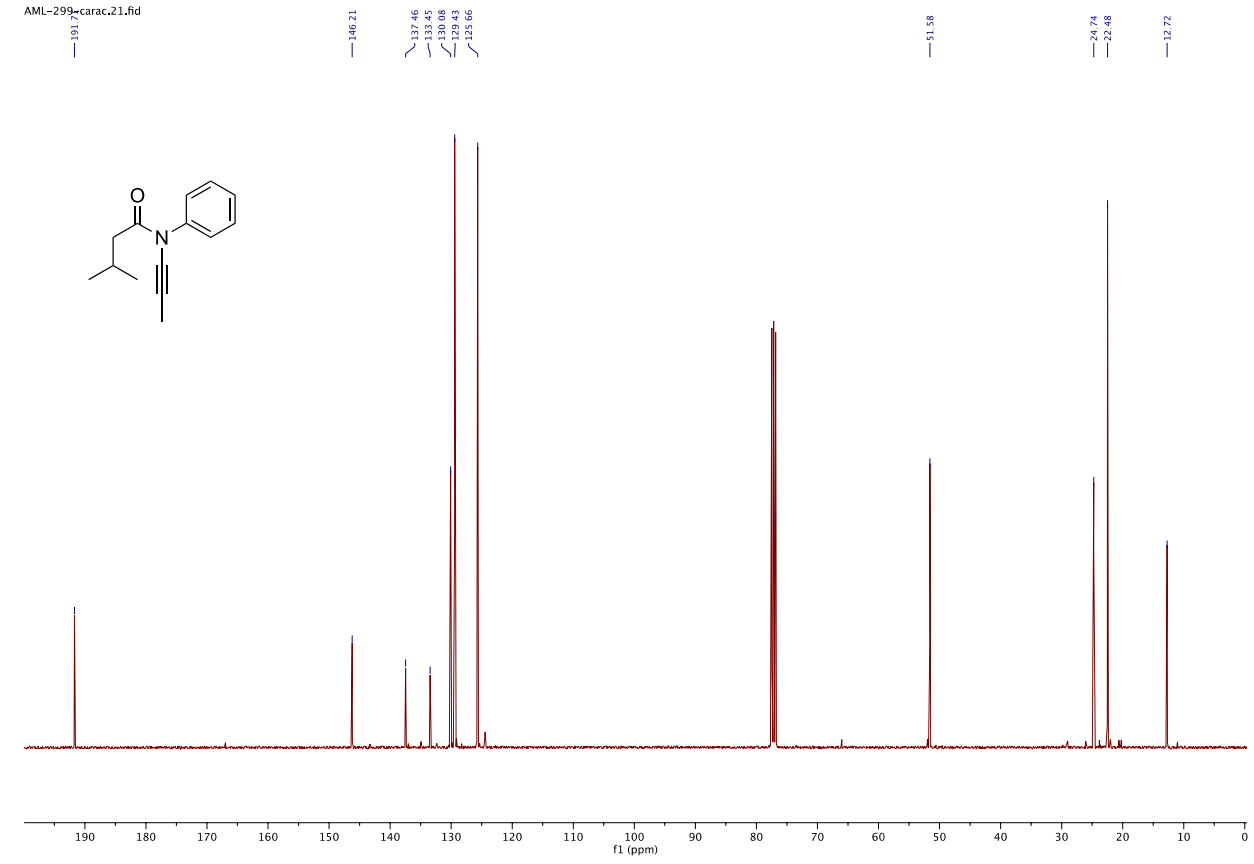
^{13}C NMR of **1x-SiR$_3$**



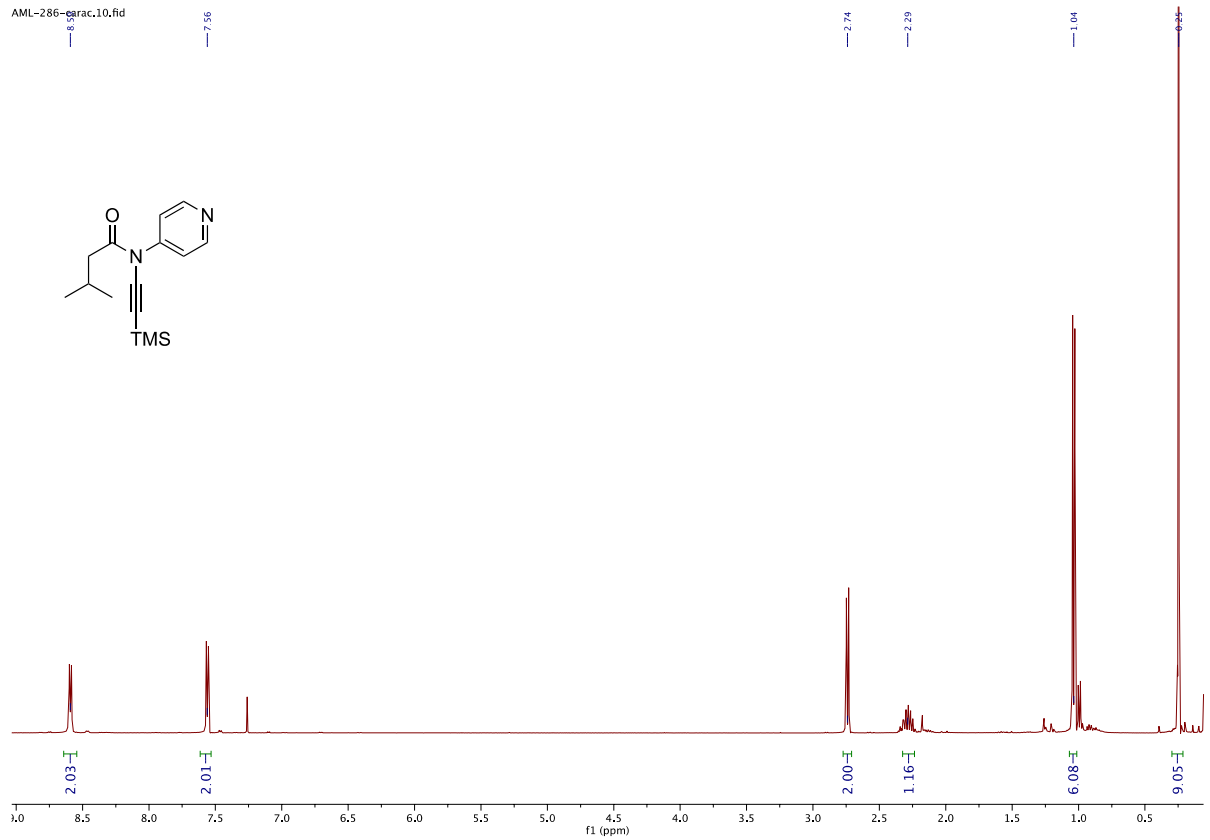
^{1}H NMR of **1ya**



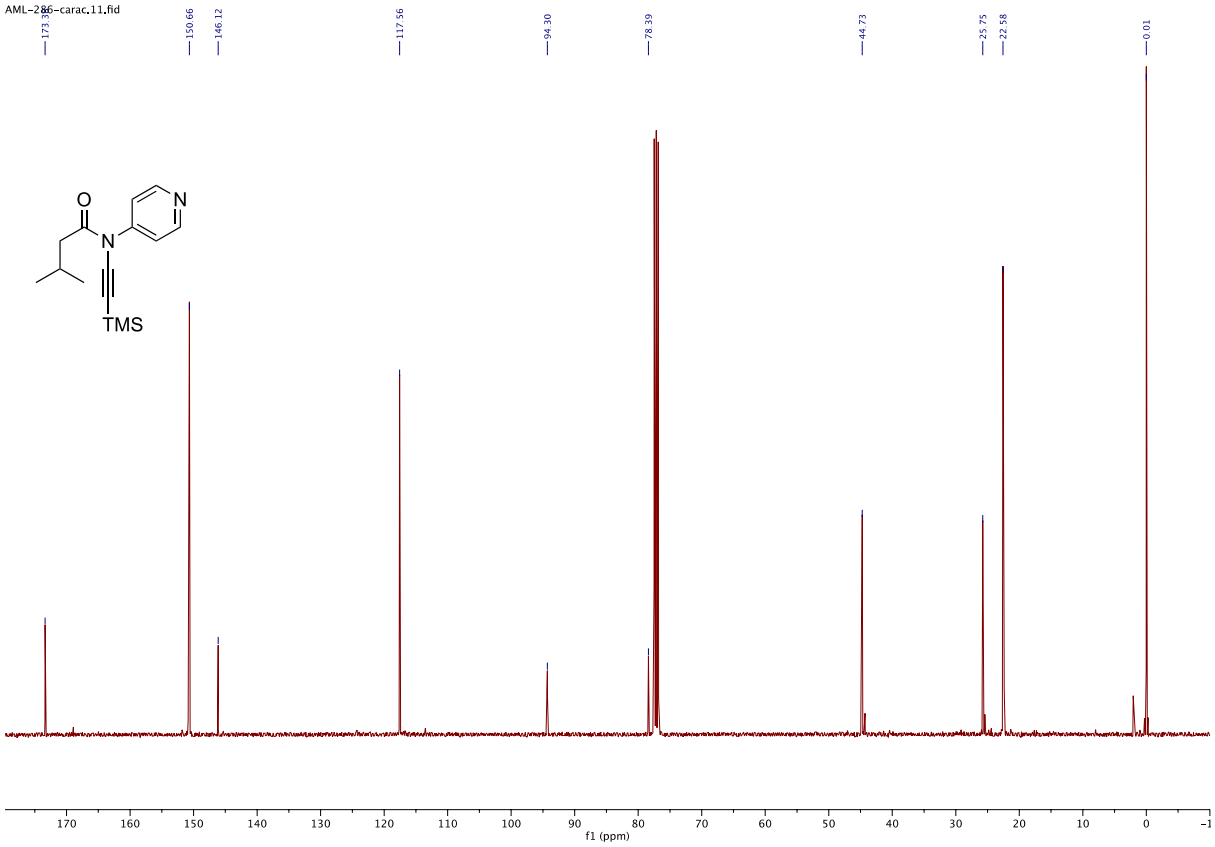
^{13}C NMR of **1ya**



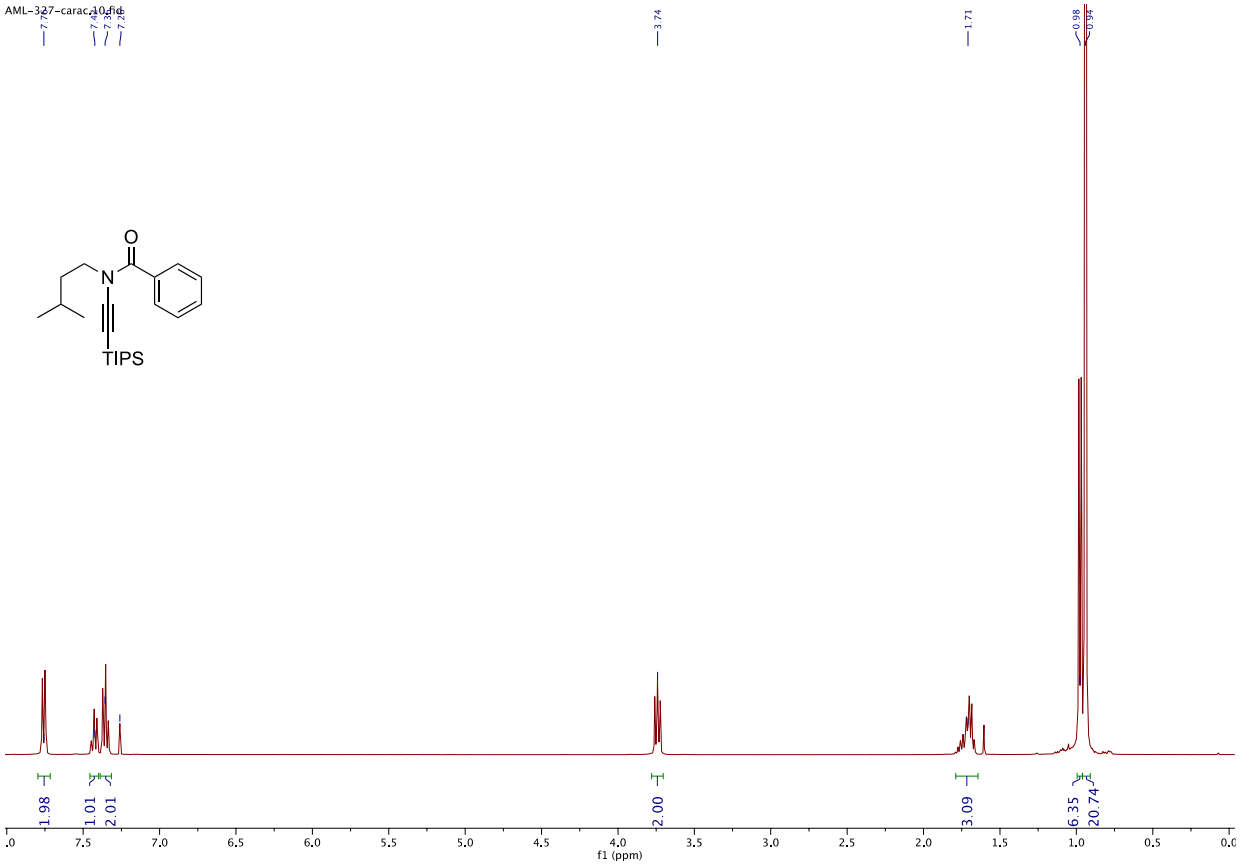
^{1}H NMR of **1yb**



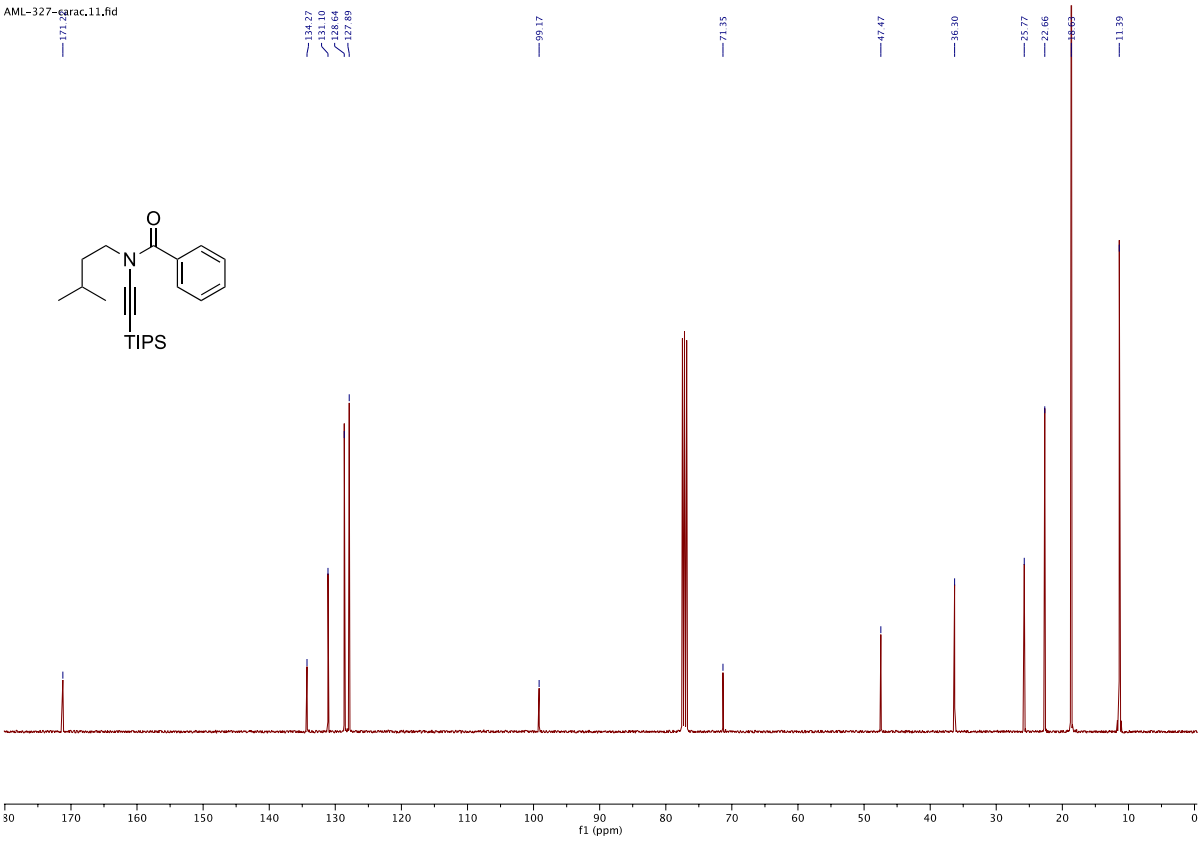
^{13}C NMR of **1yb**



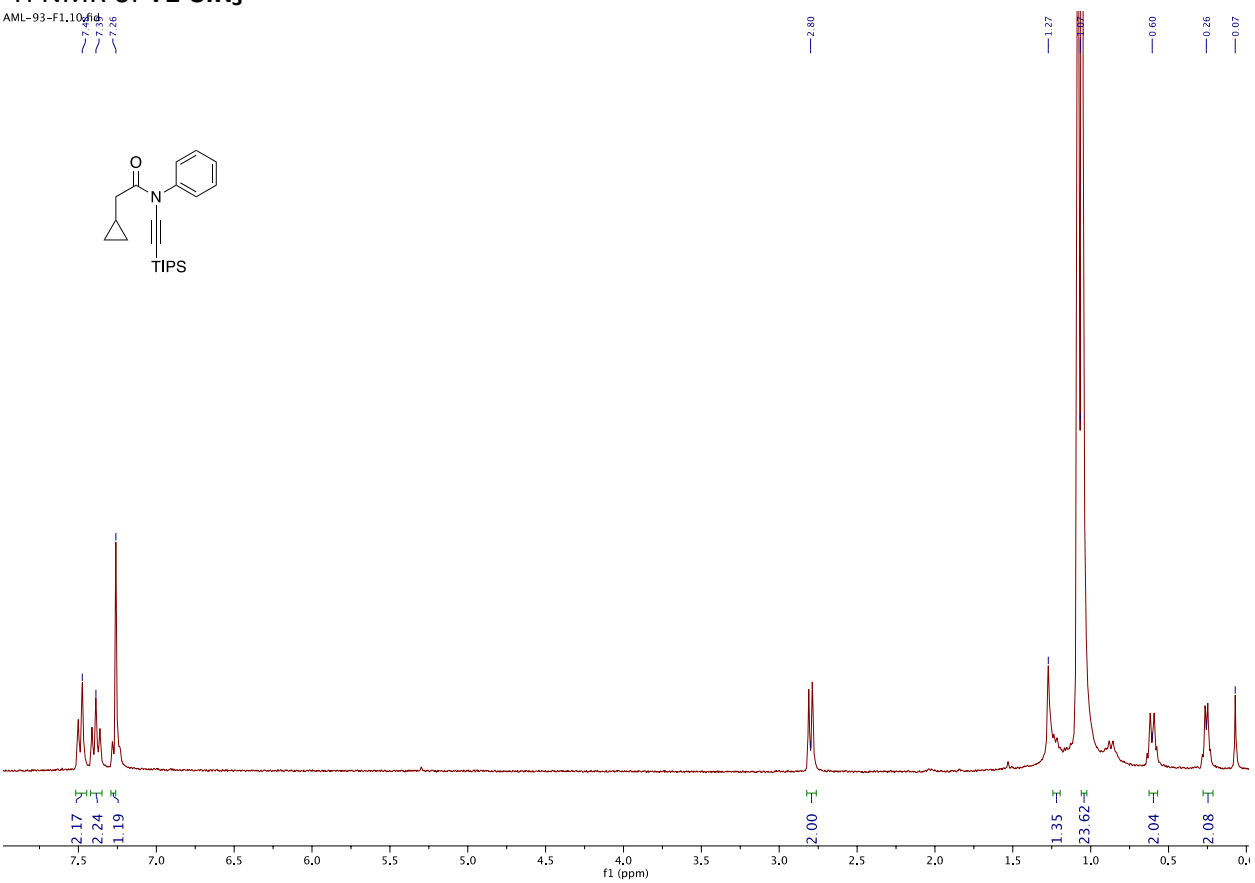
^{1}H NMR of **1z-SiR$_3$**



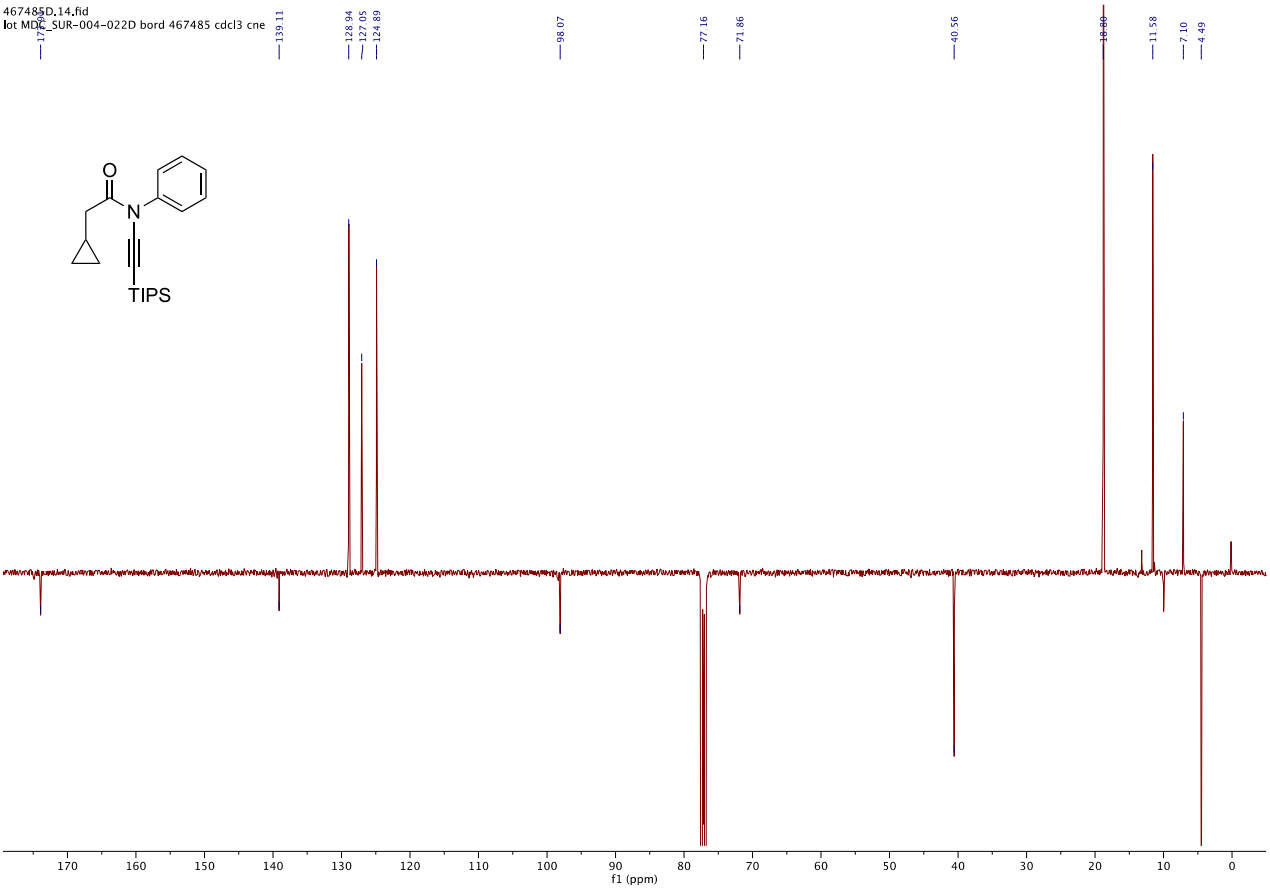
^{13}C NMR of **1z-SiR$_3$**



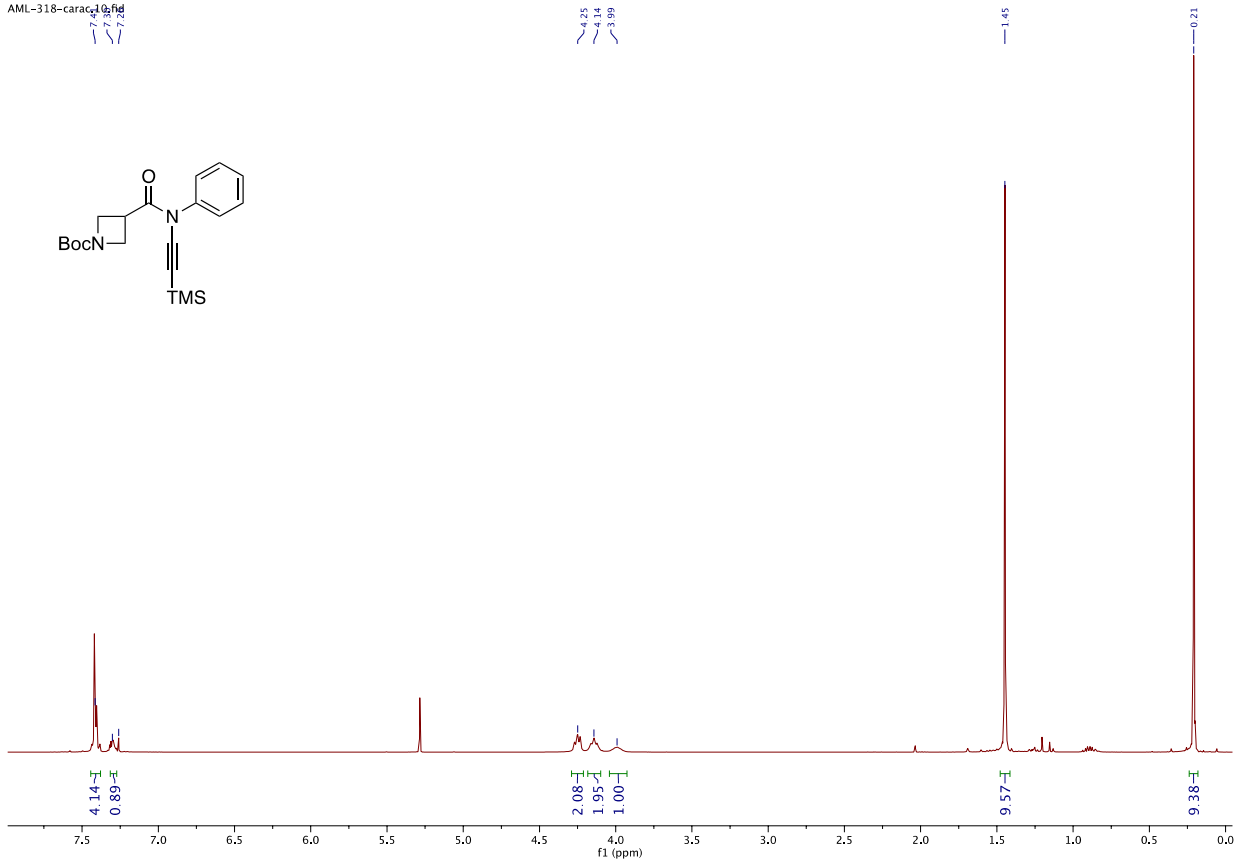
^{1}H NMR of **Y1-SiR$_3$**



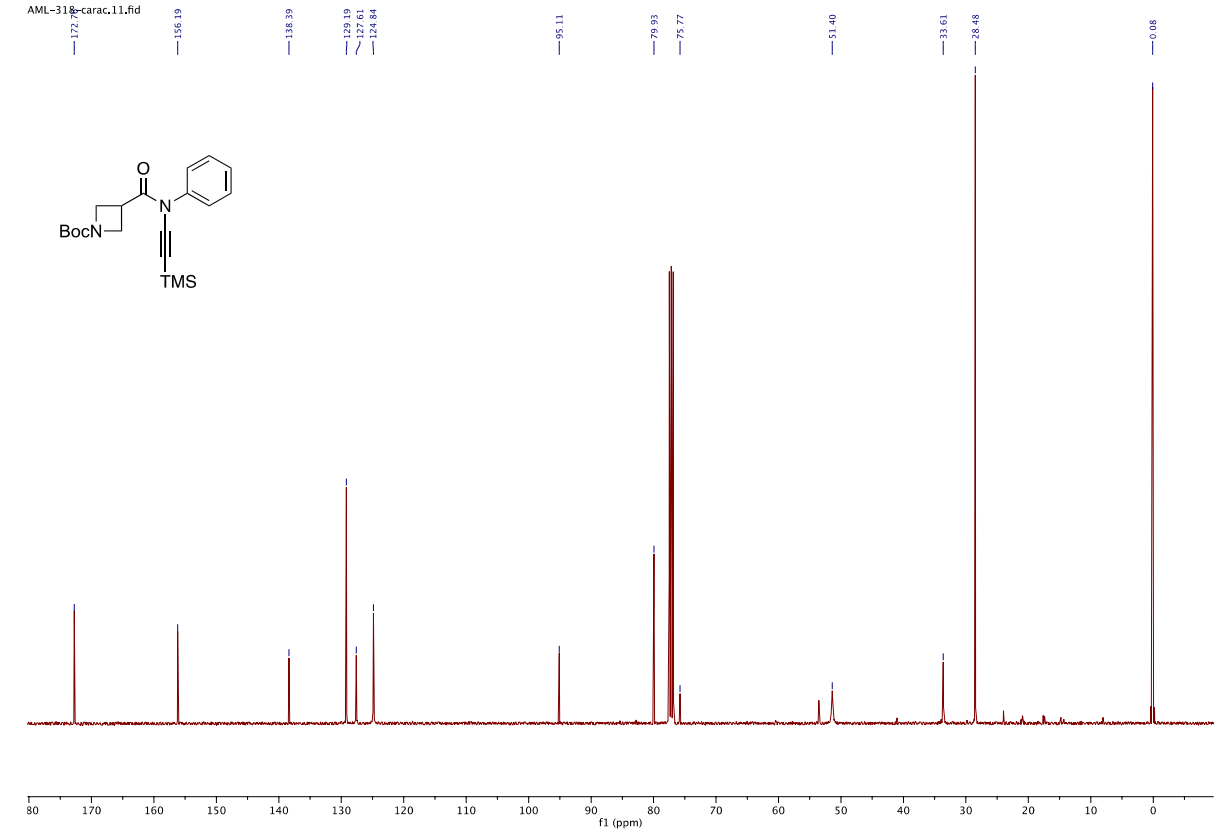
^{13}C NMR of **Y1-SiR$_3$**



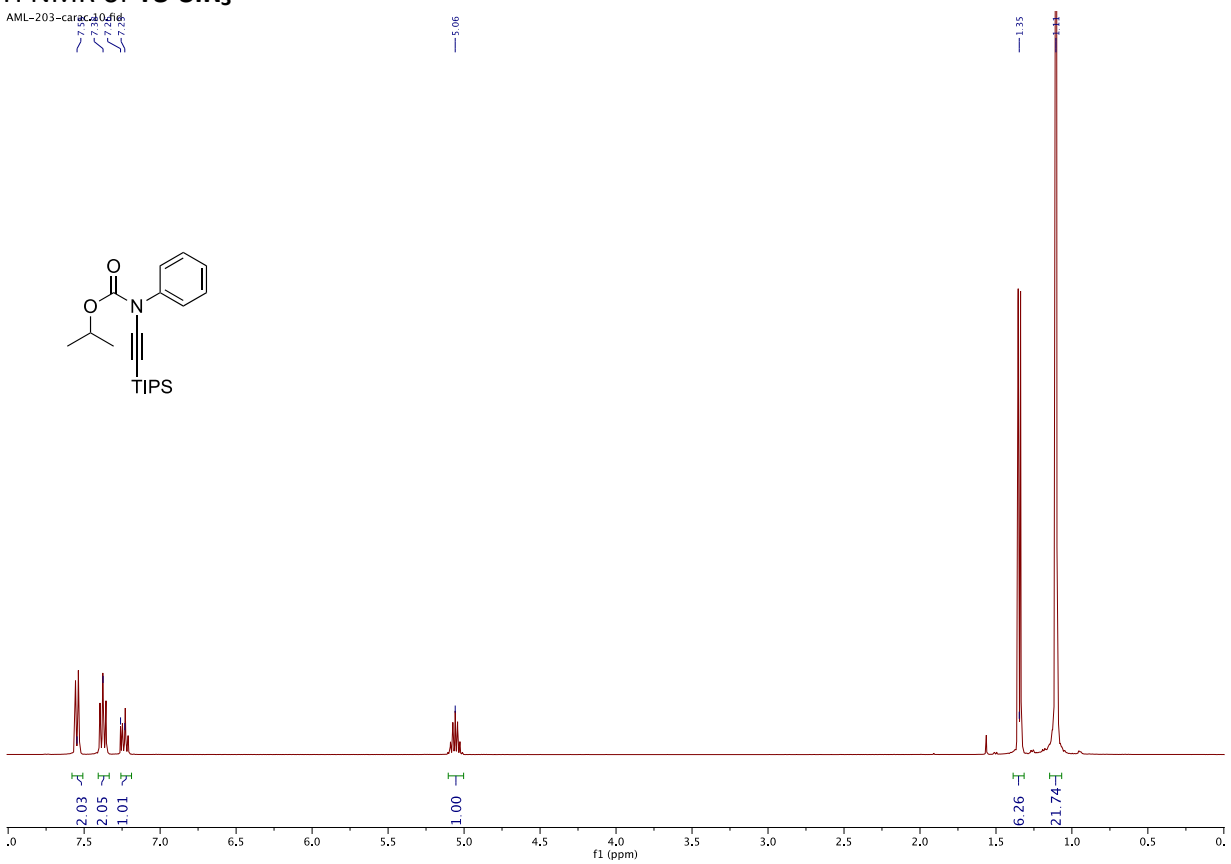
^{1}H NMR of **Y2-SiR$_3$**



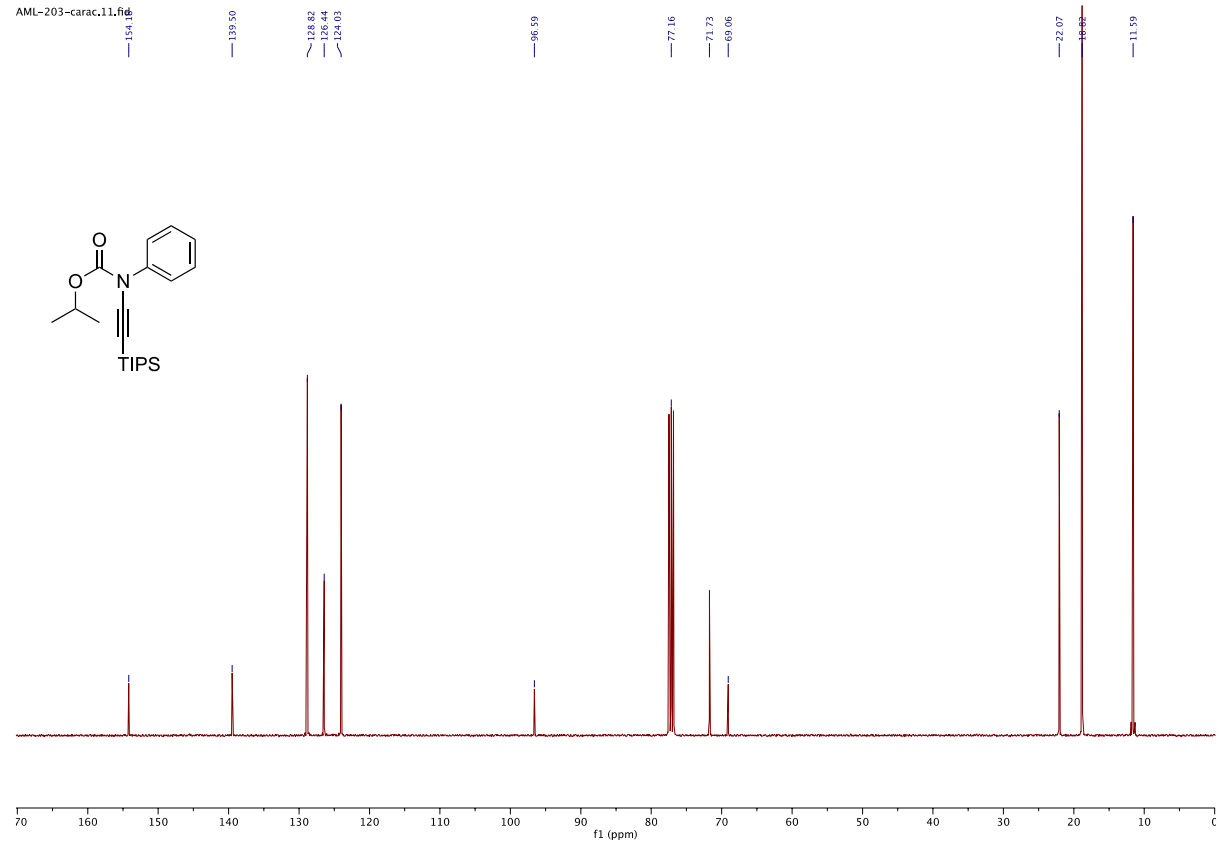
^{13}C NMR of **Y2-SiR$_3$**



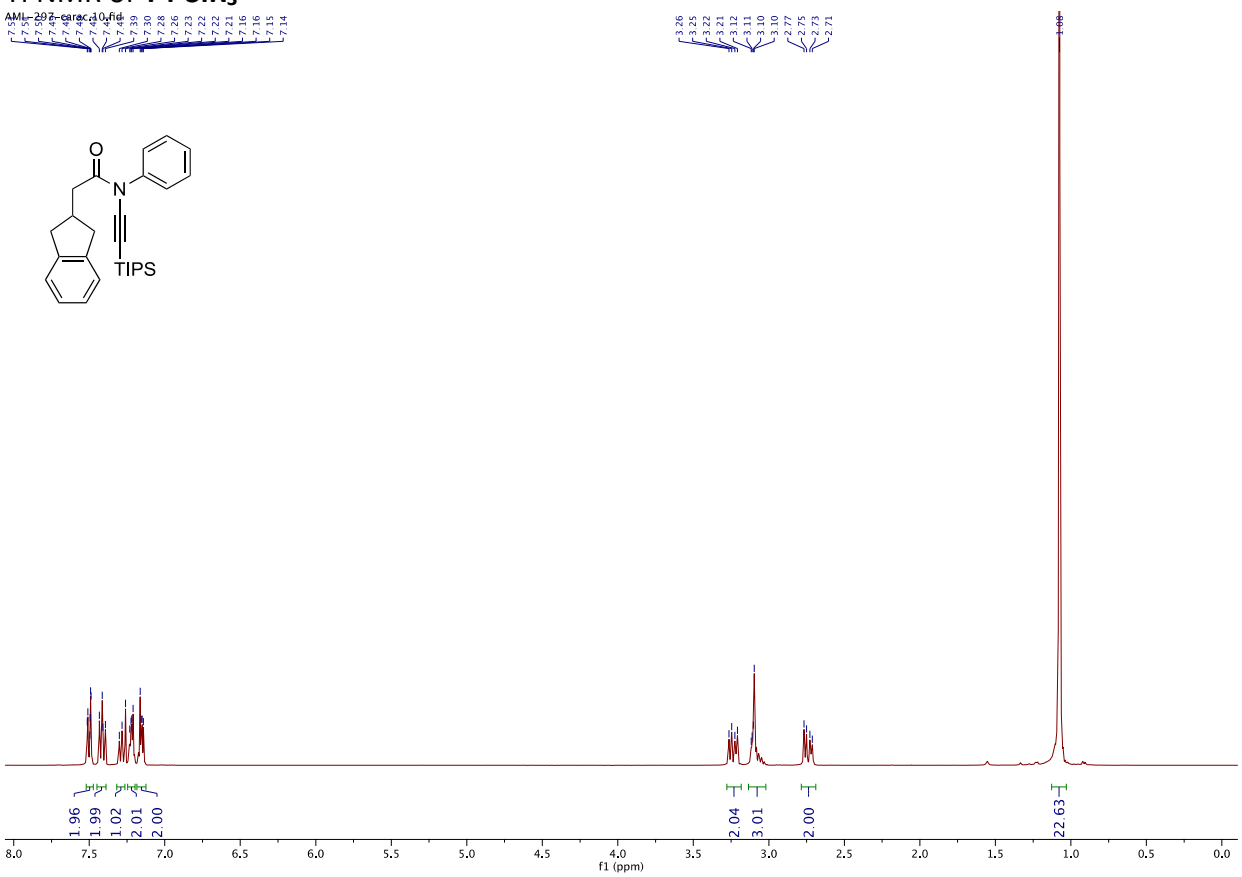
^{1}H NMR of **Y3-SiR$_3$**



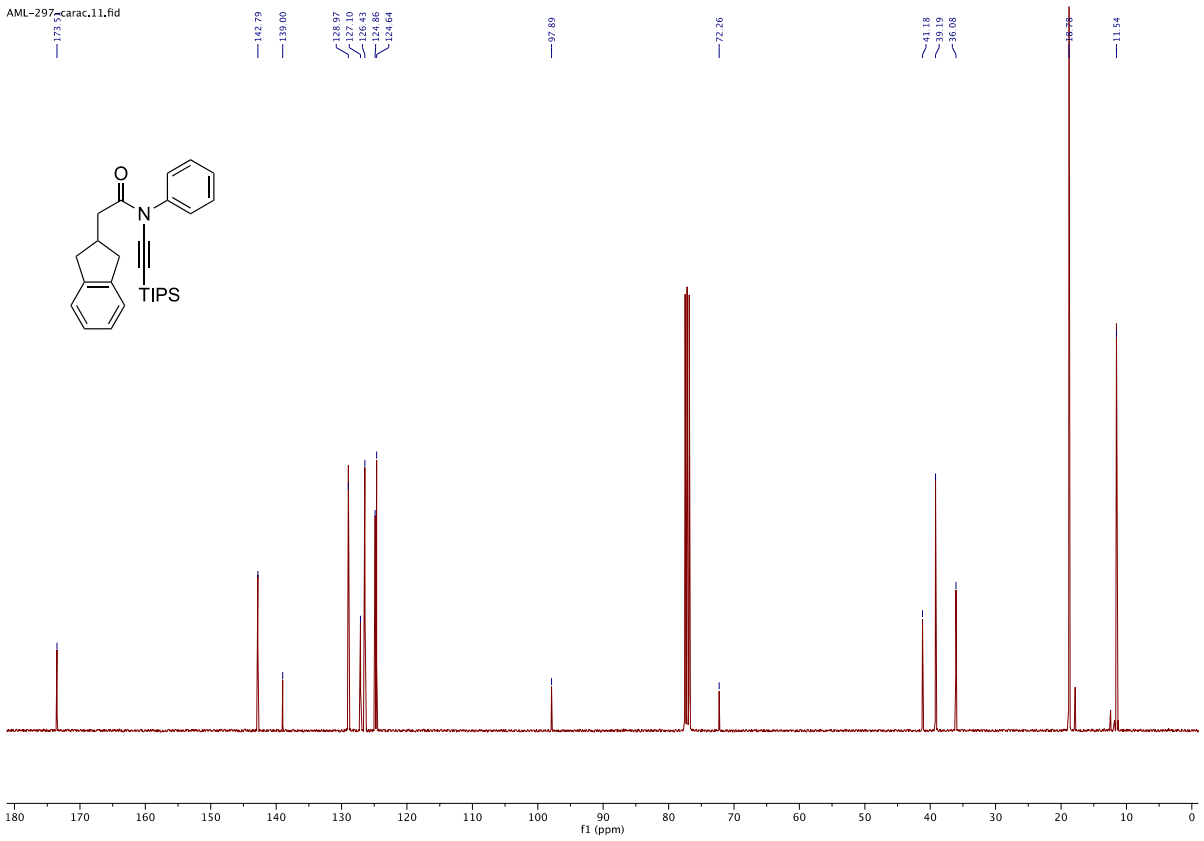
^{13}C NMR of **Y3-SiR$_3$**



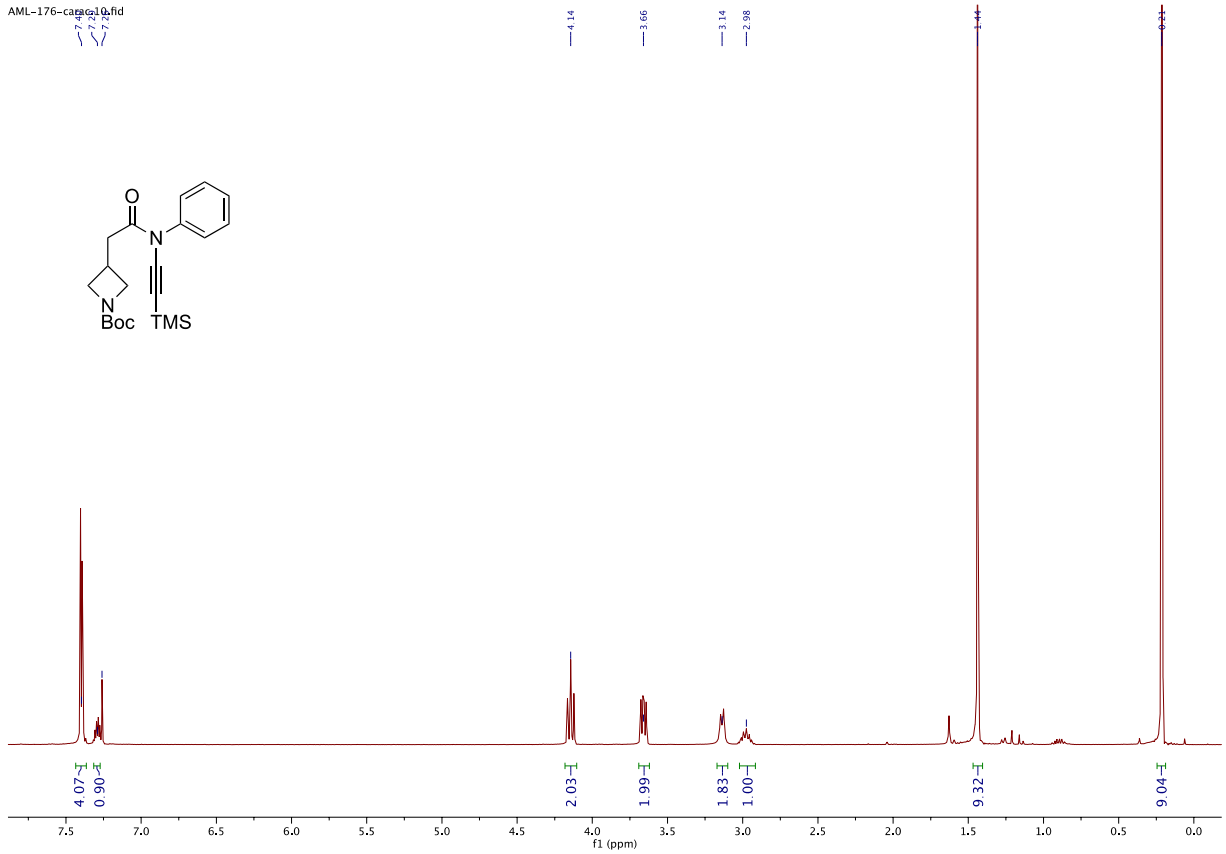
^{1}H NMR of **Y4-SiR$_3$**



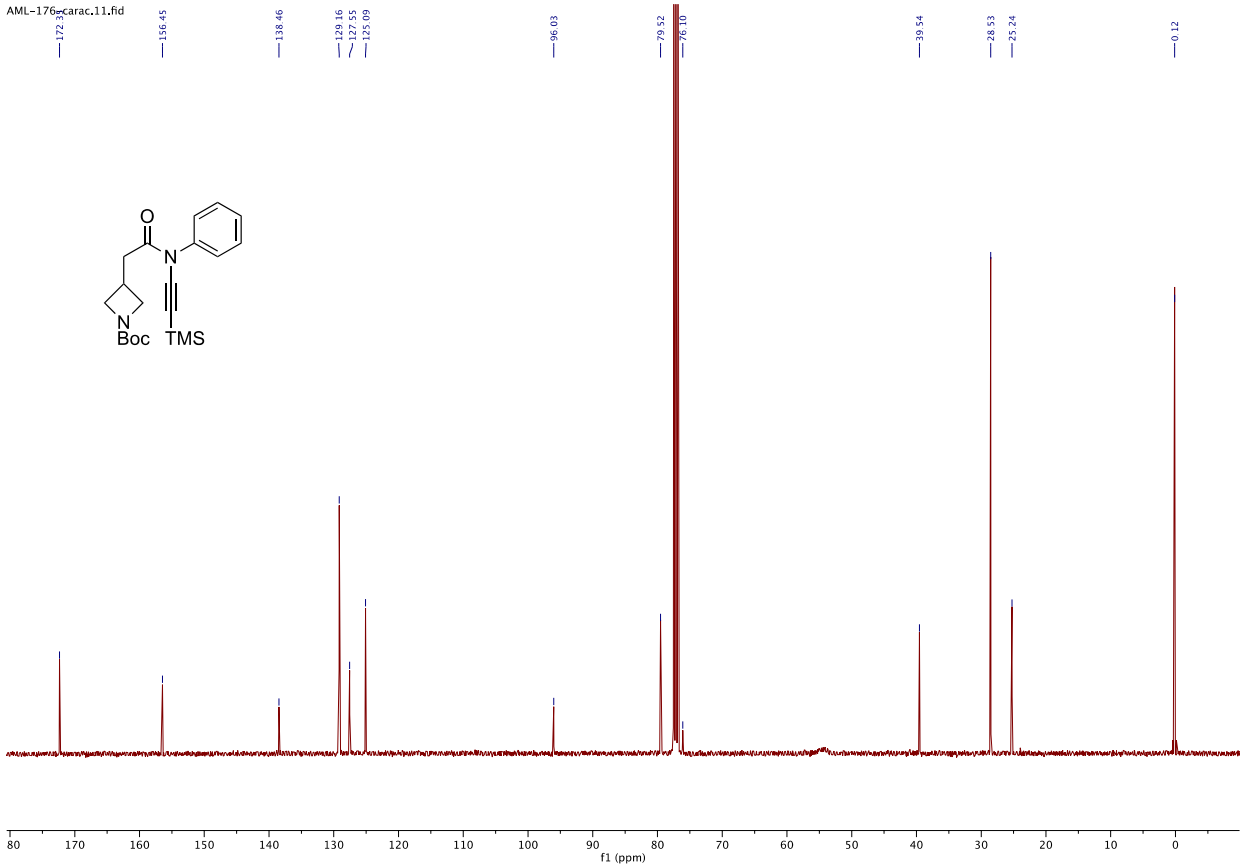
^{13}C NMR of **Y4-SiR$_3$**



^{1}H NMR of **Y5-SiR$_3$**

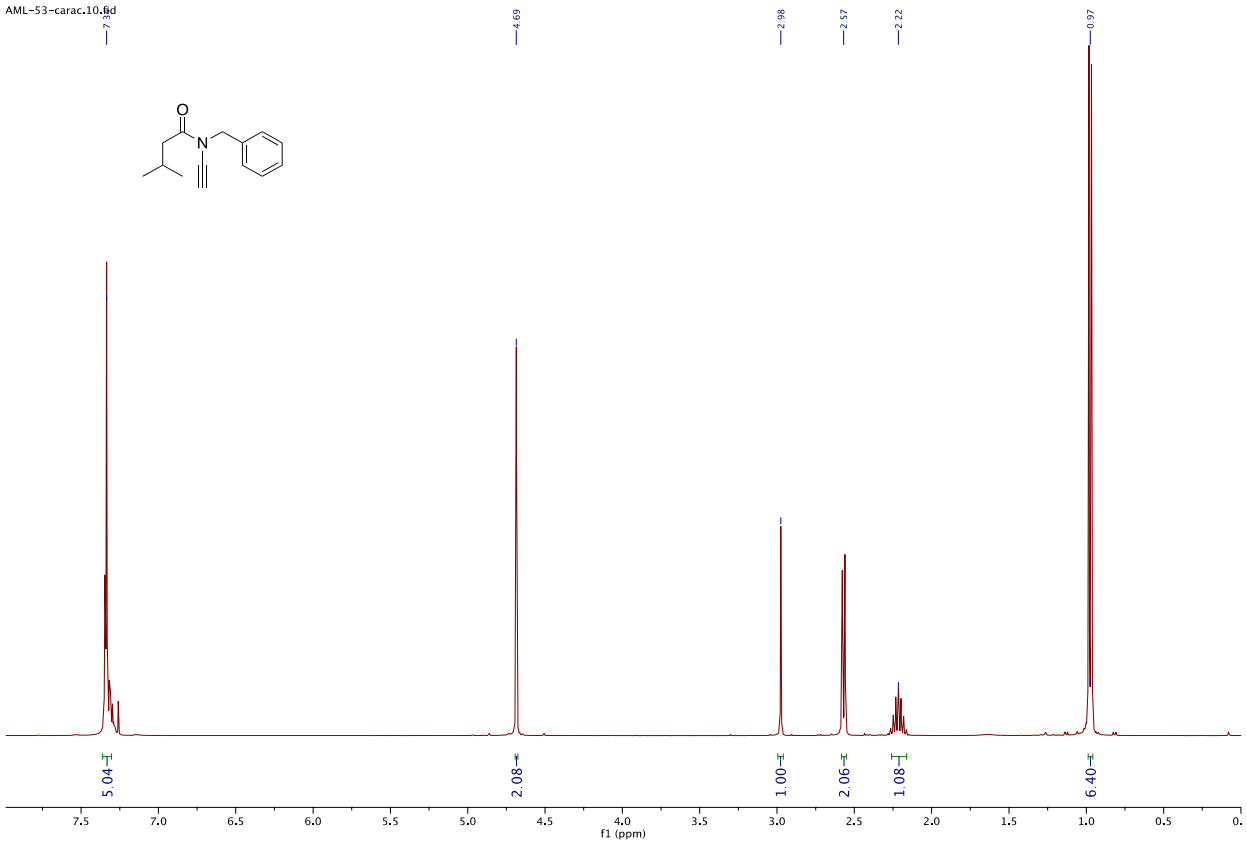


^{13}C NMR of **Y5-SiR$_3$**

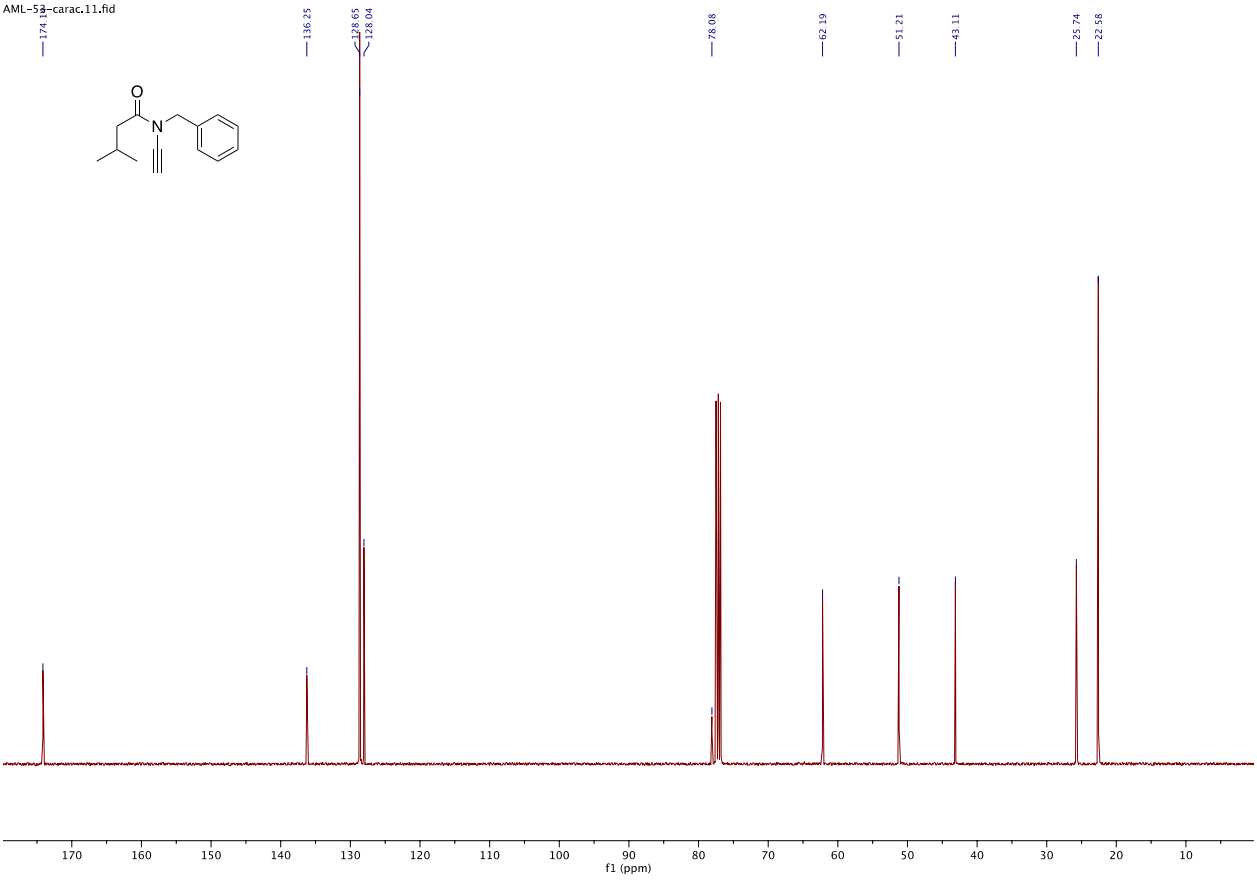


9.2 Ynamides

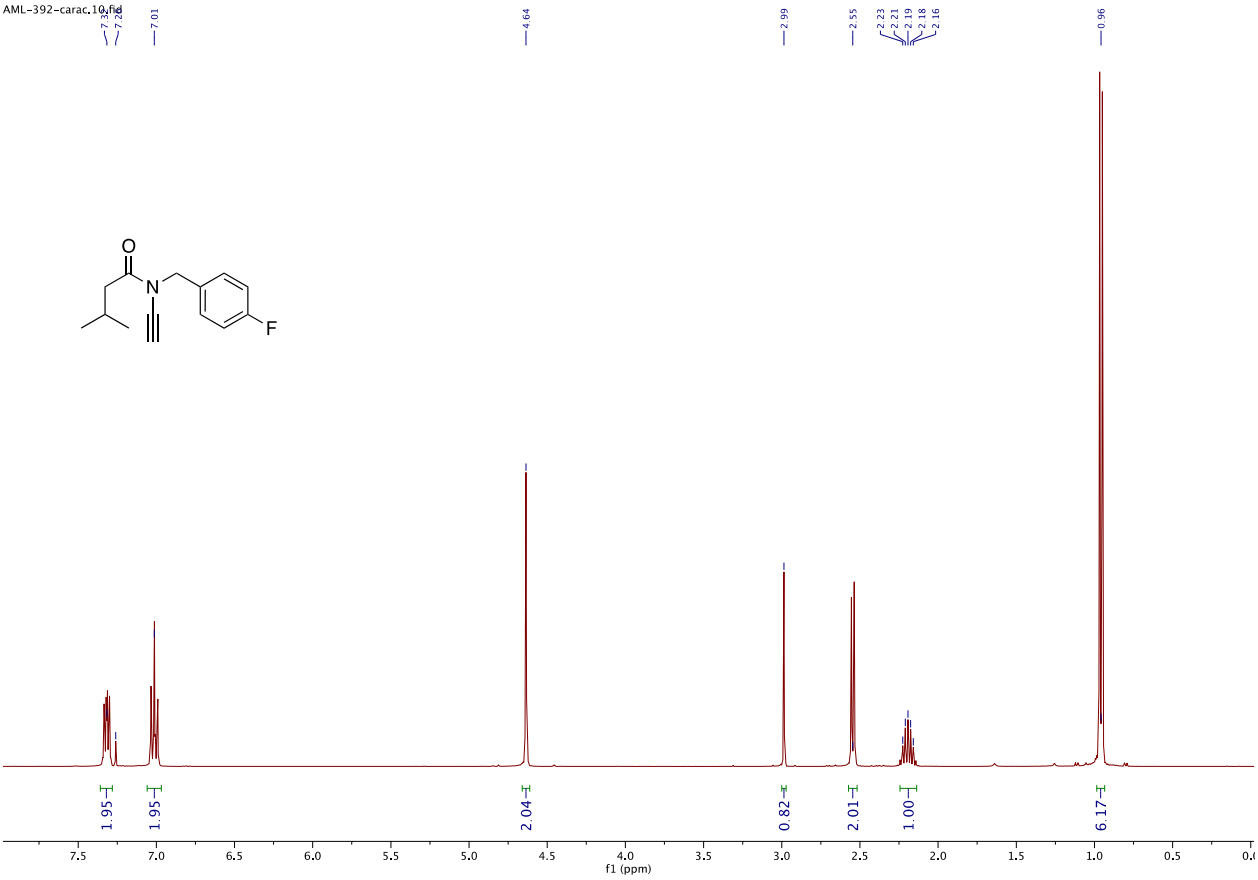
^{1}H NMR of **1a**



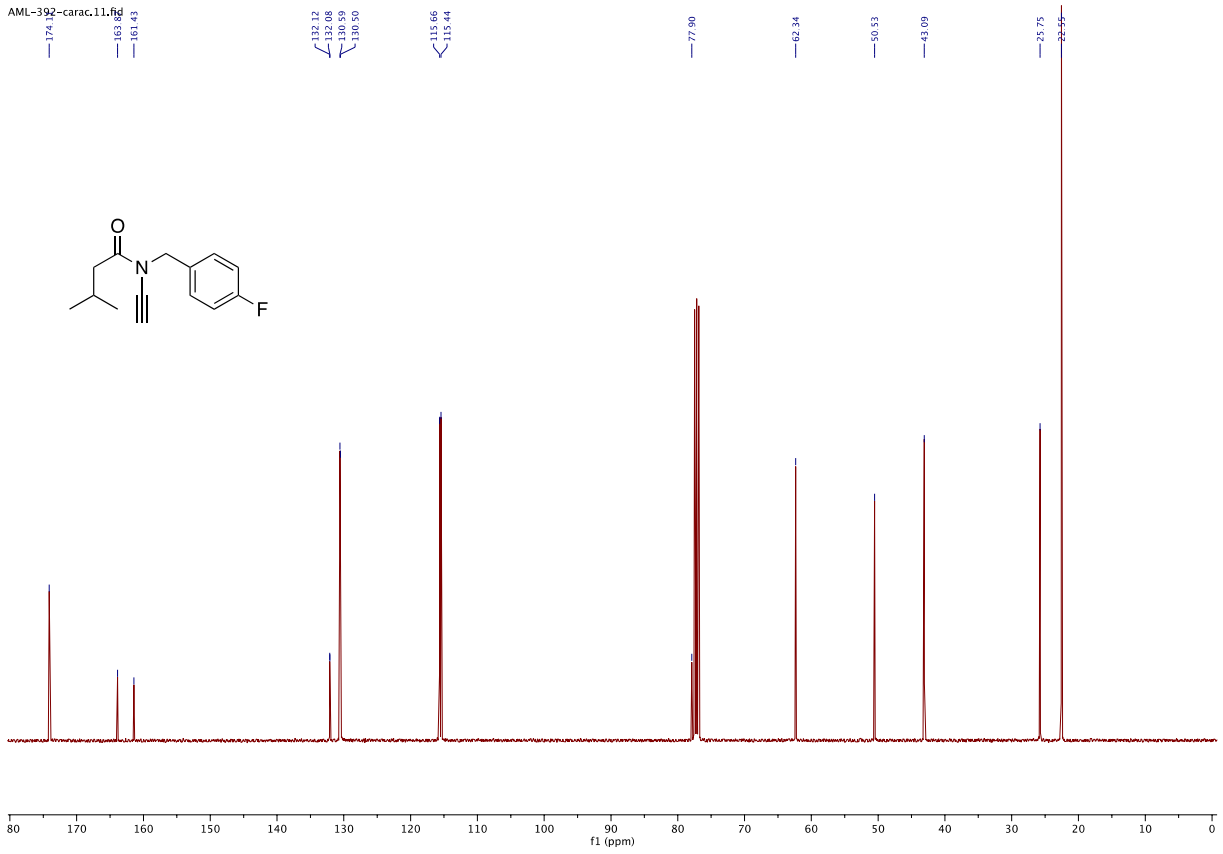
^{13}C NMR of **1a**



^{1}H NMR of **1b**

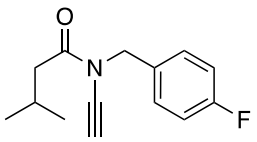


^{13}C NMR of **1b**



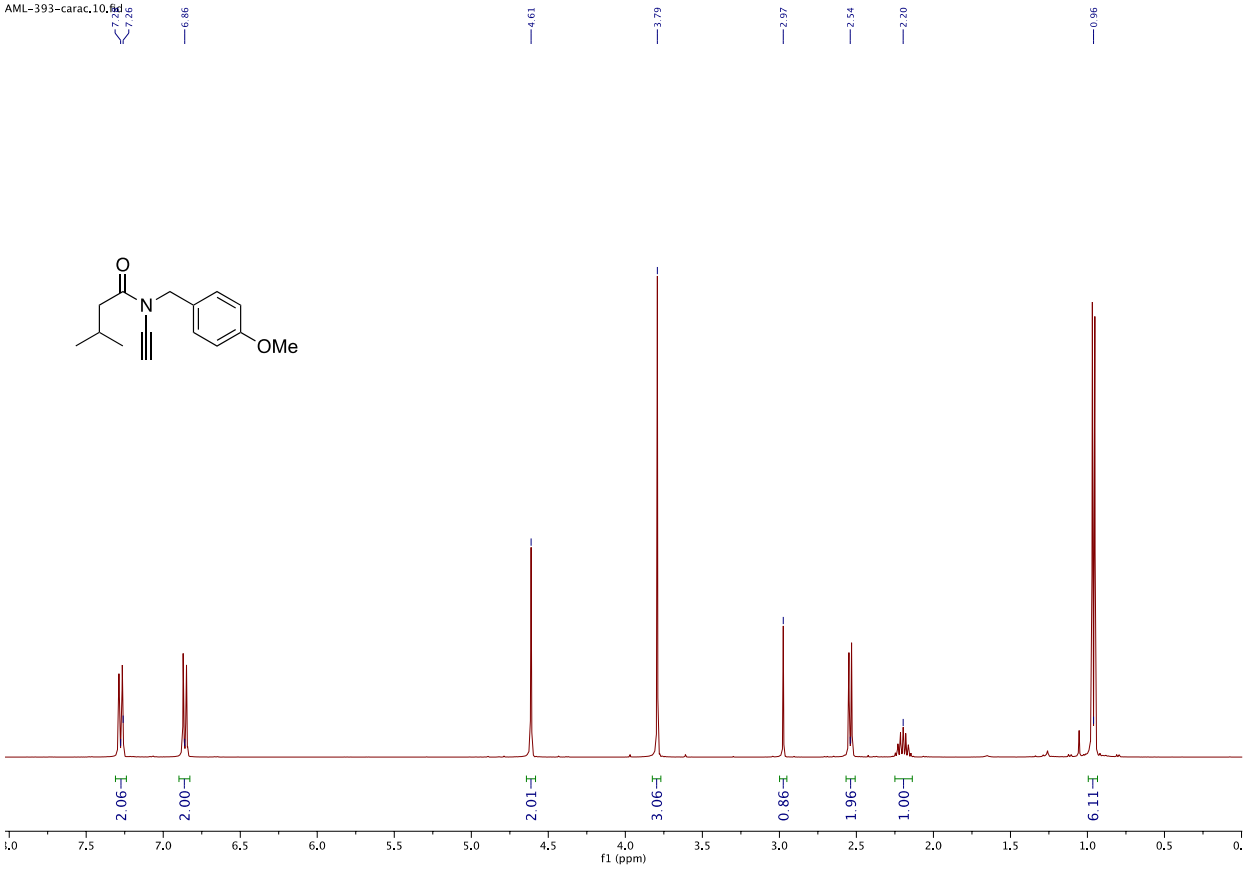
^{19}F NMR of **1b**

AML-392-1.11.fid

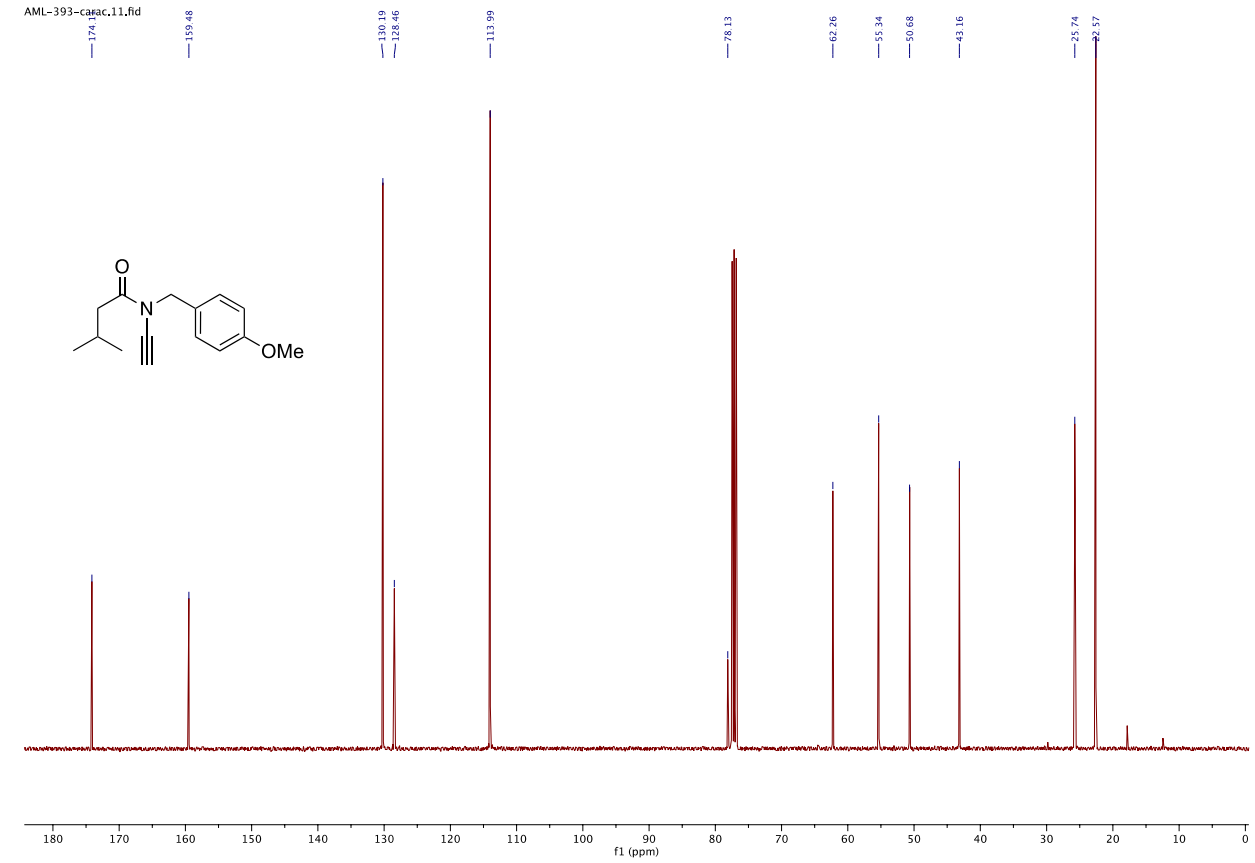


^{1}H NMR of **1c**

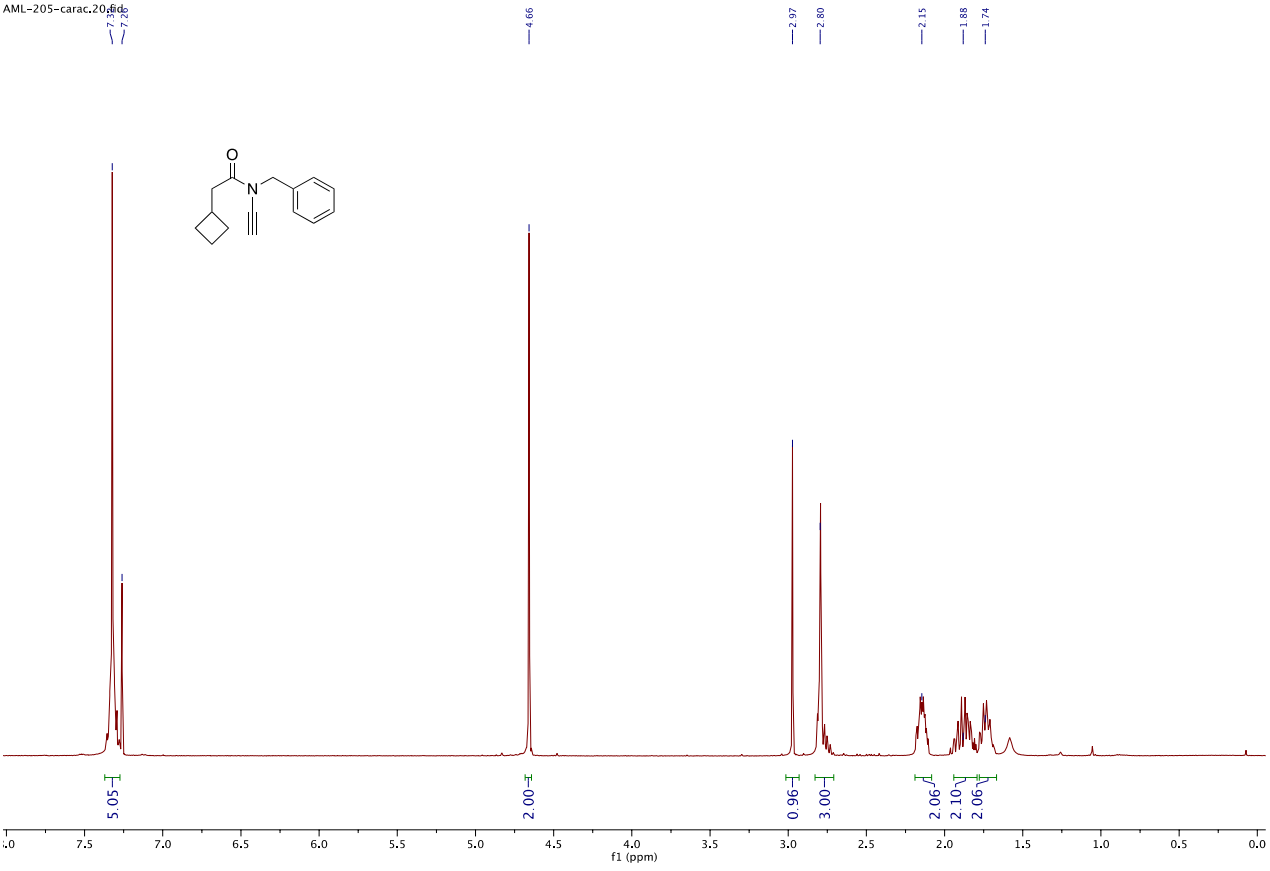
AML-393-carac.10.fid



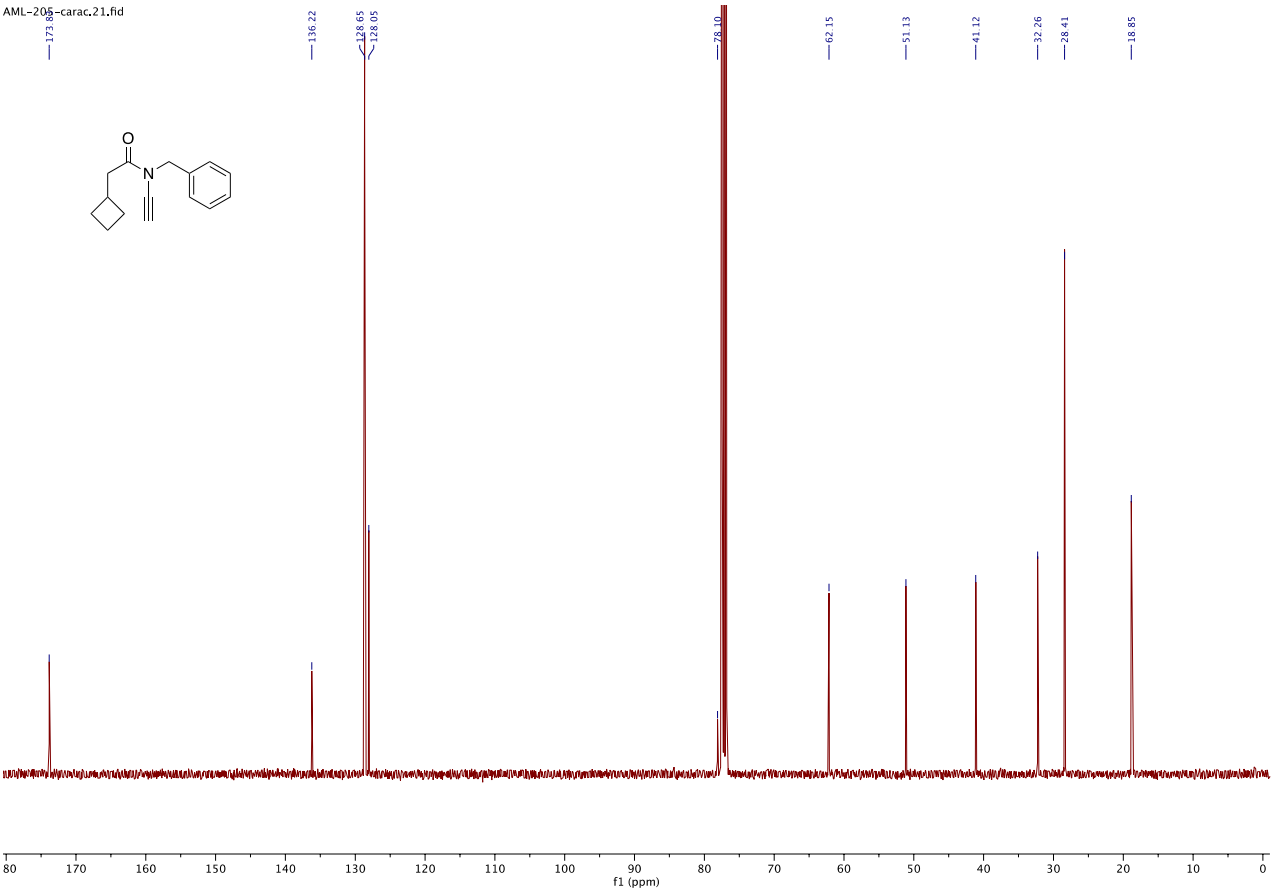
^{13}C NMR of **1c**



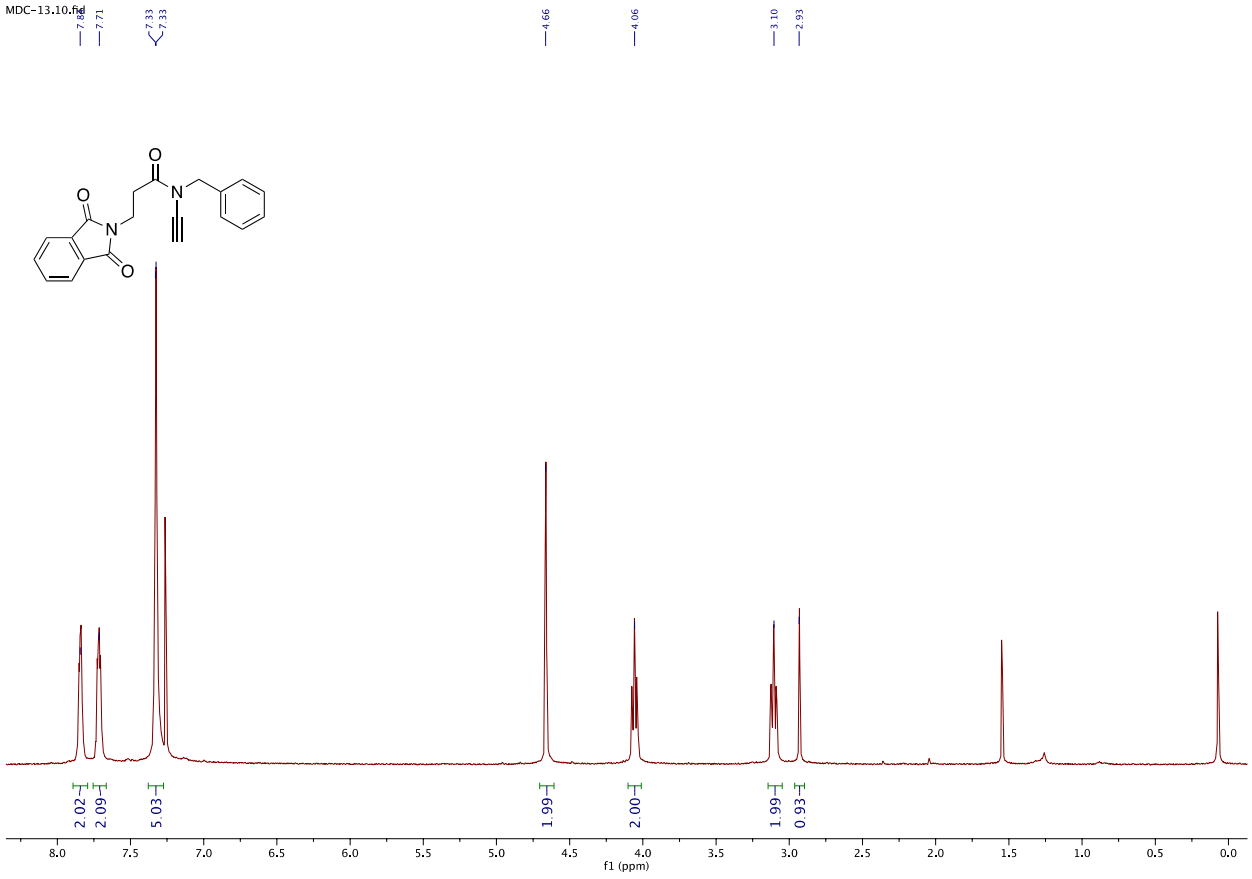
^{1}H NMR of **1d**



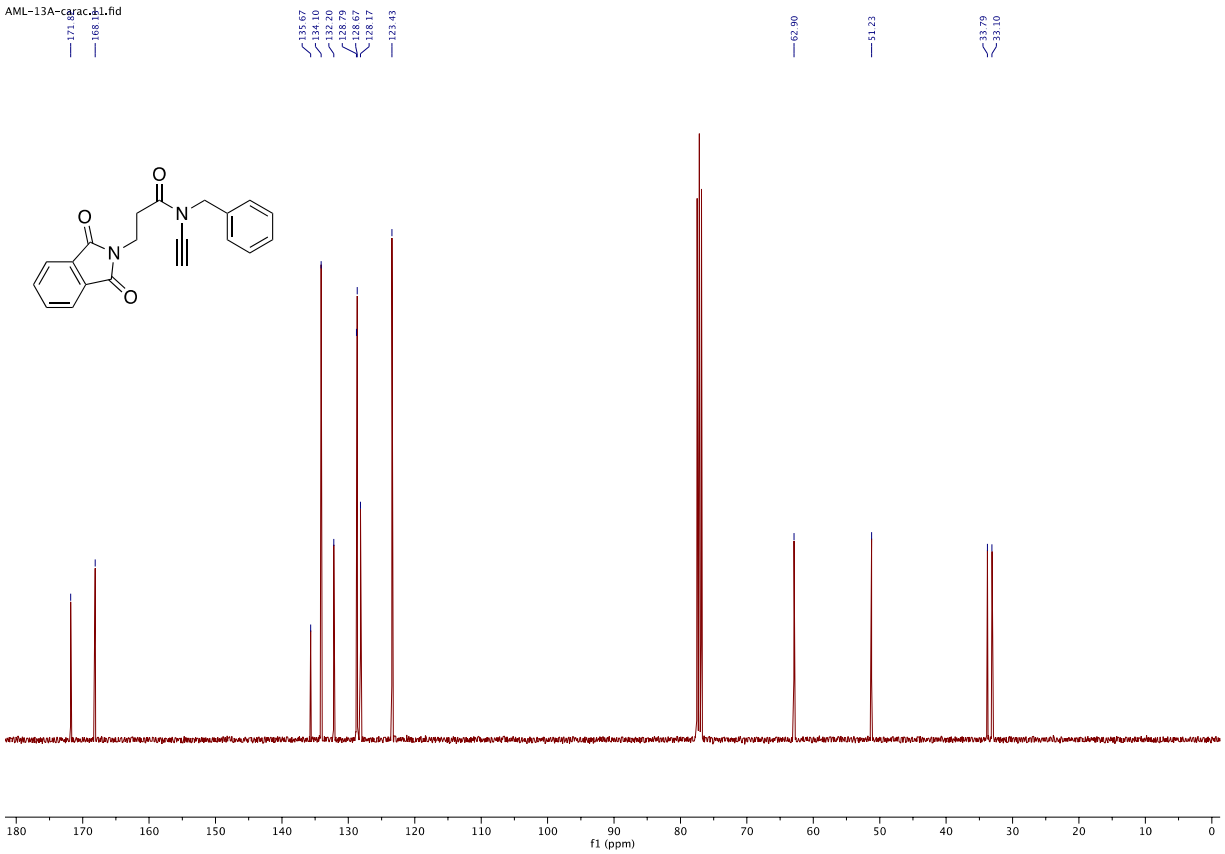
^{13}C NMR of **1d**



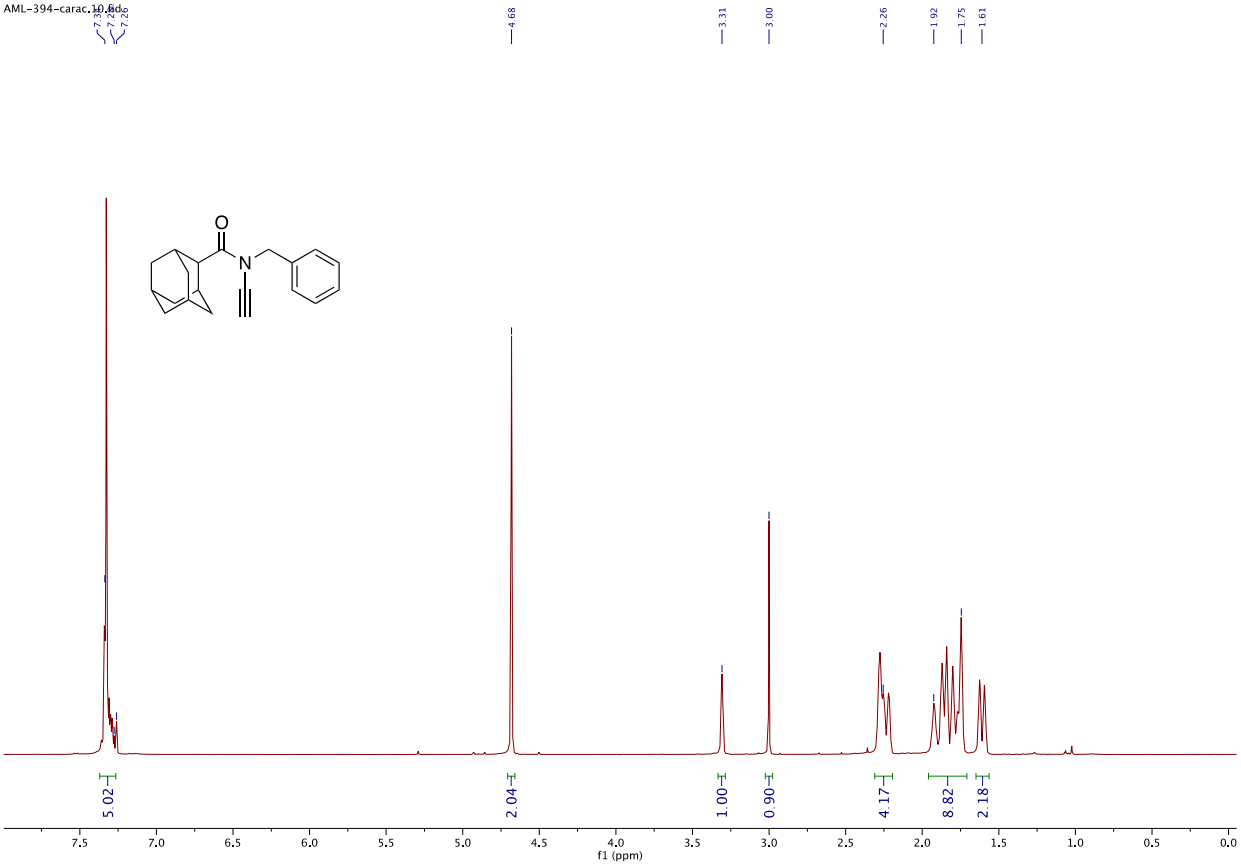
^{1}H NMR of **1e**



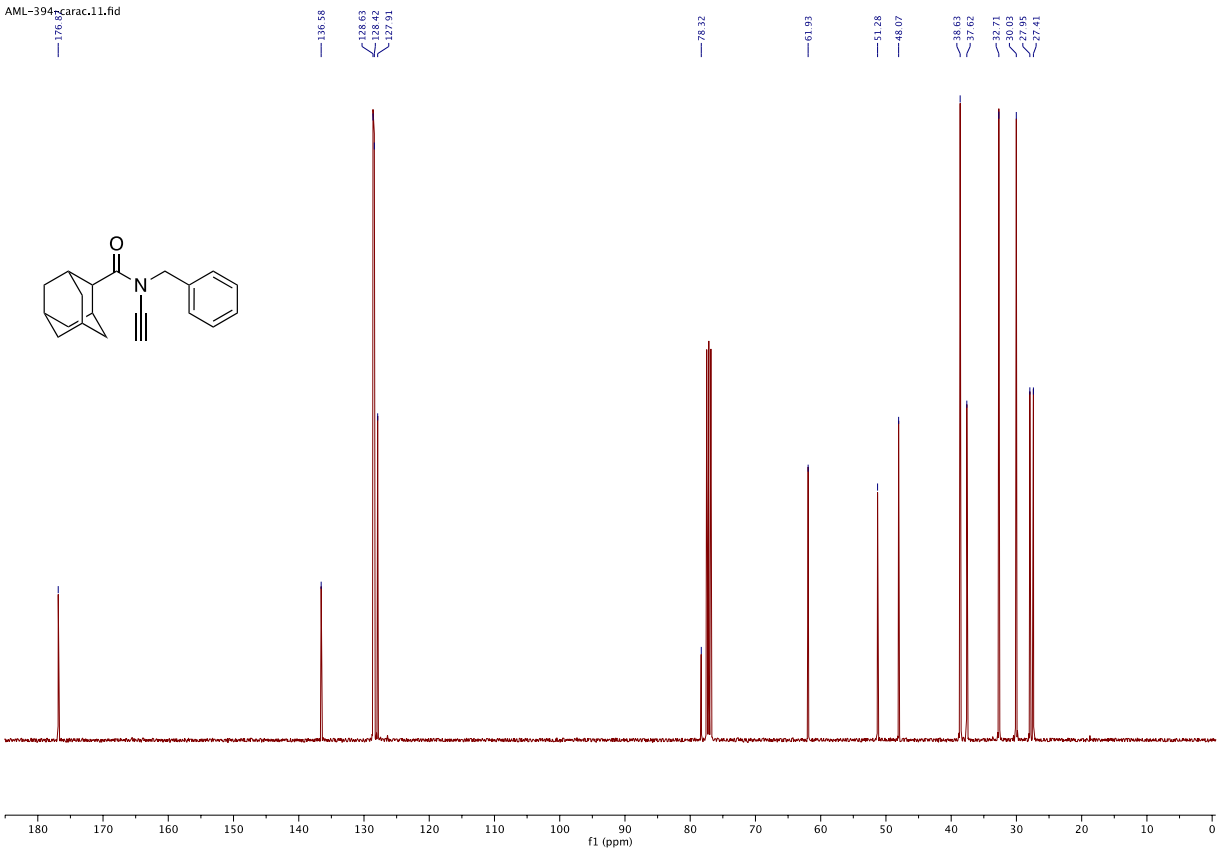
^{13}C NMR of **1e**



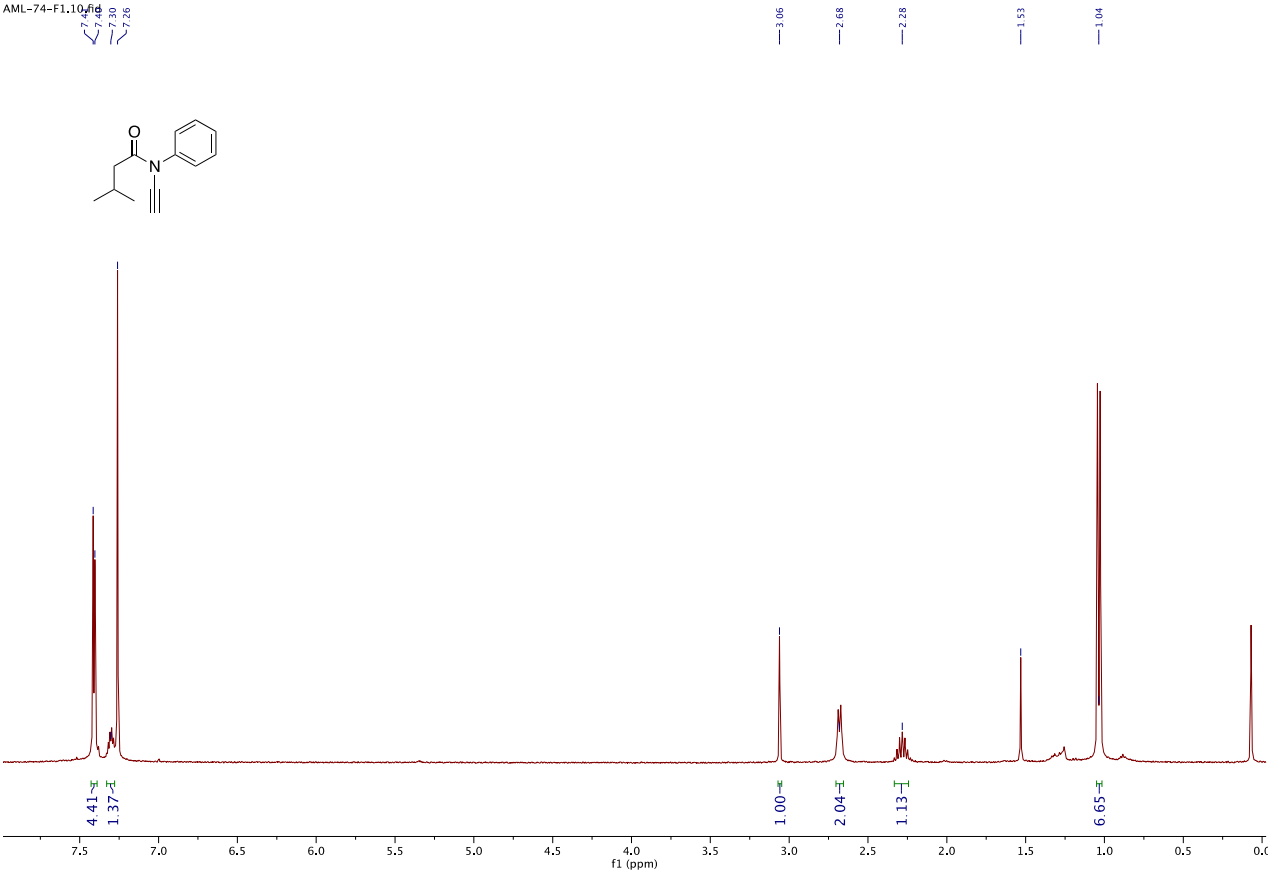
^{1}H NMR of **1f**



^{13}C NMR of **1f**

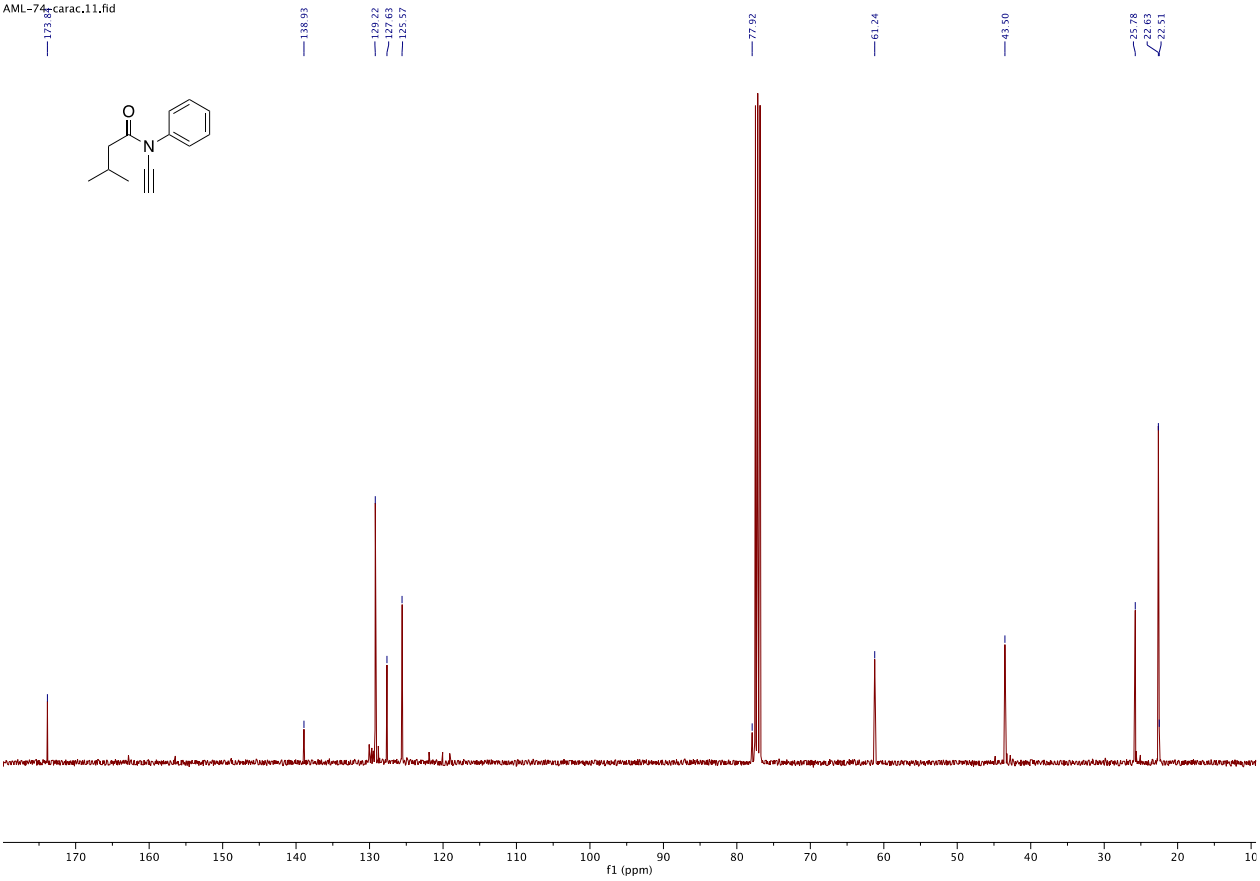


^{1}H NMR of **1g**



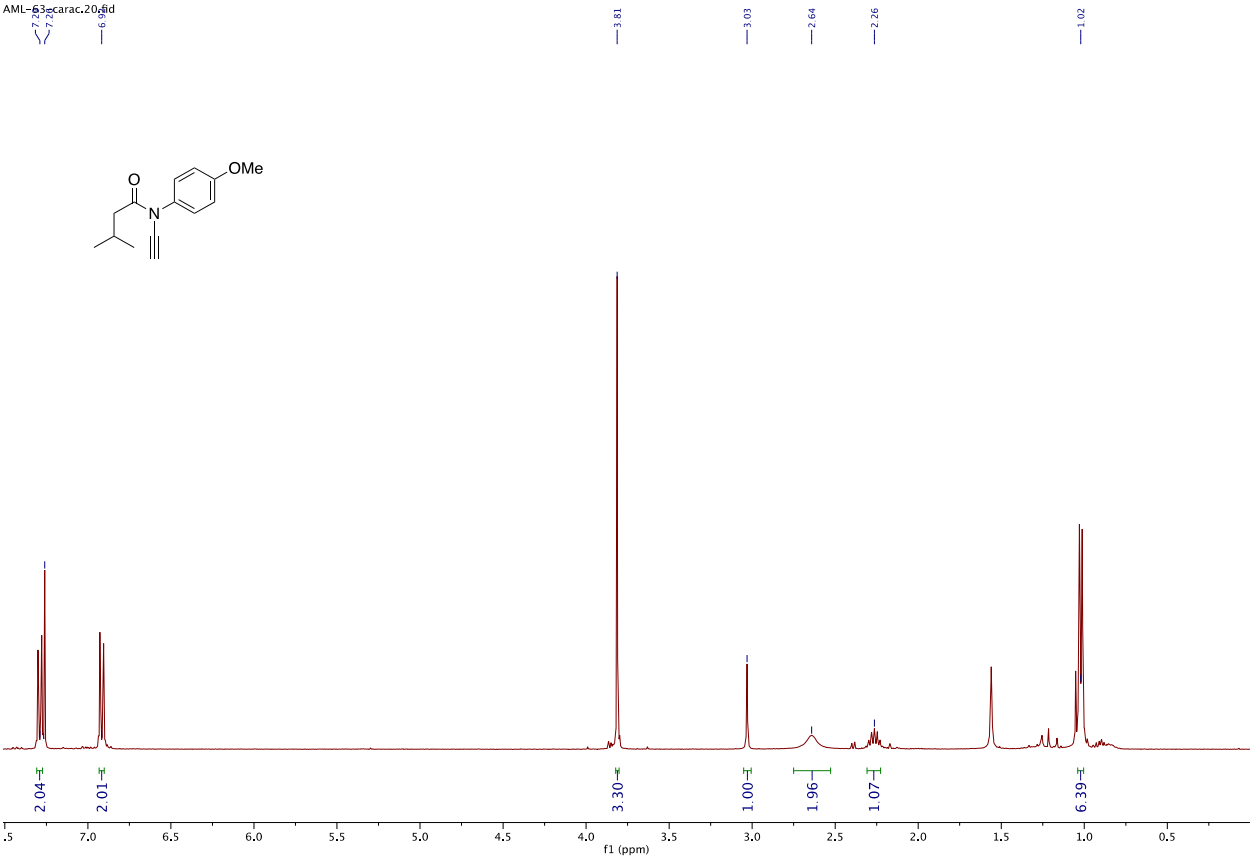
^{13}C NMR of **1g**

AML-74-carac.11.fid

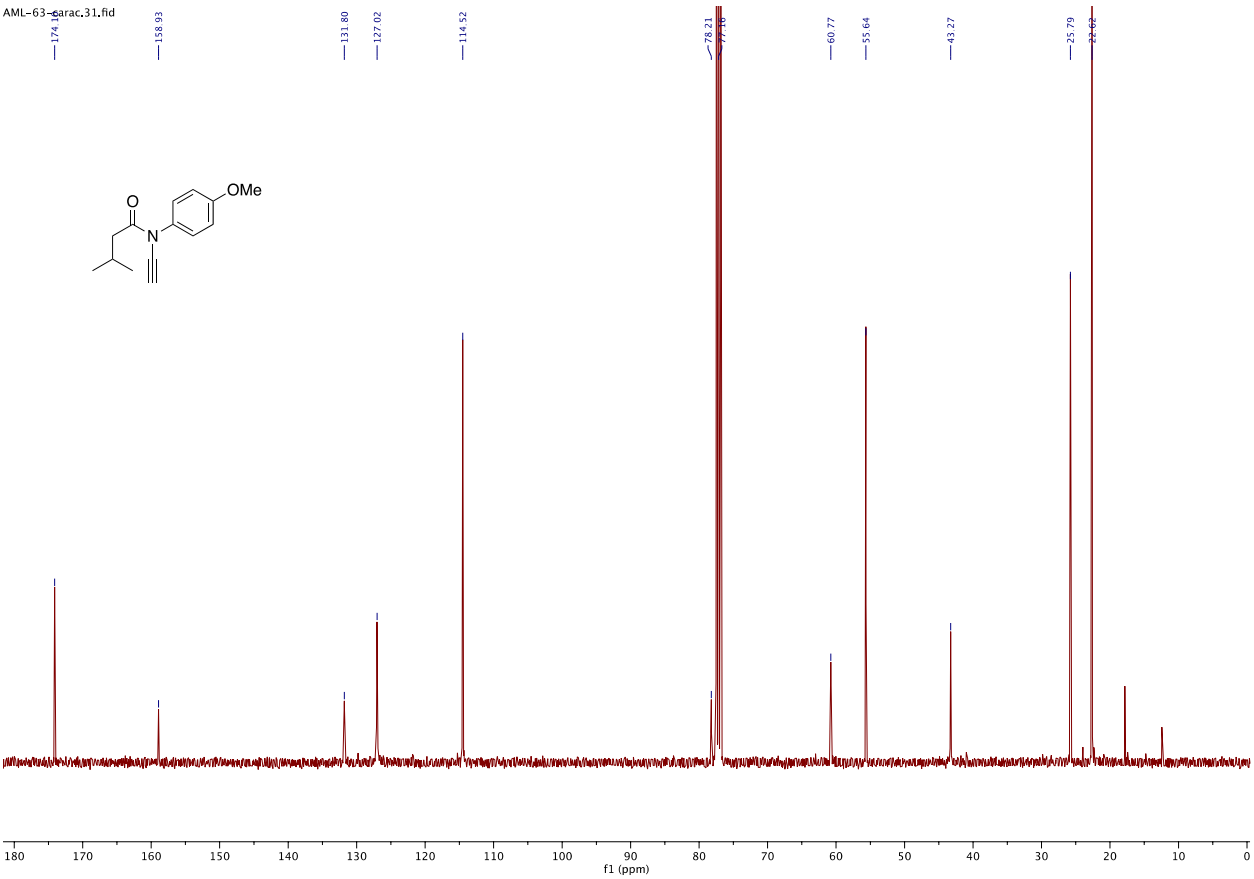


^{1}H NMR of **1h**

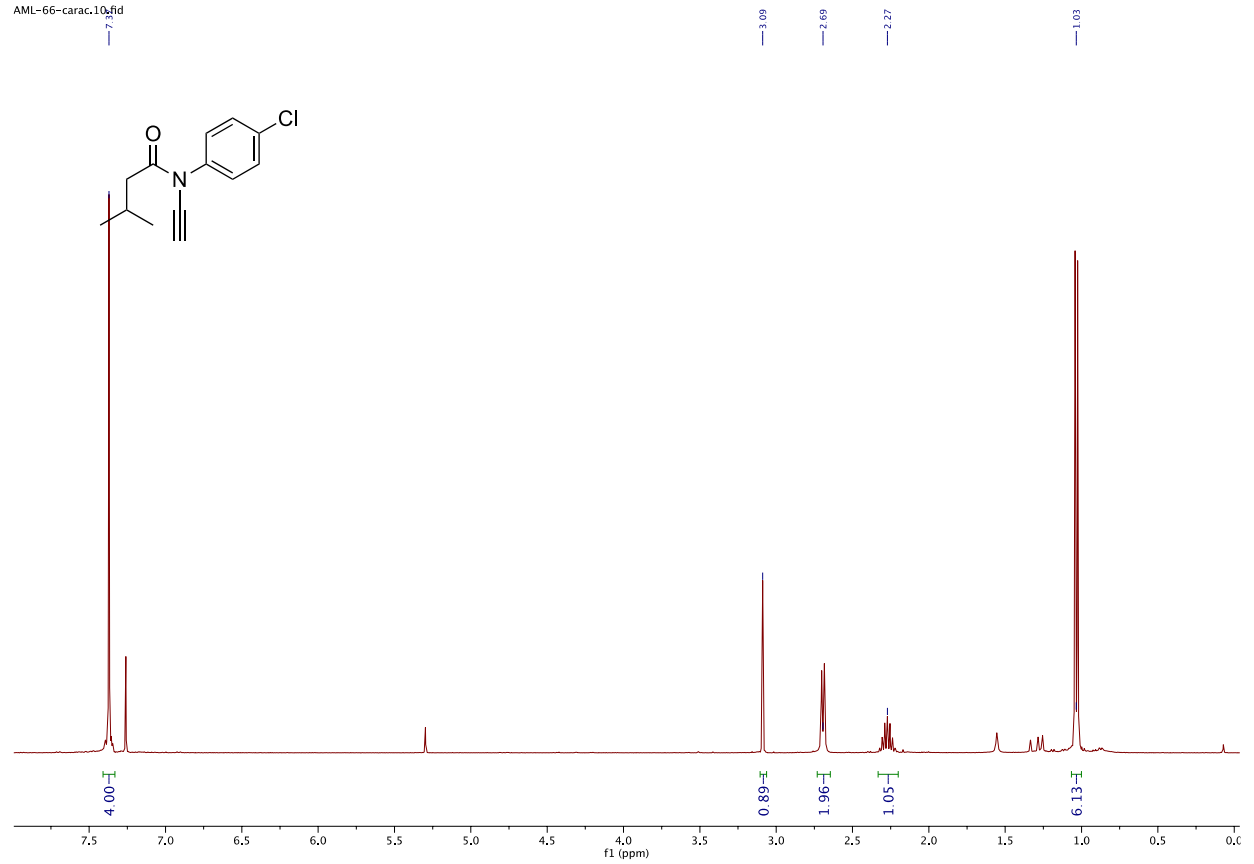
AML-63-carac.20.fid



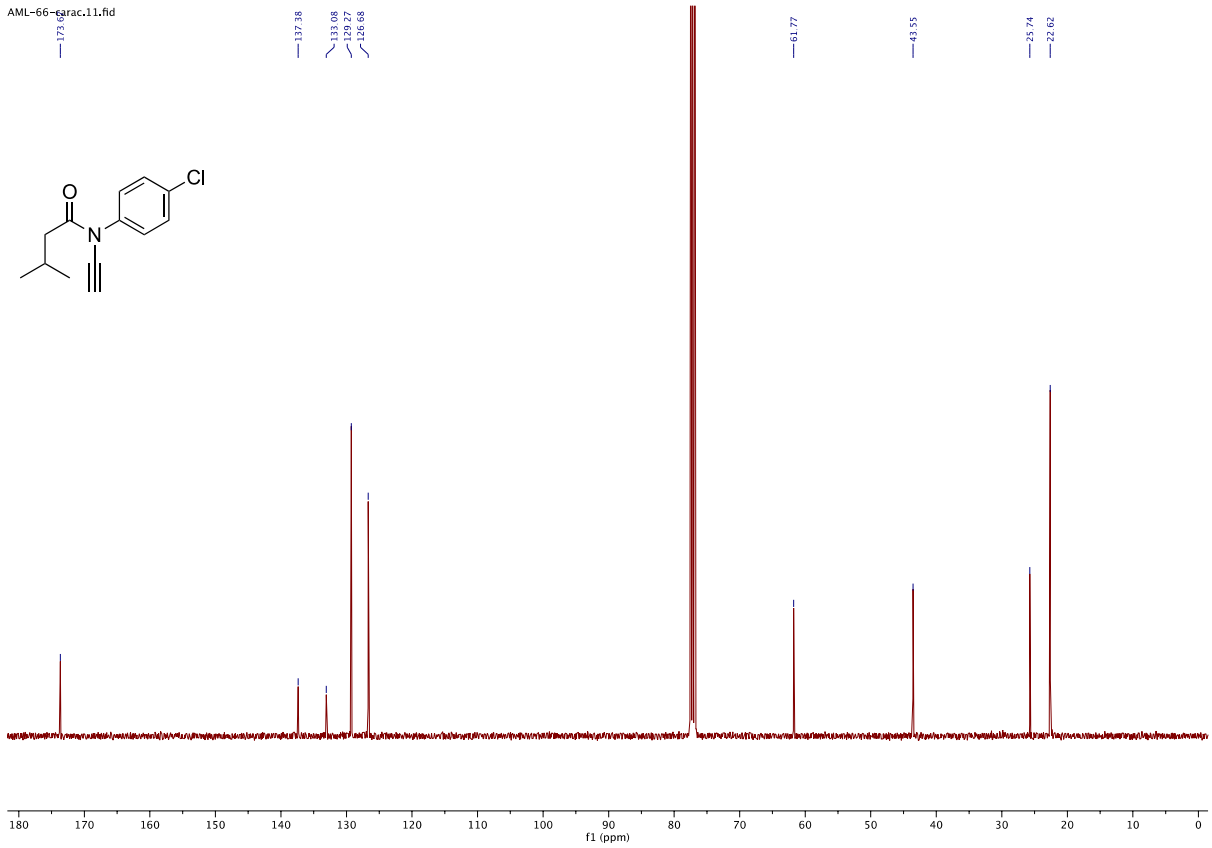
^{13}C NMR of **1h**



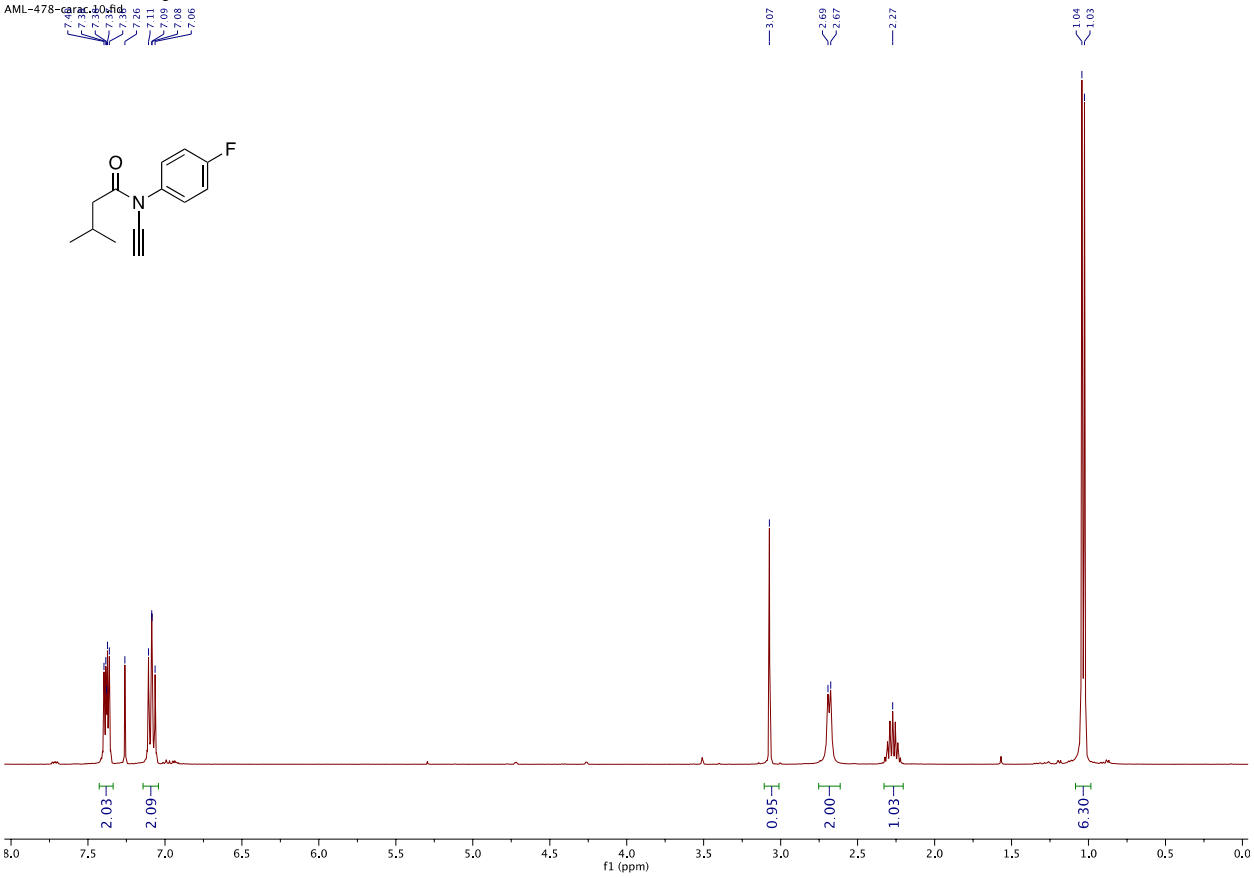
^{1}H NMR of **1i**



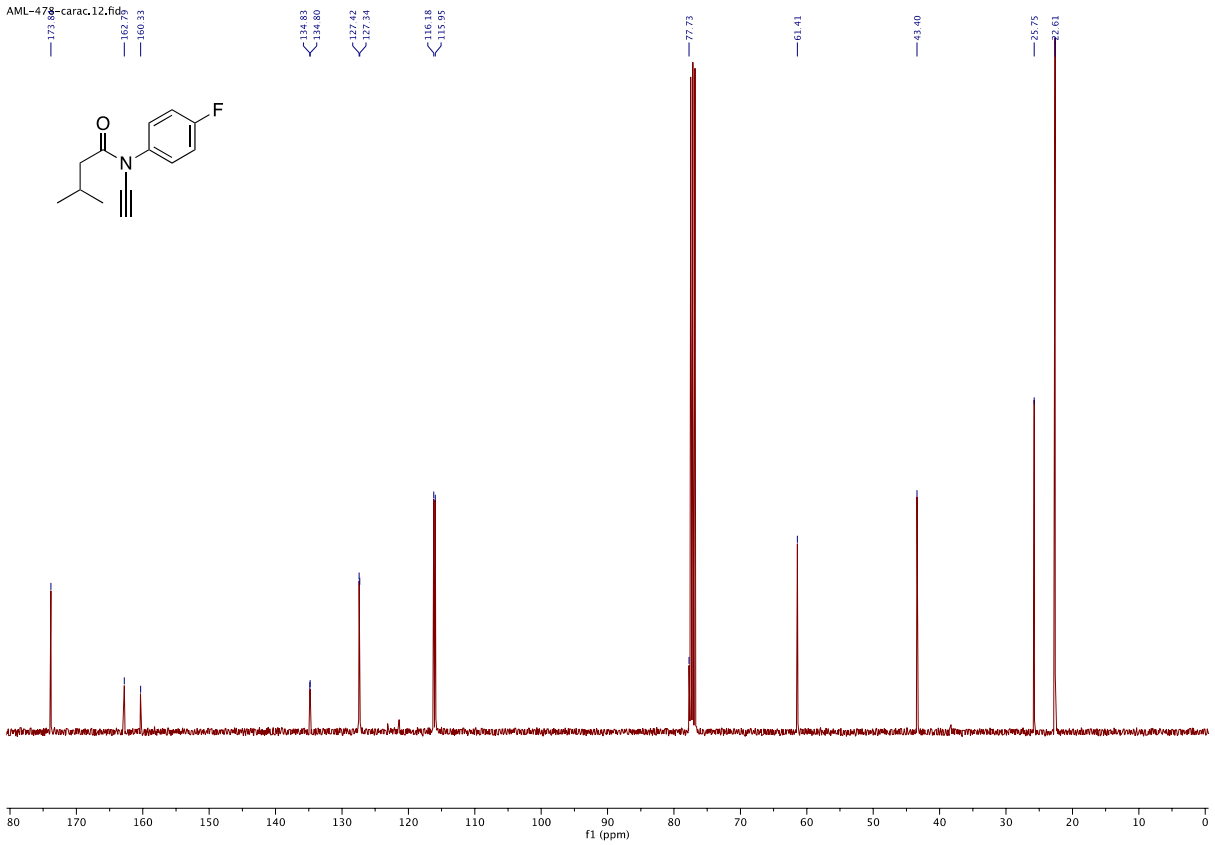
^{13}C NMR of **1i**



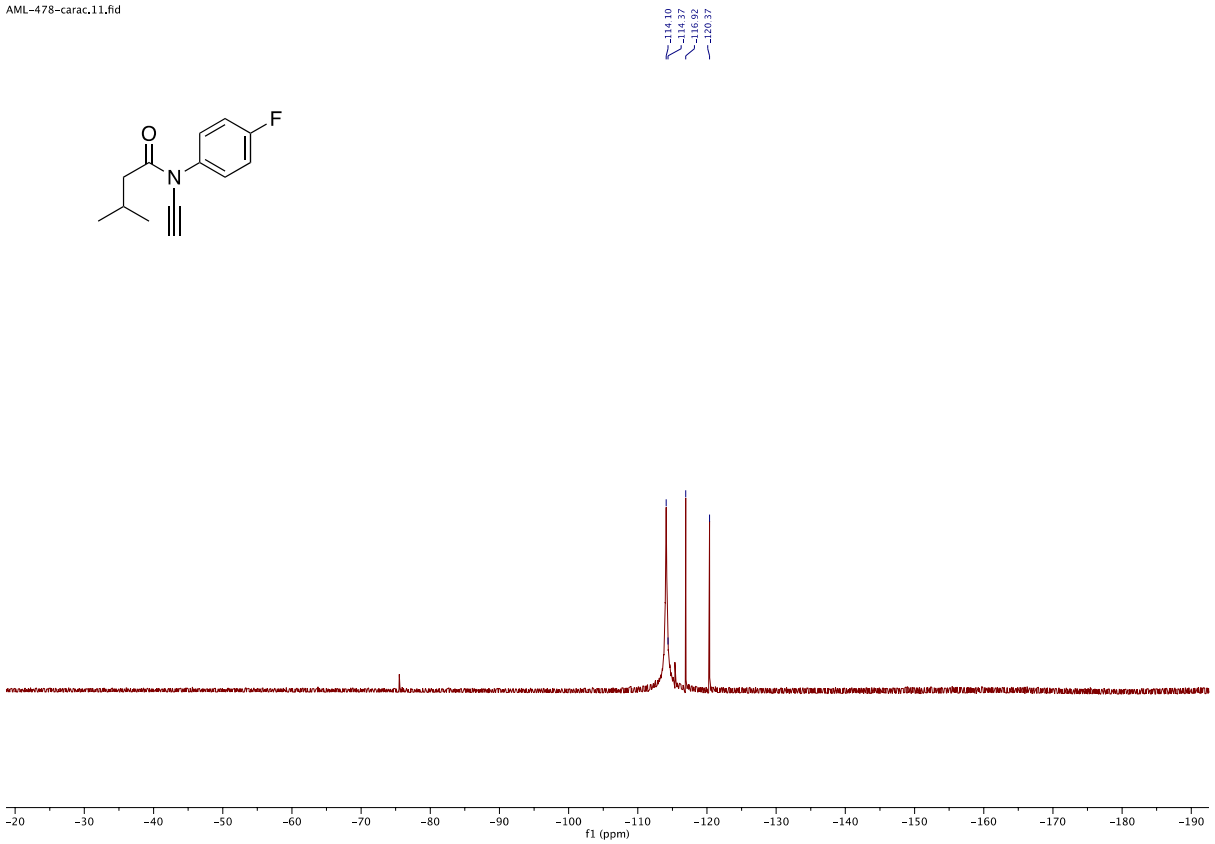
^{1}H NMR of **1j**



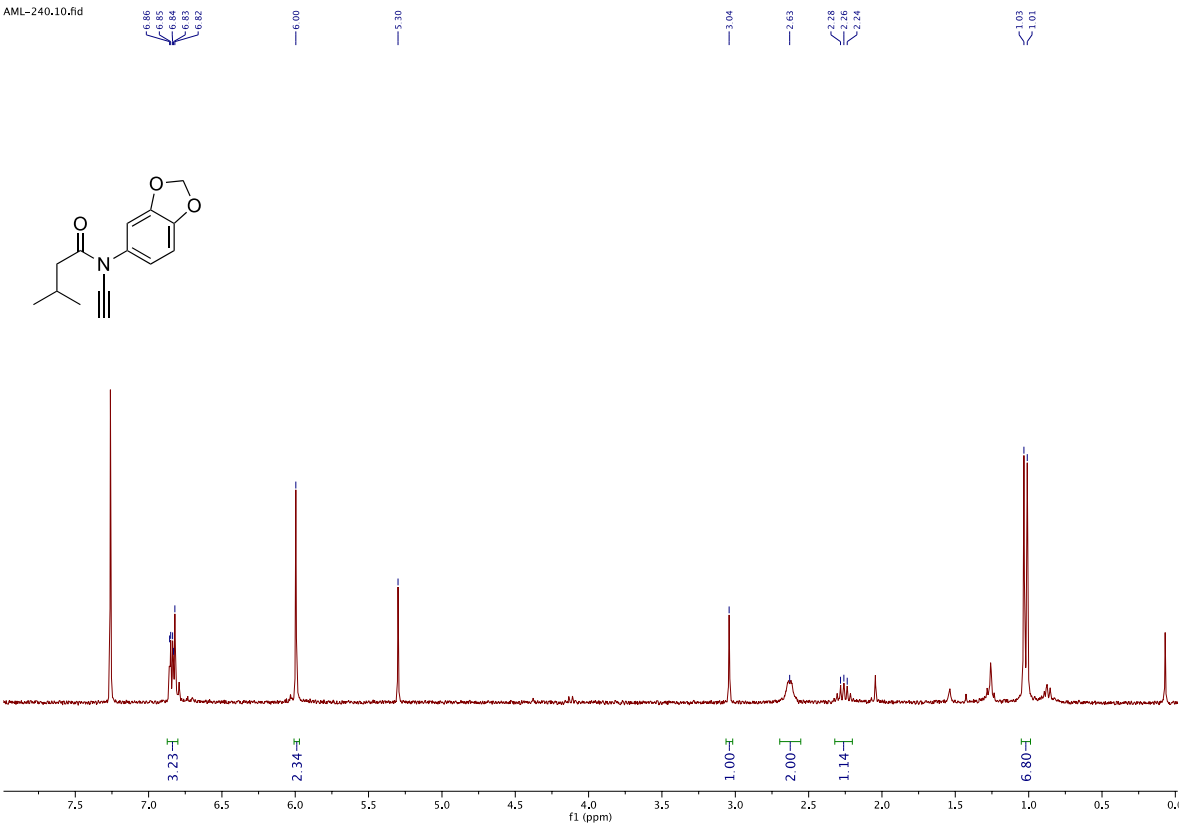
^{13}C NMR of **1j**



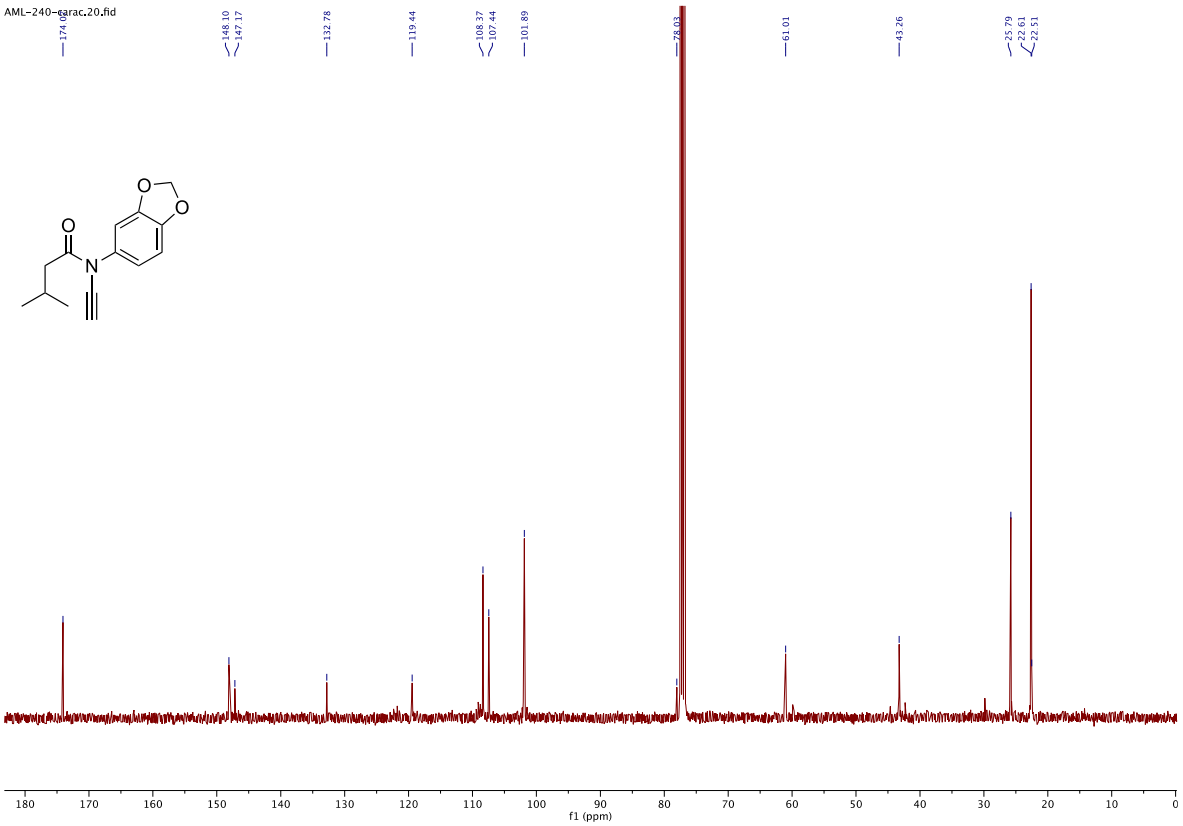
^{19}F NMR of **1j**



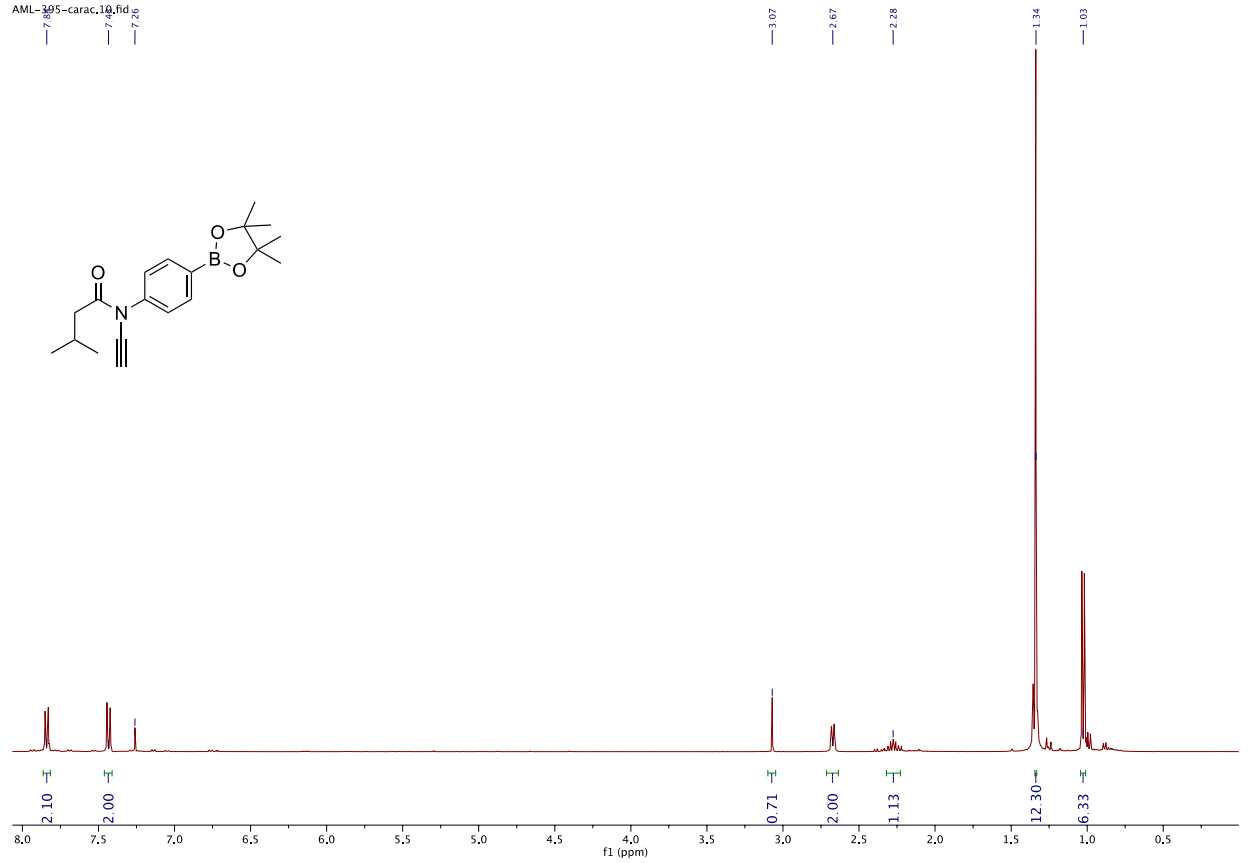
^{1}H NMR of **1k**



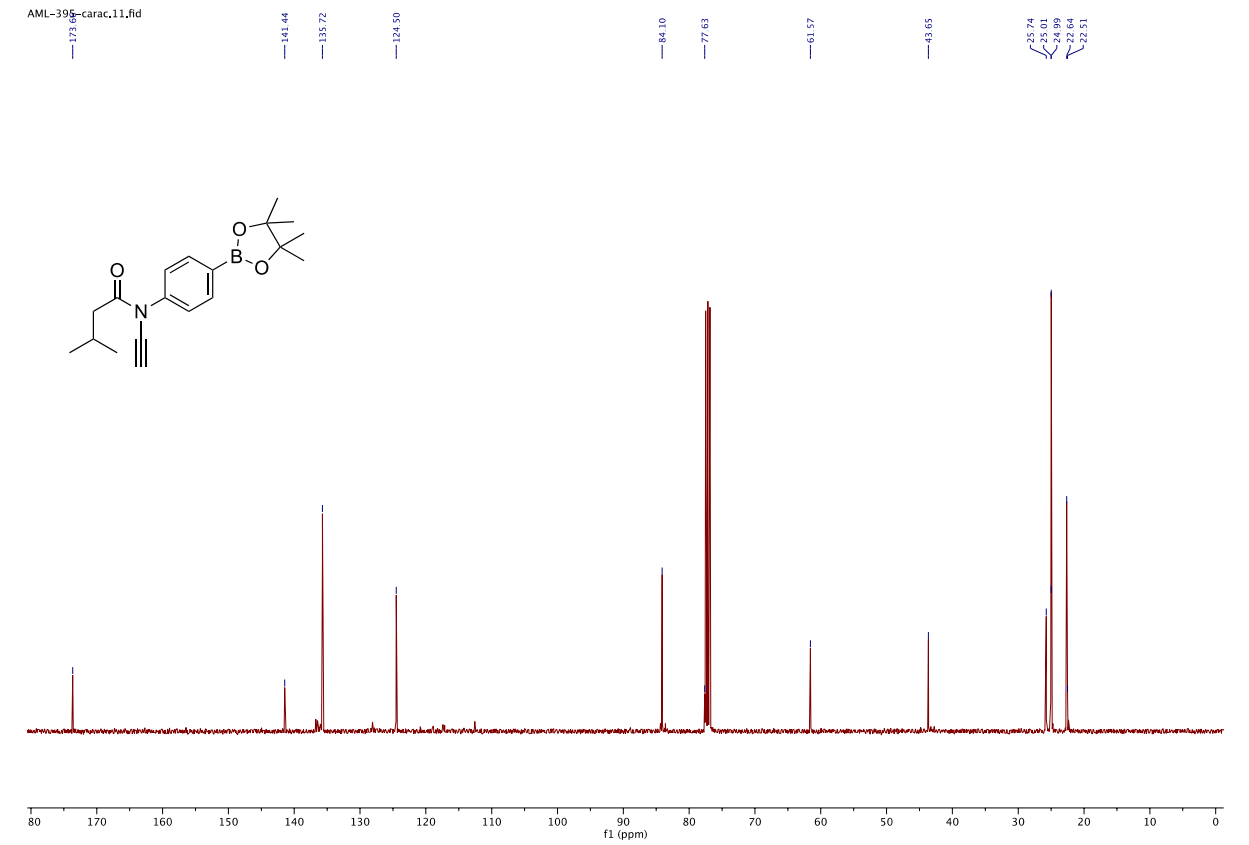
^{13}C NMR of **1k**



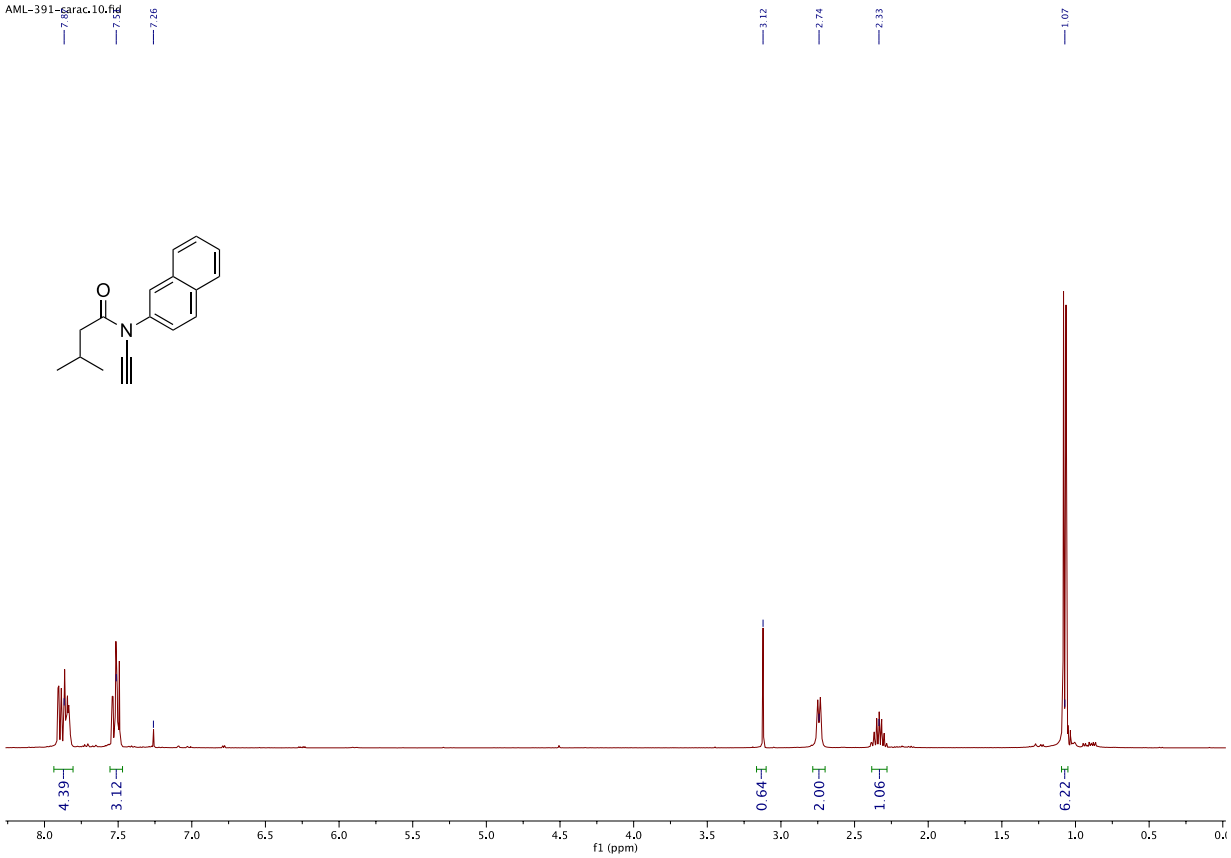
^{1}H NMR of **1l**



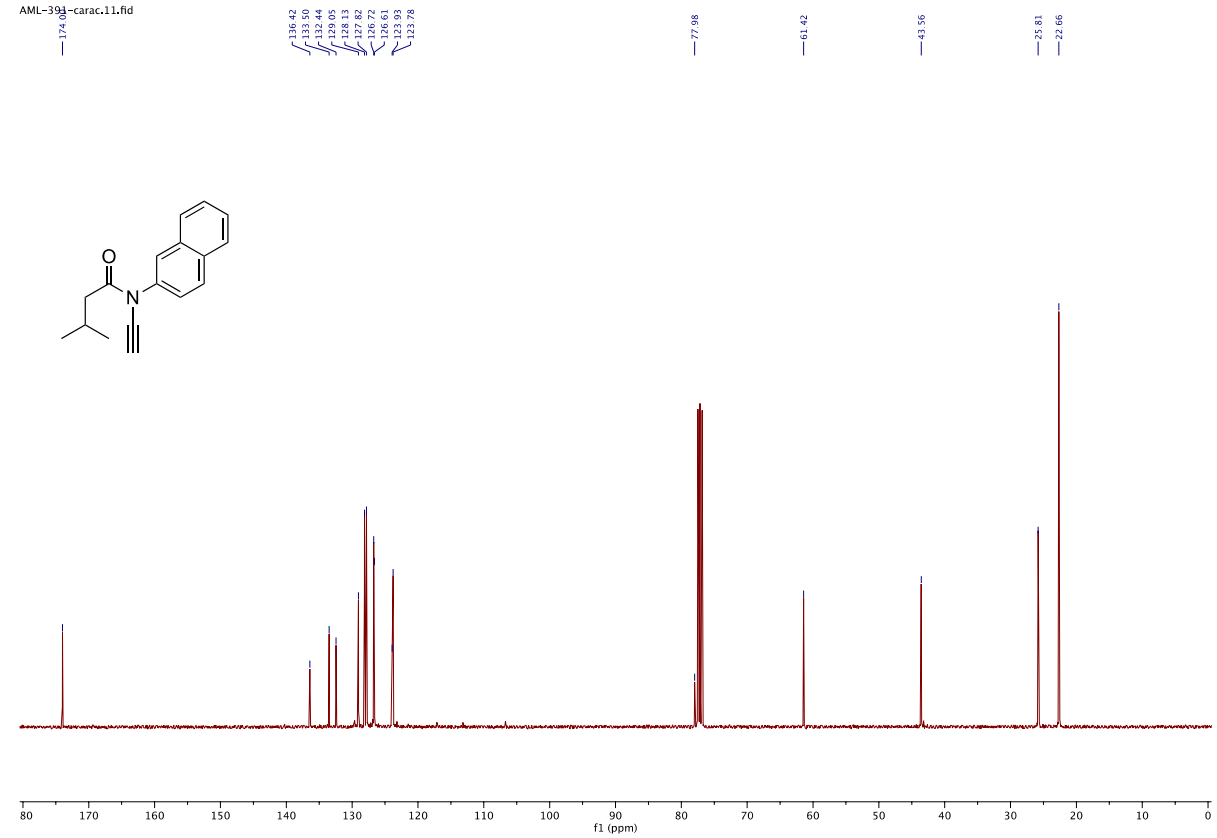
^{13}C NMR of **1l**



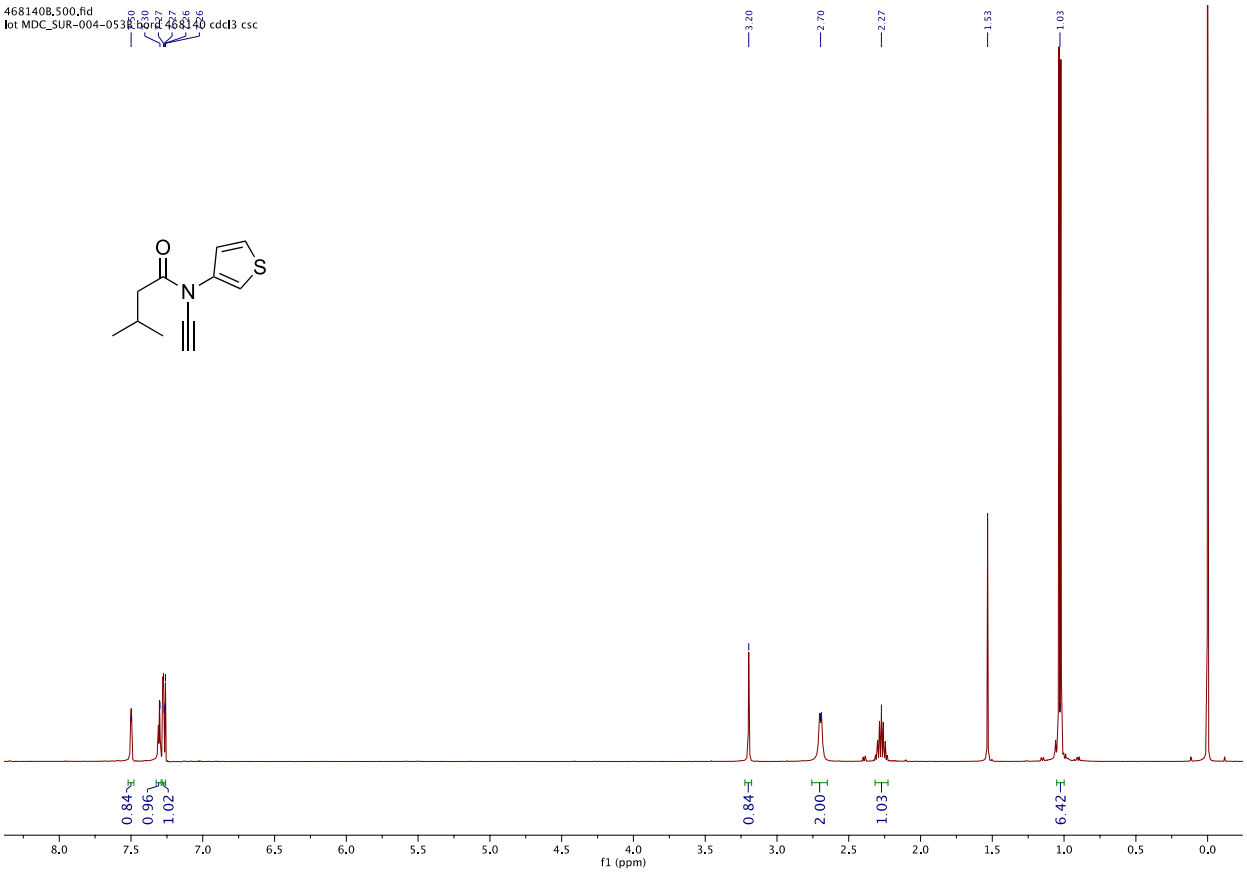
^{1}H NMR of **1m**



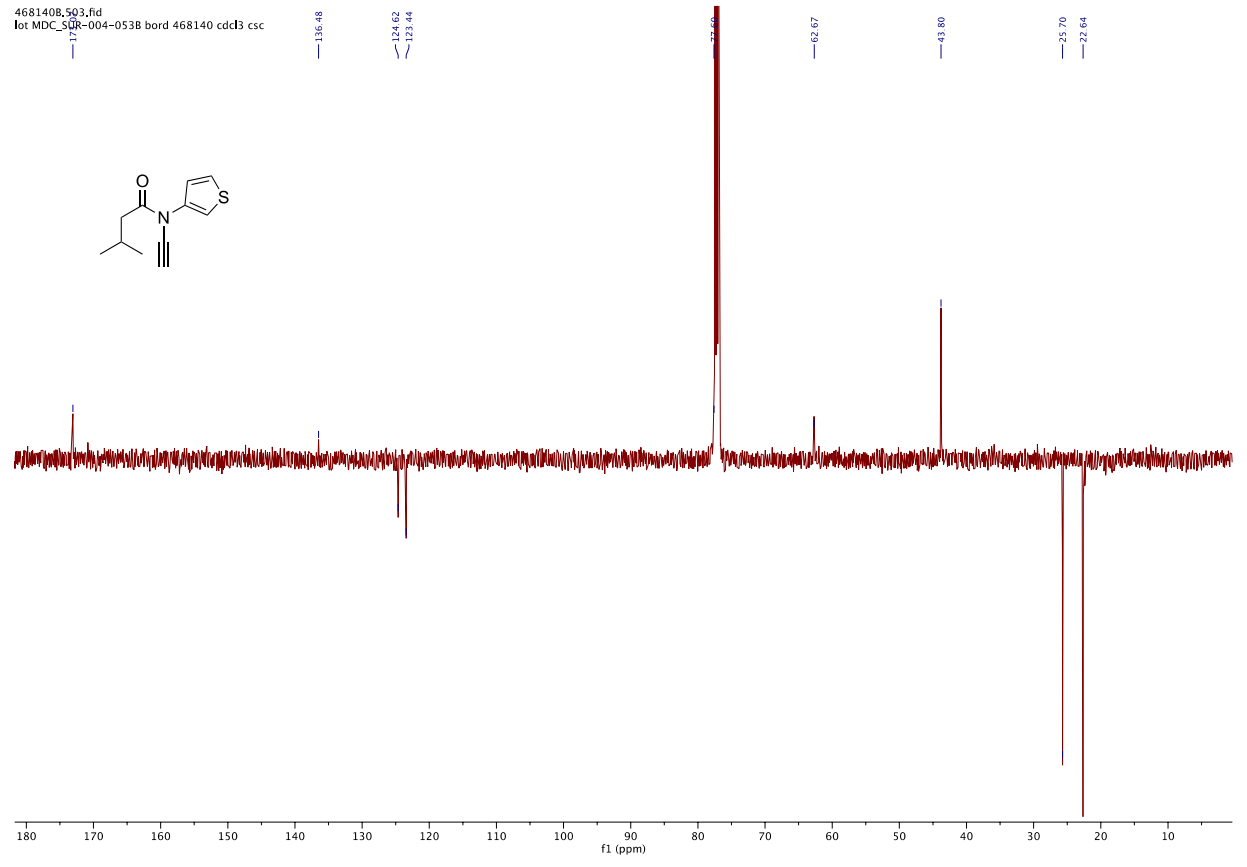
^{13}C NMR of **1m**



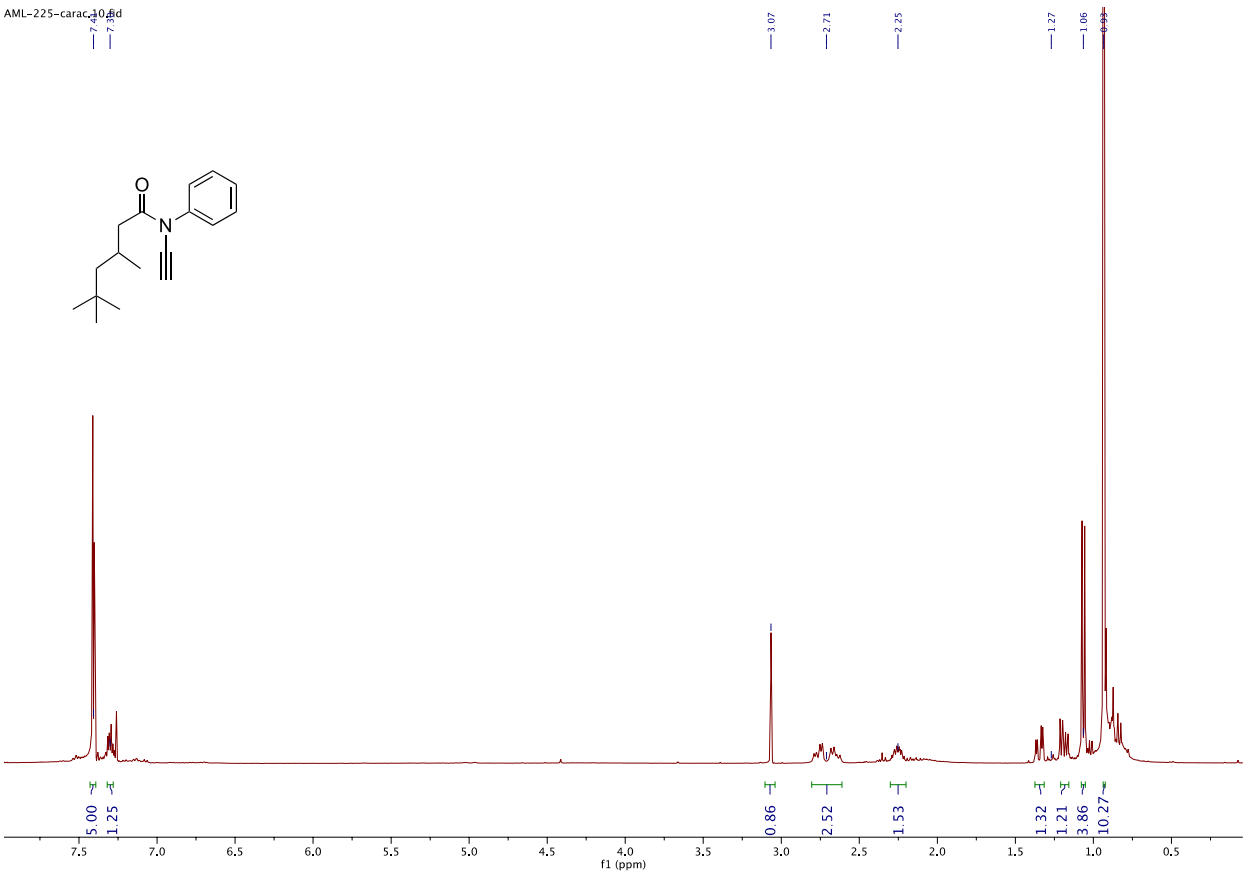
^{1}H NMR of **1n**



^{13}C NMR of **1n**



^{1}H NMR of **1o**



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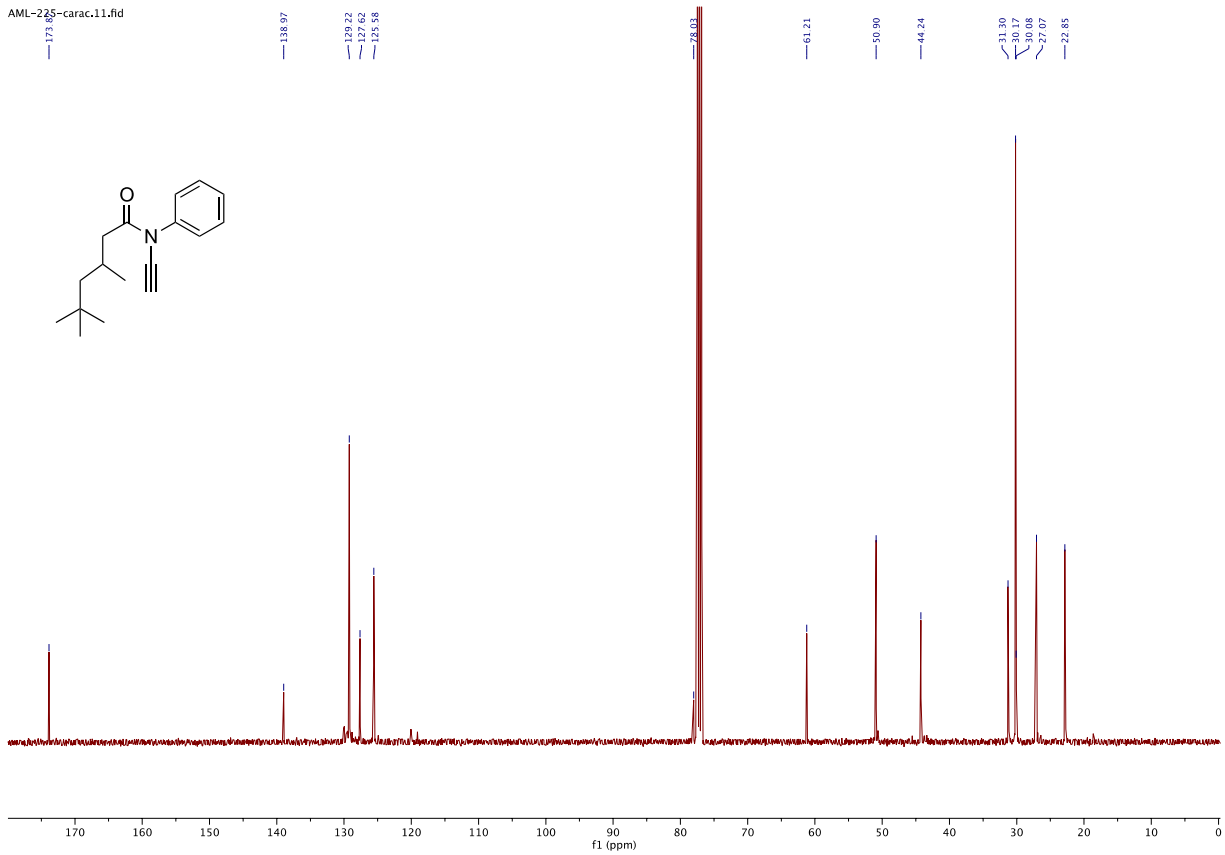
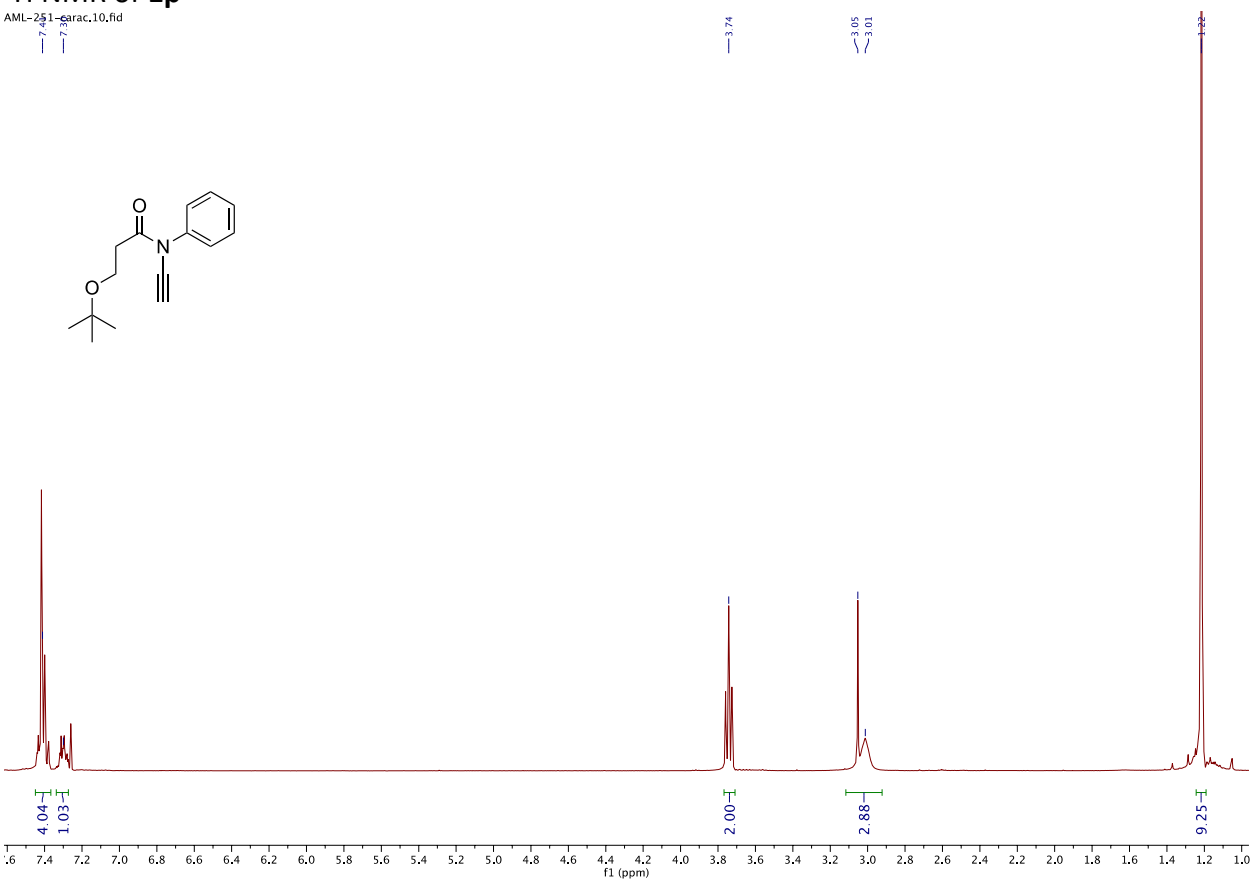
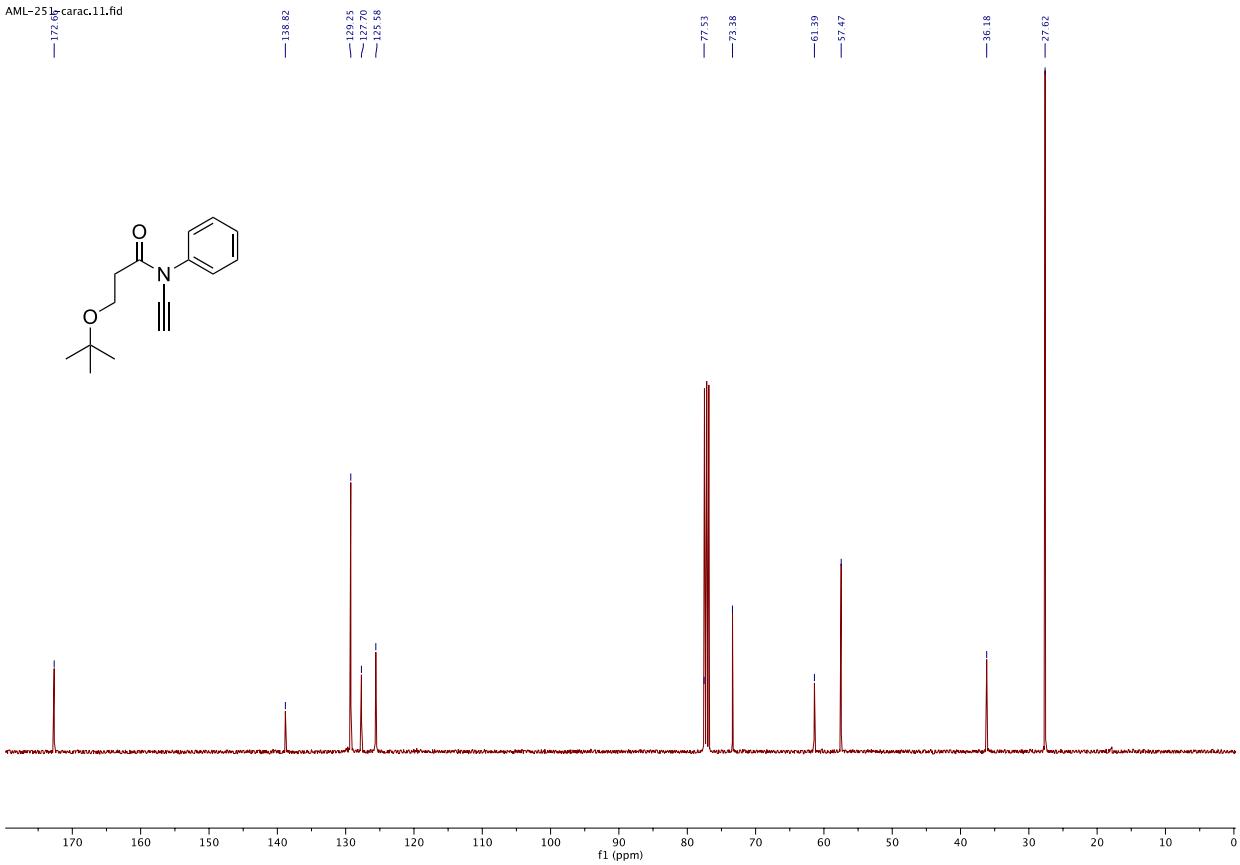


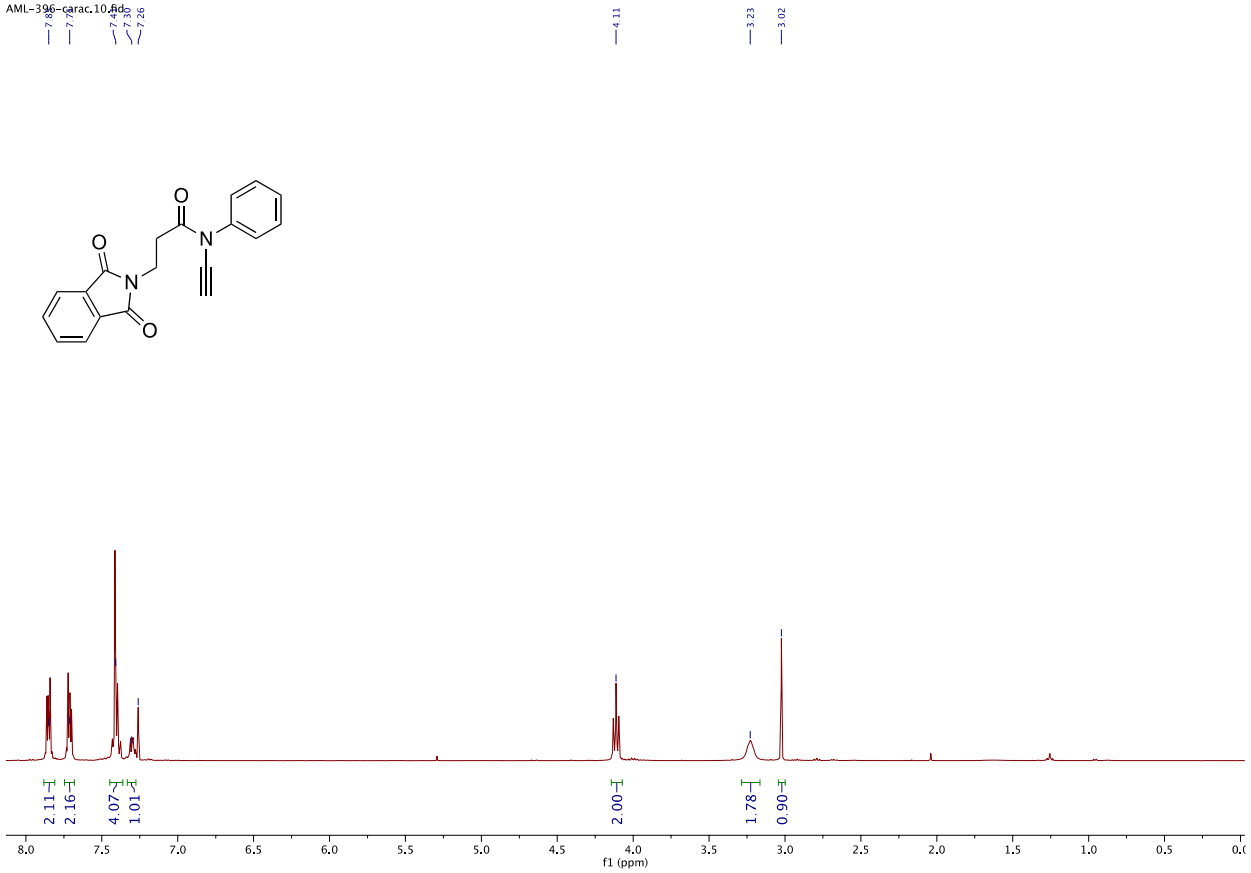
^{1}H NMR of **1p**



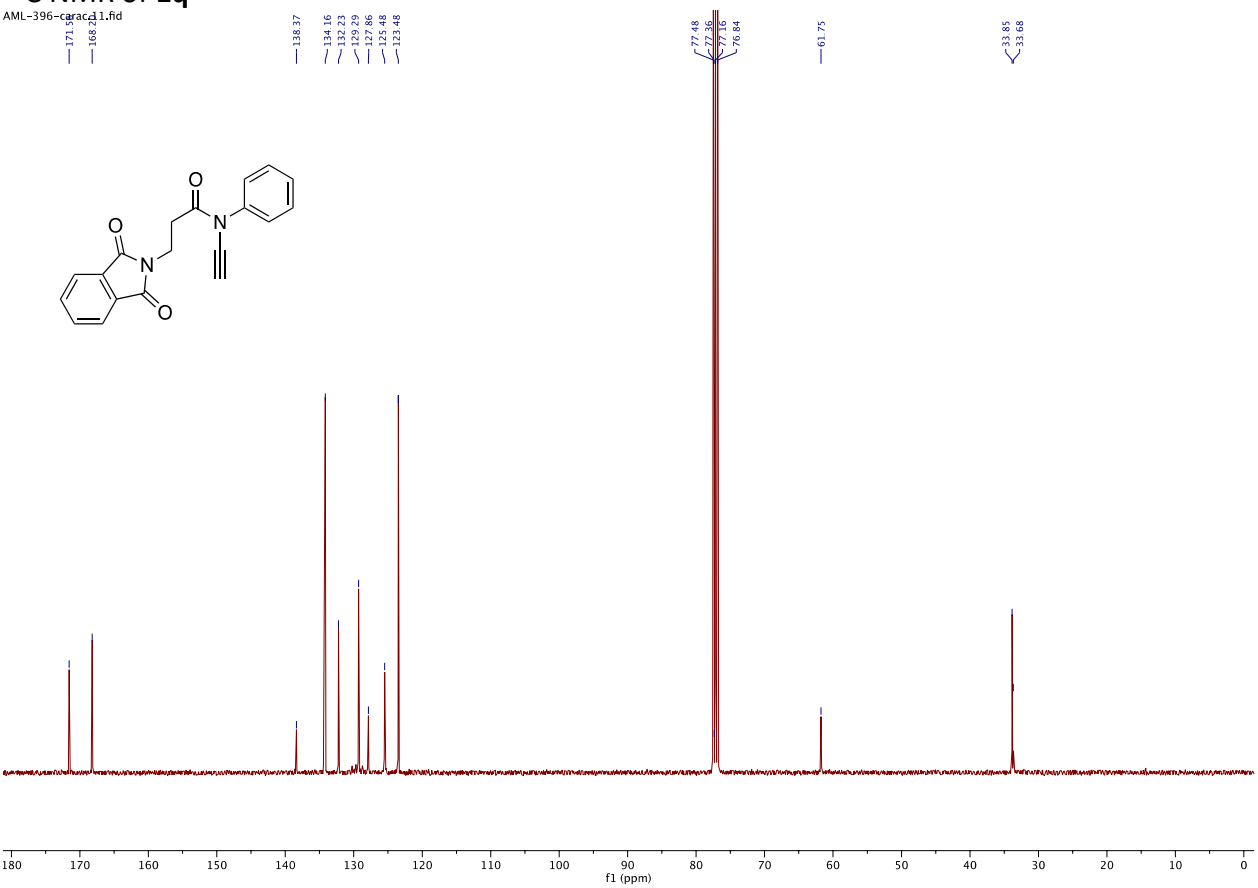
^{13}C NMR of **1p**



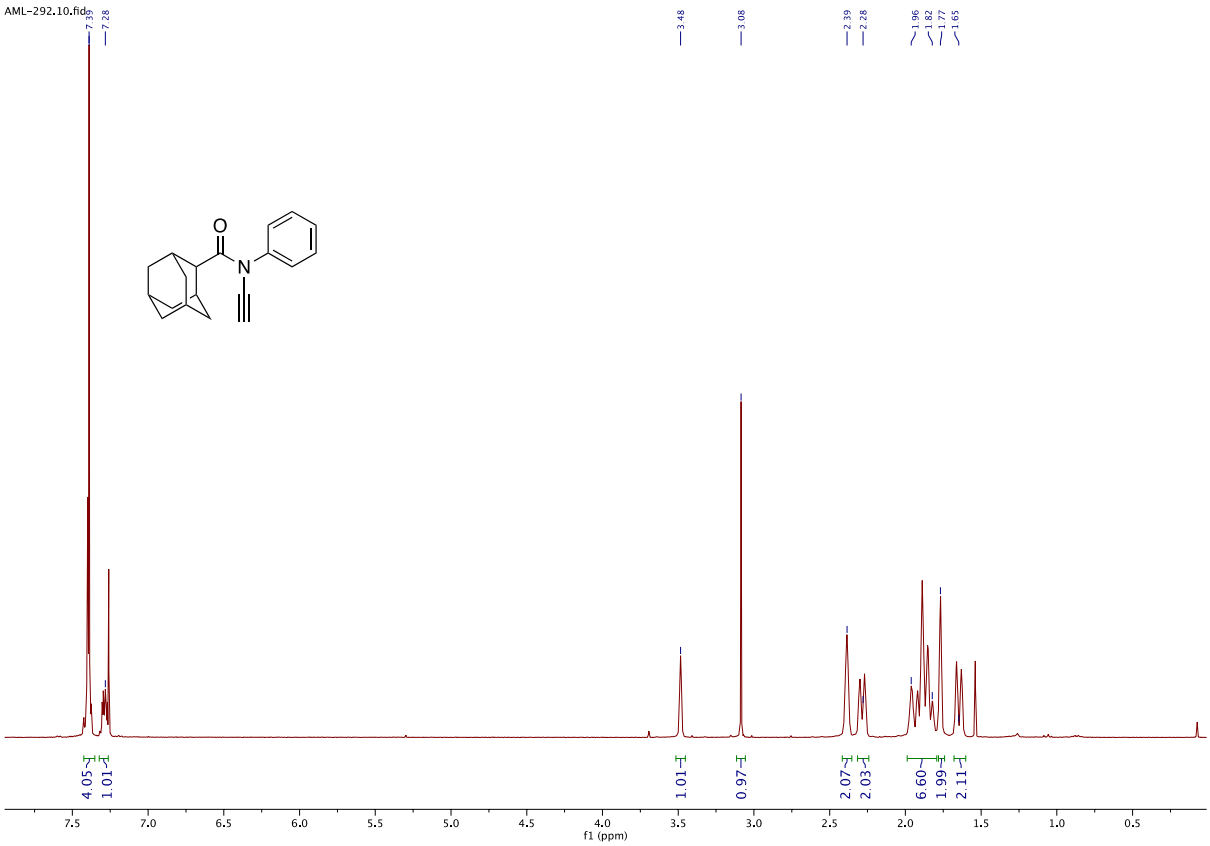
^{1}H NMR of **1q**



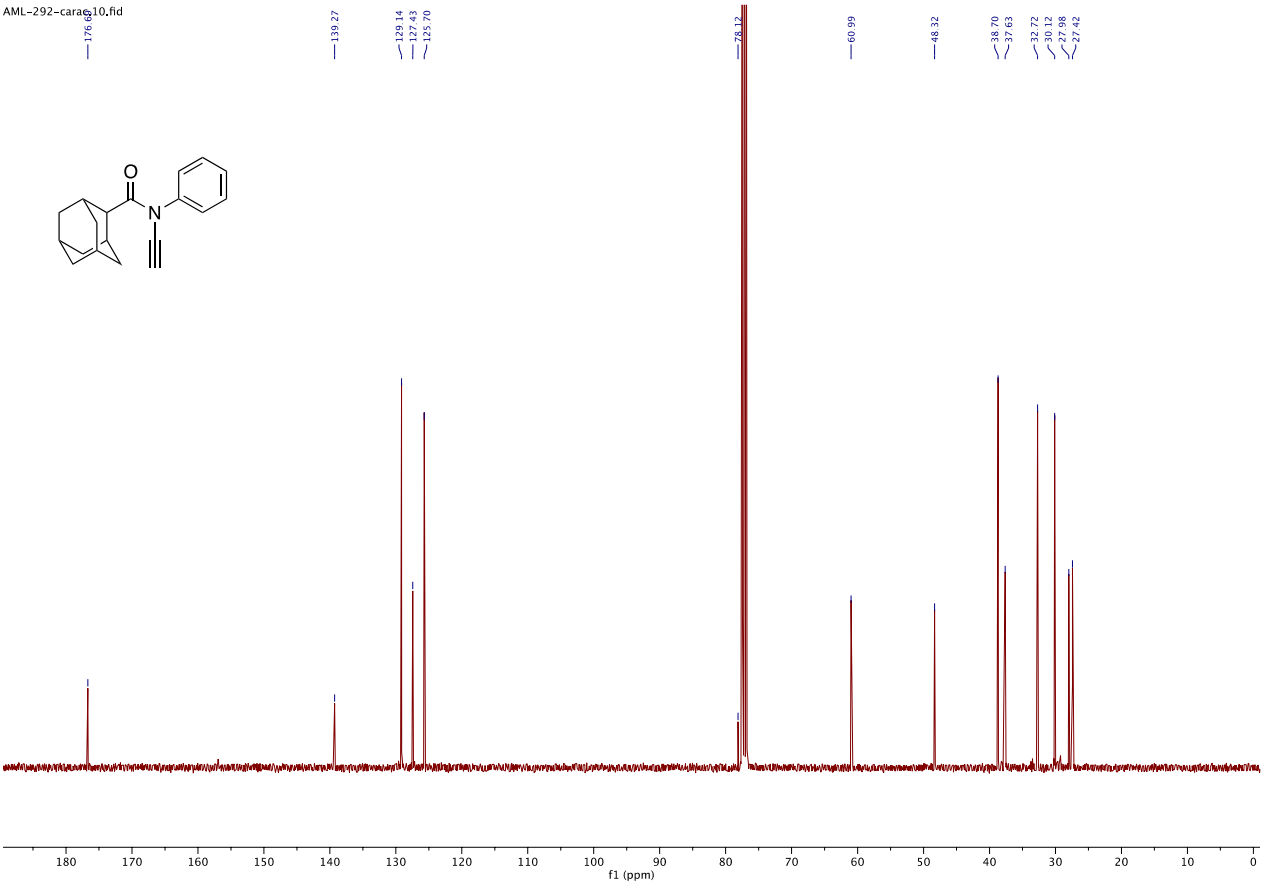
^{13}C NMR of **1q**



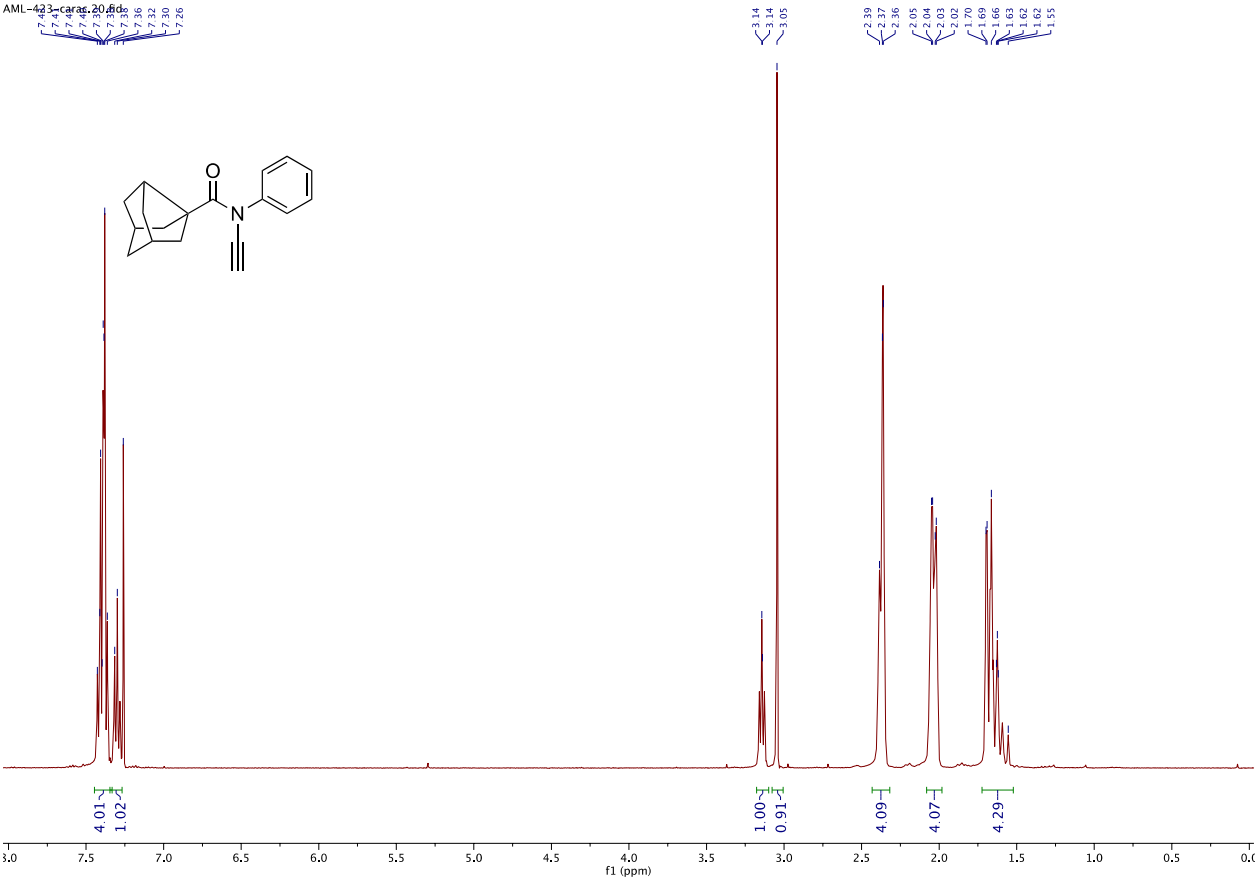
^{1}H NMR of **1r**



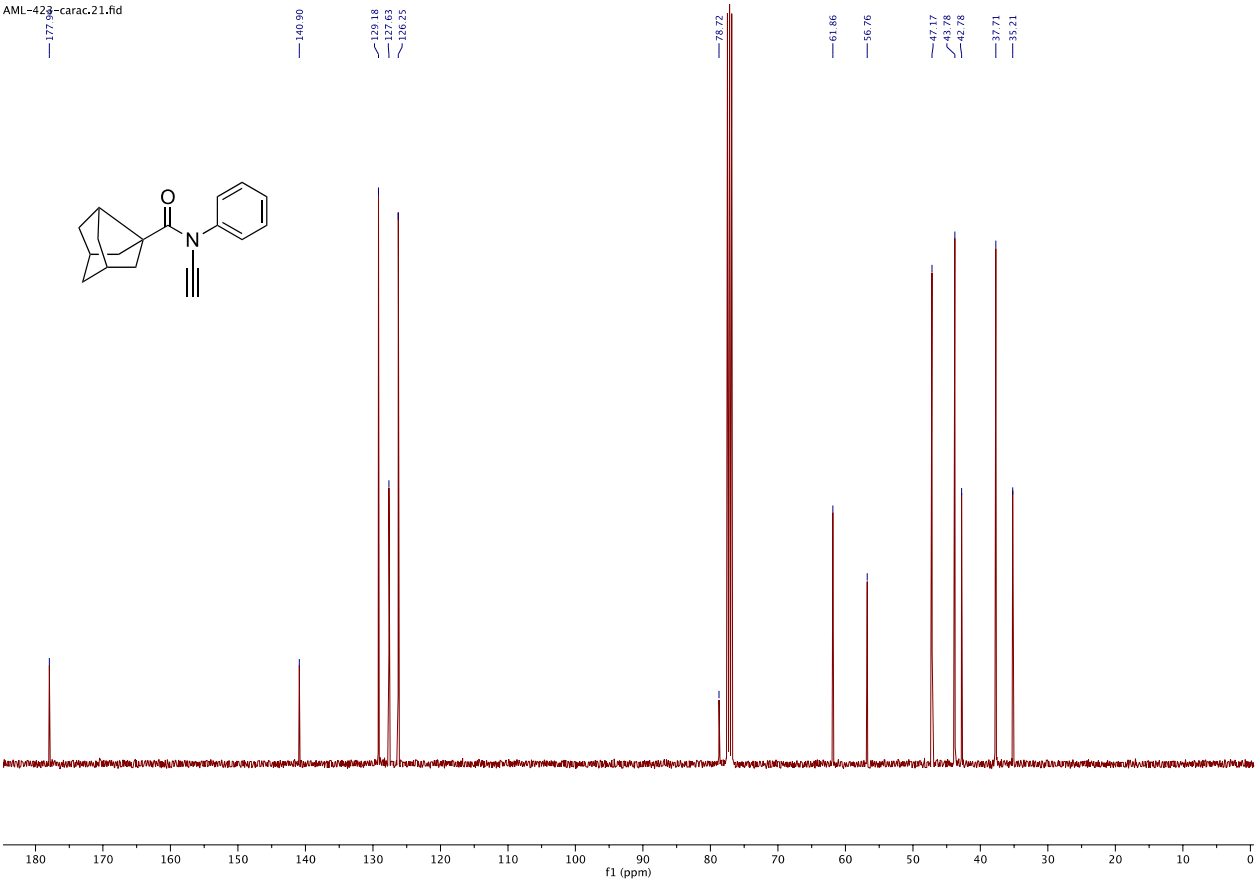
^{13}C NMR of **1r**



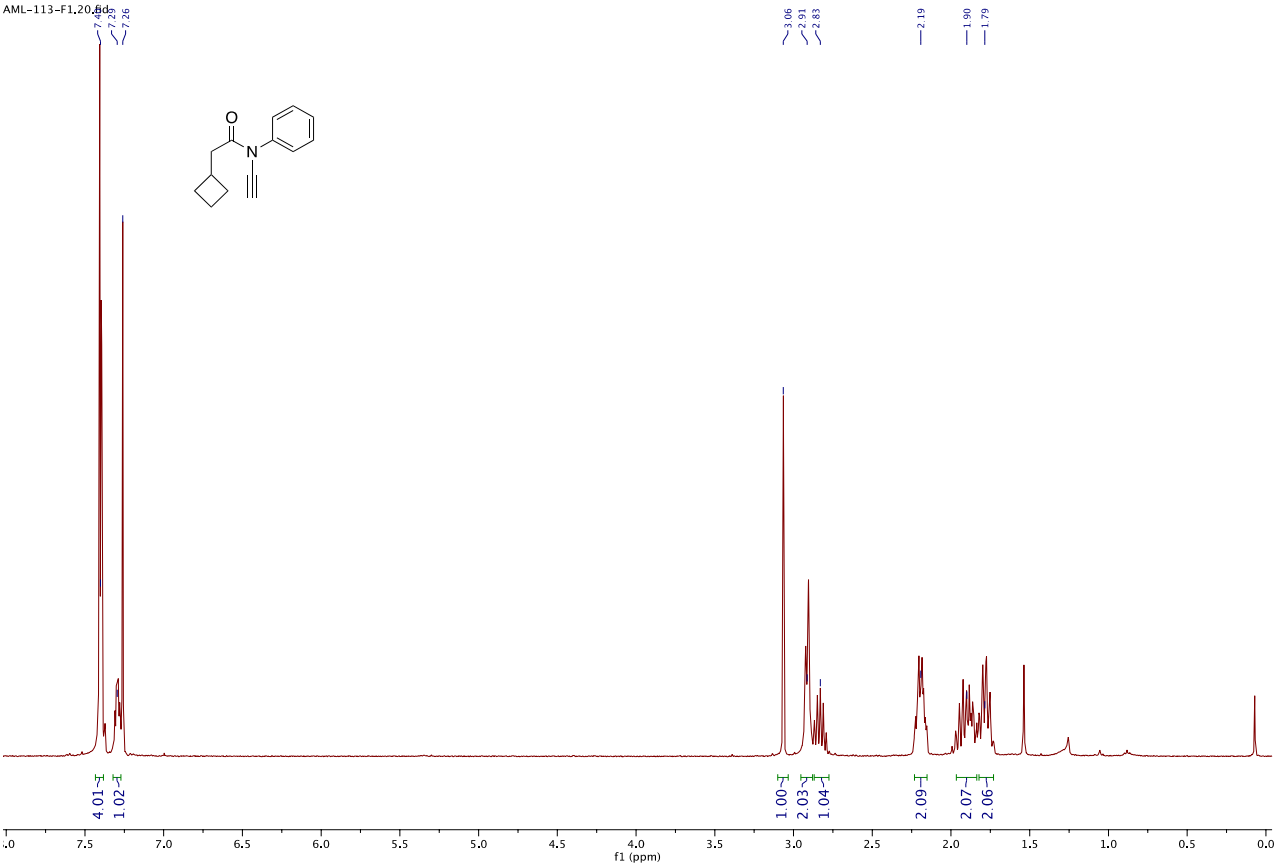
^{1}H NMR of **1s**



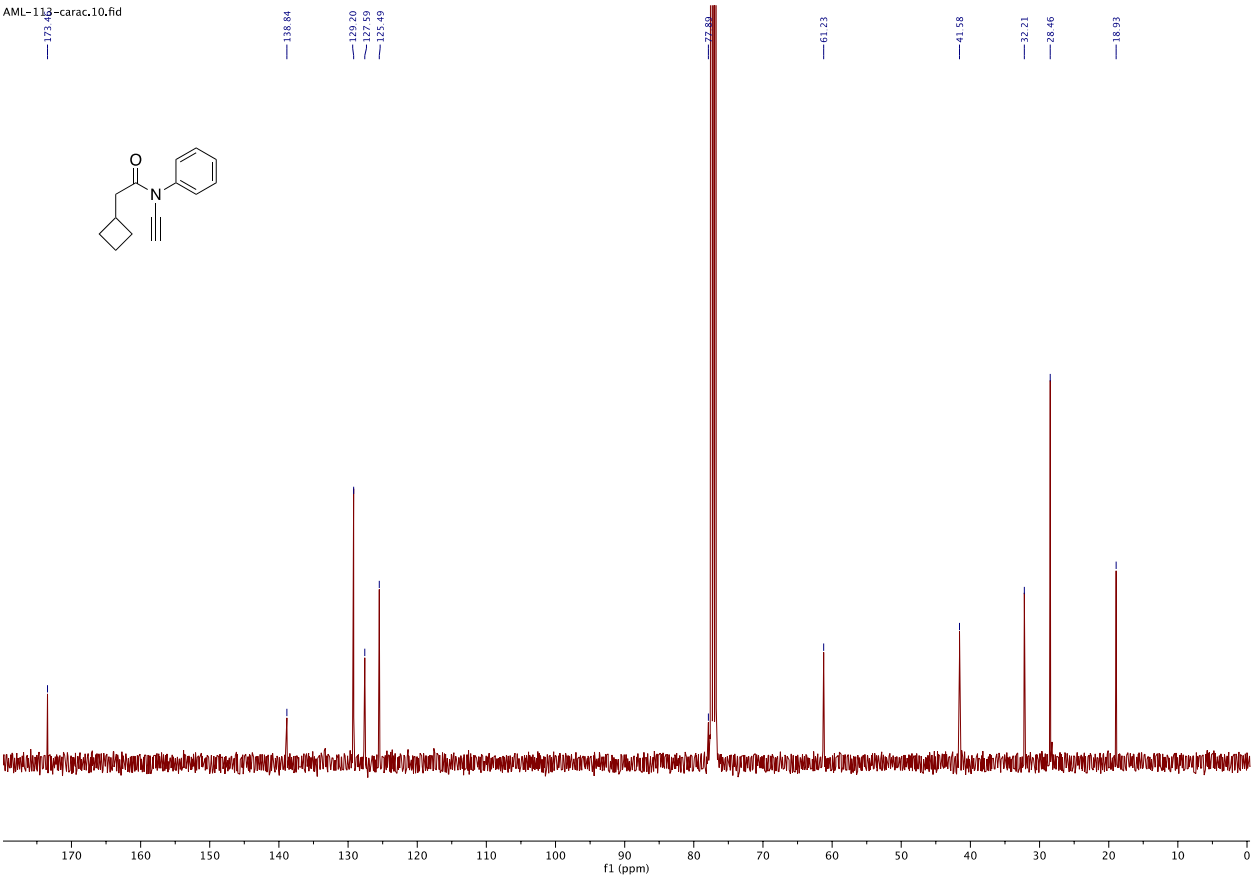
^{13}C NMR of **1s**



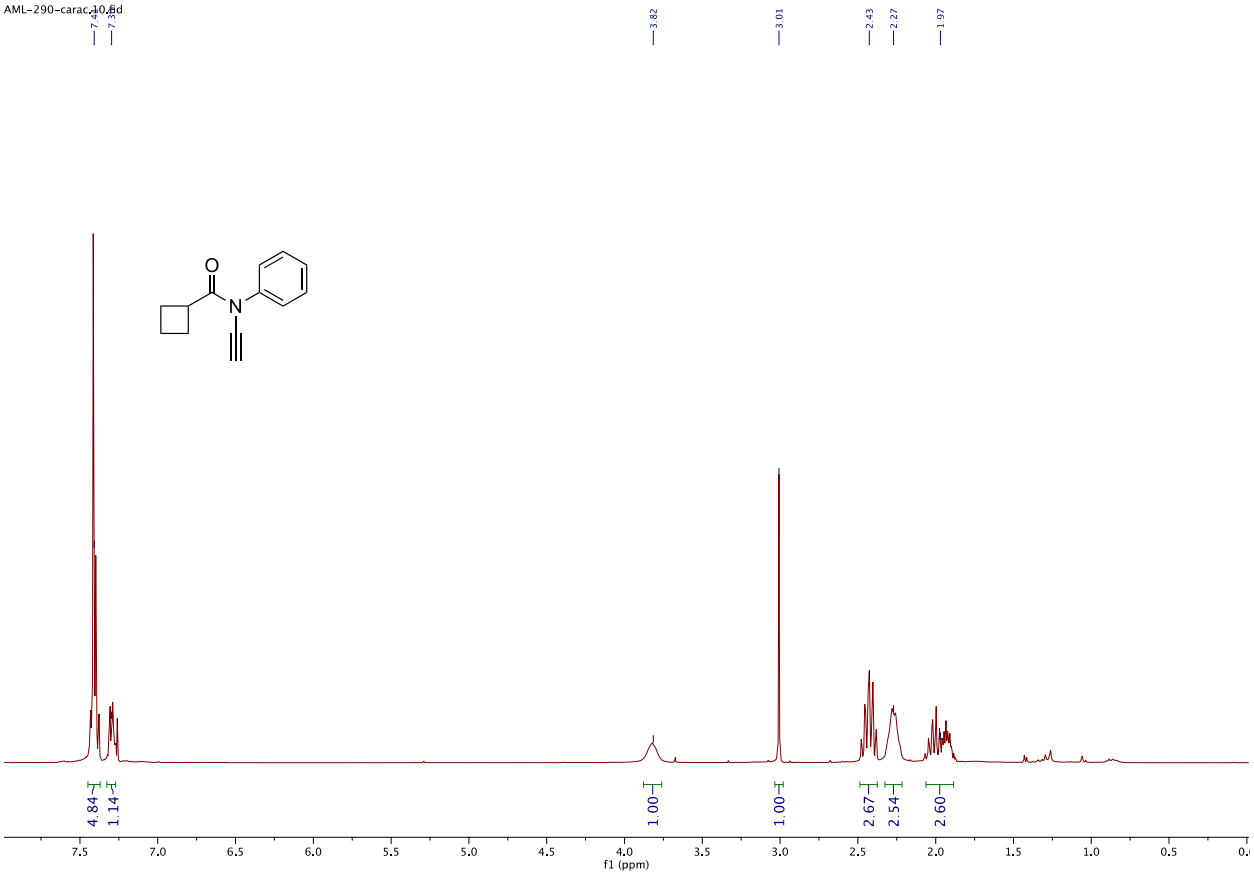
^{1}H NMR of **1t**



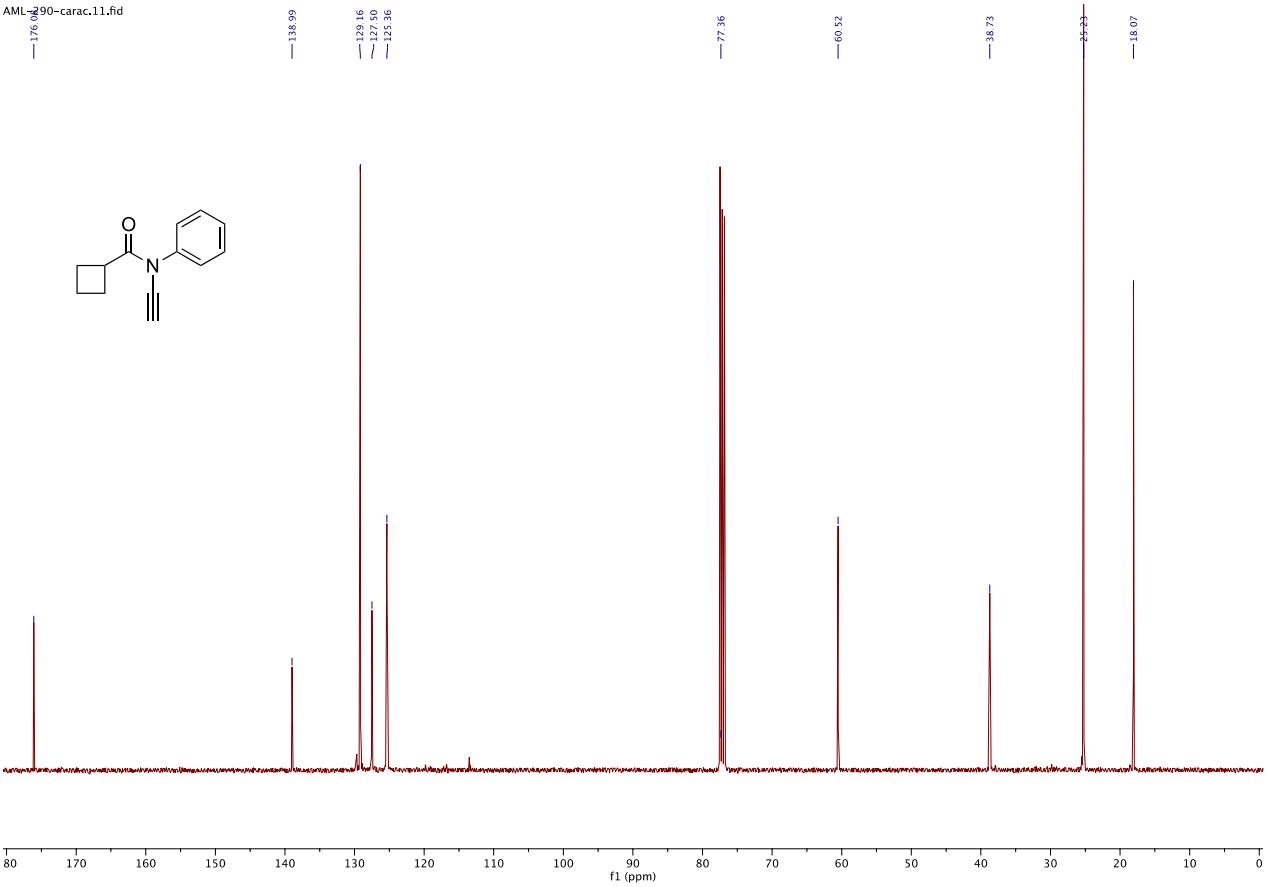
^{13}C NMR of **1t**



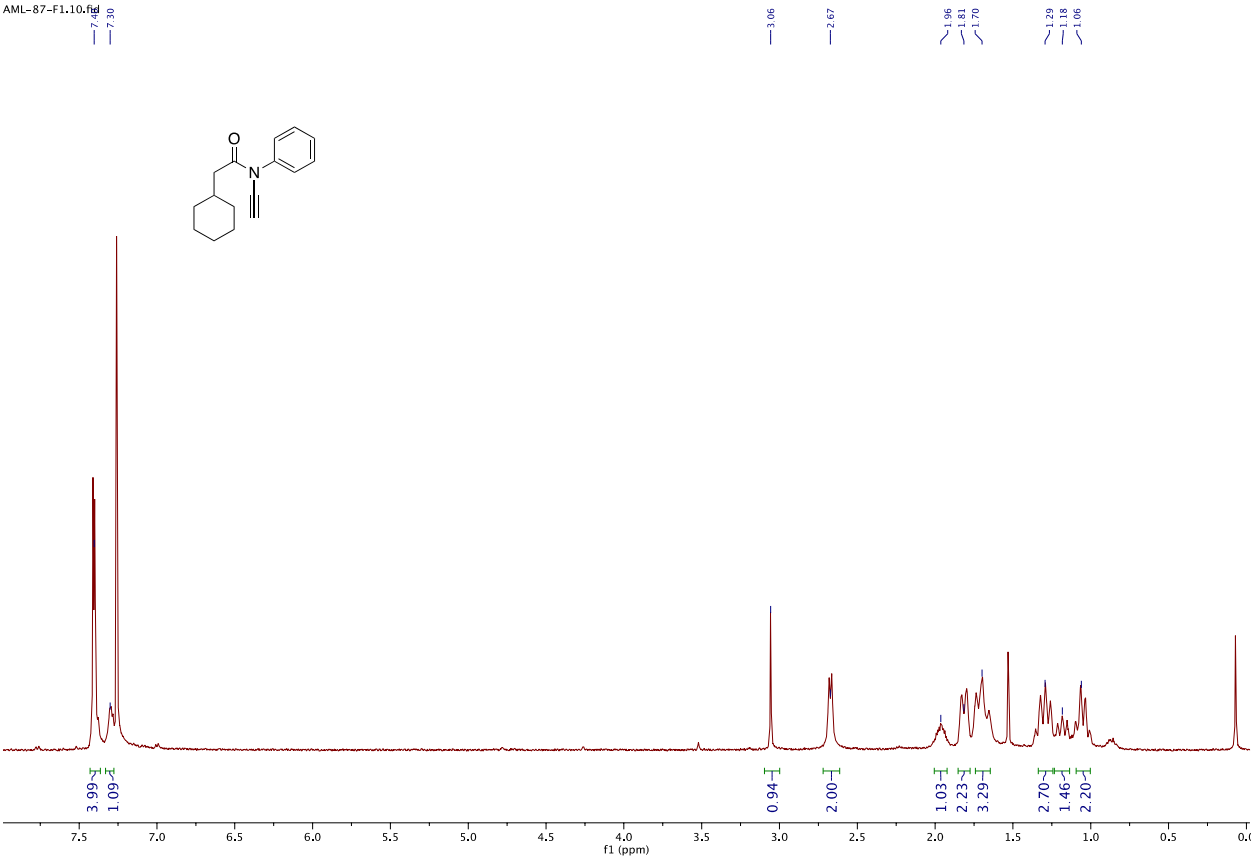
^{1}H NMR of **1u**



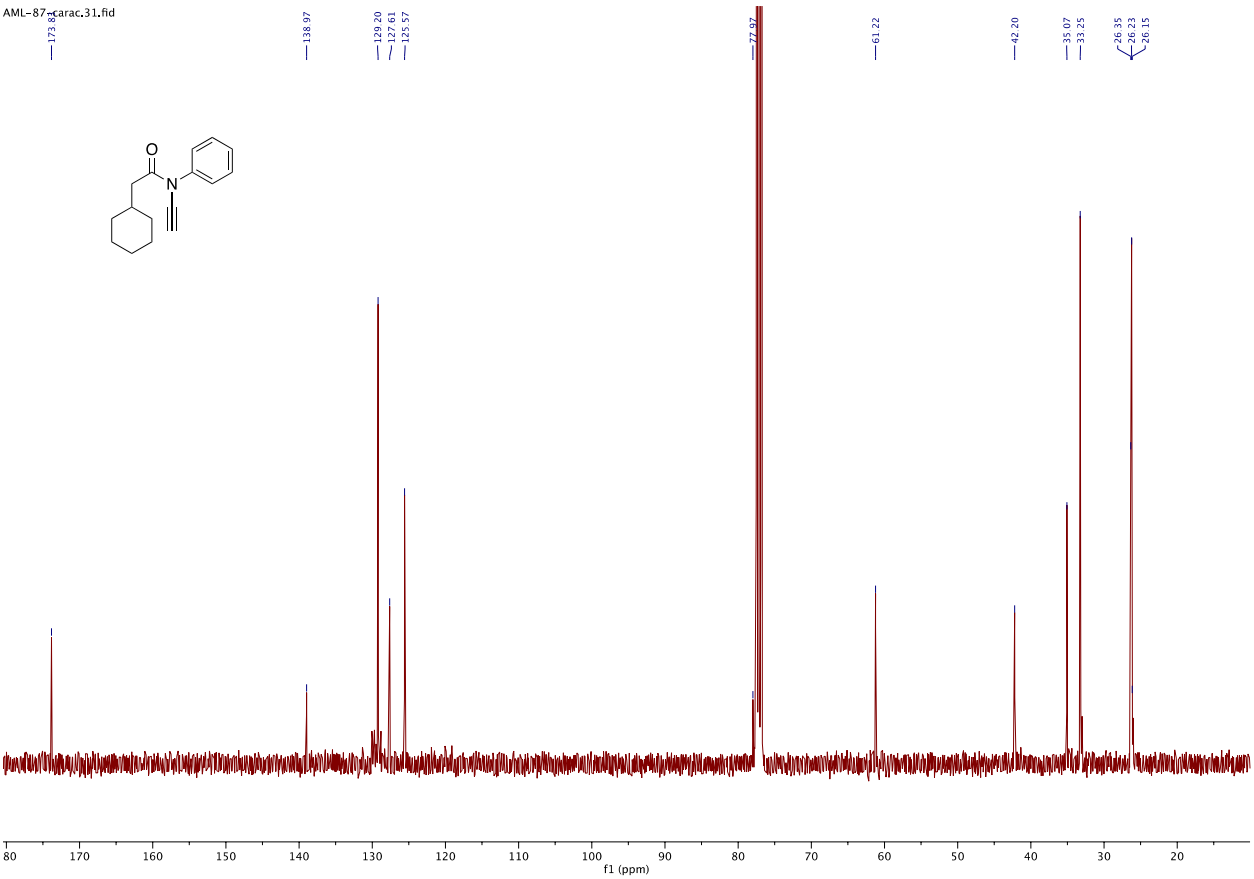
^{13}C NMR of **1u**



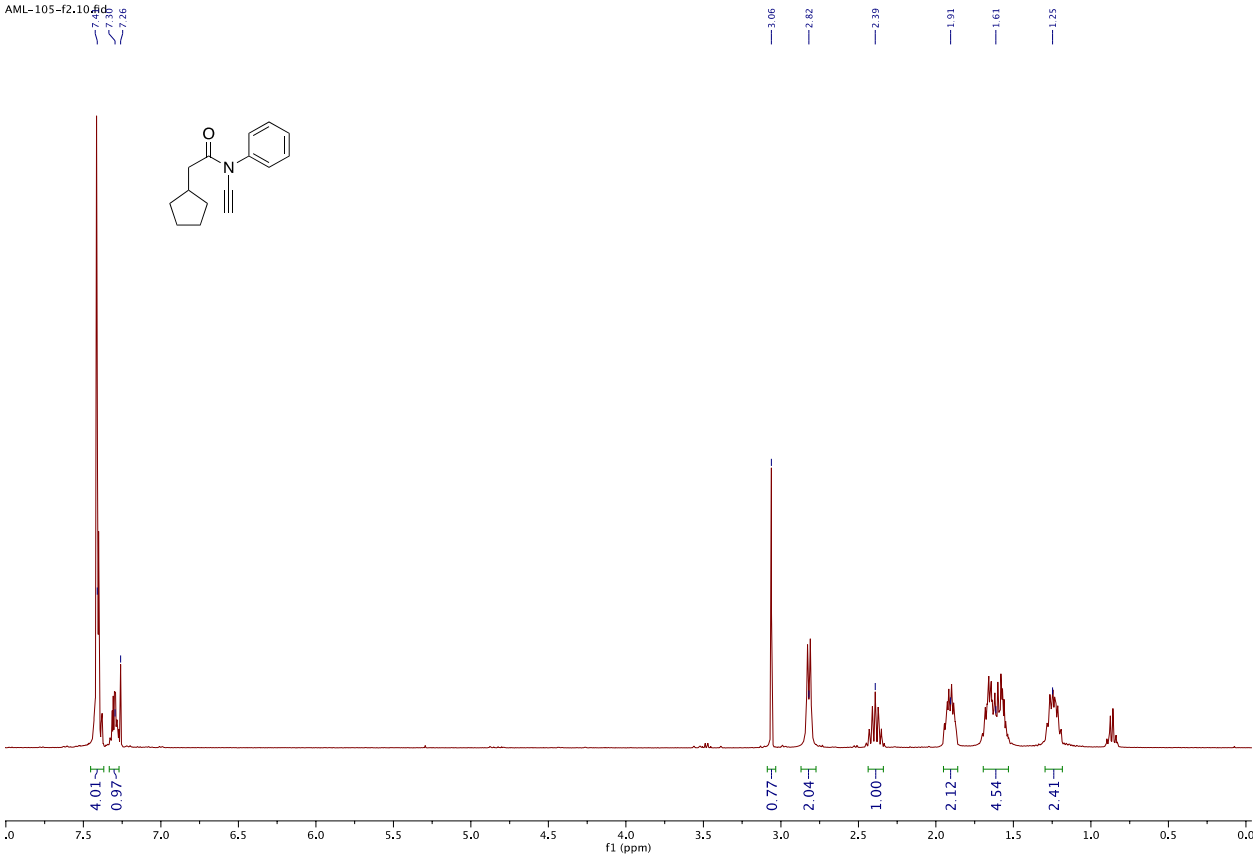
^{1}H NMR of **1v**



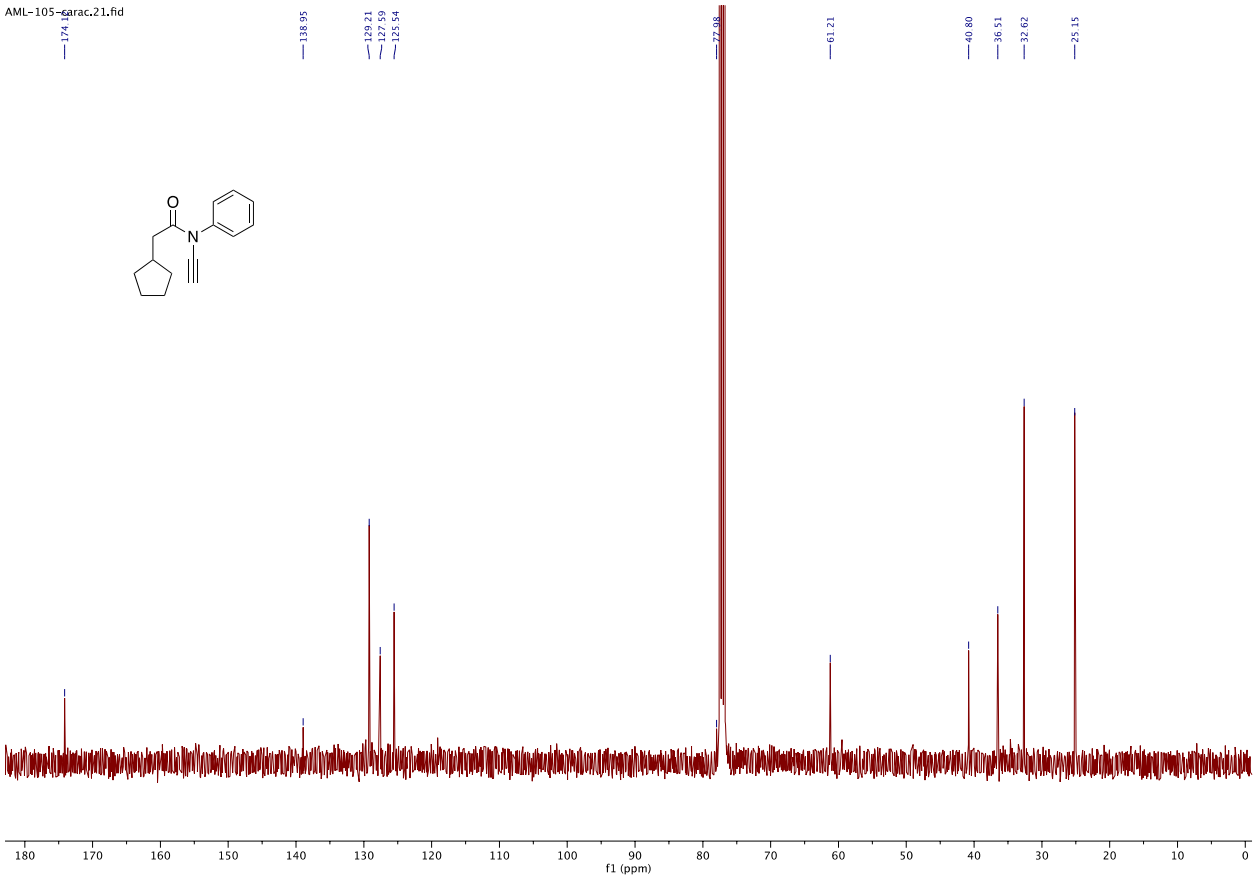
^{13}C NMR of **1v**



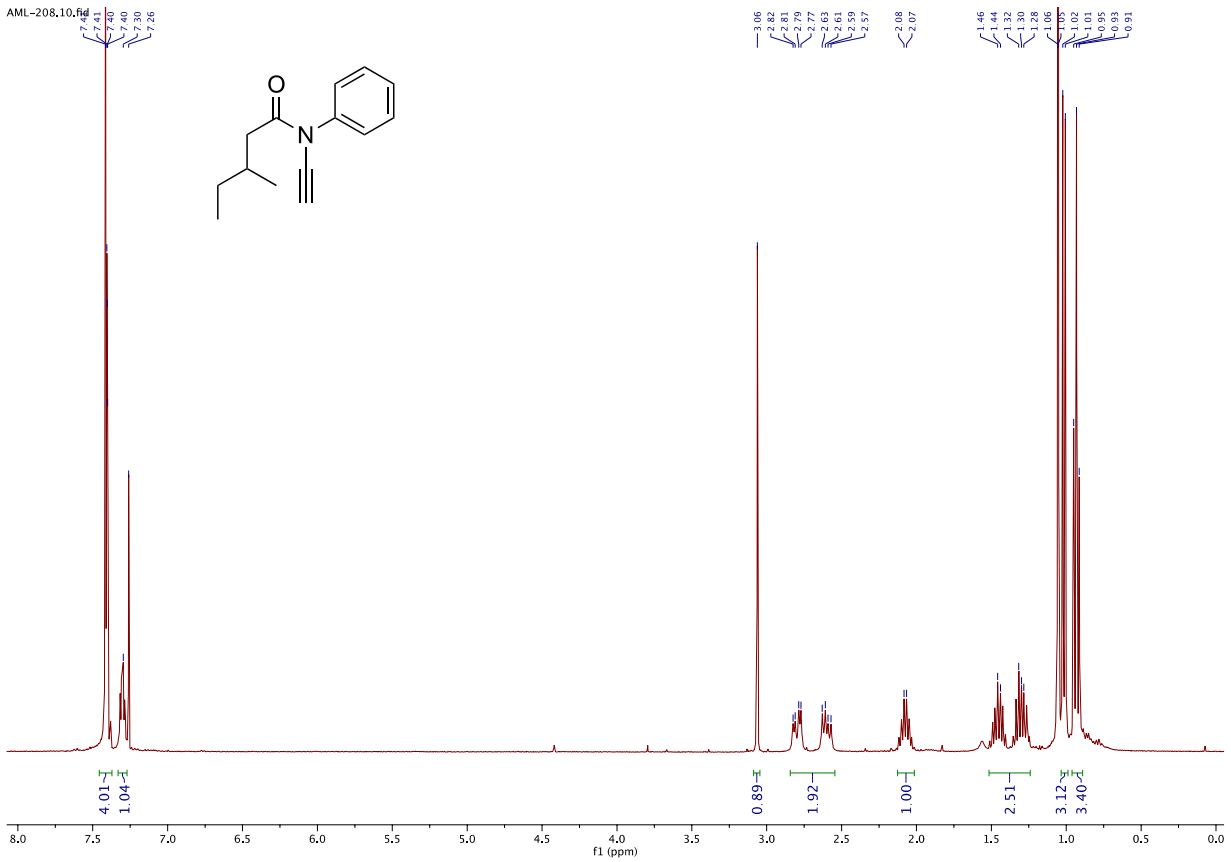
^{1}H NMR of **1w**



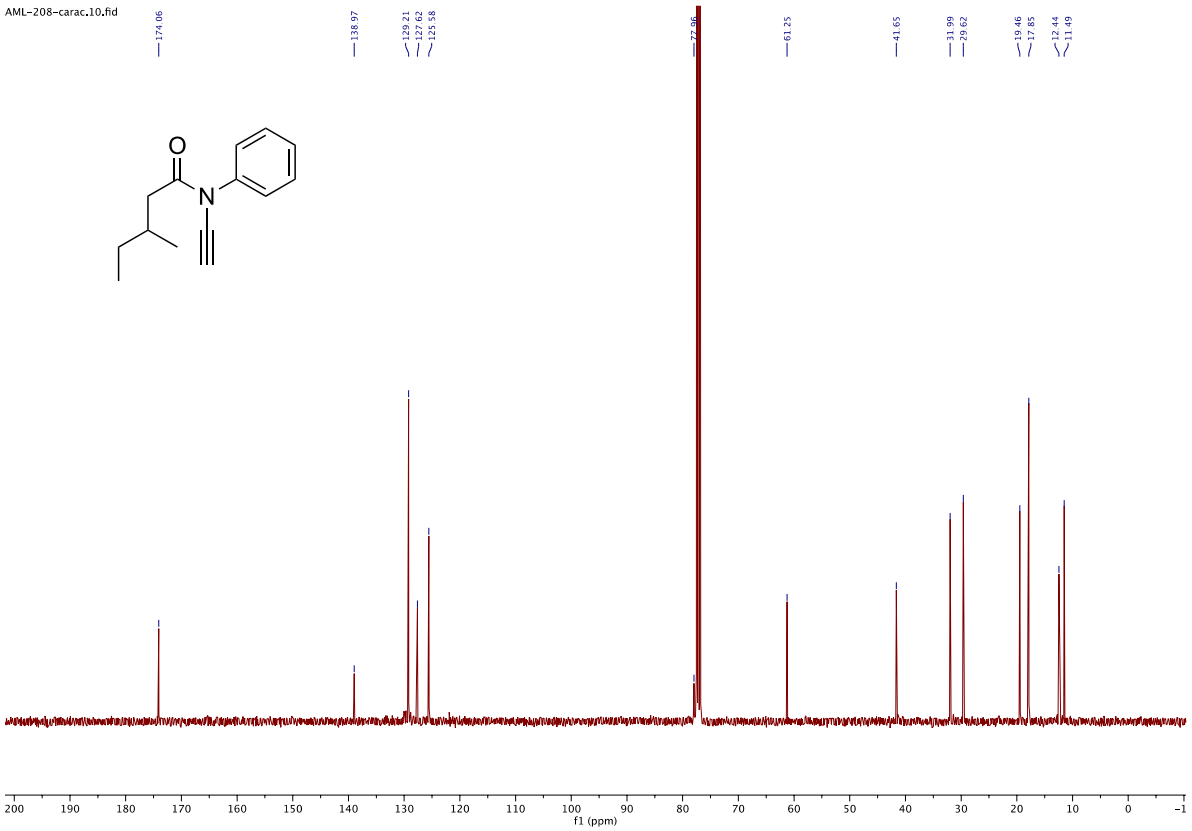
^{13}C NMR of **1w**



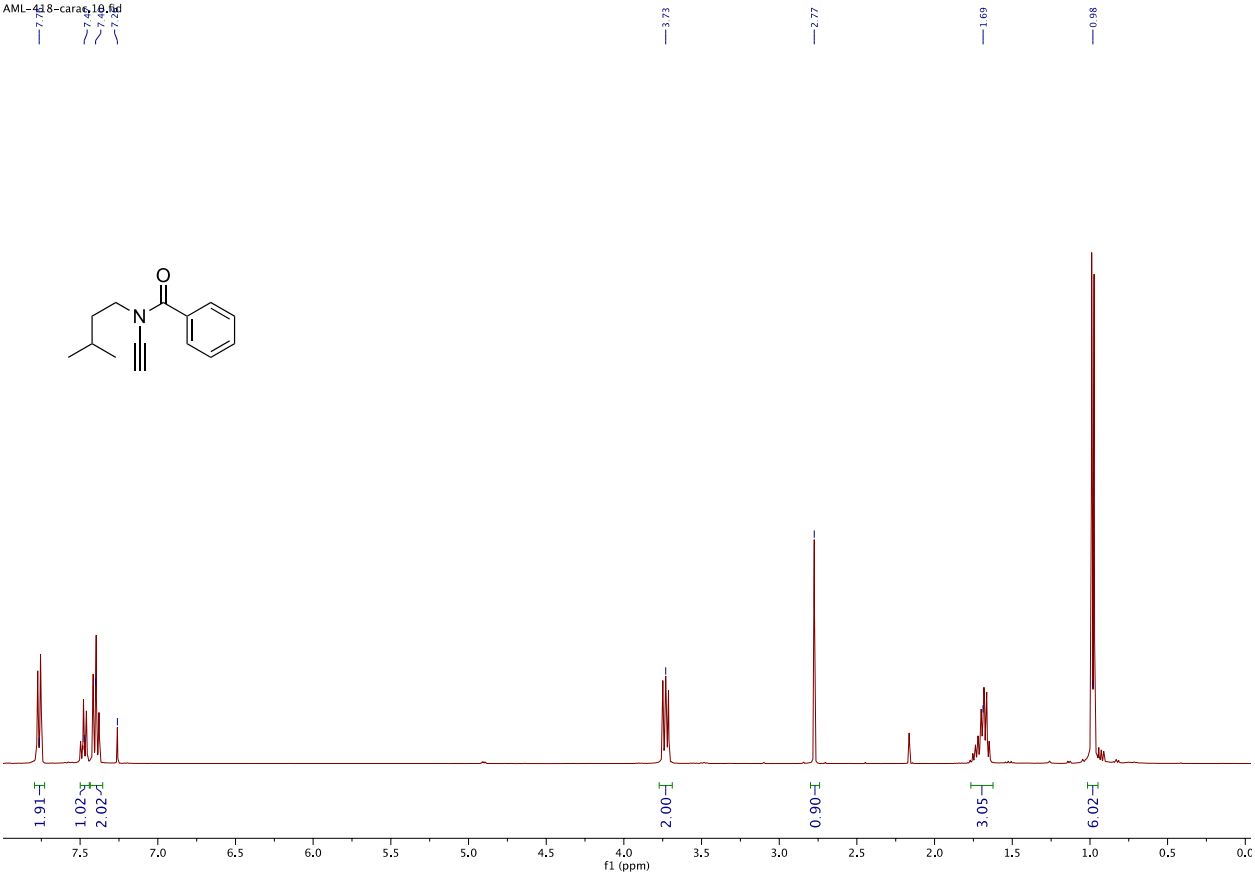
^{1}H NMR of **1x**



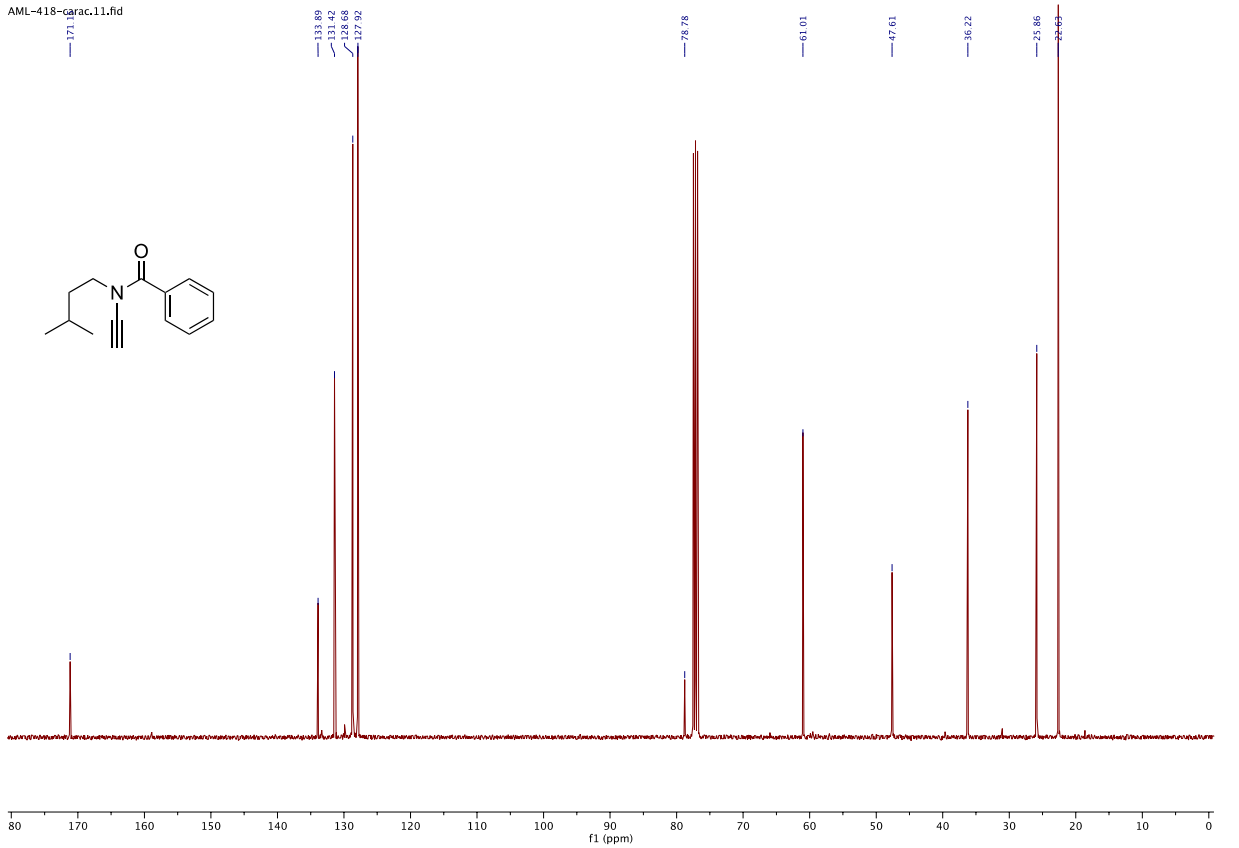
^{13}C NMR of **1x**



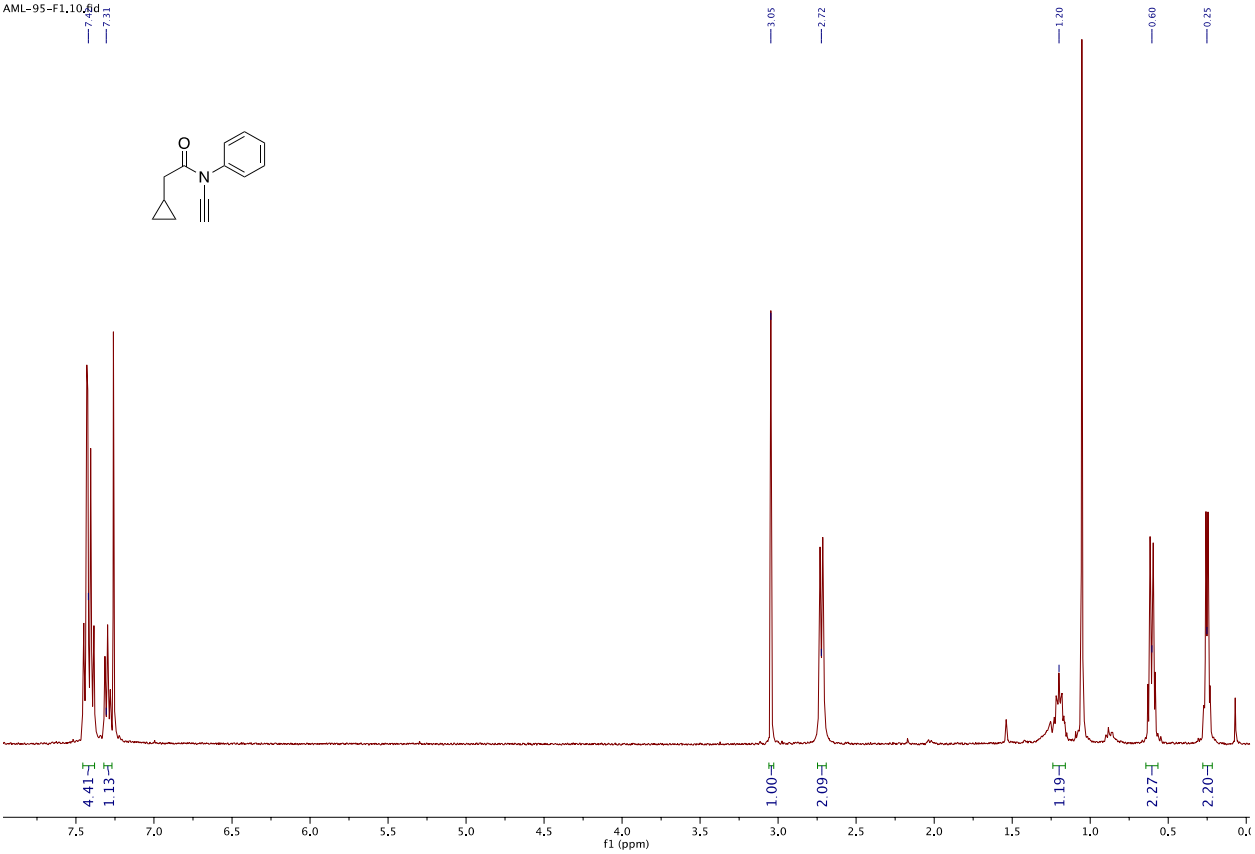
^{1}H NMR of **1z**



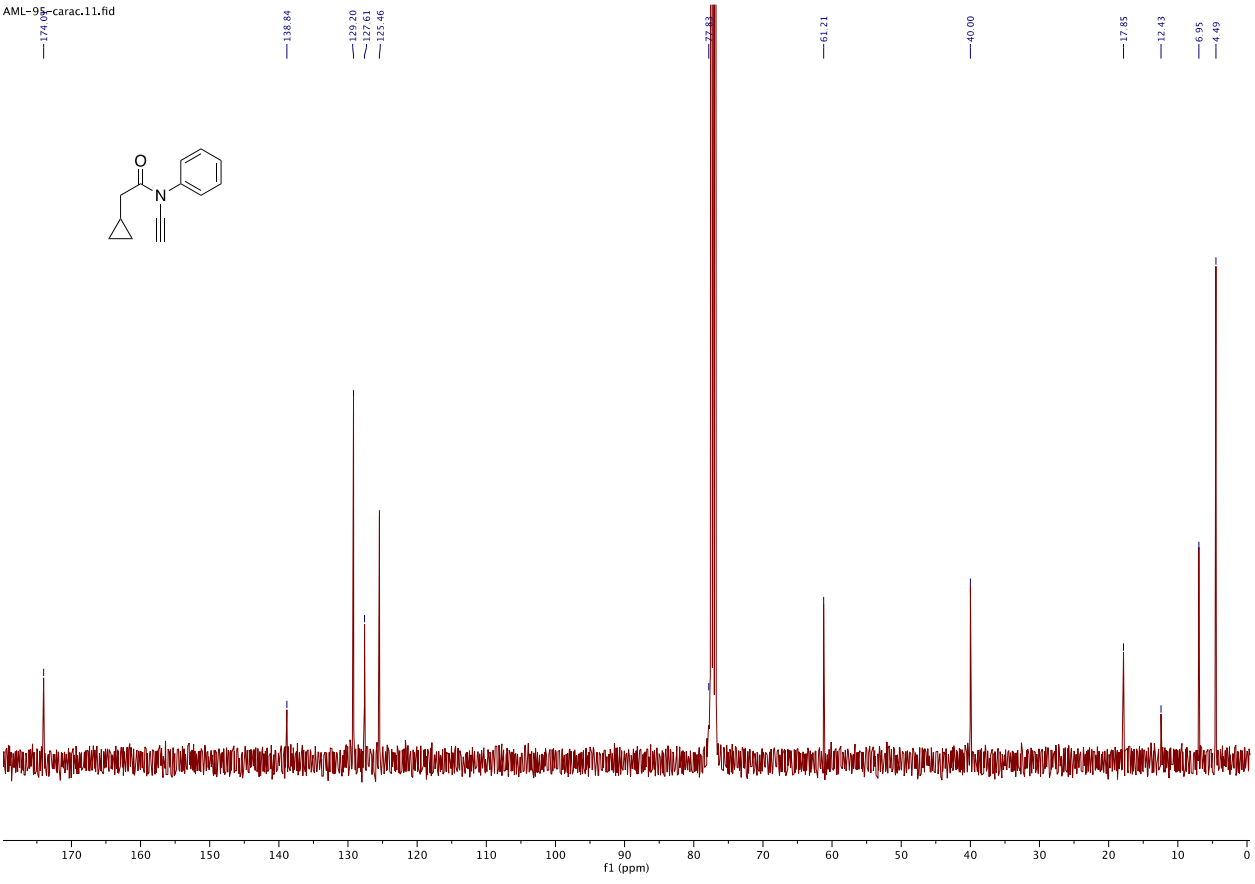
^{13}C NMR of **1z**



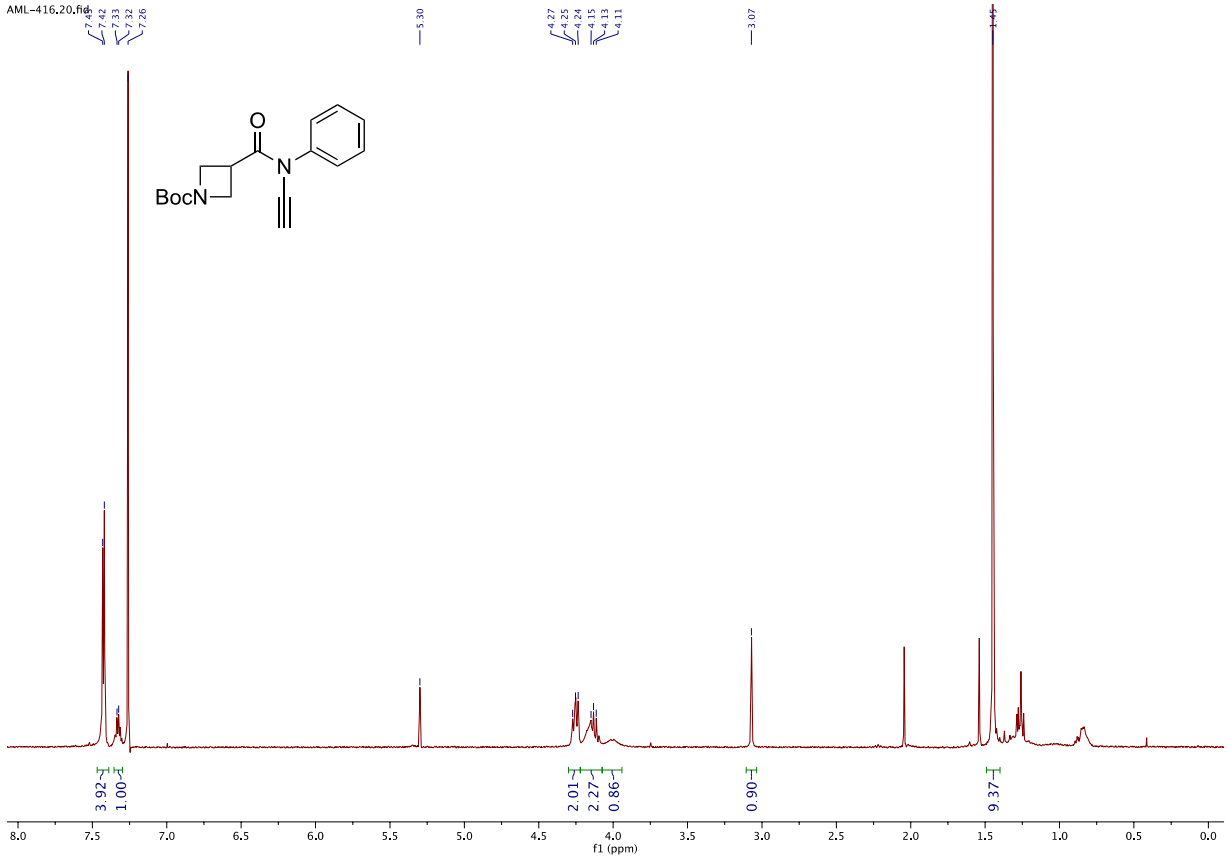
^{1}H NMR of **Y1**



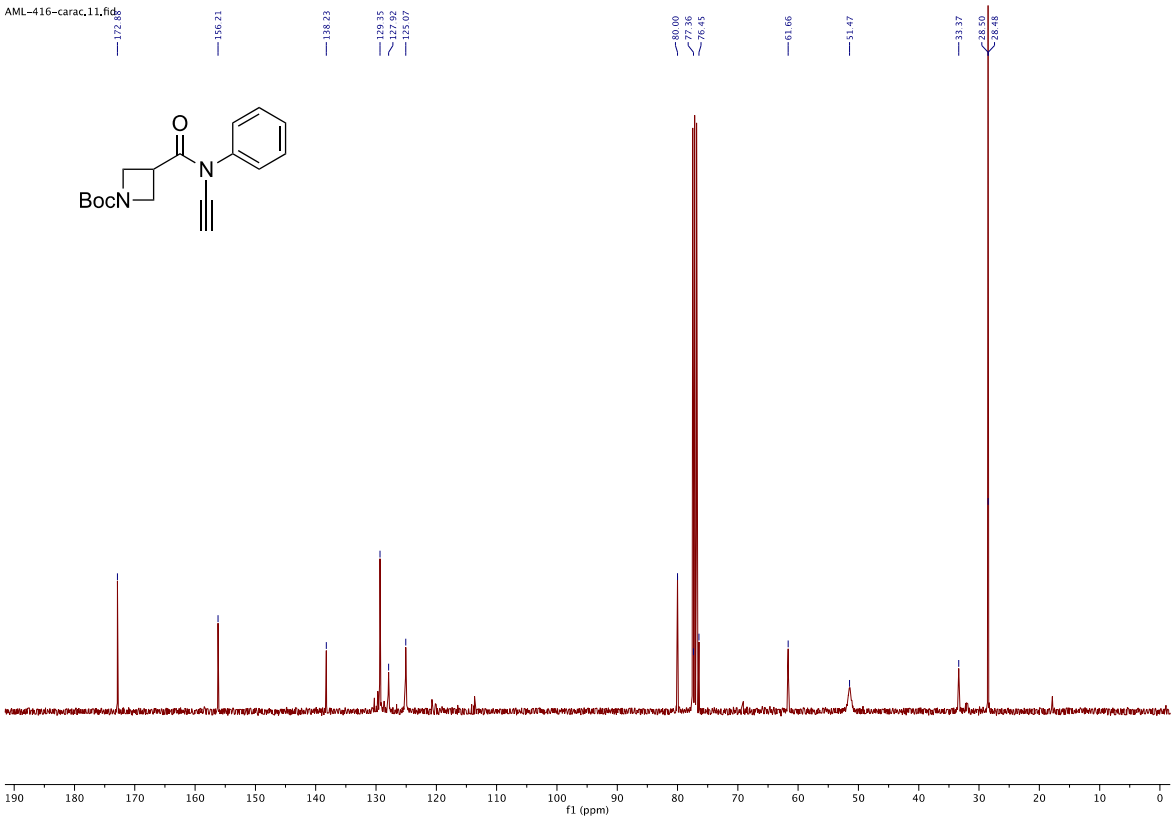
^{13}C NMR of **Y1**



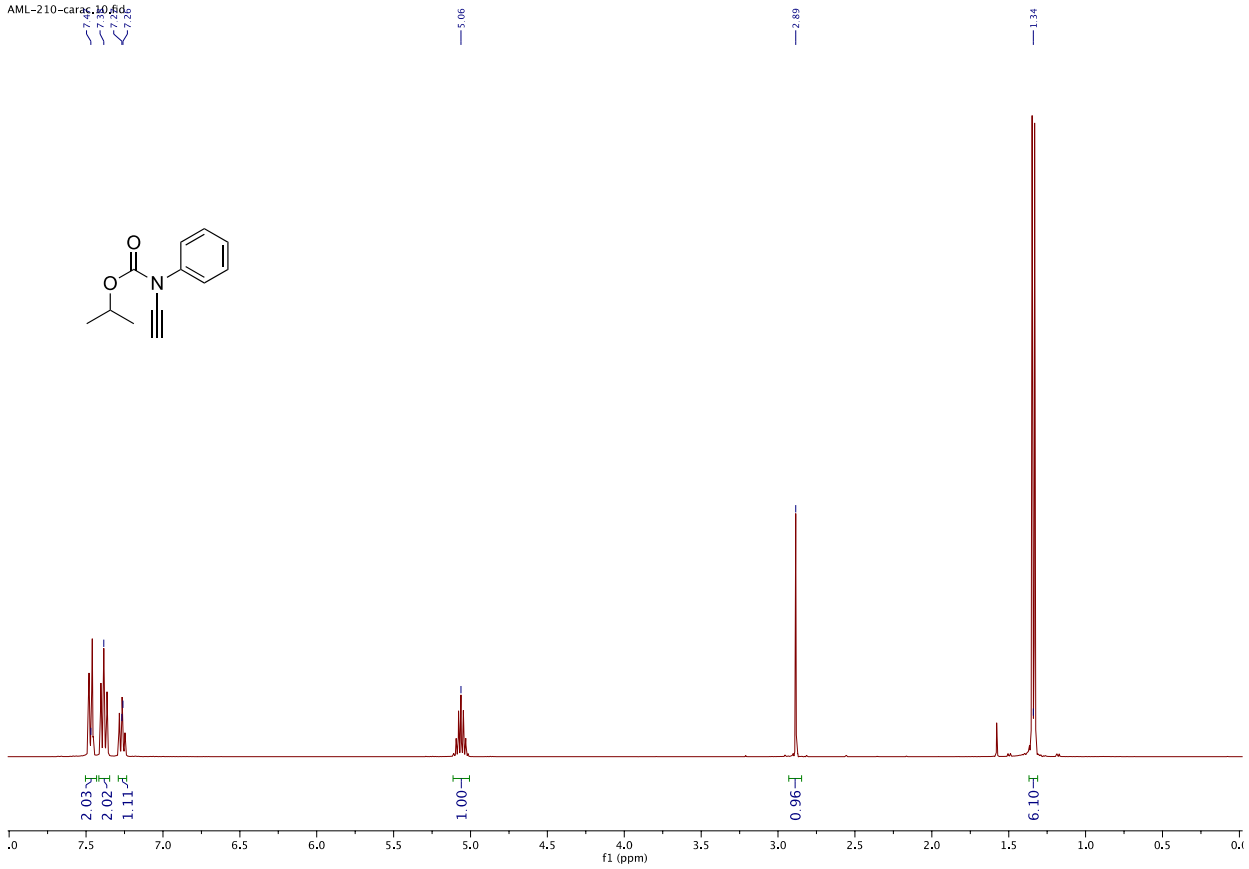
^{1}H NMR of **Y2**



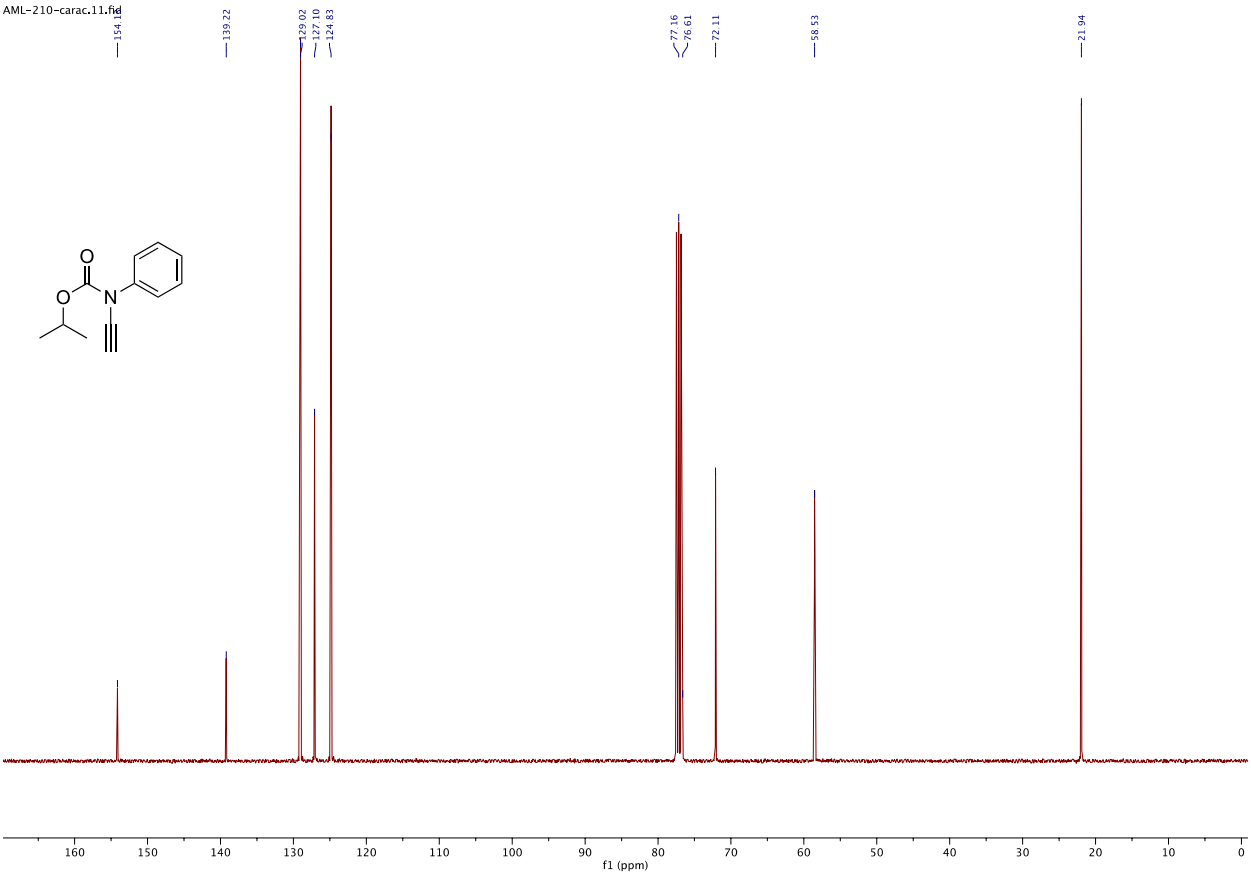
^{13}C NMR of **Y2**



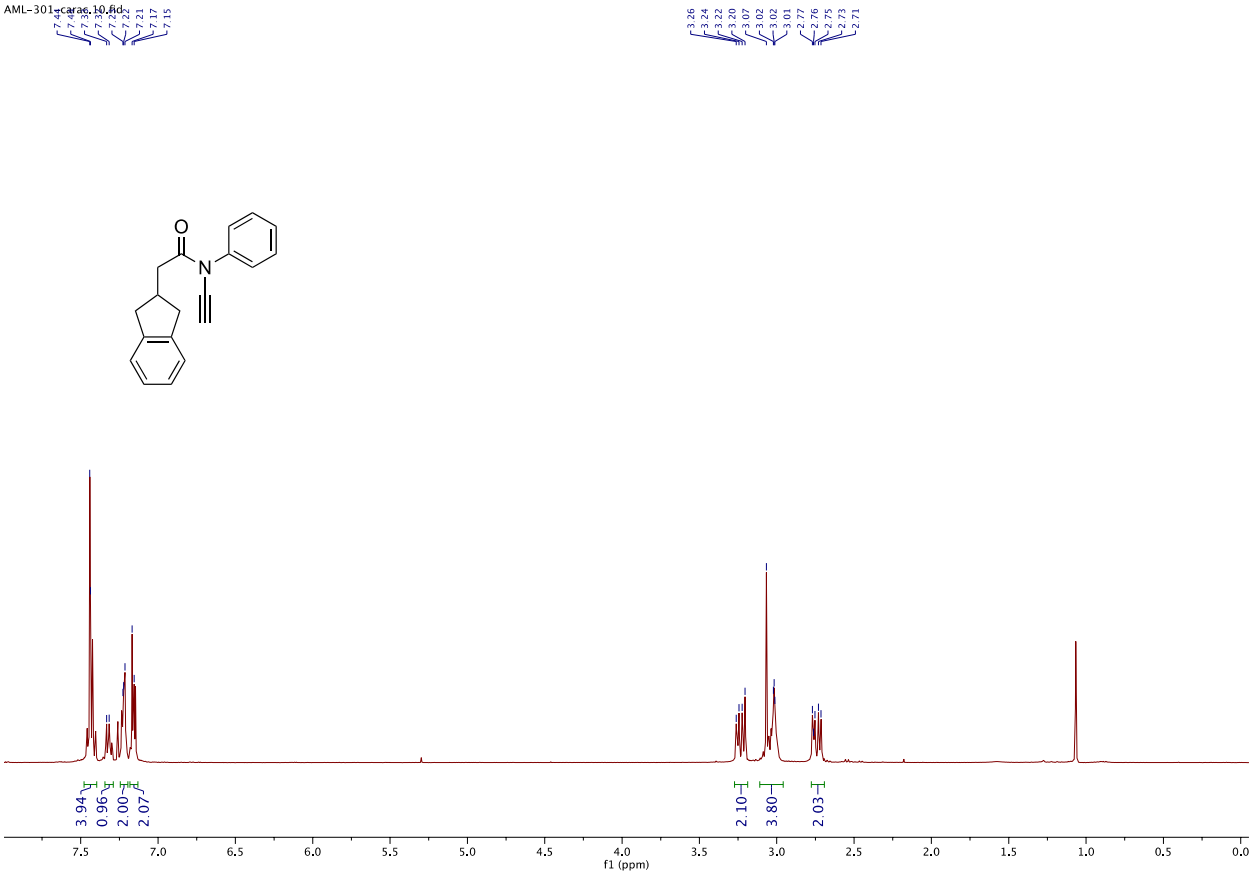
^{1}H NMR of **Y3**



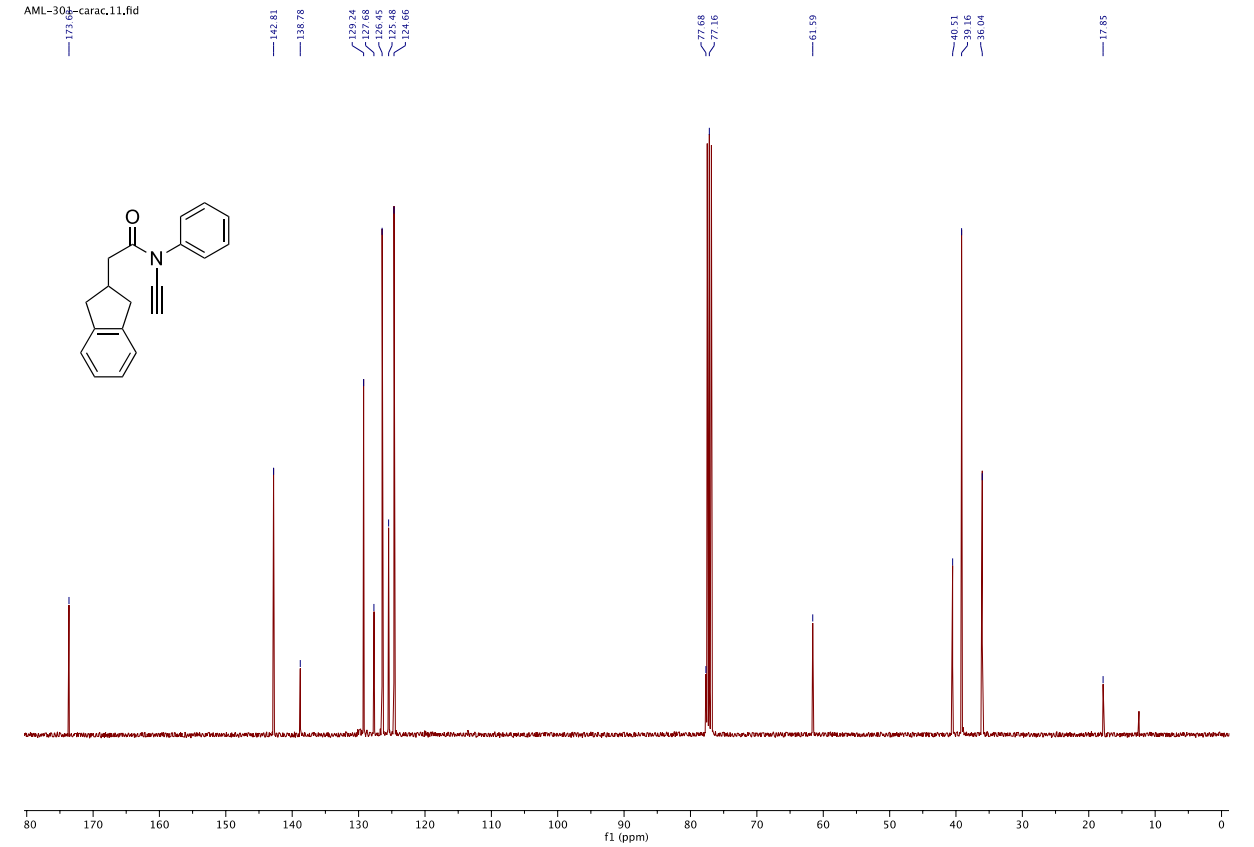
^{13}C NMR of **Y3**



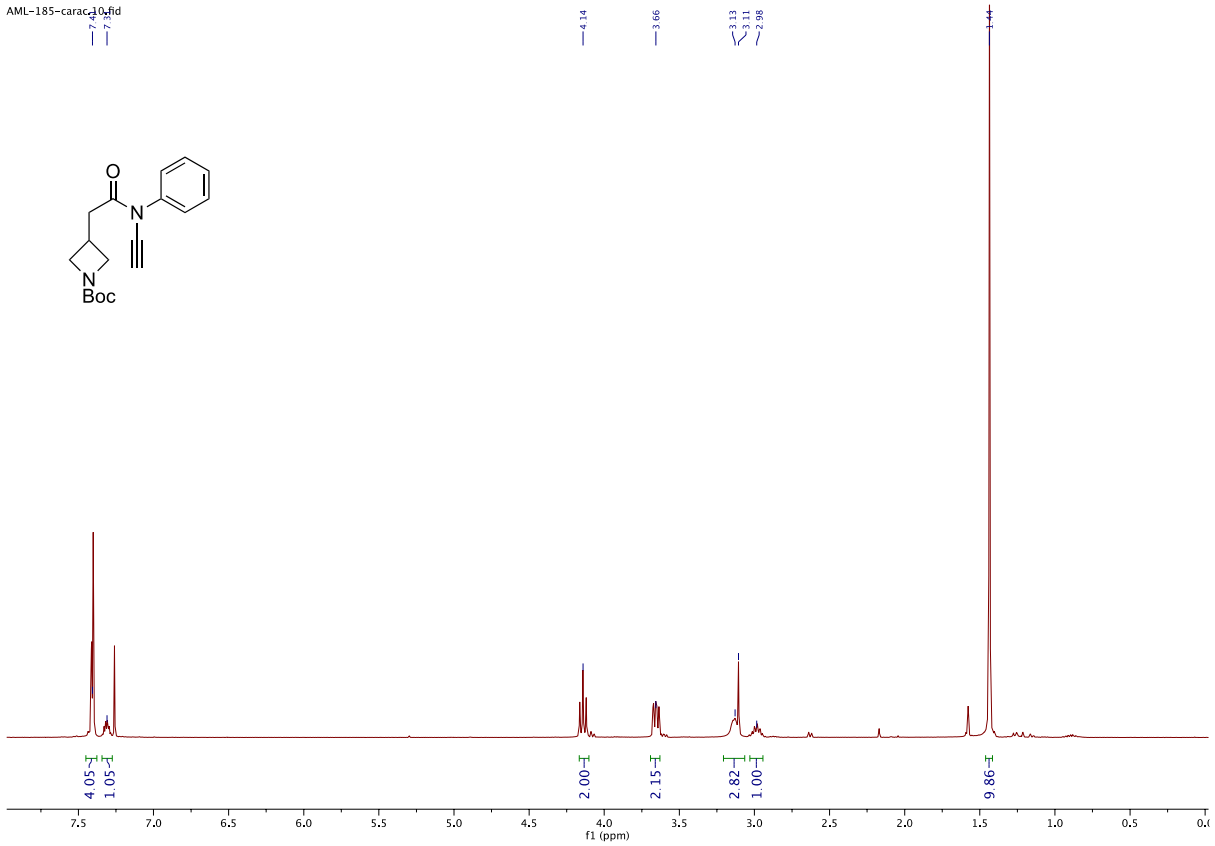
^{1}H NMR of **Y4**



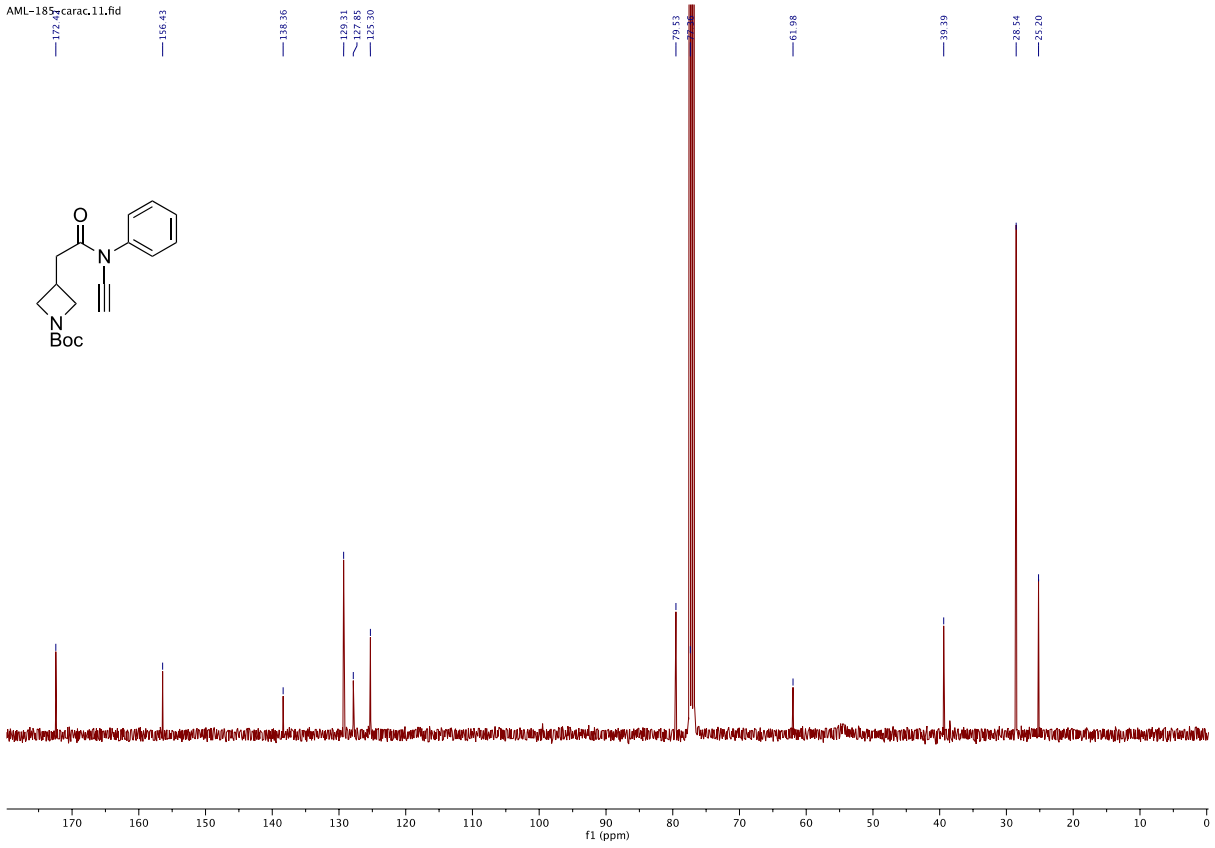
^{13}C NMR of **Y4**



^{1}H NMR of **Y5**

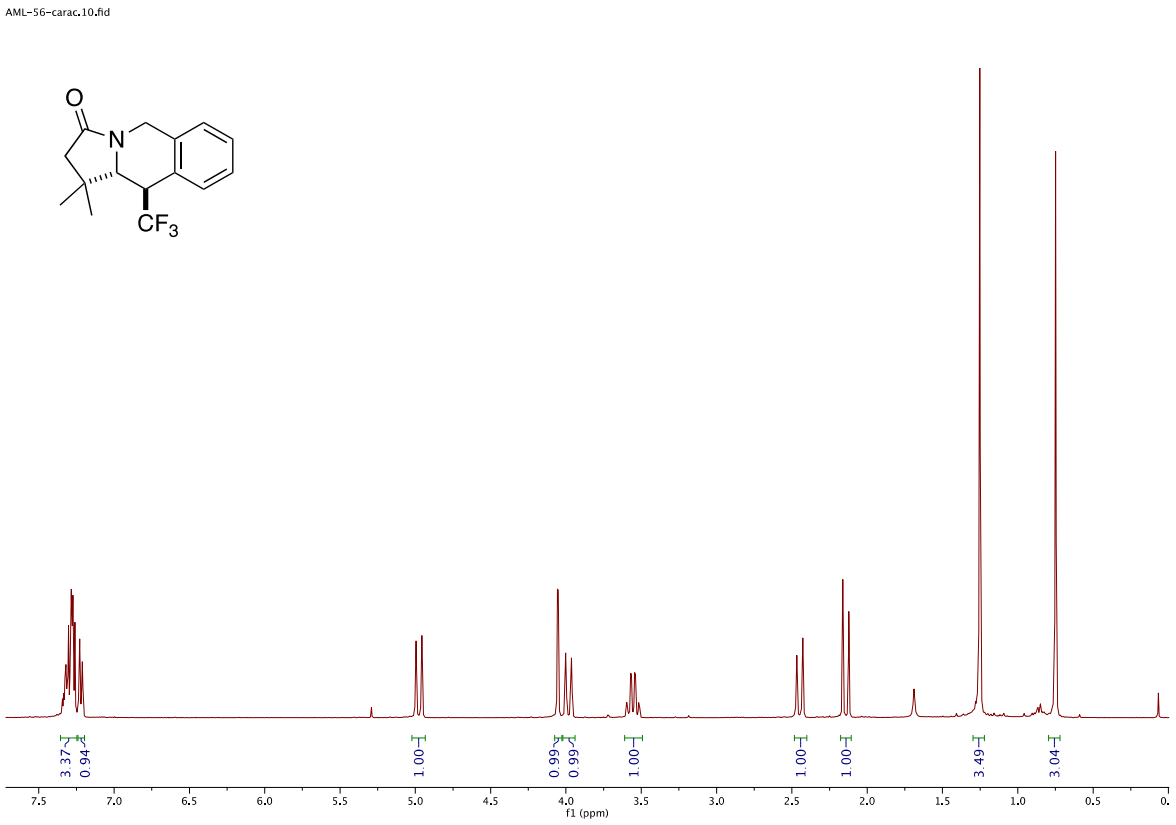


^{13}C NMR of **Y5**

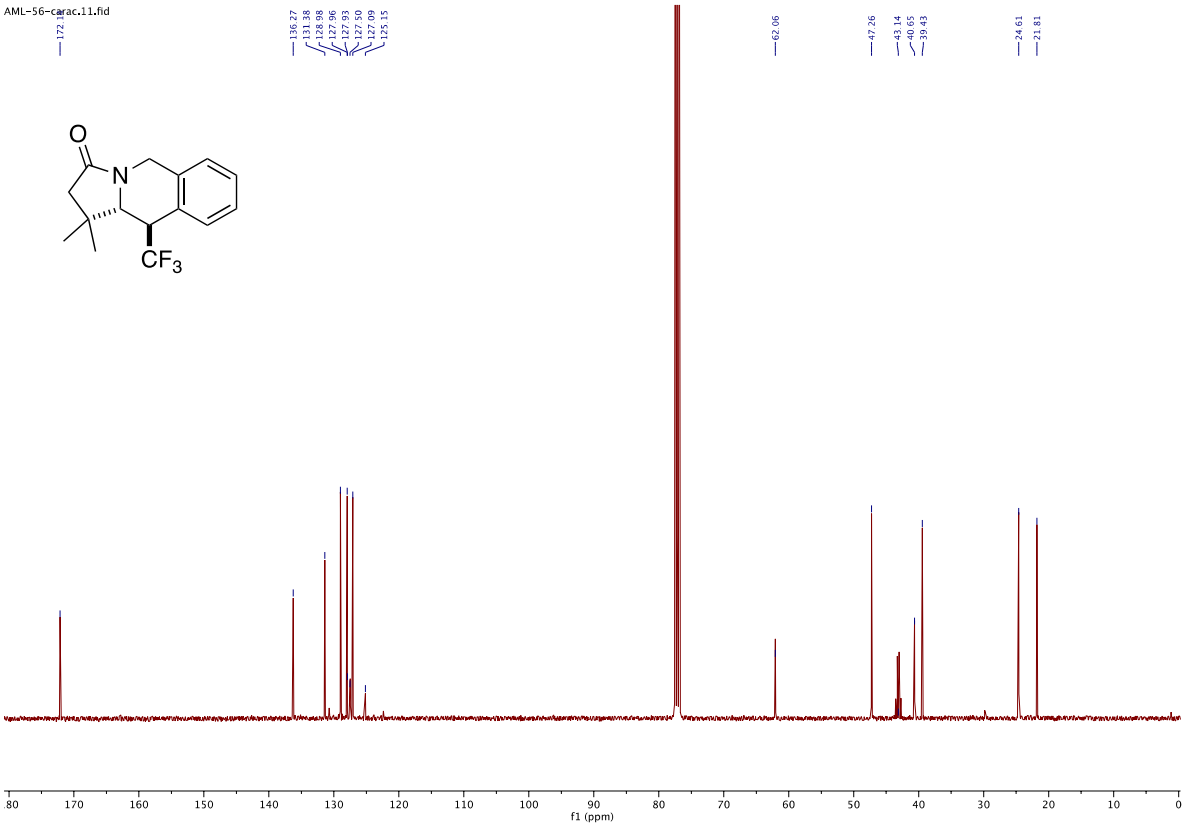


9.3 Trifluoromethylated products

^{1}H NMR of **2a**

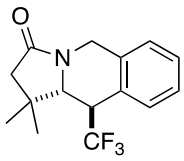


^{13}C NMR of **2a**



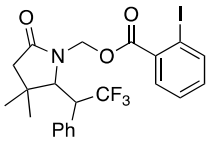
^{19}F NMR of **2a**

AML-56-F2.11.fid

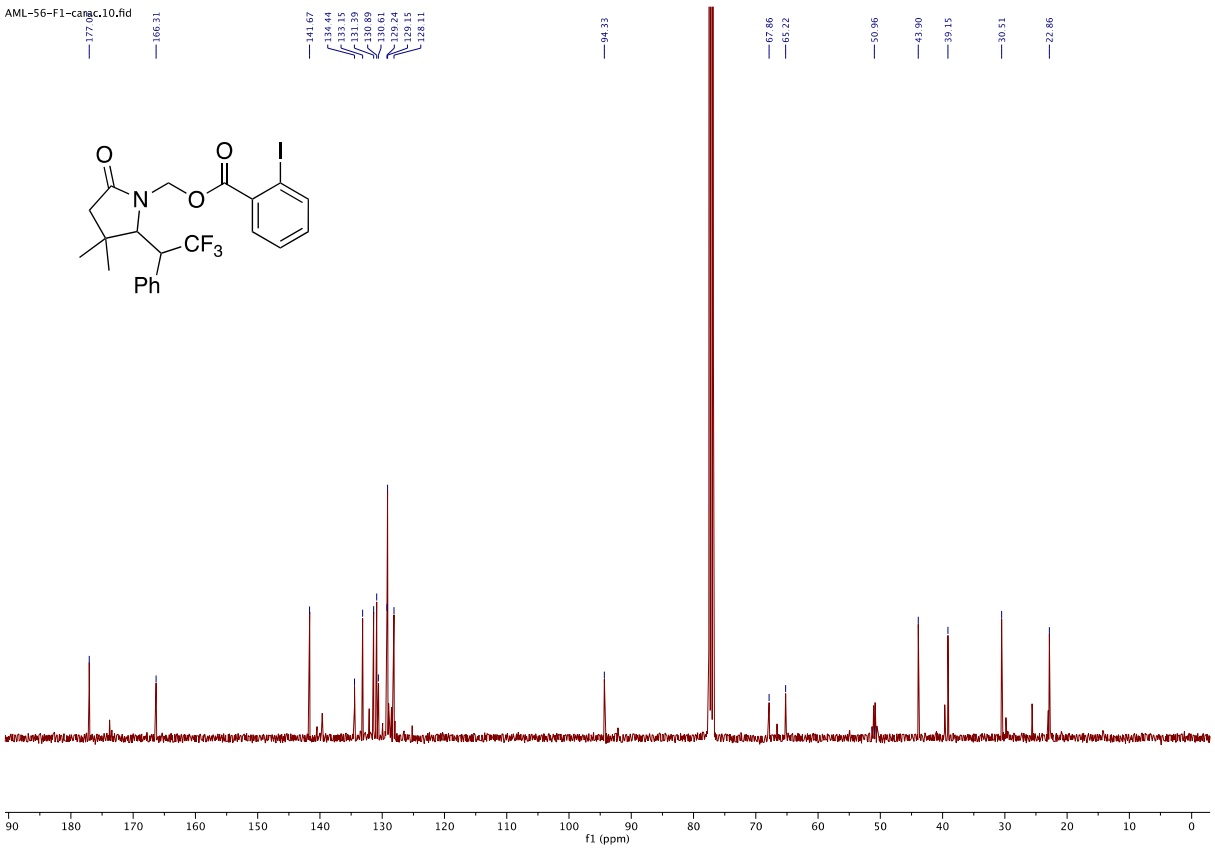


^{1}H NMR of **2aa**

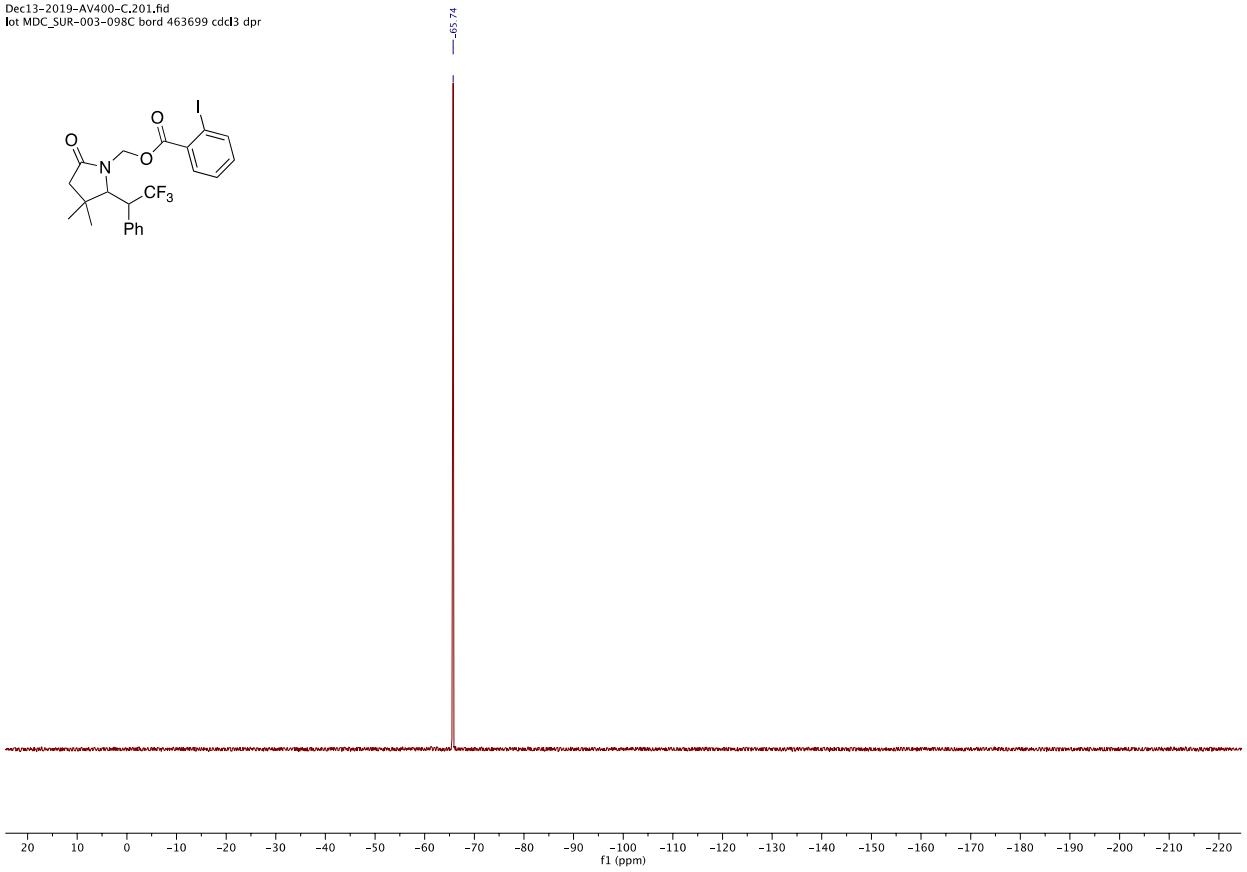
463699C.10.fid
lot MDC_SUR-003-098C bord 463699 cdcl3 cne



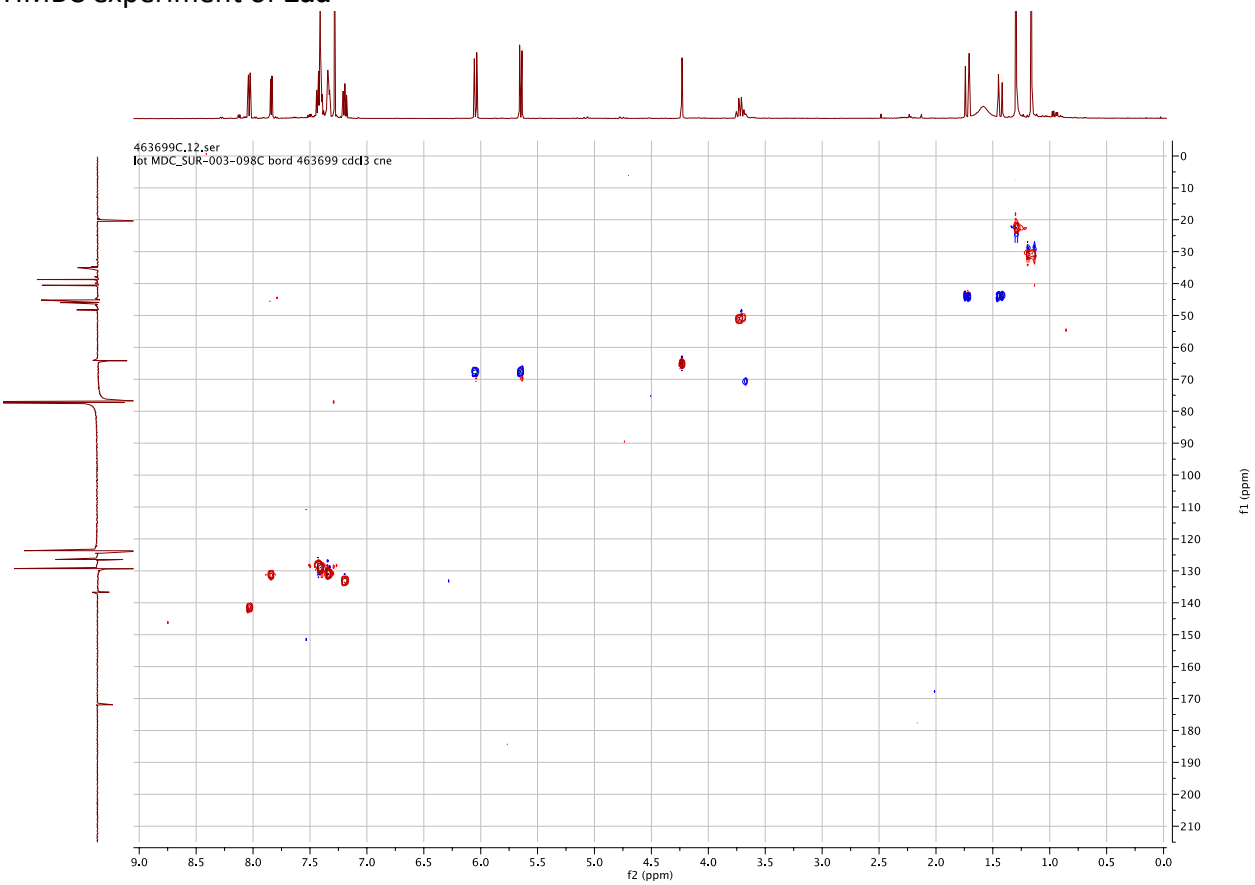
^{13}C NMR of **2aa**



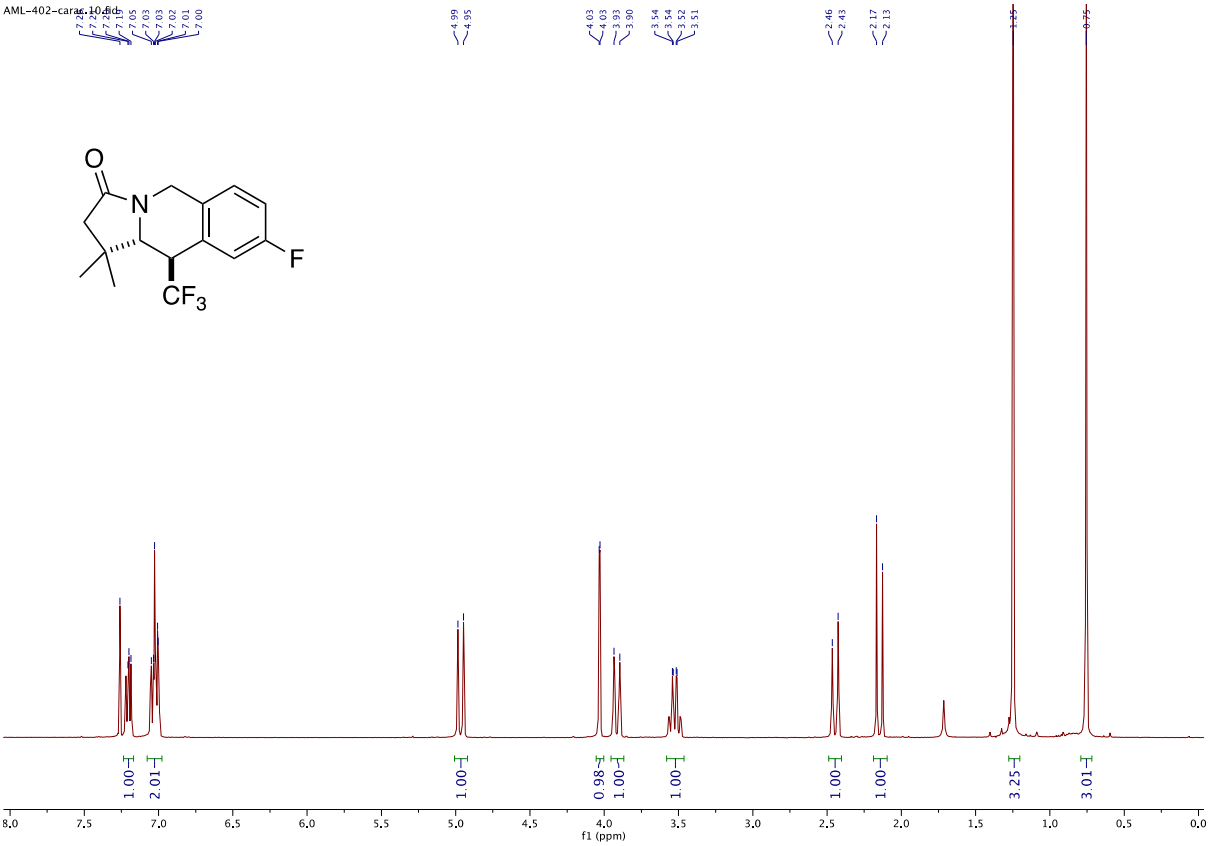
^{19}F NMR of **2aa**



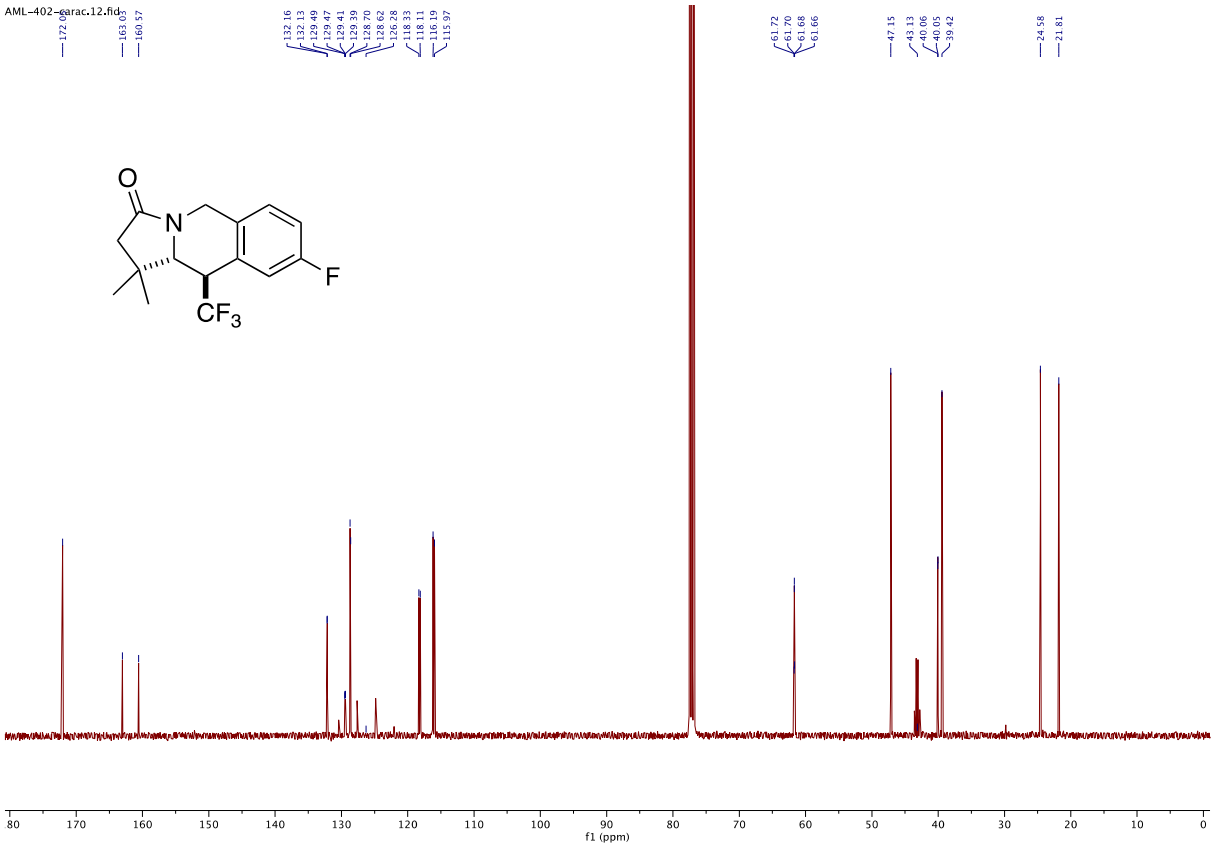
HMBC experiment of **2aa**



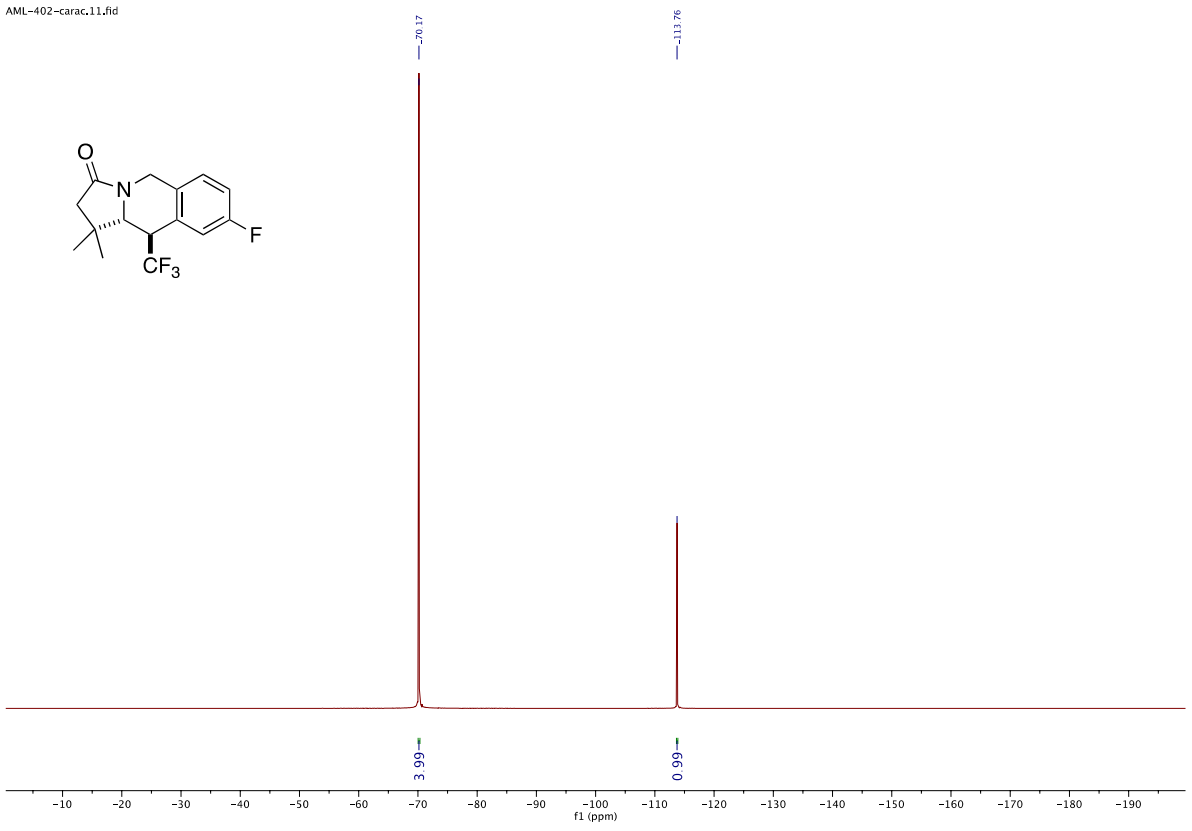
^{1}H NMR of **2b**



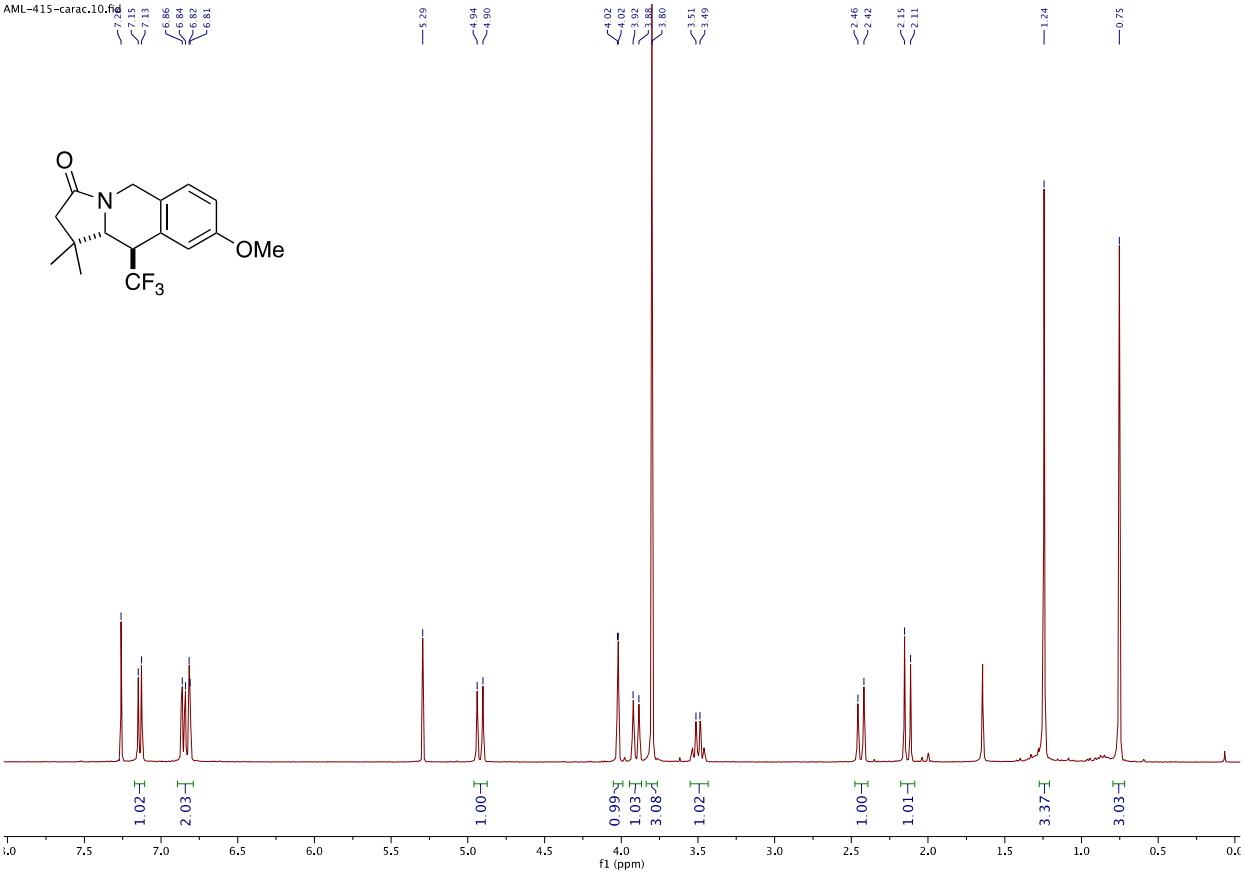
^{13}C NMR of **2b**



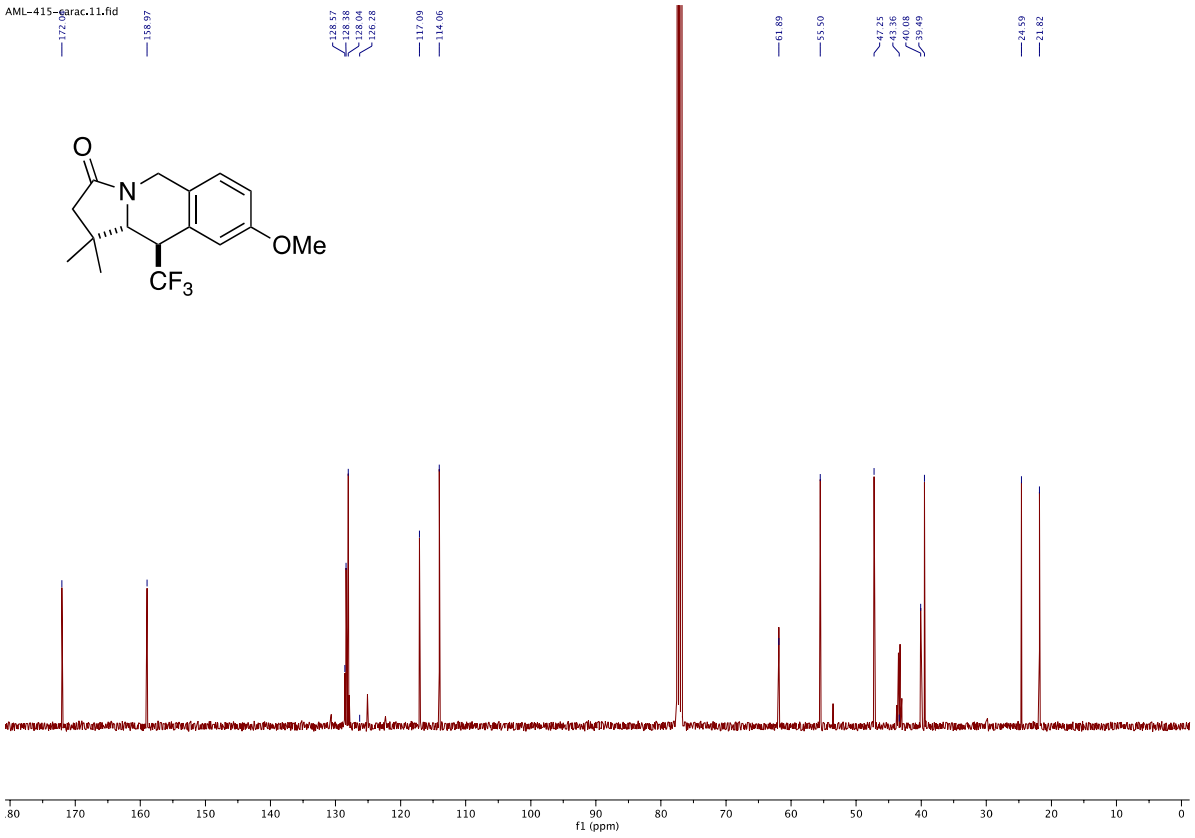
^{19}F NMR of **2b**



^{1}H NMR of **2c**

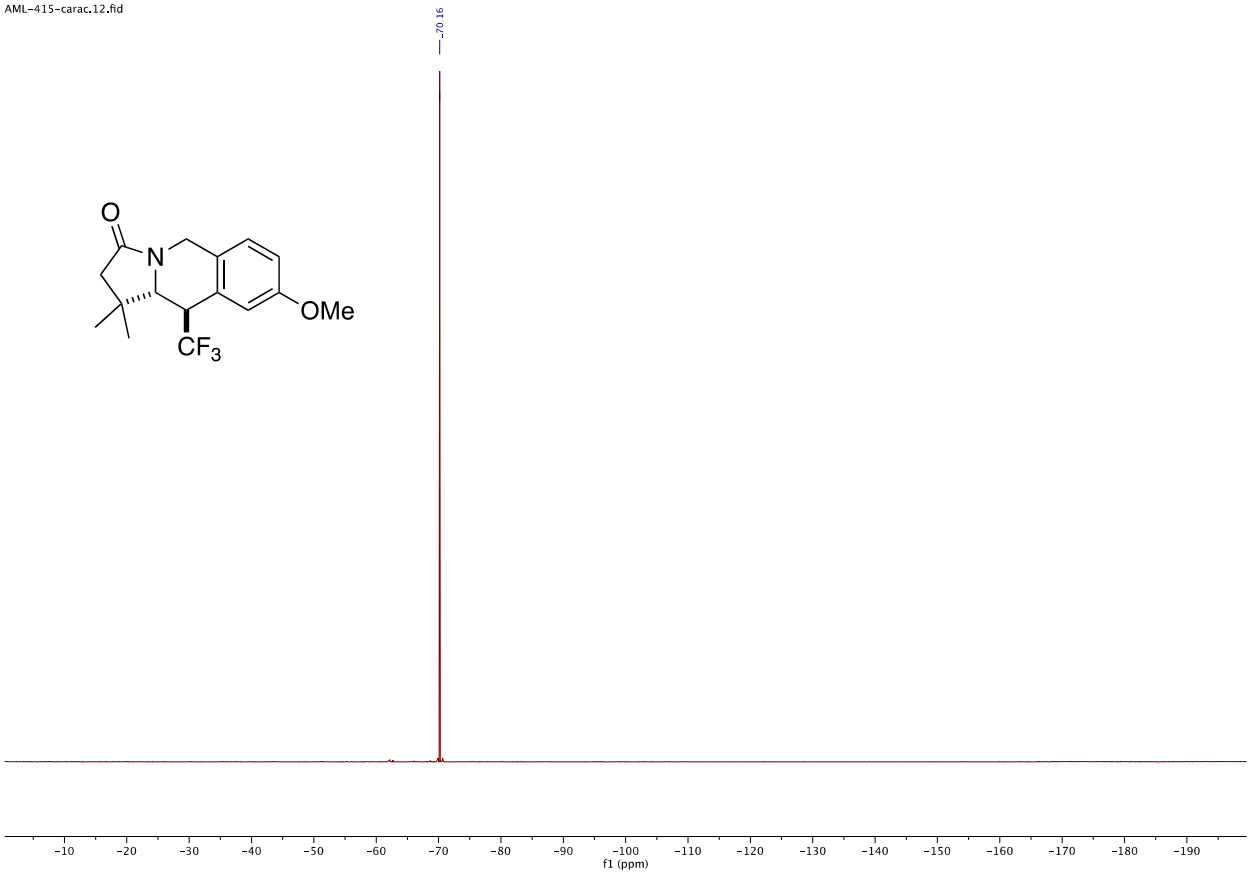


^{13}C NMR of **2c**



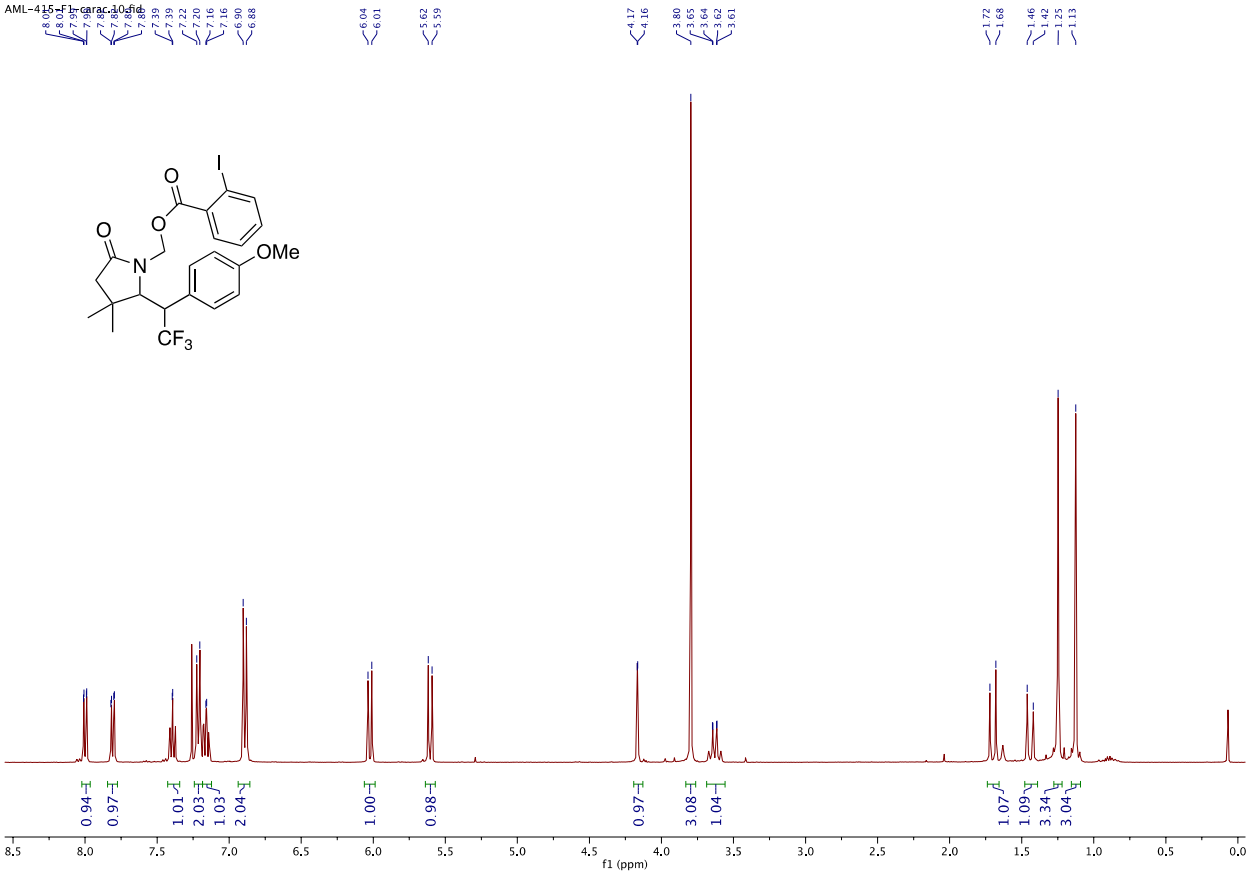
^{19}F NMR of **2c**

AML-415-carac.12.fid

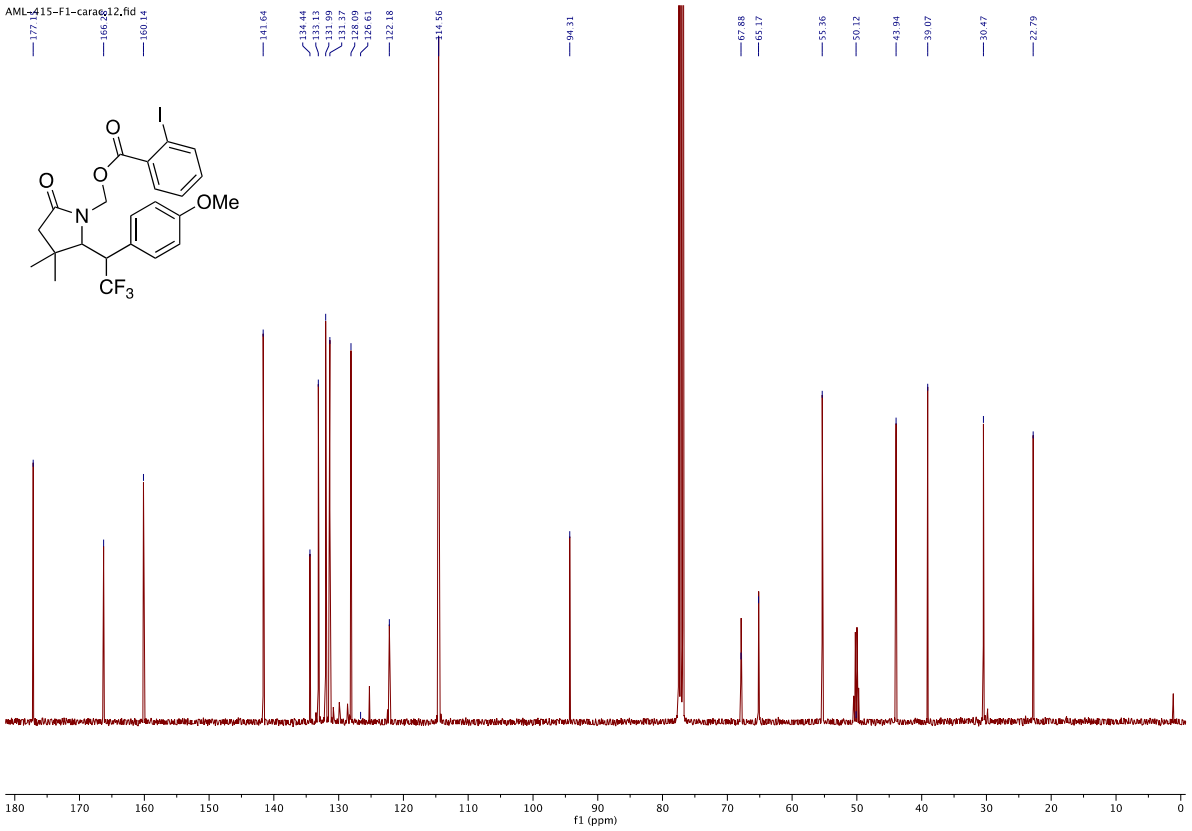


^{1}H NMR of **2ca**

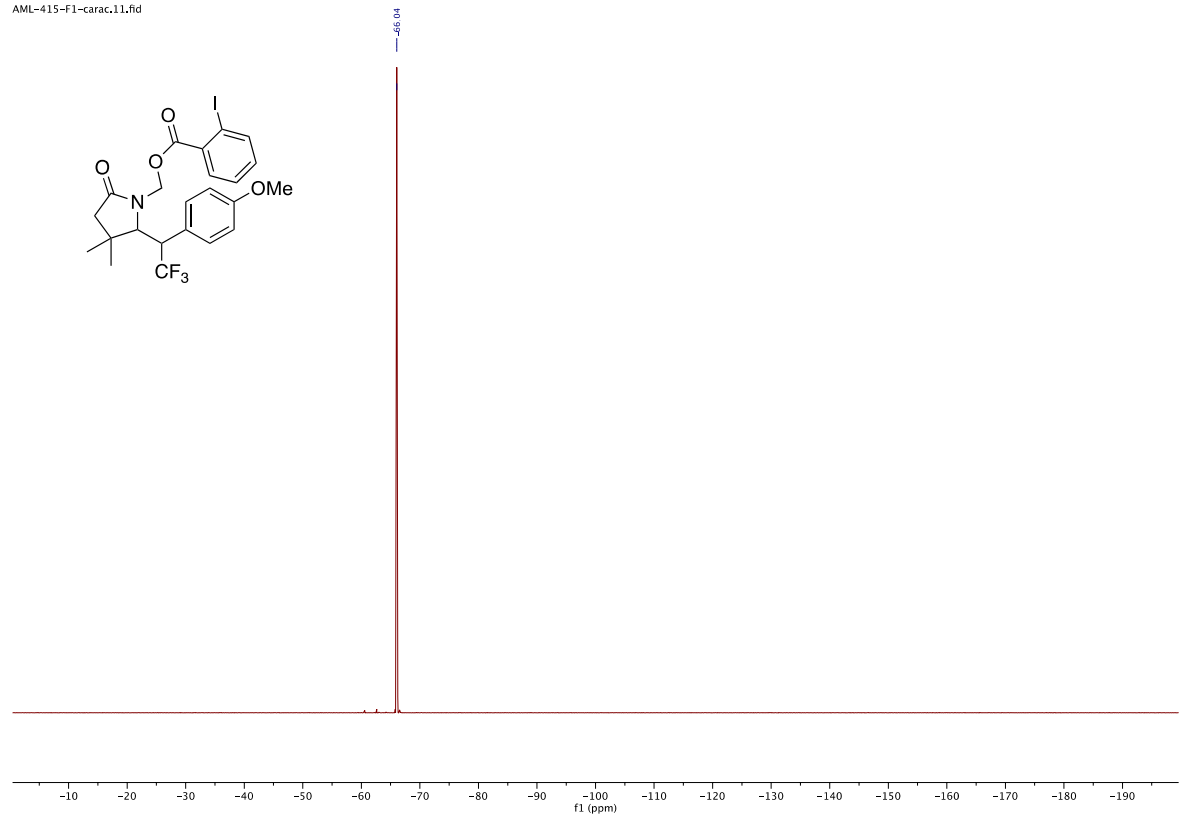
AML-415-F1-carac.10.fid



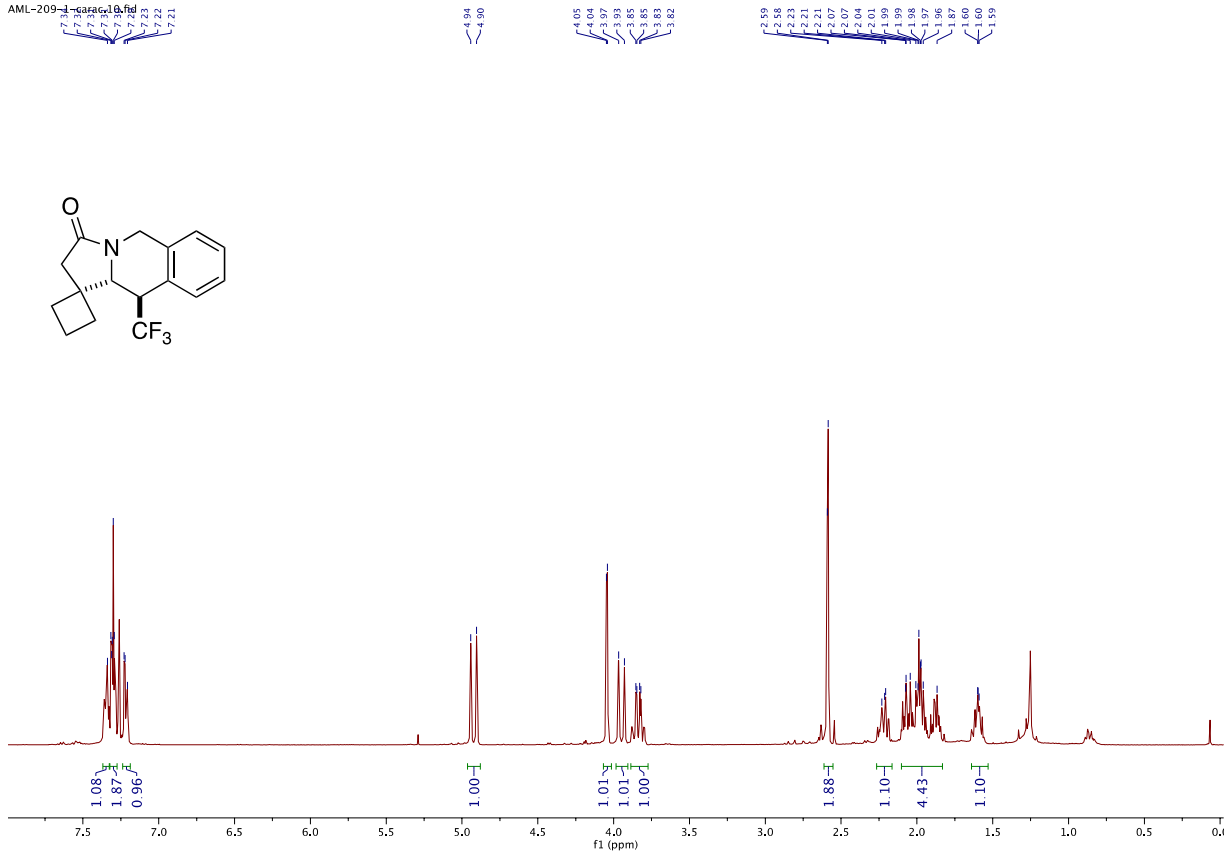
^{13}C NMR of **2ca**



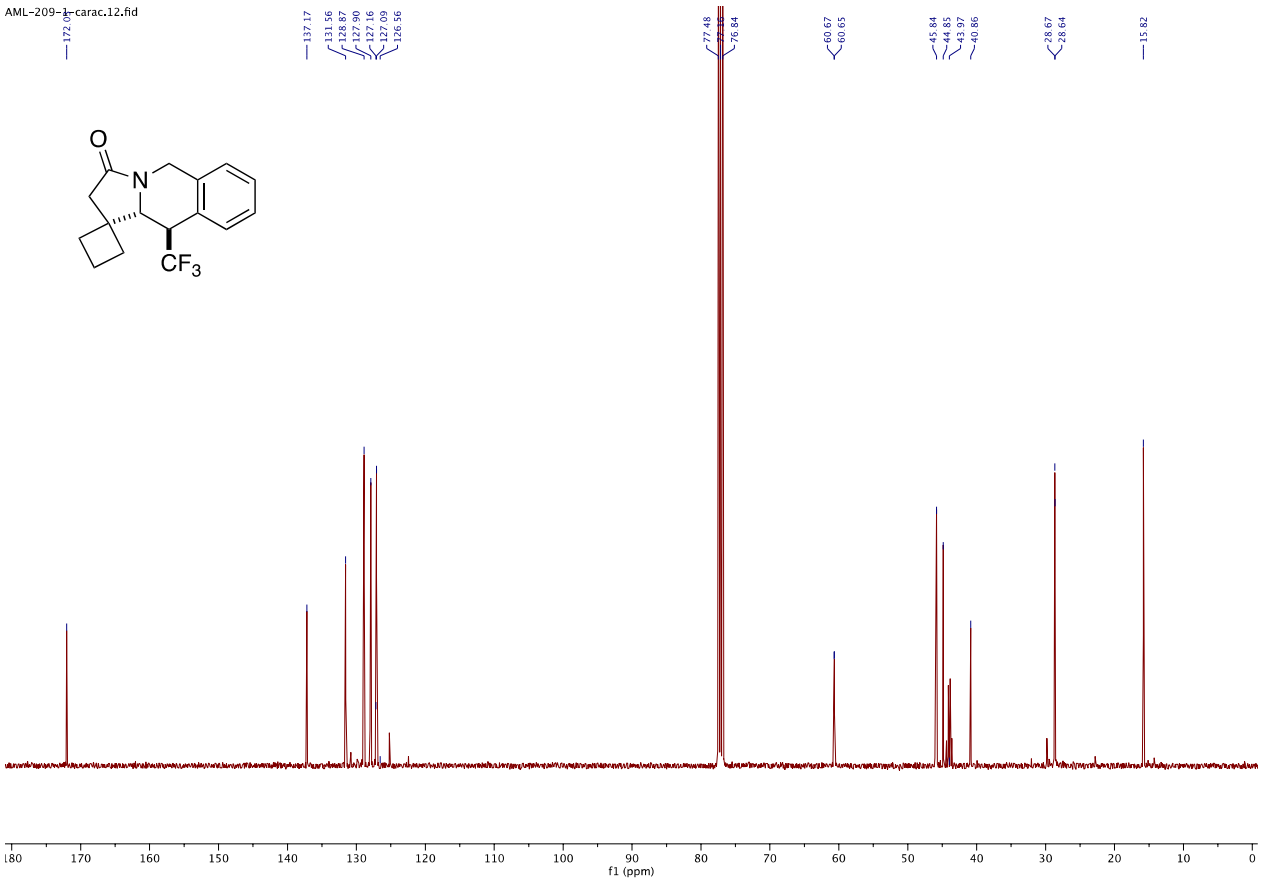
^{19}F NMR of **2ca**



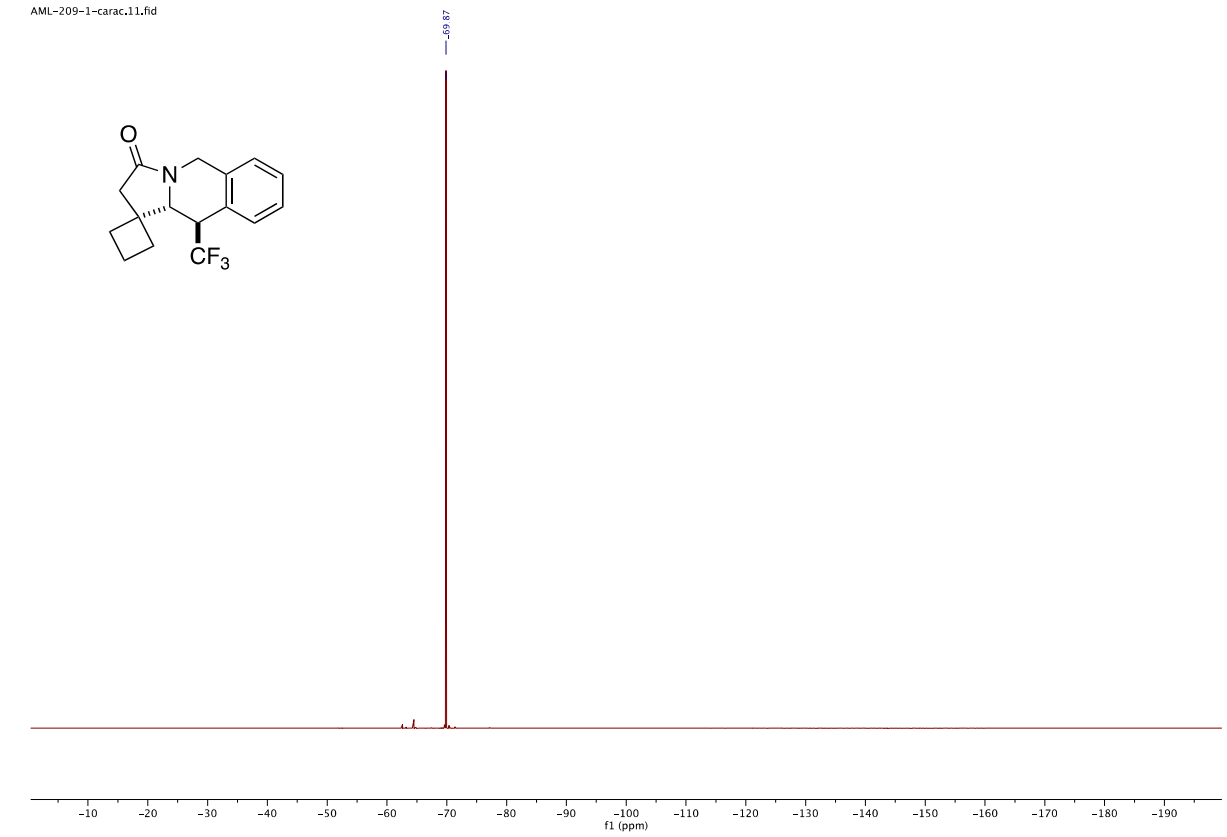
^{1}H NMR of **2d**



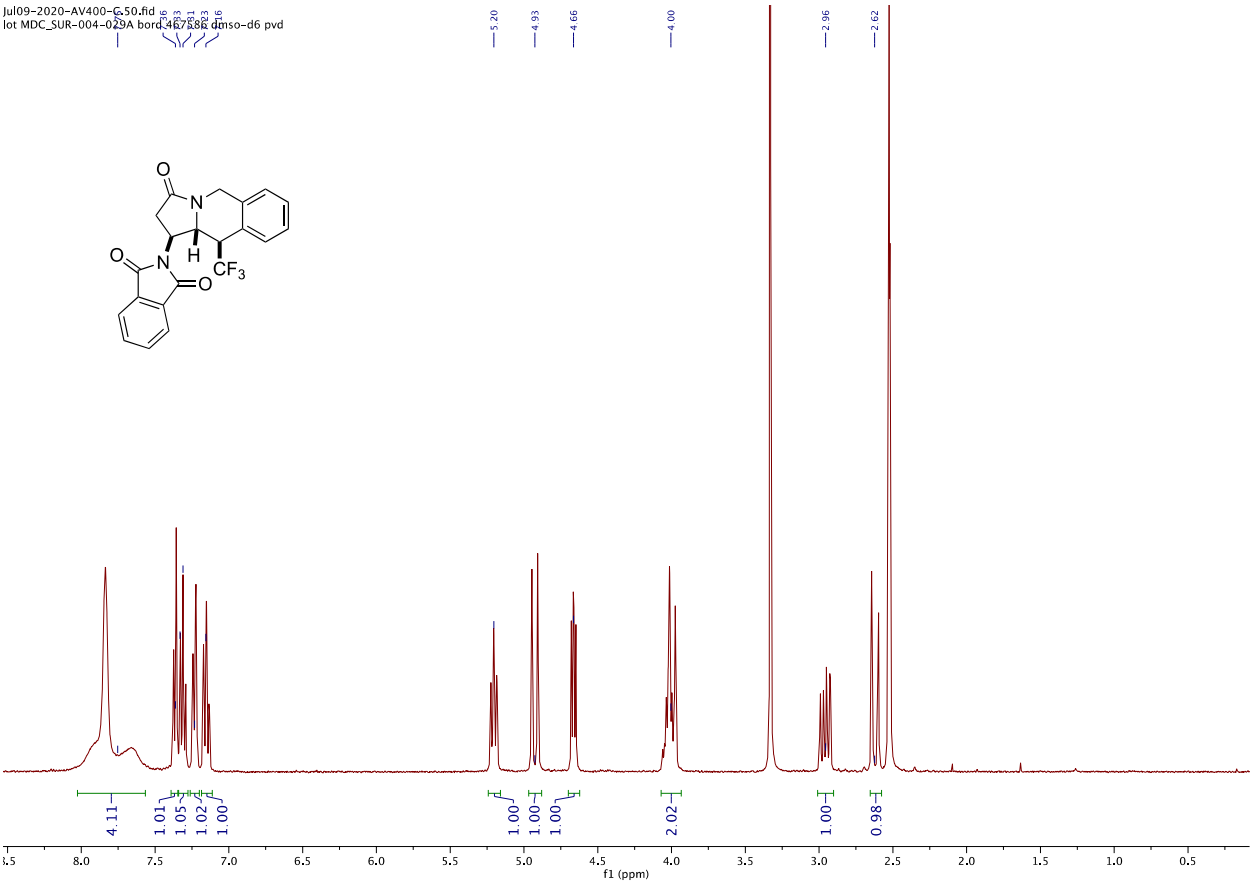
^{13}C NMR of **2d**



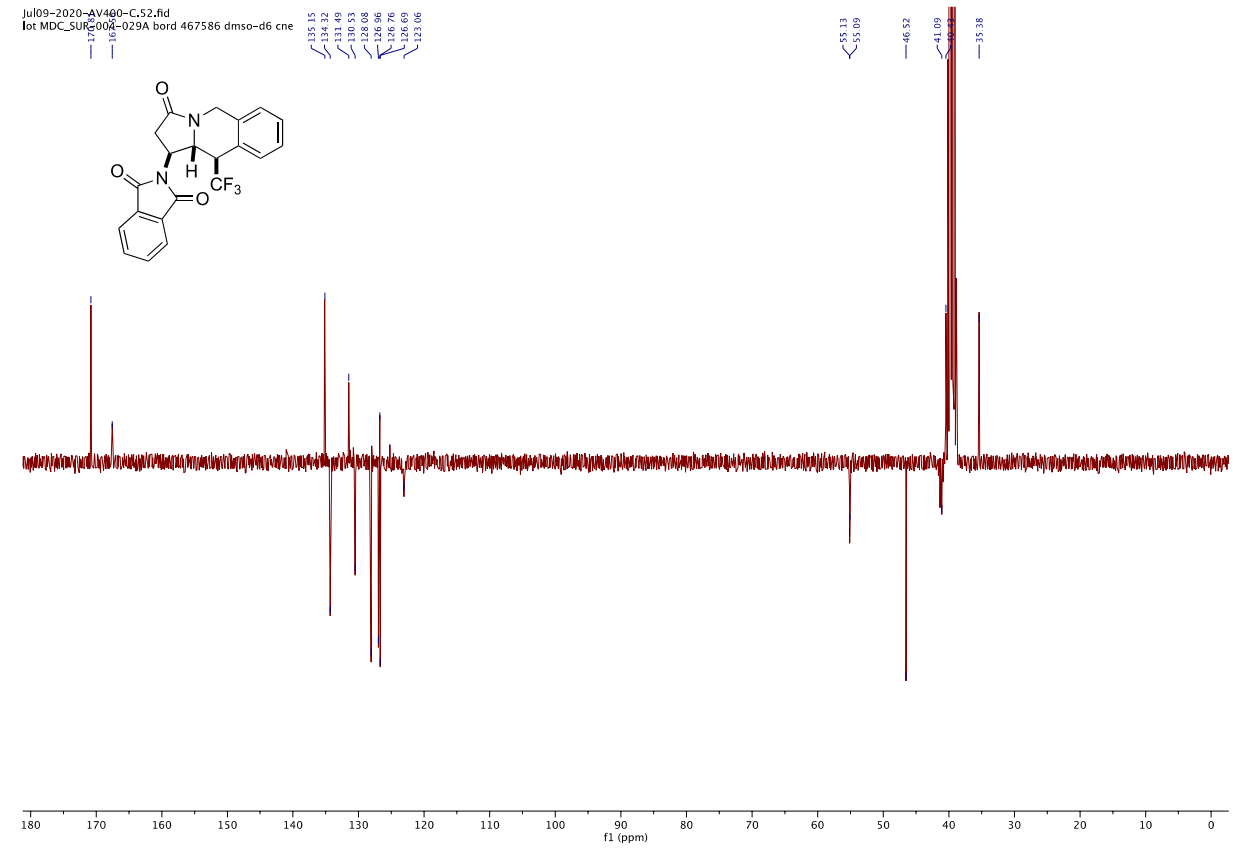
^{19}F NMR of **2d**



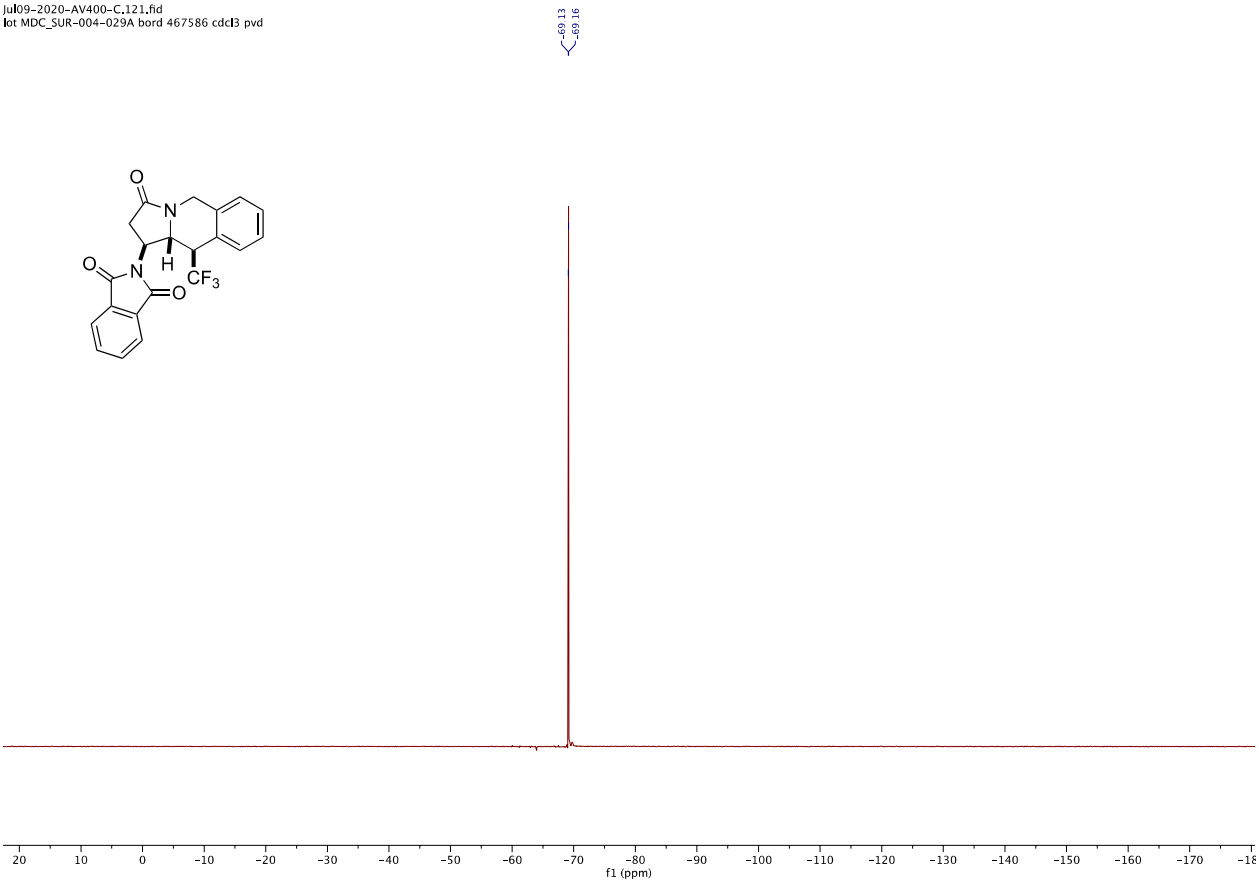
^{1}H NMR of **2e**



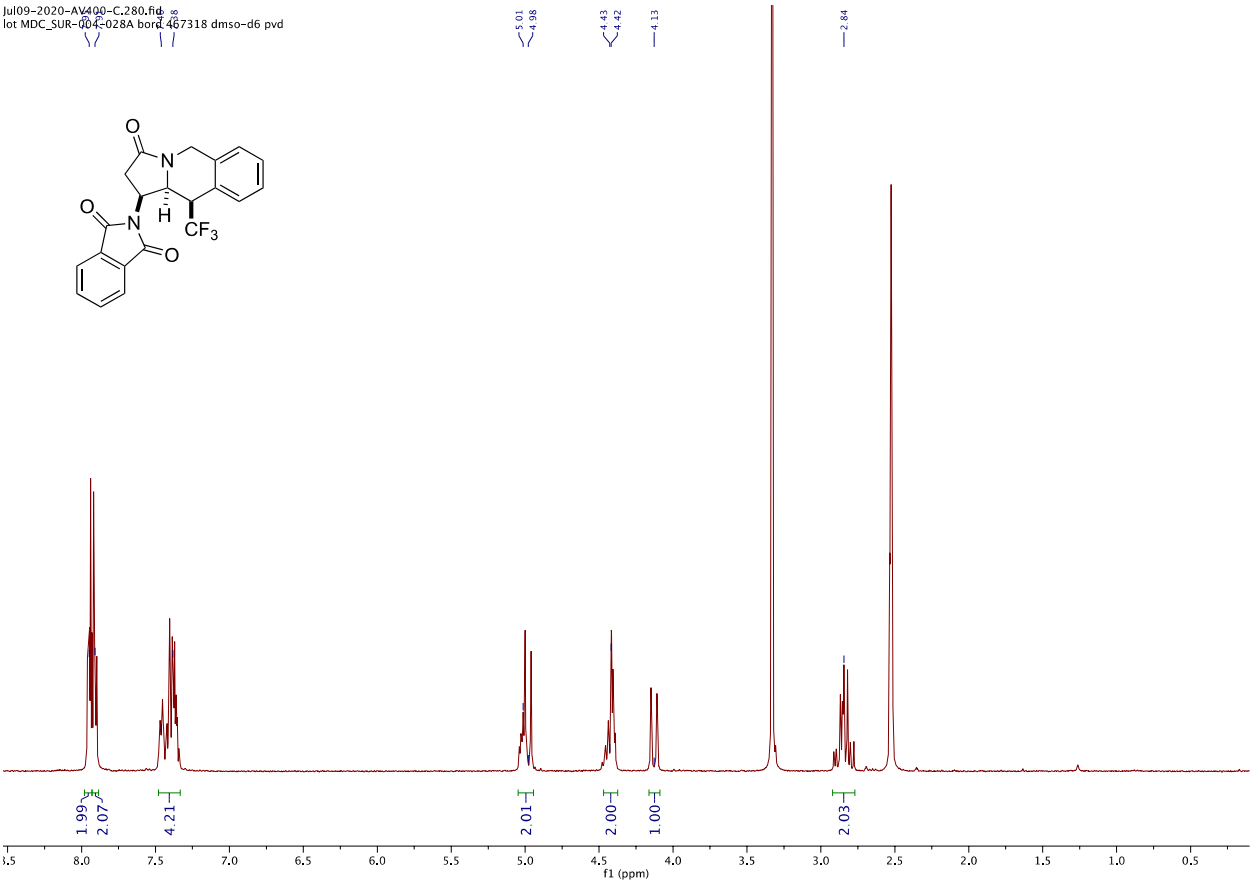
^{13}C NMR of **2e**



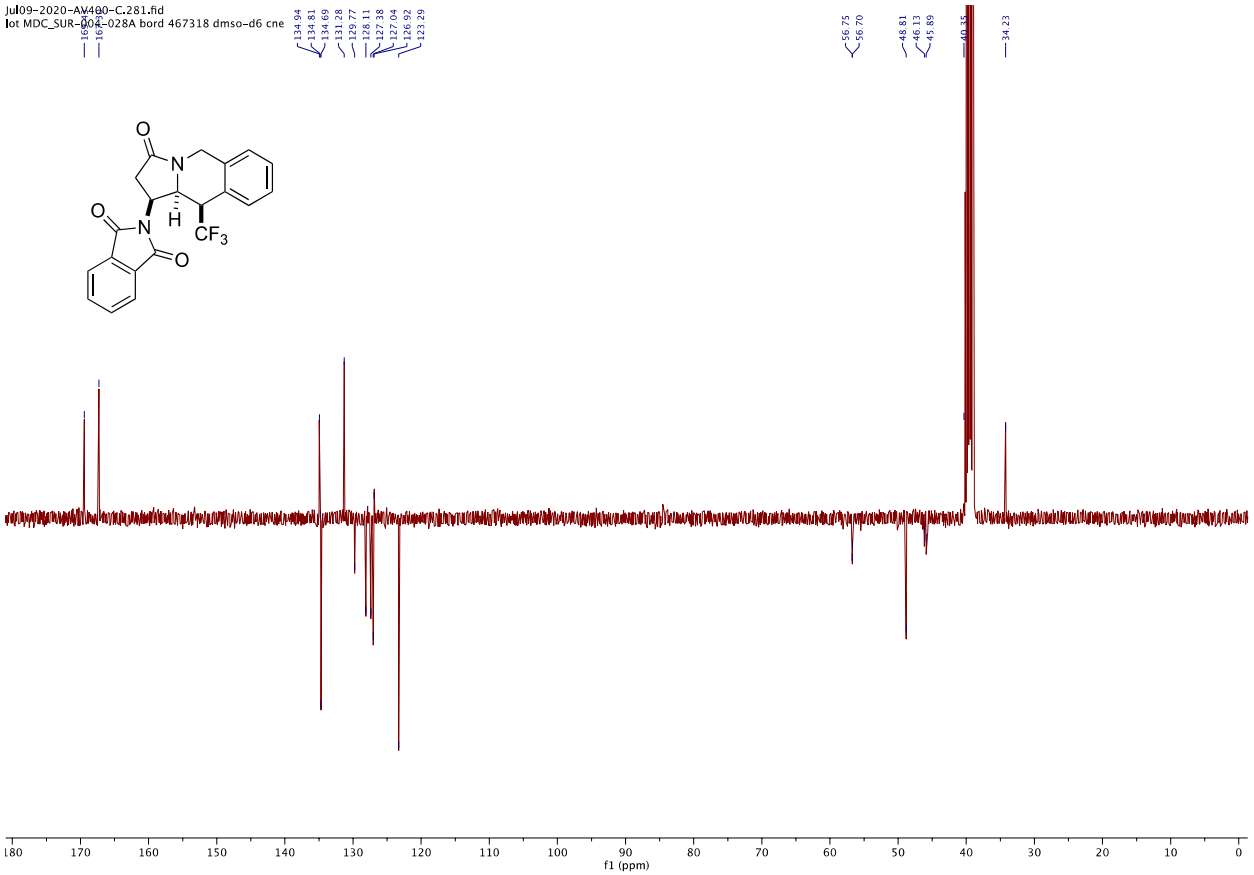
^{19}F NMR of **2e**



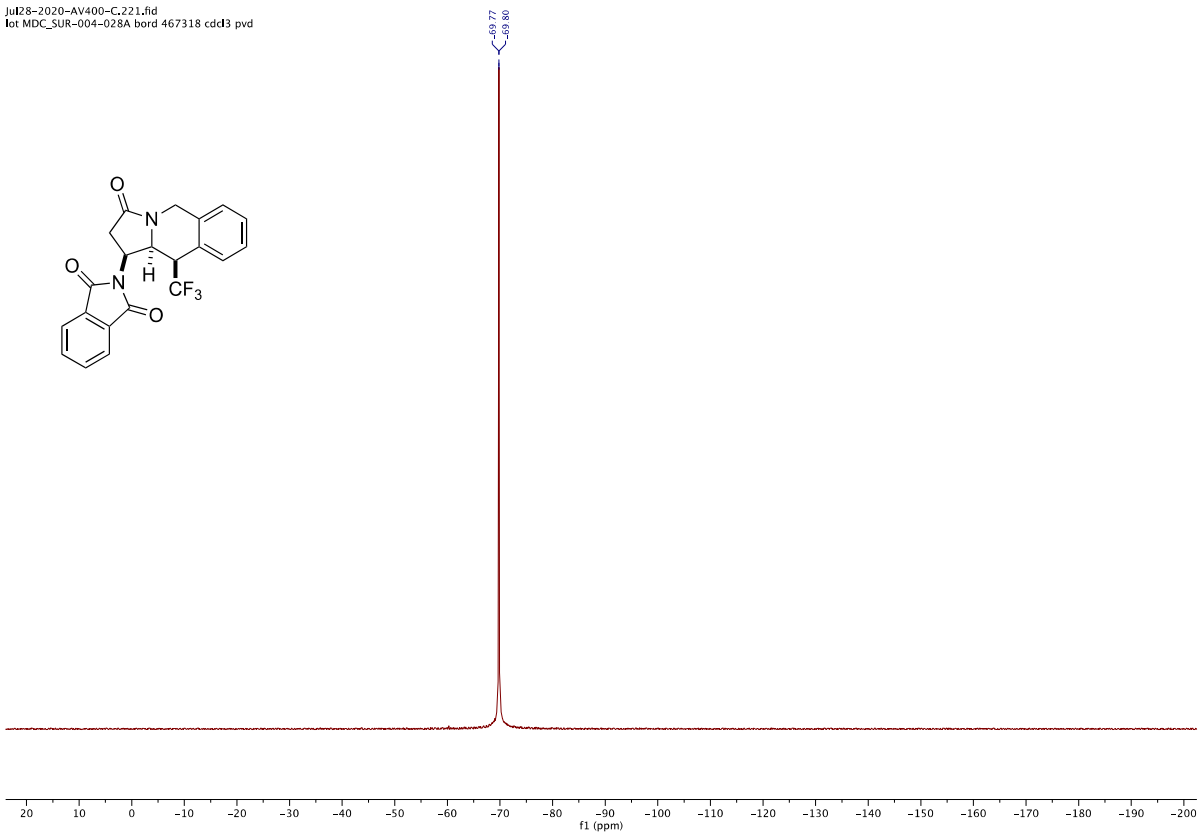
^{1}H NMR of **2e'**



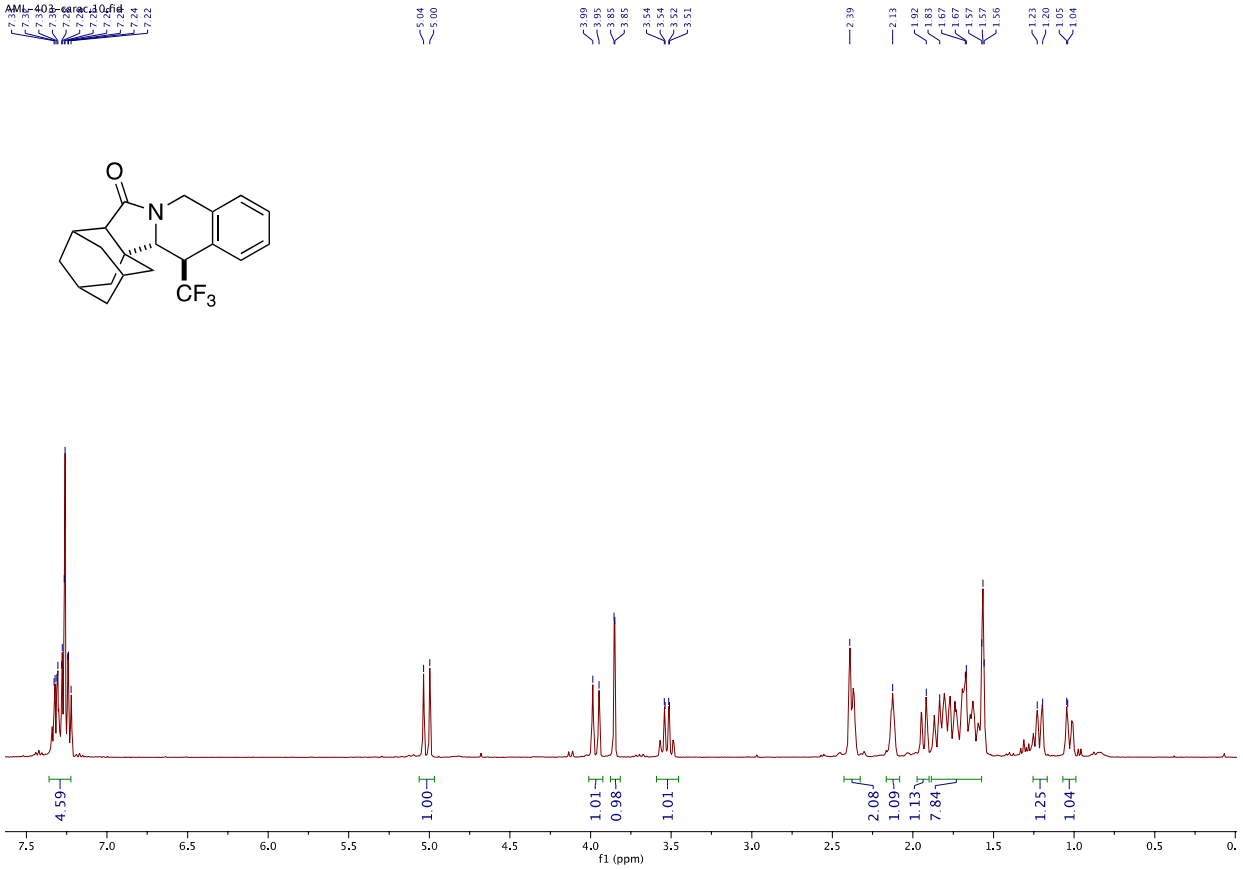
^{13}C NMR of **2e'**



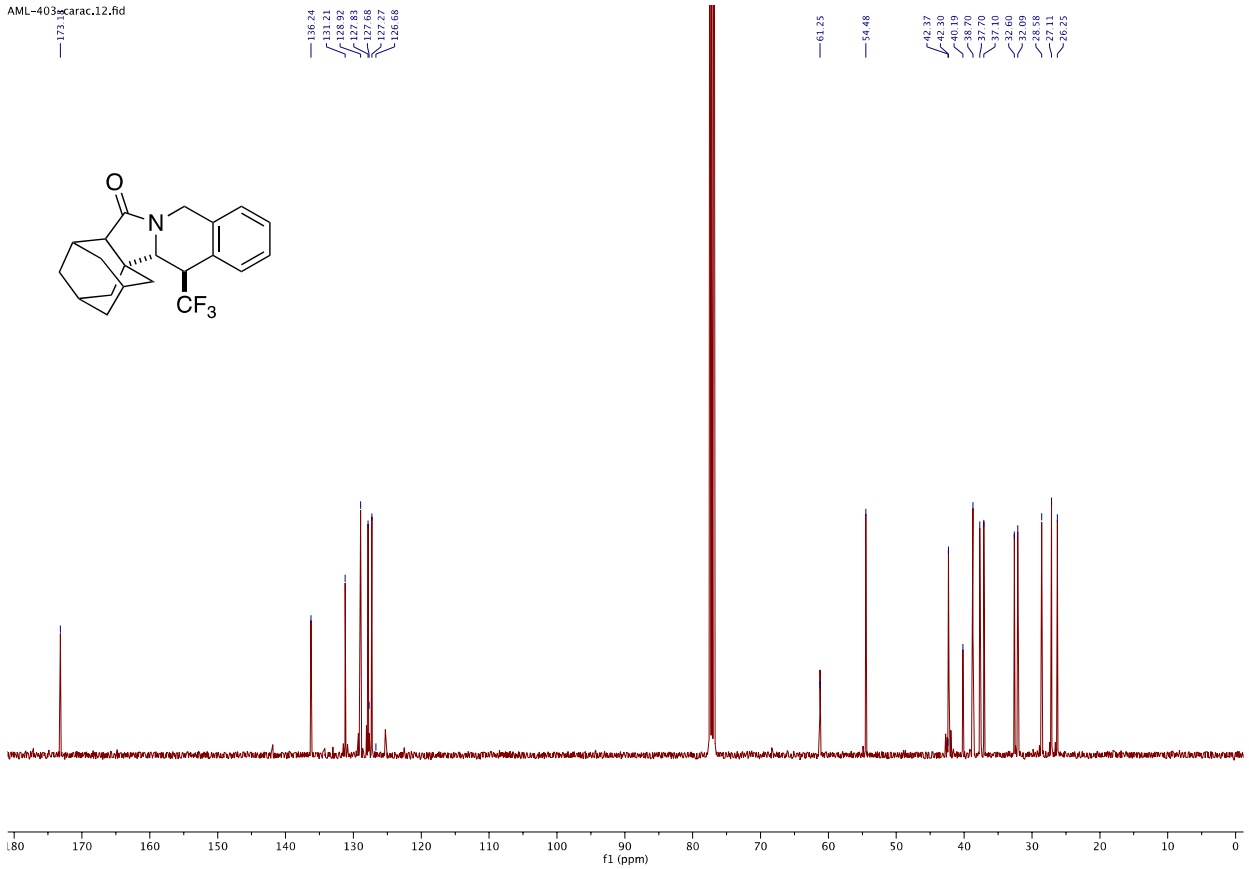
^{19}F NMR of **2e'**



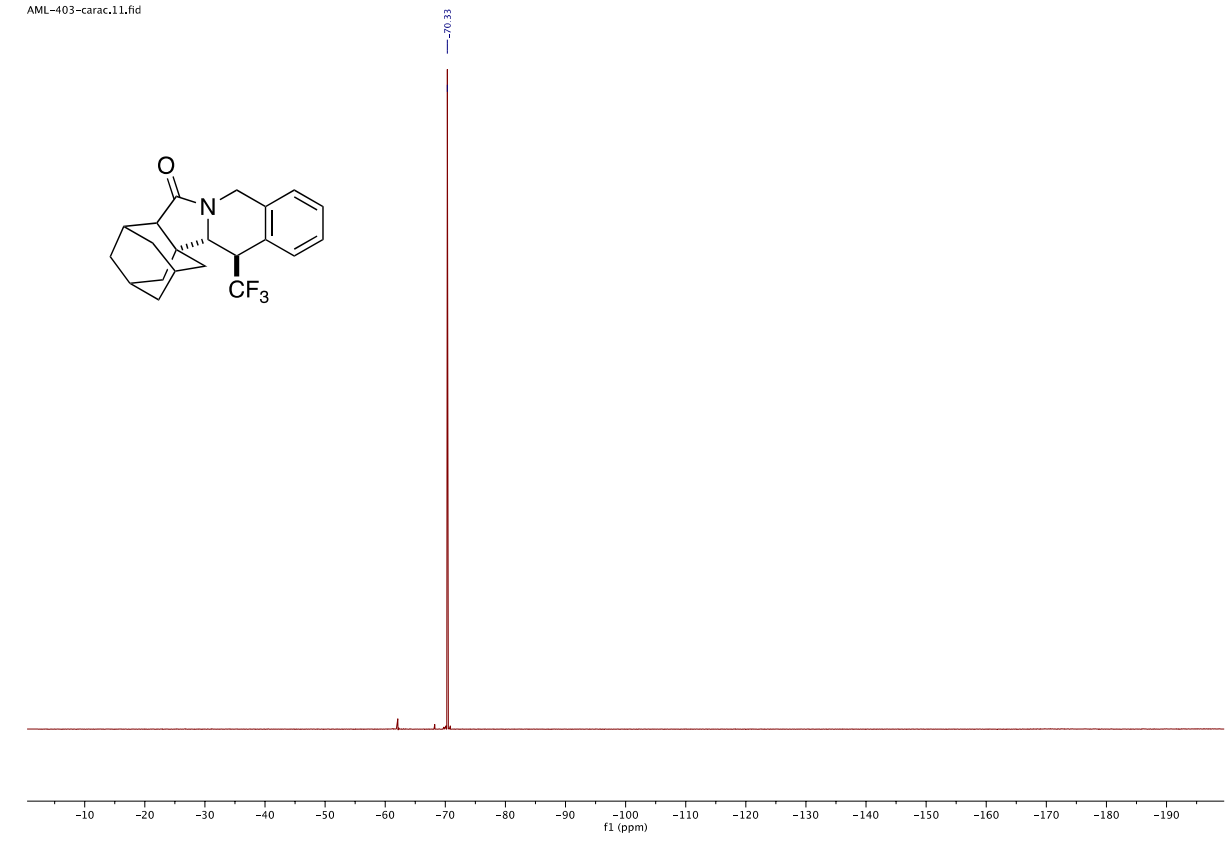
^{1}H NMR of **2f**



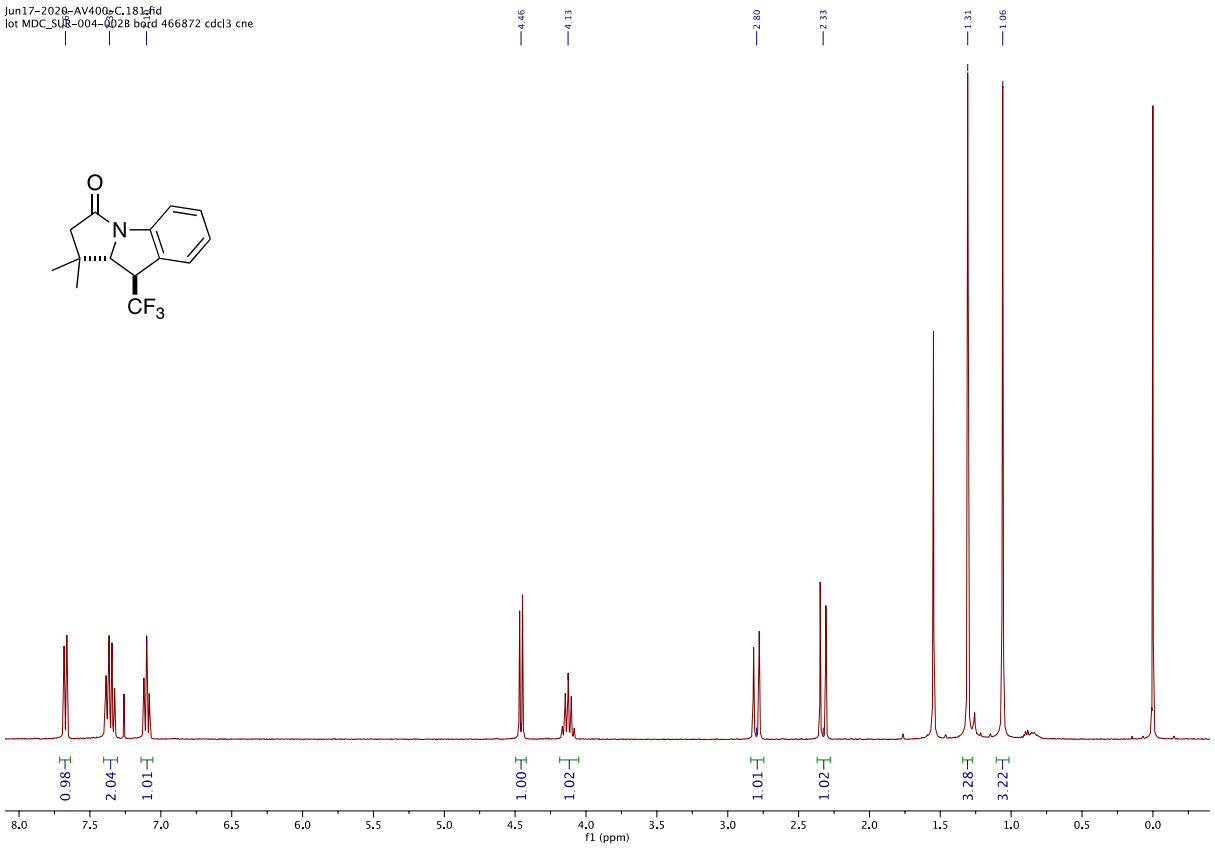
^{13}C NMR of **2f**



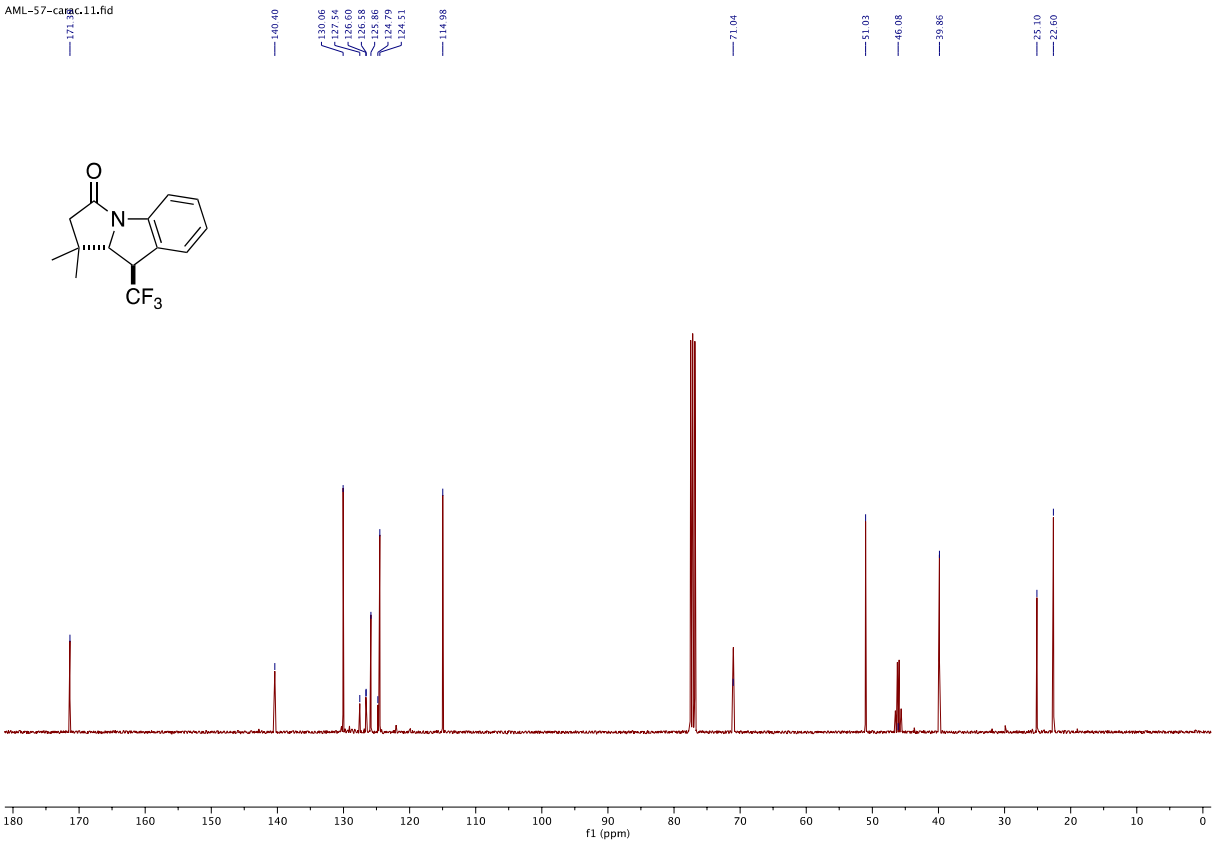
^{19}F NMR of **2f**



^{1}H NMR of **2g**



^{13}C NMR of **2g**

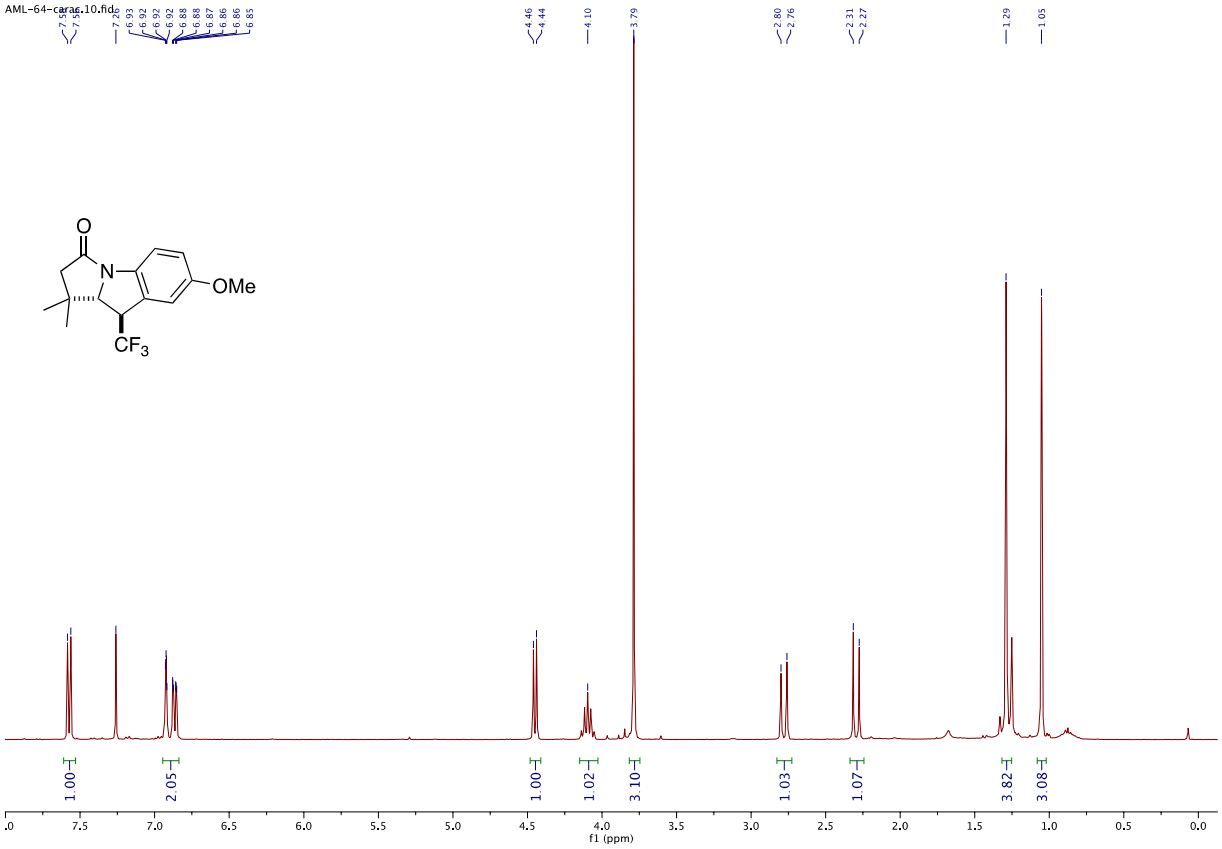


^{19}F NMR of **2g**

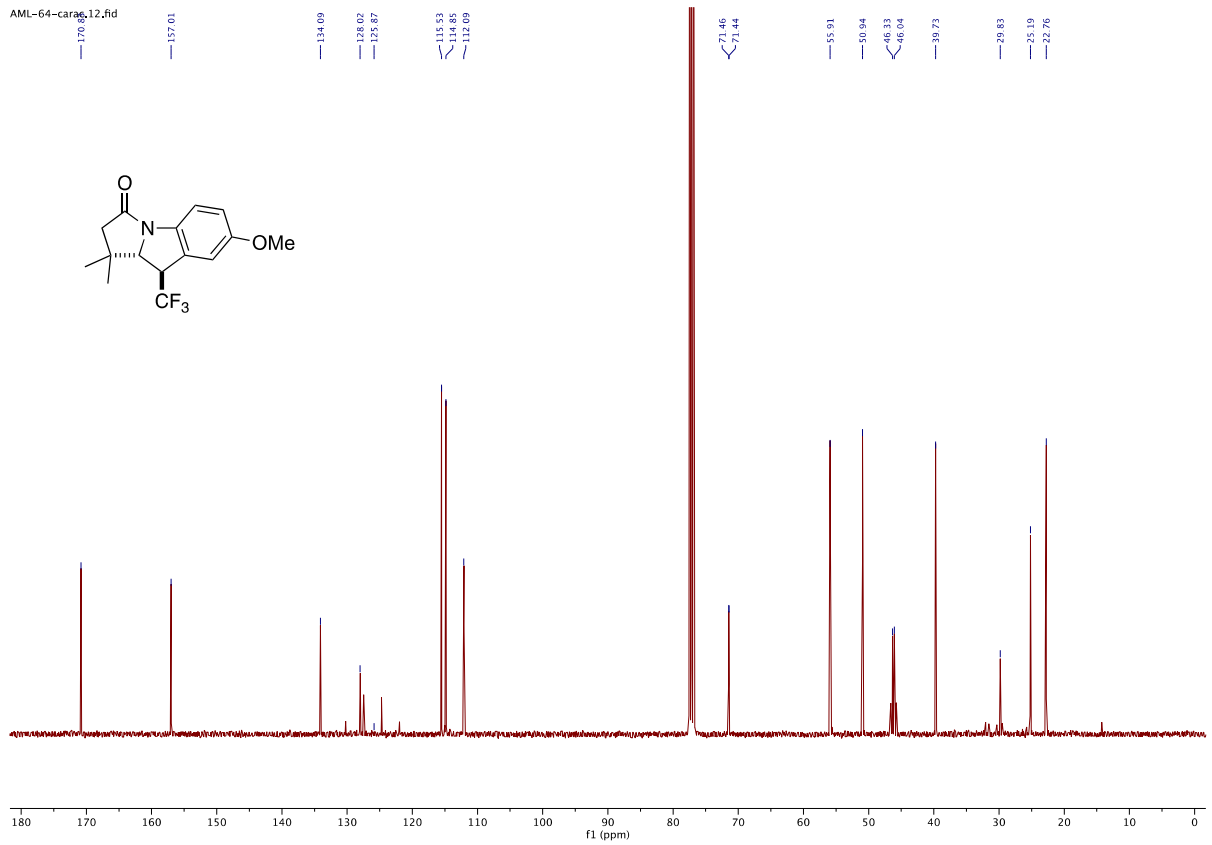
AML-57-F2.11.fid

^{1}H NMR of **2h**

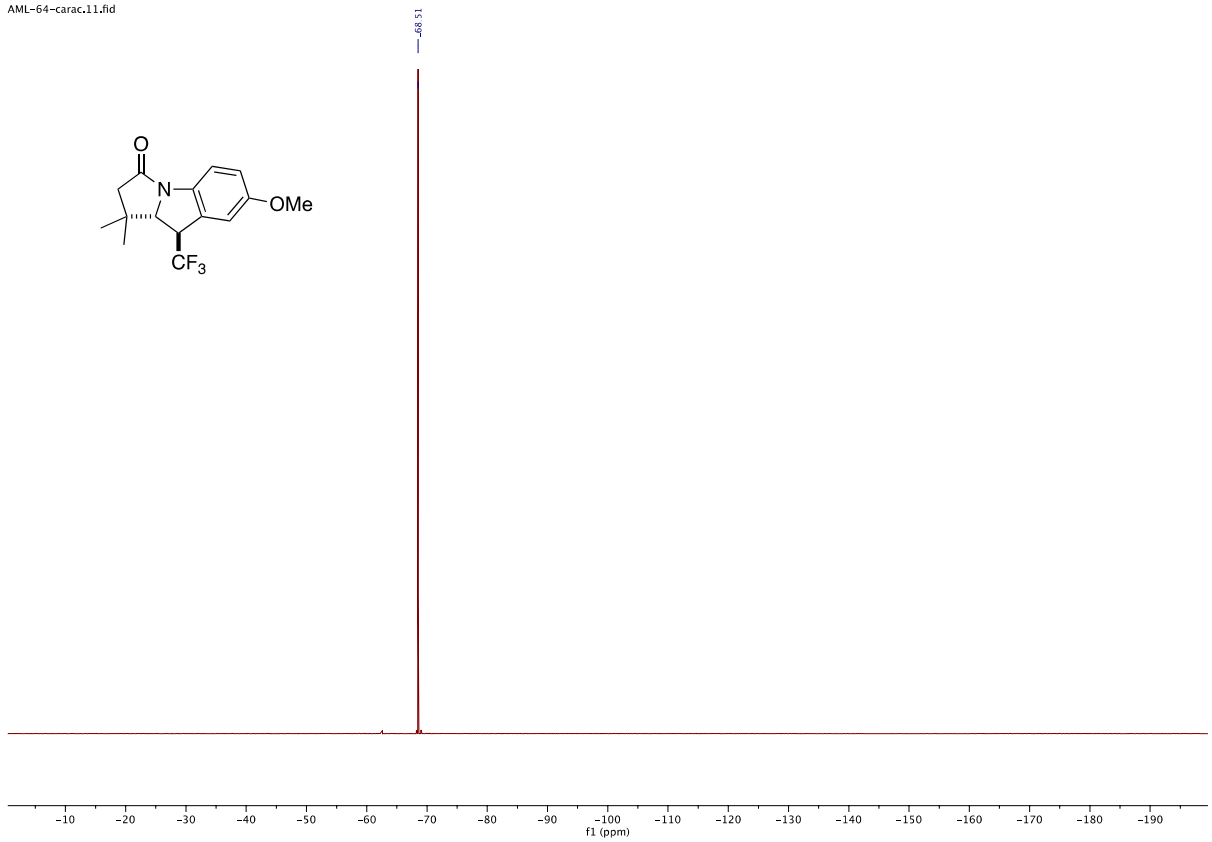
AML-64-carac.10.fid



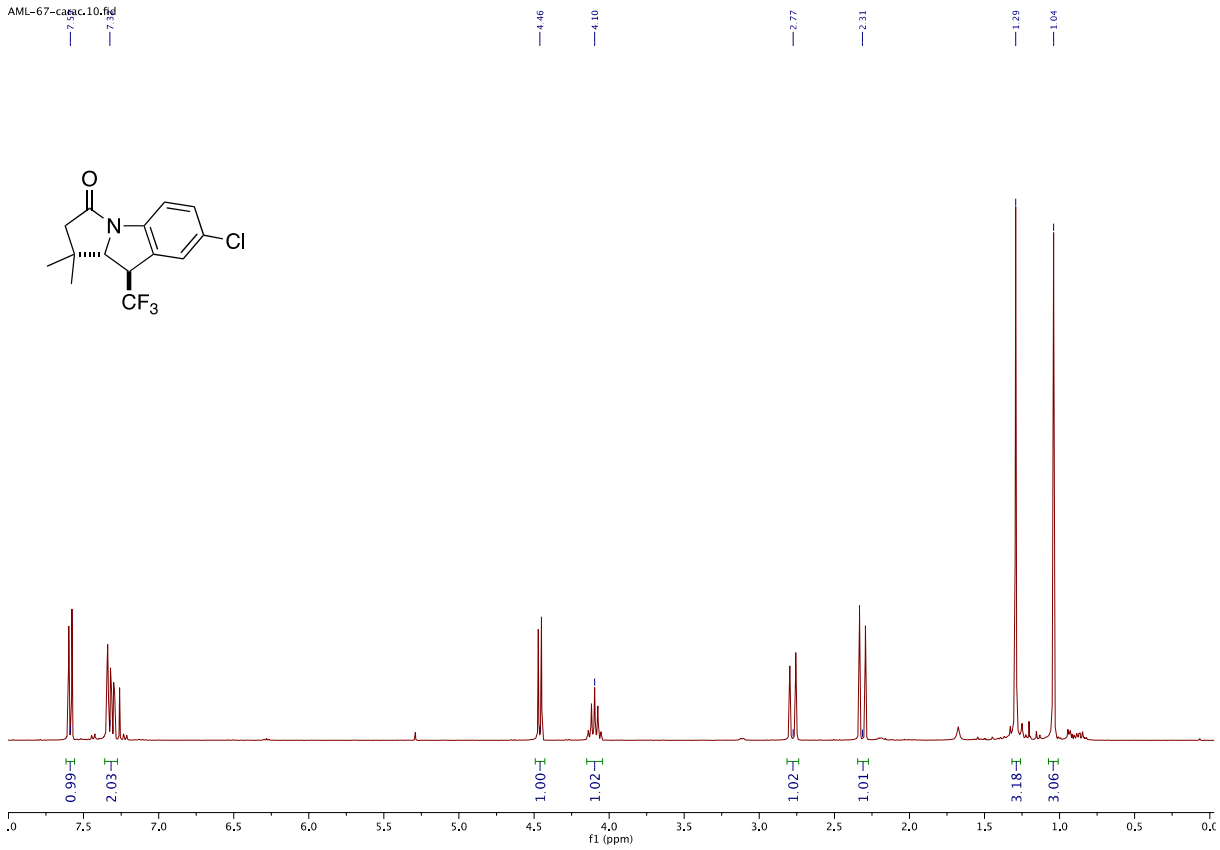
^{13}C NMR of **2h**



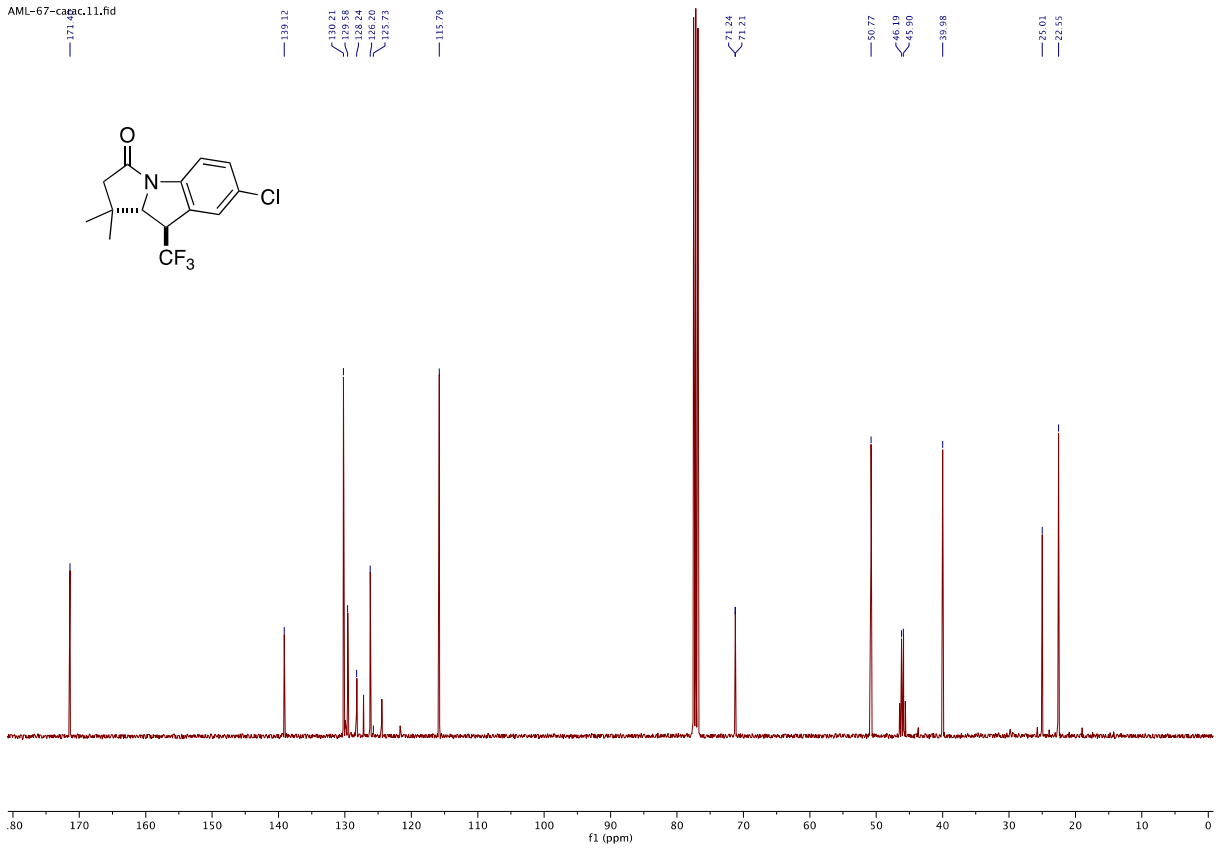
^{19}F NMR of **2h**



^{1}H NMR of **2i**

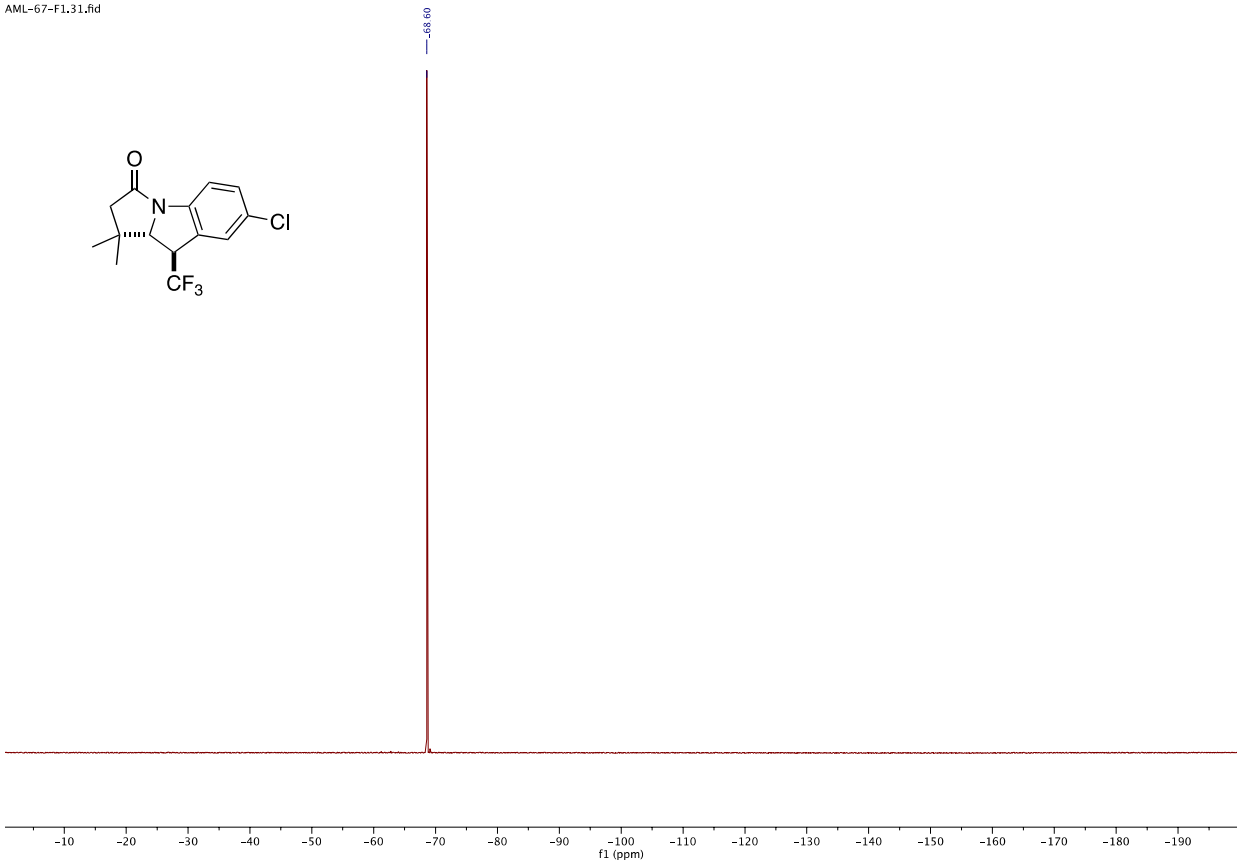


^{13}C NMR of **2i**



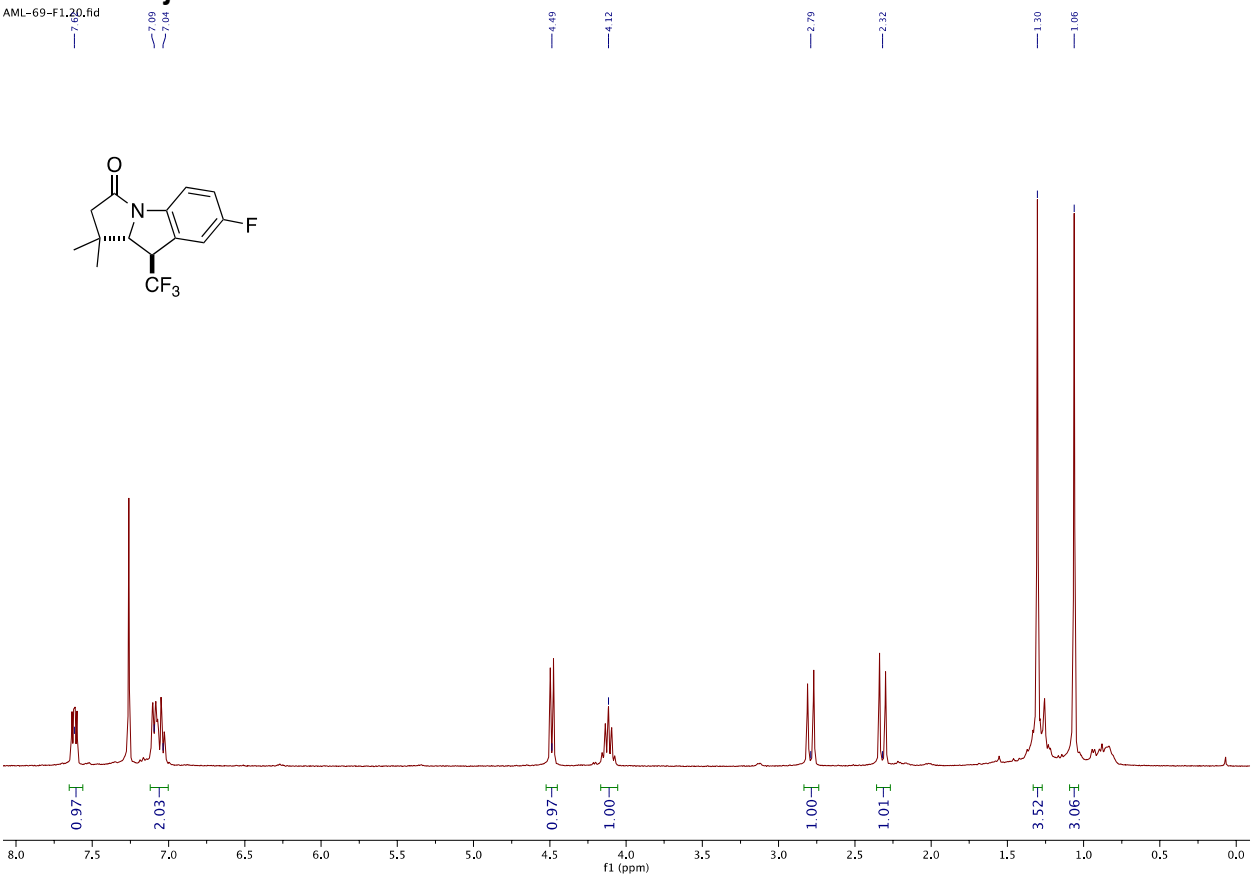
^{19}F NMR of **2i**

AML-67-F1.31.fid

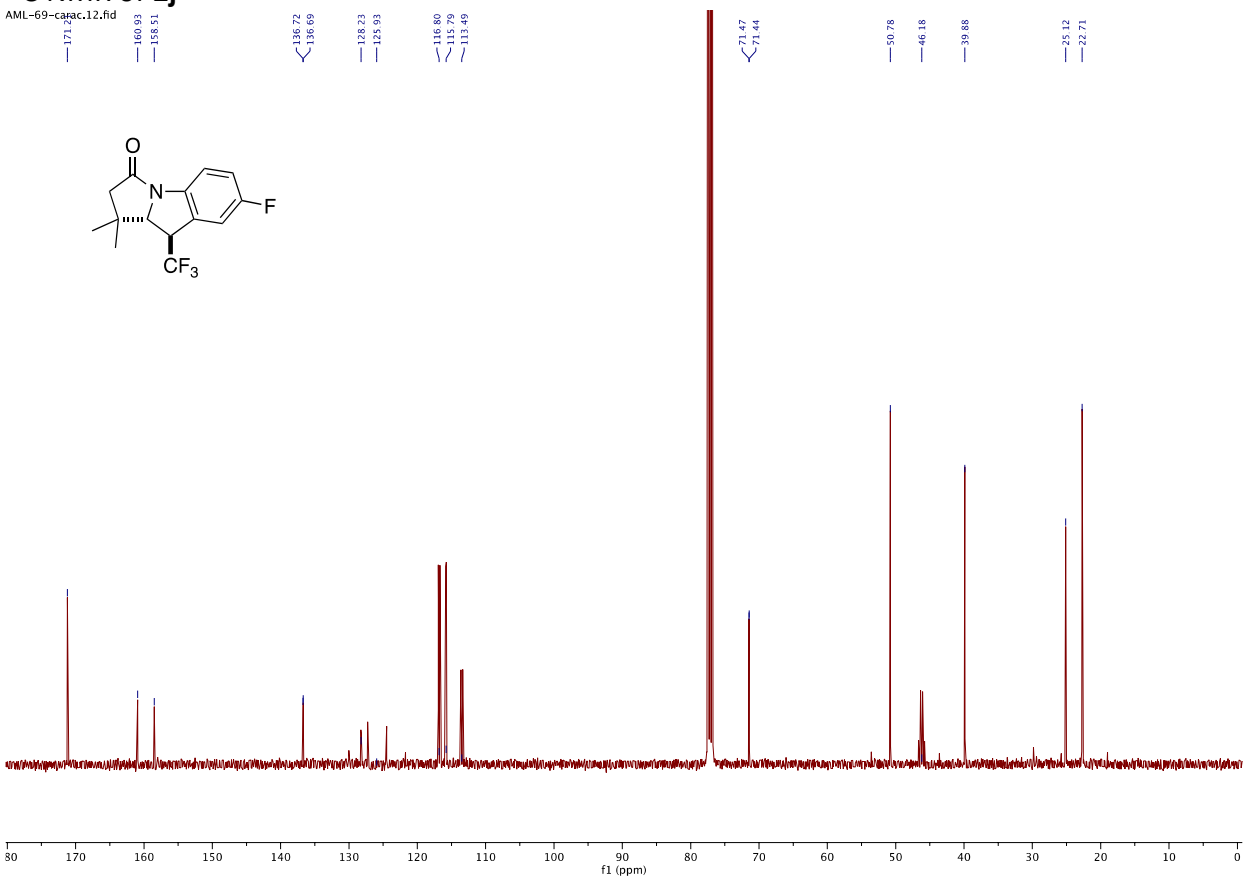


^{1}H NMR of **2j**

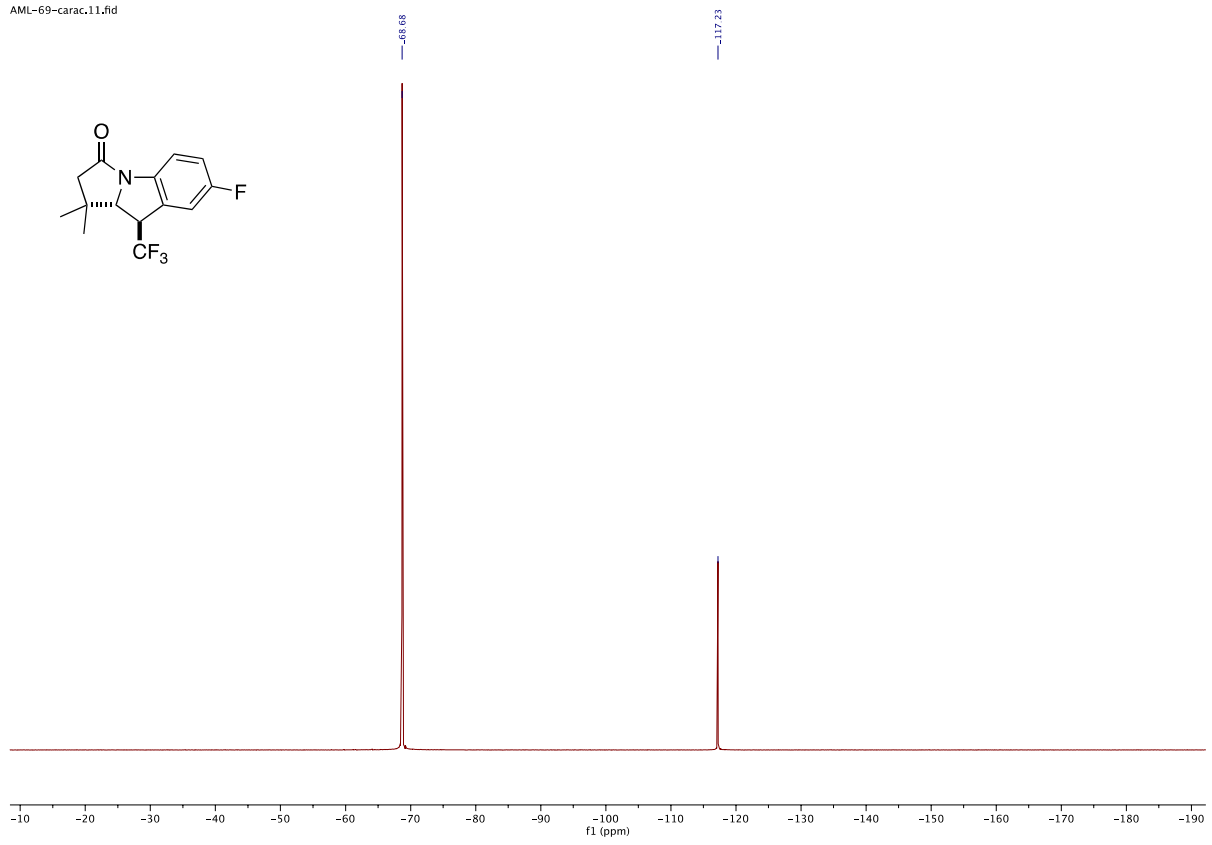
AML-69-F1.20.fid



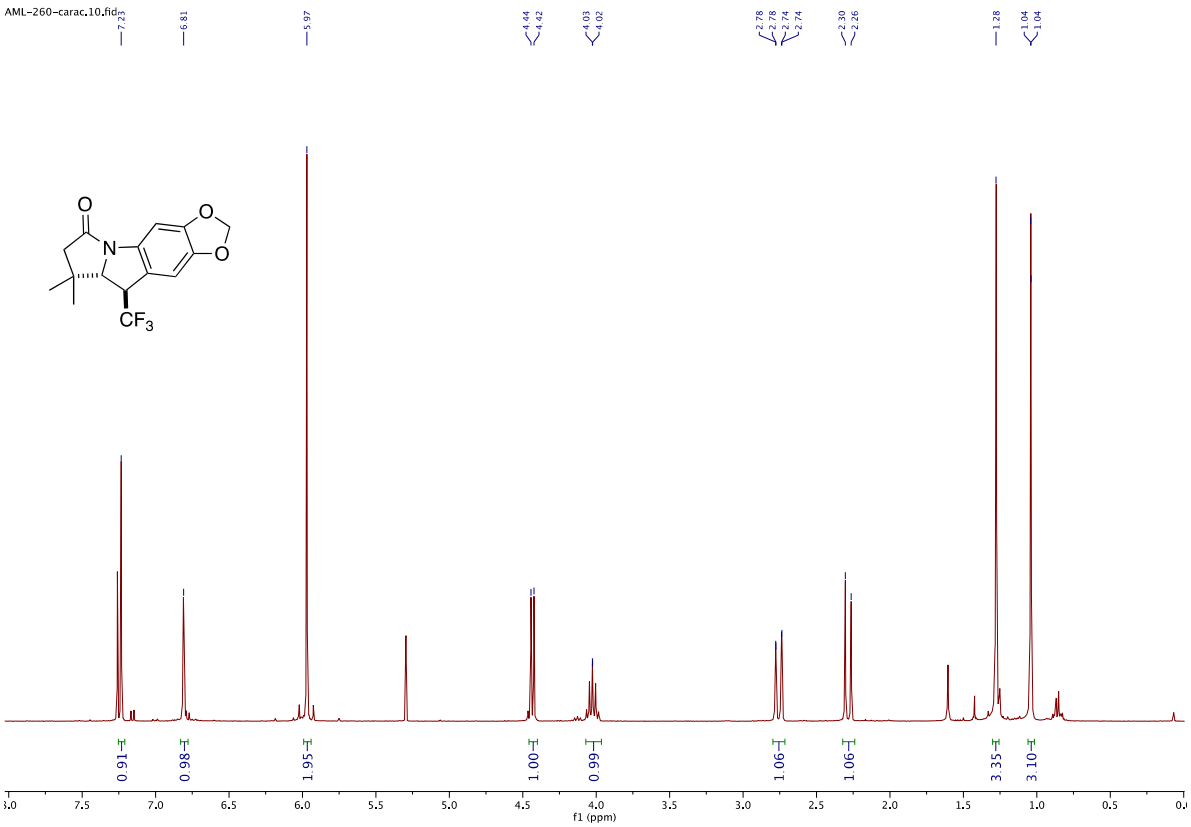
^{13}C NMR of **2j**



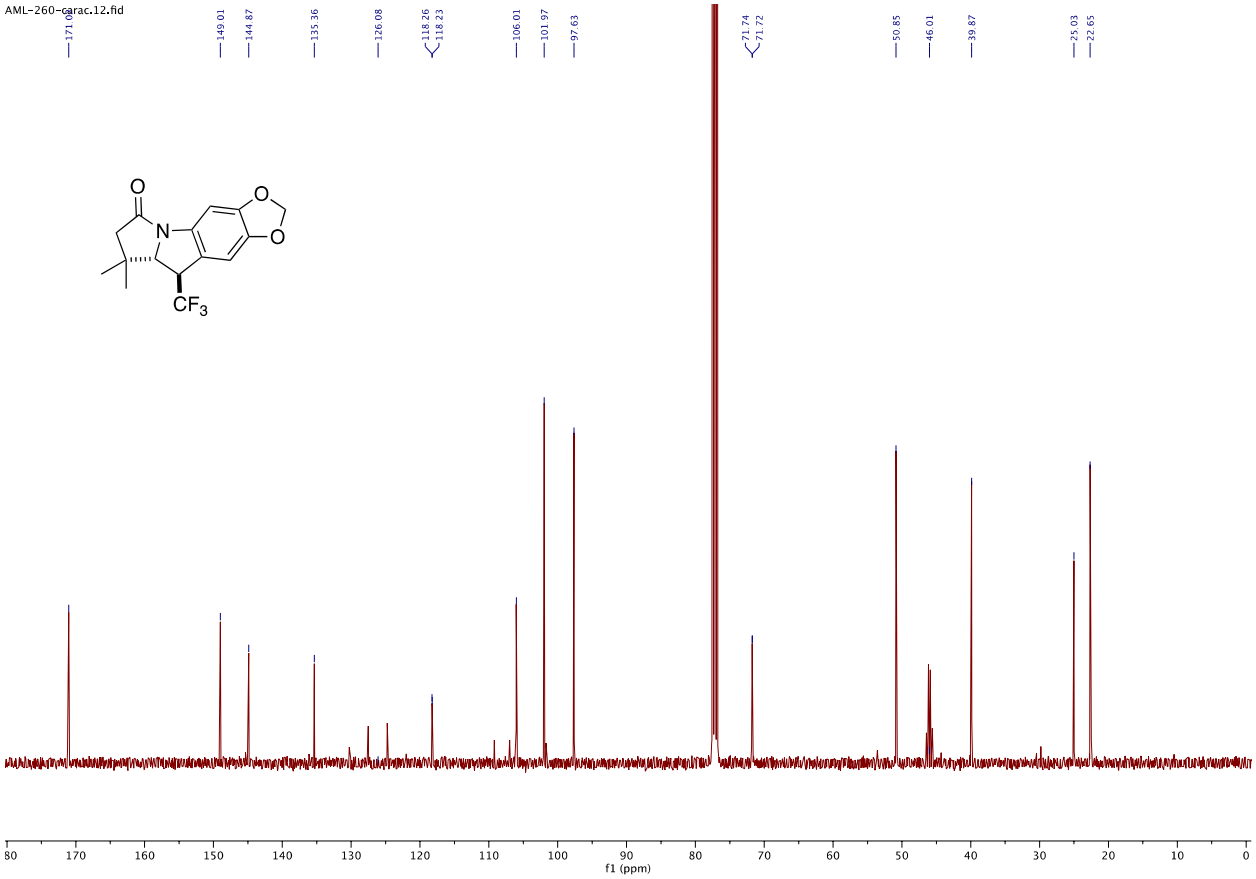
^{19}F NMR of **2j**



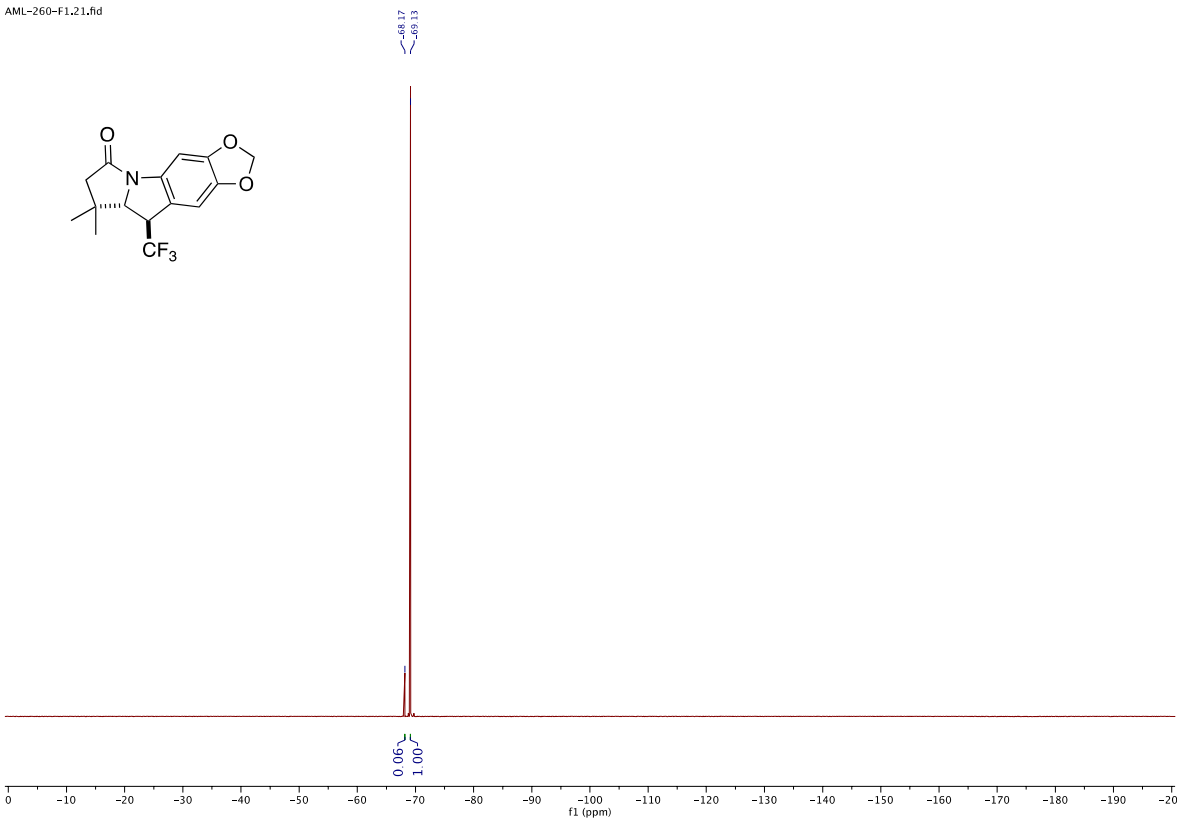
^{1}H NMR of **2k**



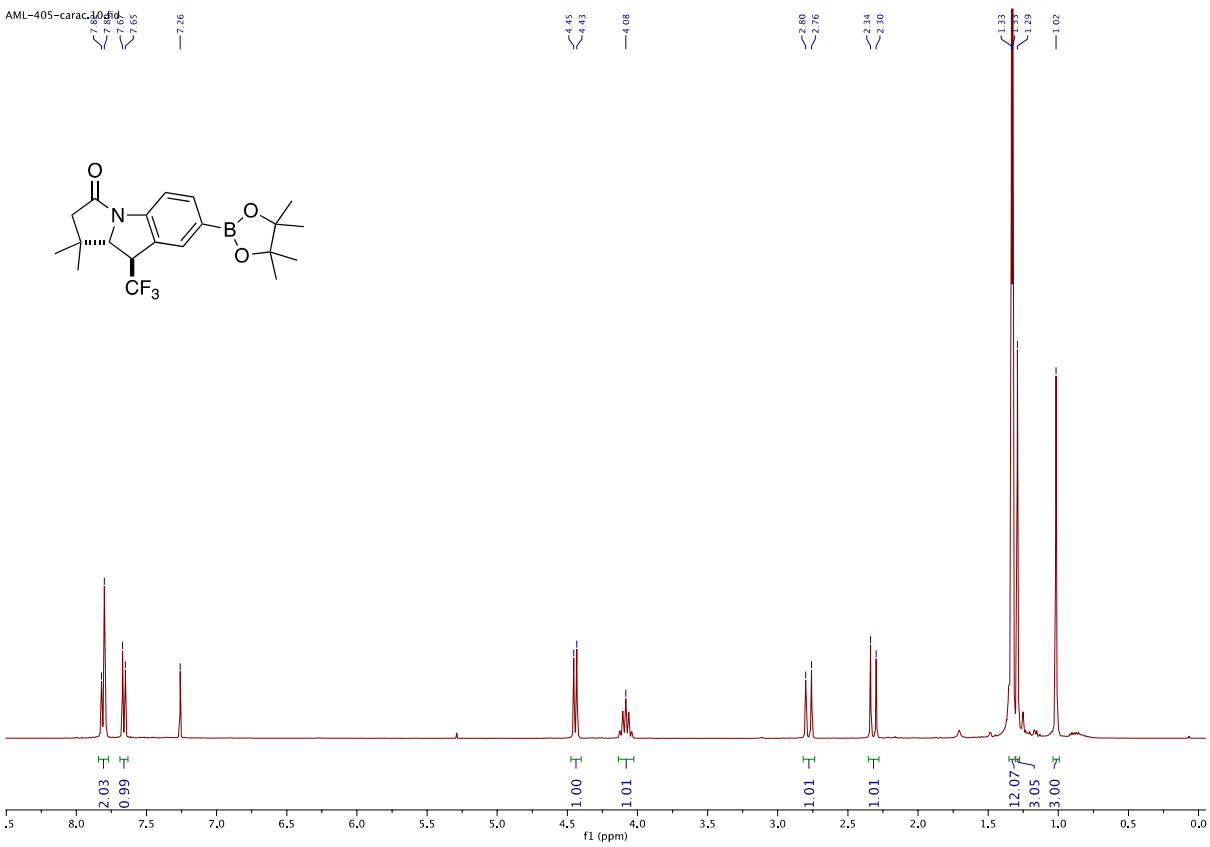
^{13}C NMR of **2k**



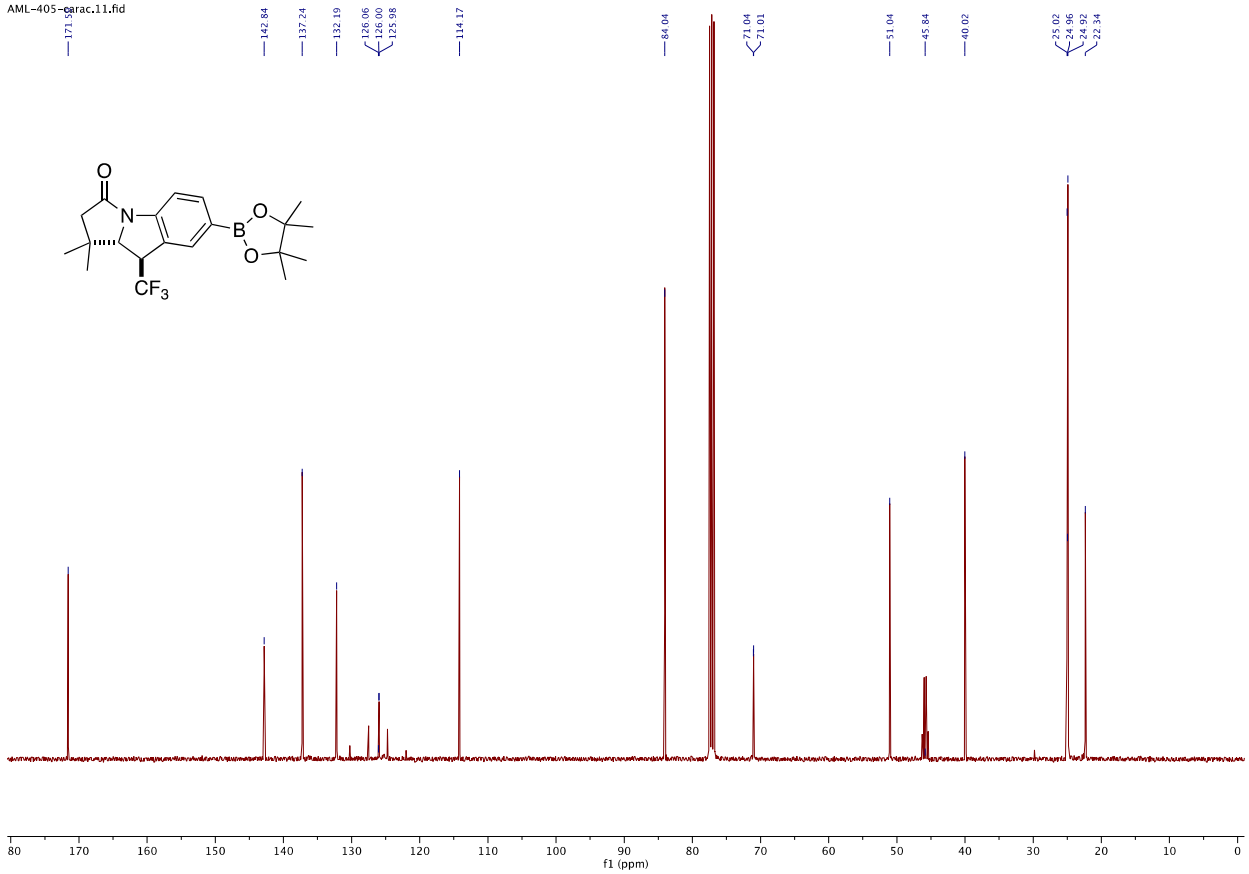
^{19}F NMR of **2k**



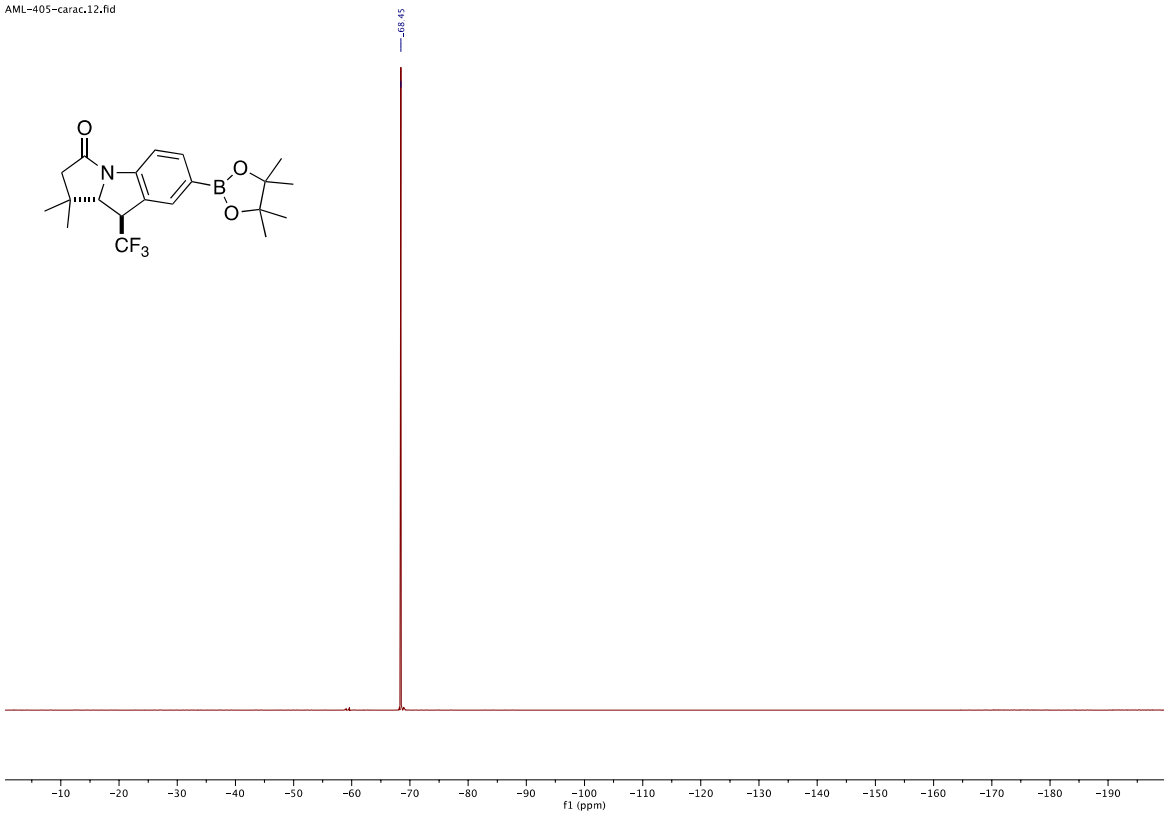
^{1}H NMR of **2l**



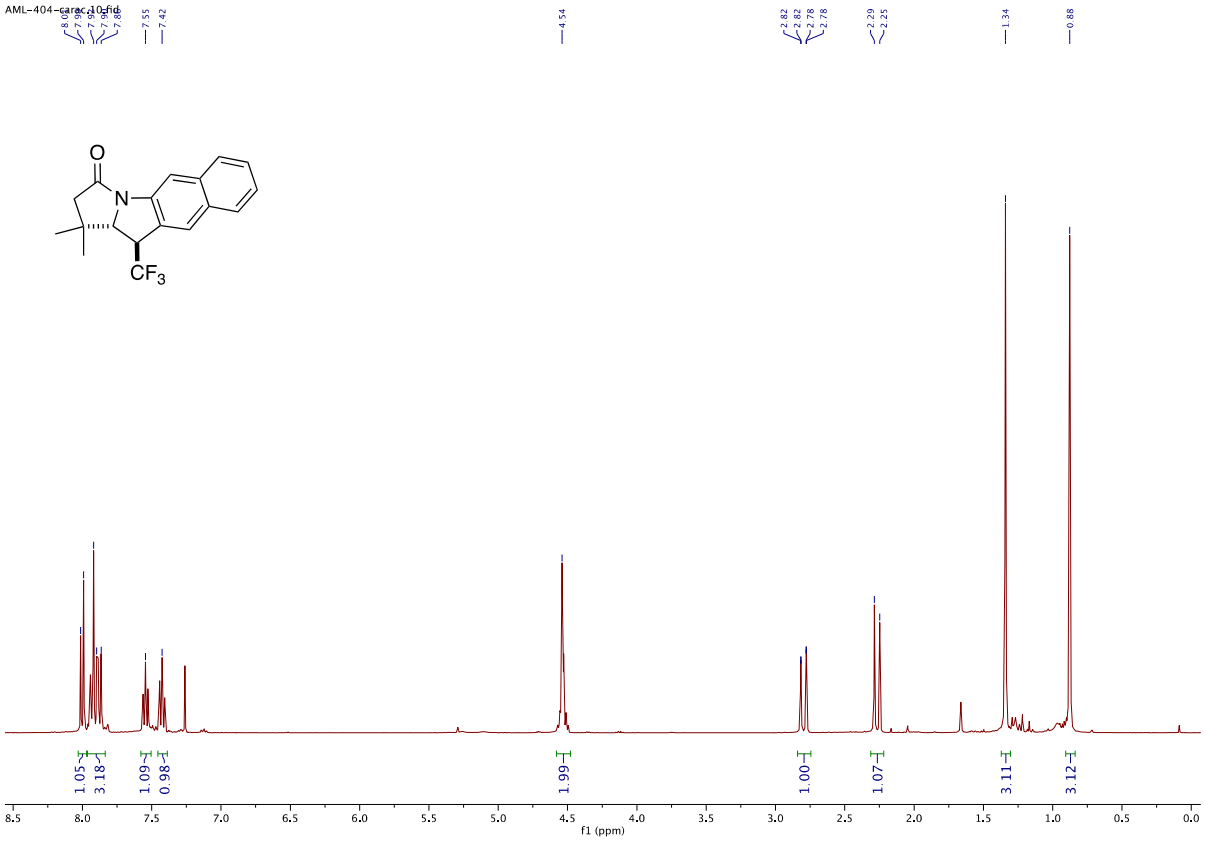
^{13}C NMR of **2l**



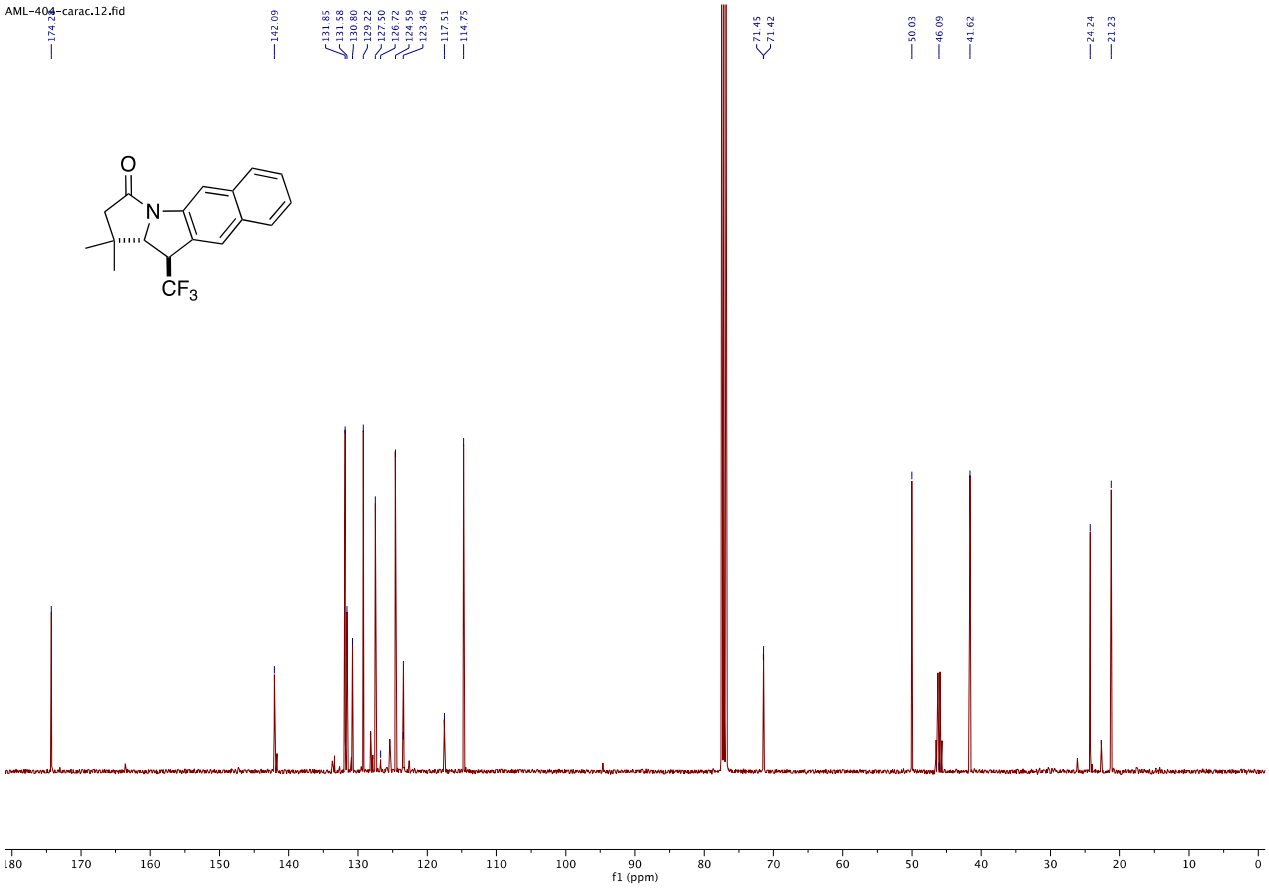
^{19}F NMR of **2l**



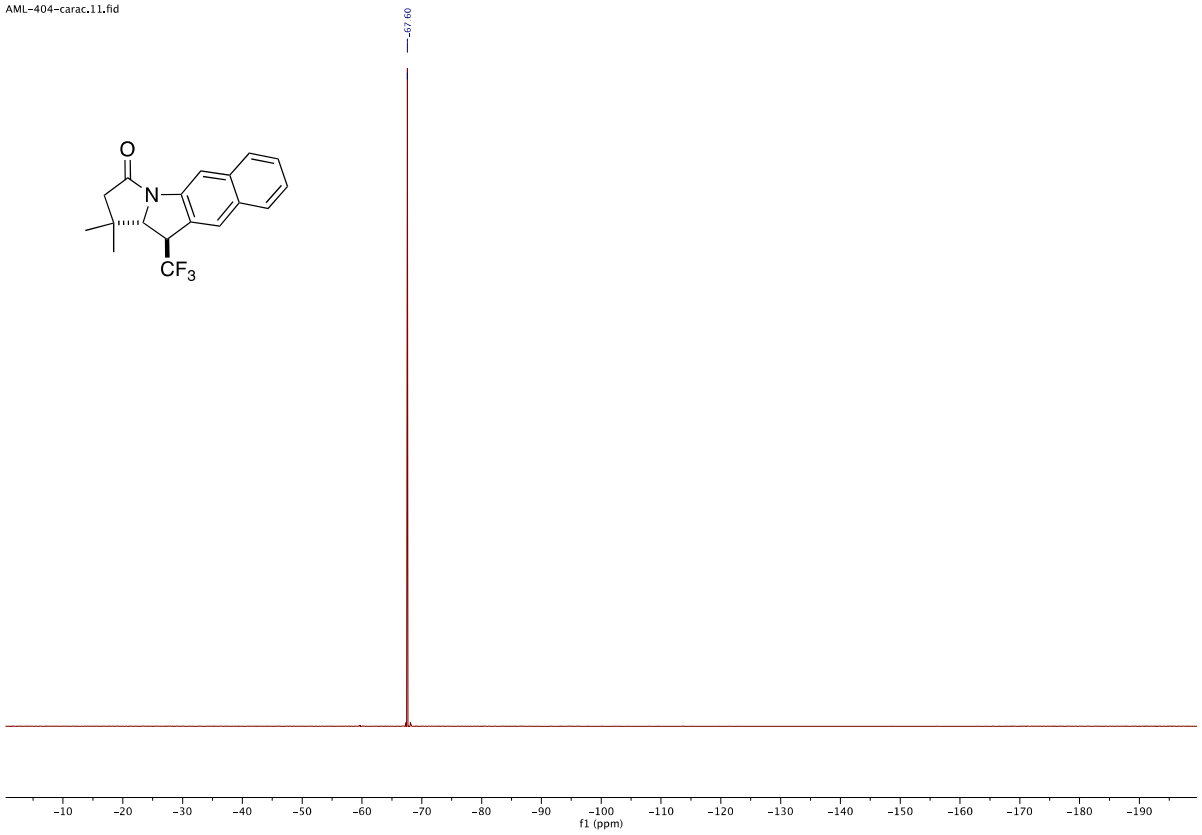
^{1}H NMR of **2m**



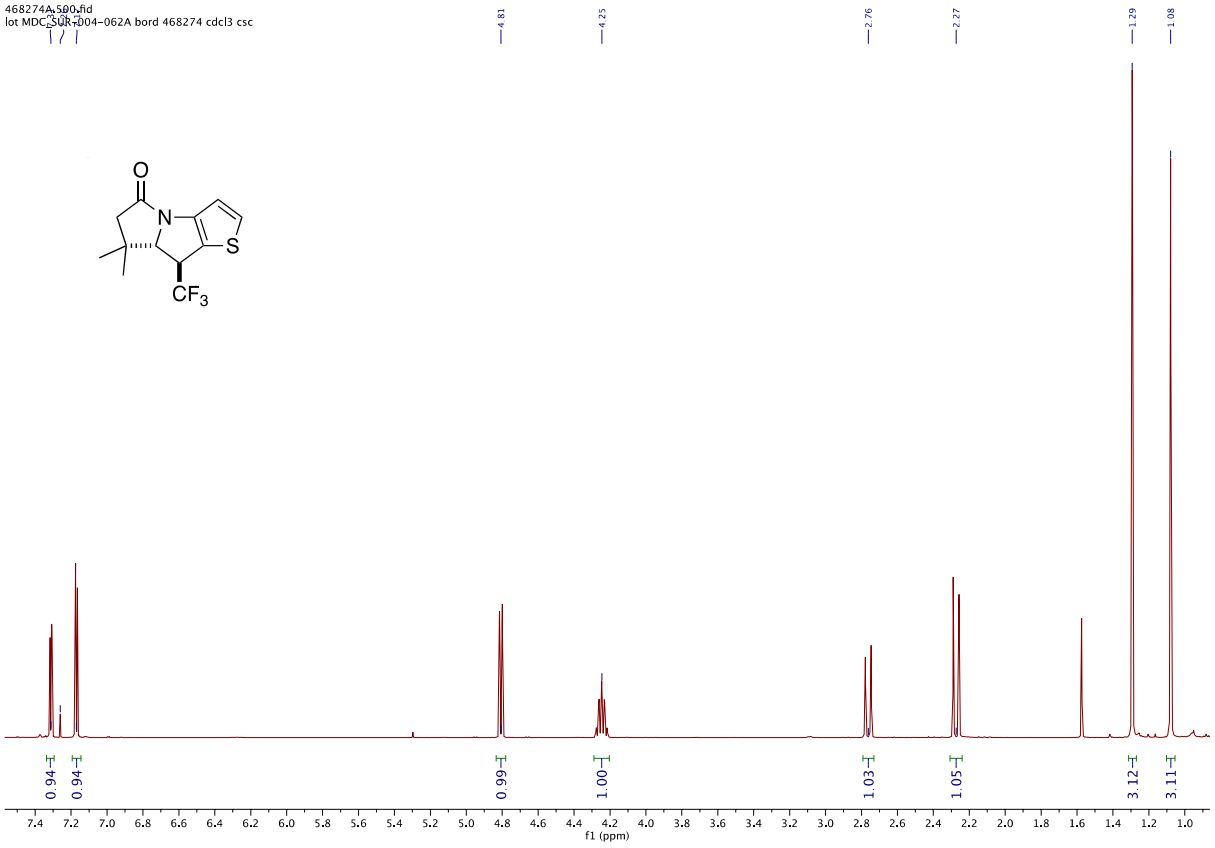
^{13}C NMR of **2m**



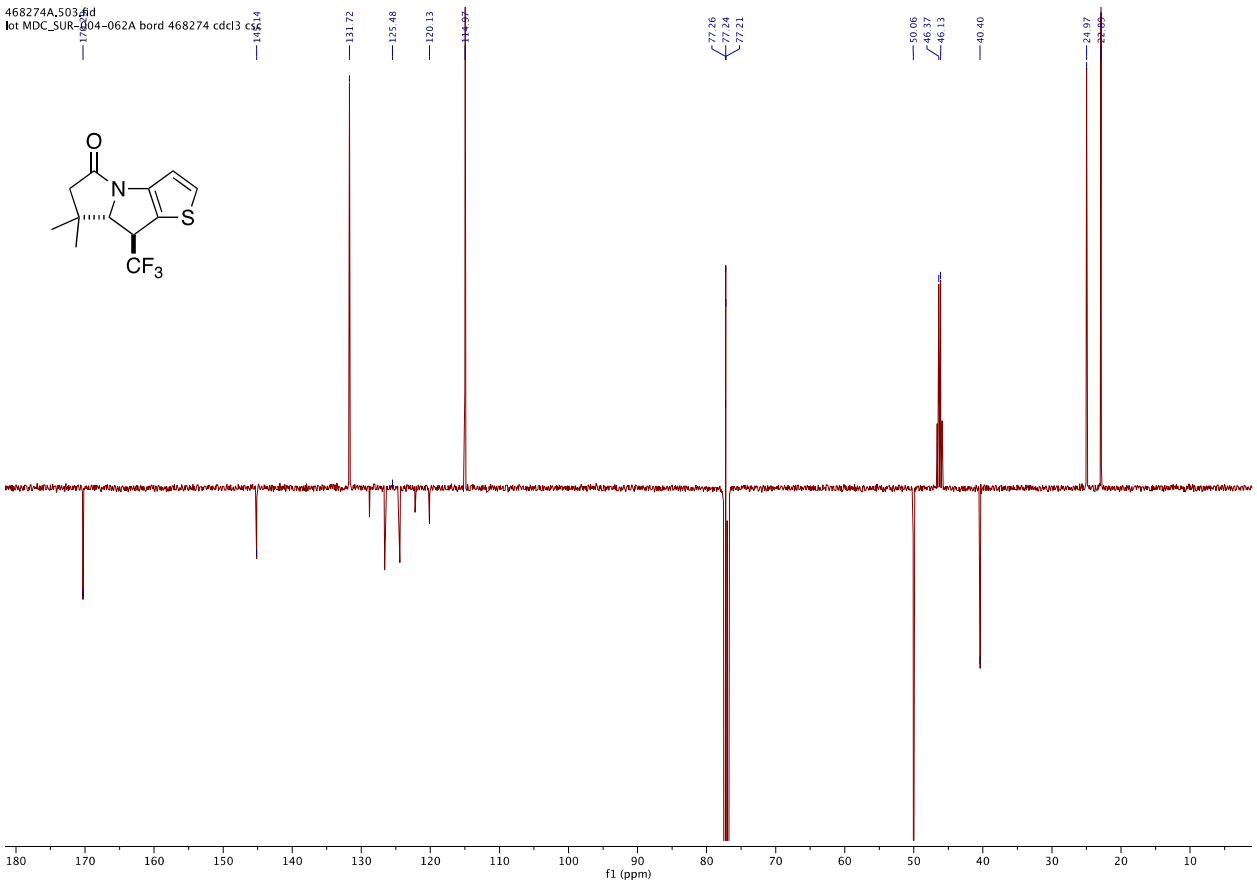
^{19}F NMR of **2m**



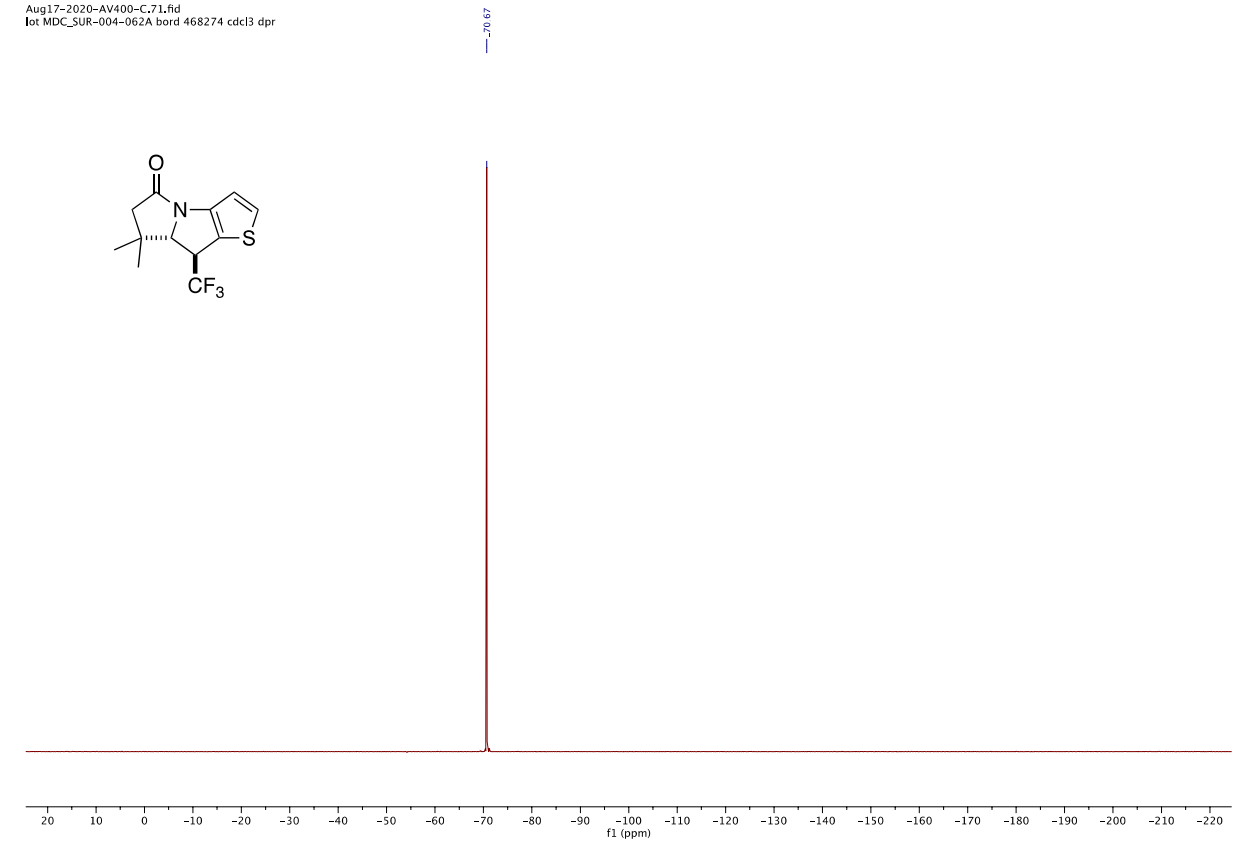
^{1}H NMR of **2n**



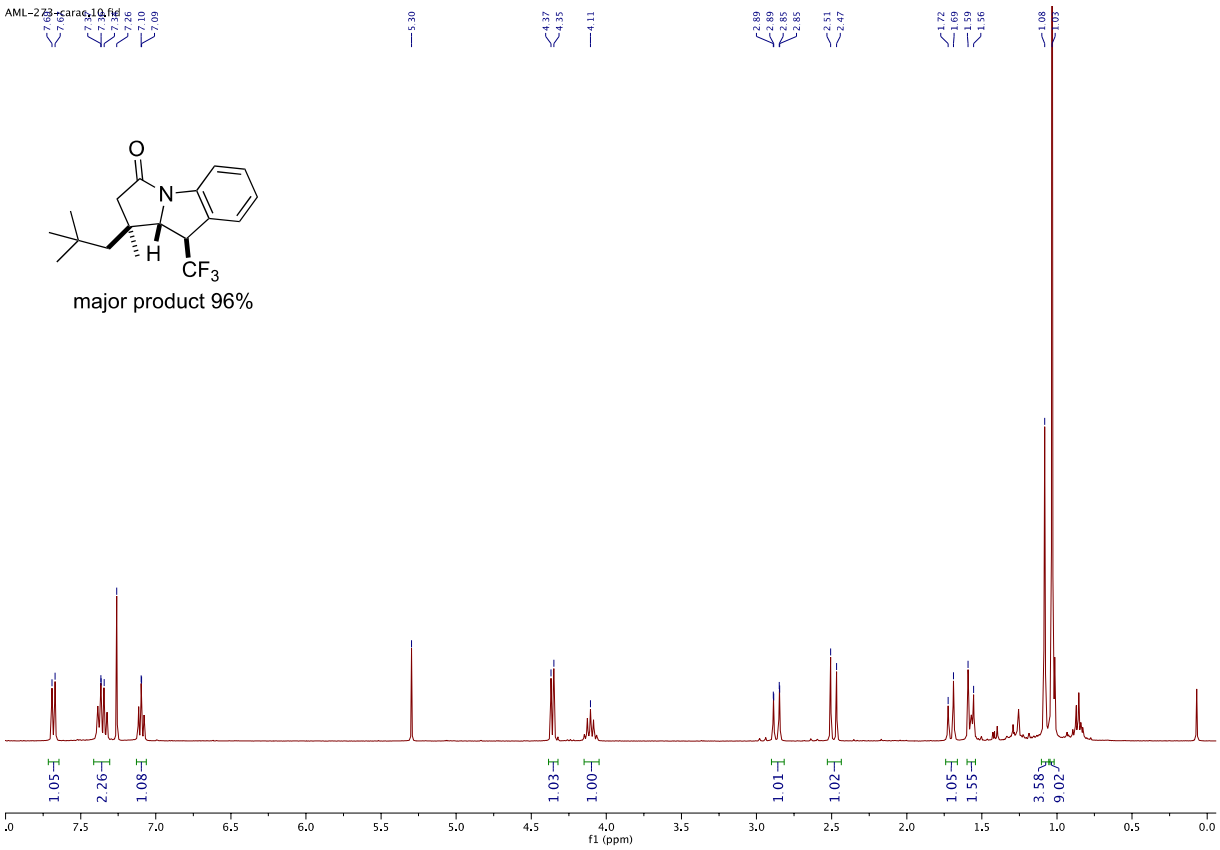
^{13}C NMR of **2n**



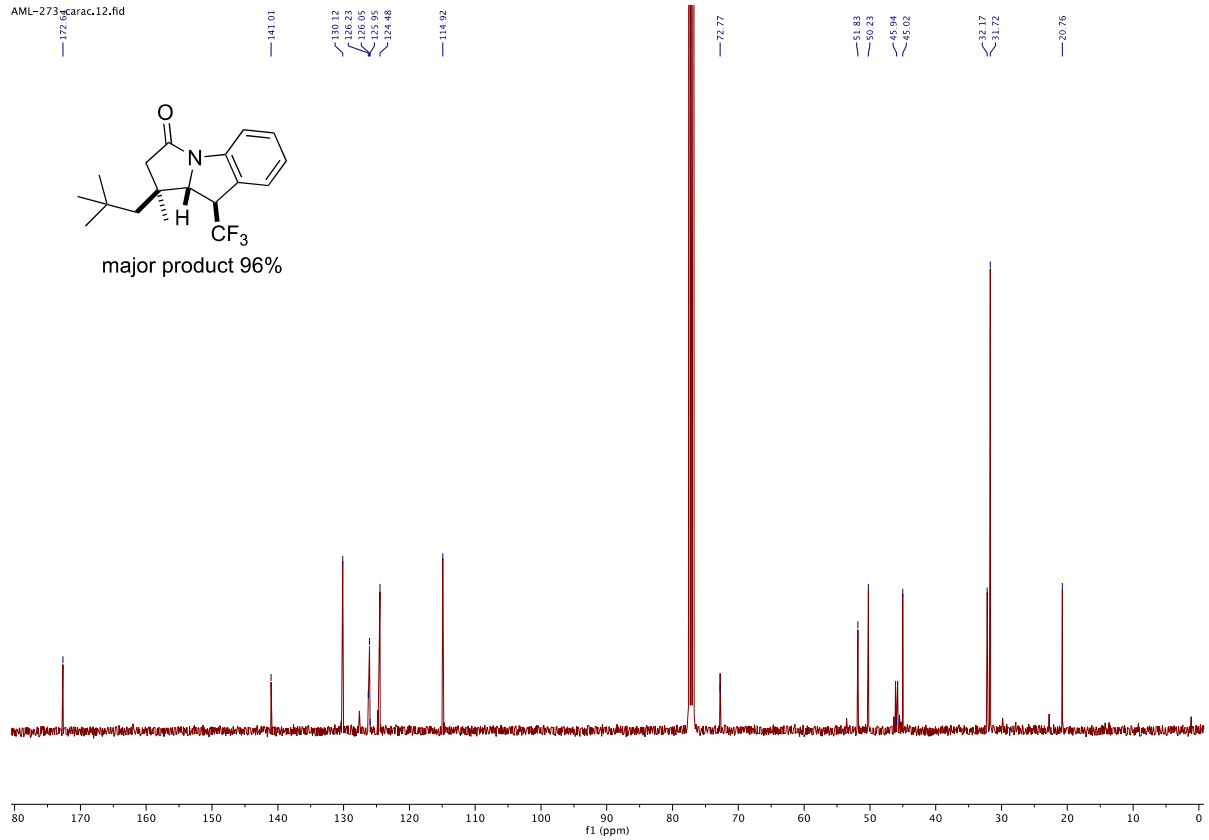
^{19}F NMR of **2n**



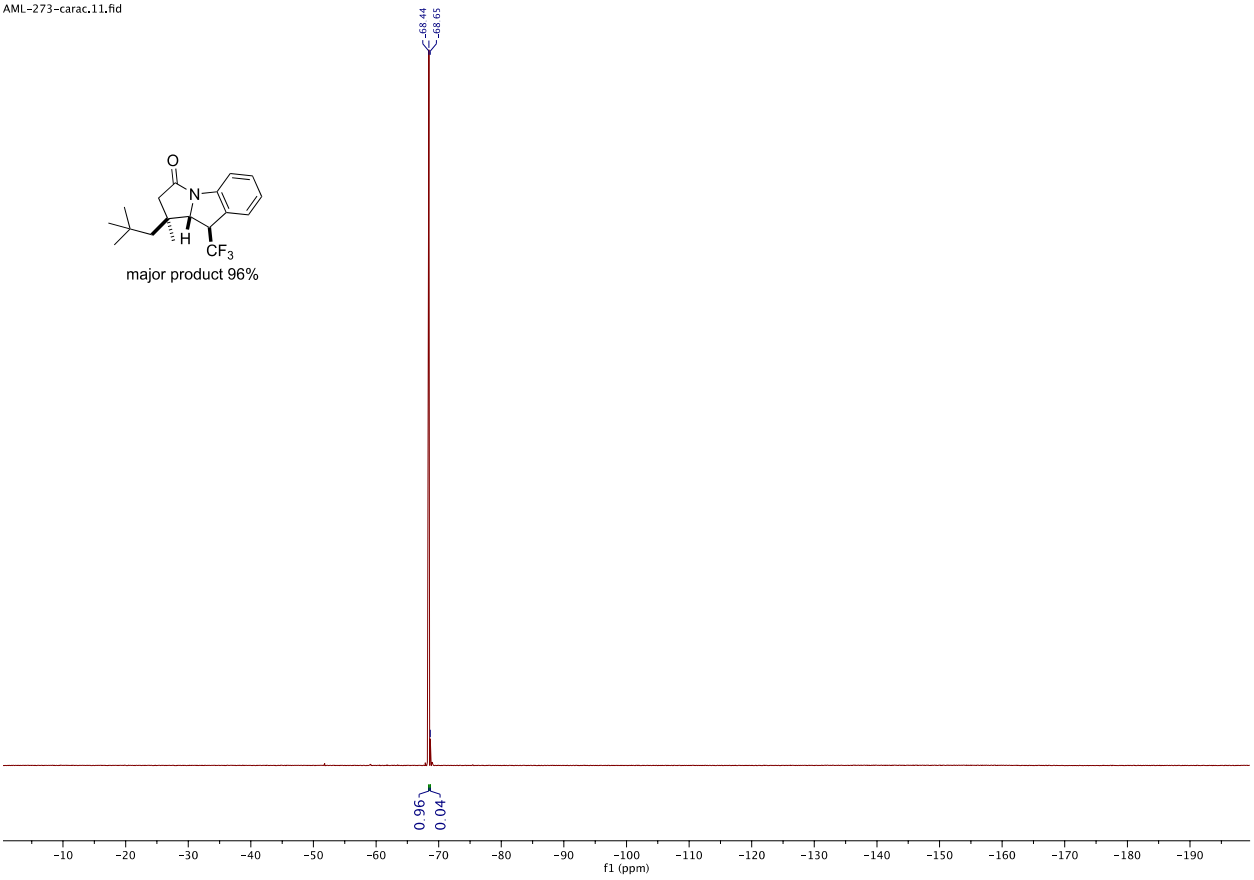
^{1}H NMR of **2o**



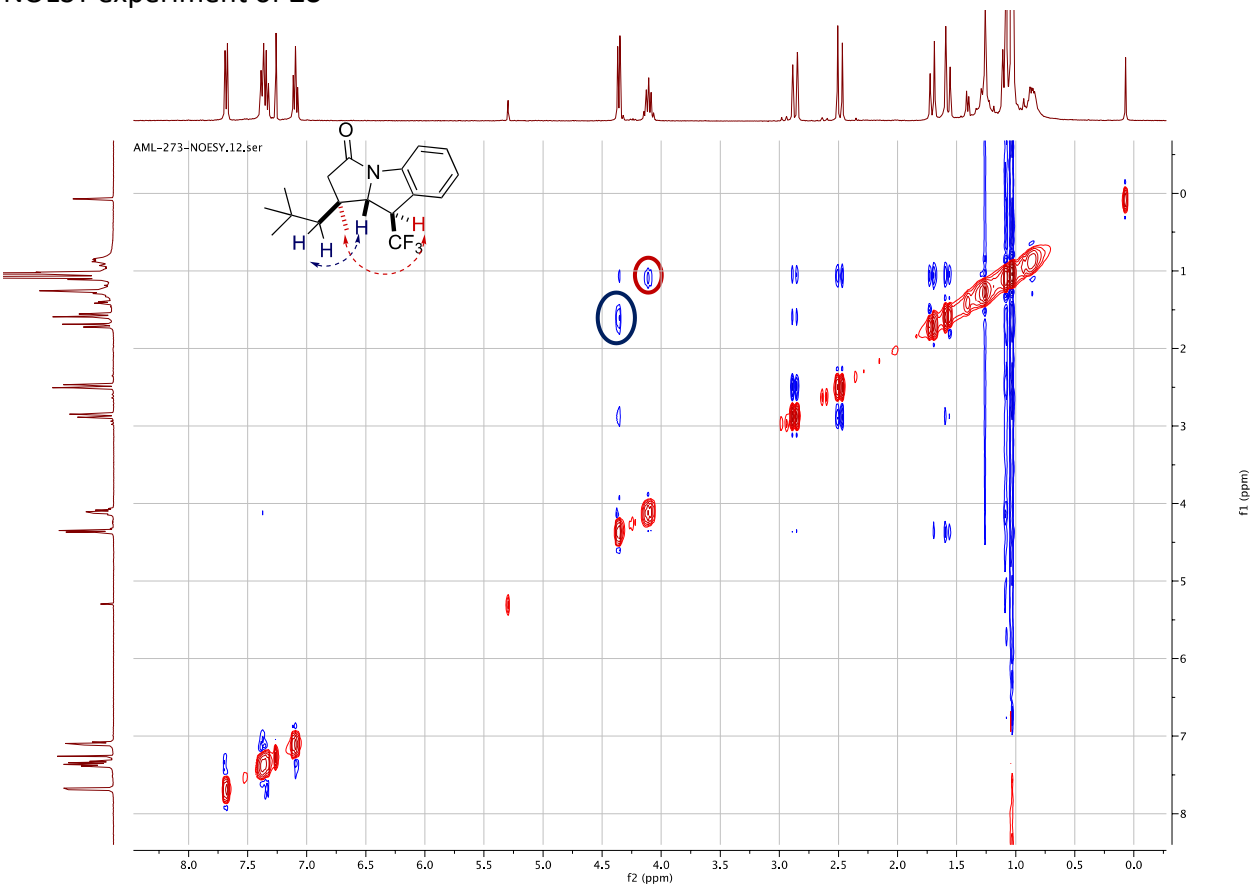
^{13}C NMR of **2o**



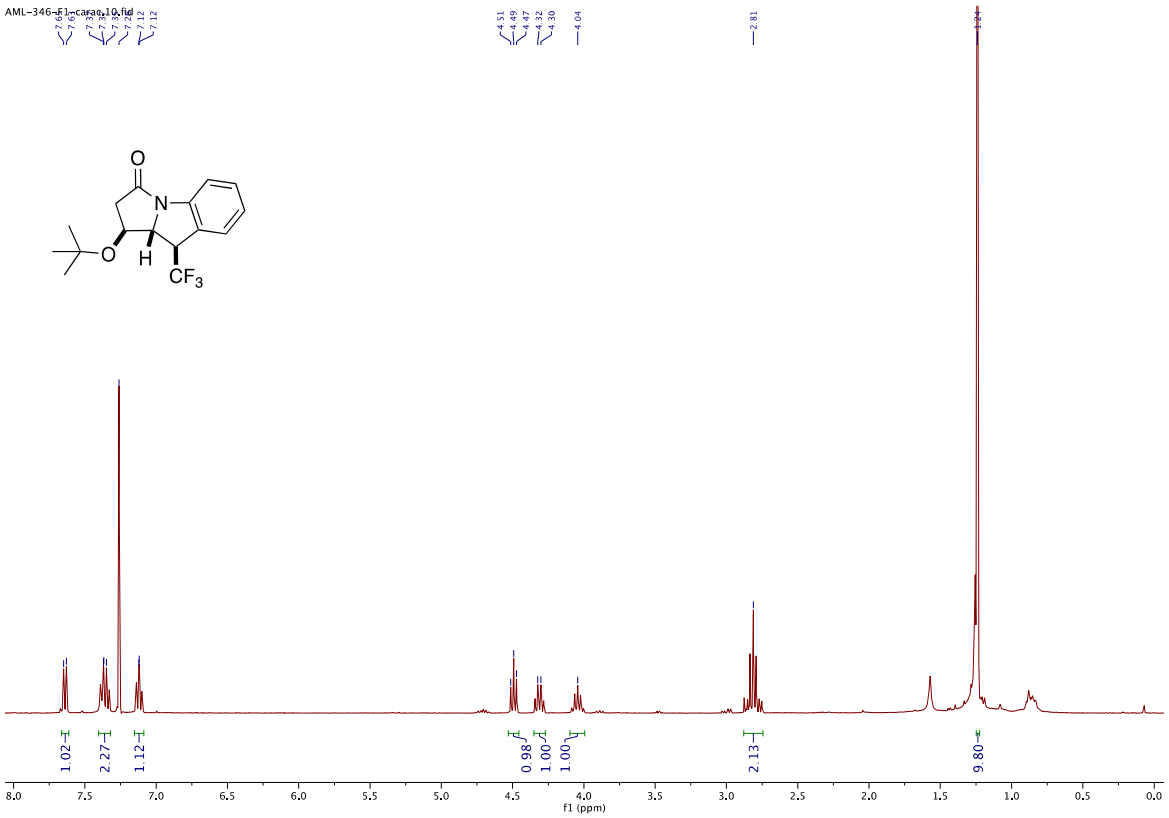
^{19}F NMR of **2o**



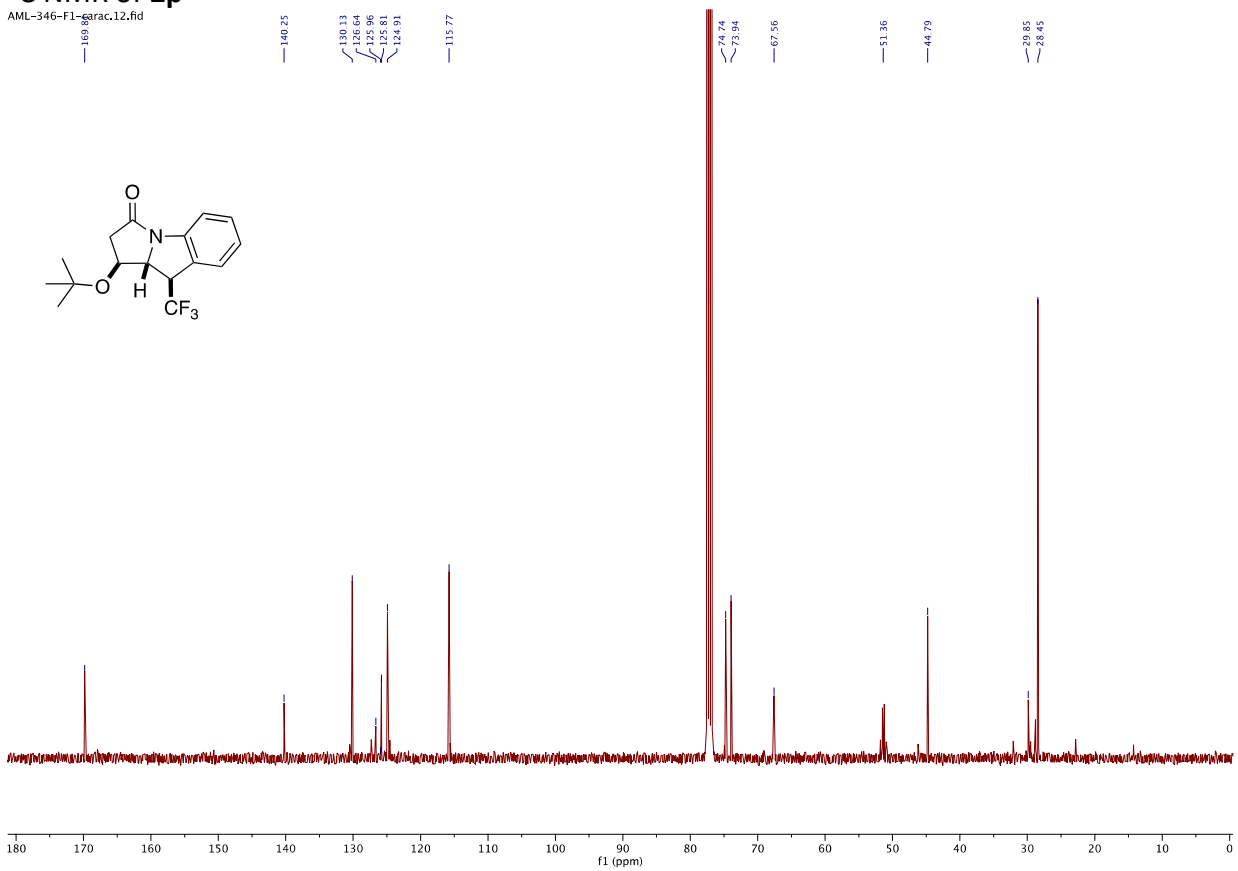
NOESY experiment of **2o**



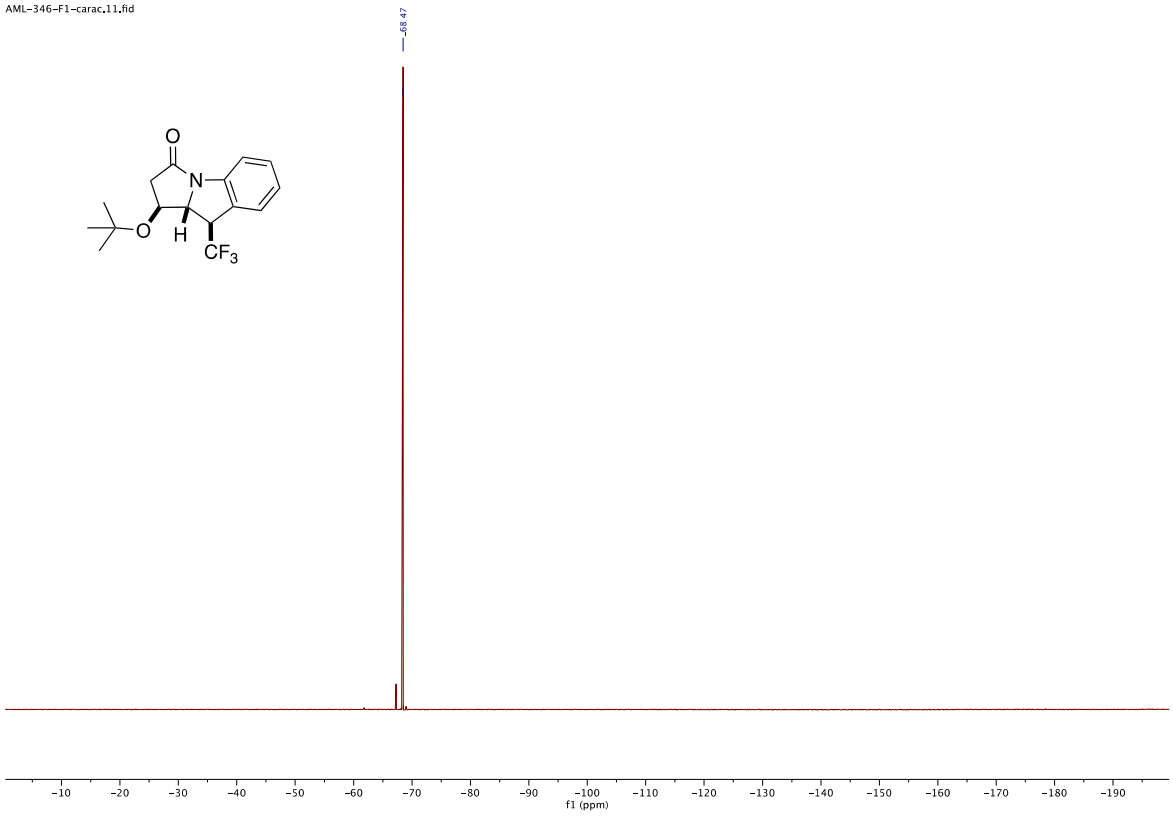
^{1}H NMR of **2p**



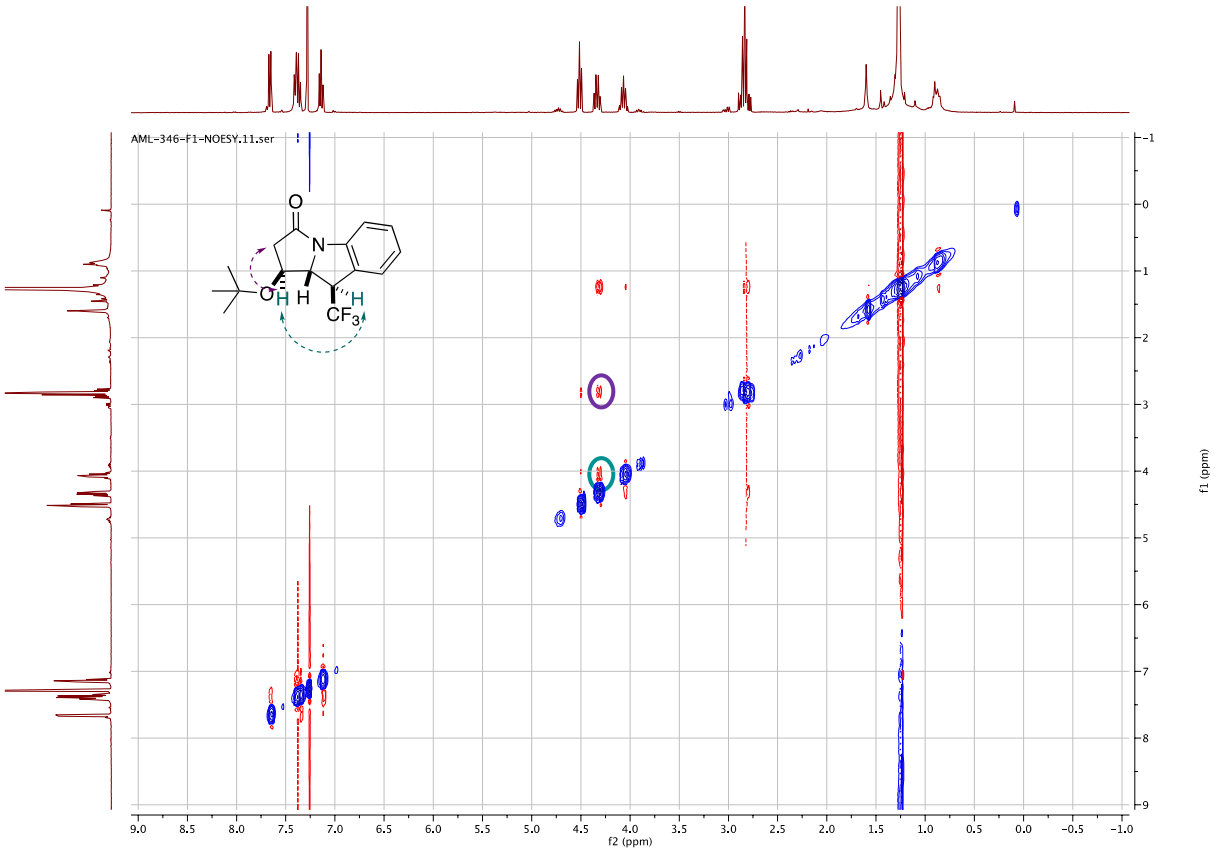
^{13}C NMR of **2p**



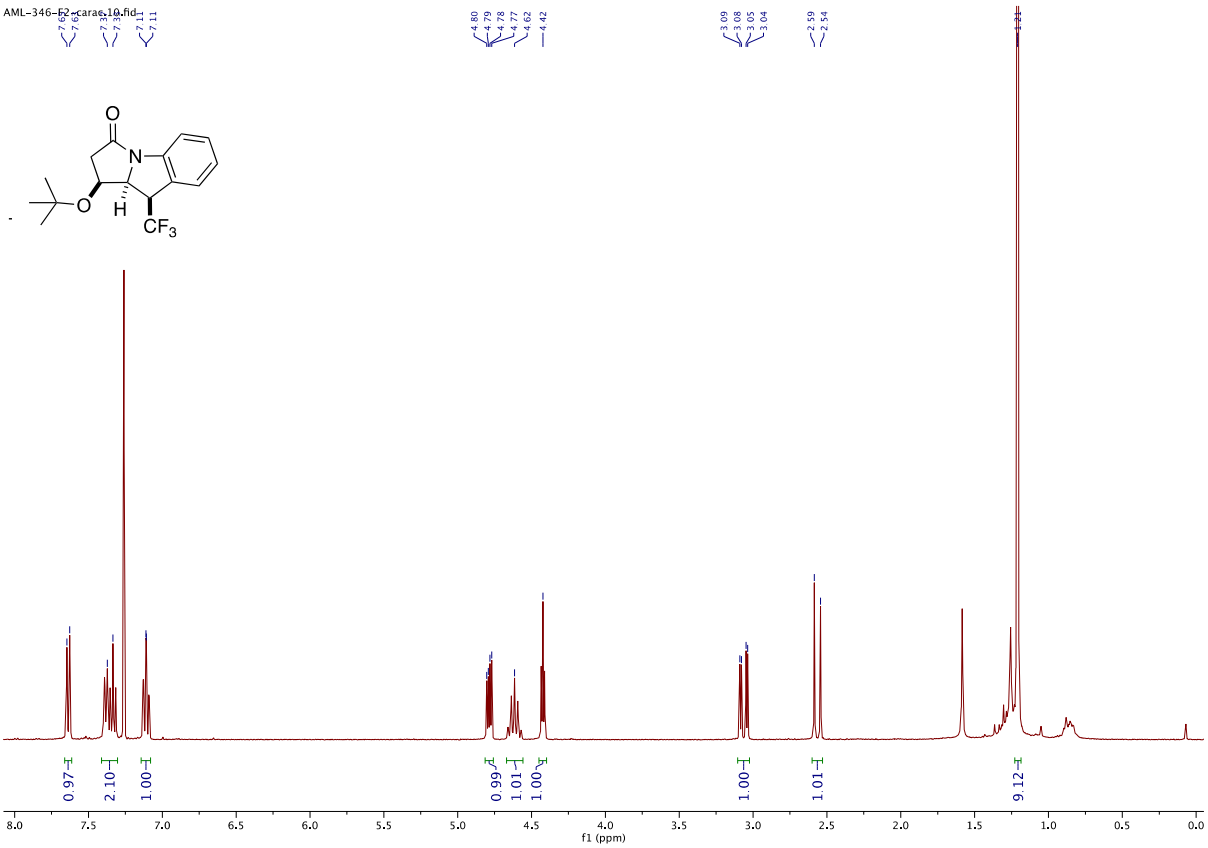
^{19}F NMR of **2p**



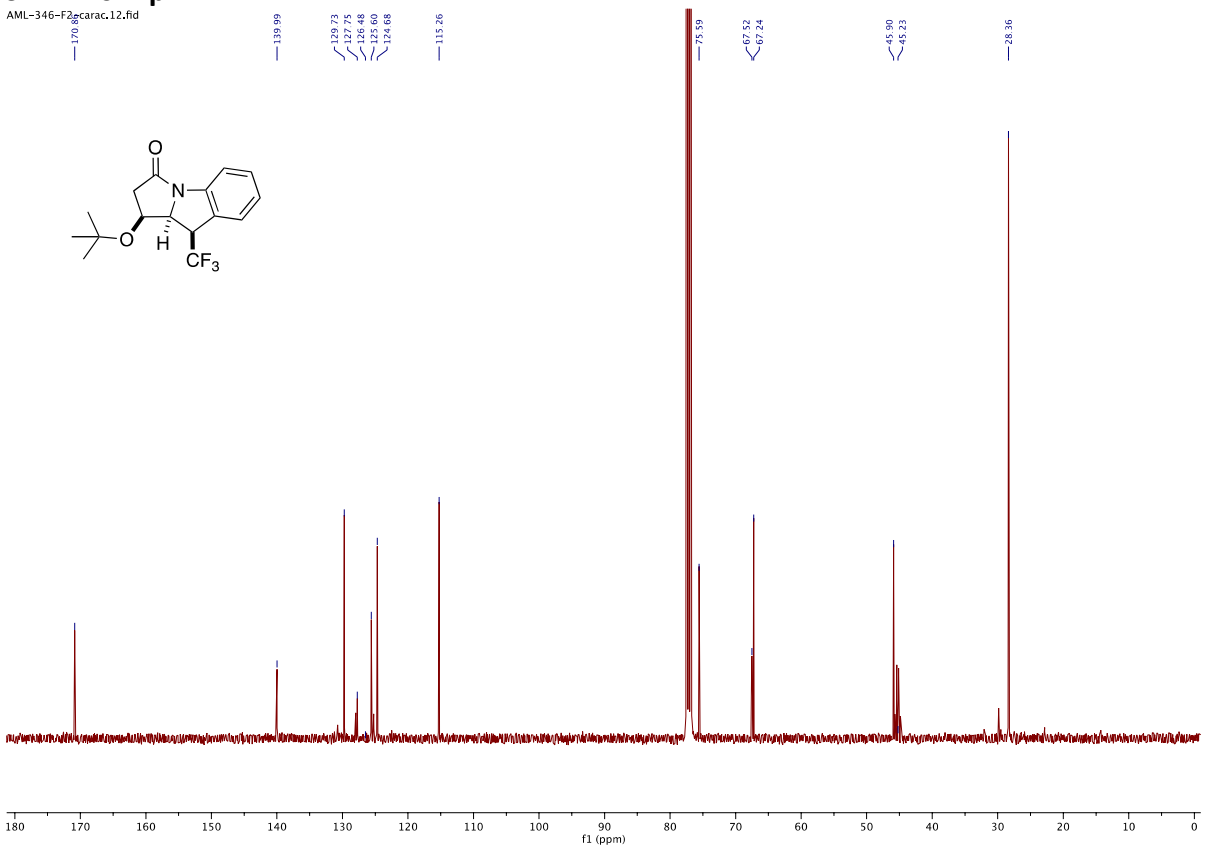
NOESY experiment of **2p**



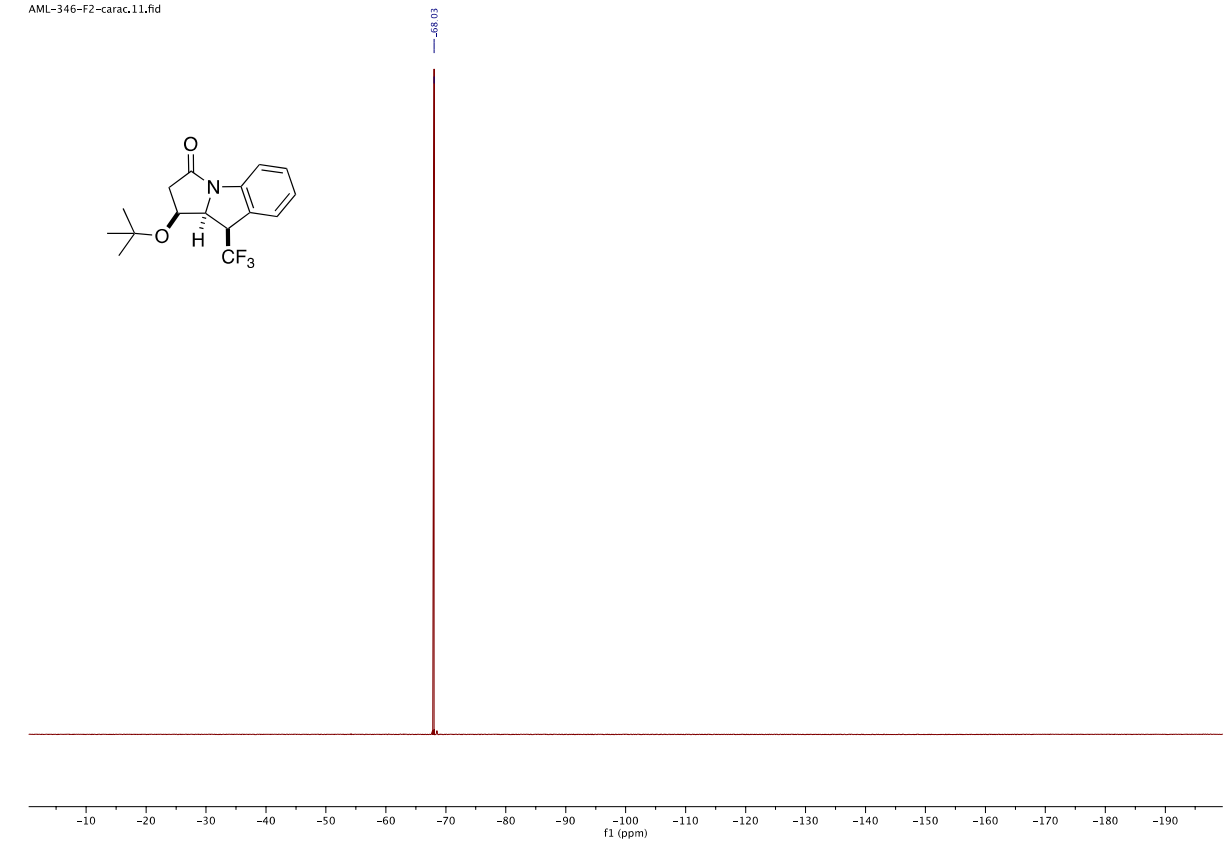
^{1}H NMR of **2p'**



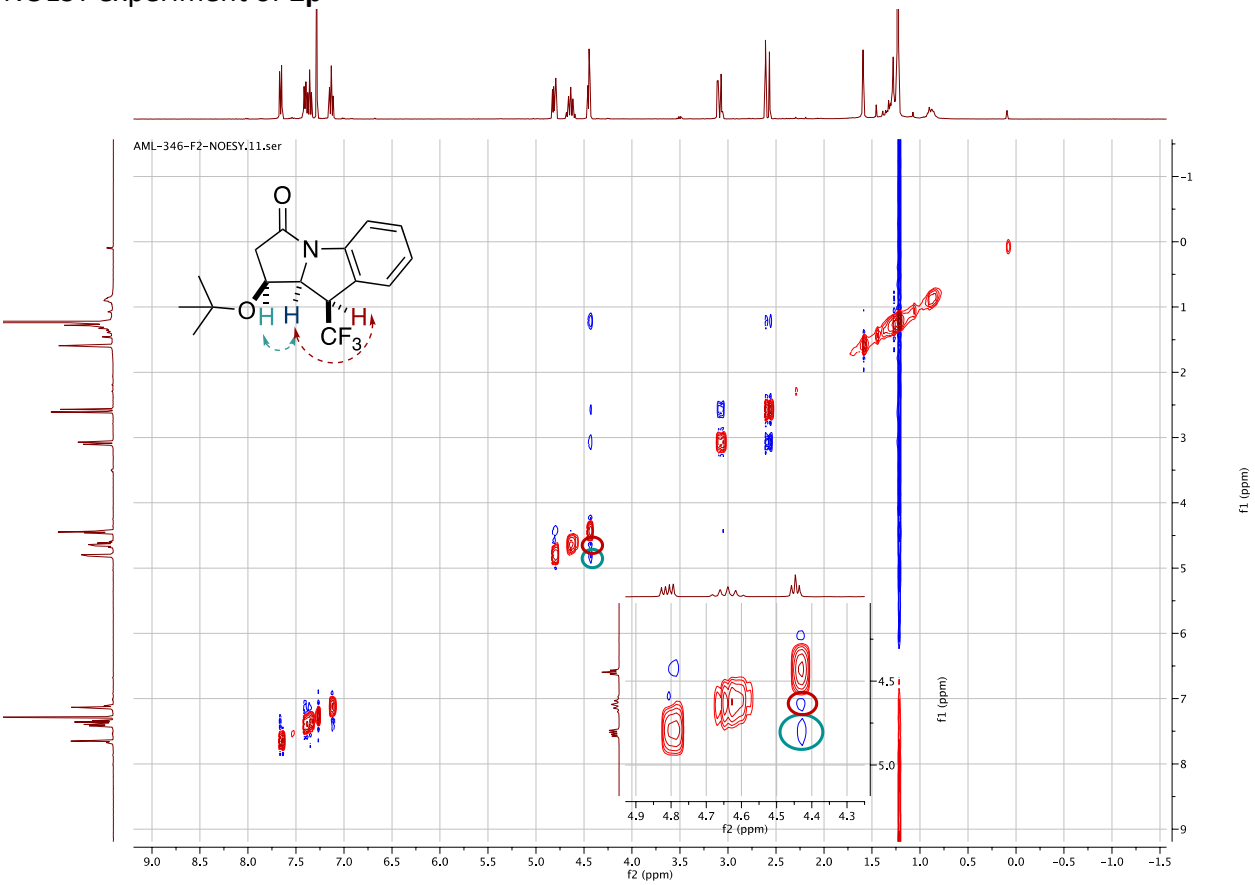
^{13}C NMR of **2p'**



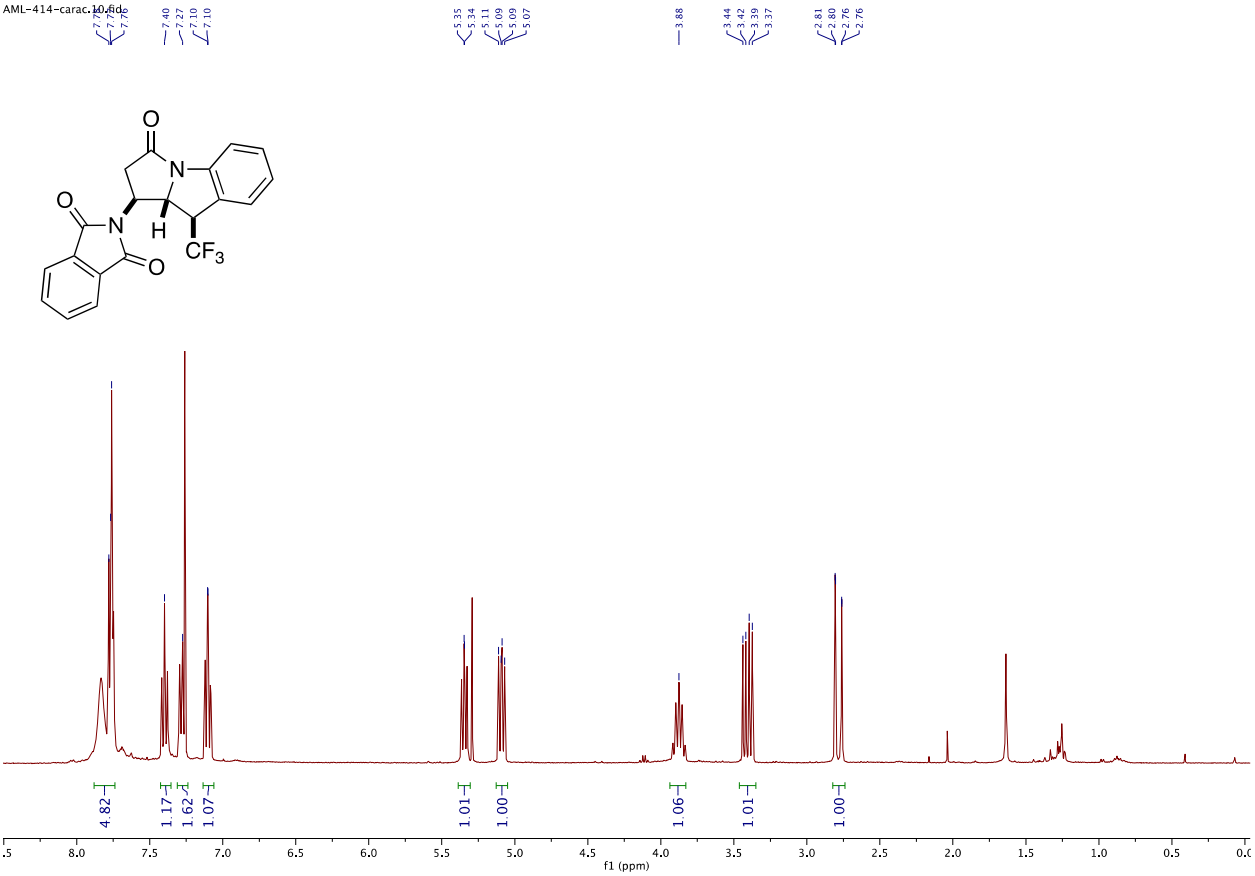
^{19}F NMR of **2p'**



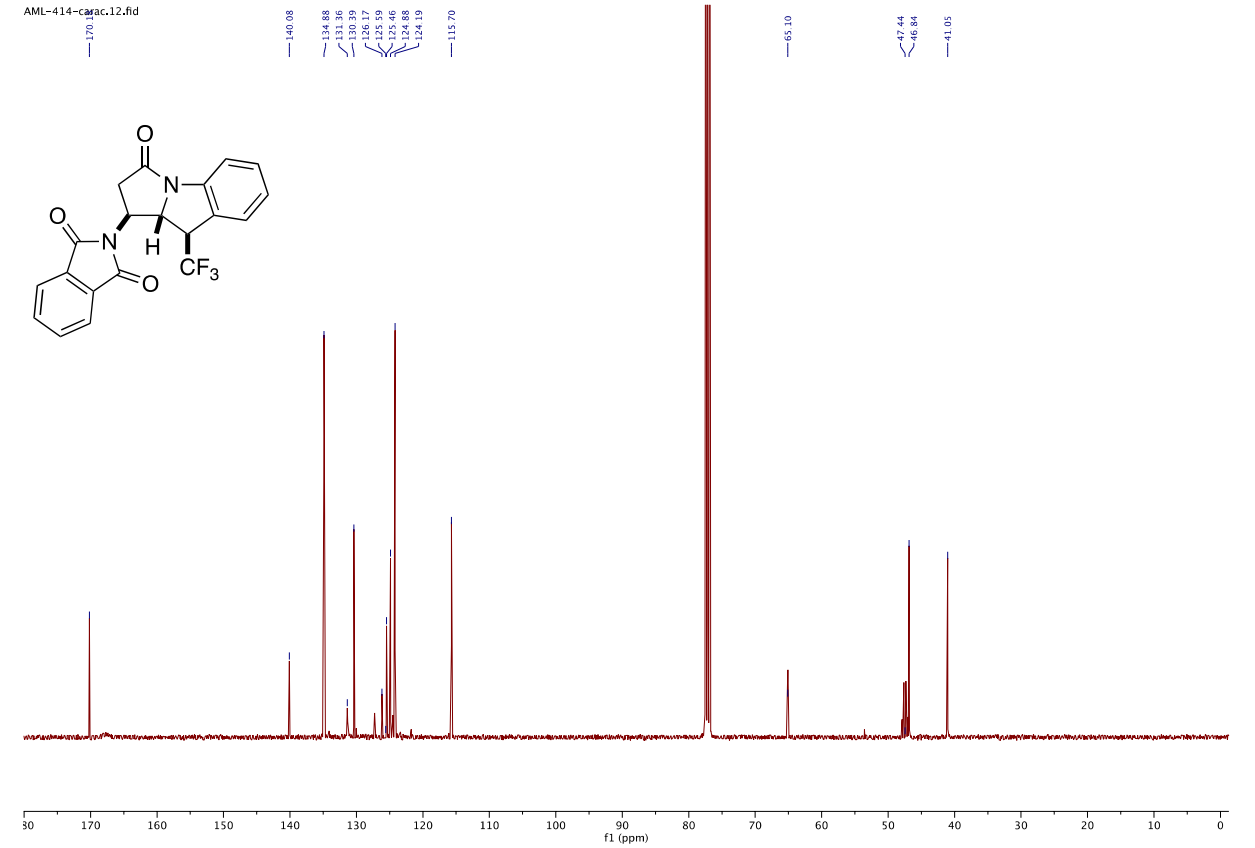
NOESY experiment of **2p'**



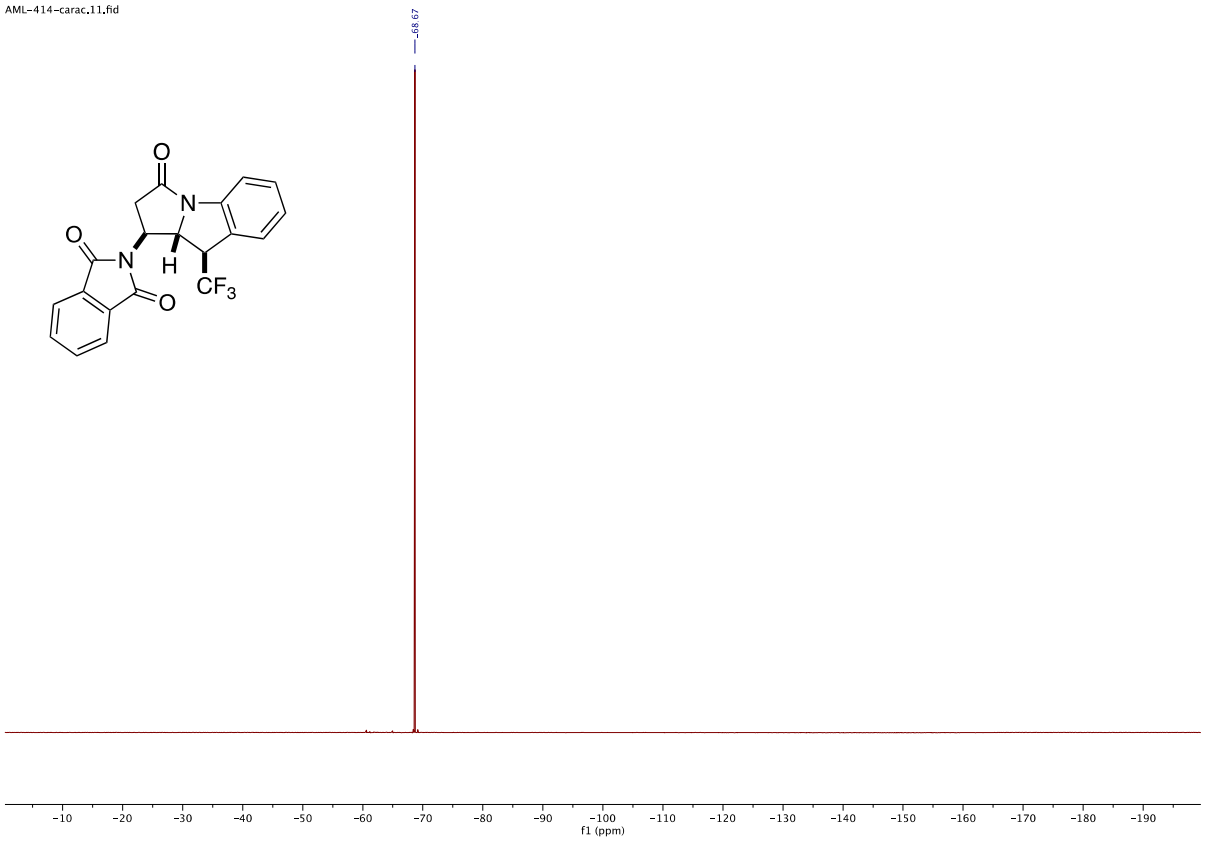
^{1}H NMR of **2q**



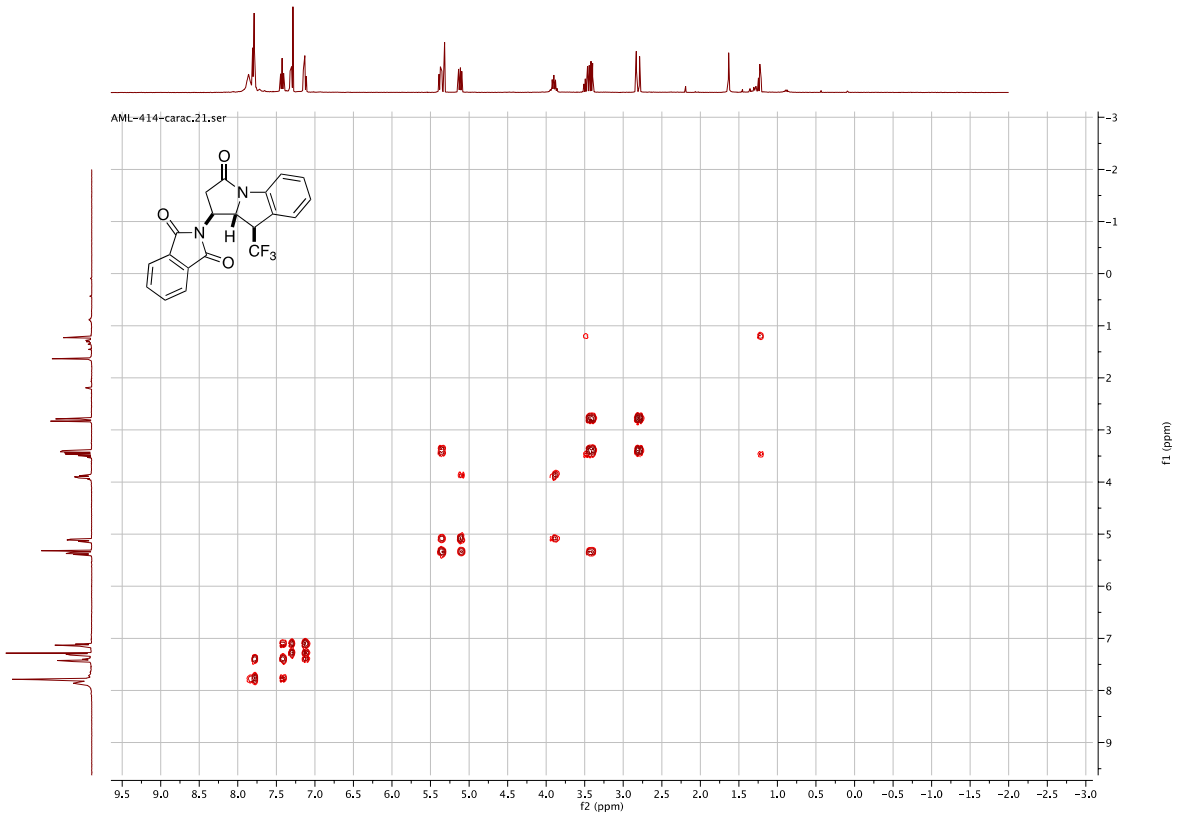
^{13}C NMR of **2q**



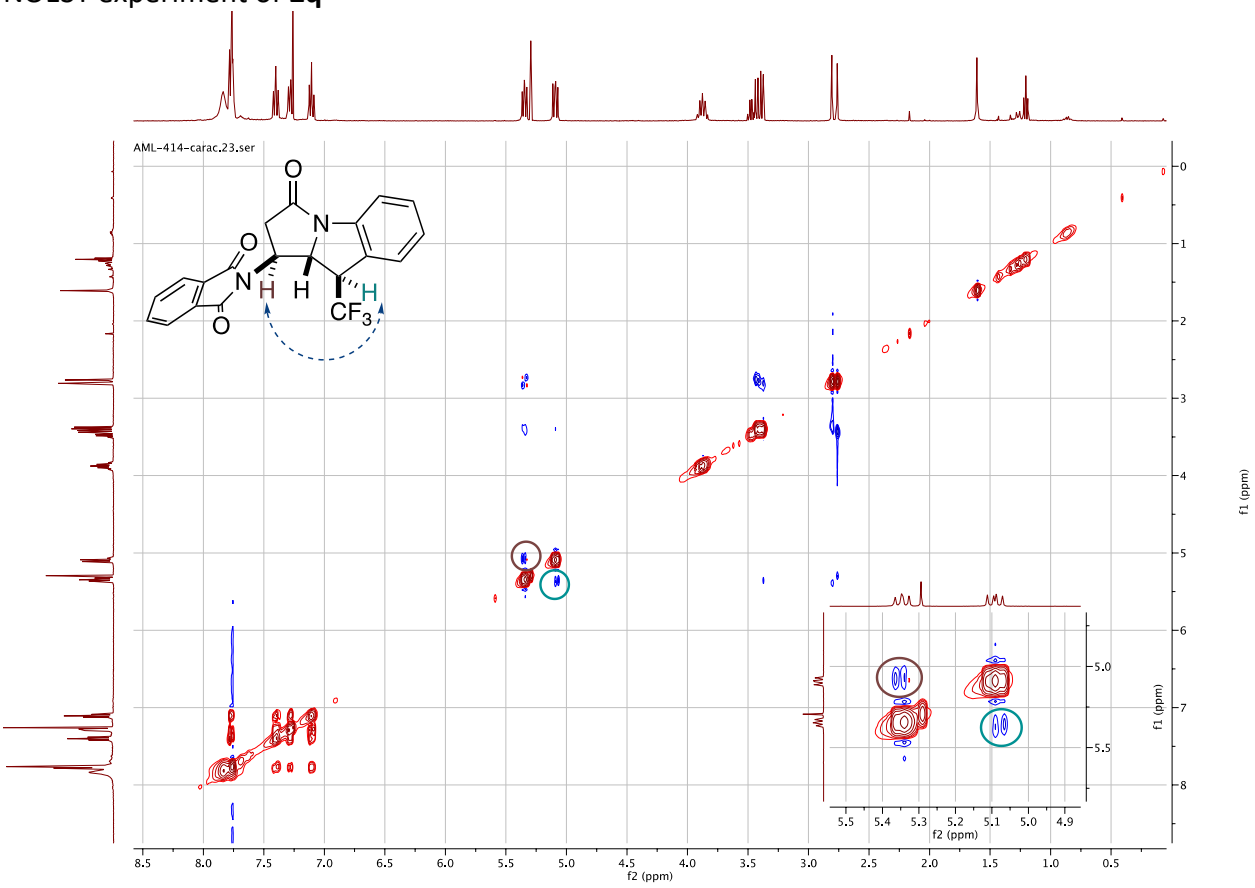
^{19}F NMR of **2q**



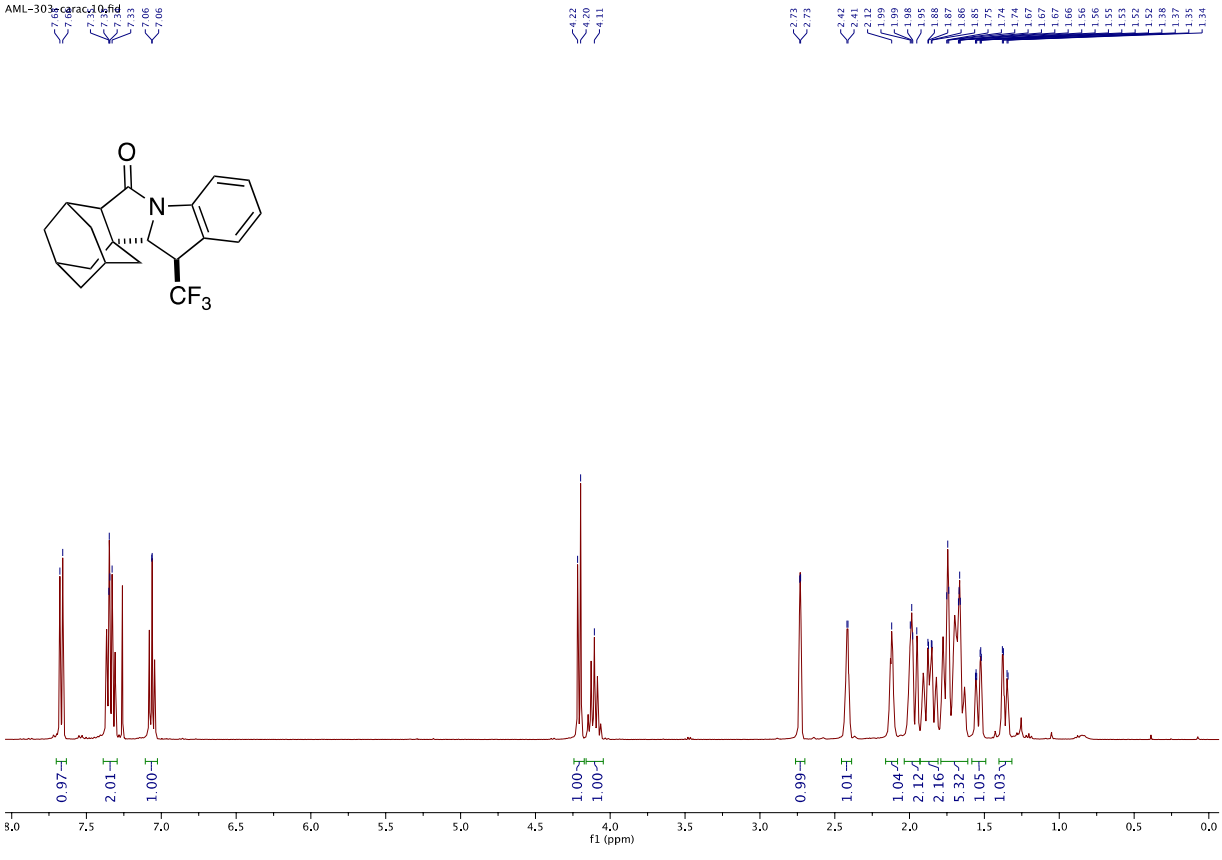
COSY experiment of **2q**



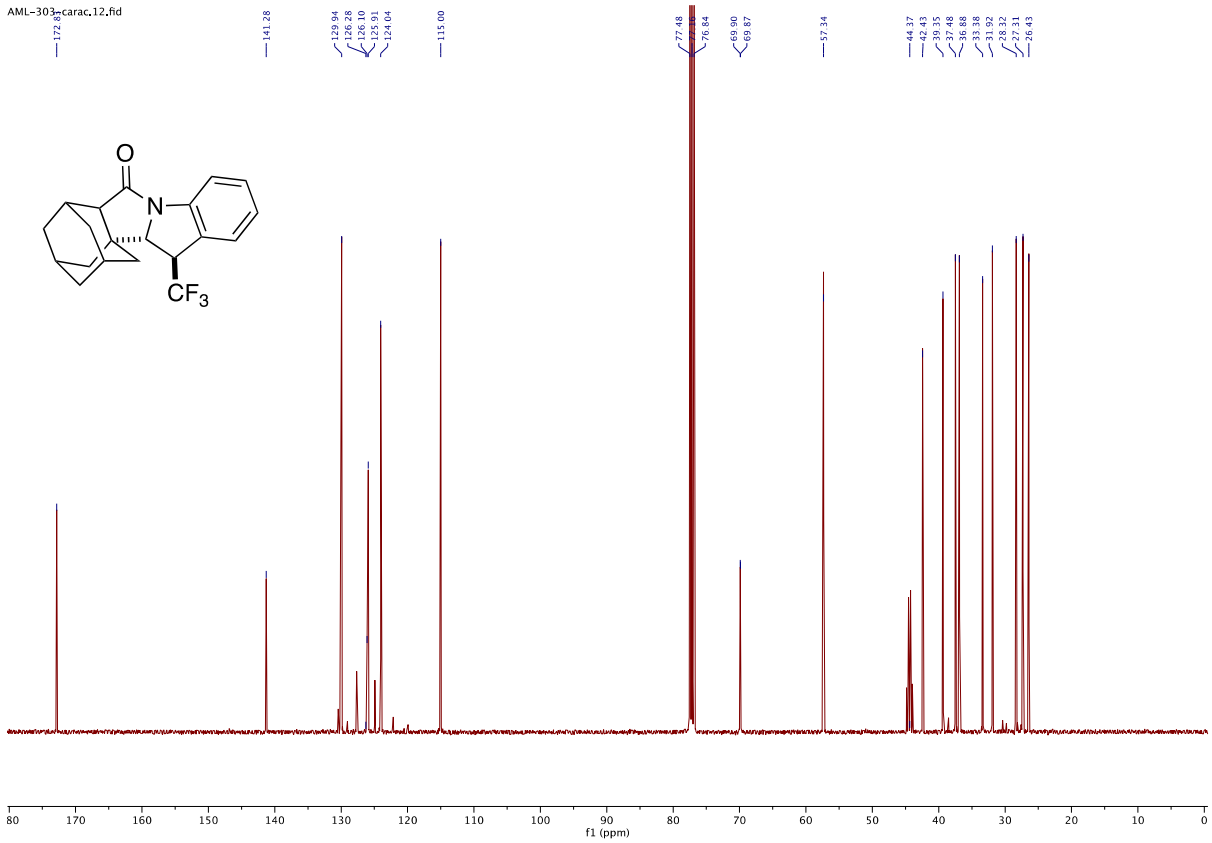
NOESY experiment of **2q**



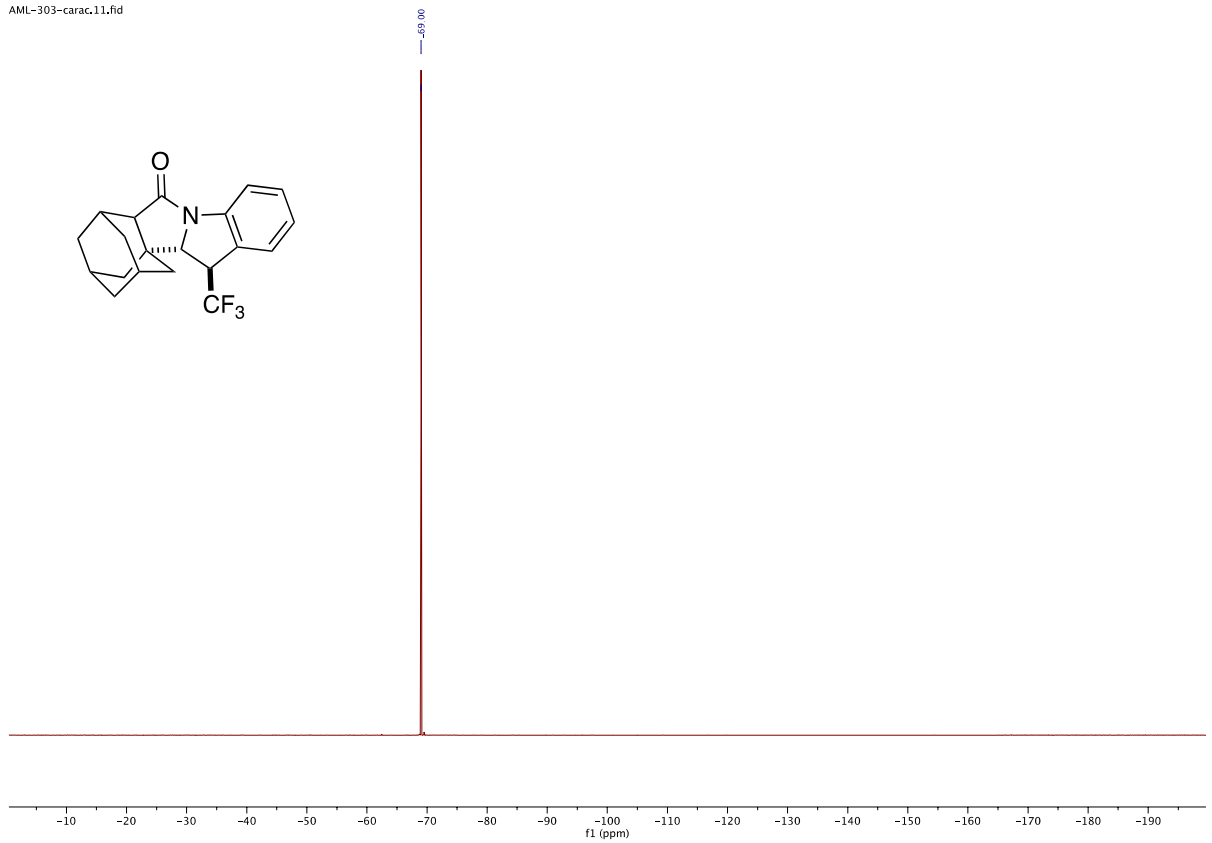
^{1}H NMR of **2r**



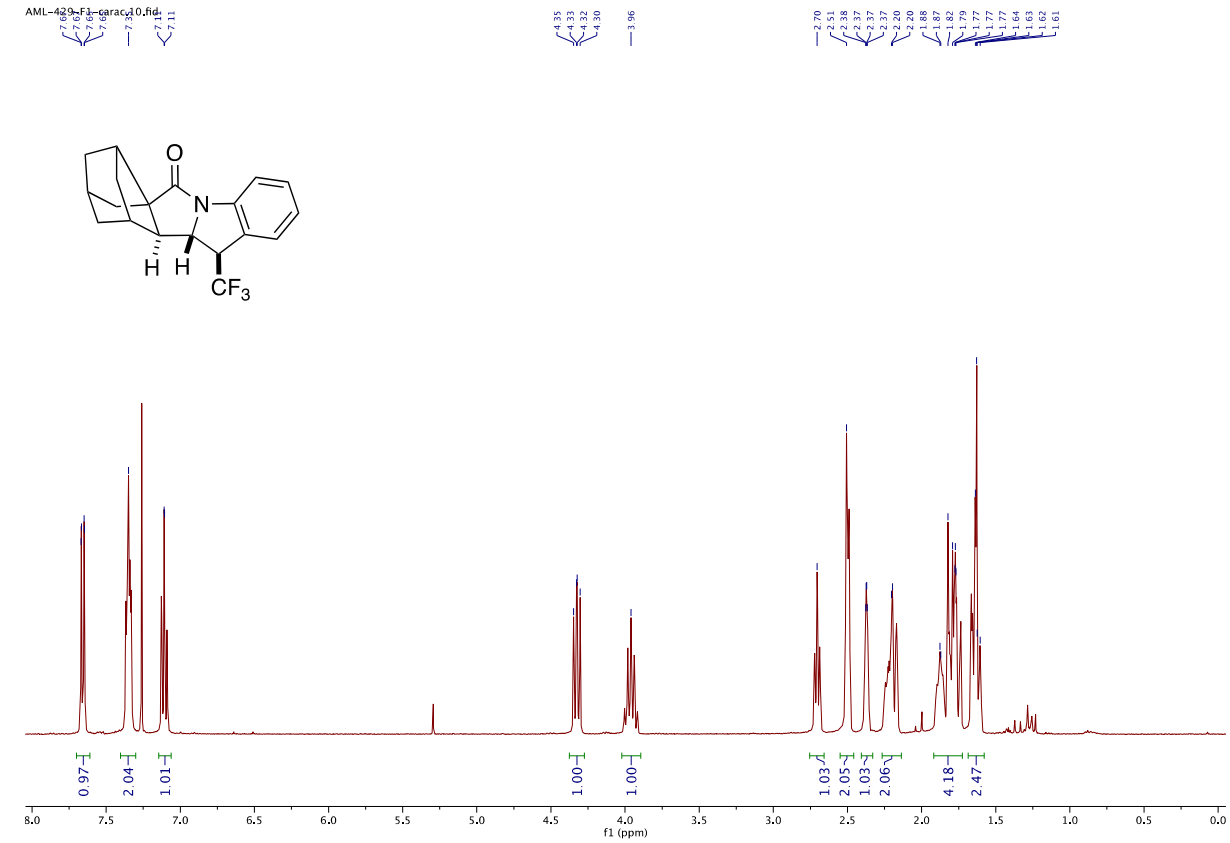
^{13}C NMR of **2r**



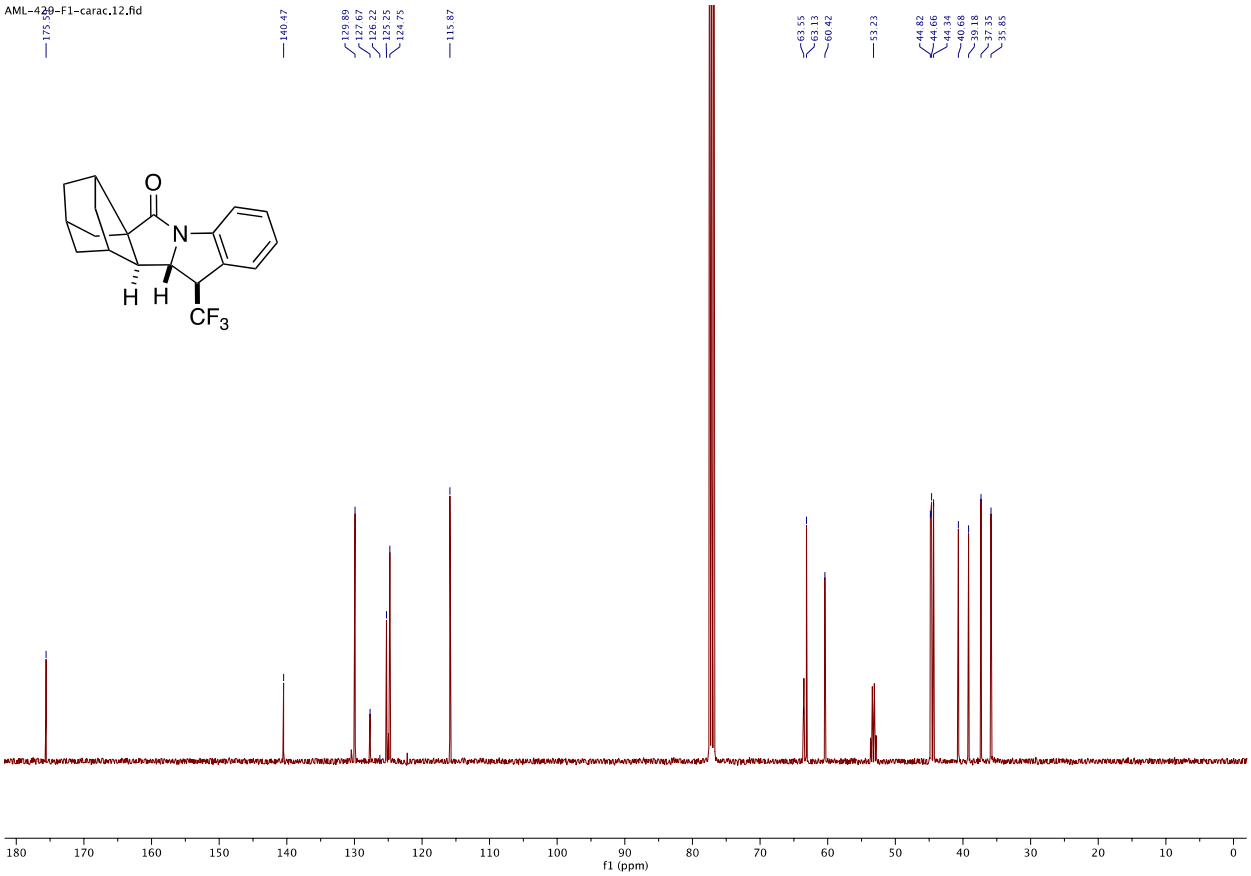
^{19}F NMR of **2r**



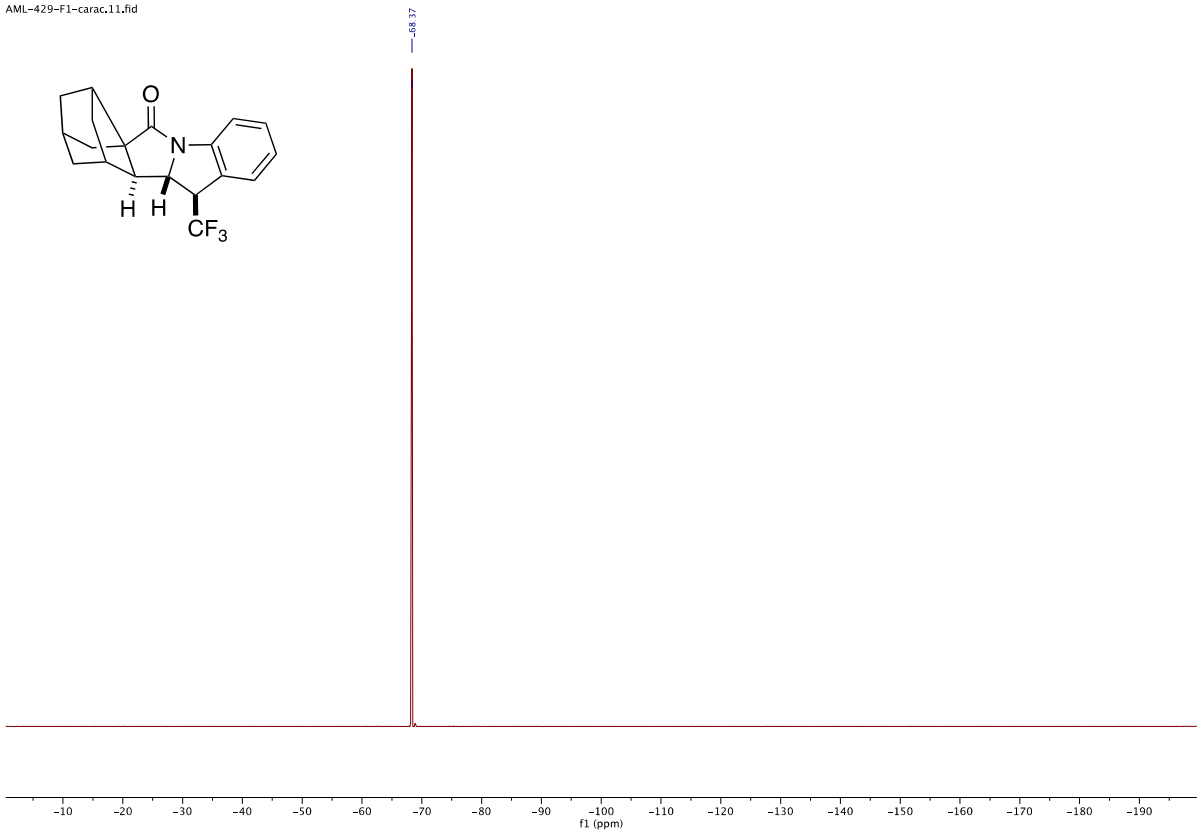
^{1}H NMR of **2s**



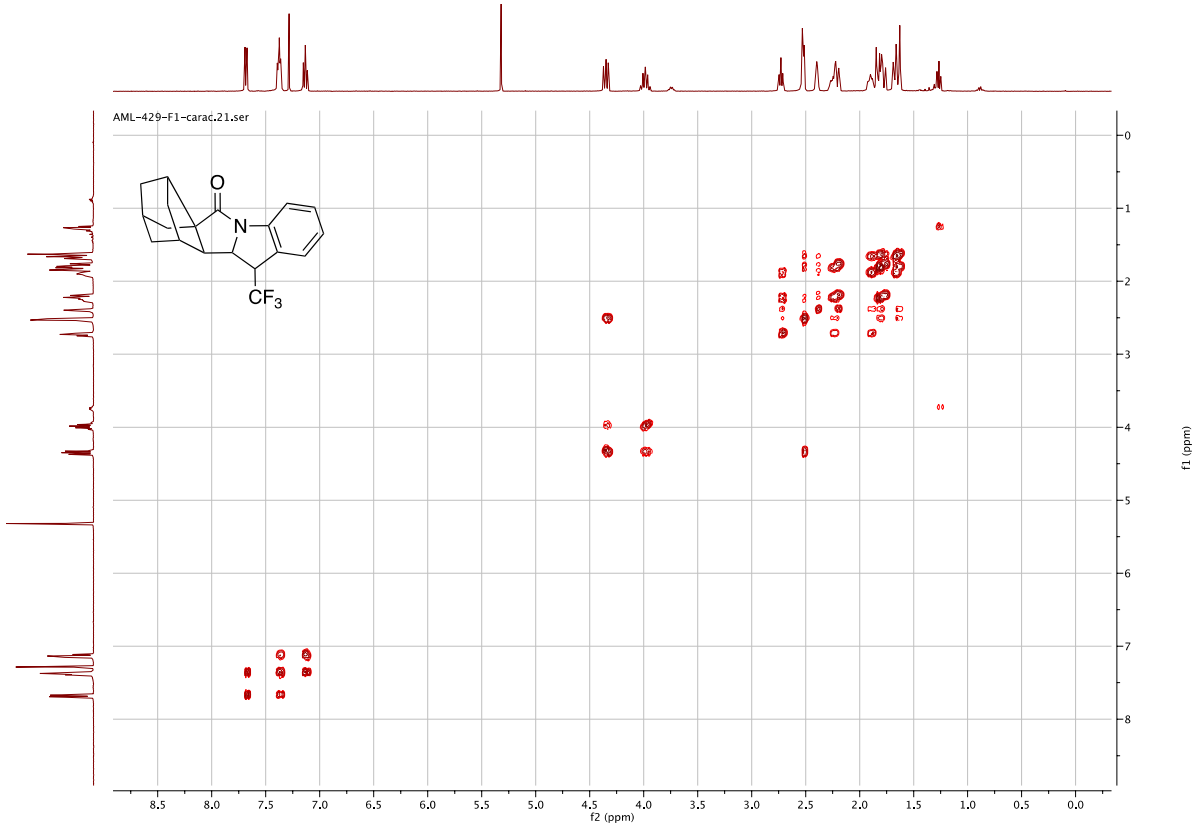
^{13}C NMR of **2s**



^{19}F NMR of **2s**

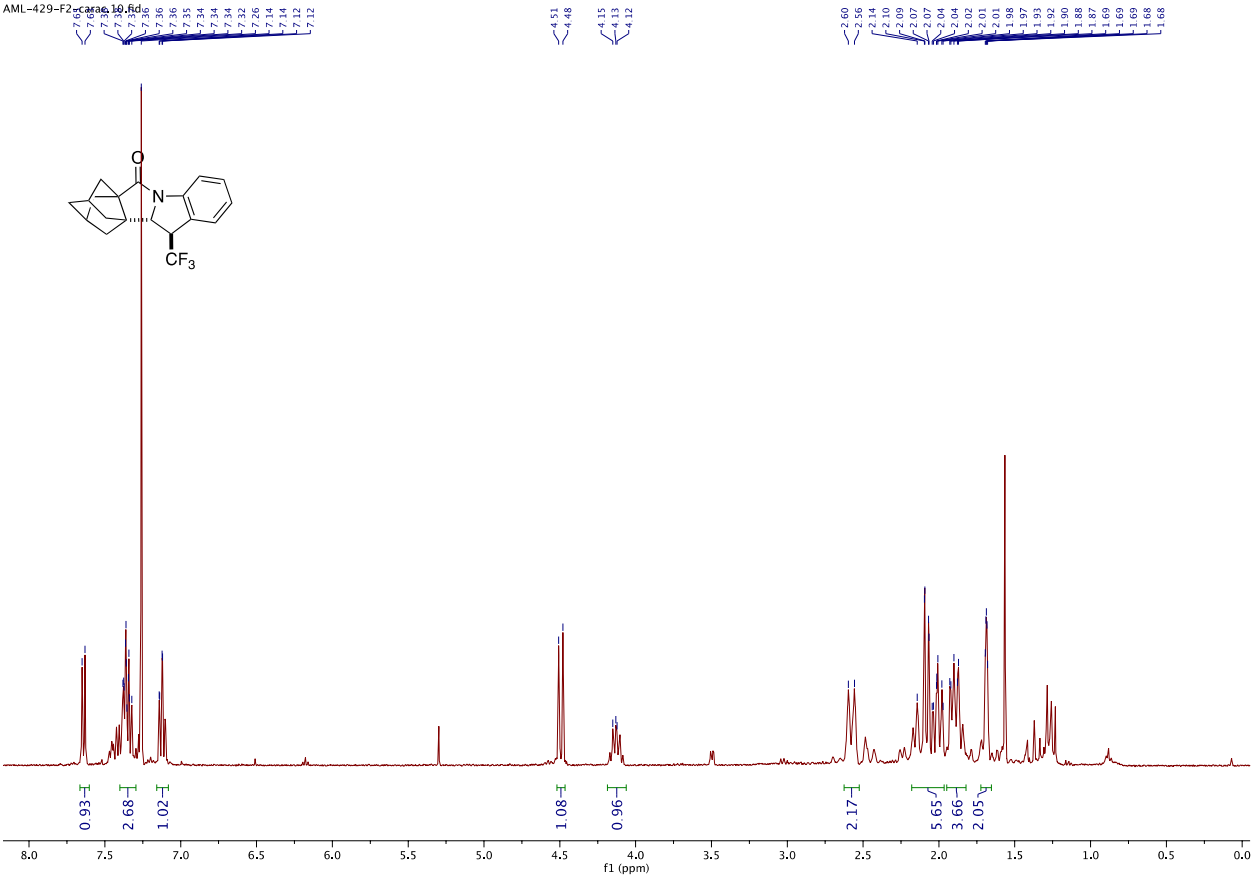


COSY experiment of **2s**

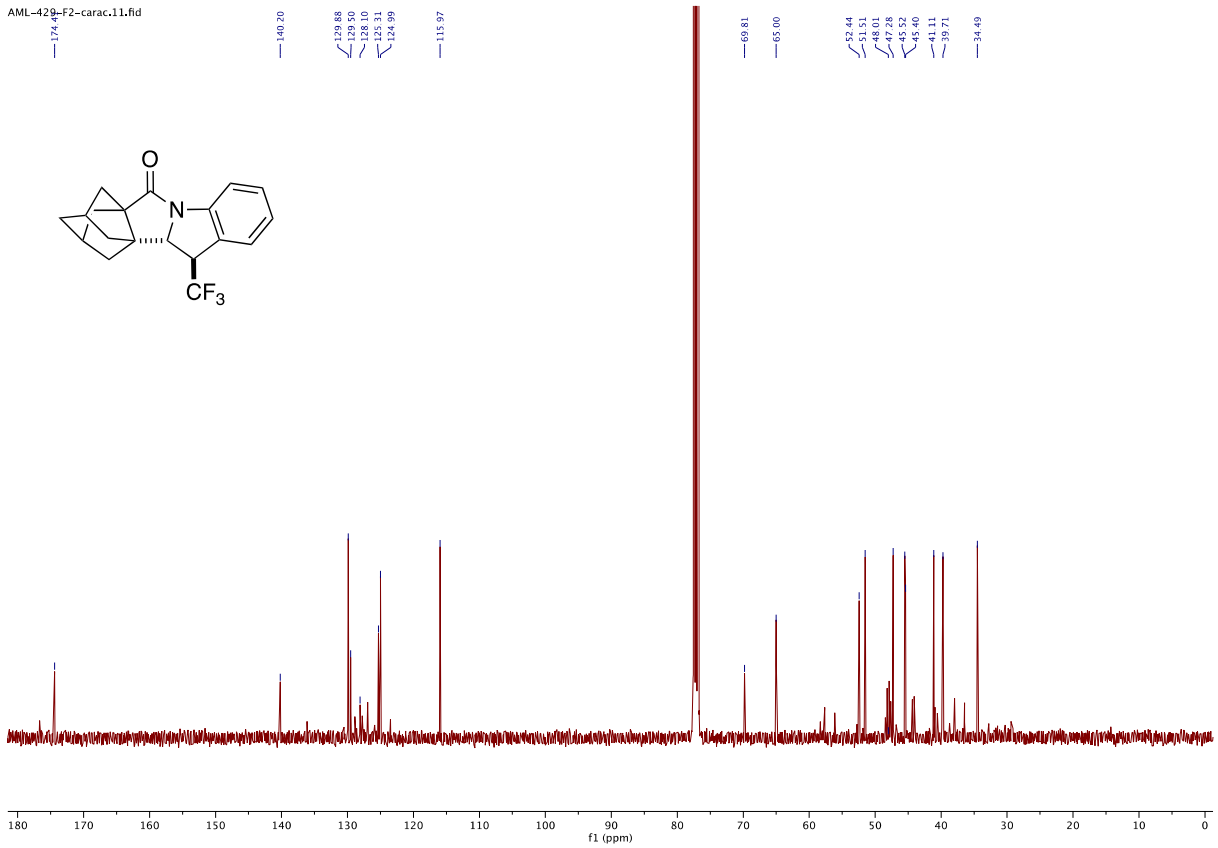


NOESY experiment of **2s**

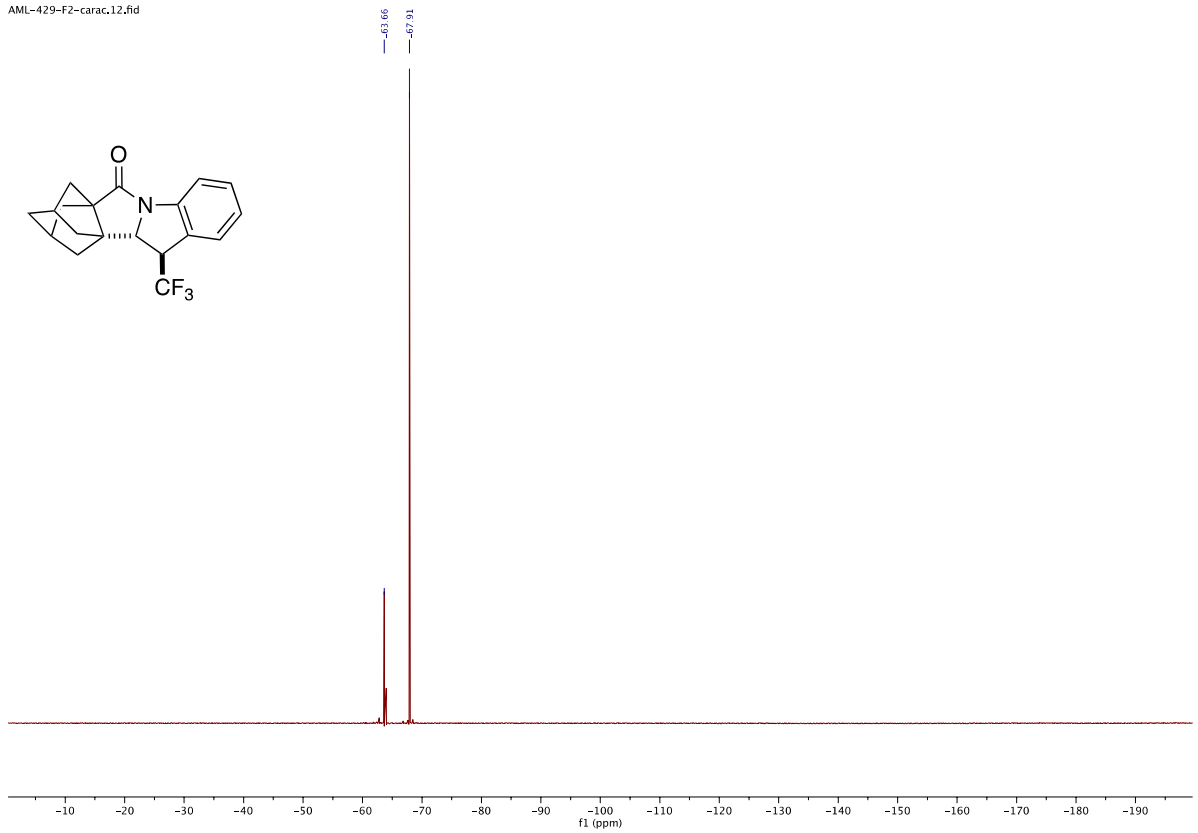
^{1}H NMR of **2sa**



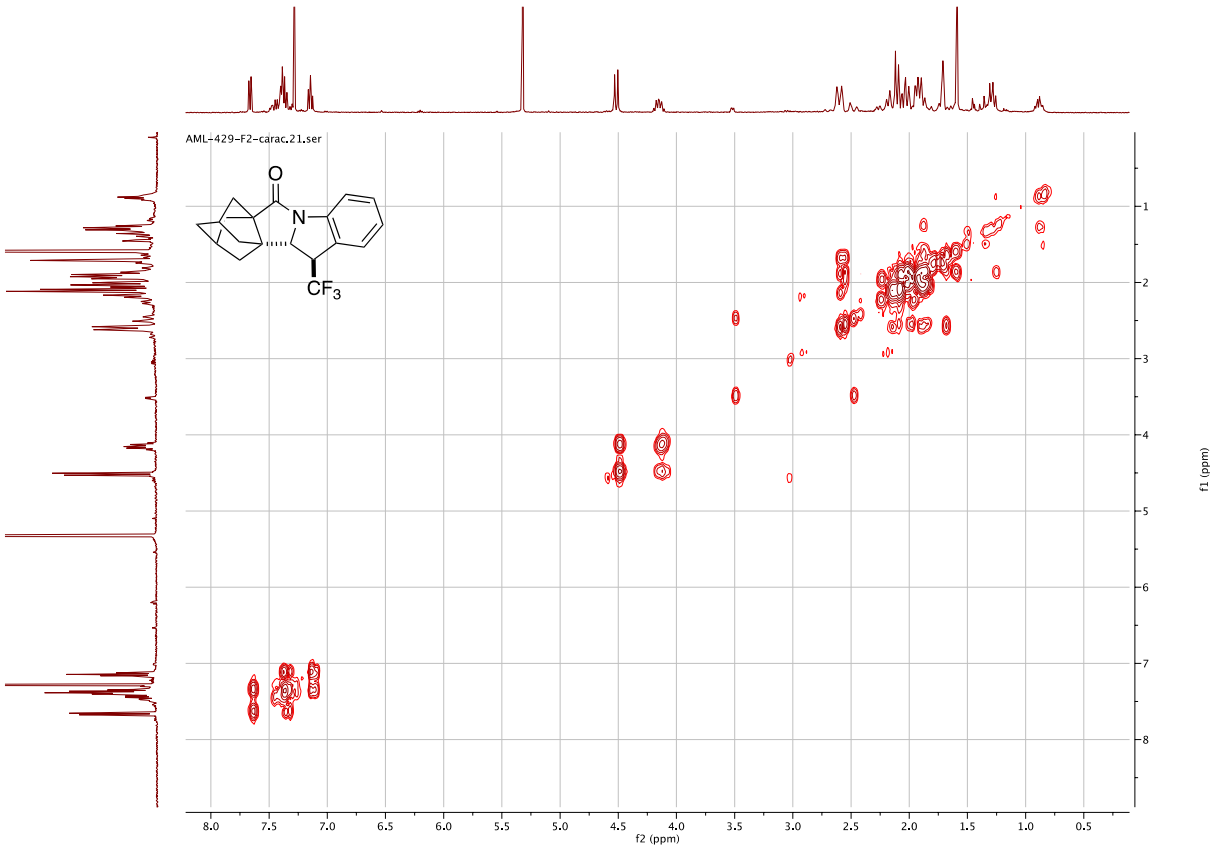
^{13}C NMR of **2sa**



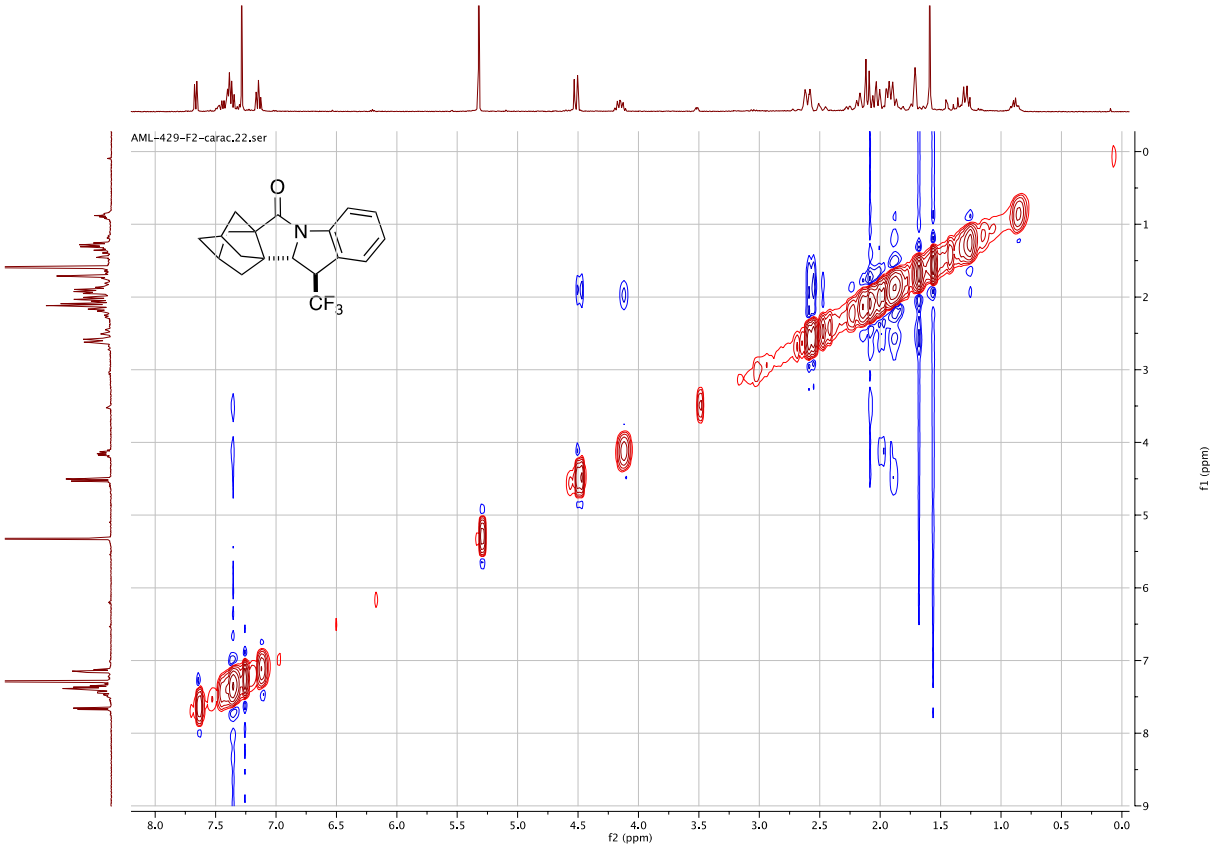
^{19}F NMR of **2sa**



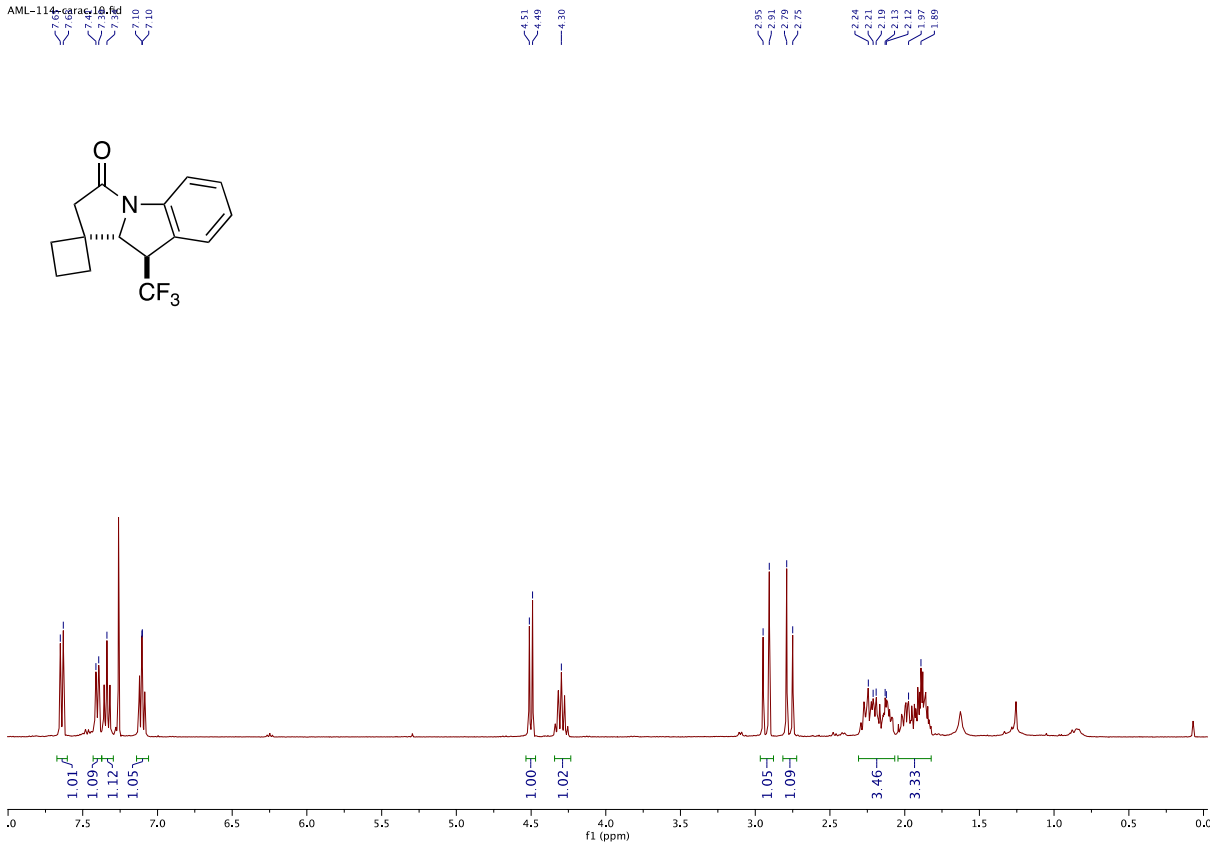
COSY experiment of **2sa**



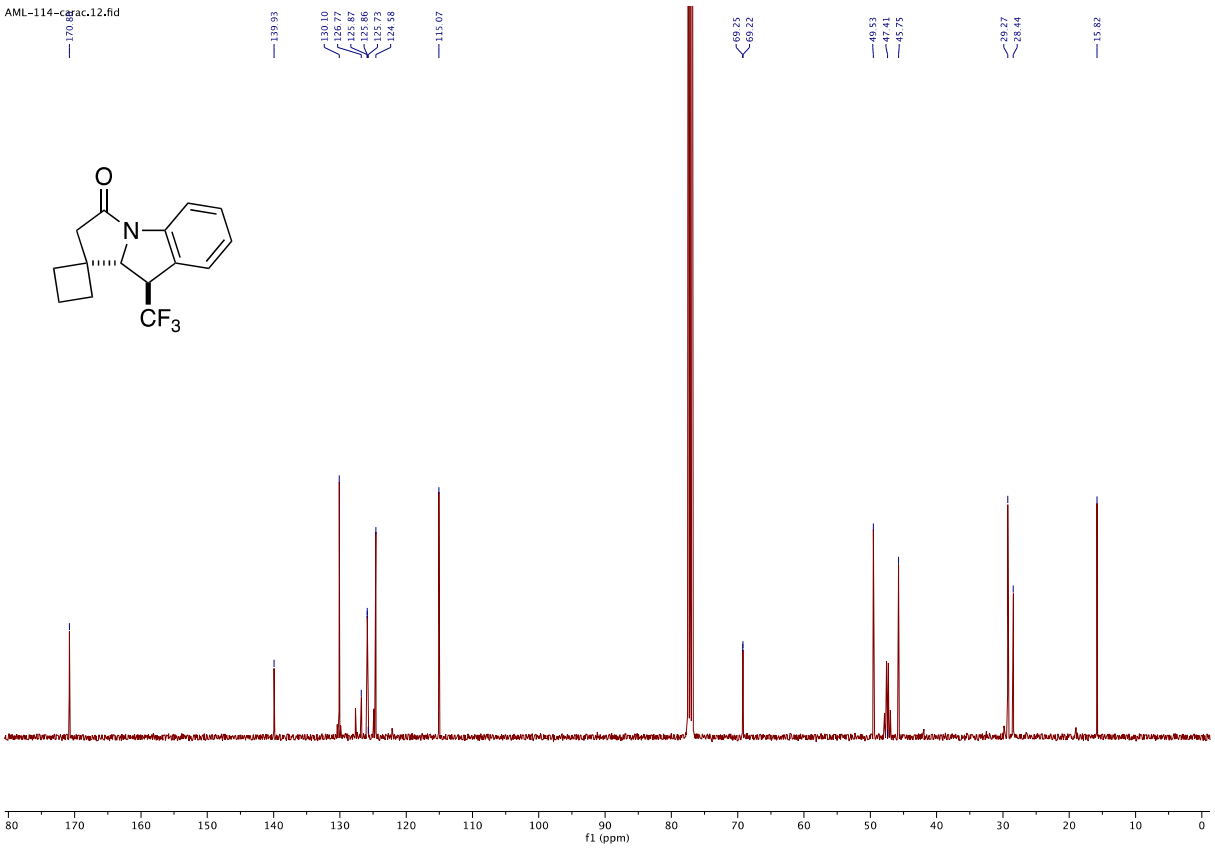
NOESY experiment of **2sa**



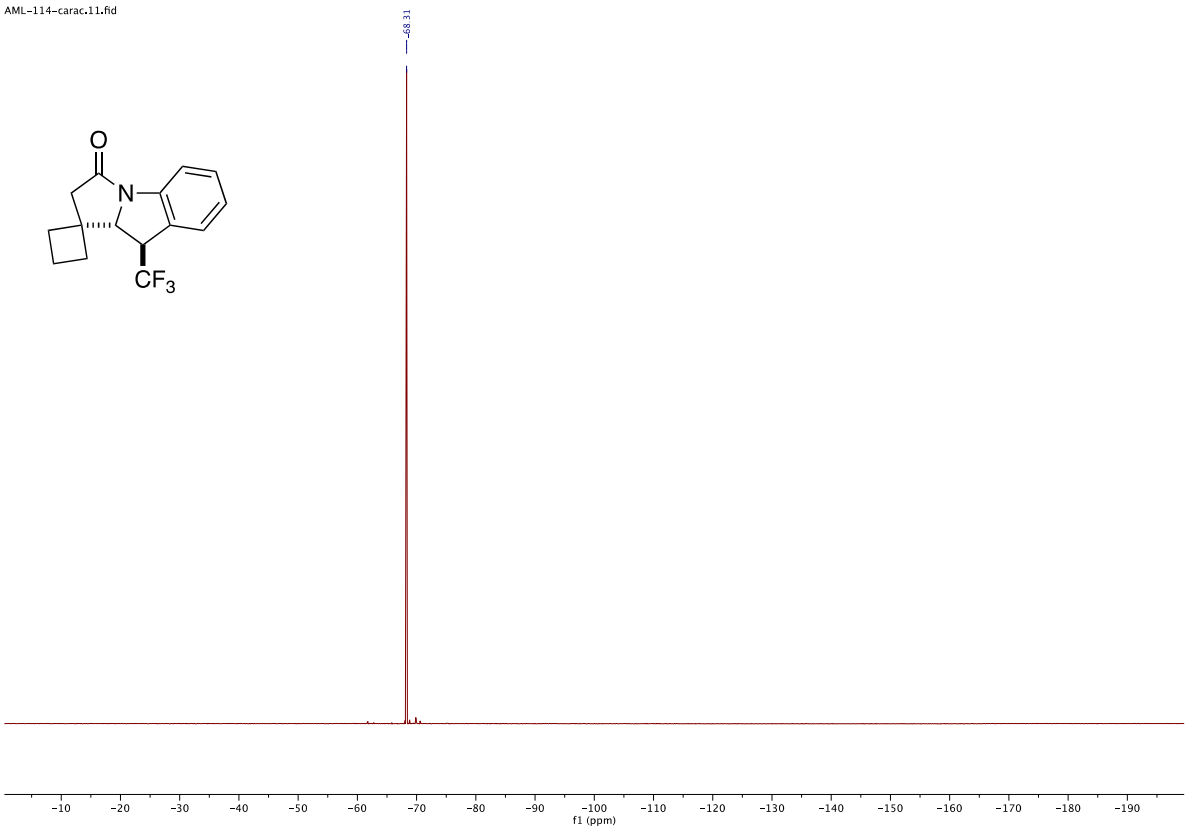
^{1}H NMR of **2t**



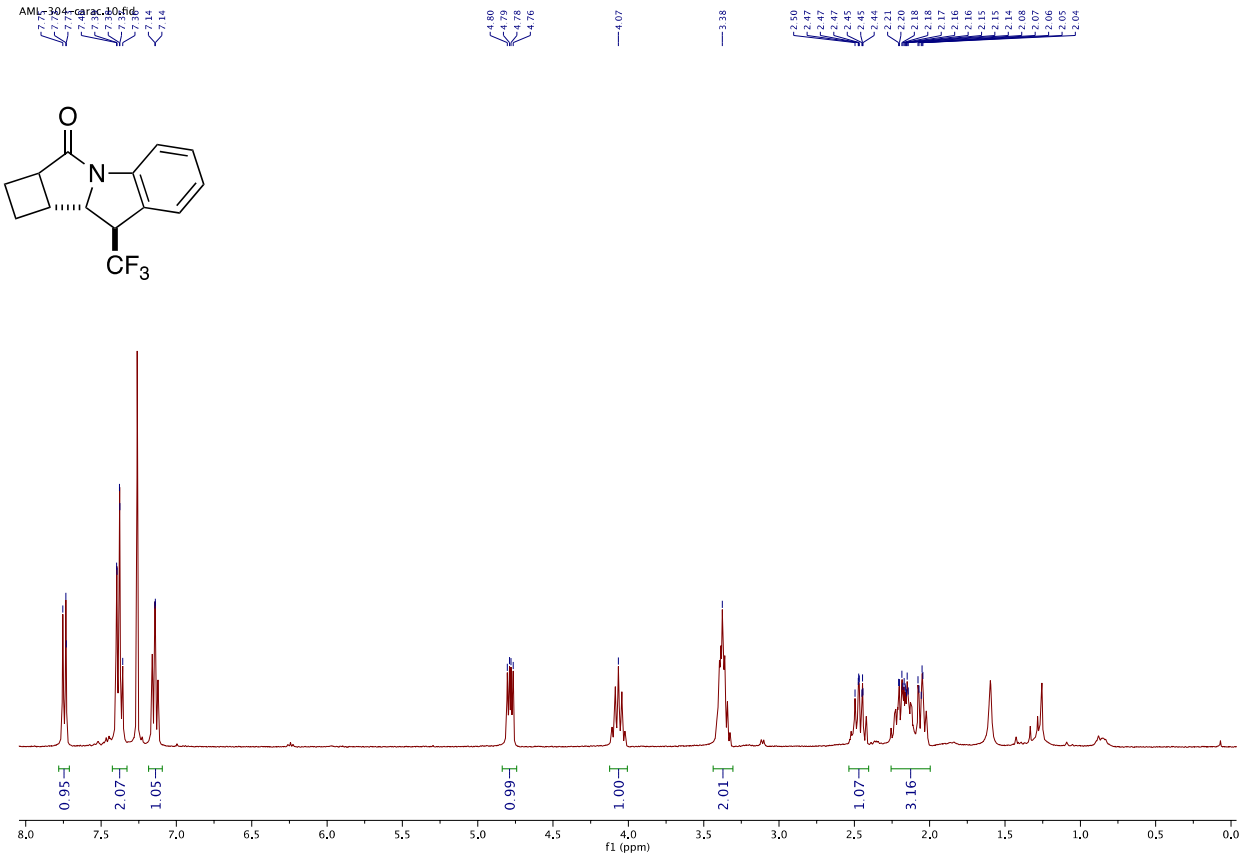
^{13}C NMR of **2t**



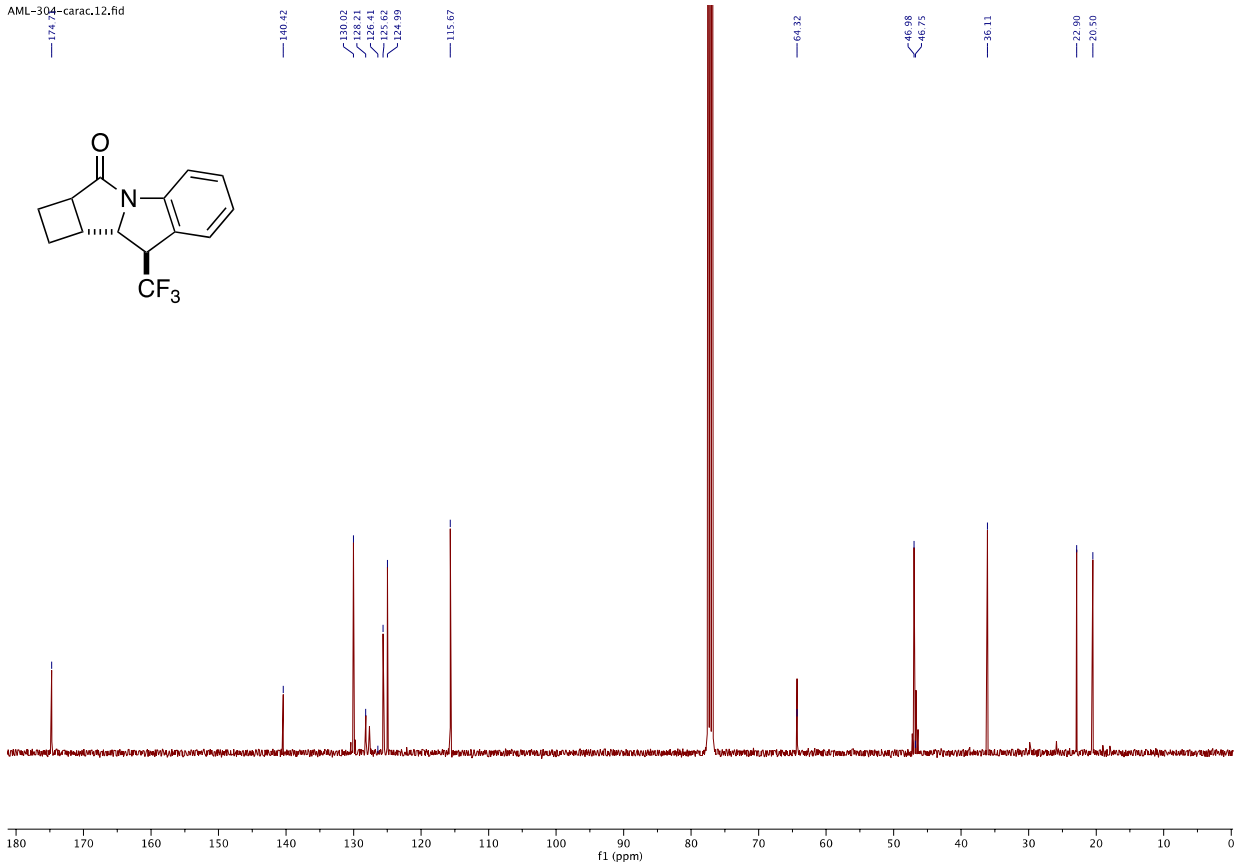
^{19}F NMR of **2t**



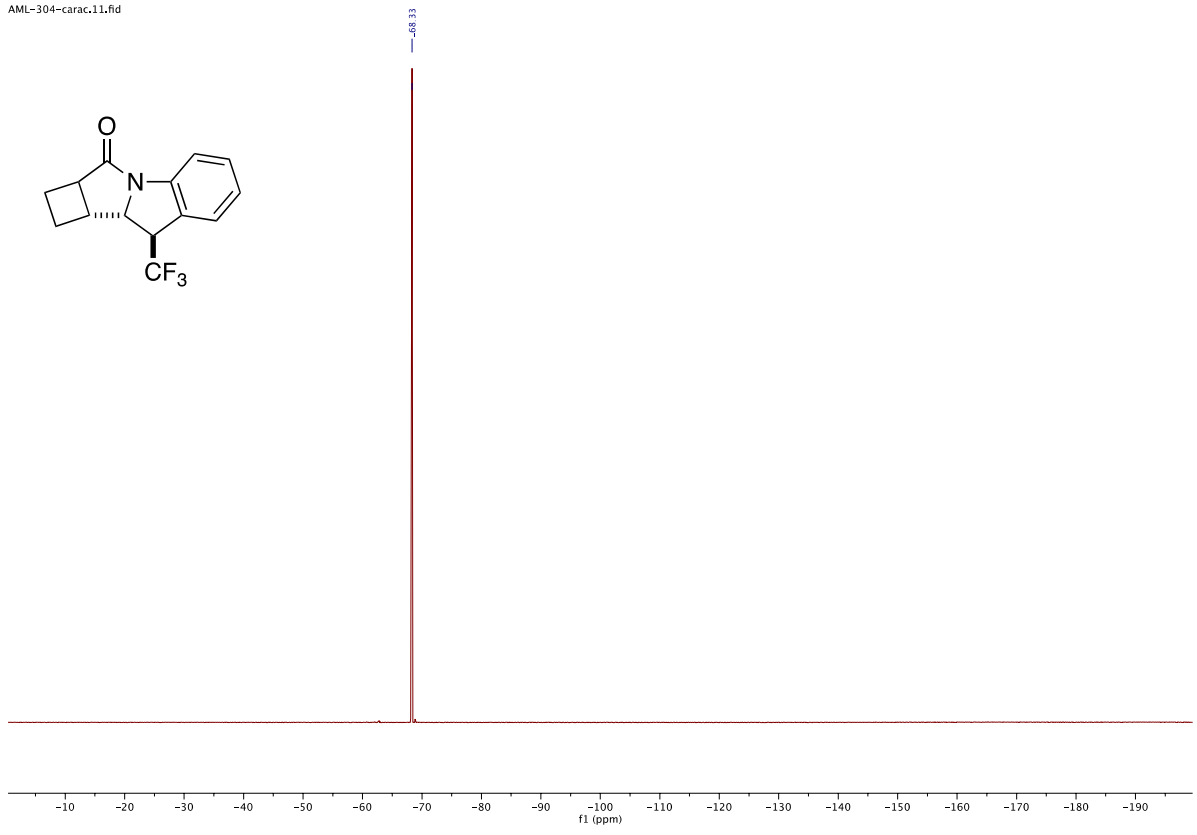
^{1}H NMR of **2u**



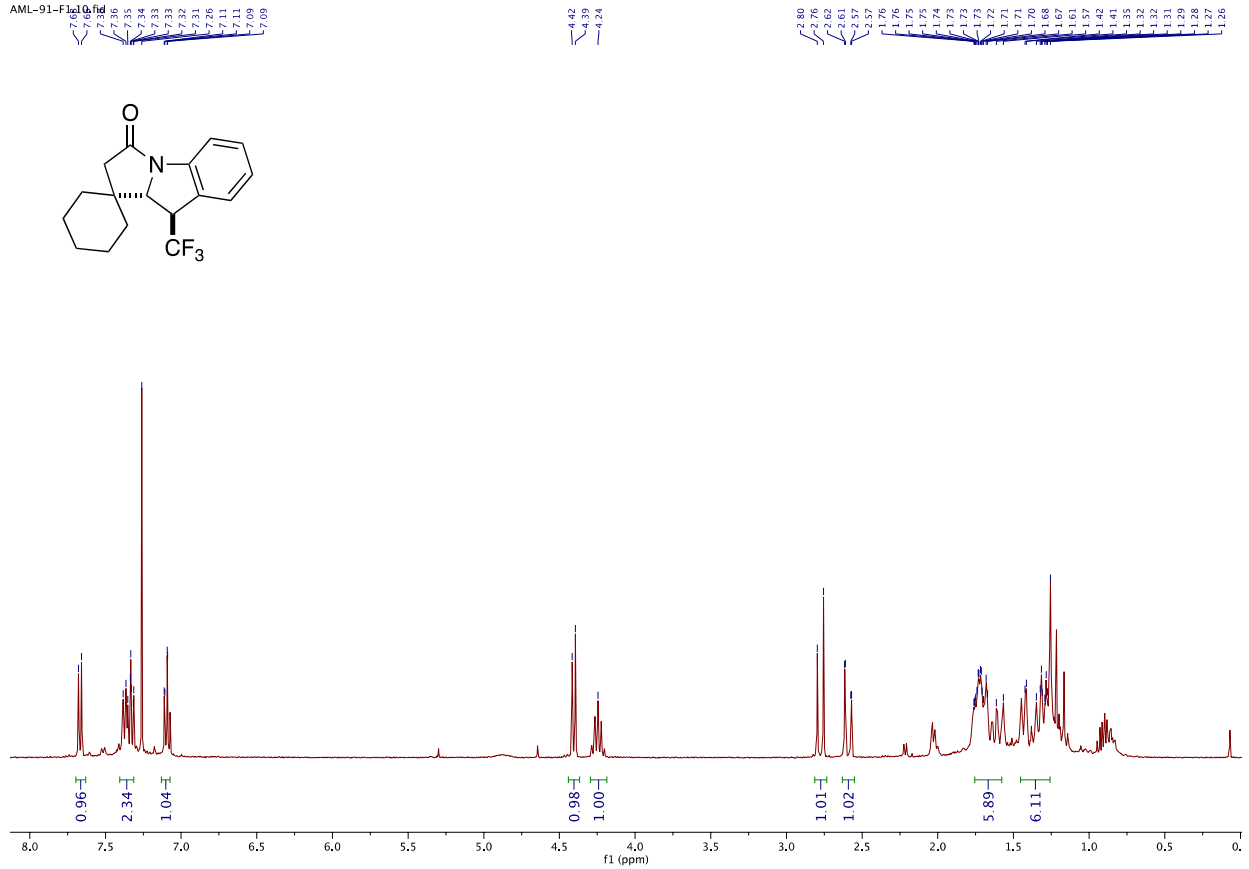
^{13}C NMR of **2u**



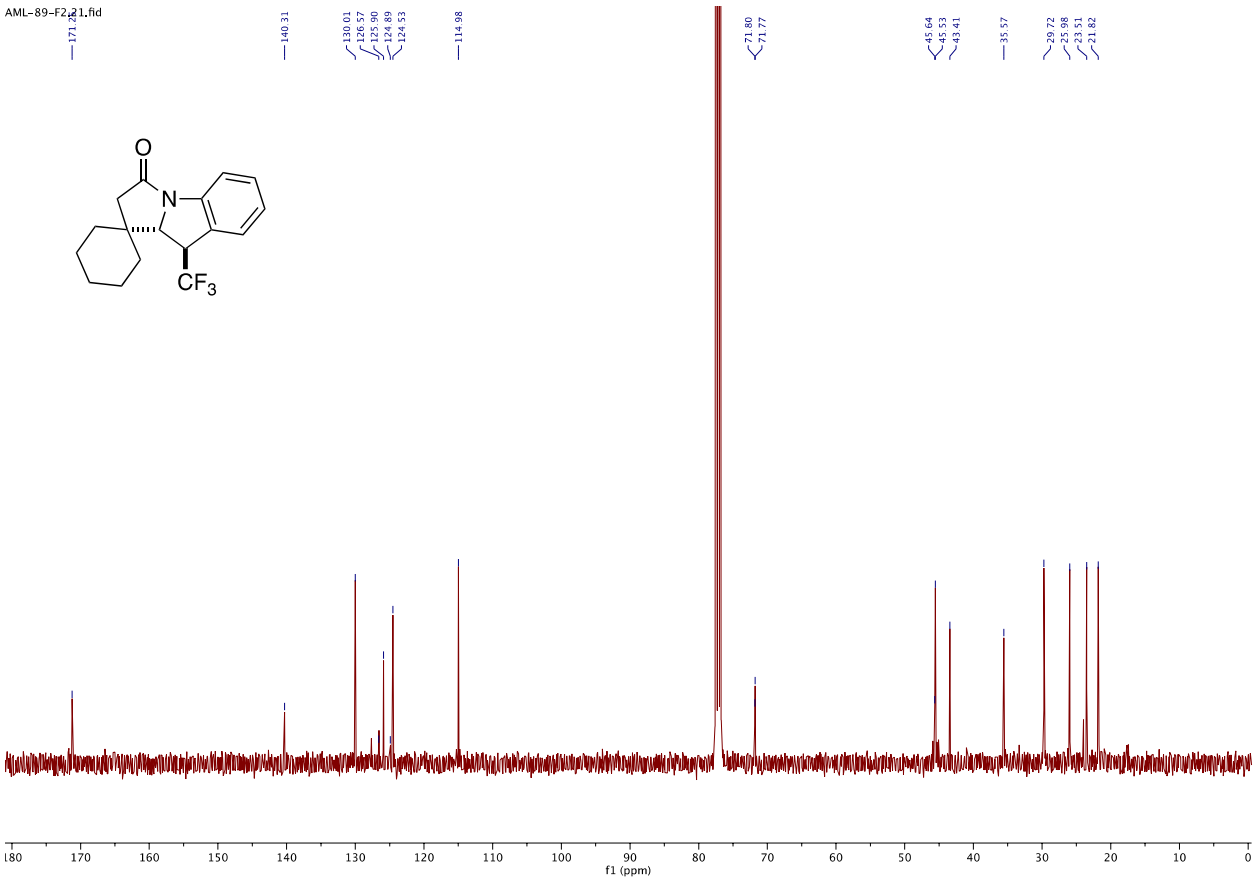
^{19}F NMR of **2u**



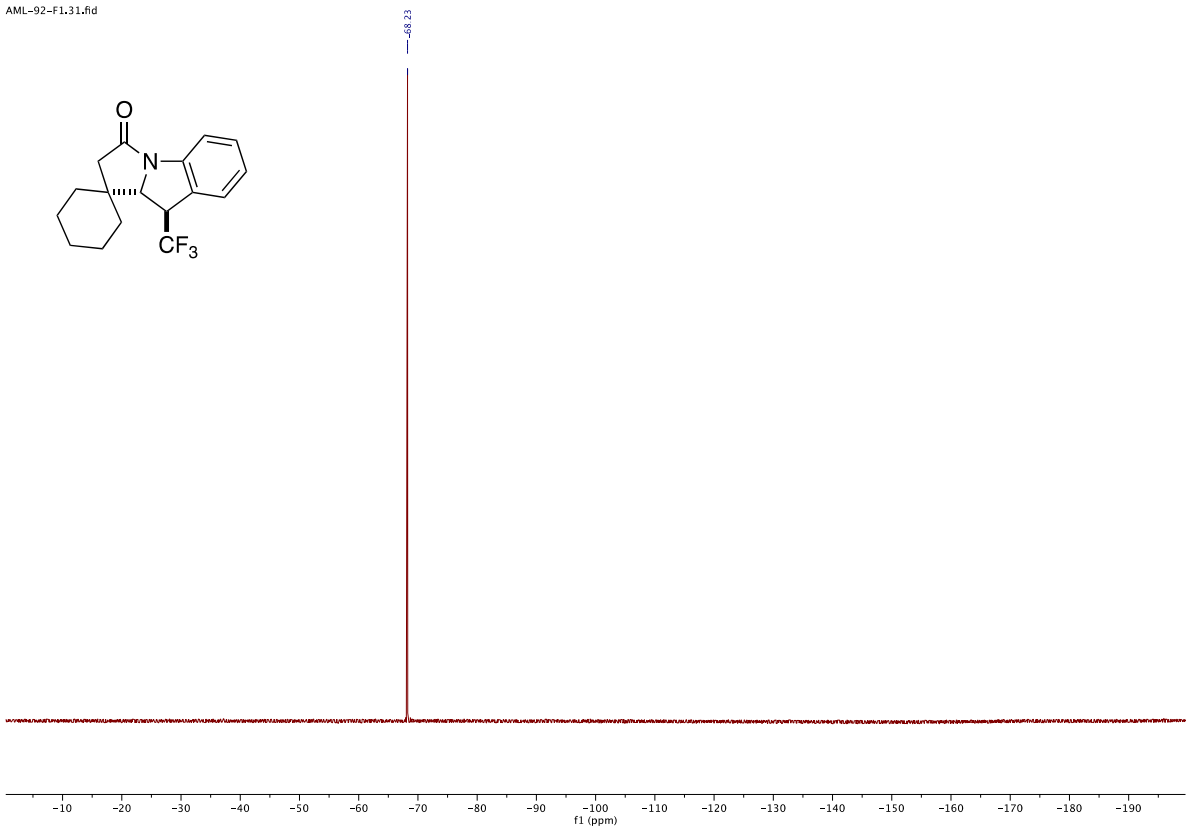
^{1}H NMR of **2v**



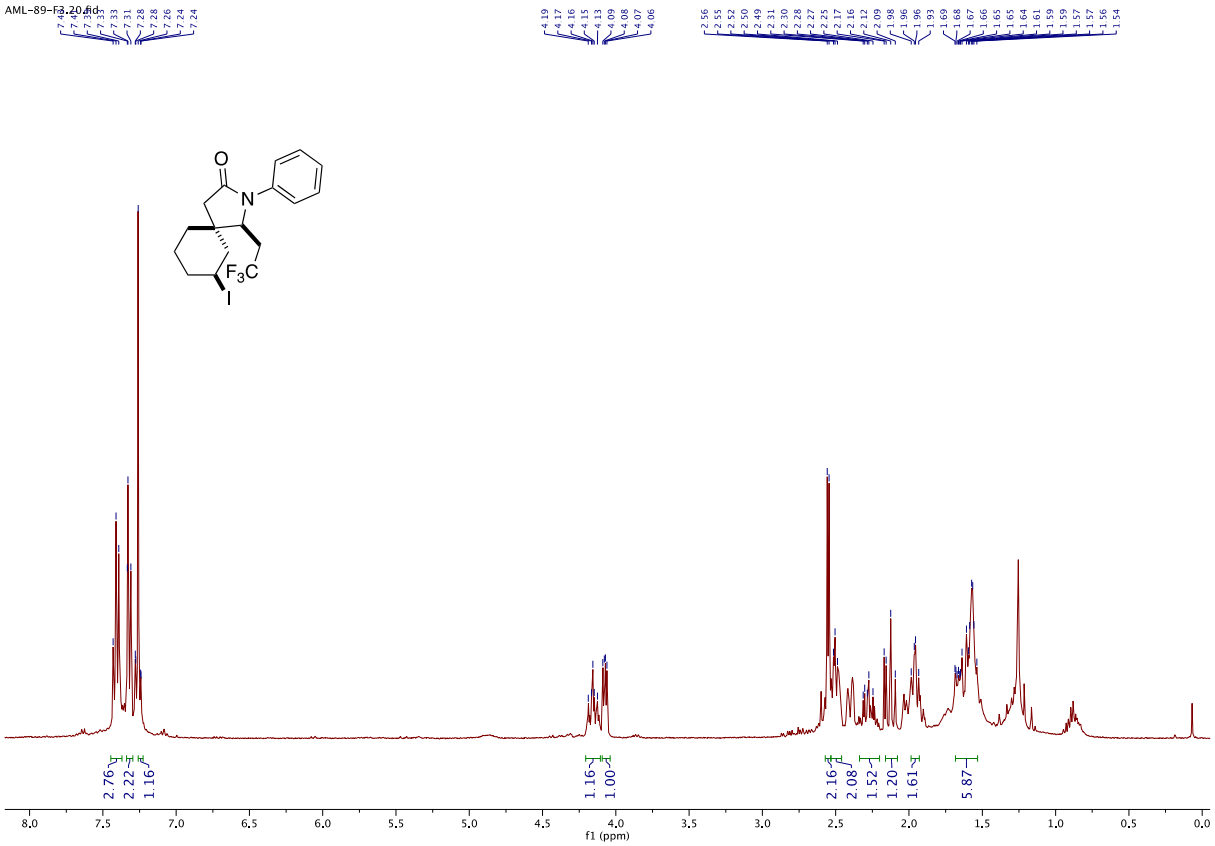
^{13}C NMR of **2v**



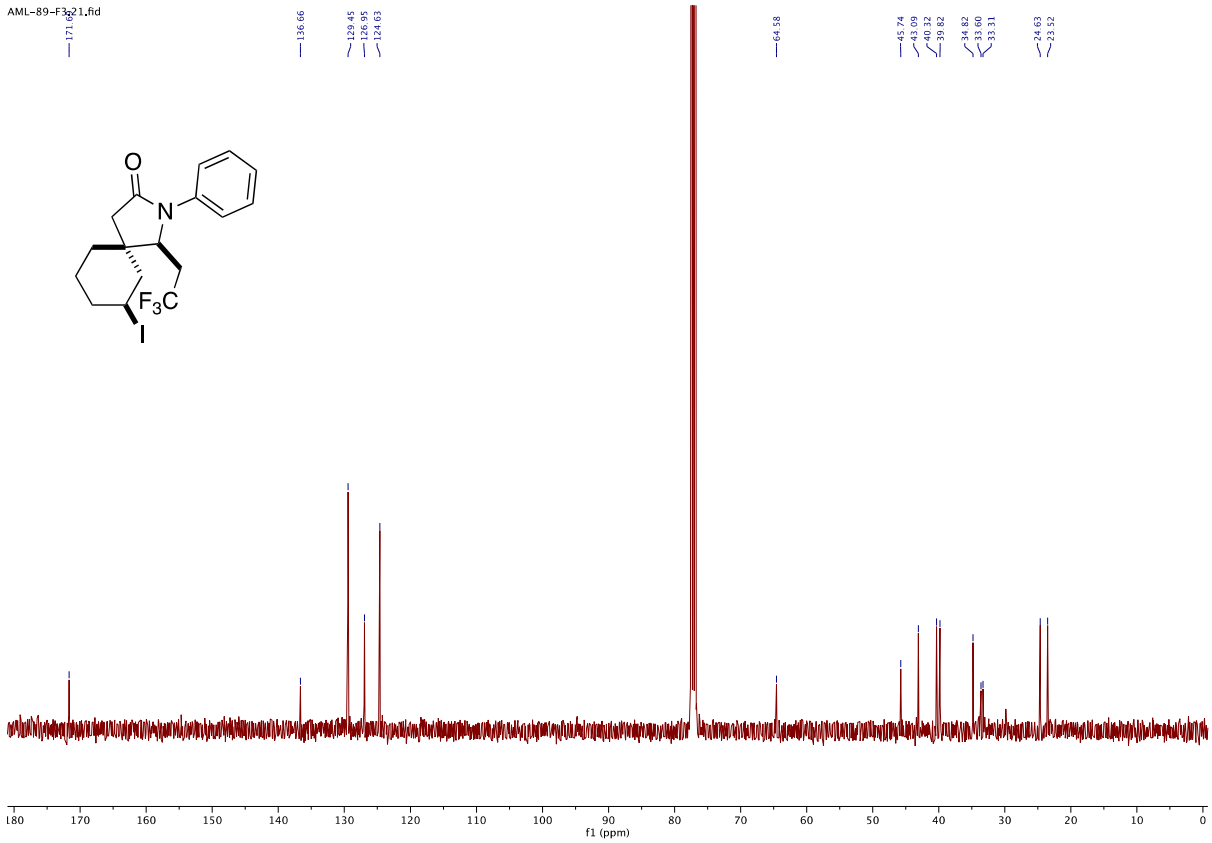
^{19}F NMR of **2v**



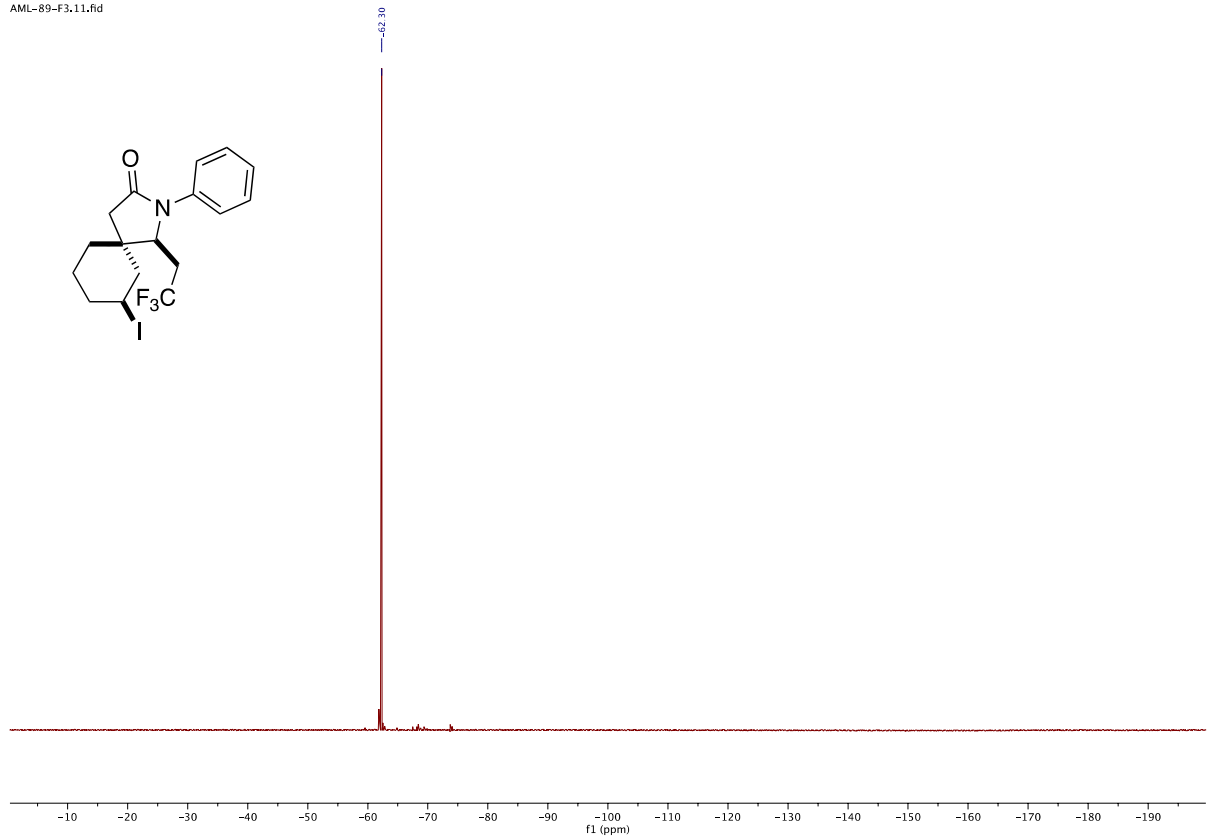
^{1}H NMR of **2va**



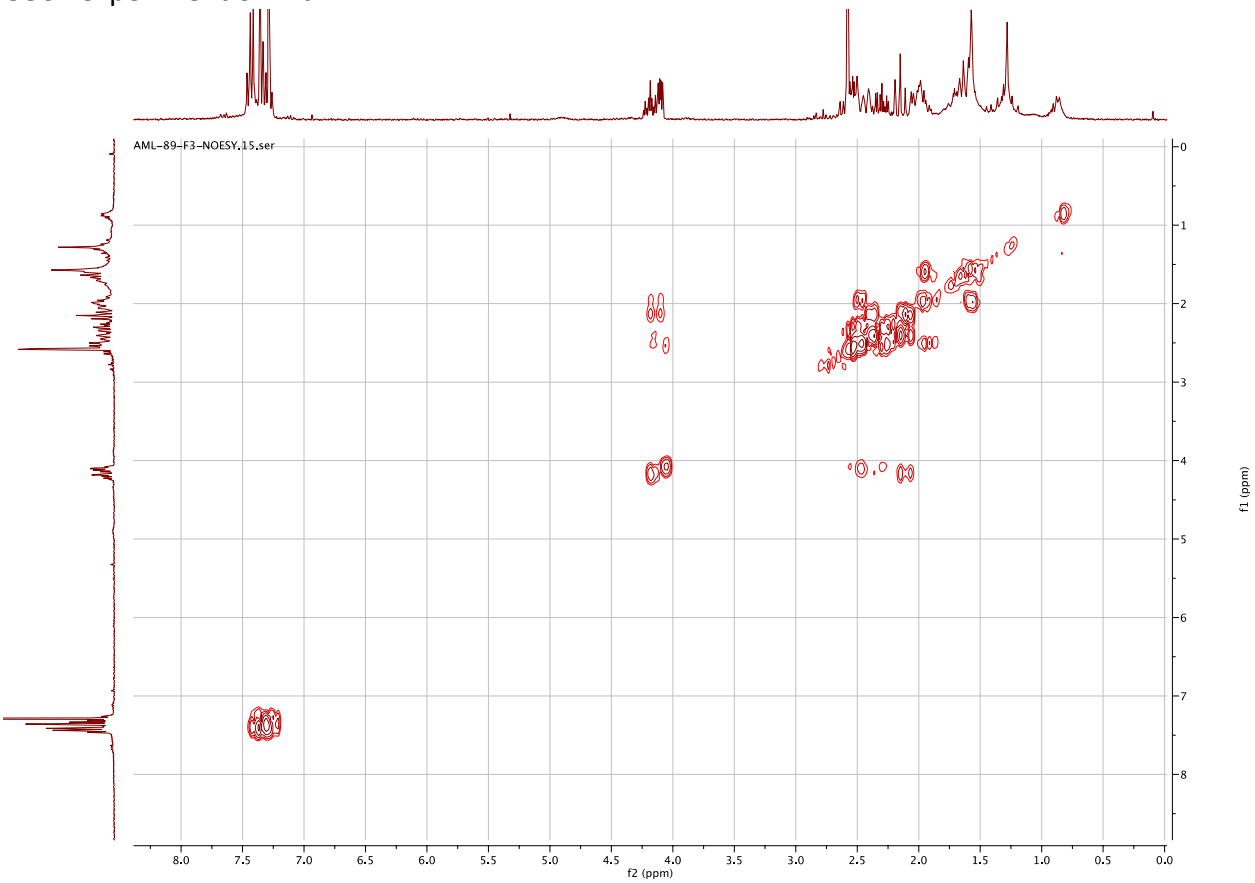
^{13}C NMR of **2va**



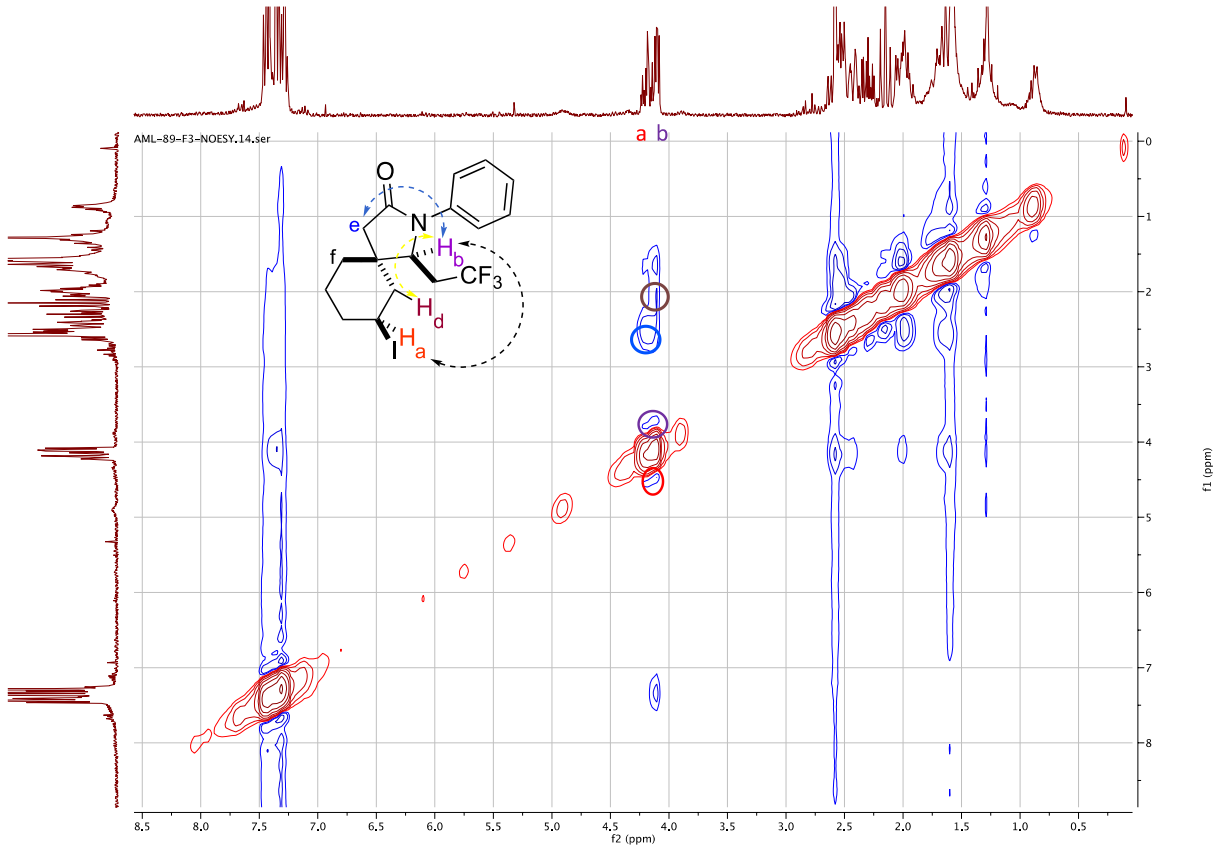
^{19}F NMR of **2va**



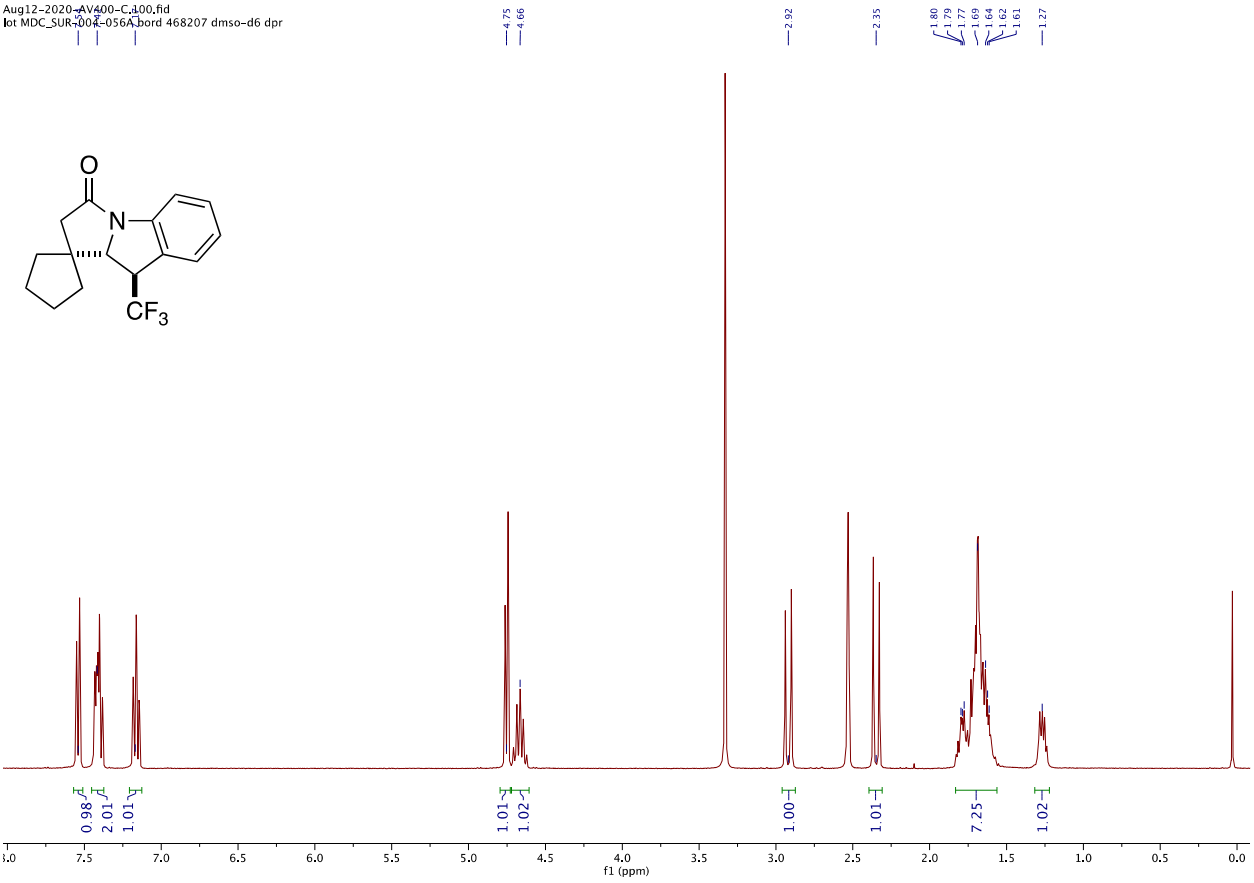
COSY experiment of **2va**



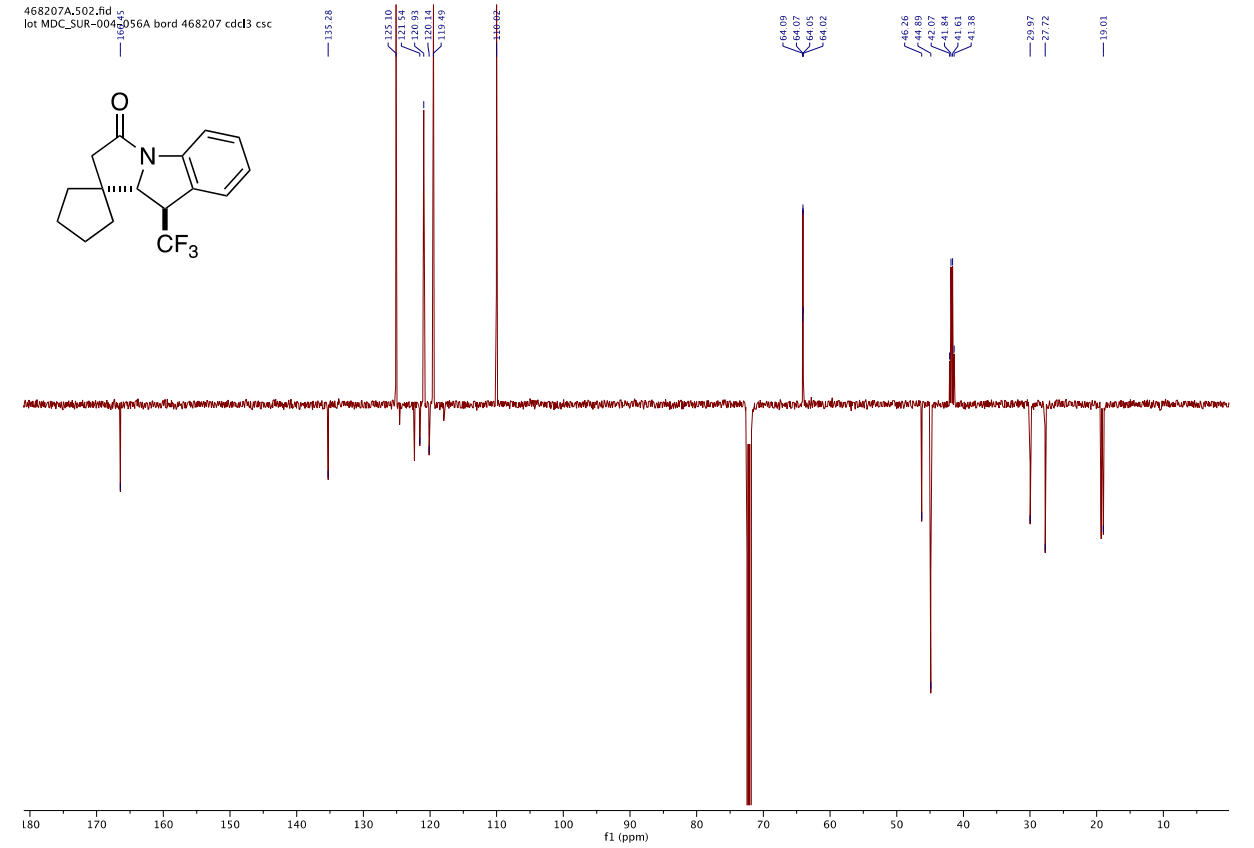
NOESY experiment of **2va**



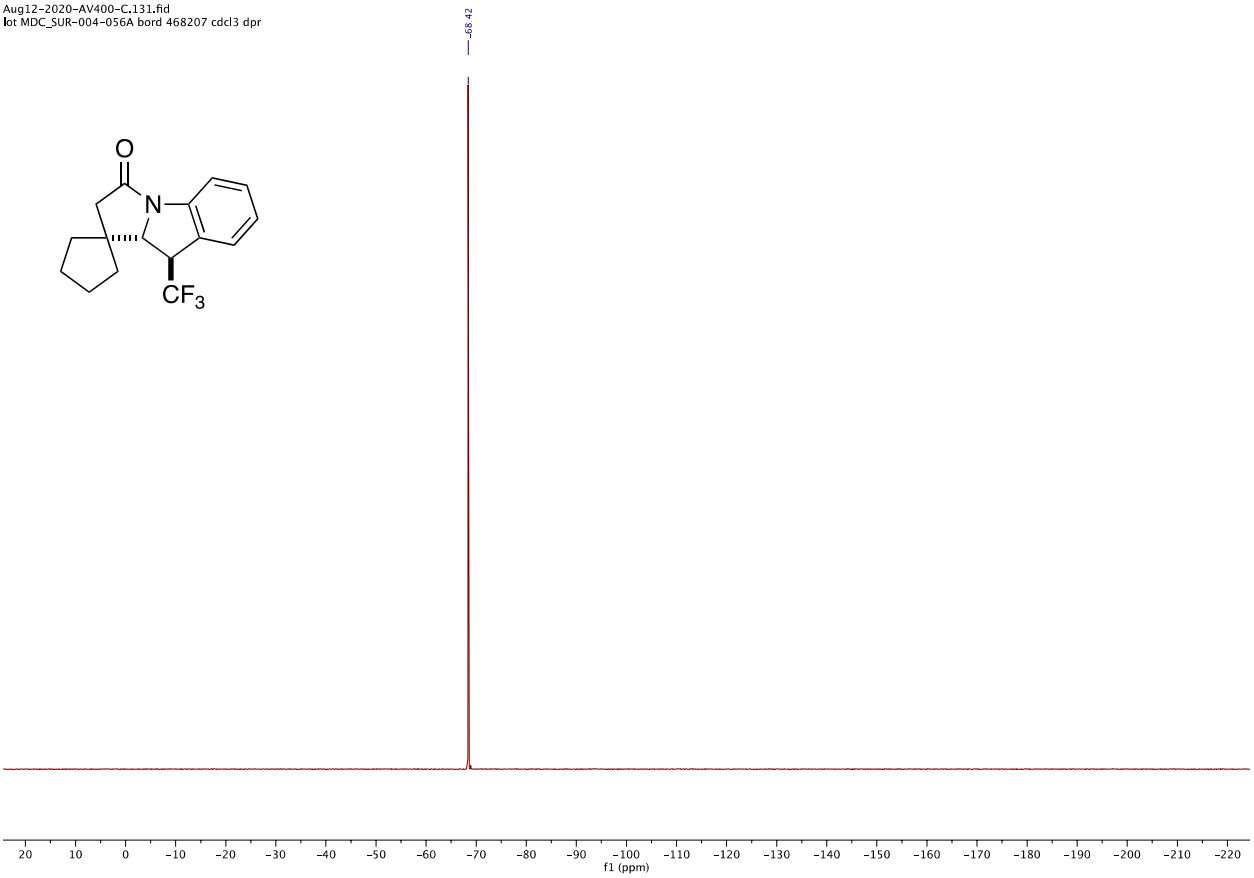
^{1}H NMR of **2w**



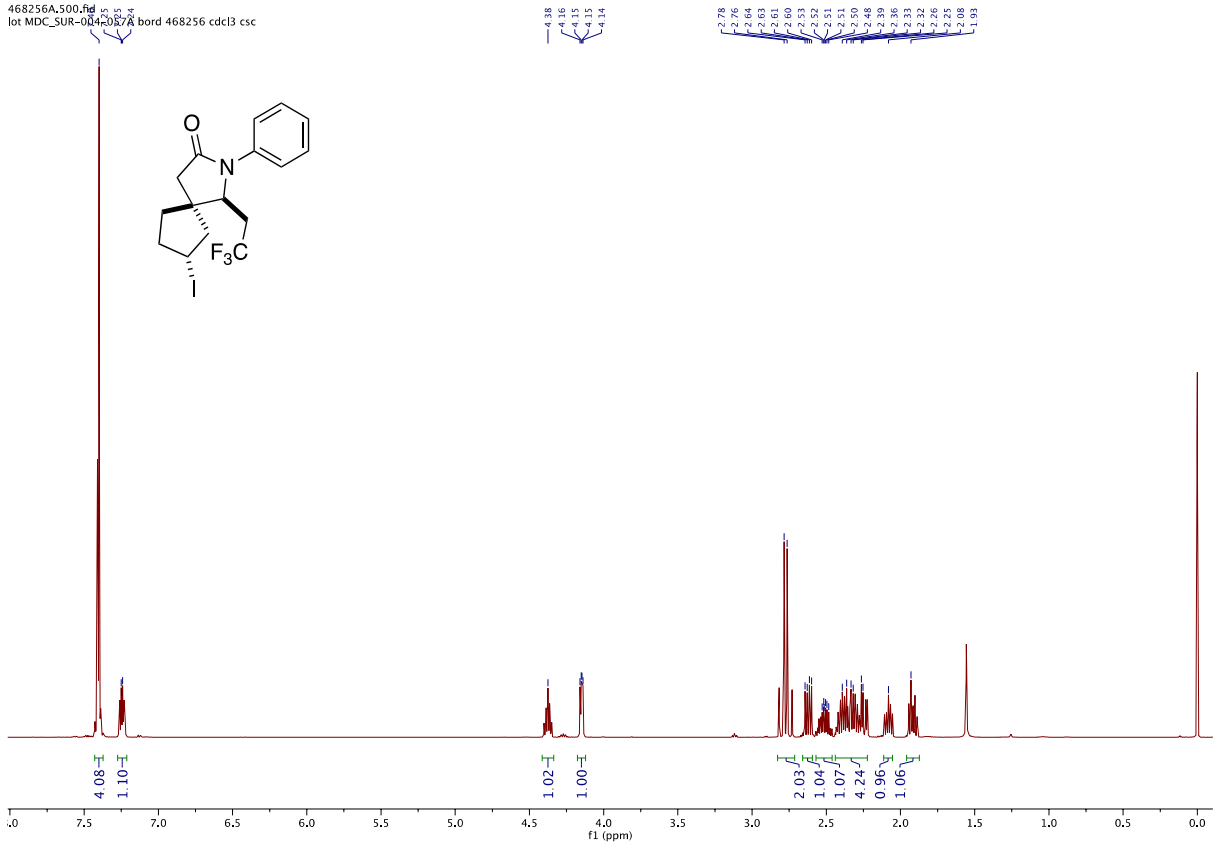
^{13}C NMR of **2w**



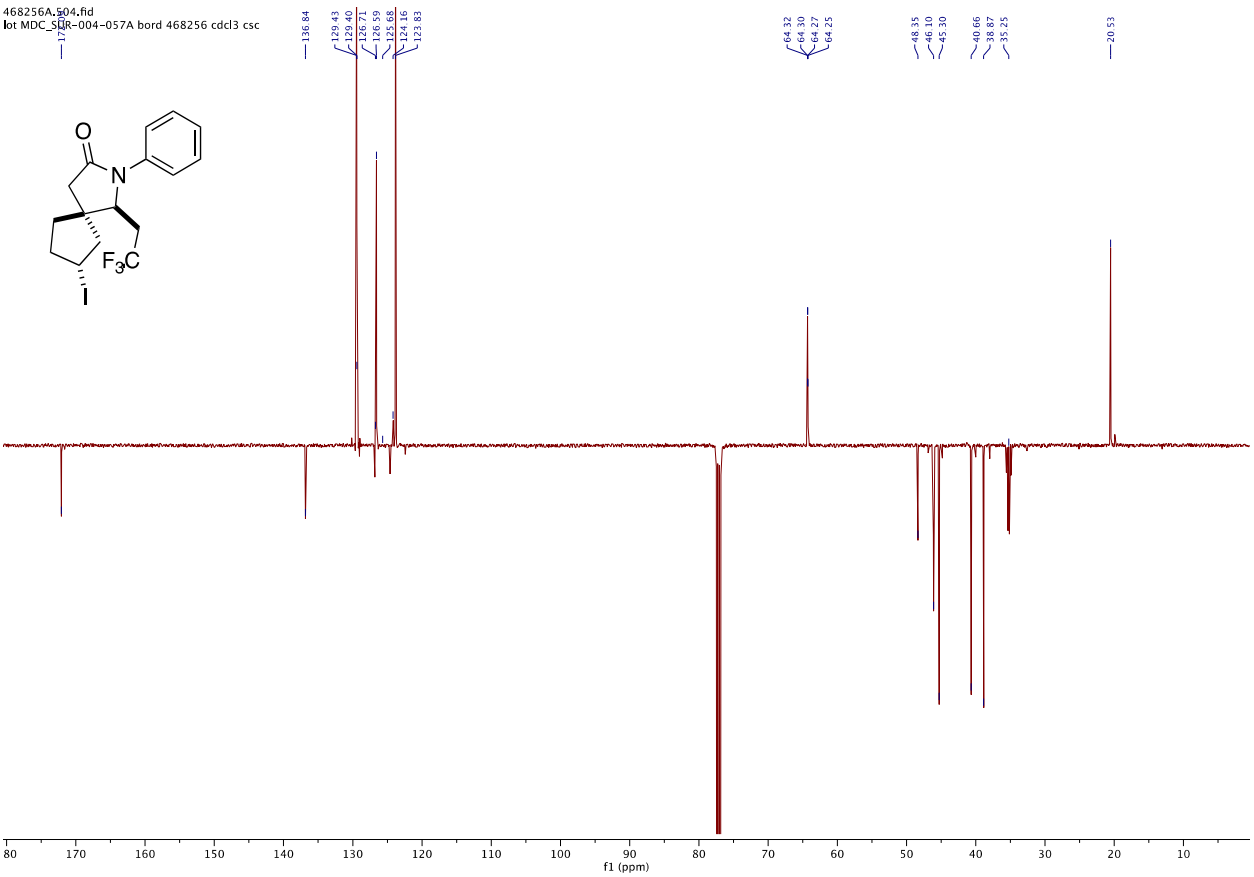
^{19}F NMR of **2w**



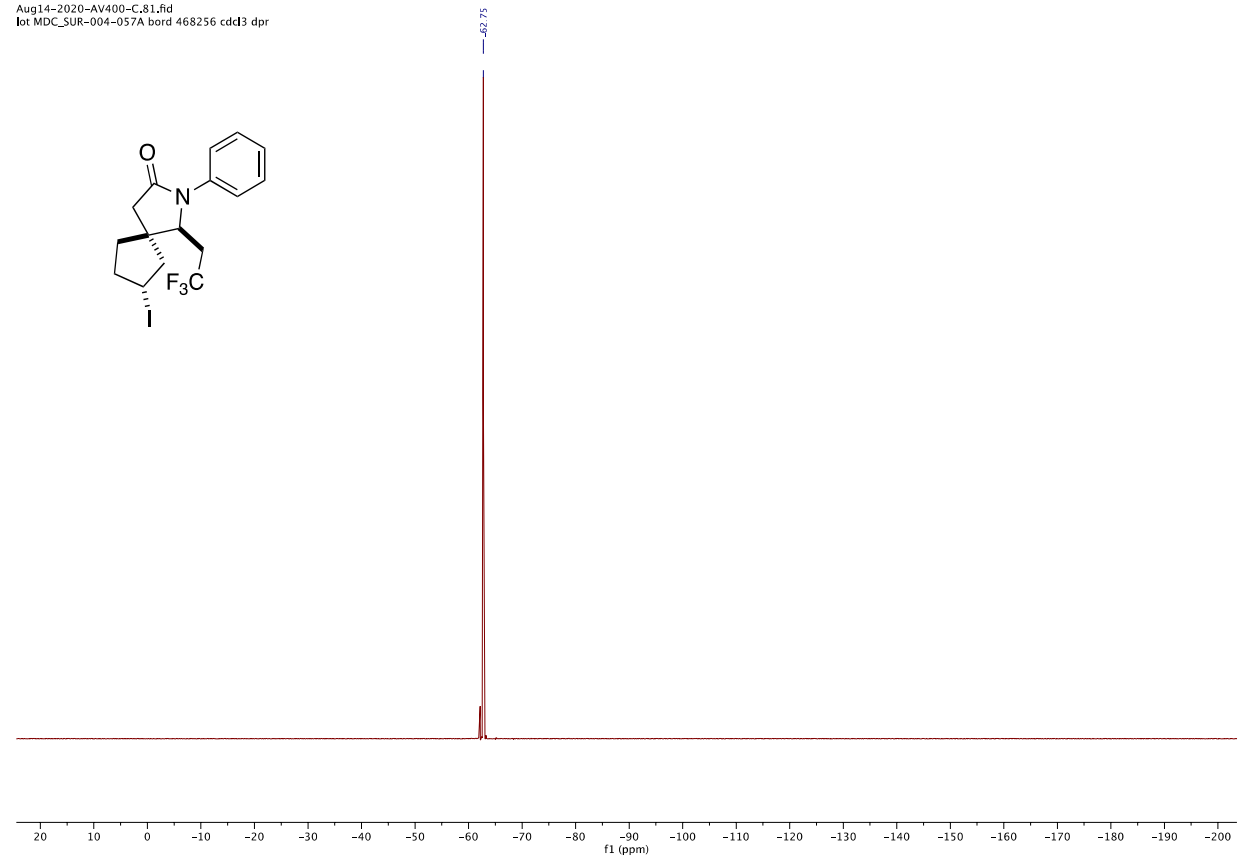
^{1}H NMR of **2wa**



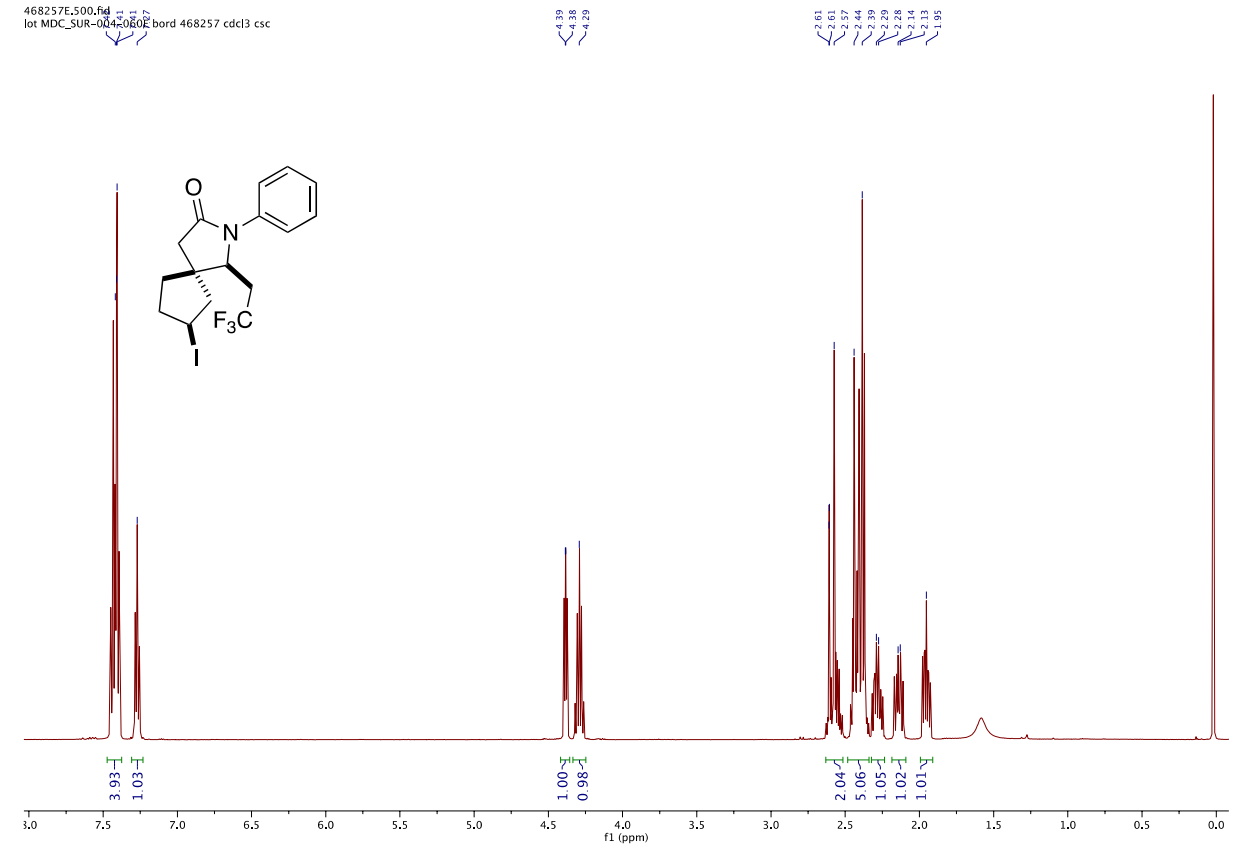
^{13}C NMR of **2wa**



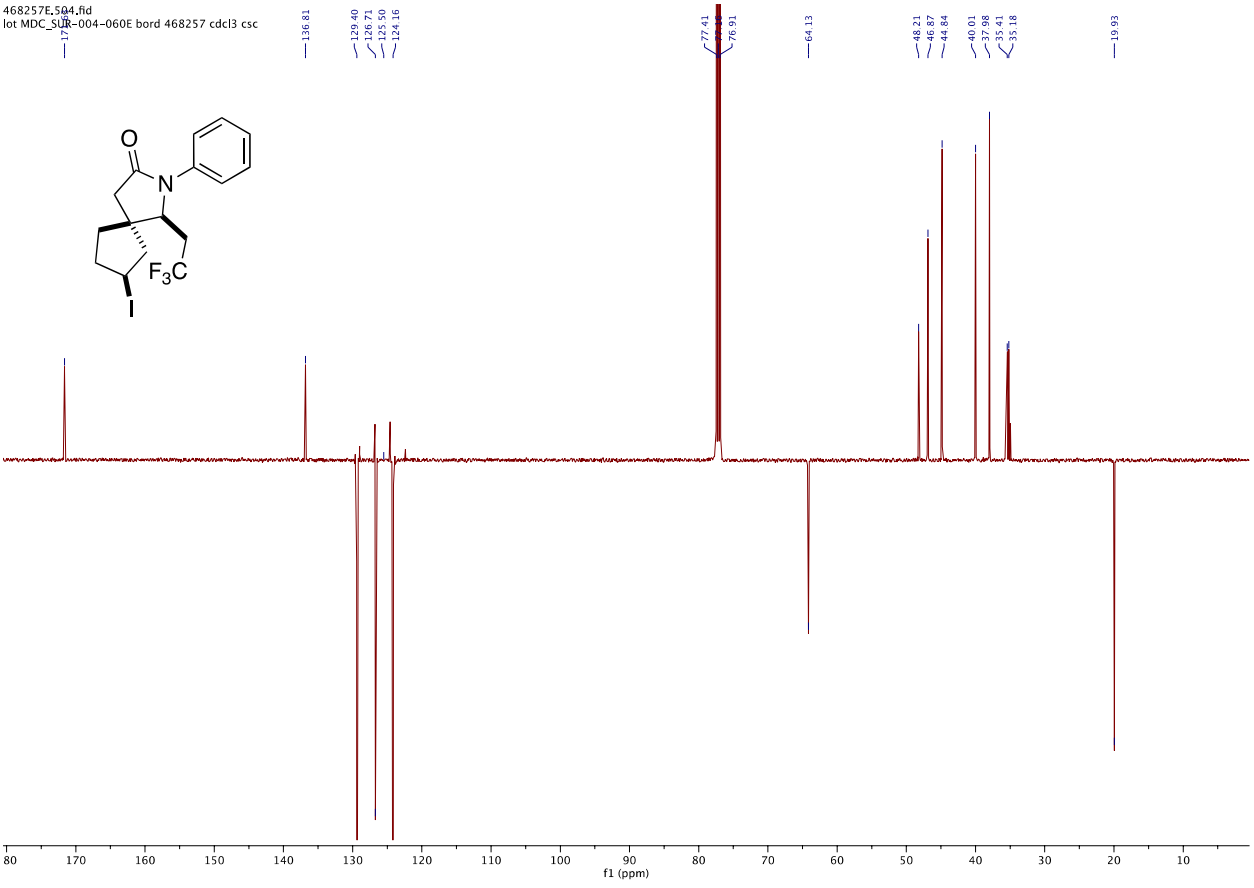
^{19}F NMR of **2wa**



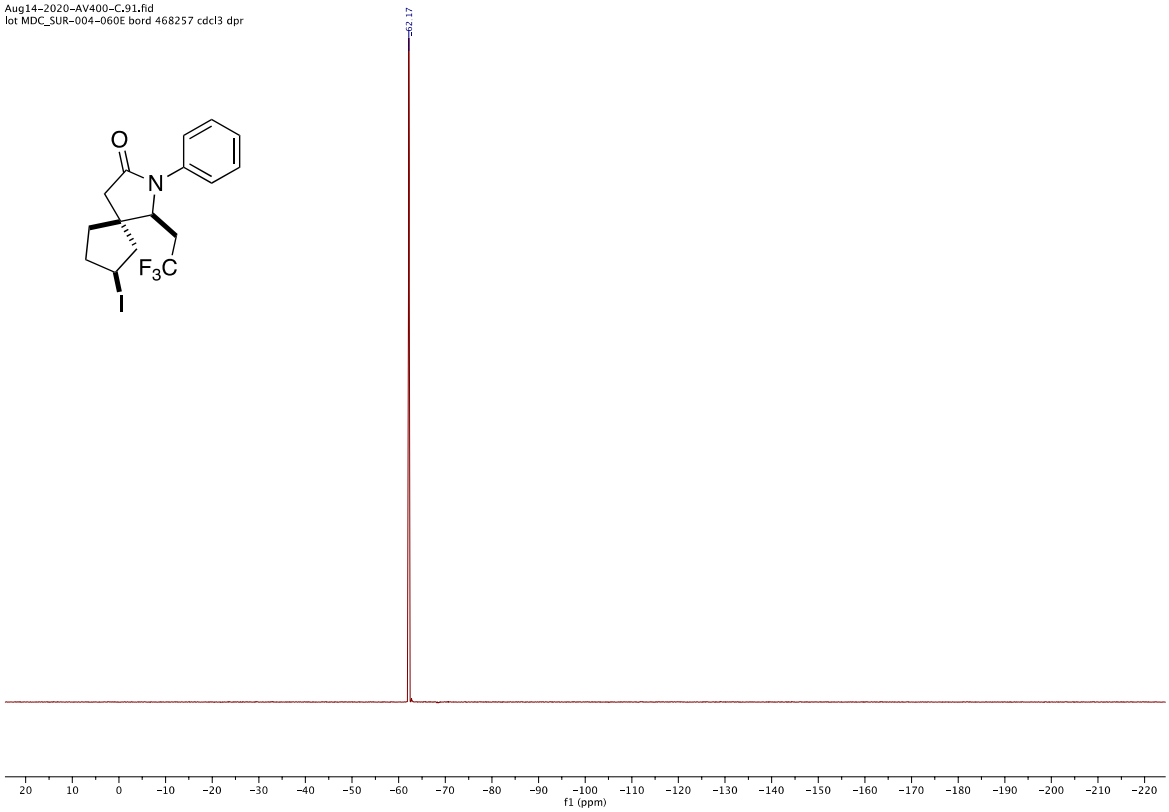
^{1}H NMR of **2wa'**



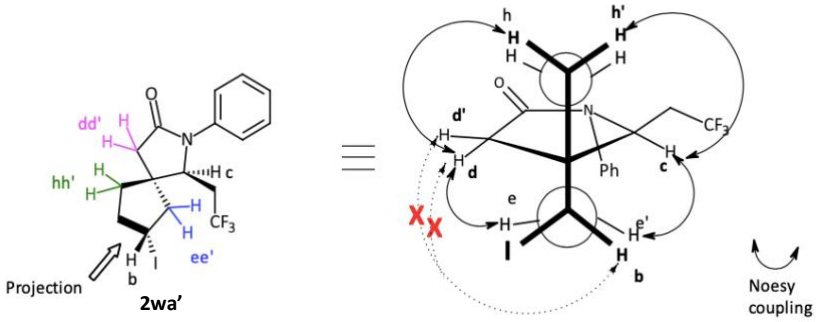
^{13}C NMR of **2wa'**

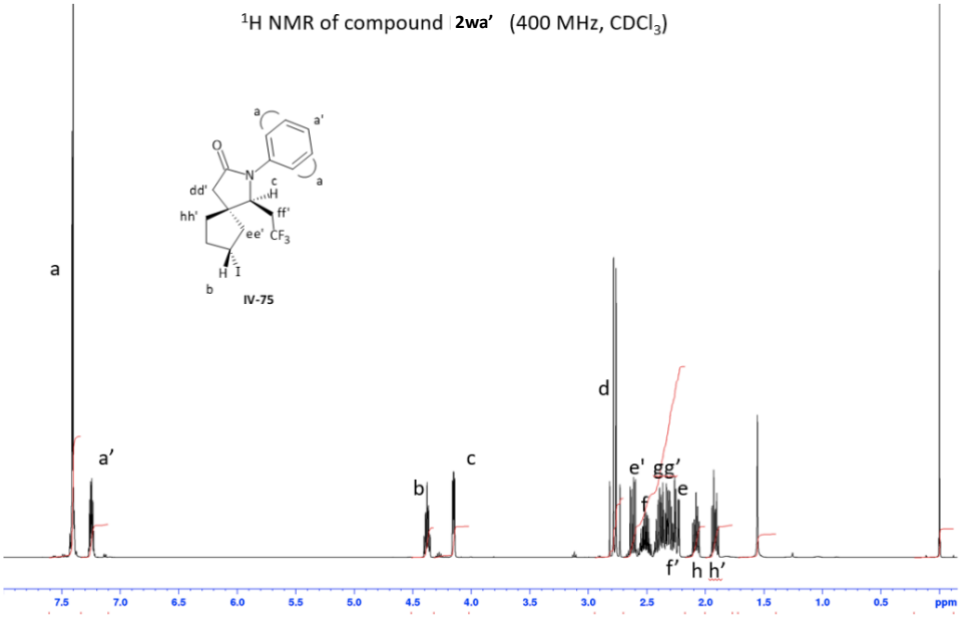


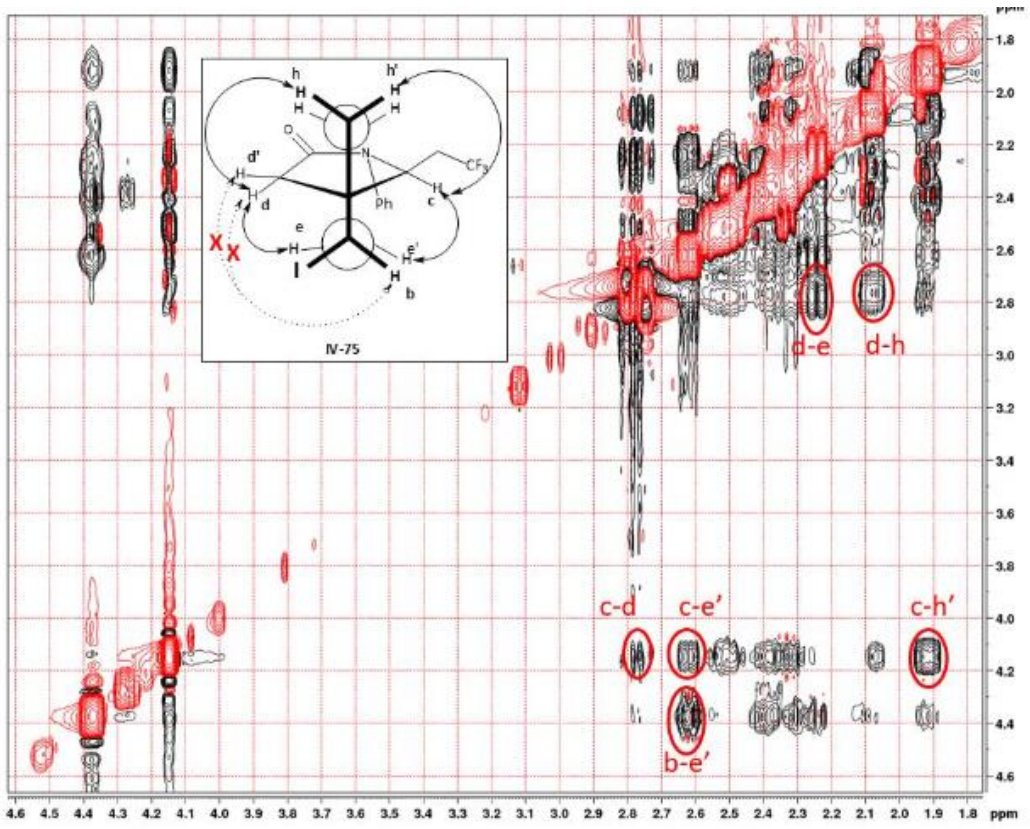
^{19}F NMR of **2wa'**



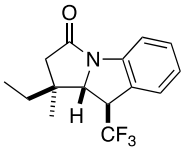
NOESY experiment of **2wa'**



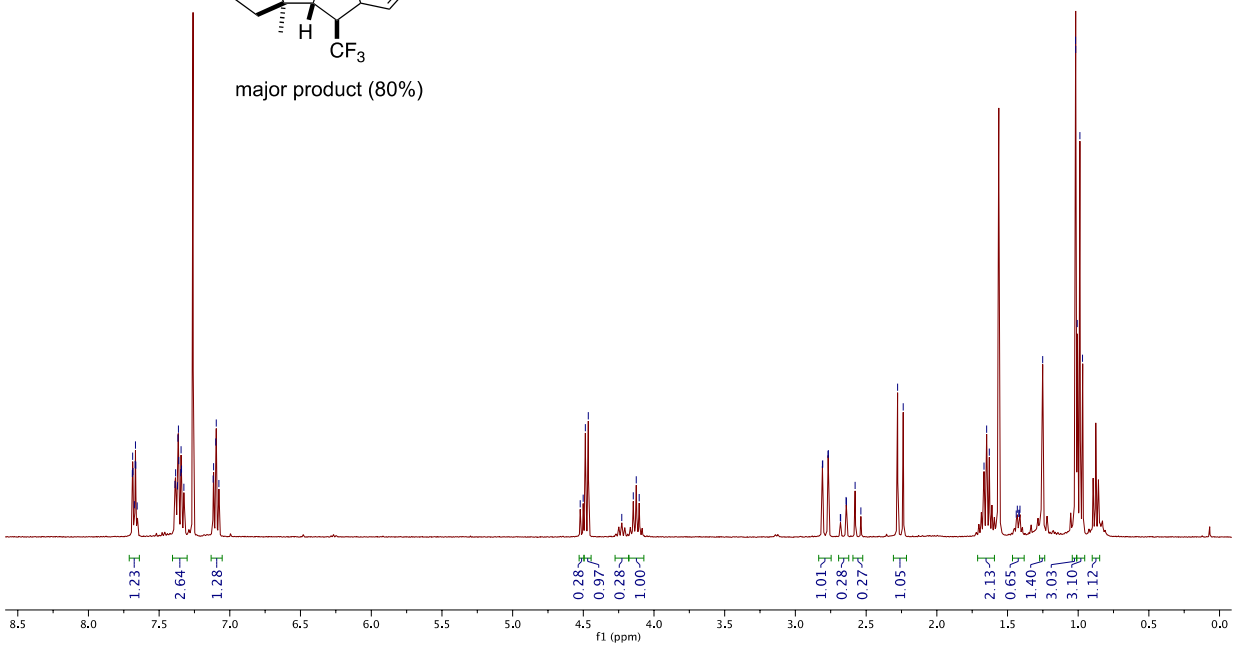




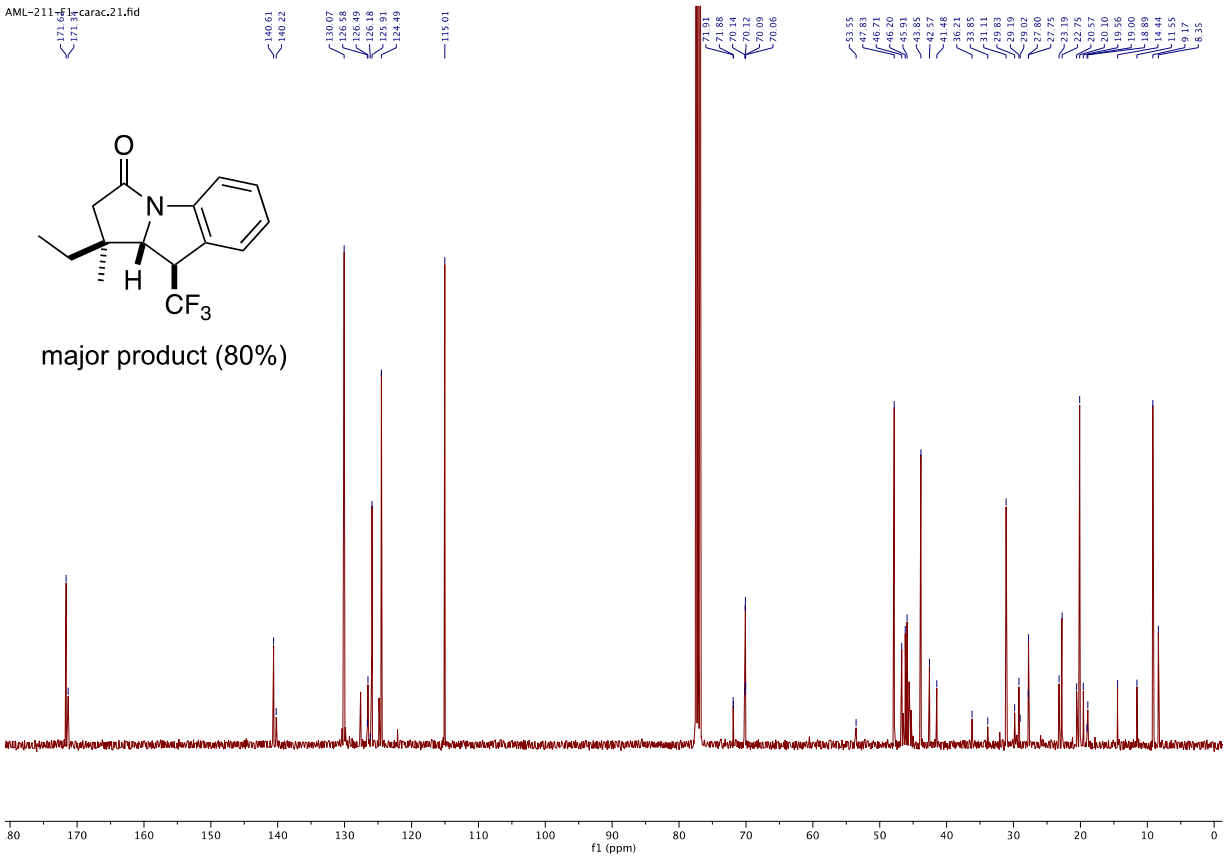
^{1}H NMR of **2x**



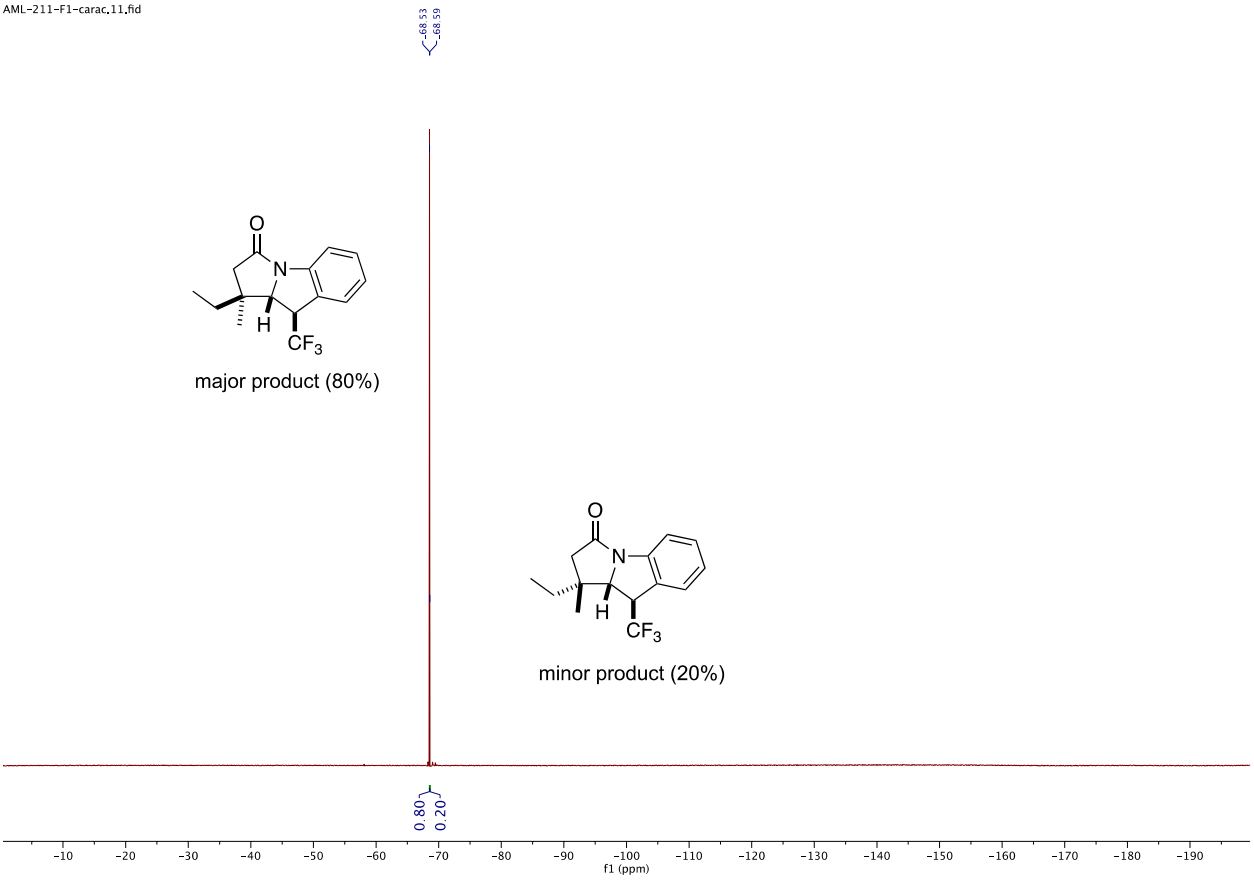
major product (80%)



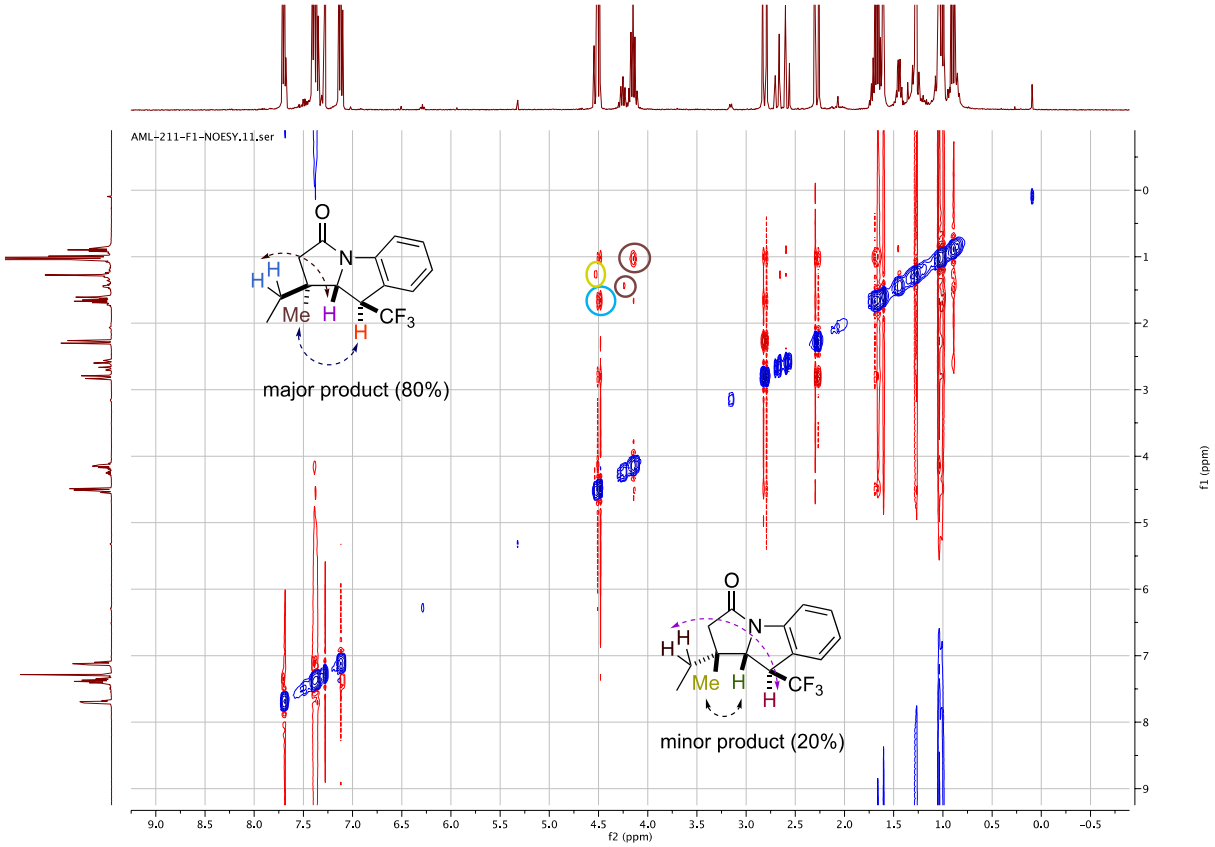
^{13}C NMR of **2x**



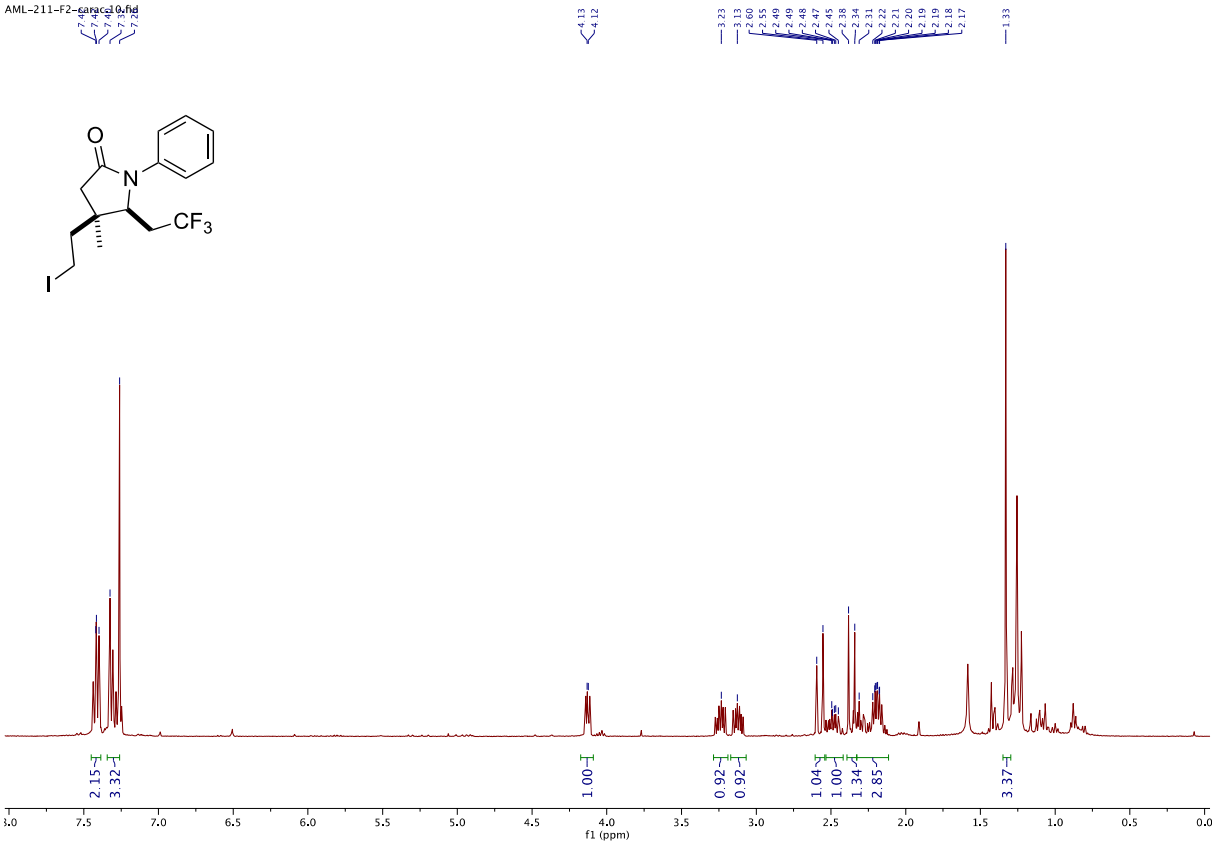
^{19}F NMR of **2x**



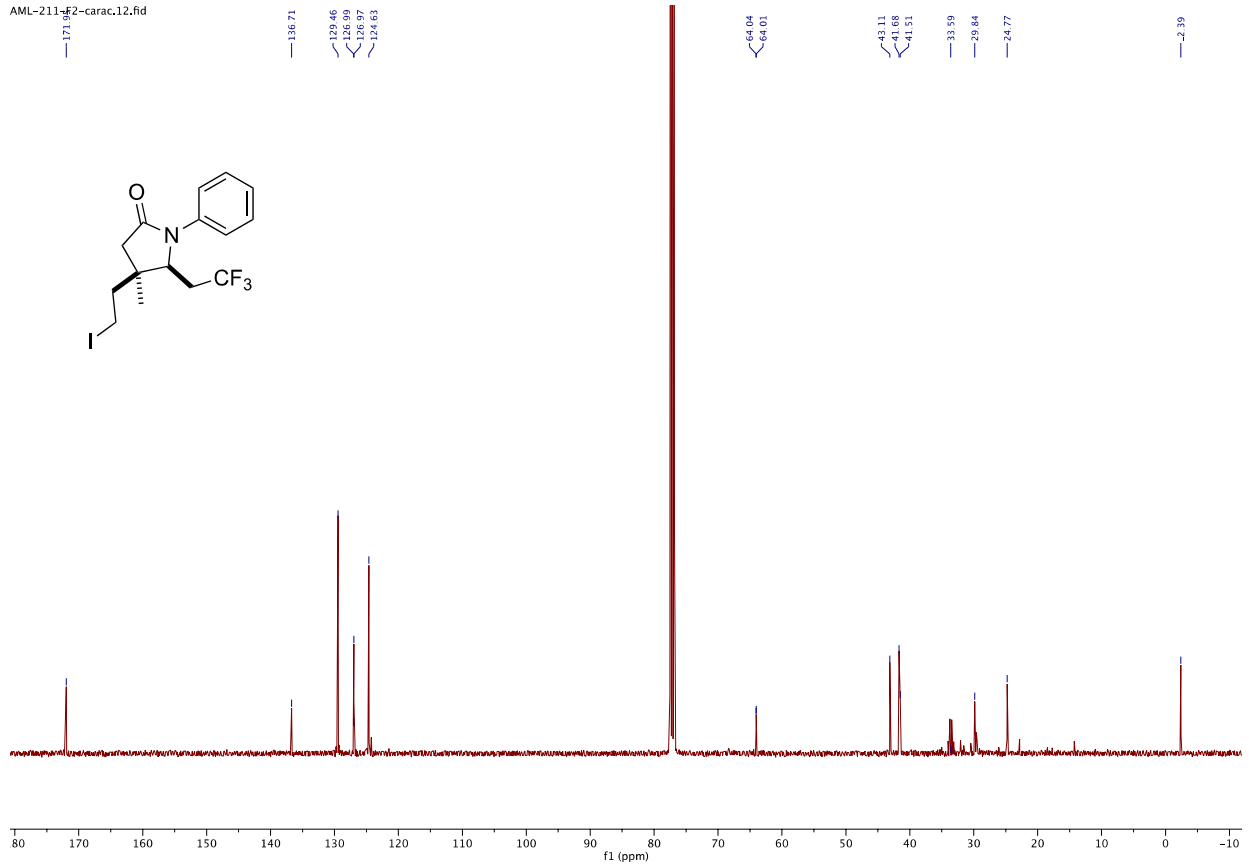
NOESY experiment of **2x**



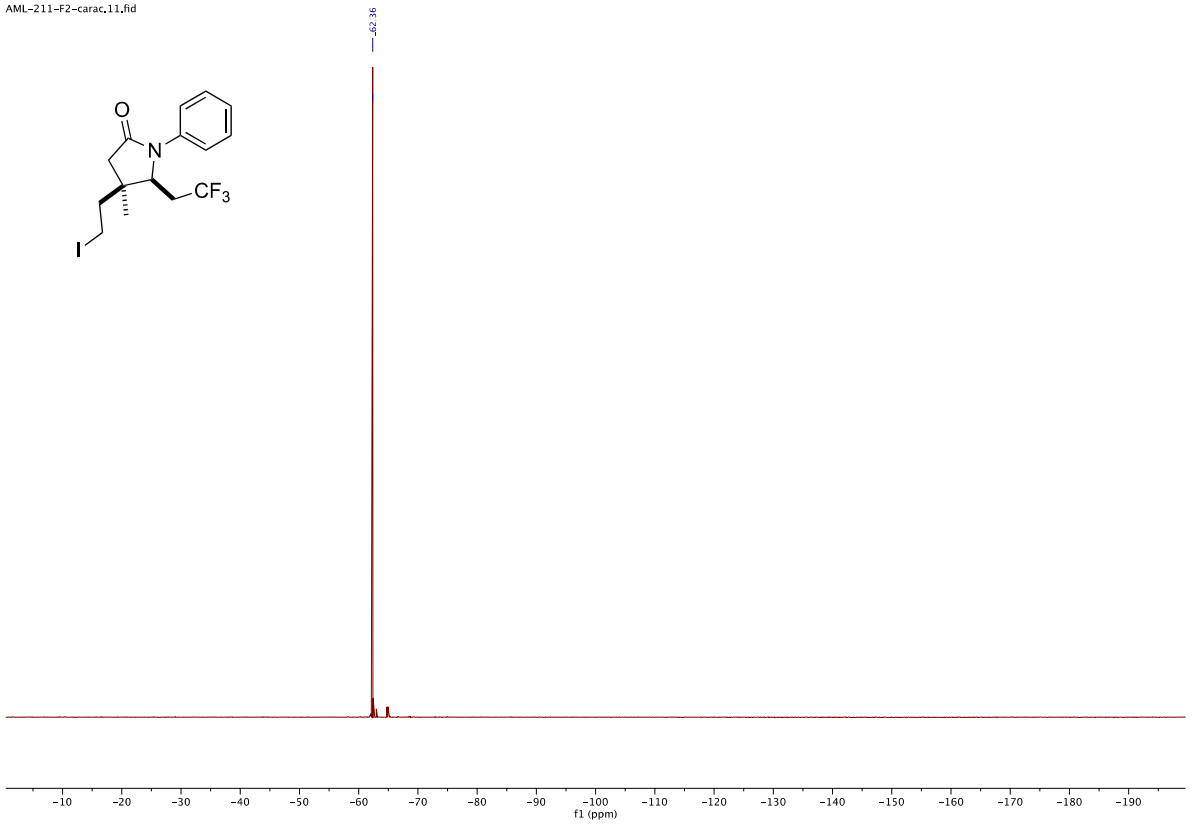
^{1}H NMR of **2xa**



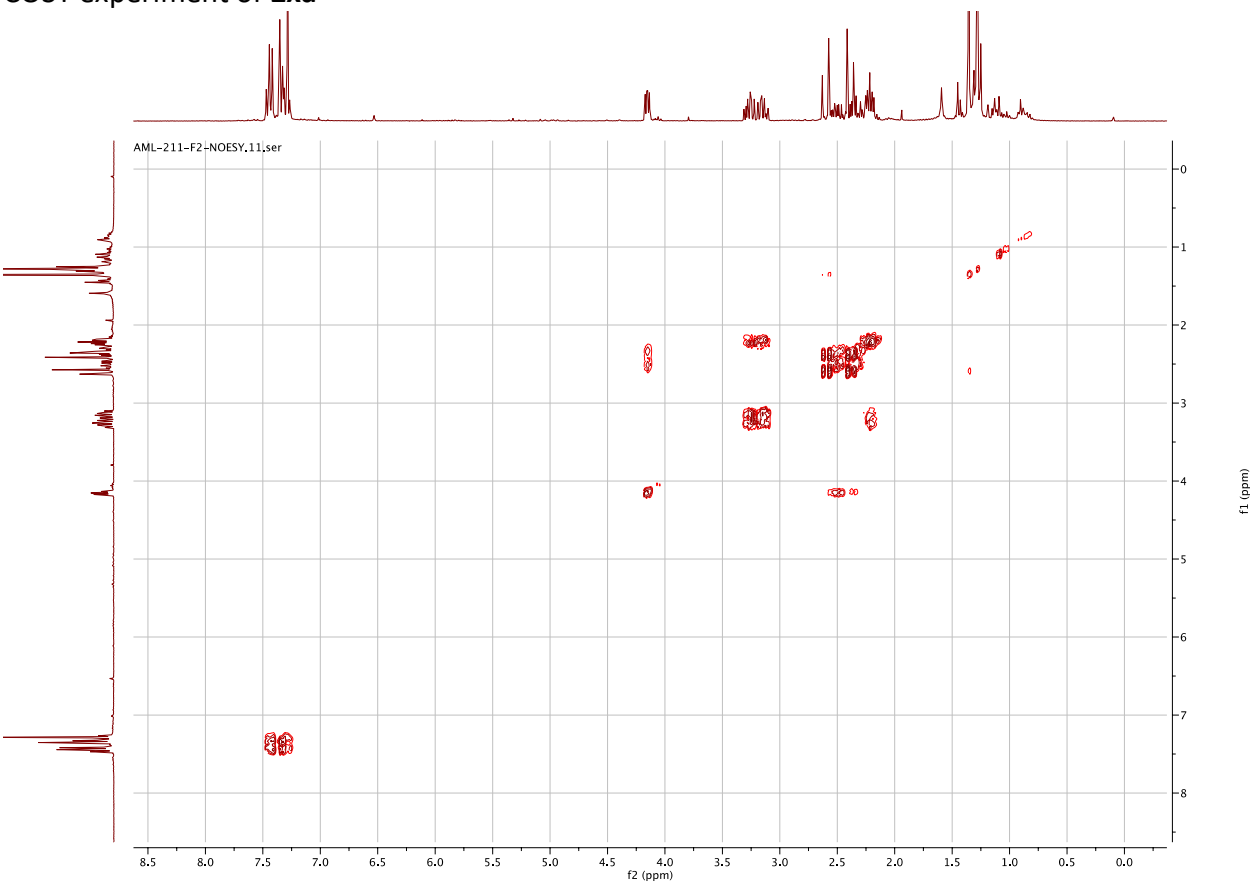
^{13}C NMR of **2xa**



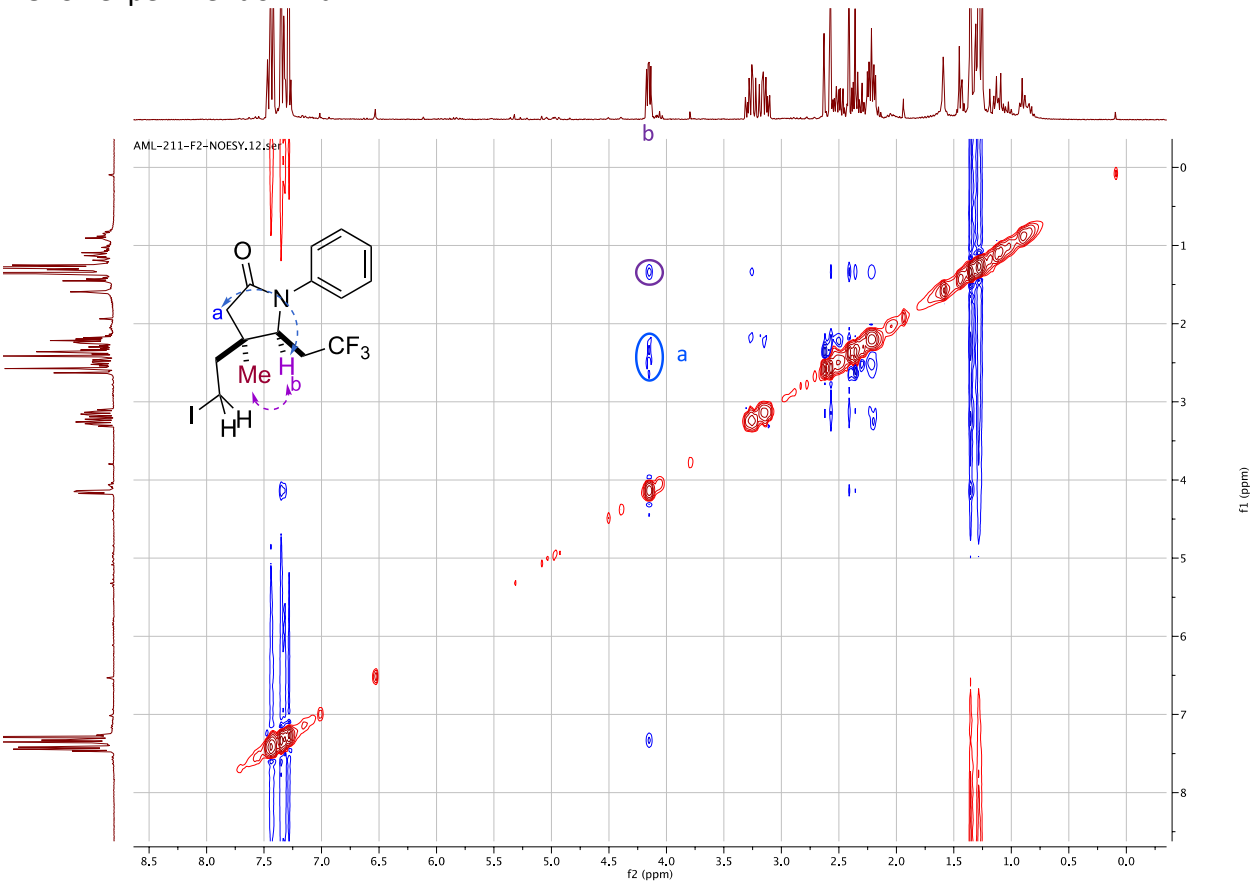
^{19}F NMR of **2xa**



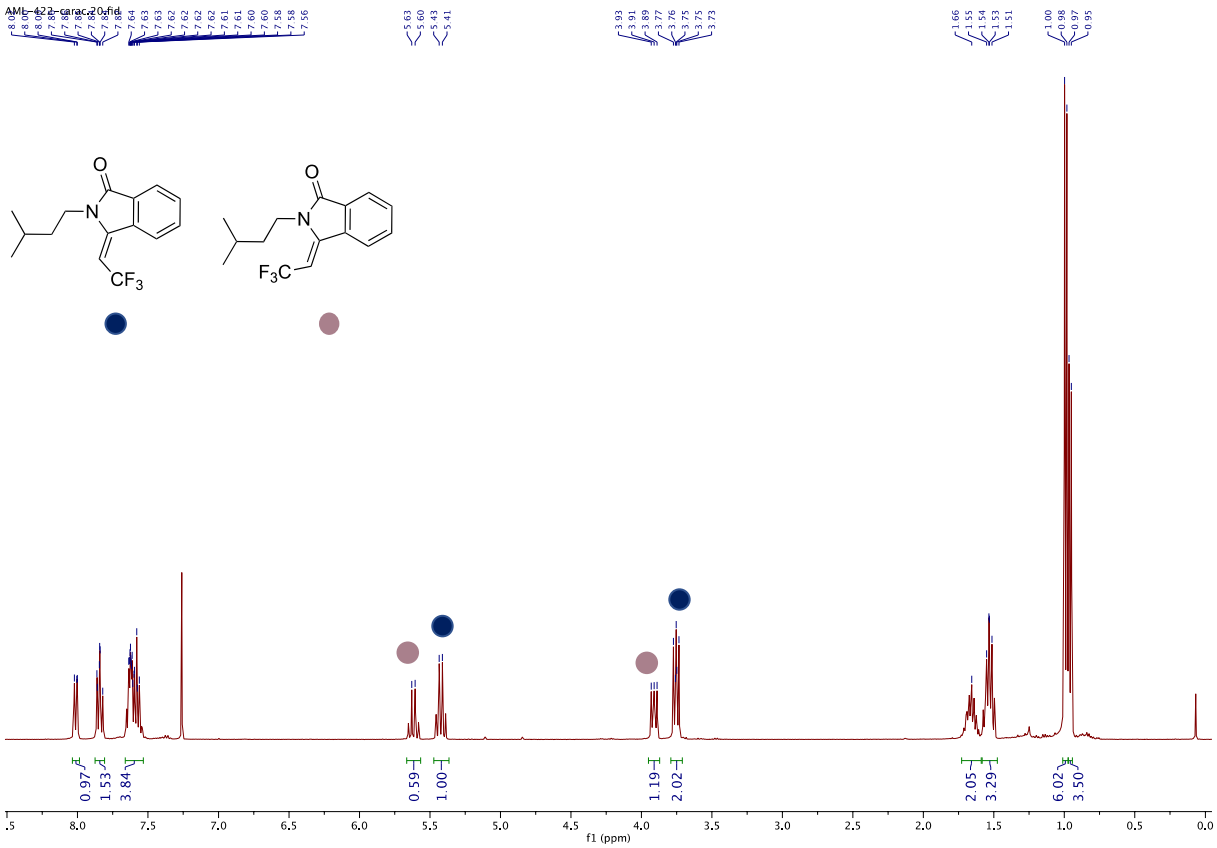
COSY experiment of **2xa**



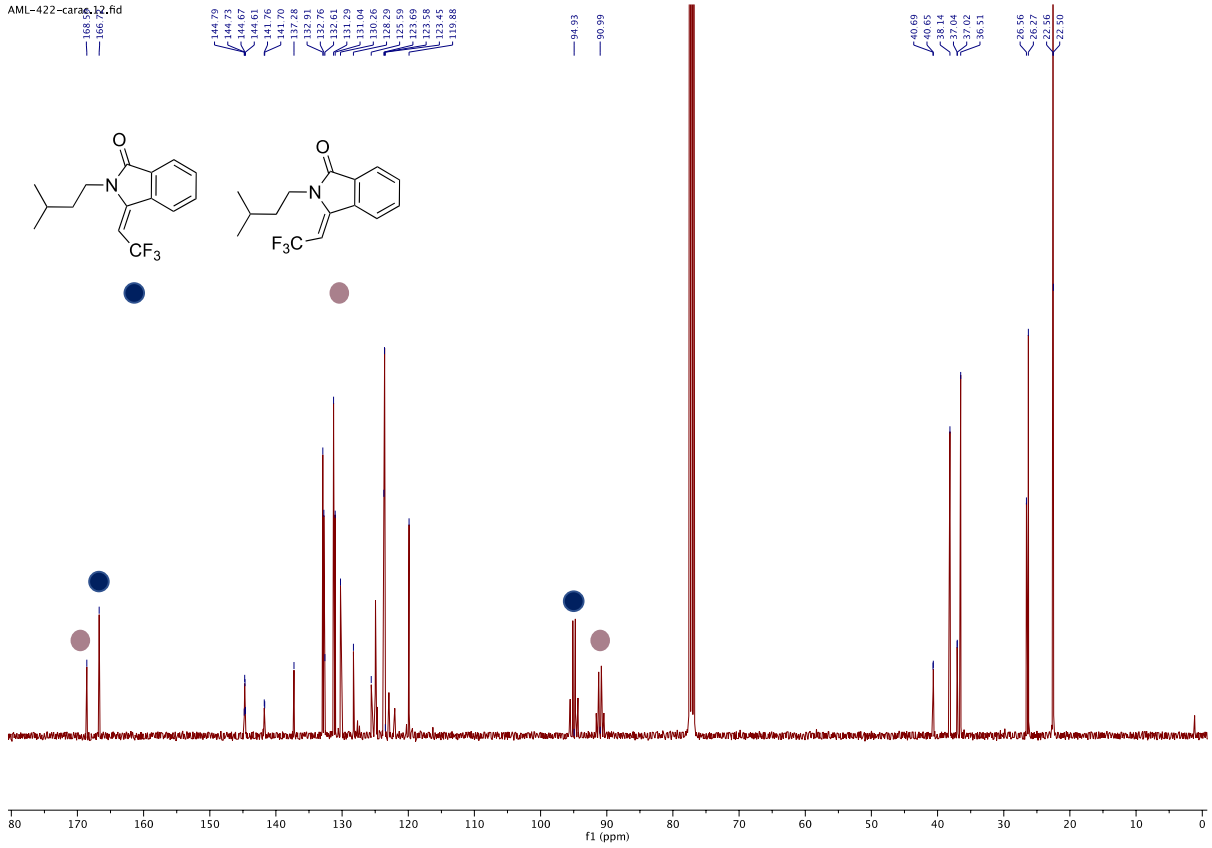
NOESY experiment of **2xa**



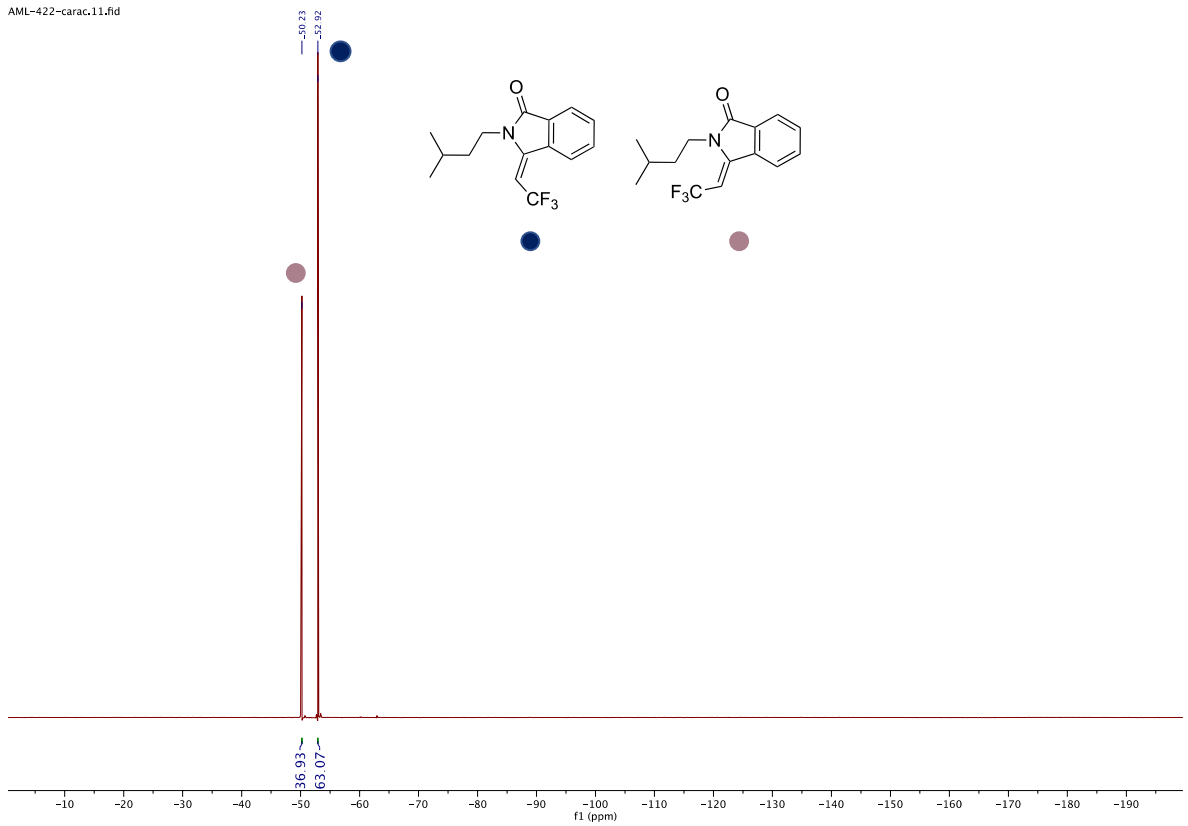
^{1}H NMR of **2z**



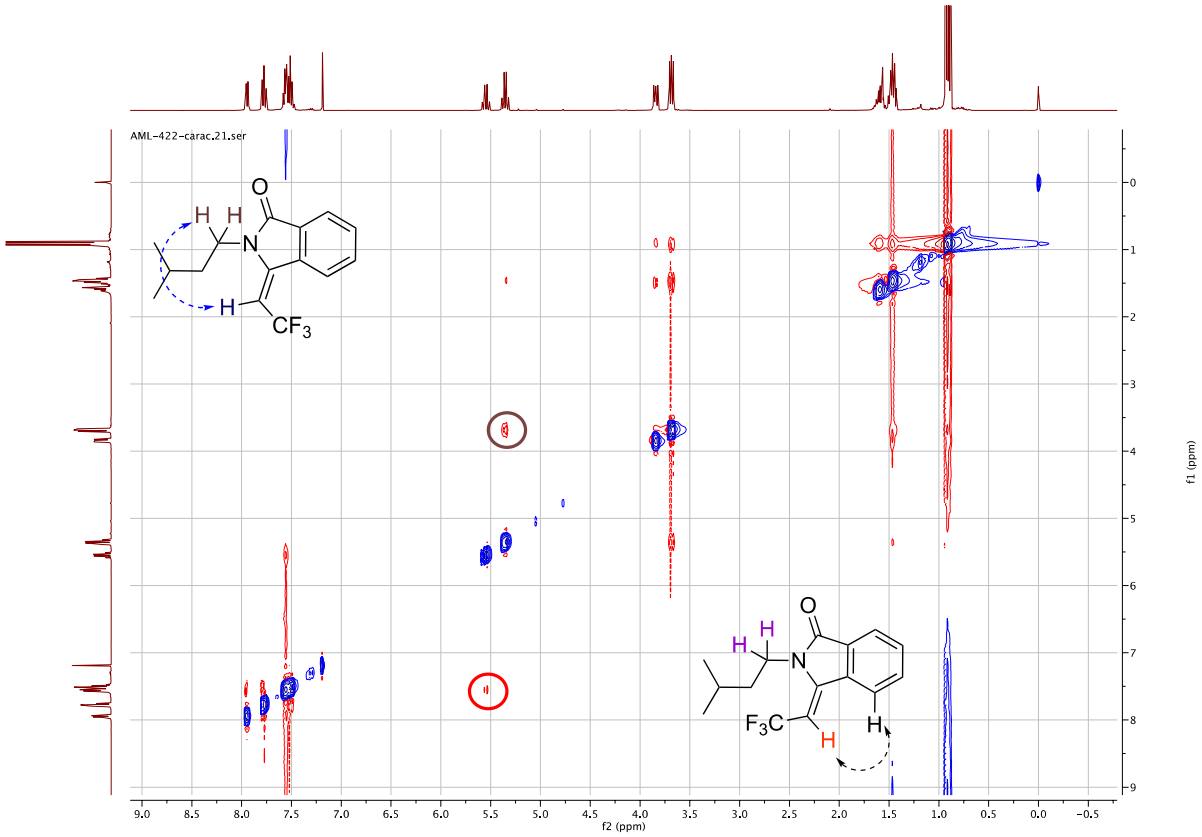
^{13}C NMR of **2z**



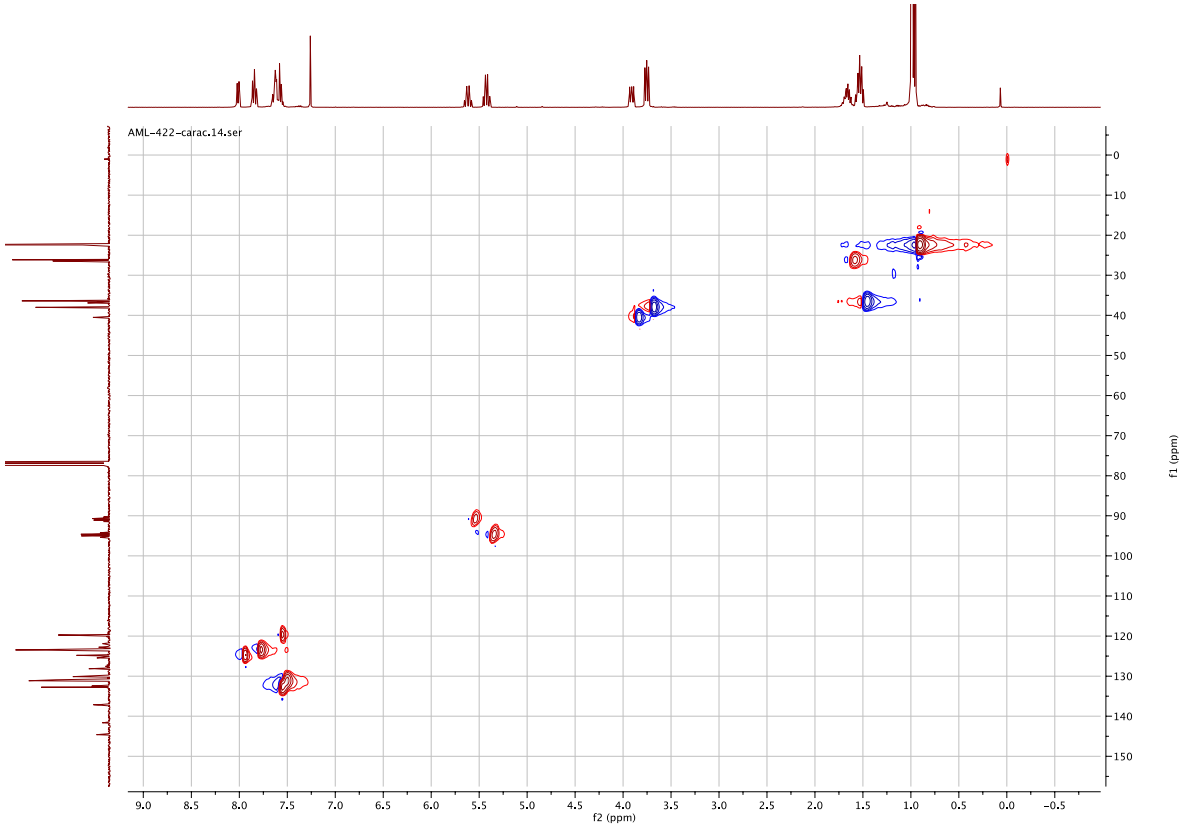
^{19}F NMR of **2z**



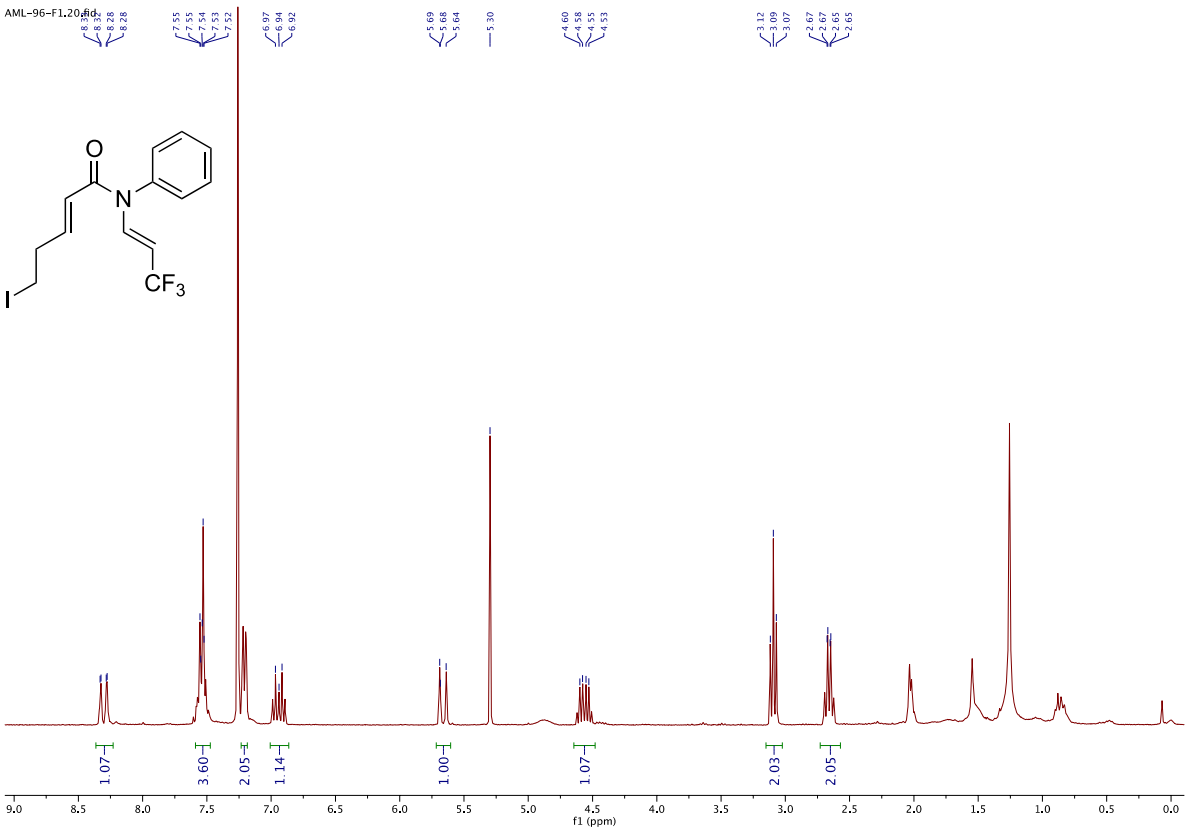
NOESY experiment of **2z**



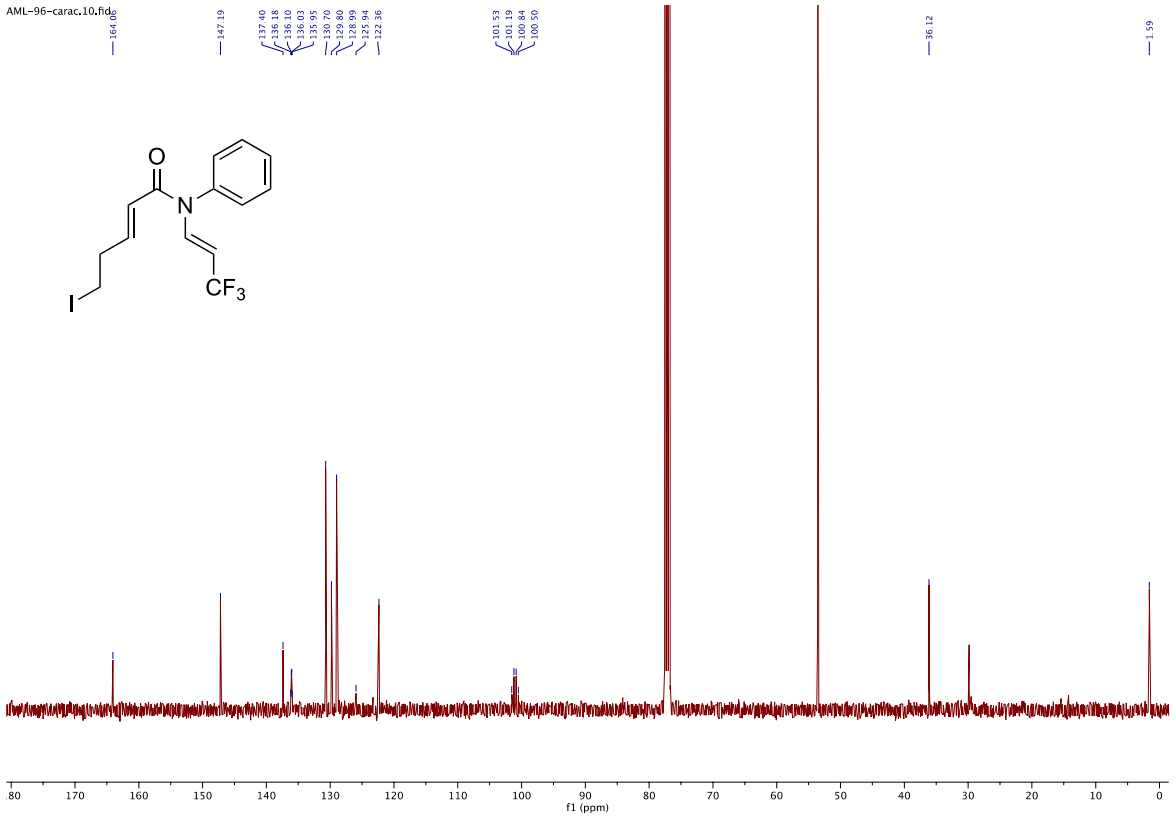
HMBC experiment of **2z**



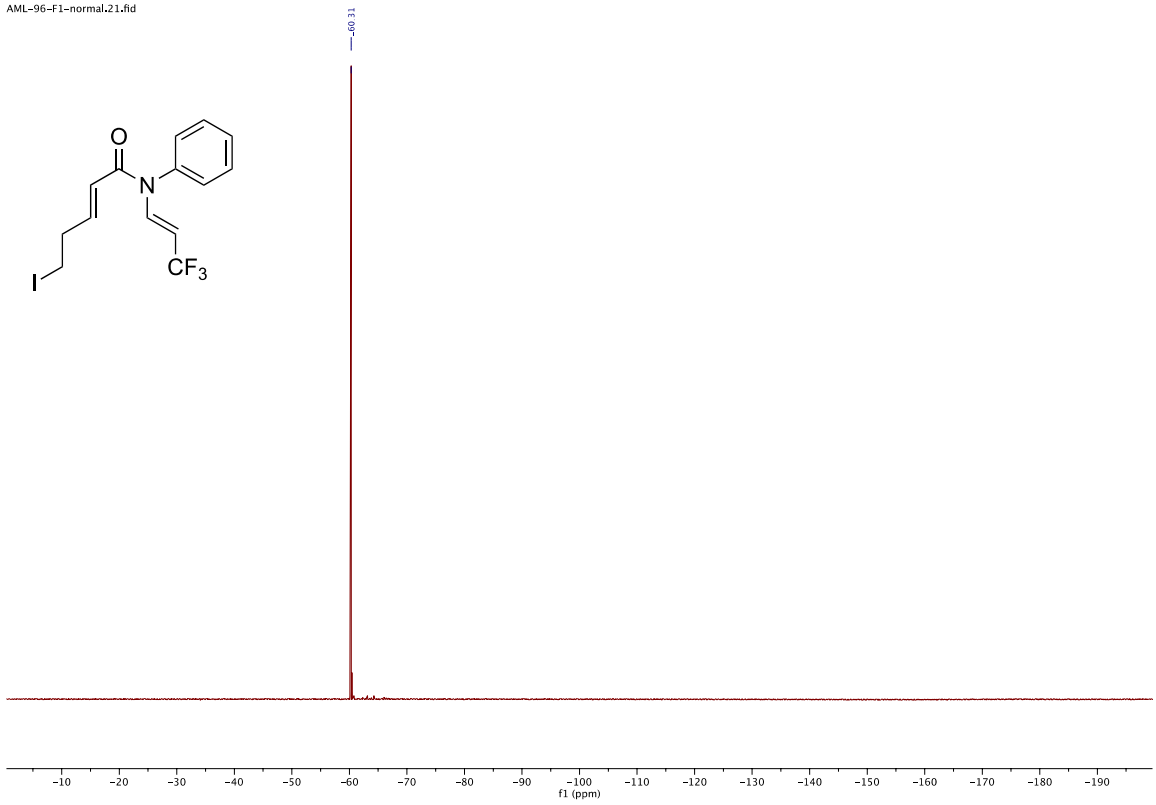
^{1}H NMR of **A1**



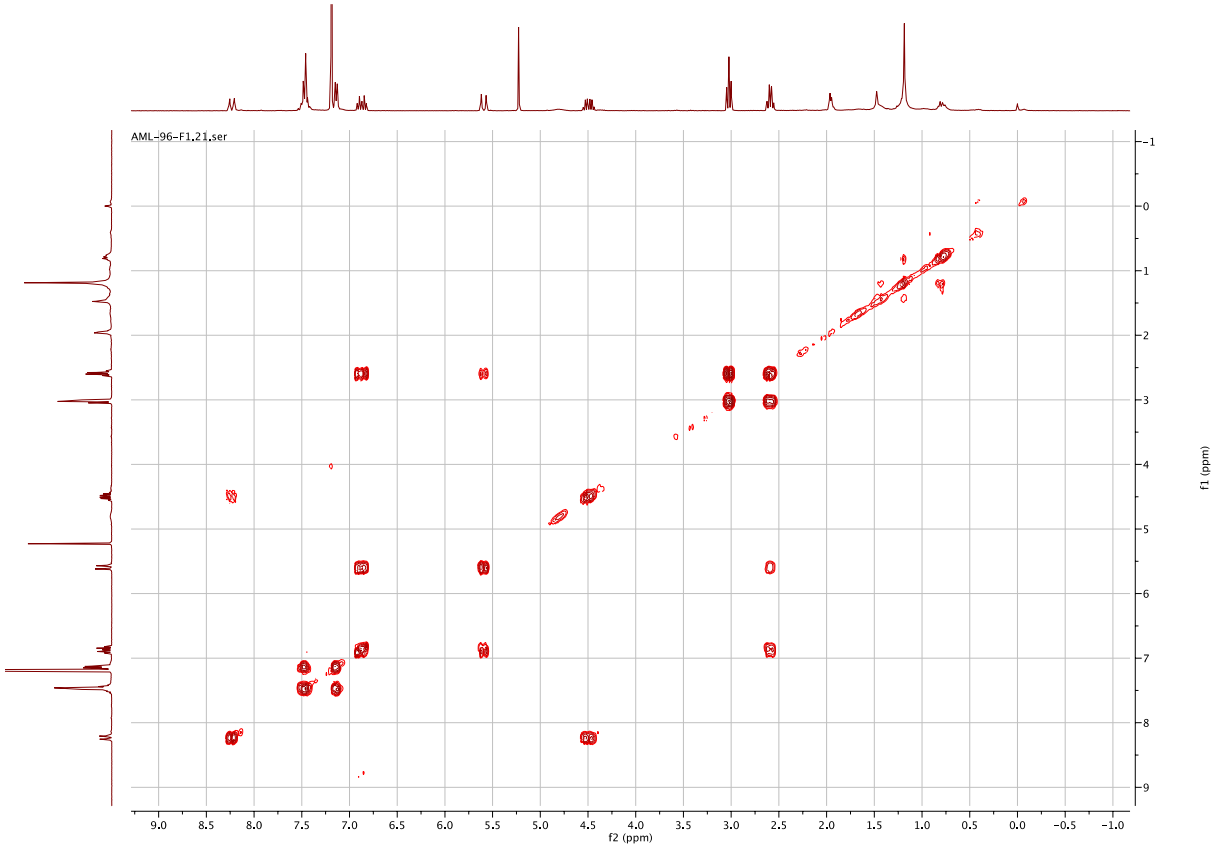
^{13}C NMR of **A1**



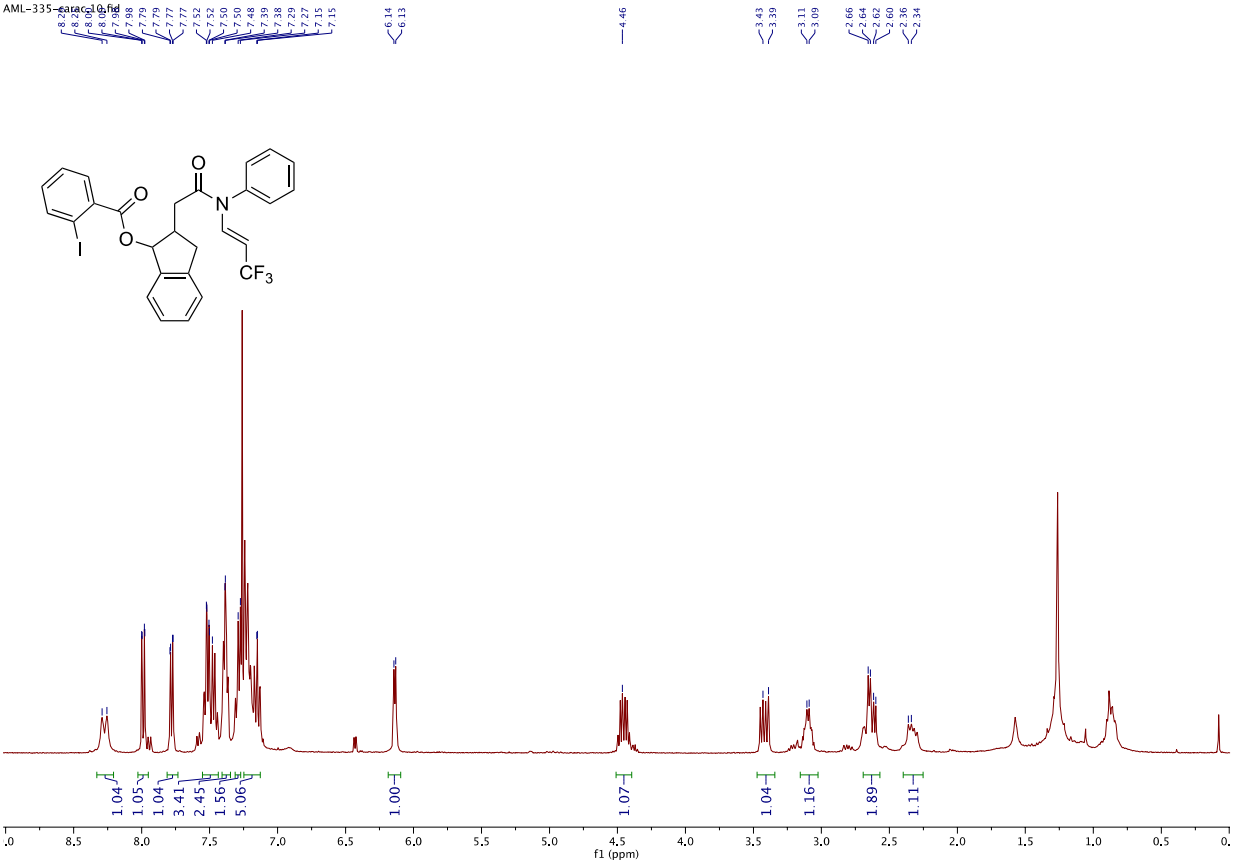
^{19}F NMR of **A1**



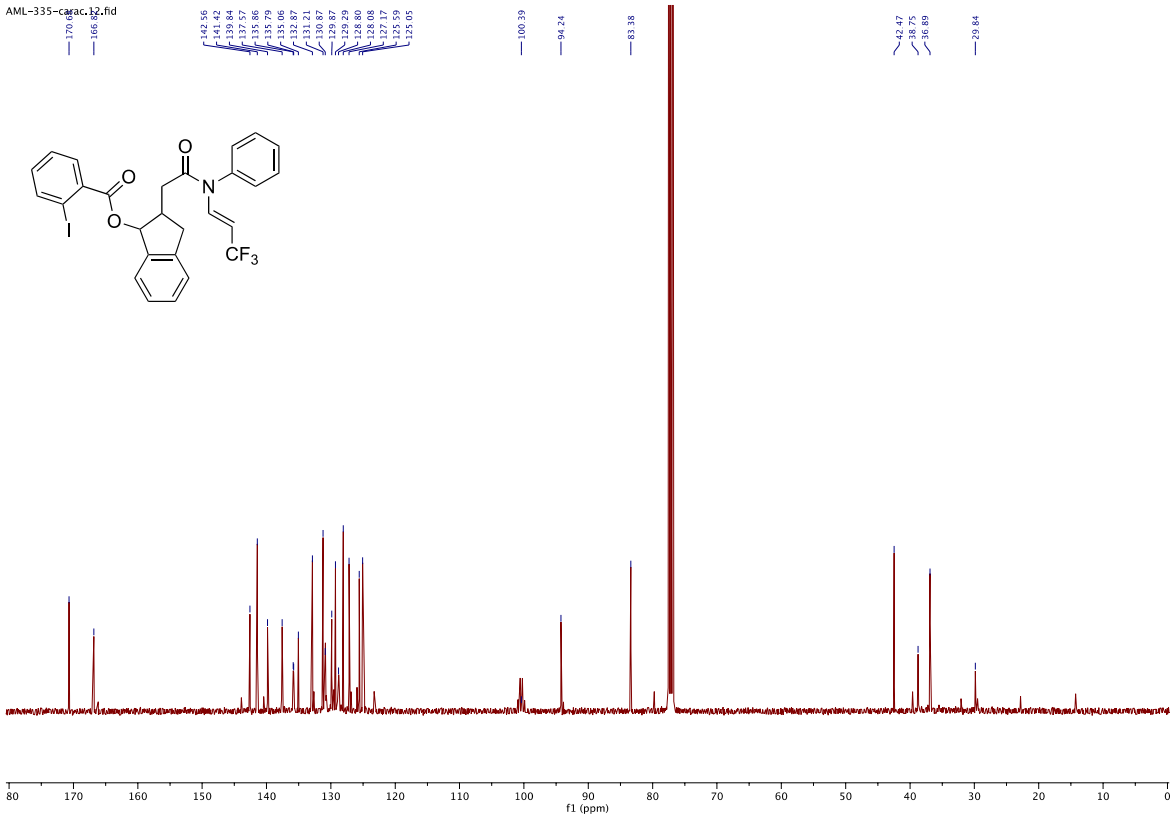
COSY experiment of **A1**



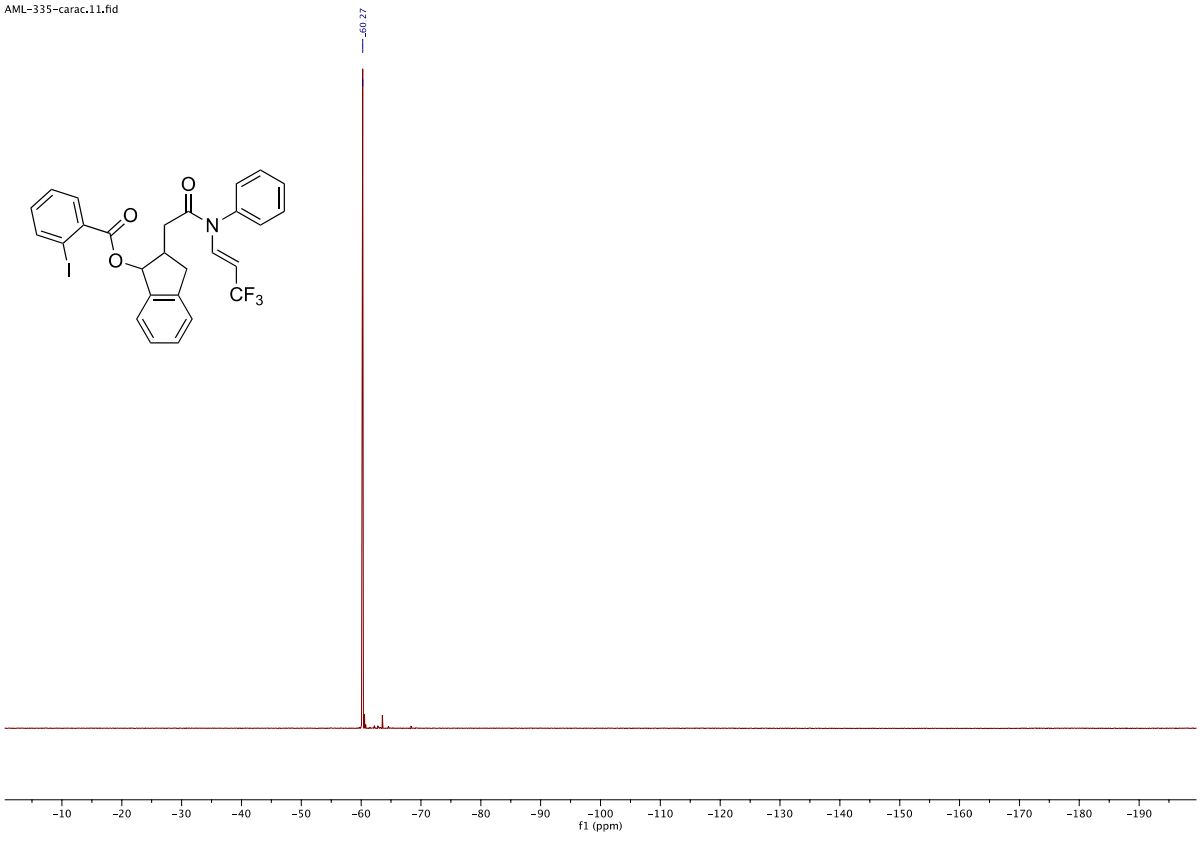
^{1}H NMR of **A4**



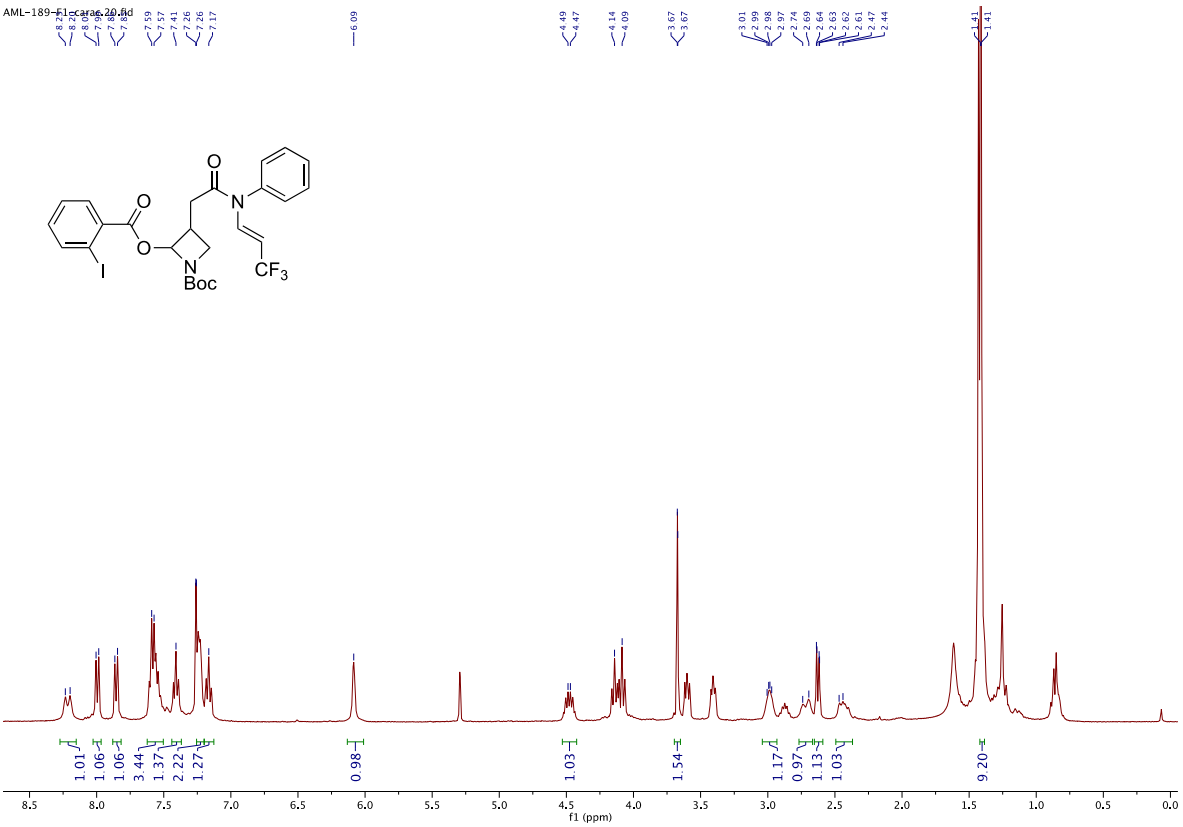
^{13}C NMR of **A4**



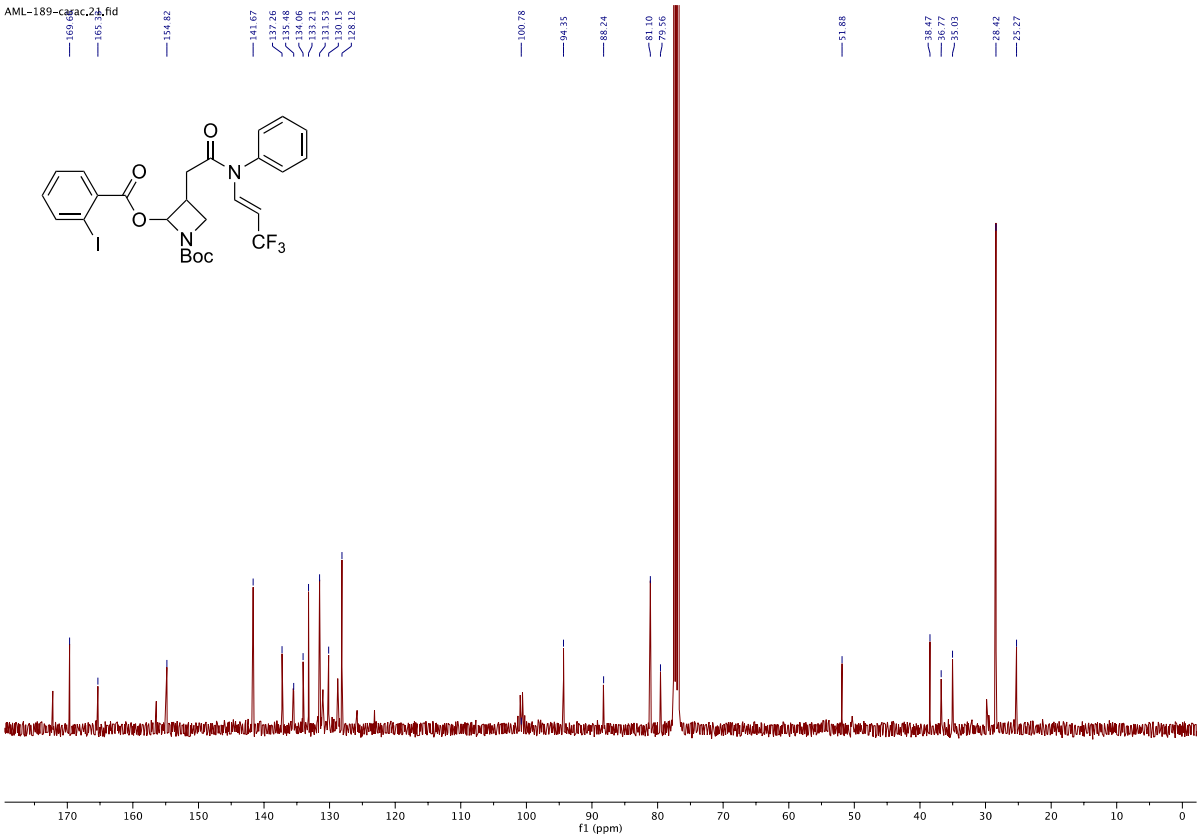
^{19}F NMR of **A4**



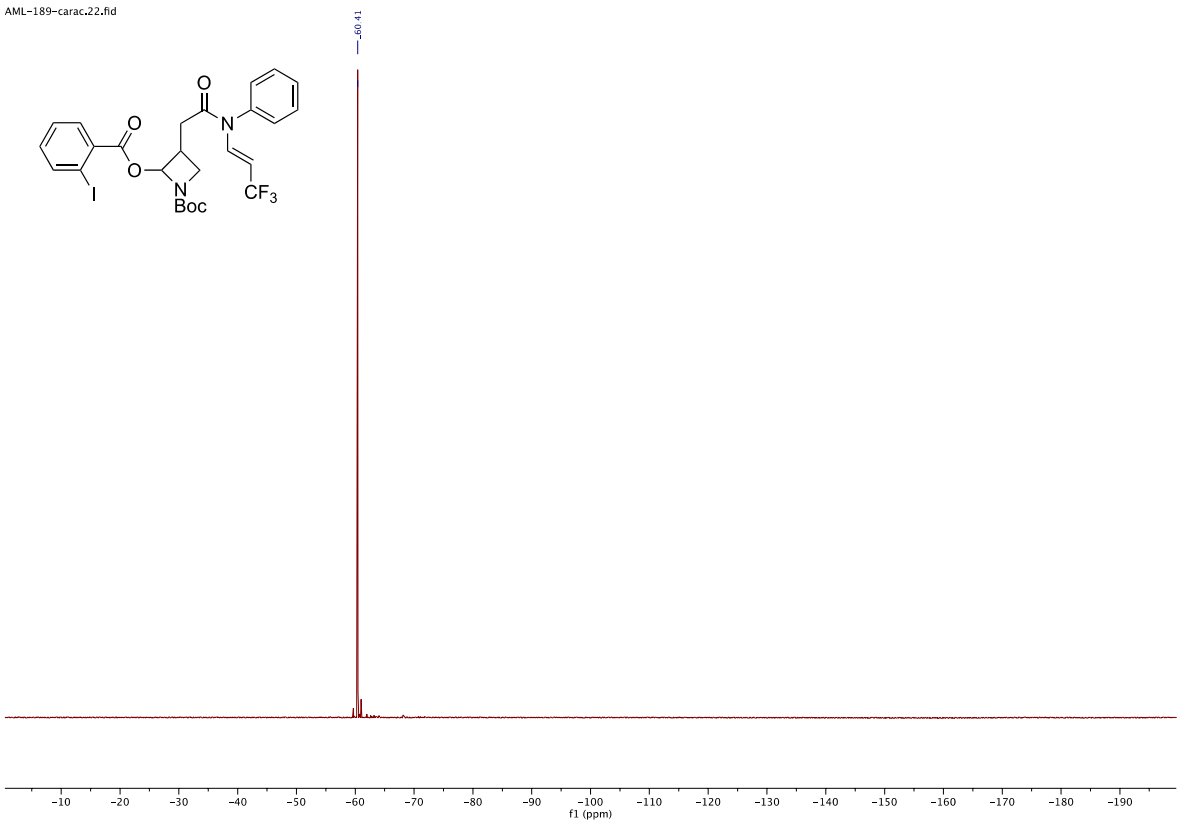
^{1}H NMR of **A5**



^{13}C NMR of **A5**



^{19}F NMR of **A5**


AML-189-carac.22.fid
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O
O
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-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

10. References

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11. X-Ray Analysis Data

Crystals were obtained by using vapor diffusion from DCM to pentane for compounds **2d**, **2a**, **2g**, **2o**. **2t** was obtained by long evaporation from DCM.

X-Ray crystal structure determination

Single crystals were selected, mounted onto a cryoloop and transferred into a cold nitrogen gas stream. Intensity data were collected with a Bruker Kappa-APEX2 CCD diffractometer using a micro-source CuKα radiation (**2a**, **2d**, **2g** and **2t**) or a graphite-monochromated MoKα radiation (**2o**). Data collection, unit-cell parameters determination, integration and data reduction were performed with the Bruker APEX4/SAINT[1] suite at 200K. The structures were solved with SHELXT[2] and refined anisotropically by full-matrix least-squares methods with SHELXL[3] using Olex2[4] software (**2d**, **2a**, **2g** and **2o**) or WinGx[5] suite of programs (**2t**).
The structures were deposited at the Cambridge Crystallographic Data Centre with numbers CCDC 2295985-2295988 and 2301768, and can be obtained free of charge via www.ccdc.cam.ac.uk.

Table S3. Crystallographic data for **2d**, **2a**, **2g**, **2t** and **2o**.

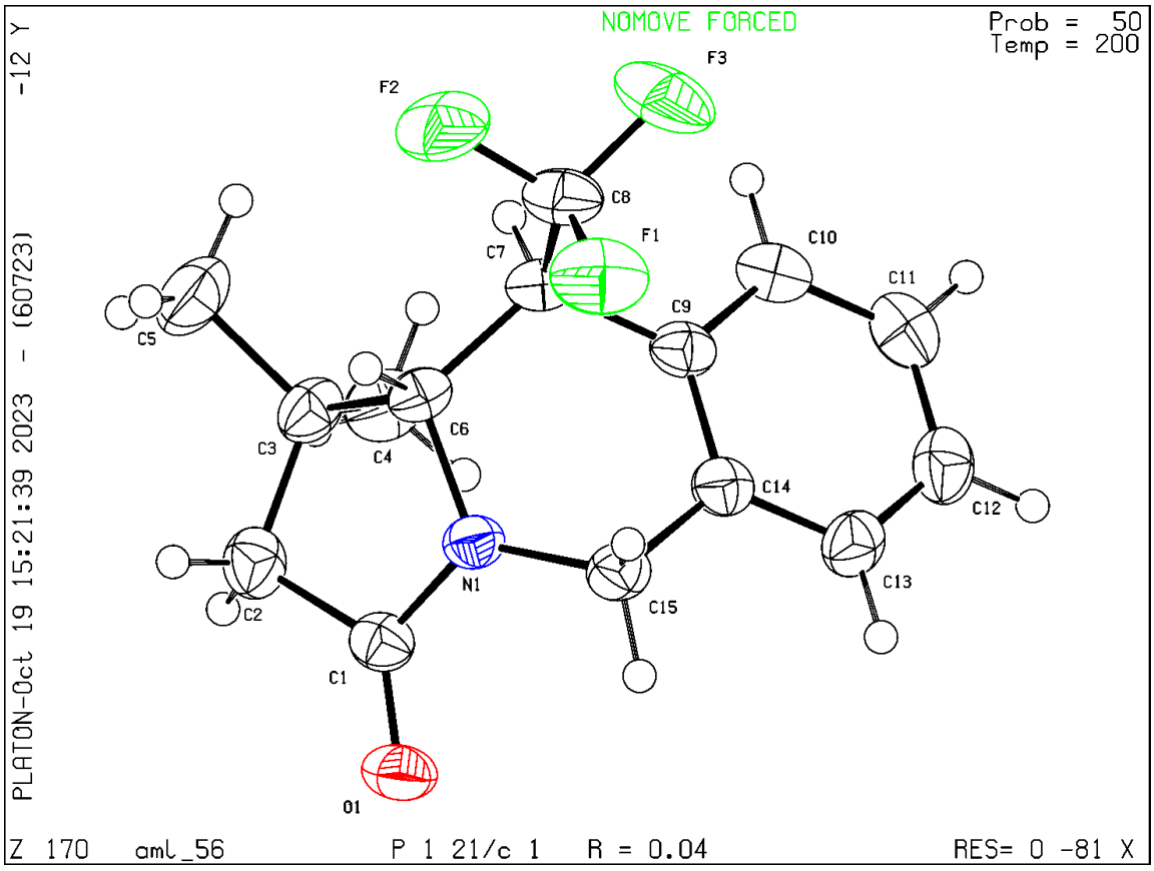
	2d	**2a**	**2g**	**2t**	**2o**
CCDC deposit number	*2295985*	*2295986*	*2295987*	*2295988*	*2301768*
Empirical formula[a]	$C_{16}H_{16}F_3NO$	$C_{15}H_{16}F_3NO$	$C_{14}H_{14}F_3NO$	$C_{15}H_{14}F_3NO$	$C_{18}H_{22}F_3NO$
Moiety Formula	$C_{16}H_{16}F_3NO$	$C_{15}H_{16}F_3NO$	$C_{14}H_{14}F_3NO$	$C_{15}H_{14}F_3NO$	$C_{18}H_{22}F_3NO$
Formula weight (g/mol)	295.30	283.29	269.26	281.27	325.36
Temperature (K)	200	200	200	200	200
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_1/c$	Pc	$P2_1/c$	$P2_12_12_1$
a (Å)	7.4696(3)	9.2596(9)	14.7284(17)	6.7312(2)	8.0465(7)

b (Å)	19.5327(8)	11.2829(10)	9.1741(8)	24.6023(7)	12.9285(12)
c (Å)	10.1253(4)	13.4672(12)	9.7832(13)	8.2365(2)	16.1143(15)
α (°)	90	90	90	90	90
β (°)	110.184(2)	103.525(6)	98.521(8)	110.277(2)	90
γ (°)	90	90	90	90	90
Volume (Å^3)	1386.57(10)	1368.0(2)	1307.3(3)	1279.46(6)	1676.4(3)
Z	4	4	4	4	4
ρ_{calc} (g/cm^3)	1.415	1.375	1.368	1.460	1.289
Absorption coefficient μ (mm^{-1})	0.987 (CuKα)	0.974 (CuKα)	0.991 (CuKα)	1.041 (CuKα)	0.102 (MoKα)
F(000)	616	592	560	584	688
Crystal size (mm²)	0.26 × 0.19 × 0.18	0.99 × 0.35 × 0.29	0.50 × 0.10 × 0.09	0.77 × 0.06 × 0.04	0.40 × 0.20 × 0.20
Wavelength λ (Å)	1.54178	1.54178	1.54178	1.54178	0.71073
2Θ range (°)	9.054 - 132.956	9.824 - 134.476	9.640 - 103.738	7.186 - 133.178	4.04 - 56.838
Miller indexes ranges	-6 ≤ h ≤ 8, -23 ≤ k ≤ 23, -12 ≤ l ≤ 11	-11 ≤ h ≤ 10, -13 ≤ k ≤ 10, -15 ≤ l ≤ 16	-14 ≤ h ≤ 15, -8 ≤ k ≤ 9, -9 ≤ l ≤ 9	-5 ≤ h ≤ 7, -29 ≤ k ≤ 29, -9 ≤ l ≤ 9	-10 ≤ h ≤ 10, -17 ≤ k ≤ 8, -21 ≤ l ≤ 21
Measured reflections	10353	10750	16063	8124	13483
Unique reflections	2418	2417	2890	2249	4206
R_{int} / R_{sigma}	0.0345 / 0.0257	0.0488 / 0.0386	0.1376 / 0.0891	0.0231 / 0.0205	0.0304 / 0.0354
Reflections [I ≥ 2σ(I)]	2027	1971	2240	1909	3361
Restraints	0	0	2	0	0
Parameters	191	184	348	181	212
Goodness-of-fit F²	1.032	1.063	1.019	1.051	1.006
Final R indexes[b] [c] [all data]	R1 = 0.0470, wR2 = 0.1020	R1 = 0.0493, wR2 = 0.1055	R1 = 0.0707, wR2 = 0.1137	R1 = 0.0496, wR2 = 0.1162	R1 = 0.0590, wR2 = 0.0936
Final R indexes[b] [c] [I ≥ 2σ(I)]	R1 = 0.0389, wR2 = 0.0972	R1 = 0.0395, wR2 = 0.0994	R1 = 0.0505, wR2 = 0.1040	R1 = 0.0422, wR2 = 0.1097	R1 = 0.0412, wR2 = 0.0867
Largest diff. peak/hole (e/Å^3)	0.24 / -0.21	0.17 / -0.18	0.14 / -0.18	0.20 / -0.29	0.19 / -0.14
Flack parameter	NC	NC	-0.2(3)	NC	0.4(3)

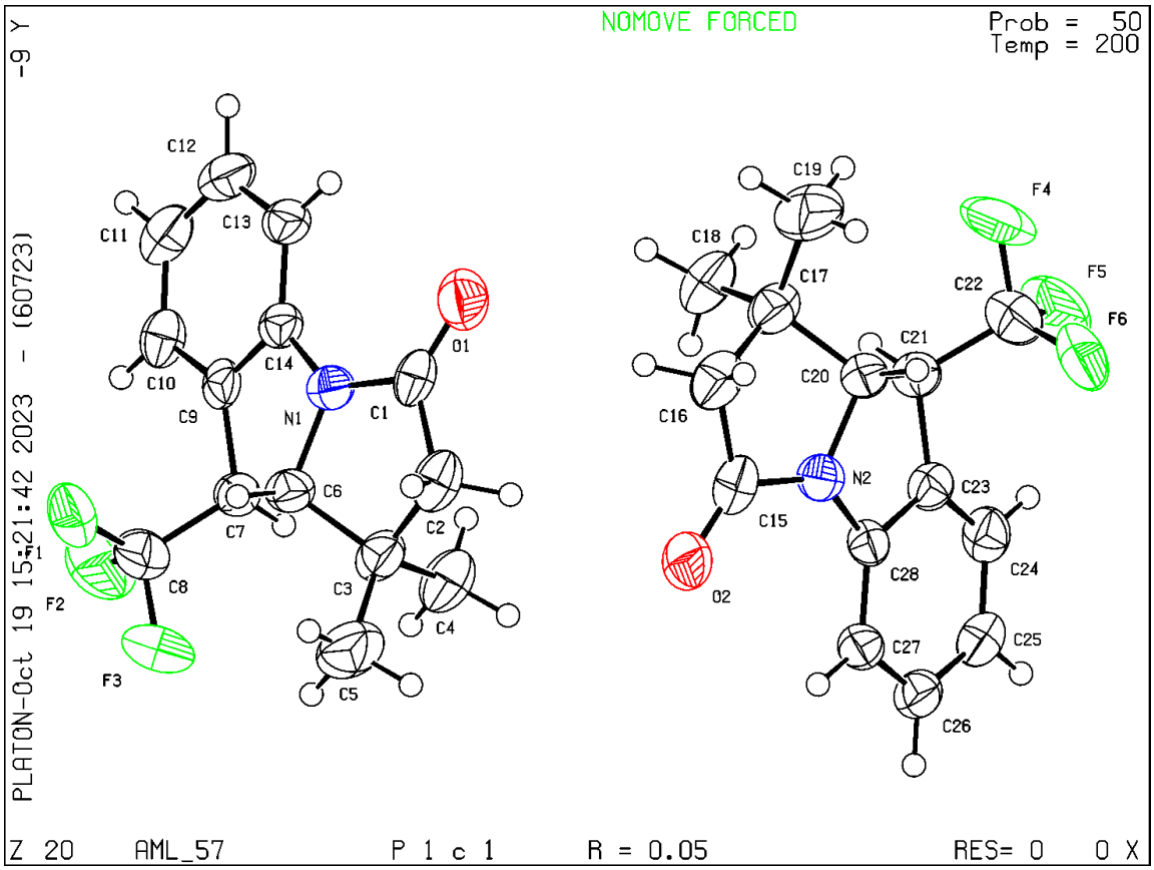
[a] Including solvent molecules (if presence)

[b] $R1 = \sum\big||F_o| - |F_c|\big| \,/ \sum |F_o|$ [c] $wR2 = \sqrt{\sum\big(w(F_o^2 - F_c^2)\big)/\sum(w(F_o^2)^2)}$

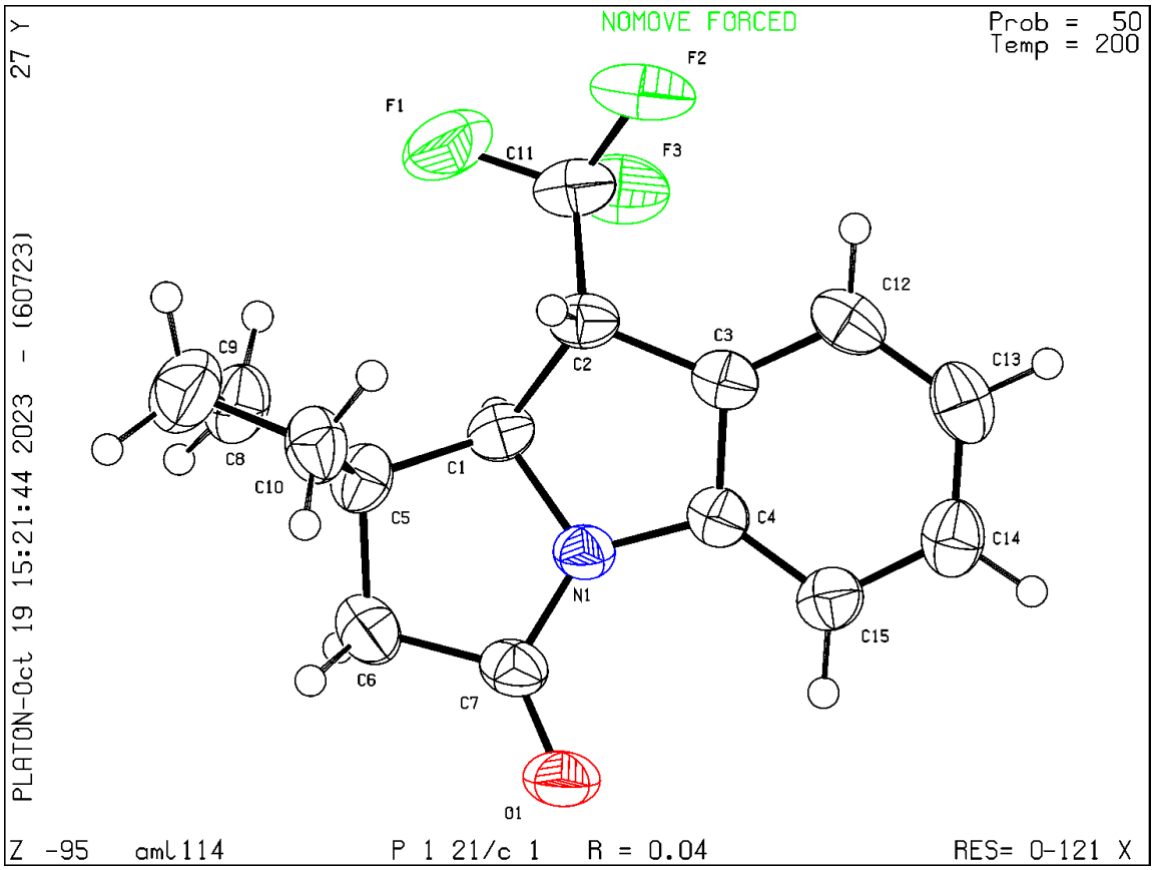
Datablock 2a - ellipsoid plot



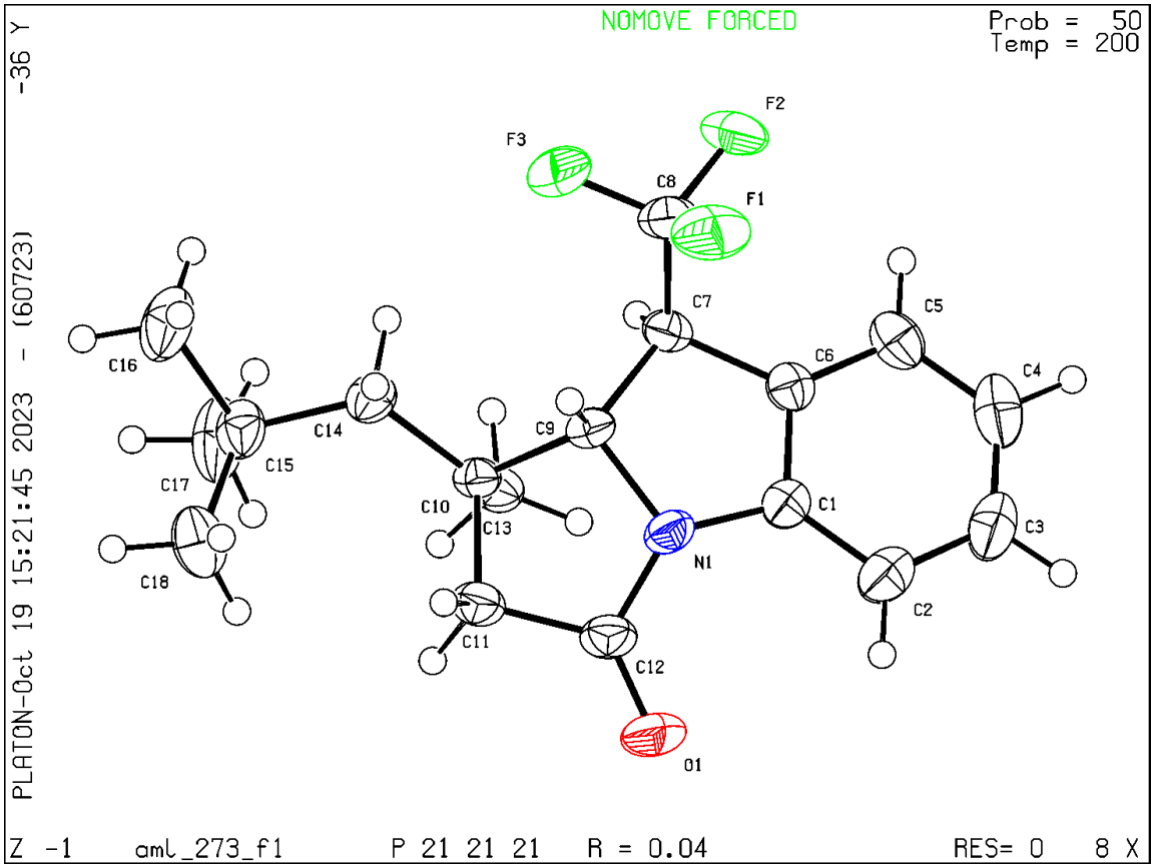
Datablock 2g - ellipsoid plot



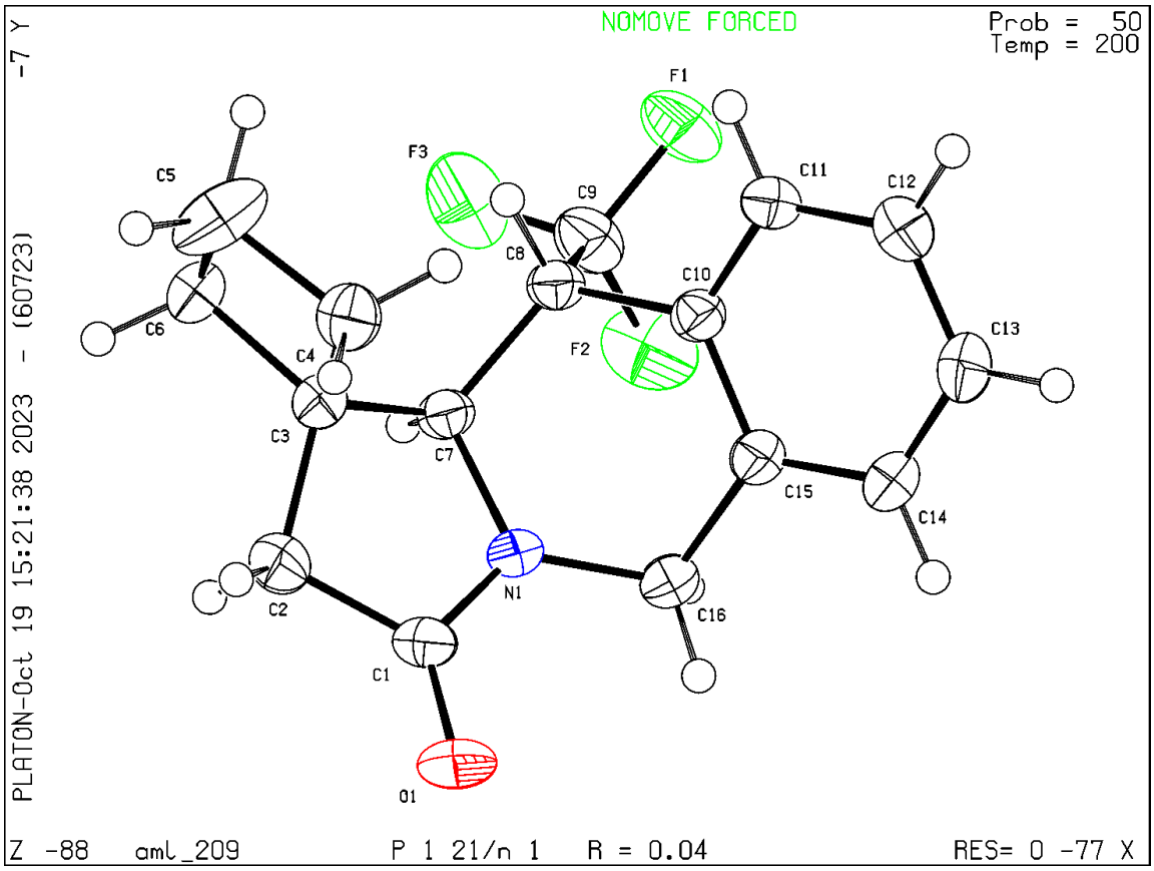
Datablock 2t - ellipsoid plot



Datablock 2o - ellipsoid plot



Datablock 2d - ellipsoid plot



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