

Supporting Information

Visible-Light-Promoted Olefinic Trifluoromethylation of Enamides with CF₃SO₂Na

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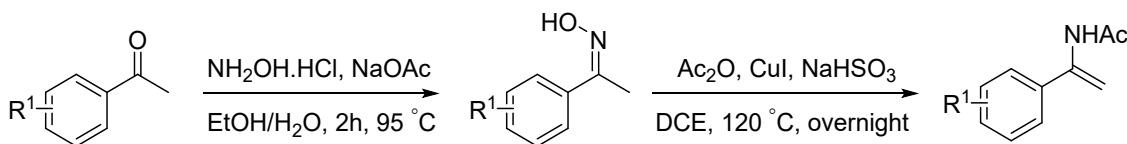
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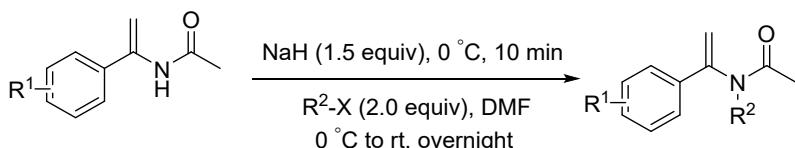
1. General Experimental Methods

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. ^1H NMR spectra were recorded at 400 MHz. The chemical shifts were reported in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift, multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *brs* = broad singlet, *p* = quintet, *h* = sextet, *hept* = septet, *m* = multiplet), coupling constants (Hz), integration. ^{13}C NMR data were collected at 100 MHz with complete proton decoupling. ^{19}F NMR data were collected at 376 MHz with complete proton decoupling. UV–Vis spectra were recorded using a Shimadzu UV-2600. Infrared spectra (IR) were measured by FT-IR apparatus. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES $^+$ mass spectrometer and acetonitrile was used to dissolve the sample. Emission intensities were recorded using Perkin-Elemer LS 55 fluorescence spectrometer. Column chromatography was carried out on silica gel (200-300 mesh).

2. Procedures for the Synthesis of Enamides 1a-1z



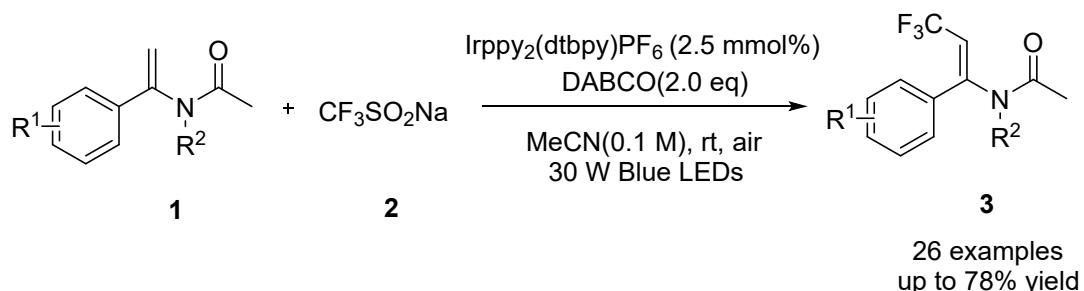
Enamides **1a-1z** were prepared according to literatures with minor modification.^{1,2} A mixture of ketone (10 mmol, 1.0 equiv), NH₂OH·HCl (1.04 g, 15 mmol, 1.5 equiv), and NaOAc (2.05 g, 25 mmol, 2.5 equiv) in EtOH (10 mL) and H₂O (30 mL) was placed into a 100 mL round-bottom flask equipped with a condenser. Then the flask was heated to 95 °C and the reaction was monitored by TLC. After full conversion, the mixture was cooled to 0 °C. The precipitate was filtered with suction, and washed with cold water and dried under vacuum. Recrystallization of the crude product with EtOH gives the pure ketoxime in nearly quantitative yields. The mixture of ketoxime (10 mmol, 1.0 equiv), Ac₂O (2.04 g, 20 mmol, 2.0 equiv), NaHSO₃ (3.15 g, 30 mmol, 3.0 equiv) and CuI (0.20 g, 1 mmol, 10 mol%) was stirred in 1,2-dichloroethane (100 mL) at 120 °C under N₂. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, diluted with EtOAc (25 mL) and washed with NaOH (2 M, 20 mL) and brine (20 mL). The organic layers were dried over anhydrous Na₂SO₄ and evaporated under vacuum. The desired enamides were obtained after purification by flash chromatography on silica gel with PE/EtOAc as the eluent.



N-acyl enamides (5 mmol, 1.0 equiv) was dissolved in 15 mL dry DMF in a 100 mL dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 7.5 mmol (1.5 equiv) sodium hydride (60% dispersion in mineral oil) was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then 10 mmol (2.0 equiv) R₂X was added dropwise and the final solution was continued to stir for overnight at room temperature. The completion of the reaction was confirmed by TLC monitoring and the excess of sodium hydride was quenched by adding 5 mL water at 0 °C. The mixture was diluted with ethyl acetate and then washed with saturated brine 3 times. The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product.

3. Detailed Optimization of Reaction Conditions and Control Experiments

3.1 Procedure for the Preparation of Compounds 3a-3z



To a 15 mL Schlenk flask equipped with a magnetic stirring bar, enamides **1** (0.2 mmol, 1.0 equiv.) $\text{CF}_3\text{SO}_2\text{Na}$ (**2**, 0.4 mmol, 2.0 equiv.), DABCO (0.4 mmol, 2.0 equiv.), $\text{Ir}(\text{ppy})_2(\text{dtbpy})\text{PF}_6$ (2.5 mmol %) and CH_3CN (2 mL) were added. The tube was screw-capped and stirred at room temperature under irradiation of 30 W blue LED (distance app. 5 cm) for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EtOAc = 1:20 to 1:9) to afford the desired product **3**.

3.2 Experimental Set-Up

The light source used for illuminating the reaction vessel (commercial supplier: Synthware) consists of blue LEDs ($\lambda_{\text{max}} = 450 \text{ nm}$) purchased from Taobao (<https://gpiled.taobao.com>).

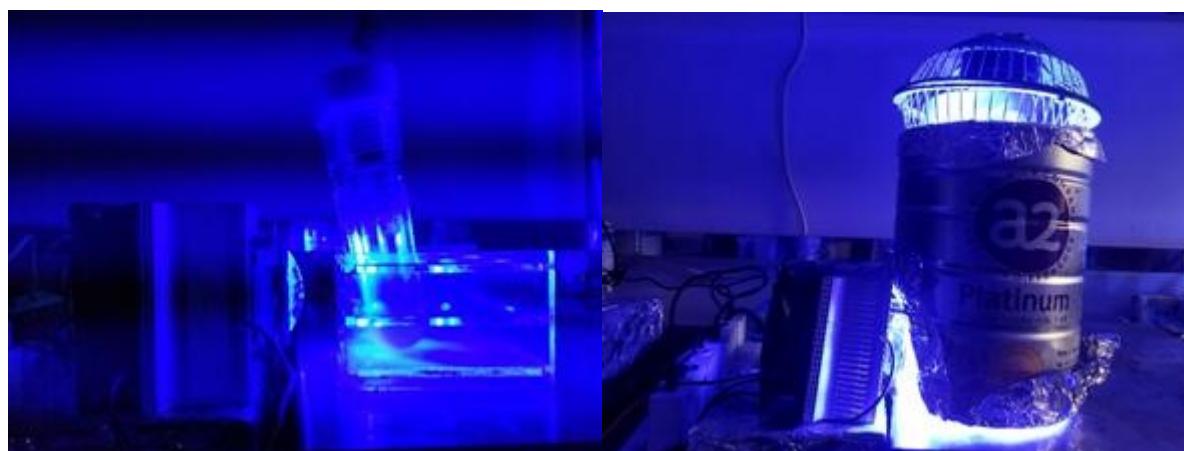


Figure S1The set-up of the reaction

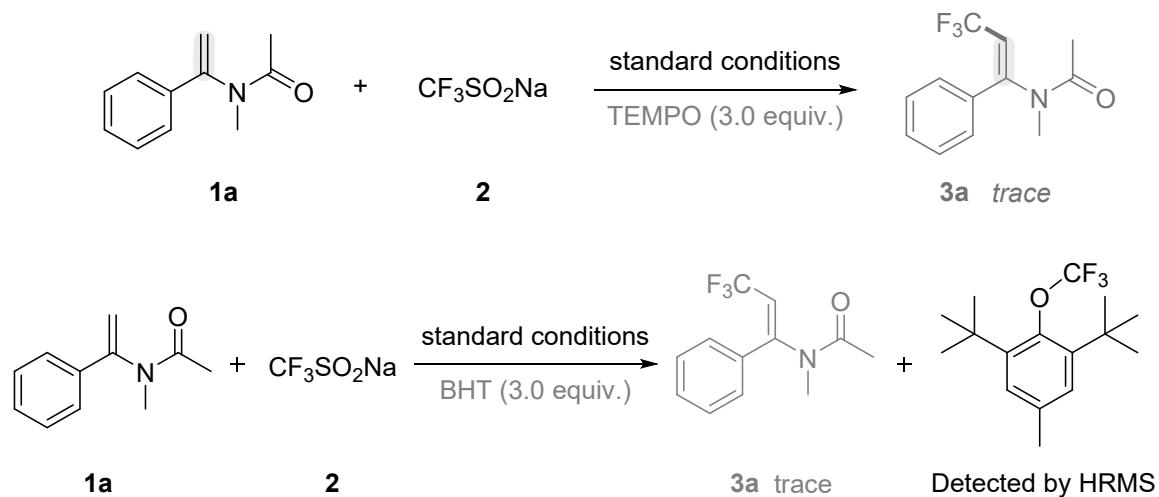
3.3 Optimization of the Reaction Conditions^a

Table S1.

Entry	Solvent	PC	Additive	Yield (%) ^e
1	CH ₃ CN	<i>fac</i> -Ir(ppy) ₃	-	21
2	CH ₃ CN	4CzIPN	-	18
3	CH ₃ CN	mpg-C ₃ N ₄	-	21
4	CH ₃ CN	Ir[dF(CF ₃)ppy]dtbpy	-	26
5	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	-	36
6	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	K ₂ HPO ₄	complex
7	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	Na ₂ CO ₃	trace
8	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DIPEA	26
9	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DMAP	42
10	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	78 ^f
11	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DTBP	trace
12	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	K ₂ S ₂ O ₈	21
13	DMF	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	66
14	DCM	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	52
15	THF	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	trace
16	DMSO	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	36
17	CH ₃ CN	-	DABCO	trace
18 ^b	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	nr
19 ^c	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	nd
20 ^d	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	trace
21 ^g	CH ₃ CN	Ir(ppy) ₂ (dtbpy)PF ₆	DABCO	76

^aThe reactions was carried out by using **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), additive (0.4 mmol, 2.0 equiv), **PC** (2.5 mol%) in solvent (2.0 mL) with closed cap at room temperature under air atmosphere for the specified time. ^bIn the dark. ^cUnder Ar atmosphere. ^dUnder O₂ atmosphere, ^eIsolated yields. ^fE/Z>20:1,determined by ¹⁹F NMR. ^gUsing open cap.

3.4 Trapping Experiment



In order to ensure whether the putative radical was trapped by BHT, ESI-MS analysis of the crude reaction mixture was performed. The resulting mass spectrum clearly shows a peak corresponding to the coupled product between BHT radical and the expected $\cdot\text{CF}_3$ radical. HRMS (ESI): $\text{C}_{16}\text{H}_{24}\text{F}_3\text{O}^+ [\text{M}+\text{H}]^+$ Calcd 289.1774, Found 289.1777.

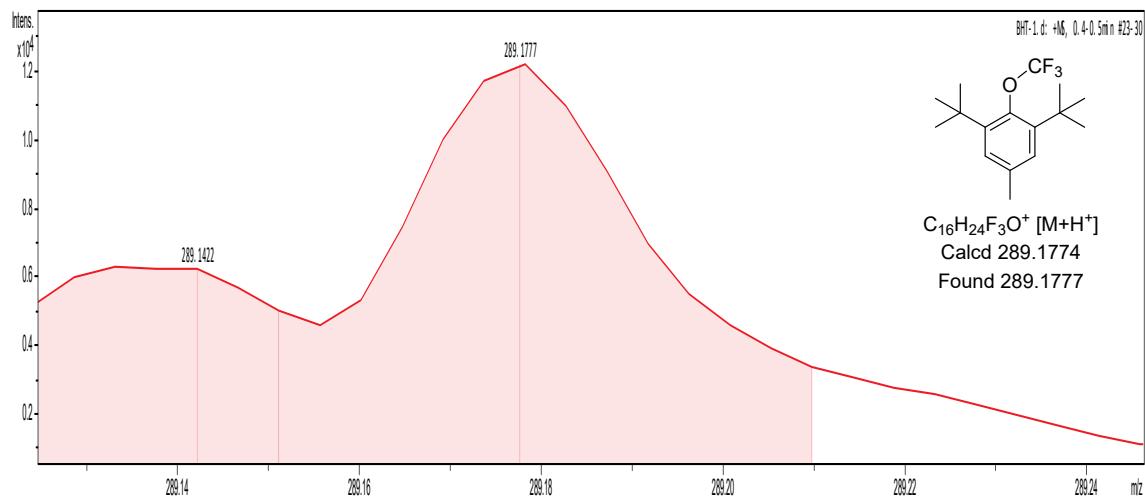


Figure S2 Crude ESI-MS of the corresponding adducts

3.5 Time Profile of the Transformation with Light On/Off over Time

Standard reactions were set up in parallel on a 0.2 mmol scale. After being irradiated for 2 h, an aliquot (100 μ L) from the reaction mixture was transferred into a nuclear magnetic tube charged with 0.5 mL of CDCl_3-d_1 . The yield of product **3a** was determined by ^{19}F NMR. Then the reaction mixture was stirred for 1 h with light-off. All of the following yields were analyzed in the identical way after 30 minutes light on then off.

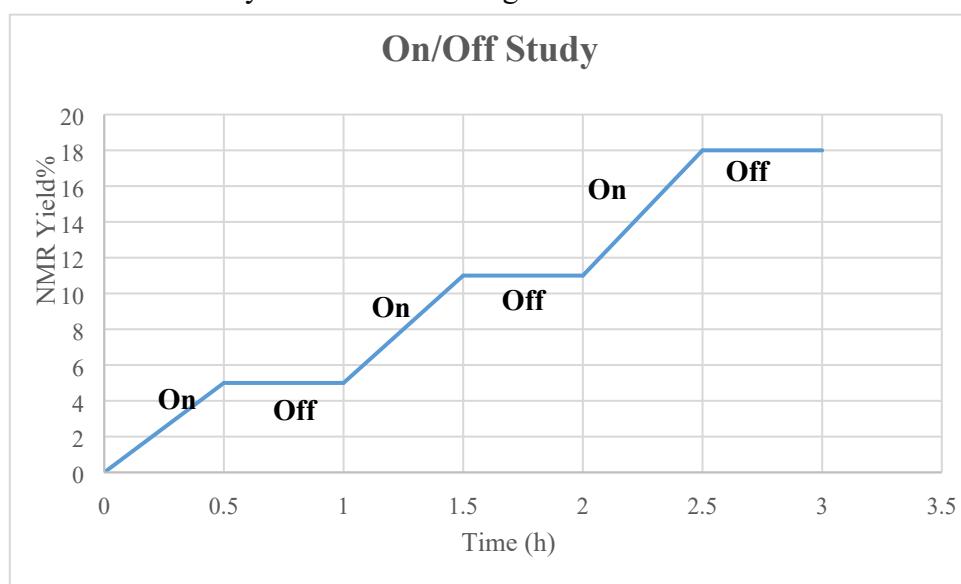


Figure S3 Time profile of the transformation with the light ON/OFF over time.

3.6 Quenching Experiments (Stern–Volmer Studies)

All fluorescence measurements were recorded using a Hitachi FL-7000 fluorometer. Quenching studies were conducted in CH₃CN. All Ir(ppy)₂dtbbpyPF₆ ($\tau_0 = 557$ ns)³ solutions (concentration: 5 μ M) were excited at 250 nm and the emission intensity was collected at 498 nm. Measurements using corresponding quenchers were taken in triplicate at different concentrations.

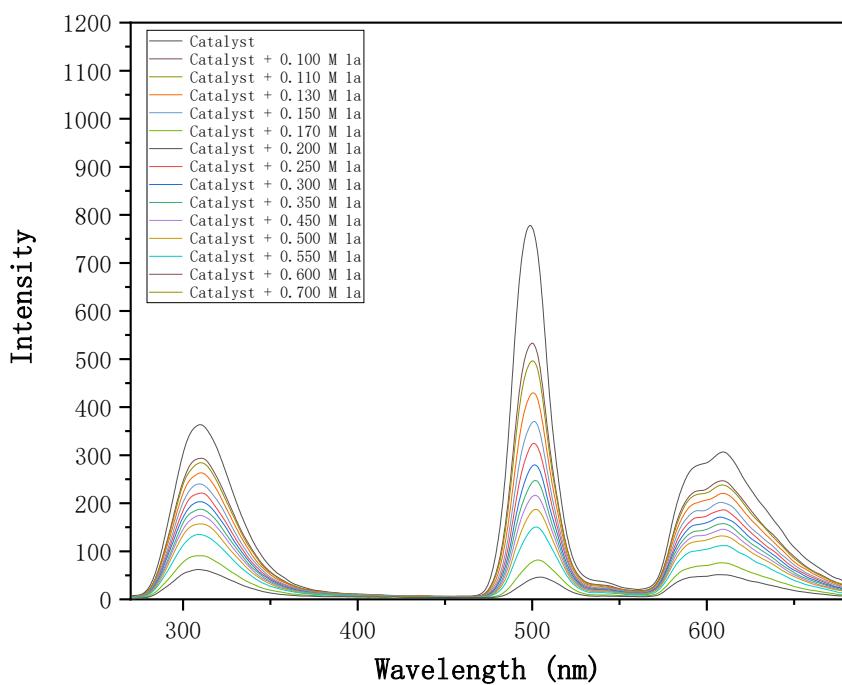
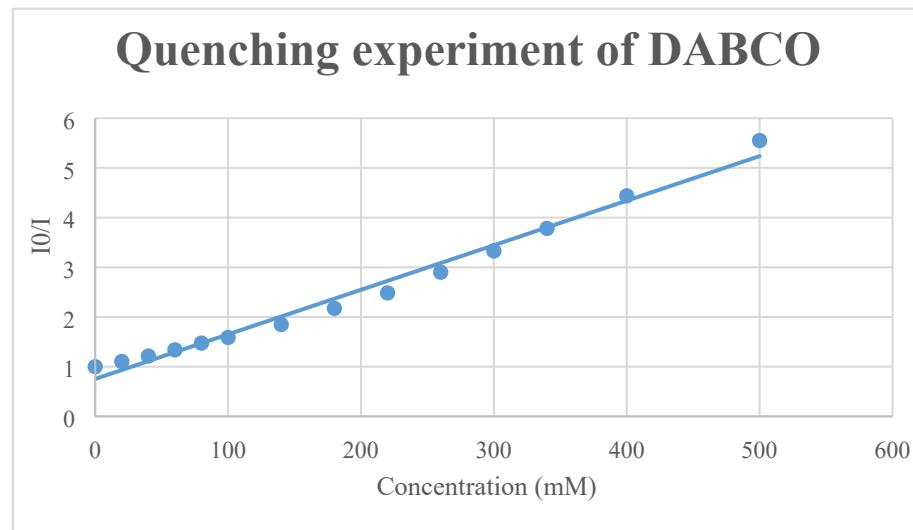


Figure S4 Stern-Volmer Experiments of DABCO in MeCN

3.7 Cyclic Voltammetry

Cyclic voltammetry was performed using a CHI650D workstation using a glassy carbon working electrode, Ag/AgCl in 3 M NaCl reference electrode, and a platinum counter electrode. The solution of **1a** was prepared by dissolving the sample (0.2 mmol) into a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in MeCN (10 mL). The potential range scanned was typically 0 V and 2.5 V at a 100mV/s.

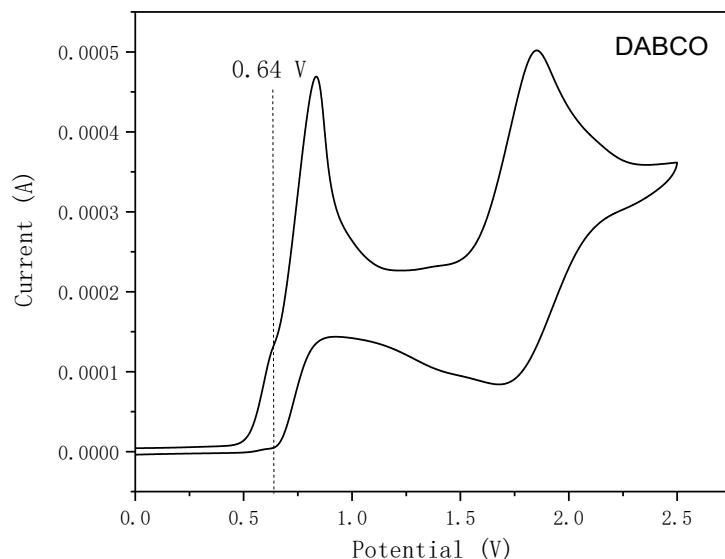


Figure S5 CV study of **DABCO** in MeCN, $E^{1/2}_{\text{ox}} = + 0.64$ V vs. SCE, (the obtained value was referenced to Ag/AgCl and converted to SCE by subtracting 0.03V) .Ir(ppy)₂(dtbbpy)PF₆ [$E^{1/2}_{\text{red}}$ (*Ir^{III}/Ir^{II}) = +0.66 V, $E^{1/2}_{\text{red}}$ (Ir^{III}/Ir^{II}) = -1.51 V vs. SCE],⁴ CF₃SO₂Na[$E^{1/2}_{\text{ox}} = +1.05$ V vs. SCE, CF₃SO₂K].⁵ O₂ [$E^{1/2}_{\text{red}} = -0.87$ V vs. SCE].⁶

3.8 NOESY Correlation Analysis

In order to assign the *cis/trans* configuration of the major product, NOESY experiments were then carried out. As shown below, the major isomer of selected product **3k** was confirmed to be (*E*)-**3k**. The peaks of isomers in the nuclear magnetic resonance of the corresponding compound are identified with small blue arrows.

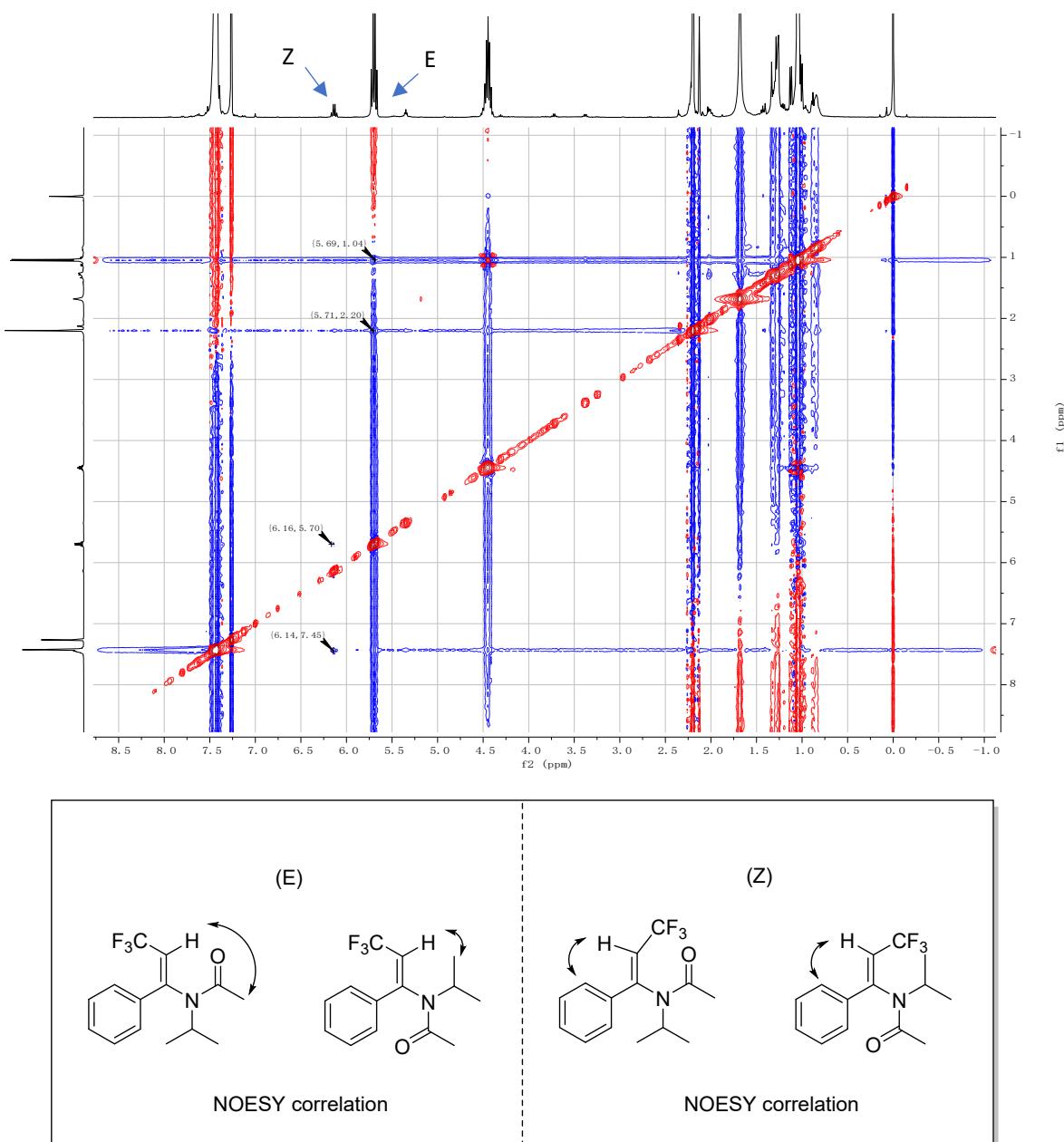


Figure S6 NOESY correlation analysis of product **3k**

3.9 Detection of Hydrogen Peroxide

To a 15 mL Schlenk flask equipped with a magnetic stirring bar, enamides **1a** (0.2 mmol, 1.0 equiv.) $\text{CF}_3\text{SO}_2\text{Na}$ **2** (0.4 mmol, 2.0 equiv.), DABCO (0.4 mmol, 2.0 equiv.), $\text{Ir}(\text{ppy})_2\text{dtbpyPF}_6$ (2.5 mmol%) and CH_3CN (2 mL) were added. The tube was screw-capped and stirred at room temperature under irradiation of 30 W blue LED (distance app. 5 cm) for 12 h. Then, 4 mL of distilled water was added to the reaction solution, and the total reaction mixture was extracted three times with dichloromethane. Adding H_2SO_4 to the separated water phase **A** and adjust the pH value to 2 to prevent further oxidation. Then 1.0 mL of 10% potassium iodide solution and 3 drops of 3% ammonium molybdate solution **B** were added to carry out the UV absorption experiment. Through the determination of I_3^- generated in the reaction process, it was indirectly proved that the H_2O_2 was obtained in the reaction process, hydrogen peroxide could oxidize I^- to I_2 , and then forming I_3^- with excess I^- .⁶ In addition, the characteristic peaks of I_3^- are 290 nm and 351 nm.⁷

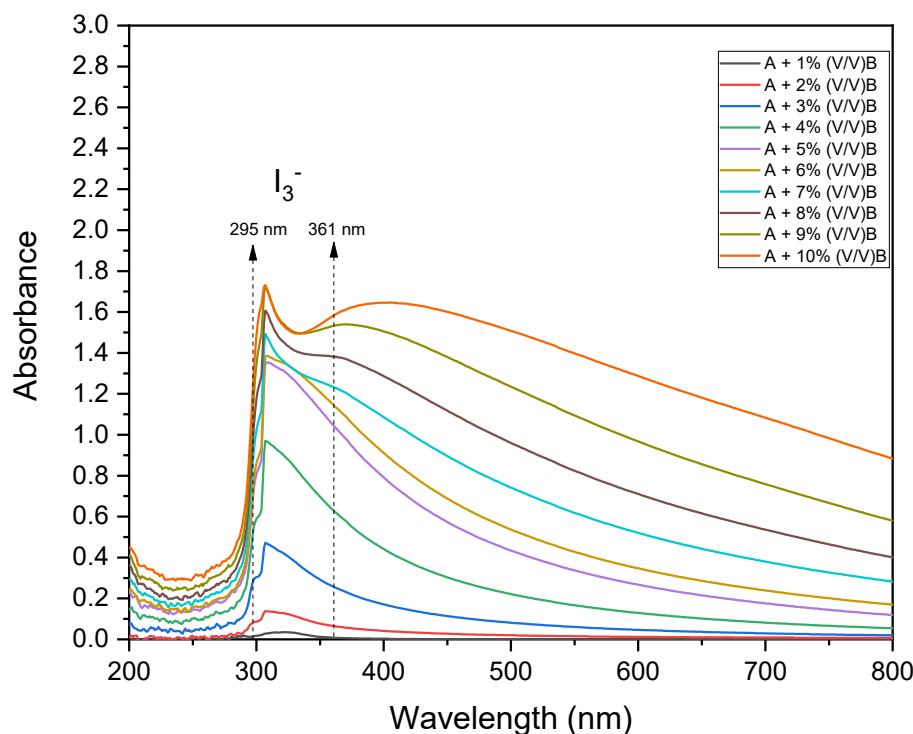


Figure S9 UV-Vis Spectra of I_3^- in presence of H_2O_2

3.10 Computational Details

All calculations were conducted using Gaussian16 software package.⁸ Optimization of all stationary points were carried out at M062X-D3/def2-SVP theoretical level.^{9,10,11,12} Frequency calculations were performed at the same level to verify the stationary points are minima (0 imaginary frequency) or saddle points (only 1 imaginary frequency). Single point calculations were carried out with Truhlar's M06-2X functional with def2-TZVPP basis set for all atoms. Dispersion effects are described using Grimme's D3 corrections. Solvation effects of acetonitrile for all calculations were considered using Truhlar's SMD solvent model.¹³ Computed structures were illustrated by CYLView software.¹⁴

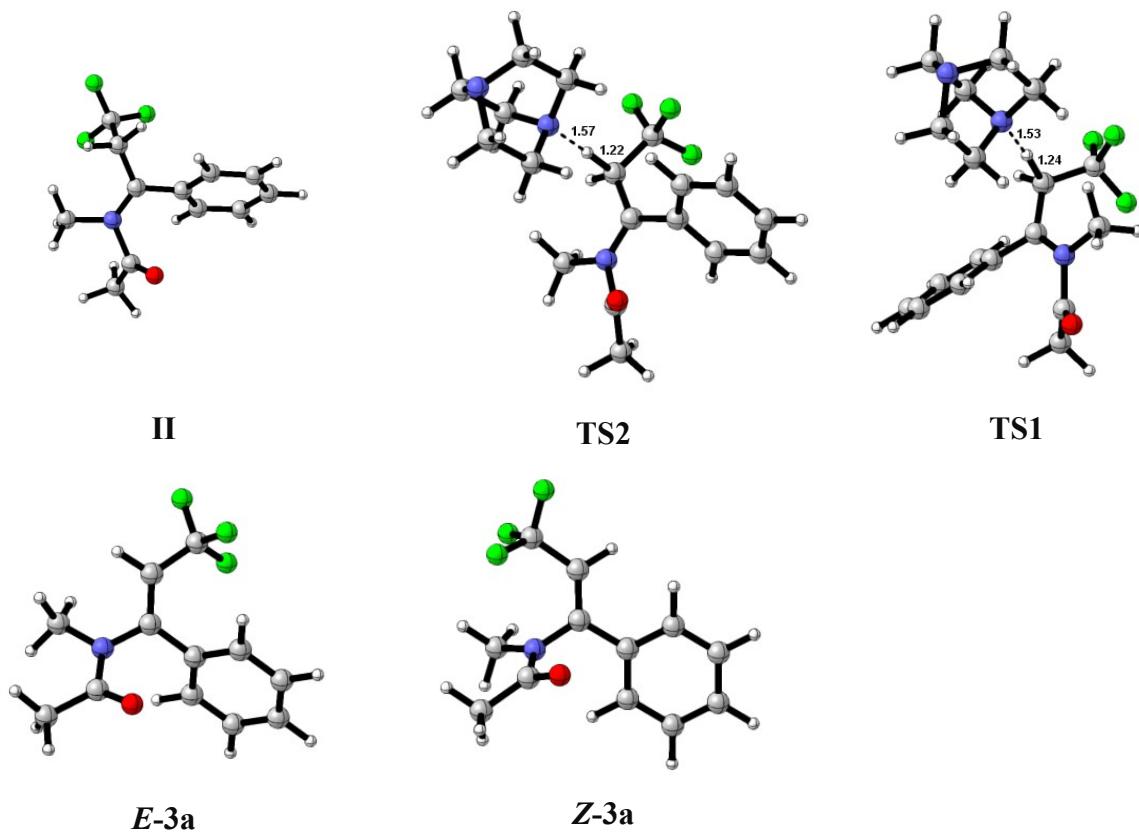


Figure S10 Computed structures of **II**, **TS1**, **TS2**, **E-3a**, **Z-3a**, selected bond distance (Å) (color code, C: grey, N: blue, O: red, H: white, F: green).

Table of energies and other thermodynamic parameters.

Structures	E _{ele}	E _{ele(SP)}	E ₀	E	H	G
II	-893.45034	-894.47934	-893.21360	-893.19777	-893.19683	-893.25771
DABCO	-344.92526	-345.31798	-344.74069	-344.73443	-344.73348	-344.77109
TS2	-1238.38670	-1239.80218	-1237.96806	-1237.94457	-1237.94362	-1238.02387
E-3a	-893.01831	-894.04746	-892.79481	-892.77898	-892.77803	-892.83924
TS1	-1238.38542	-1239.79996	-1237.96708	-1237.94379	-1237.94284	-1238.02297
Z-3a	-893.02050	-894.04984	-892.79665	-892.78095	-892.78000	-892.84073
DABCO-H⁺	-345.39618	-345.78873	-345.19595	-345.18960	-345.18865	-345.22654

Notes: E_{ele}, E₀, E, H, and G were the electronic energies, sum of electronic and zero-point energies, sum of electronic and thermal energies, sum of electronic and thermal enthalpies, and sum of electronic and thermal free energies, respectively, which were given at the M062X/def2-SVP)-SMD(acetonitrile) level. E_{ele(SP)} were single point electronic energies at the M06/def2TZVPP-SMD(acetonitrile) level.

Coordinates for all stationary points

DABCO				H	-1.205606	-2.079360	0.239713
C	0.779705	-1.321314	-0.386895	N	-1.257192	-0.001223	-0.000490
C	-0.777335	-1.322277	-0.388384	C	0.766607	1.005120	-1.000762
H	-1.174810	-1.564122	-1.385640	H	1.146309	0.683279	-1.977228
H	1.179375	-1.562550	-1.383422	C	-0.782307	0.291126	1.347551
H	-1.176460	-2.064518	0.319248	H	-1.210636	1.245277	1.680066
N	-1.274156	-0.000875	-0.001225	H	-1.135635	-0.498474	2.023269
C	0.778916	0.997057	-0.949987	C	0.764663	0.366733	1.372651
H	1.178914	0.755132	-1.946197	H	1.141628	1.374629	1.580998
C	-0.780111	0.324806	1.337797	H	1.219138	-0.343690	2.072273
H	-1.179642	1.308925	1.625606	N	1.243553	0.000763	0.001720
H	-1.179248	-0.417608	2.045283	C	-0.780683	1.020385	-0.926477
C	0.777005	0.325651	1.339397	H	-1.135424	2.000315	-0.581848
H	1.174880	1.310163	1.628152	H	-1.206389	0.830486	-1.920076
H	1.175490	-0.416421	2.047610	H	1.219979	1.966158	-0.733265
N	1.274157	0.000653	0.001352	H	1.146796	-2.055026	0.398209
C	-0.778189	0.996043	-0.951646	H	2.269895	0.001823	0.002663
H	-1.177735	1.979939	-0.663064				
H	-1.175750	0.753442	-1.948667	II			
H	1.176563	1.981427	-0.660400	C	1.832055	-1.083346	-0.774467
H	1.178396	-2.063150	0.321405	C	1.255899	-0.422407	0.322435
				C	2.071372	0.187906	1.285991
DABCO-H-cation				C	3.455511	0.099103	1.169832
C	0.767866	-1.369848	-0.368794	C	4.027470	-0.558942	0.080070
C	-0.779330	-1.313805	-0.421078	C	3.215952	-1.140428	-0.896010
H	-1.132523	-1.505533	-1.442591	H	1.199396	-1.518386	-1.551661
H	1.222712	-1.617512	-1.334527	H	1.630505	0.700510	2.142553

H	4.090161	0.551799	1.932520	H	-1.920862	-1.881132	2.481865
H	5.113260	-0.612443	-0.014051	C	-4.101887	-1.245935	-0.678369
H	3.661989	-1.637126	-1.758414	H	-4.056342	-2.084796	-1.380393
C	-0.213249	-0.320470	0.412607	H	-4.957443	-1.375400	-0.003098
C	-0.797612	1.049849	0.606313	H	-4.194577	-0.312935	-1.239503
H	-0.103457	1.650196	1.208057	C	-4.166240	1.444584	0.779048
N	-0.967504	-1.360618	0.231002	F	-4.605706	0.490390	1.610864
C	-0.383850	-2.753080	0.238855	F	-4.205033	2.597341	1.449644
O	0.307452	-3.049762	1.154866	F	-5.083555	1.548293	-0.195292
C	-0.820509	-3.605745	-0.900458	H	-2.092997	1.934407	0.698054
H	-0.155268	-4.474363	-0.953985	C	-1.420376	1.067791	-4.428002
H	-1.849048	-3.952233	-0.716971	C	-1.763220	0.765308	-2.940938
H	-0.810450	-3.037312	-1.839784	H	-2.310771	-0.182851	-2.827319
C	-2.428025	-1.349433	0.066648	H	-1.803660	0.274527	-5.085010
H	-2.657916	-1.562741	-0.985474	H	-0.861821	0.719055	-2.311386
H	-2.854223	-2.130972	0.707171	N	-2.615467	1.846340	-2.423898
H	-2.846883	-0.380194	0.340455	C	-3.475368	2.251635	-4.688717
C	-0.952647	1.762665	-0.722967	H	-3.848183	1.469244	-5.364679
F	0.219353	1.932716	-1.334803	C	-1.891534	3.124576	-2.489672
F	-1.734734	1.070796	-1.558962	H	-2.545684	3.904522	-2.075706
F	-1.499601	2.960032	-0.553634	H	-1.002240	3.044039	-1.847847
H	-1.772585	1.038131	1.105682	C	-1.515546	3.407408	-3.972315
				H	-1.946746	4.360914	-4.308164
TS1				H	-0.424887	3.466712	-4.094945
C	0.078162	-1.049520	-0.063395	N	-2.022862	2.337303	-4.829243
C	-0.757446	-0.234301	0.717628	C	-3.852615	1.931106	-3.212568
C	-0.226094	0.500682	1.788206	H	-4.487077	2.711571	-2.770985
C	1.124585	0.383481	2.098744	H	-4.378722	0.969445	-3.128937
C	1.953230	-0.432367	1.324100	H	-3.913996	3.209029	-5.003455
C	1.433506	-1.138744	0.237665	H	-0.332738	1.132275	-4.571638
H	-0.327680	-1.588210	-0.923136				
H	-0.878590	1.130775	2.395318	TS2			
H	1.534708	0.932632	2.947088	C	0.622722	-1.988322	-0.320364
H	3.014610	-0.511675	1.565072	C	0.349041	-0.978272	0.611317
H	2.085845	-1.758391	-0.378735	C	1.153776	-0.819582	1.744388
C	-2.189093	-0.136139	0.382120	C	2.221683	-1.688670	1.953393
C	-2.768176	1.189747	0.263885	C	2.500613	-2.692502	1.024680
H	-2.763083	1.482785	-0.940713	C	1.706087	-2.837806	-0.113996
N	-2.846010	-1.243683	0.079702	H	-0.004613	-2.096976	-1.208552
C	-2.383761	-2.588027	0.472250	H	0.930862	-0.030720	2.464527
O	-2.623050	-3.492563	-0.268809	H	2.839362	-1.579229	2.845692
C	-1.783104	-2.755418	1.838740	H	3.343691	-3.365643	1.188515
H	-2.275786	-3.631308	2.281926	H	1.928316	-3.617530	-0.843656
H	-0.712238	-2.982310	1.747459	C	-0.796618	-0.069830	0.373991

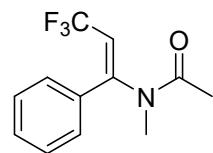
C	-0.610326	1.371586	0.344081	C	2.928279	-2.445456	-0.472741
H	-1.398569	1.902203	-0.200523	C	1.734843	-2.625198	-1.174469
N	-1.995851	-0.575911	0.206814	H	-0.306434	-1.965672	-1.435103
C	-2.285573	-1.998261	0.504100	H	1.974242	0.108554	1.571305
O	-1.933433	-2.445219	1.549230	H	3.939704	-1.322239	1.071115
C	-3.042154	-2.723493	-0.562613	H	3.791626	-3.076684	-0.690525
H	-2.697471	-3.764864	-0.565625	H	1.662866	-3.394886	-1.944948
H	-4.113082	-2.722051	-0.308265	C	-0.466888	0.044231	0.339716
H	-2.905820	-2.262928	-1.548002	C	-0.421580	1.390942	0.361972
C	-3.154175	0.250560	-0.154948	H	-1.316970	1.969848	0.591136
H	-4.041344	-0.386252	-0.211860	N	-1.712519	-0.605529	0.439814
H	-3.313922	1.009316	0.622636	C	-1.824351	-1.730786	1.255097
H	-2.983202	0.733962	-1.125010	O	-0.894413	-2.116484	1.930268
C	0.717354	1.907805	-0.118429	C	-3.160395	-2.430772	1.260248
F	1.166734	1.329811	-1.238760	H	-3.067315	-3.318017	1.894901
F	0.599571	3.216025	-0.369779	H	-3.945616	-1.775835	1.664029
F	1.690603	1.784317	0.792976	H	-3.454913	-2.728402	0.244133
H	-0.731638	1.744220	1.500463	C	-2.902792	0.073442	-0.063026
C	-0.151057	3.237477	5.069577	H	-3.644237	-0.662770	-0.389449
C	0.249122	2.714796	3.659155	H	-3.359949	0.726947	0.696252
H	0.748099	3.489451	3.059911	H	-2.621407	0.681185	-0.930659
H	0.158769	4.283919	5.200909	C	0.765467	2.238956	0.052934
H	0.919733	1.846026	3.721774	F	1.555241	1.746944	-0.907563
N	-0.969899	2.305114	2.948964	F	0.366613	3.449564	-0.362002
C	-2.255923	3.971604	4.219668	F	1.557278	2.458755	1.118645
H	-1.943632	5.017094	4.352559				
C	-1.647865	1.232764	3.689494	Z-3a			
H	-2.534371	0.929340	3.111934	C	0.544205	-2.018658	-0.608434
H	-0.966816	0.371109	3.746292	C	0.673281	-0.827768	0.119529
C	-2.029652	1.765746	5.101082	C	1.941532	-0.438855	0.571733
H	-3.116535	1.716052	5.257376	C	3.060230	-1.219538	0.288083
H	-1.546225	1.168618	5.887106	C	2.926054	-2.398896	-0.446829
N	-1.600776	3.156208	5.241322	C	1.664717	-2.796430	-0.892985
C	-1.872171	3.455473	2.803523	H	-0.441320	-2.329934	-0.961114
H	-2.754298	3.125161	2.235002	H	2.051471	0.468270	1.168815
H	-1.350560	4.221584	2.211946	H	4.041281	-0.909745	0.652214
H	-3.342999	3.920458	4.374577	H	3.802894	-3.010785	-0.665682
H	0.329012	2.640749	5.858126	H	1.551846	-3.718141	-1.466362
				C	-0.527125	0.014906	0.370418
E-3a				C	-0.433880	1.350786	0.482245
C	0.630582	-1.823703	-0.892107	N	-1.775539	-0.655077	0.396029
C	0.716090	-0.825547	0.086114	C	-1.974475	-1.599040	1.383237
C	1.911657	-0.652070	0.791338	O	-1.131215	-1.800688	2.235308
C	3.012625	-1.459638	0.511882	C	-3.284770	-2.342317	1.338420

H	-3.324938	-3.015532	2.200943	H	-2.374825	0.328033	-1.344199
H	-4.134908	-1.646447	1.371256	C	-1.564972	2.263938	0.819363
H	-3.364756	-2.926483	0.410052	F	-2.488617	1.705962	1.609959
C	-2.820240	-0.290591	-0.557498	F	-2.216589	2.714750	-0.265718
H	-3.235743	-1.191216	-1.028489	F	-1.110024	3.347217	1.459782
H	-3.635767	0.273299	-0.081163	H	0.516386	1.859407	0.317486

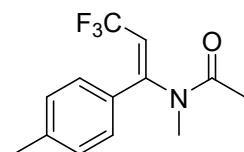
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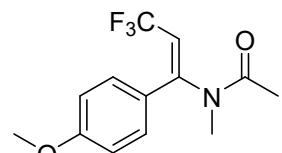
4. Characterization Data of Compounds 3a-3z



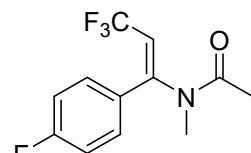
(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3a**: colorless oil (37.9 mg, yield 78%);
 IR (neat) ν 2930, 1995, 1647, 1111, 780, 626 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.40 (m, 3H), 7.39 – 7.37 (m, 2H), 5.72 (q, $J = 8.2$ Hz, 1H), 2.97 (s, 3H), 2.17 (s, 3H);
 $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.74;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.4, 151.65 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 133.1, 130.7, 128.7, 122.5 (q, $^1J_{\text{C}-\text{F}} = 269.9$ Hz), 114.7 (q, $^2J_{\text{C}-\text{F}} = 35.2$ Hz), 35.3, 22.5;
 HRMS (ESI): $\text{C}_{12}\text{H}_{12}\text{F}_3\text{NNaO}^+$ [M+Na]⁺ Calcd 266.0763, Found 266.0763.



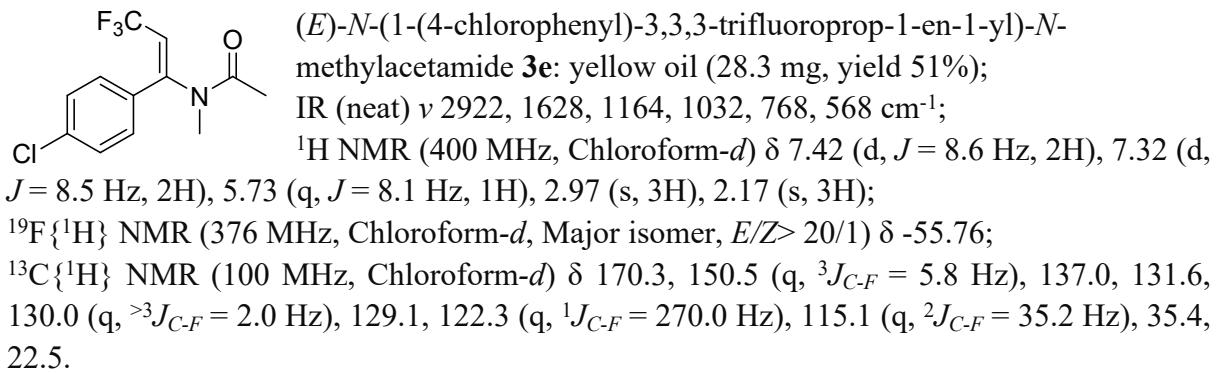
(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-(*p*-tolyl)prop-1-en-1-yl)acetamide **3b**: colorless oil (37.0 mg, yield 72%);
 IR (neat) ν 2928, 1643, 1373, 1217, 752, 669 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 6.85 (m, 4H), 5.66 (q, $J = 8.2$ Hz, 1H), 2.96 (s, 3H), 2.40 (s, 3H), 2.16 (s, 3H);
 $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.76;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.5, 151.8 (q, $^3J_{\text{C}-\text{F}} = 5.8$ Hz), 141.2, 130.1, 129.4, 128.7 (q, $^3J_{\text{C}-\text{F}} = 2.0$ Hz), 122.6 (q, $^1J_{\text{C}-\text{F}} = 269.9$ Hz), 114.1 (q, $^2J_{\text{C}-\text{F}} = 35.2$ Hz), 35.4, 22.5, 21.5;
 HRMS (ESI): $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NNaO}^+$ [M+Na]⁺ Calcd 280.0920, Found 280.0890.



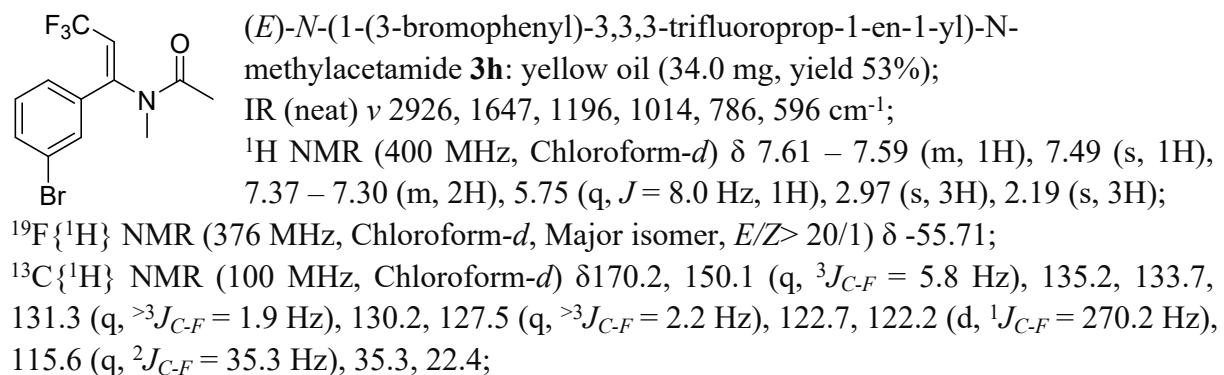
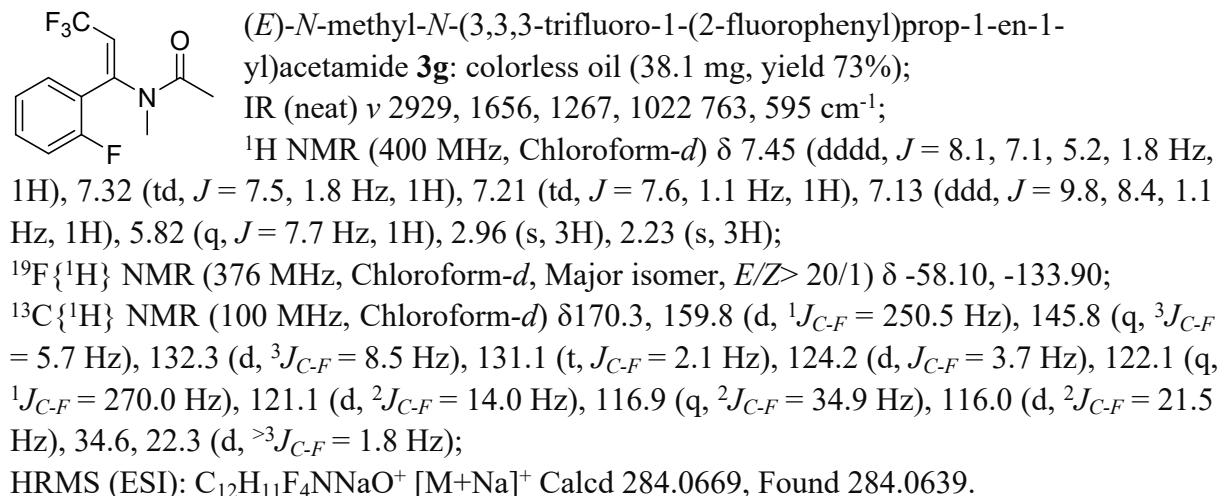
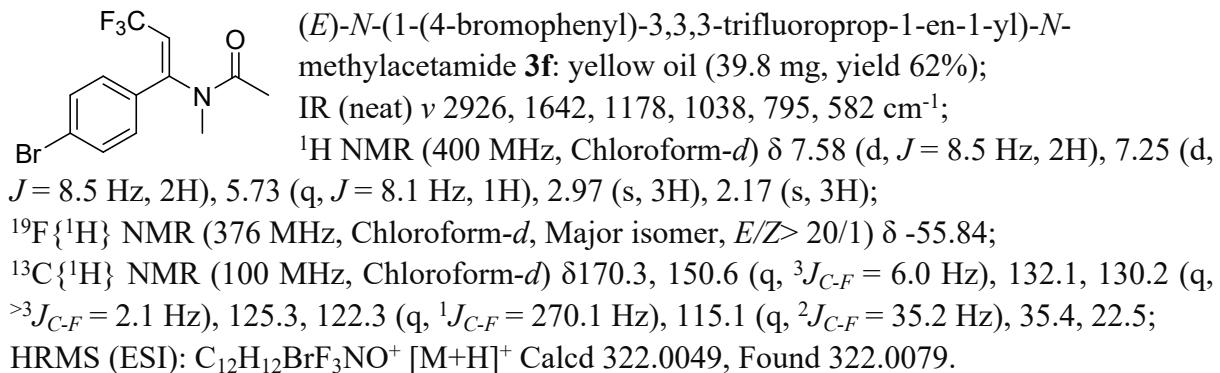
(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-(4-methoxyphenyl)prop-1-en-1-yl)acetamide **3c**: colorless oil (30.6 mg, yield 56%);
 IR (neat) ν 2918, 1645, 1064, 723, 758, 541 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.32 (d, $J = 8.8$ Hz, 2H), 6.93 (d, $J = 8.8$ Hz, 2H), 5.62 (q, $J = 8.3$ Hz, 1H), 3.85 (s, 3H), 2.98 (s, 3H), 2.14 (s, 3H);
 $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.77;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.6, 161.5, 151.5 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 130.4 (q, $^3J_{\text{C}-\text{F}} = 2.1$ Hz), 125.1, 122.7 (q, $^1J_{\text{C}-\text{F}} = 269.7$ Hz), 114.1, 113.4 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 55.4, 35.4, 22.5;
 HRMS (ESI): $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NNaO}_2^+$ [M+Na]⁺ Calcd 296.0869, Found 296.0839.



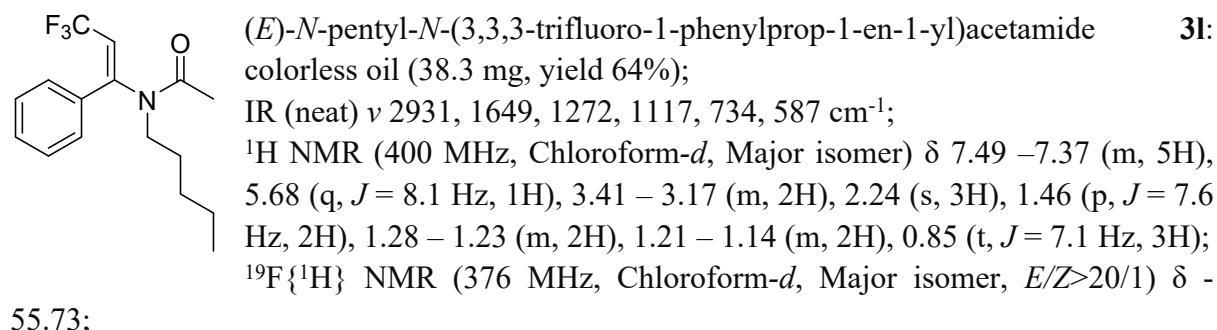
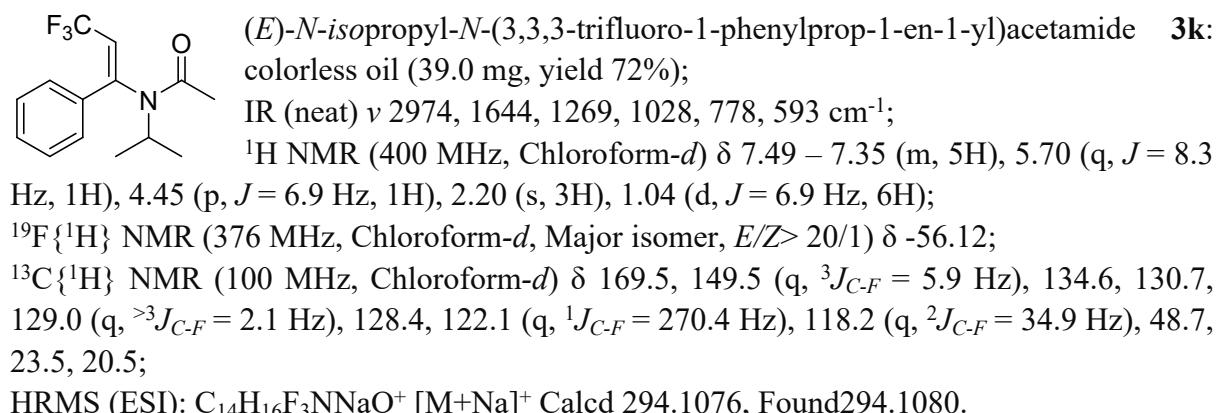
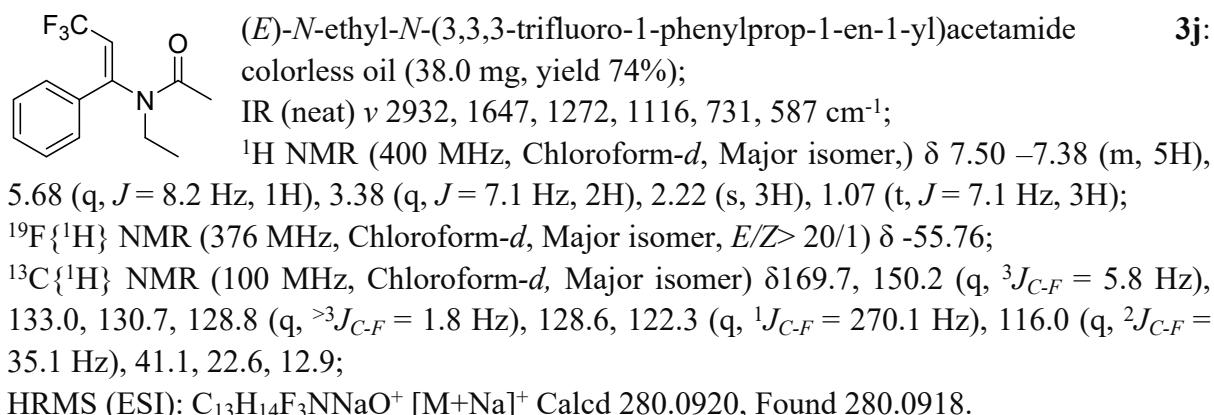
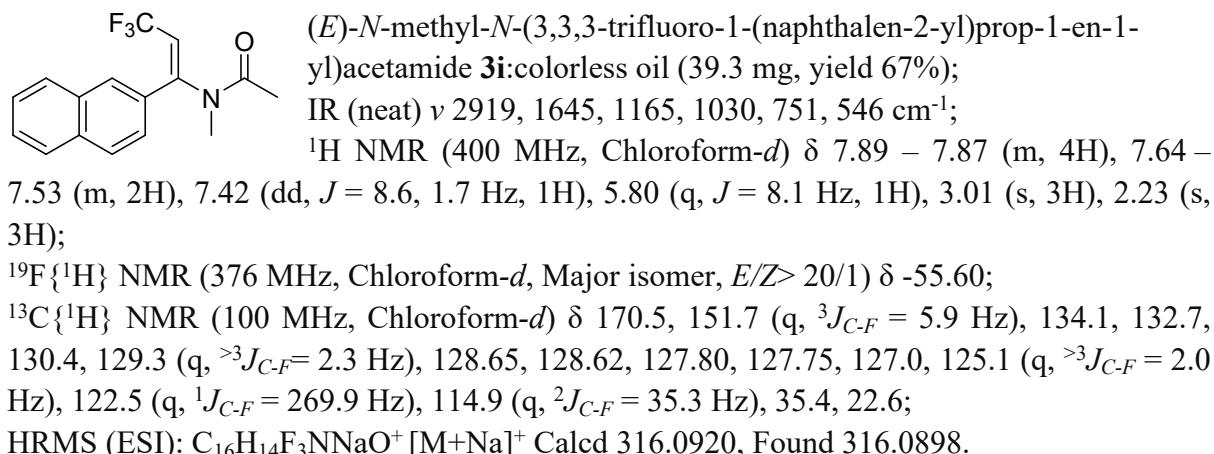
(*E*)-*N*-methyl-*N*-(3,3,3-trifluoro-1-(4-fluorophenyl)prop-1-en-1-yl)acetamide **3d**: colorless oil (33.9 mg, yield 65%);
 IR (neat) ν 2919, 1664, 1372, 1108, 828, 545 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.42 (m, 2H), 7.19 – 7.14 (m, 2H), 6.16 (q, $J = 7.6$ Hz, 1H), 3.10 (s, 3H), 1.99 (s, 3H);
 $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -59.72, -108.25;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 169.9, 164.5 (d, $^1J_{\text{C}-\text{F}} = 253.3$ Hz), 149.2 (q, $^3J_{\text{C}-\text{F}} = 5.6$ Hz), 129.9 (d, $^3J_{\text{C}-\text{F}} = 3.4$ Hz), 128.5 (d, $^3J_{\text{C}-\text{F}} = 8.8$ Hz), 122.2 (q, $^1J_{\text{C}-\text{F}} = 270.1$ Hz), 128.5 (d, $^2J_{\text{C}-\text{F}} = 22.1$ Hz), 113.7 (qd, $^{2/3}J_{\text{C}-\text{F}} = 34.0, 1.9$ Hz), 35.7 (q, $^{3/2}J_{\text{C}-\text{F}} = 1.8$ Hz), 21.2;
 HRMS (ESI): $\text{C}_{12}\text{H}_{11}\text{F}_4\text{NNaO}^+$ [M+Na]⁺ Calcd 284.0669, Found 284.0639.



HRMS (ESI): C₁₂H₁₁ClF₃NNaO⁺ [M+Na]⁺ Calcd 300.0373, Found 300.0344.

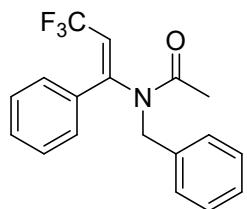


HRMS (ESI): C₁₂H₁₁BrF₃NNaO⁺ [M+Na]⁺ Calcd 343.9868, Found 343.9839.



$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 169.8, 150.4 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 132.9, 130.7, 128.7 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.6, 122.3 (q, $^1J_{\text{C}-\text{F}} = 270.1$ Hz), 116.0 (q, $^2J_{\text{C}-\text{F}} = 34.9$ Hz), 45.9, 28.8, 27.4, 22.6, 22.3, 13.9;

HRMS (ESI): $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NNaO}^+ [\text{M}+\text{Na}]^+$ Calcd 322.1389, Found 322.1371.

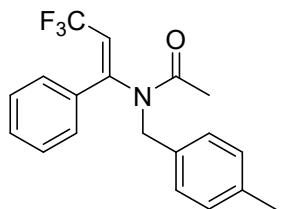


(*E*)-*N*-benzyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3m**: yellow oil (47.9 mg, yield 75%);
IR (neat) ν 2917, 1646, 1119, 1028, 885, 698 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.40 (m, 3H), 7.35 – 7.27 (m, 5H), 7.18 – 7.14 (m, 2H), 5.46 (q, $J = 8.1$ Hz, 1H), 4.52 (s, 2H), 2.26 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.93;

$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.01, 149.8 (q, $^3J_{\text{C}-\text{F}} = 5.9$ Hz), 136.5, 132.9, 130.8, 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.69, 128.65, 128.6, 127.7, 122.1 (q, $^1J_{\text{C}-\text{F}} = 270.1$ Hz), 116.9 (q, $^2J_{\text{C}-\text{F}} = 35.0$ Hz), 49.5, 22.6;

HRMS (ESI): $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}^+ [\text{M}+\text{Na}]^+$ Calcd 342.1076, Found 342.1077.

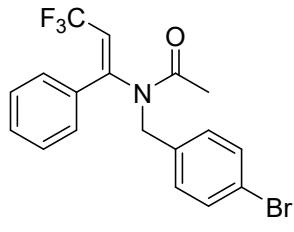


(*E*)-*N*-(4-methylbenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3n**: yellow oil (43.3 mg, yield 65%);
IR (neat) ν 2917, 1646, 1269, 1029, 739, 699 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*, Major isomer) δ 7.50 – 7.41 (m, 3H), 7.38 – 7.31 (m, 2H), 7.19 – 7.14 (t, $J = 7.5$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 1H), 7.01 – 6.91 (m, 2H), 5.46 (q, $J = 8.2$ Hz, 1H), 4.49 (s, 2H), 2.32 (s, 3H), 2.25 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.89;

$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 170.0, 149.8 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 138.2, 136.4, 132.9, 130.7, 129.4, 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.7, 128.4, 125.7, 122.2 (q, $^1J_{\text{C}-\text{F}} = 270.1$ Hz), 116.9 (q, $^2J_{\text{C}-\text{F}} = 35.0$ Hz), 49.6, 22.6, 21.4;

HRMS (ESI): $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NNaO}^+ [\text{M}+\text{Na}]^+$ Calcd 356.1233, Found 356.1232.

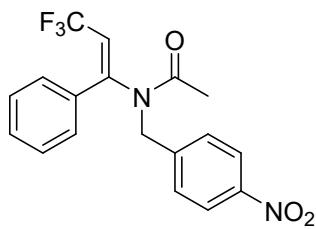


(*E*)-*N*-(4-bromobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3o**: yellow oil (51.6 mg, yield 65%);
IR (neat) ν 2938, 1650, 1270, 1123, 778, 531 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*, Major isomer) δ 7.53 – 7.40 (m, 5H), 7.35 – 7.31 (m, 2H), 7.03 (d, $J = 8.4$ Hz, 2H), 5.45 (q, $J = 8.1$ Hz, 1H), 4.44 (s, 2H), 2.27 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z = 10/1$) δ -55.92;

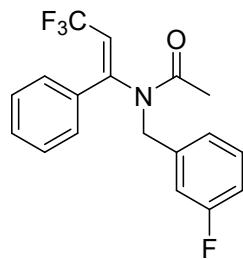
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 170.1, 149.7 (q, $^3J_{\text{C}-\text{F}} = 5.8$ Hz), 135.5, 132.6, 131.7, 131.0, 130.4, 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.8, 122.0 (q, $^1J_{\text{C}-\text{F}} = 270.2$ Hz), 121.8, 116.9 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 48.8, 22.5;

HRMS (ESI): $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{NNaO}^+ [\text{M}+\text{Na}]^+$ Calcd 420.0181, Found 420.0180.



(*E*)-*N*-(4-nitrobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3p**: yellow oil (29.8 mg, yield 41%);

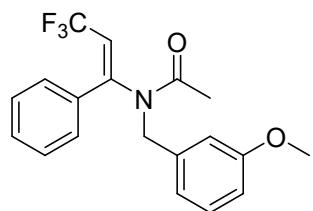
IR (neat) ν 2921, 1650, 1270, 1110, 699, 585 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*, Major isomer) δ 8.16 (d, $J = 8.6$ Hz, 2H), 7.54 – 7.44 (m, 3H), 7.34 – 7.30 (m, 4H), 5.50 (q, $J = 8.0$ Hz, 1H), 4.57 (s, 2H), 2.32 (s, 3H);
 $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* = 19/1) δ -55.94;
 $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 170.3, 149.7 (q, $^3J_{\text{C}-\text{F}} = 5.9$ Hz), 147.4, 143.8, 132.2, 131.2, 129.4, 129.0, 128.8 (q, $^{>3}J_{\text{C}-\text{F}} = 2.1$ Hz), 123.8, 121.9 (q, $^1J_{\text{C}-\text{F}} = 270.7$ Hz), 116.95 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 48.8, 22.4.;
HRMS (ESI): $\text{C}_{18}\text{H}_{15}\text{F}_3\text{N}_2\text{NaO}_3^+$ [M+Na]⁺ Calcd 387.0927, Found 387.0922.



(*E*)-*N*-(3-fluorobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3q**: yellow oil (28.3 mg, yield 42%);
IR (neat) ν 2922, 1650, 1269, 1123, 779, 698 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d* Major isomer) δ 7.52 – 7.41 (m, 3H), 7.36 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.01 – 6.85 (m, 3H), 5.48 (q, $J = 8.1$ Hz, 1H), 4.49 (s, 2H), 2.28 (s, 3H);
 $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* = 13/1) δ -55.95, -112.64;

$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d* Major isomer) δ 170.1, 162.8 (d, $^1J_{\text{C}-\text{F}} = 246.5$ Hz), 149.7 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 139.0 (d, $^3J_{\text{C}-\text{F}} = 7.1$ Hz), 132.6, 130.9, 130.1 (d, $^3J_{\text{C}-\text{F}} = 8.2$ Hz), 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.8, 124.2 (d, $^{>3}J_{\text{C}-\text{F}} = 2.9$ Hz), 122.1 (q, $^1J_{\text{C}-\text{F}} = 270.1$ Hz), 116.9 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 115.5 (d, $^2J_{\text{C}-\text{F}} = 21.7$ Hz), 114.7 (d, $^2J_{\text{C}-\text{F}} = 21.1$ Hz), 49.0 (d, $^{>3}J_{\text{C}-\text{F}} = 1.7$ Hz), 22.5;

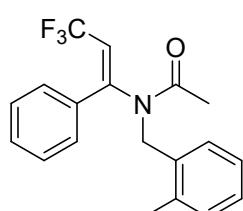
HRMS (ESI): $\text{C}_{18}\text{H}_{15}\text{F}_4\text{NNaO}^+$ [M+Na]⁺ Calcd 360.0982, Found 360.0997.



(*E*)-*N*-(3-methoxybenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3r**: yellow oil (36.3 mg, yield 52%);
IR (neat) ν 2918, 1645, 1124, 1007, 779, 587 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.40 (m, 3H), 7.34 (d, $J = 7.1$ Hz, 2H), 7.22 (t, $J = 7.8$ Hz, 1H), 6.85 – 6.79 (m, 1H), 6.78 – 6.69 (m, 2H), 5.49 (q, $J = 8.2$ Hz, 1H), 4.49 (s, 2H), 3.78 (s, 3H), 2.25 (s, 3H);
 $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* > 20/1) δ -55.86;

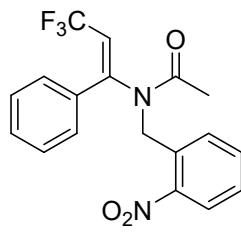
$^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.0, 159.8, 149.8 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 138.1, 132.9, 130.8, 129.6, 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 2.0$ Hz), 128.7, 122.2 (q, $^1J_{\text{C}-\text{F}} = 270.2$ Hz), 120.9, 116.9 (q, $^2J_{\text{C}-\text{F}} = 34.9$ Hz), 114.2, 113.3, 55.2, 49.6, 22.6;

HRMS (ESI): $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NNaO}_2^+$ [M+Na]⁺ Calcd 372.1182, Found 372.1183.



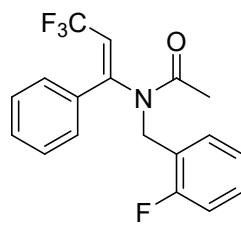
(*E*)-*N*-(2-methylbenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3s**: yellow oil (38.6 mg, yield 58%);
IR (neat) ν 2920, 1646, 1289, 1068, 772, 593 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.38 (m, 3H), 7.30 – 7.26 (m, 2H), 7.20 – 7.09 (m, 3H), 6.96 (dd, $J = 7.4, 1.7$ Hz, 1H), 5.56 (q, $J = 8.2$ Hz, 1H), 4.62 (s, 2H), 2.26 (s, 3H), 2.13 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z*> 20/1) δ -55.84;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.1, 150.1 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 136.2, 134.1, 132.8, 130.8, 130.5, 128.92 – 128.74 (m, due to C-F coupling), 128.6, 127.7, 126.0, 122.2 (d, $^1J_{\text{C}-\text{F}} = 270.2$ Hz), 116.7 (q, $^2J_{\text{C}-\text{F}} = 35.2$ Hz), 47.4, 22.7, 19.1;
HRMS (ESI): $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NNaO}^+$ [M+Na]⁺ Calcd 356.1233, Found 356.1234.



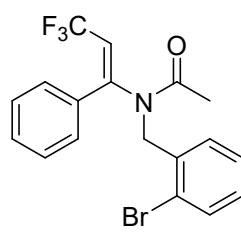
(*E*)-*N*-(2-nitrobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3t**: yellow oil (26.2 mg, yield 36%);
IR (neat) ν 2916, 1644, 1261, 1078, 801, 644 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.95 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.59 (td, $J = 7.6, 1.4$ Hz, 1H), 7.52 – 7.35 (m, 5H), 7.29 (d, $J = 7.2$ Hz, 2H), 5.63 (q, $J = 8.0$ Hz, 1H), 4.91 (s, 2H), 2.29 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z*> 20/1) δ -55.86;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.6, 150.5 (q, $^3J_{\text{C}-\text{F}} = 5.8$ Hz), 148.6, 133.3, 132.3, 131.9, 131.1, 130.1, 128.8, 128.7 (q, $^{>3}J_{\text{C}-\text{F}} = 1.9$ Hz), 128.4, 125.0, 122.1 (q, $^1J_{\text{C}-\text{F}} = 270.3$ Hz), 116.3 (q, $^2J_{\text{C}-\text{F}} = 35.4$ Hz), 47.2, 22.6;
HRMS (ESI): $\text{C}_{18}\text{H}_{15}\text{F}_3\text{N}_2\text{NaO}_3^+$ [M+Na]⁺ Calcd 387.0927, Found 387.0939.



(*E*)-*N*-(2-fluorobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3u**: yellow oil (31.7 mg, yield 47%);
IR (neat) ν 2926, 1650, 1272, 1128, 725, 648 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*, Major isomer) δ 7.49 – 7.39 (m, 3H), 7.37 – 7.24 (m, 4H), 7.09 (td, $J = 7.5, 1.2$ Hz, 1H), 7.01 (ddd, $J = 9.6, 8.2, 1.2$ Hz, 1H), 5.53 (q, $J = 8.2$ Hz, 1H), 4.59 (s, 2H), 2.26 (s, 3H);

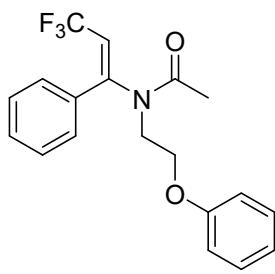
$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z*= 14/1) δ -56.14, -117.59;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 170.0, 160.9 (d, $^1J_{\text{C}-\text{F}} = 247.1$ Hz), 149.8 (q, $^3J_{\text{C}-\text{F}} = 6.0$ Hz), 132.7, 131.4 (d, $^3J_{\text{C}-\text{F}} = 4.0$ Hz), 130.8, 129.6 (d, $^3J_{\text{C}-\text{F}} = 8.2$ Hz), 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 2.1$ Hz), 128.6, 124.3 (d, $^{>3}J_{\text{C}-\text{F}} = 3.6$ Hz), 123.4 (d, $^2J_{\text{C}-\text{F}} = 14.9$ Hz), 122.1 (q, $^1J_{\text{C}-\text{F}} = 270.2$ Hz), 116.8 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 115.4 (d, $^2J_{\text{C}-\text{F}} = 21.7$ Hz), 43.4, 22.5;
HRMS (ESI): $\text{C}_{18}\text{H}_{15}\text{F}_4\text{NNaO}^+$ [M+Na]⁺ Calcd 360.0982, Found 360.0987.



(*E*)-*N*-(2-bromobenzyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3v**: yellow oil (36.5 mg, yield 46%);
IR (neat) ν 2917, 1672, 1269, 1119, 753, 521 cm^{-1} ;
 ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.44 (m, 4H), 7.32 – 7.27 (m, 3H), 7.17 – 7.11 (m, 2H), 5.66 (q, $J = 8.2$ Hz, 1H), 4.72 (s, 2H), 2.27 (s, 3H);

$^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z*> 20/1) δ -55.95;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*) δ 170.3, 150.2 (q, $^3J_{\text{C}-\text{F}} = 5.9$ Hz), 135.5, 133.0, 132.7, 130.8, 130.3, 129.2, 128.9 (q, $^{>3}J_{\text{C}-\text{F}} = 2.0$ Hz), 128.6, 127.5, 123.6, 122.1 (d, $^1J_{\text{C}-\text{F}} = 270.3$ Hz), 116.8 (q, $^2J_{\text{C}-\text{F}} = 35.1$ Hz), 50.0, 22.6;

HRMS (ESI): C₁₈H₁₅BrF₃NNaO⁺ [M+Na]⁺ Calcd 420.0181, Found 420.0180.

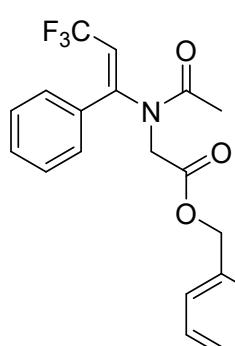


(*E*)-*N*-(2-phenoxyethyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3w**: yellow oil (39.1 mg, yield 56%);
 IR (neat) ν 2917, 1645, 1242, 1111, 754, 639 cm⁻¹;
¹H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.37 (m, 5H), 7.30 – 7.26 (m, 2H), 6.96 (t, J = 7.3, Hz, 1H), 6.92 – 6.81 (m, 2H), 5.81 (q, J = 8.2 Hz, 1H), 4.15 (t, J = 5.2 Hz, 2H), 3.71 (t, J = 5.2 Hz, 2H), 2.22 (s, 3H);

¹⁹F{¹H} NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* > 20/1) δ -55.87;

¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 170.5, 158.2, 150.8 (q, $^{3}J_{C-F}$ = 5.9 Hz), 133.1, 130.7, 129.6, 129.0 (d, $^{3}J_{C-F}$ = 1.9 Hz), 128.7, 122.4 (q, $^{1}J_{C-F}$ = 270.1 Hz), 121.1, 116.1 (q, $^{2}J_{C-F}$ = 34.9 Hz), 114.3, 65.8, 46.3, 22.6;

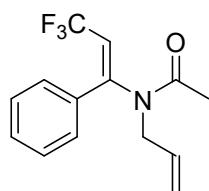
HRMS (ESI): C₁₉H₁₈F₃NNaO₂⁺ [M+Na]⁺ Calcd 372.1182, Found 372.1183.



(*E*)-*N*-(2-oxo-3-phenylpropyl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3x**: yellow oil (30.2 mg, yield 40%);
 IR (neat) ν 2919, 1677, 1270, 1127, 737, 698 cm⁻¹;
¹H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.30 (m, 10H), 5.91 (q, J = 8.2 Hz, 1H), 5.15 (s, 2H), 4.08 (s, 2H), 2.21 (s, 3H);
¹⁹F{¹H} NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* > 20/1) δ -55.97;

¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 170.6, 168.4, 145.0 (q, $^{3}J_{C-F}$ = 6.1 Hz), 135.2, 132.6, 131.0, 129.0 (q, $^{3}J_{C-F}$ = 2.0 Hz), 128.7, 128.6, 128.5, 128.3, 122.3 (q, $^{1}J_{C-F}$ = 270.1 Hz), 116.2 (q, $^{2}J_{C-F}$ = 35.3 Hz), 67.2, 48.7, 22.2;

HRMS (ESI): C₂₀H₁₈F₃NNaO₃⁺ [M+Na]⁺ Calcd 400.1131, Found 400.1148.

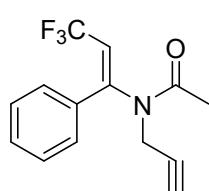


(*E*)-*N*-allyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3y**: colorless oil (25.8 mg, yield 48%);
 IR (neat) ν 2917, 1644, 1271, 1116, 779, 643 cm⁻¹;
¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 3H), 7.39 – 7.33 (m, 2H), 5.82 – 5.66 (m, 2H), 5.16 (dd, J = 10.1, 1.3 Hz, 1H), 5.03 (dd, J = 17.1, 1.5 Hz, 1H), 3.97 (dt, J = 6.3, 1.4 Hz, 2H), 2.19 (s, 3H);

¹⁹F{¹H} NMR (376 MHz, Chloroform-*d*, Major isomer, *E/Z* > 20/1) δ -55.71;

¹³C{¹H} NMR (100 MHz, Chloroform-*d*) δ 169.9, 150.2 (q, $^{3}J_{C-F}$ = 5.9 Hz), 133.2, 132.3, 130.7, 128.8 (q, $^{3}J_{C-F}$ = 2.0 Hz), 128.6, 122.3 (q, $^{1}J_{C-F}$ = 270.2 Hz), 118.5, 116.0 (q, $^{2}J_{C-F}$ = 34.9 Hz), 49.4, 22.6;

HRMS (ESI): C₁₄H₁₄F₃NNaO⁺ [M+Na]⁺ Calcd 292.0920, Found 292.0928.

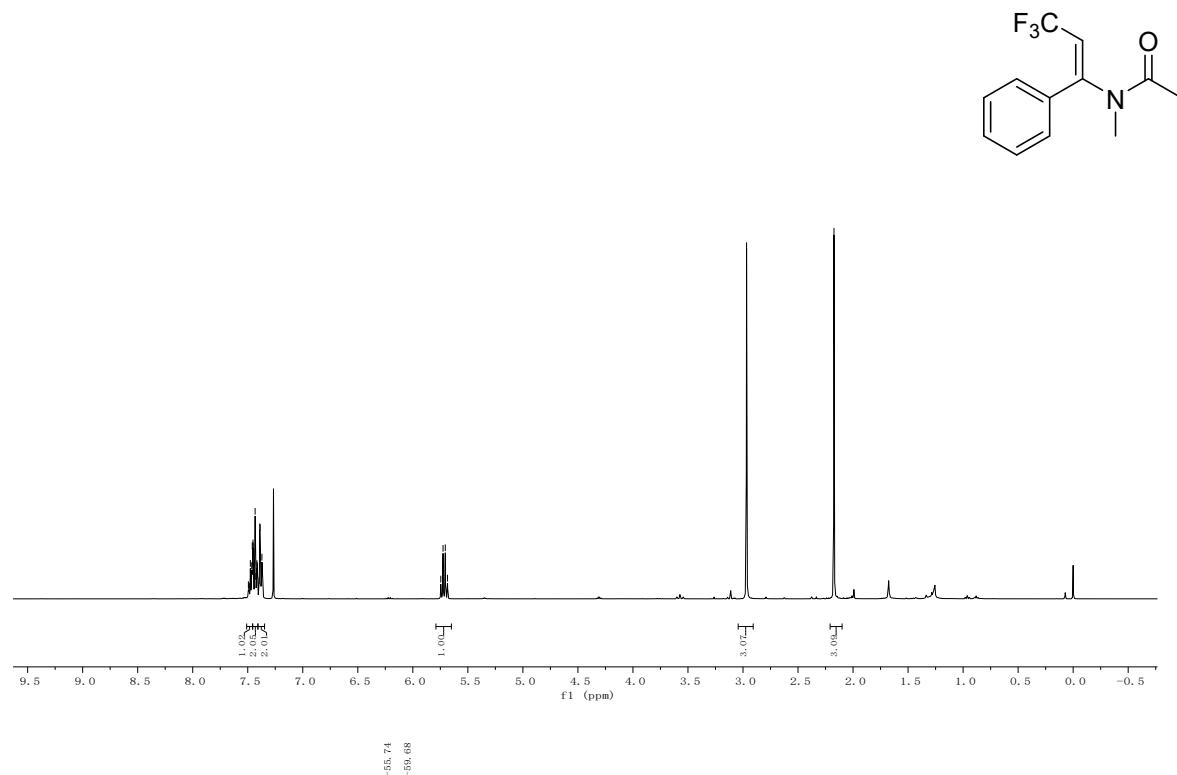


(*E*)-*N*-(prop-2-yn-1-yl)-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide **3z**: colorless oil (29.9 mg, yield 56%);
 IR (neat) ν 2918, 1673, 1270, 1123, 735, 698 cm⁻¹;
¹H NMR (400 MHz, Chloroform-*d*, Major isomer) δ 7.49 – 7.39 (m, 5H),

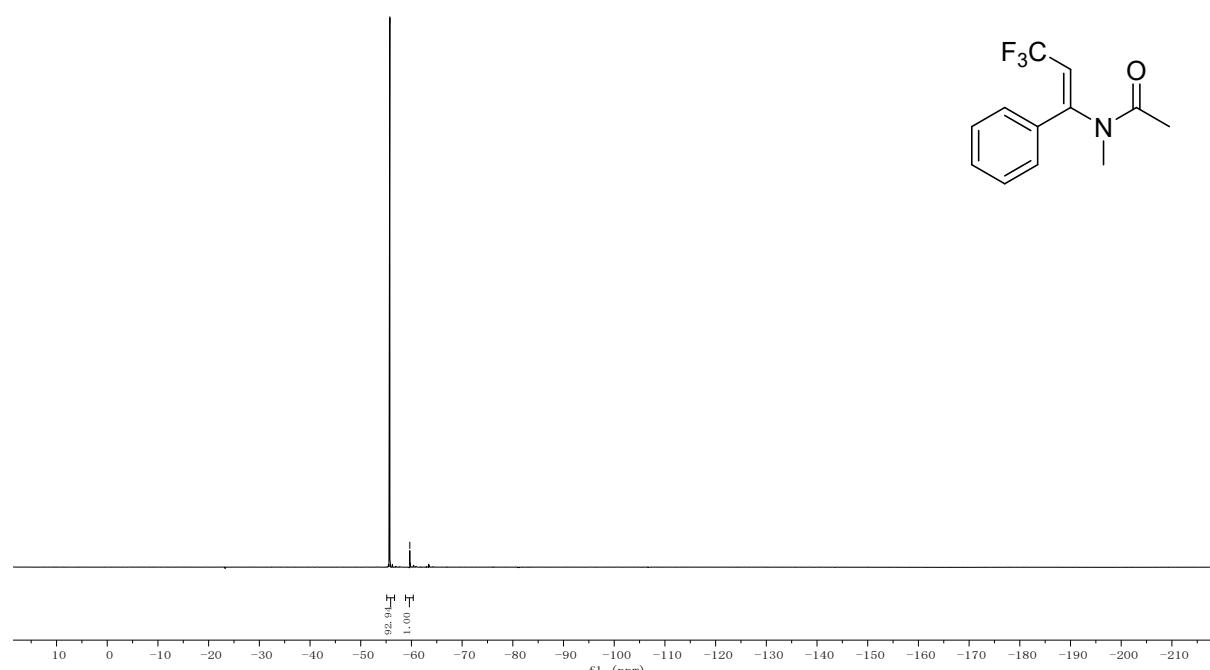
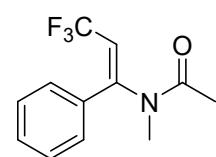
5.86 (q, $J = 8.1$ Hz, 1H), 4.20 (d, $J = 2.5$ Hz, 2H), 2.26 (t, $J = 2.5$ Hz, 1H), 2.17 (s, 3H);
 $^{19}\text{F}\{\text{H}\}$ NMR (376 MHz, Chloroform-*d*, Major isomer, $E/Z > 20/1$) δ -55.93;
 $^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, Chloroform-*d*, Major isomer) δ 169.6, 149.4 (q, $^3J_{\text{C}-\text{F}} = 5.9$ Hz),
132.7, 130.9, 128.9 (q, $^3J_{\text{C}-\text{F}} = 1.9$ Hz), 128.7, 122.3 (d, $^1J_{\text{C}-\text{F}} = 270.2$ Hz), 116.6(q, $^2J_{\text{C}-\text{F}} =$
35.3 Hz), 77.9, 72.6, 36.2, 22.5 ;
HRMS (ESI): $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NNaO}^+$ [M+Na]⁺ Calcd 290.0763, Found 290.0778.

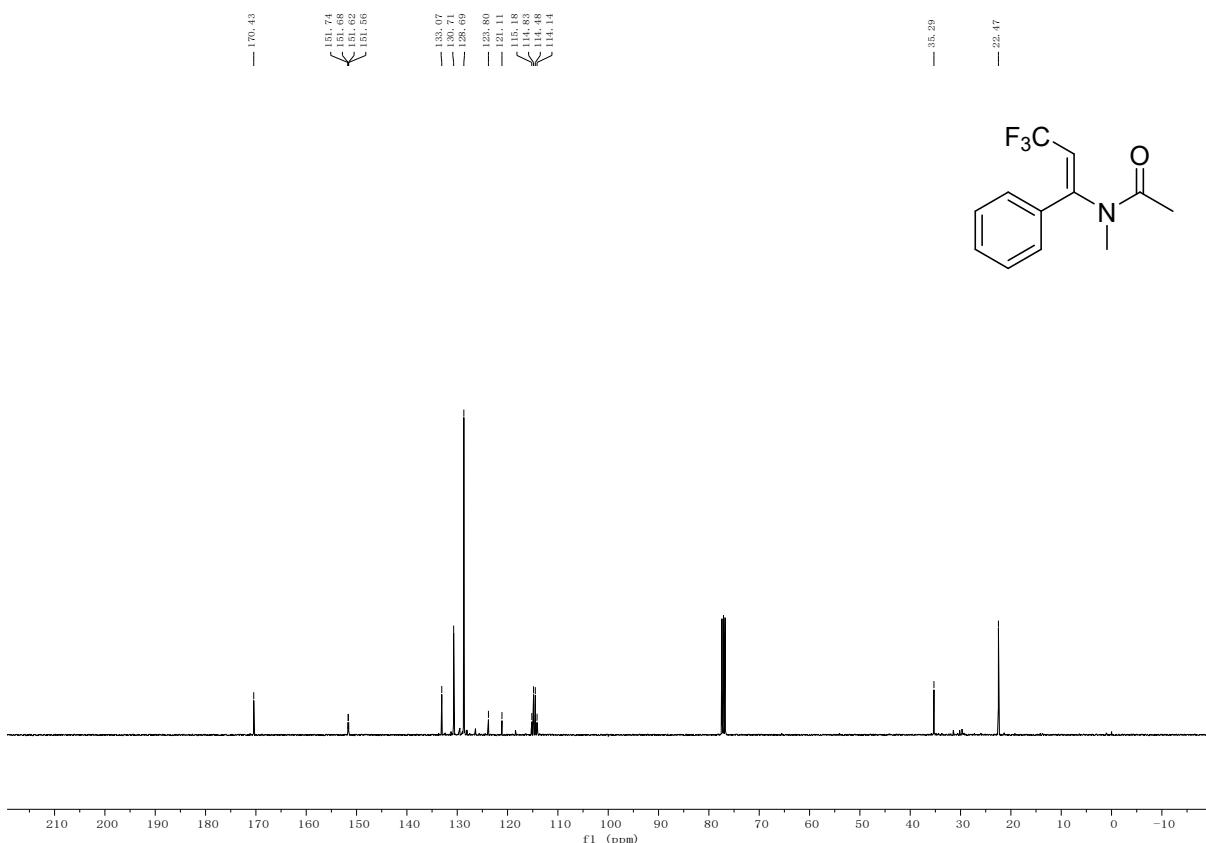
5. ^1H NMR, ^{19}F NMR and ^{13}C NMR Spectra of All Compounds

Product 3a: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).

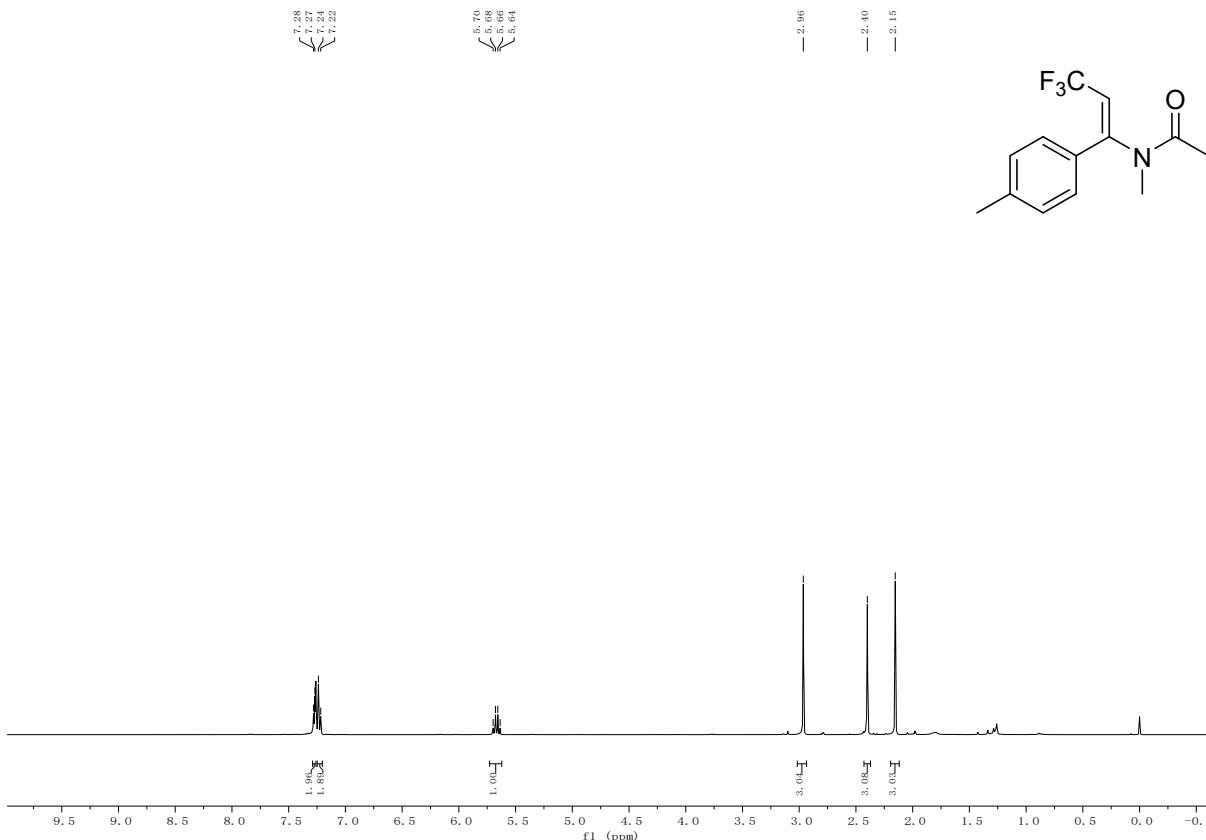


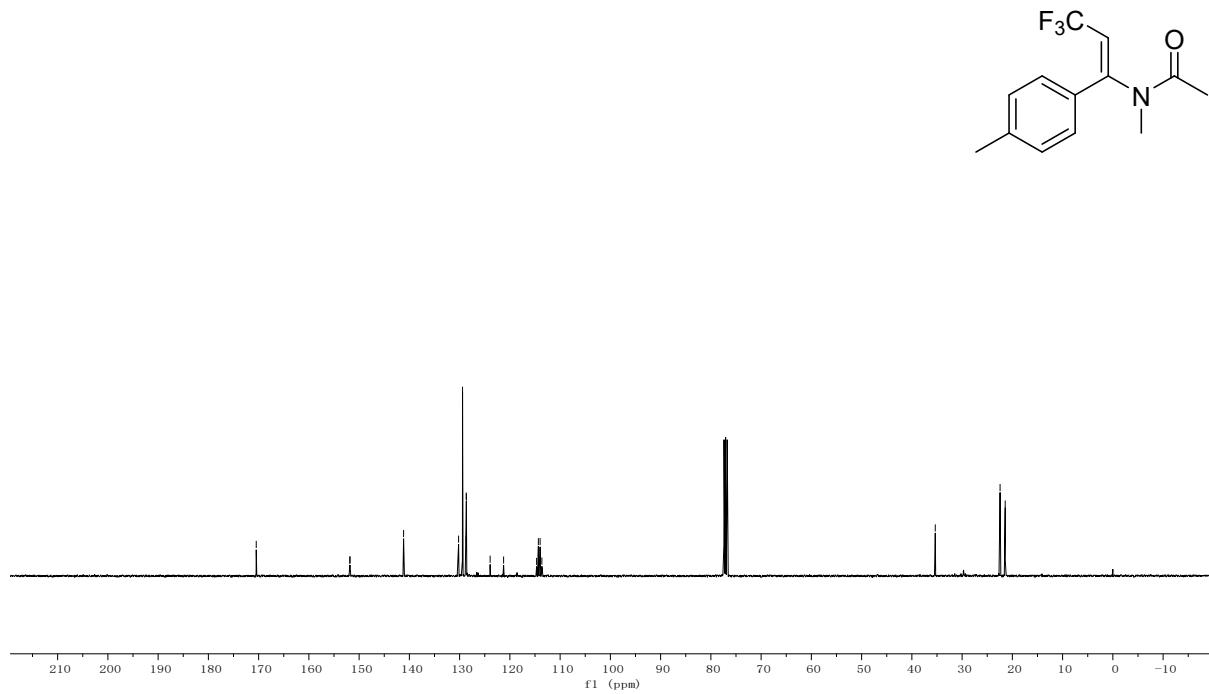
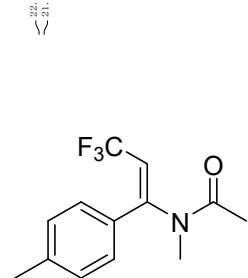
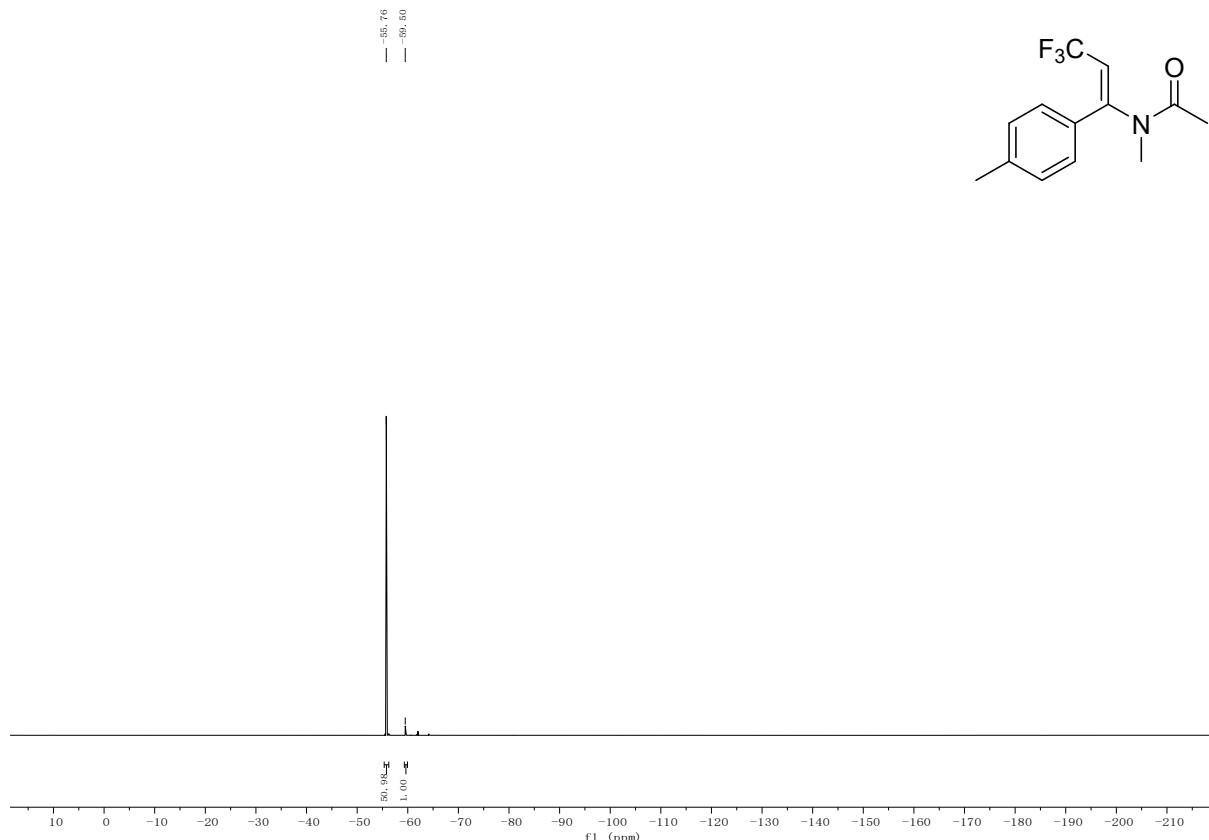
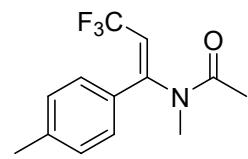
-56.74
-59.68



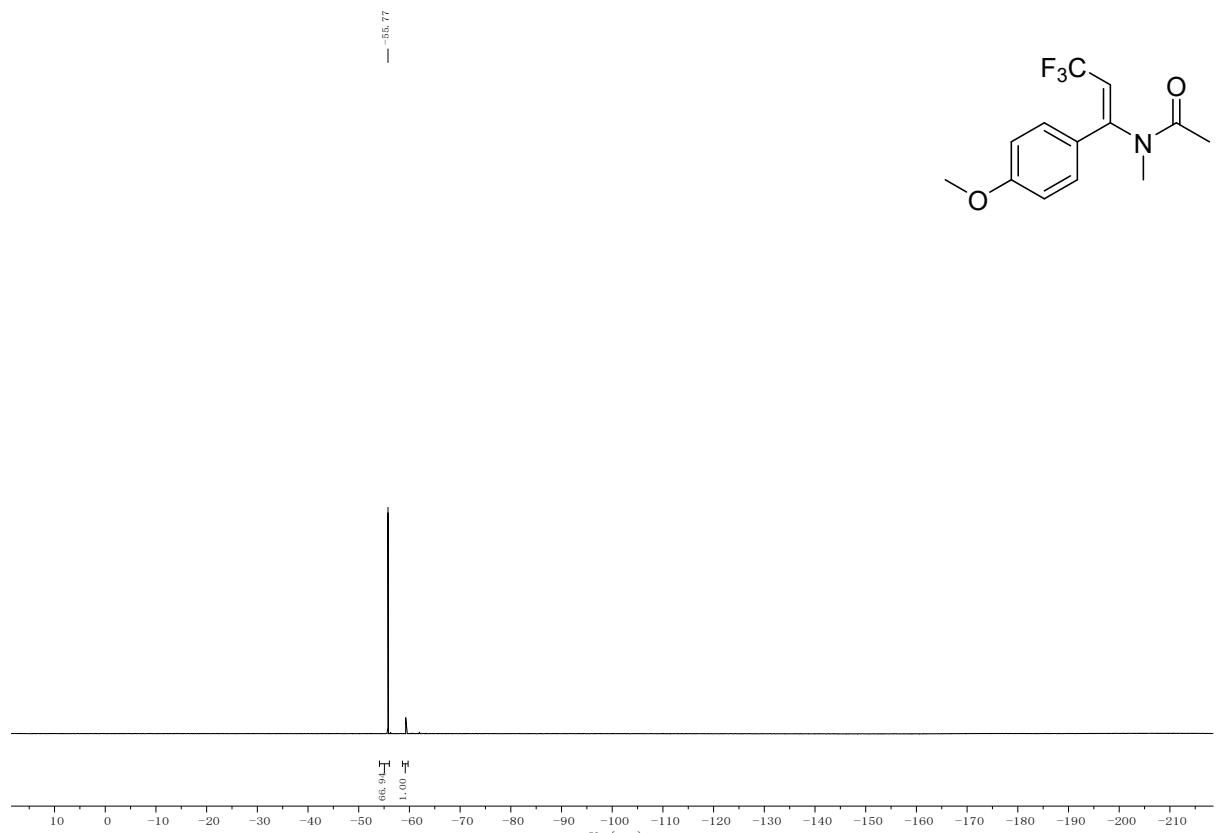
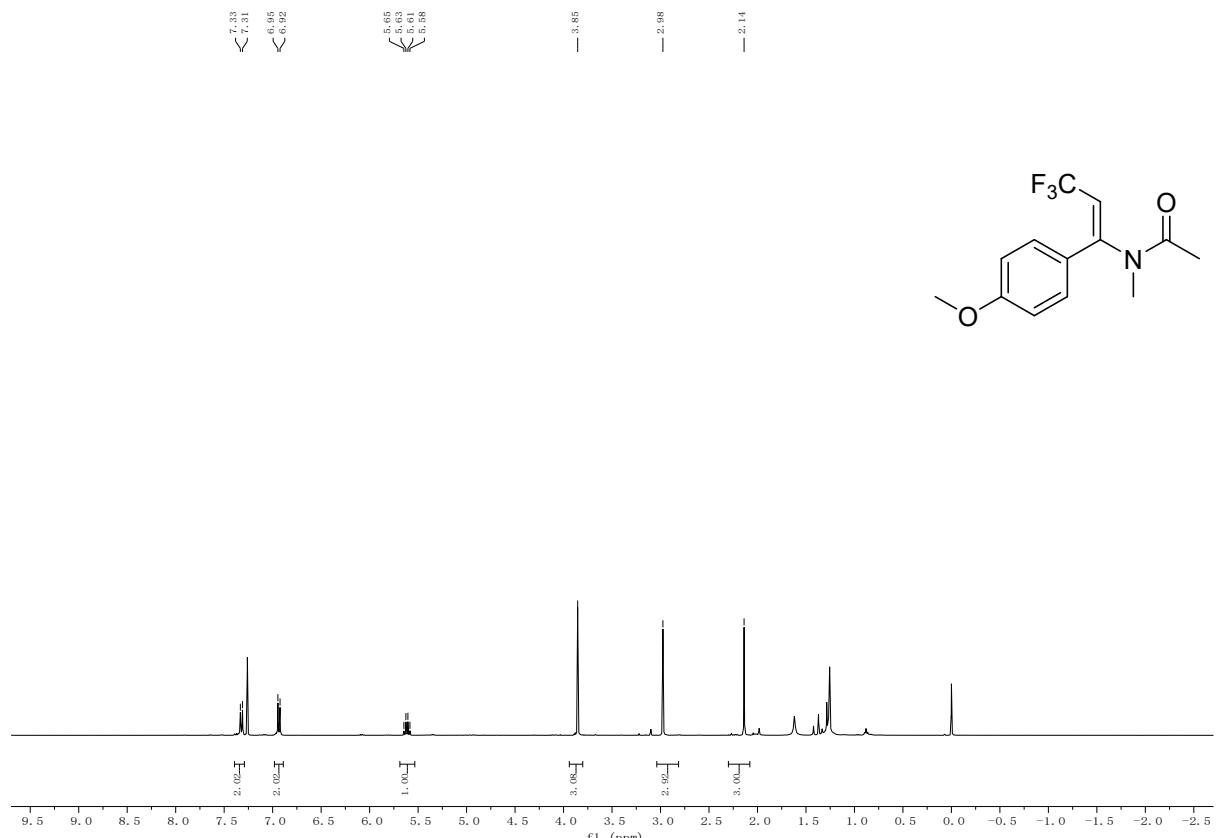


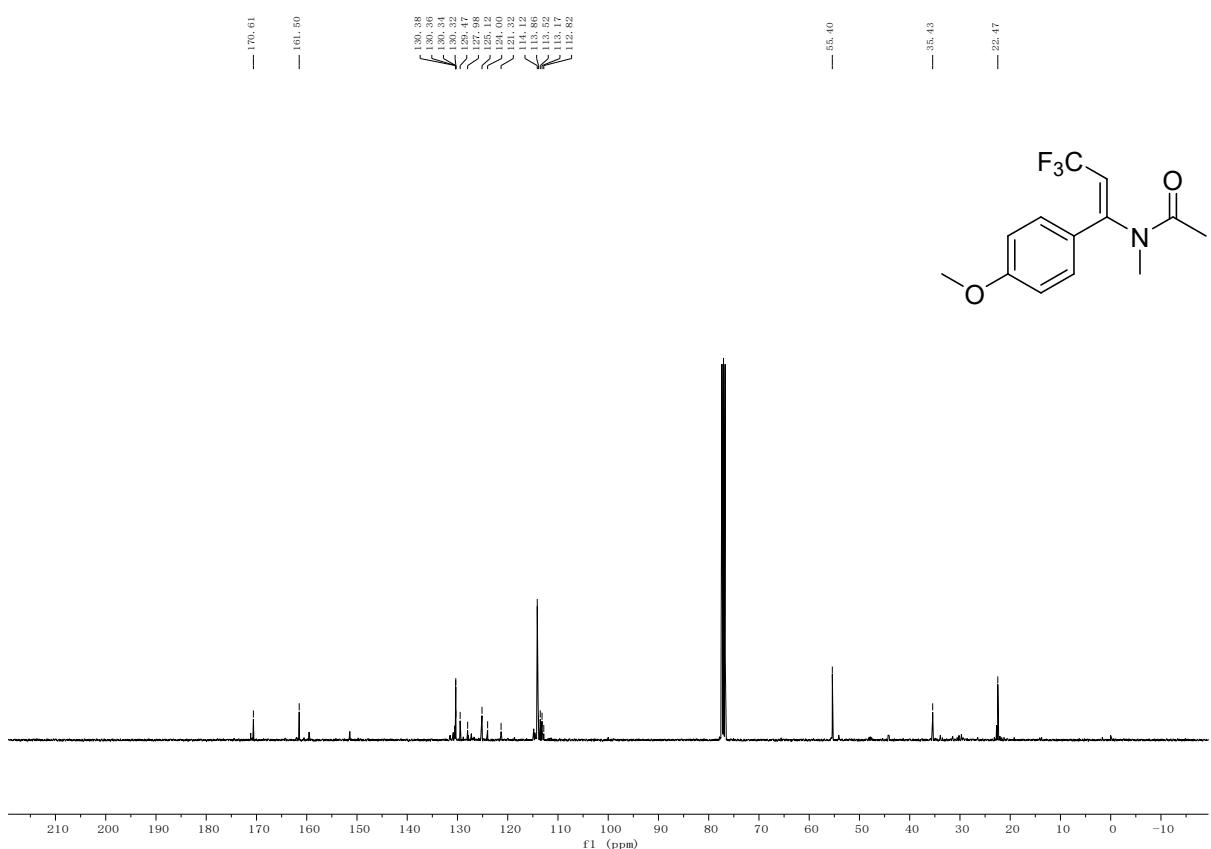
Product 3b: ^1H NMR (400 MHz, CDCl₃), ^{19}F NMR (376 MHz, CDCl₃) and ^{13}C NMR (100 MHz, CDCl₃).



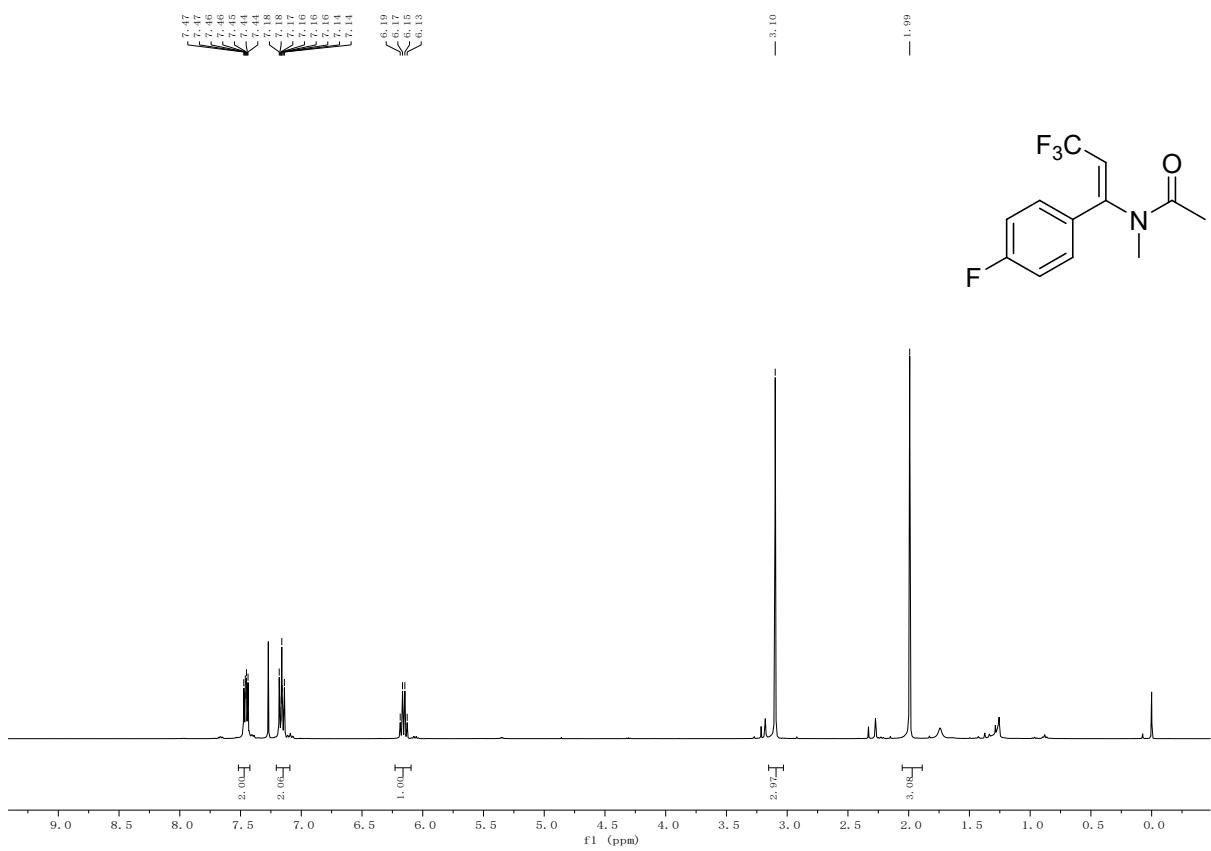


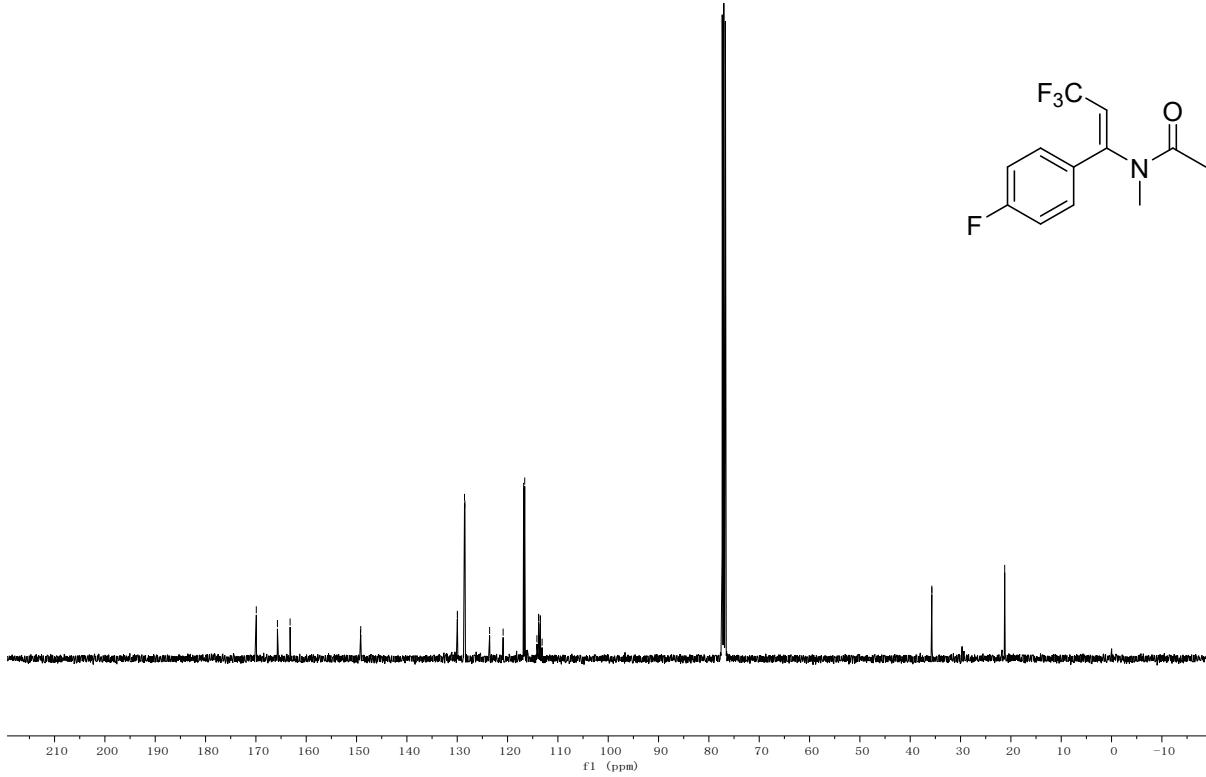
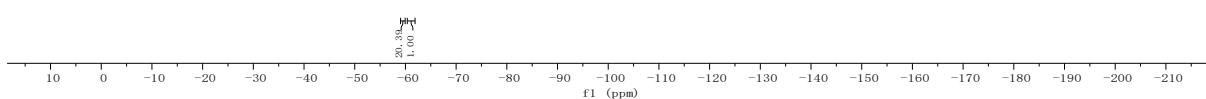
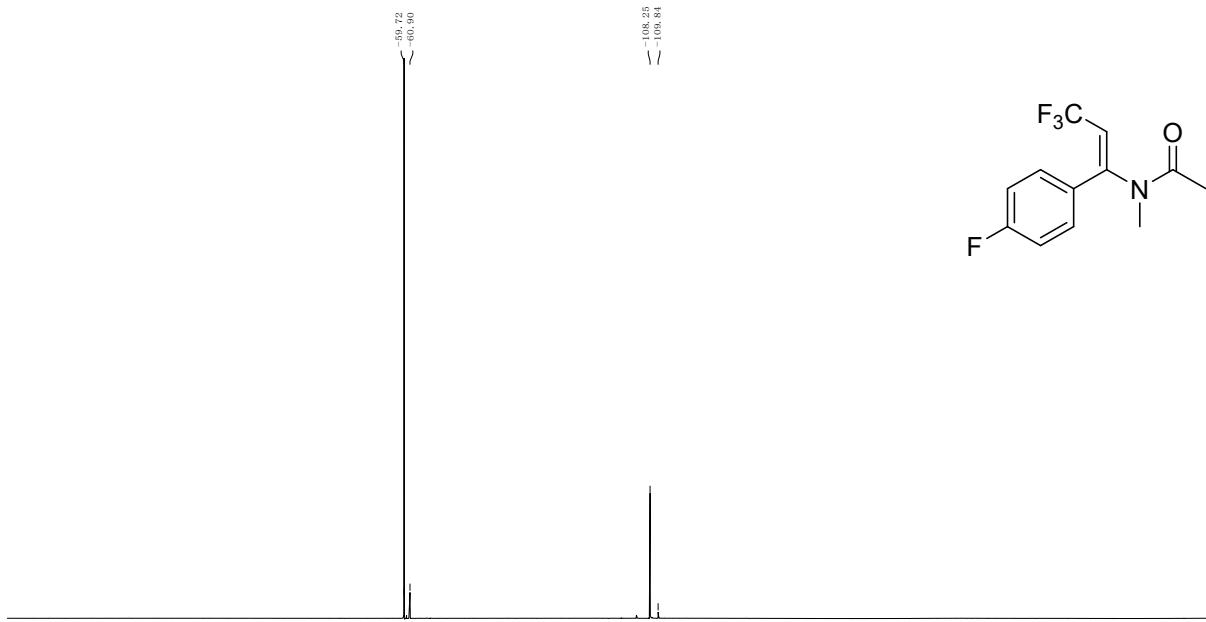
Product 3c: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



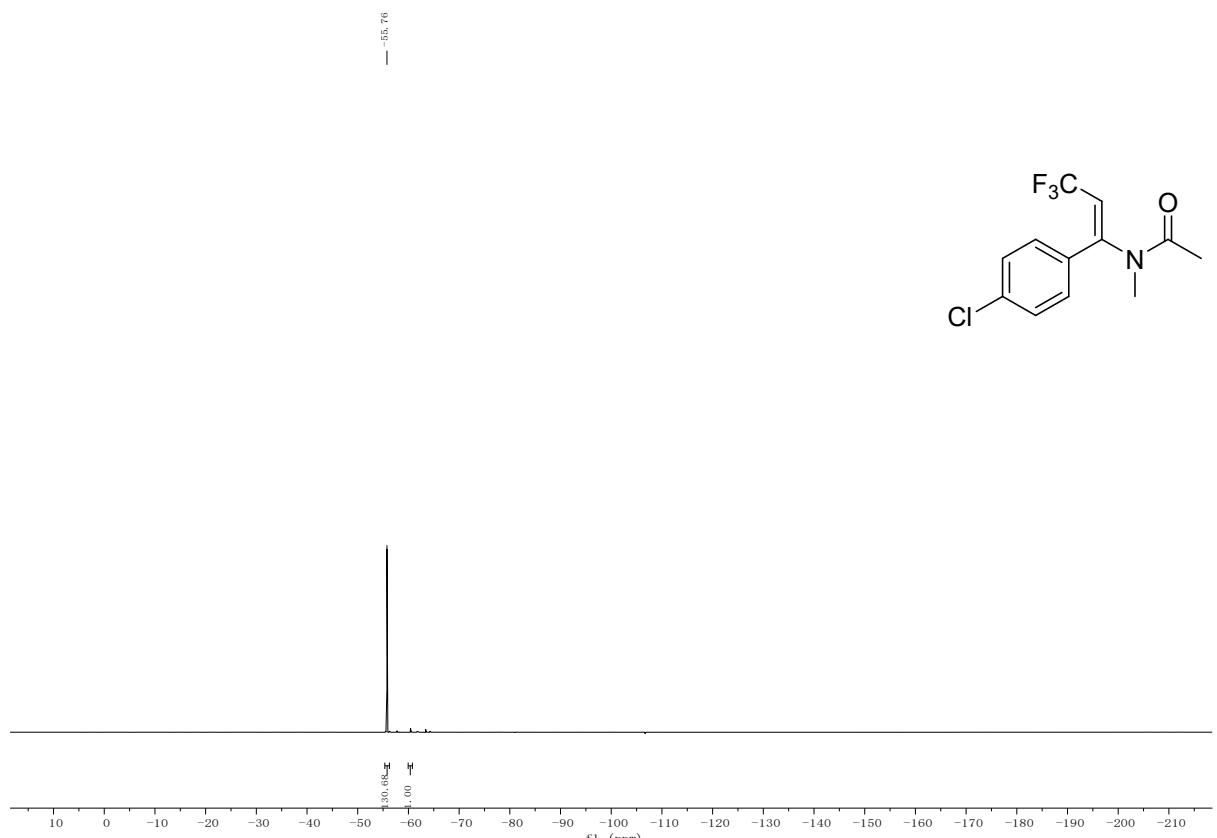
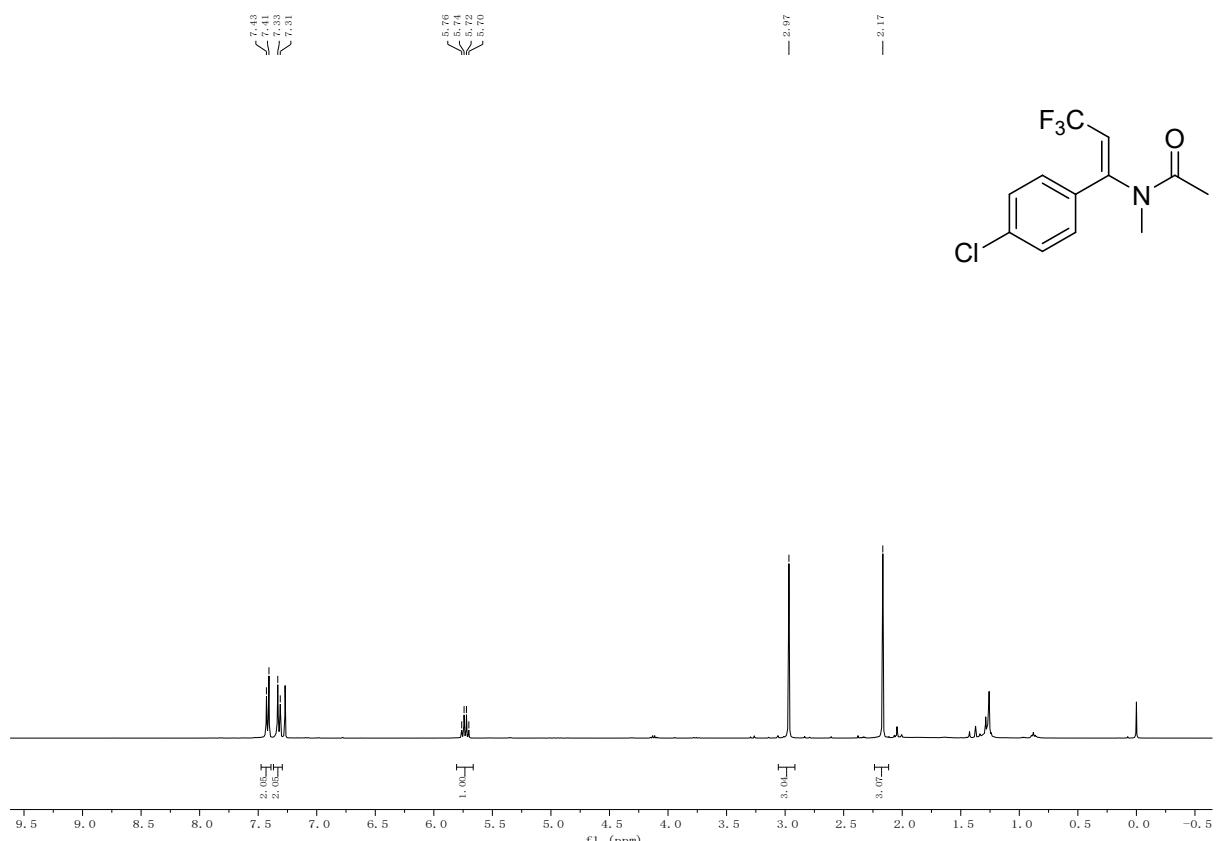


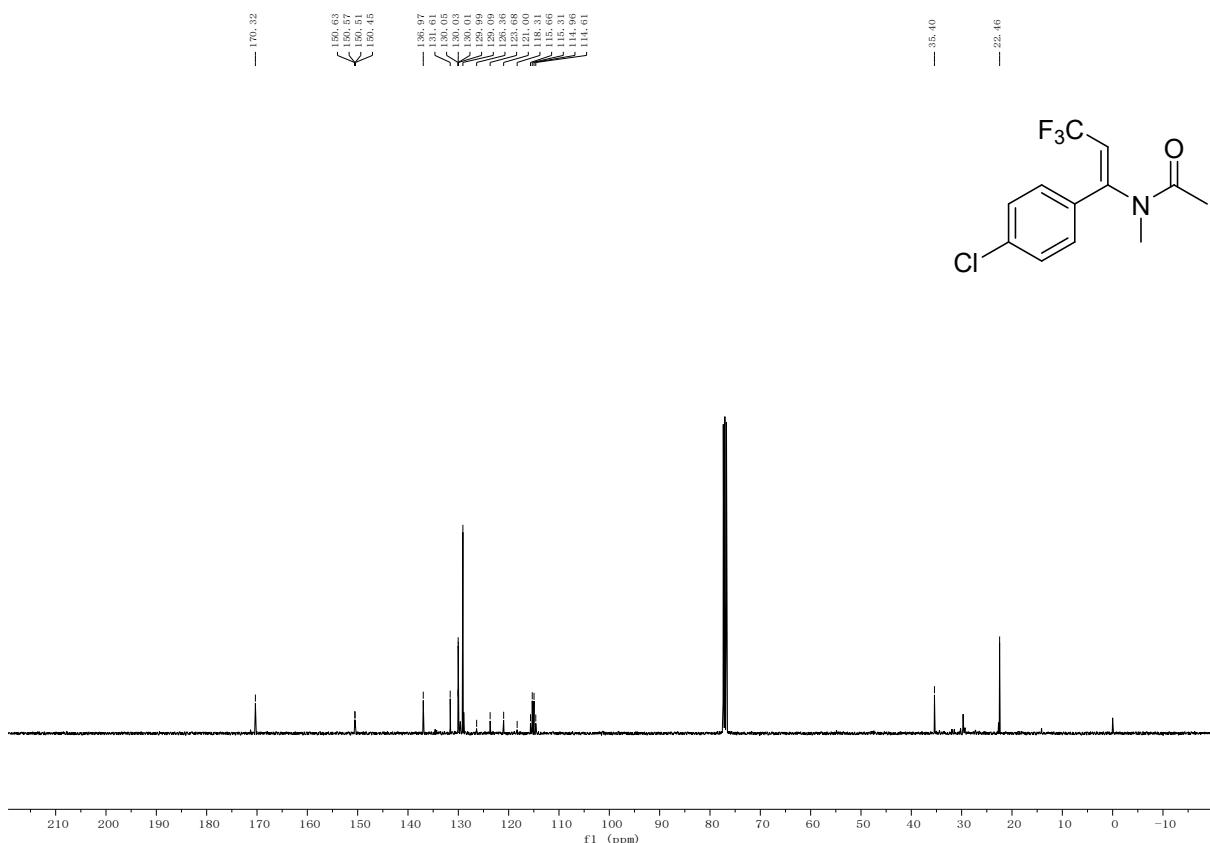
Product 3d: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



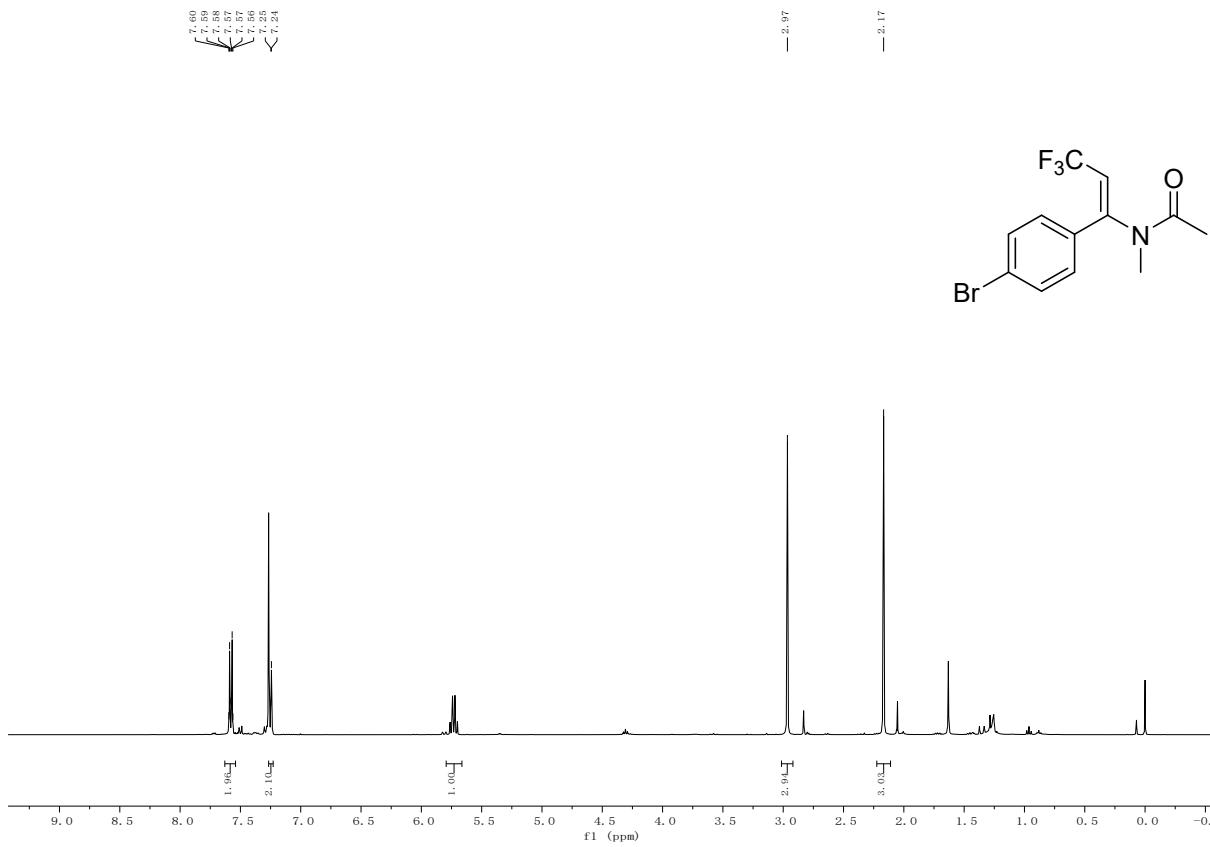


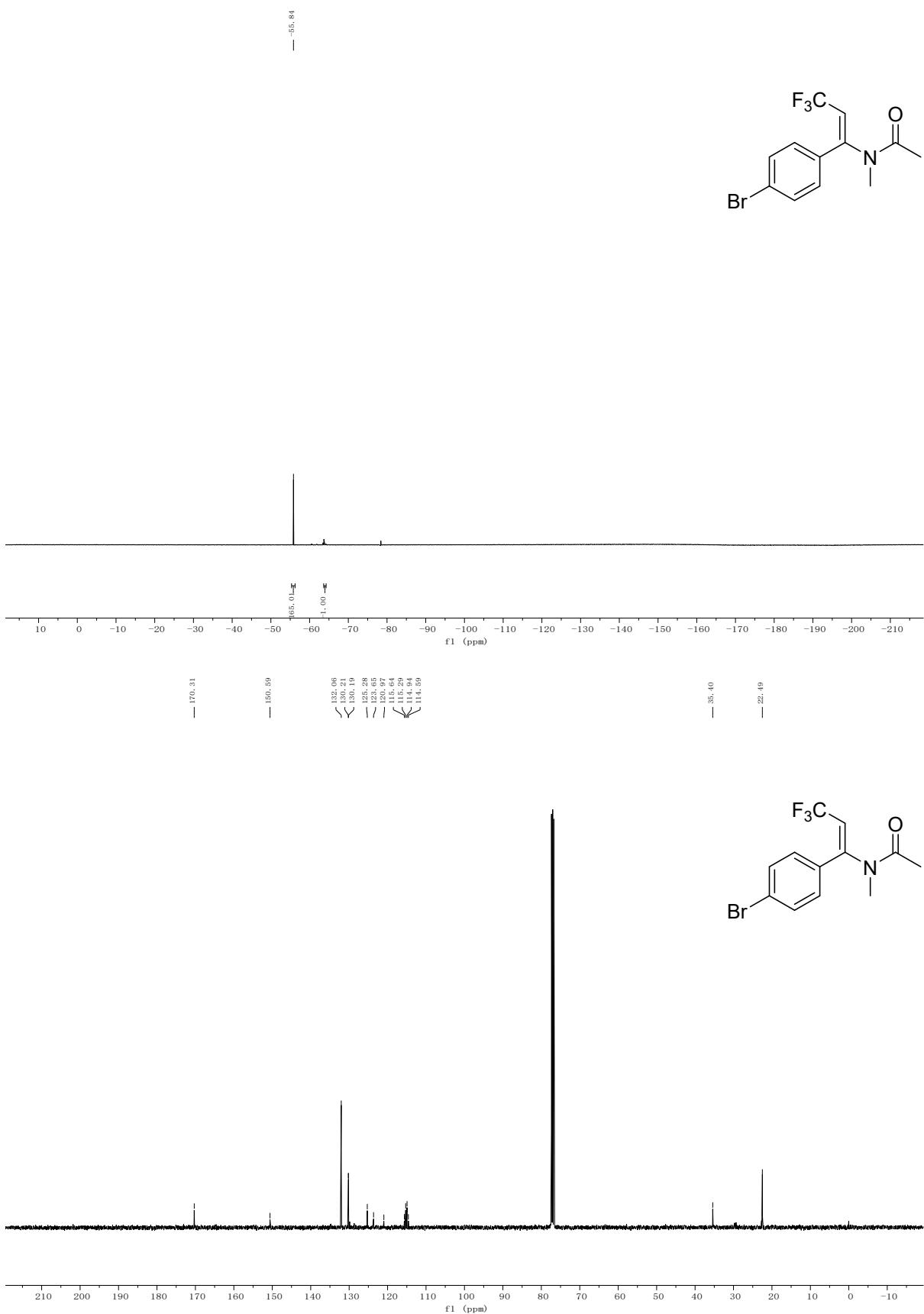
Product 3e: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



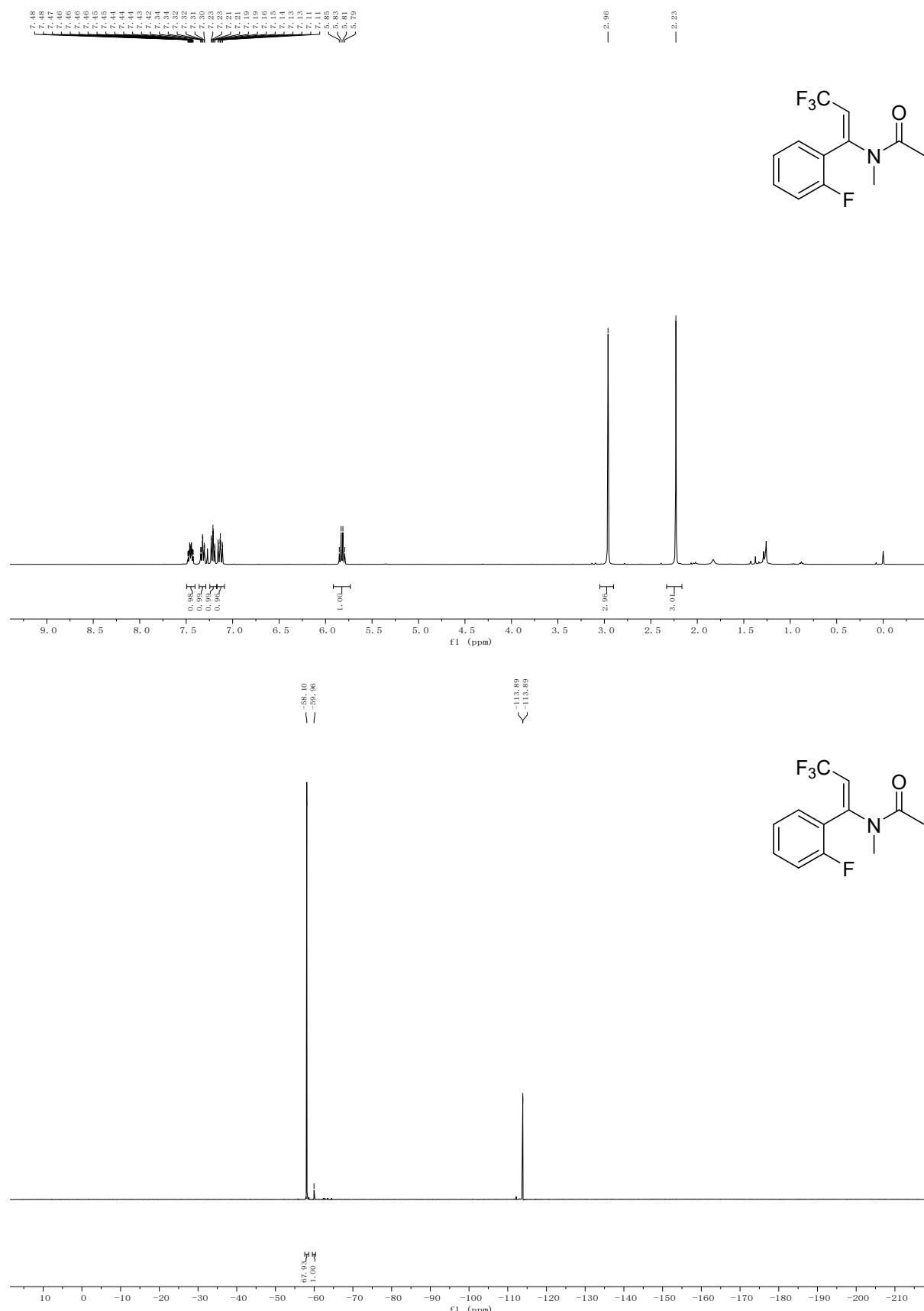


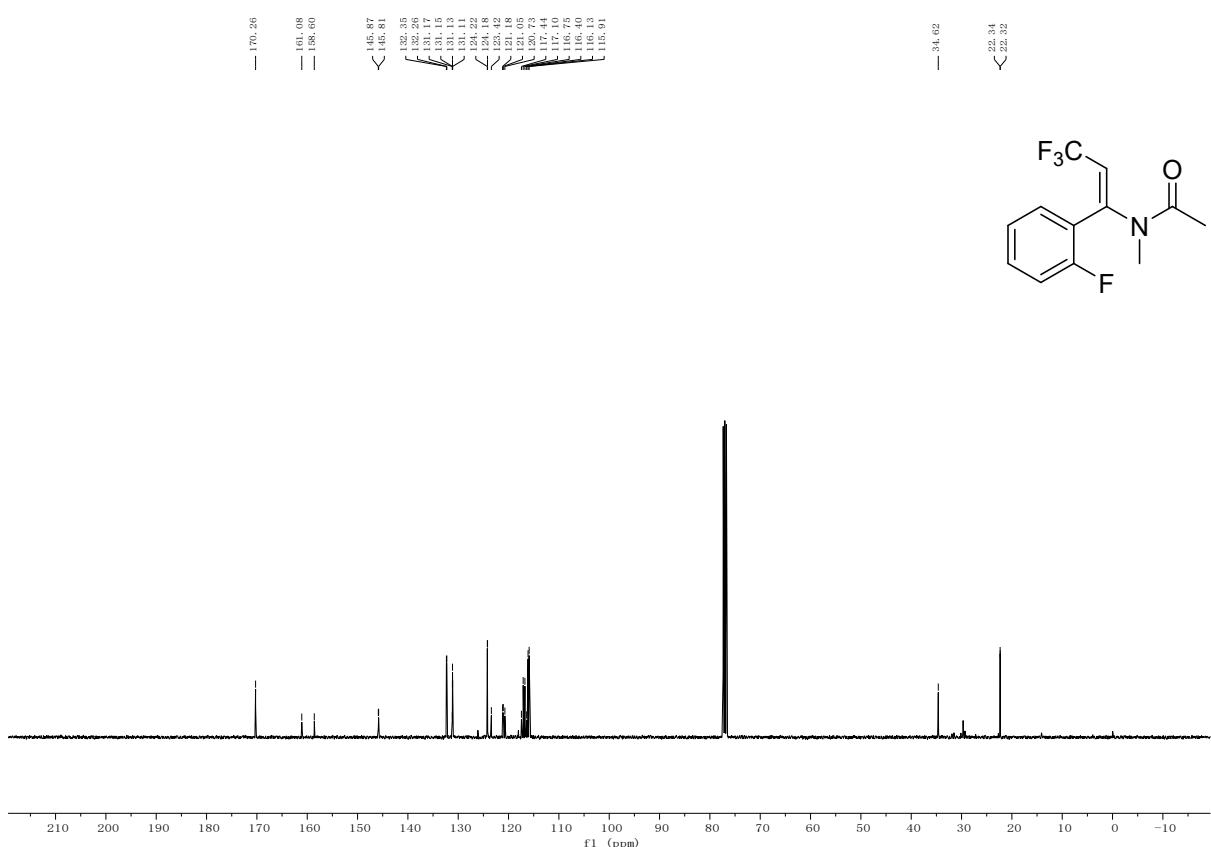
Product 3f: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



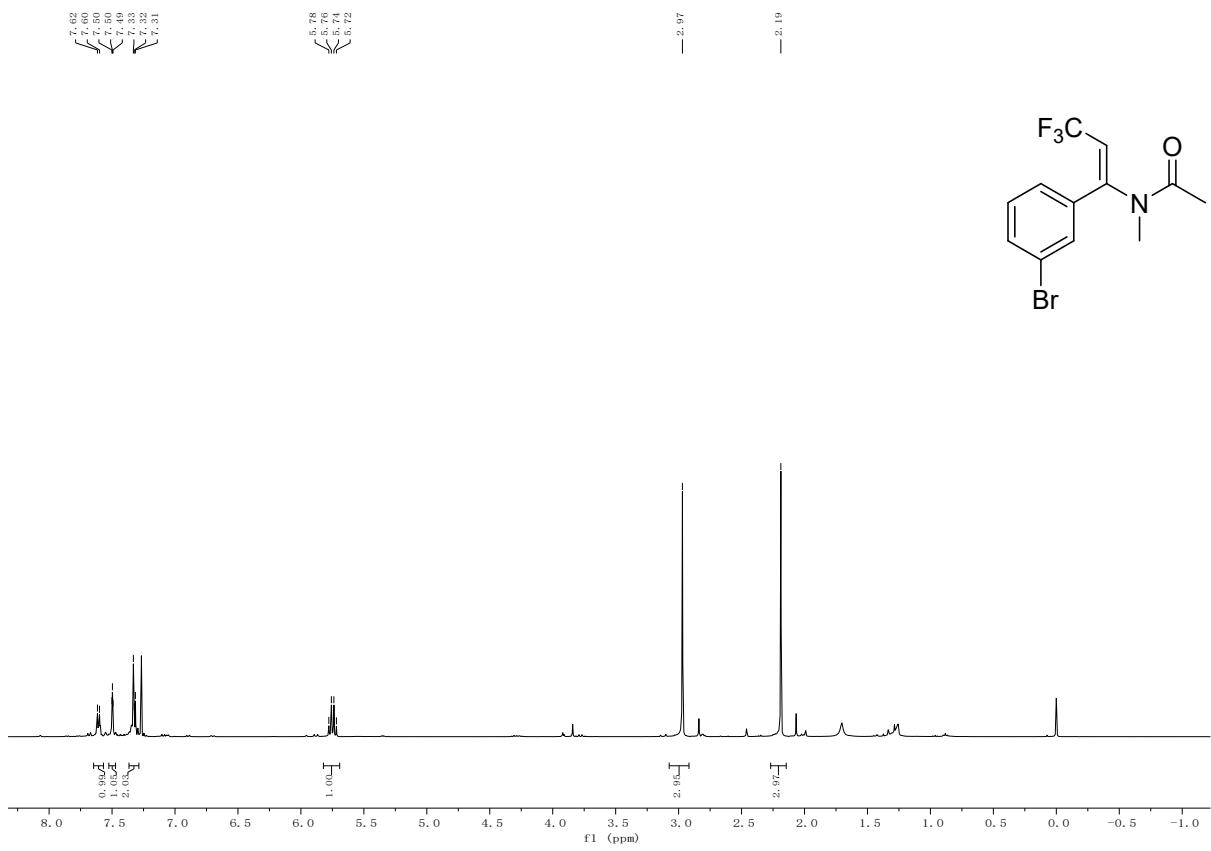


Product 3g: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).

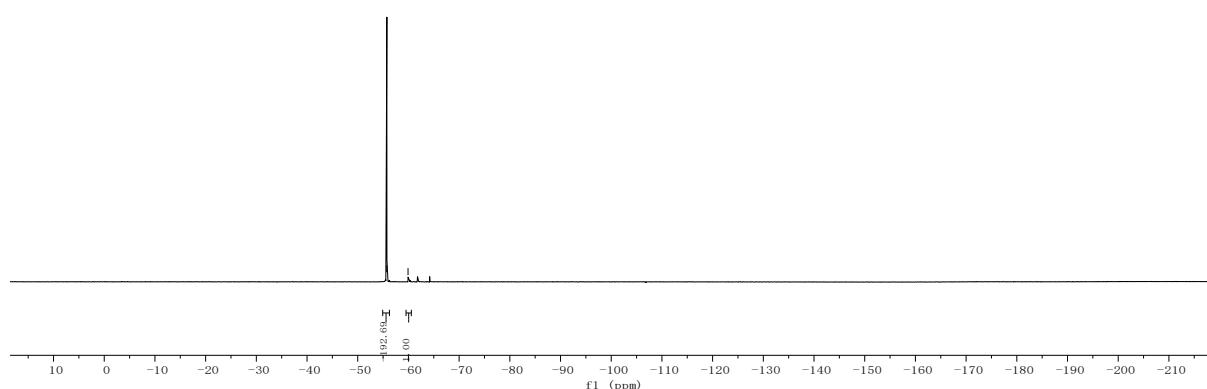
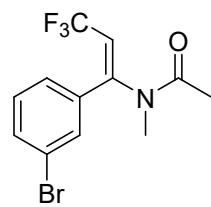




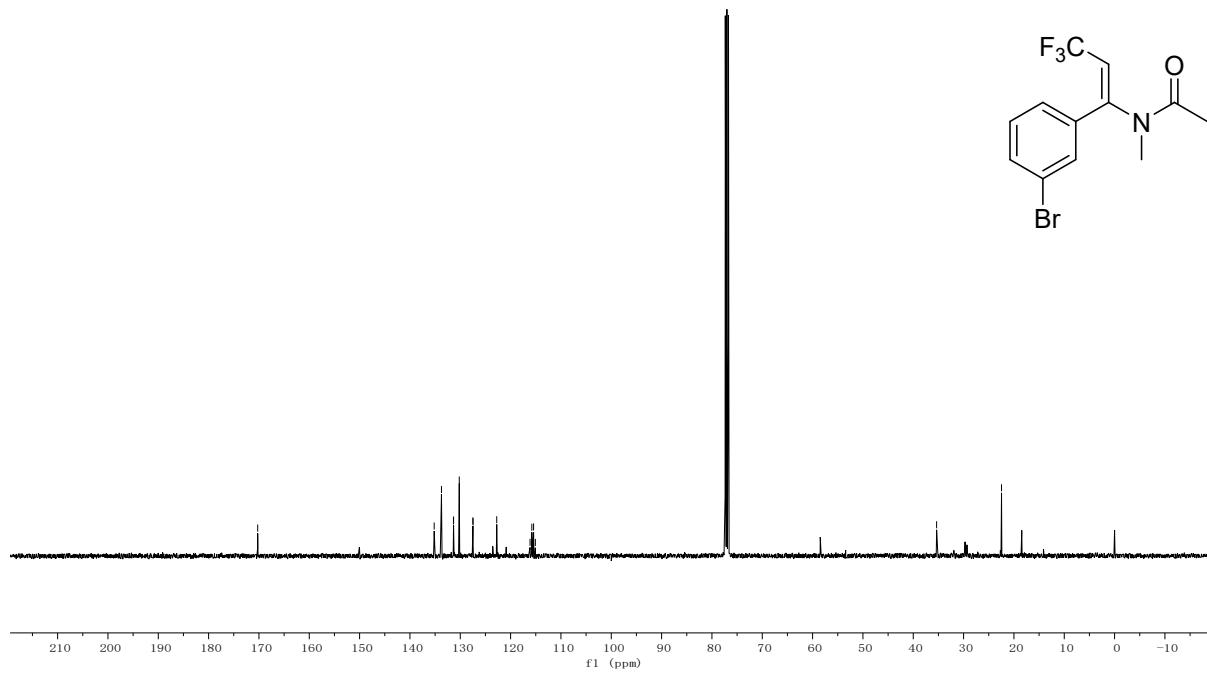
Product 3h: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



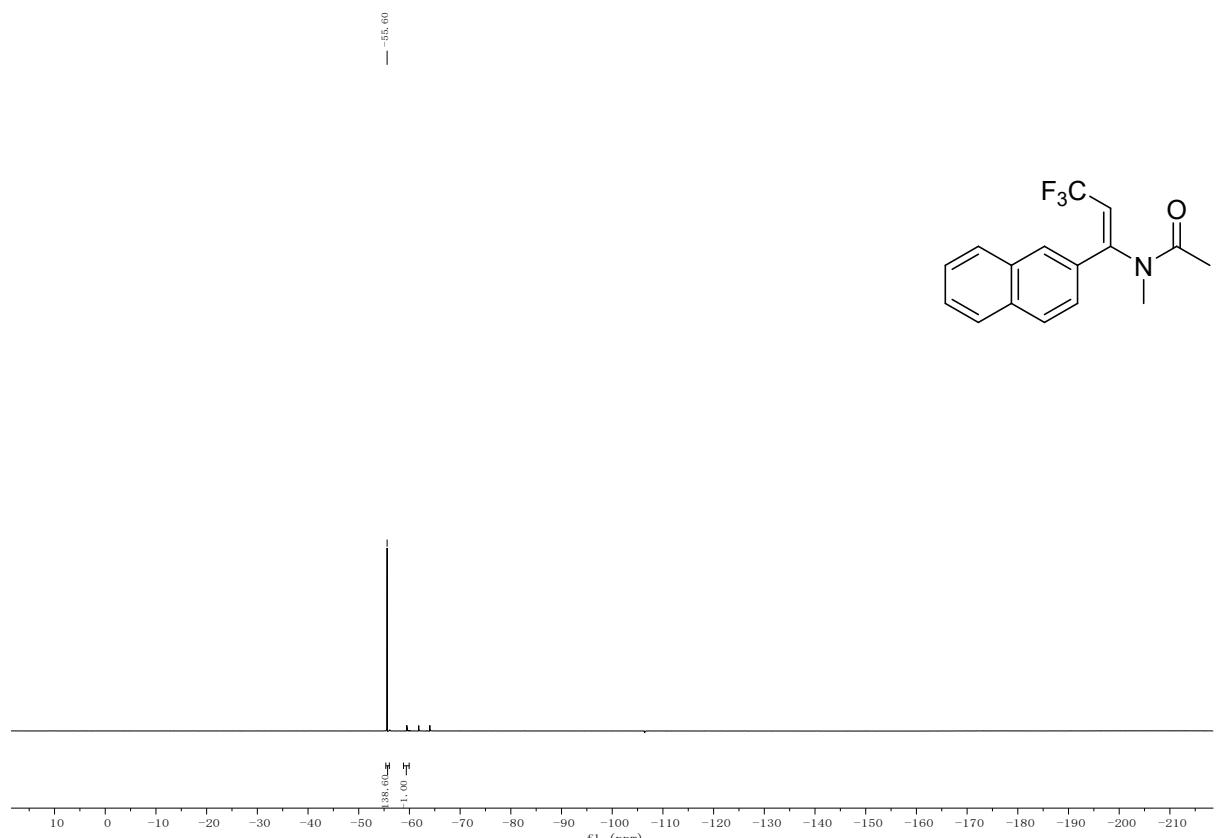
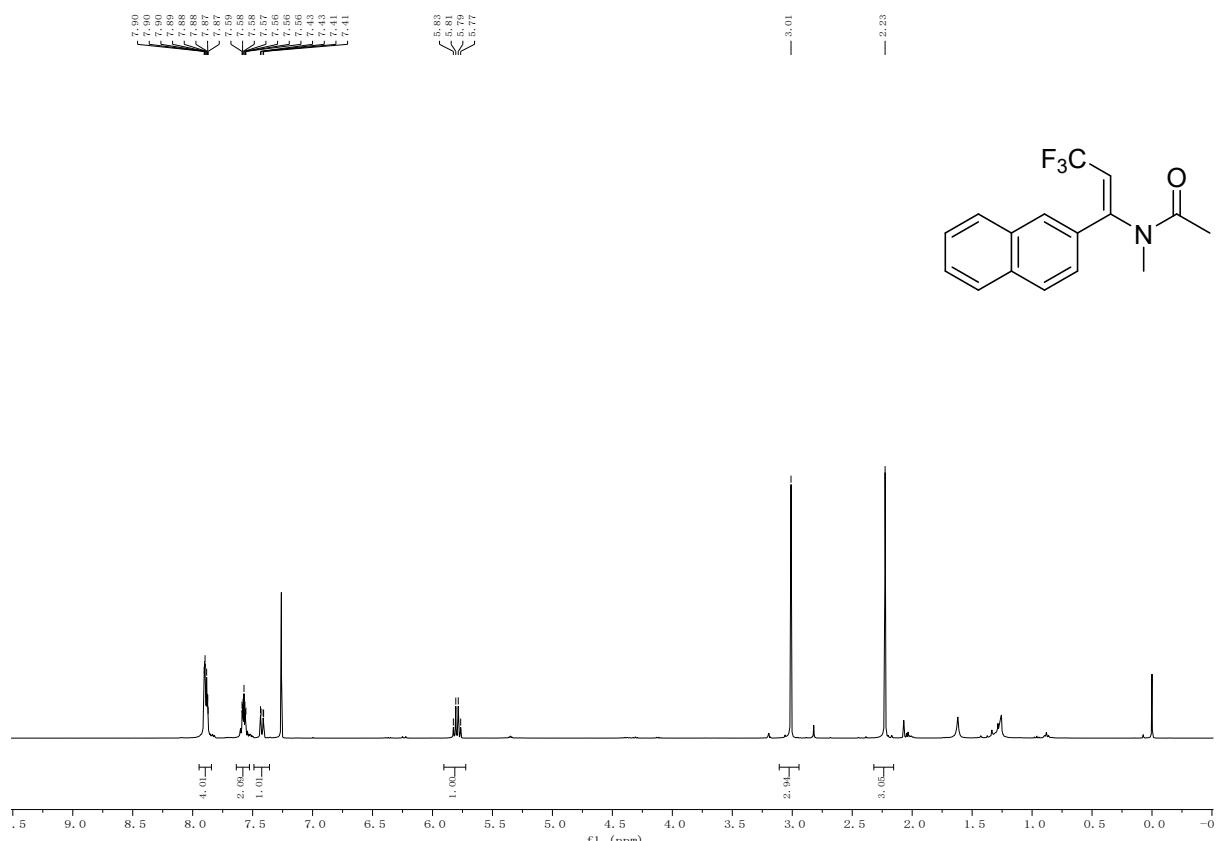
— -85.71
— -89.92

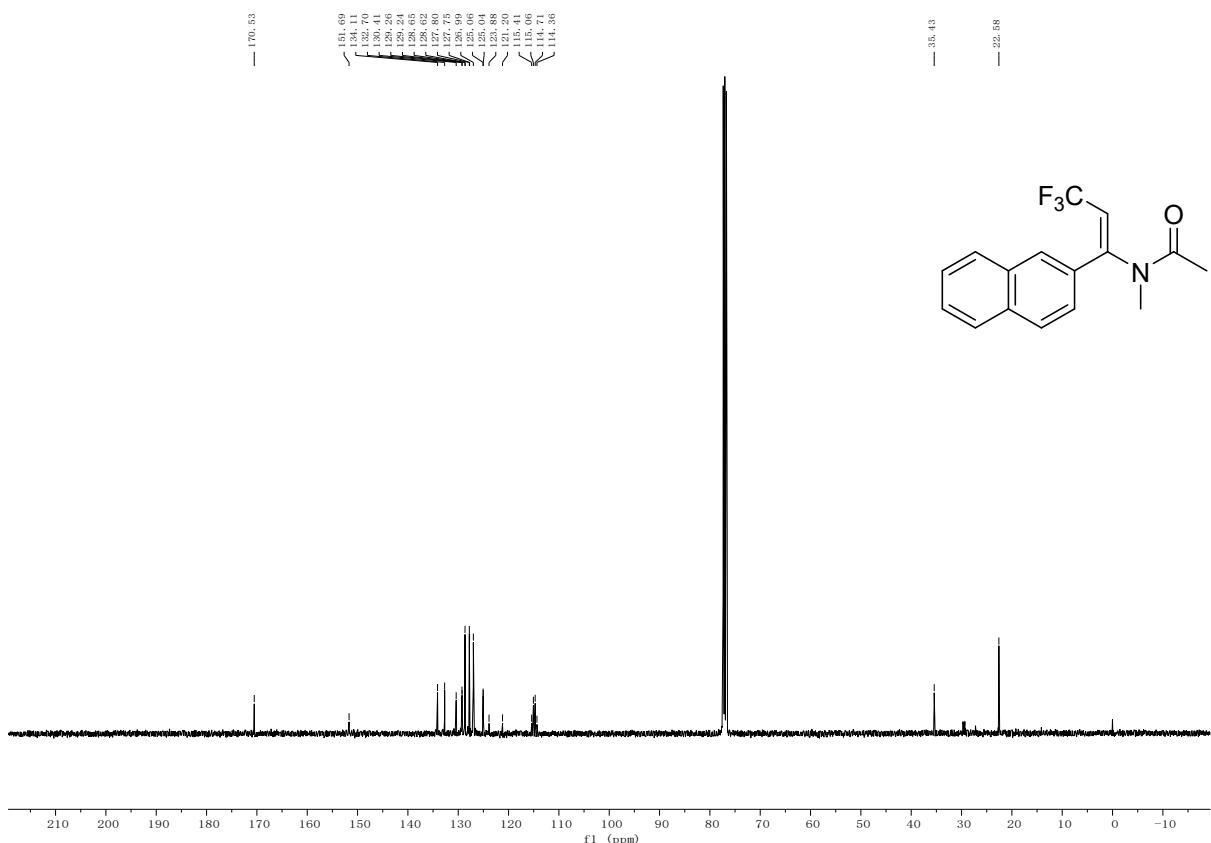


— 170.25
— 135.18
— 133.74
— 131.35
— 131.33
— 130.49
— 127.49
— 127.47
— 116.14
— 115.78
— 115.43
— 115.08
— 35.36
— 22.47

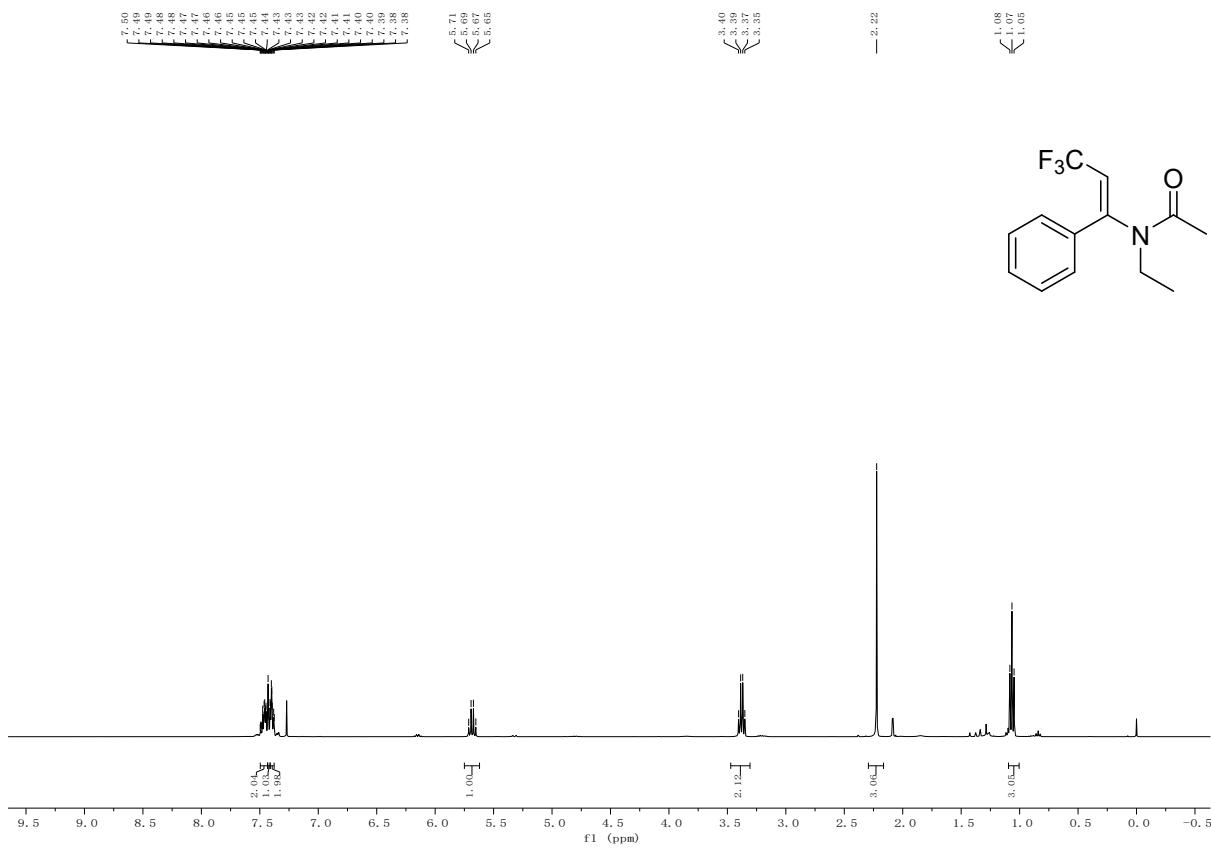


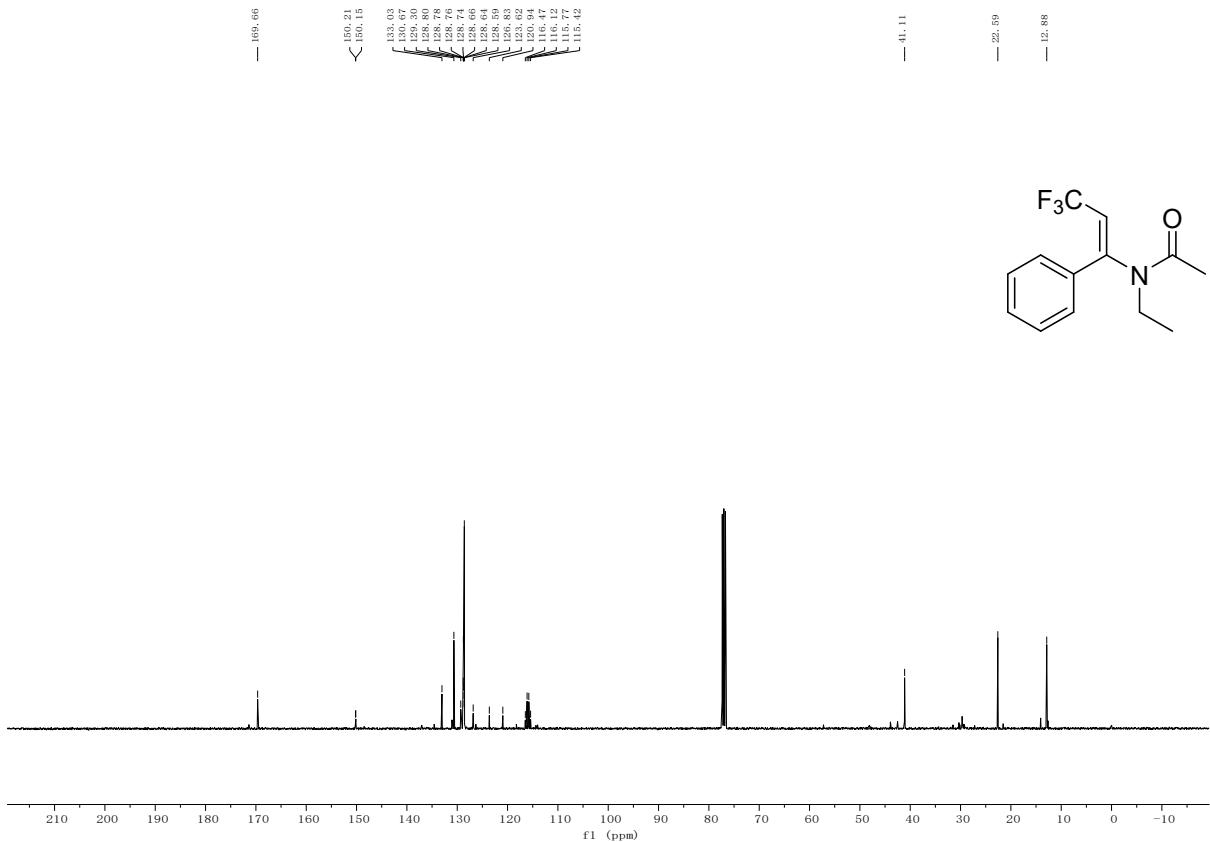
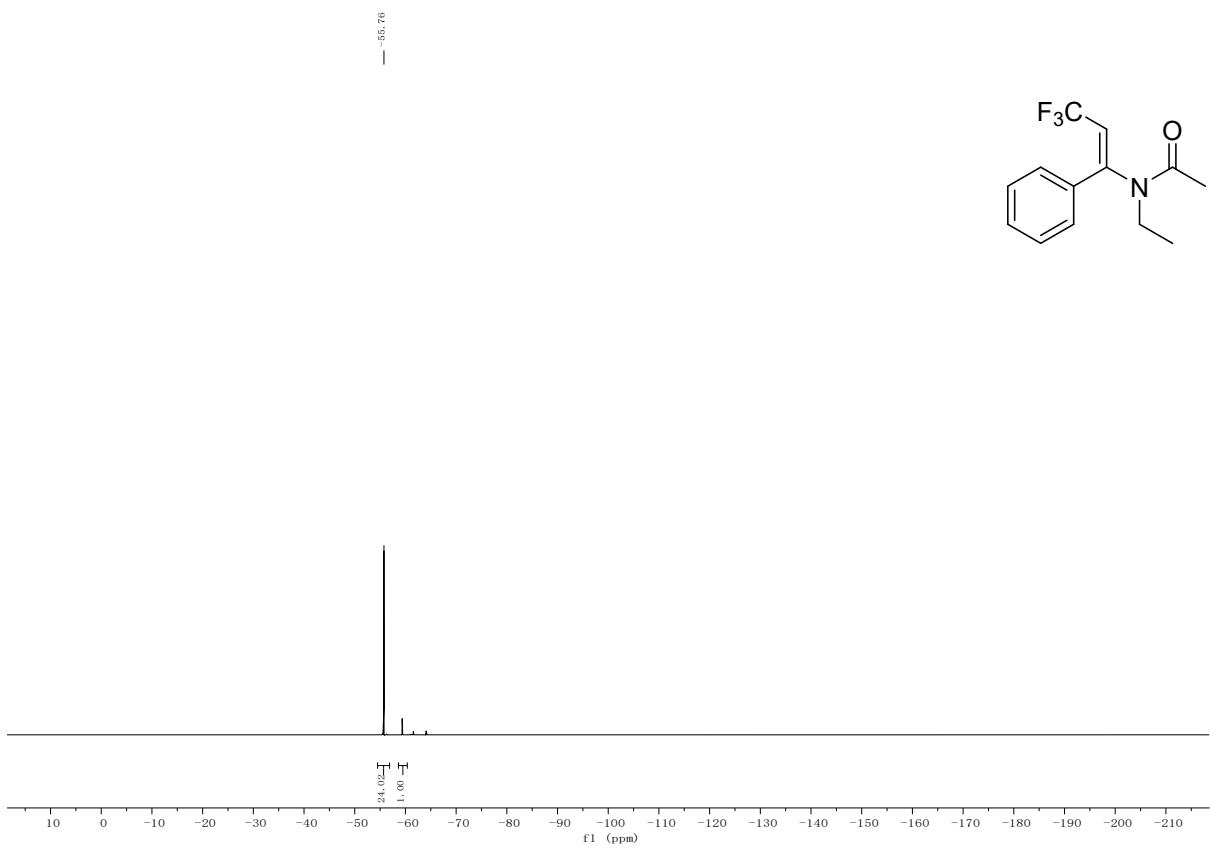
Product 3i: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



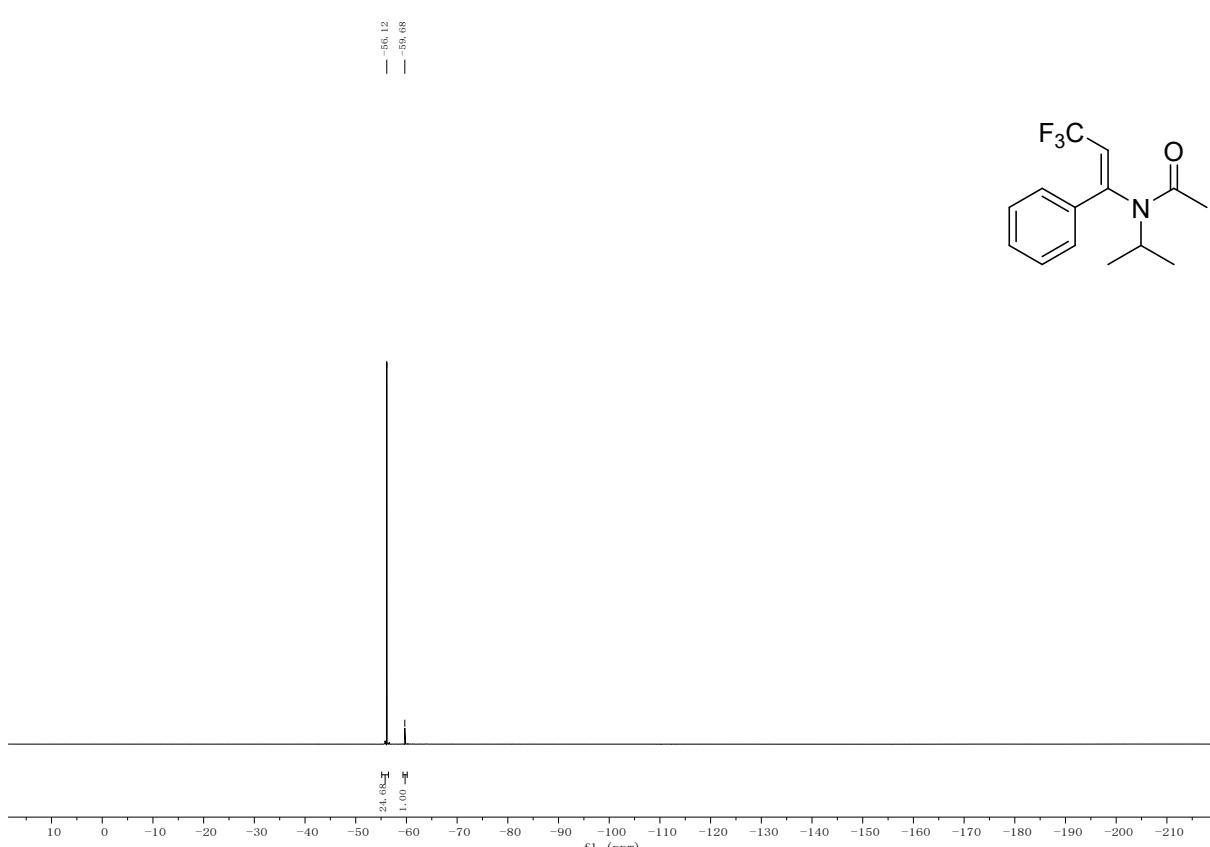
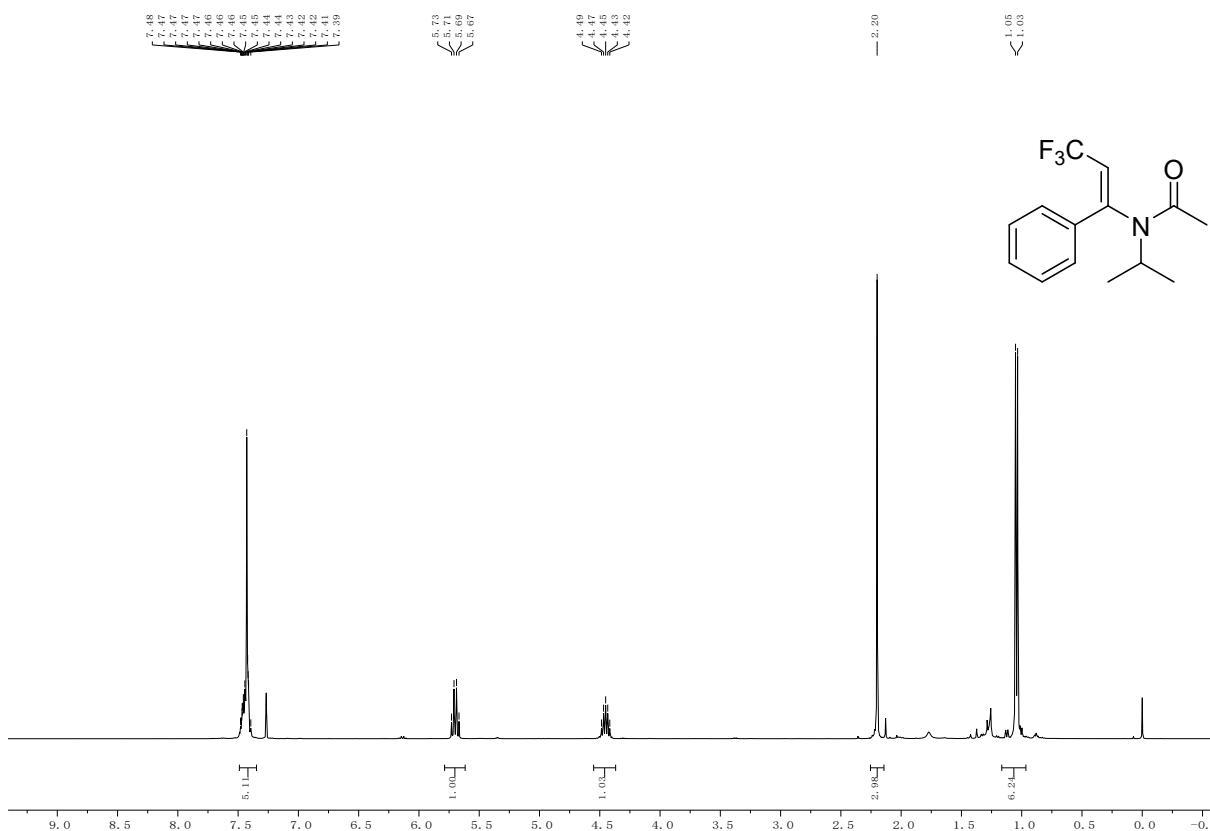


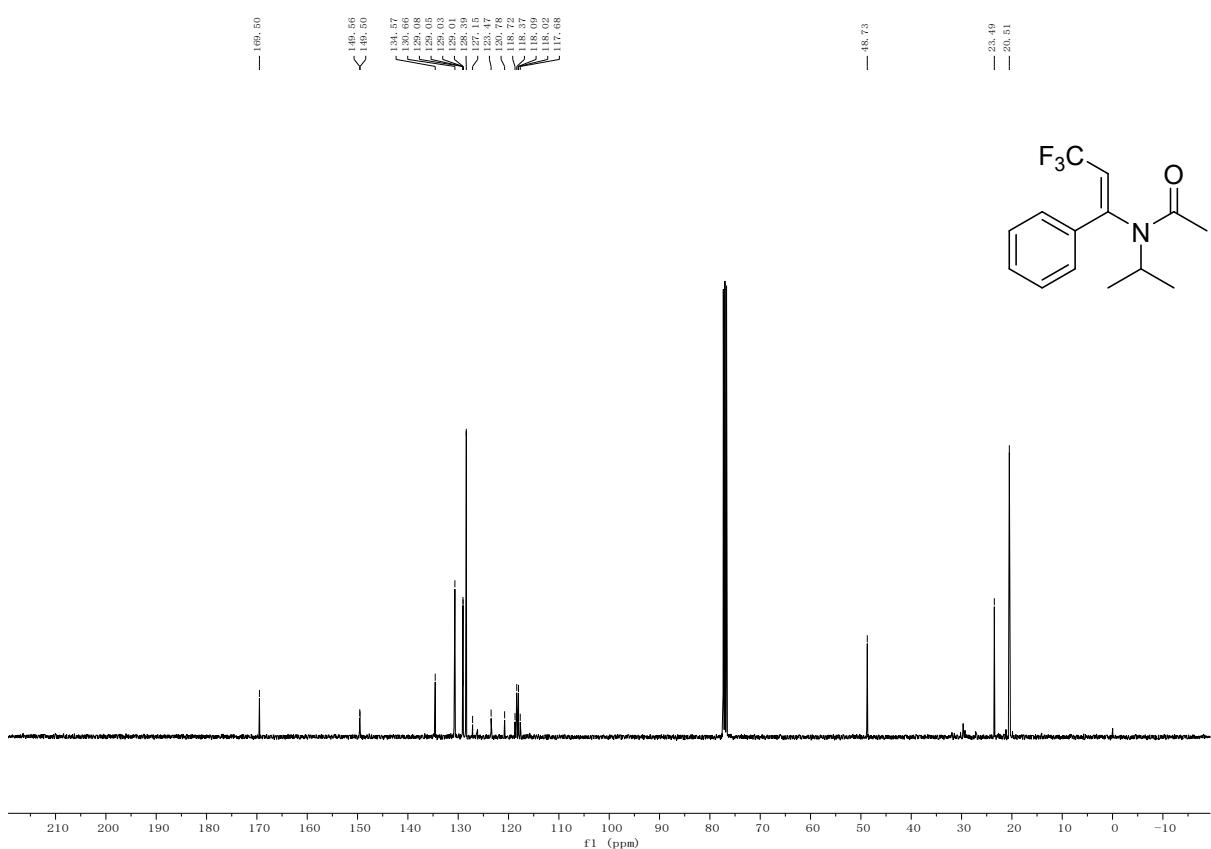
Product 3j: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



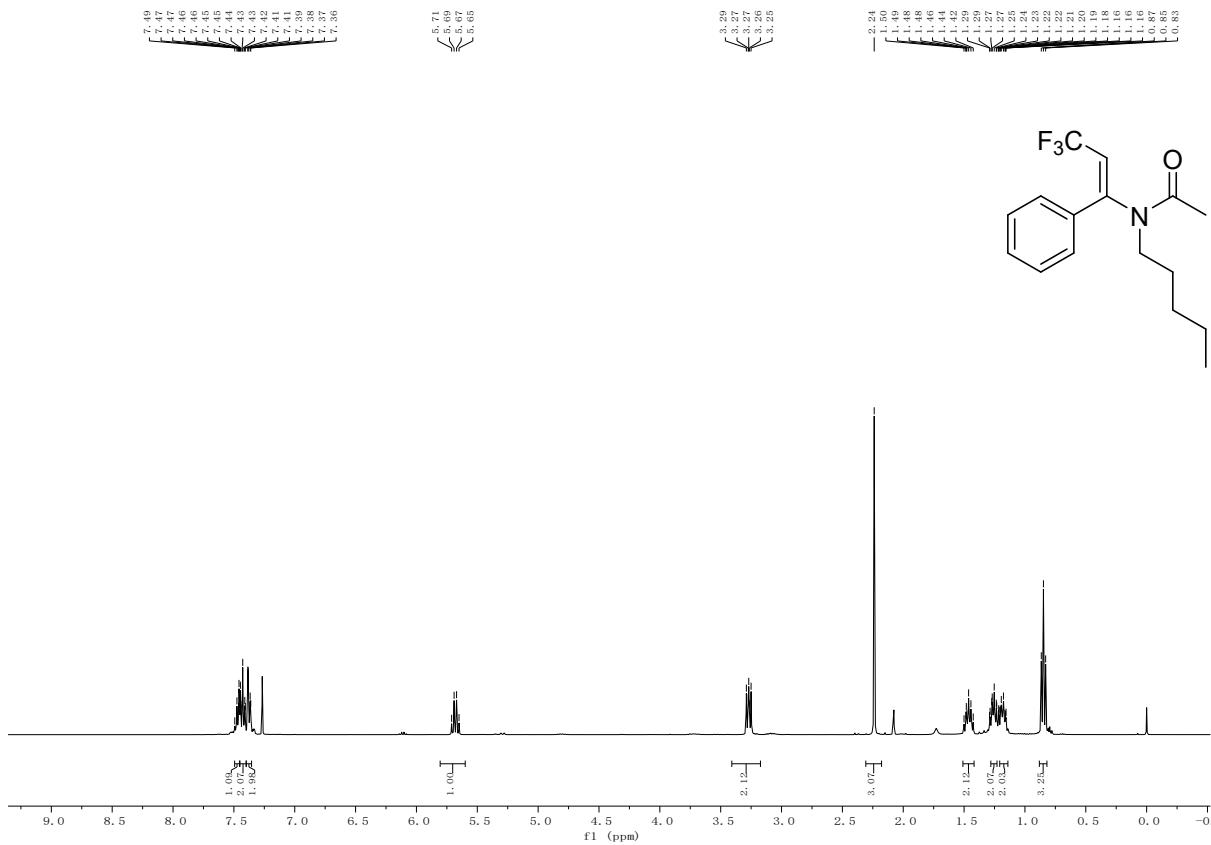


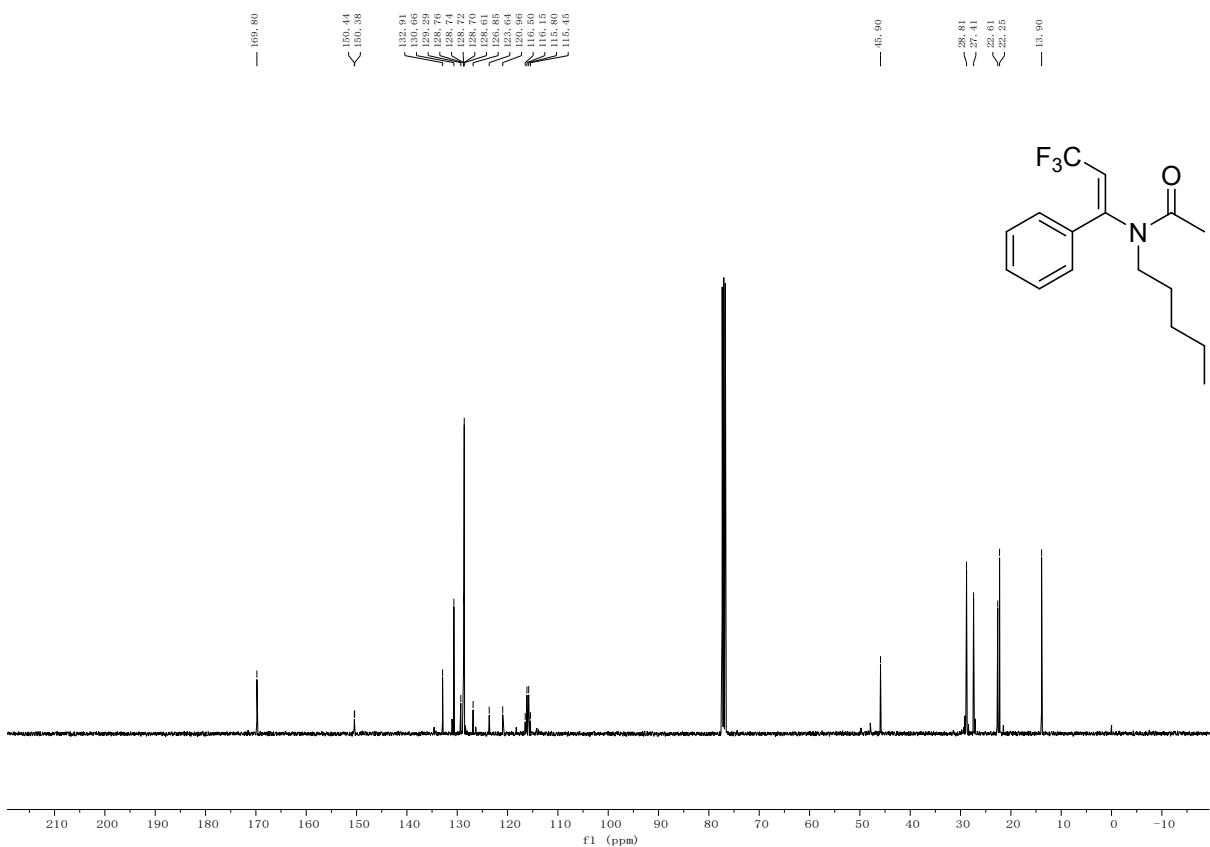
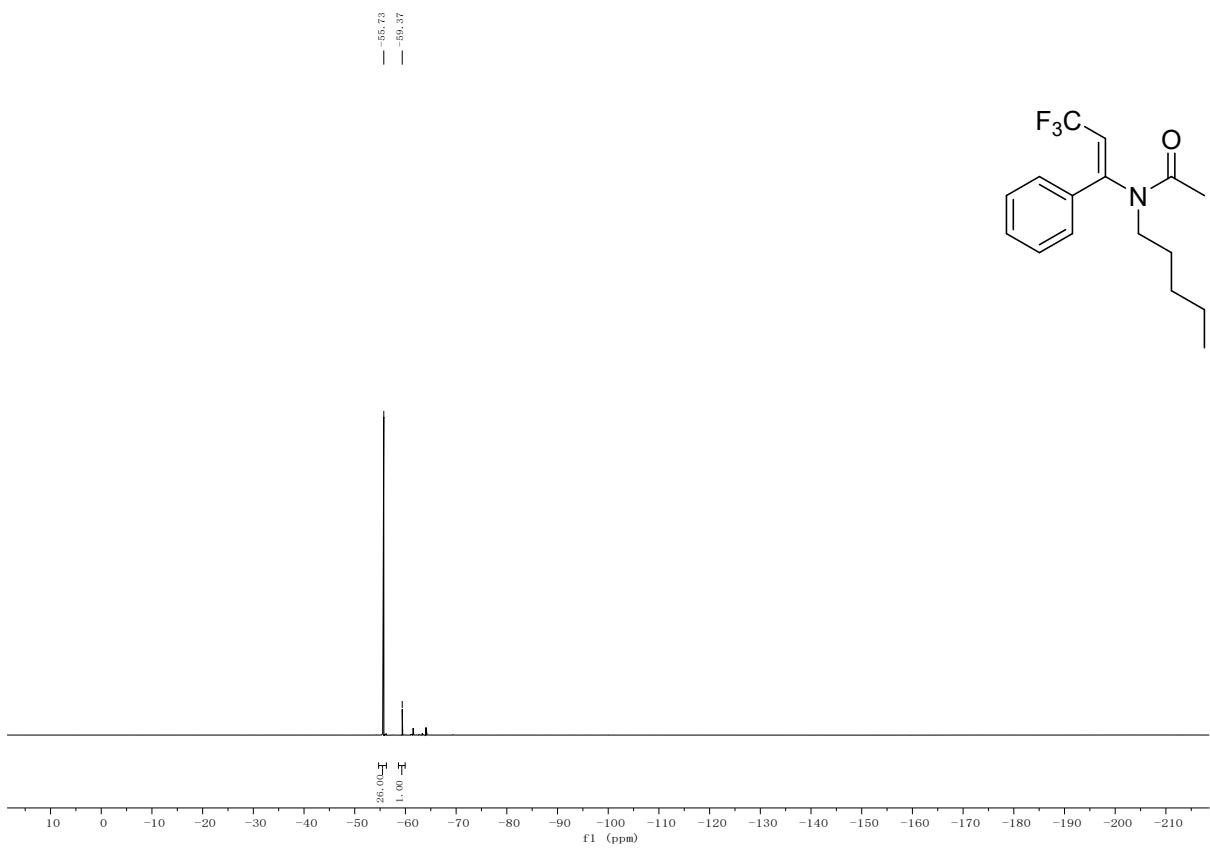
Product 3k: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



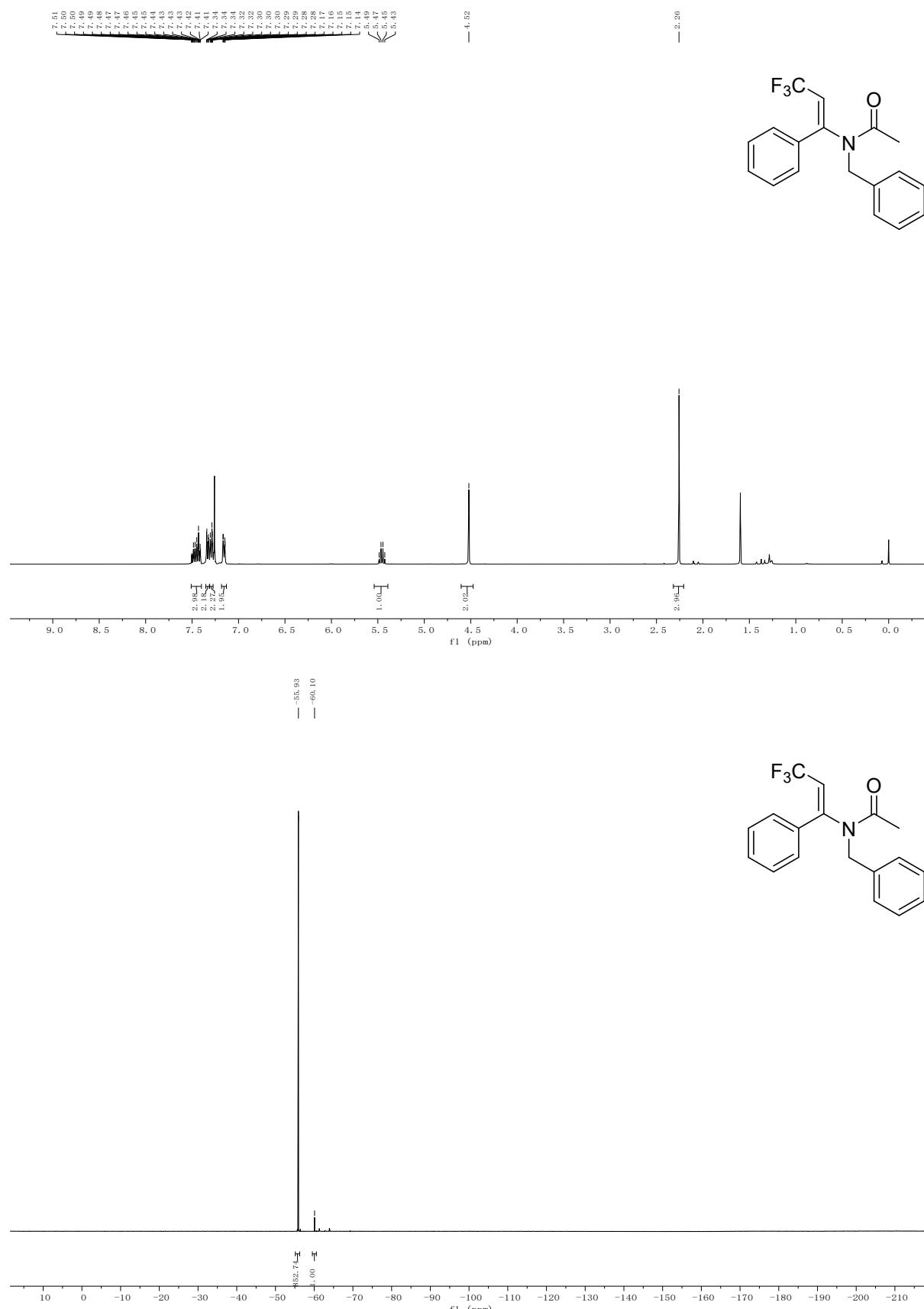


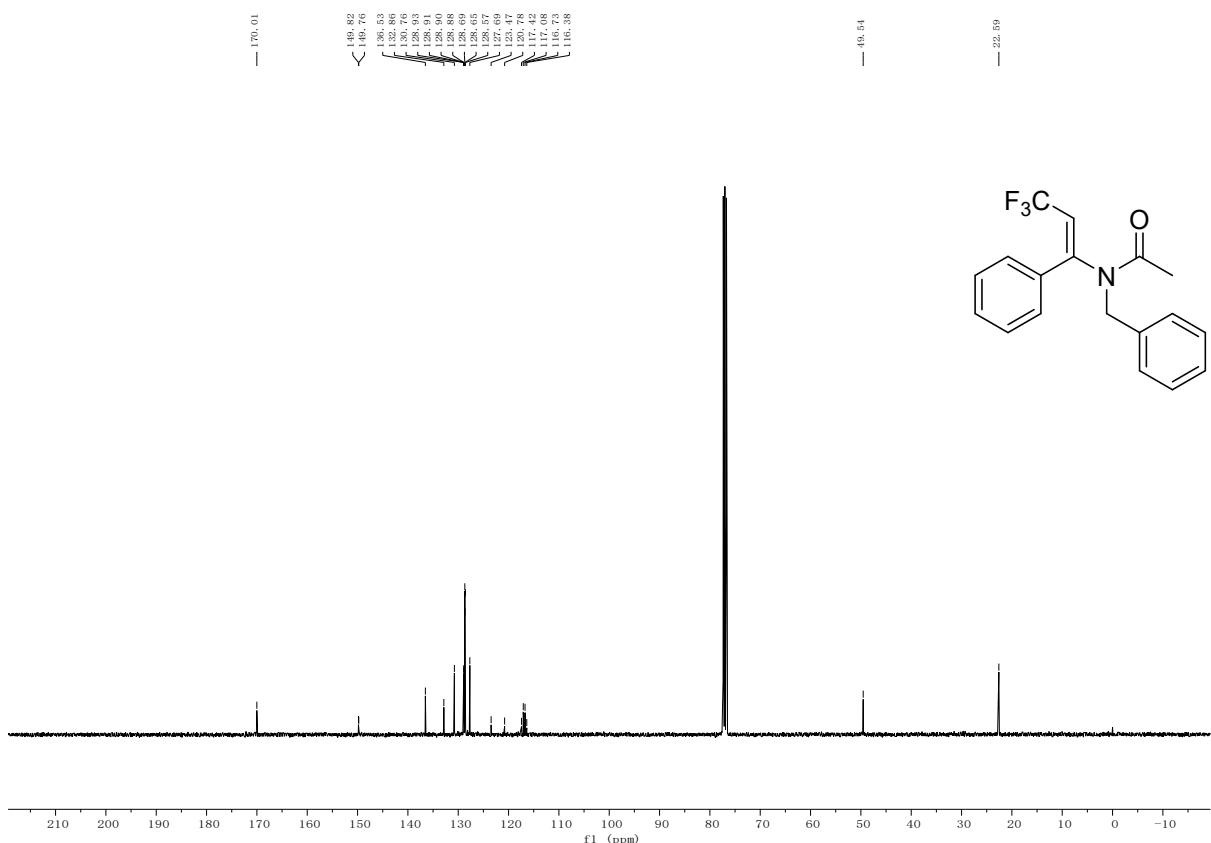
Product 3l: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



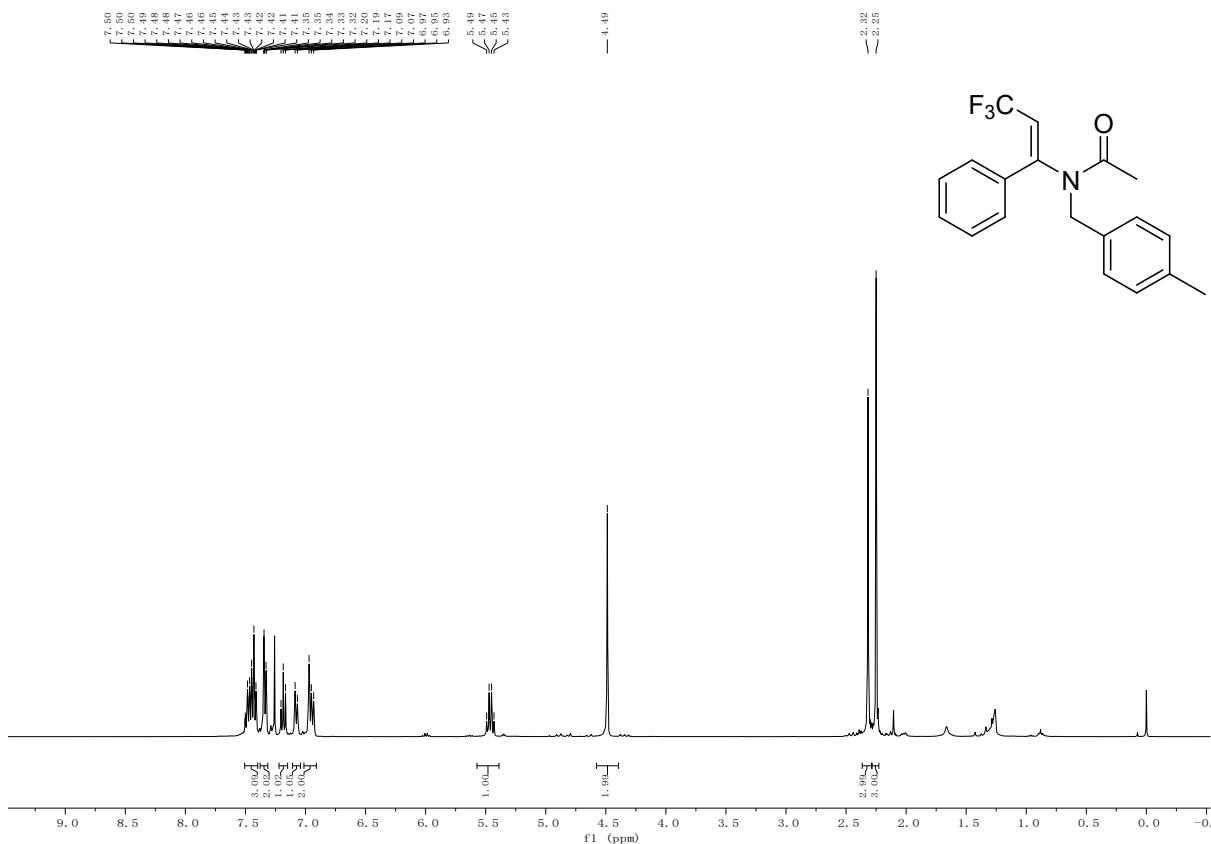


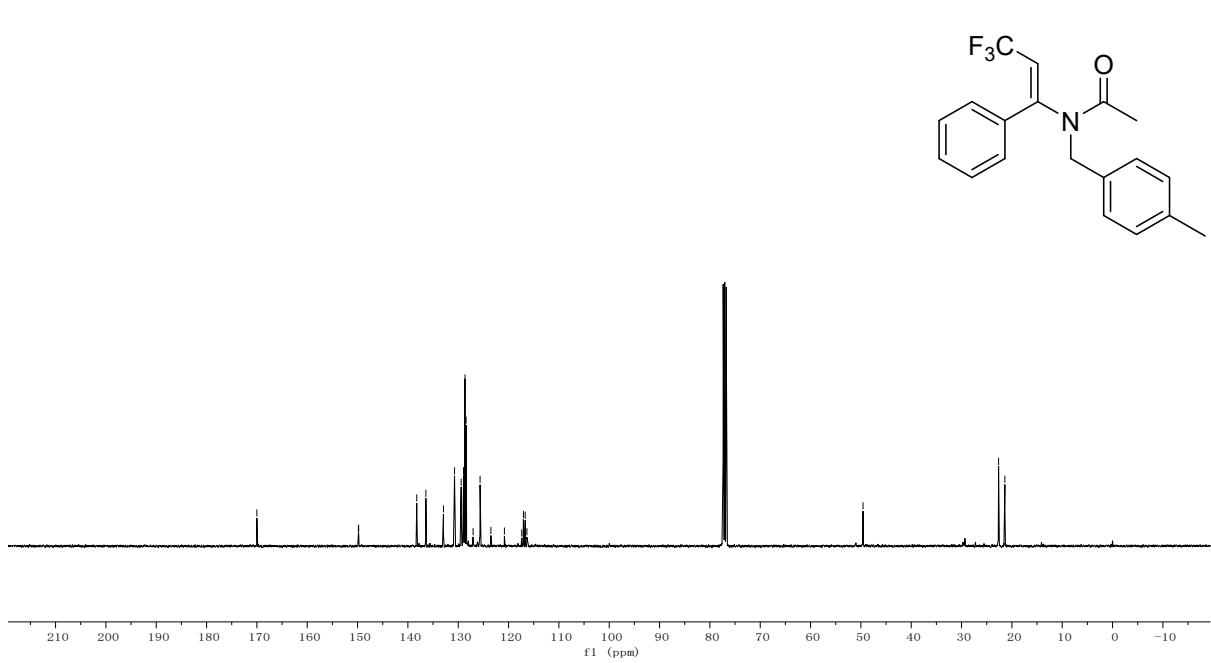
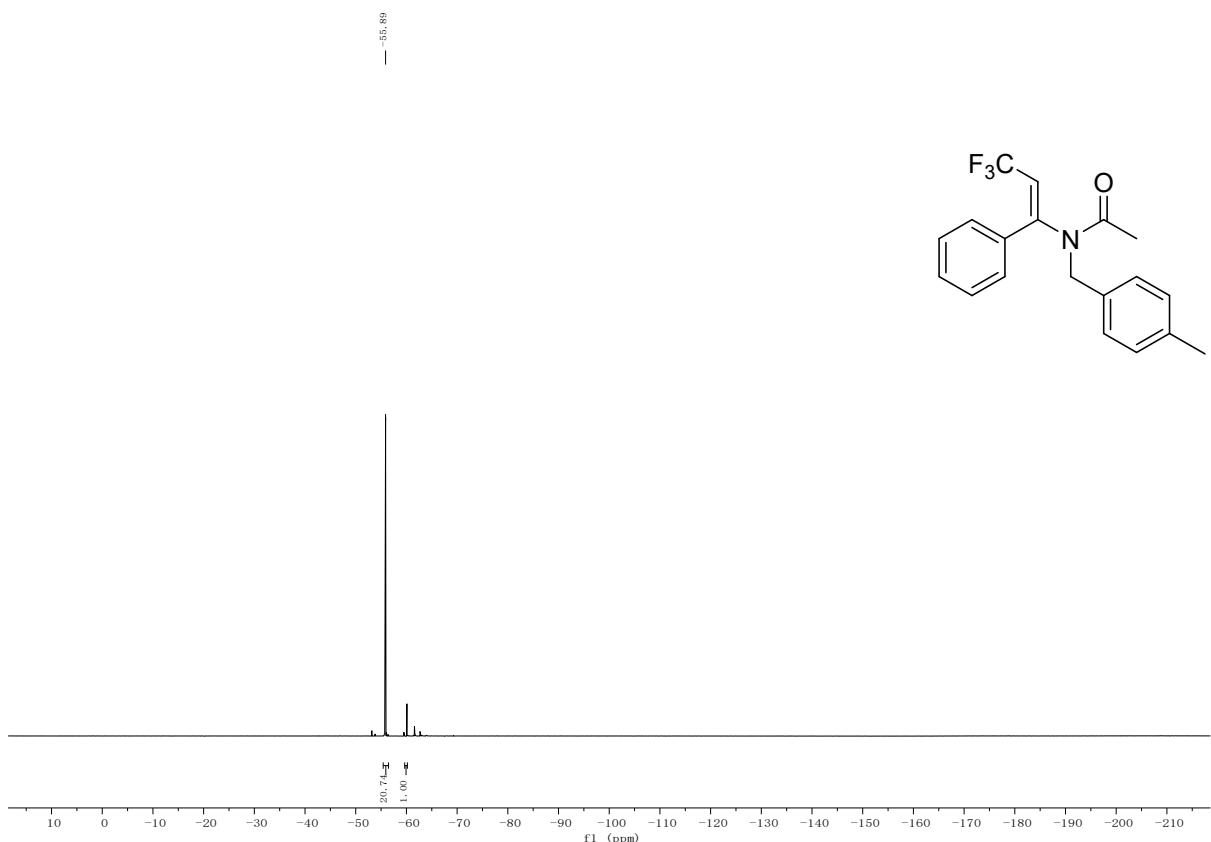
Product 3m: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



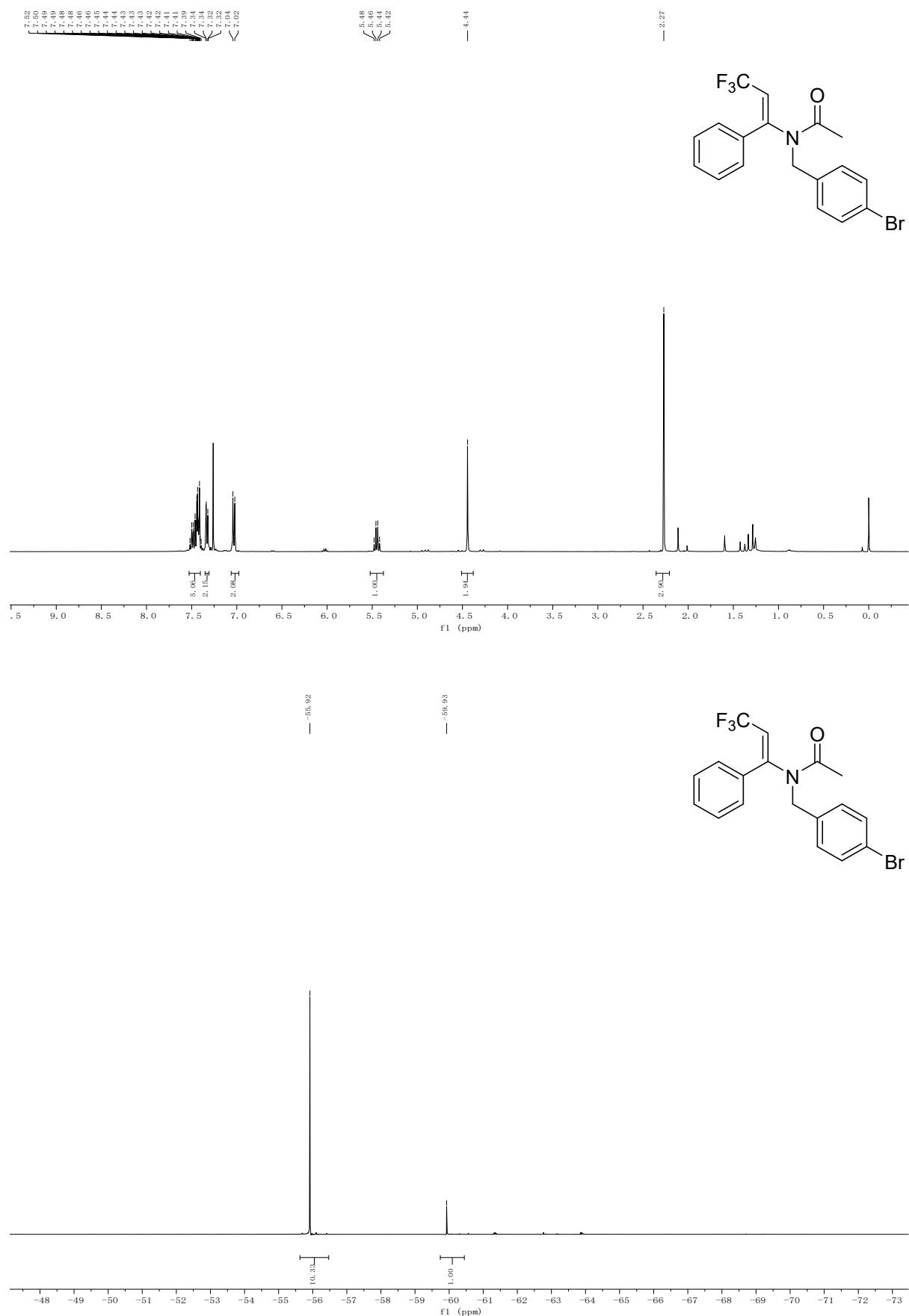


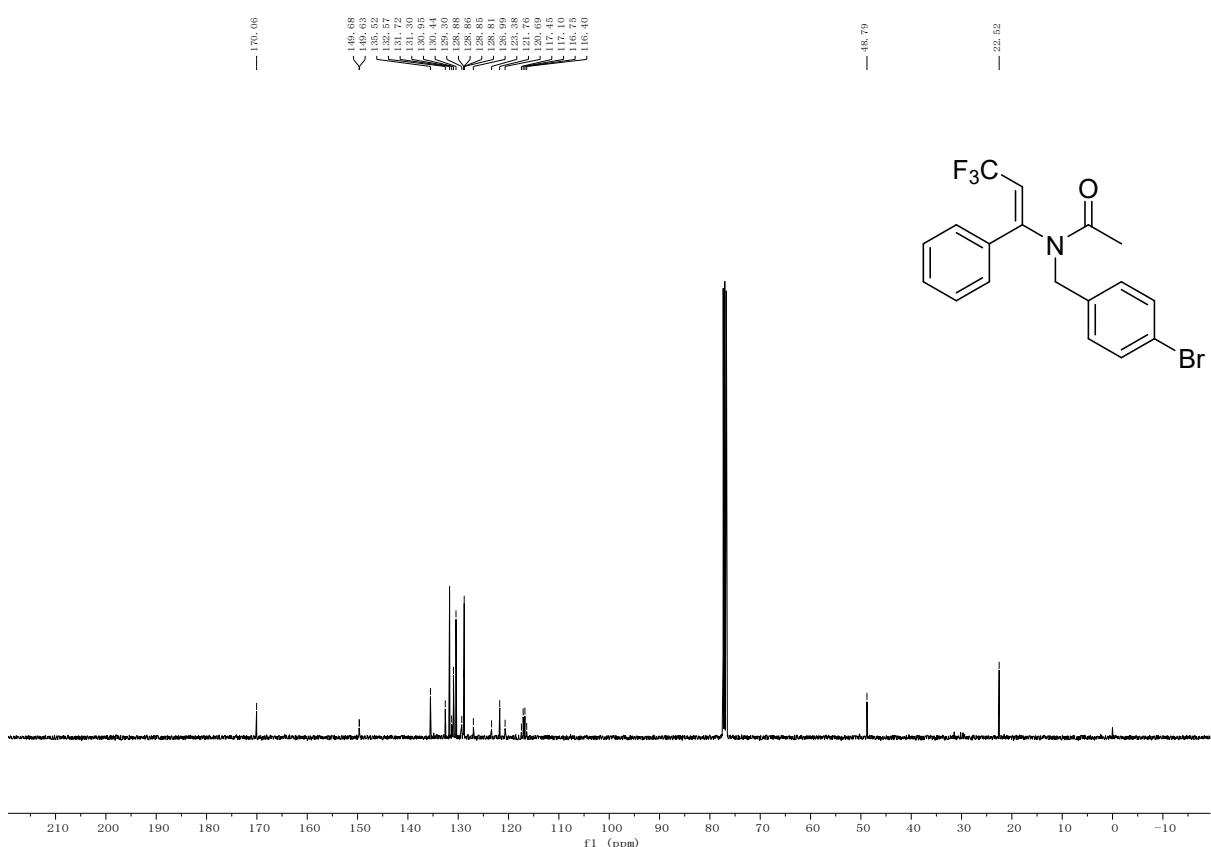
Product 3n: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



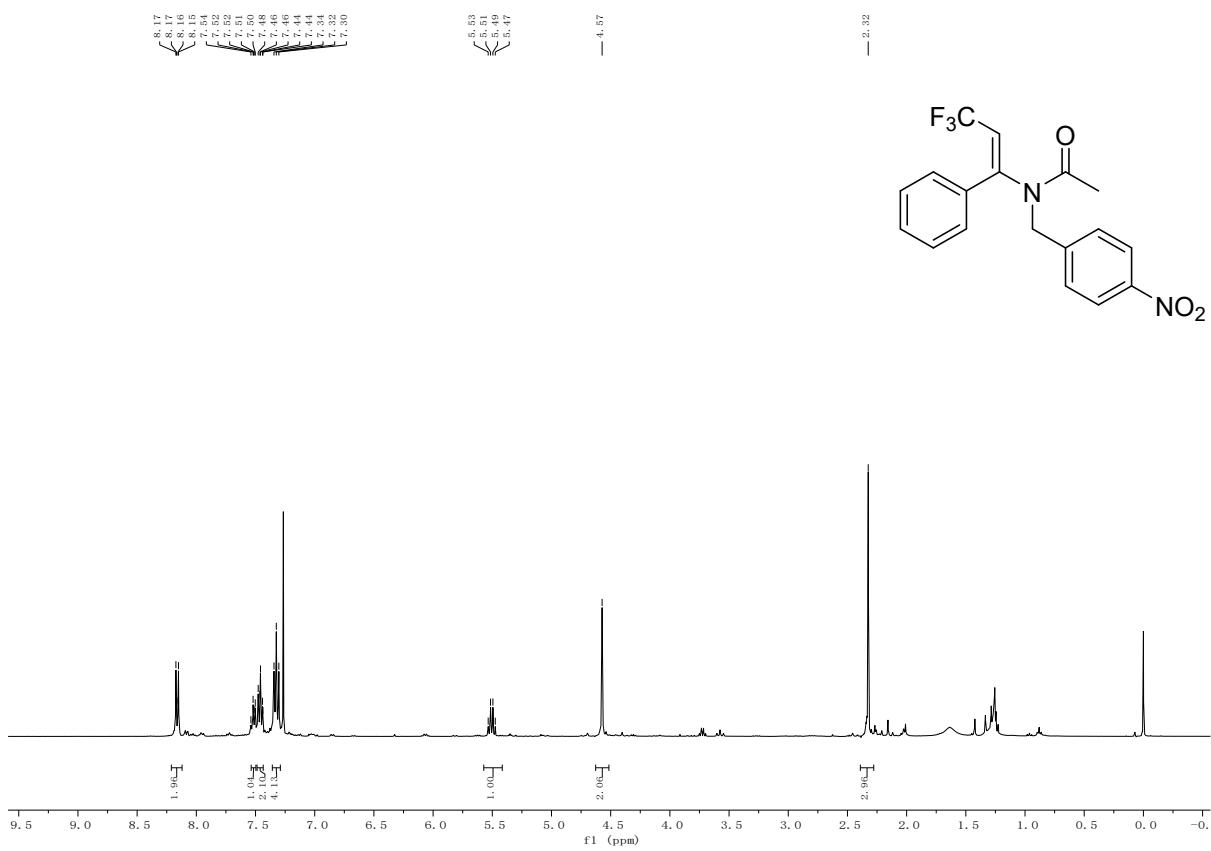


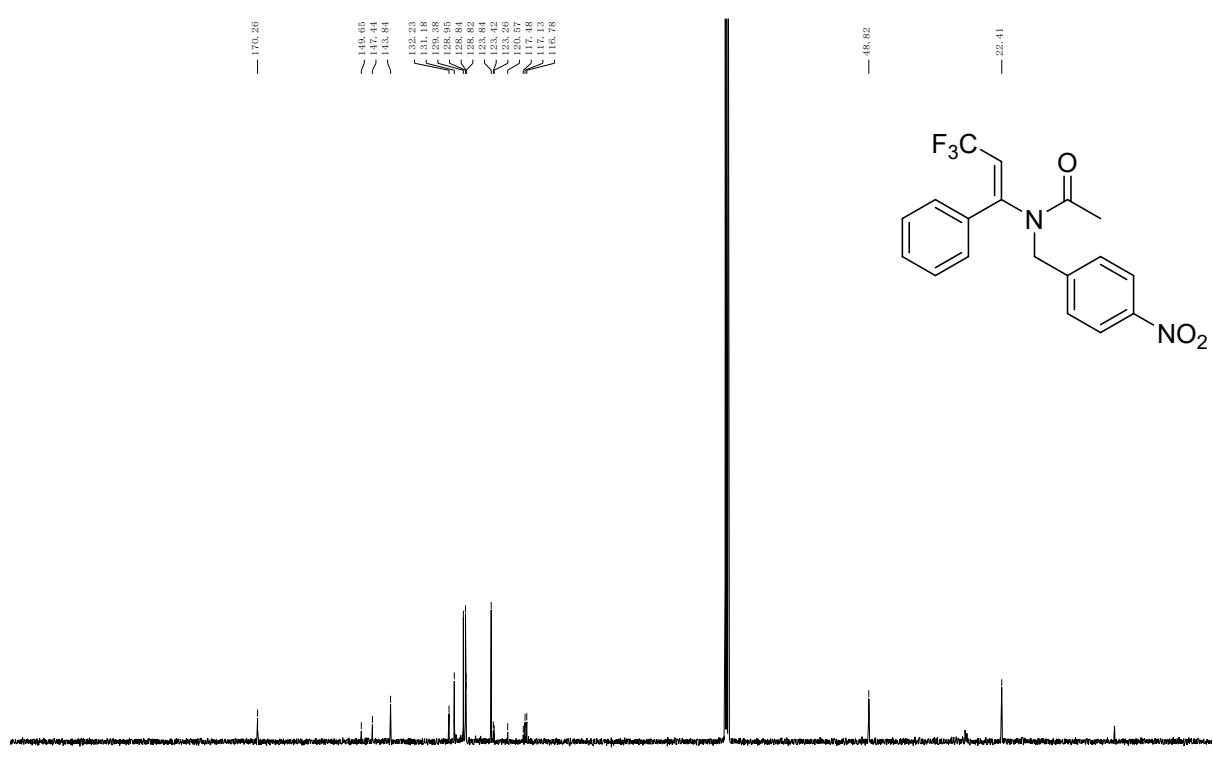
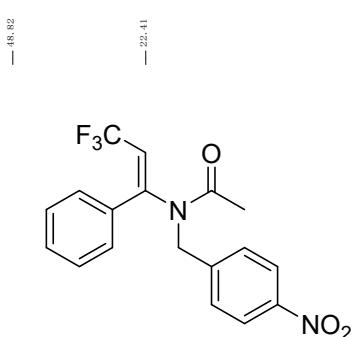
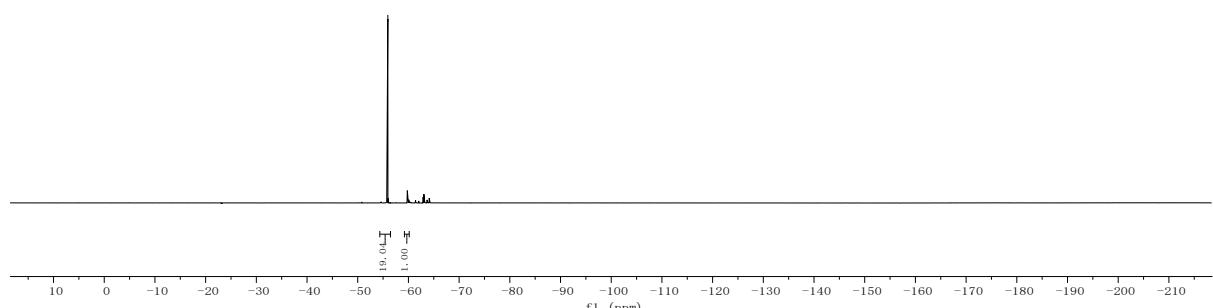
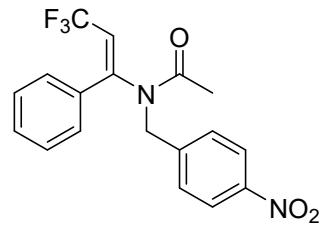
Product 3o: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



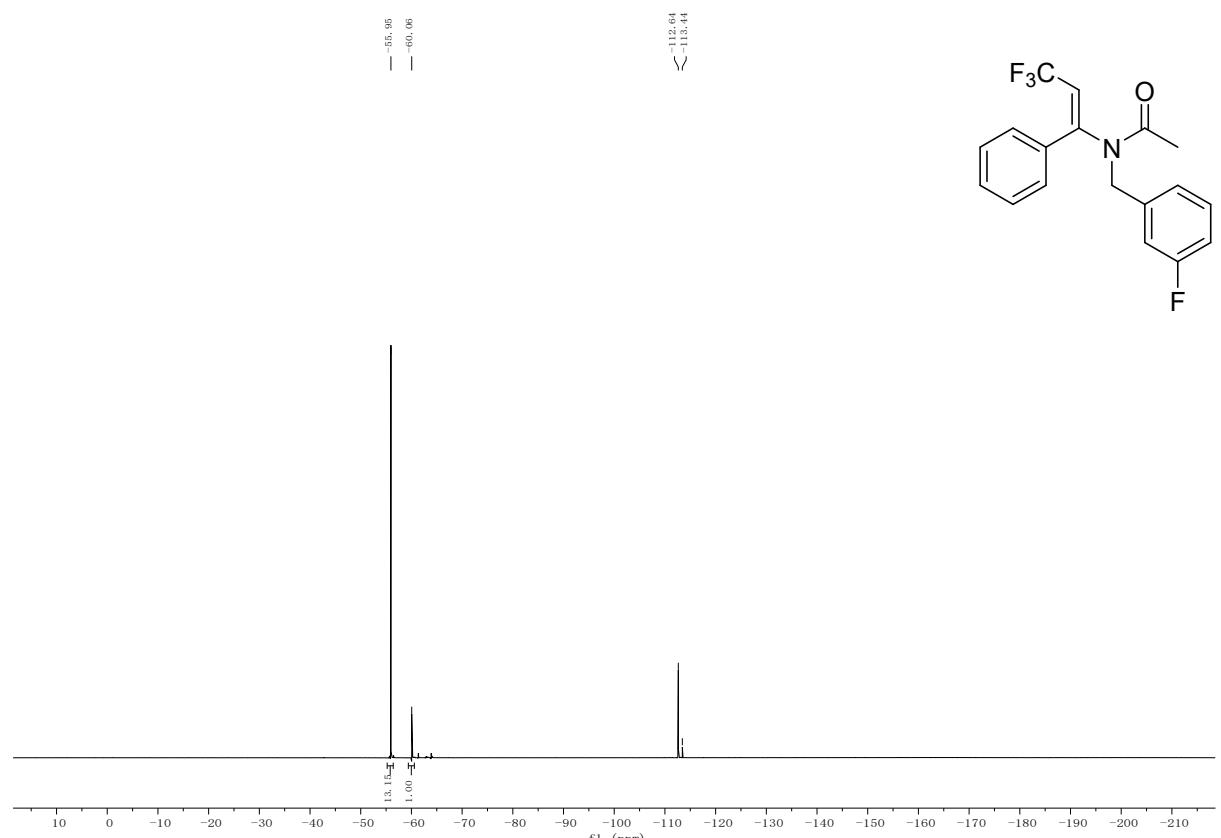
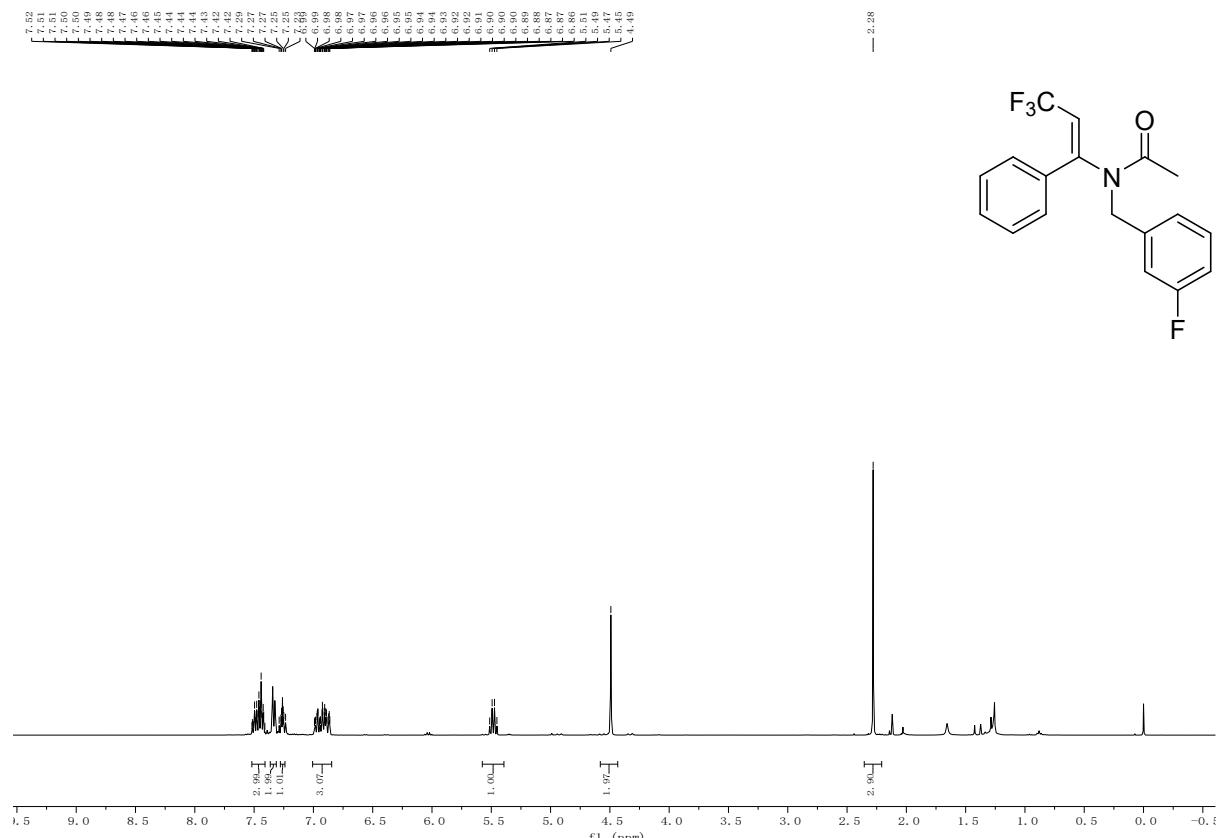


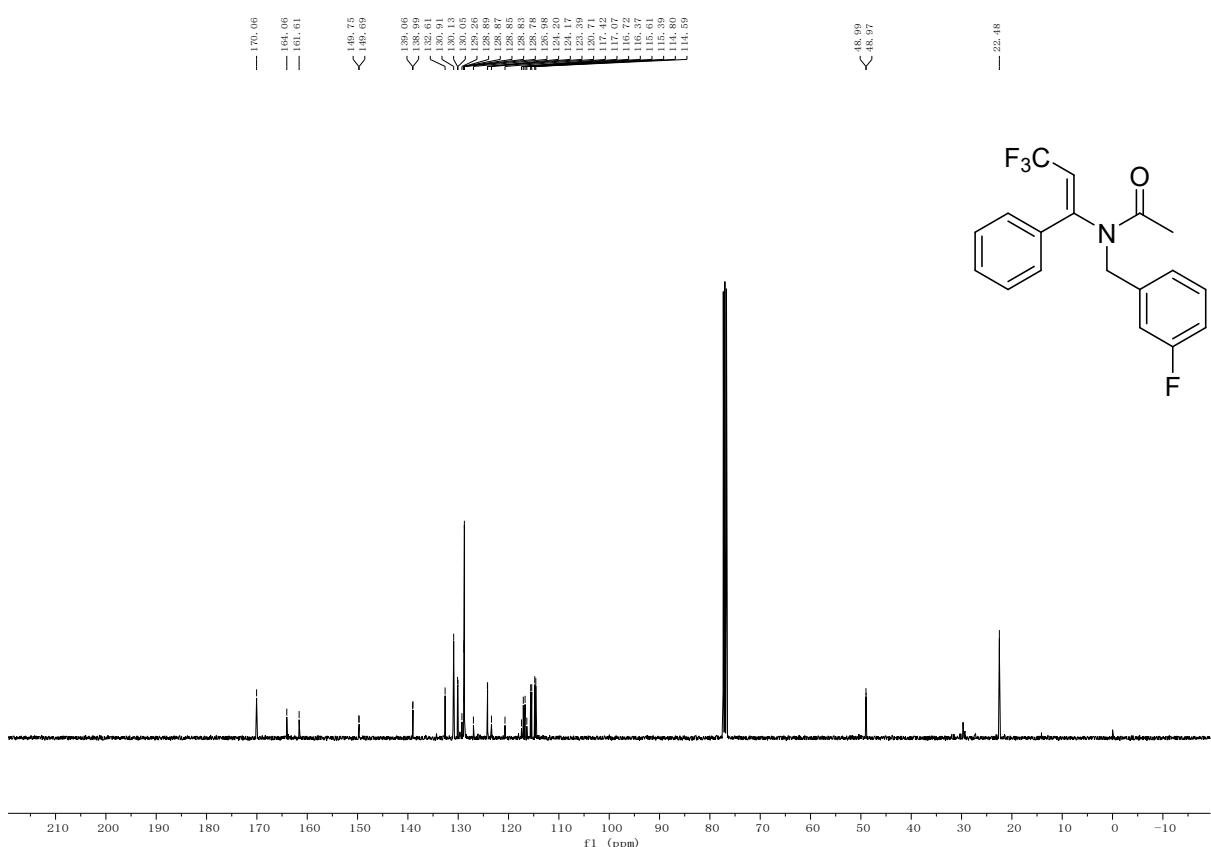
Product 3p: ¹H NMR (400 MHz, CDCl_3), ¹⁹F NMR (376 MHz, CDCl_3) and ¹³C NMR (100 MHz, CDCl_3).



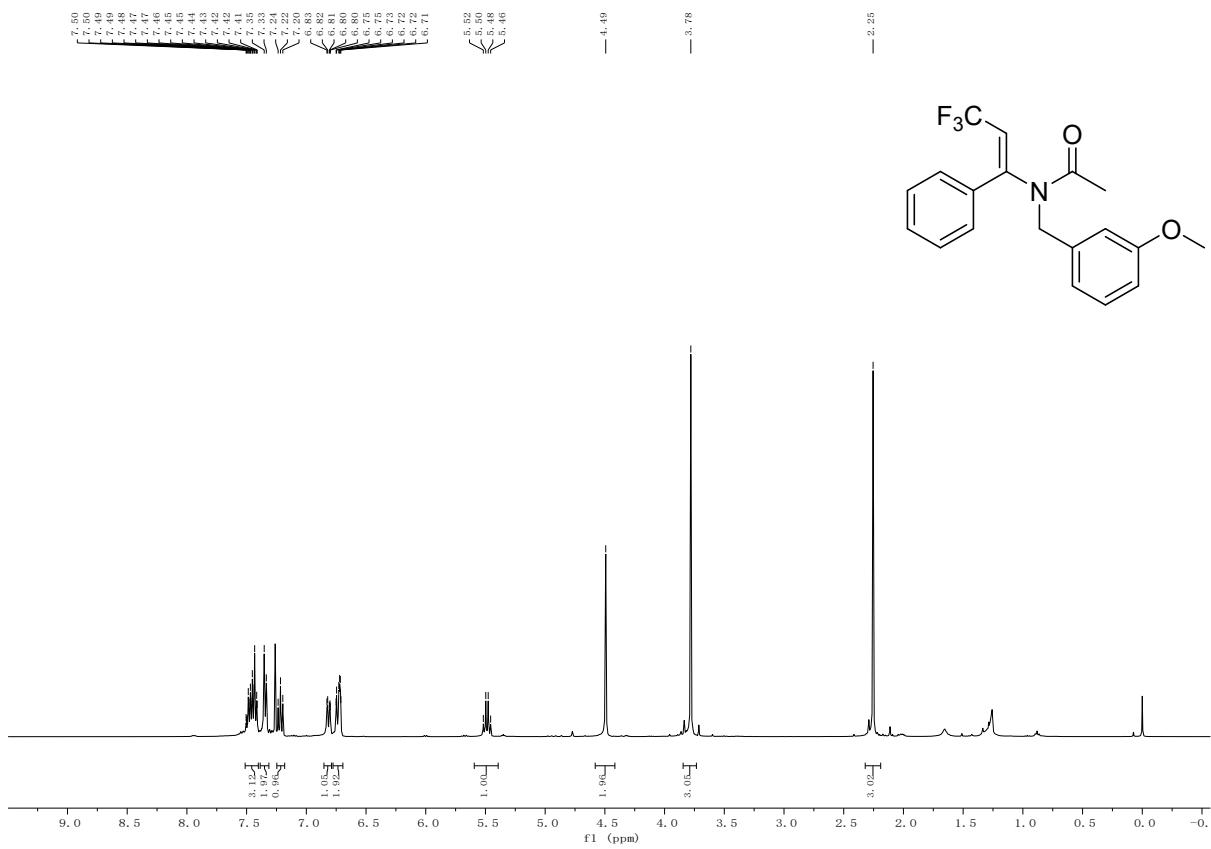


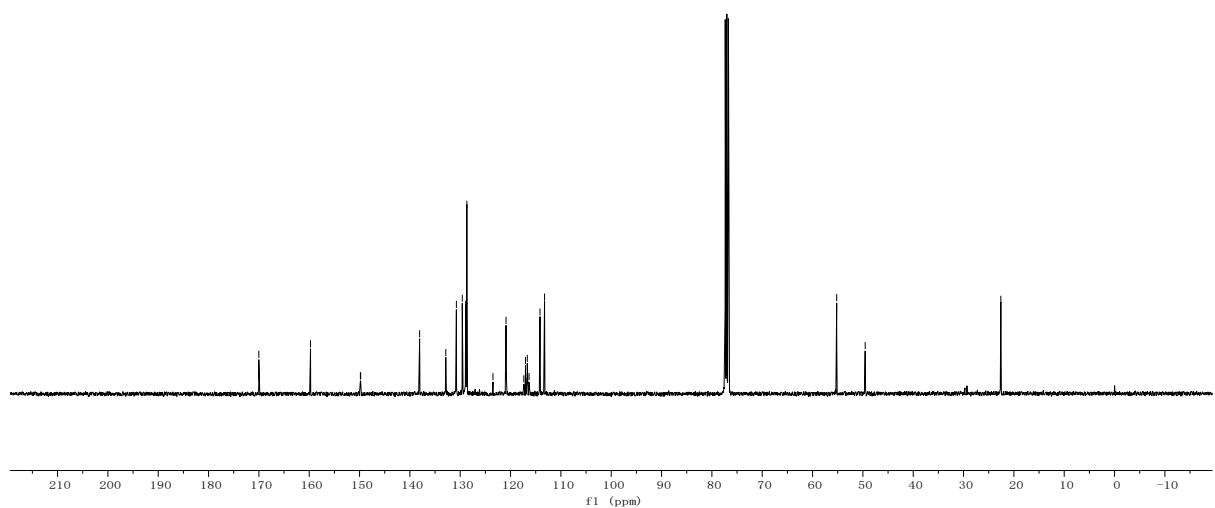
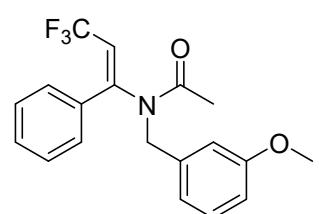
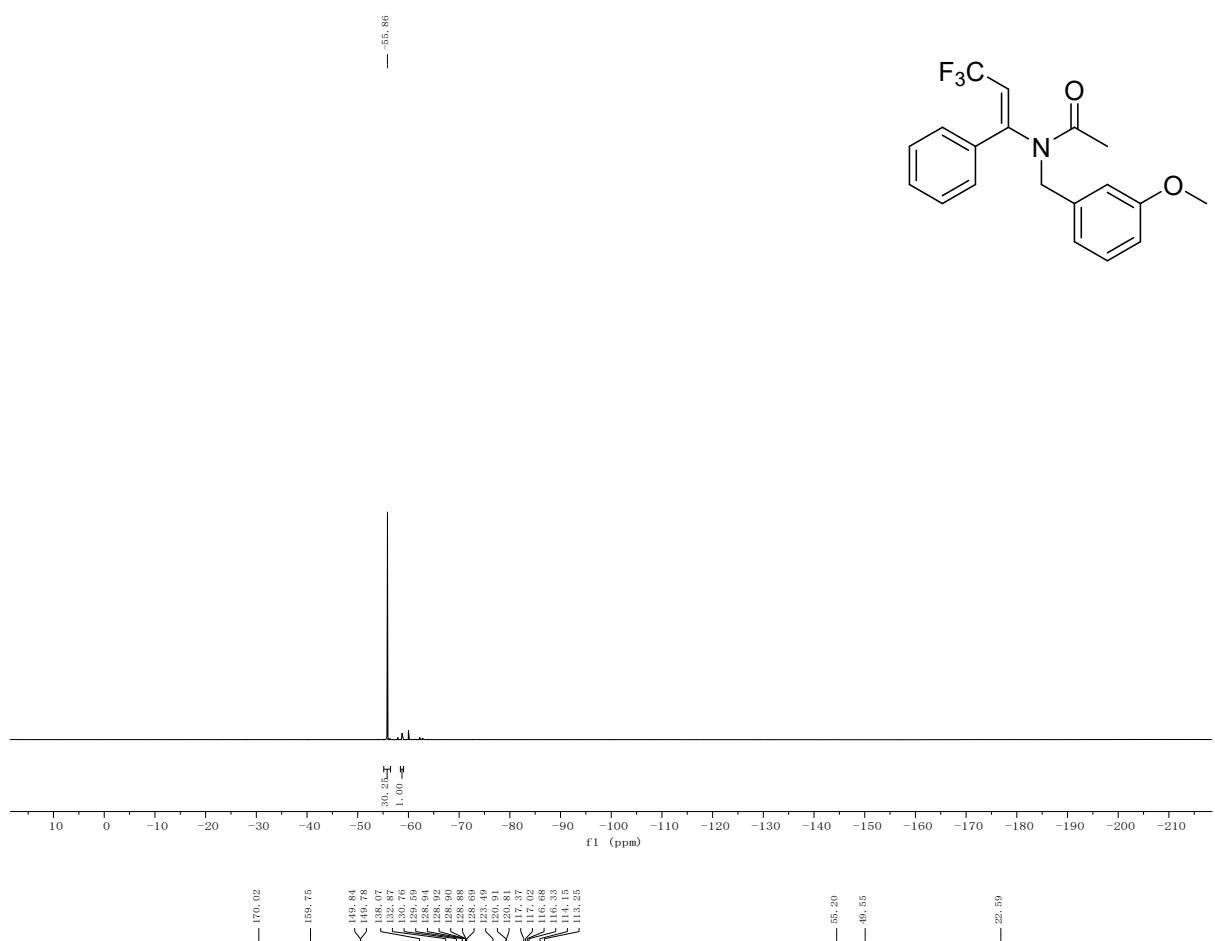
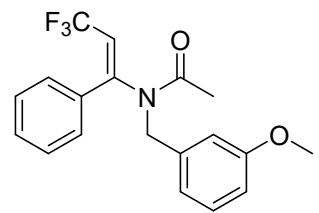
Product 3q:¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



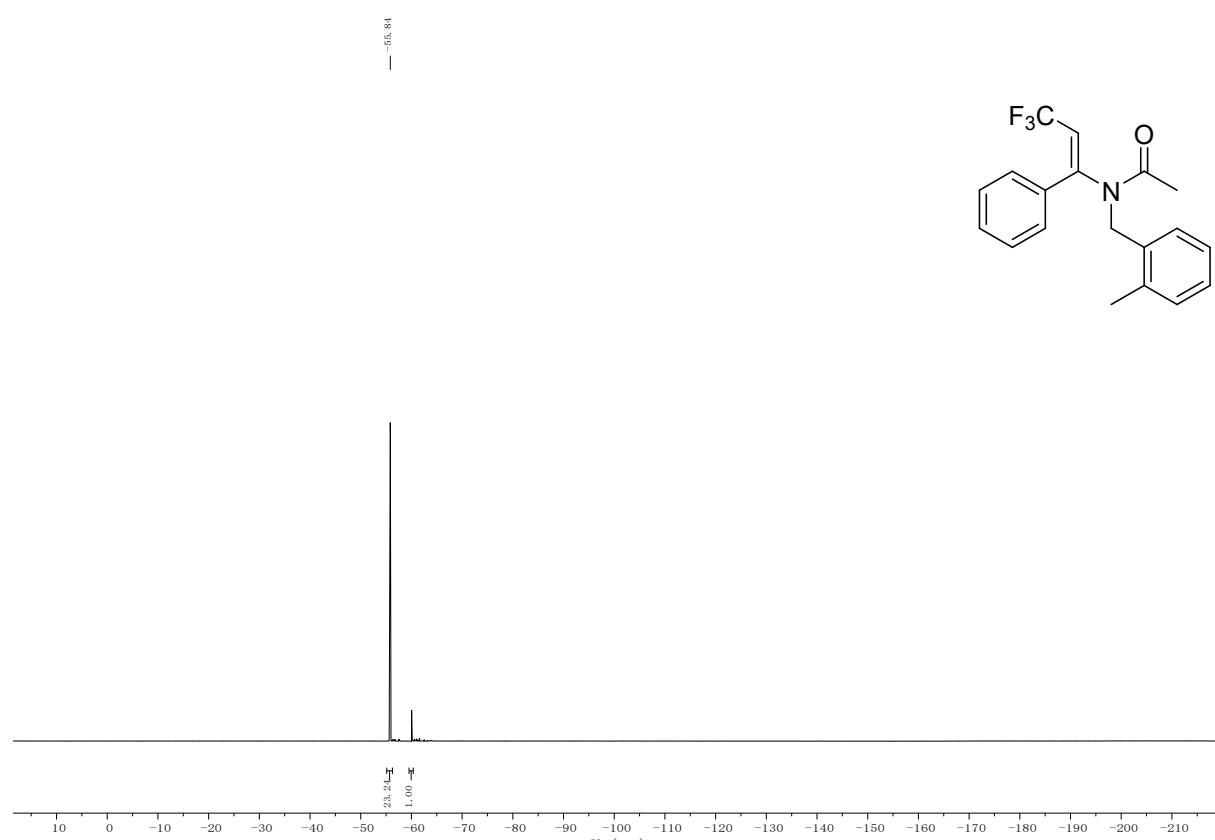
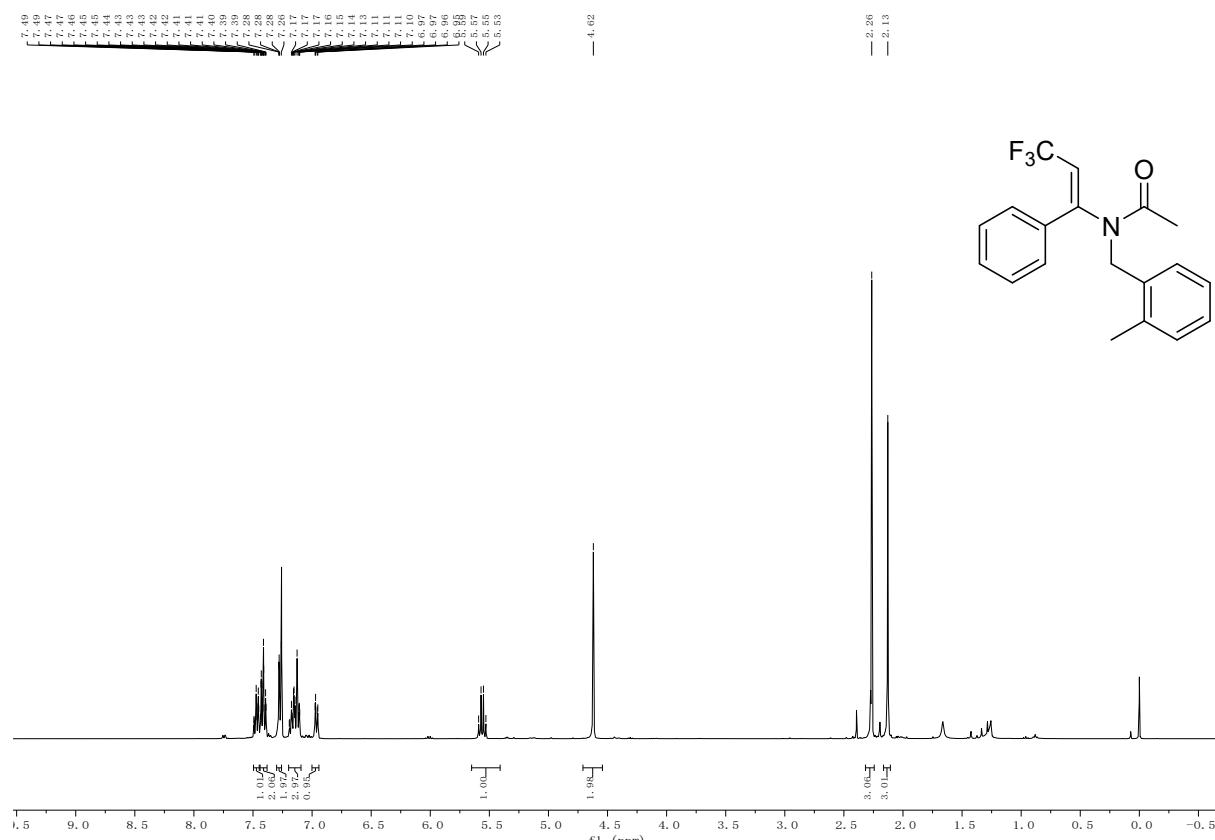


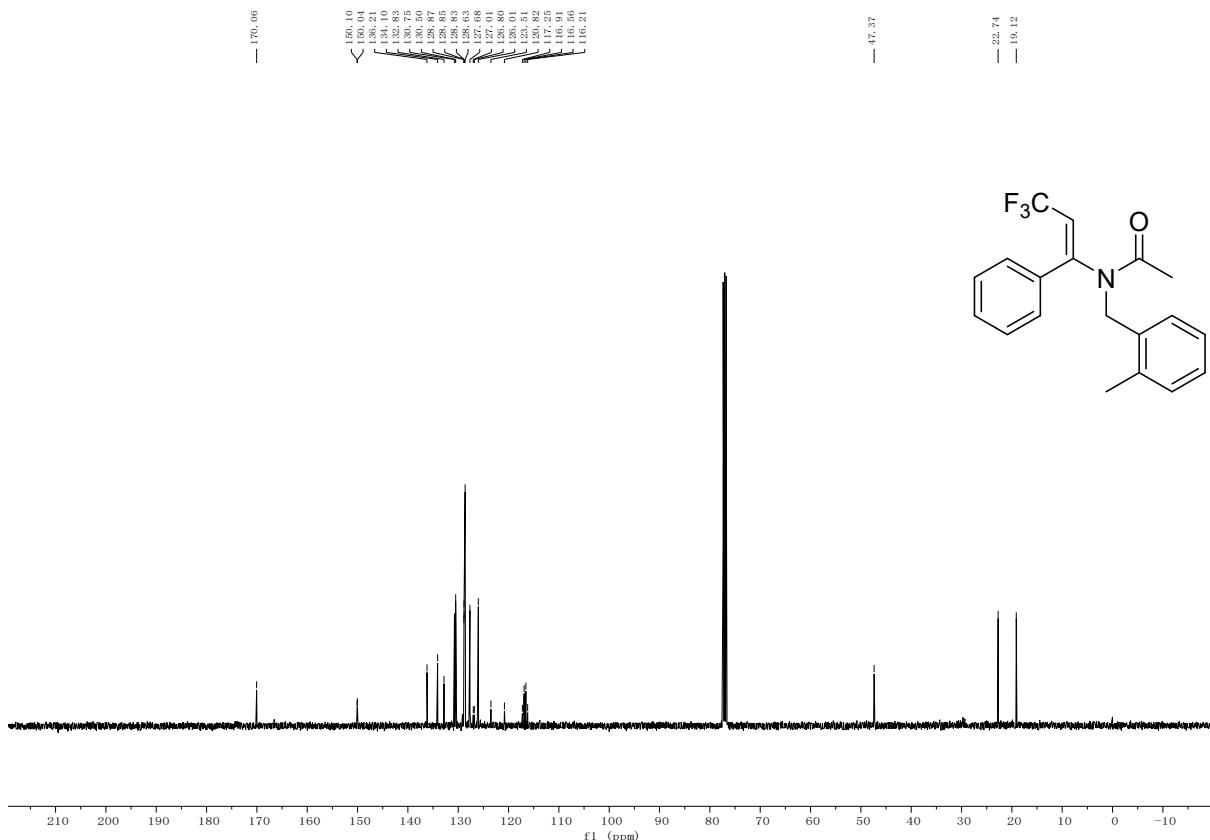
Product 3r: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



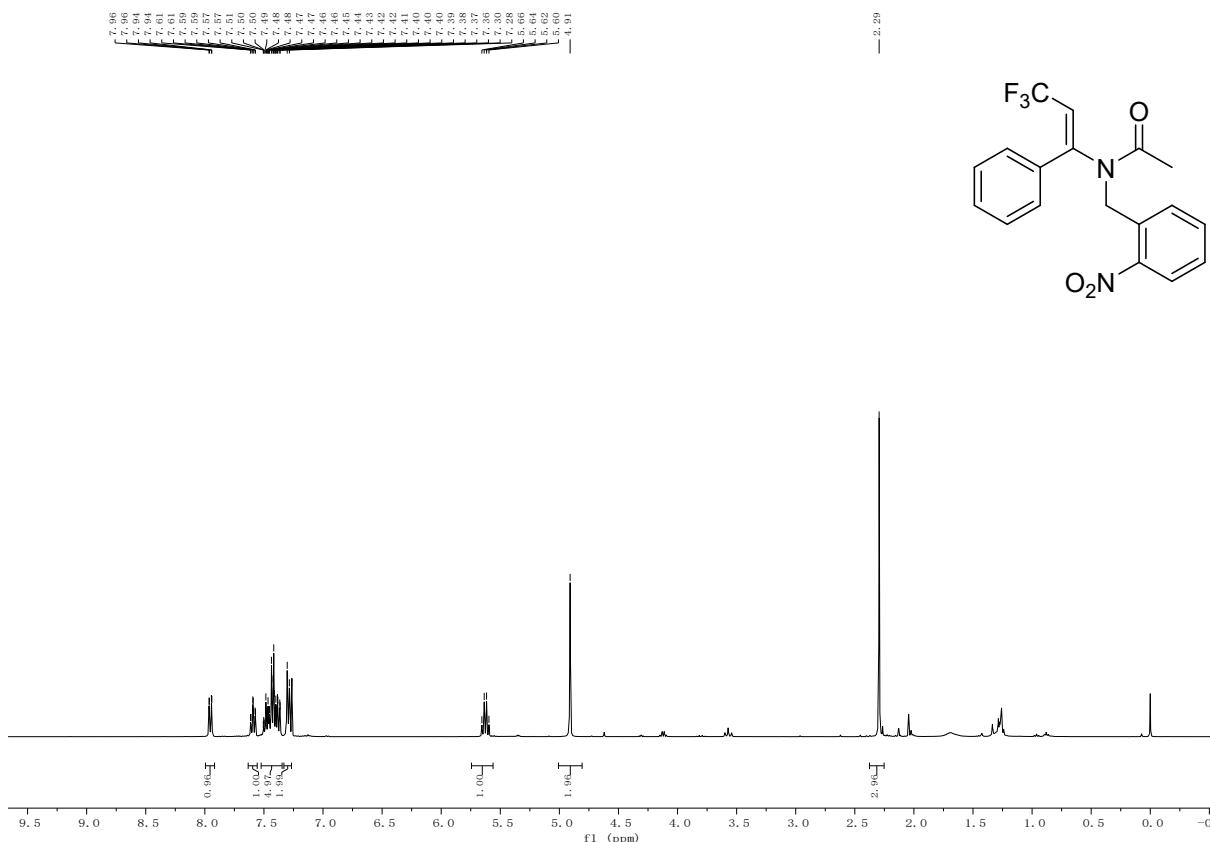


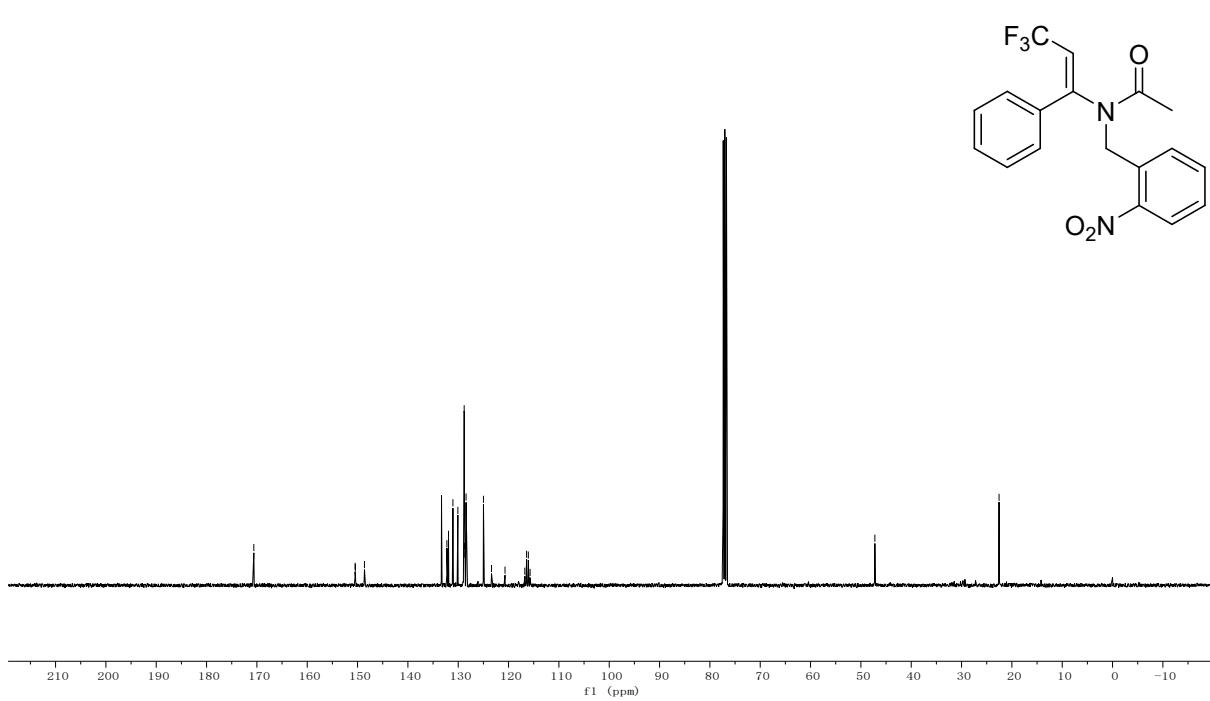
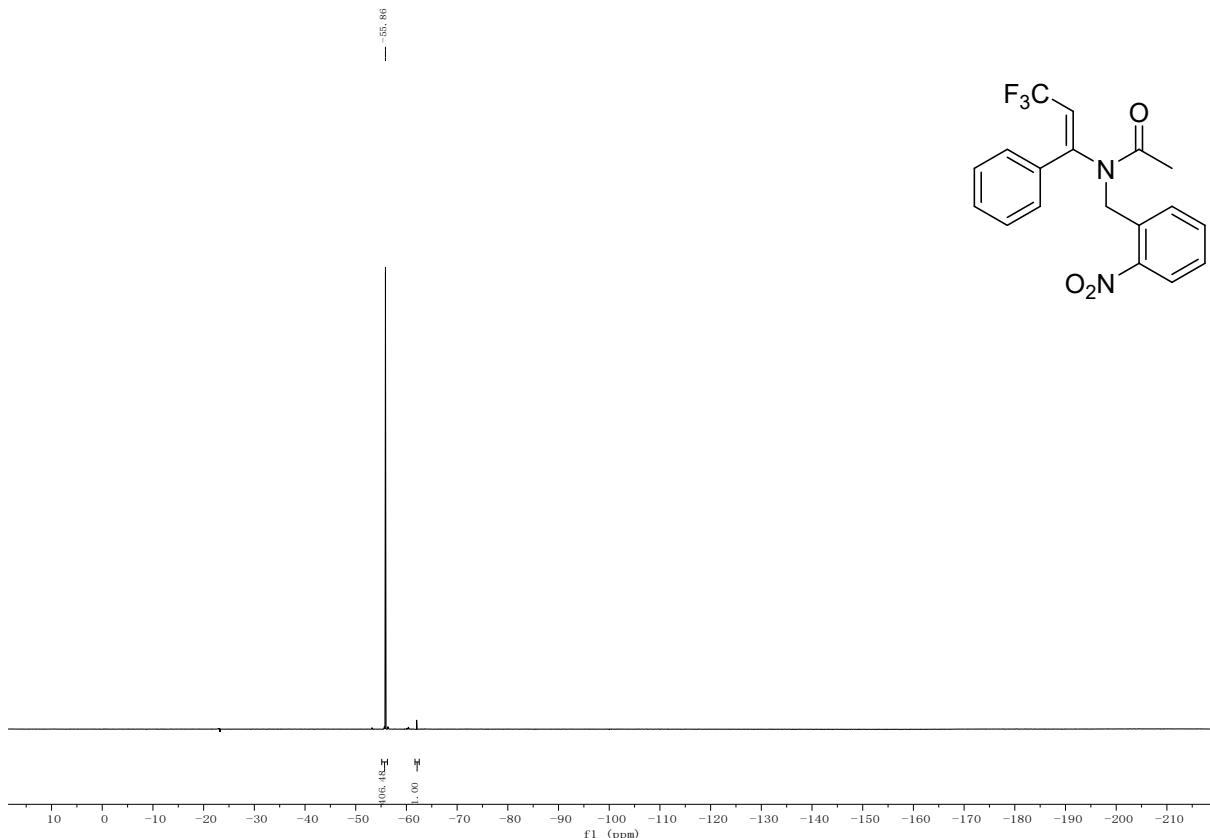
Product 3s: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



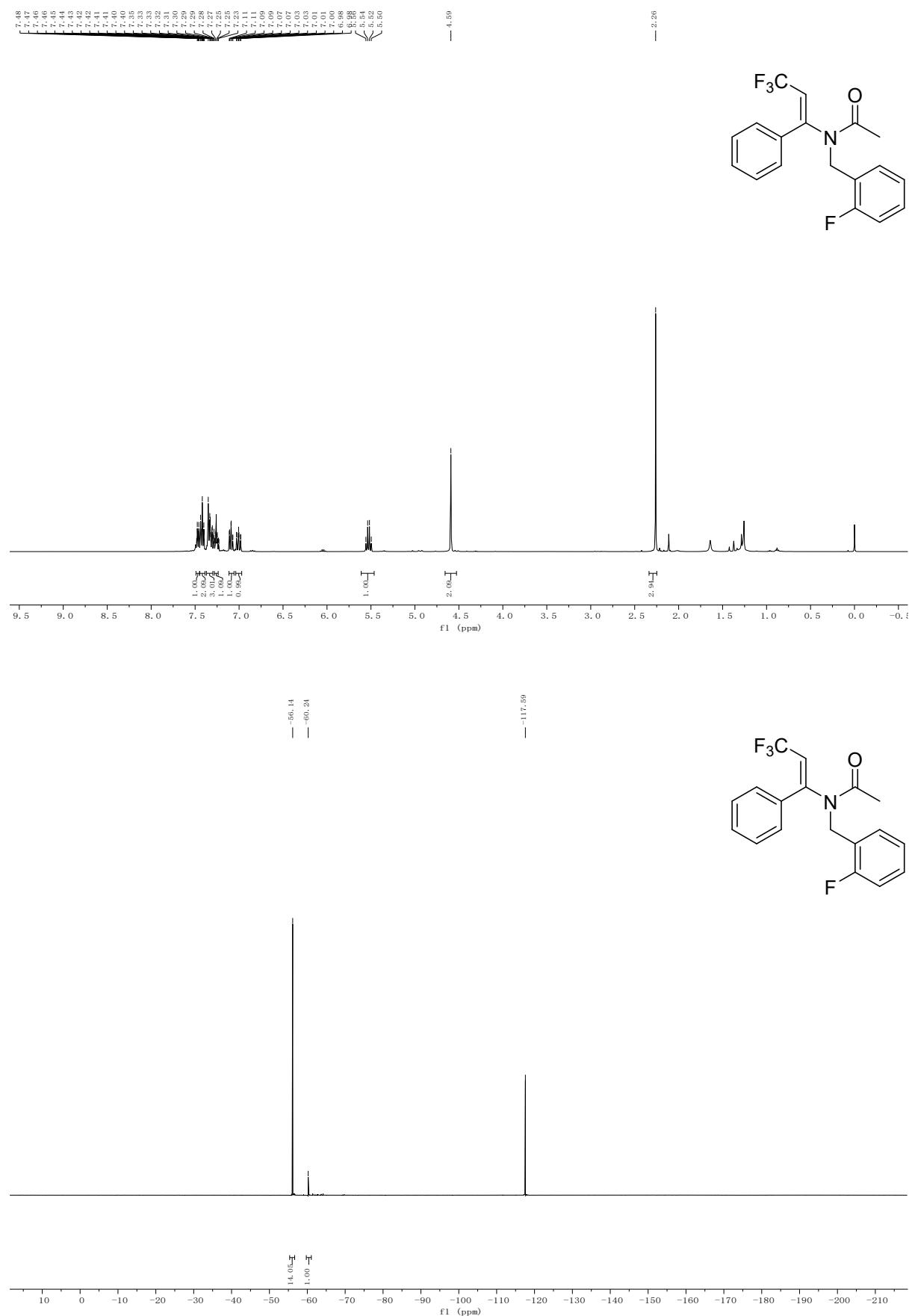


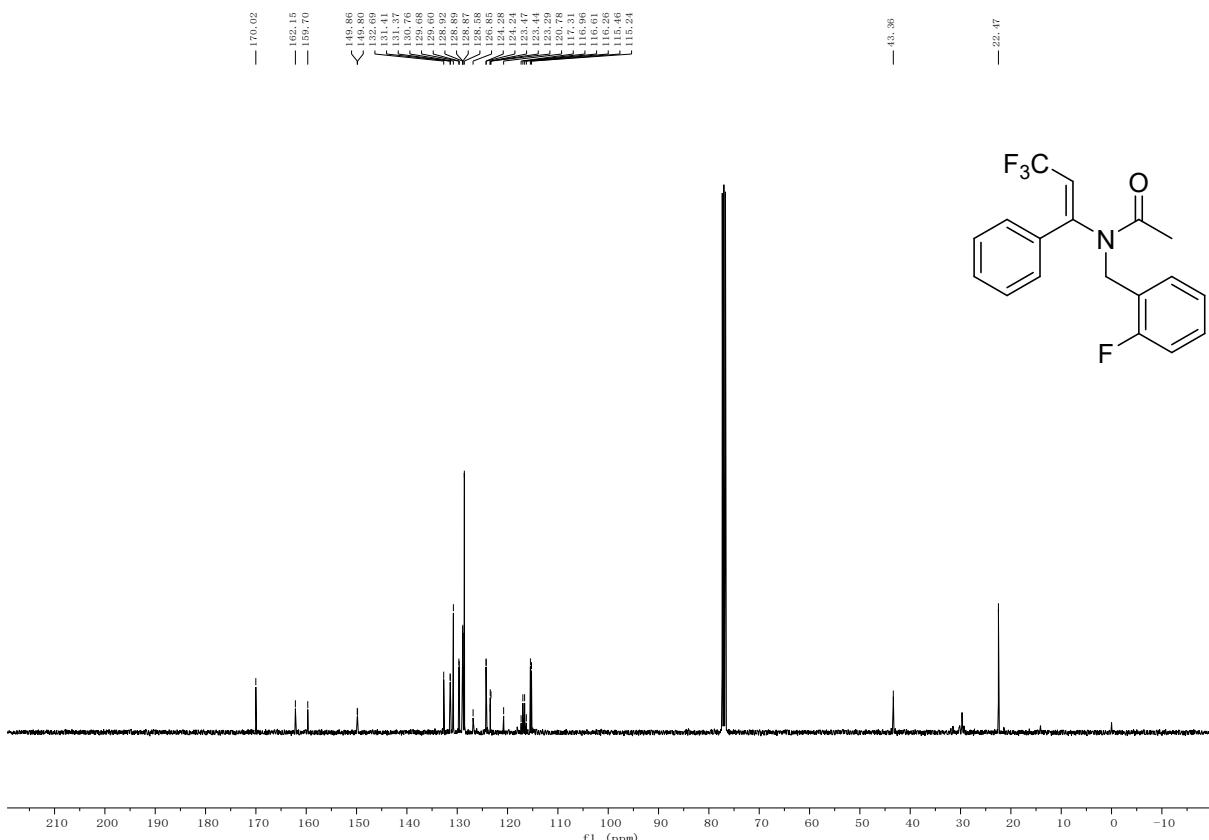
Product 3t:¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



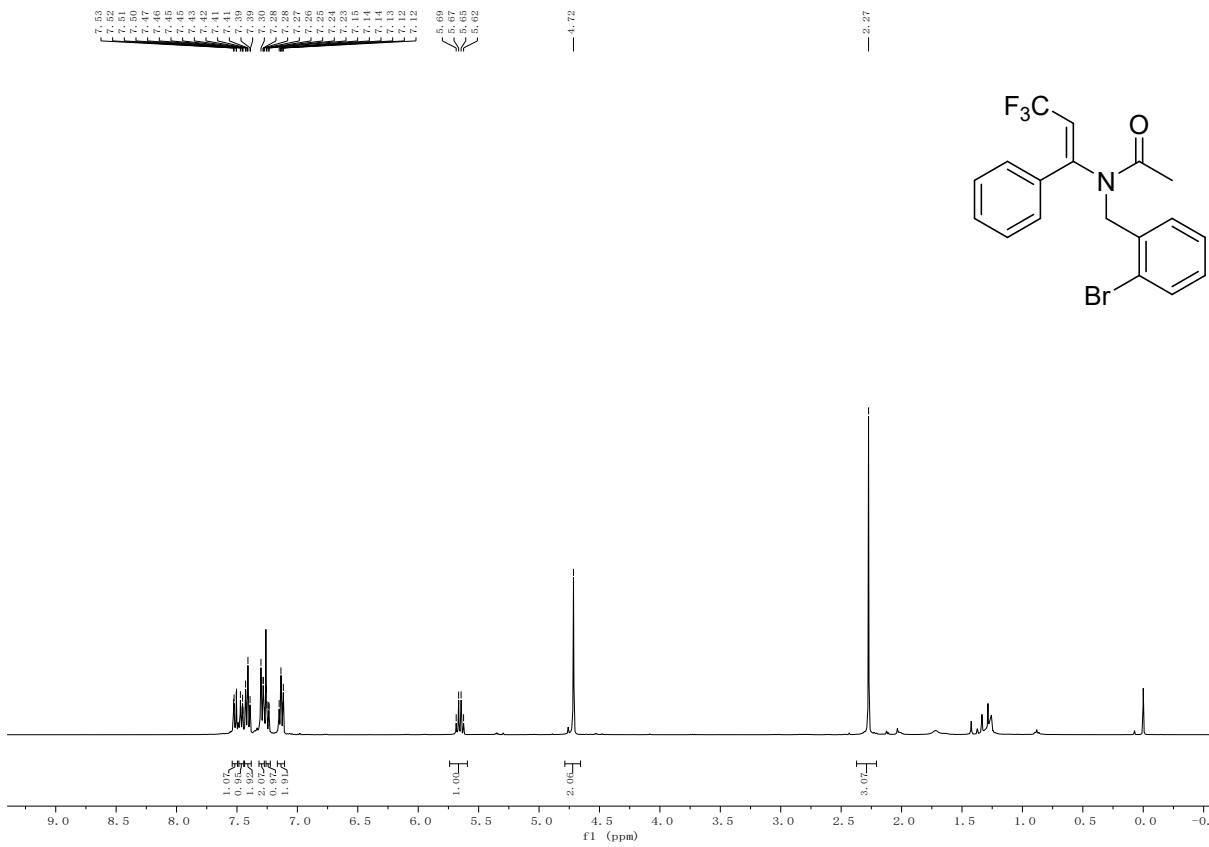


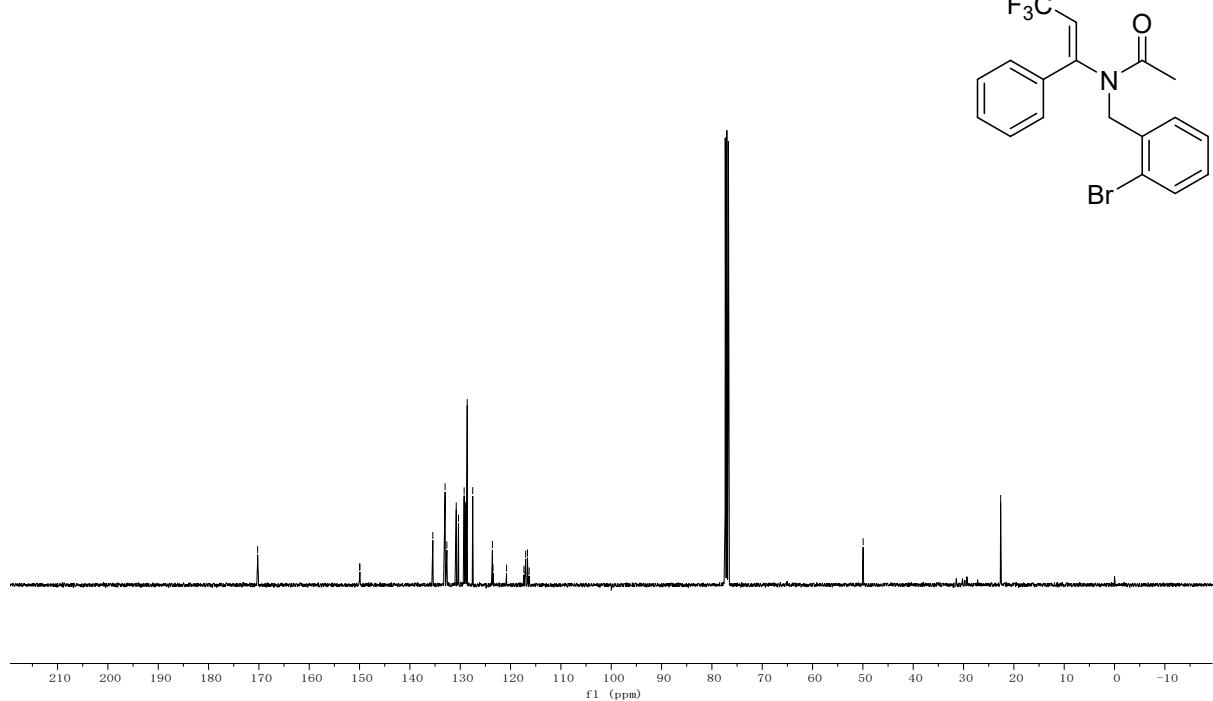
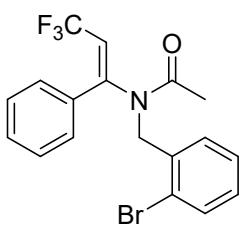
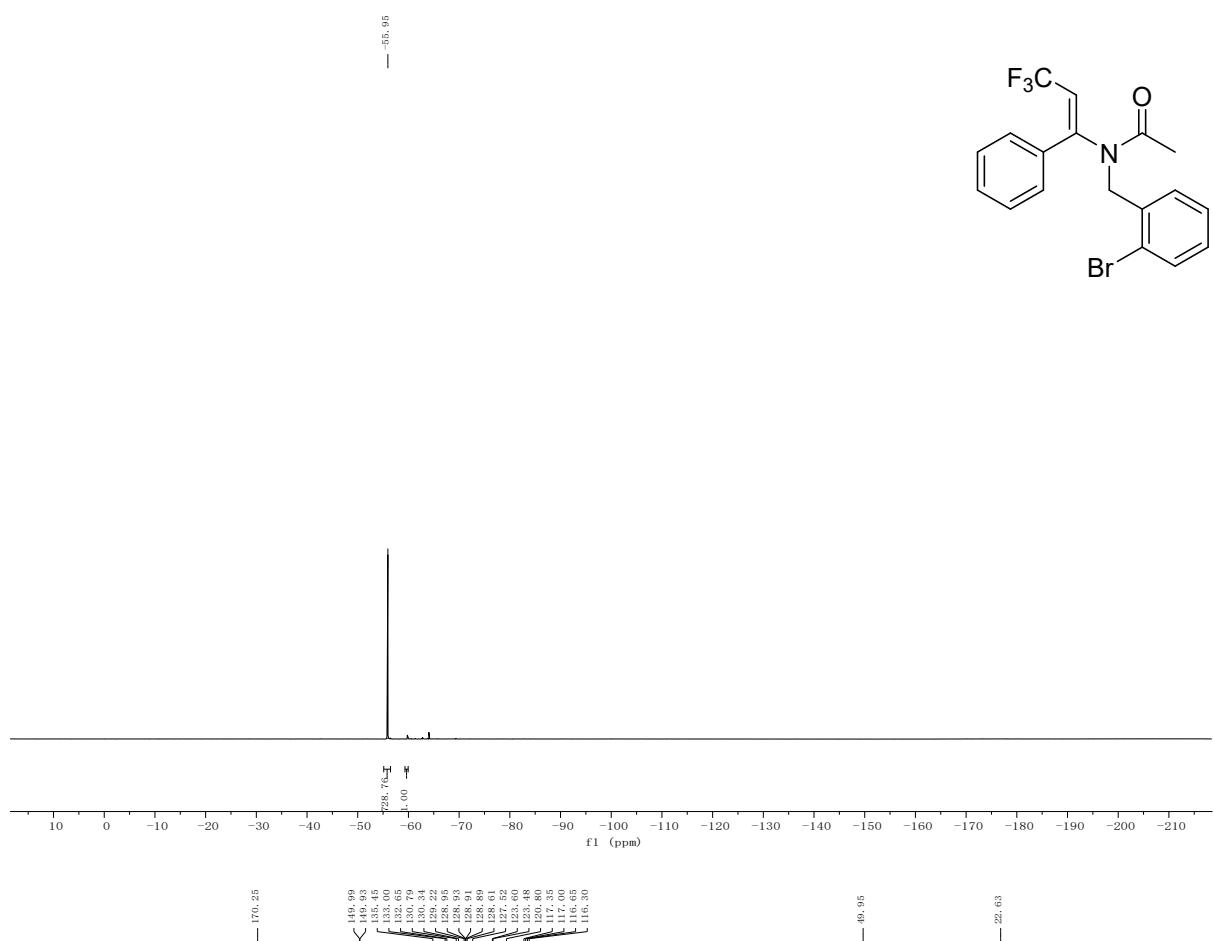
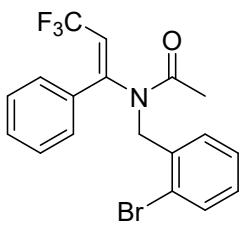
Product 3u:¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



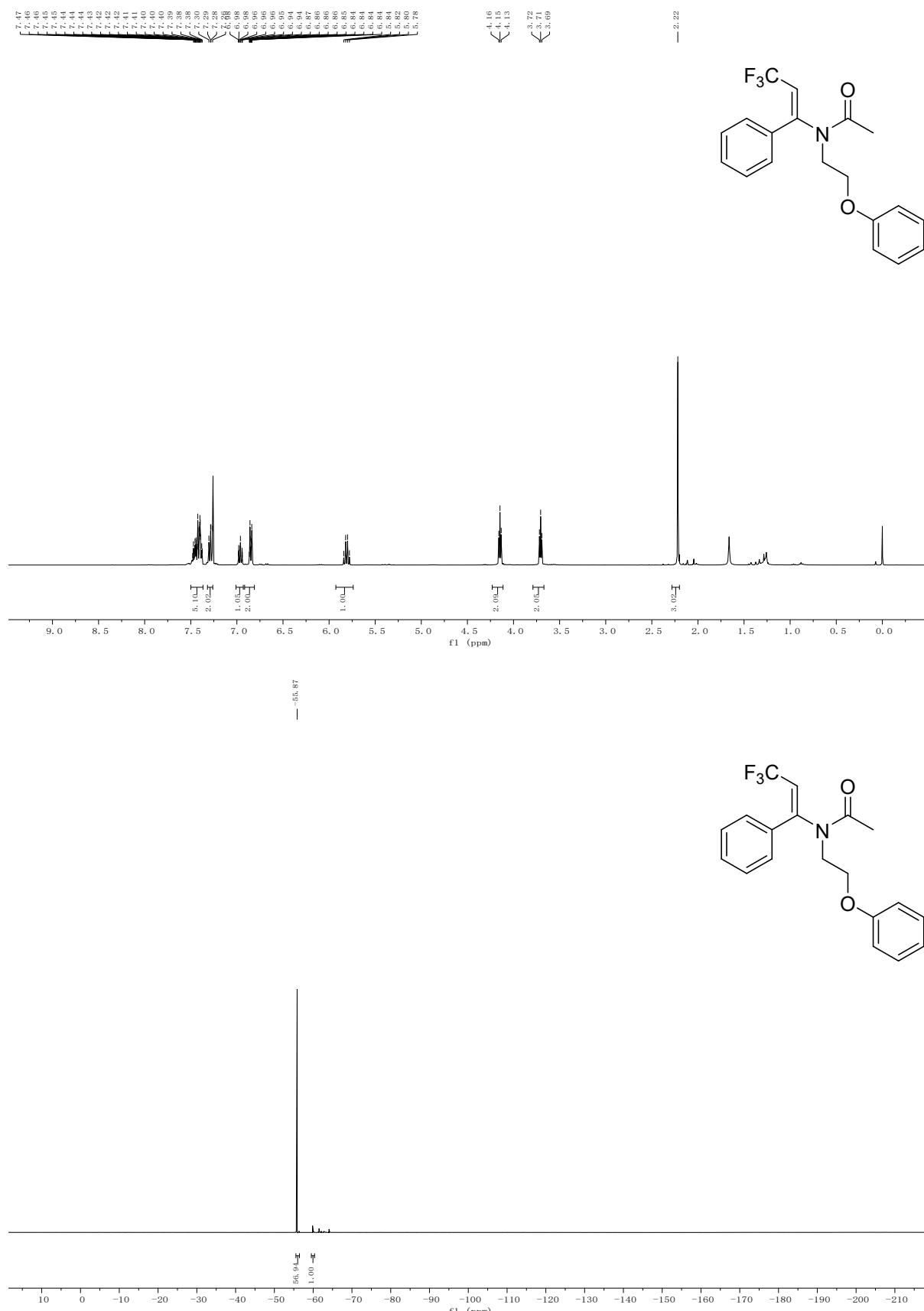


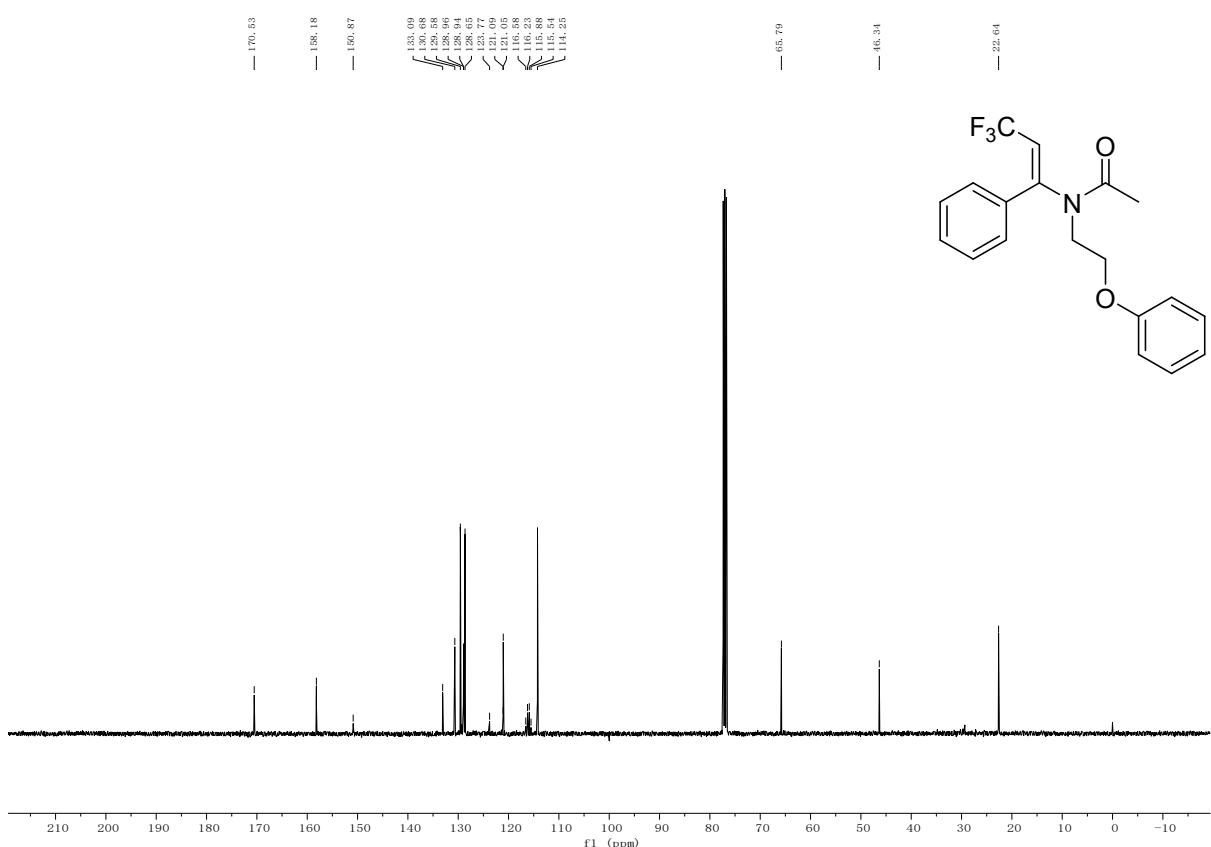
Product 3v: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).



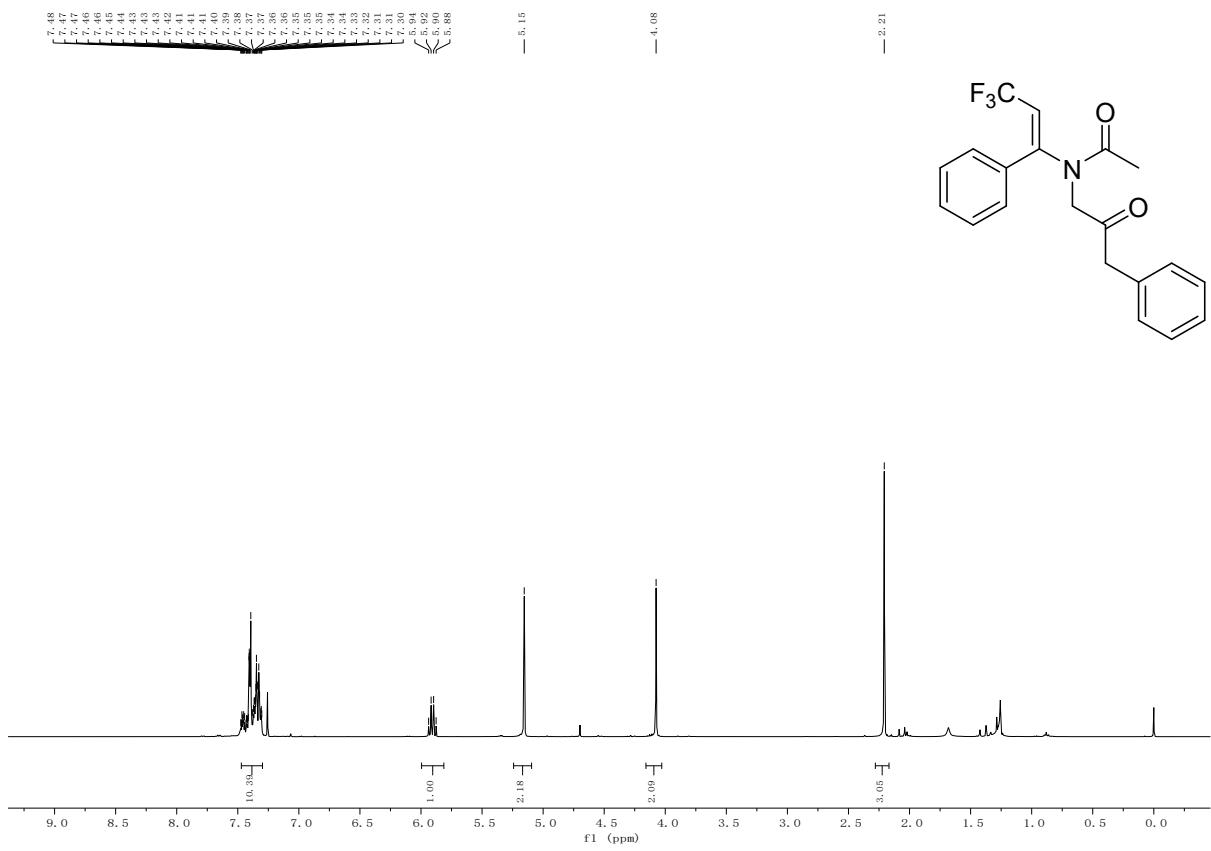


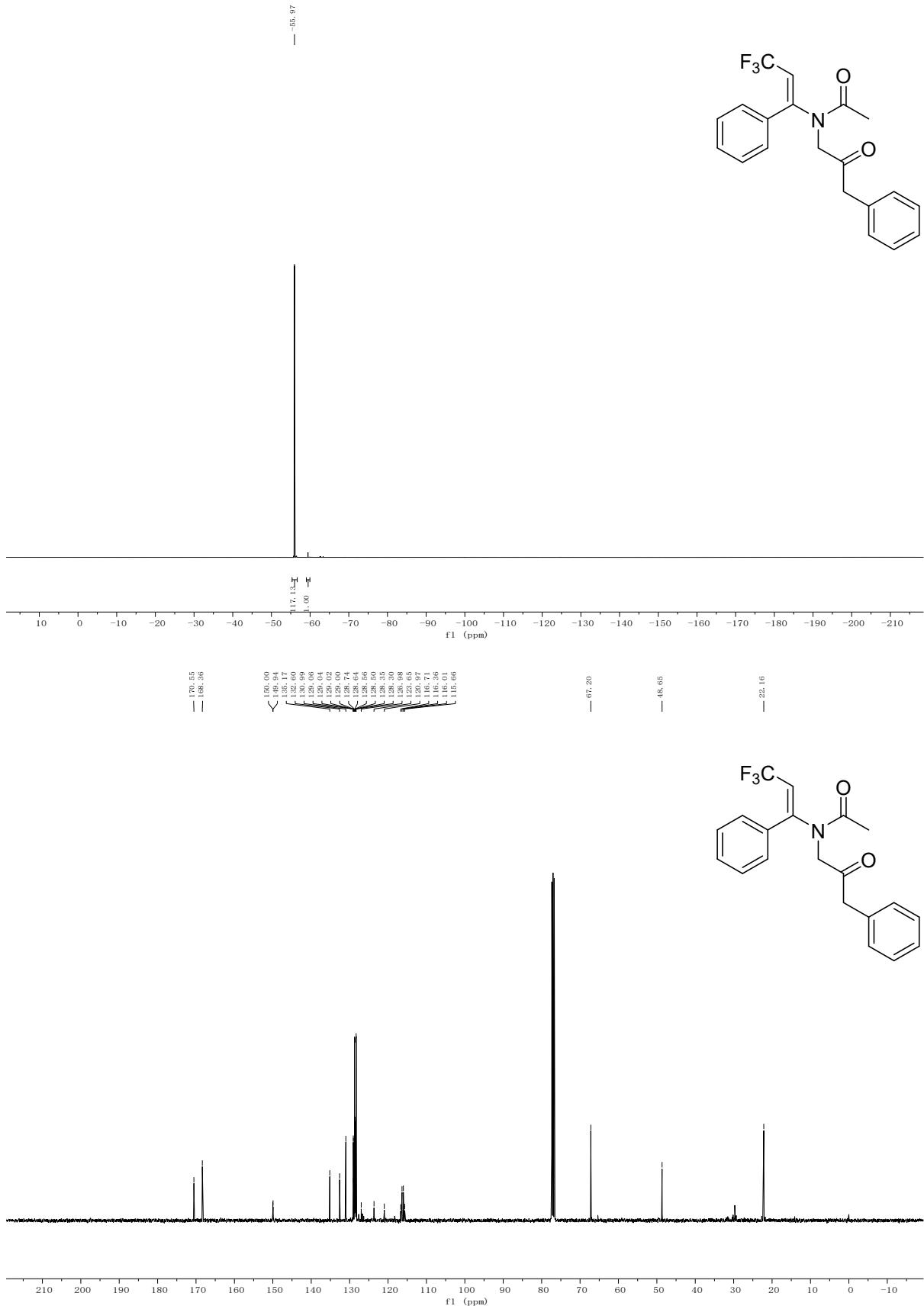
Product 3w: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).



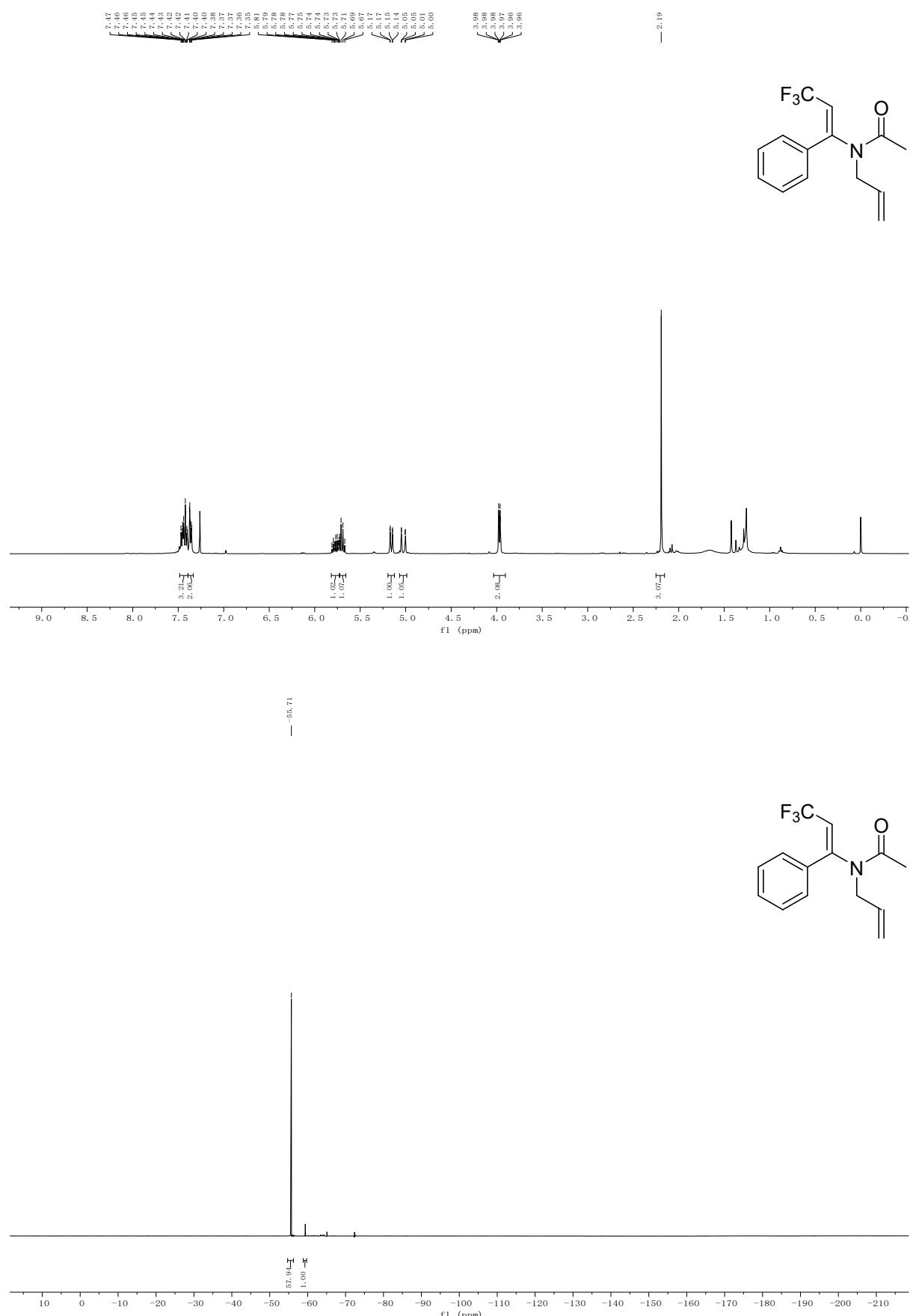


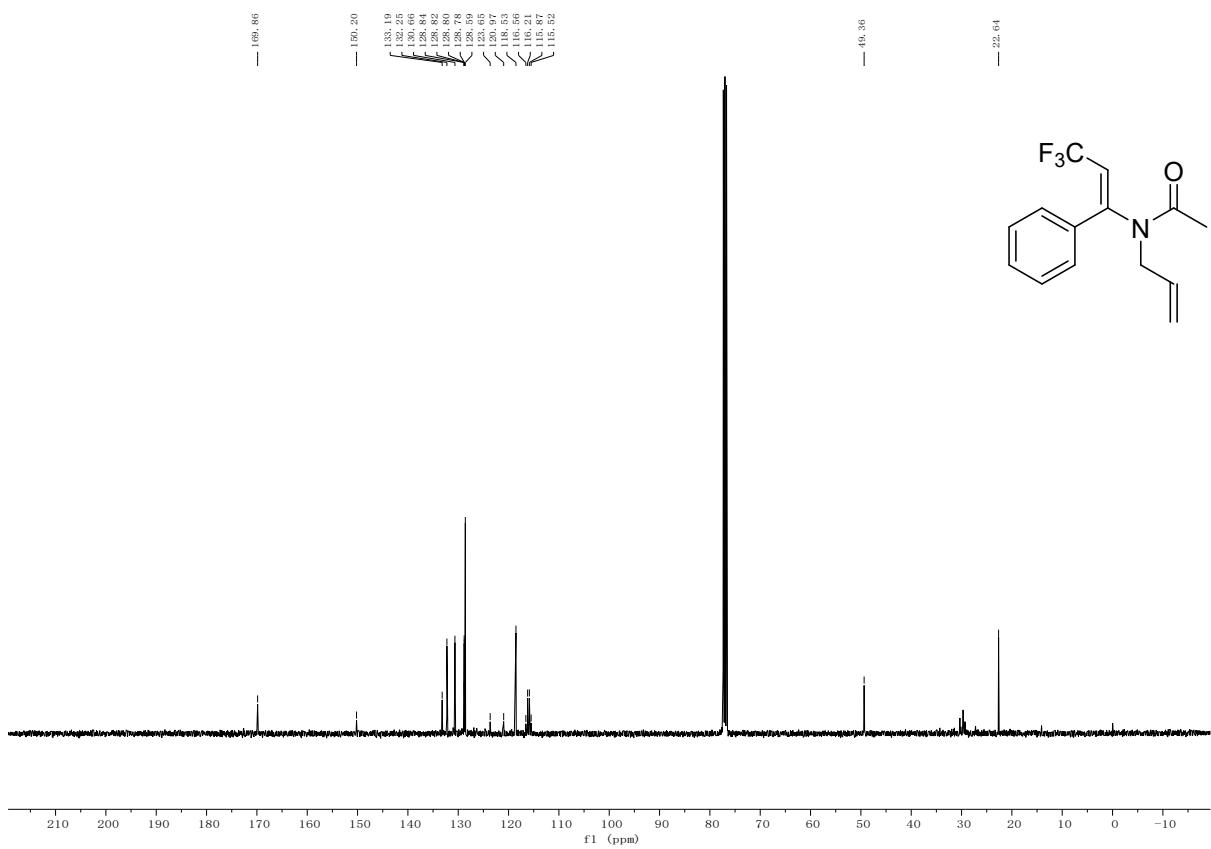
Product 3x: ^1H NMR (400 MHz, CDCl_3), ^{19}F NMR (376 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3).





Product 3y: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).





Product 3z: ¹H NMR (400 MHz, CDCl₃), ¹⁹F NMR (376 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).

