Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Catalytic Reduction of Trifluoromethylated Alkyl Bromides and Synthesis of Alkylated Heterocycles under Visible Light Irradiation: Synergetic Action of a Halogen Bond and Ni Catalysis

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Supporting Information

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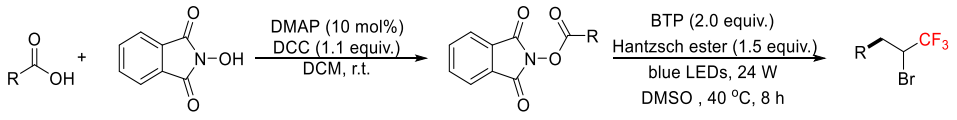
1. General information.

^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent MR400 spectrometer. ^{19}F NMR was recorded on an Agilent MR400 spectrometer. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. NMR yield was determined by ^{19}F NMR using fluorobenzene as an internal standard before working up the reaction. High-resolution mass spectra were recorded on a Thermo Scientific Q Exactive HF with Fourier-transform (orbitrap) mass spectrometer and Agilent Technologies 7250 GCQTOF in laboratory of mass spectrometry analysis at Shanghai Institute of Organic Chemistry. Melting points were taken on a SGW X-4 Melting Point Apparatus.

Materials: All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature. Anhydrous solvents THF and commercially available reagents were used without purification. All reagents were weighed and handled in air at room temperature. The starting compounds **2** were obtained from commercial suppliers and were used as received without further purification. Blue LEDs (430-490 nm) were bought online (Peak Wavelength: 455.0 nm). LED (370-375 nm, 390-395 nm, 410-415 nm, 425-430 nm, 450-455 nm) were purchased from WATTCAS^{TM}, and relevant experiments were performed in a WP-TEC-1020SL parallel reactor from WATTCAS^{TM}.

2. General procedure for the synthesis of trifluoromethylated alkyl bromides.



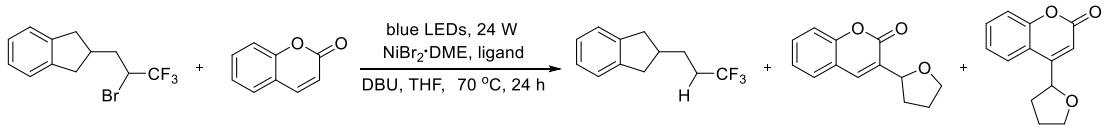
Step 1: Redox-active ester were prepared according to previous reported procedures [1]. The corresponding alkyl carboxylic acids or N-protected amino acids (5 mmol, 1.0 equiv.), N-hydroxyphthalimide (5 mmol, 1.0 equiv), and 4-dimethylaminopyridine (0.5 mmol, 10 mol%) were mixed in a flask equipped with a magnetic stirring bar, and DCM

(20 mL) was added. Then, a solution of N, N'-dicyclohexylcarbodiimide (1135 mg, 5.5 mmol, 1.1 equiv.) in DCM (5 mL) was added slowly at room temperature. After complete conversion of N-hydroxyphthalimide traced by TLC, the white precipitate was filtered off and the solution was concentrated on a rotary evaporator. The residue was purified by silica gel chromatography to give corresponding redox active esters.

Step 2: Trifluoromethyl alkyl bromide were prepared according to previous reported procedures [2]. A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with the redox active esters (4 mmol, 1.0 equiv.), Hantzsch ester (6 mmol, 1.5 equiv.). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry DMSO (25 mL) and 2-bromo-3,3,3- trifluoropropene (**BTP**) (8 mmol, 2.0 equiv.). The tube was screw capped and heated to 40°C (heat produced by blue LEDs) under irradiation of 24W blue LEDs (430-490 nm, peak wavelength:455.0 nm). After stirring for 8 h, the reaction mixture was then quenched with saturated NaCl solution and extracted with ethyl acetate. The organic layers were combined and concentrated on a rotary evaporator. The product was purified with silica gel chromatography to give corresponding pure product.

3. Reaction Conditions Optimization:

Table S1. Screening ligand



1a 2a 3a 4a-1 4a-2

Entry	Ligand	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	L1	20%, 19%, 16%
2	L2	32%, 35%, 20%
3	L3	NR
4	L4	NR
5	**L5**	**56%, 54%, 20%**
6	L6	Trace
7	L7	NR
8	L8	Trace

9	L9	NR
10	L10	47%, 45%, 27%
11	L11	14%, 16%, 15%
12	L12	Trace

[a] Reaction conditions (unless otherwise specified): **1a** (0.2 mmol), **2a** (0.1 mmol), $NiBr_2$·DME (0.005 mmol), ligand (0.005 mmol), DBU (0.15mmol), THF (1.0 mL), 24 W blue LEDs, 70 ℃, 24 h. [b] NMR yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

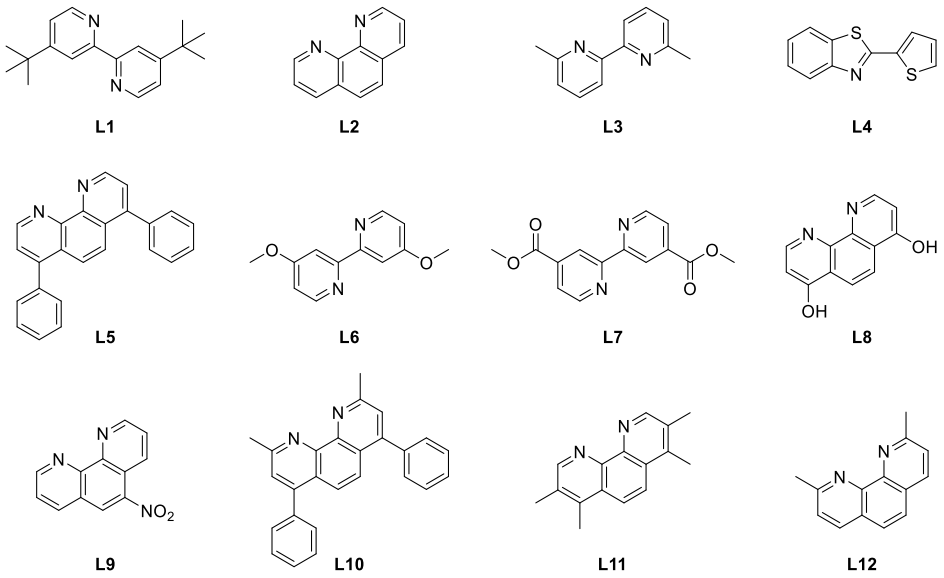
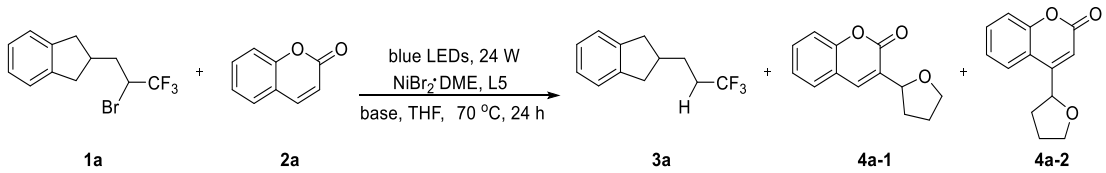


Table S2. Screening base

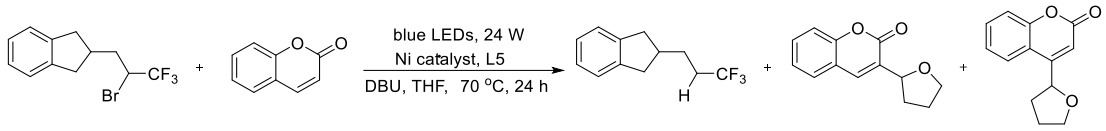


Entry	Base	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	DMAP	17%, 19%, 11%
2	N,N-dimethylpiperazine	NR
3	**DBU**	**56%, 54%, 20%**
4	DMPU	Trace
5	Et_3N	NR
6	K_2CO_3	27%, 30%, 12%
7	K_2HPO_4	NR
8	NaOAc	NR
9	Cs_2CO_3	NR

[a] Reaction conditions (unless otherwise specified): **1a** (0.2mmol), **2a** (0.1mmol), $NiBr_2$·DME (0.005 mmol), L5 (0.005 mmol), base (0.15mmol), THF (1.0 mL), 24 W blue LEDs, 70 ℃, 24 h. [b] NMR

yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

Table S3. Screening Ni catalyst

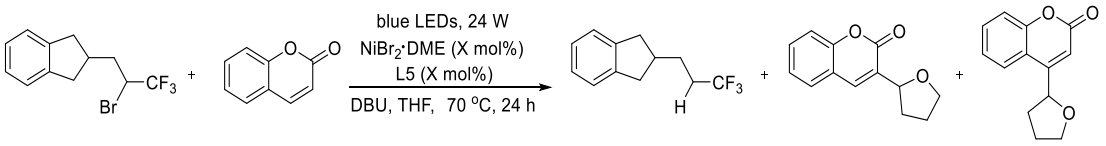


1a **2a** **3a** **4a-1** **4a-2**

Entry	Ni catalyst	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	**$Ni(OAc)_2{\cdot}4H_2O$**	**58%, 56%, 26%**
2	$NiBr_2{\cdot}DME$	56%, 54%, 20%
3	$NiBr_2$	54%, 52%, 19%
4	$NiCl_2$	51%, 52%, 20%
5	$Ni(BF_4)_2{\cdot}6H_2O$	45%, 39%, 21%
6	$Ni(ClO_4)_2{\cdot}6H_2O$	49%, 50%, 17%
7	$Ni(acac)_2$	41%, 43%, 13%

[a] Reaction conditions (unless otherwise specified): **1a** (0.2mmol), **2a** (0.1mmol), Ni catalyst (0.005 mmo), L5 (0.005 mmol), DBU (0.15mmol), THF (1.0 mL), 24 W blue LEDs, 70 °C, 24 h. [b] NMR yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

Table S4. Screening the amount of catalyst and ligand

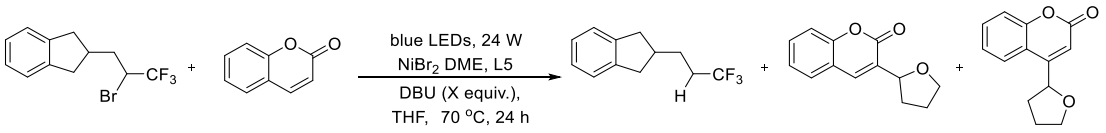


1a **2a** **3a** **4a-1** **4a-2**

Entry	Cata&Ligand (X mol%, Compared with **1a**)	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	1.25	34%, 33%, 12%
2	**2.50**	**58%, 56%, 26%**
3	3.75	45%, 45%, 13%
4	5.00	41%, 38%, 14%

[a] Reaction conditions (unless otherwise specified): **1a** (0.2mmol), **2a** (0.1mmol), DBU (0.15mmol,), THF (1.0 mL), 24 W blue LEDs, 70 °C, 24 h. [b] NMR yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

Table S5. Screening the amount of DBU

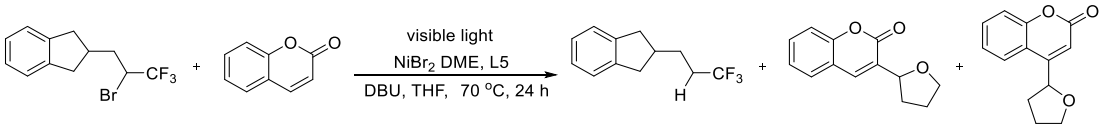


1a **2a** **3a** **4a-1** **4a-2**

Entry	DBU (X equiv., compared with **1a**)	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	**0.75**	**58%, 56%, 26%**
2	1.50	54%, 49%, 19%
3	2.25	54%, 51%, 18%

[a] Reaction conditions (unless otherwise specified): **1a** (0.2mmol), **2a** (0.1mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.005 mmol), L5 (0.005 mmol), THF (1.0 mL), 24 W blue LEDs, 70 °C, 24 h. [b] NMR yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

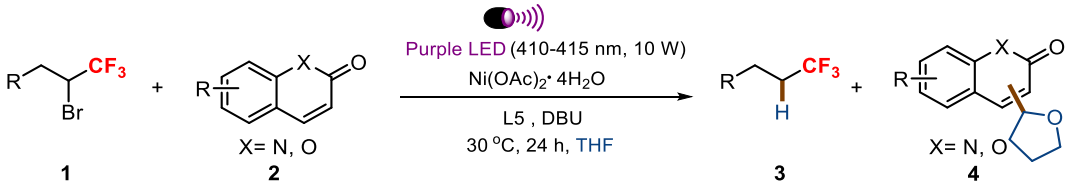
Table S6. Screening wavelength (nm)



Entry	wavelength (nm)	Yield (**3a**, **4a-1**, **4a-2**) [b]
1	370-375	NR
2	390-395	63%, 44%, 24%
3	**410-415**	**97%, 55%, 26%**
4	425-430	76%, 52%, 24%
5	450-455	63%, 46%, 15%
6	470-475	64%, 48%, 18%

[a] Reaction conditions (unless otherwise specified): **1a** (0.2mmol), **2a** (0.1mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.005 mmol), L5 (0.005 mmol), DBU (0.15mmol), THF (1.0 mL), 30°C, 24 h. [b] NMR yield of **3a**, which determined by ^{19}F NMR using fluorobenzene as internal standard and yield of isolated compounds **4a**.

4. General procedure for the synthesis of alkylated trifluoromethyl compounds and alkylated heterocycles.



General procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with compound **1** (0.2 mmol), compound **2** (0.1 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.005 mmol), L5 (0.005 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation

of Purple LEDs (410-415 nm, 10 W, the set-up is detailed in Figure S1). After stirring for 24 h, the reaction mixture was concentrated on a rotary evaporator. The product was purified with silica gel chromatography to give corresponding pure product.

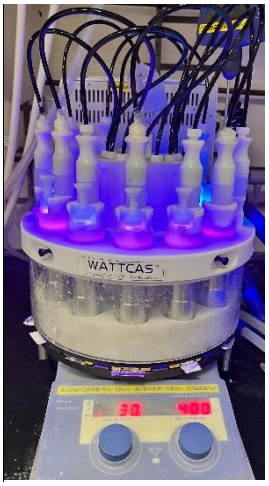
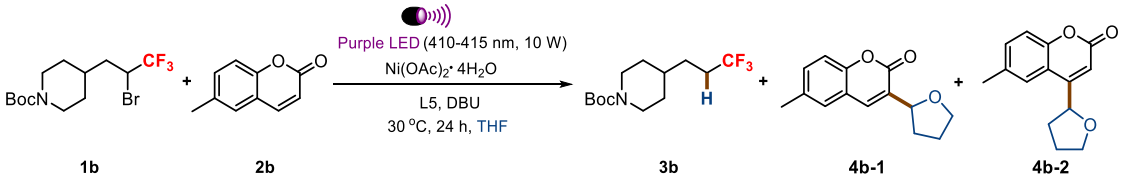


Figure S1. Experiment set-up

5. Detailed procedure for the gram scale synthesis.

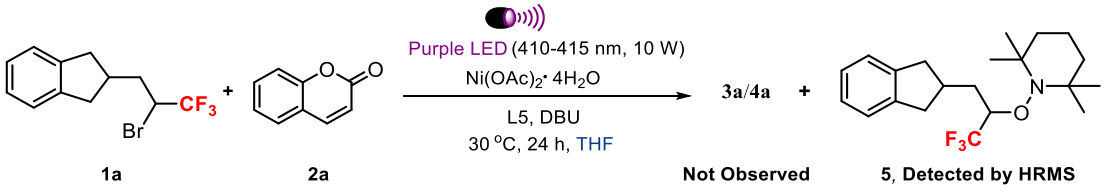


General procedure: A 100 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with compound **1b** (15 mmol), coumarin **2b** (7.5 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.375 mmol), L5 (0.375 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (35.0 mL) and DBU (11.25 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W, the set-up is detailed in Figure S2). After stirring for 48 h, the reaction mixture was concentrated on a rotary evaporator. The product **3b** (78%, 3.29 g), **4b-1** (62%, 1.09 g) and **4b-2** (20%, 0.34 g) were purified with silica gel chromatography (PE:EA=15:1 to 10:1) as white solid.

Figure S2. Experiment set-up

6. Mechanism studies

6.1 Addition of radical and SET inhibitors



Procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.2 mmol), **2a** (0.1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.005 mmol), L5 (0.005 mmol), TEMPO (0.2 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W). After stirring for 24 h, the reaction mixture was cooled to room temperature, monitored by TLC, pretreated and sent for HRMS analysis.

High resolution ESI-MS and MS/MS experiments for detecting TEMPO complex: High resolution ESI-MS and MS/MS spectra were recorded on a Q Exactive HF Orbitrap mass spectrometer (Thermo Fisher Scientific Inc.) equipped with ESI ion source. The ESI conditions were: spray voltage 3500 V; capillary temperature, 275°C; sheath gas flow rate 35 arb. units. Data acquisition and analysis were done with the Thermo Xcalibur (version 4.2.47) software package. The reaction was completely suppressed by the addition of a radical scavenger TEMPO, which suggests the potential involvement of radical intermediates during the reaction.

The elemental composition analysis of the ion at m/z 370.2347 by HRMS (Figure S3 and S4) supported the proposed structure of TEMPO complex (**5**).

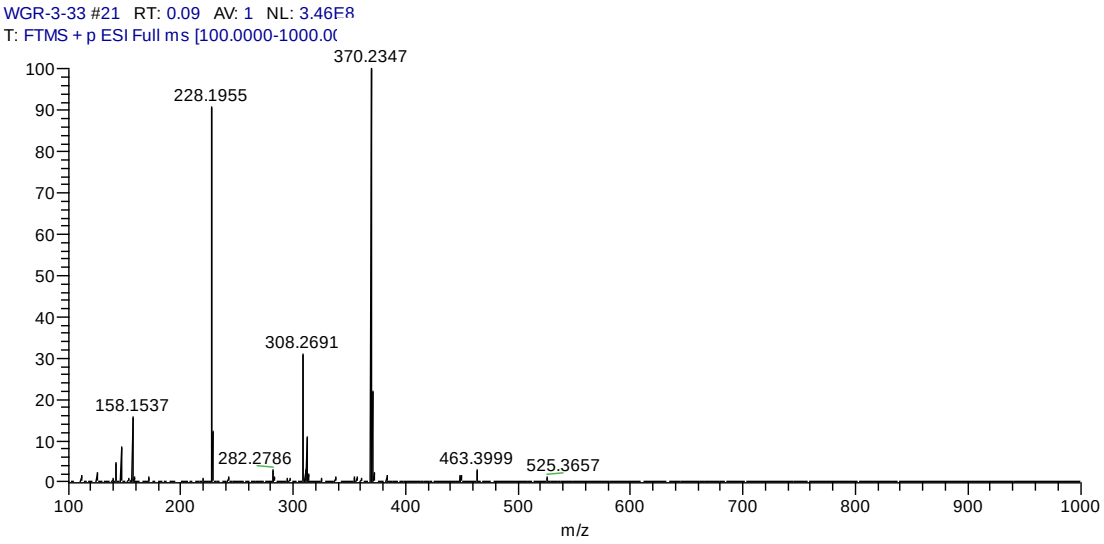


Figure S3. High resolution ESI-MS spectrum of TEMPO complex calculated for $C_{21}H_{31}ONF_3$ ($[M+H]^+$): 370.2352; Found: 370.2347.

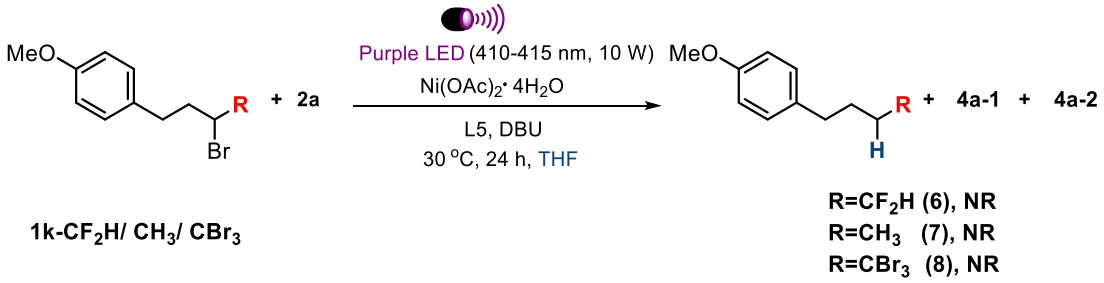
Elemental composition search on mass 370.2347

m/z= 365.2347-375.2347

m/z	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
370.2347	370.2352	-1.39	5.5	$C_{21}H_{31}ONF_3$

Figure S4. Elemental composition analysis of the ion at *m/z* 370.

6.2 Control experiment:



Procedure A: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1k-CF_2H** (0.2 mmol), **2a** (0.1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.005 mmol),

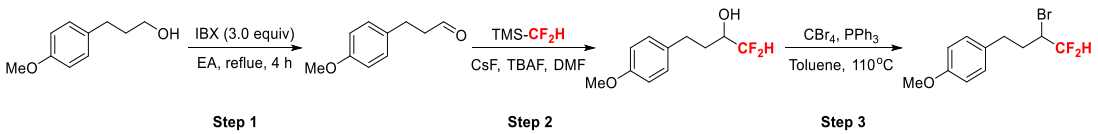
L5 (0.005 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W). After stirring for 24 h, the reaction monitored by TLC, no target products **6** and **4a** were detected.

Procedure B: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1k-CH$_3$** (0.2 mmol), **2a** (0.1 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.005 mmol), L5 (0.005 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W). After stirring for 24 h, the reaction monitored by TLC, no target products **7** and **4a** were detected.

Procedure C: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1k-CBr$_3$** (0.2 mmol), **2a** (0.1 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.005 mmol), L5 (0.005 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of dry THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W). After stirring for 24 h, the reaction monitored by TLC, no target products **8** and **4a** were detected.

Control experiments were performed by substituting the trifluoromethyl group with less electronegative analogues, such as CF_2H, CH_3, or CBr_3 substituents. However, these substitutions failed to yield the desired product, emphasizing the remarkable and pivotal role played by the trifluoromethyl group in facilitating this transformation.

Procedure for the synthesis of 1k- CF_2H:



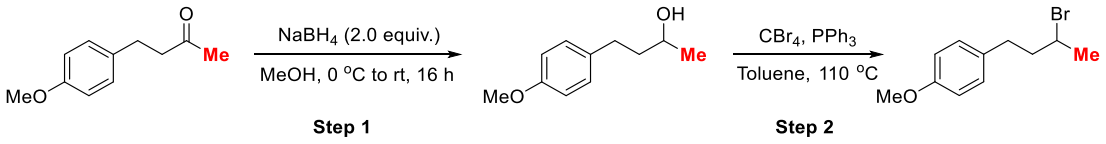
Step 1: Oxidation of the alcohol [3]. The primary alcohol (20 mmol) was dissolved in EtOAc (140 mL), and IBX (60 mmol, 16.8 g) was carefully added. The suspension was

heated to reflux for 4 h, and then the precipitate was removed via filtration. The EtOAc was then concentrated under vacuum, yielding the corresponding aldehyde in quantitative yield, which was subsequently utilized in the next step.

Step 2: Difluoromethylation of the aldehyde [4]. Add CsF (10 mg, 0.07 mmol) to a solution of 4-methoxybenzaldehyde (3 mmol) and TMS-CF_2H (2 mmol) in 6 mL of DMF under N_2 atmosphere. Stir the mixture at room temperature overnight. Add a solution of TBAF (1.5 ml, 1M in THF) to the reaction mixture. Stir the whole mixture for another 1 hour. Extract the reaction mixture with Et_2O and H_2O. Wash the organic phase with brine, then dry the organic phase using anhydrous $MgSO_4$. Filter the solution and evaporate the solvent under vacuum. Purify the residue through silica gel column chromatography.

Step 3: Bromination of the alcohol [5]. PPh_3 (2 mmol, 2.0 equiv.) and CBr_4 (2 mmol, 2.0 equiv.) were added to a solution of the alcohol (1.0 mmol) in 2.5 mL toluene. The resulting mixture was heated to 110 °C and stirred for 3 h, at which time it had turned into a yellow suspension. Then, DCM (5 mL) was added to the reaction mixture until it became a clear solution. The solvents were then evaporated, and the crude product was purified by flash chromatography on silica gel.

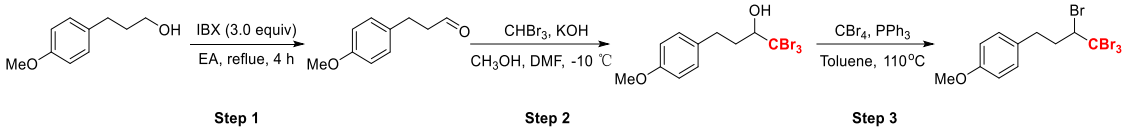
Procedure for the synthesis of 1k-CH_3:



Step 1: Reduction of the ketone to the alcohol. 4-(4-methoxyphenyl)butan-2-one (5.6 mmol, 1.0 equiv.) was dissolved in MeOH (10 mL) in a round bottom flask and placed at 0°C. Then sodium borohydride (11.2 mmol, 2.0 equiv.) was added to the solution by little portion at 0°C and the mixture was allowed to rise to room temperature, stirring overnight (16 h). Then 1 mL of acetic acid was added and the mixture was stirred briefly. A saturated solution of $NaHCO_3$ was then added (10 mL). The phases were separated and the aqueous layer was extract with ethyl acetate (10 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated

under vacuum. The product was purified with silica gel chromatography to give corresponding pure product. **Step 2:** As mentioned above.

Procedure for the synthesis of 1k-CBr_3:

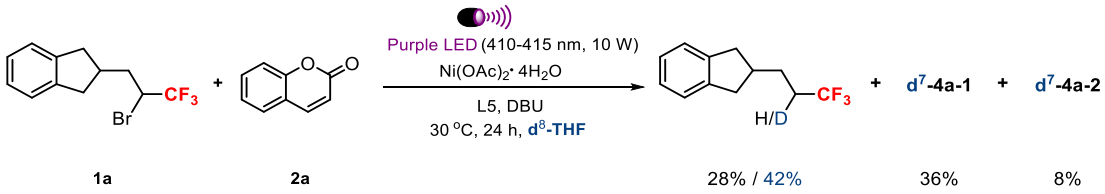


Step 1: As mentioned above.

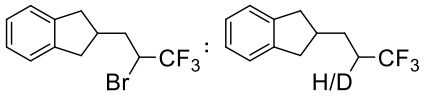
Step 2: Tribromomethylation of aldehydes of the aldehyde [6]. At -10°C, a MeOH solution (20 mL) of KOH (0.5 mmol, 0.1 equiv.) was added dropwise to a DMF(7.5mL) solution containing aldehyde (5 mmol, 1.0 equiv.) and $CHBr_3$ (11 mmol, 2.2 equiv.). The reaction progress was monitored using TLC. After complete conversion, the reaction mixture was treated with HCl (1M, 5-10 mL). After 10 minutes, ethyl acetate (EA, 10-20 mL) was added, left to stand for 30 minutes, and then extracted with ethyl acetate. The crude product obtained could be directly used for the next step.

Step 3: As mentioned above.

6.3 D-labeled experiment:

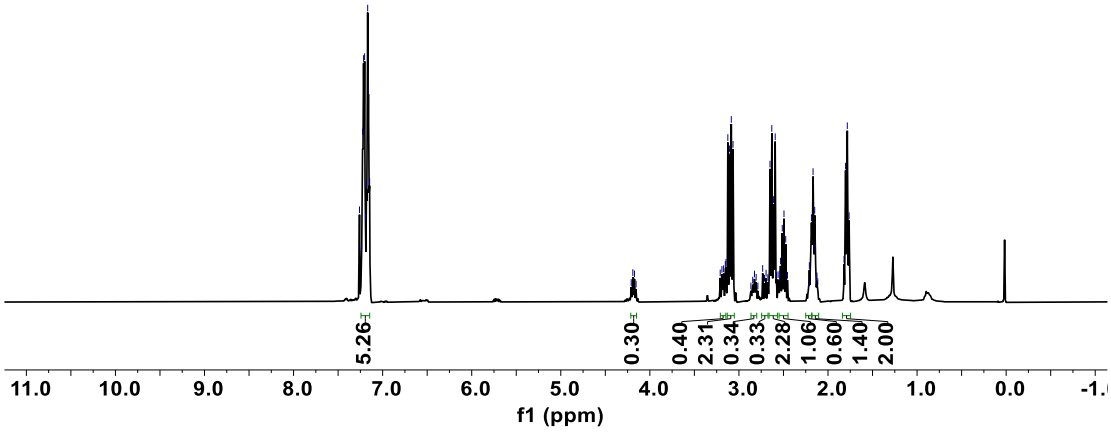


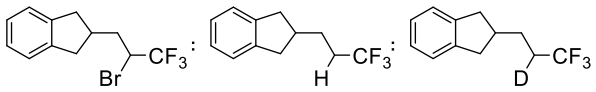
Procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.2 mmol), **2a** (0.1 mmol), $Ni(OAc)_2 \cdot 4H_2O$ (0.005 mmo), L5 (0.005 mmol). The tube was evacuated and backfilled with argon for three times, followed by the addition of d^8-THF (1.0 mL) and DBU (0.15 mmol). The tube was screw capped and heated to 30°C under irradiation of Purple LEDs (410-415 nm, 10 W). After stirring for 24 h, the reaction mixture was concentrated on a rotary evaporator. The product was purified with silica gel chromatography to give corresponding product.



0.3 : 0.7

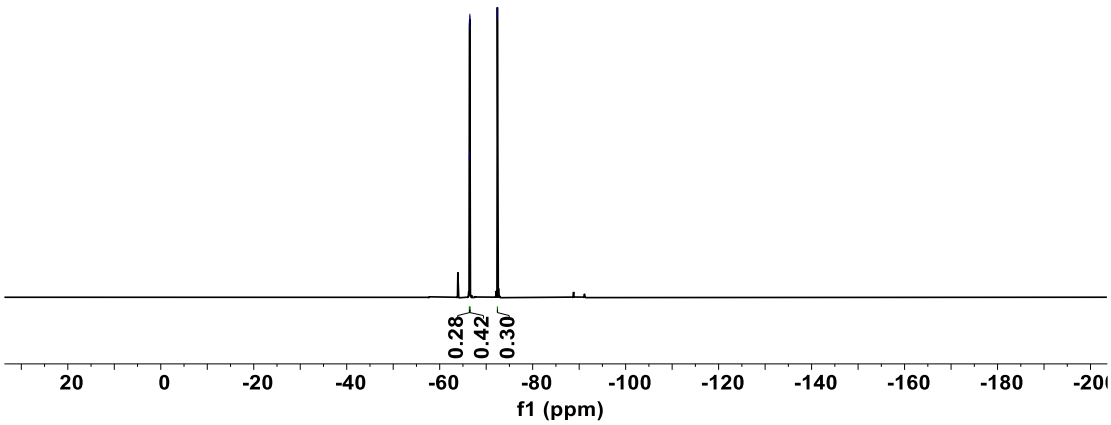
^{1}H NMR (400 MHz, $CDCl_3$)

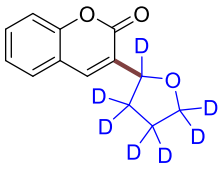




0.30 : 0.28 : 0.42

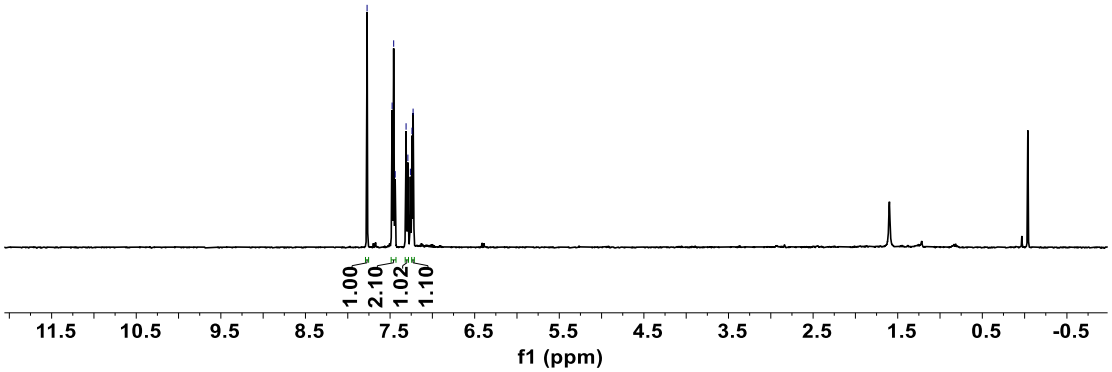
^{19}F NMR (376 MHz, $CDCl_3$)

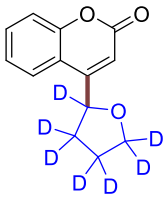




d^7-4a-1

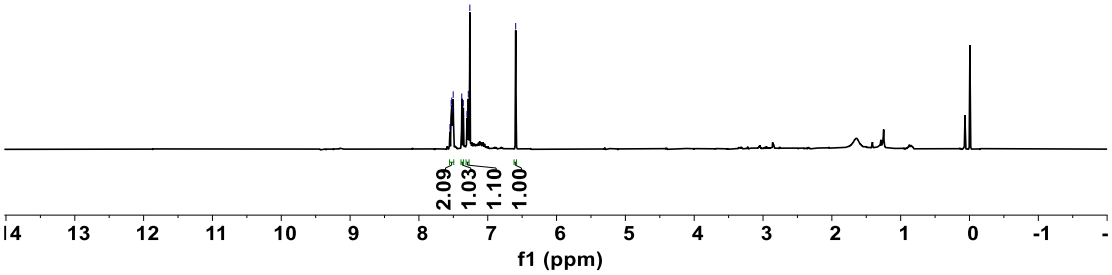
^{1}H NMR (400 MHz, $CDCl_3$)





d^7-4a-2

^{1}H NMR (400 MHz, $CDCl_3$)



6.4 UV-vis spectroscopic measurement:

Solution 1: **Ni(OAc)$_2$·4H$_2$O** (1.24 mg, 0.005 mmol) was added in THF (10 mL).

Solution 2: **L5** (1.61 mg, 0.005 mmol) was added in THF (10 mL).

Solution 3: **Ni(OAc)$_2$·4H$_2$O** (1.24 mg, 0.005 mmol) and **L5** (1.61 mg, 0.005 mmol) were added in THF (10 mL).

Solution 4: **Ni(OAc)$_2$·4H$_2$O** (1.24 mg, 0.005 mmol), **L5** (1.61 mg, 0.005 mmol) and **DBU** (0.15 mmol, 30 eq.) were added in THF (10 mL).

Solution 5: **Ni(OAc)$_2$·4H$_2$O** (1.24 mg, 0.005 mmol), **L5** (1.61 mg, 0.005 mmol), **DBU** (0.15 mmol, 30 eq.) and **1a** (0.20 mmol, 40 eq.) were added in THF (10 mL).

Solution 6: **DBU** (0.15 mmol, 30 eq.) was added in THF (10 mL).

Solution 7: **1a** (0.20 mmol, 40 eq.) was added in THF (10 mL).

Solution 8: **DBU** (0.15 mmol, 30 eq.) and **1a** (0.20 mmol, 40 eq.) were added in THF (10 mL).

These solutions were stirred at room temperature for 20 minutes and then filtered for measurement.

A / λ(nm)	Ni(OAc)$_2$·4H$_2$O	L5	Ni+L5	Ni+L5 +DBU	Ni+L5+ DBU+1a	DBU	1a	DBU+1a
330	0.024	1.134	1.944	2.023	2.223	0.067	0.009	0.090
340	0.007	0.501	1.428	1.466	2.012	0.036	0.012	0.090
350	0.007	0.212	0.843	0.912	1.364	0.032	0.006	0.109
360	0.004	0.054	0.649	0.722	1.079	0.026	0.005	0.108
370	0.004	0.016	0.262	0.366	0.583	0.017	0.007	0.096
380	0.008	0.012	0.156	0.239	0.401	0.014	0.005	0.086
390	0.010	0.01	0.111	0.176	0.309	0.013	0.004	0.077
400	0.011	0.007	0.083	0.128	0.238	0.012	0.003	0.067
410	0.010	0.007	0.061	0.091	0.177	0.012	0.002	0.057
420	0.009	0.006	0.047	0.071	0.137	0.012	0.002	0.046
430	0.008	0.006	0.035	0.055	0.103	0.011	0.001	0.035
440	0.008	0.005	0.026	0.043	0.081	0.010	0.000	0.028
450	0.007	0.005	0.020	0.035	0.065	0.010	0.000	0.023
460	0.006	0.005	0.016	0.030	0.053	0.009	0.000	0.019
470	0.006	0.005	0.013	0.024	0.044	0.009	0.000	0.017
480	0.005	0.004	0.011	0.021	0.037	0.008	0.001	0.014
490	0.006	0.004	0.010	0.019	0.032	0.008	0.001	0.012
500	0.006	0.005	0.010	0.017	0.027	0.009	0.000	0.010
510	0.006	0.004	0.009	0.016	0.024	0.008	0.000	0.008
520	0.005	0.005	0.009	0.016	0.022	0.008	0.000	0.008
530	0.006	0.006	0.011	0.016	0.021	0.008	0.002	0.008
540	0.007	0.005	0.010	0.016	0.019	0.009	0.001	0.007
550	0.007	0.006	0.01	0.015	0.018	0.008	0.003	0.007
560	0.006	0.005	0.011	0.016	0.018	0.009	0.003	0.008
570	0.006	0.004	0.011	0.016	0.017	0.007	0.003	0.007
580	0.007	0.005	0.012	0.015	0.017	0.007	0.003	0.007

590	0.006	0.005	0.012	0.015	0.016	0.008	0.003	0.007
600	0.006	0.004	0.012	0.014	0.016	0.008	0.003	0.007
610	0.007	0.004	0.012	0.014	0.014	0.007	0.003	0.007
620	0.007	0.004	0.012	0.014	0.014	0.007	0.003	0.007
630	0.007	0.004	0.013	0.013	0.013	0.007	0.004	0.007
640	0.006	0.003	0.012	0.013	0.012	0.007	0.003	0.007
650	0.007	0.003	0.012	0.012	0.011	0.007	0.003	0.007
660	0.007	0.003	0.011	0.011	0.010	0.006	0.003	0.007

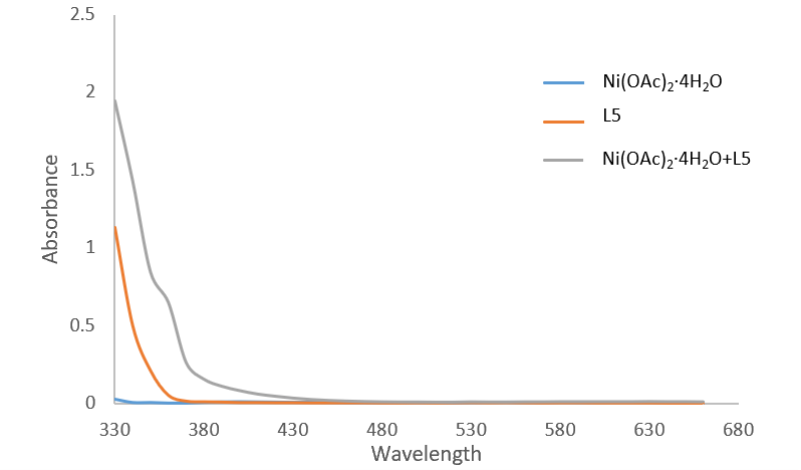


Figure S5. Absorption spectrum of $Ni(OAc)_2 \cdot 4H_2O$ +L5 [$Ni(OAc)_2 \cdot 4H_2O$ 5.0×10^{-4} M; 2 mm pathlength quartz cuvette] in THF.

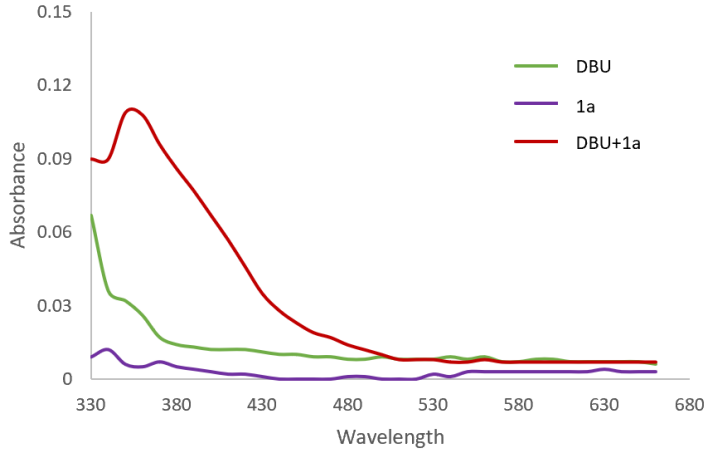


Figure S6. Absorption spectrum of DBU +1a (2 mm pathlength quartz cuvette) in THF.

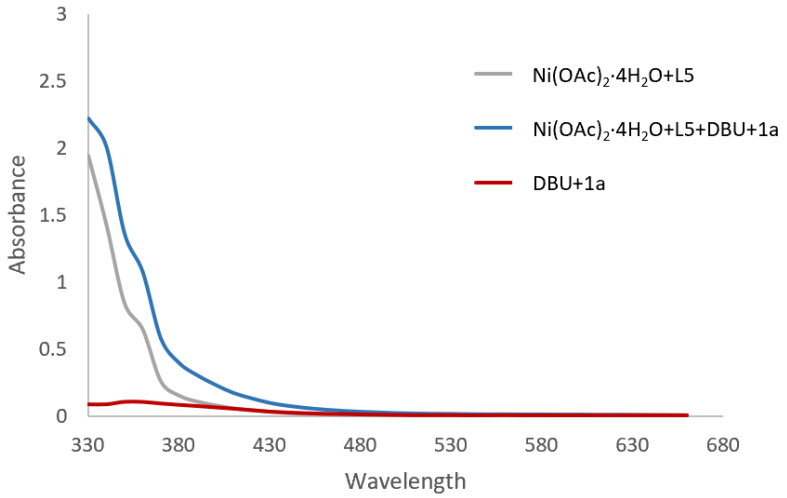


Figure S7. Absorption spectrum of $Ni(OAc)_2{\cdot}4H_2O$, L5, DBU and 1a [$Ni(OAc)_2{\cdot}4H_2O$ 5.0×10^{-4} M; 2 mm pathlength quartz cuvette] in THF.

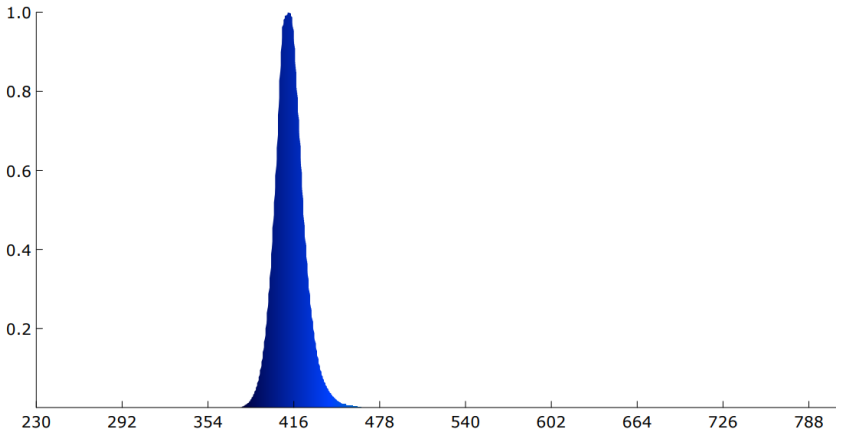
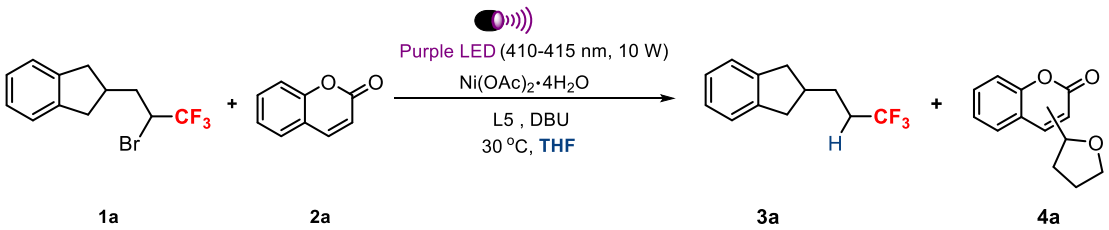


Figure S8. Emission spectra of purple LEDs used for photochemical reactions (λmax=413 nm).

6.5 Light on/off experiment:



1a 2a 3a 4a

Procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with **1a** (0.4 mmol), **2a** (0.2 mmol), $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol), L5 (0.01 mmol). The tube was evacuated and backfilled with argon for three times, followed by

the addition of dry THF (2.0 mL) and DBU (0.3 mmo). The tube was screw capped and heated to 30 °C (heat produced by purple LED) under irradiation of purple LED (410-415 nm, with cooling fan to keep the reaction temperature near 30 ℃). At constant temperature, alternating light and dark reactions were performed every 2 hours, and samples were taken monitor the yield, benzene fluoride was used as the internal standard, and ethyl acetate was used to dilute, and the yield of **3a** was detected by crude ^{19}F NMR.

Table S7. The yield of product **3a** with light on/off at different time.

Entry	Time (h)	Yield (%)
1	2	17
2	4	17
3	6	25
4	8	25
5	10	39
6	12	39
7	14	45
8	16	45

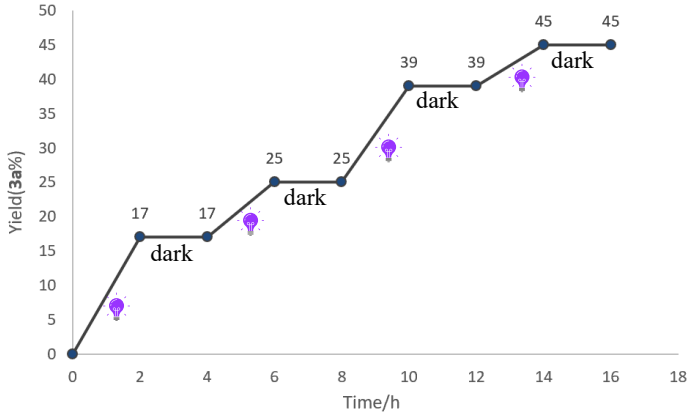
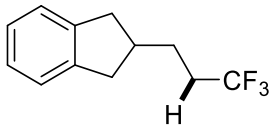


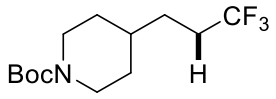
Figure S9. Light on/off experiment

7. Characterization data for the products.



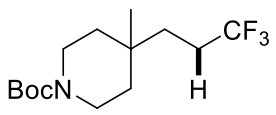
2-(3,3,3-trifluoropropyl)-2,3-dihydro-1*H*-indene (3a)

The product **3a** (38.6 mg, 90% yield) was purified with silica gel chromatography as white solid, mp: 46 – 47 °C, **4a-1** (11.9 mg, 55% yield) and **4a-2** (5.6 mg, 26% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 7.19 – 7.15 (m, 2H), 3.11 (dd, *J* = 15.2, 7.6 Hz, 2H), 2.63 (dd, *J* = 15.6, 8.2 Hz, 2H), 2.56 – 2.47 (m, 1H), 2.25 – 2.13 (m, 2H), 1.83 – 1.77 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 127.2 (q, *J* = 277.5 Hz), 126.3, 124.4, 39.0, 38.9, 32.7 (q, *J* = 28.6 Hz), 27.6 (q, *J* = 2.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.41 (t, *J* = 10.9 Hz, 3F). **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{12}H_{13}F_3$: 214.0964; Found: 214.0969.



***tert*-butyl 4-(3,3,3-trifluoropropyl)piperidine-1-carboxylate (3b)**

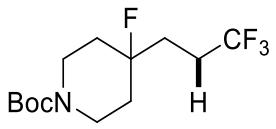
The product **3b** (49.5 mg, 88% yield) was purified with silica gel chromatography as white solid, mp: 33 – 34 °C, **4a-1** (13.0 mg, 60% yield) and **4a-2** (4.8 mg, 22% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.08 (br, 2H), 2.66 (t, *J* = 12.4 Hz, 2H), 2.14 – 2.01 (m, 2H), 1.64 (d, *J* = 12.8 Hz, 2H), 1.52 – 1.46 (m, 2H), 1.44 (s, 10H), 1.15 – 1.04 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.8, 127.2 (q, *J* = 277.5 Hz), 79.4, 43.5 (br), 35.1, 31.7, 31.0 (q, *J* = 28.6 Hz), 28.4, 28.3 (q, *J* = 2.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.52 (t, *J* = 10.7 Hz, 3F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_9H_{15}O_2NF_3$: 226.1049; Found: 226.1046.



***tert*-butyl 4-methyl-4-(3,3,3-trifluoropropyl)piperidine-1-carboxylate (3c)**

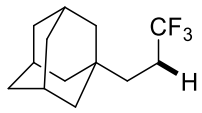
The product **3c** (47.3 mg, 80% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.7 mg, 54% yield) and **4a-2** (5.8 mg, 27% yield) were isolated

simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.62 – 3.56 (m, 2H), 3.20 – 3.14 (m, 2H), 2.09 – 1.97 (m, 2H), 1.52 – 1.48 (m, 2H), 1.44 (s, 9H), 1.35 – 1.28 (m, 4H), 0.94 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.9, 127.5 (q, *J* = 277.3 Hz), 79.4, 39.6 (br), 36.3, 33.2 (q, *J* = 2.6 Hz), 30.5, 28.4, 28.2 (q, *J* = 28.7 Hz), 22.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.52 (t, *J* = 10.5 Hz, 3F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_{10}H_{17}O_2NF_3$: 240.1206; Found: 240.1203.



***tert*-butyl 4-fluoro-4-(3,3,3-trifluoropropyl)piperidine-1-carboxylate (3d)**

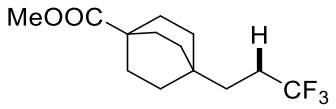
The product **3d** (38.3 mg, 64% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (12.3 mg, 57% yield) and **4a-2** (4.5 mg, 21% yield) were isolated simultaneously, eluent: (PE:EA=25:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.95 (br, 2H), 3.05 (br, 2H), 2.29 – 2.16 (m, 2H), 1.88 – 1.74 (m, 4H), 1.62 – 1.48 (m, 2H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.6, 127.0 (q, *J* = 277.0 Hz), 92.3 (d, *J* = 174.4 Hz), 79.7, 39.3 (d, *J* = 72.7 Hz), 34.3 (d, *J* = 21.8 Hz), 32.4 (qd, *J* = 2.8, 22.5 Hz), 28.3, 27.6 (qd, *J* = 29.6, 4.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.66 (t, *J* = 10.2 Hz, 3F), -165.95 (s, 1F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_9H_{14}O_2NF_4$: 244.0955; Found: 244.0953.



(3*r*,5*r*,7*r*)-1-(3,3,3-trifluoropropyl)adamantane (3e)

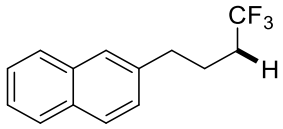
The product **3e** (43.2 mg, 93% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (12.8 mg, 59% yield) and **4a-2** (4.8 mg, 22% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.08 – 2.00 (m, 2H), 1.99 – 1.96 (m, 3H), 1.72 (d, *J* = 12.0 Hz, 3H), 1.62 (d, *J* = 12.8 Hz, 3H), 1.47 (d, *J* = 3.2 Hz, 6H), 1.33 – 1.29 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 128.0 (q, *J* = 277.4 Hz), 41.9, 37.0, 35.5 (q, *J* = 2.5 Hz), 31.3, 28.5, 27.6 (q, *J* = 28.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.49 (t, *J* = 10.9 Hz, 3F). **HRMS** (EI) m/z: $[M]^+$ Calcd for

$C_{13}H_{19}F_3$: 232.1433; Found: 232.1432.



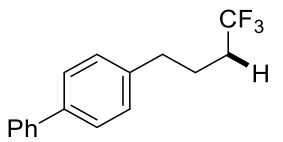
methyl 4-(3,3,3-trifluoropropyl)bicyclo[2.2.2]octane-1-carboxylate (3f)

The product **3f** (46.5 mg, 88% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (13.0 mg, 60% yield) and **4a-2** (5.4 mg, 25% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 2.02 – 1.90 (m, 2H), 1.79 – 1.75 (m, 6H), 1.41 – 1.34 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.1, 127.5 (q, *J* = 277.3 Hz), 51.6, 38.6, 32.4 (q, *J* = 2.6 Hz), 29.9, 29.6, 28.6 (q, *J* = 28.6 Hz), 28.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.63 (t, *J* = 10.5 Hz, 3F). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}O_2F_3$: 265.1410; Found: 265.1407.



2-(4,4,4-trifluorobutyl)naphthalene (3g)

This compound is known.[7] The product **3g** (42.4 mg, 89% yield) was purified with silica gel chromatography as white solid, mp: 40 – 41 °C, **4a-1** (11.9 mg, 55% yield) and **4a-2** (5.6 mg, 26% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.80 (m, 3H), 7.64 (s, 1H), 7.52 – 7.45 (m, 2H), 7.34 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.20 – 2.07 (m, 2H), 2.06 – 1.97 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.1, 133.5, 132.1, 128.2, 127.6, 127.4, 127.2 (q, *J* = 277.6 Hz), 126.9, 126.6, 126.1, 125.4, 34.7, 33.1 (q, *J* = 28.7 Hz), 23.4 (q, *J* = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.12 (t, *J* = 10.2 Hz, 3F).



4-(4,4,4-trifluorobutyl)-1,1'-biphenyl (3h)

This compound is known.[7] The product **3h** (48.6 mg, 92% yield) was purified with

silica gel chromatography as white solid, mp: 62 – 63 °C, **4a-1** (11.9 mg, 55% yield) and **4a-2** (6.1 mg, 28% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.60 (m, 2H), 7.59 – 7.56 (m, 2H), 7.49 – 7.45 (m, 2H), 7.39 – 7.35 (m, 1H), 7.30 – 7.27 (m, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.21 – 2.09 (m, 2H), 2.00 – 1.93 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 139.7, 139.2, 128.8, 128.7, 127.3, 127.2 (q, *J* = 277.8 Hz), 127.1, 127.0, 34.2, 33.1 (q, *J* = 28.6 Hz), 23.5 (q, *J* = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.11 (t, *J* = 10.9 Hz, 3F).

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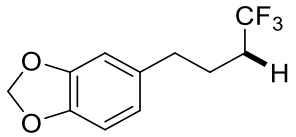
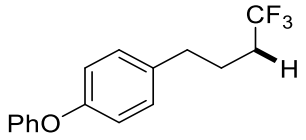


5-(4,4,4-trifluorobutyl)benzo[*d*][1,3]dioxole (3i)

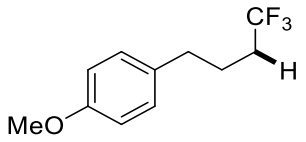
The product **3i** (41.8 mg, 90% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (13.0 mg, 60% yield) and **4a-2** (5.8 mg, 27% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* =1.6 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.94 (s, 2H), 2.61 (t, *J* = 7.4 Hz, 2H), 2.13 – 2.00 (m, 2H), 1.88 – 1.81 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 145.9, 134.4, 127.2 (q, *J* = 277.6 Hz), 121.2, 108.7, 108.2, 100.8, 34.3, 32.9 (q, *J* = 28.6 Hz), 23.7 (q, *J* = 2.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.17 (t, *J* = 10.7 Hz, 3F). **HRMS** (FI) m/z: $[M]^+$ Calcd for $C_{11}H_{11}O_2F_3$: 232.0706; Found: 232.0705.



1-phenoxy-4-(4,4,4-trifluorobutyl)benzene (3j)

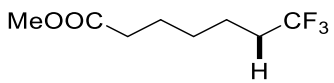
The product **4j** (50.4 mg, 90% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (12.5 mg, 58% yield) and **4a-2** (5.2 mg, 24% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.6 Hz, 2H), 7.17 – 7.10 (m, 3H), 7.02 (d, *J* =8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H),

2.69 (t, J = 8.0 Hz, 2H), 2.17 – 2.05 (m, 2H), 1.95 – 1.87 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4, 155.5, 135.5, 129.7, 129.6, 127.1 (q, J = 277.5 Hz), 123.0, 119.1, 118.6, 33.9, 33.0 (q, J = 28.7 Hz), 23.6 (q, J = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.14 (t, J = 10.9 Hz, 3F). **HRMS** (FI) m/z: $[M]^+$ Calcd for $C_{16}H_{15}OF_3$: 280.1070; Found: 280.1074.



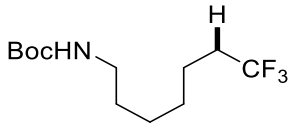
1-methoxy-4-(4,4,4-trifluorobutyl)benzene (3k)

This compound is known.[7] The product **3k** (39.7 mg, 91% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (12.3 mg, 57% yield) and **4a-2** (6.1 mg, 28% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 2.64 (t, J = 8.0 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.91 – 1.83 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 132.7, 129.3, 127.2 (q, J = 277.5 Hz), 113.9, 55.2, 33.7, 33.0 (q, J = 28.7 Hz), 23.7 (q, J = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.17 (t, J = 10.7 Hz, 3F).



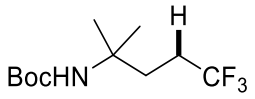
methyl 7,7,7-trifluoroheptanoate (3l)

This compound is known.[8] The product **3l** (28.5 mg, 72% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.7 mg, 54% yield) and **4a-2** (4.5 mg, 21% yield) were isolated simultaneously, eluent: (PE:EA=30:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.33 (t, J = 7.6 Hz, 2H), 2.11 – 2.04 (m, 2H), 1.69 – 1.61 (m, 2H), 1.59 – 1.53 (m, 2H), 1.44 – 1.38 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.8, 127.1 (q, J = 277.5 Hz), 51.5, 33.6, 33.5 (q, J = 28.5 Hz), 28.1, 24.4, 21.6 (q, J = 3.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.45 (t, J = 10.9 Hz, 3F).



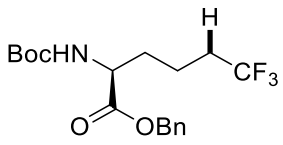
***tert*-butyl (7,7,7-trifluoroheptyl)carbamate (3m)**

The product **3m** (47.3 mg, 88% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (13.0 mg, 60% yield) and **4a-2** (5.2 mg, 24% yield) were isolated simultaneously, eluent: (PE:EA=15:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.53 (br, 1H), 3.09 (t, *J* = 7.0 Hz, 2H), 2.10 – 1.98 (m, 2H), 1.56 – 1.52 (m, 2H), 1.47 (t, *J* = 7.0 Hz, 2H), 1.43 (s, 9H), 1.37 – 1.31 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.0, 127.2 (q, *J* = 277.5 Hz), 79.1, 40.4 (br), 33.6 (q, *J* = 28.5 Hz), 29.8, 28.3, 28.2, 26.3, 21.7 (q, *J* = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.46 (t, *J* = 10.9 Hz, 3F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_8H_{15}O_2NF_3$: 214.1049; Found: 214.1047.



***tert*-butyl (5,5,5-trifluoro-2-methylpentan-2-yl)carbamate (3n)**

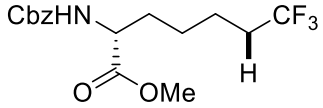
The product **3n** (46.0 mg, 90% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.7 mg, 54% yield) and **4a-2** (5.8 mg, 27% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.38 (s, 1H), 2.11 – 2.00 (m, 2H), 1.97 – 1.90 (m, 2H), 1.42 (s, 9H), 1.25 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.2, 127.4 (q, *J* = 277.3 Hz), 79.1 (br), 51.3, 31.6, 29.2 (q, *J* = 28.9 Hz), 28.3, 27.3 (br); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.27 (t, *J* = 10.5 Hz, 3F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_7H_{13}O_2NF_3$: 200.0893; Found: 200.0892.



benzyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-6,6,6-trifluorohexanoate (3o)

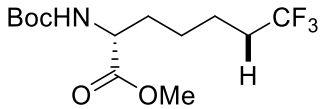
The product **3o** (63.8 mg, 85% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.9 mg, 55% yield) and **4a-2** (5.4 mg, 25% yield) were isolated simultaneously, eluent: (PE:EA=15:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 –

7.33 (m, 5H), 5.23 – 5.12 (m, 2H), 5.10 (d, J = 8.0 Hz, 1H), 4.39 – 4.34 (m, 1H), 2.15 – 1.98 (m, 2H), 1.94 – 1.84 (m, 1H), 1.74 – 1.55 (m, 3H), 1.44 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 155.3, 135.1, 128.6, 128.5, 128.3, 126.8 (q, J = 277.5 Hz), 80.1, 67.2, 52.9, 33.1 (q, J = 28.9 Hz), 31.7, 28.2, 17.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.35 (t, J = 10.5 Hz, 3F). **HRMS** (ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_{14}H_{17}O_4NF_3$: 320.1104; Found: 320.1097.



methyl (*R*)-2-(((benzyloxy)carbonyl)amino)-7,7,7-trifluoroheptanoate (3p)

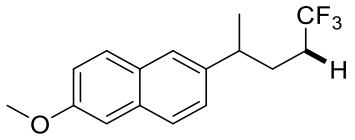
The product **3p** (59.7 mg, 86% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (10.8 mg, 50% yield) and **4a-2** (4.8 mg, 22% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 5H), 5.38 (d, J = 8.0 Hz, 1H), 5.11 (s, 2H), 4.42 – 4.37 (m, 1H), 3.74 (s, 3H), 2.11 – 1.99 (m, 2H), 1.91 – 1.82 (m, 1H), 1.72 – 1.63 (m, 1H), 1.61 – 1.51 (m, 2H), 1.45 – 1.33 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.7, 155.8, 136.1, 128.4, 128.1, 128.0, 126.9 (q, J = 277.6 Hz), 66.9, 53.5, 52.3, 33.3 (q, J = 28.7 Hz), 32.2, 24.2, 21.4 (q, J = 3.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.39 (t, J = 10.9 Hz, 3F). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{21}O_4NF_3$: 348.1417; Found: 348.1412.



methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-7,7,7-trifluoroheptanoate (3q)

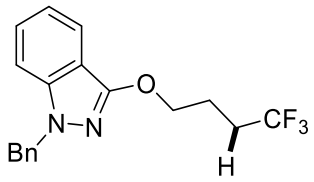
The product **3q** (53.3 mg, 85% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.9 mg, 55% yield) and **4a-2** (4.3 mg, 20% yield) were isolated simultaneously, eluent: (PE:EA=15:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.04 (d, J = 8.4 Hz, 1H), 4.29 (q, J = 6.9 Hz, 1H), 3.72 (s, 3H), 2.11 – 1.99 (m, 2H), 1.84 – 1.78 (m, 1H), 1.65 – 1.51 (m, 3H), 1.42 (s, 11H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.1, 155.3, 127.0 (q, J = 277.6 Hz), 79.8, 53.0, 52.2, 33.4 (q, J = 28.6 Hz), 32.3, 28.2, 24.4, 21.4 (q, J = 2.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.36 (t, J = 10.9 Hz, 3F). **HRMS**

(ESI) m/z: $[M+H-C_4H_8]^+$ Calcd for $C_9H_{15}O_4NF_3$: 258.0948; Found: 258.0943.



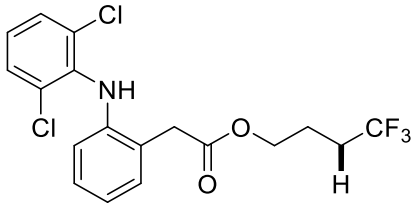
2-methoxy-6-(5,5,5-trifluoropentan-2-yl)naphthalene (3r)

The product **3r** (49.1 mg, 87% yield) was purified with silica gel chromatography as white solid, mp: 64 – 65 °C, **4a-1** (12.3 mg, 57% yield) and **4a-2** (5.0 mg, 23% yield) were isolated simultaneously, eluent: (PE:EA=1:0 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.31 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.18 – 7.14 (m, 2H), 3.93 (s, 3H), 2.92 – 2.84 (m, 1H), 2.07 – 1.89 (m, 4H), 1.37 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.4, 140.6, 133.4, 129.0, 128.9, 127.3 (q, *J* = 277.5 Hz), 127.2, 125.6, 125.2, 118.9, 105.5, 55.3, 39.0, 32.1 (q, *J* = 28.6 Hz), 30.0 (q, *J* = 2.7 Hz), 22.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.25 (t, *J* = 9.8 Hz, 3F). **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{16}H_{17}OF_3$: 282.1226; Found: 282.1230.



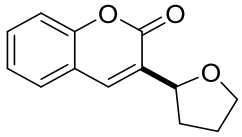
1-benzyl-3-(4,4,4-trifluorobutoxy)-1*H*-indazole (3s)

The product **3s** (61.5 mg, 92% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.9 mg, 55% yield) and **4a-2** (5.8 mg, 27% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.33 – 7.21 (m, 4H), 7.17 (t, *J* = 5.2Hz, 3H), 7.05 (t, *J* = 7.2Hz, 1H), 5.38 (s, 2H), 4.44 (t, *J* = 6.0Hz, 2H), 2.40 – 2.28 (m, 2H), 2.16 – 2.09 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 141.5, 137.3, 128.6, 127.5, 126.9, 127.1 (q, *J* = 277.1 Hz), 119.9, 119.8, 119.2, 112.8, 108.9, 67.1, 52.33, 52.27, 52.22, 30.8 (q, *J* = 29.3 Hz), 22.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ - 66.38 (t, *J* = 10.9 Hz, 3F). **HRMS** (ESI): m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}ON_2F_3$: 335.1366; Found: 335.1357.



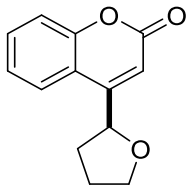
4,4,4-trifluorobutyl 2-(2-((2,6-dichlorophenyl)amino)phenyl)acetate (3t)

The product **3t** (73.1 mg, 90% yield) was purified with silica gel chromatography as colorless liquid, **4a-1** (11.9 mg, 55% yield) and **4a-2** (4.8 mg, 22% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 9.2 Hz, 1H), 7.01 – 6.95 (m, 2H), 6.86 (br, 1H), 6.56 (d, *J* = 6.4 Hz, 1H), 4.21 (t, *J* = 6.4 Hz, 2H), 3.83 (s, 2H), 2.21 – 2.09 (m, 2H), 1.97 – 1.90 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.2, 142.6, 137.7, 130.8, 129.4, 128.9, 128.1,126.8 (q, *J* = 277.6 Hz), 124.1, 122.1, 118.3, 63.5, 38.4, 30.5 (q, *J* = 29.6 Hz), 21.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.45 (t, *J* = 9.6 Hz, 3F). **HRMS** (ESI): m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}O_2NCl_2F_3$: 406.0583; Found: 406.0576.



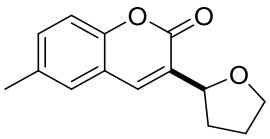
3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4a-1)

This compound is known.[9] The product **4a-1** was purified with silica gel chromatography as white solid, mp: 42 – 43 °C, eluent: (PE:EA=10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.23 (m, 1H), 4.94 (t, *J* = 6.8 Hz, 1H), 4.12 – 4.07 (m, 1H), 3.93 (q, *J* = 7.3 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.05 – 1.97 (m, 1H), 1.97 – 1.87 (m, 1H), 1.79 – 1.71 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 153.1, 136.4, 131.0, 130.9, 127.8, 124.4, 119.2, 116.4, 75.9, 68.9, 32.2, 25.6.



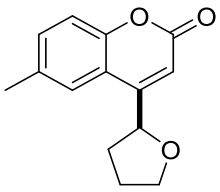
4-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4a-2)

This compound is known.[9] The product **4a-2** was purified with silica gel chromatography as colorless liquid, eluent: (PE:EA=10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.38 – 7.35 (m, 1H), 7.30 – 7.26 (m, 1H), 6.59 (d, *J* = 1.2 Hz, 1H), 5.26 – 5.22 (m, 1H), 4.17 – 4.12 (m, 1H), 4.03 – 3.97 (m, 1H), 2.58 – 2.50 (m, 1H), 2.12 – 1.95 (m, 2H), 1.92 – 1.84 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 156.9, 153.9, 131.5, 124.1, 124.0, 117.6, 117.4, 110.9, 75.7, 69.2, 32.9, 25.7.



6-methyl-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4b-1)

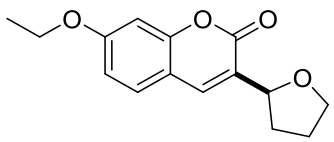
This compound is known.[10] The product **4b-1** (13.8 mg, 60% yield) was purified with silica gel chromatography as white solid, mp: 65 – 66 °C, **3b** (45.0 mg, 80% yield) and **4b-2** (4.0 mg, 17% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.30 – 7.26 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 4.96 (t, J = 6.8 Hz, 1H), 4.13 – 4.08 (m, 1H), 3.95 (q, *J* = 7.5 Hz,, 1H), 2.55 – 2.47 (m, 1H), 2.39 (s, 3H), 2.06 – 1.98 (m, 1H), 1.94 – 1.89 (m, 1H), 1.80 – 1.71 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 151.2, 136.4, 134.0, 131.9, 130.8, 127.6, 118.9, 116.1, 75.9, 68.9, 32.2, 25.6, 20.8.



6-methyl-4-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4b-2)

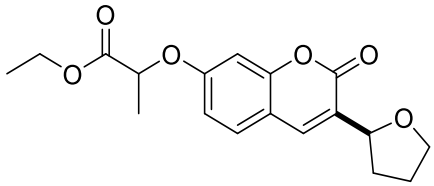
The product **4b-2** (4.0 mg, 17% yield) was purified with silica gel chromatography as colorless liquid, **3b** (45.0 mg, 80% yield) and **4b-1** (13.8 mg, 60% yield) were isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 9.2 Hz, 2H), 6.59 (s, 1H), 5.25 (t, J = 8.0 Hz, 1H), 4.13 (q, *J* = 6.9 Hz, 1H), 4.02 (q, *J* = 7.5 Hz,, 1H), 2.62 – 2.53 (m, 1H), 2.44 (s, 3H), 2.12 – 1.98

(m, 2H), 1.93 – 1.85 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 156.8, 152.0, 133.7, 132.5, 123.8, 117.2, 117.1, 110.7, 75.7, 69.1, 32.9, 25.7, 21.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}O_3$: 231.1016; Found: 231.1019.



7-ethoxy-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4c-1)

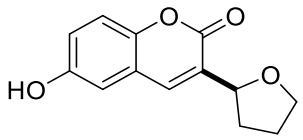
This compound is known.[11] The product **4c-1** (13.5 mg, 52% yield) was purified with silica gel chromatography as white solid, mp: 67 – 68 °C, **3b** (48.9 mg, 87% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.83 – 6.79 (m, 2H), 4.92 (t, *J* = 7.2 Hz, 1H), 4.07 (q, *J* = 7.1 Hz,, 3H), 3.93 (q, *J* = 7.5 Hz, 1H), 2.52 – 2.44 (m, 1H), 2.05 – 1.97 (m, 1H), 1.96 – 1.87 (m, 1H), 1.79 – 1.71 (m, 1H), 1.44 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 160.9, 154.8, 136.6, 128.6, 127.2, 112.9, 112.7, 100.9, 75.9, 68.8, 64.1, 32.2, 25.6, 14.5.



ethyl 2-((2-oxo-3-(tetrahydrofuran-2-yl)-2*H*-chromen-7-yl)oxy)propanoate (4d-1)

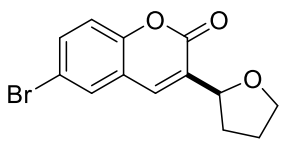
The product **4d-1** (16.6 mg, 50% yield) was purified with silica gel chromatography as colorless liquid, **3b** (50.6 mg, 90% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). Mixture of diastereomers: (dr=1:1.1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 1H, minor), 7.72 (s, 1H, major), 7.39 (d, *J* = 8.4 Hz, 1H, minor and major), 6.87 – 6.85 (m, 1H, major), 6.84 – 6.83 (m, 1H, minor), 6.74 (d, *J* = 2.4 Hz, 1H, minor), 6.73 (d, *J* = 2.4 Hz, 1H, major), 4.92 (t, *J* = 7.0 Hz, 1H, minor and major), 4.78 (q, J = 6.8 Hz, 1H, minor and major), 4.23 (q, J = 7.1 Hz, 2H, minor and major), 4.12 – 4.06 (m, 1H, minor and major), 3.93 (q, J = 7.3 Hz, 1H, minor and major), 2.53 – 2.44 (m, 1H, minor and major), 2.03 – 1.97 (m, 1H, minor and major), 1.95 – 1.89 (m, 1H,

minor and major), 1.79 – 1.71 (m, 1H, minor and major), 1.65 (d, *J* = 6.8 Hz, 3H, minor and major), 1.27 (t, *J* = 7.2 Hz, 3H, minor), 1.26 (t, *J* = 7.2 Hz, 3H, major); For the mixture: **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3 (major), 171.2 (minor), 160.7 (minor and major), 159.9 (minor and major), 154.5 (minor and major), 136.5 (minor), 136.4 (major), 128.8 (minor and major), 127.9 (major), 127.8 (minor), 113.5 (major), 113.4 (minor), 113.2 (minor), 113.0 (major), 101.6 (minor), 101.5 (major), 75.9 (major), 75.8 (minor), 72.7 (major), 72.6 (minor), 68.9 (minor), 68.8 (major), 61.6 (minor and major), 32.3 (major), 32.2 (minor), 25.6 (major), 25.5 (minor), 18.4 (minor and major), 14.1 (minor and major). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}O_6$: 333.1333; Found: 333.1332.



6-hydroxy-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4e-1)

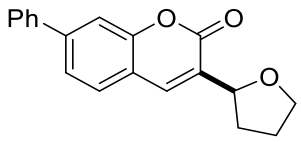
The product **4e-1** (9.3 mg, 40% yield) was purified with silica gel chromatography as white solid, mp: 134 – 135 °C, **3b** (49.5 mg, 88% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.18 (d, J = 8.8 Hz, 1H), 7.02 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.93 (d, J = 2.8 Hz, 1H), 6.69 (br, 1H), 4.98 (t, J = 6.8 Hz, 1H), 4.12 (q, *J* = 8.0 Hz, 1H), 3.96 (q, *J* = 7.2 Hz,, 1H), 2.56 – 2.47 (m, 1H), 2.07 – 1.91 (m, 2H), 1.82 – 1.74 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 152.2, 147.2, 136.2, 131.0, 119.7, 119.4, 117.4, 112.5, 76.0, 69.0, 32.2, 25.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_4$: 233.0808; Found: 233.0807.



6-bromo-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4f-1)

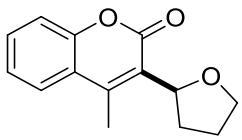
This compound is known. [10] The product **4f-1** (13.0 mg, 44% yield) was purified with silica gel chromatography as white solid, mp: 125 – 126 °C, **3b** (47.8 mg, 85% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$)

δ 7.71 (s, 1H), 7.61 (s, 1H), 7.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.19 (d, J = 8.8 Hz, 1H), 4.93 (t, J = 7.2 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 1H), 3.94 (q, *J* = 7.5 Hz,, 1H), 2.55 – 2.46 (m, 1H), 2.06 – 1.96 (m, 1H), 1.94 – 1.86 (m, 1H), 1.78 – 1.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 151.8, 135.0, 133.6, 132.3, 130.0, 120.7, 118.1, 116.9, 75.8, 68.9, 32.1, 25.6.



7-phenyl-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4g-1)

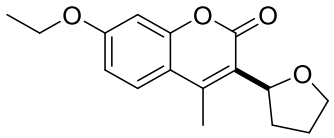
The product **4g-1** (16.1 mg, 55% yield) was purified with silica gel chromatography as white solid, mp: 109 – 110 °C, **3b** (46.1 mg, 82% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.8 Hz, 3H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 4.98 (t, *J* = 6.8 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 1H), 3.96 (q, *J* = 7.5 Hz, 1H), 2.58 – 2.49 (m, 1H), 2.08 – 2.00 (m, 1H), 1.98 – 1.90 (m, 1H), 1.83 – 1.74 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 153.4, 144.0, 139.2, 136.1 (d, *J* = 7.6 Hz), 130.7, 129.0, 128.3, 128.0, 127.1, 123.3, 118.1, 114.5 (d, *J* = 9.6 Hz), 75.9 (d, *J* = 13.7 Hz), 68.8, 32.2, 25.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}O_3$: 293.1172; Found: 293.1168.



4-methyl-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4h)

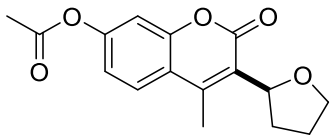
The product **4h** (13.8 mg, 60% yield) was purified with silica gel chromatography as colorless liquid, **3b** (49.5 mg, 88% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.31 – 7.30 (m, 1H), 7.29 – 7.28 (m, 1H), 5.27 (t, *J* = 8.0 Hz, 1H), 4.17 (q, *J* = 7.5 Hz, 1H), 3.93 – 3.88 (m, 1H), 2.55 (s, 3H), 2.30 – 2.23 (m, 1H), 2.21 – 2.15 (m, 1H), 2.11 – 2.02 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.3, 152.3, 148.3, 131.1, 125.3, 124.6, 124.1, 120.8, 116.7, 75.9, 68.7, 40.0, 26.8, 14.5. **HRMS** (ESI) m/z:

$[M+H]^+$ Calcd for $C_{14}H_{15}O_3$: 231.1016; Found: 231.1017.



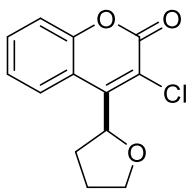
7-ethoxy-4-methyl-3-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4i)

The product **4i** (16.7 mg, 61% yield) was purified with silica gel chromatography as white solid, mp: 76 – 78 °C, **3b** (51.2 mg, 91% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.74 (d, *J* = 2.8 Hz, 1H), 5.22 (t, *J* = 7.8 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 4.05 (q, *J* = 6.9 Hz, 2H), 3.89 – 3.84 (m, 1H), 2.48 (s, 3H), 2.24 – 2.13 (m, 2H), 2.09 – 1.99 (m, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.4, 160.6, 154.0, 148.8, 125.6, 121.7, 114.1, 112.5, 100.7, 75.8, 68.6, 63.9, 30.7, 26.8, 14.5, 14.4. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}O_4$: 275.1278; Found: 275.1279.



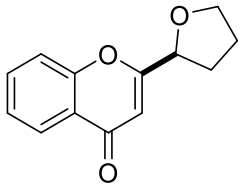
4-methyl-2-oxo-3-(tetrahydrofuran-2-yl)-2*H*-chromen-7-yl acetate (4j)

The product **4j** (15.9 mg, 55% yield) was purified with silica gel chromatography as white solid, mp: 97 – 98 °C, **3b** (50.6 mg, 90% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.8 Hz, 1H), 7.08 – 7.04 (m, 2H), 5.25 (t, *J* = 7.8 Hz, 1H), 4.16 (q, *J* = 7.5 Hz, 1H), 3.92 – 3.87 (m, 1H), 2.53 (s, 3H), 2.33 (s, 3H), 2.30 – 2.24 (m, 1H), 2.23 – 2.17 (m, 1H), 2.09 – 2.01 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 160.0, 152.9, 152.5, 147.9, 125.5, 124.8, 118.6, 117.9, 109.9, 75.9, 68.7, 31.0, 26.8, 21.1, 14.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_5$: 289.1071; Found: 289.1069.



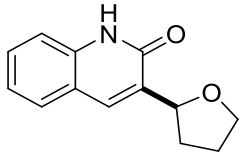
3-chloro-4-(tetrahydrofuran-2-yl)-2*H*-chromen-2-one (4k)

The product **4k** (15.3 mg, 61% yield) was purified with silica gel chromatography as white solid, mp: 112 – 113 °C, **3b** (37.7 mg, 67% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.8, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 5.47 (t, *J* = 8.4 Hz, 1H), 4.31 (q, *J* = 7.6 Hz, 1H), 4.04 – 3.98 (m, 1H), 2.51 – 2.43 (m, 1H), 2.27 – 2.14 (m, 2H), 2.05 – 1.94 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.8, 151.8, 149.5, 131.5, 126.1, 124.4, 120.2, 117.3, 117.2, 78.8, 68.9, 31.2, 26.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{12}O_3Cl$: 251.0469; Found: 251.0471.



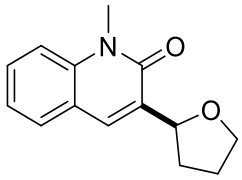
2-(tetrahydrofuran-2-yl)-4*H*-chromen-4-one (4l-1)

The product **4l-1** (11.5 mg, 53% yield) was purified with silica gel chromatography as colorless liquid, **3b** (50.6 mg, 90% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 4.81 (t, *J* = 6.6 Hz, 1H), 4.09 – 4.04 (m, 1H), 3.98 – 3.92 (m, 1H), 2.41 – 2.32 (m, 1H), 2.14 – 2.06 (m, 1H), 2.03 – 1.96 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 169.4, 156.2, 133.6, 125.7, 125.0, 123.9, 117.9, 107.6, 76.7, 69.4, 31.1, 25.3. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}O_3$: 217.0859; Found: 217.0860.



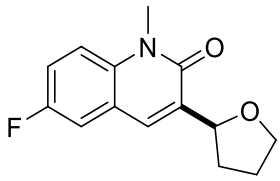
3-(tetrahydrofuran-2-yl)quinolin-2(1*H*)-one (4m)

The product **4m** (9.7 mg, 45% yield) was purified with silica gel chromatography as white solid, mp: 166 – 167 °C, **3b** (53.5 mg, 95% yield) was isolated simultaneously, eluent: (PE:EA=10:1 to 1:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 12.18 (br, 1H), 7.92 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 5.17 (t, *J* = 6.6 Hz, 1H), 4.19 – 4.14 (m, 1H), 3.99 (q, *J* = 7.2 Hz, 1H), 2.66 – 2.58 (m, 1H), 2.10 – 1.91 (m, 2H), 1.85 – 1.77 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1, 137.4, 135.1, 134.2, 129.7, 127.7, 122.6, 120.0, 115.6, 76.1, 68.7, 32.5, 25.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}O_2N$: 216.1019; Found: 216.1018.



1-methyl-3-(tetrahydrofuran-2-yl)quinolin-2(1*H*)-one (4n)

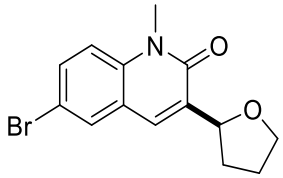
This compound is known. [12] The product **4n** (12.6 mg, 55% yield) was purified with silica gel chromatography as colorless liquid, **3b** (47.8 mg, 85% yield) was isolated simultaneously, eluent: (PE:EA=10:1 to 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 5.08 (t, *J* = 7.2 Hz, 1H), 4.12 (q, *J* = 6.9 Hz, 1H), 3.94 (q, *J* = 7.5 Hz, 1H), 3.72 (s, 3H) 2.59 – 2.51 (m, 1H), 2.03 – 1.97 (m, 1H), 1.94 – 1.87 (m, 1H), 1.76 – 1.67 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.2, 138.9, 135.0, 132.3 (d, *J* = 3.4 Hz), 129.7, 128.6, 122.1, 120.4, 113.8, 76.5 (d, *J* = 7.1 Hz), 68.6, 32.3, 29.3 (d, *J* = 5.7 Hz), 25.6.



6-fluoro-1-methyl-3-(tetrahydrofuran-2-yl)quinolin-2(1*H*)-one (4o)

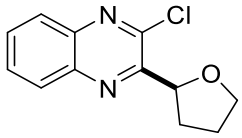
The product **4o** (11.2 mg, 45% yield) was purified with silica gel chromatography as white solid, mp: 107 – 108 °C, **3b** (50.6 mg, 90% yield) was isolated simultaneously,

eluent: (PE:EA=10:1 to 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.35 – 7.31 (m, 1H), 7.29 – 7.27 (m, 2H), 5.10 (t, *J* = 7.0 Hz, 1H), 4.14 (q, *J* = 6.9 Hz, 1H), 3.97 (q, *J* = 7.5 Hz, 1H), 3.74 (s, 3H), 2.63 – 2.54 (m, 1H), 2.06 – 1.98 (m, 1H), 1.97 – 1.90 (m, 1H), 1.77 – 1.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 158.7 (d, *J* = 424.8 Hz), 136.6, 135.5 (d, *J* = 1.4 Hz), 131.4 (dd, *J* = 7.7, 2.8 Hz), 121.3 (d, *J* = 8.6 Hz), 117.4 (d, *J* = 24.2 Hz), 115.4 (d, *J* = 7.8 Hz), 113.5 (dd, *J* = 22.6, 7.5 Hz), 76.5 (d, *J* = 12.5 Hz), 68.7, 32.3 (d, *J* = 3.6 Hz), 29.5 (d, *J* = 10.0 Hz), 25.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.24 – -121.29 (m, 1F). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}O_2NF$: 248.1081; Found: 248.1083.



6-bromo-1-methyl-3-(tetrahydrofuran-2-yl)quinolin-2(1*H*)-one (4p)

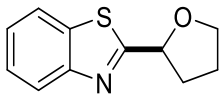
The product **4p** (15.1 mg, 49% yield) was purified with silica gel chromatography as white solid, mp: 99 – 100 °C, **3b** (48.4 mg, 86% yield) was isolated simultaneously, eluent: (PE:EA=10:1 to 3:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 1H), 3.95 (q, *J* = 7.5 Hz, 1H), 3.70 (s, 3H), 2.60 – 2.51 (m, 1H), 2.04 – 1.96 (m, 1H), 1.94 – 1.87 (m, 1H), 1.75 – 1.68 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.8, 137.9, 136.5, 132.4, 131.1 (d, *J* = 5.6 Hz), 130.7 (d, *J* = 5.5 Hz), 122.0, 115.6, 114.9, 76.5 (d, *J* = 10.3 Hz), 68.7, 32.3, 29.4 (d, *J* = 8.1 Hz), 25.7. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}O_2NBr$: 308.0281; Found: 308.0282.



2-chloro-3-(tetrahydrofuran-2-yl)quinoxaline (4q)

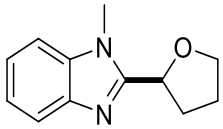
This compound is known. [13] The product **4q** (13.6 mg, 58% yield) was purified with silica gel chromatography as black liquid, **3b** (39.9 mg, 71% yield) was isolated

simultaneously, eluent: (PE:EA=20:1 to 15:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 – 8.14 (m, 1H), 8.00 – 7.98 (m, 1H), 7.77 – 7.74 (m, 2H), 5.56 (t, *J* = 6.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 2.56 – 2.48 (m, 1H), 2.27 – 2.19 (m, 1H), 2.17 – 2.05 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 145.9, 141.3, 140.6, 130.6, 130.2, 129.3, 128.0, 77.9, 69.5, 30.9, 25.7.



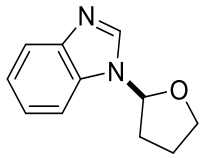
2-(tetrahydrofuran-2-yl)benzo[*d*]thiazole (4r)

This compound is known.[14] The product **4r** (12.3 mg, 60% yield) was purified with silica gel chromatography as colorless liquid, **3b** (52.3 mg, 93% yield) was isolated simultaneously, eluent: (PE:EA=10:1 to 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.38 – 7.34 (m, 1H), 5.35 (t, *J* = 6.6 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 1H), 4.00 (q, *J* = 7.5 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.31 – 2.23 (m, 1H), 2.07 – 1.99 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.4, 153.5, 134.6, 125.9, 124.7, 122.7, 121.7, 78.7 (d, *J* = 6.6 Hz), 69.4, 33.3, 25.6.



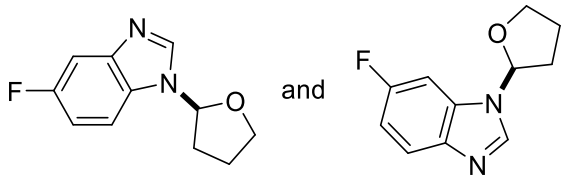
1-methyl-2-(tetrahydrofuran-2-yl)-1*H*-benzo[*d*]imidazole (4s)

This compound is known. [15] The product **4s** (10.5 mg, 52% yield) was purified with silica gel chromatography as colorless liquid, **3b** (50.6 mg, 90% yield) was isolated simultaneously, eluent: (PE:EA=10:1 to 2:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.24 (m, 2H), 5.22 (t, *J* = 7.0 Hz, 1H), 3.95 (t, *J* = 6.8 Hz, 2H), 3.87 (s, 3H), 2.85 – 2.76 (m, 1H), 2.42 – 2.33 (m, 1H), 2.24 – 2.18 (m, 1H), 2.12 – 2.03 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.5, 141.6, 136.1, 122.7, 122.1, 119.7 (d, *J* = 6.8 Hz), 109.2, 73.5 (d, *J* = 11.5 Hz), 68.7, 30.2 (d, *J* = 10.7 Hz), 29.3, 26.0.



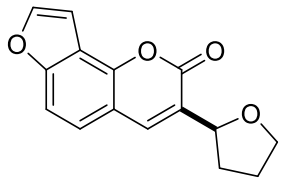
1-(tetrahydrofuran-2-yl)-1H-benzo[*d*]imidazole (4t)

This compound is known. [16] The product **4t** (10.2 mg, 54% yield) was purified with silica gel chromatography as colorless liquid, **3b** (54.0 mg, 96% yield) was isolated simultaneously, eluent: (PE:EA=1:1 to 1:3). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.80 – 7.77 (m, 1H), 7.45 – 7.43 (m, 1H), 7.28 – 7.26 (m, 2H), 6.16 – 6.13 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 1H), 4.02 (q, *J* = 7.7 Hz, 1H), 2.43 – 2.37 (m, 2H), 2.14 – 2.09 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 140.2, 132.5, 123.1, 122.5, 120.3, 110.4, 86.0, 68.9, 31.8, 24.2.



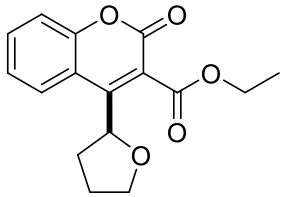
5-fluoro-1-(tetrahydrofuran-2-yl)-1H-benzo[*d*]imidazole and 6-fluoro-1-(tetrahydrofuran-2-yl)-1H-benzo[*d*]imidazole (4u)

The product **4u** (12.6 mg, 61% yield) was purified with silica gel chromatography as colorless liquid, **3b** (53.5 mg, 95% yield) was isolated simultaneously, eluent: (PE:EA=1:1 to 1:3). Mixture of isomers: (1:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.99 (s, 1H), 7.70 (q, *J* = 4.5 Hz, 1H), 7.45 (dd, *J* = 9.2, 6.8 Hz, 1H), 7.38 (q, *J* = 4.5 Hz, 1H), 7.15 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.03 (qd, *J* = 9.0, 2.8 Hz, 2H), 6.14 (t, *J* = 4.8 Hz, 1H), 6.09 (t, *J* = 4.8 Hz, 1H), 4.19 – 4.14 (m, 2H), 4.08 – 4.02 (m, 2H), 2.48 – 2.37 (m, 4H), 2.19 – 2.09 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7 (d, *J* = 30.9 Hz), 158.3 (d, *J* = 28.5 Hz), 144.6 (d, *J* = 11.4 Hz), 141.5, 141.5, 140.7 (d, *J* = 2.8 Hz), 140.5 (d, *J* = 1.0 Hz), 129.1, 121.0 (d, *J* = 10.3 Hz), 111.5 (d, *J* = 26.4 Hz), 110.9 (d, *J* = 9.2 Hz), 110.8 (d, *J* = 5.7 Hz), 106.0 (d, *J* = 24.1 Hz), 97.3 (d, *J* = 28.0 Hz), 86.1, 86.0, 68.9, 68.9, 31.8, 31.7, 24.2, 24.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.3 (s, 1F), -120.7 (s, 1F). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{11}H_{12}ON_2F$: 207.0928; Found: 207.0929.



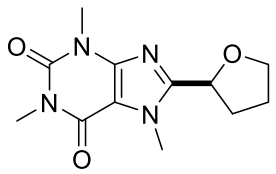
3-(tetrahydrofuran-2-yl)-2*H*-furo[2,3-*h*]chromen-2-one (4v-1)

The product **4v-1** (14.4 mg, 56% yield) was purified with silica gel chromatography as white solid, mp: 96 – 97 °C, **3b** (50.6 mg, 90% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 10:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.41 (q, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 2.0 Hz, 1H), 4.98 (t, *J* = 6.8 Hz, 1H), 4.13 (q, J = 6.9 Hz, 1H), 3.96 (q, *J* = 7.5 Hz,, 1H), 2.57 – 2.49 (m, 1H), 2.08 – 1.99 (m, 1H), 1.98 – 1.90 (m, 1H), 1.83 – 1.75 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 156.8, 147.2, 145.7, 137.6, 128.4, 123.8, 116.5, 113.8, 108.7, 104.0, 75.9, 68.9, 32.2, 25.6. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}O_4$: 257.0808; Found: 257.0710.



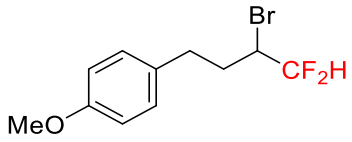
ethyl 2-oxo-4-(tetrahydrofuran-2-yl)-2*H*-chromene-3-carboxylate (4w)

The product **4w** (13.8 mg, 48% yield) was purified with silica gel chromatography as colorless liquid, **3b** (46.1 mg, 82% yield) was isolated simultaneously, eluent: (PE:EA=20:1 to 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 5.32 (t, *J* = 7.4 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.98 (q, *J* = 7.1 Hz, 1H), 3.90 (q, *J* = 7.1 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.17 – 2.08 (m, 1H), 2.07 – 1.97 (m, 2H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.2, 158.8, 152.8, 152.4, 132.2, 124.7, 124.6, 119.0, 117.4, 116.9, 76.3, 69.6, 61.7, 33.8, 26.1, 14.1. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}O_5$: 289.1071; Found: 289.1072.



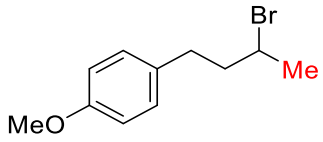
1,3,7-trimethyl-8-(tetrahydrofuran-2-yl)-1,3,6,7-tetrahydro-2*H*-purin-2-one (4x)

The product **4x** (12.5 mg, 50% yield) was purified with silica gel chromatography as white solid, mp: 115 – 116 °C, **3b** (52.3 mg, 93% yield) was isolated simultaneously, eluent: (PE:EA=1:1 to 1:5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.03 (t, *J* = 6.8 Hz, 1H), 4.03 (s, 3H), 3.99 – 3.89 (m, 2H), 3.56 (s, 3H), 3.39 (s, 3H), 2.61 – 2.52 (m, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.11 (m, 1H), 2.10 – 2.00 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.5, 152.3, 151.7, 147.2, 108.3, 72.5, 68.9, 32.2, 29.8, 29.6, 27.9, 25.9. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}O_3N_4$: 265.1295; Found: 265.1293.



1-(3-bromo-4,4-difluorobutyl)-4-methoxybenzene (1k-CF_2H)

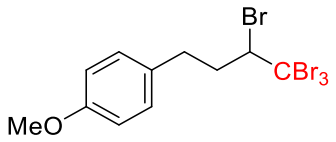
Obtained in 72% yield as a colorless liquid (0.20 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.83 (dt, *J* = 56.0, 2.4 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.80 (s, 3H), 2.96 – 2.89 (m, 1H), 2.75 – 2.67 (m, 1H), 2.28 – 2.20 (m, 1H), 2.14 – 2.04 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.2, 131.6, 129.5, 114.7 (t, *J* = 246.6 Hz), 114.0, 55.2, 49.8 (t, *J* = 24.0 Hz), 32.5 (t, *J* = 2.5 Hz), 31.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.46 (ddd, *J* = 276.7, 55.6, 10.9 Hz, 1F), -122.25 (ddd, *J* = 276.7, 56.0, 13.2 Hz, 1F). **HRMS** (DART) m/z: $[M+H]^+$ Calcd for $C_{11}H_{14}OF_2Br$: 279.0191; Found: 279.0195.



1-(3-bromobutyl)-4-methoxybenzene (1k-CH_3)

This compound is known[17]. Obtained in 81% yield as a colorless liquid (196mg). **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.11 – 4.03 (m, 1H), 3.80 (s, 3H), 2.85 – 2.78 (m, 1H), 2.73 – 2.66 (m, 1H), 2.16 – 2.06 (m, 1H), 2.05 – 1.96 (m, 1H), 1.73 (d, *J* = 4.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.9, 132.9, 129.4, 113.8, 55.2, 51.0, 42.9, 33.0, 26.5.



1-methoxy-4-(3,4,4,4-tetrabromobutyl)benzene (1k-CBr_3)

Obtained in 65% yield as a colorless liquid (311 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.40 (t, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.38 (q, *J* = 7.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.0, 137.7, 132.6, 129.3, 113.9, 89.3, 55.2, 35.0, 33.0. **HRMS** (DART) m/z: $[M+H-Br_2]^+$ Calcd for $C_{11}H_{13}OBr_2$: 318.9328; Found: 318.9340.

8. Reference：

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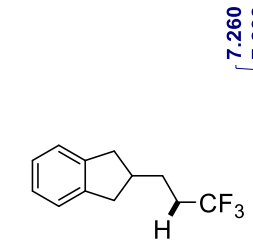
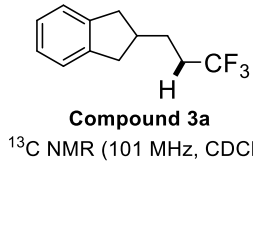
9. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR charts of the Products.



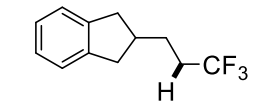
Compound 3a

^{1}H NMR (400 MHz, $CDCl_3$)



Compound 3a

^{13}C NMR (101 MHz, $CDCl_3$)

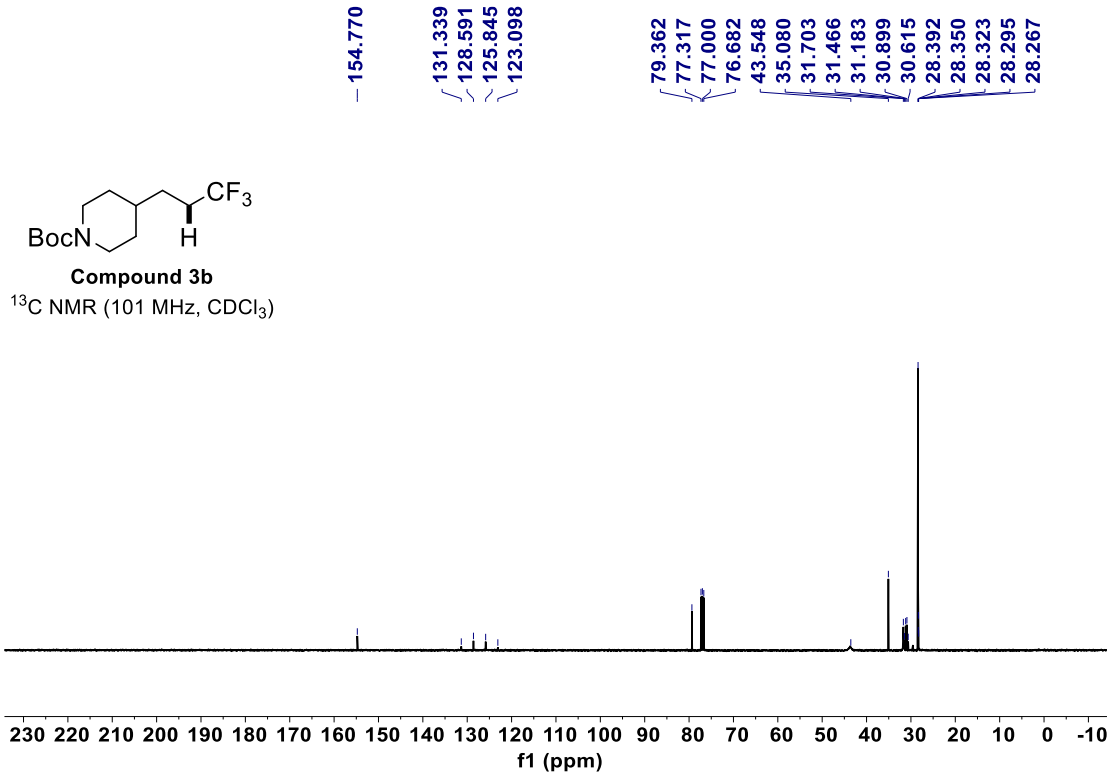


Compound 3a

^{19}F NMR (376 MHz, $CDCl_3$)

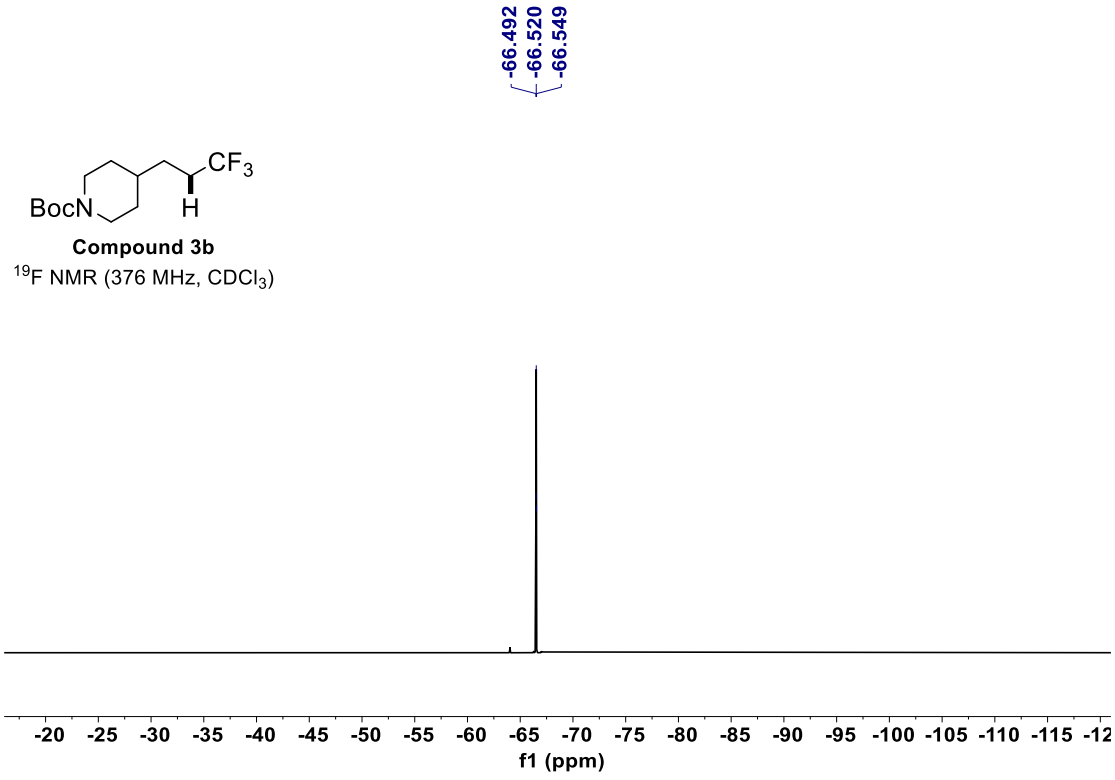
Compound 3b

^{1}H NMR (400 MHz, $CDCl_3$)



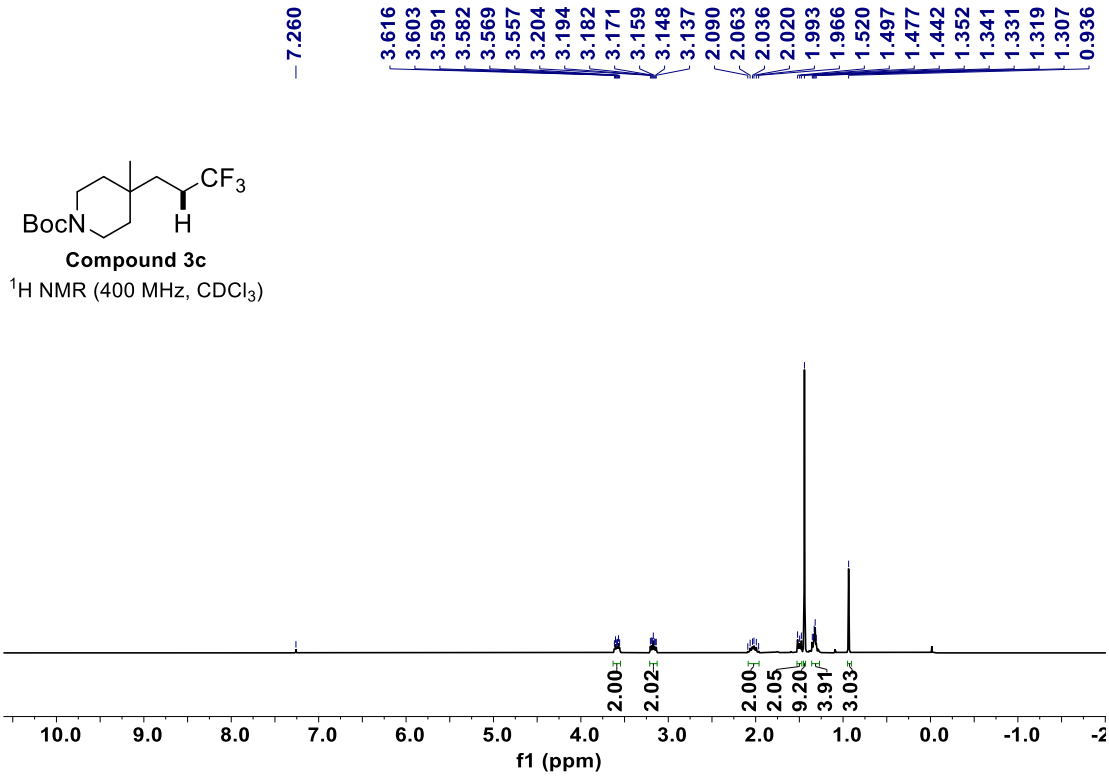
Compound 3b

^{13}C NMR (101 MHz, $CDCl_3$)



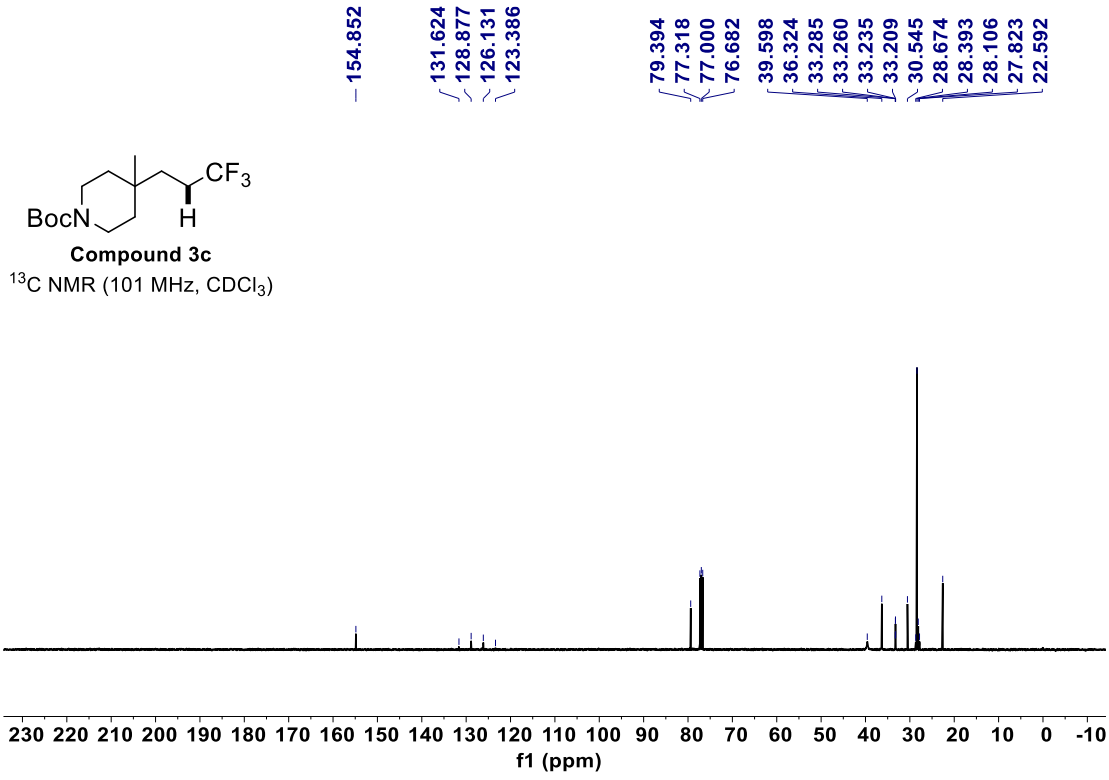
Compound 3b

^{19}F NMR (376 MHz, $CDCl_3$)



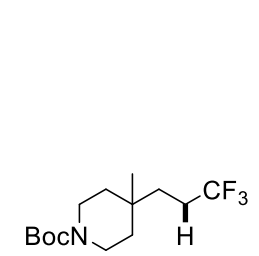
Compound 3c

^{1}H NMR (400 MHz, $CDCl_3$)



Compound 3c

^{13}C NMR (101 MHz, $CDCl_3$)

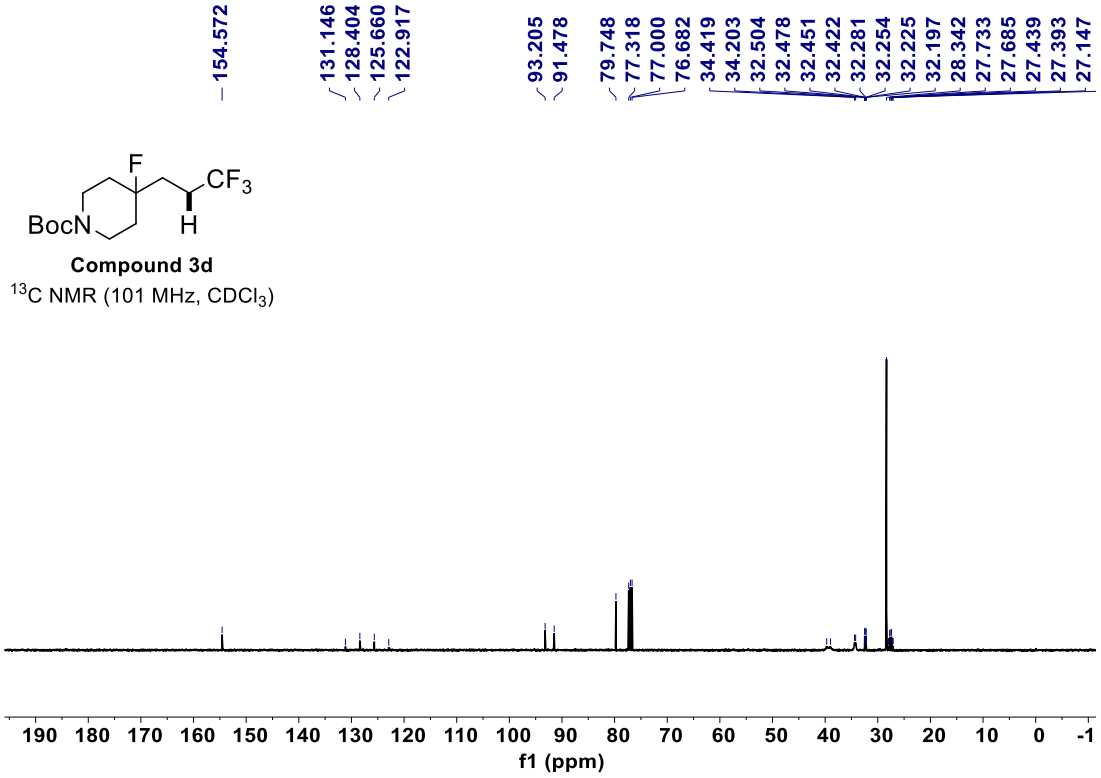


Compound 3c

^{19}F NMR (376 MHz, $CDCl_3$)

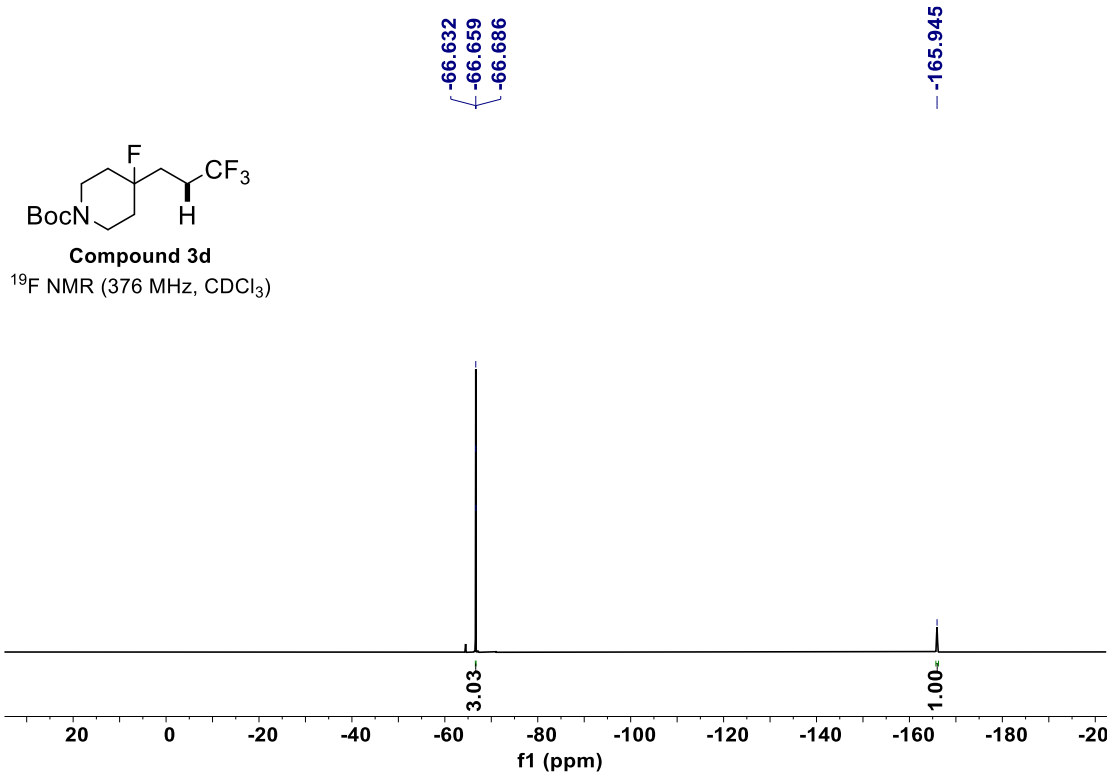
Compound 3d

^{1}H NMR (400 MHz, $CDCl_3$)



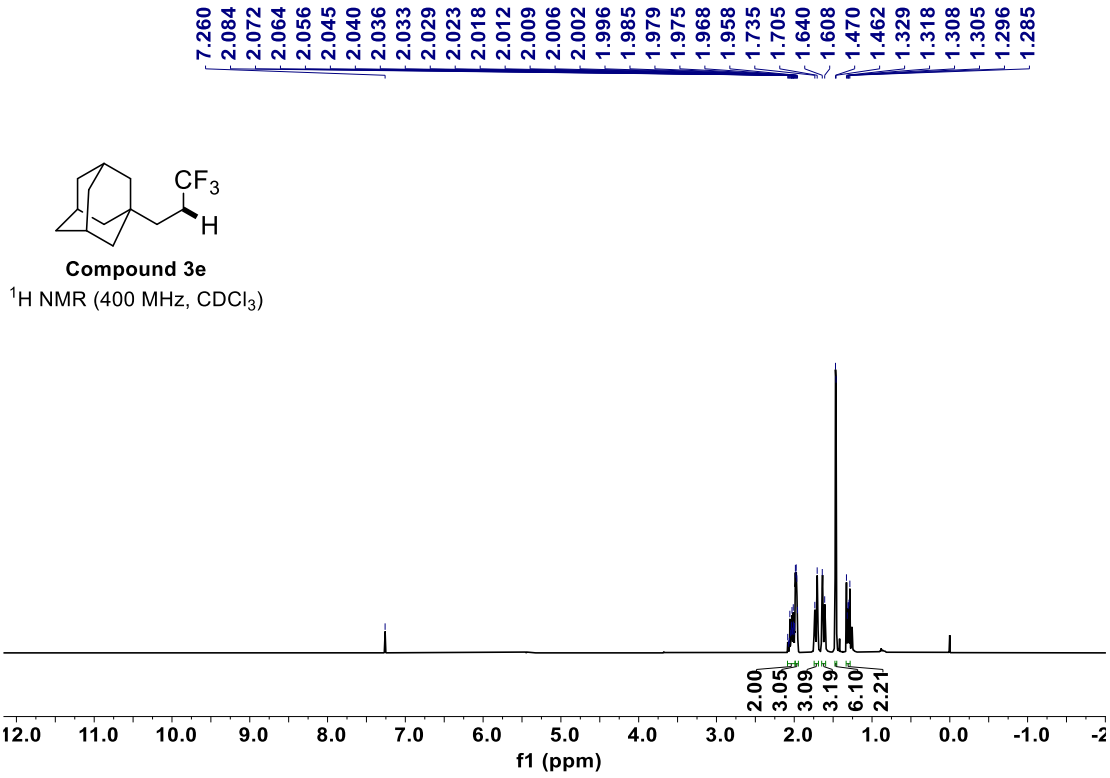
Compound 3d

^{13}C NMR (101 MHz, $CDCl_3$)



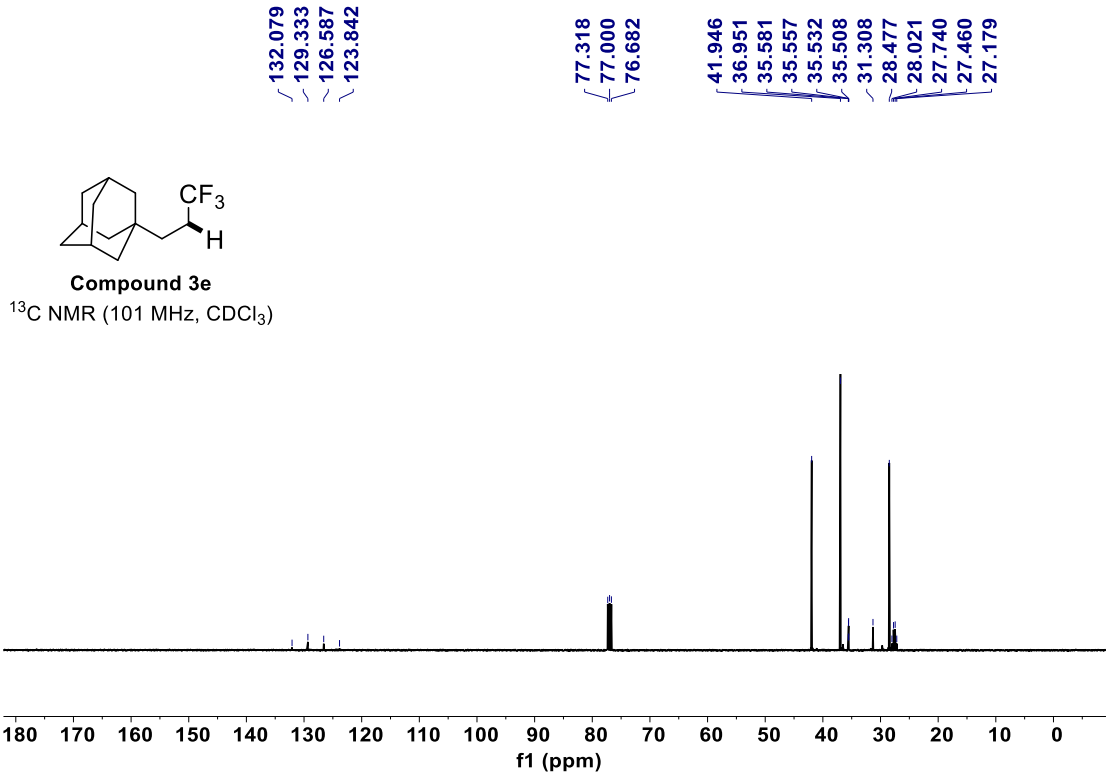
Compound 3d

^{19}F NMR (376 MHz, $CDCl_3$)



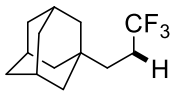
Compound 3e

^{1}H NMR (400 MHz, $CDCl_3$)



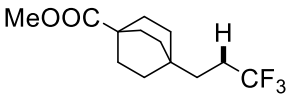
Compound 3e

^{13}C NMR (101 MHz, $CDCl_3$)



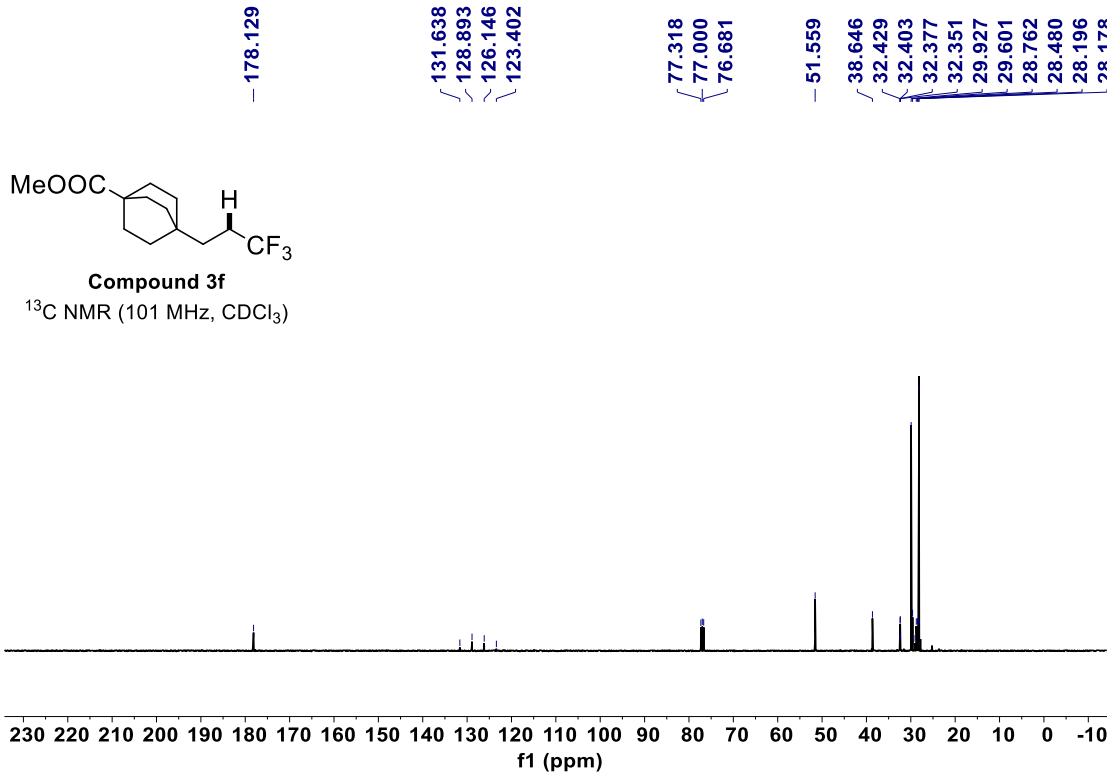
Compound 3e

^{19}F NMR (376 MHz, $CDCl_3$)



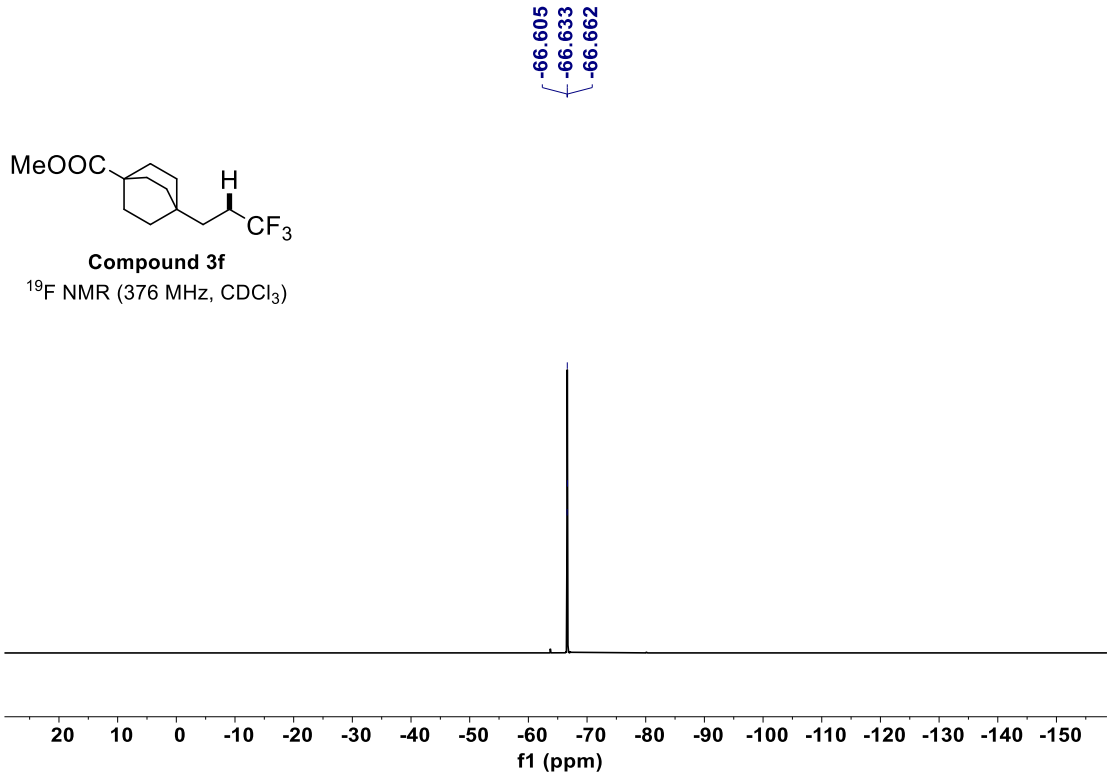
Compound 3f

^{1}H NMR (400 MHz, $CDCl_3$)



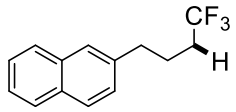
Compound 3f

^{13}C NMR (101 MHz, $CDCl_3$)



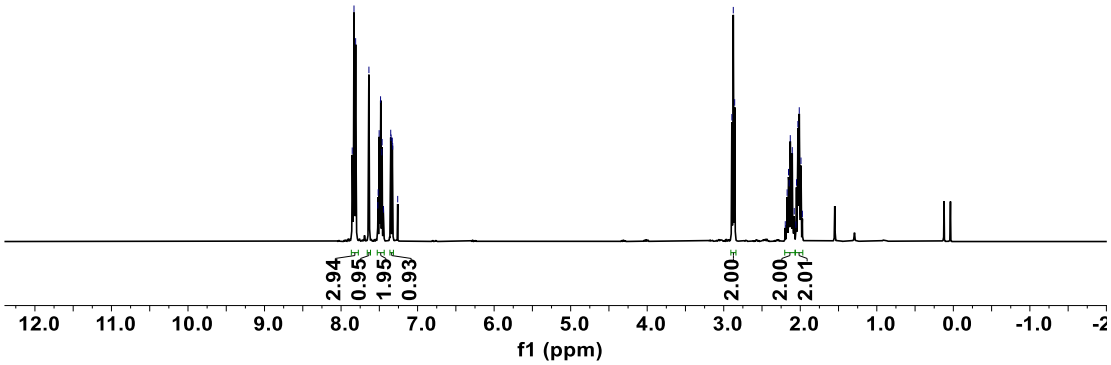
Compound 3f

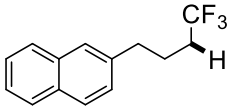
^{19}F NMR (376 MHz, $CDCl_3$)



Compound 3g

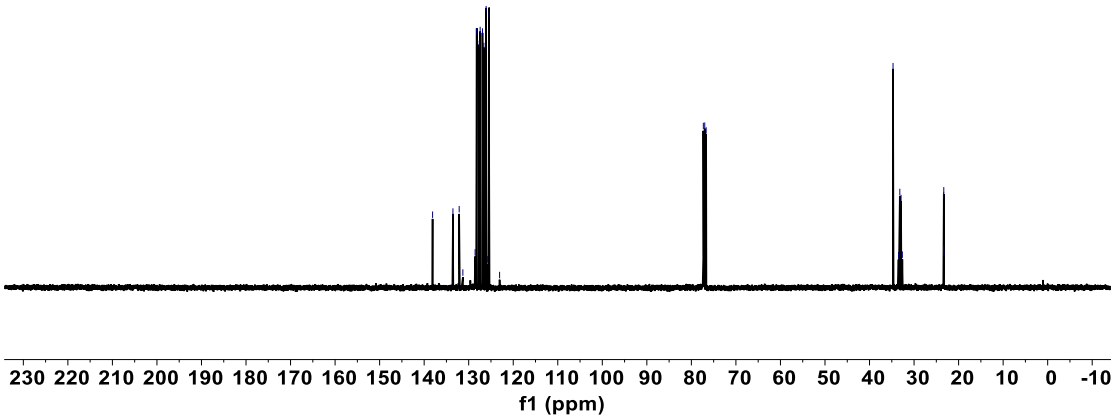
^{1}H NMR (400 MHz, $CDCl_3$)

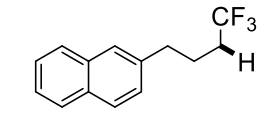




Compound 3g

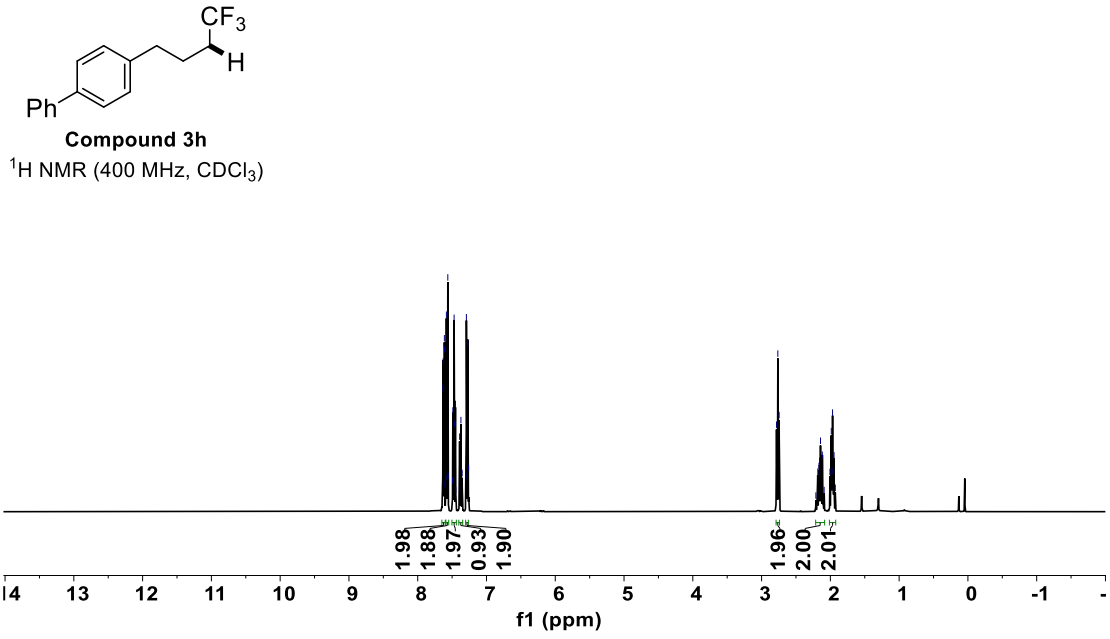
^{13}C NMR (101 MHz, $CDCl_3$)





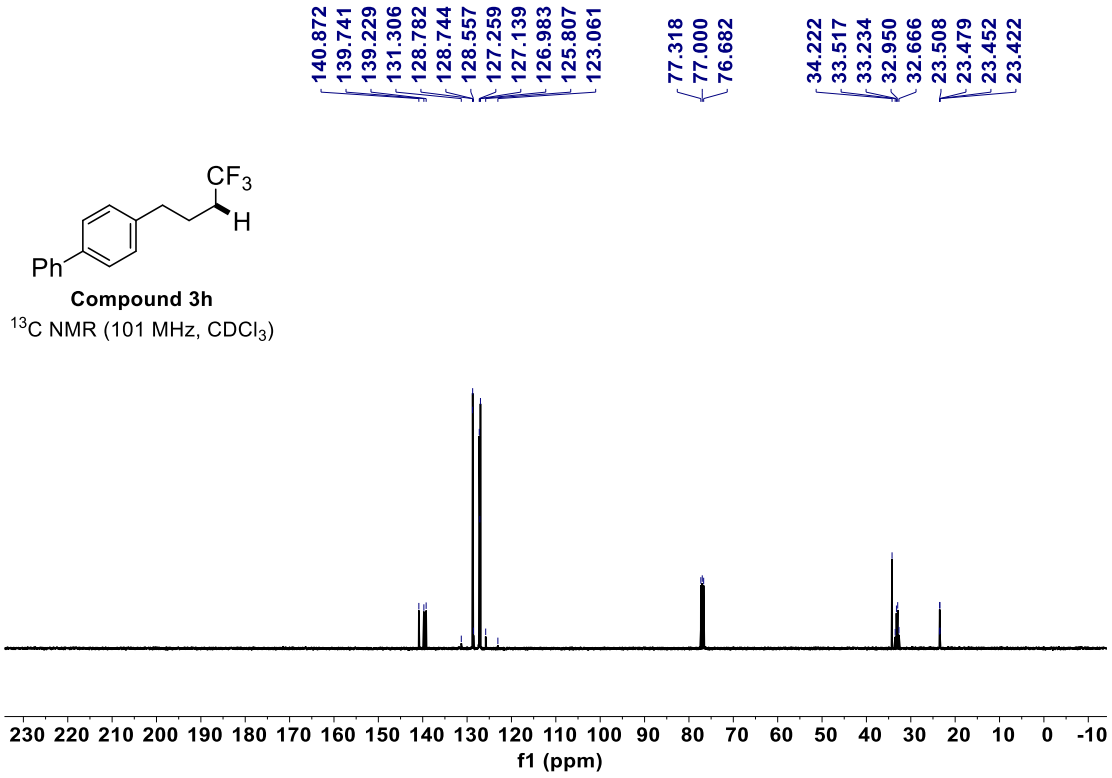
Compound 3g

^{19}F NMR (376 MHz, $CDCl_3$)



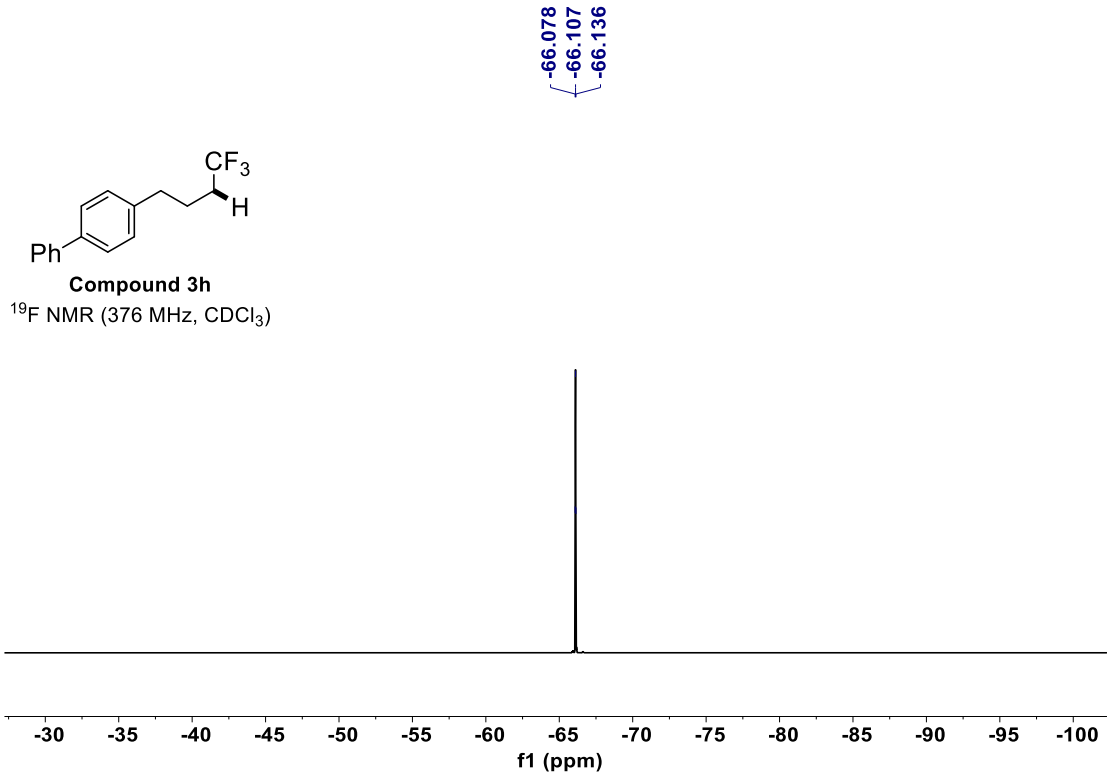
Compound 3h

^{1}H NMR (400 MHz, $CDCl_3$)



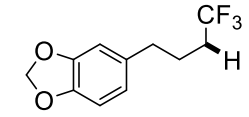
Compound 3h

^{13}C NMR (101 MHz, $CDCl_3$)



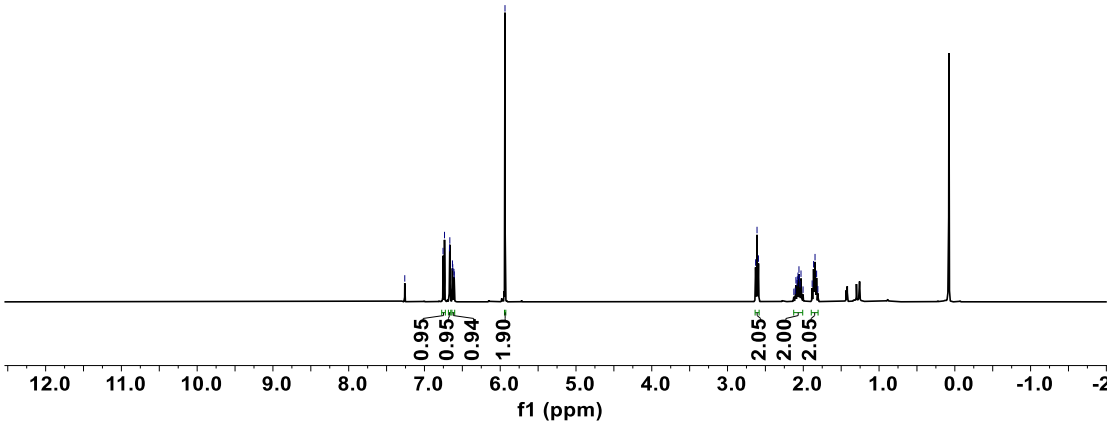
Compound 3h

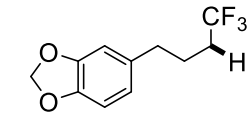
^{19}F NMR (376 MHz, $CDCl_3$)



Compound 3i

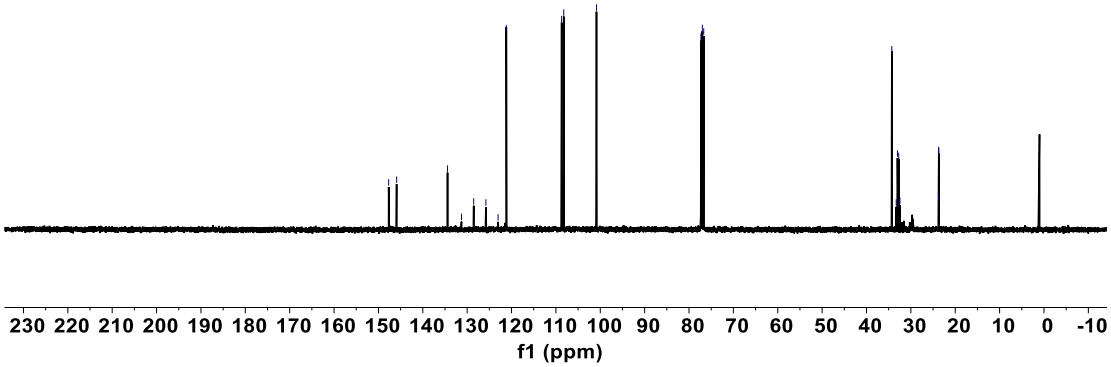
^{1}H NMR (400 MHz, $CDCl_3$)

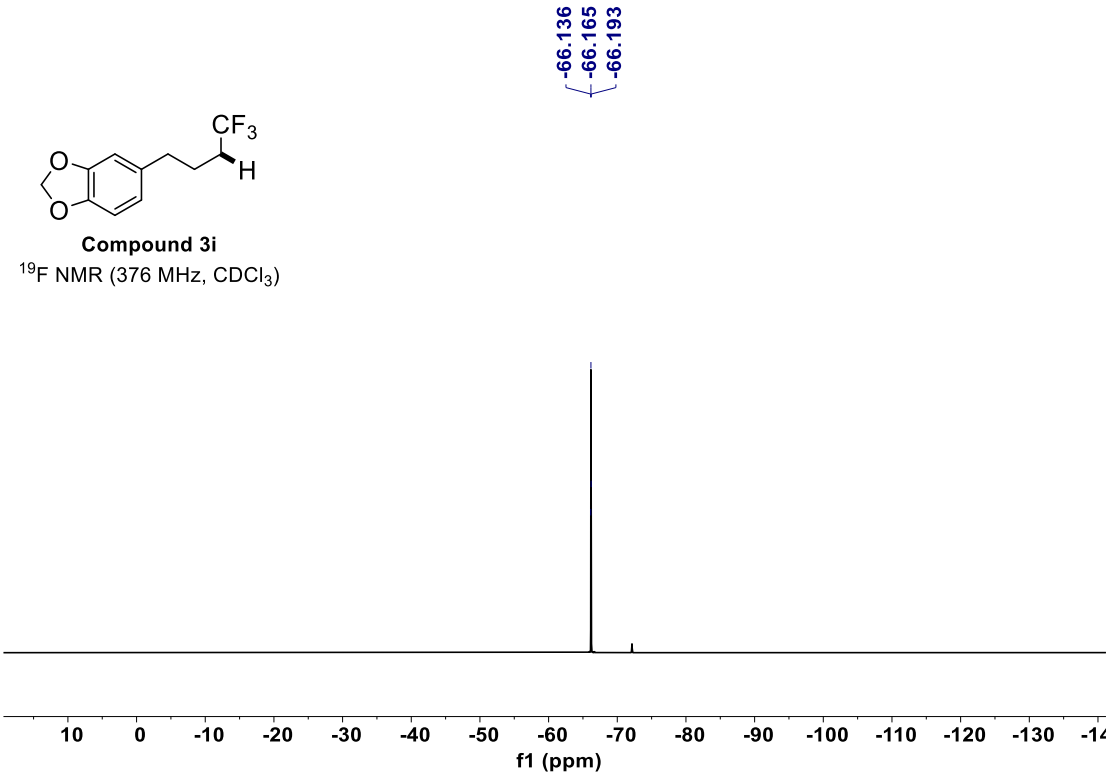




Compound 3i

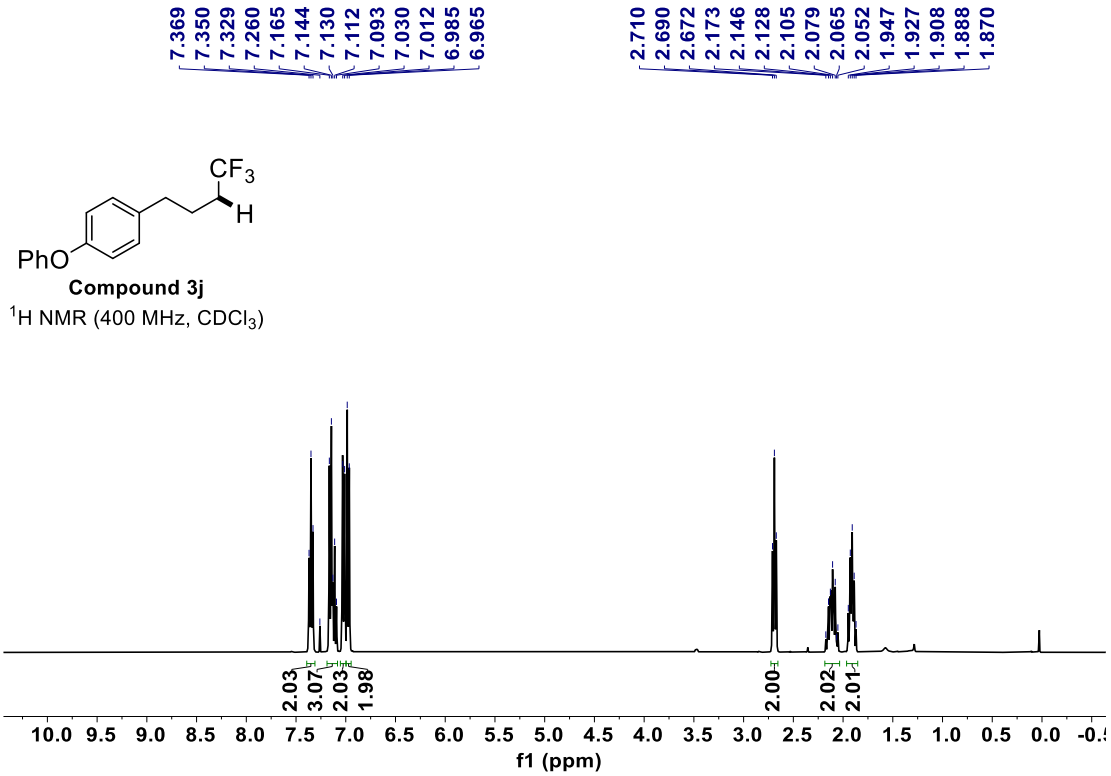
^{13}C NMR (101 MHz, $CDCl_3$)





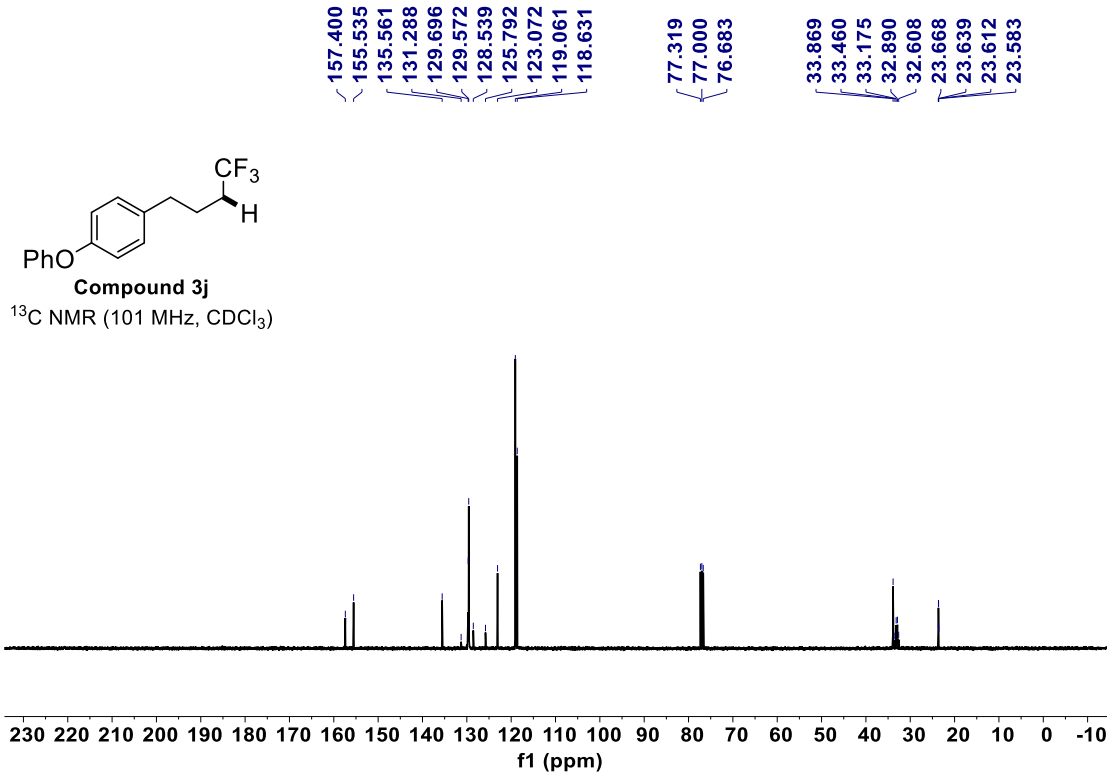
Compound 3i

^{19}F NMR (376 MHz, $CDCl_3$)



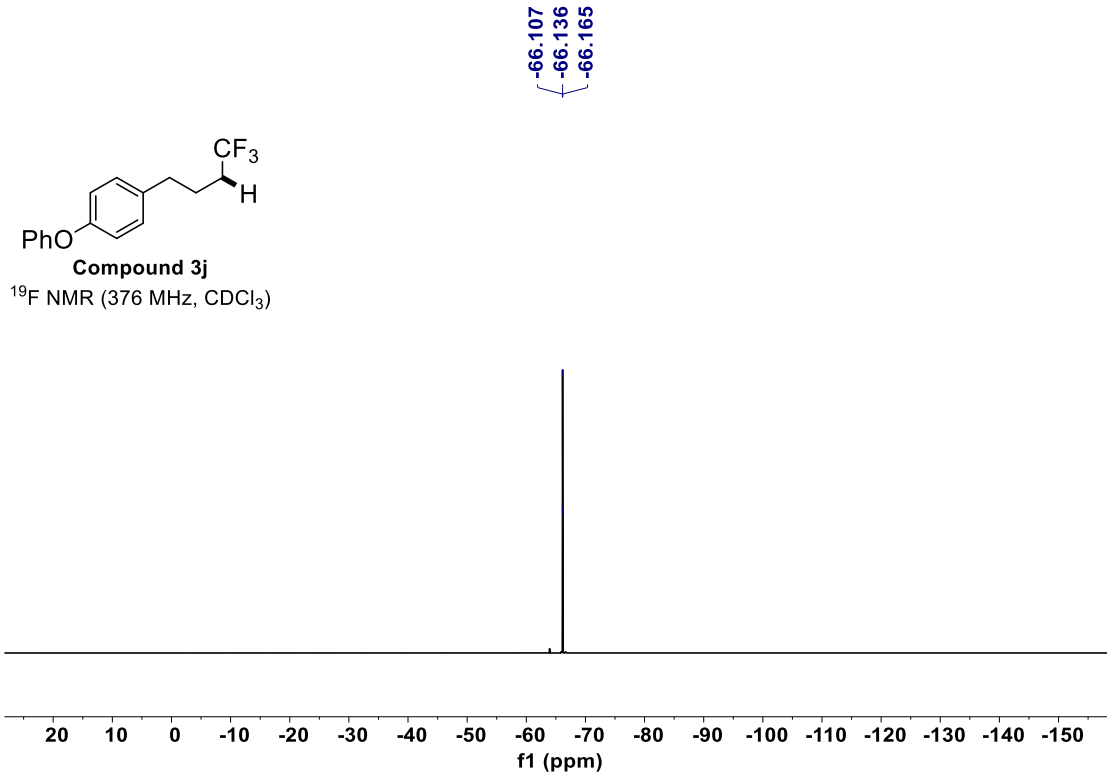
Compound 3j

^{1}H NMR (400 MHz, $CDCl_3$)



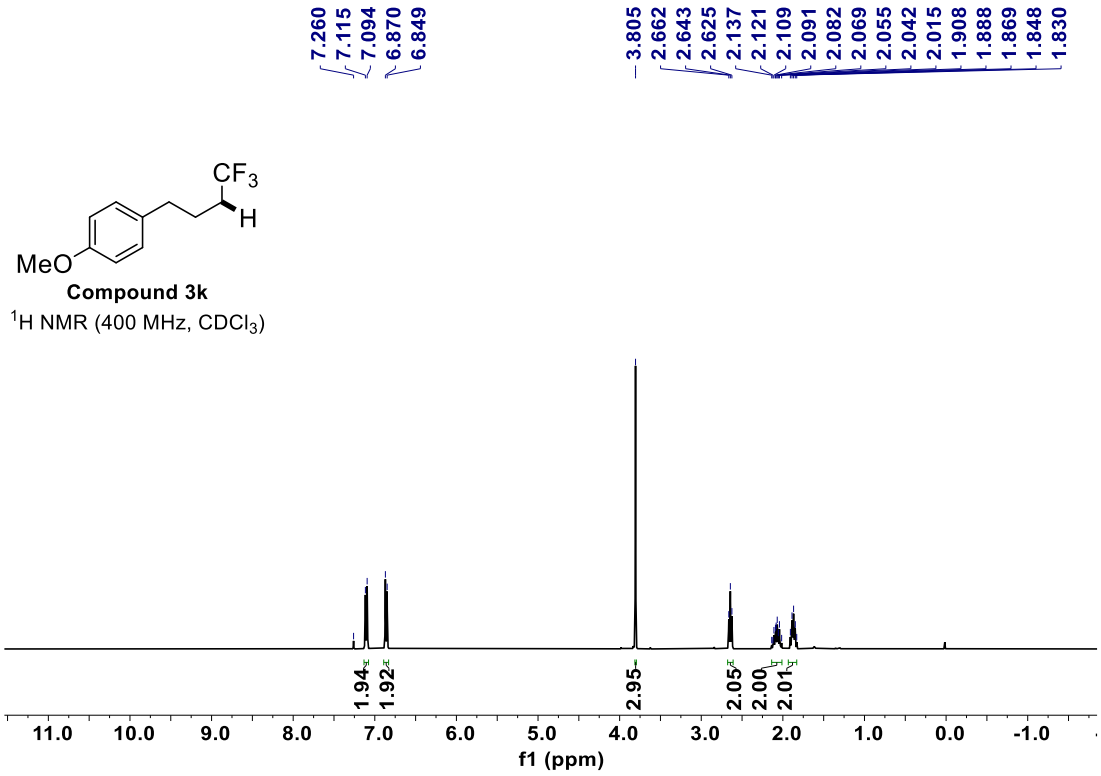
Compound 3j

^{13}C NMR (101 MHz, $CDCl_3$)



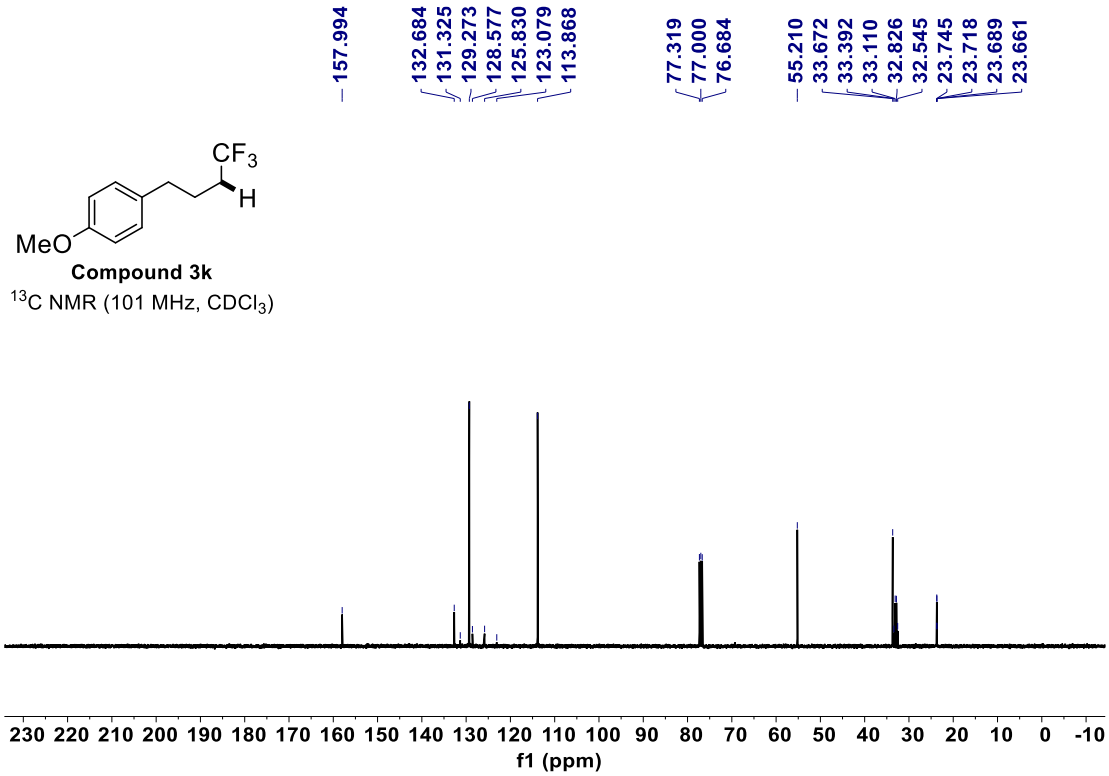
Compound 3j

^{19}F NMR (376 MHz, $CDCl_3$)



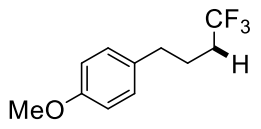
Compound 3k

^{1}H NMR (400 MHz, $CDCl_3$)



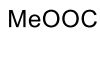
Compound 3k

^{13}C NMR (101 MHz, $CDCl_3$)



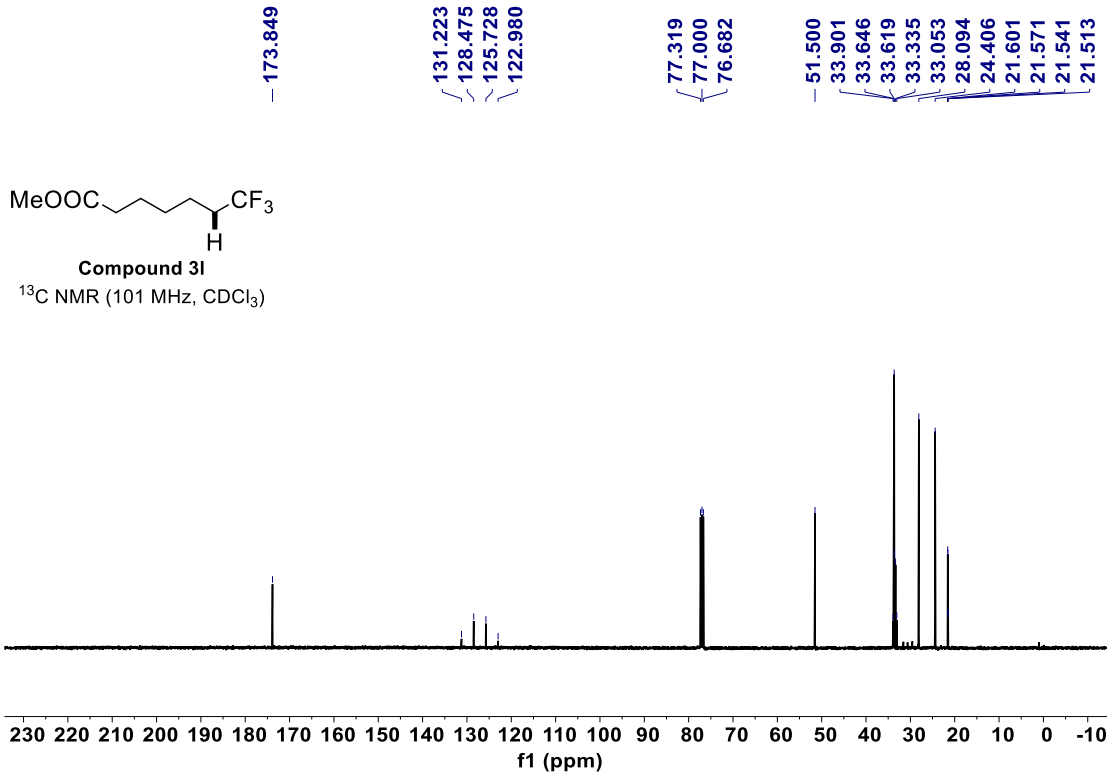
Compound 3k

^{19}F NMR (376 MHz, $CDCl_3$)



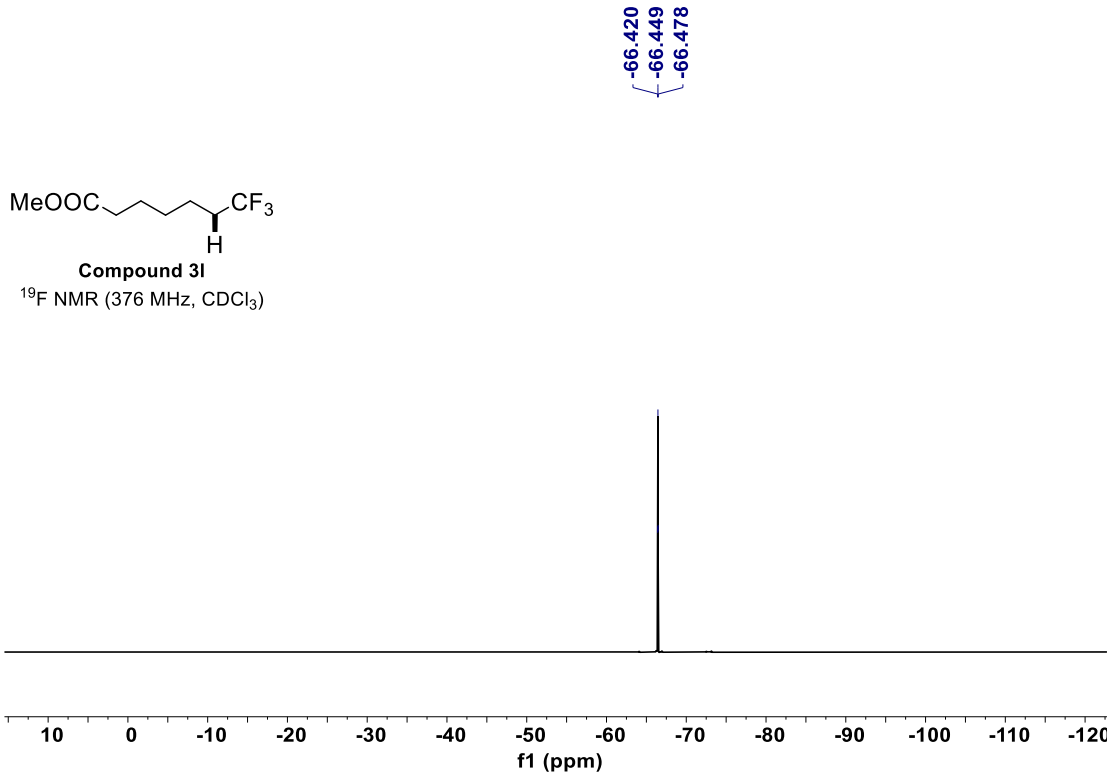
Compound 3l

^{1}H NMR (400 MHz, $CDCl_3$)



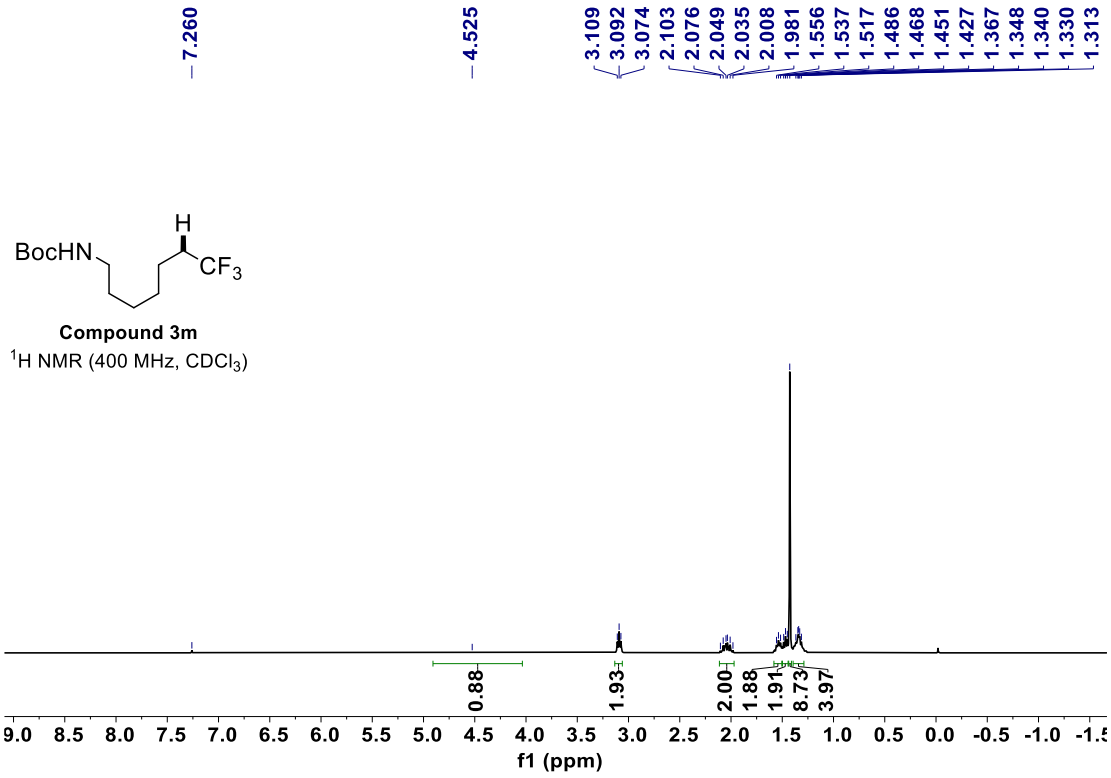
Compound 3l

^{13}C NMR (101 MHz, $CDCl_3$)



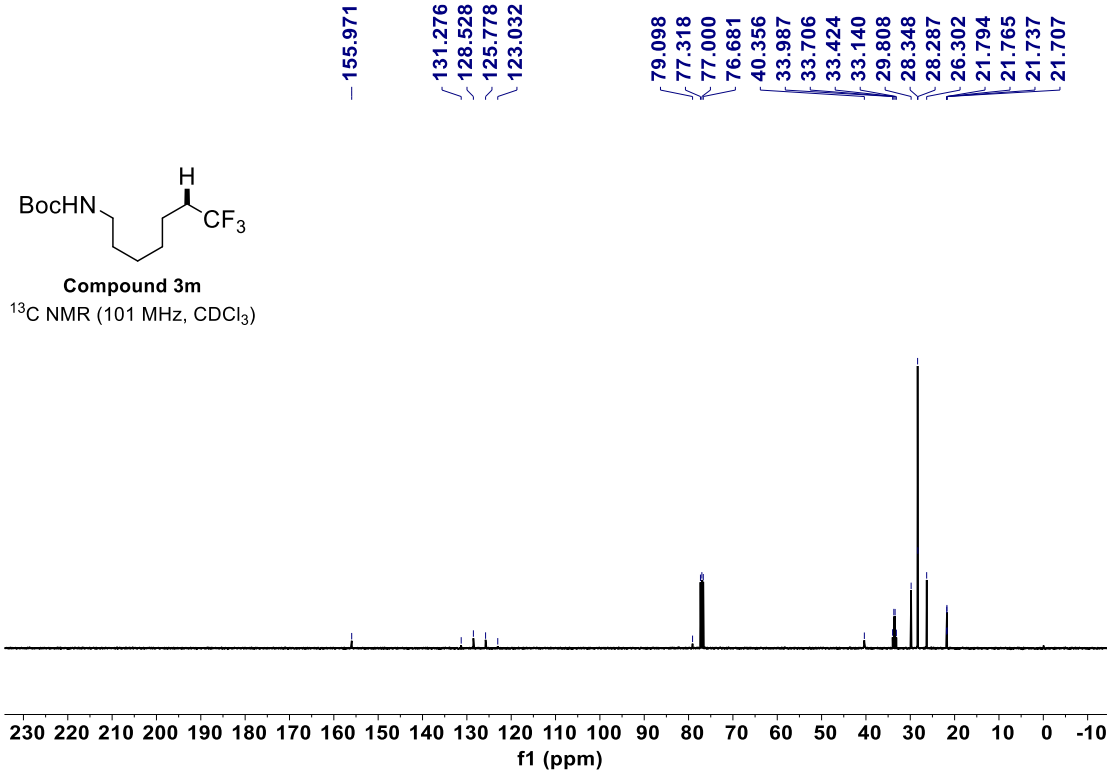
Compound 3l

^{19}F NMR (376 MHz, $CDCl_3$)



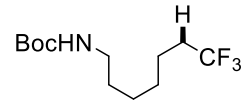
Compound 3m

^{1}H NMR (400 MHz, $CDCl_3$)



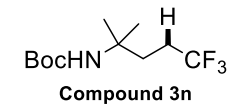
Compound 3m

^{13}C NMR (101 MHz, $CDCl_3$)



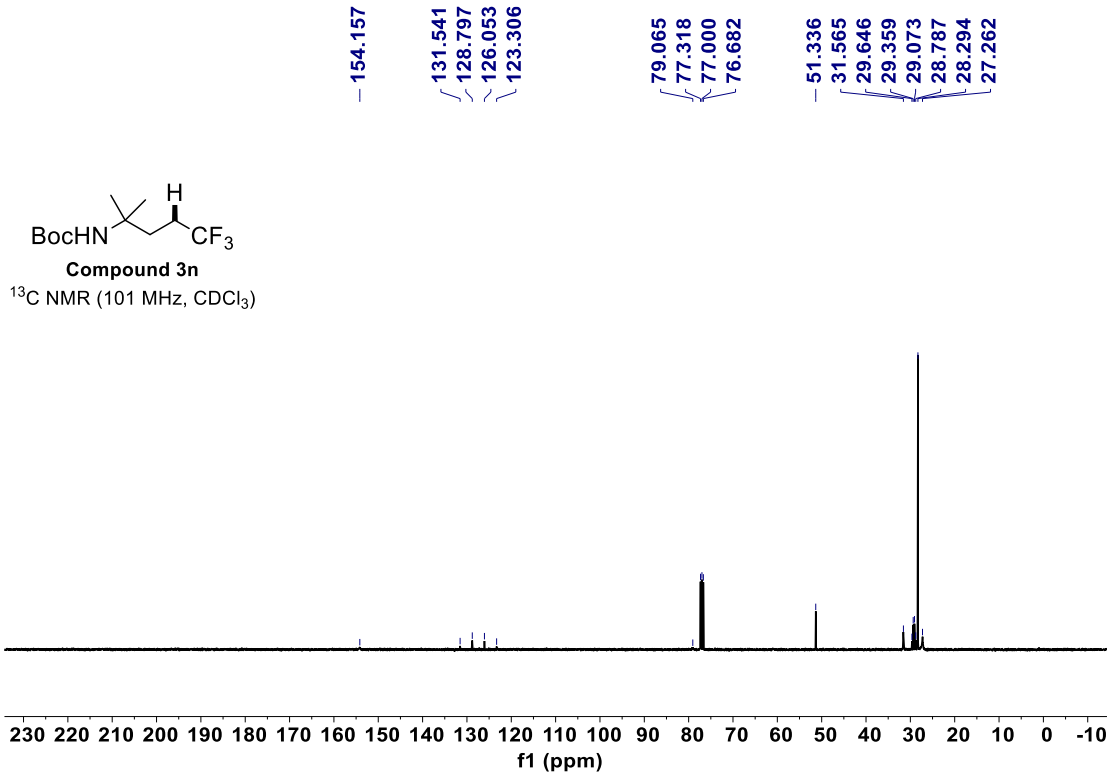
Compound 3m

^{19}F NMR (376 MHz, $CDCl_3$)



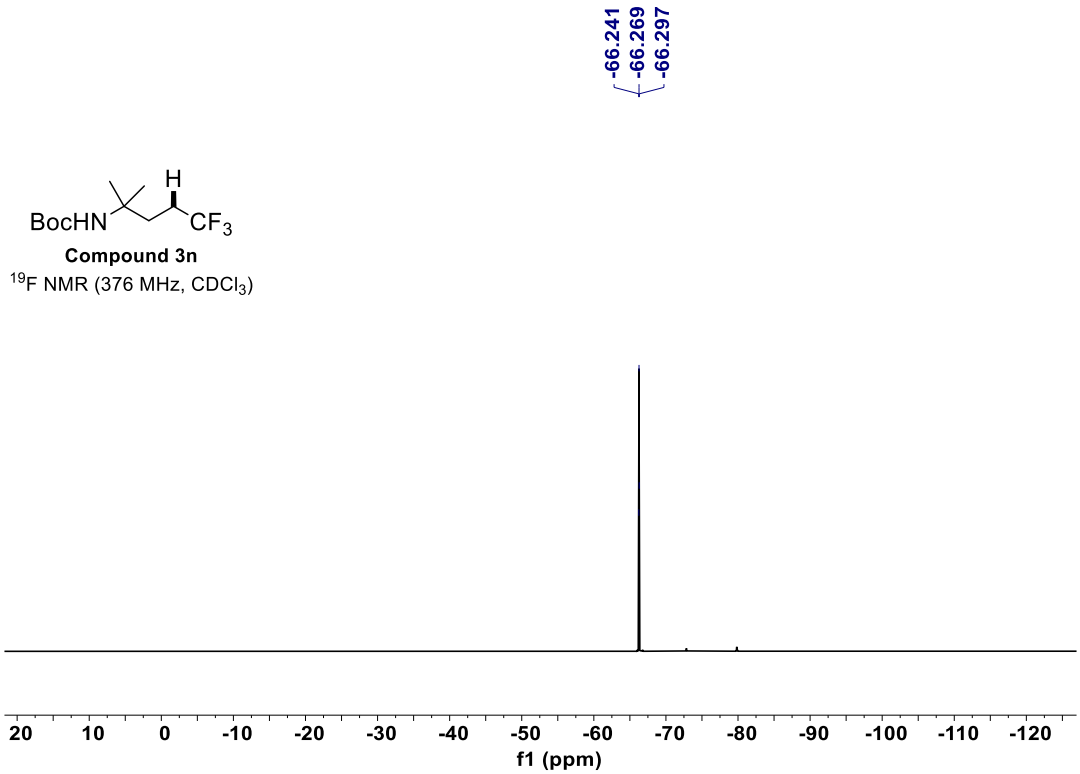
Compound 3n

^{1}H NMR (400 MHz, $CDCl_3$)



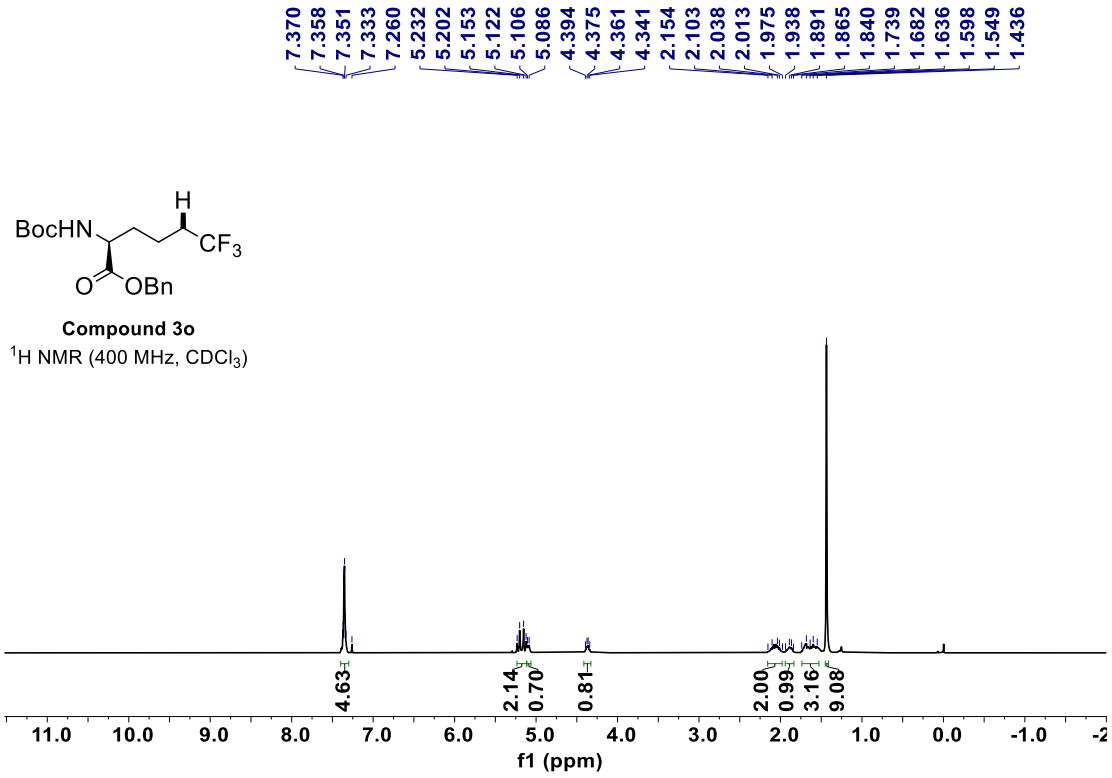
Compound 3n

^{13}C NMR (101 MHz, $CDCl_3$)



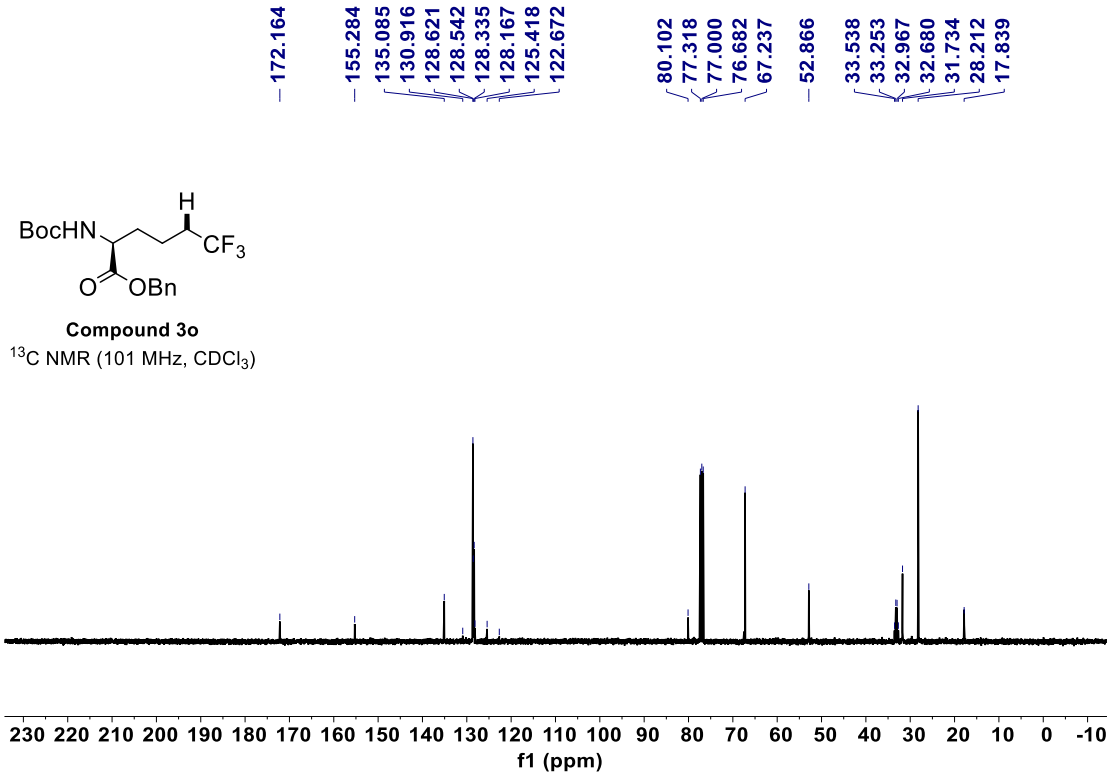
Compound 3n

^{19}F NMR (376 MHz, $CDCl_3$)



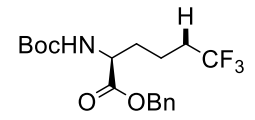
Compound 3o

^{1}H NMR (400 MHz, $CDCl_3$)



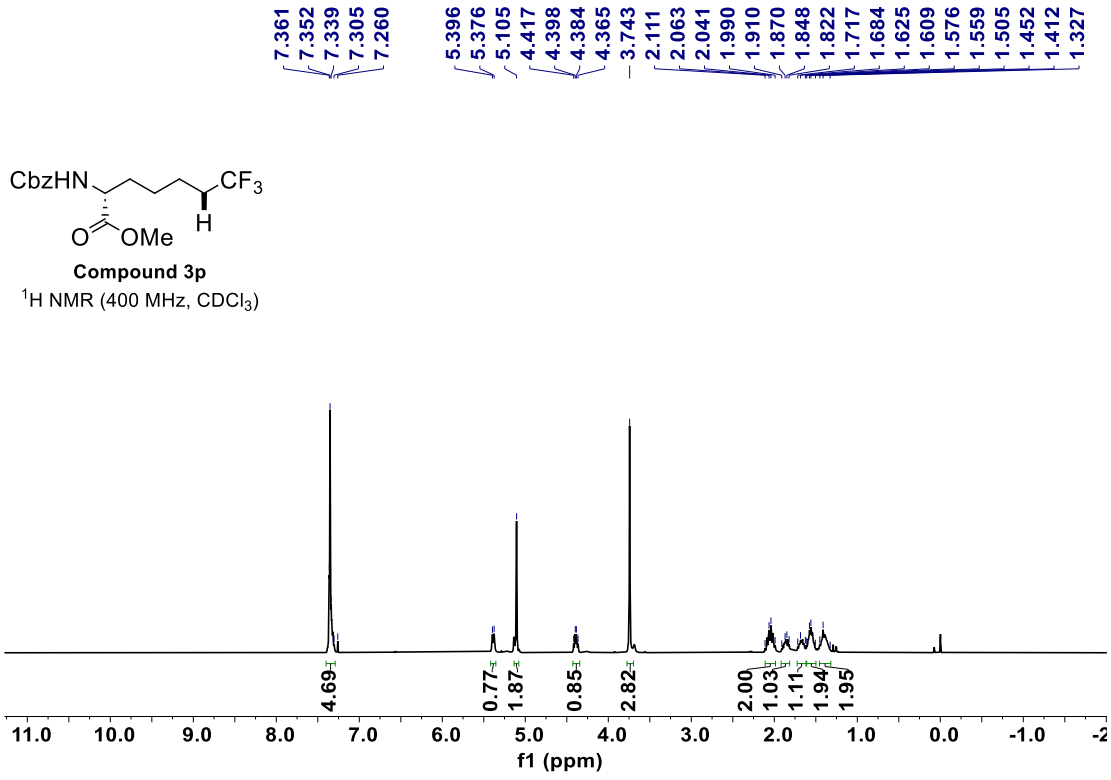
Compound 3o

^{13}C NMR (101 MHz, $CDCl_3$)



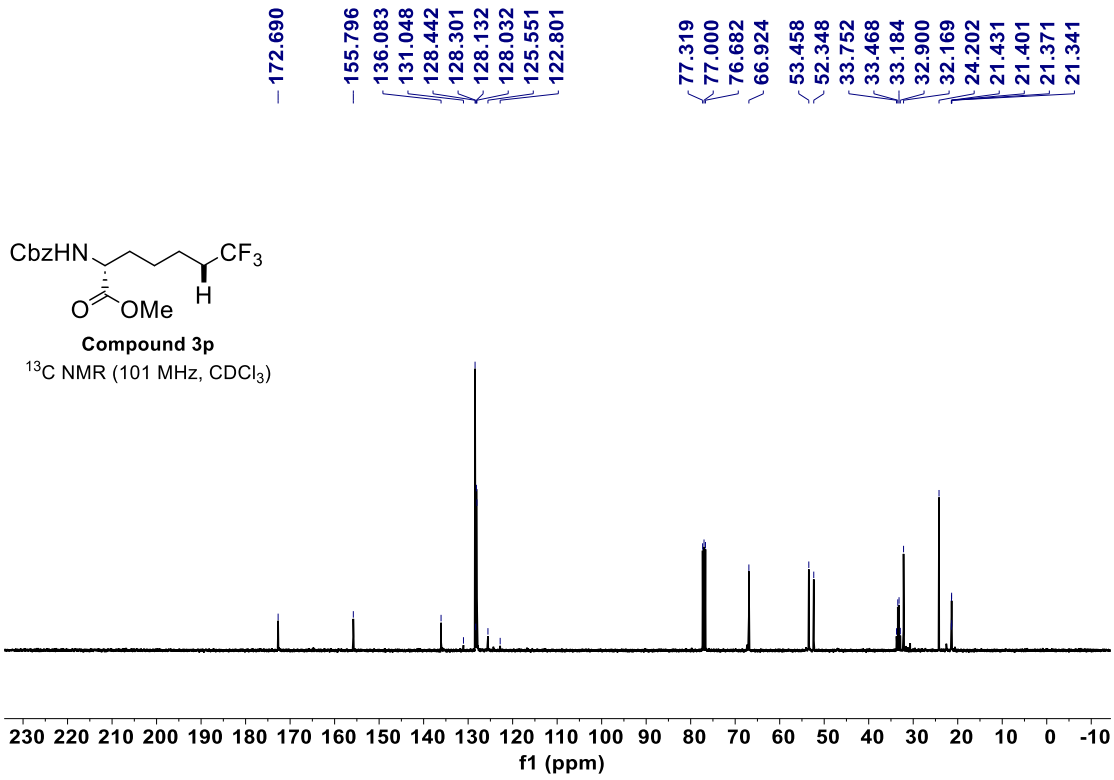
Compound 3o

^{19}F NMR (376 MHz, $CDCl_3$)



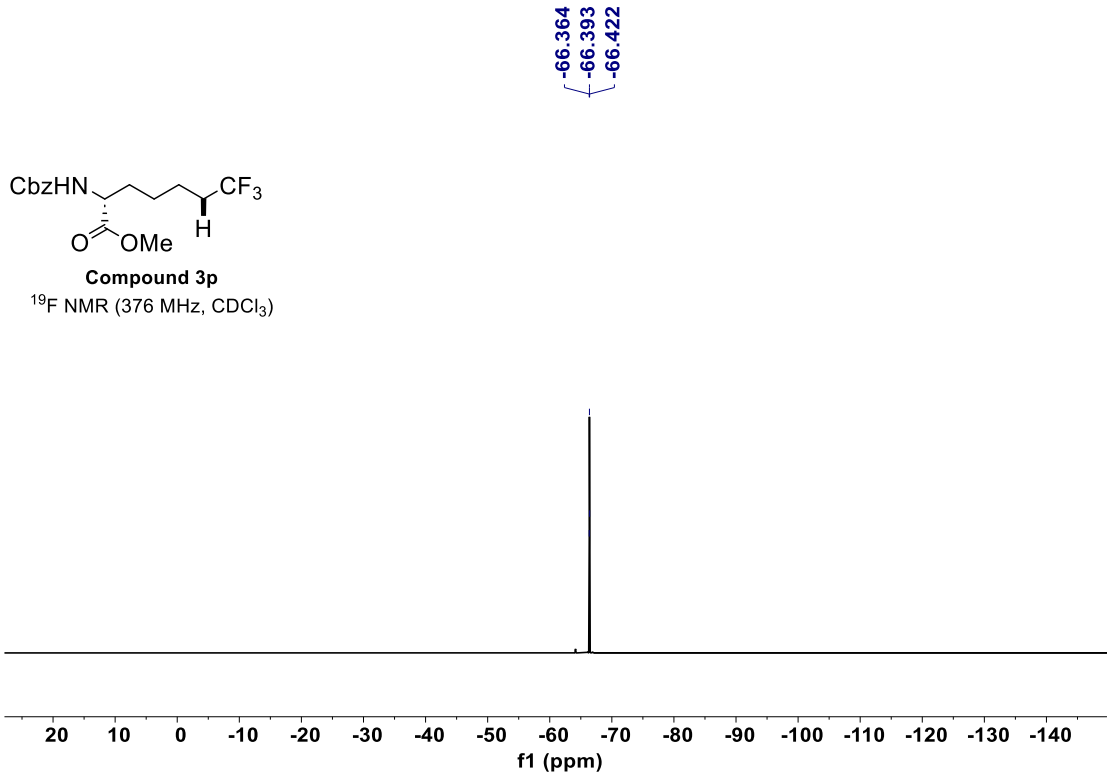
Compound 3p

^{1}H NMR (400 MHz, $CDCl_3$)



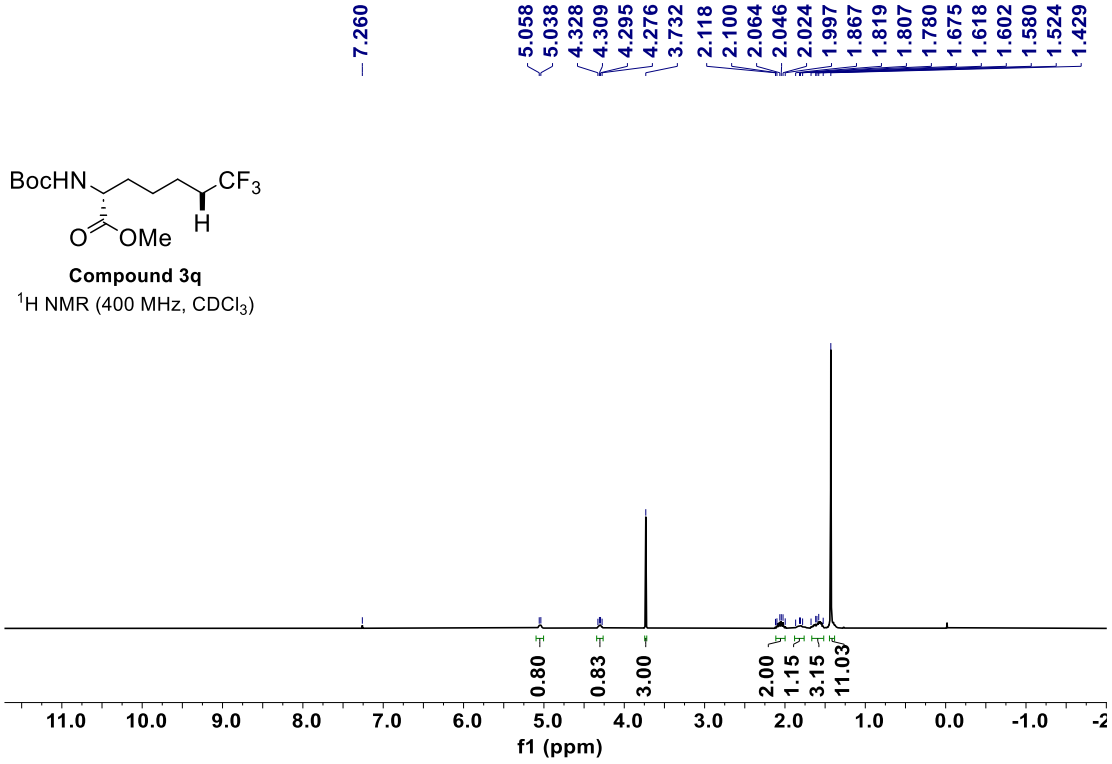
Compound 3p

^{13}C NMR (101 MHz, $CDCl_3$)



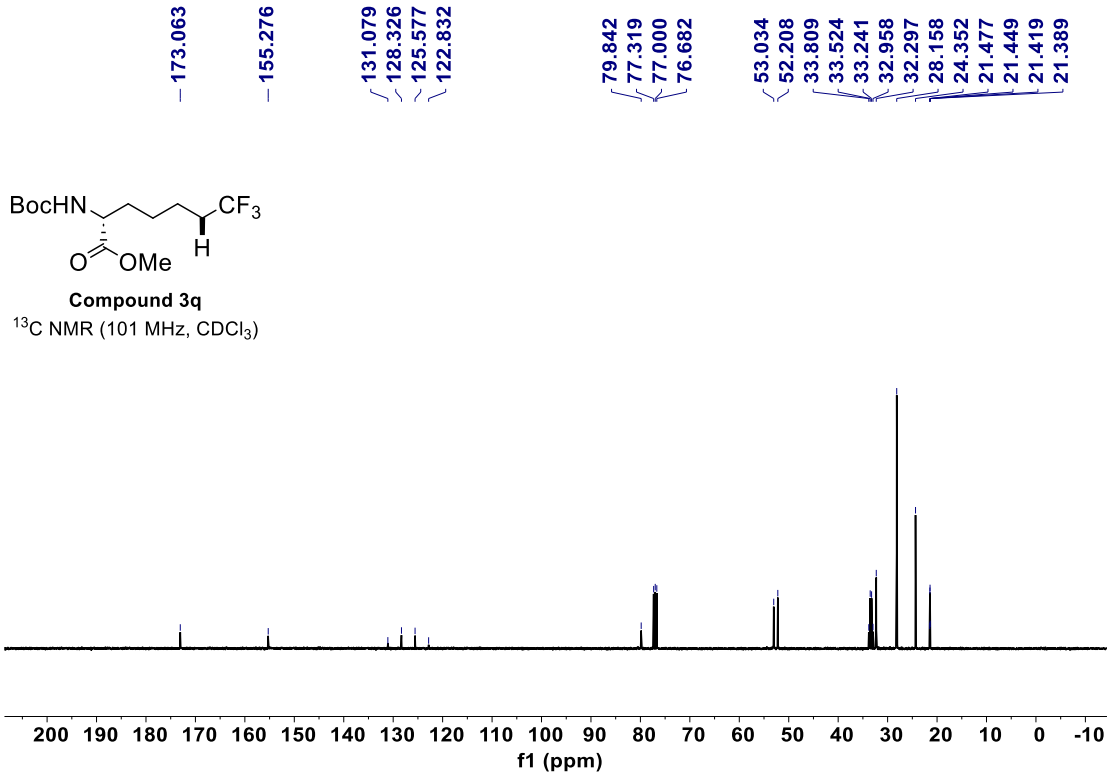
Compound 3p

^{19}F NMR (376 MHz, $CDCl_3$)



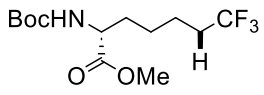
Compound 3q

^{1}H NMR (400 MHz, $CDCl_3$)



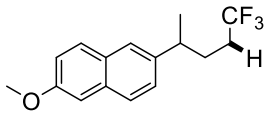
Compound 3q

^{13}C NMR (101 MHz, $CDCl_3$)



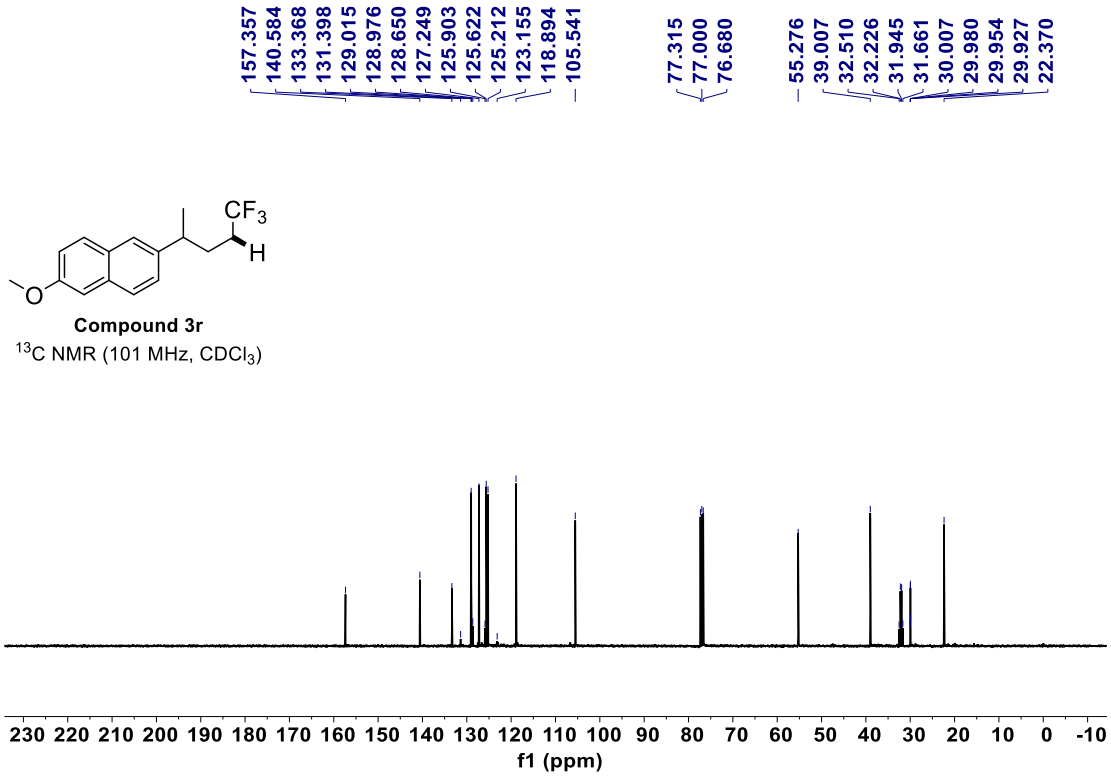
Compound 3q

^{19}F NMR (376 MHz, $CDCl_3$)



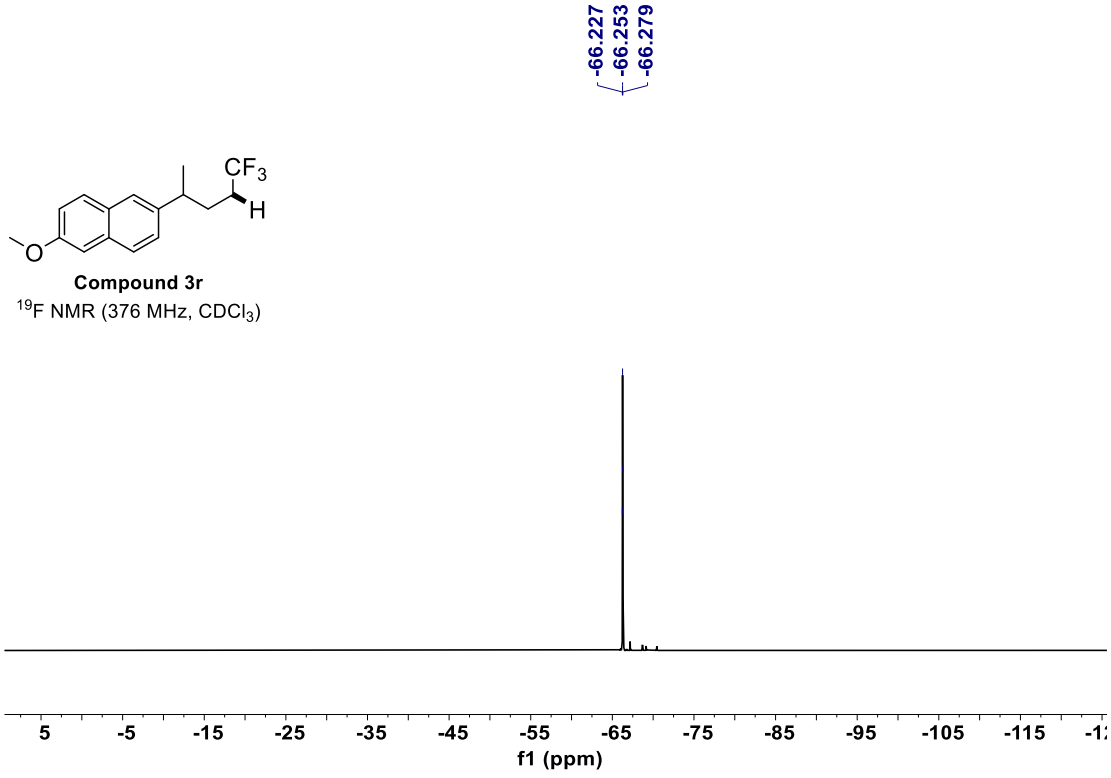
Compound 3r

^{1}H NMR (400 MHz, $CDCl_3$)



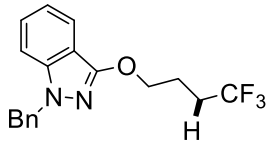
Compound 3r

^{13}C NMR (101 MHz, $CDCl_3$)



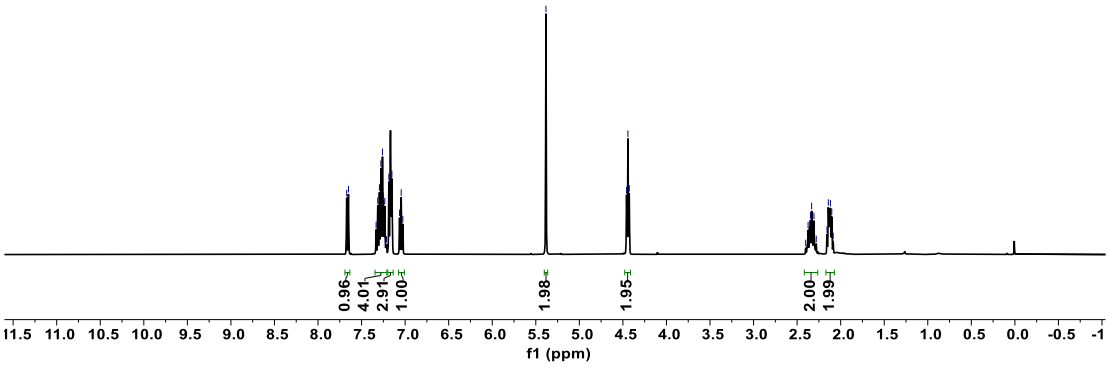
Compound 3r

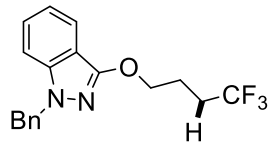
^{19}F NMR (376 MHz, $CDCl_3$)



Compound 3s

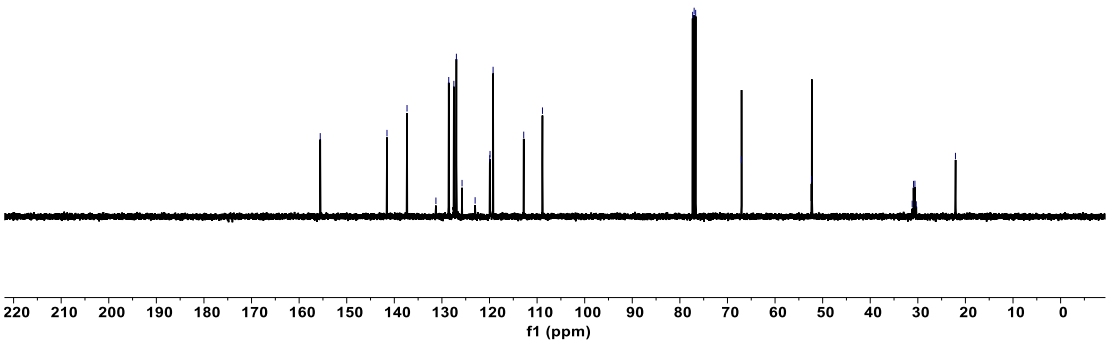
^{1}H NMR (400 MHz, $CDCl_3$)

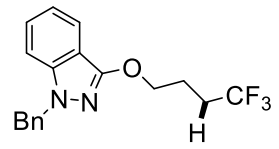




Compound 3s

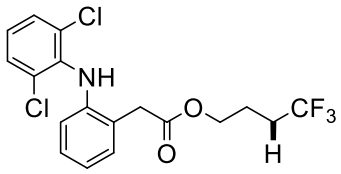
^{13}C NMR (101 MHz, $CDCl_3$)





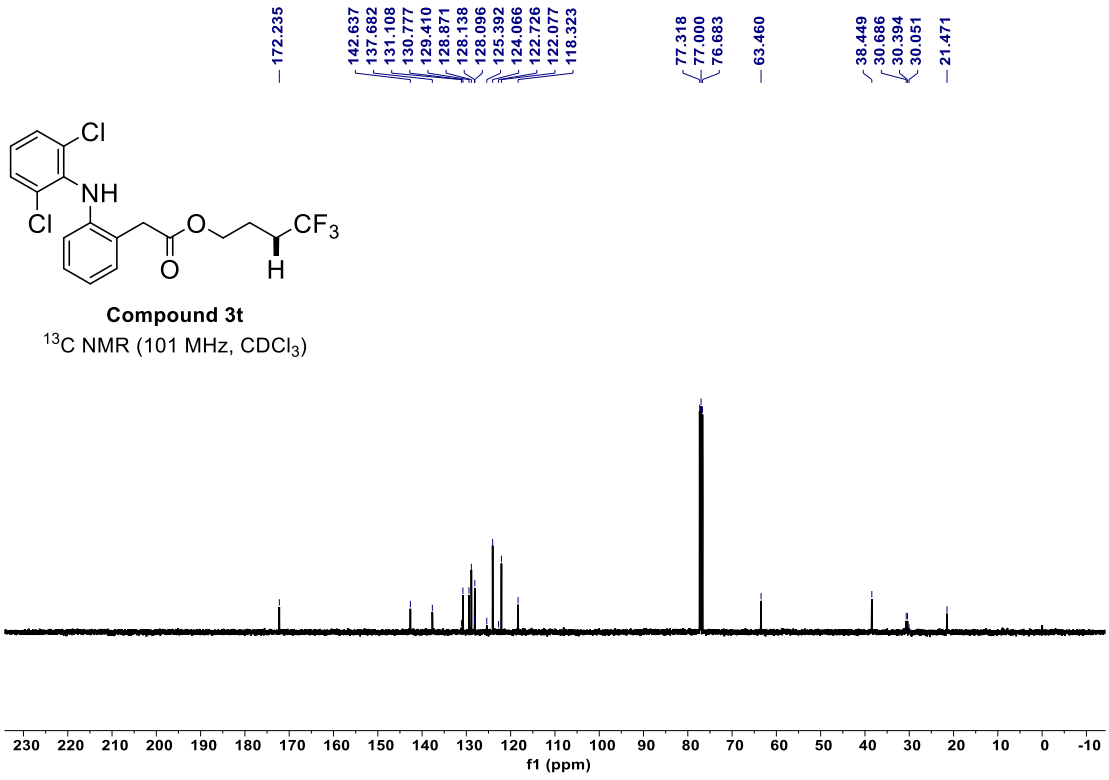
Compound 3s

^{19}F NMR (376 MHz, $CDCl_3$)



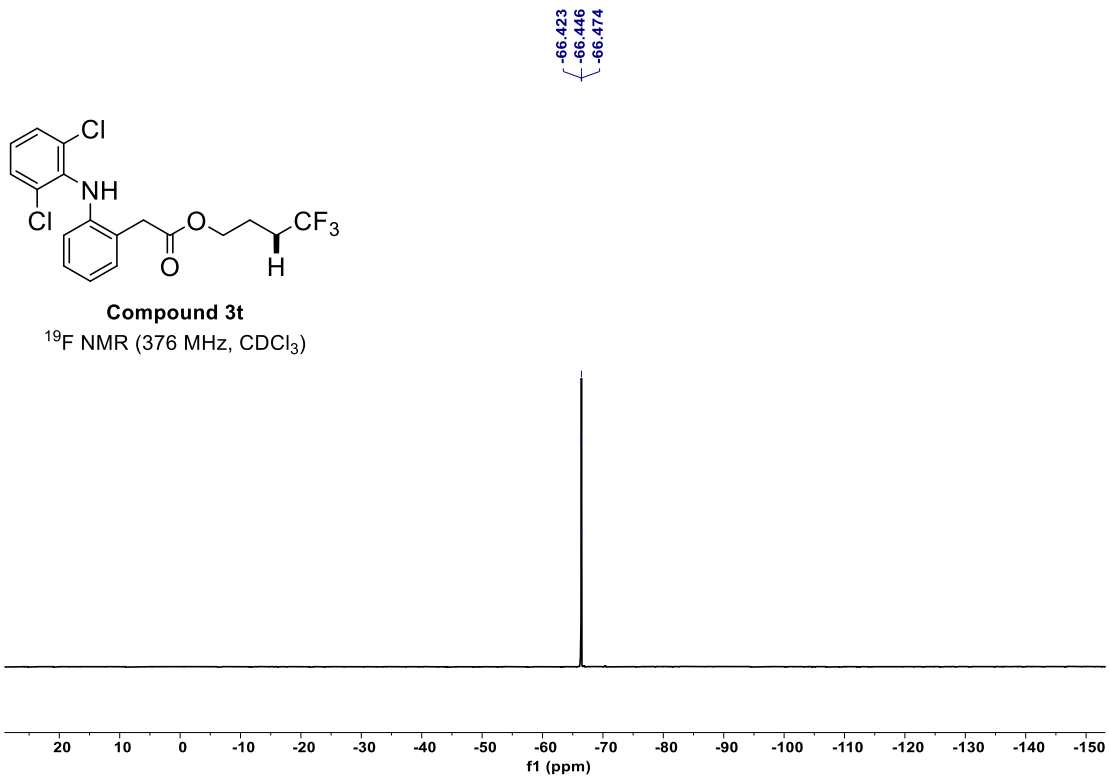
Compound 3t

^{1}H NMR (400 MHz, $CDCl_3$)



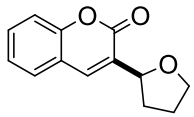
Compound 3t

^{13}C NMR (101 MHz, $CDCl_3$)



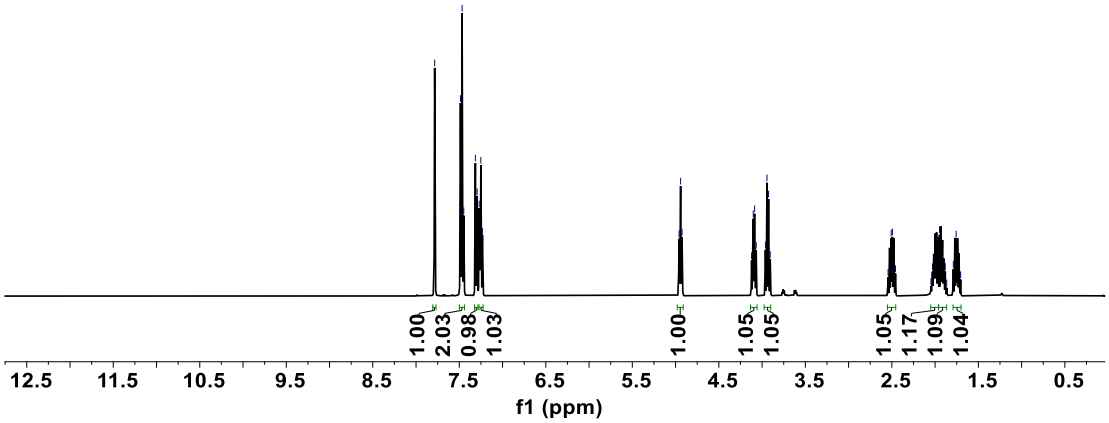
Compound 3t

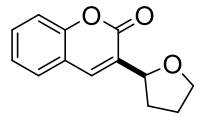
^{19}F NMR (376 MHz, $CDCl_3$)



Compound 4a-1

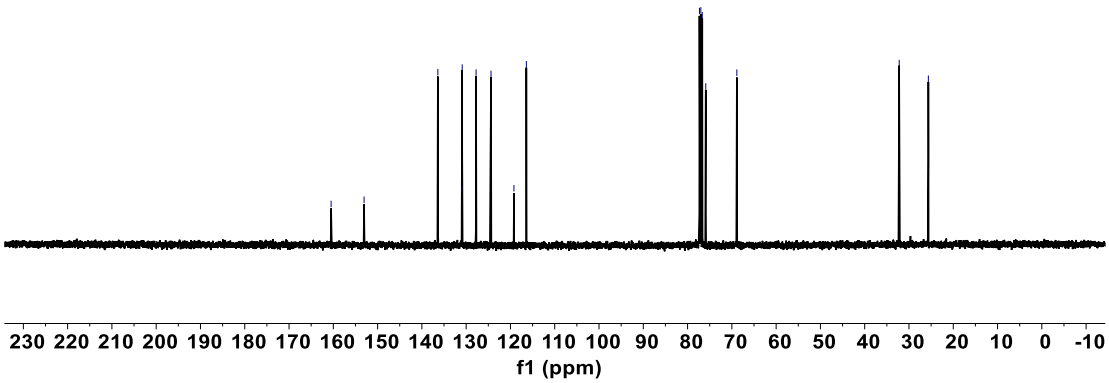
^{1}H NMR (400 MHz, $CDCl_3$)

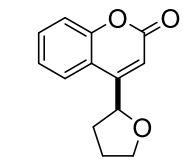




Compound 4a-1

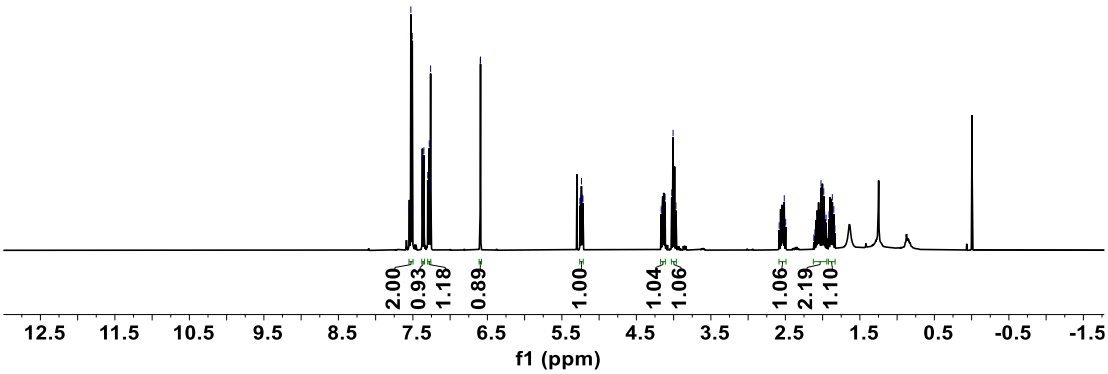
^{13}C NMR (101 MHz, $CDCl_3$)

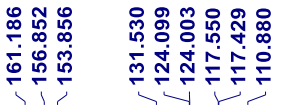


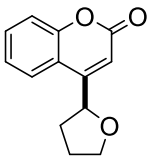


Compound 4a-2

^{1}H NMR (400 MHz, $CDCl_3$)

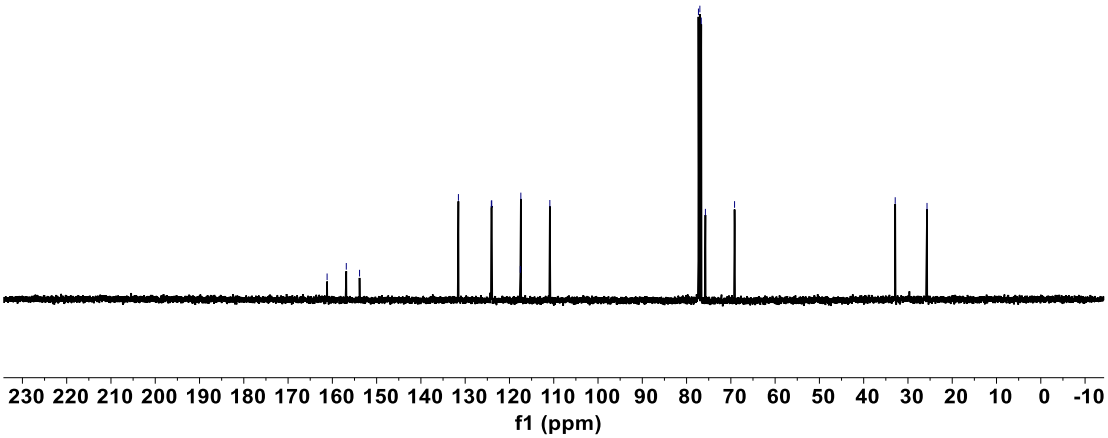


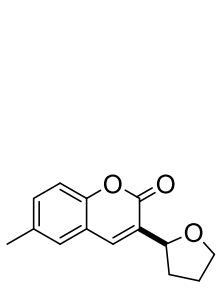




Compound 4a-2

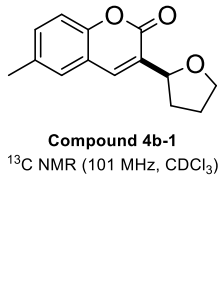
^{13}C NMR (101 MHz, $CDCl_3$)





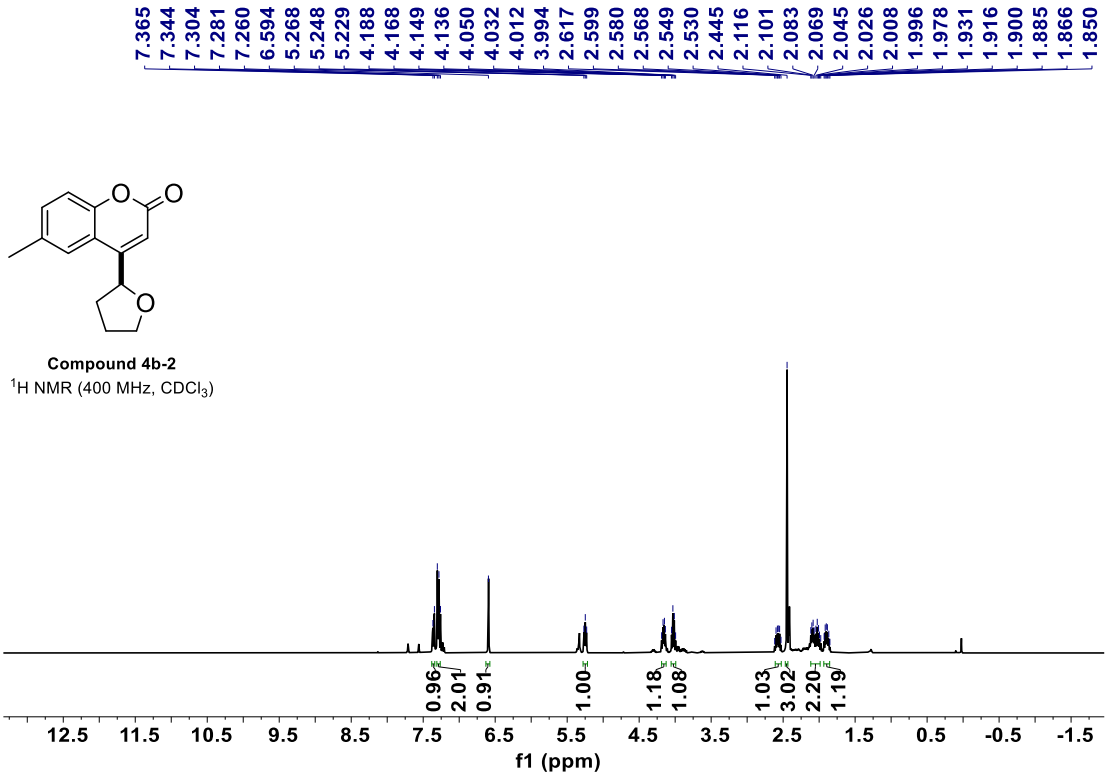
Compound 4b-1

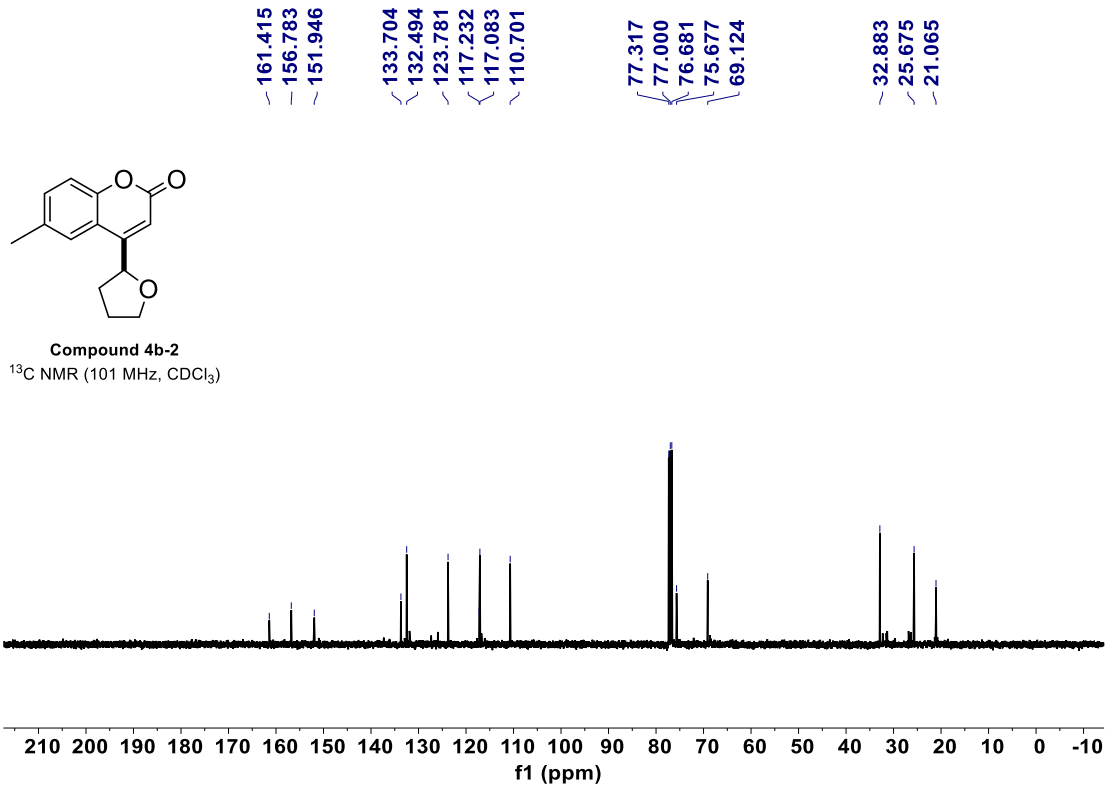
^{1}H NMR (400 MHz, $CDCl_3$)

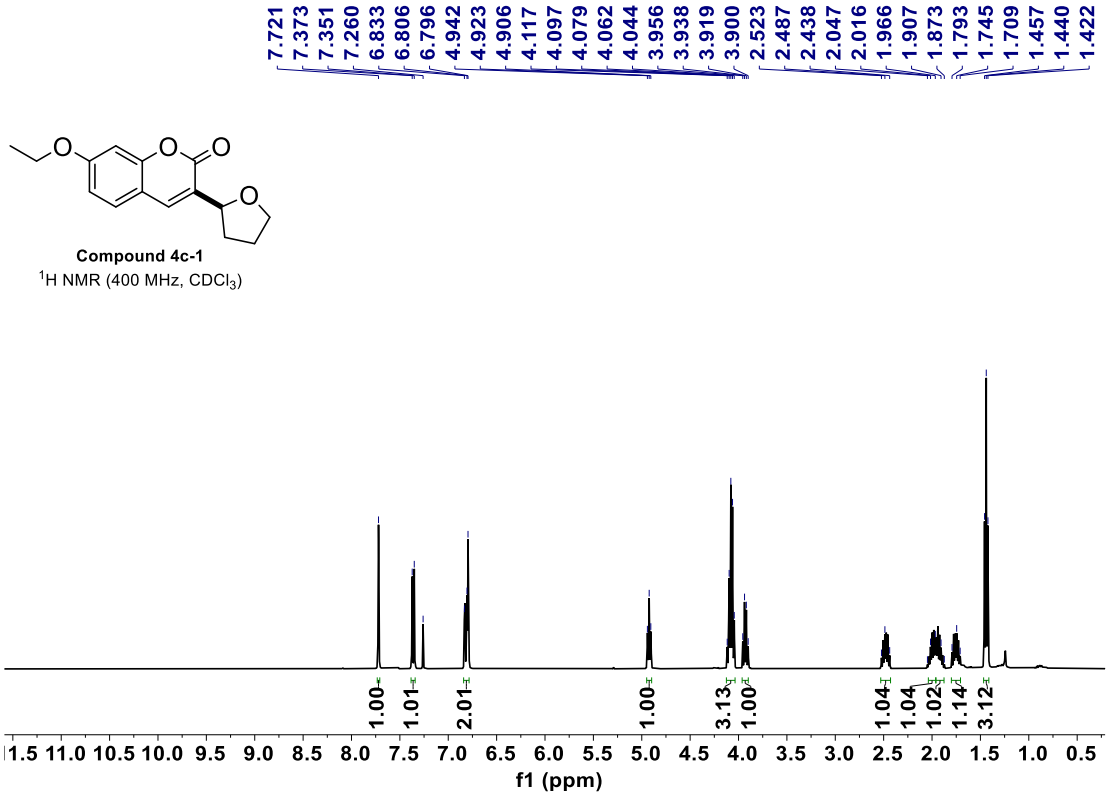


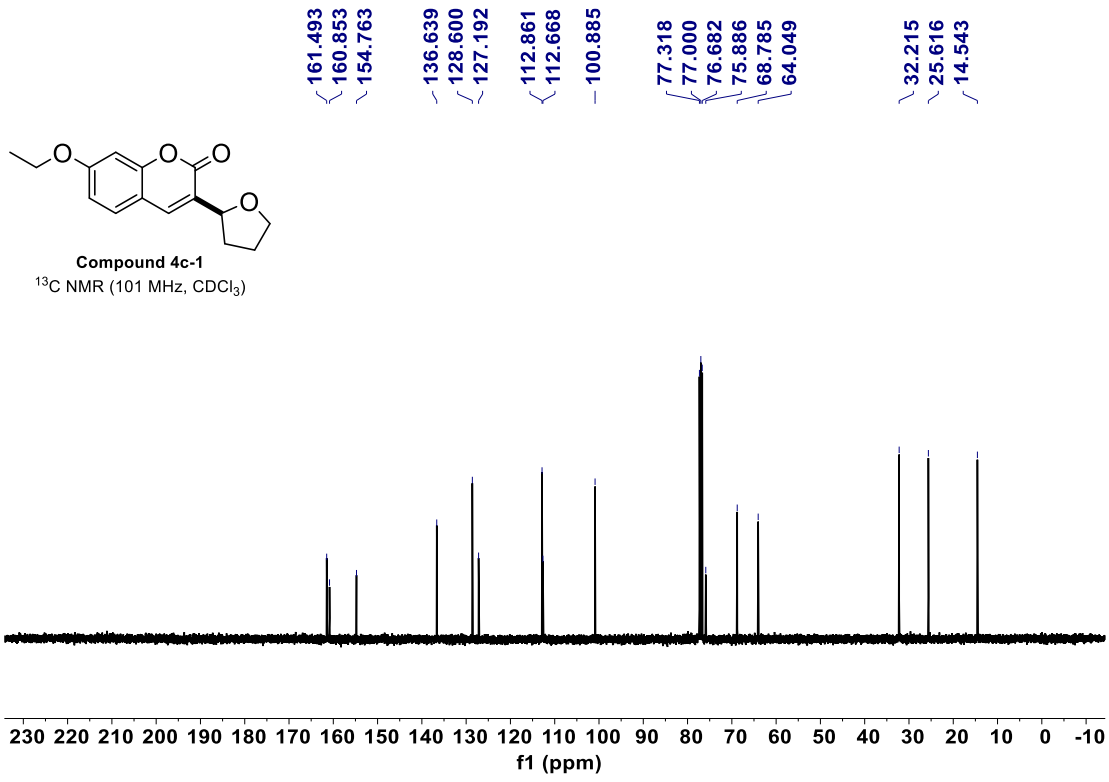
Compound 4b-1

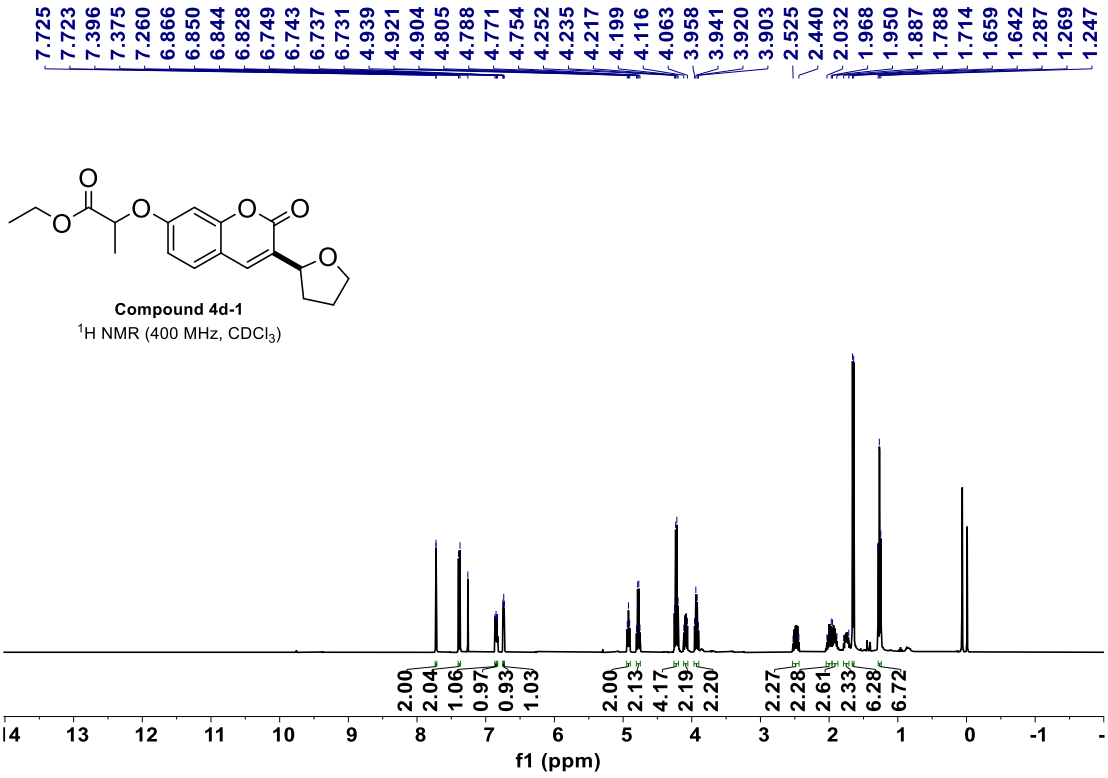
^{13}C NMR (101 MHz, $CDCl_3$)

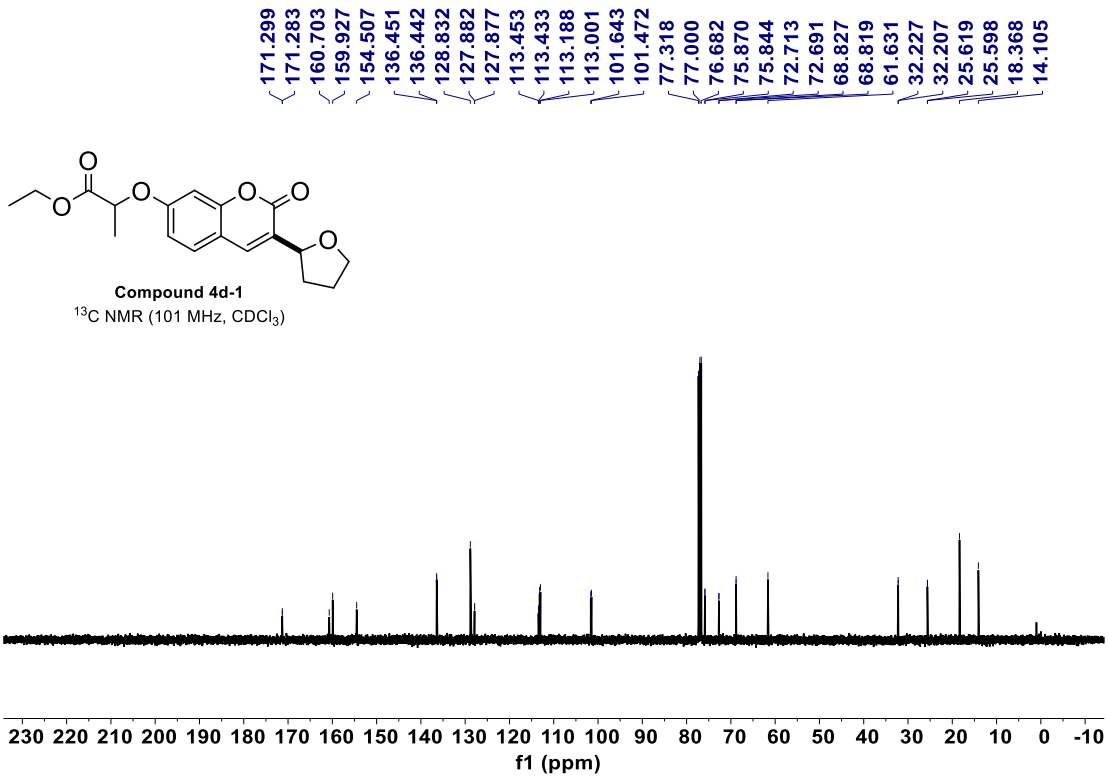

7.365
7.344
7.304
7.281
7.260
6.594
5.268
5.248
5.229
4.188
4.168
4.149
4.136
4.050
4.032
4.012
3.994
2.617
2.599
2.580
2.568
2.549
2.530
2.445
2.116
2.101
2.083
2.069
2.045
2.026
2.008
1.996
1.978
1.931
1.916
1.900
1.885
1.866
1.850
O
O
O
Compound 4b-2
1H NMR (400 MHz, CDCl3)
0.96
2.01
0.91
1.00
1.18
1.08
1.03
3.02
2.20
1.19
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)

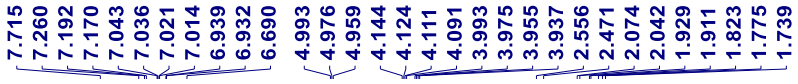

161.415
156.783
151.946
133.704
132.494
123.781
117.232
117.083
110.701
77.317
77.000
76.681
75.677
69.124
32.883
25.675
21.065
O
O
O
Compound 4b-2
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

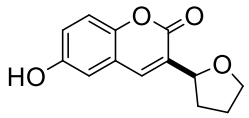

7.721
7.373
7.351
7.260
6.833
6.806
6.796
4.942
4.923
4.906
4.117
4.097
4.079
4.062
4.044
3.956
3.938
3.919
3.900
2.523
2.487
2.438
2.047
2.016
1.966
1.907
1.873
1.793
1.745
1.709
1.457
1.440
1.422
Compound 4c-1
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.01
2.01
1.00
3.13
1.00
1.04
1.04
1.02
1.14
3.12
f1 (ppm)


161.493
160.853
154.763
136.639
128.600
127.192
112.861
112.668
100.885
77.318
77.000
76.682
75.886
68.785
64.049
32.215
25.616
14.543
Compound 4c-1
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)


7.725
7.723
7.396
7.375
7.260
6.866
6.850
6.844
6.828
6.749
6.743
6.737
6.731
4.939
4.921
4.904
4.805
4.788
4.771
4.754
4.252
4.235
4.217
4.199
4.116
4.063
3.958
3.941
3.920
3.903
2.525
2.440
2.032
1.968
1.950
1.887
1.788
1.714
1.659
1.642
1.287
1.269
1.247
Compound 4d-1
^{1}H NMR (400 MHz, CDCl$_3$)
2.00
2.04
1.06
0.97
0.93
1.03
2.00
2.13
4.17
2.19
2.20
2.27
2.28
2.61
2.33
6.28
6.72
f1 (ppm)

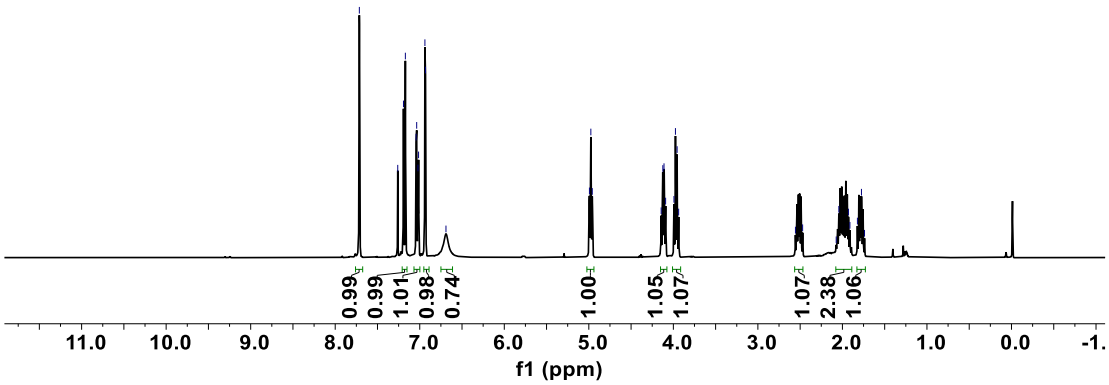

171.299
171.283
160.703
159.927
154.507
136.451
136.442
128.832
127.882
127.877
113.453
113.433
113.188
113.001
101.643
101.472
77.318
77.000
76.682
75.870
75.844
72.713
72.691
68.827
68.819
61.631
32.227
32.207
25.619
25.598
18.368
14.105
Compound 4d-1
^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

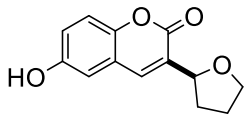




Compound 4e-1

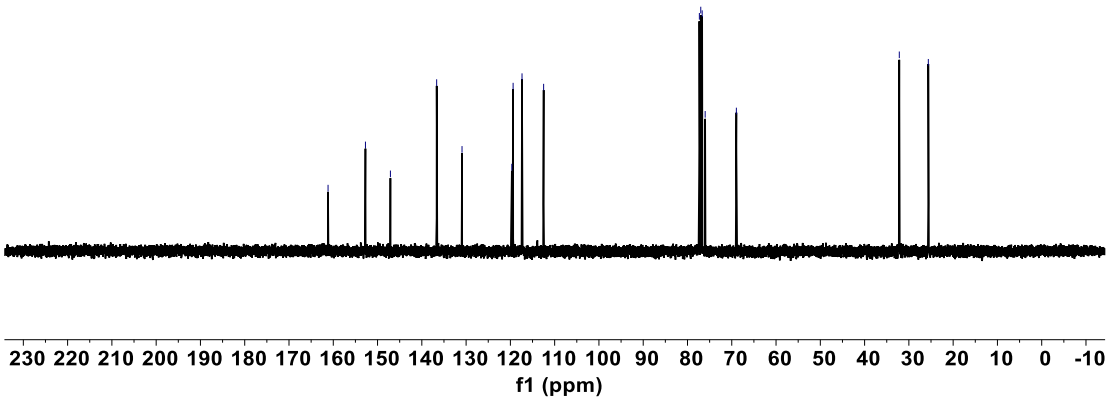
^{1}H NMR (400 MHz, $CDCl_3$)

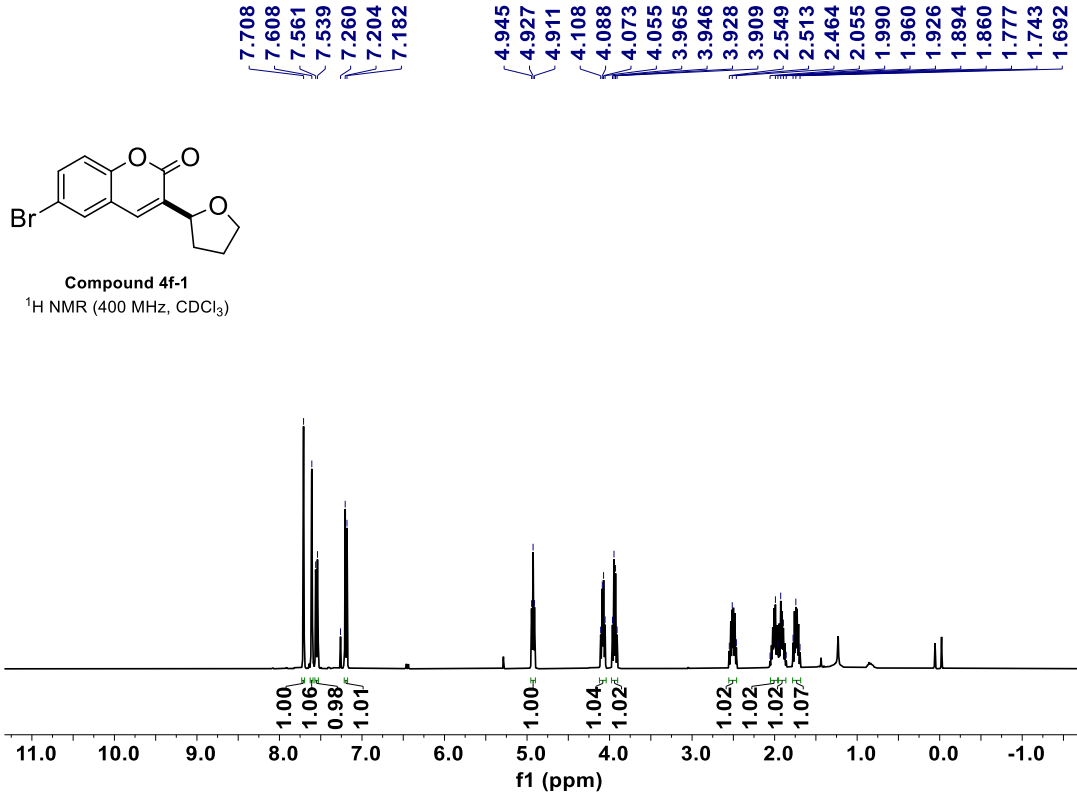




Compound 4e-1

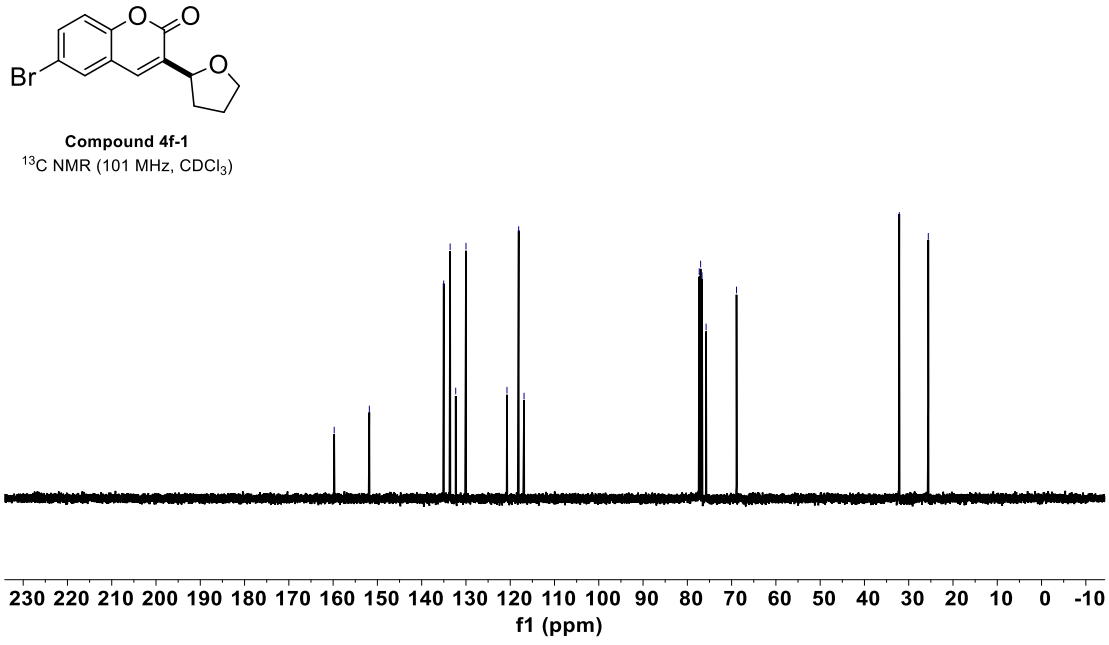
^{13}C NMR (101 MHz, $CDCl_3$)





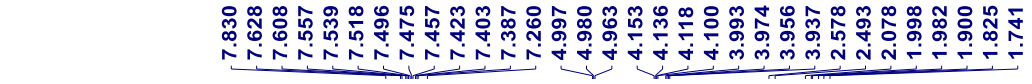
Compound 4f-1

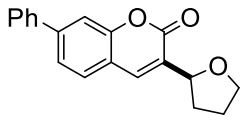
^{1}H NMR (400 MHz, $CDCl_3$)



Compound 4f-1

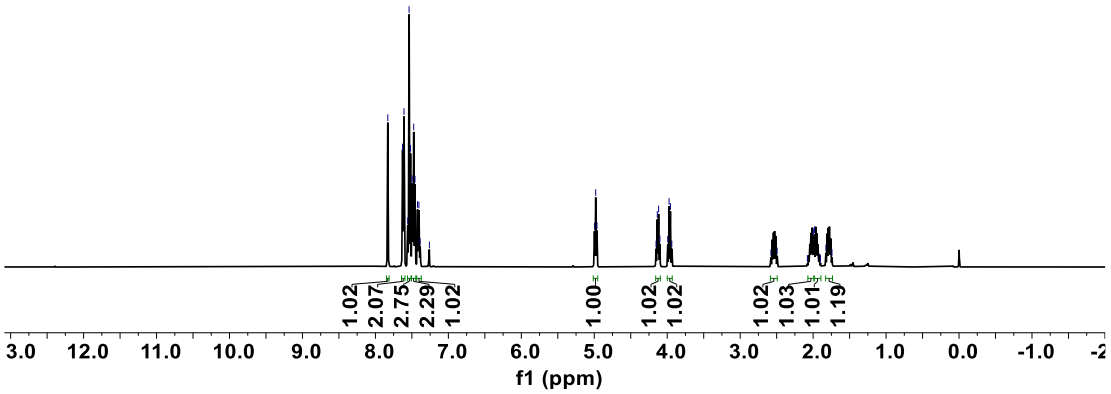
^{13}C NMR (101 MHz, $CDCl_3$)

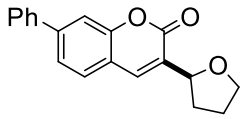




Compound 4g-1

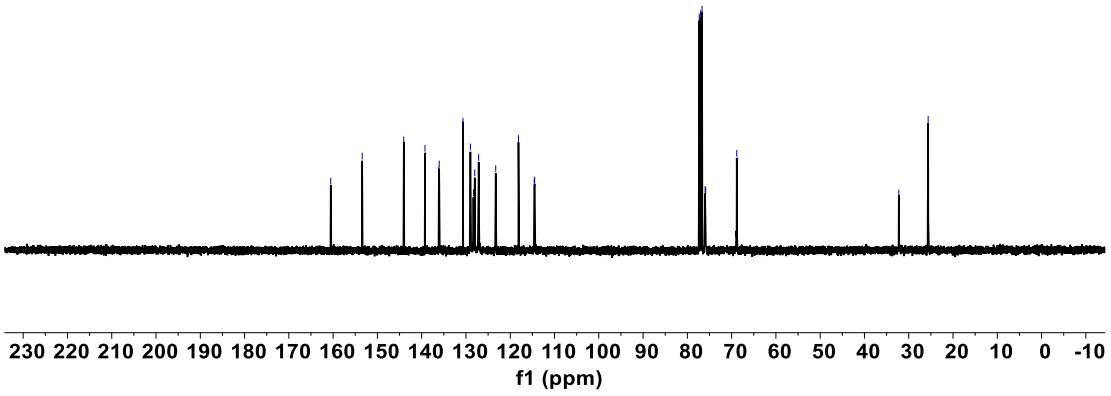
^{1}H NMR (400 MHz, $CDCl_3$)

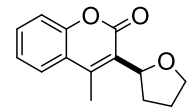




Compound 4g-1

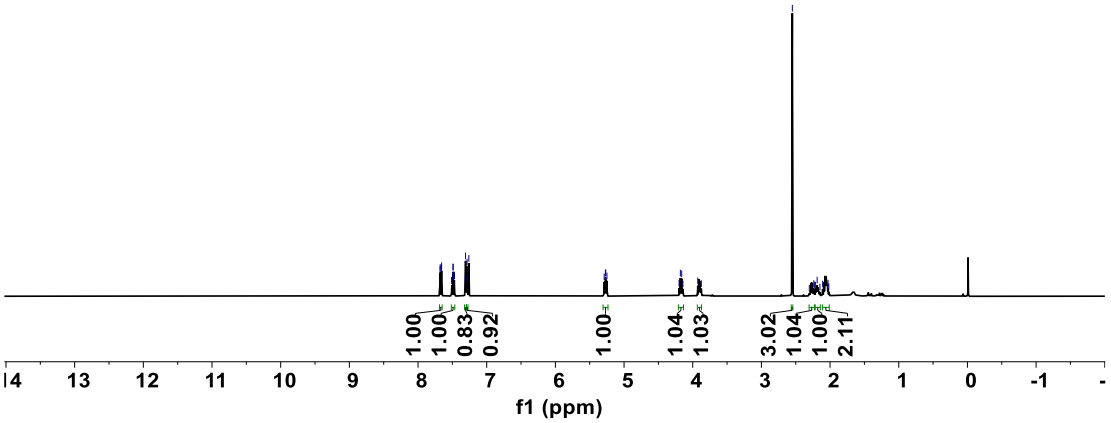
^{13}C NMR (101 MHz, $CDCl_3$)

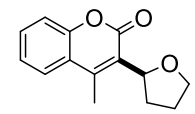




Compound 4h

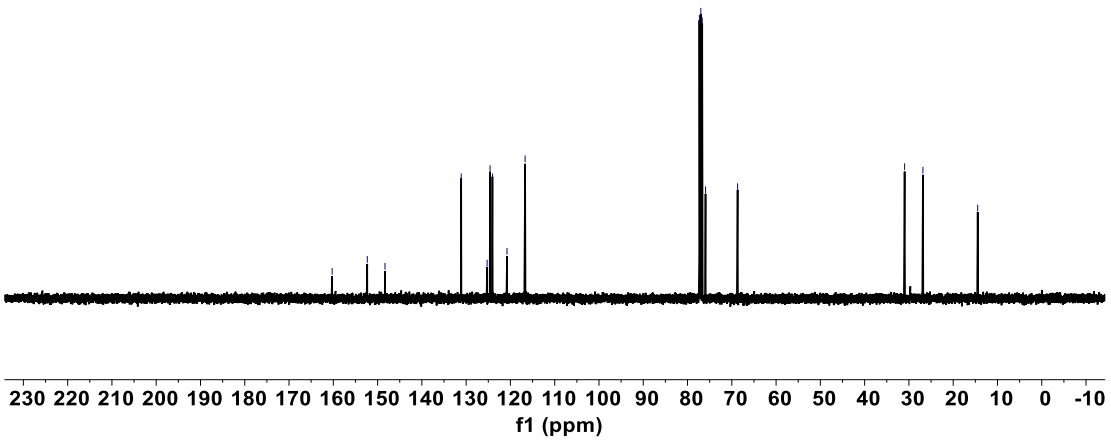
^{1}H NMR (400 MHz, $CDCl_3$)

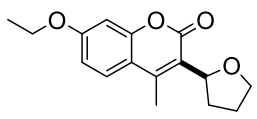




Compound 4h

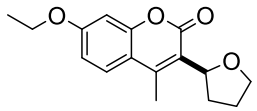
^{13}C NMR (101 MHz, $CDCl_3$)





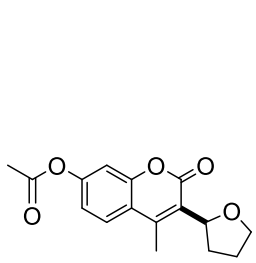
Compound 4i

^{1}H NMR (400 MHz, $CDCl_3$)



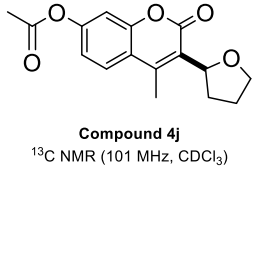
Compound 4i

^{13}C NMR (101 MHz, $CDCl_3$)



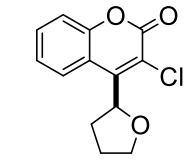
Compound 4j

^{1}H NMR (400 MHz, $CDCl_3$)



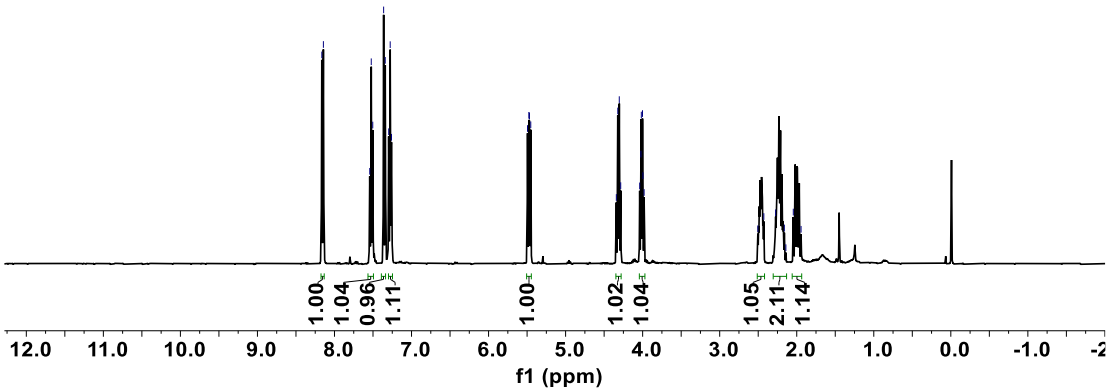
Compound 4j

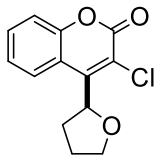
^{13}C NMR (101 MHz, $CDCl_3$)



Compound 4k

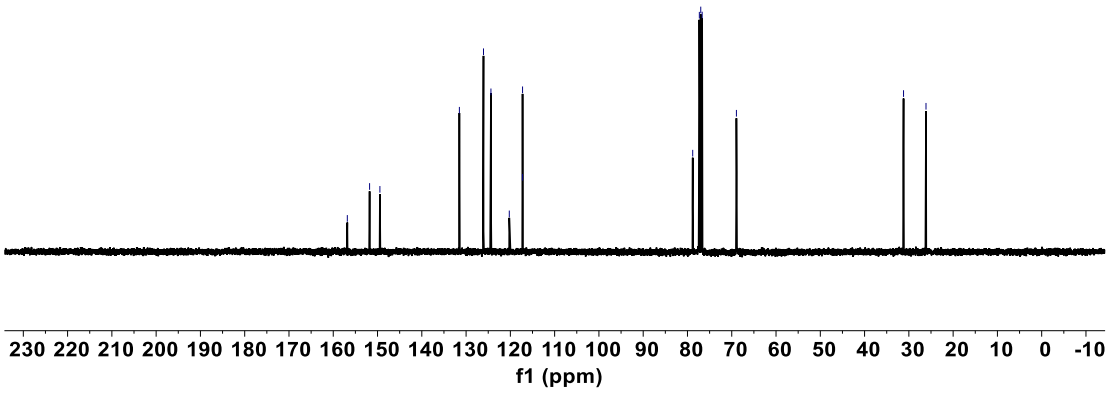
^{1}H NMR (400 MHz, $CDCl_3$)

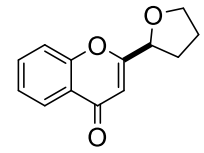




Compound 4k

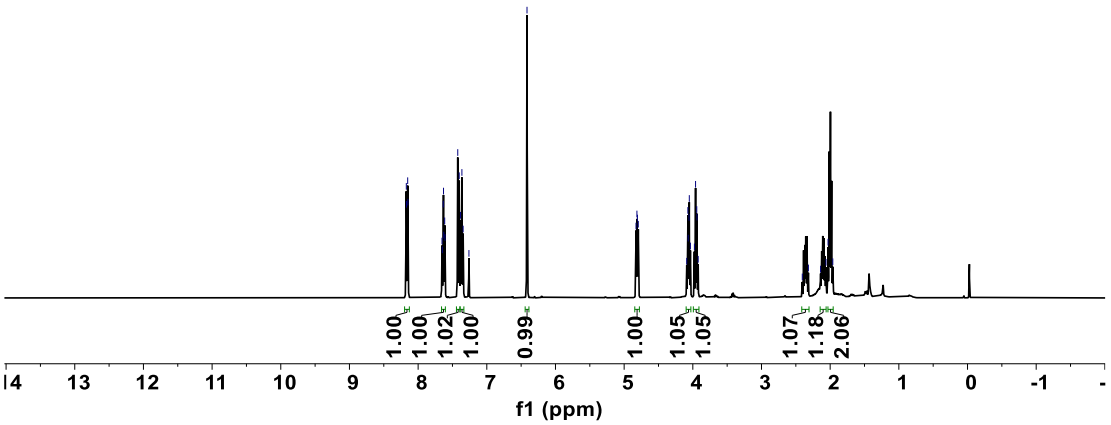
^{13}C NMR (101 MHz, $CDCl_3$)

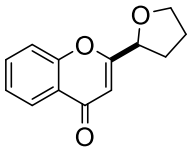




Compound 4l-1

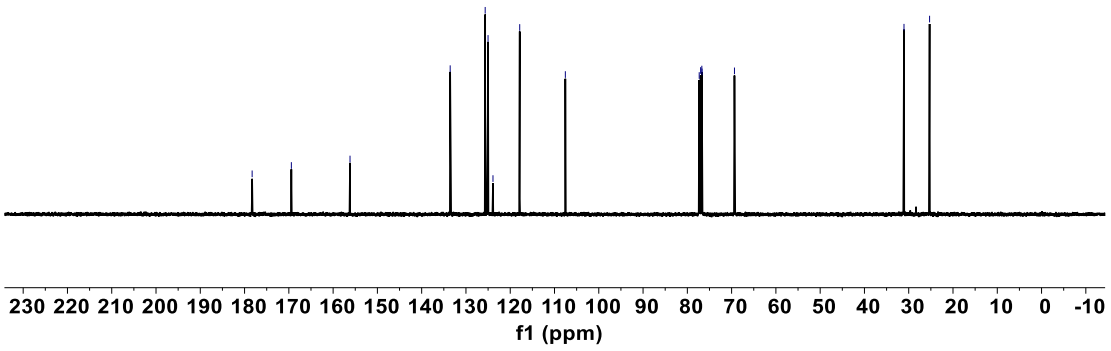
^{1}H NMR (400 MHz, $CDCl_3$)

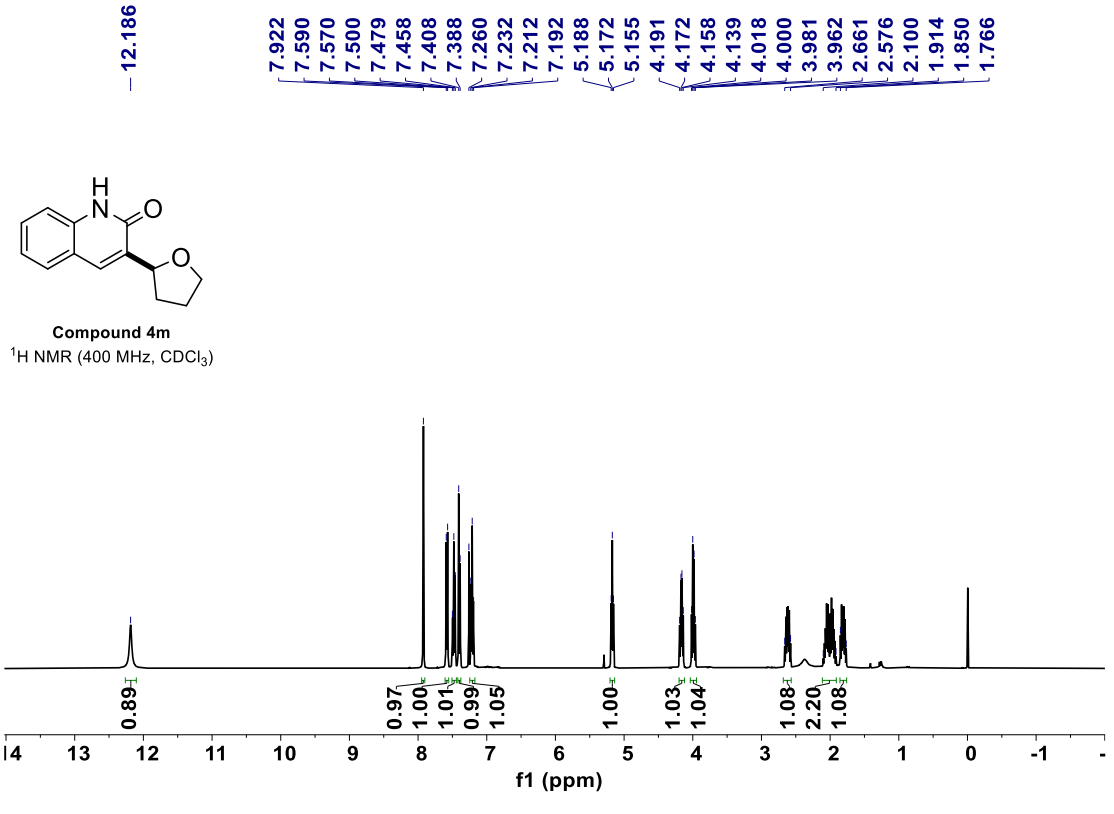




Compound 4l-1

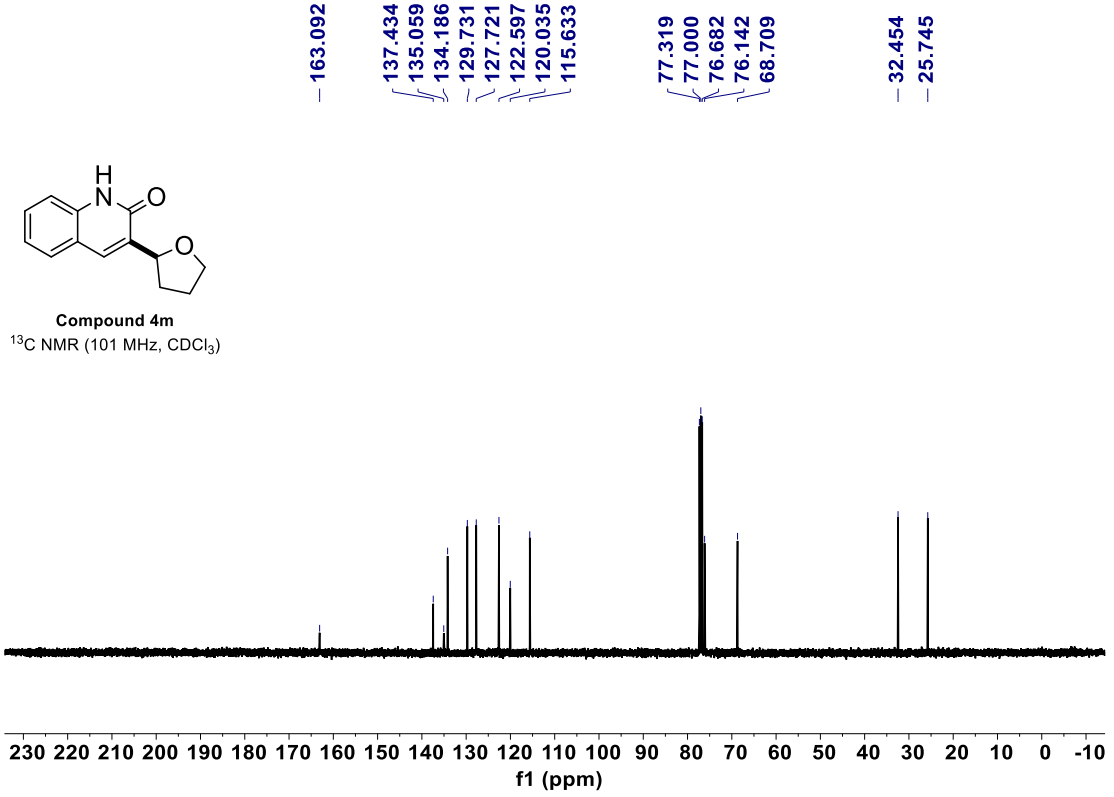
^{13}C NMR (101 MHz, $CDCl_3$)





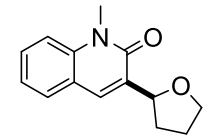
Compound 4m

^{1}H NMR (400 MHz, $CDCl_3$)



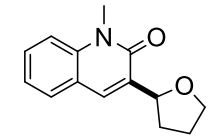
Compound 4m

^{13}C NMR (101 MHz, $CDCl_3$)



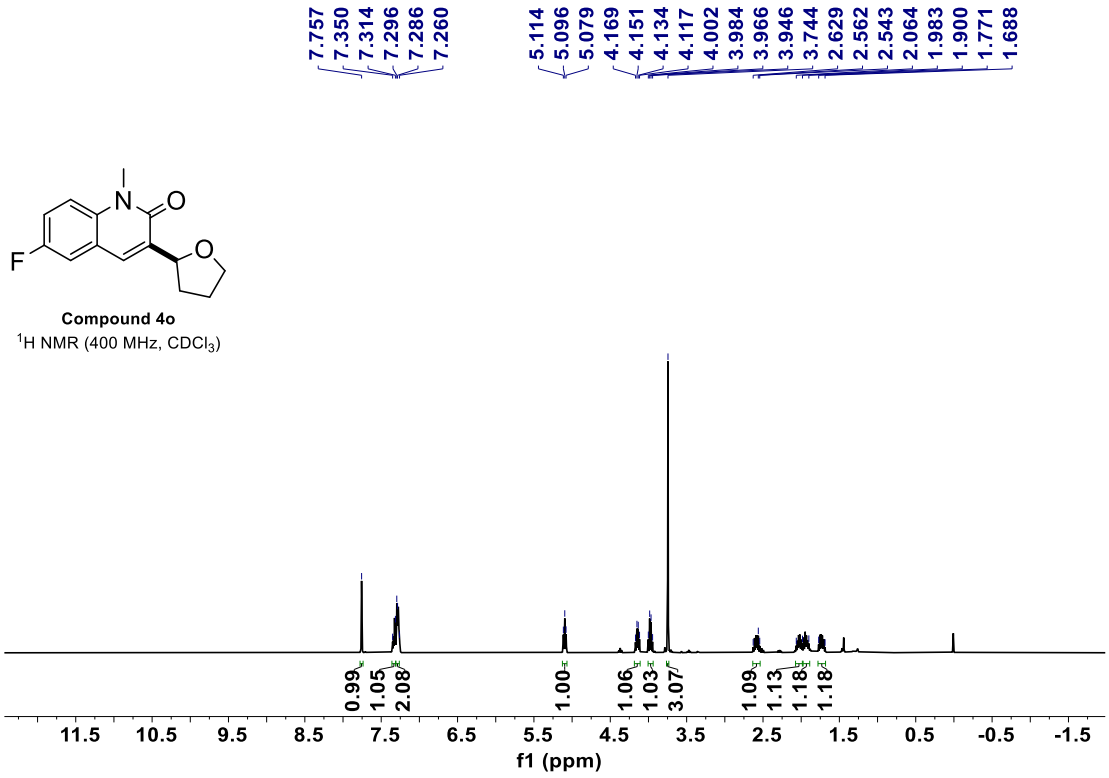
Compound 4n

^{1}H NMR (400 MHz, $CDCl_3$)



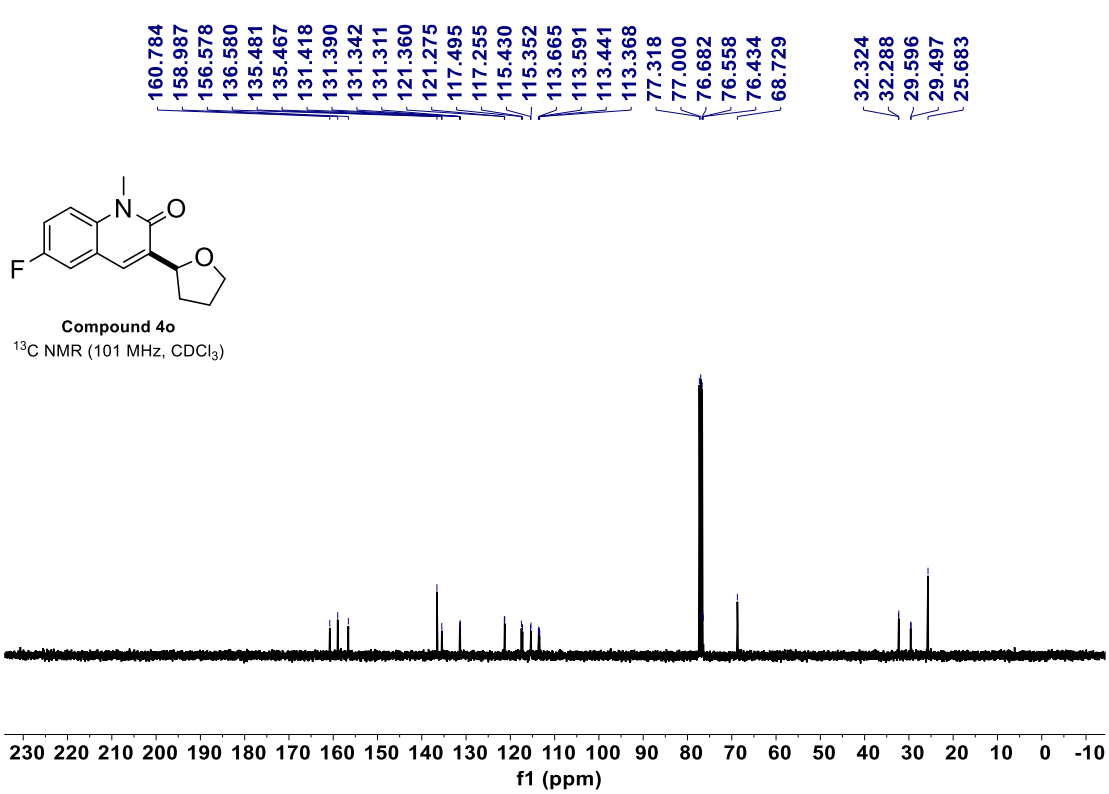
Compound 4n

^{13}C NMR (101 MHz, $CDCl_3$)



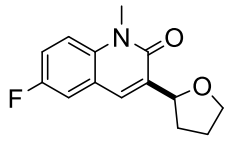
Compound 4o

^{1}H NMR (400 MHz, $CDCl_3$)



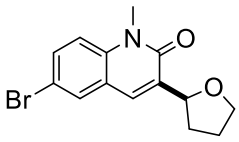
Compound 4o

^{13}C NMR (101 MHz, $CDCl_3$)



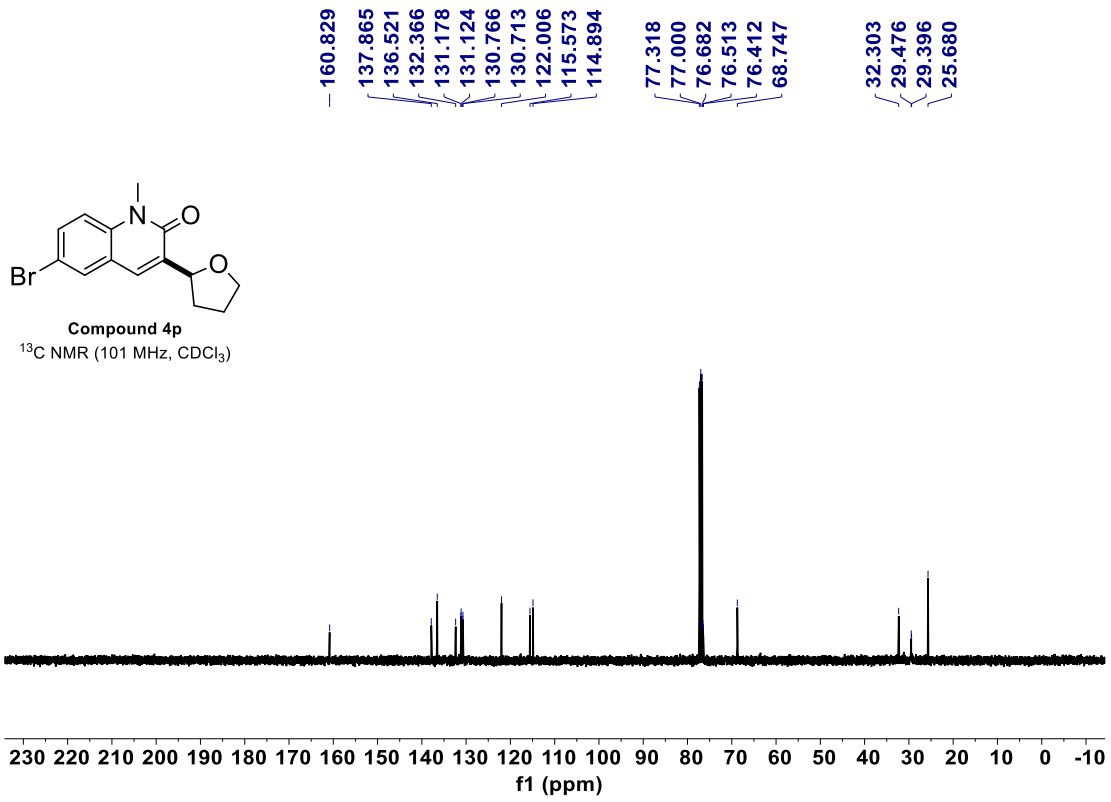
Compound 4o

^{19}F NMR (376 MHz, $CDCl_3$)



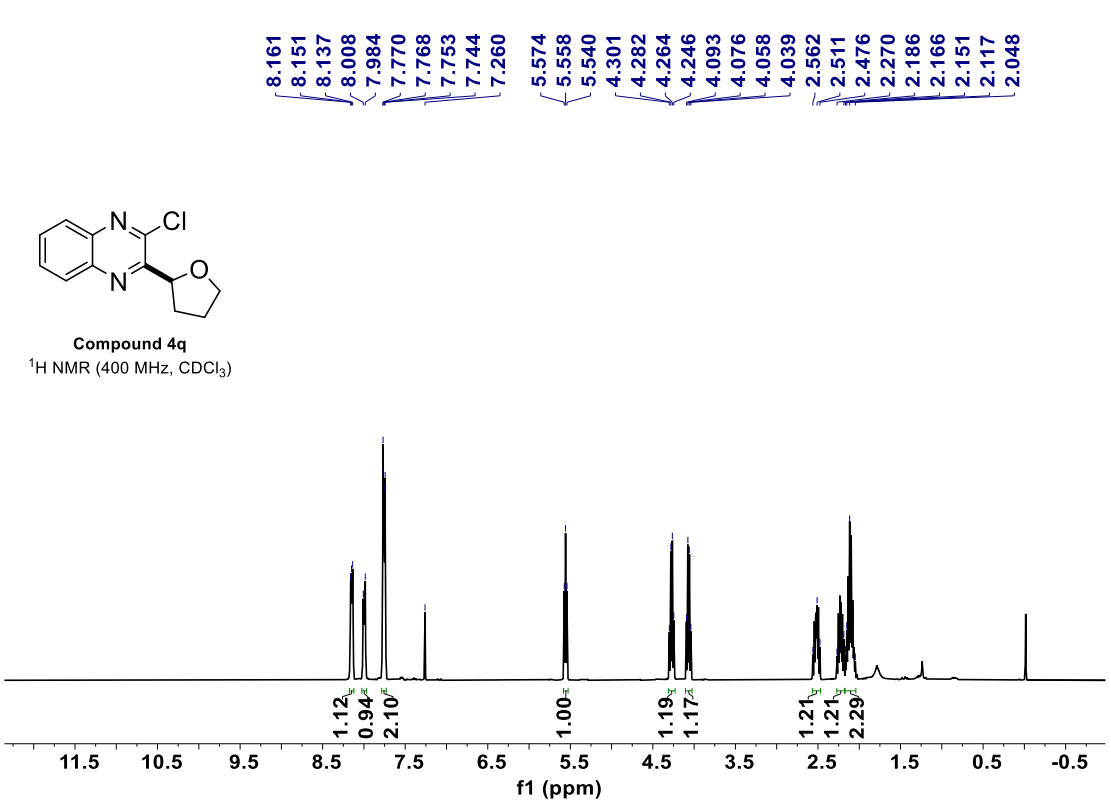
Compound 4p

^{1}H NMR (400 MHz, $CDCl_3$)



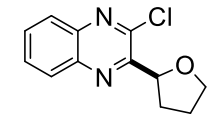
Compound 4p

^{13}C NMR (101 MHz, $CDCl_3$)



Compound 4q

^{1}H NMR (400 MHz, $CDCl_3$)

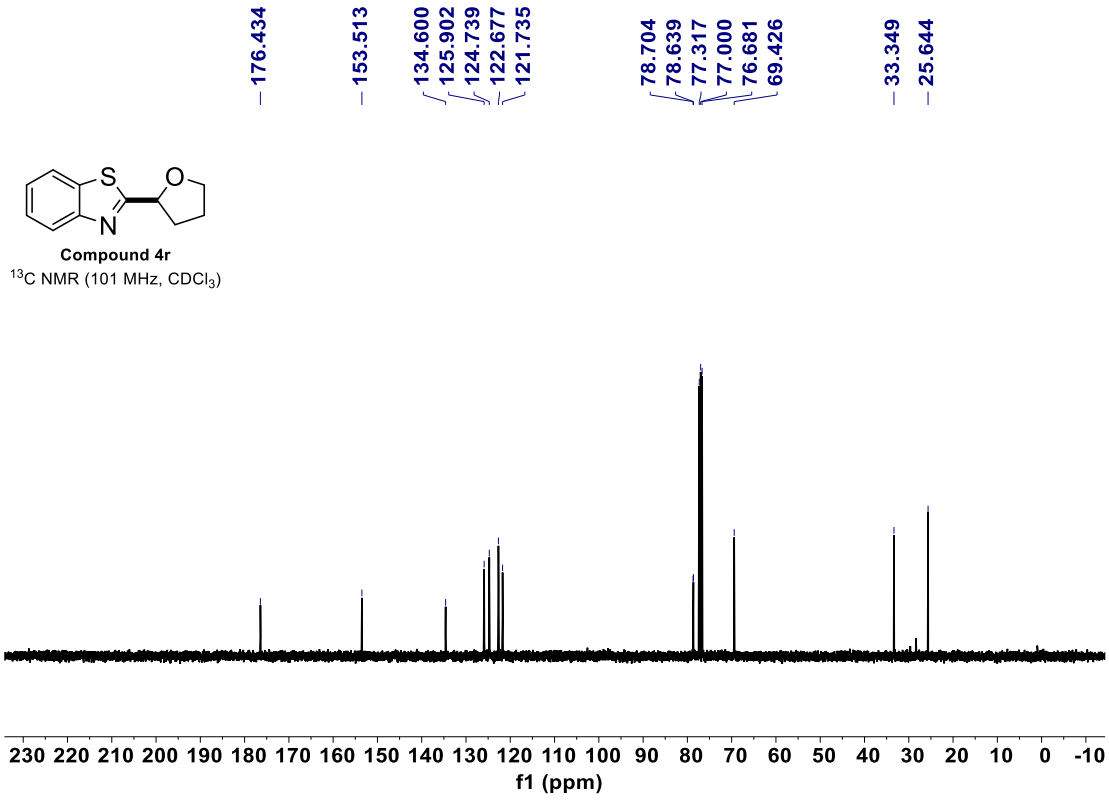


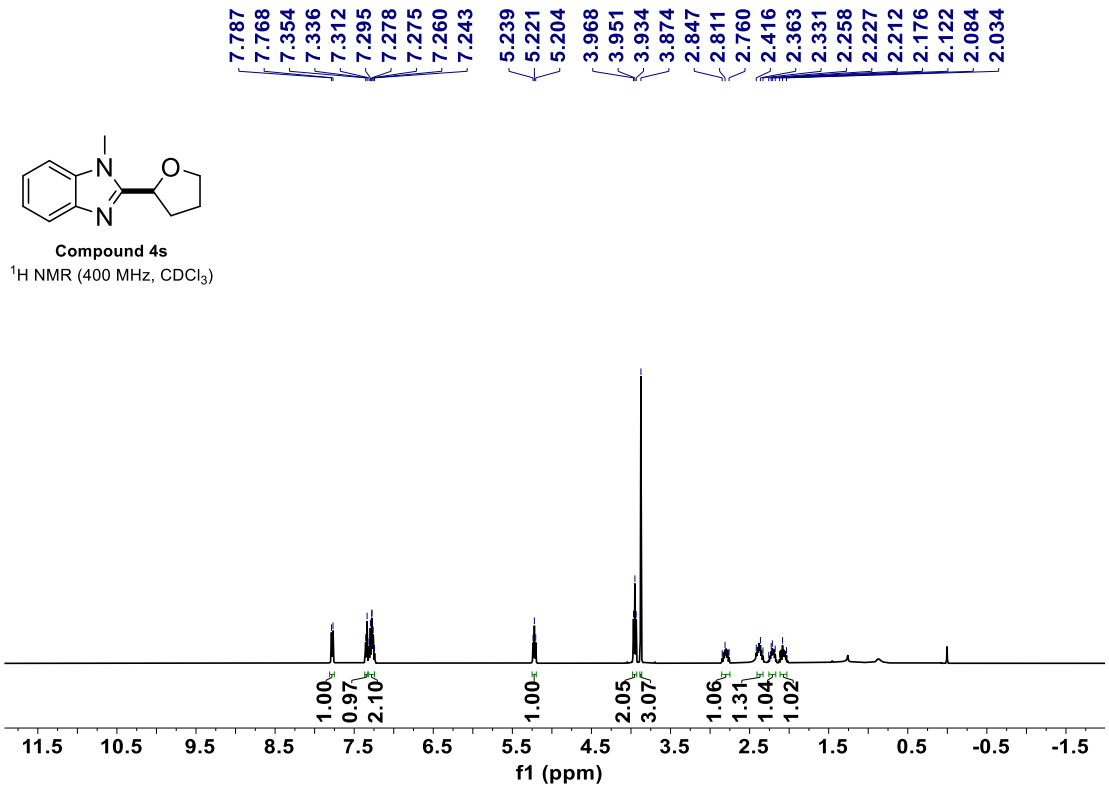
Compound 4q

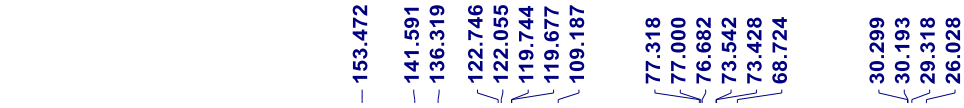
^{13}C NMR (101 MHz, $CDCl_3$)

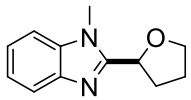
Compound 4r

^{1}H NMR (400 MHz, $CDCl_3$)


176.434
153.513
134.600
125.902
124.739
122.677
121.735
78.704
78.639
77.317
77.000
76.681
69.426
33.349
25.644
S
O
N
Compound 4r
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

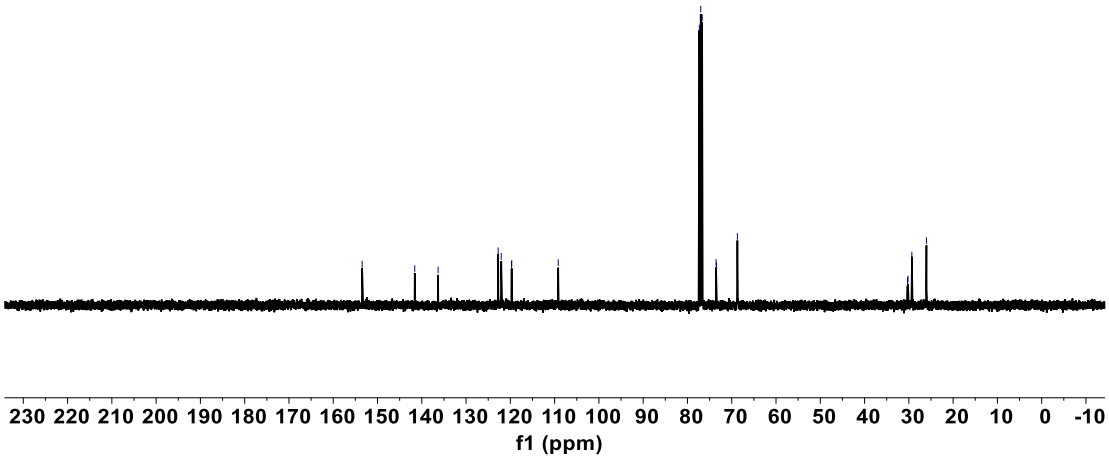

7.787
7.768
7.354
7.336
7.312
7.295
7.278
7.275
7.260
7.243
5.239
5.221
5.204
3.968
3.951
3.934
3.874
2.847
2.811
2.760
2.416
2.363
2.331
2.258
2.227
2.212
2.176
2.122
2.084
2.034
N
O
N
Compound 4s
1H NMR (400 MHz, CDCl3)
1.00
0.97
2.10
1.00
2.05
3.07
1.06
1.31
1.04
1.02
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5
f1 (ppm)

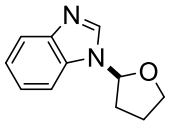




Compound 4s

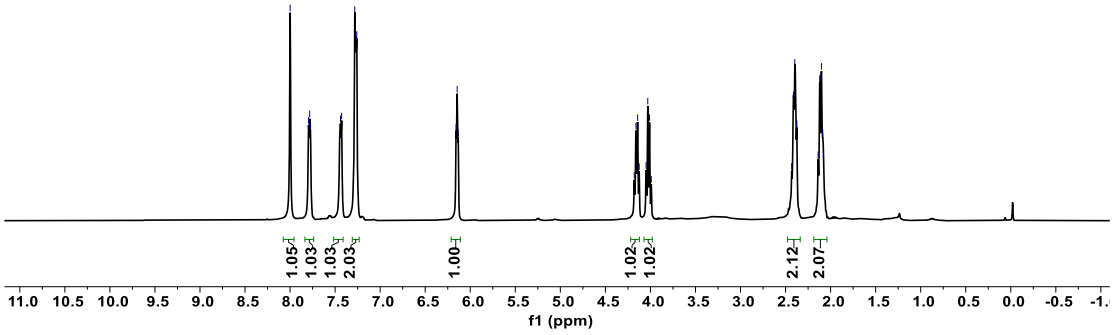
^{13}C NMR (101 MHz, $CDCl_3$)

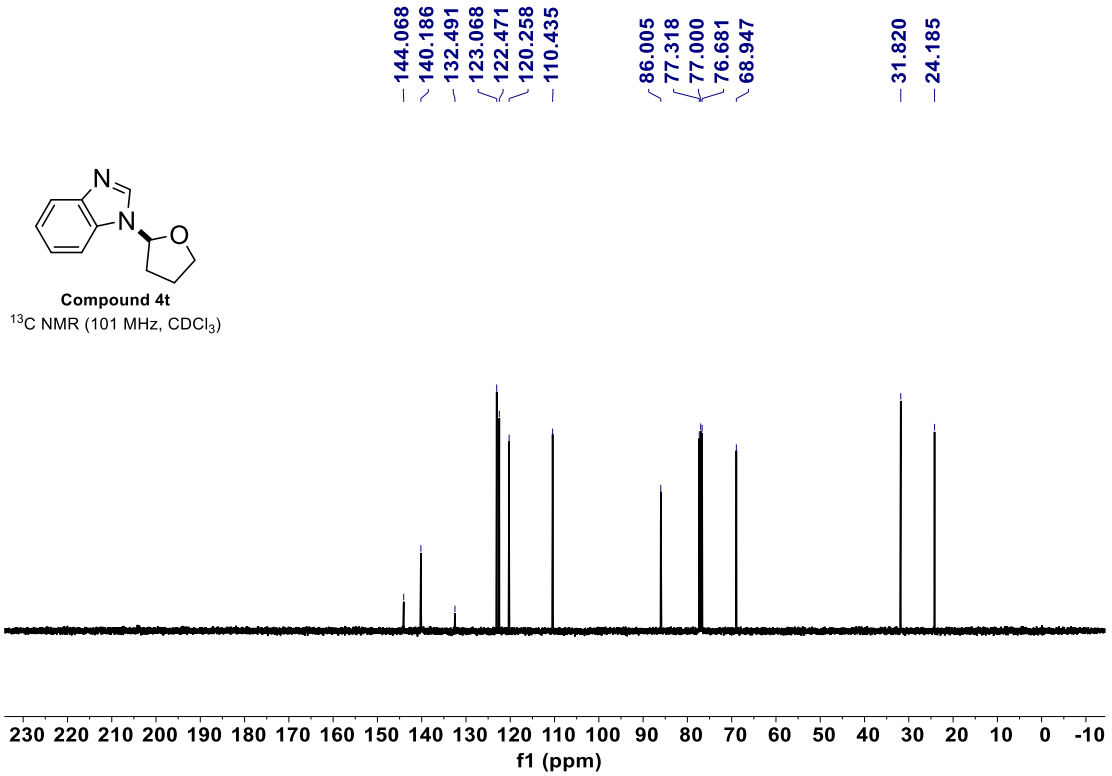




Compound 4t

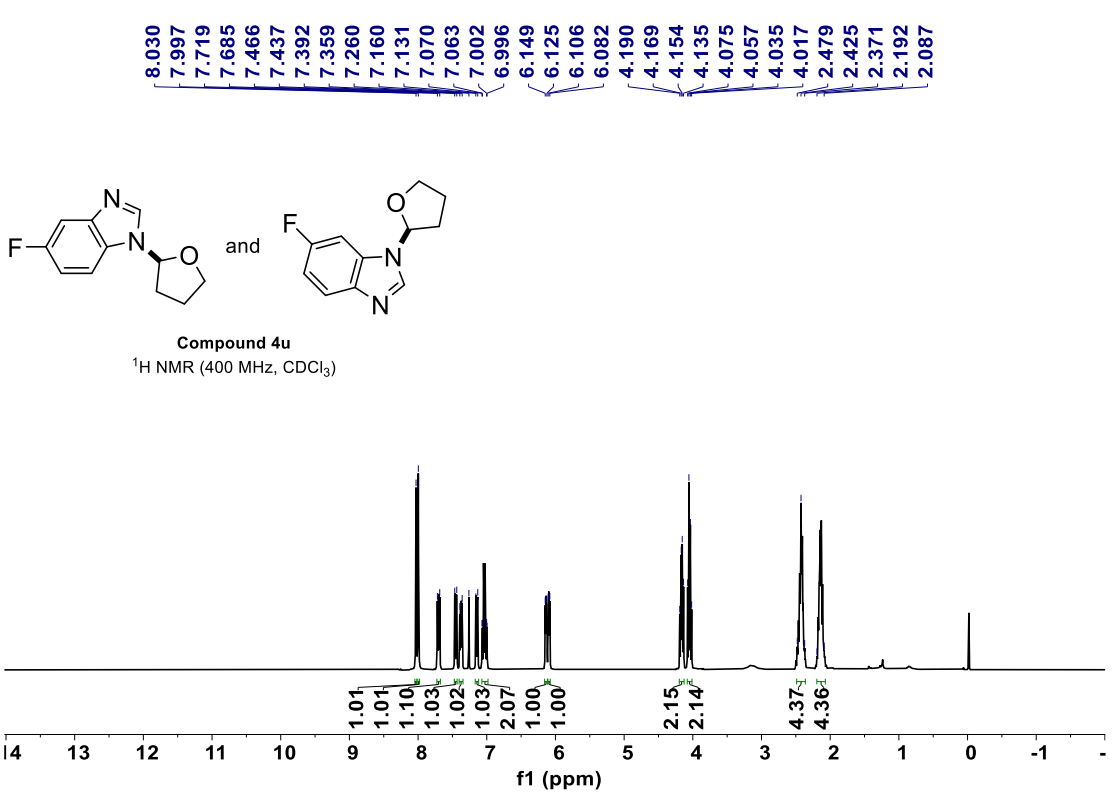
^{1}H NMR (400 MHz, $CDCl_3$)





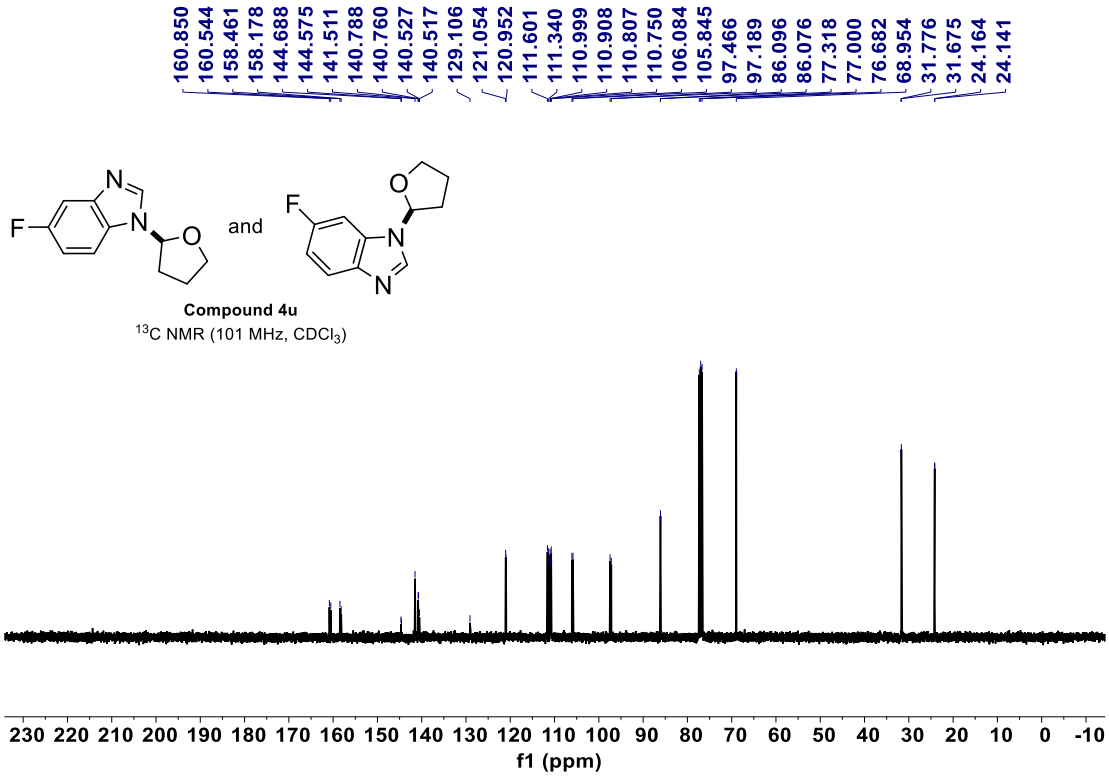
Compound 4t

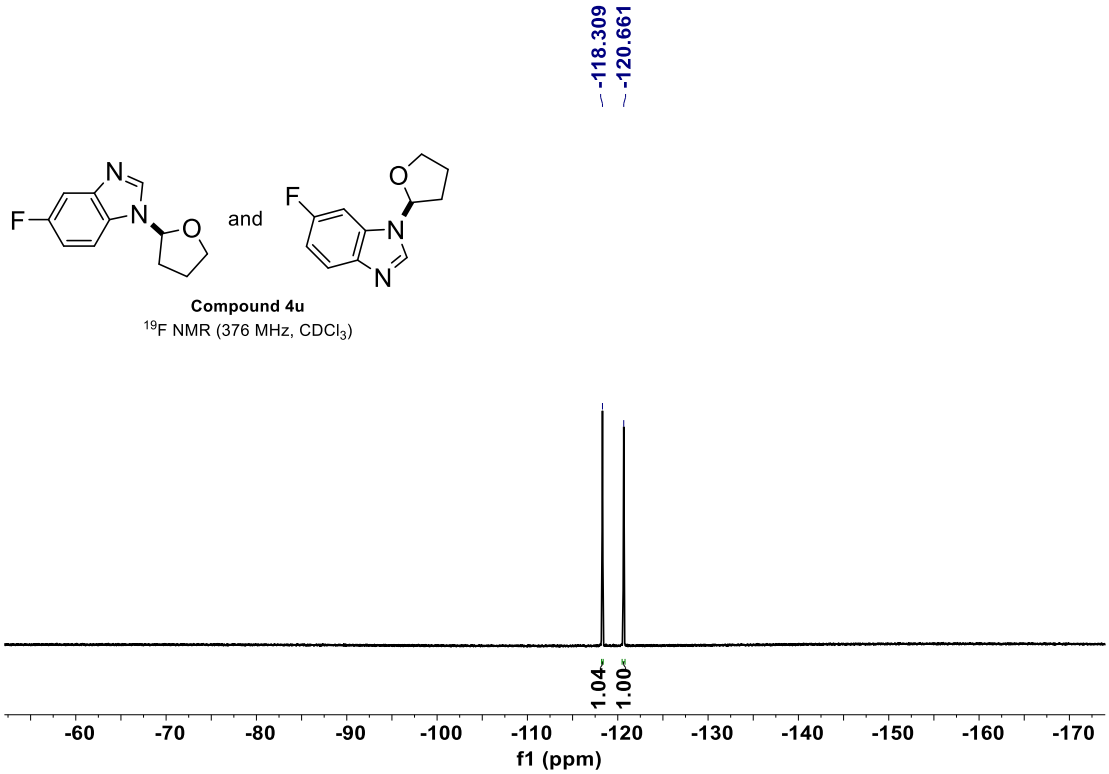
^{13}C NMR (101 MHz, $CDCl_3$)

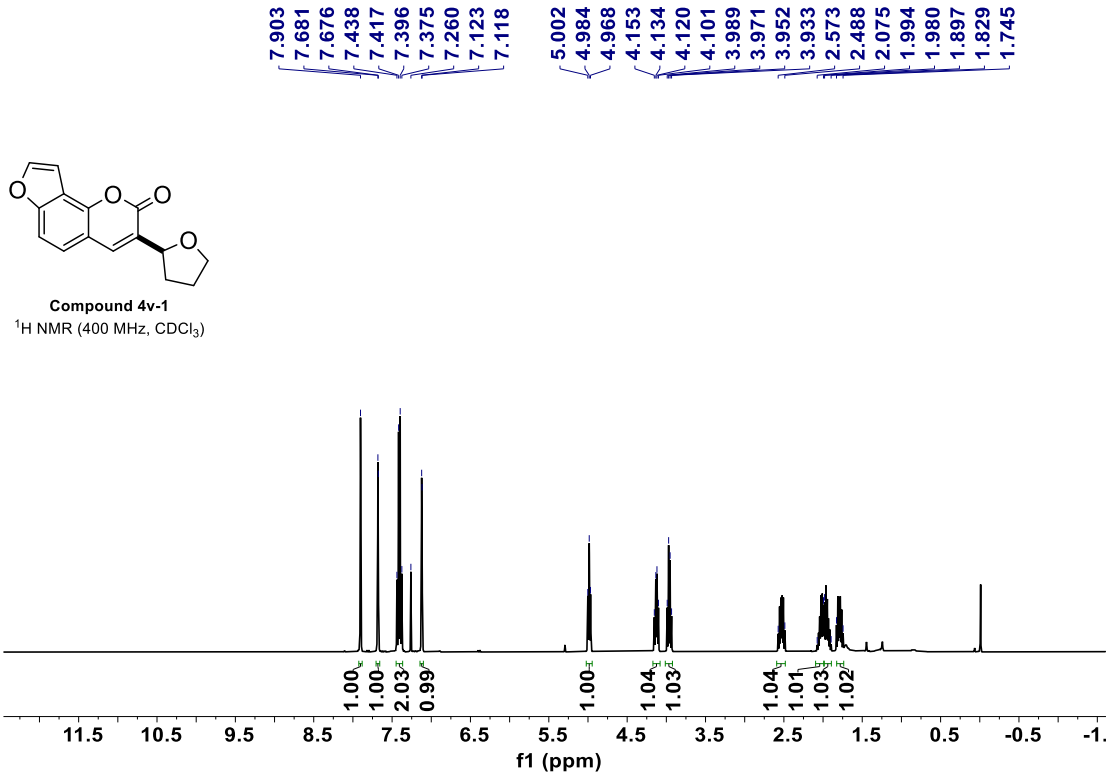


Compound 4u

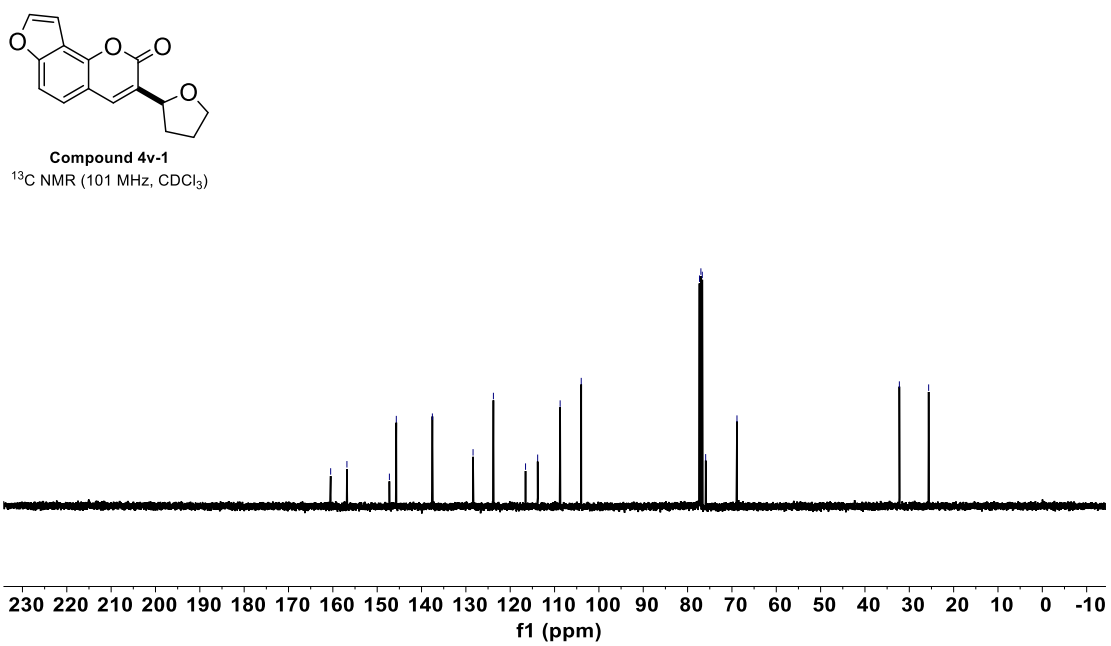
^{1}H NMR (400 MHz, $CDCl_3$)


160.850
160.544
158.461
158.178
144.688
144.575
141.511
140.788
140.760
140.527
140.517
129.106
121.054
120.952
111.601
111.340
110.999
110.908
110.807
110.750
106.084
105.845
97.466
97.189
86.096
86.076
77.318
77.000
76.682
68.954
31.776
31.675
24.164
24.141
F
N
O
and
F
O
N
N
Compound 4u
13C NMR (101 MHz, CDCl3)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

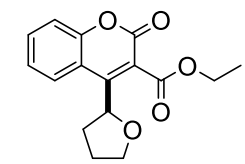

-118.309
-120.661
F
N
O
and
F
O
N
N
Compound 4u
19F NMR (376 MHz, CDCl3)
1.04
1.00
-60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)



Compound 4v-1
^{1}H NMR (400 MHz, $CDCl_3$)

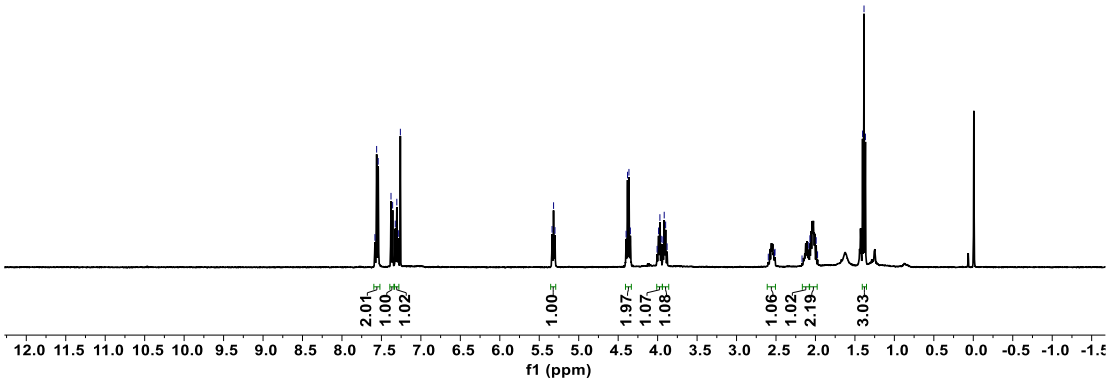


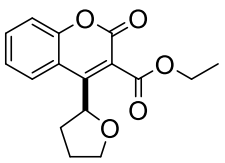
Compound 4v-1
^{13}C NMR (101 MHz, $CDCl_3$)



Compound 4w

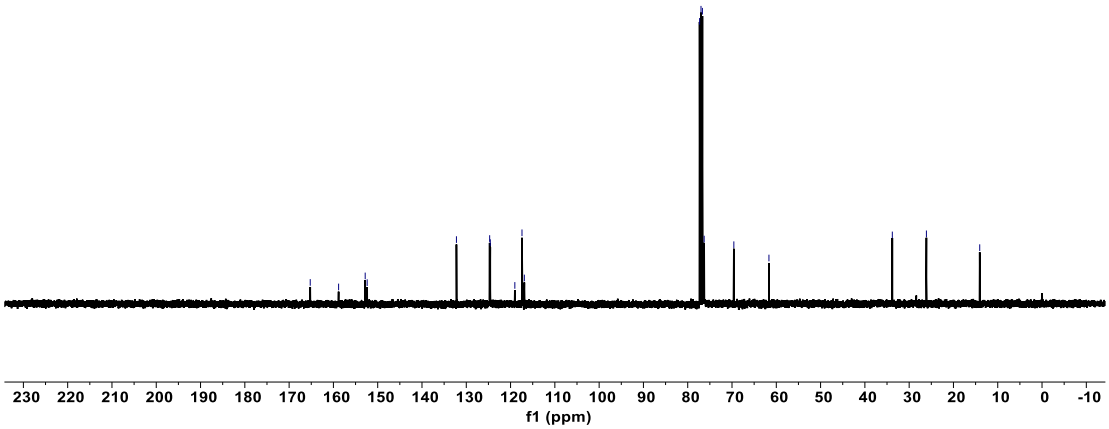
^{1}H NMR (400 MHz, $CDCl_3$)

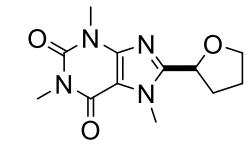




Compound 4w

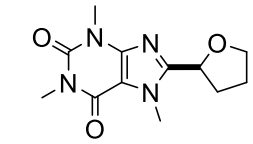
^{13}C NMR (101 MHz, $CDCl_3$)





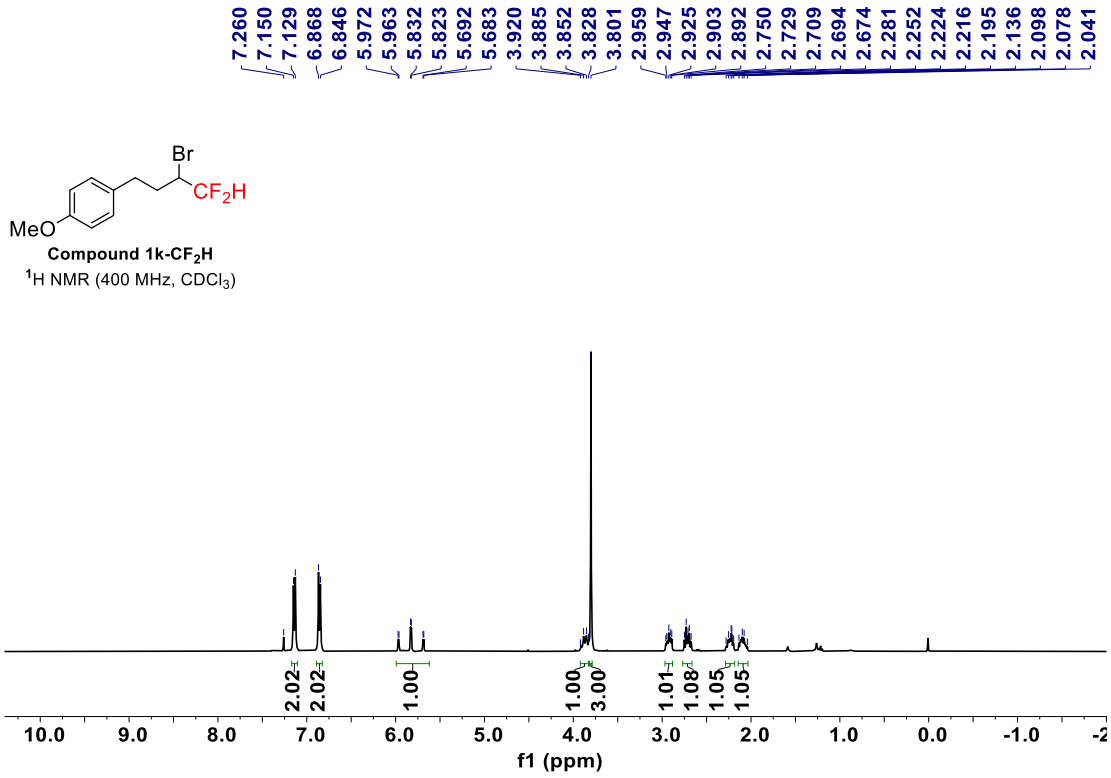
Compound 4x

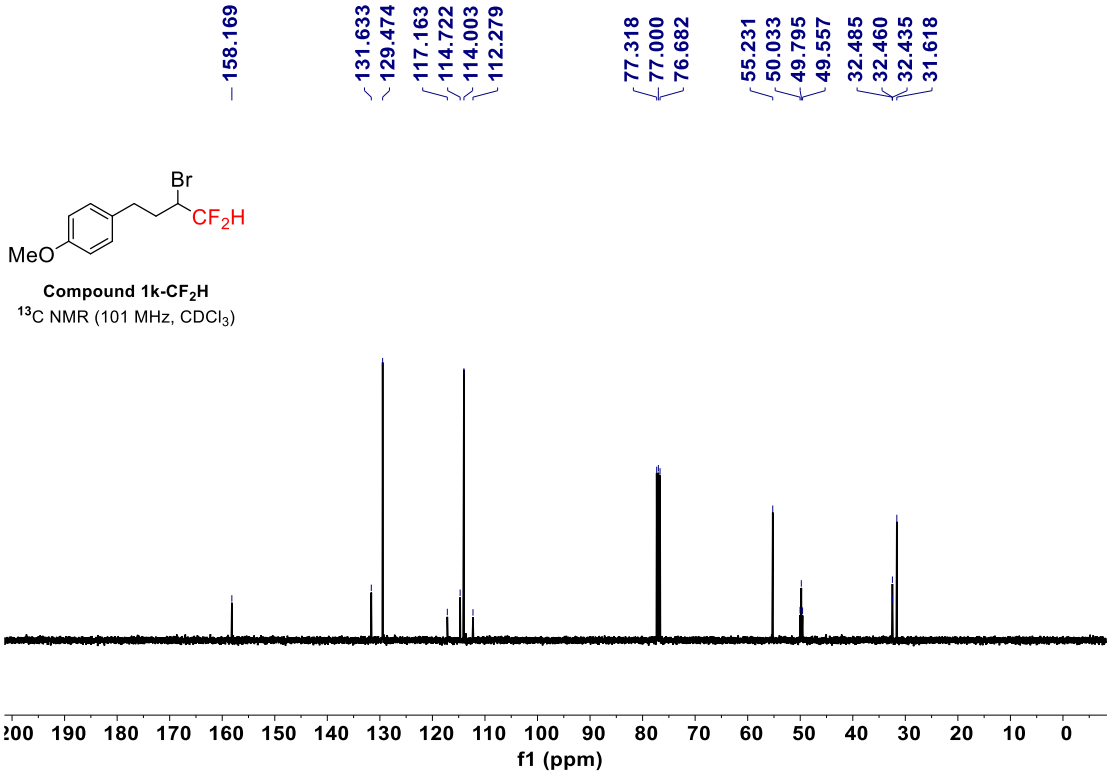
^{1}H NMR (400 MHz, $CDCl_3$)

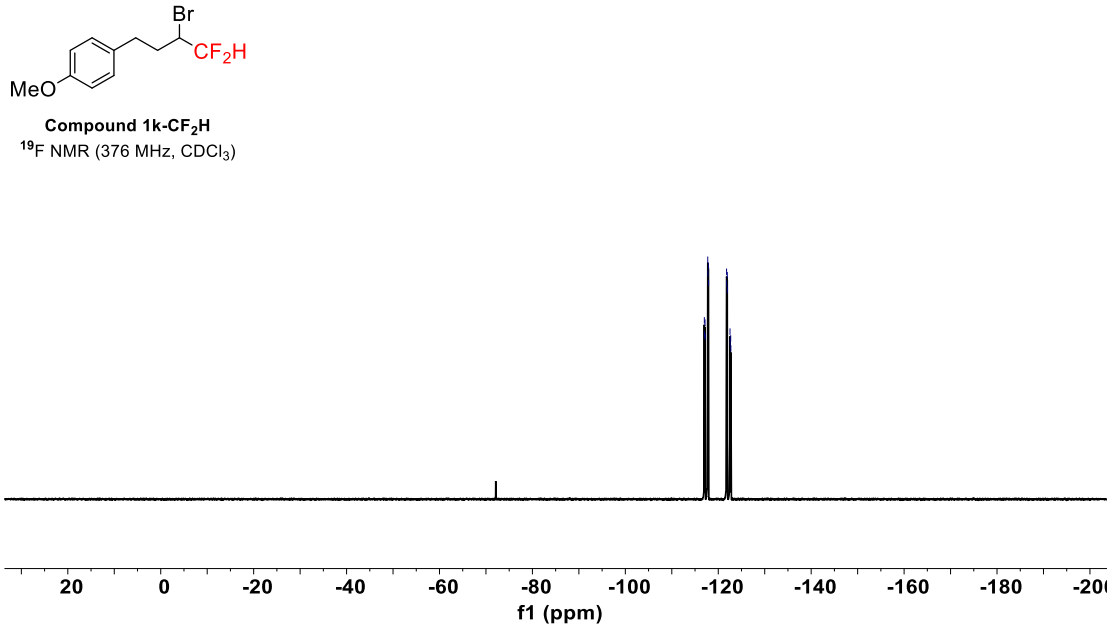


Compound 4x

^{13}C NMR (101 MHz, $CDCl_3$)

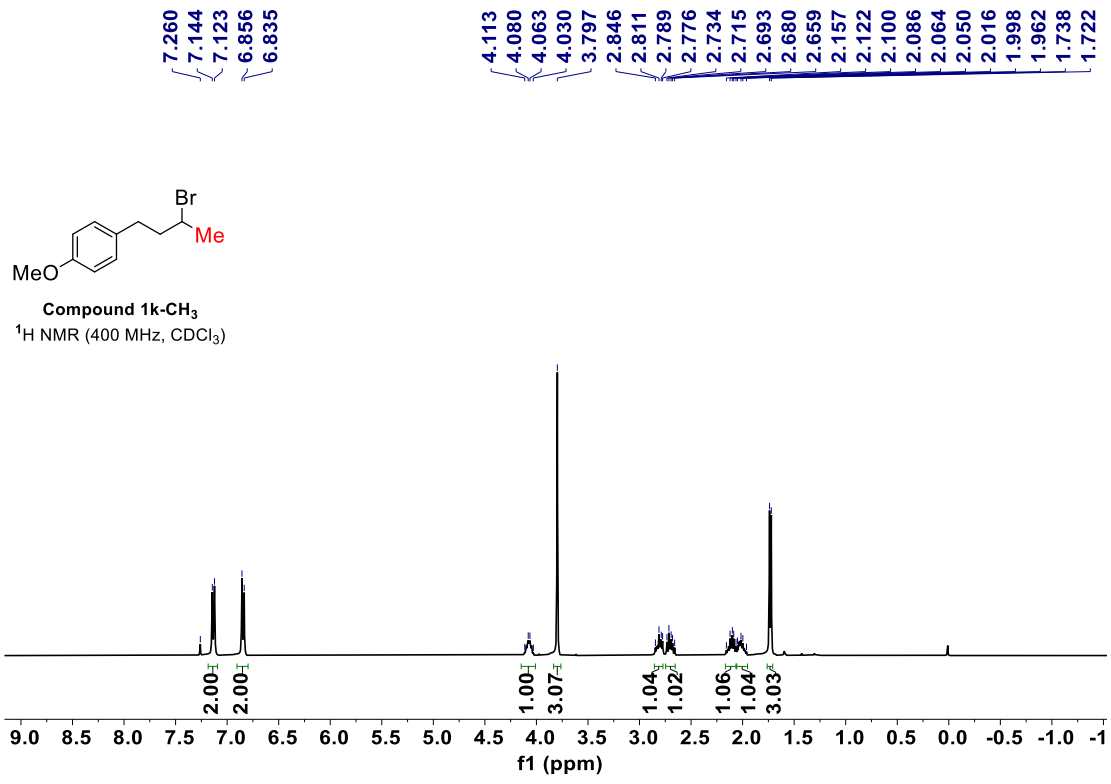

7.260
7.150
7.129
6.868
6.846
5.972
5.963
5.832
5.823
5.692
5.683
3.920
3.885
3.852
3.828
3.801
2.959
2.947
2.925
2.903
2.892
2.750
2.729
2.709
2.694
2.674
2.281
2.252
2.224
2.216
2.195
2.136
2.098
2.078
2.041
Br
CF2H
MeO
Compound 1k-CF2H
1H NMR (400 MHz, CDCl3)
2.02
2.02
1.00
1.00
3.00
1.01
1.08
1.05
1.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


158.169
131.633
129.474
117.163
114.722
114.003
112.279
77.318
77.000
76.682
55.231
50.033
49.795
49.557
32.485
32.460
32.435
31.618
Br
CF2H
MeO
Compound 1k-CF2H
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



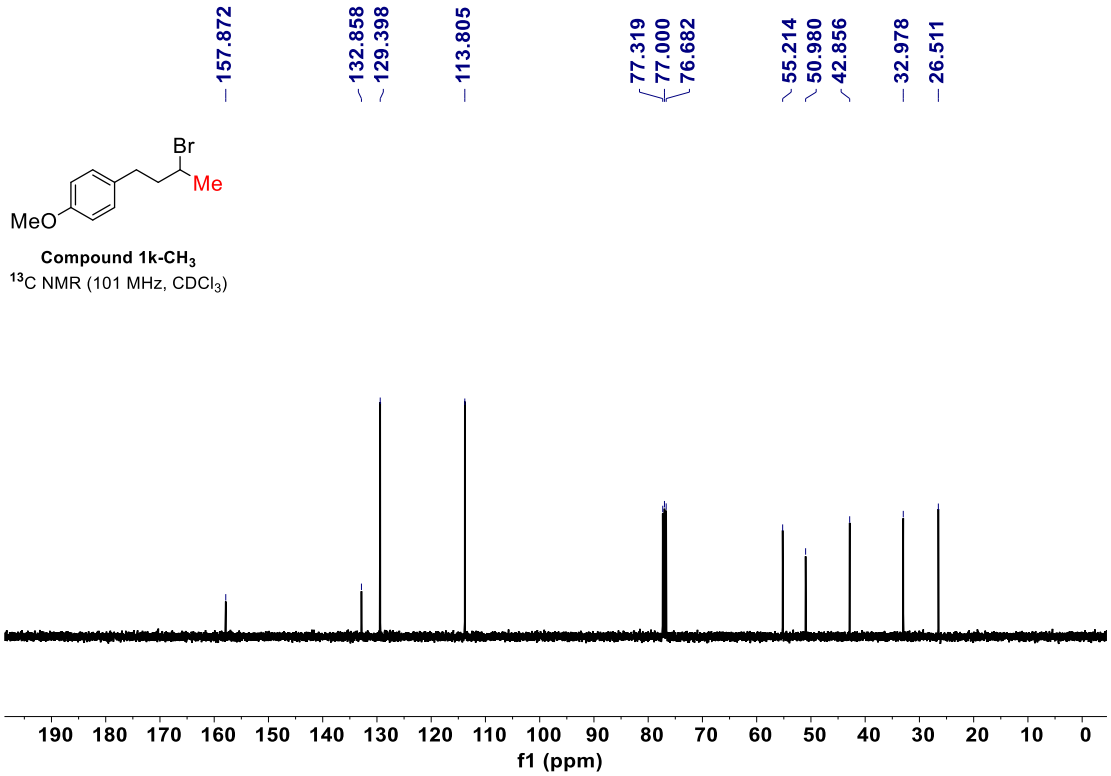
Compound 1k-CF_2H

^{19}F NMR (376 MHz, $CDCl_3$)



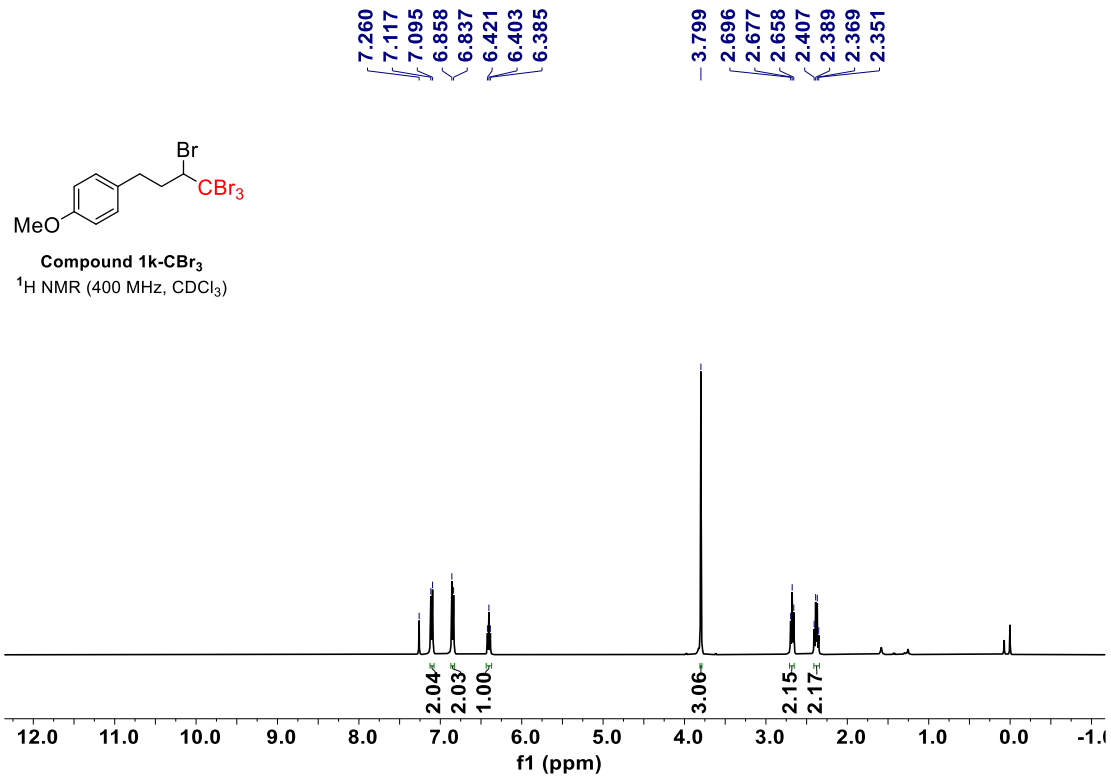
Compound 1k-CH_3

^{1}H NMR (400 MHz, $CDCl_3$)



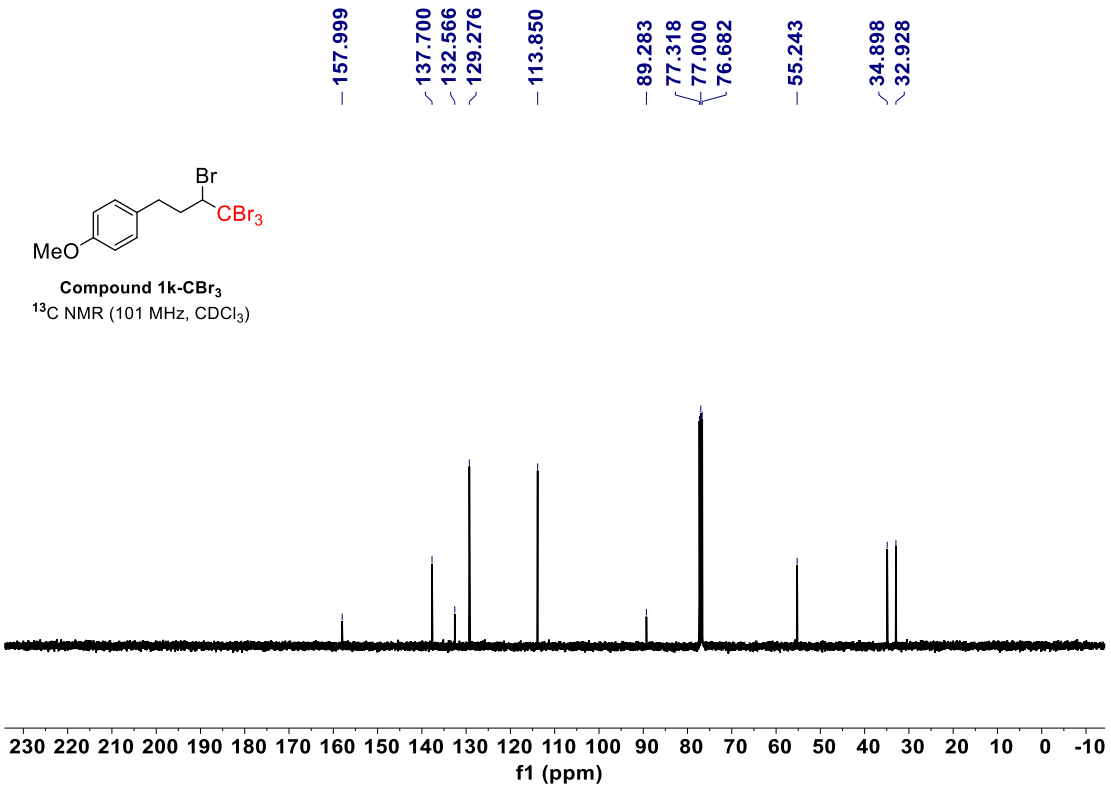
Compound 1k-CH_3

^{13}C NMR (101 MHz, $CDCl_3$)



Compound 1k-CBr_3

^{1}H NMR (400 MHz, $CDCl_3$)



Compound 1k-CBr_3

^{13}C NMR (101 MHz, $CDCl_3$)