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Supporting Information File

Metal- and Additive-Free TfOH Catalyzed Chemoselective O- and S-Trifluoroethylation of Oxindoles, Isoindolines and Thioxindoles

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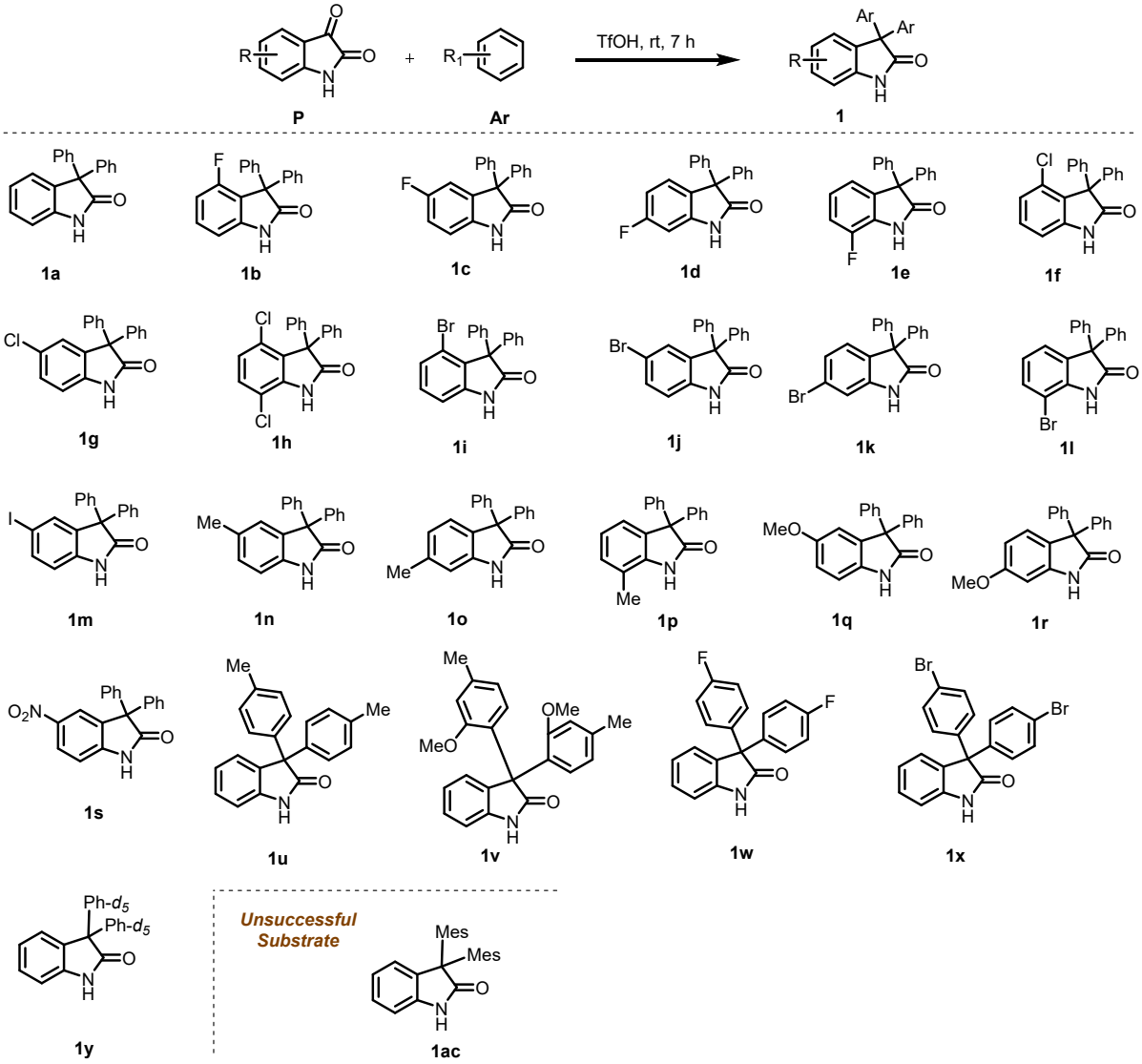
I. General Information

Unless otherwise noted, all reactions were performed on a Schlenk vacuum line or in a glovebox using oven-dried glassware and were stirred with teflon-coated magnetic stirring bars. All the chemicals and reagents were purchased from commercial suppliers Sigma Aldrich, GLR Innovations, BLD Pharma, Spectrochem and used without further purification. Solvents were dried and stored over molecular sieves under an argon atmosphere prior to use. All work-up and purification procedures were done with reagent-grade solvents in an air atmosphere. Reaction temperatures above 25 °C refer to temperatures of an aluminum heating block or a silicon oil bath, which were controlled by an electronic temperature modulator from Heidolph. Thin-layer chromatography (TLC) was performed using pre-coated plates purchased from E. Merck (silica gel 60 PF254, 0.25 mm). Column chromatography was performed using E. Merck silica gel 60 (100–200 mesh). ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded in $CDCl_3$ and d_6-DMSO, on JEOL JNM-ECS spectrometer at operating frequencies of 400 MHz {^{1}H} or 101 MHz {^{13}C} as indicated in the individual spectrum. Chemical shifts (δ) are given in parts per million (ppm) relative to residual solvent ($CDCl_3$, δ= 7.26 for ^{1}H NMR and 77.16 for ^{13}C NMR, d_6-DMSO: δ = 2.50 for ^{1}H NMR and δ = 39.52 for ^{13}C NMR) and coupling constants (*J*) in Hz. Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Multiplicity is tabulated as s for singlet, d for doublet, dd for doublet of doublet, t for triplet, q for quartet, dt for doublet of triplet, and m for multiplet. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) methods on waters mass spectrometer (XEVO G2-XS QTOF). The data collection for single crystal S-3 X-ray was performed at a 298 K on a CMOS-based Bruker D8 Venture PHOTON 100 diffractometer equipped with INCOATEC micro-focus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. *All solvents used for work-up and column chromatography were recovered by evaporation using a rota-vapor.*

II. Preparation of Starting Materials

Synthesis of 3,3 diaryl substituted 2-oxindole derivatives (1)[1]:

To a solution of Indoline-2,3-dione or isatin, P (1 eq.) in freshly distilled triflic acid, respective arene (2.5 eq.) was added at room temperature. Monitored the reaction progress with thin-layer chromatography (TLC). Upon completion (as determined by TLC analysis) of the reaction, several grams of crushed ice were added to the reaction mixture and extracted with ethyl acetate. The combined organic layer was washed once with brine, dried over sodium sulfate (Na_2SO_4), filtered, and concentrated under reduced pressure, which was further purified by silica gel column chromatography using hexane and ethyl acetate (8:2) as the eluent to afford 3,3 diaryl substituted 2-oxindoles, 1.

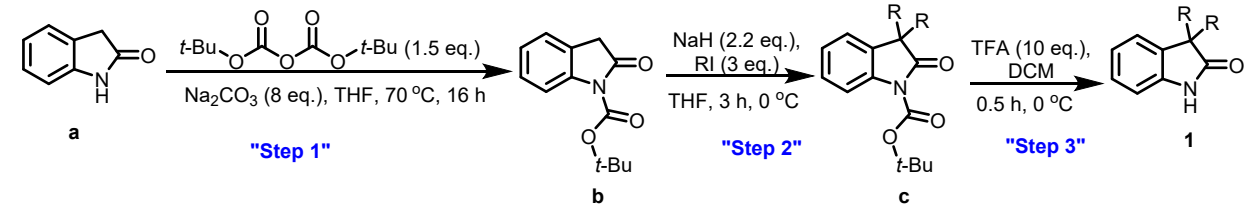


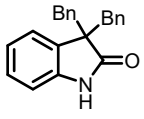
Synthesis of 3,3 dialkyl substituted 2-oxindole derivatives (1)[2]:

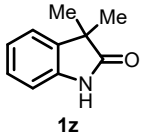
Step 1: To an oven-dried schlenk round-bottomed flask, indoline-2-one (1 eq.) was added and nitogen was purged. After that, freshly distilled THF was added and allowed to stir for 2 minutes. To this solution, Na_2CO_3 (8 eq.) was added and an ice bath was placed under the schlenk rbf. After cooling for 10 minutes, boc anhydride (1.5 eq.) was added dropwise and the ice bath was removed. Then the reaction mixture was placed over an oil bath and the reaction temperature was maintained up to 70 ^oC in the oil bath. Upon completion of the reaction, THF was recovered by evaporating on rota vapor and the reaction mixture was extracted with ethyl acetate. The crude mixture was purified through column chromatography using hexane and ethyl acetate as the eluent to obtain compound N-boc oxindole, **b** in 75 % yield.

Step 2: In an oven-dried schlenk round-bottomed flask, compound **b** (1 eq.) was added to freshly dried THF and nitrogen gas was purged. To this solution, methyl iodide or benzyl bromide (3 eq.) was added and the rbf was placed over an ice bath. Then, NaH (60 wt% mineral oil dispersion, 2.2 eq.) was added in three installments over a time lap of 15 minutes. After completion of reaction in 3 hours as monitored by TLC, THF was recovered by evaporating on rota vapor and cold water was added to the rbf. The product was extracted three times with DCM and the crude was further purified with column chromatography to afford N-boc 3,3-dialkyl oxindole, **c** in 65% yield.

Step 3: To a solution of compound **c** (1 eq.) in DCM, TFA (10 eq.) was added dropwise while placing the rbf over ice bath and the reaction mixture was allowed to stir at room temperature for half an hour. After completion of the reaction as monitored by TLC, the solvent was collected back using rota-vapor and the crude product was purified using silica gel column chromatography to afford the final compound **1.**

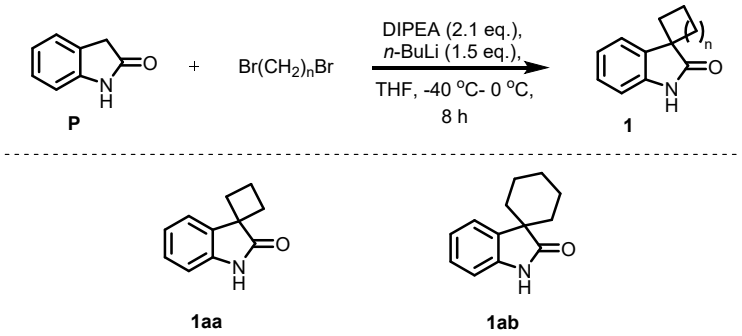



1t


1z

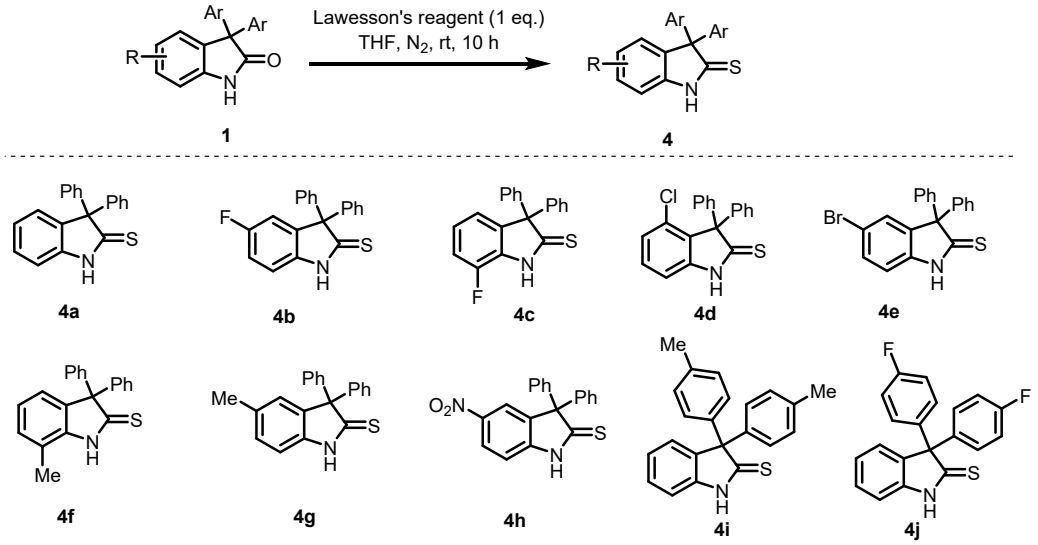
Synthesis of spirocyclic 2-oxindole derivatives (1)[3]:

To an oven-dried schlenk round-bottomed flask, indoline-2-one was dissolved in freshly dried THF and nitrogen gas was purged. The reaction mixture was transferred to the chiller having -40 ^{o}C temperature and DIPEA (2.1 eq.) was added to the solution followed by *n*-BuLi (1.5 eq.). After that, dibromopropane or dibromopentane (3 eq.) was added slowly and allowed to stir at 0 ^{o}C for 8 hours. Upon completion of the reaction as monitored by TLC, THF was recovered back by evaporating on rota-vapor and ice was added to the reaction mixture. The crude product was extracted with ethyl acetate and purified through silica gel chromatography to afford compound **1**.



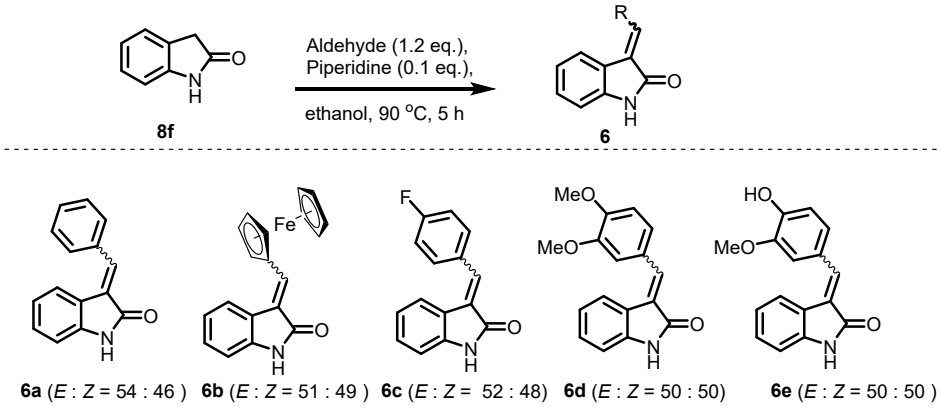
Synthesis of 3,3-disubstituted thioindolin-2-one derivatives (4)[4]:

To a solution of 3,3-disubstituted indoline-2-one, **1** (1.5 eq.) in freshly dried THF, Lawesson's reagent (1 eq.) was added. The resulting reaction mixture was stirred under an argon atmosphere at ambient temperature for 10 hours. After completion of the reaction, THF was recovered through evaporation using rota-vapor, cold water was added to it and extracted with ethyl acetate. The complete organic layer was washed with brine and dried over sodium sulfate. Upon evaporation of the organic solvent under reduced pressure, a crude product was obtained which was further purified through silica gel column chromatography.



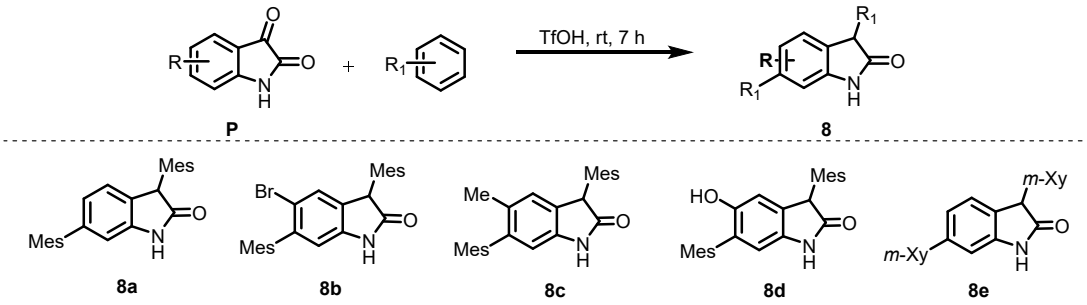
Synthesis of 3-Arylidenindolin-2-one derivatives (6)[5]:

To a solution of indolin-2-one (1 eq.) in ethanol, aldehyde (1.2 eq.), piperidine (0.1 eq.) were added and stirred at 90 °C. After the completion of the reaction in 5 hours, the reaction mixture was cooled to room temperature and ethanol was recovered through evaporation using rota-vapor. The organic layer was extracted using ethyl acetate and dried over sodium sulfate. Upon evaporation of the solvent, a crude product was obtained as diastereomers and was used for the next step.



Synthesis of 3,6-substituted indolin-2-one derivatives (8):

To a solution of isatin, P (1 eq.) in TfOH under an N_2 atmosphere, bulky arene was added and the resulting reaction mixture was stirred for 7 hours at ambient temperature. After analyzing the TLC, crushed ice was added to the reaction mixture and extracted with ethyl acetate. The complete organics were washed with brine once and dried over Na_2SO_4. The final product was isolated with excellent yield on purification through silica gel column chromatography.

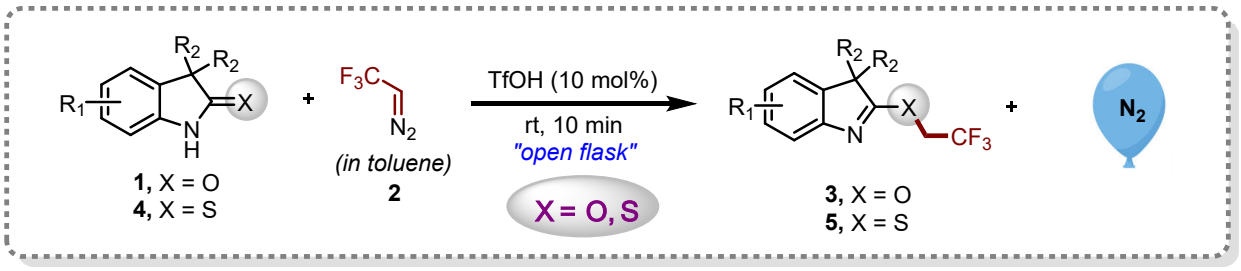


Preparation of (trifluoromethyl)diazomethane [CF_3CHN_2] in toluene (2)[6]:

A solution of $CF_3CH_2NH_2.HCl$ (100 mmol, 1 eq.) and $NaNO_2$ (125 mmol, 1.25 eq.) in toluene (200 mL) were prepared in a 500 mL round-bottomed flask (RBF) and immediately placed in an ice bath. After stirring the mixture for 15 minutes, water (20 mL) was added to it dropwise and stirred for an additional hour in the ice bath. The reaction was successful, resulting in the clear formation of aqueous and organic layers. Then, the aqueous layer was frozen in the freezer overnight at approximately -18°C and organic layer was extracted using a Teflon needle and transferred to a flame-dried round bottom flask and stored in a bottle in the freezer at -20 °C for further use.

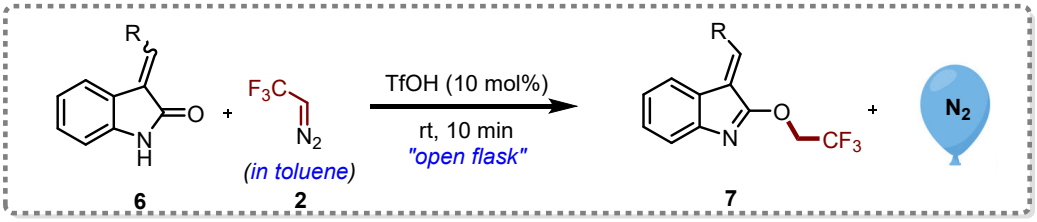
III. General Procedures

General procedure for O- and S- trifluoroethylation of 3,3-disubstituted oxindoles and thio-oxindoles (GP-1):



A vial was charged with a magnetic bead and the required amount of 3,3-disubstituted oxindole **1** or thio-oxindole **4** (0.2 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 **2** (0.22 mmol, 1.1 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added and the reaction mixture was allowed to stir at room temperature for 10 minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the product **3** or **5** was purified through silica gel column chromatography using hexane as the eluent.

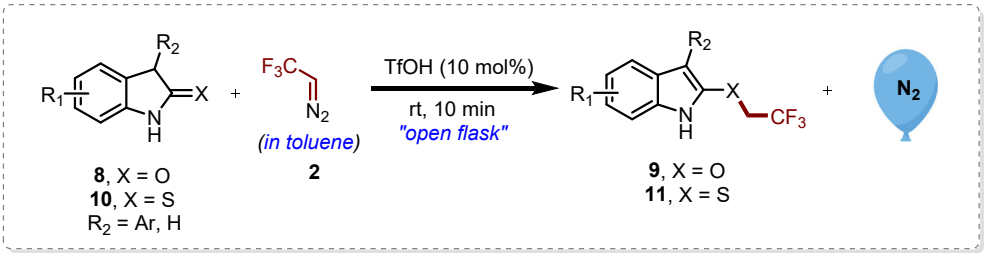
General procedure for O- trifluoroethylation of oxindole-based chalcone derivatives (GP-2):



A vial was charged with a magnetic bead and the required amount of (*E* and *Z*) oxindole-based chalcone derivative **6** (0.2 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 **2** (0.22 mmol, 1.1 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added and the reaction mixture was allowed to stir at room temperature for 10

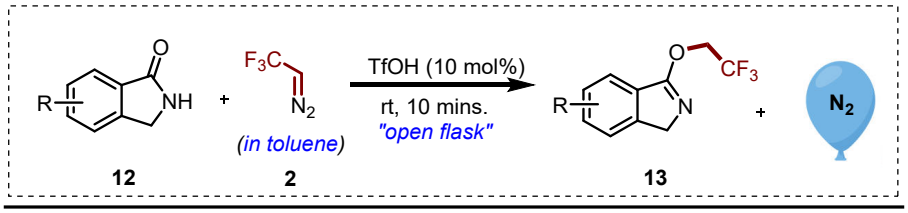
minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the product **7** was purified through silica gel column chromatography using hexane as the eluent.

General procedure for O- trifluoroethylation of mono-substituted oxindoles, unsubstituted oxindoles, and thio-oxindoles (GP-3):



A vial was charged with a magnetic bead and the required amount of respective oxindole derivative **8/10** (0.2 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 **2** (0.22 mmol, 1.1 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added and the reaction mixture was allowed to stir at room temperature for 10 minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the product **9 or 11** was purified through silica gel column chromatography using hexane as the eluent.

General procedure for O- trifluoroethylation of isoindolines (GP-4):



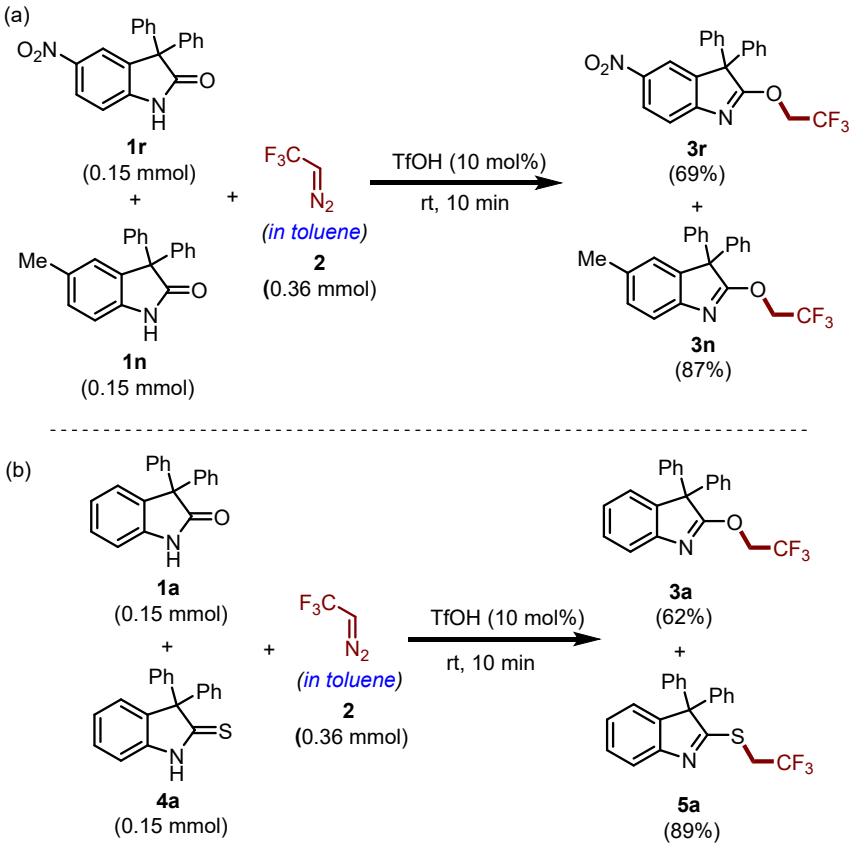
A vial was charged with a magnetic bead and the required amount of isoindoline derivative **12** (0.3 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 **2** (0.33 mmol, 1.1 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added

and the reaction mixture was allowed to stir at room temperature for 10 minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the product **13** was purified through silica gel column chromatography using hexane as the eluent.

IV. Mechanistic Studies

Competitive Experiments : a) Electron-rich *vs* electron-deficient oxindoles

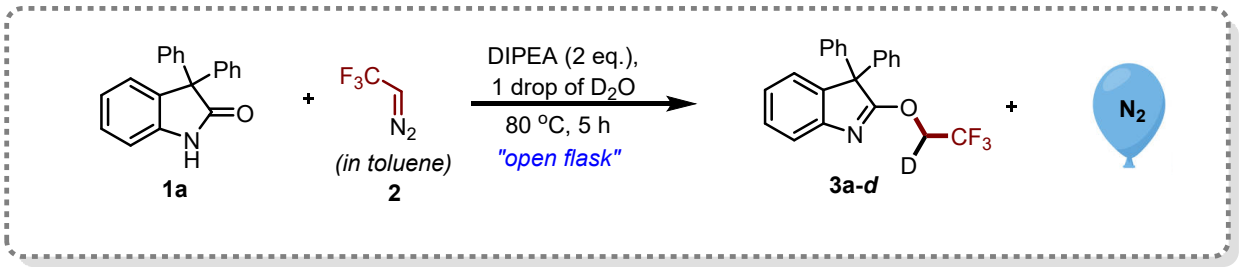
A vial was charged with a magnetic bead and the required amount of **1r** (0.15 mmol, 1 eq.) and **1n** (0.15 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 (0.33 mmol, 2.2 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added and the reaction mixture was allowed to stir at room temperature for 10 minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the crude product was analyzed through NMR spectroscopy. Then the mixture of products was separated through silica gel column chromatography by using hexane as the eluent. The effect of the substituents on the phenyl ring of oxindole was examined, and the product ratio illustrated that the -Me group on the C5 position of the oxindole facilitated the reaction while the $–NO_2$ group slowed down the reaction, **3n** was formed as the major product while **3r** was the minor.



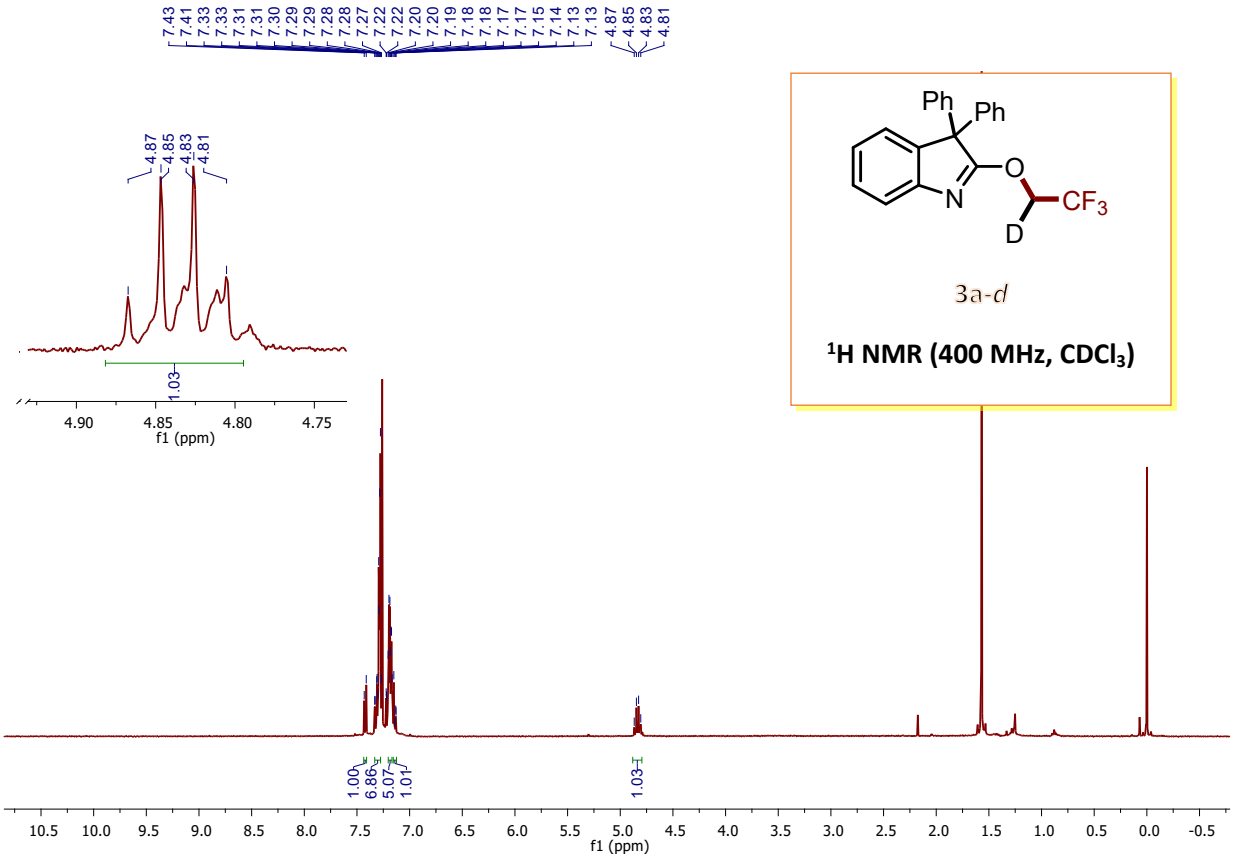
b) Oxindole *vs* Thioxindole

A vial was charged with a magnetic bead and the required amount of **1a** (0.15 mmol, 1 eq.) and **4a** (0.15 mmol, 1 eq.) was added to it. Thereafter, CF_3CHN_2 (0.33 mmol, 2.2 eq.) solution in toluene was added to the vial and after stirring for 2 minutes, catalyst triflic acid (10 mol %) was added and the reaction mixture was allowed to stir at room temperature for 10 minutes. After completion of the reaction, toluene used in the reaction was recovered through evaporation using rota-vapor. Then cold water was added to the reaction mixture and extracted with ethyl acetate (3 X 10 mL). The combined organic layer was washed with brine and dried over sodium sulfate. The solvent was evaporated and the crude product was analyzed through NMR spectroscopy. Then the mixture of products was separated through silica gel column chromatography by using hexane as the eluent. The effect of oxygen and sulfur on the protocol was examined, and the product ratio demonstrated that the reaction with thioxindole was comparatively faster and **5a** was formed as the major product in a competitive experiment with **3a**.

c) Deuterium labeling by using D_2O under basic condition



During optimization, we enquired about the proton source of trifluoroethylation in the case of base and performed a reaction in a drop of D_2O and we found through ^1H NMR that deuterium got labeled and formed O-$CHDCF_3$ (Table 1, entry 6 in main document).



V. DFT Studies

Table 1. TS structure and Gibbs Free Energy ($\Delta G^{\ddagger}$) for H-abstraction.

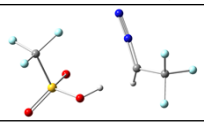
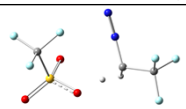
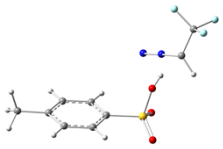
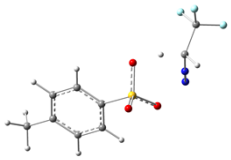
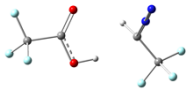
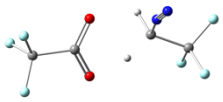
2 + acids	**Ground State (GS)**	**Transition State (TS)**	**$\Delta G^{\ddagger}$**
2 + TfOH			7.13 kcal/mol
	-1447.751627 Hartree	-1447.740250 Hartree	
2 + *p*TSA			14.83 kcal/mol
	-1381.011882 Hartree	-1380.988241 Hartree	
2 + TFA			17.51 kcal/mol
	-1012.532337 Hartree	-1012.504434 Hartree	

Table 2. Intrinsic reaction coordinate (IRC) for H-abstraction from TfOH.

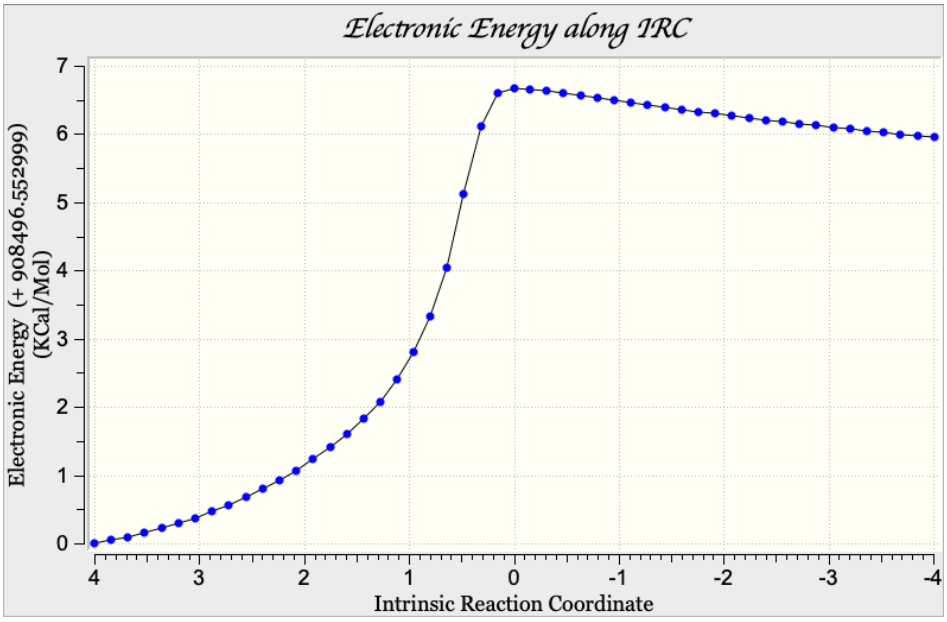


Table 3. The optimized structures (with electronic energies and imaginary frequencies, if any) of the molecules are provided in the table below.

2 + *p*-TSA (-1381.139700)

0 1

C	2.85401200	0.09826800	-0.46575300
N	2.28778400	1.09997900	-1.09468200
N	1.74653900	1.95690300	-1.60412400
C	3.90717800	0.41046200	0.54485800
F	5.15311000	0.47846200	0.02099000
F	3.93506100	-0.55564700	1.48448800
F	3.66311100	1.59406500	1.14499700
H	2.84636900	-0.85117500	-0.98626200
C	-2.04456100	0.79070900	-0.62979500
C	-3.16987900	1.57308800	-0.38170800
C	-4.25296000	1.07522300	0.35692800
C	-4.18703900	-0.24159200	0.83491400
C	-3.07211100	-1.04122600	0.59645600
C	-2.00501900	-0.51289400	-0.13204400
S	-0.56877200	-1.52687900	-0.42868400
O	-0.96149500	-2.92656700	-0.35805500
O	0.16041800	-0.99800600	-1.58920500
O	0.35431000	-1.22117600	0.88830300
C	-5.45454800	1.94237800	0.64601600
H	-1.21710900	1.17764000	-1.21493900
H	-3.21024100	2.58587100	-0.77460300
H	-5.02366200	-0.64975200	1.39629600
H	-3.03112700	-2.06459800	0.95356100
H	1.16156400	-0.73823900	0.58765700
H	-5.61136600	2.68639500	-0.14150000
H	-6.36726300	1.34506200	0.73858900
H	-5.32494800	2.48827000	1.58993300

2 + *p*-TSA (-1381.118915) *-134i*

0 1

C	2.62990900	0.12690400	0.24923200
N	2.10056500	-0.77154700	1.19749800
N	1.75825600	-1.59429300	1.86292200
C	3.78856400	-0.53097200	-0.49873600
F	4.81056100	-0.84008100	0.32304900
F	4.22420200	0.33240600	-1.41884200
F	3.38669500	-1.66243700	-1.09810200
H	2.92758700	1.02925600	0.78644500
C	-2.54755600	-0.03398700	1.13727500
C	-3.75800700	-0.70985400	0.98370500
C	-4.33341600	-0.88896900	-0.28061400
C	-3.66148700	-0.36783100	-1.39647200
C	-2.45297300	0.31045400	-1.25955500
C	-1.89857400	0.47340100	0.01203900
S	-0.38242400	1.41340600	0.21205300
O	-0.72268200	2.83905900	0.25768100
O	0.28099100	0.87006400	1.44783700
O	0.46253000	1.03256700	-1.00633300
C	-5.63113800	-1.64469300	-0.44545000
H	-2.10363000	0.09826200	2.11844300
H	-4.26425900	-1.10380900	1.86205700
H	-4.09228800	-0.49478200	-2.38719300
H	-1.93565500	0.70410400	-2.12833900
H	1.71844100	0.45015700	-0.44865400
H	-5.44999900	-2.68369700	-

0.75185700
H -6.19946400 -1.67395200
0.48972400
H -6.26546100 -1.18840800 -
1.21337900

2 + TFA (-1012.562955)

0 1
C -1.65705600 0.12791900 -0.19107800
O -0.89206100 -0.80824600 0.36749600
O -1.27598800 1.09900000 -0.80017400
C -3.15103900 -0.19177700 0.03728000
F -3.46458700 -1.36943700 -0.53101600
F -3.91552600 0.76112800 -0.49910500
F -3.41619600 -0.27114600 1.35242800
H 0.05239200 -0.56923100 0.18838100
C 1.83132500 0.33911100 -0.51143600
N 1.70831100 1.54165600 0.00836600
N 1.54244800 2.55246200 0.49178900
C 2.97529900 -0.50379500 -0.05073500
F 4.11258500 -0.30328500 -0.75505000
F 2.65732100 -1.80705400 -0.19150500
F 3.25978500 -0.26244700 1.24478500
H 1.44507500 0.22580100 -1.51706600

2 + TFA (-1012.537505) *-186i*

0 1
C -1.47903100 -0.01791800 -
0.00319900
O -0.83231200 -0.99159300
0.47879100
O -1.01686600 1.02446700 -
0.52322500
C -3.02337100 -0.16865800
0.00539400
F -3.41950800 -0.81085100 -
1.11636300
F -3.63644900 1.02636100
0.03476600
F -3.44805000 -0.88161700
1.06151500
H 0.60065200 -0.59220100
0.10408000
C 1.48614700 0.00549800 -
0.41196500

N	1.28639500	1.35176200	-0.01399700
N	1.33125600	2.36963800	0.43491400
C	2.89999000	-0.44290300	-0.04517400
F	3.84336900	0.27451200	-0.68549700
F	3.02229300	-1.72576000	-0.39915800
F	3.11318300	-0.31914700	1.27352800
H	1.29328500	-0.04819800	-1.48448800

2 + TfOH (-1447.781760)

0 1

C	1.90017300	-0.02088900	-0.64811400
N	1.52851700	1.23680400	-0.81905800
N	1.14599900	2.29625900	-0.91655600
C	3.09078700	-0.25792900	0.23002900
F	4.27135200	-0.09454400	-0.40808800
F	3.06102500	-1.52488000	0.68412600
F	3.08560600	0.58505100	1.28185900
H	1.74720700	-0.65604000	-1.51406800
S	-1.68736600	-0.84272700	-0.46702800
O	-2.68939800	-1.88754200	-0.49276400
O	-0.50890500	-1.29131900	0.53513000
O	-1.09962000	-0.27676900	-1.67911200
C	-2.38907600	0.59280400	0.49954100
F	-2.86524600	0.17280800	1.66630500
F	-3.36341200	1.15365700	-0.21176600
F	-1.41644800	1.48834700	0.70926900
H	0.34522100	-0.85461200	0.24570000

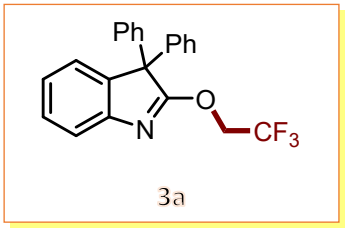
2 + TfOH (-1447.770713) *-357i*

0 1

C	1.71660400	-0.22013700	-0.55348000
N	1.34005100	1.07849400	-0.89274500
N	0.99157800	2.11849100	-1.07845000
C	2.99773200	-0.21245800	0.27754100
F	4.05251500	0.25070000	-0.42033000
F	3.25116500	-1.46838400	0.65137900
F	2.85065100	0.56118100	1.36355500
H	1.80338000	-0.79815400	-1.47579700
S	-1.54306500	-0.84040900	-0.43954200
O	-2.56927700	-1.85120500	-0.65105700
O	-0.43026700	-1.27287300	0.52453400
O	-0.95021400	-0.15563000	-1.61308000
C	-2.34418700	0.53824400	0.51995800
F	-2.82954200	0.10005900	1.68054600
F	-3.32975200	1.08736400	-0.19176800
F	-1.41735600	1.48936100	0.77238200
H	0.74227900	-0.71295900	0.05765700

VI. Characterization data

3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3a)



3a

Following the general procedure (GP-1), treatment of 3,3-diphenylindolin-2-one, **1a** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica

gel in hexane afforded 3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3a** as viscous liquid (0.066 g, 90% yield).

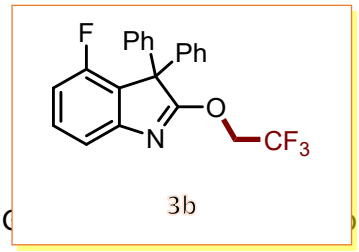
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 1H), 7.35 – 7.27 (m, 7H), 7.25 – 7.14 (m, 6H), 4.85 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.50, 151.15, 141.27, 140.40, 129.99, 128.69, 128.59, 128.20, 127.77, 127.09, 124.92, 124.82, 121.73 (q, *J* = 277.45 Hz), 119.64, 66.76, 65.31 (q, *J* = 36.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.57.

HRMS: m/z calculated for $C_{22}H_{17}NOF_3$ $[M+H]^+$ = 368.1262, found 368.1262.

4-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3b)



3b

Following the general procedure (C ro-3,3-diphenylindolin-2-one, **2b** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 4-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3b** as viscous liquid (0.070 g, 92% yield).

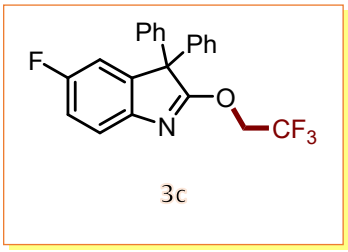
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 6H), 7.20 – 7.10 (m, 6H), 6.82 – 6.87 (m, 1H), 4.83 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.87, 164.45, 162.01, 152.63 (d, *J* = 11.7 Hz), 140.00, 136.84, 128.79, 128.09, 127.92, 126.99, 125.50, 125.41, 121.78 (q, *J* = 277.55 Hz), 111.48 (d, *J* = 22.9 Hz), 107.72 (d, *J* = 24.7 Hz), 66.39, 65.47 (q, *J* = 36.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.35, -112.22.

HRMS: m/z calculated for $C_{22}H_{17}NOF_3$ $[M+H]^+$ = 386.1168, found 386.1176.

5-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3c)



3c

Following the general procedure (GP-1), treatment of 5-fluoro-3,3-diphenylindolin-2-one, **1c** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3c** as viscous liquid (0.070 g, 91% yield).

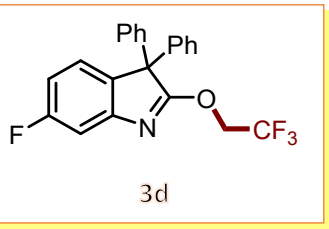
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.34 (m, 1H), 7.32 – 7.29 (m, 6H), 7.19 – 7.16 (m, 4H), 7.04 – 6.92 (m, 2H), 4.82 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.19, 161.75, 159.34, 146.93, 142.89 (d, *J* = 9.2 Hz), 139.73, 128.84, 128.75, 128.08, 128.02, 121.69 (q, *J* = 275.7 Hz), 120.39, 120.31, 115.17 (d, *J* = 21.5 Hz), 112.59 (d, *J* = 25.5 Hz), 67.21, 65.27 (q, *J* = 36.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.58, -115.95.

HRMS: m/z calculated for $C_{22}H_{16}NOF_4$ $[M+H]^+$ = 386.1168, found 386.1182.

6-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3d)



3d

Following the general procedure (GP-1), treatment of 6-fluoro-3,3-diphenylindolin-2-one, **1d** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 6-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3d** as viscous liquid (0.071 g, 93% yield).

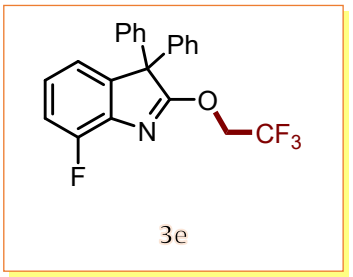
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 6H), 7.18 – 7.14 (m, 4H), 7.13 – 7.11 (m, 2H), 6.87 – 6.82 (m, 1H), 4.83 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.25, 164.27, 161.99, 152.60 (d, *J* = 11.6 Hz), 140.08, 137.41, 128.78, 128.09, 127.92, 125.50, 125.40, 120.67 (q, *J* = 276.1 Hz), 111.48 (d, *J* = 23.0 Hz), 107.71 (d, *J* = 24.7 Hz), 66.37, 65.49 (q, *J* = 36.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.60, -112.13.

HRMS: m/z calculated for $C_{22}H_{16}NOF_4$ $[M+H]^+$ = 386.1168, found 386.1167.

7-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3e)



3e

Following the general procedure (GP-1), treatment of 7-fluoro-3,3-diphenylindolin-2-one, **1e** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 7-fluoro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3e** as viscous liquid (0.070 g, 91% yield).

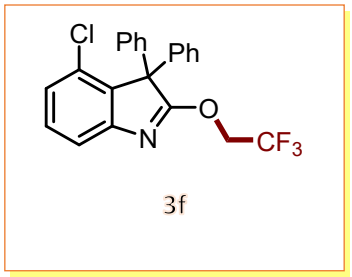
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.36 (m 1H), 7.35 – 7.27 (m, 6H), 7.22 – 7.19 (m, 4H), 7.05 – 6.94 (m, 2H), 4.84 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.20, 161.77, 159.35, 146.97, 142.93 (d, *J* = 8.5 Hz), 139.74, 128.84, 128.09, 128.01, 122.90 (q, *J* = 277.6 Hz), 120.37 (d, *J* = 8.6 Hz), 115.17 (d, *J* = 23.4 Hz), 112.59 (d, *J* = 25.3 Hz), 67.23, 65.32 (q, *J* = 37.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.60, -116.81.

HRMS: m/z calculated for $C_{22}H_{16}NOF_4$ $[M+H]^+$ = 386.1168, found 386.1166.

4-chloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3f)



3f

Following the general procedure (GP-1), treatment of 4-chloro-3,3-diphenylindolin-2-one, **1f** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 4-chloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3f** as viscous liquid (0.074 g, 92% yield).

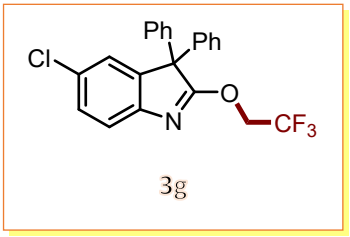
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.35 (m, 1H), 7.33 – 7.29 (m, 6H), 7.28 – 7.23 (m, 5H), 7.09 – 7.07 (m, 1H), 4.77 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.21, 153.20, 138.43, 135.60, 130.94, 130.16, 129.15, 128.34, 128.12, 126.33, 124.15 (q, *J* = 263.7 Hz), 118.31, 68.03, 65.36 (q, *J* = 36.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.21.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Cl$ $[M+H]^+$ = 402.0873, found 402.0867.

5-chloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3g)



3g

Following the general procedure (GP-1), treatment of 5-chloro-3,3-diphenylindolin-2-one, **1g** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-chloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3g** as viscous liquid (0.072 g, 90% yield).

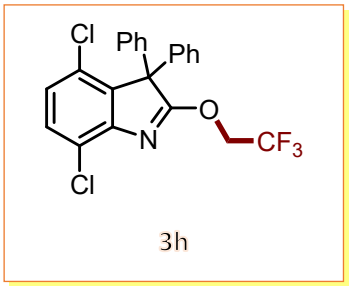
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.3 Hz, 1H), 7.32 – 7.29 (m, 6H), 7.27 – 7.26 (m, 1H), 7.19 – 7.13 (m, 5H), 4.82 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.69, 149.68, 142.88, 139.56, 130.35, 128.87, 128.79, 128.10, 125.16, 122.65 (q, *J* = 278 Hz), 67.07, 65.33 (q, *J* = 36.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.33.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Cl$ $[M+H]^+$ = 402.0873, found 402.0868.

4,7-dichloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3h)



3h

Following the general procedure (GP-1), treatment of 4,7-dichloro-3,3-diphenylindolin-2-one, **1h** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction

mixture using silica gel in hexane afforded 4,7-dichloro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3h** as viscous liquid (0.074 g, 85% yield).

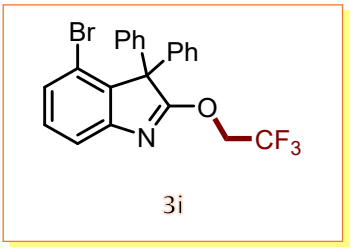
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 7H), 7.25 – 7.21 (m, 4H), 7.04 – 7.01 (m, 1H), 4.84 (q, *J* = 8.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.73, 150.02, 139.64, 134.92, 130.53, 129.33, 129.07, 128.46, 128.39, 127.14, 123.34, 121.95 (q, *J* = 279.5 Hz), 69.20, 65.74 (q, *J* = 36.1 Hz)

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.61.

HRMS: m/z calculated for $C_{22}H_{15}Cl_2F_3NO$ $[M+H]^+$ = 436.0483, found 436.0491.

4-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3i)



3i

Following the general procedure (GP-1), treatment of 4-bromo-3,3-diphenylindolin-2-one, **1i** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 4-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3i** as off white solid (0.077 g, 87% yield), m.p. 87-89 °C.

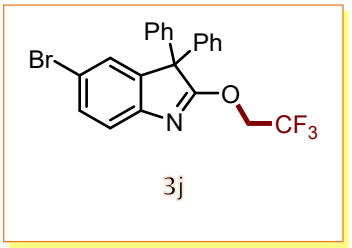
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.40 (m, 1H), 7.35 – 7.26 (m, 11H), 7.25 – 7.20 (m, 1H), 4.77 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.26, 153.58, 140.30, 135.02, 130.32, 129.48, 129.41, 128.27, 128.13, 123.63 (q, *J* = 183.0 Hz), 119.89, 118.86, 68.60, 65.31 (q, *J* = 36.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.62.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Br$ $[M+H]^+$ = 446.0367, found 446.0366.

5-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3j)



3j

Following the general procedure (GP-1), treatment of 5-bromo-3,3-diphenylindolin-2-one, **1j** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3j** as off white solid (0.072 g, 82% yield) m.p. 87-88 °C.

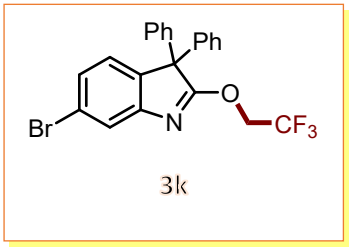
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (m, 1H), 7.37 – 7.28 (m, 8H), 7.21 – 7.14 (m, 4H), 4.84 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.67, 150.18, 143.28, 139.53, 131.71, 128.87, 128.10, 128.07, 127.94, 122.83 (q, *J* = 277.6 Hz), 121.45, 118.03, 67.07, 65.42 (q, *J* = 36.7 Hz)

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.57.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Br$ $[M+H]^+$ = 446.0367, found 446.0368.

6-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3k)



3k

Following the general procedure (GP-1), treatment of 6-bromo-3,3-diphenylindolin-2-one, **1k** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction

mixture using silica gel in hexane afforded 6-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3k** as off white solid (0.076g, 83% yield), m.p. 88-90 °C.

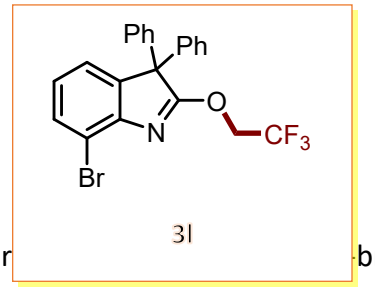
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.6 (m, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 7.36 – 7.26 (m, 6H), 7.22 – 7.10 (m, 5H), 4.82 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.58, 150.88, 143.57, 139.53, 137.73, 133.58, 128.87, 128.11, 128.06, 122.95 (q, *J* = 275.8 Hz), 121.66, 88.70, 66.91, 65.43 (q, *J* = 37.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.58.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Br$ $[M+H]^+$ = 446.0367, found 446.0372.

7-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3l)



3l

Following the general procedur -bromo-3,3-diphenylindolin-2-one, **1l** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 7-bromo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3l** as off white solid (0.076 g, 83% yield) m.p. 86-88 °C.

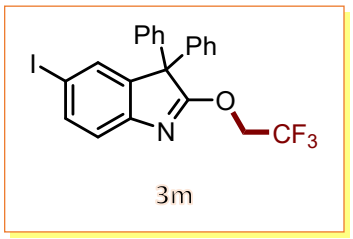
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (m, 1H), 7.34 – 7.27 (m, 6H), 7.21 – 7.12 (m, 5H), 7.05 – 6.99 (m, 1H), 4.91 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.96, 149.86, 142.69, 139.64, 131.97, 128.80, 128.13, 128.04, 126.20, 123.80, 122.86 (q, *J* = 277.3 Hz), 113.26, 68.13, 65.67 (q, *J* = 37.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.58.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3Br$ $[M+H]^+$ = 446.0367, found 446.0370.

5-iodo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3m)



Following the general procedure (GP-1), treatment of 5-iodo-3,3-diphenylindolin-2-one, **1m** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-iodo-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3m** as off white solid (0.082 g, 84% yield), m.p. 91-93 °C.

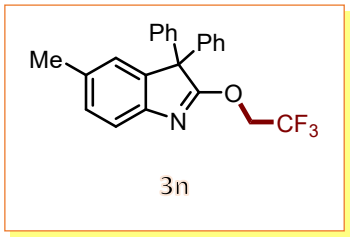
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 – 7.45 (m, 1H), 7.35 – 7.31 (m, 8H), 7.22 – 7.16 (m, 4H), 4.85 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.66, 150.16, 143.25, 139.52, 131.71, 128.87, 128.09, 127.93, 122.82 (q, *J* = 277.2 Hz), 121.11, 118.03, 67.05, 65.42 (q, *J* = 36.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.56.

HRMS: m/z calculated for $C_{22}H_{16}NOF_3I$ $[M+H]^+$ = 494.0229, found 494.0225.

5-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3n)



Following the general procedure (GP-1), treatment of 5-methyl-3,3-diphenylindolin-2-one, **1n** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3n** as viscous liquid (0.074 g, 97% yield).

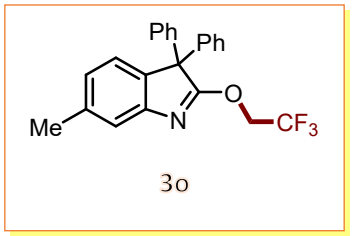
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 7H), 7.23 – 7.16 (m, 4H), 7.13 – 7.09 (m, 1H), 7.01 (m, 1H), 4.82 (q, *J* = 8.3 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.86, 148.57, 141.22, 140.43, 134.63, 129.12, 128.66, 128.23, 127.69, 125.49, 122.96 (q, *J* = 277.5 Hz), 119.18, 66.69, 65.22 (q, *J* = 36.7 Hz), 21.66.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.70.

HRMS: m/z calculated for $C_{23}H_{19}F_3NO$ $[M+H]^+$ = 332.1419, found 332.1424.

6-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3o)



3o

Following the general procedure (GP-1), treatment of 6-methyl-3,3-diphenylindolin-2-one, **1o** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 6-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3o** as viscous liquid (0.072 g, 96% yield).

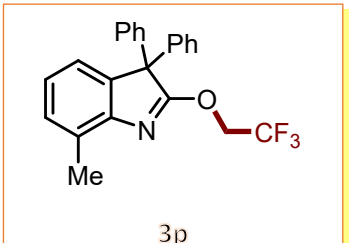
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.27 (m, 7H), 7.20 (m, 4H), 7.13 – 7.09 (m, 1H), 7.02 (s, 1H), 4.82 (q, *J* = 8.3 Hz, 2H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.88, 148.60, 141.26, 140.44, 134.63, 129.12, 128.66, 128.24, 127.69, 125.49, 122.97 (q, *J* = 277.6 Hz), 118.83, 66.71, 65.23 (q, *J* = 36.6 Hz), 21.65.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.62.

HRMS: m/z calculated for $C_{23}H_{19}F_3NO$ [M+H]+ = 332.1419, found 332.1423.

7-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3p)



3p

Following the general procedure (GP-1), treatment of 7-methyl-3,3-diphenylindolin-2-one, **1p** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 7-methyl-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3p** as viscous liquid (0.073 g, 96% yield).

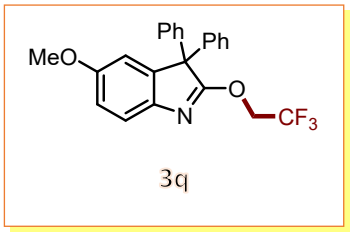
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 6H), 7.24 – 7.19 (m, 4H), 7.15 – 7.13 (m, 1H), 7.09 – 7.05 (m, 2H), 4.88 (q, *J* = 8.4 Hz, 1H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.37, 149.58, 141.06, 140.58, 129.80, 129.37, 128.61, 128.24, 127.62, 124.70, 123.09 (q, *J* = 277.9 Hz), 122.15, 66.92, 65.13 (q, *J* = 36.5 Hz).16.89.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.09.

HRMS: m/z calculated for $C_{23}H_{19}NOF_3$ $[M+H]^+$ = 381.1419, found 381.1413.

5-methoxy-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3q)



3q

Following the general procedure (GP-1), treatment of 5-methoxy-3,3-diphenylindolin-2-one, **1q** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (99/1) afforded 5-methoxy-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3q** as viscous liquid (0.078 g, 98% yield).

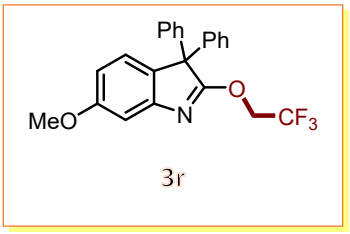
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.4 Hz, 1H), 7.31 – 7.27 (m, 6H), 7.22 – 7.17 (m, 4H), 6.84 – 6.81 (m, 1H), 6.78 (d, *J* = 2.6 Hz, 1H), 4.80 (q, *J* = 8.3 Hz, 2H), 3.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.31, 160.37, 152.25, 140.58, 133.18, 129.35, 128.65, 128.11, 127.66, 125.14, 122.90 (q, *J* = 277.6 Hz), 110.41, 105.82, 66.27, 65.30 (q, *J* = 36.7 Hz), 55.62.

^{19}F NMR (376 MHz, $CDCl_3$): δ -72.72.

HRMS: m/z calculated for $C_{23}H_{19}NO_2F_3$ $[M+H]^+$ = 398.1368, found 398.1384

6-methoxy-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3r)



3r

Following the general procedure (GP-1), treatment of 6-methoxy-3,3-diphenylindolin-2-one, **1r** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (99/1) afforded 6-methoxy-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3r** as viscous liquid (0.075 g, 95% yield).

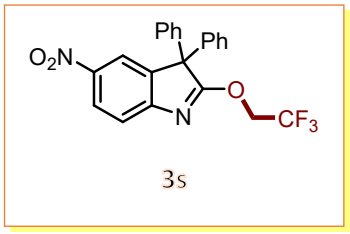
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 8.4 Hz, 1H), 7.33 – 7.27 (m, 6H), 7.24 – 7.18 (m, 4H), 6.86 – 6.78 (m, 2H), 4.81 (q, *J* = 8.4 Hz, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.08, 157.42, 144.29, 142.62, 140.30, 128.70, 128.21, 127.75, 124.36, 121.60 (q, *J* = 278.4 Hz), 112.77, 111.90, 67.06, 65.64 (q, *J* = 36.1 Hz), 55.76.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.64.

HRMS: m/z calculated for $C_{23}H_{19}NO_2F_3$ $[M+H]^+$ = 398.1368, found 398.1376.

5-nitro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3s)



3s

Following the general procedure (GP-1), treatment of 5-nitro-3,3-diphenylindolin-2-one, **1s** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (98/2) afforded 5-nitro-3,3-diphenyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3s** as off white solid (0.067 g, 82% yield), m.p. 101-103 °C.

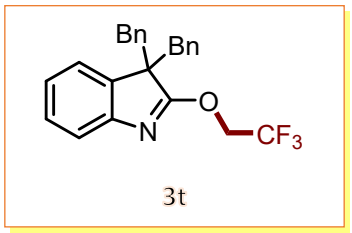
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 – 8.27 (m, 1H), 8.09 (d, *J* = 2.3 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.31 (m, 6H), 7.20 – 7.13 (m, 4H), 4.90 (q, *J* = 8.2 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 183.04, 157.31, 145.97, 145.27, 143.90, 142.39, 140.23, 138.67, 134.53, 129.12, 129.05, 128.48, 128.33, 128.23, 127.97, 126.81, 125.47, 122.57 (q, *J* = 277.9 Hz), 120.49, 119.81, 110.22, 67.13, 65.86 (q, *J* = 35.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.27.

HRMS: m/z calculated for $C_{22}H_{16}N_2O_3F_3$ $[M+H]^+$ = 413.1113, found 413.1113.

3,3-dibenzyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3t)



3t

Following the general procedure (GP-1), treatment of 3,3-dibenzylindolin-2-one, **1t** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-dibenzyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3t** as viscous liquid (0.070 g, 89% yield).

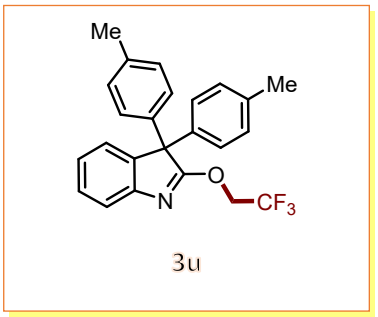
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 1H), 7.20 – 7.14 (m, 2H), 7.11 – 7.02 (m, 6H), 6.95 – 6.91 (m, 1H), 6.82 – 6.80 (m, 4H), 4.53 (q, *J* = 8.4 Hz, 2H), 3.29 (q, *J* = 13.2 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.22, 151.79, 137.87, 135.47, 129.52, 128.36, 127.89, 127.37, 123.80, 123.24 (q, *J* = 277.0 Hz), 123.15, 118.65, 64.78 (q, *J* = 36.5 Hz), 59.95, 42.59.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.31.

HRMS: m/z calculated for $C_{24}H_{21}NOF_3$ $[M+H]^+$ = 396.1575, found 396.1566.

3,3-di-*p*-tolyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3u)



3u

Following the general procedure (GP-1), treatment of 3,3-di-*p*-tolylindolin-2-one, **1u** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-di-*p*-tolyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3u** as viscous liquid (0.072 g, 91% yield).

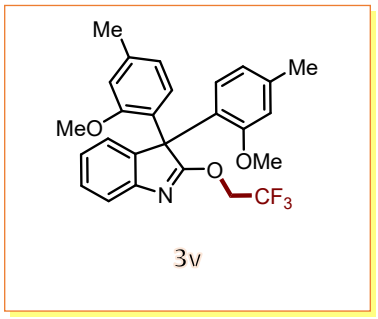
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.43 (m, 1H), 7.42 – 7.37 (m, 1H), 7.34 – 7.24 (m, 9H), 5.02 (q, *J* = 8.3 Hz, 2H), 2.50 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.82, 151.06, 141.66, 137.41, 129.35, 128.40, 128.05, 124.84, 124.68, 123.00 (q, *J* = 277.3 Hz), 119.55, 66.13, 65.24 (q, *J* = 36.7 Hz), 21.10.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.48.

HRMS: m/z calculated for $C_{24}H_{21}F_3NO$ $[M+H]^+$ = 396.1324, found 396.1290

3,3-bis(2-methoxy-4-methylphenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3v)



3v

Following the general procedure (GP-1), treatment of 3,3-bis(2-methoxy-4-methylphenyl)indolin-2-one, **1v** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (95/5) afforded 3,3-bis(2-methoxy-4-methylphenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3v** as pale yellow solid (0.084 g, 92% yield), m.p. 81-83 °C.

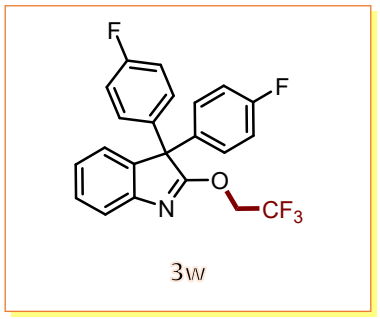
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 6.8 Hz, 1H), 7.29 – 7.21 (m, 2H), 7.11 – 6.94 (m, 3H), 6.86 – 6.68 (m, 3H), 6.63 (d, *J* = 2.0 Hz, 1H), 4.83 – 4.68 (m, 2H), 3.53 (s, 3H), 3.44 (s, 3H), 2.19 (s, 3H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.48, 156.62, 155.03, 151.54, 141.52, 129.92, 129.42, 129.35, 129.29, 128.74, 128.38, 128.32, 128.03, 127.29, 124.73, 124.32, 123.07 (q, *J* = 276.5 Hz), 118.53, 112.26, 112.12, 65.29 (q, *J* = 36.0 Hz), 62.88, 55.87, 55.51, 20.80.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.62.

HRMS: m/z calculated for $C_{26}H_{25}F_3NO_3$ $[M+H]^+$ = 456.1787, found 456.1792

3,3-bis(4-fluorophenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3w)



3w

Following the general procedure (GP-1), treatment of 3,3-bis(4-fluorophenyl)indolin-2-one, **1w** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH

(10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-bis(4-fluorophenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3w** as viscous liquid (0.070g, 88% yield).

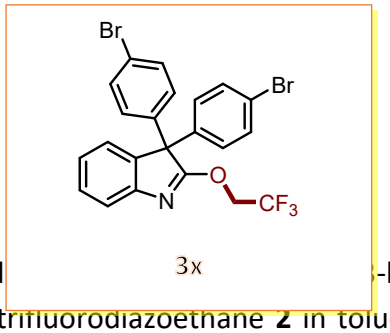
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.27 – 7.18 (m, 6H), 7.07 – 6.99 (m, 4H), 4.92 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.16, 163.66, 161.20, 150.98, 141.15, 135.86 (d, *J* = 2.8 Hz).129.82 (d, *J* = 8.0 Hz), 128.88, 125.13, 124.84 (d, *J* = 58.7 Hz), 122.96 (q, *J* = 277.6 Hz), 119.94, 115.70 (d, *J* = 21.7 Hz), 65.33 (q, *J* = 36.52 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.65, -114.13.

HRMS: m/z calculated for $C_{22}H_{15}NO_5$ $[M+H]^+$ = 404.1074, found 404.1087.

3,3-bis(4-bromophenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3x)



3x

Following the general proced -bis(4-bromophenyl)indolin-2-one, **1x** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-bis(4-bromophenyl)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3x** as off white solid (0.090 g, 87% yield), m.p. 89-91 °C.

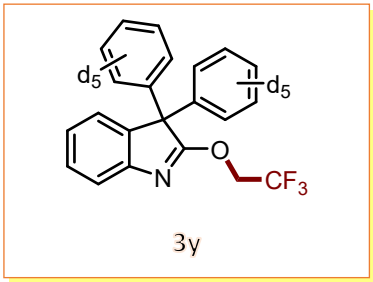
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.39 (m, 5H), 7.36 – 7.31 (m, 1H), 7.20 – 7.12 (m, 2H), 7.06 – 7.01 (m, 4H), 4.83 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 178.45, 150.91, 140.29, 138.79, 131.99, 129.80, 129.09, 125.27, 124.53, 122.25, 122.93 (q, *J* = 276.4 Hz), 119.99, 65.98, 65.88 (q, *J* = 36.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.21.

HRMS: m/z calculated for $C_{22}H_{14}NOF_3Br_2$ $[M+H]^+$ = 525.9429, found 525.9451.

3,3-bis(phenyl-d_5)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3y)



3y

Following the general procedure (GP-1), treatment of 3-(1 λ^5-phenyl-d_5)-3-(phenyl-d_5)indolin-2-one, **1y** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-bis(phenyl-d_5)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3y** as off white solid (0.068 g, 90% yield), m.p. 77-79 °C.

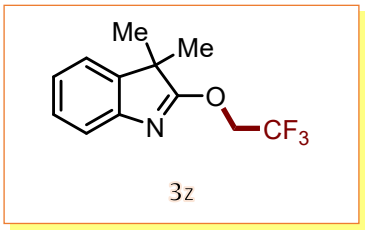
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.7 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.13 (m, 3H), 4.85 (q, *J* = 8.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.51, 151.07, 141.28, 140.18, 140.08, 128.69, 128.58, 128.47, 128.18, 128.07, 127.76, 127.65, 127.54, 124.92, 124.81, 124.70, 122.94 (q, *J* = 277.6 Hz), 119.63, 66.70, 65.30 (q, *J* = 36.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.15.

HRMS: m/z calculated for $C_{22}H_{26}NOF_3$ $[M+H]^+$ = 378.1842, found 378.1873.

3,3-dimethyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole (3z)



3z

Following the general procedure (GP-1), treatment of 3,3-dimethylindolin-2-one **1z** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica

gel in hexane afforded 3,3-dimethyl-2-(2,2,2-trifluoroethoxy)-3*H*-indole **3z** as off white solid (0.040 g, 82% yield), m.p. 70-73 °C.

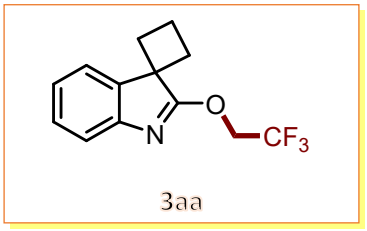
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 7.23 – 7.19 (m, 1H), 7.16 – 7.14 (m, 1H), 4.82 (q, *J* = 8.3 Hz, 1H), 1.39 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 183.39, 150.62, 143.20, 128.05, 124.38, 123.31 (q, *J* = 218.3 Hz), 121.31, 118.94, 64.88 (q, *J* = 36.5 Hz), 48.20, 23.05.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.00.

HRMS: m/z calculated for $C_{12}H_{13}NOF_3$ $[M+H]^+$ = 244.0949, found 244.0957.

2'-(2,2,2-trifluoroethoxy)spiro[cyclobutane-1,3'-indole] (3aa)



3aa

Following the general procedure (GP-1), treatment of spiro[cyclobutane-1,3'-indolin]-2'-one **1aa** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 2'-(2,2,2-trifluoroethoxy)spiro[cyclobutane-1,3'-indole] **3aa** as off white solid (0.043 g, 85% yield), m.p. 72-74 °C.

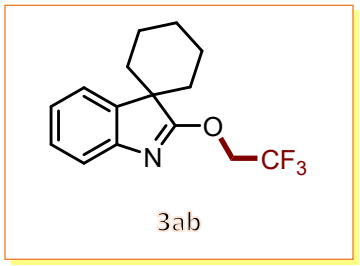
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 - 7.50 (m, 1H), 7.34 – 7.25 (m, 2H), 7.20 – 7.16 (m, 1H), 4.87 (q, *J* = 8.3 Hz, 2H), 2.68 – 2.59 (m, 2H), 2.50 – 2.43 (m, 2H), 2.40 – 2.23 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.40, 150.84, 141.27, 128.11, 124.45, 123.16 (q, *J* = 277.2 Hz), 121.39, 118.45, 64.95 (q, *J* = 36.4 Hz), 51.67, 29.49, 16.94.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.98.

HRMS: m/z calculated for $C_{13}H_{13}NOF_3$ $[M+H]^+$ = 256.0949, found 256.0960.

2'-(2,2,2-trifluoroethoxy)spiro[cyclohexane-1,3'-indole] (3ab)



3ab

Following the general procedure (GP-1), treatment of spiro[cyclohexane-1,3'-indolin]-2'-one **1ab** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 2'-(2,2,2-trifluoroethoxy)spiro[cyclohexane-1,3'-indole] **3ab** as off white solid (0.049 g, 87% yield), m.p. 72-74 °C.

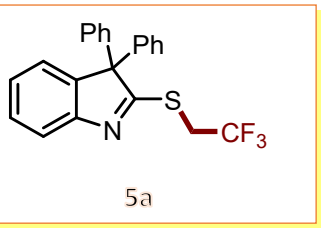
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.14 – 7.10 (m, 1H), 4.81 (q, *J* = 8.4 Hz, 2H), 1.91 – 1.78 (m, 6H), 1.70 – 1.54 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 183.20, 150.80, 142.72, 127.89, 123.84, 123.17 (q, *J* = 218.3 Hz), 123.12, 118.95, 64.92 (q, *J* = 36.4 Hz), 51.94, 31.87, 25.17, 21.54.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.92.

HRMS: m/z calculated for $C_{15}H_{17}NOF_3$ $[M+H]^+$ = 284.1262, found 284.1268.

3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5a)



5a

Following the general procedure (GP-1), treatment of 3,3-diphenylindoline-2-thione, **4a** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole, **5a** as pale yellow solid (0.073 g, 96% yield), m.p. 96-98 °C.

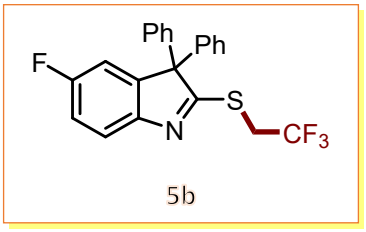
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.27 (m, 7H), 7.24 – 7.13 (m, 6H), 4.08 (q, *J* = 10.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.98, 153.37, 145.32, 140.76, 128.87, 128.48, 128.38, 127.89, 125.59, 124.84 (q, *J* = 216.4 Hz) 124.38, 119.80, 73.21, 32.61 (q, *J* = 33.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -64.79.

HRMS: m/z calculated for $C_{22}H_{17}NSF_3$ $[M+H]^+$ = 384.1034, found 384.1030.

5-fluoro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5b)



5b

Following the general procedure (GP-1), treatment of 5-fluoro-3,3-diphenylindoline-2-thione, **4b** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-fluoro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole, **5b** as pale yellow solid (0.076 g, 92% yield), m.p. 97-99 °C.

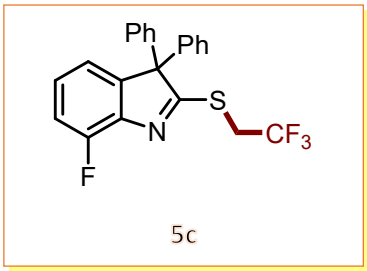
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.48 (m, 1H), 7.35 – 7.31 (m, 6H), 7.20 – 7.17 (m, 4H), 7.05 – 7.00 (m, 1H), 6.93 – 6.91 (m, 1H), 4.05 (q, *J* = 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.65, 162.27, 159.83, 149.45, 147.08 (d, *J* = 8.6 Hz), 140.20, 129.02, 128.27, 128.14, 124.67 (q, *J* = 216.9 Hz), 120.48 (d, *J* = 8.9 Hz), 115.23 (d, *J* = 23.7 Hz), 112.12 (d, *J* = 25.2 Hz), 73.52, 32.57 (q, *J* = 33.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.02, -115.91.

HRMS: m/z calculated for $C_{22}H_{16}NSF_4$ $[M+H]^+$ = 402.0940, found 402.0938.

7-fluoro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5c)



5c

Following the general procedure (GP-1), treatment of 7-fluoro-3,3-diphenylindoline-2-thione, **4c** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 7-fluoro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole, **5c** as pale yellow solid (0.074 g, 90% yield), m.p. 97-98 °C.

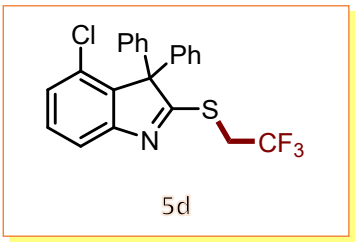
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 6H), 7.20 – 7.16 (m, 4H), 7.14 – 7.03 (m, 2H), 7.00 - 6.98 (m, 1H), 4.10 (q, *J* = 10.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 182.89, 154.40, 151.87, 148.47 (d, *J* = 2.7 Hz), 140.21, 128.98, 128.33, 128.14, 126.88 (d, *J* = 6.4 Hz), 124.68 (q, *J* = 207.3 Hz), 120.12 (d, *J* = 3.1 Hz), 115.70 (d, *J* = 18.5 Hz), 73.79, 32.71 (q, *J* = 33.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.61, -126.85.

HRMS: m/z calculated for $C_{22}H_{16}NSF_4$ $[M+H]^+$ = 402.0940, found 402.0938.

4-chloro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5d)



5d

Following the general procedure (GP-1), treatment of 4-chloro-3,3-diphenylindoline-2-thione, **4d** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH

(10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 4-chloro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5d** as pale yellow solid (0.074 g, 89% yield), m.p. 100-102 °C.

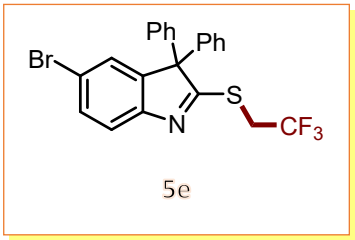
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (m, 1H), 7.37 (m, 11H), 7.14 (m, 1H), 4.07 (q, *J* = 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 183.96, 155.18, 141.85, 135.76, 130.62, 130.16, 129.14, 128.54, 128.23, 126.81, 124.43 (q, *J* = 208.1 Hz), 118.58, 74.50, 32.43 (q, *J* = 33.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.07.

HRMS: m/z calculated for $C_{22}H_{16}NSClF_3$ $[M+H]^+$ = 418.0644, found 418.0644.

5-bromo-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5e)



5e

Following the general procedure (GP-1), treatment of 5-bromo-3,3-diphenylindoline-2-thione, **4e** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-bromo-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5e** as pale yellow solid (0.082 g, 89% yield), m.p. 103-105 °C.

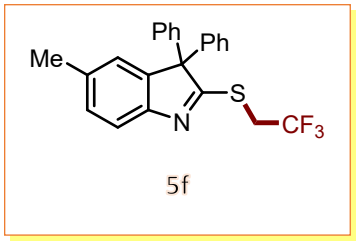
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.46 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.29 (m, 7H), 7.21 – 7.14 (m, 4H), 4.05 (q, *J* = 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 182.77, 152.37, 147.29, 140.03, 131.66, 129.05, 128.28, 128.18, 127.57, 124.75 (q, *J* = 219.8 Hz), 121.10, 119.17, 73.45, 32.62 (q, *J* = 33.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.33.

HRMS: m/z calculated for $C_{22}H_{16}NSBrF_3$ $[M+H]^+$ = 462.0139, found 462.0113.

5-methyl-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5f)



5f

Following the general procedure (GP-1), treatment of 5-methyl-3,3-diphenylindoline-2-thione, **4f** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-methyl-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5f** as pale yellow solid (0.078 g, 98% yield), m.p. 98-100 °C.

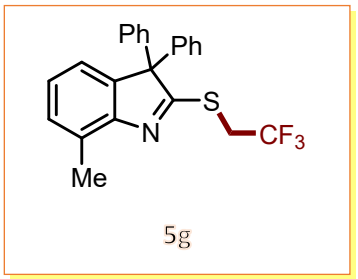
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.37 – 7.28 (m, 6H), 7.23 – 7.17 (m, 4H), 7.15 – 7.11 (m, 1H), 7.01 (s, 1H), 4.06 (q, *J* = 10.0 Hz, 2H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.71, 151.25, 145.39, 140.89, 135.46, 129.09, 128.84, 128.41, 127.81, 125.04, 124.49 (q, *J* = 219.3 Hz), 119.32, 73.06, 32.56 (q, *J* = 33.6 Hz), 21.63.

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.21.

HRMS: m/z calculated for $C_{23}H_{19}NSF_3$ $[M+H]^+$ = 398.1190, found 398.1181.

7-methyl-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5g)



5g

Following the general procedure (GP-1), treatment of 7-methyl-3,3-diphenylindoline-2-thione, **4g** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction

mixture using silica gel in hexane afforded 7-methyl-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5g** as pale yellow solid (0.076 g, 97% yield), m.p. 99-101 °C.

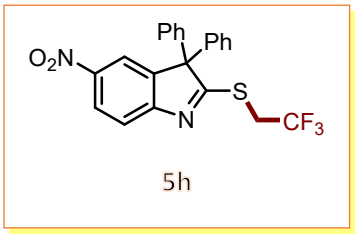
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 6H), 7.22 – 7.15 (m, 4H), 7.12 – 7.14 (m, 1H), 7.07 – 6.99 (m, 2H), 4.09 (q, *J* = 10.0 Hz, 2H), 2.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 180.22, 151.92, 145.12, 140.99, 129.70, 128.80, 128.40, 127.77, 125.45, 125.19 (q, *J* = 220.2 Hz), 121.74, 73.39, 31.40 (q, *J* = 34.2 Hz), 16.87.

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.69.

HRMS: m/z calculated for $C_{23}H_{19}NSF_3$ $[M+H]^+$ = 398.1190, found 398.1190.

5-nitro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5h)



5h

Following the general procedure (GP-1), treatment of 5-nitro-3,3-diphenylindoline-2-thione, **4h** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (97/3) afforded 5-nitro-3,3-diphenyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5h** as pale yellow solid (0.070 g, 82% yield), m.p. 105-107 °C.

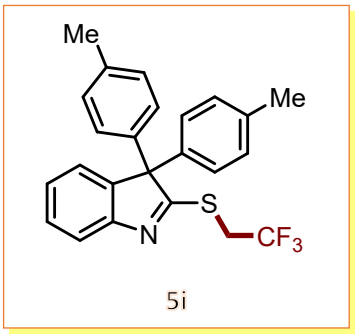
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 – 8.28 (m, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.37 – 7.32 (m, 6H), 7.20 – 7.14 (m, 4H), 4.08 (q, *J* = 9.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 188.79, 158.25, 146.44, 145.62, 139.34, 129.31, 128.59, 128.18, 125.43, 124.30 (q, *J* = 219.2 Hz), 119.98, 119.89, 73.62, 32.84 (q, *J* = 33.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.67.

HRMS: m/z calculated for $C_{22}H_{16}N_2O_2SF_3$ $[M+H]^+$ = 429.0885, found 429.0863

3,3-di-*p*-tolyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5i)



5i

Following the general procedure (GP-1), treatment of 3,3-di-*p*-tolylindoline-2-thione, **4i** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-di-*p*-tolyl-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5i** as pale yellow solid (0.074 g, 90% yield), m.p. 102-104 °C.

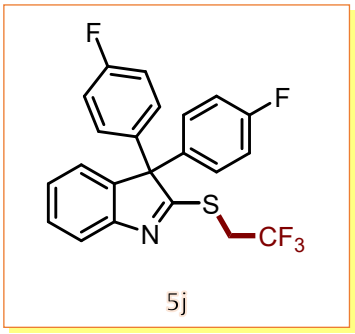
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 7.31 – 7.18 (m, 9H), 4.20 (q, *J* = 10.0 Hz, 2H), 2.46 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 182.30, 153.28, 145.69, 137.80, 137.56, 129.54, 129.30, 128.27, 125.50, 125.19 (q, *J* = 218.4 Hz), 124.19, 119.71, 72.57, 32.41 (q, *J* = 33.9 Hz), 21.07.

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.49.

HRMS: m/z calculated for $C_{24}H_{21}NSF_3$ $[M+H]^+$ = 412.1347, found 412.1345.

3,3-bis(4-fluorophenyl)-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole (5j)



5j

Following the general procedure (GP-1), treatment of 3,3-bis(4-fluorophenyl)indoline-2-thione, **4j** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3,3-bis(4-fluorophenyl)-2-((2,2,2-trifluoroethyl)thio)-3*H*-indole **5j** as pale yellow solid (0.074 g, 89% yield), m.p. 103-105 °C.

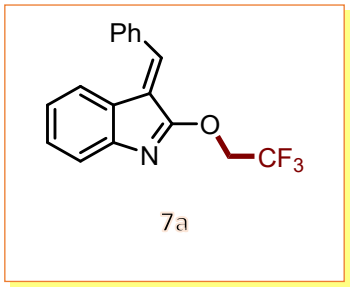
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.24 – 7.11 (m, 6H), 7.08 – 6.94 (m, 4H), 4.09 (q, *J* = 9.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 181.63, 163.70, 161.23, 153.14, 145.09, 136.30 (d, *J* = 3.3 Hz), 128.78, 125.82, 125.06 (q, *J* = 276.2 Hz), 124.11, 120.04, 115.92 (d, *J* = 21.5 Hz), 71.86, 32.50 (q, *J* = 34.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -65.78, -113.89.

HRMS: m/z calculated for $C_{22}H_{15}NSF_5$ $[M+H]^+$ = 420.0845, found 420.0844.

(*E*)-3-benzylidene-2-(2,2,2-trifluoroethoxy)-3*H*-indole (7a)



7a

Following the general procedure (GP-2), treatment of 3-benzylideneindolin-2-one **6a** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded (*E*)-3-benzylidene-2-(2,2,2-trifluoroethoxy)-3*H*-indole **7a** as yellow solid (0.054 g, 90% yield), m.p. 87-88 °C.

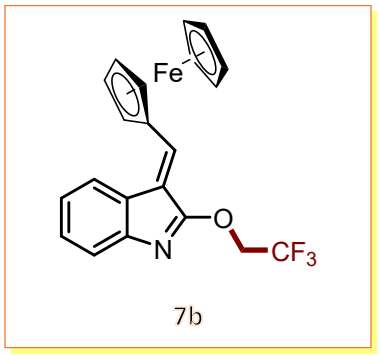
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.62 (m, 4H), 7.54 – 7.43 (m, 3H), 7.32 – 7.25 (m, 2H), 6.99 – 6.95 (m, 1H), 4.90 (q, *J* = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.17, 152.93, 137.28, 134.34, 130.19, 130.00, 129.78, 128.81, 126.87, 123.97, 123.08 (q, *J* = 282.7 Hz), 122.52, 119.09, 64.90 (q, *J* = 36.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.69.

HRMS: m/z calculated for $C_{17}H_{13}NOF_3$ $[M+H]^+$ = 304.0979, found 304.0949.

(*E*)-3-ferrocenylidene-2-(2,2,2-trifluoroethoxy)-3*H*-indole (7b)



7b

Following the general procedure (GP-2), treatment of 3-ferrocenylideneindolin-2-one **6b** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded (*E*)-3-ferrocenylidene-2-(2,2,2-trifluoroethoxy)-3*H*-indole **7b** as yellow solid (0.074 g, 90% yield), m.p. 96-98 °C.

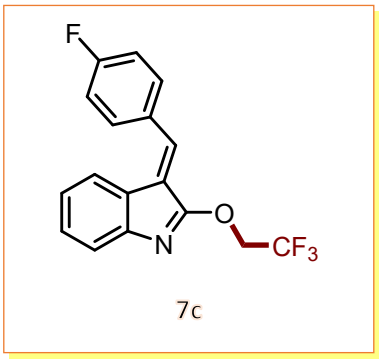
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.54 (s, 1H), 7.34 – 7.28 (m, 2H), 7.08 (t, *J* = 7.0 Hz, 1H), 4.90 (q, *J* = 7.8 Hz, 2H), 4.83 – 4.82 (m, 2H), 4.67 – 4.63 (m, 2H), 4.24 (s, 5H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 169.94, 151.94, 138.51, 128.53, 126.31 (q, *J* = 279.7 Hz), 124.04, 123.59, 122.30, 118.90, 78.16, 72.30, 71.81, 70.22, 64.73 (q, *J* = 36.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.71.

HRMS: m/z calculated for $C_{21}H_{17}NOF_3Fe$ $[M+H]^+$ = 412.0624, found 412.0612.

(*E*)-3-(4-fluorobenzylidene)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (7c)



7c

Following the general procedure (GP-2), treatment of 3-(4-fluorobenzylidene)indolin-2-one **6c** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded (*E*)-3-(4-fluorobenzylidene)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **7c** as yellow solid (0.055 g, 86% yield), m.p. 89-91 °C.

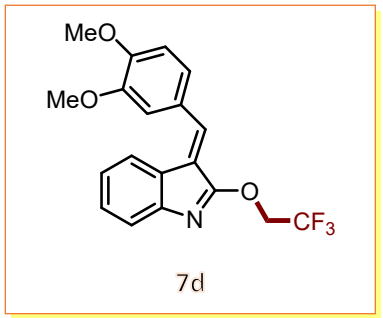
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.63 (m, 2H), 7.61 – 7.59 (m, 2H), 7.33 – 7.25 (m, 2H), 7.21 – 7.14 (m, 2H), 7.00 – 6.96 (m, 1H), 4.88 (q, *J* = 8.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.05, 164.88, 162.37, 152.94, 135.93, 131.90 (d, *J* = 8.4 Hz), 130.10, 127.37 (q, *J* = 275.2 Hz), 124.00, 122.28, 119.18, 116.04 (d, *J* = 21.9 Hz), 64.89 (q, *J* = 37.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.68, -108.90.

HRMS: m/z calculated for $C_{17}H_{12}NOF_4$ $[M+H]^+$ = 322.0855, found 322.0884.

(*E*)-3-(3,4-dimethoxybenzylidene)-2-(2,2,2-trifluoroethoxy)-3*H*-indole (7d)



7d

Following the general procedure (GP-2), treatment of 3-(3,4-dimethoxybenzylidene)indolin-2-one **6d** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (95/5) afforded (*E*)-3-(3,4-dimethoxybenzylidene)-2-(2,2,2-trifluoroethoxy)-3*H*-indole **7d** as yellow solid (0.063 g, 87% yield), m.p. 90-92 °C.

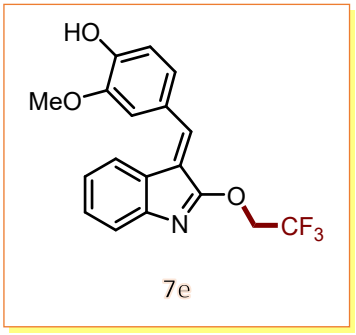
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.64 (s, 1H), 7.36 – 7.24 (m, 4H), 7.03 – 6.96 (m, 2H), 4.88 (q, *J* = 8.4 Hz, 2H), 3.97 (s, 3H), 3.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.35, 152.78, 151.05, 148.96, 137.75, 129.62, 127.05, 126.98, 126.88, 124.19, 123.76, 122.31, 122.01 (q, *J* = 244.2 Hz), 118.65, 112.71, 111.10, 64.91 (q, *J* = 36.3 Hz), 56.16.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.71.

HRMS: m/z calculated for $C_{19}H_{17}N_3OF_3$ $[M+H]^+$ = 365.1182, found 365.1161.

(*E*)-2-methoxy-4-((2-(2,2,2-trifluoroethoxy)-3*H*-indol-3-ylidene)methyl)phenol (7e)



Following the general procedure (GP-2), treatment of 3-(4-hydroxy-3-methoxybenzylidene)indolin-2-one **6e** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (90/10) afforded (*E*)-2-methoxy-4-((2-(2,2,2-trifluoroethoxy)-3*H*-indol-3-ylidene)methyl)phenol **7e** as yellow solid (0.061 g, 87% yield), m.p. 89-91 °C.

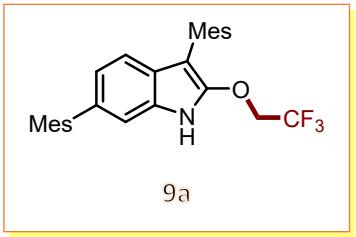
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.59 (s, 1H), 7.34 – 7.23 (m, 4H), 7.02 – 6.94 (m, 2H), 5.86 (s, 1H), 4.88 (q, *J* = 8.4 Hz, 2H), 3.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 170.33, 152.68, 148.53, 145.81, 137.66, 129.60, 127.62, 127.12, 126.97, 123.92, 123.41, 123.08 (q, *J* = 242.2 Hz), 122.48, 118.98, 116.02, 110.63, 64.90 (q, *J* = 36.2 Hz), 56.16.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.69.

HRMS: m/z calculated for $C_{18}H_{15}NO_3F_3$ $[M+H]^+$ = 350.1004, found 350.1029.

3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indole (9a)



9a

Following the general procedure (GP-3), treatment of 3,6-dimesitylindolin-2-one, **8a** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (85/15) afforded 3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indole **9a** as off white solid (0.076 g, 85% yield), m.p. 97-99 °C.

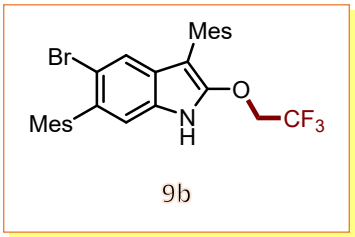
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.06 (d, *J* = 4.2 Hz, 3H), 7.03 (s, 2H), 6.88 – 6.85 (m, 1H), 4.15 (q, *J* = 8.3 Hz, 2H), 2.42 (d, *J* = 7.3 Hz, 6H), 2.23 (s, 6H), 2.11 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.81, 140.07, 138.79, 137.40, 136.72, 136.35, 134.30, 130.47, 128.50, 128.09, 126.35, 123.32 (q, *J* = 243.2 Hz), 121.95, 118.84, 110.92, 95.26, 68.55 (q, *J* = 35.4 Hz). 21.26, 21.14, 21.06, 20.67.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.66.

HRMS: m/z calculated for $C_{28}H_{29}NOF_3$ $[M+H]^+$ = 452.2201, found 452.2207.

5-bromo-3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indole (9b)



9b

Following the general procedure (GP-3), treatment of 5-bromo-3,6-dimesitylindolin-2-one, **8b** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (85/15) afforded 5-bromo-3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indole **9b** as off white solid (0.084 g, 80% yield), m.p. 103-105 °C.

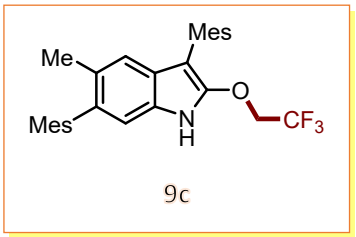
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.34 (s, 1H), 7.05 – 6.94 (m, 5H), 4.09 (q, *J* = 8.2 Hz, 2H), 2.37 (d, *J* = 5.2 Hz, 6H), 2.16 (s, 6H), 2.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.61, 139.03, 138.76, 137.84, 137.06, 136.70, 134.29, 129.86, 128.63, 127.99, 127.35, 123.12 (q, *J* = 298.5 Hz), 122.22, 115.73, 112.07, 94.74, 68.49 (q, *J* = 35.2 Hz), 21.33, 21.30, 20.70, 20.59.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.72.

HRMS: m/z calculated for $C_{28}H_{28}NOFBr$ $[M+H]^+$ = 530.1306, found 530.1309.

3,6-dimesityl-5-methyl-2-(2,2,2-trifluoroethoxy)-1*H*-indole (9c)



9c

Following the general procedure (GP-3), treatment of 3,6-dimesityl-5-methylindolin-2-one, **8c** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction

mixture using silica gel in hexane/ethyl acetate (85/15) afforded 3,6-dimesityl-5-methyl-2-(2,2,2-trifluoroethoxy)-1*H*-indole **9c** as off white solid (0.077 g, 83% yield), m.p. 99-101 °C.

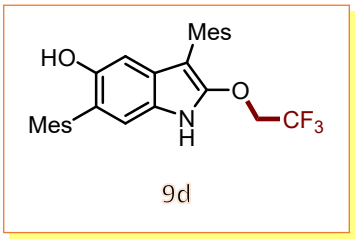
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (s, 1H), 6.95 (m, 6H), 4.08 (q, *J* = 8.3 Hz, 2H), 2.37 (d, *J* = 9.9 Hz, 6H), 2.18 (s, 6H), 1.95 (s, 6H), 1.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 145.86, 139.29, 138.83, 137.34, 136.55, 136.22, 134.39, 129.25, 128.47, 128.40, 128.02, 127.98, 127.01, 120.45 (q, *J* = 266.0 Hz), 119.58, 110.51, 94.99, 68.62 (q, *J* = 35.4 Hz), 21.31, 21.23, 20.73, 20.57, 19.84.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.74.

HRMS: m/z calculated for $C_{29}H_{31}NOF_3$ $[M+H]^+$ = 466.2358, found 466.2357.

3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indol-5-ol (9d)



9d

Following the general procedure (GP-3), treatment of 5-hydroxy-3,6-dimesitylindolin-2-one, **8d** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (82/18) afforded 3,6-dimesityl-2-(2,2,2-trifluoroethoxy)-1*H*-indol-5-ol **9d** as off white solid (0.078 g, 84% yield), m.p. 98-100 °C.

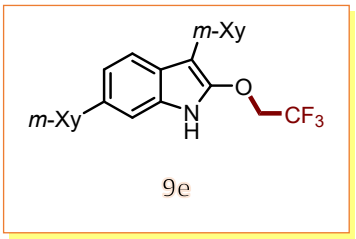
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 6.99 (d, *J* = 8.7 Hz, 4H), 6.87 (s, 1H), 6.63 (s, 1H), 4.30 (s, 1H), 4.07 (q, *J* = 8.3 Hz, 2H), 2.35 (d, *J* = 3.5 Hz, 6H), 2.16 (s, 6H), 2.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 147.27, 146.66, 138.74, 138.49, 137.93, 137.38, 132.86, 128.77, 128.63, 128.46, 128.08, 125.44, 123.52 (q, *J* = 298.8 Hz), 121.45, 111.04, 103.71, 95.29, 68.485 (q, *J* = 35.1 Hz), 21.28, 21.24, 20.68, 20.59.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.76.

HRMS: m/z calculated for $C_{28}H_{29}NO_2F_3$ $[M+H]^+$ = 468.2150, found 468.2169.

3,6-bis(2,4-dimethylphenyl)-2-(2,2,2-trifluoroethoxy)-1*H*-indole (9e)



9e

Following the general procedure (GP-3), treatment of 3,6-bis(3,5-dimethylphenyl)indolin-2-one, **8e** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (85/15) afforded 3,6-bis(2,4-dimethylphenyl)-2-(2,2,2-trifluoroethoxy)-1*H*-indole **9e** as off white solid (0.036 g, 86% yield), m.p. 93-95 °C.

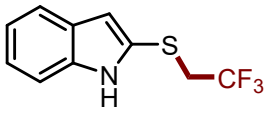
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.32 – 7.27 (m, 2H), 7.22 – 7.18 (m, 2H), 7.13 - 7.04 (m, 5H), 4.14 (q, *J* = 8.3 Hz, 2H), 2.41 (s, 3H), 2.38 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 146.50, 140.75, 139.99, 137.84, 137.42, 136.61, 135.72, 135.53, 131.36, 131.19, 130.30, 126.81, 126.53, 124.58 (q, *J* = 268.5 Hz), 122.34, 118.52, 111.12, 97.64, 68.52 (q, J = 35.5 Hz), 21.36, 21.19, 20.77, 20.18.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.66.

HRMS: m/z calculated for $C_{26}H_{25}NOF_3$ $[M+H]^+$ = 424.1901, found 424.1888.

2-((2,2,2-trifluoroethyl)thio)-1*H*-indole (11)



11

Following the general procedure (GP-3), treatment of indolin-2-thione, **10** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (85/15) afforded 2-((2,2,2-trifluoroethyl)thio)-1*H*-indole **11** as yellow solid (0.024 g, 52% yield), m.p. 93-95 °C.

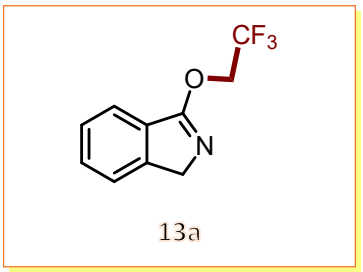
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.44 – 7.34 (m, 2H), 7.31 – 7.23 (m, 1H), 6.96 – 6.87 (m, 1H), 3.39 (q, *J* = 9.8 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.41, 128.26, 125.66, 125.34 (q, *J* = 276.0 Hz), 123.69, 120.89, 120.58, 111.30, 111.08, 39.83 (q, *J* = 32.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -66.60.

HRMS: m/z calculated for $C_{10}H_9NF_3S$ $[M+H]^+$ = 232.0408, found 232.0441.

3-(2,2,2-trifluoroethoxy)-1*H*-isoindole (13a)



13a

Following the general procedure (GP-4), treatment of isoindolin-1-one, **12a** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 3-(2,2,2-trifluoroethoxy)-1*H*-isoindole **13a** as viscous liquid (0.038 g, 90% yield).

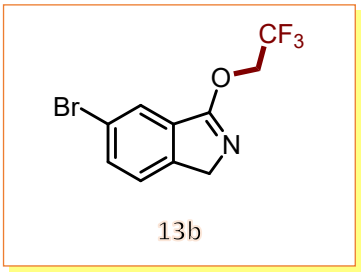
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.63 (m, 1H), 7.56 – 7.52 (m, 1H), 7.48 – 7.40 (m, 2H), 4.86 (q, *J* = 8.5 Hz, 2H), 4.63 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.92, 150.91, 131.60, 129.69, 127.44, 123 (q, *J* = 298.1 Hz), 122.63, 120.89, 64.24 (q, *J* = 36.4 Hz), 58.23.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.31.

HRMS: m/z calculated for $C_{10}H_8F_3NO$ [M+H]+ = 216.0636, found 216.0632.

5-bromo-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole (13b)



13b

Following the general procedure GP-4), treatment of 5-bromoisoindolin-1-one, **12b** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 5-bromo-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole **13b** as off white solid (0.051 g, 88% yield), m.p. 80-82 °C.

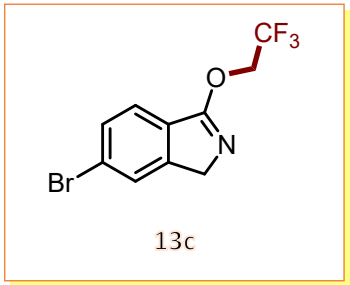
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.54 (m, 2H), 4.84 (q, *J* = 8.4 Hz, 2H), 4.60 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.20, 152.95, 130.86, 126.18 (q, *J* = 310.1 Hz), 126.13, 124.64, 122.02, 64.33 (q, *J* = 36.6 Hz), 57.97.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.81.

HRMS: m/z calculated for $C_{10}H_8NOBrF_3$ $[M+H]^+$ = 293.9741, found 293.9742.

6-bromo-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole (13c)



13c

Following the general procedure (GP-4), treatment of 6-bromoisoindolin-1-one, **12c** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane afforded 6-bromo-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole **13c** as off white solid (0.049 g, 85% yield), m.p. 79-81 °C.

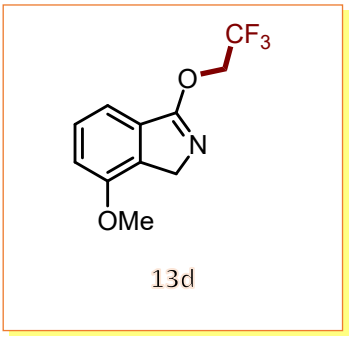
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.77 (m, 1H), 7.59 – 7.55 (m, 1H), 7.42 – 7.37 (m, 1H), 4.84 (q, *J* = 8.4 Hz, 2H), 4.59 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 167.66, 149.79, 133.64, 132.64, 124.12, 124.02, 121.42, 64.36 (q, *J* = 37.1 Hz), 58.11.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.81.

HRMS: m/z calculated for $C_{10}H_8NOBrF_3$ $[M+H]^+$ = 293.9741, found 293.9731.

7-methoxy-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole (13d)



13d

Following the general procedure (GP-4), treatment of 7-methoxyisoindolin-1-one, **12d** (0.2 mmol, 1 eq.) and 2,2,2-trifluorodiazoethane **2** in toluene (0.24 mmol, 1.2 eq.) with TfOH (10 mol %) at rt for 10 minutes followed by column chromatography of the crude reaction mixture using silica gel in hexane/ethyl acetate (99/1) afforded 7-methoxy-3-(2,2,2-trifluoroethoxy)-1*H*-isoindole **13d** as viscous liquid (0.040 g, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.84 (q, *J* = 8.4 Hz, 2H), 4.59 (s, 2H), 3.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 168.75, 154.61, 138.64, 133.40, 129.50, 123.36 (q, *J* = 277.2 Hz), 113.21, 111.22, 64.28 (q, *J* = 36.4 Hz), 56.23, 55.47, 55.46.

^{19}F NMR (376 MHz, $CDCl_3$): δ -73.81.

HRMS: m/z calculated for $C_{11}H_{11}NO_2F_3$ $[M+H]^+$ = 246.0742, found 246.0730.

VII. X-ray crystallographic data

For the determination of the X-ray crystal structure of **3y**, **5b**, **5f**, **7a**, **9b**, **13c** single crystals were selected and mounted with paratone oil on a glass fiber using the gum. The data were collected at 293 K on a CMOS-based Bruker D8 Venture PHOTON 100 diffractometer equipped with an INCOATEC micro-focus source with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. For the integration of diffraction profiles, SAINT program[7] was used. Adsorption correction was done by applying the SADABS program.[8] The crystal structure was solved by SIR 92[9] and refined by full-matrix least square method using SHELXL-97[10] WinGX system, Ver 1.70.01.[11] All the non-hydrogen atoms in the structure were located from the Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX in their ideal positions and refined using a riding model with isotropic thermal parameters.

X-ray crystallographic data of 3y (CCDC-2243514)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2243514**. Suitable single – crystals of **3y** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

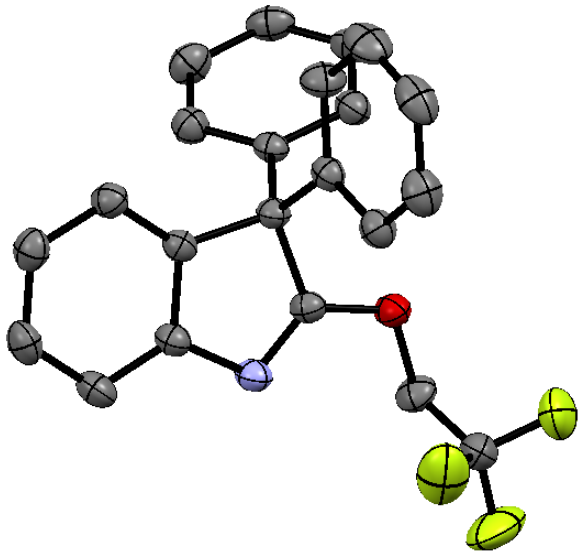


Table 4 Crystal data and structure refinement for 3y.	
Ccdc no.	2243514
Empirical formula	$C_{22}H_{16}F_3NO$
Formula weight	367.36
Temperature/K	298.00
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	6.8883(9)
b/Å	15.522(2)
c/Å	16.668(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1782.1(4)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	0.105
F(000)	760.0
Crystal size/mm^3	0.356 × 0.256 × 0.098

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.548 to 52.812
Index ranges	-8 ≤ h ≤ 8, -19 ≤ k ≤ 19, -20 ≤ l ≤ 20
Reflections collected	11776
Independent reflections	3526 [R_{int} = 0.0469, R_{sigma} = 0.0457]
Data/restraints/parameters	3526/1/309
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0387, wR_2 = 0.0883
Final R indexes [all data]	R_1 = 0.0521, wR_2 = 0.0965
Largest diff. peak/hole / e $Å^{-3}$	0.11/-0.12
Flack parameter	0.4(5)

X-ray crystallographic data of 5b (CCDC-2257366)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2257366**. Suitable single – crystals of **5b** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

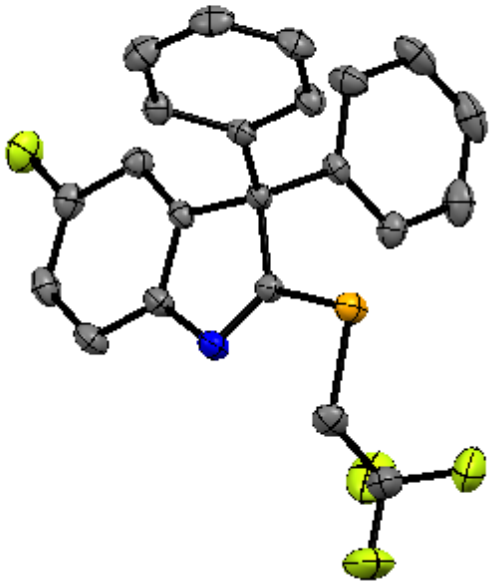


Table 5 Crystal data and structure refinement for 5b.	
Ccdc no.	2257366
Empirical formula	$C_{22}H_{15}F_4NS$
Formula weight	401.41
Temperature/K	298
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	6.8631(3)
b/Å	16.0474(5)
c/Å	16.9025(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1861.56(12)
Z	4
ρ_{calc}g/cm^3	1.432
μ/mm^{-1}	0.219
F(000)	824.0
Crystal size/mm^3	0.235 × 0.123 × 0.098
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.448 to 52.834
Index ranges	-7 ≤ h ≤ 8, -20 ≤ k ≤ 17, -21 ≤ l ≤ 20
Reflections collected	9025
Independent reflections	3786 [R_{int} = 0.0595, R_{sigma} = 0.0601]
Data/restraints/parameters	3786/1/257
Goodness-of-fit on F^2	1.045
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0496, wR_2 = 0.1112
Largest diff. peak/hole / e Å^{-3}	0.21/-0.25
Flack parameter	0.03(5)

X-ray crystallographic data of 5f (CCDC-2257371)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2257371**. Suitable single – crystals of **5f** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

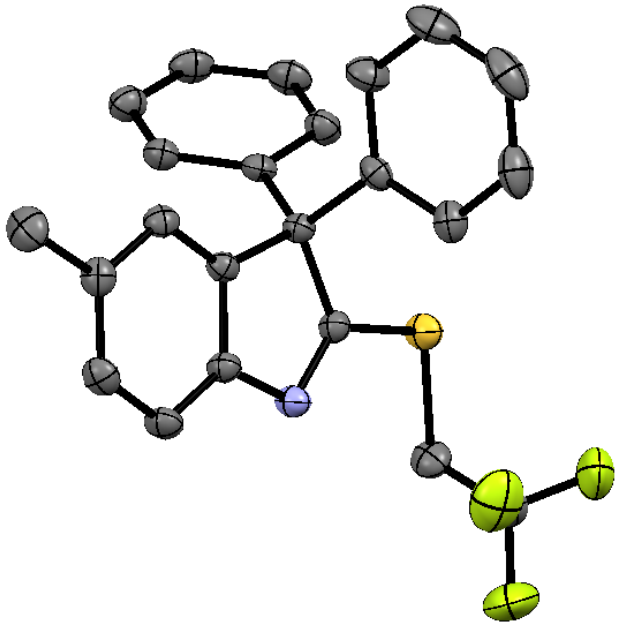


Table 6 Crystal data and structure refinement for 5f.	
Ccdc No.	2257371
Empirical formula	$C_{23}H_{18}F_3NS$
Formula weight	397.44
Temperature/K	298
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.0705(6)
b/Å	16.8461(16)
c/Å	32.575(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3880.1(6)
Z	8
ρ_{calc}g/cm^3	1.361
μ/mm^{-1}	0.202
F(000)	1648.0
Crystal size/mm^3	0.235 × 0.156 × 0.123
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.444 to 52.826

Index ranges	$-8 \le h \le 8, -21 \le k \le 20, -36 \le l \le 40$
Reflections collected	55828
Independent reflections	3971 [R_{int} = 0.0511, R_{sigma} = 0.0206]
Data/restraints/parameters	3971/0/254
Goodness-of-fit on F^2	1.151
Final R indexes [I>=2σ (I)]	R_1 = 0.0507, wR_2 = 0.1272
Final R indexes [all data]	R_1 = 0.0553, wR_2 = 0.1296
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.27

X-ray crystallographic data of 7a (CCDC-2288102)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2288102**. Suitable single – crystals of **7a** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

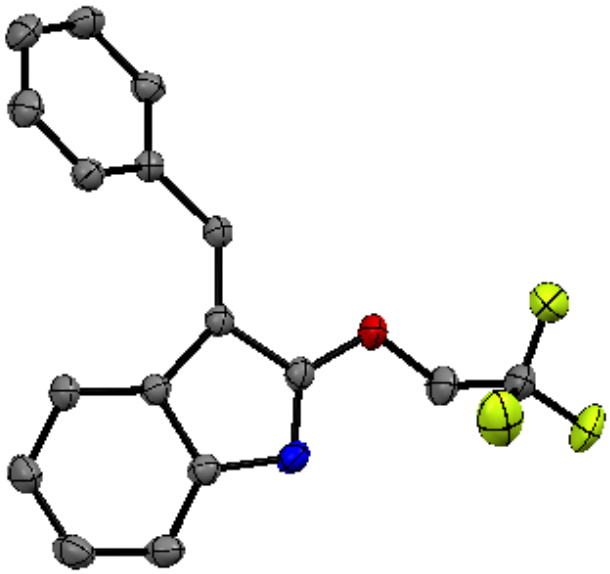


Table 7 Crystal data and structure refinement for 7a.	
Ccdc no.	2288102

Empirical formula	$C_{34}H_{26}F_6N_2O_2$
Formula weight	608.57
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	10.0648(8)
b/Å	11.6308(8)
c/Å	13.8611(10)
α/°	68.976(2)
β/°	87.671(3)
γ/°	69.921(2)
Volume/Å^3	1416.21(18)
Z	2
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	0.116
F(000)	628.0
Crystal size/mm^3	0.123 × 0.104 × 0.098
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.008 to 52.856
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	18765
Independent reflections	5794 [R_{int} = 0.0577, R_{sigma} = 0.0585]
Data/restraints/parameters	5794/0/397
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1794
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1917
Largest diff. peak/hole / e Å^{-3}	0.43/-0.48

X-ray crystallographic data of 9b (CCDC-2285990)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2285990**. Suitable single – crystals of **9b** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

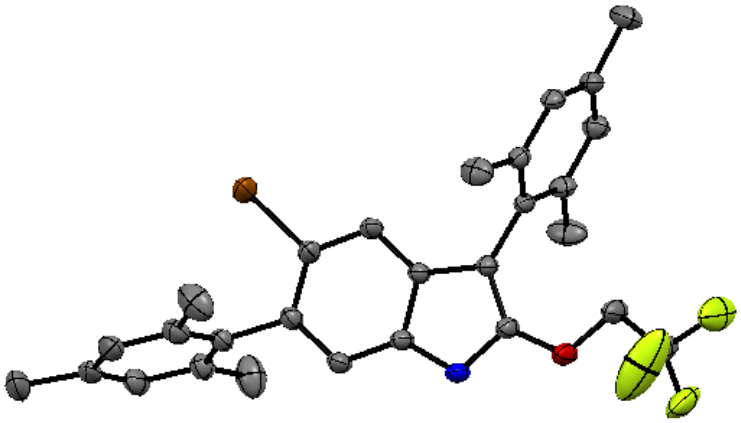


Table 8 Crystal data and structure refinement for 9b.	
Ccdc no.	2285990
Empirical formula	$C_{28}H_{26}BrF_3NO$
Formula weight	529.41
Temperature/K	298.00
Crystal system	triclinic
Space group	P-1
a/Å	7.9716(2)
b/Å	10.9315(3)
c/Å	15.7731(4)
α/°	75.9800(10)
β/°	78.6930(10)
γ/°	81.3380(10)
Volume/Å^3	1299.96(6)
Z	2
ρ_{calc}g/cm^3	1.353
μ/mm^{-1}	1.622
F(000)	542.0
Crystal size/mm^3	0.215 × 0.212 × 0.125
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.864 to 56.904
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -21 ≤ l ≤ 21
Reflections collected	35476
Independent reflections	6457 [R_{int} = 0.0576, R_{sigma} = 0.0362]
Data/restraints/parameters	6457/0/313

Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0639, wR_2 = 0.1626
Final R indexes [all data]	R_1 = 0.0766, wR_2 = 0.1725
Largest diff. peak/hole / e $Å^{-3}$	2.00/-1.42

X-ray crystallographic data of 13c (CCDC-2269435)

The crystal structure has been deposited to Cambridge Crystallographic Data Centre and the allotted deposition number is **2269435**. Suitable single – crystals of **13c** for X-ray analysis were grown up from slow crystallization in ethyl acetate at room temperature.

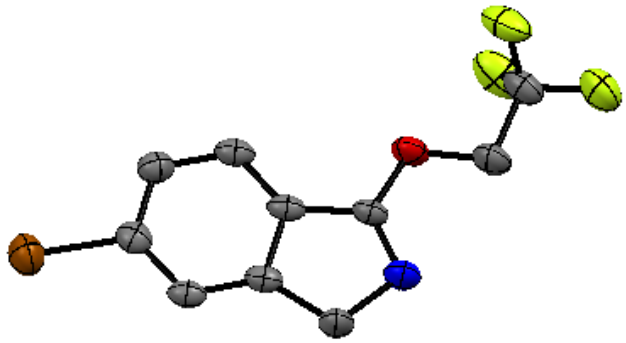


Table 9 Crystal data and structure refinement for 13c.	
Ccdc no.	2269435
Empirical formula	$C_{10}H_6BrF_3NO$
Formula weight	293.07
Temperature/K	298.00
Crystal system	monoclinic
Space group	C2
a/Å	17.093(12)
b/Å	10.057(10)
c/Å	6.991(4)
α/°	90

β/°	113.89(3)
γ/°	90
Volume/Å^3	1098.8(15)
Z	4
ρ_{calc}g/cm^3	1.772
μ/mm^{-1}	3.759
F(000)	572.0
Crystal size/mm^3	0.215 × 0.123 × 0.105
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.816 to 52.984
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -8 ≤ l ≤ 8
Reflections collected	5500
Independent reflections	2145 [R_{int} = 0.0522, R_{sigma} = 0.0635]
Data/restraints/parameters	2145/1/145
Goodness-of-fit on F^2	0.986
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.1070
Final R indexes [all data]	R_1 = 0.0497, wR_2 = 0.1132
Largest diff. peak/hole / e Å^{-3}	0.30/-0.24
Flack parameter	0.076(11)

VIII. References

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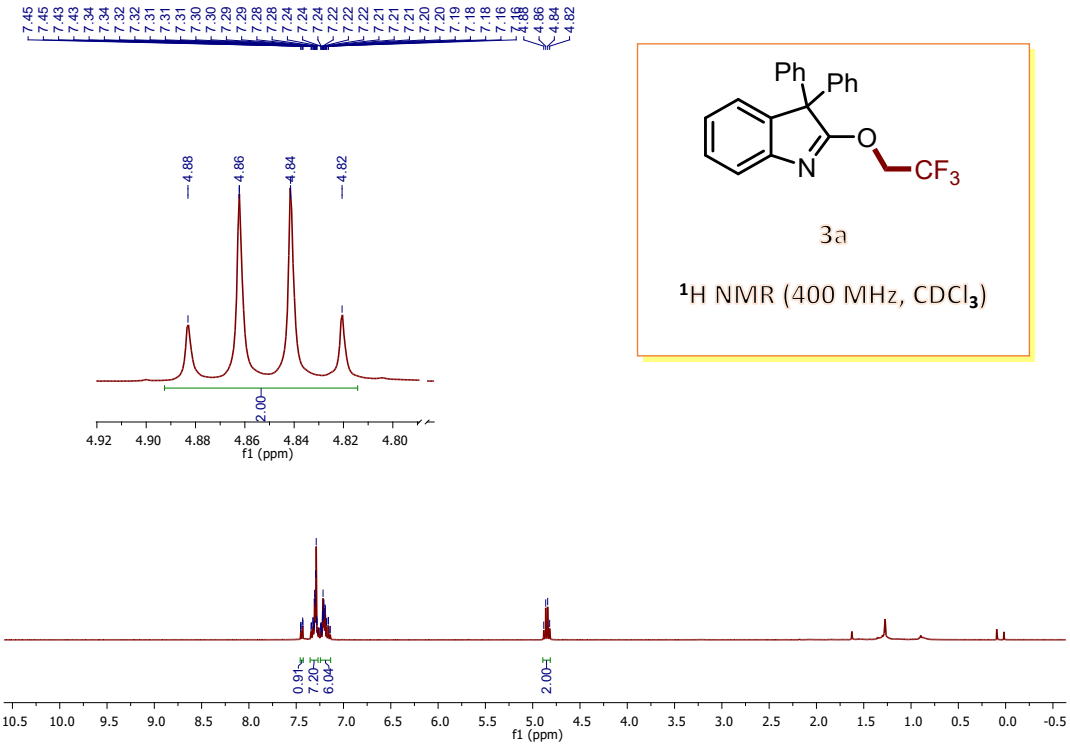
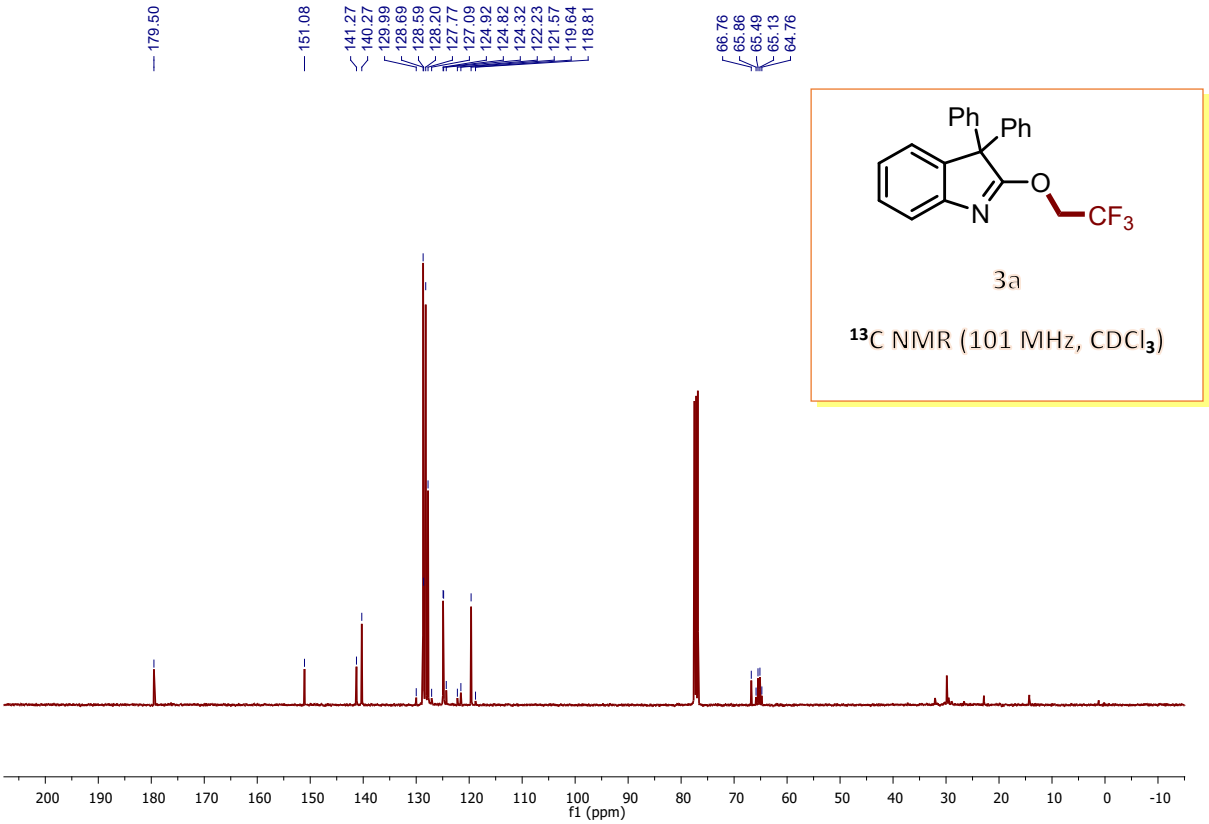
IX. NMR Spectras



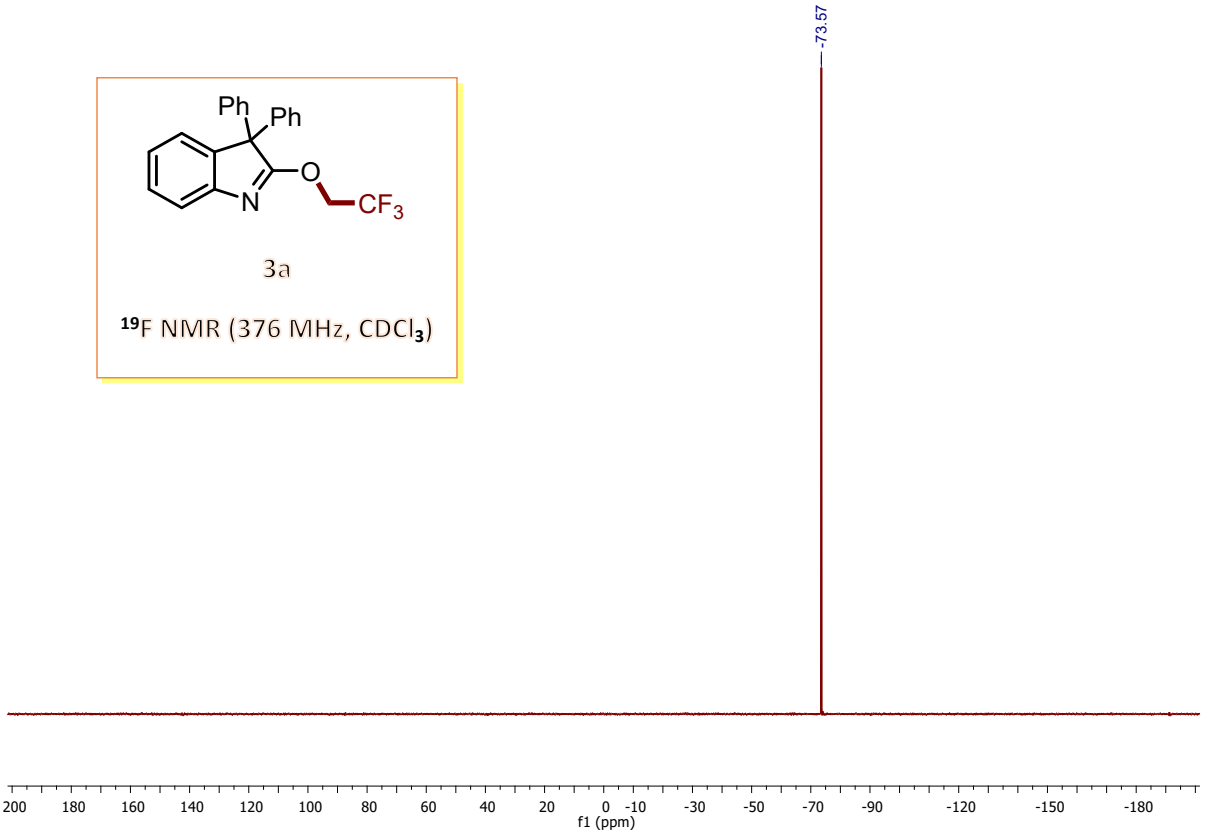
3a

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



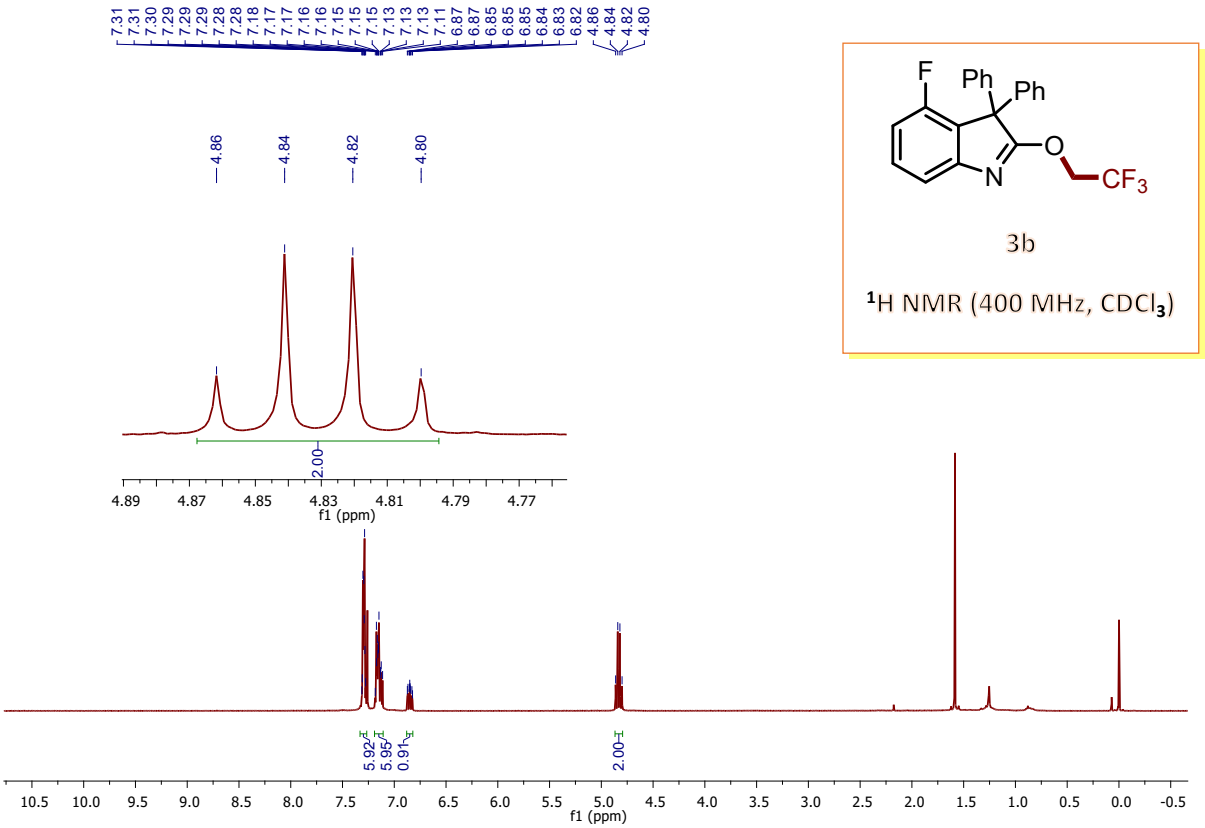
3a

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



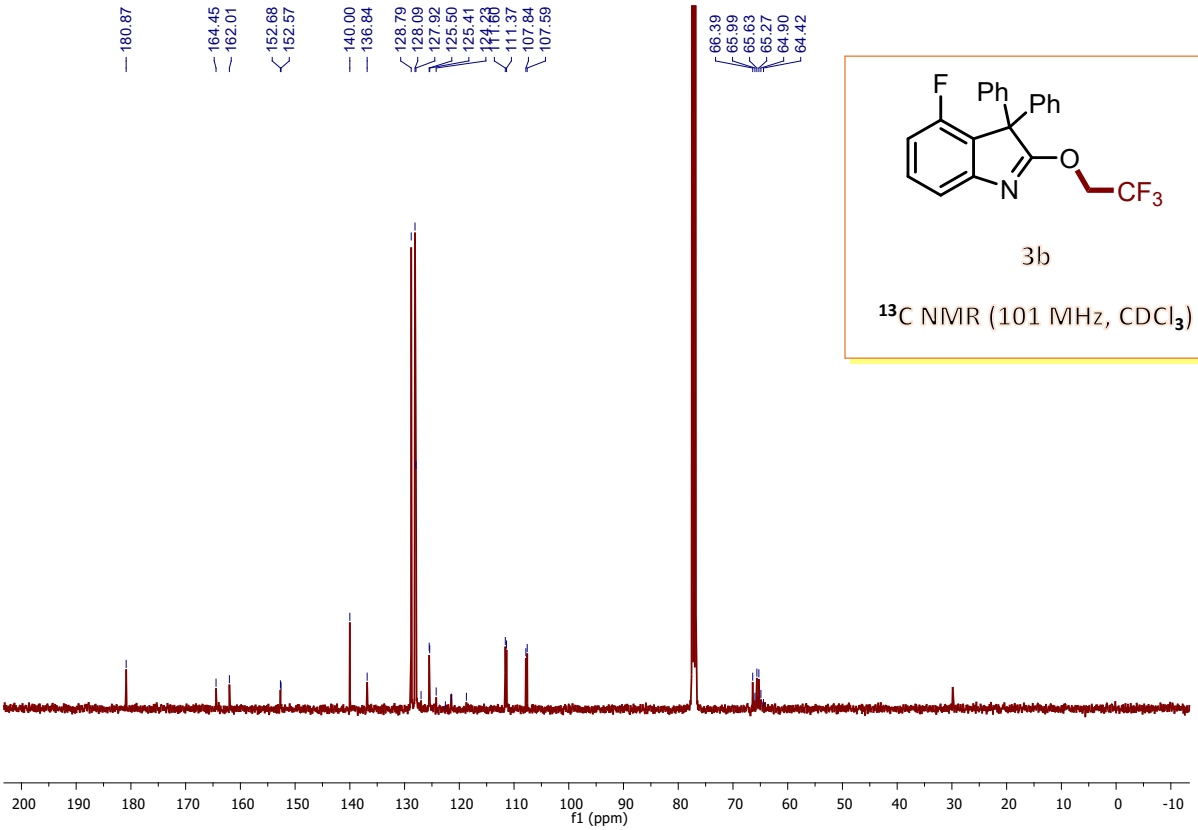
3a

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



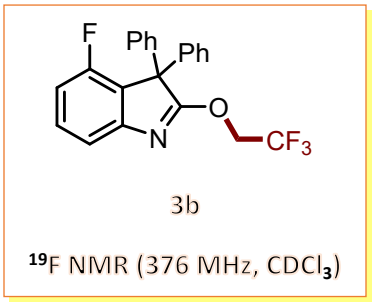
3b

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



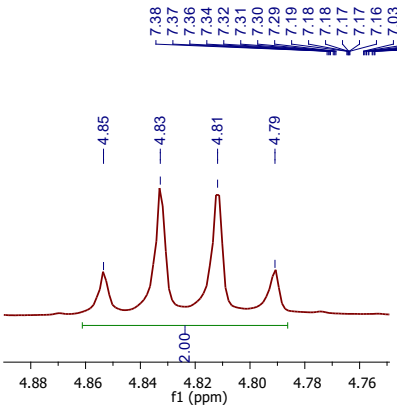
3b

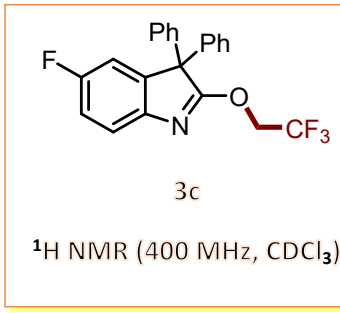
^{13}C NMR (101 MHz, $CDCl_3$)



3b

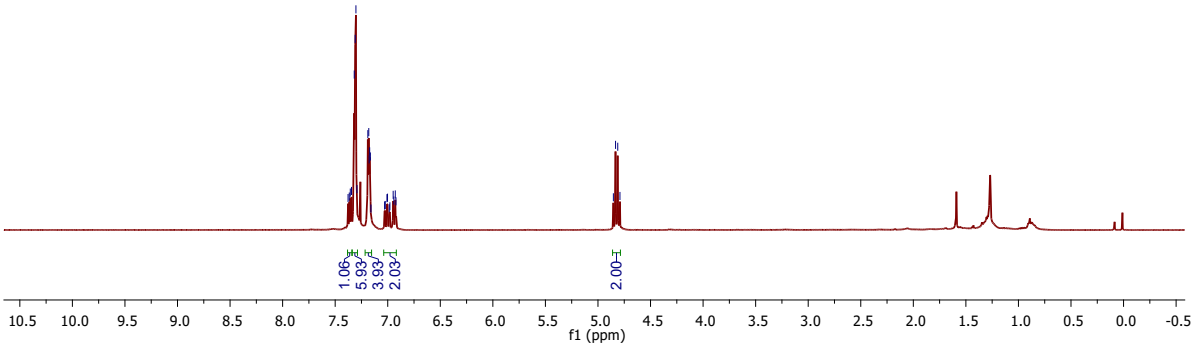
^{19}F NMR (376 MHz, $CDCl_3$)

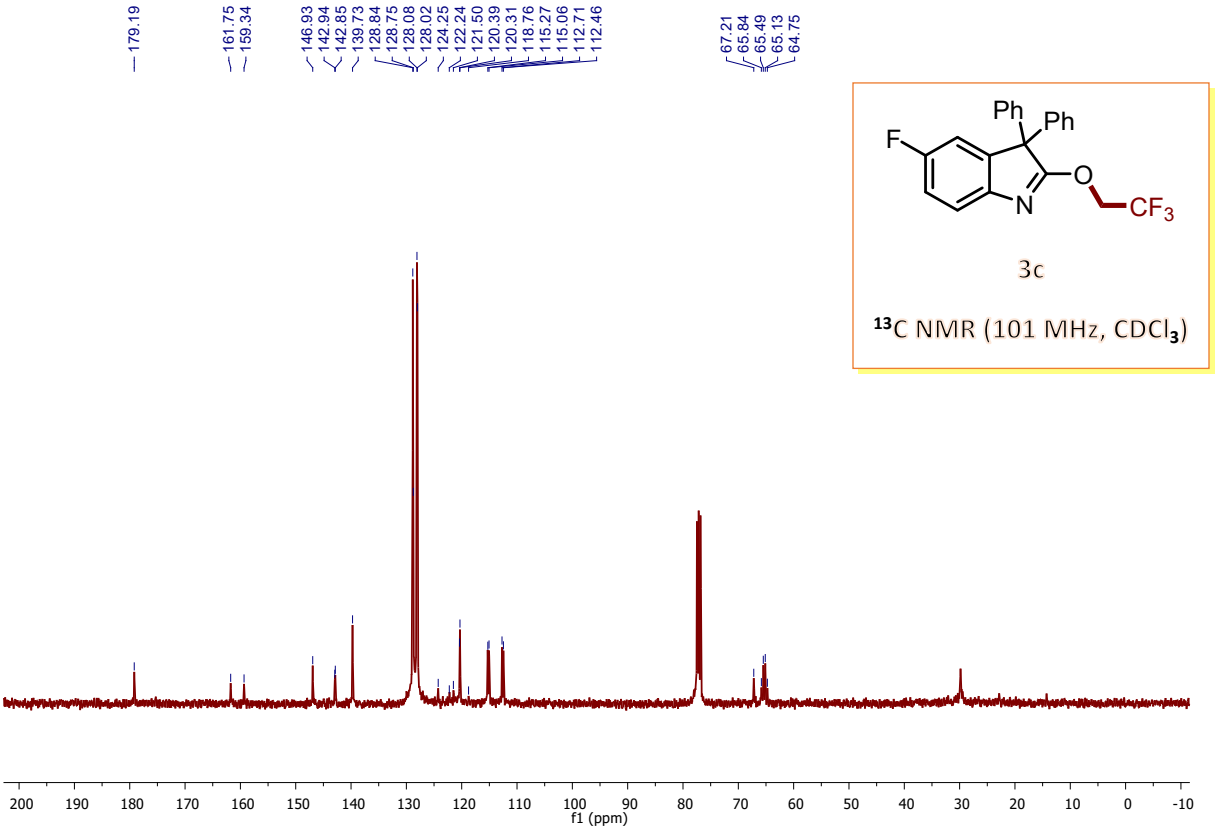




3c

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

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161.75
159.34
146.93
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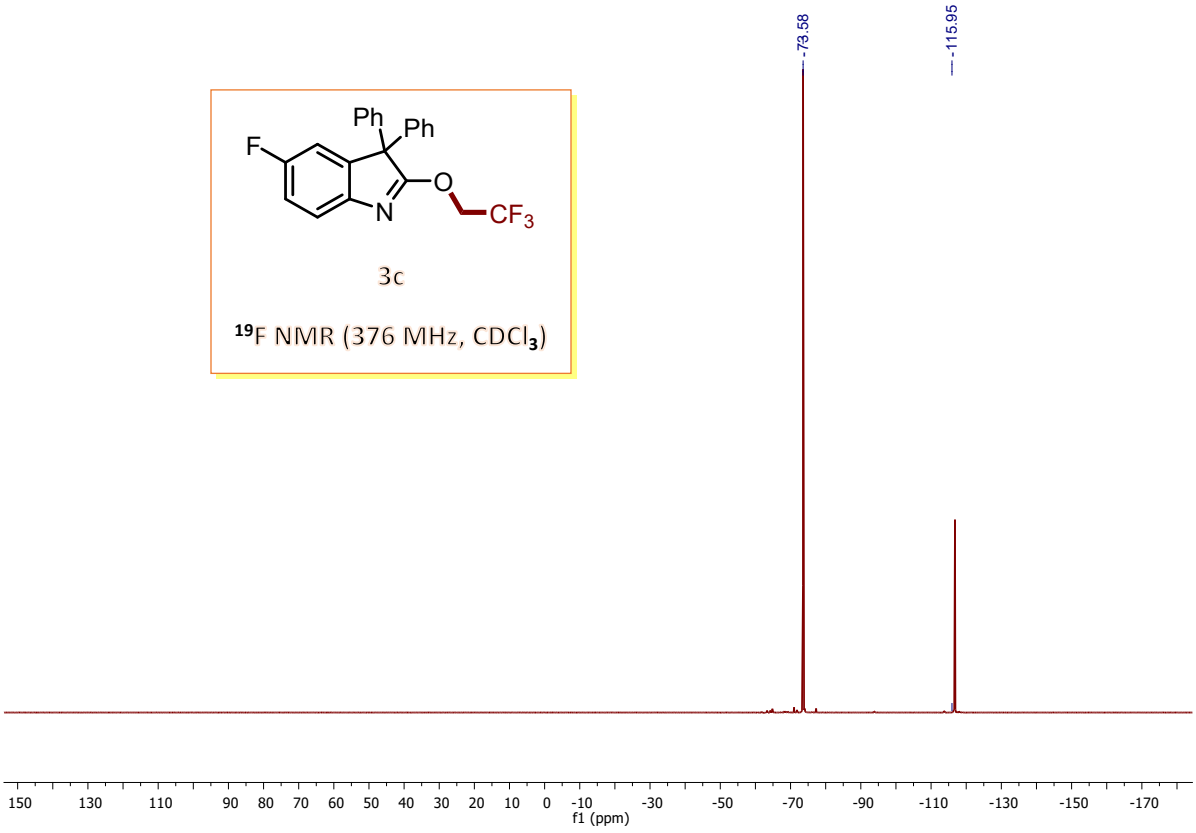
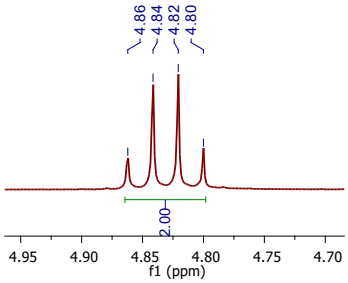
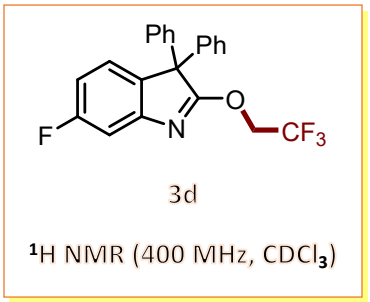
142.85
139.73
128.84
128.75
128.08
128.02
124.25
122.24
121.50
120.39
120.31
118.76
115.27
115.06
112.71
112.46
67.21
65.84
65.49
65.13
64.75
Ph
Ph
F
O
N
CF3
3c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

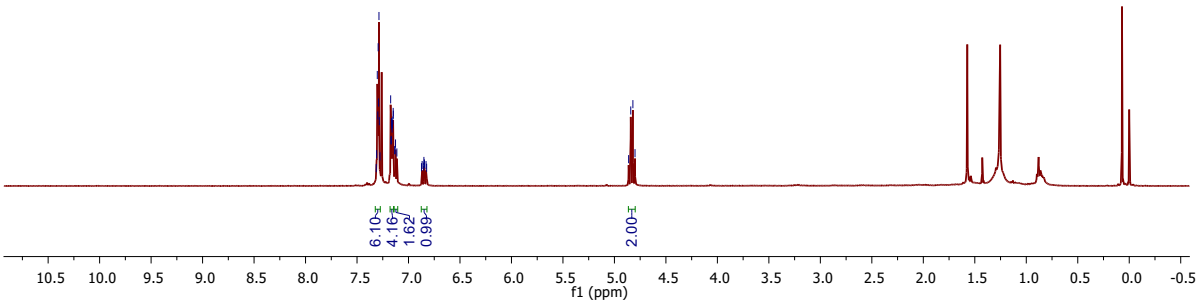

-73.58
-115.95
Ph
Ph
F
O
N
CF3
3c
19F NMR (376 MHz, CDCl3)
f1 (ppm)

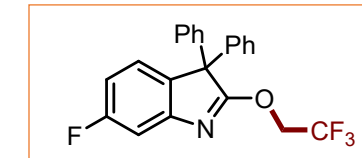




3d

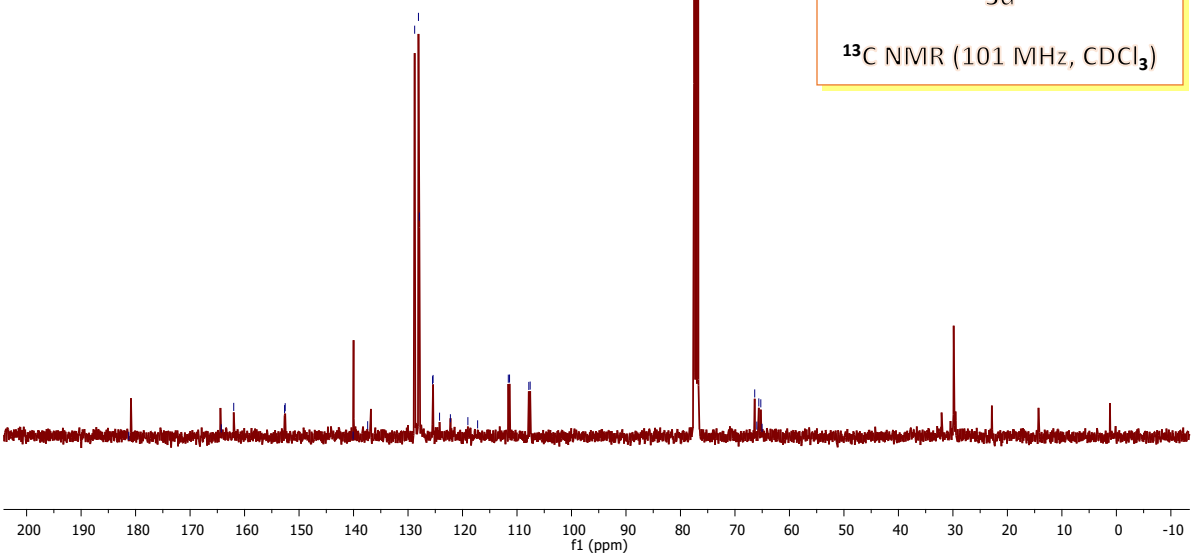
^{1}H NMR (400 MHz, $CDCl_3$)

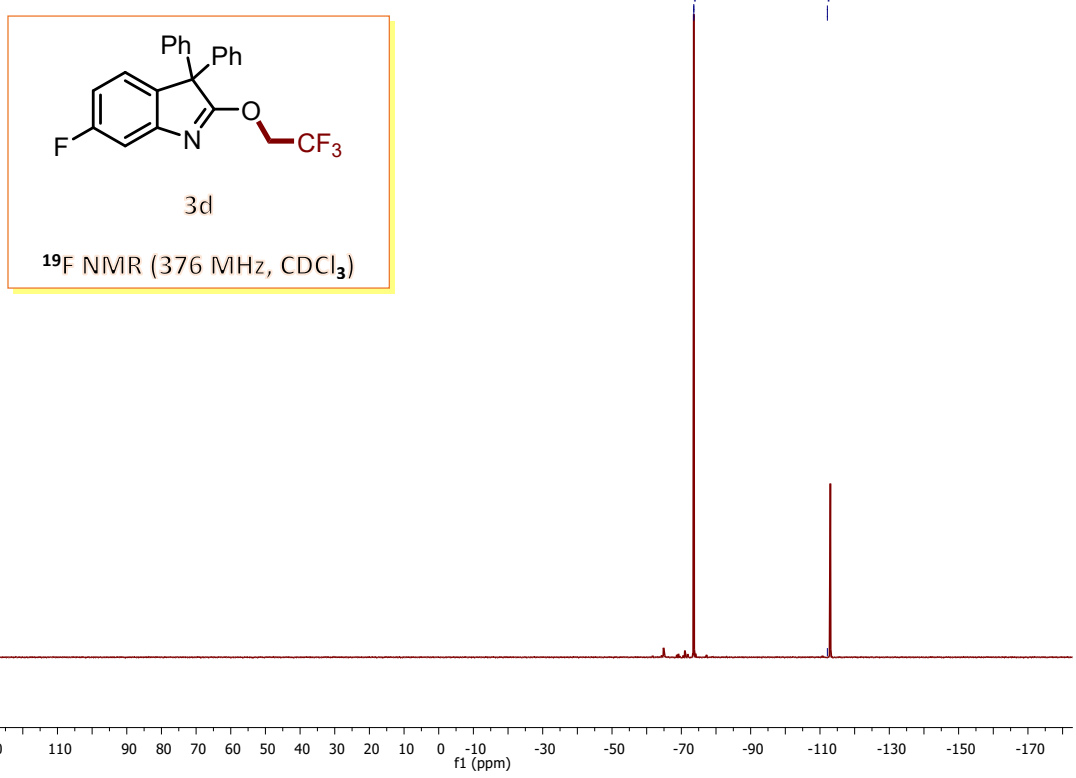


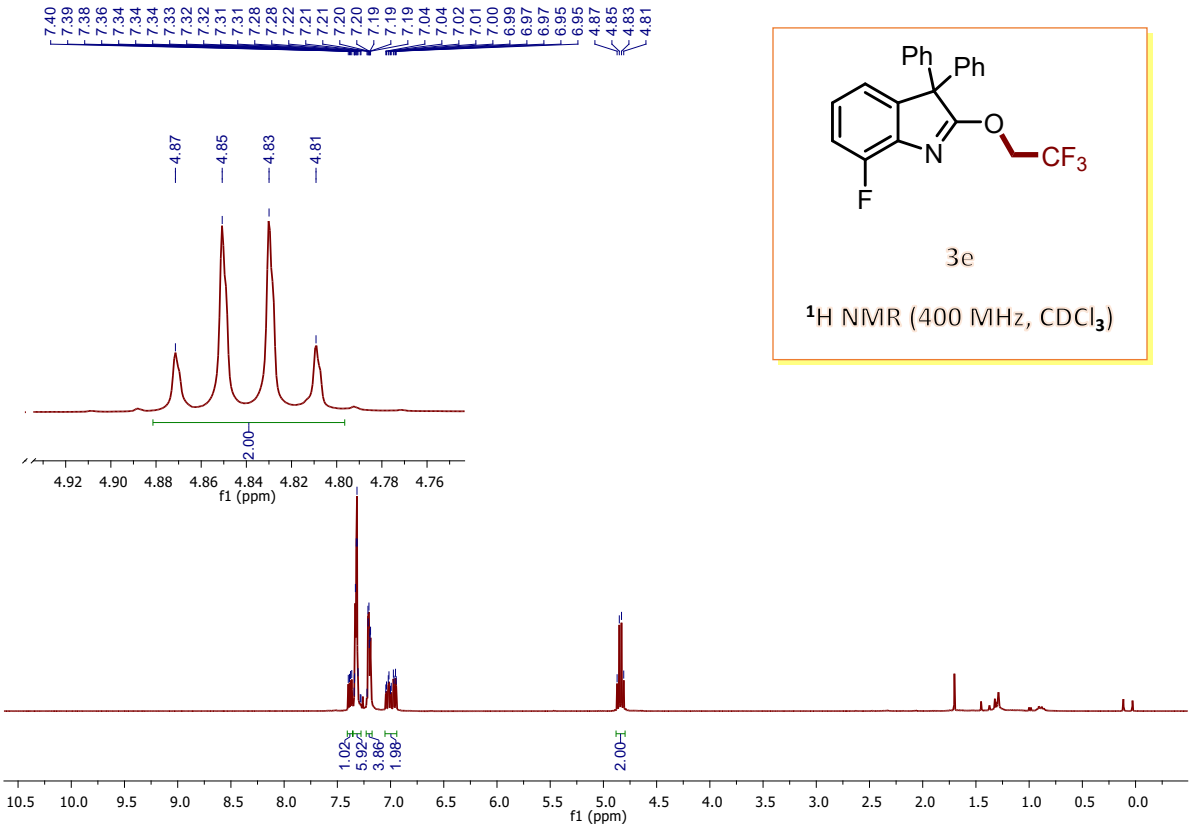


3d

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




Ph
Ph
O
N
F
CF3
3d
19F NMR (376 MHz, CDCl3)
-73.60
-112.13
f1 (ppm)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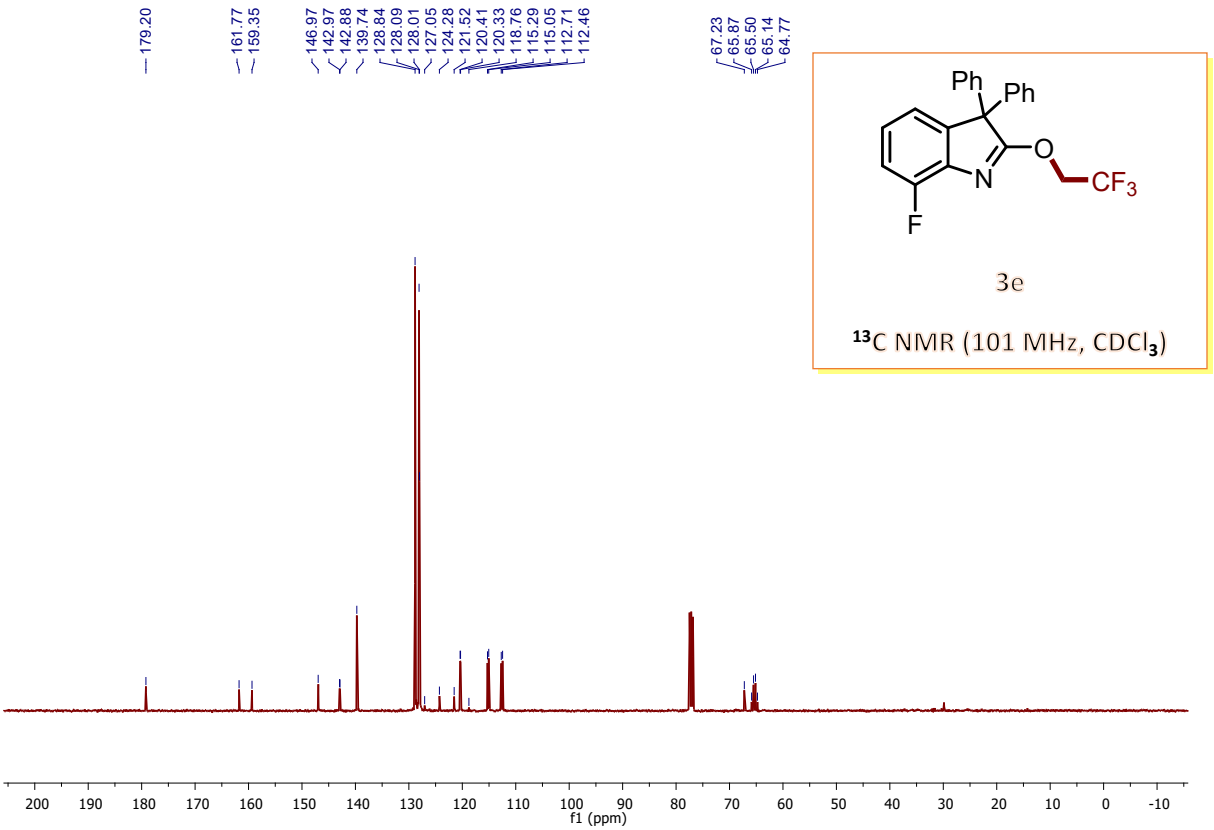
7.39
7.38
7.36
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.28
7.28
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.19
7.04
7.04
7.02
7.01
7.00
6.99
6.97
6.97
6.95
6.95
4.87
4.85
4.83
4.81
4.87
4.85
4.83
4.81
2.00
f1 (ppm)
1.02
5.92
3.86
1.98
2.00
f1 (ppm)

Ph
Ph
O
N
F
CF3
3e
1H NMR (400 MHz, CDCl3)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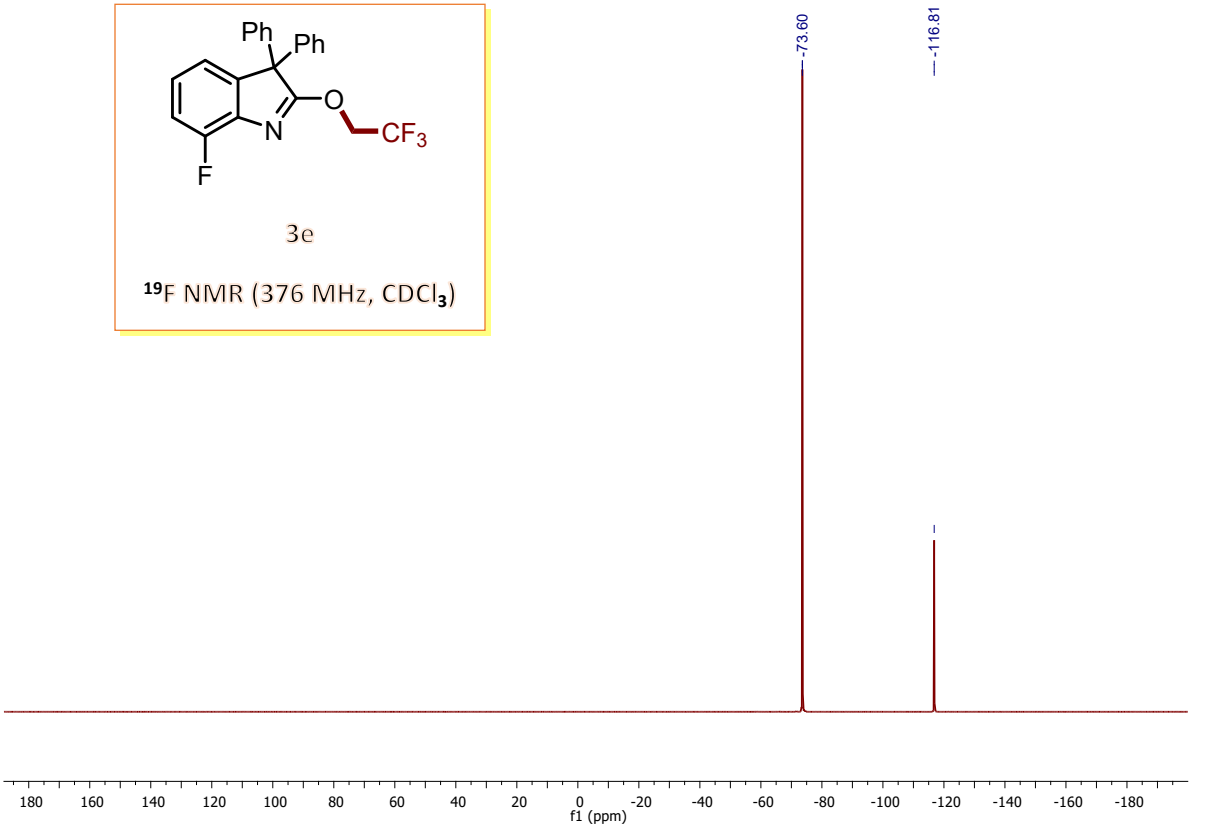
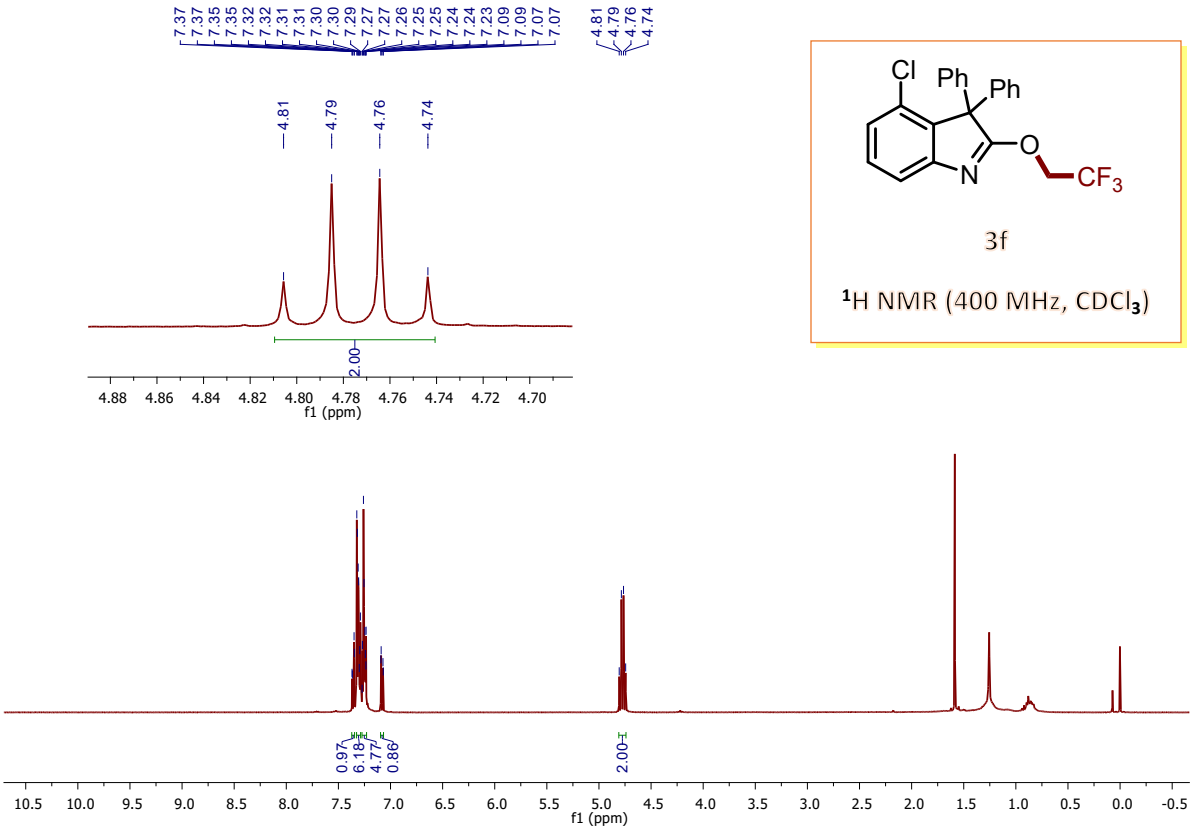
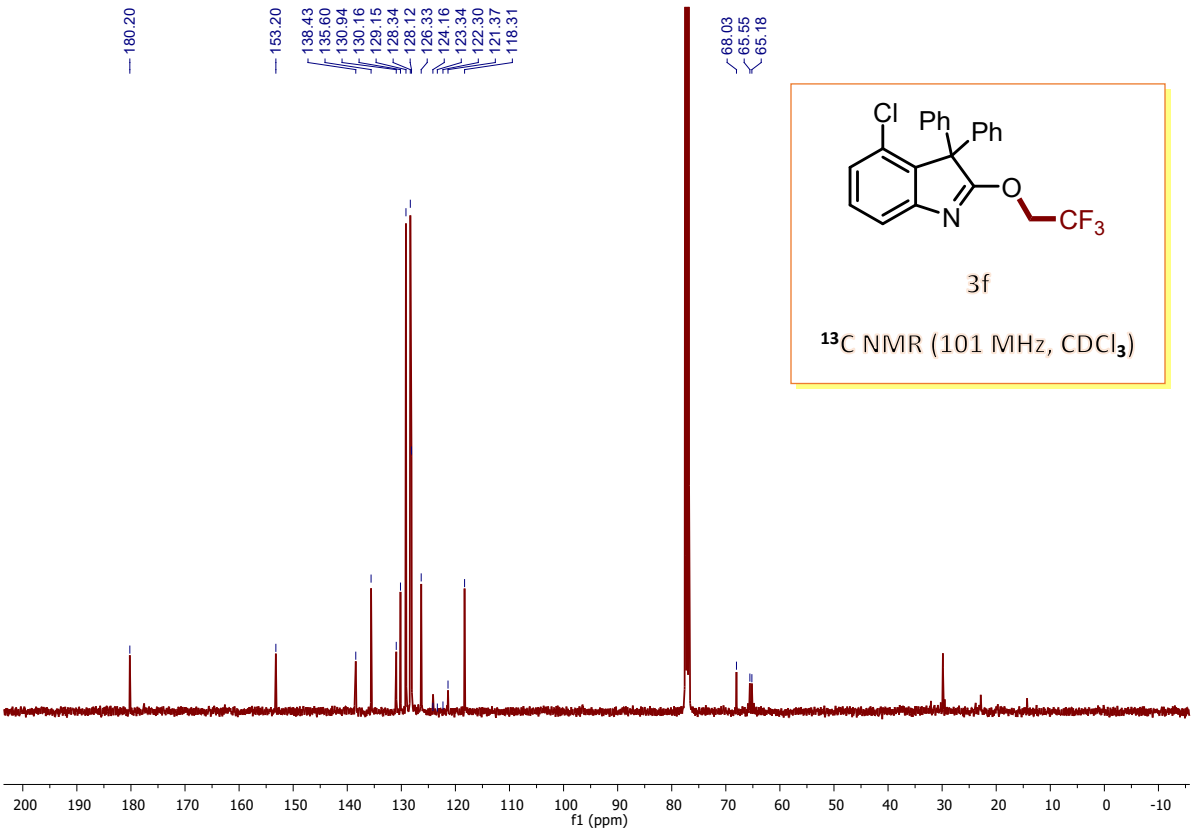
161.77
159.35
146.97
142.97
142.88
139.74
128.84
128.09
128.01
127.05
124.28
121.52
120.41
120.33
118.76
115.29
115.05
112.71
112.46
67.23
65.87
65.50
65.14
64.77
Ph
Ph
O
N
F
CF3
3e
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
Ph
O
N
F
CF3
3e
19F NMR (376 MHz, CDCl3)
-73.60
-116.81
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)



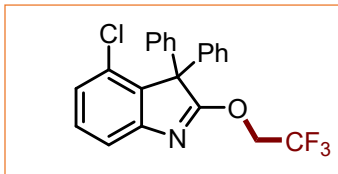
3f

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



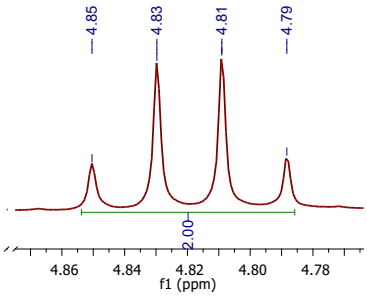
3f

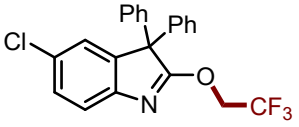
^{13}C NMR (101 MHz, $CDCl_3$)



3f

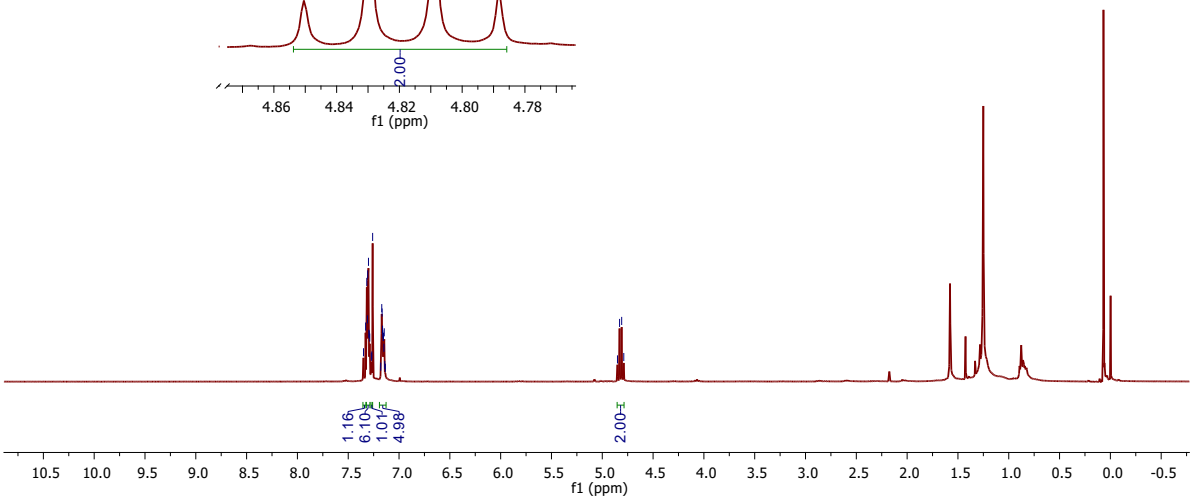
^{19}F NMR (376 MHz, $CDCl_3$)

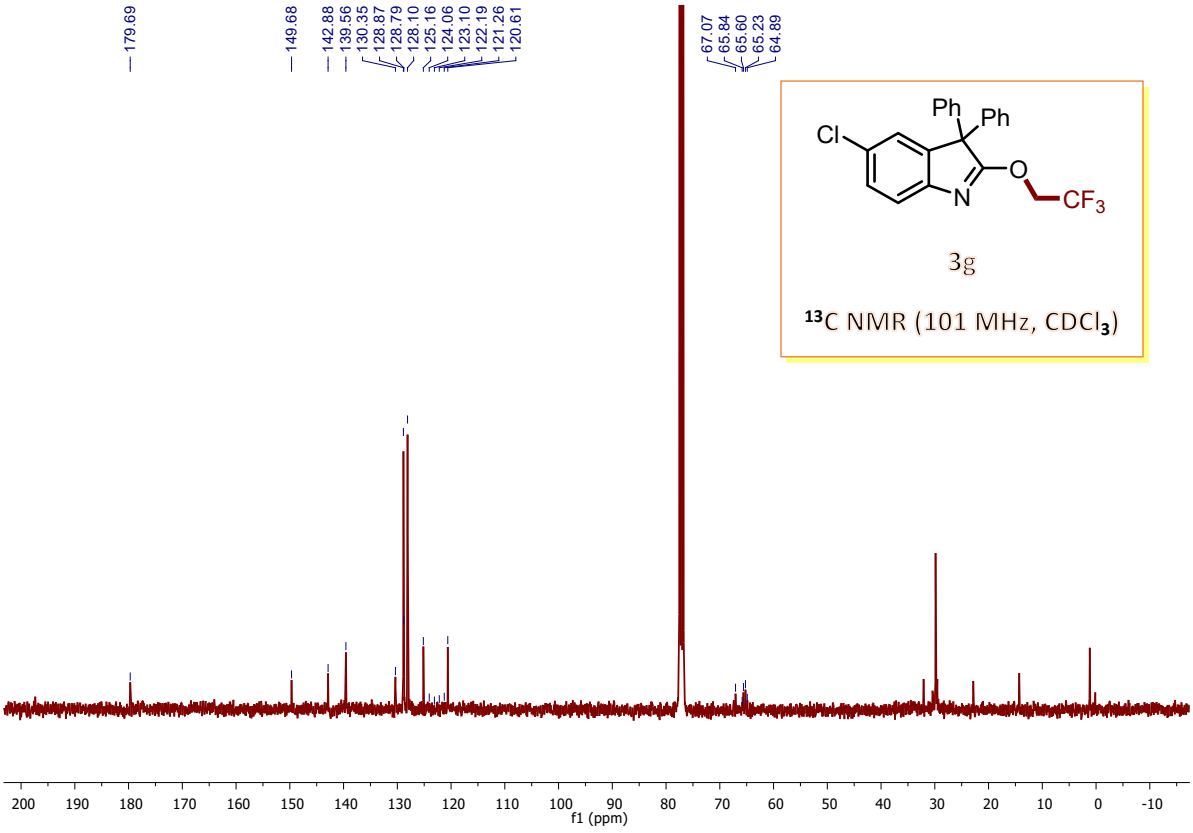




3g

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

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139.56
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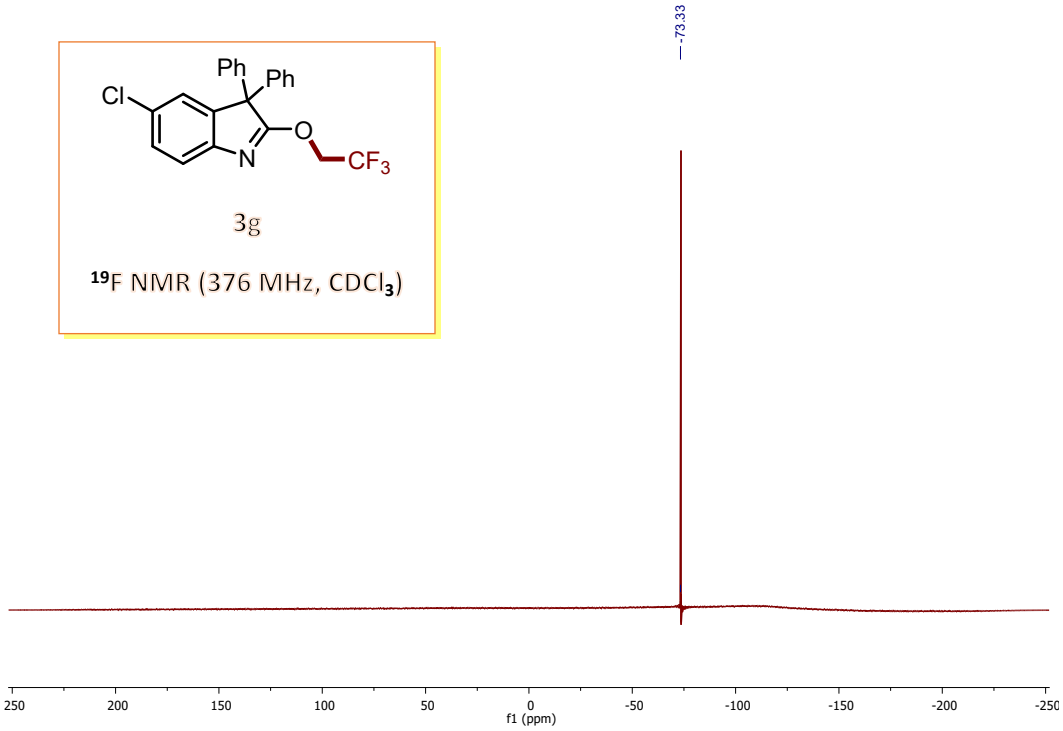
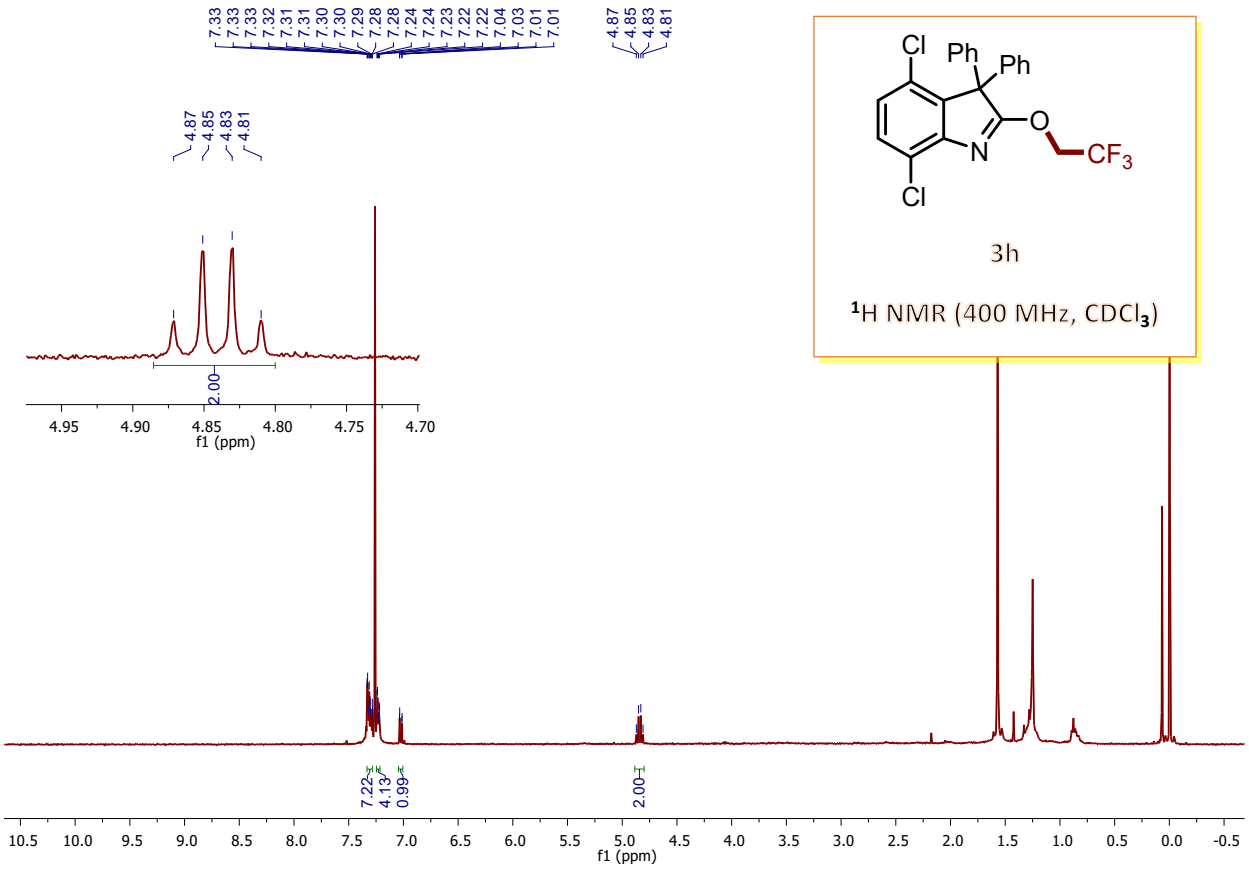
128.87
128.79
128.10
125.16
124.06
123.10
122.19
121.26
120.61
67.07
65.84
65.60
65.23
64.89
Ph
Ph
Cl
O
N
CF3
3g
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-73.33
Ph
Ph
Cl
O
N
CF3
3g
19F NMR (376 MHz, CDCl3)
250 200 150 100 50 0 -50 -100 -150 -200 -250
f1 (ppm)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7.33
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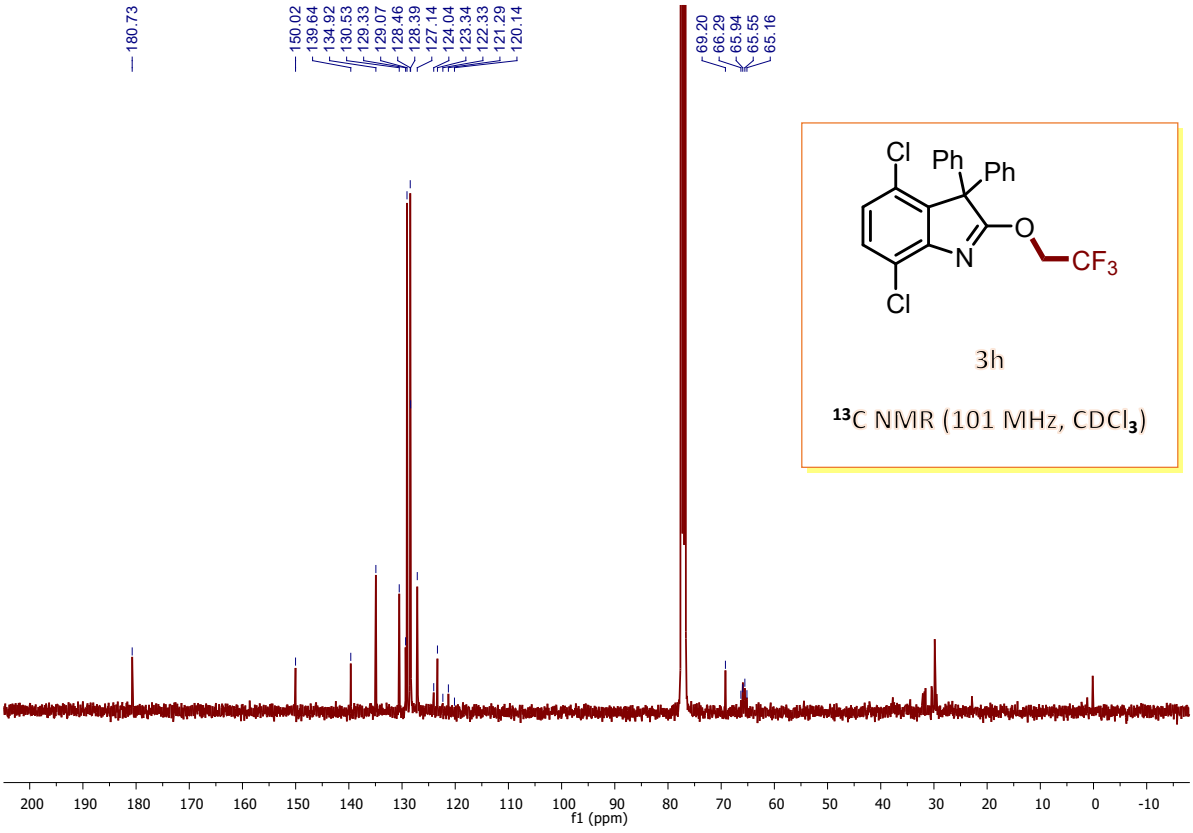
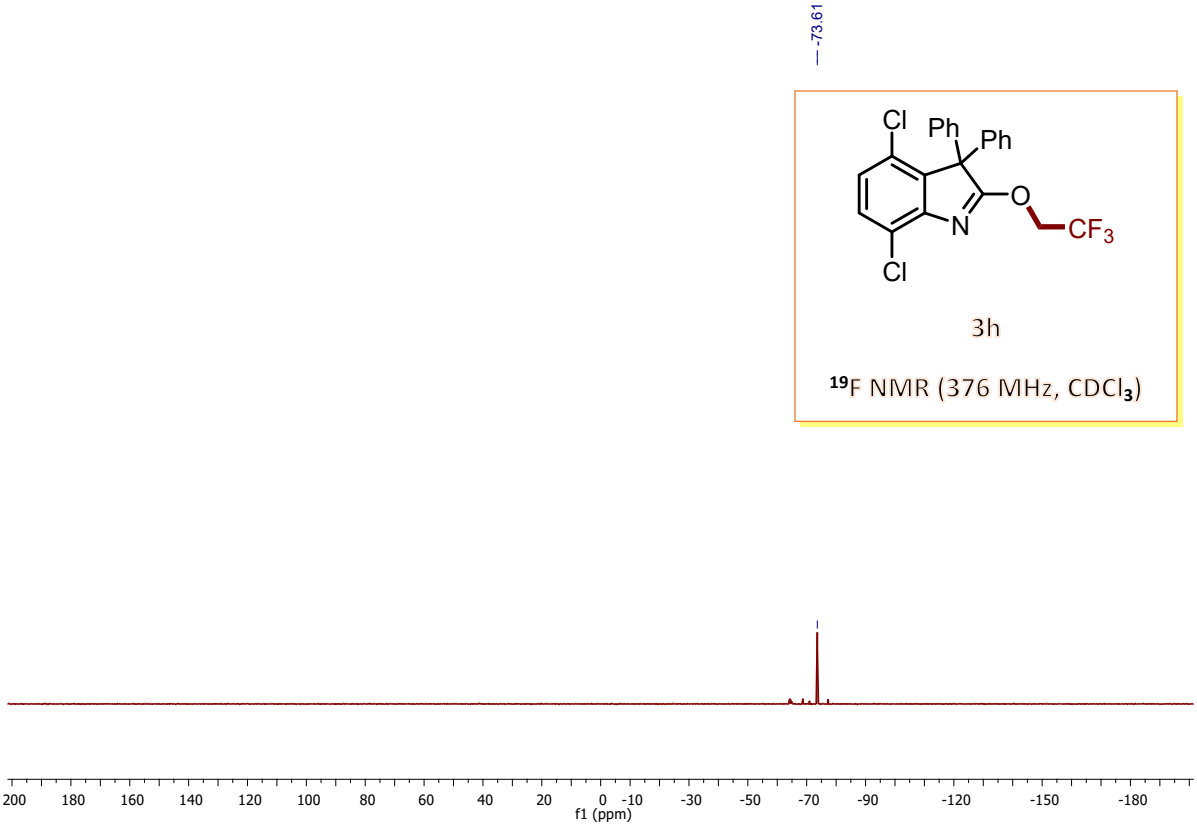
7.23
7.22
7.22
7.04
7.03
7.01
7.01
4.87
4.85
4.83
4.81
4.87
4.85
4.83
4.81
2.00
4.95
4.90
4.85
4.80
4.75
4.70
f1 (ppm)
7.22
4.13
0.99
2.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
Cl
Ph
Ph
O
N
CF3
Cl
3h
1H NMR (400 MHz, CDCl3)



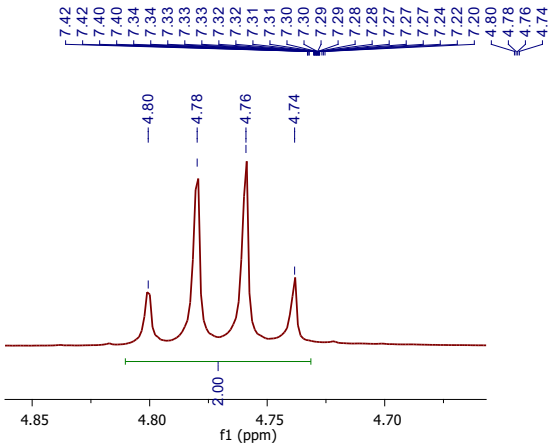
3h

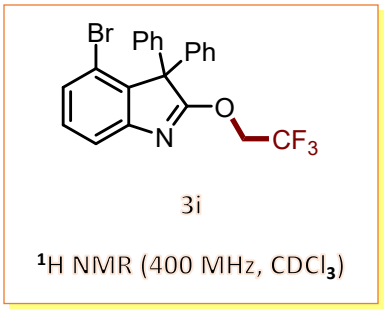
^{13}C NMR (101 MHz, $CDCl_3$)



3h

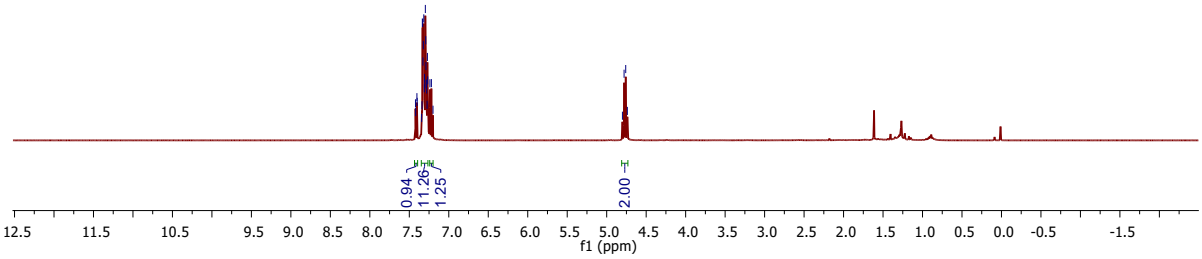
^{19}F NMR (376 MHz, $CDCl_3$)

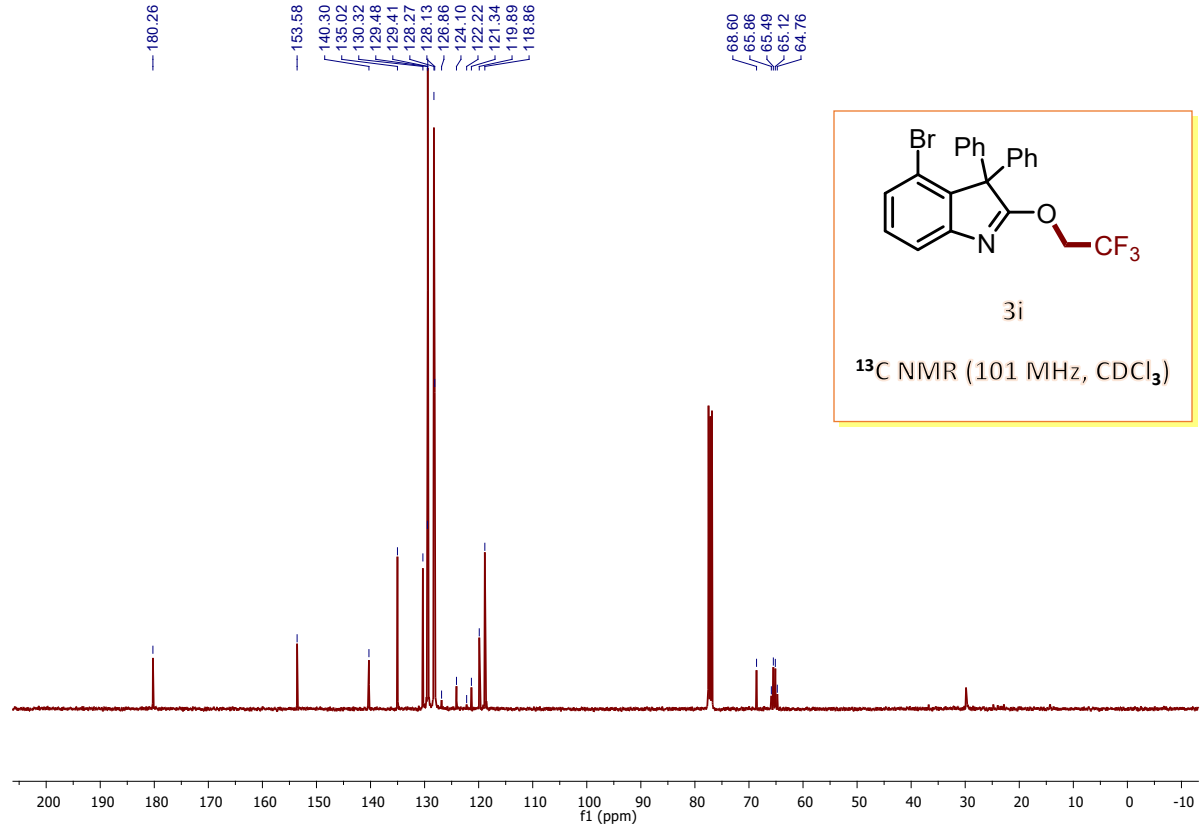




3i

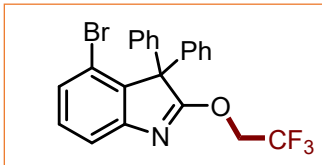
^{1}H NMR (400 MHz, $CDCl_3$)





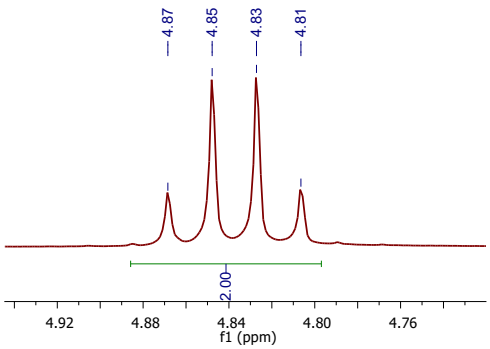
3i

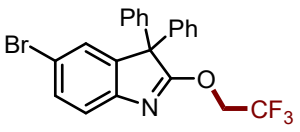
^{13}C NMR (101 MHz, $CDCl_3$)



3i

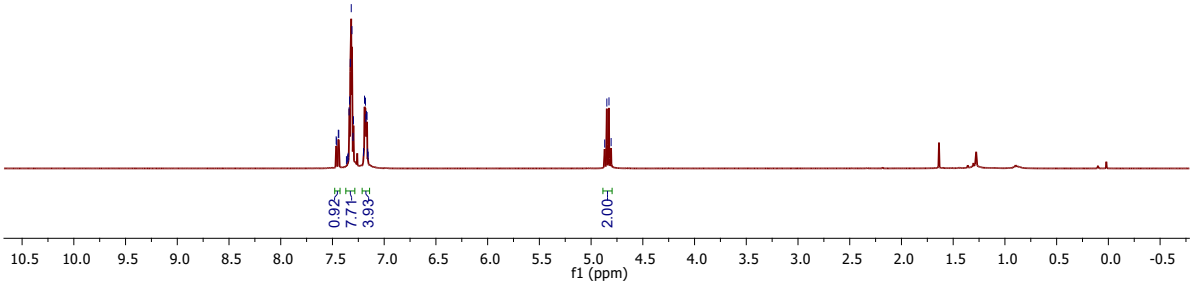
^{19}F NMR (376 MHz, $CDCl_3$)

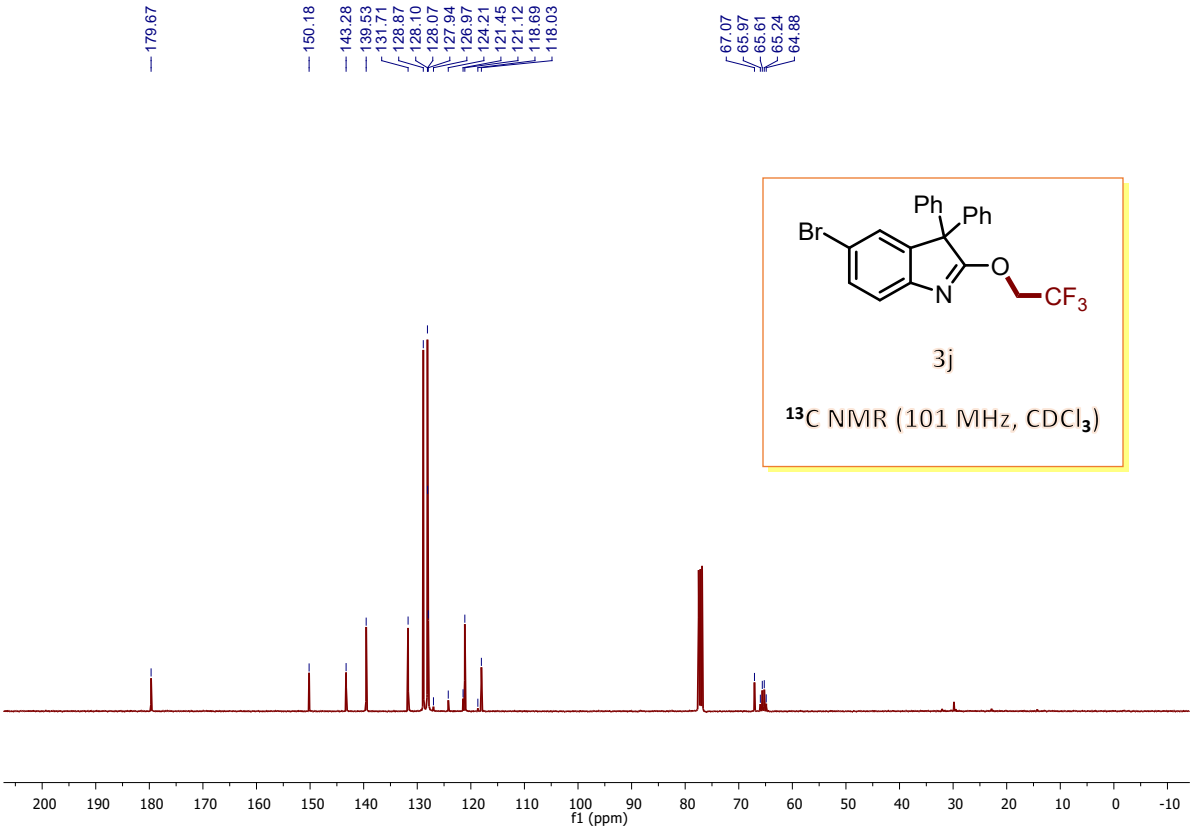


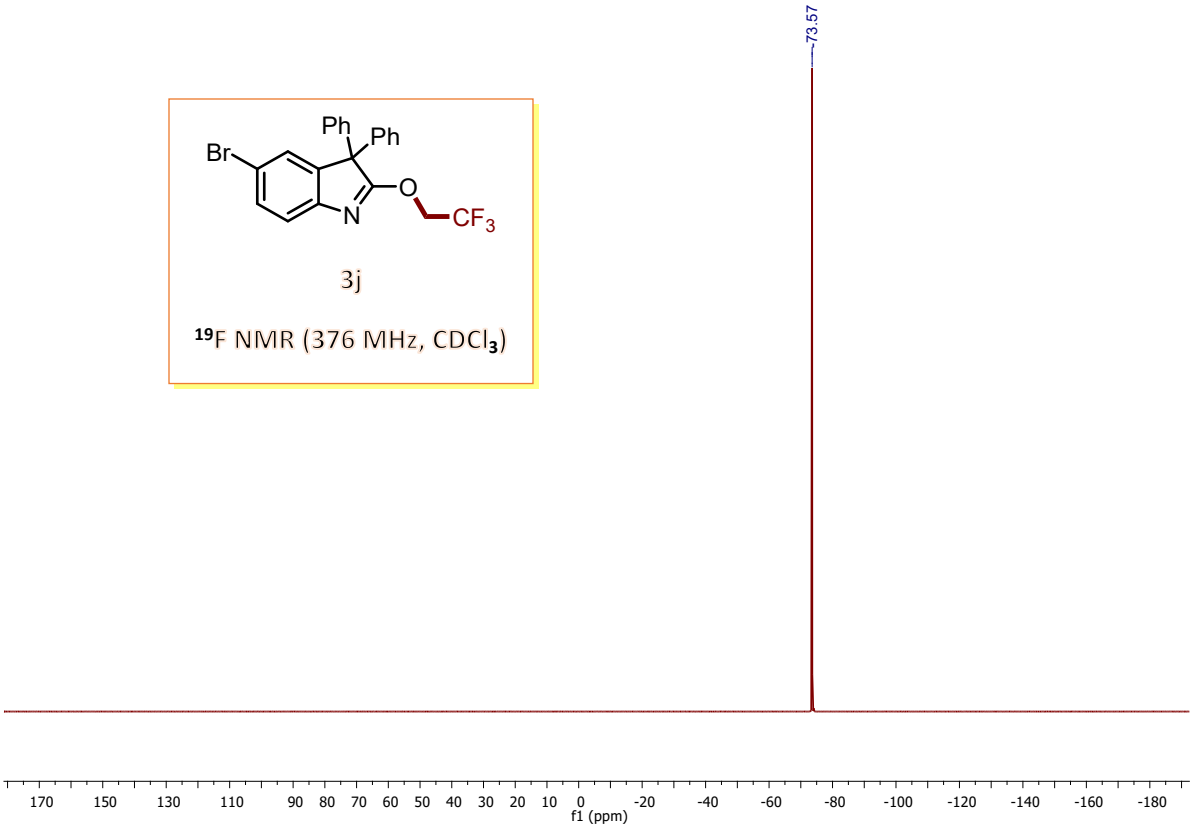


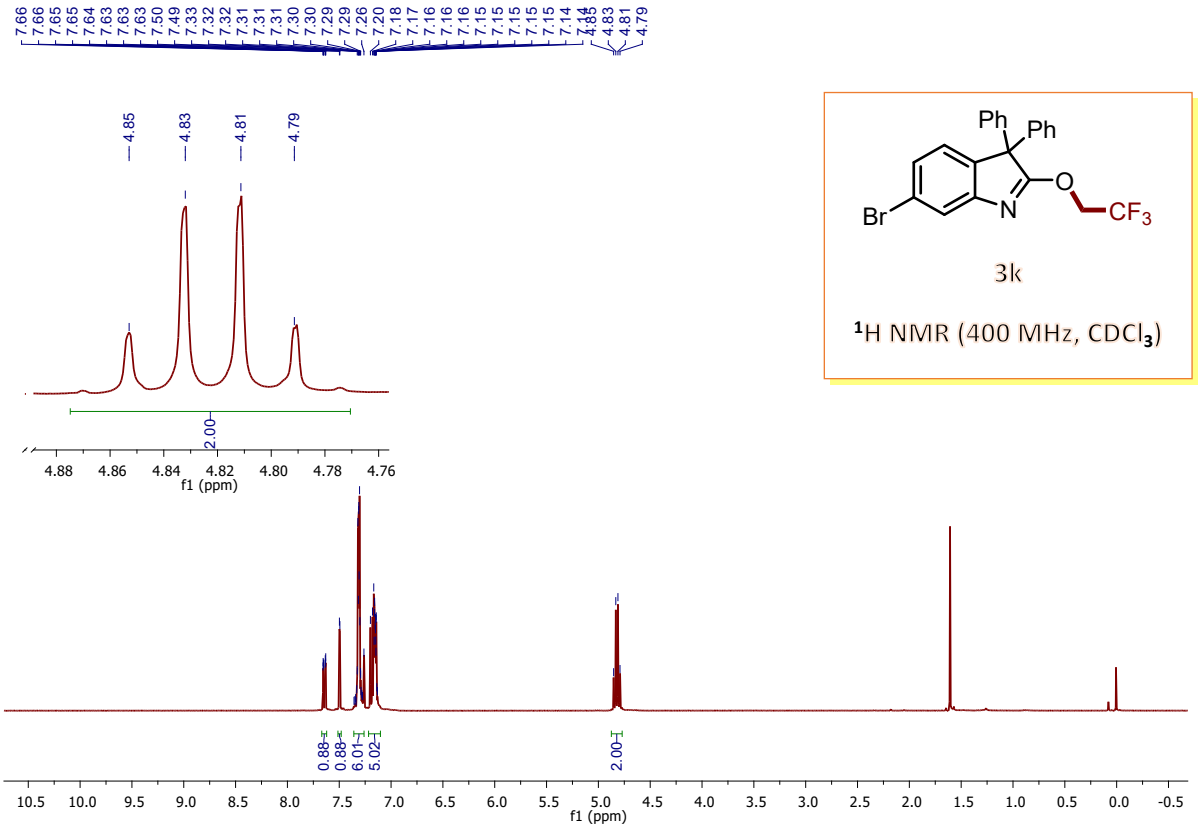
3j

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



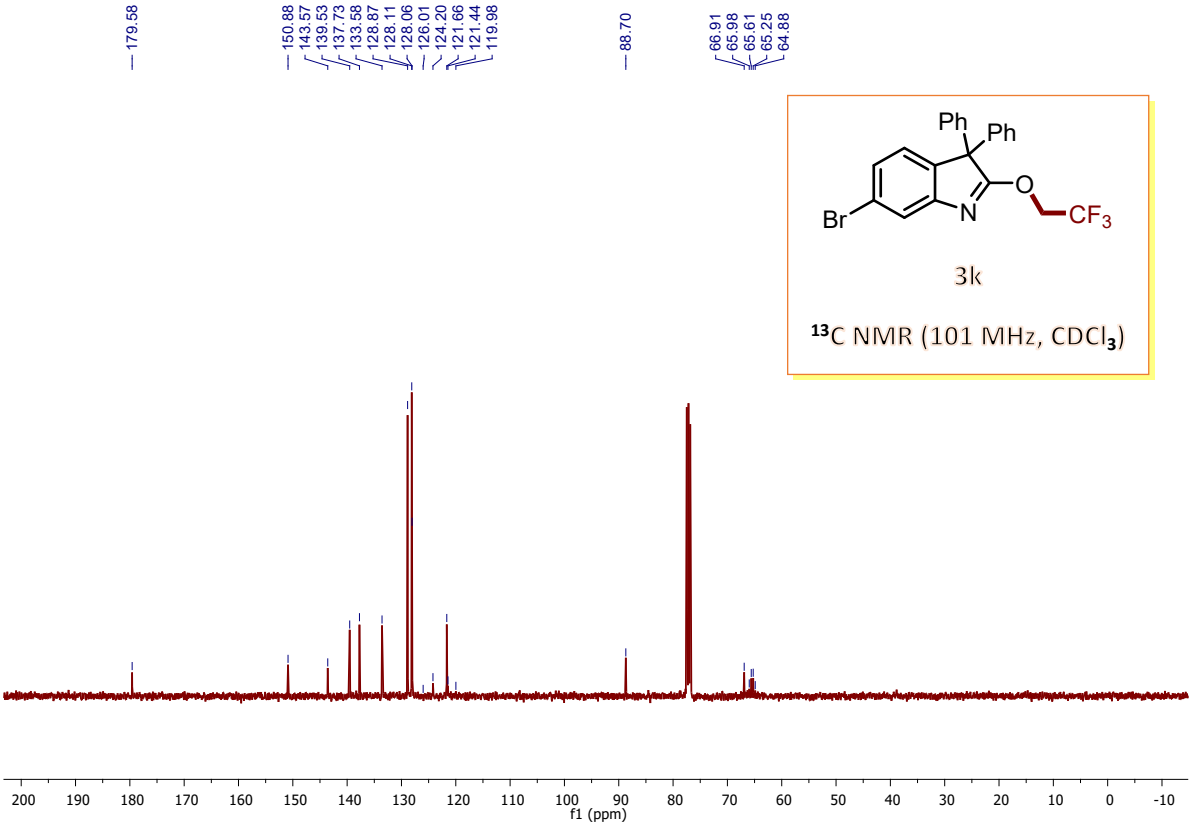

179.67
150.18
143.28
139.53
131.71
128.87
128.10
128.07
127.94
126.97
124.21
121.45
121.12
118.69
118.03
67.07
65.97
65.61
65.24
64.88
Ph
Ph
Br
O
N
CF3
3j
13C NMR (101 MHz, CDCl3)
f1 (ppm)


73.57
Ph
Ph
Br
O
N
CF3
3j
19F NMR (376 MHz, CDCl3)
f1 (ppm)



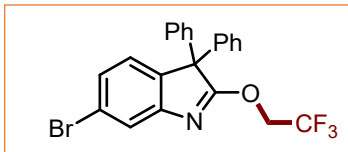
3k

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



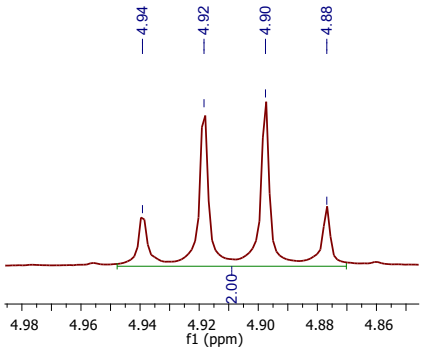
3k

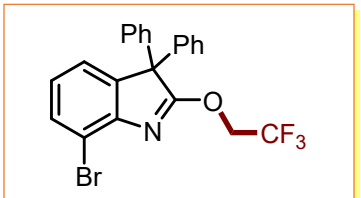
^{13}C NMR (101 MHz, $CDCl_3$)



3k

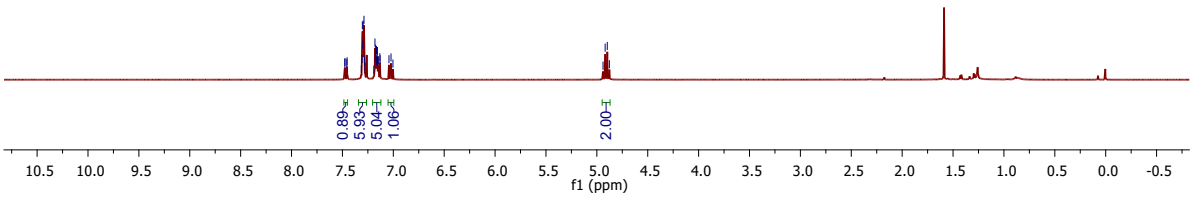
^{19}F NMR (376 MHz, $CDCl_3$)

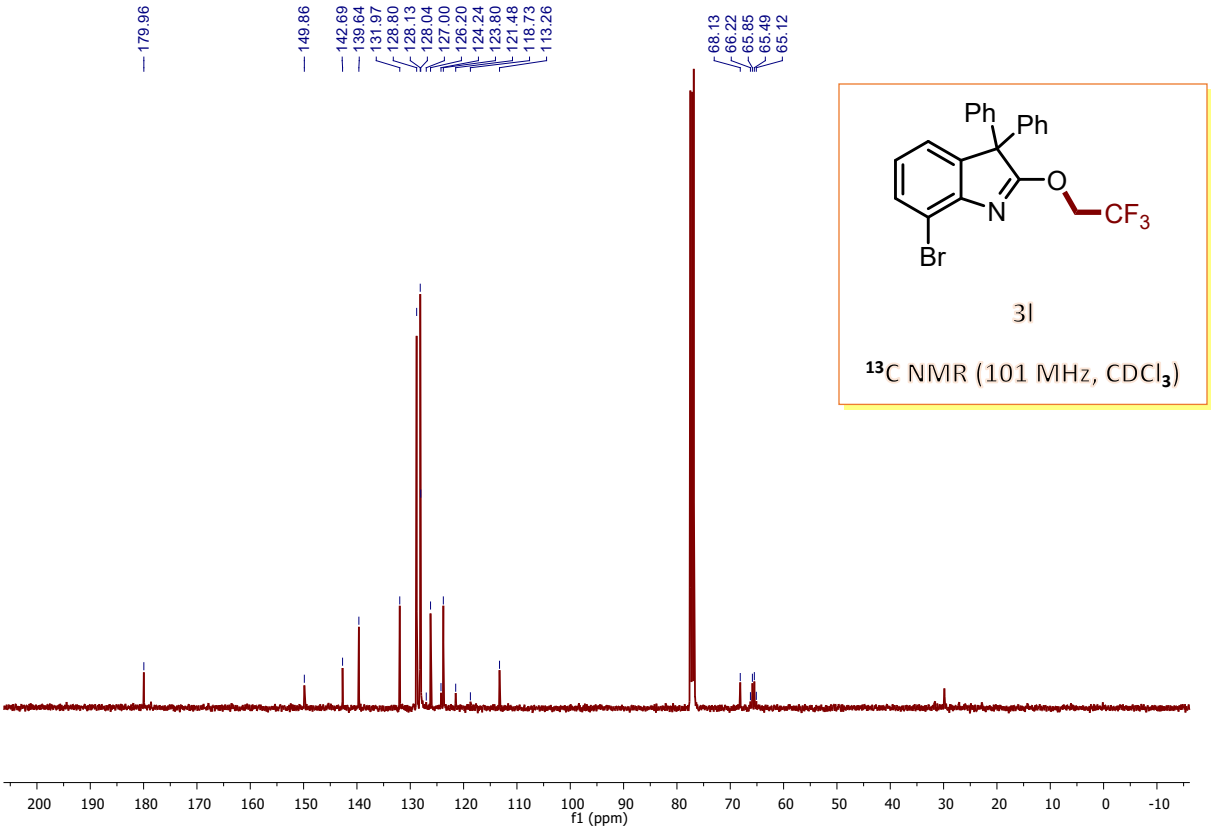




3l

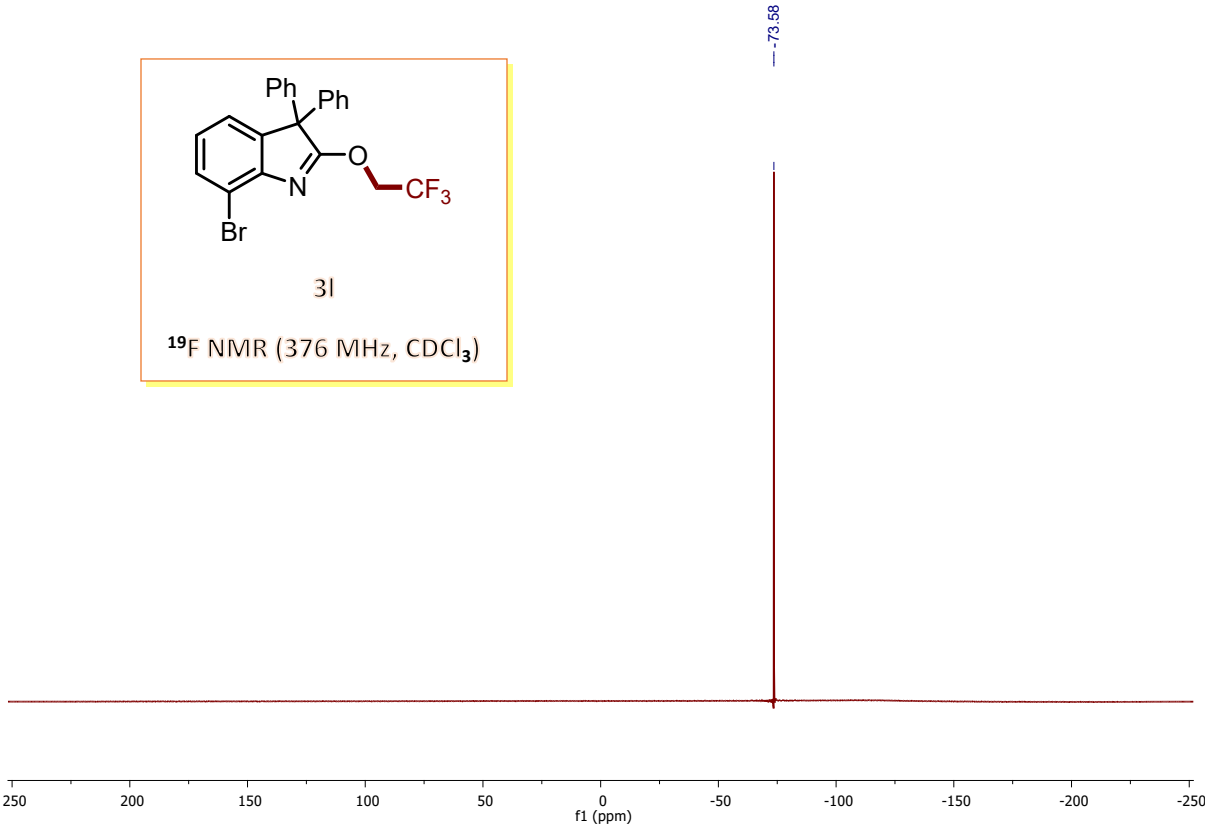
^{1}H NMR (400 MHz, $CDCl_3$)





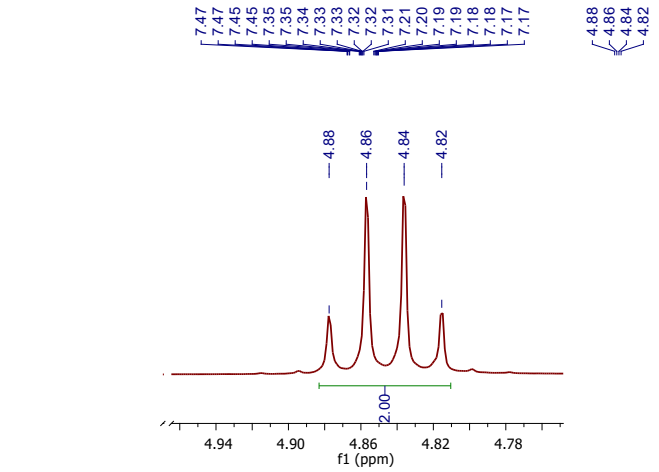
3l

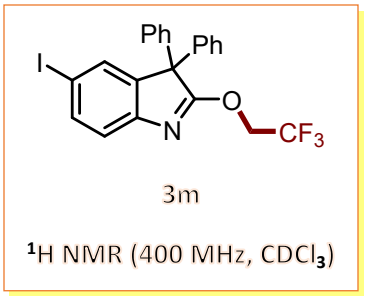
^{13}C NMR (101 MHz, $CDCl_3$)



3l

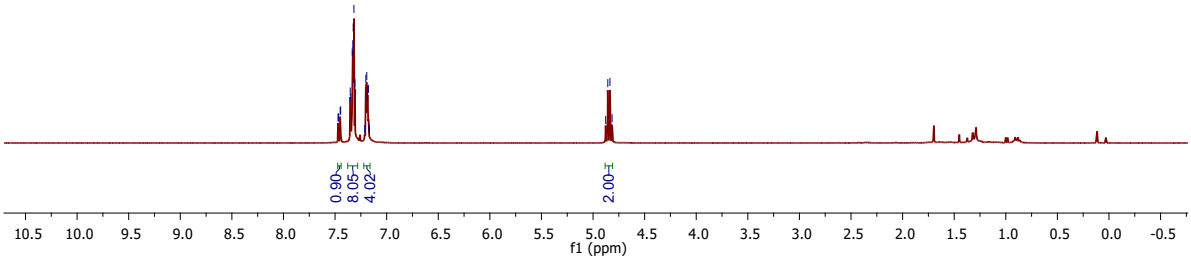
^{19}F NMR (376 MHz, $CDCl_3$)

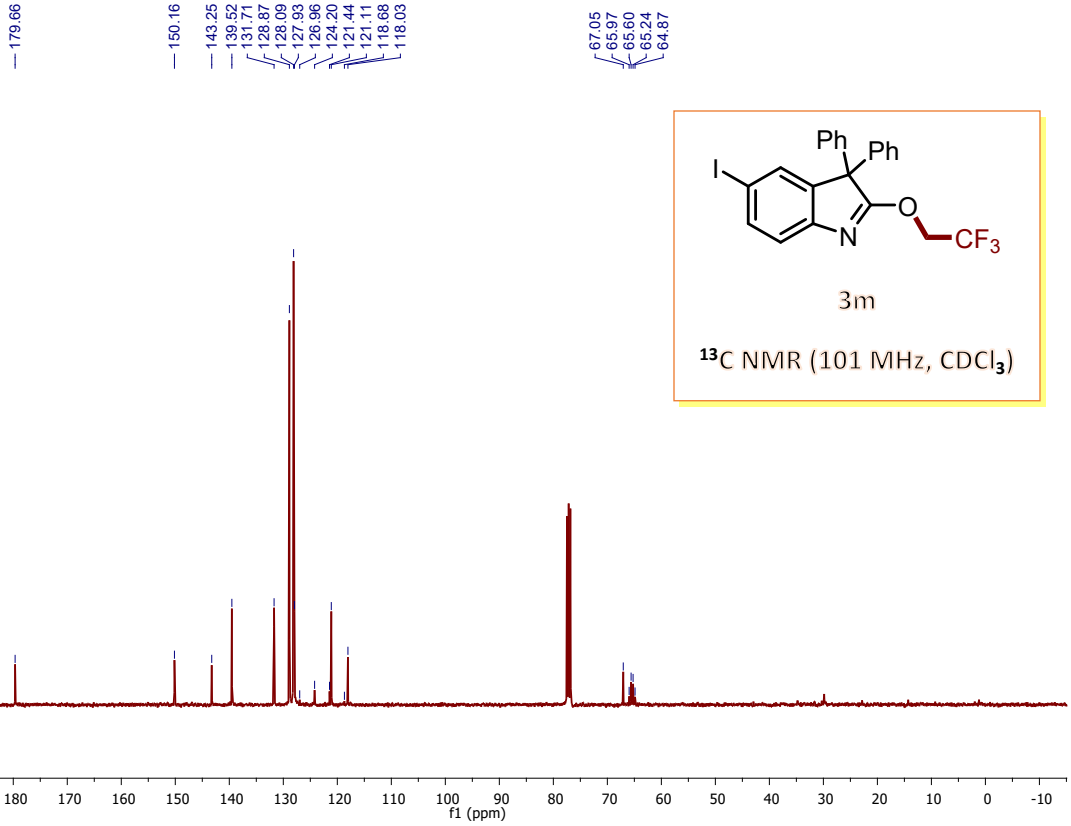




3m

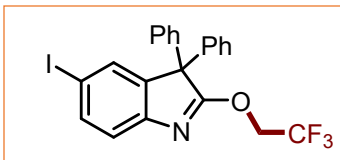
^{1}H NMR (400 MHz, $CDCl_3$)





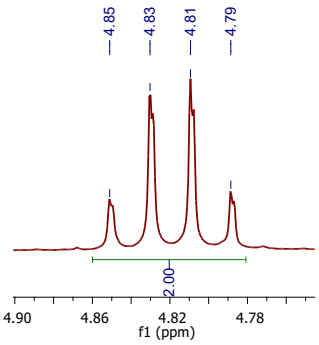
3m

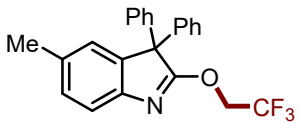
^{13}C NMR (101 MHz, $CDCl_3$)



3m

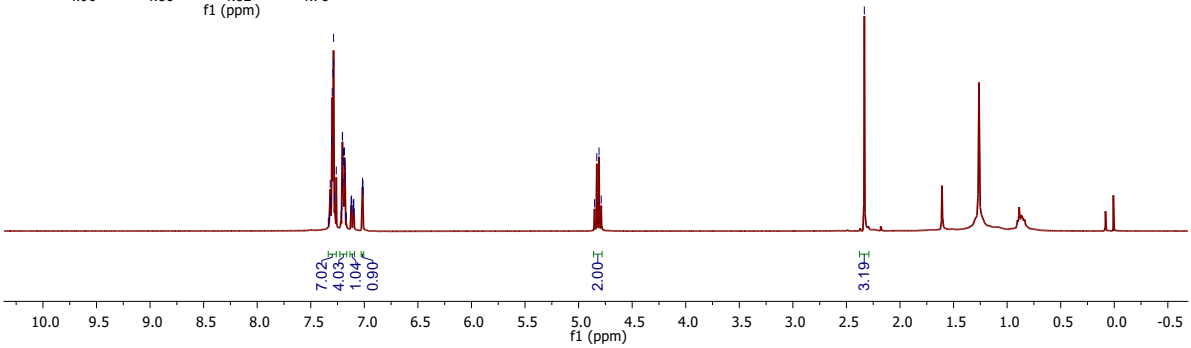
^{19}F NMR (376 MHz, $CDCl_3$)

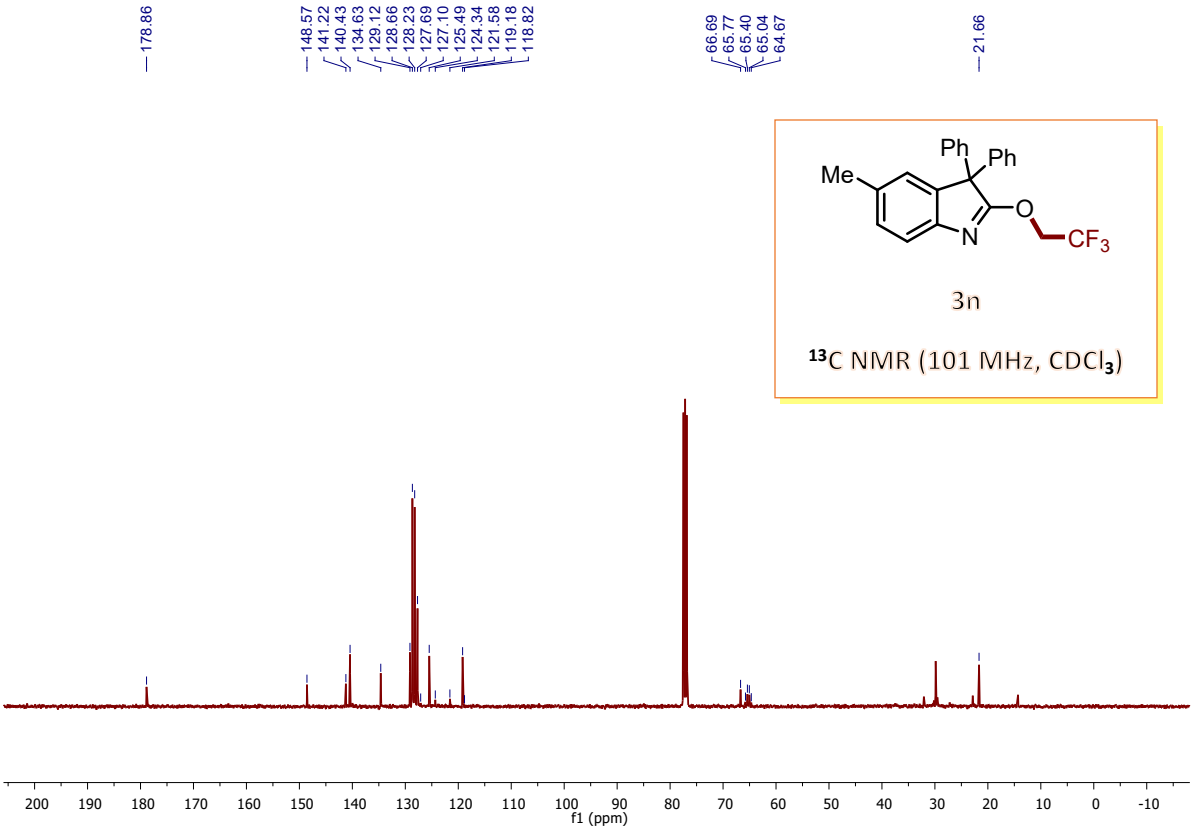


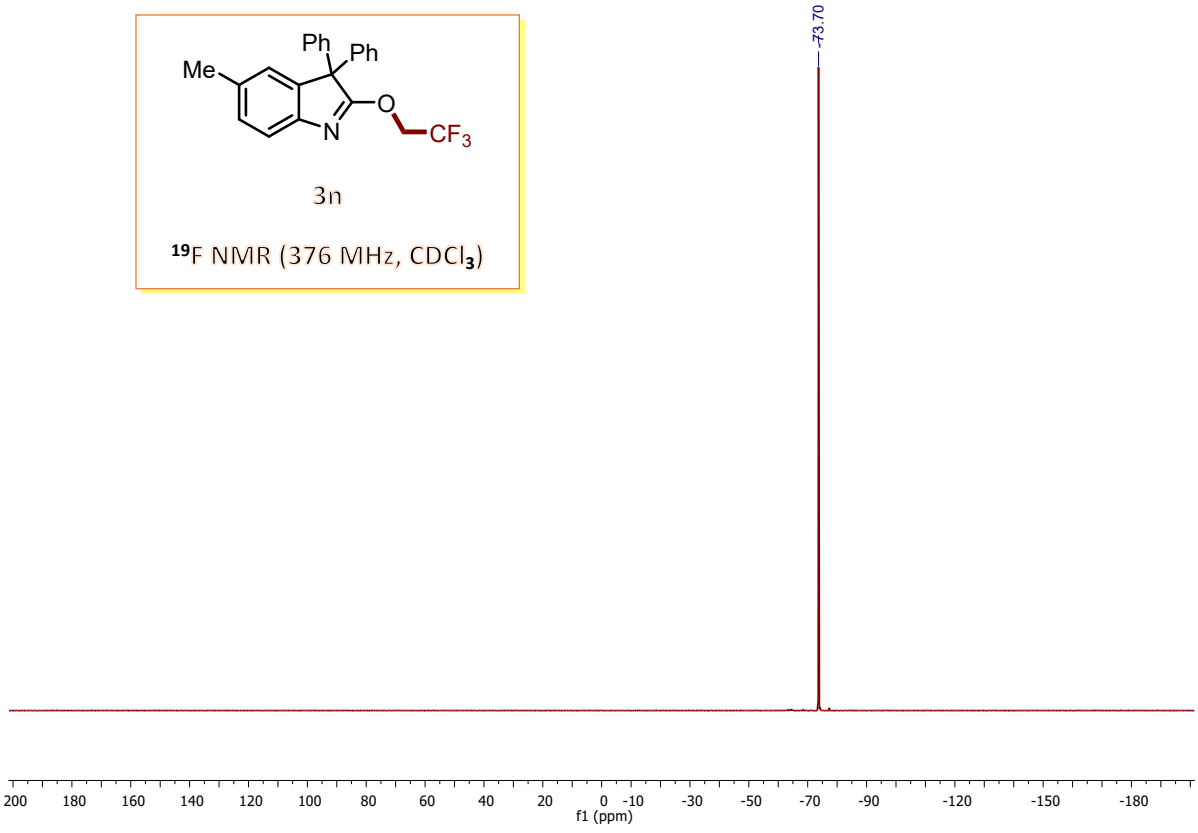


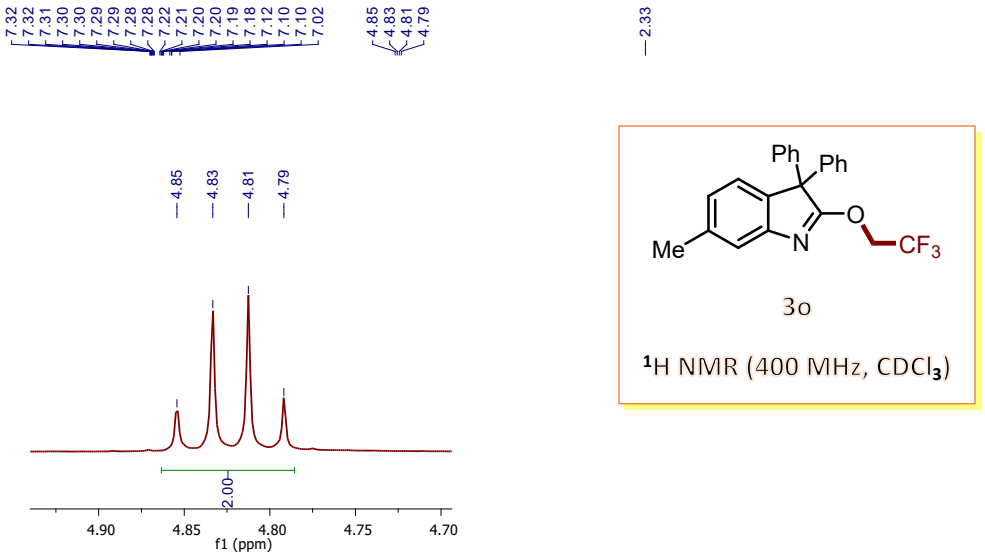
3n

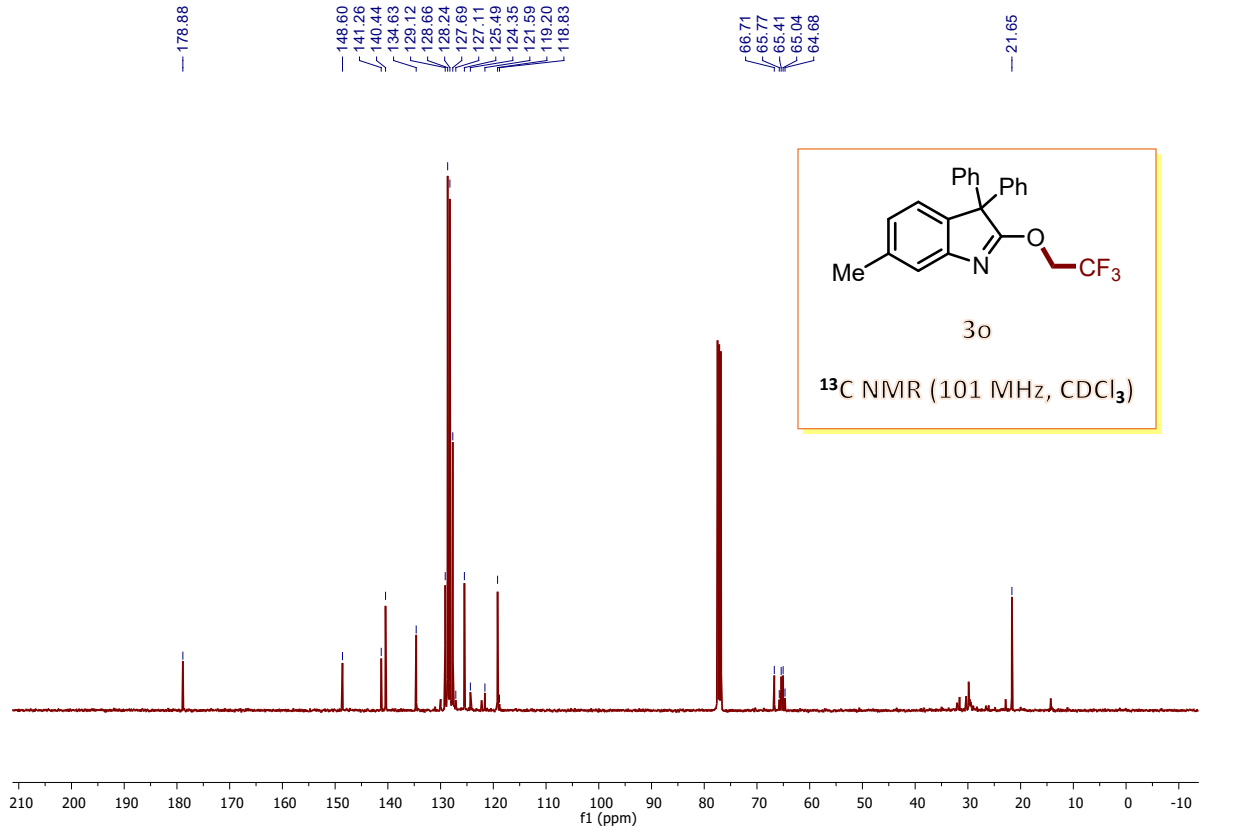
^{1}H NMR (400 MHz, $CDCl_3$)

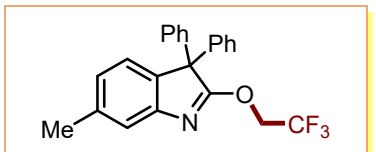



178.86
148.57
141.22
140.43
134.63
129.12
128.66
128.23
127.69
127.10
125.49
124.34
121.58
119.18
118.82
66.69
65.77
65.40
65.04
64.67
21.66
Ph
Ph
Me
O
N
CF3
3n
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-73.70
Ph
Ph
Me
O
N
CF3
3n
19F NMR (376 MHz, CDCl3)
f1 (ppm)

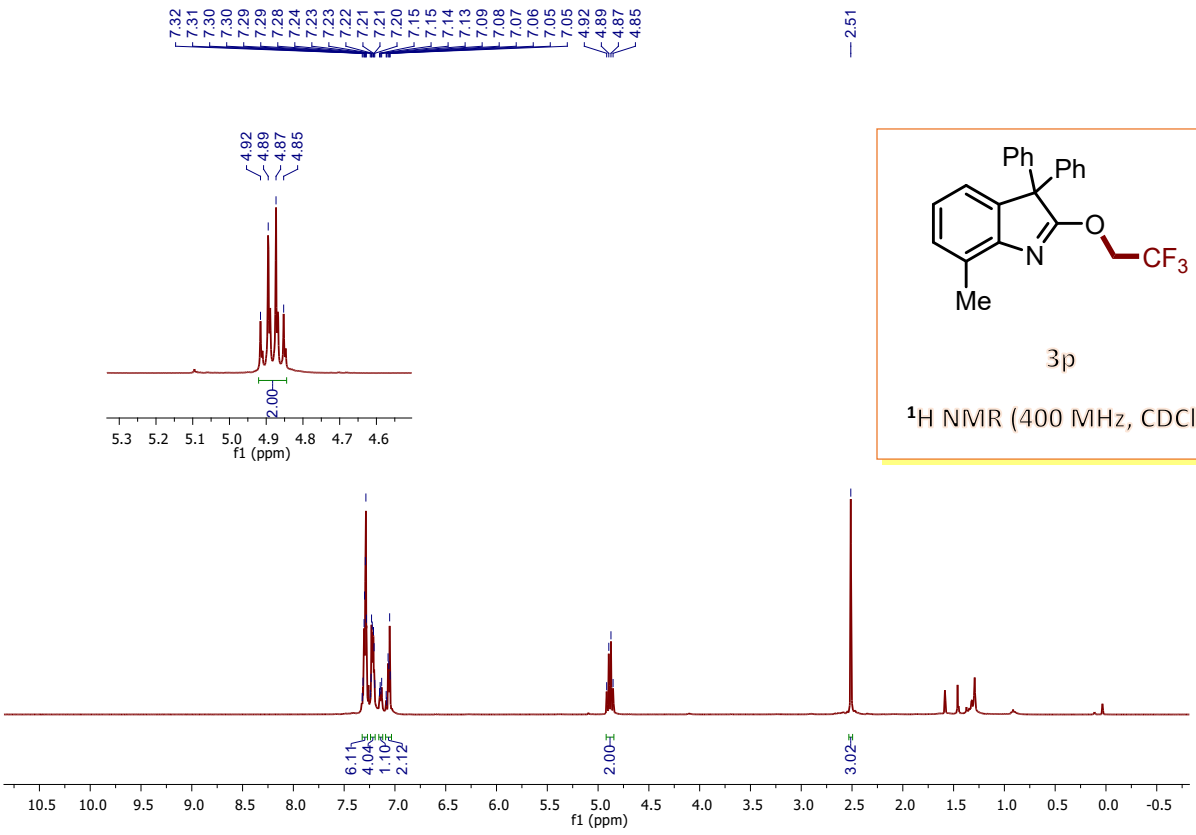

7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.22
7.21
7.20
7.20
7.19
7.18
7.12
7.10
7.10
7.02
4.85
4.83
4.81
4.79
2.33
4.85
4.83
4.81
4.79
2.00
4.90
4.85
4.80
4.75
4.70
f1 (ppm)
Ph
Ph
O
N
Me
CF3
3o
1H NMR (400 MHz, CDCl3)
7.00
4.03
1.08
0.91
2.00
3.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


178.88
148.60
141.26
140.44
134.63
129.12
128.66
128.24
127.69
127.11
125.49
124.35
121.59
119.20
118.83
66.71
65.77
65.41
65.04
64.68
21.65
Ph
Ph
O
N
Me
CF3
3o
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)



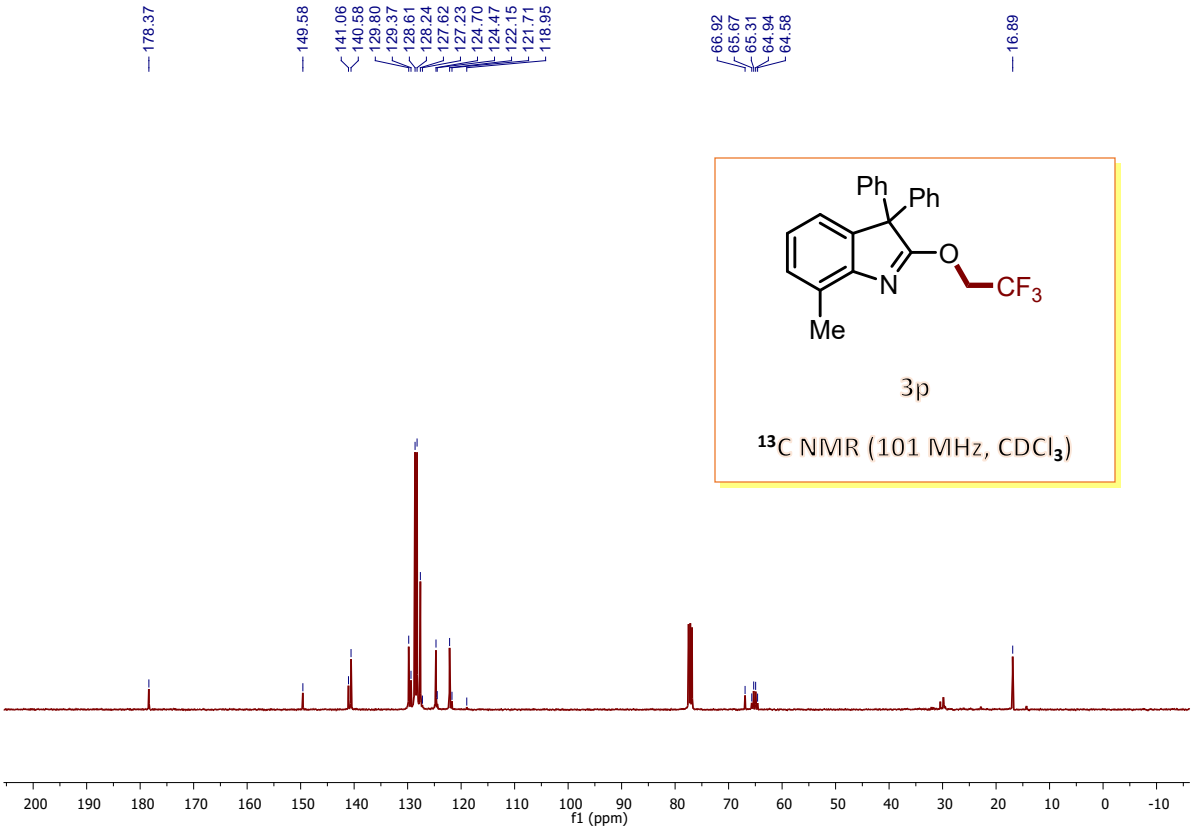
3o

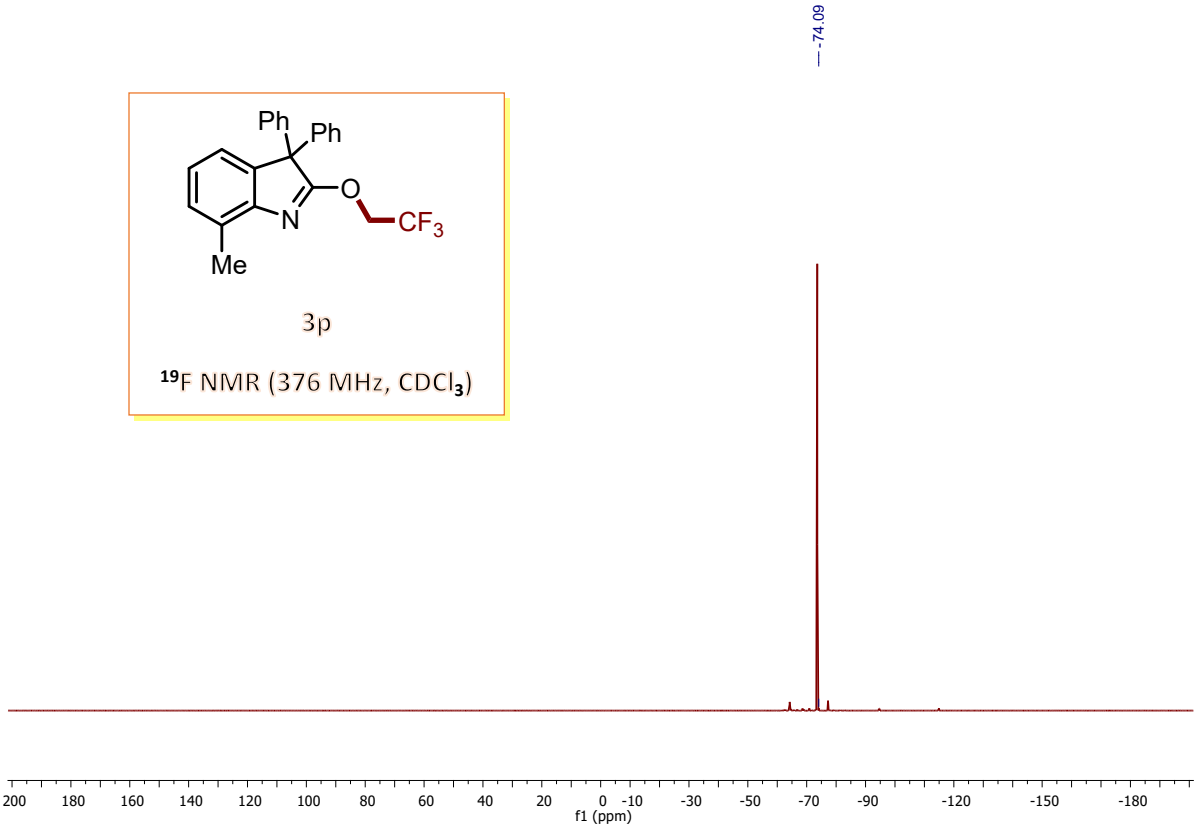
^{19}F NMR (376 MHz, $CDCl_3$)

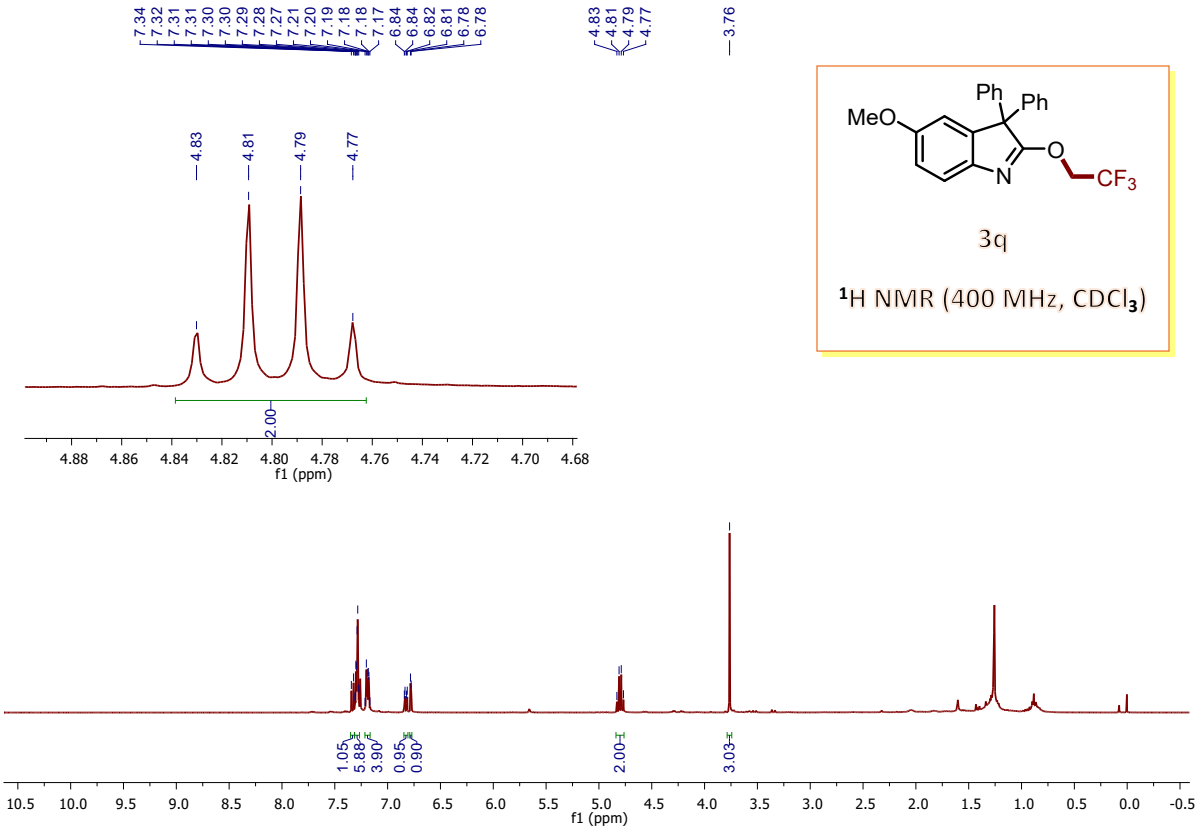


3p

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

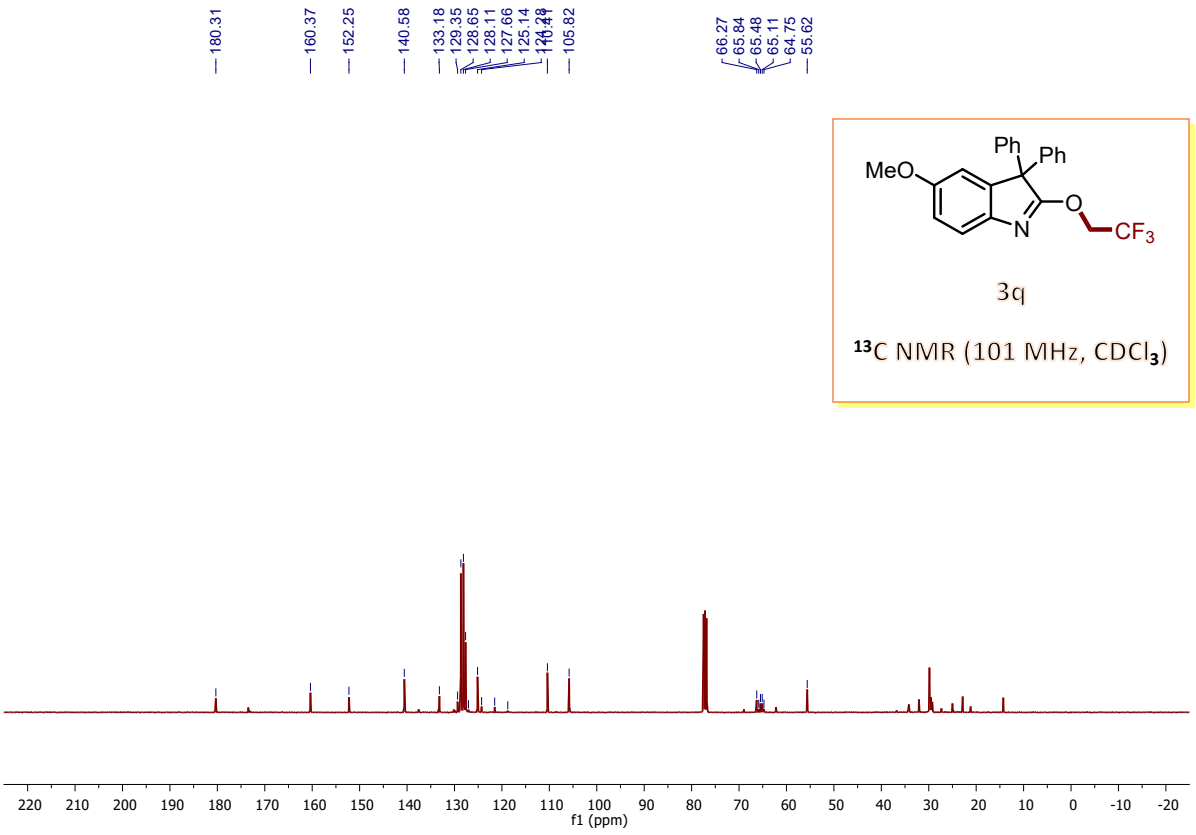

178.37
149.58
141.06
140.58
129.80
129.37
128.61
128.24
127.62
127.23
124.70
124.47
122.15
121.71
118.95
66.92
65.67
65.31
64.94
64.58
16.89
Ph
Ph
O
N
CF3
Me
3p
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-74.09
Ph
Ph
O
N
CF3
Me
3p
19F NMR (376 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)



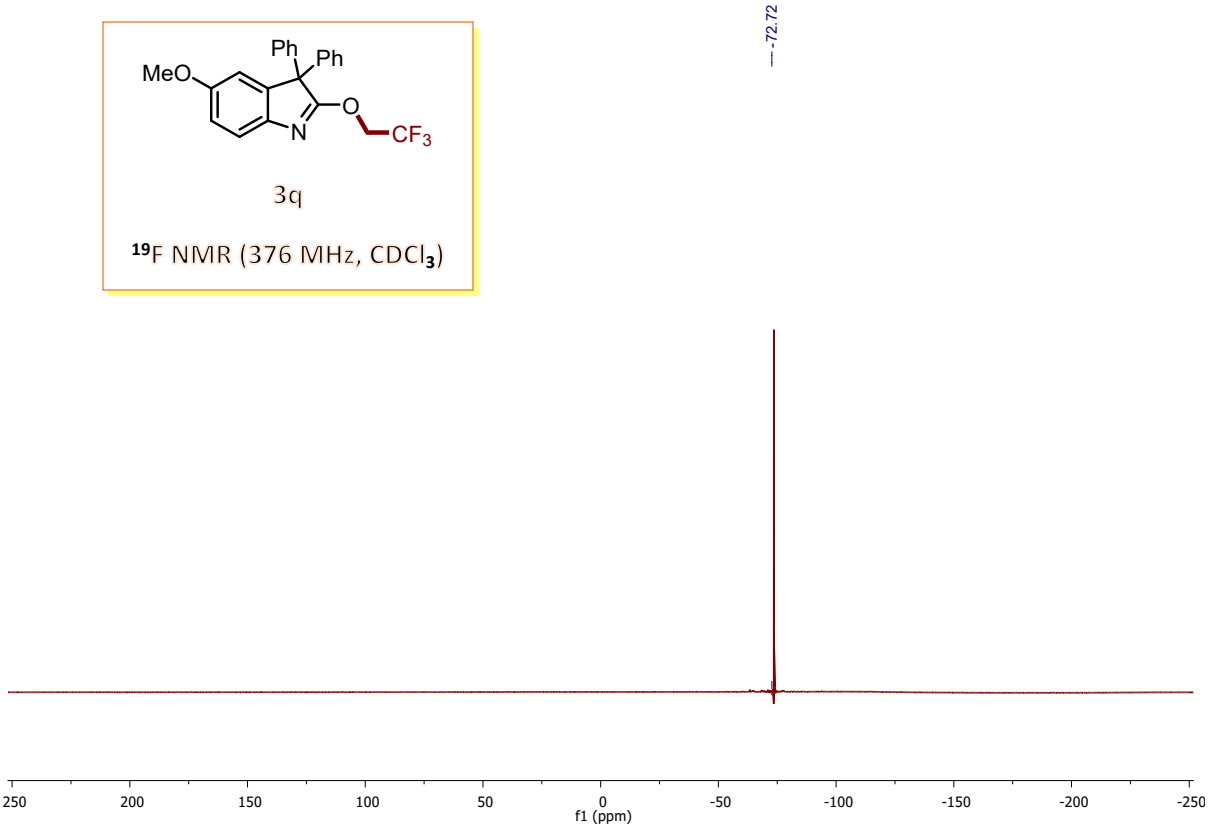
3q

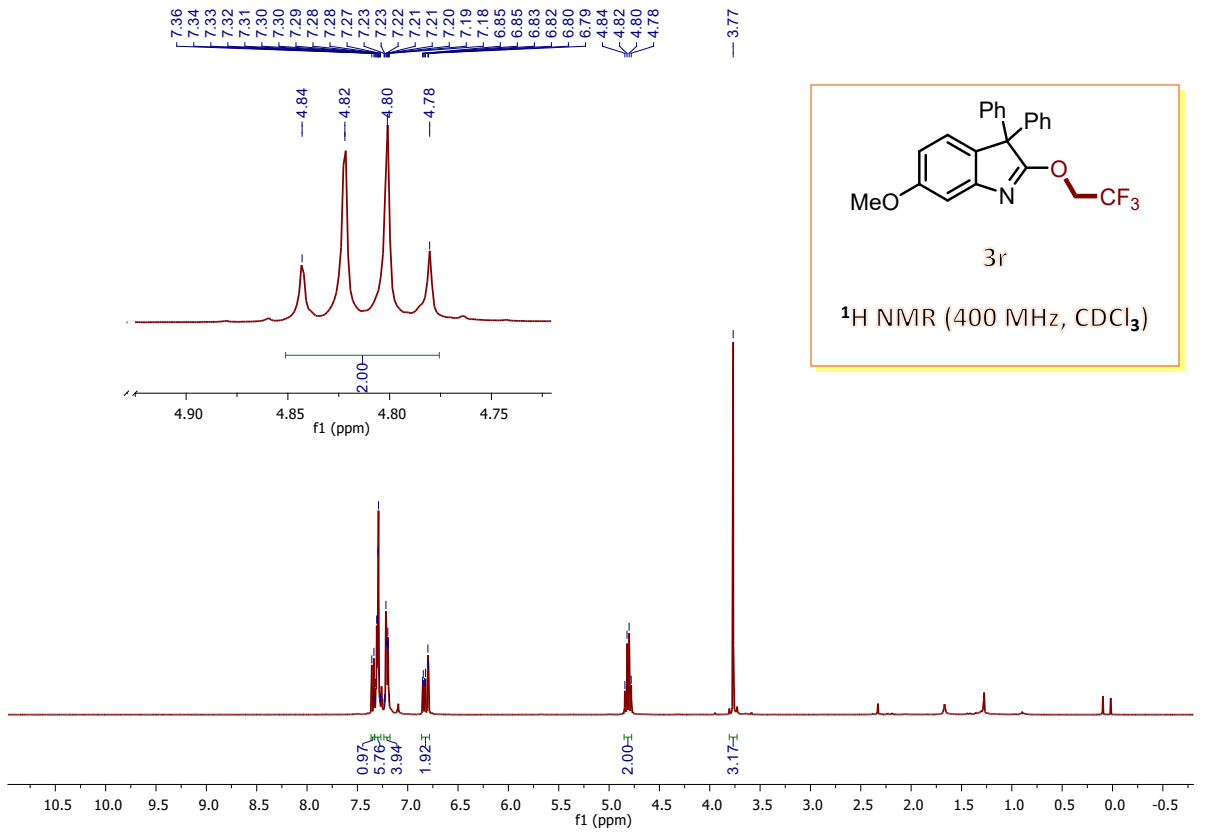
^{1}H NMR (400 MHz, $CDCl_3$)

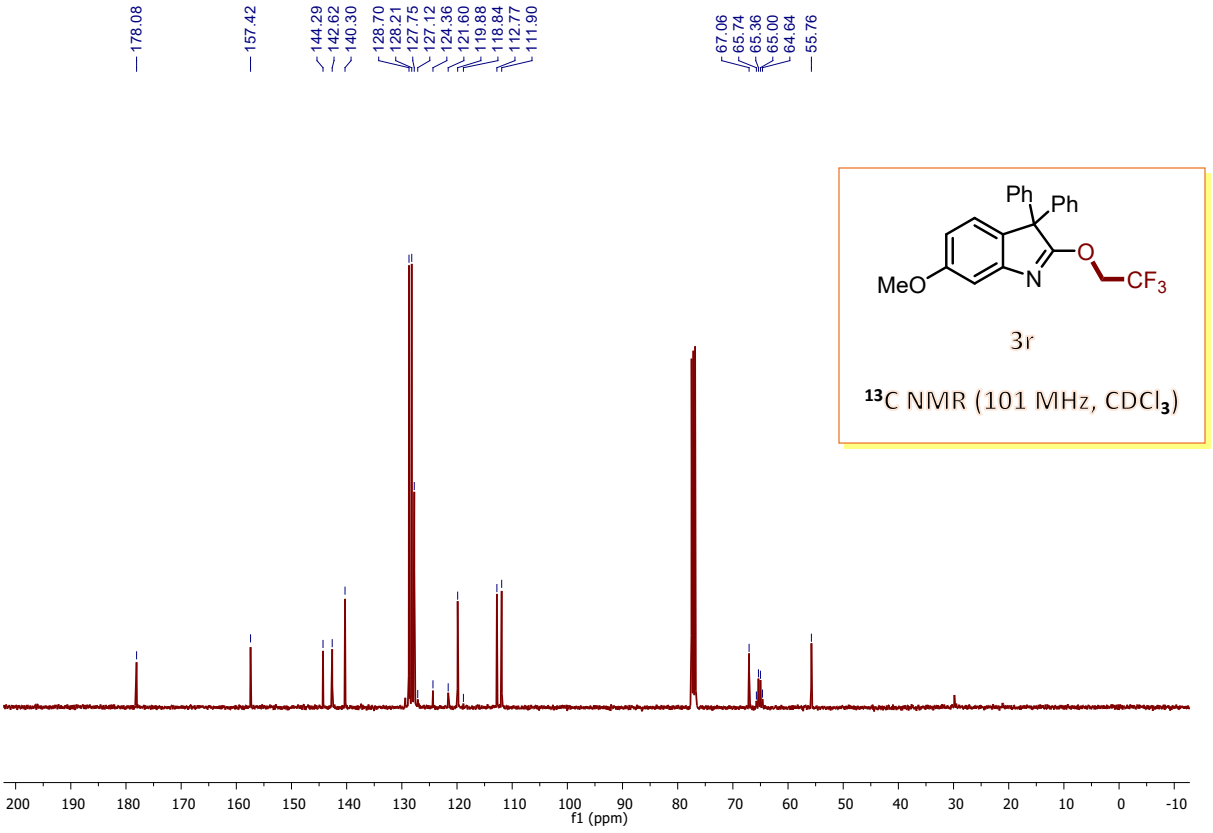


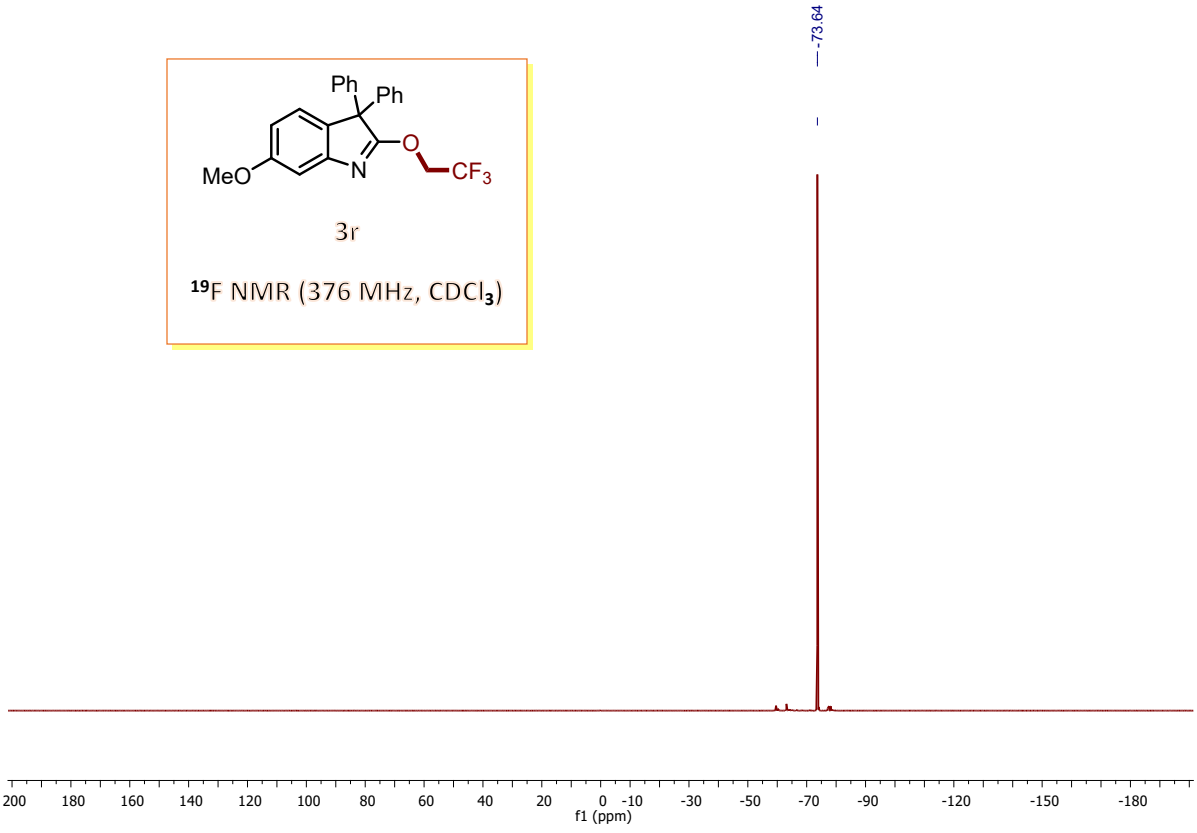
3q

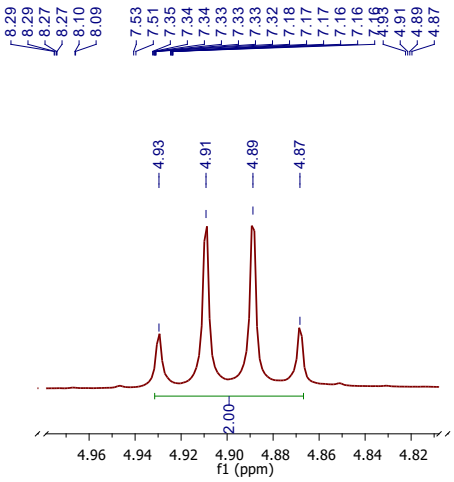
^{13}C NMR (101 MHz, $CDCl_3$)

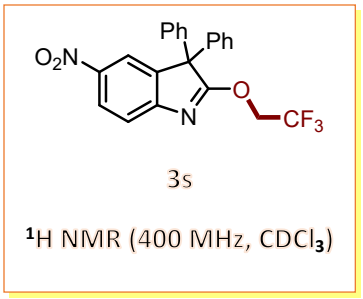

Ph
Ph
MeO
O
N
CF3
3q
19F NMR (376 MHz, CDCl3)
-72.72
250
200
150
100
50
0
-50
-100
-150
-200
-250
f1 (ppm)


7.36
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.18
6.85
6.85
6.83
6.82
6.80
6.79
4.84
4.82
4.80
4.78
3.77
4.84
4.82
4.80
4.78
2.00
4.90
4.85
4.80
4.75
f1 (ppm)
Ph
Ph
MeO
O
N
CF3
3r
1H NMR (400 MHz, CDCl3)
0.97
5.76
3.94
1.92
2.00
3.17
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


178.08
157.42
144.29
142.62
140.30
128.70
128.21
127.75
127.12
124.36
121.60
119.88
118.84
112.77
111.90
67.06
65.74
65.36
65.00
64.64
55.76
Ph
Ph
MeO
N
O
CF3
3r
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 -10
f1 (ppm)

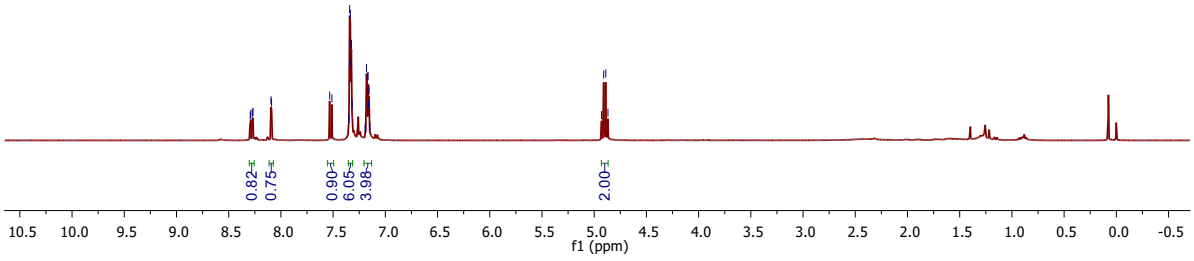

-73.64
Ph
Ph
MeO
N
O
CF3
3r
19F NMR (376 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

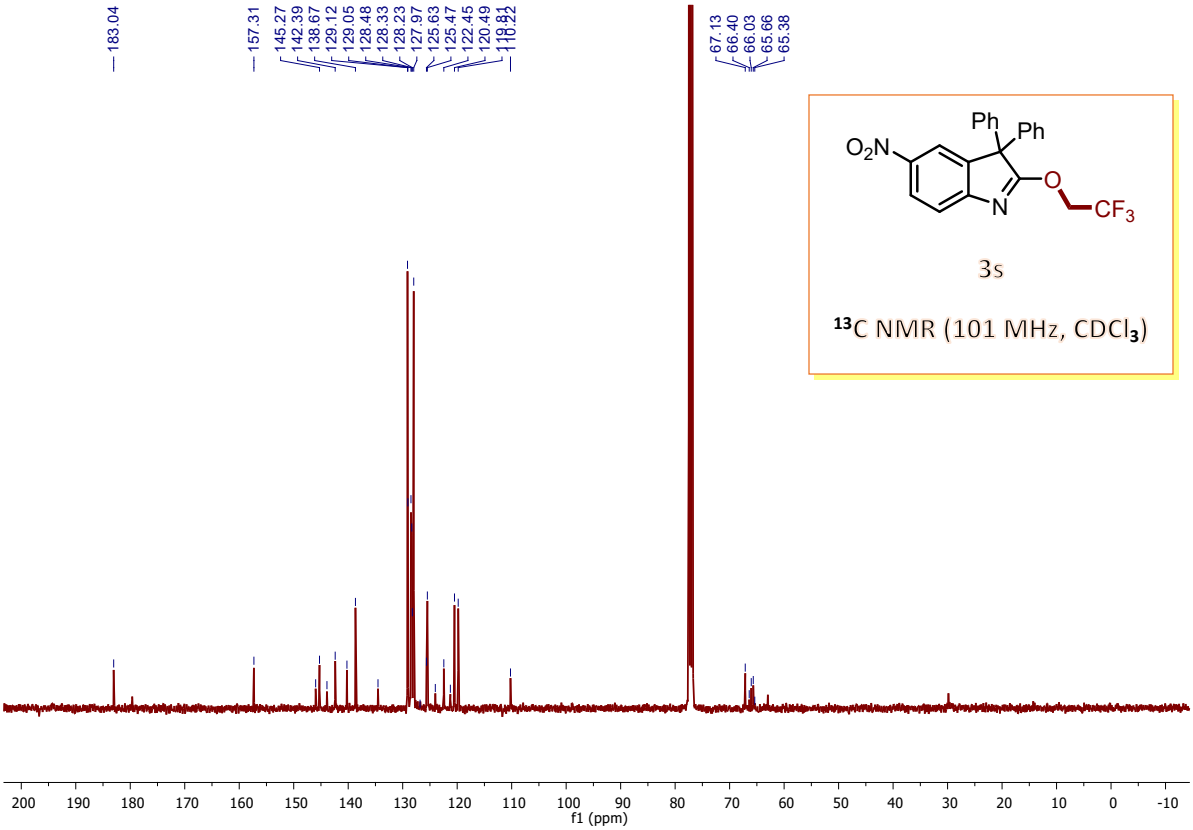




3s

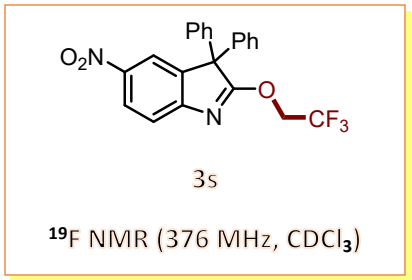
^{1}H NMR (400 MHz, $CDCl_3$)





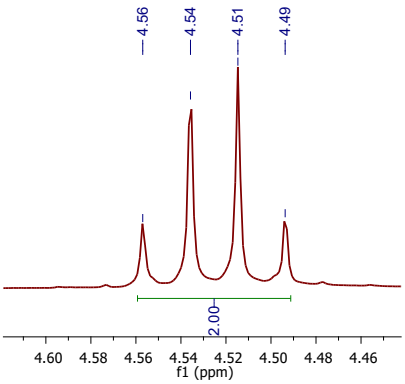
3s

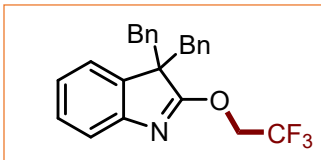
^{13}C NMR (101 MHz, $CDCl_3$)



3s

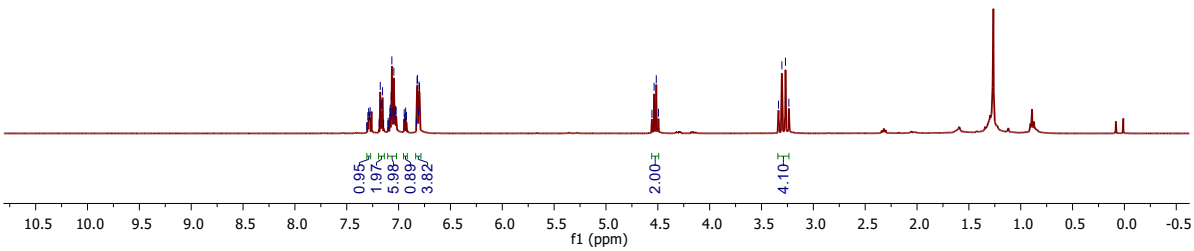
^{19}F NMR (376 MHz, $CDCl_3$)

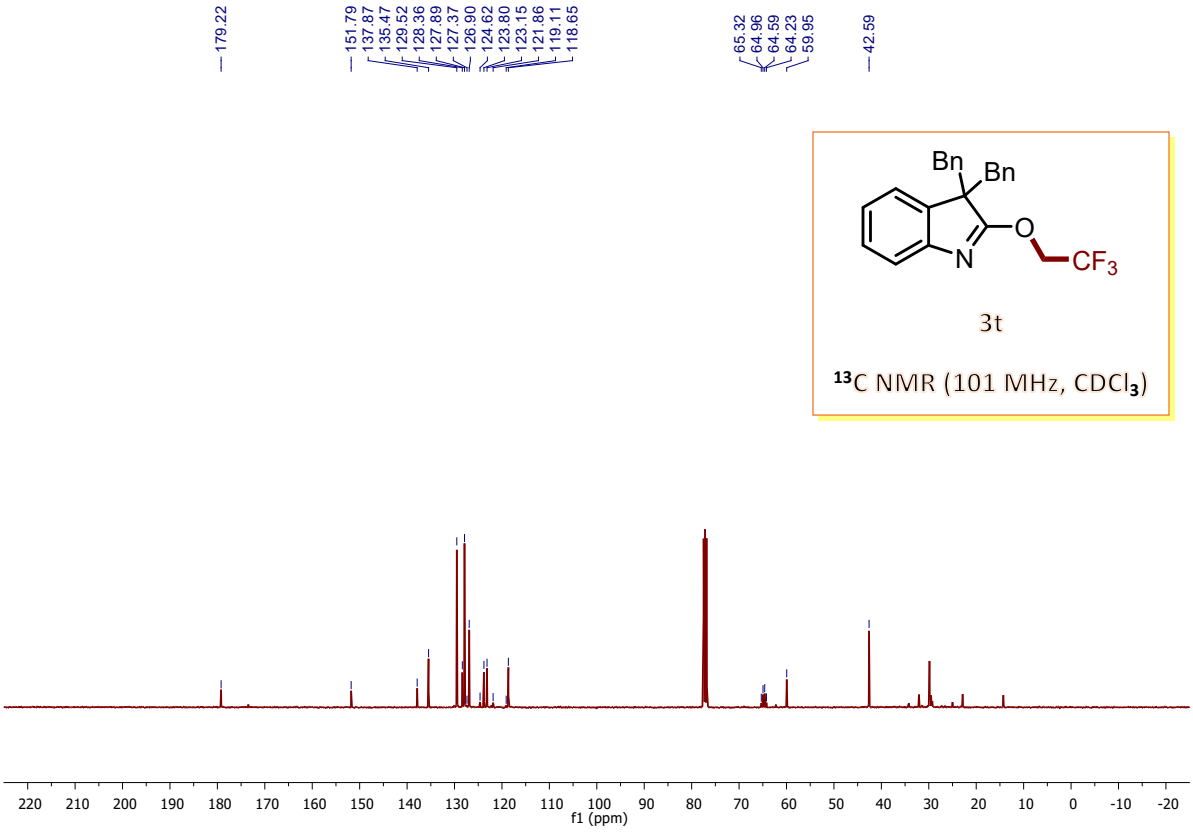


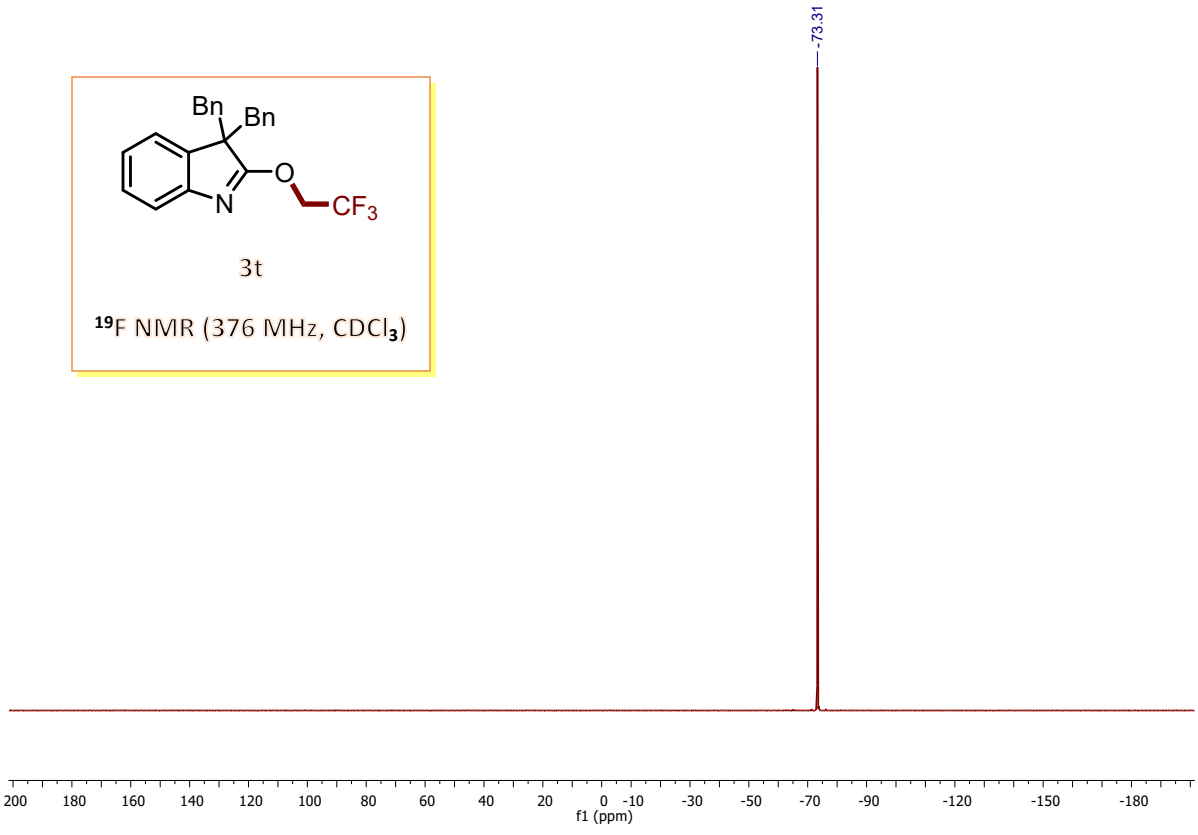


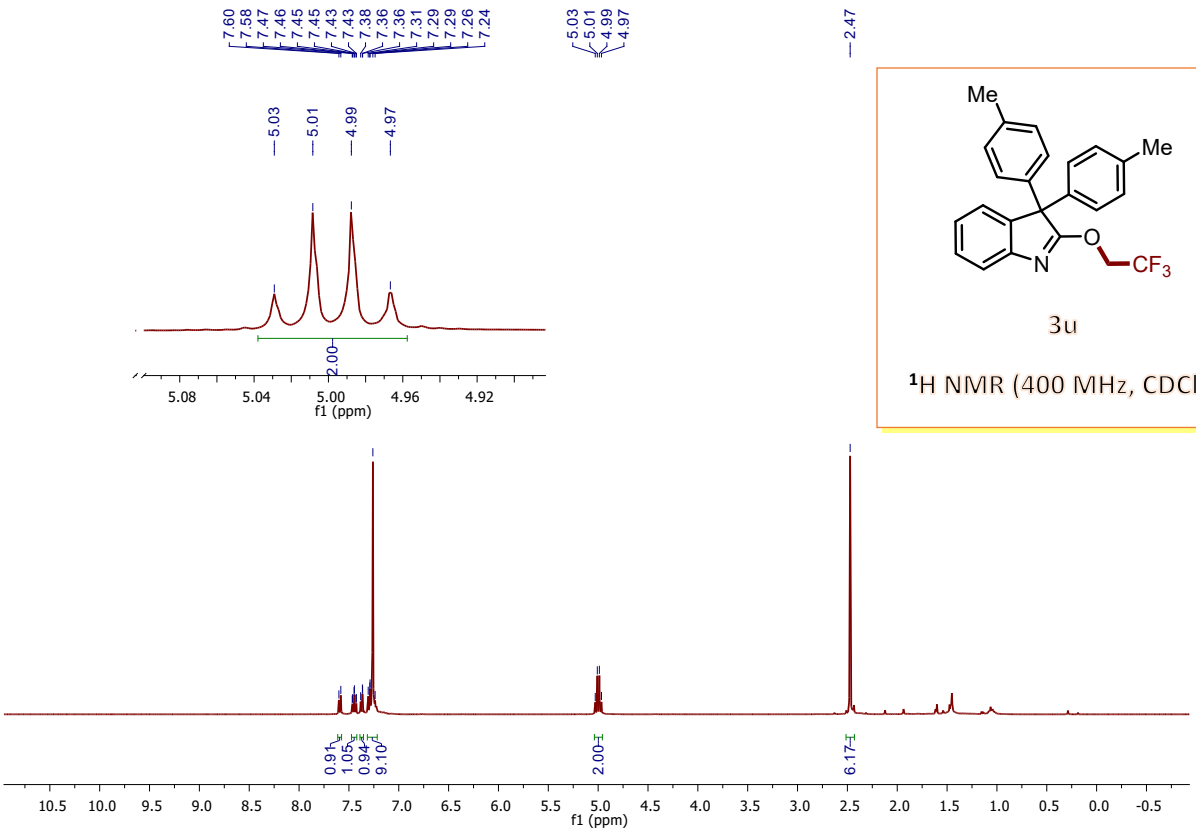
3t

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



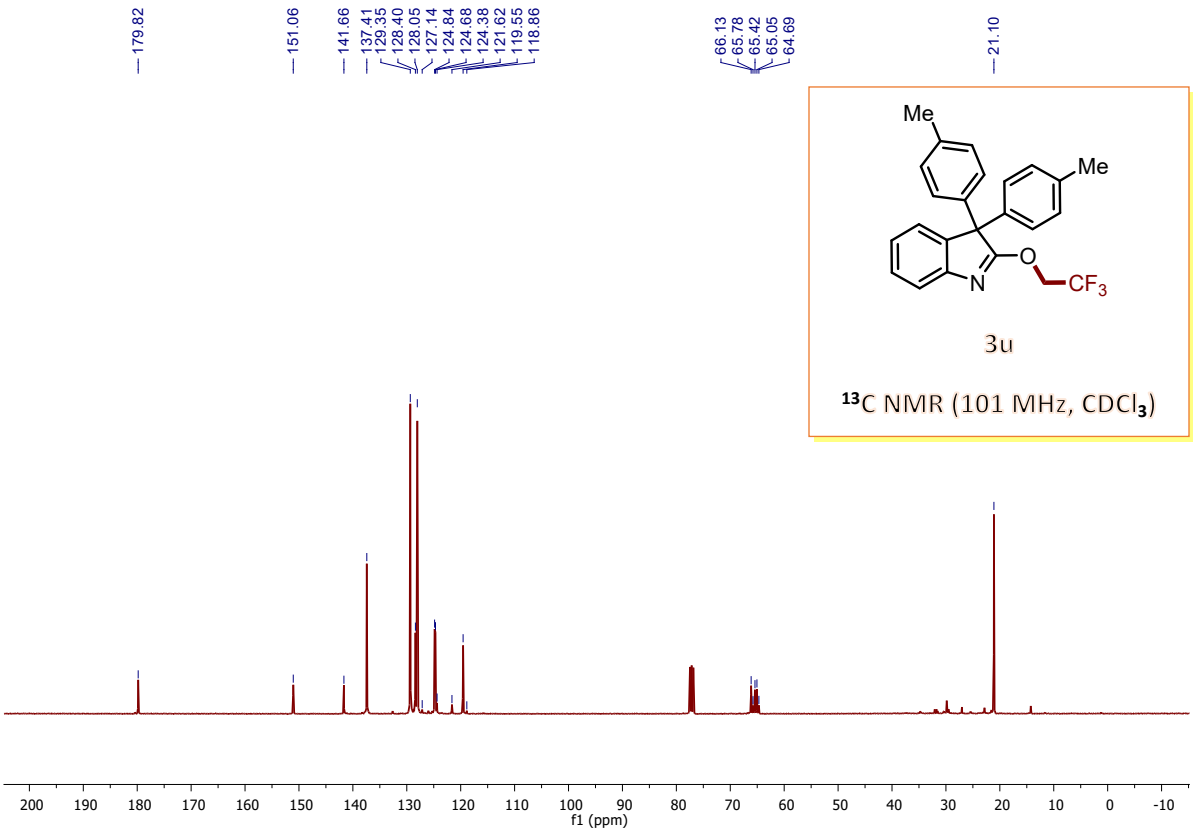

179.22
151.79
137.87
135.47
129.52
128.36
127.89
127.37
126.90
124.62
123.80
123.15
121.86
119.11
118.65
65.32
64.96
64.59
64.23
59.95
42.59
Bn
Bn
O
N
CF3
3t
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-73.31
Bn
Bn
O
N
CF3
3t
19F NMR (376 MHz, CDCl3)
f1 (ppm)



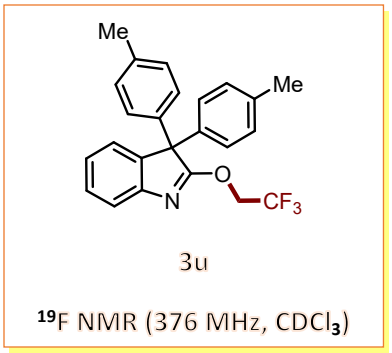
3u

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



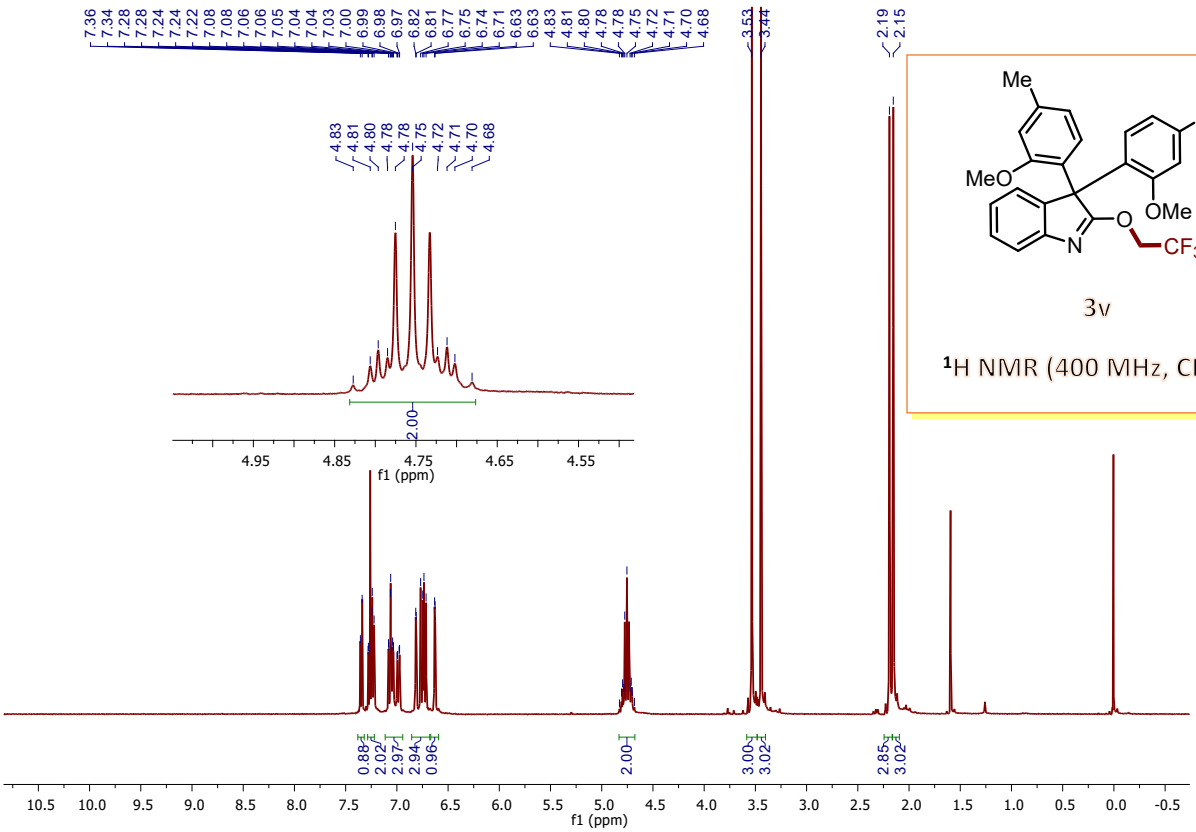
3u

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



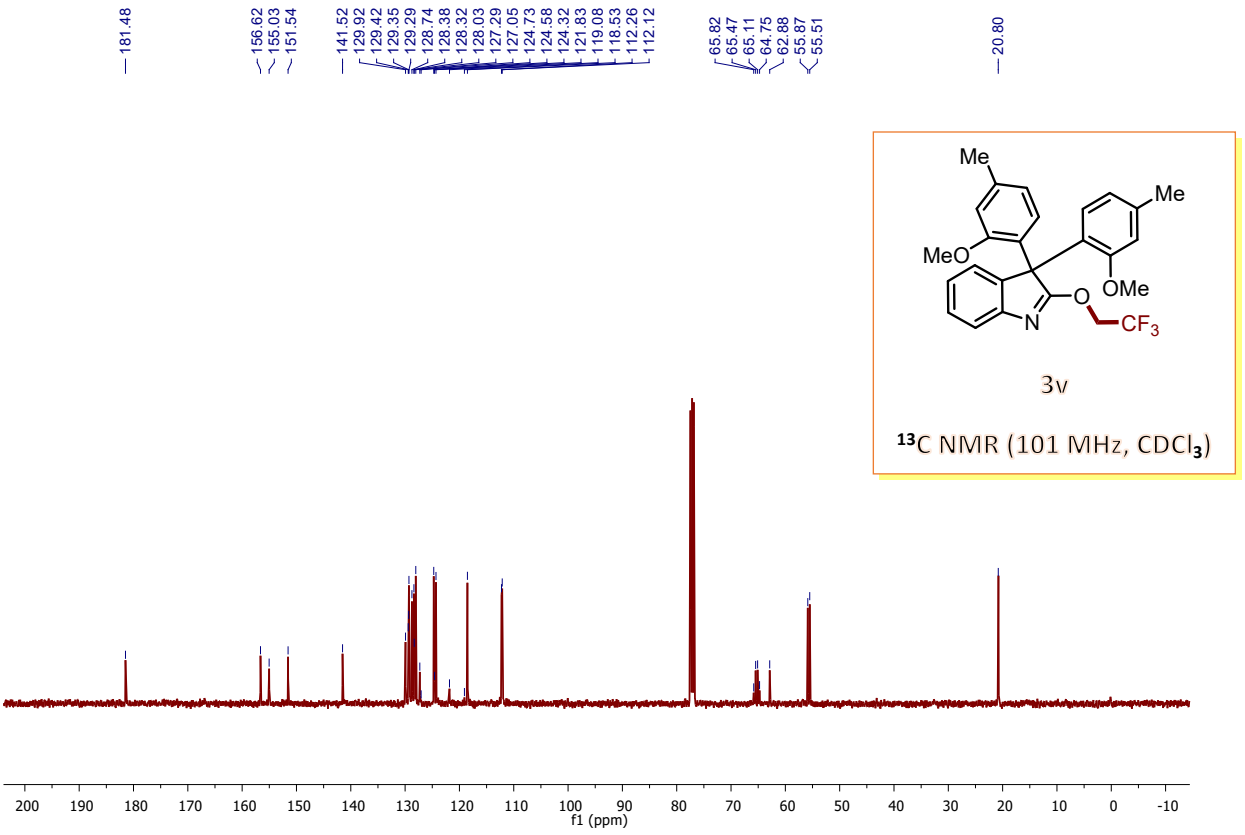
3u

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



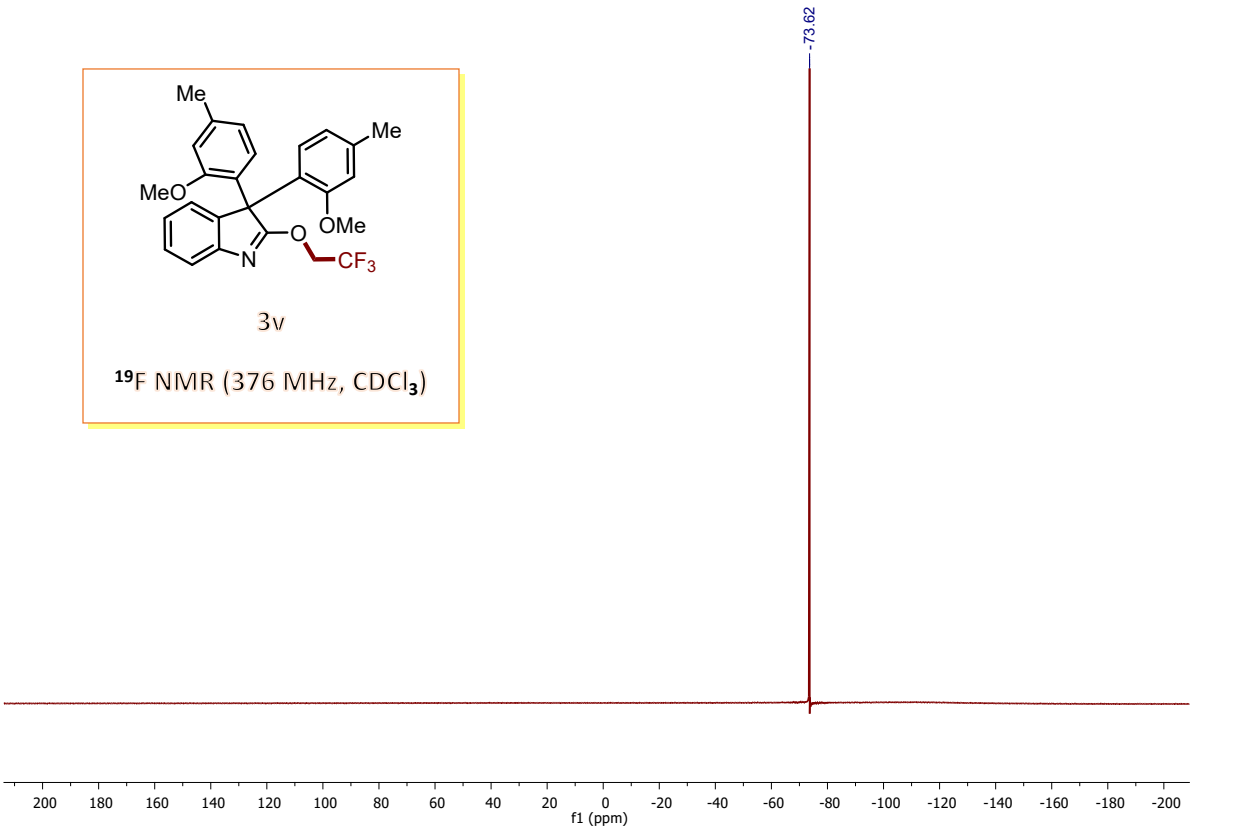
3v

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



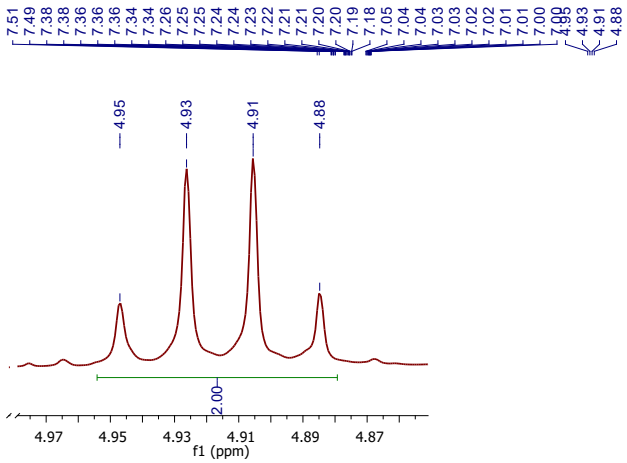
3v

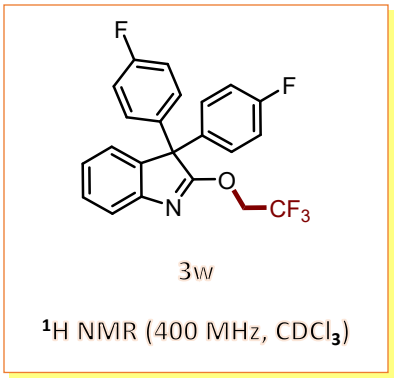
^{13}C NMR (101 MHz, $CDCl_3$)



3v

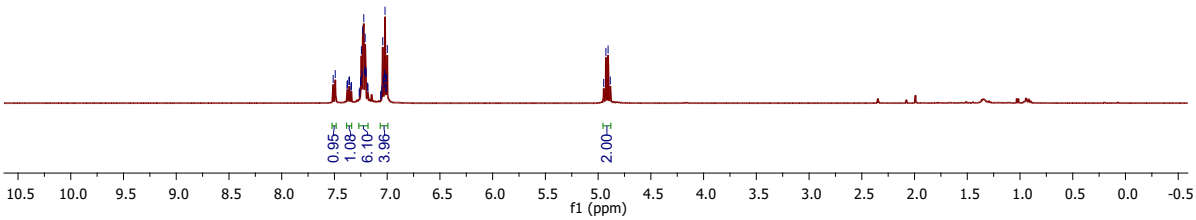
^{19}F NMR (376 MHz, $CDCl_3$)

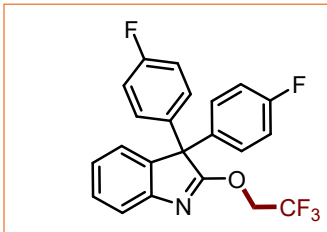




3w

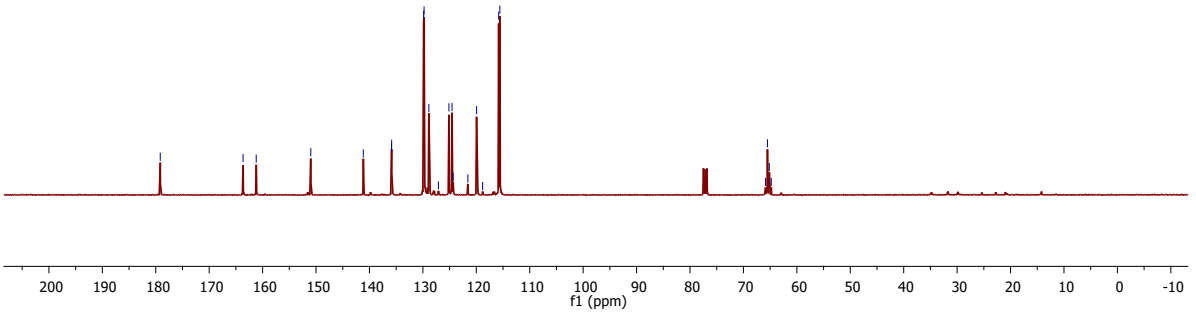
^{1}H NMR (400 MHz, $CDCl_3$)

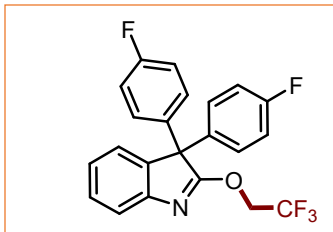




3w

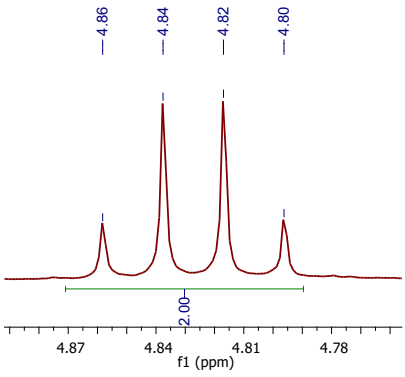
^{13}C NMR (101 MHz, $CDCl_3$)

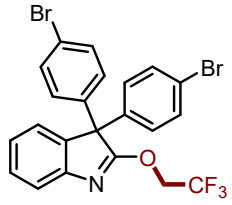




3w

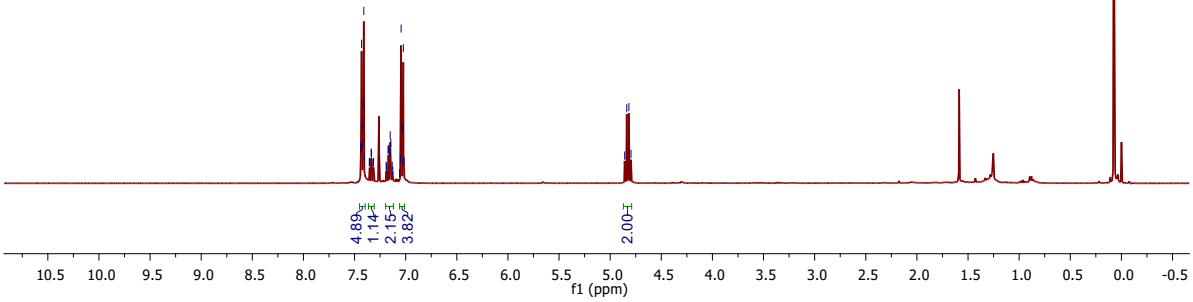
^{19}F NMR (376 MHz, $CDCl_3$)

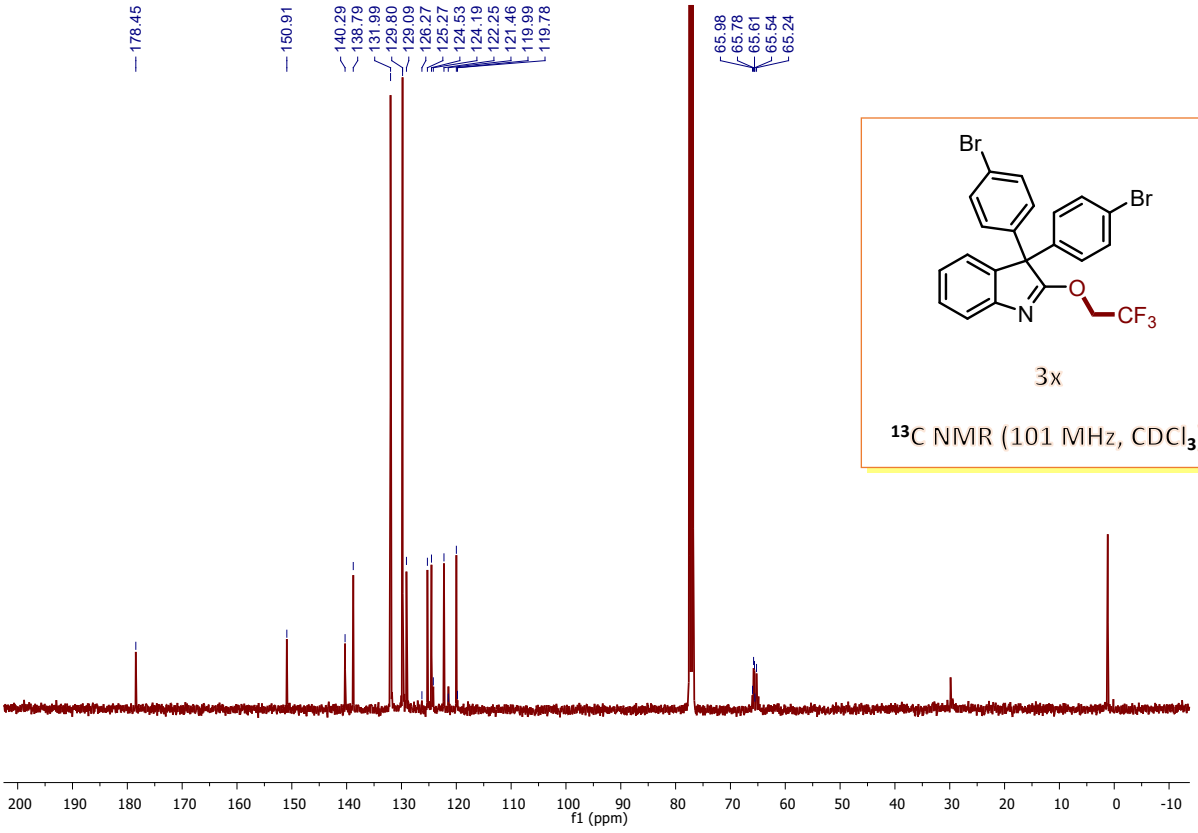




3x

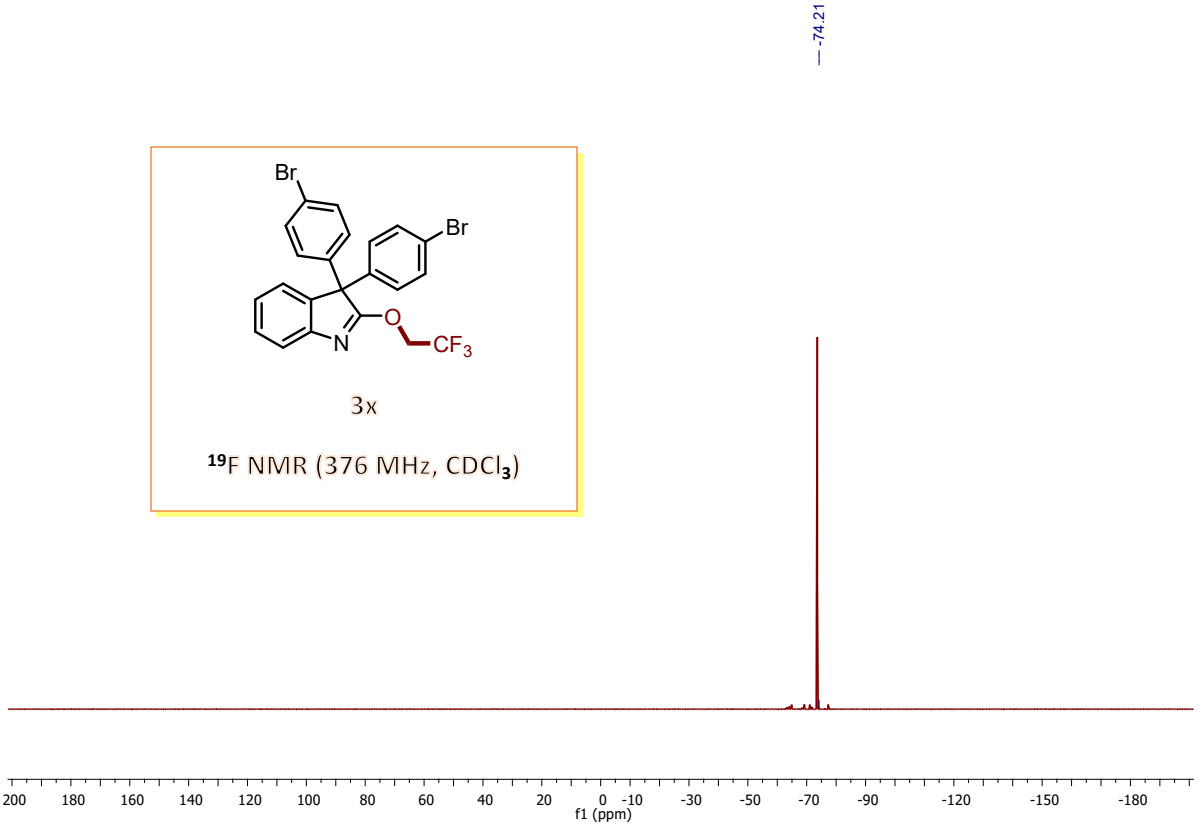
^{1}H NMR (400 MHz, $CDCl_3$)





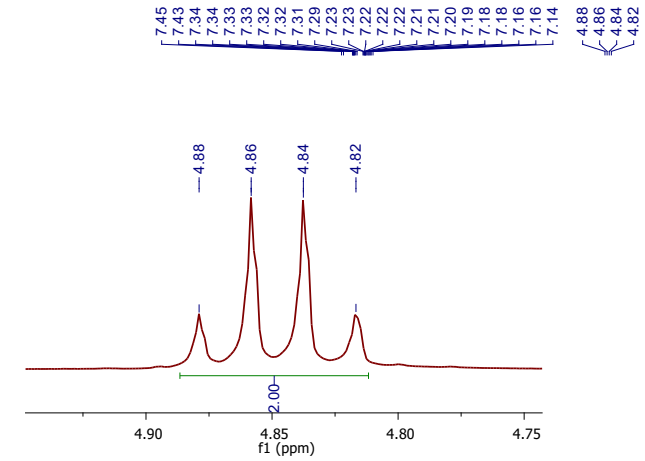
3x

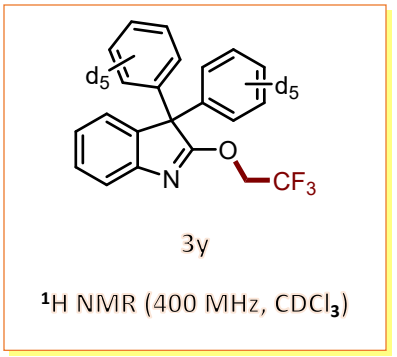
^{13}C NMR (101 MHz, $CDCl_3$)



3x

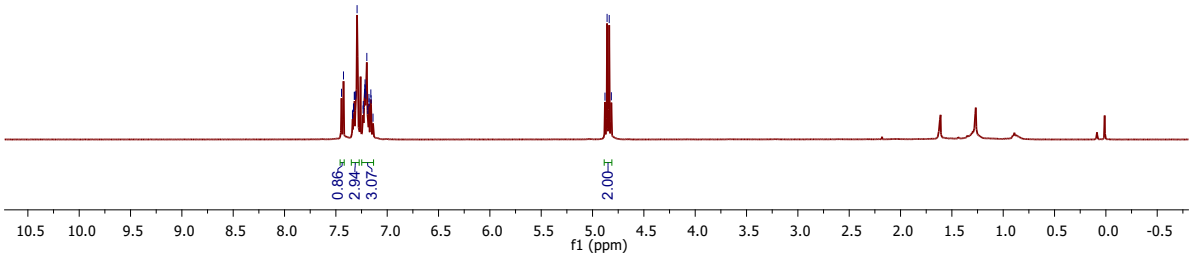
^{19}F NMR (376 MHz, $CDCl_3$)

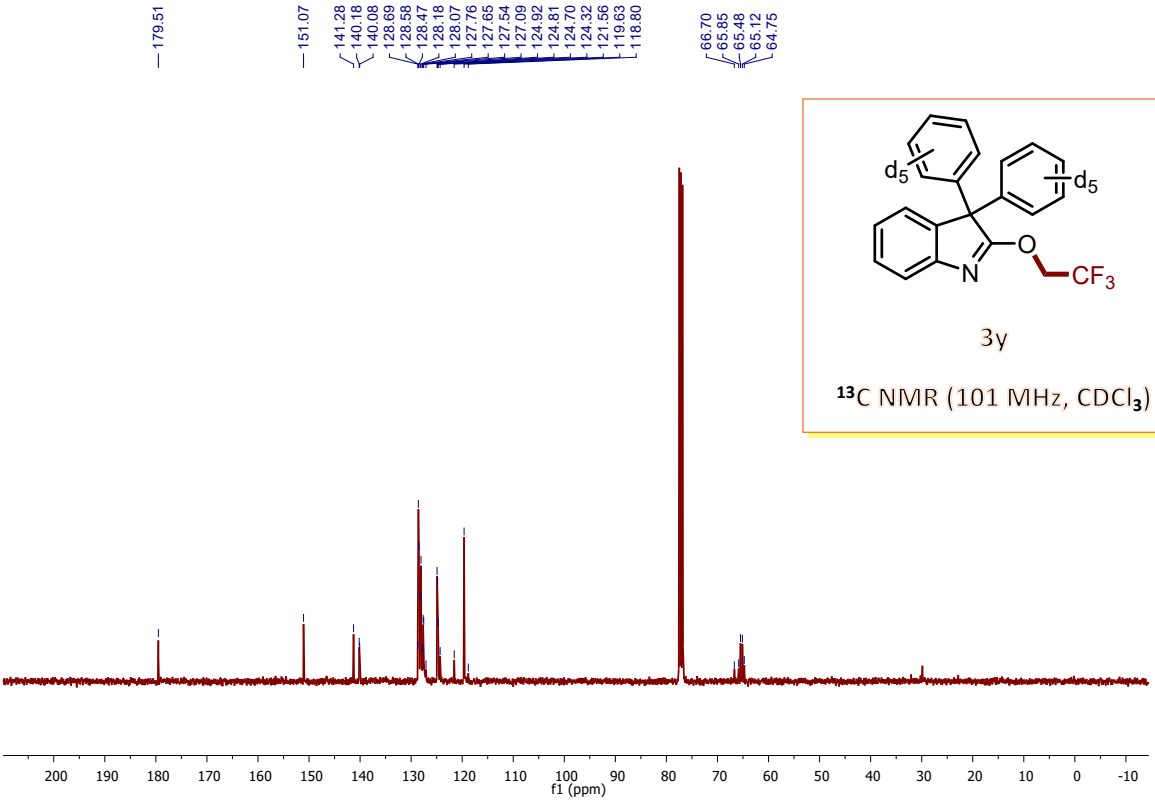




3y

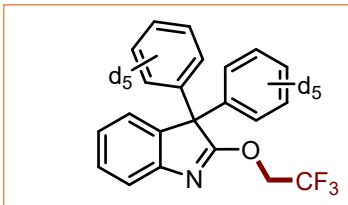
^{1}H NMR (400 MHz, $CDCl_3$)





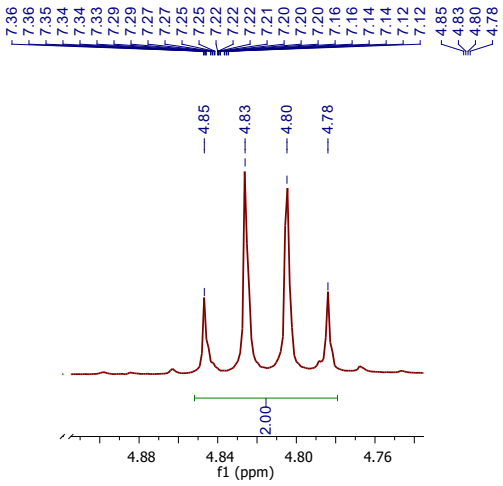
3y

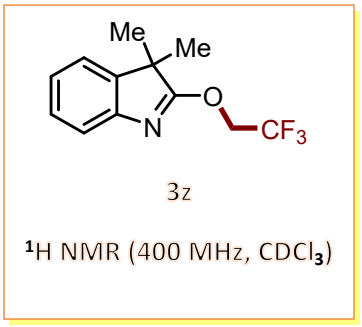
^{13}C NMR (101 MHz, $CDCl_3$)



3y

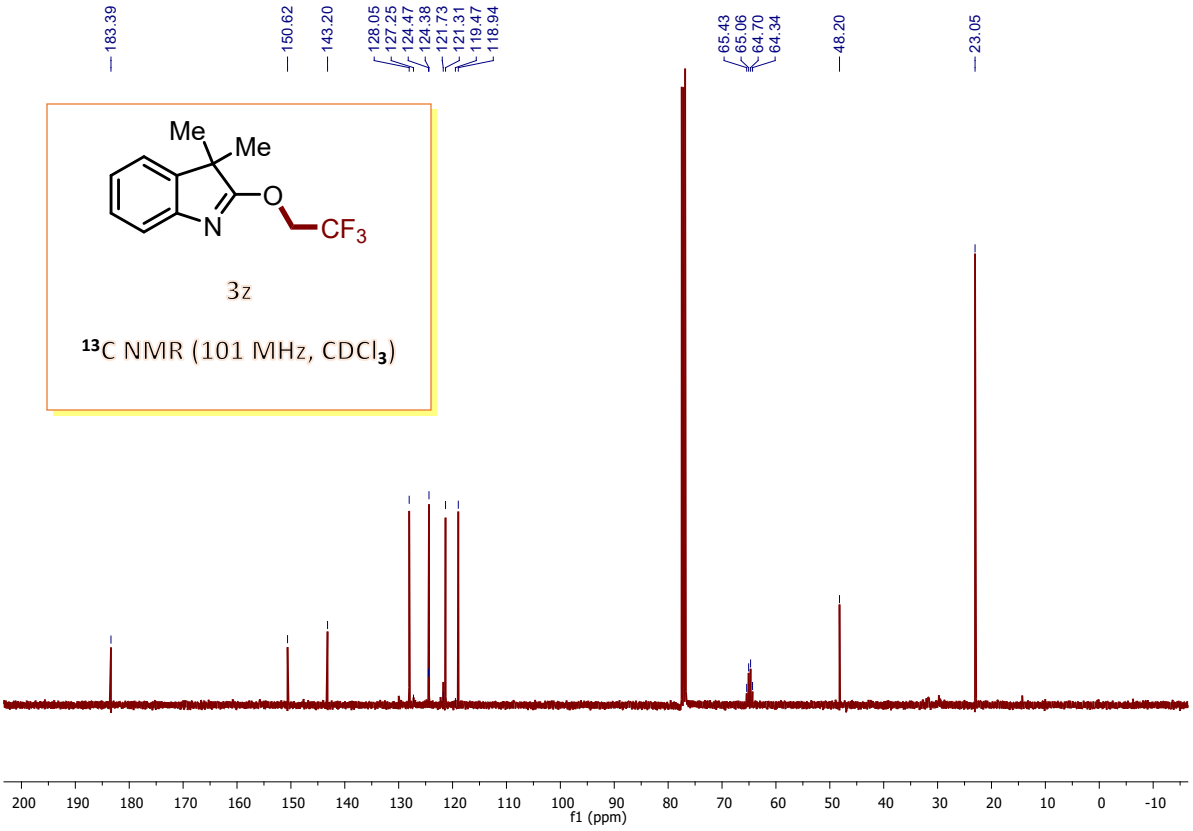
^{19}F NMR (376 MHz, $CDCl_3$)





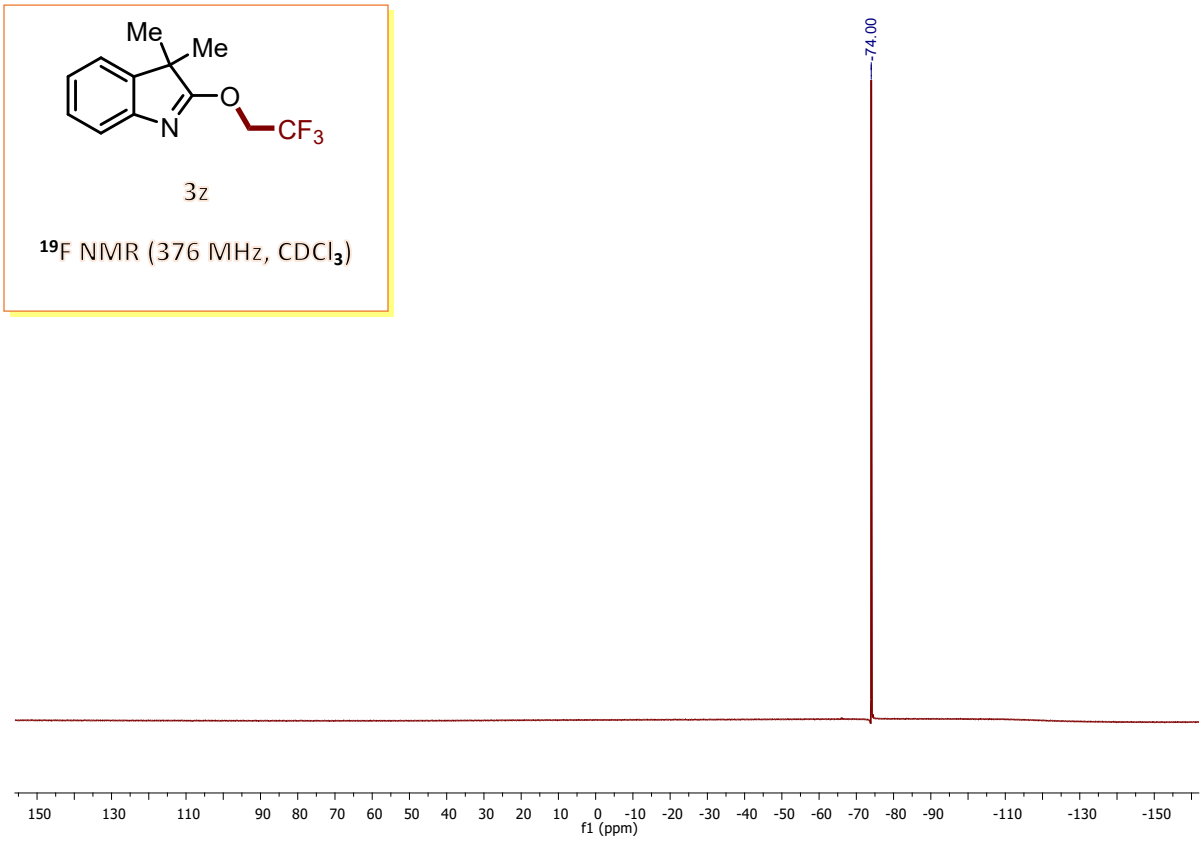
3z

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



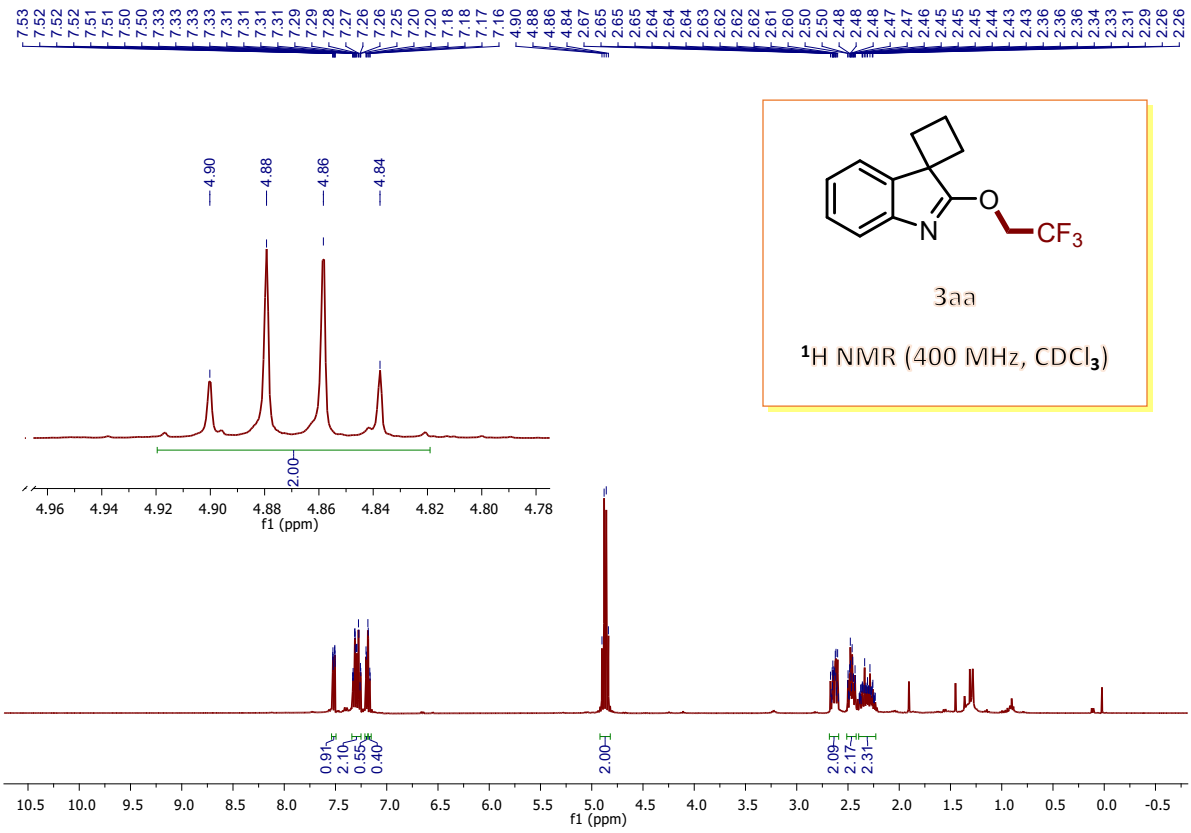
3z

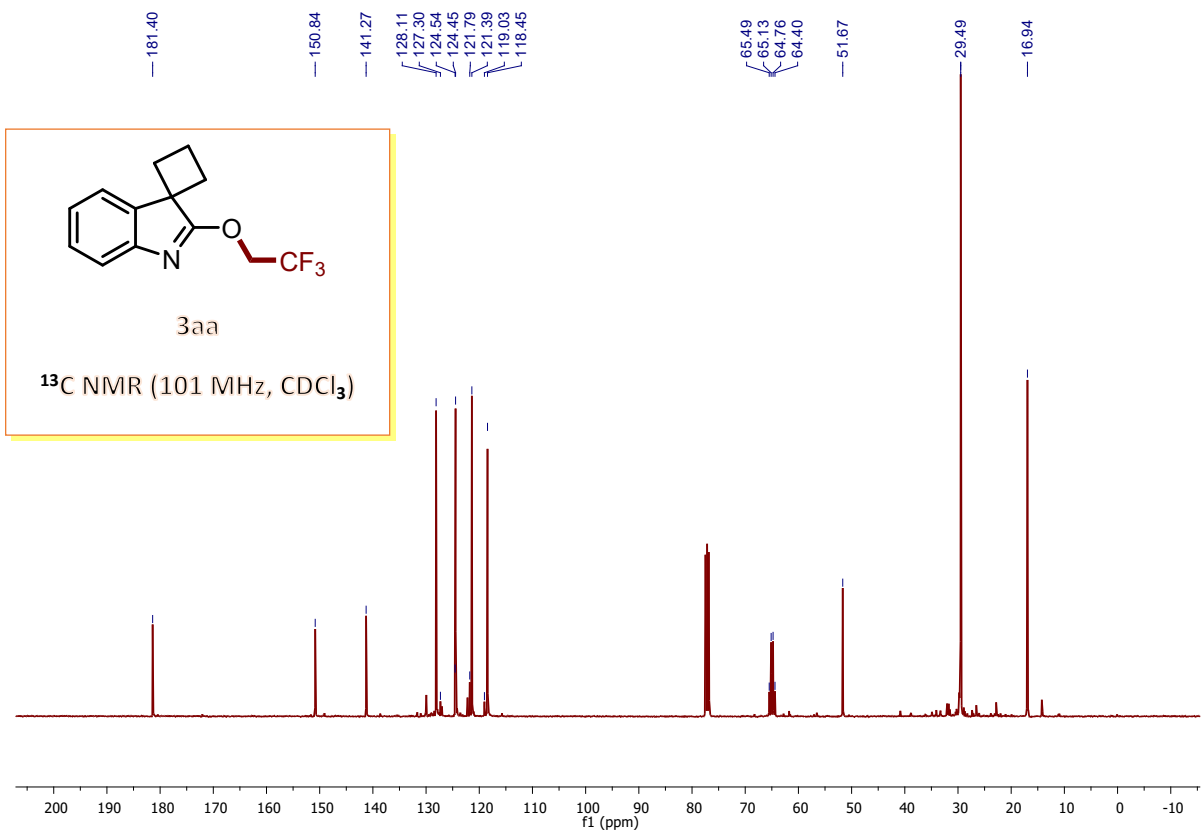
^{13}C NMR (101 MHz, $CDCl_3$)

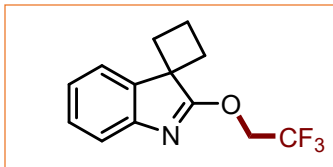


3z

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

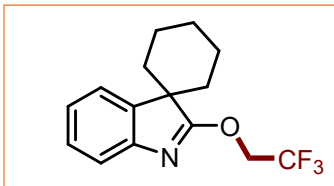

3aa
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


3aa
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)



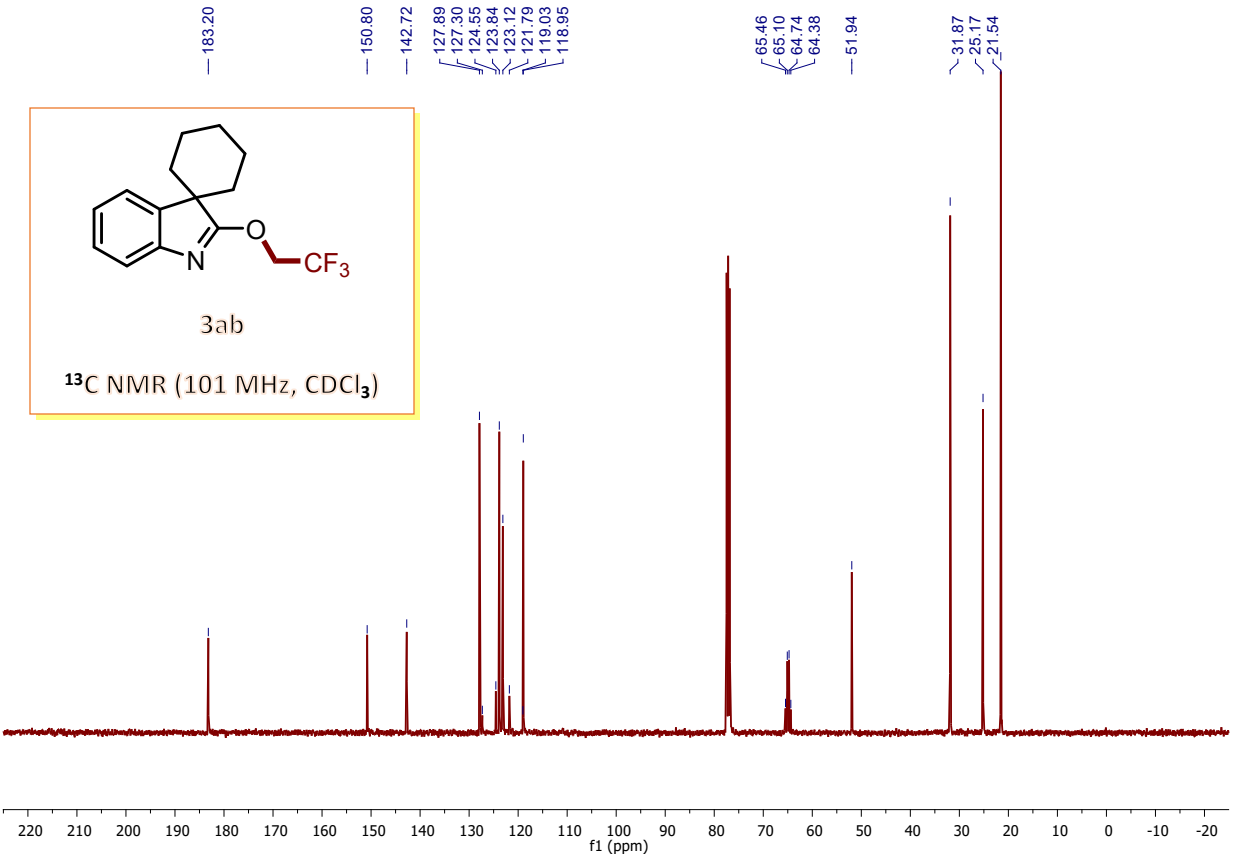
3aa

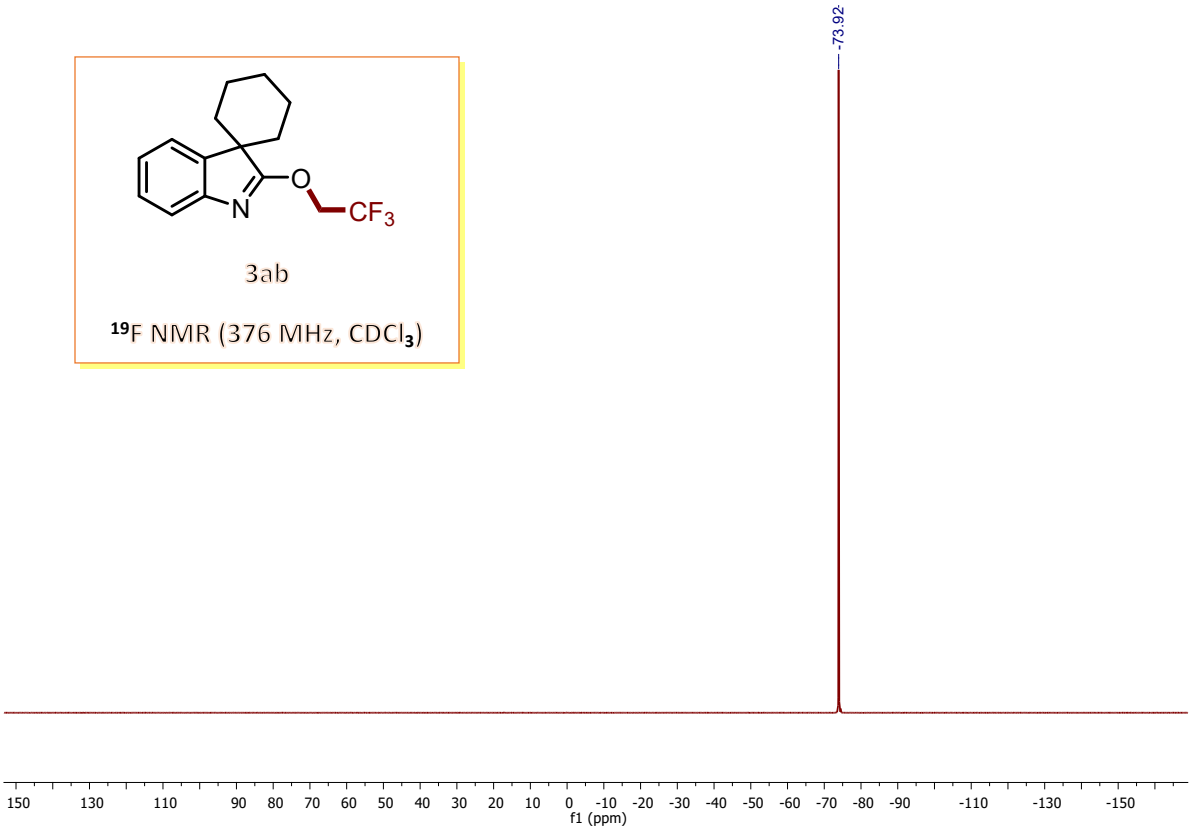
^{19}F NMR (376 MHz, $CDCl_3$)

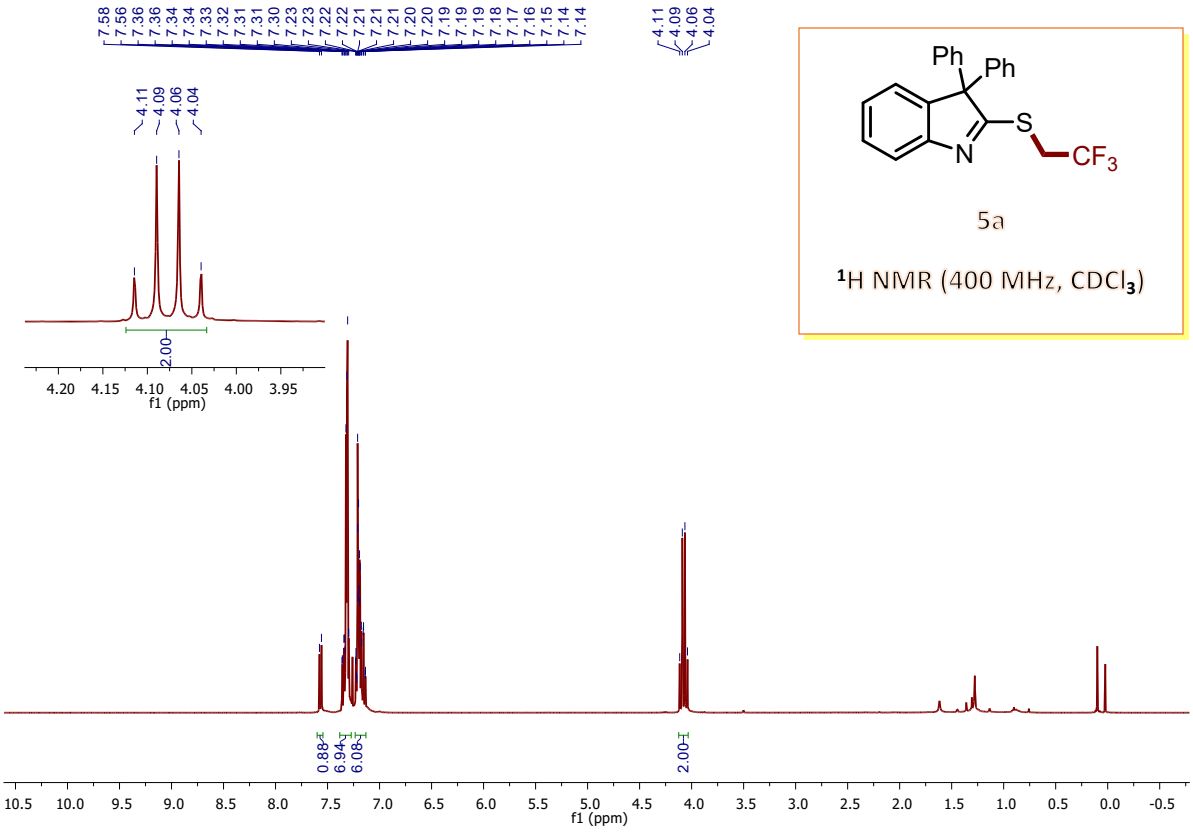


3ab

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

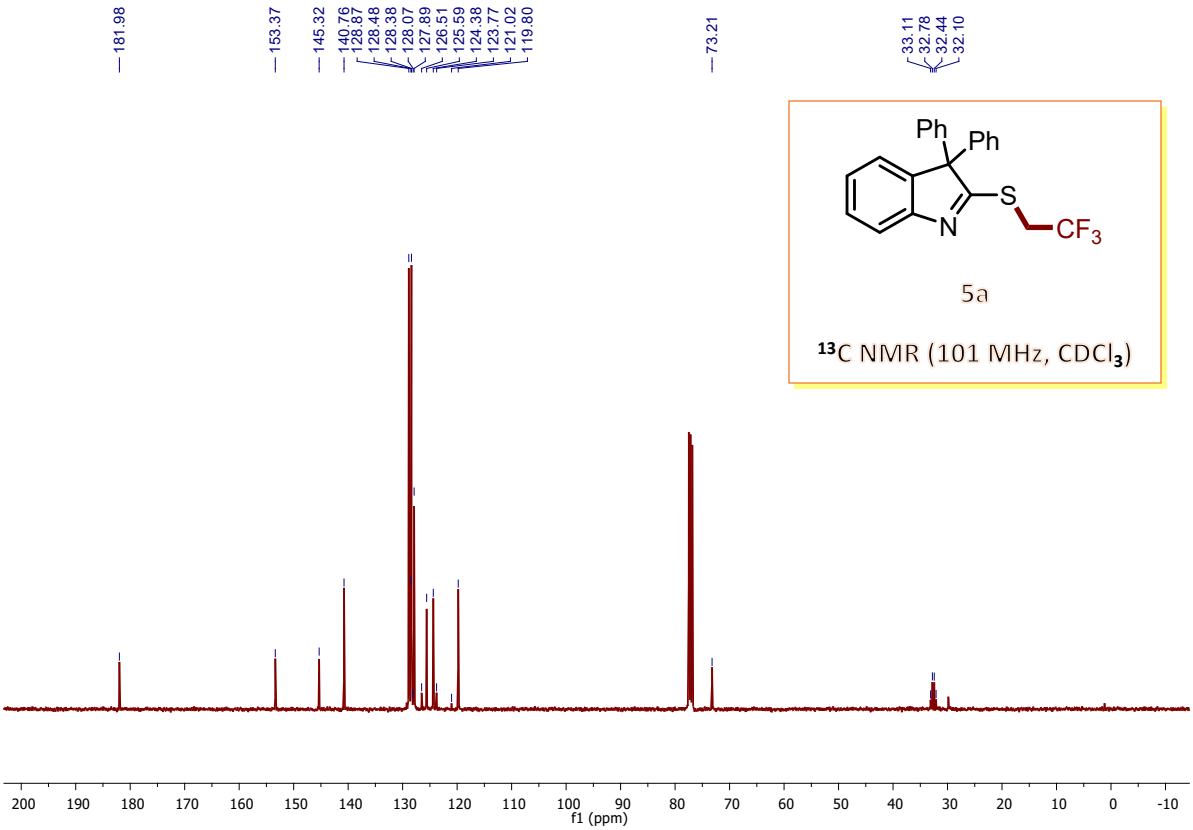

183.20
150.80
142.72
127.89
127.30
124.55
123.84
123.12
121.79
119.03
118.95
65.46
65.10
64.74
64.38
51.94
31.87
25.17
21.54
O
N
CF3
3ab
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-73.92
O
N
CF3
3ab
19F NMR (376 MHz, CDCl3)
f1 (ppm)



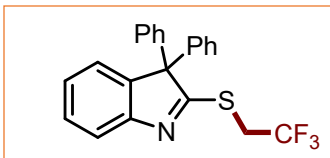
5a

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



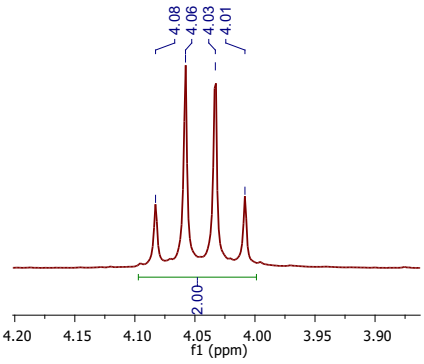
5a

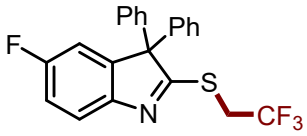
^{13}C NMR (101 MHz, $CDCl_3$)



5a

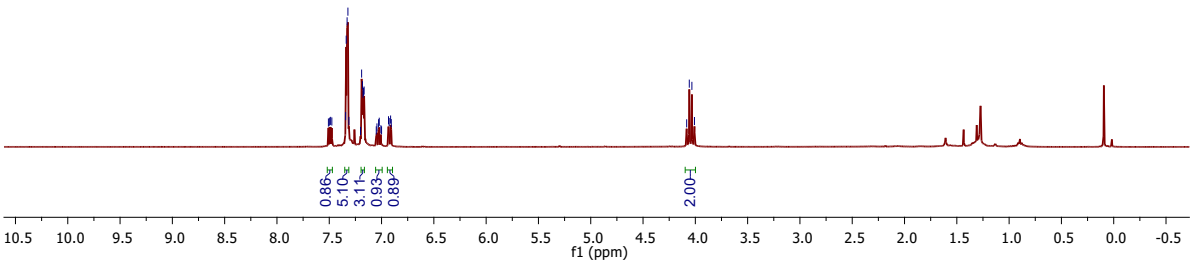
^{19}F NMR (376 MHz, $CDCl_3$)

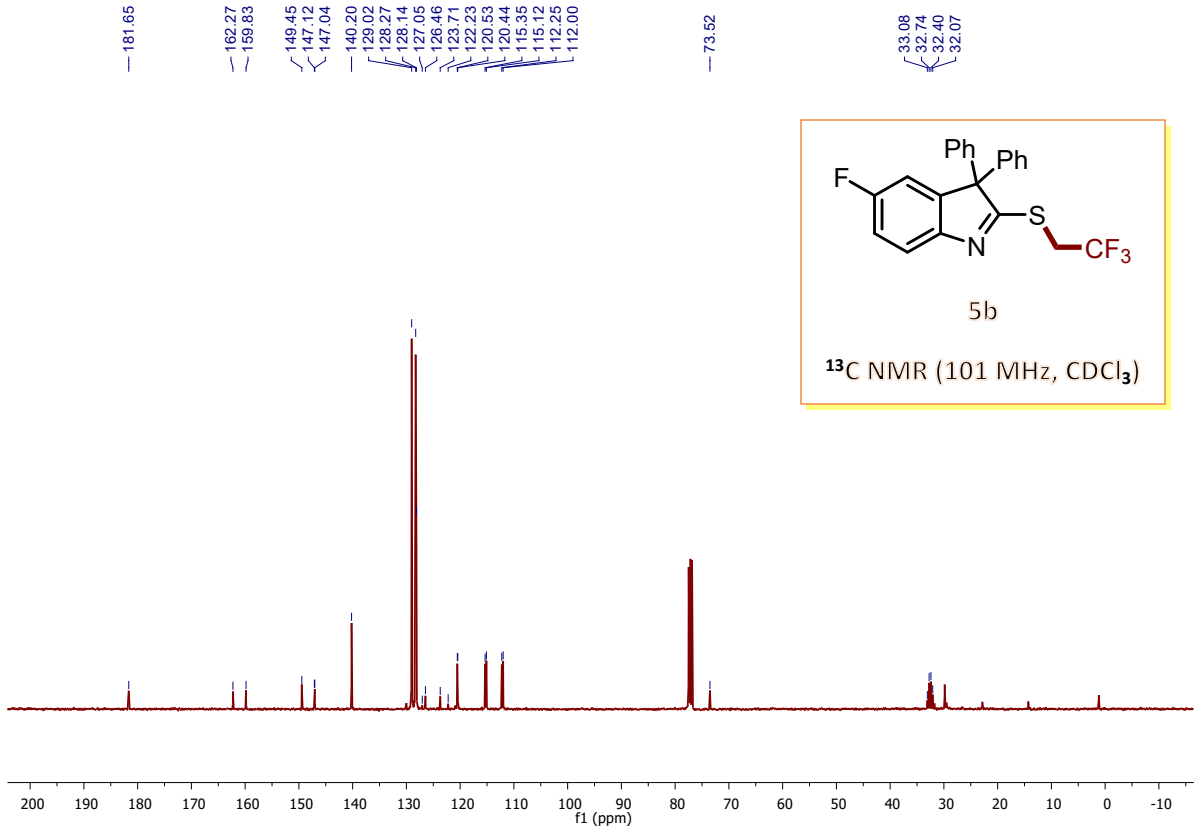


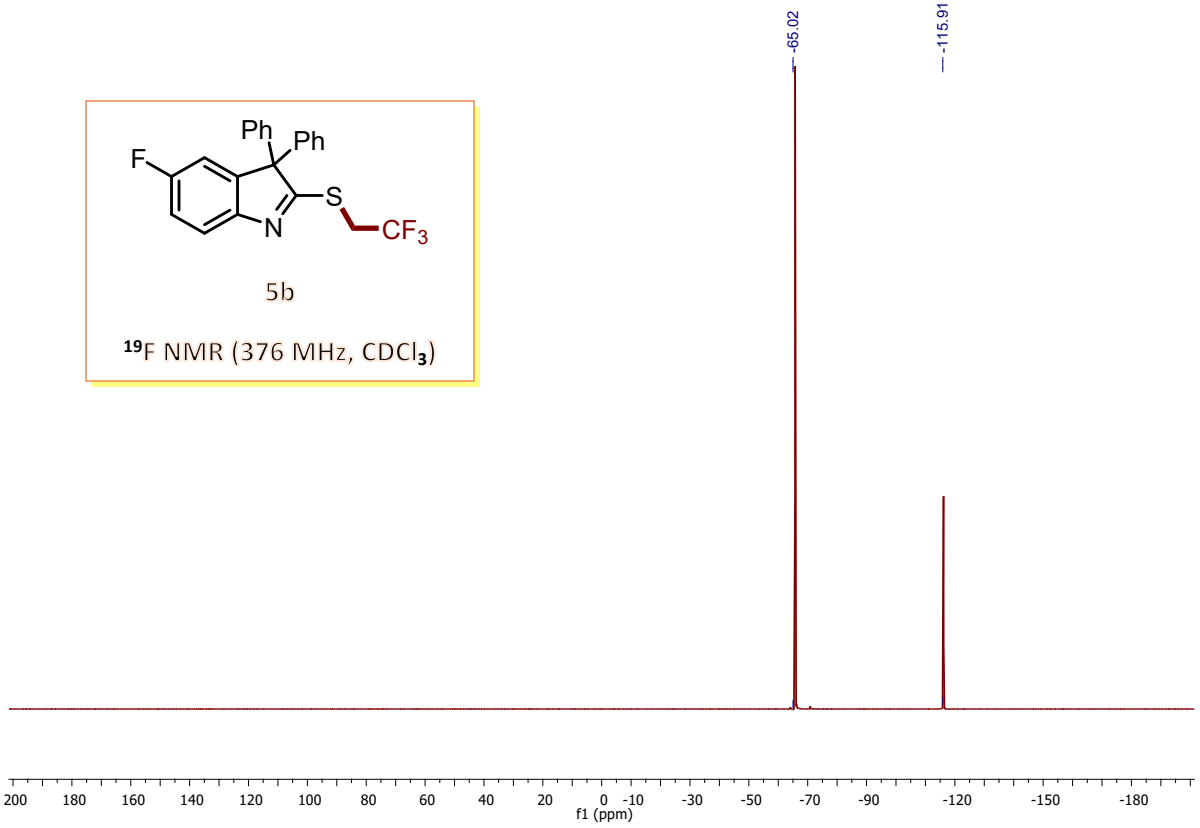


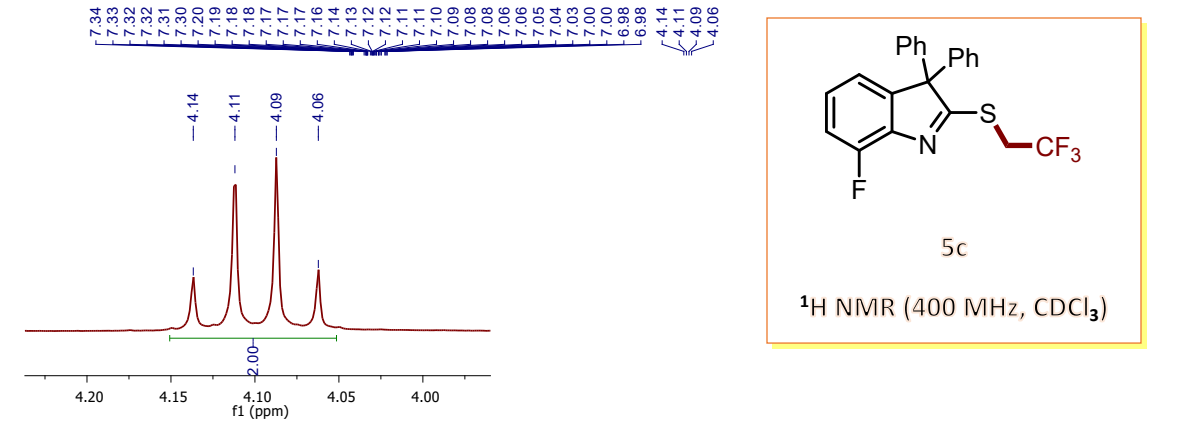
5b

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



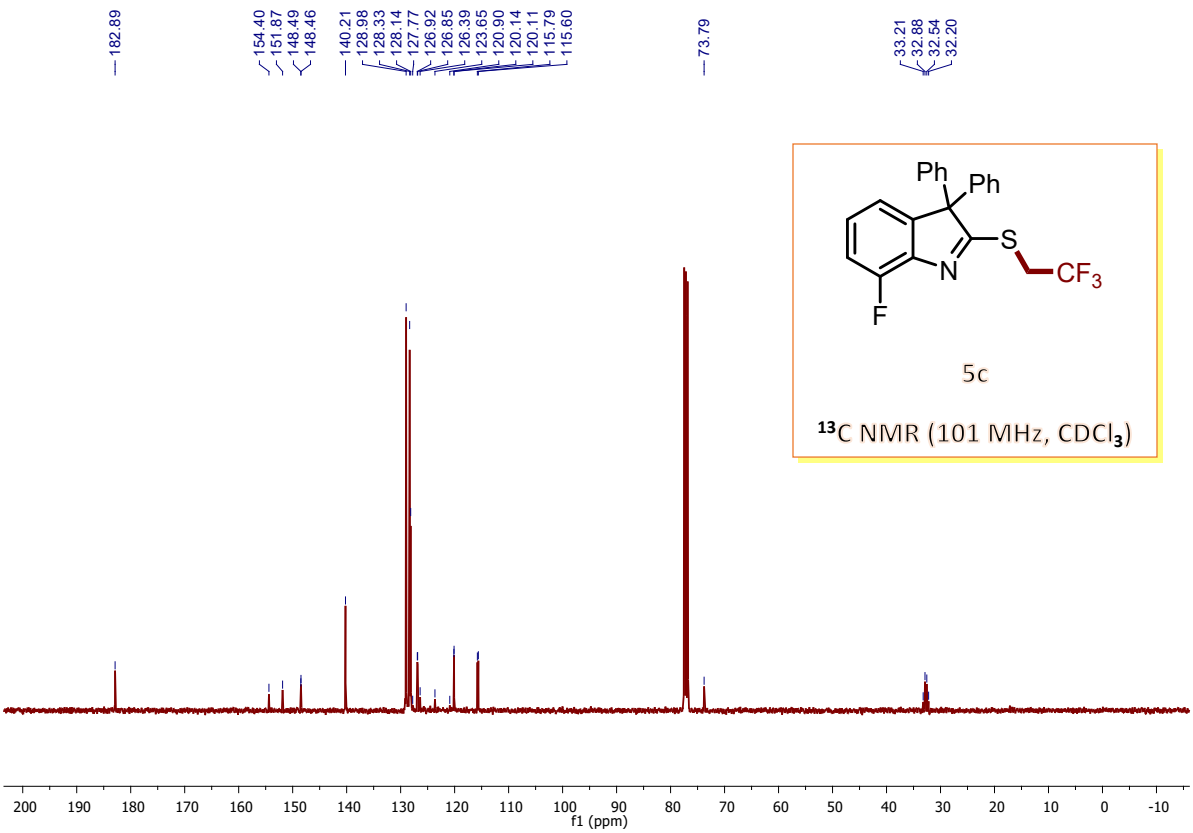

181.65
162.27
159.83
149.45
147.12
147.04
140.20
129.02
128.27
128.14
127.05
126.46
123.71
122.23
120.53
120.44
115.35
115.12
112.25
112.00
73.52
33.08
32.74
32.40
32.07
Ph
Ph
F
S
N
CF3
5b
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-65.02
-115.91
Ph
Ph
F
S
N
CF3
5b
19F NMR (376 MHz, CDCl3)
f1 (ppm)



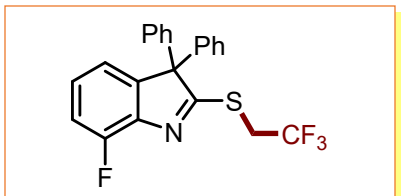
5c

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



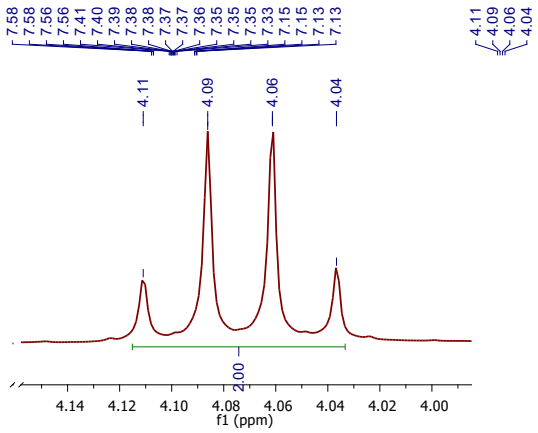
5c

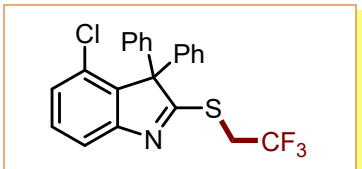
^{13}C NMR (101 MHz, $CDCl_3$)



5c

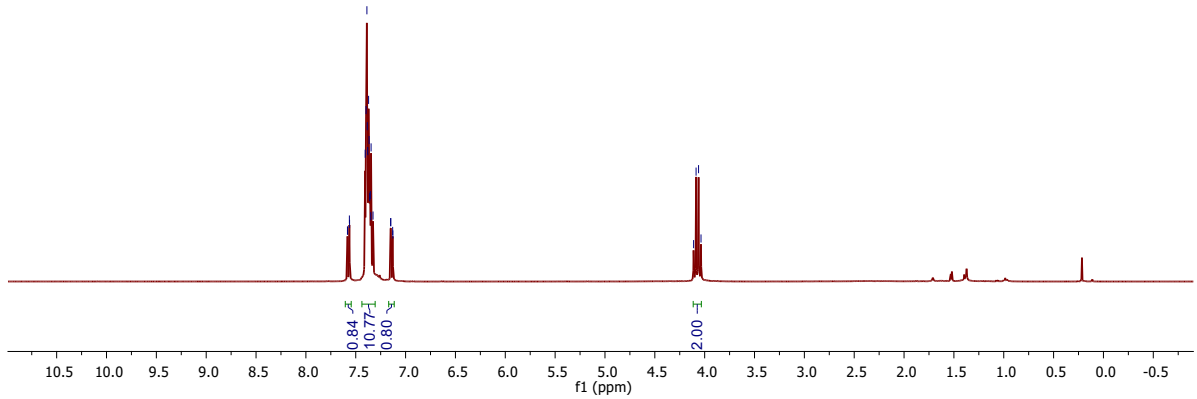
^{19}F NMR (376 MHz, $CDCl_3$)

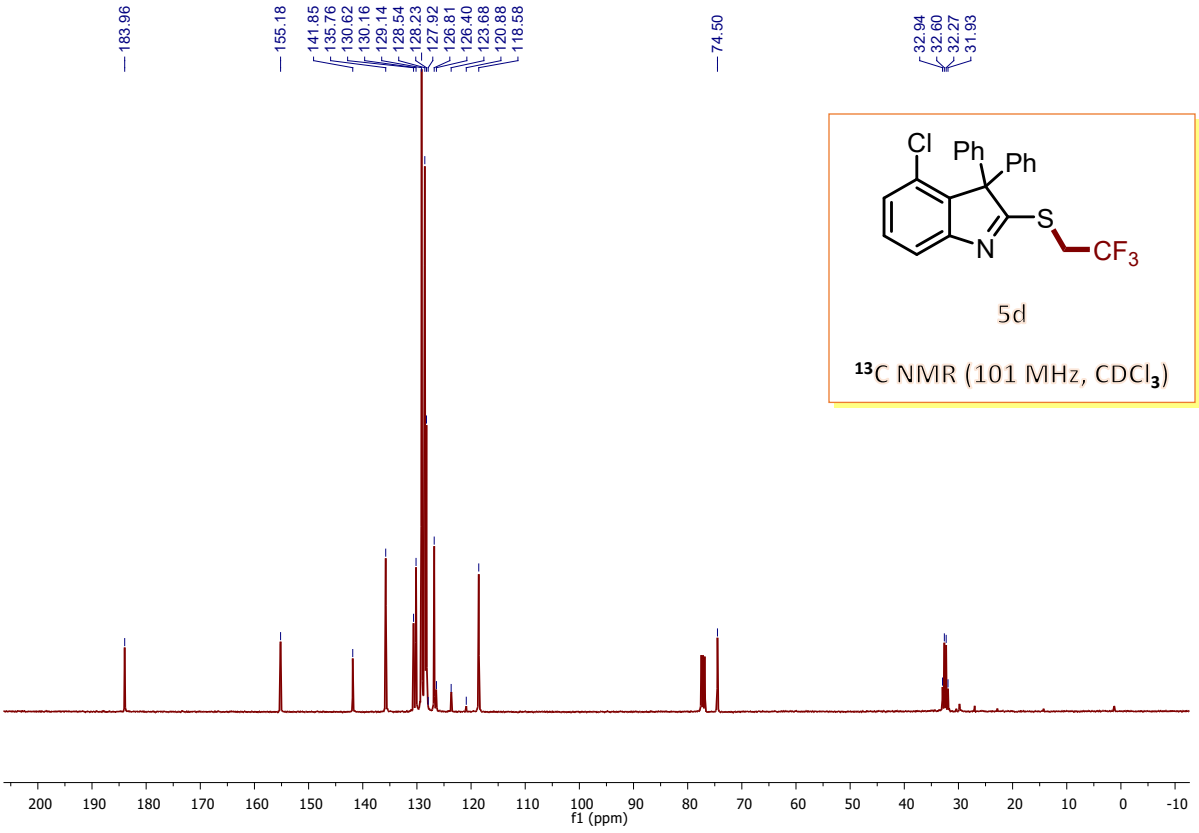


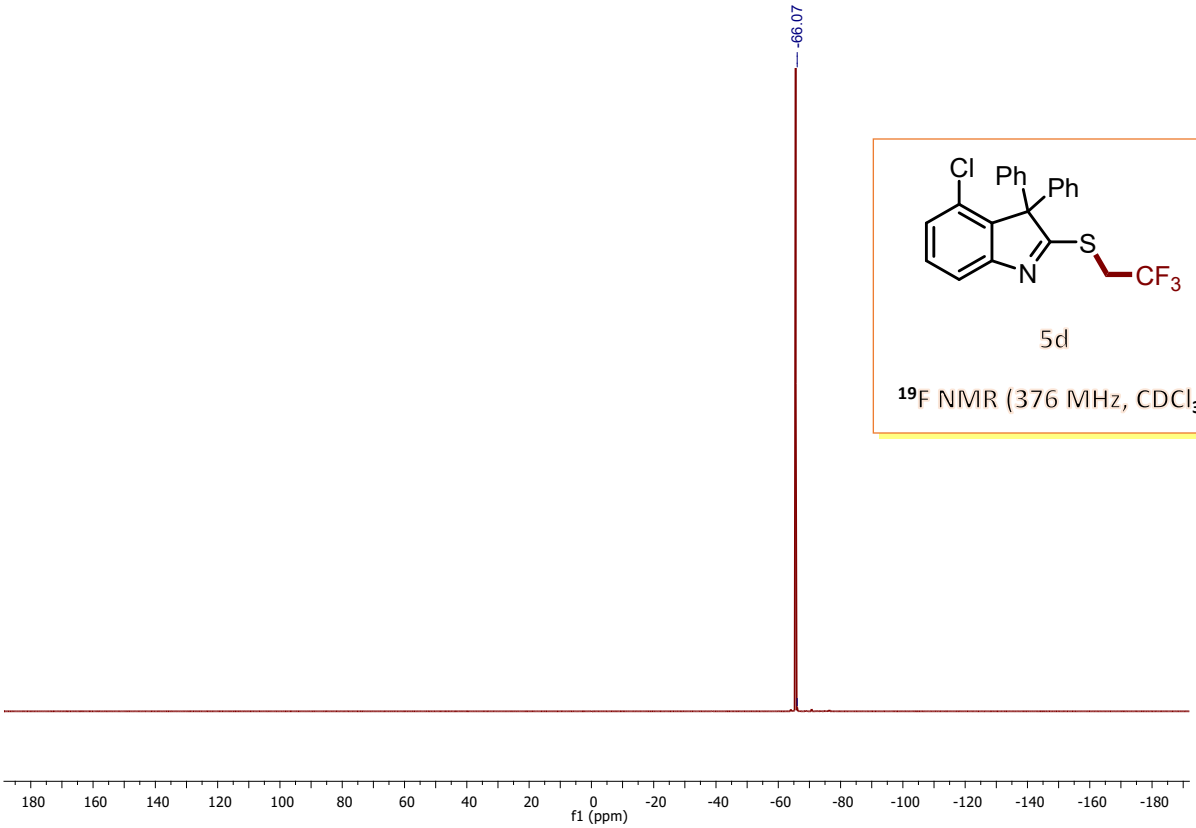


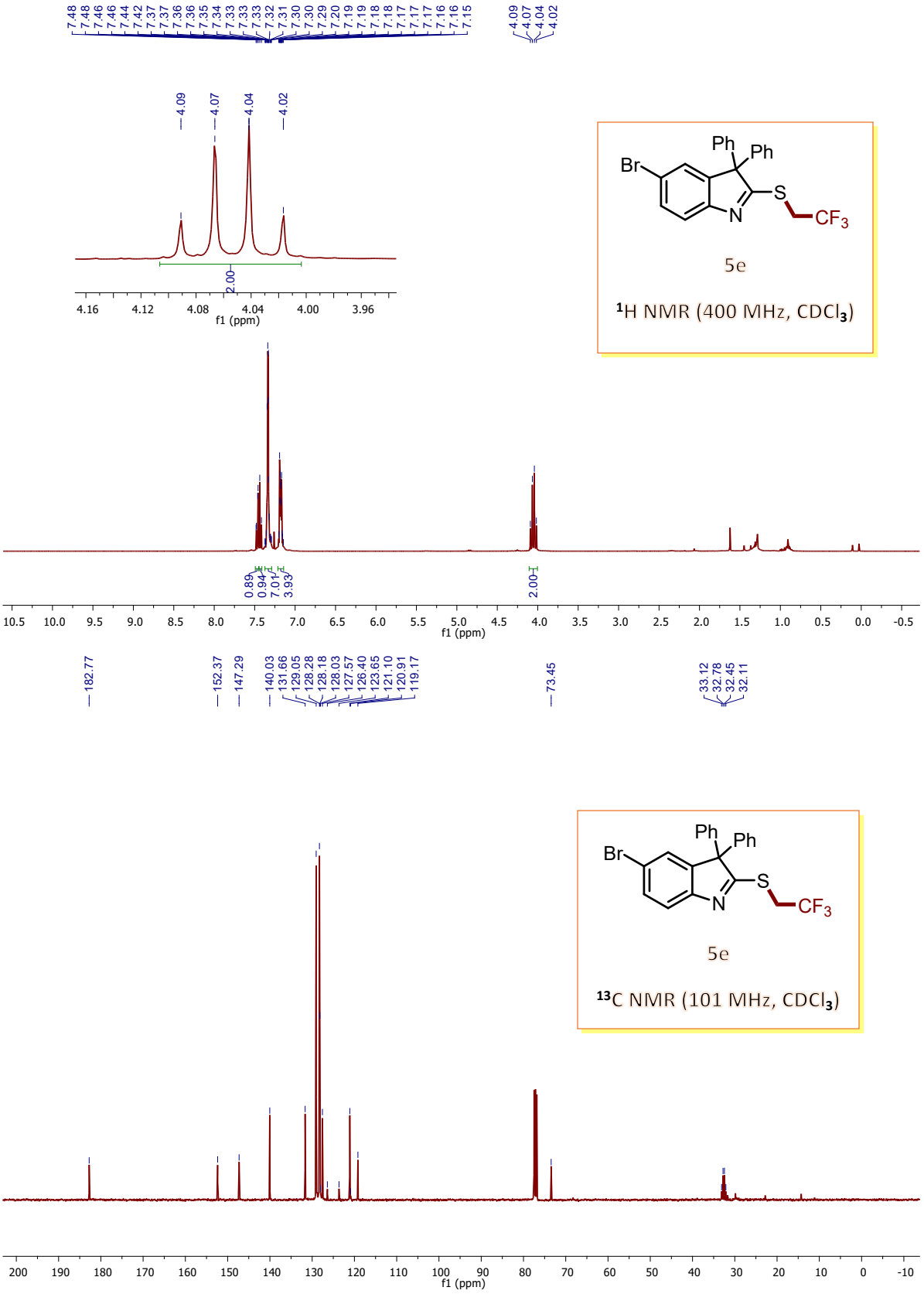
5d

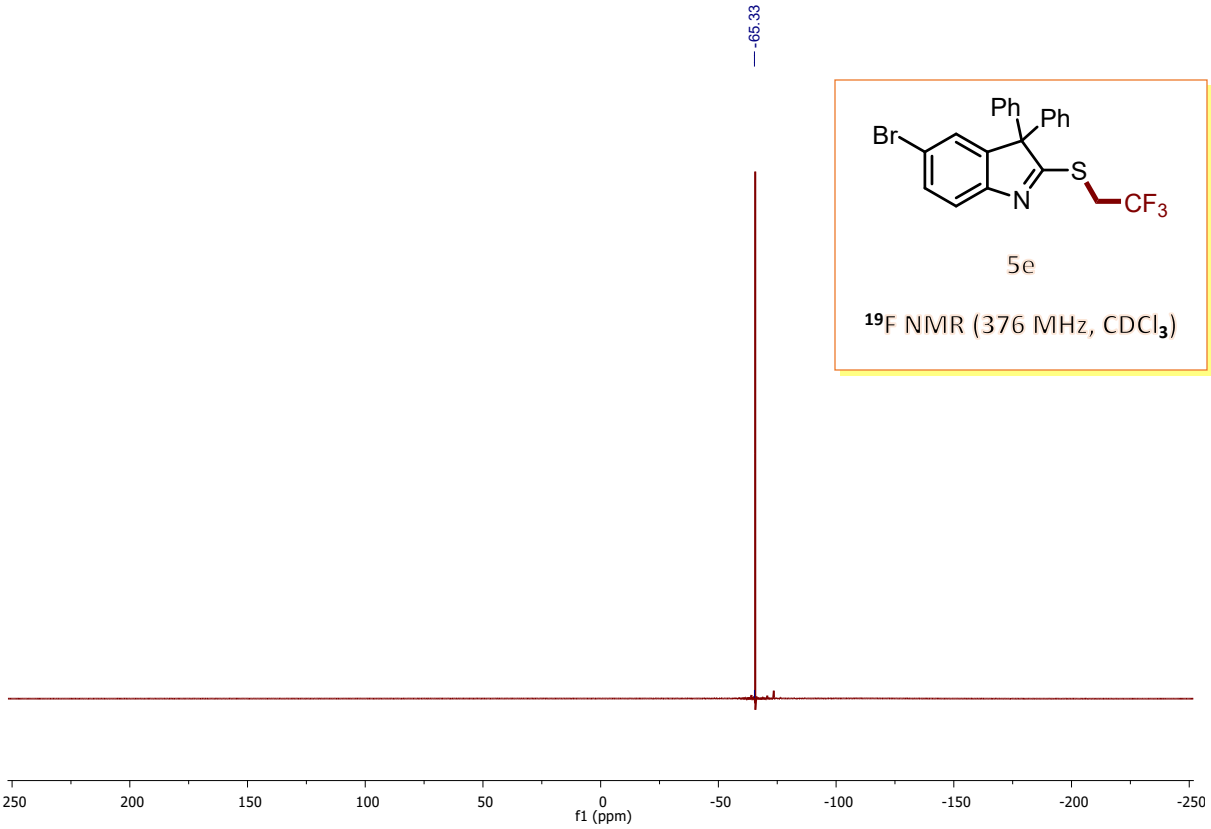
^{1}H NMR (400 MHz, $CDCl_3$)



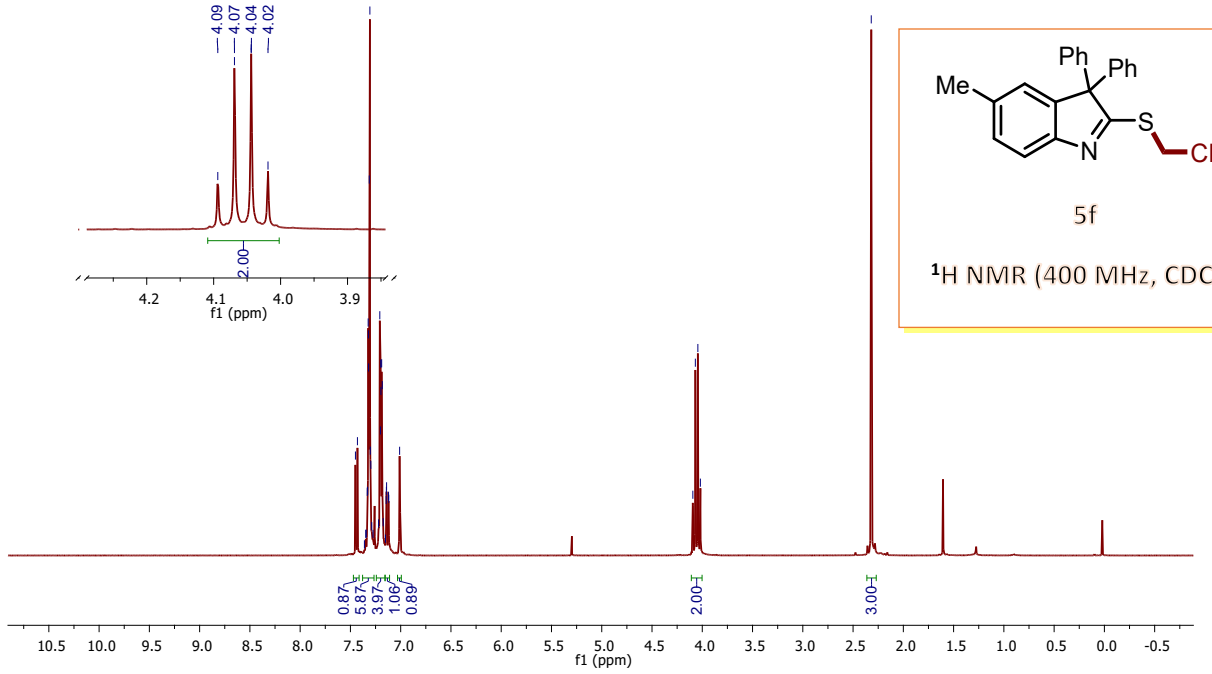

183.96
155.18
141.85
135.76
130.62
130.16
129.14
128.54
128.23
127.92
126.81
126.40
123.68
120.88
118.58
74.50
32.94
32.60
32.27
31.93
Cl
Ph
Ph
S
N
CF3
5d
13C NMR (101 MHz, CDCl3)
f1 (ppm)

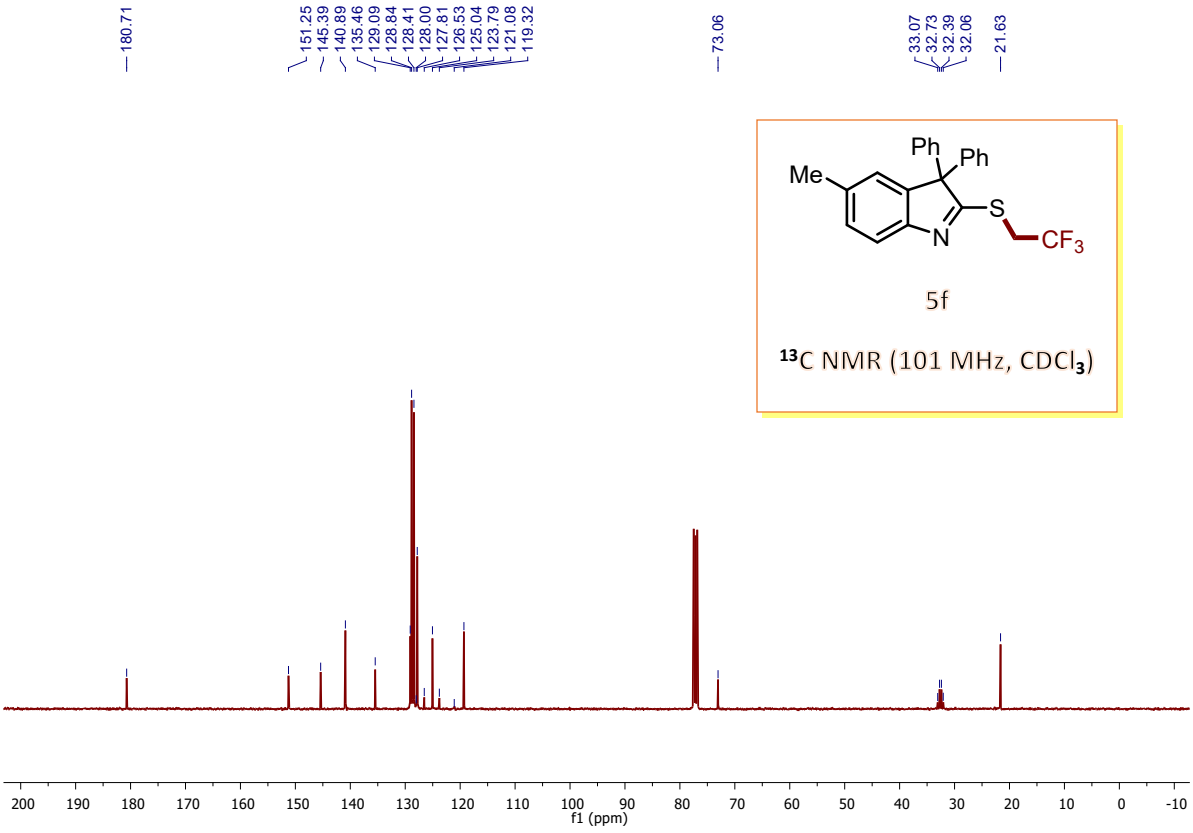

-66.07
Cl
Ph
Ph
S
N
CF3
5d
19F NMR (376 MHz, CDCl3)
f1 (ppm)

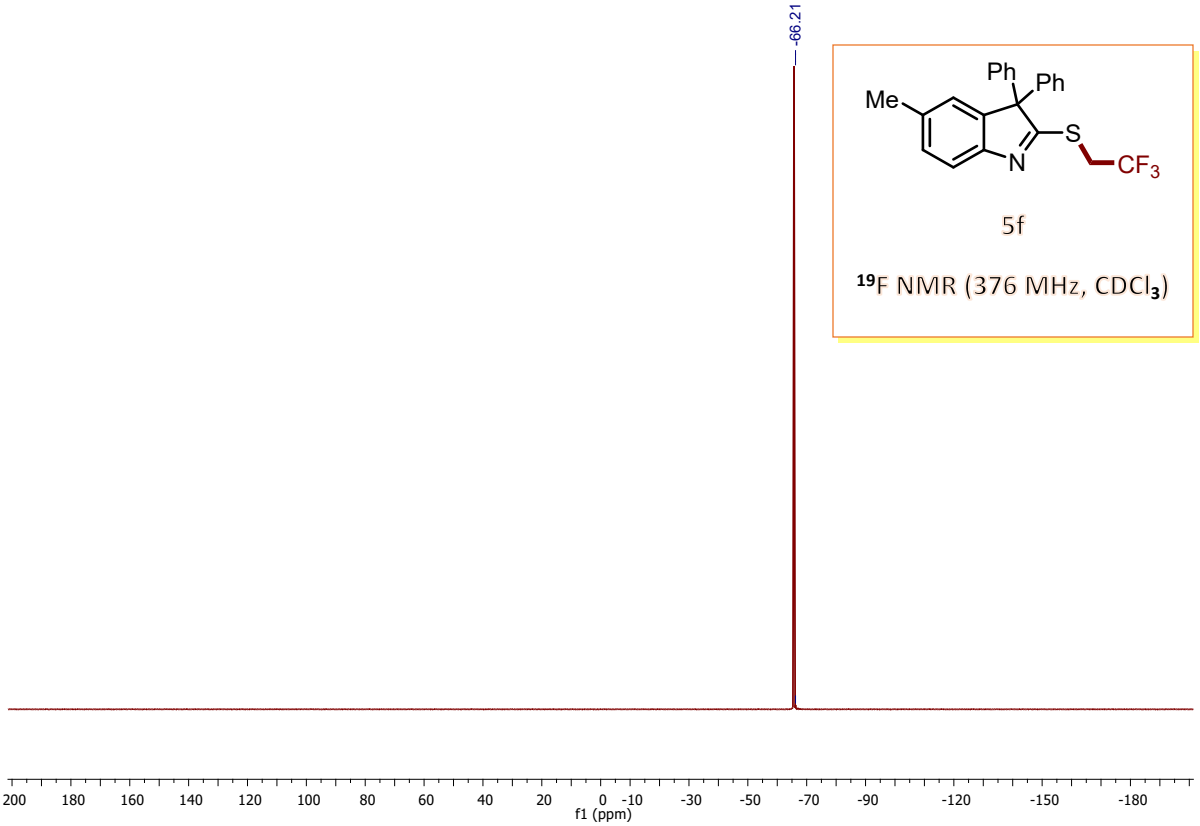

7.48 7.48 7.46 7.46 7.44 7.42 7.37 7.37 7.36 7.36 7.35 7.34 7.33 7.33 7.33 7.32 7.31 7.30 7.30 7.29 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.15
4.09 4.07 4.04 4.02
4.09 4.07 4.04 4.02
2.00
4.16 4.12 4.08 4.04 4.00 3.96
f1 (ppm)
Ph Ph Br S N CF3
5e
1H NMR (400 MHz, CDCl3)
0.89 0.94 7.01 3.93 2.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
182.77 152.37 147.29 140.03 131.66 129.05 128.28 128.18 128.03 127.57 126.40 123.65 121.10 120.91 119.17 73.45 33.12 32.78 32.45 32.11
Ph Ph Br S N CF3
5e
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 -10
f1 (ppm)

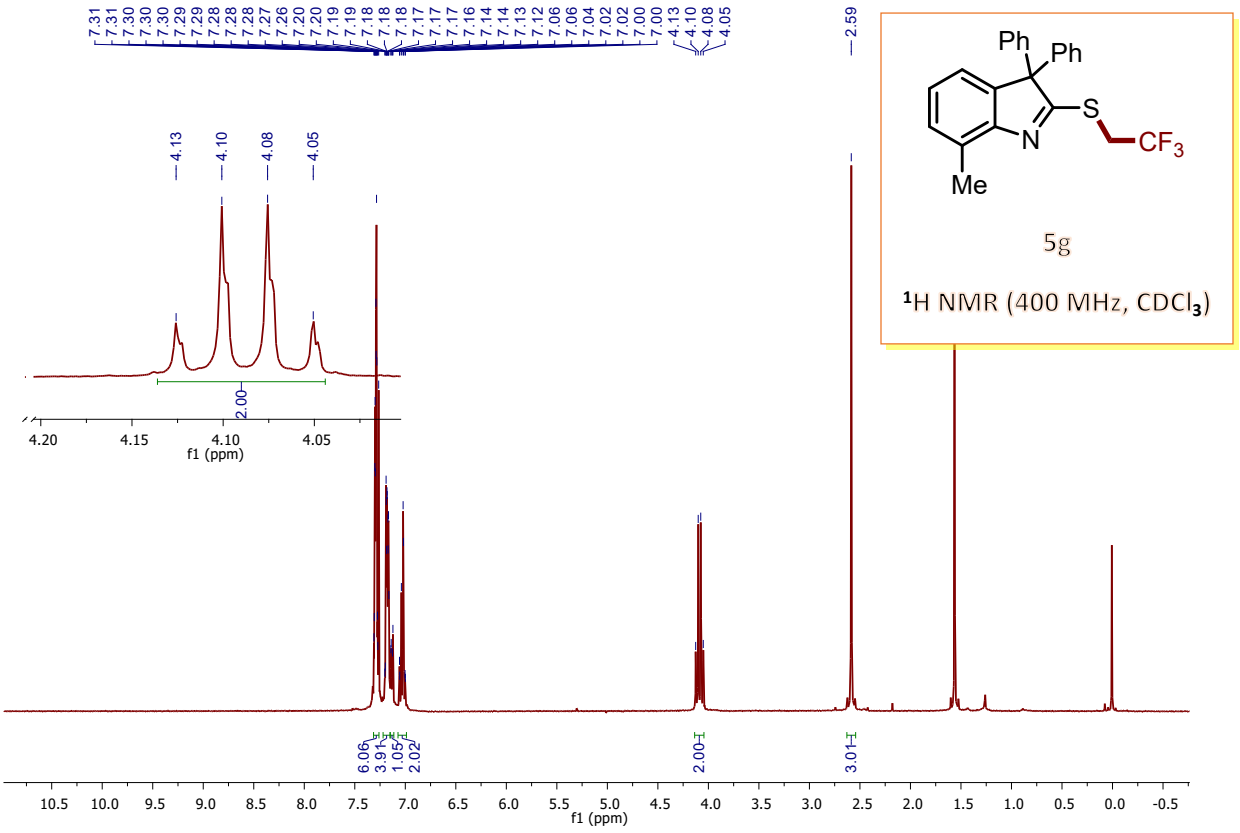

-65.33
f1 (ppm)

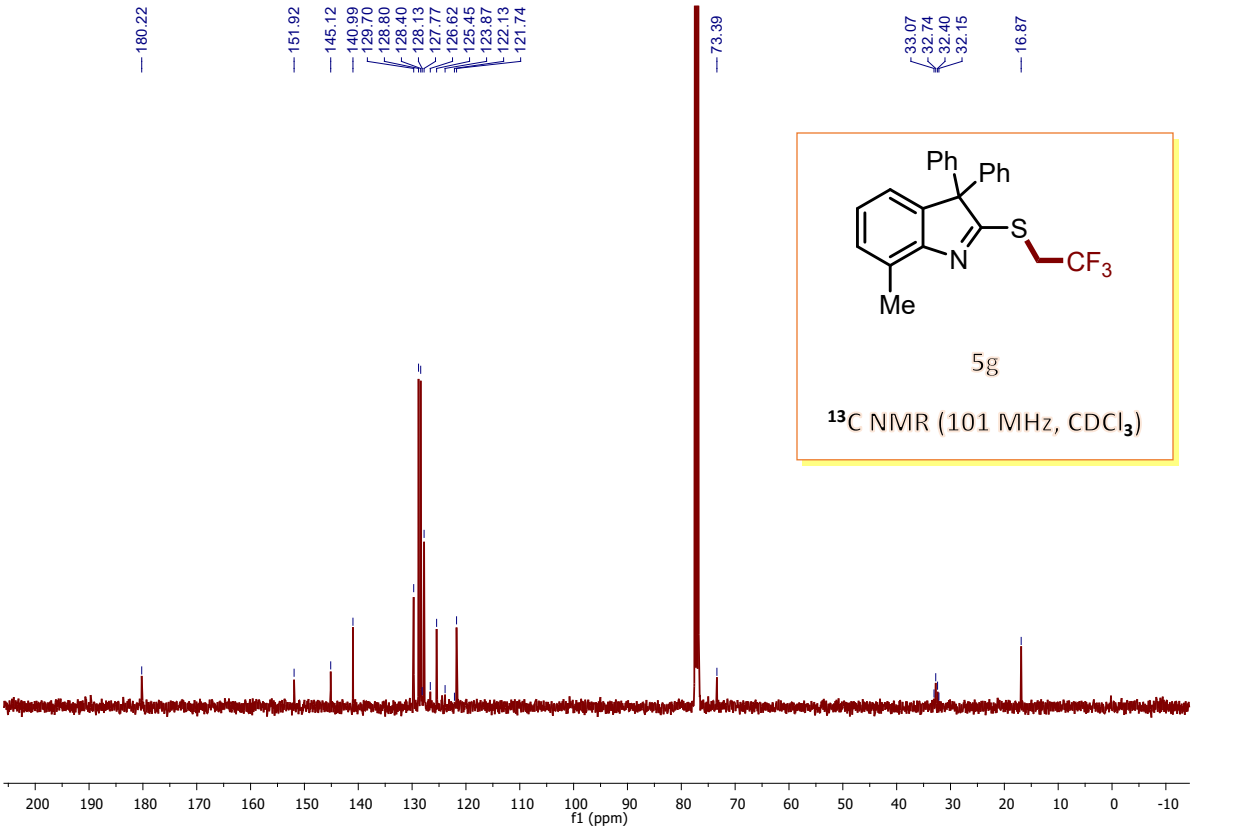

7.45
7.43
7.36
7.35
7.34
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.22
7.21
7.20
7.20
7.20
7.19
7.18
7.17
7.15
7.14
7.14
7.14
7.12
7.12
7.12
7.01
4.09
4.07
4.04
4.02
2.32

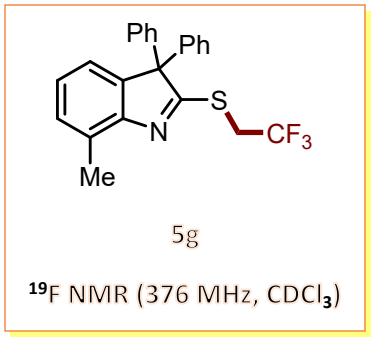

4.09
4.07
4.04
4.02
2.00
f1 (ppm)
0.87
5.87
3.97
1.08
0.89
2.00
3.00
f1 (ppm)


180.71
151.25
145.39
140.89
135.46
129.09
128.84
128.41
128.00
127.81
126.53
125.04
123.79
121.08
119.32
73.06
33.07
32.73
32.39
32.06
21.63
Ph
Ph
Me
S
N
CF3
5f
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 -10
f1 (ppm)


-66.21
Ph
Ph
Me
S
N
CF3
5f
19F NMR (376 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

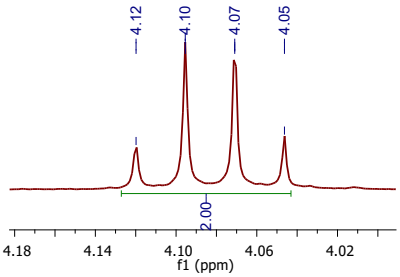

Ph
Ph
S
N
CF3
Me
5g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

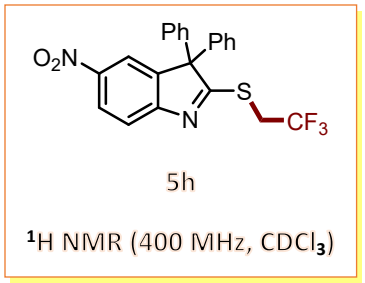

Ph
Ph
S
N
CF3
Me
5g
13C NMR (101 MHz, CDCl3)
f1 (ppm)



5g

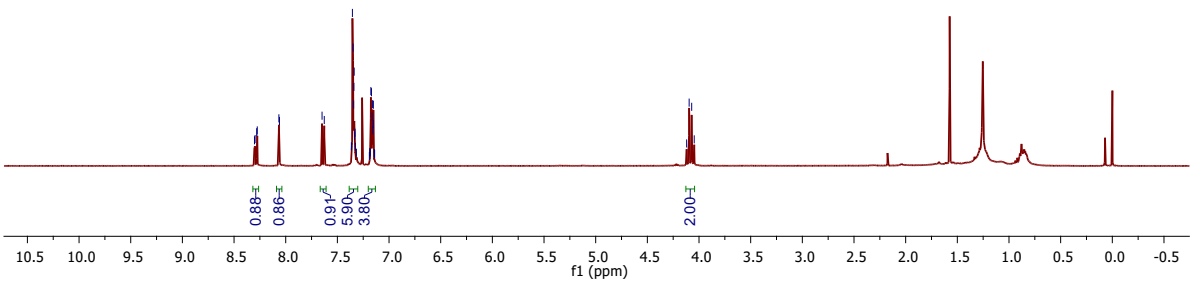
^{19}F NMR (376 MHz, $CDCl_3$)

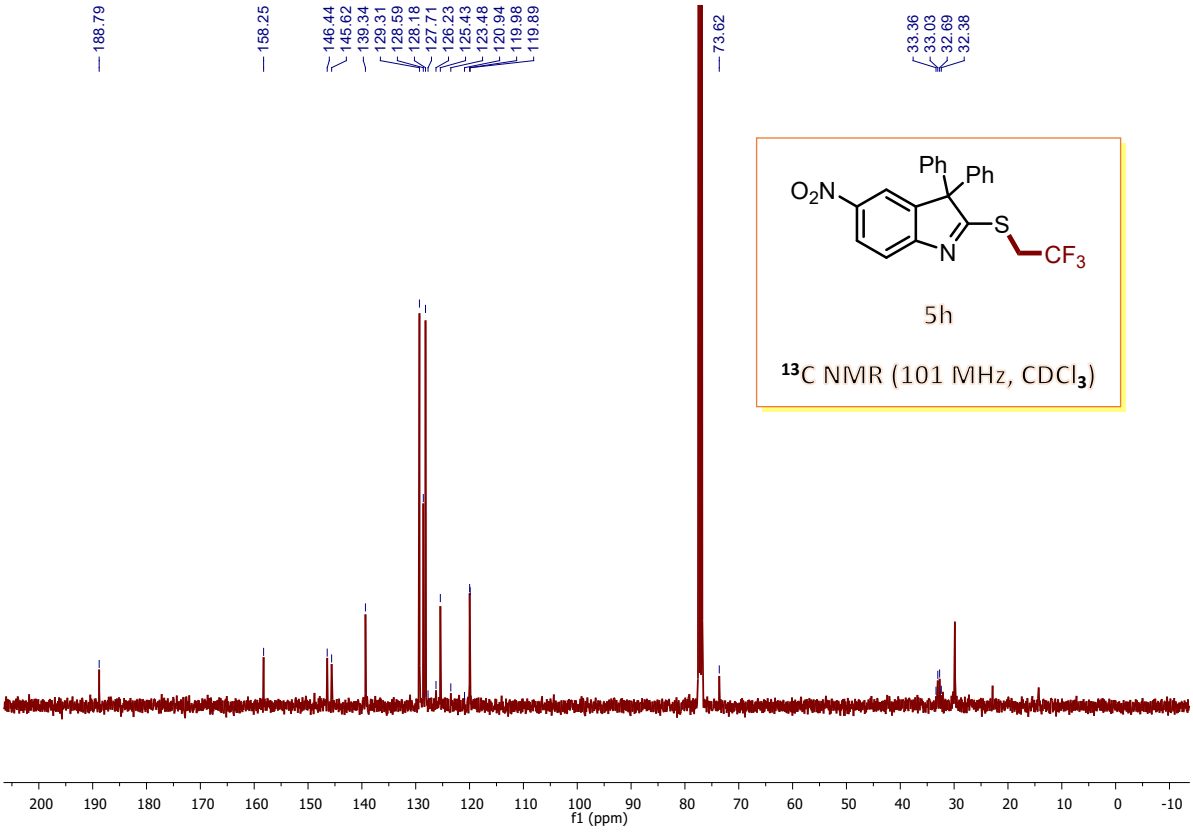


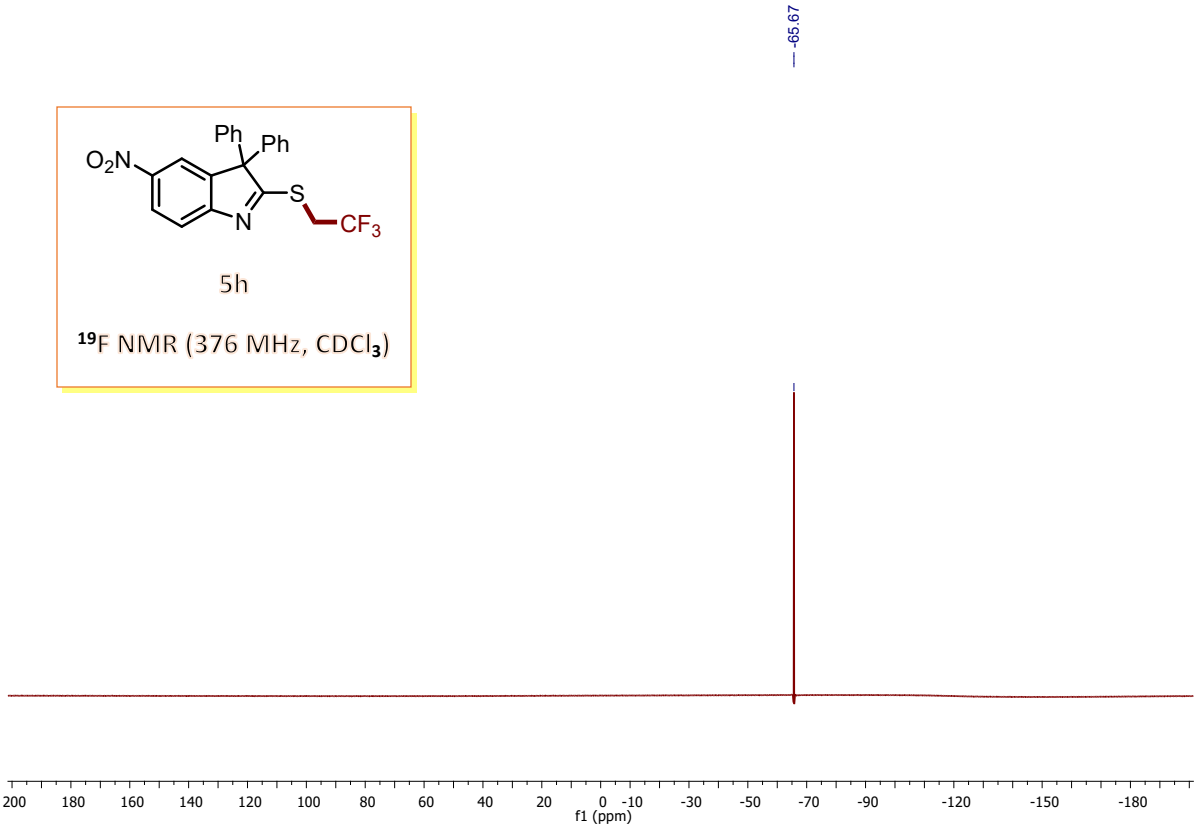


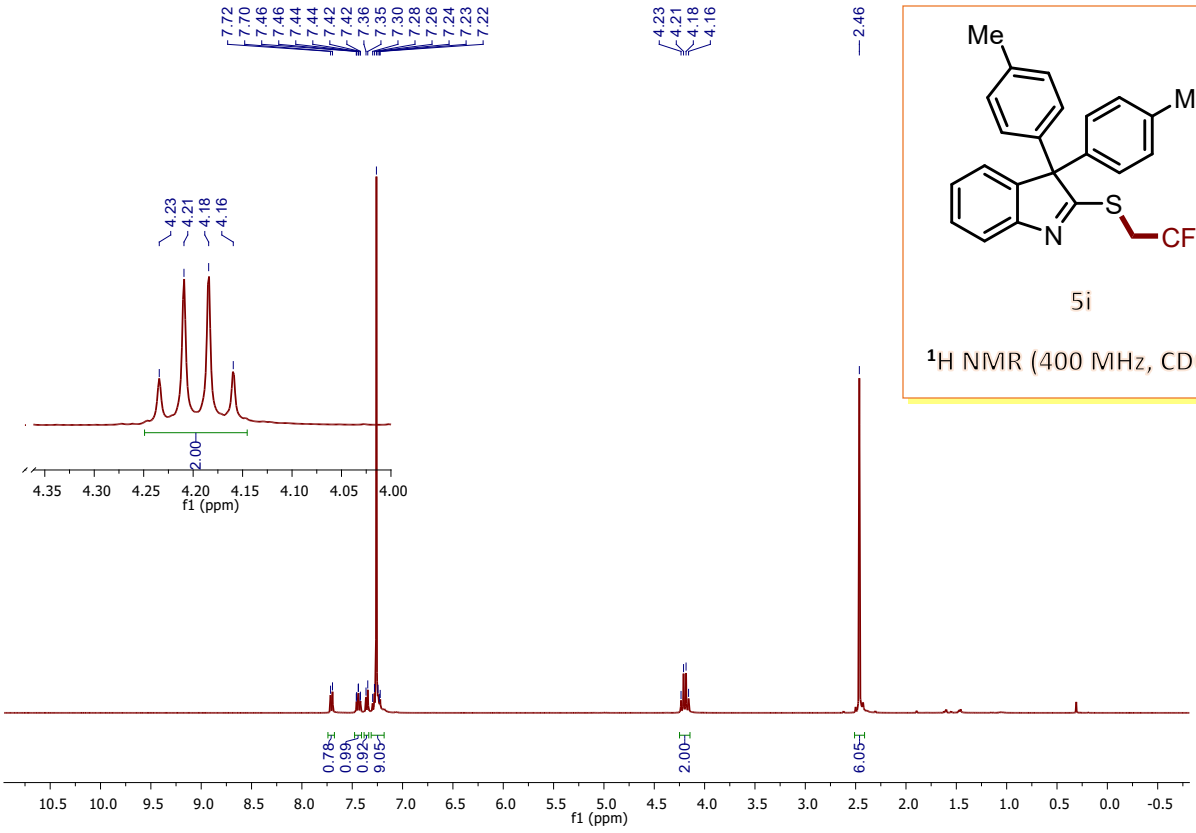
5h

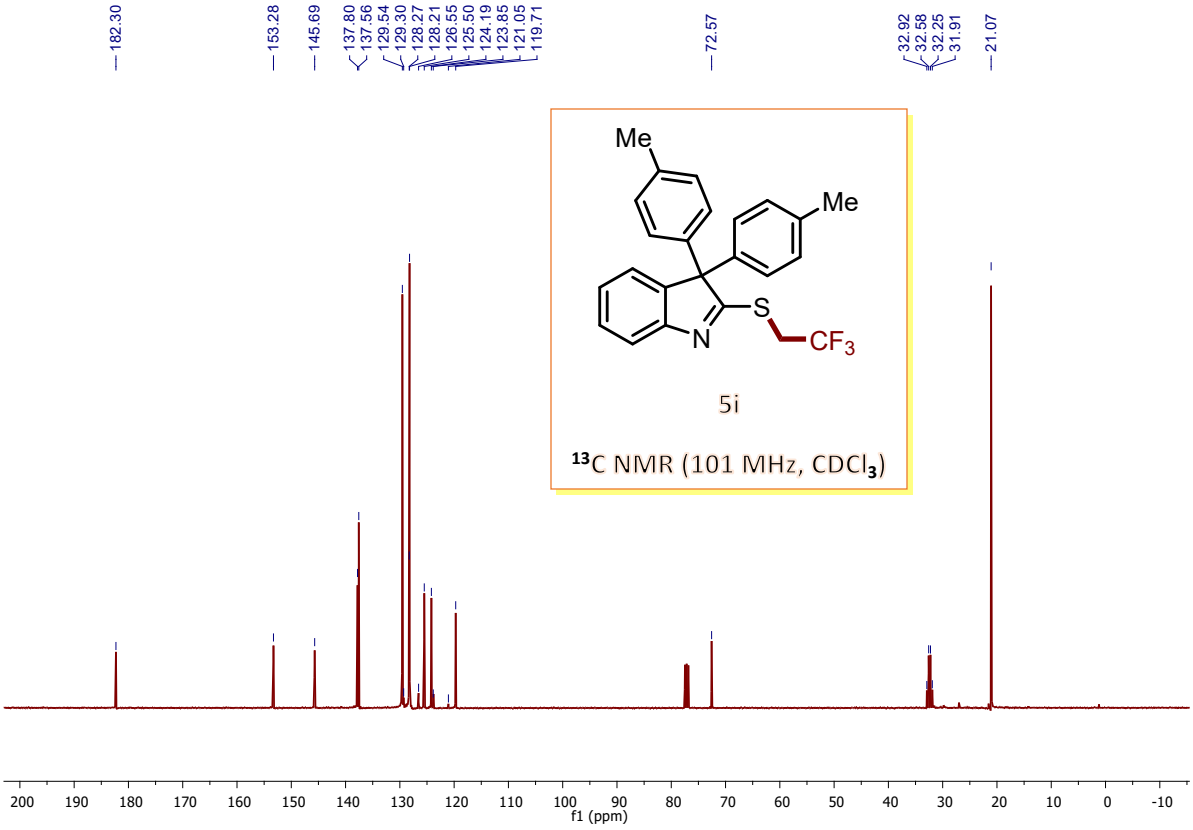
^{1}H NMR (400 MHz, $CDCl_3$)

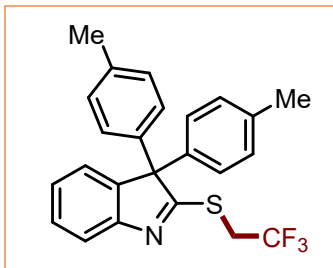



188.79
158.25
146.44
145.62
139.34
129.31
128.59
128.18
127.71
126.23
125.43
123.48
120.94
119.98
119.89
73.62
33.36
33.03
32.69
32.38
Ph
Ph
O2N
S
N
CF3
5h
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-65.67
Ph
Ph
O2N
S
N
CF3
5h
19F NMR (376 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

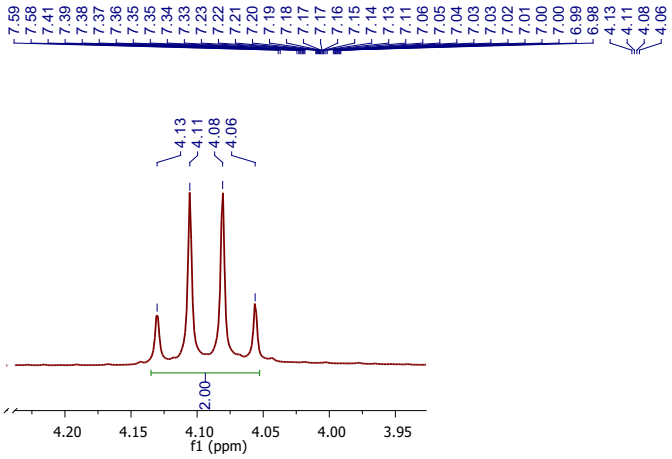

7.72
7.70
7.46
7.46
7.44
7.44
7.42
7.42
7.36
7.35
7.30
7.28
7.26
7.24
7.23
7.22
4.23
4.21
4.18
4.16
2.46
4.23
4.21
4.18
4.16
2.00
4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00
f1 (ppm)
0.78
0.99
0.92
9.05
2.00
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
Me
Me
S
N
CF3
5i
1H NMR (400 MHz, CDCl3)

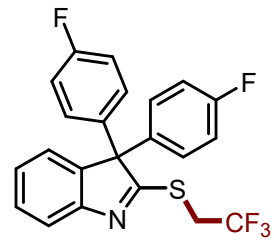

182.30
153.28
145.69
137.80
137.56
129.54
129.30
128.27
128.21
126.55
125.50
124.19
123.85
121.05
119.71
72.57
32.92
32.58
32.25
31.91
21.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
Me
Me
S
N
CF3
5i
13C NMR (101 MHz, CDCl3)



5i

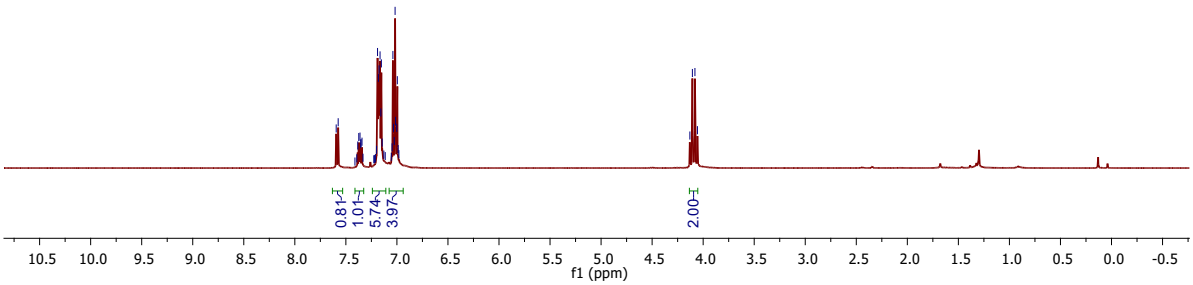
^{19}F NMR (376 MHz, $CDCl_3$)

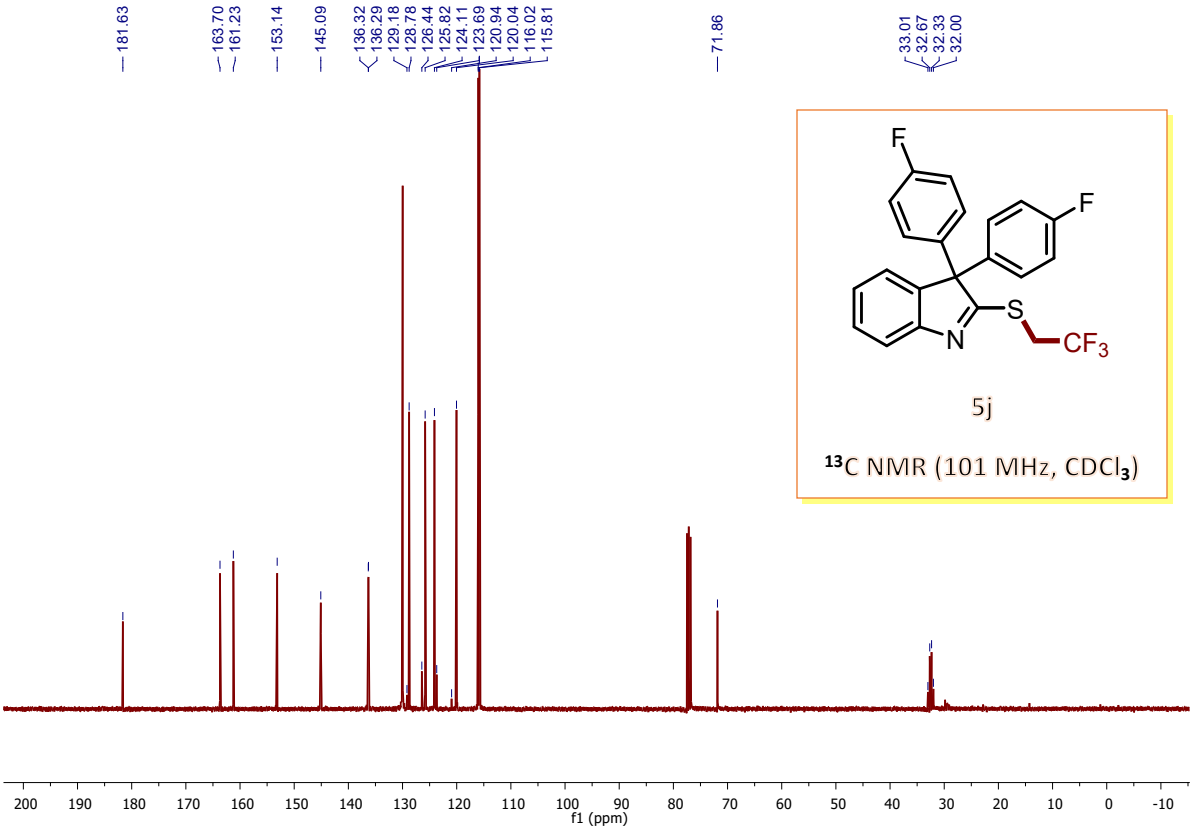


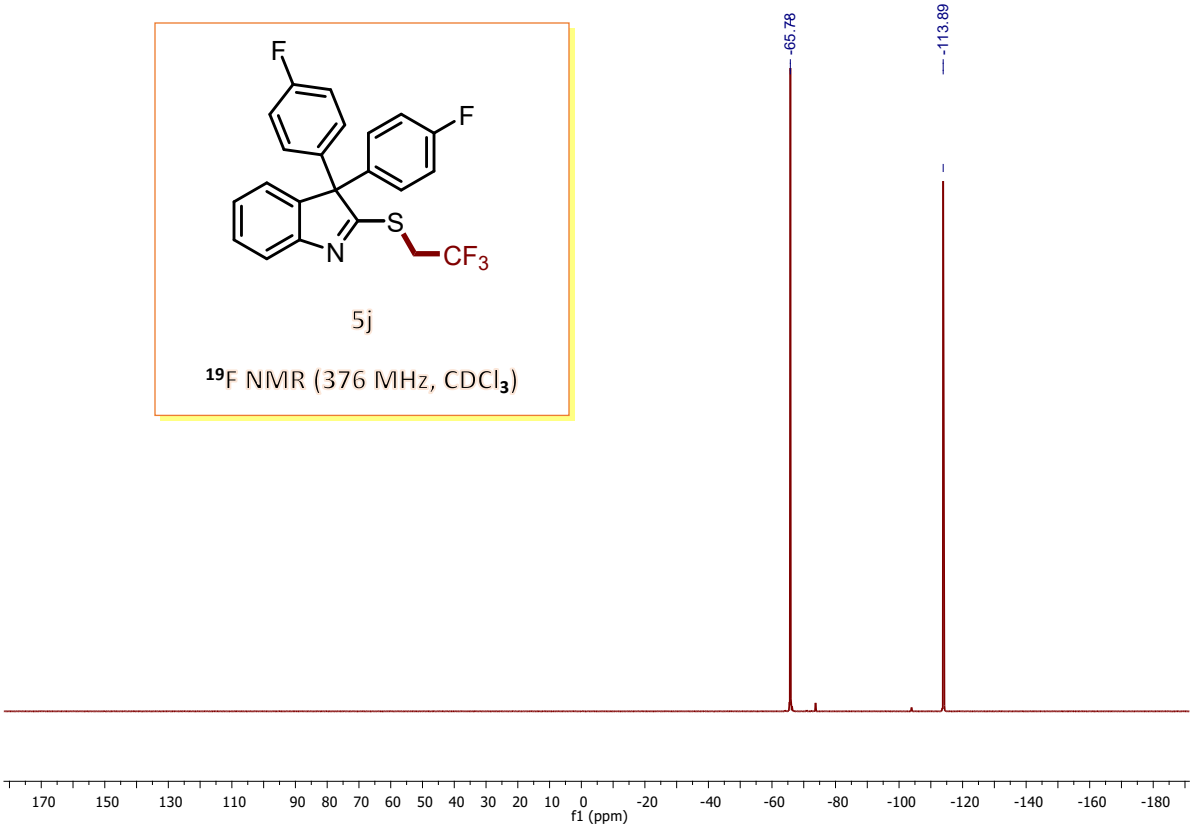


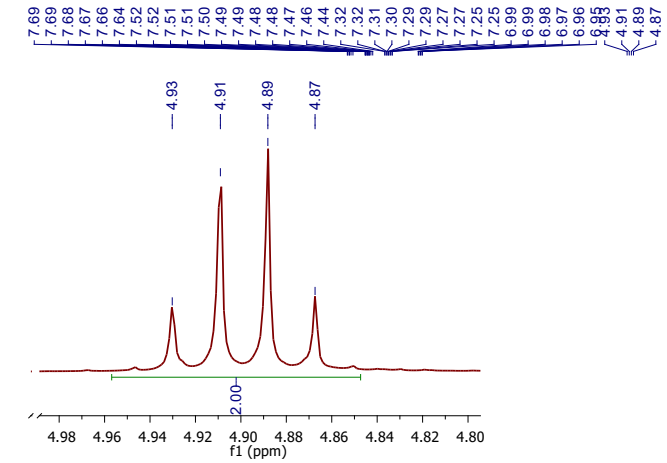
5j

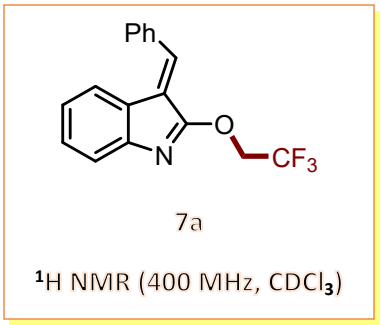
^{1}H NMR (400 MHz, $CDCl_3$)




181.63
163.70
161.23
153.14
145.09
136.32
136.29
129.18
128.78
126.44
125.82
124.11
123.69
120.94
120.04
116.02
115.81
71.86
33.01
32.67
32.33
32.00
F
F
S
N
CF3
5j
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 -10
f1 (ppm)

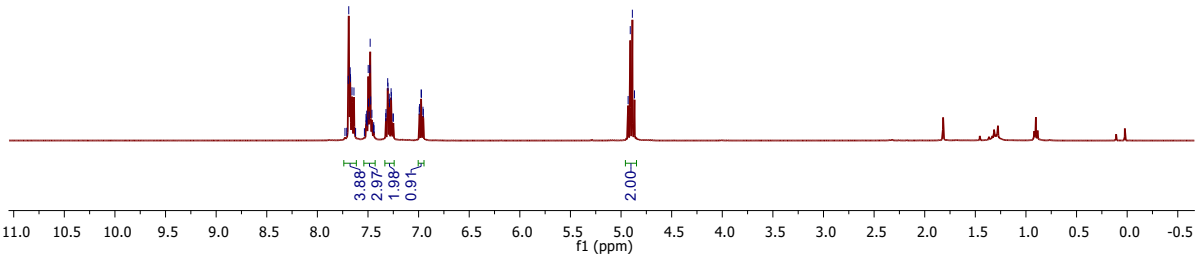

F
F
S
N
CF3
5j
19F NMR (376 MHz, CDCl3)
-65.78
-113.89
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

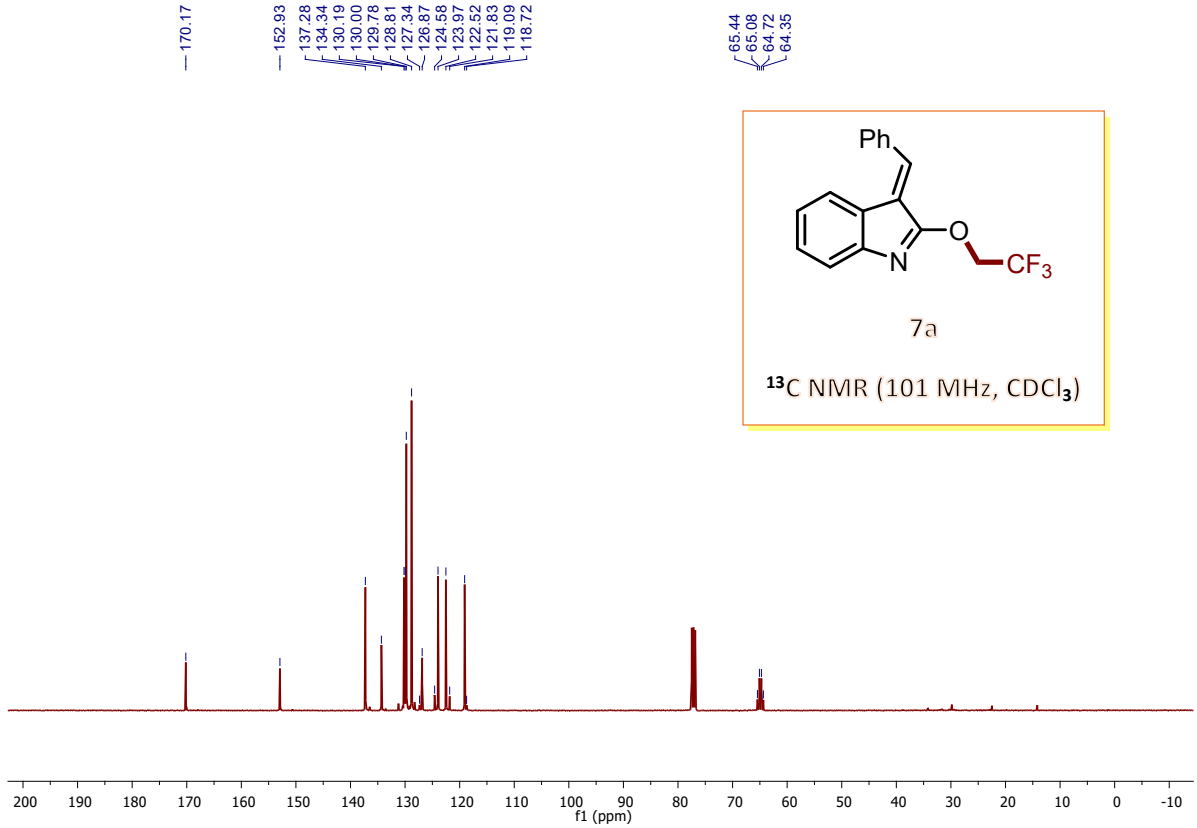




7a

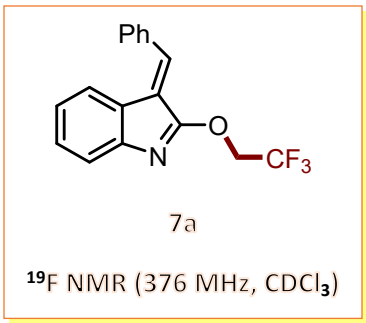
^{1}H NMR (400 MHz, $CDCl_3$)





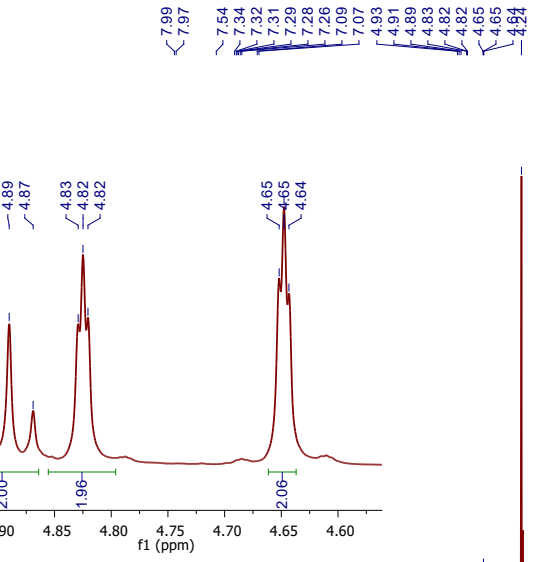
7a

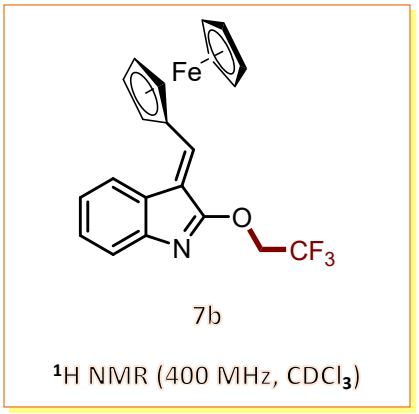
^{13}C NMR (101 MHz, $CDCl_3$)



7a

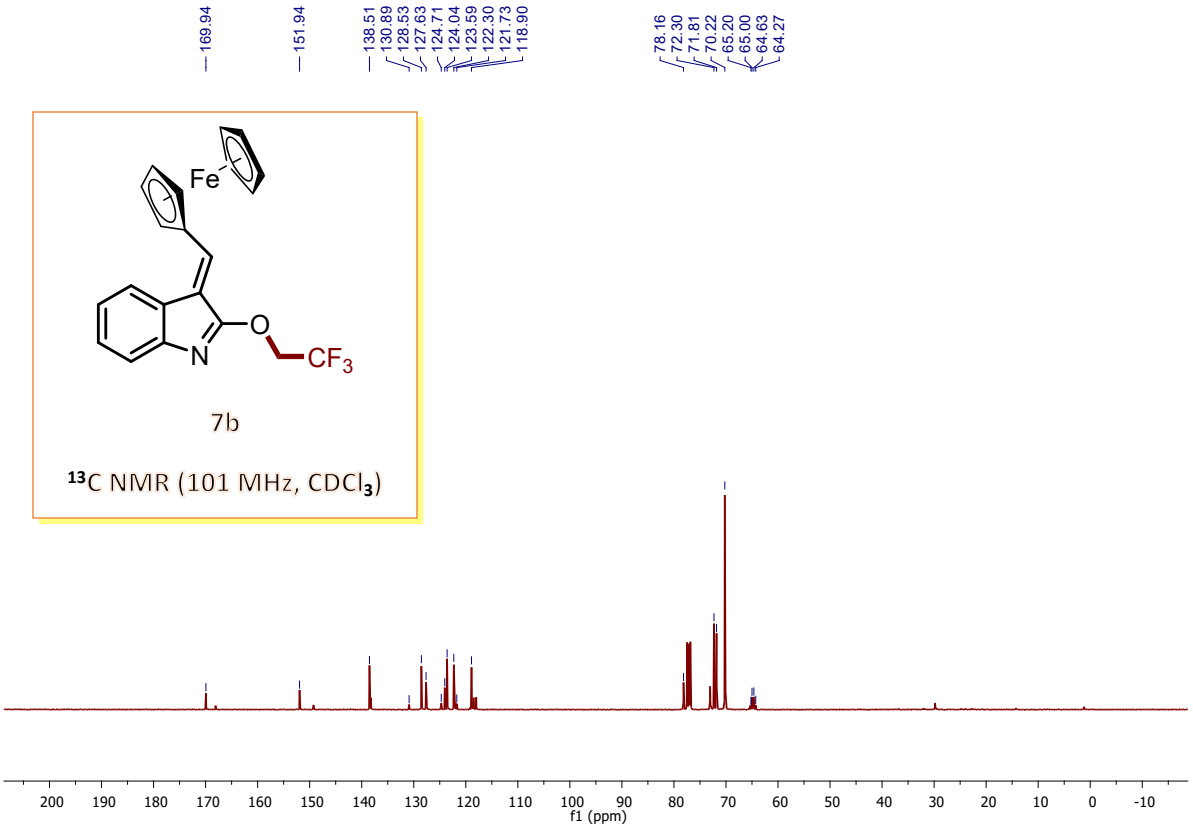
^{19}F NMR (376 MHz, $CDCl_3$)

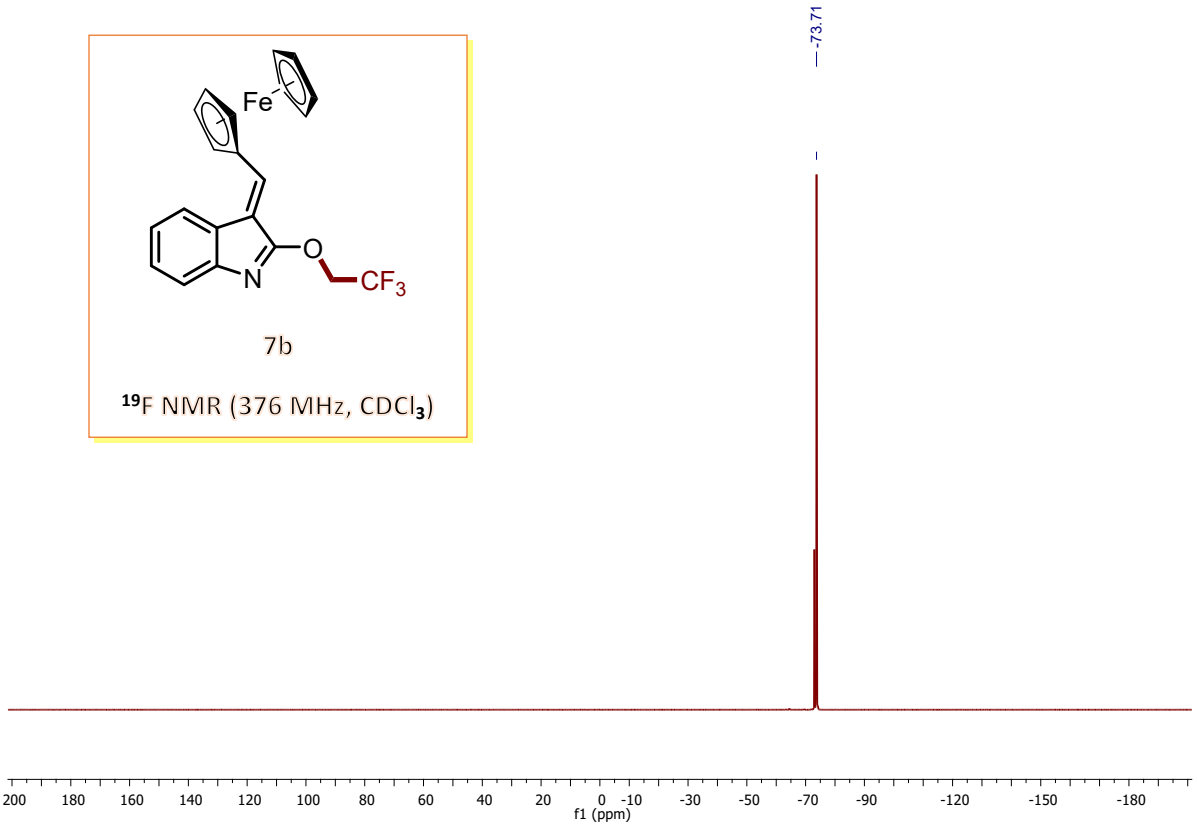


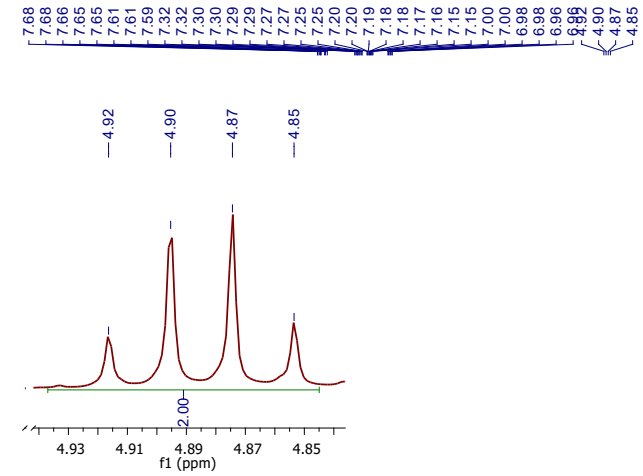


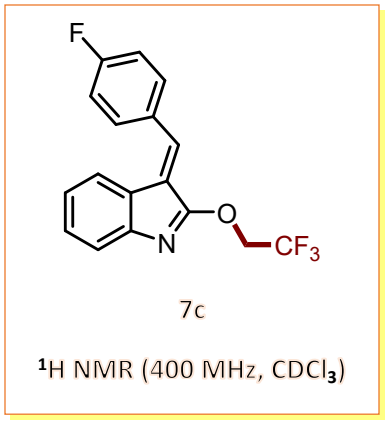
7b

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


169.94
151.94
138.51
130.89
128.53
127.63
124.71
124.04
123.59
122.30
121.73
118.90
78.16
72.30
71.81
70.22
65.20
65.00
64.63
64.27
Fe
O
N
CF3
7b
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 -10
f1 (ppm)

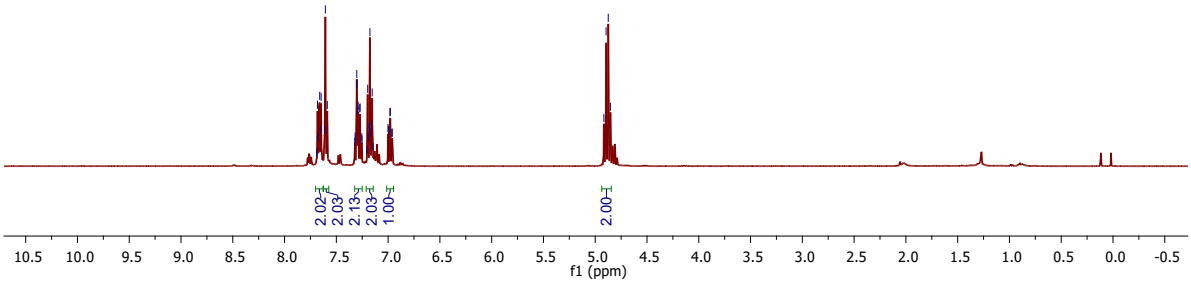

-73.71
Fe
O
N
CF3
7b
19F NMR (376 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -120 -150 -180
f1 (ppm)

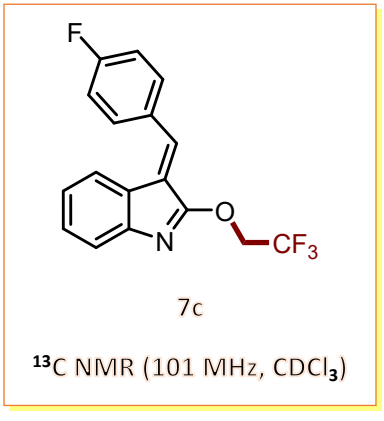




7c

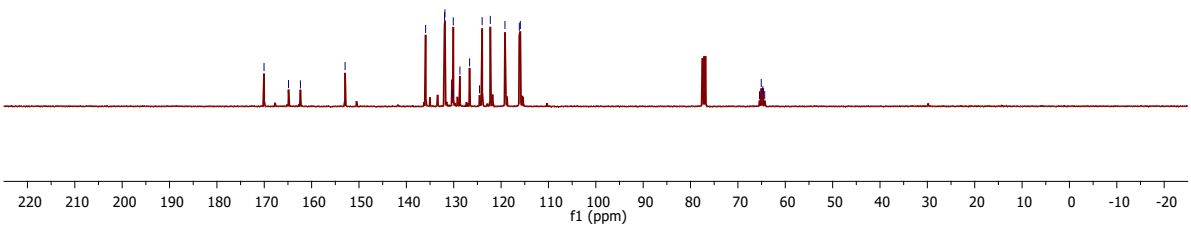
^{1}H NMR (400 MHz, $CDCl_3$)

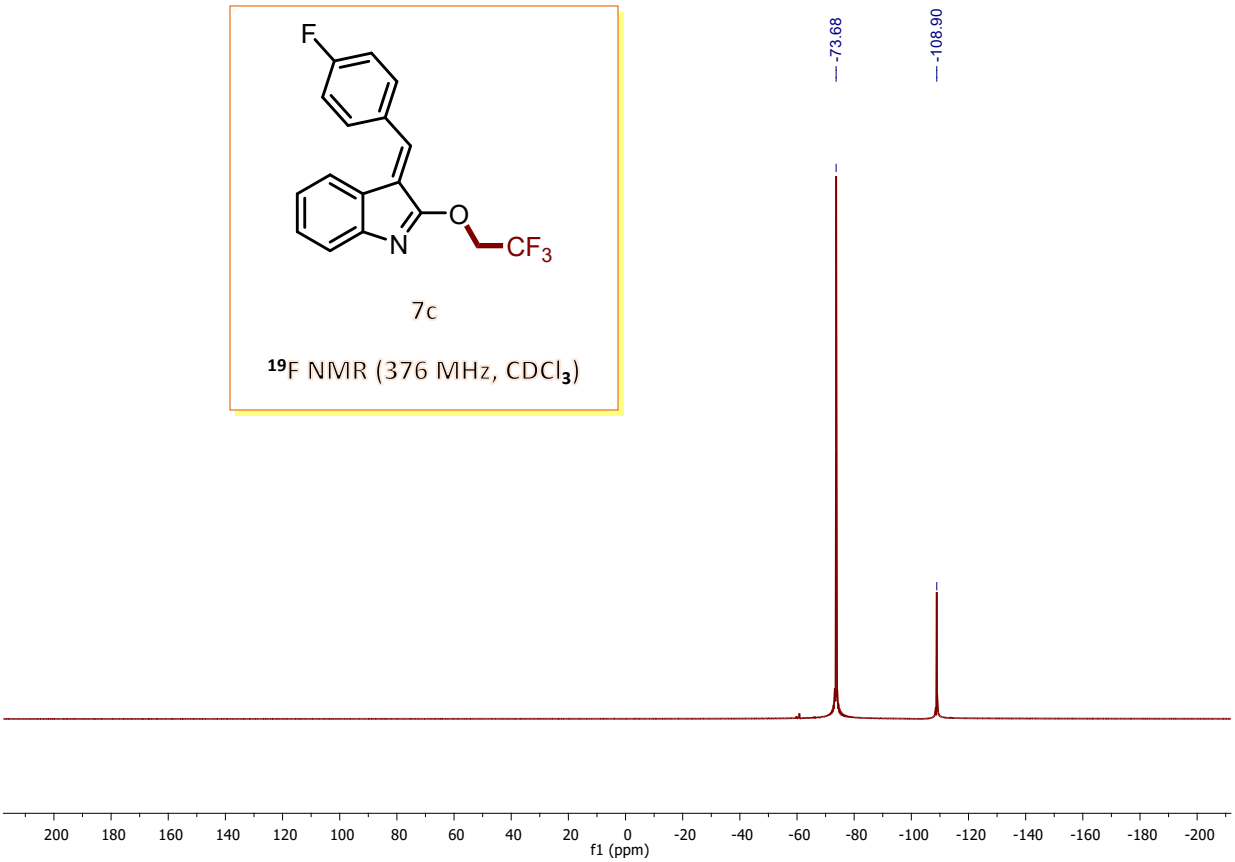


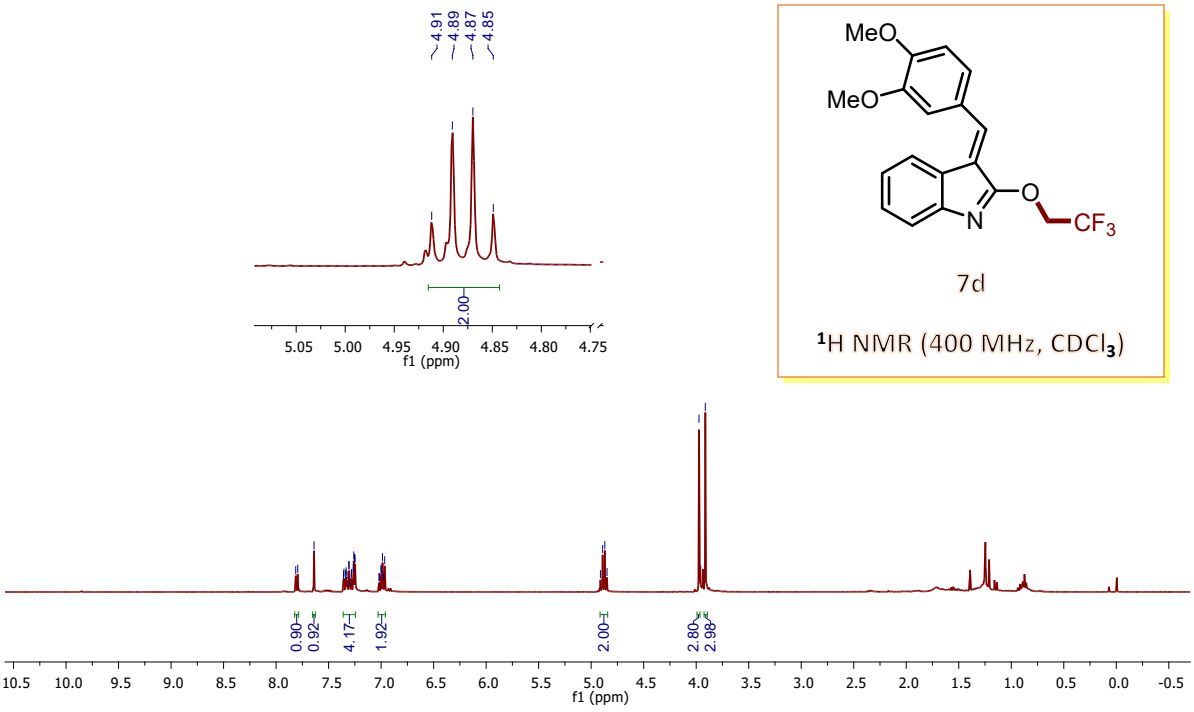


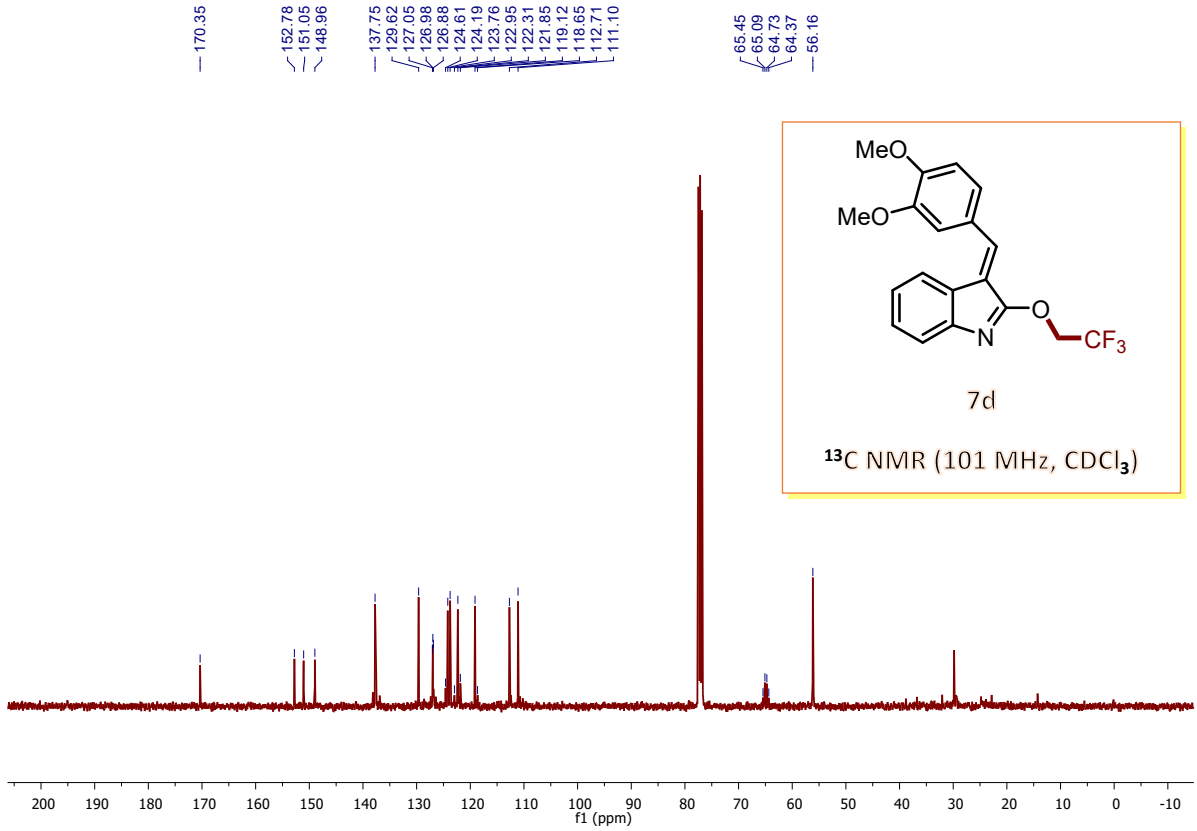
7c

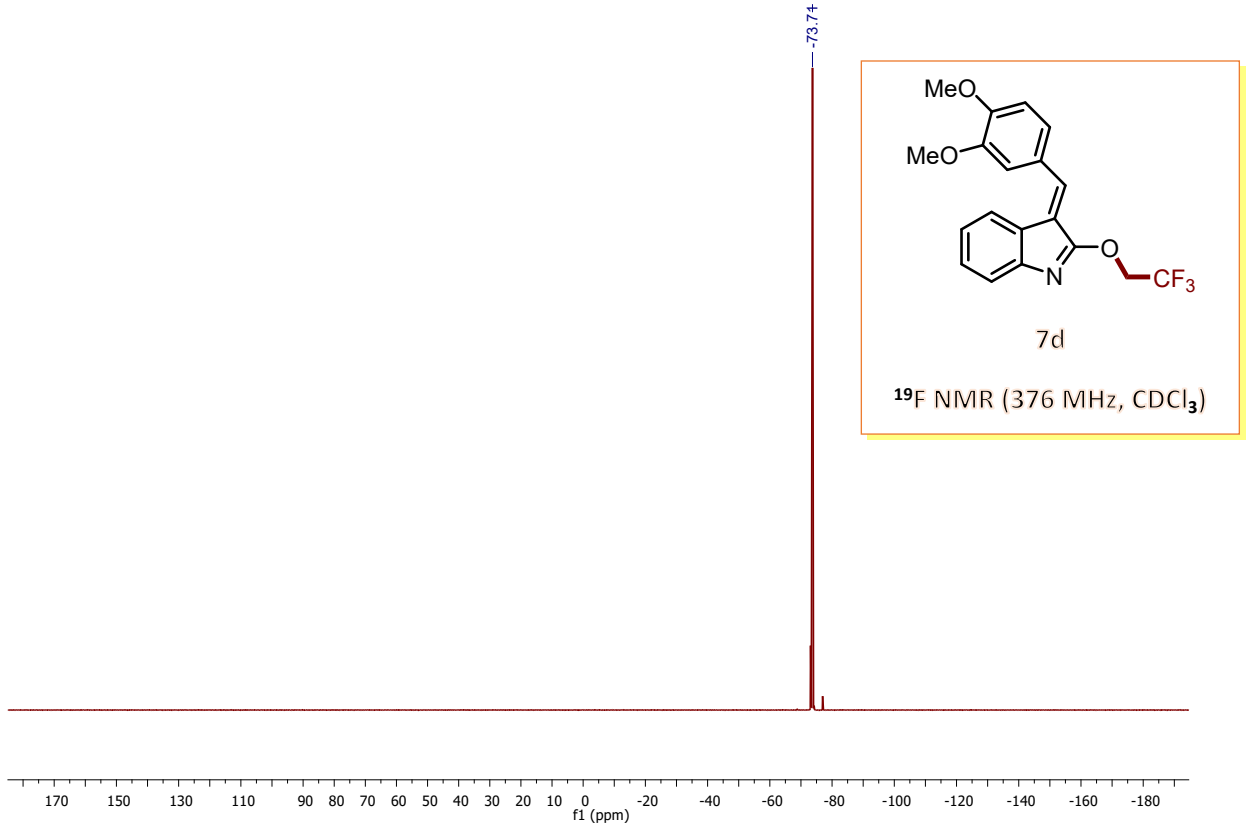
^{13}C NMR (101 MHz, $CDCl_3$)

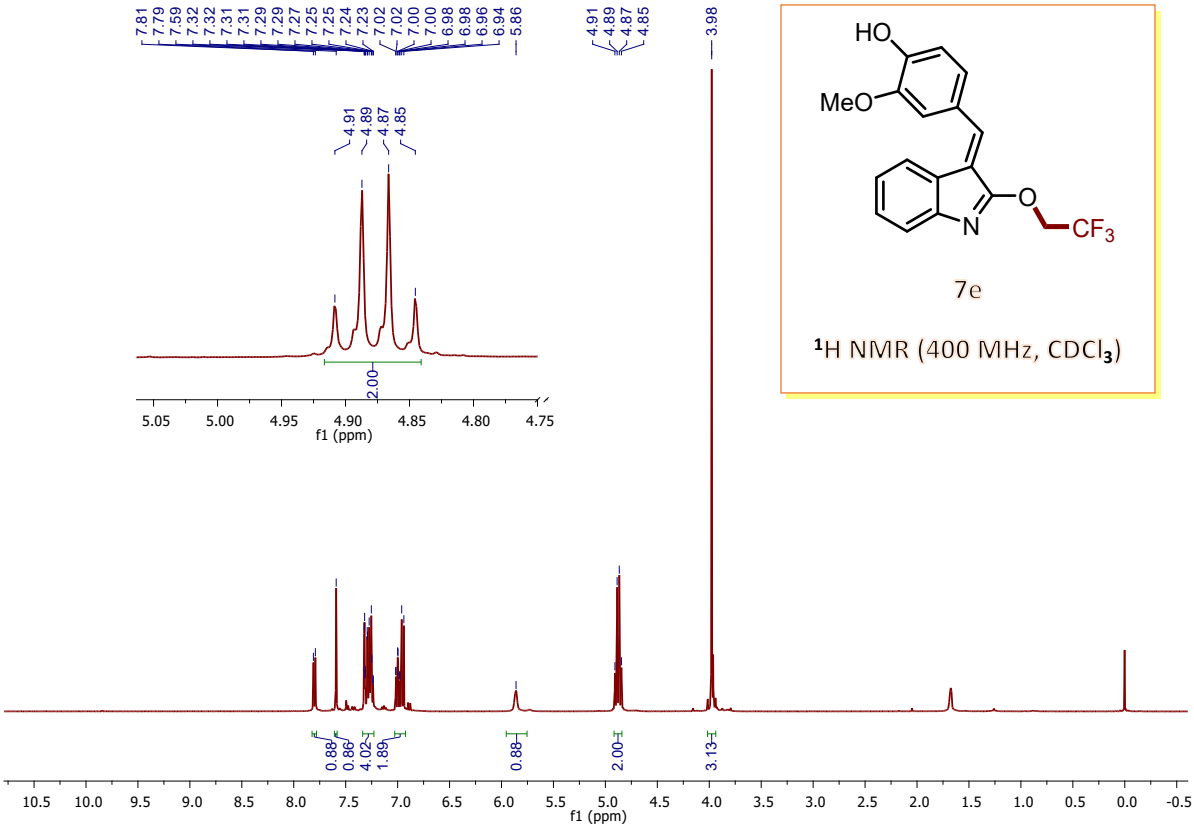


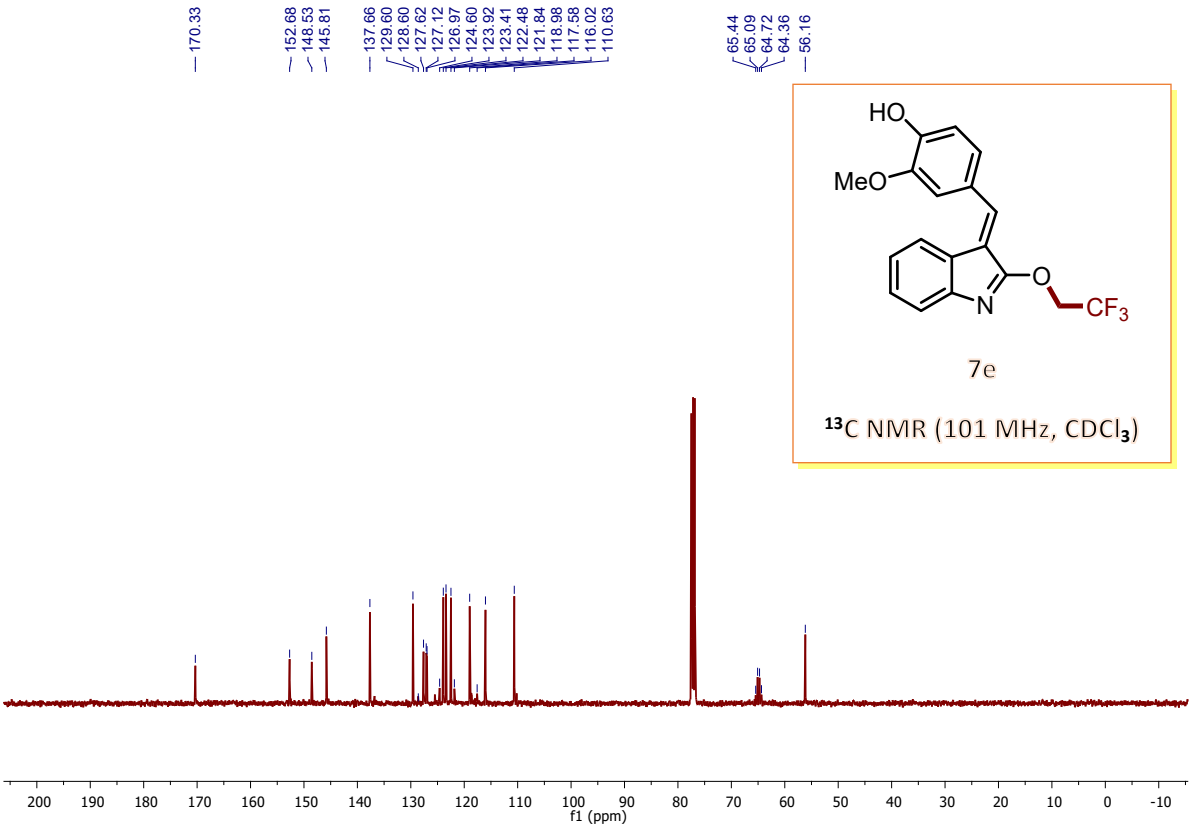

F
O
N
CF3
7c
19F NMR (376 MHz, CDCl3)
-73.68
-108.90
f1 (ppm)

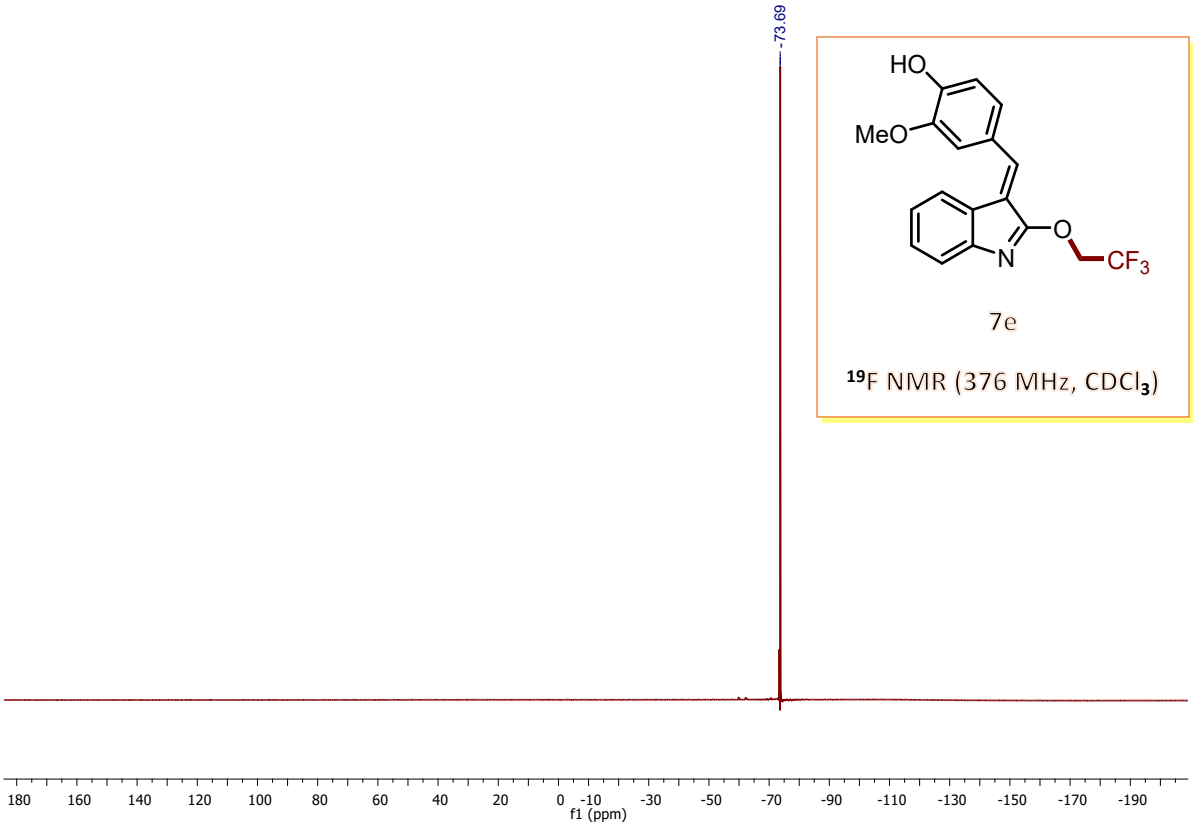

7.81
7.79
7.64
7.36
7.35
7.34
7.33
7.32
7.31
7.31
7.30
7.28
7.28
7.26
7.26
7.25
7.25
7.02
7.02
7.00
7.00
6.99
6.98
6.97
4.91
4.89
4.87
4.85
3.97
3.91
2.00
f1 (ppm)
MeO
MeO
O
N
CF3
7d
1H NMR (400 MHz, CDCl3)
0.90
0.92
4.17
1.92
2.00
2.80
2.98
f1 (ppm)


170.35
152.78
151.05
148.96
137.75
129.62
127.05
126.98
126.88
124.61
124.19
123.76
122.95
122.31
121.85
119.12
118.65
112.71
111.10
65.45
65.09
64.73
64.37
56.16
MeO
MeO
O
N
CF3
7d
13C NMR (101 MHz, CDCl3)
f1 (ppm)


-73.74
MeO
MeO
O
N
CF3
7d
19F NMR (376 MHz, CDCl3)
f1 (ppm)

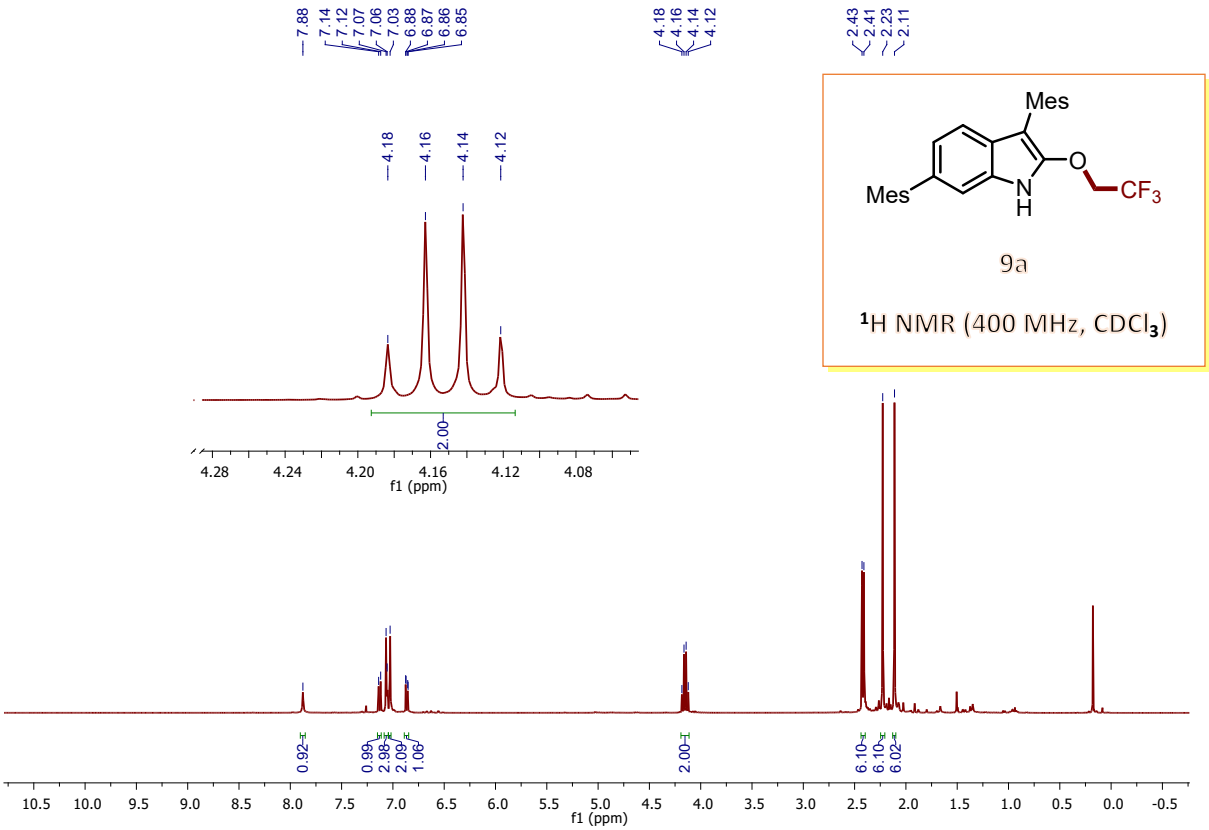

HO
MeO
O
N
CF3
7e
1H NMR (400 MHz, CDCl3)


HO
MeO
O
N
CF3
7e
13C NMR (101 MHz, CDCl3)



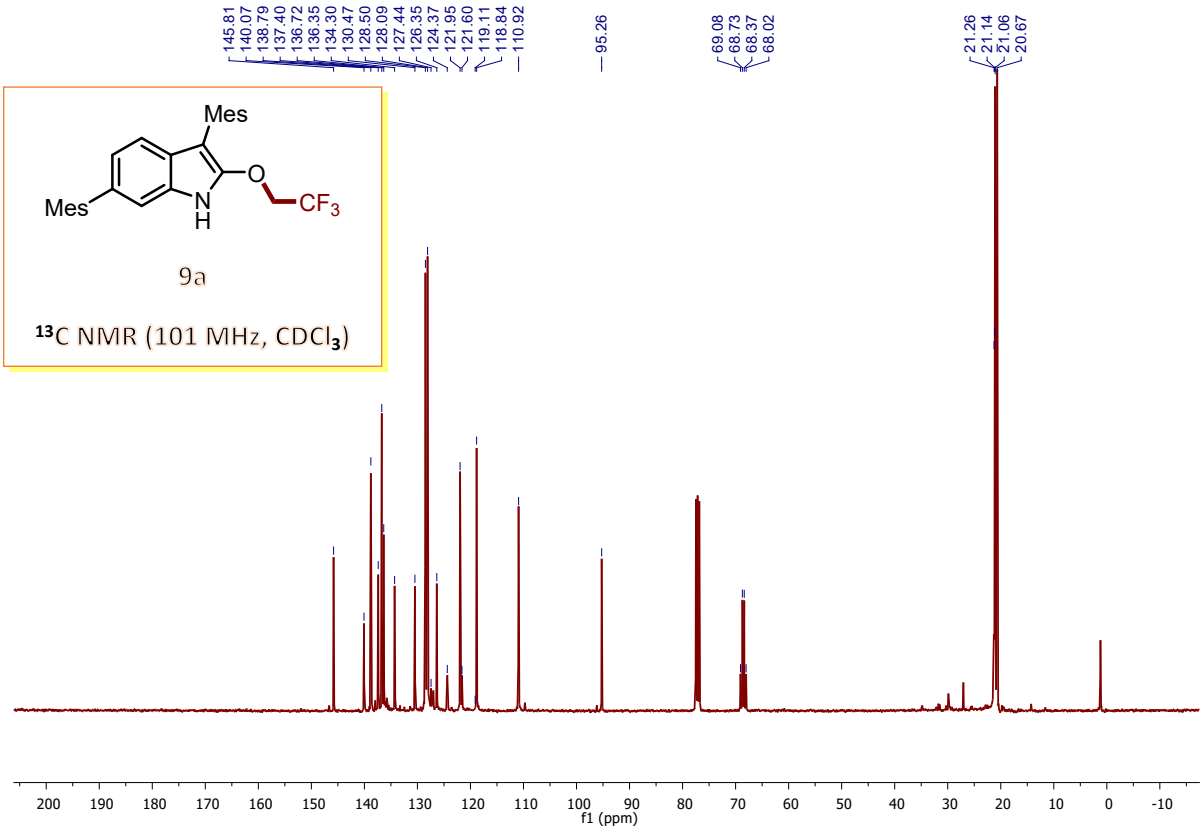
7e

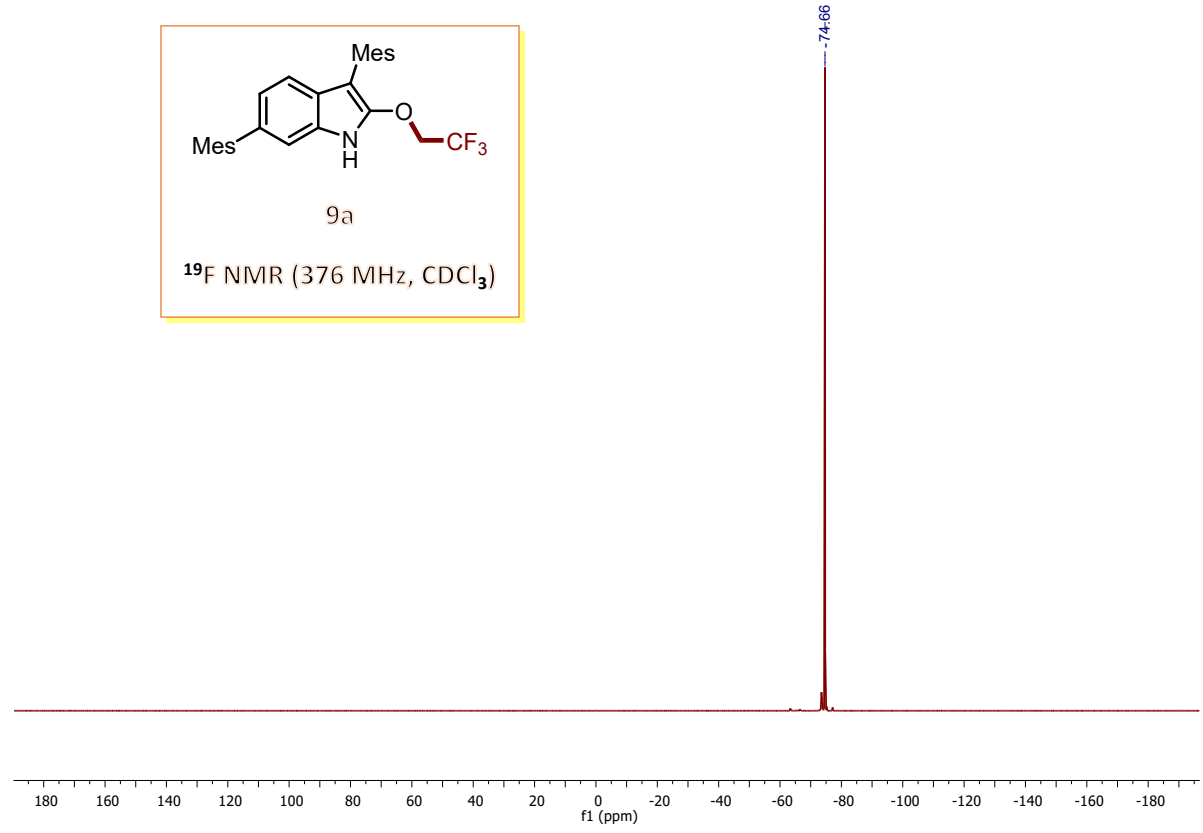
^{19}F NMR (376 MHz, $CDCl_3$)

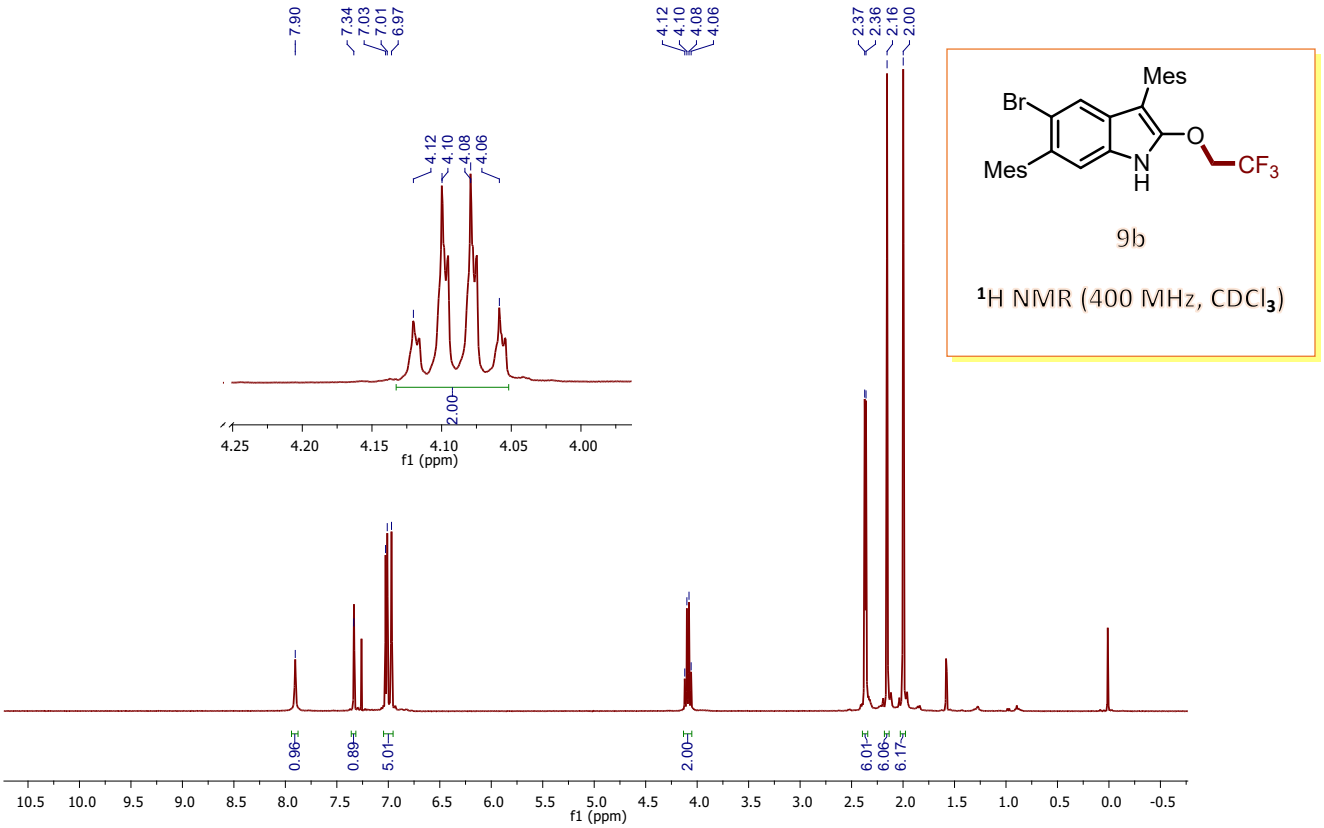


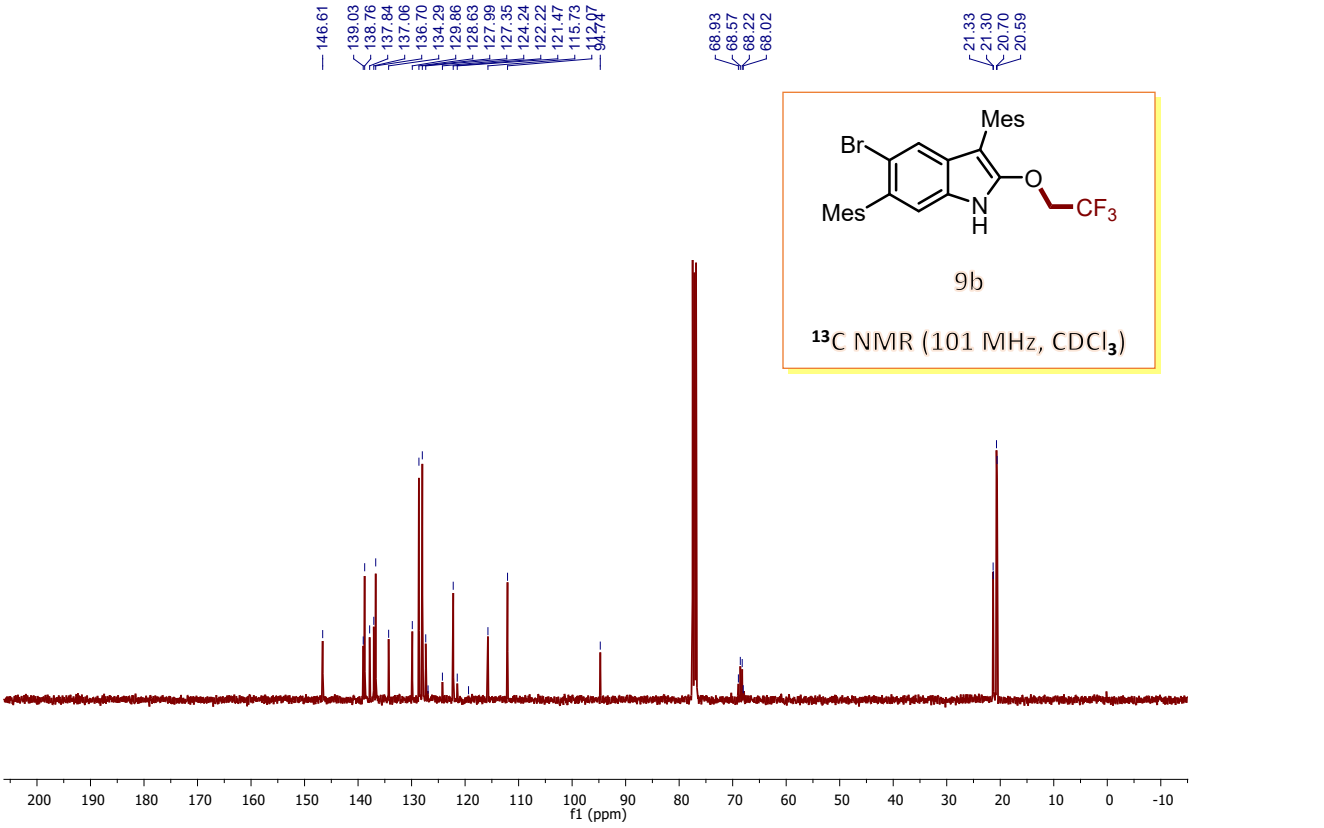
9a

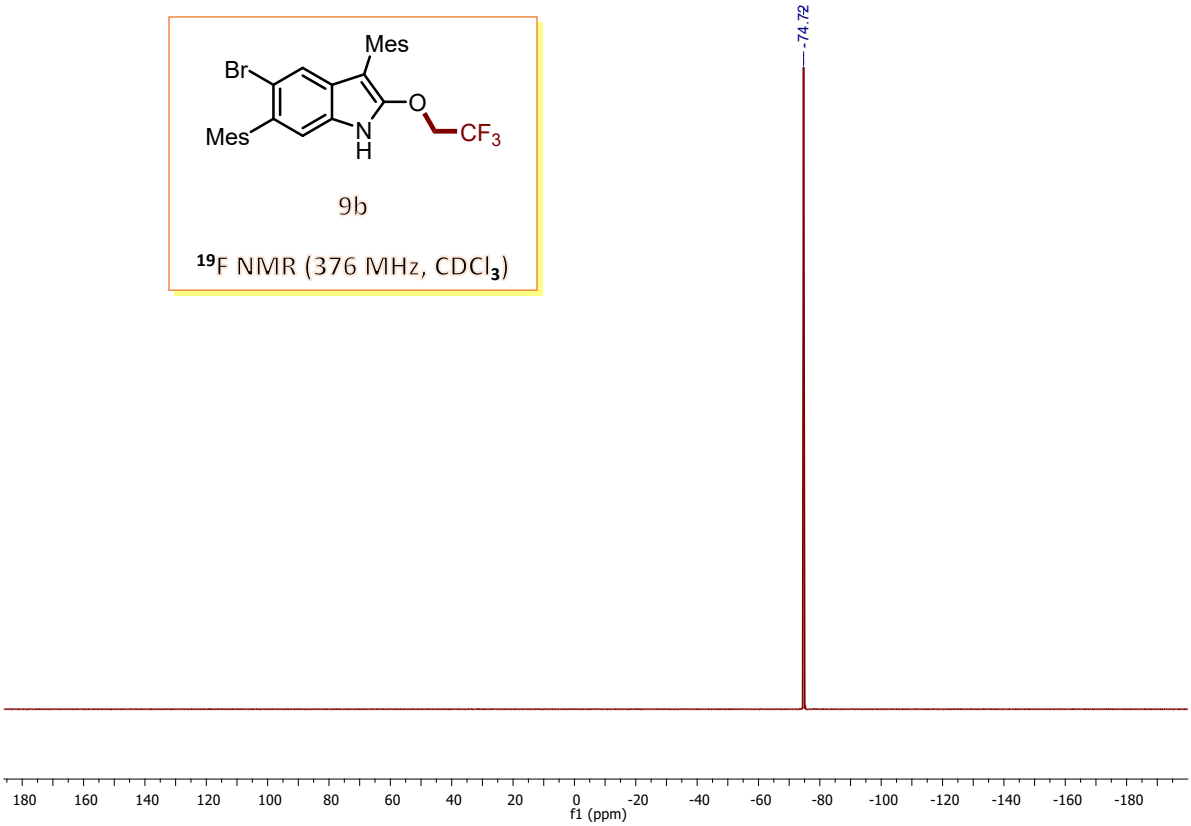
^{1}H NMR (400 MHz, $CDCl_3$)

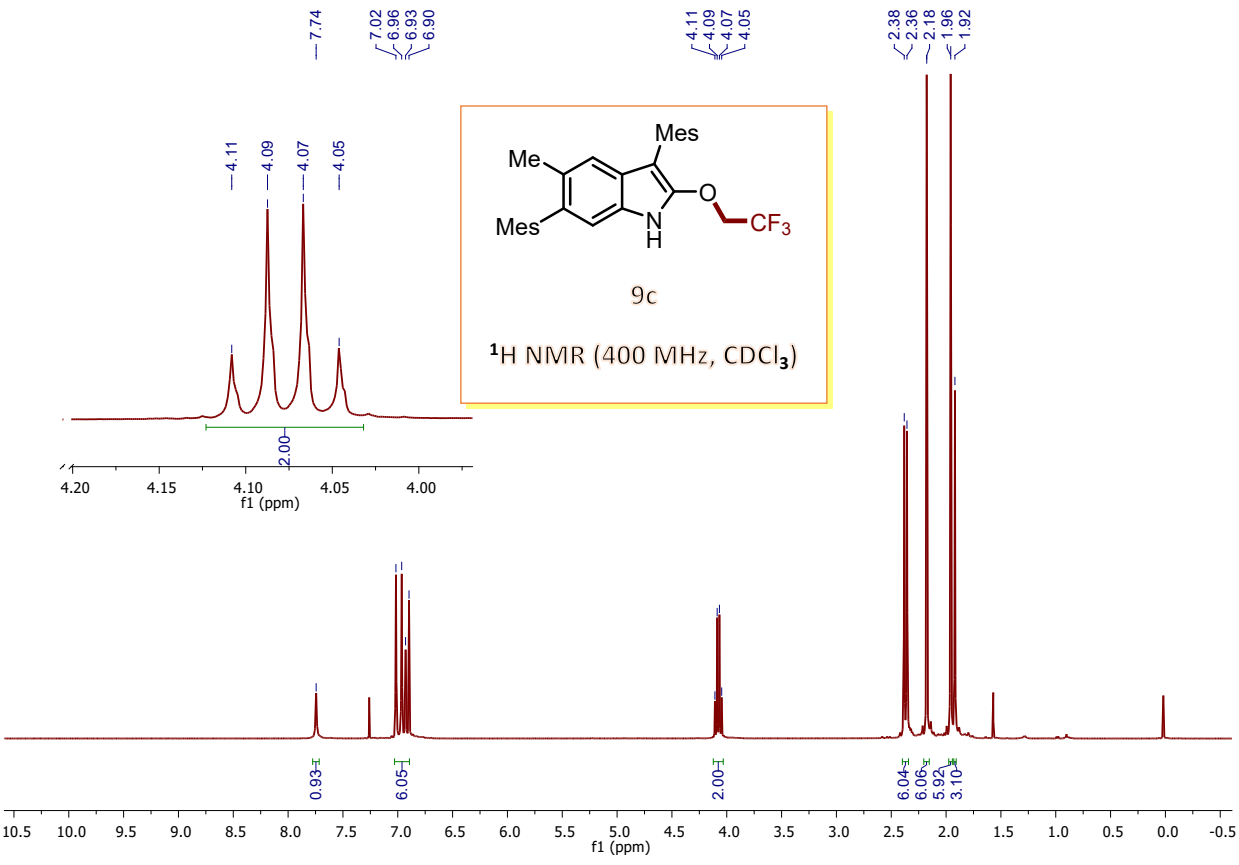

145.81
140.07
138.79
137.40
136.72
136.35
134.30
130.47
128.50
128.09
127.44
126.35
124.37
121.95
121.60
119.11
118.84
110.92
95.26
69.08
68.73
68.37
68.02
21.26
21.14
21.06
20.67
Mes
Mes
O
N
H
CF3
9a
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

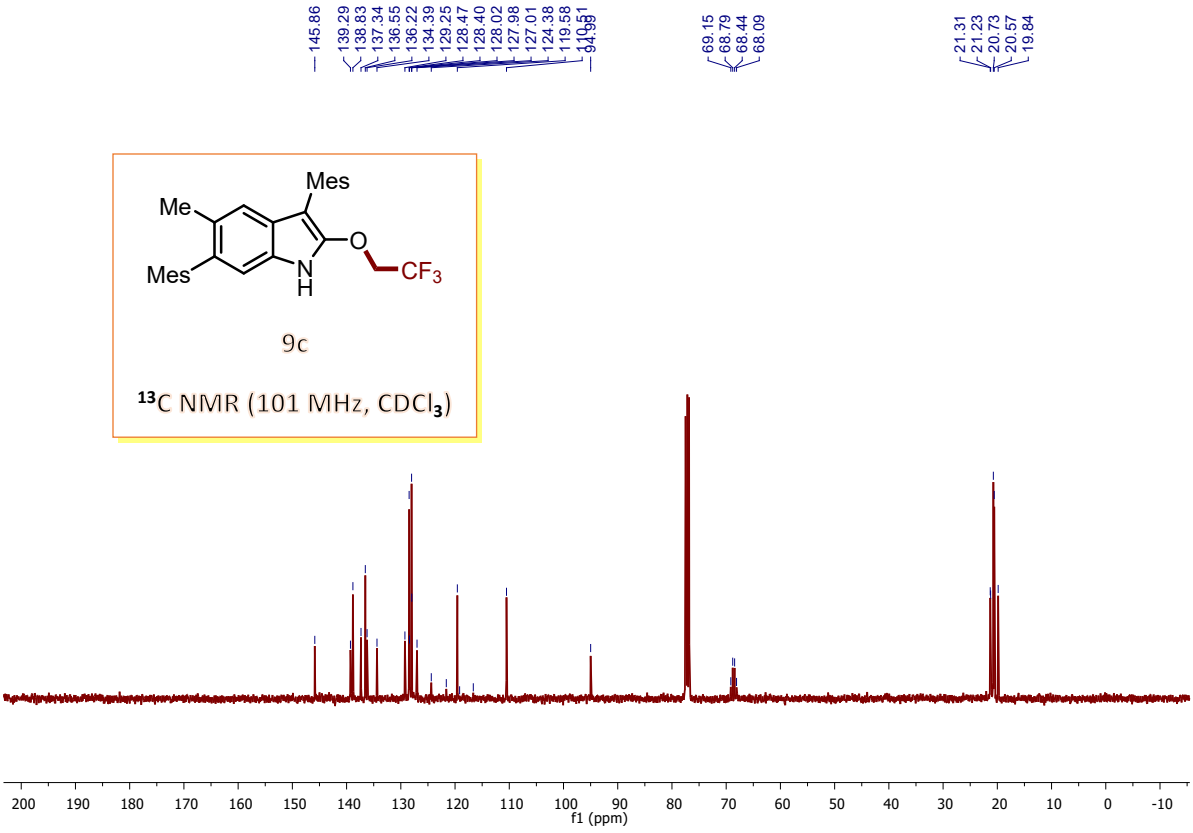

-74.66
Mes
Mes
O
N
H
CF3
9a
19F NMR (376 MHz, CDCl3)
180 160 140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
f1 (ppm)

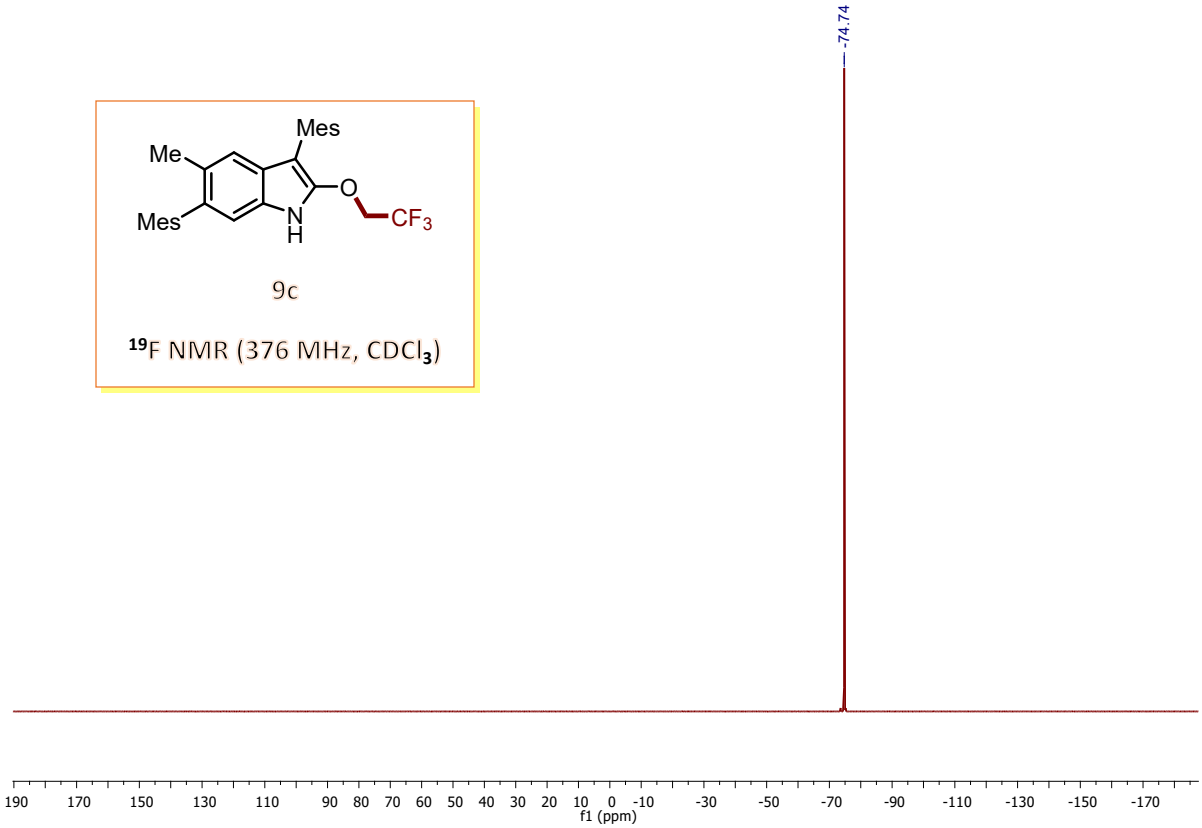

7.90
7.34
7.03
7.01
6.97
4.12
4.10
4.08
4.06
2.37
2.36
2.16
2.00
0.96
0.89
5.01
2.00
6.01
6.06
6.17
f1 (ppm)
Mes
Br
Mes
O
CF3
N
H
9b
1H NMR (400 MHz, CDCl3)

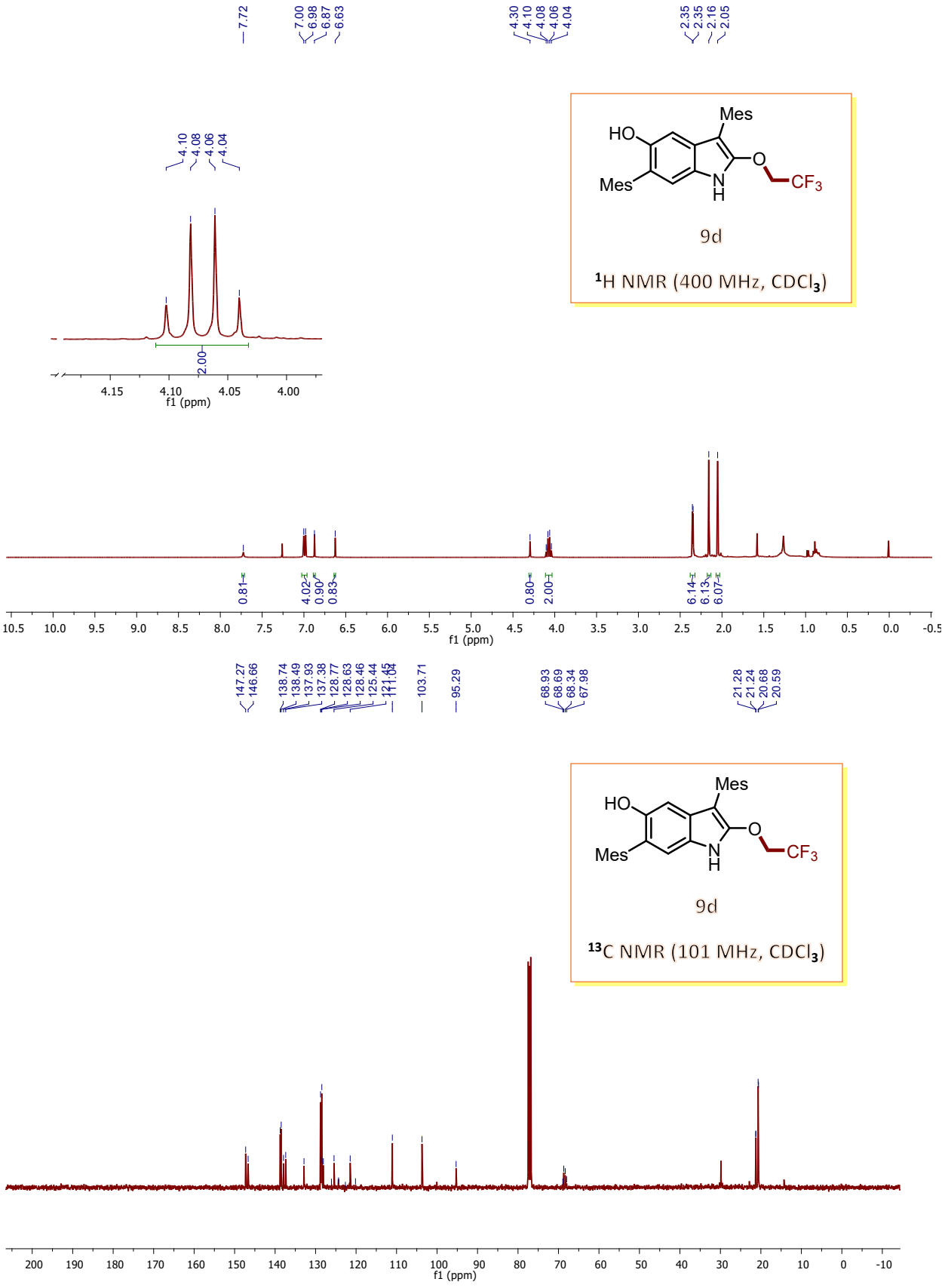

146.61
139.03
138.76
137.84
137.06
136.70
134.29
129.86
128.63
127.99
127.35
124.24
122.22
121.47
115.73
112.07
94.74
68.93
68.57
68.22
68.02
21.33
21.30
20.70
20.59
f1 (ppm)
Mes
Br
Mes
O
CF3
N
H
9b
13C NMR (101 MHz, CDCl3)

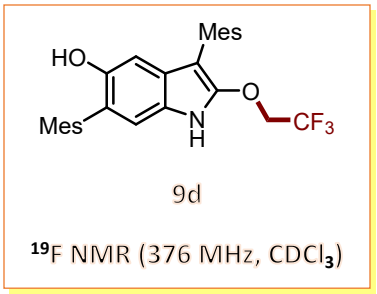

Br
Mes
Mes
O
N
H
CF3
9b
19F NMR (376 MHz, CDCl3)
-74.72
f1 (ppm)


7.74
7.02
6.96
6.93
6.90
4.11
4.09
4.07
4.05
2.38
2.36
2.18
1.96
1.92
Me
Mes
Mes
O
N
H
CF3
9c
1H NMR (400 MHz, CDCl3)
2.00
f1 (ppm)
0.93
6.05
2.00
6.04
6.06
5.92
3.10
f1 (ppm)


145.86
139.29
138.83
137.34
136.55
136.22
134.39
129.25
128.47
128.40
128.02
127.98
127.01
124.38
119.58
110.51
94.99
69.15
68.79
68.44
68.09
21.31
21.23
20.73
20.57
19.84
Mes
Me
Mes
O
N
H
CF3
9c
13C NMR (101 MHz, CDCl3)
f1 (ppm)

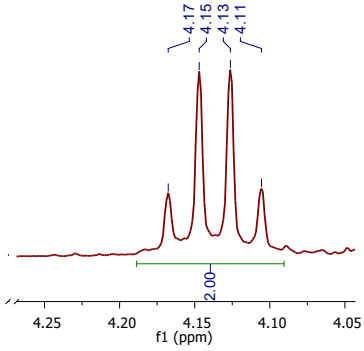

-74.74
Mes
Me
Mes
O
N
H
CF3
9c
19F NMR (376 MHz, CDCl3)
f1 (ppm)

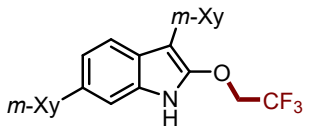

7.72
7.00
6.98
6.87
6.63
4.30
4.10
4.08
4.06
4.04
2.35
2.35
2.16
2.05
4.10
4.08
4.06
4.04
2.00
4.15
4.10
4.05
4.00
f1 (ppm)
Mes
HO
O
Mes
N
H
CF3
9d
1H NMR (400 MHz, CDCl3)
0.81
4.02
0.90
0.83
0.80
2.00
6.14
6.13
6.07
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
147.27
146.66
138.74
138.49
137.93
137.38
128.77
128.63
128.46
125.44
111.45
111.04
103.71
95.29
68.93
68.69
68.34
67.98
21.28
21.24
20.68
20.59
Mes
HO
O
Mes
N
H
CF3
9d
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
-10
f1 (ppm)



9d

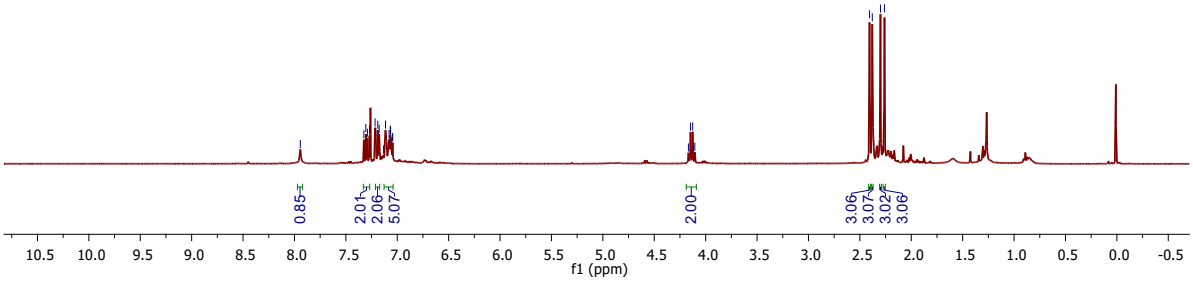
^{19}F NMR (376 MHz, $CDCl_3$)

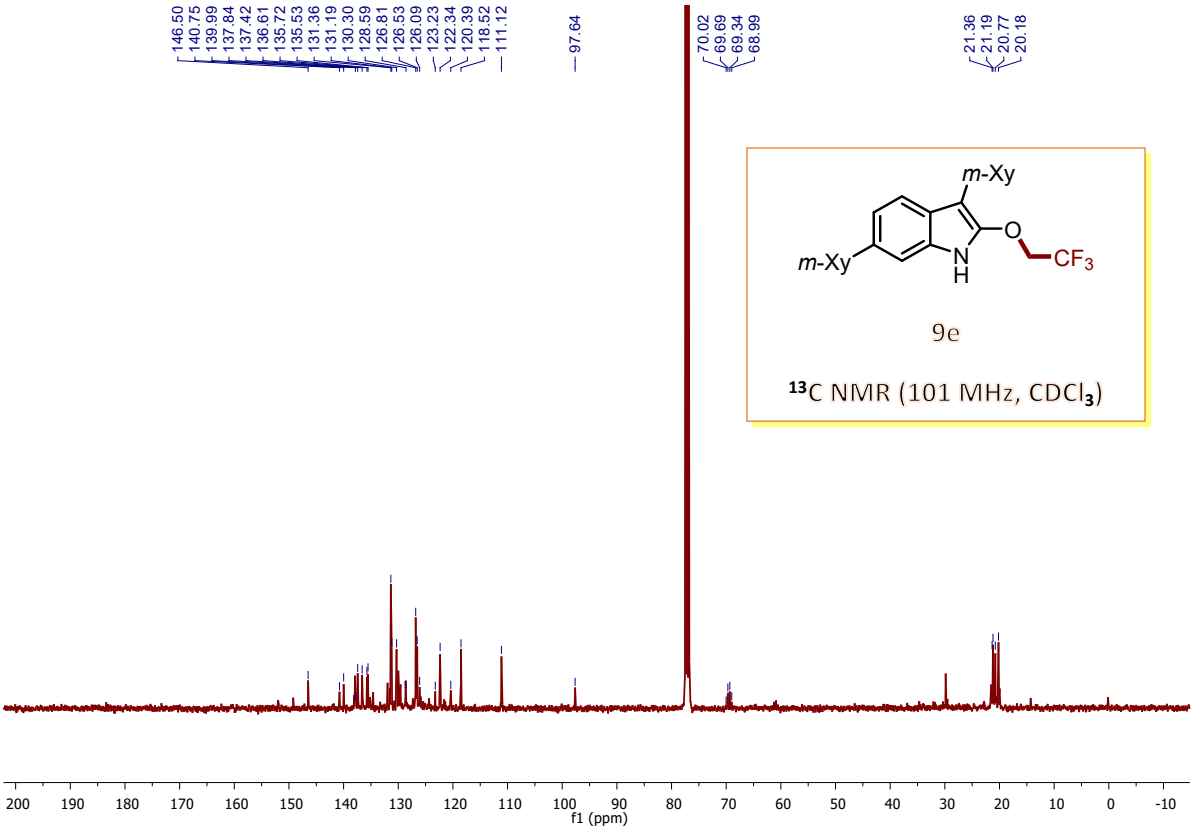


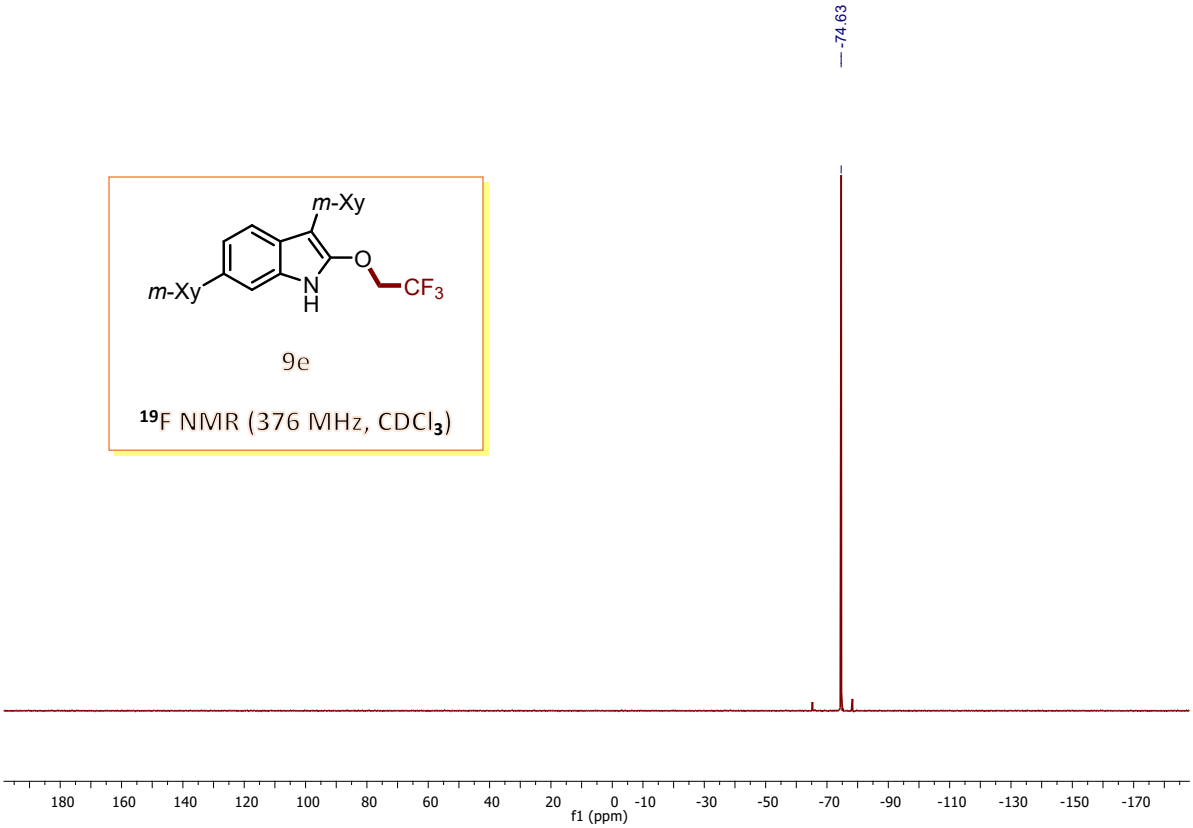


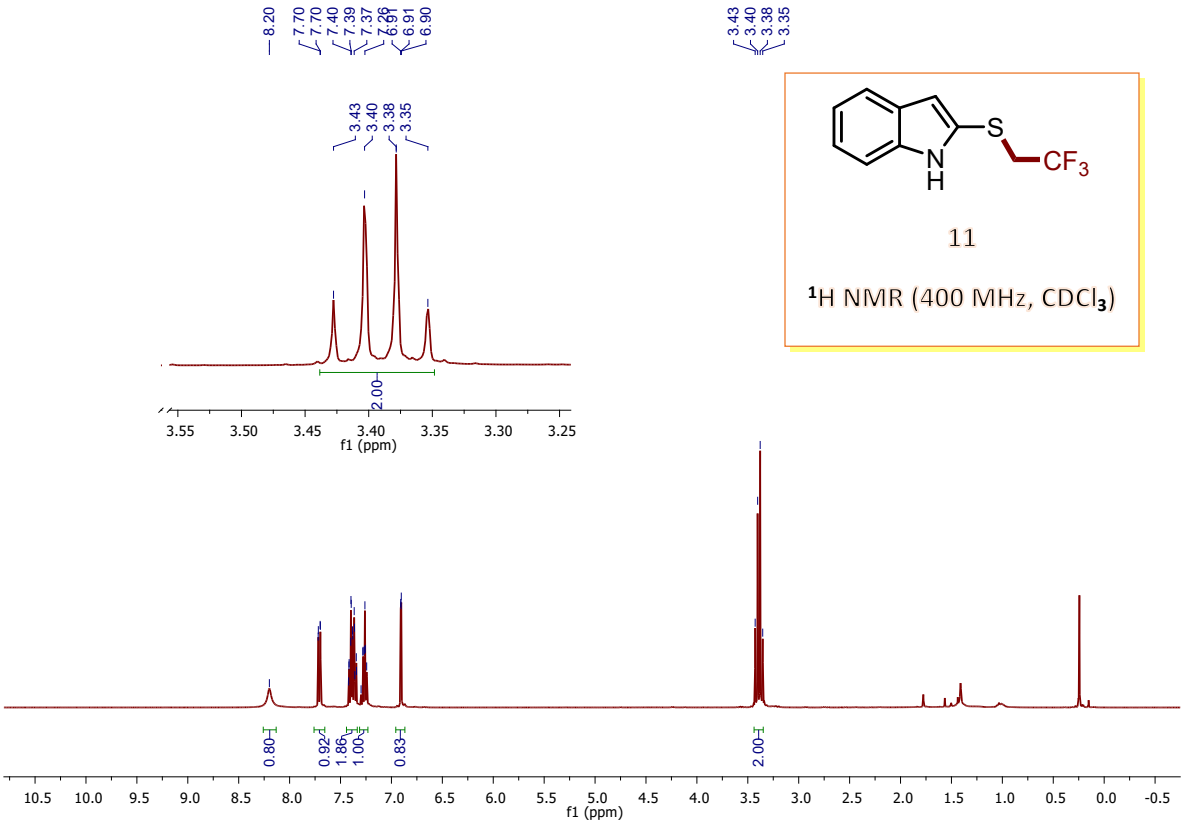
9e

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



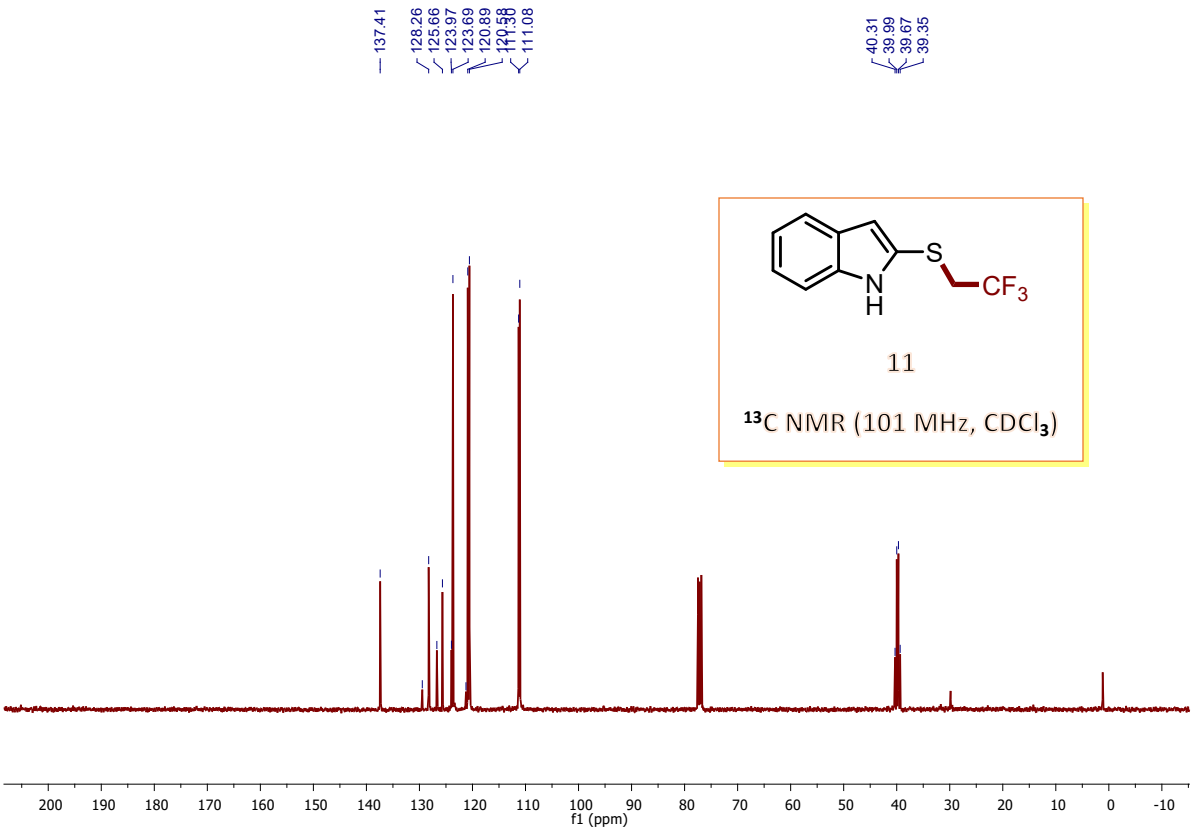

146.50
140.75
139.99
137.84
137.42
136.61
135.72
135.53
131.36
131.19
130.30
128.59
126.81
126.53
126.09
123.23
122.34
120.39
118.52
111.12
97.64
70.02
69.69
69.34
68.99
21.36
21.19
20.77
20.18
m-Xy
m-Xy
O
CF3
N
H
9e
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-74.63
m-Xy
m-Xy
O
CF3
N
H
9e
19F NMR (376 MHz, CDCl3)
180 160 140 120 100 80 60 40 20 0 -10 -30 -50 -70 -90 -110 -130 -150 -170
f1 (ppm)



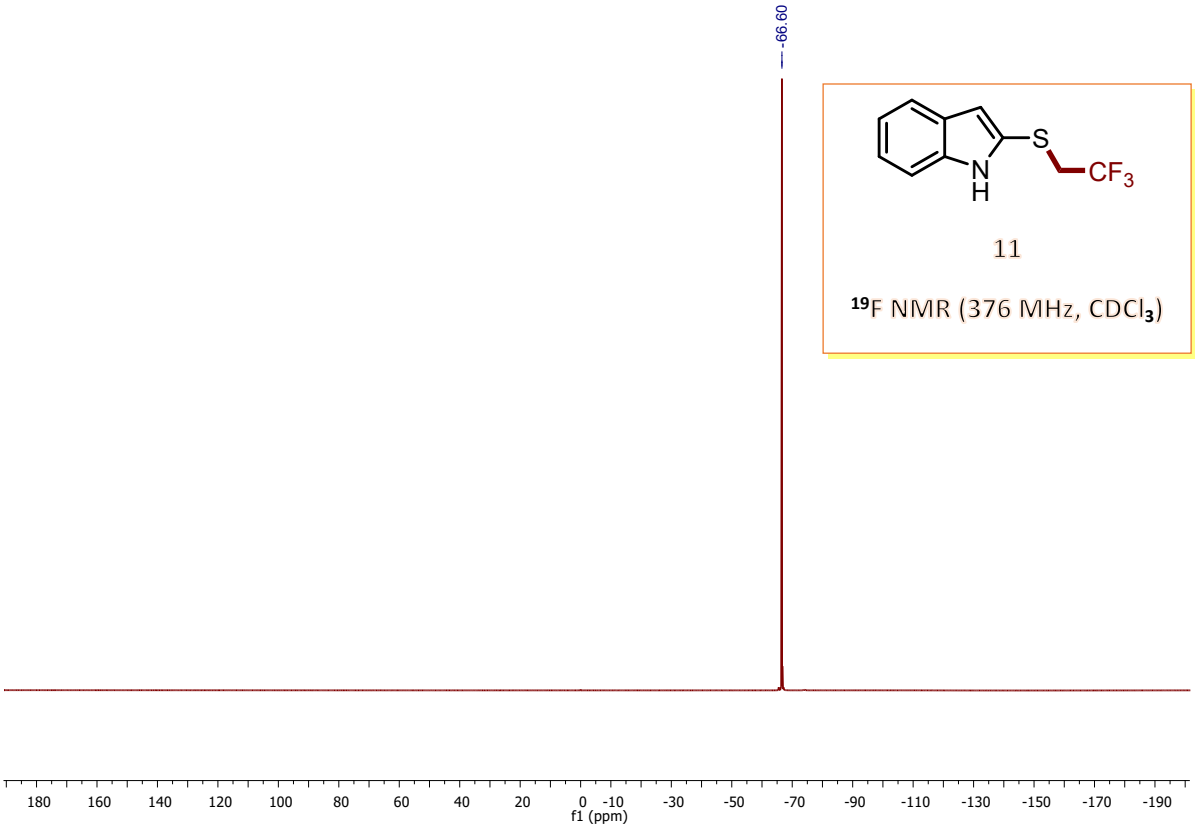
11

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



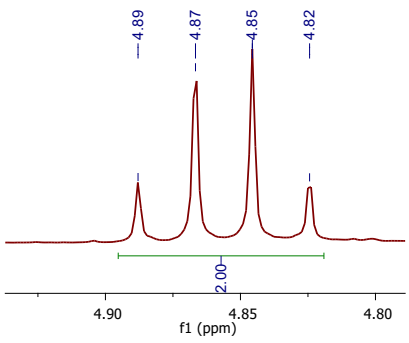
11

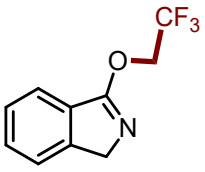
^{13}C NMR (101 MHz, $CDCl_3$)



11

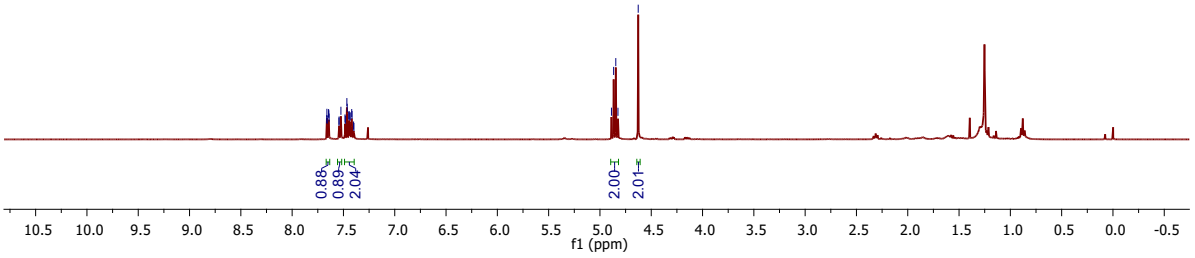
^{19}F NMR (376 MHz, $CDCl_3$)

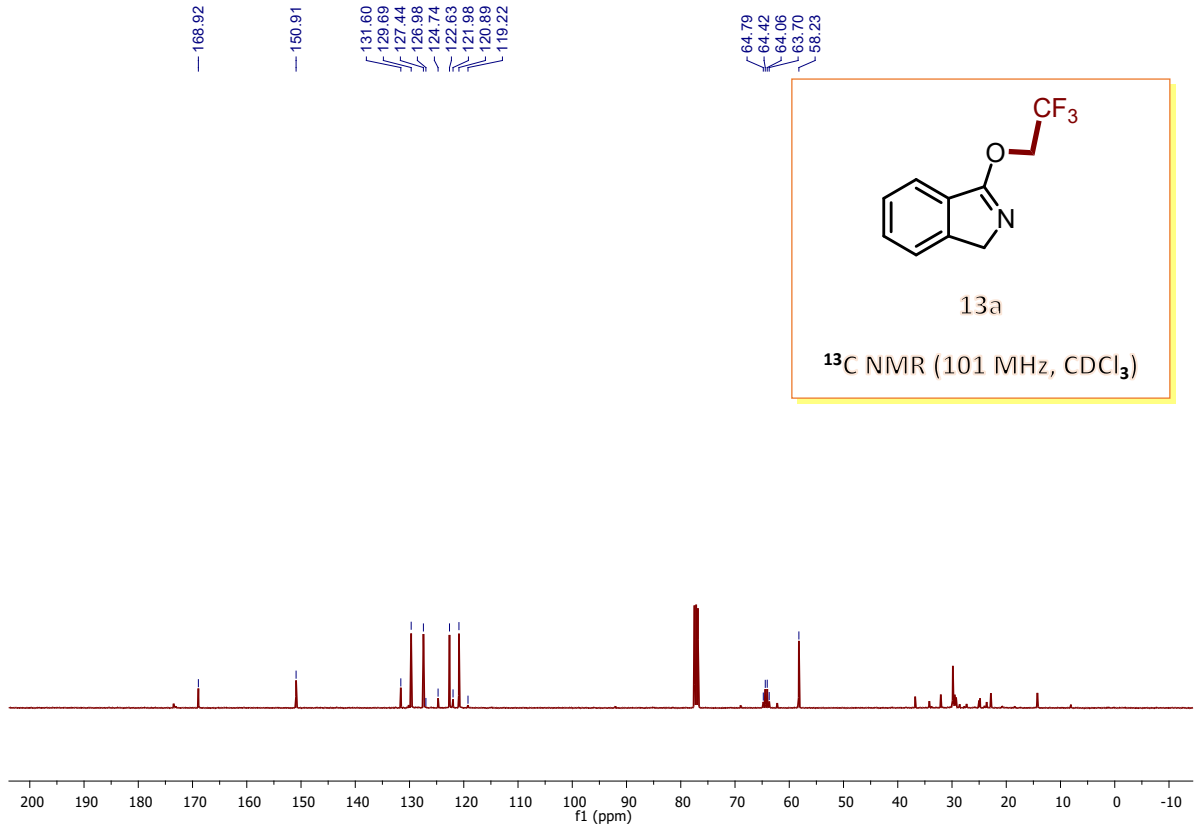


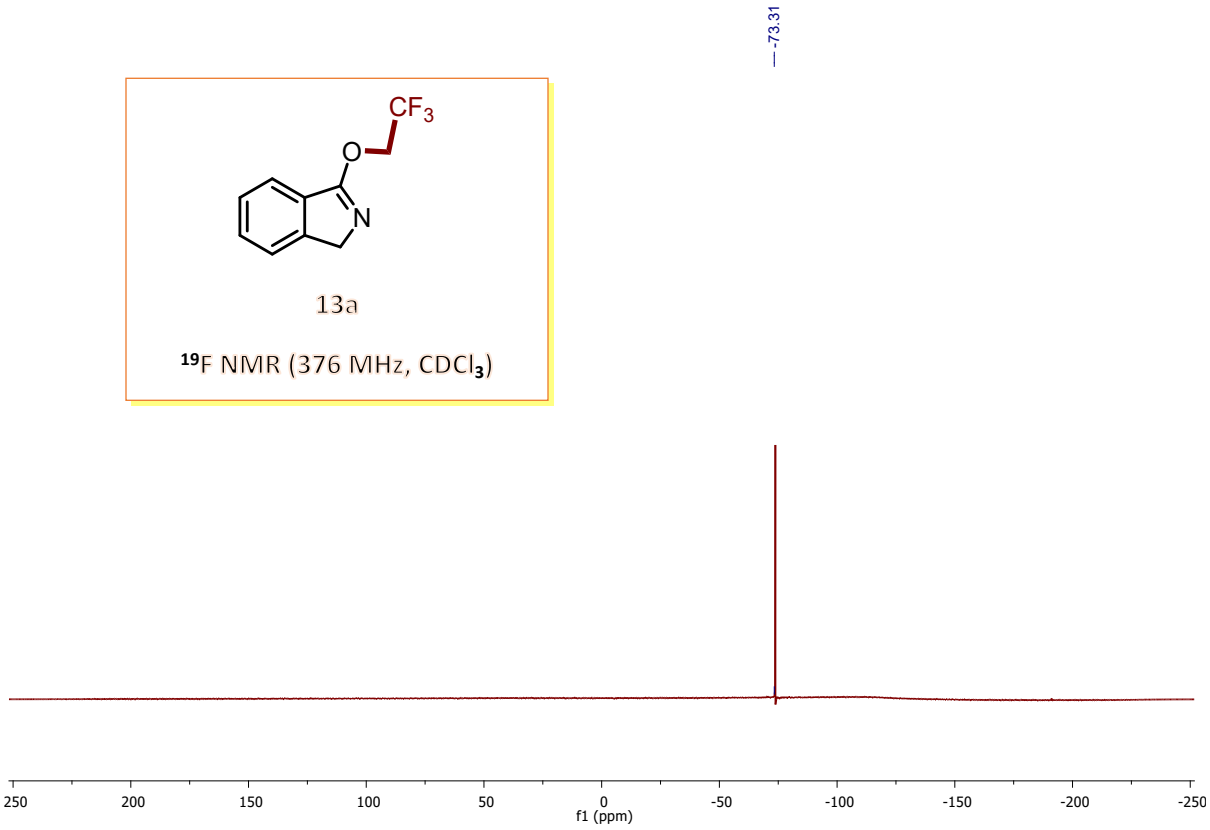


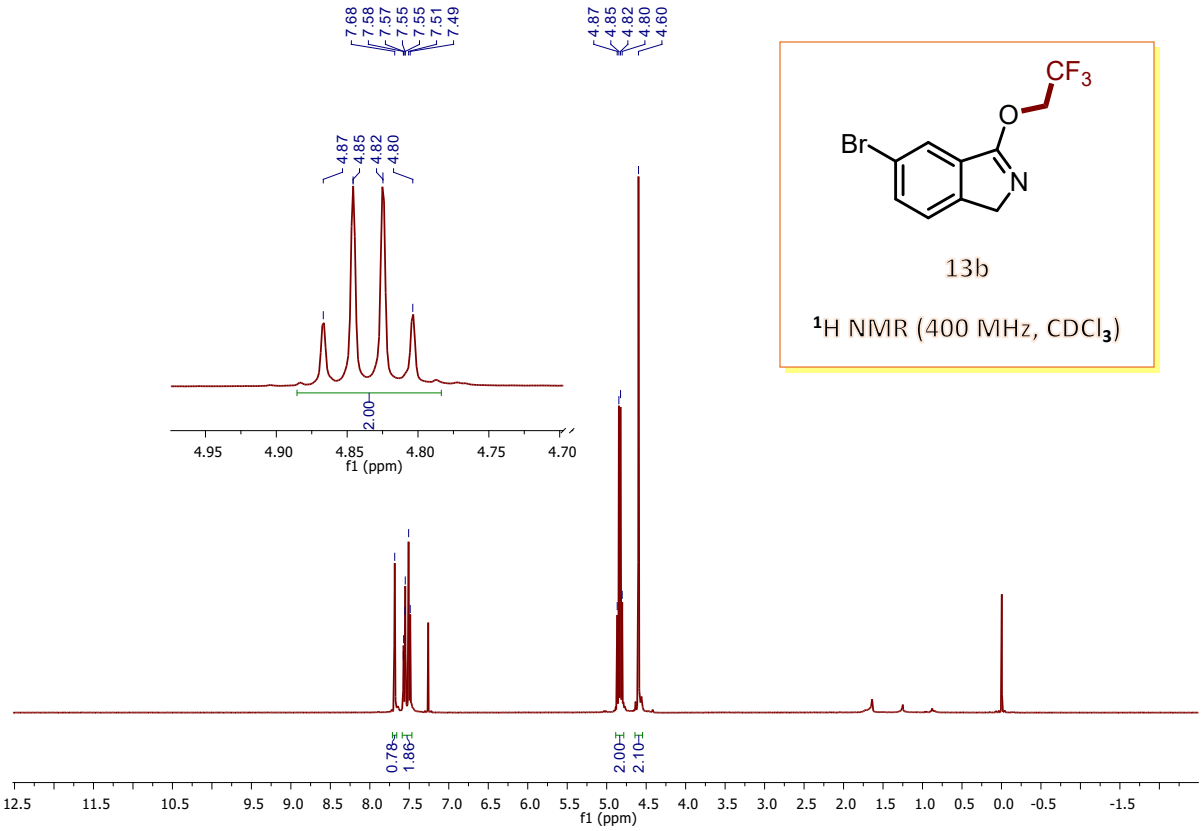
13a

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



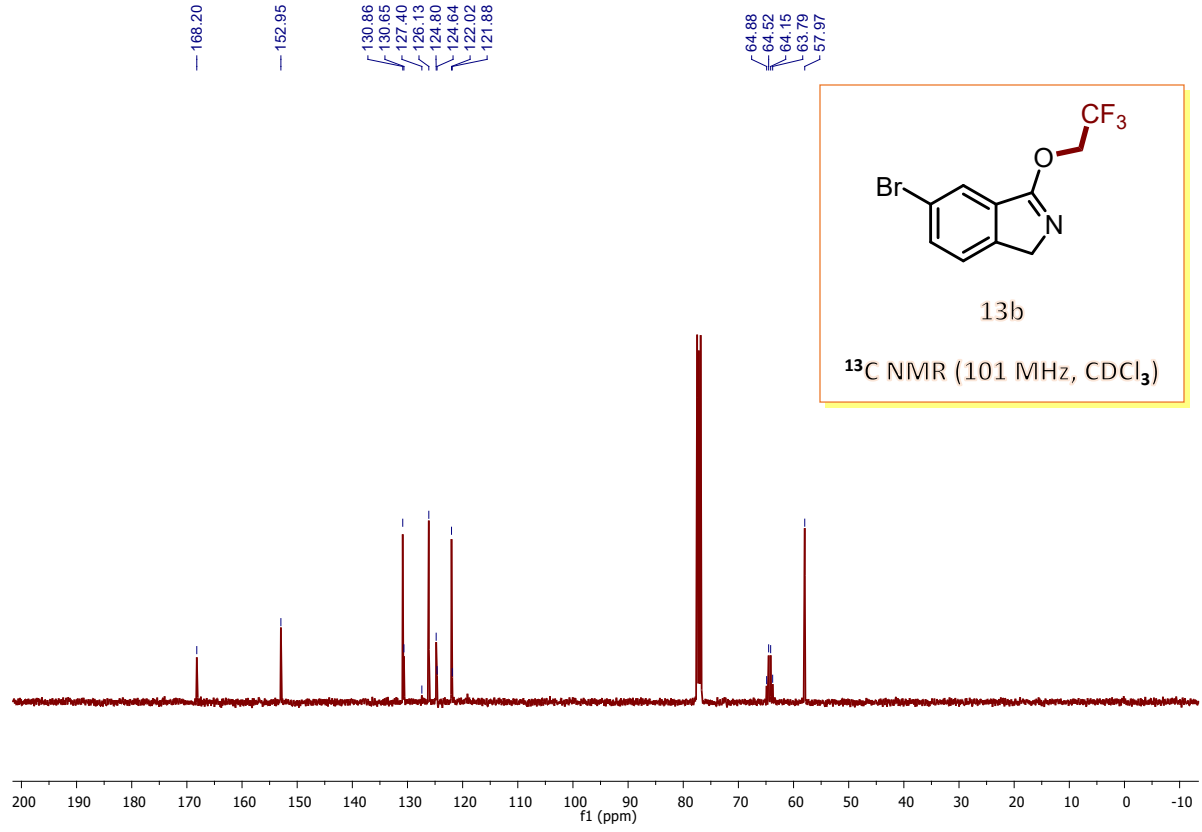

168.92
150.91
131.60
129.69
127.44
126.98
124.74
122.63
121.98
120.89
119.22
64.79
64.42
64.06
63.70
58.23
CF3
O
N
13a
13C NMR (101 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-73.31
CF3
O
N
13a
19F NMR (376 MHz, CDCl3)
250 200 150 100 50 0 -50 -100 -150 -200 -250
f1 (ppm)



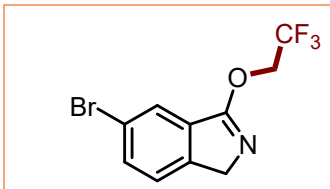
13b

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



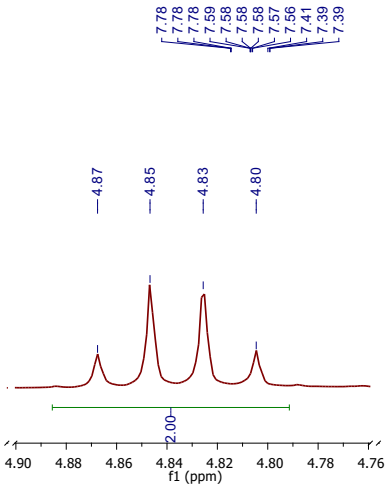
13b

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



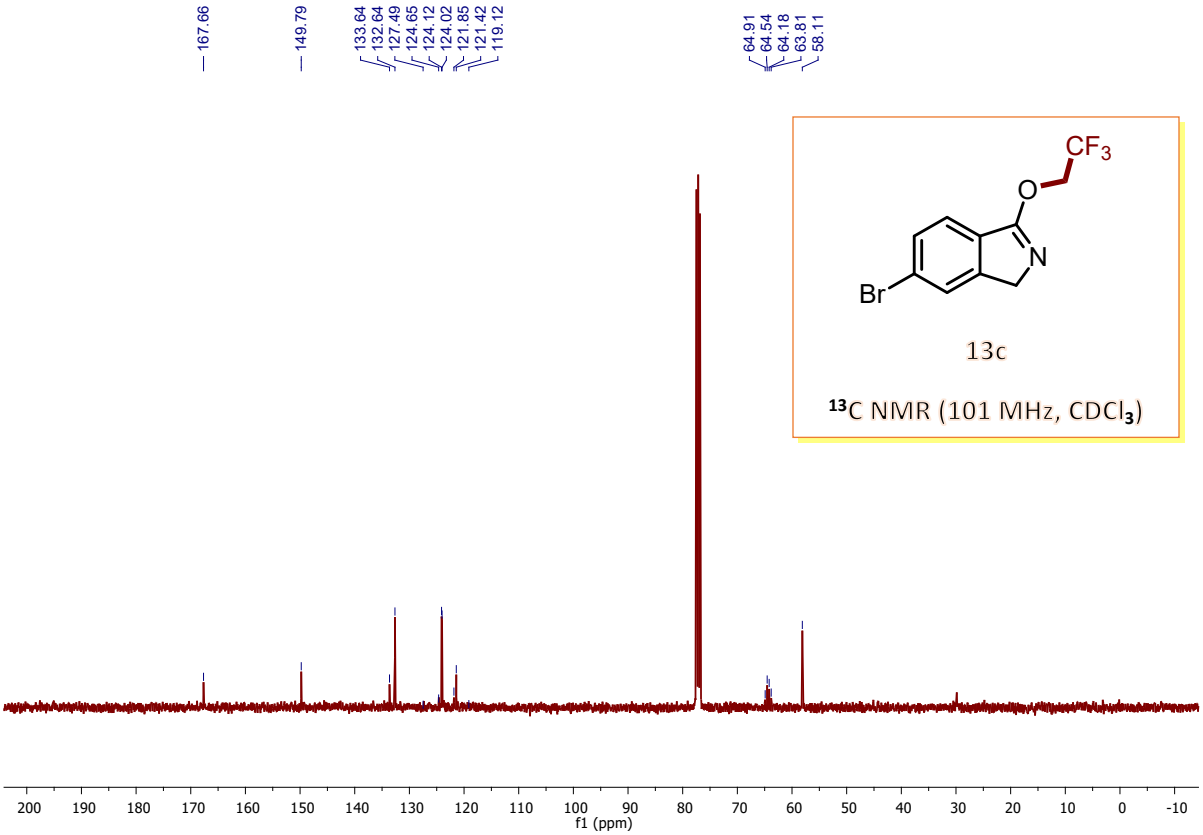
13b

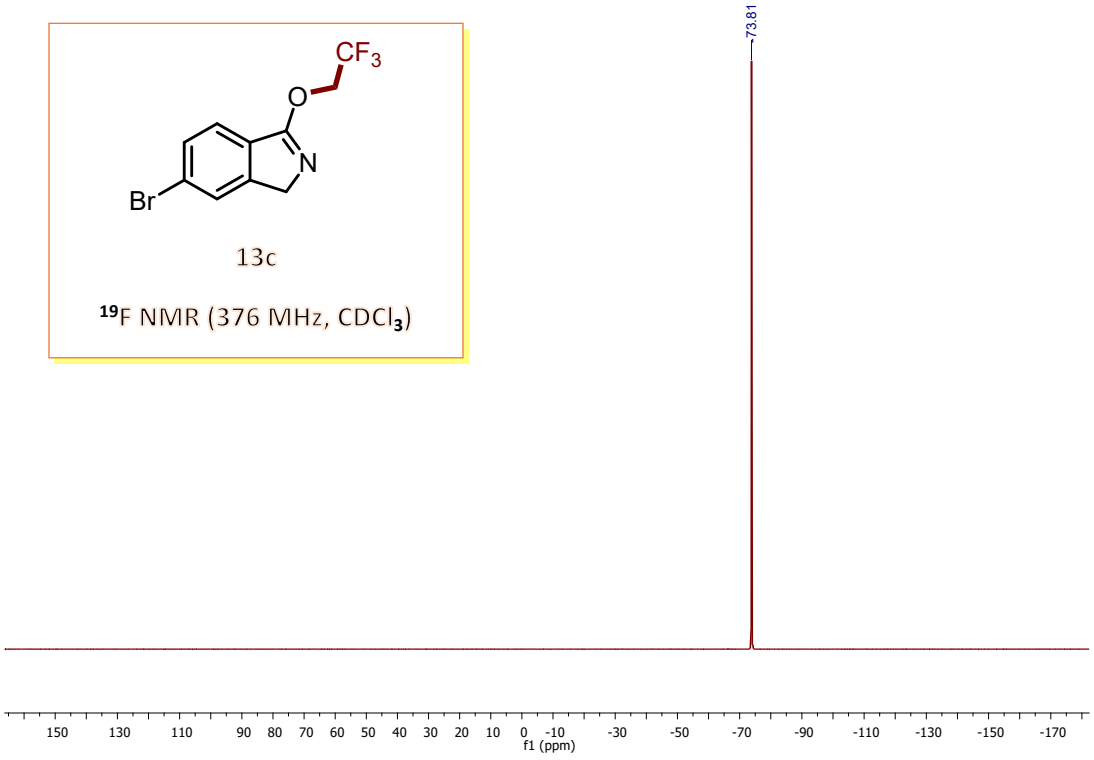
^{19}F NMR (376 MHz, $CDCl_3$)

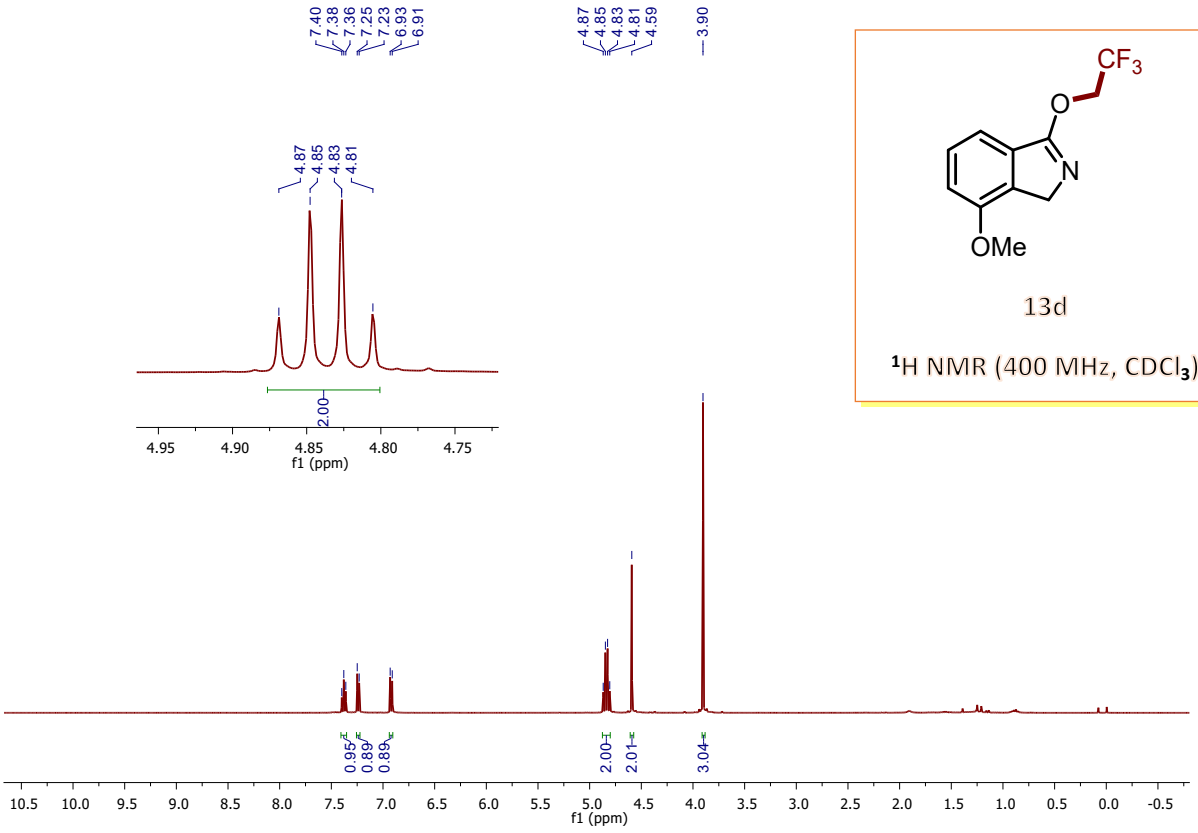


13c

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

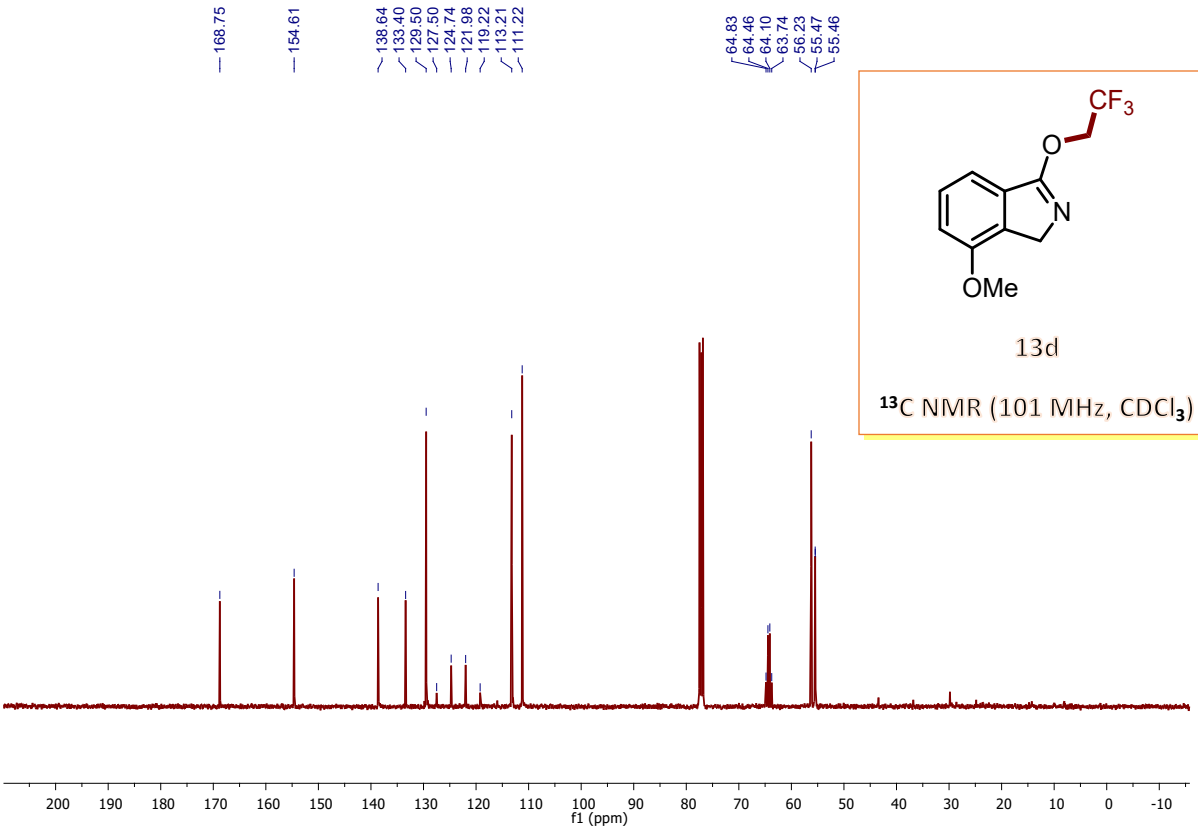

167.66
149.79
133.64
132.64
127.49
124.65
124.12
124.02
121.85
121.42
119.12
64.91
64.54
64.18
63.81
58.11
CF3
O
N
Br
13c
13C NMR (101 MHz, CDCl3)
f1 (ppm)


73.81
CF3
O
N
Br
13c
19F NMR (376 MHz, CDCl3)
f1 (ppm)



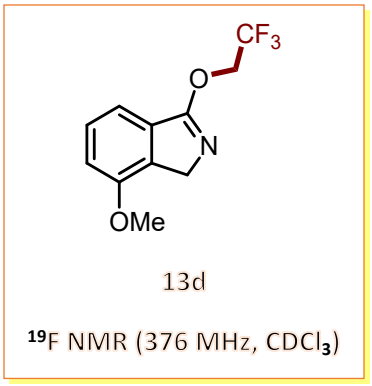
13d

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



13d

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



13d

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