Supplementary Information for

Divergent Light-Driven Strategies for the Radical Difluorosulfoximination of Unactivated Alkenes and Propellanes

Simone Baldon,[a] Julien Paut,[a,b] Elsa Anselmi,[b,c] Guillaume Dagousset,[b] Béatrice Tuccio[e], Giorgio Pelosi,[d] Sara Cuadros*,[a] Emmanuel Magnier*,[b] Luca Dell'Amico*[a]

[a]Department of Chemical Sciences, University of Padova, Via Francesco Marzolo 1, 35131, Padova (Italy)

[b]Institut Lavoisier de Versailles, Université Paris-Saclay, 45 avenue des Etats-Unis, 78035 Versailles (France)

[c] Université de Tours, Faculté des Sciences et Techniques, 37200 Tours (France)

[d]Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, Parco Area delle Scienze 17, 43124, Parma (Italy)

[e] Aix Marseille Univ, CNRS, ICR, 13013 Marseille (France)

*Correspondence to: sara.cuadroshuertas@unipd.it, emmanuel.magnier@uvsq.fr, luca.dellamico@unipd.it

Table of Contents

A. GENERAL INFORMATION

NMR spectra were recorded on Bruker AVANCE Neo 400 Nanobay equipped with a BBFO-ATM-z grad probehead, Bruker 400 AVANCE III HD equipped with a BBI-z grad probe head 5mm, Bruker 500 AVANCE III equipped with a BBI-ATM-z grad probe head 5mm, Bruker DPX 200 equipped with a QNP probehead, Bruker Avance 300 equipped with a BBO-z grad probehead or Bruker AVANCE Neo 600 equipped with a TCI Prodigy probehead. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ @ 7.26 ppm for ^{1}H NMR and @ 77.16 ppm for ^{13}C NMR). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal. NMR yields were calculated by using trichloroethylene as internal standard.

High-Resolution Mass Spectra (HRMS) were obtained on a Xevo G2-XS QToF in the Department of Pharmaceutical Sciences (University of Padua), with electron spray ionization (ESI).

Routine MS analysis and MS analysis with enantiopure sulfoximines described in section *G* were conducted in a Waters Acquity UPC^2 using CO_2/MeOH or CO_2/EtOH or CO_2/MeCN as mobile phase and a Daicel Chiralpak IG3 column as stationary phase.

Absorption spectroscopy studies have been performed on a Varian Cary 50 UV-Vis double beam spectrophotometer (more info at: www.varianinc.com). All the spectra were recorded at room temperature using a 1 mm or 1 cm path length Hellma Analytics quartz cuvettes.

Steady-state fluorescence spectra were recorded on a Varian Cary Eclipse Fluorescence spectrophotometer, using 10 mm path length Hellma Analytics quartz cuvettes.

All the cyclic voltammograms were recorded with a scan rate of 0.1 V/s. A typical three-electrode cell was employed, which was composed of a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a Ag/AgCl (3M NaCl) as reference electrode. The glass electrochemical cell was kept closed with a stopper annexed to the potentiostat. Oxygen was removed by purging the solvent with high-purity nitrogen (N_2), introduced from a line into the cell by means of a glass pipe. The potential of ferrocenium/ferrocene (Fc^+/Fc) couple was used as internal reference system to calibrate the potentiostat. All the results are subsequently converted in V vs SCE, in agreement with the value reported in literature [$E_{1/2}(Fc^+/Fc)$ = +0.38 V vs SCE].[1]

Light sources: The light sources used in this work are the following and were purchased from Kessil webpage (https://www.kessil.com/science/PR160L.php):

- **390 nm:** Kessil lamp PR160L-390 (max 52W).

- **400 nm:** Kessil lamp PR160L-400 (max 40W).

- **427 nm:** Kessil lamp PR160L-427 (max 45W).

General Procedures. Chromatographic purification of products was accomplished using flash chromatography on silica gel (SiO_2, 0.04-0.063 mm) purchased from Machery-Nagel, with the indicated solvent system according to the standard techniques; or using a Biotage Selekt® automated flash chromatography system with cartridges packed with silica (Sfär silica - high capacity duo, 20 µm). Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60 GF254, 0.25 mm). Visualization of the developed chromatography was performed by checking UV absorbance (254 nm) as well as with phosphomolybdic acid (PMA), potassium permanganate or blue Schiff stain solutions. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Oil baths were used for heating the reactions.

Materials. Commercial grade reagents and solvents were purchased at the highest commercial quality from Sigma Aldrich, FluoroChem or TCI and used as received, unless otherwise stated. All the starting materials **S1a-h, S2, S5-S7, S9, S10, S17-S20, 73, 75, 17,** were purchase from Sigma Aldrich, Fluorochem or TCI and used as received, unless otherwise stated. The alkenes **14**, **3ab**, **S21-S30** were purchase from Sigma Aldrich, Fluorochem or TCI and used as received, unless otherwise stated. The procedures for the preparation of the sulfoximines **13, 7b-7l** is detailed in Section B of this Supplementary Information (SI). **PC2** was prepared according to a reported procedure, while the synthesis of **PC3-PC12** is detailed in Section **B.9** of this SI. *Note:* dibromodifluoromethane (CF_2Br_2) is a liquid with high density (2.297 g/mL at 25 °C) and low boiling point (22-23°C). In order to handle and sample it, we generally kept the CF_2Br_2 bottle in dry ice and we transferred it using a Pasteur pipet into either a graduated 10 mL cylinder or a 1.5 mL vial also kept in dry ice. Unless otherwise stated, the CF_2Br_2 was then directly poured into the flask containing the reaction mixture or transferred with a cannula.

A.1. LIGHT SOURCES EMISSION SPECTRA

Kessil PR160L lights

The following spectrum is reported in the Kessil website (www.kessil.com/science/PR160L.php). The wavelengths used in the current study were 400, 427 and 456 nm.

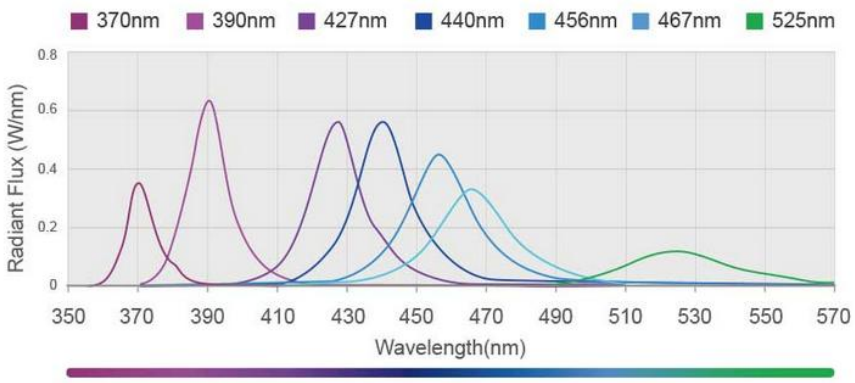


Figure S1. Emission spectra of the Kessil lights used in this work.

A.2. PHOTOCHEMICAL SET UP

Figure S2-*left* shows the general photochemical set up employed in the present study: the glass reactor (detailed in Figure S2-*right*, internal diameter = 1cm, external diameter = 2cm) containing the reaction mixture was placed at 1 cm from the light source and stirred vigorously. The temperature was kept at 20ºC with a chiller connected to the glass reactor, using water as the circulating refrigerant liquid.

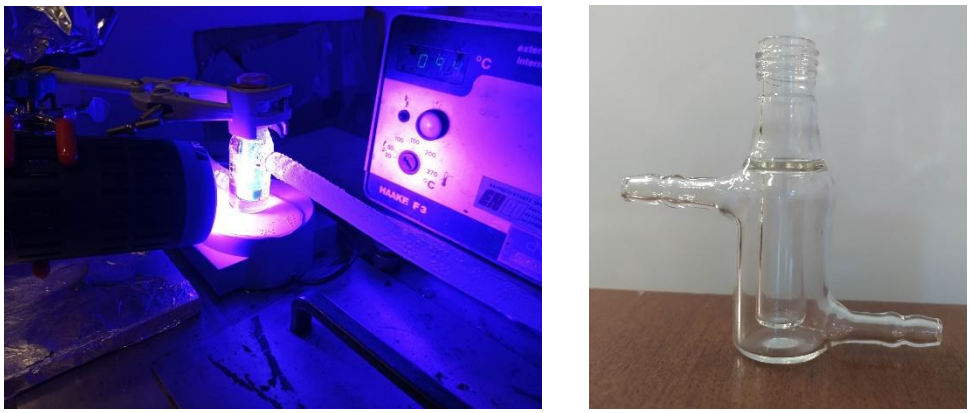


Figure S2. *Left:* Photochemical set up with cooling system. *Right:* Glass reactor.

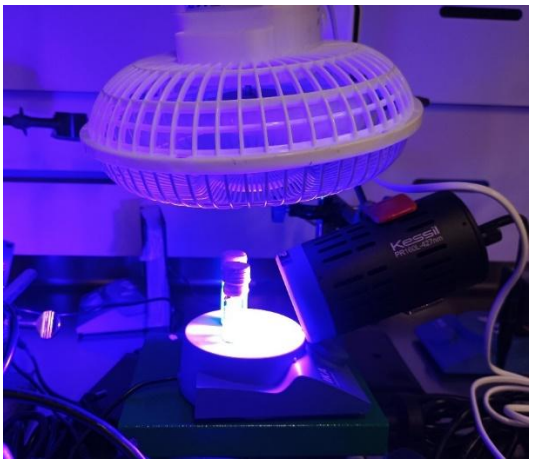
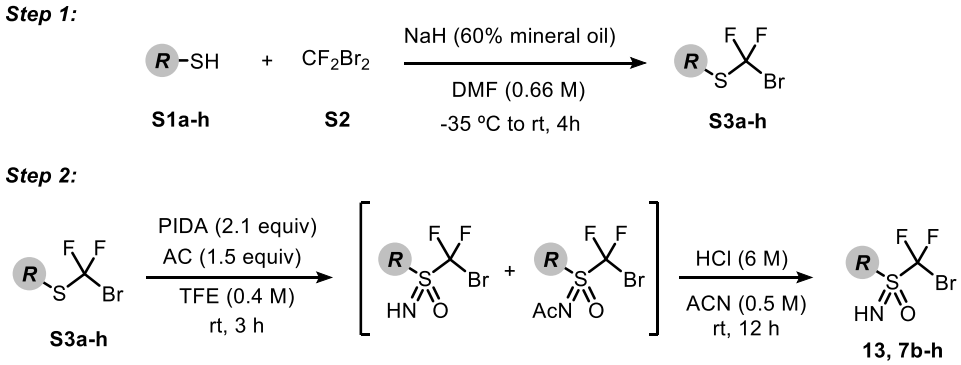


Figure S3. Photochemical set-up with a fan

B. GENERAL PROCEDURES FOR THE SYNTHESIS OF STARTING MATERIALS AND PHOTOCATALYSTS

B.1. Synthesis of aryl and heteroaryl sulfoximines (13, 7b-h)



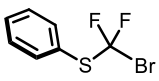
The sulfoximines **13, 7b-h** were prepared following a described procedure:[2,3]

Step 1: according to a literature procedure.[2] To solution of the thiol derivative **S1** (1 equiv.) in dry DMF (0.66 M) was slowly added NaH (60% disp. in mineral oil, 1.5 equiv) at 0°C, over a period of 30 min. The mixture was stirred at 0°C for 15 min. Then, the mixture was cooled to -35 °C in a dry ice/acetonitrile bath, and it was added dibromodifluoromethane (**S2**, 3 equiv). The reaction mixture was stirred -35 °C for 3 h, and 30 min at ambient temperature, unless otherwise stated. The reaction flask was cooled to 0 ºC, and the excess of NaH was quenched by dropwise addition of water. The aqueous phase was extracted with Et_2O (x 3 times), and the combined organic layers were washed with water (x3 times), brine, and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent under reduced pressure afforded the crude product, which

was purified by flash chromatography (hexane/EtOAc mixture) to deliver the compounds **S3** in the stated yields.

Step 2: according to literature procedure. [3] To a round bottom flask was added successively, sulfide **S3** (1 equiv.), trifluoroethanol (TFE, 0.4 M), ammonium carbamate (AC, 1.5 equiv.) and PIDA (2.1 equiv.) in one portion. The reaction mixture was stirred at room temperature for 3 h. To reach maximum conversion (checked by ^{19}F NMR with $PhOCF_3$ as internal standard), PIDA (1 equiv.) and ammonium carbamate (1 equiv.) could be added. After completion, trifluoroethanol was removed under reduced pressure. The crude mixture was diluted in an aqueous solution of HCl (6 M, 1 mL/mmol) and MeCN (2 mL/mmol), and the reaction was stirred overnight at room temperature. The pH of the aqueous phase was adjusted to 7 with $NaHCO_3$ (10% aqueous solution) then the crude mixture was extracted with DCM (3 x 10 mL). The organic layer was dried with $MgSO_4$, concentrated under reduced pressure and purified by column chromatography on silica gel affording the sulfoximines **13** and **7b-h** in the stated yield.

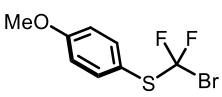
(bromodifluoromethyl)(phenyl)sulfane (S3a)



S3a

Compound **S3a** was synthesized according to the general procedure **B.1.** (step 1) using thiophenol **S1a** (2.20 g, 20 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3a** as a colorless oil (60% yield, 2.90 g, 12 mmol). The spectroscopic data agrees with the one reported in the literature.[2]

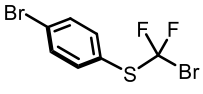
(bromodifluoromethyl)(4-methoxyphenyl)sulfane (S3b)



S3b

Compound **S3b** was synthesized according to the general procedure **B.1.** (step 1) using 4-methoxybenzenethiol **S1b** (1.37 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3b** as a colorless liquid (55% yield, 1.70 g, 6.3 mmol). The spectroscopic data is in agreement with the one reported in the literature.[4]

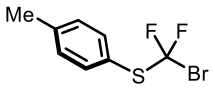
(bromodifluoromethyl)(4-bromophenyl)sulfane (S3c)



S3c

Compound **S3c** was synthesized according to the general procedure **B.1.** (step 1) using 4-bromobenzenethiol **S1c** (1.85 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3c** as a colorless liquid (37% yield, 1.17 g, 3.7 mmol). The spectroscopic data is in agreement with the one reported in the literature.[5]

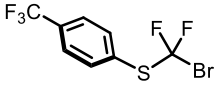
(bromodifluoromethyl)(p-tolyl)sulfane (S3d)



S3d

Compound **S3d** was synthesized according to the general procedure **B.1.** (step 1) using 4-methylbenzenethiol **S1d** (1.24 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3d** as a colorless oil (50% yield, 1.26 g, 5.0 mmol). The spectroscopic data is in agreement with the one reported in the literature.[6]

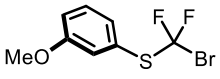
(bromodifluoromethyl)(4-(trifluoromethyl)phenyl)sulfane (S3e)



S3e

Compound **S3e** was synthesized according to the general procedure **B.1.** (step 1) using 4-(trifluoromethyl)benzenethiol **S1e** (1.78 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3e** as a colorless liquid (73% yield, 2.70 g, 6.3 mmol). The spectroscopic data is in agreement with the one reported in the literature.[4]

(bromodifluoromethyl)(3-methoxyphenyl)sulfane (S3f)

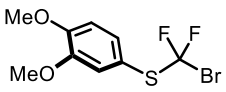


S3f

Compound **S3f** was synthesized according to the general procedure **B.1.** (step 1) using 3-methoxybenzenethiol **S1f** (1.37 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3f** as a colorless oil (71% yield, 1.90 g, 7.1 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8 Hz, 1H), 7.28 (d, *J* = 8 Hz, 1H), 7.23 (m, 1H), 7.09 (dd, *J* = 8 Hz, *J* = 2 Hz, 1H), 3.88 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 160.0, 130.3, 128.6, 128.1, 121.3, 119.3 (t, *J* = 339 Hz, 2F), 117.3, 55.6. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -22.4 (s, 2 F). **HRMS (ESI$^+$):** calculated for [$C_8H_8BrF_2OS^+$]: 268.9447 (M+H$^+$); found: 268.9455.

(bromodifluoromethyl)(3,4-dimethoxyphenyl)sulfane (S3g)

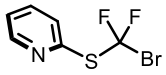


S3g

Compound **S3g** was synthesized according to the general procedure **B.1.** (step 1) using 3,4-dimethoxybenzenethiol **S1g** (1.70 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (100% hexane) to afford compound **S3g** as a colorless oil (74% yield, 2.20 g, 7.4 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8 Hz, 1H), 7.11 (m, 1H), 6.87 (dm, *J* = 8 Hz, 1H), 3.89 (s, 6H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 151.6, 149.1, 130.1, 119.8 (t, *J* = 340 Hz, 2F), 118.9, 117.9, 111.4, 56.0, 55.9. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -23.4 (s, 2 F). **HRMS (ESI$^+$):** calculated for [$C_9H_{10}BrF_2O_2S^+$]: 298.9553 (M+H$^+$); found: 298.9555.

2-((bromodifluoromethyl)thio)pyridine (S3h)

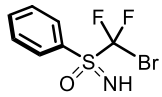


S3h

Compound **S3h** was synthesized according to the general procedure **B.1.** (step 1) using pyridine-2-thiol **S1h** (1.11 g, 10 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 95:5 hexane/EtOAc) to afford compound **S3h** as a colorless oil (32% yield, 770 mg, 3.2 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 – 8.63 (m, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.36 – 7.32 (m, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.82, 137.84, 128.98, 124.25, 118.24 (t, *J* = 338 Hz). **^{19}F NMR (188 MHz, $CDCl_3$)** δ -21.1 (s, 2 F). **HRMS (ESI^+):** calculated for [$C_6H_5BrF_2NS^+$]: 239.9289 ($M+H^+$); found: 239.9346.

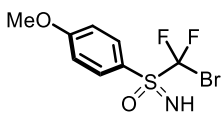
(bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone (13)



13

Compound **13** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(phenyl)sulfane **S3a** (2.90 g, 12 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **13** as a yellowish solid (85% yield, 2.75 g, 10 mmol). The spectroscopic data is in agreement with the one reported in the literature.[3]

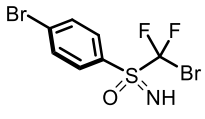
(bromodifluoromethyl)(imino)(4-methoxyphenyl)- λ^6-sulfanone (7b)



7b

Compound **7b** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(4-methoxyphenyl)sulfane **S3b** (1.70 g, 6.3 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **7b** as yellow crystals (84% yield, 1.59 g, 5.3 mmol). The spectroscopic data is in agreement with the one reported in the literature.[3]

(bromodifluoromethyl)(4-bromophenyl)(imino)- λ^6-sulfanone (7c)



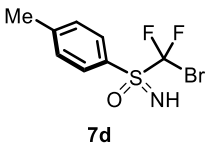
7c

Compound **7c** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(4-bromophenyl)sulfane **S3c** (1.17 g, 3.7 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **7c** as a white solid (50% yield, 645 mg, 1.9 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 3.72 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 132.91, 132.58, 131.44, 129.14, 123.90 (dd, *J* = 362 and 354 Hz).

^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$) δ -55.0 and -56.1 (AB system, J_{AB} = 135.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_7H_6Br_2F_2NOS^+$]: 347.8499 ($M+H^+$); found: 347.8546.

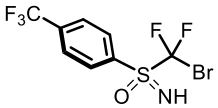
(bromodifluoromethyl)(imino)(p-tolyl)- λ^6-sulfanone (7d)



7d

Compound **7d** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(p-tolyl)sulfane **S3d** (1.26 g, 5.0 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **7d** as yellow crystals (70% yield, 994 mg, 3.5 mmol). The spectroscopic data is in agreement with the one reported in the literature.[3]

(bromodifluoromethyl)(imino)(4-(trifluoromethyl)phenyl)- λ^6-sulfanone (7e)

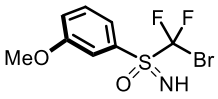


7e

Compound **7e** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(4-(trifluoromethyl)phenyl)sulfane **S3e** (2.70 g, 6.3 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **7e** as a greyish solid (34% yield, 724 mg, 2.1 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.6 Hz, 1H), 3.84 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.97 (q, *J* = 33 Hz), 134.12, 131.84, 126.56 (q, *J* = 4 Hz), 123.88 (dd, *J* = 362 and 354 Hz), 123.12 (q, *J* = 273 Hz). **^{19}F NMR decoupled ^{1}H** (377 MHz, $CDCl_3$) δ -54.9 and -56.1 (AB system, J_{AB} = 137.0 Hz, 2F), -63.4 (s, 3F). **HRMS (ESI$^+$):** calculated for [$C_8H_6BrF_5NOS^+$]: 337.9268 ($M+H^+$); found: 337.9320.

(bromodifluoromethyl)(imino)(3-methoxyphenyl)- λ^6-sulfanone (7f)

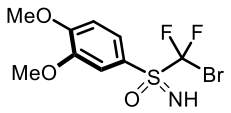


7f

Compound **7f** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(3-methoxyphenyl)sulfane **S3f** (1.90 g, 7.1 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **7f** as yellow crystals (76% yield, 1.62 g, 5.4 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 1H), 7.61 (s, 1H), 7.51 (t, *J* = 8.1 Hz, 1H), 7.29 – 7.26 (m, 1H), 3.88 (s, 3H), 3.68 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.19, 131.11, 130.43, 124.27 (dd, *J* = 362 and 354 Hz), 123.44, 122.23, 115.22, 55.95. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -54.8 and -55.9 (AB system, J_{AB} = 135.0 Hz, 2F). **HRMS (ESI$^+$)**: calculated for [$C_8H_9BrF_2NO_2S^+$]: 299.9500 ($M+H^+$); found: 299.9603.

(bromodifluoromethyl)(3,4-dimethoxyphenyl)(imino)- λ⁶-sulfanone (7g)

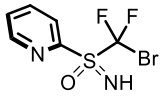


7g

Compound **7g** was synthesized according to the general procedure **B.1** (step 2) using (bromodifluoromethyl)(3,4-dimethoxyphenyl)sulfane **S3g** (2.20 g, 7.4 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **7g** as yellow crystals (80% yield, 1.95 g, 5.9 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.53 (d, *J* = 2.1 Hz, 1H), 7.03 (dd, *J* = 8.7, 1.5 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.59 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.15, 149.50, 125.96, 124.30 (dd, *J* = 361 and 354 Hz), 120.60, 112.84, 110.98, 56.52, 56.51. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -54.9 and -56.0 (AB system, J_{AB} = 137.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_9H_{11}BrF_2NO_3S^+$]: 329.9606 ($M+H^+$); found: 329.9655.

(bromodifluoromethyl)(imino)(pyridin-2-yl)- λ⁶-sulfanone (7h)

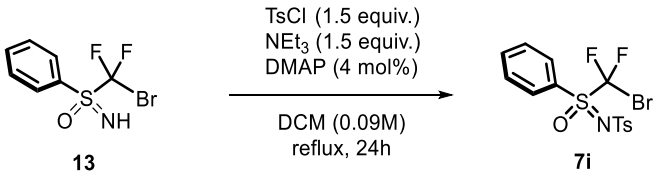


7h

Compound **7h** was synthesized according to the general procedure **B.1** (step 2) using 2-((bromodifluoromethyl)thio)pyridine **S3h** (770 g, 3.2 mmol, 1 equiv.). The crude was purified by flash column chromatography (gradient from 9:1 hexane/EtOAc to 4:6 hexane/EtOAc) to afford compound **7h** as colorless crystals (2% yield, 17 mg, 0.064 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 – 8.84 (m, 1H), 8.34 (dt, *J* = 7.9, 1.0 Hz, 1H), 8.03 (td, *J* = 7.8, 1.8 Hz, 1H), 7.69 – 7.65 (m, 1H), 4.03 (s, 1H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 150.91, 150.66, 138.55, 128.70, 126.63 (t, *J* = 1 Hz), 124.25 (t, *J* = 355 Hz). **^{19}F NMR decoupled ^{1}H (188 MHz, $CDCl_3$)** δ -53.8 and -55.4 (AB system, J_{AB} = 134.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_6H_6BrF_2N_2OS^+$]: 270.9347 ($M+H^+$); found: 270.9379

B.2. Synthesis of N-((bromodifluoromethyl)(oxo)(phenyl)-λ⁶-sulfanylidene)-4-methylbenzenesulfonamide (7i)



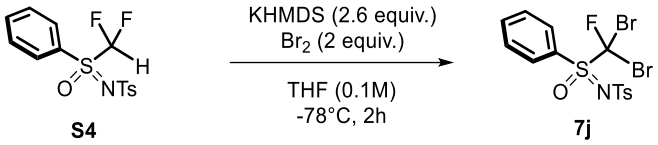
13 **7i**

In a 250 mL round-bottom flask, sulfoximine **13** (1.7 g, 6.15 mmol, 1 equiv.) is dissolved in DCM (70 mL). Tosyl chloride (TsCl) (1.8 g, 9.2 mmol, 1.5 equiv.), 4-dimethylaminopyridine (DMAP) (30 mg, 0.25 mmol, 0.04 equiv.) and triethylamine (1.3 mL, 9.2 mmol, 1.5 equiv.) are added to the solution which is stirred at reflux for 24 h. Upon completion, the reaction mixture is cooled to room temperature and quenched with HCl 1 M (30 mL). The solution is extracted with DCM

(3 x 30 mL). The combined organic layers are dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash chromatography using n-pentane/EtOAc as eluent (gradient from 9:1 n-pentane/EtOAc to 6:4 n-pentane/EtOAc)) afforded the desired compound **7i** as a white solid (62% yield, 1.6 g, 3.8 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8 Hz, 2H), 7.88 (d, *J* = 8 Hz, 2H), 7.84 (d, *J* = 8 Hz, 1H), 7.68 (t, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 2.42 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 143.8, 140.0, 136.7, 131.6, 130.1, 130.0, 129.6, 126.9, 121.2 (dd, *J* = 348 and 355 Hz, 2F), 21.7 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -54.7 and -57.3 (AB system, J_{AB} = 142.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{14}H_{13}BrF_2NO_3S_2^+$]: 423.9488 ($M+H^+$); found: 423.9482.

B.3. Synthesis of N-((dibromofluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (7j)

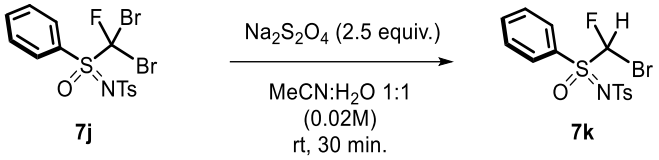


S4 **7j**

In a 25 mL round bottom flask, N-Ts S-CF_2H sulfoximine **S4** (0.25 g, 0.76 mmol) is dissolved in dry THF (8 mL) and placed under nitrogen at -78°C. KHMDS 0.5 M in Toluene (4 mL, 2 mmol, 2.6 equiv.) is added to the solution which is stirred at -78°C for 30 minutes. Bromine (0.25 g, 1.52 mmol, 2 equiv.) is then added and stirred at -78°C for 2h. Upon completion, the mixture is quenched with water and extracted with DCM (3 x 10 mL). The combined organic layers are washed with $Na_2S_2O_3$ and saturated aqueous NaCl, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by preparative TLC chromatography using petrolum ether /EtOAc (6:4) as eluent afforded the desired product **7j** as white solid (46% yield, 0.17 g, 0.35 mmol).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8 Hz, 2H), 7.89 (d, *J* = 8 Hz, 2H), 7.83 (d, *J* = 8 Hz, 1H), 7.66 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8 Hz, 2H), 2.42 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 143.5, 139.9, 136.5, 132.2, 129.6, 129.4, 129.3, 126.7, 101 (d, *J* = 361 Hz, 1F), 21.6 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -60.65 (s, 1F). **HRMS (ESI$^+$):** calculated for [$C_{14}H_{13}Br_2FNO_3S_2^+$]: 483.8688 ($M+H^+$); found: 483.8669.

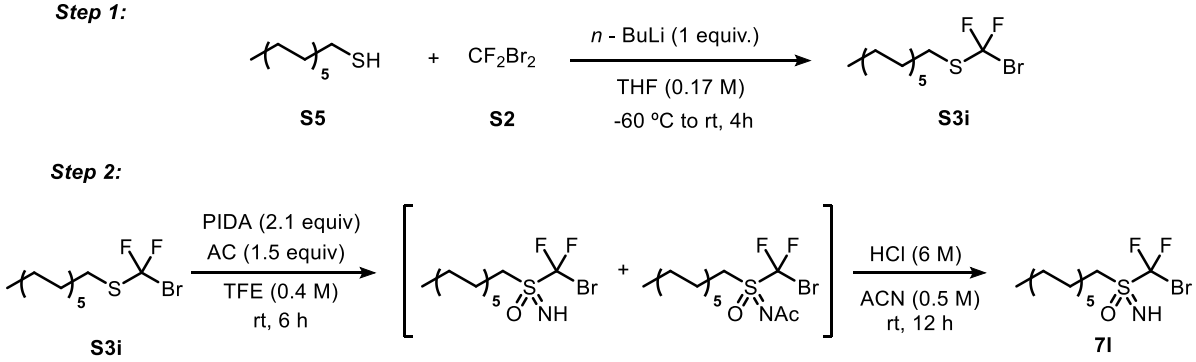
B.4. Synthesis of N-((bromofluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (7k)



To a solution of N-Ts S-CFBr$_2$ sulfoximine **7j** (0.35 g, 0.72 mmol) and MeCN (20 mL) was added $Na_2S_2O_4$ (0.31 g, 1.80 mmol, 2.5 equiv.) in 20 mL of water. The mixture was stirred at room temperature for 30 minutes. Upon completion, the mixture was extracted with DCM and the organic layer was washed with saturated aqueous NaCl, dried over $MgSO_4$ and evaporated under reduced pressure. Purification by preparative TLC chromatography using petrolum ether /EtOAc (6:4) as eluent afforded the desired product **7k** as colorless oil (52% yield, 0.15 g, 0.37 mmol, 2 diasteroisomers, 1:1 dr).

^{1}H NMR (300 MHz, CDCl$_3$) δ 8.10 (d, *J* = 8 Hz, 1H), 8.05 (d, *J* = 8 Hz, 1H), 7.90-7.98 (m, 2H), 7.82 (m, 1H), 7.66 (t, *J* = 7.7 Hz, 2H), 7.31 (d, *J* = 7 Hz, 2H), 2.42 (s, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 143.7, 139.7, 136.2 (2C min and ma*J*), 131.3 min and 130.9 ma*J*, 129.5, 129.4, 128.6 ma*J* and 128.3 min, 126.8 (2C, min and ma*J*, min 98.4 (d, *J* = 298 Hz, 1F) and ma*J* 97.4 (d, *J* = 298 Hz, 1F), 21.6 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ -134.4 (d, *J* = 47.0 Hz, 1F) and –139.0 (d, *J* = 48.0 Hz, 1F). **HRMS (ESI$^+$):** calculated for [$C_{14}H_{14}BrFNO_3S_2^+$]: 405.9583 (M+H$^+$); found: 405.9602.

B.5. Synthesis of (bromodifluoromethyl)(dodecyl)(imino)-λ^6-sulfanone 7l



Sulfoximine **7l** was prepared following a described procedure:[3]

Step 1: according to a literature procedure.[3] An oven-dried 250 mL round bottom flask was charged with 1-Dodecanethiol (**S5**, 1.2 mL, 5 mmol, 1 equiv.), in dry THF (7 mL) under inert atmosphere (Argon) at -60°C. n-Butyllithium (5 mmol, 1 equiv.) was added dropwise and the suspension was stirred at room temperature for 15 min. Then difluorodibromomethane (**S2**, 913

μL, 10 mmol, 2 equiv) was added. The resulting mixture allowed to warm to room temperature for 4h and then hydrolyzed with water, extracted with dichloromethane (3 x 10 mL), washed with brine (10 mL), dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (100% hexane) to give product **S3i** as a colorless oil (50% yield, 828 mg, 2.5 mmol). The spectroscopic data is in agreement with the one reported in the literature.[3]

Step 2: according to literature procedure.[3] To a round bottom flask was added successively, sulfide **S3i** (828 mg, 2.5 mmol, 1 equiv.), trifluoroethanol (TFE, 0.4 M), ammonium carbamate (AC, 1.5 equiv.) and PIDA (2.1 equiv.) in one portion. The reaction mixture was stirred at room temperature for 6 h. To reach maximum conversion (checked by ^{19}F NMR with $PhOCF_3$ as internal standard), PIDA (1 equiv.) and ammonium carbamate (1 equiv.) are added. After completion, trifluoroethanol was removed under reduced pressure. The crude mixture was diluted in an aqueous solution of HCl (6 M, 1 mL/mmol) and MeCN (2 mL/mmol), and the reaction was stirred overnight at room temperature. The pH of the aqueous phase was adjusted to 7 with $NaHCO_3$ (10% aqueous solution) then the crude mixture was extracted with DCM (3 x 10 mL). The organic layer was dried with $MgSO_4$, concentrated under reduced pressure and purified by flash chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) affording sulfoximine **7l** as a white powder (31% yield, 281 mg, 0.77 mmol). The spectroscopic data is in agreement with the one reported in the literature.[3]

B.6. Synthesis of alkenes

The alkenes **3a-l** depicted in Figure S4 we synthesize according to literature procedures. The corresponding references are indicated below each substrate.

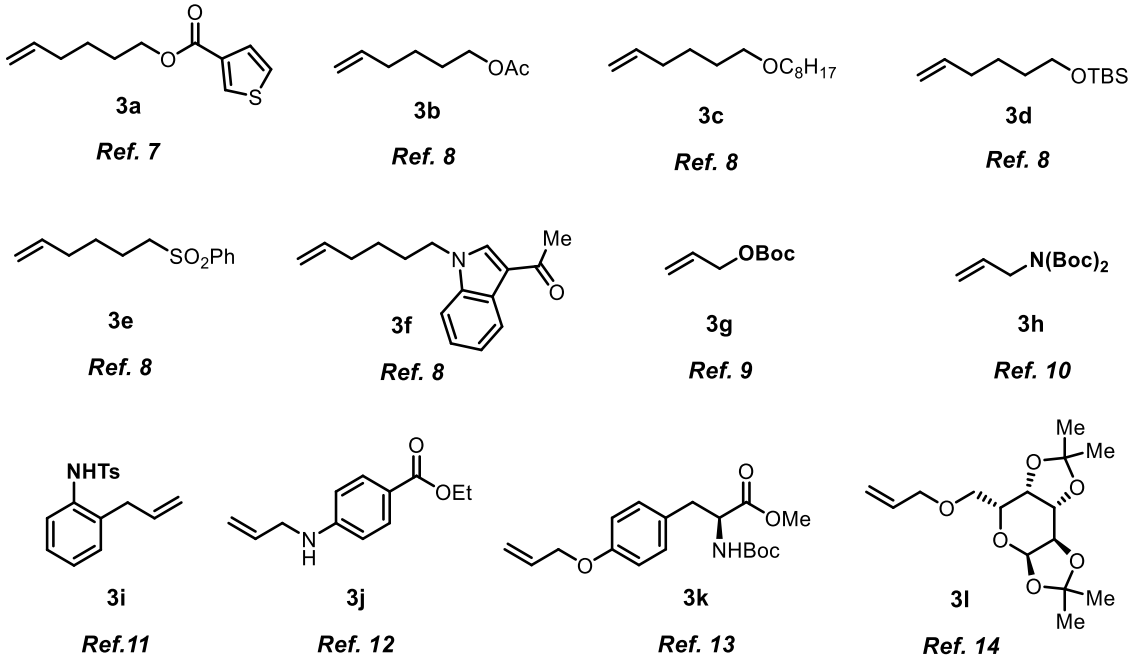
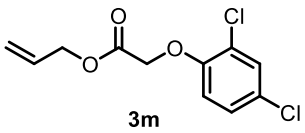


Figure S4. References for the synthesis of alkenes 3a-l.

Allyl 2-(2,4-dichlorophenoxy)acetate (3m)

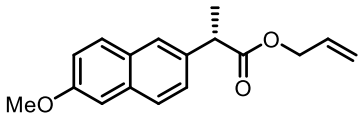


3m

Compound **3m** was synthesized according to a literature procedure.[15]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 5.91 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.42 – 5.18 (m, 2H), 4.71 (s, 2H), 4.69 (d, *J* = 5.8 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.91, 152.51, 131.32, 130.47, 127.68, 127.29, 124.43, 119.41, 114.96, 66.52, 66.15. **HRMS (ESI^+):** calculated for [$C_{11}H_{11}Cl_2O_3^+$]: 261.0080 ($M+H^+$); not found.

Allyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate (3n)

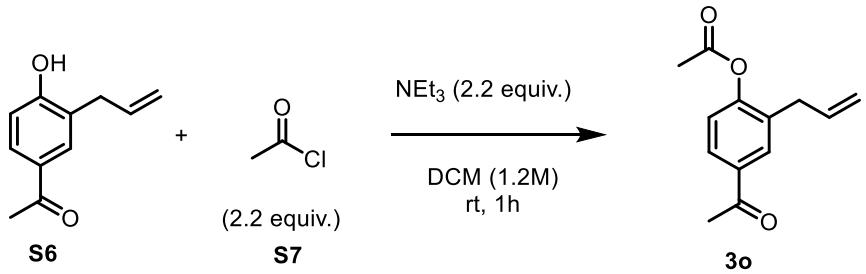


3n

Compound **3n** was synthesized according to a literature procedure.[16]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 3H), 7.41 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.20 – 7.07 (m, 2H), 6.02 – 5.70 (m, 1H), 5.31 – 5.08 (m, 2H), 4.72 – 4.44 (m, 2H), 3.91 (s, 3H), 3.92 – 3.84 (m, 1H), 1.59 (d, *J* = 7.2 Hz, 3H), 1.55 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.47, 157.79, 135.76, 133.85, 132.25, 129.43, 129.07, 127.29, 126.40, 126.13, 119.12, 118.15, 105.73, 65.47, 55.46, 45.60, 18.72. **HRMS (ESI^+):** calculated for [$C_{17}H_{18}O_3Na^+$]: 293.1148 ($M+Na^+$); found: 293.1155.

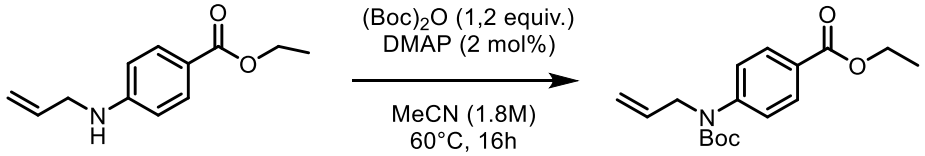
4-acetyl-2-allylphenyl acetate (3o)



A 10 mL flask was charged with a solution of 4-acetyl-2-allylphenol **S6** (232 µL, 2 mmol, 1 equiv.) in 1.7 mL DCM. Then, triethylamine (307 µL, 2.2 mmol, 2.2 equiv.) was added at 0 °C followed by the slow addition of the acetyl chloride **S7** (157 µL, 2.2 mmol, 2.2 equiv.). The reaction mixture was stirred at room temperature for 1 h, diluted with 10 mL of ethyl acetate and washed with saturated aqueous NH_4Cl (10 mL). The organic phases were dried ($MgSO_4$), concentrated, and purified by flash chromatography (hexane/EtOAc 9:1) affording compound **3o** as a yellowish oil (80% yield, 349 mg, 1.6 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.79 (m, 2H), 7.12 (dd, *J* = 8.3, 5.2 Hz, 1H), 6.04 – 5.63 (m, 1H), 5.33 – 4.94 (m, 2H), 3.32 (td, *J* = 4.9, 2.4 Hz, 2H), 2.54 (s, 3H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.02, 168.76, 152.72, 135.13, 135.03, 132.47, 130.69, 127.89, 122.73, 116.83, 34.64, 26.58, 20.88. **HRMS (ESI^+):** calculated for [$C_{13}H_{15}O_3^+$]: 219.1016 ($M+H^+$); found: 219.1081.

Ethyl 4-(allyl(tert-butoxycarbonyl)amino)benzoate (3p)

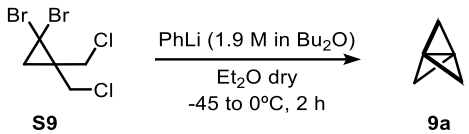


S8 **3p**

A 10 mL flask was charged with N-allyl benzocaine **S8** (1.3 g, 6.4 mmol, 1 equiv.) and DMAP (28 mg, 0.12 mmol, 0.02 equiv.) in 2.5 mL MeCN. Then, a solution of $(Boc)_2O$ (938 mg, 7.7 mmol, 1.2 equiv.) in MeCN (1 mL) was slowly added and the reaction mixture was stirred at 60°C overnight. Subsequently the solvent was evaporated under reduced pressure at 60° C, and dilute $NaHCO_3$ (10 ml) was added. This was extracted with 3x 10 ml DCM, and the combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated. The crude residue was purified by flash chromatography (hexane/EtOAc 9:1) affording compound **3p** as a colorless oil (20% yield, 391 mg, 1.3 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 5.99 – 5.76 (m, 1H), 5.27 – 5.01 (m, 2H), 4.32 (qd, *J* = 7.1, 1.3 Hz, 2H), 4.24 (dt, *J* = 5.3, 1.6 Hz, 2H), 1.42 (s, 9H), 1.34 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.07, 153.84, 147.03, 133.95, 129.98, 127.09, 125.09, 116.51, 81.01, 60.85, 52.50, 28.22, 14.33**. HRMS (ESI^+):** calculated for [$C_{17}H_{23}NO_4Na^+$]: 328.1519 ($M+Na^+$); found: 328.1602.

B.7. Preparation of the [1.1.1]-propellane solution in Et_2O (9a)



S9 **9a**

The [1.1.1]-propellane solution **9a** was prepared following a described procedure:[17] a 250 mL flame dried round-bottom flask was charged with 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane **S9** (5 g, 16.8 mmol, 1.0 equiv). The flask was evacuated and back-filled with nitrogen three times, and then anhydrous Et_2O (10 mL) was added under nitrogen atmosphere. The solution was cooled to -45ºC in a dry ice/acetonitrile bath. Then, PhLi (1.9 M in

Bu_2O, 17.8 mL, 33.7 mmol, 2.0 equiv) was added dropwise with a syringe pump (rate of addition: 1.18 mL/min) at -45 ºC, and the resulting reaction mixture was stirred at the same temperature for 15 min. The cooling bath was replaced with an ice bath, and the reaction mixture was stirred at 0ºC for 2 h. The mixture was then distilled at room temperature, using a rotatory evaporator and keeping the receiving flask in a dry ice/isopropanol bath. The distillate containing the propellane **9a** was transferred to a vial, and the solution was stored under argon atmosphere at -20ºC (volume of distillate: 10 mL). The concentration of [1.1.1]-propellane **9a** was determined by ^{1}H-NMR in $CDCl_3$ using trichloroethylene as internal standard. Generally, an aliquot of the [1.1.1]-propellane solution **9a** (50 µL), $CDCl_3$ (0.5 mL) and trichloroethylene (18 µL, 0.2 mmol) were added to an NMR tube. The ratio between internal standard (δ 6.45 ppm, 1H) and [1.1.1]-propellane (δ 2.01 ppm, 6H) was used to determine the concentration of **9a**.[18] The concentration of the propellane solution (**9a**) ranged between 0.65-1.1 M with yields of 39- 65%.

^{1}H NMR (200 MHz, $CDCl_3$ with Et_2O) δ 2.01 (s, 1H). The spectroscopic data is in agreement with those reported in the literature.[17]

B.8. Preparation of the [3.1.1]-propellane solution in Bu_2O (9b)

The [3.1.1]-propellane solution **9b** was prepared following a described procedure [19] (Figure S5):

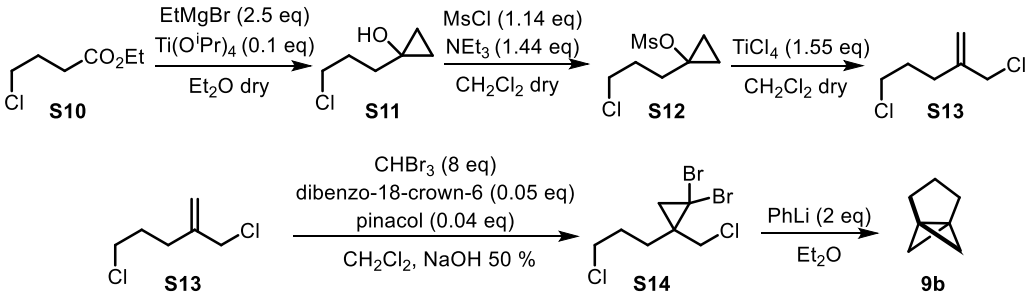


Figure S5. Synthesis of [3.1.1]-propellane **9b**.

[3.1.1]-propellane **9b** was obtained as a solution in Bu_2O. The concentration of [3.1.1]-propellane **9b** was determined by ^{1}H-NMR in $CDCl_3$ using trichloroethylene as internal standard (see Figure S6). Specifically, an aliquot of the [3.1.1]-propellane solution **9b** (50 µL), $CDCl_3$ (0.5 mL) and trichloroethylene (18 µL, 0.2 mmol) were added to an NMR tube. In the case showed in Figure S6, the ratio between internal standard (δ 6.45 ppm, 1H) and [3.1.1]-propellane **9b** (δ 2.42 ppm, 2H) was determined to be 1:0.2, which corresponds to a concentration of 0.4 M of **9b**.

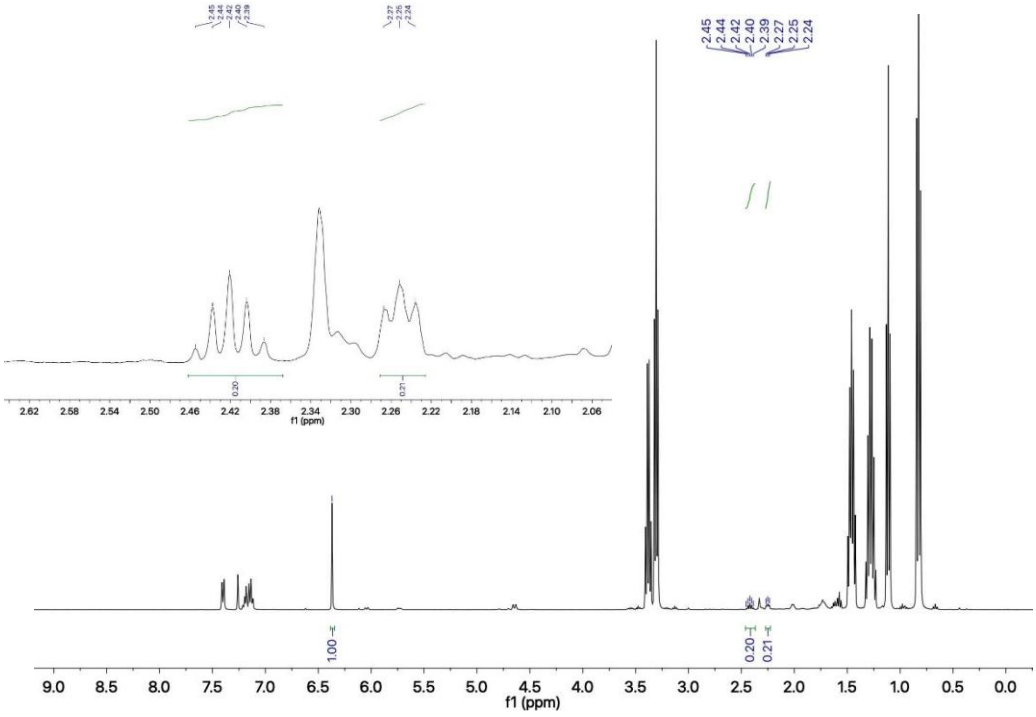
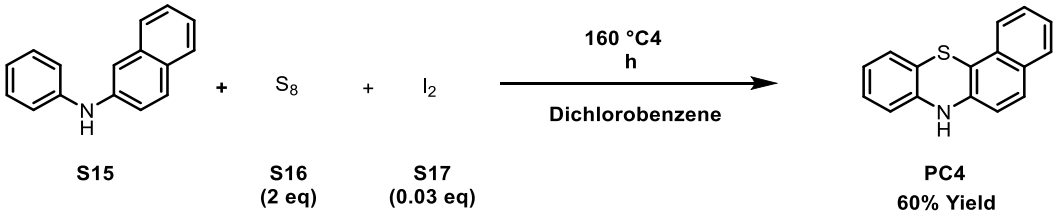


Figure S6. Determination of the concentration of the [3.1.1]-propellane solution **9b** using trichloroethylene as internal standard.

B.9. Synthesis of organic photocatalysts

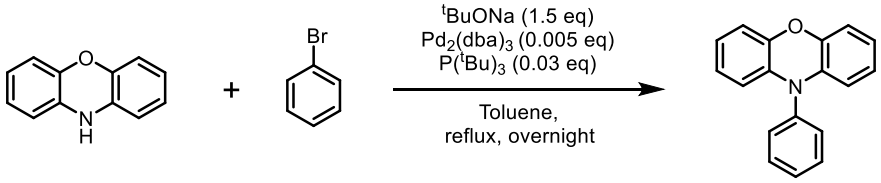
B.9.1 Synthesis of 7H-benzo[c]phenothiazine (PC4)



According to literature procedure with modifications.[20] Under nitrogen atmosphere, in a two-neck round-bottomed flask equipped with a magnetic stir bar, compound N-phenylnaphthalen-2-amine **S15** (2.19 g, 10 mmol, 1 equiv.), sulfur **S16** (0.64 g, 20 mmol, 2 equiv.) and iodine **S17** (76 mg, 0.3 mmol, 0.03 equiv.) were added. After that, 6 mL of dichloromethane solvent (DCM) is added and the system is attached to a refrigerator connected to a trap with a basic solution of NaOH 10%. The solution is stirred for 4h at 160 °C under nitrogen atmosphere. The reaction mixture is then extracted with aqueous basic solution of NaOH 10% (3 x 10 mL), dried over magnesium sulfate and concentrated under reduced pressure. The reaction crude was purified by flash column chromatography (hexane/DCM 5:1) to give the product 7H-benzo[c]phenothiazine (**PC4**) as a yellow solid (1.5 g, 60% yield).

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.02 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.30 (m, 1H), 7.12 – 7.01 (m, 3H), 6.84 (td, *J* = 7.5, 1.3 Hz, 1H), 6.86 (dd, *J* = 7.9, 1.3 Hz, 1H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 143.8, 140.9, 131.5, 131.2, 129.2, 128.6, 128.3, 127.7, 127.6, 124.2, 123.4, 122.7, 118.0, 117.6, 115.5, 109.3. **HRMS** (ESI$^+$): calculated for [$C_{16}H_{12}NS^+$]: 250.0685 (M+H$^+$); found: 250.0701.

B.7.2 Synthesis of 10-phenyl-10H-phenoxazine (PC5)

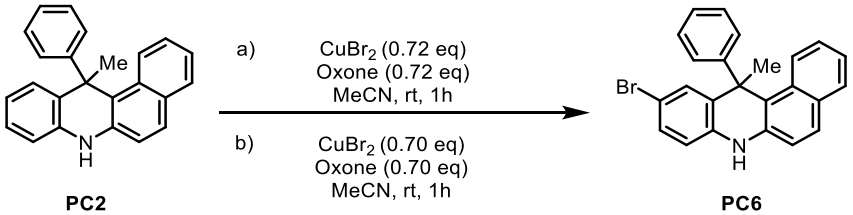


S18 **S19a** 1.2 eq **PC5**

A two-neck round bottom flask, equipped with a magnetic stir bar, was dried with vacuum/nitrogen cycles. Under nitrogen atmosphere, compound phenoxazine **S18** (183 mg, 1 mmol, 1 equiv.), phenyl bromide **S19a** (188 mg, 1.2 mmol, 1.2 equiv.), $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.05 equiv.) and ^{t}BuONa (144 mg, 1.5 mmol, 1.5 equiv.) were added sequentially, followed by 2 mL of degassed solvent Toluene. After that P(^{t}Bu)$_3$ (7 µL, 0.03 mmol, 0.03 equiv.) was added and the reaction was heated at reflux (120°C) under stirring for 6h. The reaction mixture was then extracted with ethyl acetate (3 x 10 mL). The organic phases were combined and washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/DCM 98:2) to give the corresponding product 10-phenyl-10H-phenoxazine (**PC5**) as a white solid (230 mg, 89% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.63 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.33 (m, 2H), 6.85 – 6.53 (m, 6H), 5.93 (dd, *J* = 7.8, 1.7 Hz, 2H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 144.3, 139.4, 134.9, 131.5, 131.1, 128.9, 123.7, 121.6, 115.6, 113.7. **HRMS** (ESI$^+$): calculated for [$C_{18}H_{14}NO^+$]: 260.1070 (M+H$^+$); found: 260.1111.

B.7.3 Synthesis of (S)-10-bromo-12-methyl-12-phenyl-7,12-dihydrobenzo[a]acridine (PC19).



PC2 **PC6**

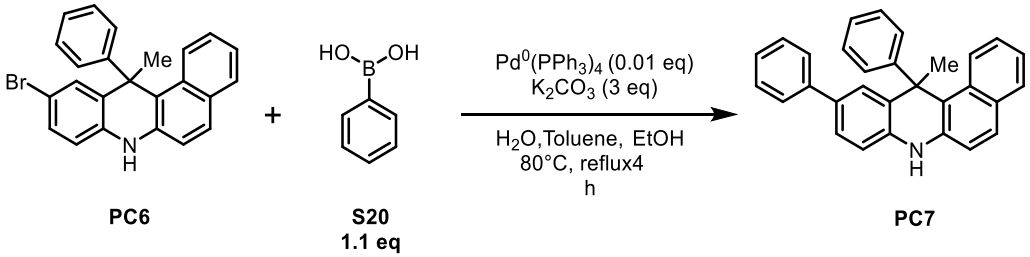
According to literature procedure with modifications.[21] Under air, a round bottom flask equipped with a magnetic stir bar was charged with **PC2** (160.7 mg, 0.50 mmol, 1 equiv.) and 5 mL of

MeCN. Then, $CuBr_2$ (82 mg, 0.36 mmol, 0.72 equiv.) and Oxone® (220 mg, 0.36 mmol, 0.72 equiv.) were added sequentially in one portion. After 1 hour, more $CuBr_2$ (78 mg, 0.35 mmol, 0.7 equiv.) and Oxone® (213 mg, 0.35 mmol, 0.7 equiv.) were added and the reaction was stirred for further 1 hour. After the reaction was completed (controlled by ^{1}H NMR), 40 mL of EtOAc were added. The organic phase was washed with H_2O (2 x 20 mL), the solvent was dried over $MgSO_4$ and removed by distillation under reduced pressure. The reaction crude was purified by flash column chromatography (hexane/EtOAc 7:3) to give the product (S)-10-bromo-12-methyl-12-phenyl-7,12-dihydrobenzo[a]acridine (**PC6**) as a white solid (135 mg, 68% yield).

*Note: In principle, 1 eq. of Oxone® should be enough for the reaction, but it decomposes over time. The reaction progress cannot be controlled by TLC because both **PC6** and **PC2** runs equally, therefore ^{1}H NMR using CD_3CN was employed instead.*

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.51 (s, 1H), 7.74 – 7.58 (m, 4H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.20 – 7.02 (m, 4H), 6.98 – 6.94 (m, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 2.24 (s, 3H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 152.5, 136.7, 136.3, 133.2, 132.9, 132.7, 131.8, 130.3, 130.3, 129.9, 129.2, 128.9, 126.5, 126.2, 126.1, 122.5, 118.0, 117.2, 116.1, 111.9, 46.6, 30.5. **HRMS** (ESI$^+$): calculated for [$C_{24}H_{19}BrN^+$]: 400.0695 (M+H$^+$); found: 400.0720.

B.7.4 Synthesis of (S)-12-methyl-10,12-diphenyl-7,12-dihydrobenzo[a]acridine (PC7).

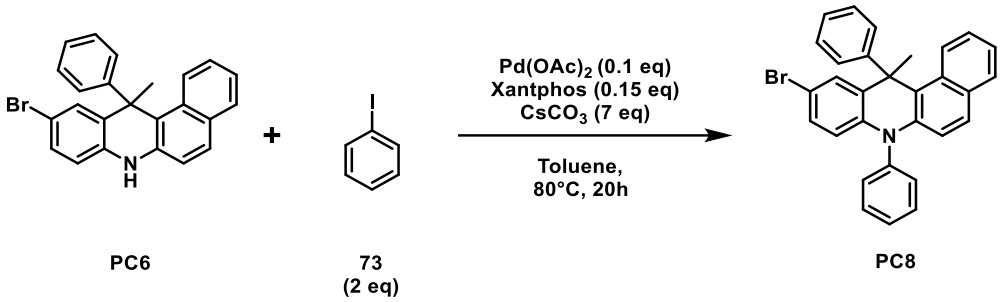


According to literature procedure with modifications.[22] A round bottom flask, equipped with a magnetic stir bar, was dried with vacuum/nitrogen cycles. Under nitrogen atmosphere, compound **PC6** (186 mg, 0.47 mmol, 1 equiv.), phenylboronic acid **S20** (63 mg, 0.52 mmol, 1.1 equiv.) and tetrakis(triphenylphosphine)palladium(0) (5.4 mg, 0.0047 mmol, 0.01 equiv.) were added sequentially, followed by 2 mL of degassed solvent. The solvent corresponds with a mixture of EtOH (0.35 mL), an aqueous solution of K_2CO_3 (193 mg in 0.7 mL, 1.4 mmol, 3 equiv., 2M) and toluene (0.95 mL), in ratio 1 : 2 : 2.7. The reaction was heated at reflux (80°C) under stirring for 4 h. After that, the crude was filtered on Celite, washed with EtOAc (10 mL) and DCM (10 mL) and the solvent was dried over $MgSO_4$ and removed by distillation under reduced pressure. The residue was purified by flash column chromatography (gradient from 100% hexane to 9:1

hexane/EtOAc) to give the product (S)-12-methyl-10,12-diphenyl-7,12-dihydrobenzo[a]acridine (**PC7**) as a white solid (110 mg, 60% yield).

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.48 (s, 1H), 7.73 – 7.62 (m, 4H), 7.59 – 7.53 (m, 1H), 7.46 – 7.25 (m, 7H), 7.23 – 7.10 (m, 4H), 7.06 – 6.95 (m, 2H), 6.88 (d, *J* = 8.3 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR (101 MHz, Acetone-d_6)** δ 153.1, 142.0, 137.0, 136.4, 133.5, 133.1, 131.7, 130.8, 130.1, 129.8, 129.5, 129.4, 129.0, 128.9, 127.0, 126.7, 126.2, 126.2, 126.1, 126.0, 122.3, 118.1, 117.5, 114.7, 54.9, 46.6. **HRMS (ESI$^+$):** calculated for [$C_{30}H_{24}N^+$]: 398.1903 (M+H$^+$); found: 398.1960.

B.7.5 Synthesis of 10-bromo-12-methyl-7,12-diphenyl-7,12-dihydrobenzo[a]acridine (PC8).

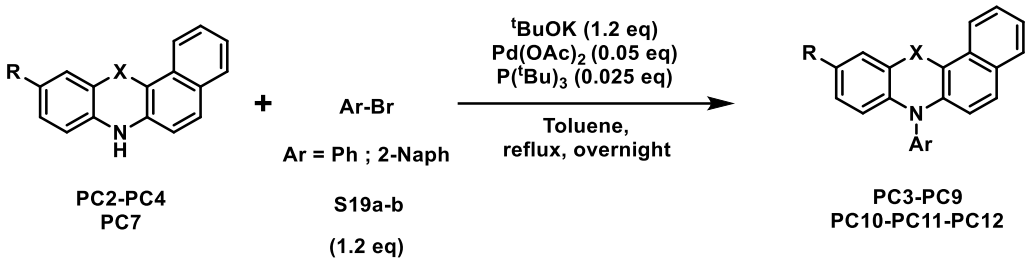


PC6 | 73 (2 eq) | PC8

According to literature procedure with modifications.[23] A round bottom flask, equipped with a magnetic stir bar, was dried with vacuum/nitrogen cycles. Under nitrogen atmosphere, compound (S)-10-bromo-12-methyl-12-phenyl-7,12-dihydrobenzo[a]acridine **PC6** (80 mg, 0.2 mmol, 1 equiv.), phenyl iodide **73** (45 µL, 0.4 mmol, 2 equiv.), Palladium (II) acetate (4.5 mg, 0.02 mmol, 0.1 equiv.), Xantphos (17 mg, 0.03 mmol, 0.15 equiv.) and Cs_2CO_3 (456 mg, 1.4 mmol, 7 equiv.) were added sequentially. After that 1 mL of degassed solvent Toluene was added and the reaction was heated at 80°C under stirring for 20h. The crude was then filtered on celite with washes of EtOAc and the solvent was removed by distillation under reduced pressure. The reaction crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC8** as a white solid (83 mg, 87% yield).

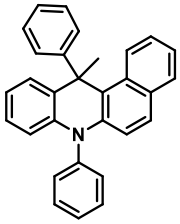
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 – 7.55 (m, 7H), 7.49 – 7.33 (m, 5H), 7.27 – 7.20 (m, 1H), 7.08 (t, *J* = 7.4 Hz, 1H), 7.03 – 6.99 (m, 1H), 6.96 (d, *J* = 2.3 Hz, 1H), 6.90 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.60 (d, *J* = 9.2 Hz, 1H), 6.06 (d, *J* = 8.8 Hz, 1H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 152.2, 142.0, 138.2, 138.0, 133.0, 132.9, 131.9, 131.7, 131.7, 130.9, 129.4, 129.2, 129.0, 129.0, 128.9, 128.4, 126.3, 126.2, 125.8, 122.7, 119.2, 117.4, 116.7, 112.8, 45.9, 31.1. **HRMS (ESI$^+$):** calculated for [$C_{30}H_{23}BrN^+$]: 476.1008 (M+H$^+$); found: 476.0977.

B.7.6 General Buchwald-Hartwig reaction procedure for N-Arylation of Photocatalysts PC3-PC9-11.



According to literature procedure with modifications.[24] A two-neck round bottom flask, equipped with a magnetic stir bar, was dried with vacuum/nitrogen cycles. Under nitrogen atmosphere, the precursor **PC2, PC4, PC7** (1 equiv.), aryl bromide **Ar-Br** (**S19a-b**, 1.1 equiv.), Palladium(II) acetate (0.05 equiv.) and ^{t}BuOK (1.2 equiv.) were added sequentially, followed by degassed solvent Toluene. After that P(^{t}Bu)$_3$ (0.025 equiv.) was added and the reaction was heated at reflux (120°C) under stirring overnight. The crude was then filtered on celite with washes of EtOAc and the solvent was removed by distillation under reduced pressure. The reaction crude was purified by flash column chromatography (hexane/DCM) to give the products **PC3** and **PC9-12** in the stated yield.

12-methyl-7,12-diphenyl-7,12-dihydrobenzo[a]acridine (PC3)

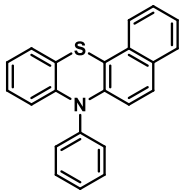


PC3

Compound **PC3** was synthesized according to the general procedure **B.7.6** using 12-methyl-12-phenyl-7,12-dihydrobenzo[a]acridine **PC2** (161 mg, 0.5 mmol, 1 equiv.), phenyl bromide (**S19a**, 86 mg, 0.55 mmol, 1.1 equiv.), Palladium (II) acetate (5.6 mg, 0.025 mmol, 0.05 equiv.), ^{t}BuOK (67 mg, 0.6 mmol, 1.2 equiv.) and P(^{t}Bu)$_3$ (3 μL, 0.0125 mmol, 0.025 equiv.) in 2.7 mL of Toluene. The crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC3** as a white solid (180 mg, 90% yield).

^{1}H NMR (400 MHz, Acetone-d$_6$) δ 7.76 (t, *J* = 7.7 Hz, 2H), 7.73 – 7.66 (m, 3H), 7.67 – 7.58 (m, 2H), 7.53 (d, *J* = 9.1 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.16 (t, *J* = 7.3, 1H), 7.08 – 7.04 (m, 1H), 7.03 – 6.96 (m, 1H), 6.92 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.83 – 6.79 (m, 1H), 6.69 – 6.65 (m, 1H), 6.61 (d, *J* = 9.2 Hz, 1H), 6.12 (dd, *J* = 8.3, 1.2 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, Acetone-d$_6$)** δ 153.4, 143.1, 139.2, 139.1, 132.7, 132.3, 132.2, 131.5, 131.3, 131.0, 129.7, 129.4, 129.1, 129.0, 127.0, 126.9, 126.2, 126.1, 122.9, 121.4, 119.9, 117.8, 115.1, 46.2, 31.3. **HRMS (ESI^{+}):** calculated for [$C_{30}H_{24}N^{+}$]: 398.1903 (M+H^{+}); found: 398.1960.

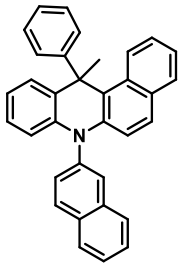
7-phenyl-7H-benzo[c]phenothiazine (PC9)


PC9

Compound **PC9** was synthesized according to the general procedure **B.7.6** using 7H-benzo[c]phenothiazine **PC4** (700 mg, 2.8 mmol, 1 equiv.), phenyl bromide **S19a** (487 mg, 3.1 mmol, 1.1 equiv.), Palladium (II) acetate (31 mg, 0.14 mmol, 0.05 equiv.), ^{t}BuOK (382 mg, 3.4 mmol, 1.2 equiv.) and P(^{t}Bu)$_3$ (17 μL, 0.07 mmol, 0.025 equiv.) in 17 mL of Toluene. The crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC9** as a yellow solid (858 mg, 94% yield).

^{1}H NMR (400 MHz, Acetone-d$_6$) δ 8.05 – 7.99 (m, 1H), 7.80 – 7.73 (m, 1H), 7.69 (t, *J* = 7.7 Hz, 2H), 7.60 – 7.45 (m, 5H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.04 – 6.86 (m, 2H), 6.66 (d, *J* = 9.0 Hz, 1H), 6.39 (dd, *J* = 8.1, 1.3 Hz, 1H). **^{13}C NMR (101 MHz, Acetone-d$_6$)** δ 145.8, 142.5, 142.4, 131.7, 131.4, 131.2, 129.1, 129.0, 128.2, 128.0, 127.9, 127.7, 125.2, 124.1, 123.3, 121.5, 118.7, 117.8, 114.3. **HRMS (ESI$^+$):** calculated for [$C_{22}H_{16}NS^+$]: 326.0998 (M+H$^+$); found: 326.0999.

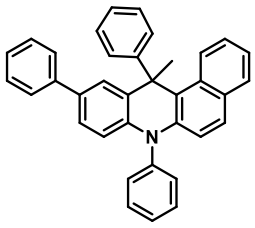
12-methyl-7-(naphthalen-2-yl)-12-phenyl-7,12-dihydrobenzo[a]acridine (PC10)


PC10

Compound **PC10** was synthesized according to the general procedure **B.7.6** using 12-methyl-12-phenyl-7,12-dihydrobenzo[a]acridine **PC2** (161 mg, 0.5 mmol, 1 equiv.) 2-bromonaphthalene (**S19b**, 114 mg, 0.55 mmol, 1.1 equiv.), Palladium (II) acetate (5.6 mg, 0.025 mmol, 0.05 equiv.), ^{t}BuOK (67 mg, 0.6 mmol, 1.2 equiv.) and P(^{t}Bu)$_3$ (3 μL, 0.0125 mmol, 0.025 equiv.) in 2.7 mL of Toulene. The crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC10** as a white solid (183 mg, 82% yield).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.19 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 8.01 – 7.90 (m, 2H), 7.77 – 7.53 (m, 6H), 7.49 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.28 – 7.15 (m, 1H), 7.12 – 6.97 (m, 2H), 6.92 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.79 – 6.75 (m, 1H), 6.70 – 6.64 (m, 2H), 6.19 (d, *J* = 8.3 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, CD$_2$Cl$_2$)** δ 153.0, 139.8, 138.8, 135.4, 133.4, 132.2, 131.8, 130.9, 130.9, 130.6, 129.3, 129.2, 128.8, 128.7, 128.4, 128.3, 127.3, 127.0, 126.5, 126.5, 125.8, 125.7, 122.5, 121.0, 119.5, 117.7, 115.0, 46.0, 31.1. **HRMS (ESI$^+$):** calculated for [$C_{34}H_{26}N^+$]: 448.2060 (M+H$^+$); found: 448.2079.

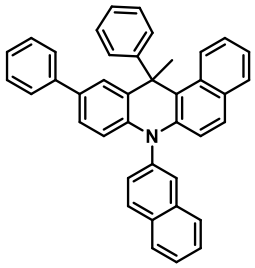
12-methyl-7,10,12-triphenyl-7,12-dihydrobenzo[a]acridine (PC11)


PC11

Compound **PC11** was synthesized according to the general procedure **B.7.6** using (S)-12-methyl-10,12-diphenyl-7,12-dihydrobenzo[a]acridine **PC7** (72 mg, 0.18 mmol, 1 equiv.), phenyl bromide (**S19a**, 31 mg, 0.2 mmol, 1.1 equiv.), Palladium (II) acetate (2 mg, 0.009 mmol, 0.05 equiv.), ^{t}BuOK (24 mg, 0.216 mmol, 1.2 equiv.) and P(^{t}Bu)$_3$ (1 μL, 4.5*10^{-3} mmol, 0.025 equiv.) in 1 mL of Toluene. The crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC11** as a white solid (55 mg, 63% yield).

^{1}H NMR (400 MHz, Acetone-d$_6$) δ 7.85 – 7.72 (m, 5H), 7.66 – 7.61 (m, 2H), 7.57 – 7.47 (m, 3H), 7.41 – 7.29 (m, 6H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.19 – 7.12 (m, 2H), 7.10 – 7.06 (m, 1H), 7.03 – 6.99 (m, 1H), 6.64 (d, *J* = 9.1 Hz, 1H), 6.23 (d, *J* = 8.6 Hz, 1H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, Acetone-d$_6$)** δ 153.4, 142.9, 141.5, 139.0, 138.7, 133.9, 132.7, 132.3, 131.7, 131.6, 129.7, 129.6, 129.5, 129.5, 129.5, 129.2, 129.0, 127.3, 127.0, 126.8, 126.3, 126.2, 125.6, 123.0, 119.9, 117.8, 115.7, 46.4, 31.4. **HRMS (ESI$^+$):** calculated for [$C_{36}H_{28}N^+$]: 474.2216 ($M+H^+$); found: 474.2264.

12-methyl-7-(naphthalen-2-yl)-10,12-diphenyl-7,12-dihydrobenzo[a]acridine (PC12)


PC12

Compound **PC23** was synthesized according to the general procedure **B.7.6** using (S)-12-methyl-10,12-diphenyl-7,12-dihydrobenzo[a]acridine **PC7** (100 mg, 0.25 mmol, 1 equiv.), 2-bromonaphthalene (**S19b**, 57 mg, 0.275 mmol, 1.1 equiv.), Palladium (II) acetate (2.8 mg, 0.0125 mmol, 0.05 equiv.), ^{t}BuOK (34 mg, 0.3 mmol, 1.2 equiv.) and P(^{t}Bu)$_3$ (2 μL, 7.5*10^{-3} mmol, 0.03 equiv.) in 1.35 mL of Toluene. The crude was purified by flash column chromatography (hexane/DCM 9:1) to afford compound **PC12** as a white solid (68 mg, 51% yield).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.23 (d, *J* = 8.6 Hz, 1H), 8.10 – 8.03 (m, 2H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.70 – 7.60 (m, 3H), 7.57 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.39 – 7.32 (m, 4H), 7.30 – 7.21 (m, 3H), 7.17 – 7.03 (m, 3H), 6.73 (d, *J* = 9.2 Hz, 1H), 6.34 (d, *J* = 8.6 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR (101 MHz, CD_2Cl_2)** δ 152.8, 141.1, 139.6, 138.6, 138.3, 135.3, 133.6, 133.4, 132.2, 131.9, 131.3, 131.0, 130.8, 129.3, 129.2, 129.2, 129.0, 128.9,

128.8, 128.5, 128.3, 127.4, 127.1, 126.9, 126.5, 126.5, 126.0, 125.8, 125.2, 122.7, 119.6, 117.7, 115.5, 46.1, 31.3.**HRMS (ESI$^+$):** calculated for [$C_{40}H_{30}N^+$]: 524.2373 (M+H$^+$); found: 524.2357.

B.8 Photoredox properties of organic photocatalysts

B.8.1 UV-Visible absorption spectra

The UV-Visible absorption spectra of the ten synthesized PCs are shown below. Each spectrum was measured in acetonitrile solution with a concentration of 0.015M, where each photocatalyst showed good solubility. Each spectrum is reported by plotting absorbance against wavelength. For a better understanding of the data obtained, the spectra of the PCs were divided into two groups: class of analogous photocatalysts in **PC1** structure (Figure S7) and class of analogous photocatalysts in **PC2** structure (Figure S8):

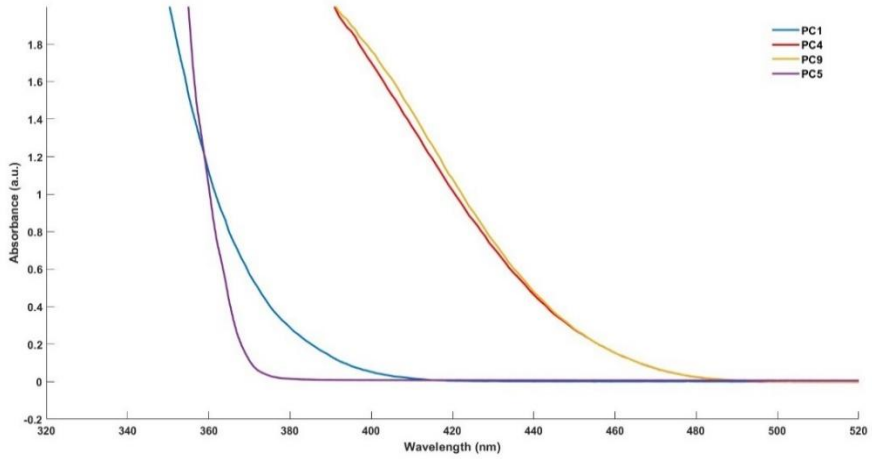


Figure S7. UV-Visible Absorption spectra of **PC1**, **PC4, PC5, PC9**. PCs were in 0.015M solutions in MeCN.

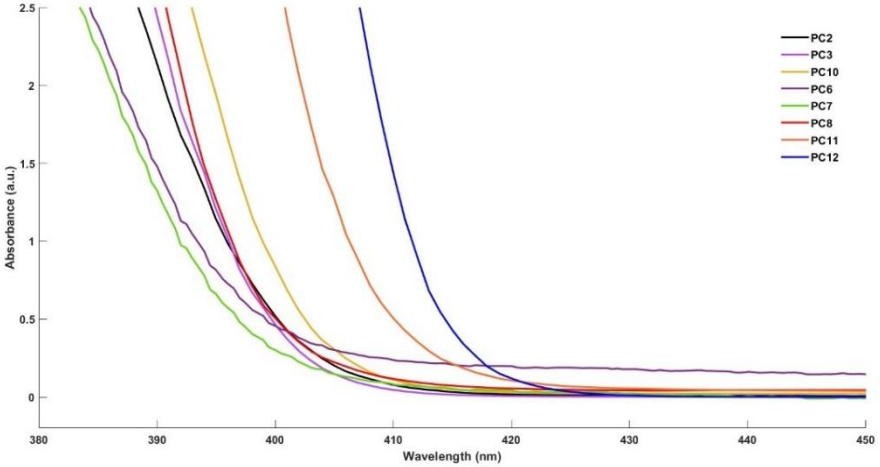


Figure S8. UV-Visible Absorption spectra of **PC2-3, PC6-8, PC10-12**. PCs were in 0.015M solutions in MeCN.

B.8.2 Fluorescence emission

The emission spectra of the PCs were recorded in acetonitrile (MeCN) solvent, irradiating the solutions at the λ_{max} of the corresponding absorption spectra (Figure S9).

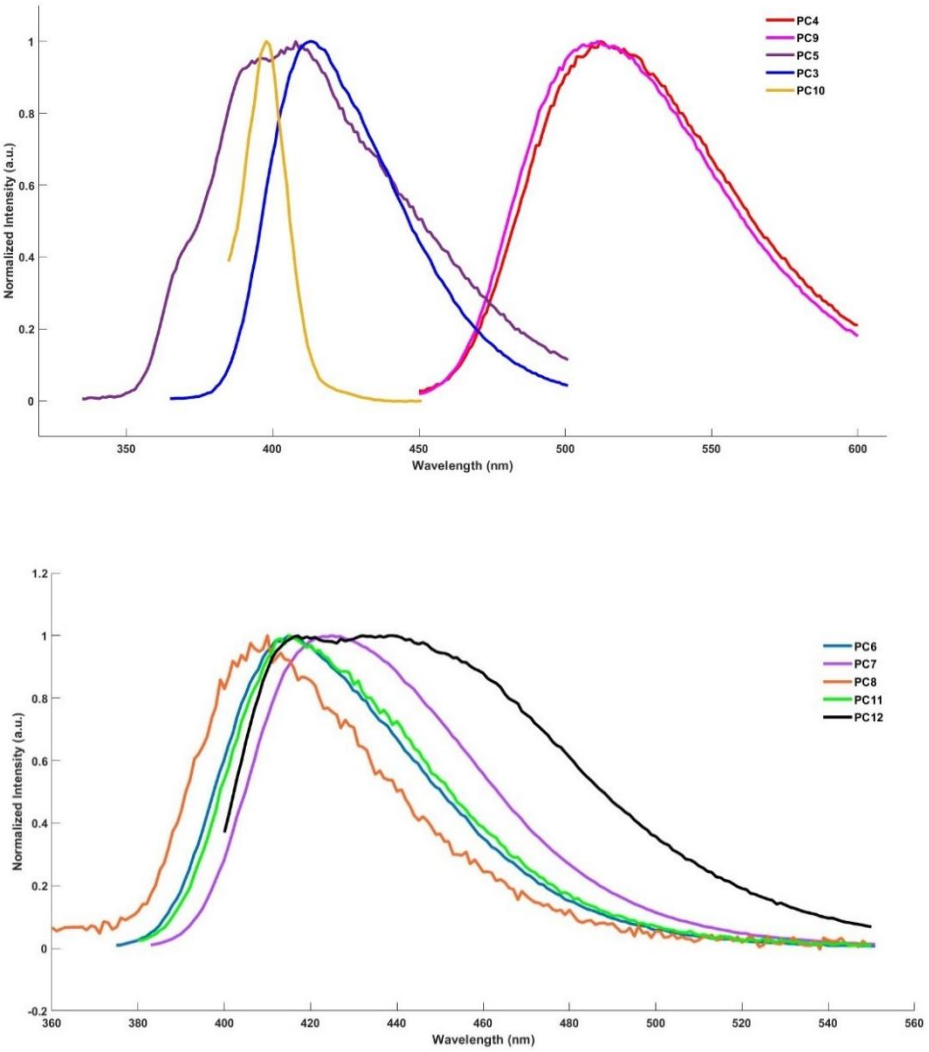


Figure S9. a) Emission spectra of **PC3-5, PC9-10**. b) Emission spectra of **PC6-8, PC11-12**.

B.8.3 Cyclic voltammetry measurements

Cyclic voltammetry measurements of the various synthesized PCs are reported below (Figure S10). Since in the reaction under analysis the PC reacts through a mechanism via oxidative quenching, only the potentials under oxidation were measured.

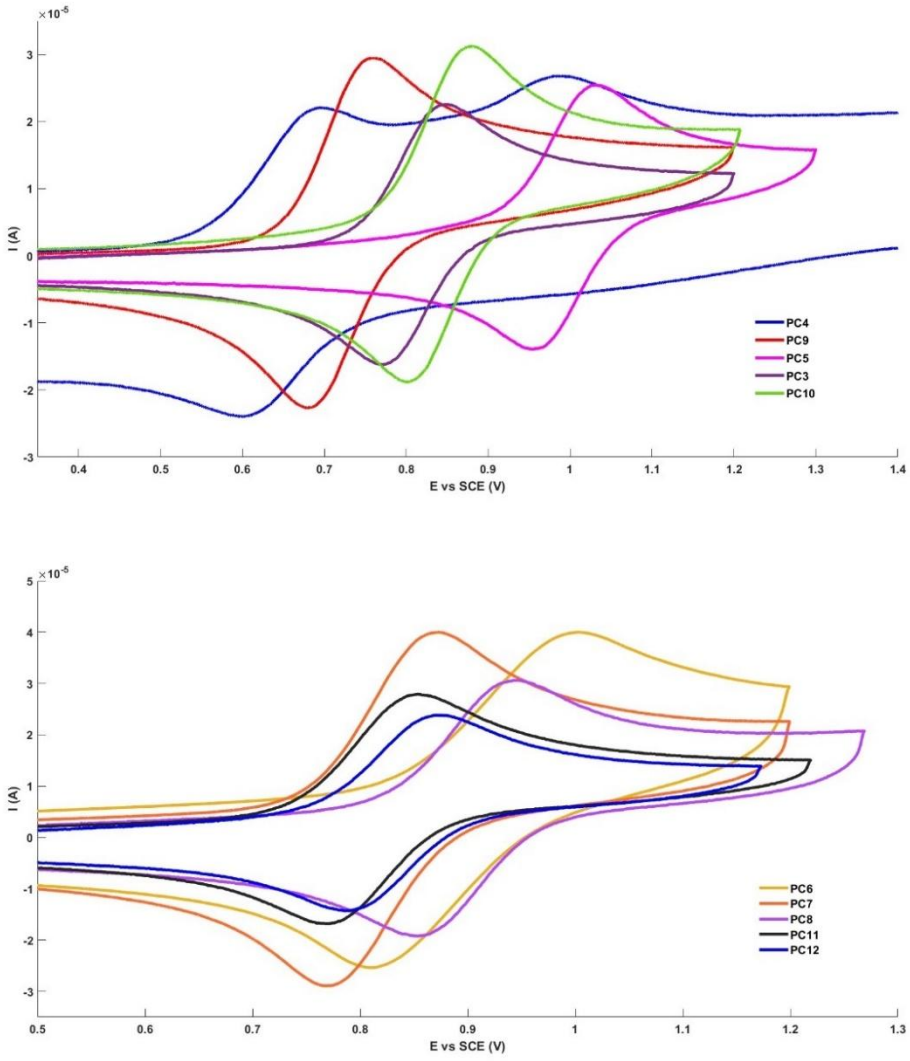


Figure S10. Cyclic voltammogram of **PC3-12** (5mM) in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Pt auxiliary electrode. The CVs are reported using the IUPAC convention.

Table S1 shows the values of the oxidation potentials of the PCs, measured through the CVs:

	PC									
	PC3	**PC4**	**PC5**	**PC6**	**PC7**	**PC8**	**PC9**	**PC10**	**PC11**	**PC12**
E_{ox}[a] (V)	0,85	0,51	0,67	0,91	0,82	0,90	0,58	0,84	0,81	0,83

[a] **Potential vs SCE in MeCN**

Table S1. Oxidation potentials of **PC3-12**.

B.8.4 Calculation of $E_{0,0}$

The excitation energy $E_{0,0}$ was determined from the intersection point between the absorption and the emission profiles of the photocatalyst.[25]

PC3

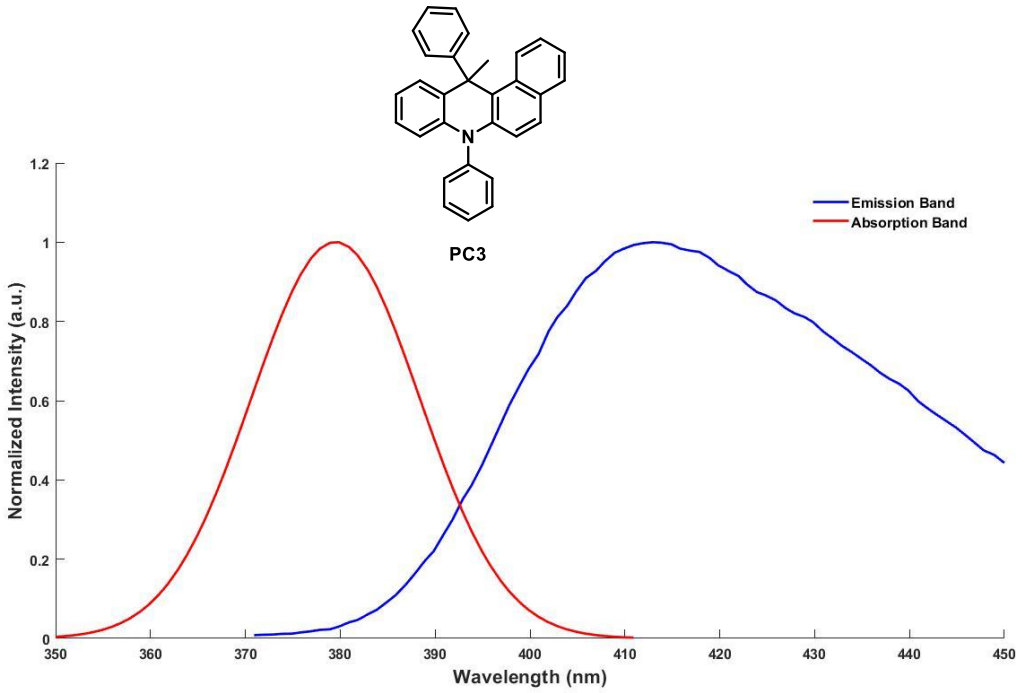


Figure S11a. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 393 nm**.

PC4

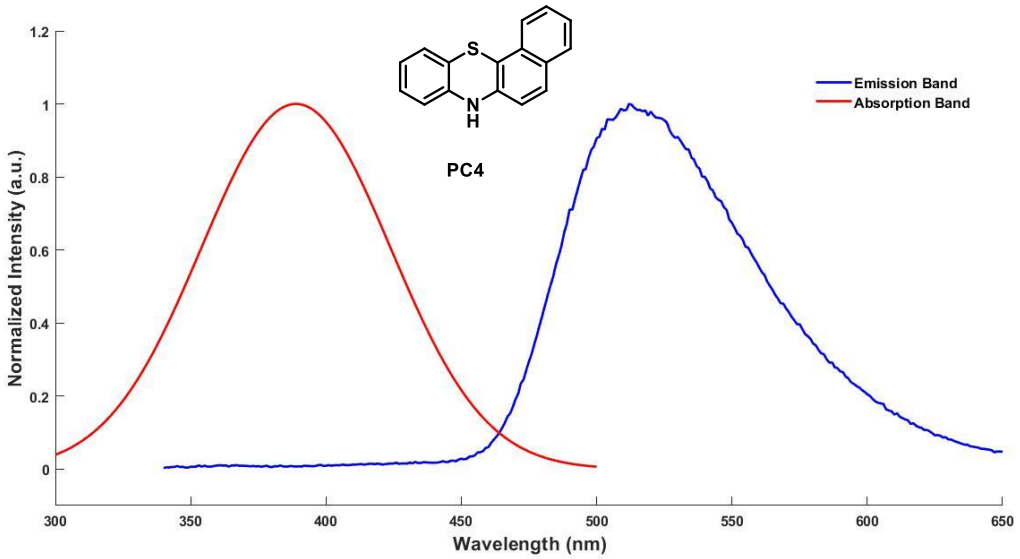


Figure S11b. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra**. λ_{int} = 464 nm**.

PC5

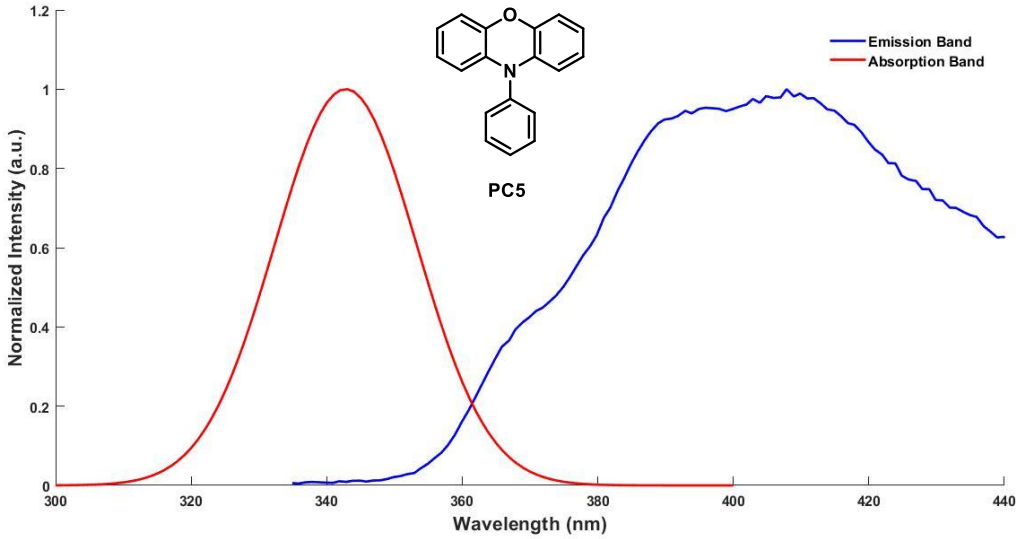


Figure S11c. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 361 nm**.

PC6

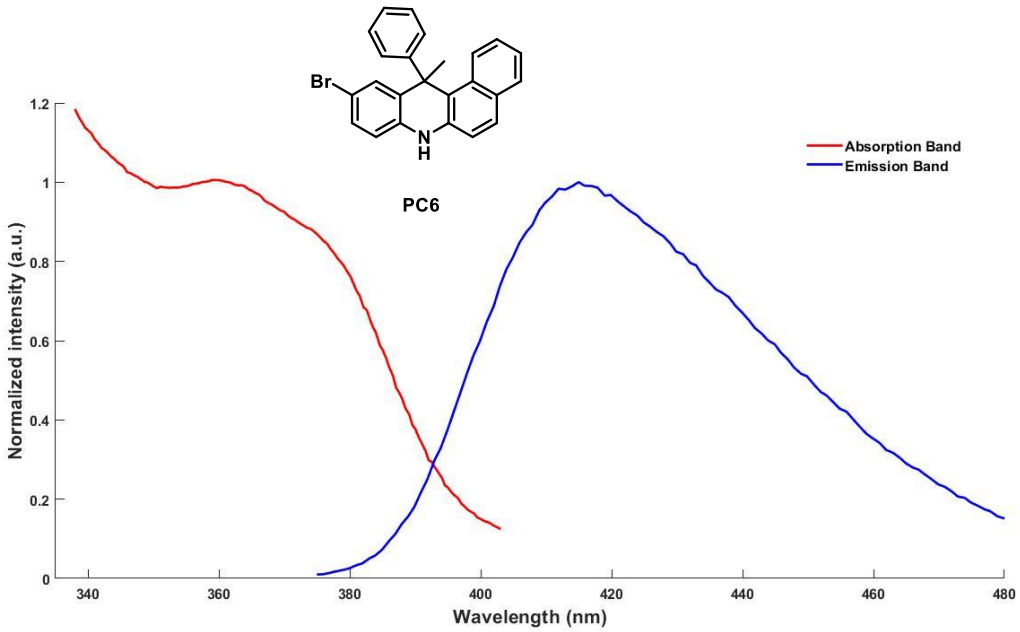


Figure S11d. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra**. λ_{int} = 392 nm**.

PC7

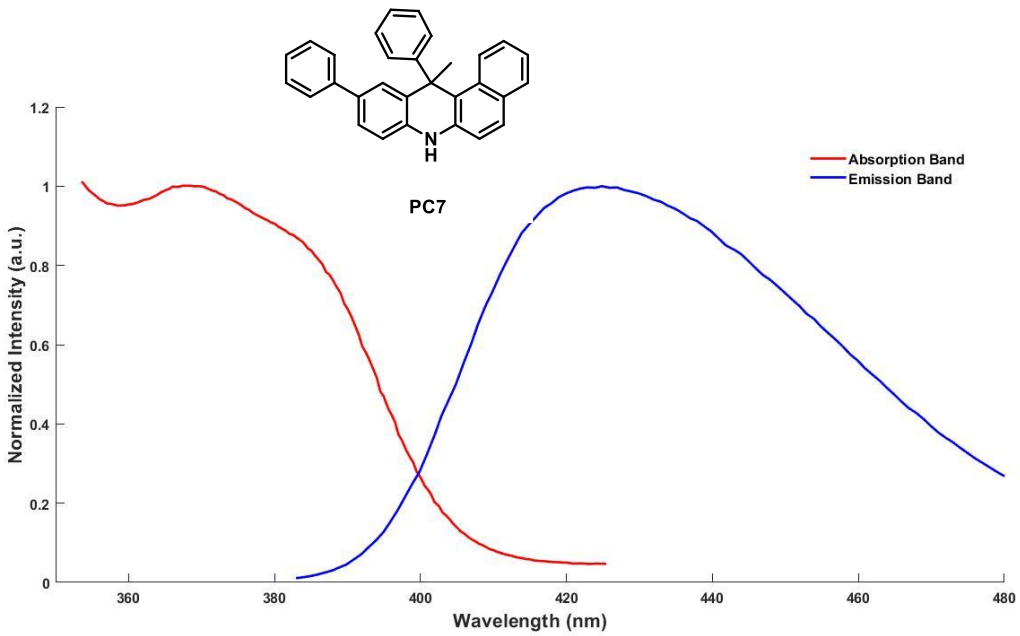


Figure S11e. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. $\boldsymbol{\lambda_{int}}$ **= 400 nm**.

PC8

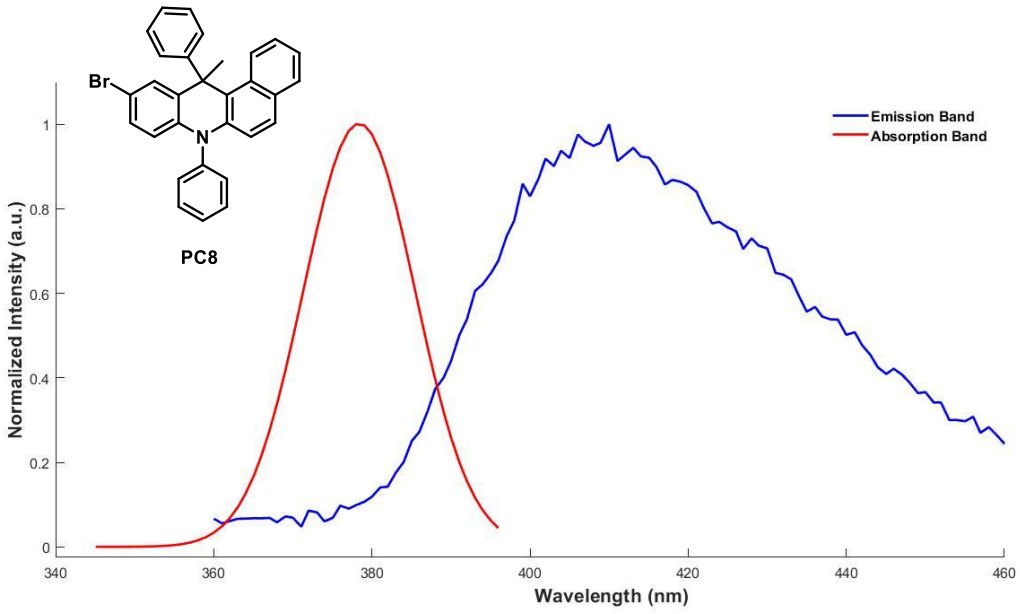


Figure S11f. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. $\boldsymbol{\lambda_{int}}$ **= 388 nm**.

PC9

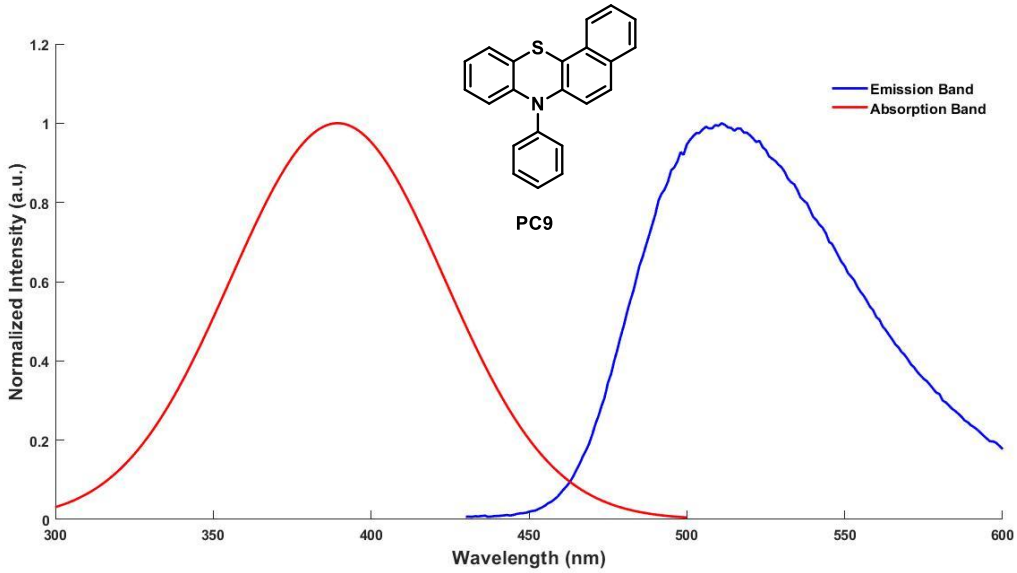


Figure S11g. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 463 nm**.

PC10

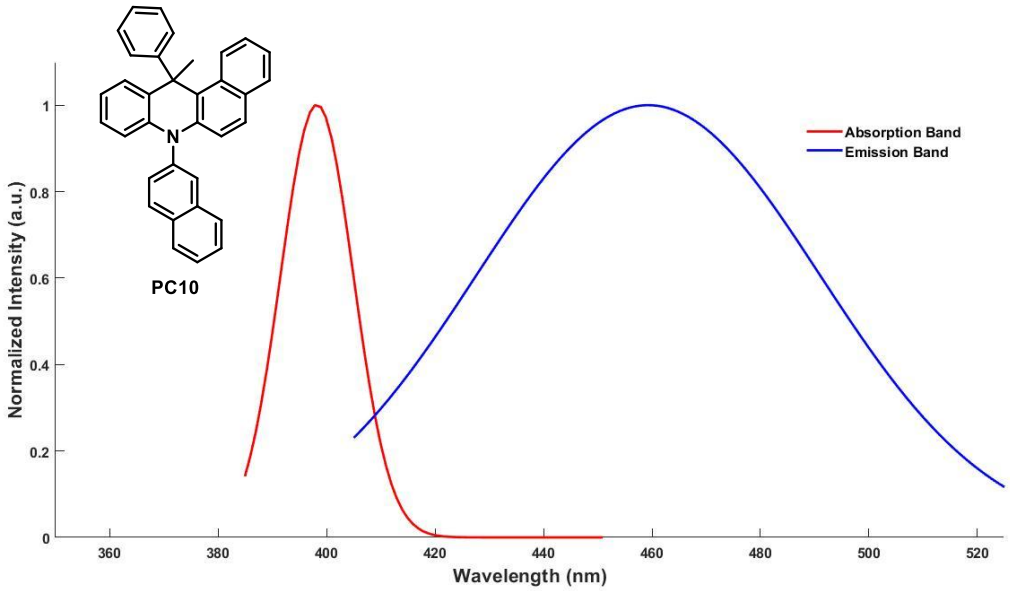


Figure S11h. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 409 nm**.

PC11

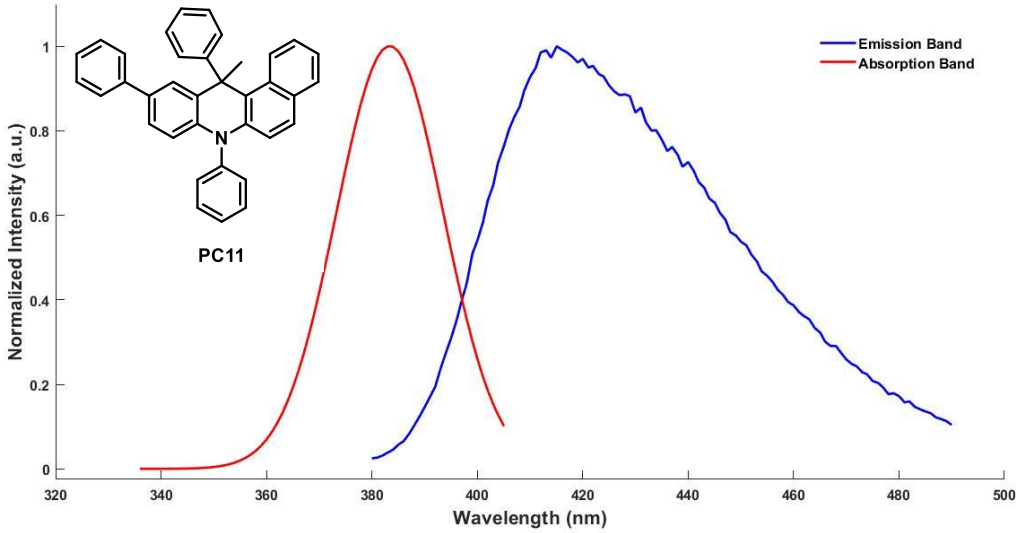


Figure S11i. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 397 nm**.

PC12

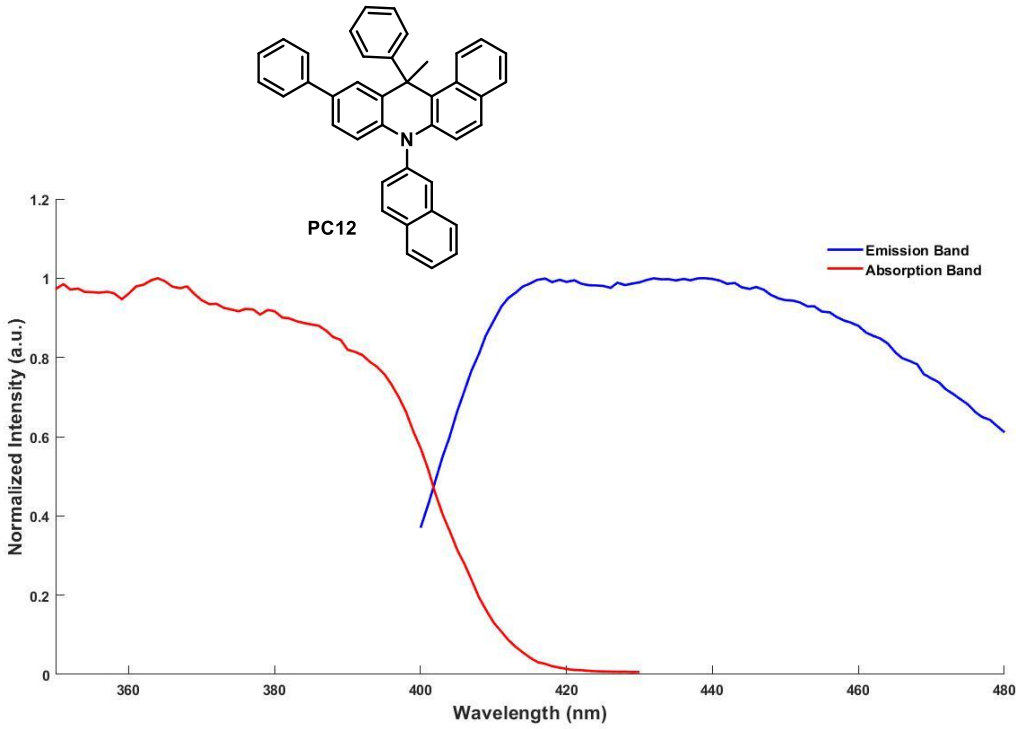


Figure S11j. Calculation of the $E_{0,0}$ from the wavelength of the intersection (λ_{int}) between normalized absorbance and emission spectra. **λ_{int} = 402 nm**.

B.8.5 Calculation of oxidation potential in excited state

The oxidation potential of the excited state photocatalysts E^*_{ox} was estimated by means of the Rehm-Weller formula:[26]

$$E^*_{ox} = E_{ox} - E_{0,0}$$

the oxidation potential E_{ox} was determined by cyclic voltammetry measurements and the excitation energy $E_{0,0}$ was determined from the intersection point between the absorption and the emission profiles.[15] Below is a table with the values of E_{ox}, $E_{0,0}$ and E^*_{ox} calculated for the synthesized **PC3-PC12** (Table S2):

PC	E_{ox} [a] (V)	$E_{0,0}$ (eV)	E^*_{ox} [a] (V)
PC1	0,68	2,78	-2,10
PC2	0,76	3,13	-2,37
PC3	0,85	3,16	-2,30
PC4	0,51	2,67	-2,16
PC5	0,67	3,43	-2,92
PC6	0,91	3,16	-2,25
PC7	0,82	3,1	-2,28
PC8	0,90	3,19	-2,29
PC9	0,58	2,68	-2,09
PC10	0,84	3,03	-2,19
PC11	0,81	3,12	-2,31
PC12	0,83	3,09	-2,26
[a] Potential vs SCE in MeCN			

Table S2. Experimental values of E_{ox}, $E_{0,0}$ and E^*_{ox} for the synthesized **PC1-12**. **PC1** and **PC2** data are derived from the literature and have been reported in the table for comparison [27,28]

B.8.6 Time-resolved emission decay of PC3

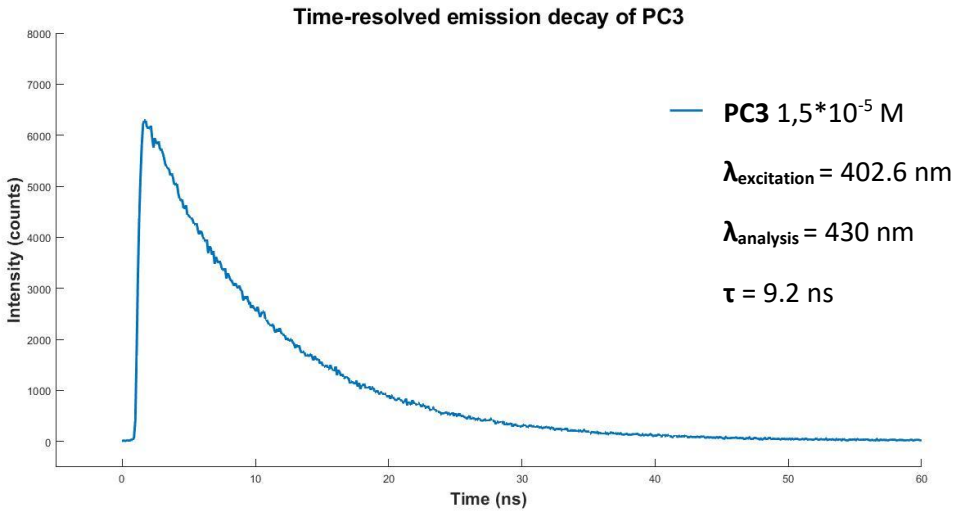


Figure S12. Time-resolved emission decay (excitation at 402.6 nm, analysis at 430 nm) of PC3 1,5*10^{-5} M in MeCN solution measured by TC-SPC (τ = 9.2 ns, from deconvolution and single-exponential fitting).

C. OPTIMIZATION OF THE REACTION CONDITIONS

C.1. ATRA WITH ALKENES

C.1.1. Preliminary screening of organic photoredox catalysts

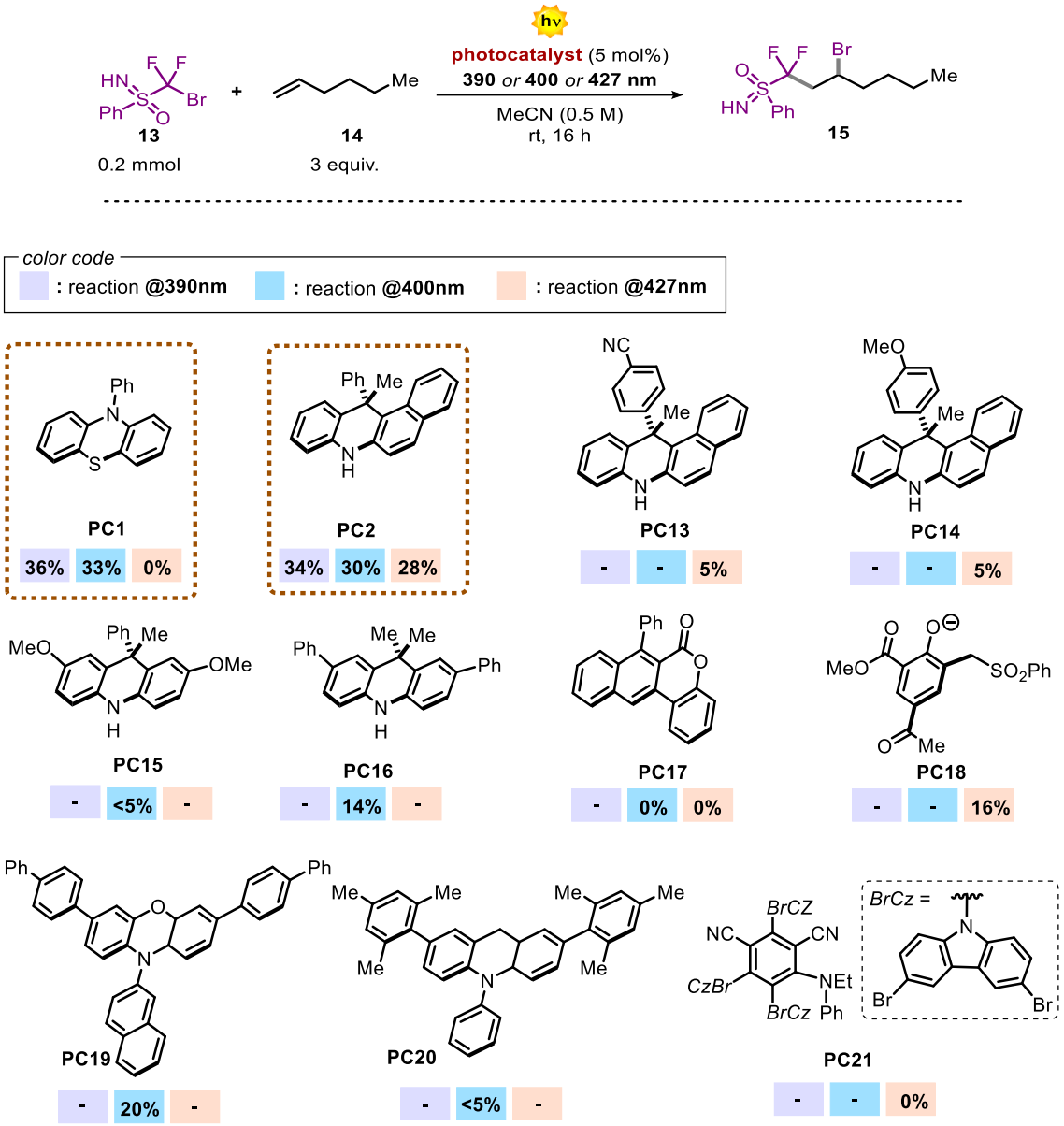
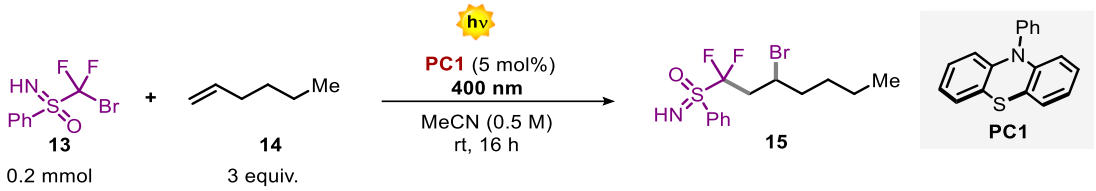


Table S3. Screening of organic photoredox catalysts. The values refer to the yield of **15** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

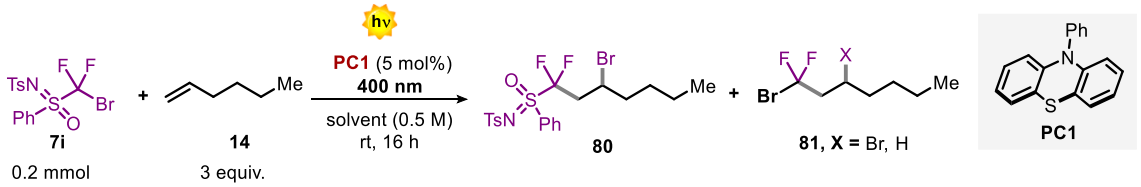
C.1.2. Solvent screening



Entry	Solvent	Conversion (%)	Yield (%)[1]
1	**MeCN**	**41**	**33**
2	DCM	29	19
3	toluene	10	>5
4	dichlorobenzene	8	0
5	DMF	0	0
6	THF	23	15

Table S4. Screening of solvents. The values refer to the conversion of **13** and yield of **15** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

C.1.3. Tests with NTs-sulfoximine



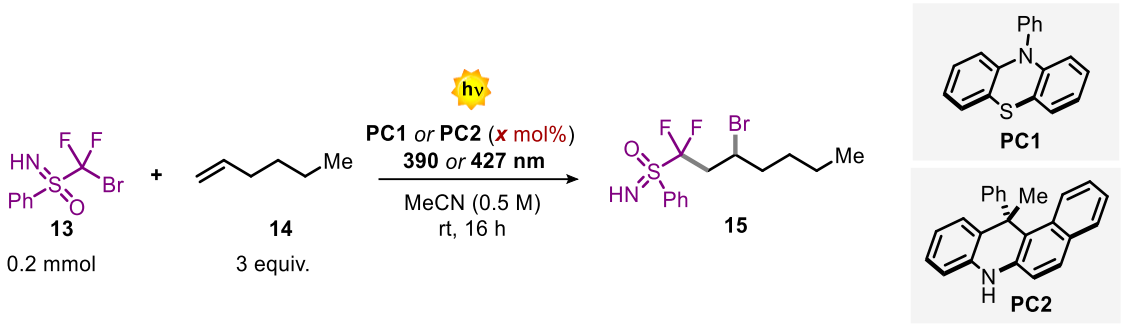
Entry	Solvent	Conversion (%)	Yield (%)[1]
1	**MeCN**	22	traces
2	DCM	67	18
3	toluene	72	12
4	dichlorobenzene	61	14

Table S5. Text with NTs-sulfoximine **7i**. The values refer to the conversion of **7i** and yield of **91** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

NOTE: From ^{19}F-NMR analysis of the reaction crude of entries 1-4, the presence of significant amounts of several byproducts is observed. Among them, the major byproduct **81** (5-12% yield)

results from the addition of the •CF_2Br radical on the olefine double bond, leading to cleavage of the S-C bond of the N-Ts sulfoximine. This type of reactivity has been previously described in the literature.[29]

C.1.4. Evaluation of the photocatalyst loading



Entry	PC	λ (nm)	mol%	Conversion (%)	Yield (%)[1]
1	PC1	400	5	41	33 (21)
2	PC1	400	10	75	51
3	**PC1**	**400**	**15**	**100**	**60 (40)**
4	PC1	400	20	100	54
5	PC2	390	5	41	34
6	PC2	390	10	62	34
7	**PC2**	**390**	**15**	**78**	**48**
8	PC2	390	20	98	22
9	PC2	427	5	21	28
10	PC2	**427**	**15**	**62**	**47**

Table S6. Evaluation of the photocatalyst loading (**PC1** and **PC2**). The values refer to the conversion of **13** and yield of **15** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

C.1.5 Tuning of the final photocatalyst scaffold

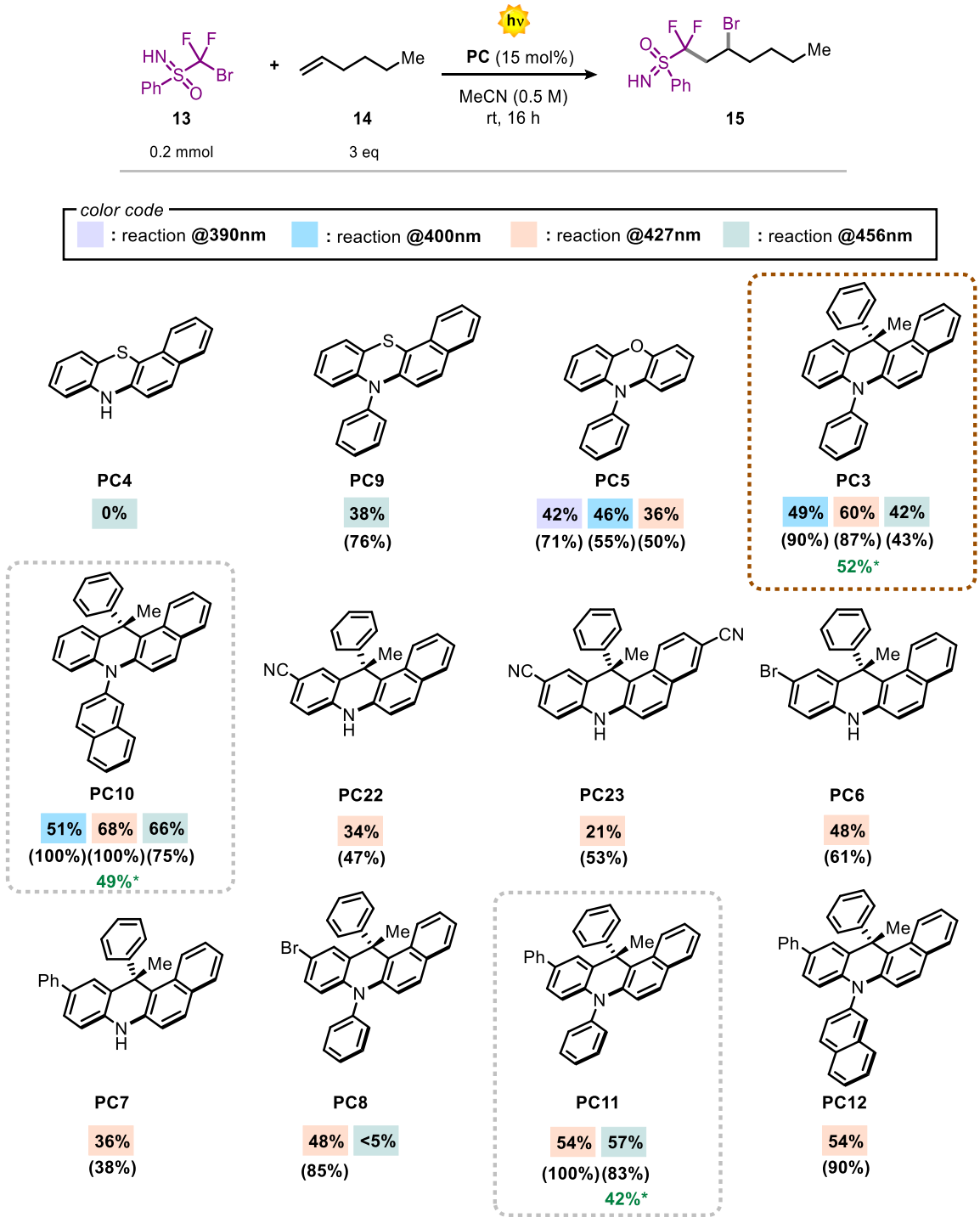
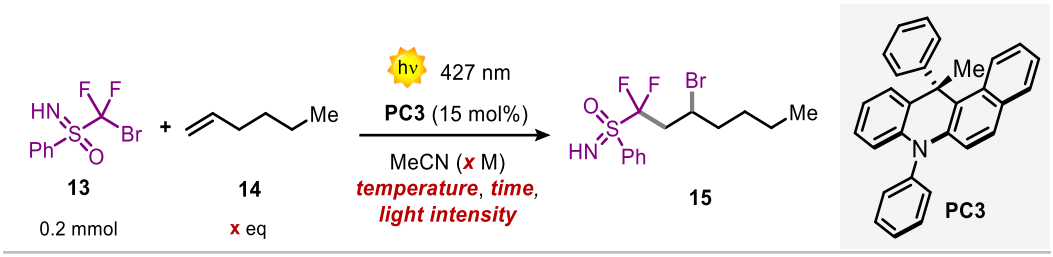


Table S7. Screening of organic photoredox catalysts. The values in colored squares refer to the yield of **15** and were determined by ^{1}H-NMR analysis of the crude reaction mixture. The values in parenthesis refer to the conversion of the starting material **13**. *Isolated yield.

C.1.6. Evaluation of concentration, reaction time, light intensity and temperature

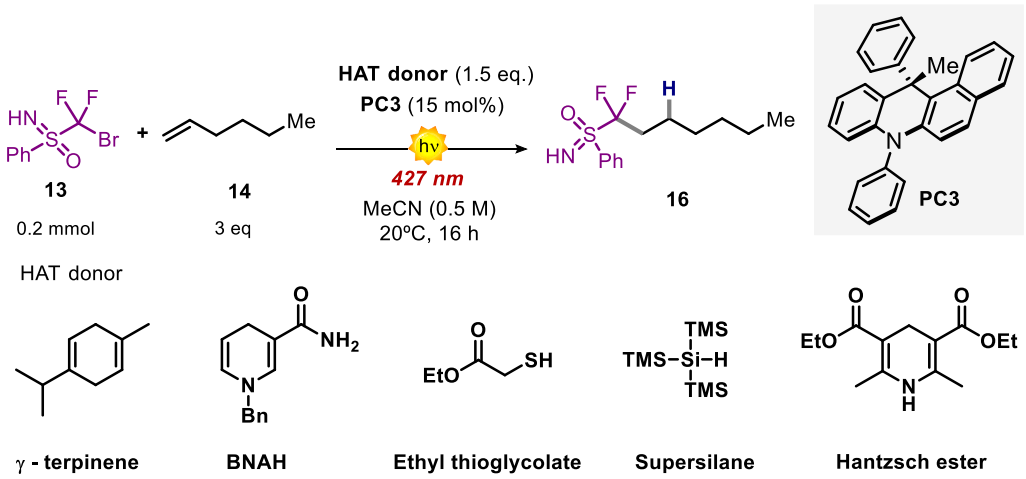


Entry	Concentration (M)	Temperature (°C)	Time (h)	% Kessil Light Intensity	Eq. 13 : 14	Conversion (%)	Yield (%)
1	0.4	rt	16	25	1 : 3	82	48
2	0.6	rt	16	25	1 : 3	85	45
3	0.5	rt	16	25	1 : 3	87	60
4	0.5	rt	16	50	1 : 3	100	49
5	0.5	rt	16	75	1 : 3	100	41
6	0.5	rt	16	100	1 : 3	100	36
7	0.5	rt	16	25	1 : 5	90	54
8	0.5	rt	16	25	1 : 2	80	49
9	0.5	rt	16	25	2 : 1	100	62
10	0.5	rt	8	25	1 : 3	81	62
11	0.5	rt	10	25	1 : 3	85	60
12	0.5	rt	24	25	1 : 3	100	54
13	0.5	10°C	10	25	1 : 3	86	57
14	0.5	20°C	10	25	1 : 3	88	59
15	0.5	50°C	16	25	1 : 3	100	30

Table S8. Evaluation of concentration, reaction time, light intensity and temperature. The values refer to the conversion of **13** and yield of **15** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

C.2. HYDROFUNCTIONALIZATION REACTION

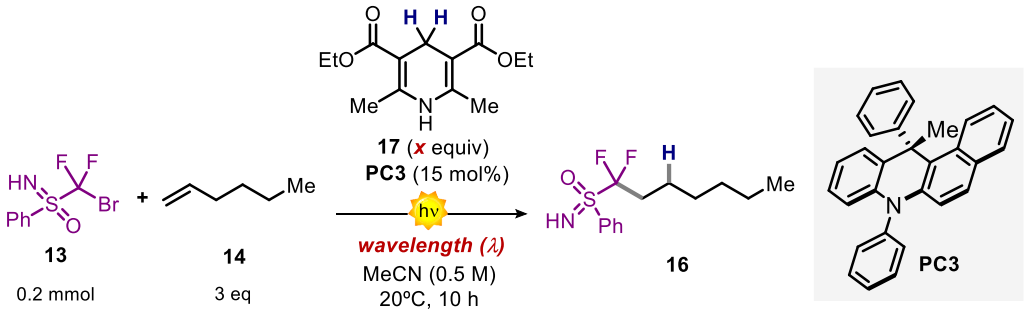
C.2.1 HAT donor screening



Entry	HAT donor	Conversion (%)	ATRA product 15 Yield (%)	Yield of 16 (%)	Isolated Yield of 16 (%)
1	γ-terpinene	90	12	40	-
2	BNAH	92	13	41	-
3	Ethyl thioglycolate	82	48	-	-
4	Supersilane	80	16	30	-
5	Hantzsch ester	100	5	51	47

Table S9. HAT donor screening for the hydrofunctionalization reaction. The values refer to the conversion of **13** and yield of **16** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

C.2.2 Reaction optimization with Hantzsch ester



Entry	PC3 loading (mol %)	Eq. of 17	λ (nm)	Conversion (%)	ATRA product 15 Yield (%)	Yield of 16 (%)	Isolated Yield of 16 (%)
1	5	1.5	427	100	5	49	43
2	15	1.5	427	100	6	50	46
3	none	1.5	427	100	<5	55	50
4	none	1	427	100	<5	48	-
5	none	2	427	100	<5	46	-
6	none	1.5	390	100	-	54	51
7	none	1.5	400	100	-	66	61

Table S10. Optimization of the hydrofunctionalization reaction with Hantzsch ester. The values refer to the conversion of **13** and yield of **16** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard.

C.3. REACTION BYPRODUCTS

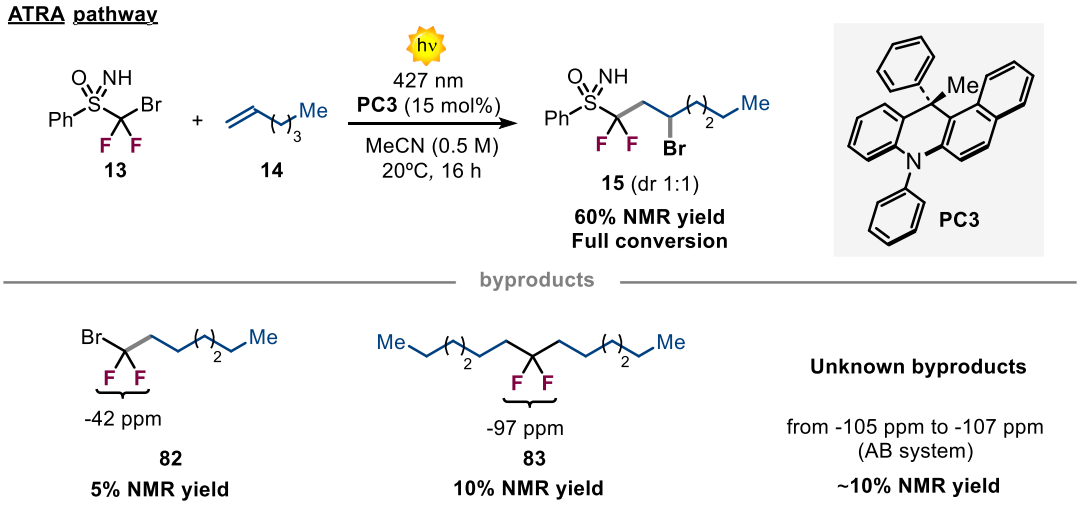


Figure S13. Analysis and quantification of reaction byproducts for the ATRA pathway. Yields are determined by ^{19}F-NMR analysis of the crude reaction mixture, using (chlorodifluoromethyl)benzene as internal standard.

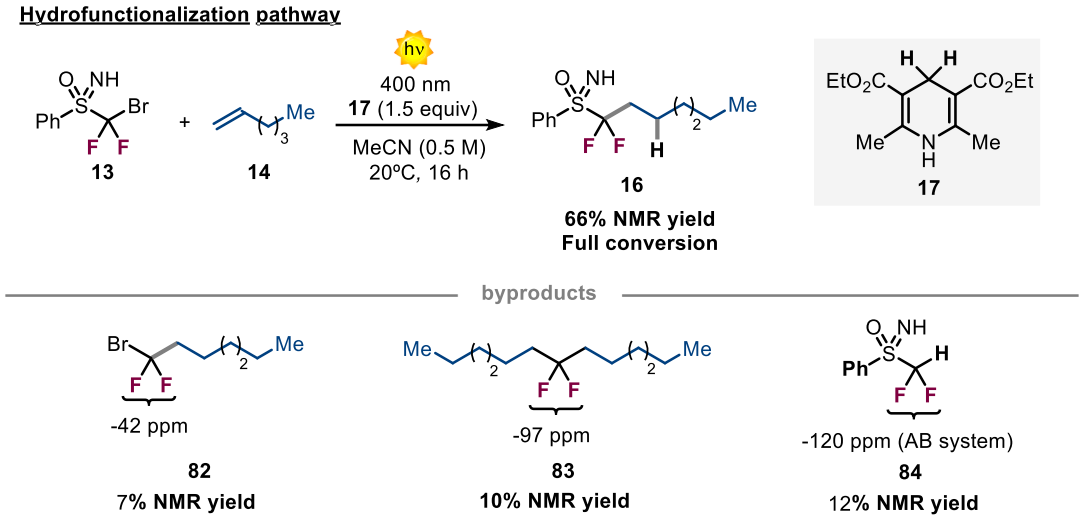


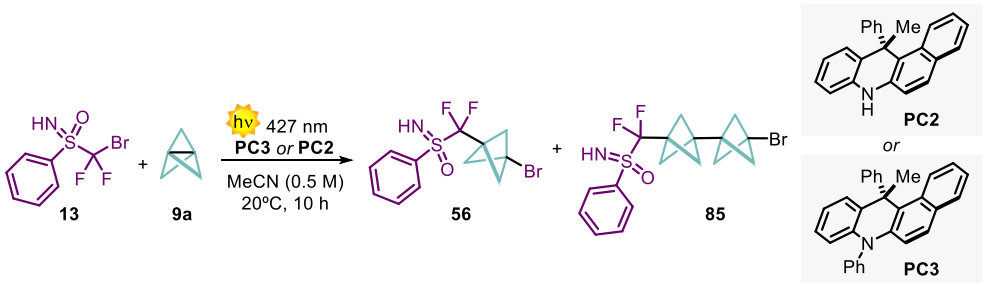
Figure S14. Analysis and quantification of reaction byproducts for the hydrofunctionalization pathway. Yields are determined by ^{19}F-NMR analysis of the crude reaction mixture, using (chlorodifluoromethyl)benzene as internal standard.

Some byproducts are found in both the ATRA and the hydrofunctionalization reactivity. The byproduct **82** results from the Giese addition of the •CF_2Br radical, generated in the competitive C-S bond cleavage of sulfoximine **13**. Subsequent reduction of the C-Br bond in **82** and second Giese addition process may lead to the formation of the byproduct **83**. The ppm values agree with what is found in the literature.[30a,b] In the ATRA reaction crude, AB system signals are also found in the range of -105 to -107 ppm. The nature of these byproducts is not certain, but it is speculated that they may consist of products from radical-radical coupling processes of some reaction intermediate species. In fact, considering the low quantum yield value for the ATRA process (ϕ =0.02) as an indication of an inefficient chain propagation mechanism, it can be hypothesized how the slow process of XAT leads to an accumulation in the reaction environment of radical intermediate species which may react with each other in homocoupling processes. This hypothesis is supported by the absence of these signals in the reaction crude of the hydrofunctionalization pathway, in which the XAT process is replaced by a faster HAT process that does not allow the accumulation of these radical intermediates.

In the case of the hydrofunctionalization reaction, it is observed the formation of the byproduct **84** resulting from debromination of substrate **13**. The signals in the reaction crude of byproduct **84** are in agreement with the values reported in the literature.[30c]

C.4. STRAIN RELEASE ATRA REACTION

Based on our previous optimal conditions for similar ATRA strain release processes,[4] we evaluated the feasibility of using **PC2** with a lower catalyst loading (Table S11).



entry	PC	PC loading (mol%)	yield 67 (%)	staffane 93 (%)
1	**PC3**	15	50	23
2	**PC3**	5	60	25
3	**PC2**	5	74 (71)	20

Table S11. Optimization of the strain-released ATRA reaction. The values refer to the yield of **56** and were determined by ^{1}H-NMR analysis of the crude reaction mixture with trichloroethylene as internal standard. The values in parenthesis refer to the isolated yield of **56**.

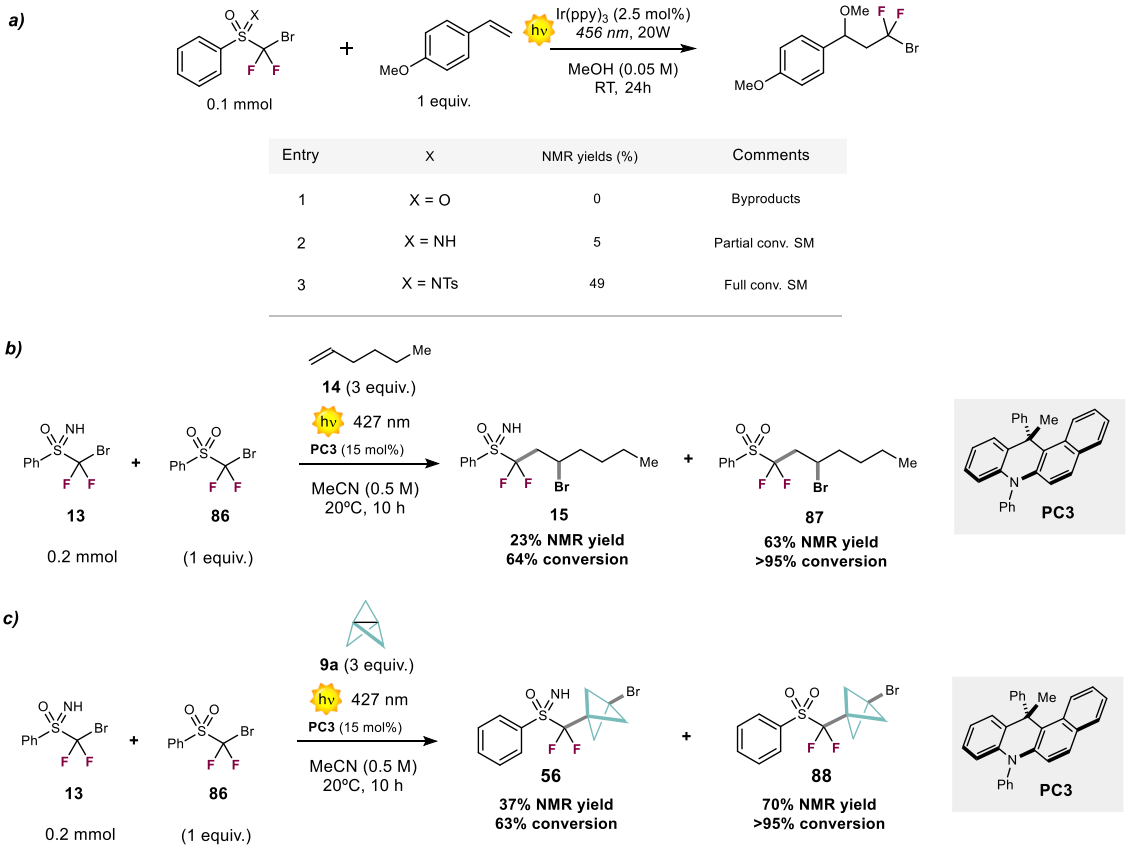
D. SULFOXIMINES VS SULFONES: REACTIVITY COMPARISON

In order to evaluate the different reactivity of sulfoximines vs. sulfones in the ATRA reaction with alkenes[31], two types of reaction were carried out: i) a methoxy bromodifluoromethylation of 4-methoxystyrene, ii) competitive ATRA functionalization of an alkene (Figure S15).

The methoxy bromodifluoromethylation under classical conditions[29b] showed a clear cut difference between the three reagents: sulfone, NH sulfoximine and the NTs sulfoximine (Figure S15 a). As already described in our earlier work[29b] the NTs sulfoximine is a good candidate for this transformation, whereas its NH analogue delivered very poor yield. The sulfone only conducted to degradation and unknown compounds. This is in accordance with the literature were, to the best of our knowledge, no fluorinated sulfone was described as a source of fluoroalkyl radical. It seems that the sulfones are limited to the formation of a sulfone difluoromethyl radical as showed in our previous work [4] This result highlight the Janus reactivity of a sulfoximine.

In a second set of experiments, an equimolar mixture of substrates **13** and **86** was tested with alkene **14** or propellane **9a** under the optimal reaction conditions (Figure S15 b and c). These experiments show that the reactivity of sulfoximines towards ATRA processes is much more challenging compared to the more reactive sulfone analogue. In particular, the reactions in presence of the single sulfone did not show the presence of any byproducts, indicating that the generation of the parasitic S-centered radical coming form the C-S reductive bond cleavage is virtually not present in this case. These findings highlight that that a seemingly minor structural

variation (O atom *vs* NH atom) of the starting reagent results in major physicochemical alteration, finally resulting in diverse and competitive reaction manifolds.

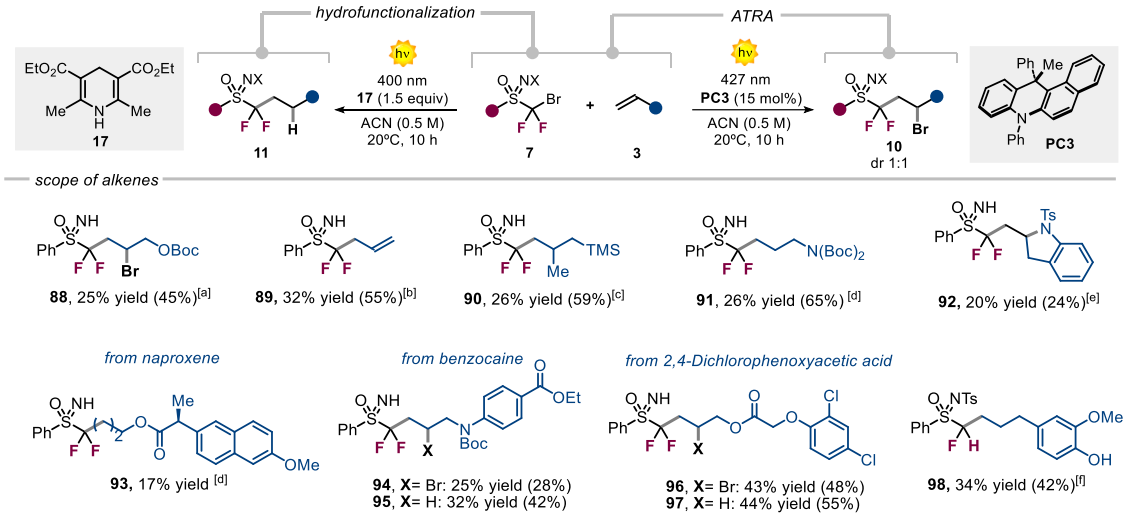


Entry	X	NMR yields (%)	Comments
1	X = O	0	Byproducts
2	X = NH	5	Partial conv. SM
3	X = NTs	49	Full conv. SM

Figure S15. Comparison of the reactivity of sulfoximine **13** and sulfone **86** in the methoxy bromodifluoromethylation of 4-methoxystyrene and in the ATRA reaction with alkene **14** and propellane **9a**. Yields and conversions are determined by ^{19}F-NMR analysis of the crude reaction mixture, using (chlorodifluoromethyl)benzene as internal standard.

E. ADDITIONAL SCOPE ENTRIES

E.1 SCOPE OF ALKENES



[a] From Boc protected allyl alcohol in the ATRA conditions.
[b] From allyl-TMS in the ATRA conditions.
[c] From methyl-substituted allyl-TMS in the hydrofunctionalization conditions.
[d] From the corresponding alkene in the hydrofunctionalization conditions.
[e] From 2-allylaniline in the ATRA conditions.
[f] From monofluorinated starting material **7k** in the hydrofunctionalization conditions.

Table S12. Scope of alkenes **3** in the light-promoted ATRA and hydrofunctionalization reactions. Reactions performed on 0.2 mmol scale. Yields refer to the isolated compounds. Values in parenthesis refer to NMR-yields. If not otherwise noted dr = 1:1.

E.2. UNSUCCESFUL SUBSTRATES

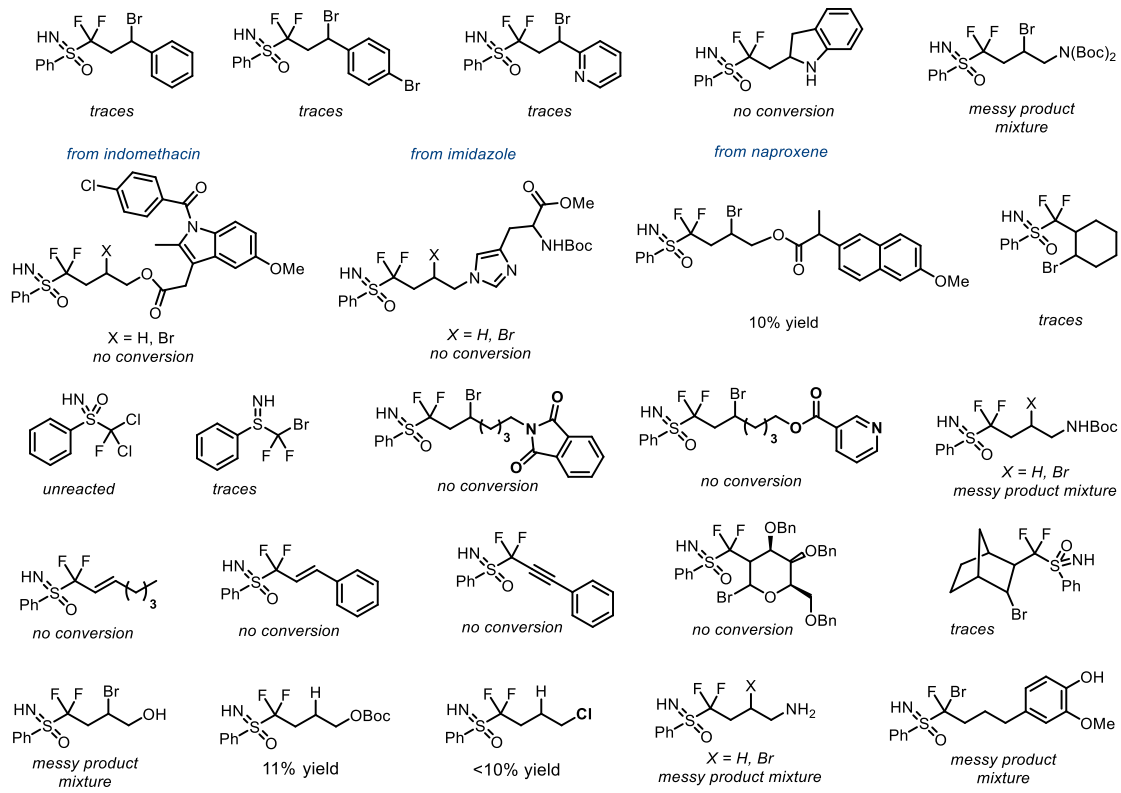
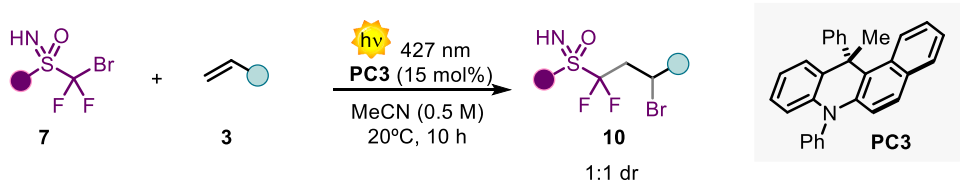


Figure S16. Unsuccessful substrates for the photochemical reaction with sulfoximine **13**.

F. GENERAL PROCEDURE FOR THE SYNTHESIS OF (DIFLUORO)ALKYL SULFOXIMINES

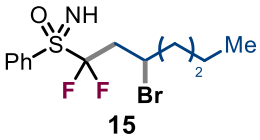
F.1. ATRA REACTION WITH ALKENES



A glass reactor (depicted in Figure S2**Figure S1**-*right*) was charged with the photocatalyst **PC3** (0.15 equiv.), the bromodifluoromethyl sulfoximine **7** (1 equiv.), the alkene **3** (if solid, 3 equiv.) and degassed acetonitrile (0.5 M). The glass reactor was closed with a septum, and the solution was degassed with nitrogen (N_2) for 1 minute. *Note: In the cases in which the alkene **3** was a liquid, the substrate was added after the addition of the solvent and degassing the solution.* Then, the vial was sealed with parafilm, and the reaction mixture was stirred for 10 h under the irradiation of a Kessil Lamp PR160L (427 nm, 45W, 25% intensity), unless otherwise stated (see set-up in Figure S2-*left*). After the irradiation period, the solvent was removed under reduced pressure and the crude product was directly purified by flash column chromatography on silica gel (hexane:EtOAc) to afford the sulfoximine products **10** in the stated yield.

Characterization data

(3-bromo-1,1-difluoroheptyl)(imino)(phenyl)-λ^6-sulfanone (15)

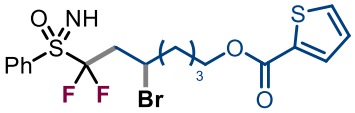


Compound **15** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), PC3 (11.9 mg, 0.03 mmol, 0.15 equiv.) and 1-hexene **14** (75 µL, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **15** as a yellowish oil (52% yield, 36.8 mg, 0.1 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 4H), 7.76 – 7.70 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 4.30 – 4.22 (m, 2H), 3.16 – 2.63 (m, 6H), 2.02 – 1.71 (m, 4H), 1.57 – 1.21 (m, 8H), 0.90 (td, *J* = 7.2, 3.0 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 134,8, 133.6 (2 dia), 130.8 (2 dia), 129.4, 129,3, 123.6 (t, *J* = 289 Hz, 2 dia), 45.8 (t, *J* = 2 Hz), 45.7 (t, *J* = 2 Hz), 39.2 (t, *J* = 19 Hz), 39.0 (t, *J* = 19 Hz), 38.9, 38.8, 29.3 (2 dia), 22.0 (2 dia), 14.0 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -102.0 and -103.7 ppm (AB system J_{AB} = 222 Hz, 2F); -

102.5 and -103.2 ppm (AB system, J_{AB} = 222 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{13}H_{19}BrF_2NOS^+$]: 354.0333 ($M+H^+$); found: 354.0336.

5-bromo-7,7-difluoro-6-(phenylsulfonimidoyl)heptyl thiophene-3-carboxylate (19)

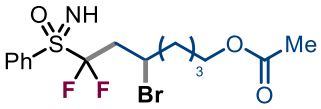


19

Compound **19** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and hex-5-en-1-yl thiophene-3-carboxylate **3a** (126 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **19** as a yellowish oil (49% yield, 47.2 mg, 0.098 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.09 (m, 2H), 8.05 (d, *J* = 7.4 Hz, 4H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.7 Hz, 4H), 7.52 (dt, *J* = 5.1, 1.2 Hz, 2H), 7.30 (dd, *J* = 5.1, 3.0 Hz, 2H), 4.33 – 4.25 (m, 6H), 3.17 – 2.69 (m, 6H), 2.04 – 1.84 (m, 4H), 1.83 – 1.65 (m, 5H), 1.65 – 1.52 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9 (2 dia), 134.9 (2 dia), 133.8 (2 dia), 133.6 (2 dia), 132.8 (2 dia), 130.8 (2 dia), 129.4 (2 dia), 128.0 (2 dia), 126.1 (2 dia), 123.5 (t, *J* = 290 Hz, 2dia), 64.3 (2 dia), 45.4 (t, *J* = 2.2 Hz), 45.3 (t, *J* = 2.3 Hz), 39.2 (t, *J* = 19.5 Hz), 39.1 (t, *J* = 19.5 Hz), 38.6, 38.5, 28.0 (2 dia), 23.9 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.8 and -103.7 (AB system, J_{AB} = 222.0 Hz, 2F), -102.4 and -103.0 (AB system, J_{AB} = 225.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{18}H_{21}BrF_2NO_3S_2^+$]: 480.0109 ($M+H^+$); found: 480.0153.

5-bromo-7,7-difluoro-7-(phenylsulfonimidoyl)heptyl acetate (21)



21

Compound **21** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and compound hex-5-en-1-yl acetate **3b** (85 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **21** as a yellowish oil (52% yield, 42.3 mg, 0.104 mmol).

Note: compound **21** was also synthesized in a higher scale following the general procedure **D.1.**, using (bromodifluoromethyl)phenylsulfoximine **13** (216 mg, 0.8 mmol, 1 equiv.), **PC3** (47.7 mg, 0.12 mmol, 0.15 equiv.) and hex-5-en-1-yl acetate **3b** (340 mg, 2.4 mmol, 3 equiv.), in the same

glass reactor (depicted in Figure S2**Figure S*1*-*right***) used for the 0.2 mmol scale reaction. Reaction time: 10 h. Yield = 48% (160 mg, 0.388 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 4H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.9 Hz, 4H), 4.31 – 4.23 (m, 2H), 4.07 – 4.03 (m, 4H), 3.21 – 2.73 (m, 4H), 2.62 (s, 2H), 2.04 (s, 6H), 2.01 – 1.77 (m, 4H), 1.69 – 1.56 (m, 6H), 1.55 – 1.44 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 171.2 (2 dia), 134.9, 134.8, 133.6 (2 dia), 130.8 (2 dia), 129.4, 129.4, 123.5 (t, *J* = 291 Hz, 2 dia), 64.1 (2 dia), 45.4 (t, *J* = 2 Hz), 45.3 (t, *J* = 2 Hz), 39.4 – 38.9 (m, 2 dia), 38.6, 38.5, 27.8 (2 dia), 23.9 (2 dia), 21.1 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.9 and -103.6 (AB system, J_{AB} = 222.0 Hz, 2F), -102.7 and -102.9 (AB system, J_{AB} = 222.5 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{15}H_{20}BrF_2NO_3SNa^+$]: 434.0208 (M+$Na^+$); found: 434.0230.

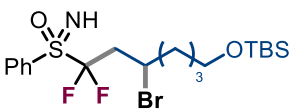
(3-bromo-1,1-difluoro-7-(octyloxy)heptyl)(imino)(phenyl)-λ^6-sulfanone (23)

23

Compound **23** was synthesized according to the general procedure D.1. using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and 1-(hex-5-en-1-yloxy)octane **3c** (127 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **23** as a yellowish oil (24% yield, 23.4 mg, 0.048 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 4H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 4H), 4.30 – 4.23 (m, 2H), 3.40 – 3.36 (m, 8H), 3.25 (s, 2H), 3.12 – 2.71 (m, 4H), 2.07 – 1.77 (m, 4H), 1.67 – 1.47 (m, 12H), 1.40 – 1.18 (m, 22H), 0.87 (t, *J* = 6.7 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 134.8, 130.8 (2 dia), 129.4, 129.3, 123.6 (t, *J* = 290 Hz, 2 dia), 71.2 (2 dia), 70.5 (2 dia), 45.6 (t, *J* = 2.2 Hz), 45.5 (t, *J* = 2.3 Hz), 39.4 – 39.1 (m, 2 dia), 39.0, 38.9, 32.0 (2 dia), 29.9 (2 dia), 29.6 (2 dia), 29.4 (2 dia), 29.0 (2 dia), 26.3 (2 dia), 24.2 (2 dia), 22.8(2 dia), 14.2 (2 dia). **^{19}F NMR decoupled 1H (377 MHz, $CDCl_3$)** δ -102.0 and -103.7 (AB system, J_{AB} = 222.0 Hz, 2F), -102.4 and -103.4 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{21}H_{35}BrF_2NO_2S^+$]: 482.1534 (M+H^+); found: 482.1569.

(3-bromo-6-((tert-butyldimethylsilyl)oxy)-1,1-difluoroheptyl)(imino)(phenyl)-λ^6-sulfanone (25)

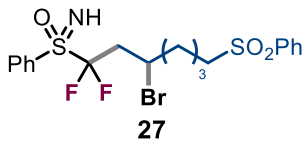


25

Compound **25** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and tert-butyl(hex-5-en-1-yloxy)dimethylsilane **3d** (129 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **25** as a yellowish oil (18% yield, 17.5 mg, 0.036 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 4H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 4H), 4.30 – 4.22 (m, 2H), 3.62 – 3.58 (m, 4H), 3.23 (s, 2H), 3.14 – 2.71 (m, 4H), 1.95 – 1.80 (m, 4H), 1.65 – 1.53 (m, 4H), 1.53 – 1.43 (m, 4H), 0.89 (d, *J* = 1.5 Hz, 18H), 0.04 (d, *J* = 1.8 Hz, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 134.8, 133.6, 133.5, 130.8 (2 dia), 129.4, 129.3, 123.6 (t, *J* = 290.3 Hz, 2 dia), 62.8 (2 dia), 45.7 (t, *J* = 2.2 Hz), 45.6 (t, *J* = 2.3 Hz), 39.3 (t, *J* = 19.3 Hz), 39.5 – 39.1 (m, 2 dia), 39.0, 38.9, 32.0 (2 dia), 29.8 (2 dia), 26.1 (2 dia), 23.8 (2 dia), 18.5 (2 dia), -5.2 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -102.0 and -103.7 (AB system, J_{AB} = 223.0 Hz, 2F), -102.6 and -103.2 (AB system, J_{AB} = 223.5 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{19}H_{33}BrF_2NO_2SSi^+$]: 484.1147 (M+H$^+$); found: 482.1182.

(3-bromo-1,1-difluoro-7-(phenylsulfonyl)heptyl)(imino)(phenyl)-λ^6-sulfanone (27)

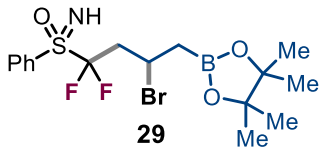


27

Compound **27** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and (hex-5-en-1-ylsulfonyl)benzene **3e** (134 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **27** as a yellowish oil (33% yield, 32.6 mg, 0.066 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.89 (d, *J* = 7.2 Hz, 4H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.67 – 7.55 (m, 12H), 4.25 – 4.18 (m, 2H), 3.24 – 3.03 (m, 4H), 3.03 – 2.62 (m, 4H), 1.93 – 1.83 (m, 2H), 1.82 – 1.57 (m, 8H), 1.56 – 1.48 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.1 (2 dia), 134.9 (2 dia), 133.9 (2 dia), 133.6 (2 dia), 130.8 (2 dia), 129.5 (2 dia), 129.4 (2 dia), 128.1 (2 dia), 123.4 (t, *J* = 290 Hz, 2 dia), 56.0 (2 dia), 44.9 (t, *J* = 2.4 Hz), 44.8 (t, *J* = 2.3 Hz), 39.3 – 38.5 (m, 2 dia), 38.3, 38.2, 26.0 (2 dia), 22.0 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.7 and -103.5 (AB system, J_{AB} = 222.0 Hz, 2F), -102.5 and -102.7 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{19}H_{23}BrF_2NO_3S_2^+$]: 494.0265 (M+H$^+$); found: 494.0307.

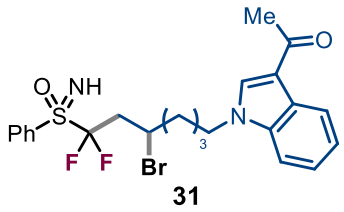
(3-bromo-1,1-difluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)(imino)(phenyl)-λ^6-sulfanone (29)



29

Compound **30** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and compound allylboronic acid pinacol ester **S21** (112 μL, 0.6 mmol, 3 equiv.) Reaction time: 10 h. NMR yield: 50%, 1:1 mixture of diastereoisomers. Due to the instability of product **29** in silica, it could not be isolated by flash chromatography.

(7-(3-acetyl-1H-indol-1-yl)-3-bromo-1,1-difluoroheptyl)(imino)(phenyl)-λ^6-sulfanone (31)

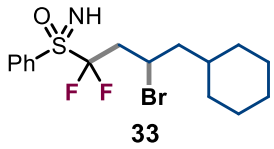


31

Compound **32** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and 1-(1-(hex-5-en-1-yl)-1H-indol-3-yl)ethan-1-one **3f** (145 mg, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **31** as a brownish oil (32% yield, 33.1 mg, 0.064 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 – 8.34 (m, 2H), 8.03 (d, *J* = 7.8 Hz, 4H), 7.75 – 7.68 (m, 4H), 7.59 (t, *J* = 7.7 Hz, 4H), 7.35 – 7.28 (m, 6H), 4.29 – 4.23 (m, 2H), 4.16 (t, *J* = 6.1 Hz, 4H), 3.21 – 2.73 (m, 4H), 2.52 (s, 6H), 1.99 – 1.77 (m, 8H), 1.69 -1.58 (m, 2H), 1.54 – 1.47 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.1 (2 dia), 136.8 (2 dia), 135.1, 135.0, 134.8 (2 dia), 133.6 (2 dia), 130.8 (2 dia), 129.4 (2 dia), 126.5 (2 dia), 123.4 (t, *J* = 290.0 Hz, 2 dia), 122.9 (2 dia), 122.7 (2 dia), 117.2 (2 dia), 109.8 (2 dia), 46.9 (2 dia), 45.2 (t, *J* = 2.3 Hz), 45.1 (t, *J* = 2.6 Hz), 39.5 – 38.9 (m, 2 dia), 38.4, 38.2, 29.0 (2 dia), 27.8 (2 dia), 24.7 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.7 and -103.3 (AB system, J_{AB} = 223.0 Hz, 2F), -102.2 and -102.6, (AB system, J_{AB} = 223.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{23}H_{26}BrF_2N_2O_2S^+$]: 511.0861 ($M+H^+$); found: 511.0911.

(3-bromo-4-cyclohexyl-1,1-difluorobutyl)(imino)(phenyl)-λ^6-sulfanone (33)

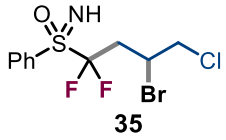


33

Compound **33** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and compound allylcyclohexane **S22** (93 µL, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **33** as a yellowish oil (40% yield, 31.3 mg, 0.08 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 4H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 4.35 – 4.27 (m, 2H), 3.25 (s, 2H), 3.12 – 2.72 (m, 4H), 1.83 – 1.47 (m, 20H), 1.22 – 1.03 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.9, 134.8, 133.6 (2 dia), 130.8 (2 dia), 129.5, 129.4, 123.6 (t, *J* = 290.1 Hz, 2 dia), 47.0, 46.9, 43.5 (t, *J* = 2.3 Hz), 43.4 (t, *J* = 2.3 Hz), 40.1 – 39.5 (m, 2 dia), 35.8 (2 dia), 33.7, 33.6, 31.6, 31.5, 26.5, 26.2, 25.9. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.5 and -103.5 (AB system, J_{AB} = 223.0 Hz, 2F), -102.3 and -102.8, (AB system, J_{AB} = 222.5 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{16}H_{23}BrF_2NOS^+$]: 394.0646 ($M+H^+$); found: 394.0687.

(3-bromo-4-chloro-1,1-difluorobutyl)(imino)(phenyl)- λ^6-sulfanone (35)

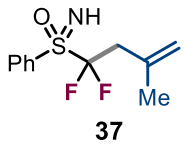


35

Compound **35** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and allyl chloride **S23** (49 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **35** as a yellowish oil (43% yield, 30.0 mg, 0.087 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.8 Hz, 4H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 4H), 4.48 – 4.41 (m, 2H), 3.97 – 3.92 (m, 2H), 3.81 – 3.76 (m, 2H), 3.41 – 3.12 (m, 4H), 2.98 – 2.68 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.0 (2 dia), 133.6, 133.5, 130.8 (2 dia), 129.4 (2 dia), 123.2 (t, *J* = 290.0 Hz, 2 dia), 48.5 (2 dia), 41.6 (t, *J* = 2.6 Hz), 41.4 (t, *J* = 2.6 Hz), 36.6 – 36.1 (m, 2 dia). **^{19}F NMR decoupled ^{1}H** (377 MHz, CDCl3) δ -101.7 and 104.3 (AB systems, J_{AB} = 224.0 Hz, 2F), -102.6 and -103.2 (AB systems, J_{AB} = 224.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{10}H_{12}BrClF_2NOS^+$]: 345.9474 ($M+H^+$); found: 345.9490

(1,1-difluoro-3-methylbut-3-en-1-yl)(imino)(phenyl)- λ⁶-sulfanone (37)

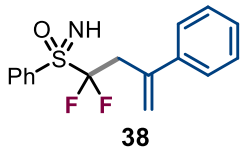


37

Compound **37** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and methallyltrimethylsilane **S25** (105 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **37** as a yellowish oil (50% yield, 24.5 mg, 0.10 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 4.70 (d, *J* = 34.8 Hz, 2H), 2.88 (s, 1H), 2.84 – 2.51 (m, 2H), 1.52 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.22, 134.61, 133.81, 130.80, 129.22, 124.06 (t, *J* = 289.6 Hz), 37.91 (t, *J* = 20.4 Hz), 23.32. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.1 and -103.4 (AB systems, J_{AB} = 220.4 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{11}H_{14}F_2NOS^+$]: 246.0759 ($M+H^+$); found: 246.0830.

(1,1-difluoro-3-phenylbut-3-en-1-yl)(imino)(phenyl)-λ⁶-sulfanone (38)

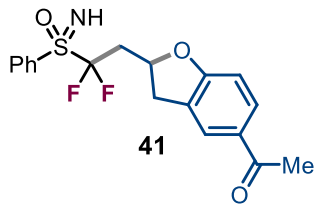


38

Compound **38** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and trimethyl(2-phenylallyl)silane **S26** (129 µL, 0.6 mmol, 3 equiv.) Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 75:25 hexane/EtOAc) to afford compound **38** as a yellowish oil (55% yield, 34.0 mg, 0.11 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.51 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.27 (m, 5H), 5.48 (d, *J* = 99.0 Hz, 2H), 3.69 – 3.27 (m, 2H), 2.93 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.13, 137.77, 134.64, 133.85, 130.82, 129.24, 128.55, 128.09, 126.20, 123.73 (t, *J* = 289.5 Hz), 120.15, 35.35 (t, *J* = 20.4 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.2 and -103.0 (AB systems, J_{AB} = 220.5 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{16}H_{16}F_2NOS^+$]: 308.0915 ($M+H^+$); found: 308.0915.

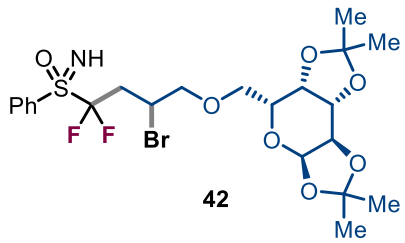
(2-(5-acetyl-2,3-dihydrobenzofuran-2-yl)-1,1-difluoroethyl)(imino)(phenyl)-λ⁶-sulfanone (41)



Compound **41** was synthesized according to the general procedure **D.1.** with modifications**:** a glass reactor (depicted in Figure S2-right) was charged with the photocatalyst **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.), (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), 4-acetyl-2-allylphenyl acetate **3o** (131 mg, 0.6 mmol, 3 equiv.) and degassed acetonitrile (0.5 M). The glass reactor was closed with a septum, and the solution was degassed with argon (Ar) for 1 minute. Then, the vial was sealed with parafilm, and the reaction mixture was stirred for 10 h under the irradiation of a Kessil Lamp PR160L (427 nm, 40W, 25% intensity). After the irradiation period, 1 mL of an aqueous solution of NaOH 2M was added and the solution stirred for further 6h. Subsequently the basic solution was neutralized until pH 7 with an aqueous solution of HCl 2M, extracted with EtOAC (3x 10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 1:1 hexane/EtOAc) to afford compound **41** as a yellowish oil (41% yield, 30.0 mg, 0.08 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 – 8.03 (m, 4H), 7.90 – 7.78 (m, 4H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.9 Hz, 4H), 6.80 (dd, *J* = 17.9, 8.3 Hz, 2H), 5.27 – 5.22 (m, 2H), 3.49 – 3.45 (m, 2H), 3.43 (s, 2H), 3.08 – 2.90 (m, 4H), 2.86 – 2.67 (m, 2H), 2.54 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.7 (2 dia), 163.0, 162.9, 135.0, 134.9, 133.6, 133.5, 131.4, 131.3, 130.9, 130.85, 130.8, 130.7, 129.5, 129.4, 126.7, 126.6, 125.7, 125.6, 123.6 (t, *J* = 289.7 Hz, 2 dia), 109.5, 109.4, 78.1 – 78.0 (m), 77.9 – 77.8 (m), 36.7 – 36.2 (m, 2 dia), 35.6, 35.5, 26.6, 26.5. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.3 and -102.3 (AB systems, J_{AB} = 225.0 Hz, 2F), -101.2 and -103.4 (AB systems, J_{AB} = 225.5 Hz, 2F). **HRMS (ESI$^+$):** HRMS (ESI$^+$): calculated for [$C_{18}H_{18}F_2NO_3S^+$]: 366.0970 (M+H$^+$); found: 366.1082.

((S)-3-bromo-1,1-difluoro-4-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)butyl)(imino)(phenyl)-λ⁶-sulfanone (42)



42

Compound **42** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenyl-sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and (3aR,5R,5aS,8aS,8bR)-5-((allyloxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran **3l** (180 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **42** as a yellowish oil (34% yield, 38.9 mg, 0.07 mmol; 1:1.3:1.3:1.4 mixture of four diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 8H), 7.72 (t, *J* = 7.5 Hz, 4H), 7.59 (t, *J* = 7.7 Hz, 8H), 5.58 – 5.54 (m, 4H), 4.69 – 4.57 (m, 4H), 4.45 – 4.29 (m, 8H), 4.24 – 4.18 (m, 4H), 3.99 – 3.94 (m, 4H), 3.92 – 3.59 (m, 16H), 3.39 – 3.14 (m, 4H), 2.90 – 2.59 (m, 8H), 1.56 (t, *J* = 5.2 Hz, 12H), 1.44 (s, 12H), 1.34 (s, 24H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.75, 134.73, 134.68, 133.41, 133.38, 133.29, 133.15, 130.86 (4 dia), 129.30, 129.28, 129.24, 123.80 (t, *J* = 292.2 Hz, 4 dia), 109.60, 109.55, 109.54, 109.01, 108.92, 108.87, 108.85, 96.45 (2 dia), 94.42 (2 dia), 75.19, 74.99, 74.93, 71.23 - 70.13 (m, 4 dia), 67.40, 67.25, 67.20, 41.11, 41.08, 40.94, 35.85 – 35.09 (m, 4 dia), 26.21, 26.19, 26.10, 25.07, 25.05, 24.56, 24.54. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.5 and -104.4 (AB systems, J_{AB} = 223.0 Hz, 2F), -100.6 and -104.1 (AB systems, J_{AB} = 222.0 Hz, 2F), -100.7 and -103.3 (AB systems, J_{AB} = 222.0 Hz, 2F), -100.8 and -103.3 (AB systems, J_{AB} = 222.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{22}H_{31}BrF_2NO_7S^+$]: 570.0967 ($M+H^+$); found: 570.1049.

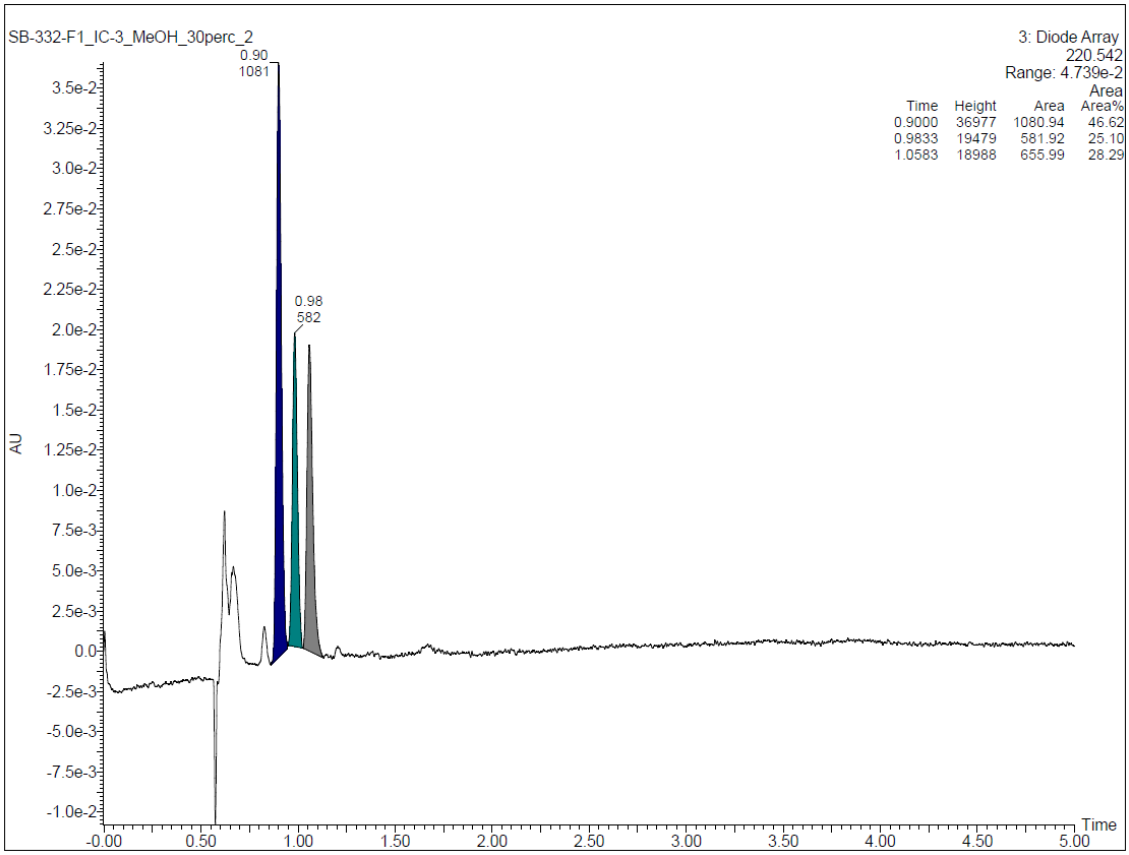
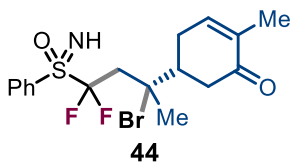


Figure S17. Chromatogram of compound **42** after isolation. UPC[2] analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 220.5 nm.

((3S)-3-bromo-1,1-difluoro-3-(4-methyl-5-oxocyclohex-3-en-1-yl)butyl)(imino)(phenyl)-λ⁶-sulfanone (44)



44

Compound **44** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and (R**)-(-)-**carvone **S27** (94 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **44** as a yellowish oil (36% yield, 30.6 mg, 0.07 mmol). Compound 54 was isolated as an inseparable mixture of four diasteroisomers in ratio 1:2:3:3.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 8H), 7.88 – 7.67 (m, 4H), 7.67 – 7.50 (m, 8H), 6.72 (s, 4H), 3.50 – 2.87 (m, 8H), 2.81 (s, 4H), 2.75 – 2.60 (m, 4H), 2.53 – 2.44 (m, 8H), 2.23 - 2.13 (m, 4H), 1.99 – 1.86 (m, 12H), 1.77 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 198.56, 198.14, 198.02, 143.71, 143.63, 143.53, 143.51, 135.49, 135.45, 135.35, 135.32, 135.04, 135.01, 134.97, 134.94, 133.29, 133.26, 133.06, 130.88, 130.85, 130.81, 129.45, 129.40, 127.86 – 120.68

(t, J = 292.3 Hz, 4 dia), 69.10, 69.08, 68.91, 45.67 – 45.62 (m, 4 dia), 41.42 – 40.77 (m, 4 dia), 30.62, 30.58, 30.45, 30.41, 29.03 (2 dia), 28.91 (2 dia), 15.65 (2 dia), 15.63 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.2 and -103.2 (AB systems, J_{AB} = 219.0 Hz, 2F), -100.3 and -103.2 (AB systems, J_{AB} = 219.0 Hz, 2F), -100.6 and -102.1 (AB systems, J_{AB} = 219.0 Hz, 2F), -101.0 and -102.1 (AB systems, J_{AB} = 219.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{21}BrF_2NO_2S^+$]: 420.0439 ($M+H^+$); found: 420.0457.

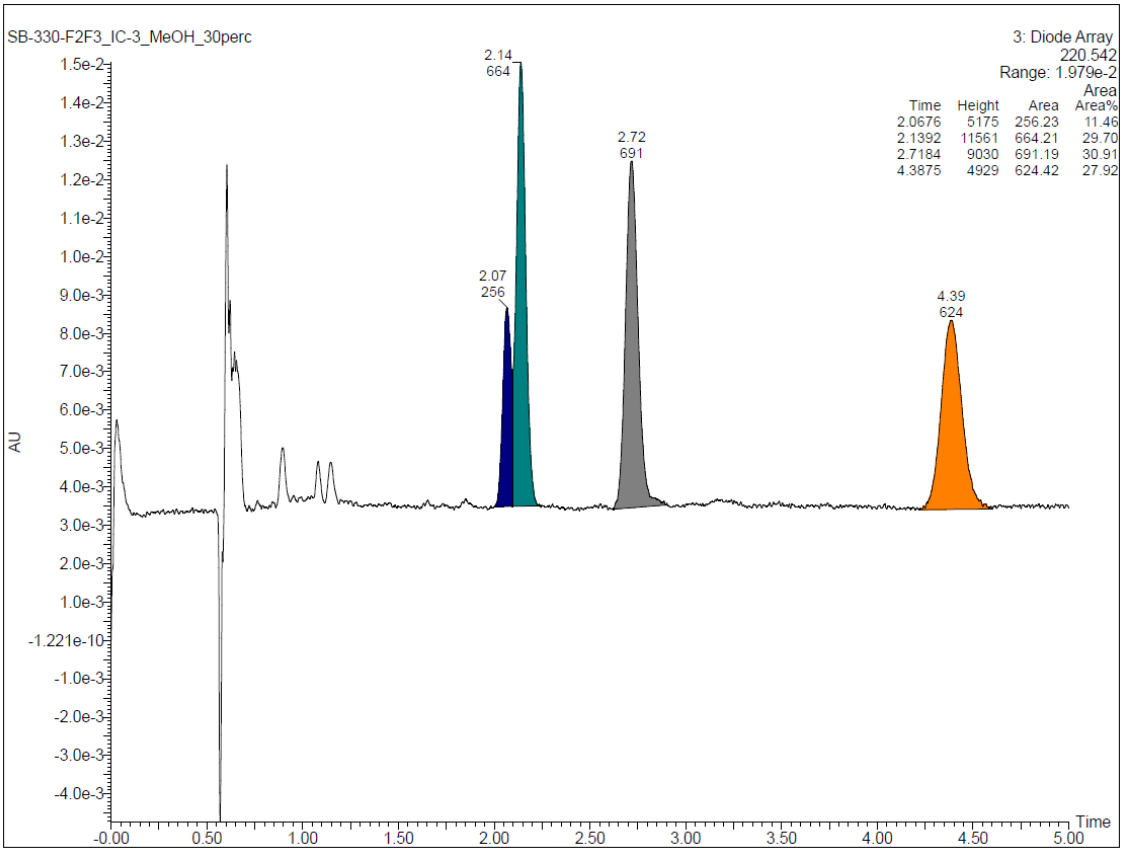
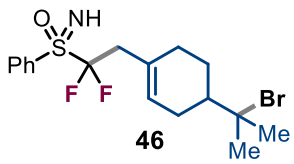


Figure S18. Chromatogram of compound **44** after isolation. UPC^2 analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 220.5 nm.

(2-(4-(2-bromopropan-2-yl)cyclohex-1-en-1-yl)-1,1-difluoroethyl)(imino)(phenyl)-λ^6-sulfanone (46)

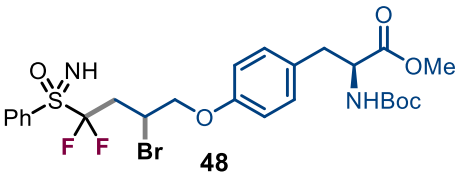


Compound **46** was synthesized according to the general procedure **D.1**. using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and β-pinene **S28** (94 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2

hexane/EtOAc) to afford compound **46** as a yellowish oil (33% yield, 26.8 mg, 0.07 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 4H), 7.71 (t, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.7 Hz, 4H), 5.74 – 5.61 (m, 2H), 3.35 – 2.74 (m, 4H), 2.70 (s, 2H), 2.54 – 1.89 (m, 10H), 1.77 (d, *J* = 1.9 Hz, 6H), 1.72 (d, *J* = 1.4 Hz, 6H), 1.64 – 1.52 (m, 2H), 1.46 – 1.28 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.6 (2 dia), 133.9, 133.8, 130.8 (2 dia), 129.2 (2 dia), 127.7, 127.6, 124.22 (t, *J* = 289.3 Hz, 2 dia), 72.5 (2 dia), 46.9, 46.8, 38.1 – 37.6 (m, 2 dia), 32.6, 32.5, 31.9 (2 dia), 30.0 (2 dia), 28.7 (2 dia), 25.9, 25.8. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -99.8 and -103.1 (AB systems, J_{AB} = 219.0 Hz, 2F), -101.2 and -102.0 (AB systems, J_{AB} = 219.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{23}BrF_2NOS^+$]: 406.0646 ($M+H^+$); found: 406.0630.

(2-(4-(2-bromopropan-2-yl)cyclohex-1-en-1-yl)-1,1-difluoroethyl)(imino)(phenyl)-λ^6-sulfanone (48)



48

Compound **48** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and methyl (S)-3-(4-(allyloxy)phenyl)-2-((tert-butoxycarbonyl)amino)propanoate **3k** (201 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 1:1 hexane/EtOAc) to afford compound **48** as a yellowish oil (28% yield, 33.5 mg, 0.06 mmol; mixture of four diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 8H), 8.05 (s, 4H), 7.73 (t, *J* = 7.5 Hz, 4H), 7.60 (t, *J* = 7.9 Hz, 8H), 7.04 – 7.01 (m, 8H), 6.88 – 6.71 (m, 8H), 4.97 (d, *J* = 8.3 Hz, 4H), 4.55 – 4.45 (m, 8H), 4.27 - 4.22 (m, 4H), 4.16 – 4.11 (m, 4H), 3.70 (s, 12H), 3.43 – 3.09 (m, 8H), 3.07 – 2.99 (m, 4H), 2.94 (s, 16H), 2.87 (s, 20H), 1.40 (s, 36H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.4 (4 dia), 162.6 (4 dia), 157.0 (4 dia), 155.2 (4 dia), 134.9 (2 dia), 134.8 (2 dia), 133.5 (2 dia), 133.4 (2 dia), 130.8 (4 dia), 130.6 (4 dia), 129.4 (2 dia), 129.3 (2 dia), 123.4 (t, *J* = 289 Hz, 4 dia), 115.0 (4 dia), 71.3 (2 dia), 71.2 (2 dia), 52.3 (4 dia), 40.2 (t, *J* = 2 Hz, 2 dia), 40.0 (t, *J* = 2.4 Hz), 36.6 (4 dia), 36.1 – 35.6 (m, 4 dia), 31.5 (4 dia), 28.4 (4 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.5 and 104.1 (AB systems, J_{AB} = 223.5 Hz, 2F), -102.7 (2F). **HRMS (ESI$^+$):** calculated for [$C_{25}H_{32}BrF_2N_2O_6S^+$]: 605.1127 ($M+H^+$); found: 605.1168.

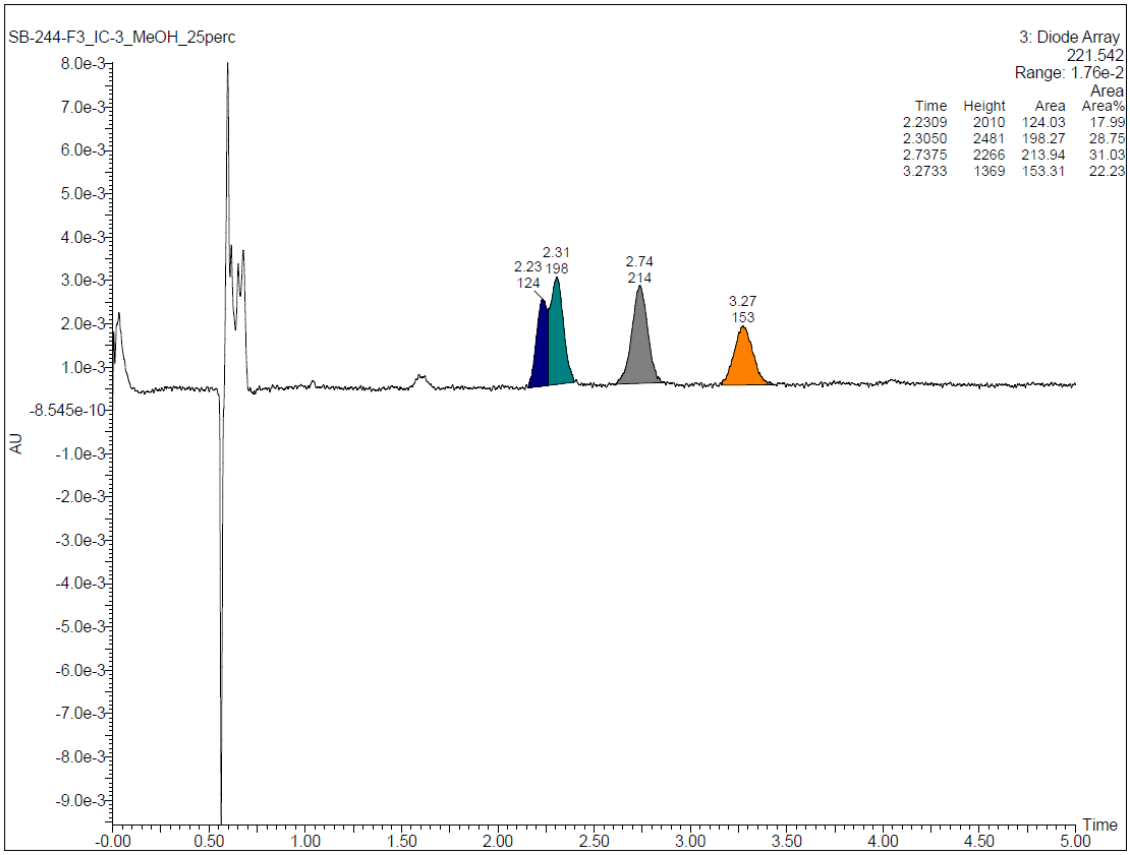
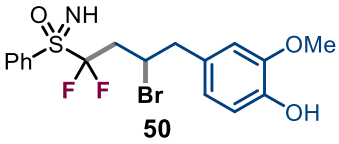


Figure S19. Chromatogram of compound **48** after isolation. UPC^2 analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 220.5 nm.

(3-bromo-1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ^6-sulfanone (50)



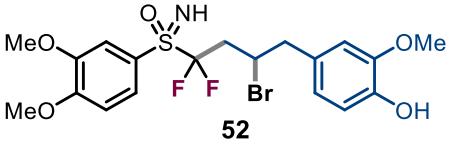
50

Compound **50** was synthesized according to the general procedure **D.1.1** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and eugenol **3ab** (92 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **50** as an orange oil (35% yield, 30.3 mg, 0.069 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 8.8 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.61 – 7.52 (m, 4H), 6.84 (dd, *J* = 10.9, 8.0 Hz, 2H), 6.72 – 6.67 (m, 2H), 6.67 – 6.60 (m, 2H), 5.62 (s, 2H), 4.49 – 4.38 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.23 – 3.06 (m, 4H), 3.05 – 2.70 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6 (2 dia), 145.0 (2 dia), 134.9, 134.8, 133.4, 133.3, 130.8, 130.7, 129.4,

129.3, 129.1, 129.0, 123.5 (t, J = 290.1 Hz, 2 dia), 122.4, 122.3, 114.5 (2 dia), 112.0, 111.9, 56.2, 56.1, 45.4 – 45.1 (m, 2 dia), 44.9 (t, J = 2.1 Hz, 2 dia), 38.4 (t, J = 19.8 Hz), 38.1 (t, J = 19.6 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.6 and -103.9 (AB systems, J_{AB} = 224.1 Hz, 2F) -102.01 and -103.22 and (AB systems, J_{AB} = 224.1 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{19}BrF_2NO_3S^+$]: 434.0232 (M+H$^+$); found: 434.0286.

(3-bromo-1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(3,4-dimethoxyphenyl) (imino)-λ^6-sulfanone (52)

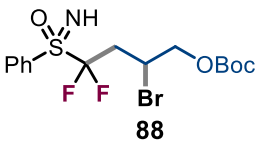


52

Compound **52** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)(3,4-dimethoxyphenyl)(imino)-λ^6-sulfanone **7g** (33 mg, 0.1 mmol, 1 equiv.), **PC3** (6 mg, 0.015 mmol, 0.15 equiv.) and eugenol **3ab** (47 μL, 0.3 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **52** as a yellowish oil (42% yield, 20.8 mg, 0.042 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, J = 15.7, 8.5, 2.2 Hz, 2H), 7.43 (dd, J = 3.7, 2.2 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.84 (t, J = 8.3 Hz, 2H), 6.73 – 6.59 (m, 4H), 5.58 (s, 2H), 4.49 – 4.36 (m, 2H), 3.97 (s, 6H), 3.93 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.26 – 3.05 (m, 5H), 3.04 – 2.70 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.7, 154.6, 149.5, 149.4, 146.6 (2 dia), 145.0 (2 dia), 129.2, 129.1, 125.2 (2 dia), 124.4, 124.3, 123.5 (t, J = 288.5 Hz, 2 dia), 122.4, 122.3, 114.5 (2 dia), 112.7, 112.6, 112.0, 111.9, 110.8 (2 dia), 56.5 (2 dia), 56.2, 56.1, 45.5 – 44.8 (m, 2 dia), 38.6 (t, J = 19.9 Hz), 38.3 (t, J = 19.8 Hz), 31.1 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.2 and -103.9 (AB systems, J_{AB} = 223.6 Hz, 2F), -102.2 and -103.3 (AB systems, J_{AB} = 223.6 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{19}H_{23}BrF_2NO_5S^+$]: 494.0443 (M+H$^+$); found: 494.0453.

2-bromo-4,4-difluoro-4-(phenylsulfonimidoyl)butyl tert-butyl carbonate (88)



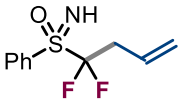
88

Compound **88** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv), and allyl tert-butyl carbonate **3g** (95 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to

afford compound **88** as a yellowish oil (25% yield, 21.1 mg, 0.05 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 4H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.8 Hz, 4H), 4.48 – 4.39 (m, 2H), 4.38 – 4.26 (m, 4H), 3.31 (s, 2H), 3.20 – 2.68 (m, 4H), 1.49 (s, 9H), 1.48 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.9, 152.8, 135.0, 134.9, 133.5, 133.4, 130.8 (2 dia), 129.5, 129.4, 123.3 (t, *J* = 285.1 Hz, 2 dia), 83.3 (2 dia), 69.3, 69.2, 39.5 (t, *J* = 2.6 Hz), 39.4 (t, *J* = 2.7 Hz), 36.1 (t, *J* = 20.1 Hz), 35.9 (t, *J* = 20.1 Hz), 27.8 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.4 and -104.2 (AB systems, J_{AB} = 224.0 Hz, 2F), -102.2 and -102.9 (AB systems, J_{AB} = 224.0 Hz, 2F). **HRMS (ESI^+):** not found.

(1,1-difluorobut-3-en-1-yl)(imino)(phenyl)- λ^6-sulfanone (89)

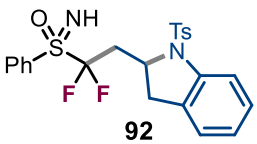


89

Compound **89** was synthesized according to the general procedure **D.1**. using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and allyltrimethylsilane **S24** (95 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **89** as a yellowish oil (32% yield, 14.8 mg, 0.06 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 5.85 – 5.74 (m, 1H), 5.47 – 5.14 (m, 2H), 3.49 – 2.78 (m, 2H), 2.65 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.69, 133.75, 130.81, 129.27, 123.69 (t, *J* = 288.4 Hz), 122.64, 35.26 (t, *J* = 21.0 Hz). **^{19}F NMR decoupled ^{1}H** (377 MHz, $CDCl_3$) δ -101.7 and -104.0 (AB systems, J_{AB} = 221.8 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{10}H_{12}F_2NOS^+$]: 232.0602 ($M+H^+$); found: 232.0643.

(1,1-difluoro-2-((S)-1-tosylindolin-2-yl)ethyl)(imino)(phenyl)-λ^6-sulfanone (92)

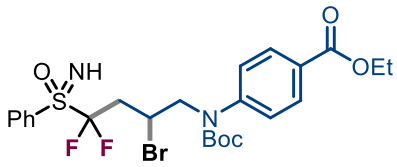


92

Compound **92** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and N-(2-allylphenyl)-4-methylbenzenesulfonamide **3i** (173 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **92** as a yellowish oil (20% yield, 19.2 mg, 0.04 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.2 Hz, 2H), 8.11 (d, *J* = 7.2 Hz, 2H), 7.73 (t, *J* = 7.5 Hz, 2H), 7.63 – 7.60 (m, 2H), 7.61 (ddd, *J* = 8.3, 7.4, 1.9 Hz, 4H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.15 (m, 4H), 7.05 – 7.00 (m, 4H), 4.77 – 4.63 (m, 2H), 3.23 – 2.96 (m, 4H), 2.96 – 2.86 (m, 2H), 2.75 (ddd, *J* = 29.9, 16.6, 3.3 Hz, 2H), 2.67 – 2.43 (m, 4H), 2.35 (s, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.5, 144.4, 140.8, 140.7, 134.8, 134.7, 134.4, 134.1, 133.2, 133.1, 131.0, 130.9, 130.8, 130.7, 130.0, 129.9, 129.4, 129.3, 128.2 (2 dia), 127.4, 127.3, 125.4, 125.3, 125.2, 125.1, 124.0 (t, *J* = 289.2 Hz), 123.9 (t, *J* = 289.2 Hz), 117.5, 117.1, 57.2, 56.8, 56.7, 38.0 (t, *J* = 18.8 Hz), 37.4 (t, *J* = 18.7 Hz), 36.4, 35.0, 21.7. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -97.2 and -105.1 (AB systems, J_{AB} = 224.0 Hz, 2F), -97.6 and -102.6 (AB systems, J_{AB} = 224.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{23}H_{23}F_2N_2O_3S_2^+$]: 477.1113 (M+H$^+$); found: 477.1238.

Ethyl 4-(((2S)-2-bromo-4,4-difluoro-4-(phenylsulfonimidoyl)butyl)(tert-butoxycarbonyl)-amino)benzoate (94)

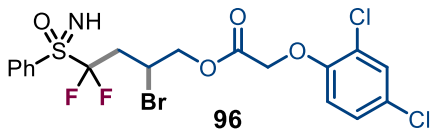


94

Compound **94** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenyl-sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and ethyl 4-(allyl(tert-butoxycarbonyl)amino)benzoate **3p** (183 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **94** as a yellowish oil (25% yield, 29.3 mg, 0.051 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (t, *J* = 7.8 Hz, 8H), 7.76 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 4H), 7.59 (d, *J* = 8.9 Hz, 4H), 5.17 – 5.01 (m, 2H), 4.37 (q, *J* = 7.1 Hz, 4H), 4.28 (t, *J* = 8.8 Hz, 2H), 3.90 – 3.87 (m, 2H), 3.06 – 2.69 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 6H), 1.25 (s, 18H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.1 (2 dia), 153.5 (2 dia), 141.7 (2 dia), 135.2 (2 dia), 133.6 (2 dia), 131.0 (2 dia), 130.9 (2 dia), 129.6 (2 dia), 126.3 (2 dia), 117.4 (2 dia), 67.5 (2 dia), 61.1 (2 dia), 50.6 (2 dia), 36.2 (2 dia), 29.9 (2 dia), 14.5 (2 dia). **^{19}F NMR decoupled ^{1}H (188 MHz, $CDCl_3$)** δ -101.2 and -102.7 (AB system, J_{AB} = 228.0 Hz, 2F), -101.3 and -101.7 (AB system, J_{AB} = 228.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{24}H_{30}BrF_2N_2O_5S^+$]: 575.1021 (M+H$^+$); found: 575.1036.

2-bromo-4,4-difluoro-4-(phenylsulfonimidoyl)butyl 2-(2,4-dichlorophenoxy)acetate (96)

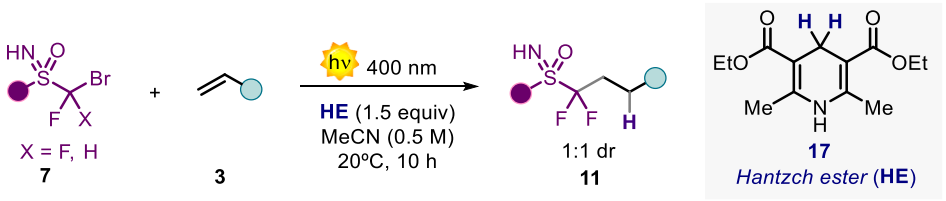


96

Compound **96** was synthesized according to the general procedure **D.1.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv.) and allyl 2-(2,4-dichlorophenoxy)acetate **3m** (157 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **96** as a yellowish oil (43% yield, 46.0 mg, 0.09 mmol; 1:1 mixture of diastereoisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.9 Hz, 4H), 7.74 (t, *J* = 6.7 Hz, 2H), 7.61 (t, *J* = 7.7 Hz, 4H), 7.40 (d, *J* = 2.5 Hz, 2H), 7.17 (dd, *J* = 8.8, 2.6 Hz, 2H), 6.80 (dd, *J* = 8.8, 2.9 Hz, 2H), 4.75 (d, *J* = 8.4 Hz, 4H), 4.56 – 4.35 (m, 6H), 3.27 – 2.72 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.6, 167.5, 152.3 (2 dia), 135.1, 135.0, 133.6, 133.5, 130.8 (2 dia), 130.6 (2 dia), 129.5, 129.4, 127.8 (2 dia), 127.5, 127.4, 124.4 (2 dia), 123.04 (t, *J* = 289.7 Hz, 2 dia), 114.9, 114.8, 67.6, 67.5, 66.2 (2 dia), 39.3 (t, *J* = 2.5 Hz), 39.2 (t, *J* = 2.6 Hz), 36.2 – 35.7 (m, 2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -102.2 and -102.9 (AB systems, J_{AB} = 223.0 Hz, 2F), -102.4 and -102.7 (AB systems, J_{AB} = 223.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{18}H_{17}BrCl_2F_2NO_4S^+$]: 529.9401 ($M+H^+$); found: 529.9441.

F.2. HYDROFUNCTIONALIZATION REACTION WITH ALKENES

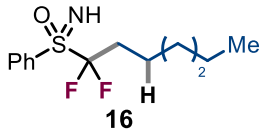


A glass reactor (depicted in Figure S2**Figure S*1-right***) was charged with Hantzsch ester (HE) **17** (1.5 equiv.), the fluorinated sulfoximine **7** (1 equiv.), the alkene **3** (if solid, 3 equiv.) and degassed acetonitrile (0.5 M). The glass reactor was closed with a septum, and the solution was degassed with nitrogen (N_2) for 1 minute. *Note: In the cases in which the alkene **3** was a liquid, the substrate was added after the addition of the solvent and degassing the solution.* Then, the vial was sealed with parafilm, and the reaction mixture was stirred for 10 h under the irradiation of a Kessil Lamp PR160L (400 nm, 40W, 25% intensity), unless otherwise stated (see set-up in Figure S2-*left*). After the irradiation period, the solvent was removed under reduced pressure and the crude product was directly purified by flash column chromatography on silica gel (hexane:EtOAc) to afford the sulfoximine products **11** in the stated yield.

NOTE: If during purification it is not possible to separate the desired product **11** from the Hantzsch ester pyridine by-product, it is possible to remove this impurity effectively by washing the organic phase with an aqueous solution 1M HCl acid. Subsequent anhydrification with $MgSO_4$ and distillation under reduced pressure allows the product **11** to be obtained in stated yield.

Characterization data

(1,1-difluorooctyl)(imino)(phenyl)-λ⁶-sulfanone (16)

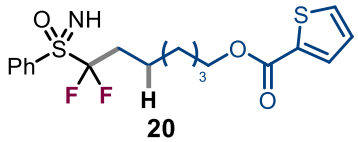


16

Compound **16** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and 1-hexene **14** (75 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **16** as a yellowish oil (61% yield, 33.6 mg, 0.12 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 2.77 (s, 1H), 2.62 – 2.00 (m, 2H), 1.77 – 1.50 (m, 2H), 1.42 – 1.30 (m, 2H), 1.34 – 1.22 (m, 4H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.2, 130.8, 129.2, 125.3 (t, *J* = 287.2 Hz), 31.5, 30.0 (t, *J* = 20.9 Hz), 29.8, 28.9, 22.5, 21.1, 14.1. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -109.0 and -109.8 (AB system, J_{AB}= 220.8 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{13}H_{20}F_2NOS^+$]: 276.1228 ($M+H^+$); found: 276.1298.

7,7-difluoro-7-(phenylsulfonimidoyl)heptyl thiophene-2-carboxylate (20)



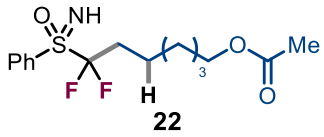
20

Compound **20** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.) Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv) .) and hex-5-en-1-yl thiophene-3-carboxylate **3a** (126 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **20** as a yellowish oil (52% yield, 38.7 mg, 0.104 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.02 (m, 3H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 5.1 Hz, 1H), 7.30 – 7.28 (m, 1H), 4.24 (t, *J* = 6.6 Hz, 2H), 3.19 (s, 1H), 2.39 – 2.10 (m, 2H), 1.76 – 1.69 (m, 2H), 1.64 – 1.56 (m, 2H), 1.46 – 1.38 (m, 4H). **^{13}C NMR (101**

MHz, $CDCl_3$) δ 162.9, 134.5, 134.1, 133.9, 132.7, 130.7, 129.2, 128.0, 126.1, 125.1 (t, *J* = 288 Hz), 64.6, 29.9 (t, *J* = 21 Hz), 28.9, 28.6, 25.8, 21.1 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.8 and -104.5 (AB system, J_{AB}= 220.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI$^+$):** calculated for [$C_{18}H_{22}F_2NO_3S_2^+$]: 402.1004 ($M+H^+$); found: 402.1076.

7,7-difluoro-7-(phenylsulfonimidoyl)heptyl acetate (22)



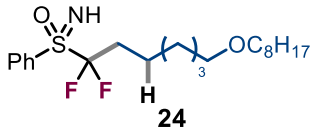
22

Compound **22** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and hex-5-en-1-yl acetate **3b** (85 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **22** as a yellowish oil (65% yield, 43.2 mg, 0.13 mmol).

Note: compound **22** was also synthesized in a higher scale following the general procedure **D.2.**, using (bromodifluoromethyl)phenylsulfoximine **13** (270 mg, 1 mmol, 1 equiv.), Hantzsch ester **17** (380 mg, 1.5 mmol, 1.5 equiv.) and hex-5-en-1-yl acetate **3b** (427 mg, 3 mmol, 3 equiv.), in the same glass reactor (depicted in Figure S2**Figure S*1-right***) used for the 0.2 mmol scale reaction. Reaction time: 10 h. Yield = 64% (215 mg, 0.645 mmol).

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 2H), 4.02 (t, *J* = 6.7 Hz, 2H), 3.20 (s, 1H), 2.42 – 2.07 (m, 2H), 2.02 (s, 3H), 1.63 – 1.54 (m, 4H), 1.44 – 1.27 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 134.5, 134.1, 130.7, 129.2, 125.1 (t, *J* = 287 Hz), 64.4, 29.9 (t, *J* = 21 Hz), 28.8, 28.4, 25.7, 21.1. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.8 and -104.5 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI$^+$):** calculated for [$C_{15}H_{22}F_2NO_3S^+$]: 334.1283 ($M+H^+$); found: 334.1352.

(1,1-difluoro-7-(octyloxy)heptyl)(imino)(phenyl)-λ^6-sulfanone (24)

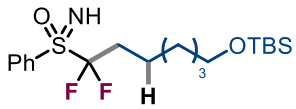


24

Compound **24** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **24** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and 1-(hex-5-en-1-yloxy)octane **3c** (127 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 85:15 hexane/EtOAc) to afford compound **24** as a yellowish oil (44% yield, 35.6 mg, 0.088 mmol).

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 3.37 (t, *J* = 6.7 Hz, 4H), 2.38 – 2.06 (m, 2H), 1.59 – 1.51 (m, 6H), 1.38 – 1.32 (m, 4H), 1.32 – 1.24 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.1, 130.7, 129.2, 125.2 (t, *J* = 288 Hz), 71.1, 70.7, 31.9, 29.9 (t, *J* = 21 Hz), 29.9, 29.6, 29.5, 29.4, 29.1, 26.3, 26.0, 22.8, 21.2 (t, *J* = 3.0 Hz), 14.2. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.8 and -104.6 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{21}H_{36}F_2NO_2S^+$]: 404.2429 ($M+H^+$); found: 404.2568.

(7-((tert-butyldimethylsilyl)oxy)-1,1-difluoroheptyl)(imino)(phenyl)-λ^6-sulfanone (26)

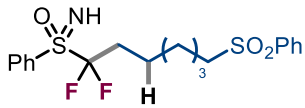


26

Compound **26** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and tert-butyl(hex-5-en-1-yloxy)dimethylsilane **3d** (129 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **26** as a yellowish oil (47% yield, 38.3 mg, 0.094 mmol).

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.43 – 1.99 (m, 2H), 1.60 – 1.43 (m, 4H), 1.43 – 1.21 (m, 4H), 0.87 (s, 9H), 0.03 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.1, 130.7, 129.2, 125.2 (t, *J* = 288 Hz), 63.1, 32.6, 30.0 (t, *J* = 21 Hz), 29.1, 26.1, 25.6, 21.2, 18.5, -5.2. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.7 and -104.6 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{19}H_{34}F_2NO_2SSi^+$]: 406.2042 ($M+H^+$); found: 406.2121.

(1,1-difluoro-7-(phenylsulfonyl)heptyl)(imino)(phenyl)-λ^6-sulfanone (28)



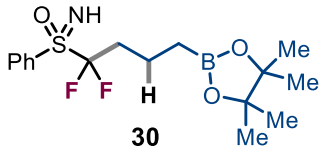
28

Compound **28** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and (hex-5-en-1-ylsulfonyl)benzene **3e** (135 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 75:25 hexane/EtOAc) to afford compound **28** as a yellowish oil (68% yield, 56.7 mg, 0.136 mmol).

^{1}H NMR (400 MHz, $CDCl_3$ δ 7.76 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.34 (m, 2H), 7.32 – 7.26 (m, 4H), 2.90 (s, 1H), 2.83 – 2.71 (m, 2H), 2.09 – 1.76 (m, 2H), 1.58 – 1.34 (m,

2H), 1.29 – 1.21 (m, 2H), 1.14 – 0.99 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 139.2, 134.6, 134.1, 133.8, 130.7, 129.4, 129.2, 128.1, 125.0 (t, *J* = 288 Hz), 56.2, 29.8 (t, *J* = 21 Hz), 28.6, 28.0, 22.5, 20.9. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.9 and -104.5 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{19}H_{24}F_2NO_3S_2^+$]: 416.1160 ($M+H^+$); found: 416.1248.

(1,1-difluoro-4-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)butyl)(imino)(phenyl)-λ^6-sulfanone (30)

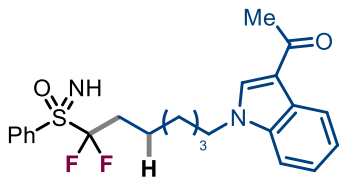


30

Compound **30** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and allylboronic acid pinacol ester **S21** (112 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **30** as a yellowish oil (48% yield, 33.1 mg, 0.096 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 3.24 (s, 1H), 2.36 – 2.09 (m, 2H), 1.73 – 1.65 (m, 2H), 1.21 (s, 12H), 0.83 (t, *J* = 7.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.4, 134.0, 130.7, 129.1, 125.2 (t, *J* = 287.6 Hz), 83.3, 32.2 (t, *J* = 20.7 Hz), 24.9, 16.1 (t, *J* = 3.5 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.3 and -104.6 (AB system, J_{AB} = 217.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{15}H_{23}BF_2NO_3S^+$]: 346.1454 ($M+H^+$); found: 348.2401.

(7-(3-acetyl-1H-indol-1-yl)-1,1-difluoroheptyl)(imino)(phenyl)-λ^6-sulfanone (32)



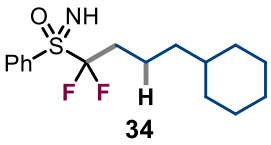
32

Compound **32** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and 1-(1-(hex-5-en-1-yl)-1H-indol-3-yl)ethan-1-one **3f** (145 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 4:6 hexane/EtOAc) to afford compound **32** as a yellowish oil (59% yield, 50.9 mg, 0.118 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 – 8.33 (m, 1H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.75 – 7.65 (m, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.21 (m, 3H), 4.12 (t, *J* = 7.1 Hz, 2H), 3.21 (s, 1H), 2.52 (s, 3H),

2.36 – 2.08 (m, 2H), 1.90 – 1.83 (m, 2H), 1.61 – 1.53 (m, 2H), 1.42 – 1.29 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.1, 136.8, 134.8, 134.6, 134.1, 130.7, 129.2, 126.4, 125.0 (t, *J* = 286 Hz), 123.3, 122.7, 122.6, 117.1, 109.9, 47.0, 29.8 (t, *J* = 21 Hz), 29.7, 28.8, 27.7, 26.6, 21.1 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.8 and -104.3 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS** (ESI^+): **HRMS (ESI^+):** calculated for [$C_{23}H_{27}F_2N_2O_2S^+$]: 433.1756 ($M+H^+$); found: 433.1855.

(4-cyclohexyl-1,1-difluorobutyl)(imino)(phenyl)-λ^6-sulfanone (34)

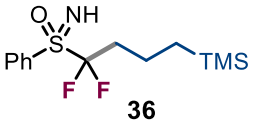


34

Compound **34** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and allylcyclohexane **S22** (93 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **34** as a yellowish oil (47% yield, 29.6 mg, 0.094 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 3.15 (s, 1H), 2.36 – 2.00 (m, 2H), 1.77 – 1.60 (m, 4H), 1.61 – 1.53 (m, 2H), 1.33 – 1.07 (m, 6H), 0.96 – 0.77 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.2, 130.7, 129.2, 125.3 (t, *J* = 287.6 Hz), 37.4, 37.0, 33.3, 30.3 (t, *J* = 20.8 Hz), 26.7, 26.4, 18.6.**^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.7 and -104.5 (AB systems, J_{AB} = 220.8 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{16}H_{24}F_2NOS^+$]: 316.1541 ($M+H^+$); found: 316.1595.

(1,1-difluoro-4-(trimethylsilyl)butyl)(imino)(phenyl)-λ^6-sulfanone (36)



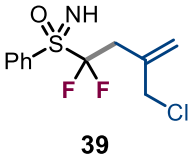
36

Compound **36** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and allyltrimethylsilane **S24** (95 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **36** as a yellowish oil (53% yield, 32.2 mg, 0.105 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 2.99 (s, 1H), 2.43 – 2.06 (m, 2H), 1.61 – 1.51 (m, 2H), 0.61 – 0.37 (m, 2H), -0.03 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.1, 130.7, 129.2, 125.1 (t, *J* = 287.3 Hz), 33.7 (t, *J* = 20.6 Hz), 16.7, 16.1, -1.7. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.8 and -104.9

(AB system, J_{AB} = 221.1 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{13}H_{22}F_2NOSSi^+$]: 306.1154 ($M+H^+$); found: 306.1222.

(3-(chloromethyl)-1,1-difluorobut-3-en-1-yl)(imino)(phenyl)-λ^6-sulfanone (39)

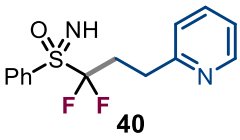


39

Compound **39** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (135 mg, 0.5 mmol, 1 equiv.), Hantzsch ester **17** (190 mg, 0.75 mmol, 1.5 equiv.) and 3-chloro-2-chloromethyl-1-propene **S29** (174 µL, 1.5 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **39** as a yellowish oil (48% yield, 67.1 mg, 0.24 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 2H), 5.34 (d, *J* = 78.5 Hz, 2H), 4.08 (s, 2H), 3.37 – 3.01 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.7, 133.6, 130.7, 129.3, 129.3, 123.6 (t, *J* = 289 Hz), 122.6, 47.9, 33.3 (t, *J* = 21 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -102.2 and -103.5 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{11}H_{13}ClF_2NOS^+$]: 280.0369 ($M+H^+$); found: 280.0339.

(1,1-difluoro-3-(pyridin-2-yl)propyl)(imino)(phenyl)-λ^6-sulfanone (40)

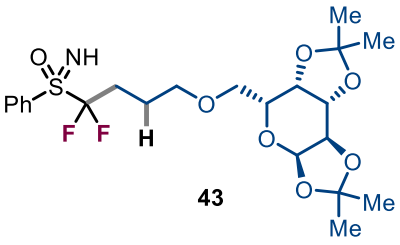


40

Compound **40** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and 2-vinylpyridine **S30** (65 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 4:6 hexane/EtOAc) to afford a clean fraction of compound **40** as a yellowish oil (54% NMR yield). The remaining fraction was contaminated with an unknown impurity that could not be separated by flash column chromatography.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.0 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.58 (m, 3H), 7.24 – 7.10 (m, 2H), 3.32 (s, 1H), 3.07 (t, *J* = 8.1 Hz, 2H), 2.89 – 2.62 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 158.9, 149.6, 136.8, 134.6, 133.8, 130.8, 129.3, 125.0 (t, *J* = 291 Hz), 123.2, 121.9, 30.0 (t, *J* = 21 Hz), 29.8 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.2 and -104.3 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{14}H_{15}F_2N_2OS^+$]: 297.0868 ($M+H^+$); found: 297.0859.

(1,1-difluoro-4-(((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methoxy)butyl)(imino)(phenyl)-λ^6-sulfanone (43)

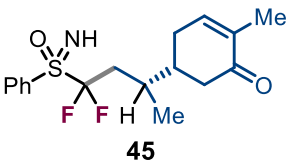


43

Compound **43** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and (3aR,5R,5aS,8aS,8bR)-5-((allyloxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran **3l** (180 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **43** as a yellowish oil (38% yield, 37.6 mg, 0.0765 mmol, 1:1 mixture of two diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 4H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 4H), 5.22 (t, *J* = 4.8 Hz, 2H), 4.28 (dd, *J* = 7.9, 2.4 Hz, 2H), 4.00 – 3.98 (m, 2H), 3.89 (dt, *J* = 7.9, 1.8 Hz, 2H), 3.61 (t, *J* = 6.2 Hz, 2H), 3.39 – 3.13 (m, 8H), 2.24 – 1.91 (m, 4H), 1.56 – 1.49 (m, 4H), 1.23 (s, 6H), 1.12 (s, 6H), 1.02 (s, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.5, 134.4, 133.9, 133.8, 130.8 (2 dia), 129.3, 129.2, 125.4 (t, *J* = 288 Hz, 2 dia), 109.6, 109.5, 109.4, 108.8, 108.7, 96.5, 96.45, 96.4, 71.7, 71.3, 71.2, 70.9, 70.8, 70.75, 70.7, 70.65, 70.6, 70.0 (2 dia), 69.6, 69.5, 68.2 (2 dia), 67.0, 66.9, 62.5 (2 dia), 27.5 – 26.6 (m, 2 dia), 26.2, 26.1, 25.0 (2 dia), 24.6, 24.4, 21.7 (dt, *J* = 6 and 3 Hz, 2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.4 and -104.2 (AB system, J_{AB} = 221.0 Hz, 2F), -103.6 and -103.9, (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{22}H_{31}F_2NO_7SNa^+$]: 514.1682 (M+Na^+); found: 514.1732.

(1,1-difluoro-3-(4-methyl-5-oxocyclohex-3-en-1-yl)butyl)(imino)(phenyl)-λ^6-sulfanone (45)



45

Compound **45** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and (R)-(-)-carvone **S27** (94 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **45** as a yellowish oil (49% yield, 33.3 mg, 0.097 mmol, 1:1.1:1.4:1.4 mixture of four diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 8H), 7.71 (t, *J* = 7.5 Hz, 4H), 7.58 (t, *J* = 7.7 Hz, 8H), 6.71 (s, 4H), 3.21 (s, 4H), 2.58 – 1.93 (m, 32H), 1.74 (s, 12H), 1.00 (t, *J* = 7.3 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.60 (4 dia), 144.65, 144.63, 144.55, 144.53, 135.64 (2 dia), 134.67 (2 dia), 133.97 (4 dia), 130.73 (4 dia), 129.27 (4 dia), 125.36 (t, J = 288 Hz, 4 dia)), 42.01 (2 dia), 41.96 (2 dia), 40.75 – 40.30 (m, 4 dia), 33.63 – 32.64 (m, 4 dia), 31.25 (4 dia), 30.02 (2 dia), 29.94 (2 dia), 28.23 (2 dia), 28.18 (2 dia), 16.83 (4 dia), 15.73 (4 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.3 and -104.1 (AB system, J_{AB} = 219.0 Hz, 2F), -101.4 and -104.0 (AB system, J_{AB} = 220.0 Hz, 2F), -101.5 and -103.7 (AB system, J_{AB} = 219.0 Hz, 2F), -101.7 and -103.5 (AB system, J_{AB} = 219.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{22}F_2NO_2S^+$]: 342.1334 ($M+H^+$); found: 342.1441.

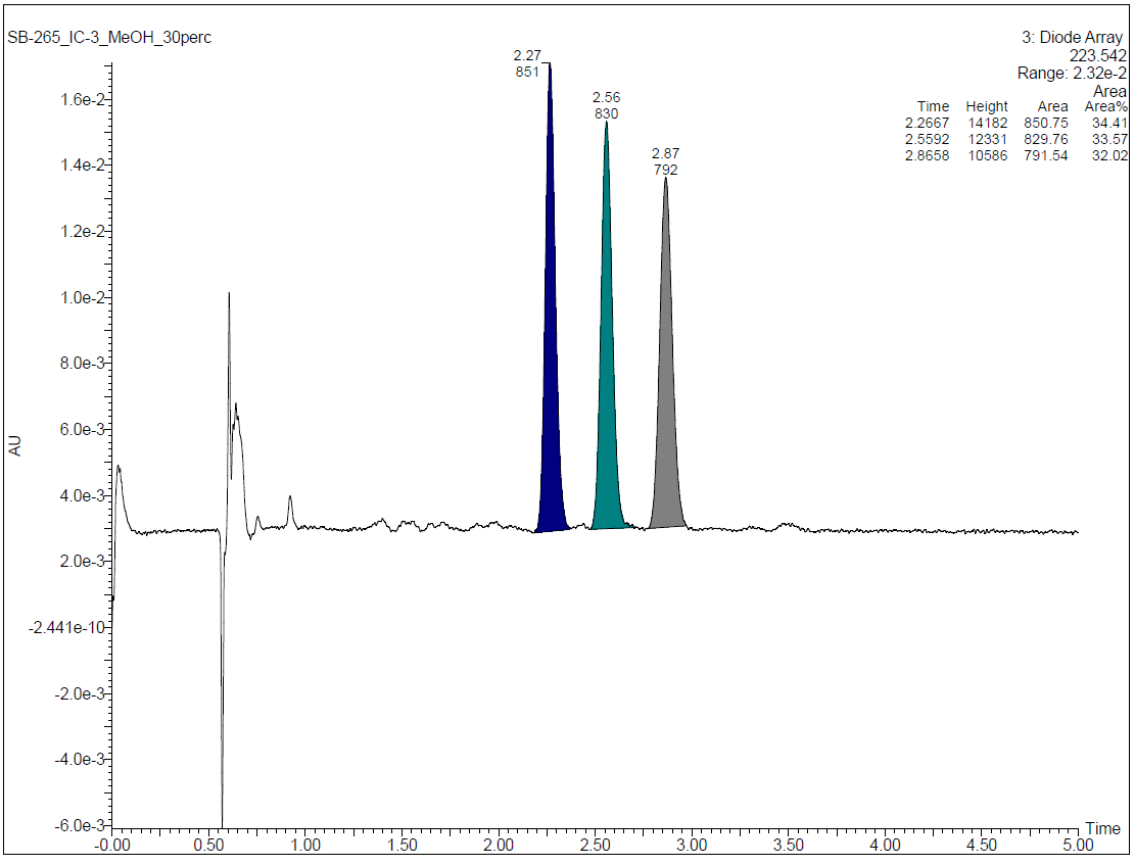
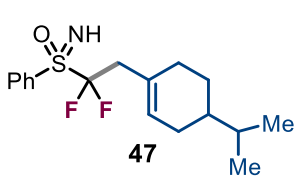


Figure S20. Chromatogram of compound **45** after isolation. UPC^2 analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 220.5 nm.

(1,1-difluoro-2-(4-isopropylcyclohex-1-en-1-yl)ethyl)(imino)(phenyl)-λ^6-sulfanone (47)

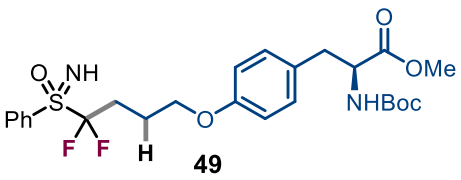


47

Compound **47** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and β-pinene **S28** (94 μL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **47** as a yellowish oil (66% yield, 43.1 mg, 0.13 mmol, 1:1 mixture of diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.4 Hz, 4H), 7.69 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 4H), 5.69 (s, 2H), 3.13 – 2.71 (m, 6H), 2.18 – 1.93 (m, 6H), 1.79 – 1.70 (m, 4H), 1.55 – 1.36 (m, 2H), 1.32 – 1.10 (m, 4H), 0.87 – 0.84 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.0, 133.9, 130.8 (2 dia), 130.3, 130.2, 129.1 (2 dia), 127.6, 127.5, 124.2 (t, *J* = 290 Hz, 2 dia), 39.6, 39.5, 38.4 – 37.8 (m, 2 dia), 32.2, 32.1, 30.0, 29.9, 29.3, 29.2, 26.4, 26.3, 20.0, 19.9, 19.7 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -99.3 and -102.8 (AB system, J_{AB} = 220.0 Hz, 2F), -100.6 and -102.0 (AB system, J_{AB} = 220.0 Hz, 2F). **HRMS (ESI+):** calculated for [$C_{17}H_{24}F_2NOS^+$]: 328.1541 ($M+H^+$); found: 328.1711.

Methyl (2S)-2-((tert-butoxycarbonyl)amino)-3-(4-(4,4-difluoro-4-(phenylsulfonimidoyl) butoxy)phenyl)propanoate (49)

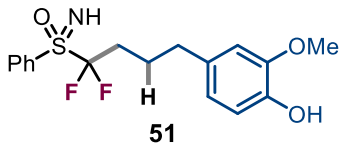


49

Compound **49** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and methyl (S)-3-(4-(allyloxy)phenyl)-2-((tert-butoxycarbonyl)amino) propanoate **3k** (201 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **49** as a yellowish oil (38% yield, 40.1 mg, 0.076 mmol, 1:1 mixture of two diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$ δ 8.07 (d, *J* = 7.0 Hz, 4H), 7.71 (t, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 4H), 7.01 (d, *J* = 8.1 Hz, 4H), 6.77 (d, *J* = 8.4 Hz, 4H), 4.97 (d, *J* = 8.3 Hz, 2H), 4.52 (d, *J* = 6.9 Hz, 2H), 3.96 (t, *J* = 5.9 Hz, 4H), 3.70 (s, 6H), 3.25 (s, 2H), 3.06 – 2.95 (m, 4H), 2.70 – 2.21 (m, 4H), 2.07 – 2.04 (m, 4H), 1.41 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.5 (2 dia), 157.8 (2 dia), 155.2 (2 dia), 134.6 (2 dia), 133.9 (2 dia), 130.7 (2 dia), 130.4 (2 dia), 129.3 (2 dia), 128.4 (2 dia), 125.0 (t, *J* = 287 Hz, 2 dia), 114.6 (2 dia), 80.0 (2 dia), 66.4 (2 dia), 54.6 (2 dia), 52.3 (2 dia), 37.6 (2 dia), 28.4 (2 dia), 27.2 (t, *J* = 21 Hz, 2 dia), 21.6 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.6 and -104.5 (AB system, J_{AB} = 223.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{25}H_{33}F_2N_2O_6S^+$]: 527.2022 ($M+H^+$); found: 527.2153.

(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ^6-sulfanone (51)

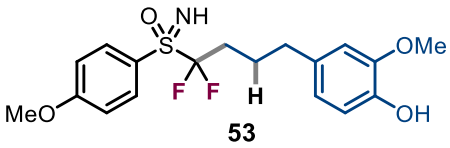


51

Compound **51** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and eugenol **3ab** (92 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **51** as a yellowish oil (62% yield, 44.0 mg, 0.124 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.62 (m, 2H), 5.60 (s, 1H), 3.85 (s, 3H), 3.19 (s, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.38 – 2.11 (m, 2H), 1.99 – 1.78 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6, 144.1, 134.6, 134.0, 132.7, 130.7, 129.2, 125.2 (t, *J* = 287 Hz), 121.1, 114.5, 111.0, 56.0, 34.8, 29.4 (t, *J* = 21 Hz), 23.2 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.2 and -104.2 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{18}F_2NO_3S^-$]: 354.0981 (M-H$^+$); found: 354.0969.

(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(4-methoxyphenyl)-λ^6-sulfanone (53)

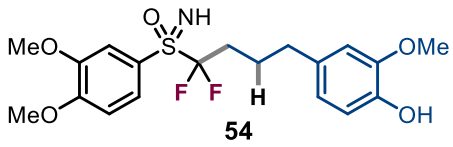


53

Compound **53** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)(4-methoxyphenyl)(imino)-λ^6-sulfanone **7b** (33 mg, 0.1 mmol, 1 equiv.), Hantzsch ester **17** (38 mg, 0.15 mmol, 1.5 equiv) and eugenol **3ab** (49 mg, 0.3 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **53** as a yellowish oil (47% yield, 18.0 mg, 0.047 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.9 Hz, 1H), 7.05 – 6.98 (m, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.50 (s, 1H), 3.90 (s, 2H), 3.87 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 1H), 2.36 – 2.10 (m, 1H), 1.94 – 1.84 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 146.6, 144.1, 133.0, 132.8, 125.1 (t, *J* = 286 Hz), 124.9, 121.1, 114.6, 114.4, 111.0, 56.0, 55.9, 34.9, 29.6 (t, *J* = 21 Hz), 23.3 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.6 and -104.6 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{18}H_{22}F_2NO_4S^+$]: 386.1232 (M+H$^+$); found: 386.1264.

(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(3,4-dimethoxyphenyl)(imino)-λ⁶-sulfanone (54)

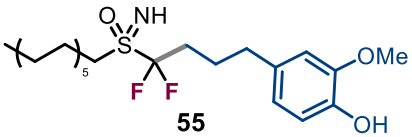


54

Compound **54** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)(3,4-dimethoxyphenyl)(imino)-λ⁶-sulfanone **7g** (33 mg, 0.1 mmol, 1 equiv.), Hantzsch ester **17** (38 mg, 0.15 mmol, 1.5 equiv) and eugenol **3ab** (49 mg, 0.3 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **54** as a yellowish oil (77% yield, 32.1 mg, 0.077 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.46 (d, *J* = 2.2 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.63 (d, *J* = 7.5 Hz, 2H), 5.50 (s, 1H), 3.97 (s, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.38 – 2.17 (m, 2H), 1.99 – 1.84 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.4, 149.3, 146.6, 144.1, 132.7, 125.2, 125.2 (t, *J* = 287 Hz), 125.0, 121.1, 114.5, 112.7, 111.0, 110.8, 56.4, 56.0, 34.9, 31.1, 29.6 (t, *J* = 21 Hz), 23.3 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.4 and -104.5 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{19}H_{24}F_2NO_5S^+$]: 416.1338 ($M+H^+$); found: 416.1410.

(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(dodecyl)(imino)-λ⁶-sulfanone (55)

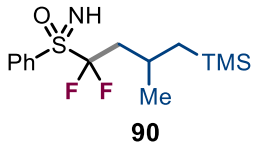


55

Compound **55** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)(dodecyl)(imino)-λ⁶-sulfanone **7l** (31 mg, 0.085 mmol, 1 equiv.), Hantzsch ester **17** (32 mg, 0.13 mmol, 1.5 equiv.) and eugenol **3ab** (39 µL, 0.26 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **55** as a white solid (43% yield, 16.5 mg, 0.037 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.5 Hz, 1H), 6.67 (s, 2H), 4.21 – 4.11 (m, 2H), 3.88 (s, 3H), 3.16 – 3.02 (m, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.35 – 2.13 (m, 2H), 1.99 – 1.83 (m, 4H), 1.48 – 1.39 (m, 2H), 1.25 (s, 14H), 0.87 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.7, 144.2, 132.6, 125.7 (t, *J* = 288 Hz), 121.1, 114.5, 111.0, 63.3, 60.9, 56.0, 53.6, 48.1, 34.9, 32.0, 29.7 (t, *J* = 11 Hz), 29.5, 29.4, 29.2, 28.7, 28.3 (t, *J* = 21 Hz), 22.8, 21.0, 14.2. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.9 and -104.8 (AB system, J_{AB} = 224.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{23}H_{40}F_2NO_3S^+$]: 448.2691 ($M+H^+$), found: 448.2721.

(1,1-difluoro-3-methyl-4-(trimethylsilyl)butyl)(imino)(phenyl)-λ^6-sulfanone (90)

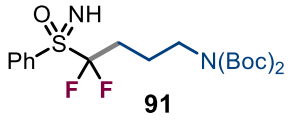


90

Compound **90** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and methallyltrimethylsilane **S25** (56 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **90** as a yellowish oil (26% yield, 16.5 mg, 0.052 mmol, 1:1 mixture of diastereoisomers).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 4H), 7.71 (t, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 15.9 Hz, 4H), 3.24 – 2.74 (m, 2H), 2.37 – 1.97 (m, 6H), 1.02 (dd, *J* = 11.1, 6.0 Hz, 6H), 0.75 – 0.78 (m, 2H), 0.56 – 0.51 (m, 2H), -0.01 (s, 9H), -0.03 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.5, 134.4, 134.0, 133.9, 130.8, 130.7, 129.2 (2 dia), 125.5 (t, *J* = 289 Hz, 2 dia), 39.1 – 38.8 (m, 2 dia), 26.3, 26.2, 24.8 (2 dia), 23.7, 23.65, 23.6, -0.6, -0.5. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.7 and -103.5 (AB system, J_{AB} = 220.0 Hz, 2F), -101.7 and -103.6 (AB system, J_{AB}= 220.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{14}H_{24}F_2NOSSi^+$]: 320.1310 (M+H$^+$); found: 320.1393.

(4-(N,N-bis(tert-butoxycarbonyl))amino-1,1-difluorobutyl)(imino)(phenyl)-λ^6-sulfanone (91)

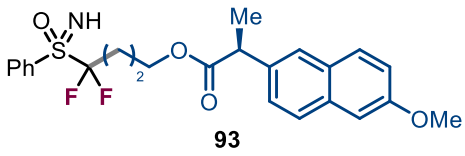


91

Compound **91** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenylsulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and N,N-bis(tert-butoxycarbonyl)allylamine **3h** (154 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **91** as a yellowish oil (26% yield, 23.2 mg, 0.052 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.22 (s, 1H), 2.48 – 2.07 (m, 2H), 2.00 – 1.79 (m, 2H), 1.48 (s, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 152.5, 134.6, 133.9, 130.7, 129.3, 124.9 (t, *J* = 289 Hz), 82.7, 45.5, 28.2, 27.8 (t, *J* = 21 Hz), 21.1 (t, *J* = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.5 and -104.9 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{20}H_{30}N_2O_5SNa^+$]: 471.1736 (M+Na$^+$); found: 471.1750.

4,4-difluoro-4-(phenylsulfonimidoyl)butyl (2S)-2-(6-methoxynaphthalen-2-yl)propanoate (93)

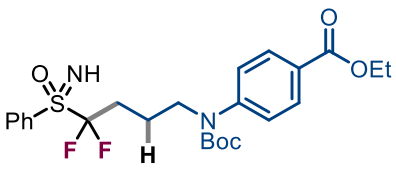


93

Compound **93** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and Allyl (S)-2-(6-methoxynaphthalen-2-yl)propanoate **3n** (162 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **93** as a yellowish oil (17% yield, 15.7 mg, 0.034 mmol, 1:1 mixture of two diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 4H), 7.76 – 7.61 (m, 8H), 7.54 (t, *J* = 7.7 Hz, 4H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.19 – 7.10 (m, 4H), 4.12 – 4.08 (m, 4H), 3.91 (s, 6H), 3.84 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 2H), 2.42 – 2.05 (m, 4H), 1.90 – 1.83 (m, 4H), 1.56 (d, *J* = 7.2 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.6 (2 dia), 157.8 (2 dia), 135.6 (2 dia), 134.6 (2 dia), 133.9 (2 dia), 130.7 (2 dia), 129.4 (2 dia), 129.2 (2 dia), 129.0 (2 dia), 127.4 (2 dia), 126.3 (2 dia), 126.0 (2 dia), 124.7 (t, *J* = 288.8 Hz, 2 dia), 119.2 (2 dia), 105.7 (2 dia), 63.4 (2 dia), 55.5 (2 dia), 45.5, 41.1, 27.0 (t, *J* = 20.9 Hz, 2 dia), 21.0 (t, *J* = 3.4 Hz, 2 dia), 18.5, 14.4. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.7 and -104.8 (AB system, J_{AB} = 221.0 Hz, 2F), -103.8 and -104.6 (AB system, J_{AB} = 221.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{24}H_{25}F_2NO_4S^+$]: 462.1545 ($M+H^+$); found: 462.1651.

Ethyl 4-((tert-butoxycarbonyl)(4,4-difluoro-4-(phenylsulfonimidoyl)butyl)amino)benzoate (95)



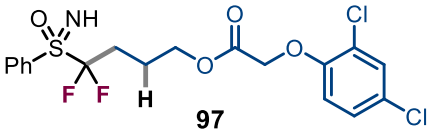
95

Compound **95** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and Ethyl 4-(allyl(tert-butoxycarbonyl)amino)benzoate **3p** (183 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **95** as a yellowish oil (32% yield, 31.8 mg, 0.064 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.88 (m, 4H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.75 (t, *J* = 7.2 Hz, 2H), 2.48 – 2.07 (m, 2H), 1.94 – 1.78 (m, 2H), 1.44 (s, 9H), 1.41 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 154.2, 146.3, 134.7, 134.0, 130.7, 130.4, 129.3, 128.1, 126.3, 124.8 (t, *J* = 287 Hz), 81.3,

61.2, 48.9, 28.4, 27.7 (t, J = 21 Hz), 20.7, 14.5. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.4 and -104.8 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{24}H_{31}F_2N_2O_5S^+$]: 497.1916 ($M+H^+$); not found.

4,4-difluoro-4-(phenylsulfonimidoyl)butyl 2-(2,4-dichlorophenoxy)acetate (97)

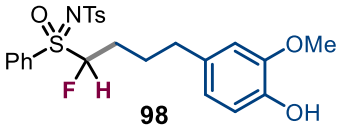


97

Compound **97** was synthesized according to the general procedure **D.2.** using (bromodifluoromethyl)phenyl sulfoximine **13** (54 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76 mg, 0.3 mmol, 1.5 equiv.) and allyl 2-(2,4-dichlorophenoxy)acetate **3m** (157 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **97** as a yellowish oil (44% yield, 39.6 mg, 0.087 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.8 Hz, 2H), 7.71 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 2.6 Hz, 1H), 7.17 (dd, J = 8.8, 2.6 Hz, 1H), 6.77 (d, J = 8.8 Hz, 1H), 4.68 (s, 2H), 4.24 (t, J = 6.2 Hz, 2H), 3.23 (s, 1H), 2.45 – 2.19 (m, 2H), 2.03 – 1.88 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.1, 152.4, 134.7, 133.9, 130.7, 130.5, 129.3, 127.7, 127.3, 124.6 (t, J = 287 Hz), 124.4, 114.8, 66.4, 64.1, 26.9 (t, J = 21 Hz), 21.0 (t, J = 3 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.9 and -104.3 (AB system, J_{AB} = 222.0 Hz, 2F). **HRMS** (ESI$^+$): **HRMS (ESI$^+$):** calculated for [$C_{18}H_{18}Cl_2F_2NO_4S^+$]: 452.0296 ($M+H^+$); found: 452.0346.

N-(((S)-1-fluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (98)



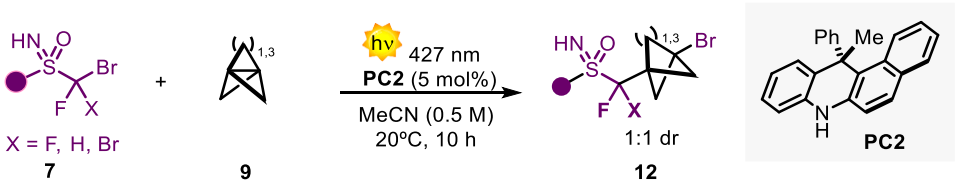
98

Compound **98** was synthesized according to the general procedure **D.2.** using **N-(((S)-**bromofluoromethyl)(oxo)(phenyl)-l6-sulfanylidene)-4-methylbenzenesulfonamide **7k** (41 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (38 mg, 0.3 mmol, 1.5 equiv.) and eugenol **3ab** (46 µL, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **98** as a yellowish oil (34% yield, 16.8 mg, 0.034 mmol, 1:1 mixture of diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 4H), 7.83 (d, J = 8.0 Hz, 4H), 7.73 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.7 Hz, 4H), 7.27 – 7.24 (m, 4H), 6.80 (d, J = 8.0 Hz, 2H), 6.62 – 6.53 (m,

4H), 5.88 (dd, *J* = 9.9, 2.7 Hz, 2H), 3.86 (s, 6H), 3.69 – 3.65 (m, 2H), 3.43 – 3.38 (m, 2H), 2.88 (s, 2H), 2.55 (t, *J* = 7.6 Hz, 4H), 2.40 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.6 (2 dia), 144.1 (2 dia), 143.2 (2 dia), 140.6 (2 dia), 135.2 (2 dia), 132.6 (2 dia), 132.2 (2 dia), 129.9 (2 dia), 129.7 (2 dia), 129.5 (2 dia), 126.8 (2 dia), 121.0 (2 dia), 114.4 (2 dia), 111.0 (2 dia), 103.6 (d, *J* = 226 Hz, 2 dia), 56.0 (2 dia), 34.8 (2 dia), 27.8 (d, *J* = 19 Hz, 2 dia), 26.6 (2 dia), 21.7 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -175.5 (s, 1F), -176.4 (s, 1F). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -175.5 (ddd, *J* = 47.2, 37.5, 14.4 Hz, 1F), -176.4 (ddd, *J* = 48.0, 38.5, 13.6 Hz, 1F). **HRMS (ESI$^+$):** calculated for [$C_{24}H_{27}FNO_5S_2$ $^+$]: 492.1309 (M+H$^+$), found: 490.1148.

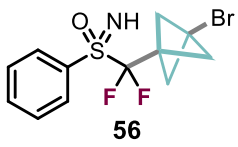
F.3. STRAIN RELEASE ATRA REACTION WITH PROPELLANES



A glass reactor (depicted in Figure S2**Figure S1**-*right*) was charged with the photocatalyst **PC2** (0.15 equiv.), the fluorinated sulfoximine **7** (1 equiv.) and degassed acetonitrile (0.5 M). The glass reactor was closed with a septum, and the solution was degassed with argon (Ar) for 1 minute. Then, the corresponding amount of [1.1.1]- or [3.1.1]-propellane solution (1.1 equiv. of **9a** or **9b**, respectively) was sequentially added to the vial, under Ar atmosphere. The vial was sealed with parafilm, and the reaction mixture was stirred for 10 h under the irradiation of a Kessil Lamp PR160L (427 nm, 45W, 25% intensity), unless otherwise stated (see set-up in Figure S2-*left*). After the irradiation period, the solvent was removed under reduced pressure and the crude product was directly purified by flash column chromatography on silica gel (hexane:EtOAc) to afford the sulfoximine products **12** in the stated yield.

Characterization Data

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(phenyl)-λ^6-sulfanone (56)

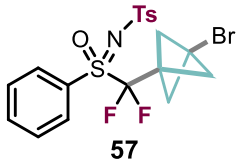


56

Compound **56** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)phenylsulfoximine **13** (54.0 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.01 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (1.1 M in Et_2O, 0.20 mL, 0.22 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by flash column chromatography (gradient from 100% hexane to 95:5 hexane/EtOAc) to afford compound **56** as a white solid (71% yield, 48.0 mg, 0.142 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.68 (m, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 3.26 (s, 1H), 2.45 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 134.8, 134.4, 130.6, 130.5 129.3, 129.2, 119.0 (t, *J* = 287 Hz), 57.9 (t, *J* = 3 Hz), 38.5 (t, *J* = 30 Hz), 35.3 (t, *J* = 2 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.2 and -103.7 (AB system, J_{AB} = 235.0 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{12}H_{13}BrF_2NOS^+$]: 335.9864 ($M+H^+$); found: 335.9854.

N-(((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (57)

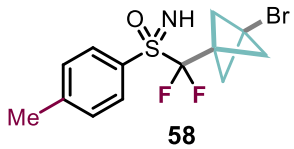


57

Compound **57** was synthesized according to the general procedure **D.3** using N-((bromodifluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide **7i** (84.8 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.87 M in Et_2O, 0.25 mL, 0.22 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by flash column chromatography (gradient from 100% hexane to 95:5 hexane/EtOAc) to afford compound **57** as a white solid (50% yield, 50.0 mg, 0.10 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.85 – 7.77 (m, 3H), 7.68 – 7.62 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 2.44 (s, 6H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.7, 140.4, 136.2, 131.9, 131.2, 131.1, 129.8, 129.75, 129.7, 129.6, 126.7, 126.6 118.7 (dd, *J* = 296 and 285 Hz), 58.2 (t, *J* = 3 Hz), 37.9 (t, *J* = 28 Hz), 35.0 (t, *J* = 2 Hz), 21.7. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -97.6 and -104.9 (AB system, J_{AB} = 226.0 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{19}H_{19}BrF_2NO_3S_2^+$]: 489.9952 ($M+H^+$); found: 489.9922.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(p-tolyl)-λ^6-sulfanone (58)



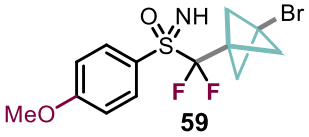
58

Compound **58** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(imino)(p-tolyl)-λ^6-sulfanone **7d** (28.4 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **58** as a yellowish solid (44% yield, 15.3 mg, 0.044 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 3.20 (s, 1H), 2.47 (s, 3H), 2.45 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 146.2, 131.3, 130.7, 130.0, 119.0 (t, *J* = 287 Hz), 58.0 (t, *J* = 3 Hz), 38.6 (t, *J* = 30 Hz), 35.4 (t, *J* = 2 Hz), 21.9 (t, *J* = 5 Hz). **^{19}F NMR**

decoupled ^{1}H (377 MHz, $CDCl_3$) δ -101.41 and -104.03 (AB system, J_{AB} = 236.0 Hz, 2F). **HRMS** (ESI^+): calculated for $[C_{13}H_{15}BrF_2NOS^+]$: 350.0020 ($M+H^+$); found: 350.0053.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(4-methoxyphenyl)-λ^6-sulfanone (59)

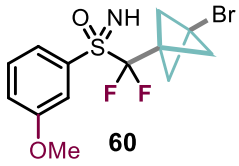


59

Compound **59** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(4-methoxyphenyl)(imino)-λ^6-sulfanone **7b** (30.1 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **59** as a yellowish solid (64% yield, 22.3 mg, 0.064 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 3.90 (s, 3H), 3.16 (s, 1H), 2.45 (s, 6H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.9, 132.9, 132.8, 125.3, 120.4 (t, *J* = 286.9 Hz), 114.6, 114.5, 58.0 (t, *J* = 3 Hz), 55.9, 38.6 (t, *J* = 30 Hz), 35.4 (t, *J* = 2 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.6 and -104.0 (AB system, J_{AB} = 235.0 Hz, 2F). **HRMS** (ESI^+): calculated for $[C_{13}H_{15}BrF_2NO_2S^+]$: 365.9969 ($M+H^+$); found: 365.9989.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(3-methoxyphenyl)-λ^6-sulfanone (60)

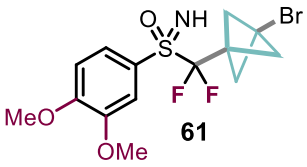


60

Compound **60** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(imino)(3-methoxyphenyl)-λ^6-sulfanone **7f** (30.1 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **60** as a yellowish oil (46% yield, 16.7 mg, 0.046 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (dd, *J* = 14.1, 5.9 Hz, 2H), 7.26 – 7.22 (m, 1H), 3.88 (s, 3H), 3.22 (s, 1H), 2.47 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.1, 135.7, 130.2, 122.9, 121.6, 119.0 (t, *J* = 287 Hz), 114.9, 57.9 (t, *J* = 3 Hz), 55.9, 50.4 (t, *J* = 3 Hz), 38.5 (t, *J* = 30 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.3 and -103.6 (AB system, J_{AB} = 235.0 Hz, 2F). **HRMS** (ESI^+): calculated for $[C_{13}H_{15}BrF_2NO_2S^+]$: 365.9969 ($M+H^+$); found: 365.9989.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(3,4-dimethoxyphenyl)(imino)-λ^6-sulfanone (**61**)

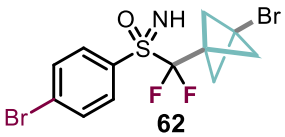


61

Compound **61** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(3,4-dimethoxyphenyl)(imino)-λ^6-sulfanone **7g** (33.0 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **61** as a yellowish solid (52% yield, 41.6 mg, 0.105 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.44 (d, *J* = 2.2 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.16 (s, 1H), 2.47 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.6, 149.3, 125.5, 125.2, 119.0 (t, *J* = 287 Hz), 112.5, 110.7, 58.0 (t, *J* = 3 Hz), 56.5, 56.4, 38.5 (t, *J* = 30 Hz), 35.3 (t, *J* = 2 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.5 and -103.6 (AB system, J_{AB} = 234.0 Hz, 2F). **HRMS** (ESI$^+$): calculated for [$C_{14}H_{17}BrF_2NO_3S^+$]: 396.0075 (M+H$^+$); found: 396.0098.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(4-bromophenyl)(imino)-λ^6-sulfanone (62)

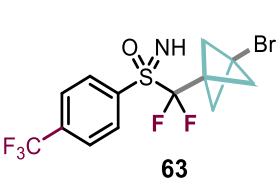


62

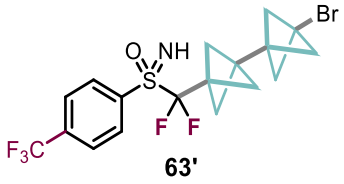
Compound **62** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(4-bromophenyl)(imino)-λ^6-sulfanone **7c** (34.9 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 9:1 hexane/EtOAc) to afford compound **62** as a yellowish solid (41% yield, 17.0 mg, 0.041 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.78 – 7.72 (m, 2H), 3.26 (s, 1H), 2.51 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.6, 132.7, 132.6, 132.1, 132.0, 130.7, 118.9 (t, *J* = 287 Hz), 58.0 (t, *J* = 3 Hz), 38.3 (t, *J* = 30 Hz), 35.2 (t, *J* = 2 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -101.0 and -102.9 (AB system, J_{AB} = 234.0 Hz, 2F). **HRMS** (ESI$^+$): calculated for [$C_{12}H_{12}Br_2F_2NOS^+$]: 413.8969 (M+H$^+$); found: 413.9001.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(4-(trifluoromethyl)phenyl)-λ⁶-sulfanone (63)



63

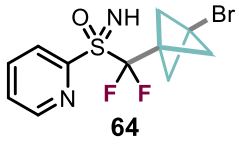


63'

Compound **63** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(imino)(4-(trifluoromethyl)phenyl)-λ⁶-sulfanone **7e** (33.8 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **63** and **63'** as a pale colourless oil (total amount: 18.3 mg, 100:77 ratio of 74:74' isolated as an inseparable mixture, 24% corrected yield of **63**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 2H), 8.00 – 7.78 (m, 2H), 3.30 (s, 1H), 2.52 (s, 6H, compound **63**), 21.12 (s, 6H compound **63'**), 1.74 (s, 4.7H, compound **63'**). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 138.4, 136.4 (q, *J* = 32 Hz), 131.3, 126.3 (q, *J* = 4 Hz), 126.2 (q, *J* = 4 Hz), 121.8 (t, *J* = 287 Hz), 58.0, 50.5 (t, *J* = 3 Hz), 31.1. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -63.2 (3F), -100.8 and -102.2 (AB system, J_{AB} = 232.0 Hz, 2F, compound **63**), -102.5 and 104.0 (AB system, J_{AB} = 232.0 Hz, 2F, compound **63'**). **HRMS** (ESI^+): calculated for [$C_{13}H_{12}BrF_5NOS^+$]: 403.9738 ($M+H^+$), found: 403.9734.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(pyridin-2-yl)-λ⁶-sulfanone (64)

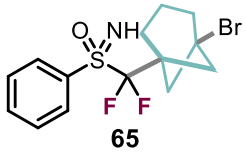


64

Compound **64** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(imino)(pyridin-2-yl)-λ⁶-sulfanone **7h** (15.7 mg, 0.06 mmol, 1 equiv.), **PC2** (1.0 mg, 0.003 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.088 mL, 0.066 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 4:6 hexane/EtOAc) to afford compound **64** as a yellowish solid (34% yield, 6.9 mg, 0.020 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81 (d, *J* = 3.9 Hz, 1H), 8.24 (d, *J* = 6.9 Hz, 1H), 8.00 (td, *J* = 7.8, 1.7 Hz, 1H), 7.64 – 7.62 (m, 1H), 2.59 – 2.48 (m, 6H).**^{13}C NMR (151 MHz, $CDCl_3$)** δ 153.6, 150.4, 138.4, 128.3, 125.9, 58.1, 38.6, 35.6. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -100.1 and -102.8 (AB system, J_{AB} = 236.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{11}H_{12}BrF_2N_2OS^+$]: 336.9816 ($M+H^+$), found: 336.9815.

((5-bromobicyclo[3.1.1]heptan-1-yl)difluoromethyl)(imino)(phenyl)-λ^6-sulfanone (65)

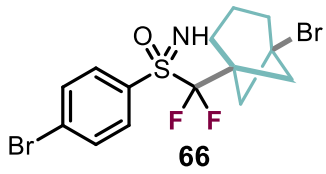


65

Compound **65** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)phenylsulfoximine **13** (27.0 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [3.1.1]-propellane solution **9b** (0.4 M in Bu_2O, 0.27 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by flash column chromatography (gradient from 100% hexane to 95:5 hexane/EtOAc) to afford compound **65** as a white solid (50% yield, 18.0 mg, 0.05 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.74 – 7.68 (m, 1H), 7.59 (t, *J* = 7.8 Hz, 2H), 3.21 – 3.16 (m, 1H), 2.81 (d, *J* = 9.6 Hz, 1H), 2.65 (d, *J* = 9.6 Hz, 1H), 2.36 (t, *J* = 7.1 Hz, 2H), 2.29 (dd, *J* = 9.6, 7.5 Hz, 1H), 2.21 – 2.02 (m, 3H), 1.97 – 1.90 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 135.6, 134.6, 130.6, 129.2, 122.1 (t, *J* = 289 Hz), 54.3, 45.6 (t, *J* = 23 Hz), 45.8 – 45.1 (m), 44.9 – 44.7 (m), 39.6, 26.0 (t, *J* = 3 Hz), 18.6. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -104.5 and -106.0 (AB system, J_{AB} = 228.0 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{14}H_{17}BrF_2NOS^+$]: 364.0177 ($M+H^+$); found: 364.0152.

(((1s,5s)-5-bromobicyclo[3.1.1]heptan-1-yl)difluoromethyl)(4-bromophenyl)(imino)-λ^6-sulfanone (66)

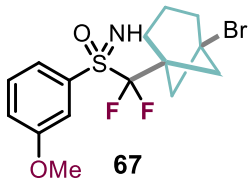


66

Compound **66** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(4-bromophenyl)(imino)-λ^6-sulfanone **7c** (69.80 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.01 mmol, 0.05 equiv.) and a [3.1.1]-propellane solution **9b** (0.4 M in Bu_2O, 0.5 mL, 0.2 mmol, 1 equiv.). Reaction time: 10 h. The crude was purified by flash column chromatography (gradient from 100:0 to 90:10 hexane/EtOAc) to afford compound **66** as a brownish solid (42% yield, 37.2 mg, 0.084 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 2H), 3.18 (s, 1H), 2.82 (d, *J* = 9.6 Hz, 1H), 2.69 (d, *J* = 9.5 Hz, 1H), 2.37 (t, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 8.6 Hz, 1H), 2.23 (t, *J* = 9.3 Hz, 1H), 2.18 – 2.01 (m, 2H), 1.99 – 1.92 (m, 2H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 134.6, 132.4, 131.9, 130.3, 121.9 (t, *J* = 289 Hz), 54.1, 45.4 (t, *J* = 23 Hz), 45.1 – 44.6 (m), 39.4, 30.95, 25.9 (t, *J* = 3 Hz), 18.5. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -104.4 and -105.1 (AB system, J_{AB} = 227.0 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{14}H_{16}Br_2F_2NOS^+$]: 441.9282 ($M+H^+$); found: 441.9317.

(((1s,5s)-5-bromobicyclo[3.1.1]heptan-1-yl)difluoromethyl)(imino)(3-methoxyphenyl)-λ^6-sulfanone (67)

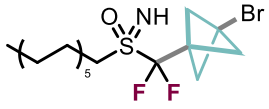


67

Compound **67** was synthesized according to the general procedure D.3 using (bromodifluoromethyl)(imino)(3-methoxyphenyl)-λ^6-sulfanone **7f** (60.2 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.01 mmol, 0.05 equiv.) and a [3.1.1]-propellane solution **9b** (0.4 M in Bu_2O, 0.5 mL, 0.2 mmol, 1 equiv.). Reaction time: 10 h. The crude was purified by flash column chromatography (gradient from 100:0 to 90:10 hexane/EtOAc) to afford compound **67** as a white solid (49% yield, 38.6 mg, 0.098 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.54 – 7.42 (m, 2H), 7.23 – 7.20 (m, 1H), 3.87 (s, 3H), 3.20 (s, 1H), 2.80 (d, *J* = 9.6 Hz, 1H), 2.66 (d, *J* = 9.6 Hz, 1H), 2.35 (t, *J* = 7.1 Hz, 2H), 2.29 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.18 (dd, *J* = 9.6, 7.6 Hz, 1H), 2.14 – 2.04 (m, 2H), 1.98 – 1.91 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.0, 136.8, 130.1, 122.7, 122.0 (t, *J* = 291 Hz), 121.3, 114.8, 55.9 (t, *J* = 5 Hz), 54.3, 45.6 (t, *J* = 23 Hz), 45.2 – 44.7 (m), 39.5, 25.9 (t, *J* = 3 Hz), 18.6. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -104.6 and -105.9 (AB system, J_{AB} = 226.0 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{15}H_{19}BrF_2NO_2S^+$]: 394.0282 ($M+H^+$); found: 394.0428.

((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(dodecyl)(imino)-λ^6-sulfanone (68)

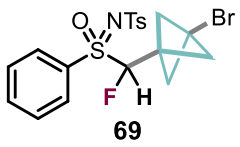


68

Compound **68** was synthesized according to the general procedure **D.3** using (bromodifluoromethyl)(dodecyl)(imino)-λ^6-sulfanone **7l** (18.1 mg, 0.05 mmol, 1 equiv.), **PC2** (0.8 mg, 0.0025 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.073 mL, 0.055 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **68** as a white solid (64% yield, 13.8 mg, 0.032 mmol).

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.19 – 2.93 (m, 2H), 2.55 (m, 2H), 2.12 (m, 2H), 2.00 (m, 2H), 1.91 (m, 2H), 1.56 (m, 2H), 1.50 – 1.38 (m, 2H), 1.26 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 57.8, 57.6, 50.3, 49.9, 49.3, 49.2, 32.0, 29.7 (t, *J* = 17 Hz), 29.5, 29.4, 29.2, 28.7, 22.8, 20.9, 14.2. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -103.1 and -104.0 (AB system, J_{AB} = 236.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{18}H_{33}BrF_2NOS^+$]: 428.1429 ($M+H^+$), found:428.1432.

N-(((S)-(3-bromobicyclo[1.1.1]pentan-1-yl)fluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (69)

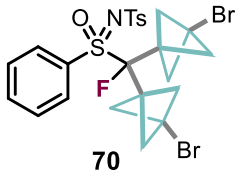


69

Compound **69** was synthesized according to the general procedure **D.3** using N-((bromofluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methyl benzenesulfonamide **7k** (40.6 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **69** as a yellowish oil (50% yield, 23.8 mg, 0.050 mmol, 1:1 mixture of diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.7 Hz, 4H), 7.81 (d, *J* = 8.2 Hz, 4H), 7.75 – 7.68 (m, 2H), 7.62 - 7.55 (m, 4H), 7.28 – 7.20 (m, 4H), 5.75 (d, *J* = 46.5 Hz, 1H), 5.65 (d, *J* = 46.8 Hz, 1H), 2.39 (s, 6H), 2.25 – 2.11 (m, 9H), 1.69 – 1.58 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 143.2, 140.6, 140.4, 135.5, 135.2, 133.9, 133.5, 129.8, 129.7, 129.6, 129.5, 129.4 (2 dia), 126.8, 126.8, 99.7 (d, *J* = 225 Hz), 99.0 (d, *J* = 227 Hz), 58.3, 58.2, 57.5 (2 dia), 53.5 – 47.1 (m, 2 dia), 40.5 (2 dia), 37.2 – 34.8 (m, 2 dia), 21.7 (2 dia). **^{19}F NMR (377 MHz, $CDCl_3$)** δ -175.0 (d, *J* = 46.0 Hz, 1F), -177.2 (d, *J* = 47.0 Hz, 1F). **HRMS (ESI$^+$):** calculated for [$C_{19}H_{20}BrFNO_3S_2^+$]: 472.0047 ($M+H^+$), found: 472.0046.

N-((bis(3-bromobicyclo[1.1.1]pentan-1-yl)fluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide (70)



70

Compound **70** was synthesized according to the general procedure **D.3** using N-((dibromofluoromethyl)(oxo)(phenyl)-λ^6-sulfanylidene)-4-methylbenzenesulfonamide **7j** (48.5 mg, 0.1 mmol, 1 equiv.), **PC2** (1.6 mg, 0.005 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (0.75 M in Et_2O, 0.15 mL, 0.11 mmol, 1.1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 8:2 hexane/EtOAc) to afford compound **70** as a yellowish oil (42% yield, 26.0 mg, 0.042 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.80 – 7.74 (m, 3H), 7.62 (t, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.36 – 2.11 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 143.5, 140.5, 135.8, 135.5, 130.5, 130.4, 129.5, 126.6, 104.3 (d, *J* = 229 Hz), 58.9 - 58.8 (m), 40.7 (d, *J* = 28 Hz), 40.4 (d, *J* = 28 Hz), 35.4 (d, *J* = 2 Hz), 35.1 (d, *J* = 2 Hz), 21.6. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -145.7 (1F). **HRMS (ESI$^+$):** calculated for [$C_{24}H_{25}Br_2FNO_3S_2^+$]: 615.9621 ($M+H^+$), found: 615.9627.

G. REACTIONS WITH ENANTIOPURE SULFOXIMINES

G.1. Separation of the enantiomers

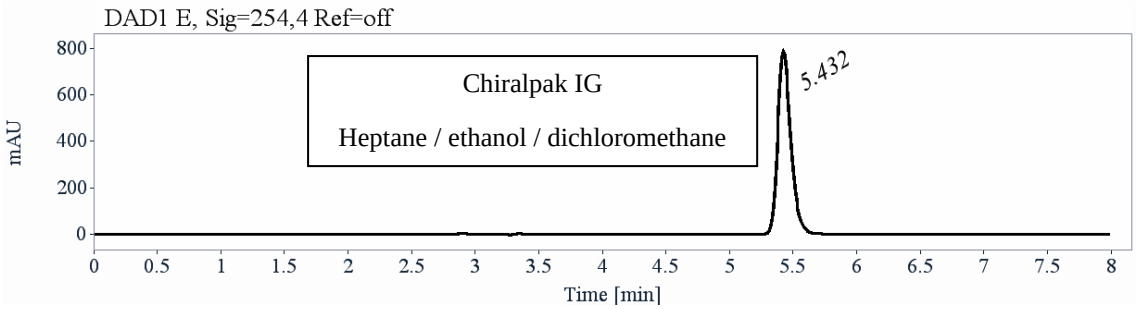
The two enantiomers of the racemic sulfoximine **13** were separated by preparative HPLC using a chiral column.

• ***Sample preparation***: About 2 g of compound **13** were dissolved in 12 mL of a mixture of hexane, ethanol and dichloromethane (60/20/20).

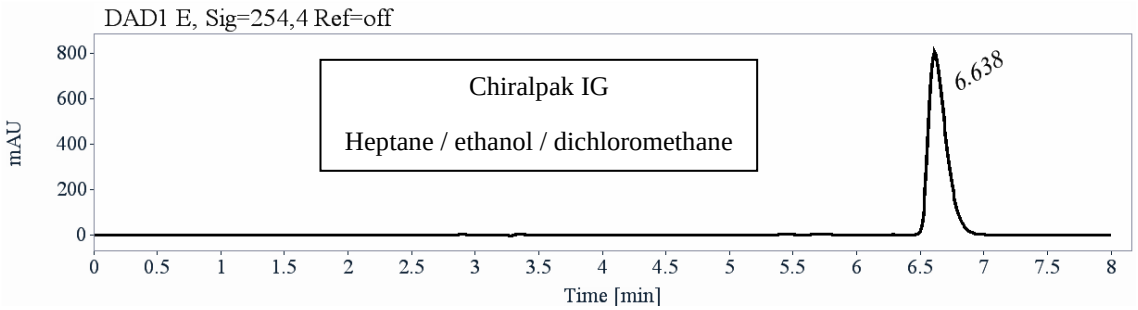
•***Chromatographic conditions:*** Lux i-Amylose-3 (250 x 10 mm), hexane / ethanol /dichloromethane (70/20/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• ***Injections:*** 120 times 100 µL, every 6 minutes.

- **First fraction**: retention time: 5.43 min; 995 mg of the first eluted enantiomer with ee > 99.5%.



- **Second fraction:** retention time: 6.64 min. 946 mg of the second eluted enantiomer with ee >99.5 %.



Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a halogen lamp (589, 578, 546, 436, 405, 365 and 325 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	**first elution on Chiralpak IG** $[\alpha]_\lambda^{25}$ **(CH_2Cl_2, c =0.21)**	**second elution on Chiralpak IG** $[\alpha]_\lambda^{25}$ **(CH_2Cl_2, c =0.39)**
589	- 12	+ 12
578	- 12	+ 12
546	- 14	+ 14
436	- 25	+ 26
405	- 33	+ 33
365	- 47	+ 49
325	- 73	+ 70

Table 13. Optical rotation of the two enantiopure sulfoximine **13**.

Electronic Circular Dichroism (ECD)

ECD and UV spectra (Figures S21 and S22, respectively) were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing. Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

- **first eluted enantiomer**: green solid line in **Figure S-S22**; concentration = 0.372 mmol/L in acetonitrile.
- **second eluted enantiomer**: red dotted line in **Figure S-S22**; concentration = 0.397 mmol/L in acetonitrile.

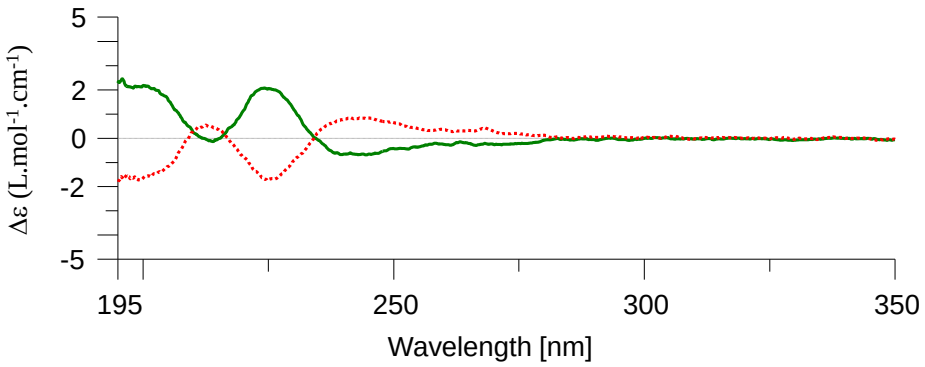


Figure S21. EDC spectrum of the two enantiomers of sulfoximine **13**.

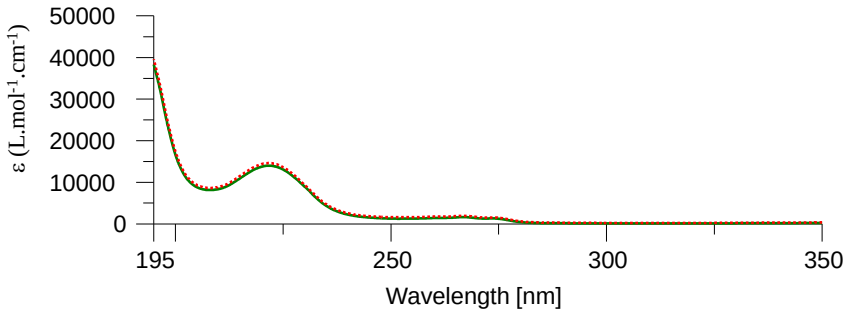


Figure S22. UV spectrum of the two enantiomers of sulfoximine **13**.

G.2. Photochemical reactions

ATRA with propellanes

The sulfoximines (-)-**13** and (+)-**13** were used in the photochemical ATRA reaction with propellane **9a**, following the general procedure **D.3.**

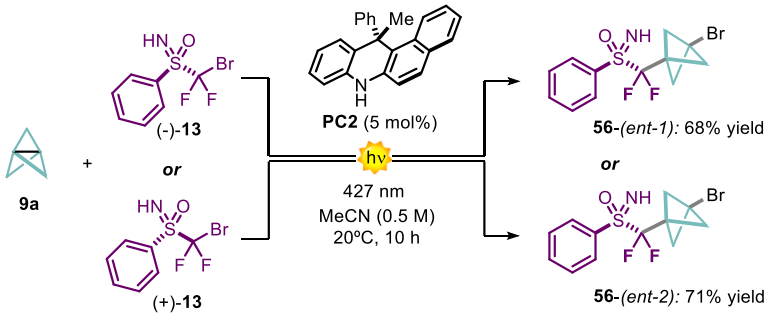
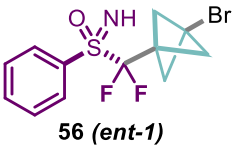


Figure S23. Photochemical ATRA reactions of enantiopure sulfoximines (-)-**13** and (+)-**13** and [1.1.1]-propellane **9a**.

Characterization Data

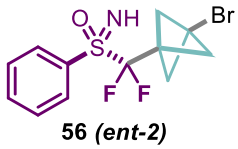
(*S*)-((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(phenyl)-λ^6-sulfanone (56 *ent-1*).



56 *(ent-1)*

Compound **56 *ent-1*** was synthesized according to the general procedure **D.3.** using (-)-(bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.01 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (1.1 M in Et_2O, 0.18 mL, 0.2 mmol, 1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% to 95:5 hexane/EtOAc) to afford compound **56 *ent-1*** as a white solid (68% yield, 45.7 mg, 0.136 mmol). The enantiomeric excess was determined by UPC^2 analysis on a Daicel Chiralpak IC3 column; isocratic method 90:10 CO_2:ACN over 5 minutes, flow rate: 3 mL/min, λ= 220 nm, τ= 2.18 min (>99.5% ee). $[\alpha]_D^{25}$ = + 2.3 (c = 1.1 in CH_2Cl_2).

(*R*)-((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(phenyl)-λ^6-sulfanone (56 *ent-2*).



56 *(ent-2)*

Compound **56 *ent-2*** was synthesized according to the general procedure **D.2.** using (+)-(bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), **PC2** (3.2 mg, 0.01 mmol, 0.05 equiv) and a [1.1.1]-propellane solution **9a** (1.1 M in Et_2O, 0.18 mL, 0.2 mmol, 1 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 95:5 hexane/EtOAc) to afford compound **56 *ent-2*** as a white solid (71% yield, 47.7 mg, 0.142 mmol). The enantiomeric excess was determined by UPC^2 analysis on a Daicel Chiralpak IC3 column; isocratic method 90:10 CO_2:ACN over 5 minutes, flow rate: 3 mL/min, λ= 220 nm, τ= 1.81 min (>99.5% ee). $[\alpha]_D^{25}$ = -5.4 (c = 1.2 in CH_2Cl_2).

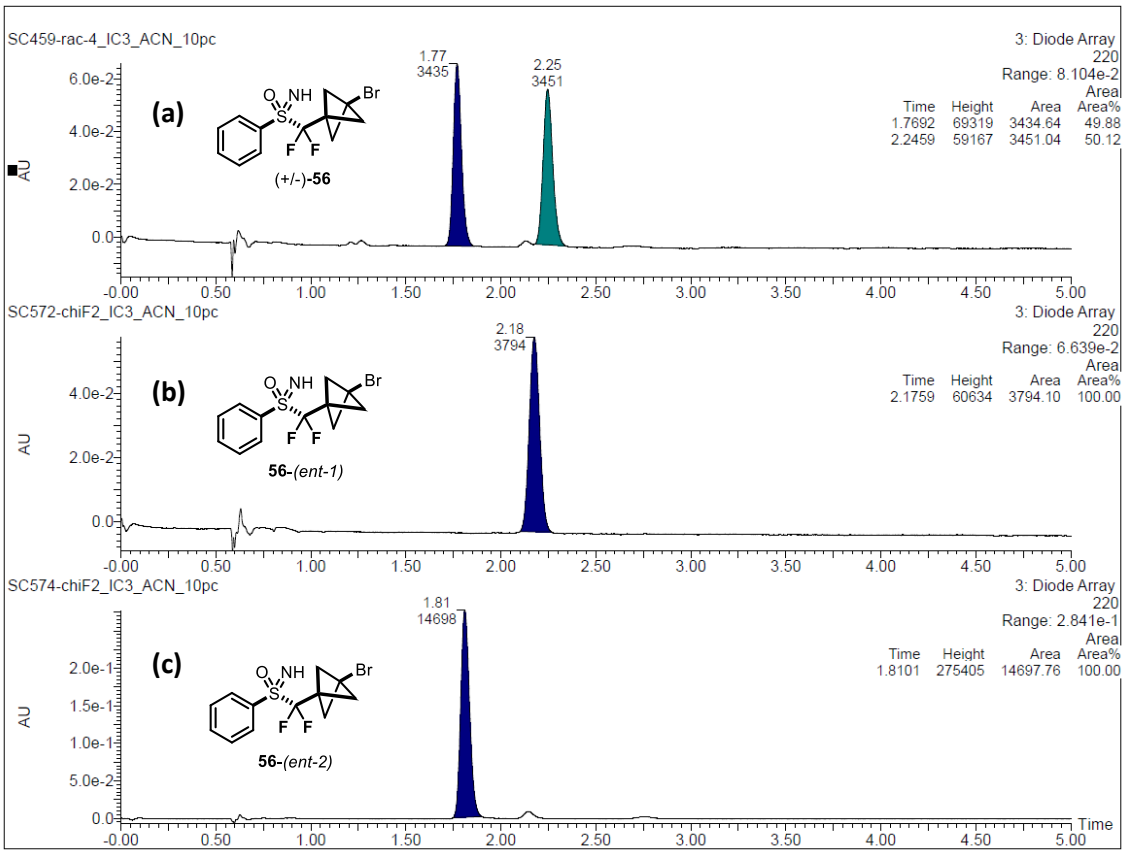


Figure S24. UPC^2 traces of **(a)** racemic **56**; **(b)** enantiopure (+)-**56**; **(c)** enantipure (-)-**56**.

Hydrofunctionalization of alkenes

The sulfoximines (-)-**13** and (+)-**13** were used in the hydrofucntionalization process with alkenes, following the general procedure **D.2.**

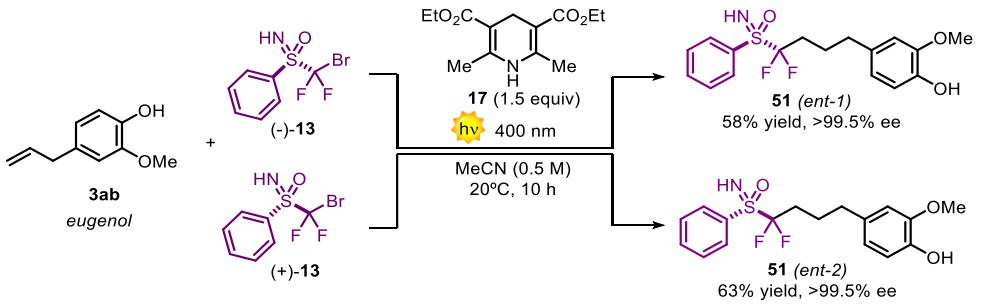
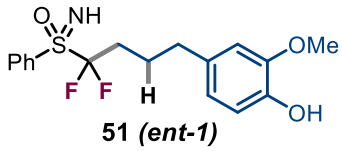


Figure S25. Photochemical hydrofunctionalization reactions of enantiopure sulfoximines (-)-**13** and (+)-**13** and eugenol **3ab.**

Characterization Data

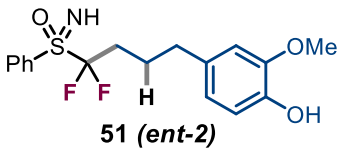
(*S*)-(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ^6-sulfanone (51 *ent-1*)



51 *(ent-1)*

Compound **51 *ent-1*** was synthesized according to the general procedure **D.2.** using (-)-(bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76.0 mg, 0.3 mmol, 1.5 equiv) and eugenol **3ab** (98.6 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **51 *ent-1*** as a yellowish oil (58% yield, 41.0 mg, 0.116 mmol). The enantiomeric excess was determined by UPC^2 analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:EtOH over 5 minutes, flow rate: 3 mL/min, λ= 220 nm, τ= 3.40 min (>99.5% ee). $[\alpha]_D^{25}$ = - 2.4 (c = 1.0 in CH_2Cl_2).

(*R*)-(1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ^6-sulfanone (51 *ent-2*)



51 *(ent-2)*

Compound **51 *ent-2*** was synthesized according to the general procedure **D.2.** using (+)-(bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), Hantzsch ester **17** (76.0 mg, 0.3 mmol, 1.5 equiv) and eugenol **3ab** (98.6 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 6:4 hexane/EtOAc) to afford compound **51 *ent-2*** as a yellowish oil (63% yield, 44.5 mg, 0.126 mmol). The enantiomeric excess was determined by UPC^2 analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:EtOH over 5 minutes, flow rate: 3 mL/min, λ= 220 nm, τ= 2.92 min (>99.5% ee). $[\alpha]_D^{25}$ = + 1.2 (c = 1.1 in CH_2Cl_2).

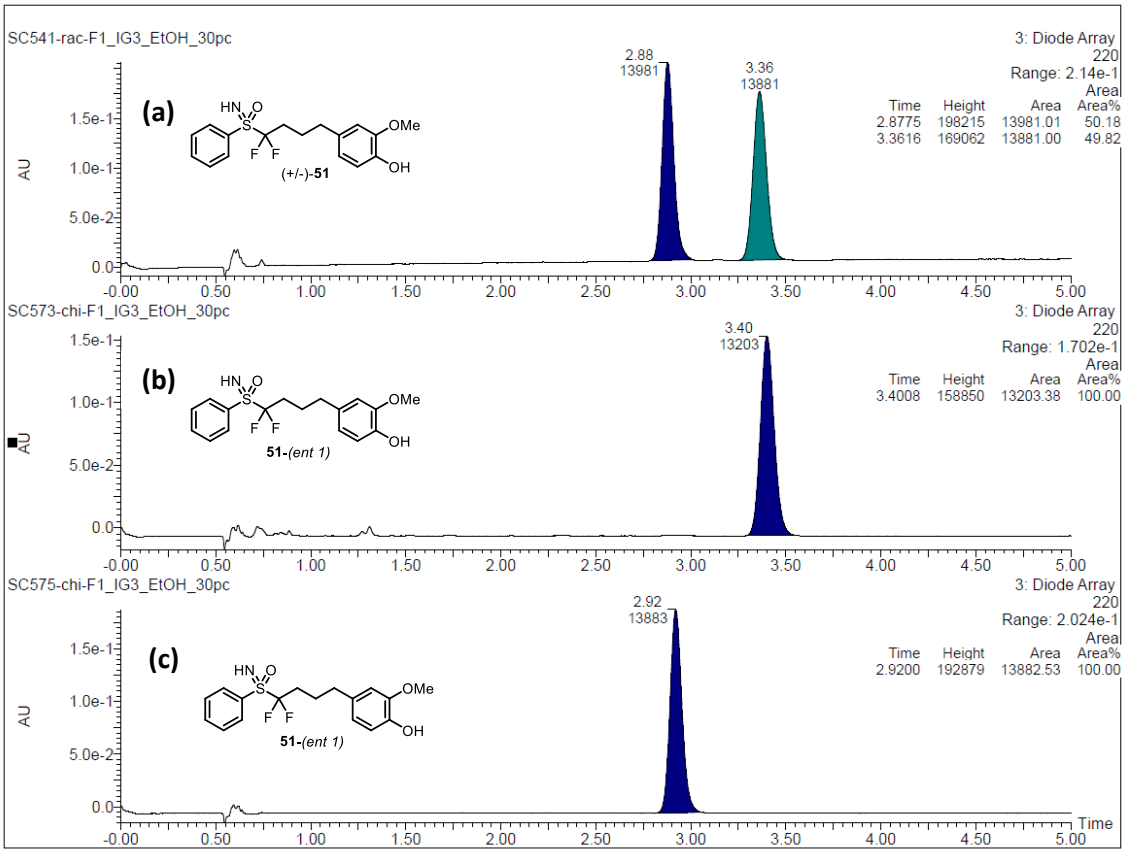


Figure S26. UPC^2 traces of **(a)** racemic **51**; **(b)** enantiopure (+)-**51**; **(c)** enantipure (-)-**51**.

ATRA with alkenes

The sulfoximines (-)-**13** and (+)-**13** were used in the photochemical ATRA process with alkenes, following the general procedure **D.1.**

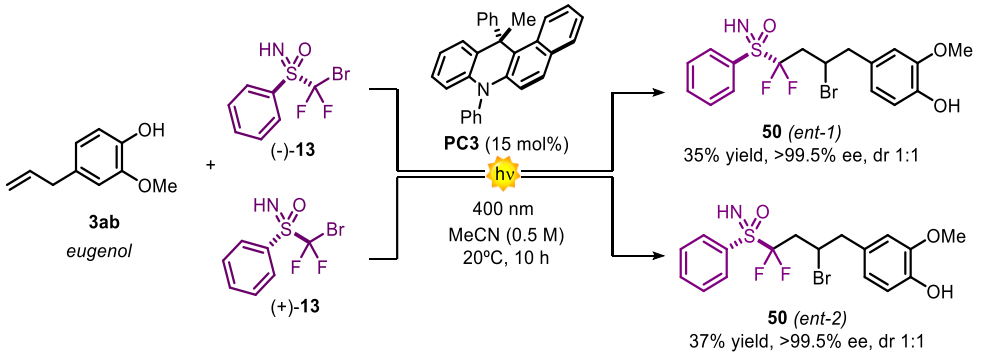
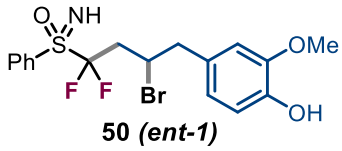


Figure S27. Photochemical ATRA reactions of enantiopure sulfoximines (-)-**13** and (+)-**13** and eugenol **3ab**.

Characterization Data

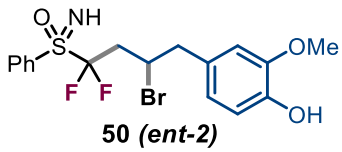
(1*S*)-(3-bromo-1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ⁶-sulfanone (50 *ent-1*)



50 *(ent-1)*

Compound **50 *ent-1*** was synthesized according to the general procedure **D.1.** using (-)-(bromodifluoromethyl)(imino)(phenyl)-λ⁶-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv) and eugenol **3ab** (98.5 mg, 0.6 mmol, 3 equiv.). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **50 *ent-1*** as a yellowish oil (34% yield, 29.8 mg, 0.068 mmol; 1:1 mixture of diastereoisomers). The enantiomeric excess was determined by UPC² analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 210 nm, τ= 2.75 min (>99.5% ee).

(1*R*)-(3-bromo-1,1-difluoro-4-(4-hydroxy-3-methoxyphenyl)butyl)(imino)(phenyl)-λ⁶-sulfanone (50 *ent-2*)



50 *(ent-2)*

Compound **50 *ent-2*** was synthesized according to the general procedure **D.1.** using (+)-(bromodifluoromethyl)(imino)(phenyl)-λ⁶-sulfanone **13** (54.0 mg, 0.2 mmol, 1 equiv.), eugenol **3ab** (98.5 mg, 0.6 mmol, 3 equiv.) and **PC3** (11.9 mg, 0.03 mmol, 0.15 equiv). Reaction time: 10 h. The crude was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to afford compound **50 *ent-2*** as a yellowish oil (35% yield, 30.3 mg, 0.069 mmol; 1:1 mixture of diastereoisomers). The enantiomeric excess was determined by UPC² analysis on a Daicel Chiralpak IG3 column; isocratic method 70:30 CO_2:MeOH over 5 minutes, flow rate: 3 mL/min, λ= 210 nm, τ= 2.55 min (>99.5% ee).

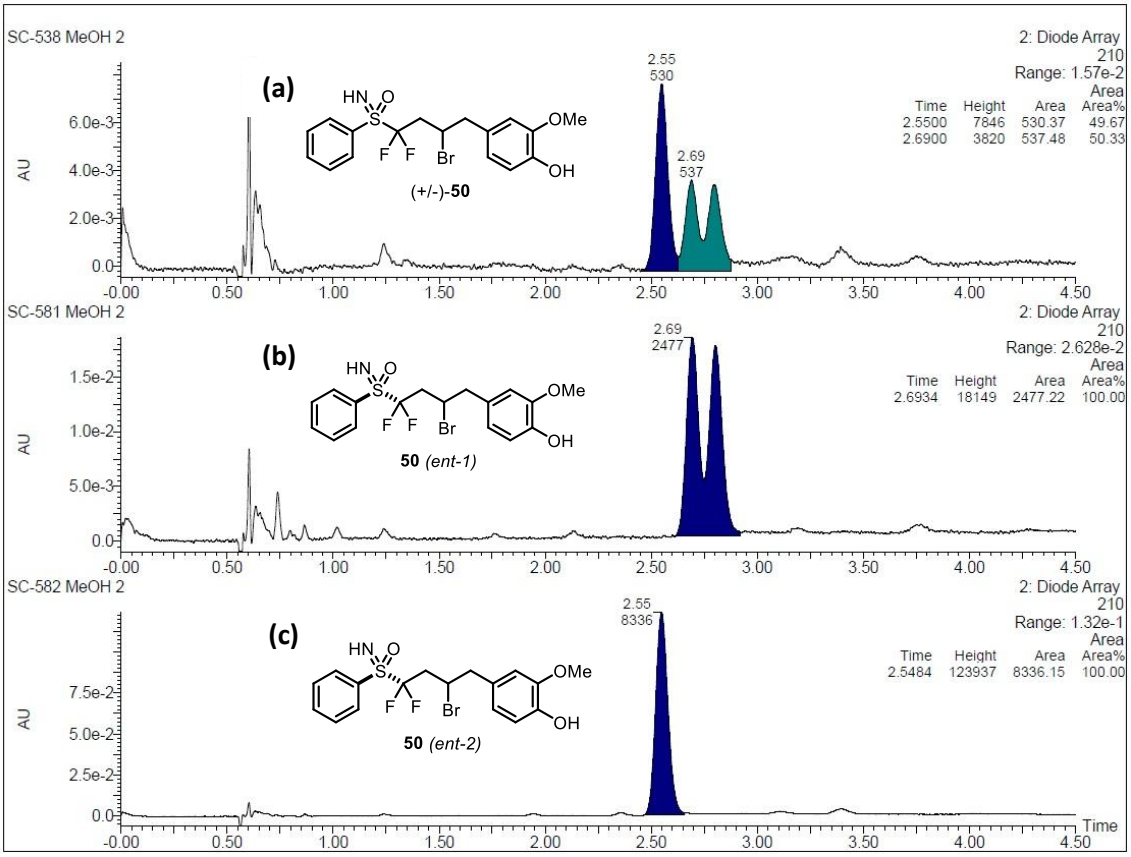


Figure S28. UPC^2 traces of **(a)** racemic **50**; **(b)** compound **50** ***(ent-1)***; **(c)** compound **50** ***(ent-2)***.

H. X-RAY CRYSTALLOGRAPHIC DATA

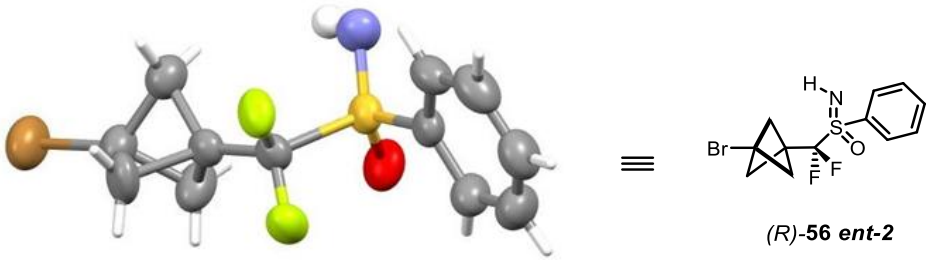
Colorless crystals of **56** ***(ent-2)*** were grown by slow evaporation of a dichloromethane solution at ambient temperature.

Single crystal data were collected with a Bruker D8 Venture diffractometer equipped with a Photon II area detector and an Oxford Cryostream 800 low temperature device (T = 200K) using a CuKα microfocus radiation source (λ = 1.54178 Å). The data collection strategy, Φ and Ω scan, covered the whole limit sphere of the reciprocal space. Data were indexed, integrated, and scaled using the CrysAlisPRO software. The structures were solved by the dual space algorithm implemented in the SHELXT code in Olex2. Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F2 implemented in SHELXL-2014. For all the structures, anisotropic displacement parameters were refined except for hydrogen atoms.

CCDC 2364218 contains the supplementary crystallographic data for the compounds **56** ***(ent-2)***. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by

emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

H.1. Single Crystal X-ray Diffraction Data for the Compound 56 (ent-2)



(R)-**56** ***ent-2***

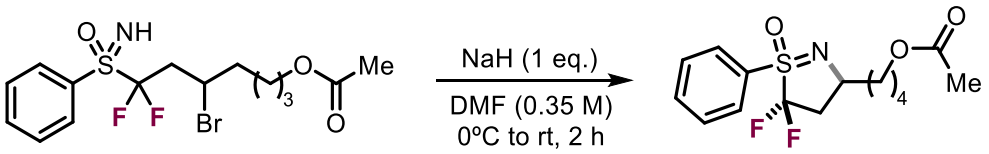
CCDC 2364218

Crystal data: $C_{12}H_{12}BrF_2NOS$ Triclinic, *P1*, a = 9.5072(6)Å, b = 11.2492(7)Å, c = 13.1335(9)Å, α = 92.018(3)°, β = 92.253(3)°, γ = 106.884(3)°, V = 1341.42(15)Å^3, Z=4; ρ_{calc}=1.665 g/cm^3, μ = 5.764 mm^{-1}, F(000)= 672, Θ range for data collection = 3.372 - 70.054°, Index range = -11<h<11, -13<k<13, -15<l<15; Reflections collected = 59085, Unique reflections = 9857, Parameters = 674, Goodness-of-fit on F^2 = 1.055, Flack parameter = 0.01(2) (Sulfur configuration R), Final R indexes [I>=2σ (I)]: R=0.059, wR2=0.1699.

I. PRODUCT DERIVATISATIONS

I.1. Cyclization reactions

I.1.1 Synthesis of 4-((3S)-5,5-difluoro-1-oxido-1-phenyl-4,5-dihydro-3H-1λ^6-isothiazol-3-yl)butyl acetate (71)



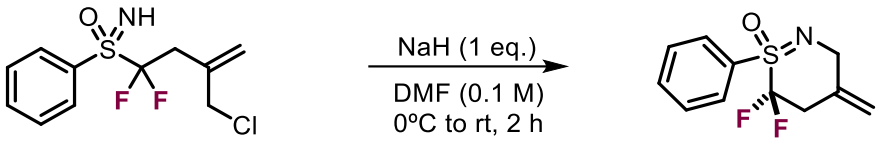
21 (1:1 dr) **71** (1:1 dr)

In a 5 mL round bottom flask, sulfoximine **21** (160.2 mg, 0.39 mmol, 1.0 equiv.) is dissolved in dry DMF (1.1 mL) and the solution was cooled at 0°C with an ice bath. NaH (15.5 mg, 60% disperiosn in mineral oil, 0.39 mmol, 1 equiv.) is added portion-wise to the solution which is then allowed to reach rt and stirred for 2h. Subsequently, the excess of NaH in the mixture is quenched at 0°C with slow addition of water (10 mL) and extracted with EtOAC (2 x 10 mL). The combined organic layers are washed with an aqueous solution of LiCl 1M (5 x 10mL), dried over $MgSO_4$

and concentrated under reduced pressure. The residue was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to give product **71** as a yellowish oil (25% yield, 32.4 mg, 0.098 mmol, 1:1 mixture of diasteroisomers).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (t, *J* = 6.7 Hz, 4H), 7.77 – 7.67 (m, 2H), 7.61 – 7.55 (m, 4H), 4.12 – 4.05 (m, 4H), 2.90 – 2.51 (m, 2H), 2.46 – 2.06 (m, 2H), 2.03 (s, 6H), 1.85 – 1.61 (m, 12H), 1.58 – 1.48 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3 (2 dia), 135.1 (2 dia), 132.1 (2 dia), 131.9 (t, *J* = 303 Hz, 2 dia), 131.4 (2 dia), 129.4 (2 dia), 64.5, 64.4, 60.8, 60.7, 59.6 (dd, *J* = 6 and J = 4 Hz, 2 dia), 39.4, 38.4, 37.4 (dd, *J* = 22 and 19 Hz), 36.0 (dd, *J* = 21 and 17 Hz), 28.6, 28.5, 22.8, 22.7, 21.10 (2 dia). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -92.2 and -98.8, (AB system, J_{AB} = 201.0 Hz, 2F), -98.0 and -104.5 (AB system, J_{AB} = 198.0 Hz, 2F). **HRMS (ESI^+):** calculated for [$C_{15}H_{20}F_2NO_3S^+$]: 332.1126 ($M+H^+$); found: 332.1216.

I.1.2 Synthesis of 6,6-difluoro-4-methylene-1-phenyl-3,4,5,6-tetrahydro-1,2-thiazine 1-oxide (72)



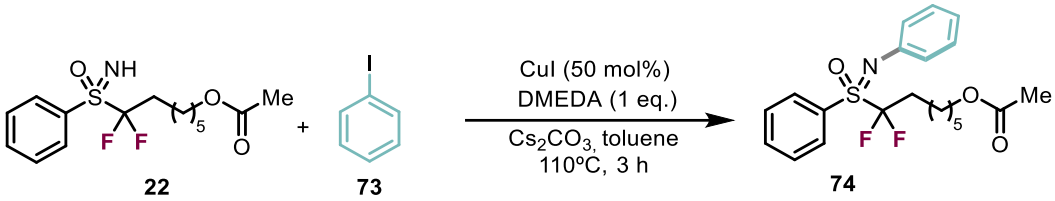
39 **72**

In a 10 mL round bottom flask, sulfoximine **39** (67.1 mg, 0.24 mmol, 1.0 equiv.) is dissolved in dry DMF (2.4 mL) and the solution was cooled at 0°C with an ice bath. NaH (9.6 mg, 60% dispersion in mineral oil, 0.24 mmol, 1 equiv.) is added portion-wise to the solution which is then allowed to reach rt and stirred for 2h. Subsequently, the excess of NaH in the mixture is quenched at 0°C with slow addition of water (10 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layers are washed with an aqueous solution of LiCl 1M (5 x 10mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to give product **72** as a yellowish oil (55% yield, 32.3 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.5 Hz, 2H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 2H), 5.05 (d, *J* = 53.7 Hz, 2H), 4.24 (d, *J* = 14.1 Hz, 1H), 3.89 (dt, *J* = 14.0, 2.0 Hz, 1H), 3.51 – 3.37 (m, 1H), 3.11 – 3.02 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 137.8, 135.0, 131.2, 130.6, 129.2, 119.5 (dd, *J* = 303 and 287 Hz), 116.0, 48.8, 40.4 (dd, *J* = 22 and 19 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -102.1 and -103.6 (AB system, J_{AB} = 221.8 Hz, 2F). **HRMS** (ESI^+): calculated for [$C_{11}H_{12}F_2NOS^+$]: 244.0602 ($M+H^+$); found: 244.0912.

I.2. N-functionalization

I.2.1. Synthesis of 7,7-difluoro-7-(N-phenylphenylsulfonimidoyl)heptyl acetate (74)

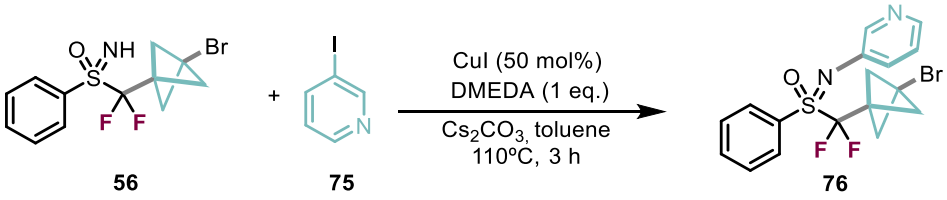


22 73 74

Compound **74** was synthesized following a method previously reported in the literature:[32] under Argon atmosphere a dry Schlenk tube was charged with sulfoximine **22** (50.0 mg, 0.15 mmol, 1.0 equiv.), iodobenzene **73** (33 µL, 0.3 mmol, 2.0 equiv.), CuI (14.3 mg, 0.075 mmol, 0.5 equiv.), DMEDA (16 µL, 0.15 mmol, 1 equiv.), Cs_2CO_3 (122.2 mg, 0.375 mmol, 2.5 equiv.), and degassed toluene (0.6 mL). After heating to 110 °C for 3 h, the mixture was cooled to room temperature and neutralized with aqueous HCl (5 mL at 1 M). The aqueous layer was extracted with dichloromethane (3x 10mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by automated flash column chromatography (gradient from 100% hexane to 7:3 hexane/EtOAc) to give product **74** as a yellowish oil (87% yield, 53.3 mg, 0.13 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.09 (d, *J* = 7.1 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 4.03 (t, *J* = 6.6 Hz, 2H), 2.49 – 2.15 (m, 2H), 2.04 (s, 3H), 1.64 – 1.56 (m, 4H), 1.47 – 1.27 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.3, 143.2, 134.5, 132.8, 131.4, 129.4, 129.2, 125.5 (t, *J* = 289 Hz), 123.8, 122.7, 64.4, 30.4 (t, *J* = 20 Hz), 28.8, 28.4, 25.6, 21.1. **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -99.0 and -102.5 (AB system, J_{AB} = 217.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{21}H_{26}F_2NO_3S^+$]: 410.1596 ($M+H^+$); found: 410.1686.

I.2.2. ((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(phenyl)(pyridin-3-ylimino)-λ^6-sulfanone (76)



56 75 76

Compound **76** was synthesized following a method previously reported in the literature with modification:[32] under Argon atmosphere a dry Schlenk tube was charged with sulfoximine **56** (0.12 mmol, 1.0 equiv.), 3-iodopyridine **75** (98.4 mg, 0.48 mmol, 4.0 equiv.), CuI (11.4 mg, 0.06 mmol, 0.5 equiv.), DMEDA (13 µL, 0.12 mmol, 1 equiv.), Cs_2CO_3 (97.8 mg, 0.3 mmol, 2.5

equiv.), and degassed toluene (0.6 mL). After heating to 110 °C for 3 h, the mixture was cooled to room temperature and neutralized with aqueous HCl (5 mL at 1 M). The aqueous layer was extracted with dichloromethane (3x 10mL). The combined organic layers were washed with an aqueous solution of ETDA 0.2 M (3 x 10mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by automated flash column chromatography (gradient from 100% DCM to 95:5 DCM/MeOH) to give product **76** as a yellowish oil.

NOTE: product **76** was obtained using as starting material a sample of ((3-bromobicyclo[1.1.1]pentan-1-yl)difluoromethyl)(imino)(phenyl)-λ^6-sulfanone **57** that was contaminated at a ratio of 100:16 with the analogous staffane derivative **57'**. The yield of product **76** was corrected considering the presence of this byproduct (50% yield, 29.6 mg, 0.06 mmol of product **76**).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.21 (d, *J* = 4.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 8.2 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 1H), 7.12 – 7.09 (m, 1H), 2.47 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 145.3, 143.8, 135.2, 131.1, 130.2, 129.7, 123.8, 119.6 (dd, *J* = 292 and 286 Hz), 58.0 (t, *J* = 3 Hz), 50.2 (t, *J* = 3 Hz), 38.5 (t, *J* = 29 Hz). **^{19}F NMR decoupled ^{1}H (377 MHz, $CDCl_3$)** δ -98.3 and -101.1 (AB system, J_{AB} = 232.0 Hz, 2F). **HRMS (ESI$^+$):** calculated for [$C_{17}H_{16}BrF_2N_2OS^+$]: 413.0129 ($M+H^+$); found: 413.0202.

J. EPR SPIN TRAPPING EXPERIMENTS

EPR measurements were carried out at room temperature on a Bruker EMX spectrometer operating at X band. The instrument settings used for spectral acquisition were as follows: modulation frequency, 100kHz; microwave power, 20 mW; modulation amplitude, 0.9 G; receiver gain, 104; time constant, 10.24 ms; sweep width, 80 G; sweep time, 5.25 s; 4 scans. All the EPR spectra recorded were simulated using the Winsim software elaborated by Dulling [33] and provided free to the EPR research community by the NIEHS.

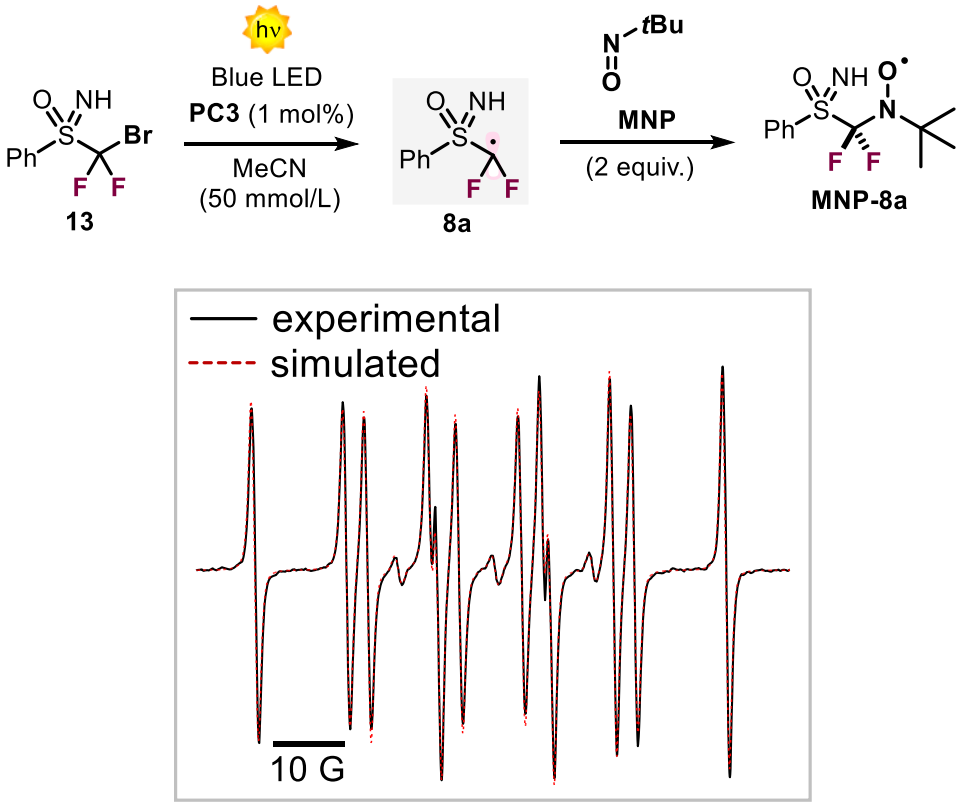


Figure S29. EPR spin trapping experiment with sulfoximine **13**.

All the spin trapping assays were carried out at room temperature in acetonitrile (MeCN). A sample containing the sulfoxime **13** (50 mmol/L), the photocatalyst **PC3** (0.5 mmol/L) and the spin trap **MNP** (100 mmol/L) was prepared in MeCN (500µL). An aliquot was then transferred into a glass capillary tube and irradiated with blue LED directly into the EPR cavity.

The EPR spectra recorded under or after irradiation (with a virtually perfect superimposition with the simulated spectra, red dotted line in Figure S29) revealed the presence of two paramagnetic species. The major one (over 90% whatever the spectrum) was assigned to the **MNP-8a** spin adduct, on the basis of its hyperfine coupling constant values (a_N =11.6G, a_{F1} = 22.1 G and a_{F2} = 14.2 G). The minor species (always lower than 10%) showed only three lines, due to a single hyperfine coupling of the unpaired electron with a nitrogen nucleus (a_N = 12.3 G). Neither of these two paramagnetic species was observed in the absence of **13**, photocatalyst **PC3**, **MNP** or light. Although the minor species could not be identified on the basis of a single hyperfine coupling constant, these blank tests clearly showed that it corresponded to a second adduct derived from sulfoxime **13**.

K. MECHANISTIC INSIGHTS

K.1. Absorption spectrum

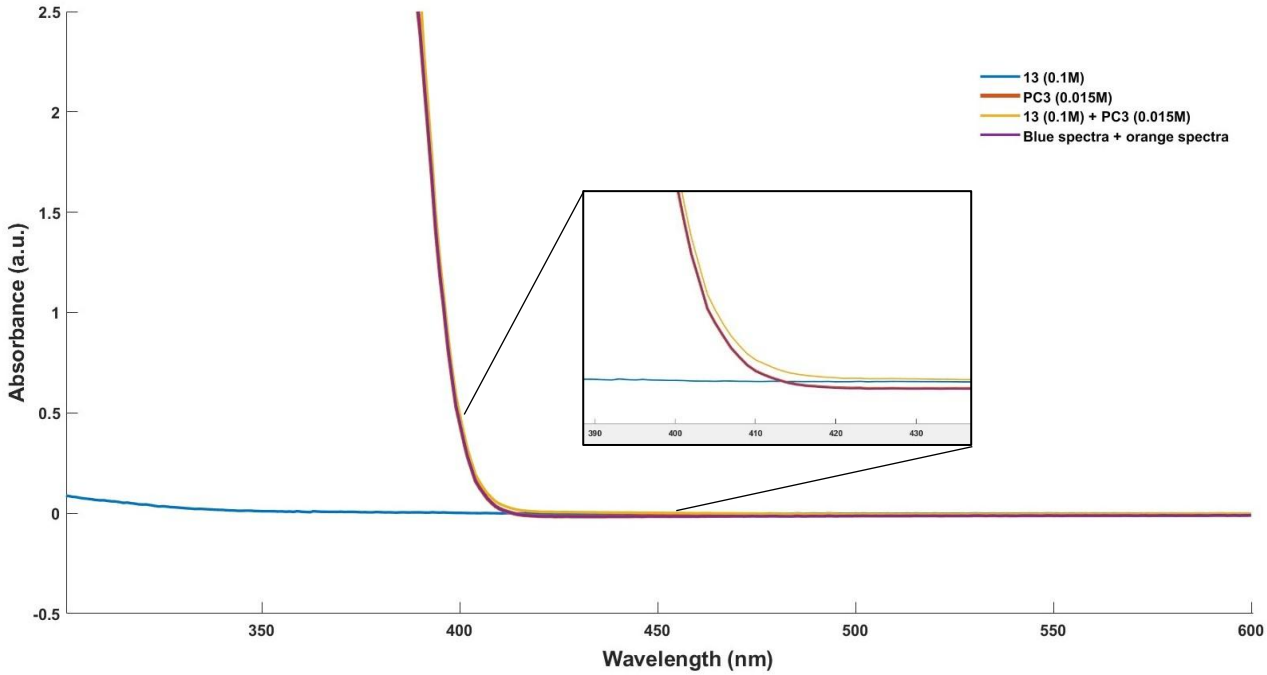


Figure S30. Optical absorption spectra of the sulfoximine **13** (blue line), the acridine catalyst **PC3** (red line) and the mixture of the acridine catalyst **PC3** with the sulfoximine **13** (yellow line). [**13**] = 0.1 M in CH_3CN, [**PC3**] = 0.015 M in CH_3CN. Recorded in quartz cuvettes, 1 mm path.

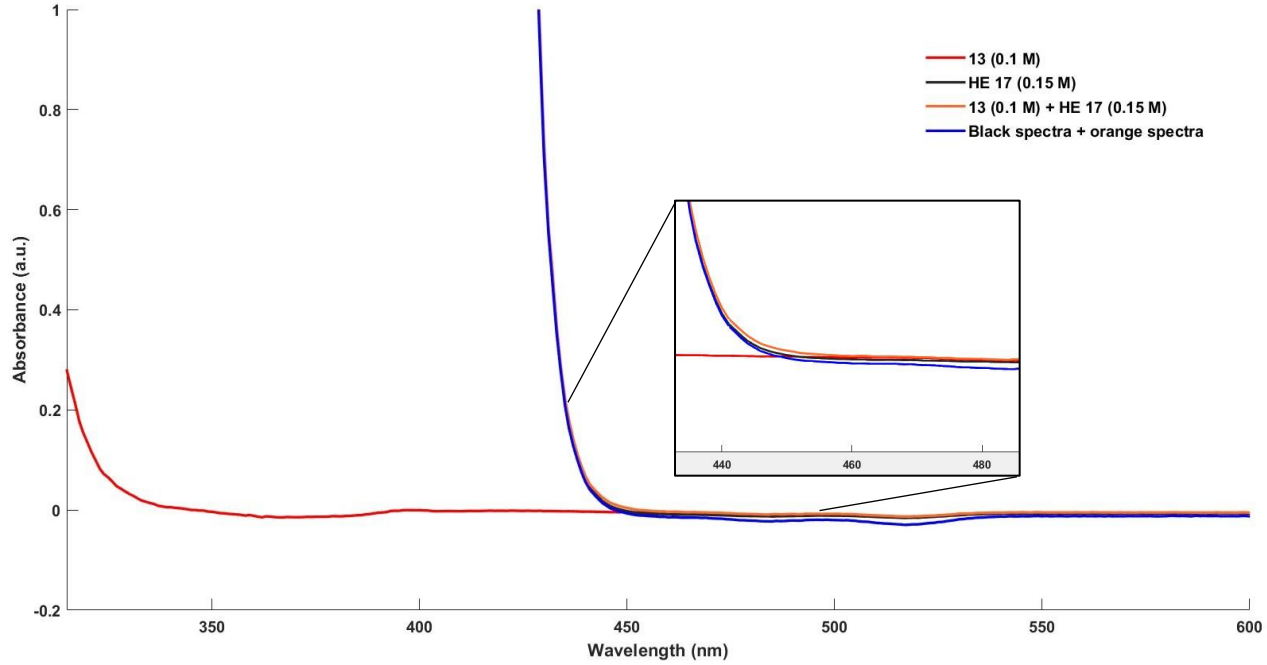


Figure S31. Optical absorption spectra of the sulfoximine **13** (red line), Hantzsch ester **17** (black line) and the mixture of **HE 17** and **13** (orange line). [**13**] = 0.1 M in DMF, [**PC3**] = 0.15 M in DMF. Recorded in quartz cuvettes, 1 mm path.

K.2. Cyclic voltammetry measurements

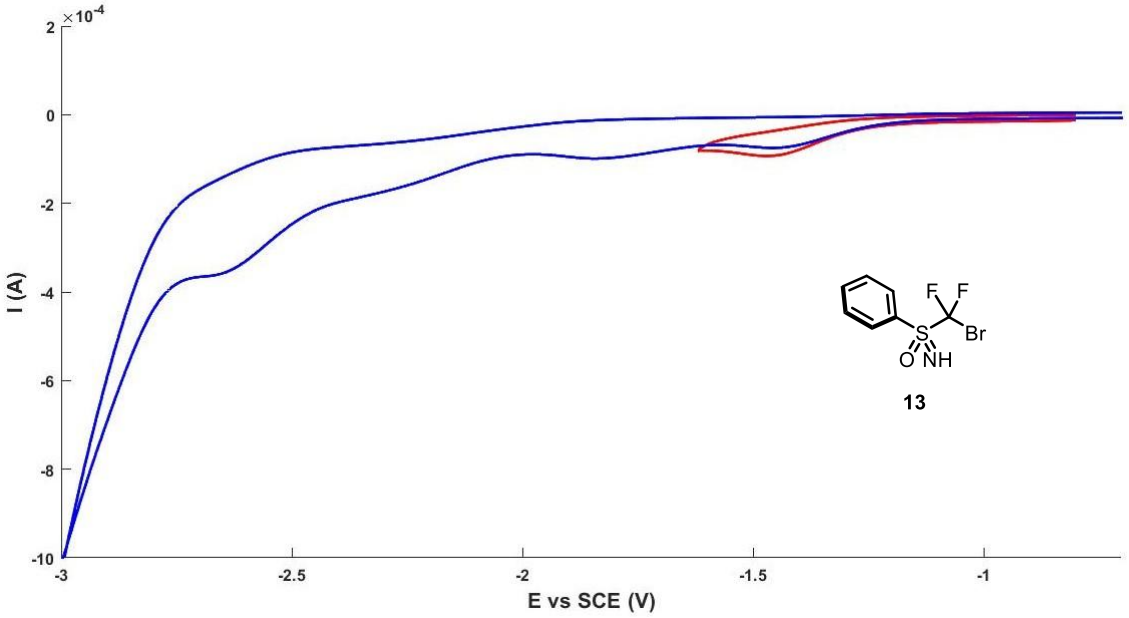


Figure S32. Cyclic voltammogram for compound **13** (5mM) in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Pt auxiliary electrode. Irreversible reduction, $E_p^C = E^{red}$(**13**/**13**$^{\bullet-}$) = -1.57 vs SCE. E_p^C refers to the cathodic peak potential, while the E^{red} value describes the electrochemical properties of **13**.

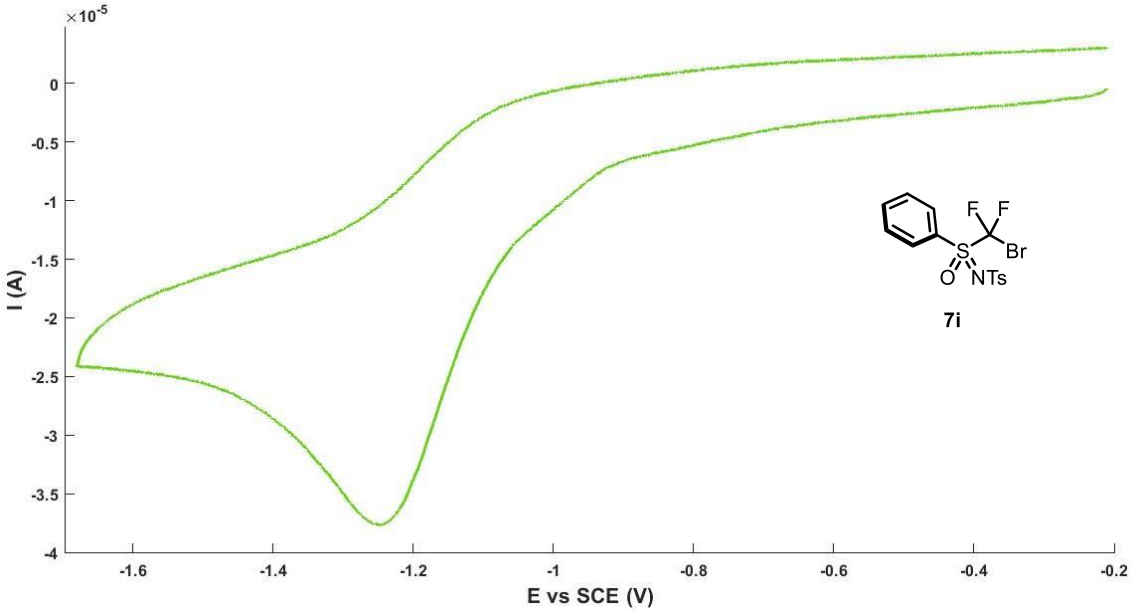


Figure S33. Cyclic voltammogram for compound **7i** (1mM) in $TBAPF_6$ in CH_3CN (0.1 M). Scan rate: 0.1 V/s. Glassy carbon working electrode; Ag/AgCl (3M, NaCl) reference electrode; Pt auxiliary electrode. Irreversible reduction, $E_p^C = E^{red}$(**7i**/**7i**$^{\bullet-}$) = -1.24 vs SCE. E_p^C refers to the cathodic peak potential, while the E^{red} value describes the electrochemical properties of **7i.**

K.3. Quantum yield measurement

A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in *Handbook of Photochemistry*.[34] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline (complete complexation takes about an hour), and monitored by UV/Vis absorbance at 510 nm.[35] The moles of iron-phenanthroline complex formed are related to moles of photons absorbed.

Actinometry

The following solutions were prepared and stored in the dark:

A) 20 mL of 1,10-phenantroline 0.2% by weight in water

B) Buffer solution:

a. 8.2 g $NaOAc \cdot H_2O$

b. 1 mL concentrated H_2SO_4 (98%)

c. Diluted to 100 mL with water

C) $Fe_2(SO_4)_3$ solution:

a. 10 g $Fe_2(SO_4)_3 \cdot nH_2O$ (approximately 20% Fe by weight)

b. 5.5 mL concentrated H_2SO_4 (98%)

c. Diluted to 100 mL with water

D) 100 mL of $K_2C_2O_4$ 1.2 M in water

The actinometric solution ($K_3Fe(C_2O_4)_3$ solution) was prepared in the dark by mixing 0.5 mL of $Fe_2(SO_4)_3$ solution with 0.5 mL of $K_2C_2O_4$ solution in a volumetric flask and diluting to 10 mL. The $K_3Fe(C_2O_4)_3$ solution was stored in the dark. The actinometric measurements were done as follows for the two Kessil lamp:

1) 1 mL of the $K_3Fe(C_2O_4)_3$ solution was added to a quartz cuvette with 1 cm optical path.

2) The cuvette was irradiated under stirring with a PR160L Kessil lamp (427 nm or 400 nm) set at 25% of its maximum output power placed at a distance of 20 cm for increasing amount of time (5, 10, 20, 30 and 45 seconds). *Note: since the absorbance of the $K_3Fe(C_2O_4)_3$ solution at 427 nm is greater than 2, all the incident photons are absorbed, and no correction factors shall be applied in the following calculations*.

3) All the irradiated solution was transferred to a 10 mL volumetric flask, to which 2 mL of the 0.2% 1,10-phenantroline solution and 0.5 mL of the buffer solution were added. The flask was filled to the mark with water and the content thoroughly mixed.

4) A blank sample was prepared repeating step 3) with 1 mL $K_3Fe(C_2O_4)_3$ solution kept in the dark without irradiation.

5) The absorbances at 510 nm of the solutions prepared according to step 3) at increasing time intervals were measured and their difference with the blank ΔA was calculated (Figures S34 and S35). The absorbance at 510 nm of the blank was lower than A = 0.06 as recommended for both the measurement with the two Kessil lamp.

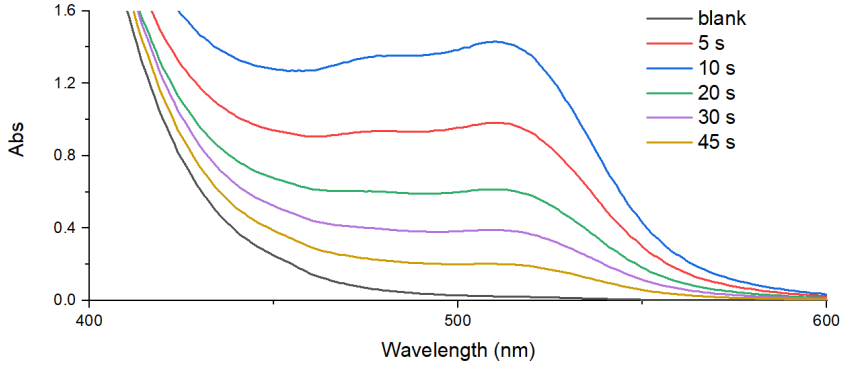


Figure S34. Absorbance spectra of the solutions prepared according to step 3 at increasing time intervals for the 427 nm Kessil lamp.

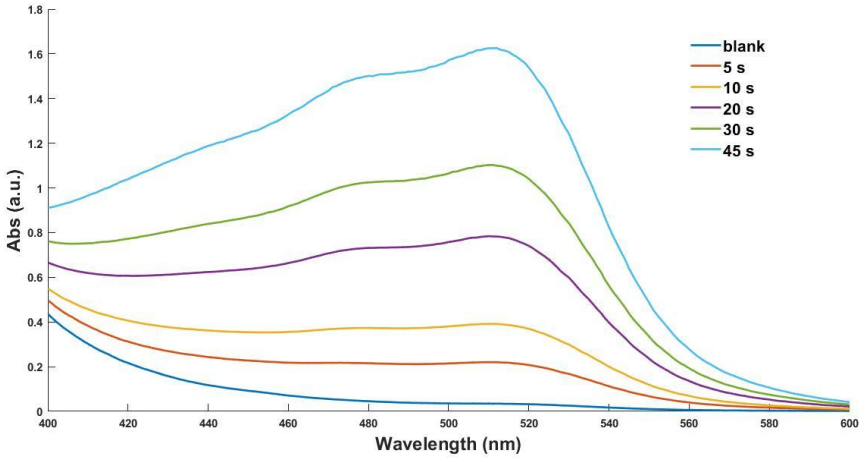


Figure S35. Absorbance spectra of the solutions prepared according to step 3 at increasing time intervals for the 400 nm Kessil lamp.

The values of ΔA obtained were plotted as a function of the irradiation time (5, 10, 20, 30 and 45 seconds) and linearly interpolated with the following function:

$$\Delta A = \frac{\varepsilon b \varphi V_1 I}{V_2 V_3} t$$

where:

ΔA: are the values obtained at each time interval in Step 5)

b: is the path length of the cuvette

ε: is the extinction coefficient of Fe-1,10-phenantroline complex at 510 nm ($1.11 \cdot 10^4$ M^{-1} cm^{-1})

φ: is the quantum yield of ferrous production at 427 or 400 nm (1.04 and 1.07 respectively)

V_1: is the volume in mL of irradiated $K_3Fe(C_2O_4)_3$ solution transferred to the 10 mL flask (1 mL)

V_2: is the volume in L of irradiated $K_3Fe(C_2O_4)_3$ solution (0.001 L)

V_3: is the volume in mL of the volumetric flask used for workup of irradiated aliquots (10 mL)

I: is the photon flux in einsteins s^{-1} (moles of photons s^{-1})

t: is the irradiation time in seconds

From the slope of the interpolation (Figure S36), the light intensity was thus calculated to be **I = $2.67 \cdot 10^{-8}$ mol s^{-1}** for the **427 nm** Kessil lamp.

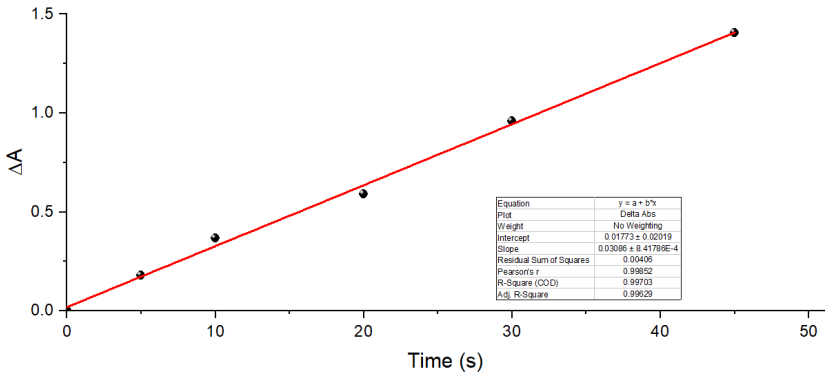


Figure S36. Plot and linear interpolation of the values of ΔA obtained according to step 5 for the **427 nm** Kessil lamp.

From the slope of the interpolation (Figure S37), the light intensity was thus calculated to be **I** = **3.01·10^{-8} mol s^{-1}** for the **400 nm** Kessil lamp.

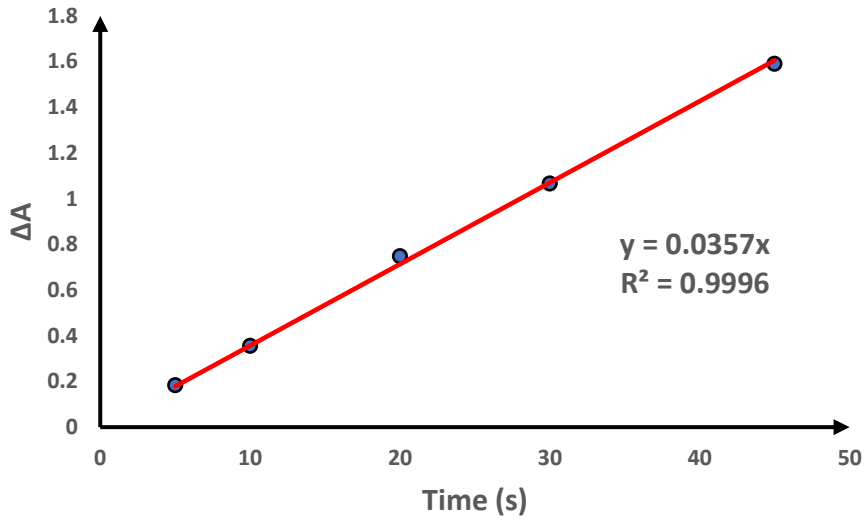
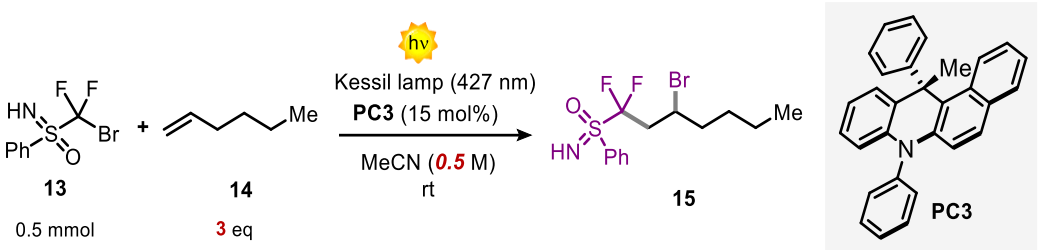


Figure S37. Plot and linear interpolation of the values of ΔA obtained according to step 5 for the **400 nm** Kessil lamp.

Quantum yield of the ATRA reaction



The same cuvette used for actinometry was charged with **13** (135 mg, 0.5 mmol, 1 eq) and the **PC3** (30 mg, 0.075 mmol, 15 mol%). The cuvette was capped with a septum and degassed with argon. 1 mL of dry and degassed MeCN were added, followed by **14** (188 µL, 1.5 mmol, 3 eq). 61 µL of $PhCF_3$ were finally added as the internal standard. The absorbance of the reaction mixture was then measured (Figure S38).

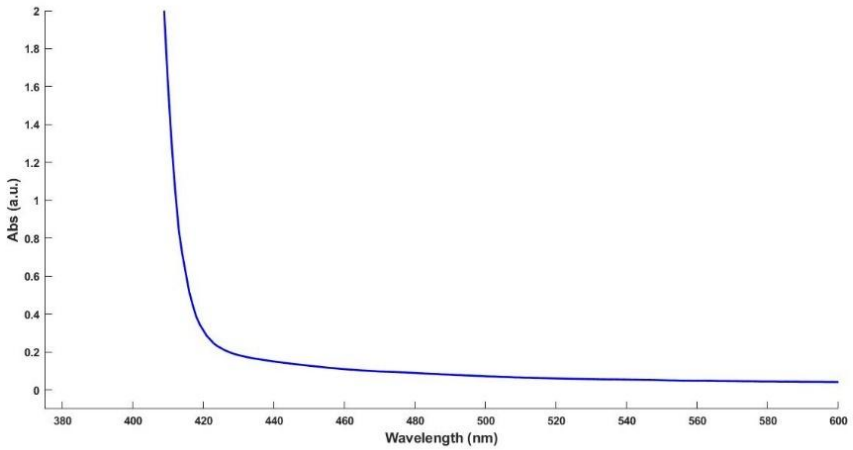


Figure S38. Absorption profile of the model reaction mixture.

The absorbance of the reaction mixture at 427 nm is **0.20**. The fraction of light absorbed (*f*) can be calculated according to $\boldsymbol{f} = 1\text{-}10^{-Abs} = 1\text{-}10^{-0.20}$ **=0.37**. Hence, the reaction mixture only absorbs 37% of the incident photons, and the effective photon flux is calculated correcting the photon flux obtained from actinometry, according to $\mathbf{I_{eff}} = f \times I = 0.37 \times 2.67 \cdot 10^{-8}$ mol s^{-1} = $\mathbf{9.95 \cdot 10^{-9}}$ **mol** $\mathbf{s^{-1}}$

The cuvette was irradiated with the same setup as in step 2 of the actinometric measurements. 50 µL aliquots of the reaction were sampled after 3, 4, 5 and 6 hours of irradiation, diluted with 500 µL of $CDCl_3$ and analyzed by ^{19}F NMR to determine the yield. The yield values (mmols of product formed) at given time intervals were plotted against the mmols of photons absorbed by the reaction mixture (obtained by multiplication of the effective photon flux with the irradiation time in seconds). The plot was linearly interpolated and the slope of the interpolation is, by definition, the quantum yield of the reaction (Figure S39). The value of quantum yield is then **0.2.**

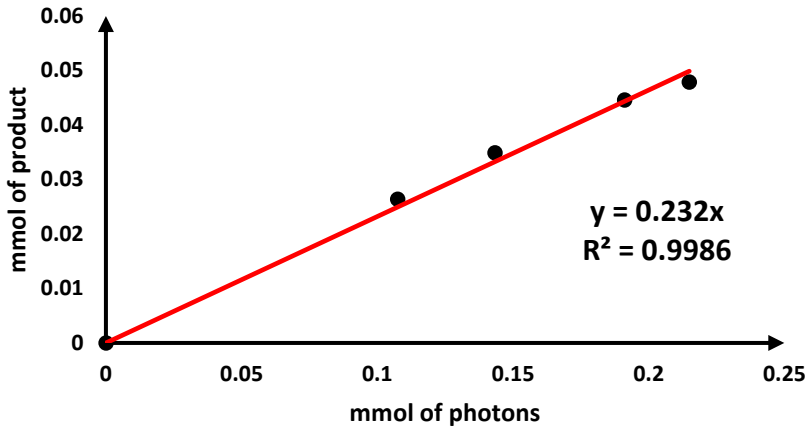
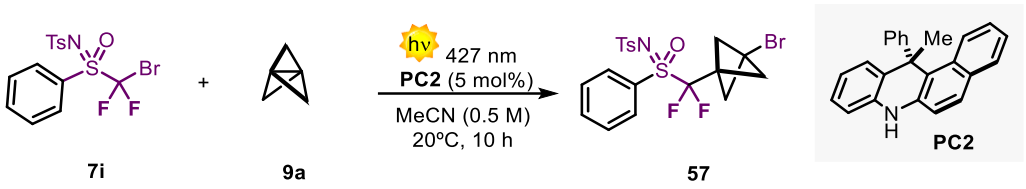


Figure S39. Plot of the mmols of product formed vs mmols of photons absorbed and linear interpolation.

Quantum yield of the strain-release ATRA reaction with [1.1.1]propellane



The same cuvette used for actinometry was charged with **7i** (212.0 mg, 0.5 mmol, 1 equiv.) and the **PC2** (8.0 mg, 0.025 mmol, 5 mol%). The cuvette was capped with a septum and degassed with argon. 1 mL of dry and degassed MeCN were added, followed by **9a** (0.77 M in Et_2O, 715 µL, 5.5 mmol, 1.1 equiv.). The absorbance of the reaction mixture was then measured (Figure S40).

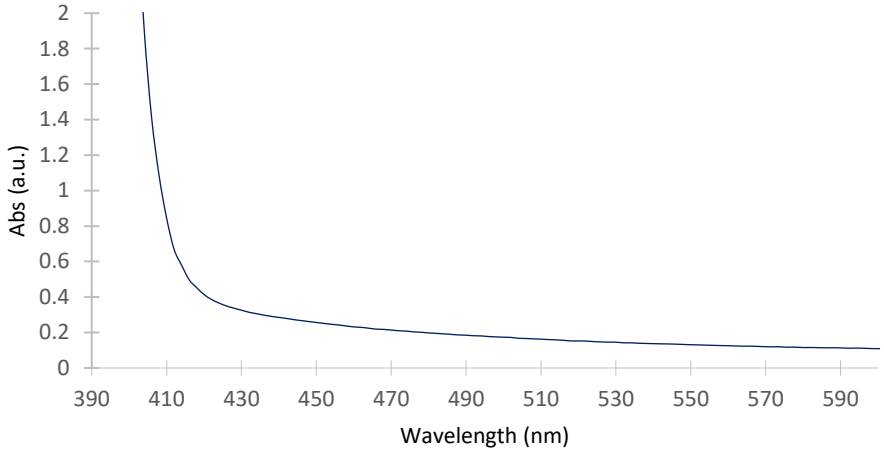


Figure S40. Absorption profile of the model reaction mixture.

The absorbance of the reaction mixture at 427 nm is **0.34**. The fraction of light absorbed (f) can be calculated according to $f = 1\text{-}10^{-Abs} = 1\text{-}10^{-0.34} =$**0.54**. Hence, the reaction mixture absorbs 54% of the incident photons, and the effective photon flux is calculated correcting the photon flux obtained from actinometry, according to $\mathbf{I_{eff}} = f \times I = 0.54 \times 2.67 \cdot 10^{-8}$ mol s^{-1} = $\mathbf{1.45 \cdot 10^{-8}\ mol\ s^{-1}}$.

The cuvette was irradiated with the same setup as in step 2 of the actinometric measurements. 6.1 µL of $PhCF_3$ as internal standard with 50 µL aliquots of the reaction were sampled after 1800, 3600, 6600, 9000 and 11400 seconds of irradiation, diluted with 500 µL of $CDCl_3$ and analyzed by ^{19}F NMR to determine the yield. The yield values (mmols of product formed) at given time intervals were plotted against the mmols of photons absorbed by the reaction mixture (obtained by multiplication of the effective photon flux with the irradiation time in seconds). The plot was linearly interpolated, and the slope of the interpolation is, by definition, the quantum yield of the reaction (Figure S41). The value of quantum yield is then **19.03**.

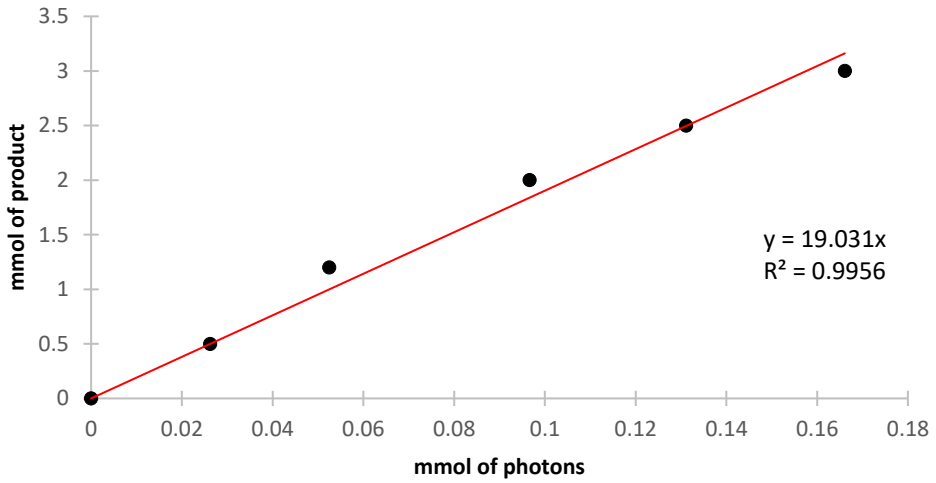
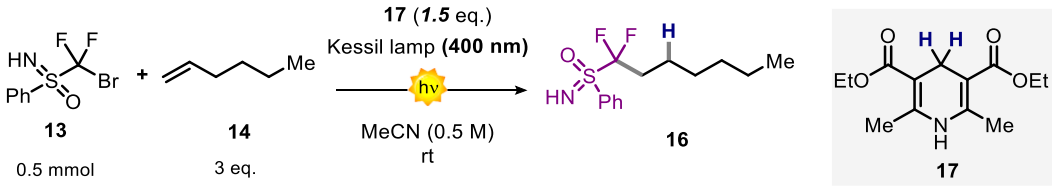


Figure S41. Plot of the mmols of product formed vs mmols of photons absorbed and linear interpolation.

Quantum yield of the hydrofunctionalization reaction



The same cuvette used for actinometry was charged with **13** (135 mg, 0.5 mmol, 1 eq) and the Hantzsch ester **17** (194 mg, 0.75 mmol, 1.5 eq.). The cuvette was capped with a septum and degassed with argon. 1 mL of dry and degassed MeCN were added, followed by **14** (188 µL, 1.5 mmol, 3 eq). 61 µL of $PhCF_3$ were finally added as the internal standard. The absorbance of the reaction mixture was then measured (Figure S42).

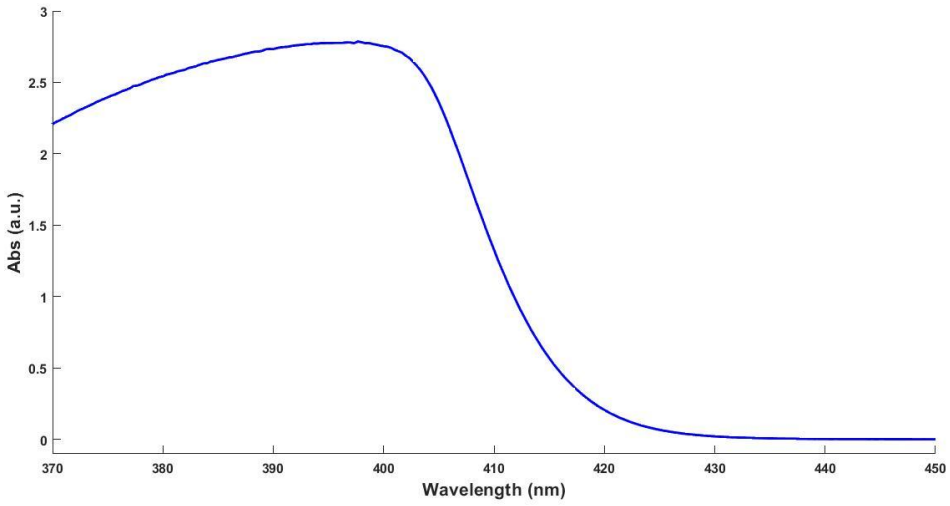


Figure S42. Absorption profile of the model reaction mixture.

The absorbance of the reaction mixture at 400 nm is **>2**. Since the absorbance of the solution at 400 nm is greater than 2 it can be assumed that all the incident photons from the lamp are absorbed by the solution. Therefore, no correction of the absorbed light needs to be affixed, and the effective photon flux corresponds to the 400 nm Kessil lamp photon flux (**$I = 3.01 \cdot 10^{-8}$ mol s^{-1}**).

The cuvette was irradiated with the same setup as in step 2 of the actinometric measurements. 50 µL aliquots of the reaction were sampled after 5h, 6h and 30 min, 7h and 30 min, and 7 hours of irradiation, diluted with 500 µL of $CDCl_3$ and analyzed by ^{19}F NMR to determine the yield. The yield values (mmols of product formed) at given time intervals were plotted against the mmols of photons absorbed by the reaction mixture (obtained by multiplication of the effective photon flux with the irradiation time in seconds). The plot was linearly interpolated and the slope of the interpolation is, by definition, the quantum yield of the reaction (Figure S43). The value of quantum yield is then **0.02**, forcing the line through the intercept (0;0).

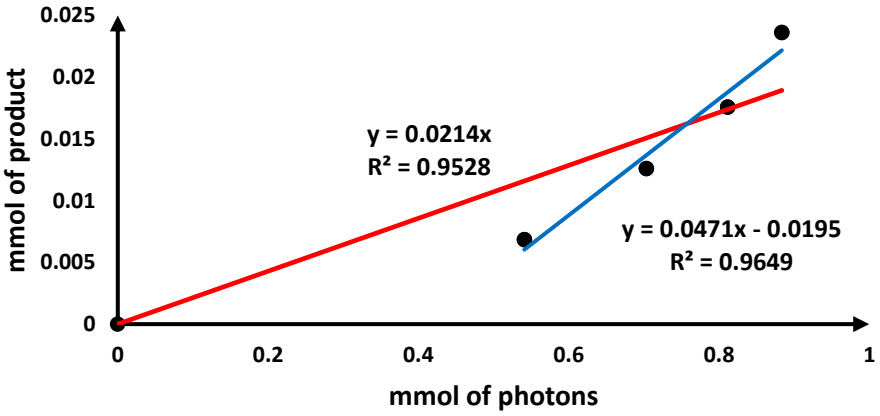


Figure S43. Plot of the mmols of product formed vs mmols of photons absorbed and linear interpolation.

Comment: The model hydrofunctionalization reaction is conducted in MeCN as the solvent. However, at the optimal concentration (0.75 M), Hantzsch ester **17** is insoluble in this medium, which complicates the acquisition of representative data during quantum yield measurements. Carrying out the reaction in other solvents did not alter the results obtained with MeCN, as at 0.75 M concentration, the Hantzsch ester **17** is only partially soluble in both DMF and DMSO. An attempt was made to perform the reaction in DMSO at a 0.07 M solution for the limiting reagent **13**, where the Hantzsch ester **17** was totally soluble (0.11 M for Hantzsch ester **17**). However, during the quantum yield measurement, ^{19}F-NMR analysis revealed that under these conditions, the dehalogenated byproduct **84** (figure S44) predominantly forms, while the desired product **16** is generated slowly and only in measurable amounts at conversions >10%.

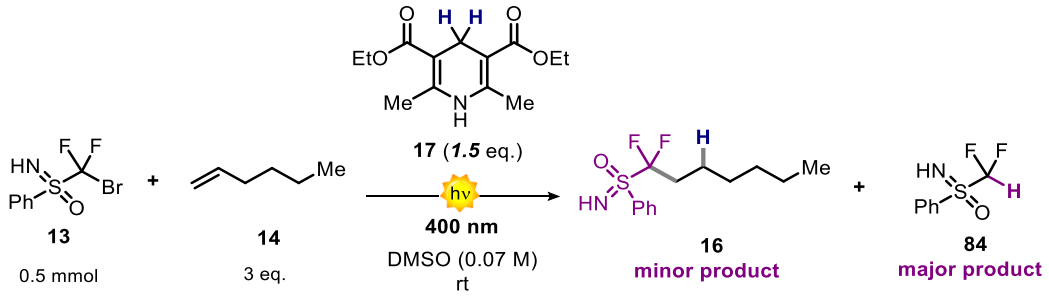
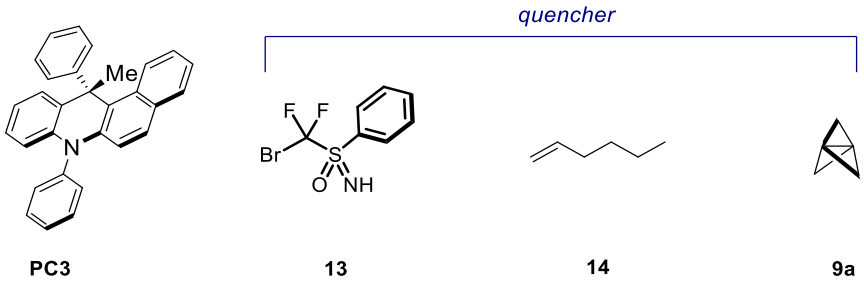


Figure S44. Outcome of the photochemical hydrofunctionalization reaction in DMSO at concentration 0.07 M.

K.4. Stern-Volmer quenching studies

Stern-Volmer quenching studies of the ATRA reaction

The Stern-Volmer quenching studies were performed without degassing. Stern-Volmer plots were initially constructed *on the excited state life-time* of the acridine catalyst **PC3** in acetonitrile ($\lambda_{excitation}$ = 402.6 nm; $\lambda_{emission}$ = 430 nm), after later additions of increasing amounts of (bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13,** 1-hexene **14** an [1.1.1]propellane **9a** as quencher.



The data points were then linearly fitted according to the Stern-Volmer equation:

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$$

where:

$\boldsymbol{\tau_0}$: initial excited state lifetime; $\boldsymbol{\tau}$: excited state lifetime in the presence of quencher; $\mathbf{K_{SV}}$: Stern-Volmer quenching constant; [**Q**]: concentration of quencher. k_q: bimolecular quenching rate.

Experimental Procedure 1

A1. The following stock solutions were initially prepared in acetonitrile:

1. **PC3** $1 \cdot 10^{-3}$ mol L^{-1}

2. Quencher 1: compound **13,** $2 \cdot 10^{-2}$ mol L^{-1}

3. Qunecher 2: 1-hexene **14,** $2 \cdot 10^{-2}$ mol L^{-1}

4. Quencher 3: [1.1.1]propellane **9a,** $2 \cdot 10^{-2}$ mol L^{-1}, prepared by dilution of a 0.88 M solution in Et_2O.

B1. The following solutions were then prepared in 2 mL volumetric flasks by dilution with MeCN of the stock solutions for every quencher.

i. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1}

ii. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $5.0 \cdot 10^{-4}$ mol L^{-1}

iii. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.0 \cdot 10^{-3}$ mol L^{-1}

iv. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.5 \cdot 10^{-3}$ mol L^{-1}

v. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $2.0 \cdot 10^{-3}$ mol L^{-1}

vi. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $3.5 \cdot 10^{-3}$ mol L^{-1}

vii. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $6.5 \cdot 10^{-3}$ mol L^{-1}

viii. **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.0 \cdot 10^{-2}$ mol L^{-1}

C1. A cuvette was each time filled with solutions **i** –**viii** (described in step B1) and the lifetime (**τ**) was each time recorded upon excitation at 402.6 nm (Figures S45-47). The ratio τ_0/τ of **PC3** was then plotted as a function of the quencher concentration [Q] (Figure S48**Error! Reference source not found.**). The fitting of the data points with the Stern Volmer equation provided the following values for the dynamic quenching of **PC3** with the quencher **13**:

$$\mathbf{K_{SV} = 85.7\ M^{-1}}$$

$$\mathbf{k_q = 9.32 \cdot 10^9\ M^{-1}\ s^{-1}}.$$

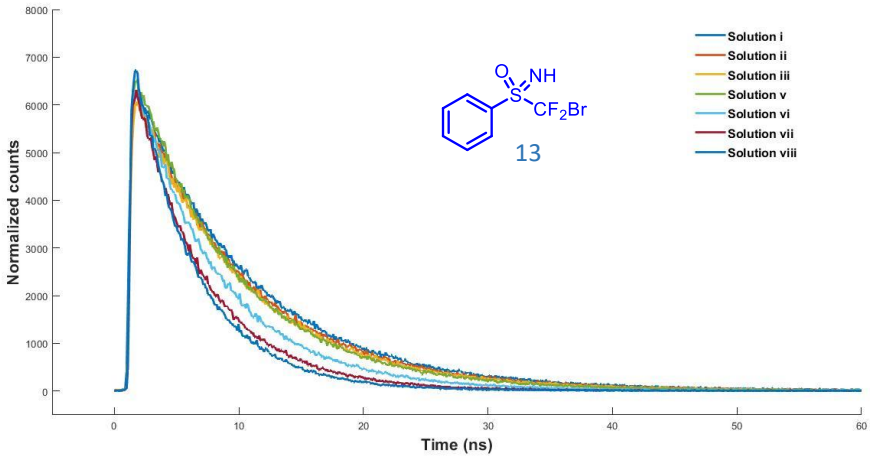


Figure S45. Time-resolved decay of the **PC3** emission upon pulse excitation, in the presence of increasing amounts of quencher **13**. (Emission 430.0 nm, excitation 402.6 nm).

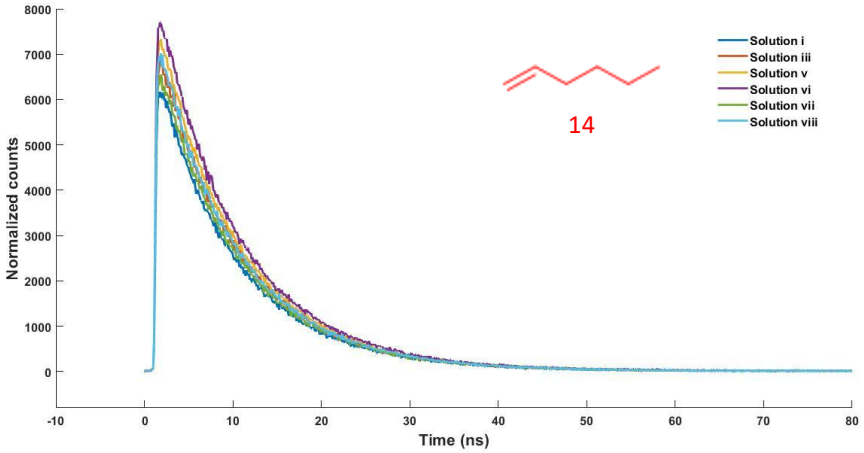


Figure S46. Time-resolved decay of the **PC3** emission upon pulse excitation, in the presence of increasing amounts of quencher **14**. (Emission 430.0 nm, excitation 402.6 nm).

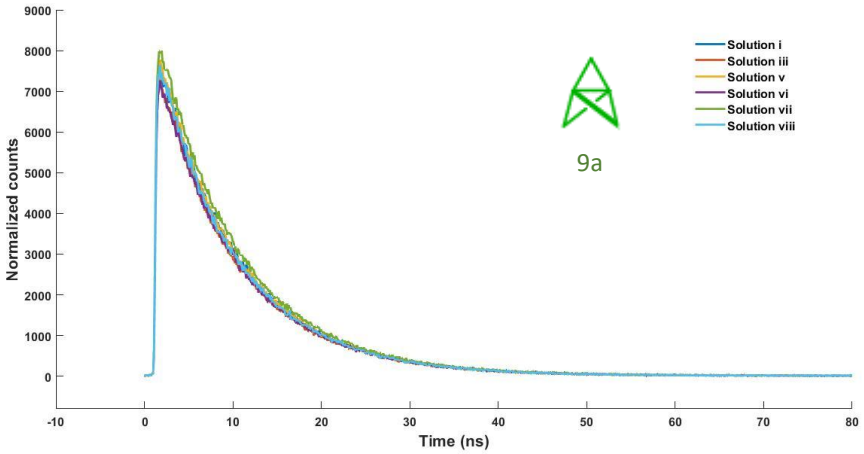


Figure S47. Time-resolved decay of the **PC3** emission upon pulse excitation, in the presence of increasing amounts of quencher **9a**. (Emission 430.0 nm, excitation 402.6 nm).

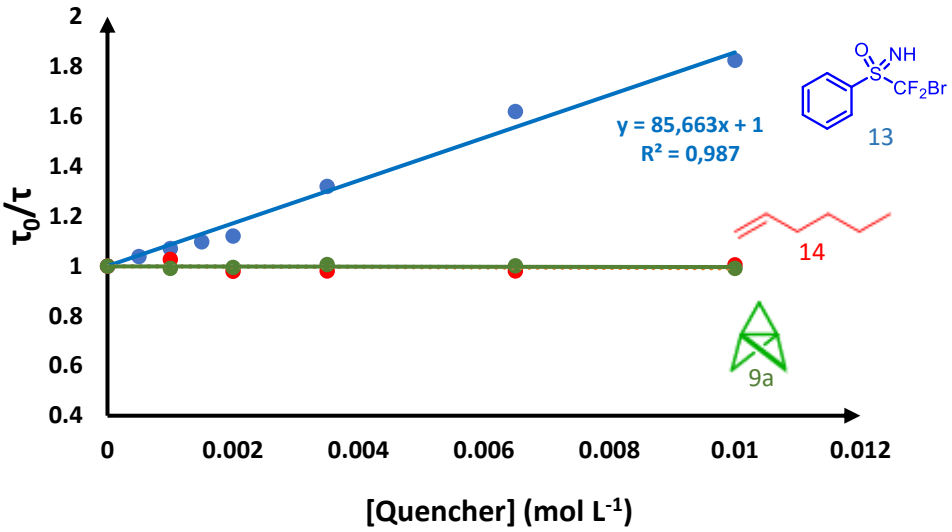


Figure S48. Plot of τ_0/τ as a function of the quencher concentration. [**PC3]** = $1.5 \cdot 10^{-5}$ M; [Q] = quencher **13** (blue line) 1-hexene **14** (red line) and [1.1.1]propellane **9a** (green line). The three different lines represent the linear fitting of the experimental data points.

Complementary to these studies, we also constructed a Stern-Volmer plot based *on the fluorescence intensity* of the acridine catalyst **PC3** in acetonitrile (λ_{ex} = 355.0 nm), after later additions of increasing amounts of quencher **13, 14** or **9a**. In this case, the rate of the quenching process was calculated according to the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}[\boldsymbol{Q}] = 1 + k_q \tau_0 [\boldsymbol{Q}]$$

where: **I**: fluorescence emission intensity; $\mathbf{I_0}$: initial fluorescence emission intensity; $\mathbf{K_{SV}}$: Stern-Volmer quenching constant; [**Q**]: concentration of quencher; k_q: bimolecular quenching rate; $\boldsymbol{\tau_0}$: excited state lifetime.

Experimental Procedure 2

A2. The following stock solutions were initially prepared in acetonitrile:

1. PC3 $1 \cdot 10^{-3}$ mol L^{-1}

2. Quencher 1: compound **13,** $2 \cdot 10^{-2}$ mol L^{-1}

3. Qunecher 2: 1-hexene **14,** $2 \cdot 10^{-2}$ mol L^{-1}

4. Quencher 3: [1.1.1]propellane **9a,** $2 \cdot 10^{-2}$ mol L^{-1}, prepared by dilution of a 0.88 M solution in Et_2O.

B2. The following solutions were then prepared in 2 mL volumetric flasks by dilution with MeCN of the stock solutions.

- **i.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1}
- **ii.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $4.88 \cdot 10^{-4}$ mol L^{-1}
- **iii.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $9.52 \cdot 10^{-4}$ mol L^{-1}
- **iv.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.82 \cdot 10^{-3}$ mol L^{-1}
- **v.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $3.33 \cdot 10^{-3}$ mol L^{-1}
- **vi.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $6.67 \cdot 10^{-3}$ mol L^{-1}
- **vii.** **PC3** $1.5 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.00 \cdot 10^{-2}$ mol L^{-1}

C2. A cuvette was each time filled with solutions **i** –**vii** (described in step B2) and the emission spectrum was each time recorded upon excitation at 355.0 nm (Figure S49-51). The emission spectra were then integrated and the area corresponding to sample **i** (*i.e.* I_0) was each time divided by the area obtained from the corresponding samples **i** – **vii** (*i.e.* I). The ratio I_0/I for both sets of data for both quenchers **13**, **14** and **9a** was then plotted as a function of the quencher concentration [Q] (Figure S52).

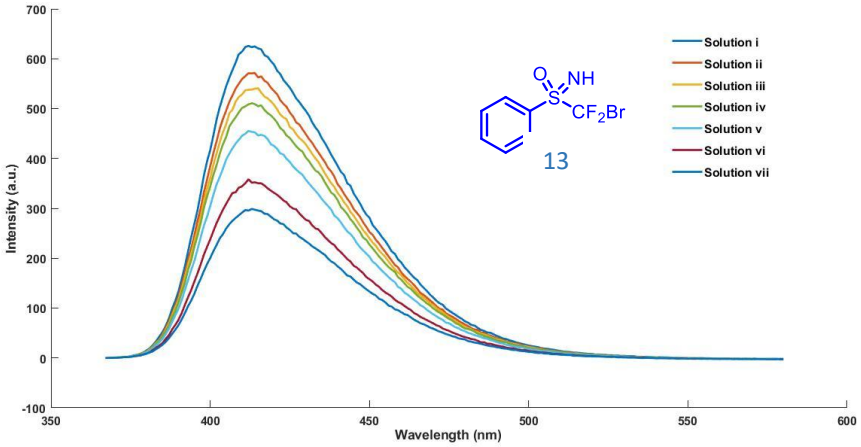


Figure S49. Fluorescence emission intensity decay of the **PC3** excitation, in the presence of increasing amounts of quencher **13** (excitation 355.0 nm).

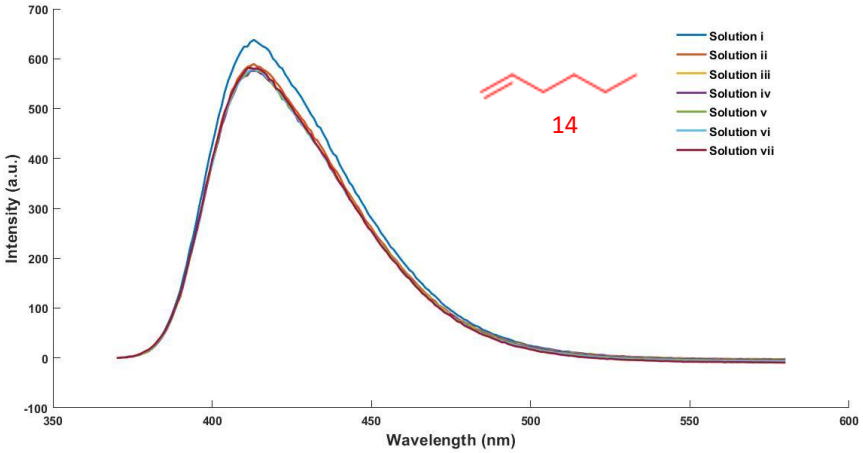


Figure S50. Fluorescence emission intensity decay of the **PC3** excitation, in the presence of increasing amounts of quencher **14** (excitation 355.0 nm).

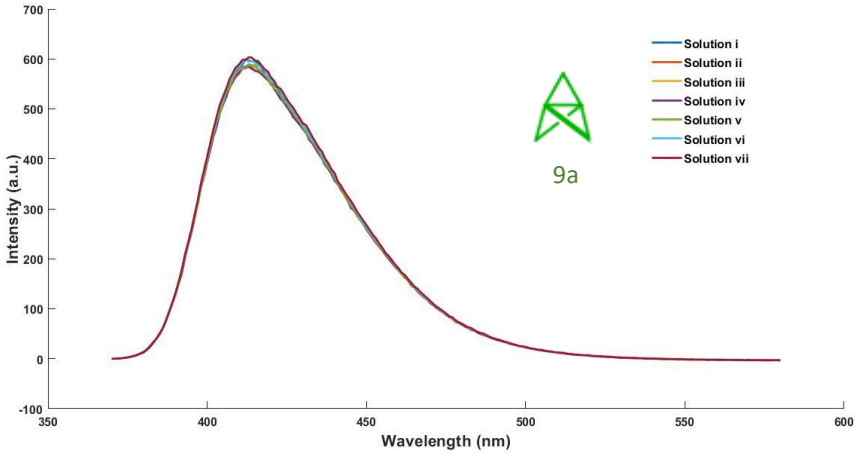


Figure S51. Fluorescence emission intensity decay of the **PC3** excitation, in the presence of increasing amounts of quencher **9a** (excitation 355.0 nm).

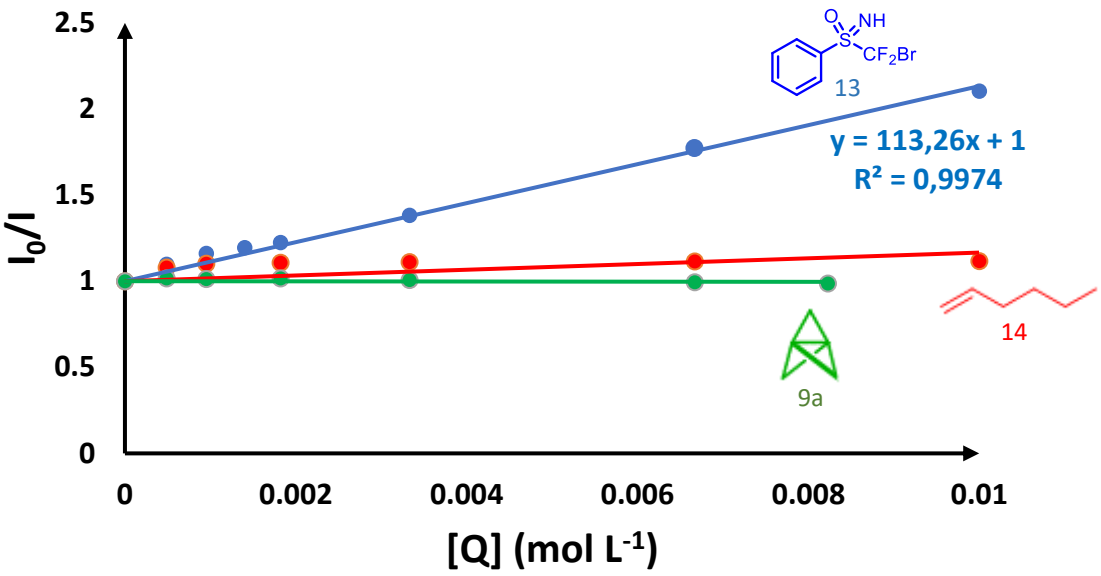


Figure S52. Plot of I_0/I as a function of the quencher concentration. [**PC3]** = $1.5 \cdot 10^{-5}$ M; [Q] = quencher **13** (blue line) 1-hexene **14** (red line) and [1.1.1]propellane **9a** (green line). The three different lines represent the linear fitting of the experimental data points.

Linear interpolation of the data points depicted in Figure S52 with the Stern-Volmer equation, provided the following absolute values of K_{SV}:

$$\mathbf{K_{SV} = 113\ L\ mol^{-1}}\ \text{(with quencher } \mathbf{13}\text{)}$$

$$\mathbf{K_{SV} = 16\ L\ mol^{-1}}\ \text{(with 1-hexene } \mathbf{14}\text{)}$$

Considering an excited state lifetime value of $\boldsymbol{\tau_0}$ **= 9.2 ns** for **PC3** and according to the Stern-Volmer equation, a value of $\mathbf{k_q = 1.2 \cdot 10^{10}\ L\ mol^{-1}\ s^{-1}}$ for quenching with quencher **13** can be calculated. This value is in the same order of magnitude as the one calculated in the *Experimental Procedure 1* of this section **K.4**. On the other hand, the resulting Stern-Volmer plot does not show any significant quenching of the excited state catalyst **PC3** with 1-hexene **14** and [1.1.1]-propellane **9a**.

Stern-Volmer quenching studies of the hydrofunctionalization reaction

The Stern-Volmer quenching studies were performed without degassing. Stern-Volmer plots were constructed *on the fluorescence intensity* of Hantzsch Ester (HE) **17** in acetonitrile ($\lambda_{excitation}$ = 392.0 nm), after later additions of increasing amounts of (bromodifluoromethyl)(imino)(phenyl)-λ^6-sulfanone **13** and 1-hexene **14** as quencher.

The data points were then linearly fitted according to the Stern-Volmer equation:

$$\frac{I_0}{I} = 1 + K_{SV}[\boldsymbol{Q}] = 1 + k_q \tau_0 [\boldsymbol{Q}]$$

where: **I**: fluorescence emission intensity; $\mathbf{I_0}$: initial fluorescence emission intensity; $\mathbf{K_{SV}}$: Stern-Volmer quenching constant; [**Q**]: concentration of quencher; k_q: bimolecular quenching rate; $\boldsymbol{\tau_0}$: excited state lifetime.

Experimental Procedure

A. The following stock solutions were initially prepared in acetonitrile:

1. Hantzsch Ester (HE) **17,** $1 \cdot 10^{-3}$ mol L^{-1}

2. Quencher 1: compound **13,** $2 \cdot 10^{-2}$ mol L^{-1}

3. Qunecher 2: 1-hexene **14,** $2 \cdot 10^{-2}$ mol L^{-1}

B. The following solutions were then prepared in 2 mL volumetric flasks by dilution with MeCN of the stock solutions.

- **i.** **HE** $2 \cdot 10^{-5}$ mol L^{-1}
- **ii.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $5 \cdot 10^{-4}$ mol L^{-1}
- **iii.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1 \cdot 10^{-3}$ mol L^{-1}
- **iv.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $2 \cdot 10^{-3}$ mol L^{-1}
- **v.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $3.5 \cdot 10^{-3}$ mol L^{-1}
- **vi.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $5 \cdot 10^{-3}$ mol L^{-1}
- **vii.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.0 \cdot 10^{-2}$ mol L^{-1}
- **viii.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $5.0 \cdot 10^{-2}$ mol L^{-1}
- **ix.** **HE** $2 \cdot 10^{-5}$ mol L^{-1} + **quencher** $1.0 \cdot 10^{-1}$ mol L^{-1}

C. A cuvette was each time filled with solutions **i** –**ix** (described in step B) and the emission spectrum was each time recorded upon excitation at 392.0 nm (Figure S53-54). The emission spectra were then integrated and the area corresponding to sample **i** (*i.e.* I_0) was each time divided by the area obtained from the corresponding samples **i** – **ix** (*i.e.* I). The ratio I_0/I for both sets of data for both quenchers **13** and **14** was then plotted as a function of the quencher concentration [Q] (Figure S55).

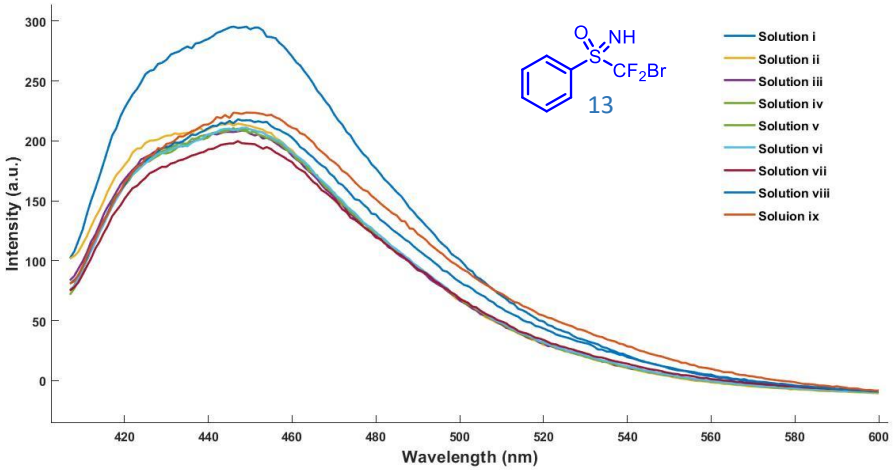


Figure S53. Fluorescence emission intensity decay of Hantzsch Ester (HE) **17** excitation, in the presence of increasing amounts of quencher **13** (excitation 392.0 nm).

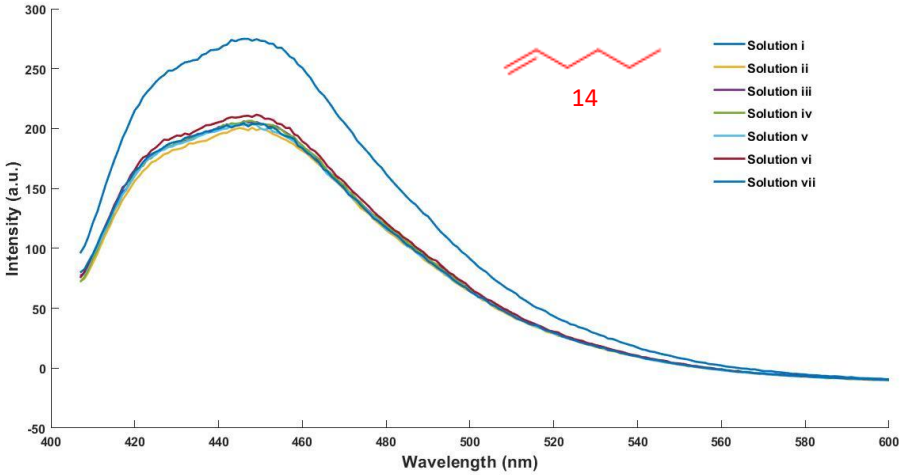


Figure S54. Fluorescence emission intensity decay of Hantzsch Ester (HE) **17** excitation, in the presence of increasing amounts of quencher 1-hexene **14** (excitation 392.0 nm).

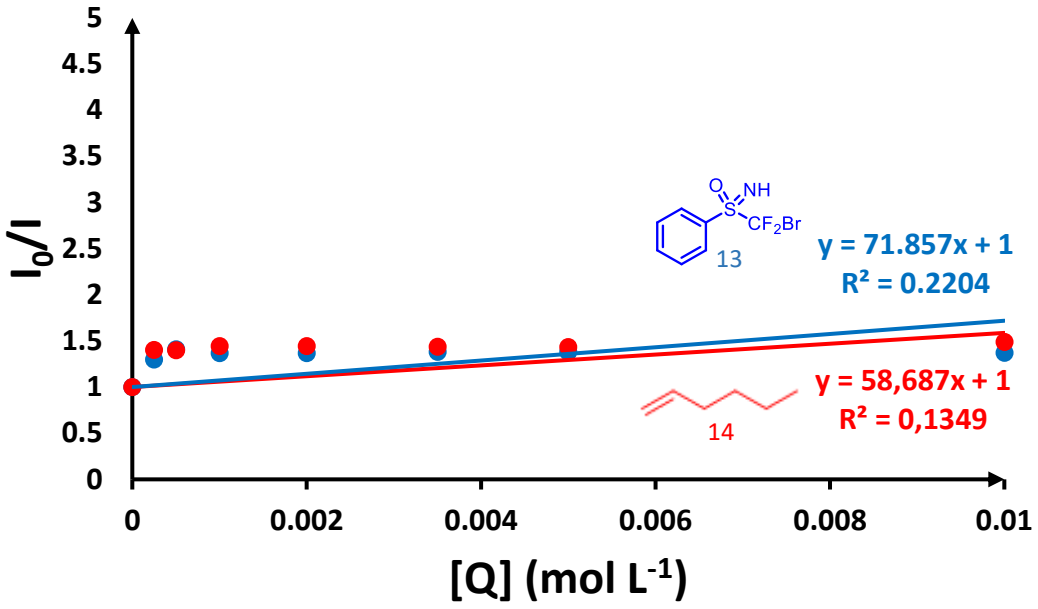


Figure S55. Plot of I_0/I as a function of the quencher concentration. [**HE]** = $1.5 \cdot 10^{-5}$ M; [Q] = quencher **13** (blue line) 1-hexene **14** (red line). The two different lines represent the linear fitting of the experimental data points.

Linear interpolation of the data points depicted in Figure S55 with the Stern-Volmer equation, provided the following absolute values of K_{SV}:

$$\mathbf{K_{SV} = 71.8\ L\ mol^{-1}}\ \text{(with quencher } \mathbf{13}\text{)}$$

$$\mathbf{K_{SV} = 58.7\ L\ mol^{-1}}\ \text{(with 1-hexene } \mathbf{14}\text{)}$$

What is observed from the fluorescence spectra of Figure S53 and Figure S54 is that for both quenchers compound **13** and 1-hexene **14**, apart from an initial decrease, no significant change in emission intensity is observed as the concentration of the two species increases, suggesting the absence of quenching of the excited state of Hantzsch Ester (HE) **17**.

L. REFERENCES

[1] (a) J. R. Aranzaes, M.-C. Daniel, D. Astruc, *Can. J. Chem.* **2006**, *84*, 288-299; (b) V. V. Pavlishchuk, A. W. Addison, *Inorganica Chim. Acta*, **2000**, *298*, 97-102.

[2] E. Ismalaj, D. Le Bars, T. Billard, *Angew. Chem. Int. Ed.* **2016**, *55*, 4790-4793.

[3] S. Chaabouni, J.-F. Lohier, A.-L. Barthelemy, T. Glachet, E. Anselmi, G. Dagousset, P. Diter, B. Pégot, E. Magnier, V. Reboul, *Chem. Eur. J.* **2018**, *24*, 17006 – 17010.

[4] S. Cuadros, G. Goti, G. Barison, A. Raulli, T. Bortolato, G. Pelosi, P. Costa, L. Dell'Amico, *Angew. Chem. Int. Ed.* **2023**, e202303585.

[5] J. Wu, Q. Zhao, T. C. Wilson, S. Verhoog, L. Lu, V. Gouverneur, Q. Shen, *Angew. Chem. Int. Ed*. **2019**, *58*, 2413 –2417.

[6] M. Pohmakotr, W. Ieawsuwan, P. Tuchinda, P. Kongsaeree, S. Prabpai, V.Reutrakul, *Org. Lett.* **2004**, *6, 24*, 4547–4550.

[7] F. Della-Felice, M. Zanini, X. Jie, E. Tan, A. M. Echavarren, *Angew. Chem. Int. Ed*. **2021**, *60*, 5693–5698.

[8] C. Rosso, S. Cuadros, G. Barison, P. Costa, M. Kurbasic, M. Bonchio, M. Prato, L. Dell'Amico, G. Filippini, *ACS Catal*. **2022**, *12*, 4290−4295.

[9] J. M. Kraus, H. C. Gits, R. B: Silverman, *Tetrahedron Letters*, **2012**, *53*, 1319–1322.

[10] M. Commandeur, C. Commandeur, J. Cossy, *Org. Lett.* **2011**, *13, 22*, 6018–6021.

[11] H. Yamamoto, E. Ho, K. Namba, H. Imagawa, M. Nishizawa, *Chem. Eur. J.* **2010**, *16*, 11271 – 11274.

[12] X.-H. Sheng, C.-C. Cui, C. Shan, Y.-Z. Li, D.-H. Sheng, B. Sun, D.-Z. Chen, *Org. Biomol. Chem*., **2018**, *16*, 3952-3960.

[13] C. T. Van, D. Nennstiel, J. Scherkenbeck *Bioorganic & Medicinal Chemistry*, **2015**, *23*, 3278–3286.

[14] S. R. Alexander, D. Lim, Z. Amso, M. A. Brimbleb, A. J. Fairbanks, *Org. Biomol. Chem*., **2017**, *15*, 2152-2156.

[15] H. Wang, P. Bellotti, X. Zhang, T. O. Paulisch, F. Glorius, *Chem*, **2021**, *7*, 3412–3424.

[16] X. Ren, Q. Liu, Z. Wang, X. Chen, *Chinese Chemical Letter*, **2023**, *34*, 107473-107477.

[17] J. Nugent, C. Arroniz, B. R. Shire, A. J. Sterling, H. D. Pickford, M. L. Wong, S. J. Mansfield, D. F. Caputo, B. Owen, J. J. Mousseau, F. Duarte, E. A. Anderson, *ACS Catal.* **2019**, *9*, 9568-9574.

[18] R. Gianatassio, J. M. Lopchuk, J. Wang, C.-M. Pan, L. R. Malins, L. Prieto, T. A. Brandt, M. R. Collins, G. M. Gallego, N. W. Sach, J. E. Spangler, H. Zhu, J. Zhu, P. S. Baran, *Science* **2016**, *351*, 241-246.

[19] N. Frank, J. Nugent, B. R. Shire, H. D. Pickford, P. Rabe, A. J. Sterling, T. Zarganes-Tzitzikas, T. Grimes, A. L. Thompson, R. C. Smith, *Nature* **2022**, *611*, 721-726.

[20] D.-G. Chen, Y. Chen, C.-H. Wu, Y.-A. Chen, M.-C. Chen, J.-A. Lin, C.-Y. Huang, J. Su, H. Tian, P.-T. Chou, *Angew. Chem. Int. Ed*., **2019**, *58*, 13297–13301.

[21] X.-L. Li, W. Wu, X.-H. Fan, L.-M. Yang, *RSC Advances*, **2013**, *3*, 12091-12095.

[22] CHANGCHUN HAIPU RUNSI TECHNOLOGY CO LTD - CN111205272, 2020, A. Location in patent: Paragraph 0103-0105.

[23] G. Goti, M. Calamante, C. Coppola, A. Dessì, D. Franchi, A. Mordini, A. Sinicropi, L. Zani, G. Reginato, *Eur. J. Org. Chem*. **2021**, 2655–2664.

[24] Y. Tian, J. Yang, Z. Liu, M. Gao, X. Li, W. Che, M. Fang, Z. Li, *Angew. Chem. Int. Ed*., **2021**, *60*, 20259 –20263.

[25] N. A. Romero, D. A. Nicewicz, *Chem. Rev*. **2016**, *116*, 10075−10166.

[26] Kavarnos, G. J. *Energetics of photoinduced electron transfer. In Fundamentals of Photoinduced Electron Transfer*; VCH: New-York, Weinheim, **1993**, pp 29–37.

[27] T. Bortolato, G. Simionato, M. Vayer, C. Rosso, L. Paoloni, E. M. Benetti, A. Sartorel, D. Lebœuf., L. Dell'Amico, *J. Am. Chem. Soc.* **2023**, *145*, 3, 1835–1846.

[28] E. H. Discekici, N. J. Treat, S. O. Poelma, K. M. Mattson, Z. M. Hudson, Y. Luo, C. J. Hawker, J. Read de Alaniz, *Chem. Commun.*, **2015**, *51*, 11705-11709.

[29] a) T. Koike, *Chem. Rec*. **2023**, *23*, e202300032; b) M. Daniel, G. Dagousset, P. Diter, P.-A. Klein, B. Tuccio, A.-M. Goncalves, G. Masson, E. Magnier, *Angew. Chem*. **2017**, *129*, 4055 –4059.

[30] a) Q.-Y. Lin, X.-H. Xu, F.-L. Qing, *Org. Biomol. Chem*., **2015**, *13*, 8740-8749; b) Z. Wang, C.-Y. Guo, C. Yang, J.-P. Chen, *J. Am. Chem. Soc*. **2019**, *141*, 5617−5622; c) N. Duchemin, R. Buccafusca, M. Daumas, V. Ferey, S. Arseniyadis, *Org. Lett.* **2019**, *21*, 8205−8210.

[31] J. Sheng, K.-J. Bian, Y.-M. Su, G.-X. Liao, R. Duan, C. Li, Z. Liu, X.-S. Wang, *Org. Chem. Front*., **2020**, *7*, 617-621.

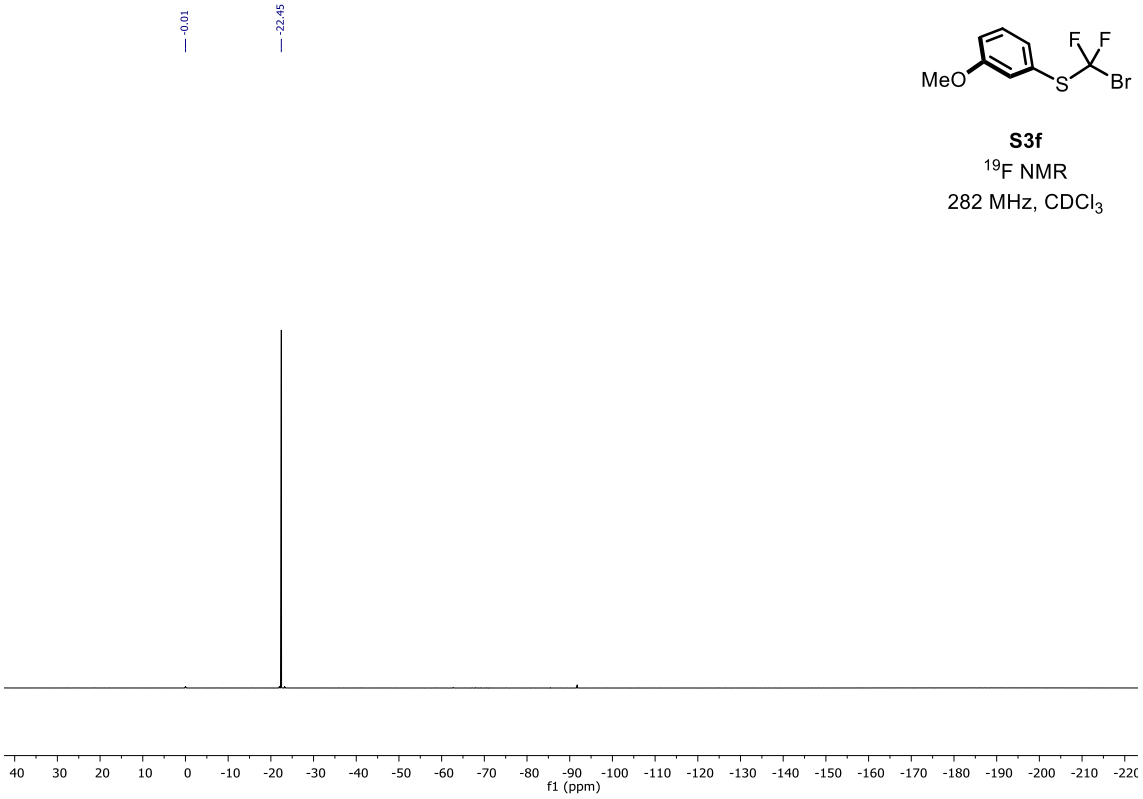
[32] Y. Macé, B. Pégot, R. Guillot, C. Bournaud, M. Toffano, G. Vo-Thanh, E. Magnier, *Tetrahedron* **2011**, *67*, 7575-7580.

[33] D. R. Duling, *J. Magn. Reson*., series B, **1994**, *104*, *2*, 105-110.

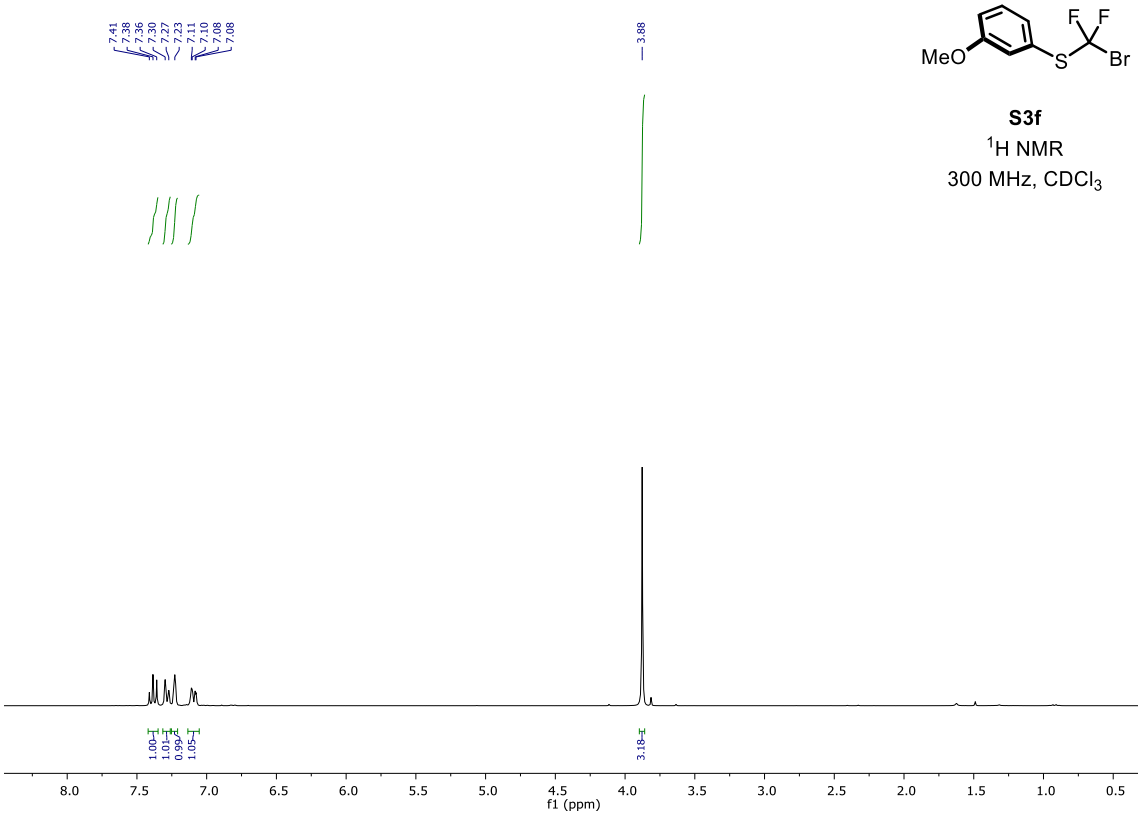
[34] S. Murov, I. Carmichael, G. Hug, *Handbook of Photochemistry*, Inc., New York **1973**, 124.

[35] H. Kuhn, S. Braslavsky, R. Schmidt, *Pure Appl. Chem.* **2004**, *76*, 2105-2146.

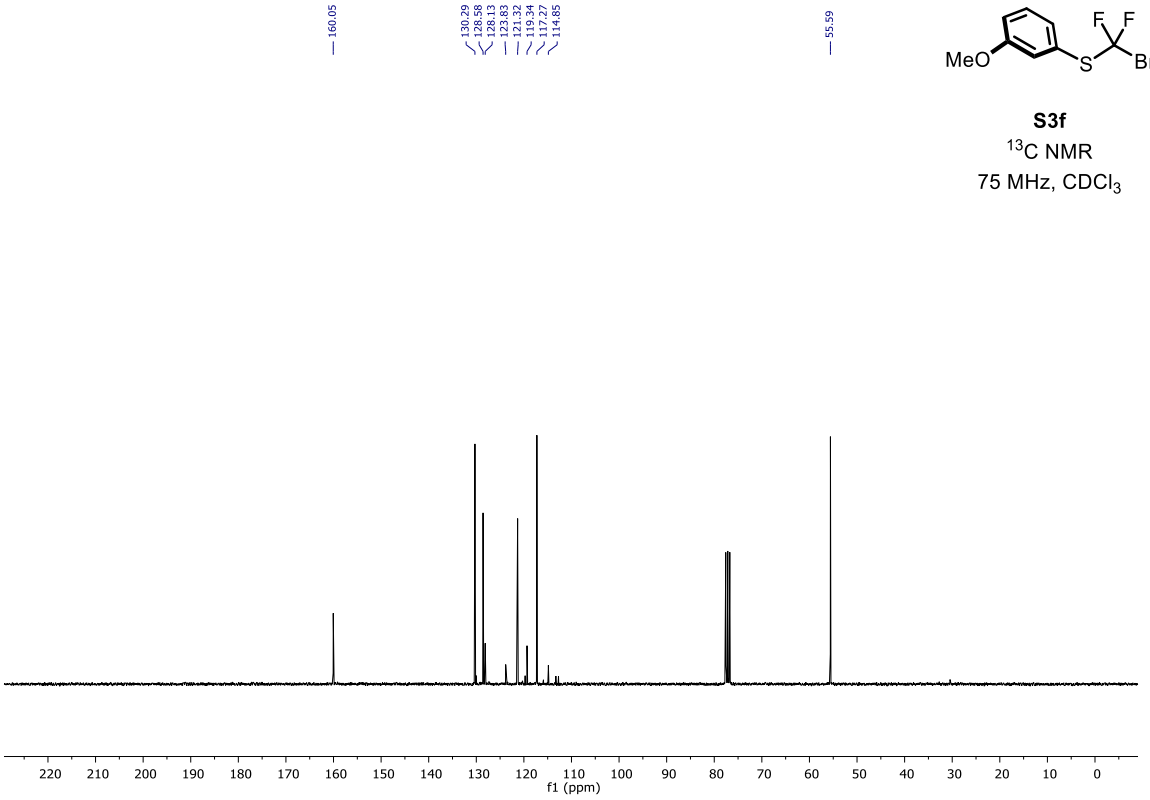
M. NMR SPECTRA



S3f
^{19}F NMR
282 MHz, $CDCl_3$



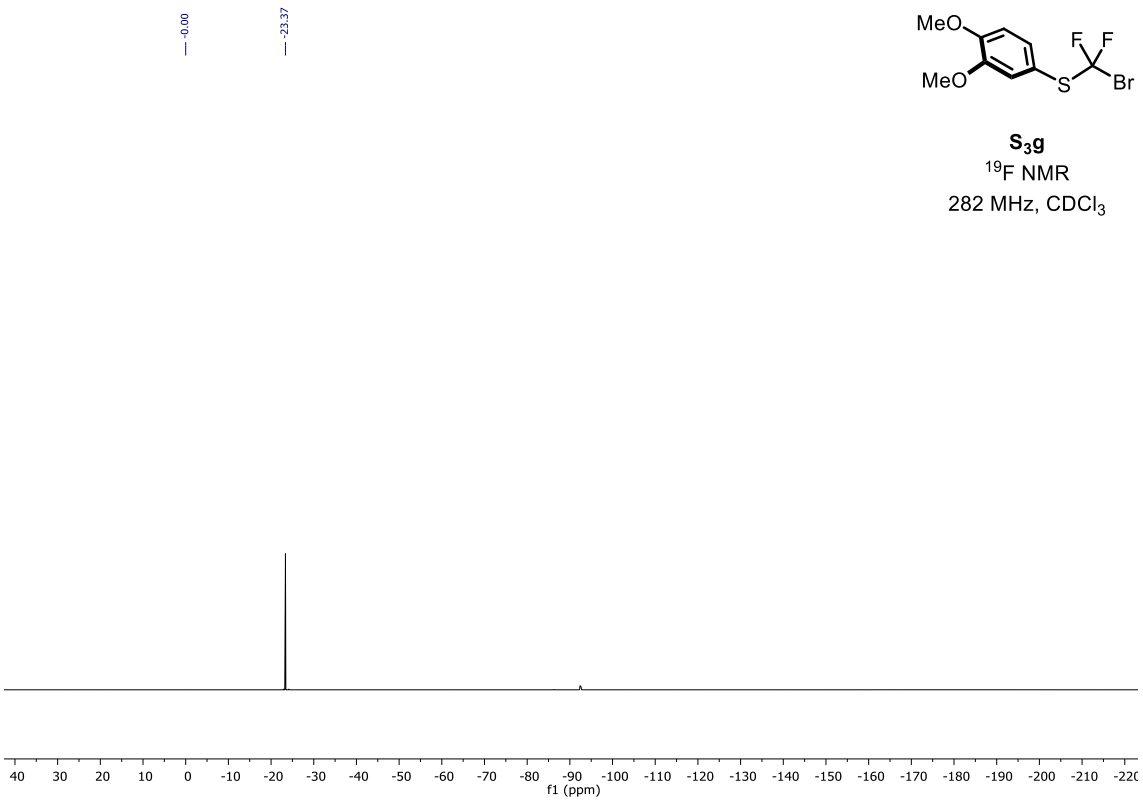
S3f
^{1}H NMR
300 MHz, $CDCl_3$



S3f

^{13}C NMR

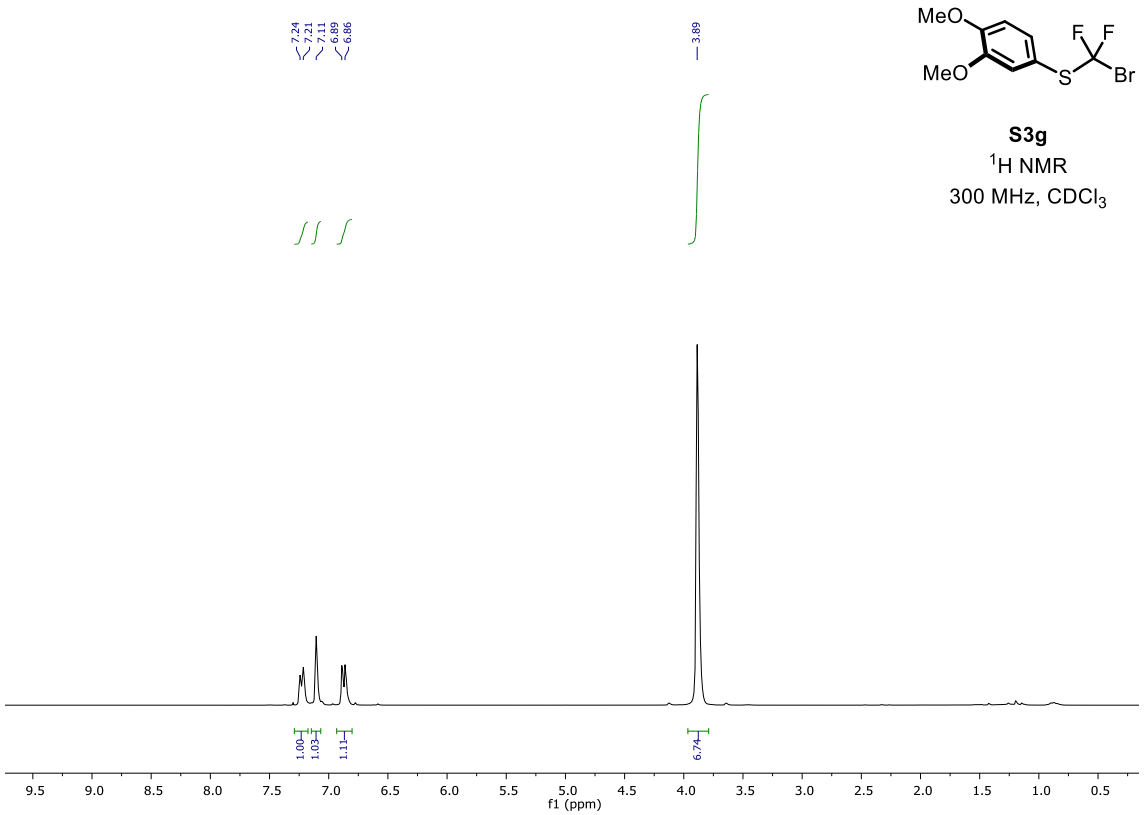
75 MHz, $CDCl_3$



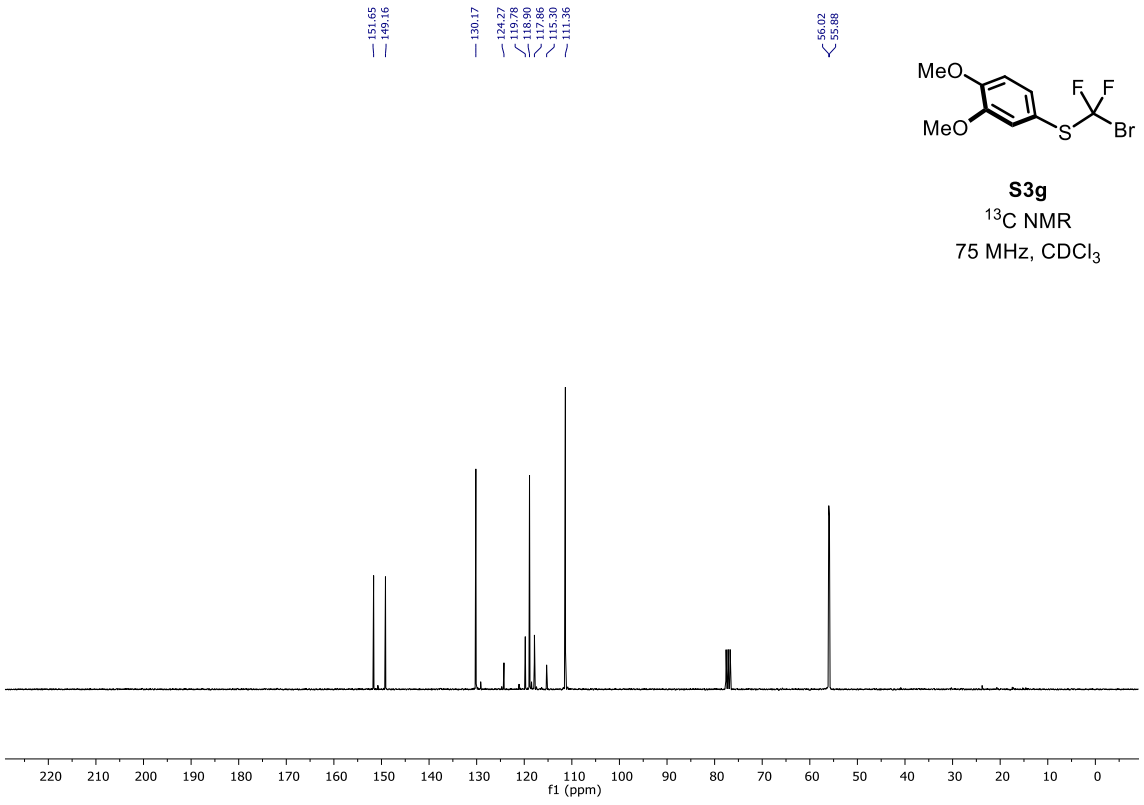
S_3g

^{19}F NMR

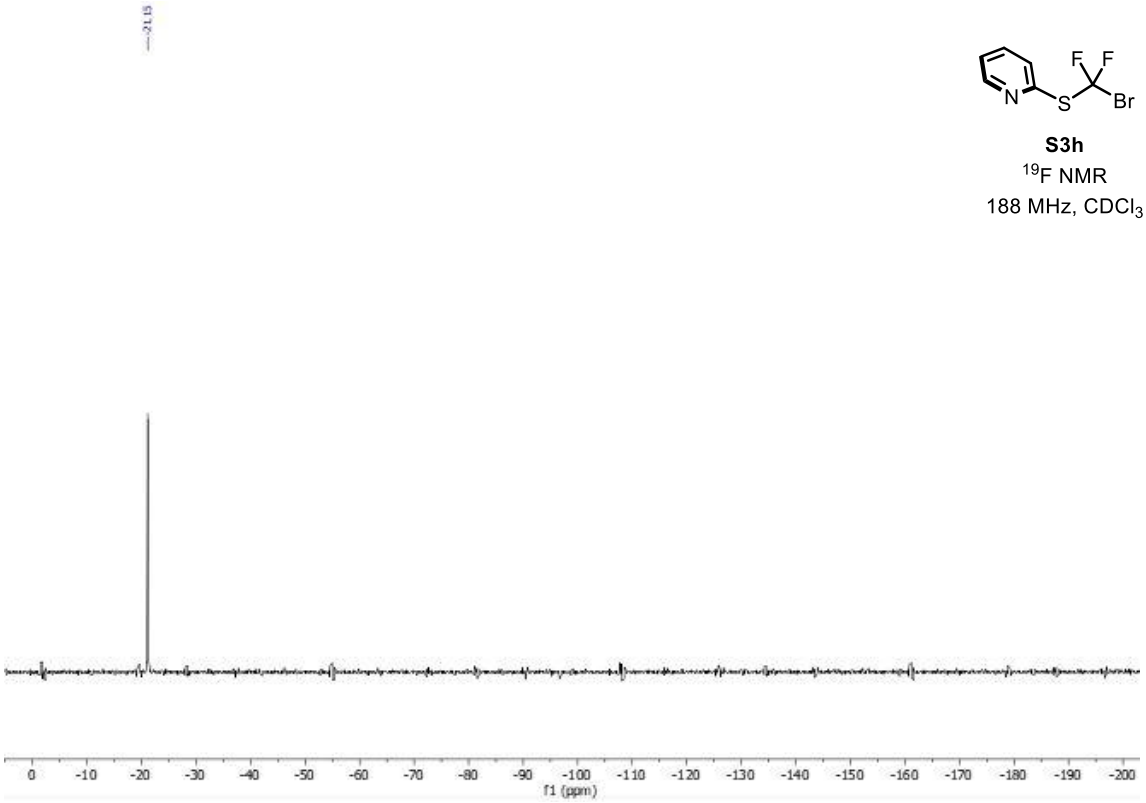
282 MHz, $CDCl_3$



S3g
^{1}H NMR
300 MHz, $CDCl_3$



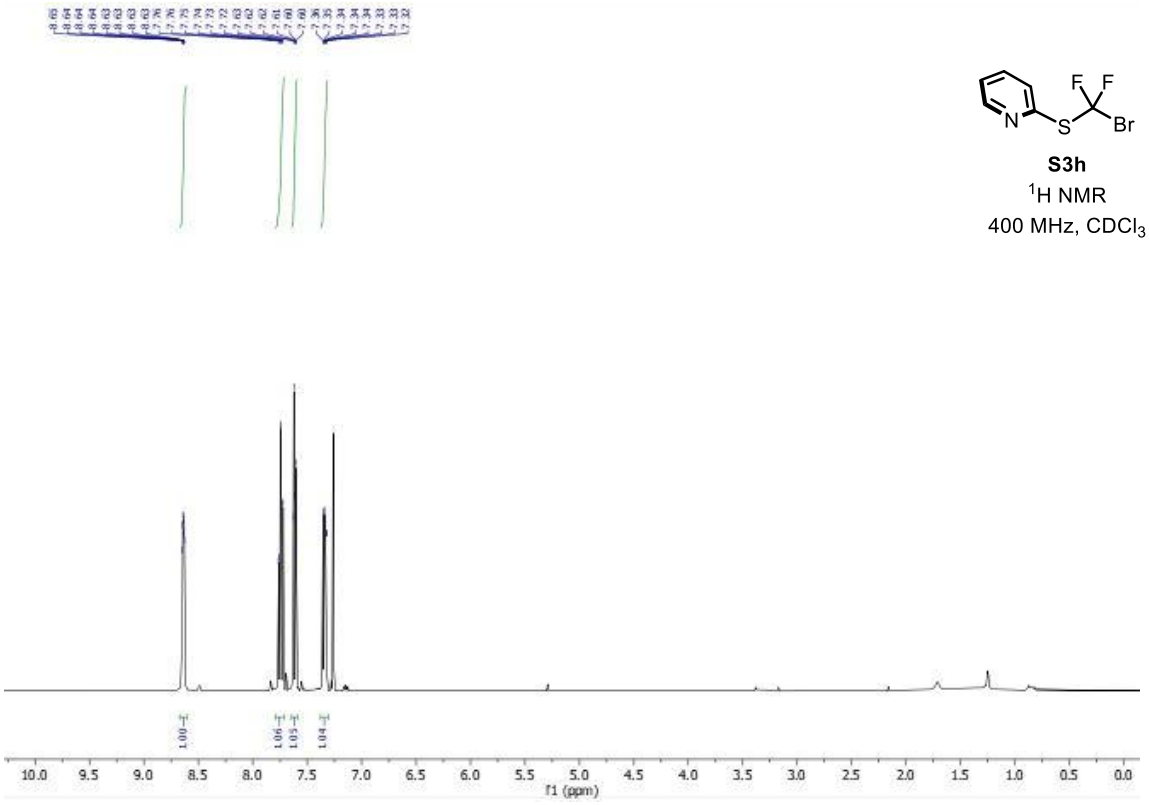
S3g
^{13}C NMR
75 MHz, $CDCl_3$



S3h

^{19}F NMR

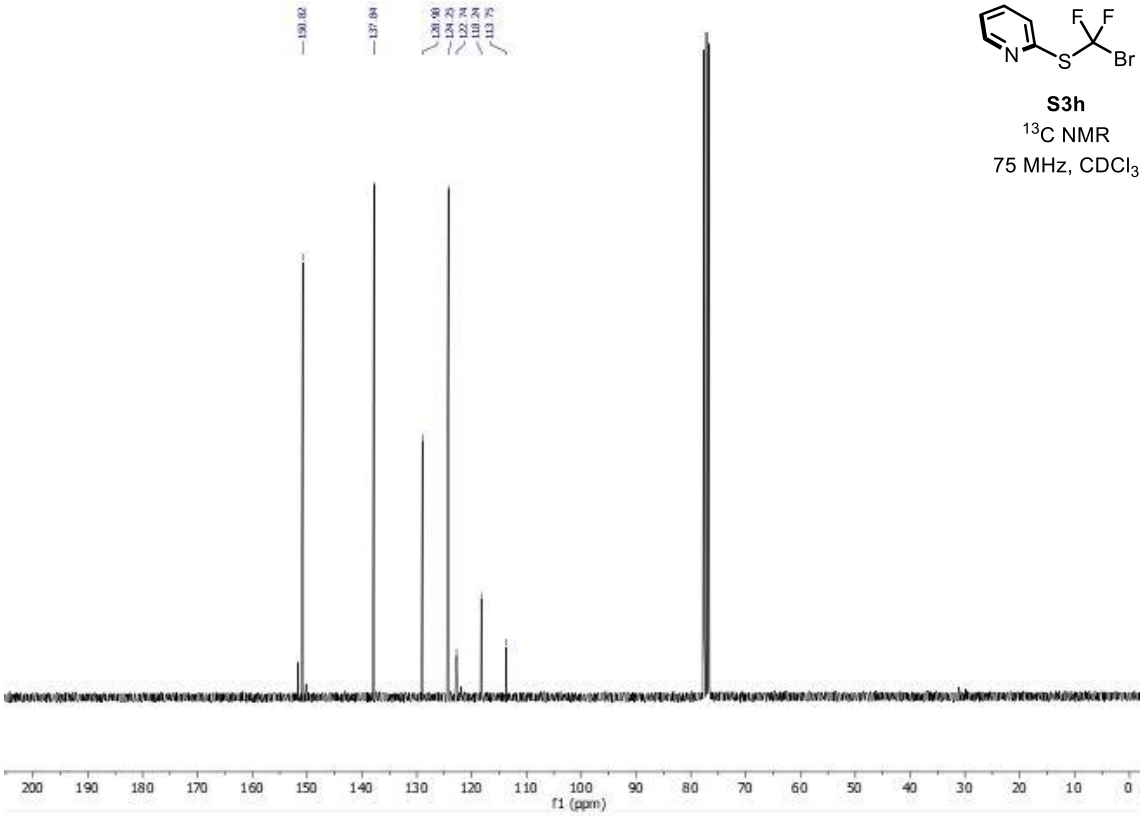
188 MHz, $CDCl_3$

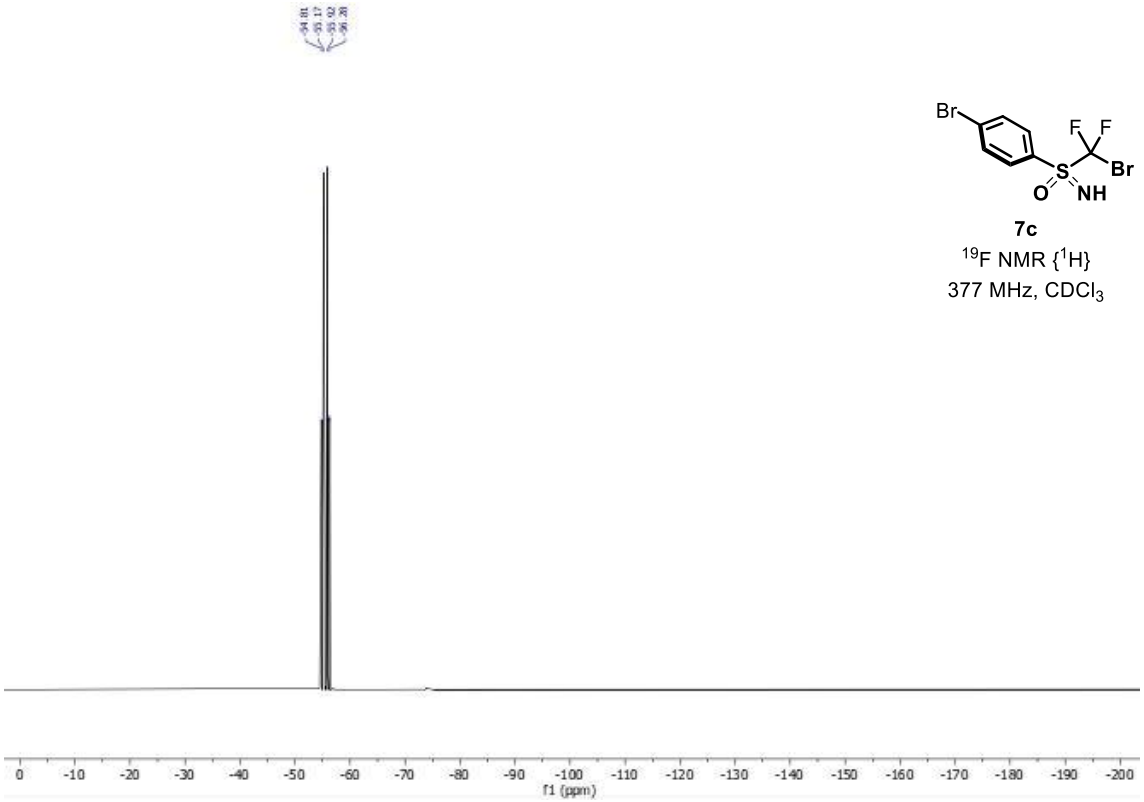


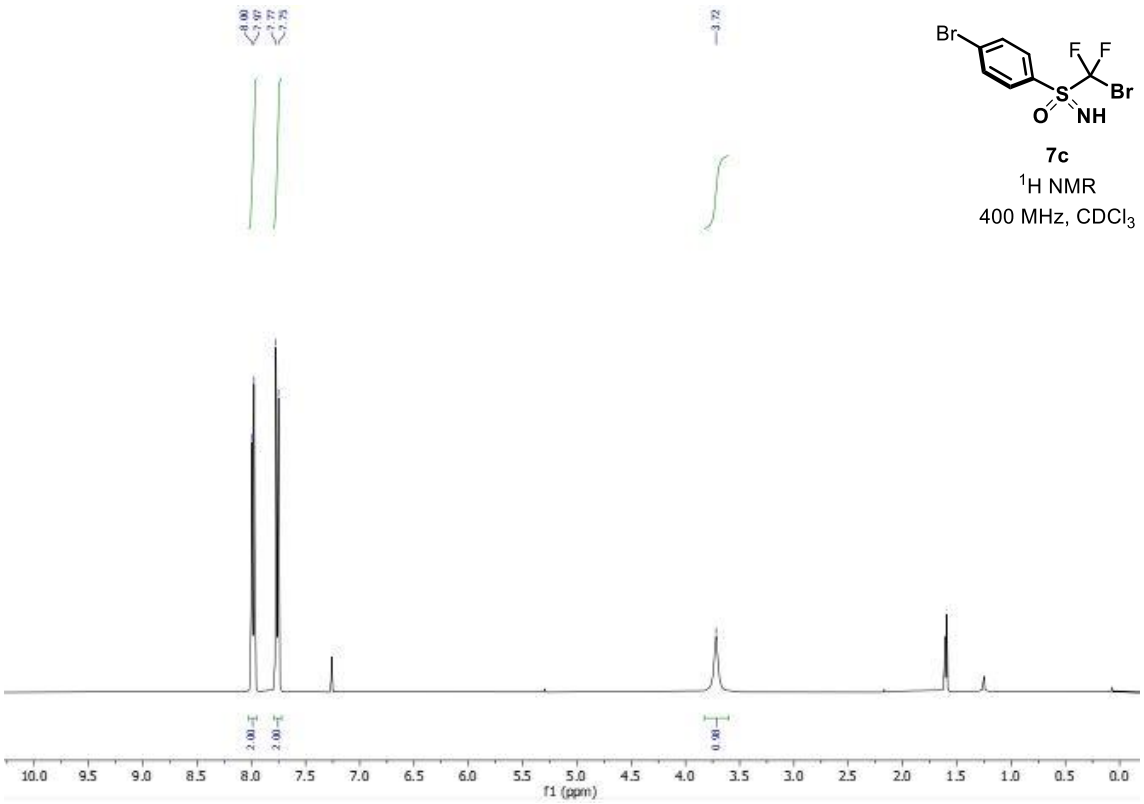
S3h

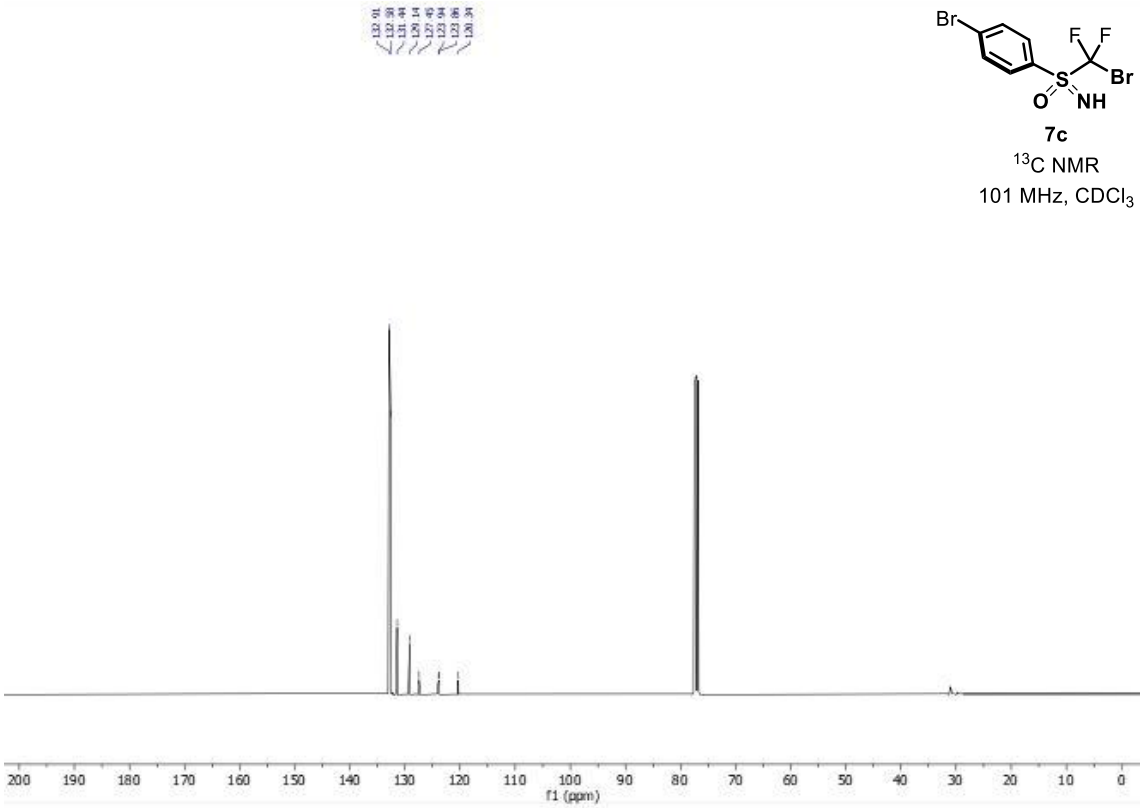
^{1}H NMR

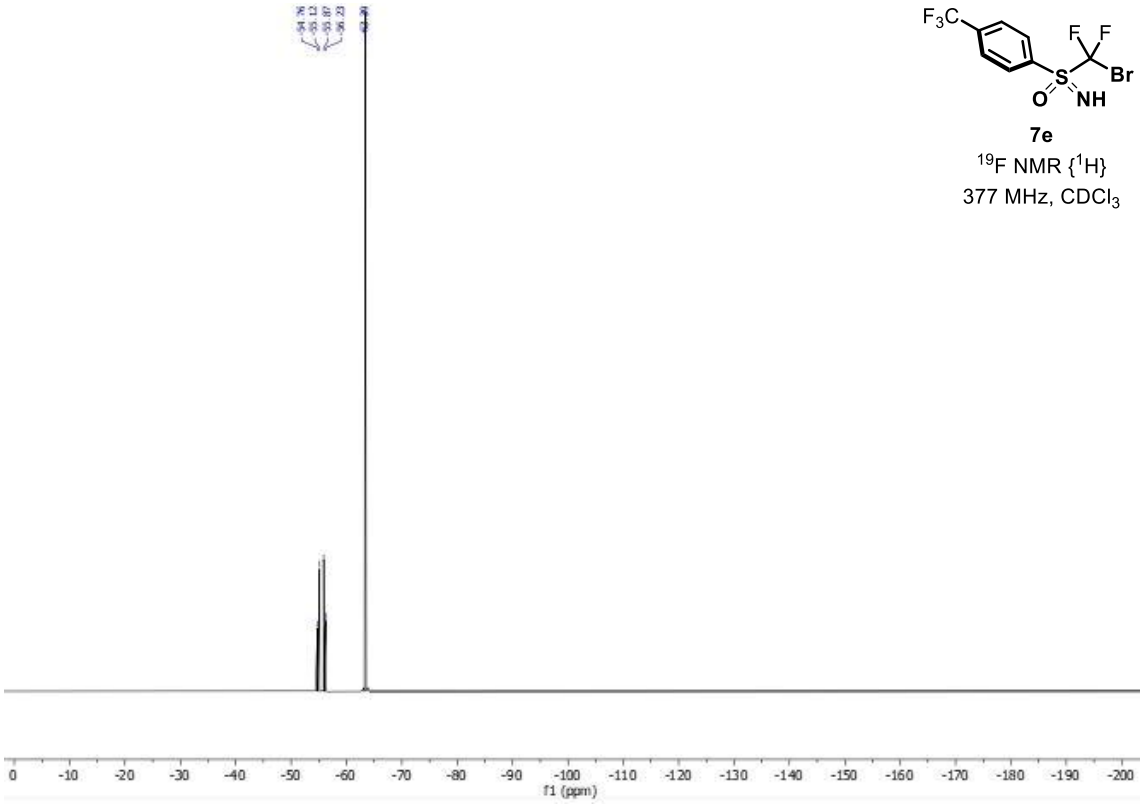
400 MHz, $CDCl_3$

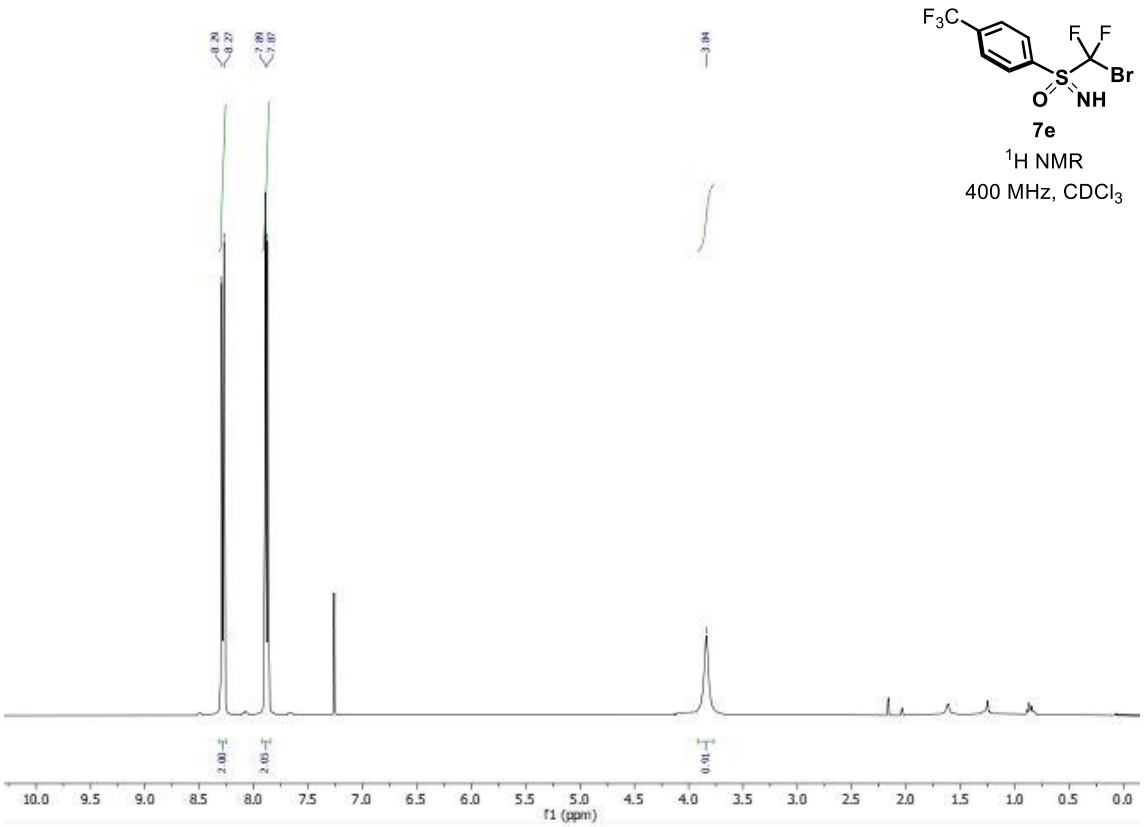

F F
N
S
Br
S3h
13C NMR
75 MHz, CDCl3
f1 (ppm)

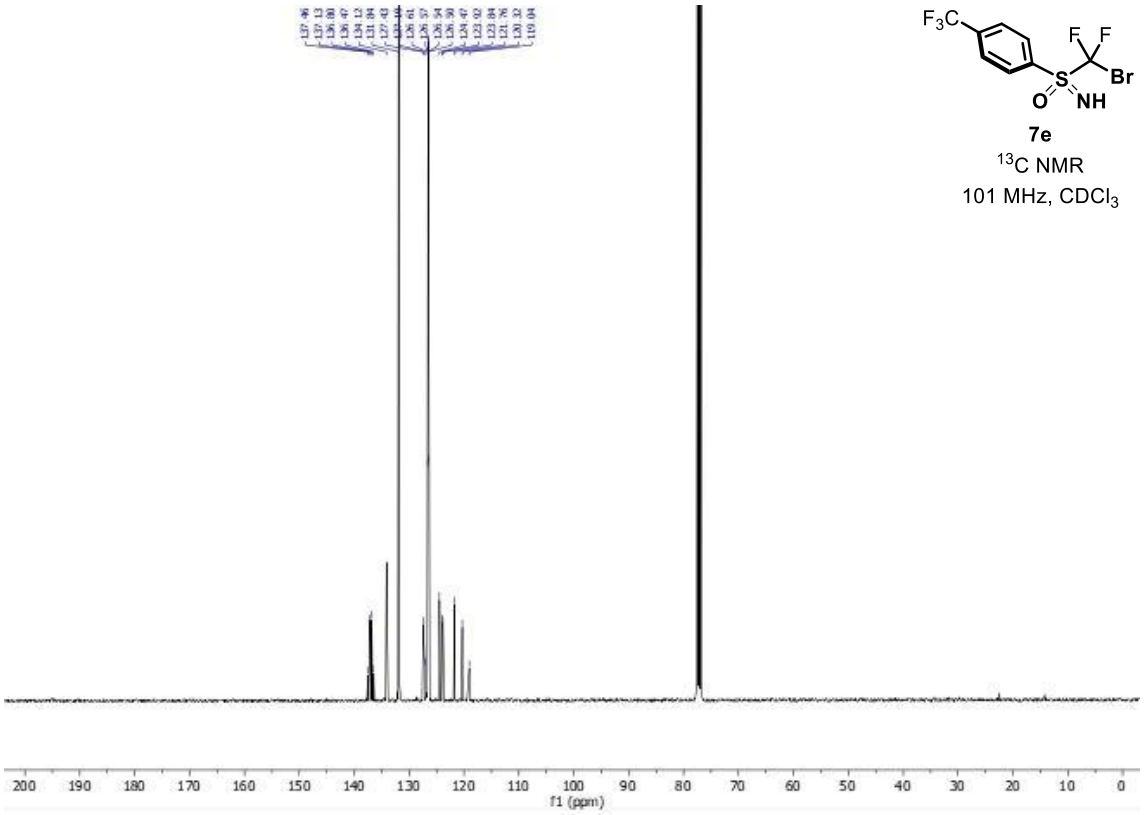

Br
F F
S
Br
O
NH
7c
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)


Br
F
F
S
Br
O
NH
7c
1H NMR
400 MHz, CDCl3
f1 (ppm)


Br
F
F
S
Br
O
NH
7c
13C NMR
101 MHz, CDCl3
f1 (ppm)


F3C
F F
Br
S
O
NH
7e
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)

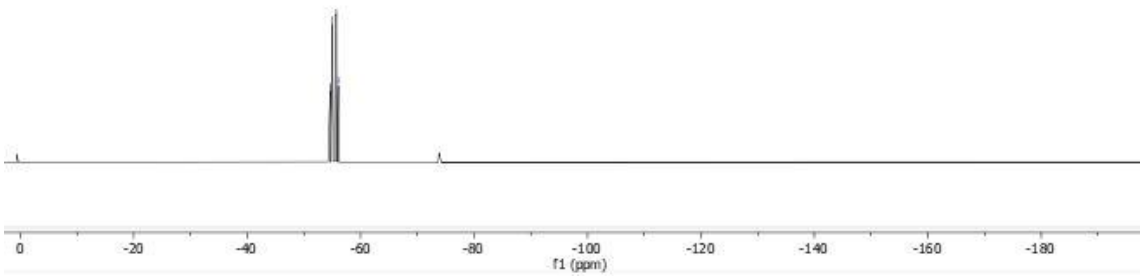

F3C
F F
Br
S
O
NH
7e
1H NMR
400 MHz, CDCl3
f1 (ppm)

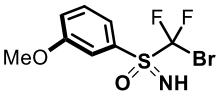


7e

^{13}C NMR

101 MHz, $CDCl_3$

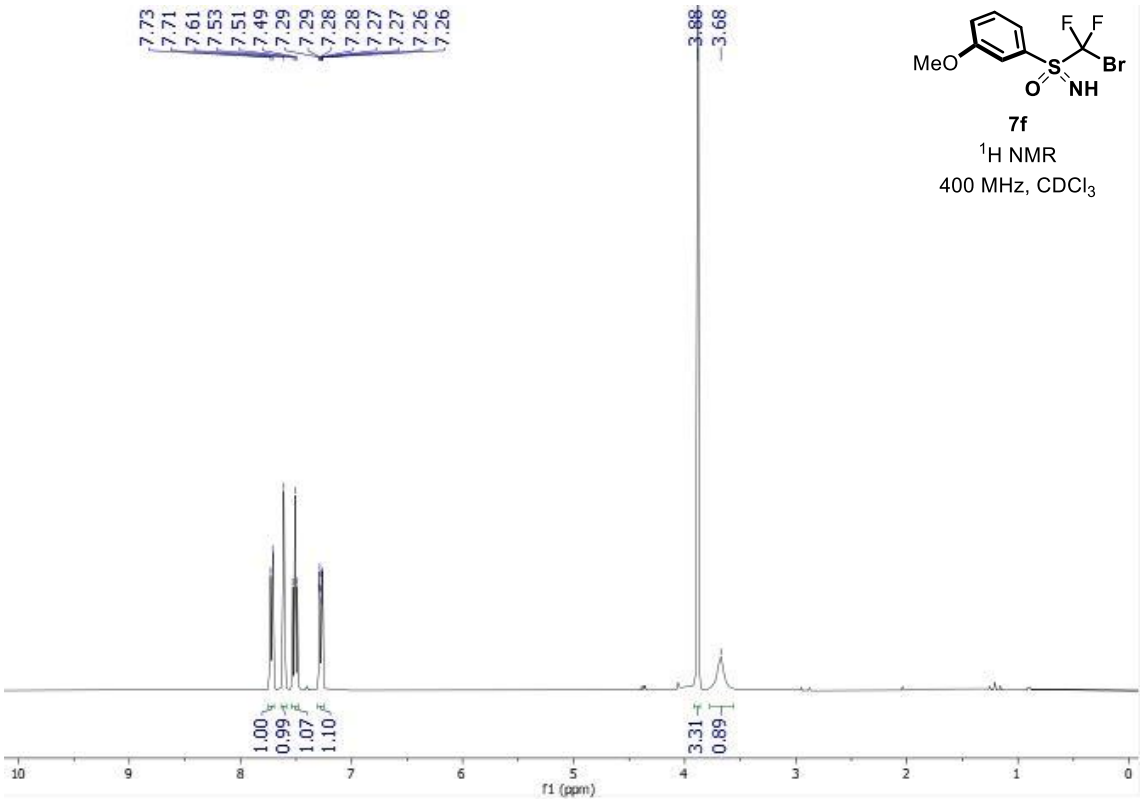




7f

^{19}F NMR {^{1}H}

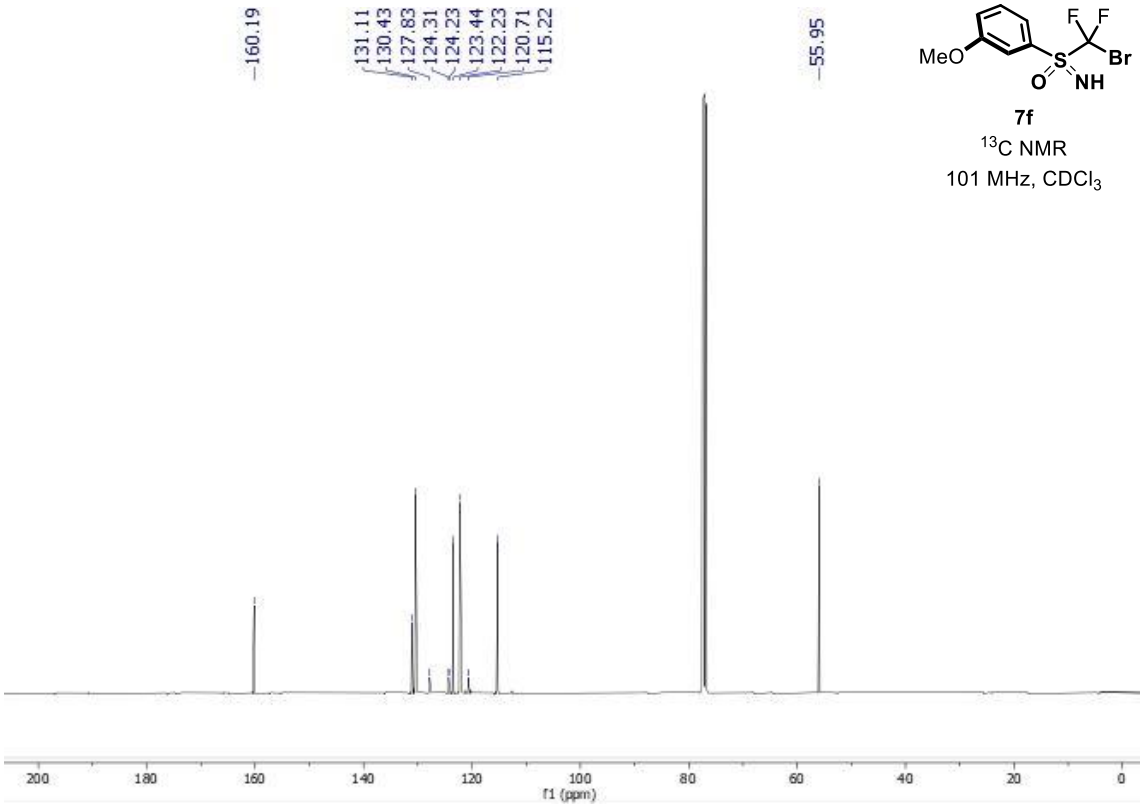
377 MHz, $CDCl_3$



7f

^{1}H NMR

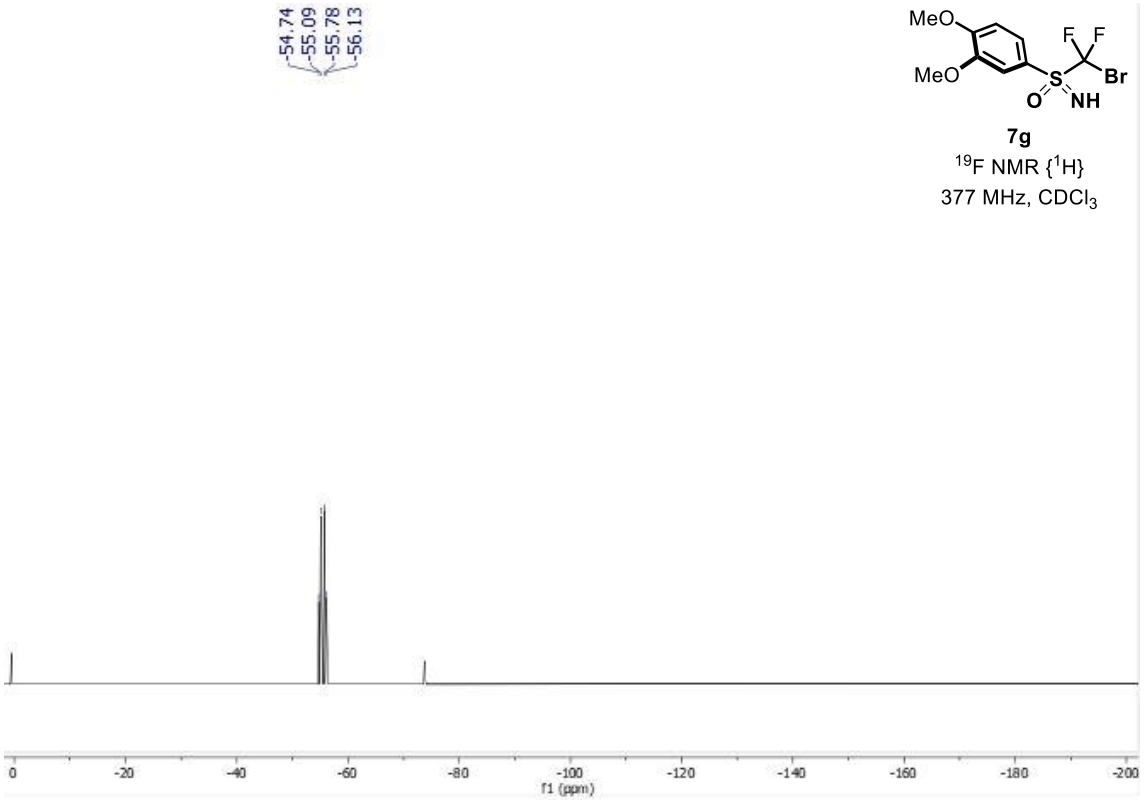
400 MHz, $CDCl_3$



7f

^{13}C NMR

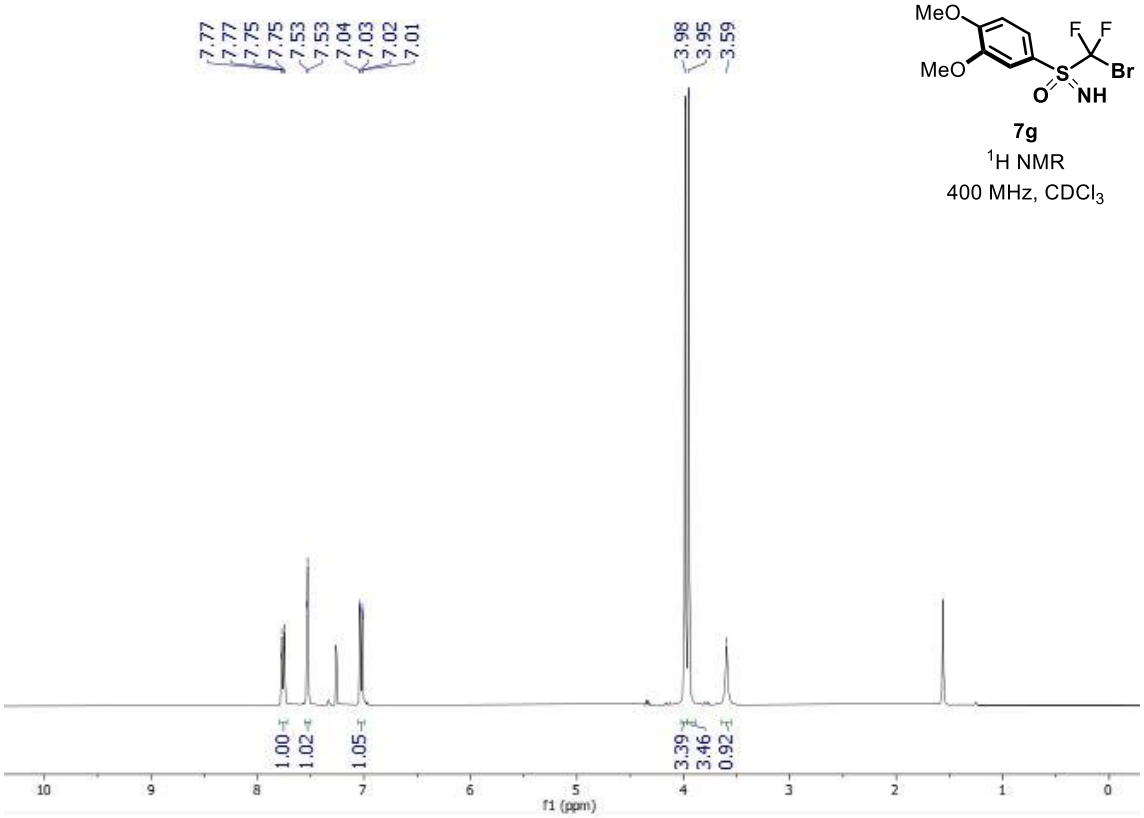
101 MHz, $CDCl_3$



7g

^{19}F NMR {^{1}H}

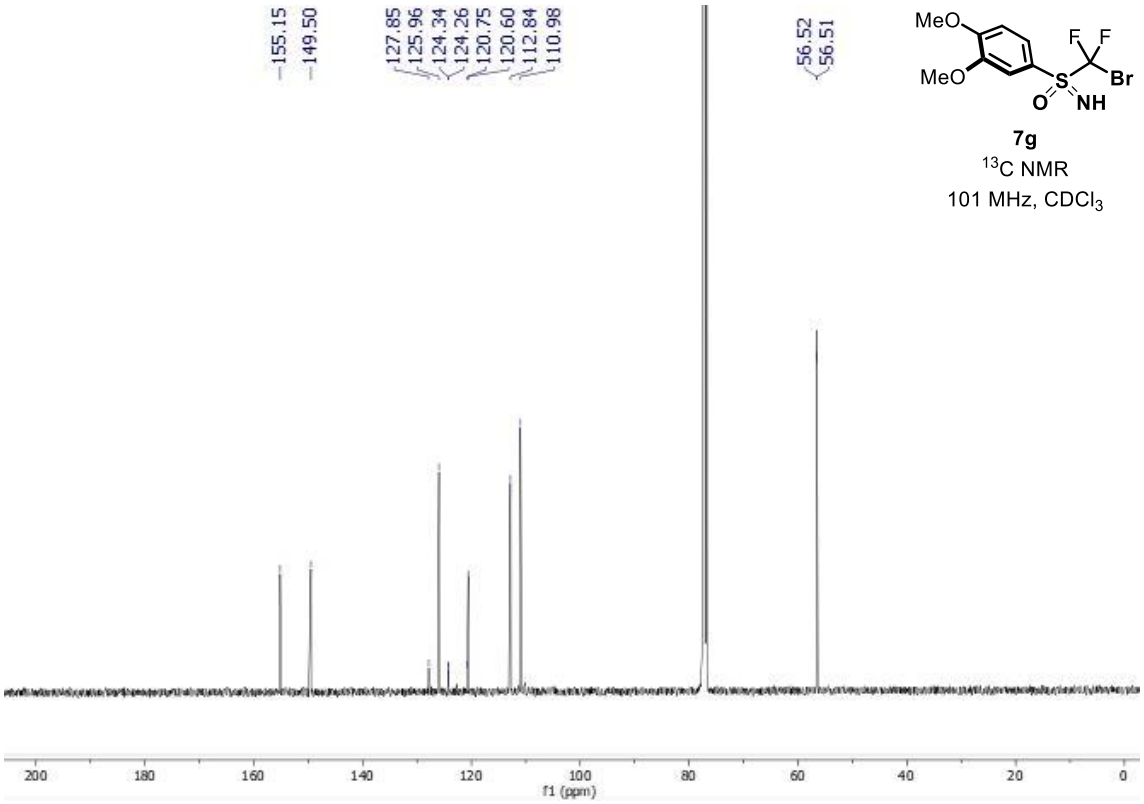
377 MHz, $CDCl_3$



7g

^{1}H NMR

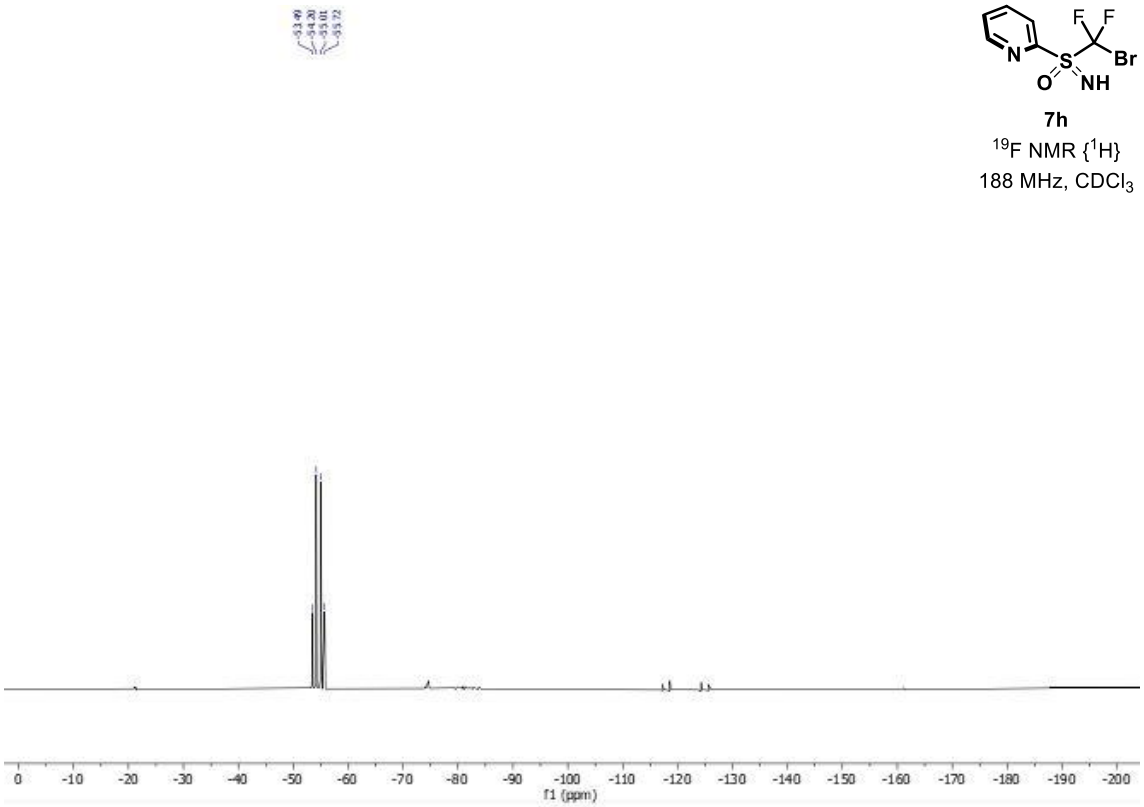
400 MHz, $CDCl_3$



7g

^{13}C NMR

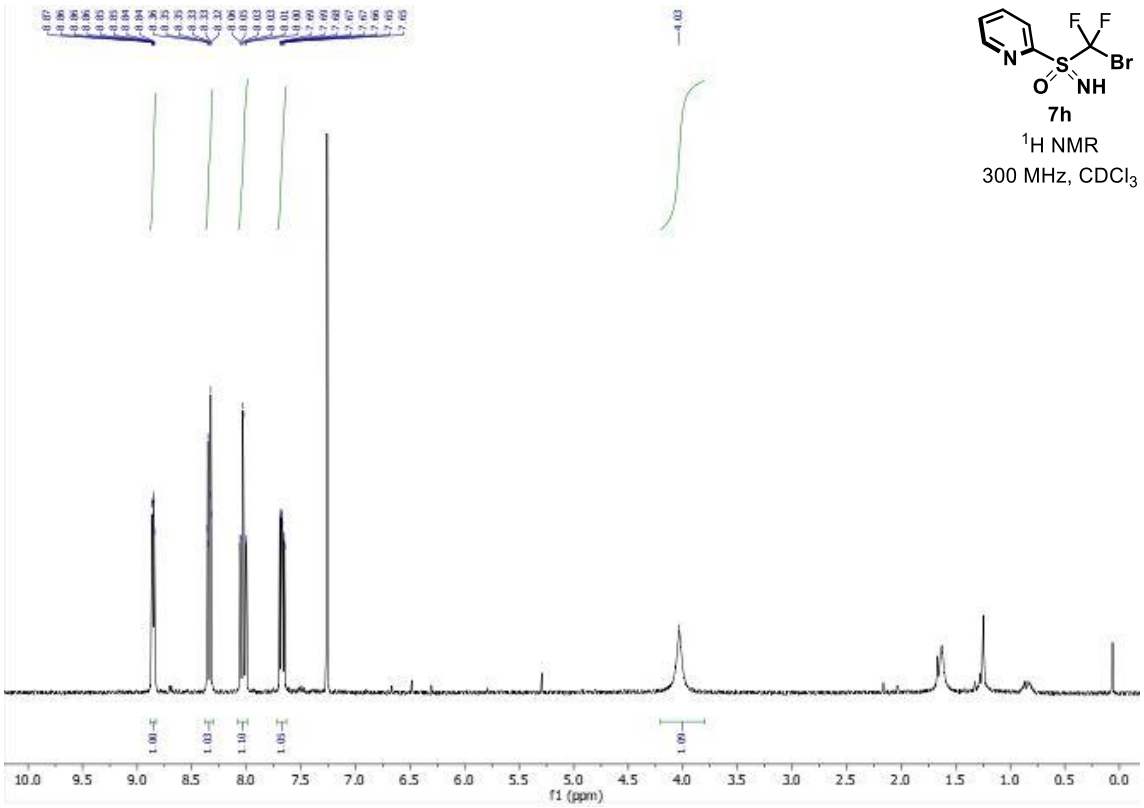
101 MHz, $CDCl_3$



7h

^{19}F NMR $\{^{1}H\}$

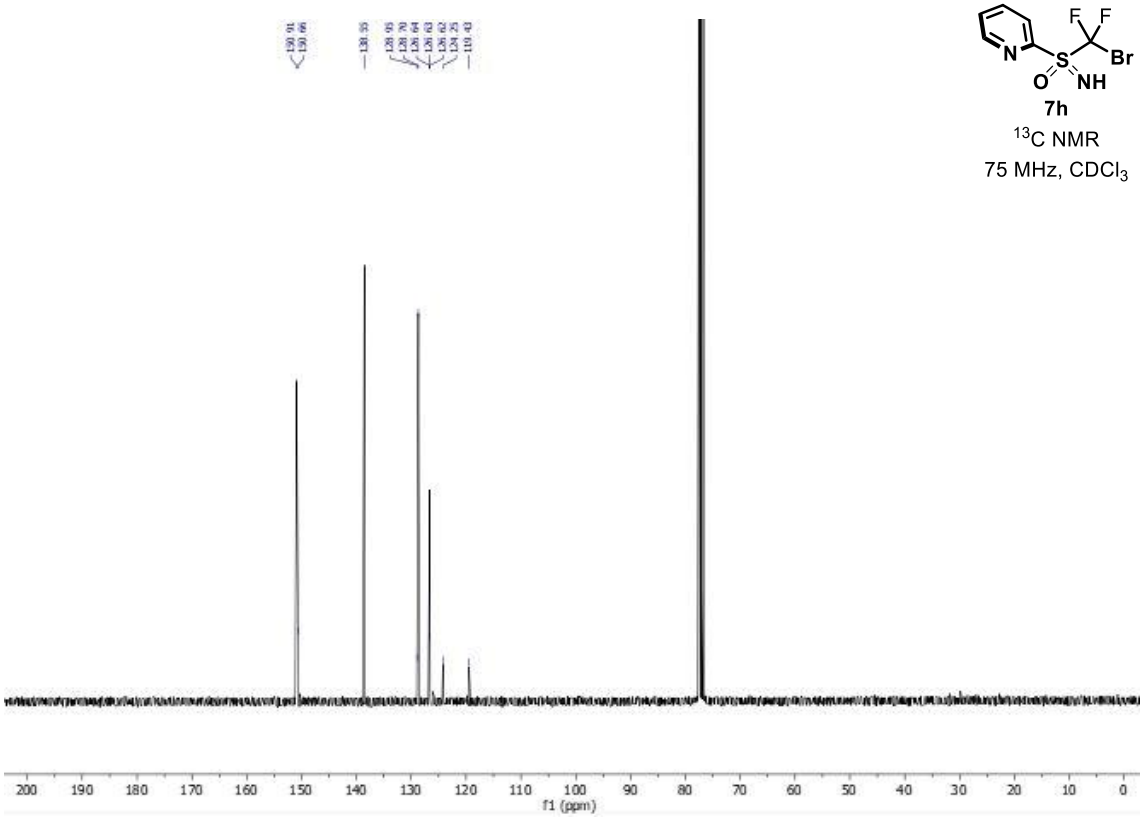
188 MHz, $CDCl_3$



7h

^{1}H NMR

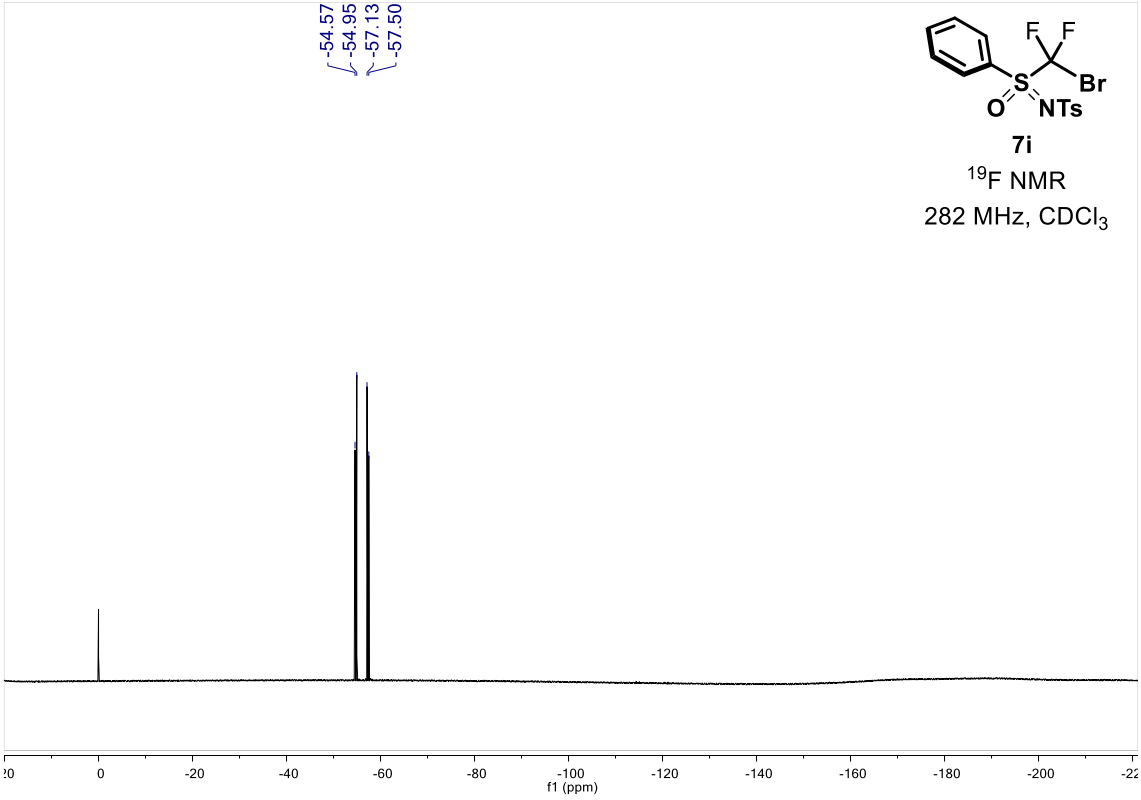
300 MHz, $CDCl_3$

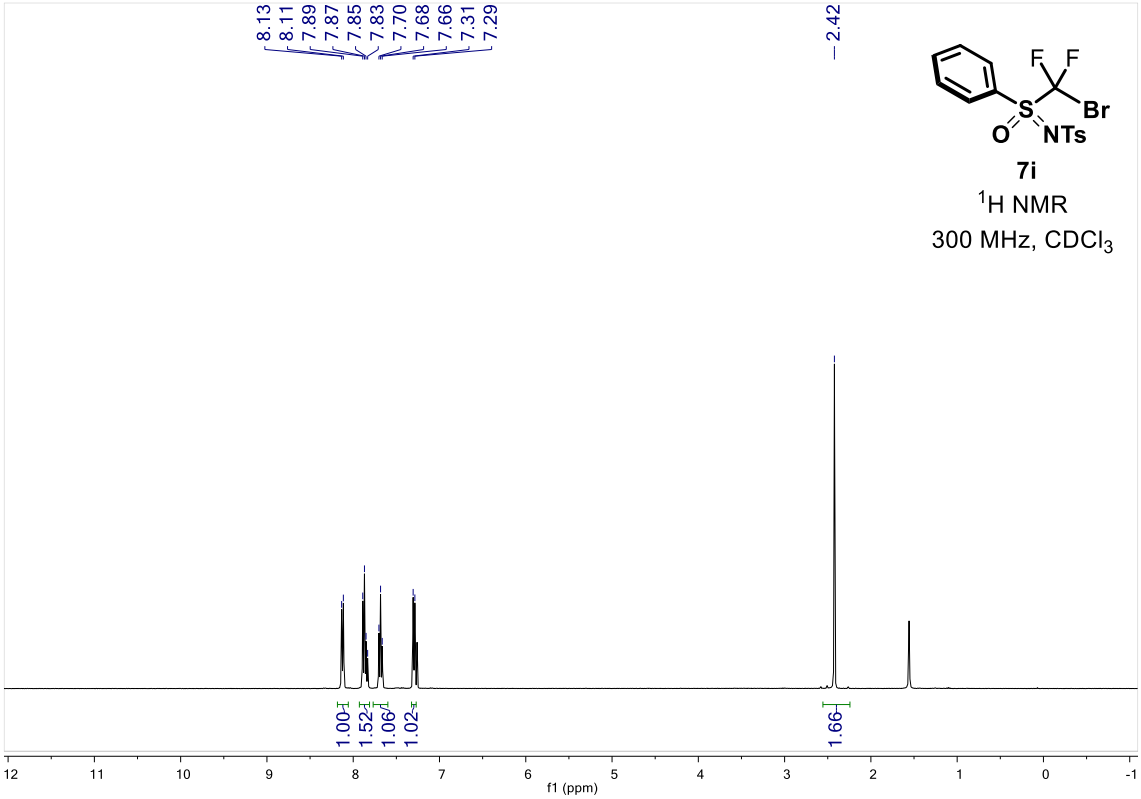


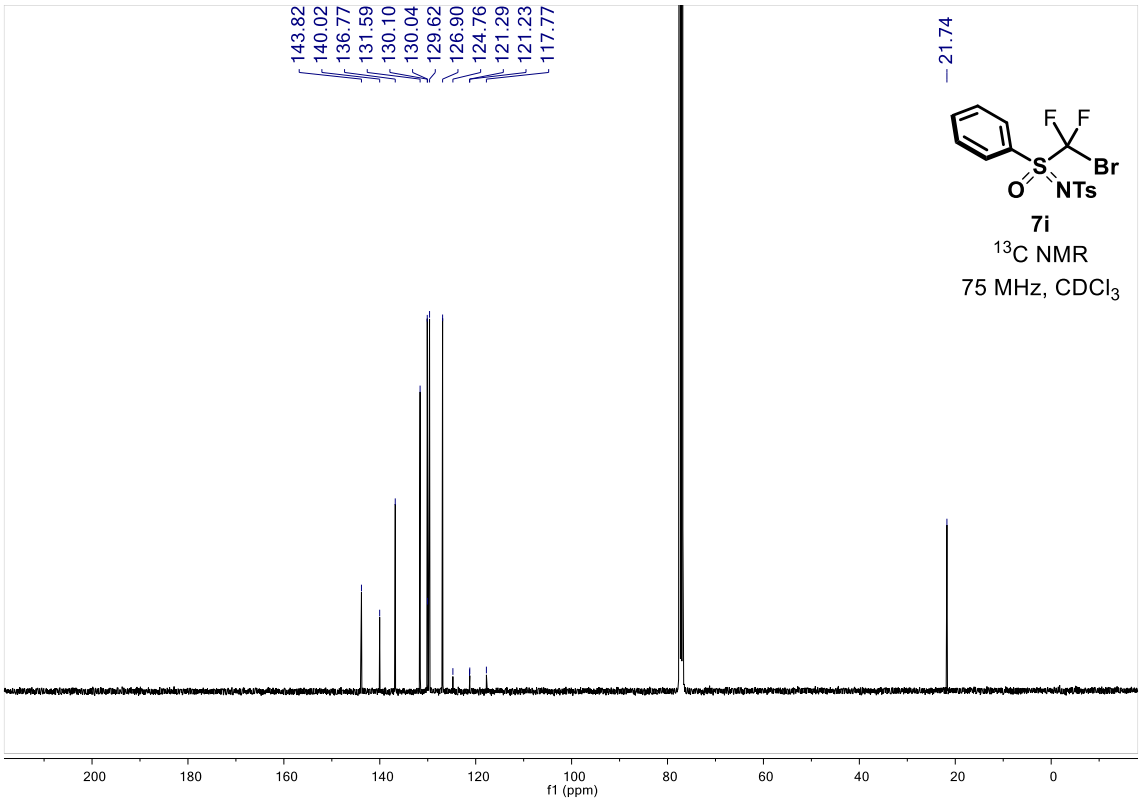
7h

^{13}C NMR

75 MHz, $CDCl_3$


-54.57
-54.95
-57.13
-57.50
F F
S
Br
O NTs
7i
19F NMR
282 MHz, CDCl3
f1 (ppm)

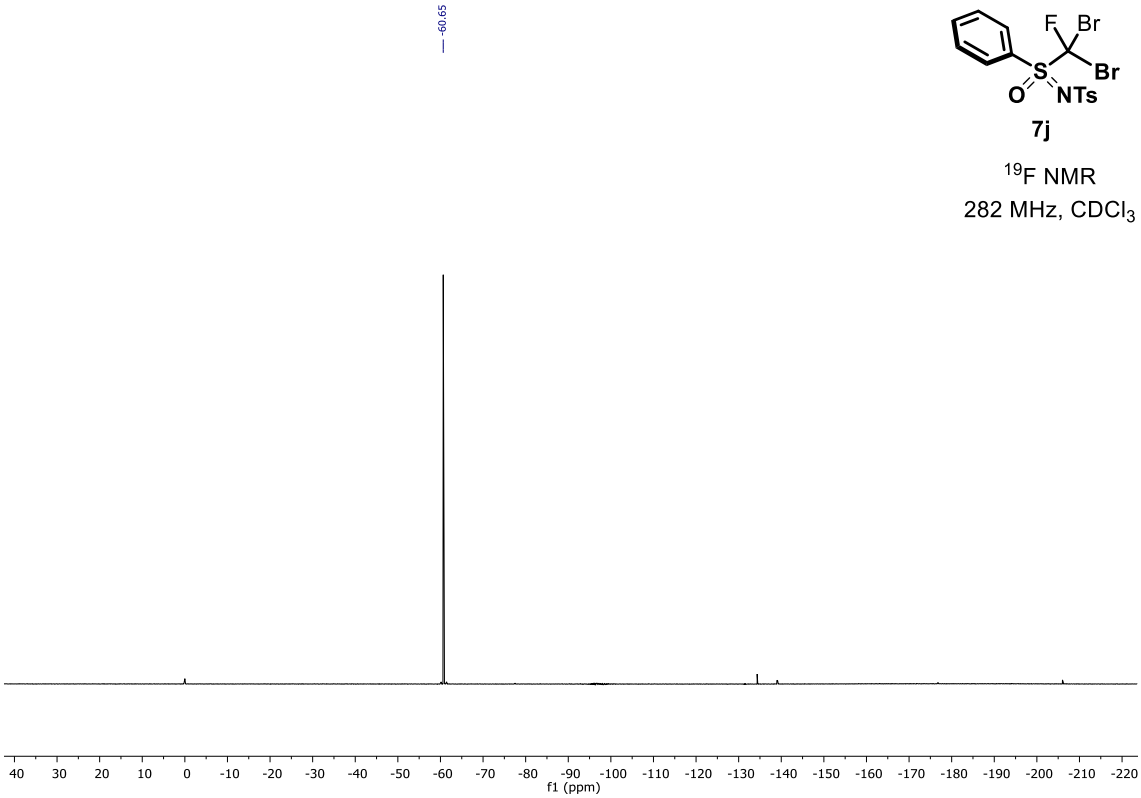

8.13
8.11
7.89
7.87
7.85
7.83
7.70
7.68
7.66
7.31
7.29
2.42
F F
S
Br
O NTs
7i
1H NMR
300 MHz, CDCl3
1.00
1.52
1.06
1.02
1.66
f1 (ppm)



7i

^{13}C NMR

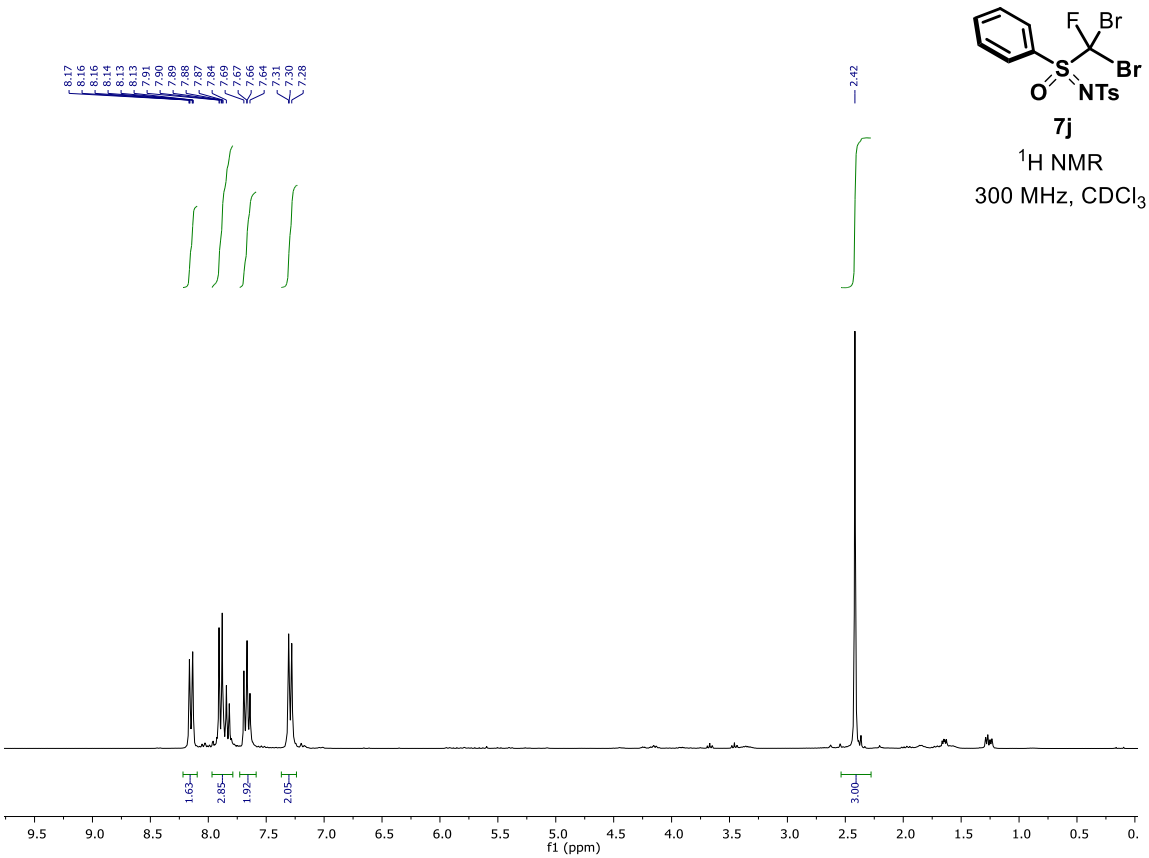
75 MHz, $CDCl_3$



7j

^{19}F NMR

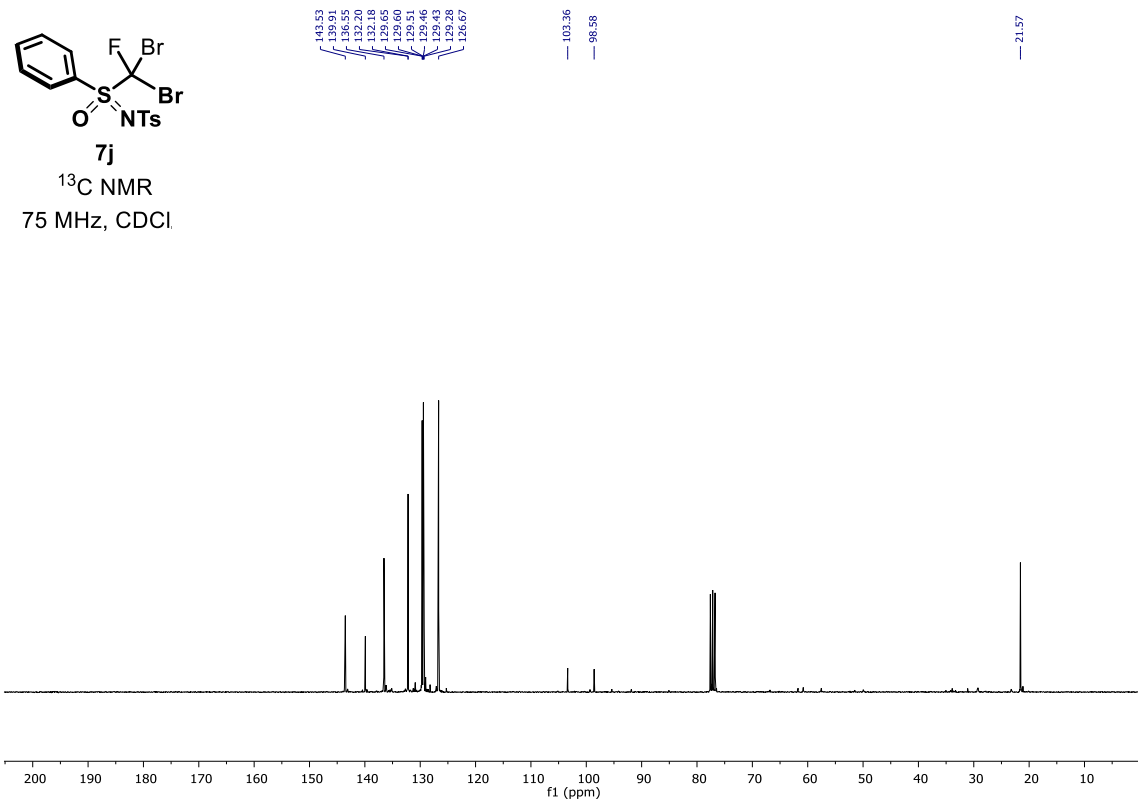
282 MHz, $CDCl_3$



7j

^{1}H NMR

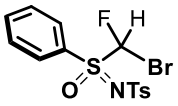
300 MHz, $CDCl_3$



7j

^{13}C NMR

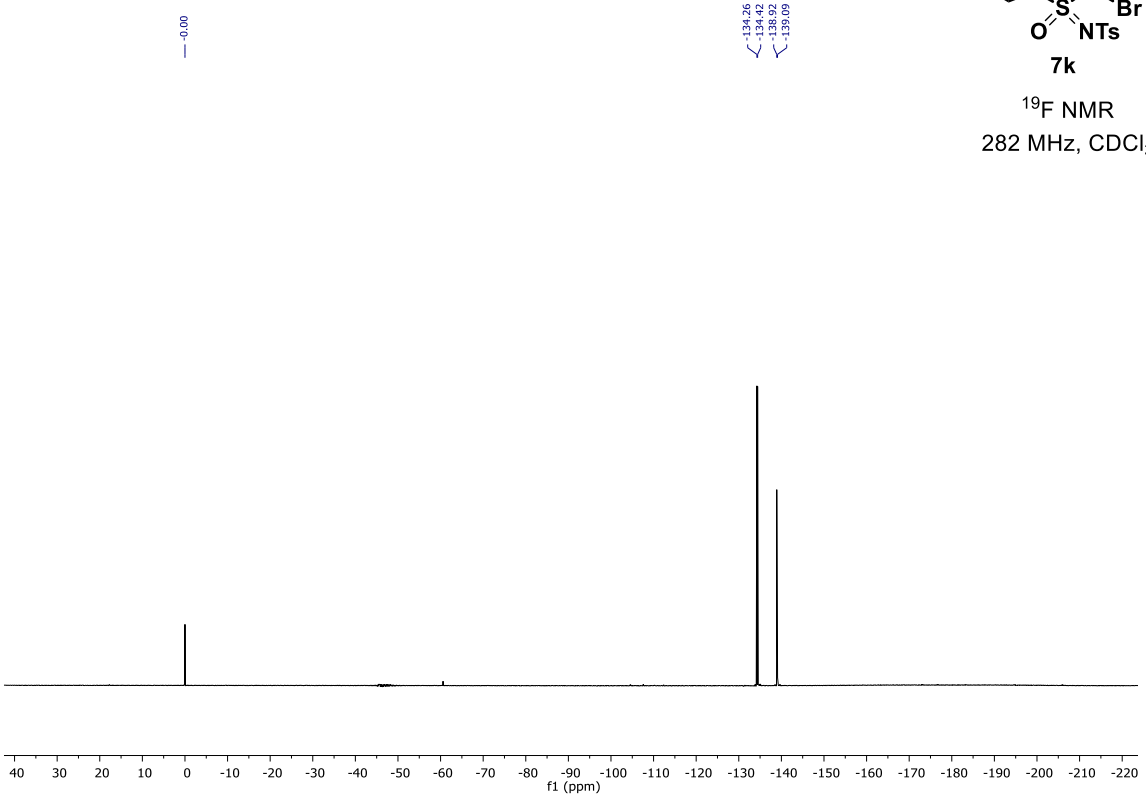
75 MHz, $CDCl_3$

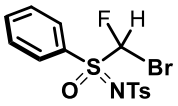


7k

^{19}F NMR

282 MHz, $CDCl_3$

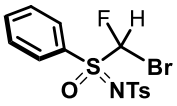




7k

^{1}H NMR

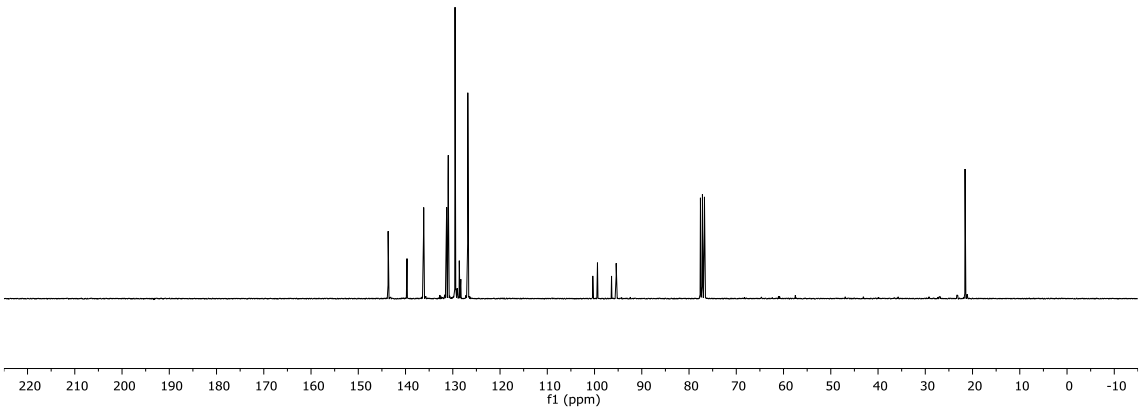
300 MHz, $CDCl_3$

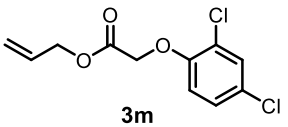


7k

^{13}C NMR

75 MHz, $CDCl_3$

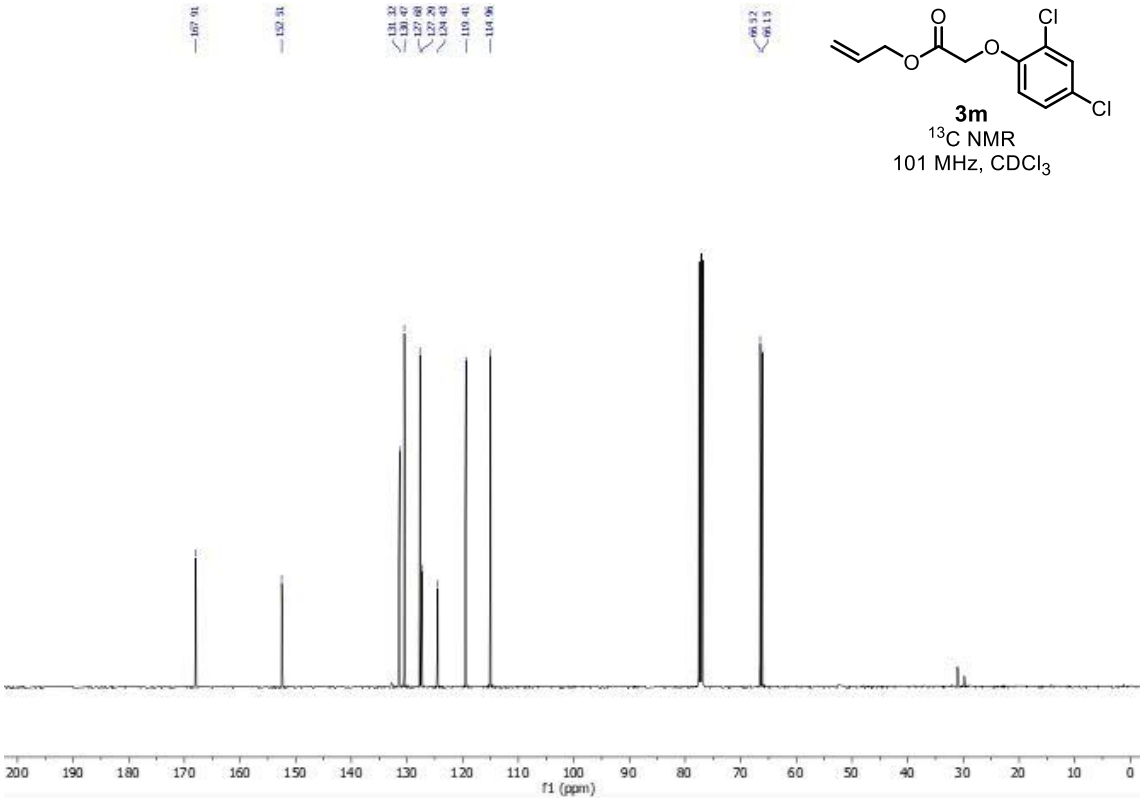




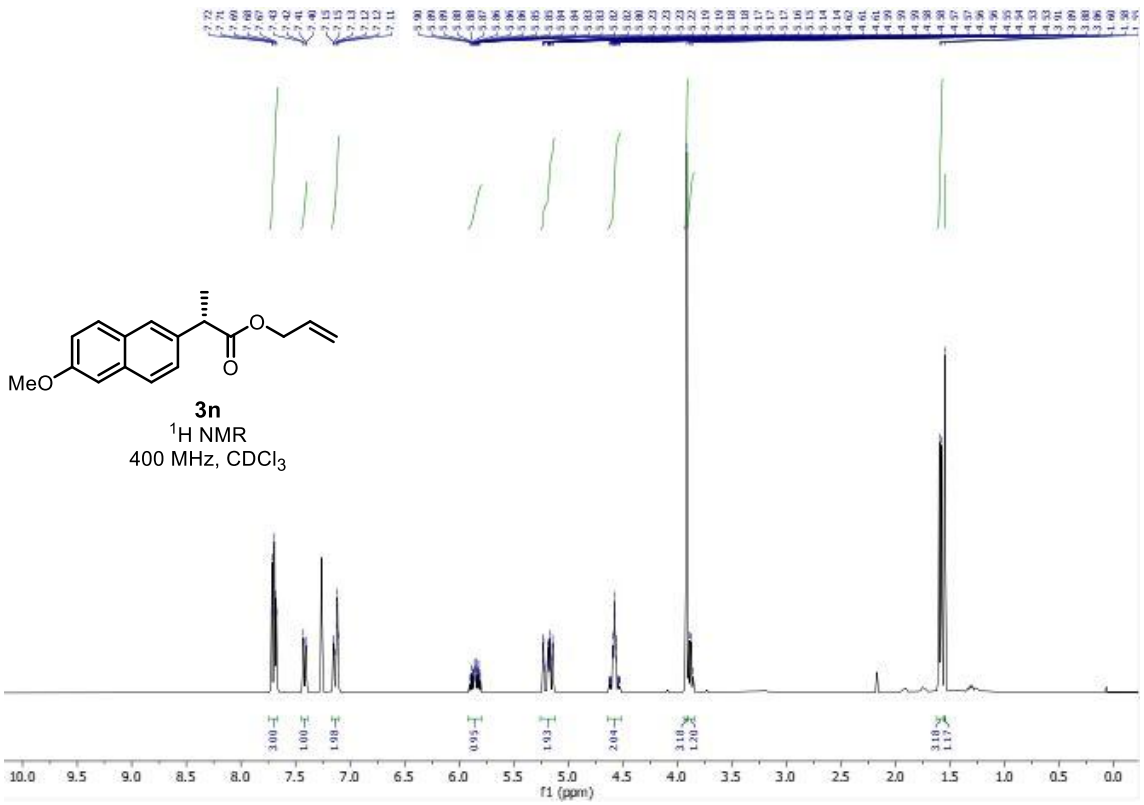
3m

^{1}H NMR

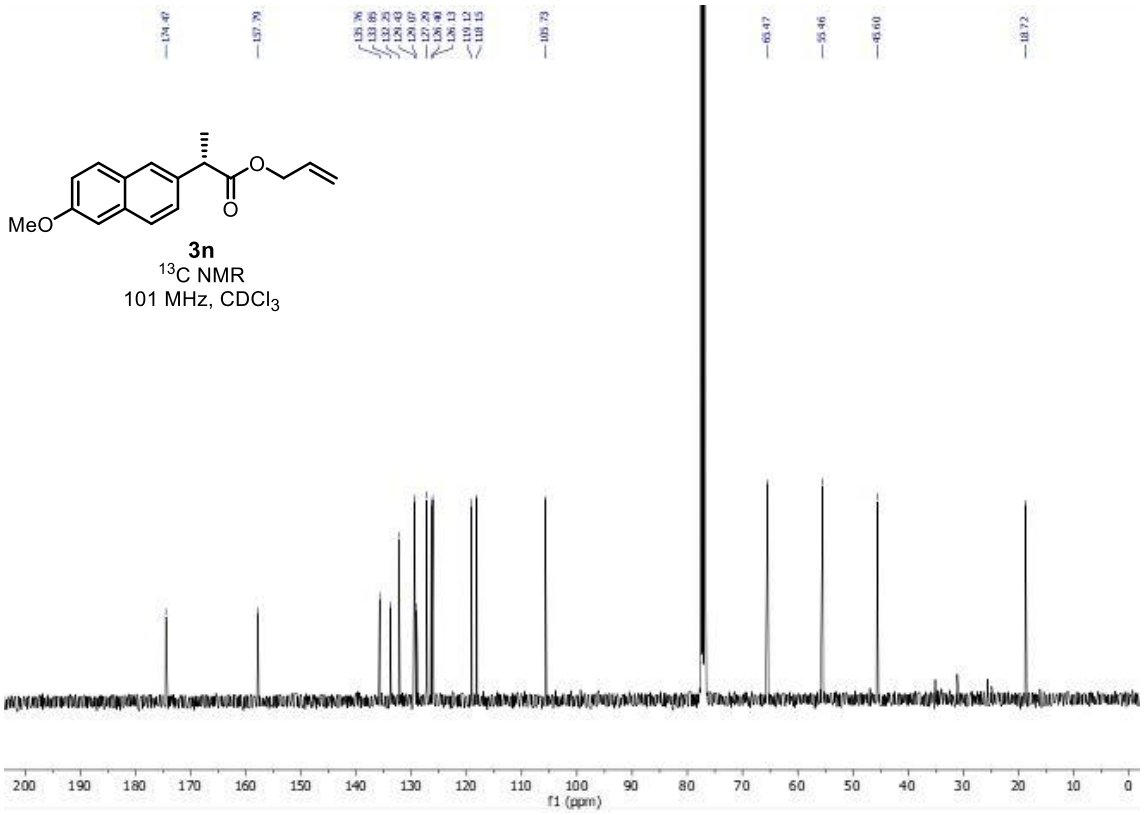
400 MHz, $CDCl_3$



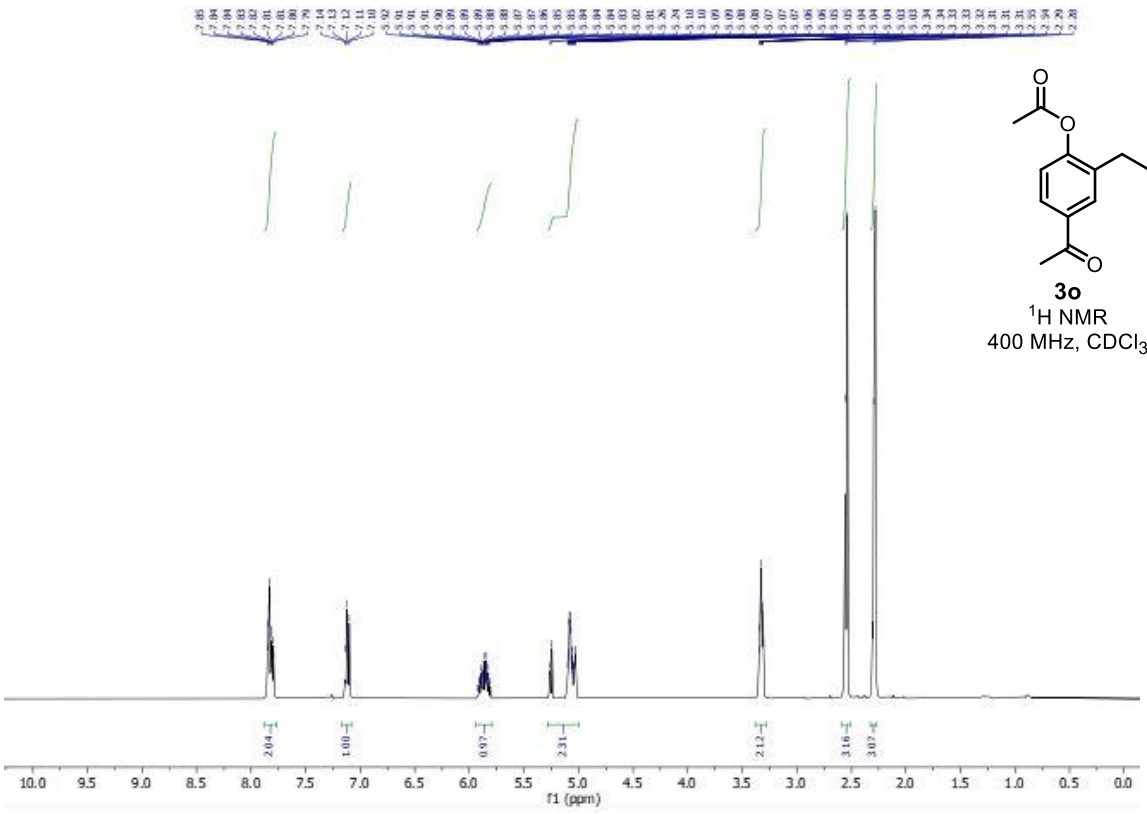
3m
^{13}C NMR
101 MHz, $CDCl_3$



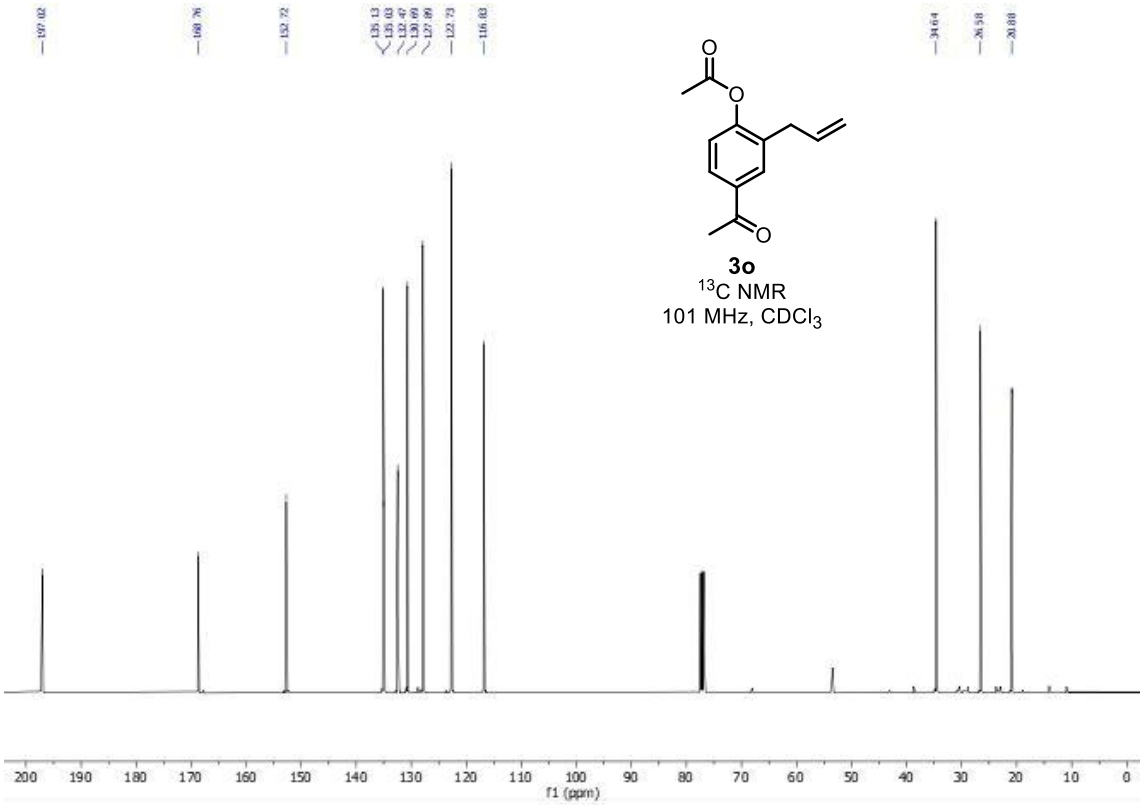
3n
^{1}H NMR
400 MHz, $CDCl_3$



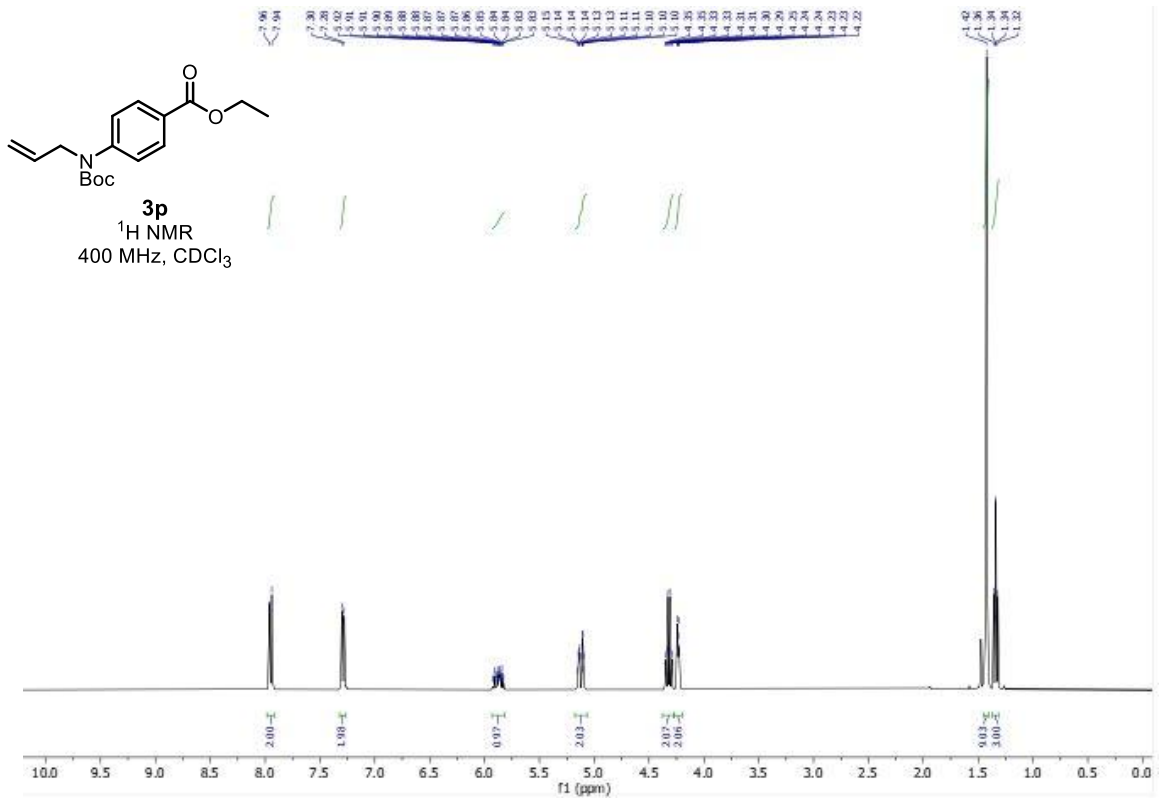
3n
^{13}C NMR
101 MHz, $CDCl_3$



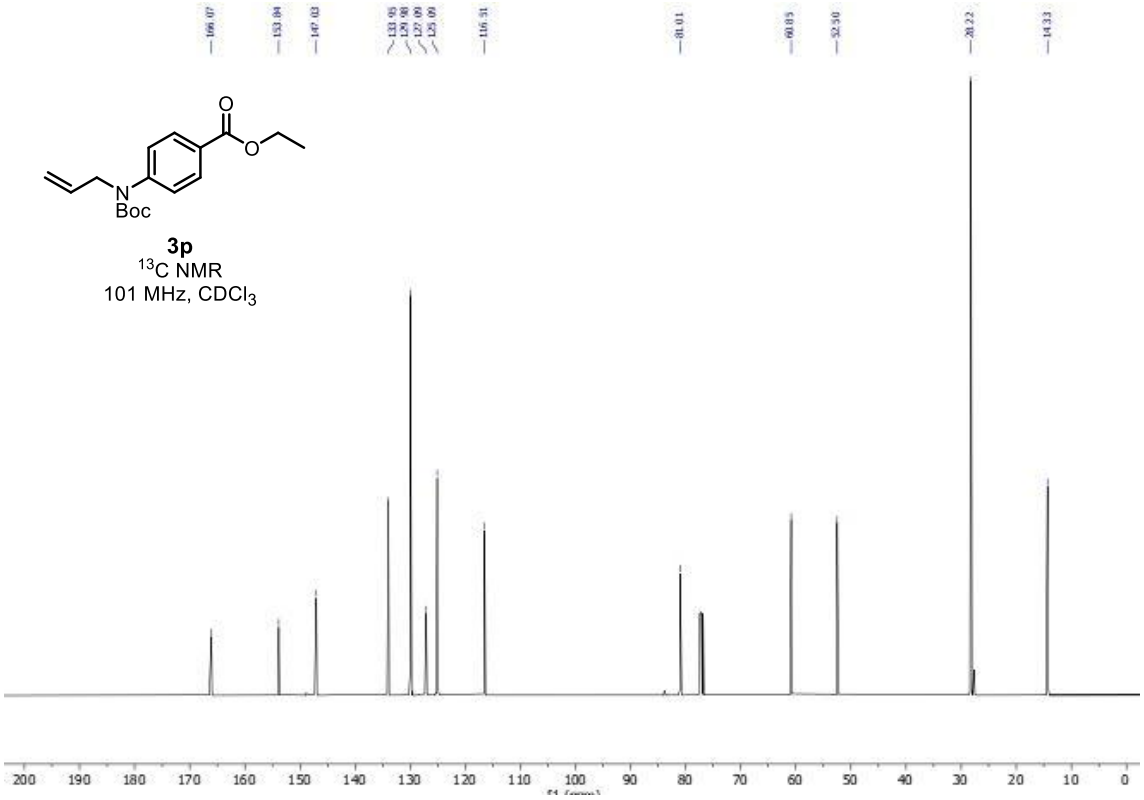
3o
^{1}H NMR
400 MHz, $CDCl_3$



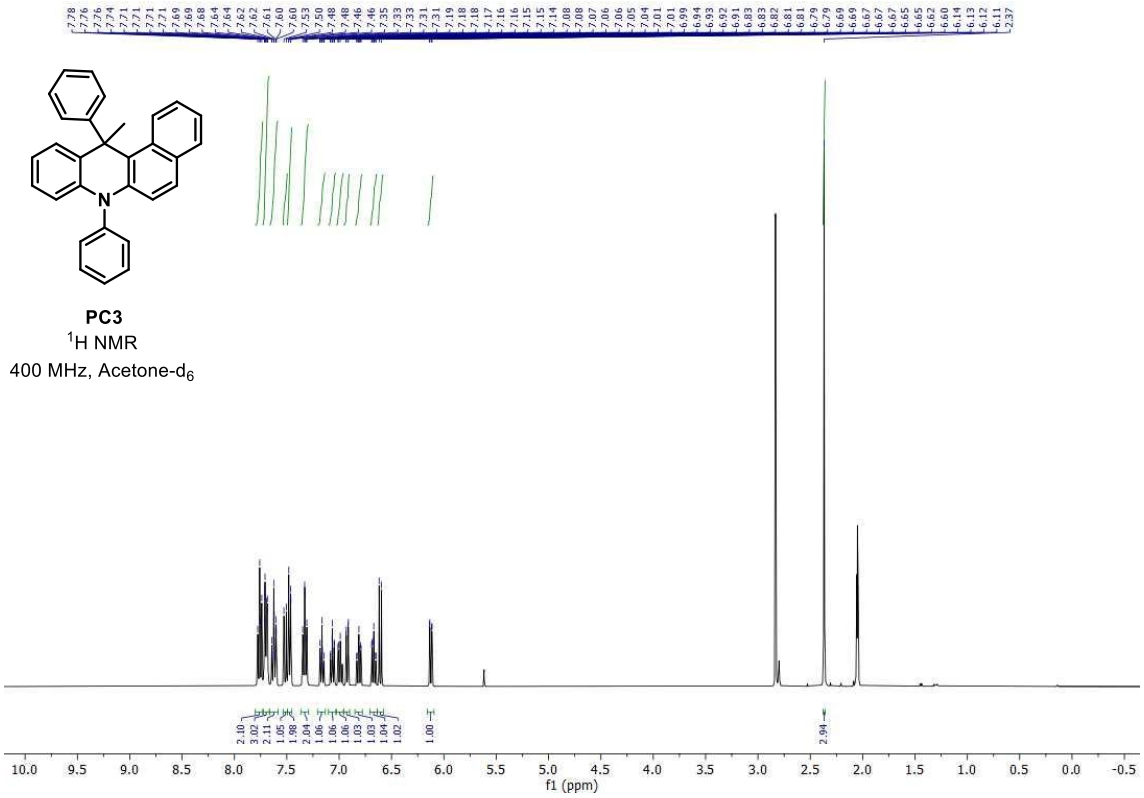
3o
^{13}C NMR
101 MHz, $CDCl_3$



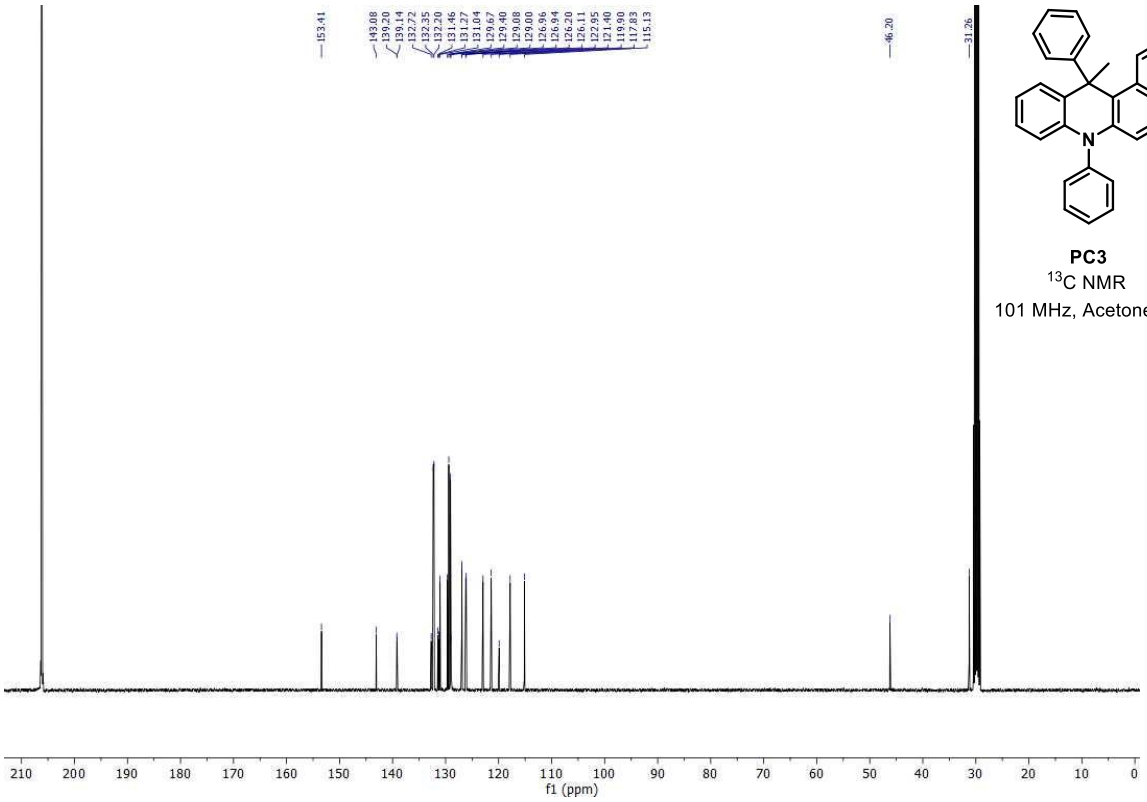
3p
^{1}H NMR
400 MHz, $CDCl_3$



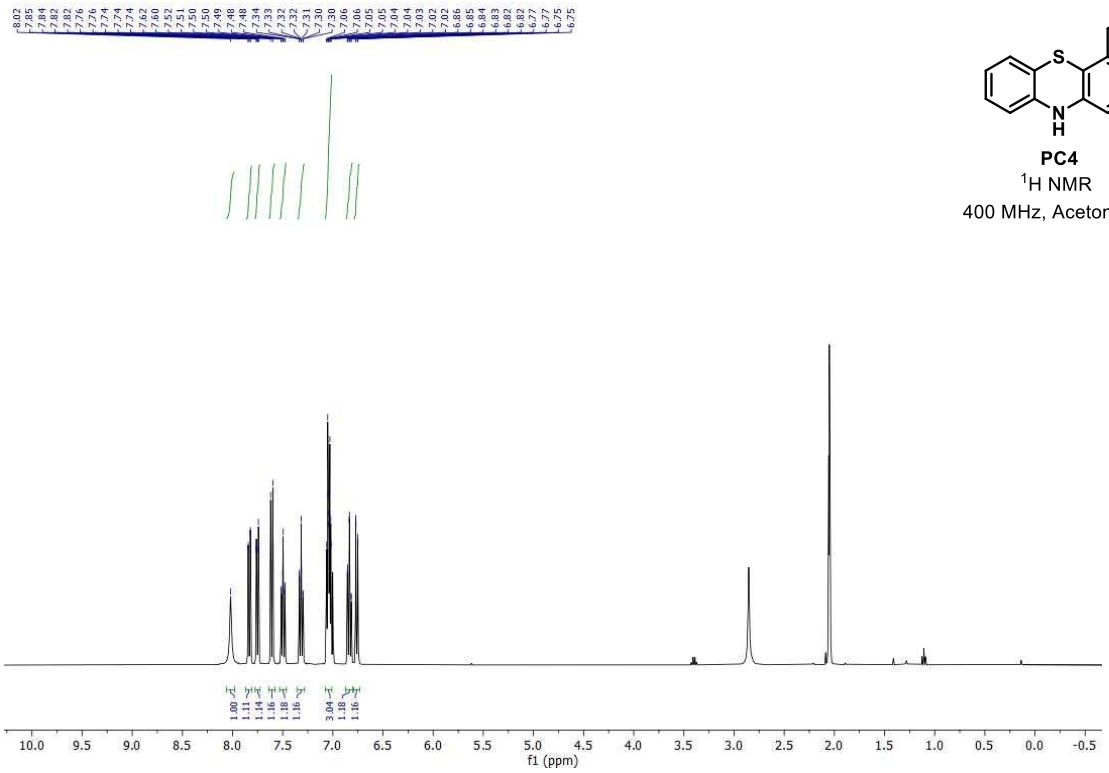
3p
^{13}C NMR
101 MHz, $CDCl_3$



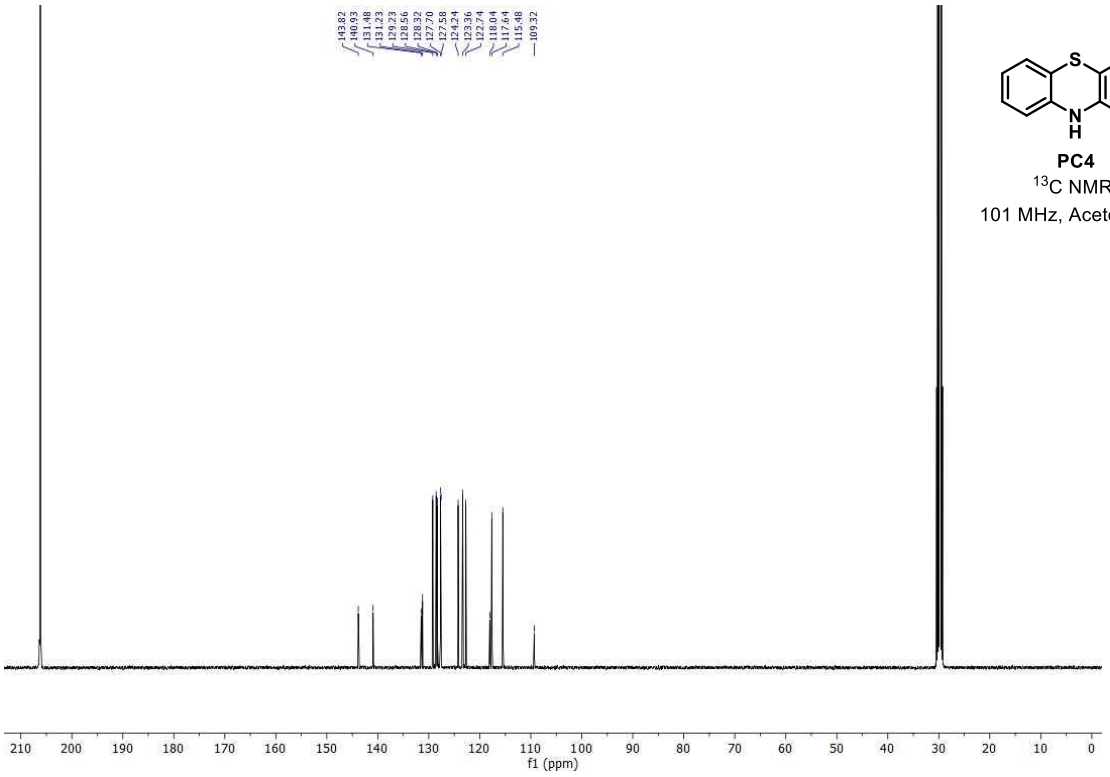
PC3
^{1}H NMR
400 MHz, Acetone-d_6



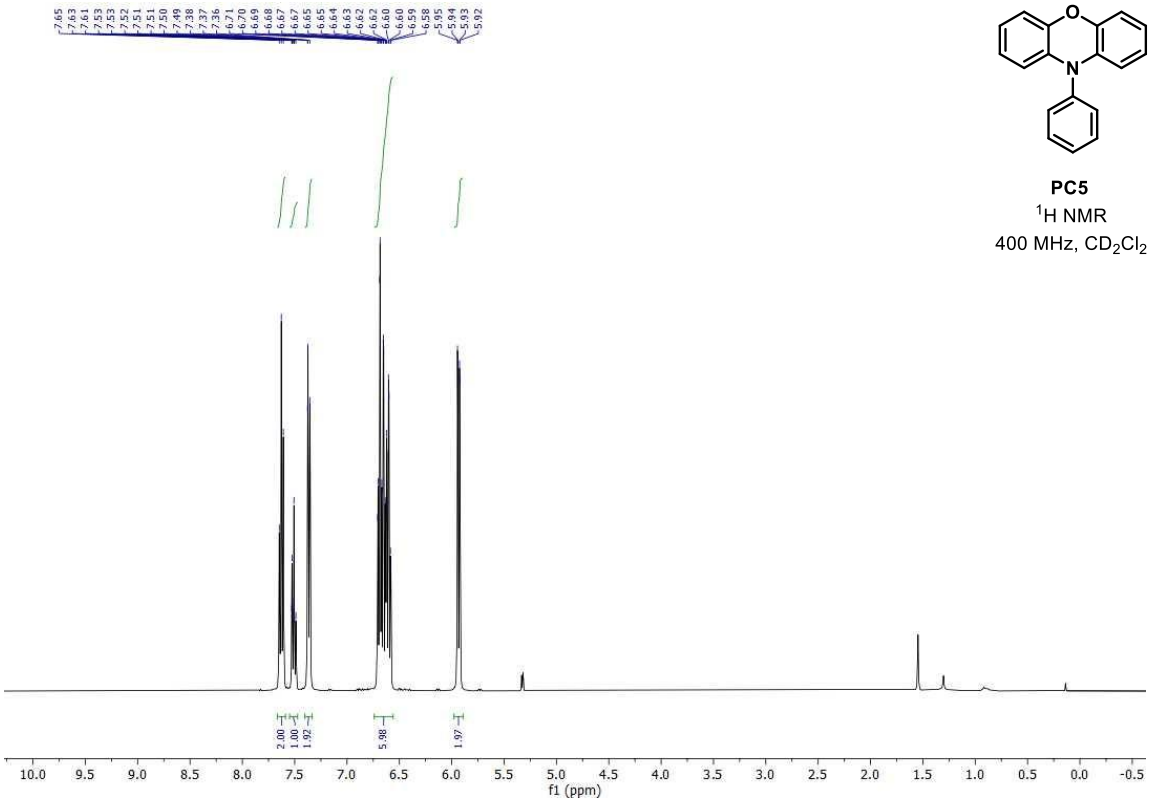
PC3
^{13}C NMR
101 MHz, Acetone-d_6



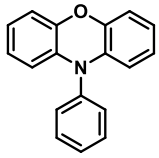
PC4
^{1}H NMR
400 MHz, Acetone-d_6



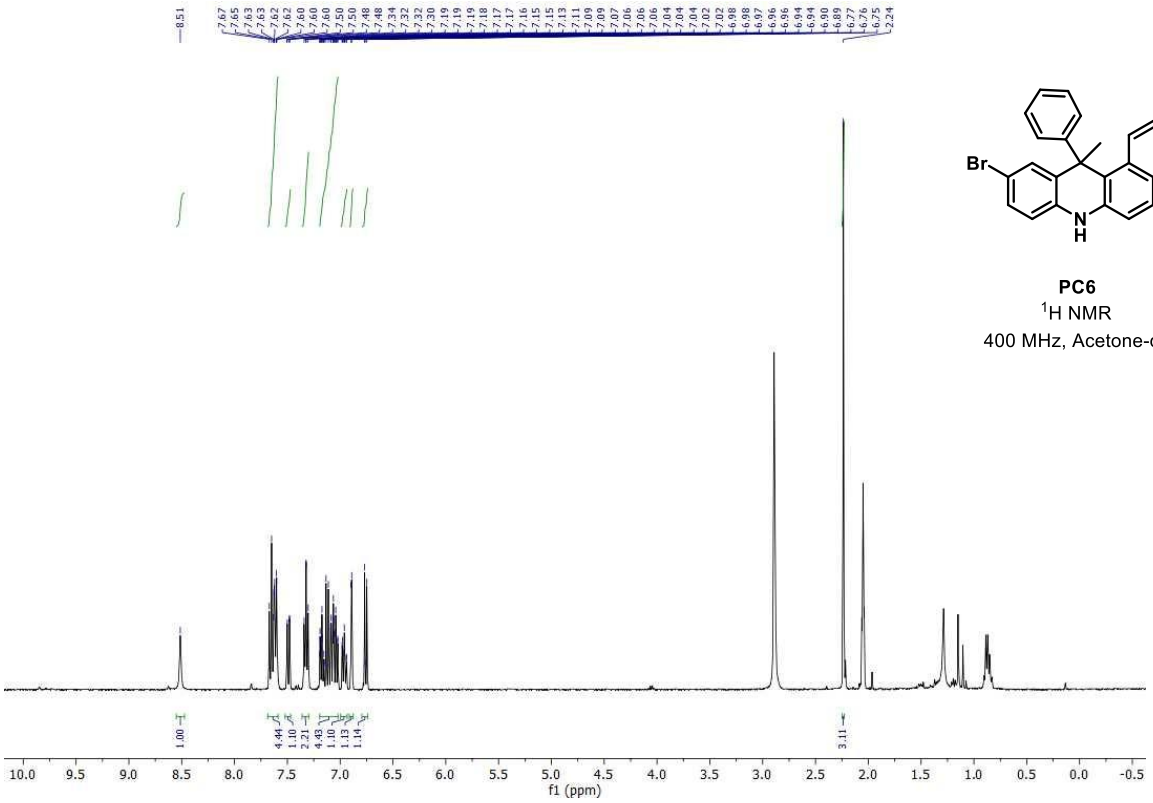
PC4
^{13}C NMR
101 MHz, Acetone-d_6



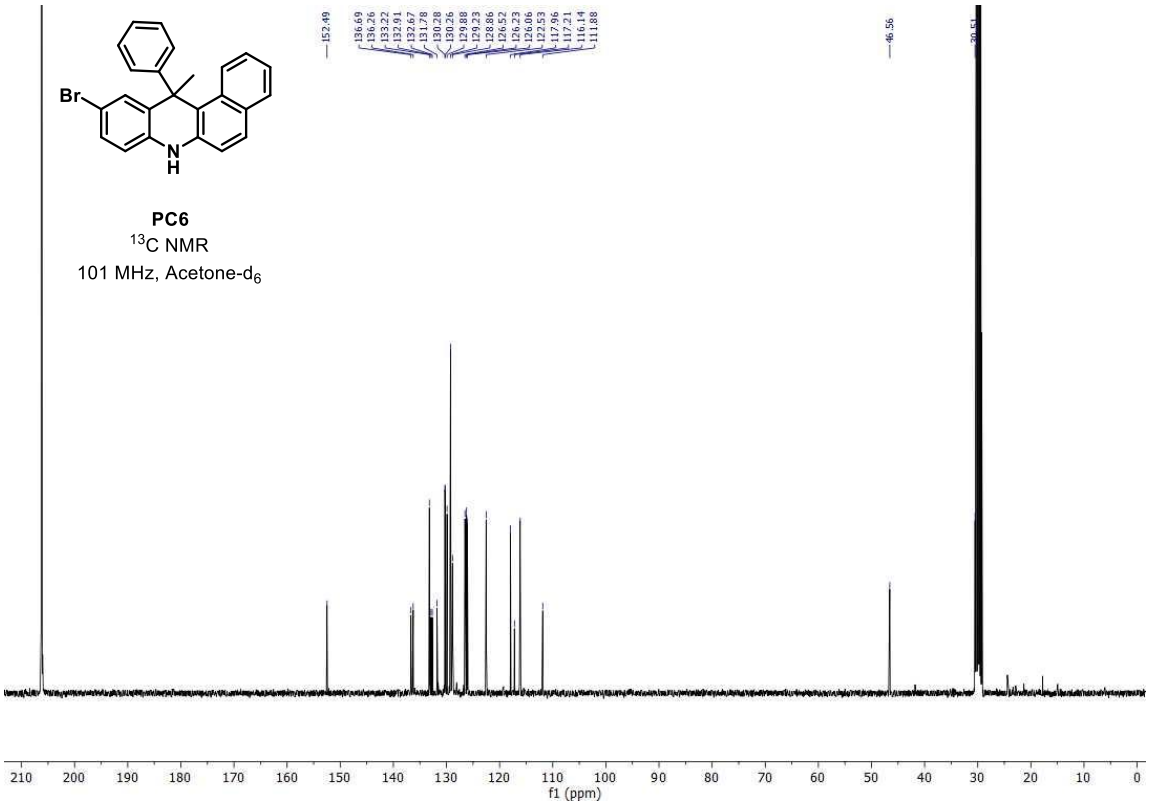
PC5
^{1}H NMR
400 MHz, CD_2Cl_2



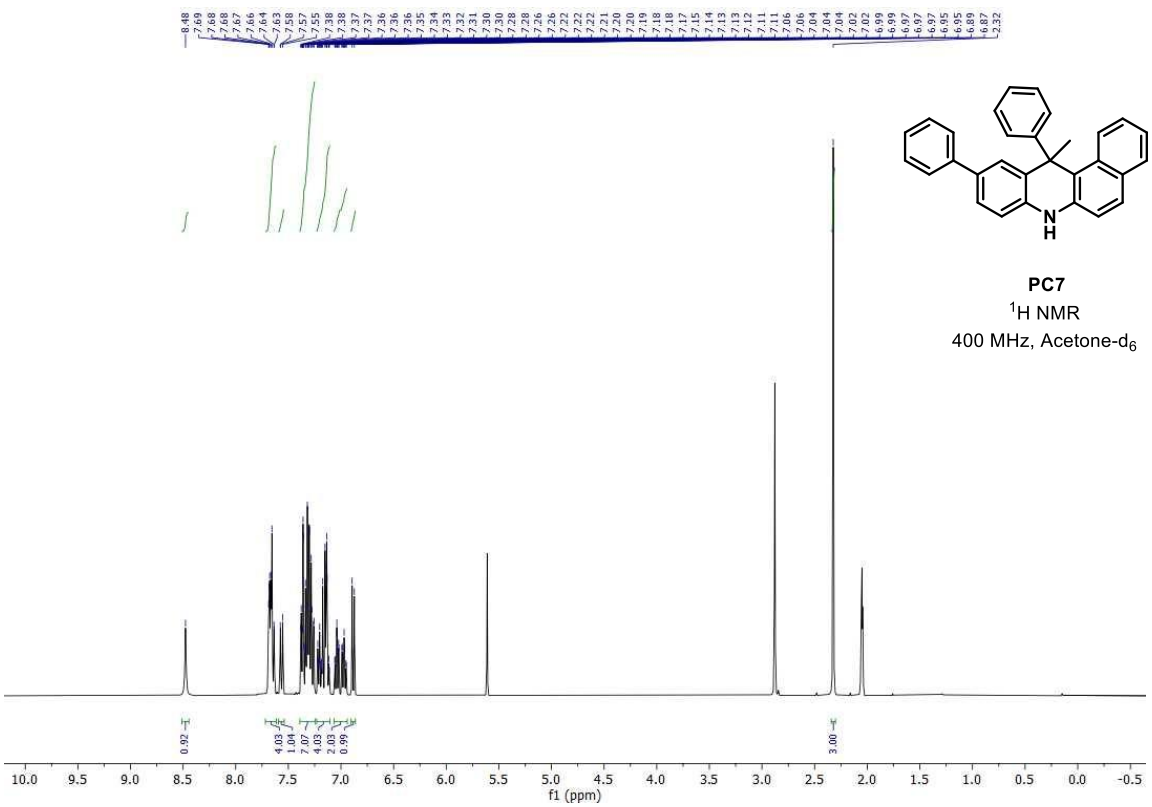
PC5
^{13}C NMR
101 MHz, CD_2Cl_2



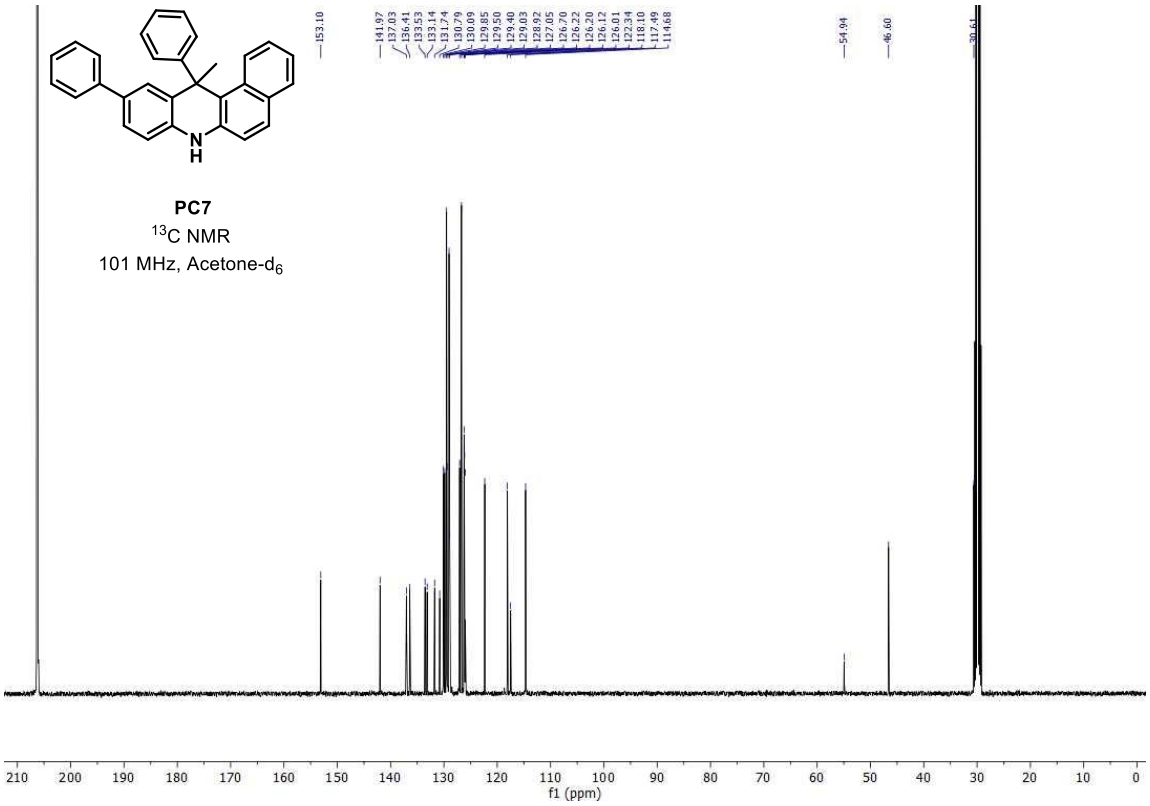
PC6
^{1}H NMR
400 MHz, Acetone-d_6



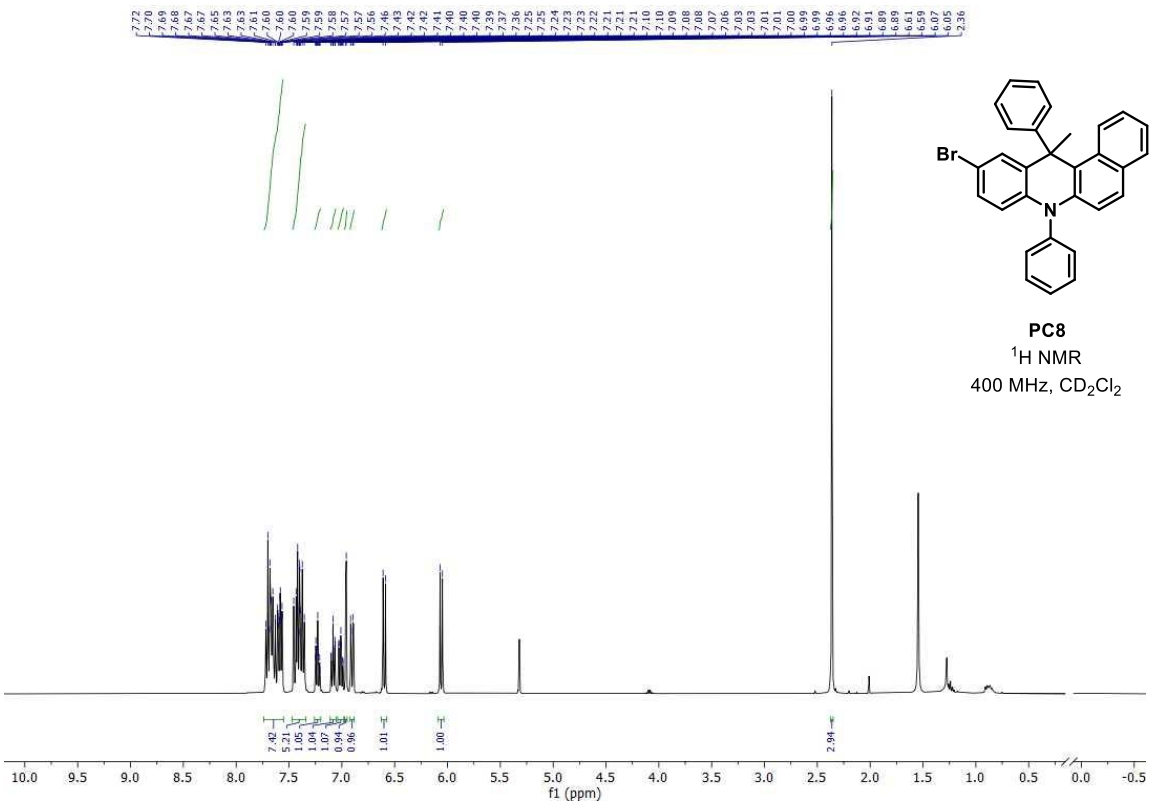
PC6
^{13}C NMR
101 MHz, Acetone-d_6



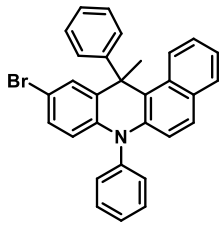
PC7
^{1}H NMR
400 MHz, Acetone-d_6



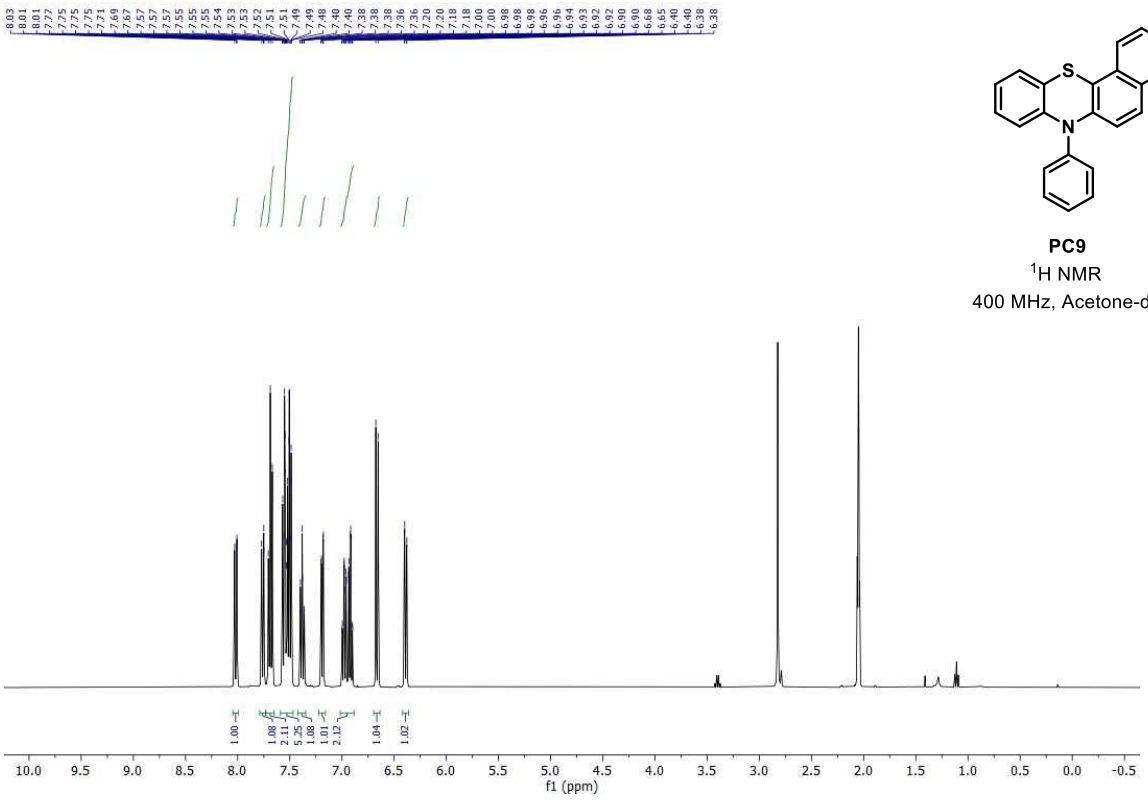
PC7
^{13}C NMR
101 MHz, Acetone-d_6



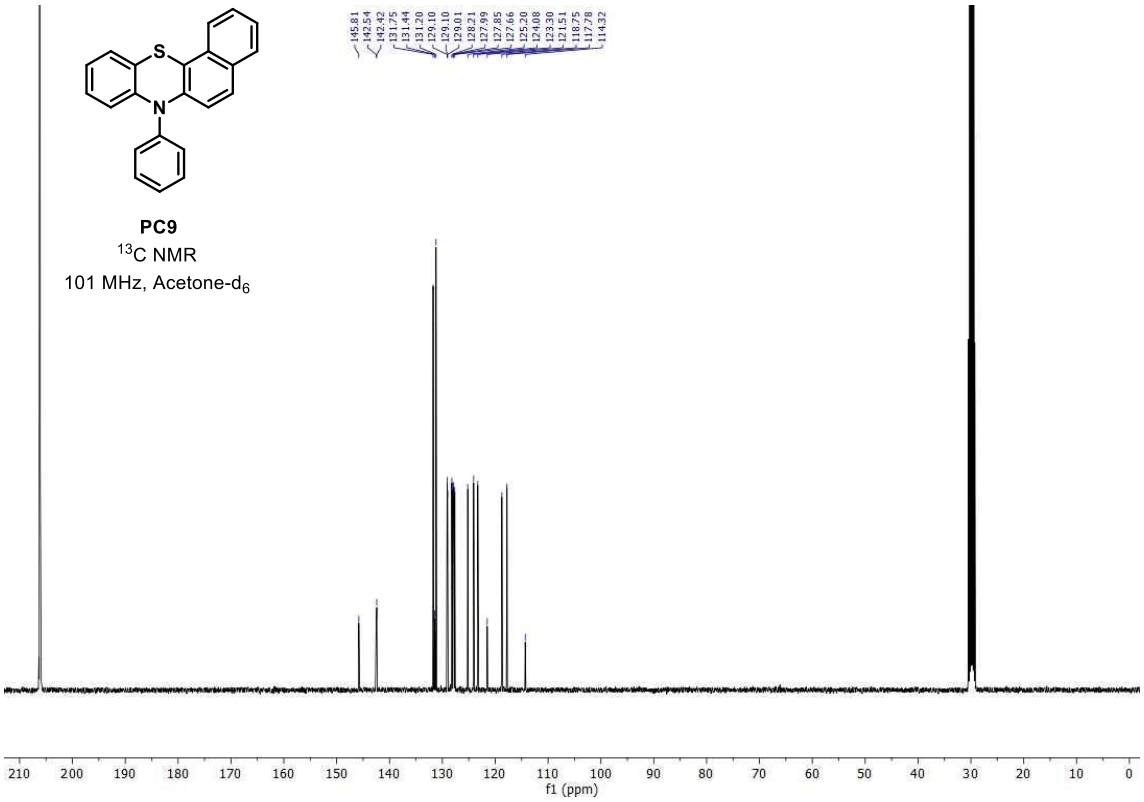
PC8
^{1}H NMR
400 MHz, CD_2Cl_2



PC8
^{13}C NMR
101 MHz, CD_2Cl_2



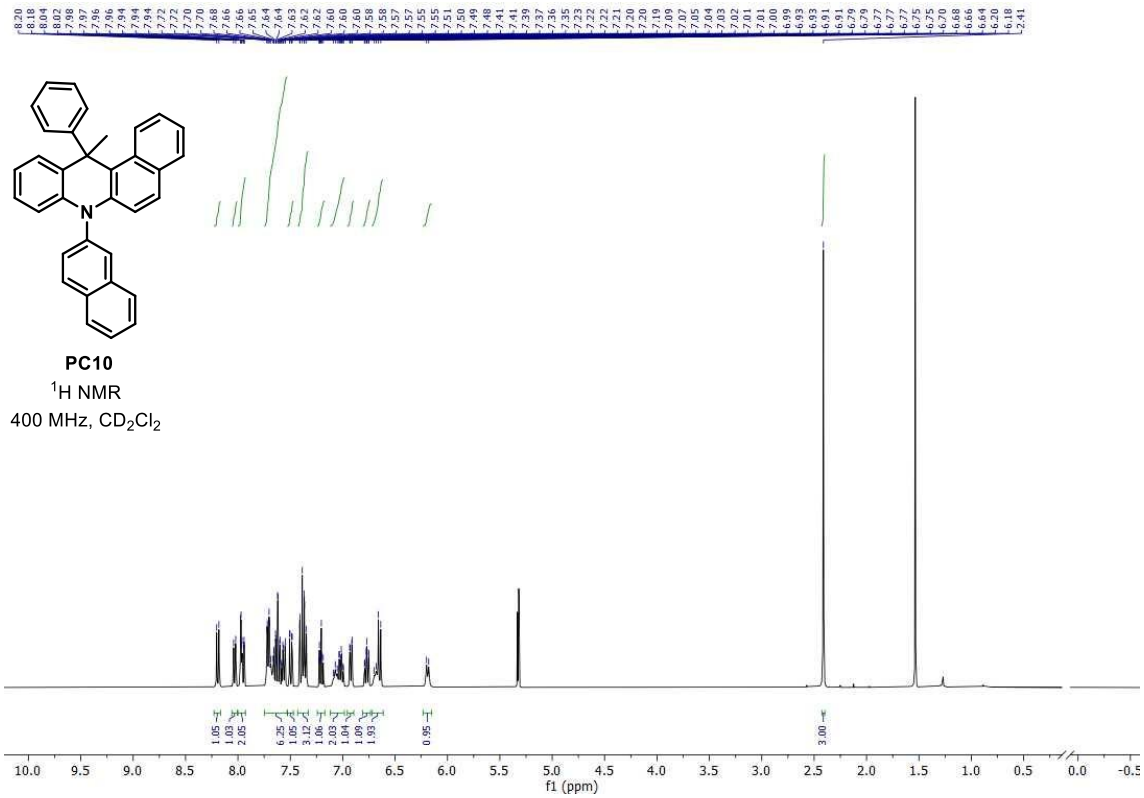
PC9
^{1}H NMR
400 MHz, Acetone-d_6



PC9

^{13}C NMR

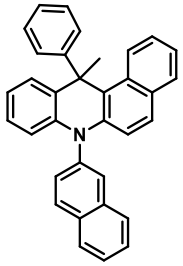
101 MHz, Acetone-d_6



PC10

^{1}H NMR

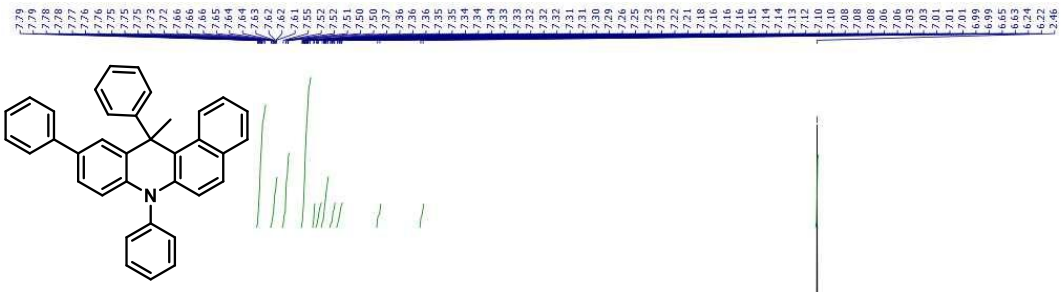
400 MHz, CD_2Cl_2



PC10

^{13}C NMR

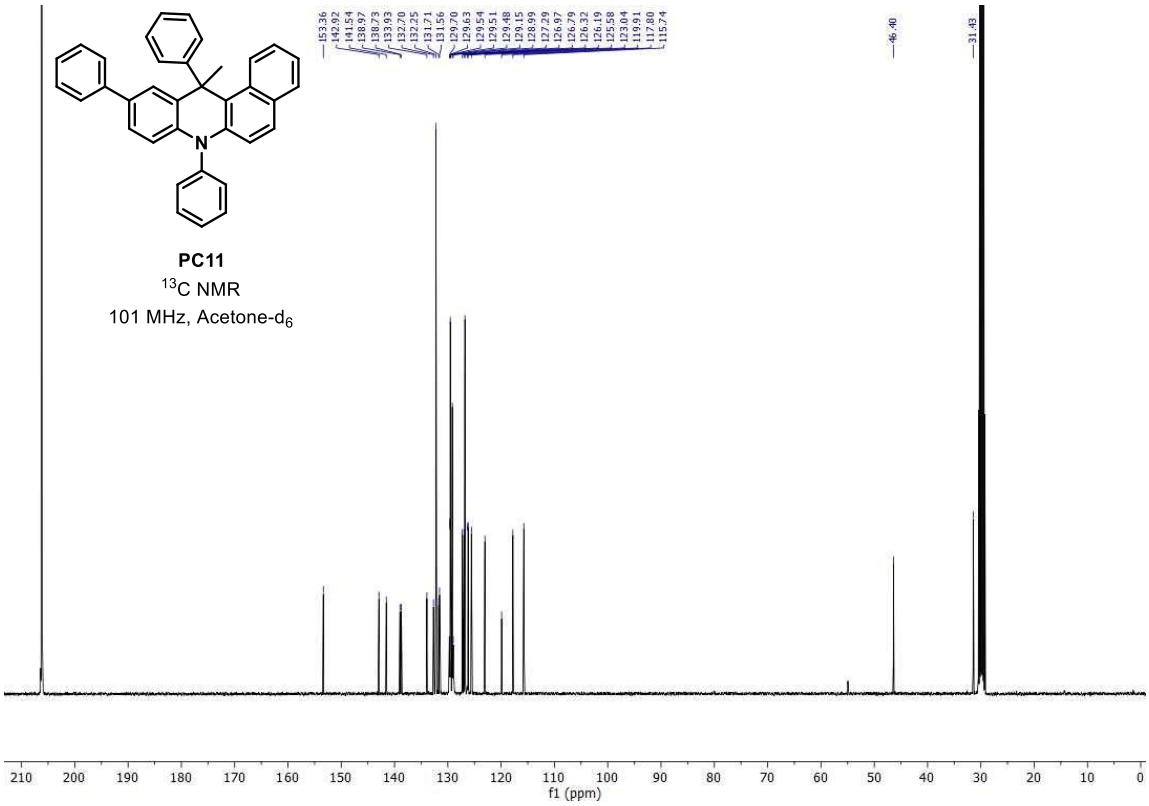
126 MHz, CD_2Cl_2

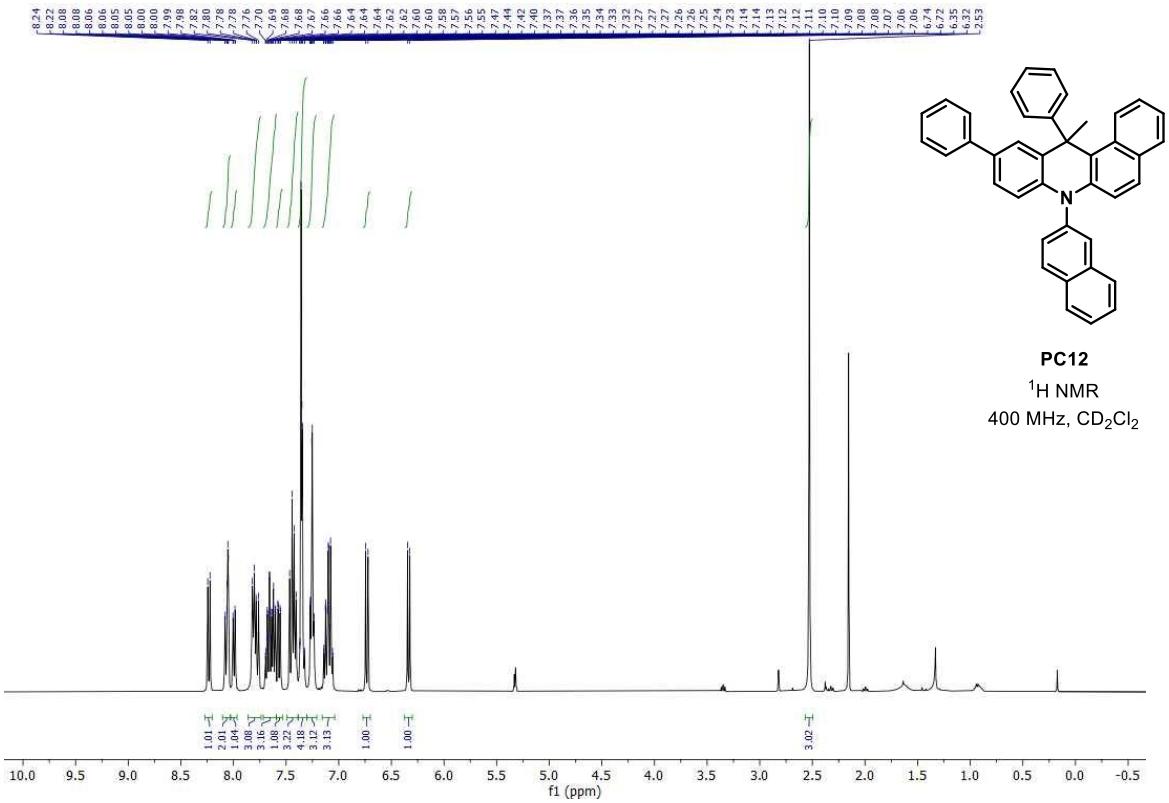


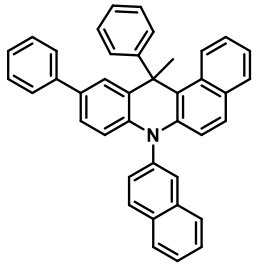
PC11

^{1}H NMR

400 MHz, Acetone-d_6


PC11
13C NMR
101 MHz, Acetone-d6
f1 (ppm)

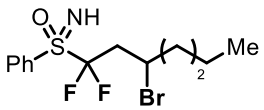

PC12
1H NMR
400 MHz, CD2Cl2
f1 (ppm)



PC12

^{13}C NMR

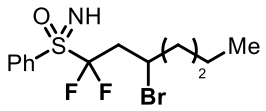
101 MHz, CD_2Cl_2



15

^{19}F NMR $\{^1H\}$

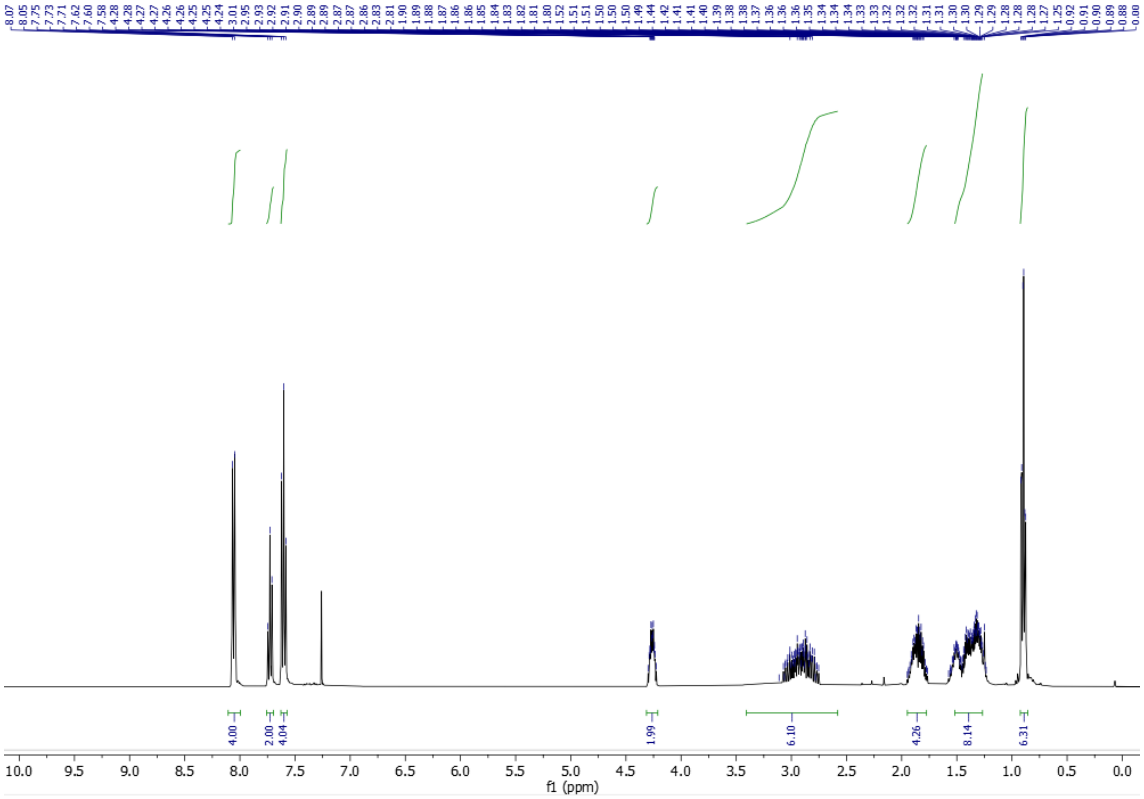
377 MHz, $CDCl_3$



15

^{1}H NMR

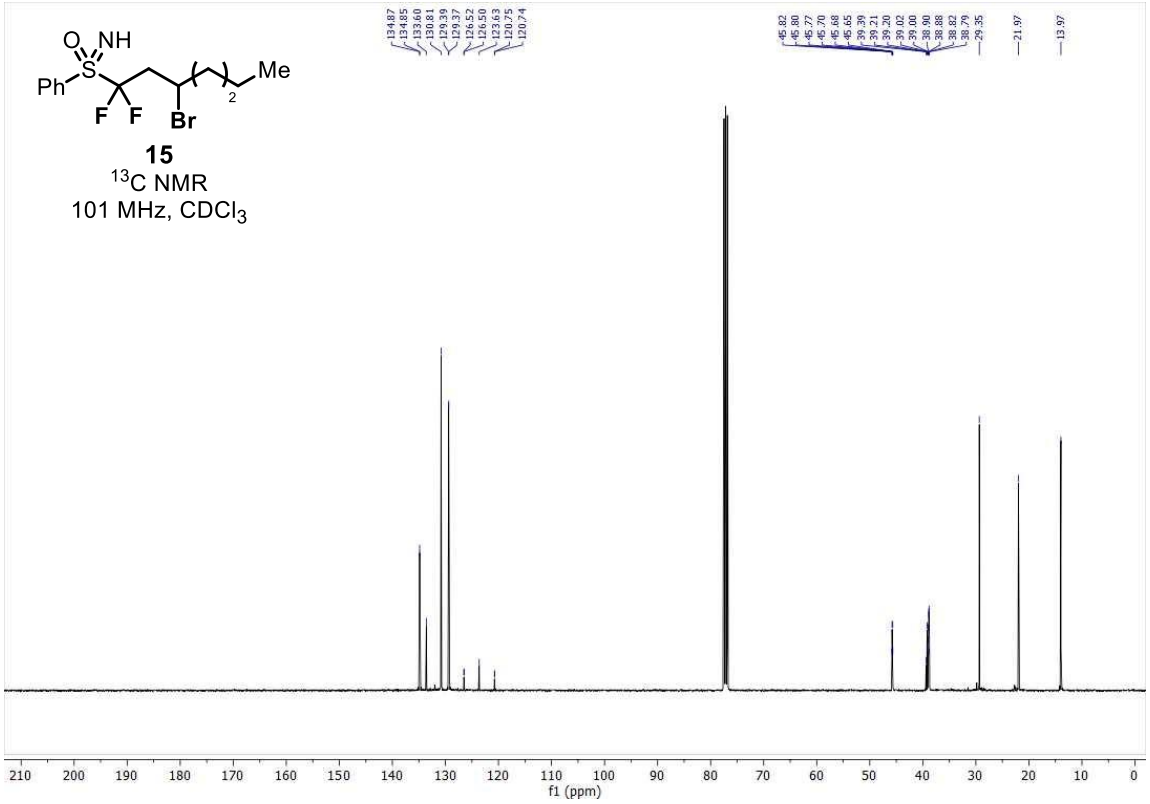
400 MHz, $CDCl_3$

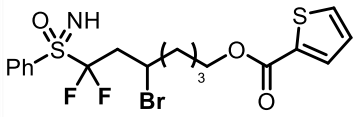


15

^{13}C NMR

101 MHz, $CDCl_3$

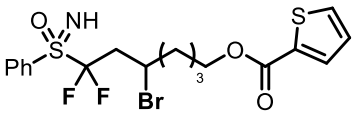




19

^{19}F NMR {^{1}H}

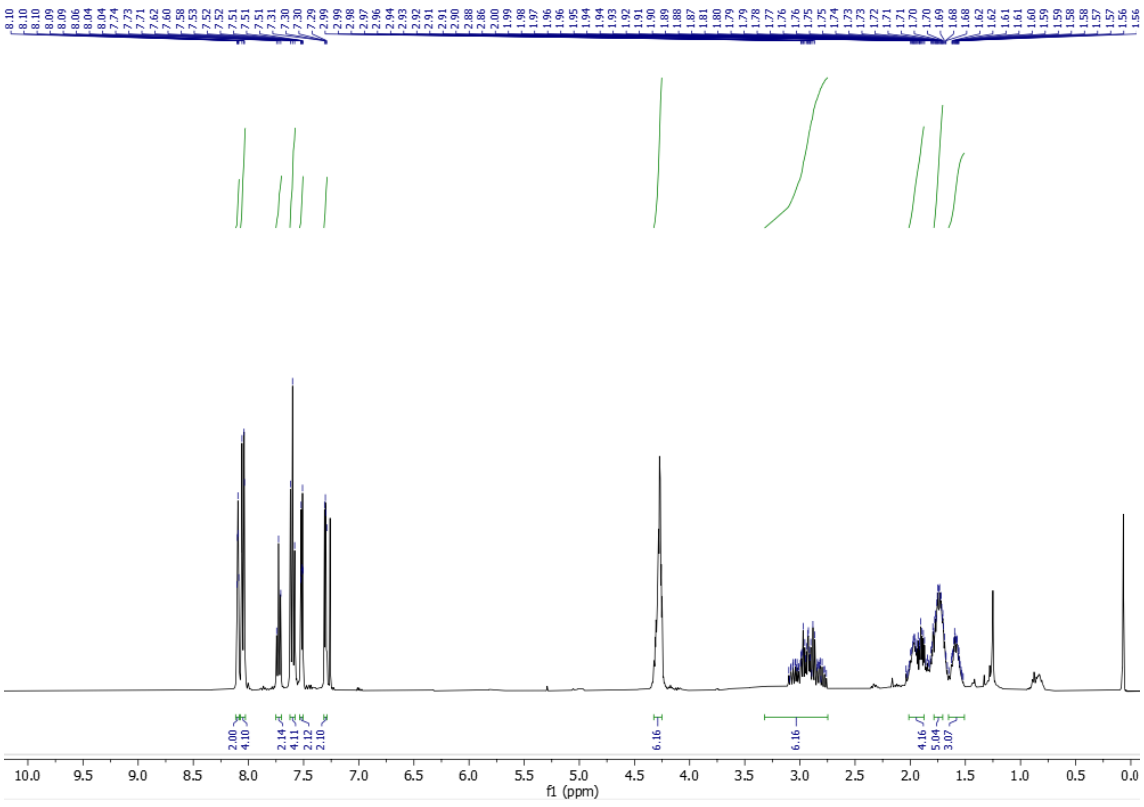
377 MHz, $CDCl_3$

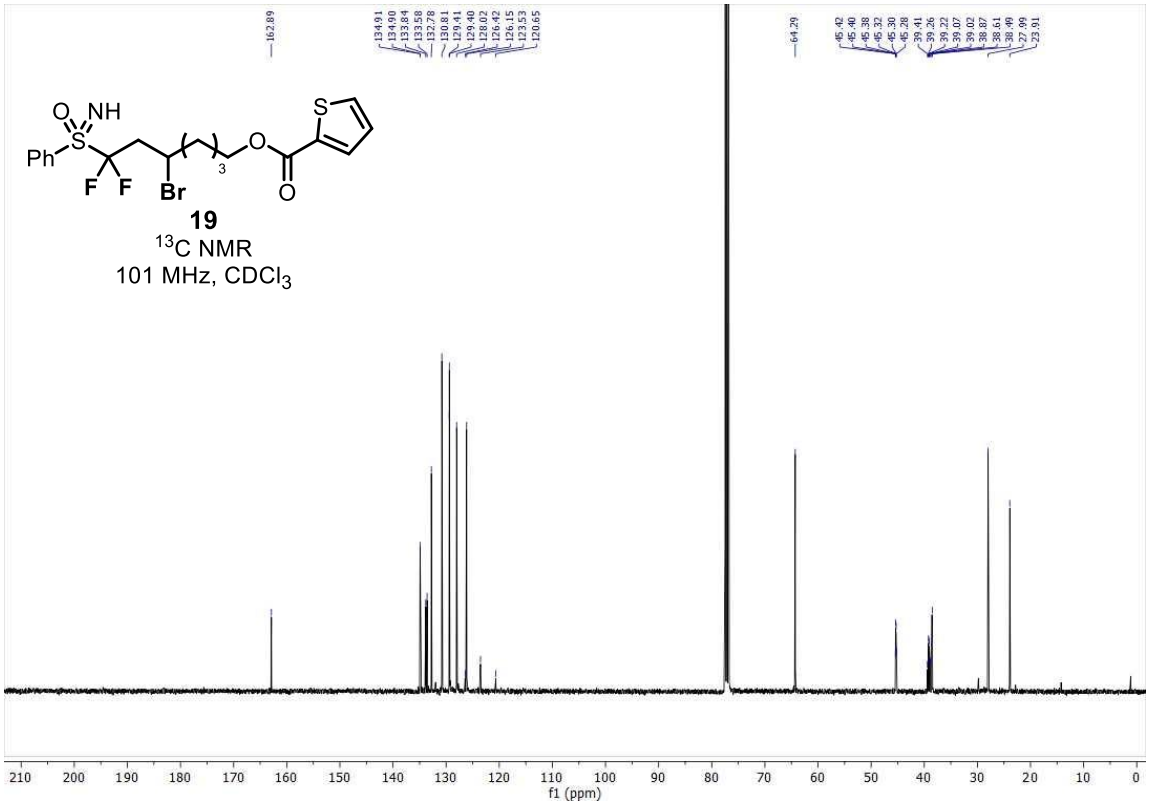


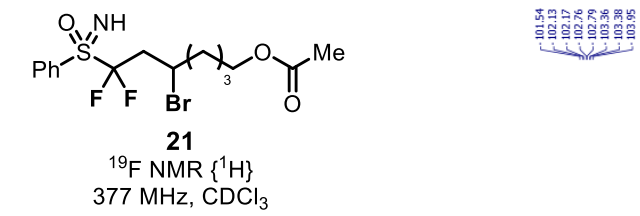
19

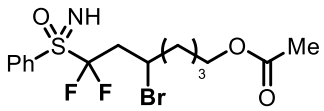
^{1}H NMR

400 MHz, $CDCl_3$




O
NH
S
Ph
F
F
Br
3
O
O
S
19
13C NMR
101 MHz, CDCl3
f1 (ppm)

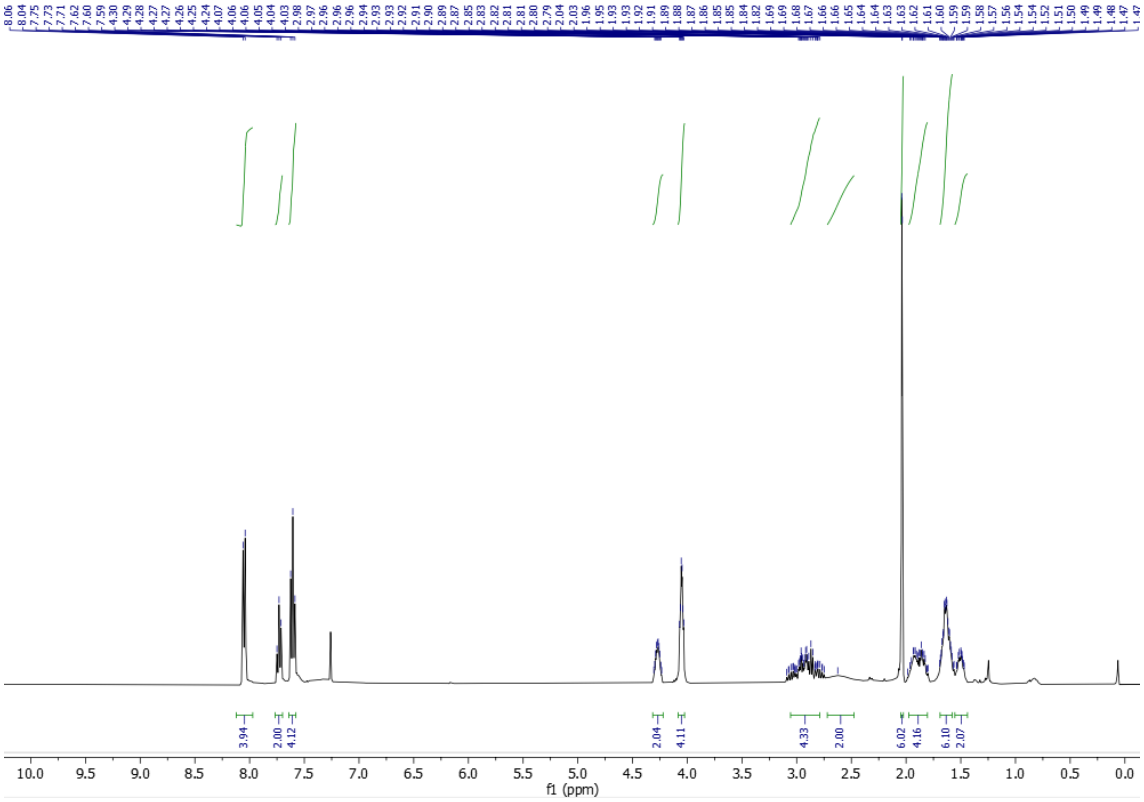

O
NH
S
Ph
F
F
Br
3
O
O
Me
21
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)

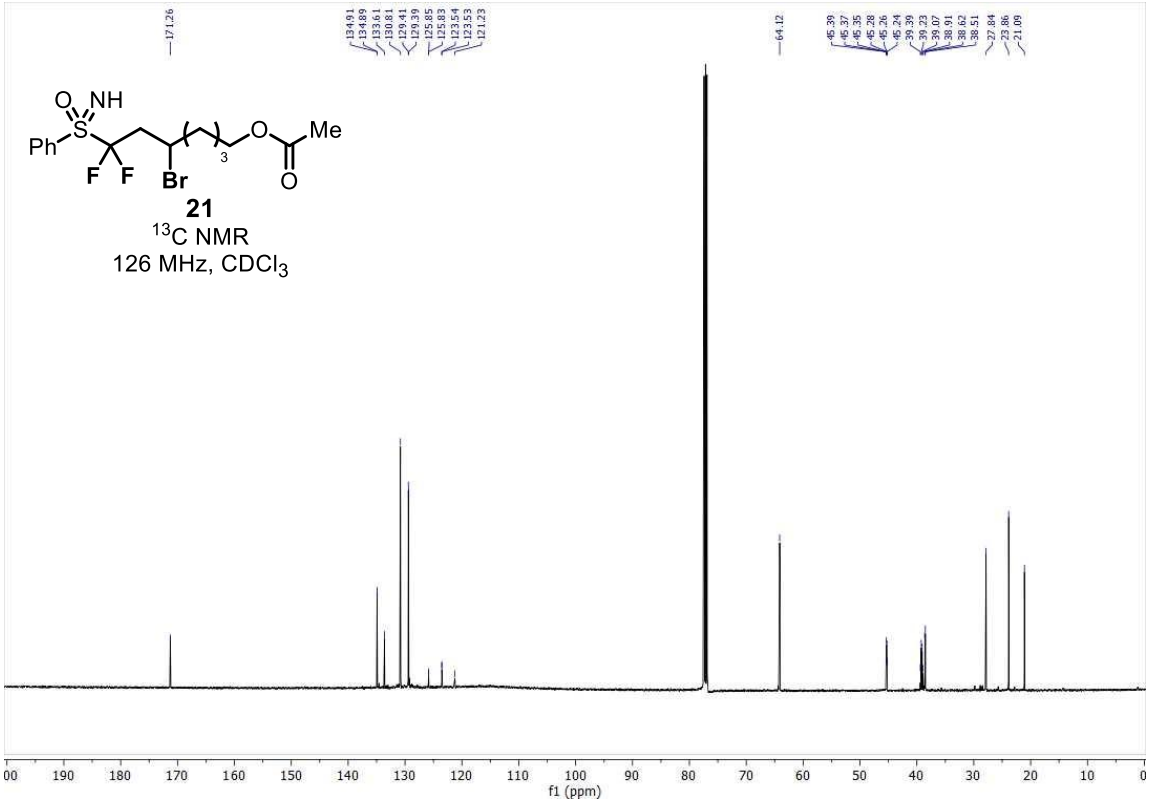


21

^{1}H NMR

400 MHz, $CDCl_3$

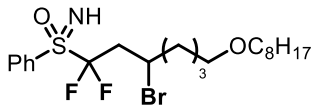




21

^{13}C NMR

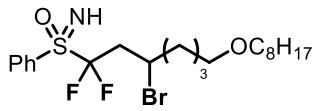
126 MHz, $CDCl_3$



23

^{19}F NMR {^{1}H}

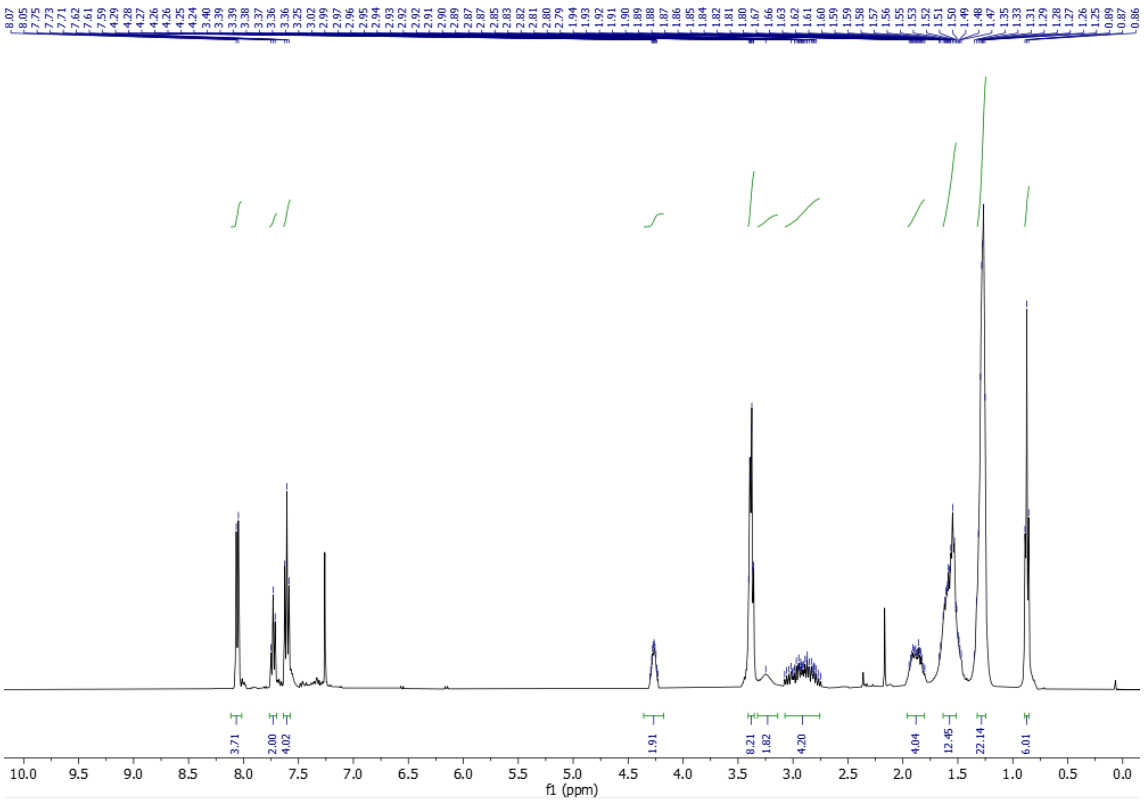
377 MHz, $CDCl_3$

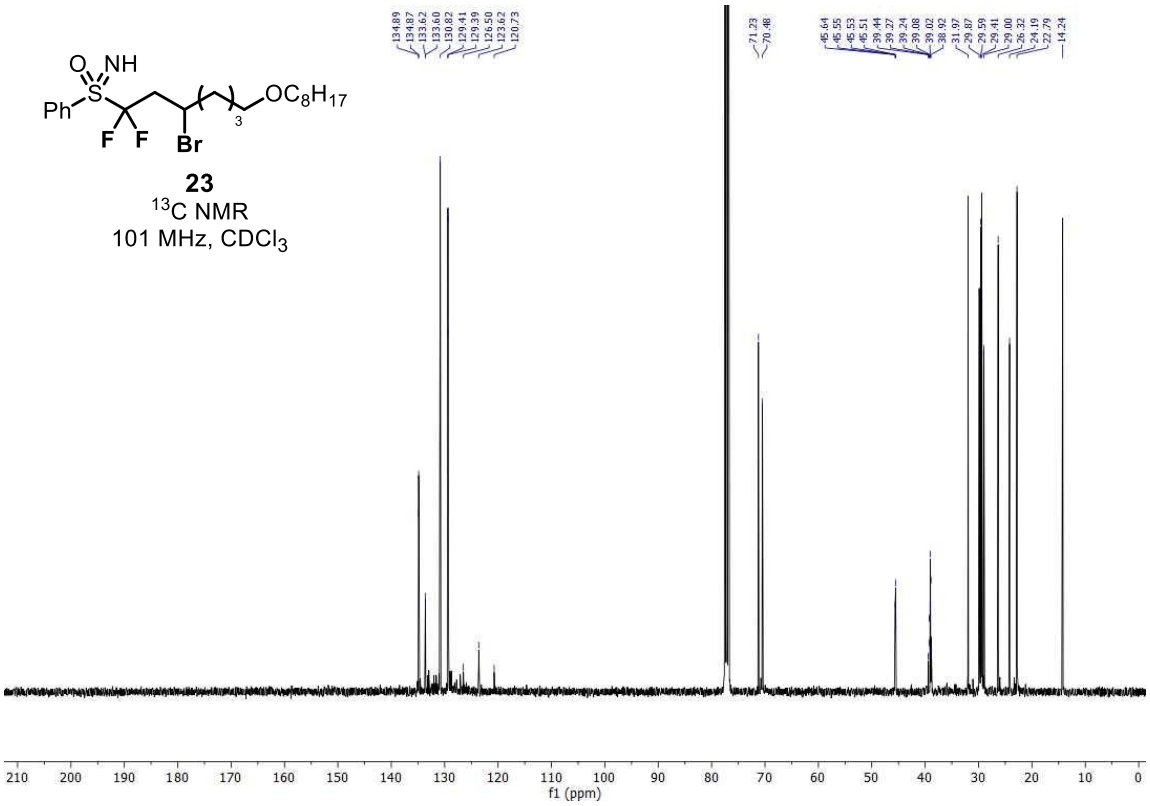


23

^{1}H NMR

400 MHz, $CDCl_3$

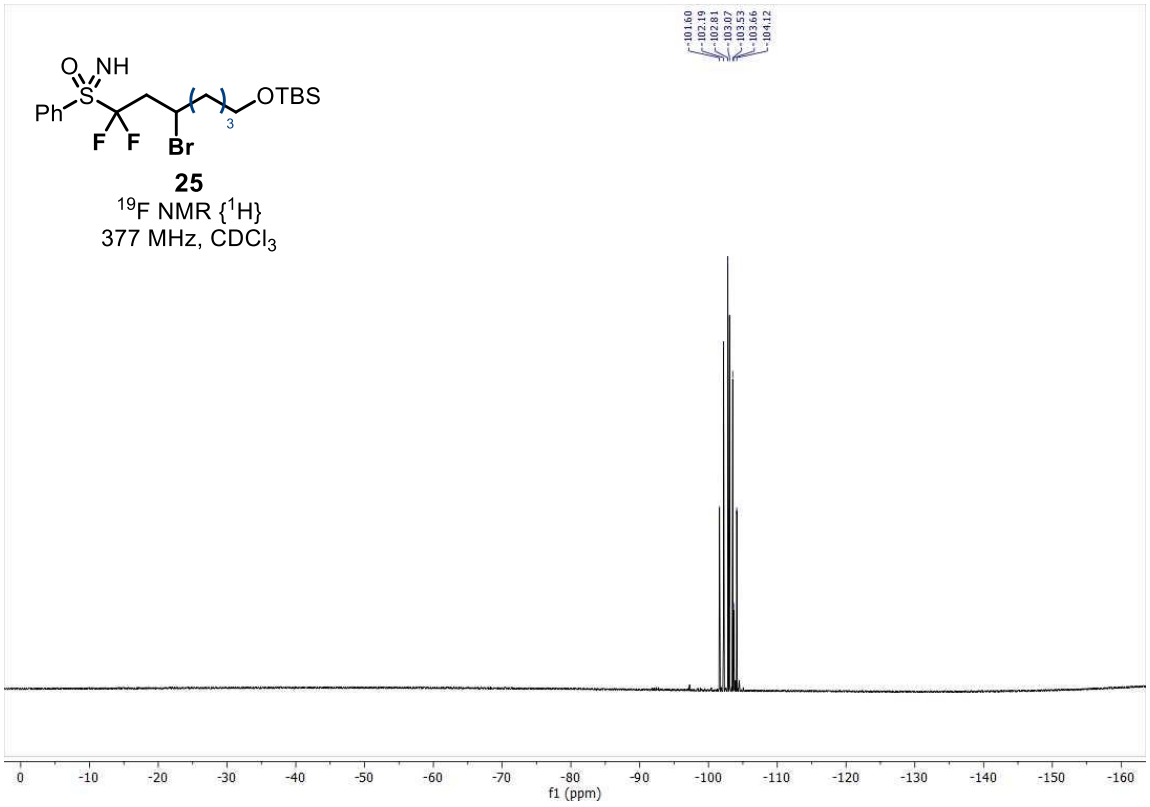




23

^{13}C NMR

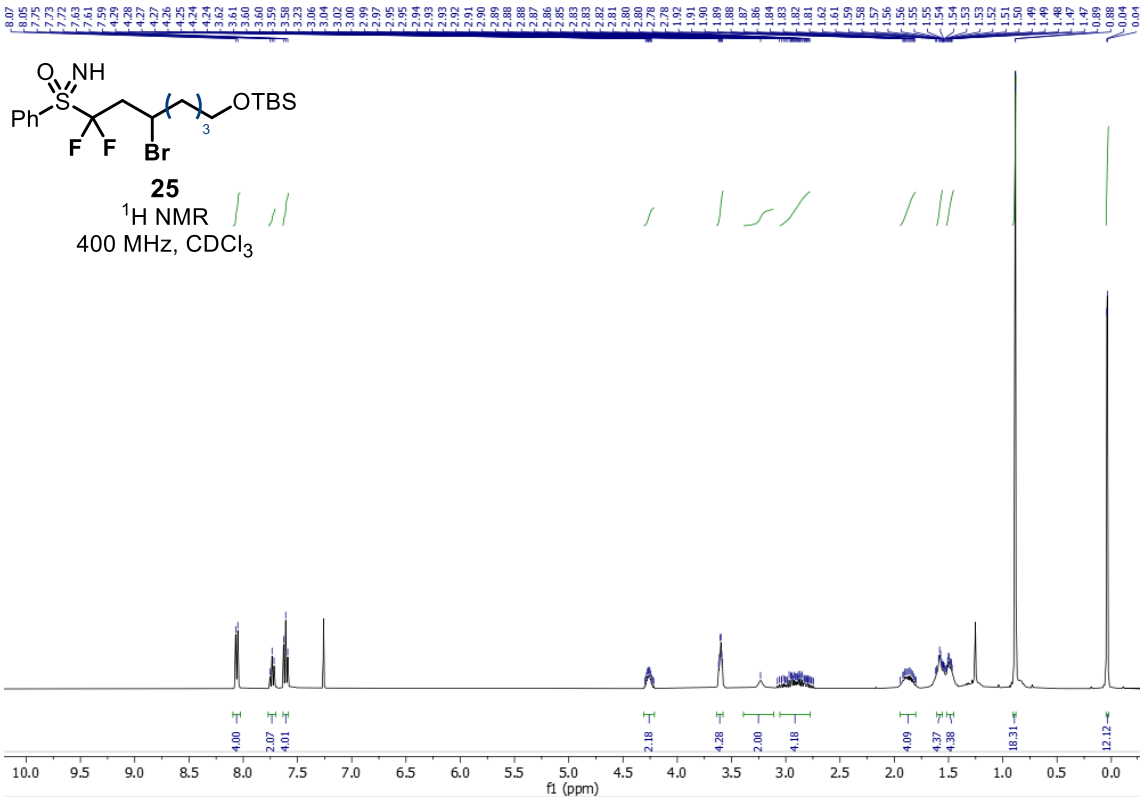
101 MHz, $CDCl_3$

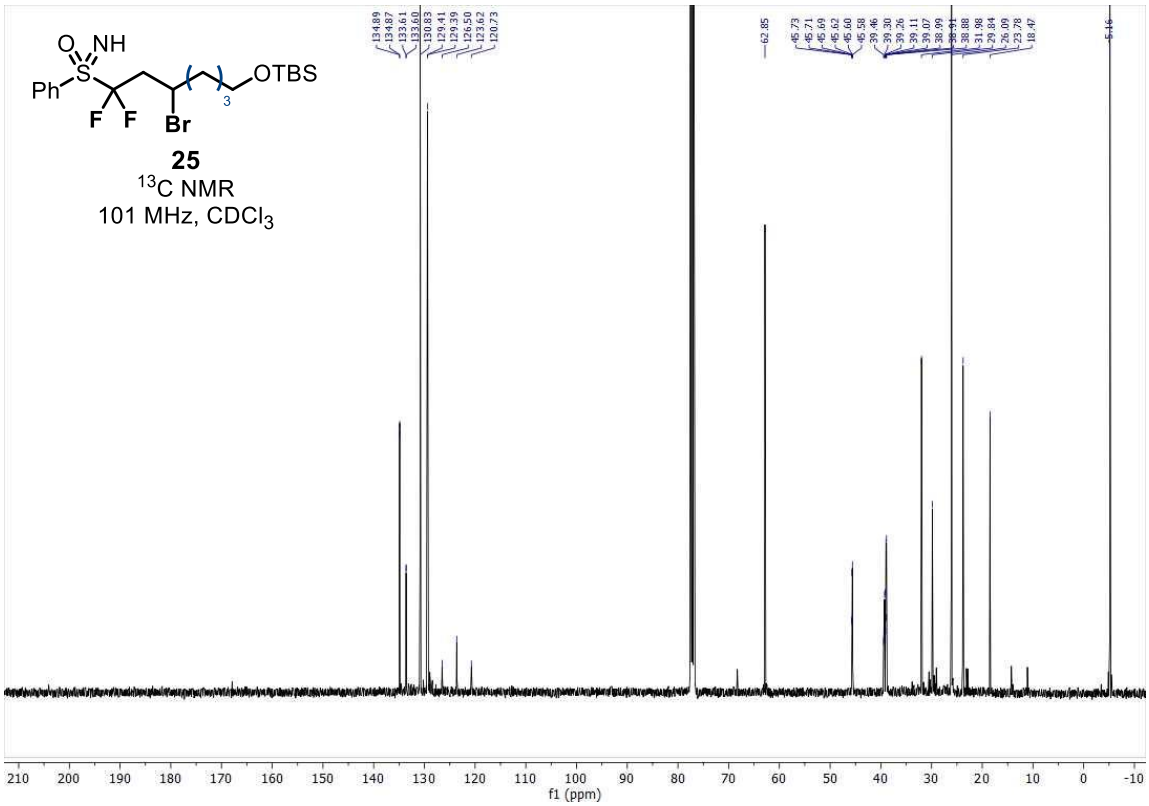


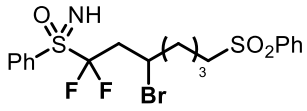
25

^{19}F NMR $\{^{1}H\}$

377 MHz, $CDCl_3$

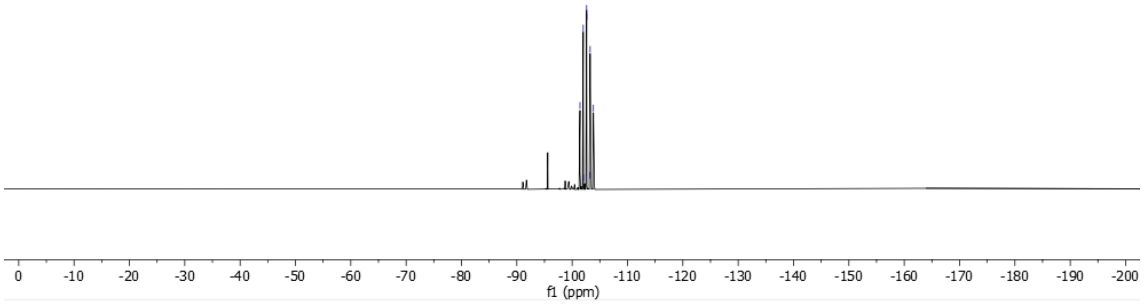

O
NH
S
Ph
F
F
Br
3
OTBS
25
1H NMR
400 MHz, CDCl3
f1 (ppm)

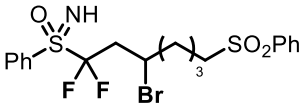

O
NH
S
Ph
F
F
Br
3
OTBS
25
13C NMR
101 MHz, CDCl3
f1 (ppm)



27

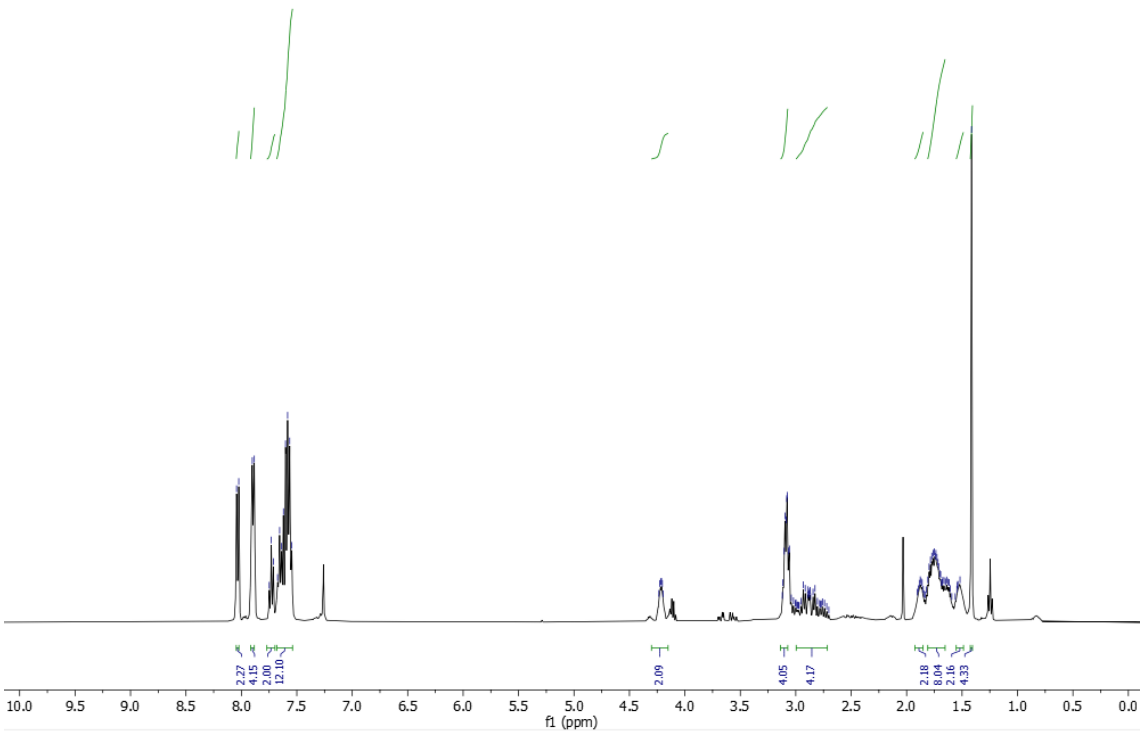
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$

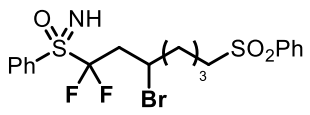




27

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

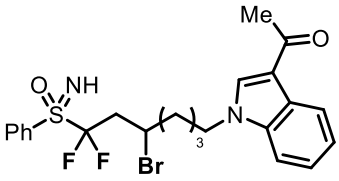




27

^{13}C NMR

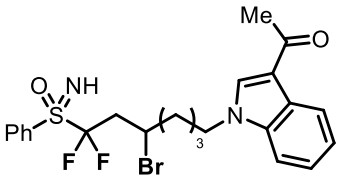
101 MHz, $CDCl_3$



31

^{19}F NMR {^{1}H}

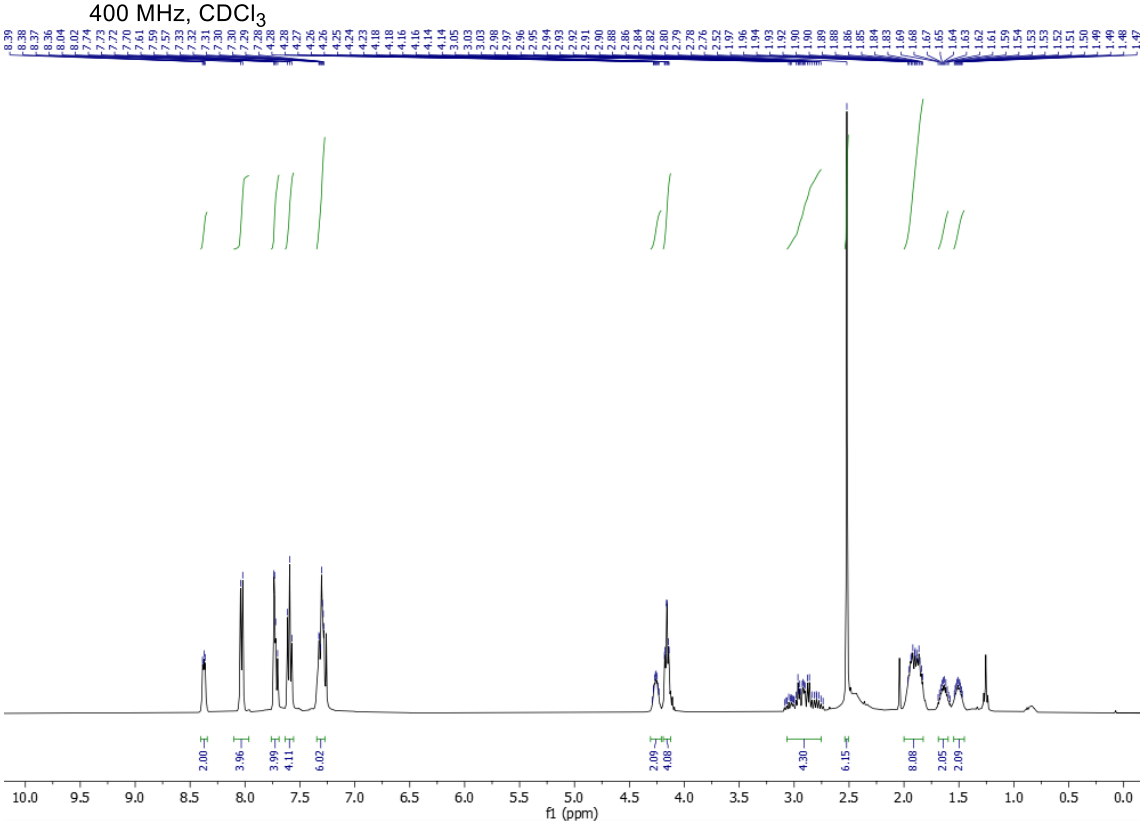
377 MHz, $CDCl_3$

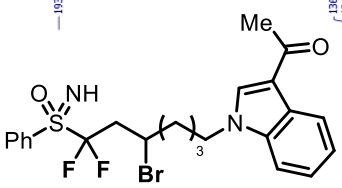


31

^{1}H NMR

400 MHz, $CDCl_3$

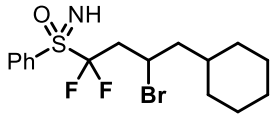




31

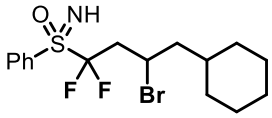
^{13}C NMR

101 MHz, $CDCl_3$



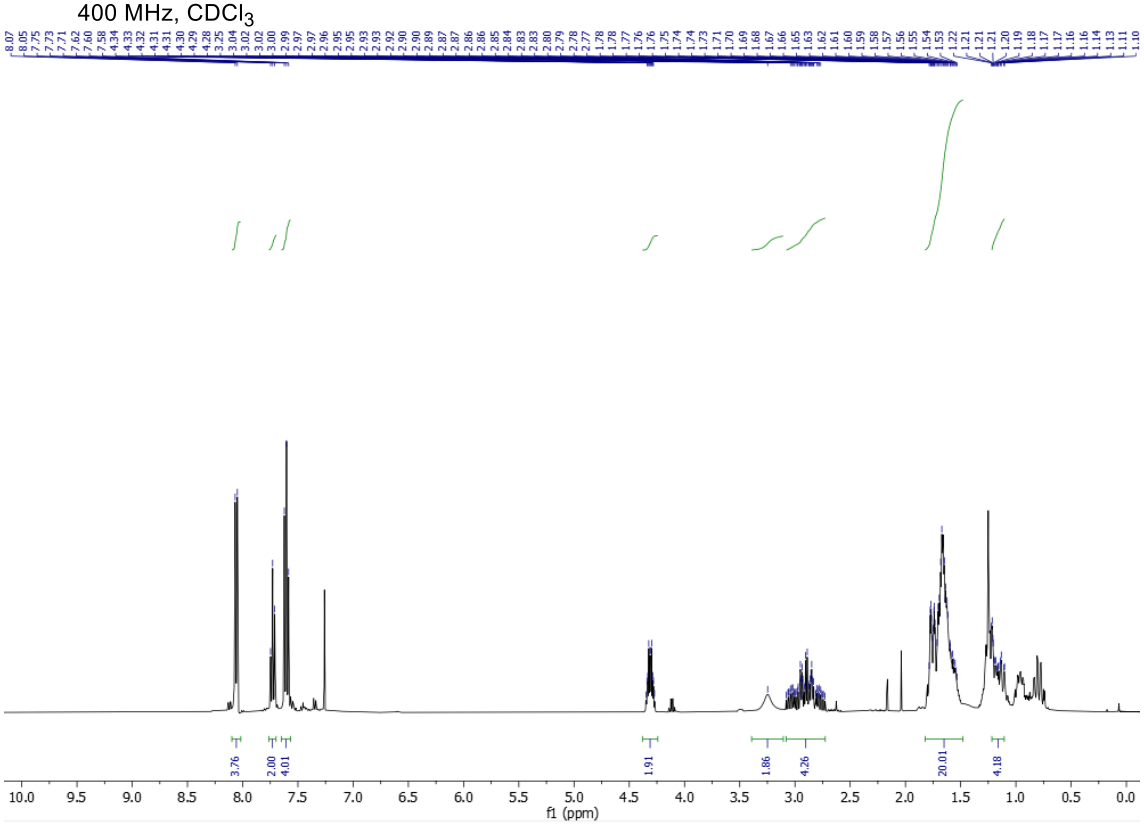
33

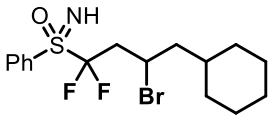
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



33

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

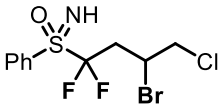




33

^{13}C NMR

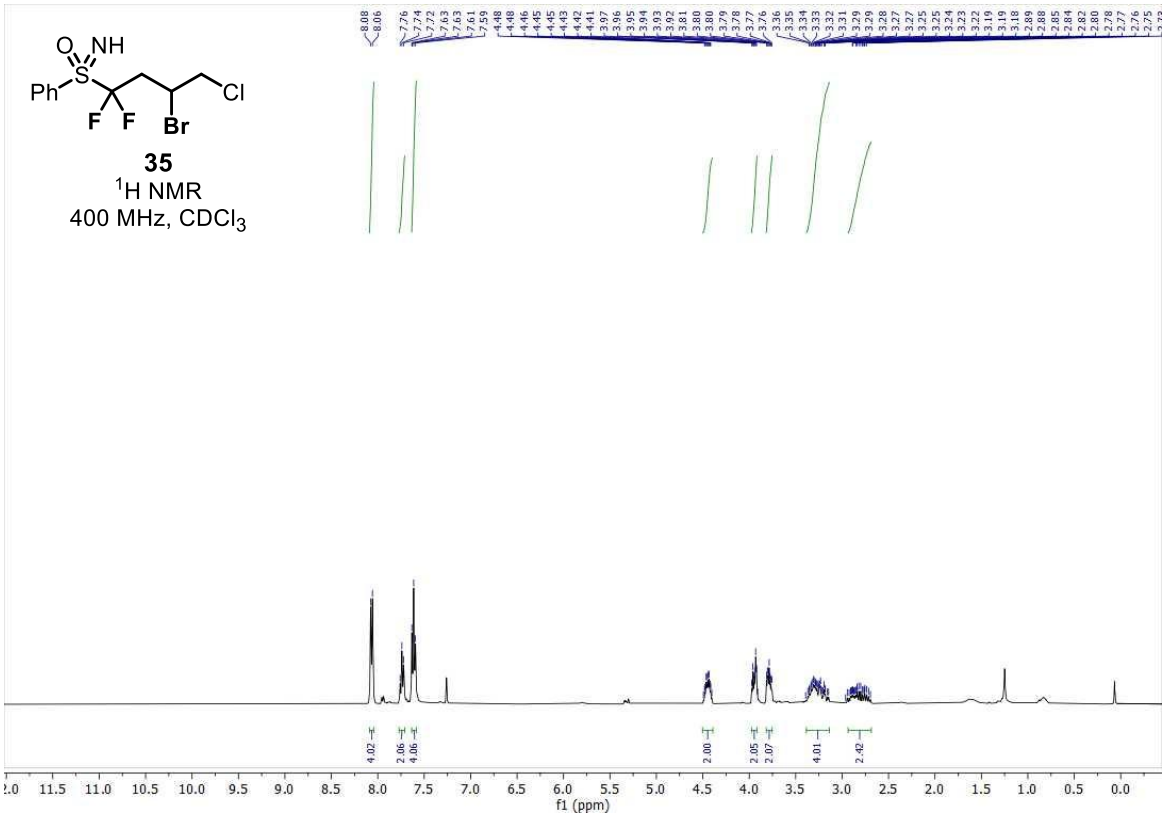
101 MHz, $CDCl_3$

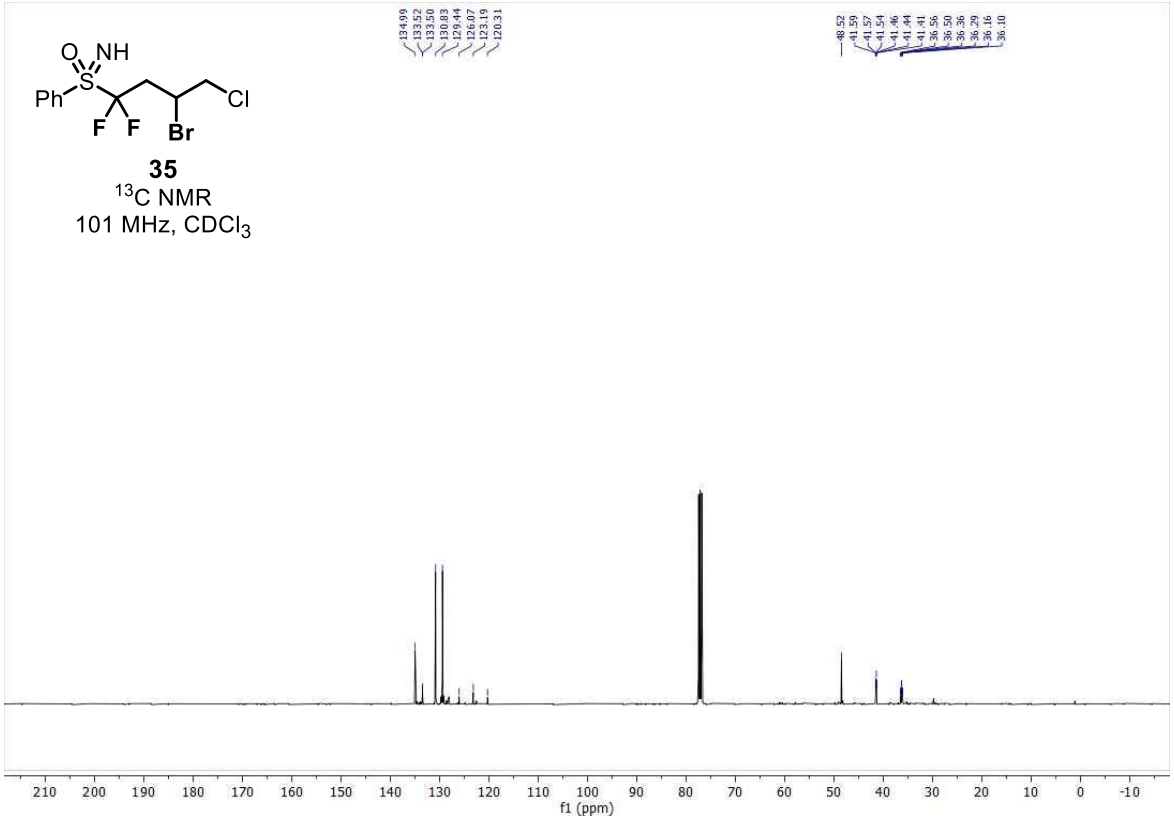


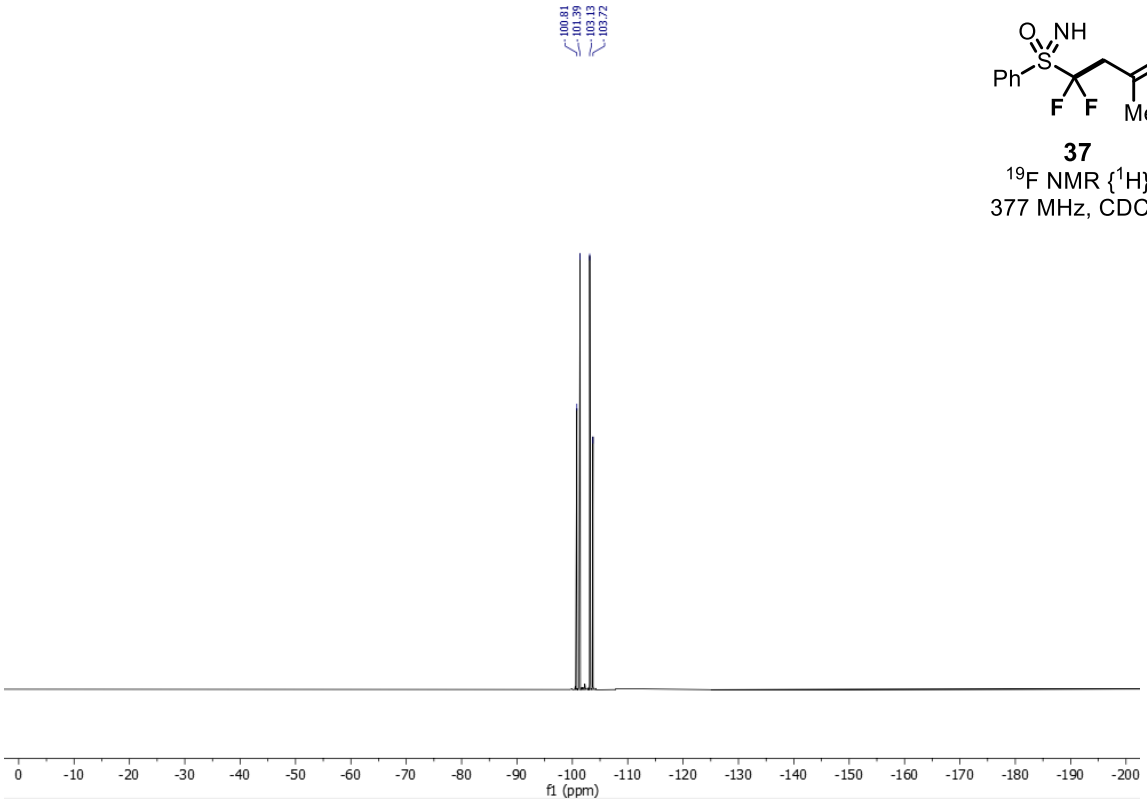
35

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$


O
NH
S
Ph
Cl
F
F
Br
35
1H NMR
400 MHz, CDCl3
f1 (ppm)

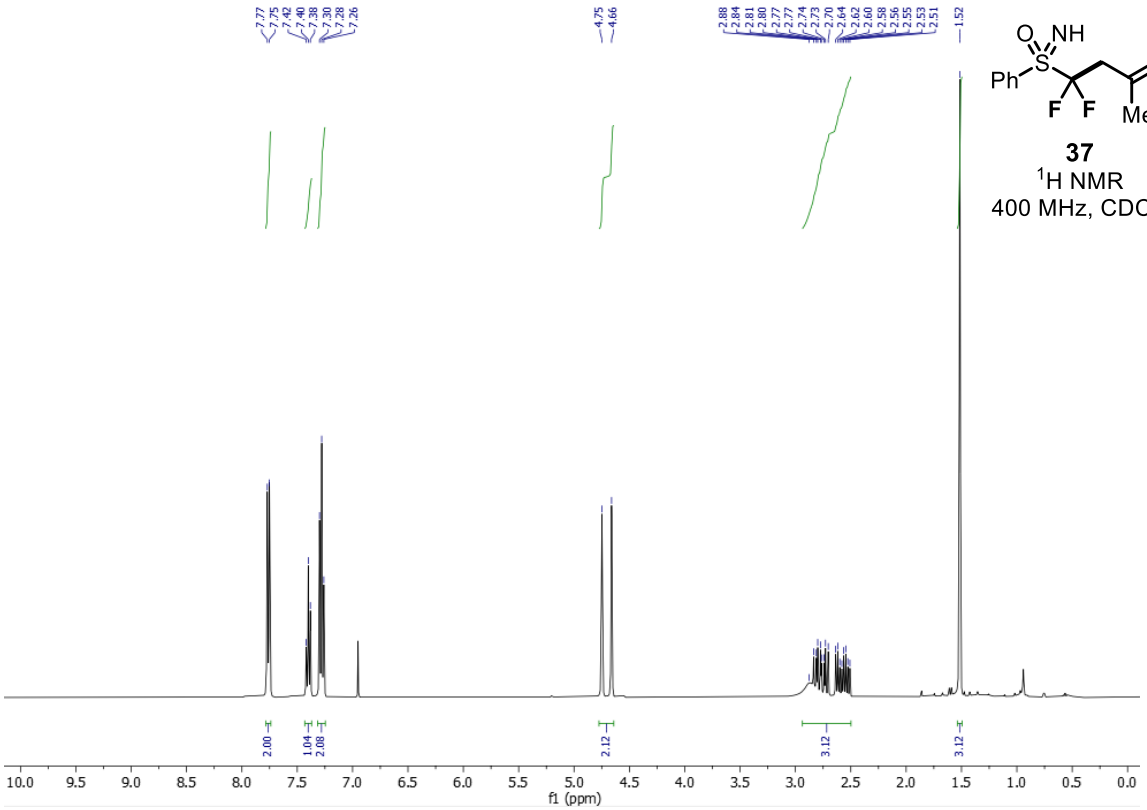

O
NH
S
Ph
Cl
F
F
Br
35
13C NMR
101 MHz, CDCl3
f1 (ppm)



37

^{19}F NMR {^{1}H}

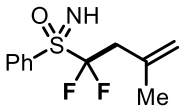
377 MHz, $CDCl_3$



37

^{1}H NMR

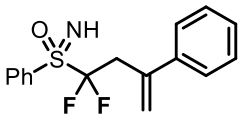
400 MHz, $CDCl_3$



37

^{13}C NMR

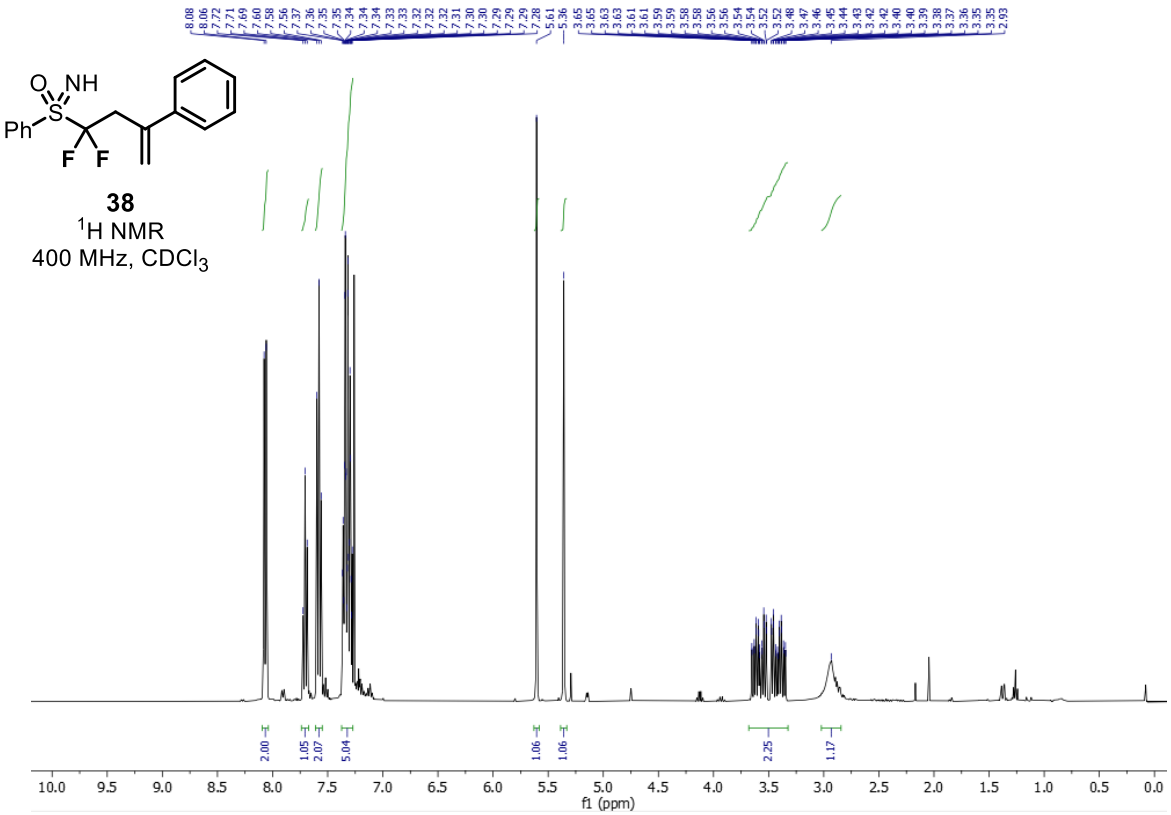
101 MHz, $CDCl_3$

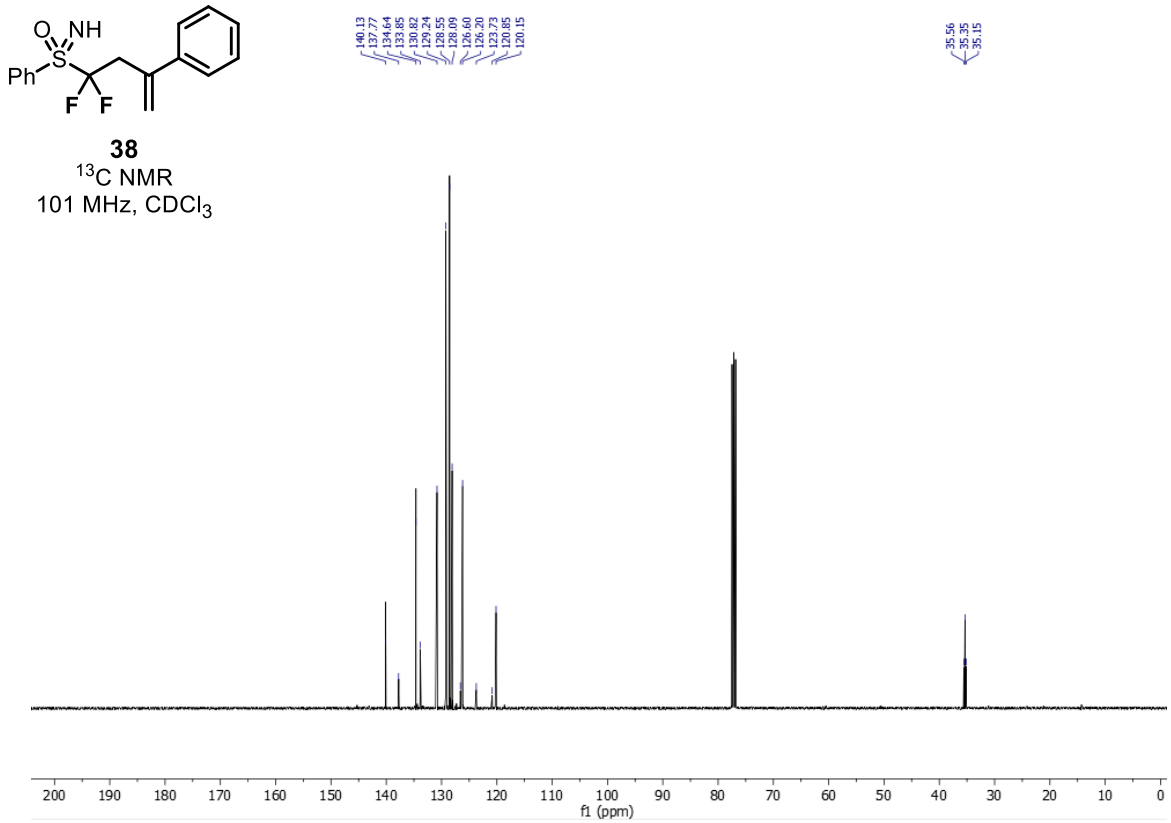


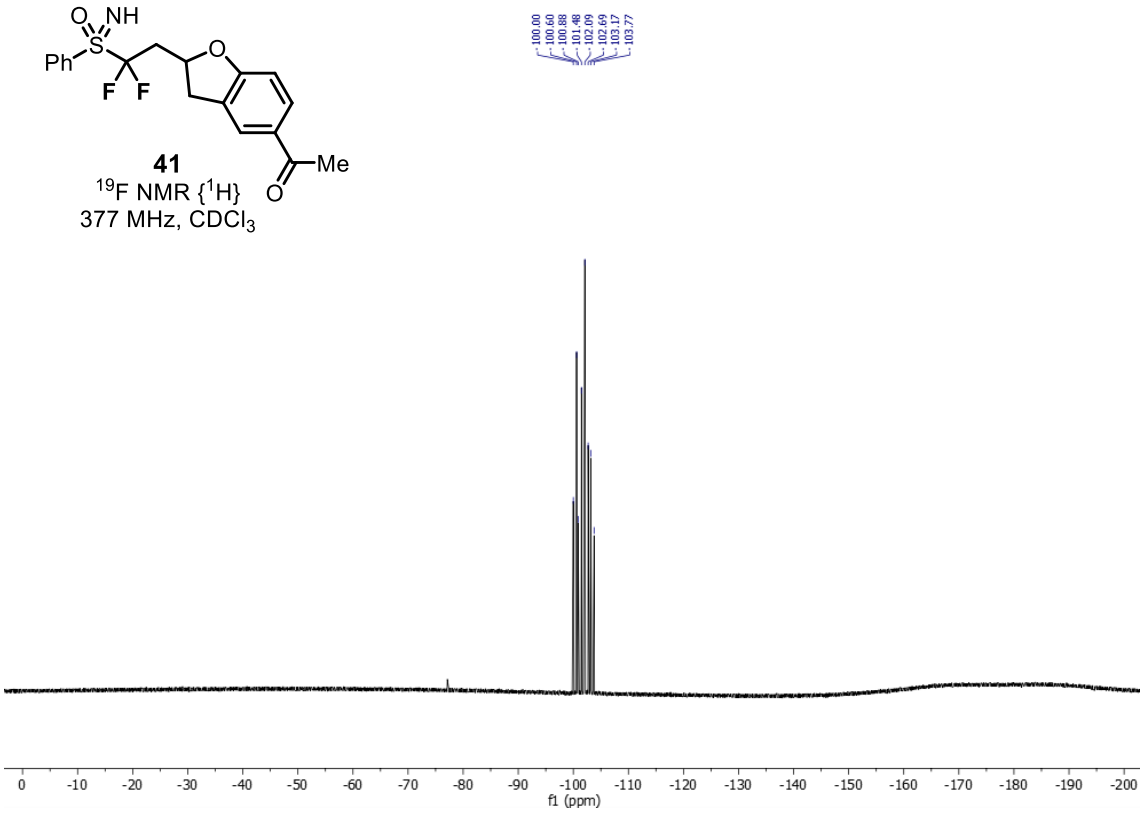
38

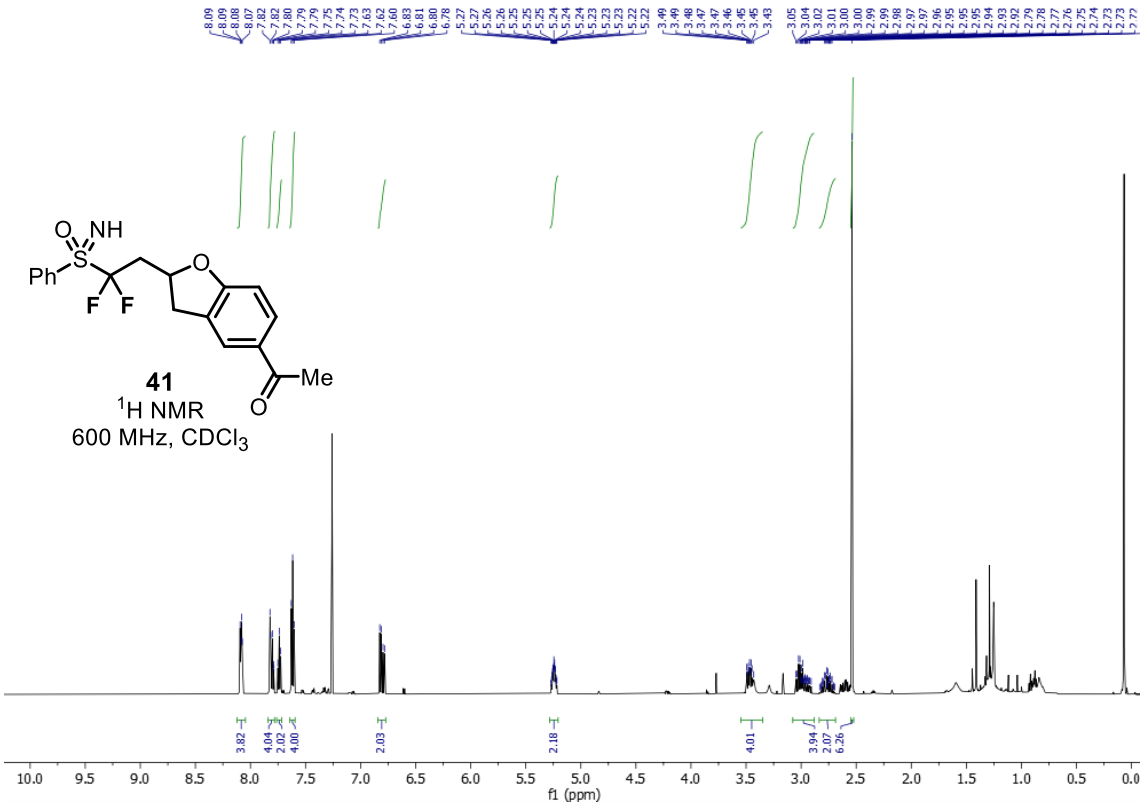
^{19}F NMR {^{1}H}

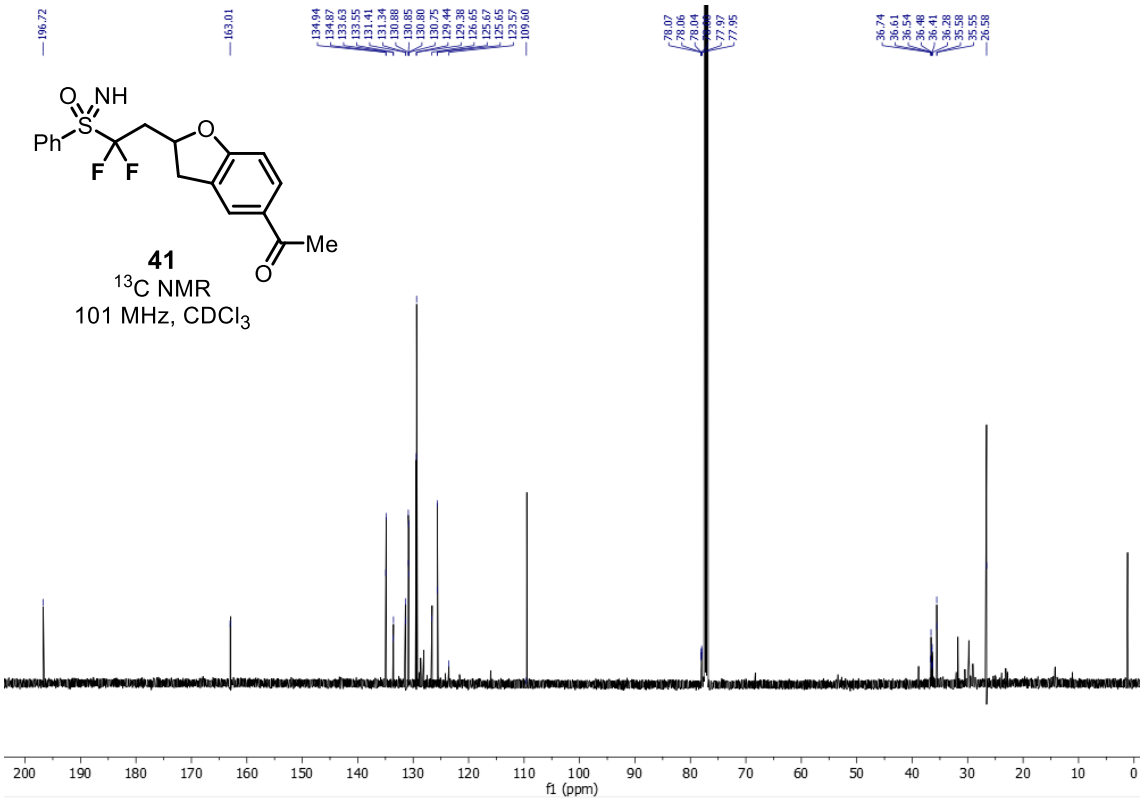
377 MHz, $CDCl_3$


O
NH
S
Ph
F
F
38
1H NMR
400 MHz, CDCl3
f1 (ppm)


O
NH
S
Ph
F
F
38
13C NMR
101 MHz, CDCl3
f1 (ppm)


O
NH
S
Ph
F F
O
Me
O
41
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$
f1 (ppm)

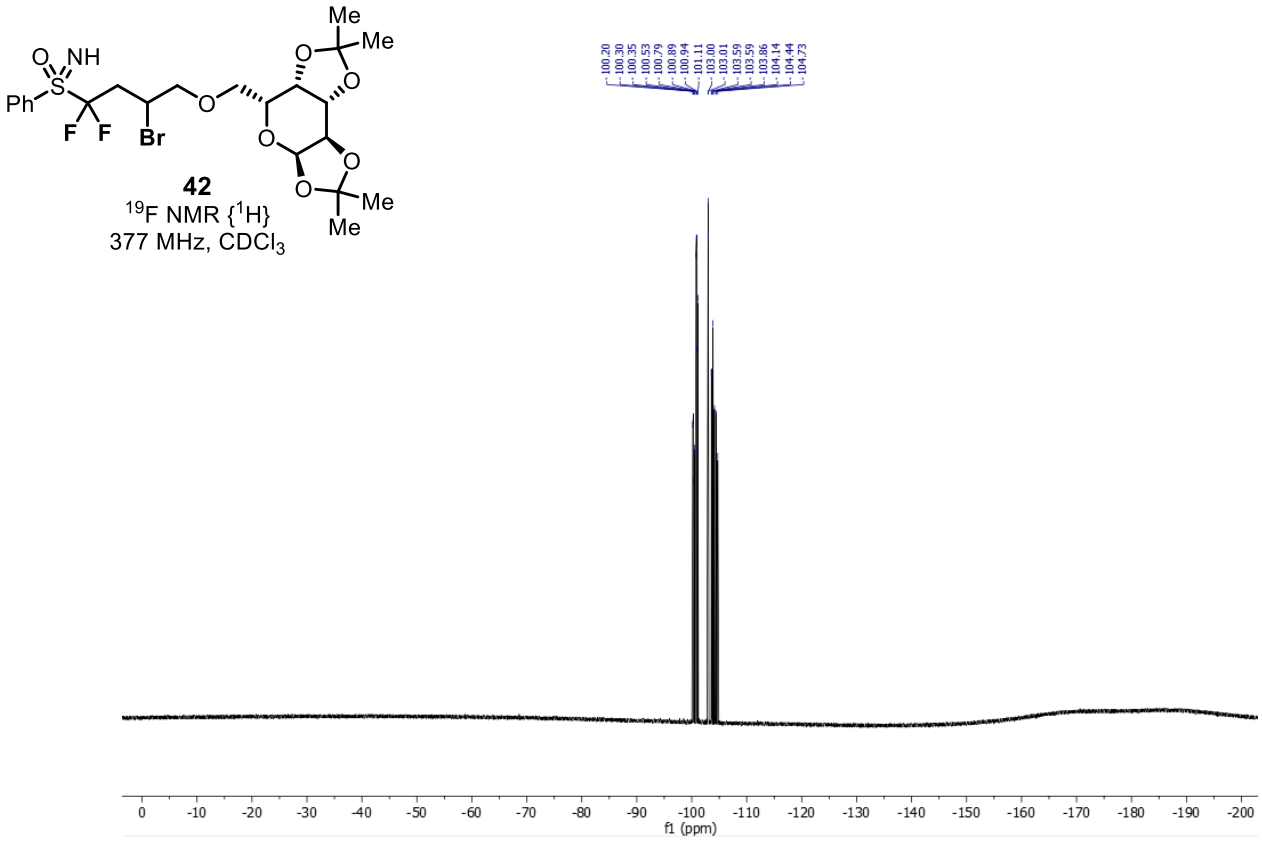

O
NH
S
Ph
F F
O
Me
O
41
^{1}H NMR
600 MHz, $CDCl_3$
f1 (ppm)



41

^{13}C NMR

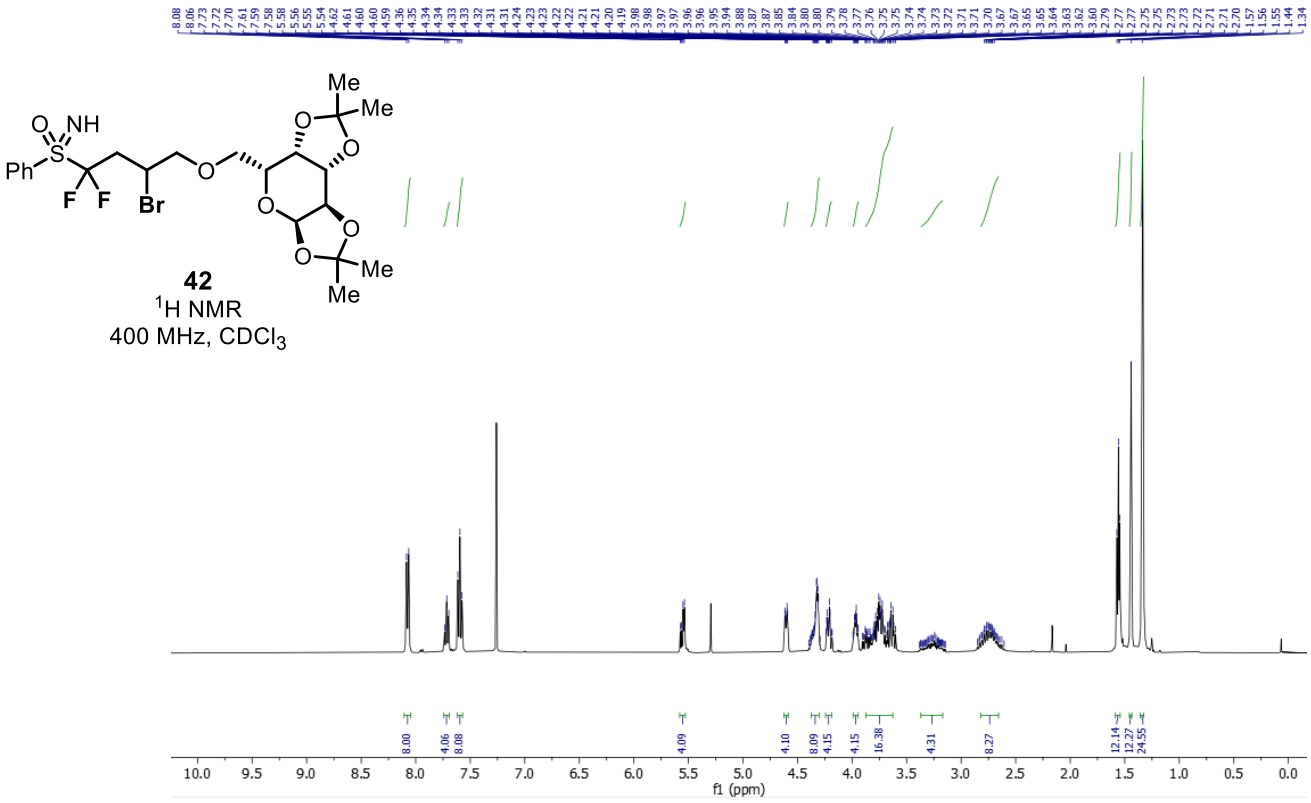
101 MHz, $CDCl_3$

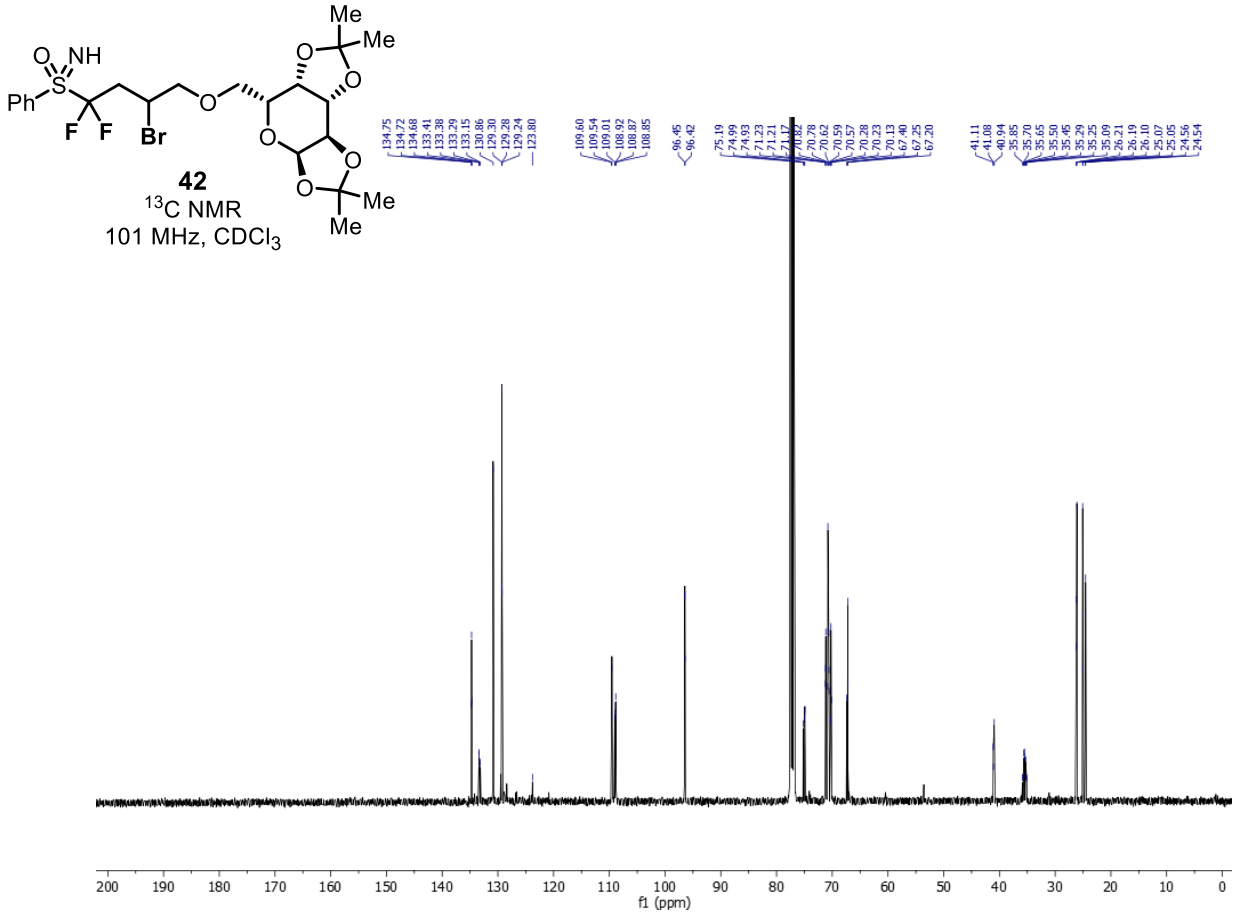


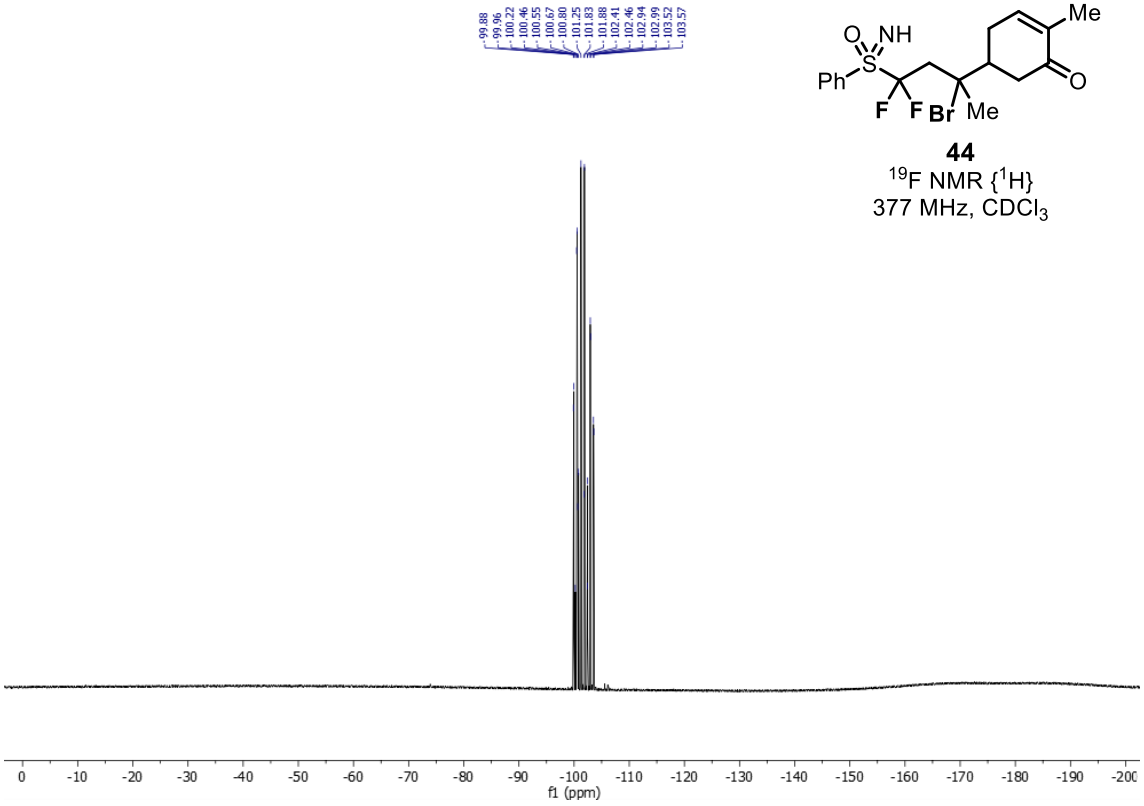
42

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$

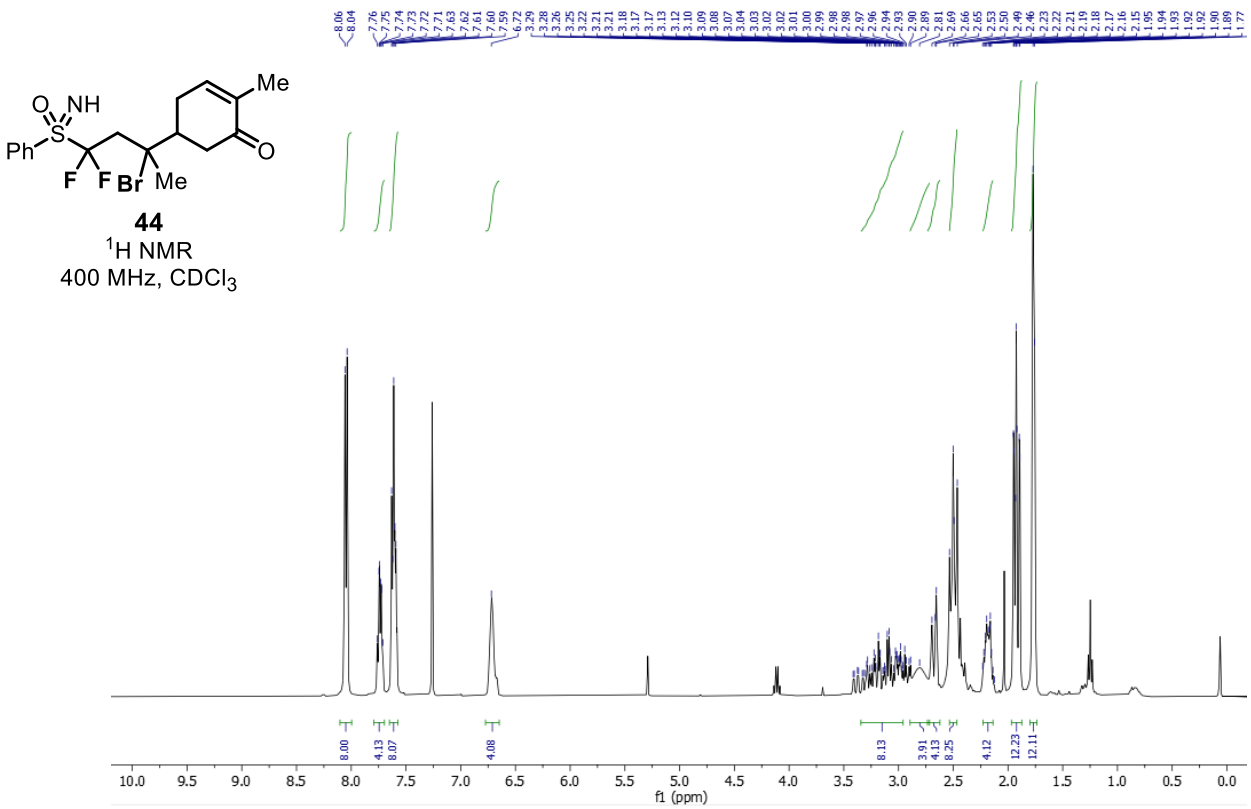

Me
Me
O
NH
S
Ph
F
F
Br
O
O
O
O
O
Me
Me
42
1H NMR
400 MHz, CDCl3
f1 (ppm)


Me
Me
O
NH
S
Ph
F
F
Br
O
O
O
O
O
Me
Me
42
13C NMR
101 MHz, CDCl3
f1 (ppm)



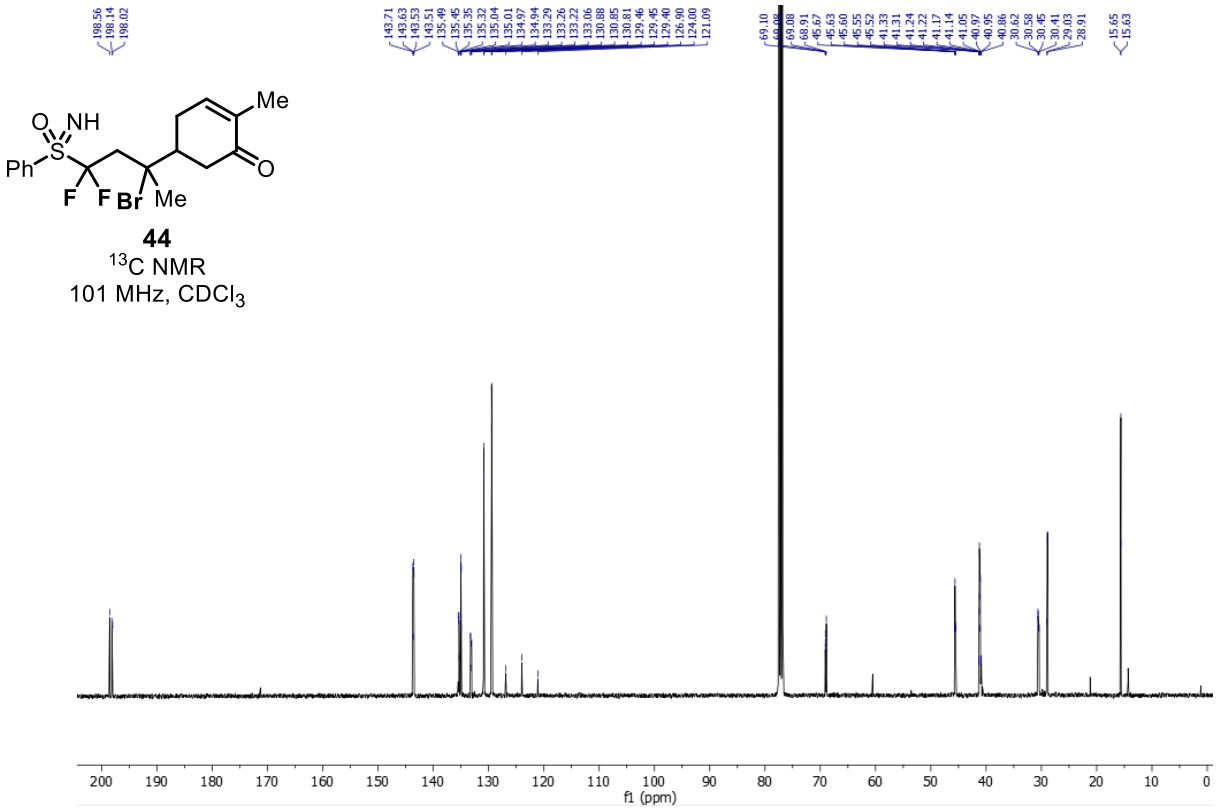
44

^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



44

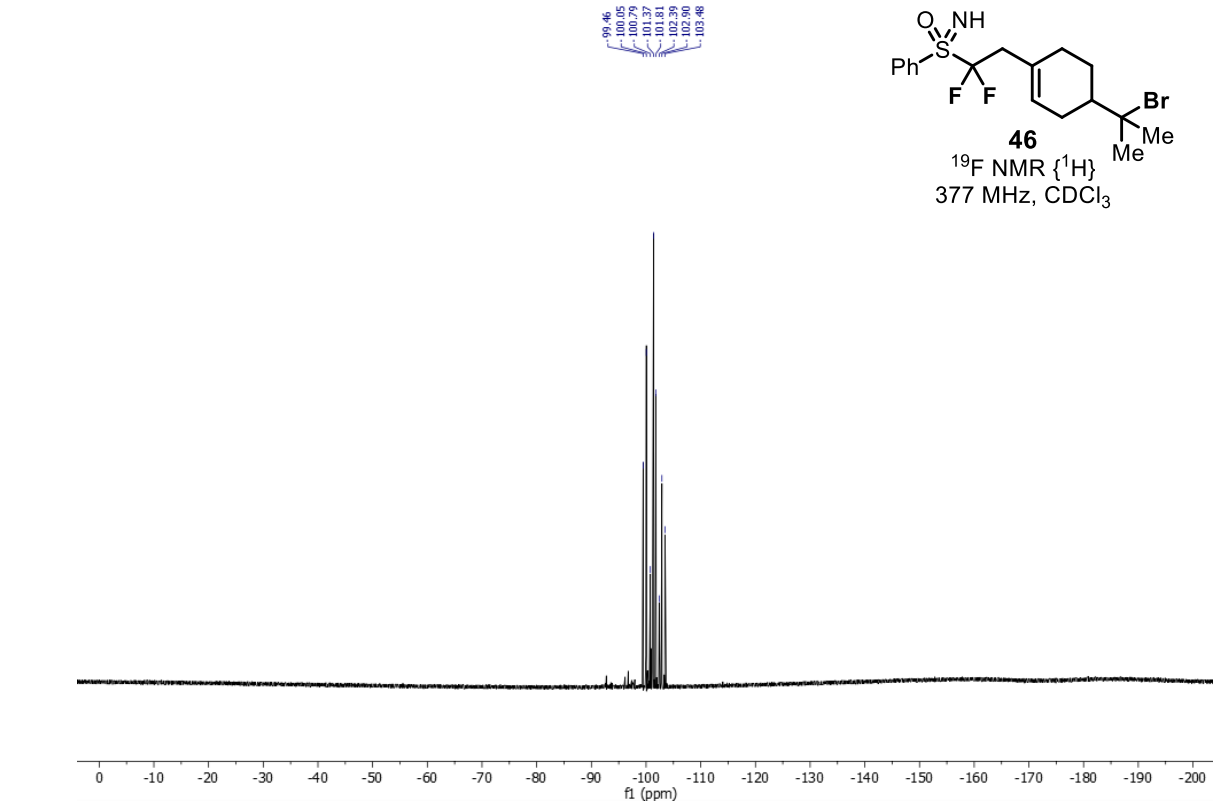
^{1}H NMR
400 MHz, $CDCl_3$



44

^{13}C NMR

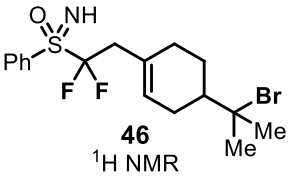
101 MHz, $CDCl_3$



46

^{19}F NMR {^{1}H}

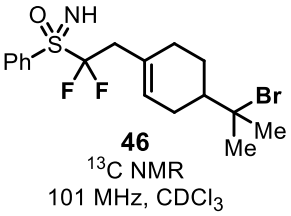
377 MHz, $CDCl_3$



46

^{1}H NMR

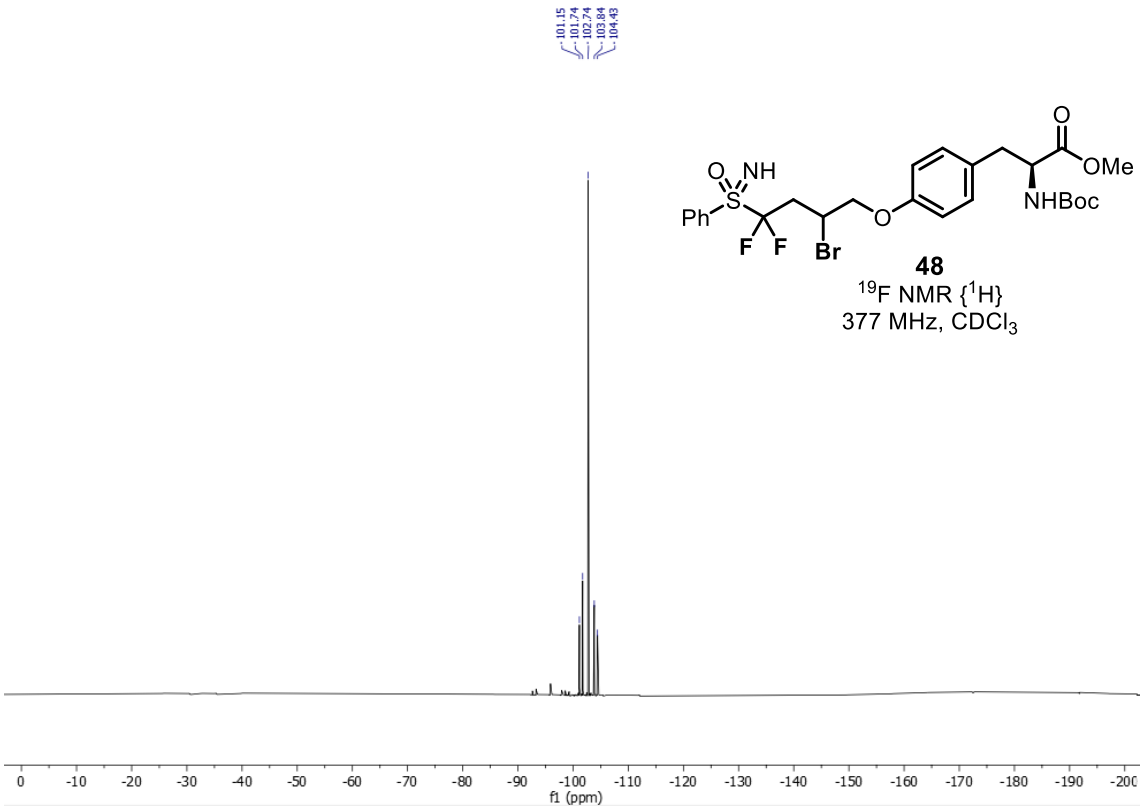
400 MHz, $CDCl_3$

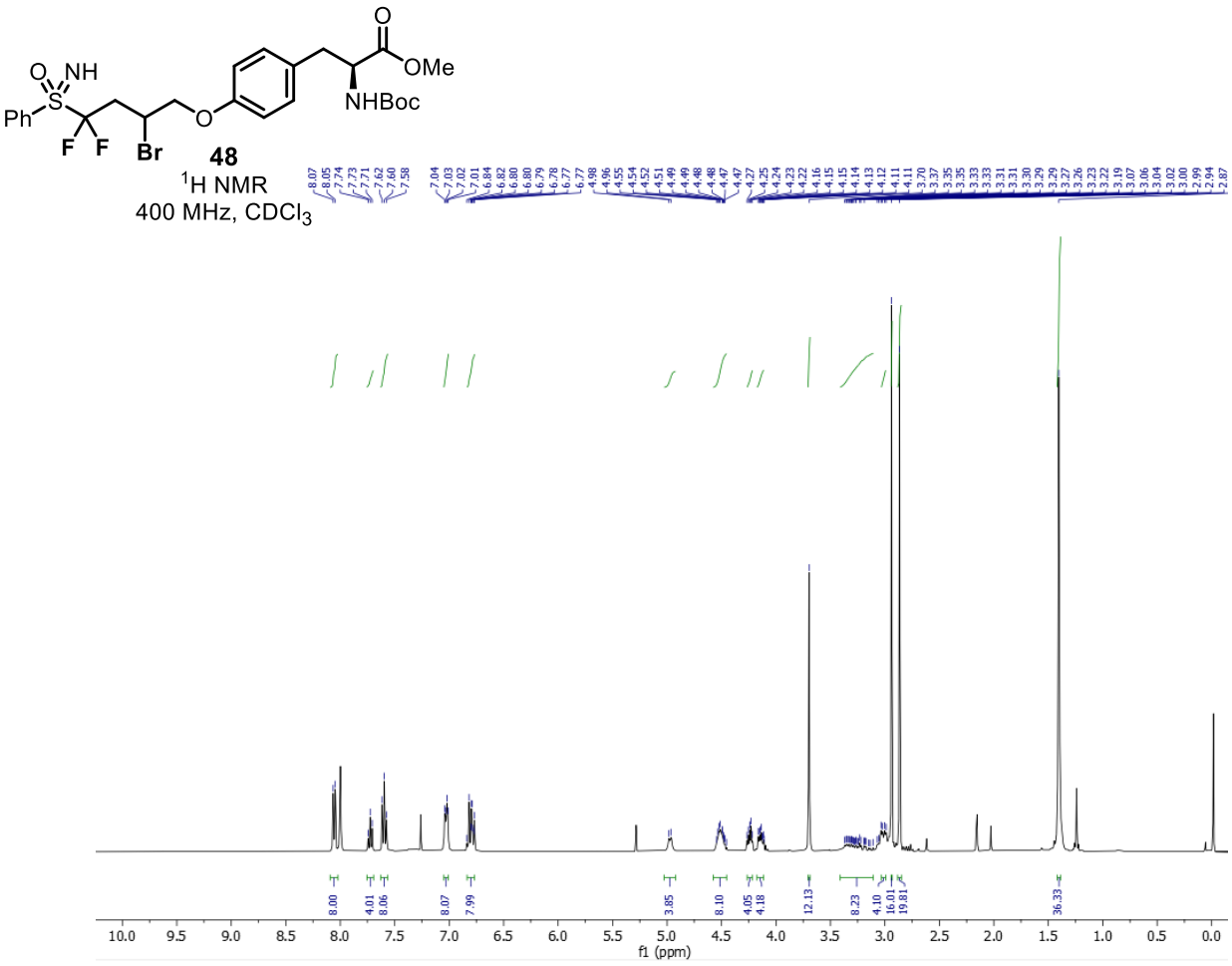


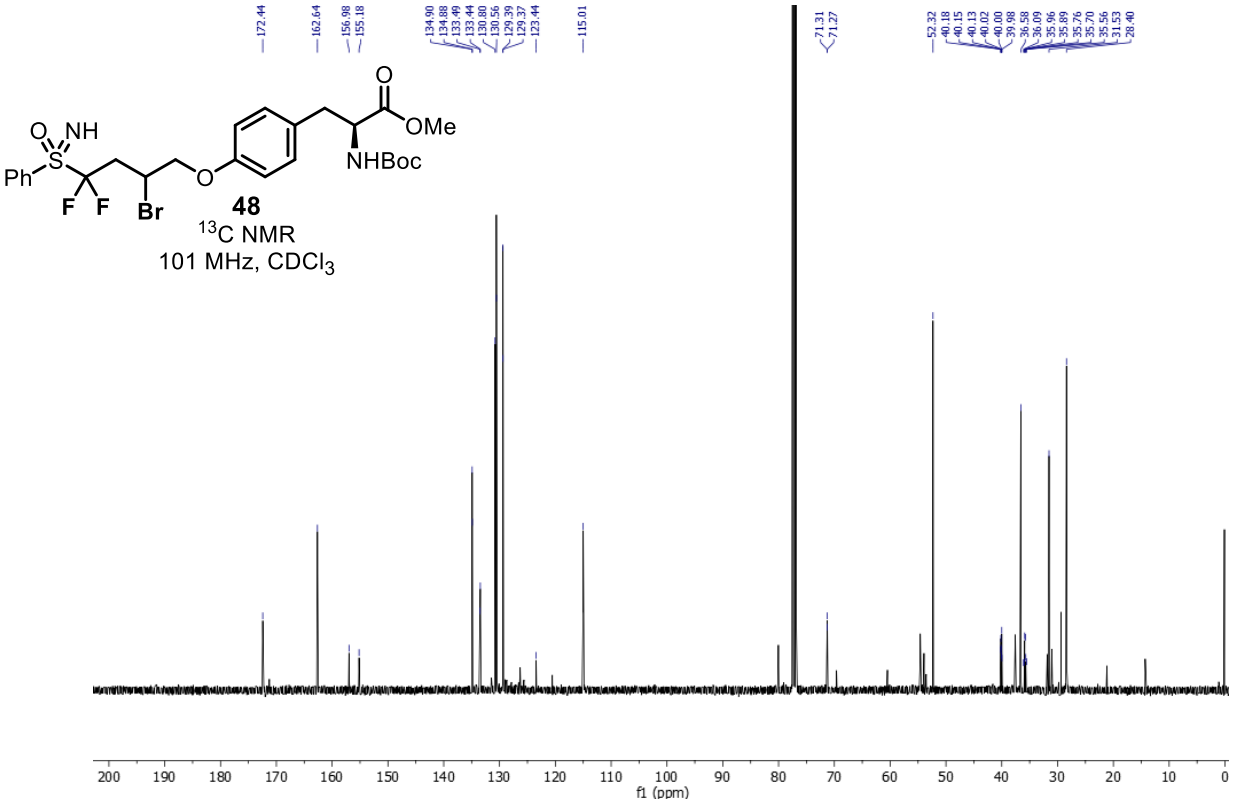
46

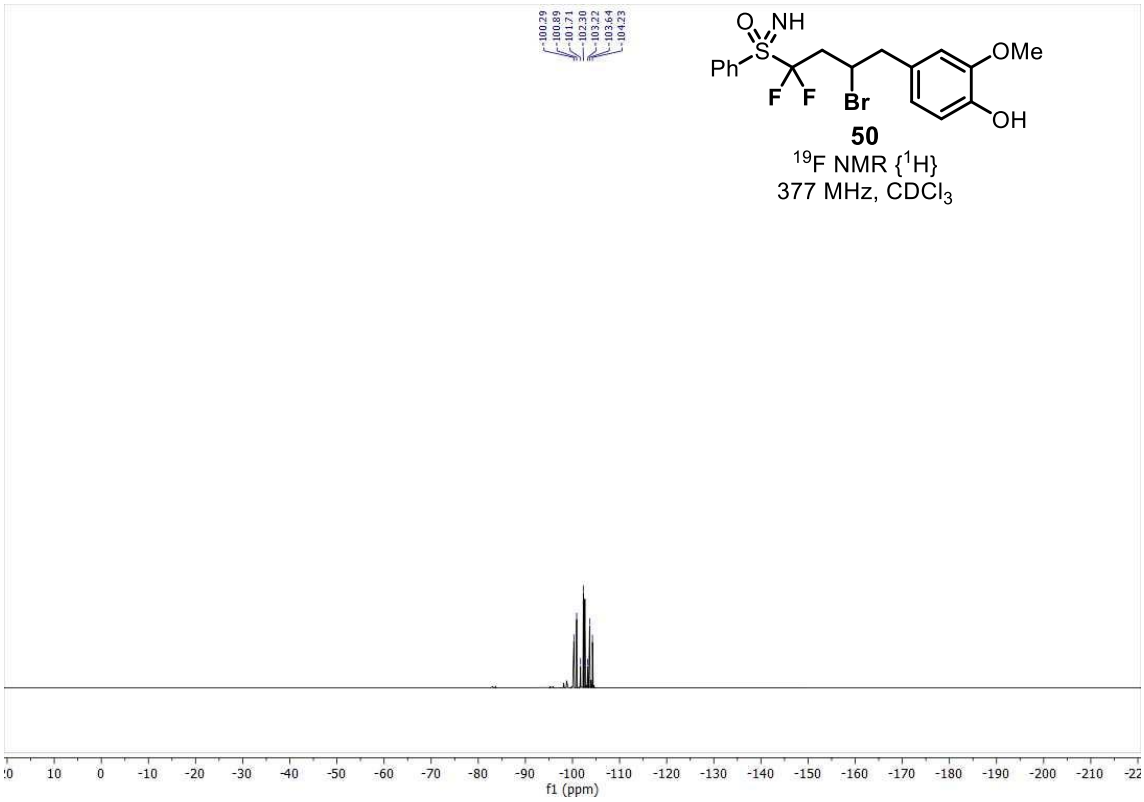
^{13}C NMR

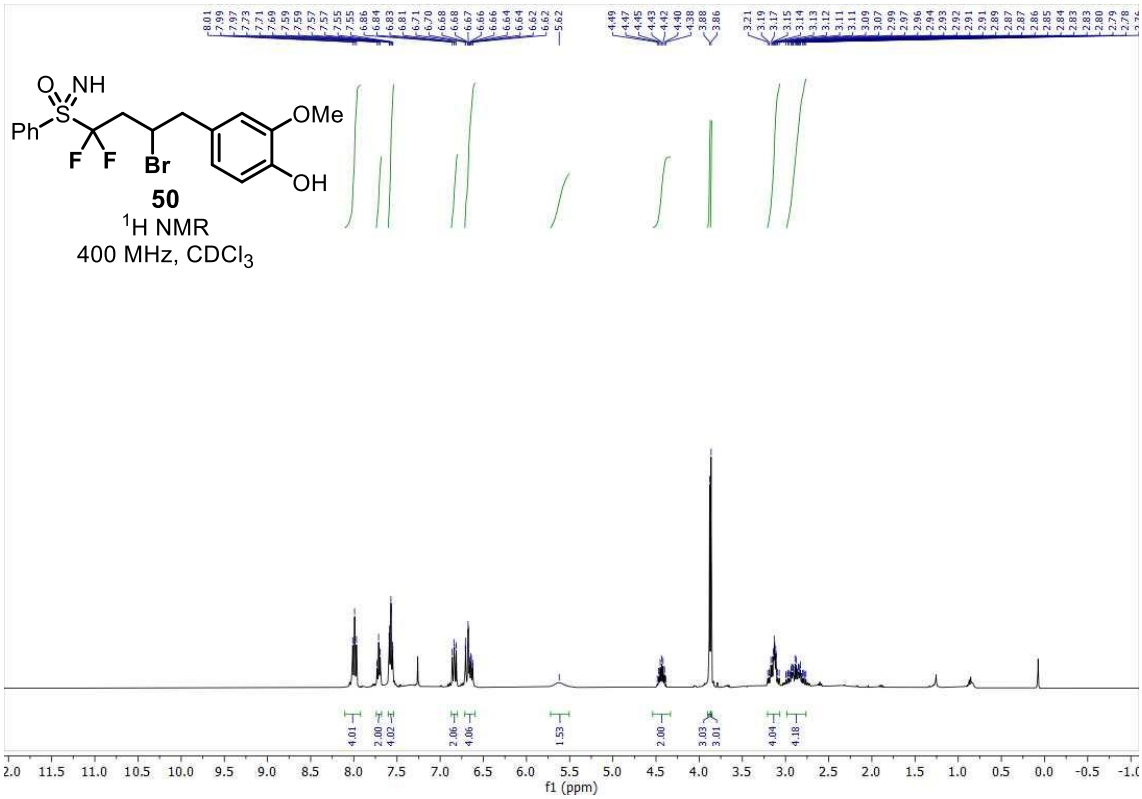
101 MHz, $CDCl_3$

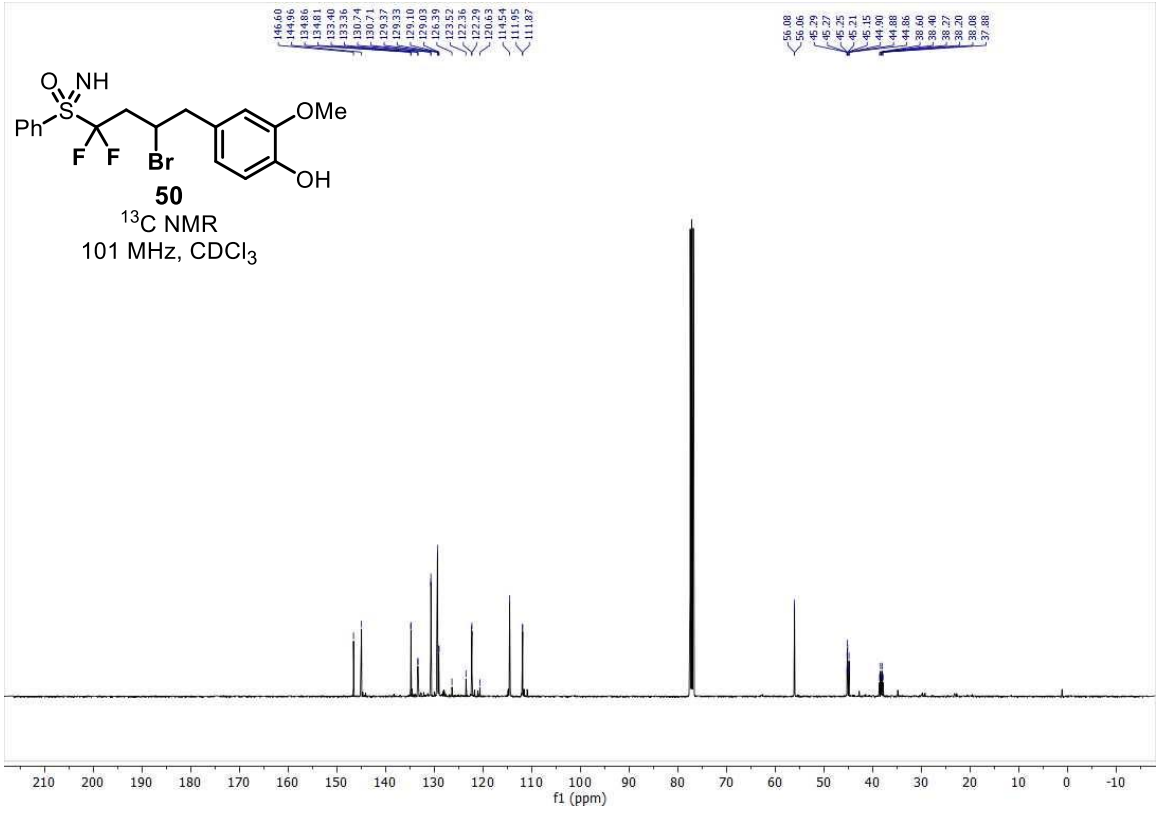

101.15
101.74
102.74
103.84
104.43
O
NH
S
Ph
F F
Br
O
OMe
NHBoc
48
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)

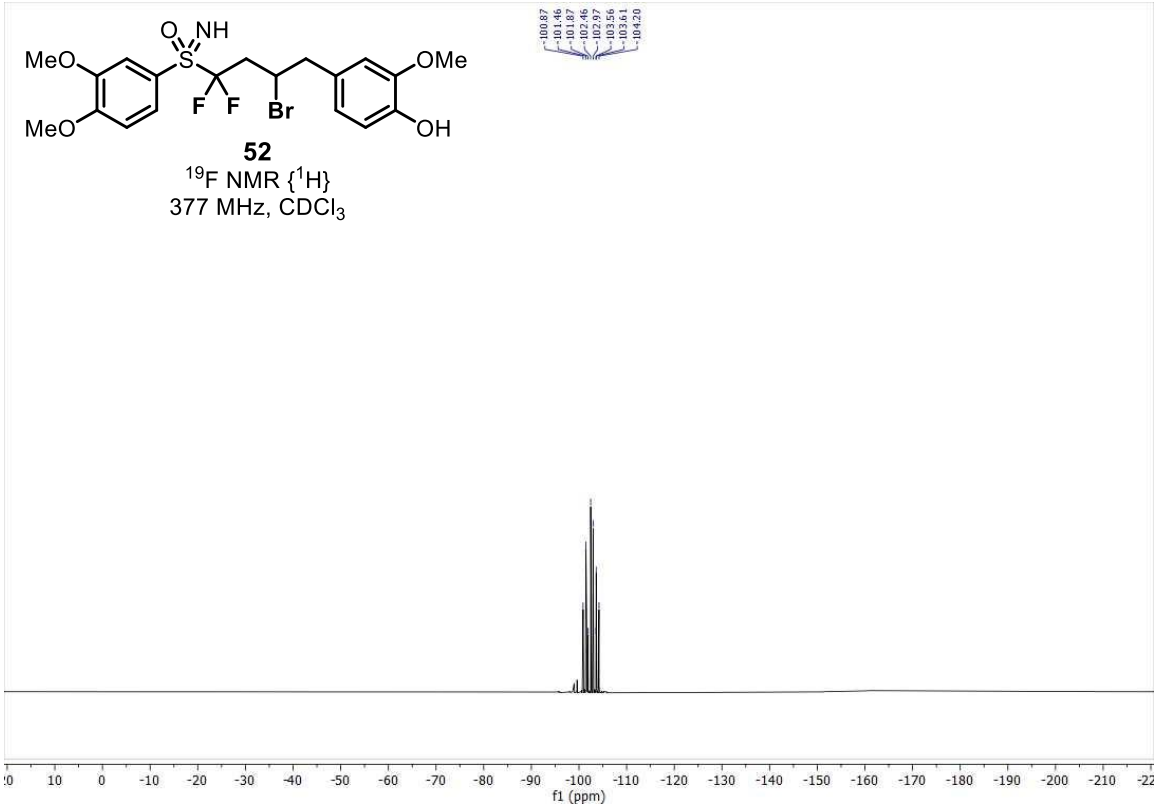

O
NH
S
Ph
F F
Br
O
OMe
NHBoc
48
1H NMR
400 MHz, CDCl3
f1 (ppm)

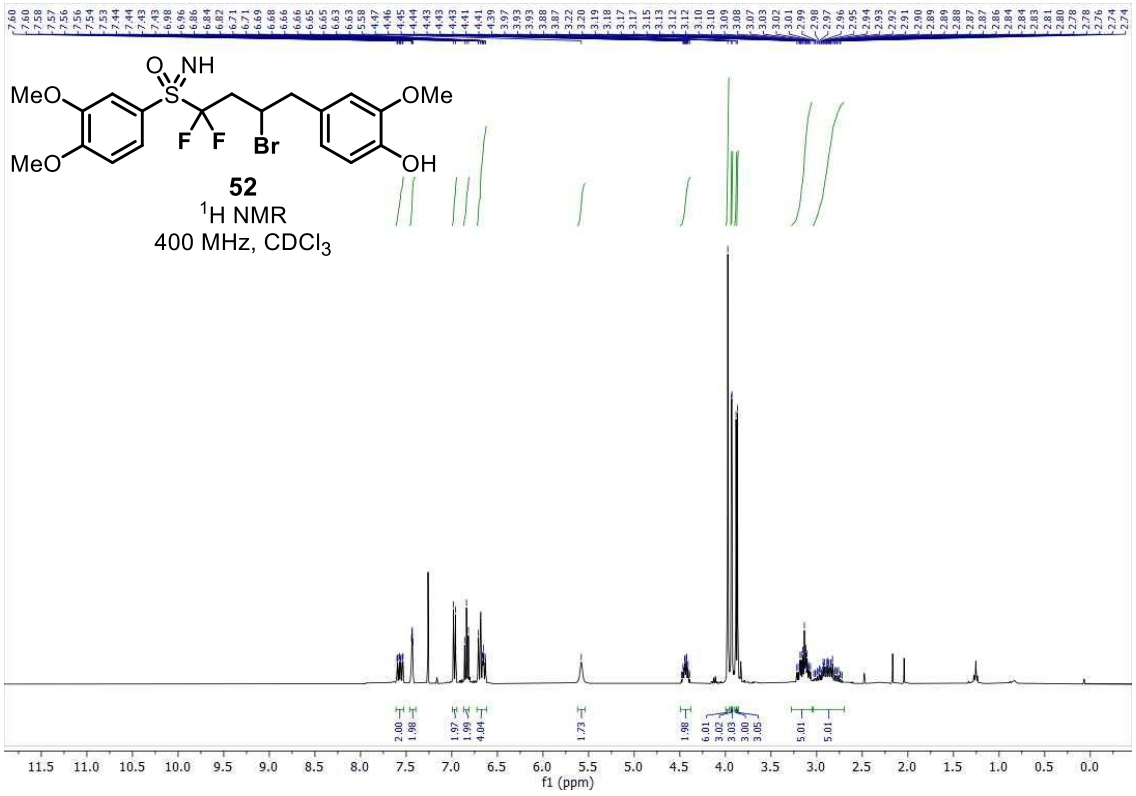

48
^{13}C NMR
101 MHz, $CDCl_3$
f1 (ppm)

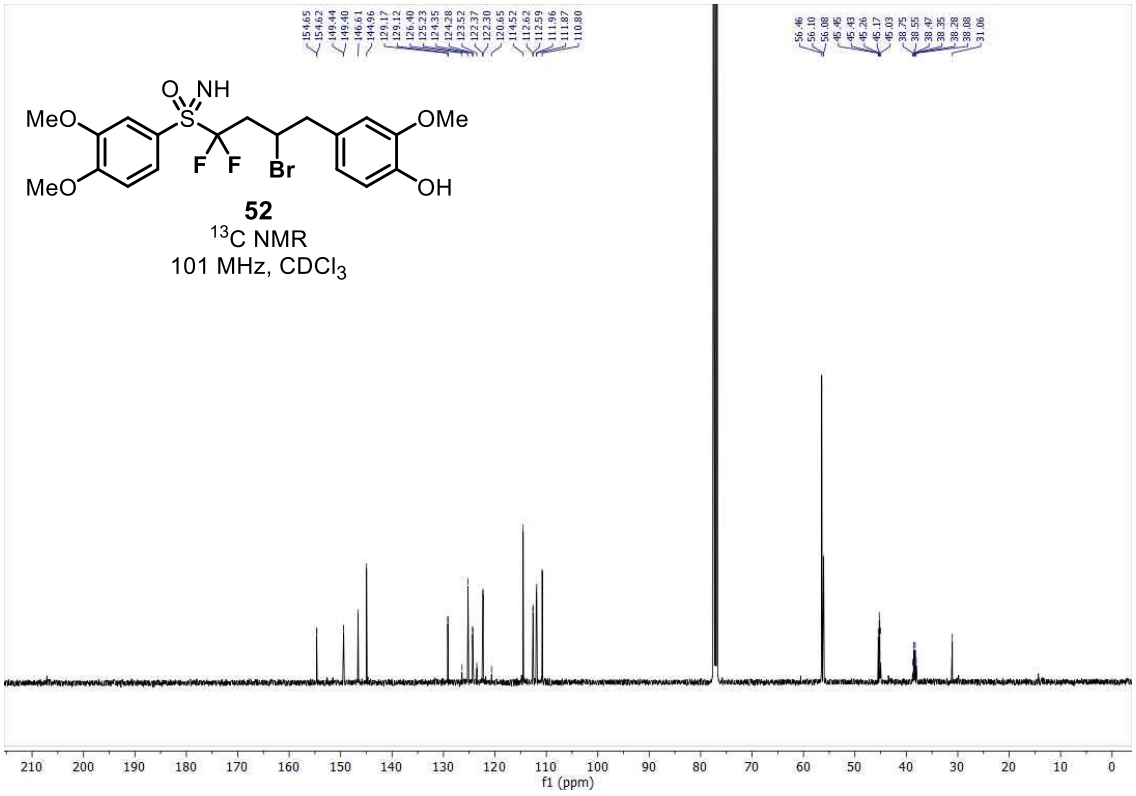

50
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$
f1 (ppm)


O
NH
S
Ph
F
F
Br
OMe
OH
50
1H NMR
400 MHz, CDCl3
f1 (ppm)

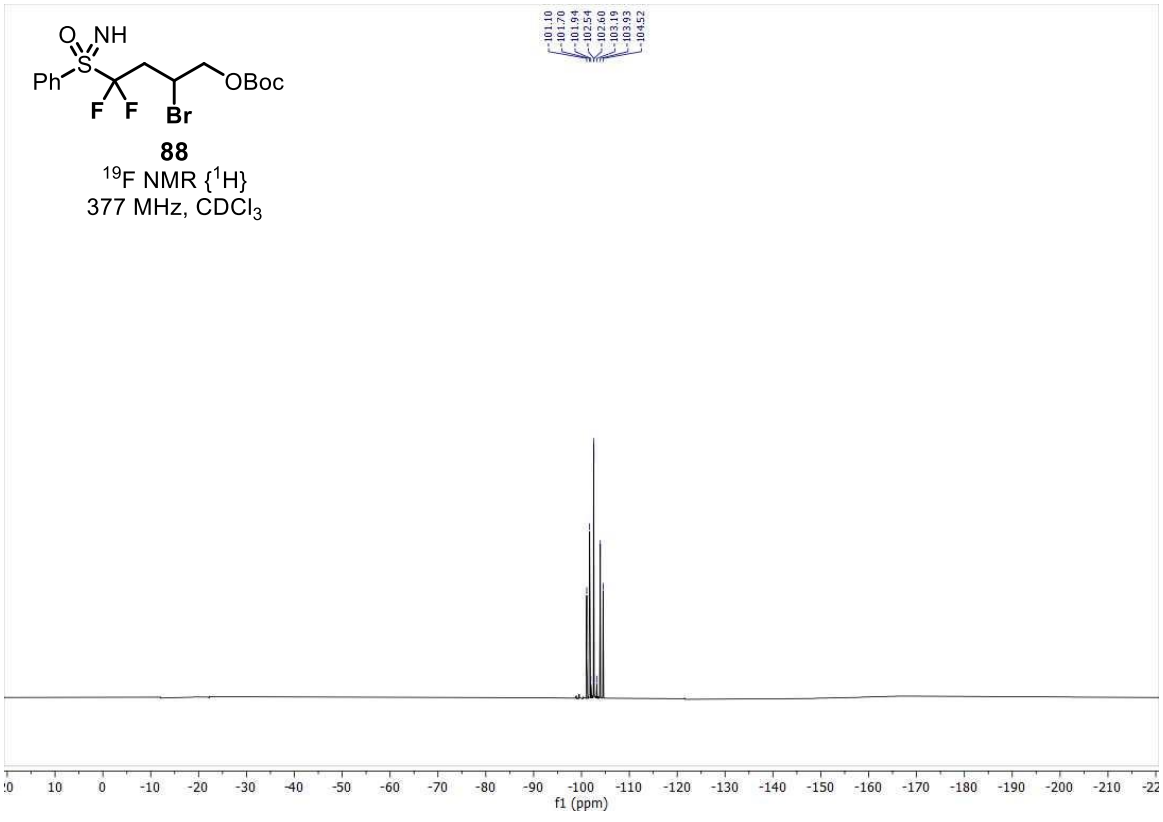

O
NH
S
Ph
F
F
Br
OMe
OH
50
13C NMR
101 MHz, CDCl3
f1 (ppm)


MeO
MeO
O
NH
S
F
F
Br
OMe
OH
52
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)

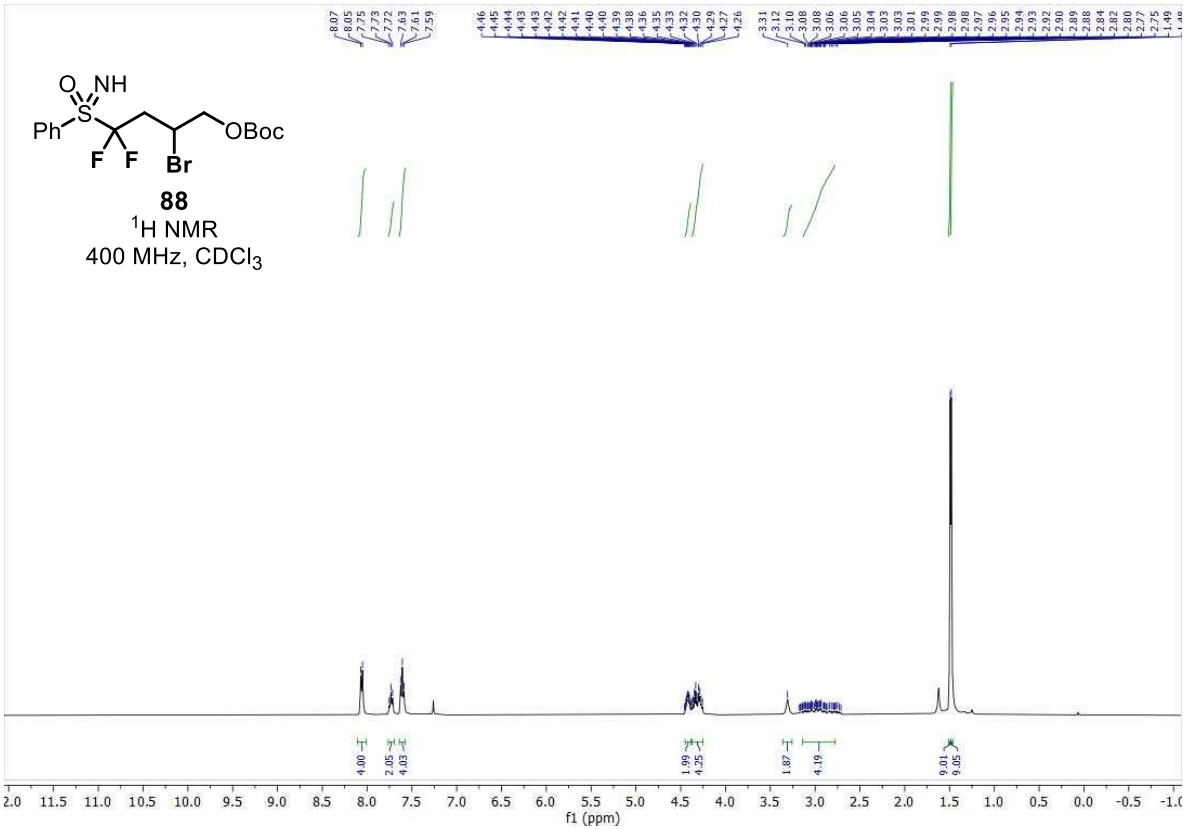

MeO
MeO
O
NH
S
F
F
Br
OMe
OH
52
1H NMR
400 MHz, CDCl3
f1 (ppm)

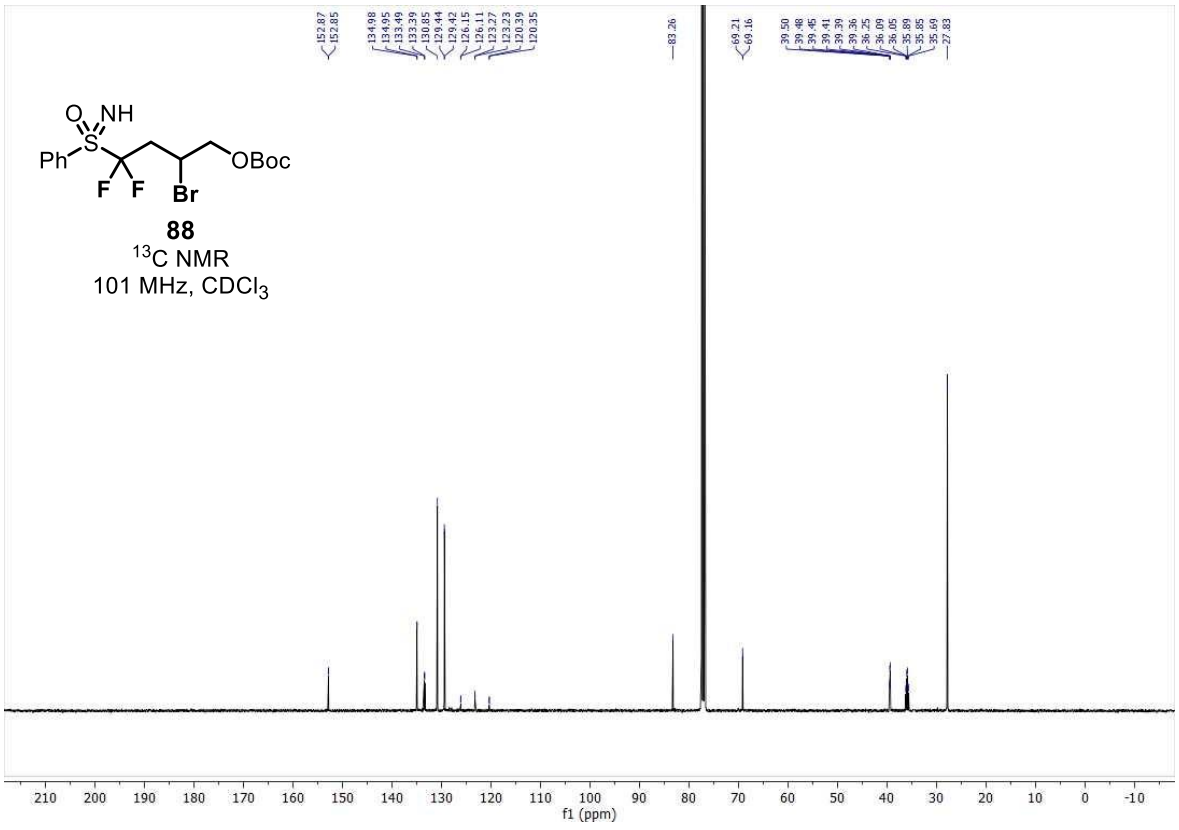


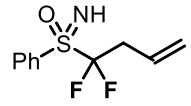
52
^{13}C NMR
101 MHz, $CDCl_3$



88
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$

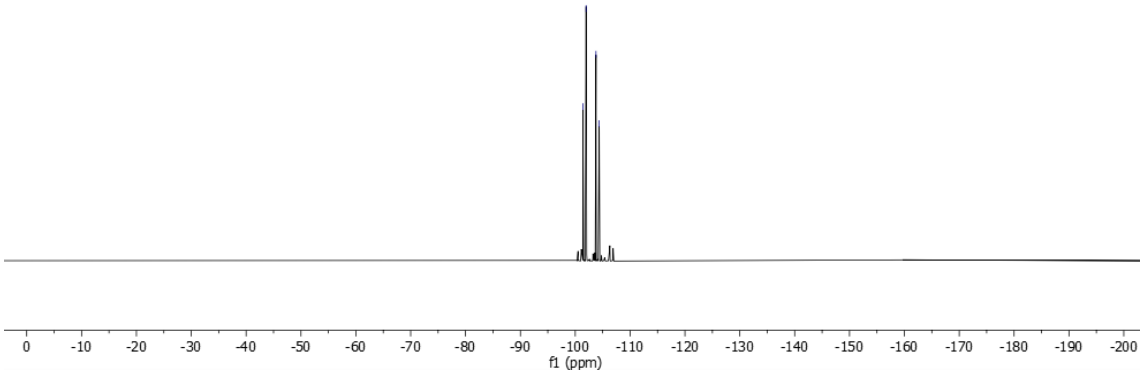

O
NH
S
Ph
F
F
Br
OBoc
88
1H NMR
400 MHz, CDCl3
f1 (ppm)

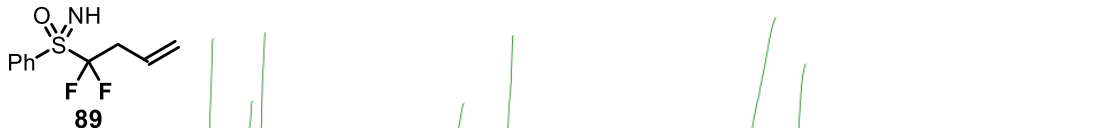

O
NH
S
Ph
F
F
Br
OBoc
88
13C NMR
101 MHz, CDCl3
f1 (ppm)



89

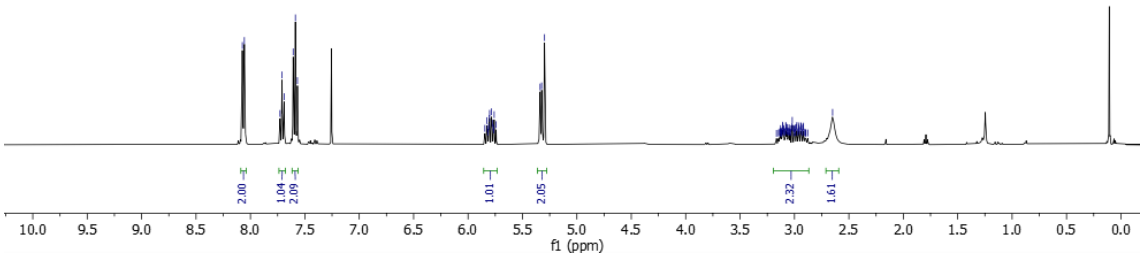
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$

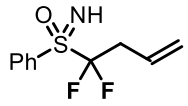




89

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

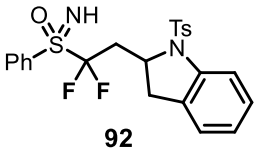




89

^{13}C NMR

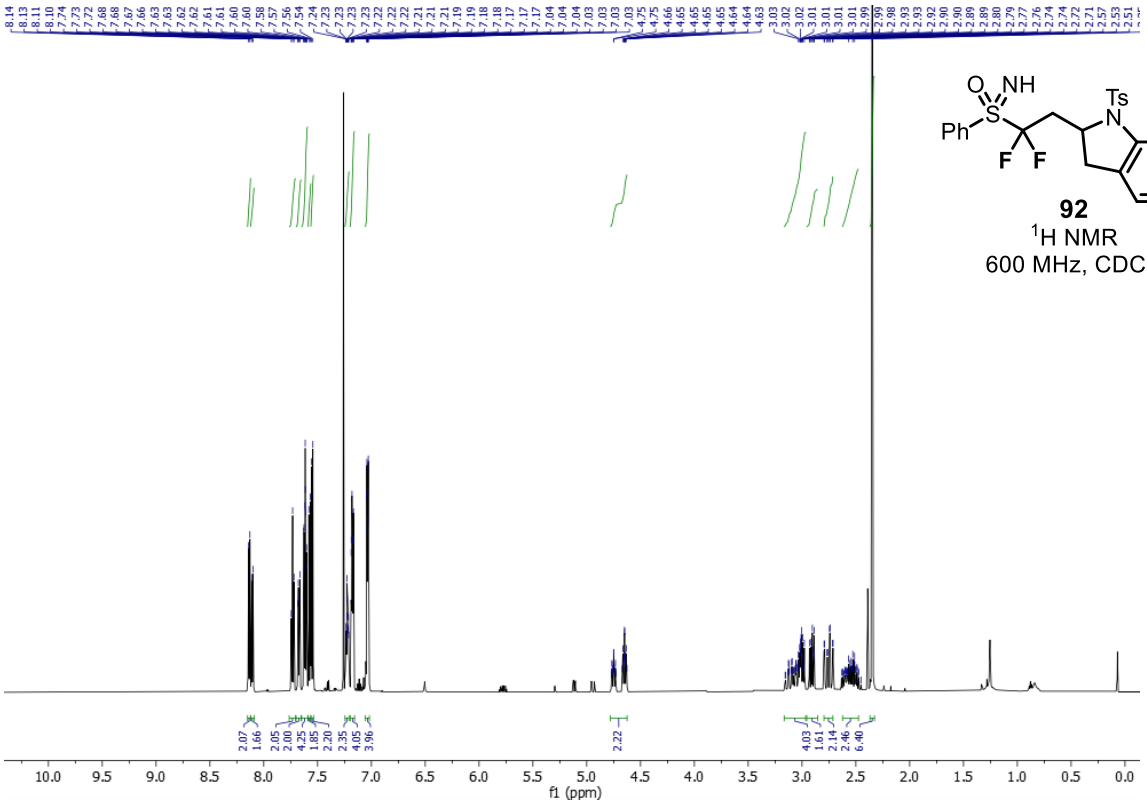
101 MHz, $CDCl_3$

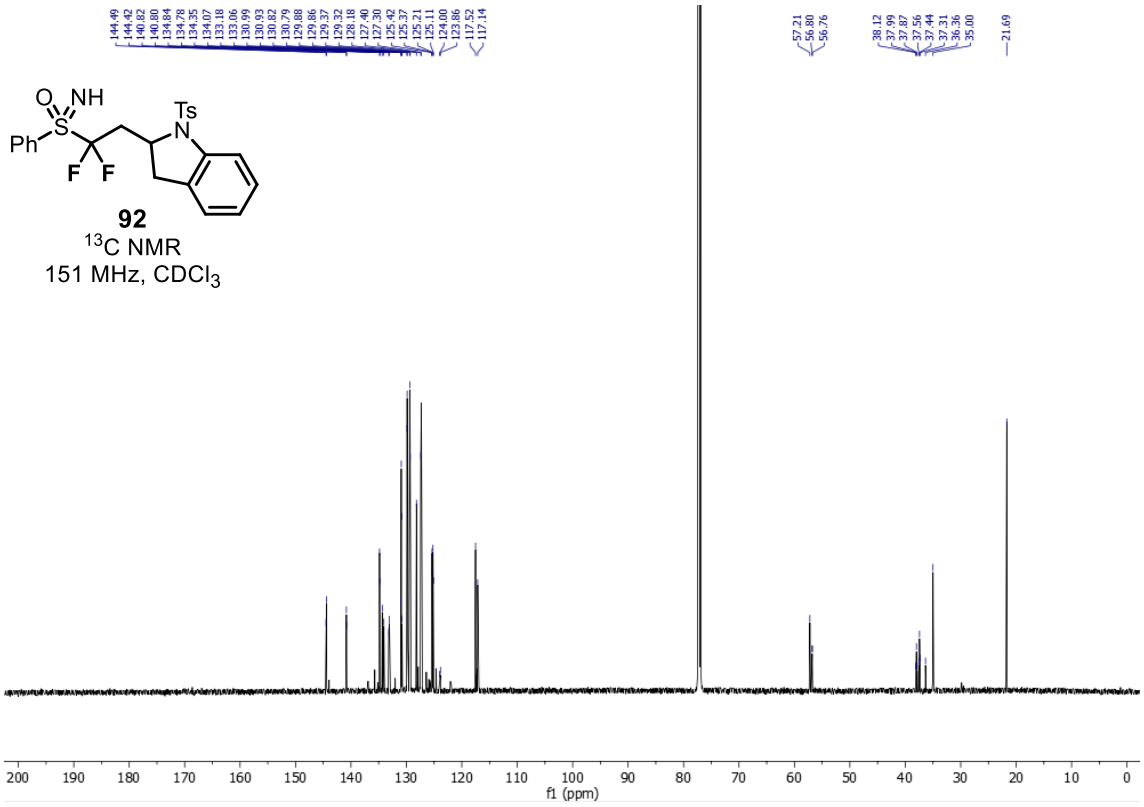


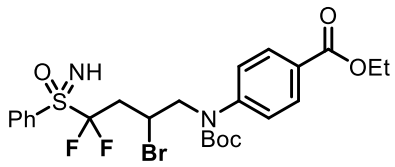
92

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$

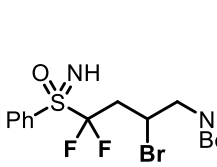

O
NH
S
Ph
F F
Ts
N
92
1H NMR
600 MHz, CDCl3
f1 (ppm)


O
NH
S
Ph
F F
Ts
N
92
13C NMR
151 MHz, CDCl3
f1 (ppm)



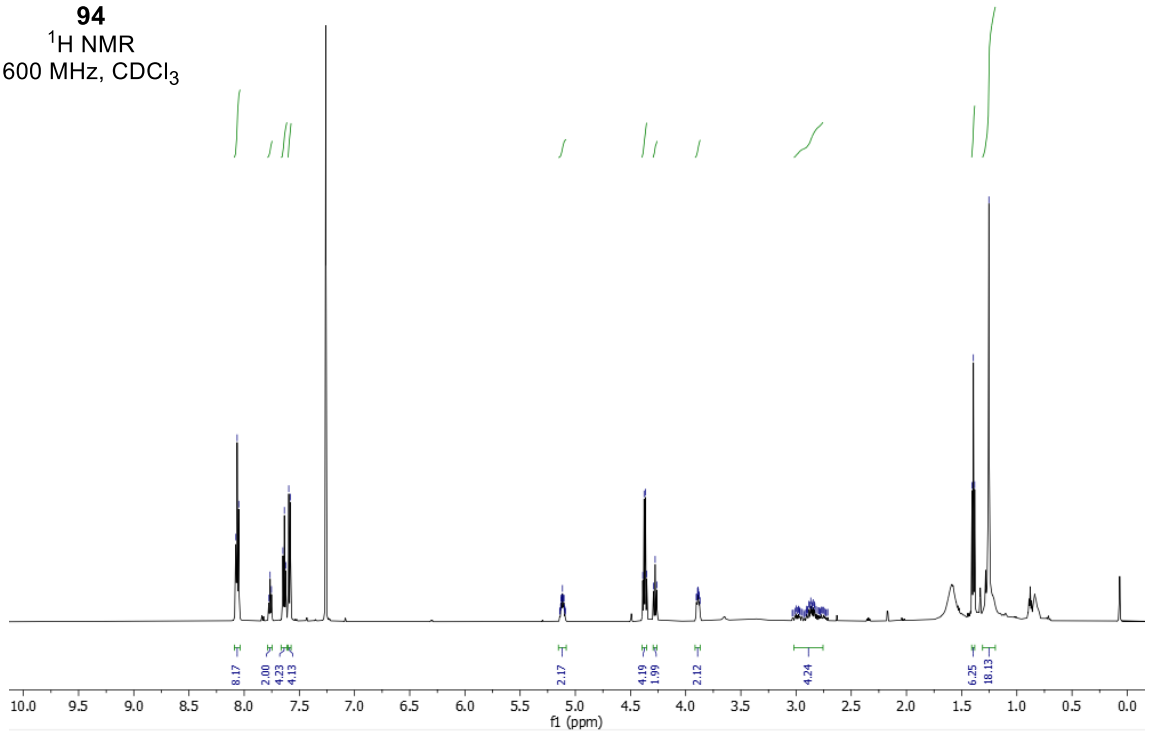
94

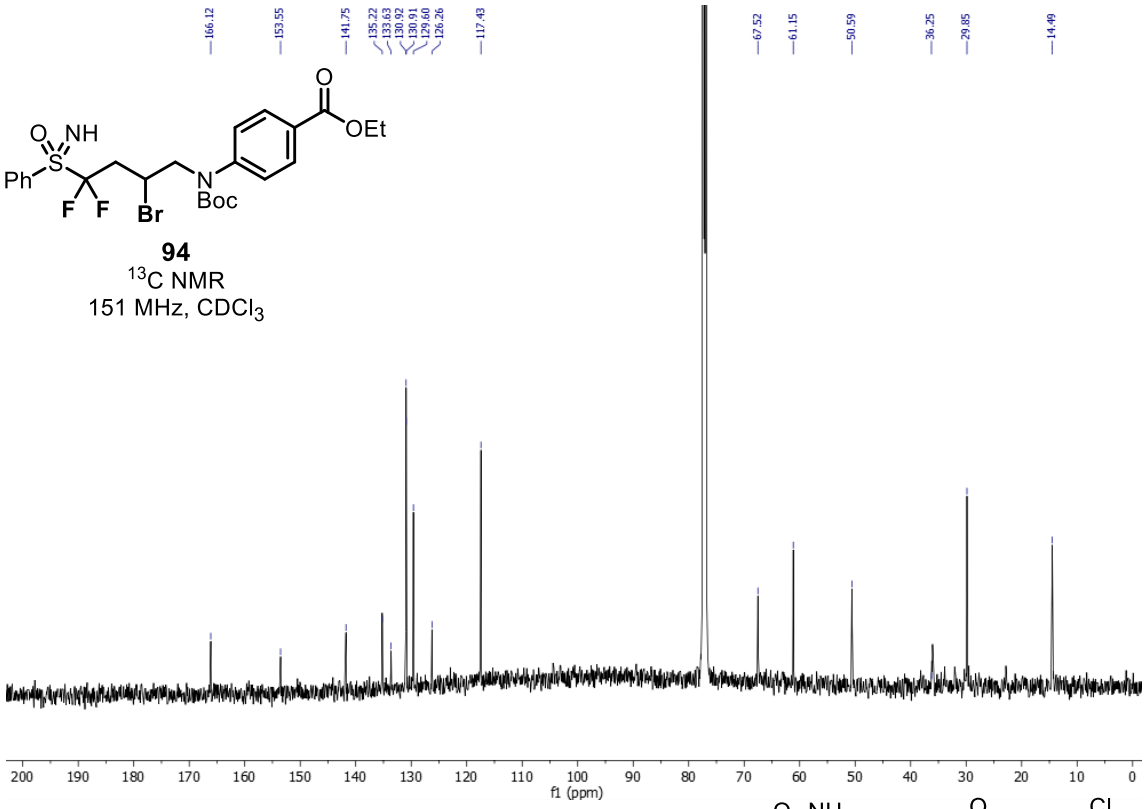
^{19}F NMR {^{1}H}
188 MHz, $CDCl_3$



94

^{1}H NMR
600 MHz, $CDCl_3$

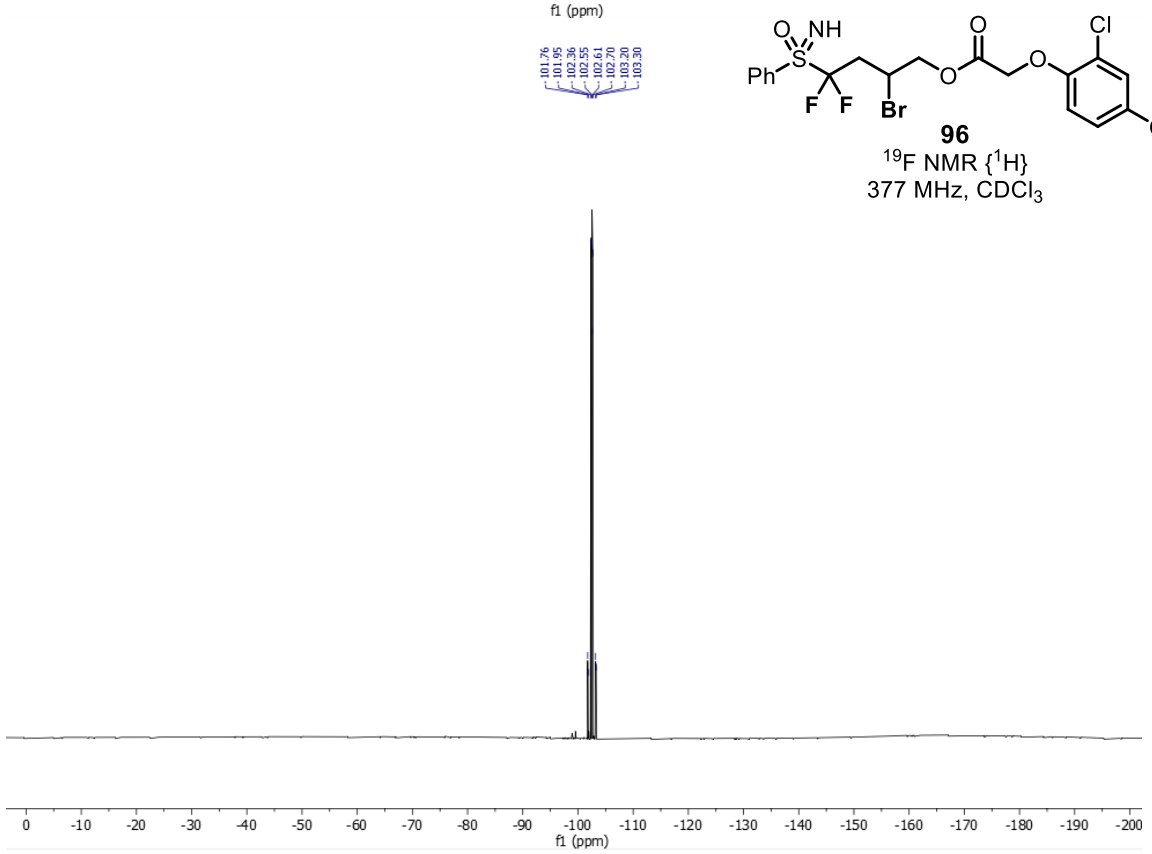




94

^{13}C NMR

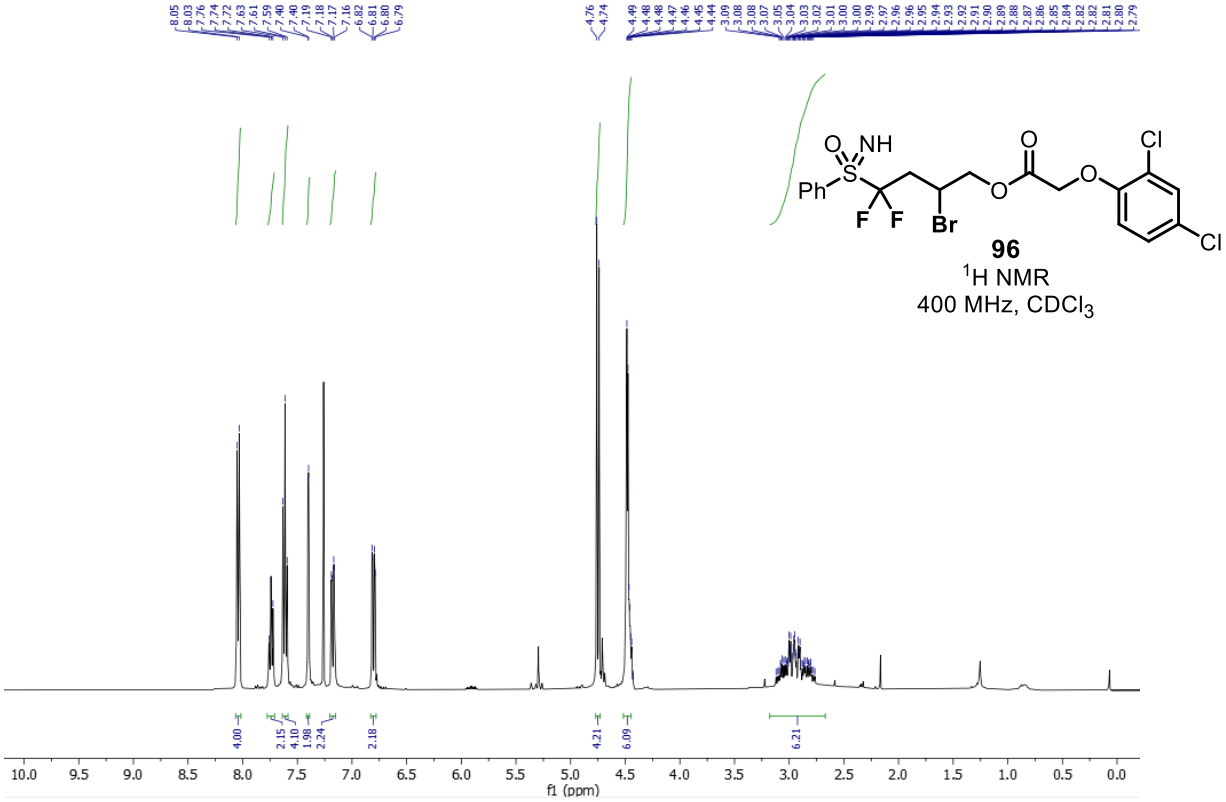
151 MHz, $CDCl_3$

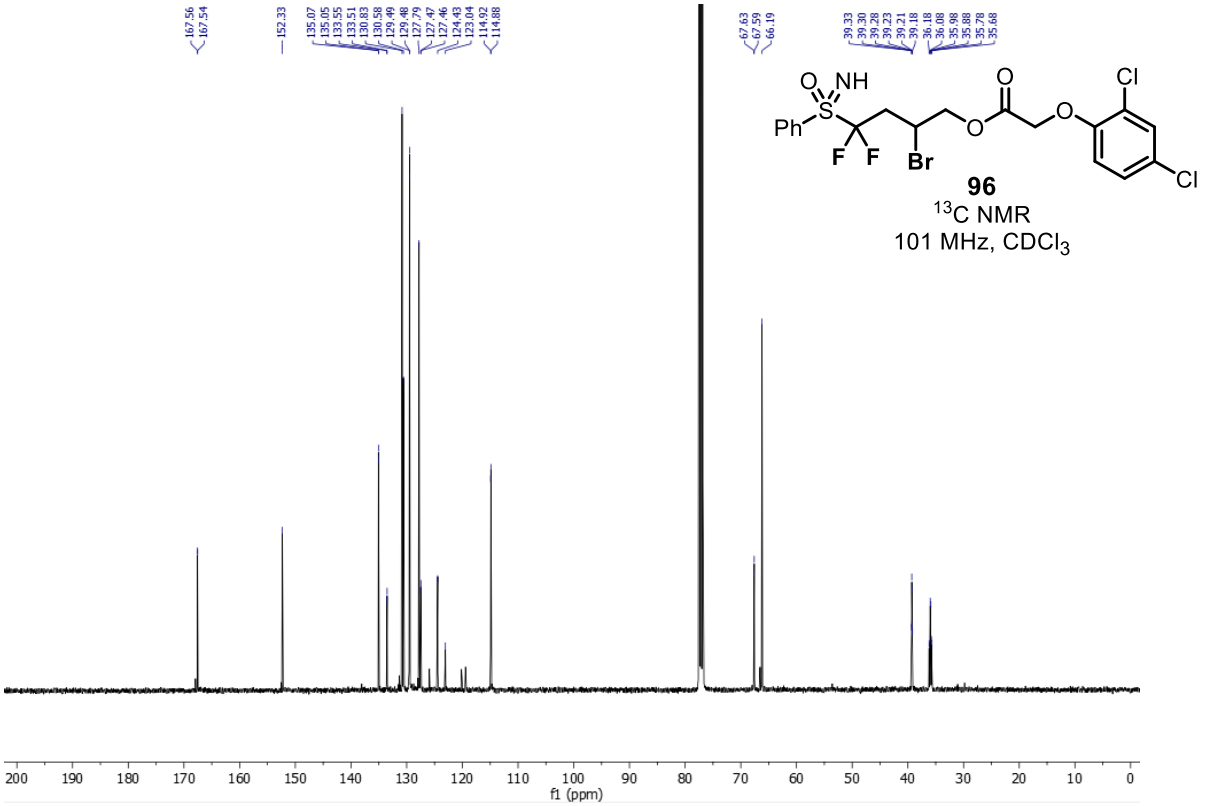


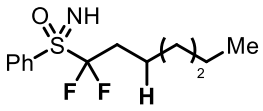
96

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$


96
^{1}H NMR
400 MHz, $CDCl_3$
f1 (ppm)

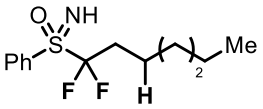

96
^{13}C NMR
101 MHz, $CDCl_3$
f1 (ppm)



16

^{19}F NMR {^{1}H}

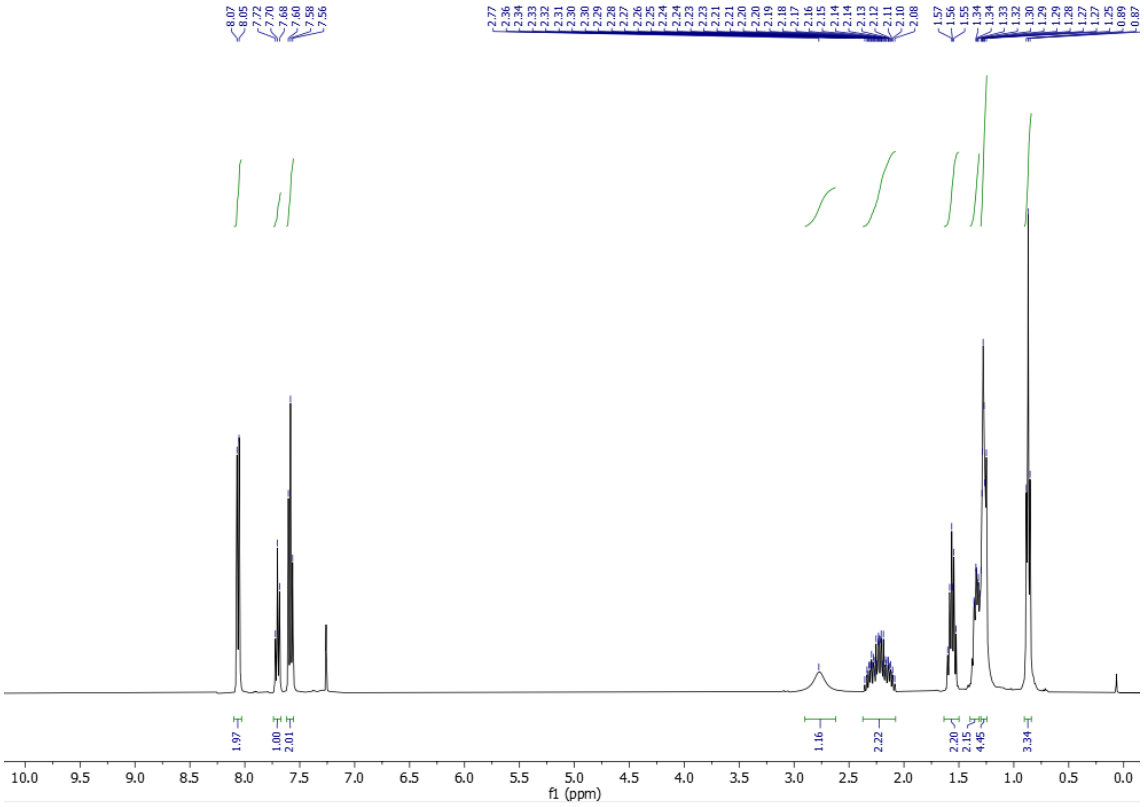
377 MHz, $CDCl_3$

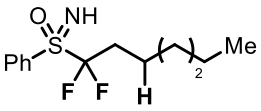


16

^{1}H NMR

400 MHz, $CDCl_3$

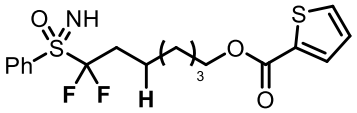




16

^{13}C NMR

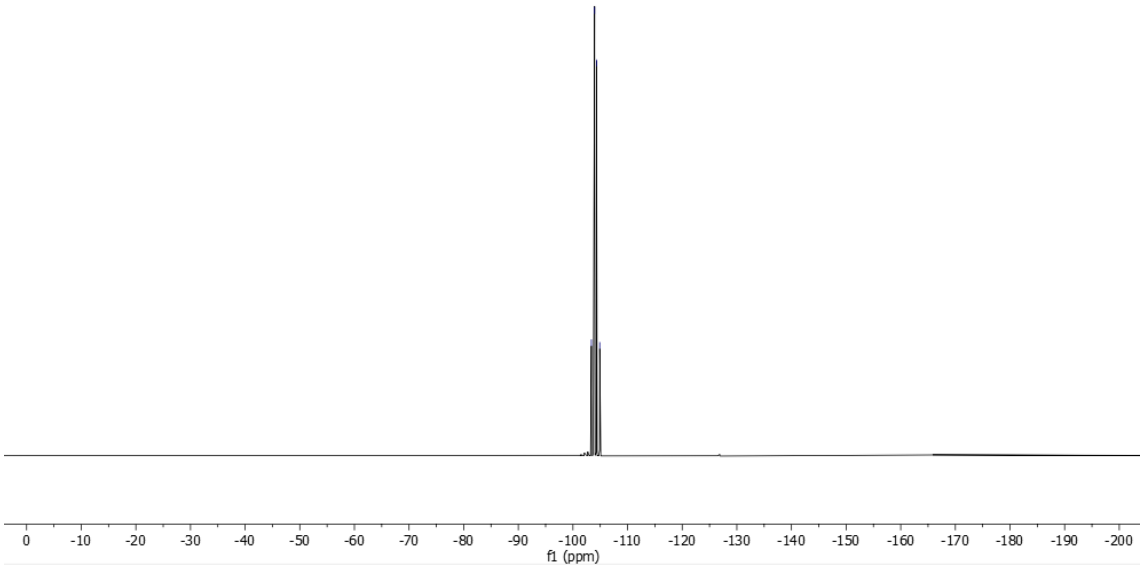
101 MHz, $CDCl_3$

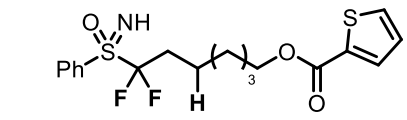


20

^{19}F NMR $\{^{1}H\}$

377 MHz, $CDCl_3$

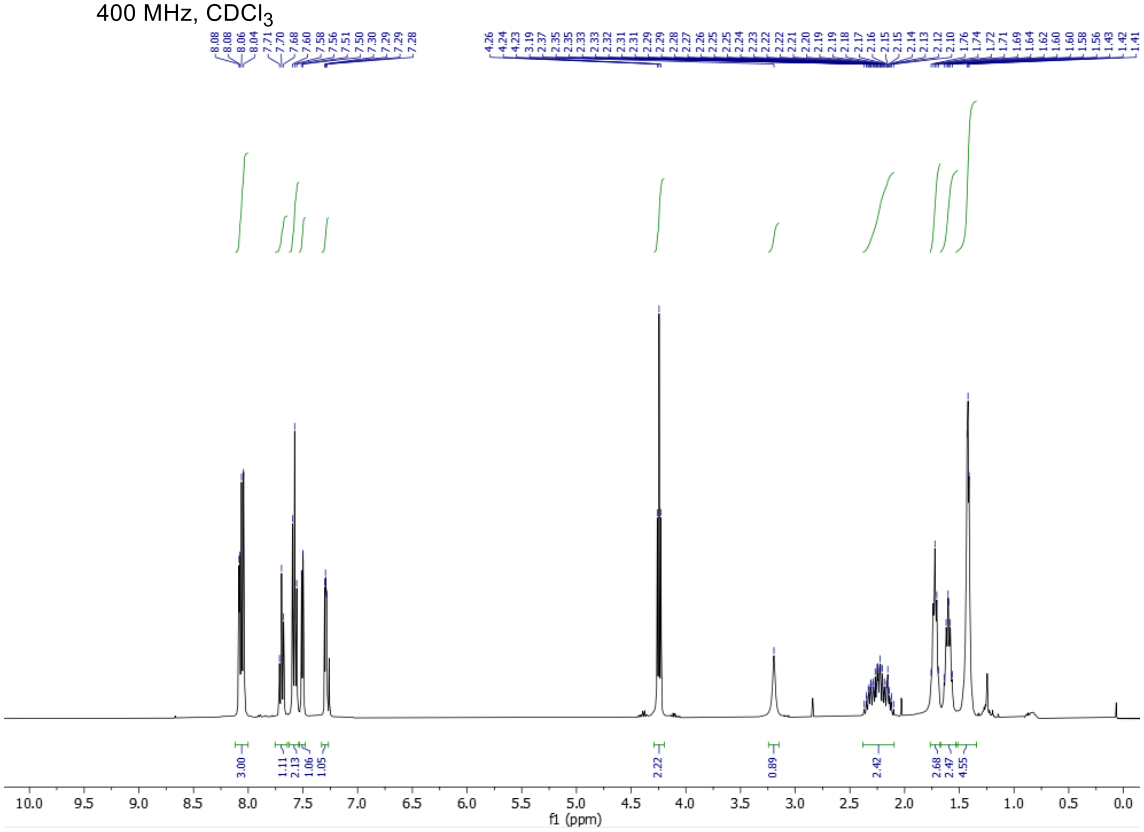


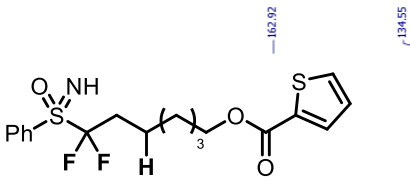


20

^{1}H NMR

400 MHz, $CDCl_3$

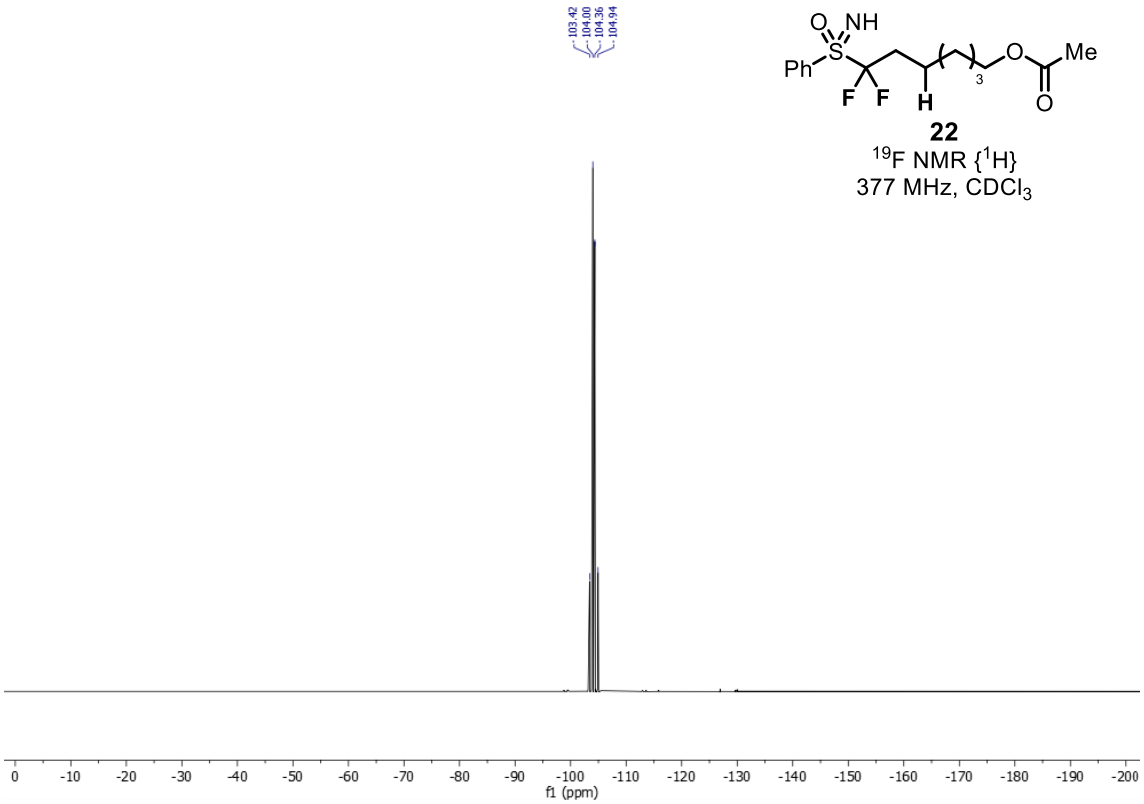


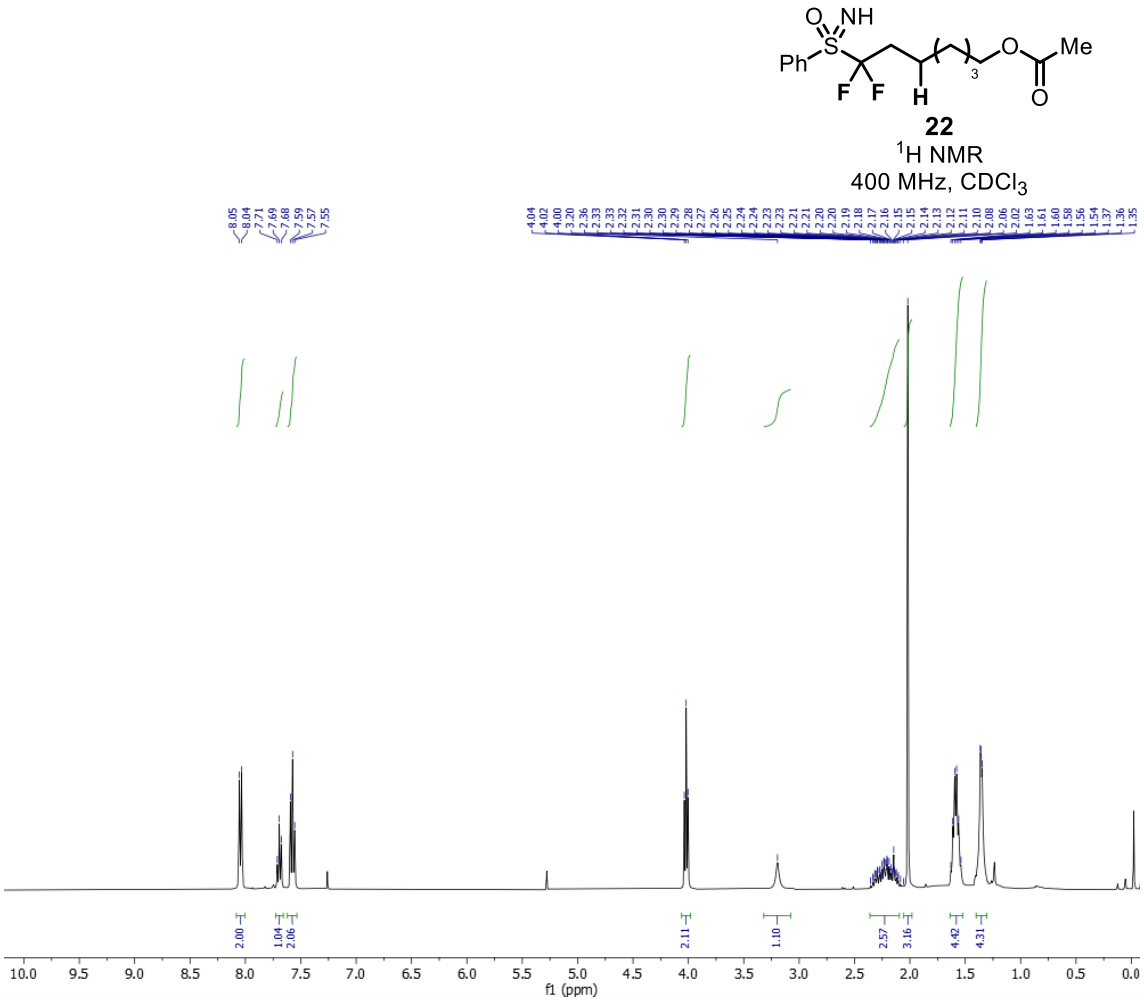


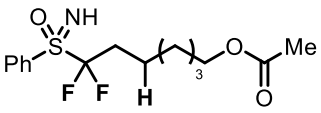
20

^{13}C NMR

101 MHz, $CDCl_3$


103.42
104.00
104.36
104.94
O NH
Ph S
F F
H
3
O
Me
O
22
19F NMR {1H}
377 MHz, CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

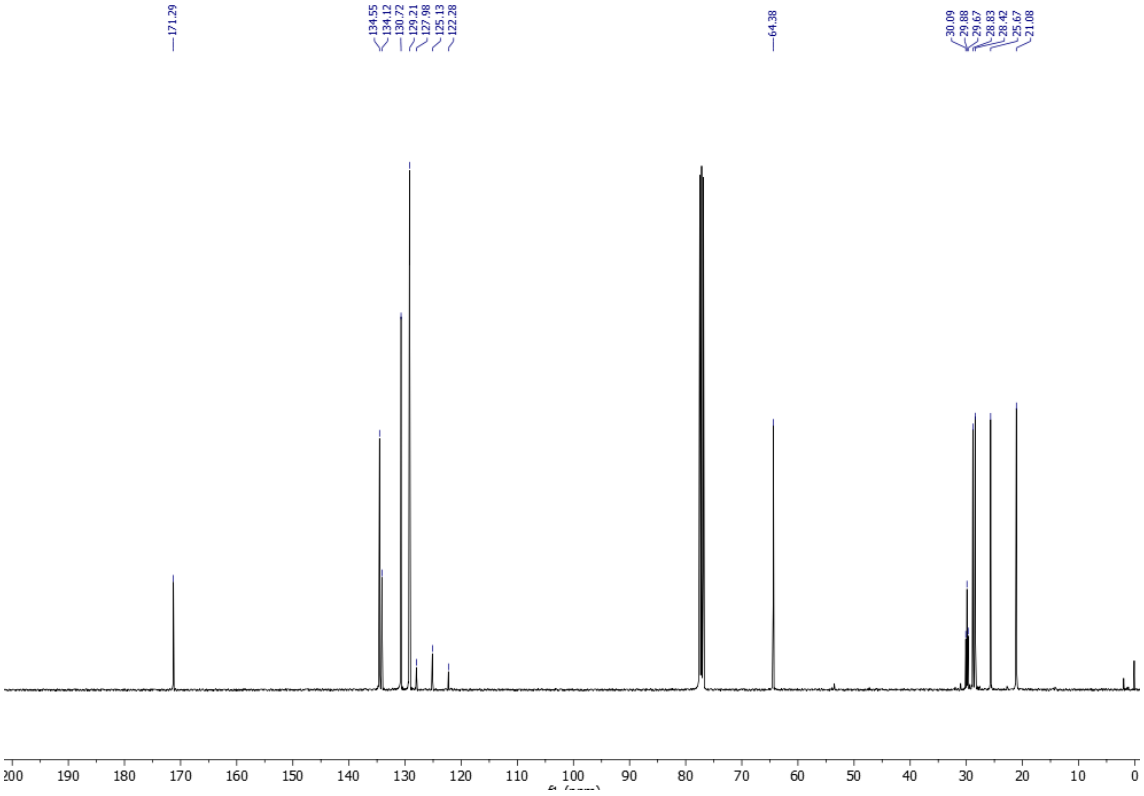

O NH
Ph S
F F
H
3
O
Me
O
22
1H NMR
400 MHz, CDCl3
8.05
8.04
7.71
7.69
7.68
7.59
7.57
7.55
2.00
1.04
2.06
2.11
1.10
2.57
3.16
4.42
4.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

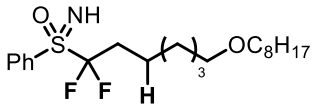


22

^{13}C NMR

101 MHz, $CDCl_3$

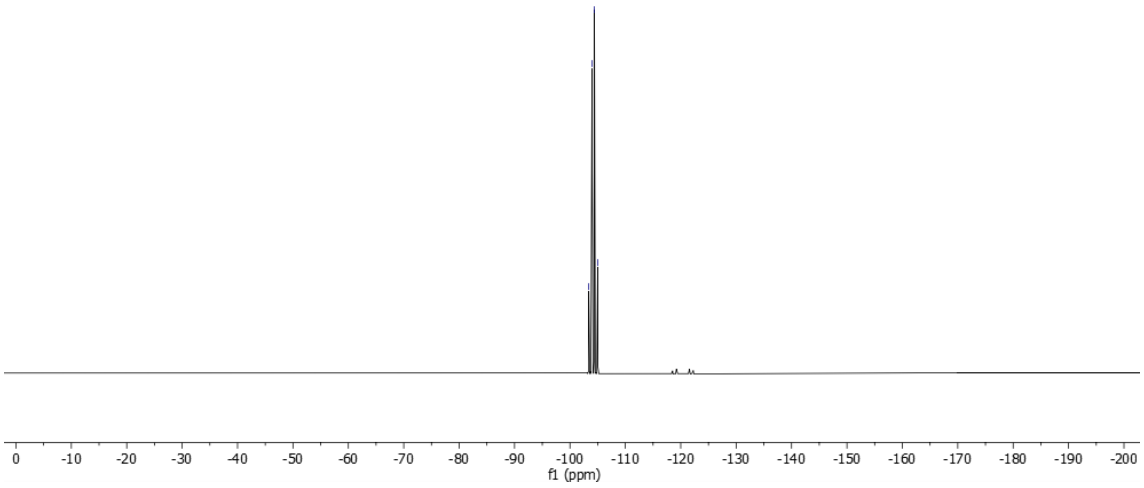


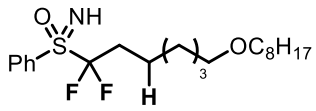


24

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$

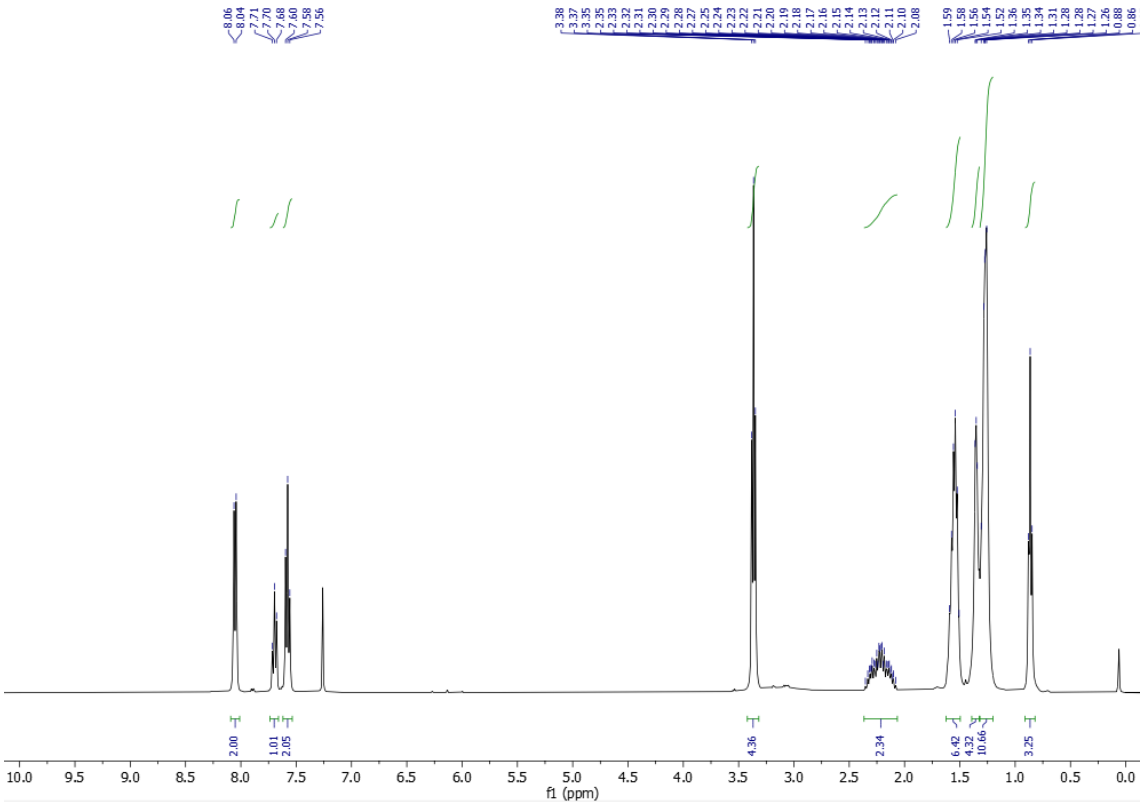


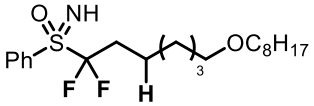


24

^{1}H NMR

400 MHz, $CDCl_3$

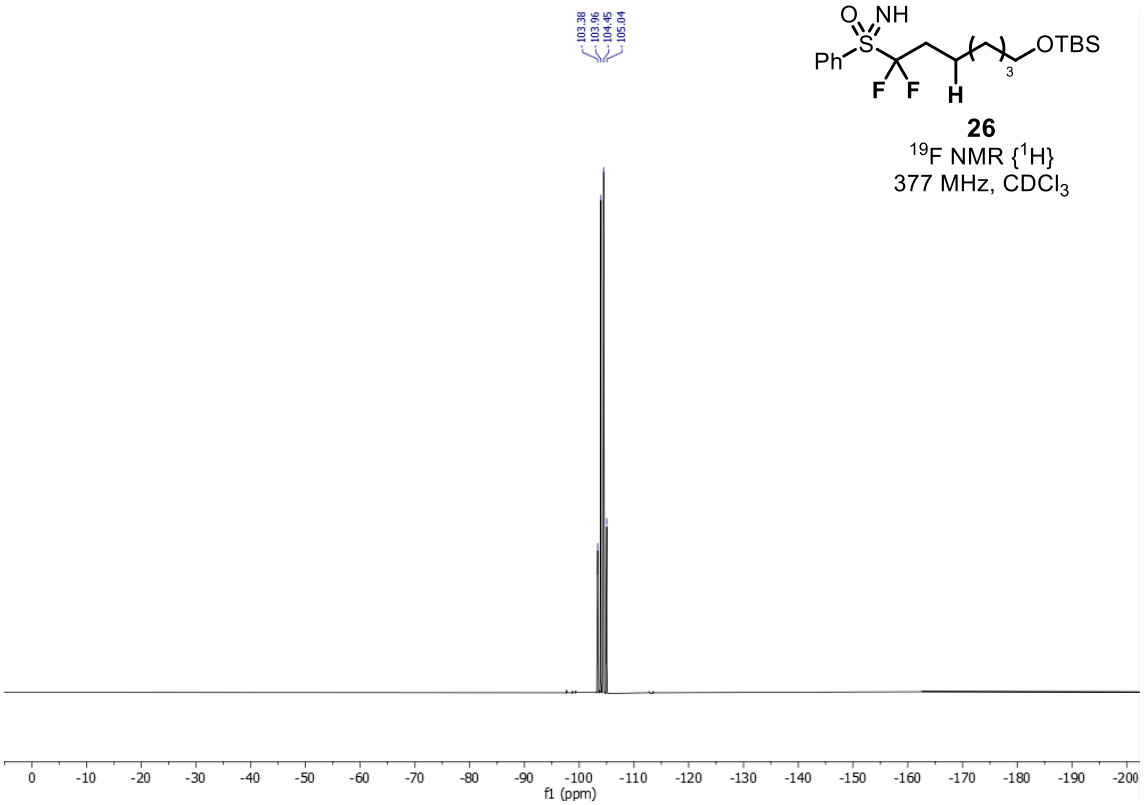




24

^{13}C NMR

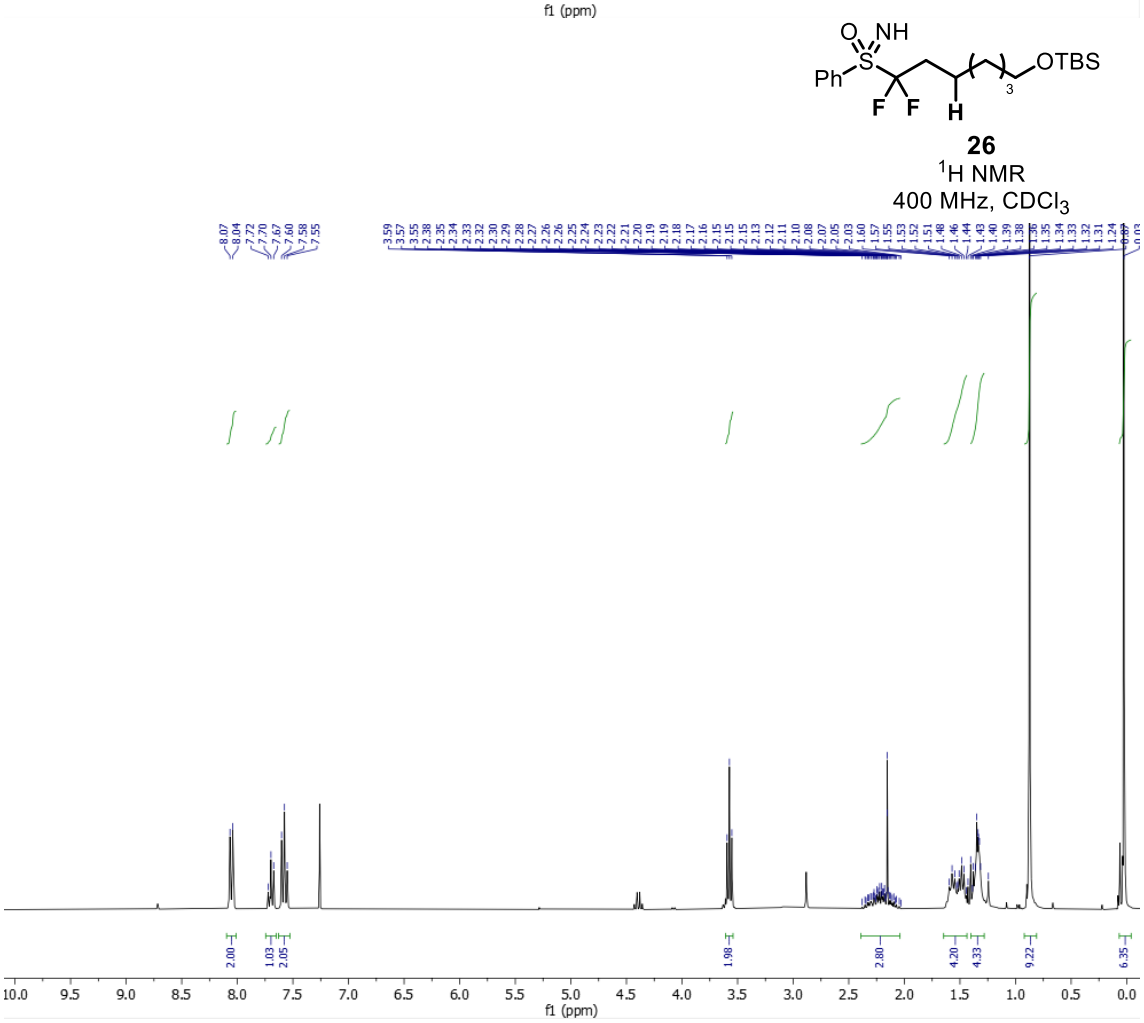
101 MHz, $CDCl_3$



26

^{19}F NMR {^{1}H}

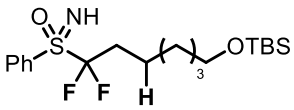
377 MHz, $CDCl_3$



26

^{1}H NMR

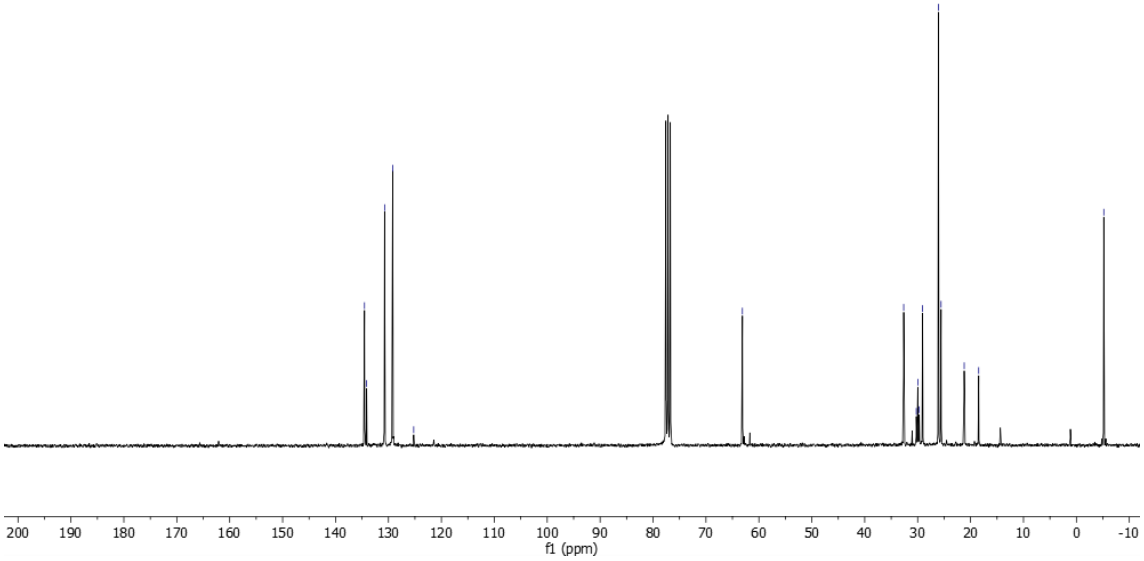
400 MHz, $CDCl_3$

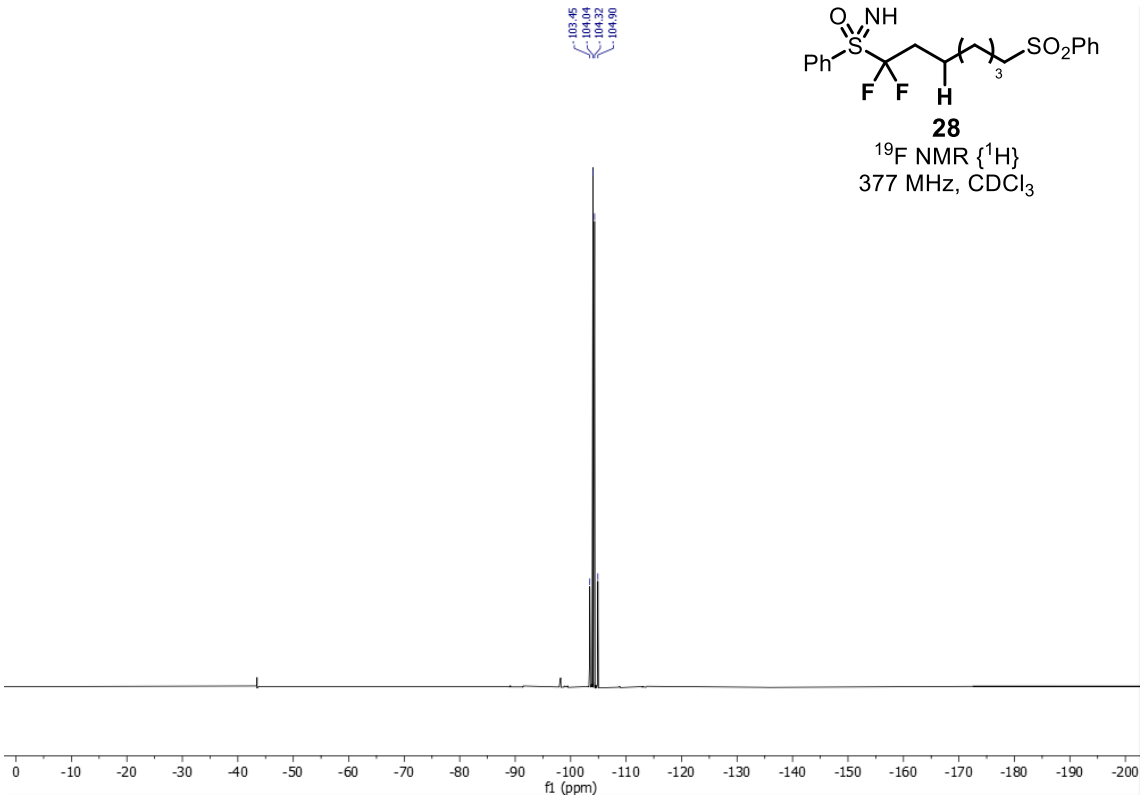


26

^{13}C NMR

101 MHz, $CDCl_3$

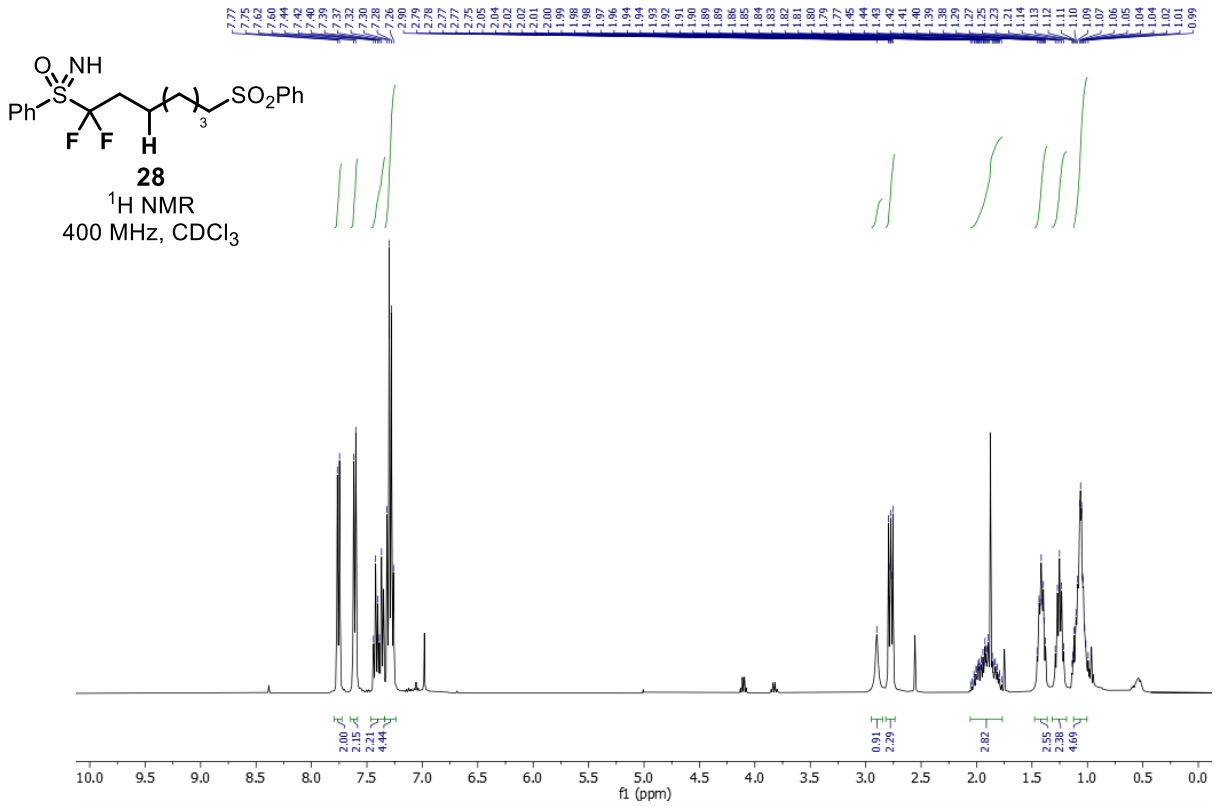


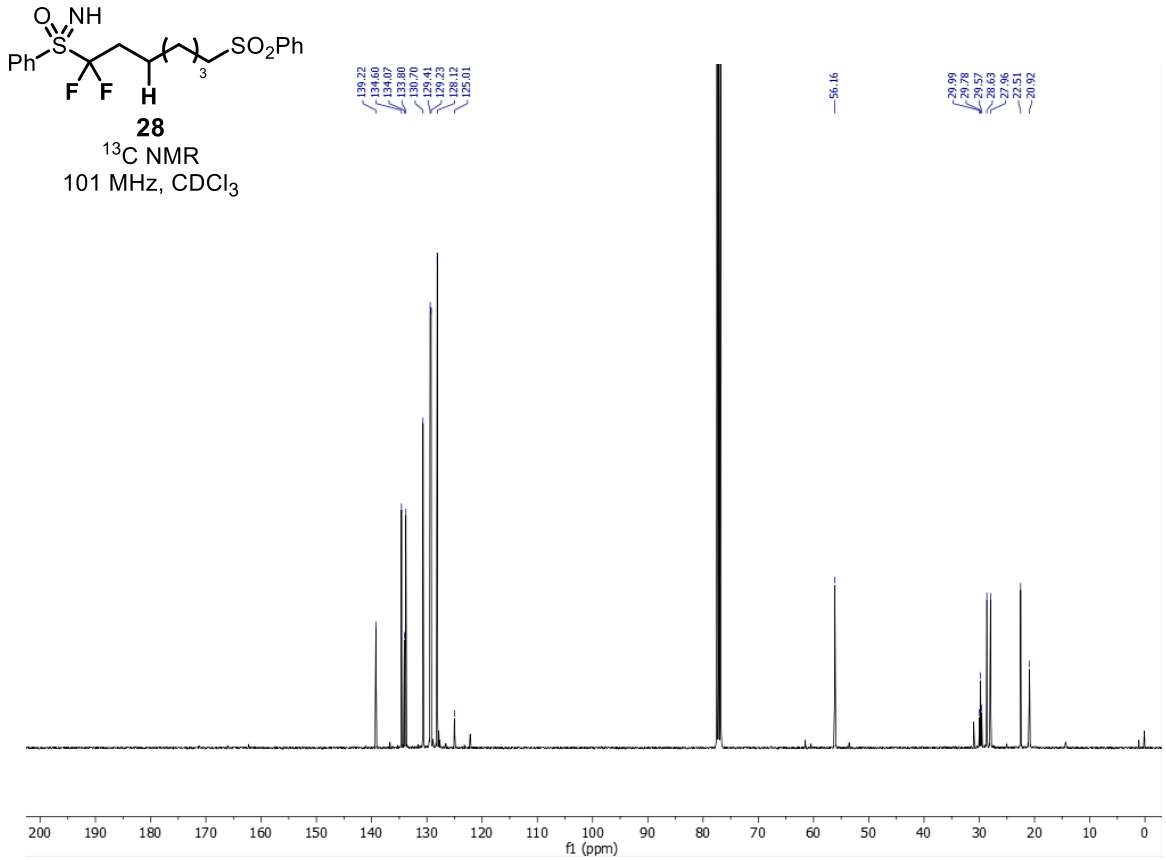


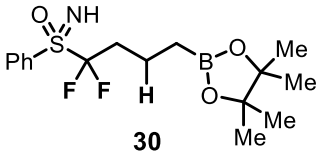
28

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$

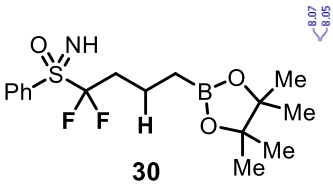

O
NH
S
Ph
F
F
H
3
SO2Ph
28
1H NMR
400 MHz, CDCl3
f1 (ppm)


O
NH
S
Ph
F
F
H
3
SO2Ph
28
13C NMR
101 MHz, CDCl3
f1 (ppm)



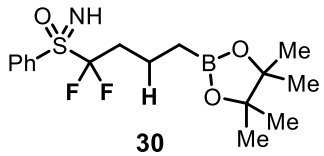
30

^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



30

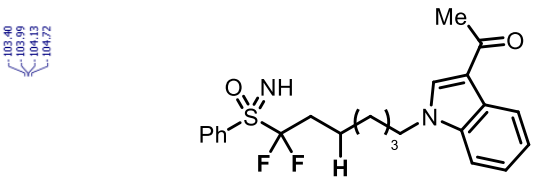
^{1}H NMR
400 MHz, $CDCl_3$



30

^{13}C NMR

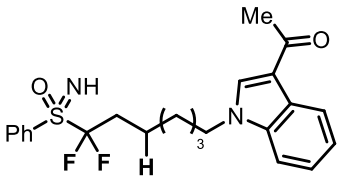
101 MHz, $CDCl_3$



32

^{19}F NMR {^{1}H}

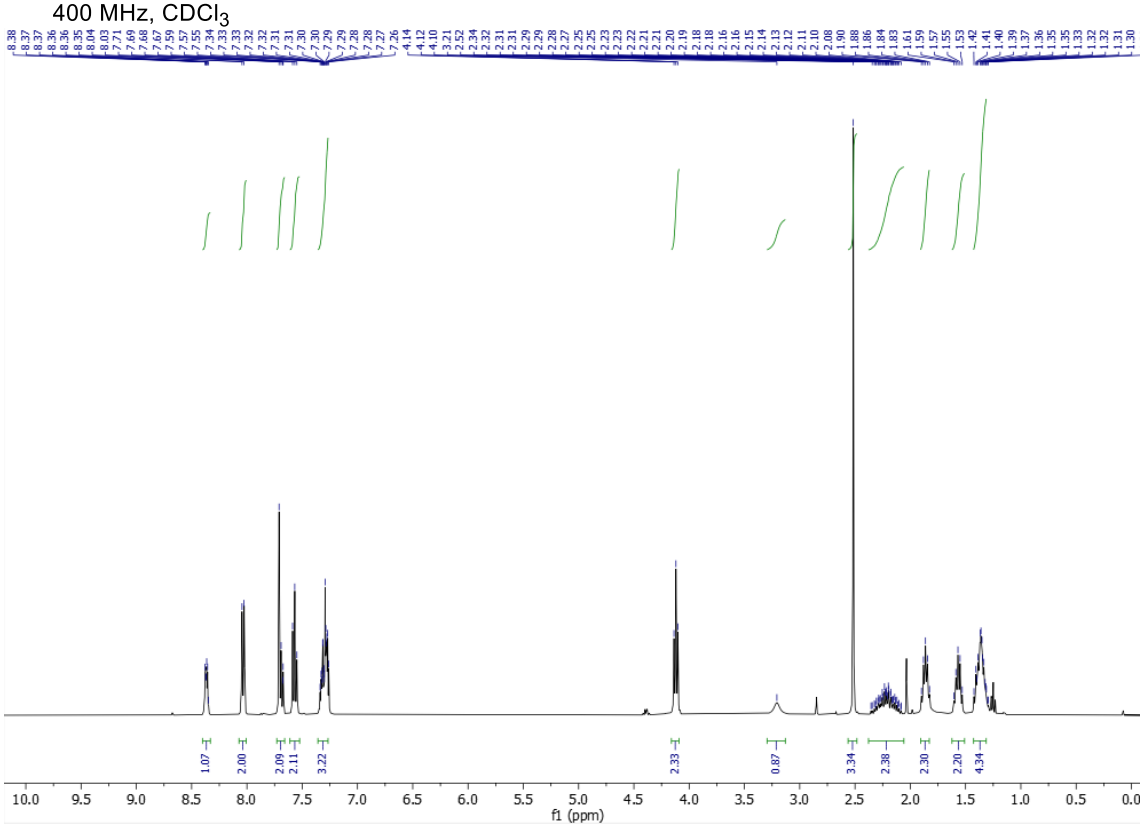
377 MHz, $CDCl_3$

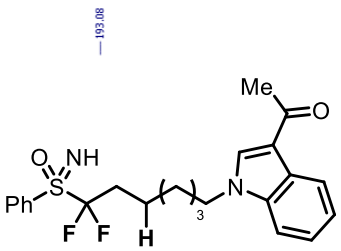


32

^{1}H NMR

400 MHz, $CDCl_3$

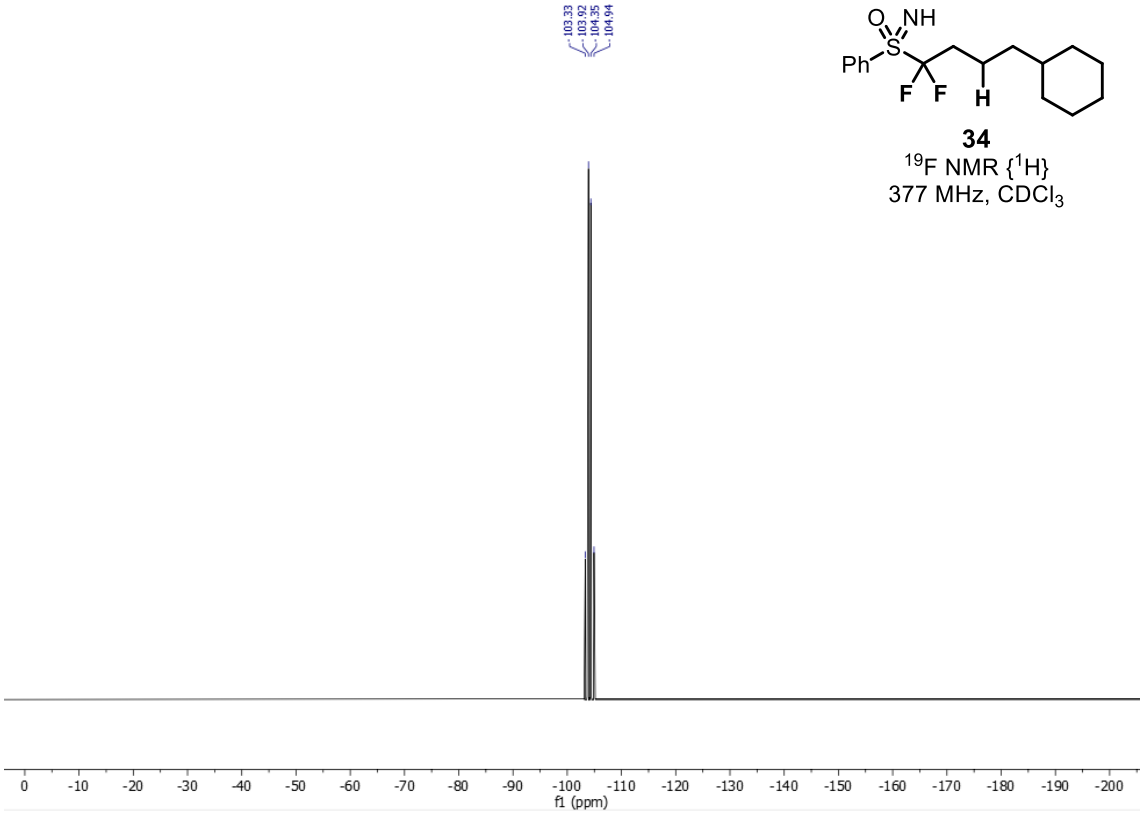




32

^{13}C NMR

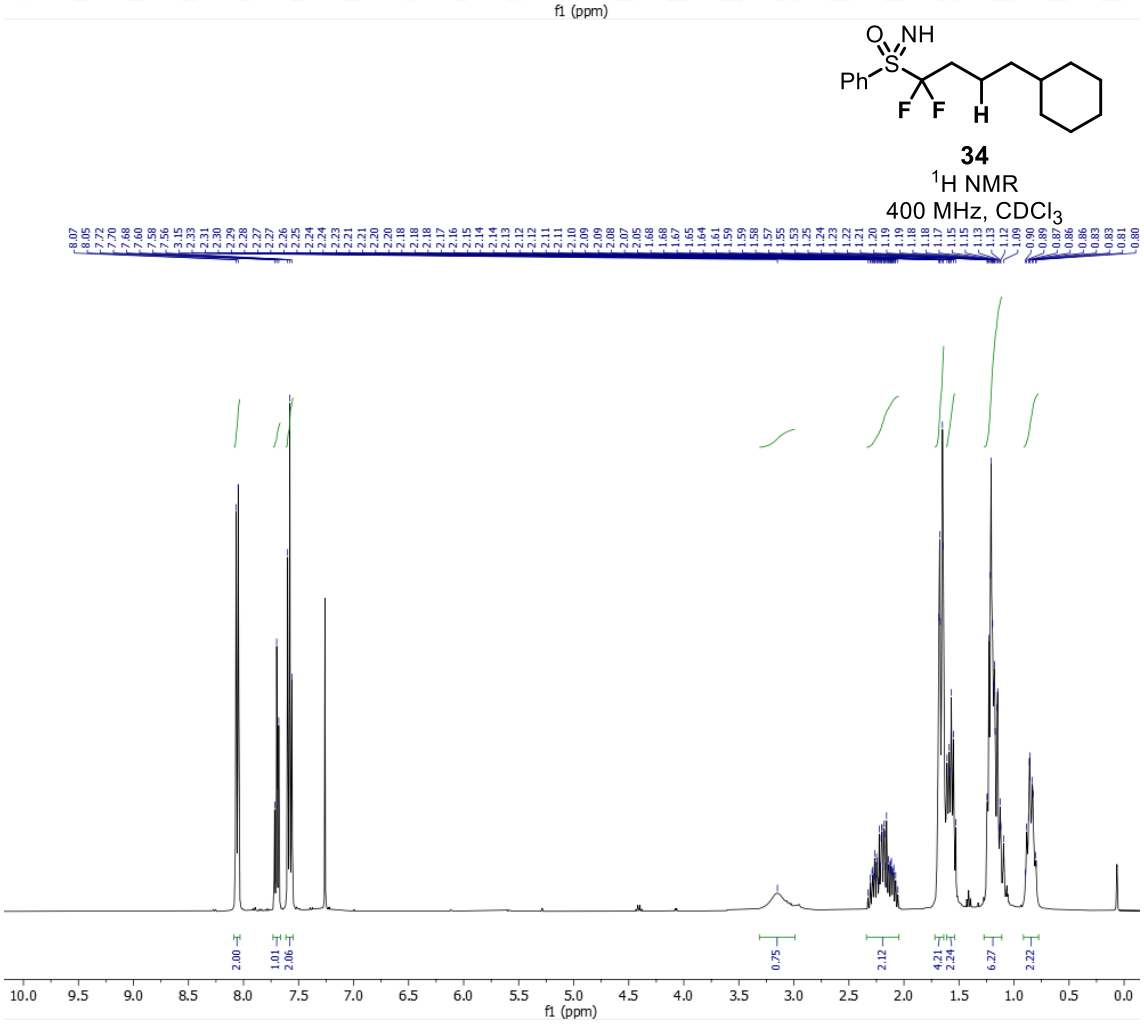
101 MHz, $CDCl_3$



34

^{19}F NMR {^{1}H}

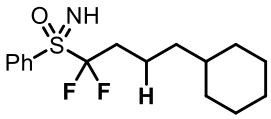
377 MHz, $CDCl_3$



34

^{1}H NMR

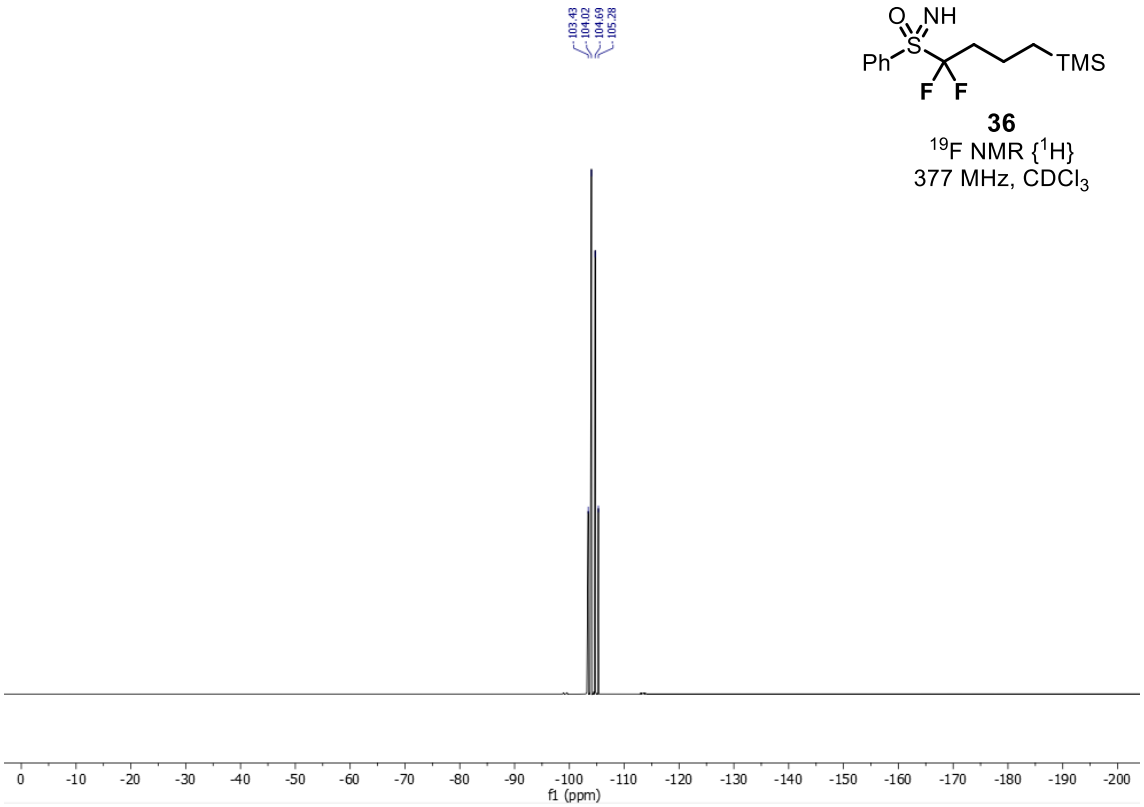
400 MHz, $CDCl_3$



34

^{13}C NMR

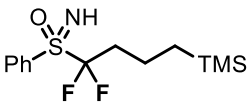
101 MHz, $CDCl_3$



36

^{19}F NMR $\{^{1}H\}$

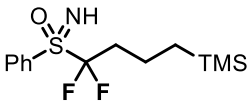
377 MHz, $CDCl_3$



36

^{1}H NMR

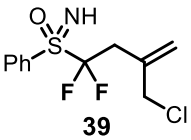
400 MHz, $CDCl_3$



36

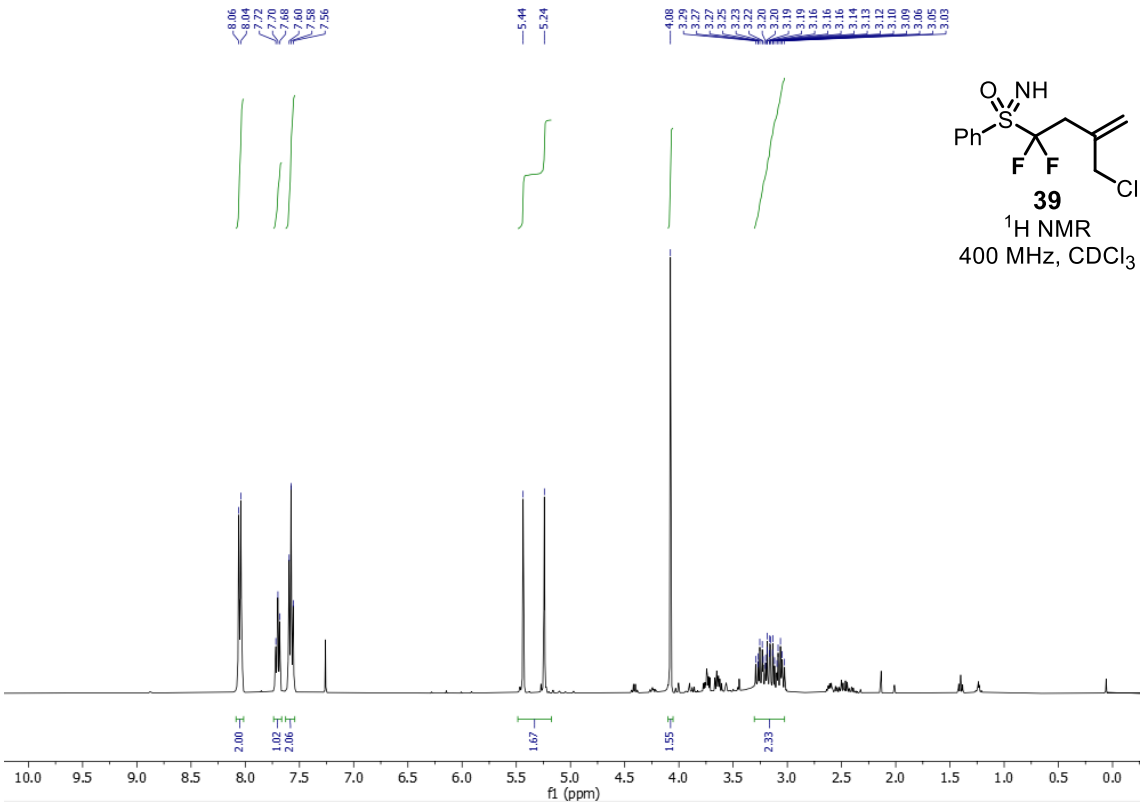
^{13}C NMR

101 MHz, $CDCl_3$



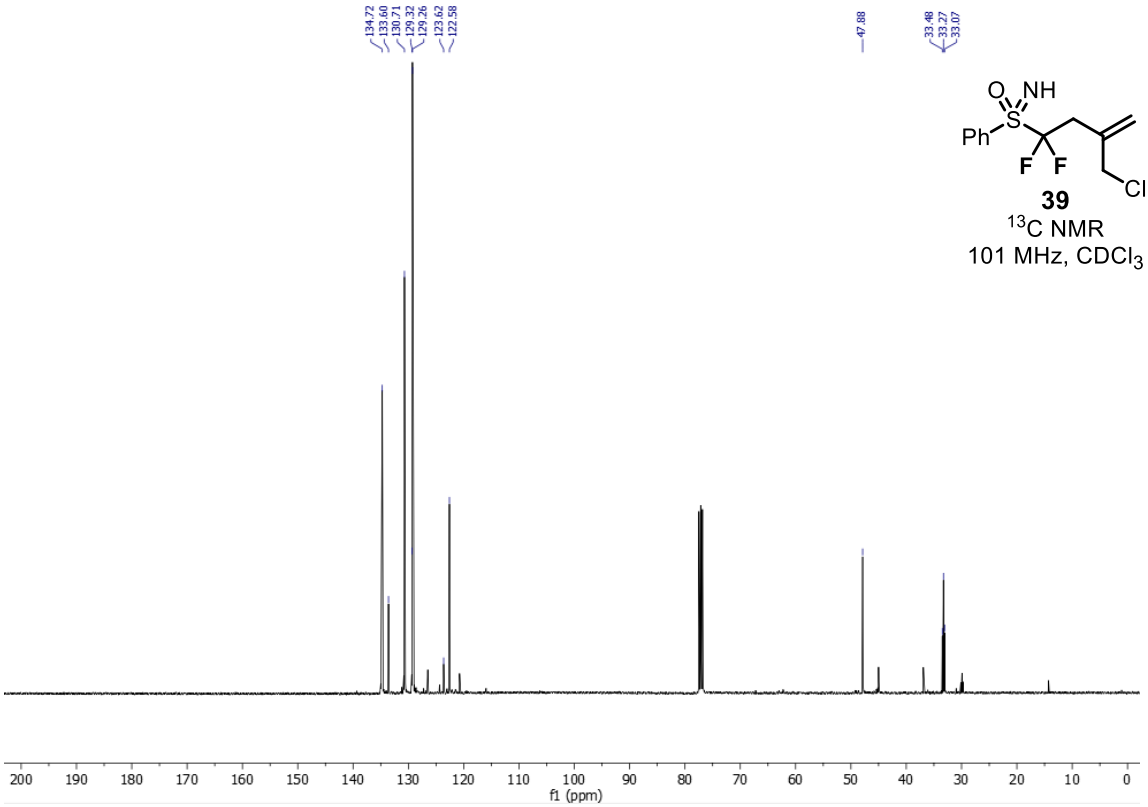
39

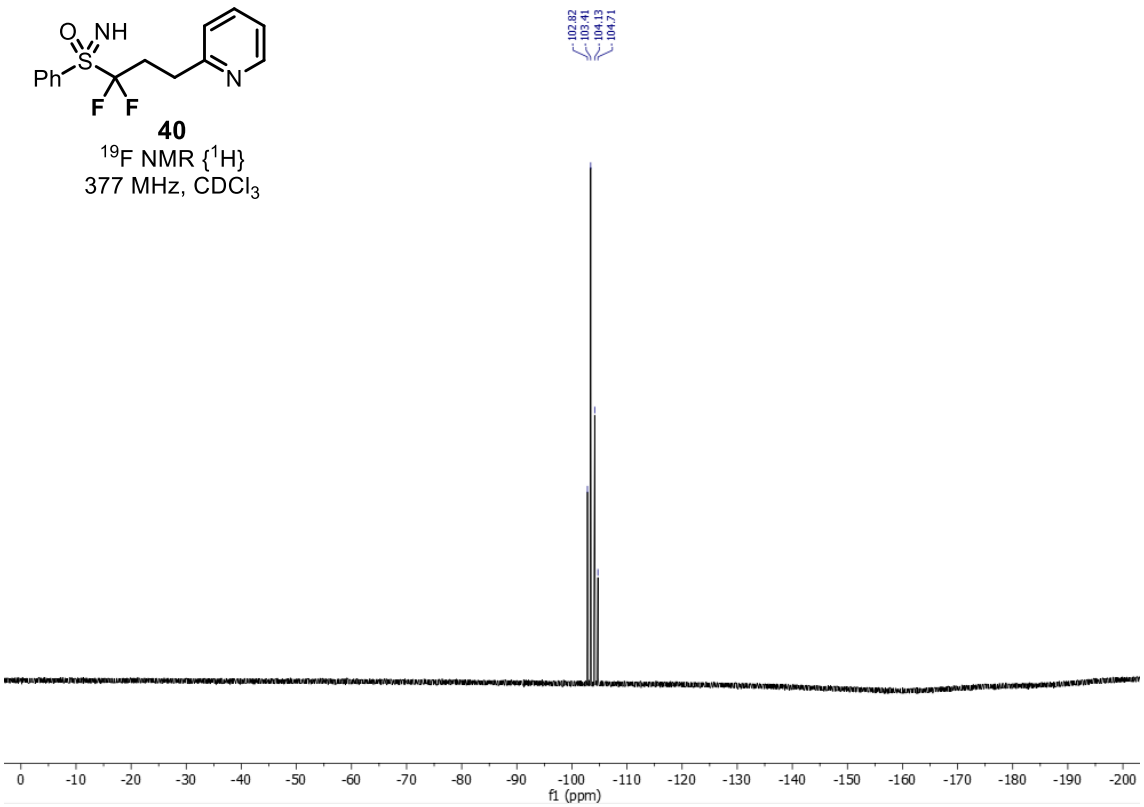
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$

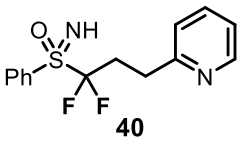


39

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


134.72
133.60
130.71
129.32
129.26
123.62
122.58
47.88
33.48
33.27
33.07
O NH
Ph S
F F
Cl
39
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

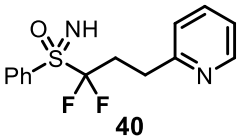

O NH
Ph S
F F
N
40
19F NMR {1H}
377 MHz, CDCl3
102.82
103.41
104.13
104.71
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



40

^{1}H NMR

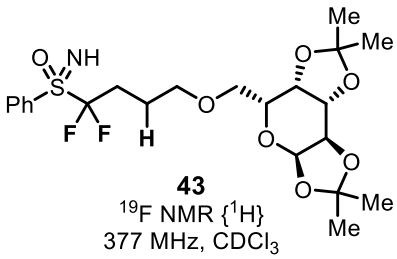
600 MHz, $CDCl_3$



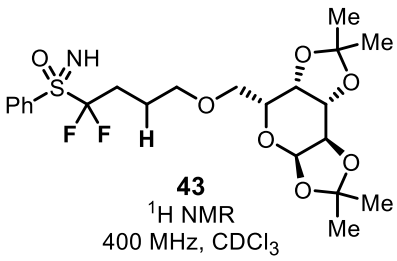
40

^{13}C NMR

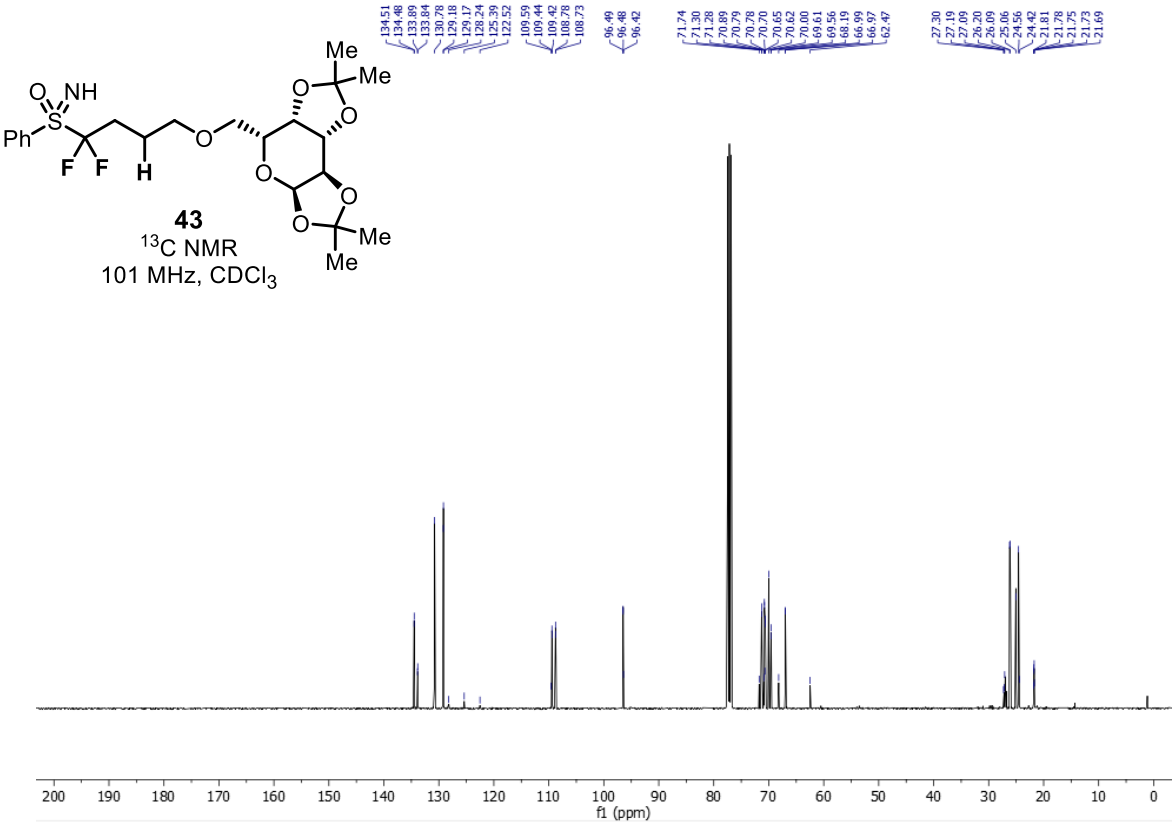
151 MHz, $CDCl_3$



43
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



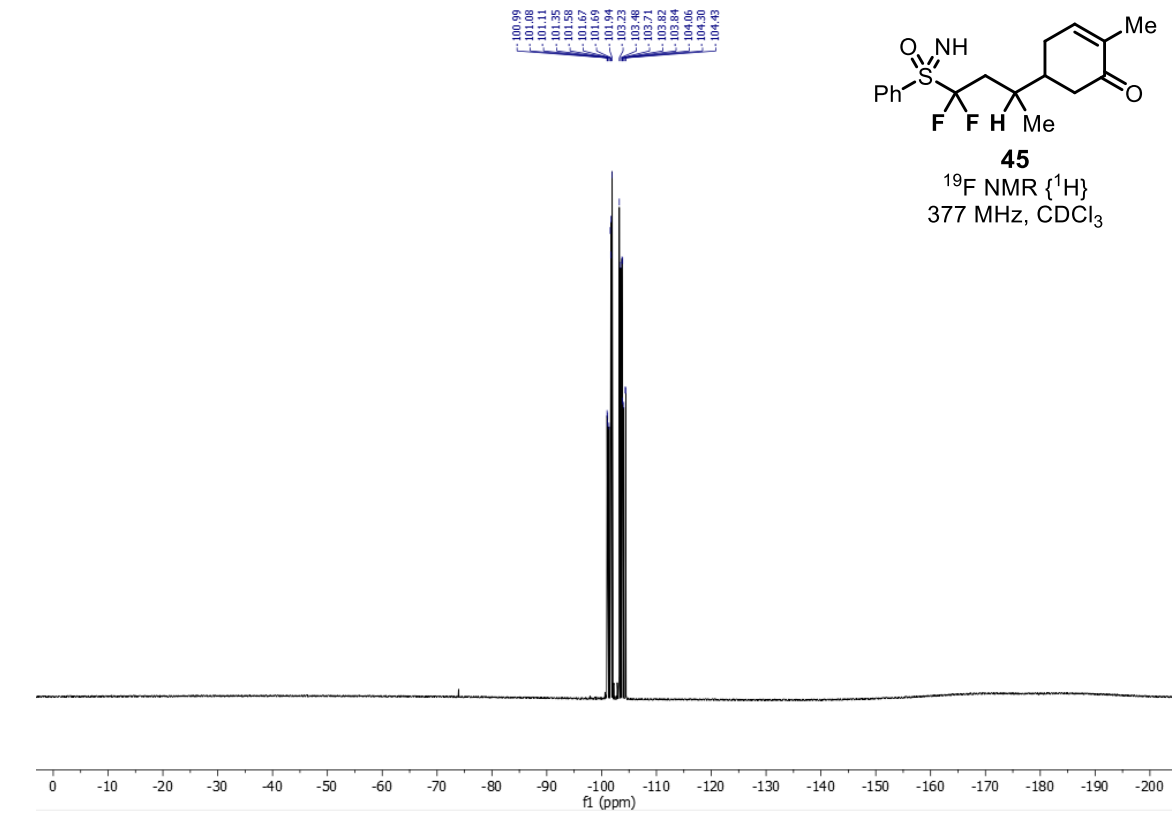
43
^{1}H NMR
400 MHz, $CDCl_3$



43

^{13}C NMR

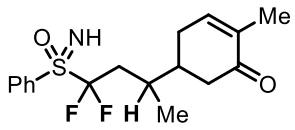
101 MHz, $CDCl_3$



45

^{19}F NMR {^{1}H}

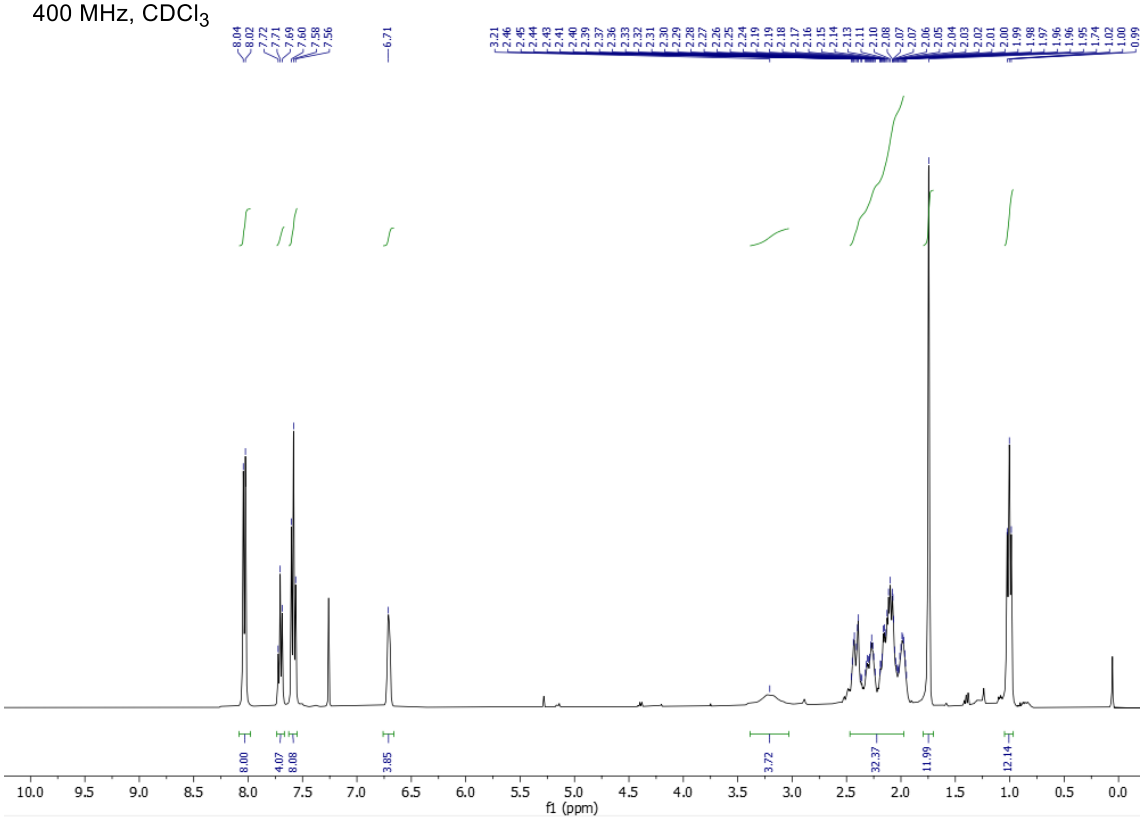
377 MHz, $CDCl_3$

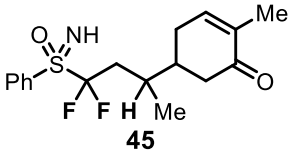


45

^{1}H NMR

400 MHz, $CDCl_3$

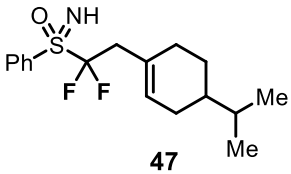




45

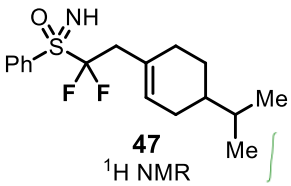
^{13}C NMR

101 MHz, $CDCl_3$



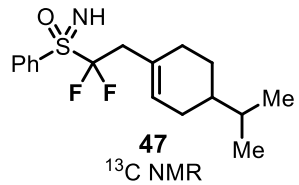
47

^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



47

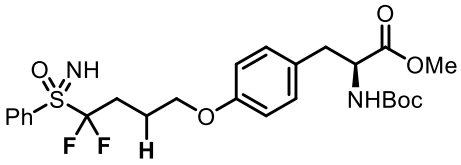
^{1}H NMR
400 MHz, $CDCl_3$



47

^{13}C NMR

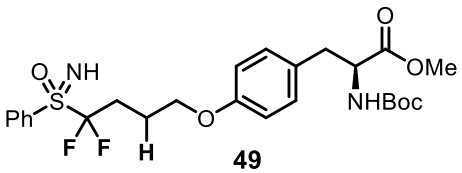
101 MHz, $CDCl_3$



49

^{19}F NMR {^{1}H}

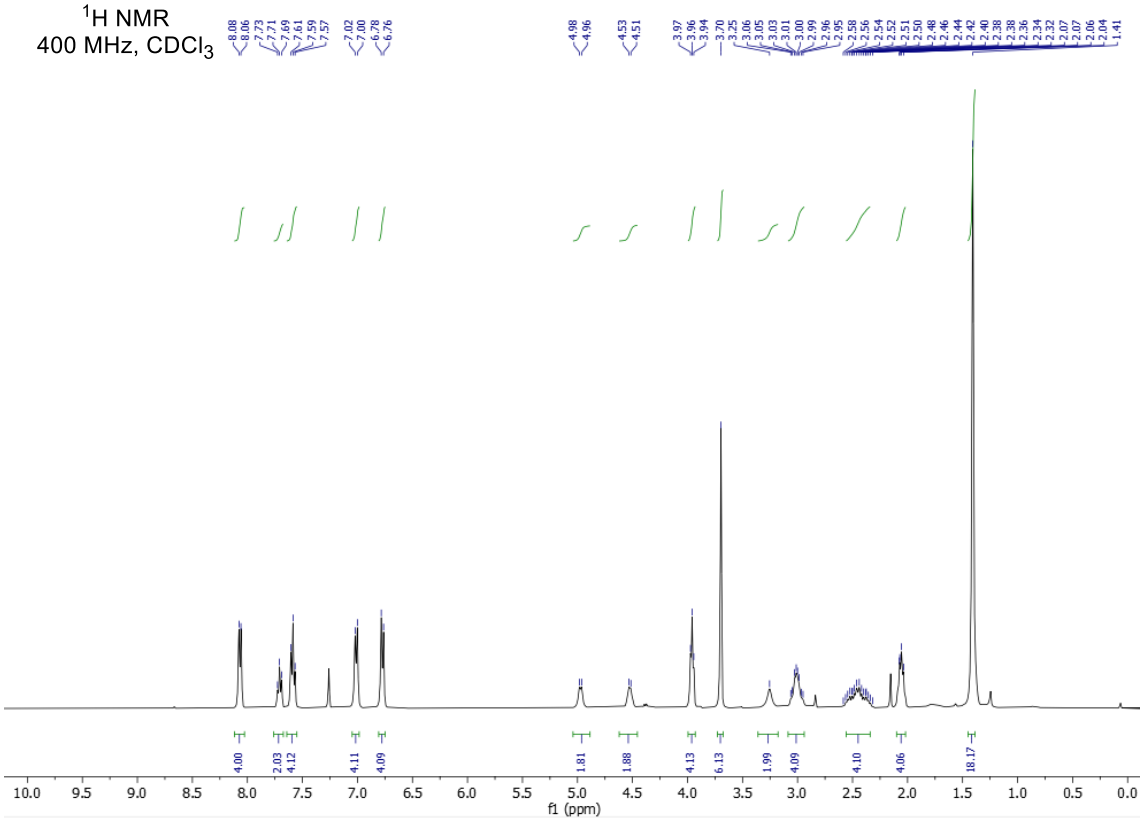
377 MHz, $CDCl_3$

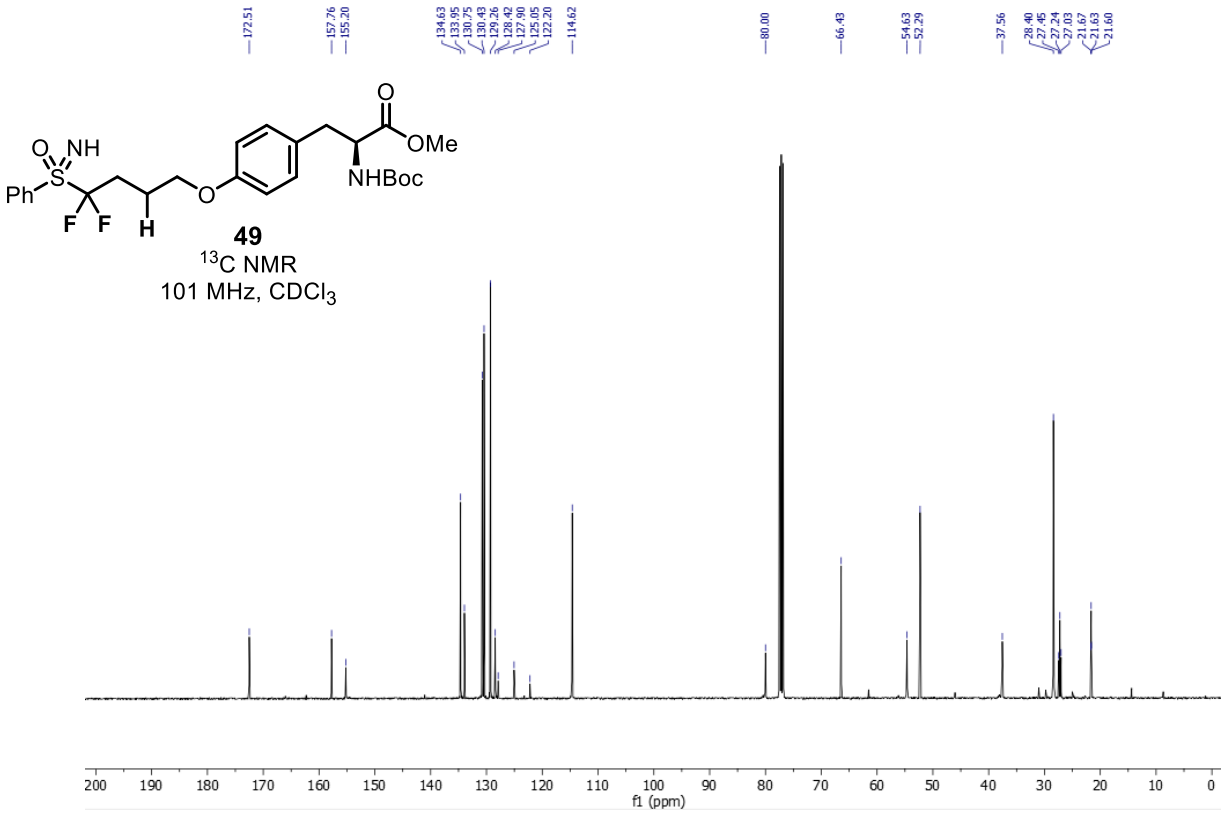


49

^{1}H NMR

400 MHz, $CDCl_3$

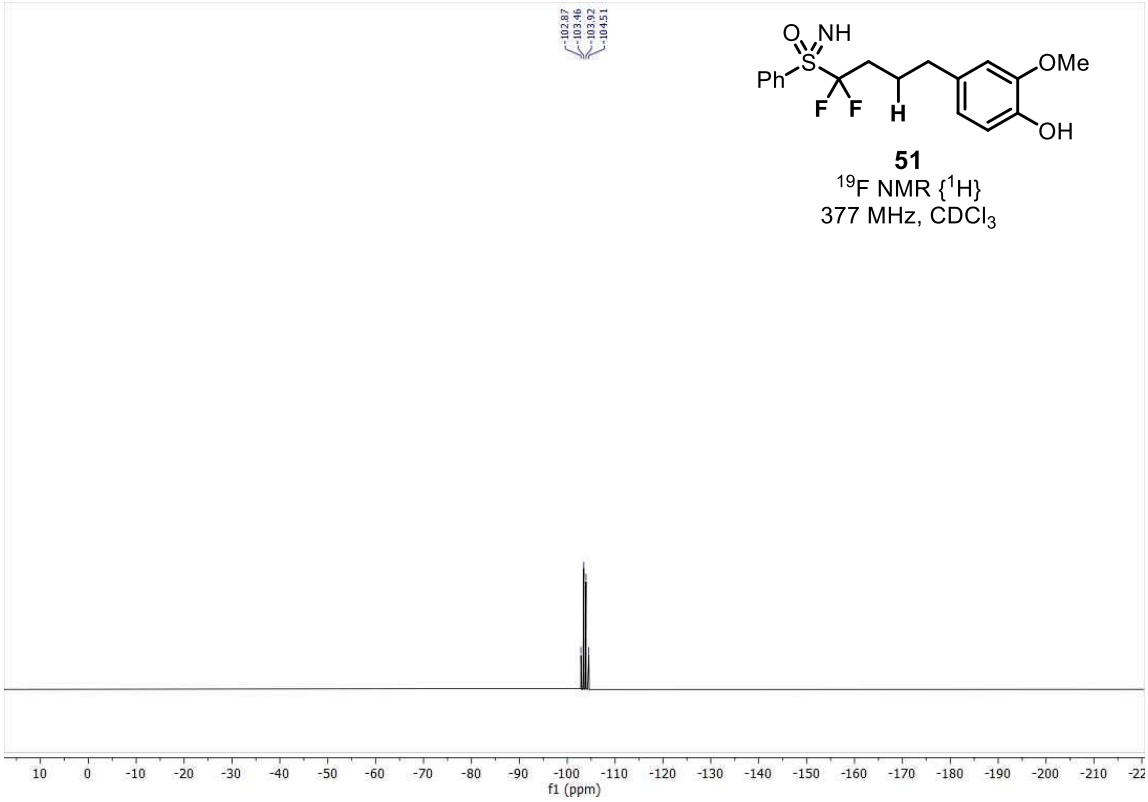




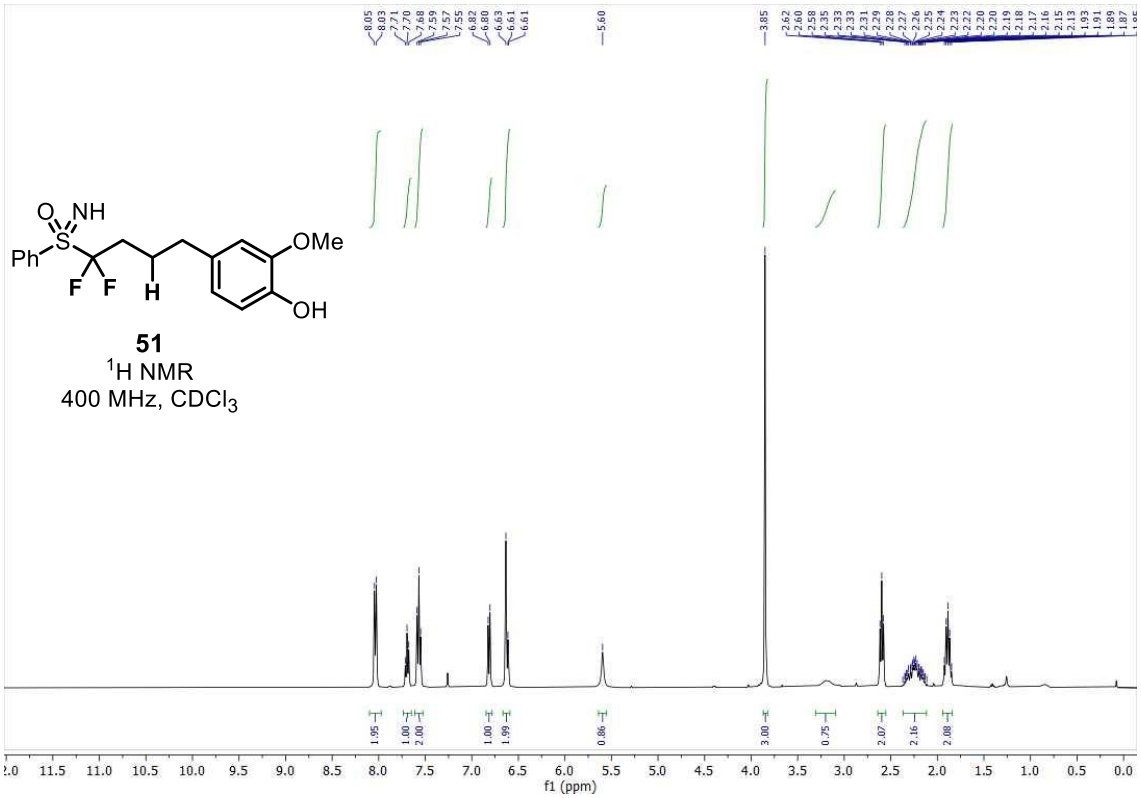
49

^{13}C NMR

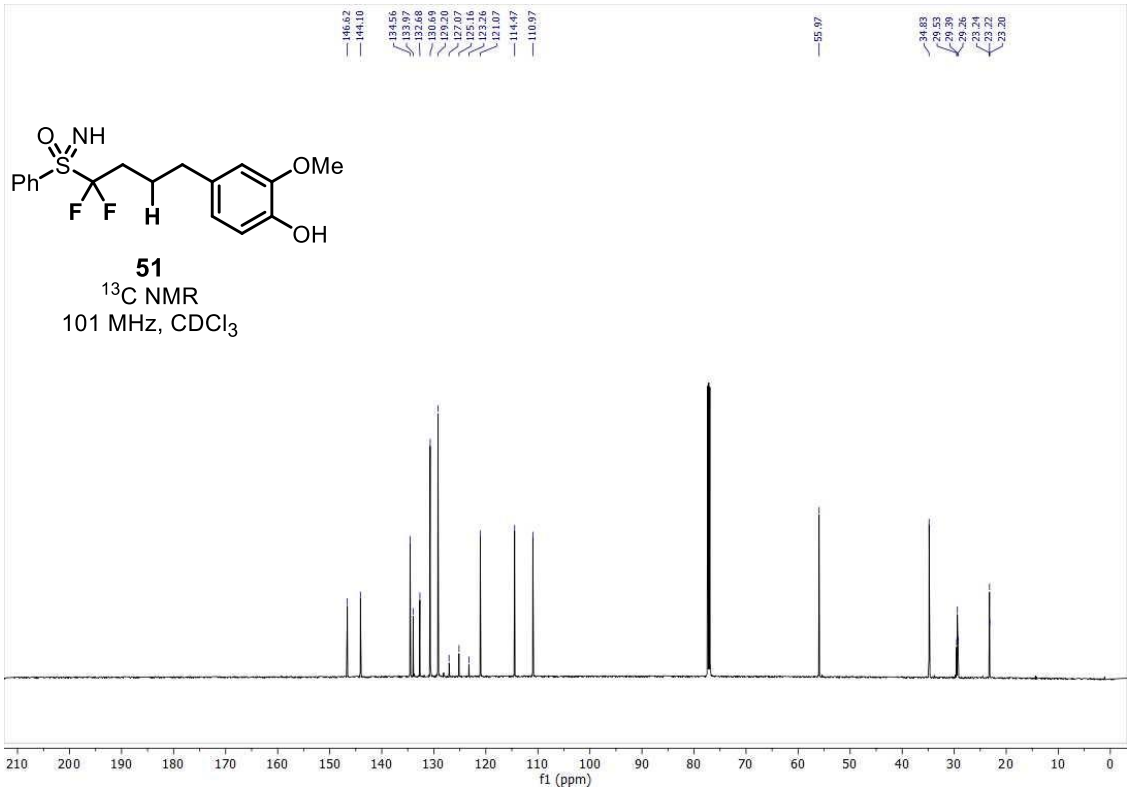
101 MHz, $CDCl_3$



51
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



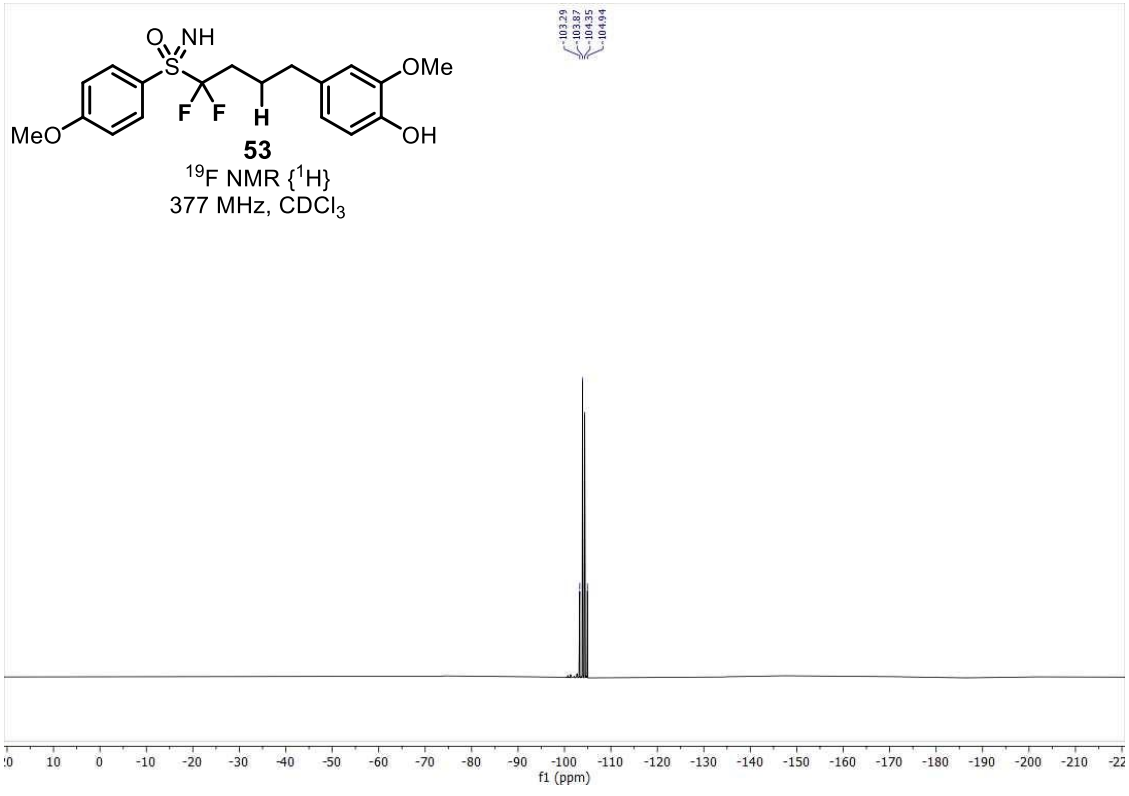
51
^{1}H NMR
400 MHz, $CDCl_3$



51

^{13}C NMR

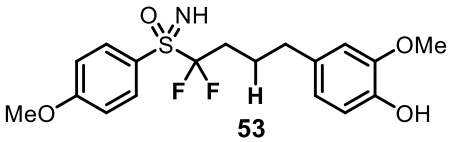
101 MHz, $CDCl_3$



53

^{19}F NMR $\{^{1}H\}$

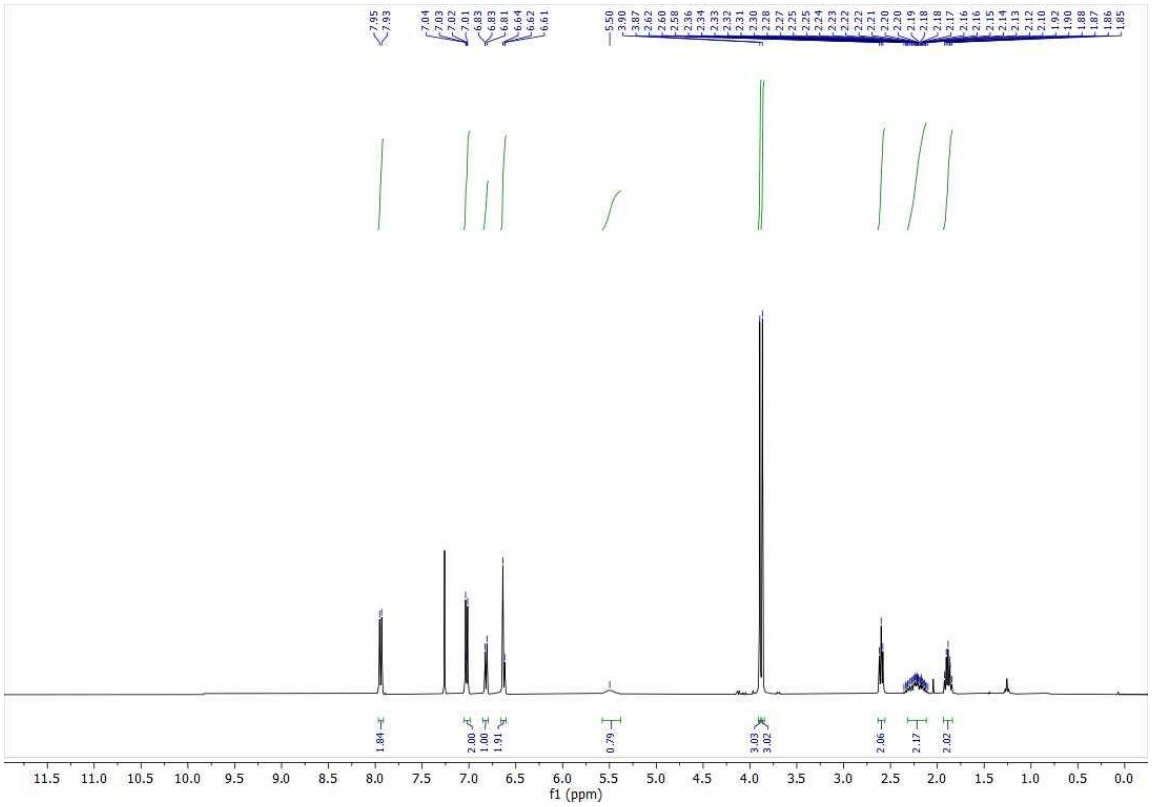
377 MHz, $CDCl_3$

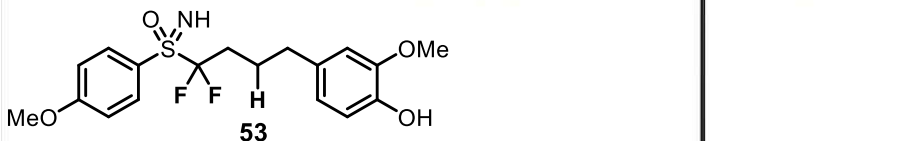


53

^{1}H NMR

400 MHz, $CDCl_3$

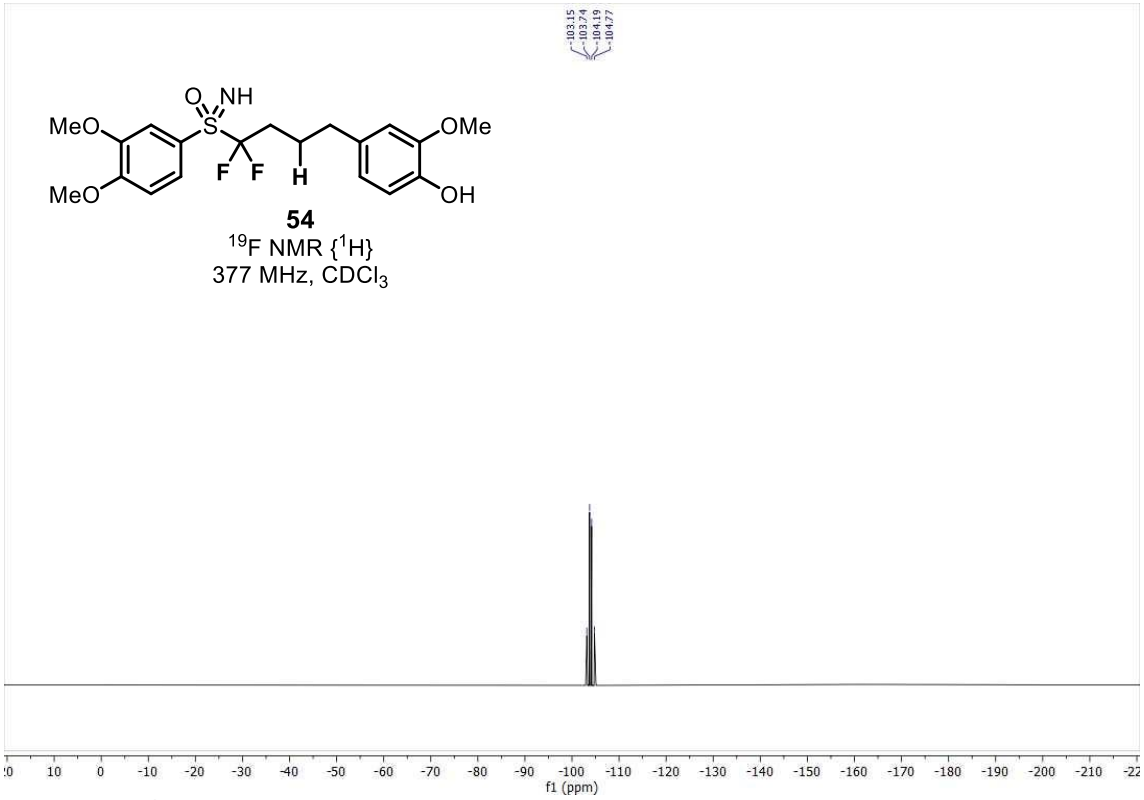




53

^{13}C NMR

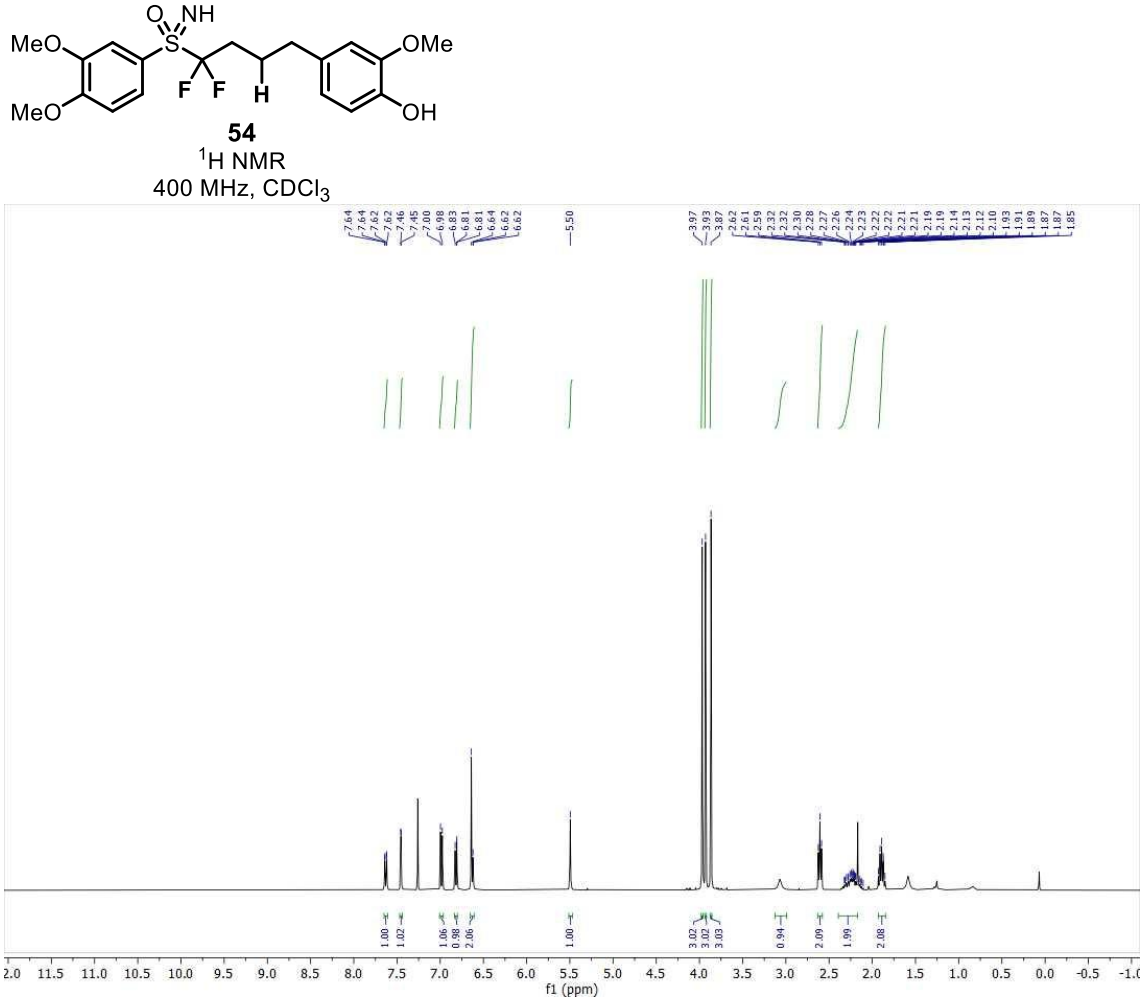
101 MHz, $CDCl_3$



54

^{19}F NMR {^{1}H}

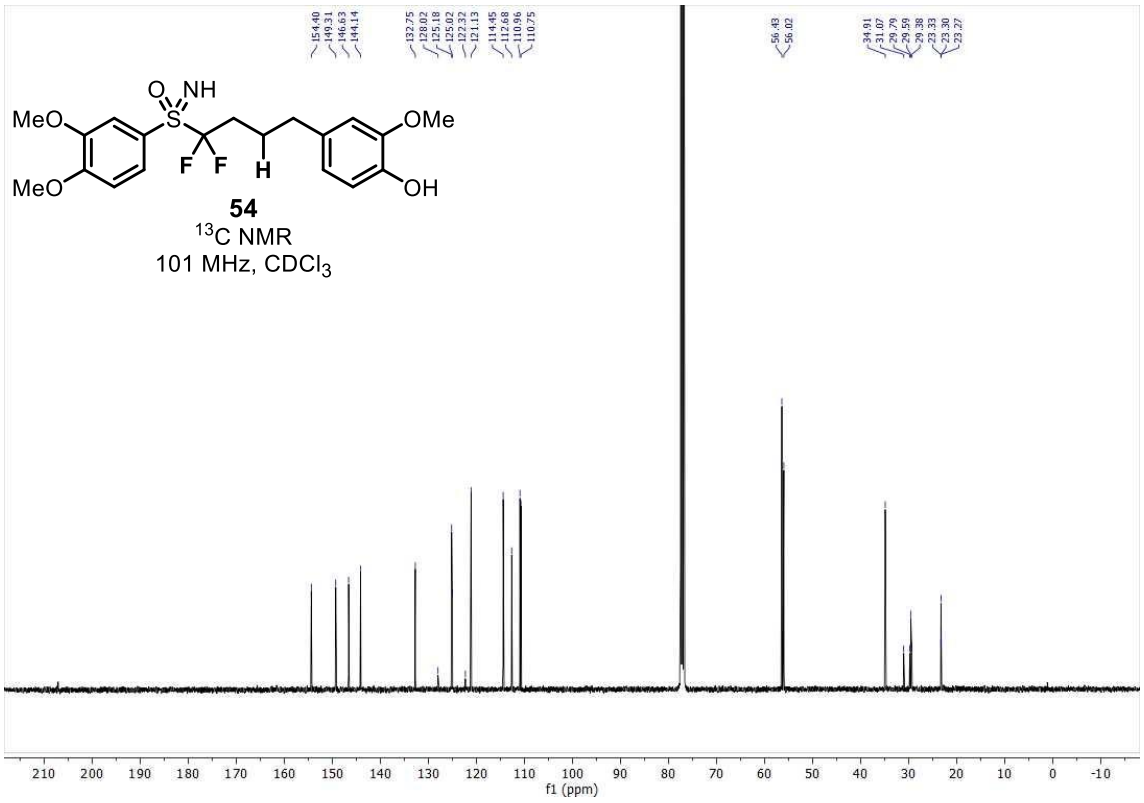
377 MHz, $CDCl_3$



54

^{1}H NMR

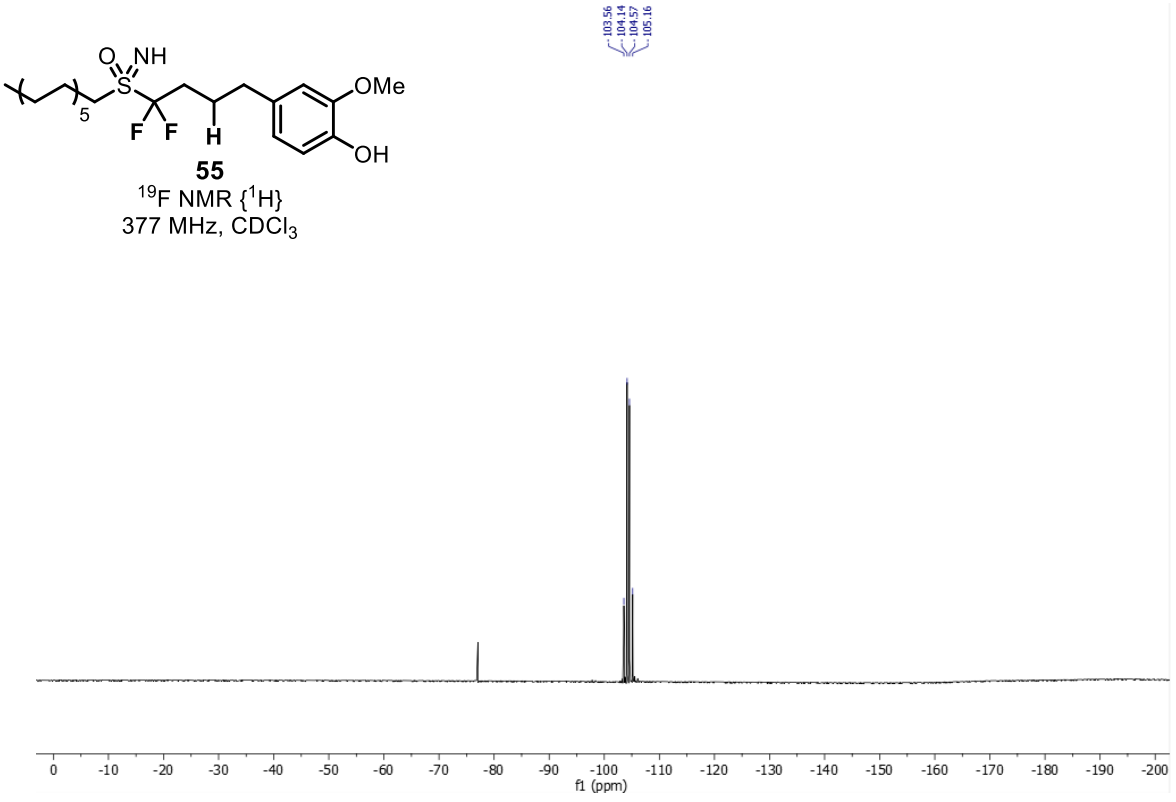
400 MHz, $CDCl_3$



54

^{13}C NMR

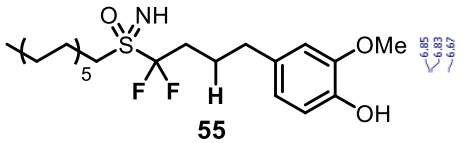
101 MHz, $CDCl_3$



55

^{19}F NMR $\{^{1}H\}$

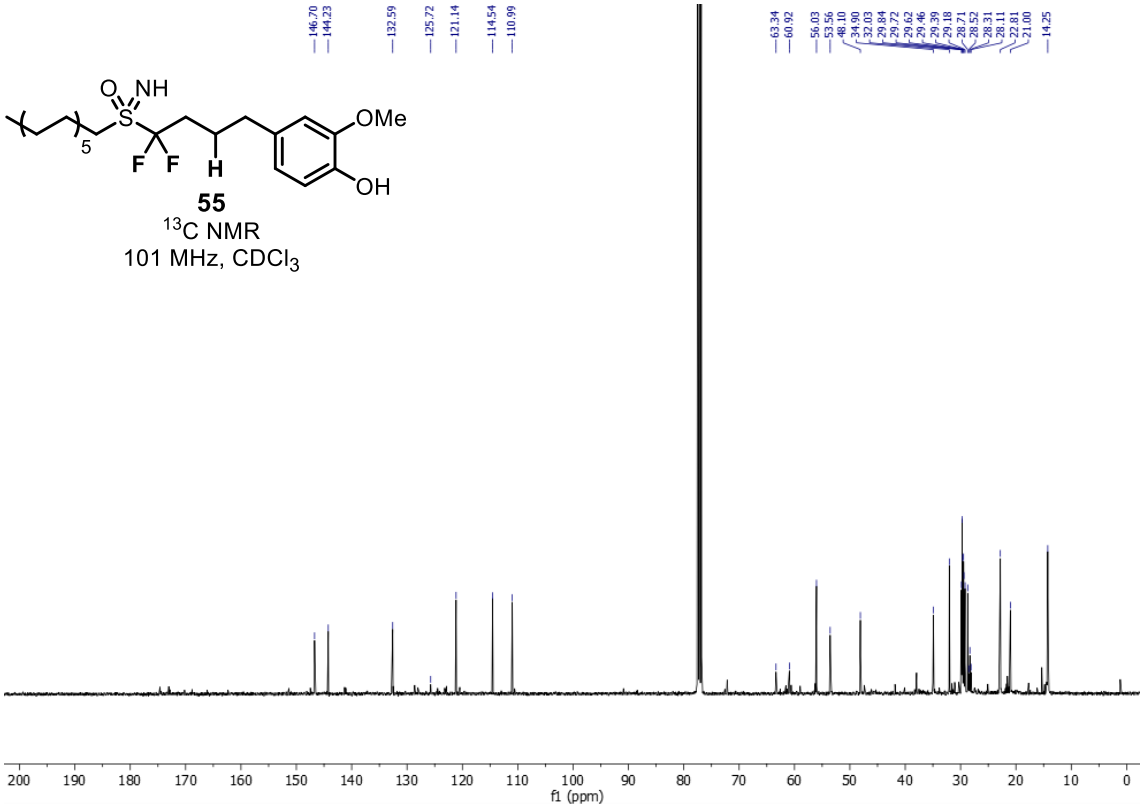
377 MHz, $CDCl_3$



55

^{1}H NMR

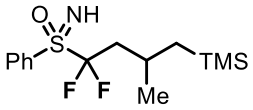
400 MHz, $CDCl_3$



55

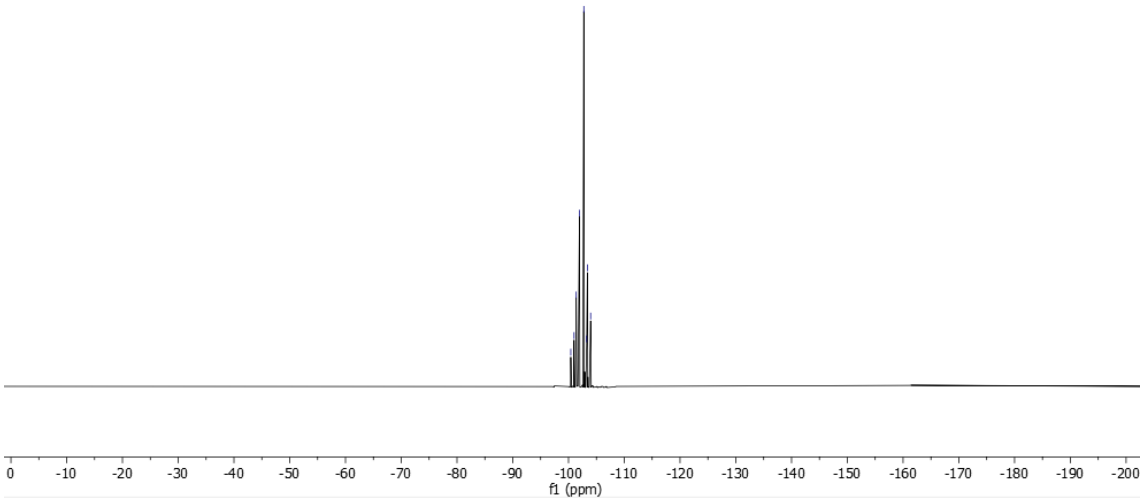
^{13}C NMR

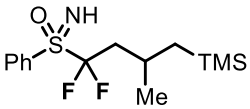
101 MHz, $CDCl_3$



90

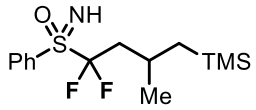
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$





90

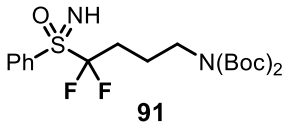
^{1}H NMR
600 MHz, $CDCl_3$



90

^{13}C NMR

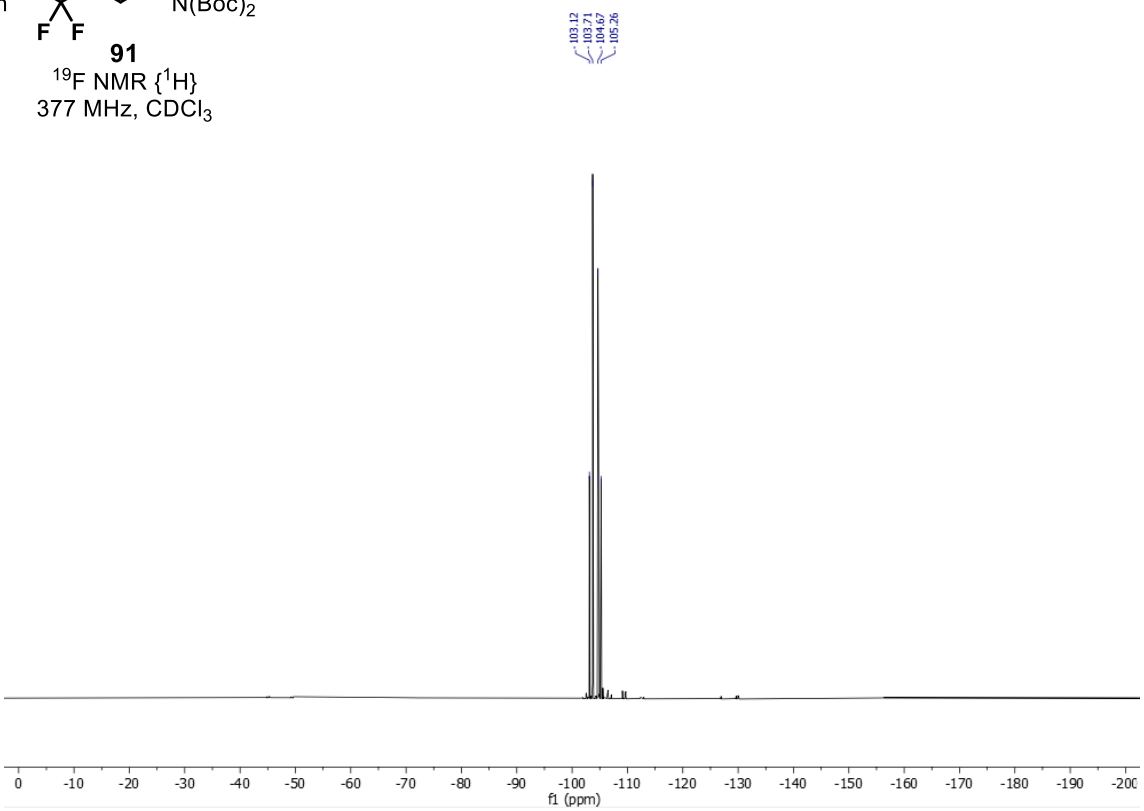
151 MHz, $CDCl_3$

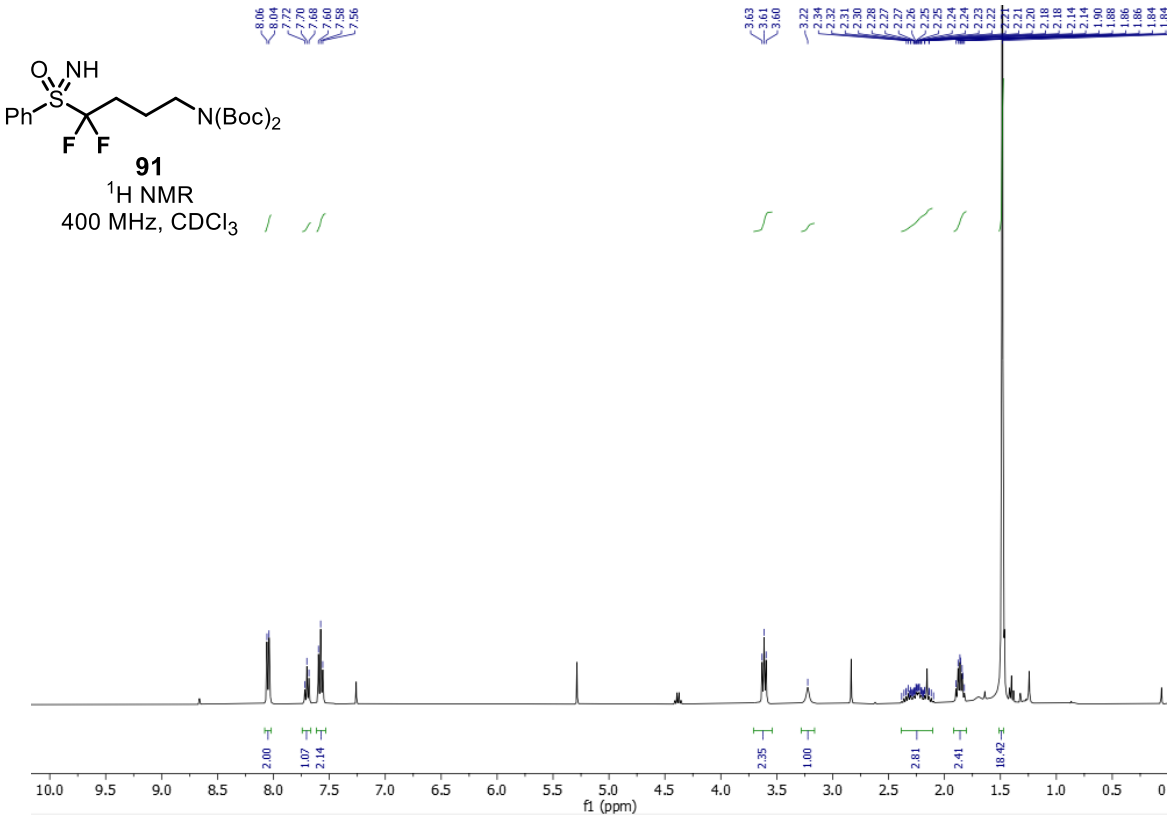


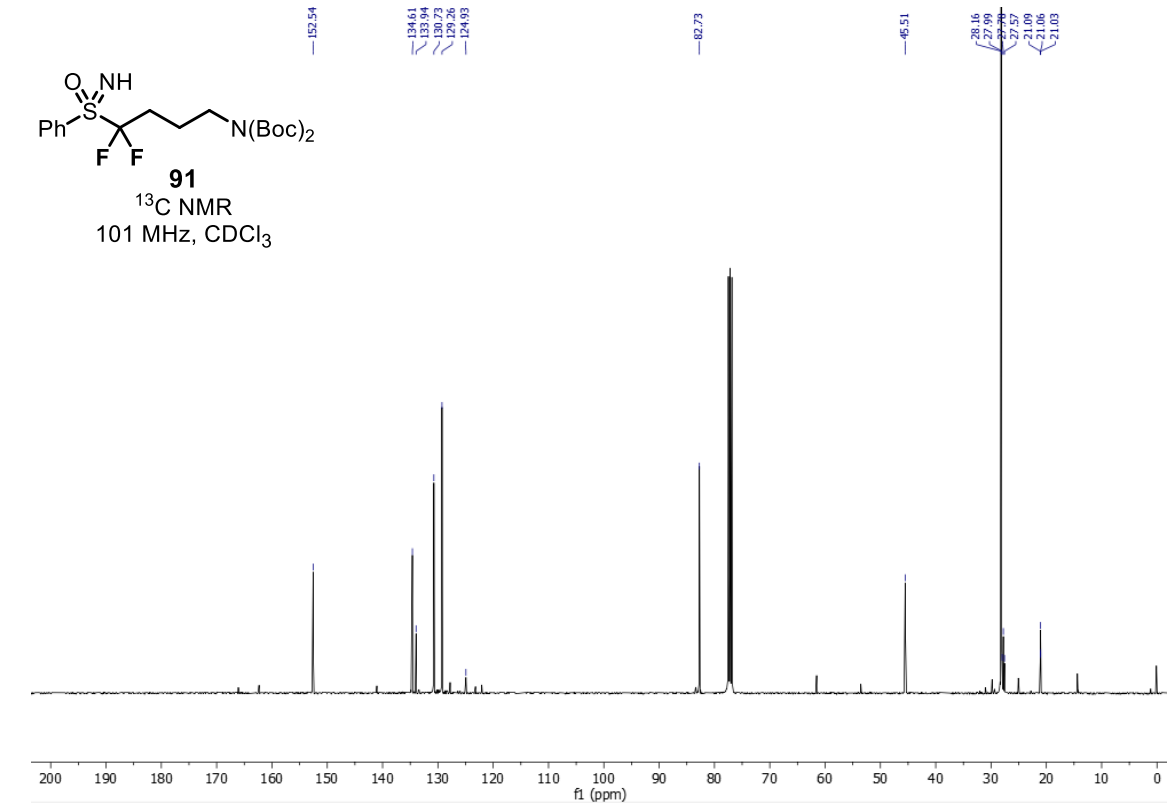
91

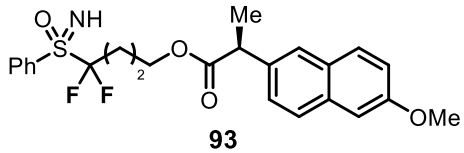
^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$



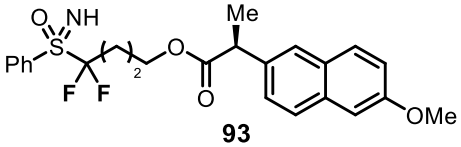

O NH
S
Ph
N(Boc)2
F F
91
1H NMR
400 MHz, CDCl3
f1 (ppm)


O NH
S
Ph
N(Boc)2
F F
91
13C NMR
101 MHz, CDCl3
f1 (ppm)



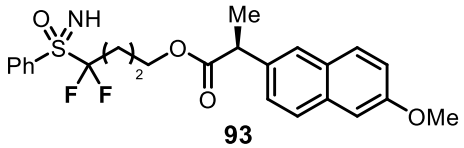
93

^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



93

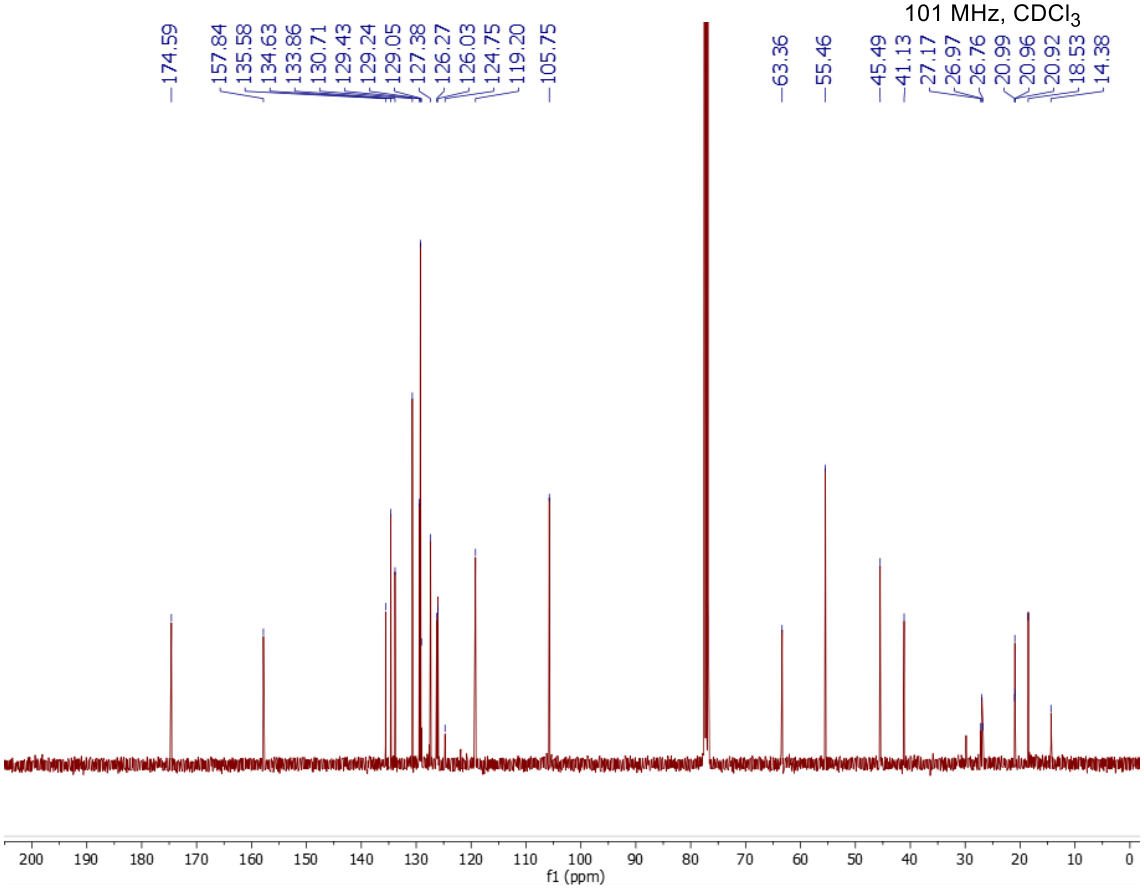
^{1}H NMR
400 MHz, $CDCl_3$

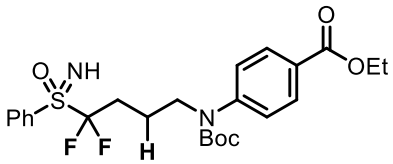


93

^{13}C NMR

101 MHz, $CDCl_3$

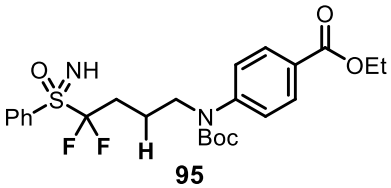




95

^{19}F NMR {^{1}H}

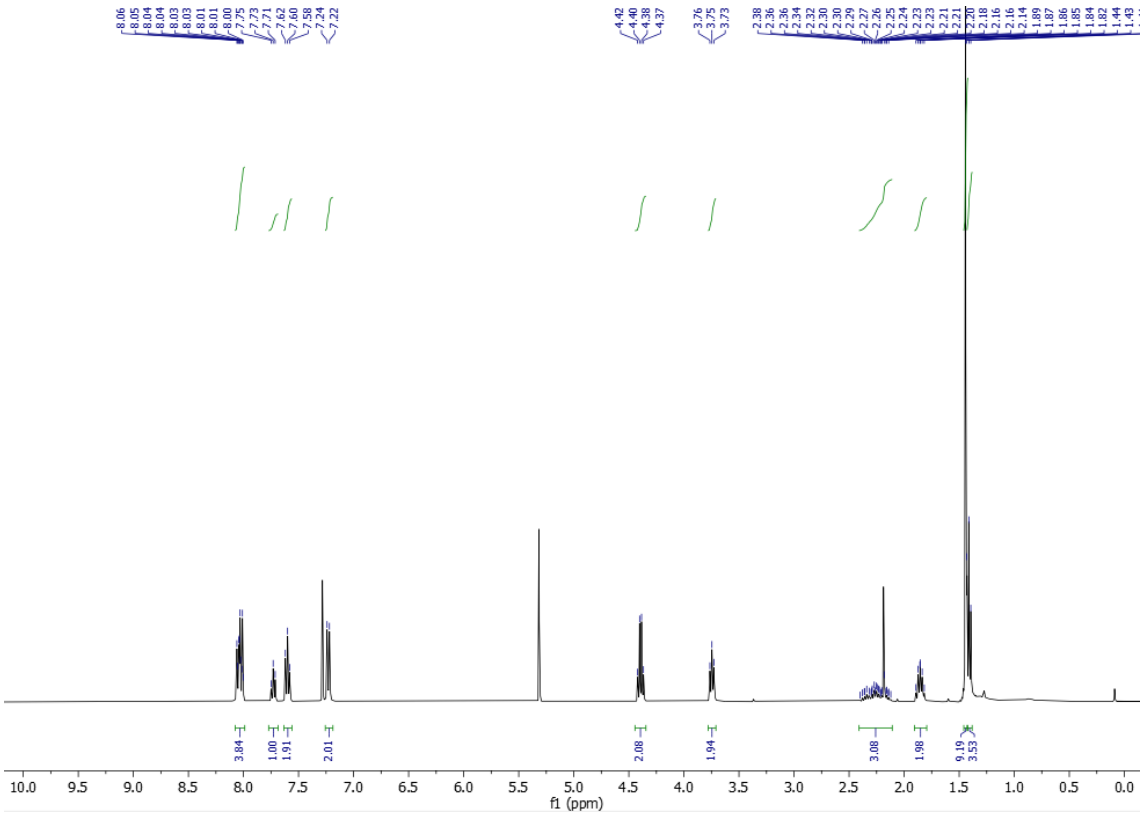
377 MHz, $CDCl_3$

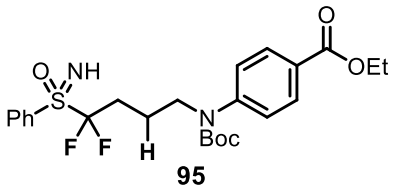


95

^{1}H NMR

400 MHz, $CDCl_3$

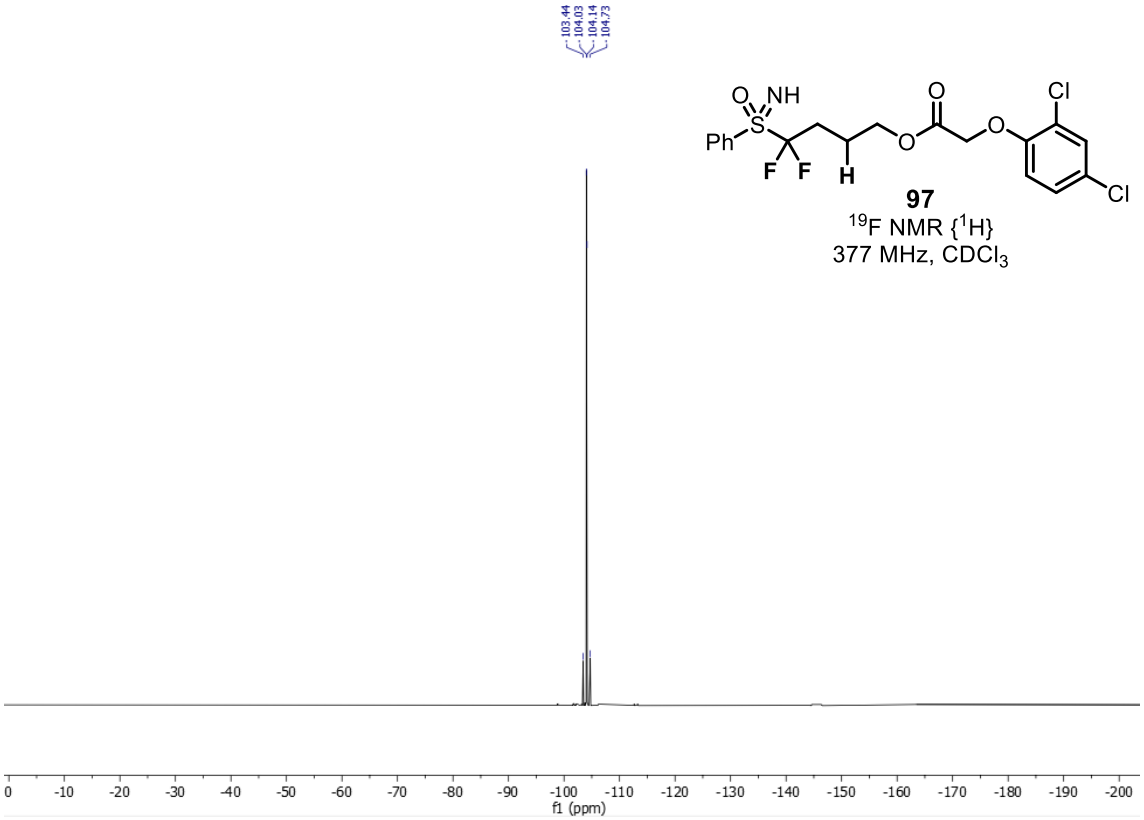


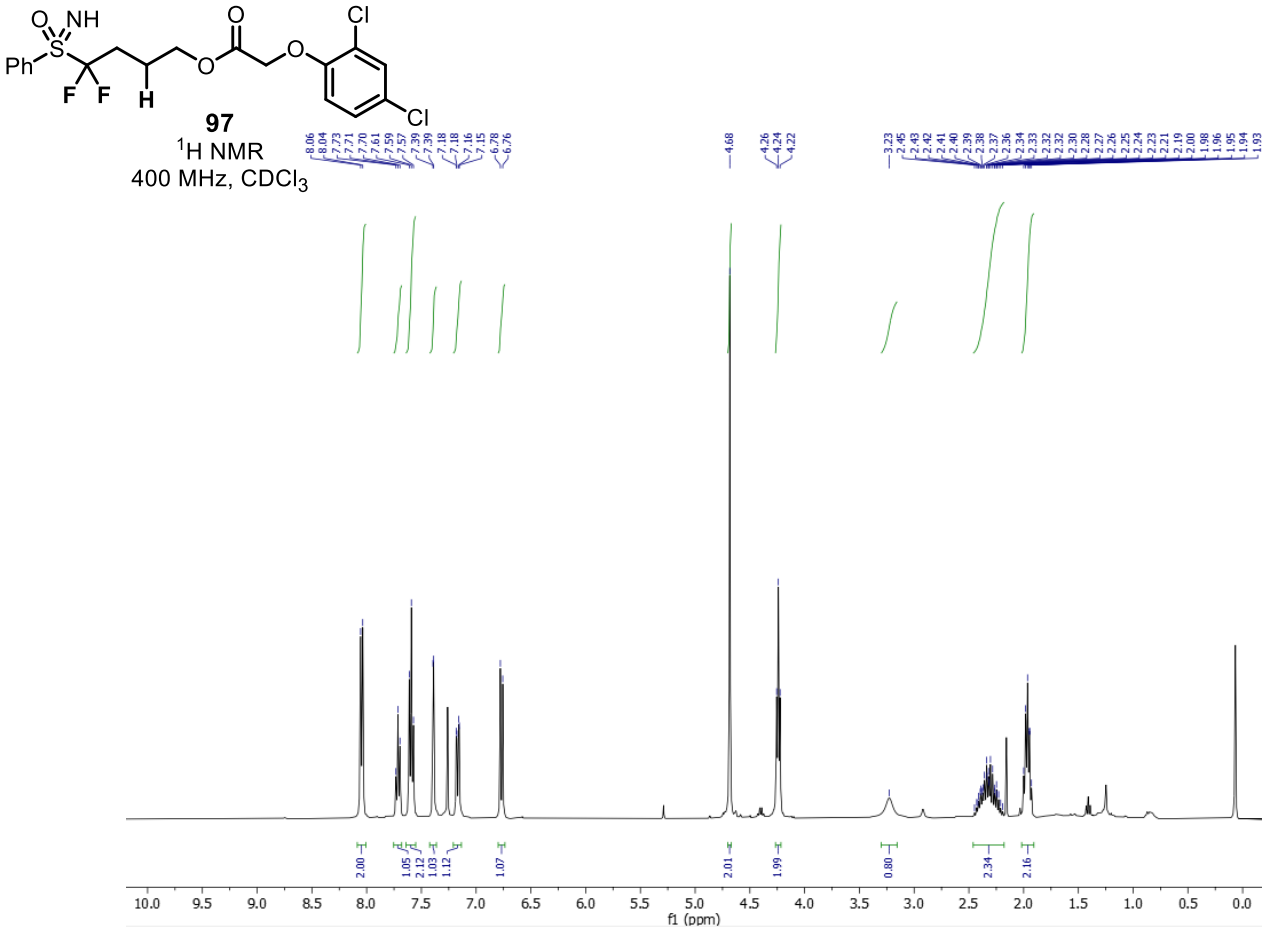


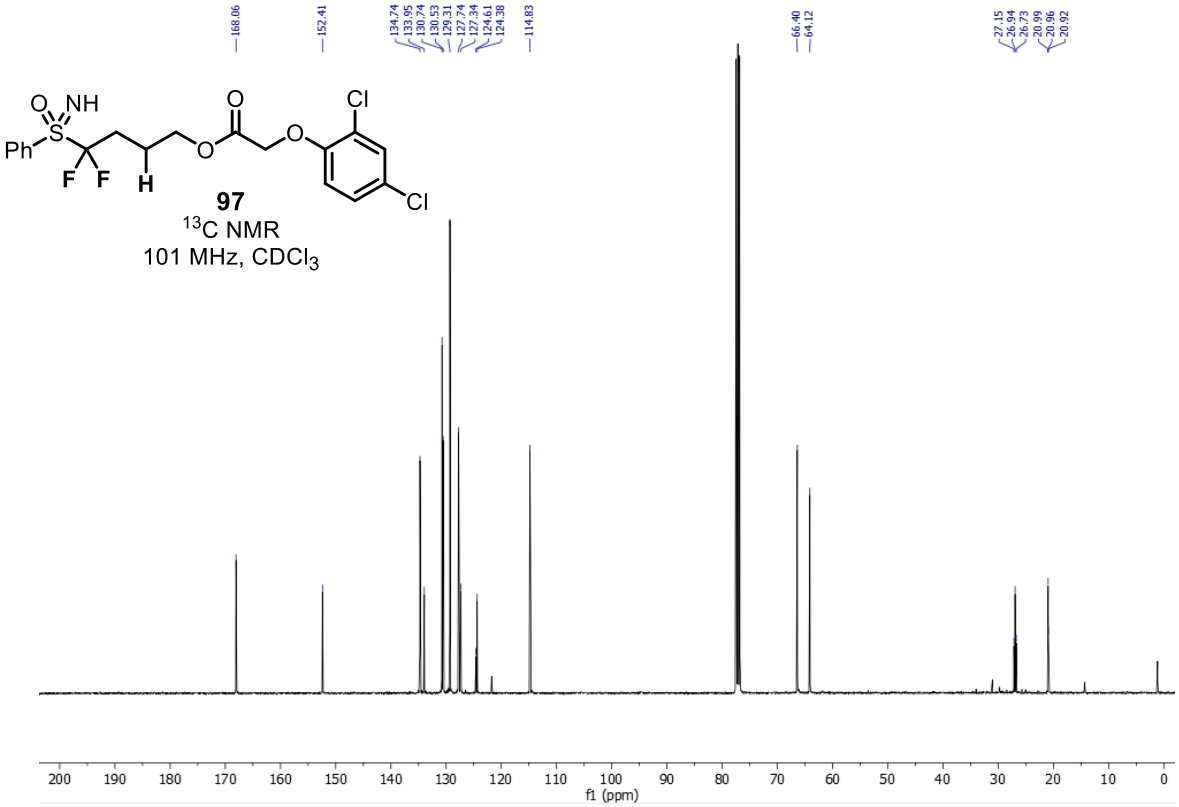
95

^{13}C NMR

101 MHz, $CDCl_3$


103.44
104.03
104.14
104.73
O NH
Ph S
F F
H
O
O
O
Cl
Cl
97
^{19}F NMR {^{1}H}
377 MHz, CDCl$_3$
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

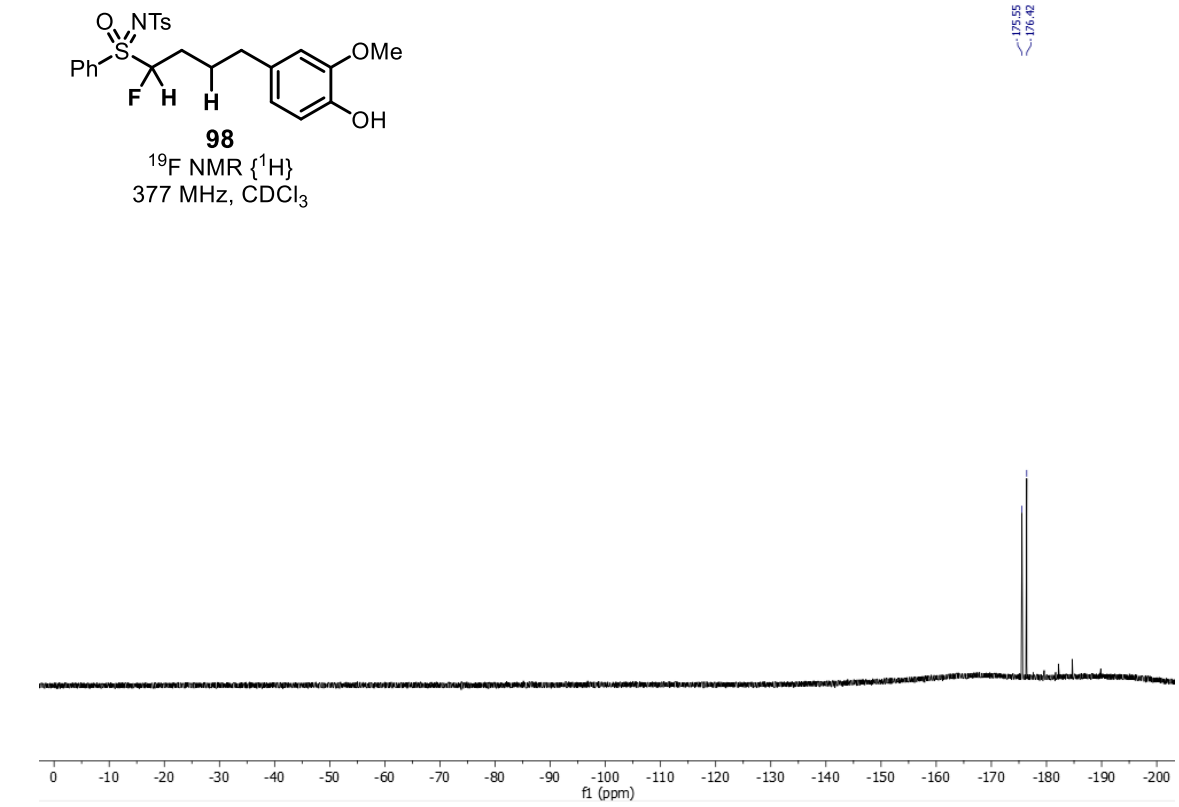

O NH
Ph S
F F
H
O
O
O
Cl
Cl
97
^{1}H NMR
400 MHz, CDCl$_3$
8.06
8.04
7.73
7.71
7.70
7.61
7.59
7.57
7.39
7.39
7.18
7.18
7.16
7.15
6.78
6.76
4.68
4.26
4.24
4.22
3.23
2.45
2.43
2.42
2.41
2.40
2.39
2.38
2.37
2.36
2.34
2.33
2.32
2.30
2.28
2.27
2.26
2.25
2.24
2.23
2.21
2.19
2.00
1.98
1.96
1.95
1.94
1.93
2.00
1.05
2.12
1.03
1.12
1.07
2.01
1.99
0.80
2.34
2.16
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
f1 (ppm)



97

^{13}C NMR

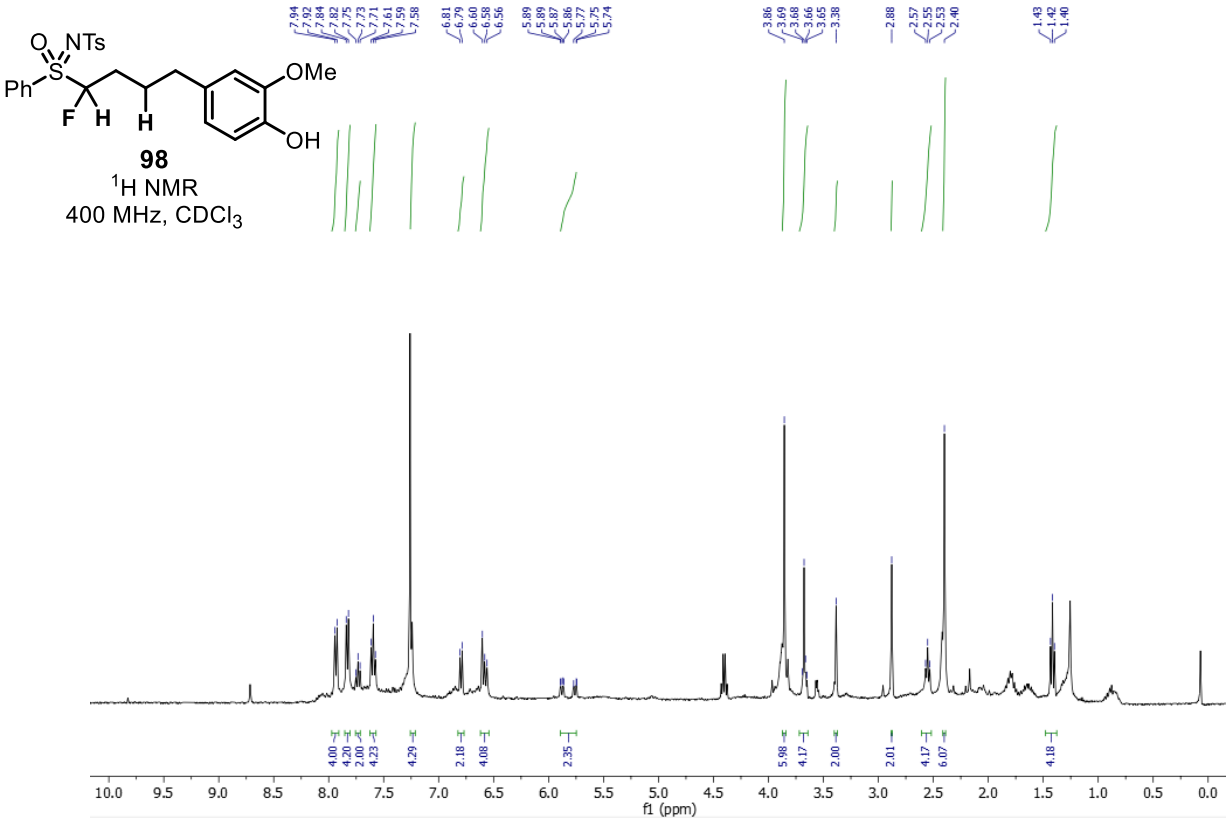
101 MHz, $CDCl_3$

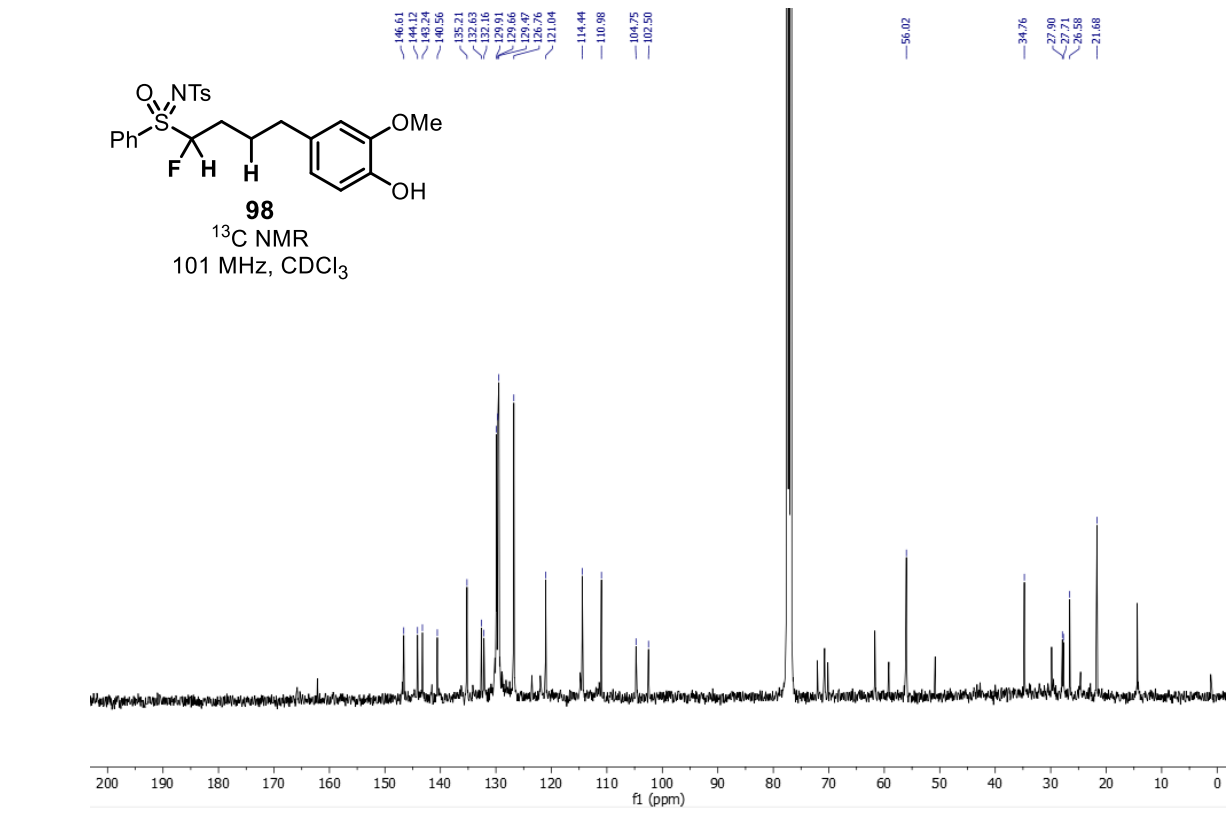


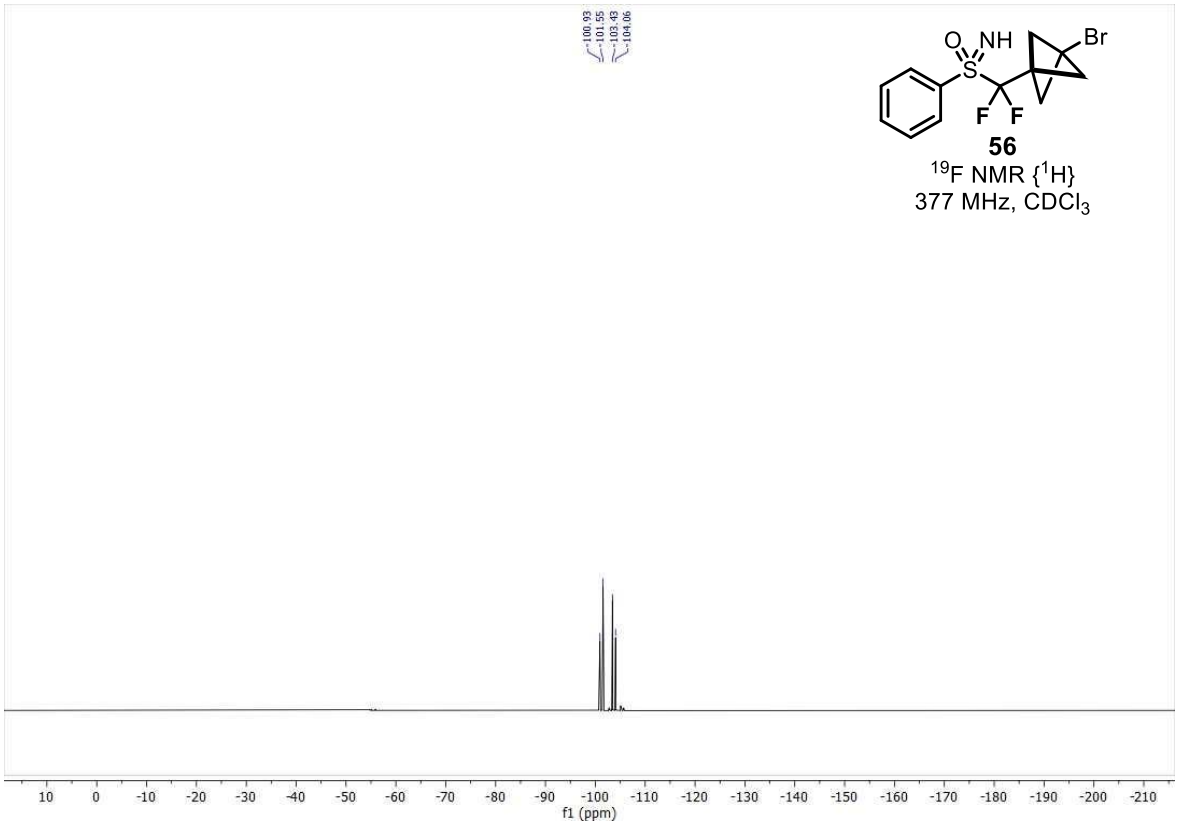
98

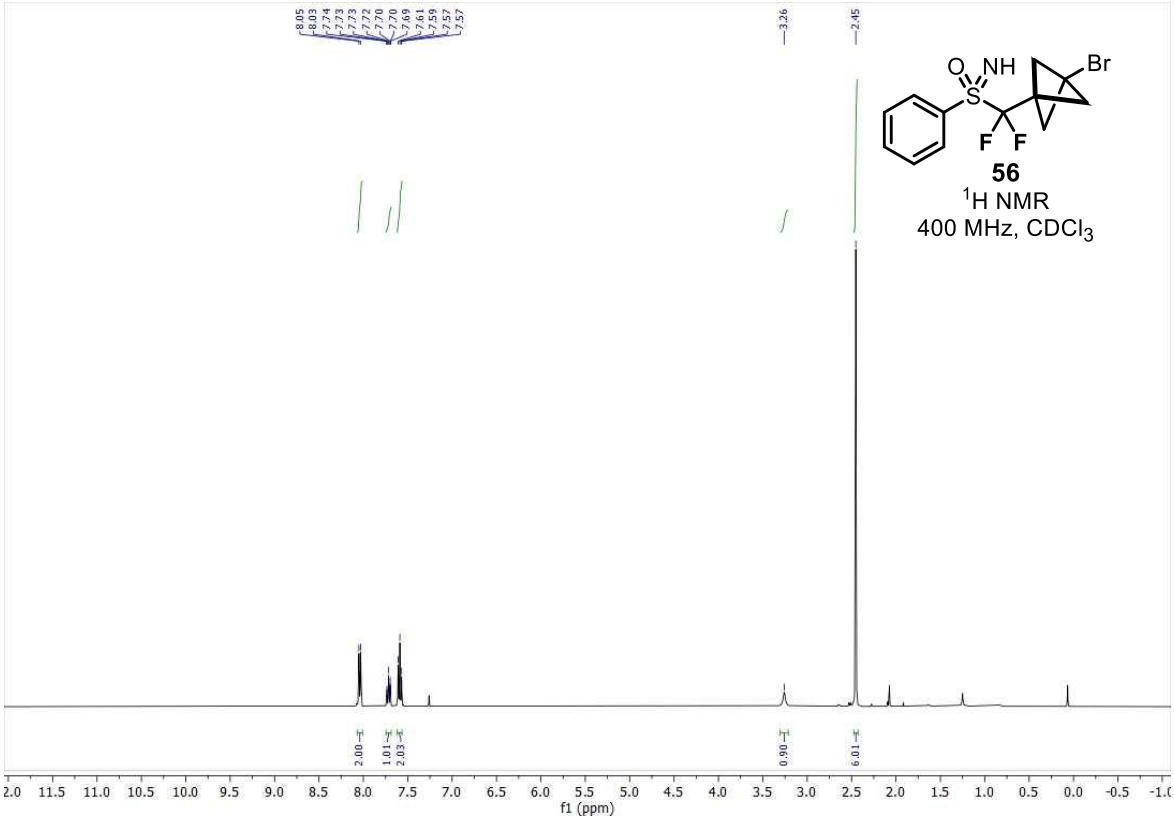
^{19}F NMR {^{1}H}

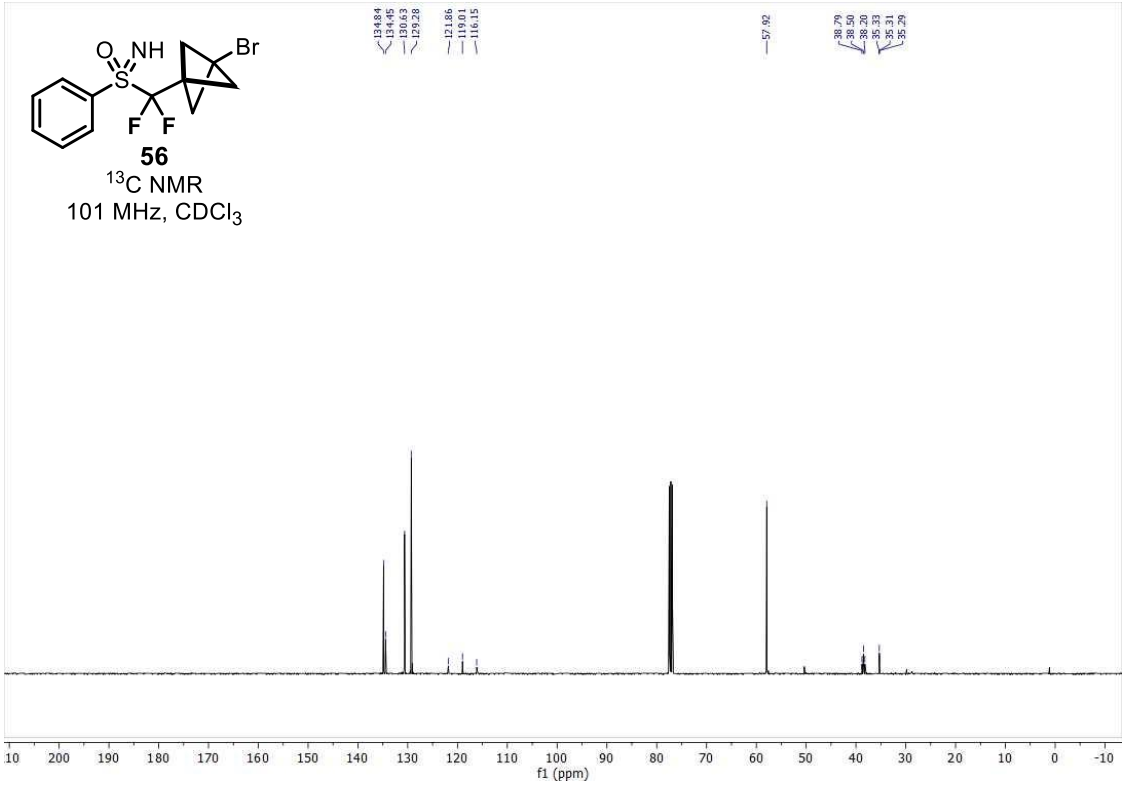
377 MHz, $CDCl_3$


O
NTs
S
Ph
F
H
H
OMe
OH
98
1H NMR
400 MHz, CDCl3
f1 (ppm)


O
NTs
S
Ph
F
H
H
OMe
OH
98
13C NMR
101 MHz, CDCl3
f1 (ppm)


-100.93
-101.55
-103.43
-104.06
O
NH
S
Br
F
F
56
19F NMR {1H}
377 MHz, CDCl3
f1 (ppm)

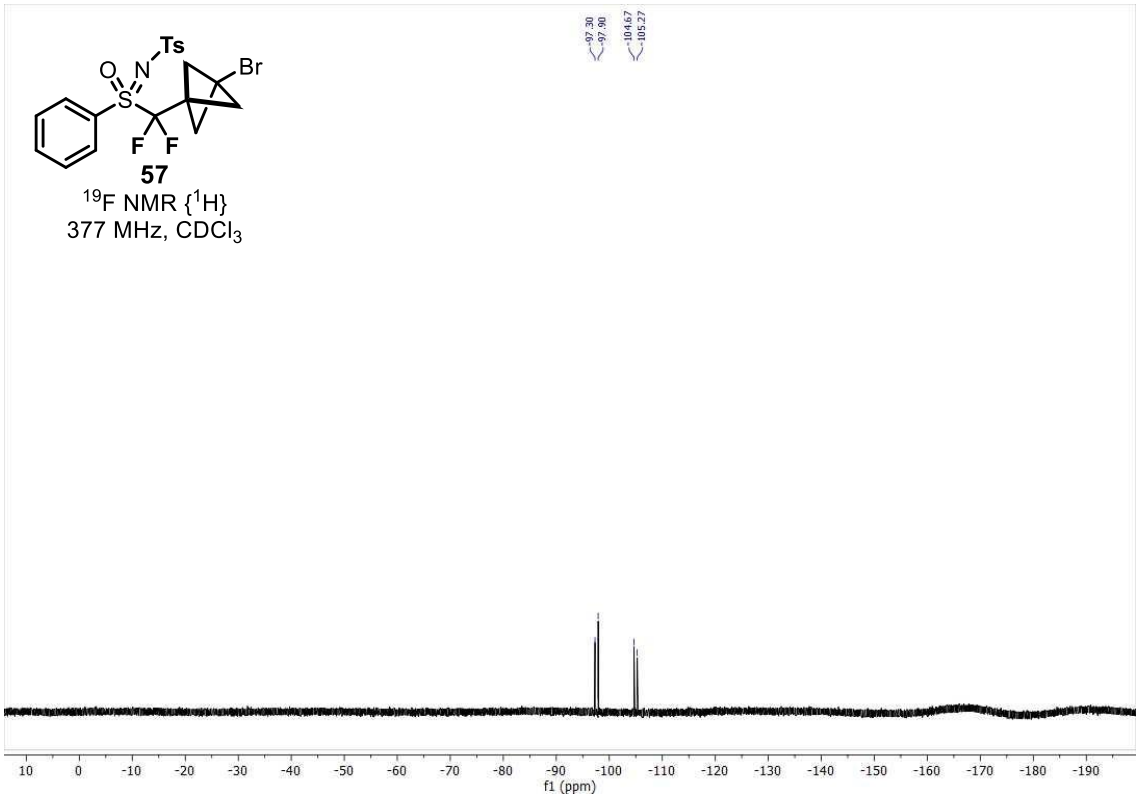

8.05
8.03
7.74
7.73
7.73
7.72
7.70
7.70
7.69
7.61
7.59
7.57
7.57
3.26
2.45
O
NH
S
Br
F
F
56
1H NMR
400 MHz, CDCl3
2.00
1.01
2.03
0.90
6.01
f1 (ppm)



56

^{13}C NMR

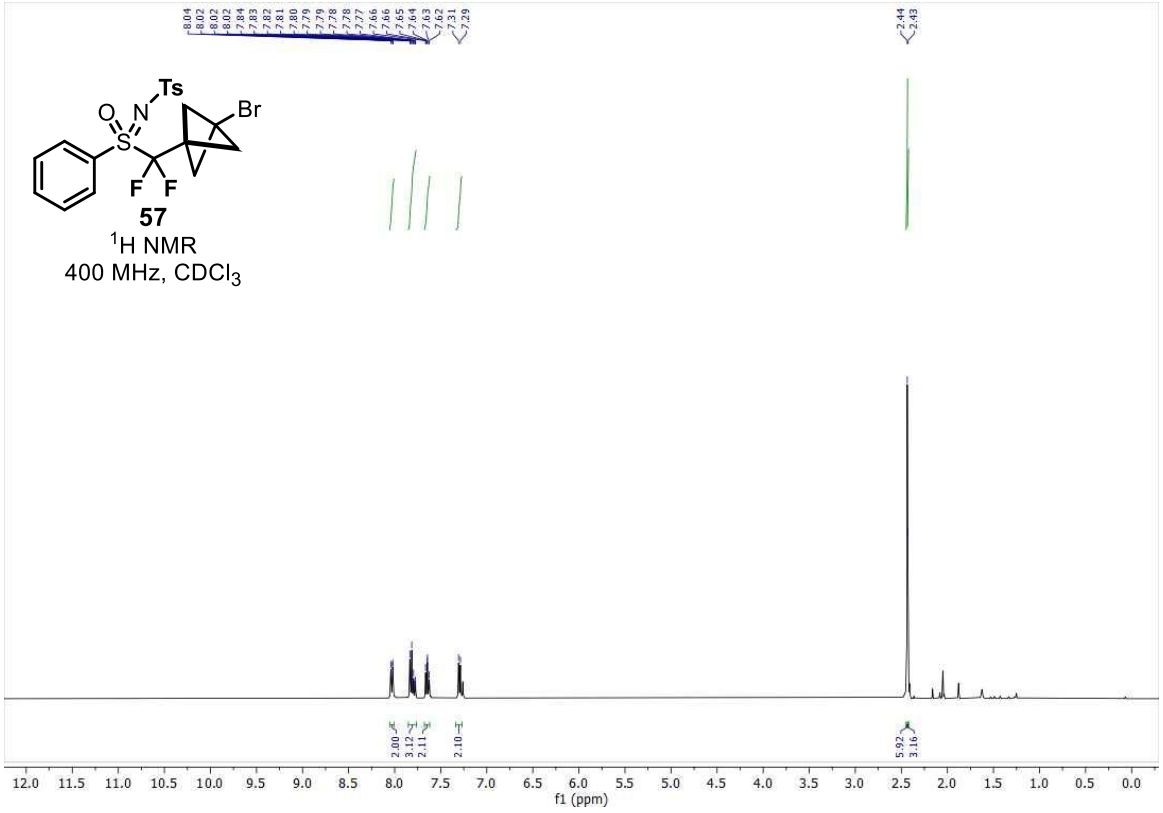
101 MHz, $CDCl_3$

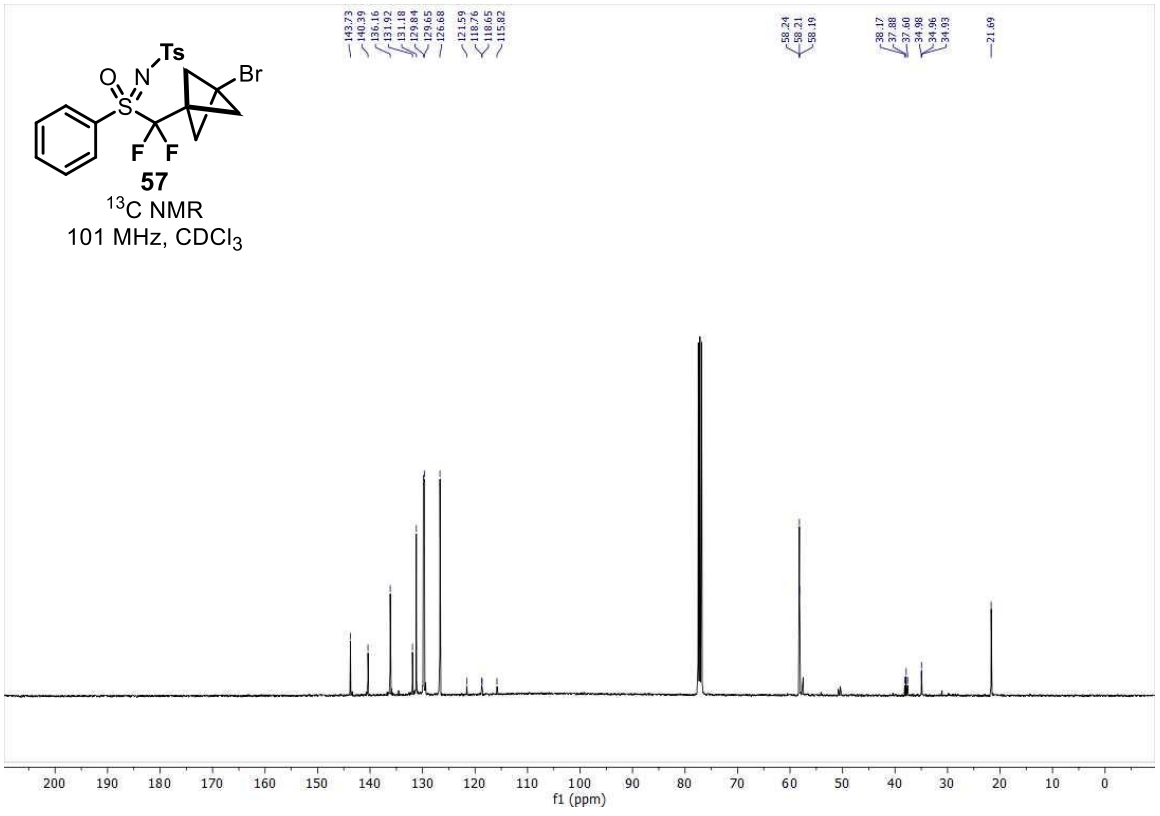


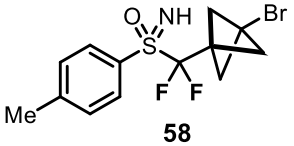
57

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$


Ts
O
N
S
Br
F F
57
1H NMR
400 MHz, CDCl3
f1 (ppm)

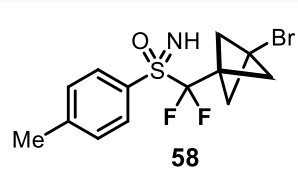

Ts
O
N
S
Br
F F
57
13C NMR
101 MHz, CDCl3
f1 (ppm)



58

^{19}F NMR {^{1}H}

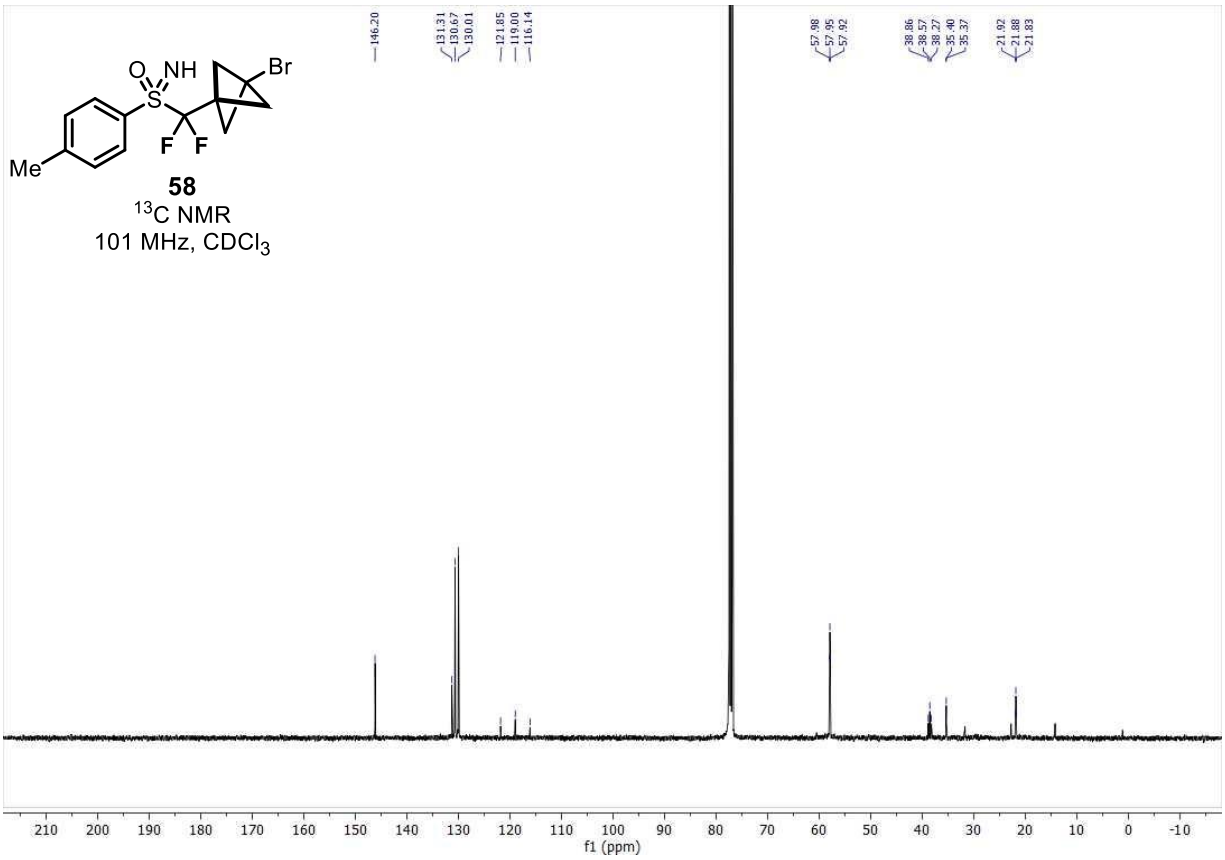
377 MHz, $CDCl_3$



58

^{1}H NMR

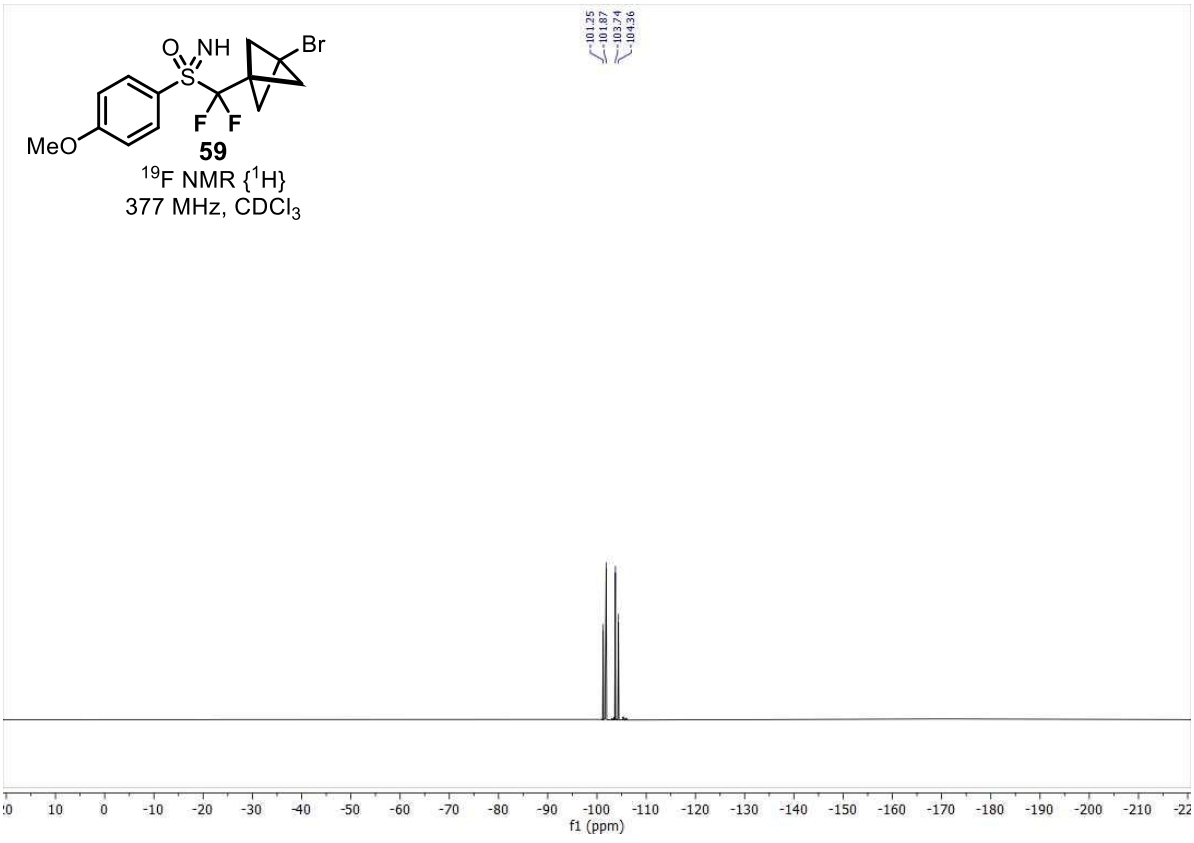
400 MHz, $CDCl_3$



58

^{13}C NMR

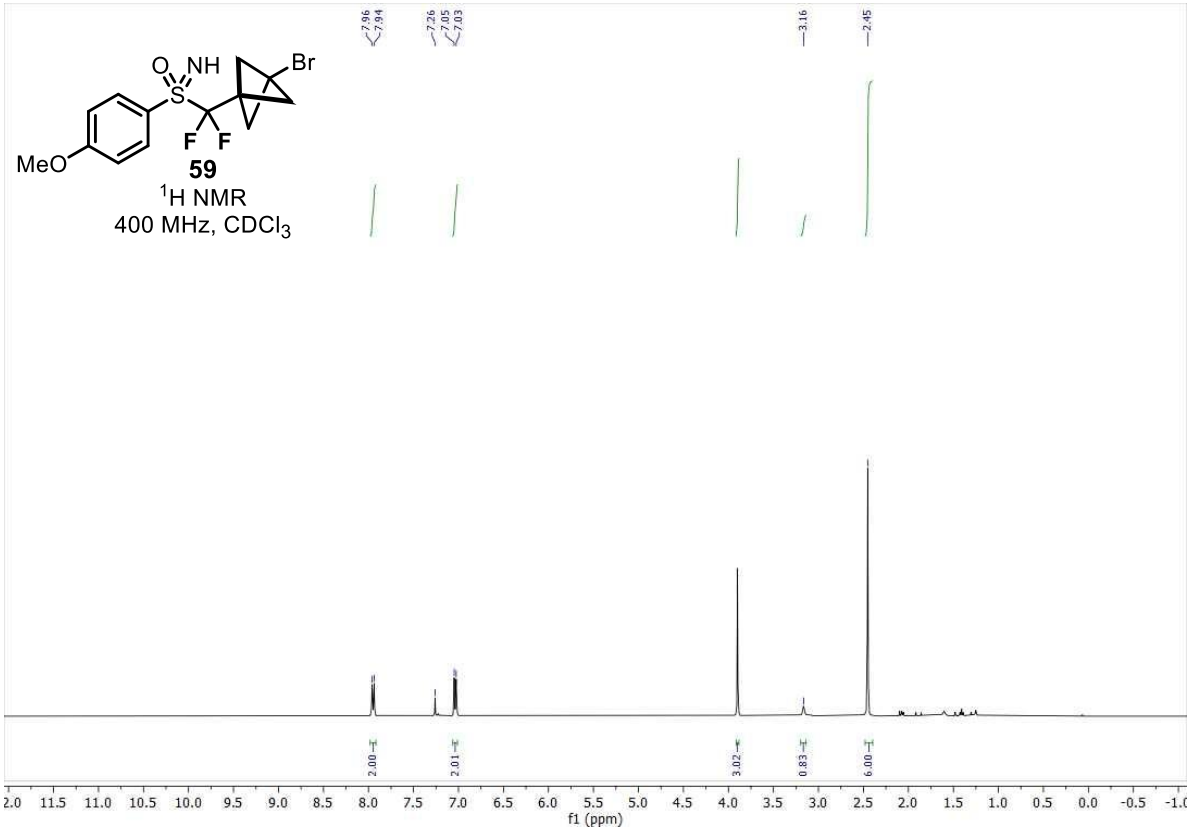
101 MHz, $CDCl_3$

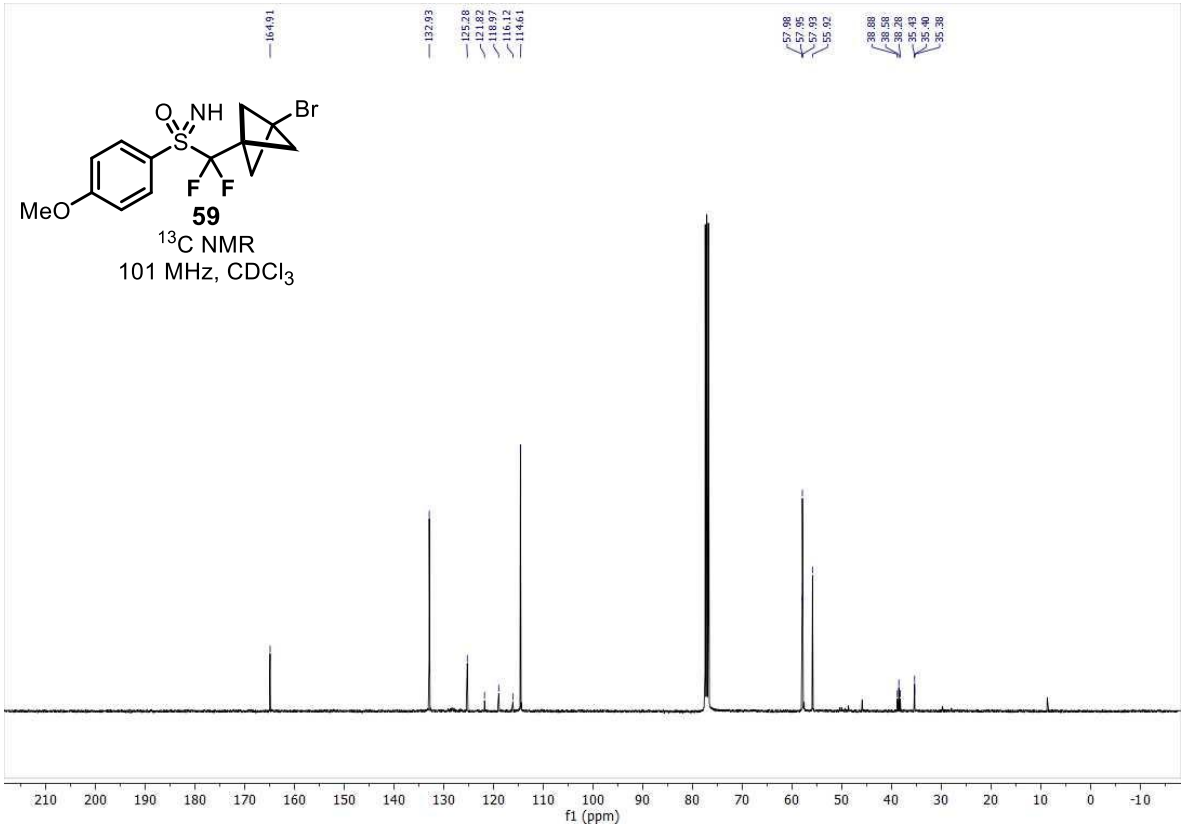


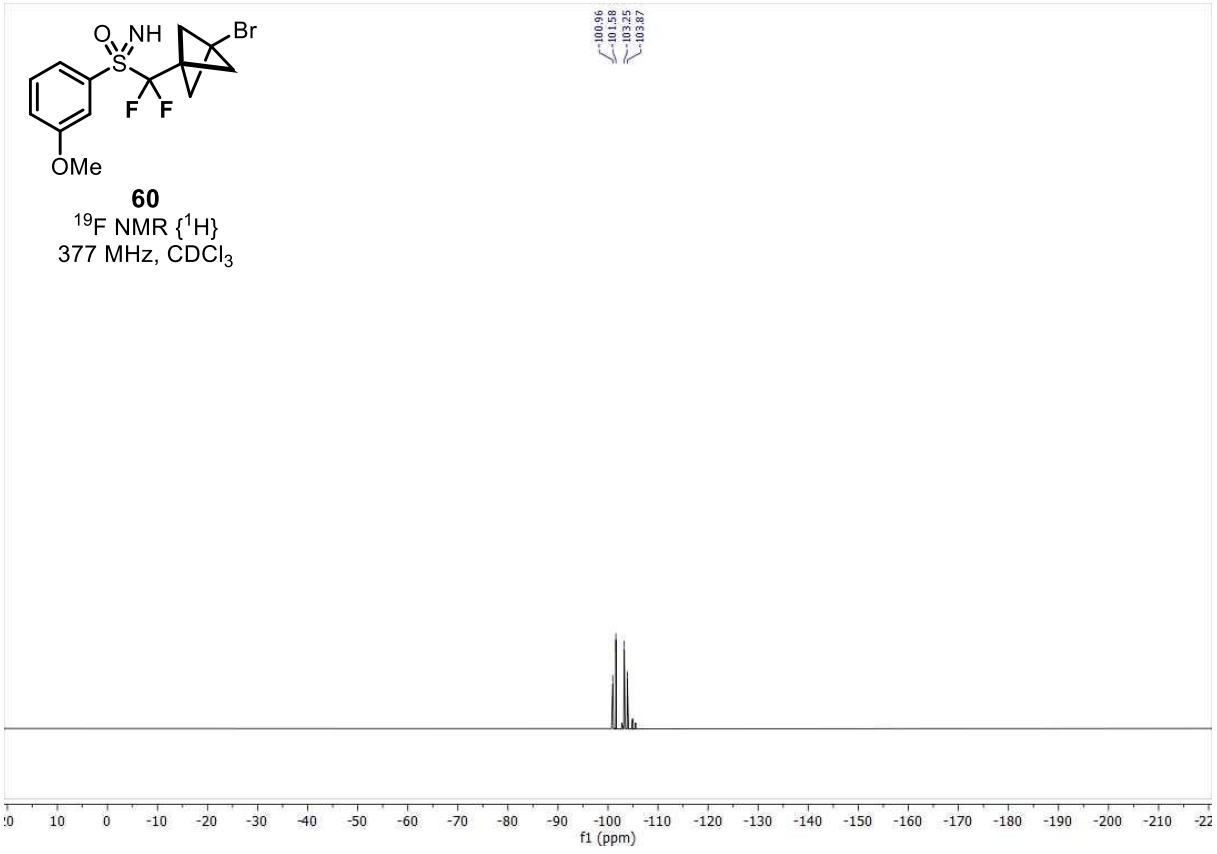
59

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$


O
NH
S
Br
F F
MeO
59
1H NMR
400 MHz, CDCl3
7.96
7.94
7.26
7.05
7.03
3.16
2.45
2.00
2.01
3.02
0.83
6.00
f1 (ppm)

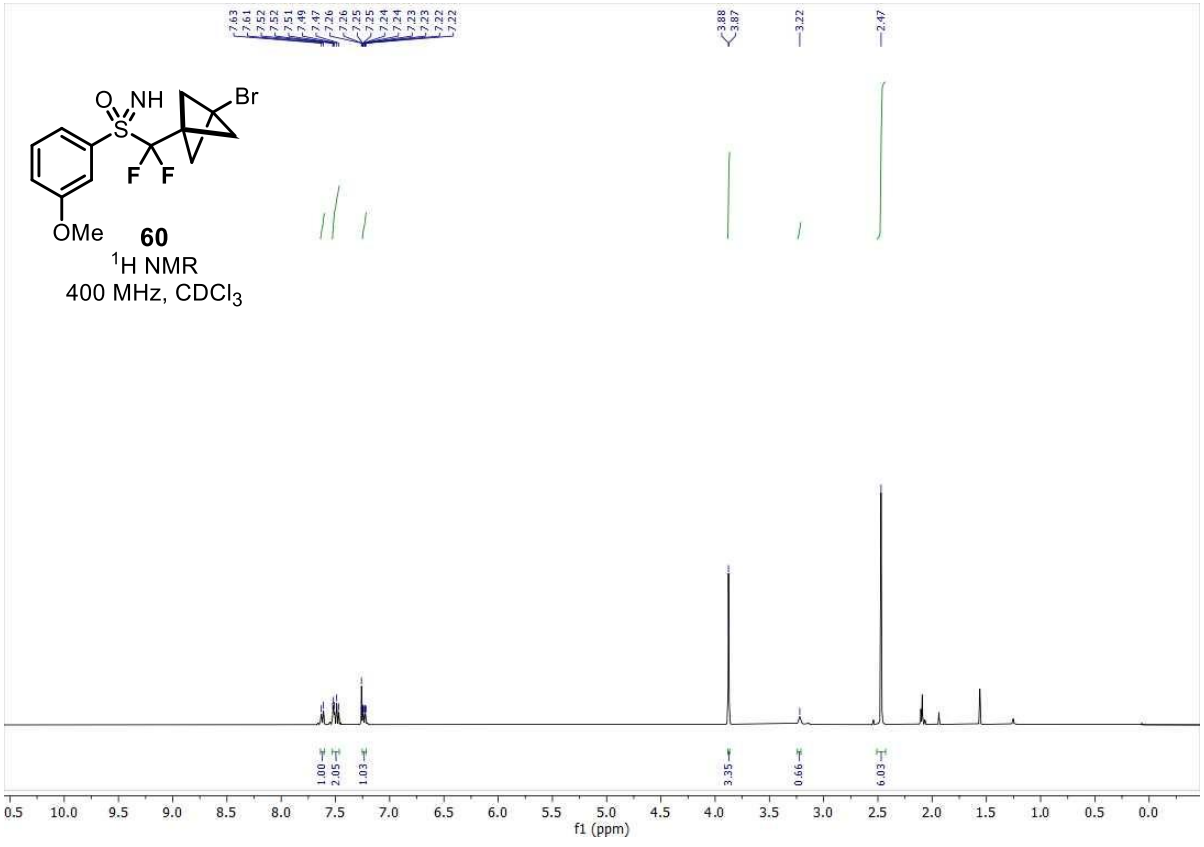

O
NH
S
Br
F F
MeO
59
13C NMR
101 MHz, CDCl3
164.91
132.93
125.28
121.82
118.97
116.12
114.61
57.98
57.95
57.93
55.92
38.88
38.58
38.28
35.43
35.40
35.38
f1 (ppm)



60

^{19}F NMR {^{1}H}

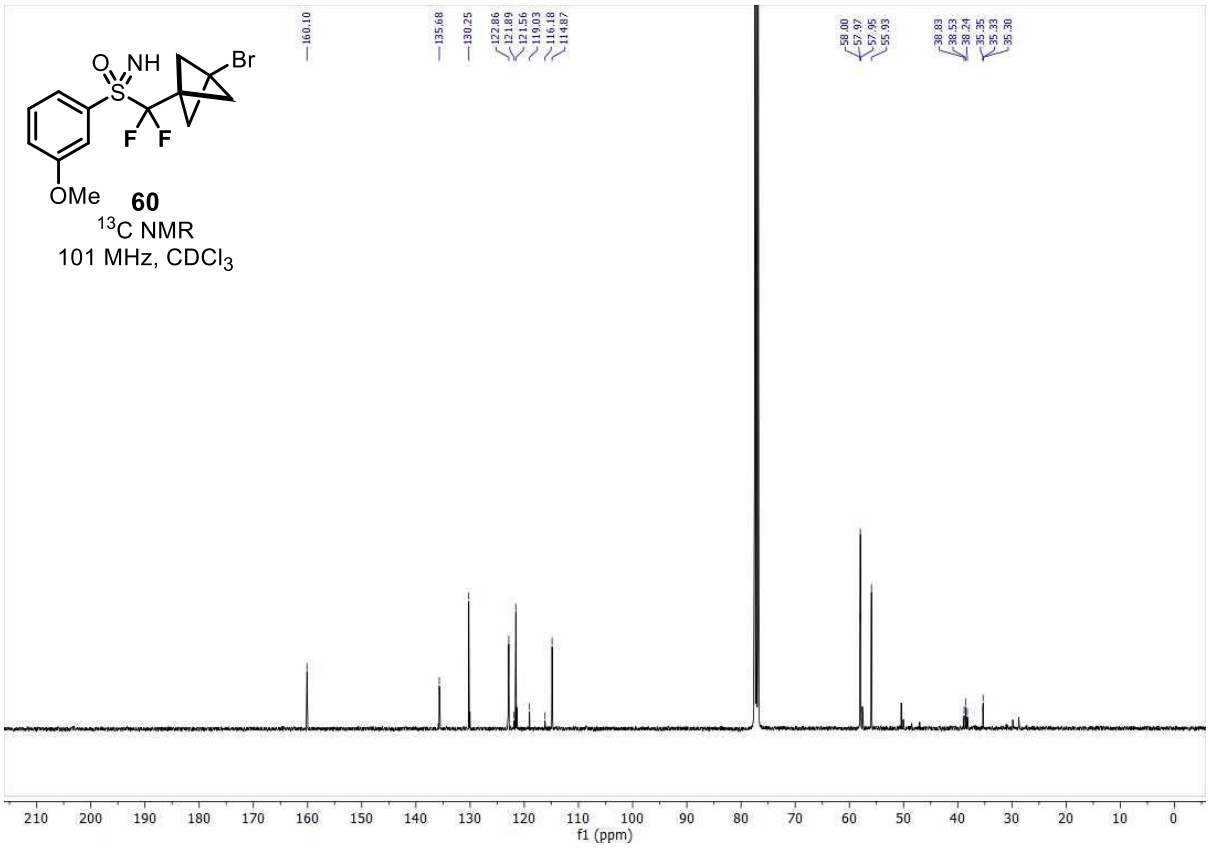
377 MHz, $CDCl_3$



60

^{1}H NMR

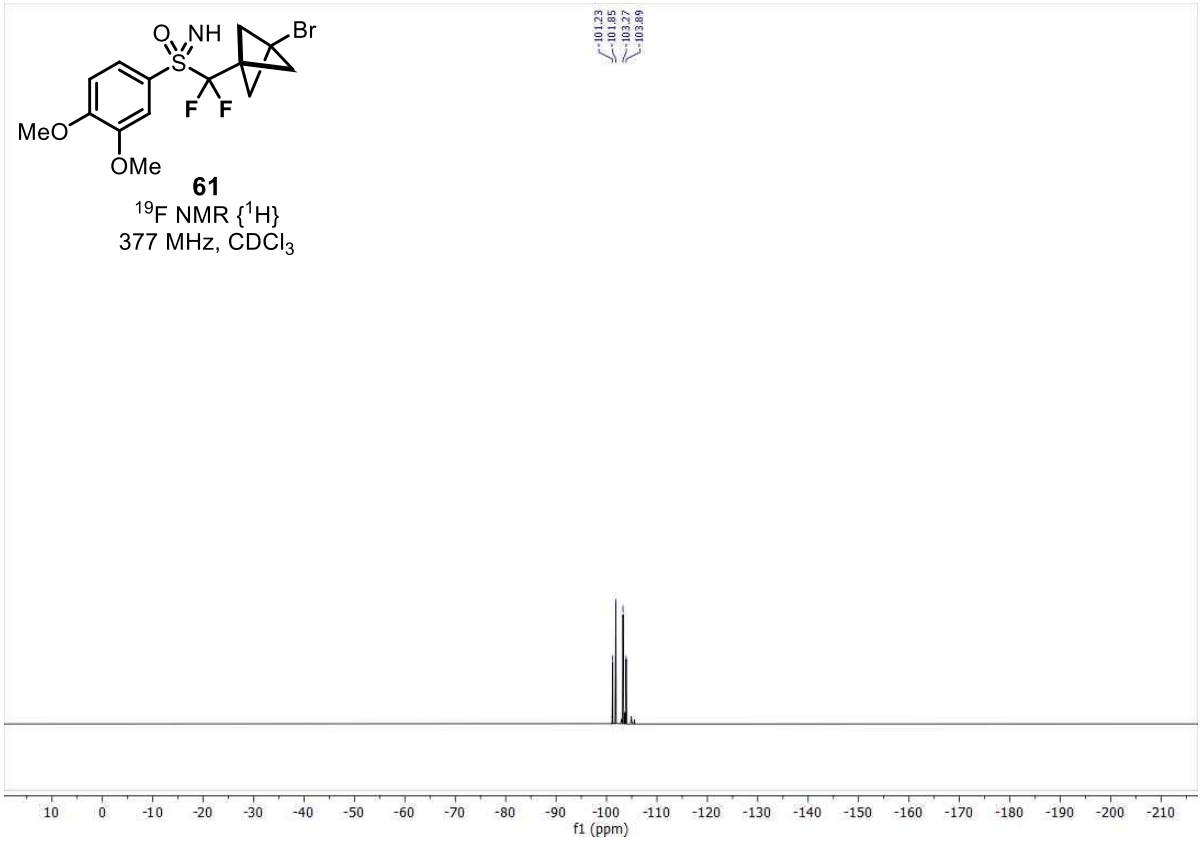
400 MHz, $CDCl_3$



60

^{13}C NMR

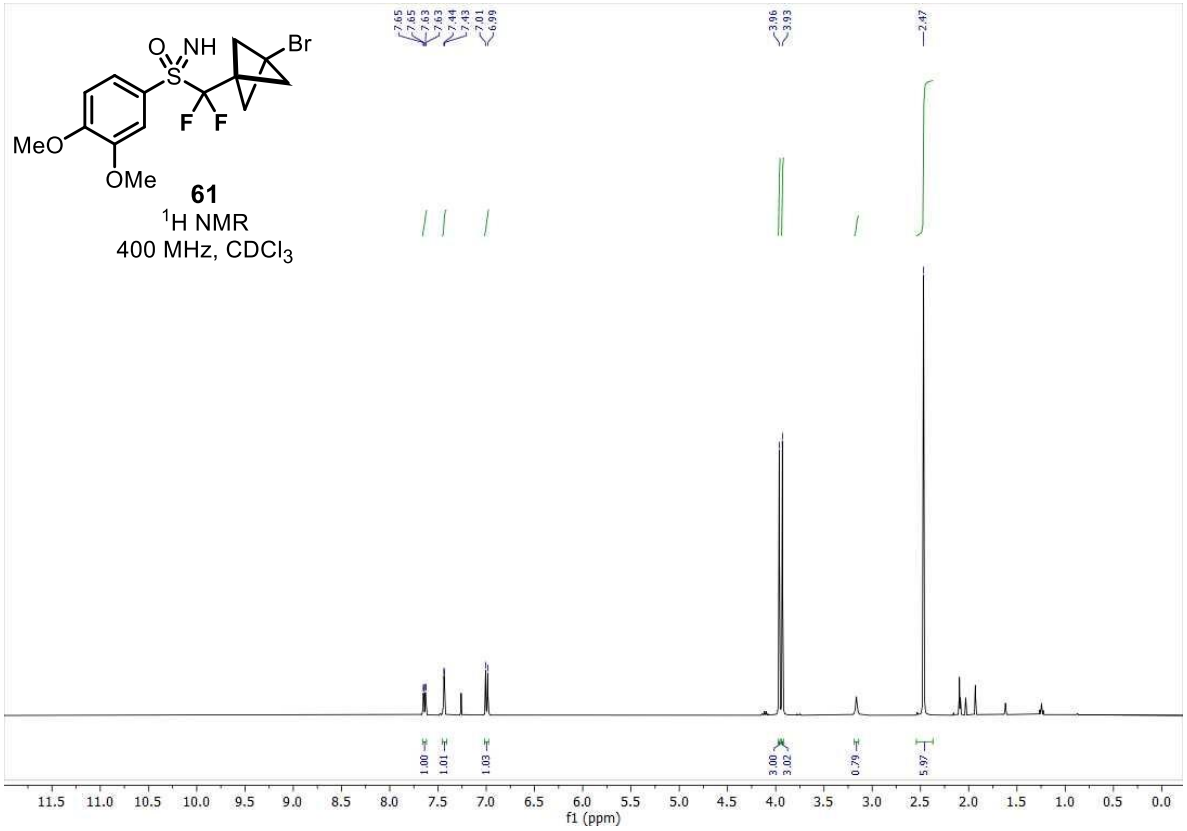
101 MHz, $CDCl_3$

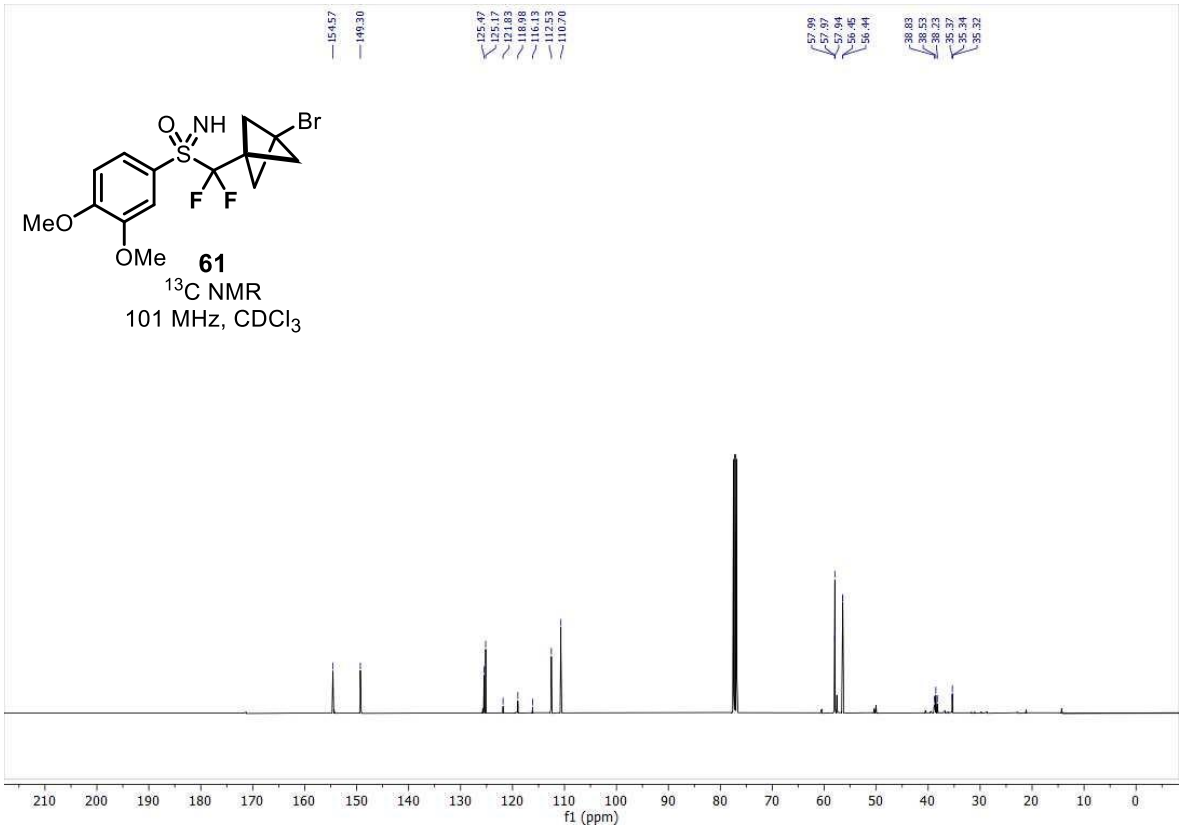


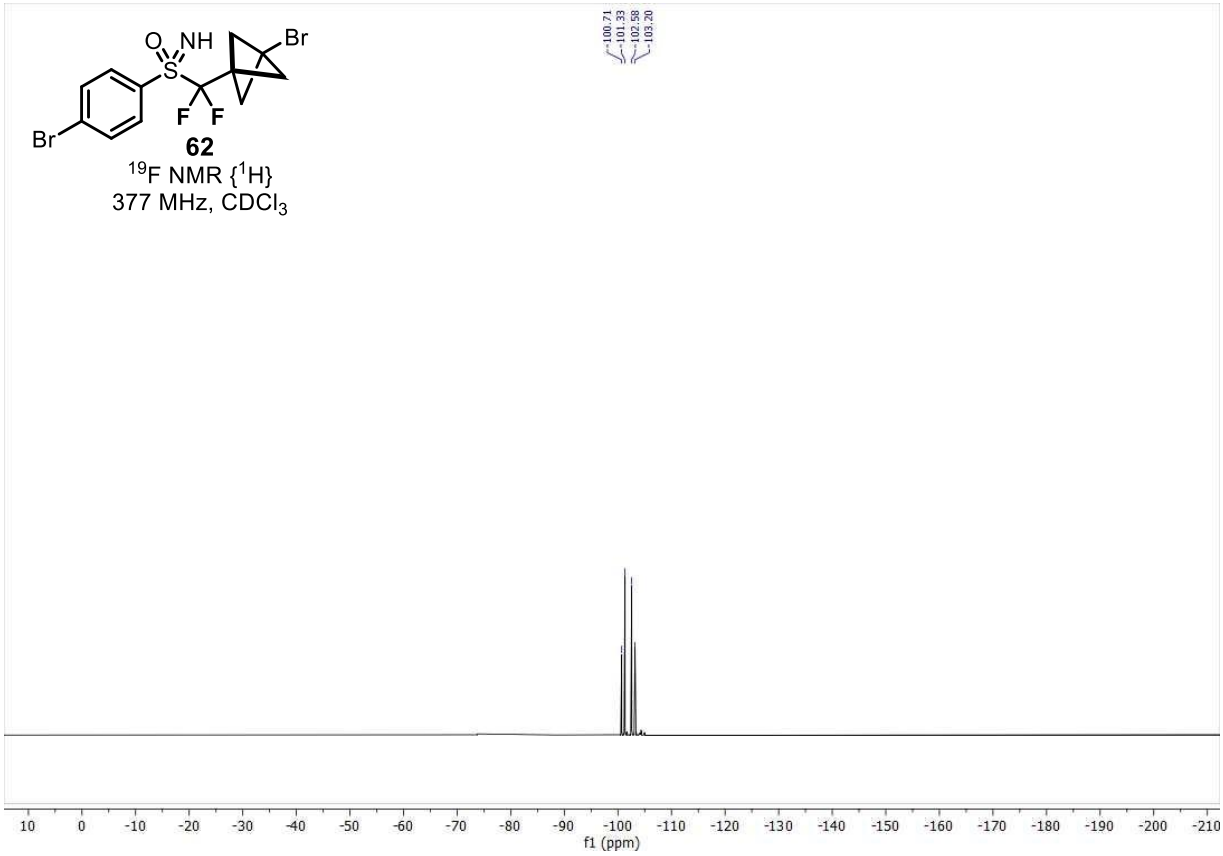
61

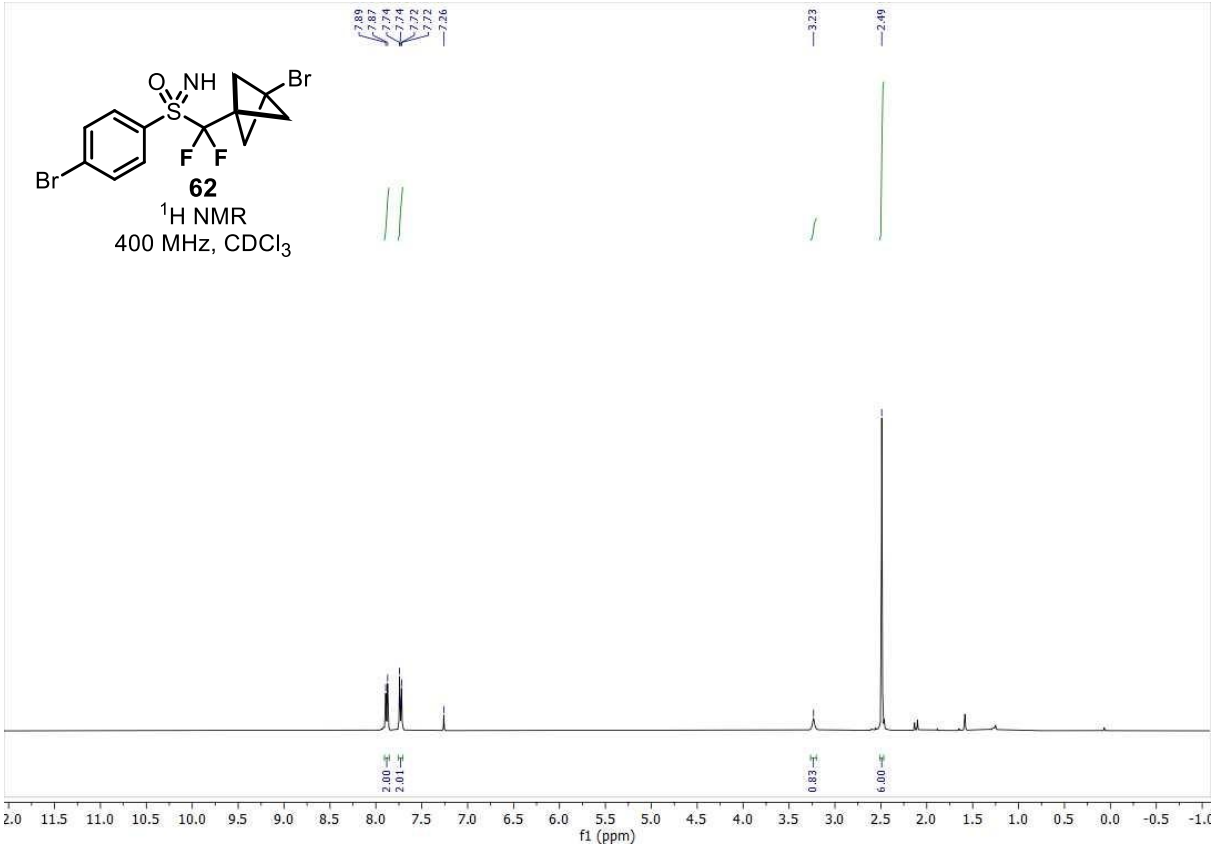
^{19}F NMR {^{1}H}

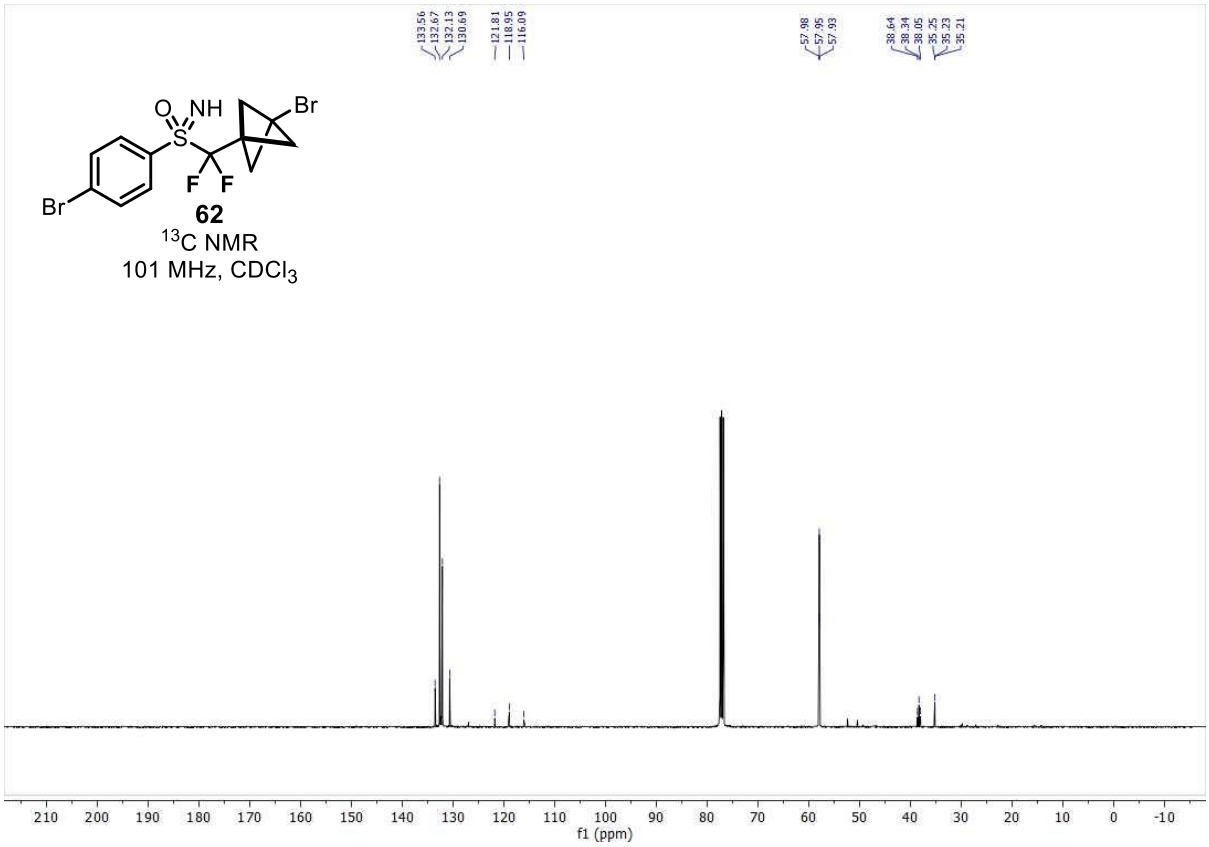
377 MHz, $CDCl_3$


61
1H NMR
400 MHz, CDCl3
f1 (ppm)


61
13C NMR
101 MHz, CDCl3
f1 (ppm)


O
NH
S
F F
Br
Br
62
19F NMR {1H}
377 MHz, CDCl3
-100.71
-101.33
-102.58
-103.20
f1 (ppm)

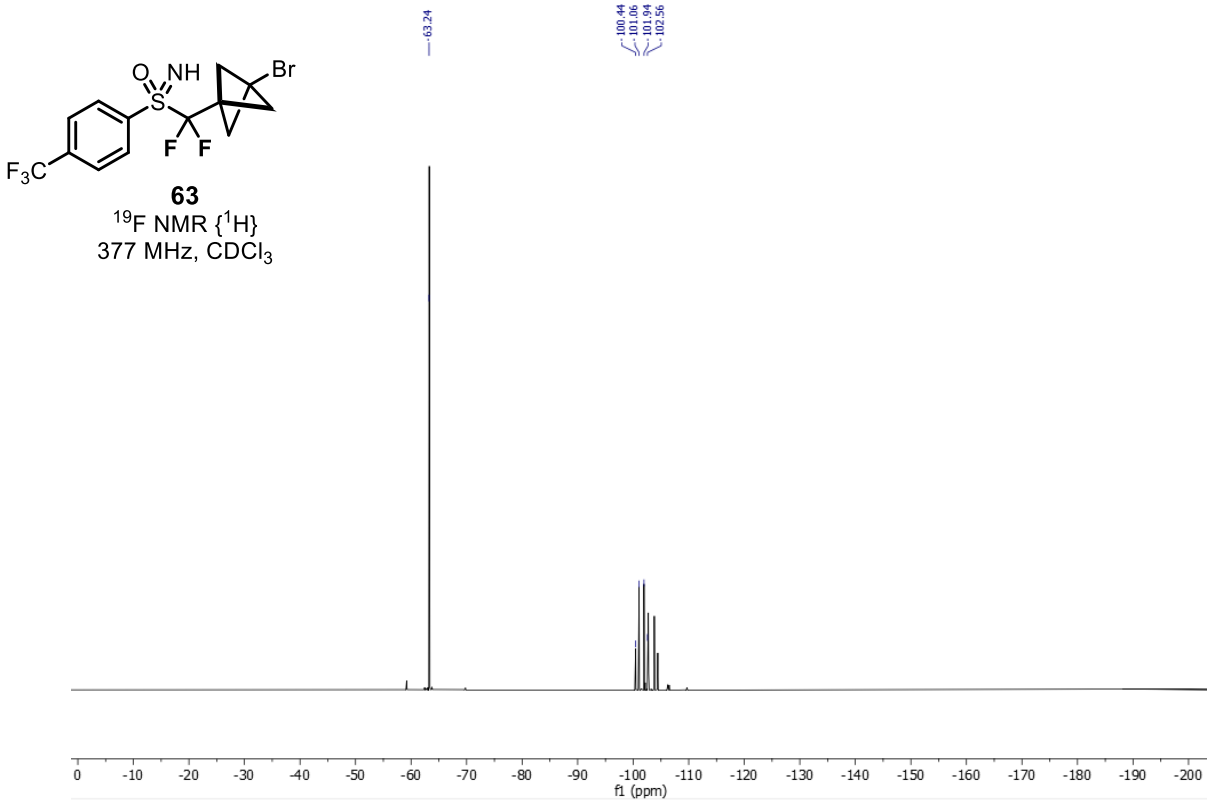

O
NH
S
F F
Br
Br
62
1H NMR
400 MHz, CDCl3
7.89
7.87
7.74
7.74
7.72
7.72
7.26
3.23
2.49
2.00
2.01
0.83
6.00
f1 (ppm)



62

^{13}C NMR

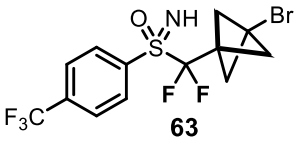
101 MHz, $CDCl_3$



63

^{19}F NMR $\{^{1}H\}$

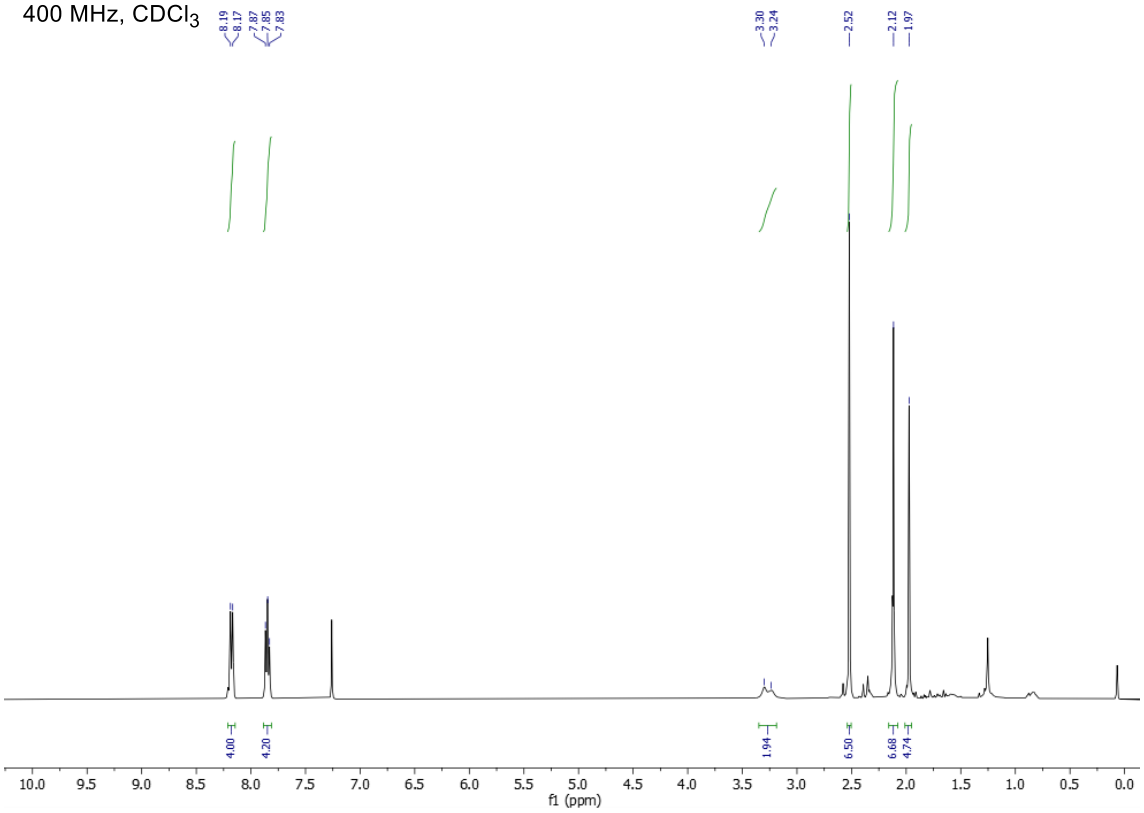
377 MHz, $CDCl_3$

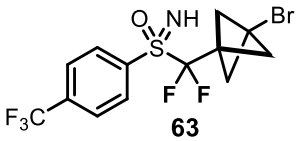


63

^{1}H NMR

400 MHz, $CDCl_3$

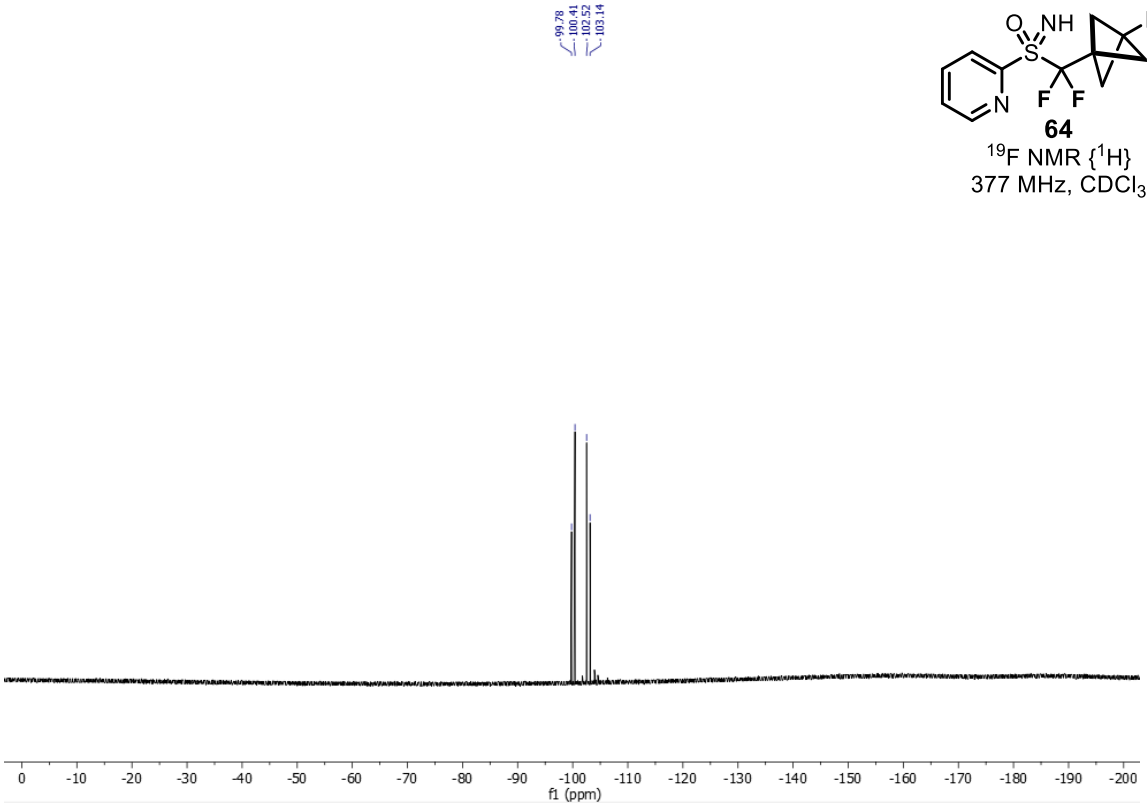


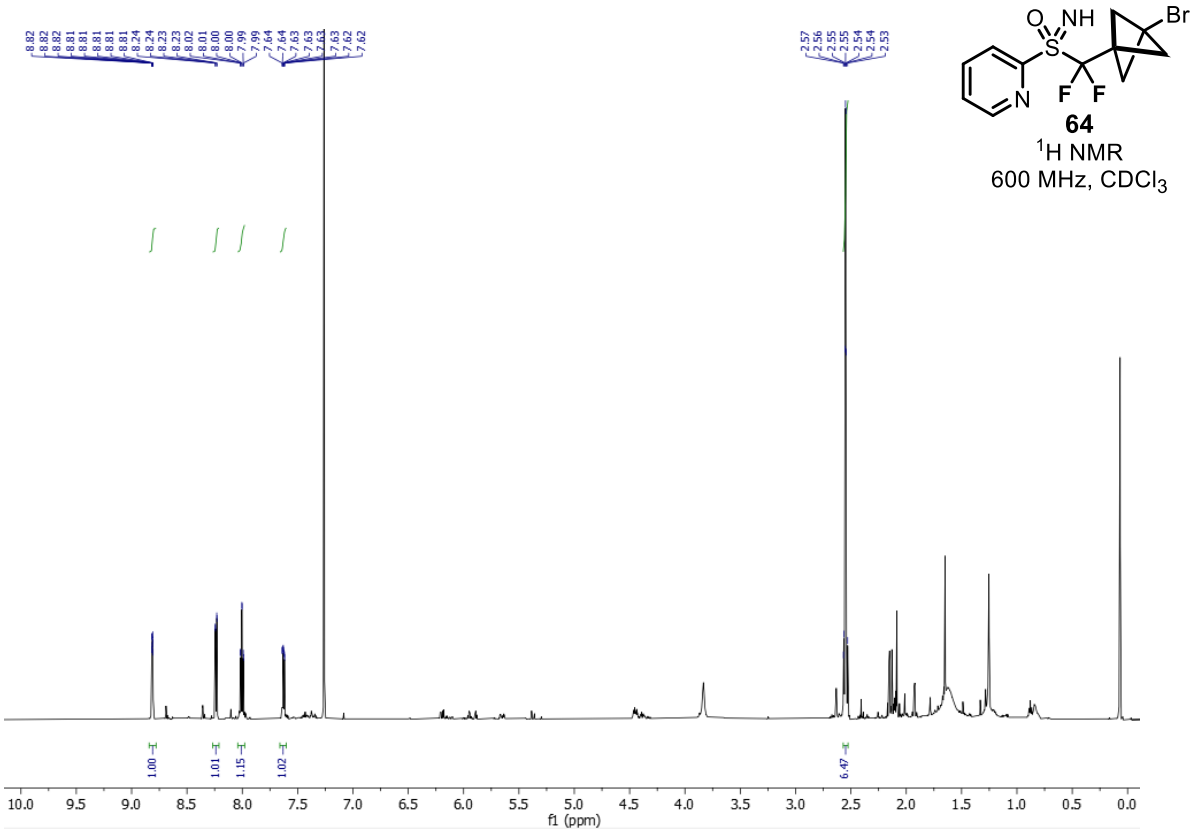


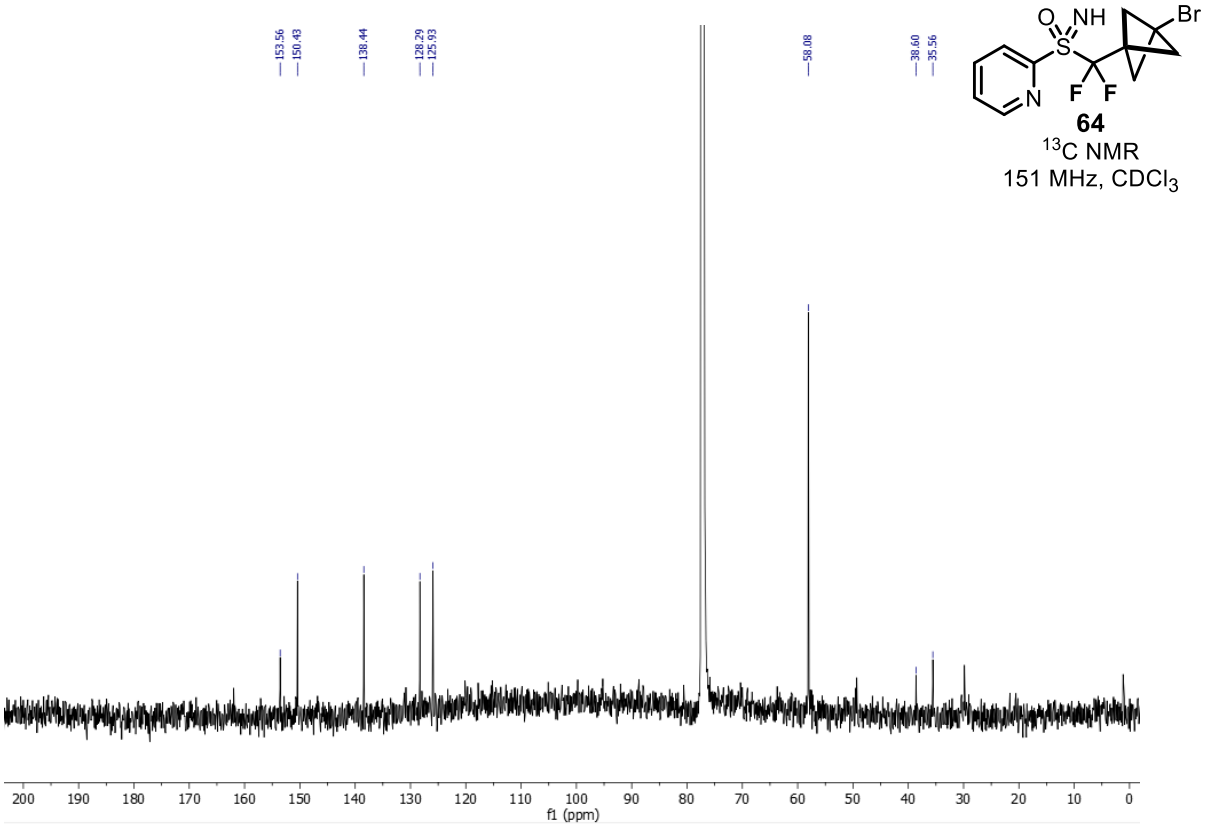
63

^{13}C NMR

101 MHz, $CDCl_3$


99.78
100.41
102.52
103.14
O
NH
S
Br
N
F F
64
19F NMR {1H}
377 MHz, CDCl3
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

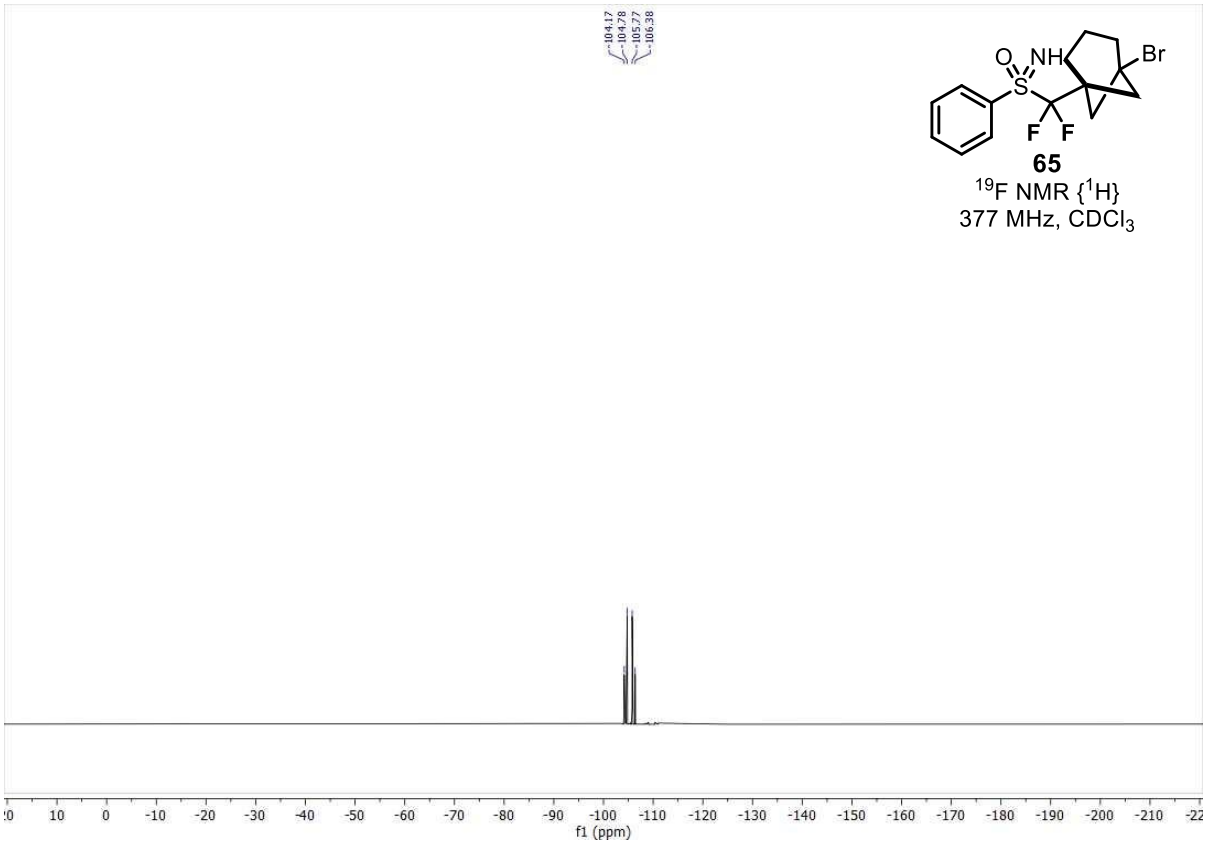

8.82
8.82
8.82
8.81
8.81
8.81
8.81
8.81
8.24
8.24
8.23
8.23
8.02
8.01
8.00
8.00
7.99
7.99
7.64
7.64
7.63
7.63
7.63
7.62
7.62
7.62
2.57
2.56
2.55
2.55
2.54
2.54
2.53
O
NH
S
Br
N
F F
64
1H NMR
600 MHz, CDCl3
1.00
1.01
1.15
1.02
6.47
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



64

^{13}C NMR

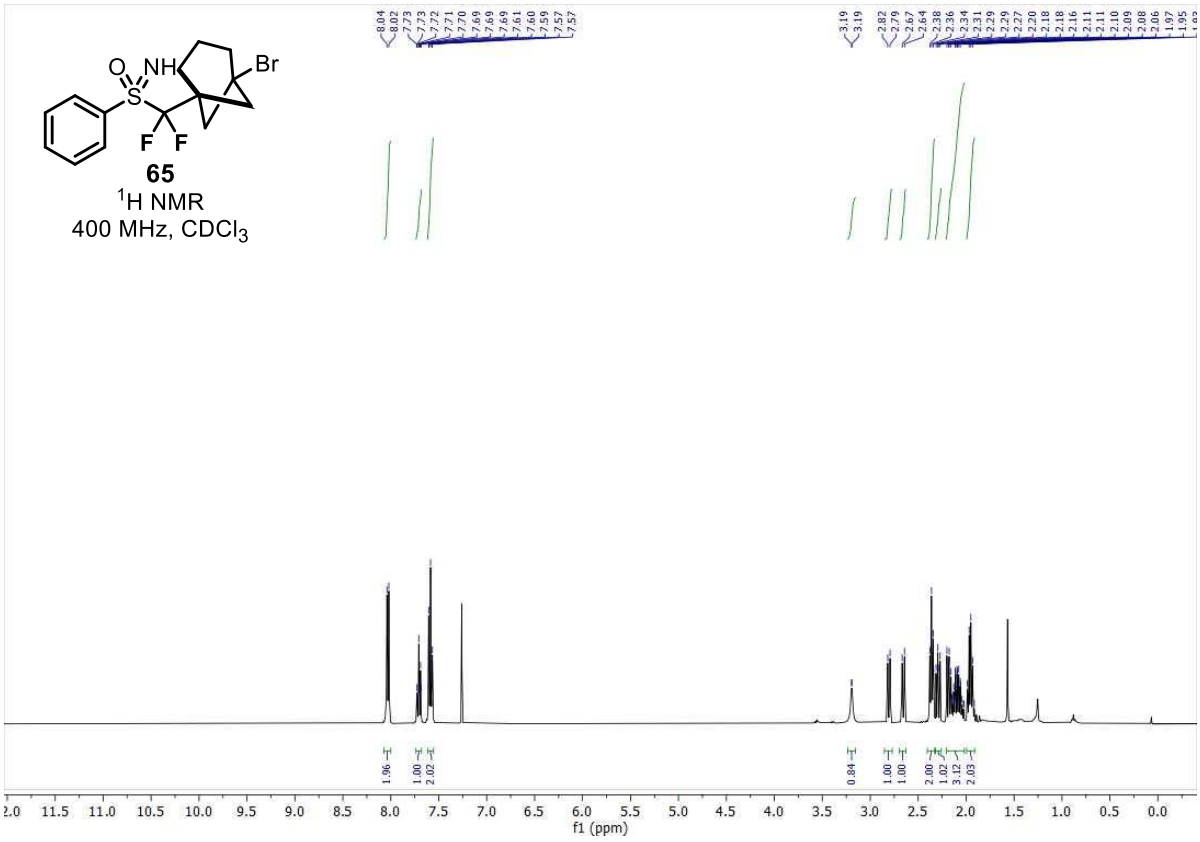
151 MHz, $CDCl_3$

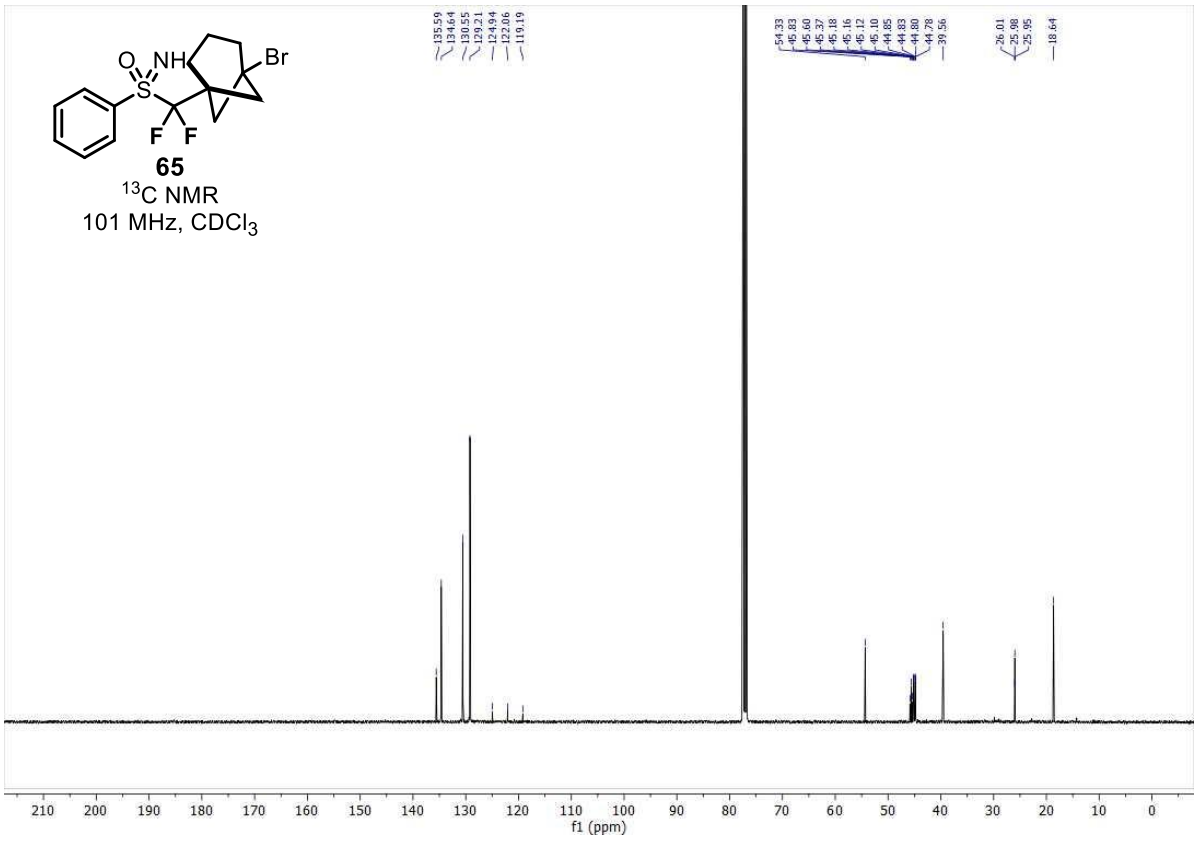


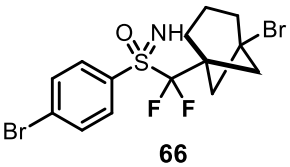
65

^{19}F NMR {^{1}H}

377 MHz, $CDCl_3$

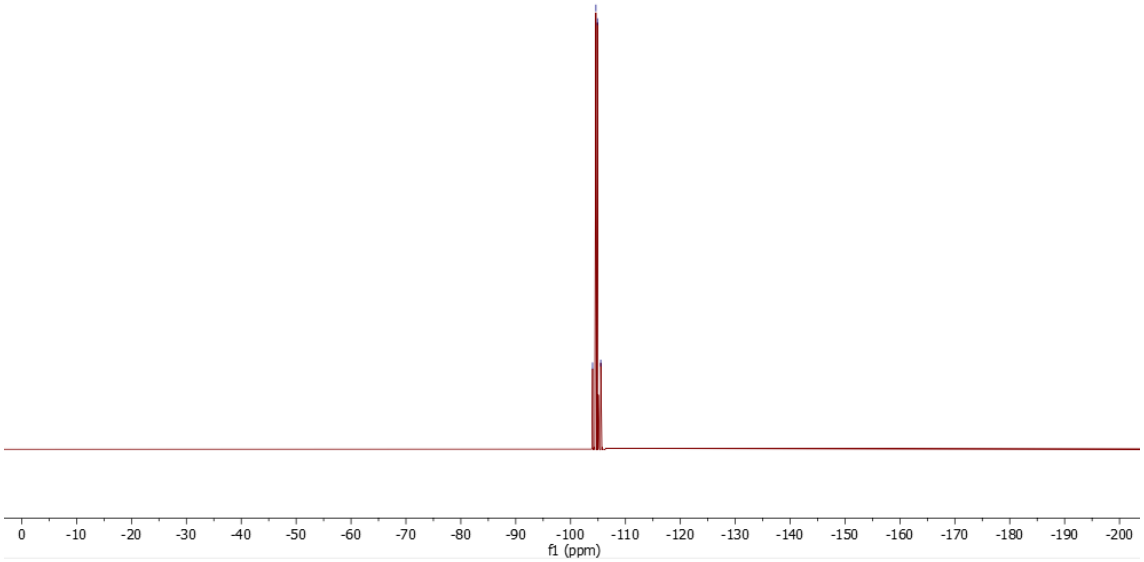

O
NH
S
Br
F F
65
1H NMR
400 MHz, CDCl3
f1 (ppm)

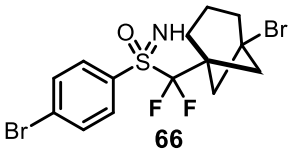

O
NH
S
Br
F F
65
13C NMR
101 MHz, CDCl3
f1 (ppm)



66

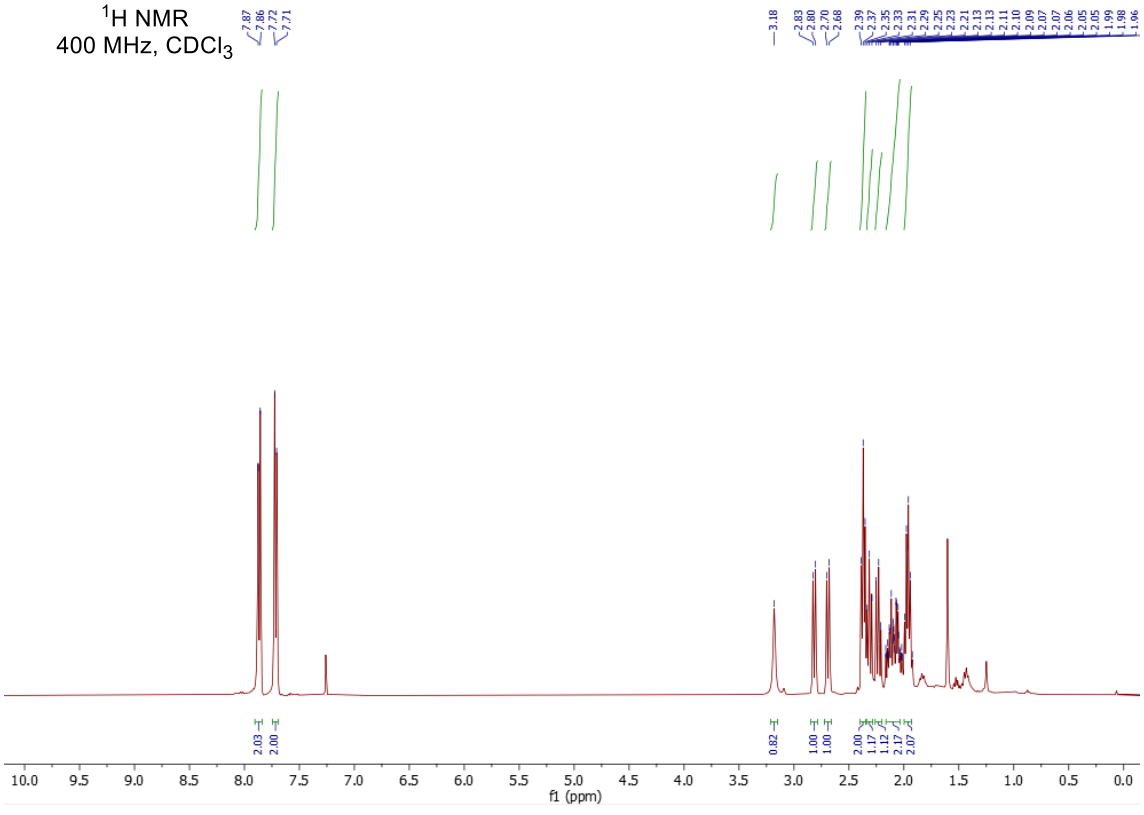
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$

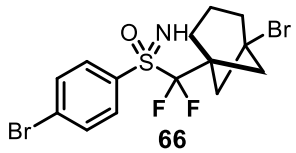




66

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

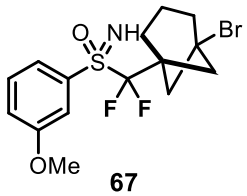




66

^{13}C NMR

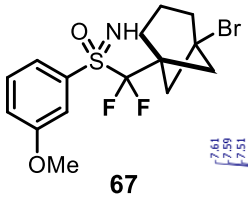
126 MHz, $CDCl_3$



67

^{19}F NMR {^{1}H}

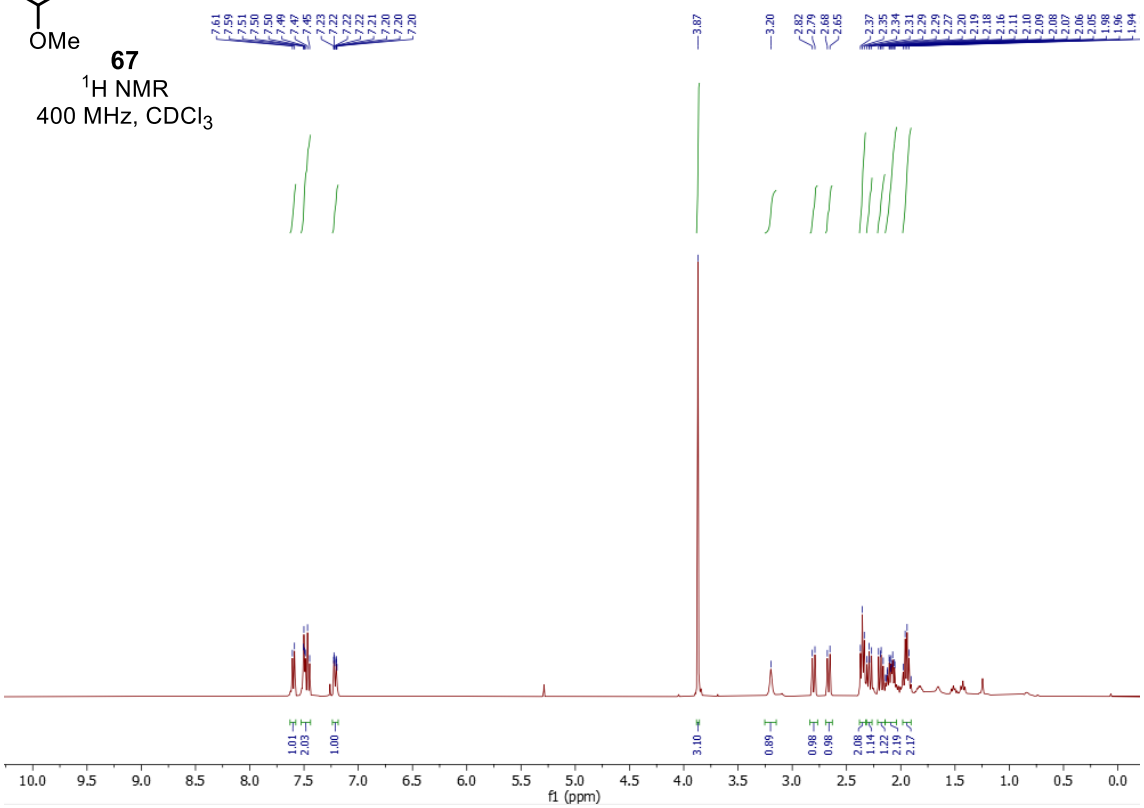
377 MHz, $CDCl_3$

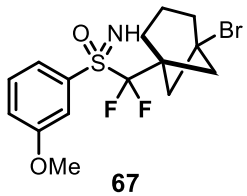


67

^{1}H NMR

400 MHz, $CDCl_3$

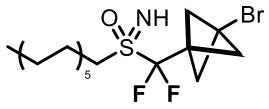




67

^{13}C NMR

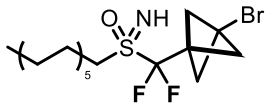
101 MHz, $CDCl_3$



68

^{19}F NMR {^{1}H}

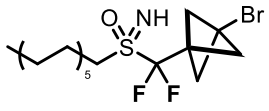
377 MHz, $CDCl_3$



68

^{1}H NMR

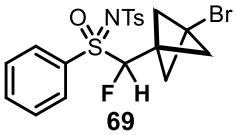
600 MHz, $CDCl_3$



68

^{13}C NMR

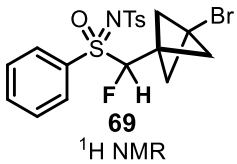
151 MHz, $CDCl_3$



69

^{19}F NMR

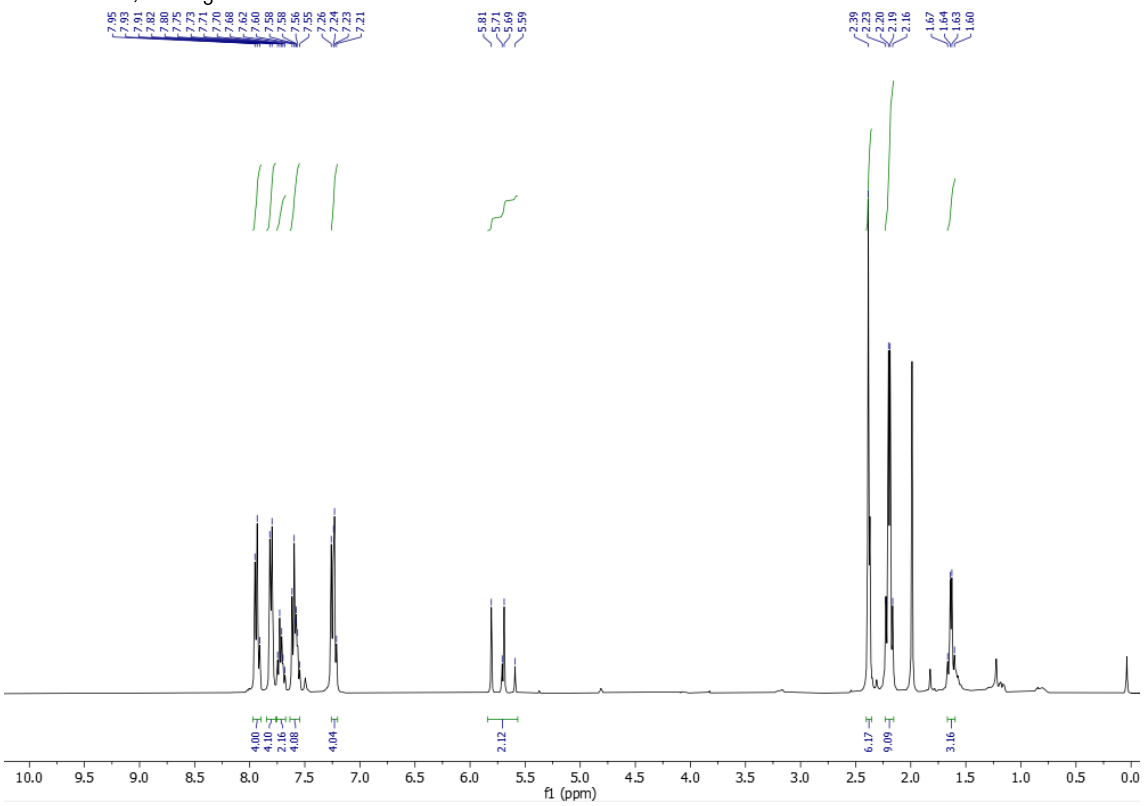
377 MHz, $CDCl_3$

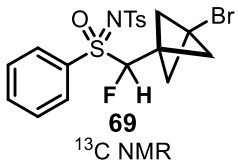


69

^{1}H NMR

400 MHz, $CDCl_3$

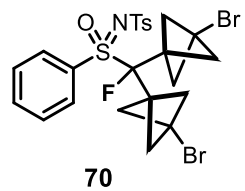




69

^{13}C NMR

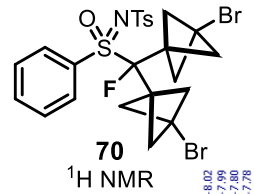
101 MHz, $CDCl_3$



70

^{19}F NMR

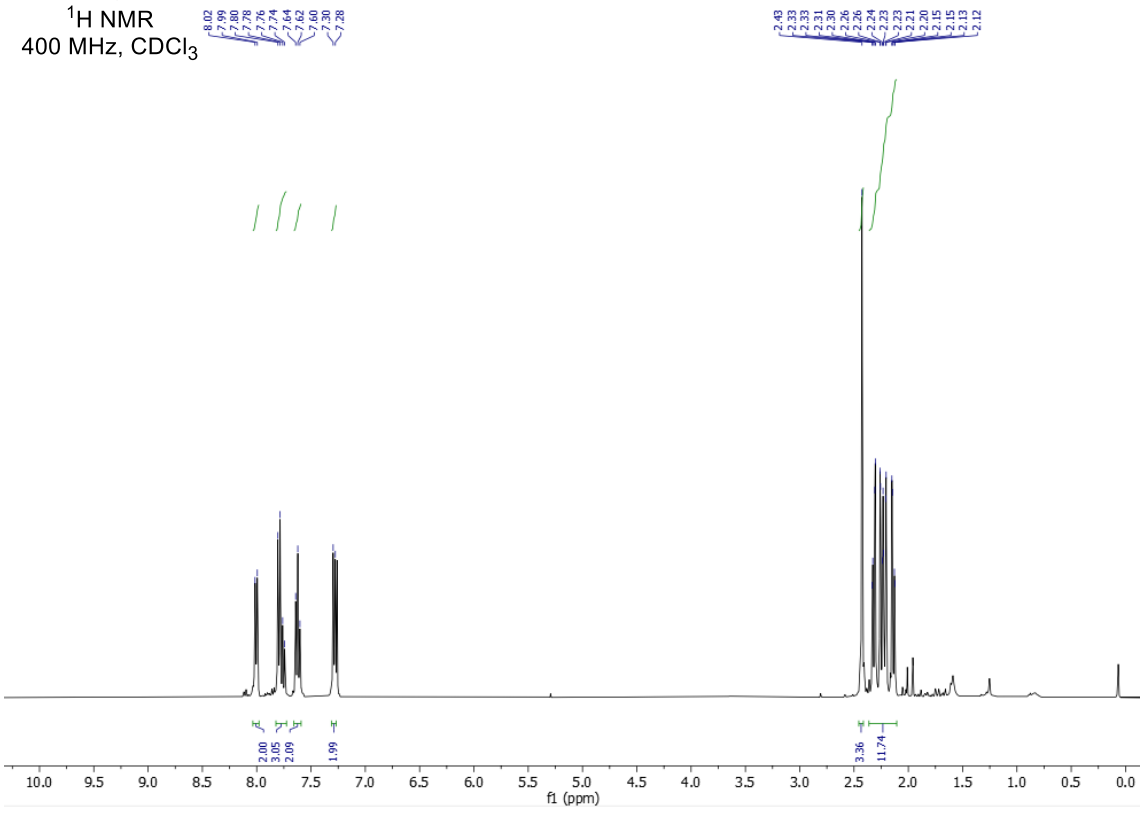
377 MHz, $CDCl_3$

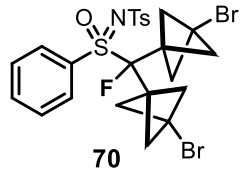


70

^{1}H NMR

400 MHz, $CDCl_3$

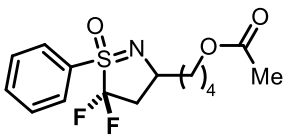




70

^{13}C NMR

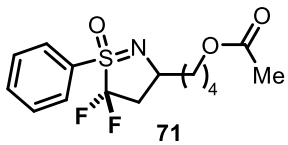
101 MHz, $CDCl_3$



71

^{19}F NMR $\{^{1}H\}$

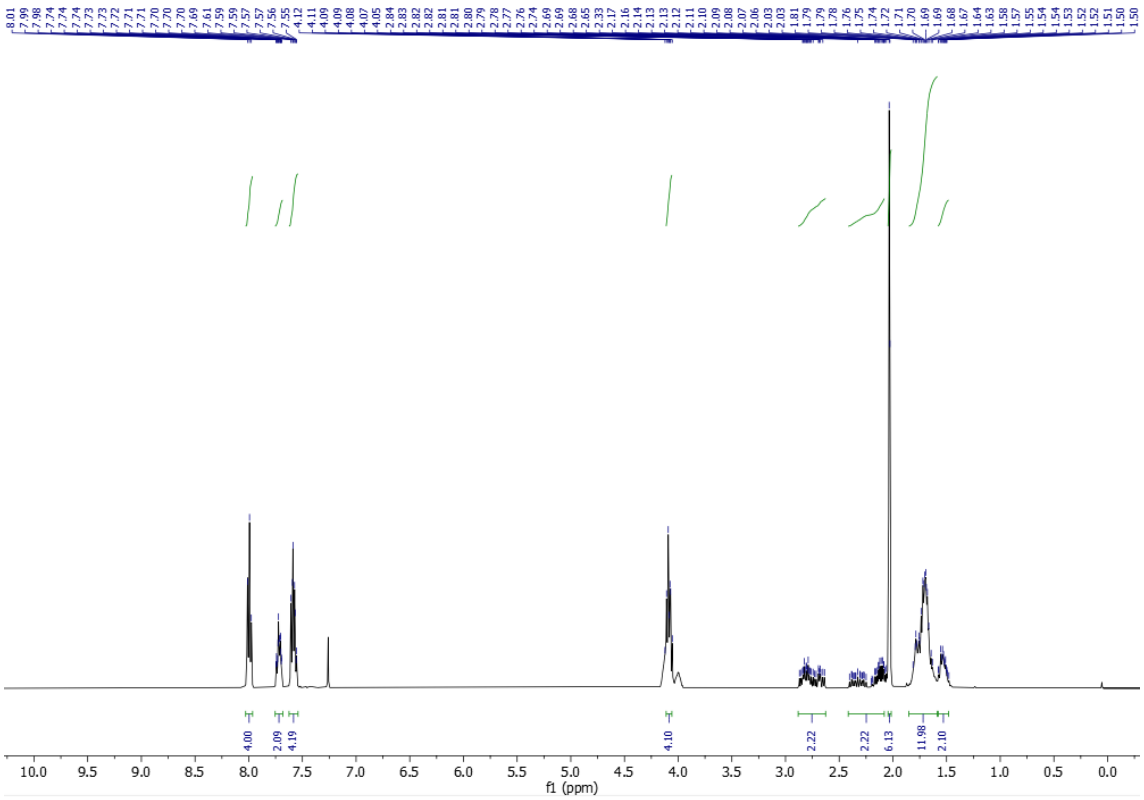
377 MHz, $CDCl_3$

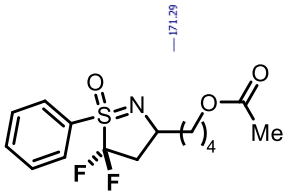


71

^{1}H NMR

400 MHz, $CDCl_3$

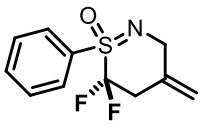




71

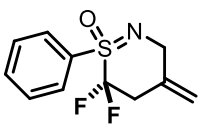
^{13}C NMR

101 MHz, $CDCl_3$



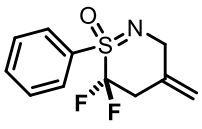
72

^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



72

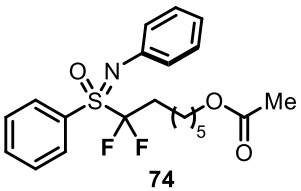
^{1}H NMR
400 MHz, $CDCl_3$



72

^{13}C NMR

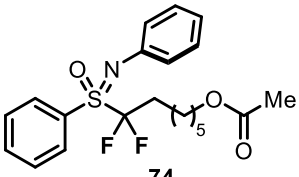
101 MHz, $CDCl_3$



74

^{19}F NMR {^{1}H}

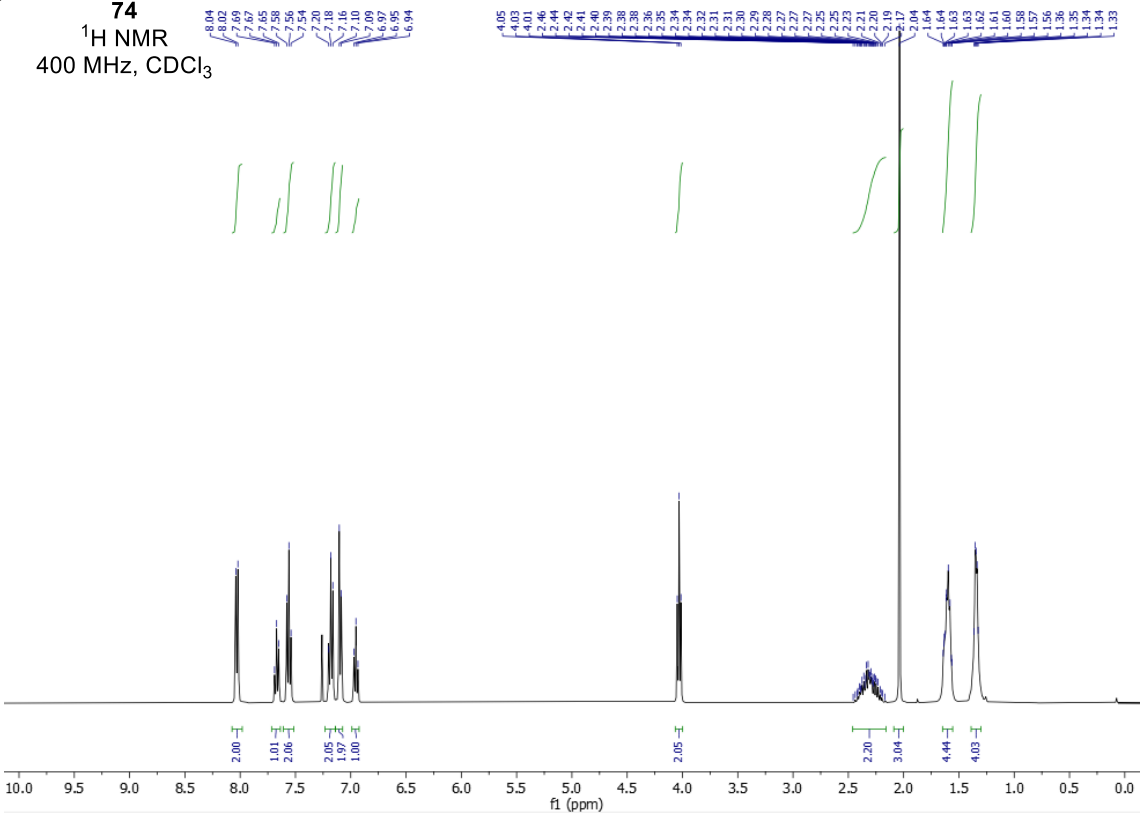
377 MHz, $CDCl_3$

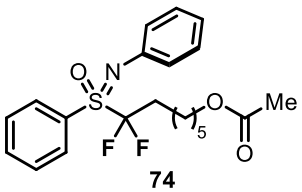


74

^{1}H NMR

400 MHz, $CDCl_3$

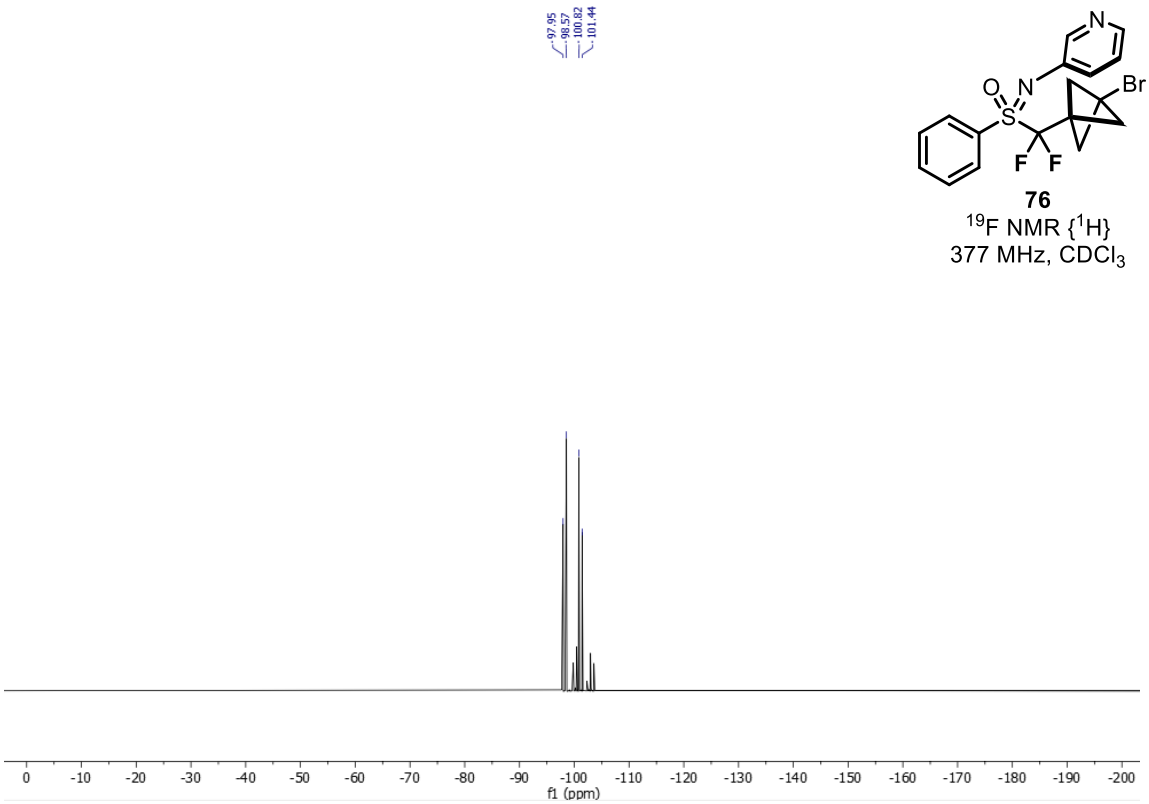




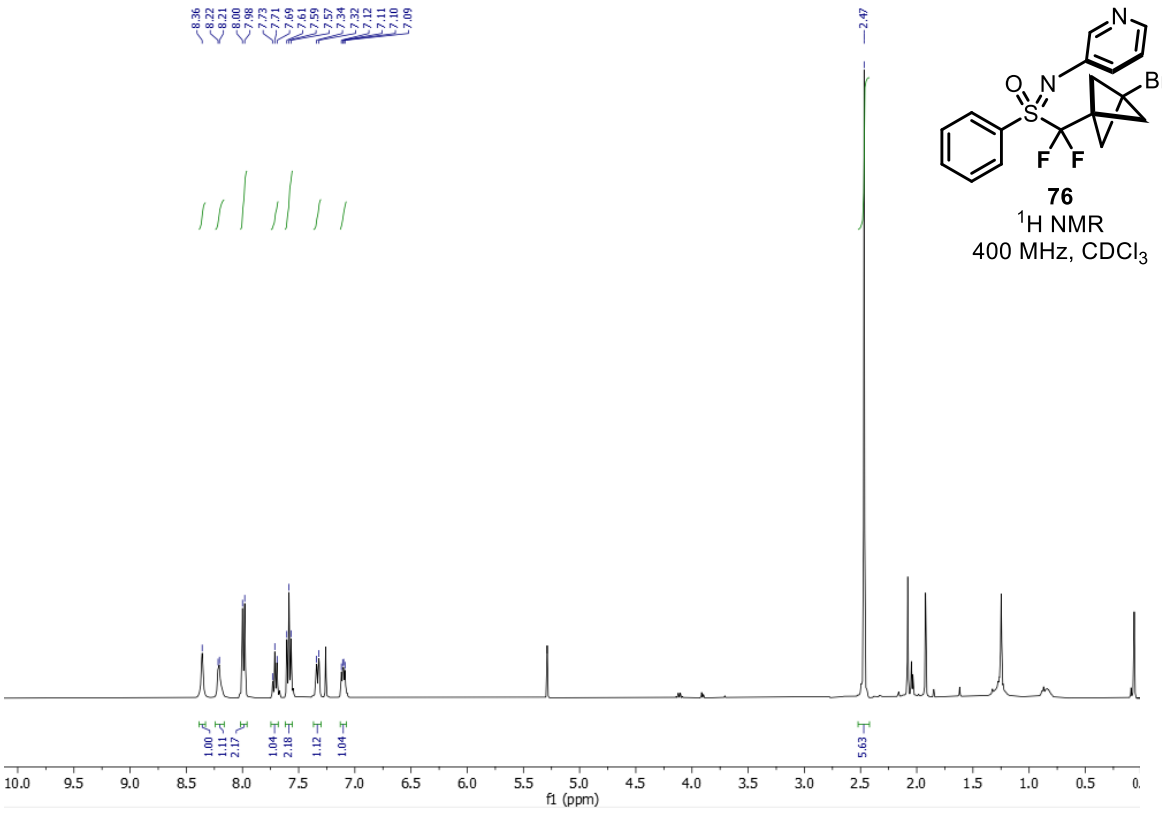
74

^{13}C NMR

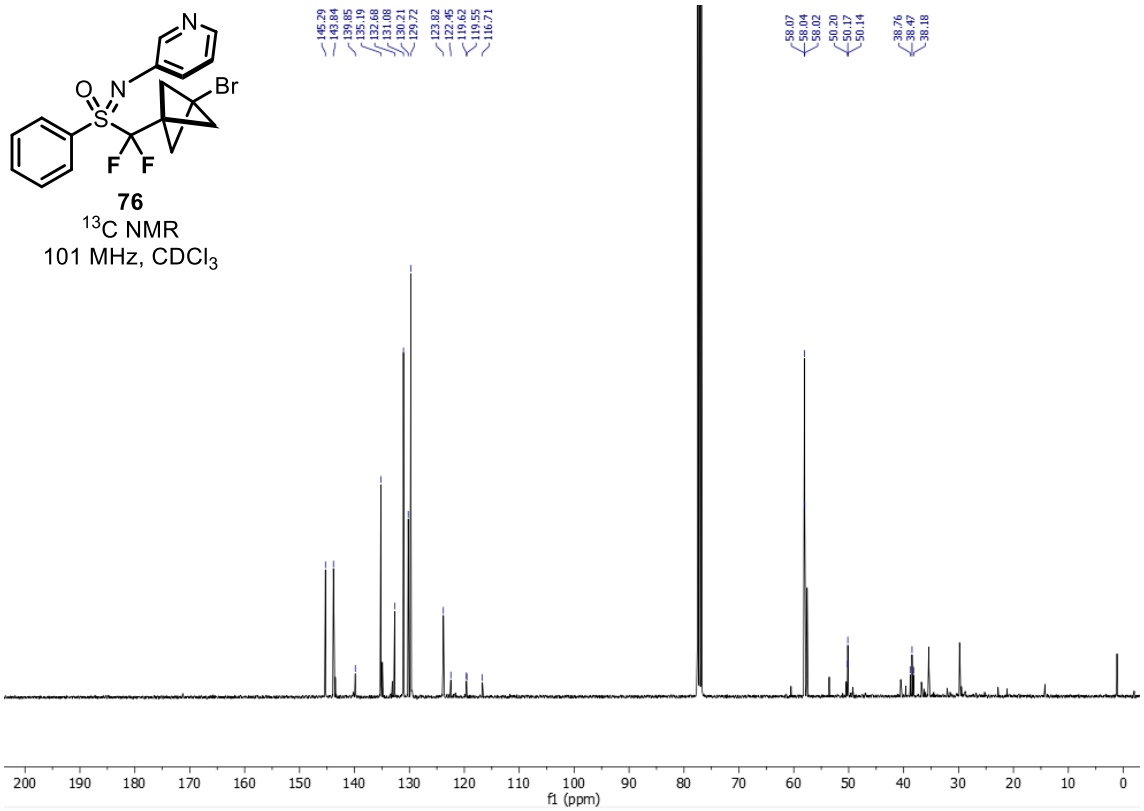
101 MHz, $CDCl_3$



76
^{19}F NMR {^{1}H}
377 MHz, $CDCl_3$



76
^{1}H NMR
400 MHz, $CDCl_3$



76

^{13}C NMR

101 MHz, $CDCl_3$