

Supporting Information

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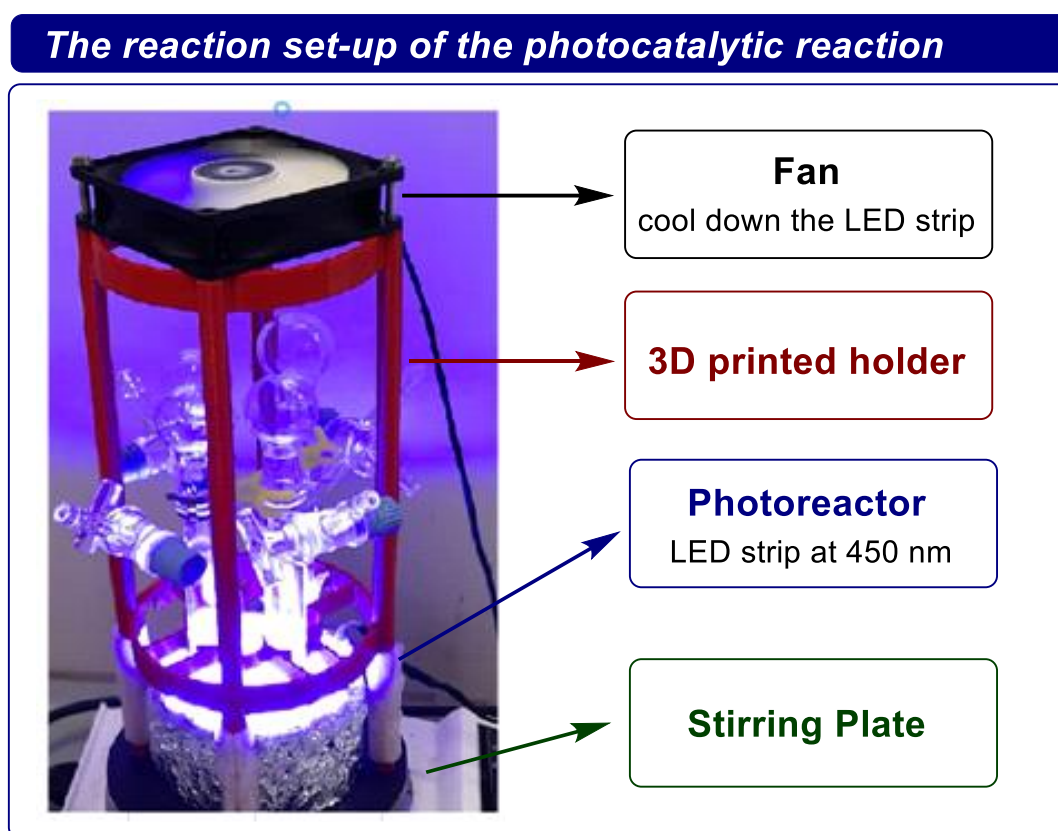
8. NMR Spectra

1. Materials and Methods

All reactions were set up under an argon atmosphere in Schlenk tubes, unless otherwise stated. Synthesis grade and anhydrous solvents were used as purchased. Chromatographic purification of products was accomplished using flash chromatography on silica gel (35-70 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF254, 0.25 mm) were employed, using UV light as the visualizing agent (254 nm), basic aqueous potassium permanganate (KMnO_4) stain solution or iodine, and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotatory evaporator. Raman spectra were acquired using an Invia Renishaw spectrometer equipped with a diode laser at 785 nm. Diffuse reflectance UV-vis spectroscopy was performed with a Thermo Scientific Evolution 600 spectrophotometer, equipped with a diffuse reflectance accessory Praying–Mantis sampling kit (Harrick Scientific Products, USA). UV-vis spectra for starting materials were performed with Shimadzu UV-2450. X-ray photoelectron microscopy (XPS) for the all nanomaterials was performed with a SPECS Sage HR 100 spectrometer with a non-monochromatic X ray source of Magnesium with a $K\alpha$ line of 1253.6 eV energy and 250 W. XPS data was fitted using CasaXPS software. Transmission electron microscopy (TEM) images were carried out on TEM Philips EM208, using an acceleration voltage of 100 kV. X-ray Diffraction (XRD) was

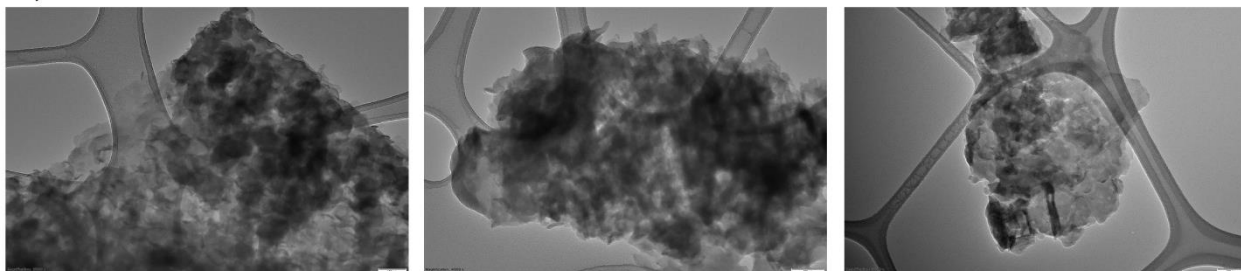
performed on a Philips X'Pert diffractometer using a monochromatized Cu K α ($\lambda = 0.154$ nm) X-ray source in the range $20^\circ < 2\theta < 100$. N₂ physisorption was performed with a Micrometrics ASAP 2020 analyzer at liquid nitrogen temperature. All the nanomaterials were degassed at 150°C for 12h at 10 μ mHg. The Specific Surface Area was calculated applying the BET method equation. Pore size distributions were determined to the adsorption branch of the isotherms with BJH method equation. CW-EPR spectra were recorded on a Bruker EMX spectrometer operating at 9.45 GHz with a modulation frequency of 100 kHz and 0.2 mT amplitude. Photoinduced EPR spectra were recorded irradiating the samples in situ using a 500 W Hg(Xe) lamp (Newport Instruments) equipped with a water filter to cut the IR emission and a cut-off filter at 420 nm.

2. Reaction set-up

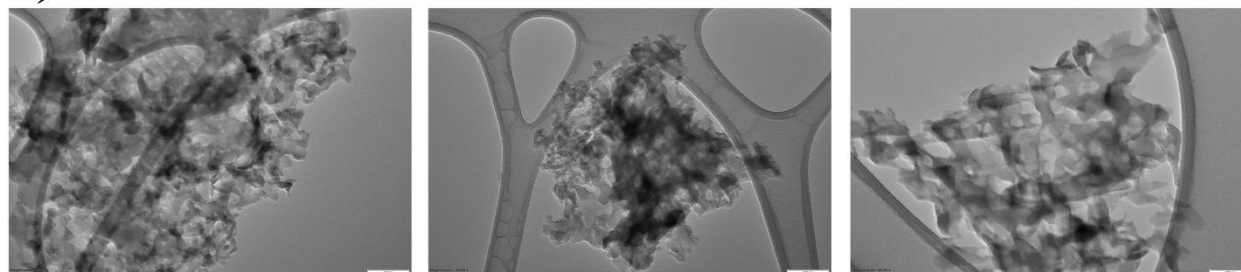


3. TEM Images

a)



b)



c)

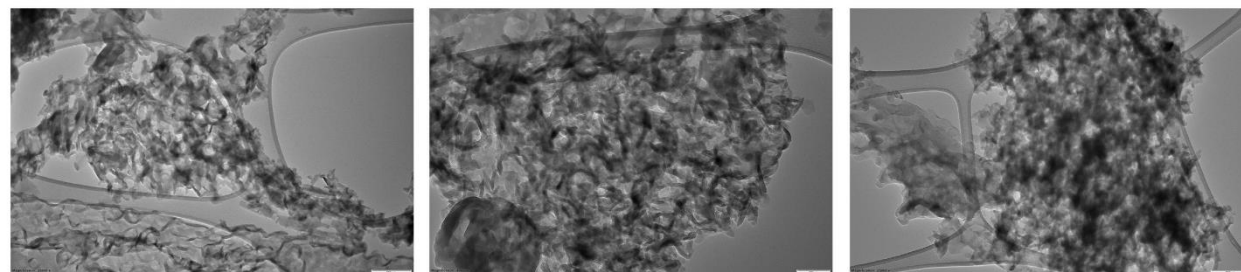


Figure S1. Representative TEM micrographs of a) am-CN, b) 4h-SACN, c) 6h-SACN

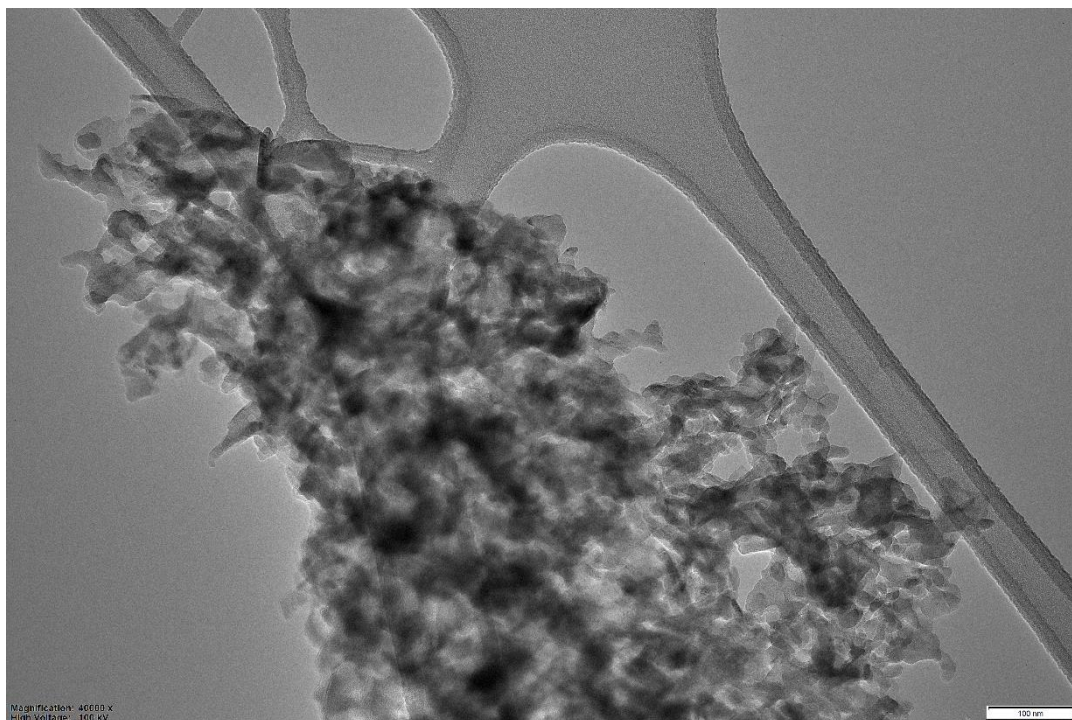


Figure S2. Representative TEM micrograph of the 6h-SACN recovered catalyst after the photocatalytic perfluoroalkylation to produce **3a**

4. Electron Paramagnetic Resonance (EPR) experiments

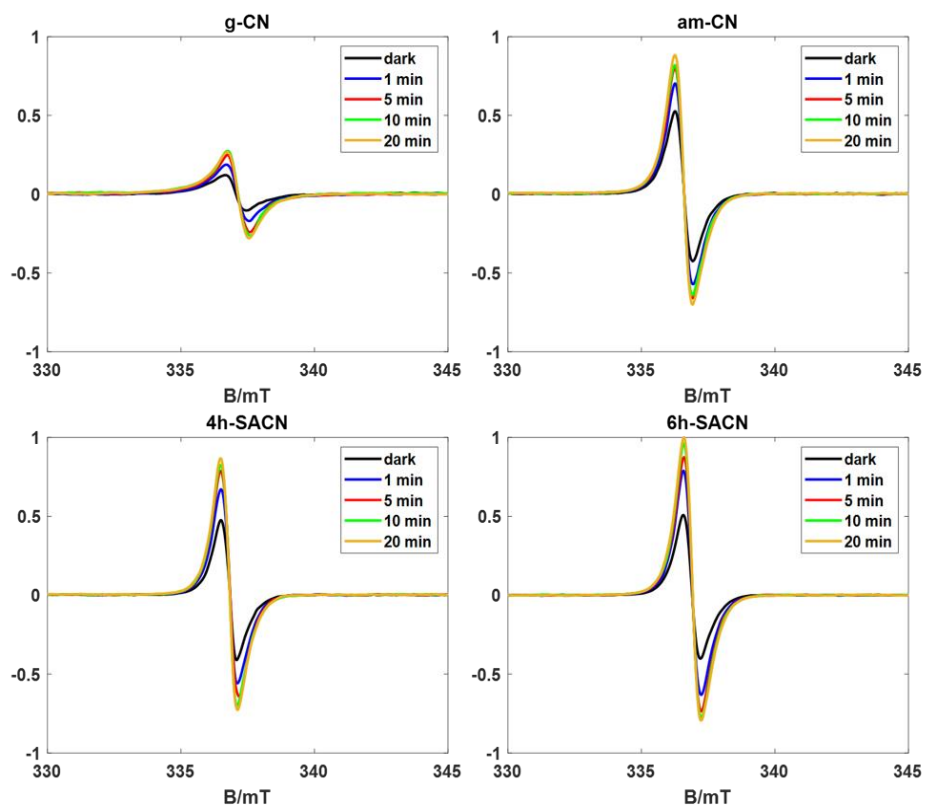


Figure S3. EPR spectra of the different CN samples recorded in air as a function of irradiation time. The spectra were recorded at 298 K at a 9.45 GHz microwave frequency and 1 mW microwave power.

5. XPS Characterization (VB measurement)

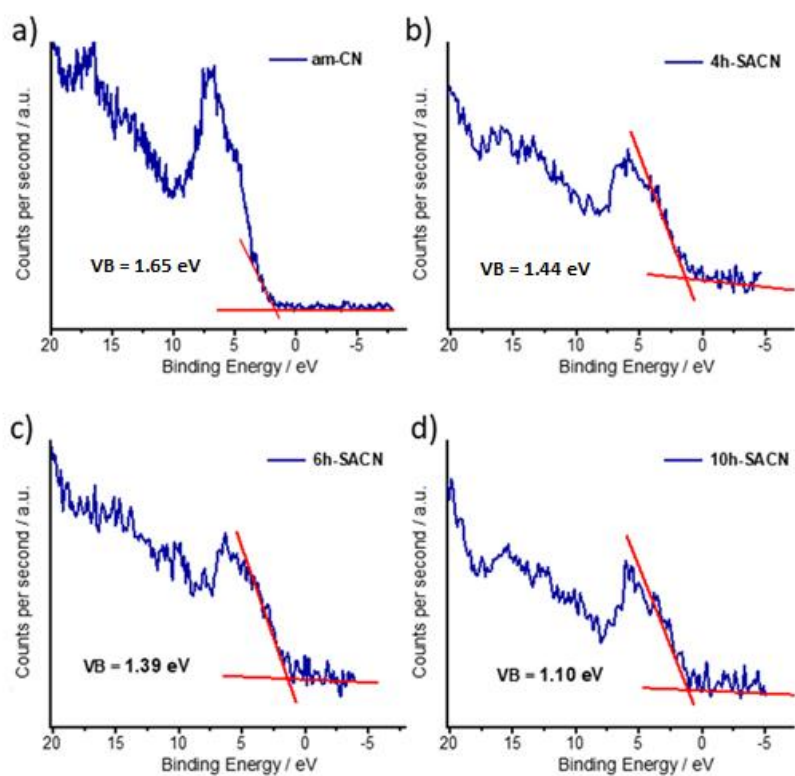


Figure S4. XPS of a) am-CN, b) 4h-SACN, c) 6h-SACN and d) 10h-SACN in the low binding energy range. The VB is calculated from the intercept of the onset of the first peak with the baseline.

6. Characterization Data

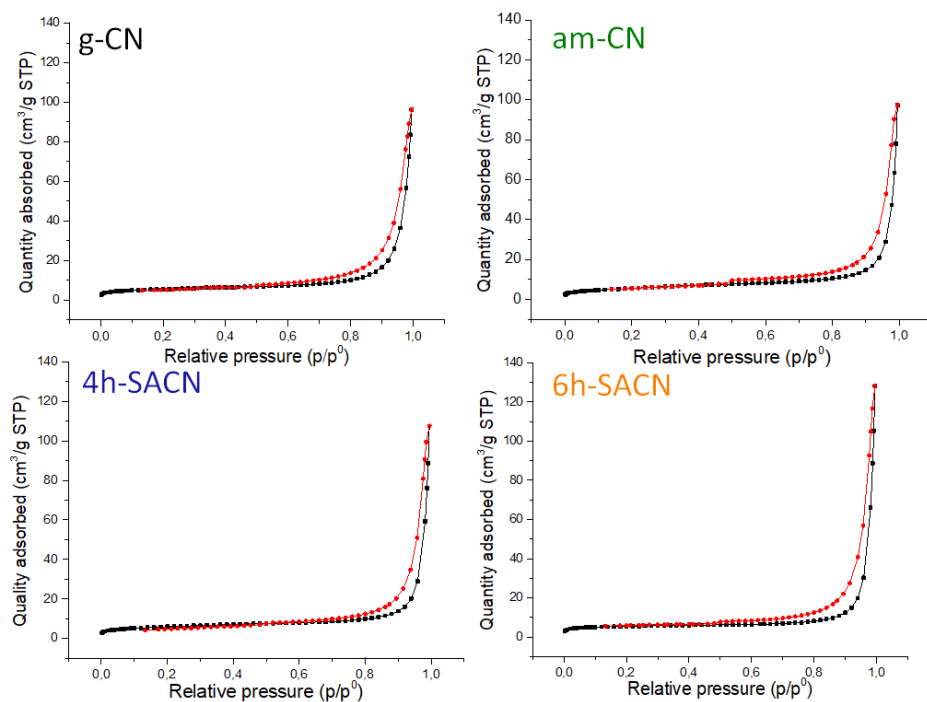


Figure S5. N₂ physisorption isotherms at 77K of the four materials.

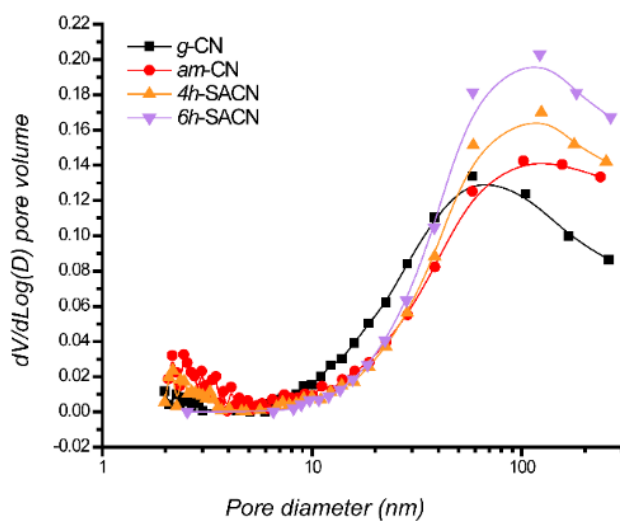


Figure S6. Pore size distribution of g-CN, am-CN, 4h-SACN, 6h-SACN

Table S1. Textural properties (pore size distribution and BET surface area) of g-CN, am-CN, 4h-SACN, 6h-SACN

Sample	Diameter pore maximum (nm)	BET surface area (m ² g ⁻¹)
<i>g</i>-CN	43	17.1
<i>am</i>-CN	118	19.0
<i>4h</i>-SACN	118	18.6
<i>6h</i>-SACN	116	15.7

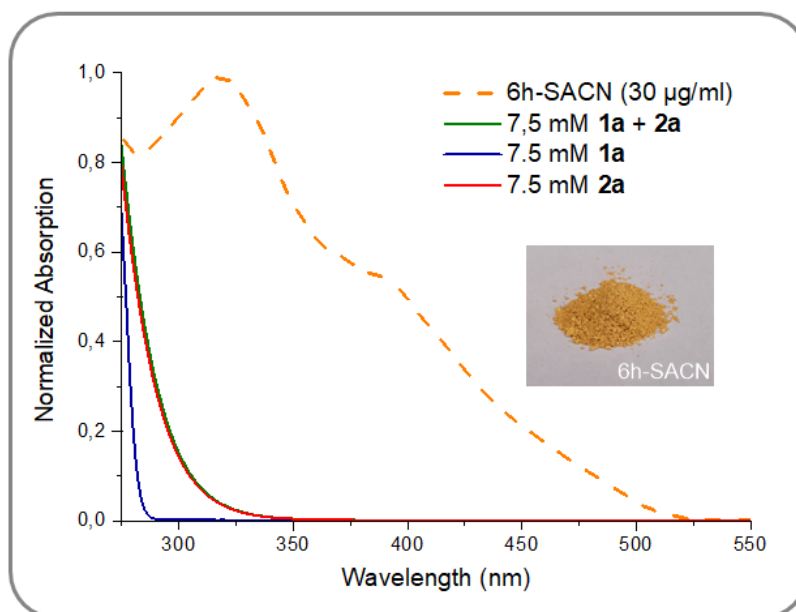


Figure S7. Normalized optical absorption spectra recorded in DMF for the best performing catalyst (6h-SACN) in the presence and absence of the reagents. In the inset, the digital picture of 6h-SACN and a graphical representation of the structure with disrupted melem strands.

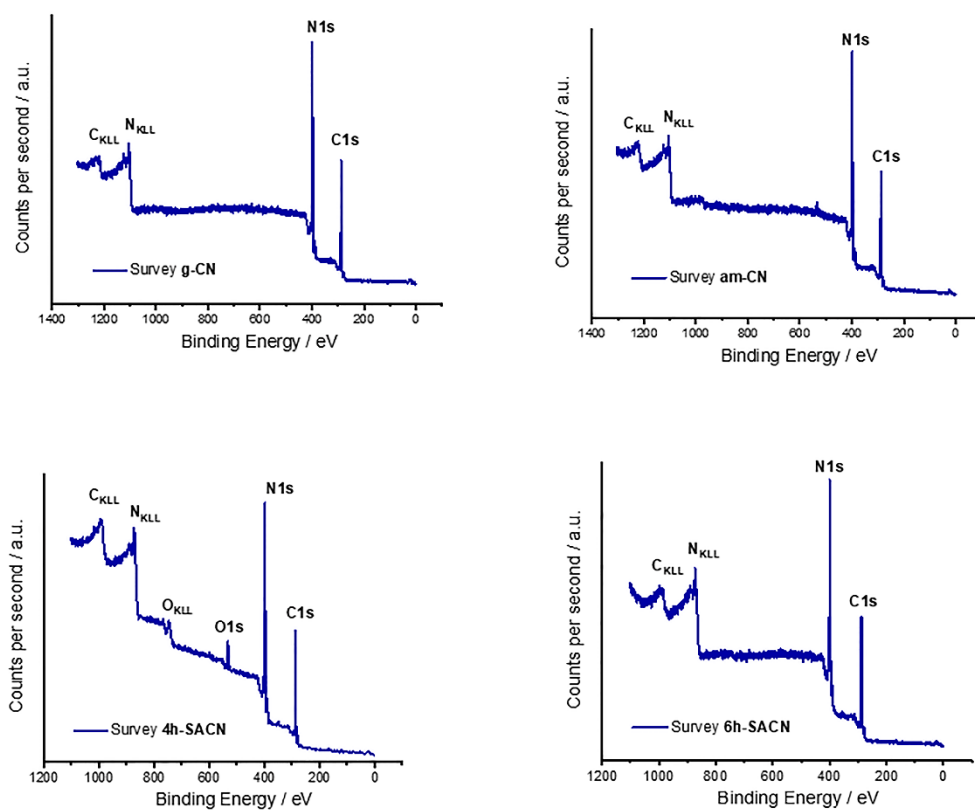


Figure S8. XPS survey of g-CN, am-CN, 4h-SACN, 6h-SACN.

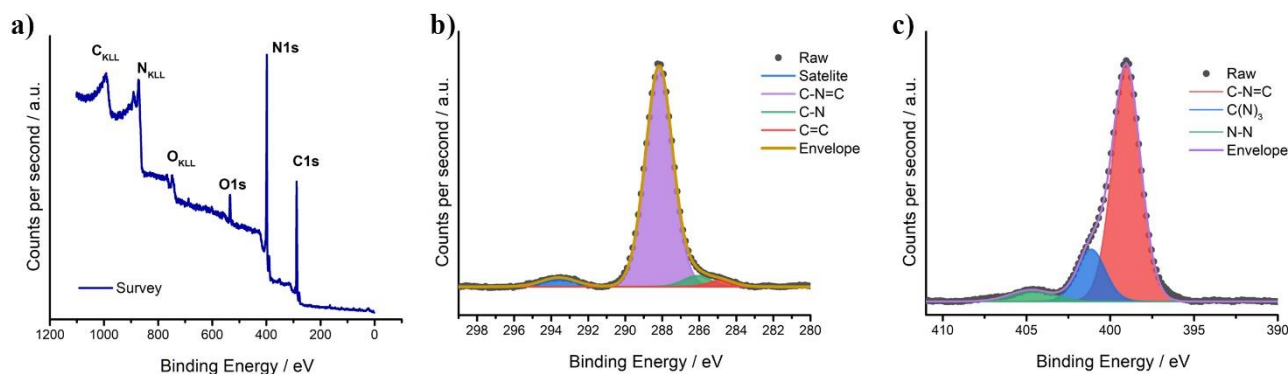


Figure S9. a) XPS survey of 10h-SACN, b) high resolution XPS in the C 1s B.E. range and in the N 1s range of 10h-SACN

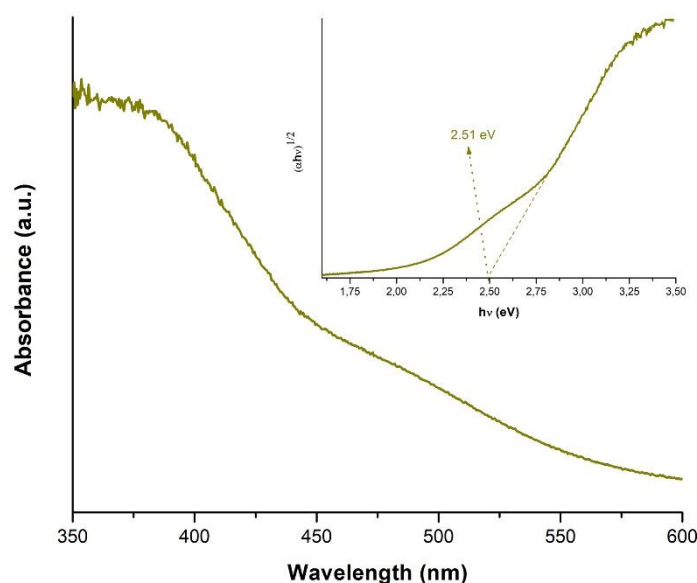
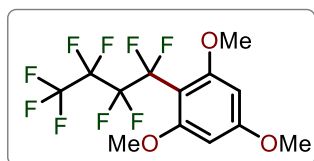


Figure S10. DR UV-Vis and corresponding Tauc plot (inset) of 10h-SACN.

Table S2. Total atomic percentages of N and C atoms as calculated by XPS

Sample	C/ at %	N/ at%
<i>g</i>-CN	43.5	56.5
<i>am</i>-CN	45.4	54.6
<i>4h</i>-SACN	41.6	58.4
<i>6h</i>-SACN	43.4	56.6

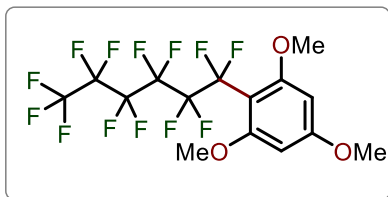
Note: Due to C-F coupling, some carbon signals of the perfluorinated products **3** were not detectable.



1,3,5-trimethoxy-2-(perfluorobutyl)benzene (3a). Prepared according to the general procedure using 1,3,5-trimethoxybenzene **1a** (0.1 mmol, 17 mg) and nonafluoro-1-iodobutane **2a** (0.6 mmol, 103 μ L). The product **3a** was obtained as white solid (35 mg, 90% yield). The characterization of the compound matches

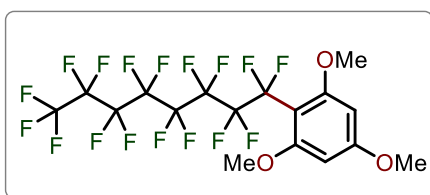
with the data reported in the literature. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 6.15 (s, 2H), 3.84 (s, 3H), 3.80 (s, 6H);

^{19}F -NMR (376 MHz, CDCl_3) δ -80.97 (m, 3F), -102.86 (m, 2F), -123.00 (m, 2F), -126.44 (m, 2F); HRMS calculated for $\text{C}_{13}\text{H}_{11}\text{F}_9\text{O}_3$ (M-Na): 409.0462, found: 409.0463.



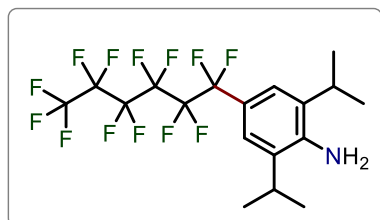
1,3,5-trimethoxy-2-(perfluorohexyl)benzene (3b). Prepared according to the general procedure using 1,3,5-trimethoxybenzene **1a** (0.1 mmol, 17 mg) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μL). The product **3b** was obtained as white solid (47 mg, 97% yield). The characterization of the compound matches with the data reported in the literature.¹ ^1H -NMR

(400 MHz, CDCl_3) δ 6.13 (s, 2H), 3.85 (s, 3H), 3.81 (s, 6H); ^{19}F -NMR (376 MHz, CDCl_3) δ -80.83 (m, 3F), -102.67 (m, 2F), -122.14 (m, 4F), -122.69 (m, 2F), -126.17 (m, 2F); HRMS calculated for $\text{C}_{15}\text{H}_{11}\text{F}_{13}\text{O}_3$ (M-Na): 509.0398, found: 509.0390.



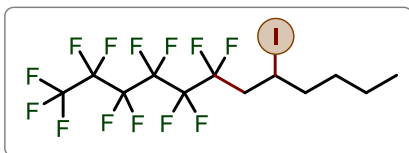
1,3,5-trimethoxy-2-(perfluorooctyl)benzene (3c). Prepared according to the general procedure using 1,3,5-trimethoxybenzene **1a** (0.1 mmol, 17 mg) and heptadecafluoro-1-iodooctane **2c** (0.6 mmol, 158 μL). The product **3c** was obtained as white solid (53 mg, 90%

yield). The characterization of the compound matches with the data reported in the literature.¹ ^1H -NMR (400 MHz, CDCl_3) δ 6.15 (s, 2H), 3.84 (s, 3H), 3.80 (s, 6H); ^{19}F -NMR (376 MHz, CDCl_3) δ -80.84 (t, $J = 10.0$ Hz, 3F), -102.66 (m, 2F), -121.75 (m, 2F), -122.05 (m, 6F), -122.79 (m, 2F), -126.15 (m, 2F); HRMS calculated for $\text{C}_{17}\text{H}_{11}\text{F}_{17}\text{O}_3$ (M-Na): 609.0334, found: 609.0335.



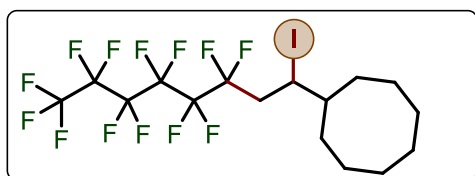
2,6-diisopropyl-4-(perfluorohexyl)aniline (3e). Prepared according to the general procedure using 2,6-diisopropylaniline **1b** (0.1 mmol, 19 μL) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μL). The product **3e** was obtained as white solid (36 mg, 72% yield). The characterization of the compound matches with the data reported in the literature.¹ ^1H NMR (400 MHz,

CDCl_3) δ 7.19 (s, 2H), 4.05 (s, 2H), 2.91 (hept, $J = 6.8$ Hz, 2H), 1.29 (d, $J = 6.8$ Hz, 12H); ^{19}F NMR (376 MHz, CDCl_3) δ -80.85 (m, 3F), -109.41 (m, 2F), -121.57 (m, 2F), -121.89 (m, 2F), -122.85 (m, 2F), -126.17 (m, 2F); HRMS calculated for $\text{C}_{18}\text{H}_{18}\text{F}_{13}\text{N}$ (M-H): 496.1309, found: 496.1306.



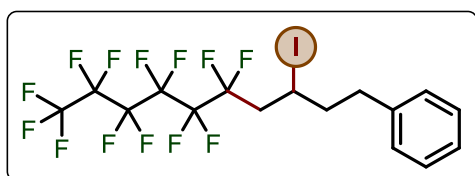
1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-8-iodododecane (3f). Prepared according to the general procedure using 1-hexene **1c** (0.1 mmol, 13 μL) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μL). The product **3f** was obtained as colorless oil (39 mg, 74% yield). The characterization of the

compound matches with the data reported in the literature.¹ ^1H NMR (400 MHz, CDCl_3) δ 4.43 – 4.26 (m, 1H), 3.04 – 2.66 (m, 2H), 1.94 – 1.72 (m, 2H), 1.58 – 1.22 (m, 4H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -80.86 (m, 3F), -111.92 (m, 1F), -114.69 (m, 1F), -121.84 (m, 2F), -122.91 (m, 2F), -123.69 (m, 2F), -126.19 (m, 2F); It was not possible to measure the HRMS (ESI-MS) of compound **3f** due to its poor tendency to ionize.



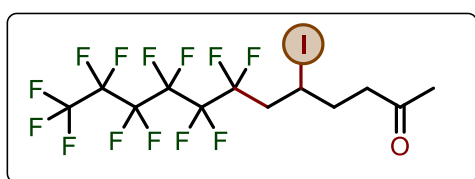
(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-iodooctyl) cyclooctane (3g) Prepared according to the general procedure using vinylcyclooctane **1d** (0.1 mmol, 14 mg) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L). The product **3g** was obtained as colorless

oil (49 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3) δ 4.38 (td, $J = 6.7, 2.6$ Hz, 1H), 2.80 (m, 2H), 1.75 (m, 2H), 1.49 (m, 12H), 1.24 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 43.12 (d, $J = 1.5$ Hz), 39.24 (t, $J = 20.8$ Hz), 36.07 (s), 34.05 (s), 31.49 (s), 29.74 (s), 26.52 (s), 26.33 (s), 26.03 (s), 25.79 (s). ^{19}F NMR (376 MHz, CDCl_3) δ -80.83 (m, 3F), -111.82 (m, 1F), -114.87 (m, 1F), -121.78 (m, 2F), -122.88 (m, 2F), -123.58 (m, 2F), -126.16 (m, 2F). It was not possible to measure the HRMS (ESI-MS) of compound **3g** due to its poor tendency to ionize.



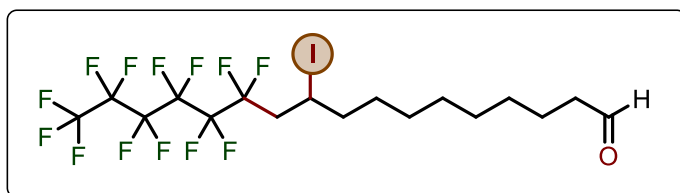
(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-3-iododecyl)benzene (3h) Prepared according to the general procedure using 4-Phenyl-1-butene **1e** (0.1 mmol, 15 μ L) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L). The product **3h** was obtained as colorless oil (54

mg, 93% yield). The characterization of the compound matches with the data reported in the literature². ^1H NMR (400 MHz, CDCl_3) δ 7.34 – 7.27 (m, 2H), 7.22 (td, $J = 6.0, 1.4$ Hz, 3H), 4.27 (ddd, $J = 13.6, 8.5, 5.2$ Hz, 1H), 3.05 – 2.68 (m, 4H), 2.21 – 2.04 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.83 (s), 128.58 (s), 128.46 (s), 126.36 (s), 41.89 (s), 41.75 (d, $J = 2.2$ Hz), 41.69 (s), 35.66 (s), 20.05 (s). ^{19}F NMR (376 MHz, CDCl_3) δ -80.50 (m, 3F), -111.34 (m, 1F), -114.37 (m, 1F), -121.79 (m, 2F), -122.89 (m, 2F), -123.67 (m, 2F), -126.17 (m, 2F). It was not possible to measure the HRMS (ESI-MS) of compound **3h** due to its poor tendency to ionize.



7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododecan-2-one (3i)

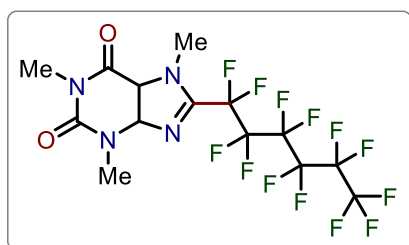
Prepared according to the general procedure using 5-Hexen-2-one **1f** (0.1 mmol, 12 μ L) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L). The product **3i** was obtained as colorless oil (50 mg, 92% yield). ^1H NMR (400 MHz, CDCl_3) δ 4.35 (m, 1H), 2.81 (m, 4H), 2.14 (m, 4H), 2.00 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 206.60 (s), 43.79 (s), 42.02 (t, $J = 20.9$ Hz), 34.21 (d, $J = 2.3$ Hz), 30.24 (s), 19.91 (s). ^{19}F NMR (376 MHz, CDCl_3) δ -80.87 (m, 3F), -111.85 (m, 1F), -114.47 (m, 1F), -121.82 (m, 2F), -122.91 (m, 2F), -123.66 (m, 2F), -126.19 (m, 2F). HRMS calculated for $\text{C}_{12}\text{H}_{10}\text{F}_{13}\text{IO}$ (M-Na): 566,9461 Found: 566,9460.



12,12,13,13,14,14,15,15,16,16,17,17,17-tridecafluoro-10-iodoheptadecanal (3j)

Prepared according to the general procedure using 5-Hexen-2-one **1g** (0.1 mmol, 20 μ L) and

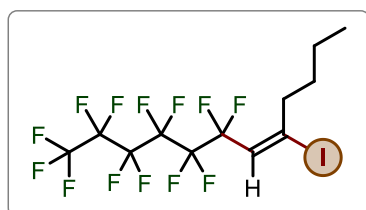
perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L). The product **3j** was obtained as colorless oil (46 mg, 75% yield). ^1H NMR (400 MHz, CDCl_3) δ 9.76 (s, 1H), 4.32 (m, 1H), 2.84 (m, 2H), 2.42 (td, $J = 7.3, 1.7$ Hz, 2H), 1.80 (m, 2H), 1.45 (m, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 202.96 (s), 44.03 (s), 41.81 (t, $J = 20.8$ Hz), 40.42 (d, $J = 2.1$ Hz), 29.65 (s), 29.36 (s), 29.27 (s), 29.22 (s), 28.55 (s), 22.17 (s), 20.97 (s). ^{19}F NMR (376 MHz, CDCl_3) δ -80.84 (m, 3F), -111.63 (m, 1F), -114.67 (m, 1F), -121.82 (m, 2F), -122.90 (m, 2F), -123.68 (m, 2F), -126.18 (m, 2F). HRMS calculated for $\text{C}_{17}\text{H}_{20}\text{F}_{13}\text{IO}$ (M-Na): 637,0243 Found: 637,0244.



1,3,7-trimethyl-8-(perfluorohexyl)-3,7-dihydro-1H-purine-2,6-dione (3k)

Prepared according to the general procedure using caffeine **1h** (0.1 mmol, 19 mg) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L) using 1.8 mg/mL of 6h-SACN. The product **3k** was obtained as white solid (25 mg, 48% yield). The characterization of the compound matches

with the data reported in the literature. ^1H NMR (400 MHz, CDCl_3) δ 4.19 (s, 3H), 3.60 (s, 3H), 3.42 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -80.74 (m, 3F), -108.96 (m, 2F), -121.01 (m, 2F), -121.39 (m, 2F), -122.71 (m, 2F), -126.06 (m, 2F); HRMS calculated for $\text{C}_{14}\text{H}_{11}\text{F}_{13}\text{N}_4\text{O}_2$ (M-K): 553.0311, found: 553.0526.

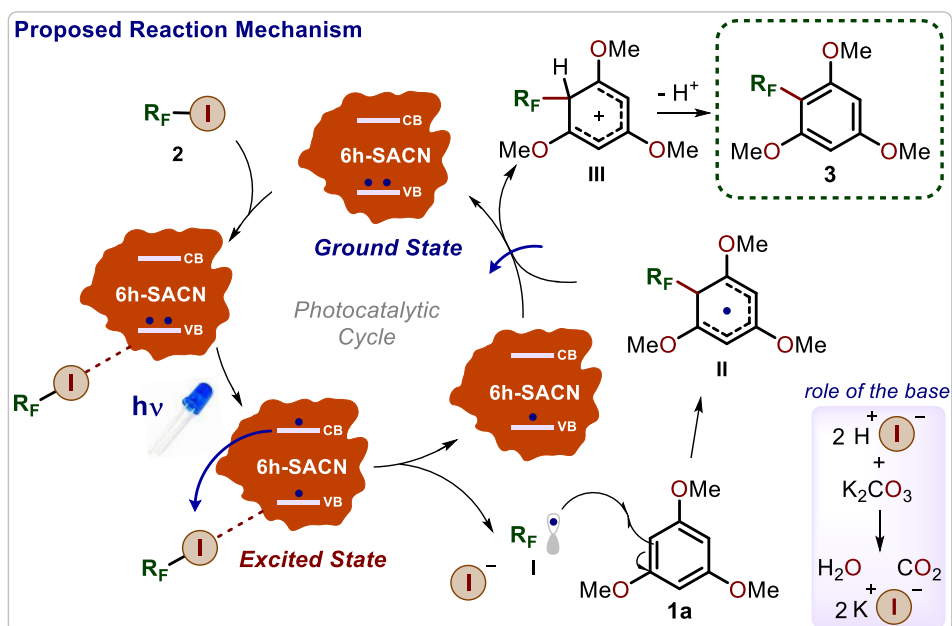


(E)-7,7,8,8,9,9,10,10,11,11,12,12,12-tridecafluoro-5-iodododec-5-ene (3l)

Prepared according to the general procedure using 1-hexyne **1i** (0.1 mmol, 12 μ L) and perfluorohexyl iodide **2b** (0.6 mmol, 130 μ L). The product **3l** was obtained as colorless oil (47 mg, 88% yield, 4:1 *E/Z*). The characterization of the compound matches with the data reported in the

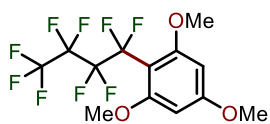
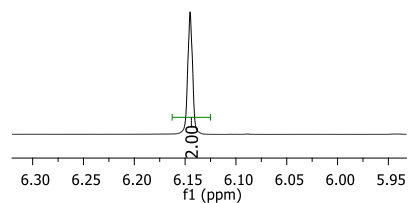
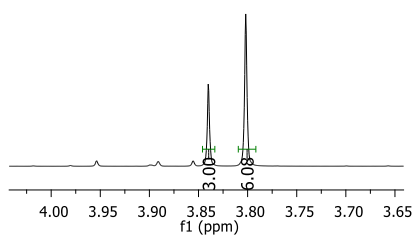
literature. 1 (*E*)-isomer: ^1H -NMR (400 MHz, CDCl_3) δ 6.35 (t, $J = 14.4$ Hz, 1H), 2.66 (t, $J = 7.6$ Hz, 2H), 1.59 (m, 2H), 1.38 (m, 2H), 0.97 (t, $J = 7.3$ Hz, 3H). The (*Z*)-isomer appears at 6.16 ppm; (*E*)-isomer: ^{19}F -NMR (376 MHz, CDCl_3) δ -80.82 (t, $J = 10.4$ Hz, 3F), -105.46 (t, $J = 13$ Hz, 2F), -121.70 (m, 2F), -122.86 (m, 2F), -123.30 (m, 2F), -126.17 (m, 2F). The (*Z*)-isomer appears at -108.50 ppm; It was not possible to measure the HRMS (ESI-MS) of compound **3l** due to its poor tendency to ionize.

7. Proposed Reaction Mechanism



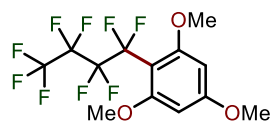
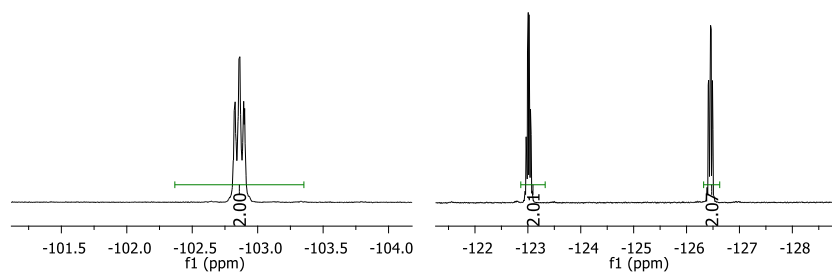
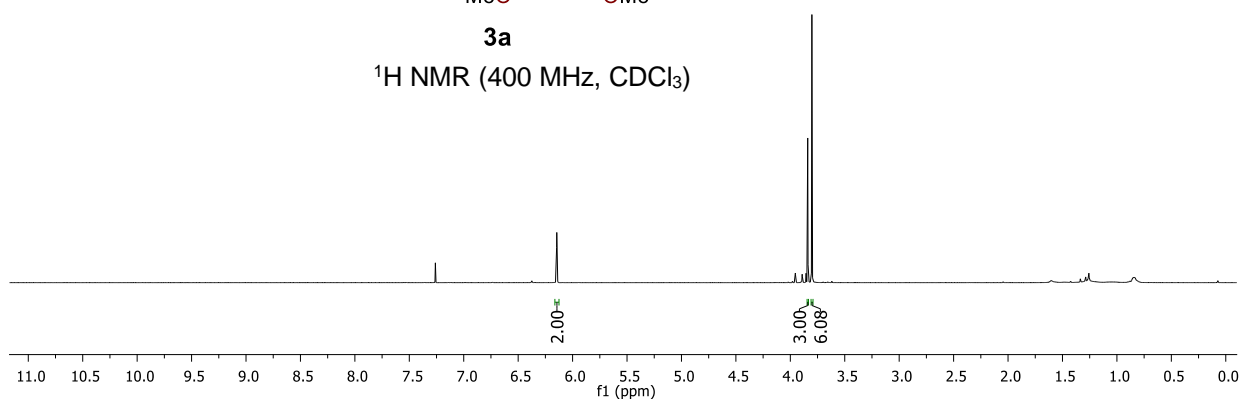
On the whole, we proposed a possible reaction mechanism which drives the photocatalytic process. The fluorinated substrates (**2**) interact with the solid surface of 6h-SACN through formation of halogen bonding. Subsequently, the photoinduced charge separation within the semiconductor trigger a radical mechanism which lead to the production of the final perfluoroalkylated adduct, namely **3a**.

8. NMR Spectra



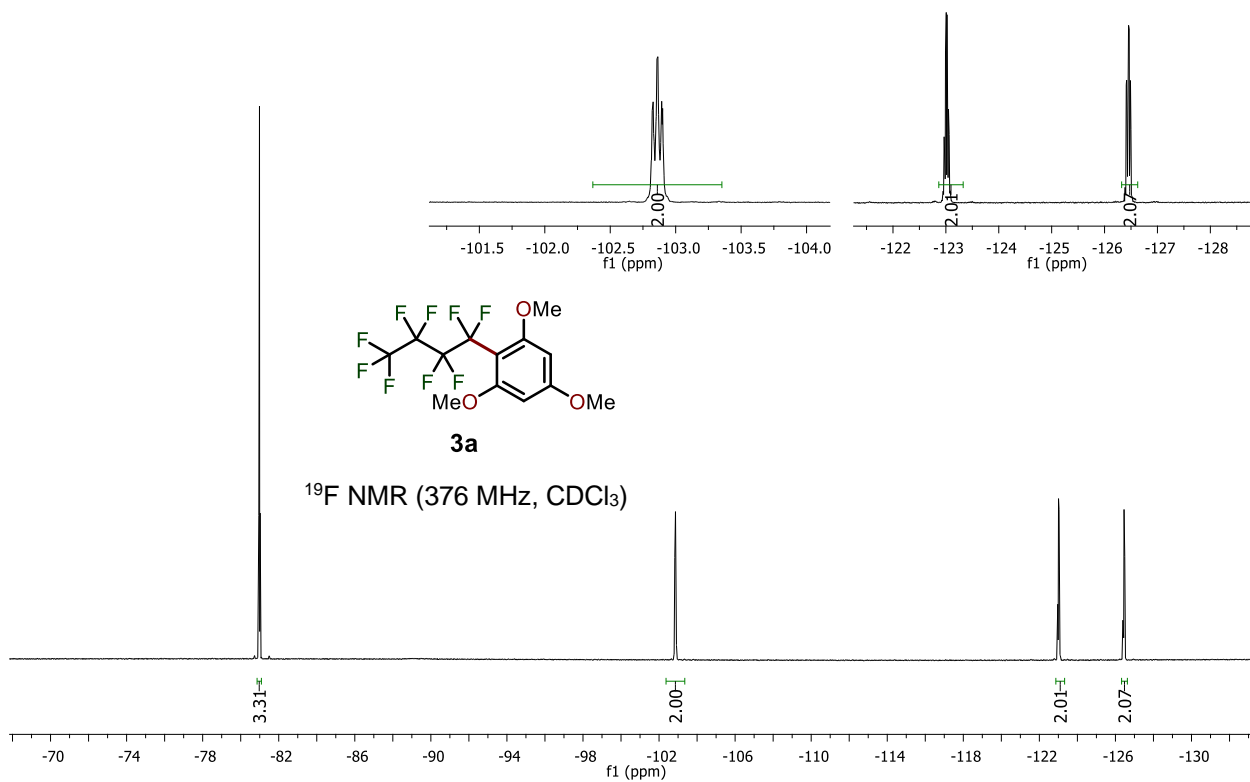
3a

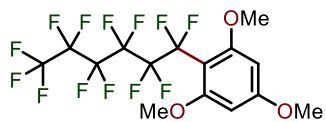
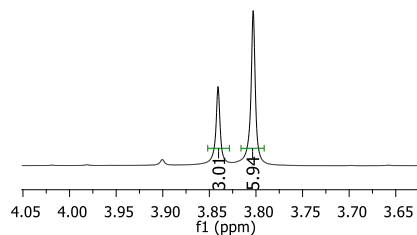
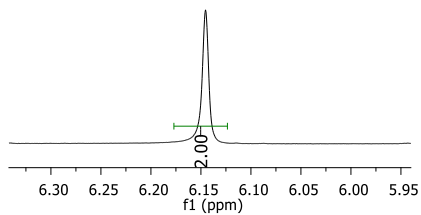
¹H NMR (400 MHz, CDCl₃)



3a

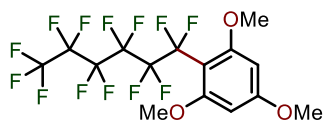
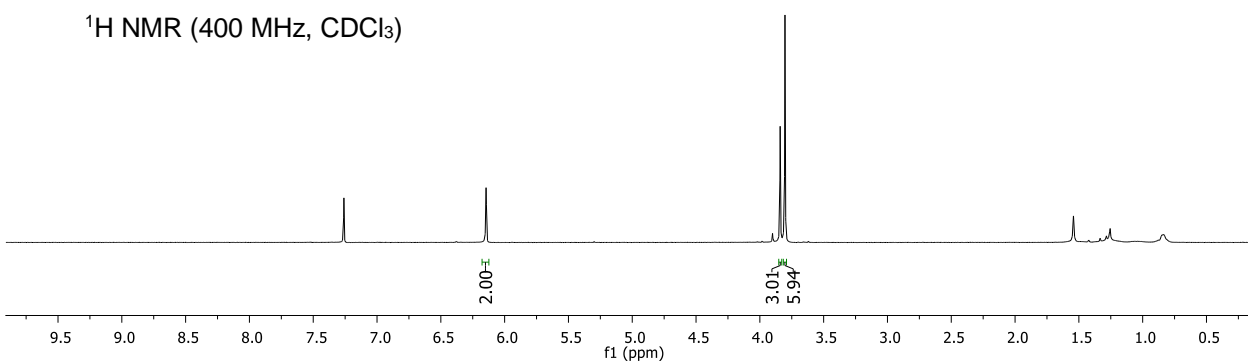
¹⁹F NMR (376 MHz, CDCl₃)





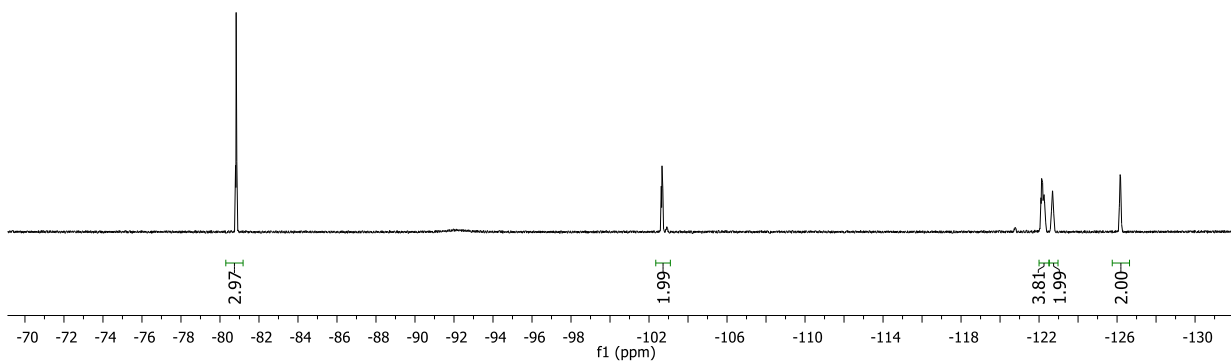
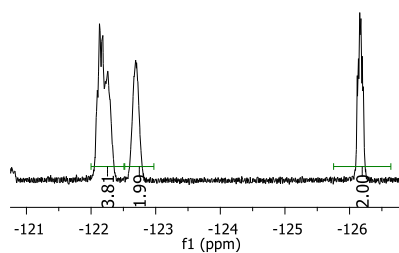
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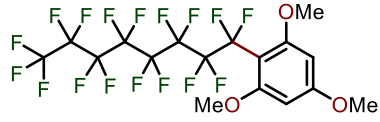
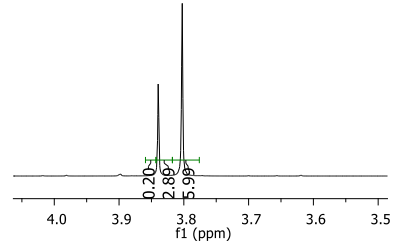
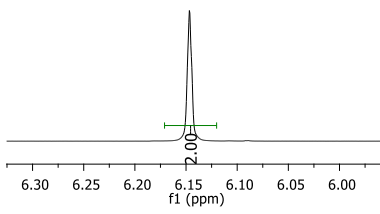
¹H NMR (400 MHz, CDCl₃)



3b

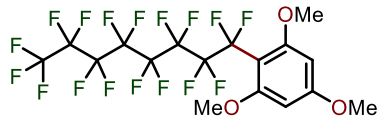
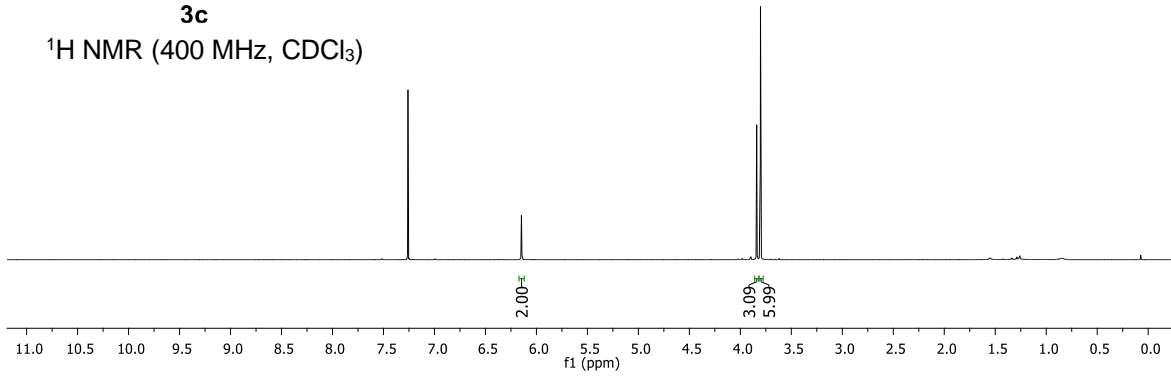
¹⁹F NMR (376 MHz, CDCl₃)





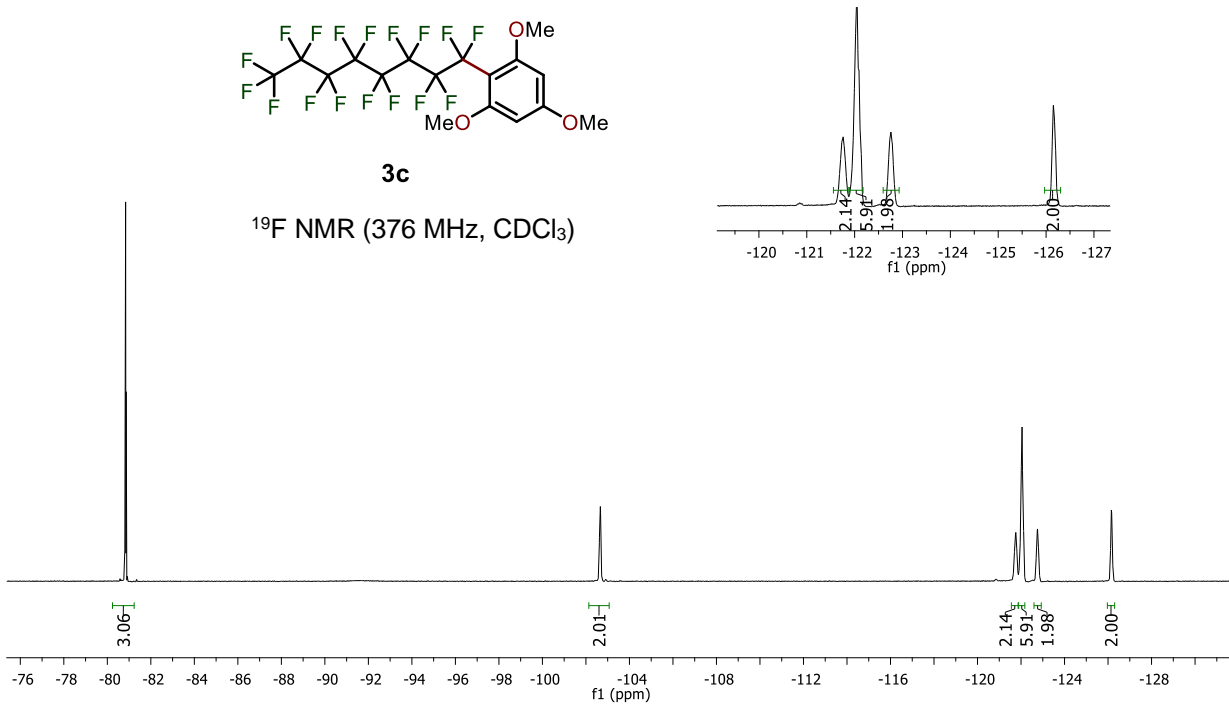
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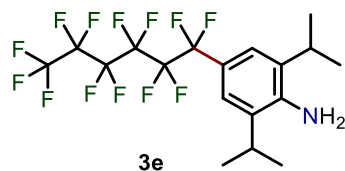
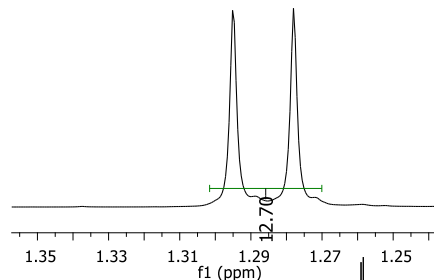
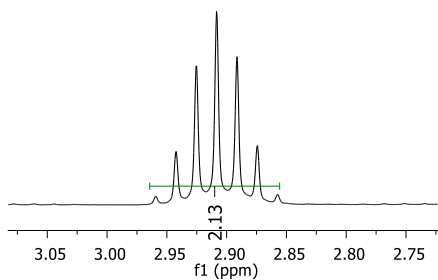
¹H NMR (400 MHz, CDCl₃)



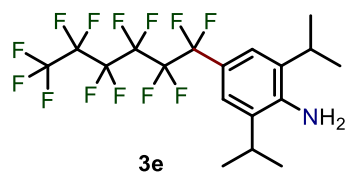
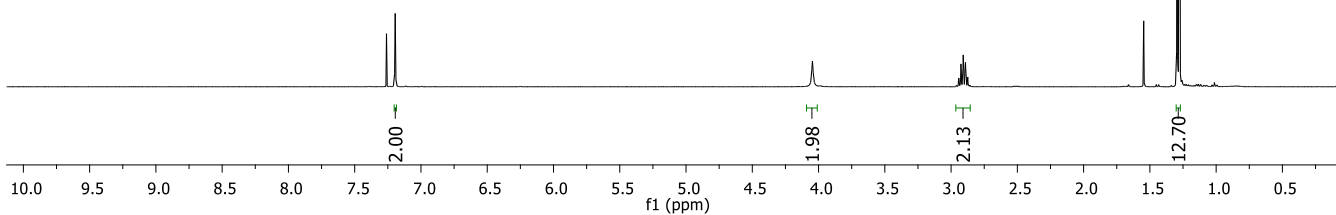
3c

¹⁹F NMR (376 MHz, CDCl₃)

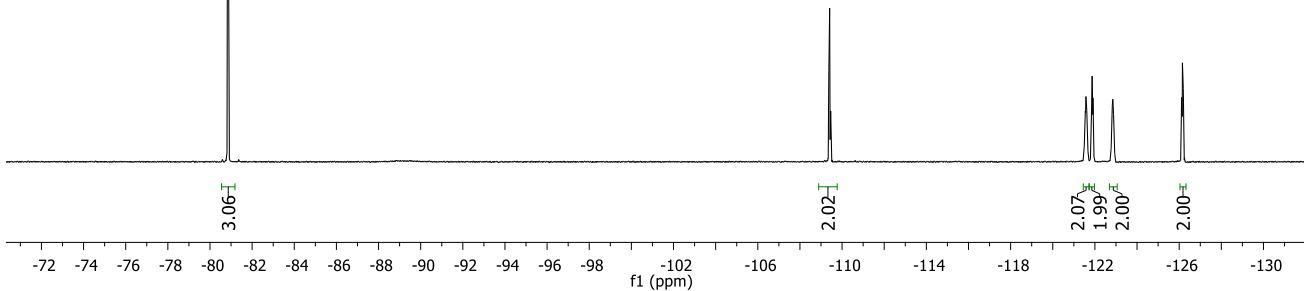
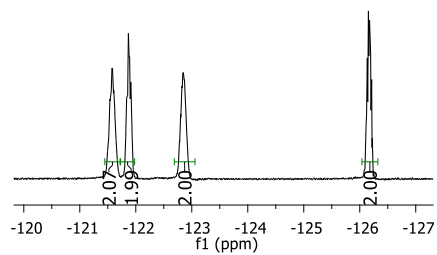


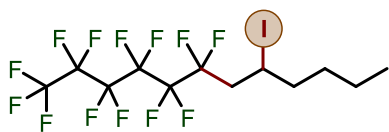


¹H NMR (400 MHz, CDCl₃)



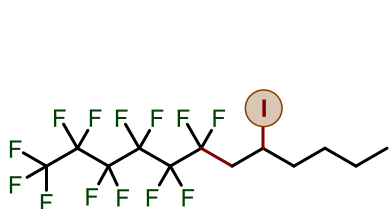
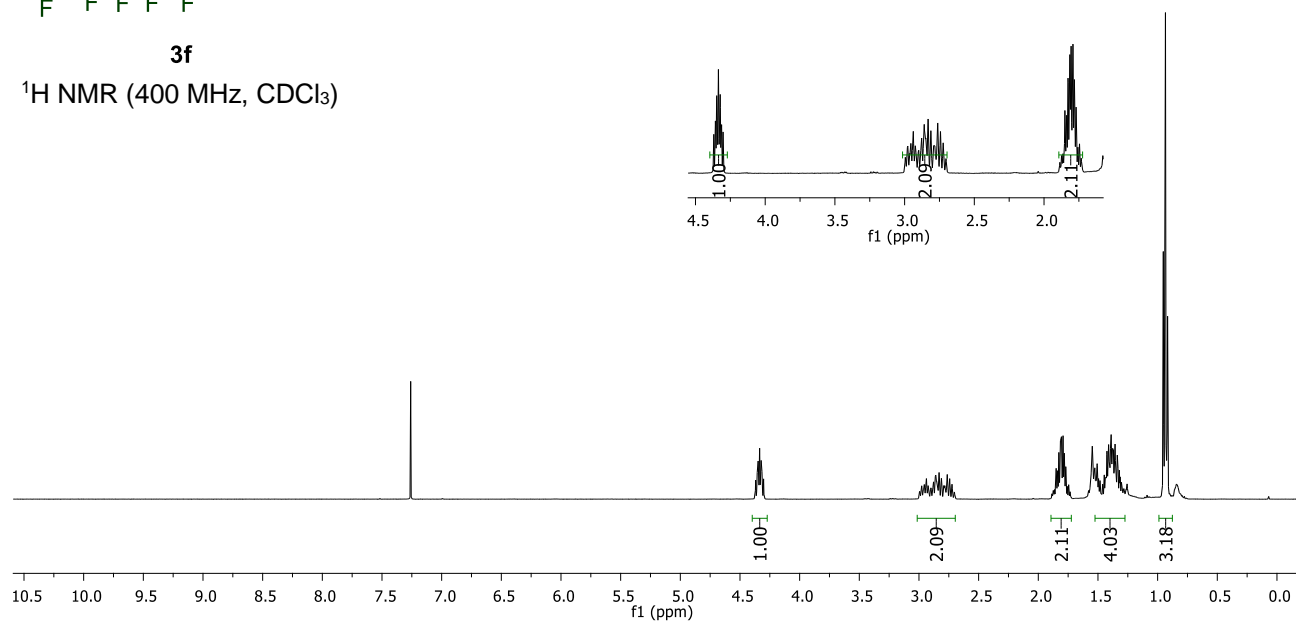
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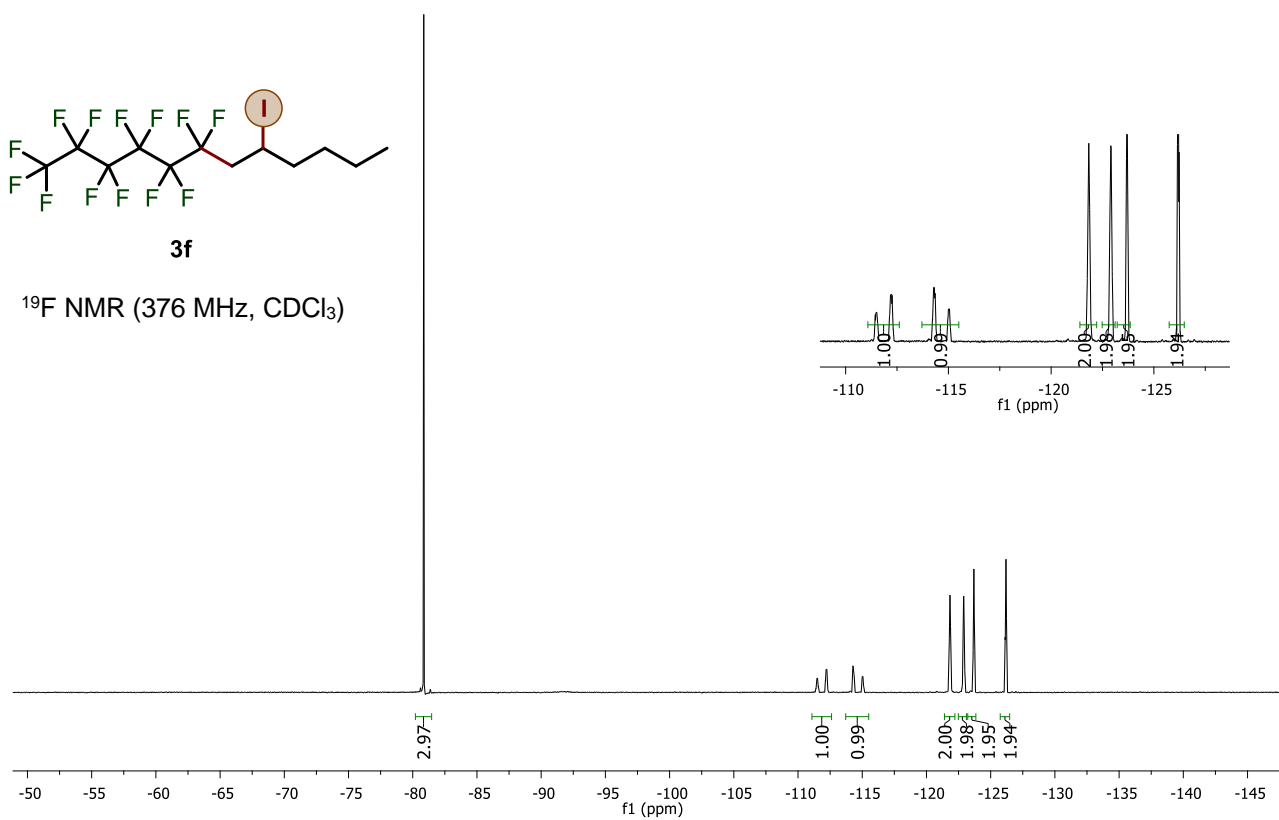
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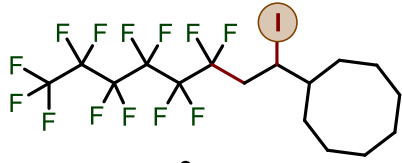
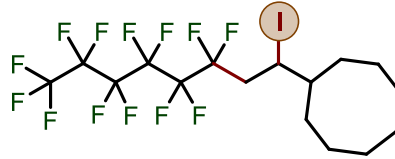
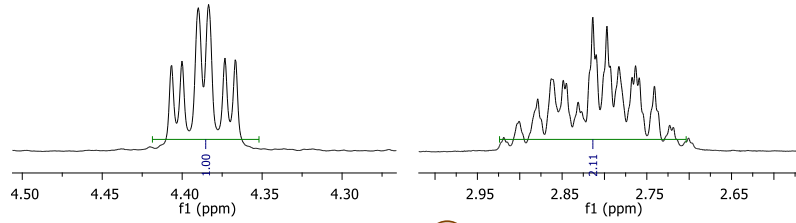
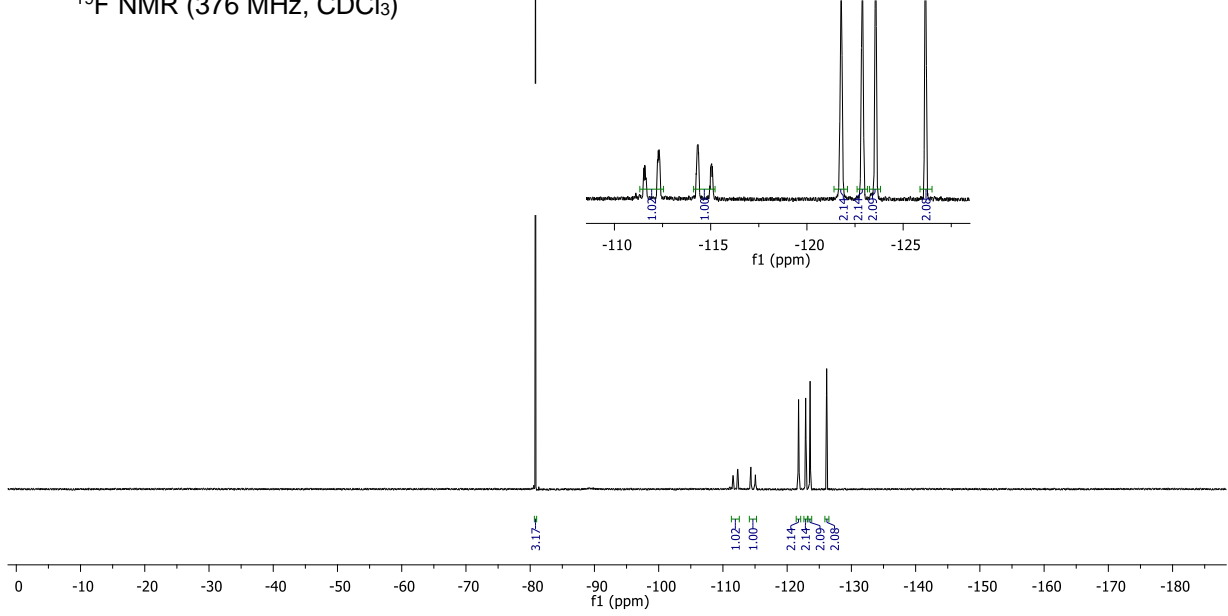
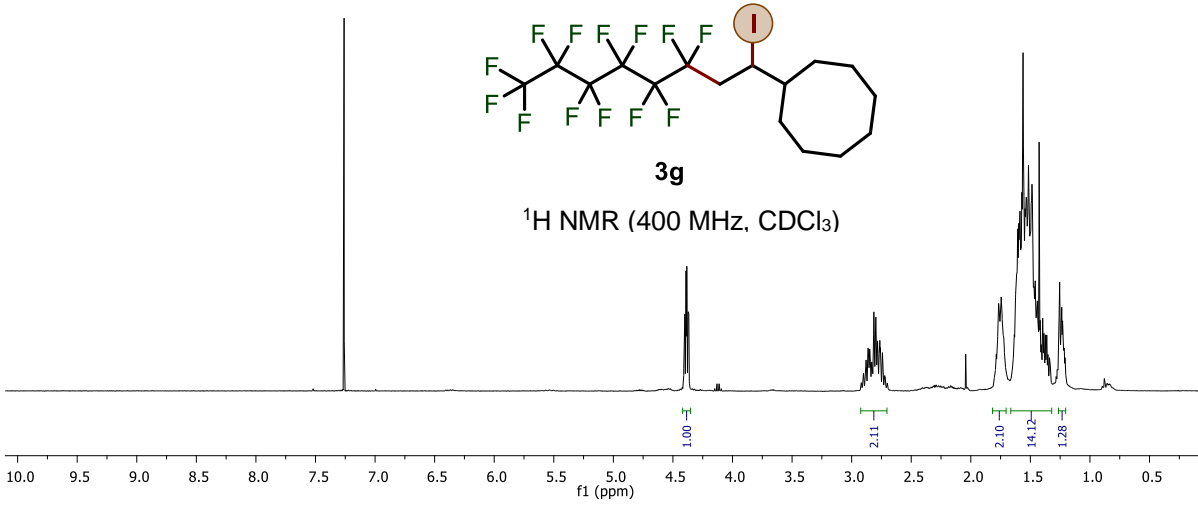
$^1\text{H NMR}$ (400 MHz, CDCl_3)

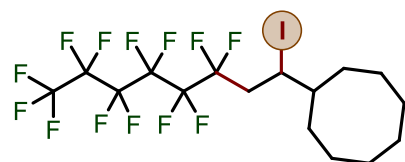


3f

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

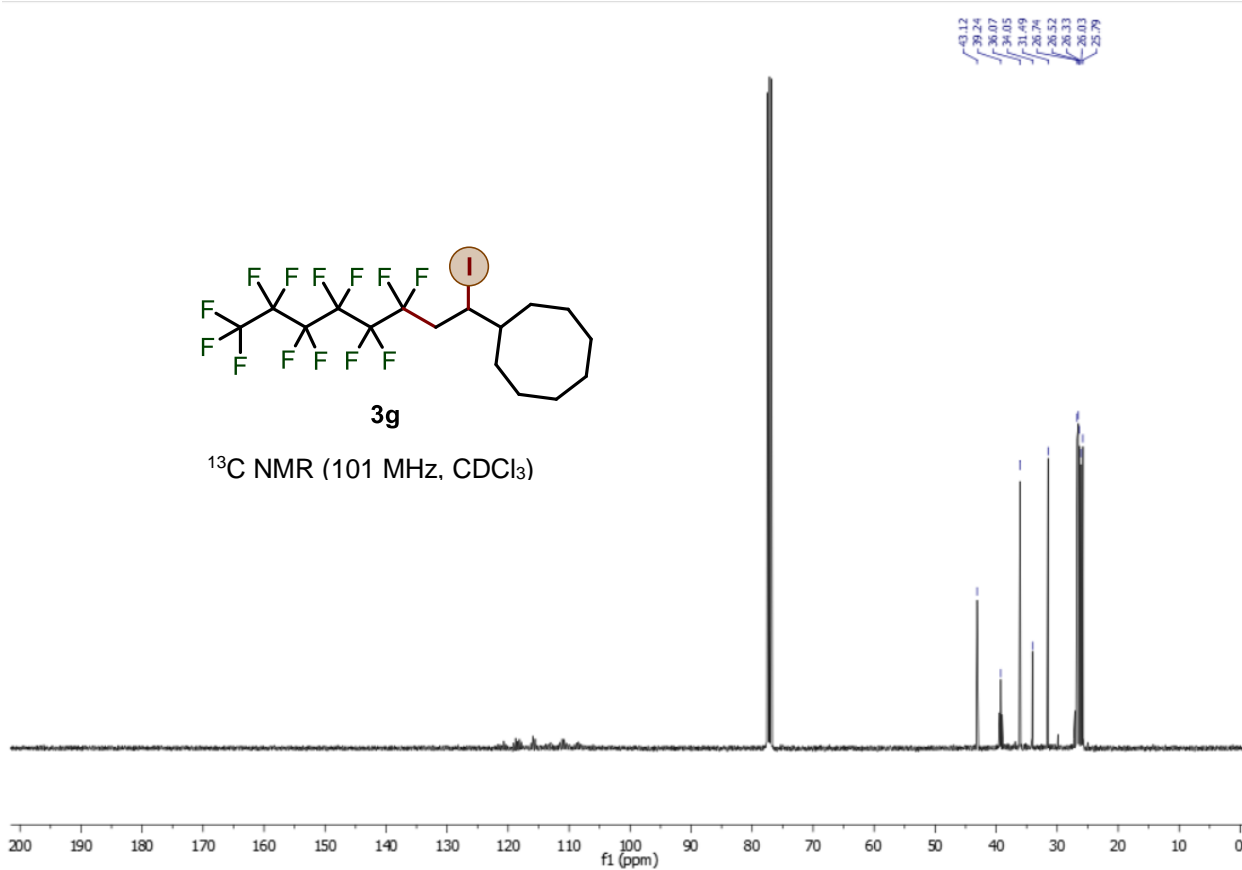


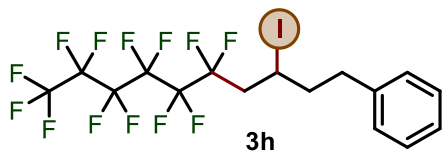
**3g**¹⁹F NMR (376 MHz, CDCl₃)**3g**¹H NMR (400 MHz, CDCl₃)



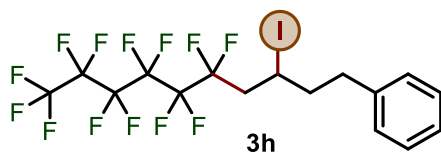
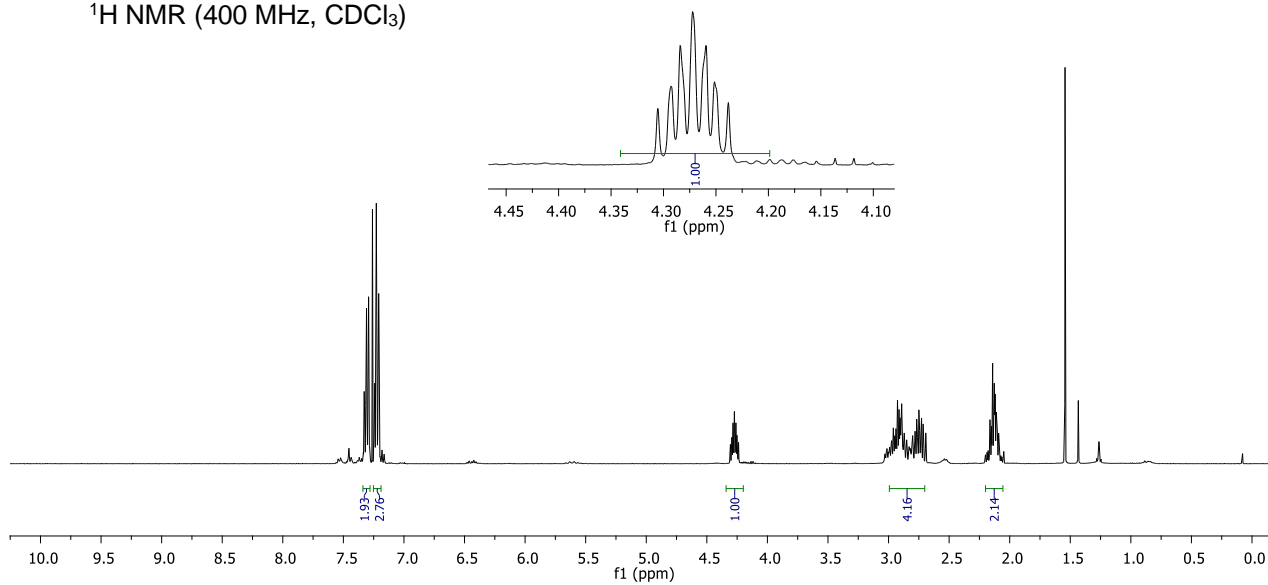
3g

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

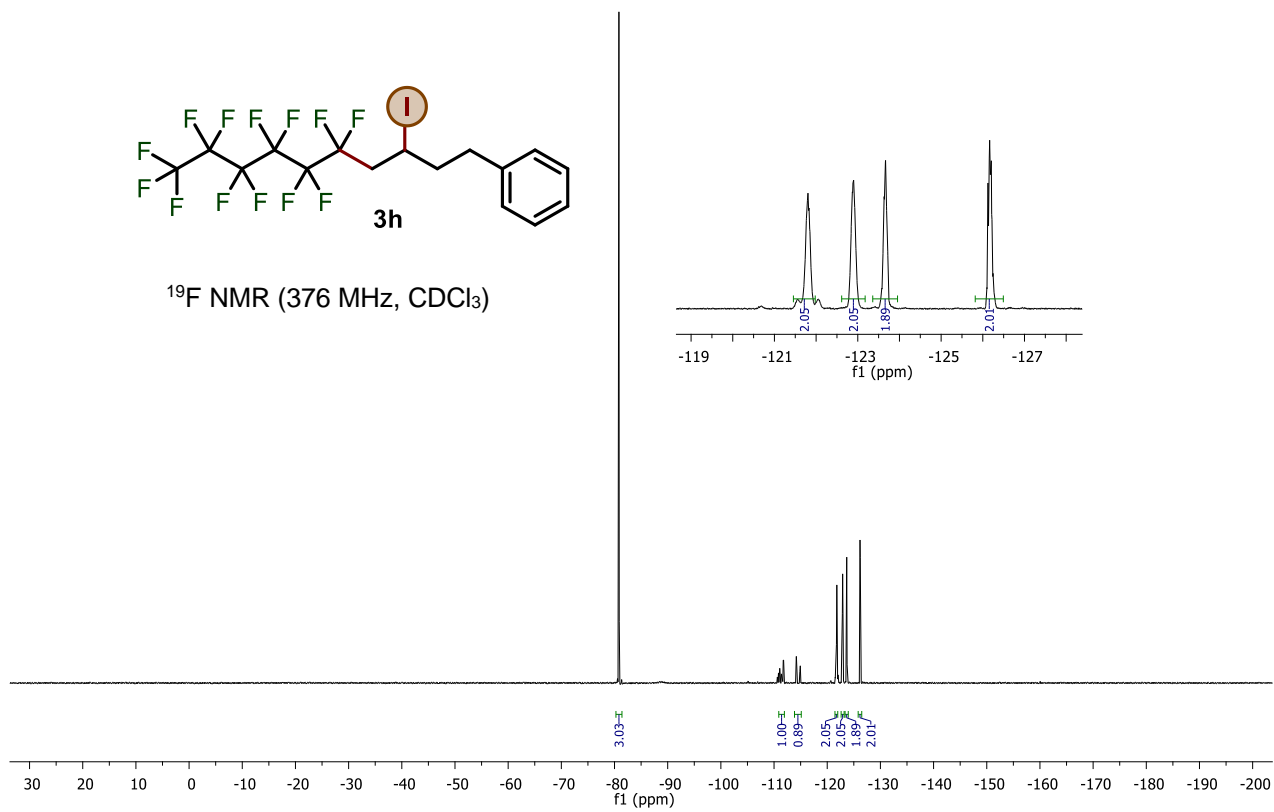


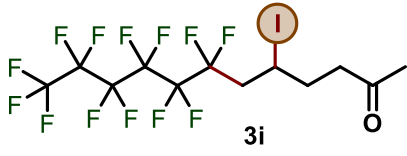


¹H NMR (400 MHz, CDCl₃)

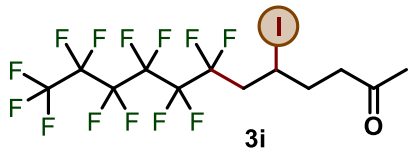
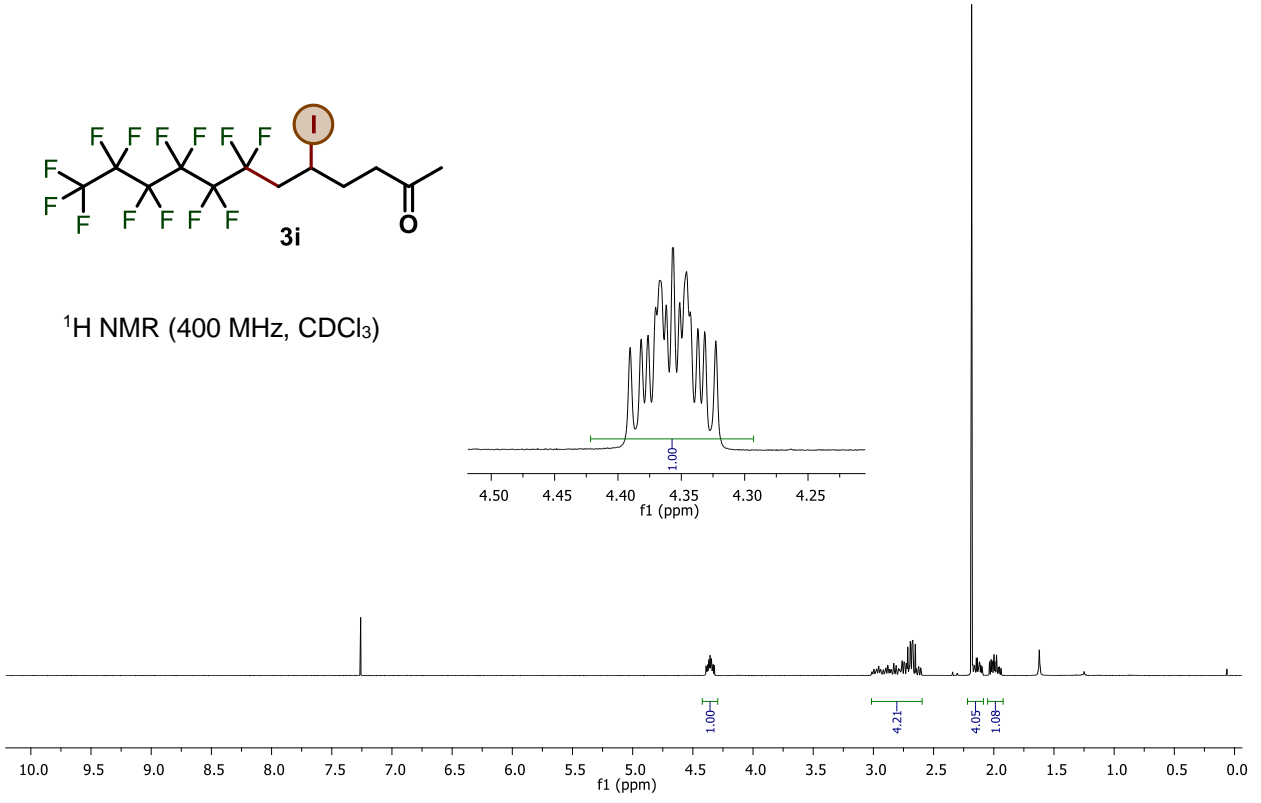


¹⁹F NMR (376 MHz, CDCl₃)

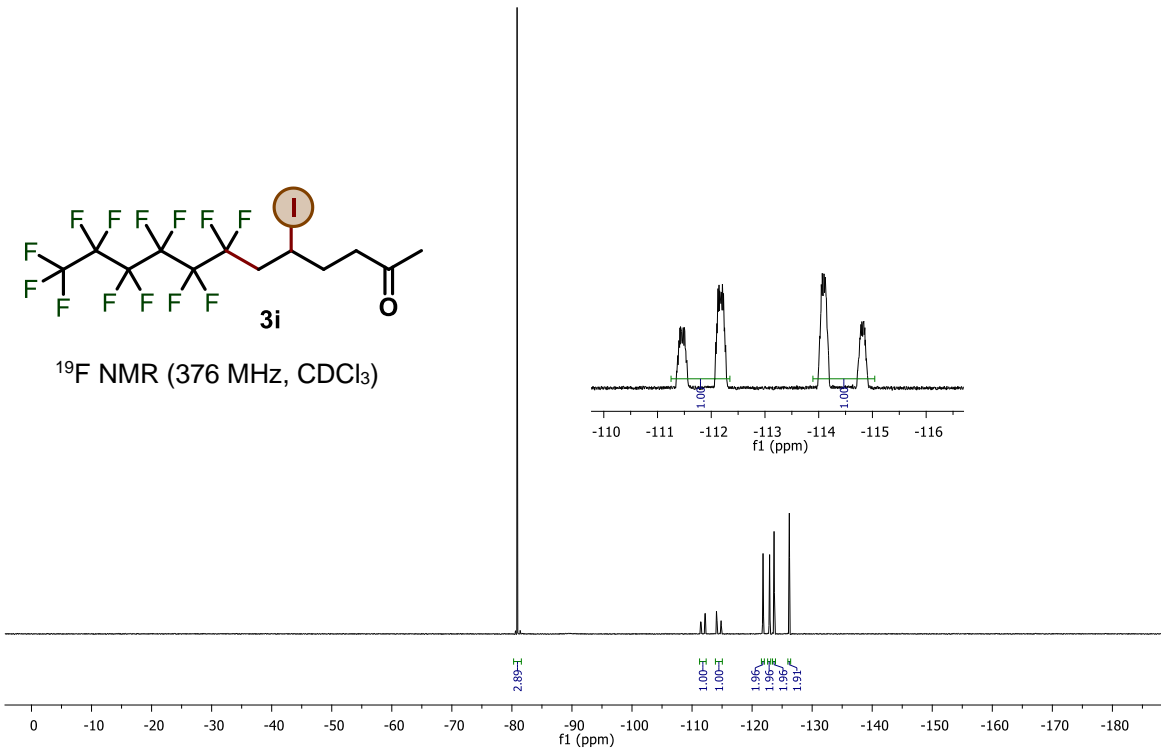


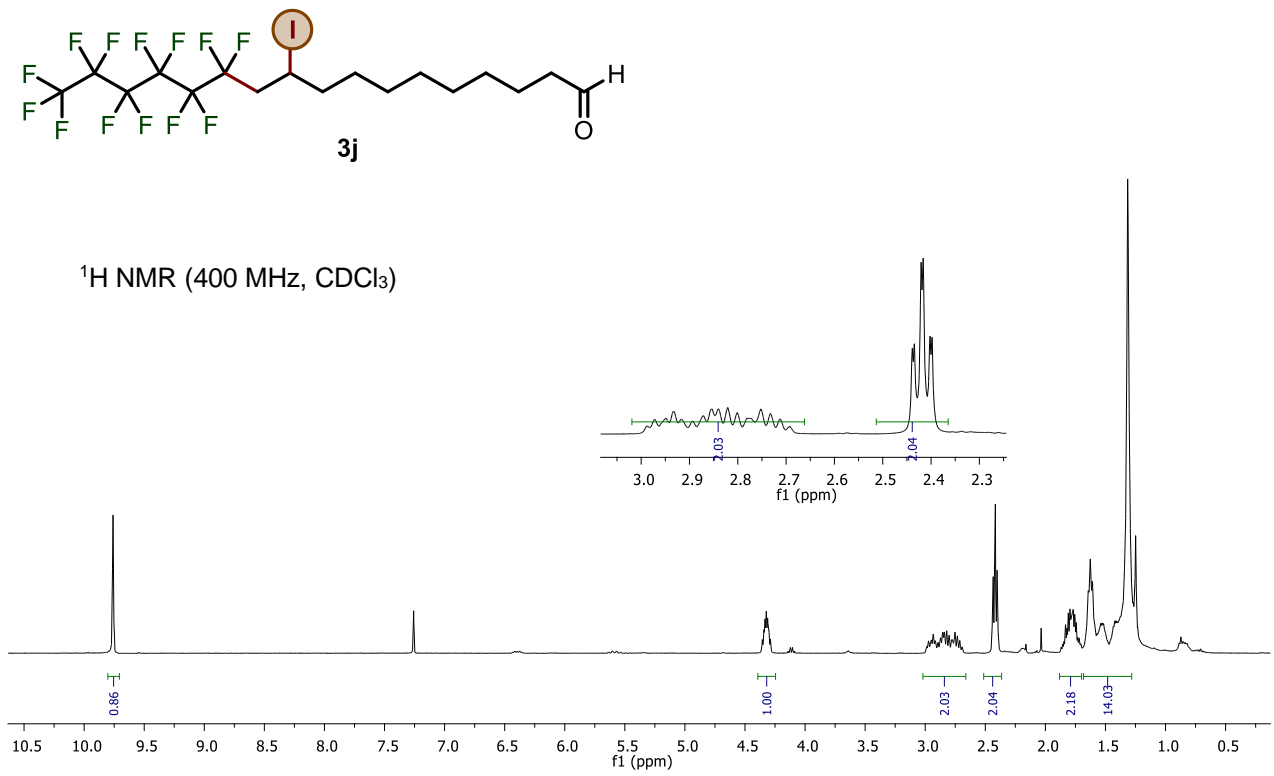
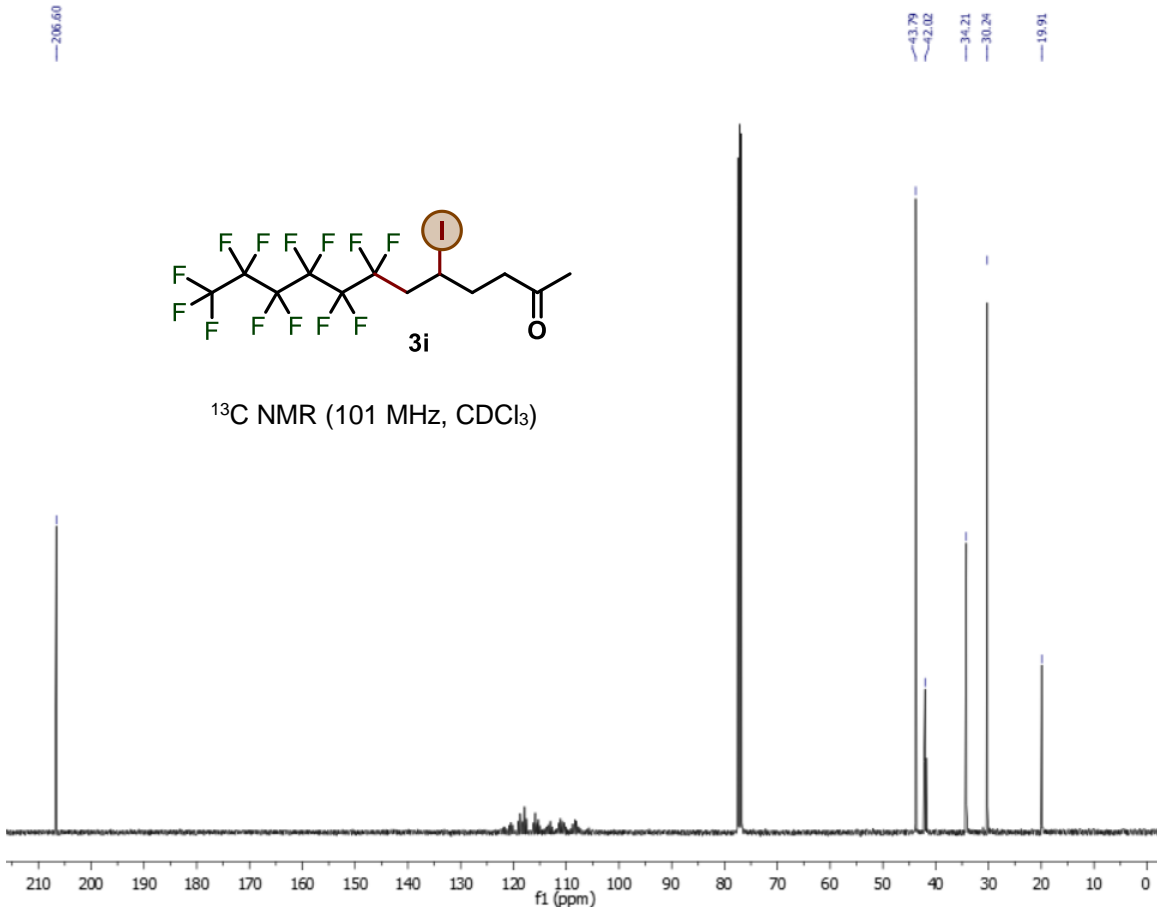


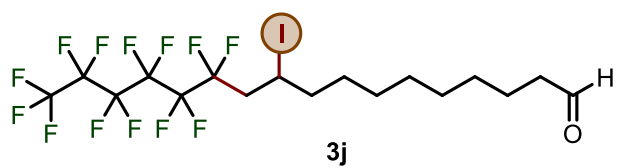
¹H NMR (400 MHz, CDCl₃)



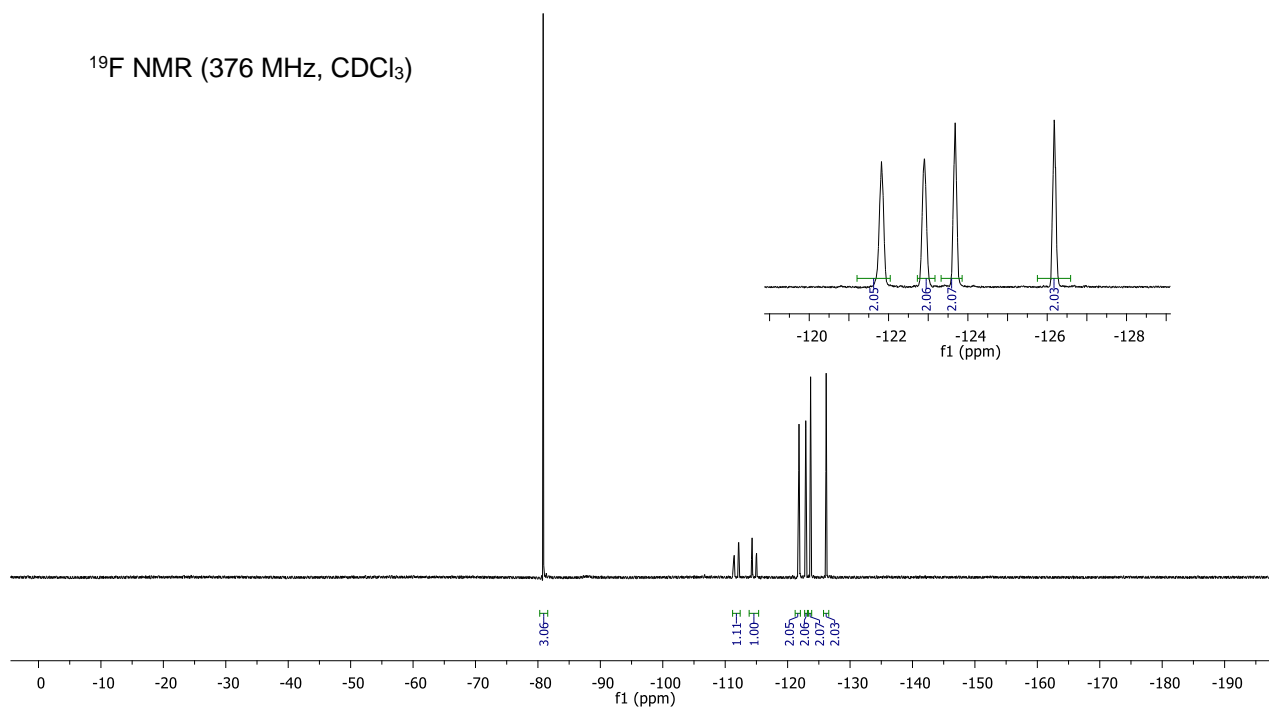
¹⁹F NMR (376 MHz, CDCl₃)



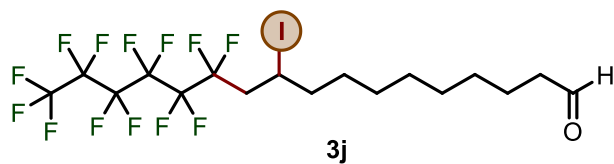




^{19}F NMR (376 MHz, CDCl_3)

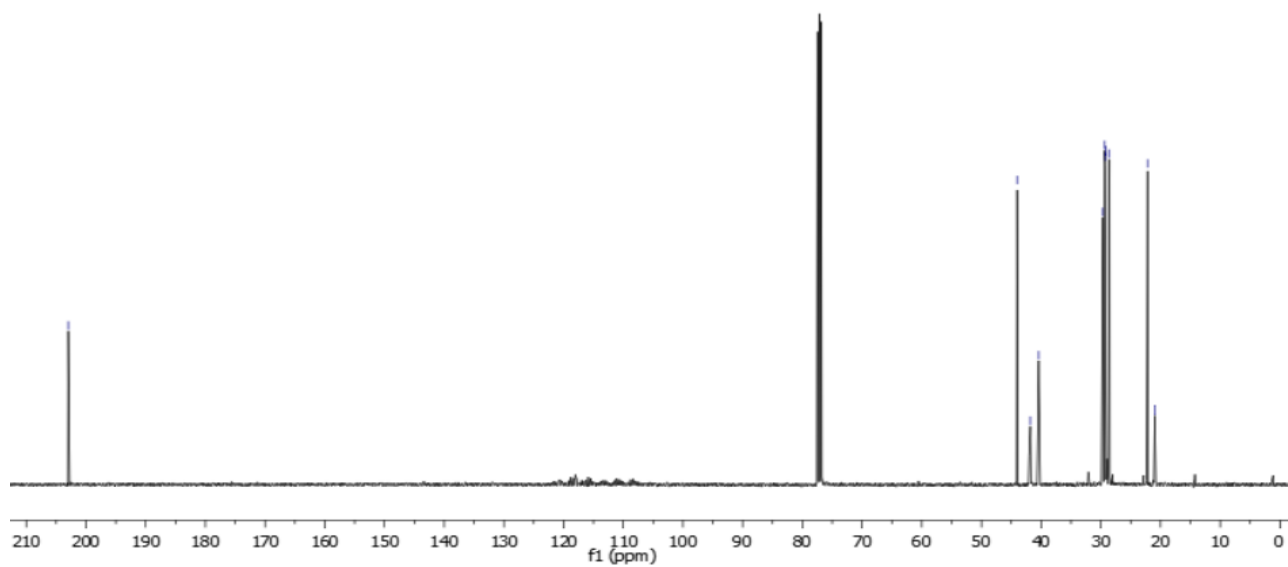


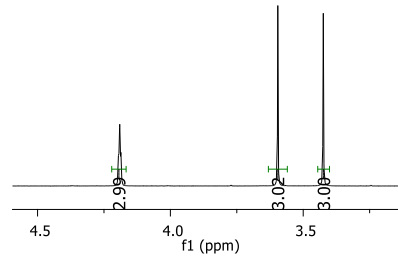
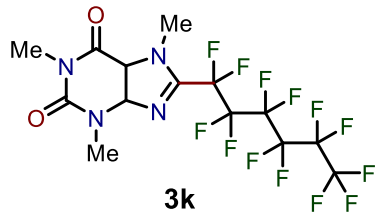
202.96



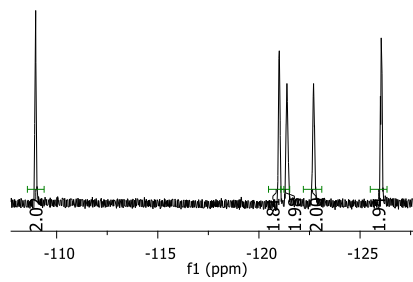
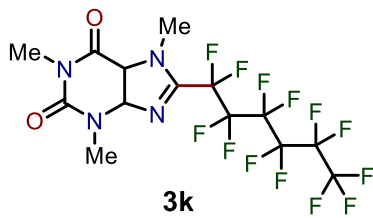
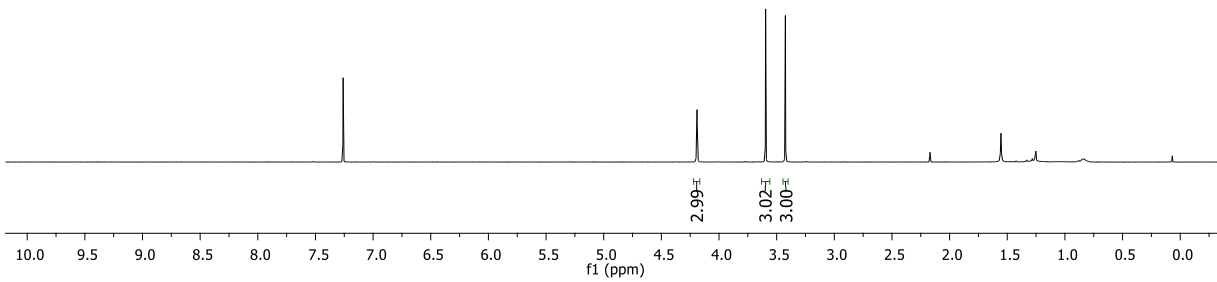
^{13}C NMR (101 MHz, CDCl_3)

44.03
29.27
-11.82
-10.41
29.22
28.39
20.97

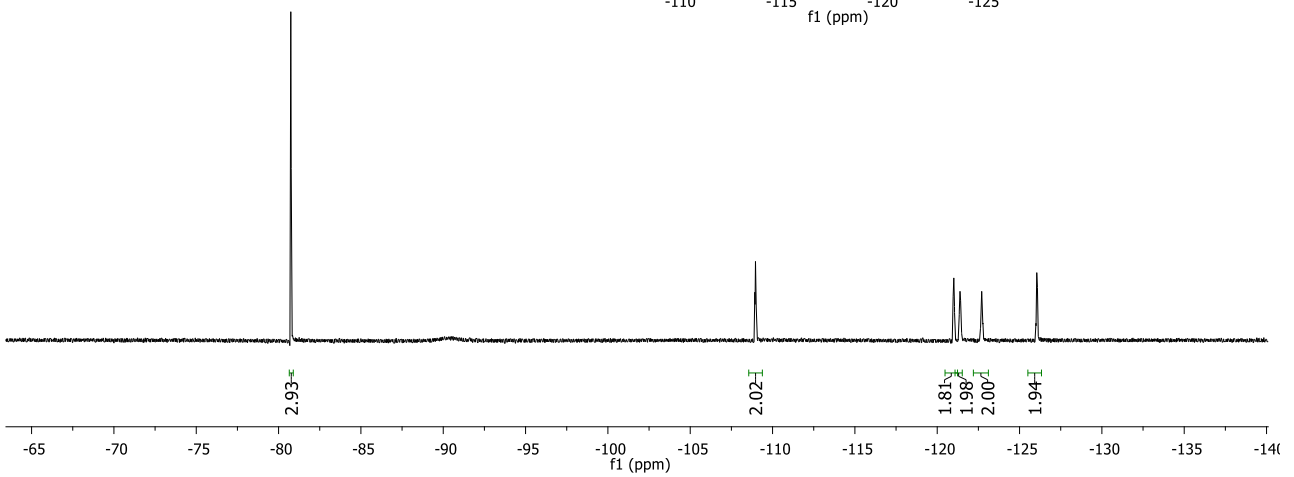


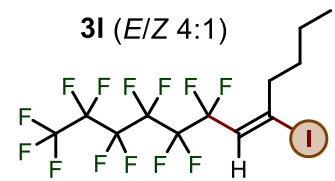


^1H NMR (400 MHz, CDCl_3)

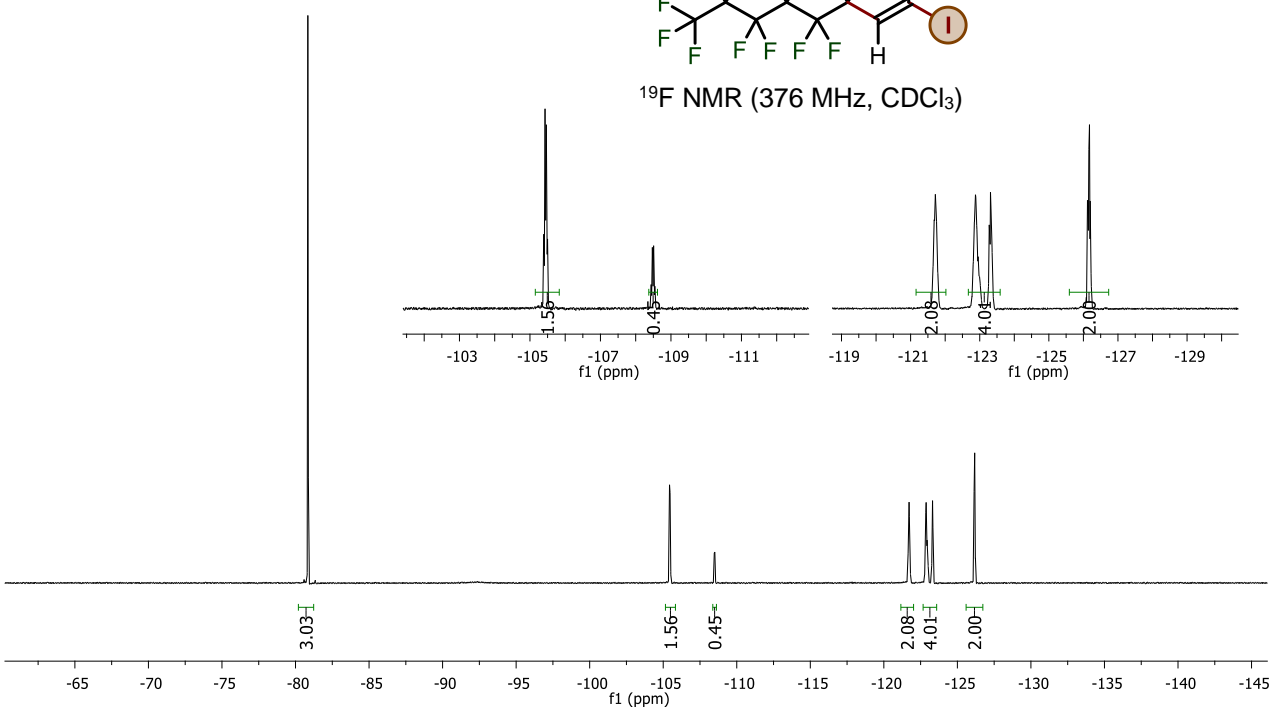
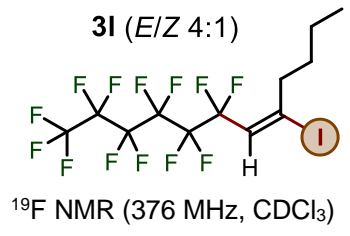
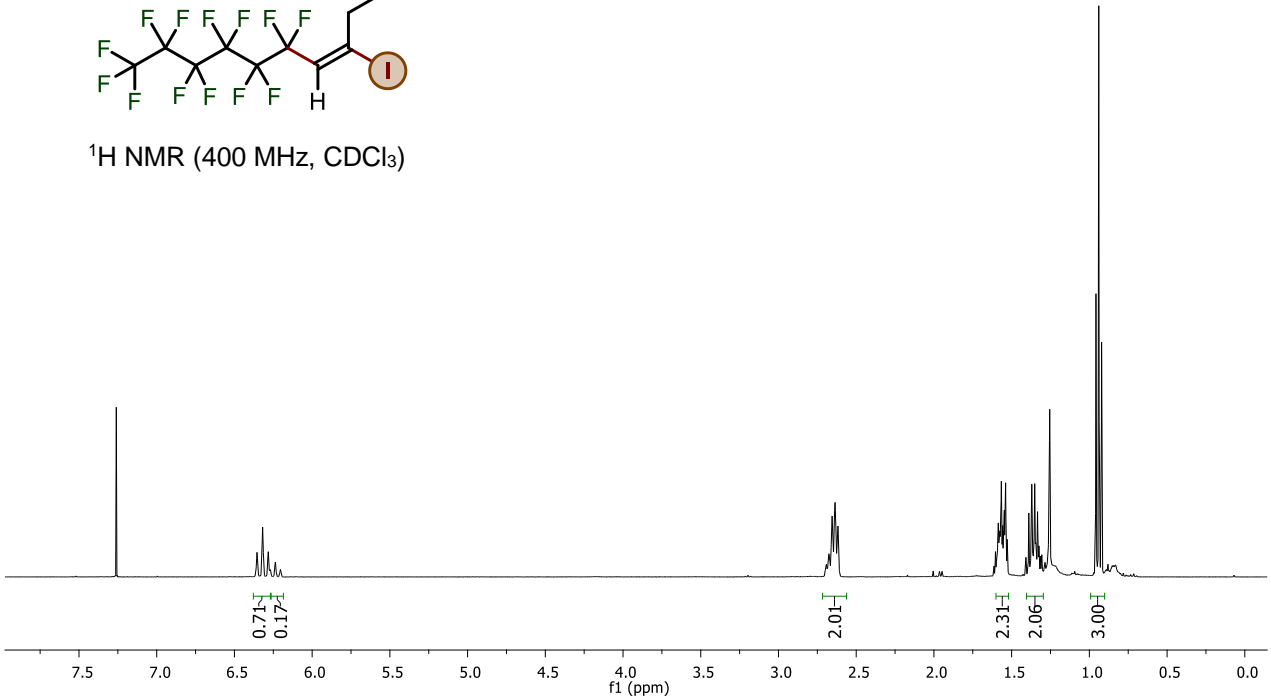


^{19}F NMR (376 MHz, CDCl_3)





¹H NMR (400 MHz, CDCl₃)



References

1. G. Filippini, F. Longobardo, L. Forster, A. Criado, G. Di Carmine, L. Nasi, C. D'Agostino, M. Melchionna, P. Fornasiero and M. Prato, *Science Adv.*, 2020, **6**, eabc9923.
2. T. Yajima, M. Murase and Yu Ofuji, *Eur. J. Org. Chem.* 2020, 3808–3811.