Supporting Information

Contents

S3 Chemical Formulae

S4 Experimental section

S4 *General Methods and Instrumentation*

S5 *Synthesis*

S14 *Photo-stability Testing*

S15 *Thermal-stability, Air-stability Testing*

S16 *Fluorescence Lifetime Measurements*

S19 *Optical Micrograph* **7b**

S20 *U.V./vis. Spectra*

S23 *EPR Spectra*

S28 *^{1}H, ^{13}C and ^{19}F NMR Spectra*

S47 *^{1}H T_1 Relaxation Time Measurements*

S49 *^{13}C T_1 Relaxation Time Measurements*

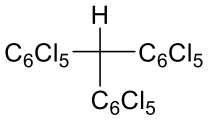
S51 *HSQC NMR* **7c**

S52 *Mass Spectra*

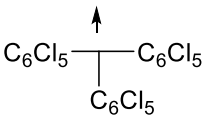
S54 *MO Calculations*

S59 References

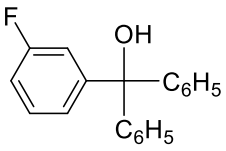
Chemical Formulae



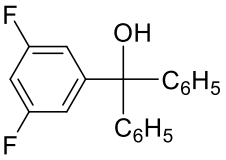
1



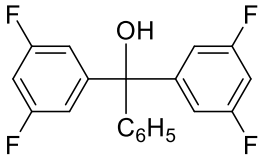
2



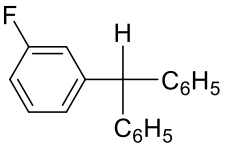
3a



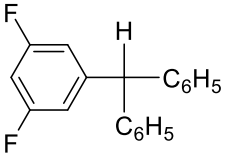
3b



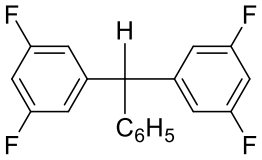
3c



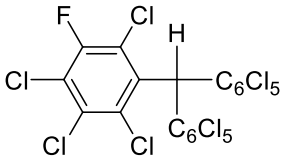
4a



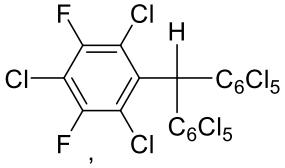
4b



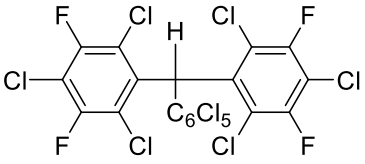
4c



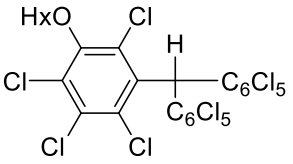
5a



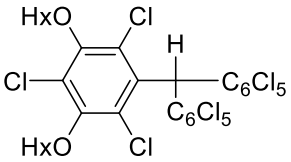
5b



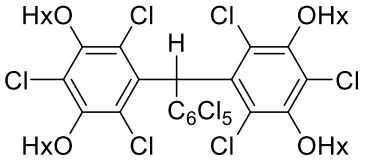
5c



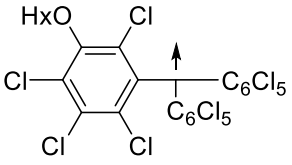
6a



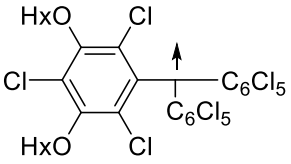
6b



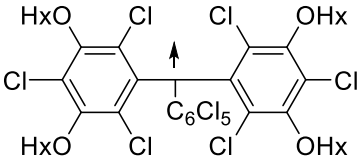
6c



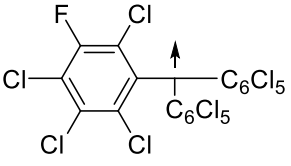
7a



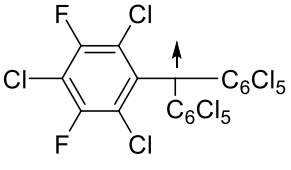
7b



7c



8a



8b

Experimental Section

General Methods and Instrumentation

Reagents were purchased commercially and were used as supplied. Reactions were performed under a nitrogen atmosphere using AR-grade solvents. Dried solvents were from a Pure Solv MD solvent purification system (Innovative Technology Inc.). The progress of reactions was monitored by TLC on pre-coated silica plates visualized by ultraviolet light. Column chromatography employed Merck Kieselgel (60 Å) F254 (230–400 mesh) silica and HPLC grade solvents. UV/vis. spectra were measured on a Perkin Elmer Lambda 35 UV/VIS Spectrometer. Steady state fluorescence spectra were measured on a Perkin Elmer LS 55. Lifetime measurements were made using an Edinburgh Instruments FLS980 fluorescence spectrophotometer. Proton, carbon and phosphorous NMR spectra were recorded on Bruker Advance 400, 500 or DPX300 spectrometers. Proton and carbon chemical shifts are quoted in parts per million (ppm) relative to $SiMe_4$, using residual non-deuterated solvent signals as the reference. Chemical shifts are corrected to $CHCl_3$ $\delta_H = 7.26$, $\delta_C = 77.36$. Coupling constants (J values) are quoted in Hertz (Hz). The splitting patterns are reported using the following abbreviations: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and combinations thereof. ^{13}C NMR Spectra (but not ^{19}F NMR Spectra) were proton decoupled. A Bruker MaXis Impact spectrometer with electrospray (ES) ionisation source was used for high-resolution mass spectrometry (HRMS). LC-MS was performed using a system comprising an Ultimate3000 HPLC instrument with a Brucker Amazon Speed MS detector. The system ran with a Phenomenex Kinetex C18 (50 mm × 2.1 mm × 2.6 μm) column and gradient elution with two binary solvent systems: MeCN/H_2O or MeCN/H_2O plus 0.1% formic acid. For polychlorinated species the accurate mass of most intense peak of the parent ion is quoted. The isotope distributions for the polychlorinated radicals, together with those calculated, are shown separately.

Synthesis

Pentadecachlorotrityl radical **2**., Pentadecachlorotriphenylmethane **1** [1] was converted to the pentadecachlorotrityl radical **2** using both the (i) NaOH/DMSO/acetone (ii) I_2 /Et_2O method [1a] and also the (i) $Bu_4N^+OH^-$ (ii) chloranil method. [2] Pentadecachlorotriphenylmethane **1** ^{1}H NMR (500 MHz, $CDCl_3$**)** δ 6.99 (s). Pentadecachlorotrityl radical **2** (UV/vis, $CHCl_3$, nm, log A) 284 (3.79), 366 (s, 4.12), 383 (4.40), 509 (2.97), 564 (2.94). Lit. (cyclohexane) 283 (3.74), 382 (4.57), 510 (3.07), 562 (3.08).

3-Fluorotriphenylmethanol **3a**. The required Grignard Reagent was prepared by refluxing 3-fluorobromobenzene (4.8 g, 33 mmol) with magnesium (795 mg, 33 mmol) in dry diethyl ether (40 mL) for 40 min. Benzophenone (5.46 g, 30 mmol) in dry diethyl ether (20 mL) was added dropwise, the solution refluxed for a further 3 h and left at RT overnight. The mixture was partitioned between dil. HCl and diethyl ether and the ether extracts washed with NaH CO_3 solution and brine, dried with $MgSO_4$, filtered and evaporated to give the almost pure 3-fluorotriphenylmethanol **3a** as a white crystalline solid (8.23 g, 93%). Further purification of a small sample by chromatography on silica (eluting first with DCM: hexane and then with DCM) followed by recrystallization from hexane gave the pure product.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.36 (m, 11H), 7.06 (m, 2H), 6.97 (m, 1H), 2.78 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.89 (d, J = 246 Hz), 149.78 (d, J = 6.5 Hz), 146.66 (d, J = 4 Hz), 129.65 (d, J = 8 Hz), 128.41 (s), 128.17 (s), 127.87 (s), 123.97 (d, J = 2.7 Hz), 115.43 (d, J = 22 Hz), 114. 44 (d, J = 21 Hz), 82.05 (d, J = 1.6 Hz).

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.28 (dd, J = 16, 9 Hz).

Positive ion HR-MS: m/z calcd. $[M\text{-}OH]^+$: 261.1074; found (ESI): 261.1071.

3,5-Difluorotriphenylmethanol **3b**. In a similar manner 3,5-difluorobromobenzene (2.58 g, 13 mmol) with benzophenone (2.7 g, 15 mmol) gave 3,5-difluorotriphenylmethanol **3b** as a white

crystalline solid which was purified by column chromatography and recrystallized from hexane (2.56 g, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.35 (m, 6H), 7.21–7.26 (m, 4H), 6.85-6.90 (m, 2H), 6.72 (tt, 1H, J = 8.4, 2.3 Hz), 2.77 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.00 (dd, J = 248, 12 Hz), 151.18 (t, J = 8.1 Hz), 146.12 (s), 128.59 (s), 128.16 (s), 128.09 (s), 111.41 (dd, J = 20, 6 Hz), 102.99 (t, J = 26 Hz), 81.94 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -109.65 (t, J = 8.4 Hz).

Positive ion HR-MS: m/z calcd. $[M\text{-}OH]^+$: 279.0980; found (ESI): 279.0976.

3,5,3',5'-Tetrafluorotriphenylmethanol **3c**. In a similar manner 3,5-difluorobromobenzene (9.65 g, 50mmol) with methyl benzoate (3.43 g, 25 mmol) gave 3,5,3',5'-tetrafluorotriphenylmethanol **3c** as a white crystalline solid which was purified by column chromatography (5.19 g, 63%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.40 (m, 3H), 7.21–7.23 (m, 2H), 7.06 (m, 2H), 6.83-6.86 (m, 4H), 6.76 (tt, 1H, J = 8.6, 2.3 Hz) 2.78 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.98 (dd, J = 248, 12 Hz), 149.86 (t, J = 8.1 Hz), 144.92 (s), 128.85 (s), 128.68 (s), 127.84 (s), 111.20 (dd, J = 20, 6 Hz), 103.49 (t, J = 26 Hz), 81.35 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.86 (t, J = 7.9 Hz).

Positive ion HR-MS: m/z calcd. $[M\text{-}OH]^+$: 315.0803; found (ESI): 315.0793.

3-Fluorotriphenylmethane **4a**. Dimethyldichlorosilane (3.04 mL, 24 mmmol) was added to a stirred ice-cooled solution of sodium iodide (7.2 g, 48 mmol) in 1:1 DCM:acetone (240 mL). 3-fluorotriphenylmethanol **3a** (5.14 g, 18.5 mmol) in DCM (120 mL) was added. The milky white solution turned brown. After a further ca. 10min the mixture was diluted with dichloromethane (1 litre) and the DCM solution washed with aqueous sodium bisulfite and saturated brine, dried with magnesium sulfate, filtered and evaporated. The crude product was purified by chromatography on silica (eluting first with DCM: hexane and then with DCM) to

give a slightly pink crystalline solid (4.60 g, 95 % crude yield; the 1H NMR spectrum showed that it still contained a small amount of polydimethylsiloxane). Since the siloxane proved very difficult to wholly remove the product was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.31 (m, 7H), 7.10 (m, 4H), 6.88 (m, 2H), 6.78 (m, 1H), 5.52 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.93 (d, J = 246 Hz), 146.59 (d, J = 6.8 Hz), 143.24 (s), 129.68 (d, J = 8 Hz), 129.37(s), 128.45 (s), 126.57 (s), 125.16 (d, J = 2.7 Hz), 116.41 (d, J = 22 Hz), 113.26 (d, J = 22 Hz) 56.55 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.28 (m).

Positive ion HR-MS: m/z calcd. $[M-H]^+$: 261.1074; found (ESI): 261.1076.

3,5-Difluorotriphenylmethane **4b**. In a similar manner 3,5-difluorotriphenylmethanol **3b** (3.08 g) gave 3,5-difluorotriphenylmethane **4b** which was purified by column chromatography (2.14 g, 74% crude yield, containing a small amount of polydimethylsiloxane). This was used for the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23–7.33 (m, 4H), 7.22–7.27 (m, 2H), 7.10 (m, 4H), 6.64 (m, 3H), 5.49 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.33 (dd, J = 248, 13 Hz), 148.39 (s), 142.86(s), 129.63 (s), 128.92 (s), 127.17 (s), 112.71 (dd, J = 20, 6 Hz), 102.24 (t, J = 26 Hz), 56.83 (s).

^{19}F NMR (470 MHz, $CDCl_3$) δ -110.1 (t, J = 8.0 Hz).

Positive ion HR-MS: m/z calcd. $[M-H]^{+\cdot}$ 279.0980; found (ESI): 279.0932.

3,5,3'5'-Tetrafluorotriphenylmethane **4c.** In a similar manner 3, 5, 3', 5'-tetrafluorotriphenylmethanol **3c** (3.32 g) gave 3,5-difluorotriphenylmethane **4c** which was purified by column chromatography (2.48 g, 78% crude yield, containing a small amount of polydimethylsiloxane). This was used for the next step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.17 (m, 3H), 7.07 (d, 2H, J = 7.3 Hz), 6.71 (tt, 2H, J = 8.8, 2.3 Hz), 6.59-6.5 (m, 4H), 5.5 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.42 (dd, J = 249, 13 Hz), 145.67 (s), 141.37 (s), 129.46 (s), 129.20 (s), 127.71 (s), 112.62 (m), 102.83 (t, J = 25 Hz), 56.32 (s).

^{19}F NMR (376 MHz, $CDCl_3$) δ -109.37 (t, J = 7.8 Hz).

Positive ion HR-MS: m/z calcd. $[M-H]^+$: 315.0803; found (ESI): 315.0791.

3-Fluorotetradecachlorotriphenylmethane **5a**. Using an apparatus equipped with a reflux condenser connected to a funnel for trapping evolved gasses in water, 3-fluorotriphenylmethane **4a** (0.75 g) and disulfurdichloride (0.25 mL) in sulfuryl chloride (20 mL) was added dropwise (45 min) to a stirred, refluxing solution of aluminium trichloride (0.19 g) in sulfuryl chloride (50 mL). Under continuing reflux the volume of the solution slowly decreased and, after about 2.5 h, more sulfuryl chloride (60 mL) needed to be added. After a total of 5h reflux, most of the remaining sulfuryl chloride was distilled off and water added dropwise to the ice-cooled flask. The white precipitate was filtered off and washed repeatedly with water, aqueous sodium bicarbonate, (again) water and dried. The product (1.99 g, essentially quantitative) was very insoluble in organic solvents but it was just possible to obtain ^{1}H and ^{19}F NMR spectra and these, together with the mass spectrum suggested that this is a roughly 1:6 mixture of **1**:**5a** (**5a** being a mixture of *syn* and *anti* isomers). Since it was so insoluble, this mixture could not be separated and the crude product was used for the next stage.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.99 (s, **1**), 6.96 (s, **5a**), 6.94 (s, **5a**).

^{19}F NMR (470 MHz, $CDCl_3$) δ -105.52 (s), -105.37 (s).

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 742.5542; found (ESI): 742.5547.

3,5-Difluorotridecachlorotriphenylmethane **5b**. In a similar manner 3,5-difluorotriphenylmethane **4b** (0.88 g) gave 3,5-difluorotridecachlorotriphenylmethane **5b** (2.2 g, essentially quantitative).

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 1H).

^{19}F NMR (470 MHz, $CDCl_3$) δ -108.90 (s, 1F), -108.53 (s, 1F).

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 726.5838; found (ESI): 726.5856.

3,5,3',5'-Tetrafluoroundecachlorotriphenylmethane **5c**. In a similar manner 3,5-difluorotriphenylmethane **4c** (0.88 g) gave 3,5,3',5'-tetrafluoroundecachlorotriphenylmethane **5c** (1.7 g, 88% crude).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (s, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.85 (s, 1F), -108.80 (s, 1F), -108.58 (s, 1F), -108.43 (s, 1F).

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 692.6458; found (ESI): 692.6463.

3-(n-Hexyloxy)-tetradecachlorotriphenylmethane **6a**. Sodium (461 mg) was dissolved in n-hexanol (10 mL) by heating at 100 ºC for 2 h under a nitrogen atmosphere. After cooling to room temperature dry DMSO (10 mL) was added giving a 1M solution of the alkoxide. The roughly 1:6 mixture of pentadecachlorotriphenylmethane **1** and 3-fluorotetradecachlorotriphenylmethane **5a** from the preparation described above was added (600 mg) and the mixture heated at 100 ºC for a further 4 h. After cooling to room temperature the mixture was acidified (dilute HCl) and extracted with Et_2O. The ether solution was washed with aqueous sodium bicarbonate solution and saturated brine solution, dried ($MgSO_4$), filtered and evaporated (heat was required to remove the n-hexanol). The crude product (2g) was purified by chromatography on silica eluting first with 10% and then 20% DCM in hexane to give 3-(n-hexyloxy)-tetradecachlorotriphenylmethane **6a** as a pale pink oil (240 mg, ca. 36%). (A ca. 3:4 mixture of *syn* and *anti* isomers)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 and 6.94 (both s, total 1H), 4.00 and 3.92 (close overlapping triplets J = 6.5 Hz and J = 6.6 Hz respectively, total 2H), 1.82 and 1.79 (m, total 2H), 1.54-1.43 (m, 2H), 1.38-1.29 (m, 4H), 0.93-0.86 (m, 3H). The sample contained a persistent impurity giving rise to a small triplet at δ 4.06

^{13}C NMR (126 MHz, $CDCl_3$) δ 14.37, 22.89, 22.92, 25.77, 30.22, 30.54, 31.93, 31.93, 56.06, 56.33, 74.27, 74.53, 130.06, 130.12, 130.64, 130.96, 131.98, 132.90, 132.34, 132.76, 132.78, 132.80, 132.83, 133.35, 133.78, 133.81, 133.86, 133.88, 133.92, 133.95, 133.97, 134.22, 134.26, 134.32, 135.39, 135.41, 135.44, 135.64, 135.73, 136.76, 136.80, 136.83, 136.88, 151.93, 152.54.

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 824.6526; found (ESI): 824.6517.

3,5-Bis-(n-hexyloxy)-tridecachlorotriphenylmethane **6b**. In a similar manner, but using a 3:1 mixture of n-hexanol and DMSO and a 5 h reaction time, 3,5-difluorotridecachlorotriphenylmethane **5b** (1 g) gave 3,5-bis-(n-hexyloxy)-tridecachlorotriphenylmethane **6b** (760 mg, 62%) as pale pink crystals.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (s, 1H), 3.99 and 3.91 (both two close overlapping triplets J = 6.5 Hz, total 4H), 1.82 and 1.79 (m, total 4H), 1.54-1.43 (m, 4H), 1.39-1.29 (m, 8H), 0.93-0.90 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$)

δ 14.39, 22.91, 25.81, 30.26, 31.93, 31.95, 55.58, 74.14, 74.40, 125.39, 127.32, 128.72, 132.64, 132.70, 133.64, 133.70, 133.79, 134.28, 134.34, 134.61, 135.36, 135.53, 137.11, 137.23, 151.58, 152.42.

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 890.7805; found (ESI): 890.7824.

In an attempt to optimise the yield, the reaction was performed/attempted using 'neat' n-hexanol; 3:1 n-hexanol: DMSO; 1:1 n-hexanol: DMSO; 1:3 n-hexanol: DMSO; and 'neat' DMSO. The best yield and purest product was obtained using the 3:1 mixture.

3,5,3',5'-Tetrakis-(n-hexyloxy)-undecachlorotriphenylmethane **6c**. In a similar manner, using a 3:1 mixture of n-hexanol and DMSO and a 6 h reaction time, *3,5,3',5'-tetrafluoroundecachlorotriphenylmethane* **5c** (1 g) gave 3,5,3'-tris-(n-hexyloxy)-5'-fluorododecachlorotriphenylmethane (434 mg, 27%) and 3,5,3',5'-tetrakis-(n-hexyloxy)-

undecachlorotriphenylmethane **6c** (195 mg, 11%) both as pale pink oils. Additional amounts (ca 200 mg, 11%) of compound **6c** were obtained by treating the trisubstitution product again in the same way.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 1H), 3.98 and 3.91 (both two close overlapping triplets J = 6.5 Hz, total 8H), 1.80 (m, 8H), 1.48 (m, 8H), 1.34 (m, 16H), 0.90 (m, 12H).

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

δ 14.38, 22.91, 22.92, 25.82, 30.27, 31.94, 54.32, 74.02, 74.30, 124.95, 127.34, 127.38, 128. 77, 128.90, 132.44, 132.26, 133.45, 134.37, 135.21, 135.26, 135.56, 151.65, 151.74, 152.19, 152.34.

Negative ion HR-MS: m/z calcd. $[M-H]^-$: 1023.0367; found (ESI): 10.230342.

3-(n-Hexyloxy)-tetradecachlorotriphenylmethyl radical **7a.** Under an atmosphere of nitrogen and in a flask protected from the light, 3-(n-hexyloxy)-tetradecachlorotriphenylmethane **6a** (75 mg) was added to a stirred mixture of tetrabutylammmonium hydroxide (0.6 mL, 40% aqueous solution), THF (15 mL) and DMSO (5 mL). After 2 h stirring at room temperature chloranil (260 mg) was added and after a further 1.5 h the mixture was partitioned between Et_2O and dilute HCl. The Et_2O solution was washed with aqueous sodium bicarbonate and saturated brine solution, dried ($MgSO_4$), filtered and evaporated. The crude product was chromatographed on silica eluting with 5% DCM in hexane to give the 3-(n-hexyloxy)-tetradecachlorotriphenylmethyl radical **7a** as a bright red solid (59 mg, 79%).

(UV/vis, $CHCl_3$, nm, log A) 282 (3.75), 366 (s, 4.18), 385 (4.47), 513 (3.02), 564 (3.02).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98 (br s, 1H), 1.84 (br s, 1H), 1.35 (br s, 4H), 1.21 (br s, 2H), 0.90 (br s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 13.93, 22.87, 25.76, 30.80, 30.86.

Negative ion HR-MS: m/z calcd. $[M]^-$: 824.6526; found (ESI): 824.6505 (isotope distribution shown below).

3,5-Bis-(n-hexyloxy)-tridecachlorotriphenylmethyl radical **7b**. In a similar manner 3,5-bis-(n-hexyloxy)-tridecachlorotriphenylmethane **6b** (175 mg) gave the 3,5-bis-(n-hexyloxy)-tridecachlorotriphenylmethyl radical **7b** (10 mg, 58%) as a bright red solid which was recrystallized from EtOH.

(UV/vis, $CHCl_3$, nm, log A) 283 (3.83), 366 (s, 4.34), 384 (4.55), 518 (3.08), 569 (3.12).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98 (br s, 2H), 1.84 (br s, 2H), 1.35 (br s, 8H), 1.21 (br s, 4H), 0.90 (br s, 6H)

^{13}C NMR (126 MHz, $CDCl_3$) δ 14.30, 22.85, 25.74, 30.64, 30.76.

Negative ion HR-MS: m/z calcd. $[M]^-$: 890.7805; found (ESI): 890.7807 (isotope distribution shown below).

3,5,3',5'-Tetrakis-(n-hexyloxy)-undecachlorotriphenylmethyl radical **7c.** Under an atmosphere of nitrogen and in a flask protected from the light, 3,5,3',5'-tetrakis-(n-hexyloxy)-undecachlorotriphenylmethane **6c** (350 mg) was added to a stirred solution of powdered NaOH (250 mg) in Et_2O (17 mL) and DMSO (3 mL). After 2 days this reaction mixture was decanted into a second flask (also protected from the light) containing iodine (2 g) in Et_2O (100 mL). After stirring for a further 2 days at room temperature this solution was washed with sodium thiosulfate, dilute HCl, aqueous sodium bicarbonate and brine, dried ($MgSO_4$), filtered and evaporated to give the 3,5,3',5'-tetrakis-(n-hexyloxy)-undecachlorotriphenylmethyl radical **7c** as a bright red oil (252 mg, 72%).

(UV/vis, $CHCl_3$, nm, log A) 283 (3.83), 365 (s, 4.30), 382 (4.54), 517 (3.03), 565 (3.18).

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (br s, 4H), 1.85 (br s, 4H), 1.35 (br s, 16H), 1.21 (br s, 8H), 0.89 (br s, 12H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 14.37, 22.92, 25.84, 30.61, 30.85.

Posative ion HR-MS: m/z calcd. $[M]^+$: 1023.0356; found (ESI): 10.230342 (isotope distribution shown below).

The 2D NMR spectra show cross-peaks indicating $^{1}H/^{1}H$ coupling between δ_H/δ_H 0.87/1.35 and 1.21/1.35 but no cross peaks for the signals at δ 1.85 and 1.99.

The HSQC $^{1}H/^{13}C$ 2D correlation spectrum shows cross-peaks between δ_H/δ_C 0.87/14.37, 1.21/25.84, 1.35/22.92, 1.35/30.85, 1.85/30.61 and 1.99/30.61.

3-Fluorotetradecachlorotriphenylmethyl radical, **10a**. Was made from 3-fluorotetradecachlorotriphenylmethane **5a** in the same manner.

Negative ion HR-MS: m/z calcd. $[M]^-$: 742.5542; found (ESI): 742.5524 (isotope distribution shown below).

This product contained ca. 20% **2** which could not be removed.

3,5-Difluorotridecachlorotriphenylmethyl radical, **10b**. Was made from 3,5-difluorotridecachlorotriphenylmethane **5c** in the same manner.

Negative ion HR-MS: m/z calcd. $[M]^-$: 726.5838; found (ESI): 726.5841 (isotope distribution shown below).

This product contained ca. 5% **10a** which could not be removed.

Photo-stability Testing

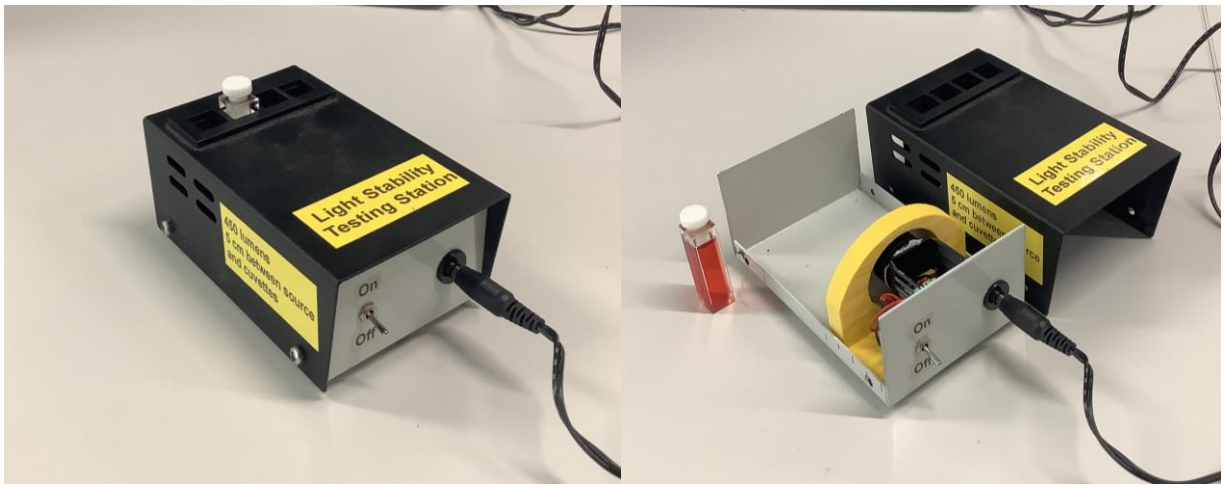


Figure S1. Apparatus used for photostability testing. (left) assembled for use. (right) cover removed.

The relative photo-stabilities of the radicals (Figure 2 and Table 2) were determined using the apparatus shown (left assembled for use; right sample and cover removed). When assembled, the 450 lumen LED light source (main emission 410-700 nm) was located 5 cm from the front of the 1 cm quartz UV cell. After a measured time interval the cell was removed and the UV/vis. spectrum recorded, the sample replaced and the process repeated. The rate of photodecomposition was determined using the disappearance of the narrow peak at ca 384 nm from the slope of the plot of $\log_{10}((A_t-A_{inf})/(A_0-A_{inf}))$ against time where A_t is the absorbance at (accumulated) time t, A_0 the initial value and A_{inf} the absorbance at long reaction time.

Thermal-stability, Air-stability Testing

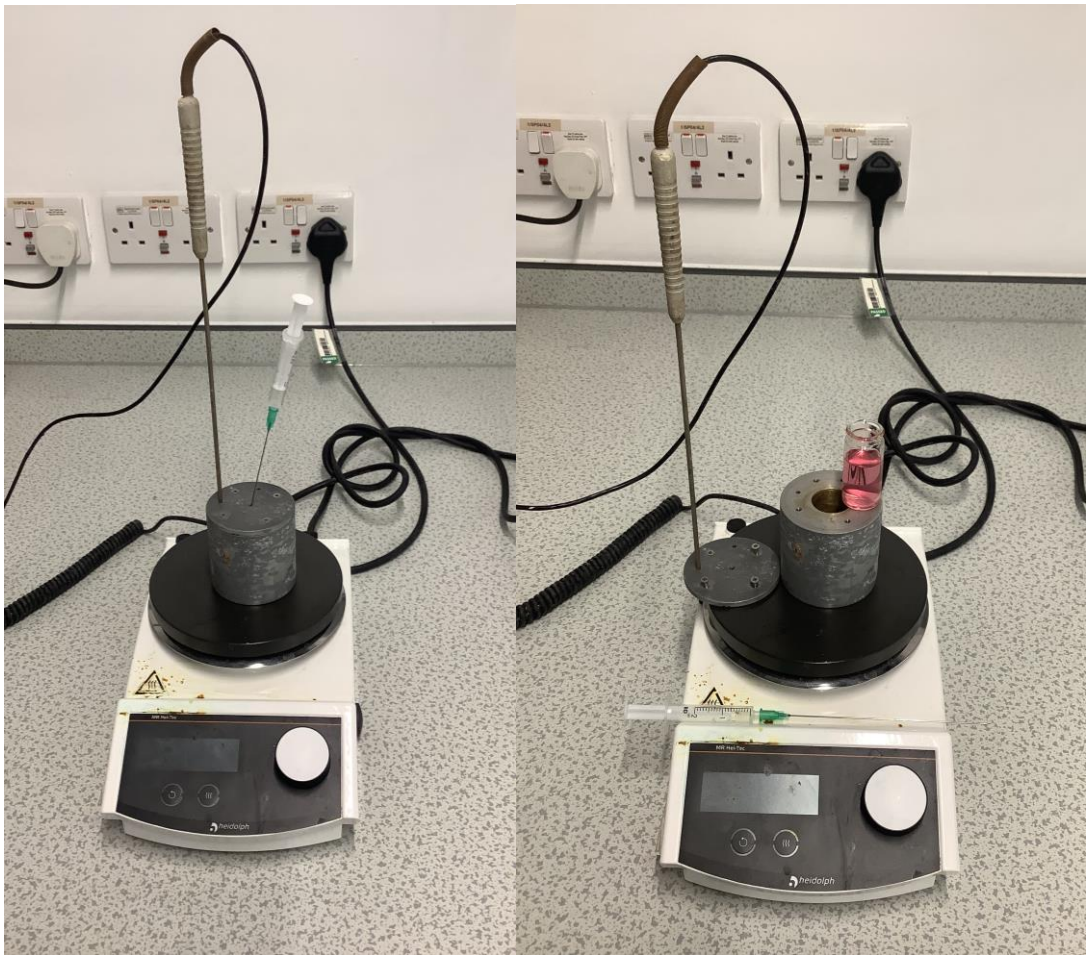


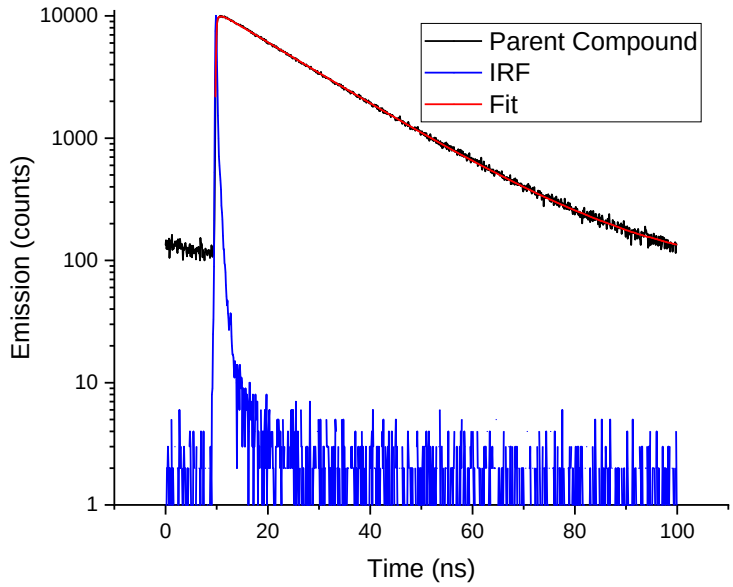
Figure S2. Apparatus used for thermal stability testing. (left) assembled for use. (right) disassembled.

The stability of solutions of the radicals when heated in the air was investigated using the apparatus shown; left assembled for use and right with the top and sample removed. In this a stirred dilute solution in mineral oil was heated within an aluminium block (which excluded the light). This top contained a hole through which the thermocouple extends half way down the wall of the block (to the level of the solution). There was also a very small hole in the centre of the lid which was just large enough to accommodate two fine syringe needles; one used to add/remove small samples and the other (for experiments using an inert atmosphere)) to introduce a gentle stream of nitrogen. Periodically small samples were removed, and the UV/vis spectrum measured in 1cm path-length quartz UV microcells.

Fluorescence Lifetime Measurements

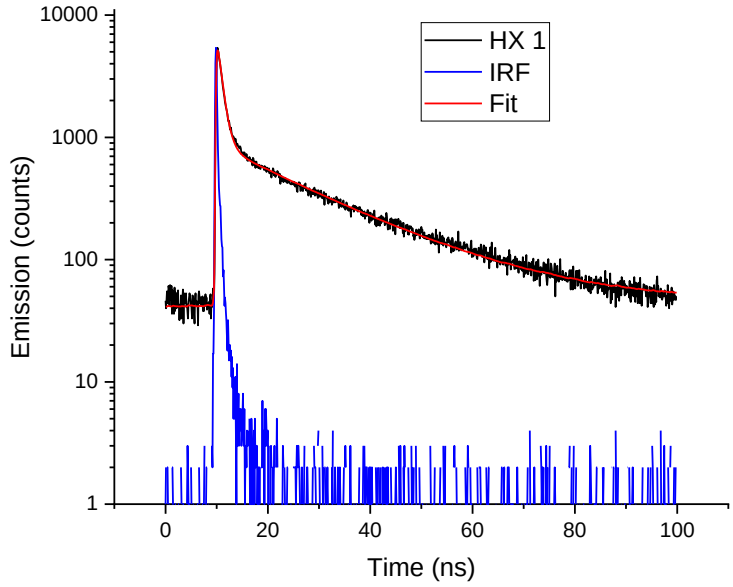
Lifetime measurements were made using an Edinburgh Instruments FLS980 fluorescence spectrophotometer. Excitation: 473 nm, pulsed diode laser (EPL-475), repetition rate: 10MHz, pulse peak power: 150 mW, laser pulse width: 79.5 ps. Detector: high-speed red-sensitive PMT (Hamamatsu H10720-20 PMT), emission slit width: 16 nm. Instrument response function (IRF) collected with colloidal silica dispersed in water (LUDOX HS-30). Lifetime fitting used Edinburgh Instruments FL980 software using the equation:

$$f(t) = \sum \beta_n e^{-t/\tau_n}$$



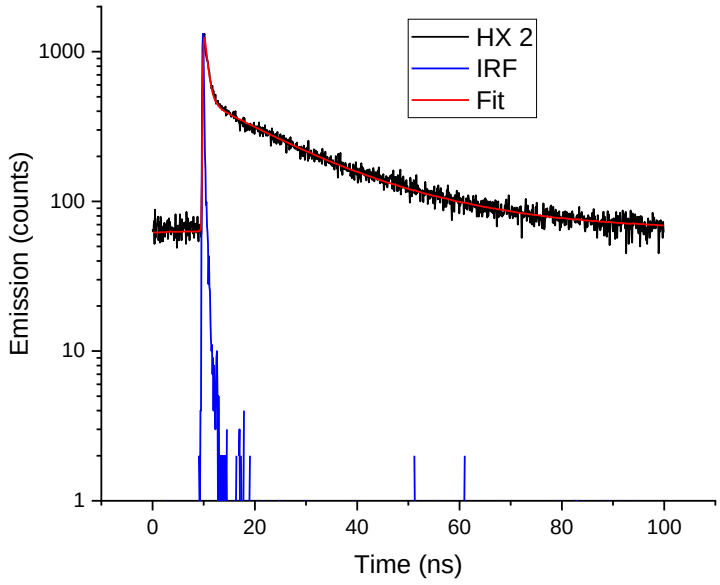
PARAM	VALUE/NS	STD. DEV./NS	PARAM	VALUE
T_1	0.24	0.05	B1	0.06
T_2	16.89	0.02	B2	0.25

Figure S3. Excited state fluorescence decay 'parent radical' **2**



PARAM	VALUE/NS	STD. DEV./NS	PARAM	VALUE
T_1	0.85	0.01	B1	0.34
T_2	20.11	0.12	B2	0.04

Figure S4. Excited state fluorescence decay $(HxO)_1$ radical **7a**



PARAM	VALUE/NS	STD. DEV./NS	PARAM	VALUE
T_1	0.58	0.02	B1	0.3

Figure S5. Excited state fluorescence decay $(HxO)_2$ radical **7b**

Optical Micrograph

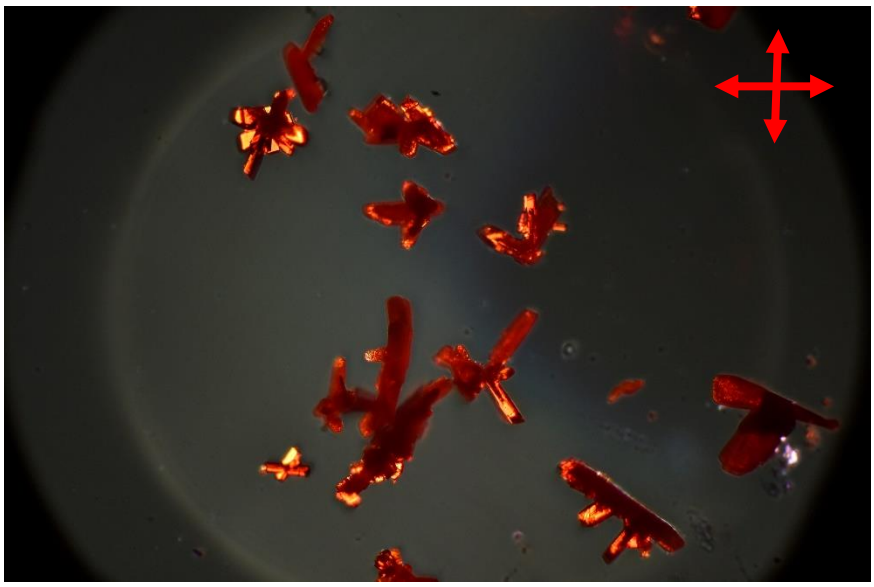


Figure S6. Optical Micrograph. Radical **7b** recrystallized from ethanol. Crossed polarizers.

UV/vis Spectra

Table S1. Radical $\lambda_{max.}$ (nm) and $\log_{10}A$ values

2, Parent radical				**7a,** HxO-1		**7b,** HxO-2		**7c,** HxO-4	
cy-hexane [1a]		Chloroform[a]		Chloroform[a]		Chloroform[b]		Chloroform[c]	
283	3.74	284	3.79	282	3.75	283	3.83	283	3.83
		366	4.12	366	4.18	366	4.24	365	4.30
382	4.57	383	4.40	385	4.47	384	4.55	382	4.54
510	3.07	509	2.97	513	3.02	518	3.08	517	3.03
562	3.08	564	2.94	564	3.02	569	3.12	565	3.18

[a] Single measurement. [b] $\log_{10}A$ Average of two measurements. [c] $\log_{10}A$ Average of three measurements.

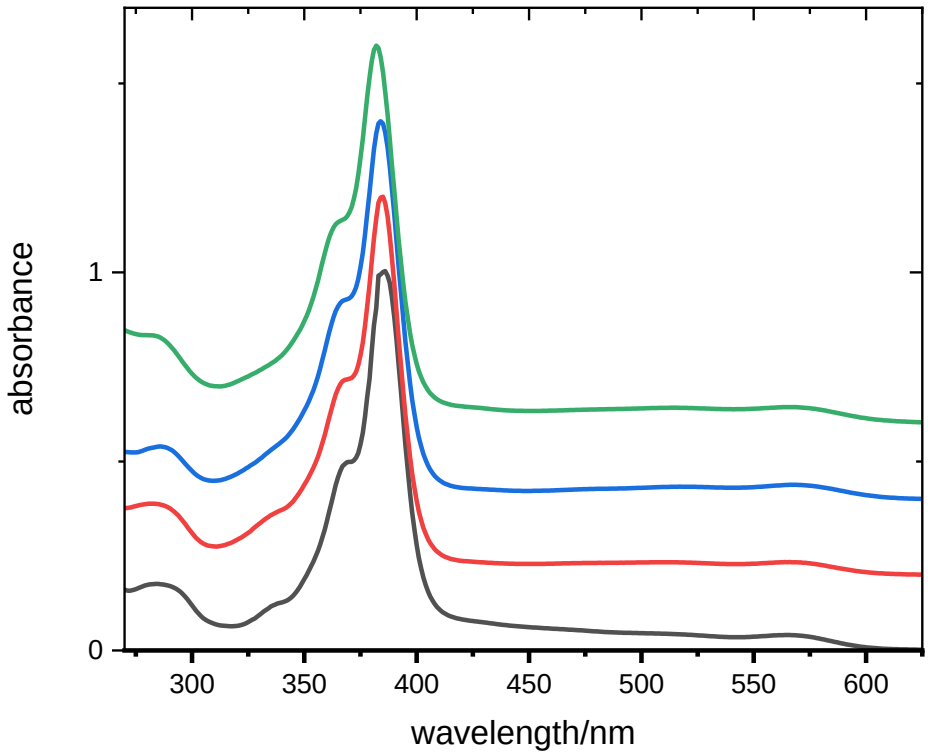


Figure S7. Normalised (Offset) UV spectra in Chloroform. Black **2,** Parent radical; Red **7a,** HxO-1; Blue **7b,** HxO-2; Green **7c,** HxO-4

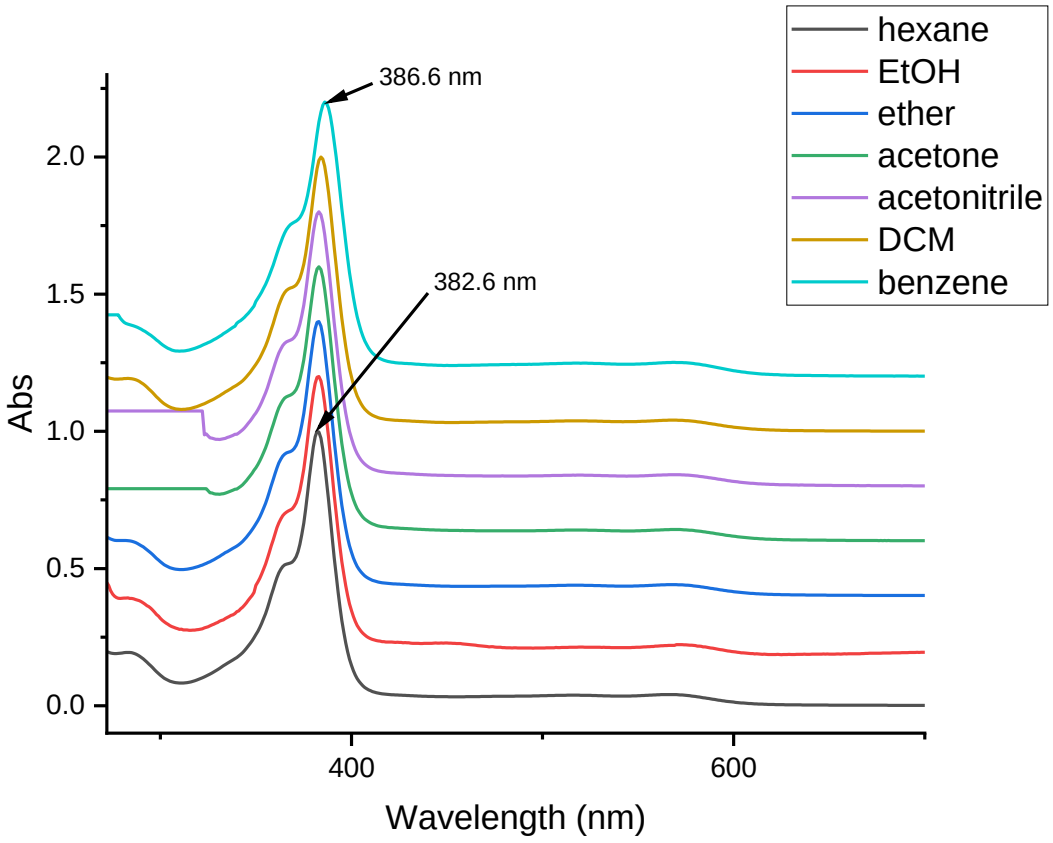


Figure S8. Solvent dependence of the UV/vis spectrum of the radical **7b,** HxO-2. (Normalised, offset) spectra in a range of solvents. Wavelength of the main maximum hexane 382.6 nm, ethanol 382.6 nm, diethyl ether 382.6 nm, acetone 382.6 nm, acetonitrile 382.9 nm, dichloromethane 384.4 nm and benzene 386.6 nm.

EPR Spectra

EPR spectra were obtained through the EPSRC National EPR Facility at the University of Manchester. A Bruker EMX Micro spectrometer, equipped with a Bruker 4122SHQ resonator was used. Sample cooling and temperature control was achieved using a Bruker ER4141VT liquid nitrogen boil-off accessory. Samples were measured in non-saturating conditions with typical measurement parameters, Microwave Power 2 mW, Modulation Amplitude 0.1 G. Reported g values were corrected using a Bruker Strong Pitch calibration standard measured at the same field sweep rate. Dilute solutions of the radicals in CH_2Cl_2 were employed and the degree of dilution and the temperature adjusted to maximise the resolution of the natural abundance ^{13}C satellites. Gererally a temperature of 200K was found to be satisfactory. For radicals **2, 8a** and **8b** great care was taken to protect the solutions from exposure to the light. Spectra were fitted and the relevant parameters extracted using Easyspin-5.2.35.

Table S2. EPR parameters.

	g-value	$\mathbf{a_{\alpha H}}$	$\mathbf{a_{ipso}}$	$\mathbf{a_{ortho}}$
2, Parent radical [a]	2.0028	84	36.3	33
2, literature values [2] [b]	2.0028	84	36.6	30.1
8a, F-1 [a, c]	2.0029	84.4	-	-
8b, F-2 [a, d]	2.0030	85	-	-
7a, HxO-1 [a]	2.0030	83.5	-	-
7b, HxO-2 [a]	2.0030	84	36.7	33

[a] CH_2Cl_2 solution 200 K. [b] $CFCl_3$ solution 163 K. [c] Contained ca. 20% **2**. [d]Contained ca. 5% **8a**.

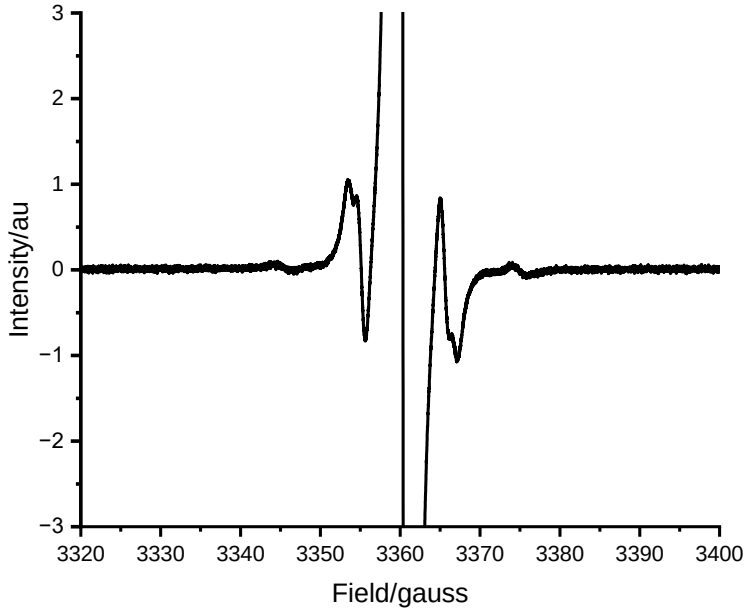


Figure S9. Parent Radical **2** showing the ^{13}C satellites, 9.439760 GHz, 200K, 0.2modAmp.

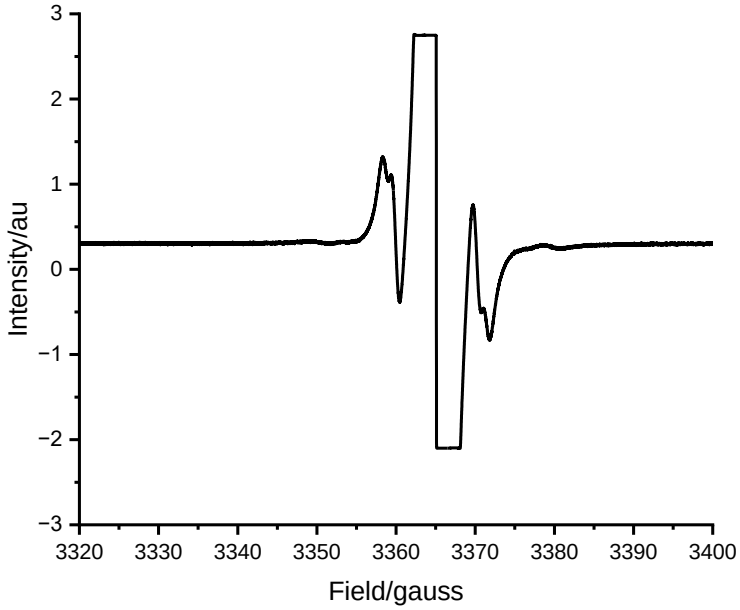


Figure S10. $(HxO)_2$ Radical **7b** showing the ^{13}C satellites, 9.453835 GHz, 200K, 0.2modAmp.

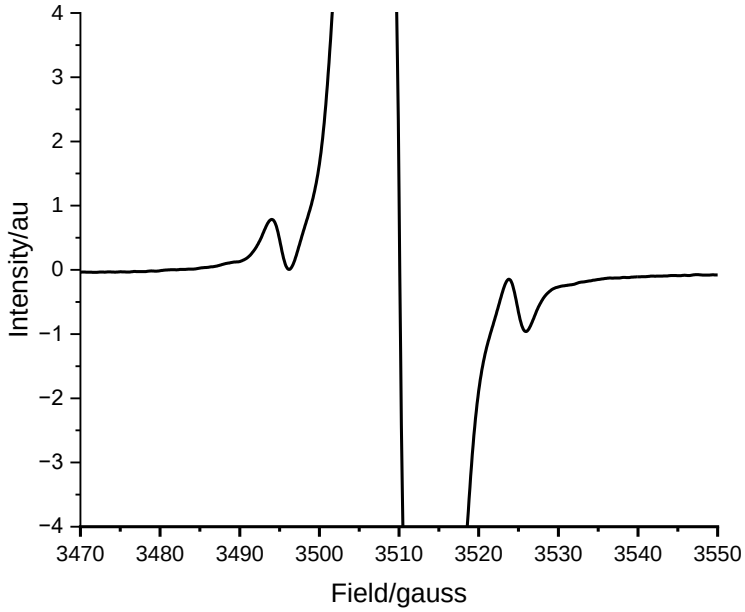


Figure S11. Parent Radical **2** enhanced gain, showing the α-carbon ^{13}C satellites, 9.860305 GHz.

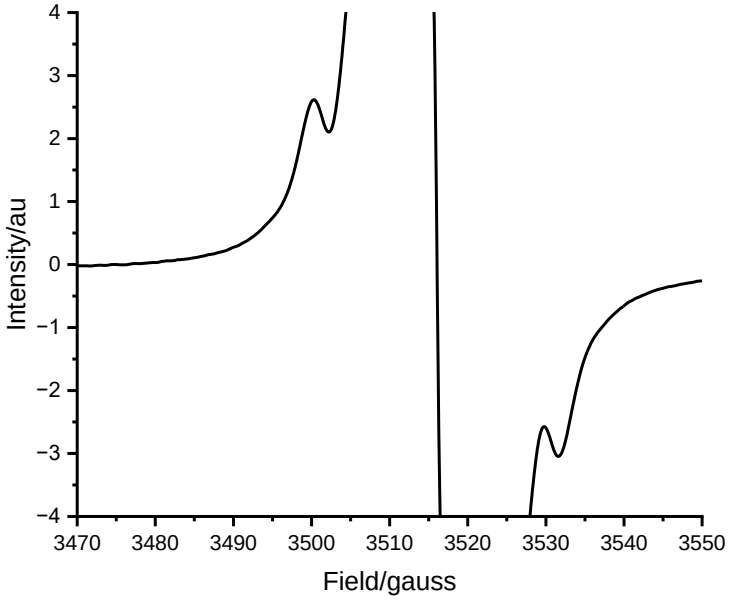


Figure S12. F_1 Radical **8a** enhanced gain, showing the α-carbon ^{13}C satellites, 9.877490 GHz.

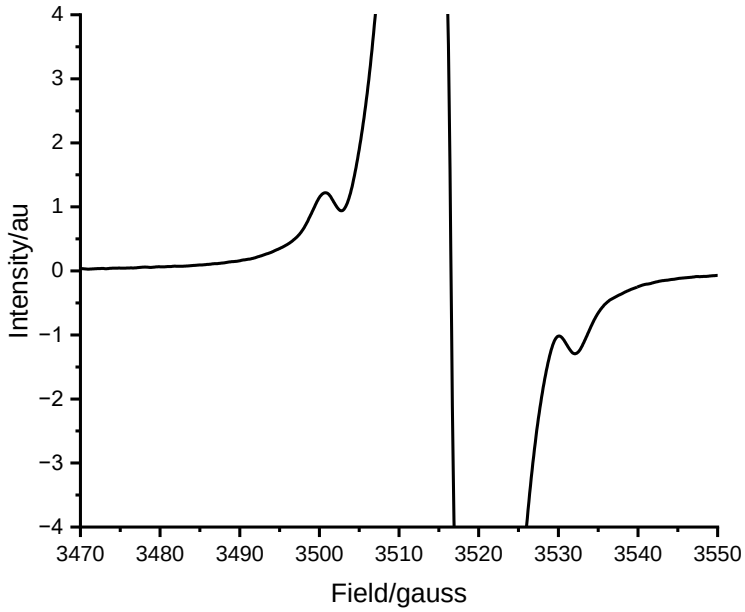


Figure S13. F_2 Radical **8b** enhanced gain, showing the α-carbon ^{13}C satellites, 9.879077 GHz.

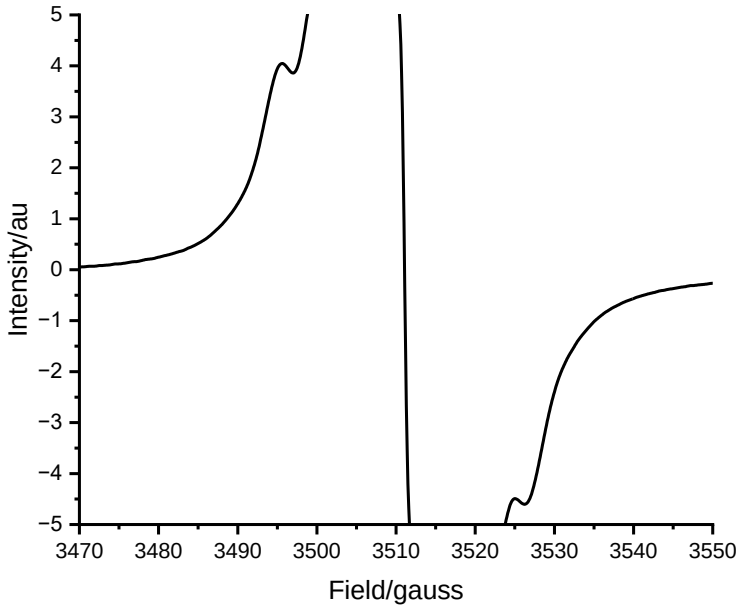


Figure S14. $(HxO)_1$ Radical **7a** enhanced gain, showing the α-carbon ^{13}C satellites, 9.863459 GHz.

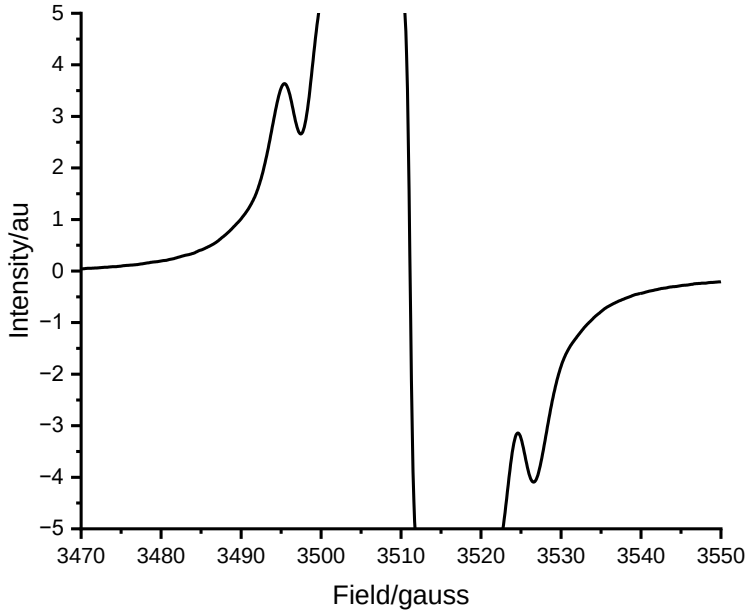


Figure S15. $(HxO)_2$ Radical **7b** enhanced gain, showing the α-carbon ^{13}C satellites, 9.864073 GHz.

^{1}H, ^{13}C and ^{19}F NMR Spectra

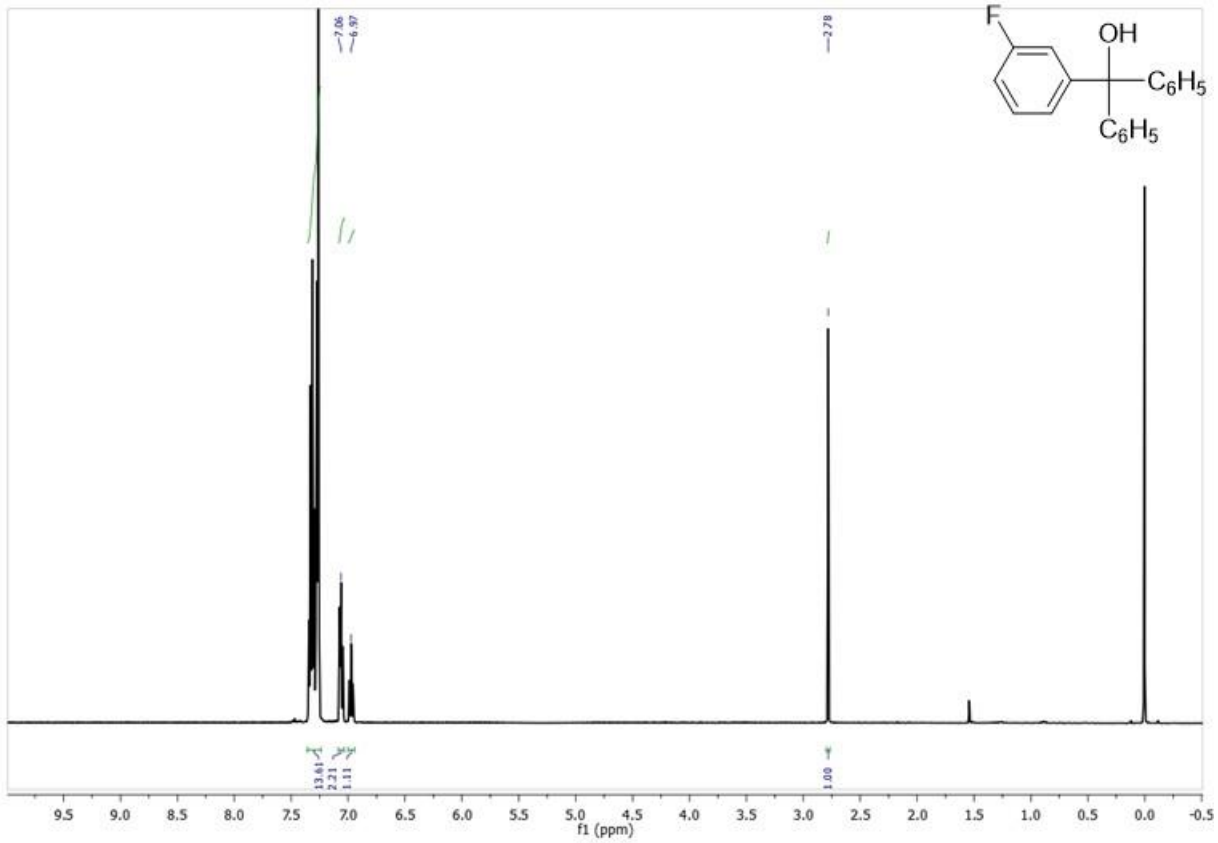


Figure S16. ^{1}H NMR (500 MHz, $CDCl_3$) **3a**

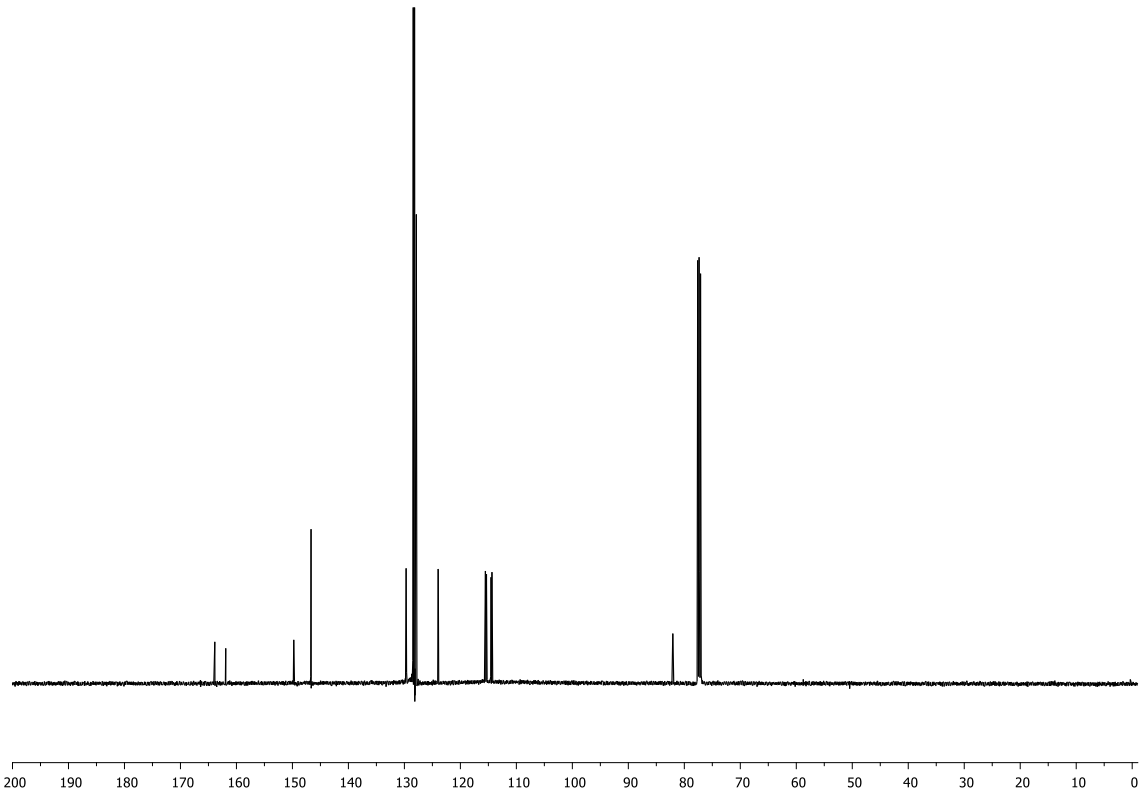


Figure S17. ^{13}C NMR (126 MHz, $CDCl_3$) **3a**

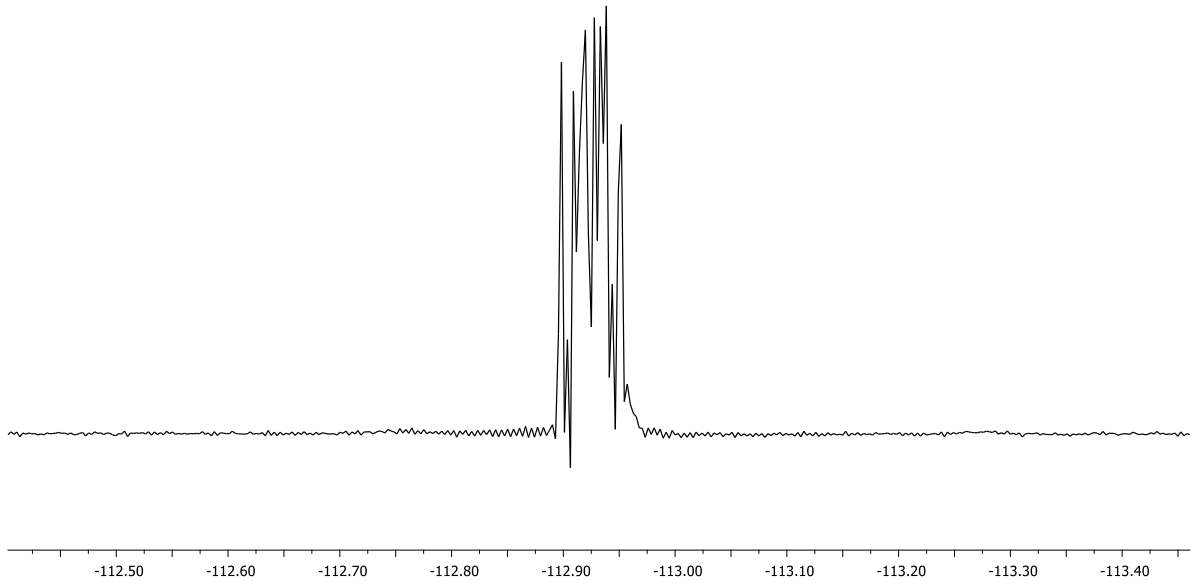


Figure S18. ^{19}F NMR (470 MHz, $CDCl_3$) **3a**

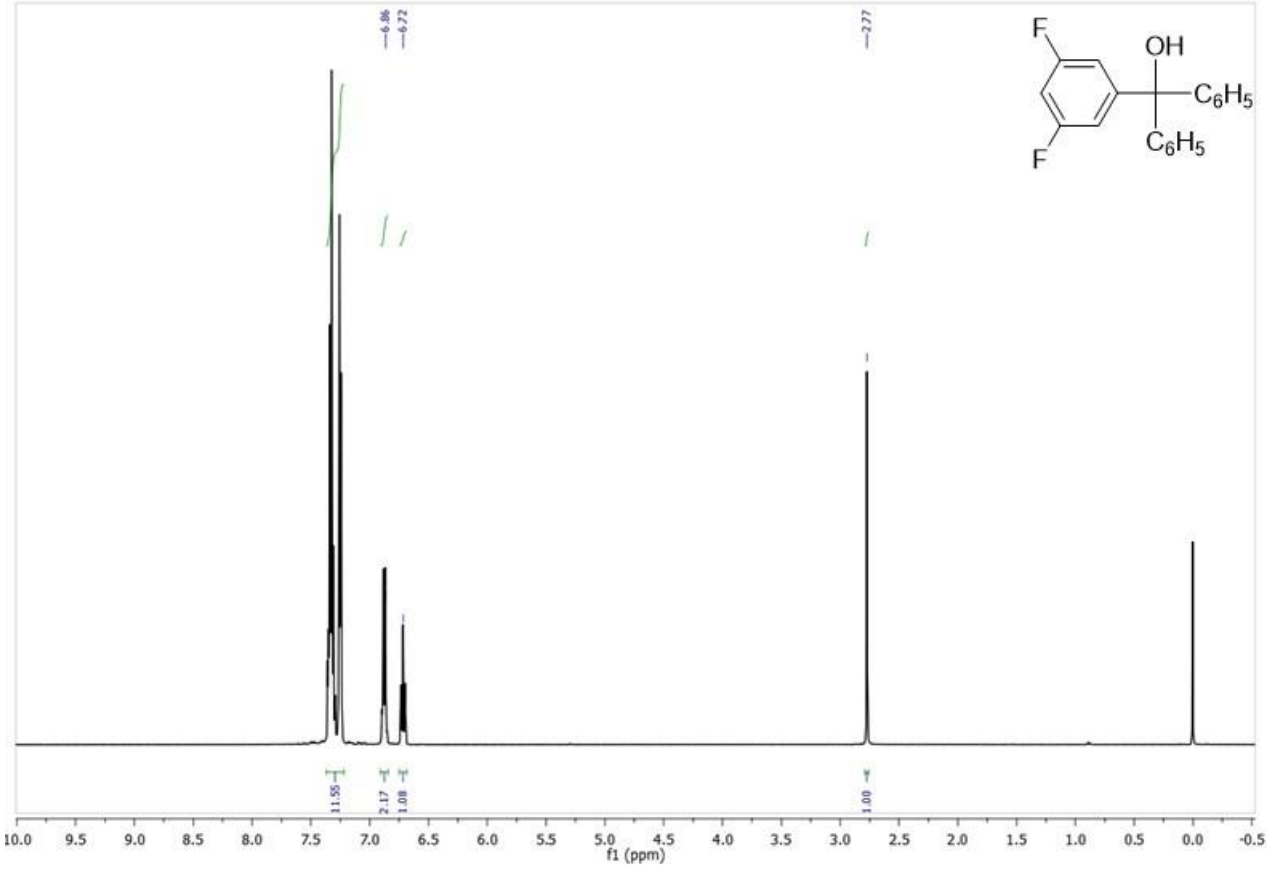


Figure S19. ^{1}H NMR (500 MHz, $CDCl_3$) **3b**

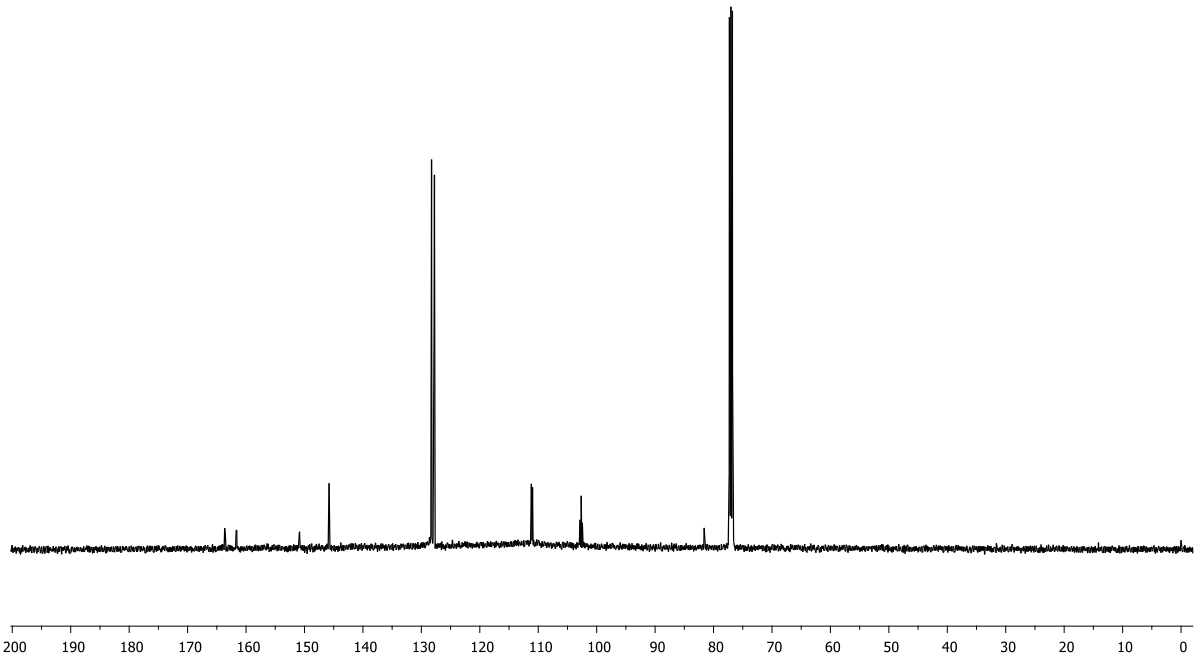


Figure S20. ^{13}C NMR (126 MHz, $CDCl_3$) **3b**

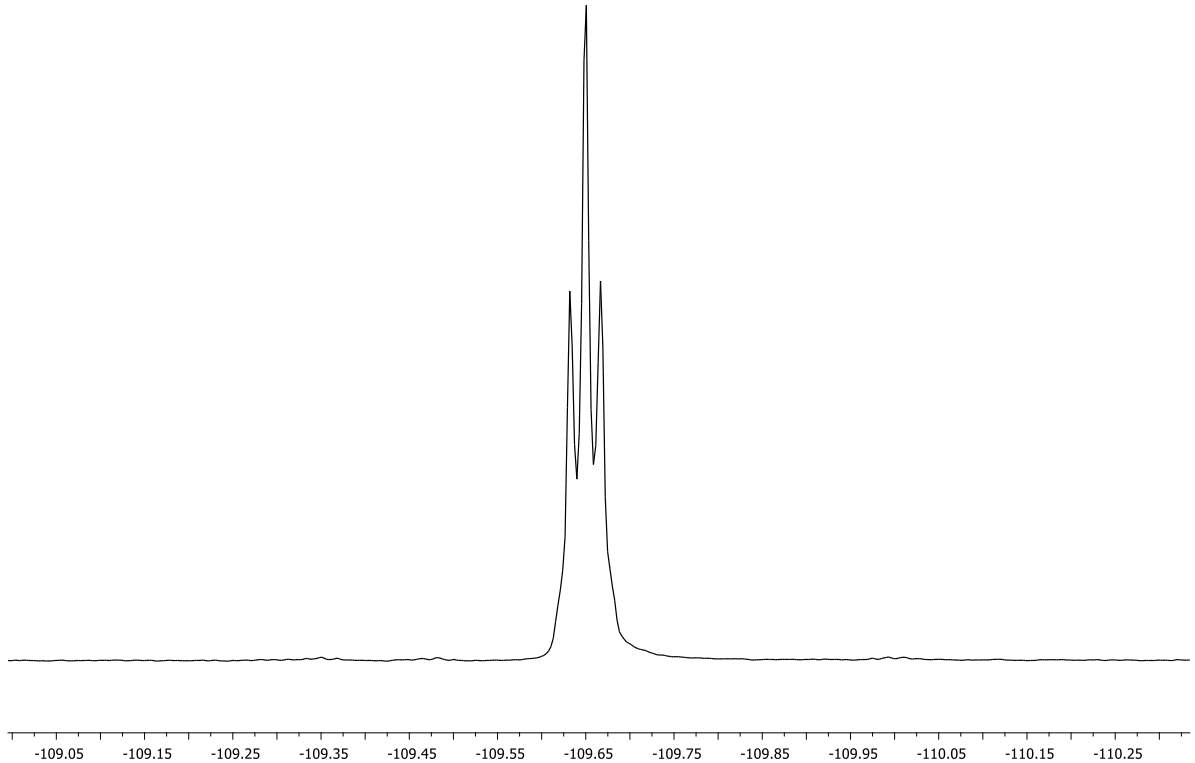


Figure S21. ^{19}F NMR (470 MHz, $CDCl_3$) **3b**

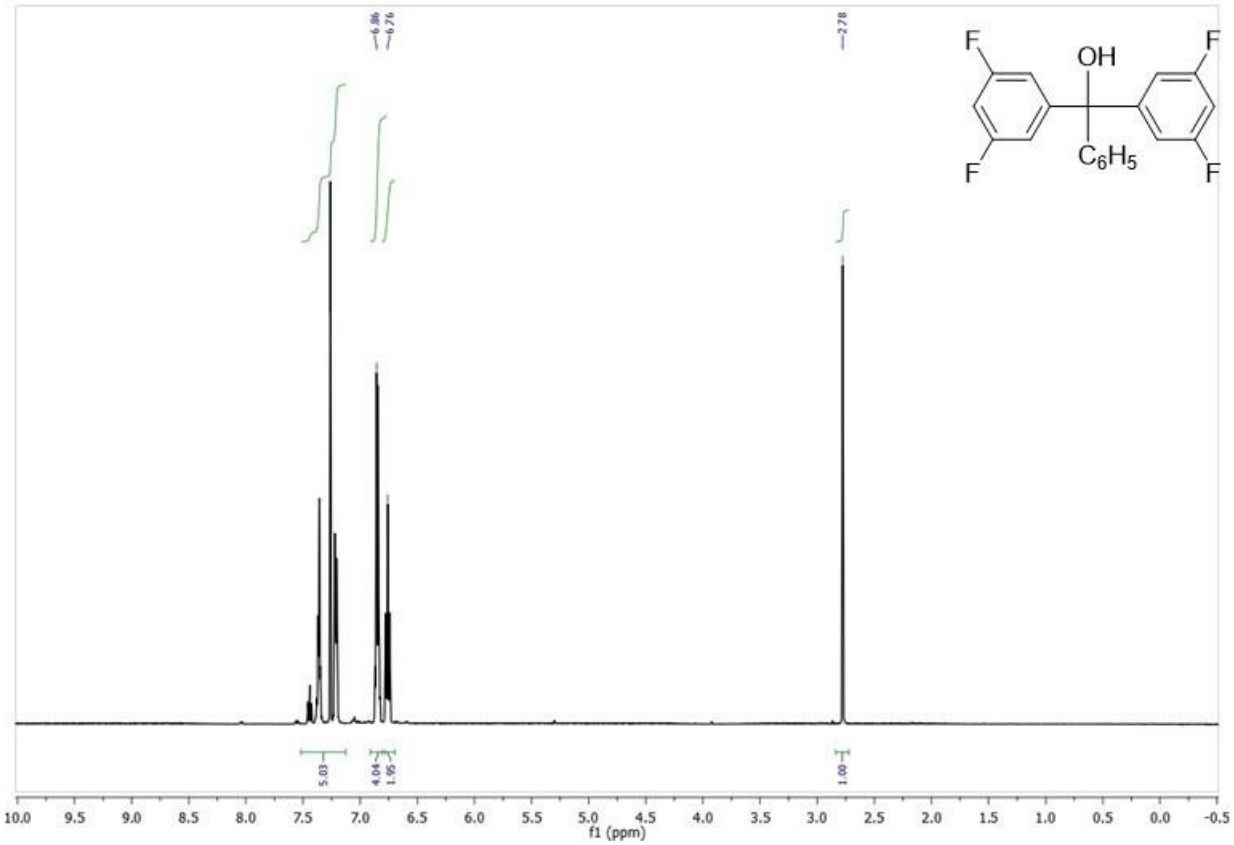


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) **3c**

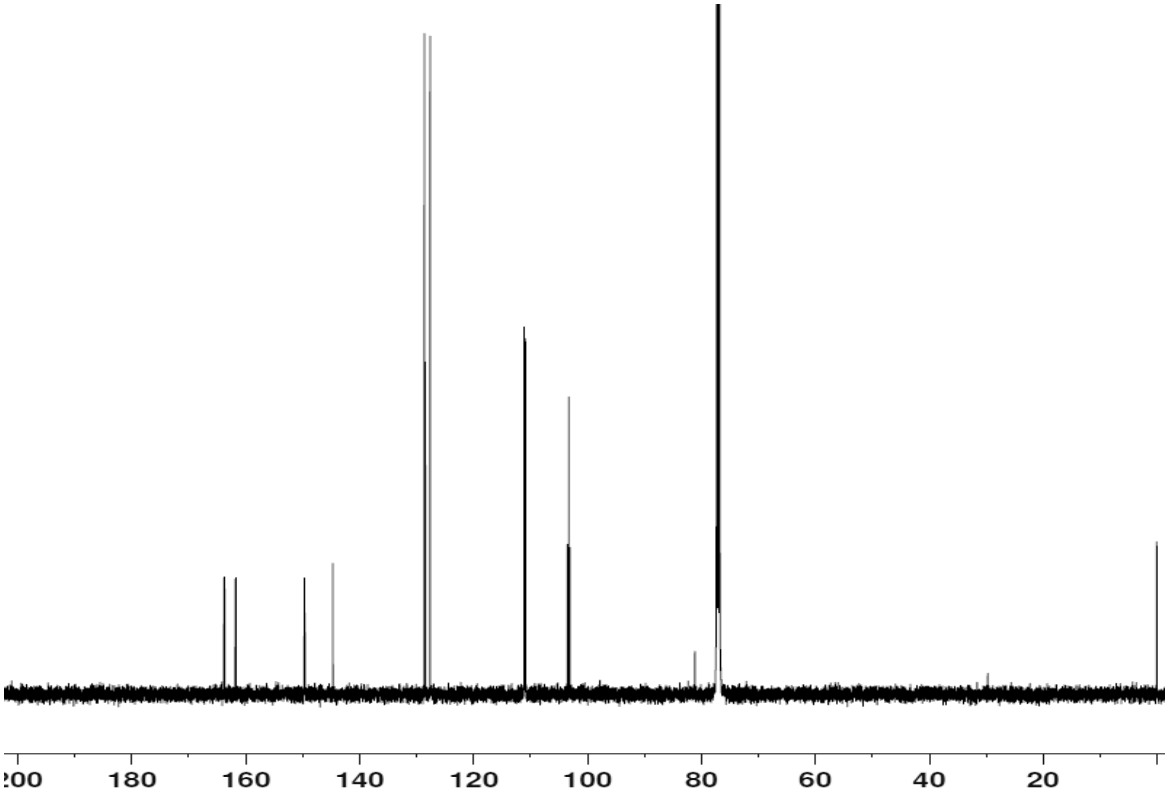


Figure S23. ^{13}C NMR (126 MHz, $CDCl_3$) **3c**

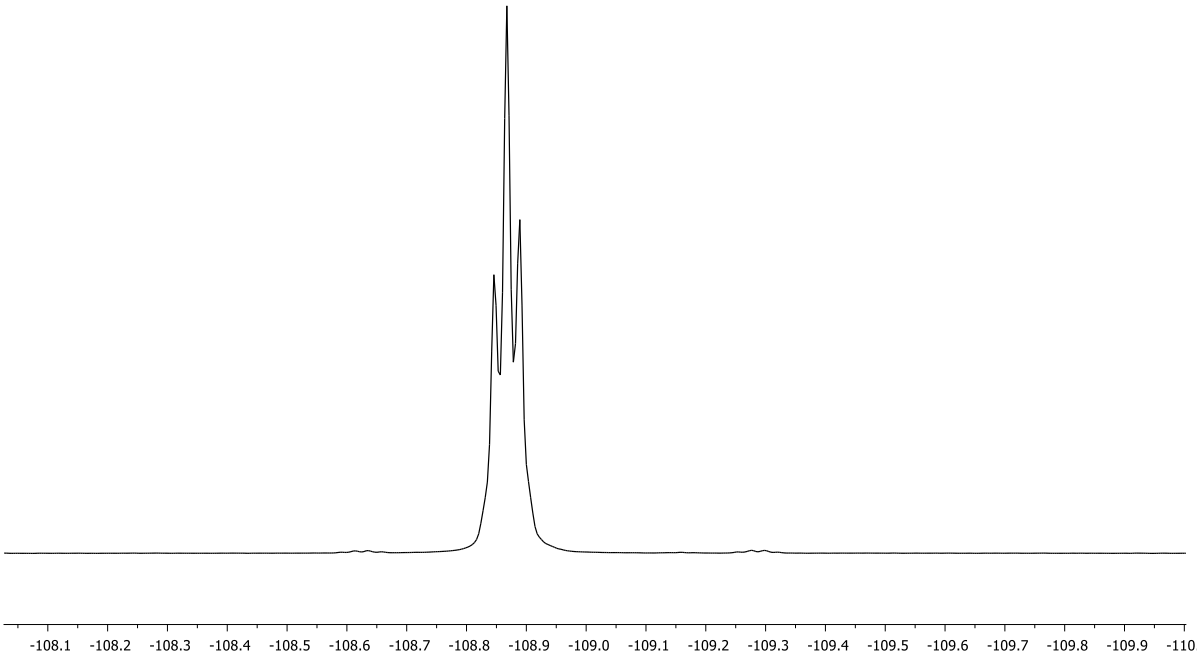


Figure S24.[19]F NMR (376 MHz, $CDCl_3$) **3c**

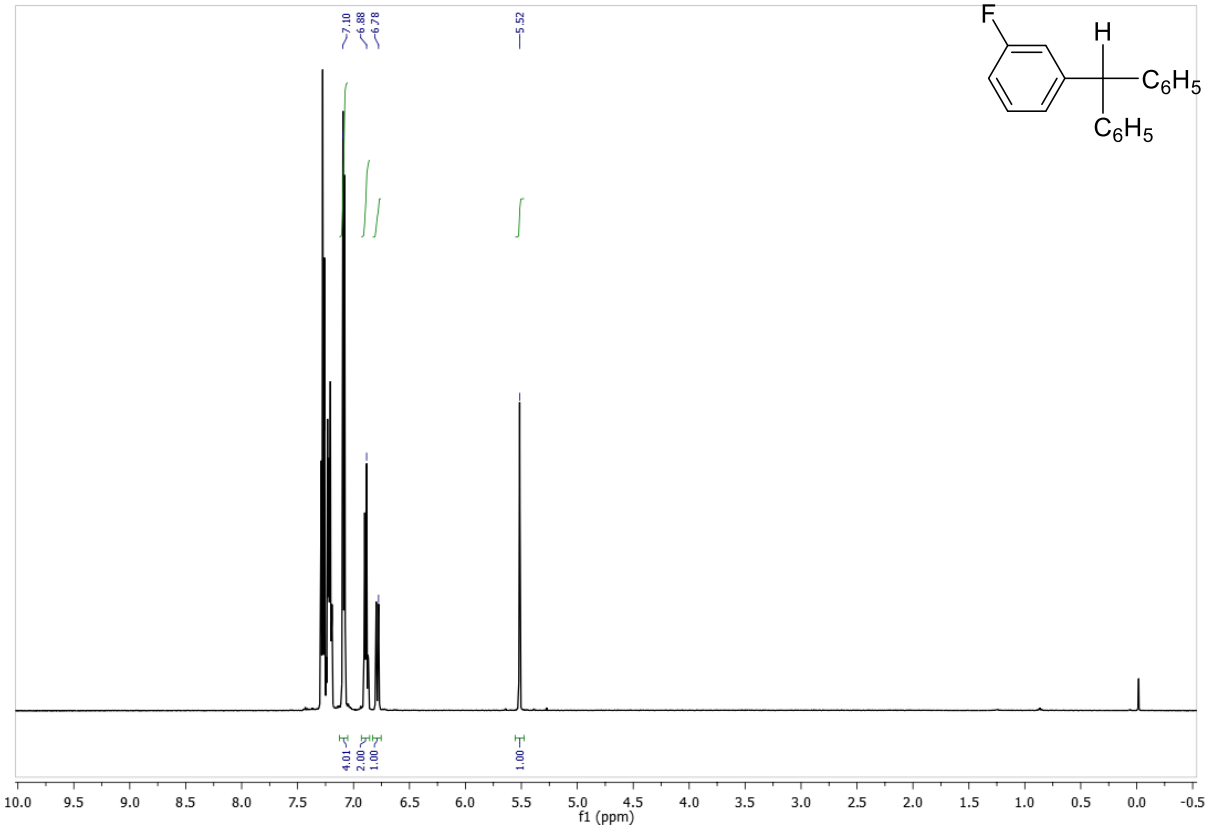


Figure S25. [1]H NMR (400 MHz, $CDCl_3$) **4a**

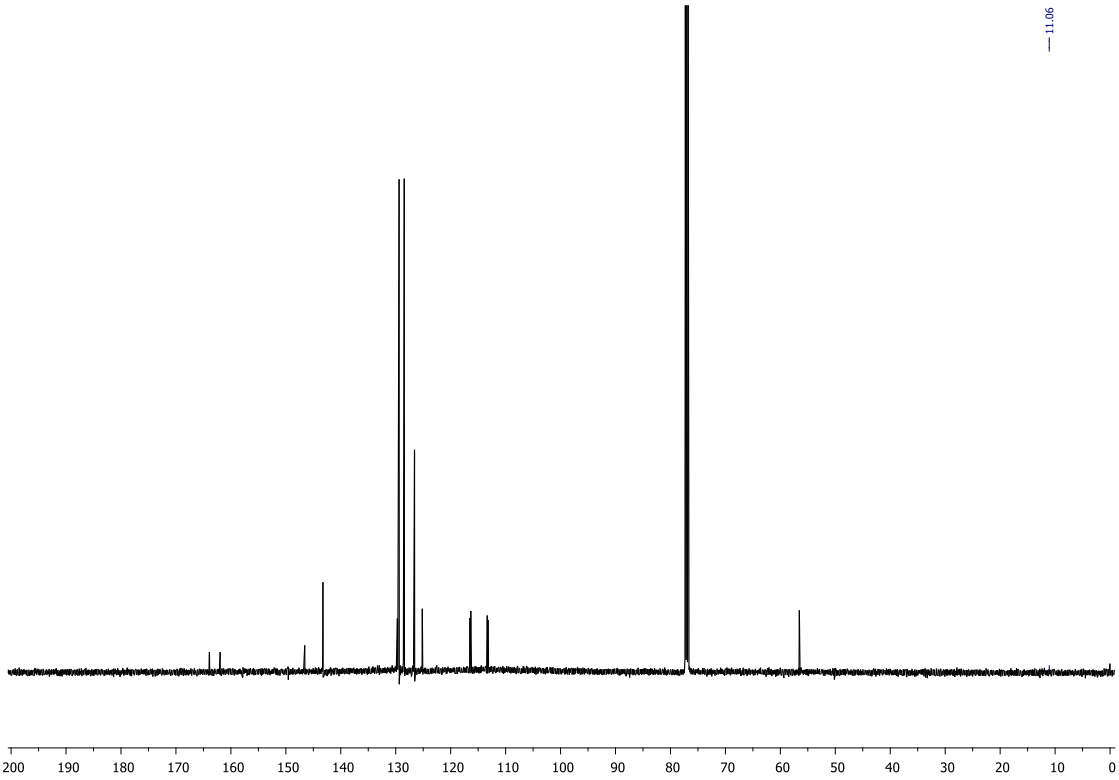


Figure S26. ^{13}C NMR (126 MHz, $CDCl_3$) **4a**

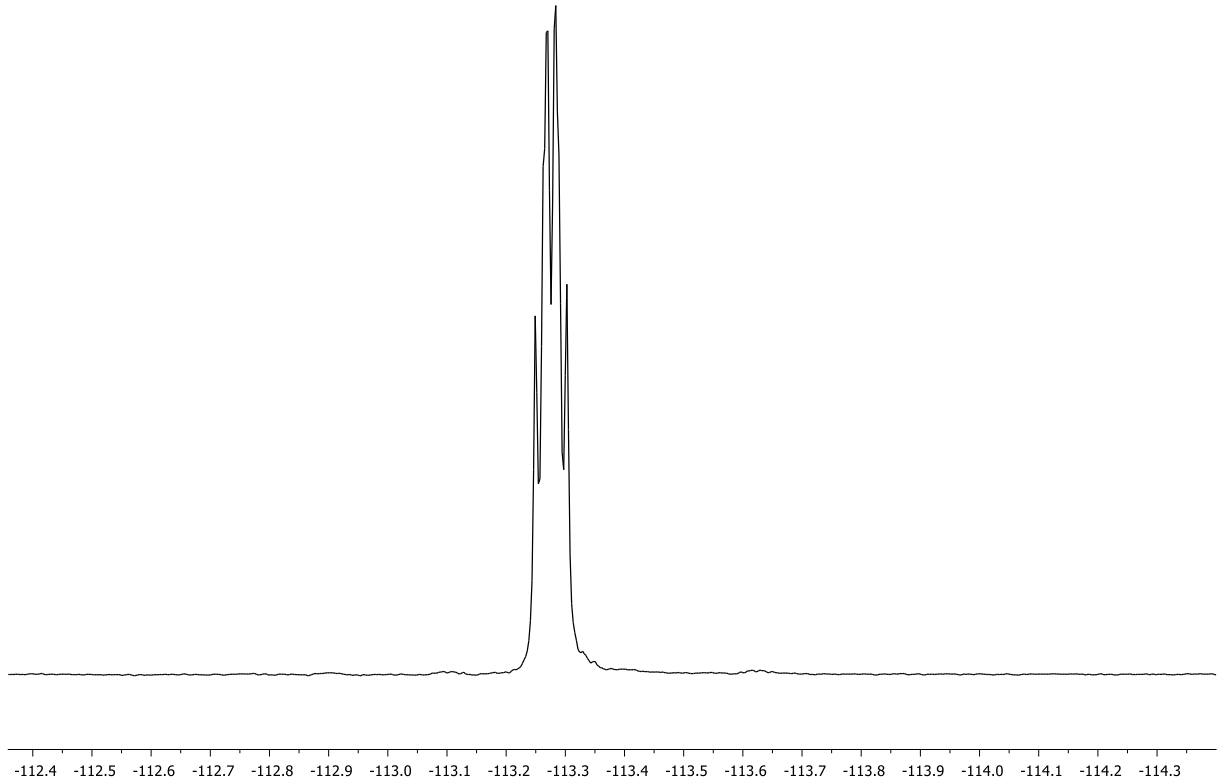


Figure S27. ^{19}F NMR (470 MHz, $CDCl_3$) **4a**

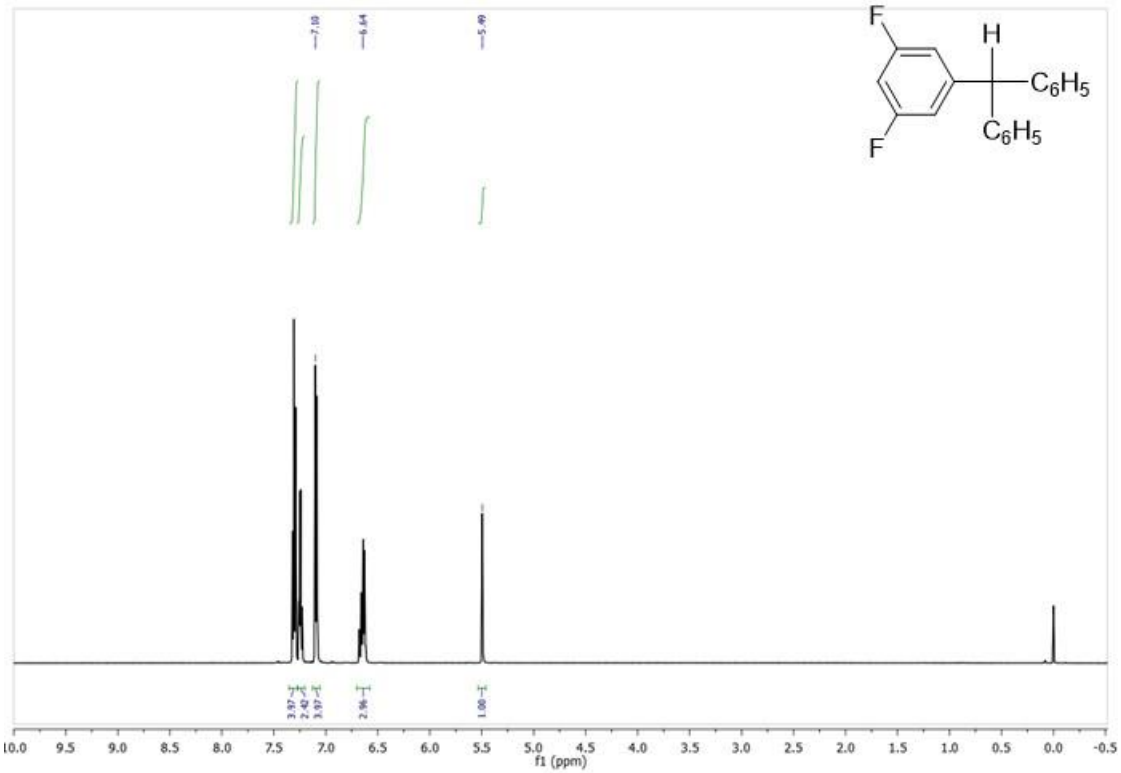


Figure S28. ^{1}H NMR (500 MHz, $CDCl_3$) **4b**

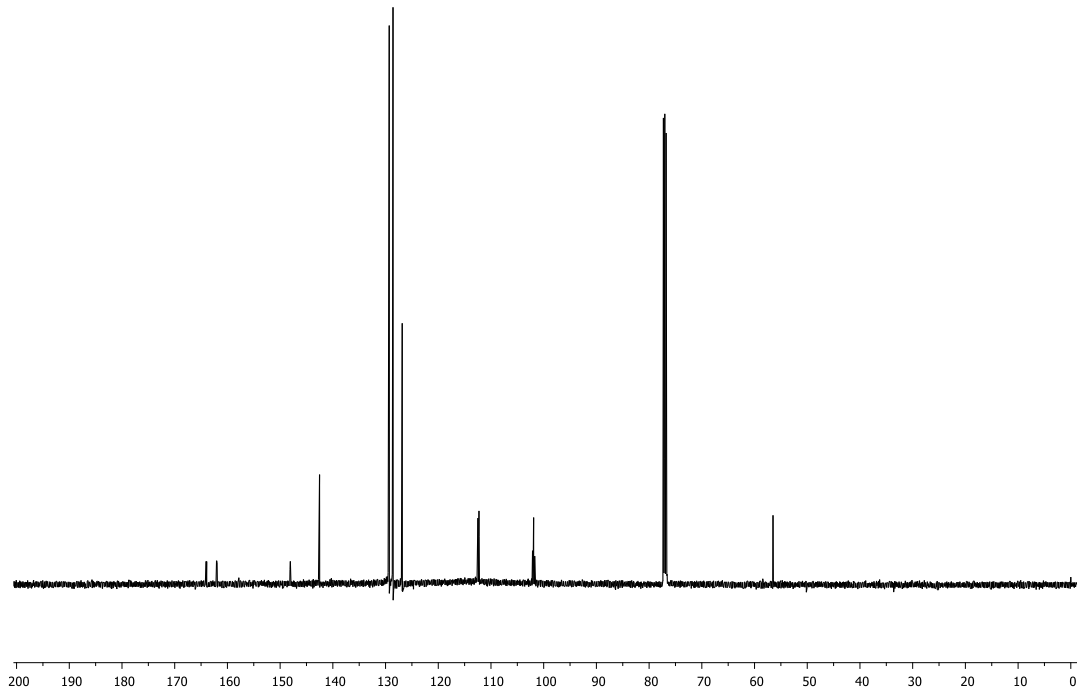


Figure S29. ^{13}C NMR (126 MHz, $CDCl_3$) **4b**

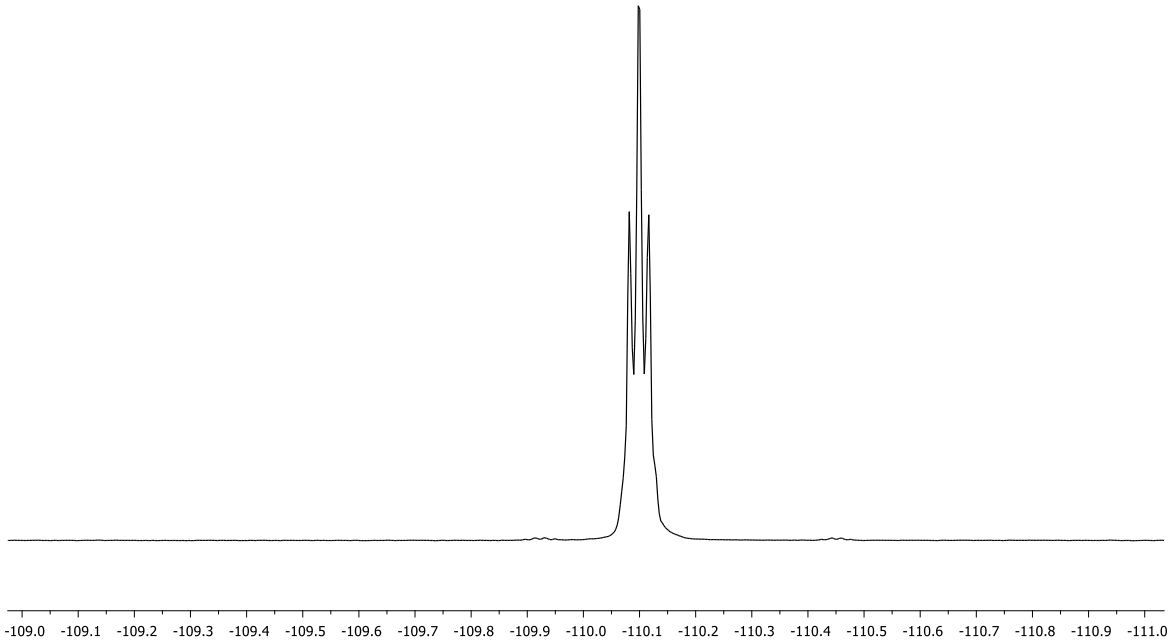


Figure S30. ^{19}F NMR (470 MHz, $CDCl_3$) **4b**

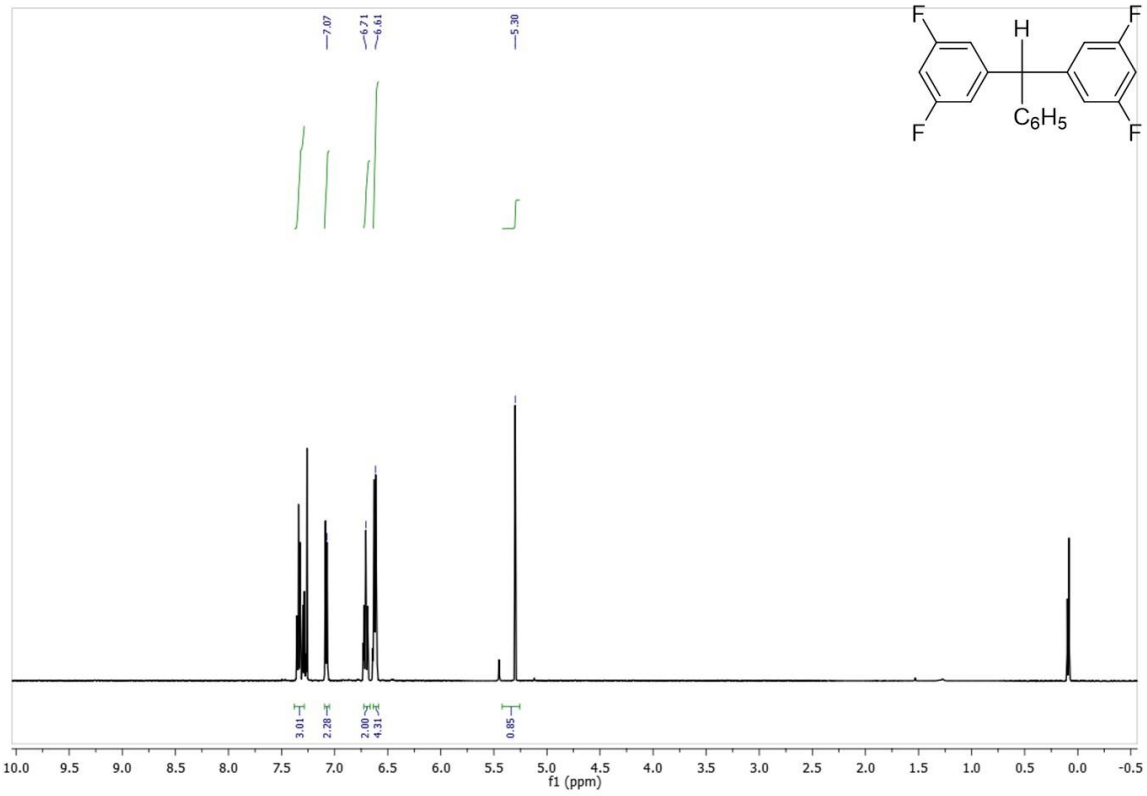


Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) **4c**

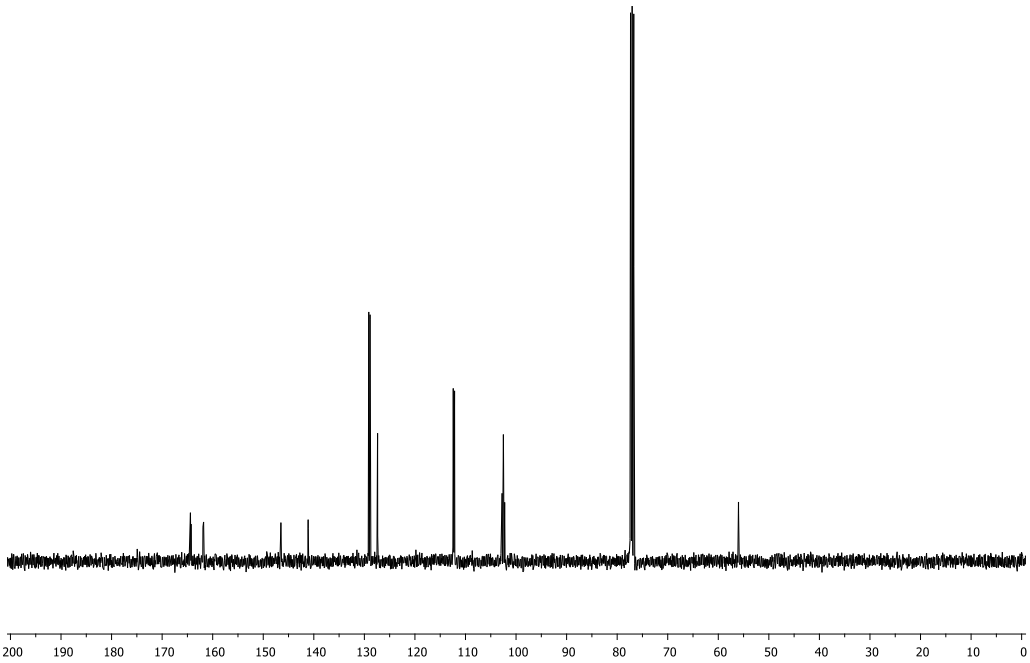


Figure S32. ^{13}C NMR (101 MHz, $CDCl_3$) **4c**

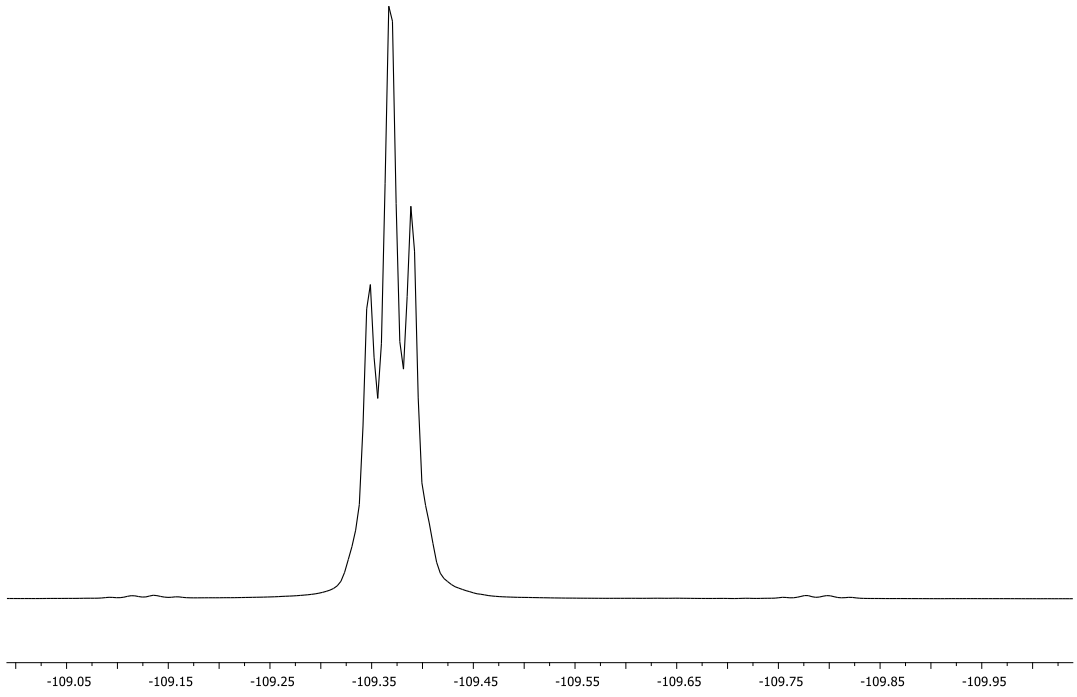


Figure S33. ^{19}F NMR (376 MHz, $CDCl_3$) **4c**

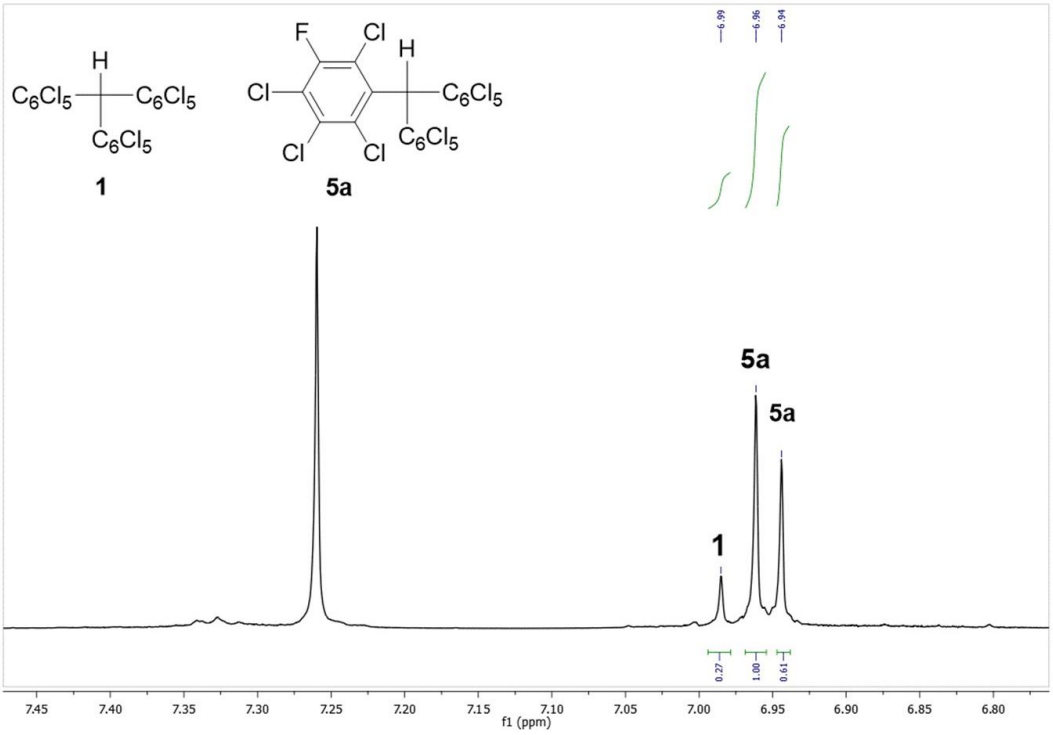


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$, expansion) saturated solution of the crude product of chlorination of **4a.** (a mixture of **5a** *syn* and *anti* isomers and **1**)

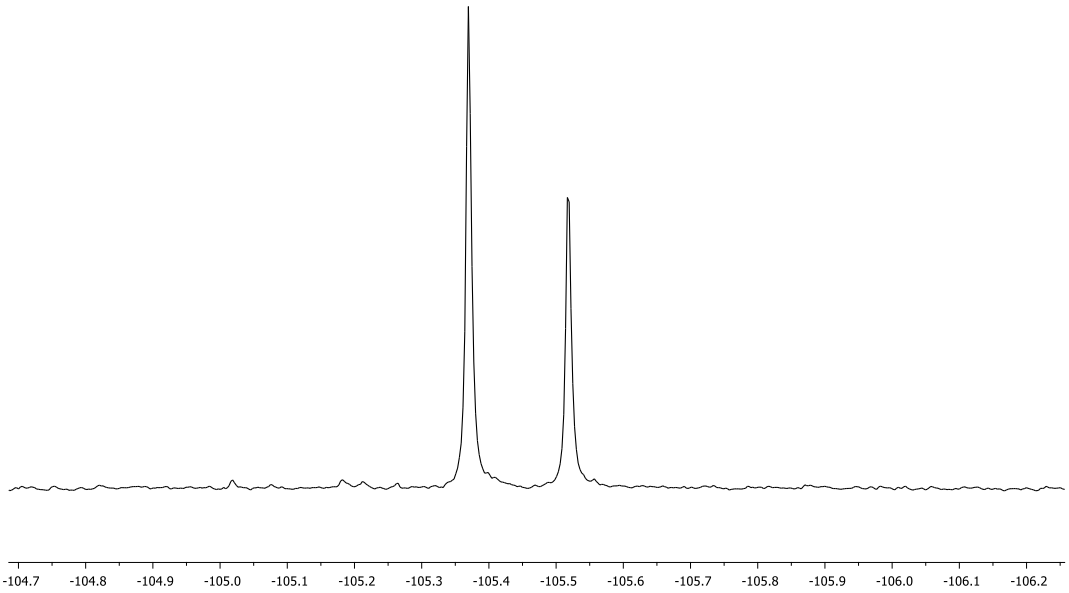


Figure S35 ^{19}F NMR (470 MHz, $CDCl_3$) saturated solution of the crude product of chlorination of **4a.** (*syn* and *anti* isomers)

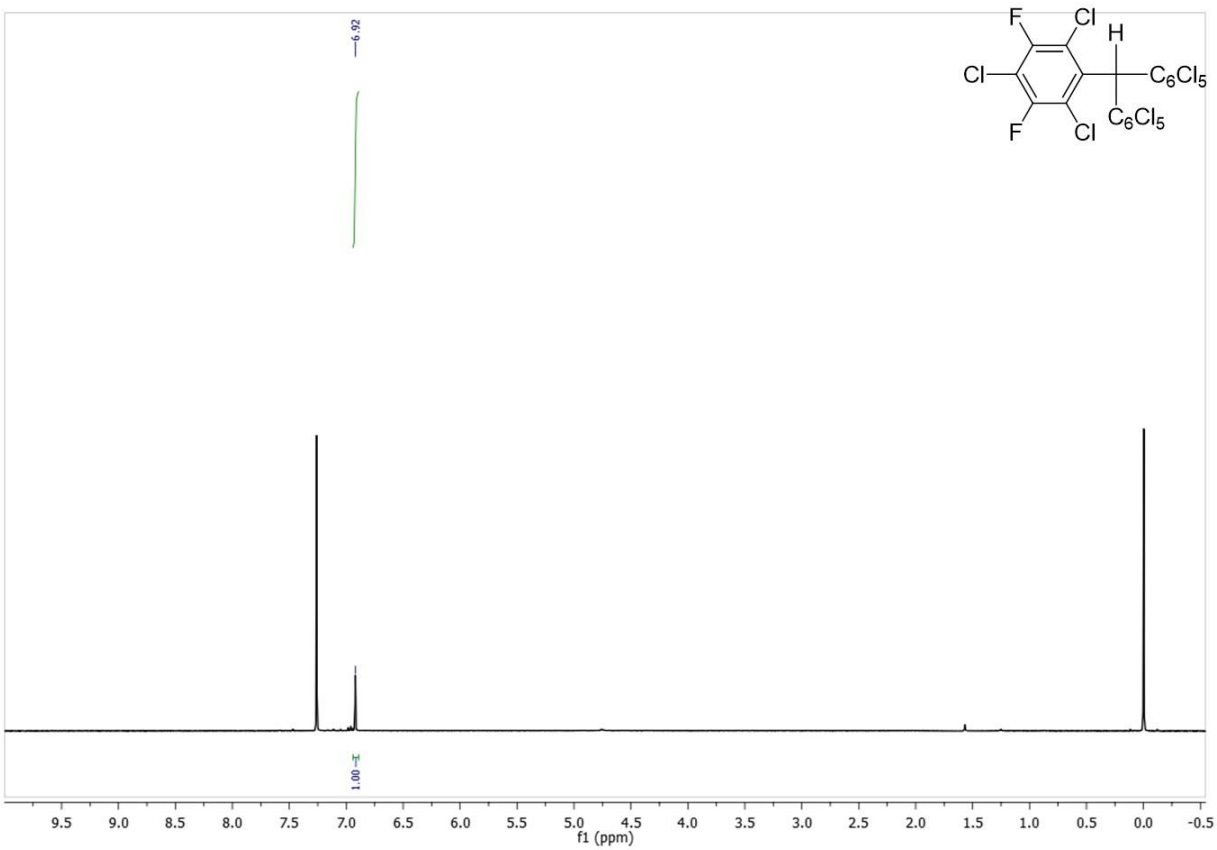


Figure S36. ^{1}H NMR (500 MHz, $CDCl_3$) crude product, saturated solution, **5b**.

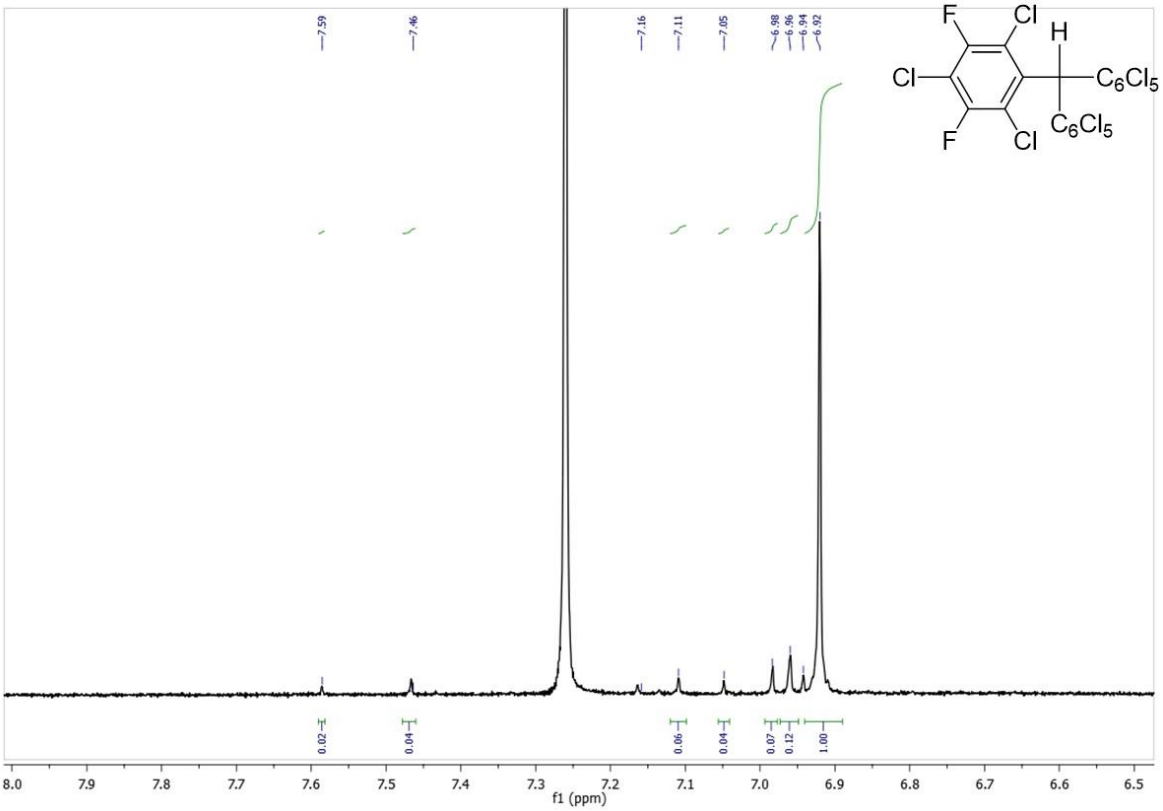


Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) **5b**, expansion showing ArH impurities in the crude product.

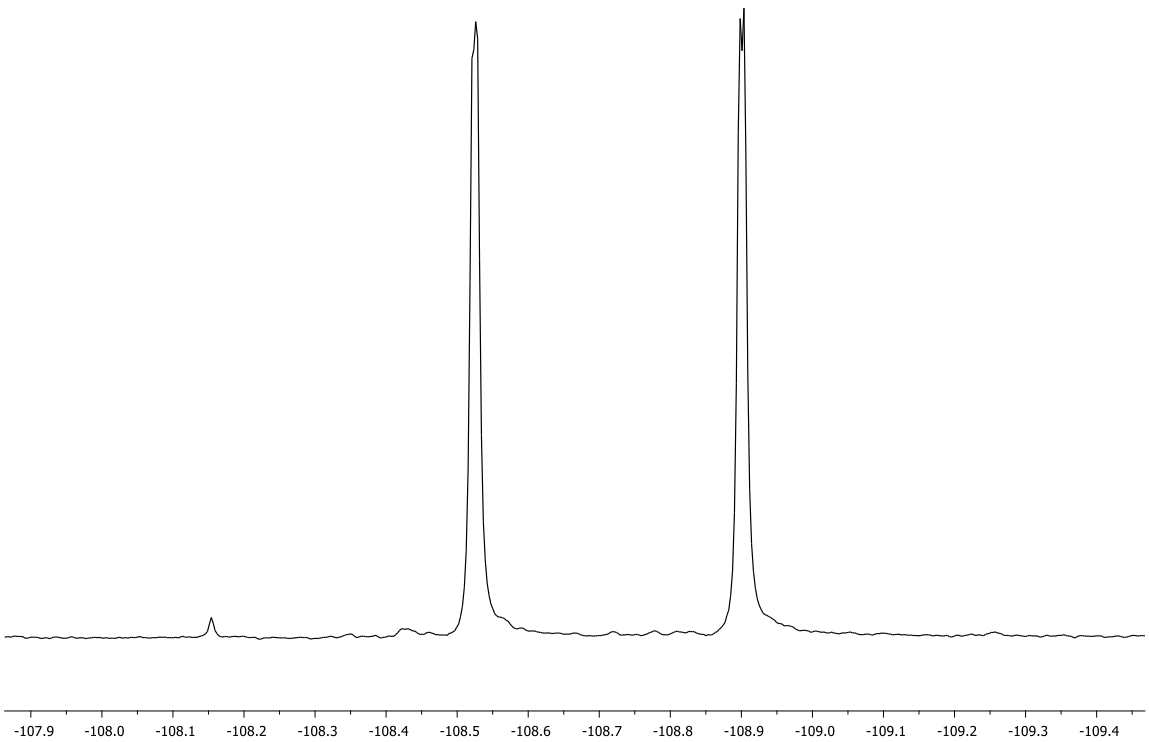


Figure S38. ^{19}F NMR (470 MHz, $CDCl_3$) crude product, saturated solution, **5b**

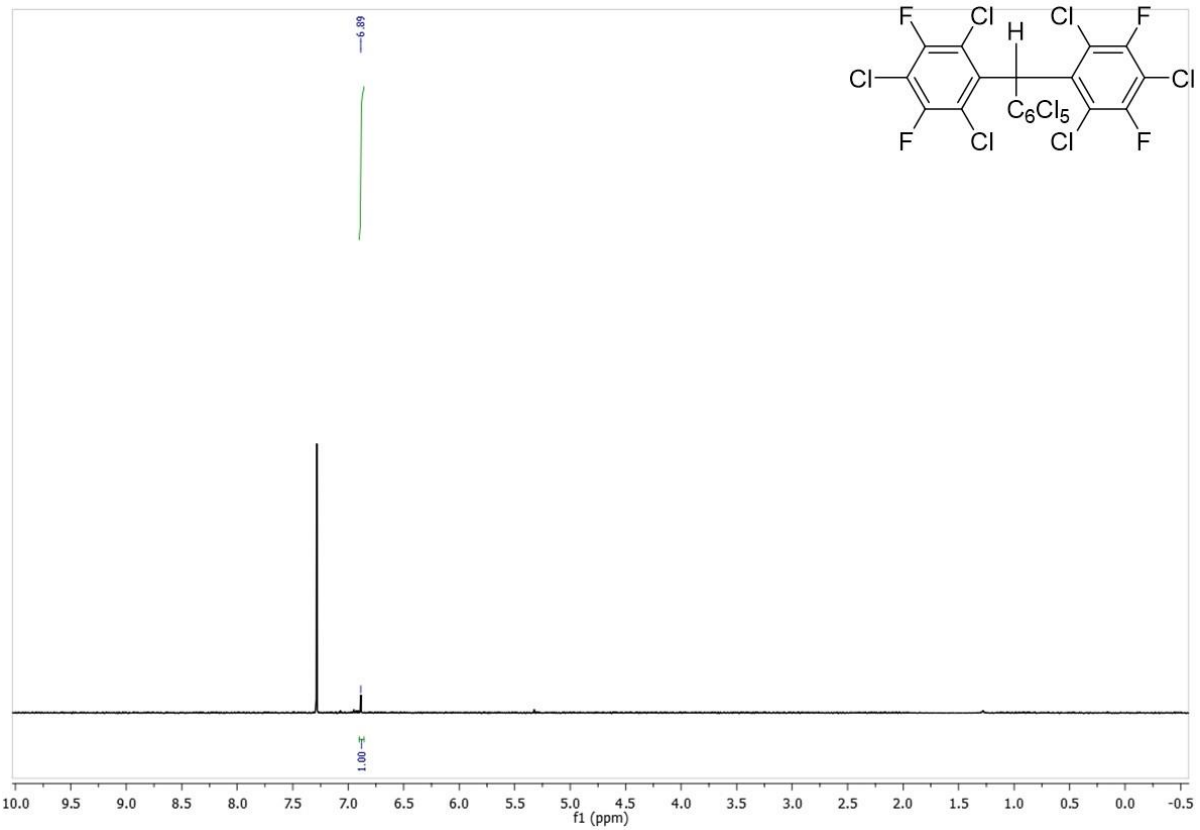


Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) crude product, saturated solution, **5c**

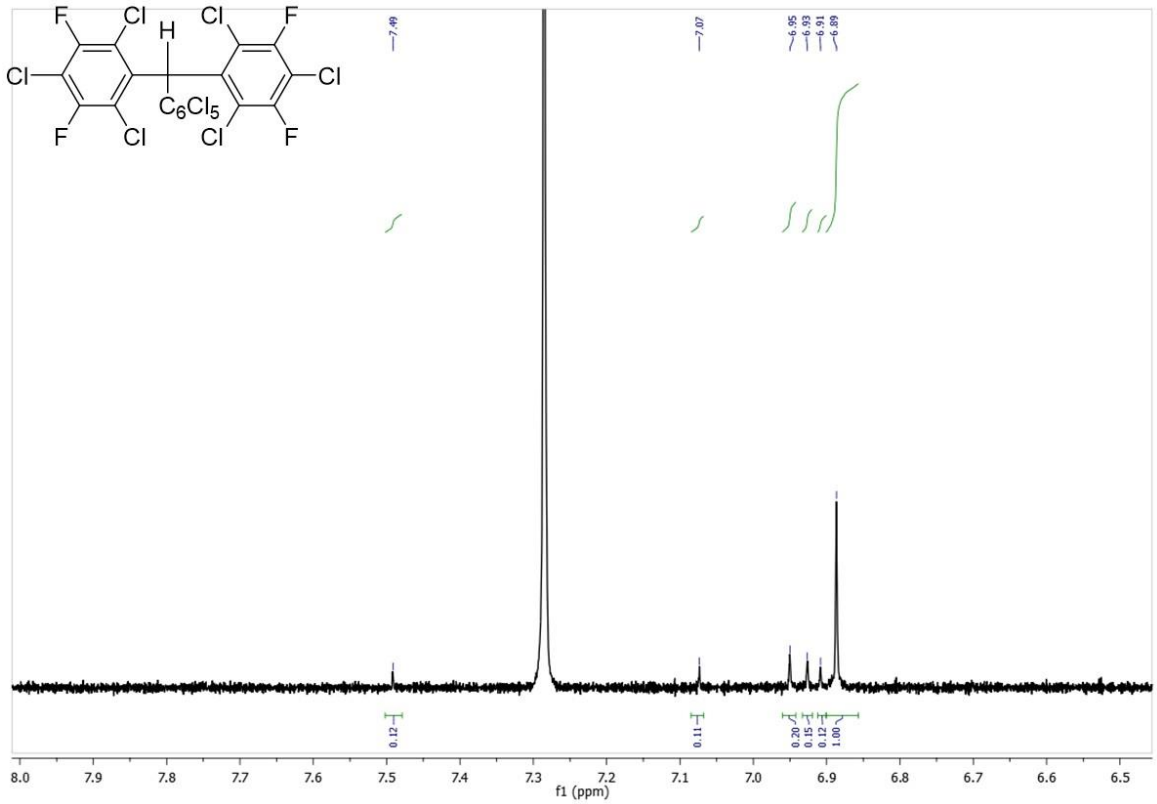


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) **5c**, expansion showing ArH impurities in the crude product.

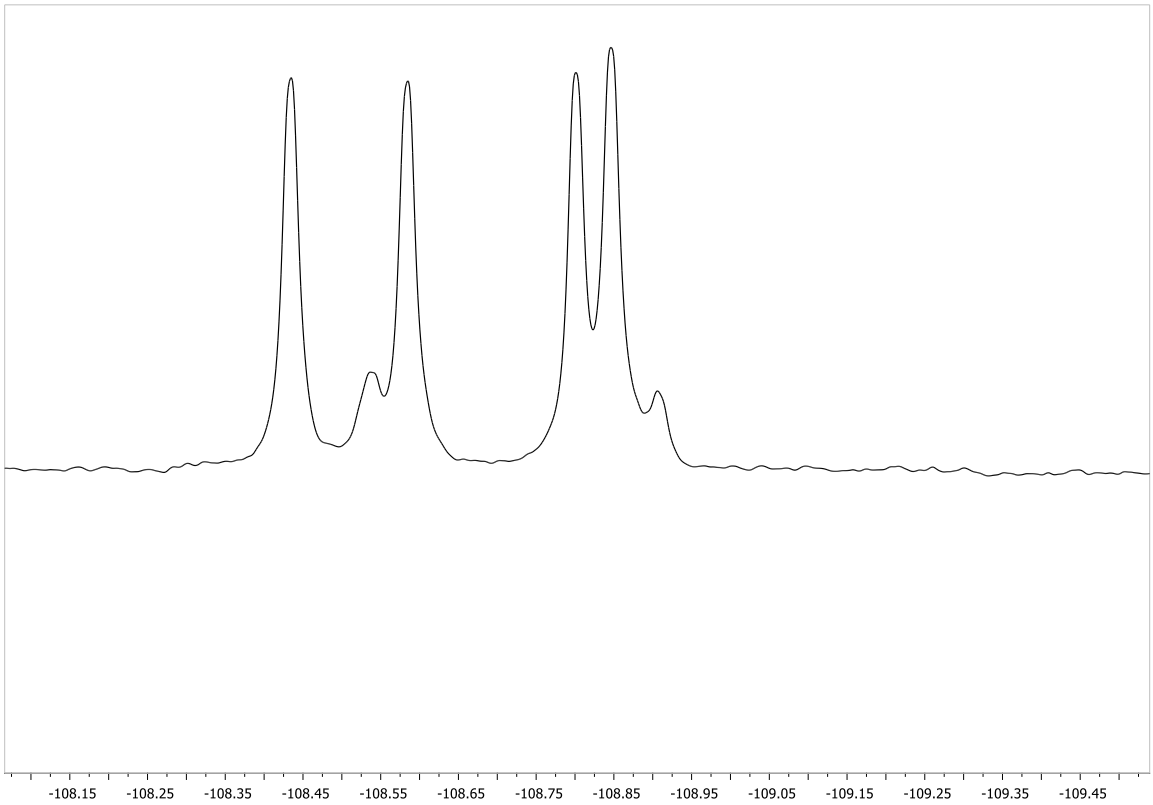


Figure S41. ^{19}F NMR (376 MHz, $CDCl_3$) crude product, saturated solution, **5c**

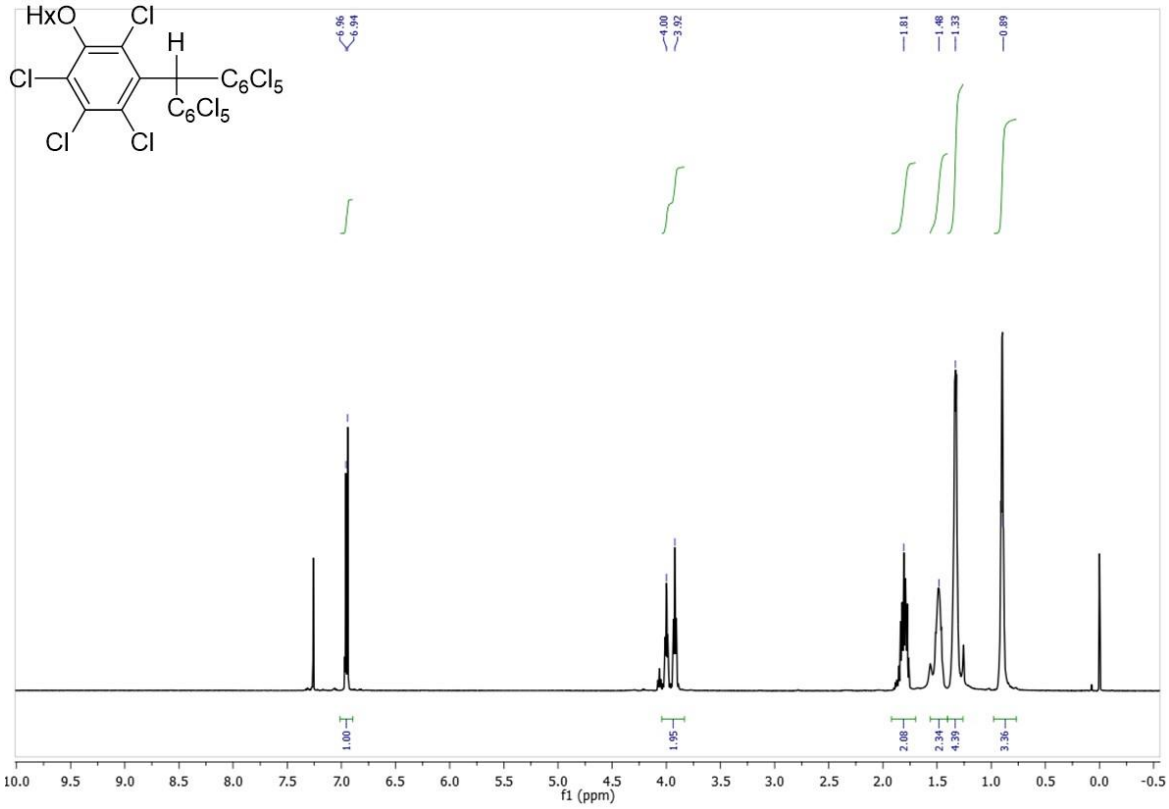


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) **6a** (*syn* and *anti* isomers)

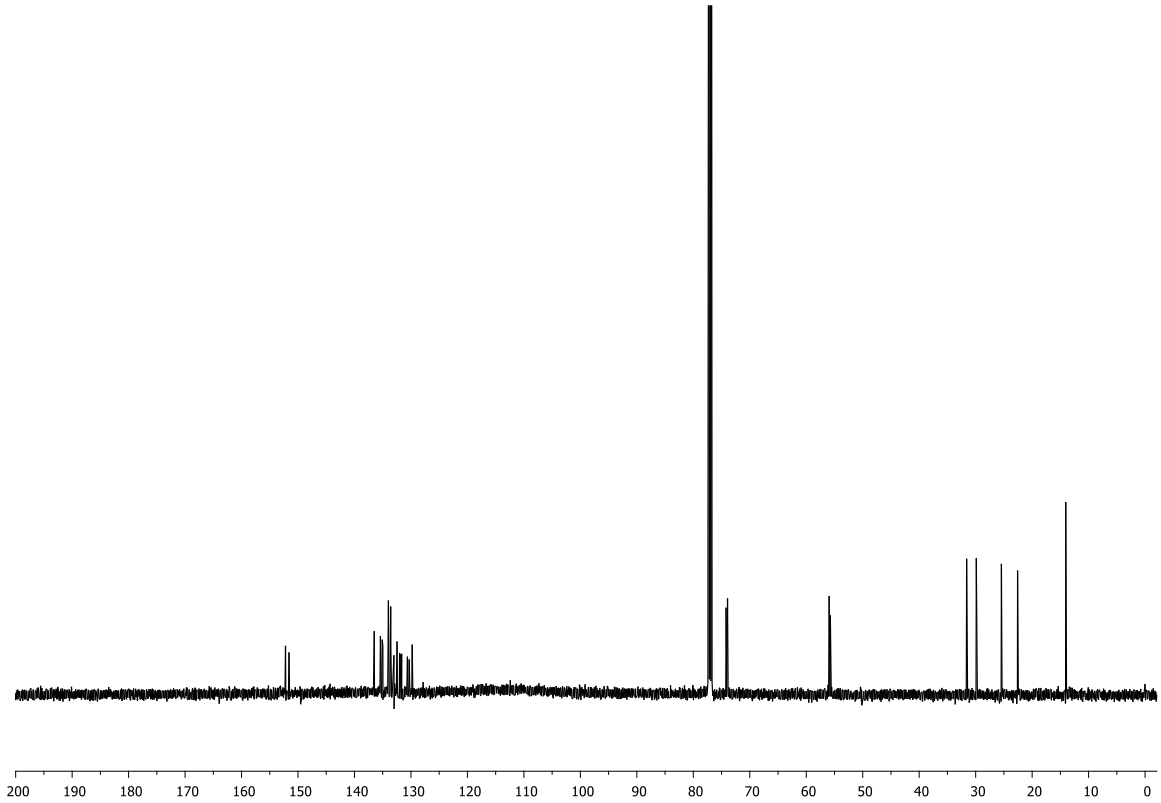


Figure S43. ^{13}C NMR (126 MHz, $CDCl_3$) **6a** (*syn* and *anti* isomers)

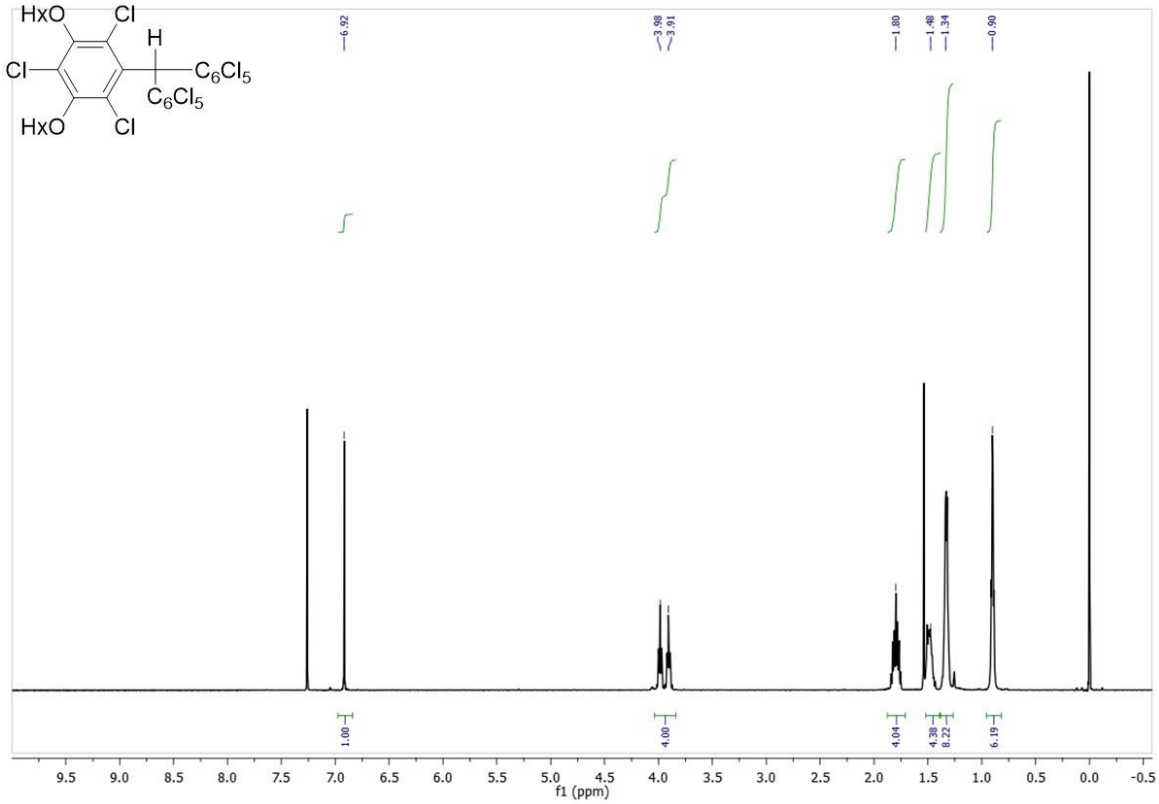


Figure S44. ^{1}H NMR (500 MHz, $CDCl_3$) **6b**

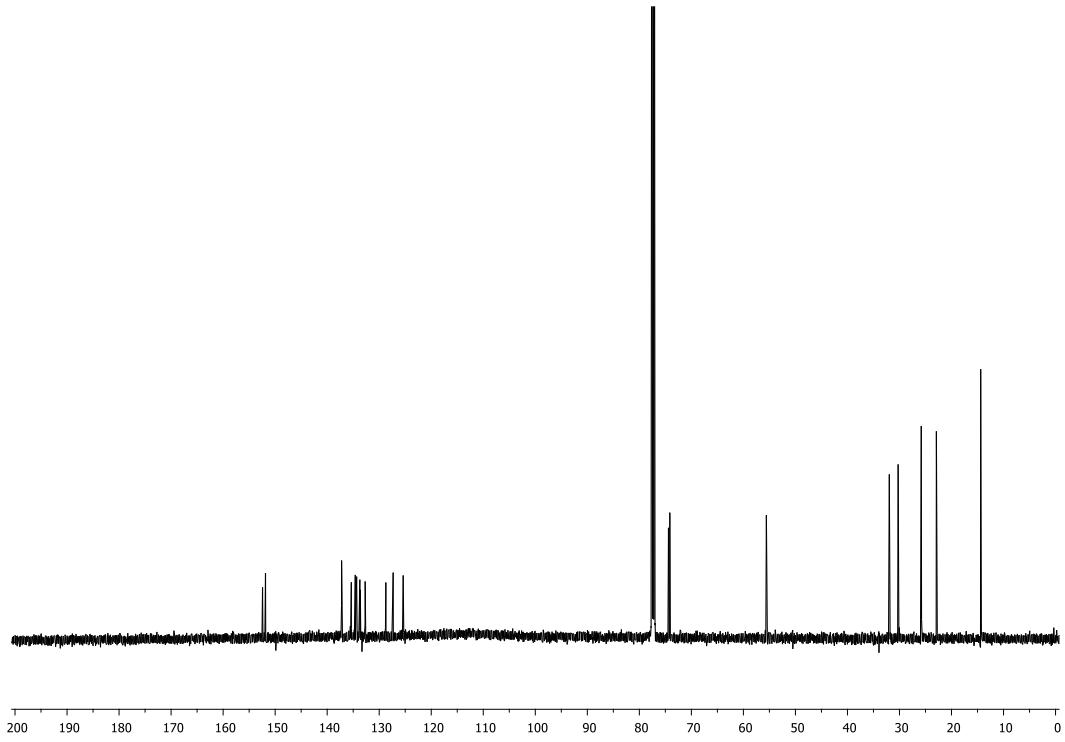


Figure S45. ^{13}C NMR (126 MHz, $CDCl_3$) **6b**

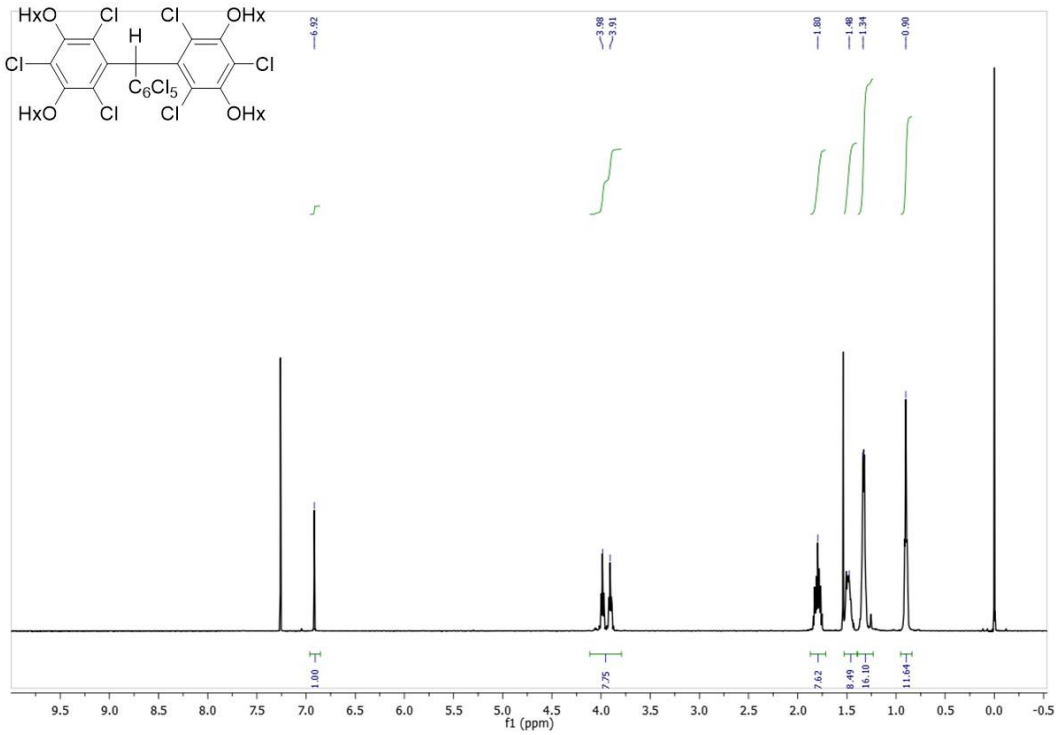


Figure S46. ^{1}H NMR (500 MHz, $CDCl_3$) **6c**

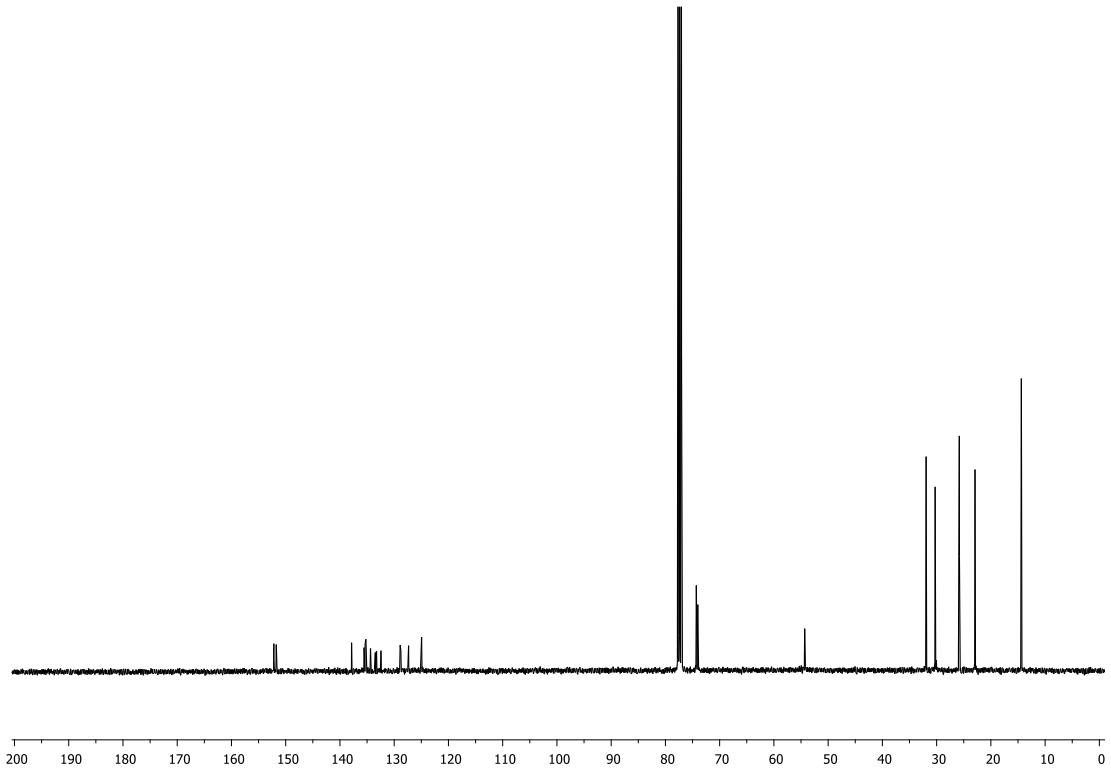


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) **6c**

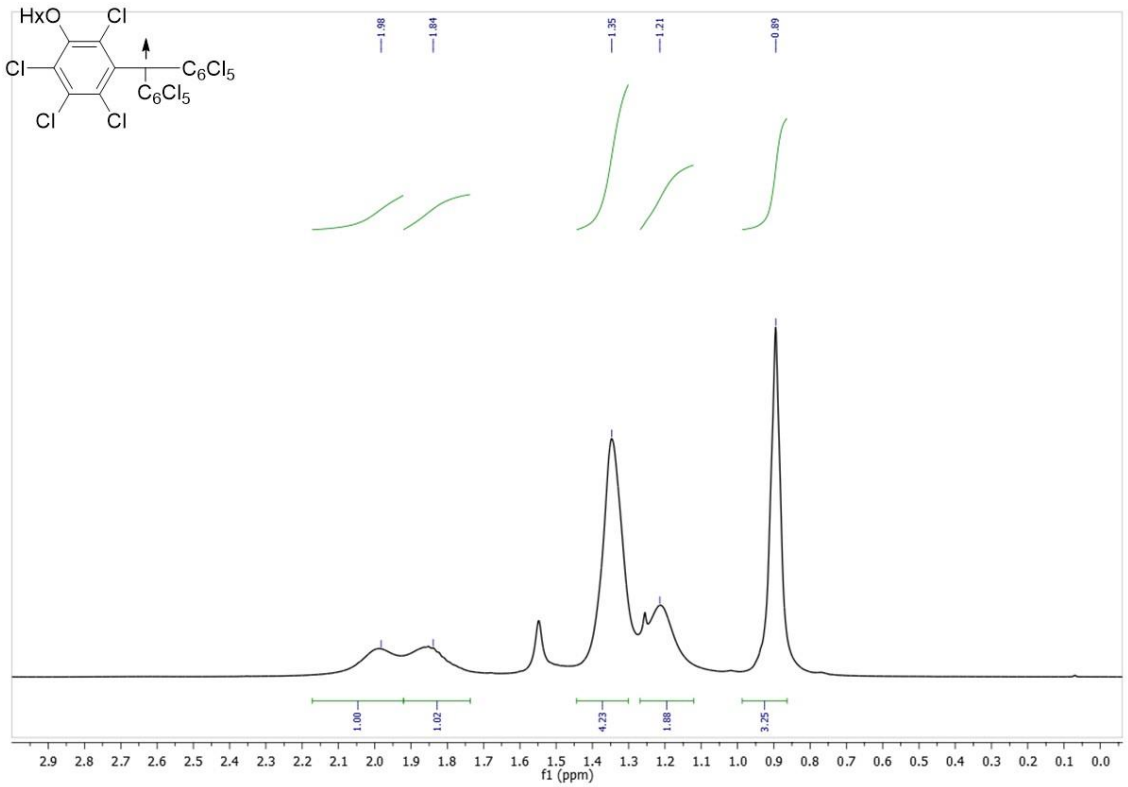


Figure S48. ^{1}H NMR (500 MHz, $CDCl_3$) **7a**

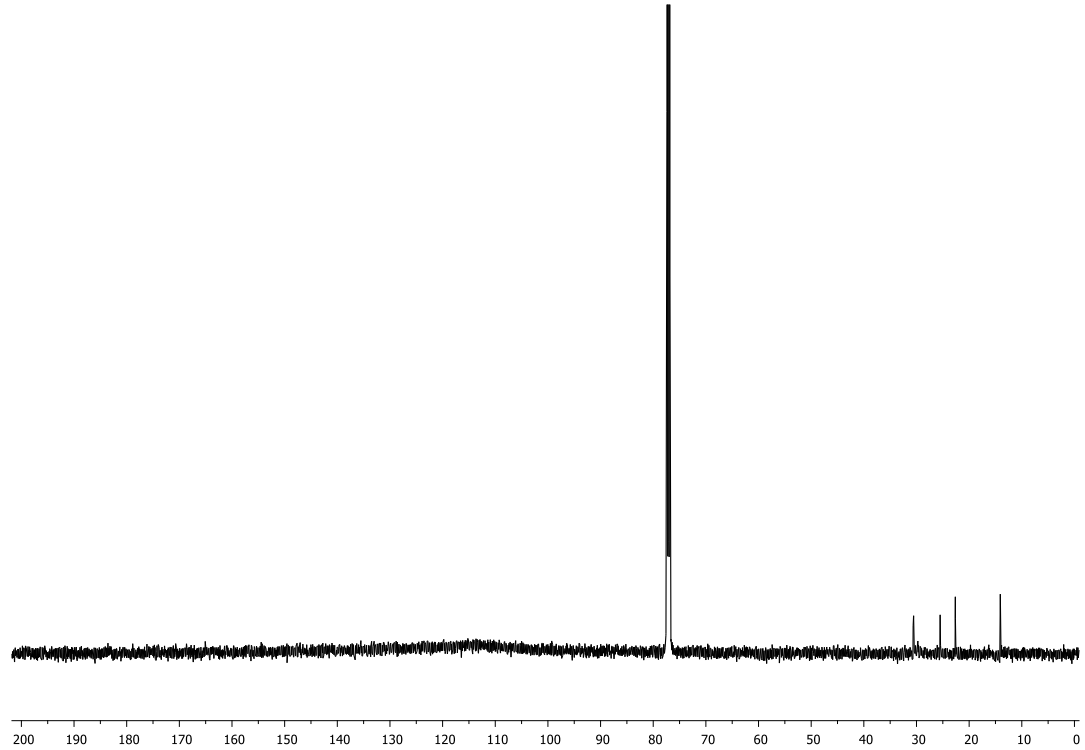


Figure S49. ^{13}C NMR (126 MHz, $CDCl_3$) **7a**

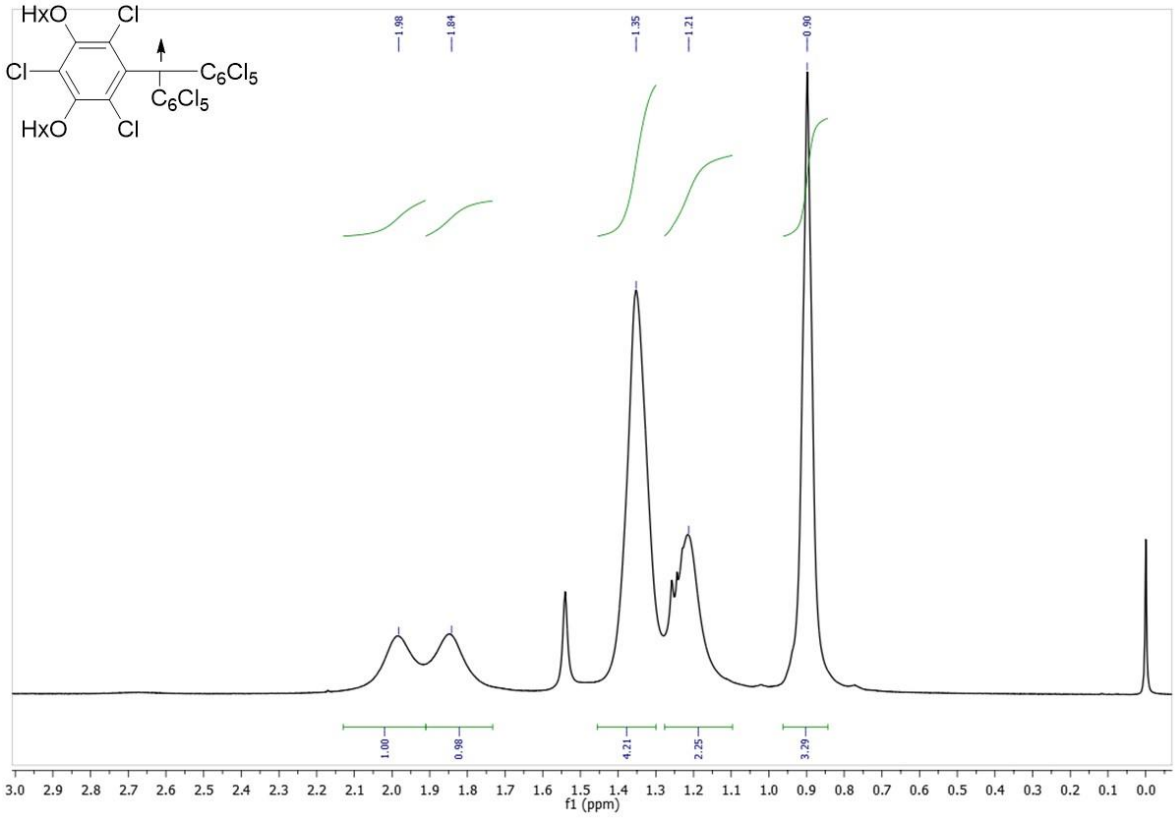


Figure S50. ^{1}H NMR (500 MHz, $CDCl_3$) **7b**

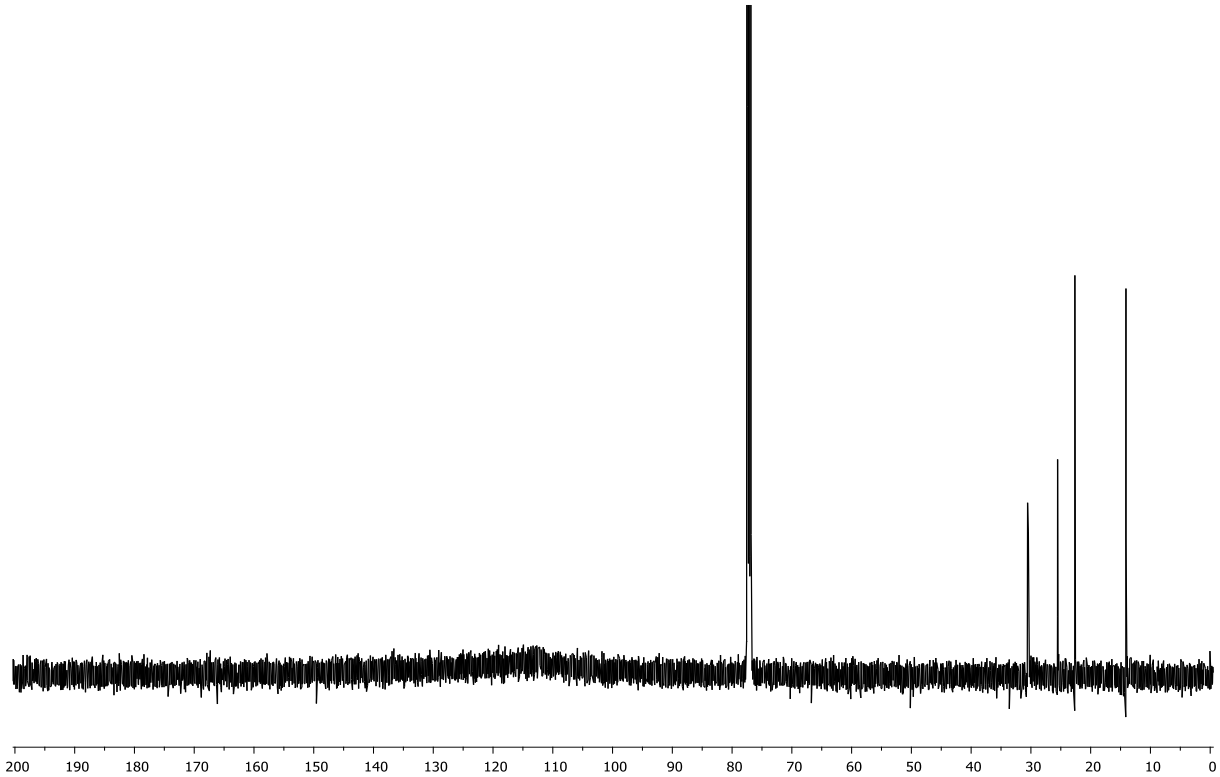


Figure S51. ^{13}C NMR (126 MHz, $CDCl_3$) **7b**

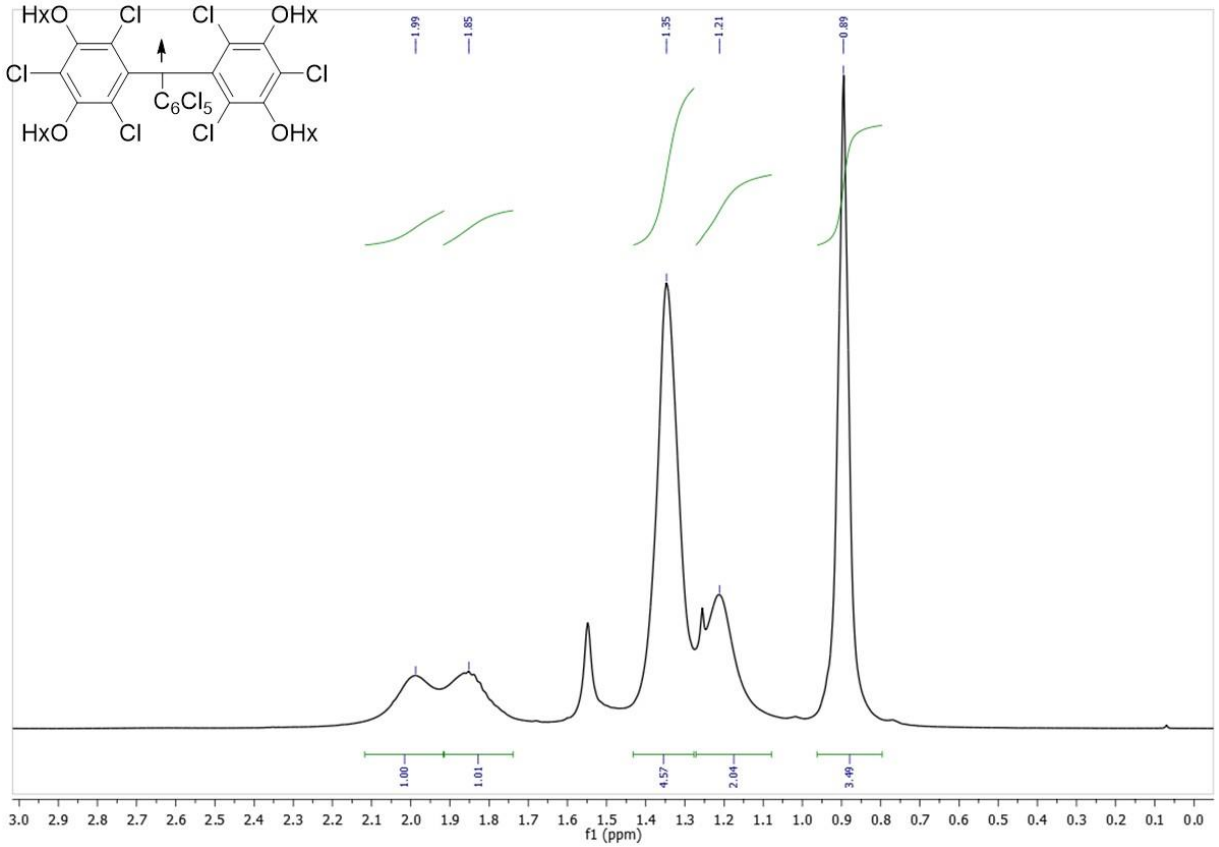


Figure 52. ^{1}H NMR (500 MHz, $CDCl_3$) **7c**

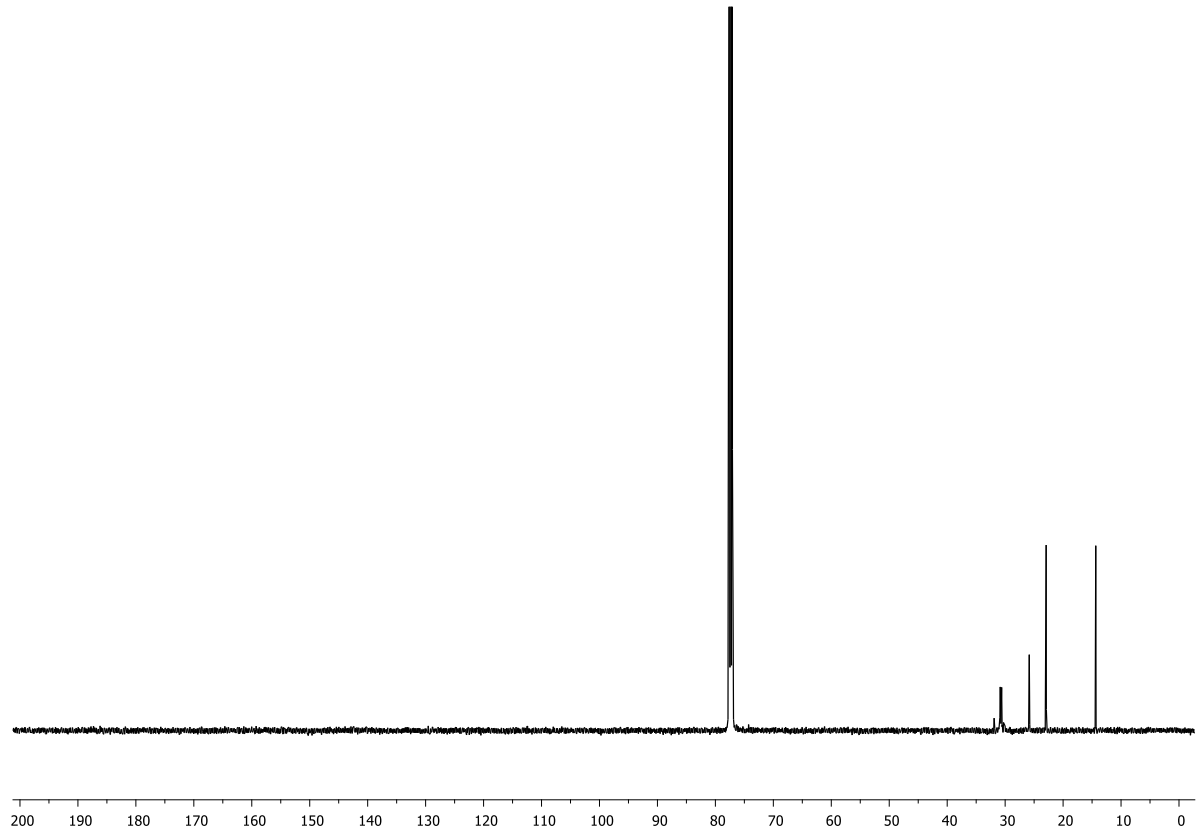


Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$) **7c**

^{1}H T_1 Relaxation Time Measurements

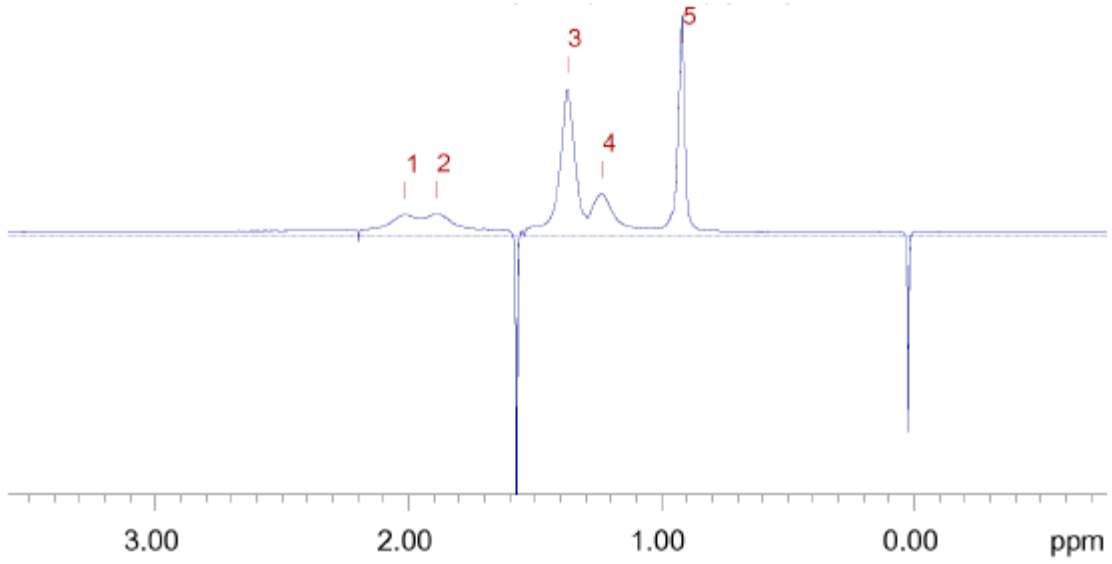


Table S3. ^{1}H NMR T_1 Relaxation times

Peak name	F2 [ppm]	T1 [s]	error	fitInfo
1	2.013	0.00946	0.003171	Done
2	1.889	0.00992	0.003021	Done
3	1.371	0.0483	0.002746	Done
4	1.236	0.0164	0.002935	Done
5	0.919	0.127	0.003996	Done

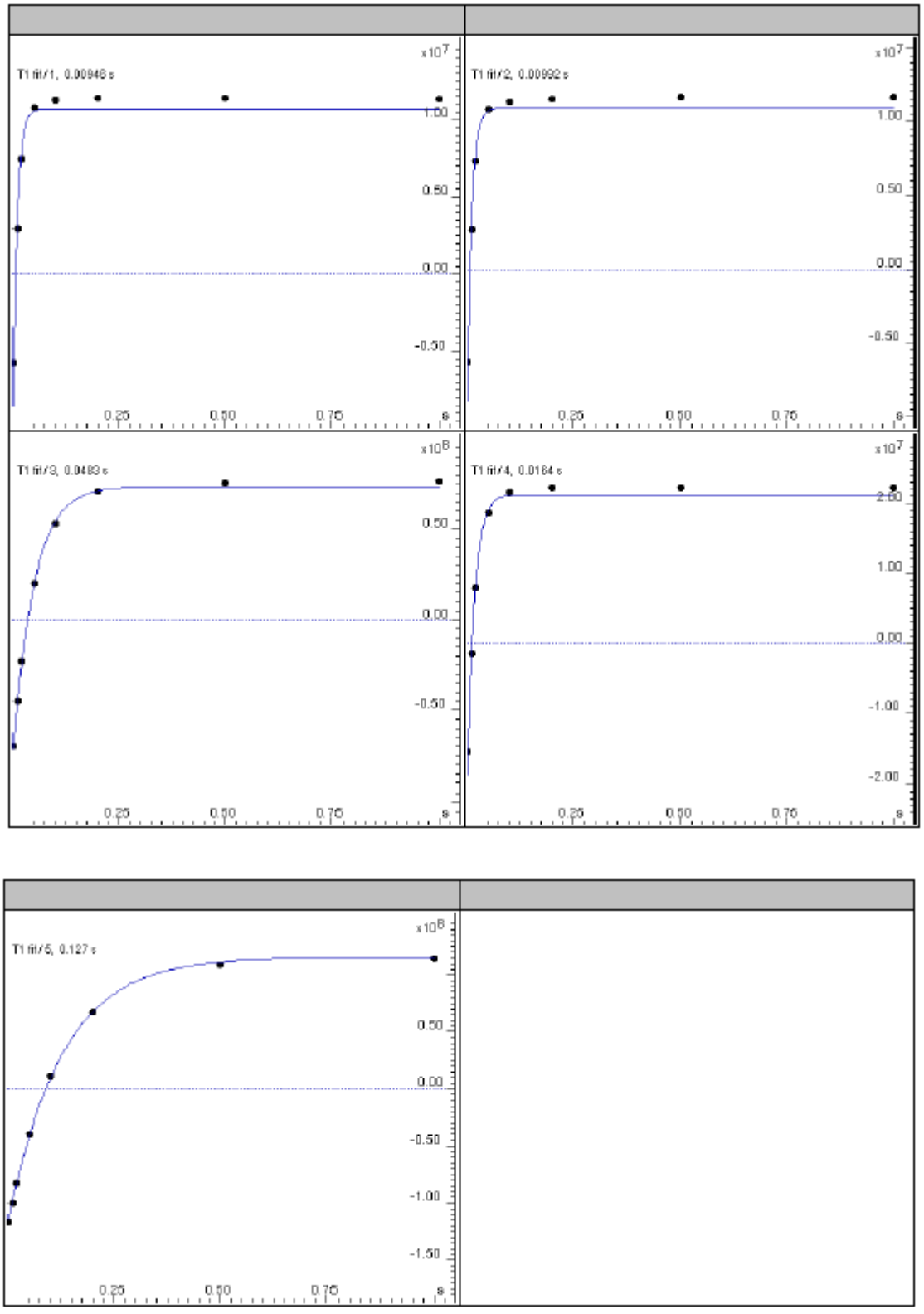


Figure S54. Fittings of ^{1}H NMR T_1 relaxation data

^{13}C T_1 Relaxation Time Measurements

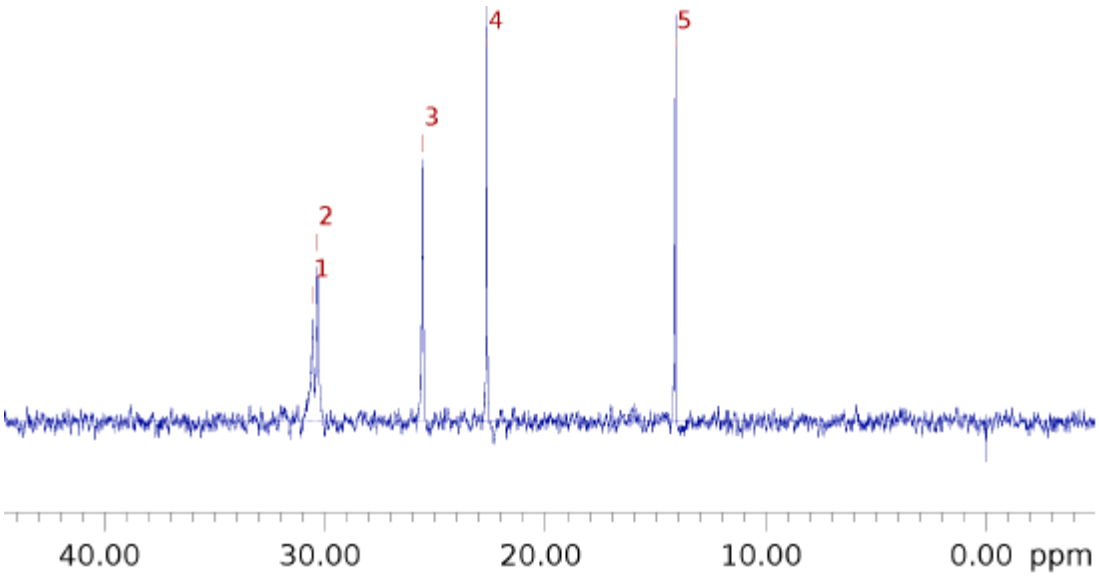


Table S4. ^{13}C NMR T_1 Relaxation times

Peak name	F2 [ppm]	Io	error	T1 [s]	error
1	30.546	1.18e+08	4.811e+06	0.310	0.02881
2	30.333	1.77e+08	7.855e+06	0.120	0.01176
3	25.548	3.08e+08	9.198e+06	0.178	0.01194
4	22.632	4.89e+08	1.322e+07	0.605	0.03616
5	14.077	4.95e+08	8.446e+06	0.907	0.03337

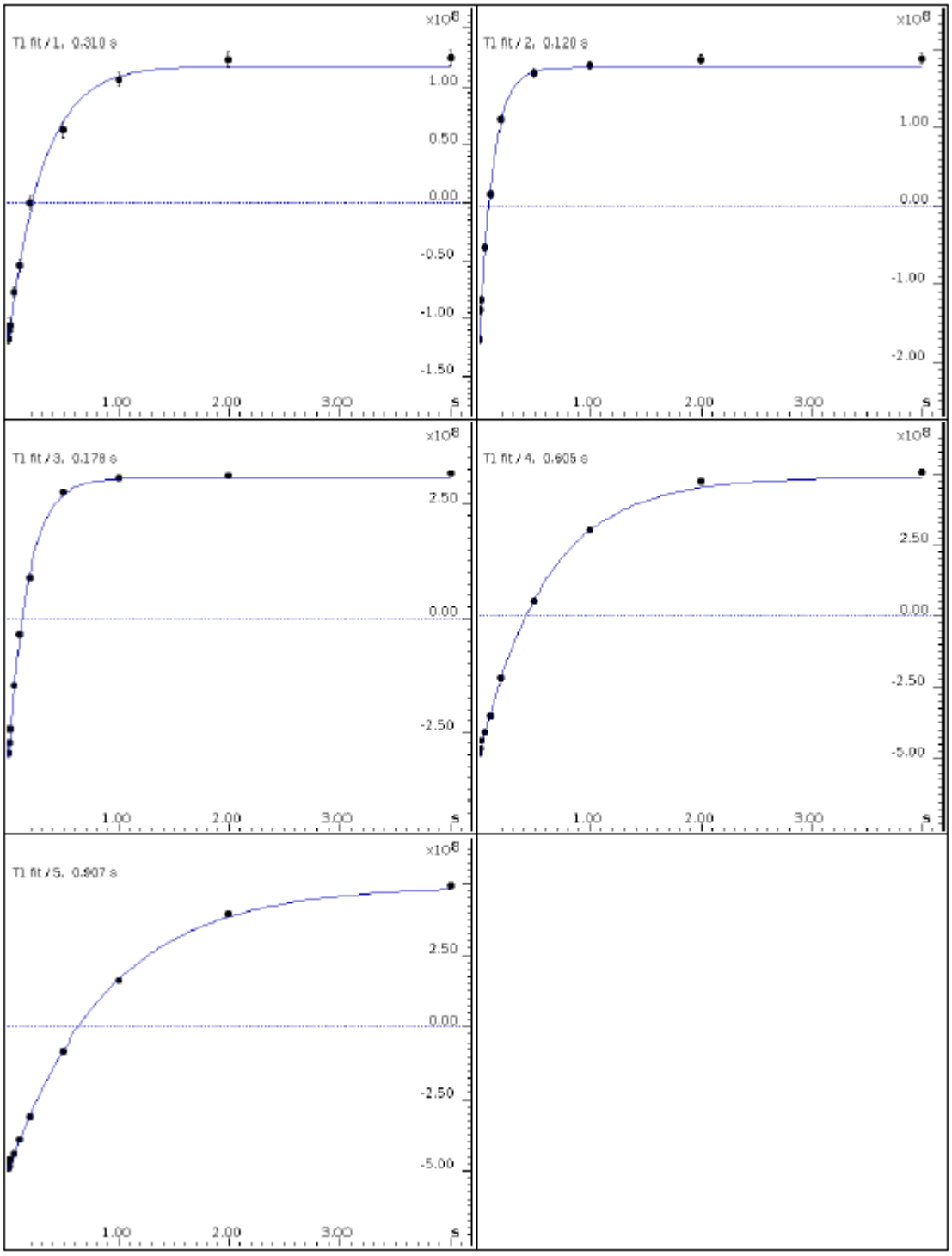


Figure S55. Fittings of ^{1}H NMR T_1 relaxation data

HSQC NMR

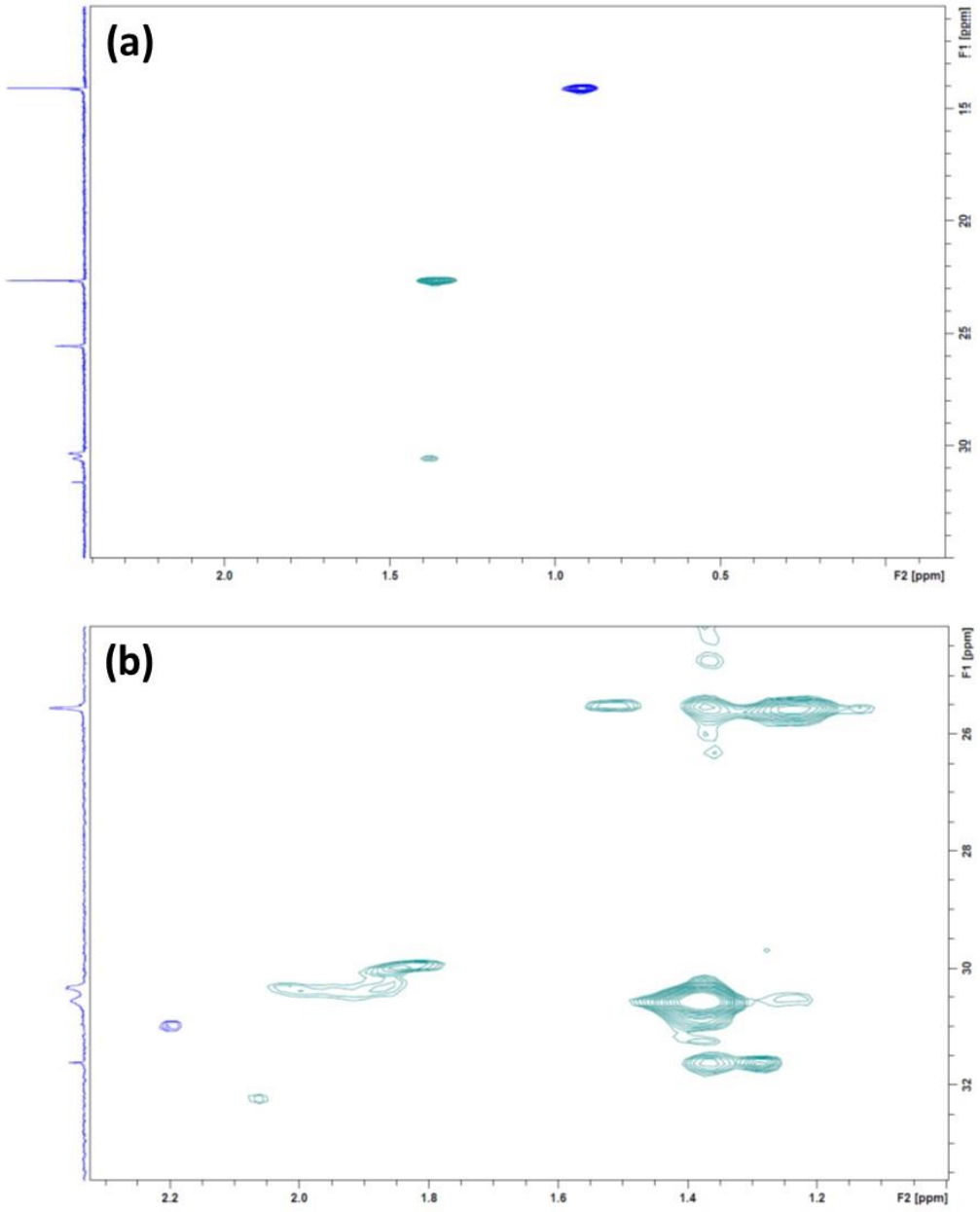
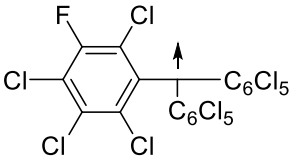


Figure S56. HSQC NMR **7c** ($CDCl_3$)

(a) Correlations: assignment/ δ_H / δ_C : CH_3-6 / 0.87 / 14.37 : CH_2-5 / 1.35 / 22.91 : CH_2-4 / 1.35 / 30.84.

(b) Enhanced sensitivity : CH_2-4 / 1.35 / 30.84 : CH_2-3 / 1.21 / 25.84 : CH_2-2 / 1.99, 1.85 / 30.61

Mass Spectra



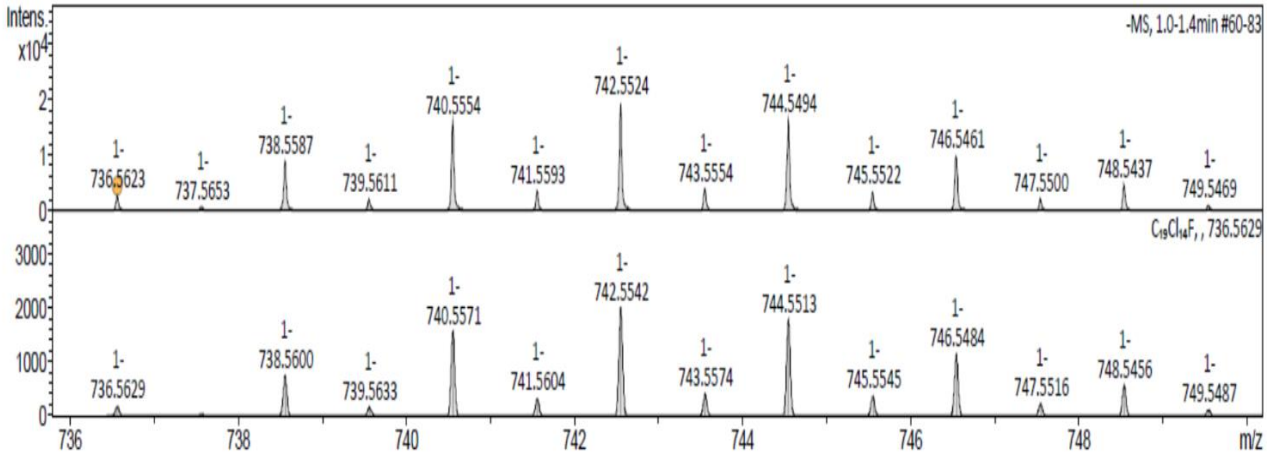
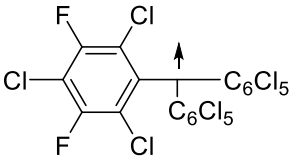


Figure S57. Radical **10a** (above), MS parent ion (M^-). (below) simulated for $C_{19}Cl_{14}F^-$



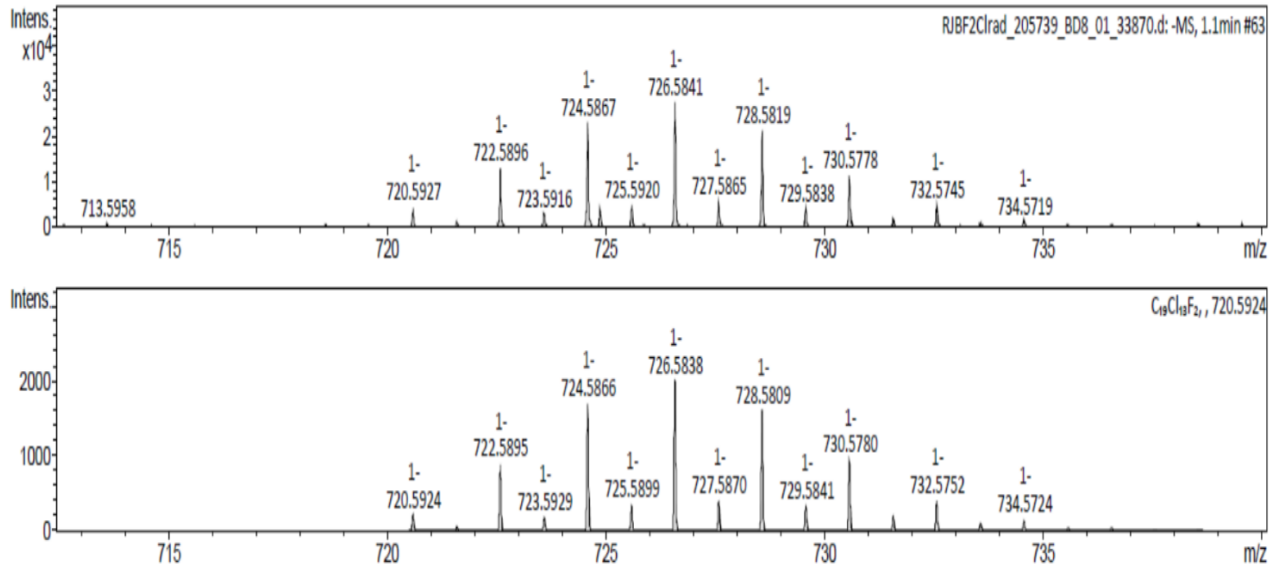


Figure S58. Radical **10b** (above) MS parent ion (M^-). (below) simulated for $C_{19}Cl_{13}F_2^-$

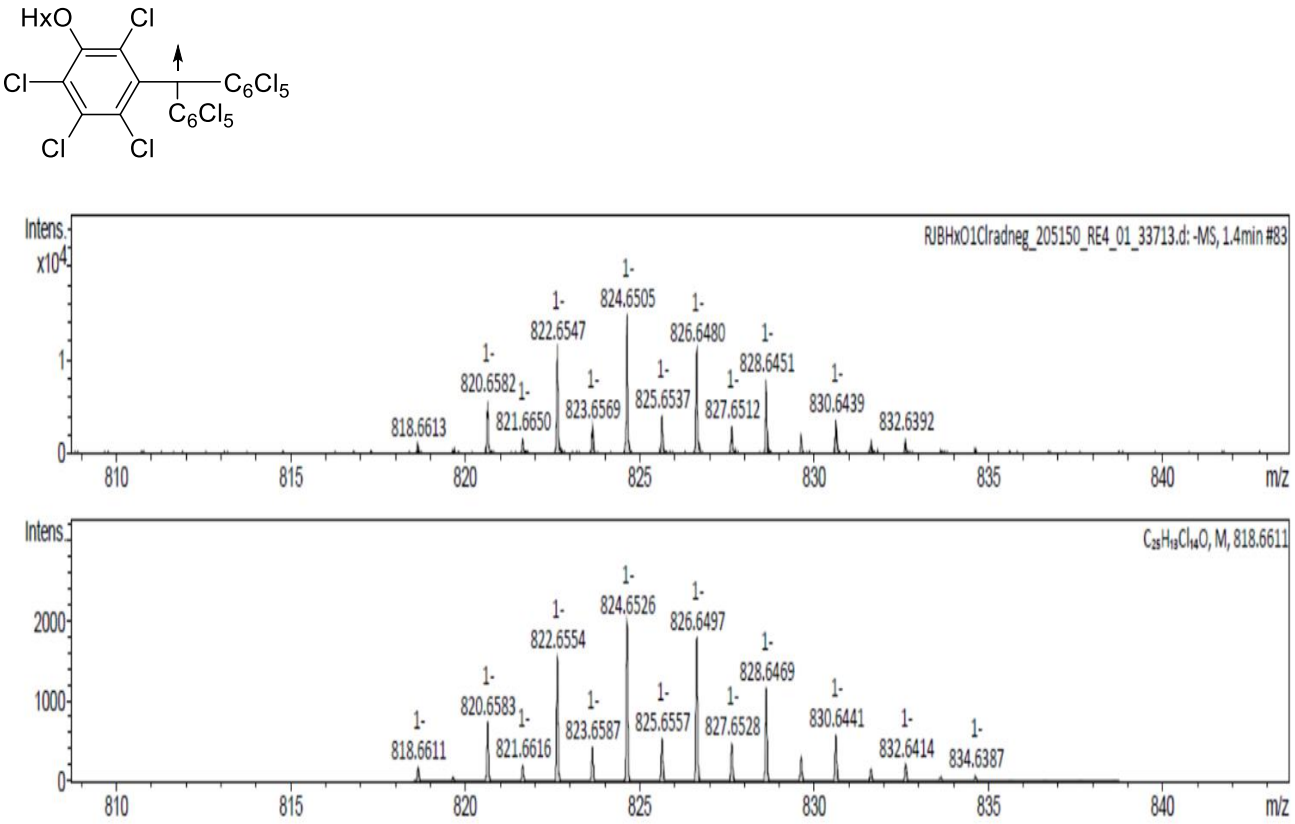


Figure S59. Radical **7a** (above) MS parent ion (M^-). (below) simulated for $C_{19}Cl_{14}(OHx)^-$

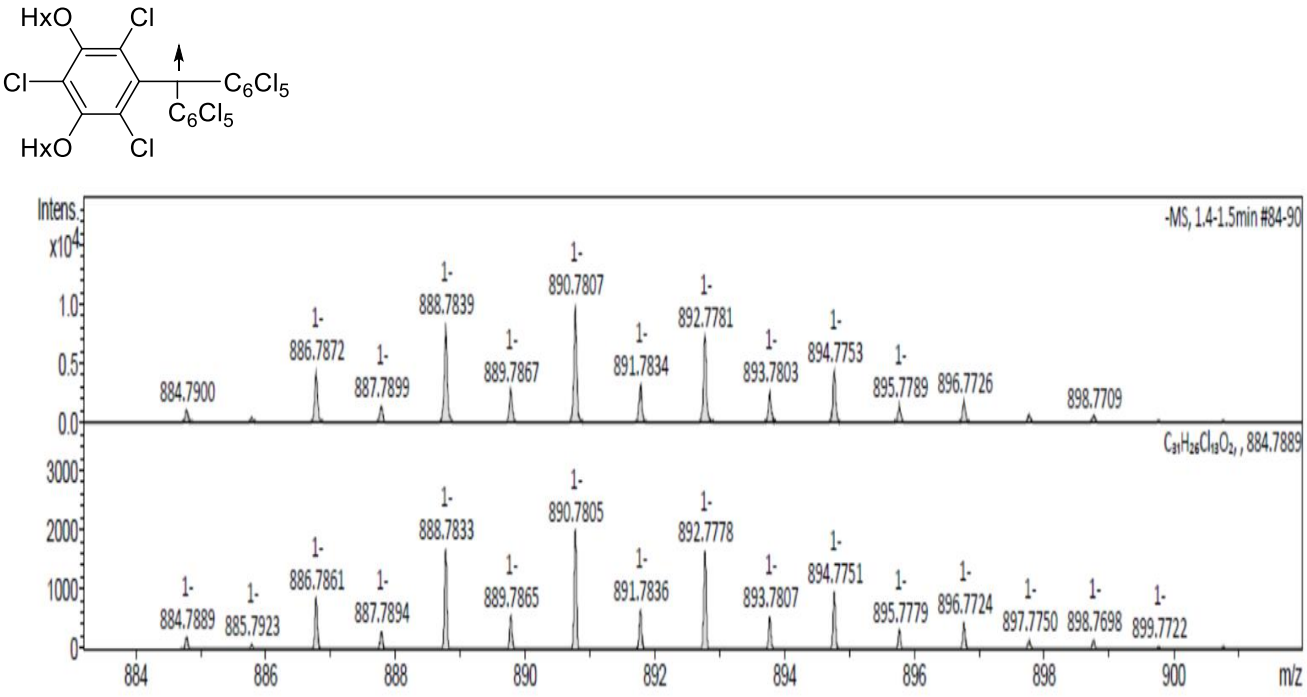
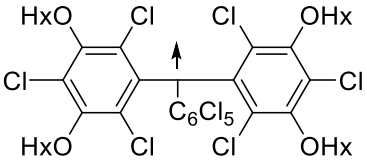


Figure S60. Radical **7b** (above) MS parent ion (M^-). (below) simulated for $C_{19}Cl_{13}(OHx)_2^-$



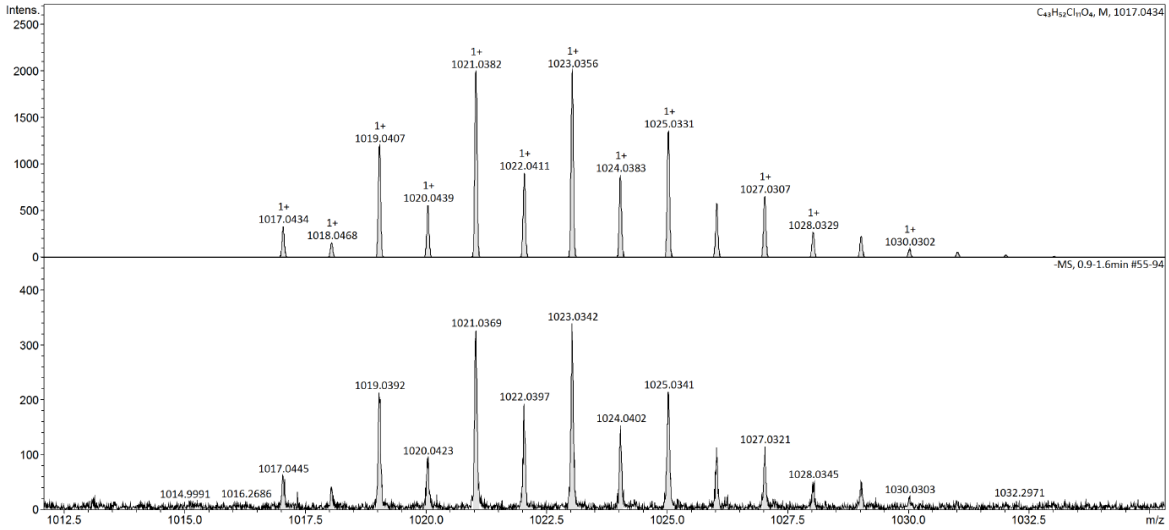
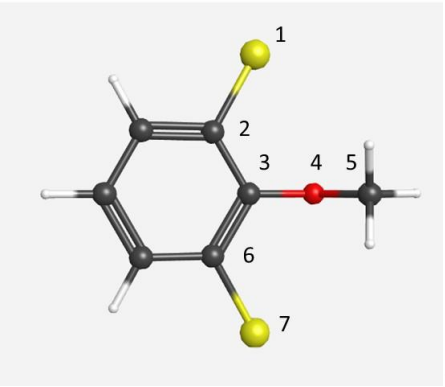


Figure S61. Radical **7c** (below) MS ion (M^+). (above) simulated for $[C_{19}Cl_{11}(OHx)_4^+]$

MO Calculations

Calculations were performed using WebMO software. In calculating the energy as a function of the dihedral angle 2-3-4-5, this angle was fixed and the rest of the geometry optimized.



+

Figure S62. 2,6-Dichloromethoxybenzene: Optimised geometry (STO 6-31G*)

Dihedral angle: 2-3-4-5 90º. Selected bond angles: 1-2-3 119.4º, 2-3-4 120º, 3-4-5 116.5º, 3-6-7 119.5º.

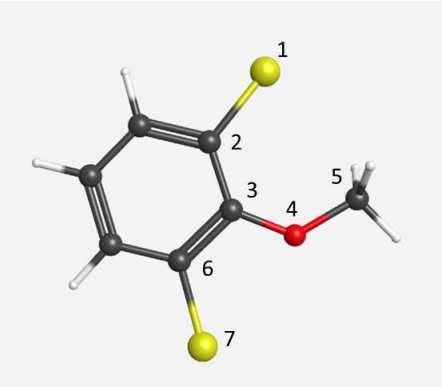


Figure S63. 2,6-Dichloromethoxybenzene: Geometry optimised with the methoxy group held in-plane (STO 6-31G*)

Dihedral angle: 2-3-4-5 0º. Selected bond angles: 1-2-3 123.6º, 2-3-4 129.5º, 3-4-5 127.9º, 3-6-7 119.1º.

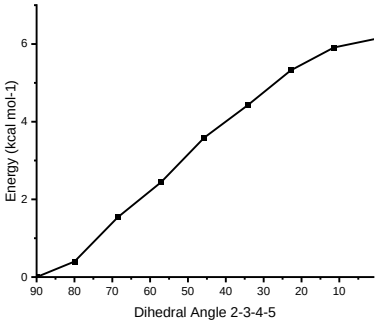


Figure S64. 2,6-Dichloromethoxybenzene: Energy (relative to the optimised geometry) as a function of the dihedral angle 2-3-4-5 (STO 6-31G*)

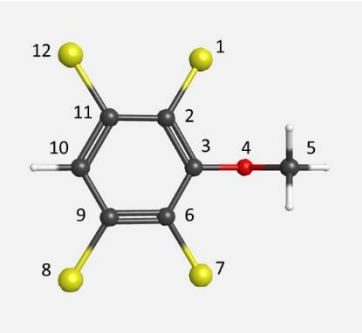


Figure S65. 2,3,5,6-Tetrachloromethoxybenzene: Optimised geometry (STO 6-31G*)

Dihedral angle: 2-3-4-5 90º. Selected bond angles: 1-2-3 118.8º, 2-3-4 120º, 3-4-5 116.8º, 3-6-7 118.8º, 8-9-10 118.1º, 10-11-12 118.0º.

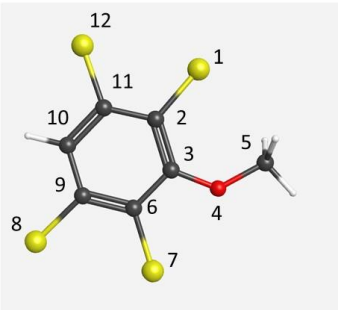


Figure S66. 2,3,5,6-Tetrachloromethoxybenzene: Geometry optimised with the methoxy group held in-plane (STO 6-31G*)

Dihedral angle: 2-3-4-5 0º. Selected bond angles: 1-2-3 122.3º, 2-3-4 128.6º, 3-4-5 129.8º, 3-6-7 118.5º, 8-9-10 117.6º, 10-11-12 117.2º.

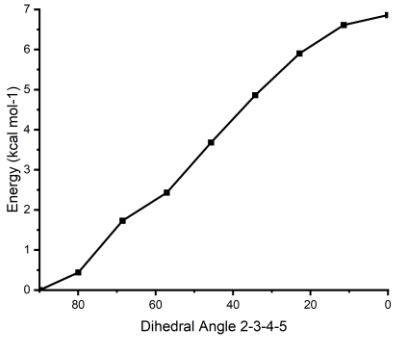


Figure S67. 2,3,5,6-Tetrachloromethoxybenzene: Energy (relative to the optimised geometry) as a function of the dihedral angle 2-3-4-5 (STO 6-31G*)

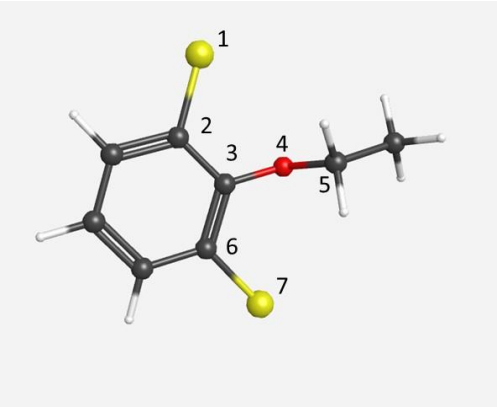


Figure S68. 2,6-Dichloroethoxybenzene: Optimised geometry (STO 6-31G*)

Dihedral angle: 2-3-4-5 90º. Selected bond angles: 1-2-3 119.0º, 2-3-4 120º, 3-4-5 116.8º, 3-6-7 119.5º.

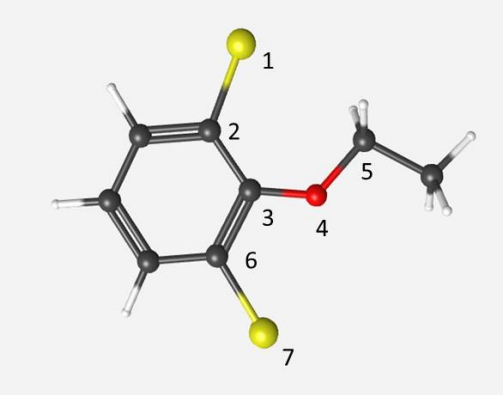


Figure S69. 2,6-Dichloroethoxybenzene: Geometry optimised with the ethoxy group held in-plane (STO 6-31G*)

Dihedral angle: 2-3-4-5 0º. Selected bond angles: 1-2-3 123.2º, 2-3-4 129.6º, 3-4-5 128.6º, 3-6-7 119.1º.

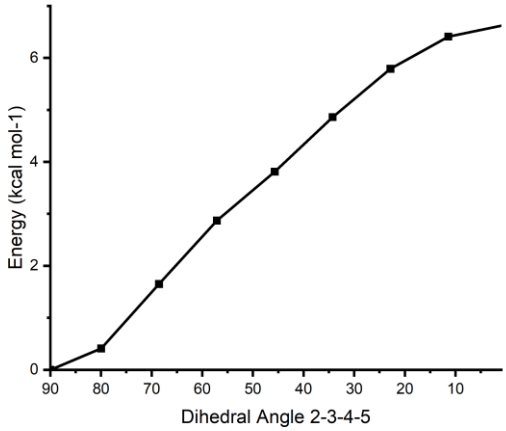


Figure S70. 2,6-Dichloroethoxybenzene: Energy (relative to the optimised geometry) as a function of the dihedral angle 2-3-4-5 (STO 6-31G*)

References

[1] a) M. Ballester, J. Riera, J. Castaner, C. Badia, J. M. Monso, *J. Am. Chem. Soc.* **1971**, *93*, 2215-2225; b) M. Ballester, J. Riera, J. Castaner, C. Rovira, O. Armet, *Synthesis* **1986**, 64-66.

[2] O. Armet, J. Veciana, C. Rovira, J. Riera, J. Castaner, E. Molins, J. Rius, C. Miravitlles, S. Olivella, J. Brichfeus, *J. Phys. Chem.* **1987**, *91*, 5608-5616.