

Supporting Information

**Photoinduced, Copper-Catalyzed Direct Perfluoroalkylation
of Heteroarenes**

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General Information

All reactions were carried out in oven-dried glassware under an argon atmosphere employing standard techniques in handling air-sensitive materials.

All solvents were reagent grade. α,α,α -Trifluorotoluene was purchased from Sigma-Aldrich and used as supplied.

Copper(I) iodide (99,999% purity) was purchased from Sigma-Aldrich and Nonafluorobutyl iodide (98+%) was purchased from Fluorochem and used as supplied. All other reagents were used as supplied.

Reactions were magnetically stirred and monitored by thin layer chromatography using Merck-Kieselgel 60F₂₅₄ plates. Flash chromatography was performed with silica gel 60 (particle size 35-70 μm) supplied by Merck. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. Photoinduced copper-catalyzed reactions were performed with commercially available blue LED strips (see p. S3).

Proton NMR spectra were recorded using an internal deuterium lock at ambient temperature on Bruker 300 MHz, Varian 400 MHz and Jeol 400 MHz spectrometers. Internal reference of δ_{H} 7.26 was used for CDCl_3 . Data are presented as follows: chemical shift (in ppm on the δ scale relative to $\delta_{\text{TMS}} = 0$), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, m = multiplet, br. = broad, app. = apparent), coupling constant (J/Hz) and integration. Resonances that are either partially or fully obscured are denoted obscured (obs.). Carbon-13 NMR spectra were recorded at 100 MHz using CDCl_3 (δ_{C} 77.16) as internal reference. For fluorinated compounds, Triply-decoupled $\{^1\text{H}\}\{^{19}\text{F}\}^{13}\text{C}$ NMR spectra have been recorded. Fluorine-19 NMR spectra were recorded at 377 MHz using α,α,α -trifluorotoluene (δ_{F} -63.24) as internal reference.

Melting points were recorded on a Stuart Scientific Analogue SMP11. Infrared spectra were recorded on a Bruker Alpha (ATR). High-resolution mass-spectra were obtained on an Agilent Technologies QTOF 6520 spectrometer.

Absorption spectra were recorded on UV-Visible Perkin Elmer Lambda 40 spectrophotometer. Emission spectra were recorded with a Shimadzu RF-5301PC spectrofluorimeter equipped with a 150 W Xenon lamp as excitation source and a Hamamatsu

R928 phototube as a detector. Corrections of the emission spectra were achieved by measuring the spectrum of a calibrated tungsten-halogen Edinburgh Analytical Instrument lamp of 10 Watts (200 to 600 nm).

The luminescence lifetimes were measured by time-correlated single-photon-counting (TC-SPC) with a LifeSpec-II Edinburgh Instruments equipped Peltier-cooled photomultiplier (R3809U-50, Hamamatsu). The sample was excited via a laser diode (PDL445, <100 ps) and the emission was measured at the maximum of emission of the complex. The data were collected by a multichannel analyser with a number of counts in the first channel ($t = 0$) minimum equal to 1000. The resulting decays were analyzed with the Edinburgh Instruments with F900 CDT software. They were deconvoluted for the instrumental response and fitted to exponential functions based on non-linear least squares regressions using a modified Marquardt algorithm thanks to Wavemetrics Igor Pro version 6.37 software. The reduced χ^2 , weighted residuals and autocorrelation function were employed for judging the quality of the fits.

Cyclic voltammetry was carried out on a carbon disk working electrode (approximate area = 3 mm²), in dry and degassed dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The potential of the working electrode was controlled by an Autolab PGSTAT 100 (Eco Chemie B. V., Utrecht, The Netherlands) potentiostat through a PC interface with a scan rate of 50 mV.s⁻¹ between -2 and +2 V vs AgCl/Ag. The counter electrode was a platinum wire (spiral diameter: 15 mm, spiral height: 70 mm), and the reference electrode a Ag/AgCl Leakless Electrode from Edaq. Ferrocene was used as an internal standard and potentials were converted vs SCE by adding 0.46 V to the value vs Fc⁺/Fc.^{S1} All measurements were performed in a single compartment cell.

^{S1} Connelly, N. G.; Geiger, W. E. *Chem. Rev.* 1996, **96**, 877.

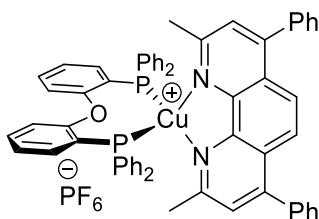
Irradiation System

The setup below made from commercially available blue LED strips has been used for the photoinduced, copper-catalyzed photoredox perfluoroalkylation of (hetero)arenes.



Experimental Procedures and Characterization Data

Synthesis and Characterization of [Cu(bcp)DPEphos]PF₆



A mixture of tetrakisacetonitrile copper(I) hexafluorophosphate (3.73 g, 10.00 mmol) and bis[(2-diphenylphosphino)phenyl] ether (DPEphos, 5.39 g, 10.00 mmol) in anhydrous dichloromethane (800 mL) was stirred for two hours at room temperature under argon in the dark. A solution of bathocuproine (bcp, 3.60 g, 10.00 mmol) in anhydrous dichloromethane (200 mL) was then added and the mixture was stirred for an additional hour in the dark. The mixture was then filtered through a pad of Celite[®] and concentrated to ca. 50-100 mL under reduced pressure. The concentrate was then added dropwise to 1 L of Et₂O with vigorous stirring in the dark. The precipitate was collected by filtration and dried under vacuum to afford [Cu(bcp)DPEphosCu]PF₆ (10.1 g, 9.12 mmol, 91%) as a bright yellow solid. The spectroscopic data correspond to those previously described in the literature.^{S2,S3}

^{S2} S.-P. Luo, E. Meja, A. Friedrich, A. Pazidis, H. Junge, A.-E. Surkus, R. Jackstell, S.; Denurra, S. Gladiali, S. Lochbrunner and M. Beller, *Angew. Chem. Int. Ed.*, 2013, **52**, 419.

^{S3} B. Michelet; C. Deldaele, S. Kajouj, C. Moucheron and G. Evano, *Org. Lett.*, 2017, **19**, 3576.

Absorption Spectrum

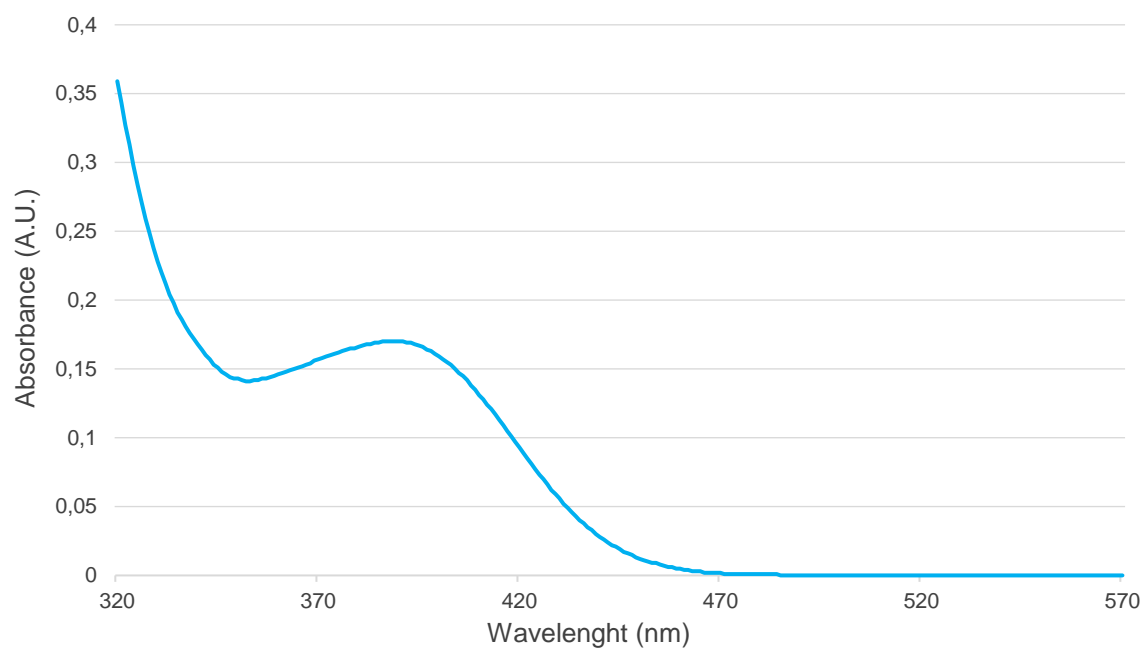


Figure S1. UV-Visible absorption spectrum of [Cu(bcp)DPEPhos]PF₆ recorded at ambient temperature under argon in DCM ($3 \cdot 10^{-5}$ M).

Mechanistic Studies

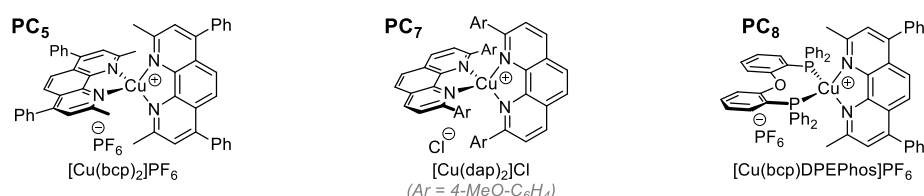
Photophysical and electrochemical characterisation of selected copper photocatalysts PC₅, PC₇ and PC₈

Photo-catalyst	Photophysical properties				Electrochemical properties			
	Absorption [nm] (ϵ [M ⁻¹ .cm ⁻¹])	Emission [nm]	ES Lifetime [ns]	Ref	E ^{Cu2+/Cu+} [V vs SCE]	E ^{Cu+/Cu} [V vs SCE]	E ^{Cu2+/Cu+*} [V vs SCE]	E ^{Cu+*/Cu} [V vs SCE]
PC ₅	478 (13200)	765	70	S4	+ 0.83 (+ 0.93 ^{S4})	-1.65	- 0.79 (- 1.05 ^{S4})	- 0.03
PC ₇	440 (4090)	685	236	S5	+ 0.75	-1.70	- 1.06	+ 0.11
PC ₈	389 (5800)	580	19400	S6	+ 1.32 (+ 1.44 ^{S7})	- 1.67 (- 1.15 ^{S7})	- 0.88	+ 0.47

Table S1: Photophysical and electrochemical characterisation of selected copper photocatalysts PC₅, PC₇ and PC₈

Photophysical properties were compiled from refs S4-S6. Electrochemical properties were measured by cyclic voltammetry in dry degassed dichloromethane with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte, using AgCl/Ag as reference electrode and ferrocene as internal standard. Potentials were converted vs SCE by adding 0.46 V to the value vs Fc⁺/Fc.^{S1} Values in italic refer to previously reported values in the literature. Excited state potentials were evaluated using the equations below from the work of Rehm and Weller:^{S8}

$$E^{\text{Cu}2+/\text{Cu}+*} = E^{\text{Cu}2+/\text{Cu}+} - \Delta E_{0-0}$$

$$E^{\text{Cu}+*/\text{Cu}} = E^{\text{Cu}+/\text{Cu}} + \Delta E_{0-0}$$

$$\text{where } \Delta E_{0-0} \approx \frac{hc}{\lambda_{\text{max}}}$$

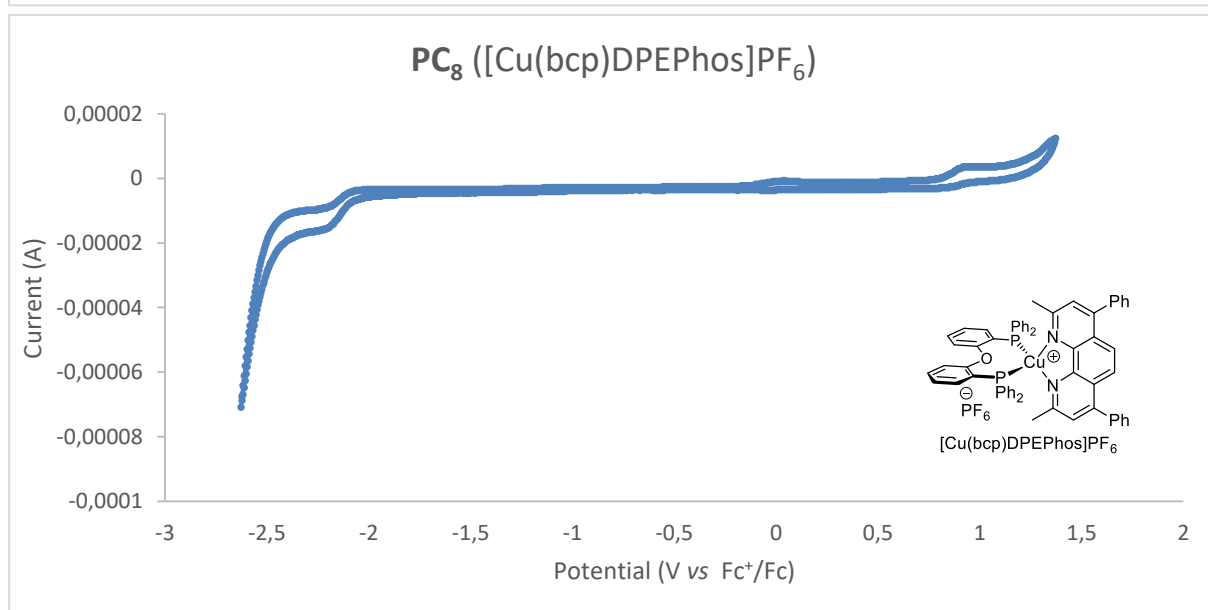
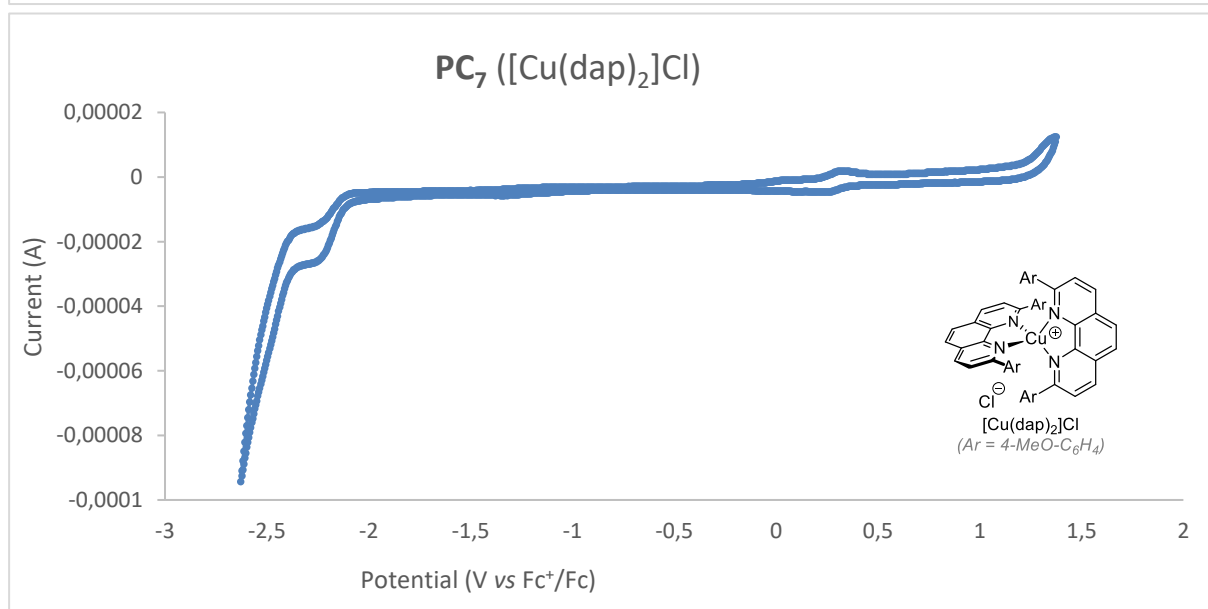
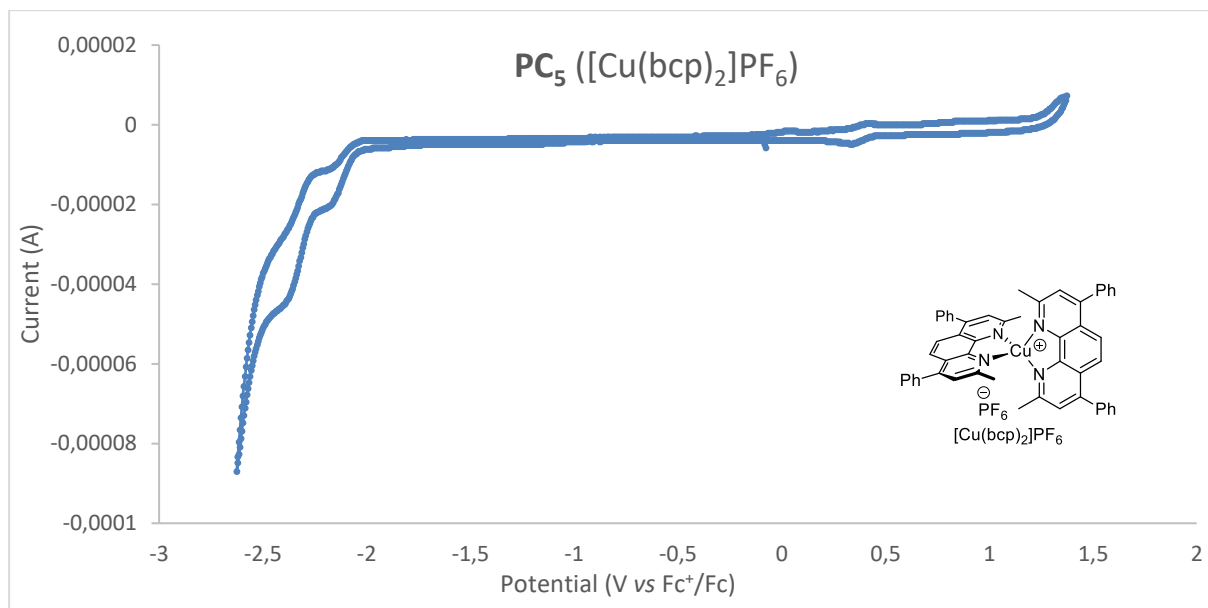
^{S4} Ruthkosky, M.; Castellano, F. N.; Meyer, G. J. *Inorg. Chem.* 1996, **35**, 6406.

^{S5} Cetin, M. M.; Hodson, R. T.; Hart, C. R.; Cordes, D. B.; Findlater, M.; Casadonte, D. J.; Cozzolino, A. F.; Mayer, M. F. *Dalton Trans.* 2017, **46**, 6553.

^{S6} Takeda, H.; Monma, Y.; Sugiyama, H.; Uekusa, H.; Ishitani, O. *Front. Chem.* 2019, **7**, 418.

^{S7} Santander-Nelli, M.; Sanhueza, L.; Navas, D.; Rossin, E.; Natali, M.; Dreyse, P. *New J. Chem.* **2022**, **46**, 1693–1703.

^{S8} Rehm, D.; Weller, A. *Isr. J. Chem.* 1970, **8**, 259–271.



Quenching experiment with IC₄F₉

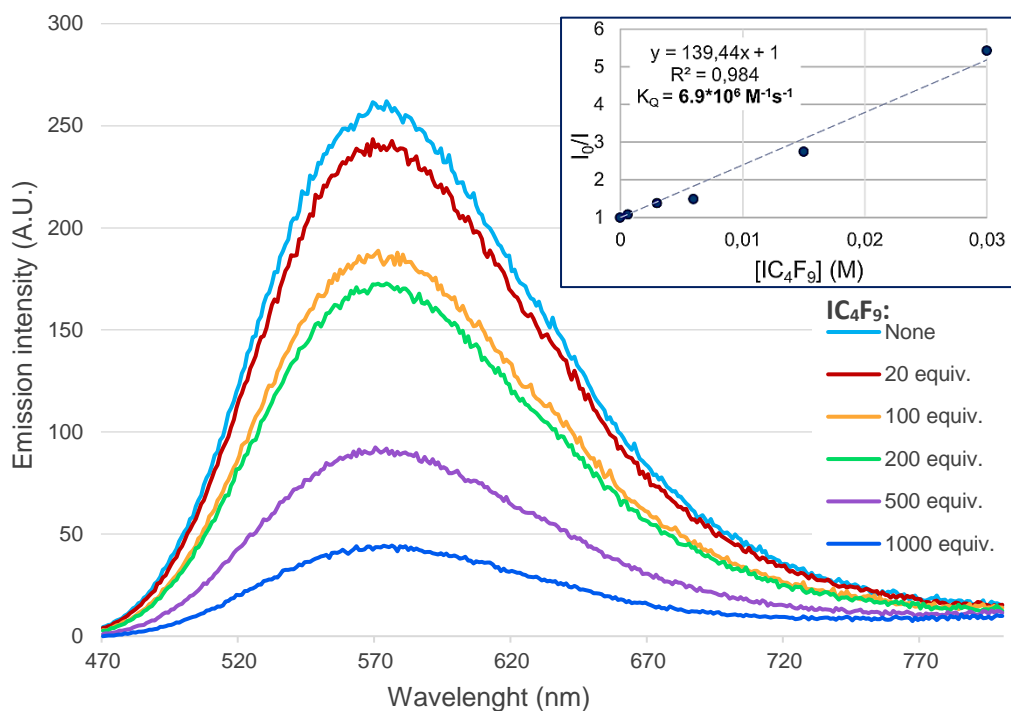


Figure S2. Quenching of the luminescence of $[\text{Cu}(\text{bcp})\text{DPEPhos}]\text{PF}_6^*$ by IC_4F_9 ($3 \times 10^{-5} \text{ M}$). Inset represents the Stern-Volmer plot for this quenching.

Quenching experiment with benzofuran

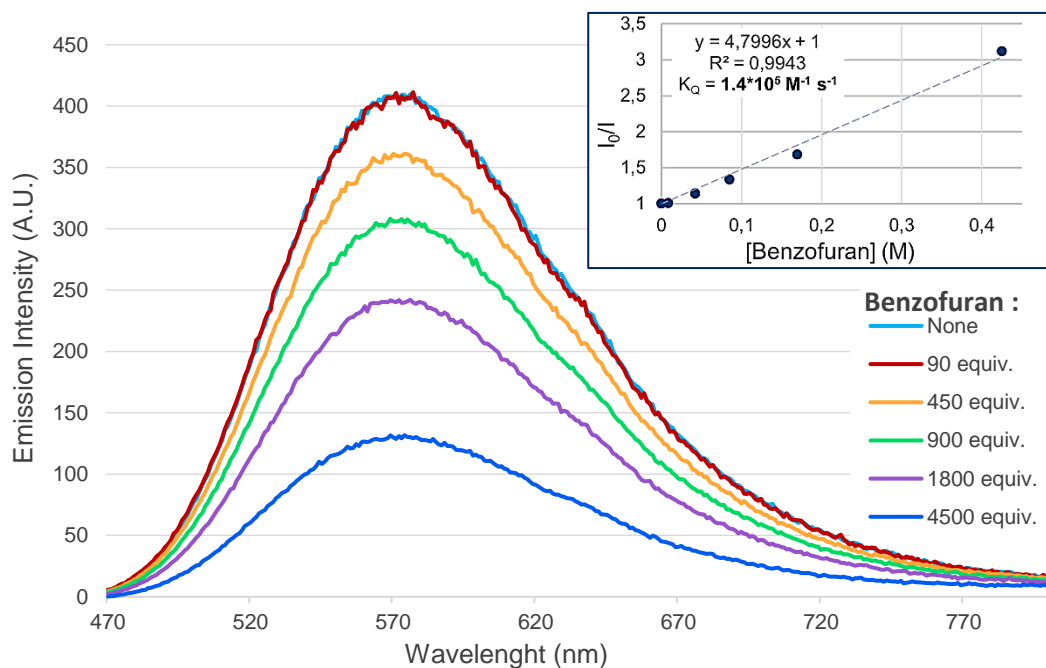


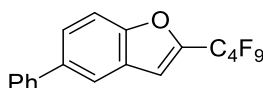
Figure S3. Quenching of the luminescence of $[\text{Cu}(\text{bcp})\text{DPEPhos}]\text{PF}_6^*$ by benzofuran ($9.5 \times 10^{-5} \text{ M}$). Inset represents the Stern-Volmer plot for this quenching.

Experimental Procedures and Characterization Data

Synthesis of Perfluoroalkylated Heteroarenes

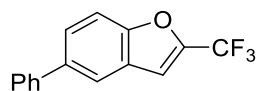
General procedure

An oven-dried vial was charged with the heteroarene (200 μmol) if solid, $[\text{Cu}(\text{bcp})\text{DPEphos}]\text{PF}_6$ (22 mg, 20 μmol , 0.10 equiv.) and potassium acetate (39 mg, 400 μmol , 2.0 equiv.). The vial was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. The perfluoroalkyl iodide (1.2 mL), the heteroarene (200 μmol) if liquid, and dry dichloromethane (300 μL) were then added and the reaction mixture was stirred under blue LED irradiation (using blue LED strips, see p. S3 for experimental setup) overnight at room temperature. The resulting mixture was concentrated under reduced pressure. The crude residue was then purified by flash column chromatography over silica gel.



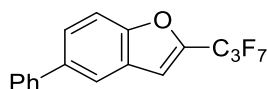
3a

5-Phenyl-2-nonafluorobutyl-benzofuran 3a. Prepared according to the general procedure starting from 200 μmol of 5-phenyl-benzofuran. Yield: 66% (54 mg, 131 μmol). Solvent system for flash column chromatography: pentane. Colorless solid; Mp: 52 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.86 (dd, $J = 1.8$ and 0.7 Hz, 1H), 7.69 (dd, $J = 8.7$ and 1.8 Hz, 1H), 7.66 – 7.60 (m, 3H), 7.51 – 7.45 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 (q, $J = 1.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.5, 143.7, 141.0, 138.1, 129.1, 127.6, 127.5, 127.0, 126.9, 120.9, 117.6, 112.4, 111.7, 111.0, 110.4, 108.9; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -112.5, -123.8, -126.5; IR (FTIR): ν_{max} 1465, 1233, 1204, 1135, 1033, 884, 861, 792, 698 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{18}\text{H}_{13}\text{F}_9\text{ON}$ $[\text{M}+\text{H}]^+$ 430.0848, found 430.0872.



3b

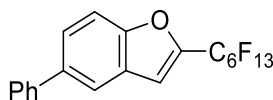
5-Phenyl-2-trifluoromethyl-benzofuran 3b. A sealed tube was charged with [Cu(bcp)DPEphos]PF₆ (22 mg, 20 μmol, 0.10 equiv.), potassium acetate (39 mg, 400 μmol, 2.0 equiv.) and 5-phenyl-benzofuran (39 mg, 201 μmol, 1.0 equiv.). The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry dichloromethane (300 μL) was added and trifluoromethyl iodide was condensed at -78 °C in order to reach around 2 mL of volume. The rubber septum was replaced by a Teflon-coated screw tap that was carefully sealed with Teflon-tape and Parafilm, and the reaction mixture was stirred under blue LED irradiation (using blue LED strips, see p. S3 for experimental setup) overnight at room temperature. The resulting mixture was diluted with dichloromethane and concentrated under reduced pressure. The crude residue was then purified by flash column chromatography over silica gel (pentane) to afford the desired product **3b** as a white solid (11 mg, 42 μmol, 21%). Mp: 48 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 1.6 Hz, 1H), 7.69 – 7.59 (m, 4H), 7.47 (td, *J* = 6.9 and 1.7 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.23 – 7.21 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 154.9, 144.3, 141.0, 138.0, 129.0 (2C+C), 127.6 (2C+C), 127.5, 126.9, 121.0, 112.4, 108.5; ¹⁹F NMR (377 MHz, CDCl₃): δ -65.4; IR (FTIR): ν_{max} 2937, 2930, 2923, 1357, 1340, 1310, 1184, 1157, 1136, 1074, 934, 764 cm⁻¹; ESIHRMS *m/z* calcd for C₁₅H₁₃F₃ON₂ [M+H]⁺ 281.0976, found 281.0984.



3c

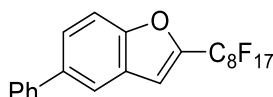
2-Heptafluoropropyl-5-phenyl-benzofuran 3c. Prepared according to the general procedure starting from 201 μmol of 5-phenyl-benzofuran. Yield: 43% (31 mg, 87 μmol). Solvent system for flash column chromatography: pentane. White solid; Mp: 45 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 1.5 Hz, 1H), 7.70 – 7.59 (m, 4H), 7.50 – 7.45 (m, 2H), 7.41 – 7.36 (m, 1H), 7.30 (q, *J* = 1.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 155.5, 143.5, 141.0, 138.1, 129.1, 127.6, 127.5, 127.0, 126.9, 120.9, 118.0, 112.5, 111.2, 110.9, 108.8; ¹⁹F NMR (377 MHz, CDCl₃): δ -80.9, -

113.3, -127.3;⁵⁹ IR (FTIR): ν_{\max} 3183, 3118, 1361, 1222, 1194, 1154, 1118, 957, 864, 764 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{17}\text{H}_{10}\text{F}_7\text{O}$ $[\text{M}+\text{H}]^+$ 363.0614, found 363.0619.



3d

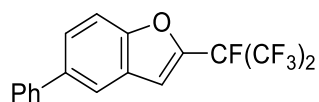
2-Perfluorohexyl-5-phenylbenzofuran 3d. Prepared according to the general procedure starting from 200 μmol of 5-phenylbenzofuran. Yield: 53% (54 mg, 105 μmol). Solvent system for flash column chromatography: pentane. White solid; Mp: 57 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.86 (d, $J = 1.8$ Hz, 1H), 7.71 – 7.58 (m, 4H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.42 – 7.36 (m, 1H), 7.31 – 7.28 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.5, 143.7, 141.0, 138.1, 129.1, 127.7, 127.5, 127.0, 126.9, 121.0, 117.4, 112.5, 111.8, 111.2, 111.0 (2C), 110.5, 108.6; ^{19}F NMR (377 MHz, CDCl_3): δ -81.3, -112.3, -122.4, -122.9, -123.2, -126.6; IR (FTIR): ν_{\max} 3675, 1235, 1196, 1182, 1161, 1145, 1123, 1093, 889, 763 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{20}\text{H}_{10}\text{F}_{13}\text{O}$ $[\text{M}+\text{H}]^+$ 513.0519, found 513.0527.



3e

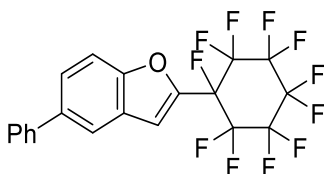
2-Perfluorooctyl-5-phenylbenzofuran 3e. Prepared according to the general procedure starting from 200 μmol of 5-phenylbenzofuran. Yield: 39% (47 mg, 78 μmol). Solvent system for flash column chromatography: pentane. White solid; Mp: 74 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.86 (dd, $J = 1.9$ and 0.7 Hz, 1H), 7.73 – 7.56 (m, 4H), 7.53 – 7.42 (m, 2H), 7.43 – 7.33 (m, 1H), 7.29 (q, $J = 1.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.5, 143.7, 141.0, 138.1, 129.1, 127.6, 127.5, 127.0, 126.9, 120.9, 117.3, 112.5, 111.8, 111.3, 110.9 (2C+2C), 110.4, 108.6; ^{19}F NMR (377 MHz, CDCl_3): δ -81.3, -112.3, -122.2, -122.3 (2F+2F), -122.8, -123.2, -126.6; IR (FTIR): ν_{\max} 2921, 1306, 1238, 1208, 1148, 821, 764 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{22}\text{H}_{10}\text{F}_{17}\text{O}$ $[\text{M}+\text{H}]^+$ 613.0455, found 613.0448.

⁵⁹ An unidentified residual signal at -75.9 ppm is present in the ^{19}F NMR spectrum (integration: 0.40).



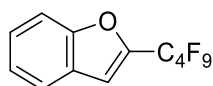
3f

2-Perfluoropropan-2-yl-5-phenyl-benzofuran 3f. Prepared according to the general procedure starting from 210 μmol of 5-phenyl-benzofuran. Yield: 52% (39 mg, 109 μmol). Solvent system for flash column chromatography: pentane. White solid; Mp: 50 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.85 (dd, $J = 1.7$ and 0.8 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.64 – 7.59 (m, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.37 (m, 1H), 7.26 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.4, 141.1, 138.1, 129.1, 127.7, 127.5, 127.0, 126.7, 120.7, 120.2, 119.9, 112.3, 110.7, 89.7; ^{19}F NMR (377 MHz, CDCl_3): δ -75.8, -180.1; IR (FTIR): ν_{max} 2992, 2933, 1304, 1271, 1224, 1004, 977, 886, 763 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{17}\text{H}_{10}\text{F}_7\text{O}$ $[\text{M}+\text{K}]^+$ 401.0173, found 401.0161.



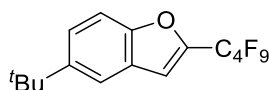
3g

2-Perfluorocyclohexyl-5-phenyl-benzofuran 3g. Prepared according to the general procedure starting from 200 μmol of 5-phenyl-benzofuran. Yield: 60% (57 mg, 120 μmol). Solvent system for flash column chromatography: pentane. White solid; Mp: 66 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3): δ 7.87 (dd, $J = 1.8$ and 0.8 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 – 7.44 (m, 2H), 7.41 – 7.34 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.5, 141.0 (2C), 138.1, 129.1, 127.7, 127.5, 127.0, 120.7 (2C), 112.6 (2C+C), 112.4 (2C+C+C); ^{19}F NMR (377 MHz, CDCl_3): δ -117.5, -122.7, -123.9, -123.1, -139.3, -142.2, -174.9; IR (FTIR): ν_{max} 3180, 1261, 1194, 1180, 1157, 1120, 1083, 960, 854, 763 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{20}\text{H}_9\text{F}_{11}\text{OK}$ $[\text{M}+\text{K}]^+$ 513.0109, found 513.0129.



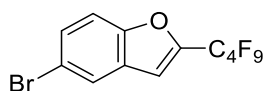
3h

2-Nonafluorobutyl-benzofuran 3h. Prepared according to the general procedure starting from 200 μmol of benzofuran. Yield: 49% (33 mg, 98 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.70 (dt, $J = 7.8$ and 1.0 Hz, 1H), 7.60 (dt, $J = 8.4$ and 0.9 Hz, 1H), 7.47 (ddd, $J = 8.5$, 7.2 and 1.4 Hz, 1H), 7.36 (ddd, $J = 8.0$, 7.4 and 1.0 Hz, 1H), 7.26 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.9, 143.1, 127.2, 126.3, 124.2, 122.6, 117.6, 112.3, 111.7, 110.7, 110.4, 108.9; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -112.5, -123.8, -126.5; IR (FTIR): ν_{max} 2955, 2924, 2854, 1456, 1353, 1235, 1205, 1135, 1061, 1033, 797, 740 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{12}\text{H}_6\text{F}_9\text{O}$ $[\text{M}+\text{H}]^+$ 337.0269 found 337.0274.



3i

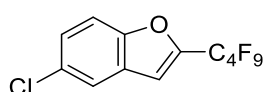
5-tert-Butyl-2-nonafluorobutyl-benzofuran 3i. Prepared according to the general procedure starting from 206 μmol of 5-tert-butylbenzofuran. Yield: 62% (50 mg, 127 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.67 (dd, $J = 1.9$ and 0.9 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.21 (q, $J = 1.0$ Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.2, 147.5, 143.0, 126.0, 125.4, 118.5, 117.6, 111.7, 111.6, 110.9, 110.4, 108.9, 35.0, 31.9 (3C); ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -112.4, -123.8, -126.5; IR (FTIR): ν_{max} 2967, 2911, 1235, 1204, 1136, 1016, 883, 813, 734 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{16}\text{H}_{13}\text{F}_9\text{ONa}$ $[\text{M}+\text{Na}]^+$ 415.0715, found 415.0709.



3j

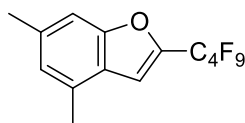
5-Bromo-2-nonafluorobutyl-benzofuran 3j. Prepared according to the general procedure starting from 200 μmol of 5-bromobenzofuran during two days. Yield: 30% (25 mg, 60 μmol).

Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, $J = 2.1$ Hz, 1H), 7.56 (dd, $J = 8.8$ and 2.0 Hz, 1H), 7.47 (dt, $J = 8.9$ and 0.8 Hz, 1H), 7.20 (q, $J = 1.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.7, 144.3, 130.3, 128.2, 125.3, 117.5, 117.4, 113.8, 111.4, 110.3, 110.1, 108.9; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -112.7, -123.8, -126.5; IR (FTIR): ν_{max} 1356, 1234, 1204, 1161, 1136, 1033, 833, 789, 745, 698, 674, 650 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{12}\text{H}_4\text{BrF}_9\text{OK}$ $[\text{M}+\text{K}]^+$ 452.8933, found 452.8991.



3k

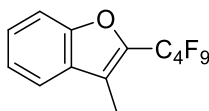
5-Chloro-2-nonafluorobutyl-benzofuran 3k. Prepared according to the general procedure starting from 202 μmol of 5-chlorobenzofuran. Yield: 36% (27 mg, 73 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 2.1$ Hz, 1H), 7.52 (dt, $J = 8.9$ and 0.8 Hz, 1H), 7.42 (dd, $J = 8.9$ and 2.1 Hz, 1H), 7.20 (q, $J = 1.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 154.3, 144.5, 130.0, 127.7, 127.6, 122.1, 117.5, 113.4, 111.4, 110.3 (2C), 108.8; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -112.7, -123.8, -126.5; IR (FTIR): ν_{max} 2914, 1236, 1137, 908, 861, 807, 734 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{12}\text{H}_5\text{ClF}_9\text{O}$ $[\text{M}+\text{H}]^+$ 370.9880, found 370.9884.



3l

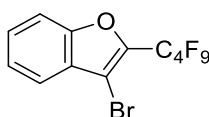
4,6-Dimethyl-2-nonafluorobutyl-benzofuran 3l. Prepared according to the general procedure starting from 133 μmol of 4,6-dimethylbenzofuran. Yield: 53% (25 mg, 70 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.21 (s, 2H), 6.96 (s, 1H), 2.51 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.4, 141.8, 137.8, 132.1, 126.0, 123.9, 117.6, 111.8, 110.4, 109.7, 109.4, 108.9, 21.9, 18.5; ^{19}F NMR

(377 MHz, CDCl₃): δ -81.5, -112.3, -123.8, -126.6; IR (FTIR): ν_{\max} 2929, 1356, 1234, 1204, 1091, 1017, 862, 745 cm⁻¹; ESIHRMS m/z calcd for C₁₄H₁₃F₉ON [M+NH₄]⁺ 382.0848 found 382.0875.



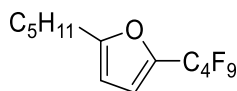
3m

3-Methyl-2-nonafluorobutyl-benzofuran 3m. Prepared according to the general procedure starting from 200 μ mol of 3-methylbenzofuran. Yield: 45% (31 mg, 89 μ mol). Solvent system for flash column chromatography: pentane. Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.62 (dt, J = 7.8 and 1.1 Hz, 1H), 7.53 (dt, J = 8.3 and 0.9 Hz, 1H), 7.44 (ddd, J = 8.4, 7.1 and 1.3 Hz, 1H), 7.34 (ddd, J = 8.1, 7.1 and 1.0 Hz, 1H), 2.42 (t, J = 2.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 154.8, 137.5, 128.7, 127.2, 123.5, 121.3, 120.7, 117.6, 113.1, 112.1, 110.7, 108.9, 7.9; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.4, -112.0, -124.1, -126.8; IR (FTIR): ν_{\max} 1455, 1375, 1234, 1205, 1135, 1091, 915, 880, 837, 746, 735 cm⁻¹; ESIHRMS m/z calcd for C₁₃H₇F₉OK [M+K]⁺ 388.9985, found 388.9973.



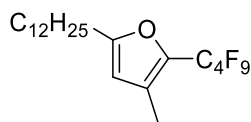
3n

3-Bromo-2-nonafluorobutyl-benzofuran 3n. Prepared according to the general procedure starting from 198 μ mol of 3-bromobenzofuran during two days. Yield: 67% (55 mg, 132 μ mol). Solvent system for flash column chromatography: pentane. Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.67 (dt, J = 7.8 and 1.0 Hz, 1H), 7.58 (dt, J = 8.4 and 1.0 Hz, 1H), 7.52 (ddd, J = 8.4, 7.0 and 1.3 Hz, 1H), 7.43 (ddd, J = 8.0, 7.0 and 1.1 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 154.4, 138.6, 128.5, 127.6, 124.8, 121.5, 117.5, 112.4, 112.2, 110.5, 108.8, 102.6; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.4, -112.2, -123.6, -126.7; IR (FTIR): ν_{\max} 3491, 2929, 1355, 1234, 1204, 1136, 995, 893, 841, 746, 734, 652 cm⁻¹; ESIHRMS m/z calcd for C₁₂H₅BrF₉O [M+H]⁺ 414.9375, found 414.9313.



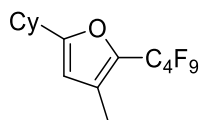
4a

2-Nonafluorobutyl-5-pentyl-furan 4a. Prepared according to the general procedure starting from 208 μmol of 5-pentylfuran. Yield: 69% (51 mg, 143 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 6.74 (d, $J = 3.4$ Hz, 1H), 6.10 (d, $J = 3.4$ Hz, 1H), 2.66 (t, $J = 7.6$ Hz, 2H), 1.66 (quint., $J = 7.3$ Hz, 2H), 1.34 (dq, $J = 8.5$ and 4.9 Hz, 4H), 0.90 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.0, 139.1, 117.6, 114.8, 111.5, 110.4, 108.9, 106.5, 31.3, 28.1, 27.5, 22.4, 14.0; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -111.5, -124.2, -126.7; IR (FTIR): ν_{max} 2962, 2935, 2866, 1353, 1234, 1205, 1136, 1114, 1019, 854, 735 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{13}\text{H}_{13}\text{F}_9\text{O}$ [M+Na] $^+$ 379.0715, found 379.0730.



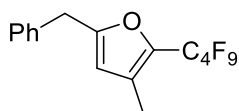
4b

5-Dodecyl-3-methyl-2-nonafluorobutyl-furan 4b. Prepared according to the general procedure starting from 201 μmol of 5-dodecyl-3-methylfuran. Yield: 61% (57 mg, 122 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.94 (s, 1H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.12 (t, $J = 2.6$ Hz, 3H), 1.61 (quint., $J = 7.3$ Hz, 2H), 1.32 – 1.23 (m, 18H), 0.91 – 0.84 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 159.5, 133.7, 126.7, 117.7, 112.8, 110.7, 110.3, 109.0, 32.1, 29.8 (3C), 29.7, 29.5, 29.4, 29.2, 28.0, 27.8, 22.9, 14.2, 10.0; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -111.3, -124.5, -126.9; IR (FTIR): ν_{max} 2927, 2856, 1351, 1234, 1206, 1135, 1085, 970, 863, 818, 735, 647 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{21}\text{H}_{30}\text{F}_9\text{O}$ [M+H] $^+$ 469.2147, found 469.2155.



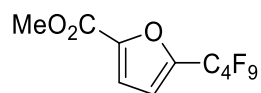
4c

5-Cyclohexyl-3-methyl-2-nonafluorobutyl-furan 4c. Prepared according to the general procedure starting from 202 μmol of 5-cyclohexyl-3-methylfuran. Yield: 54% (42 mg, 110 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 5.91 (s, 1H), 2.65-2.54 (m, 1H), 2.12 (t, $J = 2.5$ Hz, 3H), 2.04-1.93 (m, 2H), 1.85 – 1.75 (m, 2H), 1.74 – 1.67 (m, 1H), 1.42 – 1.29 (m, 4H), 1.28 – 1.18 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 133.5, 126.5, 117.7, 112.9, 110.8, 109.0, 108.3, 37.2, 31.2, 26.1, 25.9, 10.0; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -111.4, -124.6, -127.0; IR (FTIR): ν_{max} 2934, 2859, 1234, 1206, 1175, 1134, 1085, 865, 809, 736 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{15}\text{H}_{16}\text{F}_9\text{O}$ $[\text{M}+\text{H}]^+$ 383.1052, found 383.0993.



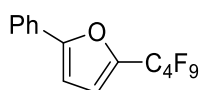
4d

5-Benzyl-3-methyl-2-nonafluorobutylfuran 4d. Prepared according to the general procedure starting from 197 μmol of 5-benzyl-3-methylfuran. Yield: 65% (50 mg, 128 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 3H), 5.93 (s, 1H), 3.98 (s, 2H), 2.14 (t, $J = 2.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 157.6, 134.0, 134.5, 128.9, 128.8, 127.0, 126.9, 117.7, 112.8, 111.6, 110.7, 108.9, 34.5, 10.0; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -111.4, -124.4, -126.9; IR (FTIR): ν_{max} 3035, 2946, 1406, 1351, 1234, 1206, 1134, 1085, 979, 863, 819, 739, 728, 699 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{16}\text{H}_{12}\text{F}_9\text{O}$ $[\text{M}+\text{H}]^+$ 391.0739, found 391.0746.



4e

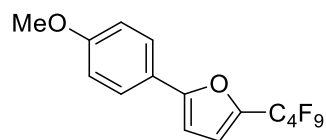
5-Methoxycarbonyl-2-nonafluorobutyl-furan 4e. Prepared according to the general procedure starting from 200 μmol of methyl furan-2-carboxylate. Highly volatile product, ^{19}F NMR Yield: 51%.^{S10} Solvent system for flash column chromatography: pentane/Et₂O (70/30). Colorless oil; ^1H NMR (400 MHz, CDCl₃): δ 7.24 (dd, J = 2.9 and 1.8 Hz, 1H), 6.95 (dt, J = 3.7 and 1.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl₃): δ 158.2, 147.6, 144.0, 118.0, 117.5, 115.3, 110.9, 110.1, 108.8, 52.6; ^{19}F NMR (377 MHz, CDCl₃): δ -81.4, -112.4, -123.8, -126.5; IR (FTIR): ν_{max} 2961, 2920, 2851, 1740, 1297, 1228, 1201, 1113, 1022, 804, 737 cm^{-1} ; ESIHRMS m/z calcd for C₁₀H₆F₉O₃ [M+H]⁺ 345.0168, found 345.0182.



4f

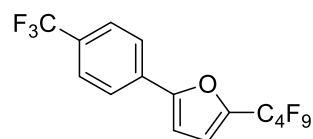
5-Phenyl-2-nonafluorobutyl-furan 4f. Prepared according to the general procedure starting from 201 μmol of 5-phenylfuran. Yield: 58% (42 mg, 116 μmol). Solvent system for flash column chromatography: pentane. Yellow oil; ^1H NMR (400 MHz, CDCl₃): δ 7.72 (dd, J = 7.2 and 1.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.94 (dt, J = 3.5 and 1.2 Hz, 1H), 6.74 (dt, J = 3.6 and 1.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl₃): δ 157.7, 140.1, 129.4, 129.1 (2C+C), 124.7 (2C), 117.6, 116.0, 111.5, 110.4, 108.9, 105.8; ^{19}F NMR (377 MHz, CDCl₃): δ -81.5, -110.6, -124.0, -126.5; IR (FTIR): ν_{max} 3069, 1234, 1219, 1204, 1135, 1110, 1023, 855, 745, 735 cm^{-1} ; ESIHRMS m/z calcd for C₁₄H₈F₉O [M+H]⁺ 363.0426, found 363.0432.

^{S10} ^{19}F NMR yield was determined using α,α,α -trifluorotoluene as an internal standard.



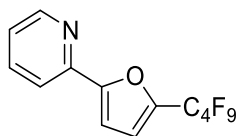
4g

5-(4-Methoxyphenyl)-2-nonafluorobutyl-furan 4g. Prepared according to the general procedure starting from 207 μmol of 5-(4-methoxyphenyl)furan. Yield: 71% (58 mg, 148 μmol). Solvent system for flash column chromatography: pentane/Et₂O (95/05). Yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.64 (dt, $J = 8.9$ and 2.9 Hz, 2H), 6.96 (dt, $J = 8.9$ Hz and 2.9 Hz, 2H), 6.90 (dt, $J = 3.6$ and 1.3 Hz, 1H), 6.59 (dt, $J = 3.6$ and 0.9 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 160.4, 157.8, 139.4, 126.2, 122.4, 117.6, 116.0, 114.5, 111.6, 110.4, 109.0, 104.3, 55.5; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.5, -111.4, -124.0, -126.5; IR (FTIR): ν_{max} 2915, 1497, 1235, 1135, 1024, 909, 835, 790, 734 cm^{-1} ; ESIHRMS m/z calcd for C₁₅H₁₀F₉O₂ [M+H]⁺ 393.0532, found 393.0540.



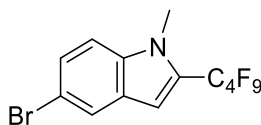
4h

5-(4-trifluoromethylphenyl)-2-(nonafluorobutyl)-furan 4h. Prepared according to the general procedure starting from 204 μmol of 5-(4-trifluoromethylphenyl)furan. Yield: 57% (50 mg, 116 μmol). Solvent system for flash column chromatography: pentane/Et₂O (95/05). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, $J = 8.2$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 6.97 (dt, $J = 3.6$ and 1.2 Hz, 1H), 6.85 (d, $J = 3.6$ Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 156.0, 141.2, 132.5, 130.8, 126.1, 124.8, 124.1, 117.6, 116.1, 111.3, 110.4, 108.9, 107.7; ¹⁹F NMR (377 MHz, CDCl₃): δ -63.3, -81.5, -111.8, -123.9, -126.5; IR (FTIR): ν_{max} 3068, 2862, 1325, 1235, 1116, 856, 796 cm^{-1} ; ESIHRMS m/z calcd for C₁₅H₇F₁₂O [M+K]⁺ 468.9859, found 468.9871.



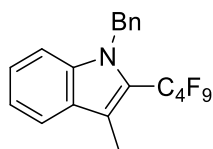
4i

2-Nonafluorobutyl-5-(pyridine-2-yl)-furan 4i. Prepared according to the general procedure starting from 200 μmol of 2-(furan-2-yl)pyridine. Yield: 66% (48 mg, 132 μmol). Solvent system for flash column chromatography: pentane/Et₂O (50/50). Yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 8.65 (dt, J = 4.8 and 1.4 Hz, 1H), 7.79 (dd, J = 4.9 and 1.4 Hz, 2H), 7.27 (dd, J = 8.8 and 4.4 Hz, 1H), 7.19 (dt, J = 3.6 and 1.0 Hz, 1H), 7.00 (dt, J = 3.6 and 1.2 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 157.0, 150.0, 148.2, 141.1, 137.1, 123.4, 119.5, 117.6, 116.2, 111.4, 110.4, 109.2, 108.9; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.5, -111.7, -123.9, -126.5; IR (FTIR): ν_{max} 1428, 1278, 1236, 1136, 908, 781, 733 cm⁻¹; ESIHRMS m/z calcd for C₁₃H₇F₉ON [M+H]⁺ 364.0378, found 364.0385.



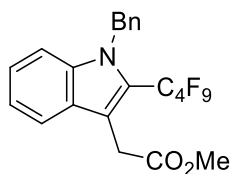
5a

N-Methyl-5-bromo-2-nonafluorobutyl-indole 5a. Prepared according to the general procedure starting from 205 μmol of *N*-methyl-5-bromo-indole. Yield: 31% (27 mg, 63 μmol). Solvent system for flash column chromatography: petroleum ether/EtOAc (90/10). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.81 (d, J = 1.9 Hz, 1H); 7.45 (dd, J = 8.9 and 1.9 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 6.90 (s, 1H), 3.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 138.0, 127.8, 127.6, 126.6, 124.7, 117.6, 114.2 (2C), 111.7, 110.6, 109.1, 106.9, 31.9; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.4, -106.1, -122.0, -126.2; IR (FTIR): ν_{max} 2948, 2847, 1234, 1209, 1134, 792, 728 cm⁻¹; ESIHRMS m/z calcd for C₁₃H₈F₉BrN [M+H]⁺ 427.9691, found 427.9710.



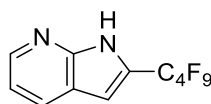
5b

N-Benzyl-3-methyl-2-nonafluorobutyl-indole 5b. Prepared according to the general procedure starting from 203 μmol of *N*-benzyl-3-methyl-indole. Yield: 55% (49 mg, 112 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.74 (dd, J = 7.7 and 1.3 Hz, 1H), 7.34 – 7.20 (m, 6H), 6.99 – 6.95 (m, 2H), 5.48 (s, 2H), 2.54 (t, J = 2.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.5, 137.9, 128.8, 127.9, 127.4, 125.7, 125.2, 120.9, 120.5, 120.3, 118.4, 117.7, 115.8, 111.0, 110.9, 109.2, 48.9, 9.4; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -112.7, -123.8, -126.5; IR (FTIR): ν_{max} 3039, 2927, 1349, 1232, 1204, 1133, 1108, 871, 839, 733 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{20}\text{H}_{15}\text{F}_9\text{N}$ $[\text{M}+\text{H}]^+$ 440.1055, found 440.1066.



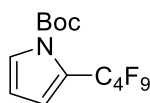
5c

Methyl 2-(1-benzyl-2-(nonafluorobutyl)-1H-indol-3-yl)acetate 5c. Prepared according to the general procedure starting from 198 μmol of methyl 2-(1-benzyl-1H-indol-3-yl)acetate. Yield: 24% (24 mg, 48 μmol). Solvent system for flash column chromatography: petroleum ether/EtOAc : 90/10. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.72 – 7.68 (m, 1H), 7.32 – 7.19 (m, 6H + CHCl_3), 6.98 – 6.93 (m, 2H), 5.47 (s, 2H), 3.98 (t, J = 2.0 Hz, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 138.4, 137.4, 128.9, 127.5, 127.4, 125.7, 125.5, 122.0, 121.3, 120.5, 117.6, 115.5, 114.8, 111.2, 110.7, 109.1, 52.3, 49.1, 30.4; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -103.8, -122.4, -126.3; IR (FTIR): ν_{max} 2956, 2925, 2851, 1746, 1466, 1349, 1233, 1204, 1170, 1134, 869, 734 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{22}\text{H}_{17}\text{F}_9\text{NO}_2$ $[\text{M}+\text{H}]^+$ 498.1110, found 498.1112.



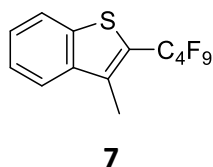
5d

2-Nonafluorobutyl-pyrrolo[2,3-*b*]pyridine 5d. Prepared according to the general procedure starting from 210 μmol of pyrrolo[2,3-*b*]pyridine. Yield: 87% (61 mg, 182 μmol). Solvent system for flash column chromatography: pentane/Et₂O (50/50). Yellow solid; Mp: 108 °C; ¹H NMR (400 MHz, CDCl₃): δ 14.2 (s, 1H), 8.46 (dd, J = 4.9 and 1.5 Hz, 1H), 8.12 (dd, J = 8.0 and 1.5 Hz, 1H), 7.23 (dd, J = 8.0 and 4.8 Hz, 1H), 6.95 (t, J = 1.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 149.1, 144.9, 131.5, 125.9, 120.2, 117.6, 117.2, 113.7, 110.5, 109.1, 103.9; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.5, -110.0, -123.5, -126.1; IR (FTIR): ν_{max} 2853, 1351, 1327, 1231, 1207, 1134, 859, 834, 791, 745, 648 cm⁻¹; ESIHRMS m/z calcd for C₁₁H₆F₉N₂ [M+H]⁺ 337.0382, found 337.0390.

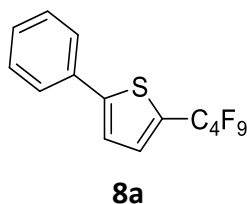


6

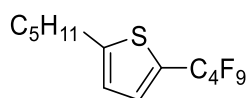
***N*-tert-Butoxycarbonyl-2-nonafluorobutyl-pyrrole 6.** Prepared according to the general procedure starting from 200 μmol of *N*-tert-Butoxycarbonyl-pyrrole. Yield: 43% (33 mg, 86 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (dd, J = 3.3 and 2.0 Hz, 1H), 6.77 (ddt, J = 3.7, 1.9 and 0.9 Hz, 1H), 6.25 (t, J = 3.5 Hz, 1H), 1.60 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 147.7, 127.8, 120.4, 119.9, 117.7, 113.5, 110.7, 110.0, 109.2, 85.8, 27.8; ¹⁹F NMR (377 MHz, CDCl₃): δ -81.4, -100.9, -120.0, -126.0; IR (FTIR): ν_{max} 2985, 1779, 1755, 1348, 1234, 1134, 897, 848, 819, 800, 734 cm⁻¹; ESIHRMS m/z calcd for C₁₃H₁₂F₉NO₂Na [M+Na]⁺ 408.0617, found 408.0608.



3-Methyl-2-nonafluorobutylbenzo[*b*]thiophene 7. Prepared according to the general procedure starting from 200 μmol of 3-methyl-benzo[*b*]thiophene. Yield: 51% (37 mg, 101 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.89 – 7.80 (m, 2H), 7.51 – 7.45 (m, 2H), 2.57 (tt, $J = 2.0$ and 0.9 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.0, 139.7, 136.9, 126.8, 124.9, 123.6, 123.3, 122.6, 117.7, 116.2, 110.9, 109.2, 12.6; ^{19}F NMR (377 MHz, CDCl_3): δ -81.4, -101.0, -122.1, -126.2; IR (FTIR): ν_{max} 2923, 1352, 1232, 1204, 1134, 929, 786, 731, 718 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{13}\text{H}_7\text{F}_9\text{SNa}$ $[\text{M}+\text{Na}]^+$ 389.0017, found 389.0013.

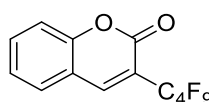


2-Nonafluorobutyl-5-phenylthiophene 8a. Prepared according to the general procedure starting from 200 μmol of 2-phenylthiophene. Yield: 63% (48 mg, 126 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.59 (m, 2H), 7.46-7.37 (m, 4H), 7.30 (dt, $J = 3.9$ and 1.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 149.9, 133.0, 131.3, 129.3, 129.0, 128.1, 126.4, 123.2, 117.6, 114.8, 110.2, 109.1; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -101.9, -122.9, -126.0; IR (FTIR): ν_{max} 3040, 1545, 1462, 1354, 1270, 1233, 1205, 1134, 1083, 988, 855, 797, 756, 733, 702, 689 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{14}\text{H}_{11}\text{F}_9\text{NS}$ $[\text{M}+\text{NH}_4]^+$ 396.0463, found 396.0460.



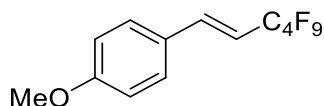
8b

2-Nonafluorobutyl-5-pentylthiophene 8b. Prepared according to the general procedure starting from 200 μmol of 2-pentylthiophene. Yield: 75% (56 mg, 150 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 3.7$ Hz, 1H), 6.80 (dt, $J = 3.7$ and 1.1 Hz, 1H), 2.84 (td, $J = 7.7$ and 0.8 Hz, 2H), 1.74-1.66 (m, 2H), 1.39-1.33 (m, 4H), 0.93-0.89 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 151.9, 130.4, 126.4, 124.6, 117.7, 114.9, 110.2, 109.1, 31.3, 31.3, 30.2, 22.5, 14.1; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -101.5, -123.0, -126.0; IR (FTIR): ν_{max} 2962, 2937, 2862, 1549, 1474, 1354, 1234, 1205, 1134, 1078, 985, 857, 797, 745, 733, 702 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{13}\text{H}_{13}\text{F}_9\text{S}$ $[\text{M}]^+$ 372.0589, found 372.0586.



9

Nonafluorobutyl-coumarin 9. Prepared according to the general procedure starting from 198 μmol of coumarin. Yield: 46% (33 mg, 91 μmol). Solvent system for flash column chromatography: pentane/ Et_2O (40/60). Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 8.14 (d, $J = 0.9$ Hz, 1H), 7.72 – 7.61 (m, 2H), 7.42 – 7.36 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 155.6, 155.1, 146.6, 134.9, 129.7, 125.4, 117.6, 117.2, 117.1, 116.8, 114.3, 110.7, 109.0; ^{19}F NMR (377 MHz, CDCl_3): -81.3, -111.7, -122.1, -126.3; IR (FTIR): ν_{max} 3677, 2924, 1749, 1233, 1215, 1135, 873, 758, 743, 720 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{13}\text{H}_6\text{F}_9\text{O}_2$ $[\text{M}+\text{H}]^+$ 365.0219, found 365.0220.



10a

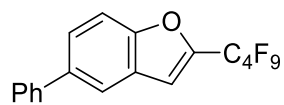
***p*-Methoxy- β -Nonafluorobutyl-styrene 10a.** Prepared according to the general procedure starting from 200 μmol of *p*-methoxy-styrene. Yield: 50% (35 mg, 99 μmol). Solvent system for flash column chromatography: pentane. Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.46 – 7.39

(m, 2H), 7.11 (dt, $J = 16.1$ and 2.4 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.06 (dt, $J = 16.1$ and 12.3 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 161.4, 139.3, 129.4, 126.4, 117.7, 115.4, 114.5, 111.8, 110.6, 109.0, 55.5; ^{19}F NMR (377 MHz, CDCl_3): δ -81.5, -111.3, -124.6, -126.2; IR (FTIR): ν_{max} 2964, 2844, 1656, 1232, 1132, 975, 886, 818, 728 cm^{-1} ; ESIHRMS m/z calcd for $\text{C}_{13}\text{H}_{10}\text{F}_9\text{O}$ $[\text{M}+\text{H}]^+$ 353.0582, found 353.0569.

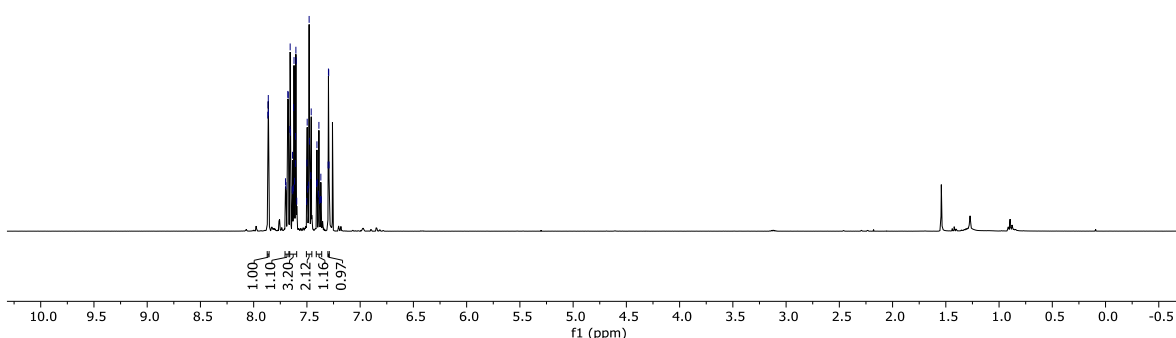
Supporting Information

Copies of ^1H , ^{13}C and ^{19}F spectra

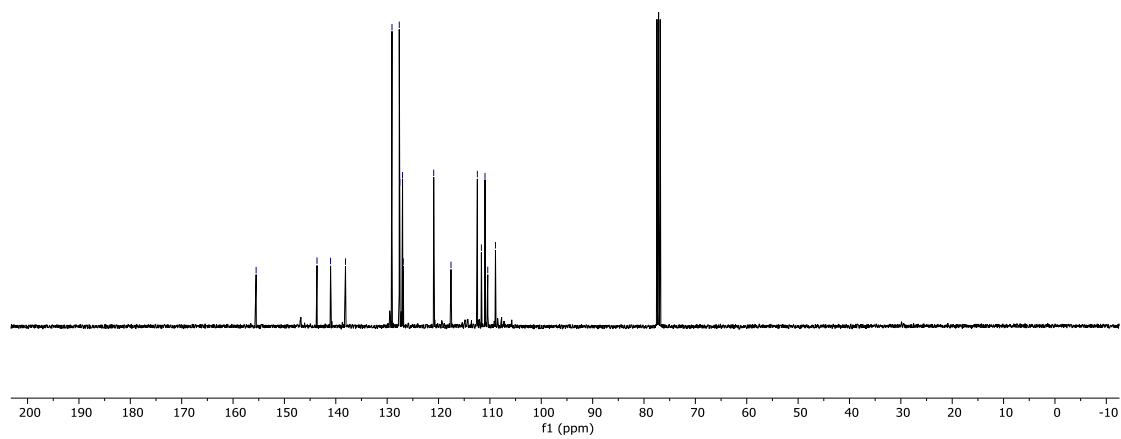
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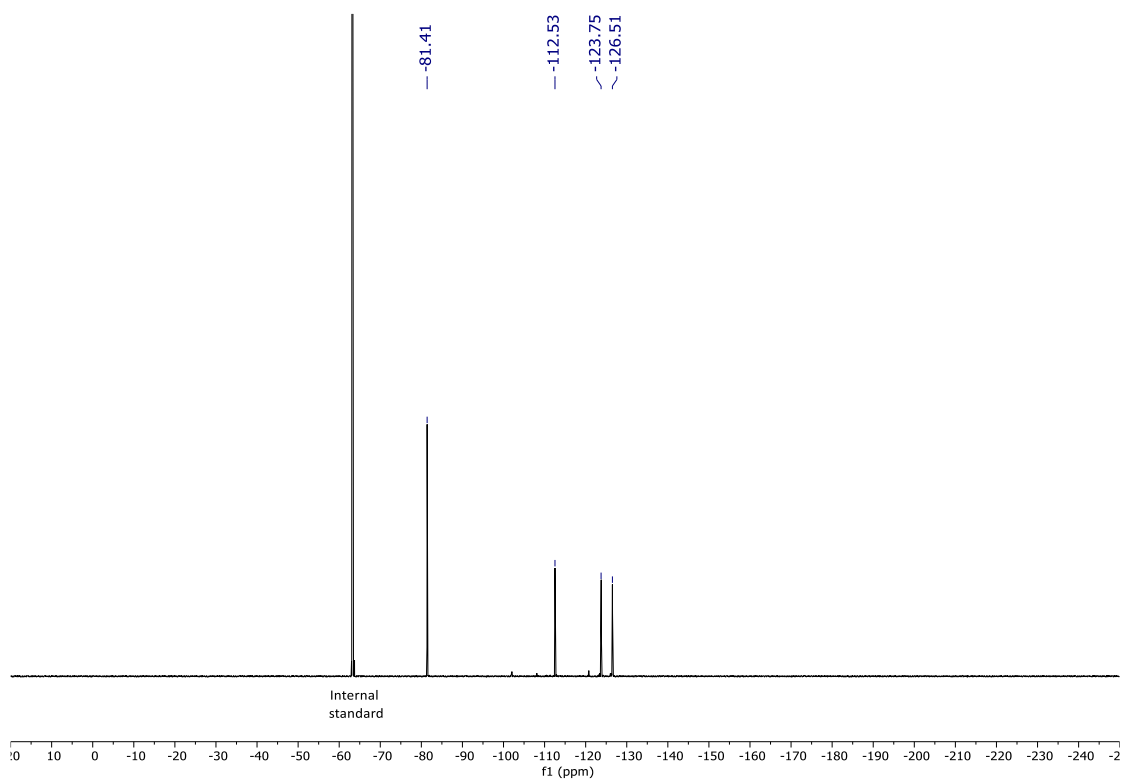


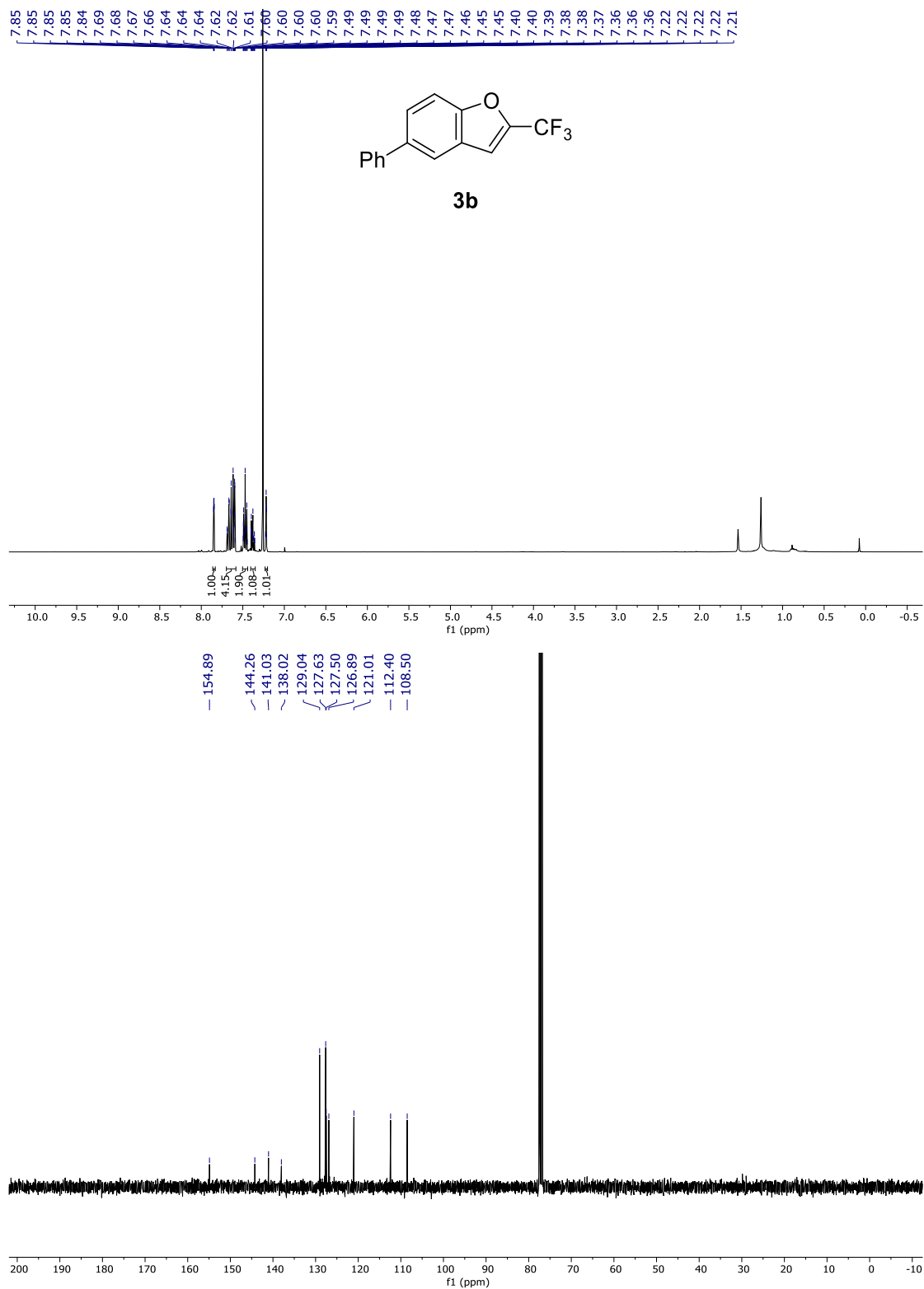
3a

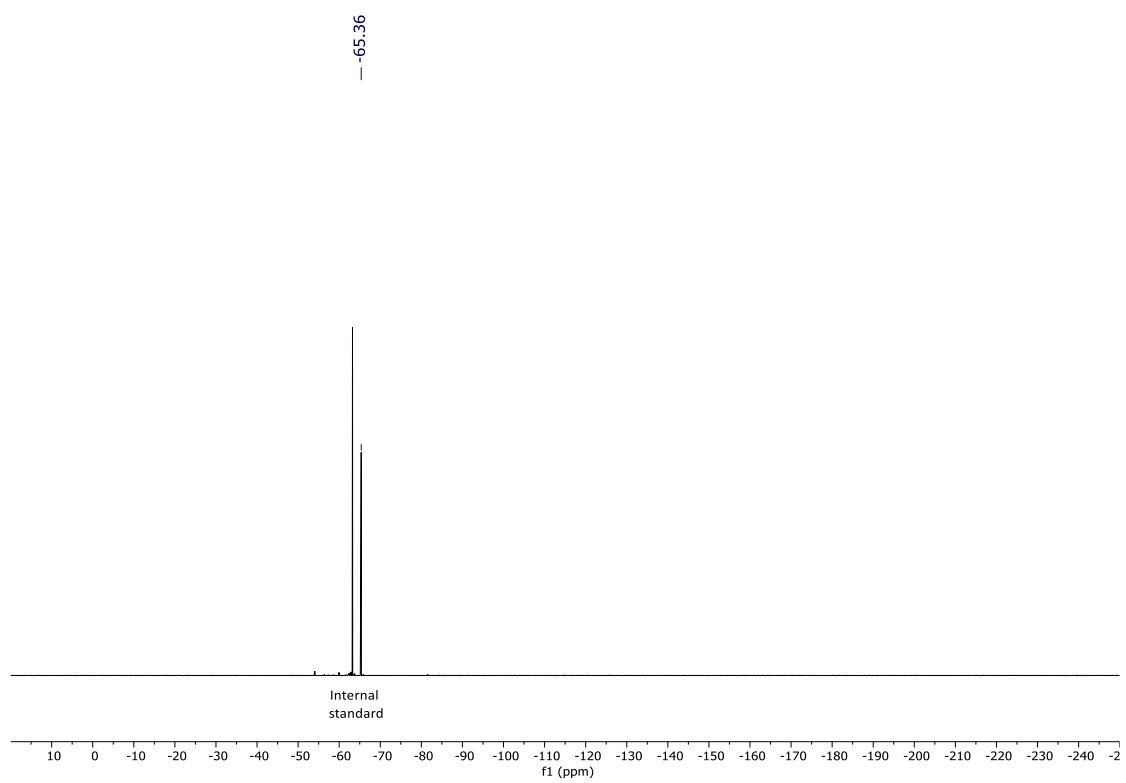


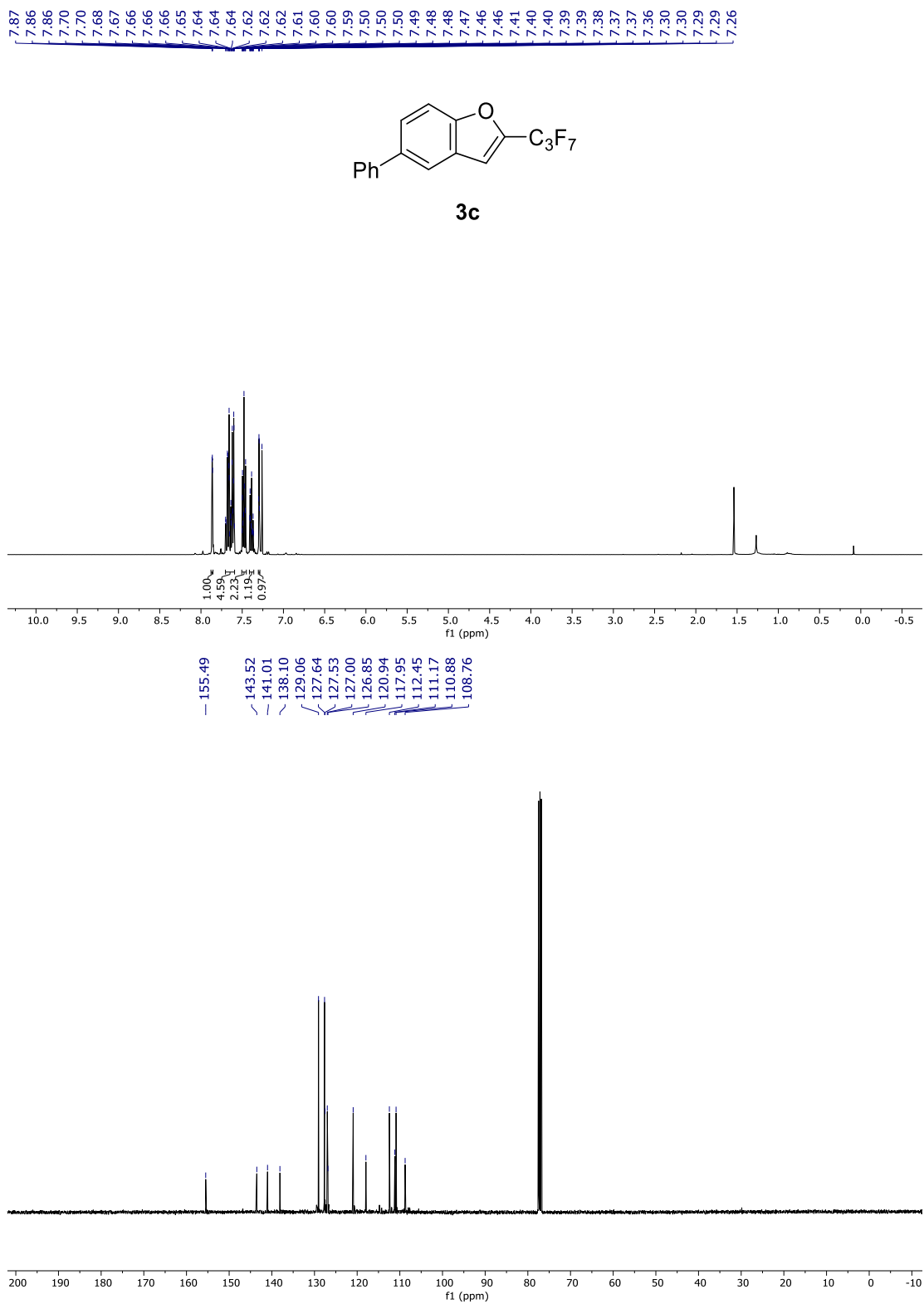
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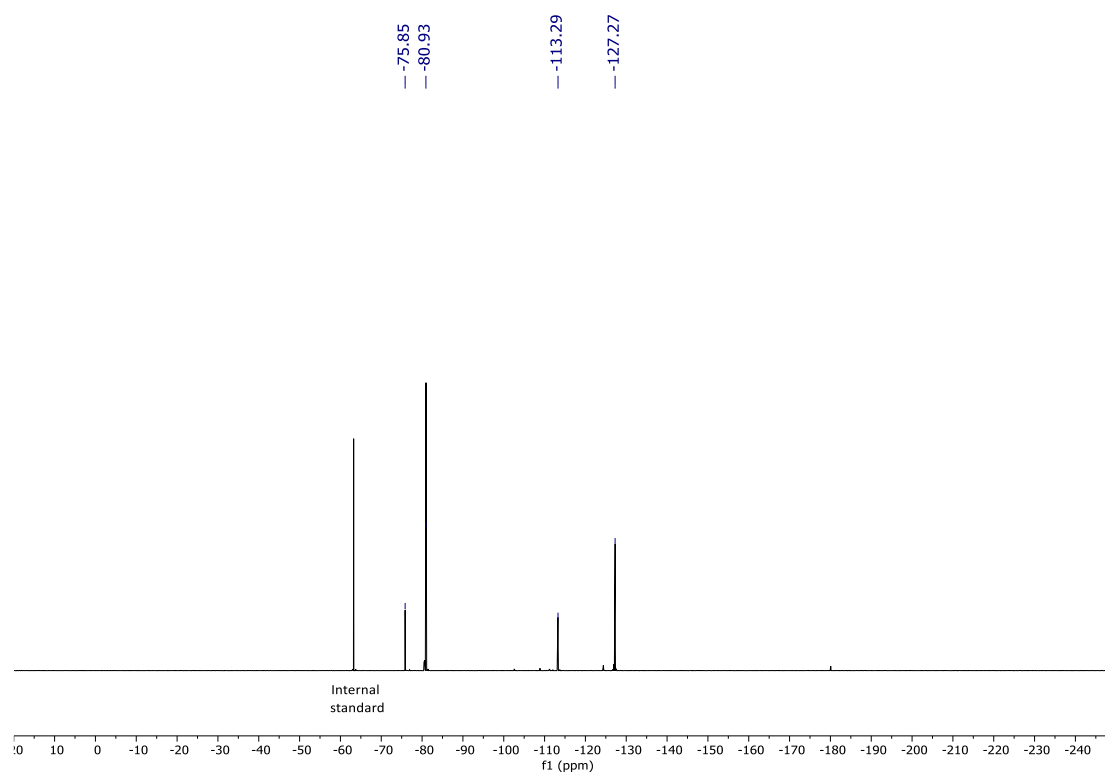




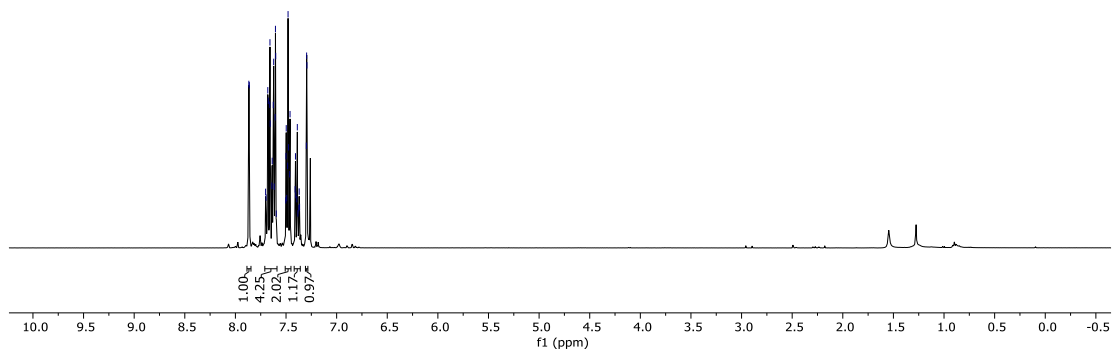
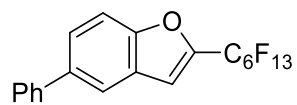




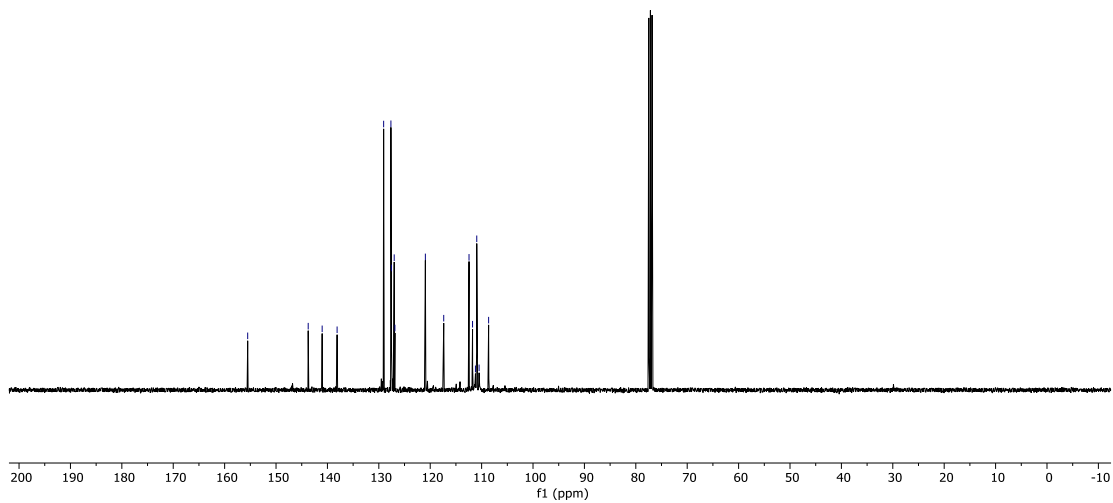


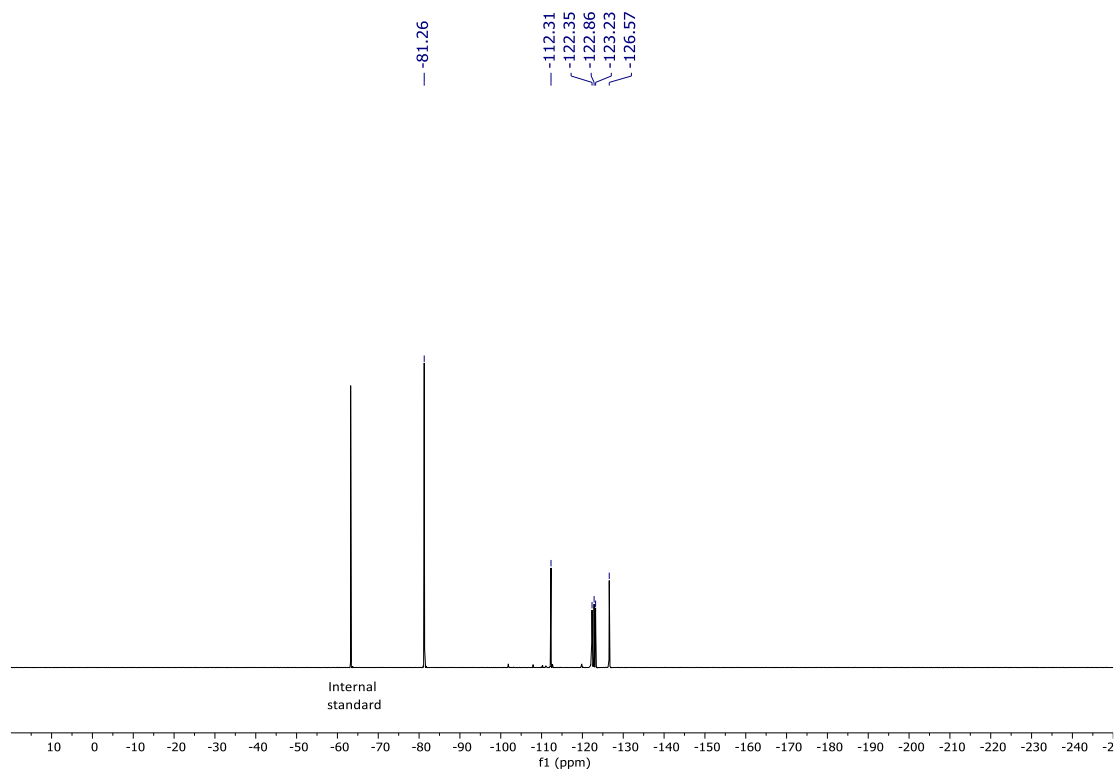


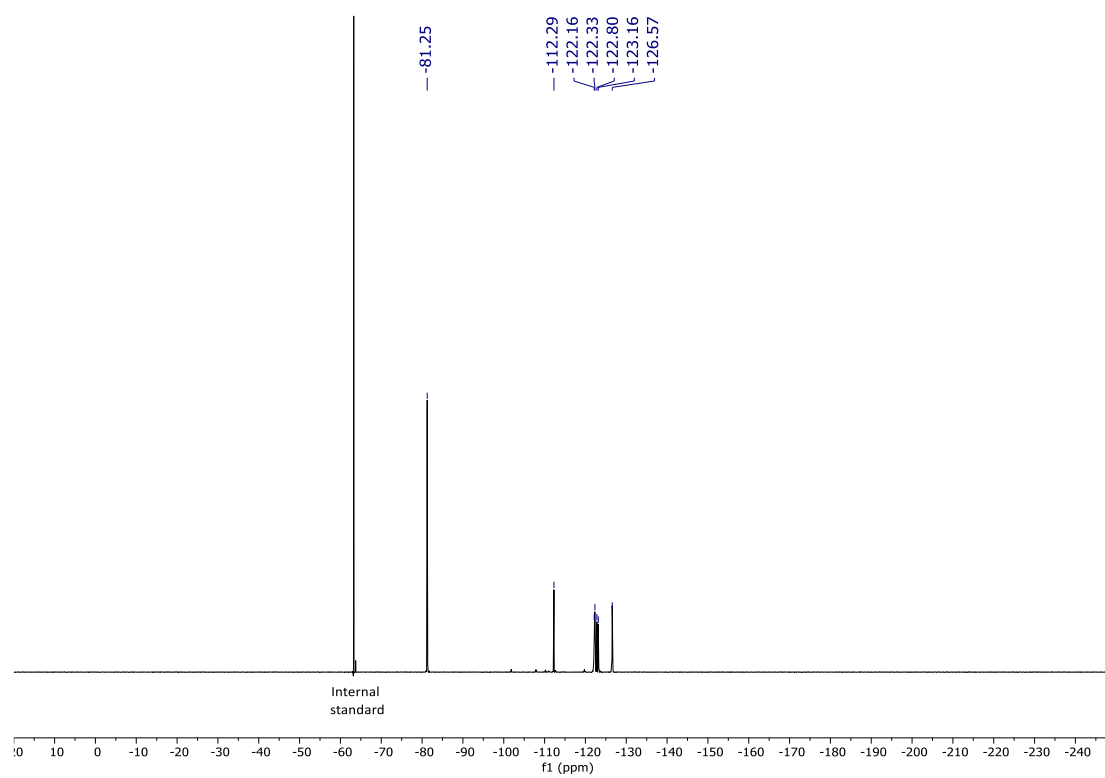
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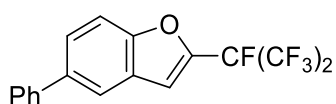
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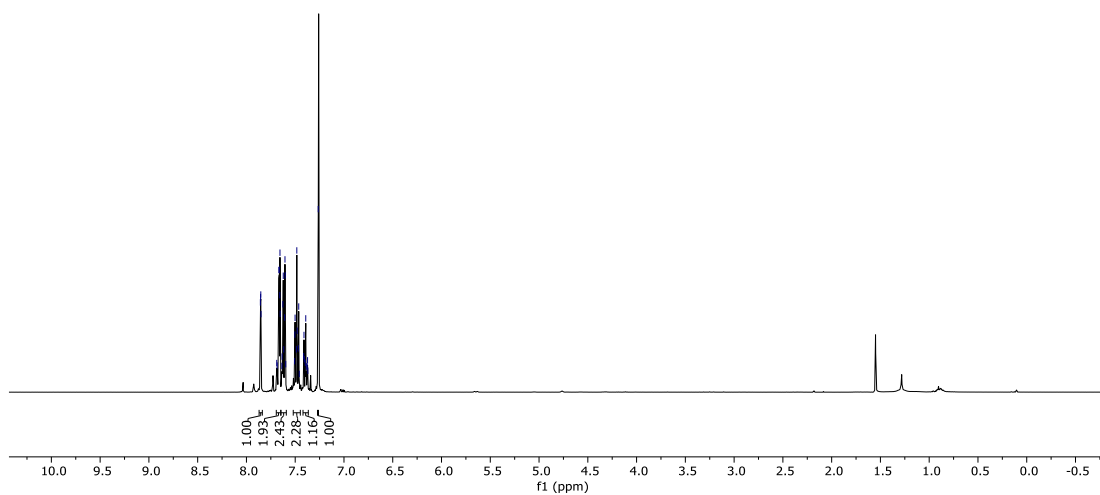




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3f



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