Supporting Information

Metal-free Iodoperfluoroalkylation: Photocatalysis vs. Frustrated Lewis Pair Catalysis

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General Experimental Procedures

All syntheses involving air- and moisture-sensitive compounds were carried out inside a glovebox (_Vacuum Atmospheres_ model OMNI-LAB) under N₂ atmosphere (_Air Liquide ALPHAGAZ™ 5.0_). Glassware was dried for 2 hours at 120 °C and cooled down in vacuo.

Reagents, as well as solvents, were purchased from Acros, Sigma Aldrich, abcr, TCI, J & K scientific, Fluorochem, or Avantor. Chemicals were used without further purification or purified according to laboratory methods.¹ Nonafluoro-1-iodobutane was filtered through a column packed with aluminum oxide 90 basic 0.063 - 0.200 mm (activity stage I) and activated molecular sieve (4 Å) under N₂ atmosphere. The clear liquid was stored in amber glass vials under N₂ atmosphere. Solvents were dried with the solvent purification system MP-SPS 800 from _M.Braun_, distilled and, if necessary, degassed with freeze-pump-thaw. For Grignard reactions, magnesium turnings (purchased, for Grignard reactions, ≥ 99.5%) were activated by stirring with 1 M hydrochloric acid for 1 min. They were subsequently washed with water, ethanol, and finally Et₂O. The solvent was decanted off after each washing step. To dry the activated magnesium turnings a rotary evaporator and then a high vacuum pump was used.

Reactions were monitored by thin-layer chromatography (TLC) using _Macherey-Nagel_ silica gel plates ALUGRAM® Xtra SIL G/UV254 (0.20 mm thickness) and visualized by UV light or staining reagents if necessary. As staining reagent self-prepared potassium permanganate solution (KMnO₄ (3.0 g), K₂CO₃ (20 g), NaOH (5.0 ml 5.0%), H₂O (300 mL)) was used. Chromatographic purification of products was performed on _Macherey-Nagel_ 60 M (0.04 - 0.063 mm) silica gel.

¹H-, ¹¹B-, ¹³C-, and ¹⁹F-NMR spectra were recorded on _Bruker_ Avance III 300 and 600 NMR spectrometer. Chemical shifts are reported in parts per million (ppm) to the corresponding solvent. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, ddd = doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons, and d) assignment. Coupling constants (J) were reported in Hertz (Hz). The attributions of the chemical shifts were determined by means of COSY and HSQC experiments. If not described differently the NMR-spectra were measured at 298 K.

IR spectra were recorded using a _Jasco_ FT/IR-6200 spectrometer. Samples were measured as film on a NaCl single crystal. The absorption bands were given in wavenumbers (cm⁻¹).

GC experiments were conducted on a Shimadzu GC-2010 equipped with an auto injector AOC-20i (syringe code: 10R-S-0.63C). A ZB-Wax Plus column (30 m x 0.25 mm x 0.25 μm) was used. As internal standard n-decane (Acros Organics, purity 99+%, LOT: 1283567) was added to the reaction solution.

High-resolution mass spectra (HRMS) were measured with a _Bruker Daltonics_ UHR-QTOF maXis 4G.
Melting points were recorded on a Büchi B-540.

Elemental analyses were measured on an elementar Vario Micro Cube.

If mentioned all reactions inside the fume hood were conducted under red light (Jedi Lightning E27 ID60, 806 lm, 11W) and best possible light exclusion. Inside the glovebox all reactions were prepared with an RGB LED-strip as light source. Addition of the individual perfluoroalkyl iodide was conducted under red light by a LED-strip.

The used photoreactor is self-assembled and is described in literature.\(^2\)

Unless otherwise stated all perfluoroalkylation reactions were conducted inside 4 ml screw neck glass vials with a septa screw cap or a glass screw-cap vial with a Teflon-insert screw cap.

**General procedure (GP-A)**

Inside the glovebox \(\text{tBu}_3\text{P}\) (10 mol%) as well as the borane (10 mol%) were weighed into an amber glass screw-top vial, dissolved in \(\text{CH}_2\text{Cl}_2\) (2.1 mL) and a Teflon stirring bar was added. The educt and the corresponding perfluoroalkyl iodide (1.10 mmol) were added. The reaction vial was sealed and stirred for the indicated reaction time, the solvent was evaporated under a stream of nitrogen. Purification was conducted by chromatography.

**General procedure B (GP-B)**

Inside the glovebox \(\text{tBu}_3\text{P}\) (10 mol%) and the educt were weighed into an aluminum foil-wrapped reaction glass. \(\text{CH}_2\text{Cl}_2\) (2 mL) and a Teflon stirring bar were added. Under red light conditions the corresponding perfluoroalkyl iodide (1.10 mmol) was added. The reaction vial was sealed, transferred into the photoreactor, and was irradiated for the indicated time. After the stated reaction time the irradiation was stopped, and the solvent was evaporated under a stream of nitrogen. Purification was conducted by chromatography.
1. FLP-catalyzed Iodoperfluoroalkylations

1.1. 1-Methoxy-4-(4,4,5,6,6,7,7-nonafauro-2-iodoheptyl)benzene (15)

Following GP-A, 'Bu3P (16.7 mg, 0.0825 mmol, 10.0 mol%), B(C6F5)3 (40.5 mg, 0.0791 mmol, 9.61 mol%), 4-allylanisole (63) (122 mg, 0.823 mmol, 1.00 equiv) and nonafluoro-1-iodobutane (282 mg, 0.815 mmol, 0.990 equiv) were weighed out into an amber glass screw-top vial, dissolved in CH2Cl2 (2.5 mL) and stirred for 6 d. Purification was conducted by chromatography on SiO2 (n-pentane:acetone 99:1) and (cyclohexane:acetone 99:1) yielding pure product 15 (114 mg, 0.232 mmol, 28 %).

1H NMR (300 MHz, Chloroform-d) δ [ppm] 7.18 – 7.07 (m, 2H, Ar–H), 6.94 – 6.82 (m, 2H, Ar–H), 4.43 (dq, J = 8.4, 6.4 Hz, 1H, −CH2I−), 3.81 (s, 3H, −OMe), 3.28 – 3.08 (m, 2H, Ar–CH2–), 3.01 – 2.73 (m, 2H, −CH2–R).

13C{1H} NMR (75.5 MHz, Chloroform-d) δ [ppm] 159.0, 130.8, 130.2, 114.1, 121.3-110.3 (m, CF2, CF3), 55.4, 46.4, 40.6 (t, 2JCF = 20.9 Hz, −H2CCFRf), 20.3.

19F NMR (282 MHz, Chloroform-d) δ [ppm] −81.1 (tt, J = 9.7, 3.2 Hz, 3F), −111.6 − −114.7 (m, 2F), −124.5 − −124.7 (m, 2F), −125.8 − −126.0 (m, 2F).

IR (film on NaCl), [cm−1] 2838, 1613, 1585, 1514, 1467, 1442, 1351, 1246, 1135, 1037, 881, 832, 726, 518.

m/z calculated for C14H13F9IO [M + H+]: 494.9862, found: 494.9857.

This substance has been described in former publications4, but due to one missing signal at 100.1 ppm in the 13C-NMR-spectrum and variations of multiplicities in the 1H- as well as 19F-NMR-spectra, the material was fully characterized.

1.2. 1-Bromo-4-((7,7,8,8,9,9,10,10,10-nonafluoro-5-iododecyl)oxy)benzene (16)

Following GP-A, 'Bu3P (14.9 mg, 0.0736 mmol, 10.1 mol%), B(C6F5)3 (37.4 mg, 0.0738 mmol, 10.1 mol%), (Hex-5-en-1-yl)-4-bromophenylether (67) (186 mg, 0.729 mmol, 1.00 equiv) as well as nonafluoro-1-iodobutane (251 mg, 0.726 mmol, 0.996 equiv) were weighed into an amber glass screw-cap vial and were reacted in CH2Cl2 (2.1 mL). After 24 h a sample was withdrawn for a control by NMR
spectroscopy outside the glovebox. Purification was conducted by chromatography on SiO$_2$ (n-hexane:EtOAc 99:1, twofold n-pentane:Et$_2$O 99:1) yielded pure product 16 (349 mg, 0.581 mmol, 80%).

$^1$H NMR (300 MHz, Chloroform-$_d$) $\delta$ 7.42 – 7.33 (m, 2H), 6.81 – 6.73 (m, 2H), 4.35 (tt, $J$ = 8.2, 5.3 Hz, 1H), 3.95 (t, $J$ = 6.0 Hz, 2H), 3.07 – 2.66 (m, 2H), 1.98 – 1.68 (m, 5H), 1.68 – 1.54 (m, 1H).

$^{19}$F NMR (282 MHz, Chloroform-$_d$) $\delta$ –81.0 (tt, $J$ = 9.6, 3.3 Hz), –111.2 – –113.0 (m), –113.6 – –116.1 (m), –124.3 – –124.8 (m), –125.7 – –126.1 (m).

Analytic data are consistent with literature-known values.$^4$

1.3. 5,5,6,6,7,7,8,8,9,9,10,10-Tridecafluoro-3-iododecyl acetate$^3$ (17)

Following GP-A, $^t$Bu$_3$P (16.7 mg, 0.0825 mmol, 10.5 mol%), B(C$_6$F$_5$)$_3$ (40.9 mg, 0.0799 mmol, 10.2 mol%), 3-butenyl acetate (64) (89.9 mg, 0.786 mmol, 1.00 equiv) and perfluorohexyl iodide (357 mg, 0.801 mmol, 1.02 equiv) were weighed out into an amber glass screw-top vial and then dissolved in CH$_2$Cl$_2$ (2.5 mL). The resulting solution was stirred at r.t. sealed with a Teflon-insert screw cap inside the glovebox. After 44 h and 6 d, respectively, samples for controls by NMR spectroscopy were taken inside the glovebox. The reaction solution was then transferred into a transparent screw-top vial. After 12 d, 21 d and 35 d, respectively, samples for controls by NMR spectroscopy were taken inside the glovebox. Most of the solvent was evaporated, and purification was conducted by chromatography on SiO$_2$ (cyclohexane:CH$_2$Cl$_2$ 65:35) yielded pure product 17 (333 mg, 0.595 mmol, 76%).

$^1$H NMR (600 MHz, Chloroform-$_d$) $\delta$ [ppm] 4.45 – 4.36 (m, 1H, $-CH_2CO_2^-$), 4.35 – 4.27 (m, 1H, $-CH_2I$), 4.21 – 4.10 (m, 1H, $-CH_2CO_2^-$), 3.03 – 2.90 (m, 1H, $R_3CH_2^-$), 2.90 – 2.76 (m, 1H, $R_3CH_2^-$), 2.22 – 2.14 (m, 1H, $-CH_2CH_2^-$), 2.14 – 2.07 (m, 1H, $-CH_2CH_2^-$), 2.08 – 2.02 (m, 3H, $-CH_3$).

$^{13}$C($^1$H) NMR (151 MHz, Chloroform-$_d$) $\delta$ [ppm] 170.8, 119.7-108.7 (m, CF$_2$, CF$_3$), 64.2, 42.0 ($t$, $^2J_{CF} = 20.8$ Hz, $-H_2CCF_3R_F$), 39.0, 20.9, 15.3.

$^{19}$F NMR (282 MHz, Chloroform-$_d$) $\delta$ [ppm] –80.8 (tt, $J$ = 10.1, 2.6 Hz, 3F), –110.9 – –115.1 (m, 2F), –121.6 – –122.0 (m, 2F), –122.7 – –123.1 (m, 2F), –123.5 – –123.9 (m, 2F), –126.0 – –126.4 (m, 2F).

IR (film on NaCl), [cm$^{-1}$] 2962, 1747, 1433, 1366, 1237, 1042, 845, 812, 733, 699, 657, 606, 553, 530.

$m/z$ calculated for C$_{12}$H$_{11}$F$_{13}$IO$_2$ [M + H$^+$] = 560.9591, found 560.9593.
1.4. 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl acetate\(^3\) (18)

\[\text{O} \quad + \quad \text{C}_4\text{F}_8\text{I} \quad \xrightarrow{\text{tBuP} (9.66 \text{ mol\%}), \text{B(C}_6\text{F}_5)_3 (9.82 \text{ mol\%})} \quad \text{O} \quad \text{C}_4\text{F}_9\text{I} \]

Following GP-A, tBuP (16.4 mg, 0.0811 mmol, 9.66 mol%), B(C\(_6\)F\(_5\))\(_3\) (42.2 mg, 0.0824 mmol, 9.82 mol%), nonafluoro-1-iodobutane (282 mg, 0.815 mmol, 0.972 equiv) and allyl acetate (65) (84.0 mg, 0.839 mmol, 1.00 equiv) were weighed out into an amber glass screw-top vial and then dissolved in CH\(_2\)Cl\(_2\) (2.5 mL). After 3, 7, 18 and 25 d, respectively, samples for a control by NMR spectroscopy were taken inside the glovebox. After 35 d, most of the solvent was evaporated, and purification was conducted by chromatography on SiO\(_2\) (n-pentane:CH\(_2\)Cl\(_2\) 80:20) yielded pure product 18 (92.2 mg, 0.207 mmol, 25%).

\(^1\)H NMR (300 MHz, Chloroform-\(d\)) \(\delta [\text{ppm}] 3.98 – 3.79 (\text{m}, 3\text{H}, \text{–CHI} \quad \text{+ R}_4\text{CF}_2\text{H})\), 2.57 – 2.22 (\text{m}, 2\text{H}, \text{–CH}_2\text{CO}_2\text{H}), 1.56 (\text{s}, 3\text{H}, \text{–CH}_3).

\(^{13}\)C\(^{1\text{H}}\) NMR (75.5 MHz, C\(_6\)D\(_6\)) \(\delta [\text{ppm}] 169.1, 121.2-110.5 (\text{m}, \text{CF}_2, \text{CF}_3), 68.4, 37.9 (\text{t}, J_{\text{CF}} = 21.2 \text{ Hz}, \text{–H}_2\text{CCF}_2\text{R}_4\text{F}), 20.0, 12.0.

\(^{19}\)F MR (282 MHz, Chloroform-\(d\)) \(\delta [\text{ppm}] -81.0 – -81.3 (\text{m}, 3\text{F}), -112.4 – -114.8 (\text{m}, 2\text{F}), -124.2 – -124.5 (\text{m}, 2\text{F}), -125.7 – -126.1 (\text{m}, 2\text{F}).

IR (film on NaCl), [\text{cm}^{-1}] 2958, 1750, 1432, 1382, 1356, 1233, 1135, 1043, 1026, 881, 739, 725.

m/z calculated for C\(_9\)H\(_8\)F\(_9\)I\(\text{NaO}_2\) [\(\text{M} + \text{Na}^+\)] = 468.9318, found 468.9316.

1.5. 6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodononyl 4-chlorobenzoate\(^3\) (19)

1.5.1. Reaction with B(C\(_4\)F\(_3\))\(_3\)

\[\text{O} \quad + \quad \text{C}_4\text{F}_8\text{I} \quad \xrightarrow{\text{tBuP} (9.83 \text{ mol\%}), \text{B(C}_6\text{F}_5)_3 (9.92 \text{ mol\%})} \quad \text{O} \quad \text{C}_4\text{F}_9\text{I} \]

Following GP-A, tBuP (14.6 mg, 0.0722 mmol, 9.83 mol%), B(C\(_6\)F\(_5\))\(_3\) (37.3 mg, 0.0729 mmol, 9.92 mol%) were weighed into a glass vial and then dissolved in CH\(_2\)Cl\(_2\) (1.7 mL). Pent-4-en-1-yl 4-chlorobenzoate (66) (165 mg, 0.734 mmol, 1.00 equiv) as well as nonafluoro-1-iodobutane (256 mg, 0.740 mmol, 1.01 equiv) were weighed into an amber glass screw-cap vial and were then dissolved in CH\(_2\)Cl\(_2\) (0.40 mL). The catalyst solution was transferred to the alkene. The resulting solution was sealed with a Teflon insert screw cap and stirred at r.t. After 24 h the reaction was quenched by the addition of desalinated water (10 \(\mu\)L) and a sample was withdrawn for a control by NMR spectroscopy.
Purification was conducted by chromatography on SiO\textsubscript{2} (n-pentane:Et\textsubscript{2}O 98:2) yielded pure product 19 (364 mg, 0.638 mmol, 87%).

\textsuperscript{1}H NMR (300 MHz, Chloroform-\textit{d}) \( \delta \) [ppm] 8.00 – 7.93 (m, 2H), 7.47 – 7.38 (m, 2H), 4.46 – 4.32 (m, 3H), 3.09 – 2.69 (m, 2H), 2.14 – 1.84 (m, 4H).

\textsuperscript{19}F NMR (282 MHz, Chloroform-\textit{d}) \( \delta \) –81.1 (tt, \( J = 9.7, 3.3 \) Hz), –111.1 – –112.4 (m), –114.4 – –115.5 (m), –124.4 – –124.8 (m), –125.7 – –126.2 (m).

Analytic data are consistent with literature-known values.\textsuperscript{4}

### 1.5.2. Reaction with B(2,3,6-Cl\textsubscript{3}C\textsubscript{6}H\textsubscript{2})(2,3,6-F\textsubscript{3}C\textsubscript{6}H\textsubscript{2})\textsubscript{3} 22

Following GP-A, \textsuperscript{1}Bu\textsubscript{3}P (10.0 mg, 0.0494 mmol, 10.0 mol\%), B(2,3,6-Cl\textsubscript{3}C\textsubscript{6}H\textsubscript{2})(2,3,6-F\textsubscript{3}C\textsubscript{6}H\textsubscript{2}) \textsubscript{3} 22 (23.8 mg, 0.0525 mmol, 10.6 mol\%) as well as nonafluoro-1-iodobutane (171 mg, 0.494 mmol, 1.00 equiv) were weighed into an amber glass screw-cap vial and were reacted in CH\textsubscript{2}Cl\textsubscript{2} (1.4 mL). After 27 h and 12 d a sample was withdrawn for a control by NMR spectroscopy. Purification was conducted by chromatography on SiO\textsubscript{2} (n-pentane:Et\textsubscript{2}O 98.3:1.7) yielded the pure product 19 (37.8 mg, 0.0662 mmol, 13%) as well as educt 66 (67.2 mg, 0.299 mmol, 61%).

### 1.6. 2-(7,7,8,8,9,9,10,10,10-Nonafluoro-5-iododecyl)isoindoline-1,3-dione\textsuperscript{3} 20

Following GP-A, \textsuperscript{1}Bu\textsubscript{3}P (8.3 mg, 0.041 mg, 10 mol\%), B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (20.7 mg, 0.040 mmol, 9.89 mol\%), 2-(hex-5-en-1-yl)isoindoline-1,3-dione (68) (93.5 mg, 0.408 mmol, 1.00 equiv) as well as nonafluoro-1-iodobutane (70.0 \( \mu \)L, 0.407 mmol, 0.997 equiv) were weighed into an amber glass screw-cap vial and were reacted in CH\textsubscript{2}Cl\textsubscript{2} (2.1 mL). After 24 h a sample was withdrawn for a control by NMR spectroscopy outside the glovebox. Purification was conducted by chromatography on SiO\textsubscript{2} (n-hexane:EtOAc 93:7) yielded pure product 20 (135 mg, 0.235 mmol, 58%).

\textsuperscript{1}H NMR (300 MHz, Chloroform-\textit{d}) \( \delta \) 7.90 – 7.77 (m, 2H), 7.77 – 7.67 (m, 2H), 4.30 (tt, \( J = 8.1, 5.3 \) Hz, 1H), 3.71 (t, \( J = 7.1 \) Hz, 2H), 3.06 – 2.64 (m, 2H), 1.93 – 1.57 (m, 5H), 1.53 – 1.40 (m, 1H).
\[ ^{19}\text{F NMR} \ (282 \text{ MHz, Chloroform-}d) \ \delta -81.01 \ (tt, \ J = 9.7, 3.3 \text{ Hz}), -111.01 - -112.75 \text{ (m), } -114.04 - -115.89 \text{ (m), } -124.23 - -124.79 \text{ (m), } -125.40 - -126.64 \text{ (m).} \]

Analytic data are consistent with literature-known values.\(^4\)

### 1.7. 1,1,1,2,2,3,3,4,4,4-Decafluoro-6-iodododec-5-ene\(^3\) (35)

\[
\text{52} \quad + \quad \text{C}_4\text{F}_8 \quad \xrightarrow{\text{tBu}_3\text{P} (10.5 \text{ mol}%), \text{B}(2,6-\text{F}_2\text{C}_6\text{H}_3)_3 (10.0 \text{ mol}%) \ 21} \quad \text{CH}_2\text{Cl}_2, \text{ r.t., } 32 \text{ d} \quad \text{55}
\]

Following GP-A, tBu3P (16.8 mg, 0.0830 mmol, 10.5 mol%), B(2,6-F2C6H3)3 21 (27.7 mg, 0.0791 mmol, 10.0 mol%), 1-octyne (52) (86.9 mg, 0.789 mmol, 1.00 equiv) and nonafluoro-1-iodobutane (300 mg, 0.867 mmol, 1.10 equiv) were weighed out into an amber glass screw-top vial and then dissolved in CH2Cl2 (2.5 mL). It was stirred at r.t. sealed with a Teflon-insert screw cap inside the glovebox. After 1, 4, and 6 d, respectively, samples for a control by NMR spectroscopy were withdrawn inside the glovebox, which were filled up with CDCl3 outside the glovebox. After 12 d another NMR-control was conducted, but the sample was directly filled up with C6D6 inside the glovebox. Afterwards, the reaction solution was filled into a transparent vial, and the slightly yellowish solution stirred for another 8 d before a control by NMR spectroscopy was conducted. After overall 32 d the last sample was withdrawn. Purification was conducted by chromatography on SiO₂ (n-pentane) yielded the pure product 35 as E-isomer (110 mg, 0.236 mmol, 30%) and as E/Z-mixture (48.9 mg, 0.107 mmol, 14%, E:Z = 1.0:0.42)

\[ ^1\text{H NMR} \ (300 \text{ MHz, Chloroform-}d) \ \delta 6.32 \ (t, \ J = 14.5 \text{ Hz, 1H}), 2.63 \ (t, \ J = 7.4 \text{ Hz, 3H}), 1.57 \ (ddt, \ J = 11.7, 9.3, 4.8 \text{ Hz, 2H}), 1.40 - 1.24 \ (m, \ J = 4.6 \text{ Hz, 6H}), 0.95 - 0.85 \ (m, 3H). \]

\[ ^{19}\text{F NMR} \ (282 \text{ MHz, Chloroform-}d) \ \delta -80.9 - -81.5 \text{ (m, 3F), } -105.4 - -106.0 \text{ (m, 2F), } -124.1 - -124.5 \text{ (m, 2F), } -125.7 - -126.1 \text{ (m, 2F).} \]

Analytic data are consistent with literature-known values.\(^5\)

### 1.8. (3,3,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)benzene (23)

#### 1.8.1. Reaction with B(C₆F₅)s₃\(^3\)

\[
\text{69} \quad + \quad \text{C}_6\text{F}_{13} \quad \xrightarrow{\text{tBu}_3\text{P} (10 \text{ mol}%), \text{B}(\text{C}_6\text{F}_5)_3 (10.1 \text{ mol}%) \ 21} \quad \text{CH}_2\text{Cl}_2, \text{ r.t., } 23 \text{ d} \quad \text{70}
\]

Following GP-A, tBu3P (16 mg, 0.079 mmol, 10 mol%), B(C₆F₅)₃ (40.4 mg, 0.0789 mmol, 10.1 mol%), phenylacetylene (69) (82.0 mg, 0.783 mmol, 1.00 equiv) as well as 1-iodoperfluorohexane (0.366 g, 0.821 mmol, 1.05 equiv) were weighed into an amber glass screw-top vial, dissolved in CH2Cl2 (2 mL)
and sealed with a Teflon-insert screw cap. The brownish solution was stirred at r.t. for 23 d. Purification was conducted by chromatography on SiO$_2$ (n-pentane:CH$_2$Cl$_2$ = 98:2) yielded pure product 70 as a colourless liquid (48.5 mg, 0.0885 mmol, 10%)

$^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.40 – 7.27 (m, 5H, Aryl-H), 6.60 (t, $J = 13.4$ Hz, 1H, CICH).

$^{19}$F NMR (282 MHz, Chloroform-d) $\delta$ [ppm] $-80.7$ – $-81.0$ (m, 3F), $-105.1$ – $-105.4$ (m, 2F), $-121.5$ – $-122.0$ (m, 2F), $-122.7$ – $-123.1$ (m, 4F), $-126.0$ – $-126.4$ (m, 2F).

Analytic data are consistent with literature-known values.$^6$

1.8.2. Reaction with B(2,6-F$_2$C$_6$H$_3$)$_3$ (21)$^3$

\[
\begin{align*}
\text{Ar} & \quad + \quad \text{C}_6\text{F}_{13}\text{I} \\
\text{69} & \quad \xrightarrow{^3\text{Bu}_3\text{P} (9.3 \text{ mol\%})} \\
\text{CH}_2\text{Cl}_2, \text{r.t.}, 17 \text{ d} & \quad \rightarrow \quad \text{70}
\end{align*}
\]

Following GP-A, $^3$Bu$_3$P (16 mg, 0.079 mmol, 9.3 mol%), B(2,6-F$_2$C$_6$H$_3$)$_3$ (27 mg, 0.078 mmol, 9.2 mol%), phenylacetylene (69) (86.5 mg, 0.847 mmol, 1.00 equiv) and C$_6$F$_{13}$I (0.393 g, 0.881 mmol, 1.04 equiv) were reacted. The solution turned yellowish. After 17 d purification was conducted by chromatography on SiO$_2$ (cyclohexane) yielded product 70 (92.6 mg, 0.169 mmol, 20%) and several side-products.

$^1$H NMR (300 MHz, Chloroform-d) $\delta$ 7.40 – 7.27 (m, 5H, Aryl-H), 6.60 (t, $J = 13.4$ Hz, 1H, CICH).

$^{19}$F NMR (282 MHz, Chloroform-d) $\delta$ $-80.7$ – $-81.0$ (m, 3F), $-105.1$ – $-105.4$ (m, 2F), $-121.5$ – $-122.0$ (m, 2F), $-122.7$ – $-123.1$ (m, 4F), $-126.0$ – $-126.4$ (m, 2F).

Analytic data are consistent with literature-known values.$^6$

2. Photomediated Iodoperfluoroalkylations

2.1. 1,1,1-Trifluoro-3-iodonon-2-ene (34)

\[
\begin{align*}
\text{52} & \quad + \quad \text{F}_3\text{C} \text{I} \\
\text{CH}_2\text{Cl}_2, 30 \text{ ^\circ C}, 3 \text{ h} & \quad \xrightarrow{^3\text{Bu}_3\text{P} (10.7 \text{ mol\%})} \\
461 \text{ nm} & \quad \rightarrow \quad \text{34}
\end{align*}
\]

Inside the glovebox $^3$Bu$_3$P (10.7 mg, 0.0529 mmol, 10.0 mol%) and 1-octyne (52) (58.0 mg, 0.527 mmol) were weight into an aluminum foil wrapped two-necked round-bottom flask with stopcock and dissolved with CH$_2$Cl$_2$ (2 mL). A stirring bar was added, and the flask was sealed with a septum. Outside the glovebox a balloon with CF$_3$I was connected to the reaction flask and under red light, the aluminum foil was removed inside the photoreactor. The reaction was stirred vigorously under irradiation for 3 h. Purification of the yellow reaction solution by column chromatography on SiO$_2$ (pentane) yielded pure product 34 as a mixture of isomers (79.5 mg, 0.258 mmol, 50%, $E/Z = 81:19$).
Analytic data are consistent with literature-known values.\textsuperscript{5b}

2.2. \textit{1,1,2,2,3,3,4,4-Nonafluoro-6-iododec-5-ene} (35)

Following GP-B, \textsuperscript{5}Bu\textsubscript{3}P (10.6 mg, 0.0524 mmol, 9.32 mol%), 1-octyne (52) (61.9 mg, 0.562 mmol) and nonafluoro-1-iodobutane (100 \textmu L, 0.583 mmol, 1.04 equiv) were irradiated in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) for 1 h. Purification was conducted by chromatography on SiO\textsubscript{2} (pentane) yielded pure product 35 as colourless liquid (243 mg, 0.533 mmol, 95 \%, \textit{E/Z} = 89:11).

\textbf{1H NMR} (300 MHz, Chloroform-\textit{d}) \(\delta [\text{ppm}] 6.24 (t, J = 13.1 \text{ Hz}, 1H, CI\text{CH}, \text{E-isomer}), 2.67 (t, J = 7.2 \text{ Hz}, 2H, Z-isomer, CH\text{H}\text{CICH}), 2.63 (t, J = 7.5 \text{ Hz}, 2H, E-isomer, CH\text{H}\text{CICH}), 1.61 – 1.55 (m, 2H, CH\text{H}\text{CICH}), 1.36 – 1.27 (m, 6H, CH\text{H}((CH\text{H})\text{CICH}), 0.90 (t, J = 6.9, 3H, CH\text{H})).

\textbf{19F NMR} (565 MHz, Chloroform-\textit{d}) \(\delta [\text{ppm}] -105.67 (2F, CF\text{H}, \text{Z-isomer}), -108.65 – -108.76 (m, 2F, CF\text{H}, E-isomer), -123.85 – -123.99 (m, 2F, CF\text{H}, Z-isomer), -124.11 – -124.31 (m, 2F, CF\text{H}, E-isomer), -125.71 – -125.92 (m, 2F, CF\text{H}).

Analytic data are consistent with literature-known values.\textsuperscript{5a}

\textbf{Large scale reaction with 1-octyne (52) and nonafluoro-1-iodobutane}

Inside the glovebox \textsuperscript{5}Bu\textsubscript{3}P (403 mg, 1.99 mmol, 10.0 mol%) was weight into a two-necked round-bottom flask with stopcock, a stirring bar was added and sealed with a septum. Outside the glovebox CH\textsubscript{2}Cl\textsubscript{2} (24 mL), 1-octyne (52) (2.93 ml, 19.9 mmol) and nonafluoro-1-iodobutane (3.75 ml, 21.9 mmol, 1.10 equiv) under red light. The reaction was stirred under irradiation for 2 h. Purification of the yellow reaction solution by column chromatography on SiO\textsubscript{2} (pentane) yielded pure product 35 as a colourless oil yield (8.48 g, 18.6 mmol, 93 \%, \textit{E/Z} = 89:11).

Analytic data are consistent with literature-known values.\textsuperscript{5a}
2.3. \(1,1,1,2,3,3,4,4,5,5,6,6\)-Tridecafluoro-8-iodotetradec-7-ene (36)

Following GP-B, \(^1\text{BuP}\) (10.8 mg, 0.0534 mmol, 9.50 mol%), 1-octyne (52) (61.9 mg, 0.562 mmol) and perfluoro-1-iodohexane (126 µL, 0.583 mmol, 1.04 equiv) were irradiated in \(\text{CH}_2\text{Cl}_2\) (2 mL) for 1 h. Purification was conducted by chromatography on SiO\(_2\) (pentane) yielded pure product 36 as colourless liquid (262 mg, 0.471 mmol, 84\%, \(E/Z = 85:15\)).

\(^1\text{H} \text{NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) [ppm] 6.32 (t, \(J = 14.4\) Hz, 1H, CICH, \(E\)-isomer), 6.24 (t, \(J = 13.2\) Hz, 1H, CICH, Z-isomer), 2.69 – 2.65 (m, 2H, \(\text{CH}_2\text{CICH}\), \(Z\)-isomer), 2.65 – 2.60 (m, 2H, \(\text{CH}_2\text{CICH}\), \(E\)-isomer), 1.62 – 1.55 (m, 2H, \(\text{CH}_2\text{CICH}\)), 1.35 – 1.26 (m, 6H, \(\text{CH}_3\text{(CH}_2\text{)}_2\text{CICH}\)), 0.93 – 0.87 (m, 3H, \(\text{CH}_3\)).

\(^{19}\text{F} \text{NMR}\) (565 MHz, Chloroform-\(d\)) \(\delta\) [ppm] -80.75 – -80.89 (m, 3F, CF\(_3\)), -105.40 (t, \(J = 13.3\) Hz, 2F, CF\(_2\), \(E\)-isomer), -108.46 (t, \(J = 13.2\) Hz, 2F, CF\(_2\), \(Z\)-isomer), -121.50 – -121.83 (m, 2F, CF\(_2\)), -122.70 – -122.92 (m, 2F, CF\(_2\)), -123.21 – -123.38 (m, 2F, CF\(_2\), \(Z\)-isomer), -125.99 – -126.25 (m, 2F, CF\(_2\)).

Analytic data are consistent with literature-known values.\(^8\)

2.4. \(9,9,10,11,11,12,13,13,14,14,15,15,16,16\)-Heptadecafluoro-7-iodohexadec-7-ene (37)

Inside the glovebox \(^1\text{BuP}\) (10.9 mg, 0.0539 mmol, 10.1 mol%), 1-octyne (52) (58.9 mg, 0.535 mmol) were weighed into a reaction vial and \(\text{CH}_2\text{Cl}_2\) (2 mL) was added. Outside the glovebox under a stream of nitrogen and best possible light exclusion perfluorooctyl iodide (154 µL, 0.583 mmol, 1.09 equiv) was added. The reaction solution was irradiated for 4 h. Purification was conducted by chromatography on SiO\(_2\) (pentane) yielded pure product 37 (343 mg, 0.524 mmol, 98\%, \(E/Z = 85:15\))

\(^1\text{H} \text{NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) [ppm] 6.32 (t, \(J = 14.4\) Hz, 1H, CICH, \(E\)-isomer), 6.23 (t, \(J = 13.1\) Hz, 1H, CICH, \(Z\)-isomer), 2.68 (t, \(J = 6.9\) Hz, 2H, \(\text{CH}_2\text{CICH}\), \(Z\)-isomer), 2.63 (t, \(J = 7.7\) Hz, 2H, \(\text{CH}_2\text{CICH}\), \(E\)-isomer), 1.60 – 1.55 (m, 2H, \(\text{CH}_2\text{CH}_2\text{CICH}\)), 1.33 – 1.27 (m, 6H, \(\text{CH}_3\text{(CH}_2\text{)}_2\text{CICH}\)), 0.90 (t, \(J = 7.2\) Hz, 3H, \(\text{CH}_3\)).

\(^{19}\text{F} \text{NMR}\) (565 MHz, Chloroform-\(d\)) \(\delta\) [ppm] -80.80 (t, \(J = 9.9\) Hz, 3F, CF\(_3\)), -105.40 (t, \(J = 13.4\) Hz, 2F, CF\(_2\), \(E\)-isomer), -108.46 (t, \(J = 13.3\) Hz, 2F, CF\(_2\), \(Z\)-isomer), -121.33 – -121.58 (m, 2F, CF\(_2\)), -121.75
-122.07 (m, 5F, CF₂), -122.60 -122.83 (m, 3F, CF₂), -122.87 -123.02 (m, 2F, CF₂, Z-isomer), -123.17 -123.35 (m, 2F, CF₂), -125.99 -126.29 (m, 2F, CF₂).

Analytic data are consistent with literature-known values.⁵

2.5. (3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)benzene (38)

Following GP-B, ‘Bu₃P (10.5 mg, 0.0519 mmol, 9.30 mol%), phenylacetylene (69) (57.0 mg, 0.558 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.04 equiv) were irradiated in CH₂Cl₂ (2 mL) for 2 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded pure product 38 as mixture of isomers (202 mg, 0.450 mmol, 81%, E/Z = 95:5)

¹H NMR (600 MHz, Chloroform-d) δ [ppm] 7.38 – 7.35 (m, 5H, -Aryl, Z-isomer), 7.35 – 7.27 (m, 5H, -Aryl, E-isomer), 6.59 (t, J = 13.3 Hz, 1H, CICH, E-isomer), 6.54 – 6.46 (m, 1H, CICH, Z-isomer).

¹⁹F NMR (565 MHz, Chloroform-d) δ [ppm] -80.89 – -80.99 (m, 3F, CF₃, Z-isomer), -81.05 (t, J = 9.6 Hz, 3F, CF₃, E-isomer), -105.44 (t, J = 12.6 Hz, 2F, CF₂, E-isomer), -109.08 – -109.26 (m, 2F, CF₂, Z-isomer), -123.60 – -123.97 (m, 2F, CF₂), -125.56 – -125.76 (m, 2F, CF₂, Z-isomer), -125.76 – -125.99 (m, 2F, CF₂, E-isomer).

Analytic data are consistent with literature-known values.⁷

2.6. 1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (39)

Inside the glovebox ‘Bu₃P (10.9 mg, 0.0539 mmol, 10.2 mol%) was weighed into a reaction vial, dissolved in CH₂Cl₂ (2 mL) and a stirring bar was addd. Outside the glovebox under a stream of nitrogen and best possible light exclusion 1-ethynyl-4-methylbenzene (71) (67 µL, 0.530 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.10 equiv) were added. The reaction vial was sealed with a septa screw cap and irradiated for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded a light yellow oil as pure product 39 in a mixture of diastereomers (201.6 mg, 0.436 mmol, 82%, E/Z = 95:5).

¹H NMR (300 MHz, Chloroform-d) δ [ppm] 7.38 (m, 2H, Aryl, Z-isomer), 7.21 (d, J = 8.27 Hz, 2H, Aryl, E-isomer), 7.14 (d, J = 8.18 Hz, 2H, Aryl, E-isomer), 7.03 (m, 2H, Aryl, Z), 6.57 (t, J = 13.41 Hz,
1H, -CH-RF, E-isomer), 6.47 (t, \( J = 1.18 \) Hz, 1H, -CH-RF, E-isomer), 2.39 (s, 3H, Aryl-CH3, Z-isomer), 2.36 (s, 3H, Aryl-CH3, E-isomer).

\(^{19}\text{F NMR}\) (282 MHz, Chloroform-\( d\)) \( \delta \) [ppm] -80.88 – -80.97 (m, 3F, CF3, Z-isomer), -80.98 – -81.12 (m, 3F, CF3, E-isomer), -105.20 – -105.43 (m, 2F, CF2, E-isomer), -108.83 – -109.02 (m, 2F, CF2, Z-isomer), -123.76 – -123.93 (m, 2F, CF2, E-isomer), -125.64 – -125.75 (m, 2F, CF2, Z-isomer), -125.76 – -125.95 (m, 2F, CF2, E-isomer).

Compound is named differently in literature, but analytic data are consistent with literature-known values.\(^b\)

2.7. 1-Methoxy-4-(3,3,4,4,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (40)

Inside the glovebox \(^t\)BuP (10.9 mg, 0.0539 mmol, 10.2 mol\%) was weighed into a reaction vial and dissolved in CH2Cl2 (2 mL). Outside the glovebox under a stream of nitrogen and best possible light exclusion 4-methoxyphenylacetylene (72) (69 \( \mu L \), 0.530 mmol) and nonafluoro-1-iodobutane (100 \( \mu L \), 0.583 mmol, 1.10 equiv) were added. The reaction vial was sealed with a septa screw cap and irradiated for 3 h. Purification was conducted by chromatography on SiO2 (pentane:Et2O = 98:2) yielded a yellow liquid as pure product 40 in a mixture of diastereomers (220 mg, 0.460 mmol, 84%, \( E/Z \) = 92:8).

\(^1\text{H NMR}\) (300 MHz, Chloroform-\( d\)) \( \delta \) [ppm] 7.46 (m, 2H, Aryl, Z-isomer), 7.27 (m, 2H, Aryl, E-isomer), 6.89 (m, 2H, Aryl, Z-isomer), 6.85 (m, 2H, Aryl, E-isomer), 6.56 (t, \( J = 13.9 \) Hz, 1H, -CH-RF, E-isomer), 6.43 (t, \( J = 13.4 \) Hz, 1H, -CH-RF, Z-isomer), 3.85 (s, 3H, OCH3, Z-isomer), 3.83 (s, 3H, OCH3, E-isomer).

\(^{13}\text{C}\( ^{1}\text{H} \) NMR\) (75.5 MHz, Chloroform-\( d\)) \( \delta \) [ppm] 160.4, 133.8, 135.7 (m, CF2, CF3), 128.95 (t, \( J = 2.61 \) Hz), 123.2-115.5 (m, CF2, CF3), 126.4 (t, \( J = 21.8 \) Hz), 113.9, 113.7 (t, \( J = 5.96 \) Hz), 113.5, 55.4

\(^{19}\text{F NMR}\) (282 MHz, Chloroform-\( d\)) \( \delta \) [ppm] -80.94 (tt, \( J = 9.9 \), 3.1 Hz, 3F, CF3, Z-isomer), -81.04 (tt, \( J = 9.6 \), 3.2 Hz, 3F, CF3, E-isomer), -105.00 – -105.18 (m, 2F, E-isomer), -108.52 – -108.69 (m, 2F, Z-isomer), -123.67 – -123.77 (m, 2F, E-isomer), -123.76 – -123.96 (m, 2F, Z-isomer), -125.63 – -125.76 (m, 2F, Z-isomer), -125.77 – -125.96 (m, 2F, E-isomer).

\( \text{IR} \) (film on NaCl), \( \nu \) [cm\(^{-1}\)] 3064, 3007, 2960, 2938, 2910, 2841, 2548, 2318, 2241, 2055, 1977, 1891, 1634, 1604, 1575, 1508, 1466, 1442, 1415, 1352, 1294, 1237, 1134, 1110, 1054, 1033, 929, 905, 890, 872, 855, 832, 749, 722, 664, 631, 590, 569, 553, 530
**Elemental analysis** for C₁₃H₃₇I₀ calculated: C: 32.66 %, H: 1.69 %
measured: C: 32.61 %, H: 1.73 %

2.8. 1-(tert-Butyl)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (41)

Inside the glovebox 'Bu₃P (10.7 mg, 0.0559 mmol, 9.94 mol%) was weighed into the reaction glass vial, dissolved in CH₂Cl₂ (2 mL) and a stirring bar was added. Outside the glovebox under a stream of nitrogen and best possible light exclusion 4-tert-butylphenylacetylene (73) (96 µL, 0.532 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.10 equiv) were added. The reaction vial was sealed with the septa screw cap and irradiated for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded a light yellow oil as pure product 41 in a mixture of diastereomers (192.7 mg, 0.366 mmol, 69%, E/Z = 95:5).

**¹H NMR** (300 MHz, Chloroform-d) δ [ppm] 7.36 – 7.32 (m, 2H, Aryl- E), 7.31 – 7.24 (m, 2H, Aryl- Z), 7.23 – 7.14 (m, 2H, Aryl- Z), 6.51 (t, J = 13.8 Hz, 1H, CHI, E-isomer), 6.43 (t, J = 13.4 Hz, 1H, CHI, Z-isomer), 1.27 (s, 9H, Z-isomer), 1.26 (s, 9H, E-isomer).

**¹³C[¹H] NMR** (75.5 MHz, Chloroform-d) δ [ppm] 153.9, 152.8, 138.4, 128.2, 127.0 (t, J = 2.63 Hz), 126.5 (t, J = 22.08 Hz), 125.1, 113.8 (t, J = 2.63 Hz), 34.93, 31.31

**¹⁹F NMR** (282 MHz, Chloroform-d) δ [ppm] -80.92 – -81.00 (m, 3F, CF₃, Z-Isomer), -81.06 (tt, J = 9.3, 2.7 Hz, 3F, CF₃, E-Isomer), -105.06 – -105.40 (m, 2F, CF₂, E-Isomer), -108.80 – -109.14 (m, 2F, CF₂, Z-Isomer), -123.65 – -124.08 (m, 2F, CF₂), -125.65 – -126.06 (m, 2F, CF₂).

**IR** (film on NaCl), v [cm⁻¹] 3087, 3035, 2966, 2908, 2872, 2326, 1910, 1790, 1636, 1604, 1506, 1465, 1405, 1352, 1296, 1234, 1134, 1109, 1055, 1026, 930, 892, 874, 842, 750, 737, 694, 674, 591, 526.

**Elemental analysis** for C₆₆H₄₅F₂I calculated: C: 38.12 %, H: 2.80 %
measured: C: 38.19 %, H: 2.81 %

2.9. 1-Bromo-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (42)

Following GP-B, 'Bu₃P (10.9 mg, 0.0559 mmol, 10.2 mol%), 1-bromo-4-ethenylbenzene (74) (95.6 mg, 0.528 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.10 equiv) were irradiated in CH₂Cl₂.
(2 mL) for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded a light yellow oil as pure product 42 in a mixture of diastereomers (173.4 mg, 0.3296 mmol, 62%, E/Z = 94:6).

³H NMR (300 MHz, Chloroform-d) δ [ppm] 7.53 (m, 2H, Aryl, Z-isomer), 7.48 (m, 2H, Aryl, E-isomer), 7.35 (m, 2H, Aryl, Z-isomer), 7.17 (m, 2H, Aryl, E-isomer), 6.61 (t, J = 13.4 Hz, 1H, -CH-Rₛ, E-isomer), 6.50 (d, J = 12.8 Hz, 1H, -CH-Rₛ, Z-isomer).

¹³C{³H} NMR (75.5 MHz, Chloroform-d) δ [ppm] 140.3, 131.5, 128.6 (t, J = 2.55 Hz), 127.2 (t, J = 22.21 Hz), 123.8, 119.74 – 113.37 (m, CF₂, CF₃), 111.1 (t, J = 6.34 Hz)

¹⁹F NMR (282 MHz, Chloroform-d) δ [ppm] -80.98 – -81.16 (m), -105.47 (t, J = 11.2 Hz), -109.40 (t, J = 12.2 Hz), -123.68 – -123.92 (m), -125.65 – -125.77 (m), -125.75 – -125.97 (m).


Elemental analysis for C₁₂H₃BrF₃I  measured: C: 27.60 %, H: 0.85 %

2.10.  (E)-(3,3,4,5,6,6,6-Nonafluoro-1-iodo-2-methylhex-1-en-1-yl)benzene (43)

Following GP-B, ⁵Bu₃P (10.6 mg, 0.0524 mmol, 9.24 mol%), 1-Propyn-1-ylbenzene (75) (65.9 mg, 0.567 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.03 equiv) were irradiated in CH₂Cl₂ (2 mL) for 2 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded colourless crystals 43 (218.8 mg, 0.473 mmol, 83%).

³H NMR (600 MHz, Chloroform-d) δ [ppm] 7.33 – 7.18 (m, 5H, Aryl-), 2.30 (s, 3H, -CH₃).

¹³C{³H} NMR (75.5 MHz, Chloroform-d) δ [ppm] 144.3, 130.1 (t, J = 20.80 Hz), 128.3, 127.8, 126.9, 119.4-110.5 (m, CF₂, CF₃), 115.0 (t, J = 4.50 Hz), 26.77.

¹⁹F NMR (565 MHz, Chloroform-d) δ [ppm] -81.01 (t, J = 9.3 Hz, 3F, CH₃), -103.30 – -103.49 (m, 2F, CF₂), -120.39 – -120.60 (m, 2F, CF₂), -126.11 – -126.35 (m, 2F, CF₂).


m.p.: 72.4 – 76.9 °C
Elemental analysis for C₁₃H₃F₉I  
  calculated: C: 33.79 %, H: 1.75 %
  measured: C: 33.95 %, H: 1.68 %

2.11. (5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodooct-3-en-1-yl)benzene (44)

Inside the glovebox 'Bu₃P (10.7 mg, 0.0529 mmol, 9.53 mol%) was weighed into the reaction glass vial, dissolved in CH₂Cl₂ (2 mL) and a stirring bar was added. Outside the glovebox under a stream of nitrogen and best possible light exclusion 4-phenyl-1-butene (76) (78 µL, 0.5354 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.05 equiv) were added. The reaction vial was sealed with a septa screw cap and irradiated for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded a colourless liquid as pure product 44 in mixture of diastereomers (169.1 mg, 0.355 mmol, 64%, E/Z = 70:30)

¹H NMR (300 MHz, Chloroform-d) δ [ppm] 7.35 (m, 2H, Aryl, E-isomer), 7.26 (m, 3H, Aryl, E-isomer), 6.39 (t, J = 14.4 Hz, 1H, -CH-R₈), 2.95 (m, 4H, Aryl-CH₂-CH₂-, E-isomer).

¹³C[¹H] NMR (75.5 MHz, Chloroform-d) δ [ppm] 139.5, 128.75, 128.65, 127.1 (t, J = 23.9 Hz), 126.7, 121.1 (t, J = 6.30 Hz), 119.83 – 113.8 (m, CF₃, CF₃), 43.63 (t, J = 3.01), 36.4.

¹⁹F NMR (282 MHz, Chloroform-d) δ [ppm] -81.04 (m, 3F, CF₃), -105.91 – -106.17 (m, 2F), -124.03 – -124.38 (m, 2F), -125.63 – -125.97 (m, 2F).

IR (film on NaCl), ν [cm⁻¹] 3088, 3067, 3029, 2933, 2866, 1617, 1496, 1456, 1426, 1353, 1315, 1237, 1137, 1103, 1063, 1032, 947, 935, 918, 878, 841, 824, 811, 736, 698, 643, 557, 529.

Elemental analysis for C₁₄H₁₀F₉I  
  calculated: C: 35.32 %, H: 2.12 %
  measured: C: 35.21 %, H: 2.07 %

2.12. (E)-6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-5-propynon-4-ene (45)

Following GP-B, 'Bu₃P (10.5 mg, 0.0519 mmol, 9.96 mol%), 4-octyne (77) (57.4 mg, 0.521 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.12 equiv) were irradiated in CH₂Cl₂ (2 mL) for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded pure product 45 (125.2 mg, 0.0274 mmol, 52%).
**1H NMR** (300 MHz, Chloroform-d) δ [ppm] 2.69 (t, J = 7.6 Hz, 2H, CI\(_2\)RfH₂), 2.46 – 2.23 (m, 2H, H₂CI\(_2\)Rf), 1.79 – 1.46 (m, 4H, (CH\(_3\)(CH₂))₂), 0.95 (dt, J = 12.7, 7.3 Hz, 6H, (CH\(_3\)₂CH₂)₂).

**19F NMR** (565 MHz, Chloroform-d) δ [ppm] -80.97 (t, J = 9.8 Hz, 3F, CF₃), -102.96 (t, J = 14.9 Hz, 2F, CF₂), -122.11 – -122.38 (m, 2F, CF₂), -125.95 – -126.22 (m, 2F, CF₂).

Analytic data are consistent with literature-known values.⁹

2.13. (3,3,4,4,5,5,6,7,7,8,8,9,9,10,10-Heptadecafluoro-1-iododec-1-en-1-yl)trimethylsilane (46)

Inside the glovebox, ¹Bu₃P (11.1 mg, 0.0549 mmol, 10.3 mol%) and trimethylsilylacetylene (80) (52.4 mg, 0.534 mmol) were weighed into the reaction glass vial. A stirring bar and CH₂Cl₂ (2 mL) were added. The reaction vial was sealed with a septa screw cap. Outside the glovebox under a stream of nitrogen and best possible light exclusion perfluorooctyl iodide (325, 0.596 mmol, 1.12 equiv) was added. The reaction vial was sealed with the septa screw cap and irradiated for 2 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded a colourless liquid as pure product 46 in mixture of diastereomers (315.3 mg, 0.486 mmol, 92%, E/Z = 63:37)

**1H NMR** (300 MHz, Chloroform-d) δ [ppm] 7.53 (t, J = 15.7 Hz, 1H, -CH-Rf, E-isomer), 7.03 (t, J = 13.5 Hz, 1H, -CH-Rf, Z-isomer), 0.36 (t, J = 1.5 Hz, 9H, -SiMe₃, E-isomer), 0.30 (s, 5H, 9H, -SiMe₃, Z-isomer).

**13C(1H) NMR** (75.5 MHz, Chloroform-d) δ [ppm] 139.3 (t, J = 23.1 Hz), 131.9 (t, J = 23.0 Hz), 129.3, 123.8 – 107.7, 1.2, -1.8

**19F NMR** (282 MHz, Chloroform-d) δ [ppm] -81.61 – -81.80 (m, 3F), -106.03 – -106.31 (m, 2F), -109.44 – -109.61 (m, 2F), -121.79 – -122.22 (m, 2F), -122.17 – -122.64 (m, 4F), -122.89 – -123.14 (m, 1F), -123.14 – -123.47 (m, 3F), -126.61 – -126.93 (m, 2F).

**IR** (film on NaCl), ν [cm⁻¹] 2962, 2904, 2370, 2346, 1588, 1413, 1369, 1353, 1325, 1242, 1213, 1150, 1136, 1116, 1061, 984, 848, 776, 766, 745, 736, 725, 705, 658, 618, 595, 559, 528

In literature the multiplicity of the signals at 0.36 ppm and 0.30 ppm in the ¹H-NMR spectra are listed as singlet.¹⁰ Here, the signal at 0.36 ppm is a triplet. The other analytical data are consistent with literature-known values.¹⁰
2.14. 2-(4,4,5,6,6,7,7,7-Nonafluoro-2-iodohept-2-en-1-yl)isoindoline-1,3-dione (47)

Following GP-B, 'Bu.P (10.8 mg, 0.0534 mmol, 9.84 mol%), 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (78) (100 mg, 0.542 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.05 equiv) were irradiated in CH₂Cl₂ (2 mL) for 3 h. Purification was conducted by chromatography on SiO₂ (pentane:Et₂O 5:1) yielded colourless crystals as pure product 47 in mixture of diastereomers (201.4 mg, 0.379 mmol, 70%, E/Z = 69:31)

¹H NMR (300 MHz, Chloroform-d) δ [ppm] 7.97 – 7.85 (m, 2H, Aryl), 7.83 – 7.72 (m, 2H, Aryl), 6.62 (t, J = 15.0 Hz, 1H, -C₆H₄F), 4.72 – 4.64 (m, 2H, N-C₂H₅Cl).

¹³C{¹H} NMR (75.5 MHz, Chloroform-d) δ [ppm] 167.1, 134.6, 131.9, 128.6 (t, J = 24.5 Hz), 123.9, 119.8 – 110.3 (m, CF₂, CF₃), 116.9 (t, J = 5.76 Hz), 43.0.

¹⁹F NMR (282 MHz, Chloroform-d) δ [ppm] -80.96 (tt, J = 9.2, 2.9 Hz, 3F), -105.42 – -106.68 (m, 2F), -123.41 – -124.25 (m, 2F), -125.19 – -126.45 (m, 2F).

IR (film on NaCl), ν [cm⁻¹] 3064, 2937, 2332, 1776, 1725, 1634, 1469, 1419, 1394, 1352, 1234, 1135, 1109, 1089, 1032, 1006, 985, 940, 919, 903, 879, 793, 772, 743, 713, 694, 666, 588, 528.

m.p. = 58.5-59.5 °C
m/z calculated for C₃₁H₁₃F₉IN₂O₂ [M + NH₄⁺] 548.9721, found 548.9715

2.15. O-tert-Butyl-(4,4,5,6,6,7,7,7-nonafluoro-2-iodohept-2-en-1-yl)-(N-phenyl)carbamate (48)

Inside the glovebox 'Bu₃P (10.9 mg, 0.0538 mmol, 10.1 mol%) was weighed into a reaction glass vial, dissolved in CH₂Cl₂ (2 mL) and a stirring bar was added. Outside the glovebox under a stream of nitrogen and best possible light exclusion N-(tert-butoxycarbonyl)-N-(prop-2-ynyl)aniline (79) (123 mg, 0.530 mmol) and nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.05 equiv) were added. The reaction vial was sealed with e septa screw cap and irradiated for 3 h. Purification was conducted by
chromatography on SiO₂ (pentane:Et₂O 95:5) yielded a colourless liquid as pure product 48. Only the E-isomer was isolated (135.7 mg, 0.235 mmol, 44%)

\( ^1H \) NMR (300 MHz, Chloroform-\( d \)) \( \delta \) [ppm] 7.29 (m, 5H, Aryl), 6.43 (t, \( J = 15.2 \) Hz, 1H, -CH-R₆, E-isomer), 4.66 (s, 2H, N-CH₂-CI), 1.48 (s, 9H, CH₃).

\( ^13C(\text{H}) \) NMR (75.5 MHz, Chloroform-\( d \)) \( \delta \) [ppm] 157.4, 154.3, 141.1, 128.9, 127.3, 126.8, 121.9–114.4 (m, CF₂, CF₃), 81.7, 77.4, 54.1, 28.4

\( ^19F \) NMR (282 MHz, Chloroform-\( d \)) \( \delta \) [ppm] -81.06 (tt, \( J = 9.7, 2.9 \) Hz, 3F), -105.65 – -106.14 (m, 2F), -123.92 – -124.28 (m, 2F), -125.65 – -126.07 (m, 2F).

IR (film on NaCl), \( \nu \) [cm\(^{-1}\)] 3348, 3065, 3043, 2979, 2933, 1705, 1652, 1634, 1598, 1522, 1496, 1478, 1456, 1430, 1412, 1382, 1369, 1355, 1317, 1297, 1237, 1169, 1135, 1047, 1022, 936, 918, 881, 862, 831, 799, 758, 741, 731, 696, 582, 526.

\( \text{m/z} \) calculated for C\(_{18}\)H\(_{32}\)F\(_9\)N\(_2\)O\(_2\) [M + NH\(_3\)] = 595.0504, found 595.0493

2.16. \( \text{(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)cyclopropane (61) and 6,6,7,7,8,8,9,9,10,10,11,11-tridecafluoro-1-iodoundeca-3,4-diene (62)} \)

Following GP-B, \( ^1\text{Bu}_3\text{P} \) (11.3 mg, 0.0559 mmol, 10.5 mol%), ethynylcyclopropane (59) (45.0 mg, 0.532 mmol) and perfluorohexyl iodide (126 µL, 0.583 mmol, 1.10 equiv) were irradiated in CH₂Cl₂ (2 mL) for 3 h. Purification was conducted by chromatography on SiO₂ (pentane) yielded the vinylcyclopropane product 61 as mixture of isomers (69%, \( E/Z = 82:18 \); determined from the NMR-spectrum) and the fluorinated ring-opened allene 62 (31%, determined from the NMR-spectrum).

\( \text{(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)cyclopropane (61)} \)

\( ^1H \) NMR (300 MHz, Chloroform-\( d \)) \( \delta \) [ppm] 6.39 (t, \( J = 14.8 \) Hz, 1H, E-isomer), 6.37 – 6.27 (m, 1H, Z-isomer), 1.76 – 1.64 (m, 1H, Z-isomer), 1.57 – 1.45 (m, 1H, E-isomer), 0.89 – 0.82 (m, 4H).

\( ^19F \) NMR (282 MHz, Chloroform-\( d \)) \( \delta \) [ppm] -80.84 (t, \( J = 10.0 \) Hz, E-isomer), -104.51 (t, \( J = 13.5 \) Hz, E-isomer), -107.29 (t, \( J = 13.4 \) Hz, Z-isomer), -121.40 – -122.05 (m, 2F), -122.64 – -123.08 (m, 2F), -123.08 – -123.43 (m, 2F), -125.99 – -126.37 (m, 2F).

\( \text{6,6,7,7,8,8,9,9,10,10,11,11-Tridecafluoro-1-iodoundeca-3,4-diene (62)} \)

\( ^1H \) NMR (300 MHz, Chloroform-\( d \)) \( \delta \) [ppm] 5.83 – 5.69 (m, 1H), 5.56 – 5.40 (m, 1H), 3.21 (td, \( J = 7.1, 1.1 \) Hz, 2H), 2.70 (tdd, \( J = 7.0, 2.9 \) Hz, 2H).
\[ ^{19}\text{F NMR} \text{(282 MHz, Chloroform-}d\text{)} \delta \text{ [ppm]} -80.84 \text{ (t, } J = 10.0 \text{ Hz)}, -108.23 \text{ (t, } J = 13.2 \text{ Hz)}, -107.29 \text{ (t, } J = 13.4 \text{ Hz)}, -121.40 - 122.05 \text{ (m, 2F)}, -122.64 - 123.08 \text{ (m, 2F)}, -123.08 - 123.43 \text{ (m, 2F)}, -125.99 - 126.37 \text{ (m, 2F).} \]

Products were isolated as mixtures. Differentiation of the cyclopropyl-containing product 61 and the fluorinated allene 62 were possible by comparing with analytical data from literature. Some signals of the fluorinated cyclopropyl derivative 61 and fluorinated allene 62 have the same shift.

3. Reaction with Ethyldifluoroiodoacetate

3.1. Reaction of 1-octene (49) with ethyl difluoroiodoacetate (50)

Inside the glovebox 1\text{Bu}_3\text{P (10.3 mg, 0.0539 mmol, 10.3 mol%)}, 1-octene (49) (58.5 mg, 0.521 mmol) were weighed into a reaction glass vial and dissolved in CH\text{2Cl}_2 (2 mL). Outside the glovebox under a stream of nitrogen and best possible light exclusion ethyl difluoroiodoacetate (50) (86 µL, 0.583 mmol, 1.12 equiv) was added. The reaction vial was sealed with a septa screw cap and irradiated for 2 h. Purification was conducted by chromatography on SiO\text{2} (pentane:Et\text{2}O 98:2) yielded a colourless liquid as pure product 51 (170.1 mg, 0.469 mmol, 90%).

\[ ^{1}\text{H NMR} \text{(300 MHz, Chloroform-}d\text{)} \delta \text{ [ppm]} 4.34 \text{ (q, } J = 7.2 \text{ Hz, 2H), 4.29 – 4.12 \text{ (m, 1H), 3.02 – 2.79 \text{ (m, 1H), 2.80 – 2.62 \text{ (m, 1H), 1.89 – 1.64 \text{ (m, 2H), 1.63 – 1.40 \text{ (m, 1H), 1.40 – 1.16 \text{ (m, 10H), 0.93 – 0.82 \text{ (m, 3H).}}}}\]

\[ ^{19}\text{F NMR} \text{(282 MHz, Chloroform-}d\text{)} \delta \text{ [ppm]} -101.32 – -102.71 \text{ (m, 1F), -105.65 – -107.62 \text{ (m, 1F).}}\]

Analytic data are consistent with literature-known values.\textsuperscript{11}

3.2. Reaction of 1-octyne (52) with ethyl difluoroiodoacetate (50)

Inside the glovebox 1\text{Bu}_3\text{P (10.7 mg, 0.0528 mmol, 9.90 mol%)}, 1-octyne (52) (58.5 mg, 0.534 mmol) were weighed into a reaction glass vial and dissolved in CH\text{2Cl}_2 (2 mL). Outside the glovebox under a stream of nitrogen and best possible light exclusion ethyl difluoroiodoacetate (50) (86 µL, 0.583 mmol, 1.12 equiv) was added. The reaction vial was sealed with a septa screw cap and irradiated for 2 h. Purification was conducted by chromatography on SiO\text{2} (pentane:Et\text{2}O 99:1) yielded a colourless liquid as pure product 53 in a mixture of diastereomers (187 mg, 0.519 mmol, 97\%, E/Z = 84:16).
$^1$H NMR (300 MHz, Chloroform-\textit{d}) $\delta$ [ppm] 6.40 (t, $J = 13.2$ Hz, 1H, \textit{E}-isomer), 6.37 – 6.31 (m, 1H, \textit{Z}-isomer), 4.45 – 4.38 (m, 2H, \textit{Z}-isomer), 4.33 (q, $J = 7.2$ Hz, 2H, \textit{E}-isomer), 2.64 – 2.54 (m, 2H, \textit{E}-isomer), 1.56 – 1.51 (m, 2H, \textit{E}-isomer), 1.40 – 1.27 (m, 9H, \textit{E}-isomer), 0.94 – 0.84 (m, 3H, \textit{E}-isomer).

$^{19}$F NMR (282 MHz, Chloroform-\textit{d}) $\delta$ [ppm] -97.72 (s, 1F, \textit{E}-isomer), -97.89 (s, 1F, \textit{Z}-isomer).

Analytic data are consistent with literature-known values.$^8$

4. Reactions in the presence of iodides

![Reactions in the presence of iodides](image)

General procedure: Triphenylphosphine (14 mg, 0.053 mmol, 10 mol%) and TBAI or NaI (1.50 equiv) were weighed into a reaction vial. Under a stream of N\textsubscript{2} and under red light 1-octene (49) (84 $\mu$L, 0.53 mmol), the corresponding solvent (2 mL), and nonafluoro-1-iodobutane (100 $\mu$L, 0.583 mmol, 1.1 equiv) were added. The reaction vial was sealed and irradiated for 1 h inside the photoreactor. After 1 h a sample of the reaction solution was withdrawn, and the conversion was determined from the measured $^{19}$F-NMR spectrum (Table 1). NaI was not completely dissolved in both solvents after the indicated reaction time.

<table>
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<th>solvent</th>
<th>conversion [%]</th>
</tr>
</thead>
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<td>1 MeCN</td>
<td>26</td>
</tr>
<tr>
<td>2 CH\textsubscript{2}Cl\textsubscript{2}</td>
<td>45</td>
</tr>
<tr>
<td>3 MeCN NaI</td>
<td>68</td>
</tr>
<tr>
<td>4 CH\textsubscript{2}Cl\textsubscript{2} NaI</td>
<td>56</td>
</tr>
<tr>
<td>5 MeCN TBAI</td>
<td>36</td>
</tr>
<tr>
<td>6 CH\textsubscript{2}Cl\textsubscript{2} TBAI</td>
<td>66</td>
</tr>
</tbody>
</table>

5. Interval irradiation

![Interval irradiation](image)

Inside the glovebox $^{1}$Bu\textsubscript{3}P (10.6 mg, 0.0524 mmol, 10.0 mol%), 1-octene (49) (58.5 mg, 0.522 mmol) and \textit{n}-decane (33.5 mg) as internal standard were weighed into a 10 ml round-bottom Schlenk flask. CH\textsubscript{2}Cl\textsubscript{2} (2 mL) and a Teflon stirring bar were added, and the flask was sealed with a septum. Outside the glovebox, the Schlenk flask was attached to an N\textsubscript{2} stream and positioned inside the photoreactor.
The flask and the photoreactor were wrapped with aluminum foil (Figure 1). Under red light conditions and best possible light exclusion nonafluoro-1-iodobutane (100 μL, 0.583 mmol, 1.11 equiv) was added. Irradiation and dark periods are listed in Table 2. Samples were withdrawn under red light with a 1.0 ml syringe (Braun) flushed with N₂. 0.10 ml of the reaction solution were withdrawn and diluted with 0.4 ml CH₂Cl₂ in a short amber thread vial. The vial was sealed with a black screw cap and to exclude ambient light, covered with aluminum foil.

**Figure 1:** Reaction flask inside the photoreactor wrapped with aluminium foil.

**Table 2:** Irradiation, dark periods and conversion in the photomediated iodoperfluoroalkylation of 1-octene (49).

<table>
<thead>
<tr>
<th>Time [h:min]</th>
<th>Conversion [%]</th>
<th>Details</th>
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<td>32</td>
</tr>
<tr>
<td>2</td>
<td>00:21</td>
<td>37</td>
</tr>
<tr>
<td>3</td>
<td>00:26</td>
<td>45</td>
</tr>
<tr>
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<td>00:46</td>
<td>48</td>
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<tr>
<td>5</td>
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<tr>
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<td>01:51</td>
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<tr>
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<td>02:11</td>
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<tr>
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<td>02:31</td>
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<td>12</td>
<td>02:51</td>
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</tr>
<tr>
<td>13</td>
<td>03:11</td>
<td>≥99</td>
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</tbody>
</table>
Figure 2: Interval irradiation of a reaction of 1-octene (49) with nonafluoro-1-iodobutane.

6. Reactions at elevated temperatures

Inside the glovebox 'Bu₃P (10.9 mg, 0.0538 mmol, 9.63 mol%), 1-octene (49) (62.7 mg, 0.559 mmol), and n-decane (29.6 mg) as internal standard was weighed into a two necked 10 ml round-bottom flask with a stopcock. CH₂Cl₂ (2 mL) and a Teflon stirring bar were added, and the flask was sealed with a septum. Outside the glovebox, the flask was attached to an N₂ stream and was connected to a condenser in an N₂ counterflow. The reaction flask and the condenser were covered with aluminum foil (Figure 3).

Under red light and best possible light exclusion nonafluoro-1-iodobutane (100 µL, 0.583 mmol, 1.04 equiv) was added in an N₂ counterflow. The reaction was heated up with a water bath at 30 °C. After 1 h a sample was withdrawn under red light with a 1.0 ml syringe (Braun) flushed with N₂. 0.10 ml of the reaction solution were withdrawn and diluted with 0.4 ml CH₂Cl₂ in a short thread vial. The vial was sealed with a black screw cap and to exclude ambient light, covered with aluminum foil. ¹⁹F-NMR showed 29 % conversion. The reaction solution was heated for 1 h at 40 °C, and another sample was withdrawn in the same procedure as mentioned. ¹⁹F-NMR analysis showed 34 % conversion.
7. Determination of the association constants (Kₐ)

The association constants (Kₐ) for 'Bu₃P, Ph₃P, and (MeO)₃P, were determined by ¹⁹F-NMR spectroscopy. The individual phosphine or phosphite, respectively was weighed into an NMR tube (Table 3 - Table 12), and a stock solution of C₄F₉I in CH₂Cl₂ (0.03 mmol, 0.05 M) was added. The total volume of the mixture was 0.6 ml inside the NMR tube. As internal standard CFCl₃ in C₆D₆ (0.25 M), molten into a glass capillary, was added to every NMR tube. The ¹⁹F-NMR shifts were reported in ppm and referenced to CFCl₃ in C₆D₆. The shift was determined by using the MestReNova “Multiplet Analysis” (Version: 11.0.0-17609). 'Bu₃P was weighed in the NMR tube inside the glovebox, and after the stock solution was added the NMR tube was sealed with a cap and adhesive tape. All ¹⁹F-NMR spectra were recorded at 298 K, and the chemical shift (Δδ) for the –CF₂I group were used as reference.
7.1. Association constant for \( {^t \text{Bu}_3 \text{P}} \) and nonafluoro-1-iodobutane in CH\(_2\)Cl\(_2\)

The association constant of \( {^t \text{Bu}_3 \text{P}} \) and nonafluoro-1-iodobutane in CH\(_2\)Cl\(_2\) was calculated to be \( = 14.60 \text{ M}^{-1} \) (average of four experiments (Table 3-Table 6)).

Table 3 Determination of the association constant of \( {^t \text{Bu}_3 \text{P}} \) and \( \text{C}_4\text{F}_9\text{I} \) in CH\(_2\)Cl\(_2\) (trail 1).

<table>
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<tr>
<th>trail 1</th>
<th>m [mg]</th>
<th>n [mmol]</th>
<th>c [mmol/ml]</th>
<th>l/c [ml/mmol]</th>
<th>( \delta ) [ppm]</th>
<th>( \Delta \delta ) [ppm]</th>
<th>( 1/\Delta \delta ) [ppm(^{-1})]</th>
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<td>1</td>
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<td>1.20</td>
<td>0.500</td>
<td>80.11</td>
<td>19.55</td>
<td>0.0512</td>
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<tr>
<td>2</td>
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<td>0.667</td>
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<td>1.00</td>
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</table>

\[
K_{^t \text{Bu}_3 \text{P}} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.04806}{0.00342} = 14.15 \text{ M}^{-1}
\]

Figure 4: Determination of the association constant of \( {^t \text{Bu}_3 \text{P}} \) and \( \text{C}_4\text{F}_9\text{I} \) in CH\(_2\)Cl\(_2\) (trail 1).
Table 4 Determination of the association constant of tBu₃P and C₆F₉I in CH₂Cl₂ (trail 2).

<table>
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\[
K_{tBu_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.04779}{0.00354} = 13.66 \text{ M}^{-1}
\]

Figure 5: Determination of the association constant of tBu₃P and C₆F₉I in CH₂Cl₂ (trail 2).
**Table 5** Determination of the association constant of tBu₃P and C₄F₉I in CH₂Cl₂ (trail 3).

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\[ K_{tBu_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.04844}{0.00329} = 14.70 \text{ M}^{-1} \]

**Figure 6**: Determination of the association constant of tBu₃P and C₄F₉I in CH₂Cl₂ (trail 3).
Table 6 Determination of the association constant of tBu3P and C4F9I in CH2Cl2 (trail 4).

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\[
K_{K_{Bu3P}} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.04923}{0.00306} = 16.90 \text{ M}^{-1}
\]

Figure 7: Determination of the association constant of tBu3P and C4F9I in CH2Cl2 (trail 4).
7.2. Association constant for Ph₃P and nonafluoro-1-iodobutane in CH₂Cl₂

The association constant of Ph₃P and C₄F₉I in CH₂Cl₂ was calculated to be $K_{\text{Ph₃P}} = 0.96$ M⁻¹ (average of four experiments (Table 7-Table 9).

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Equation $y = a + b \cdot x$

Pearson's r 0.99752
Residual Sum of Squares 0.12921
Adj. R-Square 0.99442

$K_{\text{Ph₃P}} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.28488}{0.30216} = 1.06$ M⁻¹

Figure 8: Determination of the association constant of Ph₃P and C₄F₉I in CH₂Cl₂ (trail 1).

28
Table 8 Determination of the association constant of Ph₃P and C₄F₉I in CH₂Cl₂ (trail 2).

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\[
K_{Ph_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.27357}{0.26765} = 1.02 \text{ M}^{-1}
\]

**Figure 9:** Determination of the association constant of Ph₃P and C₄F₉I in CH₂Cl₂ (trail 2).
**Table 9** Determination of the association constant of Ph$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 3).

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\[ K_{\text{Ph}_3\text{P}} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.22544}{0.28675} = 0.79 \text{ M}^{-1} \]

**Figure 10:** Determination of the association constant of Ph$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 3).
7.3. **Association constant for (MeO)$_3$P and nonafluoro-1-iodobutane in CH$_2$Cl$_2**

The association constant of (MeO)$_3$P and nonafluoro-1-iodobutane in CH$_2$Cl$_2$ was calculated to be $0.46$ M$^{-1}$ (average of four experiments (Table 10-Table 12)).

**Table 10** Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 1).

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$K_{(MeO)_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.71878}{1.58338} = 0.45$ M$^{-1}$

**Figure 11**: Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 1).
Table 11 Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 2).

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<td>0.352</td>
<td>2.84</td>
<td>60.74</td>
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<td>3.98</td>
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<td>0.199</td>
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<td>8</td>
<td>11.1</td>
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<td>6.71</td>
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<td>9</td>
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<td>0.101</td>
<td>9.93</td>
<td>60.62</td>
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<td>–</td>
<td>–</td>
<td>–</td>
<td>60.56</td>
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</tbody>
</table>

K$_{(\text{MeO})_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.81493}{1.59197} = 0.51 \text{ M}^{-1}$

Figure 12: Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 2).
Table 12: Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 3).

<table>
<thead>
<tr>
<th>m</th>
<th>n</th>
<th>c</th>
<th>1/c</th>
<th>δ</th>
<th>Δδ</th>
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<td>1.00</td>
<td>1.00</td>
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<td>4</td>
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<td>0.498</td>
<td>2.01</td>
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<tr>
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<td>26.2</td>
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<td>0.352</td>
<td>2.84</td>
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<tr>
<td>6</td>
<td>18.8</td>
<td>0.152</td>
<td>0.253</td>
<td>3.96</td>
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<tr>
<td>7</td>
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<td>0.06</td>
</tr>
<tr>
<td>10</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>60.56</td>
<td>–</td>
</tr>
</tbody>
</table>

$K_{(MeO)_3P} = \frac{\text{Intercept}}{\text{Slope}} = \frac{0.66332}{1.5536} = 0.43 \text{ M}^{-1}$

![Figure 13: Determination of the association constant of (MeO)$_3$P and C$_4$F$_9$I in CH$_2$Cl$_2$ (trail 3).](image)
8. Borane synthesis

8.1. Tris(pentafluorophenyl)borane $\text{B(C}_6\text{F}_5)_3$ (2)

The synthesis of tris(pentafluorophenyl)borane (2) was conducted in a modified version of the literature-known procedure.$^{12}$ In a one-liter three-necked round bottom flask, cooled dropping funnel and internal thermometer bromopentafluorobenzene (81) (18.5 g, 75.0 mmol, 3.00 equiv) was dissolved in pentane (400 mL) and cooled to $-78 \, ^\circ\text{C}$. In the dropping funnel $n$-BuLi in hexane (2.49 M, 29.5 mL, 73.7 mmol, 2.95 equiv) was cooled to $-78 \, ^\circ\text{C}$ and was added slowly. The temperature of the reaction solution was kept at $<-70 \, ^\circ\text{C}$. After completion, the reaction was stirred 1 h at $-78 \, ^\circ\text{C}$ and $\text{BCl}_3$ (25 mL, 25 mmol, 1.0 equiv) was added rapidly in one stream with a syringe. The cooling bath was removed and the reaction mixture was allowed to reach room temperature. The solution was filtered via Schlenk-filtration over Celite, the solution was removed under reduced pressure until a solid precipitated and the solution was cooled to $-78 \, ^\circ\text{C}$ again. With another Schlenk-filtration the solvent was removed from the solid and the precipitate was allowed to reach room temperature. The solution was filtered via Schlenk-filtration over Celite, the solution was removed under reduced pressure until a solid precipitated and the solution was cooled to $-78 \, ^\circ\text{C}$ again. With another Schlenk-filtration the solvent was removed from the solid and the precipitate was allowed to reach room temperature. The solution was filtered via Schlenk-filtration over Celite, the solution was removed under reduced pressure until a solid precipitated and the solution was cooled to $-78 \, ^\circ\text{C}$ again. With another Schlenk-filtration the solvent was removed from the solid and the precipitate was dried in vacuo overnight. Inside the glovebox the colourless cotton-like solid (2.40 g) was separated from grey solid. The grey solid was sublimed two times ($88 \, ^\circ\text{C} \rightarrow 95 \, ^\circ\text{C} \rightarrow 100 \, ^\circ\text{C}$, $1 \times 10^{-3}$ mbar) yielding colourless cotton-like solid (4.75 g) and was combined with the already isolated product 2 (7.15 g, 14.0 mmol, 56%).

$^{19}\text{F NMR}$ (282 MHz, $\text{C}_6\text{D}_6$) $\delta$ [ppm] $\sim$128.29 $-$ $\sim$129.15 (m, 6F, $o$-$\text{C}_6\text{F}_5$), $\sim$141.22 $-$ $\sim$141.86 (m, 3F, $p$-$\text{C}_6\text{F}_5$), $\sim$159.47 $-$ $\sim$160.44 (m, 6F, $m$-$\text{C}_6\text{F}_5$).

$^{11}\text{B NMR}$ (96 MHz, $\text{C}_6\text{D}_6$) $\delta$ [ppm] 56.94.

Analytic data are consistent with literature-known values.$^{13}$

8.2. Tris(2,6-difluorophenyl)borane $\text{B}(2,6$-$\text{F}_2\text{C}_6\text{H}_3)_3$ (21)

The synthesis of tris(2-fluorophenyl)borane (21) was conducted similar to a literature-known procedure.$^{14}$ $1$-Bromo-2,6-difluorobenzene (82) (5.21 g, 27.0 mmol, 3.00 equiv) was dissolved in dry
THF (200 mL) and cooled to −25 °C with a cryostat. A solution of PrMgCl (13.5 ml, 2.0 M in THF, 27 mmol, 3.0 equiv) was added dropwise within 23 min. After stirring at −25 °C for 30 min, the solution was stirred at 0 °C for 1 h. The resulting grey/brownish solution was cooled to −50 °C. In another flask BF₃ · OEt₂ (1.14 ml, 9.00 mmol, 1.00 equiv) was dissolved in dry THF (36 mL), cooled with an acetone/dry ice bath and then slowly added to the other solution via transfer-cannula. The resulting clear solution was stirred at −50 °C for 1 h, then the solution was allowed to reach r.t. within 1 h. By removal of all volatiles using a secondary cold trap a slightly grey substance was obtained. By extraction with toluene (1 x 16 ml, 1 x 12 ml, 1 x 8 mL) and subsequent filtration via syringe filter, a clear yellowish solution was obtained. A colourless residue (< 1 g) remained behind. By removal of all volatiles using a second cold trap a grey solid was obtained. The substance was sublimed (120 °C, 3·10⁻³ mbar) and inertly recrystallised from boiling n-hexane (34.8 mL). Inert filtration with a Schlenk frit, rinsing with n-hexane (3 mL) of the collected needle shaped crystals and drying in high vacuum yielded colourless needles 21 (1.2 g, 3.4 mmol, 38%, purity ≥ 96%).

¹H NMR (300 MHz, CD₂Cl₂) δ [ppm] 7.60 – 7.42 (m, 1H), 6.95 – 6.85 (m, 2H).

¹⁹F NMR (282 MHz, CD₂Cl₂) δ [ppm] −99.8.

Analytic data are consistent with literature-known values.¹⁴b

8.3. (2,3,6-Trichlorophenyl)-bis(2,3,6-trifluorophenyl)borane B(2,3,6-Cl₃C₆H₂)(2,3,6-F₃C₆H₂)₂(22)³

8.3.1. (2,3,6-Trichlorophenyl)boronic acid (84)

The synthesis of (2,3,6-trichlorophenyl)boronic acid (84) was conducted according to a literature-known procedure.¹⁵

1,2,4-Trichlorobenzene (83) (5.30 g, 24.0 mmol, 1.00 equiv) was dissolved in dry THF (31 ml, 0.7 M) and cooled to −78 °C. n-Butyllithium (32.1 ml, 2.49 M in hexane, 32.1 mmol, 1.10 equiv) was added to the cooled solution dropwise. After the addition of around 9 ml n-butyllithium solution a suspension was formed and the n-butyllithium addition was continued very slowly. After 2 h stirring at −78 °C, trimethyl borate (7.0 ml, 63 mmol, 2.1 equiv) was added dropwise via syringe and a clear solution was obtained. The solution was allowed to warm up overnight, resulting in a colourless suspension. The suspension was cooled with an ice bath and hydrochloric acid (1 M, 40 mL) was added. After stirring at r.t. for 2 h the phases were separated and the aqueous phase was extracted with Et₂O (3 x 20 mL). The combined organic phases were washed with brine (3 x 15 mL) and then dried with Na₂SO₄. The drying
agent was filtered off and the solvents were removed thoroughly (60 °C, 13 mbar) at a rotary evaporator. A partly wet, colourless solid (6.7 g) was obtained, which washed on a frit with n-hexane (2 x 10 mL) and then dried at a rotary evaporator (45 °C, 15 mbar). A colourless solid was obtained (5.23 g, 23.2 mmol, 80%).

**m.p.** = 152-154 °C (lit. 149-150 °C)

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ [ppm] 8.72 (s, 2H), 7.57 (d, $J = 8.6$ Hz, 1H), 7.39 (d, $J = 8.6$ Hz, 1H).

$^{11}$B NMR (96 MHz, DMSO-$d_6$) $\delta$ 27.6.

Analytic data are consistent with literature-known values.$^{15}$

8.3.2. Potassium (2,3,6-trichlorophenyl)trifluoroborate (85)$^3$

(2,3,6-Trichlorophenyl)boronic acid (84) (4.39 g, 19.5 mmol, 1.00 equiv) was dissolved in methanol (30 mL, 0.65 M). A solution of potassium hydrogen difluoride (6.09 g, 78.0 mmol, 4.00 equiv) in desalinated water (22 mL, 3.5 M) was added to the educt solution, resulting in the precipitation of a colourless solid and a noticeable temperature rise. After stirring over night, acetone (30 mL) was added and nearly all solid was dissolved. The suspension was filtered and the residue was washed with acetone (3 x 8 mL). After a thorough removal of the solvent at a rotary evaporator (60 °C, 7 mbar) a colourless solid was obtained, which was dissolved in acetone (35 mL). Small amounts of a colourless solid stayed undissolved and the yellow solution was filtered. The solvent was removed thoroughly (60 °C, 13 mbar) once more and the resulting yellowish solid was washed with n-hexane (3 x 15 mL) on a frit. The pure colourless powder (5.45 g) was dried in a vacuum oven at 70 °C and 7 mbar for 24 h yielding product 85 (5.42 g, 18.9 mmol, 97%).

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ [ppm] 7.28 (d, $J = 8.5$ Hz, 1H), 7.13 (d, $J = 8.5$ Hz, 1H).

$^{19}$F NMR (282 MHz, DMSO-$d_6$) $\delta$ [ppm] $-132.5$ (dd, $J = 88.5$, 40.6 Hz).

$^{11}$B NMR (96 MHz, DMSO-$d_6$) $\delta$ [ppm] 1.8 (q, $J = 46.3$ Hz).

Analytic data are consistent with literature-known values.$^{15}$
8.3.3. (2,3,6-Trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (22) \(^3\)

\[
\begin{align*}
\text{F} & \quad \text{F} & \quad \text{F} & \quad \text{Br} & \quad \text{86} & \quad \overset{\text{iPrMgCl}}{\longrightarrow} & \quad \text{F} & \quad \text{F} & \quad \text{MgBr} & \quad \text{87} & \quad \overset{\text{BF}_3\text{K}}{\longrightarrow} & \quad \text{F} & \quad \text{F} & \quad \text{B} & \quad \text{F} & \quad \text{F} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{22} & \quad \text{85}
\end{align*}
\]

The synthesis of (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (22) was conducted according to a literature-known procedure.\(^15\)

1-Bromo-2,3,6-trifluorobenzene (86) (2.30 g, 10.9 mmol, 2.3 equiv) was dissolved in dry THF (31 ml, 0.35 M) and cooled to −24 °C. Within 8 min iPrMgCl (5.5 ml, 2.0 M in THF, 11 mmol, 2.3 equiv) was added, resulting in a yellowish solution. The solution was warmed to 0 °C with an icebath, stirred at this temperature for 30 min and then for 1 h at r.t. Potassium (2,3,6-trichlorophenyl)-trifluoroborate (85) (1.36 g, 4.74 mmol, 1.00 equiv) was suspended in dry THF (1.4 ml, 1.4 M). The solution of the Grignard reagent as well as the fluoroborate suspension were cooled to 0 °C with an icebath and the solution of the Grignard reagent was transferred within 12 min. After 40 min the icebath was removed and the solution was stirred at r.t. for 15 h. Volatiles were removed inertly and then the solid was dried (75 °C, 12 mbar) with a rotary evaporator. The resulting yellow-orange foam was extracted with toluene (3 x 15 mL). Volatiles were removed and the solid was dried (75 °C, 13 mbar), yielding a yellow-orange resin (1.9 g). n-Pentane (2.5 mL) was added, resulting in no precipitation. After storage in the refrigerator for 2 d, a white solid precipitated, which was filtered off. The crystals were washed with ice-cooled n-pentane (3 x 1.5 mL) and dried. Two subsequent sublimations (120 °C, 1·10⁻² mbar) yielded the product 22 as amorphous crystals (1.05 g, 2.31 mmol, 49%).

\(^1\)H NMR (300 MHz, C₆D₆) δ [ppm] 6.73 (d, \(J = 8.6\) Hz, 1H), 6.59 (d, \(J = 8.6\) Hz, 1H), 6.44 (qd, \(J = 9.2, 5.2\) Hz, 2H), 6.16 – 6.02 (m, 2H).

\(^19\)F NMR (282 MHz, C₆D₆) δ [ppm] −103.1 (d, \(J = 15.8\) Hz), −122.7 (d, \(J = 21.8\) Hz), −142.2 (dd, \(J = 21.8, 15.7\) Hz).

Analytic data are consistent with literature-known values.\(^15\)
9. Educt synthesis

9.1. Pent-4-en-1-yl 4-chlorobenzoate (66)

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{O} & \quad \text{O} \\
\text{CH}_2\text{Cl}_2, 0 \degree \text{C} & \quad \text{r.t.} \\
\text{Et}_3\text{N} & \quad \text{Et}_3\text{N} \\
88 & \quad 89 \\
\end{align*}
\]

The synthesis of pent-4-en-1-yl 4-chlorobenzoate (66) was conducted similar to a literature-known procedure. A solution of 4-chlorobenzoyl chloride (88) (3.50 g, 20.0 mmol, 1.00 equiv) in CH₂Cl₂ (30 mL) was cooled with an ice bath. Pent-4-en-1-ol (89) (1.72 g, 20.0 mmol, 1.00 equiv) was added in one portion, followed by dropwise addition of Et₃N (4.2 ml, 30 mmol, 1.5 equiv). The cooling bath was removed and the white suspension was stirred at r.t. for 20 h. After addition of desalinated water (15 mL) and brine (1 mL), phases were separated. The organic layer was washed with brine (2 x 10 mL) and then dried over Na₂SO₄. After removal of all volatiles, purification by column chromatography on SiO₂ (n-hexane:EtOAc 98:2) yielded pure product 66 (4.02 g, 17.9 mmol, 89%).

\[^{1}H\text{ NMR} (300 \text{ MHz, Chloroform-}d) \delta [ppm] 8.02 – 7.93 (m, 2H), 7.45 – 7.38 (m, 2H), 5.84 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.13 – 4.95 (m, 2H), 4.33 (t, J = 6.6 Hz, 2H), 2.29 – 2.13 (m, 2H), 1.97 – 1.77 (m, 2H).

Analytic data are consistent with literature-known values.

9.2. (Hex-5-en-1-yl)-4-bromophenylether(67)

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{OH} & \quad \text{OH} \\
\text{a) NaOEt/EtOH, r.t., 2 h} & \quad \text{b) 6-bromohex-1-ene, reflux, 3 h} \\
90 & \quad 67 \\
\end{align*}
\]

The synthesis of 1-bromo-4-(hex-5-en-1-yl)oxy)benzene (67) was conducted similar to a literature-known procedure. Sodium (0.76 g, 33 mmol, 1.5 equiv) was dissolved in dry EtOH (20 mL) and then 4-bromophenol (90) (3.8 g, 22 mmol, 1.0 equiv) was added. After stirring at r.t. for 2 h, 6-bromohex-1-ene (45 w%, 3.9 g, 24 mmol, 1.1 equiv) was added and the solution was refluxed for 3 h. After stirring for additional 14 h at r.t. the yellow suspension was filtered and all volatiles were removed. The solid was dissolved in EtOAc (50 mL) and the resulting organic phase was washed with a mixture of desalinated water and brine (4:1, 25 mL) as well as undiluted brine (5 mL). It was dried over Na₂SO₄. After removal of all volatiles, purification by column chromatography on SiO₂ (n-hexane → n-hexane:EtOAc 97:3) gave pure product 67 (3.60 g, 14 mmol, 64%).

\[^{1}H\text{ NMR} (300 \text{ MHz, Chloroform-}d) \delta [ppm] 7.40 – 7.32 (m, 2H), 6.82 – 6.72 (m, 2H), 5.83 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.93 (m, 2H), 3.93 (t, J = 6.4 Hz, 2H), 2.19 – 2.06 (m, 2H), 1.86 – 1.71 (m, 2H), 1.63 – 1.49 (m, 2H).\]
Analytic data are consistent with literature-known values.\(^4\)

9.3. 2-(Prop-2-yn-1-yl)isoindoline-1,3-dione (78)

\[
\begin{array}{c}
\text{93} \\
\text{6K} \\
\text{O} \\
\end{array} + \begin{array}{c}
\text{Br} \\
\text{92} \\
\end{array} \xrightarrow{\text{DMF, 80 °C}} \begin{array}{c}
\text{O} \\
\text{93} \\
\end{array}
\]

The synthesis of 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (78) was conducted similar to a literature-known procedure.\(^1\) Potassium phthalimide (93) (4.81 g, 26.0 mmol, 1.00 equiv) was suspended in DMF (31 mL) and propargyl bromide (92) (80 wt% in toluene, 5.4 ml, 31 mmol, 1.2 equiv) was added at room temperature. The reaction mixture was stirred at 80 °C until the starting material was consumed. The hot reaction mixture was poured onto a mixture of cold water and crushed ice, the solid filtered on a Büchner funnel and washed with small amounts of ice-cold water. The colourless to light beige solid was dried in a vacuum desiccator over orange gel for three days yielded pure product 78 (3.28 g, 17.7 mmol, 68%)

m.p.: 141.7 – 144.4 ºC

\(^1\)H NMR (300 MHz, Chloroform-d) \(\delta \) [ppm] 7.92 – 7.83 (m, 2H, aryl), 7.79 – 7.70 (m, 2H, aryl), 4.45 (d, \(J = 2.5 \) Hz, 2H, NCH\(_2\)), 2.22 (t, \(J = 2.5 \) Hz, 1H, \(\equiv CH\)).

Analytic data are consistent with literature-known values.\(^2\)

9.4. \(N\)-(tert-butoxycarbonyl)-\(N\)-(prop-2-ynyl)aniline (79)

\[
\begin{array}{c}
\text{91} \\
\text{H} \\
\text{O} \\
\end{array} \xrightarrow{\text{a) NaH}} \begin{array}{c}
\text{92} \\
\text{Br} \\
\end{array} \xrightarrow{\text{THF, 0 ºC}} \begin{array}{c}
\text{79} \\
\text{O} \\
\text{N} \\
\end{array} \xrightarrow{\text{r.t.}} \begin{array}{c}
\text{O} \\
\text{N} \\
\end{array}
\]

The synthesis of \(N\)-(tert-butoxycarbonyl)-\(N\)-(prop-2-ynyl)aniline (79) was conducted similar to a literature-known procedure.\(^1\) A solution of \(N\)-Boc-aniline (91) (5.03 g, 26.0 mmol, 1.00 equiv) in THF (110 mL) was treated with sodium hydride (60 wt% in mineral oil, 1.81 g, 45.5 mmol, 1.75 equiv) at 0 ºC and stirred for 1 h 25 min. Propargyl bromide (92) (80 wt% in toluene, 4 ml, 37.5 mmol, 1.44 equiv) was added to the mixture at 0 ºC over 15 min. The reaction was stirred over 23 h at room temperature and was quenched with saturated NH\(_4\)Cl (50 mL) at 0 ºC and extracted with diethyl ether (5 x 50 mL). The combined organic layers were washed with brine (75 mL), dried with Na\(_2\)SO\(_4\), filtered and evaporated. Purification was conducted by chromatography on SiO\(_2\) (Hexane:EtOAc = 30:1) yielded 79 (5.99 g, 25.9 mmol, 99%) as a pale yellow oil.
\textbf{^1H NMR} (300 MHz, Chloroform-\textit{d}) \( \delta \) [ppm] 7.41 – 7.31 (m, 4H), 7.30 – 7.19 (m, 1H), 4.39 (d, \( J = 2.4 \) Hz, 2H), 2.27 (t, \( J = 2.4 \) Hz, 1H), 1.48 (s, 9H).

Analytic data are consistent with literature-known values.\textsuperscript{18}
10. Spectral Data

10.1. 1-Methoxy-4-(4,4,5,5,6,6,7,7,8,8-nonafluoro-2-iodoheptyl)benzene (15)

\[
\text{H NMR spectrum (300 MHz, CDCl}_3\text{)}
\]

\[
\text{F NMR spectrum (282 MHz, CDCl}_3\text{)}
\]
$^{13}$C-$^1$H NMR spectrum (75.5 MHz, CDCl$_3$)

DEPT spectrum (75.5 MHz, CDCl$_3$)
HSQC spectrum (300, 75.5 MHz, CDCl₃)

IR spectrum (film on NaCl)
10.2. 1-Bromo-4-((7,7,8,9,10,10,10-nonafluoro-5-iododecyl)oxy)benzene (16)

\[ \text{O} \quad \text{C}_4\text{F}_9 \]

\[ \text{Br} \]

1H NMR spectrum (300 MHz, CDCl₃)

\[ \text{O} \quad \text{C}_4\text{F}_9 \]

\[ \text{Br} \]

19F NMR spectrum (282 MHz, CDCl₃)
10.3. $5,5,6,6,7,7,8,8,9,9,10,10,10$-Tridecafluoro-3-iododecyl acetate (17)

$\text{F}_{13}\text{C}_6$ \hspace{1cm} O \hspace{1cm} 17

$^1\text{H}$ NMR spectrum (600 MHz, CDCl$_3$)

$\text{F}_{13}\text{C}_6$ \hspace{1cm} O \hspace{1cm} 17

$^{13}\text{C}^{1\text{H}}$ NMR spectrum (151 MHz, CDCl$_3$)
\[ F_{13}C_6 \text{O} \]

**$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)**

**COSY spectrum (600 MHz, CDCl$_3$)**
HSQC spectrum (600, 151 MHz, CDCl₃)

IR spectrum (film on NaCl)
10.4. 4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl acetate (18)

\[ \text{F}_9\text{C}_4 - \text{O} - \text{O} \]

1H NMR spectrum (300 MHz, CDCl₃)

\[ \text{F}_9\text{C}_4 - \text{O} - \text{O} \]

13C\{1H\} NMR spectrum (151 MHz, CDCl₃)
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

DEPT spectrum (75.5 MHz, CDCl$_3$)
HSQC spectrum (300, 75.5 MHz, CDCl$_3$)

IR spectrum (film on NaCl)
10.5.  6,6,7,7,8,9,9,9-Nonafluoro-4-iodononyl 4-chlorobenzoate (19)

\[
\text{\textsuperscript{1}H NMR spectrum (300 MHz, CDCl}_3)\\
\]

\[
\text{\textsuperscript{19}F NMR spectrum (282 MHz, CDCl}_3)\\
\]
10.6. 2-(7,7,8,8,9,9,10,10,10-Nonafluoro-5-iododecyl)isoindoline-1,3-dione (20)

\[
\begin{align*}
\text{H NMR spectrum (300 MHz, CDCl}_3) \\
\end{align*}
\]

\[
\begin{align*}
\text{F NMR spectrum (282 MHz, CDCl}_3) \\
\end{align*}
\]
10.7. 1,1,1-Trifluoro-3-iodonon-2-ene (34)

\[ \text{34} \text{CF}_3 \]

\[ \text{H NMR spectrum (600 MHz, CDCl}_3\text{)} \]

\[ \text{F NMR spectrum (282 MHz, CDCl}_3\text{)} \]
10.8. 1,1,2,2,3,3,4,4,4-Nonafluoro-6-iodododec-5-ene (35)

\[
\text{\(\text{H NMR spectrum (300 MHz, CDCl}_3\))}
\]

\[
\text{\(\text{\(19\)F NMR spectrum (282 MHz, CDCl}_3\))}
\]
10.9. 1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodotetradec-7-ene (36)

\[ \text{H NMR spectrum (300 MHz, CDCl}_3\]}

\[ \text{F NMR spectrum (282 MHz, CDCl}_3\]}

\[ \text{H NMR spectrum (300 MHz, CDCl}_3\]}

\[ \text{F NMR spectrum (282 MHz, CDCl}_3\]}

55
10.10. 9,9,10,10,11,12,12,13,13,14,14,15,15,16,16-Heptadecafluoro-7-
iodohexadec-7-ene (37)

\[
\text{\textsuperscript{1}H NMR spectrum (300 MHz, CDCl}_3\]

\[
\text{\textsuperscript{19}F NMR spectrum (282 MHz, CDCl}_3\]

56
10.11. (3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)benzene (38)

\[ \text{H NMR spectrum (300 MHz, CDCl} \text{3)} \]

\[ \text{F NMR spectrum (282 MHz, CDCl} \text{3)} \]
10.12. 1-Methyl-4-(3,3,4,4,5,6,6,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (39)

\[
\text{Me} \quad \text{C}_4\text{F}_9
\]

\[
\begin{array}{c|c|c}
\text{H} & \text{F} \\
7.14 & 0.18 \\
6.47 & 13.10 \\
7.21 & 38.27 \\
6.57 & 13.41 \\
7.36 & \\
\end{array}
\]

\[
1^H \text{ NMR spectrum (300 MHz, CDCl}_3\]

\[
\text{Me} \quad \text{C}_4\text{F}_9
\]

\[
\begin{array}{c|c|c}
\text{m} & \text{s} & \text{s} \\
-0.23 & -108.92 & -123.81 \\
-81.04 & -105.30 & -125.86 \\
\end{array}
\]

\[
\text{F} \text{NMR spectrum (282 MHz, CDCl}_3\]

\[
0.08 \ 2.04 \\
1.86 \ 0.12 \\
1.50 \ 0.08 \ 1.90
\]

\[19^F \text{ NMR spectrum (282 MHz, CDCl}_3\]
10.13. 1-Methoxy-4-(3,3,4,5,5,6,6,6-nonfluoro-1-iodohex-1-en-1-yl)benzene (40)

![Chemical Structure](image)

**\(^1\)H NMR spectrum (300 MHz, CDCl\(_3\))**

![NMR Spectrum](image)

**\(^{13}\)C\(^{\text{1H}}\) NMR spectrum (75.5 MHz, CDCl\(_3\))**

![NMR Spectrum](image)
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

DEPT spectrum (75.5 MHz, CDCl$_3$)
COSY spectrum (300, 300 MHz, CDCl3)

HSQC spectrum (300, 75.5 MHz, CDCl3)
IR spectrum (film on NaCl)

10.14. 1-(tert-Butyl)-4-(3,3,4,5,6,6,6-nonfluoro-1-iodohex-1-en-1-yl)benzene (41)

![Chemical structure of 1-(tert-Butyl)-4-(3,3,4,5,6,6,6-nonfluoro-1-iodohex-1-en-1-yl)benzene (41)]

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
$^{13}$C$^{[1]H}$ NMR spectrum (75.5 MHz, CDCl$_3$)

$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)
DEPT spectrum (75.5 MHz, CDCl₃)

COSY spectrum (300, 300 MHz, CDCl₃)
HSQC spectrum (300, 75.5 MHz, CDCl₃)

IR spectrum (film on NaCl)
10.15. 1-Bromo-4-(3,3,4,4,5,5,6,6,6-nonfluoro-1-iodohex-1-en-1-yl)benzene (42)

\[
\begin{align*}
\text{Br} & \quad \text{C}_9 \text{F}_9 \\
\end{align*}
\]

\[
\begin{array}{c}
\text{(m)} \\
7.53 \\
\text{(m)} \\
7.48 \\
\text{A (m)} \\
7.17 \\
\text{(m)} \\
6.51 \\
\text{(m)} \\
6.41 \\
\text{(s)} \\
7.36
\end{array}
\]

\[
\begin{array}{c}
(0) \\
122.7 (22.21) \\
(0) \\
111.1 (20.39)
\end{array}
\]

\[
\begin{array}{c}
(0) \\
128.6 (22.55) \\
(0) \\
127.7 (22.21)
\end{array}
\]

\[
\begin{array}{c}
(131.1) \\
(133.1) \\
(132.1)
\end{array}
\]

\[
\begin{array}{c}
(0) \\
129.8
\end{array}
\]

\[
\begin{array}{c}
130 \\
128 \\
126 \\
124 \\
122 \\
120 \\
118 \\
116 \\
114 \\
112 \\
110 \\
108
\end{array}
\]

\[
\begin{array}{c}
180 \\
170 \\
160 \\
150 \\
140 \\
130 \\
120 \\
110 \\
100 \\
90 \\
80 \\
70 \\
60 \\
50 \\
40 \\
30 \\
20 \\
10 \\
0
\end{array}
\]

\[\text{^1H NMR spectrum (300 MHz, CDCl}_3\text{)}\]

\[
\begin{align*}
\text{Br} & \quad \text{C}_9 \text{F}_9 \\
\end{align*}
\]

\[
\begin{array}{c}
\text{(m)} \\
7.05 \\
\text{(m)} \\
7.02 \\
\text{A (m)} \\
6.71 \\
\text{(m)} \\
6.43 \\
\text{(m)} \\
6.30 \\
\text{(s)} \\
7.30
\end{array}
\]

\[
\begin{array}{c}
(0) \\
122.7 (22.21) \\
(0) \\
111.1 (20.39)
\end{array}
\]

\[
\begin{array}{c}
(0) \\
128.6 (22.55) \\
(0) \\
127.7 (22.21)
\end{array}
\]

\[
\begin{array}{c}
(131.1) \\
(133.1) \\
(132.1)
\end{array}
\]

\[
\begin{array}{c}
(0) \\
129.8
\end{array}
\]

\[
\begin{array}{c}
130 \\
128 \\
126 \\
124 \\
122 \\
120 \\
118 \\
116 \\
114 \\
112 \\
110 \\
108
\end{array}
\]

\[
\begin{array}{c}
180 \\
170 \\
160 \\
150 \\
140 \\
130 \\
120 \\
110 \\
100 \\
90 \\
80 \\
70 \\
60 \\
50 \\
40 \\
30 \\
20 \\
10 \\
0
\end{array}
\]

\[\text{^13C\text{^1H} NMR spectrum (75.5 MHz, CDCl}_3\text{)}\]

66
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

DEPT spectrum (75.5 MHz, CDCl$_3$)
COSY spectrum (300, 300 MHz, CDCl3)

HSQC spectrum (300, 75.5 MHz, CDCl3)
IR spectrum (film on NaCl)

10.16. \((E)-(3,3,4,5,6,6,6\text{-Nonafluoro}-1\text{-iodo}-2\text{-methylhex}-1\text{-en}-1\text{-yl})\text{benzene (43)}\)

![Chemical structure of compound 43]

\(\text{C}_4\text{F}_9\text{Me}\)

\(\text{H}^1\) NMR spectrum (300 MHz, CDCl₃)
$^{13}$C\(^1\)H NMR spectrum (75.5 MHz, CDCl\(_3\))

$^{19}$F NMR spectrum (282 MHz, CDCl\(_3\))
DEPT spectrum (75.5 MHz, CDCl₃)

COSY spectrum (300, 300 MHz, CDCl₃)
HSQC spectrum (300, 75.5 MHz, CDCl3)

IR spectrum (film on NaCl)
10.17.  (5,5,6,6,7,8,8,8-Nonafluoro-3-iodooct-3-en-1-yl)benzene (44)

\[ \text{H NMR spectrum (300 MHz, CDCl}_3\]}

\[ \text{C}^1\text{H} \] NMR spectrum (75.5 MHz, CDCl\textsubscript{3})

\[ \text{C}^{13}\text{H} \] NMR spectrum (75.5 MHz, CDCl\textsubscript{3})
$^{19}$F NMR spectrum (282 MHz, CDCl₃)

DEPT spectrum (75.5 MHz, CDCl₃)
COSY spectrum (300, 300 MHz, CDCl₃)

HSQC spectrum (300, 75.5 MHz, CDCl₃)
IR spectrum (film on NaCl)

10.18. \((E)-6,6,7,7,8,8,9,9,9\)-Nonafluoro-4-iodo-5-propynon-4-ene (45)

\[
\begin{align*}
C_4F_9 & \quad \text{I} \\
\end{align*}
\]

\text{H} NMR spectrum (300 MHz, CDCl\textsubscript{3})
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

10.19. (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Heptadecafluoro-1-iododec-1-en-1-yl)trimethylsilane (46)

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
$\text{Me}_3\text{SiC}_8\text{F}_{17}$

$\text{13C}^{1}\text{H} \text{NMR-spectrum (75.5 MHz, CDCl}_3\text{)}$

$\text{Me}_3\text{SiC}_8\text{F}_{17}$

$\text{19F NMR spectrum (282 MHz, CDCl}_3\text{)}$
IR spectrum (film on NaCl)

10.20. 2-(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodohept-2-en-1-yl)isoindoline-1,3-dion (47)
$^{13}$C{[H]} NMR spectrum (75.5 MHz, CDCl$_3$)

$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)
DEPT spectrum (75.5 MHz, CDCl₃)

COSY spectrum (300, 300 MHz, CDCl₃)
HSQC spectrum (300, 75.5 MHz, CDCl₃)

IR spectrum (film on NaCl)
10.21. \textit{O-}\textit{tert-}Butyl-(4,4,5,6,6,7,7,7-octafluoro-2-iodohept-2-en-1-yl)-(N-phenyl)-carbamate (48)

\textbf{1H NMR spectrum (300 MHz, CDCl$_3$)}

\textbf{13C[1H] NMR spectrum (75.5 MHz, CDCl$_3$)}
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

DEPT spectrum (75.5 MHz, CDCl$_3$)
COSY spectrum (300, 300 MHz, CDCl3)

HSQC spectrum (300, 75.5 MHz, CDCl3)
IR spectrum (film on NaCl)

10.22. (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)benzene (70)

![IR spectrum](image)

1H NMR spectrum (300 MHz, CDCl₃)
19F NMR spectrum (282 MHz, CDCl3)

10.23. Ethyl-2,2-difluoro-4-iododecanoate (51)

1H NMR spectrum (300 MHz, CDCl3)
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

10.24. Ethyl-2,2-difluoro-4-iododec-3-enoate (53)

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
$^{19}$F NMR spectrum (282 MHz, CDCl$_3$)

10.25. (3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)cyclopropane (61)

6,6,7,7,8,8,9,9,10,10,11,11-Tridecafluoro-1-iodoundeca-3,4-diene (62)

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
$^{19}$F NMR spectrum (282 MHz, CDCl₃)

$^1$H NMR spectrum (300 MHz, CDCl₃)
$^19$F NMR spectrum (282 MHz, CDCl$_3$)

10.26. Tris(pentafluorophenyl)borane (2)

$^19$F NMR spectrum (282 MHz, C$_6$D$_6$)
11B NMR spectrum (96 MHz, C6D6)

10.27. Tris(2,6-difluorophenyl)borane (21)

1H NMR spectrum (300 MHz, CD2Cl2)
$^{19}F$ NMR spectrum (282 MHz, CD$_2$Cl$_2$)

10.28. (2,3,6-Trichlorophenyl)boronic acid (84)

$^1$H NMR spectrum (300 MHz, DMSO-d$_6$)
$^{11}$B NMR spectrum (96 MHz, DMSO-d$_6$)

10.29. Potassium (2,3,6-trichlorophenyl)trifluoroborate (85)

$^1$H NMR spectrum (300 MHz, DMSO-d$_6$)

94
$^{19}$F NMR spectrum (282 MHz, DMSO-d$_6$)

10.30. (2,3,6-Trichlorophenyl)-bis(2,3,6-trifluorophenyl)borane (22)

$^1$H NMR spectrum (300 MHz, C$_6$D$_6$)
\(^{19}\text{F} \text{NMR spectrum (282 MHz, C}_{6}\text{D}_{6})\)

10.31. Pent-4-en-1-yl 4-chlorobenzoate (66)

\(^{1}\text{H} \text{NMR spectrum (300 MHz, CDCl}_3\)
10.32. (Hex-5-en-1-yl)-4-bromophenylether (67)

![Diagram of 67]

$^1$H NMR spectrum (300 MHz, CDCl$_3$)

10.33. 2-(Prop-2-yn-1-yl)isoindoline-1,3-dione (78)

![Diagram of 78]

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
10.34. *N*-(tert-butoxycarbonyl)-*N*-(prop-2-ynyl)aniline (79)

![Chemical structure](image)

$^1$H NMR spectrum (300 MHz, CDCl$_3$)
10.35. Crystallographic details

A single-crystal of (E)-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodo-2-methylhex-1-en-1-yl)benzene (43) was mounted using a microfabricated polymer film crystal-mounting tool (dual-thickness MicroMount MiTeGen) using low viscosity oil (perfluoropolyalkylether; viscosity 1800 cSt. ABCR) to reduce the X-ray absorption and scattering. A Bruker D8 Venture single-crystal X-ray diffractometer with area detector using Mo-Kα (λ = 0.71073 Å) radiation was used for data collection at the temperature stated for each compound. Multiscan absorption corrections implemented in SADABS\textsuperscript{21} were applied to the data. The structure was solved by intrinsic phasing (SHELXT-2013)\textsuperscript{22} and refined by full-matrix least-squares methods on $F^2$ (SHELXL-2014).\textsuperscript{23} The hydrogen atoms were placed at calculated positions and refined by using a riding model. CCDC 1998315 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Figure 14:** Single-crystal X-ray data of 43 showing the asymmetric unit with thermal ellipsoids set at 50% probability. The structure was measured at 100 K and solved in the monoclinic space group $P2_1/c$ with $R_{	ext{int}} = 0.0393$. $R_1 = 0.0227$ and $wR_2 = 0.0564$. Selected bond lengths [Å]: I1–C7 2.128(2) and C7–C8 1.338(3).
Figure 15: View of the unit cell of 43 along the crystallographic $b$ axis.

Figure 16: View of the elongated unit cell of 43 along the crystallographic $c$ axis. The separation of the fluous chains and the hydrocarbon parts within the crystal can be noticed.
11. Literature


(3) Spittler, M. Frustrated Lewis Pair-Catalysed Functionalisation of Alkenes with Iodoperfluoroalkanes and Gold-Catalysed Desymmetrisation of 1,4-Diynes. Heinrich-Heine-Universität Düsseldorf, docserv.uni-duesseldorf.de/servlets/DocumentServlet?id=50212, 2018.


