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Metal-Free Iodoperfluoroalkylation: Photocatalysis versus Frustrated Lewis Pair Catalysis

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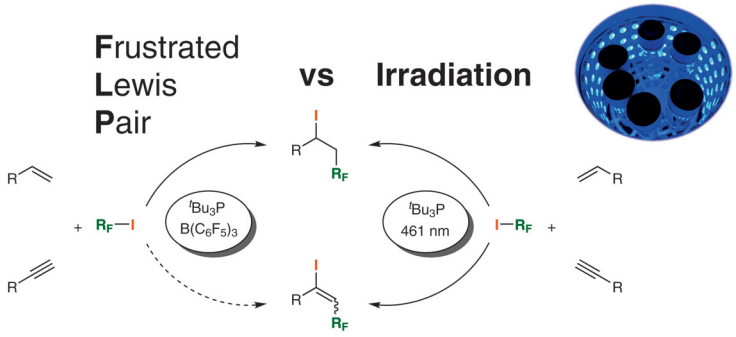
In memoriam Professor Rolf Huisgen



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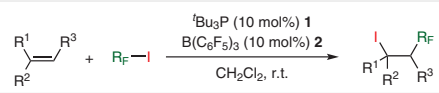
Abstract A comparison of two catalytic, metal-free iodoperfluoroalkylation protocols is presented. Frustrated Lewis pairs [^{t}Bu$_3$P/B(C$_6$F$_5$)$_3$] or phosphines/phosphites under visible light irradiation efficiently mediate the functionalization of non-activated alkenes and alkynes. A comprehensive account of the corresponding substrate scopes as well as insights into the mechanistic details of both reaction pathways are provided.

Key words iodoperfluoroalkylation, frustrated Lewis pair, electron donor–acceptor complex, halogenations, radicals

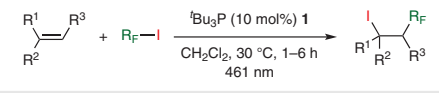
The introduction of fluorine or large perfluoroalkyl groups can significantly alter the electronic properties, lipophilicity, and metabolic stability of an organic molecule.[1] In particular, the fine chemical industry,[2] pharmaceutical research[3] and materials sciences[4] strive for new methods for the introduction of fluorinated functional groups.[5] Over the last few years, the portfolio of synthetic methodology has changed and a plethora of new methods have been developed.[6] Tailor-made fluorinating reagents,[7] transition-metal catalysts[8] and metal-free methods[9] have been developed, providing milder reaction conditions compared to established transformations such as UV-light-mediated[10] reactions. Transition-metal complexes[11] (based on ruthenium, iridium, copper) or organic dyes[12] (eosin Y, rose bengal, riboflavin) are nowadays popular catalysts for photochemical reactions.[9a,13]

In 2016, we reported the frustrated Lewis pair (FLP)-catalyzed iodoperfluoroalkylation of unsaturated hydrocarbons,[14] which was followed by further mechanistic studies in 2019 (Scheme 1).[15] For these transformations, we used the popular FLP consisting of tris(pentafluorophenyl)-borane (**2**) (often abbreviated as BCF) and tri-*tert*-butylphosphine (**1**).[16]



Scheme 1 FLP-catalyzed iodoperfluoroalkylation of alkenes using ^{t}Bu$_3$P (**1**) (10 mol%) and B(C$_6$F$_5$)$_3$ (**2**) (10 mol%) as catalysts[14,15]

As this FLP-mediated iodoperfluoroalkylation showed some peculiar characteristics, we investigated the mechanism of this reaction more thoroughly.[15] While activation of the iodoperfluoroalkane by the Lewis base was indicated by NMR spectroscopy, kinetic studies revealed strong evidence for an additional photomediated process. Lewis base mediated photochemical perfluoroalkylations have been documented earlier.[17,18] Chen and co-workers[17] used *N*,*N*,*N*′,*N*′-tetraethylethylene diamine (TEEDA) to activate the iodoperfluoroalkane by forming an electron donor–acceptor (EDA) complex. Moreno-Mañas[18b] as well as Huang and Zhang[18a] reported that triphenylphosphine and related phosphorus(III) compounds can catalyze iodoperfluoroalkylations. However, a photomediated process was not considered in these publications. An electron donor–acceptor complex formed from an electron-deficient perfluoroalkyl iodide and an electron-rich phosphine can absorb light of lower energy than the individual components. This can lead to homolytic bond cleavage and radical formation.[19] Developing this concept further, we presented the photomediated iodoperfluoroalkylation of alkenes in the presence of ^{t}Bu$_3$P (**1**) (Scheme 2).[20]



Scheme 2 Photomediated iodoperfluoroalkylation of alkenes using ^{t}Bu$_3$P (**1**) (10 mol%) as the catalyst[20]

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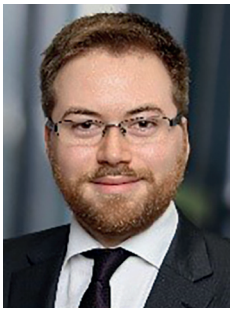
Other research groups have also recently reported the effective use of phosphorus compounds as catalysts for similar transformations. Zhao, Li and He developed a difluoroalkylation of alkenes by using organophosphine reagents (DPPM) at higher temperature.[21] Zhang and co-workers presented the phosphine-catalyzed difluoroalkylation of arenes and heterocycles by using visible light.[22] The group of Dilman successfully developed the iododifluoromethylation of alkenes by utilizing (phosphonio)-difluoromethyl radical cations.[23] Furthermore, phenols,[24] amines[25] and even acetone[26] as a solvent were investigated as Lewis base mediators in this context.

When we started our investigation on the FLP-catalyzed reaction, one of the first observations was the formation of $[^tBu_3PI][FB(C_6F_5)_3]$ (**3**) upon mixing $^tBu_3P$ and $B(C_6F_5)_3$ with various perfluoroalkyl iodides (Scheme 3).[14] The formation

Biographical Sketches



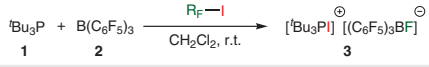
Lucas Helmecke was born in 1992 in Germany. He studied chemistry at Heinrich-Heine-Universität Düsseldorf and graduated in 2017 with a master´s degree in chemistry. He is currently a Ph.D. student under the supervision of Constantin Czekelius. His work is mainly focused on the development and investigation of metal-free iodoperfluoroalkylation reactions and the activation of perfluoroalkyl iodides with phosphorus compounds.

Michael Spittler was born in 1988 in Germany. After undergraduate studies at Krefeld, where he studied chemistry and biotechnology in combination with an apprenticeship as a chemical laboratory assistant at Evonik, he finished his master's studies in chemistry at Heinrich-Heine-Universität in 2015. He earned his Ph.D. under the supervision of Constantin Czekelius for his work in the field of asymmetric gold catalysis and the investigation of frustrated Lewis pair (FLP)-catalyzed iodoperfluoroalkylation reactions. Together with Lucas Helmecke, he has started to develop the activation of perfluoroalkyl iodides with phosphorus compounds.

Bernd M. Schmidt researches responsive and functional supramolecular systems. Born and raised in Berlin, Germany, he performed his Ph.D. with Dieter Lentz at the Freie Universität Berlin and with Hidehiro Sakurai at the IMS in Okazaki, Japan, working on bowl-shaped aromatic hydrocarbons (corannulene and sumanene). Bernd undertook postdoctoral studies with Makoto Fujita at the University of Tokyo, Japan and with Stefan Hecht at the Humboldt University of Berlin, Germany, to learn more about supramolecular chemistry, physical–organic chemistry and molecular photoswitches. Since February 2018, he has been an independent research group leader at Heinrich-Heine-Universität Düsseldorf, Germany.

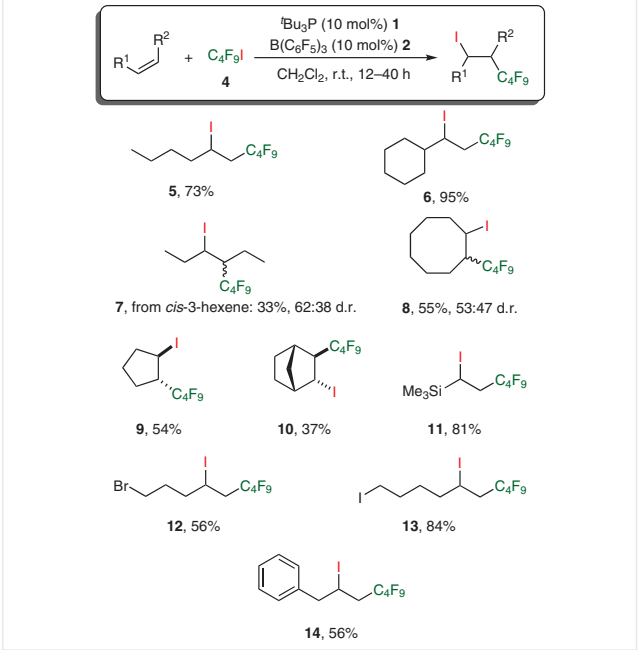
Constantin Czekelius was born in Germany in 1974. After undergraduate studies at Freiburg and Würzburg, he obtained a diploma in chemistry at the ETH Zurich in 2000. Under the supervision of Erick M. Carreira he earned a Ph.D. in 2004. After postdoctoral studies in the group of Richard R. Schrock at MIT, he joined the Freie Universität Berlin as an independent research group leader. Since 2013, he has been a chemistry professor at Heinrich-Heine-Universität Düsseldorf. His interests include enantioselective catalytic methods for the facile preparation of synthetically interesting building blocks, the synthesis of halogenated compounds, and research on medicinal chemistry.

of this iodophosphonium fluoroborate salt suggested that the Lewis pair was capable of activating the C–I bond. It was proposed that upon its cleavage, either α-fluoro- or β-fluoro elimination leads to the ion pair. It is noteworthy that the salt is completely unreactive towards alkenes and neither the fluoride nor the iodonium ion are transferred to cyclohexene or hex-1-ene.



Scheme 3 Formation of iodophosphonium fluoroborate salt **3** from iodoperfluoroalkanes[14]

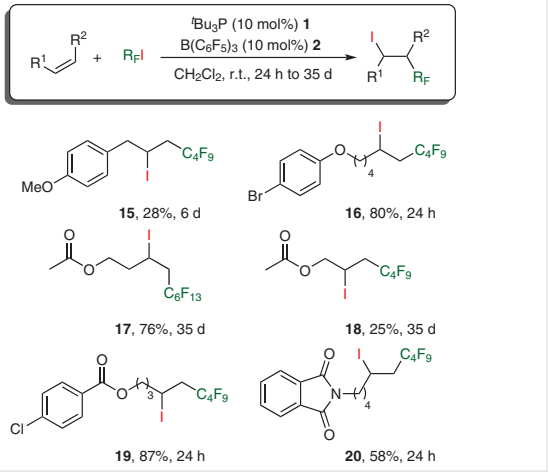
In contrast to this observation, when employing $^tBu_3P$ and $B(C_6F_5)_3$ as an FLP together with nonafluoro-1-iodobutane (**4**) in the presence of different alkenes, the corresponding iodoperfluoroalkylated products were isolated (Scheme 4).[14] Herein, iodine was always regioselectively incorporated at the higher substituted carbon. When using (*Z*)-3-hexene it was shown that the reaction was not diastereoselective and that a mixture of isomers was isolated. This implies that ring opening of a putative *epi*-iodonium intermediate by nucleophilic substitution was less likely. In contrast, when (*E*)-3-hexene was tested, no reaction was observed over the period of 24 hours. Neither a reaction nor polymerization were observed when styrene was used as the starting material.[14] Styrene even quenches the FLP-catalyzed iodoperfluoroalkylation of other substrates.[15] Moreno-Mañas et al. reported a similar behavior and ascribed it to the high stability of potentially formed benzylic radicals.[18b]



Scheme 4 FLP-catalyzed iodoperfluoroalkylation of alkenes[14]

Non-functionalized internal and terminal alkenes as well as cyclic alkenes were successfully transformed. Other halides (**12** and **13**) and silanes (**11**) were also tolerated in this iodoperfluoroalkylation. However, further investigations of the functional group tolerance showed that many polar substituents were not compatible with this catalyst system.

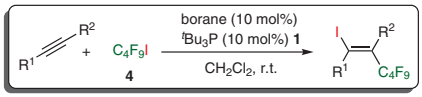
For example, alcohols were unsuitable as starting materials, presumably due to interaction with the empty orbital of the borane. In contrast, substrates with aliphatic as well as aromatic esters, phenol ethers or phthalimides were successfully iodoperfluoroalkylated (Scheme 5), but sometimes slow conversions and low yields were observed. Due to demethylation and concomitant deactivation of the borane, 4-allylanisole proved to be a challenging substrate as well.



Scheme 5 FLP-catalyzed iodoperfluoroalkylation of alkenes incorporating polar substituents

When changing to non-functionalized, terminal or internal alkynes as substrates using $B(C_5F_6)_3$ (**2**) as the Lewis acid, the corresponding monoaddition products for terminal and internal alkynes were isolated in 10% yield after long reaction times of up to 23 d (Table 1). Dureen and Stephan reported boron alkynylide formation from $^tBu_3P$, $B(C_6F_5)_3$ and phenylacetylene.[27] We assumed that this formation of a stable $[^tBu_3PH][PhC{\equiv}CB(C_6F_5)]$ intermediate might be a faster and more efficient process than the iodoperfluoroalkylation of the alkyne. To overcome this problem of potential catalyst deactivation and potentially improving tolerance towards heteroatoms, electronically tuned boranes such as tris(2,6-difluorophenyl)borane (**21**) and the more water-stable (2,3,6-trichlorophenyl)bis(2,3,6-trifluorophenyl)borane (**22**) were investigated (Table 1 and Table 2). However, the transformation of demanding alkenes or terminal alkynes was not substantially improved.

Table 1 FLP-Catalyzed Iodoperfluoroalkylation of Non-Functionalized Alkynes Using Different Boranes



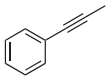
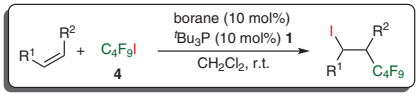
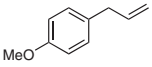
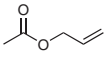
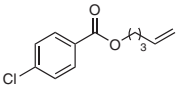
Entry	Substrate	Borane	Yield (%) *E*/*Z*
1		$B(C_6F_5)_3$ (**2**)	18[14] *E*-isomer
2		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	44 70:30
3		$B(C_6F_5)_3$ (**2**)	10 *E*-isomer
4		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	20 *E*-isomer
5		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	–

Table 2 FLP-Catalyzed Iodoperfluoroalkylation Using Electronically Modified Boranes



Entry	Substrate	Borane	Yield (%)
1		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	–
2		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	–
3		$B(2,6\text{-}F_2C_6H_3)_3$ (**21**)	–
4		$B(2,3,6\text{-}Cl_3C_6H_2)(2,3,6\text{-}F_3C_6H_2)_2$ (**22**)	13

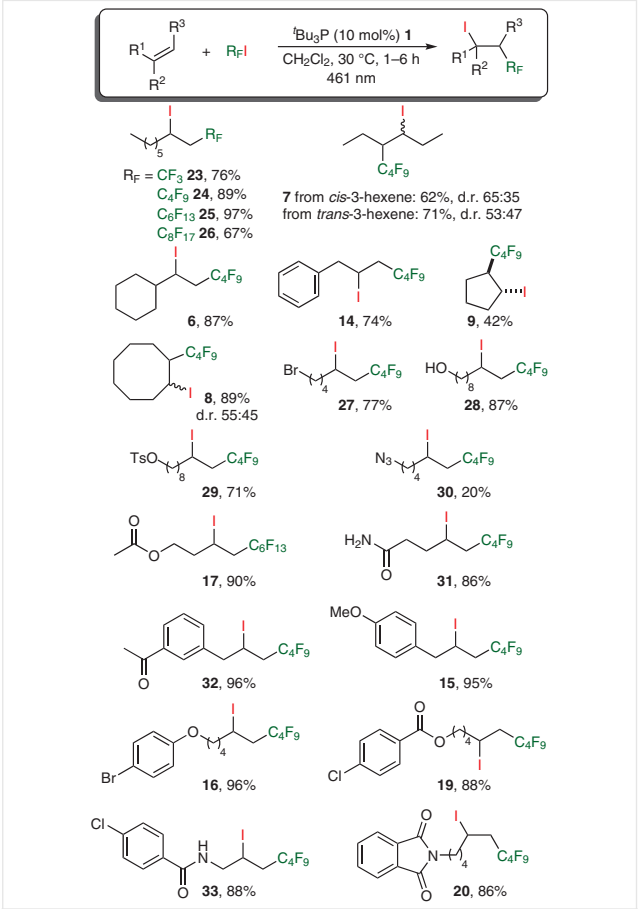
Only in the case of phenylacetylene (Table 1, entry 4) a better yield was obtained by by changing the Lewis acid from $B(C_6F_5)_3$ (**2**) to $B(2,6\text{-}F_2C_6H_3)_3$ (**21**). With respect to the phosphine catalyst partner, we found that only $^tBu_3P$ (**1**) promoted the reaction efficiently.[15] Kinetic experiments on the FLP-catalyzed reaction showed a first-order dependency with respect to the perfluoroalkyl iodide. In the catalytic cycle the phosphine most likely coordinates to the perfluoroalkyl iodide and is involved in a fast-starting reaction, but then conversion slows down rapidly. This initial coordination and interaction can be detected by ^{19}F and ^{31}P NMR spectroscopy. Only a moderate rate increase could be observed when using higher concentrations of the Lewis acid. In contrast, higher concentrations of the alkene slow down the reaction rate, presumably by coordination of the Lewis acid to the double bond as mentioned earlier in the case of an alkyne.[15]

While we investigated the FLP-catalyzed reaction, we obtained more and more evidence for a very efficient competing photocatalytic process involving the perfluoroalkyl iodide and the used phosphine $^tBu_3P$. Therefore, we examined this catalytic reaction in more detail. We started by visible light irradiation of a mixture of 1-octene and C_4F_9I with or without added $^tBu_3P$ under similar conditions as those of the FLP-catalyzed reaction.[20] Surprisingly, we obtained a yield of 89% after a reaction time of 1 hour in the presence of $^tBu_3P$ (10 mol%). Without the phosphine, no conversion was detected after 72 hours and only 32% after 49 days.[20]

Starting from this observation, we aimed at providing a solution for issues described above, such as functional group tolerance or poor alkyne transformation. Screening of different phosphorus compounds showed that other phosphines or phosphites were also capable of catalyzing the reaction, although electron-rich and sterically demanding $^tBu_3P$ (**1**) remained as the most efficient catalyst. Dichloromethane was the best solvent in this case having the additional positive side effect that it can be easily removed from the volatile products.

Reactions at higher wavelengths (531 nm, 29%; 630 nm, 10%) did not lead to complete conversion. Only at 461 nm full conversion was detected after 1 hour. At even lower wavelengths (405 nm), an increasing occurrence of C_4F_9H in the ^1H and ^{19}F NMR spectra could be detected.[20] In contrast to the FLP-catalyzed reaction, various terminal or internal alkenes, carrying polar functional groups, such as alcohols, ethers, esters, and amides, as well as halides, were cleanly transformed in the photocatalytic iodoperfluoroalkylation and good to excellent yields were obtained (Scheme 6).[20] Moreover, alkenes incorporating *E*-configured double bonds were now also suitable substrates. An exception was an azide-functionalized alkene giving a low yield, which was due to the difficulty in the purification process. The potentially expected Staudinger product could not be observed in this reaction. Electron-deficient alkenes still represent difficult substrates as no product could be isolated when ethyl acrylate or related substrates were used (see the Supporting Information).[20]

With these promising results in hand, we next investigated the substrate scope by further extending it towards alkynes (Scheme 7). Using 1-octyne as a model alkyne, we were able to isolate the corresponding addition products as efficiently as for the reactions with alkenes. Terminal, internal and phenylacetylenes gave the corresponding products in 50–98% yield as isomeric mixtures with the *E*-iodoalkene as the major product. In the case of 1-phenyl-1-propyne the configuration was confirmed by crystal structure analysis (see Figure 14 in the Supporting Information,). The carbamate product **48** was obtained in low yield and only the *E*-

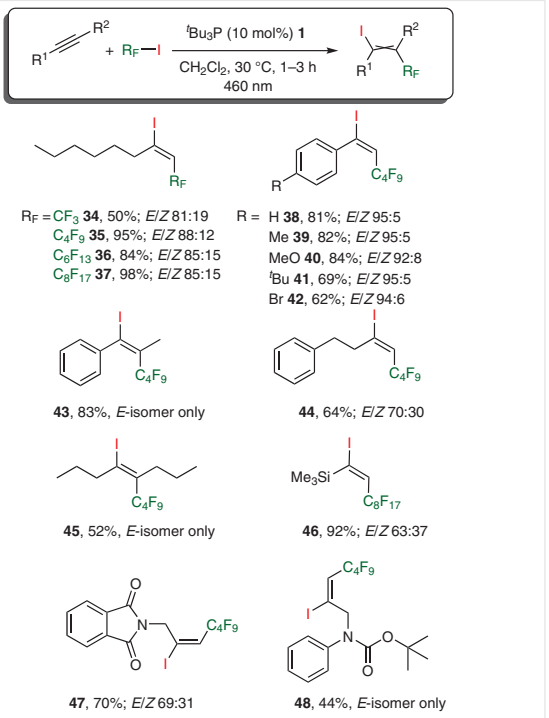


Scheme 6 Photocatalytic iodoperfluoroalkylation of alkenes[20]

isomer was isolated. The *Z*-alkene was not isolated but only detected in the ^{1}H and ^{19}F NMR spectra. Overall, the reaction times were quite similar to those for the transformations of alkenes (1–3 h).

Employing the optimized reaction conditions, we tested the scalability of the reaction and effectively prepared the perfluoroalkylated product of 1-octene (**49**) with C_4F_9I (**4**) in a quantity of 8.90 g (19.5 mmol, 98%).[20] Similarly, 1-octyne (**52**) was transformed into 8.48 g of the corresponding product **35** (18.6 mmol, 93%) (see the Supporting Information).

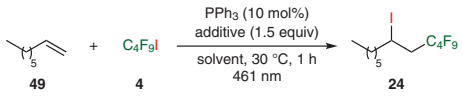
In 2019, Fu et al. published the photocatalytic decarboxylative alkylation with sodium iodide (1.5 equiv) as additive and triphenylphosphine (20 mol%) as the catalyst.[28] We reacted 1-octene (**49**) with C_4F_9I (**4**) under these standard conditions and added sodium iodide (NaI) or tetrabutylammonium iodide (TBAI) in MeCN or CH_2Cl_2, respectively (Table 3). Without an additive, the conversion in CH_2Cl_2 (entry 2) was higher than that in MeCN (entry 1). In theoretical studies (*vide infra*), we found evidence for a Lewis pair interaction between the perfluoroalkyl iodide and solvent molecules.[29a] Given the more pronounced donor ability of



Scheme 7 Photocatalytic iodoperfluoroalkylation of alkynes using tri-*tert*-butylphosphine

the nitrile in this context, competition of the more abundant solvent with the phosphine is likely to result in slower conversion. While the reaction rate substantially increased in acetonitrile in the presence of sodium iodide (entry 3), the more soluble TBAI additive led to a higher conversion in dichloromethane (entry 6).

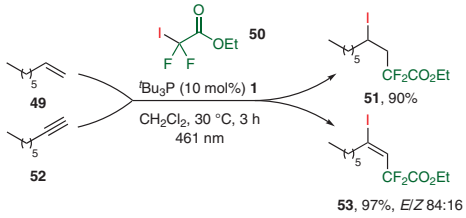
Table 3 Reactions of 1-Octene with C_4F_9I and PPh_3 in the Presence of Iodide Salts



Entry	Solvent	Additive	Conversion (%)
1	MeCN	–	26
2	CH_2Cl_2	–	45
3	MeCN	NaI	68
4	CH_2Cl_2	NaI	56
5	MeCN	TBAI	36
6	CH_2Cl_2	TBAI	66

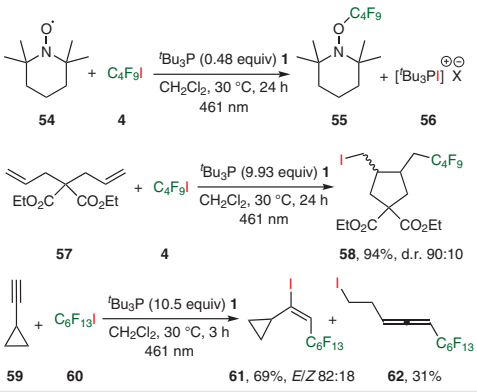
In 2019, Zhao, Li, and He presented the phosphine-catalyzed difluoroalkylation of alkenes.[21] For the reaction with ethyl 2,2-difluoro-1-iodoacetate they used bis(diphenylphosphino)methane (DPPM) as the catalyst (10 mol%) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone

(DMPU) as the additive to reduce the formation of HCF_2COOEt. They conducted this reaction at 80–90 °C in THF for 20–30 hours. It is noteworthy that we were able to perform the addition of ethyl 2,2-difluoro-1-iodoacetate (**50**) to 1-octene (**49**) or 1-octyne (**52**) using $^tBu_3P$ as the catalyst in our setup over 3 hours at room temperature (Scheme 8).



Scheme 8 Phosphine-catalyzed reactions of 1-octene (**49**) and 1-octyne (**52**) with ethyl 2,2-difluoro-1-iodoacetate (**50**)

Mechanistic experiments confirmed the assumption of a radical mechanism. When 2,2,6,6-tetramethylpiperidin-1-yl-oxyl (**54**) (TEMPO) was added as radical scavenger to the reaction mixture the corresponding TEMPO-C_4F_9 product **55** was detected (Scheme 9).



Scheme 9 Radical scavenger and radical clock experiments[20]

By using diethyl 2,2-diallylmalonate (**57**) as the starting material for the iodoperfluoroalkylation, the functionalized cyclopentane derivative **58**, most likely formed via a radical 5-*exo*-*trig*-ring closure, was isolated (Scheme 9). As a second radical clock, we tested ethynylcyclopropane (**59**) and isolated the perfluoroalkylated vinylcyclopropane product **61** together with the ring-opened allene **62** (Scheme 9). Test reactions showed that the addition of nonafluoro-1-iodobutane (**4**) to 1-octene (**49**) was very slow in the absence of the phosphine (32% conversion after 49 d) or without light irradiation (12% conversion after 1 h).[20] We attributed the latter observation to the fact that light could not be completely excluded during the reaction setup or sample withdrawal. An interval irradiation experiment was conducted to demonstrate the requirement of continuous light irradiation (Figure 1). Once a solution of 1-octene (**49**) and C_4F_9I (**4**) together with the catalyst had been irradiated for 1 minute, rapid conversion was detected after the first sample withdrawal. The solution was then stirred in the dark for 20 minutes and only a minor increase in conversion was detected. Next, irradiation was continued in increasing intervals (as depicted) during which complete conversion was observed after 3 hours.

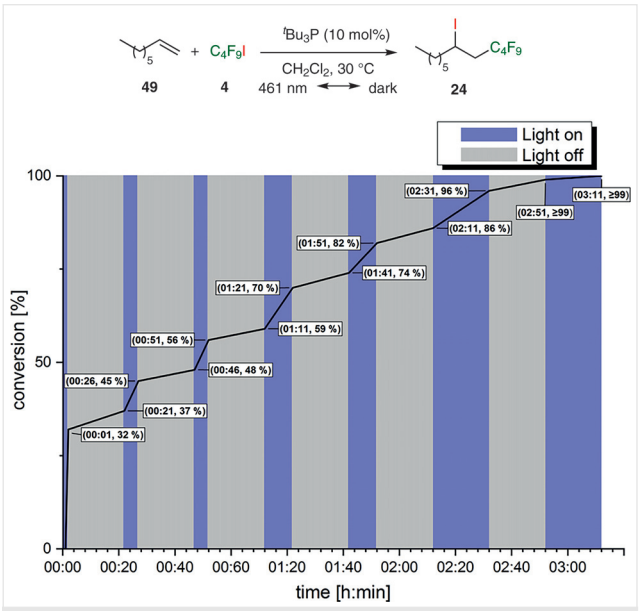
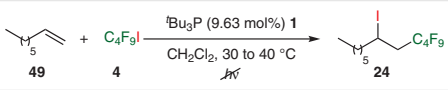


Figure 1 Interval irradiation of the reaction of 1-octene (**49**) with C_4F_9I (**4**)

To exclude the possibility that C_4F_9I is thermally activated by the LEDs, we heated a solution of 1-octene (**49**) and C_4F_9I (**4**) for 1 hour at 30 °C under best possible light exclusion conditions (Scheme 10). After 1 hour at 30 °C, we monitored 29% conversion, and after further heating to reflux for another hour, 34% conversion was observed. This indicates that thermal activation is negligible in this range.



Scheme 10 Reaction at elevated temperatures and under exclusion of light

As is known in the literature, perfluoroalkyl iodides can form a halogen bond (XB) with a Lewis base (LB) such as amines and phosphines.[19a,29] We have already shown that the interaction between C_4F_9I (**4**) and $^tBu_3P$ (**1**) is observable in the ^{19}F and ^{31}P NMR spectra of such a mixture.[15] When we screened various phosphorus(III) compounds as potential catalysts, we observed the best conversions for $^tBu_3P$

(1 h, ≥99%) followed by $(MeO)_3P$ (6 h, 94%) and Ph_3P (2 h, 88%).[20] Noteworthy, $^nBu_3P$ was almost inactive. Using a ^{19}F NMR spectroscopy titration method, we determined the association constants (K_a) for $^tBu_3P$ (14.15 M^{-1}), PPh_3 (0.96 M^{-1}), and $(MeO)_3P$ (0.46 M^{-1}), respectively. Taylor et al. showed that the binding constant differs substantially in various solvents.[30] For this reason, we determined the binding constant in CH_2Cl_2 and used an internal standard as a reference (see the Supporting Information).

During the mechanistic investigations of the photocatalyzed reaction the nature of the light absorption process caught our interest. Interestingly, the reaction solutions containing different phosphine or phosphite catalysts appear completely colorless. Additionally, their UV–vis spectra showed almost no overlap with the blue LED irradiation profile (Figure 2).[29a]

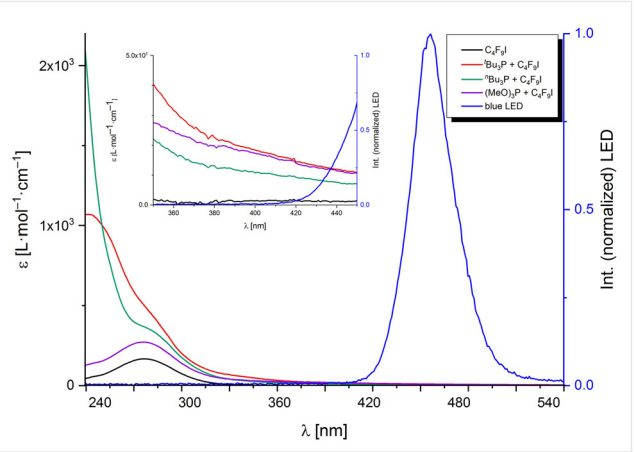


Figure 2 UV–vis absorption spectra of the reaction solutions and the blue LED irradiation profile[29a] Int. = intensity. Intensitiy of the used LED was normalized to 1.

In contrast to sensitizer-mediated processes, for example involving transition-metal photocatalysts, binding of the iodoperfluoroalkane to the phosphine does not result in a red-shift of the absorption maximum. Instead, a significant increase in the absorption coefficient with concomitant broader tailing into the visible light region was found. This could be rationalized by relativistic density functional theory and multireference configuration interaction methods. This detailed study also allowed addressing the seemingly puzzling observation that both $^tBu_3P$ and $P(OMe)_3$ are active catalysts, but that closely related $^nBu_3P$ is not. In the case of the electron-rich and bulky $^tBu_3P$, the high Lewis base donor ability drives the formation of the biradical triplet state. However, the adducts of tri-*n*-butylphosphine show larger coordinate displacements for the ground and the excited state leading to inefficient vibrational wave function overlap. In contrast, phosphites are much less electron-rich but seem to allow for oxygen lone pair participation in the HOMO. In the flexible trimethyl phosphite this is possible for a small fraction of reactive conformers resulting in strong spectral tailing. In contrast, conformationally locked phosphites $(^tBuO)_3P$ or $MeC(CH_2O)_3P$ are both unreactive.

In summary, two metal-free, mild and catalytic (10 mol%) iodoperfluoroalkylations have been compared: One using a frustrated Lewis pair ($BC_6F_5/^tBu_3P$) as the catalyst, and the other a photomediated process catalyzed by just a Lewis base ($^tBu_3P$). It has been shown that FLPs can activate perfluoroalkyl iodides for their reaction with unfunctionalized alkenes.[14] In the presence of functionalized substrates bearing polar substituents or in the transformation of alkynes the original catalyst system is deactivated, presumably by competitive interaction with the highly electron-deficient borane. Reactivity is restored to some extent when employing a modified catalyst system based on partially fluorinated aryl boranes. When $^tBu_3P$ as a Lewis base is used as the sole catalyst and the reaction medium is irradiated by blue light, the restriction in substrate scope is overcome rendering the process more efficient and operationally simple. By forming an electron donor–acceptor (EDA) complex between the Lewis base and the perfluoroalkyl iodide, light-induced radical formation takes place. Various alkenes or alkynes with different polar functional groups are efficiently transformed in good to very good yields. By switching from perfluoroalkylated iodides to ethyl 2,2-difluoro-1-iodoacetate, the corresponding addition products could be obtained as well. Mechanistic investigations using radical clocks or radical scavengers support the assumption of a radical mechanism. Apart from the Lewis acid mediated or photochemically induced activation of the EDA complex, its thermal activation has also been investigated, but this process is not competitive in terms of reaction rate. The association constants for the EDA complexes of different phosphines and phosphites were determined. These studies provide a basis for correlation with theoretical calculations, which have shown the intricacy of the photocatalytic mode of action of phosphorus(III) compounds. It was found that seemingly small variations of the electronic properties and conformational flexibility result in stark differences in the excitation and relaxation profiles. These findings should also contribute to a deeper understanding of related photocatalytic processes involving EDA complexes in general.

Reagents and solvents were purchased from Acros, Sigma-Aldrich, abcr, TCI, J&K Scientific or Avantor. Solvents were dried with a MP-SPS 800 solvent purification system from M. Braun and degassed by freeze-pump-thaw cycles. Reactions were monitored by thin-layer chromatography (TLC) using Macherey-Nagel silica gel plates (ALUGRAM® XtraSIL G/UV_{254}, 0.20 mm thickness). Melting points were recorded on a Büchi B-540 instrument. IR spectra were recorded as films on a NaCl single crystal using a Jasco FT/IR-6200 spectrophotometer. ^1H,^{11}B, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance III 300 and 600 spectrometers. Chemical shifts are reported in

parts per million (ppm) and referenced to the corresponding solvent; m_c = complex multiplet; *E* and *Z* refer to the assigned isomers. High-resolution mass spectrometry (HRMS) was performed with a Bruker Daltonics UHR-QTOF maXis 4G spectrometer. Elemental analyses were recorded on an Elementar Vario Micro Cube.

FLP-Catalyzed Iodoperfluoroalkylation; General Procedure A (GP-A)

Using a glovebox (N_2 atmosphere), $^tBu_3P$ (10 mol%) and the borane (10 mol%) were weighed into an amber glass screw-top vial, dissolved in CH_2Cl_2 (2.1 mL) and a Teflon stir bar was added. The alkene or alkyne substrate and the corresponding perfluoroalkyl iodide (1.10 mmol) were added. The reaction vial was sealed and the contents stirred for the indicated reaction time. The solvent was evaporated under a stream of nitrogen. Purification was conducted by silica gel column chromatography.

Photomediated Iodoperfluoroalkylation; General Procedure B (GP-B)

Using a glovebox (N_2 atmosphere), $^tBu_3P$ (10 mol%) and the alkene or alkyne substrate were weighed into an aluminum-foil-wrapped reaction glass. CH_2Cl_2 (2 mL) and a Teflon stir bar were added. Under red light conditions the corresponding perfluoroalkyl iodide (1.10 mmol) was added. The reaction vial was sealed, transferred into a photoreactor[20] and was irradiated for the indicated time. After the stated reaction time, irradiation was stopped and the solvent was evaporated under a stream of nitrogen. Purification was conducted by silica gel column chromatography.

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

The title compound was prepared following GP-A.

Yield: 114 mg (28%); colorless liquid.

IR (film): 2838, 1613, 1585, 1514, 1467, 1442, 1351, 1246, 1135, 1037, 881, 832, 726, 518 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.18–7.07 (m, 2 H, Ar–H), 6.94–6.82 (m, 2 H, Ar–H), 4.43 (dq, *J* = 8.4, 6.4 Hz, 1 H, –CHI–), 3.81 (s, 3 H, –OMe), 3.28–3.08 (m, 2 H, Ar–CH_2–), 3.01–2.73 (m, 2 H, –CH_2–R_F).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.0, 130.8, 130.2, 114.1, 121.3–110.3 (m, CF_2, CF_3), 55.4, 46.4, 40.6 (t, $^2J_{CF}$ = 20.9 Hz, –$H_2CCF_2R_F$), 20.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.1 (tt, *J* = 9.7, 3.2 Hz, 3 F), –111.6 to –114.7 (m, 2 F), –124.5 to –124.7 (m, 2 F), –125.8 to –126.0 (m, 2 F).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{13}F_9IO$: 494.9862; found: 494.9857.

1-Bromo-4-[(7,7,8,8,9,9,10,10,10-nonafluoro-5-iododecyl)oxy]benzene (16)[17]

The title compound was prepared following GP-A.

Yield: 349 mg (80%); light yellow oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.33 (m, 2 H), 6.81–6.73 (m, 2 H), 4.35 (tt, *J* = 8.2, 5.3 Hz, 1 H), 3.95 (t, *J* = 6.0 Hz, 2 H), 3.07–2.66 (m, 2 H), 1.98–1.68 (m, 5 H), 1.68–1.54 (m, 1 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.0 (tt, *J* = 9.6, 3.3 Hz), –111.2 to –113.0 (m), –113.6 to –116.1 (m), –124.3 to –124.8 (m), –125.7 to –126.1 (m).

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-3-iododecyl Acetate (17)

The title compound was prepared following GP-A.

Yield: 333 mg (76%); colorless liquid.

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

^1H NMR (600 MHz, $CDCl_3$): δ = 4.45–4.36 (m, 1 H, –CH_2CO_2–), 4.35–4.27 (m, 1 H, –CHI–), 4.21–4.10 (m, 1 H, –CH_2CO_2–), 3.03–2.90 (m, 1 H, R_FCH_2–), 2.90–2.76 (m, 1 H, R_FCH_2–), 2.22–2.14 (m, 1 H, –CH_2CH_2–), 2.14–2.07 (m, 1 H, –CH_2CH_2–), 2.08–2.02 (m, 3 H, –CH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.8, 119.7–108.7 (m, CF_2, CF_3), 64.2, 42.0 (t, $^2J_{CF}$ = 20.8 Hz, –$H_2CCF_2R_F$), 39.0, 20.9, 15.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.8 (tt, *J* = 10.1, 2.6 Hz, 3 F), –110.9 to –115.1 (m, 2 F), –121.6 to –122.0 (m, 2 F), –122.7 to –123.1 (m, 2 F), –123.5 to –123.9 (m, 2 F), –126.0 to –126.4 (m, 2 F).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{11}F_{13}IO_2$: 560.9591; found: 560.9593.

4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptyl Acetate (18)

The title compound was prepared following GP-A.

Yield: 92.2 mg (25%); colorless liquid.

IR (film): 2958, 1750, 1432, 1382, 1356, 1233, 1135, 1043, 1026, 881, 739, 725 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 3.98–3.79 (m, 3 H, –CHI–, R_FCH_2–), 2.57–2.22 (m, 2 H, –CH_2CO_2–), 1.56 (s, 3 H, –CH_3).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 169.1, 121.2–110.5 (m, CF_2, CF_3), 68.4, 37.9 (t, $^2J_{CF}$ = 21.2 Hz, –$H_2CCF_2R_F$), 20.0, 12.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.0 to –81.3 (m, 3 F), –112.4 to –114.8 (m, 2 F), –124.2 to –124.5 (m, 2 F), –125.7 to –126.1 (m, 2 F).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_8F_9INaO_2$: 468.9318; found: 468.9316.

6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodononyl 4-Chlorobenzoate (19)[17]

The title compound was prepared following GP-A.

Yield: 364 mg (87%); colorless oil.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.00–7.93 (m, 2 H), 7.47–7.38 (m, 2 H), 4.46–4.32 (m, 3 H), 3.09–2.69 (m, 2 H), 2.14–1.84 (m, 4 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.1 (tt, *J* = 9.7, 3.3 Hz), –111.1 to –112.4 (m), –114.4 to –115.5 (m), –124.4 to –124.8 (m), –125.7 to –126.2 (m).

2-(7,7,8,8,9,9,10,10,10-Nonafluoro-5-iododecyl)isoindoline-1,3-dione (20)[17]

The title compound was prepared following GP-A; yield: 135 mg (58%); light brown oil

^1H NMR (300 MHz, $CDCl_3$): δ = 7.90–7.77 (m, 2 H), 7.77–7.67 (m, 2 H), 4.30 (tt, *J* = 8.1, 5.3 Hz, 1 H), 3.71 (t, *J* = 7.1 Hz, 2 H), 3.06–2.64 (m, 2 H), 1.93–1.57 (m, 5 H), 1.53–1.40 (m, 1 H).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.01 (tt, *J* = 9.7, 3.3 Hz), –111.01 to –112.75 (m), –114.04 to –115.89 (m), –124.23 to –124.79 (m), –125.40 to –126.64 (m).

1,1,1-Trifluoro-3-iodonon-2-ene (34)[31a]

1,1,1-Trifluoro-3-iodonon-2-ene (**34**) was synthesized using a procedure similar to GP-B. $^tBu_3P$ (**1**) and 1-octene (**49**) were dissolved in this case before a balloon with CF_3I was connected.

Yield: 79.5 mg (50%, *E*/*Z* = 81:19); colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.39 (q, *J* = 7.7 Hz, 1 H, ClC*H*, *E*), 6.29 (qt, *J* = 7.2, 1.4 Hz, 1 H, ClC*H*, *Z*), 2.63–2.57 (m, 2 H, CH_2ClCH), 1.60–1.53 (m, 2 H, CH_2CH$_2$ClCH), 1.34–1.27 [m, 6 H, CH$_3$(CH_2)$_3$CH$_2$ClCH], 0.90 (t, *J* = 6.7 Hz, 3 H, CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –57.81 (s, CF_3, *E*), –60.00 (s, CF_3, *Z*).

1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodododec-5-ene (35)[31]

Following GP-A: Yield: 158.9 mg (44%, *E*/*Z* = 1.0:0.42); colorless liquid.

Following GP-B: Yield: 243 mg (95%, *E*/*Z* = 89:11); colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.32 (t, *J* = 14.5 Hz, 1 H, ClC*H*, *E*), 6.24 (t, *J* = 13.1 Hz, 1 H, ClC*H*, *Z*), 2.67 (t, *J* = 7.2 Hz, 2 H, CH_2ClCH, *Z*), 2.63 (t, *J* = 7.5 Hz, 2 H, CH_2ClCH, *E*), 1.61–1.55 (m, 2 H, CH_2CH$_2$ClCH), 1.36–1.27 [m, 6 H, CH$_3$(CH_2)$_3$CH$_2$ClCH], 0.90 (t, *J* = 6.9 Hz, 3 H, CH_3).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.92 to –81.13 (m, 3 F, CF_3), –105.55 to –105.67 (m, 2 F, CF_2, *E*), –108.65 to –108.76 (m, 2 F, CF_2, *Z*), –123.85 to –123.99 (m, 2 F, CF_2, *Z*), –124.11 to –124.31 (m, 2 F, CF_2, *E*), –125.71 to –125.92 (m, 2 F, CF_2).

1,1,1,2,2,3,3,4,4,5,5,6,6-Tridecafluoro-8-iodotetradec-7-ene (36)[32]

The title compound was prepared following GP-B.

Yield: 262 mg (84%, *E*/*Z* = 85:15); colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.32 (t, *J* = 14.4 Hz, 1 H, ClC*H*, *E*), 6.24 (t, *J* = 13.2 Hz, 1 H, ClC*H*, *Z*), 2.69–2.65 (m, 2 H, CH_2ClCH, *Z*), 2.65–2.60 (m, 2 H, CH_2ClCH, *E*), 1.62–1.55 (m, 2 H, CH_2ClCH), 1.35–1.26 [m, 6 H, CH$_3$(CH_2)$_3$CH$_2$ClCH], 0.93–0.87 (m, 3 H, CH_3).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.75 to –80.89 (m, 3 F, CF_3), –105.40 (t, *J* = 13.3 Hz, 2 F, CF_2, *E*), –108.46 (t, *J* = 13.2 Hz, 2 F, CF_2, *Z*), –121.50 to –121.83 (m, 2 F, CF_2), –122.70 to –122.92 (m, 2 F, CF_2), –122.92 to –123.06 (m, 2 F, CF_2, Z), –123.21 to –123.38 (m, 2 F, CF_2), –125.99 to –126.25 (m, 2 F, CF_2).

9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluoro-7-iodohexadec-7-ene (37)[31a]

Yield: 343 mg (98%, *E*/*Z* = 85:15); colorless liquid.

9,9,10,10,11,11,12,12,13,13,14,14,15,15,16,16,16-Heptadecafluoro-7-iodohexadec-7-ene (**37**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) and 1-octyne (**52**) were dissolved in this case before addition of $C_8F_{17}I$ under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.32 (t, *J* = 14.4 Hz, 1 H, ClC*H*, *E*), 6.23 (t, *J* = 13.1 Hz, 1 H, ClC*H*, *Z*), 2.68 (t, *J* = 6.9 Hz, 2 H, CH_2ClCH, *Z*), 2.63 (t, *J* = 7.7 Hz, 2 H, CH_2ClCH, *E*), 1.60–1.55 (m, 2 H, CH_2CH$_2$ClCH), 1.33–1.27 [m, 6 H, CH$_3$(CH_2)$_3$CH$_2$ClCH], 0.90 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.80 (t, *J* = 9.9 Hz, 3 F, CF_3), –105.40 (t, *J* = 13.4 Hz, 2 F, CF_2, *E*), –108.46 (t, *J* = 13.3 Hz, 2 F, CF_2, *Z*), –121.33 to –121.58 (m, 2 F, CF_2), –121.75 to –122.07 (m, 5 F, CF_2), –122.60 to –122.83 (m, 3 F, CF_2), –122.87 to –123.02 (m, 2 F, CF_2, *Z*), –123.17 to –123.35 (m, 2 F, CF_2), –125.99 to –126.29 (m, 2 F, CF_2).

(3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodohex-1-en-1-yl)benzene (38)[33]

The title compound was prepared following GP-B.

Yield: 202 mg (81%, *E*/*Z* = 95:5); colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.35 (m, 5 H, Ar–H, *Z*), 7.35–7.27 (m, 5 H, Ar–H, *E*), 6.59 (t, *J* = 13.3 Hz, 1 H, ClC*H*, *E*), 6.54–6.46 (m, 1 H, ClC*H*, *Z*).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.89 to –80.99 (m, 3 F, CF_3, *Z*), –81.05 (t, *J* = 9.6 Hz, 3 F, CF_3, *E*), –105.44 (t, *J* = 12.6 Hz, 2 F, CF_2, *E*), –109.08 to –109.26 (m, 2 F, CF_2, *Z*), –123.60 to –123.97 (m, 2 F, CF_2), –125.56 to –125.76 (m, 2 F, CF_2, *Z*), –125.76 to –125.99 (m, 2 F, CF_2, *E*).

1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (39)[31a]

1-Methyl-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (**39**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) was dissolved in this case before addition of 1-ethynyl-4-methylbenzene and C_4F_9I (**4**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 201.6 mg (82%, *E*/*Z* = 95:5); light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (m_c, 2 H, Ar–H, *Z*), 7.21 (d, *J* = 8.3 Hz, 2 H, Ar–H, *E*), 7.14 (d, *J* = 8.2 Hz, 2 H, Ar–H, *E*), 7.03 (mc, 2 H, Ar-H, Z), 6.57 (t, *J* = 13.4 Hz, 1 H, –C*H*–R_F, *E*), 6.47 (t, *J* = 1.2 Hz, 1 H, –C*H*–R_F, *Z*), 2.39 (s, 3 H, Ar–CH_3, *Z*), 2.36 (s, 3 H, Ar–CH_3, *E*).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.88 to –80.97 (m, 3 F, CF_3, *Z*), –80.98 to –81.12 (m, 3 F, CF_3, *E*), –105.20 to –105.43 (m, 2 F, CF_2, *E*), –108.83 to –109.02 (m, 2 F, CF_2, *Z*), –123.76 to –123.93 (m, 2 F, CF_2, *E*), –125.64 to –125.75 (m, 2 F, CF_2, *Z*), –125.76 to –125.95 (m, 2 F, CF_2, *E*).

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

1-Methoxy-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (**40**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) was dissolved in this case before addition of 4-methoxyphenylacetylene and C_4F_9I (**4**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 220 mg (84%, *E*/*Z* = 92:8); yellow liquid.

IR (film): 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 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (m_c, 2 H, Ar-H, *Z*), 7.27 (m_c, 2 H, Ar-H, *E*), 6.89 (m_c, 2 H, Ar-H, *Z*), 6.85 (m, 2 H, Ar-H, *E*), 6.56 (t, *J* = 13.9 Hz, 1 H, -C*H*-R_F, *E*), 6.43 (t, *J* = 13.4 Hz, 1 H, -C*H*-R_F, *Z*), 3.85 (s, 3 H, OCH_3, *Z*), 3.83 (s, 3 H, OCH_3, *E*).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 160.4, 133.8, 135.7 (m, CF_2, CF_3), 129.0 (t, *J* = 2.61 Hz), 123.2–115.5 (m, CF_2, CF_3), 126.4 (t, *J* = 21.8 Hz), 113.9, 113.7 (t, *J* = 6.0 Hz), 113.5, 55.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.94 (tt, *J* = 9.9, 3.1 Hz, 3 F, CF_3, *Z*), –81.04 (tt, *J* = 9.6, 3.2 Hz, 3 F, CF_3, *E*), –105.00 to –105.18 (m, 2 F, *E*), –108.52 to –108.69 (m, 2 F, *Z*), –123.67 to –123.77 (m, 2 F, *E*), –123.76 to –123.96 (m, 2 F, *Z*), –125.63 to –125.76 (m, 2 F, *Z*), –125.77 to –125.96 (m, 2 F, *E*).

Anal. Calcd for $C_{13}H_8F_9IO$: C, 32.66; H, 1.69. Found: C, 32.61; H, 1.73.

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

1-(*tert*-Butyl)-4-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohex-1-en-1-yl)benzene (**41**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) was dissolved in this case before addition of 4-*tert*-butylphenylacetylene and C_4F_9I (**4**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 192.7 mg (69%, *E*/*Z* = 95:5); light yellow oil.

IR (film): 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 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.36-7.32 (m_c, 2 H, Ar-H, *E*) 7.31-7.42 (m_c, 2 H, Ar-H, *Z*), 7.32-7.14 (m_c, 2 H, Ar-H, *Z*), 6.51 (t, *J* = 13.8 Hz, 1 H, C*H*I, *E*), 6.43 (t, *J* = 13.4 Hz, 1 H, C*H*I, *Z*), 1.27 (s, 9 H, *Z*), 1.26 (s, 9 H, *E*).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 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), 34.9, 31.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.92 to –81.00 (m, 3 F, CF_3, *Z*), –81.06 (tt, *J* = 9.3, 2.7 Hz, 3 F, CF_3, *E*), –105.06 to –105.40 (m, 2 F, CF_2, *E*), –108.80 to –109.14 (m, 2 F, CF_2, *Z*), –123.65 to –124.08 (m, 2 F, CF_2), –125.65 to –126.06 (m, 2 F, CF_2).

Anal. Calcd for $C_{16}H_{14}F_9I$: C, 38.12; H, 2.80. Found: C, 38.19; H, 2.81.

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

The title compound was prepared following GP-B.

Yield: 173.4 mg (62%, *E*/*Z* = 94:6); light yellow oil.

IR (film): 3065, 1902, 1780, 1638, 1584, 1561, 1484, 1393, 1352, 1296, 1235, 1134, 1072, 1057, 1028, 1013, 923, 906, 891, 873, 816, 761, 745, 713, 693, 668, 636, 590, 562, 529 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (m_c, 2 H, Ar–H, *Z*), 7.48 (m_c, 2 H, Ar–H, *E*), 7.35 (m_c, 2 H, Ar–H, *Z*), 7.17 (m_c, 2 H, Ar–H, *E*), 6.61 (t, *J* = 13.4 Hz, 1 H, –C*H*–R_F, *E*), 6.50 (d, *J* = 12.8 Hz, 1 H, –C*H*–R_F, *Z*).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 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, CF_2, CF_3), 111.1 (t, *J* = 6.34 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.98 to –81.16 (m), –105.47 (t, *J* = 11.2 Hz), –109.40 (t, *J* = 12.2 Hz), –123.68 to –123.92 (m), –125.65 to –125.77 (m), –125.75 to –125.97 (m).

Anal. Calcd for $C_{12}H_5BrF_9I$: C, 27.35; H, 0.96. Found: C, 27.60; H, 0.85.

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

The title compound was prepared following GP-B.

Yield: 218.8 mg (83%); colorless crystals; mp 72.4–76.9 °C.

IR (film): 3081, 3061, 3019, 2973, 2934, 2869, 2548, 2433, 2401, 2337, 1959, 1891, 1809, 1767, 1633, 1594, 1575, 1489, 1443, 1389, 1350, 1300, 1244, 1216, 1198, 1173, 1137, 1106, 1073, 1013, 999, 919, 881, 872, 861, 833, 765, 740, 707, 698, 674, 648, 624, 602, 569, 553, 532 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.33–7.18 (m, 5 H, Ar–H), 2.30 (s, 3 H, $–CH_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 144.3, 130.1 (t, *J* = 20.80 Hz), 128.3, 127.8, 126.9, 119.4–110.5 (m, CF_2, CF_3), 115.0 (t, *J* = 4.50 Hz), 26.8.

^{19}F NMR (565 MHz, $CDCl_3$): δ = –81.01 (t, *J* = 9.3 Hz, 3 F, CH_3), –103.30 to –103.49 (m, 2 F, CF_2), –120.39 to –120.60 (m, 2 F, CF_2), –126.11 to –126.35 (m, 2 F, CF_2).

Anal. Calcd for $C_{13}H_8F_9I$: C, 33.79; H, 1.75. Found: C, 33.95; H, 1.68.

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

(5,5,6,6,7,7,8,8,8-Nonafluoro-3-iodooct-3-en-1-yl)benzene (**44**) was synthesized using a procedure similar to GP-B. $^tBu_3P$ (**1**) was dissolved in this case before addition of 4-phenyl-1-butyne and C_4F_9I (**4**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 169.1 mg (64%, *E*/*Z* = 70:30); colorless liquid.

IR (film): 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 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (m_c, 2 H, Ar–H, *E*), 7.26 (m_c, 3 H, Ar–H, *E*), 6.39 (t, *J* = 14.4 Hz, 1 H, –C*H*–R_F, *E*), 2.95 (m, 4 H, Ar-CH_2-CH_2-Cl, *E*).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.5, 128.8, 128.7, 127.1 (t, *J* = 23.9 Hz), 126.7, 121.1 (t, *J* = 6.3 Hz), 119.8–113.8 (m, CF_2, CF_3), 43.6 (t, *J* = 3.0 Hz), 36.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.04 (m, 3 F, CF_3), –105.91 to –106.17 (m, 2 F), –124.03 to –124.38 (m, 2 F), –125.63 to –125.97 (m, 2 F).

Anal. Calcd for $C_{14}H_{10}F_9I$: C, 35.32; H, 2.12. Found: C, 35.21; H, 2.07.

(*E*)-6,6,7,7,8,8,9,9,9-Nonafluoro-4-iodo-5-propylnon-4-ene (45)[14]

The title compound was prepared following GP-B.

Yield: 125.2 mg (52%); colorless liquid.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.69 (t, *J* = 7.6 Hz, 2 H, $ClC_{RF}H_2$), 2.46–2.23 (m, 2 H, H_2ClC_{RF}), 1.79–1.46 [m, 4 H, $(CH_3(CH_2))_2$], 0.95 [dt, *J* = 12.7, 7.3 Hz, 6 H, $(CH_3(CH_2))_2$].

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.97 (t, *J* = 9.8 Hz, 3 F, CF_3), –102.96 (t, *J* = 14.9 Hz, 2 F, CF_2), –122.11 to –122.38 (m, 2 F, CF_2), –125.95 to –126.22 (m, 2 F, CF_2).

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iododec-1-en-1-yl)trimethylsilane (46)[34]

(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iododec-1-en-1-yl)trimethylsilane (**46**) was synthesized using a procedure similar to GP-B. $^tBu_3P$ (**1**) and trimethylsilylacetylene were dissolved in this case before addition of perfluorooctyl iodide under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 315.3 mg (92%, *E*/*Z* = 63:37); colorless liquid.

IR (film): 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 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (t, *J* = 15.7 Hz, 1 H, –C*H*–R_F, *E*), 7.03 (t, *J* = 13.5 Hz, 1 H, –C*H*–R_F, *Z*), 0.36 (t, *J* = 1.5 Hz, 9 H, $–SiMe_3$, *E*), 0.30 (s, 5 H, 9 H, $–SiMe_3$, *Z*).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 139.3 (t, *J* = 23.1 Hz), 131.9 (t, *J* = 23.0 Hz), 129.3, 123.8–107.7, 1.2, –1.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.61 to –81.80 (m, 3 F), –106.03 to –106.31 (m, 2 F), 109.44 to –109.61 (m, 2 F), –121.79 to –122.22 (m, 2 F), –122.17 to –122.64 (m, 4 F), –122.89 to –123.14 (m, 1 F), –123.14 to –123.47 (m, 3 F), –126.61 to –126.93 (m, 2 F).

2-(4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodohept-2-en-1-yl)isoindoline-1,3-dione (47)

The title compound was prepared following GP-B.

Yield: 201.4 mg (70%, *E*/*Z* = 69:31); colorless crystals; mp 58.5–59.5 °C.

IR (film): 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 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.97–7.85 (m, 2 H, Ar–H), 7.83–7.72 (m, 2 H, Ar–H), 6.62 (t, *J* = 15.0 Hz, 1 H, –C*H*–R_F), 4.72–4.64 (m, 2 H, N–CH_2–Cl).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.1, 134.6, 131.9, 128.6 (t, *J* = 24.5 Hz), 123.9, 119.8–110.3 (m, CF_2, CF_3), 116.9 (t, *J* = 5.8 Hz), 43.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –80.96 (tt, *J* = 9.2, 2.9 Hz, 3 F), –105.42 to –106.68 (m, 2 F), –123.41 to –124.25 (m, 2 F), –125.19 to –126.45 (m, 2 F).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{15}H_{11}F_9IN_2O_2$: 548.9721; found: 548.9715.

tert-Butyl (4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodohept-2-en-1-yl)(phenyl)carbamate (48)

tert-Butyl (4,4,5,5,6,6,7,7,7-nonafluoro-2-iodohept-2-en-1-yl)(phenyl)carbamate (**48**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) was dissolved in this case before addition of *N*-(*tert*-butoxycarbonyl)-*N*-(prop-2-ynyl)aniline and C_4F_9I (**4**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 135.7 mg (44%); colorless liquid.

IR (film): 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 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (m_c, 5 H, Ar–H), 6.43 (t, *J* = 15.2 Hz, 1 H, –C*H*–R_F, *E*), 4.66 (s, 2 H, N–C*H*$_2$–Cl), 1.48 (s, 9 H, C*H*$_3$).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 157.4, 154.3, 141.1, 128.9, 127.3, 126.8, 121.9–114.4 (m, CF_2, CF_3), 81.7, 77.4, 54.1, 28.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –81.06 (tt, *J* = 9.7, 2.9 Hz, 3 F), –105.65 to –106.14 (m, 2 F), –123.92 to –124.28 (m, 2 F), –125.65 to –126.07 (m, 2 F).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{18}H_{21}F_9IN_2O_2$: 595.0504; found 595.0493.

Ethyl 2,2-Difluoro-4-iododecanoate (51)[21,24]

Yield: 170.1 mg (90%); colorless liquid.

Ethyl 2,2-difluoro-4-iododecanoate (**51**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) and 1-octene (**49**) were dissolved in this case before addition of ethyl difluoroiodoacetate (**50**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.34 (q, *J* = 7.2 Hz, 2 H), 4.29–4.12 (m, 1 H), 3.02–2.79 (m, 1 H), 2.80–2.62 (m, 1 H), 1.89–1.64 (m, 2 H), 1.63–1.40 (m, 1 H), 1.40–1.16 (m, 10 H), 0.93–0.82 (m, 3 H).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –101.32 to –102.71 (m, 1 F), –105.65 to –107.62 (m, 1 F).

Ethyl 2,2-Difluoro-4-iododec-3-enoate (53)[32]

Ethyl 2,2-difluoro-4-iododec-3-enoate (**53**) was synthesized using a procedure similar to GP-B. ^{t}Bu$_3$P (**1**) and 1-octyne (**52**) were dissolved in this case before addition of ethyl difluoroiodoacetate (**50**) under a stream of nitrogen and with the best possible light exclusion outside the glovebox.

Yield: 187 mg (97%, *E*/*Z* = 84:16); colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.40 (t, *J* = 13.2 Hz, 1 H, *E*), 6.37–6.31 (m, 1 H, *Z*), 4.45–4.38 (m, 2 H, *Z*), 4.33 (q, *J* = 7.2 Hz, 2 H, *E*), 2.64–2.54 (m, 2 H, *E*), 1.56–1.51 (m, 2 H, *E*), 1.40–1.27 (m, 9 H, *E*), 0.94–0.84 (m, 3 H, *E*).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –97.72 (s, 1 F, *E*), –97.89 (s, 1 F, *Z*).

(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)cyclopropane (61)[32]

The title compound was prepared following GP-B.

Yield 241 mg. In a mixture with product **62**. (69%, *E*/*Z* = 82:18); colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.39 (t, *J* = 14.8 Hz, 1 H, *E*), 6.37–6.27 (m, 1 H, *Z*), 1.76–1.64 (m, 1 H, *Z*), 1.57–1.45 (m, 1 H, *E*), 0.89–0.82 (m, 4 H).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.84 (t, *J* = 10.0 Hz, *E*), –104.51 (t, *J* = 13.5 Hz, *E*), –107.29 (t, *J* = 13.4 Hz, *Z*), –121.40 to –122.05 (m, 2 F), –122.64 to –123.08 (m, 2 F), –123.08 to –123.43 (m, 2 F), –125.99 to –126.37 (m, 2 F).

6,6,7,7,8,8,9,9,10,10,11,11,11-Tridecafluoro-1-iodoundeca-3,4-diene (62)[32]

The title compound was prepared following GP-B.

Yield 241 mg. In a mixture with product **61**. (31%); colorless liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.83–5.69 (m, 1 H), 5.56–5.40 (m, 1 H), 3.21 (td, *J* = 7.1, 1.1 Hz, 2 H), 2.70 (tdd, *J* = 7.0, 2.9 Hz, 2 H).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.84 (t, *J* = 10.0 Hz), –108.23 (t, *J* = 13.2 Hz), –107.29 (t, *J* = 13.4 Hz), –121.40 to –122.05 (m, 2 F), –122.64 to –123.08 (m, 2 F), –123.08 to –123.43 (m, 2 F), –125.99 to –126.37 (m, 2 F).

(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodooct-1-en-1-yl)benzene (70)[35]

Following GP-A with $B(C_6F_5)_3$: Yield: 48.5 mg (10%); colorless liquid.

Following GP-A with $B(2,6\text{-}F_2C_6H_3)_3$: Yield: 92.6 mg (20%); colorless liquid.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38–7.35 (m, 5 H, Ar–H, *Z*), 7.35–7.27 (m, 5 H, Ar–H, *E*), 6.59 (t, *J* = 13.3 Hz, 1 H, ClC*H*, *E*), 6.54–6.46 (m, 1 H, ClC*H*, *Z*).

^{19}F NMR (565 MHz, $CDCl_3$): δ = –80.89 to –80.99 (m, 3 F, CF_3, *Z*), –81.05 (t, *J* = 9.6 Hz, 3 F, CF_3, *E*), –105.44 (t, *J* = 12.6 Hz, 2 F, CF_2, *E*), –109.08 to –109.26 (m, 2 F, CF_2, *Z*), –123.60 to –123.97 (m, 2 F, CF_2), –125.56 to –125.76 (m, 2 F, CF_2, *Z*), –125.76 to –125.99 (m, 2 F, CF_2, *E*).

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Supporting Information

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