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苯基吩噻嗪多孔有机聚合物催化的非活化末端烯烃的卤代全氟烷基化反应

王 睿[†,a] 高 朗[†,a] 周 岑[b] 张 霄[*,a]
([a]福建师范大学化学与材料学院 福建省先进材料化工基础重点实验室 福建省高分子材料重点实验室 福州 350007)
([b]闽江学院材料与化学工程学院 福建省中国漆新型材料工程研究中心 福州 350108)

摘要 以苯基吩噻嗪多孔有机聚合物作为无金属、可回收的异相光催化剂, 在可见光的作用下实现了非活化末端烯烃的氯代三氟甲基化和碘代全氟烷基化反应, 高效地合成了一系列具有重要价值的含氟化合物.
关键词 氯代三氟甲基化; 非均相; 多孔有机聚合物; 可循环; 无过渡金属

Haloperfluoroalkylation of Unactivated Terminal Alkenes over Phenylphenothiazine-Based Porous Organic Polymers

Wang, Rui[†,a] Gao, Lang[†,a] Zhou, Cen[b] Zhang, Xiao[*,a]
([a] *Fujian Key Laboratory of Polymer Materials*, *Fujian Provincial Key Laboratory of Advanced Materials Oriented Chemical Engineering*, *College of Chemistry and Materials Science*, *Fujian Normal University*, *Fuzhou 350007*)
([b] *Fujian Engineering and Research Center of New Chinese Lacquer Materials*, *College of Materials and Chemical Engineering*, *Minjiang University*, *Fuzhou 350108*)

Abstract Photocatalytic heterogeneous chlorotrifluoromethylation and iodoperfluoroalkylation of unactivated terminal alkenes have been achieved under the catalysis of phenylphenothiazine-based porous organic polymer (PTH-POP). This method offers a transition-metal-free and recyclable platform to access valuable perfluoroalkylated compounds in a highly efficient fashion.
Keywords chlorotrifluoromethylation; heterogeneous; porous organic polymer; recyclability; transition-metal-free

1 Introduction

The high-value utilization of renewable energy represents a promising solution to address the energy crises and the associated environmental problems. In this regard, the development of photocatalysts that are capable of converting abundant solar energy into chemical energy has received privileged attention.[1] Due to the outstanding photophysical properties, homogeneous ruthenium-/iridium-based polypyridyl complexes are the most frequently used. However, the catalyst residual issues as well as high price and strong toxicity of noble metals are recognized as significant disadvantages. Thus, the implementation of heterogeneous photocatalysts, particularly in a metal-free fashion for sustainable organic synthesis is highly desirable.[2-3]

Trifluoromethyl (CF_3) group is regarded as one of the most important structural motifs in the realm of medicinal chemistry because its incorporation into small molecules often enhances lipophilicity, binding selectivity, metabolic stability, and bioavailability.[4] Continuing efforts have been devoted to selectively introducing these fluorine-containing substituents.[5] Particularly, trifluoromethylation-chloration difunctionalization of alkenes constitutes a straightforward and useful method.[6] However, a brief survey of the literature reveals that heterogeneous approaches to chlorotrifluoromethylation of alkenes are much

* Corresponding author. E-mail: zhangxiao@fjnu.edu.cn
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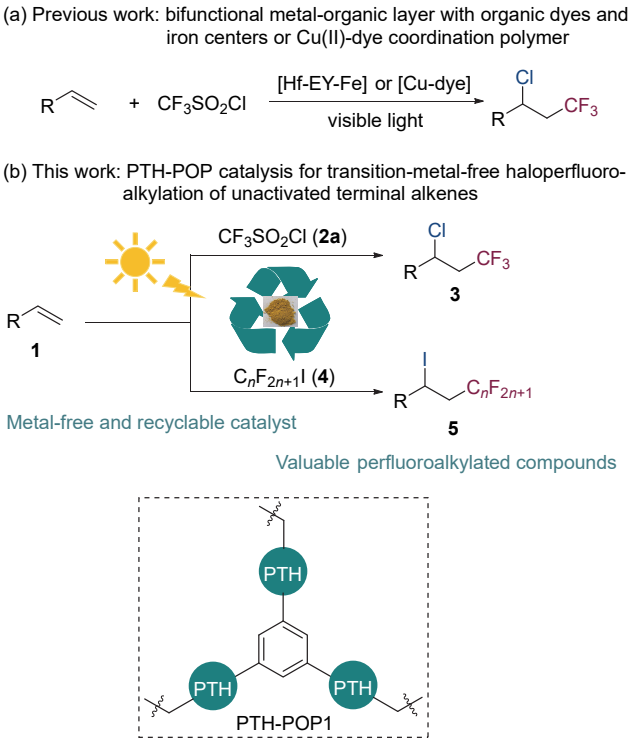
† 共同第一作者(These authors contributed equally to this work).

less explored, possibly due to the lack of suitable heterogeneous photocatalysts. In this regard, the groups of Lin[7] and Duan[8] have independently developed a bifunctional metal-organic layer with organic dyes and iron centers, and Cu(II)-dye coordination polymer for synergistically catalyzing chlorotrifluoromethylation of alkenes, respectively (Scheme 1a). The two examples are of significance; nevertheless, transition-metals were used in both cases, which is not ideal from the perspective of green chemistry.



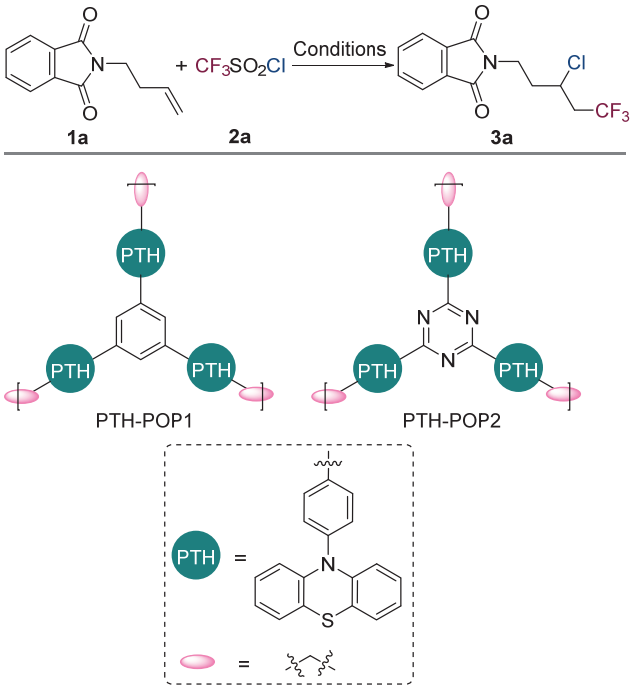
Scheme 1 Photocatalytic heterogeneous chlorotrifluoromethylation of alkenes

On the other hand, *N*-phenylphenothiazines (PTHs) have been emerged as excellent photocatalysts in organic synthesis. However, ultraviolet-light irradiation is required to access their excited states, which somewhat hampered the wide applications.[9a-9d] To circumvent the problem, PTH-based porous organic polymers (PTH-POP1 and PTH-POP2) as a class of metal-free, stable, and reusable visible-light heterogeneous photocatalysts were recently introduced.[9e] Notably, the structural manipulation and polymeric networks not only allow visible-light absorption, but also enable divergent bromoalkylation and cyclopropanation of unactivated terminal alkenes by simply tuning the solvents. As our continuing study, we envisioned that PTH-POP catalysis might provide a complementary method toward the synthesis of valuable fluoroalkylated compounds in a transition-metal free fashion. Here heterogeneous transition-metal-free chlorotrifluoromethylation of unactivated terminal alkenes has been achieved over PTH-POP catalysis. In addition, this method can be applicable to iodoperfluoroalkylation under slightly modified conditions (Scheme 1b).[10]

2 Results and discussion

At the outset, the model reactions between unactivated terminal alkene (**1a**) and CF_3SO_2Cl (**2a**) were investigated using K_2HPO_4 as the base and acetonitrile as the solvent. Under irradiation with blue LEDs, both PTH-POP1 and PTH-POP2 provided the desired yields (Table 1, Entries 1～2). After screening of the bases including Na_2HPO_4, $NaHCO_3$, Et_3N, and 1,5-dizzabicyclo[5.4.0]undecen-5-ene (DBU), it was confirmed that K_2HPO_4 was optimal (Table 1, Entries 3～6). Notably, the reaction could proceed even without any external base (Table 1, Entry 7). Further optimizations revealed that the solvents had a profound effect

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Base	Solvent	Yield[b]/% of **3a**
1	PTH-POP1	K_2HPO_4	CH_3CN	96 (88)[c]
2	PTH-POP2	K_2HPO_4	CH_3CN	95
3	PTH-POP1	Na_2HPO_4	CH_3CN	94
4	PTH-POP1	$NaHCO_3$	CH_3CN	57
5	PTH-POP1	Et_3N	CH_3CN	47
6	PTH-POP1	DBU	CH_3CN	22
7	PTH-POP1	—	CH_3CN	89
8	PTH-POP1	K_2HPO_4	DMF	37
9	PTH-POP1	K_2HPO_4	Acetone	79
10	PTH-POP1	K_2HPO_4	THF	39
11	PTH-POP1	K_2HPO_4	DCE	94
12[d]	—	K_2HPO_4	CH_3CN	0
13[e]	PTH-POP1	K_2HPO_4	CH_3CN	0

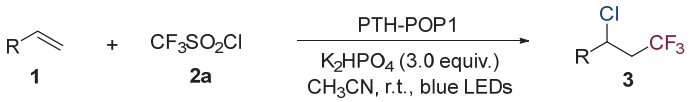
[a] Reaction conditions: a solution of catalyst (4.0 mg), **1a** (0.2 mmol, 1.0 equiv.), **2a** (3.0 equiv.), and base (3.0 equiv.) in the indicated solvent (1.6 mL, 0.125 mol/L) was irradiated by blue LEDs (30 W) at room temperature under nitrogen atmosphere for 26 h. [b] Determined by ^1H NMR yield using CH_2Br_2 as an internal standard. [c] Isolated yield. [d] Without a catalyst. [e] Under dark conditions.

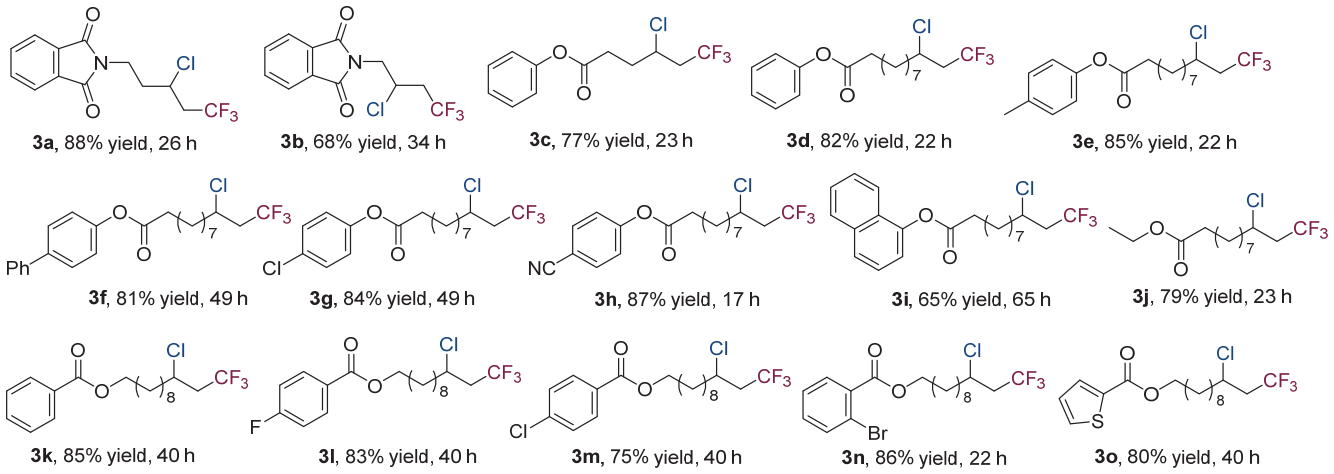
on the reaction outcome and acetonitrile gave the best yield (96% yield, Entries 1, 8～11). Finally, the control reactions performed either in the absence of a catalyst or under dark conditions failed to give any conversion, demonstrating the importance of both visible light and photocatalysts (Entries 12～13).

With the optimized reaction conditions in hand, the substrate scope for chlorotrifluoromethylation of alkenes was evaluated (Table 2). A variety of unactivated terminal olefins bearing diverse functionalities were well accommodated, furnishing the corresponding chlorotrifluoromethylated products **3a**～**3o** in 65%～88% yields. For instance, the reactions of ester-tethered alkenes possessing either an electron-donating (Me) or electron-withdrawing group (F, Cl, Br, CN) on the aromatic rings, regardless of the chain length all occurred smoothly. Notably, the aliphatic and heteroaryl esters were also viable substrates, thereby delivering **3j** and **3o** in 79% and 80% yields, respectively.

Next, we were delighted to discover that iodoperfluoroalkylation of unactivated terminal alkenes was readily achieved under slightly modified conditions. By employing sodium ascorbate as the additive and the mixture of acetonitrile and methanol as the solvent instead, the model reaction of alkene **1a** with C_4F_9I (**4a**) proceeded well to afford the expected product **5a** in excellent yield in the presence of PTH-POP1 or PTH-POP2 upon irradiation with blue LEDs (Table 3, Entries 1～2). Purely organic reductants such as *N*,*N*-diisopropylethylamine (DIPEA) and Et_3N also proved feasible (Table 3, Entries 3～4). Finally, the control experiments confirmed that a reductant,

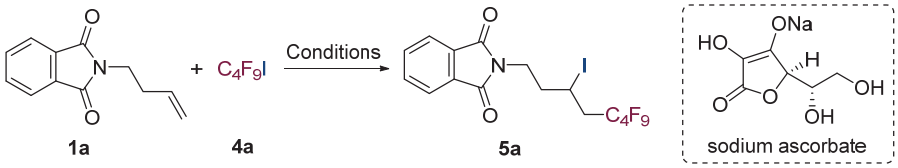
Table 2 Substrate scope for chlorotrifluoromethylation of unactivated terminal alkenes[a,b]





[a] Reaction conditions: a solution of PTH-POP1 (5.9 mg), **1** (0.3 mmol), **2a** (0.9 mmol, 3.0 equiv.), and K_2HPO_4 (0.9 mmol, 3.0 equiv.) in CH_3CN (2.4 mL, 0.125 mol/L) was irradiated by blue LEDs (30 W) at room temperature under nitrogen atmosphere. [b] Isolated yield.

Table 3 Optimization of the reaction conditions[a]



Entry	Catalyst	Reductant	Solvent	Yield[b]/% of **5a**
1	PTH-POP1	Sodium ascorbate	CH_3CN/CH_3OH	99 (86)[c]
2	PTH-POP2	Sodium ascorbate	CH_3CN/CH_3OH	97
3	PTH-POP1	DIPEA	CH_3CN/CH_3OH	79
4	PTH-POP1	Et_3N	CH_3CN/CH_3OH	96
5[d]	PTH-POP1	—	CH_3CN/CH_3OH	5
6[e]	—	Sodium ascorbate	CH_3CN/CH_3OH	2
7[f]	PTH-POP1	Sodium ascorbate	CH_3CN/CH_3OH	0

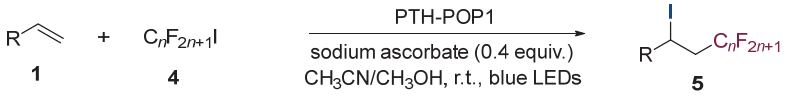
[a] Reaction conditions: a solution of PTH-POP1 (4.0 mg), **1a** (0.2 mmol), **4a** (0.3 mmol, 1.5 equiv.), and reductant (0.08 mmol, 0.4 equiv.) in CH_3CN/CH_3OH (V∶V=4∶3, 1.75 mL) was irradiated by blue LEDs (30 W) at room temperature under nitrogen atmosphere for 11 h. [b] Determined by ^1H NMR yield using CH_2Br_2 as an internal standard. [c] Isolated yield. [d] Without sodium ascorbate. [e] Without a catalyst. [f] Under dark conditions.

a photocatalyst and visible-light irradiation are all essential, as their absence shut down the reaction dramatically (Table 3, Entries 5～7). The scope with respect to olefins was then explored (Table 4). Similarly, a series of amides or ester-tethered alkenes could be transformed into the corresponding perfluoroalkyl tagged iodides **5a** ～ **5j** (83%～99% yields). Changing the perfluoroalkylation reagent to $C_8F_{17}I$ also proved feasible, leading to the formation of **5k** in 54% yield.

To gain insights into the reaction mechanisms, the control experiments were performed in the presence of various scavengers under standard conditions (Figure 1). Both chlorotrifluoromethylation and iodoperfluoroalkylation reactions were completely inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) was present, confirming the operation of radical processes in each case. Moreover, the addition of $CuSO_4$ as an electron scavenger and KI as a hole scavenger uniformly deteriorated the formation of the corresponding products (**3a** and **5a**). These results suggested that the electron and hole intermediates were involved in these transformations.

Based on the experimental observations and known literatures,[6,10] the reaction mechanisms for photocatalytic chlorotrifluoromethylation and iodoperfluoroalkylation of unactivated terminal alkenes were proposed. As shown in Figure 2, POP absorbs visible light to generate its excited state species POP* (POP: PTH-POP1). The chlorotrifluoromethylation reaction was initiated by oxidatively quenching of POP* with CF_3SO_2Cl (−0.18 V vs SCE)[11] to produce $POP^{\bullet+}$ and CF_3 radical upon the release of sulfur dioxide and the chloride ion. The CF_3 radical then adds to

Table 4 Substrate scope for iodoperfluoroalkylation of unactivated terminal alkenes[a,b]



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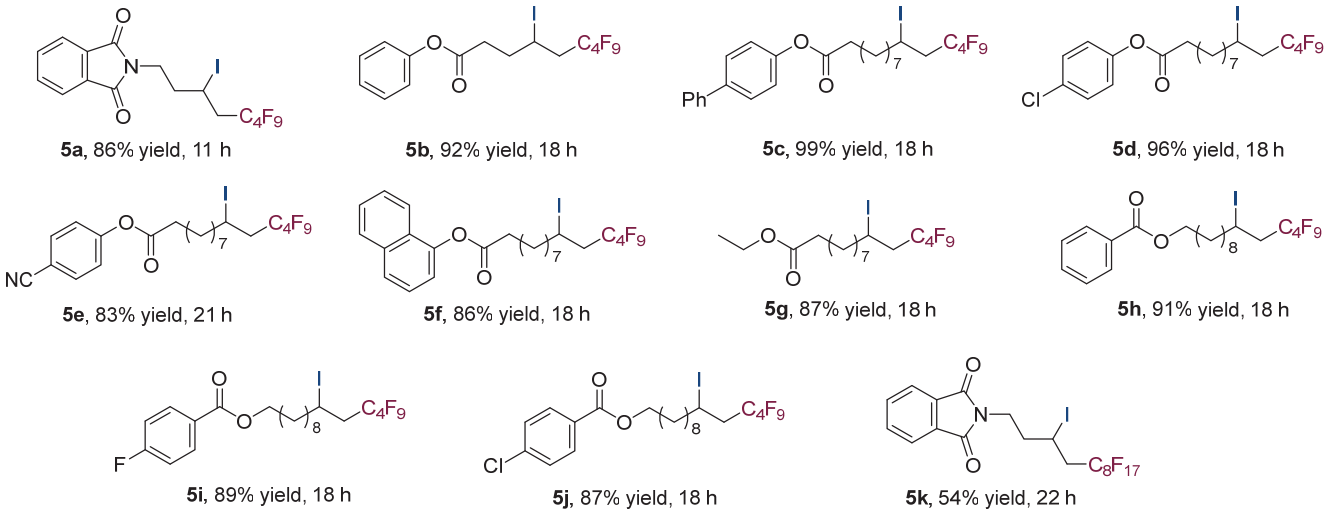

[a] Reaction conditions: a solution of PTH-POP1 (4.0 mg), **1** (0.2 mmol), **4** (0.3 mmol, 1.5 equiv.), and sodium ascorbate (0.08 mmol, 0.4 equiv.) in CH_3CN/CH_3OH (V∶V=4∶3, 1.75 mL) was irradiated by blue LEDs (30 W) at room temperature under nitrogen atmosphere. [b] Isolated yield.

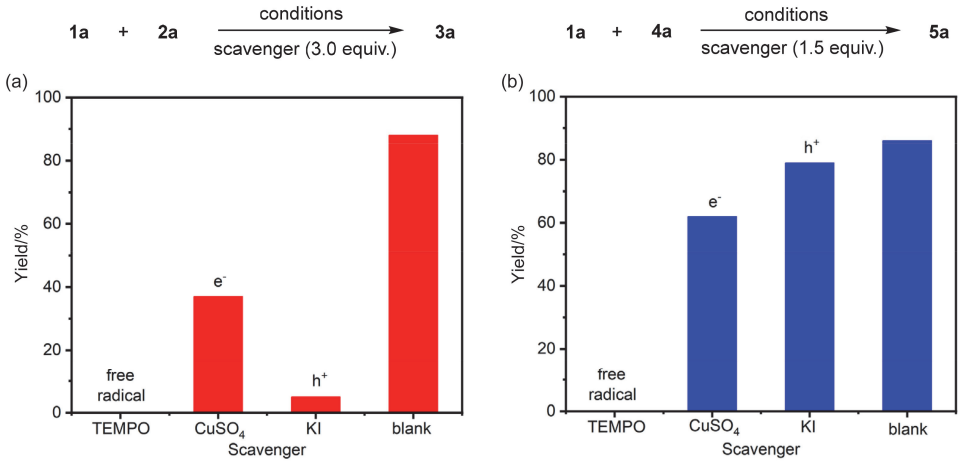

Figure 1 Effect of scavengers on chlorotrifluoromethylation (a) and iodoperfluoroalkylation (b) of unactivated terminal alkenes

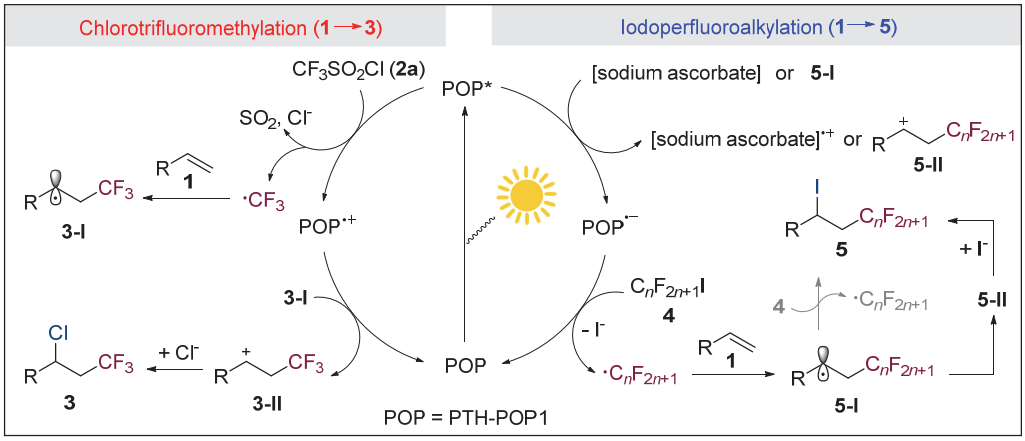

Figure 2 Proposed mechanisms for photocatalytic chlorotrifluoromethylation (left) and iodoperfluoroalkylation (right) of unactivated terminal alkenes

alkene **1** to form **3-I**. Single-electron oxidation of **3-I** by $POP^{\bullet+}$ affords cation **3-II** and meanwhile completes the catalytic cycle. The corresponding chlorotrifluoromethylation product **3** can be obtained after nucleophilic trapping by chloride ion. Notably, the iodoperfluoroalkylation reaction only proceeds with the addition of sodium ascorbate, which acts as a reductant to convert POP* into reduced $POP^{\bullet-}$. Then $POP^{\bullet-}$ is capable of donating an electron to $C_nF_{2n+1}I$ to produce C_nF_{2n+1} radical, which undergoes addition to alkene **1**. The iodoperfluoroalkylation compound **5** can subsequently be delivered via radical-polar crossover mechanism. Notably, the chain processes[12] might be excluded based on the quantum yields determined for both reactions.

Lastly, the recycling experiments regarding chlorotrifluoromethylation of unactivated terminal alkenes were conducted. The catalyst PTH-POP1 can easily be separated from the reaction mixtures through filtration and reused for at least five cycles without obvious decline in the photocatalytic activity (Figure 3a). By employing a single batch of catalyst added at the beginning, the sequential formation of **3h**, **3g**, **3i**, **3e**, and **3k** was achieved in comparable yields to those with fresh catalyst (Figure 3b). Thus, PTH-POP1 functions as a metal-free and recyclable photocatalyst for the synthesis of valuable perfluoroalkylated compounds.

3 Conclusions

In summary, the heterogeneous chlorotrifluoromethylation and iodoperfluoroalkylation of unactivated terminal alkenes have been realized over phenylphenothiazine-based porous organic polymers. The salient features of this method include a metal-free and reusable photocatalyst, mild reaction conditions, and wide substrate scope. A variety of important multi-fluorinated compounds can be accessed in a precisely controlled fashion with a single operation. This study represents a rare example on the applications of POPs in fluorine chemistry.[13]

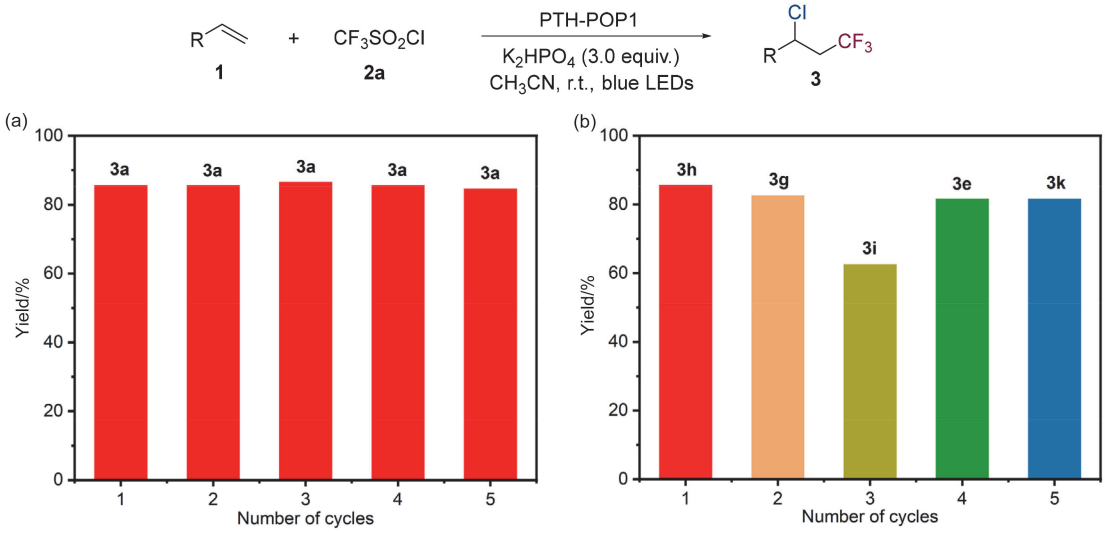

Figure 3 Recycling experiments: (a) formation of **3a**, and (b) sequential formation of **3h**, **3g**, **3i**, **3e** and **3k**

Reaction conditions: a solution of PTH-POP1 (5.9 mg), **1** (0.3 mmol), **2a** (0.9 mmol, 3.0 equiv.), and K_2HPO_4 (0.9 mmol, 3.0 equiv.) in CH_3CN (2.4 mL, 0.125 mol/L) was irradiated by blue LEDs (30 W) at room temperature under nitrogen atmosphere.

4 Experimental section

4.1 Instruments and reagents

Melting points were determined on an INESA Physico-Optical Instrument SGW X-4A Microscopic melting point apparatus. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker instrument (400 MHz, 100 MHz and 376 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protic solvent signals. High resolution mass spectrum (HRMS) were obtained on an Agilent qtof 6540 LC-MS (ESI) mass spectrometer with the use of quadrupole analyzer. Fourier transform infrared spectra were recorded on a Nicolet iS50 FT-IR spectrophotometer. Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry nitrogen atmosphere. All reagents were commercially purchased and used without any further purification.

4.2 General procedure for photocatalytic chlorotrifluoromethylation of unactivated terminal alkenes

To a sealed tube were added the substrate **1** (0.3 mmol, 1.0 equiv.), **2a** (0.9 mmol, 3 equiv.), PTH-POP1 (5.9 mg), K_2HPO_4 (0.9 mmol, 3 equiv.), and acetonitrile (2.4 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 2～3 cm from 30 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by thin-layer chromatography, TLC) under nitrogen atmosphere. Afterwards, the catalyst and K_2HPO_4 were separated by filtration and washed with dichloromethane. Then the filtrate was concentrated by rotary evaporation and the residue was purified by silica gel flash column chromatography using ethyl acetate/petroleum ether as the eluent to afford the desired products **3**.

2-(3-Chloro-5,5,5-trifluoropentyl)isoindoline-1,3-dione (**3a**):[6b] White solid, 55.0 mg, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89～7.84 (m, 2H), 7.76～7.72 (m, 2H), 4.20～4.14 (m, 1H), 3.98～3.85 (m, 2H), 2.76～2.56 (m, 2H), 2.33～2.25 (m, 1H), 2.17～2.08 (m, 1H).

2-(2-Chloro-4,4,4-trifluorobutyl)isoindoline-1,3-dione (**3b**):[6d] White solid, 64.5 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92～7.88 (m, 2H), 7.80～7.75 (m, 2H), 4.56～4.49 (m, 1H), 4.09～3.93 (m, 2H), 2.72～2.63 (m, 2H).

Phenyl 4-chloro-6,6,6-trifluorohexanoate (**3c**): Colorless oil, 62.0 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 (t, J=8.0 Hz, 2H), 7.24 (t, J=7.6 Hz, 1H), 7.08 (d, J=7.6 Hz, 2H), 4.31～4.24 (m, 1H), 2.91～2.52 (m, 4H), 2.39～2.31 (m, 1H), 2.12～2.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 150.4, 129.5, 126.0, 125.0 (q, J=275.0 Hz), 121.4, 53.1 (q, J=3.0 Hz), 42.5 (q, J=28.0 Hz), 32.8, 30.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.70 (t, J=11.3 Hz); IR (film) ν_{max}: 2927, 1755, 1593, 1493, 1424, 1388, 1242, 1194, 1135, 1082, 1024, 935, 814, 755, 690, 666, 631, 500, 434, 415 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{16}ClF_3NO_2$ $[M+NH_4]^+$ 298.0816, found 298.0815.

Phenyl 10-chloro-12,12,12-trifluorododecanoate (**3d**): Colorless oil, 86.0 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (t, J=7.2 Hz, 2H), 7.24～7.20 (m, 1H), 7.07 (d, J=8.4 Hz, 2H), 4.13～4.07 (m, 1H), 2.67～2.45 (m, 4H), 1.86～1.69 (m, 4H), 1.59～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 150.7, 129.3, 125.7, 125.3 (q, J=276.0 Hz), 121.5, 54.1 (q, J=3.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 34.3, 29.14, 29.05, 29.0, 28.7, 25.8, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.80 (t, J=11.3 Hz); IR (film) ν_{max}: 2928, 2856, 1757, 1593, 1493, 1457, 1388, 1240, 1195, 1138, 930, 814, 749, 690, 665, 631, 499 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{28}ClF_3NO_2$ $[M+NH_4]^+$ 382.1755, found 382.1754.

p-Tolyl 10-chloro-12,12,12-trifluorododecanoate (**3e**): White solid, 94.5 mg, 85% yield. m.p. 29.1～31.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16 (d, J=8.8 Hz, 2H), 6.94 (d, J=8.4 Hz, 2H), 4.13～4.07 (m, 1H), 2.69～2.47 (m, 4H), 2.33 (s, 3H), 1.86～1.69 (m, 4H), 1.57～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 148.5, 135.3, 129.8, 125.3 (q, J=276.0 Hz), 54.1 (q, J=3.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 34.3, 29.1, 29.04, 28.96, 28.7, 25.8, 24.9, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.80 (t, J=11.3 Hz); IR (film) ν_{max}: 2925, 2856, 1743, 1508, 1469, 1390, 1336, 1274, 1236, 1198, 1140, 1117, 1092, 1057, 1020, 920, 837, 817, 752, 725, 668, 626, 578, 506, 451 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{30}ClF_3NO_2$ $[M+NH_4]^+$ 396.1912, found 396.1911.

[1,1'-Biphenyl]-4-yl 10-chloro-12,12,12-trifluorododecanoate (**3f**): White solid, 108.7 mg, 81% yield. m.p. 30.9～34.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (t, J=8.4 Hz, 4H), 7.41 (t, J=8.0 Hz, 2H), 7.32 (t, J=8.0 Hz, 1H), 7.14 (d, J=8.8 Hz, 2H), 4.13～4.06 (m, 1H), 2.66～2.44 (m, 4H), 1.85～1.68 (m, 4H), 1.58～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 150.1, 140.3, 138.8, 128.7, 128.0, 127.3, 127.0, 125.3 (q, J=276.0 Hz), 121.8, 54.1 (q, J=3.0 Hz), 42.3 (q, J=29.0 Hz), 38.0, 34.3, 29.1, 29.04, 28.95, 28.7, 25.8, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.72 (t, J=11.3 Hz); IR (film) ν_{max}: 2929, 2850, 1758, 1518, 1486, 1391, 1336, 1276, 1233, 1207, 1187, 1168, 1133, 1061, 1008, 918, 850, 769, 743, 696, 667, 635, 578, 549, 496, 455 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}ClF_3NO_2$ $[M+NH_4]^+$ 458.2068, found 458.2067.

4-Chlorophenyl 10-chloro-12,12,12-trifluorododecanoate (**3g**): White solid, 100.1 mg, 84% yield. m.p. 52.5～55.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (d, J=8.8 Hz, 2H), 7.02 (d, J=8.4 Hz, 2H), 4.14～4.07 (m, 1H), 2.68～2.46 (m, 4H), 1.86～1.69 (m, 4H), 1.56～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 149.2, 131.0, 129.4, 125.3 (q, J=275.0 Hz), 54.1 (q, J=3.0 Hz), 42.4 (q, J=29.0 Hz), 38.0, 34.2, 29.1, 29.0, 28.9, 28.7, 25.8, 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.80 (t, J=11.3 Hz); IR (film) ν_{max}: 2927, 2849, 1743, 1489, 1471, 1395, 1276, 1231, 1201, 1146, 1120, 1089, 1059, 1029, 1015, 948, 922, 835, 807, 753, 723, 666, 630, 576, 503, 433 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}Cl_2F_3NO_2$ $[M+NH_4]^+$ 416.1365, found 416.1365.

4-Cyanophenyl 10-chloro-12,12,12-trifluorododecanoate

(**3h**): White solid, 103.0 mg, 87% yield. m.p. 64.1～67.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70～7.67 (m, 2H), 7.24～7.21 (m, 2H), 4.14～4.08 (m, 1H), 2.69～2.47 (m, 4H), 1.87～1.70 (m, 4H), 1.60～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 154.0, 133.6, 125.2 (q, J=276.0 Hz), 122.7, 118.2, 109.5, 54.1 (q, J=3.0 Hz), 42.3 (q, J=28.0 Hz), 37.9, 34.2, 29.1, 29.0, 28.9, 28.7, 25.8, 24.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.79 (t, J=11.3 Hz); IR (film) ν_{max}: 2928, 2853, 2228, 1748, 1601, 1500, 1471, 1396, 1276, 1232, 1207, 1167, 1121, 1088, 1059, 1029, 927, 851, 835, 752, 723, 665, 628, 549, 473 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{27}ClF_3N_2O_2$ $[M+NH_4]^+$ 407.1708, found 407.1707.

Naphthalen-1-yl 10-chloro-12,12,12-trifluorododecanoate (**3i**): Yellow oil, 78.0 mg, 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88～7.85 (m, 2H), 7.74 (q, J=8.0 Hz, 1H), 7.52～7.44 (m, 3H), 7.26～7.23 (m, 1H), 4.14～4.08 (m, 1H), 2.74 (t, J=7.2 Hz, 2H), 2.66～2.47 (m, 2H), 1.90～1.70 (m, 4H), 1.51～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 146.6, 134.7, 128.0, 126.9, 126.4, 125.9, 125.4, 121.1, 118.1, 54.2 (q, J=3.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 34.4, 29.2, 29.1, 28.8, 25.9, 25.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.80 (t, J=11.3 Hz); IR (film) ν_{max}: 2928, 2855, 1758, 1599, 1508, 1389, 1224, 1123, 914, 797, 773, 631, 553 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{30}ClF_3NO_2$ $[M+NH_4]^+$ 432.1912, found 432.1912.

Ethyl 10-chloro-12,12,12-trifluorododecanoate (**3j**): Colorless oil, 71.0 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.15～4.07 (m, 3H), 2.69～2.47 (m, 2H), 2.29 (t, J=7.2 Hz, 2H), 1.86～1.24 (m, 17H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.8, 125.3 (q, J=276.0 Hz), 60.1, 54.1 (q, J=4.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 34.3, 29.14, 29.06, 29.0, 28.7, 25.8, 24.9, 14.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.88 (t, J=7.5 Hz); IR (film) ν_{max}: 2929, 2857, 1732, 1464, 1373, 1241, 1146, 1036, 836, 725, 666, 631 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{28}Cl$- F_3NO_2 $[M+NH_4]^+$ 334.1755, found 334.1754.

10-Chloro-12,12,12-trifluorododecyl benzoate (**3k**): Colorless oil, 91.1 mg, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (d, J=7.2 Hz, 2H), 7.55 (t, J=7.6 Hz, 1H), 7.44 (t, J=7.6 Hz, 2H), 4.32 (t, J=6.4 Hz, 2H), 4.14～4.07 (m, 1H), 2.68～2.46 (m, 2H), 1.86～1.69 (m, 4H), 1.54～1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.7, 132.8, 130.5, 129.5, 128.3, 125.3 (q, J=275.0 Hz), 65.1, 54.2 (q, J=3.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 29.33, 29.27, 29.2, 28.8, 28.7, 26.0, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.82 (t, J=11.3 Hz); IR (film) ν_{max}: 2921, 2852, 1756, 1520, 1487, 1470, 1352, 1216, 1168, 1131, 1020, 1007, 880, 850, 769, 741, 723, 692, 510, 410 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{30}ClF_3NO_2$ $[M+NH_4]^+$ 396.1912, found 396.1911.

10-Chloro-12,12,12-trifluorododecyl 4-fluorobenzoate (**3l**): White solid, 97.9 mg, 83% yield. m.p. 26.9～28.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.08～8.03 (m, 2H), 7.11 (t, J=8.4 Hz, 2H), 4.31 (t, J=6.8 Hz, 2H), 4.14～4.07 (m, 1H), 2.69～2.47 (m, 2H), 1.87～1.69 (m, 4H), 1.54～1.28 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.70, 165.69 (d, J=251.0 Hz), 132.0 (d, J=9.0 Hz), 125.3 (q, J=281.0 Hz), 115.4 (d, J=22.0 Hz), 65.2, 54.2 (q, J=4.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 29.33, 29.28, 29.2, 28.8, 28.7, 26.0, 25.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.83 (t, J=11.3 Hz, 3F), −105.98～−106.08 (m, 1F); IR (film) ν_{max}: 2928, 2856, 1760, 1599, 1508, 1463, 1390, 1350, 1217, 1132, 1014, 879, 797, 773, 723, 553 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{29}ClF_4NO_2$ $[M+NH_4]^+$ 414.1817, found 414.1817.

10-Chloro-12,12,12-trifluorododecyl 4-chlorobenzoate (**3m**): White solid, 91.8 mg, 75% yield. m.p. 99.1～104.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (d, J=8.8 Hz, 2H), 7.41 (d, J=8.8 Hz, 2H), 4.31 (t, J=6.8 Hz, 2H), 4.14～4.07 (m, 1H), 2.67～2.47 (m, 2H), 1.86～1.69 (m, 4H), 1.54～1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 139.2, 130.9, 128.9, 128.6, 125.3 (q, J=276.0 Hz), 65.3, 54.1 (q, J=4.0 Hz), 42.4 (q, J=29.0 Hz), 38.0, 29.31, 29.26, 29.15, 28.8, 28.6, 25.9, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.82 (t, J=11.3 Hz); IR (film) ν_{max}: 2927, 2856, 1718, 1452, 1350, 1314, 1272, 1218, 1133, 1070, 1027, 879, 711, 688 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{26}Cl_2F_3O_2$ $[M+H]^+$ 413.1256, found 413.2652.

10-Chloro-12,12,12-trifluorododecyl 2-bromobenzoate (**3n**): Colorless oil, 118.6 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.77 (d, J=6.8 Hz, 1H), 7.65 (d, J=7.6 Hz, 1H), 7.38～7.30 (m, 2H), 4.34 (t, J=6.8 Hz, 2H), 4.14～4.06 (m, 1H), 2.68～2.46 (m, 2H), 1.86～1.69 (m, 4H), 1.55～1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.3, 134.2, 132.6, 132.3, 131.1, 127.1, 125.3 (q, J=276.0 Hz), 121.5, 65.7, 54.1 (q, J=4.0 Hz), 42.4 (q, J=28.0 Hz), 38.0, 29.3, 29.2, 29.1, 28.7, 28.5, 25.9, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.81 (t, J=11.3 Hz); IR (film) ν_{max}: 2928, 2856, 1729, 1647, 1591, 1502, 1433, 1408, 1292, 1239, 1145, 1107, 1044, 1028, 1012, 968, 951, 929, 855, 821, 804, 761, 745, 674, 627, 576, 494, 427, 415, 403 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{29}BrClF_3NO_2$ $[M+NH_4]^+$ 476.0997, found 476.0996.

10-Chloro-12,12,12-trifluorododecyl thiophene-2-carboxylate (**3o**): Colorless oil, 78.0 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J=3.6 Hz, 1H), 7.54 (d, J=5.2 Hz, 1H), 7.09 (t, J=4.4 Hz, 1H), 4.29 (t, J=6.8 Hz, 2H), 4.14～4.07 (m, 1H), 2.68～2.46 (m, 2H), 1.86～1.69 (m, 4H), 1.54～1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.3, 134.1, 133.2, 132.1, 127.6, 125.3 (q, J=276.0 Hz), 65.2, 54.1 (q, J=4.0 Hz), 42.3 (q, J=28.0 Hz), 38.0, 29.3, 29.2, 29.1, 28.7, 28.6, 25.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −63.82 (t, J=11.3 Hz); IR (film) ν_{max}: 2927, 2855, 1707, 1526, 1465, 1419, 1387, 1359, 1259, 1144, 1094, 860, 751, 721, 665, 631 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{28}ClF_3NO_2S$ $[M+NH_4]^+$ 402.1476, found 402.1476.

4.3 General procedure for photocatalytic iodoperfluoroalkylation of unactivated terminal alkenes

To a sealed tube were added the substrate **1** (0.2 mmol, 1.0 equiv.), **4** (0.3 mmol, 1.5 equiv.), PTH-POP1 (4.0 mg),

sodium ascorbate (0.08 mmol, 0.4 equiv.), methanol (0.75 mL) and acetonitrile (1.0 mL). The reaction mixture was degassed via freeze-pump-thaw for 3 cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 2～3 cm from 30 W blue LEDs. The mixture was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the catalyst was separated by filtration and washed with dichloromethane. Then the filtrate was concentrated by rotary evaporation and the residue was purified by silica gel flash column chromatography using ethyl acetate/petroleum ether as the eluent to afford the desired products **5**.

2-(8,8,8,8,8,8,8,8,8-Nonafluoro-3-iodo-8λ^{12}-octa-5,7-diyn-1-yl)isoindoline-1,3-dione (**5a**): White solid, 98.0 mg, 86% yield. m.p. 64.6～69.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88～7.86 (m, 2H), 7.75～7.73 (m, 2H), 4.35～4.28 (m, 1H), 3.96～3.80 (m, 2H), 3.04～2.79 (m, 2H), 2.35～2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 134.1, 131.9, 123.4, 41.4 (t, J=21.0 Hz), 38.6, 38.2, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.01～−81.08 (m, 3F), −110.52～−115.00 (m, 2F), −124.51～−124.60 (m, 2F), −125.87～−125.98 (m, 2F); IR (film) ν_{max}: 2932, 1770, 1704, 1464, 1435, 1402, 1374, 1354, 1330, 1213, 1179, 1128, 1099, 1073, 1027, 1004, 983, 869, 840, 800, 763, 720, 690, 648, 619, 552, 531, 515, 415 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{15}F_9IN_2O_2$ $[M+NH_4]^+$ 565.0029, found 565.0027.

Phenyl 9,9,9,9,9,9,9,9,9-nonafluoro-4-iodo-9λ^{12}-nona-6,8-diynoate (**5b**): Colorless oil, 92.3 mg, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.37 (m, 2H), 7.26～7.22 (m, 1H), 7.11～7.07 (m, 2H), 4.50～4.43 (m, 1H), 3.07～2.73 (m, 4H), 2.34～2.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6, 150.5, 129.5, 126.0, 121.4, 41.7 (t, J=20.0 Hz), 35.2, 34.7, 18.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −80.99～−81.05 (m, 3F), −111.28～−115.10 (m, 2F), −124.43～−124.53 (m, 2F), −125.83～−125.93 (m, 2F); IR (film) ν_{max}: 2971, 1756, 1593, 1352, 1195, 1163, 1132, 931, 879, 727, 689, 499 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}F_9INO_2$ $[M+NH_4]^+$ 540.0077, found 540.0075.

[1,1'-Biphenyl]-4-yl 15,15,15,15,15,15,15,15,15-nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diynoate (**5c**): White solid, 137.2 mg, 99% yield. m.p. 28.6～33.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.60～7.54 (m, 4H), 7.45～7.41 (m, 2H), 7.36～7.31 (m, 1H), 7.17～7.13 (m, 2H), 4.36～4.30 (m, 1H), 3.00～2.70 (m, 2H), 2.58 (t, J=7.6 Hz, 2H), 1.88～1.72 (m, 4H), 1.43～1.26 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 150.1, 140.4, 138.9, 128.8, 128.1, 127.3, 127.1, 121.8, 41.5 (t, J=21.0 Hz), 40.3, 34.4, 29.5, 29.1, 29.1, 29.0, 28.4, 24.9, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −80.98～81.05 (m, 3F), −111.55～−115.28 (m, 2F), −124.49～−124.58 (m, 2F), −125.83～−125.94 (m, 2F); IR (film) ν_{max}: 2921, 2852, 1756, 1520, 1487, 1470, 1352, 1216, 1168, 1131, 1020, 1007, 880, 850, 769, 741, 723, 692, 510, 410 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{32}F_9INO_2$ $[M+NH_4]^+$ 700.1329, found 700.1325.

4-Chlorophenyl 15,15,15,15,15,15,15,15,15-nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diynoate (**5d**): Colorless oil, 124.9 mg, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35～7.31 (m, 2H), 7.04～7.00 (m, 2H), 4.36～4.30 (m, 1H), 2.99～2.70 (m, 2H), 2.55 (t, J=7.2 Hz, 2H), 1.88～1.71 (m, 4H), 1.55～1.29 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 149.2, 131.1, 129.4, 123.0, 41.5 (t, J=21.0 Hz), 40.3, 34.2, 29.5, 29.12, 29.08, 29.0, 28.4, 24.8, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.01～−81.08 (m, 3F), −111.56～−115.32 (m, 2F), −124.52～−124.62 (m, 2F), −125.87～−125.97 (m, 2F); IR (film) ν_{max}: 2928, 2856, 1759, 1487, 1351, 1200, 1163, 1133, 1086, 1014, 879, 842, 723, 506 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}ClF_9INO_2$ $[M+NH_4]^+$ 658.0626, found 658.0624.

4-Cyanophenyl 15,15,15,15,15,15,15,15,15-nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diynoate (**5e**): Colorless oil, 108.0 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70～7.67 (m, 2H), 7.24～7.21 (m, 2H), 4.37～4.30 (m, 1H), 3.00～2.70 (m, 2H), 2.59 (t, J=7.6 Hz, 2H), 1.88～1.72 (m, 4H), 1.56～1.29 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.3, 154.0, 133.6, 122.7, 118.2, 109.6, 41.5 (t, J=22.0 Hz), 40.2, 34.2, 29.5, 29.1, 29.0, 28.9, 28.4, 24.7, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.00～−81.07 (m, 3F), −110.51～−115.32 (m, 2F), −124.52～−124.62 (m, 2F), −124.57～−125.98 (m, 2F); IR (film) ν_{max}: 2928, 2857, 2230, 1762, 1602, 1505, 1411, 1351, 1213, 1166, 1132, 879, 723, 549 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{27}F_9IN_2O_2$ $[M+NH_4]^+$ 649.0968, found 649.0966.

Naphthalen-1-yl 15,15,15,15,15,15,15,15,15-nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diynoate (**5f**): Colorless oil, 106.1 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88～7.85 (m, 2H), 7.73 (d, J=8.0 Hz, 1H), 7.51～7.44 (m, 3H), 7.25～7.23 (m, 1H), 4.36～4.30 (m, 1H), 3.00～2.70 (m, 4H), 1.90～1.71 (m, 4H), 1.51～1.28 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 146.6, 134.6, 128.0, 126.9, 126.4, 125.9, 125.4, 121.1, 118.1, 41.5 (t, J=21.0 Hz), 40.3, 34.4, 29.5, 29.2, 29.1, 29.1, 28.4, 25.0, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.00～−81.04 (m, 3F), −111.52～−115.27 (m, 2F), −124.49～−124.58 (m, 2F), −125.83～−125.95 (m, 2F); IR (film) ν_{max}: 2928, 2856, 1760, 1599, 1508, 1463, 1390, 1350, 1217, 1132, 1014, 879, 797, 773, 723, 553, 513 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}F_9INO_2$ $[M+NH_4]^+$ 674.1172, found 674.1172.

Ethyl 15,15,15,15,15,15,15,15,15-nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diynoate (**5g**):[14] Colorless oil, 91.8 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.36～4.30 (m, 1H), 4.13 (q, J=7.2 Hz, 2H), 2.99～2.70 (m, 2H), 2.29 (t, J=7.6 Hz, 2H), 1.88～1.71 (m, 2H), 1.67～1.24 (m, 15H).

15,15,15,15,15,15,15,15,15-Nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diyn-1-yl benzoate (**5h**): Colorless oil, 103.5 mg, 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.07～8.04 (m, 2H), 7.57～7.53 (m, 1H), 7.46～7.41 (m,

2H), 4.32 (t, J=6.7 Hz, 3H), 2.99～2.70 (m, 2H), 1.87～1.71 (m, 4H), 1.58～1.27 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.6, 132.8, 130.5, 129.5, 128.3, 65.0, 41.5 (t, J=21.0 Hz), 40.3, 29.5, 29.4, 29.2, 29.2, 28.7, 28.4, 26.0, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.03～−81.10 (m, 3F), −111.57～−115.33 (m, 2F), −124.53～−124.63 (m, 2F), −125.88～−126.00 (m, 2F); IR (film) ν_{max}: 2927, 2856, 1718, 1452, 1350, 1314, 1272, 1218, 1133, 1070, 1027, 879, 711, 688 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{30}F_9INO_2$ $[M+NH_4]^+$ 638.1172, found 638.1170.

15,15,15,15,15,15,15,15,15,15-Nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diyn-1-yl 4-fluorobenzoate (**5i**): Colorless oil, 116.0 mg, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.09～8.03 (m, 2H), 7.11 (t, J=8.8 Hz, 2H), 4.36～4.29 (m, 3H), 3.00～2.70 (m, 2H), 1.88～1.72 (m, 4H), 1.58～1.27 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.67, 165.67 (d, J=252.0 Hz), 132.1, 132.0, 126.7, 115.5, 115.3, 65.2, 41.5 (t, J=21.0 Hz), 40.3, 29.5, 29.4, 29.3, 29.24, 29.17, 28.7, 28.4, 26.0, 20.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.05～−81.11 (m, 3F), −106.04～−106.16 (m, 1F), −111.59～−115.33 (m, 2F), −124.55～−124.65 (m, 2F), −125.89～−126.01 (m, 2F); IR (film) ν_{max}: 2928, 2856, 1717, 1604, 1508, 1350, 1271, 1218, 1153, 1133, 1090, 1015, 879, 854, 768, 723, 688, 608, 502 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{29}F_{10}INO_2$ $[M+NH_4]^+$ 656.1078, found 656.1076.

15,15,15,15,15,15,15,15,15,15-Nonafluoro-10-iodo-15λ^{12}-pentadeca-12,14-diyn-1-yl 4-chlorobenzoate (**5j**): Colorless oil, 113.4 mg, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99～7.96 (m, 2H), 7.43～7.39 (m, 2H), 4.36～4.30 (m, 3H), 2.99～2.70 (m, 2H), 1.88～1.71 (m, 4H), 1.56～1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.8, 139.2, 130.9, 128.9, 128.6, 65.3, 41.5 (t, J=21.0 Hz), 40.3, 29.5, 29.3, 29.24, 29.16, 28.6, 28.4, 26.0, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −81.01～−81.08 (m, 3F), −111.57～−115.32 (m, 2F), −124.53～−124.62 (m, 2F), −125.87～−125.97 (m, 2F); IR (film) ν_{max}: 2927, 2856, 1720, 1595, 1489, 1465, 1402, 1350, 1271, 1218, 1170, 1133, 1092, 1016, 879, 850, 760, 723, 685, 526 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{29}ClF_9INO_2$ $[M+NH_4]^+$ 672.0782, found 672.0780.

2-(12,12,12,12,12,12,12,12,12,12,12,12,12,12,12,12,12,12,12-heptadecafluoro-3-iodo-12λ^{20}-dodeca-5,7,9,11-tetrayn-1-yl)isoindoline-1,3-dione (**5k**): White solid, 88.9 mg, 54% yield. m.p. 95.5～99.0 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89～7.84 (m, 2H), 7.76～7.71 (m, 2H), 4.35～4.28 (m, 1H), 3.96～3.80 (m, 2H), 3.04～2.79 (m, 2H), 2.35～2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.1, 134.1, 131.9, 123.4, 41.6 (t, J=20.0 Hz), 38.7, 38.3, 14.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −80.80 (t, J=7.52 Hz, 3F), −111.24～−114.77 (m, 2F), −121.57 (s, 2F), −121.94 (s, 4F), −122.75 (s, 2F), −123.59 (s, 2F), −126.14 (s, 2F); IR (film) ν_{max}: 2934, 1771, 1706, 1464, 1434, 1401, 1370, 1330, 1198, 1145, 1077, 1018, 1007, 984, 947, 868, 800, 764, 721, 712, 703, 658, 619, 580, 555, 531, 510 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{15}F_{17}IN_2O_2$ $[M+NH_4]^+$ 764.9901, found 764.9897.

Supporting Information Synthesis and characterization of PTH-POP1, PTH-POP2; ^{1}H NMR spectra of compounds **3a**, **3b**, **5g**; ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra of new compounds **3c**～**3o**, **5a**～**5f**, **5h**～**5k**. The Supporting Information is available free of charge via the Internet at http://siocjournal.cn/.

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