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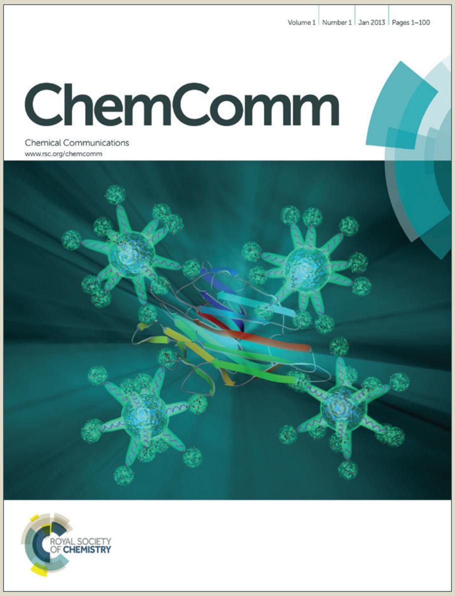

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Photoinduced Reductive Perfluoroalkylation of Phosphine Oxides: Synthesis of *P*-Perfluoroalkylated Phosphines Using TMDPO and Perfluoroalkyl Iodides

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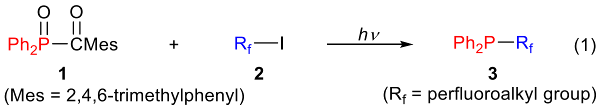
Yuki Sato, Shin-ichi Kawaguchi, and Akiya Ogawa *

A photoinduced reaction between TMDPO ((2,4,6-trimethylbenzoyl)diphenylphosphine oxide) and perfluoroalkyl iodides successfully affords *P*-(perfluoroalkyl)diphenylphosphines as promising ligands for recyclable catalysts. Interestingly, the perfluoroalkylation reaction involves the reduction of phosphorus(V) compounds to phosphorus(III) species. Advantages of the present reaction include the use of an air-stable phosphorus source and good yields of *P*-perfluoroalkylphosphines in short reaction times.

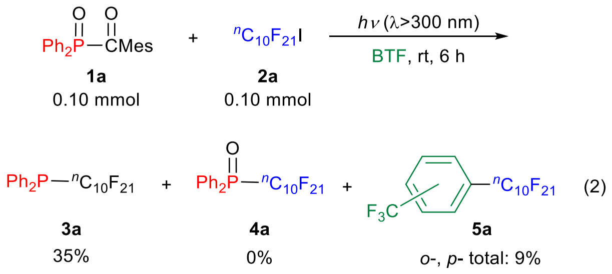
Organophosphine compounds[1] are widely used as ligands for metal catalysts and as reagents in Wittig[2] and Mitsunobu reactions.[3] However, the synthesis of organophosphines is often difficult owing to their oxophilicity. As such, phosphines are usually converted to air- and moisture-stable phosphine derivatives such as phosphine sulfides, phosphine oxides, and phosphine-borane complexes prior to modification and isolation. Alternatively, the introduction of fluorous tags onto phosphines is another way to handle phosphines without oxidation. Phosphines with fluorous moieties exhibit fluorous affinity and can be manipulated using fluorous/organic biphasic systems (FBS) without any prior organic transformations.[4] *P*-perfluoroalkylated phosphines such as $Ph_2P^nC_{10}F_{21}$, in which a perfluoroalkyl group is directly linked to the phosphorus atom, have sufficient fluorous affinity for manipulation via FBS. *P*-perfluoroalkylated phosphines can form a complex with palladium(II) in spite of its electron deficiency, and the formed Pd(II) complex catalyzes common coupling reactions such as Suzuki-Miyaura coupling, Sonogashira coupling, and the Heck reaction.[5] Therefore, *P*-perfluoroalkylated phosphines are attractive phosphines; however, synthetic routes toward *P*-perfluoroalkylated phosphines are limited to methods, which require strict reaction conditions,[6] such as Birch reduction conditions,[6h] or trivalent phosphine species, which are unstable in the presence of moisture and oxygen.[5, 6a,f,g,i] Therefore, synthetic methods which utilize shelf-stable phosphorus sources under mild conditions are strongly desired. During exploration of air- and moisture-stable phosphorus sources, we focused on diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO).[7] TMDPO is commercially available and is a shelf-stable solid; it is typically used as a photoinitiator,[8] as it releases phosphinoyl radicals. We expected perfluoroalkylation using this phosphorus-centered radical and photoinduced reaction between TMDPO and perfluoroalkyl iodide was conducted. As a result, a trivalent phosphorus compound, *P*-perfluoroalkylphosphine, was obtained in spite of the use of a pentavalent phosphorus source, i.e., TMDPO (Eq. 1). Such transformations accompanied with the reduction of pentavalent phosphorus compounds to trivalent phosphorus compounds are rare, with the exception of simple reductions.[9] Moreover, there are only a few examples of reactions which utilize TMDPO as a phosphorus source.[10] Therefore, we were set out to investigate the reductive perfluoroalkylation of TMDPO in detail.



$$\mathrm{Ph_2P(=O)-C(=O)Mes} + \mathrm{R_f{-}I} \xrightarrow{h\nu} \mathrm{Ph_2P{-}R_f} \qquad (1)$$

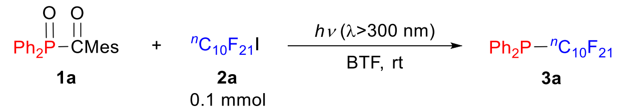
1 (Mes = 2,4,6-trimethylphenyl) **2** **3** (R_f = perfluoroalkyl group)

When a mixture of TMDPO (**1a**, 0.30 mmol) and $^nC_{10}F_{21}I$ (**2a**, 0.30 mmol) was irradiated in BTF (benzotrifluoride, 0.60 mL) with a Xenon lamp (500 W) through a sealed Pyrex NMR tube for 6 h at room temperature, perfluoroalkylated phosphine oxide **4a** was not obtained at all.[11] Surprisingly, however, *P*-(perfluorodecyl)diphenylphosphine **3a** was obtained in a moderate yield (Eq. 2). Perfluoroalkylated arenes (**5a**) from BTF were also obtained, albeit only in a small quantity.



In an attempt to improve the yield of **3a**, several reaction conditions were examined (Table 1). Specifically, the reaction time and ratio of **1a**:**2a** were evaluated. When excessive amounts of **1a** were used, **2a** was consumed completely in 1.5 h to afford the desired **3a** in good yields (entries 4, 5). Irradiation with a tungsten lamp (450 W) also afforded **3a** in a good yield, although a prolonged reaction time was required (entry 6). Notably, BTF was used as the solvent in all cases, because the starting materials, TMDPO and ${}^{n}C_{10}F_{21}I$, were not sufficiently soluble in solvents such as $CHCl_3$, C_6H_6, and 1,1,1,3,3-pentafluorobutane. The reaction mixtures were extracted with an FBS (FC-72/MeOH) to afford the pure product, **3a**.

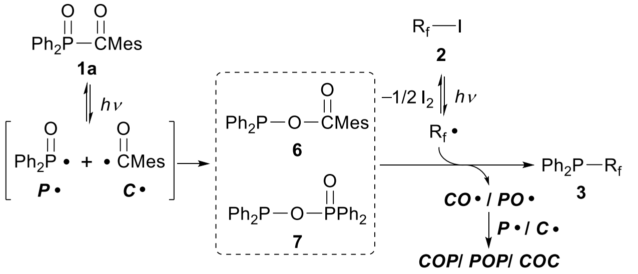
Table 1. Optimization of reaction conditions.[a]



Entry	1a : 2a[b]	Time	Yield [%][c] 3a	Yield [%][c] 5a	Conversion of 2a [%][c]
1	1 : 1	6 h	35	9	64
2	1 : 1	1.5 h	34	8	65
3	3 : 1	1.5 h	67	7	96
4	4 : 1	1.5 h	77	7	100
5	5 : 1	1.5 h	78	6	100
6[d]	4 : 1	24 h	81	2	99

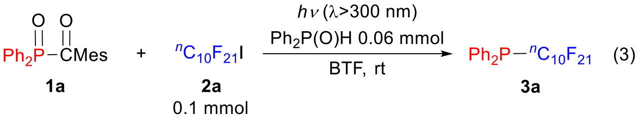
[a]Reaction conditions: ${}^{n}C_{10}F_{21}I$ (**2a**; 0.1 mmol), BTF (0.6 mL), Xenon lamp (500 W), room temperature. [b]Molar ratios. [c]Determined by ${}^{19}F$ NMR. [d]Irradiation with tungsten lamp (450 W).

We propose that the reductive perfluoroalkylation of TMDPO proceeds via the pathway shown in Scheme 1, on the basis of related studies.[12] Near-UV light irradiation induces the homolytic P–C bond cleavage of **1a**, resulting in the formation of diphenylphosphinoyl radical (***P·***) and 2,4,6-trimethylbenzoyl radical (***C·***). These radicals recombine to give intermediate **6** and **7**. The formation of **6** from TMDPO under photoirradiation was supported by a diode laser-based, time-resolved IR study by George et al.[12d] and ${}^{31}P$-NMR-CIDNP (chemically induced dynamic nuclear polarization) spectroscopy described by Wirtz et al.[12e] Subsequently, intermediate **6** reacts with a perfluoroalkyl radical (R_f·), which is generated from R_f–I upon near-UV irradiation,[13] to give **3** with concomitant release of MesC(O)O· (***CO·***). The generation of **7** from TMDPO is also supported by ${}^{31}P$-NMR-CIDNP[12e] and **7** reacts with R_f· to give **3** with concomitant release of $Ph_2P(O)O$· (***PO·***). Furthermore, the formation of MesC(O)OP(O)Ph_2 (***COP***)[15] and $Ph_2P(O)OP(O)Ph_2$ (***POP***)[15] generated by the coupling of ***CO·*** and ***PO·*** with ***P·*** was observed, thus further supporting the proposed mechanism.



Scheme 1. A plausible reaction pathway for the photoinduced reaction of **1a** with **2**. ***COP*** = MesC(O)OP(O)Ph_2, ***POP*** = $Ph_2P(O)OP(O)Ph_2$, ***COC*** = MesC(O)OC(O)Mes.

To enhance the synthetic utility of the reaction, additives were investigated. On the basis of the proposed reaction pathway, the efficient formation of intermediate **6** or **7** would improve the yield of **3a**. The intermediate **6** cannot be influenced by any additive because it is generated mainly in a cage[12d, e] and $Ph_2P(O)H$ cannot penetrate the cage; however, the generation of **7** can be increased by the addition of $Ph_2P(O)H$, which has a diphenylphosphinoyl unit. When $Ph_2P(O)H$ (**8a**, 60 mol%, 0.06 mmol) was added to the reaction system, the yield of **3a** was improved as expected, and the generation of **5a**, which cannot be separated using FBS, was completely suppressed (Eq. 3).[14] Furthermore, upon addition of $Ph_2P(O)H$, the amount of **1a** could be reduced to 2 equivalent amounts, although a prolonged reaction time was required. Notably, when $Ph_2P(O)H$ was added, the amount of $Ph_2P(O)OP(O)Ph_2$, generated through the reaction of **7** with R_f·, increased, indicating that the addition of $Ph_2P(O)H$ promoted the formation of **7**.



1a (0.4 mmol), 1.5 h	99% (96%)
1a (0.3 mmol), 2 h	88%
1a (0.2 mmol), 9 h	92%

(Determined by ${}^{19}F$ NMR. Isolated yield is shown in paretheses.)

Next, the scope of viable substrates was investigated. Notably, several aryl substituted *P*-perfluoroalkylphosphines could be synthesized from TMDPO analogues (Table 2). TMDPO analogues **1b**, **1c**, and **1e**, bearing –^{t}Bu, –OMe, and –F groups, respectively, at the *para*-position of the diaryl unit of phosphine oxide, reacted with **2a** to afford the corresponding *P*-perfluoroalkylphosphines **3b**, **3c**, and **3e** in good yields. TMDPO analogue **1d**, with an –OMe group at the *meta*-position, also produced *P*-perfluoroalkylphosphine **3d** in a good yield. In addition, the reaction could be scaled up to 2 mmol, and yielded >1 g of *P*-perfluoroalkylphosphine **3a**.

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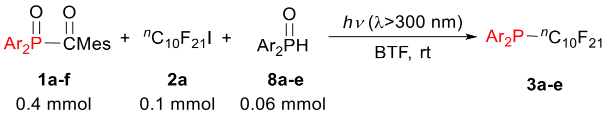
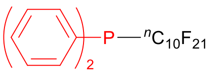
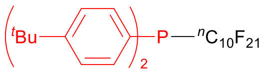
Table 2. Photoinduced synthesis of *P*-perfluoroalkylphosphines from several TMDPO derivatives and $^{n}C_{10}F_{21}I$.[a]

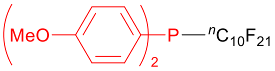




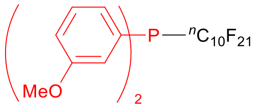
1.5 h, 96%[b] **3a**
(18 h, *1.2 g*, 88%)[c]



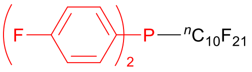
4 h, 78%[b] **3b**



3 h, 67%[b] **3c**



10 h, 74%[b] **3d**

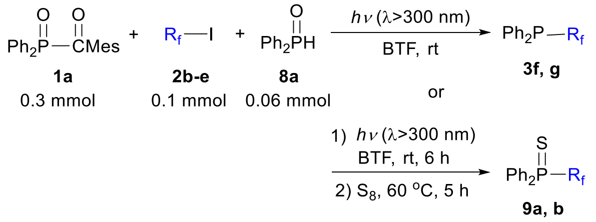


4 h, 82%[b] **3e**

[a] Reaction conditions: diaryl(2,4,6-trimethylbenzoyl)phosphine oxide (**1**: 0.4 mmol), heneicosafluorodecyl iodide (**2a**: 0.1 mmol), diarylphosphine oxide (**8**: 0.06 mmol), and BTF (0.6 mL) were added into a sealed Pyrex NMR tube under an inert atmosphere and the mixture was irradiated with a Xenon lamp for the specified reaction times. [b] Isolated yield after purification using MeOH /FC-72 biphasic system. [c] The reaction was conducted using 8 mmol of **1a**, 2 mmol of **2a**, 1.2 mmol of **8a** and BTF (12 mL) were used.

The viability of several perfluoroalkyl iodides was also evaluated (Table 3). Phosphines with long perfluoroalkyl chains (more than eight carbons) were purified using a MeOH/FC-72 biphasic system and were obtained in good yields (entries 1 and 2). On the other hand, phosphines bearing less than seven carbons were treated with S_8 after the reaction, and were purified by silica gel column chromatography because their fluorous character was insufficient for manipulation via FBS (entries 3 and 4). Secondary perfluoroalkyl iodides such as perfluorocyclohexyl iodide **2d** did not give the corresponding phosphine sulfide **9a** in a satisfactory yield (entry 3). Notably, 1,6-diiodoperfluorohexane **2e** gave the corresponding phosphine sulfide **9b** in an excellent yield (entry 4).

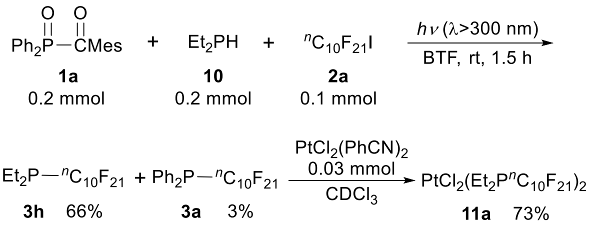
Table 3. Photoinduced synthesis of *P*-perfluoroalkylphosphines from TMDPO and several perfluoroalkyl iodides.[a]



Entry	R_f-I	Time	Product	Yield [%][b]
1[c]	**2b** : $^{n}C_{12}F_{25}I$	**6 h**	**3f** : $Ph_2P–{}^{n}C_{12}F_{25}$	98
2[c]	**2c** : $^{n}C_8F_{17}I$	**3 h**	**3g** : $Ph_2P–{}^{n}C_8F_{17}$	82
3[d]	**2d** : $^{c}C_6F_{11}I$	**6 h**	**9a** : $Ph_2P(S)–{}^{c}C_6F_{11}$	(31)
4[d]	**2e**: $I(CF_2)_6I$	**6 h**	**9b** : $Ph_2P(S)–(CF_2)_6–P(S)Ph_2$	96

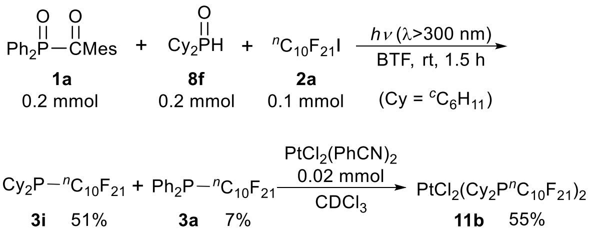
[a] Reaction conditions: TMDPO (**1a**; 0.30 mmol), perfluoroalkyl iodide (**2**; 0.10 mmol), diphenyl phosphine oxide (**8a**, 0.06 mmol), and BTF (0.60 mL) were added to a sealed Pyrex NMR tube under an inert atmosphere and the mixture was irradiated with a Xenon lamp for the specified reaction times. [b] Isolated yield. The yield of **9a** (shown in parenthesis) was determined by ^{19}F NMR. [c] TMDPO (**1a**; 0.40 mmol) was used. Products **3f** and **3g** were isolated using a MeOH/FC-72 biphasic system. [d] After the reaction, the mixture was treated with S_8 (0.60 mmol) for 5 h. The products were isolated by silica gel column chromatography (eluent: *n*-hexane/AcOEt).

This reaction could be utilized in the synthesis of dialkyl *P*-perfluoroalkylphosphines. When 2 equivalent amounts of **1a** and Et_2PH relative to **2a** were used, $Et_2P–{}^{n}C_{10}F_{21}$ was obtained in a moderate yield along with a trace amount of **3a**, after separation using the MeOH/FC-72 biphasic system (Eq. 4).[16] In this reaction, $Et_2P–P(O)Ph_2$ was generated in situ and reacted with a R_f• to give **3h**. In order to obtain a transition metal/**3h** complex, $PtCl_2(PhCN)_2$ was added to separate **3a**, diethyl *P*-perfluoroalkylphosphine **3h** was successfully complexed with platinum and **11a**, which is a promising recyclable catalyst, was isolated in 73% yield.



(4)

Moreover, dialkylphosphine oxides could also be used for the synthesis of dialkyl *P*-perfluoroalkylphosphines. When 2 equivalent amounts of **1a** and $(^{c}C_6H_{11})_2P(O)H$ relative to **2a** were used, $(^{c}C_6H_{11})_2P–{}^{n}C_{10}F_{21}$ was obtained in a moderate yield (Eq. 5).[17] In this reaction, $(^{c}C_6H_{11})_2POP(O)Ph_2$ was generated and reacted with a R_f• prior to intermediates **6** and **7**, derived from **1a**. The phosphine was successfully converted to a platinum complex, **11b**, in 55% yield.



(5)

In conclusion, we developed a method for the rapid synthesis of *P*-perfluoroalkyl phosphines using TMDPO as a phosphorus source. This reaction generates phosphorus(III) compounds from phosphorus(V) species via perfluoroalkylation. This method is viable for the synthesis of a variety of *P*-perfluoroalkylphosphines. In addition, the generated *P*-perfluoroalkylphosphines could be complexed with a transition-metal, platinum(II). Therefore, the generated *P*-perfluoroalkylphosphines can be used as ligands, and in the near future, new reactions are expected to be developed using the produced *P*-perfluoroalkylphosphine ligand-metal complexes.

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Notes and references

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, Gakuen-cho 1-1, Nakaku, Sakai, Osaka 599-8531, Japan. *Corresponding author E-mail (A. Ogawa.): ogawa@chem.osakafu-u.ac.jp

Electronic Supplementary Information (ESI) available: [details experimental procedure for the synthesis of substrates and products, spectral and analytical data of products, and copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and ^{31}P NMR spectra of products and included here]. See DOI: 10.1039/c000000x/

1. (a)L. D. Quin, *A Guide to Organophosphorus Chemistry*, John Wiley & Sons, New York, 2000; (b)H. Yorimitsu, *Beilstein J. Org. Chem.*, 2013, **9**, 1269-1277; (c)Q. Xu, Y.-B. Zhou, C.-Q. Zhao, S.-F. Yin and L.-B. Han, *Mini-Rev. Med. Chem.*, 2013, **12**, 824-835.
2. (a)G. Wittig and U. Schöllkopf, *Chem. Ber.*, 1954, **87**, 1318-1330; (b)B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, 1989, **89**, 863-927.
3. (a)O. Mitsunobu, M. Yamada and T. Mukaiyama, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 935-939; (b)O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Jpn.*, 1967, **40**, 2380-2382; (c)S. Dandapani and D. P. Curran, *Chem. Eur. J.*, 2004, **10**, 3130-3138.
4. (a)J. A. Gladysz, D. P. Curran and I. T. Horváth, *Handbook of Fluorous Chemistry*, Wiley-VCH, Weinheim, Germany, 2004; (b)I. T. Horváth and J. Rábai, *Science*, 1994, **266**, 72-75.
5. S-i. Kawaguchi, Y. Minamida, T. Ohe, A. Nomoto, M. Sonoda and A. Ogawa, *Angew. Chem. Int. Ed.*, 2013, **52**, 1748-1752.
6. (a)A. K. Brisdon and C. J. Herbert, *Chem. Commun.*, 2009, 6658-6660; (b)K. K. Banger, A. K. Brisdon, C. J. Herbert, H. A. Ghaba and I. S. Tidmarsh, *J. Fluorine Chem.*, 2009, **130**, 1117-1129; (c)D. Y. Mikhaylov, T. V. Gryaznova, Y. B. Dudkina, F. M. Polyancev, S. K. Latypov, O. G. Sinyashin and Y. H. Budnikova, *J. Fluorine Chem.*, 2013, **153**, 178-182; (d)E. Lindner and H. Kranz, *Chem. Ber.*, 1968, **101**, 3438-3444; (e)M. B. Murphy-Jolly, L. C. Lewis and A. J. M. Caffyn, *Chem. Commun.*, 2005, 4479-4480; (f)J. D. Palcic, P. N. Kapoor, D. M. Roddick and R. Gregory Peters, *Dalton Trans.*, 2004, 1644-1647; (g)K. Gosling, D. J. Holman, J. D. Smith and B. N. Ghose, *J. Chem. Soc. A*, 1968, 1909-1914; (h)S. E. Vaillard, A. Postigo and R. A. Rossi, *Organometallics*, 2004, **23**, 3003-3007; (i)M. N. Lanteri, R. A. Rossi and S. E. Martín, *J. Organomet. Chem.*, 2009, **694**, 3425-3430.
7. (a)*US Pat.*, 4 710 523, 1987; (b)*US Pat.*, 4 324 744, 1982.
8. (a)K. Ikemura, Y. Kadoma and T. Endo, *Dent. Mater. J.*, 2011, **30**, 769-789; (b)R. Nazir, P. Danilevicius, D. Gray, M. Farsari and D. T. Gryko, *Macromolecules*, 2013, **46**, 7239-7244; (c)Y. Tian, Y.-L. Zhang, J.-F. Ku, Y. He, B.-B. Xu, Q.-D. Chen, H. Xia and H.-B. Sun, *Lab Chip*, 2010, **10**, 2902-2905; (d)T. Griesser, A. Wolfberger, U. Daschiel, V. Schmidt, A. Fian, A. Jerrar, C. Teichert and W. Kern, *Polym. Chem.*, 2013, **4**, 1708-1714; (e)L. Gonsalvi and M. Peruzzini, *Angew. Chem. Int. Ed.*, 2012, **51**, 7895-7897.
9. (a)C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. D. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277-4280; (b)M. Berthod, A. Favre-Réguillon, J. Mohamad, G. Mignani, G. Docherty and M. Lemaire, *Synlett*, 2007, **2007**, 1545-1548; (c)Y. Li, S. Das, S. Zhou, K. Junge and M. Beller, *J. Am. Chem. Soc.*, 2012, **134**, 9727-9732; (d)H. Fritzsche, U. Hasserodt and F. Korte, *Chem. Ber.*, 1964, **97**, 1988-1993; (e)R. Köster and Y. Morita, *Angew. Chem.*, 1965, **77**, 589-590; (f)M. Masaki and K. Fukui, *Chem. Lett.*, 1977, **6**, 151-152; (g)T. Coumbe, N. J. Lawrence and F. Muhammad, *Tetrahedron Lett.*, 1994, **35**, 625-628; (h)K. L. Marsi, *J. Org. Chem.*, 1974, **39**, 265-267; (i)L. Horner, H. Hoffmann and P. Beck, *Chem. Ber.*, 1958, **91**, 1583-1588; (j)S. Griffin, L. Heath and P. Wyatt, *Tetrahedron Lett.*, 1998, **39**, 4405-4406.
10. (a)E. Lindner and G. Vordermaier, *Chem. Ber.*, 1979, **112**, 1456-1463; (b)G. Frey, H. Lesiecki, E. Lindner and G. Vordermaier, *Chem. Ber.*, 1979, **112**, 763-772; (c)C. H. Cho, S. Kim, M. Yamane, H. Miyauchi and K. Narasaka, *Bull. Chem. Soc. Jpn.*, 2005, **78**, 1665-1672; (d)N. Said, S. Touil, A. B. Akacha and M. L. Efrit, *Phosphorus, Sulfur, Silicon Relat. Elem.*, 2008, **183**, 2726-2733; (e)E. Lindner and H. Kern, *Chem. Ber.*, 1984, **117**, 355-365; (f)H. Lesiecki, E. Lindner and G. Vordermaier, *Chem. Ber.*, 1979, **112**, 793-798.
11. The reaction condition was referred to our previous report, ref. 5.
12. (a)T. Sumiyoshi, M. Katayama and W. Schnabel, *Chem. Lett.*, 1985, **14**, 1647-1650; (b)T. Sumiyoshi, W. Schnabel, A. Henne and P. Lechtken, *Polymer*, 1985, **26**, 141-146; (c)G. W. Sluggett, C. Turro, M. W. George, I. V. Koptyug and N. J. Turro, *J. Am. Chem. Soc.*, 1995, **117**, 5148-5153; (d)C. S. Colley, D. C. Grills, N. A. Besley, S. Jockusch, P. Matousek, A. W. Parker, M. Towrie, N. J. Turro, P. M. W. Gill and M. W. George, *J. Am. Chem. Soc.*, 2002, **124**, 14952-14958; (e)U. Kolczak, G. Rist, K. Dietliker and J. Wirz, *J. Am. Chem. Soc.*, 1996, **118**, 6477-6489.
13. (a)M. H. Habib and T. E. Mallouk, *J. Fluorine Chem.*, 1991, **53**, 53-60; (b)Z.-M. Qiu and D. J. Burton, *J. Org. Chem.*, 1995, **60**, 3465-3472; (c)A. Ogawa, M. Imura, N. Kamada and T. Hirao, *Tetrahedron Lett.*, 2001, **42**, 2489-2492; (d)K. Tsuchii, M. Imura, N. Kamada, T. Hirao and A. Ogawa, *J. Org. Chem.*, 2004, **69**, 6658-6665; (e)T. Yajima, I. Jahan, T. Tonoi, M. Shinmen, A. Nishikawa, K. Yamaguchi, I. Sekine and H. Nagano, *Tetrahedron*, 2012, **68**, 6856-6861.
14. When $Ph_2P(O)H$ (0.1 mmol) was added to the reaction system in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 10% yield, along with the desired product in 19% yield.
15. After the reaction, ***COP*** and ***POP*** were obtained in 6% and 81% yields (***COP***, δ_P = 30 ppm; ***POP***, δ_P = 29 ppm). These chemical shifts are supported from reference 12e for ***COP*** and H. G. Korth, J. Lusztyk and K. U. Ingold, *J. Org. Chem.*, 1990, **55**, 624-631. for ***POP***.
16. When Et_2PH (0.2 mmol) and $^{n}C_{10}F_{21}I$ (0.1 mmol) were irradiated under the same condition in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 13% yield, along with $Et_2P^{n}C_{10}F_{21}$ in 47% yield.
17. When $Cy_2P(O)H$ (0.2 mmol) and $^{n}C_{10}F_{21}I$ (0.1 mmol) were irradiated under the same condition in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 21% yield, along with $Cy_2P^{n}C_{10}F_{21}$ in 18% yield.