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Copper- and nickel- catalyzed C–P coupling reactions between P(O)–H compounds and alkyl radicals generated from alkylsilyl peroxides

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Dedicated to Prof. Léon Ghosez on the occasion of his honorary special issue.

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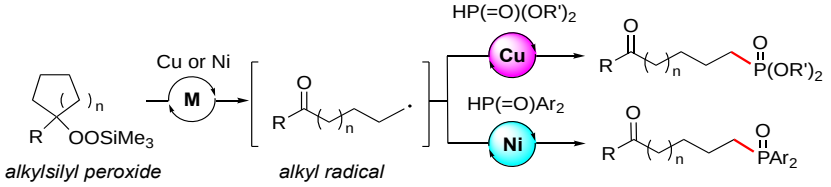
Abstract

Organophosphorus compounds are among the most fundamental and versatile bioactive molecules in medicinal and agricultural fields. Phosphonate ($R^1P(=O)(OR^2)$) compounds, in particular, are garnering considerable attention as prodrugs. Herein transition-metal-catalyzed C–P cross-coupling reaction between P(O)–H compounds and a series of alkylsilyl peroxides as alkyl radical precursors is reported. The reaction proceeded under mild conditions and various coupling products were synthesized from the corresponding dialkyl phosphonates and diarylphosphine oxides using copper and nickel catalysts. Mechanistic studies suggested that a silyl group is necessary to obtain the desired coupling products from dialkyl phosphonates under mild conditions.



Keywords: C–P coupling reactions, alkyl radicals, alkylsilyl peroxides, P(O)–H compounds, metal catalysts

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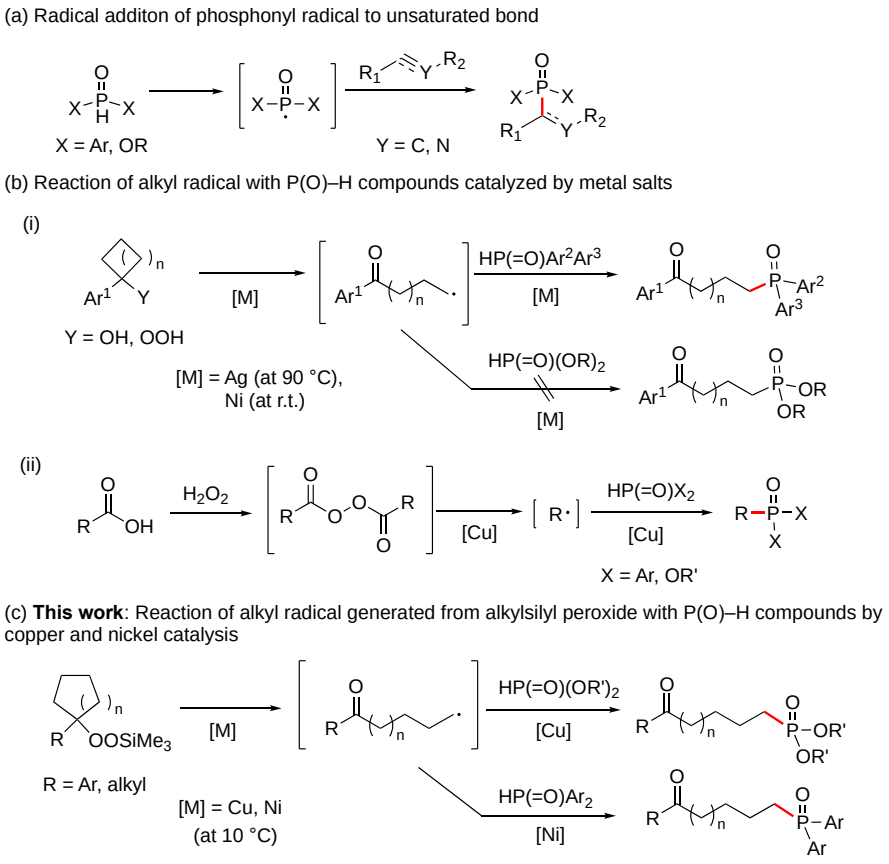
Introduction

Organophosphorus compounds are one of the most fundamental and versatile bioactive molecules and they are used in both the medicinal and agricultural fields.[1–4] Phosphonate ($R^1P(=O)(OR^2)$) compounds, in particular, have attracted considerable attention as prodrugs in recent years.[5] Thus, much effort has been devoted to the development of C–P coupling reactions with various transformations having been reported in this area.[6–10] In recent decades, the radical-mediated C–P coupling reactions of P(O)–H compounds, such as phosphonates and phosphine oxides, have been developed (Scheme 1). The main approach used for these coupling reactions involves the radical addition of a phosphonyl radical, generated from a P(O)–H compound, to various unsaturated bonds (Scheme 1a).[11–16] The converse approach, a C–P coupling reaction between an alkyl radical and a P(O)–H compounds has, thus far, not been developed to a synthetically useful level. For example, metal-catalyzed reactions of alkyl radicals, generated from cyclic alcohols[17] and hydroperoxides,[18] with diarylphosphine oxides has only been reported very recently (Scheme 1b-i). The formation of alkyl radicals from an *in situ*-generated diacyl peroxide, which was prepared from the corresponding carboxylic acid and its subsequent coupling reaction with P(O)–H compounds, has also been demonstrated (Scheme 1b-ii).[19] In this context, we have reported the metal-promoted[20] and photo- promoted[21, 22] *in situ* generation of alkyl radicals from alkylsilyl peroxide, and their subsequent coupling reactions with coupling partners to furnish C–C,[22–26] C–N,[22, 27, 28] C–O,[28, 29] C–B,[30] C–Si,[30] and C–X[31] bond formations. Alkylsilyl peroxides are stable radical precursors, and various structures can be prepared easily from alcohols and olefinic compounds. Herein, we report Cu- and Ni-catalyzed C–P coupling reactions of alkyl radicals, generated from alkylsilyl peroxides, with dialkyl phosphonates and diarylphosphine oxides under mild conditions (Scheme 1c).



Scheme 1. Radical-mediated C–P coupling reactions.

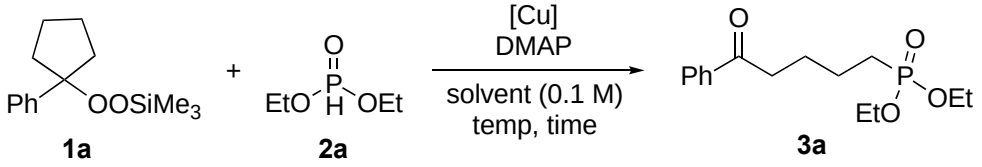
Results and Discussion

We initially examined the coupling reaction of alkylsilyl peroxide **1a** with diethyl phosphonate (**2a**) in the presence of a copper catalyst (Table 1). When the reaction was conducted using a catalytic amount of CuBr (5 mol%) and 1,10-phenanthroline (1,10-Phen, 5 mol%) in benzene at 25 °C for 6 h, a trace amount of the desired product **3a** was detected (entry 1, Table 1). The use of an equimolar amount of 4-dimethylaminopyridine (DMAP; 1–2 equiv), which was used as a ligand, and a base, improved the yield, and product **3a** was obtained in 37% yield (entry 2). When the reaction was conducted at 60 °C, undesired side reactions were promoted and **3a** was reduced to an 11% yield (entry 3). In contrast, the reaction at 10 °C resulted in a slight improvement of the product yield (entry 4). Increasing the amounts of catalyst, alkylsilyl peroxide **1a**, and DMAP were found to be effective and, as a result, the use of CuBr (15 mol%), **1a** (1.5 equiv) and DMAP (2.0 equiv) furnished the coupling product **3a** in 69% yield (entries 5–7). Other solvents such as DMF, acetonitrile (MeCN) and THF were also tested and found to be less effective for this reaction (entries 8–10). The choice of copper salt was critical and the reaction using copper(I) acetate (CuOAc) under the aforementioned conditions gave product **3a** in a quantitative yield (entries 11–13). A lower catalyst loading (10 mol%) also gave product **3a** in a similar yield (entry 14). For more details on the reaction optimization, see Tables S1 and S2 in the supplementary material.

With the optimized reaction conditions in hand, we examined the scope of the P(O)–H compounds tolerated by the conditions when using 10 mol% of CuOAc (Table 2). The reaction of **1a** with three different dialkyl phosphonates afforded the corresponding products **3a**–**c** in excellent yields (entries 1–3). Other dialkyl substrates such as dibenzyl and diisobutyl phosphonates **2d** and **2e**, also gave products **3d** and **3e** in moderate and excellent yields, respectively (entries 4 and 5). The use of *sec*-alkyl derivatives, such as diisopropyl phosphonate (**2f**) and bis((*R*)-1-phenylethyl) phosphonate (**2g**), gave coupling products **3f** and **3g** in 64% and 83% yields, respectively (entries 6 and 7). The reaction of **1a** with diphenylphosphine oxide (**2h**) did not work well under these conditions. The use of $NiCl_2$ and 1,3-bis(diphenylphosphino)propane (DPPP) as the catalyst and ligand in THF, however, furnished the desired coupling product **3h** in 70% yield (entry 8). The use of other diarylphosphine oxides such as **2i** and **2j** under the alternate conditions also gave the desired coupling products **3i** and **3j** in moderate yields (entries 9 and 10).

Next, the substrate scope of the alkylsilyl peroxides tolerated by the reaction was investigated (Table 3). Reactions involving five-, seven- and twelve-membered cyclic alkylsilyl peroxides **1a**–**c** afforded the corresponding coupling products in excellent yields (entries 1–3). A variety of aryl derivatives **1d**–**f** such as 4-tolyl-, 4-fluoropnehyl- and thiophenyl-substituted derivatives were also investigated, and the corresponding products **4d**, **4e** and **4f** were produced in 89%, 84% and 58% yields, respectively (entries 4–6). The use of methyl- and ethyl-substituted alkylsilyl peroxides **1g** and **1h** successfully afforded products **4g** and **4h** in excellent yields (entries 7 and 8).

Table 1. Optimization of the reaction conditions[a]

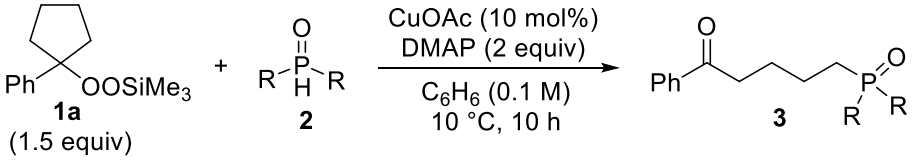


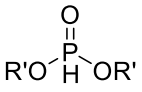
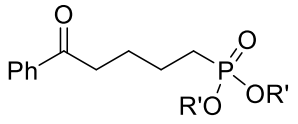
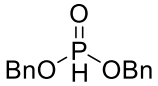
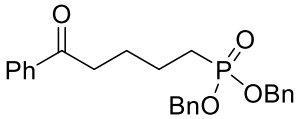
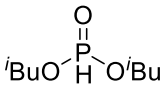
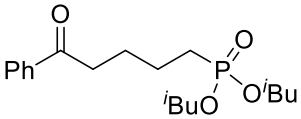
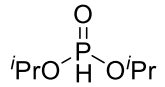
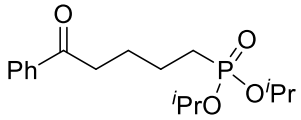
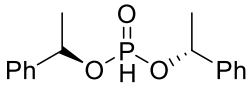
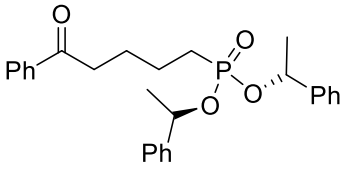
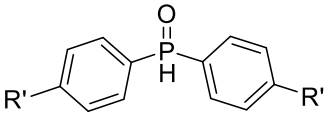
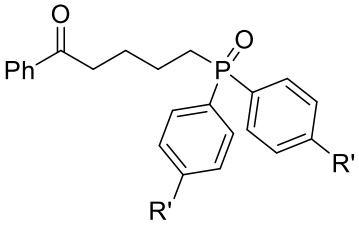
entry	[Cu] (mol%)	**1a** (equiv)	DMAP (equiv)	solvent	temp (°C), time (h)	yield (%)[b]
1[c]	CuBr (5)	1.2	-	C_6H_6	25, 6	<5
2	CuBr (5)	1.2	1.0	C_6H_6	25, 6	37
3	CuBr (5)	1.2	1.0	C_6H_6	60, 6	11
4	CuBr (5)	1.2	1.0	C_6H_6	10, 6	43
5	CuBr (15)	1.2	1.0	C_6H_6	10, 6	51
6	CuBr (15)	1.2	2.0	C_6H_6	10, 6	54
7	CuBr (15)	1.5	2.0	C_6H_6	10, 10	69
8	CuBr (15)	1.5	2.0	DMF	10, 10	42
9	CuBr (15)	1.5	2.0	MeCN	10, 10	31
10	CuBr (15)	1.5	2.0	THF	10, 10	35
11	CuCl (15)	1.5	2.0	C_6H_6	10, 10	67
12	CuSCN (15)	1.5	2.0	C_6H_6	10, 10	47
13	CuOAc (15)	1.5	2.0	C_6H_6	10, 10	99 (99)[d]
14	CuOAc (10)	1.5	2.0	C_6H_6	10, 10	96 (93)[d]

[a]Reactions were carried out using diethyl phosphonate **2a** (0.2 mmol), alkylsilyl peroxide **1a** (1.2–1.5 equiv), copper salt (5–15 mol%) and DMAP (1–2 equiv) in a solvent (2 mL). [b] ^{31}P NMR yield using triphenyl phosphate as an internal standard. [c] 1,10-Phen (5 mol%) was used instead of DMAP. [d]Isolated yield.

Control experiments were carried out to gain insight into the reaction mechanism (Scheme 2). The reaction of alkylsilyl peroxide **1a** with diethyl phosphonate (**2a**) in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) as a radical scavenger gave the radical adduct **5** in 79% yield without the formation of product **3a** (Scheme 2a). The same TEMPO radical-trapping reaction was performed in the absence of alkylsilyl peroxide **1a** and no radical adducts, such as compound **6**, were detected (Scheme 2b). Next, reactions utilizing 1-phenylcyclopentan-1-ol (**7**) or 1-phenylcyclopentyl hydroperoxide (**8**), instead of alkylsilyl peroxide **1a**, were carried out (Scheme 2c). Alcohol **7** did not react at all under the standard conditions, and the alkyl hydroperoxide **8** was consumed under these conditions, resulting in a trace amount of the target-coupling product **3a**. These results indicated that the reaction proceeds via a radical mechanism and that the alkylsilyl-peroxide functional group is necessary for a successful reaction.

Table 2. Scope of P(O)–H compounds[a]

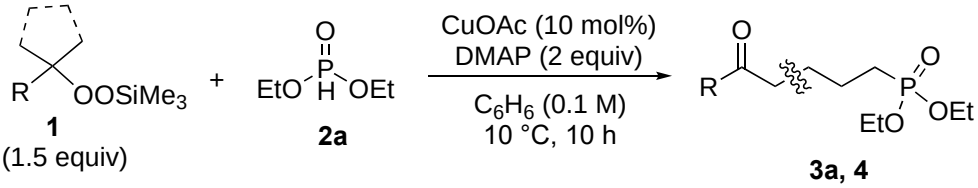


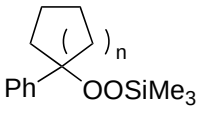
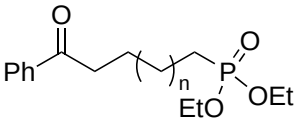
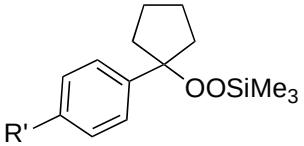
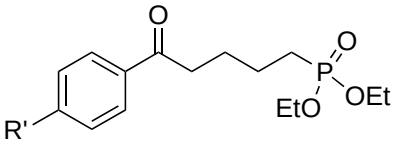
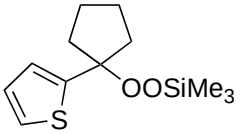
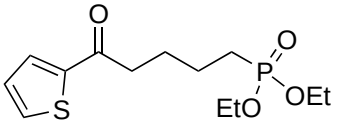
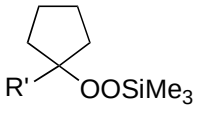
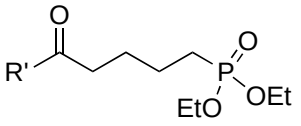
entry	substrate **2**	product **3**[b]
		
1	**2b** (R' = Me)	**3b** (R' = Me): 87%
2	**2a** (R' = Et)	**3a** (R' = Et): 93%
3	**2c** (R' = ^{n}Bu)	**3c** (R' = ^{n}Bu): 91%
		
4	**2d**	**3d**: 66%
		
5	**2e**	**3e**: 93%
		
6	**2f**	**3f**: 64%
		
7	**2g**	**3g**: 83%
		
8	**2h** (R' = H)	**3h** (R' = H): 6% (70%)[c]
9	**2i** (R' = OMe)	**3i** (R' = OMe): (43%)[c]
10	**2j** (R' = CF_3)	**3j** (R' = CF_3): (68%)[c]

[a]Reactions were carried out in the presence of P(O)–H compound **2** (0.2 mmol), alkylsilyl peroxide **1a** (1.5 equiv), CuOAc (10 mol%) and DMAP (2 equiv) in benzene (2 mL) at 10 °C for 10 h. [b]Isolated yield. [c]$NiCl_2$ (10 mol%) and DPPP (12 mol%) was used instead of CuOAc and DMAP in THF.

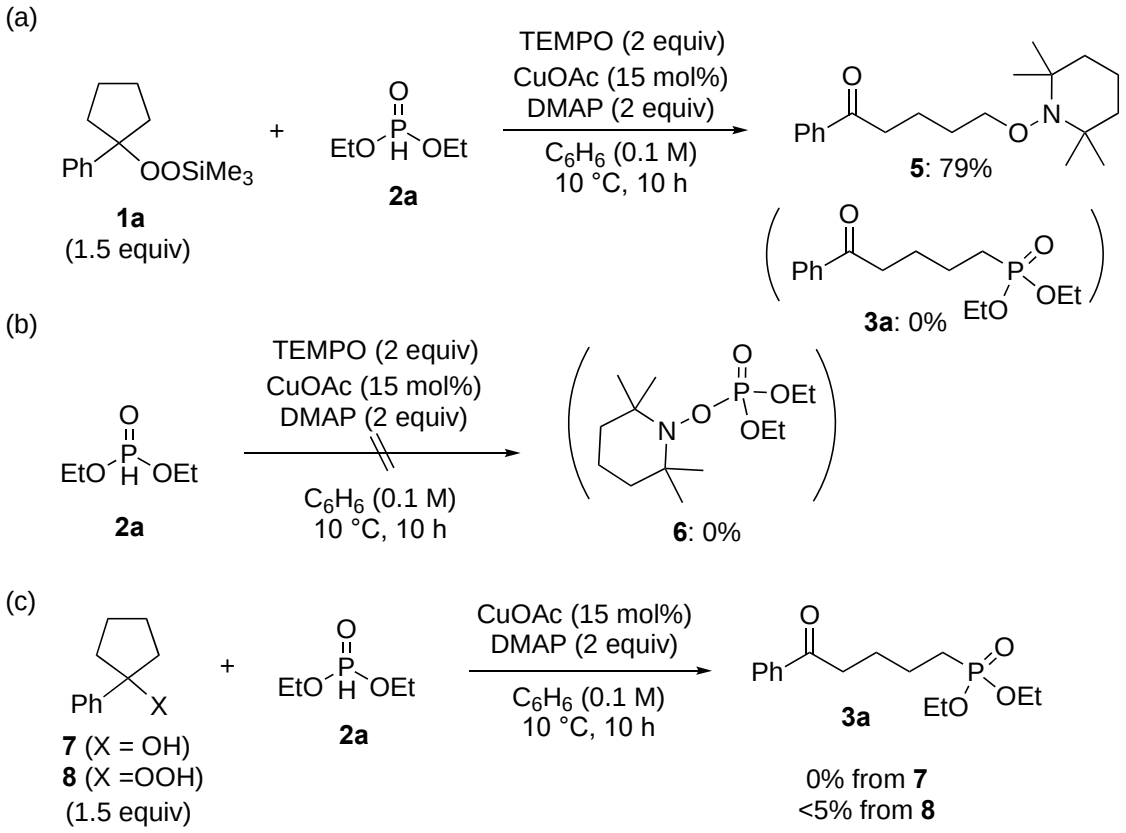
Based on these results and our previous observations,[20] a plausible reaction mechanism for the Cu-catalyzed coupling reaction of **1a** with **2a** is illustrated in Scheme 3. Initially, the O–O bond of alkylsilyl peroxide **1a** is cleaved by the copper catalyst via a single-electron transfer (SET) process, yielding the alkoxy radical **9** and copper–silanoxide complex **10**. The subsequent β-scission of alkoxy radical **9** generates alkyl radical **11**, while transmetallation between copper–silanoxide complex **10** and diethyl phosphonate **2a** affords phosphonate–copper complex **12**. A subsequent reaction of alkyl radical **11** and phosphonate–copper complex **12** finally affords the coupling product **3a.**

Table 3. Scope of alkysilyl peroxides[a]

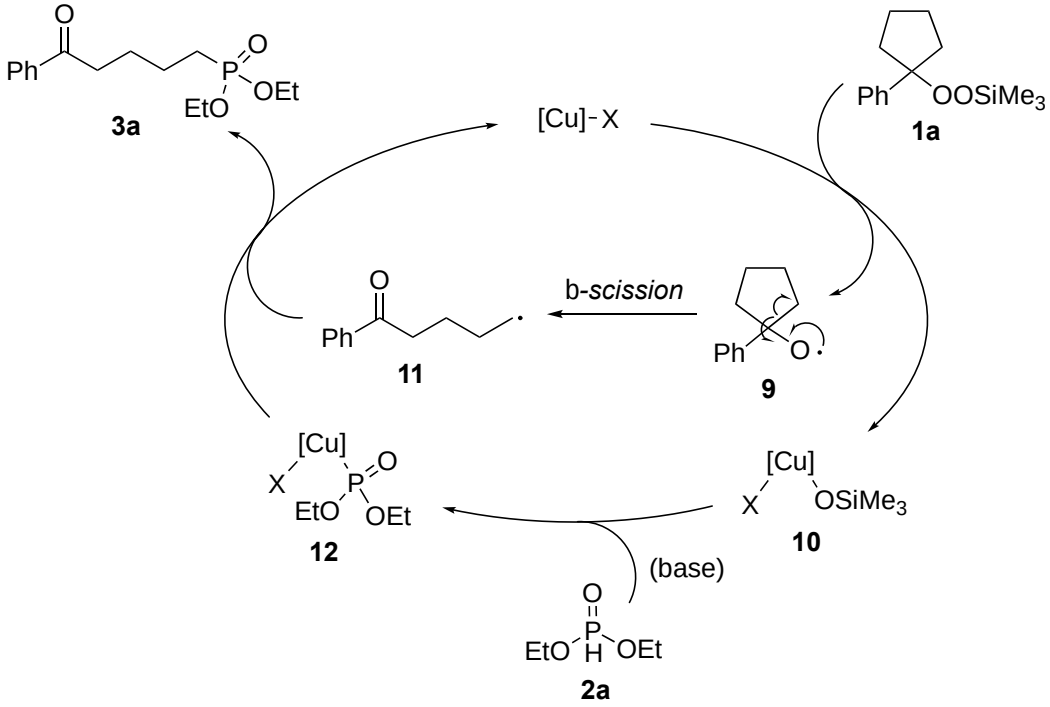


entry	alkylsilyl peroxide **1**	product **3a** or **4**[b]
		
1	**1a** (n = 1)	**3a** (n = 1): 93%
2	**1b** (n = 3)	**4b** (n = 3): 82%
3	**1c** (n = 8)	**4c** (n = 8): 76%
		
4	**1d** (R' = Me)	**4d** (R' = Me): 89%
5	**1e** (R' = F)	**4e** (R' = F): 84%
		
6	**1f**	**4f**: 58%
		
7	**1g** (R' = Me)	**4g** (R' = Me): 91%
8	**1h** (R' = Et)	**4h** (R' = Et): 99%

[a]Reactions were carried out in the presence of diethyl phosphonate **2a** (0.2 mmol), alkylsilyl peroxide **1** (1.5 equiv), CuOAc (10 mol%) and DMAP (2 equiv) in benzene (2 mL) at 10 °C for 10 h. [b]Isolated yield.



Scheme 2. Control experiments.



Scheme 3. Proposed reaction mechanism.

Conclusions

We have developed Cu- and Ni-catalyzed C–P cross-coupling reactions between P(O)–H compounds and alkylsilyl peroxides. The reactions of phosphonate compounds with alkylsilyl peroxides proceeded smoothly under mild conditions in the presence of a Cu catalyst, and the desired coupling products were obtained in up to 99% isolated yield. Reactions between diarylphosphine oxides and alkylsilyl peroxides were also demonstrated using a Ni catalyst. Control experiments suggested that the alkyl silyl peroxide acts as an alkyl radical source, and that the silyl group on the alkylsilyl peroxide plays an important role in allowing the reaction to proceed effectively under mild conditions.

Experimental Section

General: ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR, and 162 MHz for ^{31}P NMR) and a JEOL JNM-ECZ500R/S1 spectrometer (125 MHz for ^{13}C NMR). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz), and assignment. Tetramethylsilane (TMS) was used as the internal standard (0 ppm) for the ^{1}H NMR spectra, and $CDCl_3$ was used as the internal standard (77.16 ppm) for the ^{13}C NMR spectra. High-resolution mass spectra (HRMS) were recorded on a Thermo-Fisher Q-Exactive Orbitrap spectrometer in electrospray ionization (ESI) mode. Infrared (IR) spectra were obtained on a Thermo-Fisher Nicolet 6700 spectrometer. All reactions were performed under an argon atmosphere. Reactions were monitored using thin-layer chromatography (TLC, silica gel HSGF 254, 0.25±0.02 mm). NMR yields were determined using ^{31}P NMR spectroscopy with triphenyl phosphate as an internal standard. The reaction products were purified by column chromatography on silica gel (Qingdao Haiyang Chemical, zcx-II, 300-400 mesh). Dry solvents, such as benzene, tetrahydrofuran (THF), acetonitrile (MeCN) and *N,N*-dimethylformamide (DMF) were purchased from reagent companies as "Dehydrated". Alkylsiyl peroxides **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g** and **1h** were synthesized according to their respective literature methods.[22, 27, 32] 1-Phenylcyclopenthyl hydroperoxide **7**[33] was synthesized according to the literature. Other reagents and solvents were purchased from reagent companies and used as received.

General procedure for copper-catalyzed C-P coupling reaction of alkylsilyl peroxide with P(O)–H compound. To a solution of copper(I) acetate (CuOAc, 2.4 mg, 0.02 mmol), 4-dimethylaminopyridine (DMAP, 48.8 mg, 0.4 mmol) and P(O)–H compound **2** (0.2 mmol) in dry benzene (2 mL) was added alkylsilyl peroxide **1** (0.3 mmol) at 10 °C under an argon atmosphere. The reaction mixture was stirred at the same temperature for 10 h. The resulting mixture was diluted with ethyl acetate and washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the coupling product.

Diethyl (5-oxo-5-phenylpentyl)phosphonate (3a). Reaction was performed using 15 mol% of CuOAc. Colorless oil, 99% isolated yield (59.1 mg, 0.19 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* 7.0 Hz, 2H), 7.55 (t, *J* 7.3 Hz, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 4.16 – 4.00 (m, 4H), 2.99 (t, *J* 7.2 Hz, 2H), 1.88 – 1.78 (m, 4H), 1.77 – 1.65 (m, 2H), 1.31 (t, *J* 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8 , 137.0 , 133.2 , 128.7 , 128.1 , 61.7 (d, *J* 6.5 Hz), 38.1 (d, *J* 1.3 Hz), 25.8 (d, *J* 141.1 Hz), 25.2 (d, *J* 17.6 Hz), 22.4 (d, *J* 5.0 Hz), 16.6 (d, *J* 6.1 Hz); ^{31}P NMR (162 MHz,

$CDCl_3$): δ 31.9; FT-IR (KBr): 2924, 2854, 1742, 1632, 1456, 1377, 1352, 1259, 1024, 960, 800, 755, 691 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{24}O_4P^+$ 299.1407; Found 299.1405.

Dimethyl (5-oxo-5-phenylpentyl)phosphonate (3b). Colorless oil, 87% isolated yield (47.1 mg, 0.17 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* 7.2 Hz, 2H), 7.55 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 3.73 (d, *J* 10.8 Hz, 6H) 2.99 (t, *J* 7.1 Hz, 2H), 1.89–1.77 (m, 4H), 1.75–1.63 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 137.0, 133.2, 128.7, 128.1, 52.5 (d, *J* 6.6 Hz), 38.0 (d, *J* 1.1 Hz), 25.1 (d, *J* 17.4 Hz), 24.8 (d, *J* 140.9 Hz), 22.3 (d, *J* 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.5; FT-IR (KBr): 2955, 1681, 1632, 1449, 1352, 1222, 1030, 815, 692 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{20}O_4P^+$ 271.1094; Found 271.1091.

Dibutyl (5-oxo-5-phenylpentyl)phosphonate (3c). Colorless oil, 91% isolated yield (64.5 mg, 0.18 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (m, 2H), 7.58–7.52 (m, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 4.07–3.94 (m, 4H), 2.98 (t, *J* 7.2 Hz, 2H), 1.87–1.78 (m, 4H), 1.77–1.67 (m, 2H), 1.66–1.59 (m, 4H) , 1.44-1.33 (m, 4H), 0.92 (t, *J* 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 137.0, 133.2 , 128.7, 128.1, 65.4 (d, *J* 6.8 Hz), 38.1, 32.7 (d, *J* 6.1 Hz), 25.6 (d, *J* 141.0 Hz), 25.2 (d, *J* 17.6 Hz), 22.4 (d, *J* 5.1 Hz), 18.9, 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.8; FT-IR (KBr): 2959, 2874, 1687, 1597, 1449, 1379, 1222, 1023, 903, 800, 742, 692 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{32}O_4P^+$ 355.2033; Found 355.2030.

Dibenzyl (5-oxo-5-phenylpentyl)phosphonate (3d). Colorless oil, 66% isolated yield (55.9 mg, 0.13 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* 7.0 Hz, 2H), 7.55 (t, *J* 7.3 Hz, 1H), 7.45 (t, *J* 7.7 Hz, 2H), 7.37–7.28 (m, 10H), 5.10–4.91 (m, 4H), 2.91 (t, *J* 7.2 Hz, 2H), 1.86–1.73 (m, 4H), 1.72–1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 137.0, 136.6 (d, *J* 5.9 Hz), 133.2, 128.7, 128.7, 128.5, 128.1, 128.1, 67.3 (d, *J* 6.5 Hz), 38.0 (d, *J* 1.1 Hz), 26.1 (d, *J* 140.3 Hz), 25.1 (d, *J* 18.0 Hz), 22.3 (d, *J* 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.0; FT-IR (KBr): 3064, 3033, 2950, 1683, 1632, 1455, 1220, 996, 857, 736, 695 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{28}O_4P^+$ 423.1720; Found 423.1719.

Diisobutyl (5-oxo-5-phenylpentyl)phosphonate (3e). Colorless oil, 93% isolated yield (65.6 mg, 0.19 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* 7.3 Hz, 2H), 7.54 (t, *J* 7.3 Hz, 1H), 7.44 (t, *J* 7.6 Hz, 2H), 3.84–3.68 (m, 4H), 2.98 (t, *J* 7.2 Hz, 2H), 1.96–1.86 (m, 2H), 1.85–1.64 (m, 6H), 0.91 (d, *J* 6.7 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8 , 137.0 , 133.1 , 128.7 , 128.1 , 71.6 (d, *J* 7.0 Hz), 38.1 , 29.4 (d, *J* 6.3 Hz), 25.5 (d, *J* 141.5 Hz), 25.2 (d, *J* 17.5 Hz), 22.4 (d, *J* 5.2 Hz), 18.8 ; ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.6; FT-IR (KBr): 2961, 1686, 1632, 1449, 1352, 1223, 1010, 963, 858, 755, 692 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{32}O_4P^+$ 355.2033; Found 355.2031.

Diisopropyl (5-oxo-5-phenylpentyl)phosphonate (3f). Colorless oil, 64% isolated yield (41.8 mg, 0.13 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* 7.1 Hz, 2H), 7.55 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 4.76–4.60 (m, 2H), 2.98 (t, *J* 7.2 Hz, 2H), 1.88–1.62 (m, 6H), 1.31 (d, *J* 1.8 Hz, 6H), 1.29 (d, *J* 1.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 137.0, 133.2, 128.7, 128.1, 70.0 (d, *J* 6.7 Hz), 38.2, 27.1 (d, *J* 142.3 Hz), 25.3 (d, *J* 18.0 Hz), 24.2 (d, *J* 4.6 Hz), 24.2 (d, *J* 3.9 Hz), 22.6 (d, *J* 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.8; FT-IR (KBr): 2978, 2933, 1684, 1632, 1597, 1449, 1385, 1352, 1220, 1179, 1107, 984, 692 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{28}O_4P^+$ 327.1720; Found 327.1718.

(*R*)-1-Phenylethyl ((*S*)-1-phenylethyl) (5-oxo-5-phenylpentyl)phosphonate (3g). Colorless oil, 83% isolated yield (74.4 mg, 0.17 mmol). ^1H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* 7.1 Hz, 2H), 7.55 (t, *J* 7.3 Hz, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 7.43–7.33 (m, 4H), 7.32–7.22 (m, 6H), 5.64–5.55 (m, 1H), 5.40–5.31 (m, 1H), 2.85–2.80 (m, 2H), 1.72–1.47 (m, 9H), 1.30 (d, *J* 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 142.4 (d, *J* 3.5 Hz), 142.2 (d, *J* 4.0 Hz), 137.0, 133.1, 128.7, 128.6, 128.6, 128.1, 128.1, 128.1, 126.1, 126.0, 74.9 (d, *J* 6.1 Hz), 74.4 (d, *J* 6.9 Hz), 38.0, 38.0, 27.0 (d, *J* 141.0 Hz), 25.0 (d, *J* 18.3 Hz), 24.9 (d, *J* 5.4 Hz), 24.3 (d, *J* 4.5 Hz), 22.2 (d, *J* 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.8; FT-IR (KBr): 2980, 2930, 2872, 1683, 1632, 1449, 1375, 1219, 1065, 1008, 966, 743, 699, 547 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{27}H_{31}NaO_4P^+$ 473.1852; Found 473.1850.

5-(Diphenylphosphoryl)-1-phenylpentan-1-one (3h).[16] The reaction was performed using $NiCl_2$ (2.6mg, 0.02 mmol) and 1,3-bis(diphenylphosphino)propane (DPPP, 9.9 mg, 0.024 mmol) instead of CuOAc and DMAP, in THF. White solid, 70% isolated yield (50.7 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.90 (d, *J* 7.2 Hz, 2H), 7.77–7.70 (m, 4H), 7.58–7.40 (m, 9H), 2.96 (t, *J* 7.2 Hz, 2H), 2.38–2.27 (m, 2H), 1.93–1.80 (m, 2H), 1.77–1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 199.8, 136.9, 133.2, 133.0 (d, *J* 99.0 Hz), 131.9 (d, *J* 2.9 Hz), 130.9 (d, *J* 9.4 Hz), 128.8 (d, *J* 11.6 Hz), 128.7, 128.1, 38.2, 29.8 (d, *J* 72.0 Hz), 25.6 (d, *J* 15.4 Hz), 21.5 (d, *J* 3.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) *δ* 32.3.

5-(Bis(4-methoxyphenyl)phosphoryl)-1-phenylpentan-1-one (3i).[18] The reaction was performed using $NiCl_2$ (2.6mg, 0.02 mmol) and DPPP (9.9 mg, 0.024 mmol) instead of CuOAc and DMAP, in THF. White solid, 43% isolated yield (36.4 mg, 0.09 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.90 (d, *J* 7.6 Hz, 2H), 7.62 (dd, *J* 10.9, 8.3 Hz, 4H), 7.54 (t, *J* 7.4 Hz, 1H), 7.43 (t, *J* 7.5 Hz, 2H), 6.95 (d, *J* 7.2 Hz, 4H), 3.82 (s, 6H), 2.95 (t, *J* 7.2 Hz, 2H), 2.31–2.23 (m, 2H), 1.88–1.78 (m, 2H), 1.74–1.63 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): *δ* 199.9, 162.3 (d, *J* 2.9 Hz), 136.9, 133.1, 132.7 (d, *J* 10.9 Hz), 128.7, 128.1, 124.4 (d, *J* 104.7 Hz), 114.3 (d, *J* 12.6 Hz), 55.4, 38.2, 30.3 (d, *J* 72.7 Hz), 25.6 (d, *J* 15.4 Hz), 21.6 (d, *J* 3.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 32.6.

5-(Bis(4-(trifluoromethyl)phenyl)phosphoryl)-1-phenylpentan-1-one (3j). The reaction was performed using $NiCl_2$ (2.6mg, 0.02 mmol) and DPPP (9.9 mg, 0.024 mmol) instead of CuOAc and DMAP, in THF. White solid, 68% isolated yield (69.7 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.92–7.84 (m, 6H), 7.78–7.72 (m, 4H), 7.54 (t, *J* 7.4 Hz, 1H), 7.43 (t, *J* 7.7 Hz, 2H), 2.98 (t, *J* 7.1 Hz, 2H), 2.43–2.35 (m, 2H), 1.94–1.83 (m, 2H), 1.77–1.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 199.6 , 136.8 , 136.8 (d, *J* 95.5 Hz), 134.1 (dd, *J* 32.9, 2.7 Hz), 133.3 , 131.3 (d, J 9.5 Hz), 128.8, 128.1, 125.9 (dq, J 11.8, 3.7 Hz), 123.5 (q, *J* 272.8 Hz), 37.9, 29.5 (d, *J* 72.2 Hz), 25.4 (d, *J* 15.6 Hz), 21.2 (d, *J* 3.8 Hz); ^{31}P NMR (162 MHz, CDCl3): δ 30.5; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* –63.3 ; FT-IR (KBr): 2937, 2867, 1685, 1632, 1402, 1335, 1226, 1182, 1125, 1103, 1063, 1018, 1010, 840, 833, 798, 788, 767, 727, 710, 697, 689, 601, 562 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{25}H_{21}F_6NaO_2P^+$ 521.1076; Found 521.1075.

Diethyl (7-oxo-7-phenylheptyl)phosphonate (4b). Colorless oil, 82% isolated yield (53.5 mg, 0.16 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.94 (d, *J* 7.0 Hz, 2H), 7.54 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.6 Hz, 2H), 4.16–3.99 (m, 4H), 2.95 (t, *J* 7.3 Hz, 2H), 1.78–1.67 (m, 4H), 1.66–1.53 (m, 2H), 1.47–1.35 (m, 4H), 1.30 (t, *J* 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 200.4, 137.0, 132.9, 128.6, 128.0, 61.4 (d, *J* 6.5 Hz), 38.4, 30.4 (d, *J* 16.8 Hz), 28.8, 25.6 (d, *J* 140.7 Hz), 24.0, 22.3 (d, *J* 5.2 Hz), 16.5 (d, *J* 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 32.4; FT-IR (KBr): 2983, 2934, 2865, 1683, 1449, 1215, 1054, 1027, 965, 754, 693, 547 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{17}H_{28}O_4P^+$ 327.1720; Found 327.1714.

Diethyl (12-oxo-12-phenyldodecyl)phosphonate (4c). Colorless oil, 76% isolated yield (60.3 mg, 0.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.95 (d, *J* 7.0 Hz, 2H), 7.54 (t, *J* 7.4 Hz, 1H), 7.45 (t, *J* 7.5 Hz, 2H), 4.16–3.99 (m, 4H), 2.95 (t, *J* 7.4 Hz, 2H), 1.77–1.66 (m, 4H), 1.63–1.52 (m, 2H), 1.43–1.21 (m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 200.6, 137.1, 132.8, 128.5, 128.0, 61.4 (d, *J* 6.5 Hz), 38.6, 30.6 (d, *J* 16.9 Hz), 29.5, 29.5, 29.4, 29.4, 29.1, 29.1, 25.7 (d, *J* 140.2 Hz), 24.4, 22.4 (d, *J* 5.2 Hz), 16.5 (d, *J* 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 32.7; FT-IR (KBr): 2981, 2927, 2854, 1686, 1632, 1449, 1235, 1057, 1029, 963, 742, 692 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{38}O_4P^+$ 397.2502; Found 397.2497.

Diethyl (5-oxo-5-(*p*-tolyl)pentyl)phosphonate (4d). Colorless oil, 89% isolated yield (55.6 mg, 0.18 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.85 (d, *J* 8.2 Hz, 2H), 7.26 (d, *J* 8.0 Hz, 2H), 4.19–4.00 (m, 4H), 2.97 (t, *J* 7.2 Hz, 2H), 2.41 (s, 3H), 1.87–1.76 (m, 4H), 1.74–1.63 (m, 2H), 1.32 (t, *J* 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 199.5, 143.9, 134.5, 129.4, 128.3, 61.6 (d, *J* 6.5 Hz), 38.0 (d, *J* 1.1 Hz), 25.8 (d, *J* 141.0 Hz), 25.3 (d, *J* 17.7 Hz), 22.4 (d, *J* 5.1 Hz), 21.8, 16.6 (d, *J* 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 32.0; FT-IR (KBr): 2982, 2934, 1683, 1607, 1445,

1407, 1392, 1368, 1227, 1181, 1164, 1098, 1027, 962, 816 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{16}H_{25}NaO_4P^+$ 335.1383; Found 335.1377.

Diethyl (5-(4-fluorophenyl)-5-oxopentyl)phosphonate. Colorless oil, 84% isolated yield (51.8 mg, 0.16 mmol). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.99–7.94 (m, 2H), 7.12 (t, *J* 8.6 Hz, 2H), 4.16–4.00 (m, 4H), 2.96 (t, *J* 7.1 Hz, 2H), 1.85–1.62 (m, 6H), 1.31 (t, *J* 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 198.2, 165.8 (d, *J* 254.5 Hz), 133.4 (d, *J* 3.0 Hz), 130.7 (d, *J* 9.3 Hz), 115.8 (d, *J* 21.8 Hz), 61.6 (d, *J* 6.6 Hz), 38.0 (d, *J* 1.4 Hz), 25.7 (d, *J* 141.1 Hz), 25.1 (d, *J* 17.6 Hz), 22.4 (d, *J* 5.0 Hz), 16.6 (d, *J* 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 31.8; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* –105.4; FT-IR (KBr): 2984, 1685, 1632, 1598, 1227, 1158, 1056, 1026, 962 cm^{-1}; HRMS (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{15}H_{22}FNaO_4P^+$ 339.1132; Found 339.1127.

Diethyl (5-oxo-5-(thiophen-2-yl)pentyl)phosphonate (4f). Colorless oil, 58% isolated yield (35.2 mg, 0.12 mmol). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.70 (dd, *J* 3.8, 1.2 Hz, 1H), 7.62 (dd, *J* 4.9, 1.1 Hz, 1H), 7.12 (dd, *J* 5.0, 3.8 Hz, 1H), 4.16–4.00 (m, 4H), 2.92 (t, *J* 7.3 Hz, 2H), 1.88–1.78 (m, 4H), 1.72–1.62 (m, 2H), 1.31 (t, *J* 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 192.7, 144.2, 133.5, 131.8, 128.1, 61.5 (d, *J* 6.5 Hz), 38.7 (d, *J* 1.2 Hz), 25.6 (d, *J* 141.1 Hz), 25.4 (d, *J* 17.6 Hz), 22.3 (d, *J* 5.1 Hz), 16.5 (d, *J* 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 31.8; FT-IR (KBr): 2982, 2933, 1659 1632, 1416, 1232, 1053, 1025, 963 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{13}H_{22}O_4PS^+$ 305.0971; Found 305.0965.

Diethyl (5-oxohexyl)phosphonate (4g). Colorless oil, 91% isolated yield (42.8 mg, 0.18 mmol). ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.16–3.98 (m, 4H), 2.45 (t, *J* 6.9 Hz, 2H), 2.13 (s, 3H), 1.79–1.52 (m, 6H), 1.31 (t, *J* 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 208.5, 61.6 (d, *J* 6.5 Hz), 43.2 (d, *J* 1.3 Hz), 30.1, 25.7 (d, *J* 141.2 Hz), 24.7 (d, *J* 17.5 Hz), 22.2 (d, *J* 5.1 Hz), 16.6 (d, *J* 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 31.8; FT-IR (KBr): 2918, 1712, 1632, 1226, 1054, 1027, 964 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{10}H_{22}O_4P^+$ 237.1250; Found 237.1247.

Diethyl (5-oxoheptyl)phosphonate (4h). Colorless oil, 99% isolated yield (49.3 mg, 0.19 mmol). ^1H NMR (400 MHz, $CDCl_3$): *δ* 4.16–3.95 (m, 4H), 2.40 (q, *J* 7.1 Hz, 4H), 1.76–1.51 (m, 6H), 1.29 (t, *J* 7.1 Hz, 6H), 1.03 (t, *J* 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 211.2, 61.6 (d, *J* 6.5 Hz), 41.8, 36.1 , 25.7 (d, *J* 141.1 Hz), 24.8 (d, *J* 17.5 Hz), 22.3 (d, *J* 5.1 Hz), 16.6 (d, *J* 6.0 Hz), 7.9; ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 31.9; FT-IR (KBr): 2981, 1712, 1632, 1385, 1240, 1055, 1029, 962 cm^{-1}; HRMS (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{24}O_4P^+$ 251.1407; Found 251.1402.

Radical trapping experiment (Scheme 2a). To a solution of CuOAc (2.4 mg, 0.02 mmol), DMAP, (48.8 mg, 0.4 mmol), diethyl phosphonate **2a** (27.6 mg, 0.2 mmol) and (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, 62.5 mg, 0.4 mmol) in dry benzene (2 mL) was added alkylsilyl peroxide **1a** (75.1 mg, 0.3 mmol) at 10 °C under argon atmosphere. The reaction mixture was stirred at same temperature for 10 h and resulting mixture was diluted with ethyl acetate. The mixture was washed with water and brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give TEMPO adduct **5.**

1-Phenyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentan-1-one (5).[33] Colorless oil, 79% isolated yield (74.8 mg, 0.24 mmol). ^1H NMR (400 MHz, $CDCl_3$): *δ* 8.01–7.96 (m, 2H), 7.57 (t, *J* 7.4 Hz, 1H), 7.48 (t, *J* 7.6 Hz, 2H), 3.81 (t, *J* 6.4 Hz, 2H), 3.04 (t, *J* 7.4 Hz, 2H), 1.91–1.82 (m, 2H), 1.71–1.59 (m, 2H), 1.49–1.42 (m, 4H), 1.37–1.27 (m, 2H), 1.17 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 200.1, 136.8, 132.6, 128.3, 127.8, 76.2, 59.4, 39.3, 38.4, 32.8, 28.2, 21.2, 19.9, 16.9.

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Supplementary Material

Tables S1 and S2 and copies of ^{1}H, ^{13}C ^{19}F and ^{31}P NMR spectra are provided in the Supplementary Material file associated with this manuscript.

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