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SYNTHESIS OF ARYLTHIOCHLOROCYCLOTRIPHOSPHAZENES

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Abstract – We investigated the reaction between hexachlorocyclotriphosphazene ($(NPCl_2)_3$: HCCP) and thiols in the presence of bases. In MeCN/Et_3N, two and/or four arylthio units were introduced in *gem*-mode selectively by controlling the amount of thiols: thus, HCCP was treated with 2 and/or 4 equivalents of ArSH/Et_3N in MeCN to afford 2,2-dithiolated and/or 2,2,4,4-tetrathiolated products, respectively. Neither mono-thiosubstituted products, tri-thiosubstituted products, nor regioisomers (non-geminal products) were obtained. In contrast, when other solvents such as THF and Et_2O or other bases such as NaH or K_2CO_3 were used, a mixture of dithiolated products, tetrathiolated products, and hexathiolated products was obtained.

INTRODUCTION

Cyclotriphosphazene has a 6-membered heterocyclic ring in which three P atoms and three N atoms are alternately connected. A typical cyclotriphosphazene derivative is hexachlorocyclotriphosphazene (HCCP), which is industrially synthesized from PCl_5 and NH_4Cl.[1] HCCP has an interesting structure that Cl atoms are bonded and oriented upwards and downwards with respect to the phosphazene ring. Since HCCP is reactive to nucleophiles with its six Cl atoms, HCCP possesses potential to introduce six substituents into a small structural unit of 6-membered ring. Therefore, HCCP is expected to be a starting material to form functional materials integrating various functions compactly. Indeed, a number of phosphazene derivatives have been synthesized by nucleophilic substitution of HCCP, and they have been used as flame retardant compounds,[2] fertilizers,[3] hard coat agents,[4] lubricants for hard disk drives,[5] dental resin cements,[6] non-flammable additives for electrolyte of Li secondary batteries,[7] and so on. Though thiolatad chlorocyclotriphosphazenes are used for starting material of thiolated polyphosphazenes[8] and anti-cancer drugs,[9] preparation of thiophenoxyphosphazenes remains much less studied than the synthesis of the analogous aryloxy and amino derivatives;[10] there are few reports dealing

with synthesis of tetrathiocyclotriphosphazenes, and mixture of dithio, tetrathio, and hexathio derivatives were obtained.

In substitution of HCCP, product ratio and selectivity (number of introduced nucleophiles, regio-, and stereochemistry) depends on nucleophiles and reaction conditions. Thus, when 2 equivalents of nucleophiles are introduced, geminal disubstituted isomer, non-geminal *trans* disubstituted isomer, and non-geminal *cis* disubstituted isomer would be obtained (Figure 1).[11]

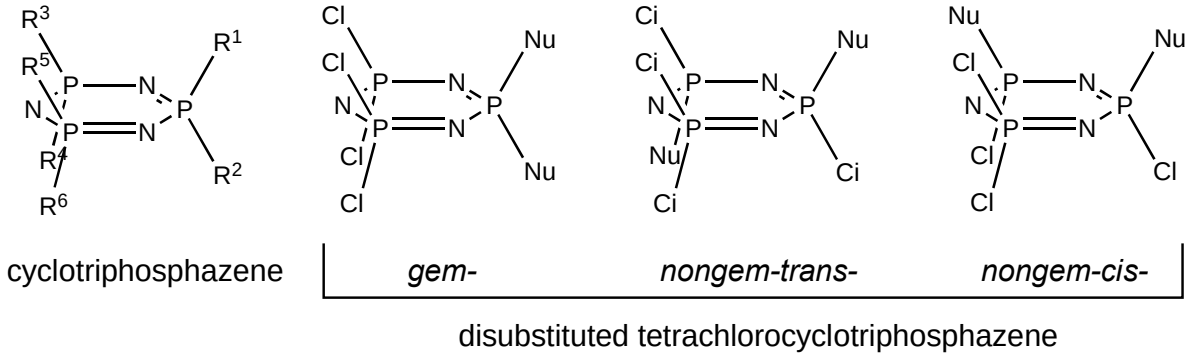
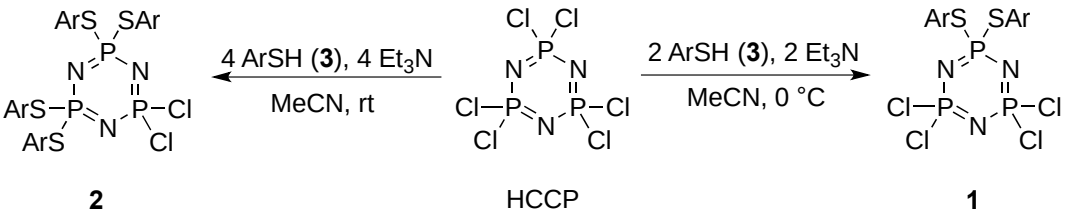


Figure 1. Cyclotriphosphazene and disubstituted tetrachlorocyclotriphosphazenes

In this study, we examined reaction of HCCP with thiols under several reaction conditions to find that two and/or four arylthio units were introduced in *gem*-mode selectively by controlling solvents, bases, and amount of thiols. In acetonitrile, HCCP was treated with 2 and/or 4 equivalents of ArSH/Et_3N to afford 2,2-dithiolated and/or 2,2,4,4-tetrathiolated products, respectively (Scheme 1). Neither mono-thiosubstituted products, tri-thiosubstituted products, nor regioisomers (non-geminal products) were obtained. In contrast, when other solvents such as THF and Et_2O or other bases such as NaH or K_2CO_3 were used, a mixture of dithiolated products, tetrathiolated products, and hexathiolated products was obtained.



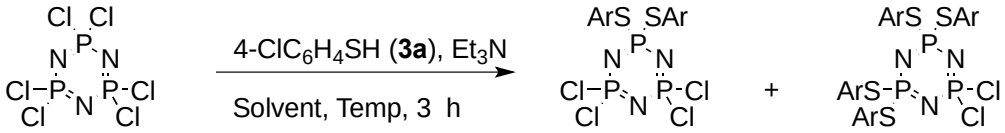
Scheme 1. Partial thiolation with ArSH/Et_3N/MeCN system

RESULTS AND DISCUSSION

A typical procedure for synthesis of 2,2-dichloro-4,4,6,6-tetrakis(4-chlorophenylthio)cyclotriphosphazene (**2a**) is as follows. Triethylamine (1.2 mmol) was added

dropwise to a mixture of HCCP (0.30 mmol), 4-chlorobenzenethiol (**3a**, 1.2 mmol), and MeCN (4 mL) at room temperature (18-23 ºC). The solution was stirred for 3 hours at room temperature under argon atmosphere (completion of tetrathiolation was confirmed after 2 hours by ^{31}P NMR analysis of the reaction mixture). After usual work-up and purification by silica gel column chromatography, 2,2-dichloro-4,4,6,6-tetrakis(4-chlorophenylthio)cyclotriphosphazene (**2a**, 0.28 mmol, 93%) was obtained. The reaction was carried out in several solvents and with several bases, and amount of **3a** and base were varied. The results are summarized in Tables 1 and 2.

Table 1. Thiolation of HCCP with 4-chlorothiophenol (**3a**): Effect of solvent

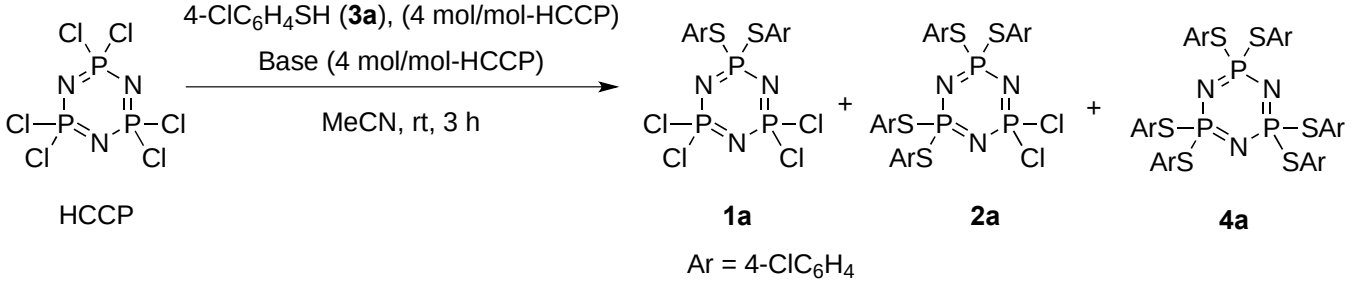


HCCP **1a** **2a** Ar = 4-ClC$_6$H$_4$

	Solvent	Dielectric const. ε	Amount of Base/eq.	Amount of **3a**/eq	Temp.	Yield[a]		
						1a	**2a**	HCCP
1	MeCN	36.6	4	4	rt	trace	99	n.d.[b]
2	MeCN		2	2	rt	99	trace	n.d.[b]
3	MeCN		1	1	rt	60	n.d.[b]	40
4	EtCN	29.7	4	4	rt	trace	99	n.d.[b]
5	MEK	18.6	4	4	rt	7	92	n.d.[b]
6	1,2-DCE	10.4	4	4	rt	61	39	n.d.[b]
7	THF	7.5	4	4	rt	50	50	n.d.[b]
8	AcOEt	6.4	4	4	rt	61	39	n.d.[b]
9	PhCl	5.7	4	4	rt	75	22	3
10	$CHCl_3$	4.8	4	4	rt	87	13	n.d.[b]
11	Et_2O	4.3	4	4	rt	22	33	44
12	EtCN	29.7	2	2	0 ºC	99	trace	n.d.[b]
13	MEK	18.6	2	2	0 ºC	99	trace	n.d.[b]
14	1,2-DCE	10.4	2	2	0 ºC	99	trace	trace
15	THF	7.5	2	2	0 ºC	92	3	5
16	AcOEt	6.4	2	2	0 ºC	87	4	9
17	PhCl	5.7	2	2	0 ºC	76	5	19
18	$CHCl_3$	4.8	2	2	0 ºC	56	2	42
19	Et_2O	4.3	2	2	0 ºC	15	10	75

[a]Determined by ^{31}P NMR. [b]Not detected.

Table 2. Thiolation of HCCP with 4-chlorothiophenol (**3a**): Effect of base



Entry	Base	p*K*a of conjugate acid (H_2O)	Time/h	Yield/%[a]			
				1a	**2a**	**4a**	HCCP
1	Et_3N	10.8	3	trace	99	trace	n.d.[b]
2	DBU	12	3	n.d.[b]	87	8	n.d.[b]
3	2,6-lutidine	6.8	3	98	2	n.d.[b]	n.d.[b]
4	2,6-lutidine	6.8	24	92	8	n.d.[b]	n.d.[b]
5	pyridine	5.2	3	84	n.d.[b]	n.d.[b]	15
6	pyridine	5.2	15	95	4	n.d.[b]	n.d.[b]
7	NaH		3	28	70	2	n.d.[b]
8	K_2CO_3	10.2	3	9	74	12	n.d.[b]
9	NaOH	16	3	Complex			

[a]Determined by ^{31}P NMR. [b]Not detected.

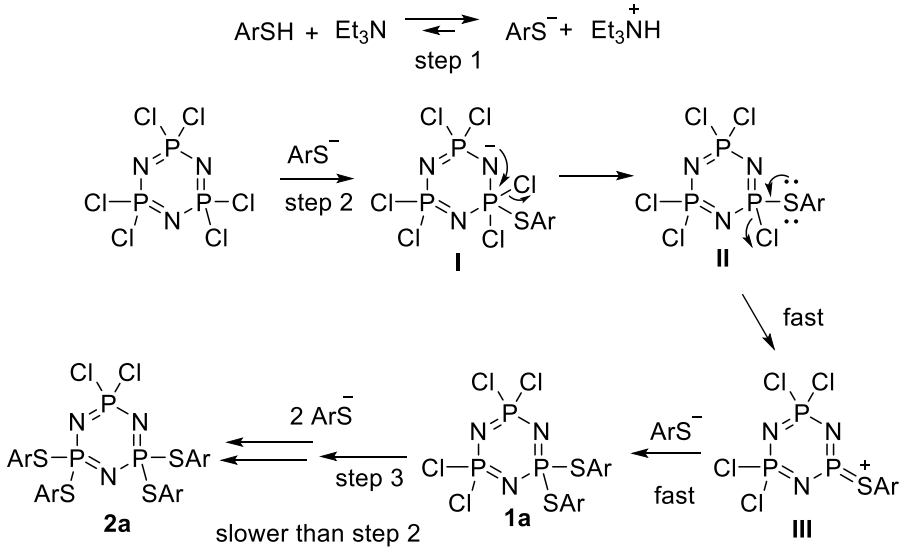
The feature of the reaction is as follows:

1) In MeCN, number of introduced thiols is dependent on the amounts of thiol and Et_3N used: When 2 equivalents of thiol and NEt_3 were used, gem-dithiolated derivative **1a** was obtained (Table 1, Entry 2), whereas 4 equivalents of thiol and Et_3N were used, 2,2,4,4-tetrathiolato derivative **2a** was obtained predominantly (Entry 1). Other compounds such as mono, tri, penta-thiolato, and non-geminal isomers were not detected. When 1 eqivalent of thiol and Et_3N were used, a mixture of **1a** and HCCP was obtained and monothiolated derivative was not detected (Entry 3). It means that the second substitution was faster process than the first substitution.
2) When solvents having high dielectric constant, such as MeCN and EtCN, was used, **1a** or **2a** was generated exclusively: in other solvents, a mixture of **1a** and **2a** was obtained in various proportions (Entries 4-19).
3) When 4 equivalents of thiophenol **3a** and amine were used, aliphatic amines such as Et_3N and DBU gave tetrathiolated derivative **2a** (Table 2, Entries 1, 2), whereas aromatic amines such as 2,6-lutidine and pyridine gave dithiolated derivative **1a** (Entries 3-6). Inorganic bases such as

NaH and K_2CO_3 gave a mixture of **1a**, **2a**, and hexathiolated product **4a** (Entries 7, 8), and NaOH gave only a complex mixture (Entry 9).

4) Only substitution of Cl with thiolate occurred, and side reactions such as ring opening did not occur.

A plausible mechanism is as follows. Thiolation of HCCP could be represented as a bond-recombination reaction. Thiolation of HCCP of **1a** and/or **2a** would be an exothermic reaction since the enthalpy change (ΔH) of the bond-exchange reaction was estimated to be negative (bond dissociation energy at 298 K (kJ/mol): P-Cl 289, S-H 344, P-S 346, H-Cl 432: enthalpy change ΔH = (289 + 344) - (346 + 432) = -145 kJ/mol) from each bond dissociation energy. **2a** would be more thermodynamically stable than **1a** since it is thermodynamically favored to replace P-Cl bond with P-S bond. ArS^-, generated from reaction of ArSH and NEt_3, would add to HCCP to give the adduct **I**. 2-Steps of dechlorination would occur to afford intermediates **II** and **III**. Second addition of ArS^- to **III** would give the dithiolated product **1a**. Thus, it would be suggested that step 3 is kinetically controlled since **1a** was obtained exclusively and no **2a** was detected when 2 mol eq. of **3a** and Et_3N was used.



Scheme 2. A plausible mechanism

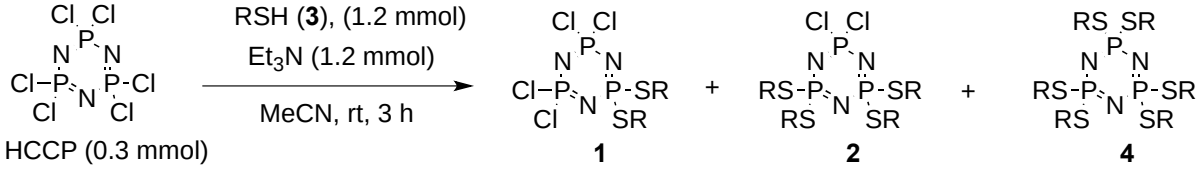
$[Et_3NH^+][ArS^-]$ would disassociate in a highly polar solvent, so that ArS^- would get closer to the naked state and the nucleophilicity of ArS^- would increase in an aprotic solvent having high dielectric constant (ε value). In addition, ionic intermediates **I** and **III** would be stabilized by solvation. As the result, the thiolation would be accelerated.

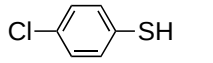
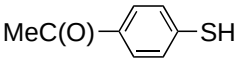
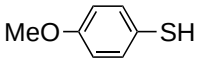
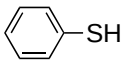
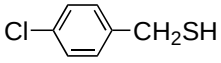
p*K*a Values of the conjugated acids of the bases would be a key factor of these product ratio. Concentration of ArS^- generated in step 1 at the earliest stage in the reaction could be estimated from the

p*K*a values. p*K*a of 4-chlorobenzenethiol is 5.9. When Et_3N (p*K*a of the conjugated acid $[Et_3NH]^+$ = 10.8) is used, the equilibrium constant of the step 1 is $10^{4.9}$, therefore most of ArSH would turn in ArS^- . On the other hand, when pyridine (p*K*a of the conjugated acid $[PyH]^+$ = 5.2) was used, the equilibrium constant of the step 1 is $10^{-0.7}$, and about 20% of ArSH would change to ArS^-.

Scope and limitations of tetrathiolation was examined with several thiols (Table 3). When the thiophenol derivatives containing electron-withdrawing groups (Cl, Ac), tetrathiosubstituted products **2** were obtained in good yields (Entries 1, 2). Though the thiophenol derivatives having π-electron-donating groups (OMe) gave tetrathiosubstituted product **2c**, the products were isolated in moderate yield, due to their unstability (Entry 3).

Table 3. Thiolation of HCCP



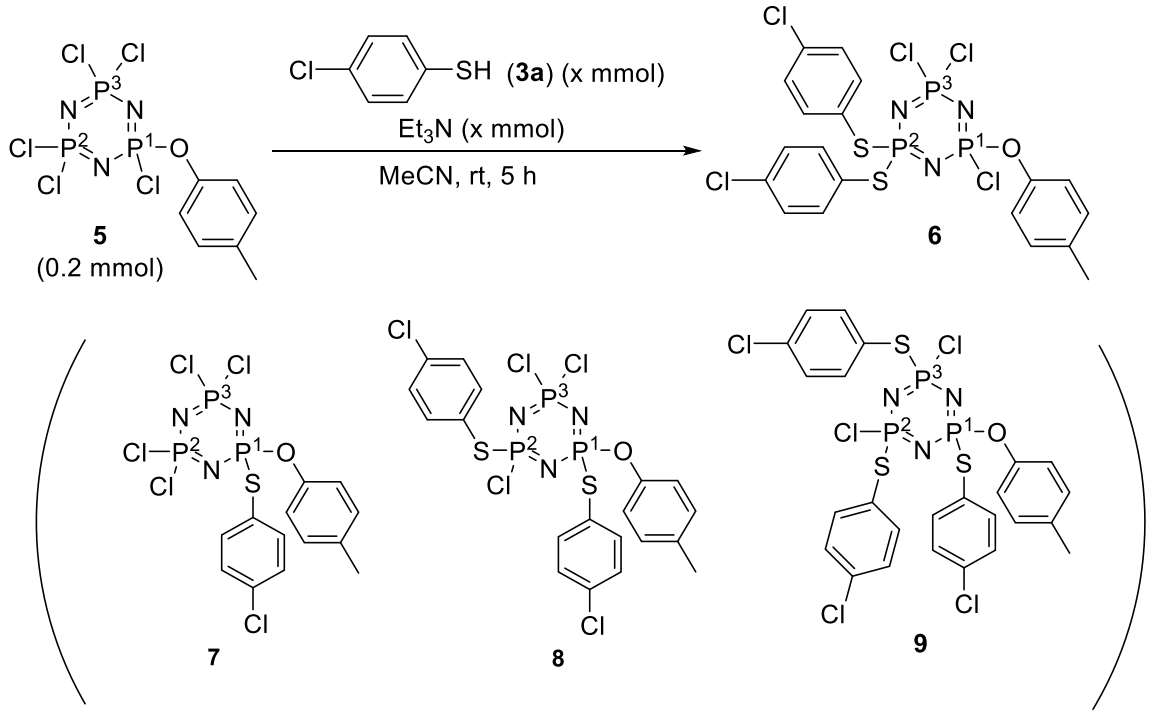
Entry	RSH		pKa	Ratio in crude (%)[a]			Yield of **2** (%)[b]
				1	**2**	**4**	
1		**3a**	6.1	trace	99	trace	93
2		**3b**		n.d.[c]	94	5	84
3		**3c**		9	88	n.d.[c]	40[d]
4		**3d**	6.8	4	96	n.d.[c]	77
5		**3e**	6.6	n.d.[c]	94	n.d.[c]	80
6		**3f**	9.2	25	57	5	
7[e]		**3f**		2	69	n.d.[c]	57
8	Pr−SH	**3g**	10.9	99	n.d.[c]	n.d.[c]	93 (**1g**)
9[e]		**3g**		43	54	n.d.[c]	
10[f]		**3g**		n.d.[c]	77	22	63

[a] Determined by ^{31}P NMR of the reaction mixture. [b] Isolated yields. [c] Not detected. [d] The solubility of **2c** was low. [e] NaH (1.2 mmol) was used as the base. [f] NaH (1.5 mmol) and **3g** (1.5 mmol) were used.

p-Toluenethiol (**3d**) and thiophenol (**3e**) gave **2d** and **2e** in high yields (Entries 4, 5). The tetrathiolation proceeded fast with ArSH having low p*K*a value since ArS^- would be generated smoothly. HCCP was treated with 4 equivalents of 4-chlorobenzyl mercaptan (**1f**) and base. When Et_3N was used as a base, the thiolation proceeded slowly, and a mixture of dithiolated product **2f**, tetrathiolated product **3f**, and hexathiolated product **4f** (25/57/5) was obtained (Entry 6). On the other hand, when NaH was used as a base, **3f** was obtained as the main product with many by-product detected in ^{31}P NMR (Entry 7). The thiolation with 4 mol eq. of propanethiol (**1g**) and Et_3N gave dithiosubstituted product **2g** predominantly (Entry 8). When HCCP was allowed to react with **3g (**1.2 mmol) and NaH (1.2 mmol), a mixture of dithiolated product **1g** and tetrathiolated product **2g** (43/54) was obtained (Entry 9), whereas when **3g** (1.5 mmol) and NaH (1.5 mmol) was used, a mixture of tetrathiolated product **2g** and hexathiolated product **4g** (77/22) was obtained (Entry 10). From these results, it would be difficult to control the number of thiolates introduced using **3g**/NaH system. Tetrathiolation would likely proceed under conditions RS^- was easily generated since **1g** was selectively obtained without formation of **2g** and **4g** despite using 4 mol eq. of **3g** and Et_3N, whereas thiolation with 4 mol eq. of **3g** and NaH gave **1g** and **2g** as a mixture. In addition, monothiolated and *non-gem*-substituted products were not obtained, so that sulfur atom would have a greater influence on the determination of substitution mode rather than R and Ar groups since both RS^- and ArS^- were introduced in *gem*-substitution mode.

Thiolates were introduced in *gem*-substitution mode for unsubstituted HCCP. Then, we investigated the introduction behavior of ArS^- to substituted cyclotriphosphazene derivatives since it would be a basic study on the synthesis of multifunctional cyclotriphosphazene derivatives. We chose pentachloroaryloxycyclotriphosphazene **5** as a starting material which is easily synthesized from HCCP, *p*-cresol, and NaH[8] (Table 4). When 1 equivalent of **3a** and Et_3N were allowed to react with **5**, a mixture of **6** and **5** (molar ratio was approximately 1:1) was obtained and no monothiolated products were detected (Entry 1). When **5** was treated with 2 equivalents of **3a** and Et_3N, **6** was selectively obtained in 92% yield (Entry 2). Isomers such as **7** or **8** were not obtained when both 1 mol eq. and 2 mol eq. of **3a** and Et_3N were used. Therefore, ArS^- was selectively introduced into P^2 (or P^3) in *gem*-substitution mode and was not introduced into P^1, which was a predictable result from the fact that ArO^- is introduced in *non-gem*-mode and ArS^- is introduced in *gem*-mode. It was suggested that P^1 is less reactive to nucleophiles than P^2 (or P^3). Thus, the reactivity of P center into which one S is introduced would be improved, whereas the reactivity of P center into which one O is introduced would decrease.

Table 4. Investigation of introduction behavior of thiolates to **5**



Entry	x	Ratio[a]			Yield of **6** (%)[b]	Recover of **5** (%)[b]
		6	**5**	others		
1	0.2	45	55	n.d.[c]		
2	0.4	99	n.d.[c]	trace	92	n.d.[c]

[a] Determined by ^{31}P NMR of reaction mixture. [b] Isolated yields. [c] Not detected.

In conclusion, we examined reaction of HCCP with thiol derivatives under several reaction conditions to find that ArS^- was introduced in *gem*-substitution mode. Proper choice of solvents and bases was very important to control the number of thiolates introduced. It was suitable to use MeCN as a solvent and Et_3N as a base, and 2,2-dithiolated and/or 2,2,4,4-tetrathiolated products were obtained exclusively by using 2 and/or 4 equivalents of ArSH, respectively. In contrast, when other solvents such as THF and Et_2O or other bases such as NaH or K_2CO_3 was used, a mixture of dithiolated products, tetrathiolated products, and hexathiolated products was obtained. On the other hand, neither mono-substituted products, tri-substituted products, nor regioisomers were not obtained.

EXPERIMENTAL

Dithiolation of HCCP: Triethylamine (0.08 mL, 0.6 mmol) was added slowly to a mixture of HCCP (103.0 mg, 0.30 mmol), 4-chlorobenzenethiol (**3a**, 88.7 mg, 0.61 mmol), and MeCN (4 mL) at 0 ºC to give white precipitates. The solution was stirred for 3 h at 0 ºC under argon atmosphere. The reaction

mixture was poured into a mixture of AcOEt (5 mL) and sat. aq. NH_4Cl (10 mL). The mixture was extracted with AcOEt (10 mL × 3). The organic layers were combined and washed with H_2O (5 mL) and sat. aq. NaCl (5 mL), successively, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/toluene = 3/1) to afford 2,2,4,4-tetrachloro-6,6-bis(4-chlorophenylthio)cyclotriphosphazene (**1a**, 147.0 mg, 0.26 mmol, 88%). **1a**: colorless solids; mp 126.0-127.0 ºC; R_f = 0.40 (hexane/toluene = 3/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.23 (2P), 46.92 (1P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.4 Hz, 4H), 7.52 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.65, 123.78, 130.12, 130.15, 137.38, 137.43, 137.69, 137.75; IR (KBr) 587, 1012, 1188, 1473, 1571, 3086 cm^{-1}; Anal. Calcd for $C_{12}H_8Cl_6N_3P_3S_2$: C, 25.56; H, 1.43; N, 7.45. Found: C, 25.67; H, 1.06; N, 7.37.

2,2,4,4-Tetrachloro-6,6-bis(4-methoxyphenylthio)cyclotriphosphazene (**1c**): colorless solids; $\boldsymbol{R_f}$ = 0.53 (hexane/AcOEt = 7/2); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 19.85 (d, *J* = 10.3 Hz, 2P), 48.93 (t, *J* = 10.3 Hz, 1P); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.82 (s, 6H), 6.91 (d, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 8.4, 4H).

2,2,4,4-Tetrachloro-6,6-bis(4-methylphenylthio)cyclotriphosphazene (**1d**): colorless solids; mp 129.5-131.0 ºC; R_f = 0.30 (hexane/toluene = 3/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.92 (d, *J* = 7.4 Hz, 2P), 48.60 (t, *J* = 7.4 Hz 1P); ^{31}P NMR (162 MHz, acetone-d_6) δ 19.38 (2P), 48.05 (1P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.37 (s, 3H), 7.20 (d, *J* = 8.4 Hz, 4H), 7.48 (d, *J* = 8.4 Hz, 4H); ^{1}H NMR (400 MHz, acetone-d_6) δ 2.38 (s, 6H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.51 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.50, 121.69, 121.77, 130.61, 130.65, 136.43, 136.48, 140.93, 140.97; ^{13}C NMR (100 MHz, acetone-d_6) δ 21.27, 122.19, 122.27, 131.48, 131.51, 137.12, 137.17, 142.07, 142.17; IR (KBr) 580, 1017, 1193, 1489, 2918, 3026 cm^{-1}.

X-Ray crystallographic data of 1d: 1d was recrystallized from MeCN/AcOEt (1:1) solution with slow vaporization of the solvents at room temperature. $C_{14}H_{14}Cl_4N_3P_3S_2$, M = 523.14, monoclinic, *a* = 7.868(2), *b* = 24.337(7), *c* = 11.763(3) Å, β = 106.9.1(11)º, V = 2155.1(10) $Å^3$, calculated density is 1.612 g/cm^3, T = 100 K, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-Kα) = 0.971 mm^{-1}, 27445 reflections measured, 4863 unique (Rim = 0.0867), which were used in all calculations. The final R1 = 0.0472 ($I > 2\sigma(I)$, 4285 reflections) and R*w* = 0.0989 (all data).

X-Ray data for **1d** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1921878. Copies of the data may be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

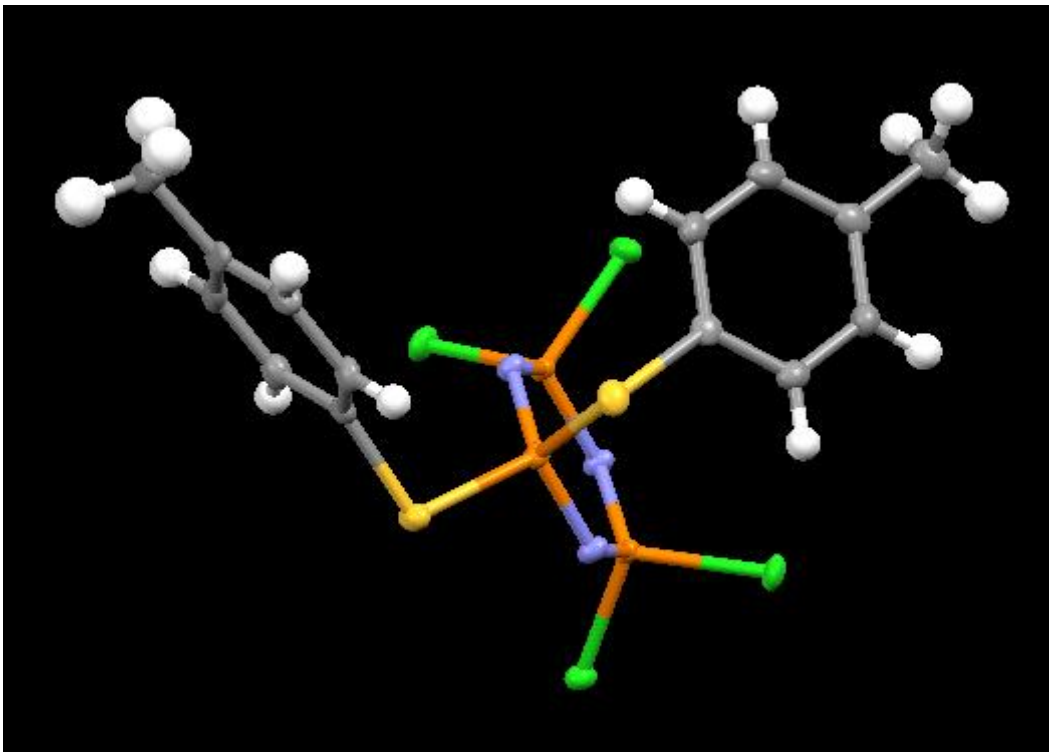


Figure 2. Single-crystal X-ray diffraction analysis of **1d**

Tetrathiolation of HCCP: Triethylamine (0.18 mL, 1.3 mmol) was added to a mixture of HCCP (105.1 mg, 0.30 mmol), **3a** (185.2 mg, 1.28 mmol), and MeCN (4 mL) at room temperature (18-23 ºC). White precipitates formed immediately. The solution was stirred for 3 h at room temperature under argon atmosphere. The reaction mixture was poured into a mixture of AcOEt (5 mL) and sat. aq. NH_4Cl (10 mL). The mixture was extracted with AcOEt (10 mL × 3). The organic layers were combined and washed with H_2O (5 mL) and sat. aq. NaCl (5 mL), successively, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/toluene = 3/1, gradient) to afford 2,2-dichloro-4,4,6,6-tetrakis(4-chlorophenylthio)cyclotriphosphazene (**2a**, 194.6 mg, 0.28 mmol, 93%) **2a**: colorless solids; mp 104.5-106.0 ºC; R_f = 0.27 (hexane/toluene = 3/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.75 (1P), 45.36 (2P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.6 Hz, 8H), 7.42 (d, J = 7.6 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.28, 129.82, 136.67, 137.08; IR (KBr) 582, 1166, 1389, 1474, 1898, 3084 cm^{-1}; Anal. Calcd for $C_{24}H_{16}Cl_6N_3P_3S_4$: C, 36.94; H, 2.07; N, 5.39. Found: C, 37.06; H, 2.00; N, 5.45.

X-Ray crystallographic data of 2a: 2a was recrystallized from AcOEt solution with slow vaporization of the solvent at room temperature. $C_{24}H_{16}Cl_6N_3P_3S_4$, M = 780.29, primitive triclinic, a = 12.902(2), b = 15.549(2), c = 16.6007(16) Å, α = 95.279(4)º, β = 96.321(7)º, γ = 104.902(8)º, V = 3202.8(7) Å^3, calculated density is 1.618 g/cm^3, T = 100 K, space group P-$_1$ (no. 2), Z = 4, μ(Mo-Kα) = 0.970 mm^{-1},

51694 reflections measured, 14626 unique (Rim = 0.0830), which were used in all calculations. The final R1 = 0.0367 ($I > 2\sigma(I)$, 7896 reflections) and R*w* = 0.0633 (all data).

X-Ray data for **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1921877. Copies of the data may be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033. E-mail: deposit@ccdc.cam.ac.uk).

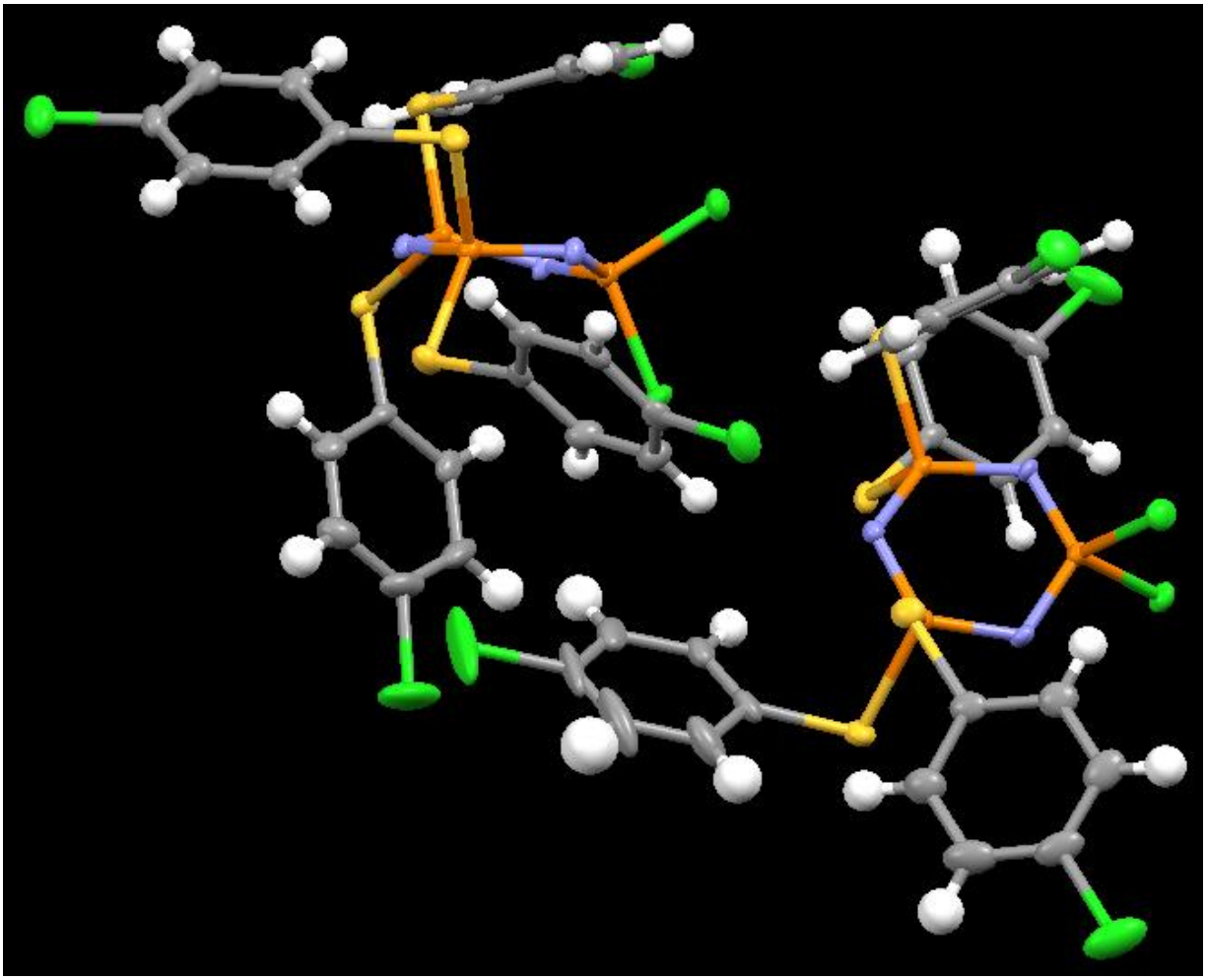


Figure 3. Single-crystal X-ray diffraction analysis of **2a**

4,4,6,6-Tetrakis(4-acetylphenylthio)-2,2-dichlorocyclotriphosphazene (**2b**): colorless solids; mp 164.5-165.5 ºC; R_f = 0.40 (hexane/AcOEt = 3/4); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.97 (1P), 44.61 (2P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 12H), 7.59 (d, *J* = 8.0 Hz, 8H), 7.92 (d, *J* = 8.0 Hz, 8H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 26.97, 129.37, 132.74, 135.86, 138.34, 197.35; IR (KBr) 587, 1169, 1395, 1685, 2994, 3063 cm^{-1}; Anal. Calcd for $C_{32}H_{28}Cl_2N_3O_4P_3S_4$: C, 47.41; H, 3.48; N, 5.18. Found: C, 47.27; H, 3.20; N, 5.11.

2,2-Dichloro-4,4,6,6-tetrakis(4-methoxyphenylthio)cyclotriphosphazene (**2c**): colorless solids; mp 112.0-113.5 ºC; R_f = 0.30 (hexane/AcOEt = 7/2); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.40 (t, *J* = 5.7 Hz, 1P), 46.80 (d, *J* = 5.7 Hz, 2P); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 12H), 6.88 (d, *J* = 8.8 Hz, 8H), 7.44 (d, *J* = 8.8 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.50, 115.01, 117.68, 137.51, 161.05; IR (KBr) 582, 1164, 1251, 1493, 1591, 2836, 2939 cm^{-1}; Anal. Calcd for $C_{28}H_{28}Cl_2N_3O_4P_3S_4$: C, 44.10; H, 3.70; N, 5.51. Found: C, 44.38; H, 3.43; N, 5.46.

2,2-Dichloro-4,4,6,6-tetrakis(4-methylphenylthio)cyclotriphosphazene (**2d**): colorless solids; mp 98.5-99.5 ºC; R_f = 0.17 (hexane/toluene = 3/2), 0.43 (hexane/AcOEt = 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.44 (1P), 46.32 (2P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 12H), 7.16 (d, *J* = 8.0 Hz, 8H), 7.41 (d, *J* = 8.0 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.45, 123.71, 130.17, 135.80, 139.91; IR (KBr) 582, 806, 1170, 1490, 2919, 3022 cm^{-1}; Anal. Calcd for $C_{28}H_{28}Cl_2N_3P_3S_4$: C, 48.14; H, 4.04; N, 6.01. Found: C, 48.19; H, 3.80; N, 5.95.

2,2-Dichloro-4,4,6,6-tetrakis(phenylthio)cyclotriphosphazene (**2e**): colorless oil; R_f = 0.10 (hexane/toluene = 3/2), 0.30 (hexane/AcOEt = 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.71 (1P), 46.07 (2P) (coupling constant was too small to measure.); ^{31}P NMR (162 MHz, acetone-d_6) δ 17.82 (1P), 45.72 (2P) (coupling constant was too small to measure.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.42 (m, 12H), 7.51-7.55 (m, 8H); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.42-7.52 (m, 12H), 7.55-7.57 (m, 8H); ^{13}C NMR (100 MHz, Aceton-d_6) δ 127.67, 130.38, 130.79, 136.53; IR (neat) 581, 742, 1023, 1140, 1168, 3059 cm^{-1}.

Reaction between HCCP and alkanethiol: NaH (60% dispersion in oil, 59.9 mg, 1.5 mmol) was washed with hexane (3 mL × 4) and suspended in MeCN (0.5 mL). HCCP (103.8 mg, 0.30 mmol) and 4-chlorobenzyl mercaptan (**3f**, 0.17 mL, 1.2 mmol) were dissolved in MeCN (3.5 mL), and the mixture was added to the NaH suspension. The solution was stirred for 3 h at room temperature under argon atmosphere. An aliquot of the reaction mixuture was analyzed by ^{31}P NMR to find that a mixture of tetrasubstituted product **2f**, disubstituted product **1f**, and unidentified mixture (69/2/28) was obtained. The reaction mixture was poured into a mixture of AcOEt (5 mL) and sat. aq. NH_4Cl (10 mL). The mixture was extracted with AcOEt (10 mL × 3). The organic layers were combined and washed with H_2O (5 mL) and sat. aq. NaCl (5 mL), successively, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified twice by column chromatography (SiO_2, hexane/AcOEt = 50/1, gradient, and hexane/AcOEt = 3/1) to afford 2,2-dichloro-4,4,6,6-tetrakis(4-chlorobenzylthio)cyclotriphosphazene (**2f**, 142.2 mg, 0.17 mmol, 57 %). **2f:** colorless oil; R_f = 0.37 (hexane/AcOEt = 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.81 (t, *J* = 4.5 Hz, 1P), 48.34 (d, *J* = 4.5 Hz, 2P); ^{31}P NMR (162 MHz, ^{1}H-nondecoupling, $CDCl_3$) δ 18.81 (t, *J* = 4.5 Hz, 1P), 48.34 (dquint, *J* = 4.5 Hz, 14.8 Hz, 2P); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.02 (d, *J* = 14.8 Hz, 8H),

7.23-7.30 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.17, 128.99, 130.61, 133.76, 134.59; IR (neat) 589, 830, 1171, 1490, 1596, 2929, 3029 cm^{-1}; Anal. Calcd for $C_{28}H_{24}Cl_6N_3P_3S_4$: C, 40.21; H, 2.89; N, 5.02. Found: C, 40.23; H, 2.69; N, 5.00.

2,2,4,4-Tetrachloro-6,6-bis(propylthio)cyclotriphosphazene (**1g**): colorless liquid; R_f = 0.53 (hexane/AcOEt = 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.31 (2P), 52.54 (1P) (coupling constant was too small to measure.); ^{31}P NMR (162 MHz, ^{1}H-nondecoupling, $CDCl_3$) δ 19.31 (2P), 52.54 (quint, J = 17.1 Hz, 1P); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J = 7.2 Hz, 6H), 1.79 (sext, J = 7.2 Hz, 4H), 2.91 (dt, J = 17.2, 7.2 Hz, 4H); IR (neat) 513, 597, 1191, 1457, 2932, 2967 cm^{-1}.

2,2-Dichloro-4,4,6,6-tetrakis(propylthio)cyclotriphosphazene (**2g**): colorless liquid; R_f = 0.40 (hexane/AcOEt = 10/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.00 (1P), 50.30 (2P) (coupling constant was too small to measure.); ^{31}P NMR (162 MHz, ^{1}H-nondecoupling, $CDCl_3$) δ 18.00 (1P), 50.30 (quint, J = 16.0 Hz, 2P); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, J = 7.2 Hz, 12H), 1.78 (sext, J = 7.2 Hz, 8H), 2.90 (dt, J = 16.4, 7.2 Hz, 8H); IR (neat) 512, 591, 1169, 1456, 2931, 2965 cm^{-1}.

Thiolation of 2,2,4,4,6-Pentachloro-6-(4-methylphenoxy)cyclotriphosphazene (5): Triethylamine (0.06 mL, 0.5 mmol) was added to a mixture of **5** (97.8 mg, 0.23 mmol), **3a** (68.0 mg, 0.47 mmol), and MeCN (4 mL) at room temperature to give white precipitates. The solution was stirred for 5 h at room temperature under argon atmosphere. The reaction mixture was poured into a mixture of AcOEt (5 mL) and sat. aq. NH_4Cl (10 mL). The mixture was extracted with AcOEt (10 mL × 3). The organic layers were combined and washed with sat. aq. K_2CO_3 (5 mL × 2), H_2O (5 mL × 2), and sat. aq. NaCl (5 mL), successively, dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, hexane/AcOEt = 15/1) to afford 2,2,6-trichloro-4,4-bis(4-chlorophenylthio)-6-(4-methylphenoxy)cyclotriphosphazene (**6**, 134.76 mg, 0.21 mmol, 92%). **6:** colorless oil; R_f = 0.43 (hexane/AcOEt = 15/1); ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.61 (dd, J = 10.3, 55.3 Hz, 1P), 22.71 (d, J = 55.3 Hz, 1P), 47.64 (d, J = 10.3 Hz, 1P); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 7.03 (d, J = 8.4 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.00, 120.92, 124.26, 124.33, 129.87, 129.99, 130.38, 136.08, 136.94, 137.09, 137.50, 137.69, 147.73; IR (neat) 583, 819, 1173, 1504, 2923, 3033 cm^{-1}; Anal. Calcd for $C_{19}H_{15}Cl_5N_3OP_3S_2$: C, 35.90; H, 2.38; N, 6.61. Found: C, 36.26; H, 2.27; N, 6.56.

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