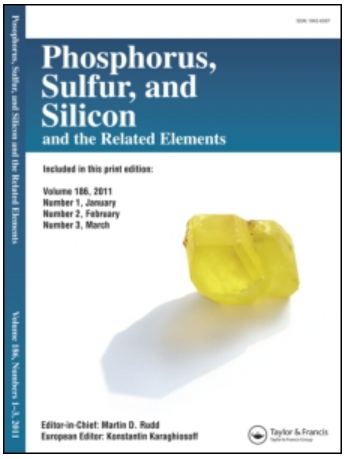

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Synthesis and Properties of Phosphoroselenoic Acids and Their salts Bearing Binaphthyl Groups

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SYNTHESIS AND PROPERTIES OF PHOSPHOROSELENOIC ACIDS AND THEIR SALTS BEARING BINAPHTHYL GROUPS

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Phosphoroselenoyl chlorides were prepared by reacting four types of substituted 1,1′-bi-2-naphthols, PCl_3, and elemental selenium in the presence of Et_3N. The chlorides were converted to the corresponding acids via acid ammonium salts with high efficiency. The spectroscopic properties of these derivatives were used to elucidate the structures of the acids. Finally, the acids were applied to the hydrogenation reaction of imines using Hantzsch ester as a hydrogen donor.

Keywords Binaphthyl groups; organocatalysts; phosphoroselenoic acid salts; phosphoroselenoyl chlorides

INTRODUCTION

The synthesis of phosphoric acids bearing binaphthyl groups and their application to asymmetric synthesis as organocatalysts are some of the most active areas of study in organic chemistry.[1] The replacement of an oxygen atom in phosphoric acids with heavier atoms such as sulfur and selenium might enhance the acidity of the resulting acids. Two precedents of phosphorothioic acids with binaphthyl groups have been reported. The first contained an unsubstituted binaphthyl group and was used as a chiral equivalent of H_2S.[2] For the second, the catalytic activity of phosphorothioic acid derived from a chiral 3,3′-substituted BINOL was examined, but it almost did not catalyze the protonation of an enol silyl ether.[3] Therefore, acids with higher acidity are needed, and this can be realized by replacing an oxygen atom of phosphoric acids with a selenium atom. Very recently we found that phosphoroselenoyl chlorides **1** (Scheme 1) were stable under neutral conditions

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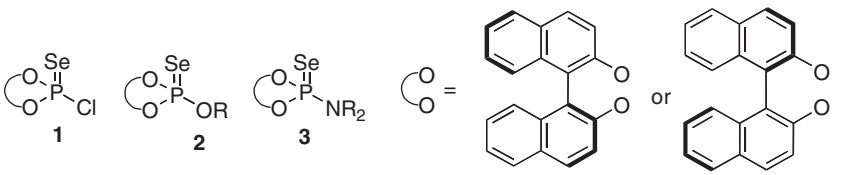


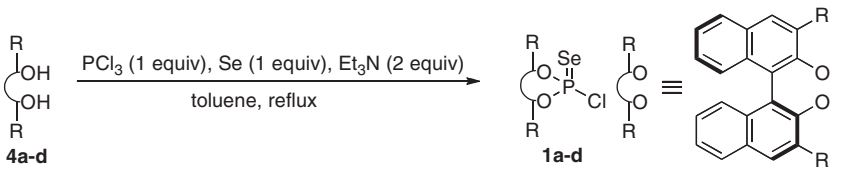
Scheme 1

and were not susceptible to hydrolysis, whereas **1** readily reacted with alcohols in the presence of bases and with amines to give esters **2** and amides **3**.[4]

The selenation of phosphates bearing substituted binaphthyl groups has been reported to lead to the corresponding esters.[5]As part of our studies on a series of phosphoroselenoic acid derivatives,[6] we report in this article the synthesis of chlorides, acids, and acid salts, and their spectroscopic properties. The catalytic reaction using chiral phosphoroselenoic acids is also described.

RESULTS AND DISCUSSION

Initially, phosphoroselenoyl chlorides **1** were prepared by treating PCl_3 with (*S*)-(–)-1,1′-bi-2-naphthol (**4a**) in the presence of Et_3N in toluene (Scheme 2 and Table I). The reaction was complete within 6 h, and the corresponding chloride **1a** was obtained in 90% isolated yield. The chloride **1a** was purified by column chromatography on silica gel, and no decomposition of **1a** was observed during purification. The reaction was then extended to 3,3′-substituted 1,1′-bi-2-naphthols. The reaction was monitored by the observation of ^{31}P NMR spectra to confirm the consumption of PCl_3. In all cases, longer reaction times were necessary to complete the reaction. For 3,3′-dibromo derivative, the corresponding **1b** was obtained in moderate yield, whereas the use of 3,3′-bis- (triphenylsilyl) and 3,3′-bis(triisopropylphenyl) derivatives gave chlorides **1c** and **1d** in better yields (Table I). In the ^{31}P NMR spectra, the substituents scarcely affected the chemical shifts, and the signals of 3,3′-substituted derivatives **1b**–**1d** were at $\delta = 63.2 \pm 1.2$. In contrast, the signals of Se atoms in ^{77}Se NMR spectra were affected by the 3,3′-substituents. The ^{77}Se signal of **1a** was at $\delta = -69.2$, and the introduction of substituents at the 3,3′ positions shifted the signal to lower field by more than 28 ppm.



Scheme 2

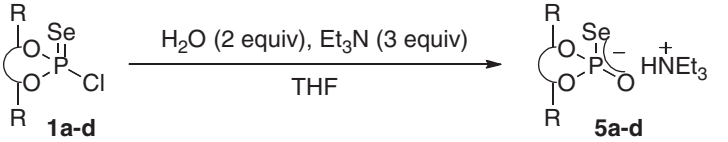
Next, the hydrolysis of chlorides **1** in the presence of Et_3N was carried out in THF (Scheme 3 and Table II). As in the synthesis of chlorides **1**, the substituted chlorides required longer reaction times to be converted to the corresponding salts **5**, but in all cases the salts **5** were obtained in very high yields. The differences in the chemical shifts in the ^{31}P and ^{77}Se NMR spectra of **5** showed a tendency similar to that seen with **1**, i.e., much smaller

Table I Synthesis and properties of phosphoroselenoyl chlorides **1**

entry	**4**	time h	product	yield %	^{31}PNMR δ	^{77}Se NMR δ	$^{1}J_{P\text{-}Se}$[a] Hz
1	**4a** R = H	6	**1a**	90	69.0	−69.2	1060.9
2	**4b** R = Br	9.5	**1b**	48	64.4	−60.3	1079.4
3	**4c** R = $SiPh_3$	24	**1c**	78	63.2	−41.0	1066.6
4	**4d** R = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$	17	**1d**	70	62.2	−41.0	1066.6

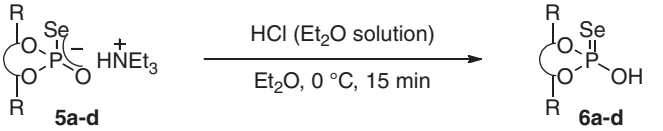
[a]The mean values observed in ^{31}P and ^{77}Se NMR spectra are shown.

differences were observed in ^{31}P NMR than in ^{77}Se NMR. The coupling constants between ^{31}P and ^{77}Se atoms in **5** were lower than those in **1** by about 191 Hz. This indicates that the double bond character between P and Se atoms in salts **5** is weaker than that in **1**.



Scheme 3

Finally, acid hydrolysis of the salts **5** was carried out leading to phosphoroselenoic acids **6** (Scheme 4 and Table III).



Scheme 4

The salts **5** were stirred with an Et_2O solution of HCl, and the reaction was complete within 15 min. The precipitates were removed by filtration, and concentration of the solution gave the corresponding acids **6a**, **6b**, and **6d** as a rare example of *O*,*O*-diaryl phosphoroselenoic acids.[7] In these cases, Et_2O could not be completely removed, and the

Table II Synthesis of phosphoroselenoic acid salts **5**

entry			conditions	yield %	^{31}PNMR% δ	^{77}SeNMR δ	$^{1}J_{P\text{-}Se}$[a] Hz
1	**1a** R = H	reflux, 2 h	**5a**	96	62.1	−235.0	876.3
2	**1b** R = Br	rt, 2h	**5b**	96	60.6	−227.4	898.8
3	**1c** R = $SiPh_3$	rt, 24 h then reflux, 4 h	**5c**	92	57.6	−184.2	889.4
4	**1d** R = 2,4,6-(i-Pr)$_3$C$_6$H$_2$	reflux, 12 h	**5d**	95	57.7	−210.5	860.8

[a]The mean values observed in ^{31}P and ^{77}Se NMR spectra are given.

Table III Synthesis of phosphoroselenoic acids **6**

entry	5	HCl (equiv)	product	yield %	^{31}P NMR δ	^{77}Se NMR δ	$^{1}J_{P\text{-}Se}$[a] Hz
1	**5a** R = H	2	**6a**	88	71.5	−278.2	989.2
2	**5b** R = Br	4	**6b**	82	69.7	−268.4	993.1
3	**5c** R = $SiPh_3$	4	**6c**	84	67.9	−245.6	1012.6
4	**5d** R = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$	2	**6d**	75	69.6	−264.5	996.0

[a]The mean values observed in ^{31}P and ^{77}Se NMR spectra are given.

acids were formed as adducts with less than one equiv. of Et_2O and H_2O based on their ^{1}H NMR spectra. For synthesis of the acid **6c**, the reaction mixture was washed with THF after the reaction to dissolve the reaction product, and this was followed by aqueous workup. Concentration of the organic layer gave acid **6c**, but it contained THF and H_2O. Attempts to remove Et_2O, THF, and H_2O by drying under reduced pressure failed, and the elemental analyses of **6a**, **6c**, and **6d** supported their inclusion. The resulting acids were readily soluble in a variety of solvents such as toluene, THF, and CH_2Cl_2, which is in marked contrast to phosphoric acids bearing a binaphthyl group. The stability of these acids **6** in the solid state depended on the substituents at 3,3′-positions. While unsubstituted acid **6a** is labile, acids **6c** and **6d** can be subjected to prolonged storage at room temperature.

To elucidate the structure of the acids **6**, and particularly the location of the acidic proton, the mean values of NMR data of analogous compounds **2** and **5**–**7** were examined in Table IV.

In the ^{31}P NMR spectra, the signals of **2**, **5**, and **6** were in the range 60 to 80 ppm, whereas those of phosphoroselenoic acid *Se*-esters **7**, which formally possess a P–Se single bond, were at around 31 ppm. Based on these data, in phosphoroselenoic acids **6**, the proton is located on the oxygen atom of **6**. Formally, P–Se bonds are double bonds and P–O bonds are single bonds, and the proton is located at the oxygen atom in solution. This observation is close to that for *t*-BuPhP(Se)OH,[8] but is in strong contrast to those for sulfur isologues of phosphoric acids, which are formulated as a P–O double bond and a P–S single bond.[3,4] Additionally, the effect of the solvent on the location of the proton was examined since selenoic acids have been known to be present as ArC(Se)OH or ArC(O)SeH forms depending on the solvent.[9]

NMR spectra of the acid **6a** were measured in toluene-d_8, $CDCl_3$, methanol-d_4, and THF-d_8 (Table V). In all cases, ^{31}P NMR signal was observed at around 72 ppm and ^{77}Se NMR signal was found at around –280 ppm. No dramatic difference was observed for these

Table IV ^{31}P and ^{77}Se NMR data of phosphoroselenoic acid *O*-esters **2**, acids **6**, acid salts **5**, and *Se*-esters **7** in $CDCl_3$

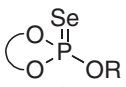
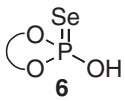
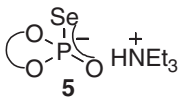
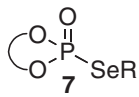
		 **2**	 **6**	 **5**	 **7**
^{31}PNMR	δ	76–80	68–72	62.1	30–32
	$^{1}J_{P\text{-}Se}$	1020–1030	989–1013	874.1	520–580
^{77}Se NMR	δ	−324–327	−246–278	−184–235	200–340

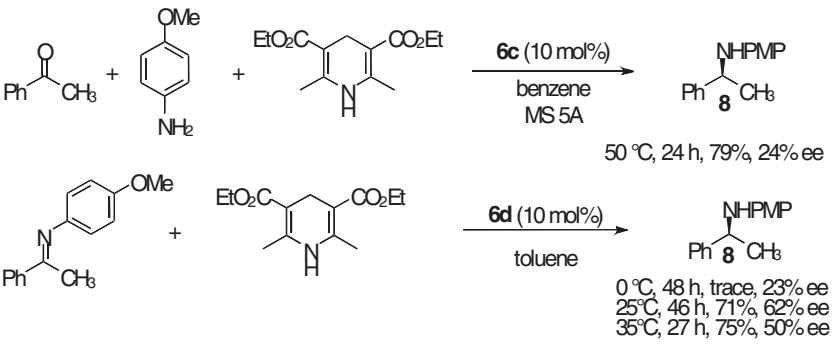
Table V ^{31}P NMR data of phosphoroselenoic acid **6a** in toluene-d_8, $CDCl_3$, methanol-d_4, and THF-d_8

		toluene-d_8	$CDCl_3$	Methanol-d_4	THF-d_8
^{31}PNMR	δ	73.3	72.4	70.4	72.4
	$^1J_{P\text{-}Se}$	1003.6	988.8	951.1	998.5
^{77}Se NMR		–[a]	−278.2	−284.3	−287.9
		–[a]	988.8	970.5	1025.4

[a]Not observed.

chemical shifts or for $^1J_{P\text{-}Se}$ couplings. Therefore, the phosphoroselenoic acid **6a** adopts a structure with O–H bond, and this form was almost independent of the solvent.

Finally, the applicability of phosphoric acid **6** as an organocatalyst was tested. The hydrogenation reaction of an imine with Hantzsch ester was reported independently by Rueping et al.[10] We carried out the reduction reaction for an in-situ generated or isolated imine with Hantzsch ester in the presence of catalytic amount of phosphoroselenoic acid **6** (Scheme 5).



Scheme 5

The acids **6c** and **6d** catalyzed the reaction at room temperature or above to give the desired amine **8** in good yield. The acid **6c** showed only low enantioselectivity for **9**, whereas the reaction catalyzed by **6d** gave **8** in better enantioselectivity, although the phosphoric acids bearing identical substituents have been reported to give **9** in higher enantioselectivities.[10]

In summary, procedures for the synthesis of phosphoroselenoyl chlorides, phosphoroselenoic acids, and ammonium salts with a 1,1′-bi-2-naphthyl group have been described. While the synthesis of derivatives with substituents at the 3,3′-positions required longer reaction times in some cases, all derivatives were obtained in good to high yields. The stability of the chlorides and ammonium salts was independent of the substituents on the binaphthyl group, whereas the unsubstituted acid was more labile than acids with substituents. The structure of the acid was elucidated on the basis of spectroscopic properties, and it adopts a form with a P–Se double bond and an O–H single bond. Finally, the applicability of the acids as organocatalysts was proven in the hydrogenation reaction of the imine with Hantzsch ester.

EXPERIMENTAL

Melting points were measured by a Yanagimoto micro melting point apparatus (uncorrected). IR spectra were obtained on a Jasco FT/IR 410 spectrophotometer. ^{1}H (399.7 MHz), ^{13}C (100.4 MHz), ^{31}P (162.0 MHz), and ^{77}Se (376.0 MHz) NMR spectra were measured on a JEOL α-400 spectrometer. The ^{1}H and ^{13}C chemical shifts are reported in δ values with reference to Me_4Si and $CDCl_3$ as internal standards, respectively. All spectra were acquired in the proton-decoupled mode. Mass (MS) and high-resolution mass spectra (HRMS) were measured on a JEOL JMS-700 spectrometer. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. All the manipulations were carried out under Ar atmosphere.

(S_{ax})-4-Chloro-2,6-dibromodinaphtho[2,1-d:1′,2′-f][1,3,2] dioxaphosphepin-4-selenide (1b)

To a 100 mL three-necked flask, (S_{ax})-3,3′-dibromo-1,1′-binaphthol (3.55 g, 8.0 mmol), selenium powder (0.695 g, 8.8 mmol), and toluene (20 mL) were added under Ar atmosphere. To this mixture, trichlorophosphine (0.698 mL, 8.0 mmol) and triethylamine (2.23 mL, 16 mmol) were added with vigorous stirring. After adding, the mixture was warmed up to 110°C, and stirred for 9.5 h. Then the reaction mixture was filtered, washed with THF, and the filtrate was concentrated. The resulting solid was purified by column chromatography on silica gel (CH_2Cl_2:hexane = 1:2, Rf = 0.50) to give (S_{ax})-4-chloro-2,6-dibromodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphophepin-4-selenide (2.35 g, 48%) as an orange solid: mp: 196–199°C; IR (KBr): 1578, 1498, 1444, 1393, 1357, 1321, 1227, 1151, 1140, 1082, 998, 965, 859, 823, 768, 747, 725, 667, 641, 630, 607, 580, 562, 510, 443, 418 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.21 (d, J = 8.8 Hz, 2H, arom-H), 7.32 (dd, J = 6.8, 8.8 Hz, 2H, arom-H), 7.54 (dd, J = 7.3, 7.8 Hz, 2H, arom-H), 7.89 (d, J = 7.8 Hz, 2H, arom-H), 8.36 (s, 2H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 113.7, 114.3, 123.8, 123.9, 124.1, 127.0, 127.1, 127.3, 127.4, 127.5, 127.7, 131.3, 131.5, 132.3, 132.5, 134.4, 134.5, 143.5, 143.6, 144.4, 144.6 (Ar); ^{31}P NMR ($CDCl_3$): δ = 64.4 ($^{1}J_{SeP}$ = 1078.5 Hz); ^{77}Se NMR ($CDCl_3$): δ = −60.3 ($^{1}J_{SeP}$ = 1080.3 Hz); MS (EI) m/z 586 (M^+); HRMS Calcd for $C_{20}H_{10}Br_2ClO_2PSe$: 585.7633, Found: 585.7620.

(S_{ax})-4-Chloro-2,6-bis(triphenylsilyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-selenide (1c). White solid: mp: >300°C; IR (KBr): 3068, 1617, 1563, 1492, 1428, 1384, 1301, 1276, 1255, 1190, 1149, 1107, 974, 952, 907, 881, 729, 704, 644, 633, 611, 597, 574, 522, 499 445, 410; ^{1}H NMR ($CDCl_3$): δ = 7.19–7.23 (m, 2H, arom-H), 7.29–7.42 (m, 20H, arom-H), 7.44–7.49 (m, 2H, arom-H), 7.61–7.66 (m, 12H, arom-H), 7.83 (t, J = 8.3 Hz, 2H, arom-H), 8.19 (d, J = 7.8 Hz, 2H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 122.5, 122.8, 125.9, 126.0, 126.8, 126.9, 127.0, 127.1, 127.7, 128.0, 128.8, 129.6, 129.7, 130.8, 131.0, 133.5, 134.1, 134.2 (Ar); ^{31}P NMR ($CDCl_3$): δ = 63.2 ($^{1}J_{SeP}$ = 1065.7 Hz); ^{77}Se NMR ($CDCl_3$): δ = –41.0 ($^{1}J_{SeP}$ = 1067.5 Hz), MS (ESI) m/z: 969 $[M+Na]^+$.

(S_{ax})-4-Chloro-2,6-bis(triisoproylphenyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]-dioxaphosphepin-4-selenide (1d). White solid: mp: >300°C, IR (KBr): 3054, 2960, 2930, 2869, 1714, 1607, 1567, 1496, 1460, 1407, 1383, 1362, 1314, 1236, 1196, 1169, 1148, 1115, 1068, 1054, 1029, 988, 966, 938, 889, 874, 854, 821, 777, 750, 731, 714, 675, 660, 646, 633, 620, 587, 555, 531, 513, 499, 474, 461, 448, 431; ^{1}H NMR ($CDCl_3$): δ = 0.89–0.94 (m, 6H, $CH(C\underline{H}_3)_2$), 1.13–1.18 (m, 6H, $CH(C\underline{H}_3)_2$), 1.23–1.29 (m, 6H, $CH(C\underline{H}_3)_2$), 1.31–1.37 (m, 18H, $CH(C\underline{H}_3)_2$), 2.63–2.75 (m, 2H, $C\underline{H}(CH_3)_2$), 2.80–2.87

(m, 1H, C<u>H</u>(CH$_3$)$_2$), 2.92–3.03 (m, 3H, C<u>H</u>(CH$_3$)$_2$), 7.04 (s, 1H, arom-H), 7.08 (s, 1H, arom-H), 7.13–7.22 (m, 4H), 7.29–7.33 (m, 2H), 7.51–7.55 (m, 2H), 7.93–8.00 (m, 4H, arom-H); ^{13}C NMR (CDCl$_3$): δ = 23.4, 23.6, 23.7, 24.05, 24.12, 25.2, 25.3, 27.4, 27.5, 30.9, 31.0, 31.2, 31.3, 34.2 (CH(CH$_3$)$_2$), 120.5, 121.1, 121.7, 121.8, 122.8, 122.9, 126.2, 126.6, 127.3, 127.4, 128.4, 130.4, 130.8, 131.3, 131.4, 131.6, 132.2, 132.5, 132.6, 133.4, 133.6, 145.8, 145.9, 146.8, 146.9, 147.1, 147.7, 147.8, 148.8, 148.9 (Ar); ^{31}P NMR (CDCl$_3$): δ = 62.2 ($^1J_{SeP}$ = 1065.7 Hz); ^{77}Se NMR (CDCl$_3$): δ = –41.0 ($^1J_{SeP}$ = 1067.5 Hz); MS (ESI) m/z: 857 [M+Na]$^+$; Anal. Calcd for $C_{50}H_{56}ClO_2PSe$ (834.3652): C, 71.98; H, 6.76, Found: C, 71.68; H, 6.53%.

(S_{ax})-2,6-Dibromodinaphtho[2,1-d:1′,2′-f][1,3,2] dioxaphosphepin-4-selenoic Acid Triethyl Ammonium Salt (5b)

To a 50 mL two-necked flask, (S_{ax})-3,3′-dibromobinaphthylphosphoro-selenoyl chloride (1.55 g, 2.5 mmol), THF (9.5 mL), H_2O (0.090 mL, 5.0 mmol), and Et_3N (1.05 mL, 7.5 mmol) were added under Ar atmosphere, and the mixture was stirred at room temperature for 2 h. Then, the reaction mixture was diluted with CH_2Cl_2, washed with water, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give a white solid. The solid was purified by recrystallization (CH_2Cl_2/Et_2O) to give (S_{ax})-2,6-dibromodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-selenoic acid triethylammonium salt (1.60 g, 96%) as a white solid: mp: 254–264°C; IR (KBr): 3060, 2979, 2665, 1577, 1496, 1474, 1461, 1445, 1413, 1392, 1357, 1325, 1238, 1221, 1174, 1032, 1008, 967, 903, 830, 804, 754, 729, 662, 639, 622, 608, 572, 511, 456 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 1.34 (t, J = 7.3 Hz, 9H, HN(CH$_2$C<u>H</u>$_3$)$_3$), 3.13 (m, 6H, HN(C<u>H</u>$_2$CH$_3$)$_3$), 7.21 (m, 4H, arom-H), 7.41 (s, 2H, arom-H), 7.79 (d, J = 7.8 Hz, 1H, arom-H), 7.81 (d, J = 8.3 Hz, 1H, arom-H), 8.22 (s, 1H, arom-H), 8.28 (s, 1H, arom-H), 11.3 (br s, 1H, <u>H</u>N(CH$_2$CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$): δ = 8.7 (HN(CH$_2$<u>C</u>H$_3$)$_3$), 46.0 (HN(<u>C</u>H$_2$CH$_3$)$_3$), 116.1, 124.1, 124.2, 124.5, 125.8, 126.3, 126.4, 127.0, 127.1, 127.3, 127.4, 131.6, 131.9, 132.8, 133.3, 145.4, 145.5, 145.8, 145.9 (Ar); ^{31}P NMR (CDCl$_3$): δ = 60.6 ($^1J_{SeP}$ = 894.8 Hz); ^{77}Se NMR (CDCl$_3$): δ = −227.4 ($^1J_{SeP}$ = 902.8 Hz); MS (FAB) m/z: 567 (M$^-$).

(S_{ax})-2,6-Bis(triphenylsilyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-selenoic acid triethylammonium salt (5c). Pale yellow solid: mp: 265–275°C; IR (KBr): 3067, 3047, 2607, 2466, 1565, 1486, 1428, 1390, 1210, 1148, 1105, 978, 836, 755, 705, 672, 625, 584, 504, 494, 416; ^{1}H NMR (CDCl$_3$): δ = 0.69 (t, J = 7.3 Hz, 9H, HN(CH$_2$C<u>H</u>$_3$)$_3$), 2.14 (m, 3H, HN(C<u>H</u>$_2$CH$_3$)$_3$), 2.26 (m, 3H, HN(C<u>H</u>$_2$CH$_3$)$_3$), 7.13–7.75 (m, 38H, arom-H), 7.96 (s, 1H, arom-H), 8.04 (s, 1H, arom-H), 10.7 (br s, 1H, <u>H</u>N(CH$_2$CH$_3$)$_3$); ^{13}C NMR (CDCl$_3$): δ = 8.7 (HN(CH$_2$<u>C</u>H$_3$)$_3$), 46.0 (HN(<u>C</u>H$_2$CH$_3$)$_3$), 116.1, 124.1, 124.2, 124.5, 125.8, 126.3, 126.4, 127.0, 127.1, 127.3, 127.4, 131.6, 131.9, 132.8, 133.3, 145.4, 145.5, 145.8, 145.9 (Ar); ^{31}P NMR (CDCl$_3$): δ = 57.6 ($^1J_{SeP}$ = 888.1 Hz); ^{77}Se NMR (CDCl$_3$): δ = -184.2 ($^1J_{SeP}$ = 890.6 Hz); MS (FAB) m/z: 927 (M$^-$).

(S_{ax})-2,6-Bis(triisopropylphenyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-selenoic acid triethyl ammonium salt (5d). Pale yellow solid: mp: 185–191°C; IR (KBr): 2956, 2607, 2455, 1606, 1567, 1494, 1460, 1408, 1381, 1361, 1315, 1243, 1214, 1138, 1068, 996, 967, 938, 884, 859, 831, 777, 749, 709, 661, 630, 612, 574, 520, 457; ^{1}H NMR (CDCl$_3$): δ = 0.71 (d, J = 6.8 Hz, 3H), 0.79 (t, J = 7.3 Hz, 9H, NCH$_2$C<u>H</u>$_3$), 0.90 (d, J = 6.8 Hz, 3H), 1.03 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 1.19–1.23 (m, 15H), 1.27 (t, J = 6.8 Hz, 6H), 2.60–2.87

(m, 11H), 3.41 (m, 1H), 6.87 (d, $J = 2.0$ Hz, 1H, arom-H), 6.97 (d, $J = 3.9$ Hz, 2H, arom-H), 7.05–7.19 (m, 5H, arom-H), 7.32 (dd, $J = 6.8$ Hz, 7.8 Hz, 2H, arom-H), 7.71 (s, 1H, arom-H), 7.75–7.80 (m, 3H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 8.3$, 23.2, 23.8, 24.1, 24.2, 24.3, 24.7, 25.0, 25.1, 26.1, 27.4, 30.5, 30.6, 31.1, 31.2, 34.2, 45.2 (alkyl part), 119.6, 120.5, 120.6, 121.5, 123.1, 123.2, 124.5, 124.6, 125.4, 127.2, 127.6, 127.9, 128.0, 130.4, 130.5, 131.4, 132.3, 132.7, 132.9, 133.1, 13.4, 133.8, 147.2, 147.3, 147.4, 147.8, 148.0, 148.4, 148.5, 148.7 (Ar); ^{31}P NMR ($CDCl_3$): $\delta = 57.7$ ($^1J_{SeP} = 861.5$ Hz); ^{77}Se NMR ($CDCl_3$): $\delta = -210.5$ ($^1J_{SeP} = 860.1$ Hz); MS (ESI) m/z: 918 $[M+H]^+$.

(S_{ax})-Dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide (6a)

To a 20 mL two-necked flask, phosphoroselenoic acid triethylammonium salt (0.512 g, 1.0 mmol) and Et_2O (10 mL) were added under Ar atmosphere, and the mixture was cooled to 0°C. To this solution was added hydrogen chloride (1.0 M Et_2O solution, 2 mL, 2.0 mmol), and the mixture was stirred at that temperature for 15 min. The insoluble part was filtered. Removal of the solvent from the filtrate under reduced pressure gave a white solid containing (S_{ax})-dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide and Et_2O in approximately 1:0.78 ratio (^{1}H NMR) (0.407 g, 88%): mp (decomp.): 100–140°C; IR (KBr): 3426, 3056, 2978, 2933, 2881, 2342, 1908, 1685, 1619, 1589, 1508, 1462, 1433, 1385, 1361, 1322, 1223, 1200, 1155, 1069, 980, 951, 857, 841, 814, 793, 772, 750, 712, 697, 654, 617, 575, 563, 529, 507, 485, 456, 418 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.72$ (brs, 2H, OH), 7.26–7.62 (m, 8H, arom-H), 7.93–8.06 (m, 4H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 120.9$, 121.4, 122.2, 122.5, 125.7, 126.5, 126.6, 127.1, 127.2, 128.4, 128.5, 130.8, 131.0, 131.7, 131.9, 132.4, 132.5, 146.6, 146.7, 147.9, 148.1 (Ar); ^{31}P NMR ($CDCl_3$): $\delta = 71.5$ ($^1J_{SeP} = 989.6$ Hz); ^{77}Se NMR ($CDCl_3$): $\delta = -278.2$ ($^1J_{SeP} = 988.8$ Hz); Anal. Calcd for $C_{20}H_{13}O_3PSe \cdot 0.5\ Et_2O \cdot 0.3\ H_2O$ (453.7152): C, 58.41; H, 3.19, Found: C, 58.24; H, 4.13%.

(S_{ax})-2,6-Dibromodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide (6b)

To a 20 mL two-necked flask, the (S_{ax})-3,3′-dibromobinaphthylphosphoro-selenoic acid triethylammonium salt (0.335 g, 0.50 mmol) and Et_2O (5 mL) were added under Ar atmosphere, and the mixture was cooled to 0°C. To this solution, hydrogen chloride (1.0 M Et_2O solution, 2 mL, 2.0 mmol) was added, and the mixture was stirred at that temperature for 15 min. The insoluble part was filtered. Removal of the solvent from the filtrate under reduced pressure gave a white solid containing (S_{ax})-2,6-dibromodinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide and Et_2O in approximately 1:0.83 ratio (^{1}H NMR) (0.260 g, 82%): mp: 90–130°C (dec.); IR (KBr): 3057, 2976, 1699, 1616, 1578, 1498, 1444, 1392, 1323, 1231, 1003, 966, 854, 747, 666, 627, 571, 508 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 5.70$ (br s, 3H), 7.18–7.27 (m, 4H, arom-H), 7.48 (dd, $J = 11.7$, 7.3 Hz 2H, arom-H), 7.85 (dd, $J = 8.3$, 4.9 Hz, 2H, arom-H), 8.29 (s, 1H, arom-H), 8.32 (s, 1H, arom-H); ^{13}C NMR ($CDCl_3$): $\delta = 114.6$, 115.0, 123.6, 124.0, 126.7, 127.0, 127.1, 127.6, 131.4, 131.5, 131.6, 132.1, 133.6, 134.0, 143.5, 144.7, 144.8; ^{31}P NMR ($CDCl_3$): $\delta = 69.7$ ($^1J_{SeP} = 1016.3$ Hz); ^{77}Se NMR ($CDCl_3$): $\delta = -268.4$ ($^1J_{SeP} = 969.9$ Hz); MS (EI) m/z 568 (M^+); HRMS Calcd for $C_{20}H_{11}O_3PSe$: 567.7972, Found: 567.7973.

(S_{ax})-2,6-Bis(triphenylsilyl)dinaphtho[2,1-d:1′,2′-f][1,3,2] dioxaphosphepin-4-hydroxy-4-selenide (6c)

To a 20 mL two-necked flask, the (S_{ax})-3,3′-bis(triphenylsilyl)binaphthylphosphoroselenoic acid triethylammonium salt (0.542 g, 0.50 mmol) and Et_2O (5 mL) were added under Ar atmosphere, and the mixture was cooled to 0°C. To this solution, hydrogen chloride (1.0 M Et_2O solution, 2 mL, 2.0 mmol) was added, and the mixture was stirred at that temperature for 15 min. Then, the reaction mixture was dilluted with THF, washed with water, and the aqueous layer was extracted with Et_2O. The combined organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give a white solid containing (S_{ax})-2,6-bis(triphenylsilyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide and THF in approximately 1:1.8 ratio (^{1}H NMR) (0.441 g, 84%): mp: 140–205°C (dec.); IR (KBr): 3067, 3048, 1563, 1487, 1428, 1388, 1217, 1107, 978, 954, 858, 743, 700, 591, 504, 428, 407; ^{1}H NMR ($CDCl_3$): δ = 7.13–7.35 (m, 24H, arom-H), 7.56–7.60 (m, 12H, arom-H), 7.66 (d, J = 8.3 Hz, 1H, arom-H), 7.72 (d, J = 8.3 Hz, 1H, arom-H), 7.99 (s, 1H, arom-H), 8.08 (s, 1H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 122.2, 122.6, 125.4, 125.9, 126.8, 127.0, 127.3, 127.4, 127.7, 127.9, 128.1, 128.7, 129.3, 129.6, 129.9, 130.7, 130.8, 133.9, 134.2, 134.3, 134.9, 136.5, 136.7, 136.8, 137.0, 137.3, 141.7, 142.0, 150.7, 150.8, 152.2, 152.4; ^{31}P NMR ($CDCl_3$): δ = 67.9 ($^1J_{SeP}$ = 1006.5 Hz); ^{77}Se NMR ($CDCl_3$): δ = -245.6 ($^1J_{SeP}$ = 1018.7 Hz); Anal. Calcd for $C_{56}H_{41}O_3PSeSi_2 \cdot 1$ THF $\cdot$ 1.5 H_2O (1027.1564): C, 70.16; H, 5.10, Found: C, 70.23; H, 5.06.

(S_{ax})-2,6-Bis(triisopropylphenyl)dinaphtho[2,1-d:1′,2′-f][1,3,2] dioxaphosphepin-4-hydroxy-4-selenide (6d)

To a 20 mL two-necked flask, the (S_{ax})-3,3′-bis(triisopropylphenyl)-binaphthylphosphoroselenoic acid triethylammonium salt (0.459 g, 0.50 mmol) and Et_2O (5 mL) were added under Ar atmosphere, and the mixture was cooled to 0°C. To this solution, hydrogen chloride (1.0 M Et_2O solution, 1 mL, 1.0 mmol) was added, and the mixture was stirred at that temperature for 15 min. The insoluble part was filtered. Removal of the solvent from the filtrate under reduced pressure gave a pale yellow solid containing (S_{ax})-2,6-bis(triisopropylphenyl)dinaphtho[2,1-d:1′,2′-f][1,3,2]dioxaphosphepin-4-hydroxy-4-selenide and Et_2O in approximately 1:0.60 ratio (^{1}H NMR) (0.330 g, 75%): mp: 196–200°C (dec.); IR (KBr): 3569, 3049, 2964, 2869, 2354, 1606, 1567, 1496, 1461, 1407, 1383, 1362, 1315, 1238, 1207, 1149, 1116, 1068, 968, 938, 872, 821, 778, 750, 715, 661, 632, 616, 571, 515, 455, 410 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 0.85 (d, J = 6.3 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 0.99 (d, J = 6.8 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.06 (d, J = 6.8 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.13 (d, J = 6.3 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 1.24–1.32 (m, 21H, CH(C$\underline{H}_3$)$_2$), 1.35 (d, J = 6.3 Hz, 3H, CH(C$\underline{H}_3$)$_2$), 2.68 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 2.81 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 2.93 (m, 2H, C$\underline{H}$(CH$_3$)$_2$), 3.11 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 7.00 (d, J = 1.5 Hz, 1H, arom-H), 7.10–7.13 (m, 3H, arom-H), 7.19–7.34 (m, 4H, arom-H), 7.47–7.51 (m, 2H, arom-H), 7.89–7.92 (m, 3H, arom-H), 7.97 (s, 1H, arom-H); ^{13}C NMR ($CDCl_3$): δ = 23.2, 23.8, 24.11, 24.13, 24.15, 24.20, 24.22, 25.2, 25.3, 26.8, 27.5, 30.6, 30.9, 31.0, 31.3, 34.3 (CH(CH$_3$)), 120.1, 120.8, 121.2, 121.6, 122.5, 122.6, 122.92, 122.94, 125.6, 125.7, 126.1, 126.2, 127.3, 127.6, 128.2, 128.3, 131.0, 131.5, 131.8, 132.02, 132.05, 132.37, 132.41, 132.5, 132.59, 132.61, 133.1, 145.5, 145.6, 146.9, 147.0, 147.1, 147.9, 148.1, 148.2, 148.3, 148.5; ^{31}P NMR ($CDCl_3$): δ = 69.6 ($^1J_{SeP}$ = 997.7 Hz); ^{77}Se NMR ($CDCl_3$): δ = −264.5

($^1J_{SeP} = 994.3$ Hz); Anal. Calcd for $C_{50}H_{57}O_3PSe \cdot 1\ H_2O$ (834.3317): C, 72.01; H, 7.13, Found: C, 71.82; H, 7.11%.

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