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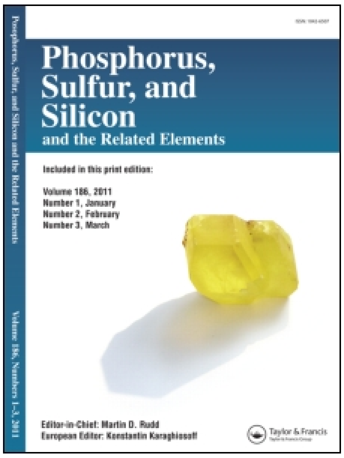

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Synthesis and Fugicidal Activities of 2-Silatranyl Propylamino-4-substitued Phenyl(Hydrogen)-5,5-dimethyl-1,3,2-dioxaphosphinanes-2-oxides (Sulfides)

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*Phosphoryl-aminopropyl-silatranes **4** were synthesized by nucleophilic reactions of 2-Cl-1,3,2- dioxaphosphinanes **2** with γ-aminopropyl-silatrane **3**, which was obtained by the cyclization reaction of triethanolamine and γ-aminopropyltriethoxysilane. The structures of the products were characterized by ^{1}H NMR, ^{31}P NMR, IR, MS, and elemental analyses. The target compounds **4** exhibited fungicidal activity.*

Keywords 2-Cl-1,3,2-Dioxaphosphinanes; fungicidal activity; synthesis; nucleophilic reactions; phosphoryl-aminopropyl-silatranes; γ-aminopropyl silatrane

INTRODUCTION

2-Cl-1,3,2-dioxaphosphinane is an important heterocycle which shows good biological and pharmaceutical activity. Some derivatives were found to exhibit good fungicidal or antitumor activities.[1–5] As an important intermediate compound, γ-aminopropyl silatrane has been found to have good biological activity.[6–9] Therefore, we became interested in the synthesis of phosphoryl-aminopropyl-silatranes. Herein we have synthesized a series of 2-Cl-4-substitued-1,3, 2-dioxaphosphinanes, which were reacted with γ-aminopropyl silatrane to give the target compounds phosphoryl-aminopropyl–silatranes **4**. The synthetic route

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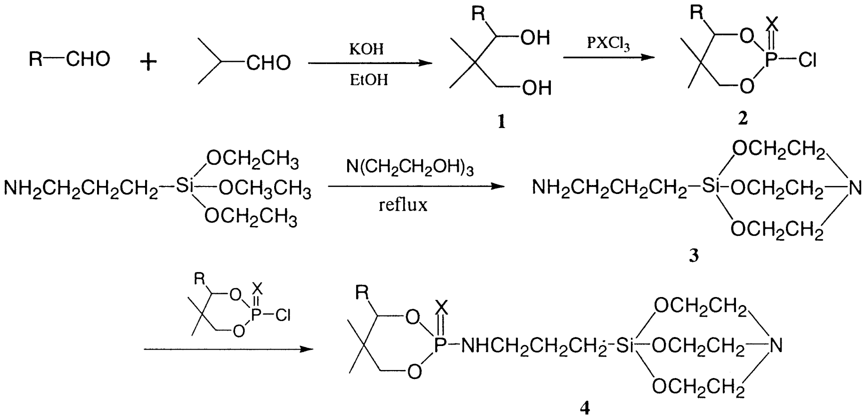
is shown in Scheme 1. The structures of the products was verified by ^{1}H NMR, ^{31}P NMR, IR, MS, and elemental analyses. Some of the products possess potential fungicidal activity.



SCHEME 1

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RESULTS AND DISCUSSION

The easily accessible substituted benzaldehydes reacted with isobutyraldehyde in the presence of potassium hydroxide to give diols **1**, which readily were reacted with phosphorus oxychloride or phosphorus thiochloride to give 2-Cl-1,3,2-dioxaphosphinanes **2**. Reaction of **2** with γ-aminopropyl silatrane **3** gave target compounds **4** in good yields (see Table I).

The formation of **4** was a nucleophilic substitution reaction. Initially, 2-Cl-1,3,2-dioxaphosphinanes **2** in methylene dichloride were added dropwise to γ-aminopropyl silatrane **3** to obtain target compounds **4**, but the reaction required 5–6 h and the yields were low. Next, triethylamine was used as an acid-binding agent. In the presence of triethylamine, the reaction times were shorter and the yields were higher. Although the reactivity of $\mathbf{2_{a\sim f}}$ were different from $\mathbf{2_{g\sim l}}$, when the reactions were carried out at 20$\sim$30°C, only the reaction times were different. With the use of triethylamine, the best reaction time was 2–4 h and the yields were about 80% (see Table I).

The structures of **4** have been verified spectroscopically. For example, the ^{1}H NMR spectral data for **4c** showed the signals of Si—CH$_2$ at 0.14–0.17 ppm as a triplet; the protons of the 5-position methyl groups of the phosphorus heterocycle appeared as two single peaks at 0.73 ppm and 0.92 ppm, as the two methyl groups are located in different magnetic

TABLE I Preparation of Phosphoryl-Aminopropyl-Silatranes 4

Compound	X	R	Reaction time (h)	Yield (%)[a]
4a	O	H	2	85
4b	O	Ph	2	83
4c	O	4-Cl-C_6H_4	2	78
4d	O	4-CH_3-C_6H_4	2	76
4e	O	4- CH_3O-C_6H_4	3	70
4f	O	2,4-Cl_2- C_6H_4	3	79
4g	S	H	3	80
4h	S	Ph	3	79
4i	S	4-Cl-C_6H_4	3	77
4j	S	4-CH_3-C_6H_4	3	75
4k	S	4- CH_3O-C_6H_4	4	65
4l	S	2,4-Cl_2- C_6H_4	4	74

[a]Isolated yields based on 2-Cl-1,3,2-dioxaphosphinanes used. The reactions were run in the presence of Et_3N.

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environments; and the chemical shift of the multiplets due to P—N—CH_2 overlapped with the multiplets due to N—CH_2 at 2.52–2.79 ppm and O—CH_2 at 3.29–3.60 ppm. An addition of the silatrane unit resonances include a triplet for —NH at 5.18–5.24 ppm, and a singlet for O—CH at 5.30 ppm . The aromatic signals of the R group appear at 7.39–7.47 ppm as multiplets. For ^{31}P NMR spectra, the phosphorus atom appeared as a singlet with a chemical shift of 7.65 ppm. In the IR spectral data of **4c**, the NH stretching frequency of N—H appears as a broad peak at 3234 cm^{-1}, the strong stretching frequency of P=O appears at 1211 cm^{-1}, the stretching frequency of P—O—C showed a strong absorption at 1089 cm^{-1} and 995 cm^{-1}, and the strong absorption due to Si—O—C appeared at 1045 cm^{-1}. The MS spectrum of **4c** showed a molecule ion peak at m/z 490.5 with a 19% abundance and the other main fragmentation peaks were in accordance with the structure of **4c**. As for the corresponding compound of **4i**, the ^{1}H NMR spectral data and MS spectrum are similar to **4c**; in the IR spectral data of **4i**, the strong stretching frequency of P=S appears at 752 cm^{-1}; and for the ^{1}P NMR spectra of **4i**, the chemical shift for the phosphorus atom appeared at 69.9 ppm.

The biological activity of **4** was investigated, and the results indicated a moderate-to-good fungicidal activity. For example, **4l** showed 87% inhibition of *Botrytis cinerepers* and **4f** showed 85% inhibition of *Bipilaris maydis* in 50 mg/L (see Table II).

EXPERIMENTAL

All reagents were analytically pure. Solvents were purified according to standard procedures. Melting points were uncorrected. MS data were

TABLE II The Fungicidal Activities of Phosphoryl-Aminopropyl-Silatranes 4 (50 mg/L, Relative Inhibition Ratio %)

Compound	*Fusarium oxysporium*	*Rhizoctonia solani*	*Botrytis cinerepers*	*Gibberella zeae*	*Dothiorella gregaria*	*Bipilaris maydis*
4a	24	54	70	37	58	79
4b	15	16	57	12	37	65
4c	29	30	40	37	16	55
4d	29	53	20	37	27	45
4e	28	51	72	31	45	63
4f	39	58	80	40	43	85
4g	29	33	64	37	43	70
4h	29	6	70	33	6	45
4i	34	40	30	37	32	60
4j	24	55	61	46	43	55
4k	30	52	59	35	41	70
4l	43	60	87	55	64	81

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obtained on a Finnigan Trace MS spectrometer. IR were recorded on a PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^{1}H NMR and ^{31}P NMR spectra were recorded on a VARIAN MERCURY-PLUS 400 spectrometer with TMS and 85% H_3PO_4 as the internal and external reference, respectively, in DMSO-d_6 as the solvent. Resonnces are given in ppm (δ). Elementary analysis were obtained on a Perkin-Elmer CHN 2400 elementary analysis instrument.

Preparation of Phosphoryl-Aminopropyl-Silatranes 4[10–16]

100 mmol (substitued) and benzaldehyde and 200 mmol isobutyraldehyde were added into a 250 mL three-necked flask, and a solution of 100 mmol KOH in 90 mL dry ethanol was added dropwise at a bath temperature between 50~60°C with for stirring 5 h. Then the solvent was removed under reduced pressure, and 100 mL of cold water was added to the residual mixture. After standing for 12 h, filtration provided a solid which was washed twice with heptane and was recrystallized from toluene to give the diols **1**.

To a solution of 10 mmol **1** prepared as above in 50 mL dry methylene dichloride, 10 mmol phosphorus oxychloride was added dropwise over 1 h at 35°C, and the mixtrre was stirred under reflux for 2 h. The solvent was removed under reduced pressure, and the residual mixture was recrystallized from toluene to give 2-Cl-1,3,2-dioxaphosphinanes $\mathbf{2_{a\sim f}}$.

10 mmol of **1**, 10 mmol of phosphorus thiochloride and 16 mL of dry tetrahydrofuran were added to a 100 mL three necked-flask. A solution of 20 mmol triethylamine in 8 mL dry tetrahydrofuran was added dropwise over 1 h at ice-bath temperatures from the foltrate, then at

room temperture with stirring for 14 h. After filtration, the solvent was removed under reduced pressure, and the residual mixture was recrystallized from cyclohexane to give 2-Cl-1,3,2-dioxaphosphinanes $\mathbf{2_{g\sim l}}$.

100 mmol of triethanolamine and 100 mmol of γ-aminopropyltriethoxysilane were added to a 250 mL three-necked flask, which was fitted with a thermometer and a Dean Stark trap. The mixture was heated slowly to reflux, and reflux continued until the ethanol substantially was removed. The reaction product remaining in the flask was γ-aminopropyl-silatrane **3**, which was used directly without further purification.

5 mmol of γ-aminopropyl-silatrane **3**, 5 mmol of triethylamine, and 30 mL of dry methylene dichloride were added to a 100 mL three-necked flask; a solution of 5 mmol **2** in 8 mL of dry methylene dichloride was added dropwise for 1 h at a bath temperture of 10°C and kept at room temperture with stirring for 2∼4 h. The solvent was removed under reduced pressure and the residual mixture was washed twice with a little water and was recrystallized from ethanol–water to give phosphorylaminopropyl-silatranes **4**.

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2-Silatranyl Propylmino-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4a)

White crystals, m.p. 228–229°C, ^{1}H NMR (DMSO-d$_6$, 400 MHz) $\delta =$ 4.93–4.97 (t, 1H, —NH), 3.76–3.98 (m, 10H, O-CH$_2$), 2.63–2.76 (m, 8H, N-CH$_2$), 1.40–1.42 (m, 2H, C-CH$_2$), 1.02 (s, 3H, CH$_3$), 0.87 (s, 3H, CH$_3$), 0.06–0.10 (t, 2H, Si-CH$_2$); ^{31}P NMR (DMSO-d$_6$, 400 MHz) $\delta =$ 7.71; IR (KBr) (υ_{max}/cm^{-1}), 3283 (N—H), 1263 (P=O), 1096 and 1006 (P—O—C), 1052 (Si—O—C); MS(m/z, %), 380 (M, 14.9), 336 (50.4), 322 (93.8), 207 (7.2), 174 (100), 149 (2.9), 129 (51.0). Elemental anal. calcd. for $C_{14}H_{29}N_2O_6PSi$: C, 44.21; H, 7.63; P, 8.16. Found: C, 44.28; H, 7.69; P, 8.08.

2-Silatranyl Propylmino-4-phenyl-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4b)

White crystals, m.p. 186–188°C, ^{1}H NMR (DMSO-d$_6$, 400 MHz) $\delta =$ 7.31–7.39 (m, 5H, Ph—H), 5.32 (s, 1H, O—CH), 5.21–5.27 (t, 1H, —NH), 3.32–3.63 (m, 8H, O—CH$_2$), 2.51–2.80 (m, 8H, N—CH$_2$), 1.41–1.43 (m, 2H, C—CH$_2$), 0.89 (s, 3H, CH$_3$), 0.70 (s, 3H, CH$_3$), 0.12–0.16 (t, 2H, Si-CH$_2$); ^{31}P NMR (DMSO-d$_6$, 400MHz) $\delta = 7.68$; IR (KBr) (υ_{max}/cm^{-1}), 3210 (N—H), 1229 (P=O), 1098 and 993 (P—O—C), 1051 (Si—O—C); MS(m/z), 456 (M$^+$, 1.3), 411 (5.9), 313 (1.0), 283 (2.0), 254 (4.1), 174 (100), 129 (4.9), 91 (10.8). Elemental anal. calcd. for $C_{20}H_{33}N_2O_6PSi$: C, 52.63; H, 7.24; P, 6.80. Found: C, 52.57; H, 7.29; P, 6.85.

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2-Silatranyl Propylmino-4-(4-chloro-phenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4c)

White crystals, m.p. 210–211°C, ^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.39–7.47 (m, 4H, Ph—H), 5.30 (s, 1H, O—CH), 5.18–5.24 (t, 1H, —NH), 3.29–3.60 (m, 8H, O—CH_2), 2.52–2.79 (m, 8H, N—CH_2), 1.46–1.53 (m, 2H, C—CH_2), 0.92 (s, 3H, CH_3), 0.73 (s, 3H, CH_3), 0.14–0.17 (t, 2H, Si-CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta = 7.65$; IR (KBr) (υ_{max}/cm^{-1}), 3234 (N-H), 1211 (P=O), 1089 and 995 (P—O—C), 1045 (Si—O—C); (m/z), 490.5 (M^+, 19.2), 460 (11.2), 313 (27.7), 281 (37.1), 254 (69.0), 174 (100), 129 (25.4), 91 (12.0). Elemental anal. calcd. for $C_{20}H_{32}ClN_2O_6PSi$: C, 48.93; H, 6.52; P, 6.32. Found: C, 48.86; H, 6.60; P, 6.38.

2-Silatranyl Propylmino-4-(4-methyl-phenyl) -5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4d)

White crystals, m.p. 209–210°C,^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.20–7.21 (m, 4H, Ph—H), 5.26 (s, 1H, O—CH), 5.20-5.23 (t, 1H,—NH), 3.34–3.63 (m, 8H, O—CH_2), 2.51–2.80 (m, 8H, N-CH_2), 2.31 (s, 3H, Ar–CH_3), 1.45–1.54 (m, 2H, C—CH_2), 0.93 (s, 3H, CH_3), 0.67 (s, 3H, CH_3), 0.12–0.16 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta =$ 7.78; IR (KBr) (υ_{max}/cm^{-1}), 3215 (N—H), 1211 (P—O), 1095 and 994 (P—O—C), 1047 (Si—O—C); MS (m/z), 470 (M^+, 0.1), 313 (2.5), 281 (5.6), 254 (24.3), 174 (100), 129 (9.0), 91 (11.0). Elemental anal. calcd. for $C_{21}H_{35}N_2O_6PSi$: C, 53.62; H, 7.45; P, 6.60. Found: C, 53.58; H, 7.41; P, 6.63.

2-Silatranyl propylmino-4-(4-methoxyl-phenyl) -5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4e)

Pale yellow crystals, m.p. 205–206°C, ^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.32–7.38 (m, 4H, Ph—H), 5.33 (s, 1H, O—CH), 5.20–5.25 (t, 1H, —NH), 3.71 (s, 3H, O—CH_3) 3.30–3.62 (m, 8H, O—CH_2), 2.53–2.78 (m, 8H, N—CH_2), 1.48–1.56 (m, 2H, C—CH_2), 0.86 (s, 3H, CH_3), 0.68 (s, 3H, CH_3), 0.11–0.15 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta = 7.70$; IR (KBr) (υ_{max}/cm^{-1}), 3243 (N-H), 1238 (P=O), 1091 and 995 (P—O—C), 1045 (Si—O—C); MS (m/z), 486 (M^+, 3.0), 313 (4.1), 281 (7.2), 254 (20.5), 174 (100), 129 (11.3), 91 (16.6). Elemental anal. calcd. for $C_{21}H_{35}N_2O_7PSi$: C, 51.85; H, 7.20; P, 6.38. Found: C, 51.79; H, 7.18; P, 6.42.

2-Silatranyl Propylmino-4-(2,4-dichlorophenyl) -5,5-dimethyl-1,3,2-dioxaphosphinane-2-oxide (4f)

White crystals, m.p. 249–250°C ,^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.46–7.69 (m, 3H, Ph—H), 5.67 (s, 1H, O—CH), 5.35–5.40 (t, 1H, —NH), 3.33–3.62 (m, 8H, O—CH_2), 2.57–2.80 (m, 8H, N—CH_2), 1.44–1.50 (m, 2H, C—CH_2), 1.00 (s, 3H, CH_3), 0.74 (s, 3H, CH_3), 0.12–0.16 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta = 7.69$; IR (KBr) (υ_{max}/cm^{-1}), 3235 (N—H), 1243 (P=O), 1097 and 996 (P—O—C), 1048 (Si—O—C); MS (m/z), 525 (M^+, 0.2), 313 (1.6), 281 (7.1), 254 (21.5), 174 (100), 129 (5.1), 91 (3.1). Elemental anal. calcd. for $C_{20}H_{31}Cl_2N_2O_6PSi$: C, 45.71; H, 5.90; P, 5.90. Found: C, 45.66; H, 5.87; P, 5.94.

2-Silatranyl PropyImino-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4g)

White crystals, m.p. 179–180°C, ^{1}H NMR (DMSO-d_6 ,400 MHz) $\delta =$ 5.70–5.75 (t, 1H, —NH), 3.70–4.13 (m, 10H, O—CH_2), 2.75–2.82 (m, 8H, N—CH_2), 1.43–1.46 (m, 2H, C–CH_2), 1.14 (s, 3H, CH_3), 0.79 (s, 3H, CH_3), 0.07–0.11 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6 ,400MHz) $\delta =$ 69.6; IR (KBr) (υ_{max}/cm^{-1}), 3219 (N—H), 1104 and 1009 (P—O—C), 1035 (Si—O—C), 757 (P=S); MS (m/z), 396 (M^+, 2.1), 353 (5.3), 339 (26.0), 223 (7.4), 174 (100), 129 (14.2). Elemental anal. calcd. for $C_{14}H_{29}N_2O_5PSSi$: C, 42.42; H, 7.32; P, 7.83. Found: C, 42.38; H, 7.37; P, 7.86.

2-Silatranyl PropyImino-4-phenyl-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4h)

Pale yellow crystals, m.p. 156–158°C, ^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.32–7.41 (m, 5H, Ph—H), 5.95–5.99 (t, 1H, —NH), 5.35 (s, 1H, O—CH), 3.35–3.90 (m, 8H, O—CH_2), 2.51–2.98 (m, 8H, N—CH_2), 1.51–1.60 (m, 2H, C—CH_2), 0.90 (s, 3H, CH_3), 0.73 (s, 3H, CH_3), 0.15–0.19 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta = 69.8$; IR (KBr) (υ_{max}/cm^{-1}), 3231 (N—H), 1091 and 1019 (P—O—C), 1027 (Si—O—C), 751 (P=S); MS (m/z), 472 (M^+, 3.9), 329 (3.3), 299 (3.4), 270 (6.2), 174 (100), 129 (8.0), 91 (16.9). Elemental anal. calcd. for $C_{20}H_{33}N_2O_5PSSi$: C, 50.85; H, 6.99; P, 6.57. Found: C, 50.80; H, 7.05; P, 6.63.

2-Silatranyl PropyImino-4-(4-chloro-phenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4i)

Pale yellow crystals, m.p. 165–167°C, ^{1}H NMR (DMSO-d_6, 400 MHz) $\delta =$ 7.41-7.49 (m, 4H, Ph—H), 5.91–5.97 (t, 1H, —NH), 5.36 (s, 1H, O—CH), 3.36–3.85 (m, 8H, O—CH_2), 2.52–2.93 (m, 8H, N—CH_2), 1.49–1.58 (m, 2H, C—CH_2), 0.89 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 0.16–0.19 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) $\delta = 69.9$; IR (KBr) (υ_{max}/cm^{-1}), 3238 (N—H), 1079 and 1001 (P—O—C), 1028 (Si—O—C), 752 (P=S); MS (m/z), 506.5 (M^+,6.2), 329 (2.5), 299 (0.8), 270 (4.1), 174 (100), 129 (6.4), 91 (3.6). Elemental anal. calcd. for $C_{20}H_{32}ClN_2O_5PSSi$: C, 47.38; H, 6.32; P, 6.12. Found: C, 47.31; H, 6.37; P, 6.15.

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2-Silatranyl Propylmino-4-(4-methyl-phenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4j)

Pale yellow crystals, m.p. 167–168°C, ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.17–7.22 (m, 4H, Ph—H), 5.91–5.96 (t, 1H, —NH), 5.29 (s, 1H, O—CH), 3.43–3.88 (m, 8H, O—CH_2), 2.51–2.96 (m, 8H, N—CH_2), 2.31 (s, 3H, Ar—CH_3),1.50–1.59 (m, 2H, C—CH_2), 0.89 (s, 3H, CH_3), 0.70 (s, 3H, CH_3), 0.15–0.19 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) δ = 70.2; IR (KBr) (υ_{max}/cm^{-1}), 3237 (N—H), 1084 and 1002 (P—O—C), 1028 (Si—O—C), 751 (P=S); MS (m/z), 486 (M^+, 0.2), 329 (1.5), 299 (0.2), 270 (4.7), 174 (100), 129 (6.5), 91 (6.8). Elemental anal. calcd. for $C_{21}H_{35}N_2O_5PSSi$: C, 51.85; H, 7.20; P, 6.38. Found: C, 51.78; H, 7.25; P, 6.34.

2-Silatranyl Propylmino-4-(4-methoxyl-phenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4k)

Pale yellow crystals, m.p. 163–164°C, ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.31–7.37 (m, 4H, Ph—H), 5.91–5.97 (t, 1H, —NH), 5.35 (s, 1H, O—CH), 3.75 (s, 3H, O—CH_3) 3.32—3.67 (m, 8H, O—CH_2), 2.54–2.90 (m, 8H, N—CH_2), 1.49–1.57 (m, 2H, C—CH_2), 1.05 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 0.14–0.18 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO—d_6, 400MHz) δ = 70.1; IR (KBr) (υ_{max}/cm^{-1}), 3233 (N—H), 1089 and 1001 (P—O—C), 1031 (Si—O—C), 752 (P=S); MS (m/z), 502 (M^+,1.2), 329 (2.3), 299 (0.7), 270 (6.2), 174 (100), 129 (7.5), 91 (11.8). Elemental anal. calcd. for $C_{21}H_{35}N_2O_6PSSi$: C, 50.20; H, 6.97; P, 6.18. Found: C, 50.27; H, 6.91; P, 6.23.

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2-Silatranyl Propylmino-4-(2,4-dichloro-phenyl)-5,5-dimethyl-1,3,2-dioxaphosphinane-2-sulfide (4l)

Pale yellow crystals, m.p. 184–185°C, ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 7.45–7.70 (m, 3H, Ph—H), 6.04–6.08 (t, 1H, —NH), 5.80 (s, 1H, O—CH), 3.33–3.94 (m, 8H, O—CH_2), 2.51–2.94 (m, 8H, N—CH_2), 1.49–1.55 (m, 2H, C—CH_2), 1.48 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 0.14–0.18 (t, 2H, Si—CH_2); ^{31}P NMR (DMSO-d_6, 400MHz) δ = 70.1; IR (KBr) (υ_{max}/cm^{-1}), 3229 (N-H), 1096 and 1005 (P—O—C), 1027 (Si—O—C), 751 (P=S); MS (m/z), 541 (M^+,0), 329 (0.6), 299 (1.5), 270 (6.7), 174 (100), 129 (7.8), 91 (2.6). Elemental anal. calcd. for $C_{20}H_{31}Cl_2N_2O_5PSSi$: C, 44.36; H, 5.73; P, 5.73. Found: C, 44.39; H, 5.70; P, 5.77.

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