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Ring Opening of Lactones and Anhydrides Induced by [Cp$_2$ZrHCl]$_n$

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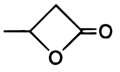
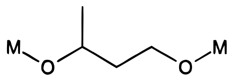
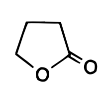
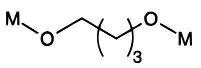
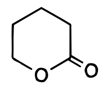
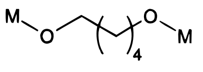
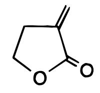
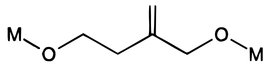
For several years we have been involved in the study of interactions between main group elements and group 4 elements, especially zirconium derivatives. Our goal is to take advantage of the properties of group 4 elements to develop new synthetic approaches for the synthesis of organic or inorganic species.[1]

Although the Schwartz reagent [Cp$_2$ZrHCl]$_n$ (**1**)[2] has been known for a long time and has been employed in a variety of reactions, its use in reagent-promoted ring-opening reactions is rare and is limited to a few examples.[3,4] In the course of studying the reaction of **1** with unsaturated heterocycles, we have discovered a useful ring-opening process of oxygen, nitrogen, or phosphorus five-membered rings.[4] Herein we report on the extension of this useful methodology which allows the mild cleavage of various lactones and anhydrides and a one-pot synthesis of di-, tri-, or tetraphosphinites.

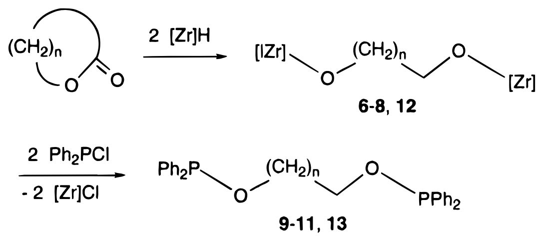
Addition of **1** (2 equiv) to a THF solution of lactone **2**, **3**, or **4** at 0 °C leads quantitatively to the isolated and fully characterized linear dizirconated compounds **6**, **7**, or **8**. Further addition of an electrophile such as chlorodiphenylphosphine to those derivatives affords the 1,3-, 1,4-, or 1,5-diphosphinites **9**, **10**, or **11** (Scheme 1); the latter transformation is simple and highly selective, and no side products were generally detected. For example, the same reaction performed with the α-methylene-γ-butyrolactone **5** using 2 (or more) equiv of **1** gives rise to the unsaturated dizirconated derivative **12**, which reacted with chlorodiphenylphosphine to give the new diphosphinite **13**. No hydrozirconation of the 1,1-disubstituted olefinic moiety of **5** is observed.

Table 1. Synthesis of Bis(zirconocenyloxy)alkyls 6−8 and 12 and the Corresponding Bisphosphinites 9−11 and 13

Lactones	Products	Yield(%)
 **2**		
	6 M = [Zr]	95
	9 M = PPh$_2$	70*
 **3**		
	7 M = [Zr]	95
	10 M = PPh$_2$	70
 **4**		
	8 M = [Zr]	90
	11 M = PPh$_2$	80
 **5**		
	12 M = [Zr]	90
	13 M = PPh$_2$	80*

(*)isolated yield from the corresponding phosphorus disulfide derivative

Scheme 1. Ring-Opening Reaction of Lactones 2−5 with [Cp$_2$ZrHCl] Followed by the Exchange Reaction with Ph$_2$PCl



[Zr]H = Cp$_2$ZrHCl

The general applicability of the method has been assessed using a variety of lactones. The ratio of the number of equivalents of **1** versus the number of equivalents of lactone necessary for a clean reaction is dependent on the specific lactone.

The full transformation of 1,6-dioxaspiro[4.4]nonane-2,7-dione (**14**) into the unexpected trizirconated linear derivative **18**, fully characterized by NMR spectroscopy, and the well-known oxide (Cp$_2$ZrCl)$_2$O (**17**) necessitates 5 equiv of **1** (Scheme 2). Such a result can be explained if one considers that 4 equiv of **1** are used for the ring-opening process of the bis lactone **14**, affording the transient tetrazirconated form **15**. This could be followed by intramolecular elimination of **17**, leading to the ketone

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† Laboratoire de Chimie de Coordination du CNRS.

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(1) See for example: (a) Majoral, J.-P.; Dufour, N.; Meyer, F.; Caminade, A.-M.; Choukroun, R.; Gervais, D. *J. Chem. Soc., Chem. Commun.* **1990**, 507. (b) Dufour, N.; Majoral, J.-P.; Caminade, A.-M.; Choukroun, R.; Dromzée, R. *Organometallics* **1991**, *10*, 45. (c) Boutonnet, F.; Dufour, N.; Straw, T.; Igau, A.; Majoral, J.-P. *Organometallics* **1991**, *10*, 3939. (d) Dufour, N.; Caminade, A.-M.; Basso-Bert, M.; Igau, A.; Majoral, J.-P. *Organometallics* **1992**, *11*, 1131. (e) Zablocka, M.; Igau, A.; Majoral, J.-P.; Pietrusiewicz, K. M. *Organometallics* **1993**, *12*, 603. (f) Colombo-Khater, D.; Caminade, A.-M.; Delavaux-Nicot, B.; Majoral, J.-P. *Organometallics* **1993**, *58*, 2861. (g) Boutonnet, F.; Zablocka, M.; Igau, A.; Majoral, J.-P.; Jaud, J.; Pietrusiewicz, K. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1487. (h) Boutonnet, F.; Zablocka, M.; Igau, A.; Majoral, J.-P.; Raynaud, B.; Jaud, J. *J. Chem. Soc., Chem. Commun.* **1993**, 1866. (i) Igau, A.; Dufour, N.; Mahieu, A.; Majoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1993**, *1*, 95. (j) Zablocka, M.; Boutonnet, F.; Igau, A.; Dahan, F.; Majoral, J.-P.; Pietrusiewicz, K. M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1735. (k) Mahieu, A.; Igau, A.; Jaud, J.; Majoral, J.-P. *Organometallics* **1995**, *14*, 944. (l) Boutonnet, F.; Zablocka, M.; Igau, A.; Jaud, J.; Majoral, J.-P.; Schamberger, J.; Erker, G.; Werner, S.; Krüger, C. *J. Chem. Soc., Chem. Commun.* **1995**, 823. (m) Zablocka, M.; Igau, A.; Cénac, N.; Donnadieu, B.; Dahan, F.; Majoral, J.-P.; Pietrusiewicz, K. M. *J. Am. Chem. Soc.* **1995**, *117*, 8083.

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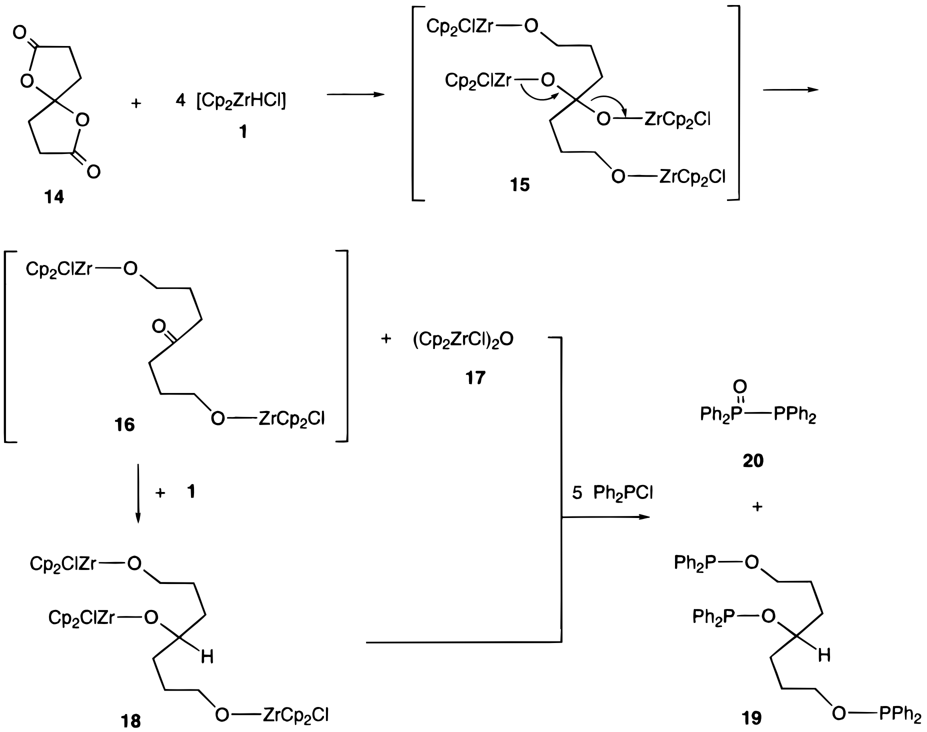
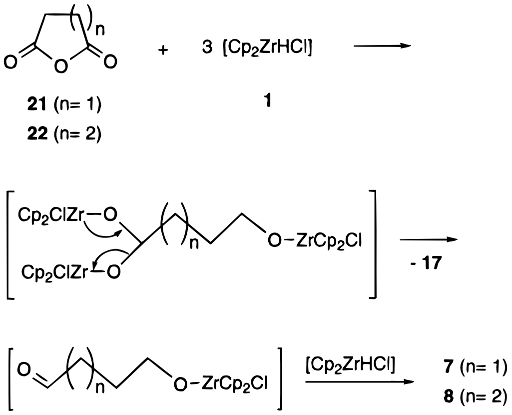
Scheme 2



Scheme 3



16. Hydrozirconation of **16** with the 5th equivalent of **1** finally gives **18**. Further addition of five equiv of chlorodiphenylphosphine to the mixture of compounds **17** and **18** leads to the triphosphinite **19** and to the phosphine–phosphine oxide **20**. Triphosphinite **19** arises from an exchange reaction between **18** and the chlorophosphine while **20** comes from the reaction of the oxide **17** with the same chlorophosphine.[5]

Such a zirconium-promoted ring-opening procedure can be extended to other oxygen heterocycles such as anhydrides. For instance, cleavage of C–O bonds of the succinic anhydride **21** takes place when **21** is treated with 4 equiv of **1**, the two zirconium oxides **7** and **17** being quantitatively obtained (Scheme 3). Addition of 4 equiv of chlorodiphenylphosphine to **7** and **17** leads to the diphosphinite **10** and to **20**. The same sequence occurs rapidly in a one-pot synthesis involving 4 equiv of **1**, glutaric anhydride (**22**), and 4 equiv of chlorodiphenylphosphine, giving rise to the diphosphinite **11** and **20**.

The conversion of ethylenediaminetetraacetic dianhydride (**23**) to the tetrazirconated species **24** and then into the new hexadentate ligand **25** (Scheme 4) follows the same reaction sequence outline in Scheme 3 but needs 8 equiv of **1** for each equivalent of the dianhydride **23** and then 8 equiv of chlorodiphenylphosphine. Such a conversion illustrates the potentiality of this ring-opening process for the formation of polydentate ligands which are of interest for the development of more efficient catalytic systems.[6]

Extension of this methodology, using various heterocycles and electrophiles, to the one-pot synthesis of a large variety of organic and inorganic compounds is underway.

Experimental Section

General. All manipulations were carried out under an argon atmosphere, either on a high-vacuum line using standard Schlenk techniques or in a drybox. Solvents were freshly distilled from dark purple solutions of sodium/benzophenone ketyl (THF, diethyl ether), lithium aluminum hydride (pentane), P_2O_5 (CH_3CN), or CaH_2 (CH_2Cl_2). C_6D_6 and $CDCl_3$ were treated respectively with $LiAlH_4$ and CaH_2, distilled, and stored under argon. $[Cp_2ZrHCl]_n$ (Schwartz reagent) (**1**) was synthesized by the method of Buchwald.[7]

NMR chemical shifts are expressed in ppm upfield from Me_4Si (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). The ^{13}C NMR assignments were confirmed by proton-decoupled and/or selective heteronuclear-decoupled spectra.

Typical Procedure for Ring Opening of Lactones 2–5 and 14 and Anhydrides 21–23. To a suspension of **1** (0.644

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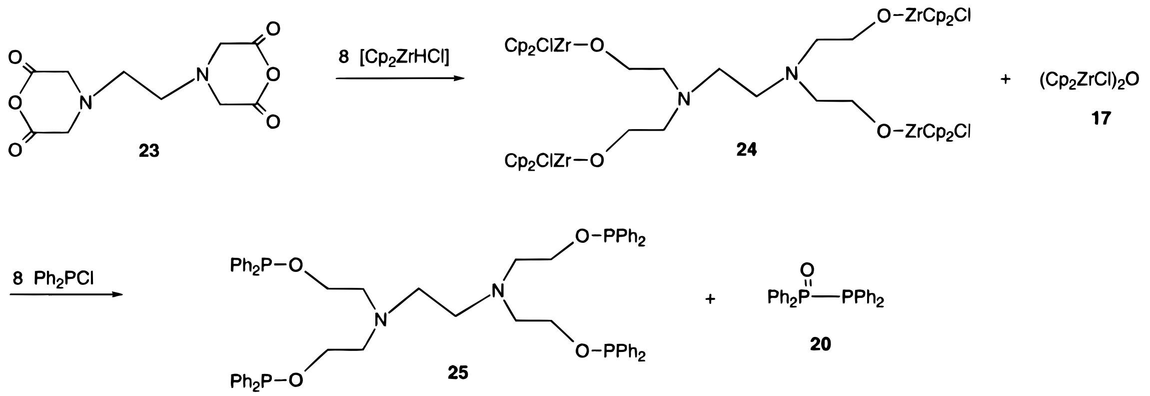
[5] Addition of chlorodiphenylphosphine (2 equiv) to $(Cp_2ZrCl)_2O$ (1 equiv), separately prepared by a conventional method,[8] leads to **20**. The first step of the reaction consists of the formation of the transient species $Cp_2Zr(OPPh_2)Cl$ (and Cp_2ZrCl_2) which reacts further with a second equivalent of chlorodiphenylphosphine to give Cp_2ZrCl_2 and Ph_2POPPh_2. Isomerization of Ph_2POPPh_2 lastly affords $Ph_2PP(O)Ph_2$: Cénac, N.; Zablocka, M.; Igau, A.; Majoral, J.-P.; Skowronska, A. Unpublished results.

[6] See for example: van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34.

[7] Buchwald, S. L.; LaMaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, *28*, 3895.

[8] Reid, A. F.; Shannon, J. M.; Wailes, P. C. *Aust. J. Chem.* **1965**, *18*, 173.

Scheme 4



g, 2.5 mmol) in 5 mL of THF at 0 °C was added the lactone **2**, **3**, **4** or **5** (1.25 mmol) in solution in 5 mL of THF. The resulting mixture was warmed up to room temperature and stirred for 1 h. Evaporation of the solvent gave **6**, **7**, **8**, or **12** as a colorless oil in a quantitative yield. Ring opening of lactone **14** is conducted similarly with **1** (0.644 g, 2.5 mmol) and the lactone **14** (0.05 mmol), giving rise quantitatively to **17** and **18**. The same procedure is used for reactions involving anhydrides **21**, **22** (4 mmol of **1**, 1 mmol of **21** or **22**), and **23** (8 mmol of **1**, 1 mmol of **23**).

1,3-Bis[(chlorodicyclopentadienylzirconio)oxy]butane (6): ^{13}C{^{1}H} NMR (C_6D_6) δ 25.2, 44.4, 72.9, 77.3, 114.0, 114.2; ^{1}H NMR (C_6D_6) δ 1.05 (d, 3H), 1.52 (m, 2H), 3.92–4.35 (m, 3H), 6.01, 6.02, 6.07, 6.09 (s, 20H).

1,4-Bis[(chlorodicyclopentadienylzirconio)oxy]butane (7): ^{13}C{^{1}H} NMR (C_6D_6) δ 30.9, 75.9, 113.9; ^{1}H NMR (C_6D_6) δ 1.52 (m, 4H), 3.93 (m, 4H), 6.05 (s, 20H).

1,5-Bis[(chlorodicyclopentadienylzirconio)oxy]pentane (8): ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.1, 33.0, 75.6, 113.3; ^{1}H NMR ($CDCl_3$) δ 1.25–1.51 (m, 6H), 3.99 (t, 4H), 6.28 (s, 20H).

1,4-Bis[(chlorodicyclopentadienylzirconio)oxy]-2-methylenebutane (12): ^{13}C{^{1}H} NMR ($CDCl_3$) δ 36.6, 74.2, 78.2, 110.0, 113.6, 113.7, 146.6; ^{1}H NMR ($CDCl_3$) δ 2.12 (t, 2H, $CH_2C{=}$), 4.10 (t, 2H), 4.44 (s, 2H), 4.83 (s, 1H), 5.00 (s, 1H), 6.28 (s, 10H), 6.31 (s, 10H).

1,4,7-Tris[(chlorodicyclopentadienylzirconio)oxy]heptane (18): ^{13}C{^{1}H} NMR ($CDCl_3$) δ 29.8, 34.3, 75.7, 84.5, 114.0; ^{1}H NMR ($CDCl_3$) δ 1.33–2.19 (m, 8H), 3.92–4.11 (m, 5H), 6.29 (s, 30H).

***N,N,N′,N′*-Tetrakis[(chlorodicyclopentadienylzirconio)oxy]ethyl-1,4-ethylenediamine (24):** ^{13}C{^{1}H} NMR ($CDCl_3$) δ 52.7, 57.8, 74.3, 114.1.

Typical Procedure for Exchange Reactions with Zirconated Species 6, 7, 8, 12, 18, and 24 and Chlorodiphenylphosphine. To the zirconated species (1 mmol) in solution in 10 mL of THF at −78 °C was added chlorodiphenylphosphine (2, 4, 5, or 8 mmol), depending on the considered zirconated compound. The resulting mixture was stirred for 12 h at room temperature. After evaporation of the solvent diphosphinites **10** and **11** were extracted with pentane (40 mL). The diphosphinites **9** and **12**, the triphosphinite **19**, or the tetraphosphinite **25** were treated with sulfur (1.1 equiv per phosphinite function) for 12 h at room temperature. The resulting phosphinite sulfides were purified by chromatography eluting with a dichloromethane/pentane (1/3) solution for **9′** and **12′** or with an acetonitrile/dichloromethane (1/1) solution for **19′** and **26**.

1,3-Butanediyl bis(diphenylphosphinite) (9) (^{31}P{^{1}H} NMR ($CDCl_3$) δ 107.0 and 112.3) was isolated as its disulfide form **9′**: yield 80%; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 79.2 and 81.6 (s, $Ph_2P(S)O$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 21.9, 29.7, 60.9, 70.6, 128.3, 128.4, 130.7, 131.0, 131.2, 131.4, 131.7, *i*-Ph not detected; ^{1}H NMR ($CDCl_3$) δ 1.21 (d, 3H), 2.06 (m, 2H), 4.07 (m, 2H), 5.04 (m, 1H), 7.32–7.47 and 7.73–7.93 (m, 20H); MS *m/z* 523 (M + 1)$^+$. Anal. Calcd for $C_{28}H_{28}O_2P_2S_2$: C, 64.35; H, 5.40. Found: C, 64.29; H, 5.37.

1,4-Butanediyl bis(diphenylphosphinite) (10): yield 70%; ^{31}P{^{1}H} NMR (C_6D_6) δ 112.0; ^{13}C{^{1}H} NMR (C_6D_6) δ 28.0, 69.5, 128.3, 129.1, 130.9, *i*-Ph not detected; ^{1}H NMR (C_6D_6) δ 1.55 (m, 4H), 3.66 (m, 4H), 6.93–7.16 and 7.55–8.05 (m, 20H). The corresponding disulfide derivative **10′** has also been identified: ^{31}P{^{1}H} NMR (C_6D_6) δ 80.1 (s, $Ph_2P(S)O$); MS *m/z* 523 (M + 1)$^+$. Anal. Calcd for $C_{28}H_{28}O_2P_2S_2$: C, 64.35; H, 5.40. Found: C, 64.32; H, 5.55.

1,5-Pentanediyl bis(diphenylphosphinite) (11): yield 80%; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 111.3; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 22.1, 30.9, 69.8, 128.1, 129.0, 130.1, *i*-Ph not detected; ^{1}H NMR ($CDCl_3$) δ 1.50 (m, 2H), 1.70 (tt, 4H), 3.82 (td, 4H), 7.31–7.37 and 7.44–7.53 (m, 20H). The corresponding disulfide derivative **11′** has also been identified: ^{31}P{^{1}H} NMR (C_6D_6) δ 79.9; MS *m/z* 537 (M + 1)$^+$. Anal. Calcd for $C_{29}H_{30}O_2P_2S_2$: C, 64.91; H, 5.63. Found: C, 64.82; H, 5.75.

2-Methylene-1,4-butanediyl bis(diphenylphosphinite) (13) (^{31}P{^{1}H} NMR ($CDCl_3$) δ 112.2 and 114.0) was isolated as its disulfide form **13′**: yield 80%; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 81.3 and 82.3 (s, $Ph_2P(S)O$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 33.7, 62.7, 66.8, 115.75, 128.7, 128.8, 131.7, 132.1, 132.2, 134.4, 134.5, 140.6; ^{1}H NMR ($CDCl_3$) δ 2.51 (t, 2H), 4.13 (td, 2H), 4.44 (d, 2H), 5.05 (d, 1H), 5.21 (d, 1H), 7.38–7.46 and 7.77–7.91 (m, 20H); MS *m/z* 535 (M + 1)$^+$. Anal. Calcd for $C_{29}H_{28}O_2P_2S_2$: C, 65.15; H, 5.28. Found: C, 65.11; H, 5.36.

1,4,7-Heptanetriyl tris(diphenylphosphinite) (19) (^{31}P{^{1}H} NMR ($CDCl_3$) δ 113.0 (broad)) was isolated as its disulfide form **19′**: yield 45%; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 79.5 and 81.0; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 25.8, 31.1, 64.5, 76.0, 128.4, 128.5, 130.7, 131.0, 131.2, 131.4, 131.7, *i*-Ph not detected; ^{1}H NMR ($CDCl_3$) δ 1.66 (m, 8H), 3.87 (m, 4H), 4.77 (m, 1H), 7.34–7.51 and 7.75–7.87 (m, 30H); MS *m/z* 797 (M + 1)$^+$. Anal. Calcd for $C_{43}H_{43}O_3P_3S_3$: C, 64.81; H, 5.44. Found: C, 64.78; H, 5.37.

***N,N,N′,N′*-Tetrakis[[(diphenylphosphanyl)oxy]ethyl]-1,4-ethylenediamine (25)** (^{31}P{^{1}H} NMR ($CDCl_3$) δ 115.3) was isolated as its disulfide form **26**: yield 50%; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 82.5; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 53.2, 54.5, 62.7, 128.3, 131.0, 131.7, 134.1; ^{1}H NMR ($CDCl_3$) δ 2.55 (m, 4H), 2.79 (t, 8H), 3.93 (td, 8H), 7.35–7.41 and 7.76–7.87 (m, 40H); MS *m/z* 1102 (M + 1)$^+$. Anal. Calcd for $C_{58}H_{60}N_2O_4P_4S_4$: C, 63.26; H, 5.49. Found: C, 63.18; H, 5.39.

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