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Synthesis, Structure, and Reactivity of a Symmetrically Substituted 9-Phosphatriptycene Oxide and Its Derivatives

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ABSTRACT: *Novel 9-phosphatriptycenes were synthesized by utilizing ortho-lithiation of a triarylphosphine oxide as a key step. The structural analysis of the 9-phosphatriptycene oxide revealed its highly distorted structure around the phosphorus atom, which is consistent with the up-field shift in the ^{31}P NMR spectrum. The 9-phosphatriptycene and its chalcogenides were synthesized by ordinary methods, and the spectral comparisons of these chalcogenides indicated the large s-character of the lone-pair orbital or the phosphorus–chalcogen σ bonds of those species. The 9-phosphatriptycene oxide was reacted with lithium naphthalenide to give the ring-opened products.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:437–446, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20038

INTRODUCTION

Heterotriptycenes have attracted great interest of organic and inorganic chemists because of their unique structures and spectroscopic properties. 9-Phosphatriptycene, which was first synthesized by Bickelhaupt in 1974, has interesting characteristics [1]. For example, its C_{aryl}—P—C_{aryl} angle is narrowed compared to that of triphenylphosphine, which is revealed by the X-ray crystallographic analysis of 2-(*t*-butyl)-9-phosphatriptycene [2,3]. Such a distorted structure around the phosphorus atom is suggested in the solution as well as in the solid by the up-field shifted signal in the ^{31}P NMR spectrum.

The key step of the synthetic route to 9-phosphatriptycene reported by Bickelhaupt is the intramolecular nucleophilic attack of the carbanion to the benzyne generated by *ortho*-lithiation of aryl chloride followed by elimination of chloride anion (Scheme 1). However, it is difficult to apply this method to the synthesis of 9-phosphatriptycenes with various substituents on the aromatic rings because of difficulties in the preparation of starting materials. On the other hand, several heterotriptycenes were synthesized utilizing *ortho*-metalation as a key step [4].

Recently we reported the synthesis of a 9-phosphatriptycene oxide utilizing *ortho*-lithiation of a triarylphosphine oxide, and its structure was revealed by the X-ray crystallographic analysis [5]. The large *s*-characters of the lone pair or the phosphorus–chalcogen σ bond were also elucidated by the NMR spectroscopy. Here we describe the synthesis of 9-phosphatriptycenes as well as the structures of the multisubstituted 9-phosphatriptycene oxides and the spectroscopic properties of the 9-phosphatriptycene chalcogenides. Some reactions of the 9-phosphatriptycene oxide are also described. A part of this work has been communicated [5].

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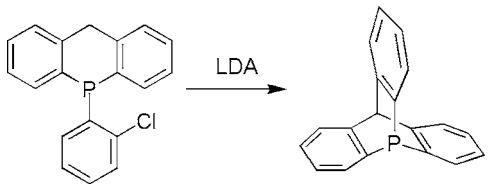


SCHEME 1

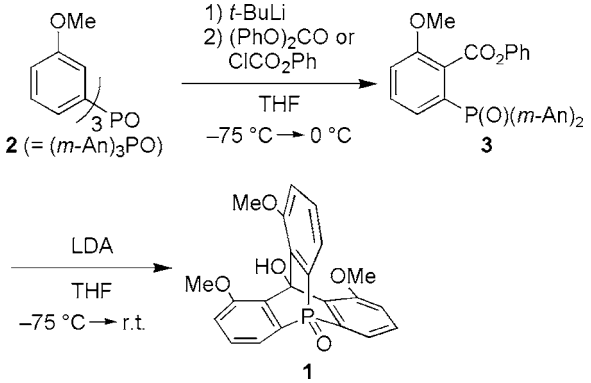
RESULTS AND DISCUSSION

Syntheses of 9-Phosphatriptycene Oxide and 9,10-Diphosphatriptycene Oxide

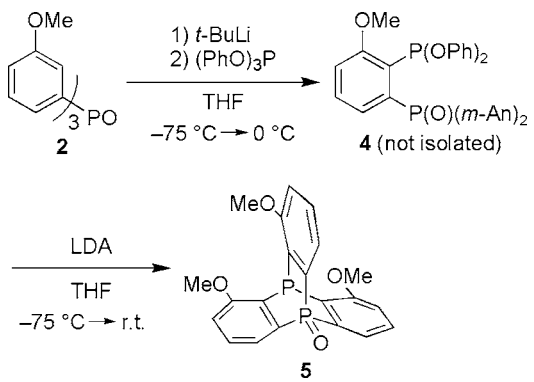
The synthesis of 9-phosphatriptycene oxide **1** is shown in Scheme 2. Although the *ortho*-lithiation of tris(3-methoxyphenyl)phosphine oxide (**2**) was accomplished with *t*-BuLi or lithium diisopropylamide (LDA), the reactivity of the lithio-derivatives against carbon electrophiles were dramatically changed by the difference of base. When LDA was used as a base, the reactivity of the carbanion decreased and the reaction with carbonates did not proceed at all. The coordination of $(i\text{-Pr})_2NH$ to the carbanion probably hampered the reaction. On the other hand, the anion generated with *t*-BuLi reacted with $(PhO)_2CO$ or $ClCO_2Me$ to give phenoxycarbonyl derivative **3**. Multisubstituted 9-phosphatriptycene oxide (**1**) was obtained by treatment of **3** with 2 equiv of LDA in 51% yield. The overall yield of **1** is 33% from **2**, which can be easily obtained quantitatively from commercially available 3-bromoanisole. So this synthetic methodology of the 9-phosphatriptycene derivative has an advantage in both yield and number of steps compared to the reported methods.

This synthetic route to a phosphatriptycene framework could be applied to the synthesis of a multisubstituted 9,10-diphosphatriptycene oxide. 9,10-Diphosphatriptycene was synthesized by Weinberg from *o*-dichlorobenzene and white phosphorus [6]. This synthesis, however, has several problems in an application to the synthesis of multisubstituted diphosphatriptycenes, because of the low regioselectivity, as well as high reaction temperature and low yield. As shown in Scheme 3, multisubstituted 9,10-diphosphatriptycene oxide **5** was synthesized from **2** in 2 steps. The lithio-derivative of **2** was treated with $(PhO)_3P$ to give phosphonite **4**, the generation of which was confirmed by the characteristic doublet signals at δ_P 162.9 and 29.4, corresponding to diaryl arylphosphonite and triarylphosphine oxide fragments, respectively. Because the isolation of **4** was difficult due to its low stability against oxygen and water, the mixture containing **4** was treated with an excess amount of LDA to give **5** in 6% yield from **2**. The reason of the low yield is probably side reactions caused by the nucleophilic attack of LDA to the phosphonite.

The ^{31}P NMR spectrum of **1** showed the signal at δ_P 2.1, which was up-field shifted by 28 ppm compared to that of **2** (δ_P 30.3). This phenomenon is attributable to the distortion around phosphorus atom of **1**, which was confirmed by the X-ray crystallographic analysis of **1**. The signal of the hydroxy proton of **1** was observed at δ_H 6.18 in ^1H NMR, indicating the existence of intramolecular hydrogen bond between the hydroxy group and the methoxy group at the peri-position, compared to that of tris(2-methoxyphenyl)methanol (δ_H 5.44). This intramolecular hydrogen bond also affected the reactivity of the hydroxy group; that is, the H–D exchange of the hydroxy proton did not occur with D_2O, and a stronger acid, DCl/D_2O, was necessary for the exchange reaction. As shown in Scheme 4, the hydroxy group could not be methylated with MeI, because of the steric hindrance by the three methoxy groups at the peri-positions as well as the stabilization of the anionic species by intramolecular chelating of the counter



SCHEME 2



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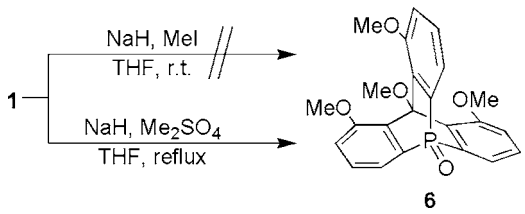


SCHEME 4

cation. The methyl derivative **6** was obtained in 94% yield by the use of a more powerful methylating reagent, Me_2SO_4.

The ^{31}P NMR spectrum of **5** showed the doublet signals at δ_P −134.7 and 7.6, corresponding to the triarylphosphine and the triarylphosphine oxide fragments, respectively. The signal due to the phosphine site of **5** was up-field shifted compared to those of 9,10-diphosphatriptycene (δ_P −43). This phenomenon is attributed to the steric compression effect caused by the three methoxy groups at peri-positions to the phosphorus atom. Because these methoxy groups protect the phosphorus atom sterically, **5** is unreactive against oxygen in both the solid and the solution states. Neither the reactions of **5** with elemental sulfur and selenium at 75°C nor that with H_2O_2 at room temperature in $CDCl_3$ proceeded at all.

X-ray Crystallographic Analysis of 9-Phosphatriptycene Oxide

The single crystal of **6** was obtained by recrystallization from CH_2Cl_2/MeOH, and the X-ray crystallographic analysis was performed. The ORTEP drawing is shown in Fig. 1. The C_{aryl}—P—C_{aryl} angles of **6** [98.10(6), 99.72(6), and 100.32(6)] were also substantially narrowed as well as those of **1**. The structural difference between **1** and **6** was observed in the C_{aryl}—C10—C_{aryl} angles. The differences between the three C_{aryl}—C10—C_{aryl} angles of **6** [104.76(9), 104.50(9), and 111.41(9)] are bigger than those of **1** [106.2(4), 105.6(2), and 109.0(4)], which suggest the deviation from the C_{3v} symmetry of the phosphatriptycene framework of **6** due to the steric repulsion between the methyl group at C10 and the three methoxy groups at the peri-positions.

The decrease in the bond angles around bridgehead phosphorus atom is also observed in 9-phosphatriptycene (95.0°) and its analogs, 9,10-azaphosphatriptycene (93.5°) and 9,10-diphosphatriptycene (97.0°), revealed by X-ray crystallographic analyses [7,8].

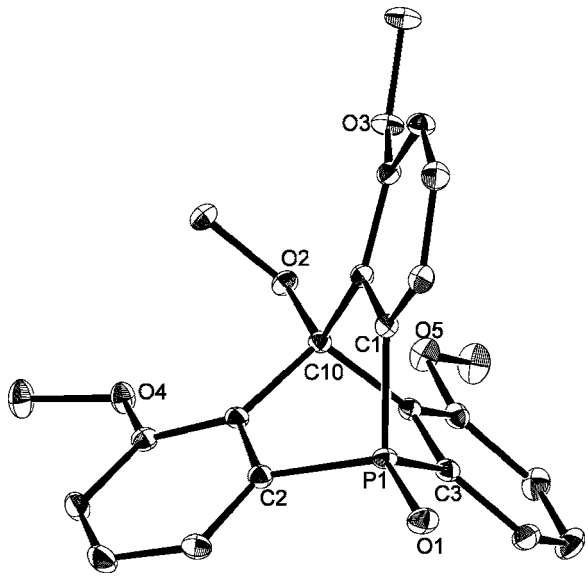
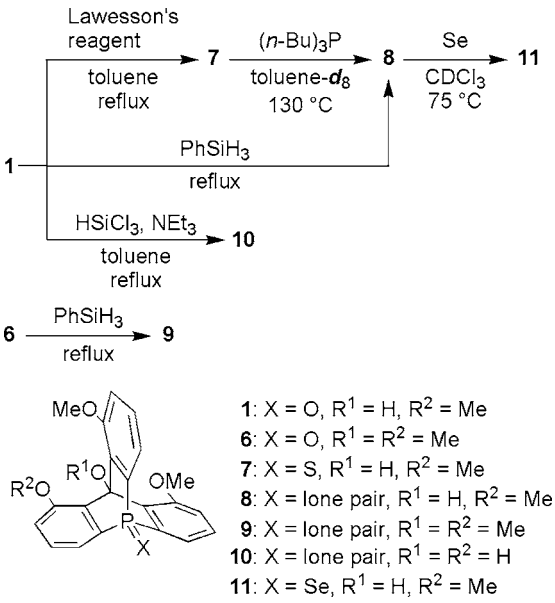


FIGURE 1 ORTEP drawing of **6** (50% probability). Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)–O(1) 1.4855(11), P(1)–C(1) 1.7798(13), P(1)–C(2) 1.7714(13), P(1)–C(3) 1.8009(14), C(1)–P(1)–C(2) 100.32(6), C(2)–P(1)–C(3) 98.10(6), C(1)–P(1)–C(3) 99.72(6).

Syntheses of a 9-Phosphatriptycene and its Chalcogenides

In order to evaluate orbital hybridization and electronic state of phosphorus atoms in 9-phosphatriptycene derivatives, the 9-phosphatriptycene and its chalcogenides (Ch = S, Se) were synthesized from **1** (Scheme 5).

The sulfurization of **1** proceeded by treatment of **1** with an excess amount of Lawesson's reagent almost quantitatively estimated by ^1H and ^{31}P NMR spectra; however, the isolated yield was low due to poor solubility of 9-phosphatriptycene sulfide **7**. 9-Phosphatriptycene **8** was obtained by desulfurization of **7** with $(n\text{-Bu})_3P$. **8** was also obtained by the direct reduction of **1** with $PhSiH_3$. The ^{31}P NMR spectrum of **8** showed the signal at δ_P −68.7, which is largely up-field shifted compared to that of tris(3-methoxyphenyl)phosphine (δ_P −2.6) and nearly the same as that of 9-phosphatriptycene (δ_P −64.8), indicating the increase of magnetic shielding against the phosphorus nuclei caused by distortion around them. The $PhSiH_3$ reduction could be applied to **6** and tetramethoxy-9-phosphatriptycene **9** was obtained quantitatively. On the other hand, when $HSiCl_3$ was used for the reduction of **1**, demethylated derivative **10** was obtained [4e]. Further demethylated products were not observed in this reaction, even when the large excess amount of $HSiCl_3$ was



SCHEME 5

used. When **8** was allowed to react with elemental selenium, the corresponding 9-phosphatriptycene selenide **11** was obtained. Although the ^{1}H and ^{31}P NMR spectra showed that **8** was converted to **11** quantitatively, the low solubility of **11** decreased its isolated yield, unfortunately. The spectroscopic property of 9-phosphatriptycene chalcogenides **1**, **7**, and **11** is discussed in the next section.

Spectroscopic Comparisons of 9-Phosphatriptycene Chalcogenides

The selected NMR spectral data of **1**, **7**, and **11** are summarized in Table 1. The spectral data of tris(3-methoxyphenyl)phosphine chalcogenides **2**, **12**, and **13** are also listed for comparisons. For **1, 7**, and **11**, the ^{31}P NMR spectra showed up-field signals with a decrease in the $^{1}J_{PC}$ values for **1**, **7**, and **11**, compared with those of the reference compounds **2**, **12**, and **13**, respectively (Fig. 2). On the other hand, the $^{1}J_{PSe}$ value of **11** is larger than that of **13**.

TABLE 1 Selected NMR Data of 9-Phosphatriptycene Chalcogenides and Tris(3-methoxyphenyl)phosphine Chalcogenides

	δ_P	$^{1}J_{PC}$ (Hz)	$^{1}J_{PSe}$ (Hz)
1	2.1	93.0	—
7	10.0	75.9	—
11	3.9	67.8	827
2	30.3	103.1	—
12	44.6	84.3	—
13	38.1	76.0	732

The C_{aryl}—P—C_{aryl} angles of the 9-phosphatriptycene chalcogenides are thought to be narrower than those of tris(3-methoxyphenyl)phosphine chalcogenides, as shown in the X-ray crystallographic analysis of **1**. The deviation of the C_{aryl}—P—C_{aryl} angles from that of tetrahedral structure (109.5°) makes it difficult for the phosphorus atom to take sp^3 hybridization in 9-phosphatriptycene chalcogenides. Because of the decrease in the extent of the hybridization in 9-phosphatriptycene chalcogenides, the P—C_{aryl} bonds consist of more $3p$ orbitals of the phosphorus atom and the P—Ch σ bond consists of more $3s$ orbitals than those of usual triarylphosphine chalcogenides do. Absolute value of $^{1}J_{AB}$ reflects participation of s orbital to σ bond between atom A and atom B. Taking into account these theoretical considerations, the trends in $^{1}J_{PC}$ and $^{1}J_{PSe}$ values are quite reasonable [9]. On the other hand, the up-field shift in ^{31}P NMR spectra are attributed to the fact that the bonding electron pair has more population near the phosphorus atom and the magnetic shielding against the phosphorus nuclei strengthens, because the P—Ch σ bonds have large phosphorus $3s$ character in 9-phosphatriptycene selenide.

The ^{77}Se NMR spectrum of **11** showed a significantly up-field shifted signal at δ_{Se} −601.3 compared to that of **13** (δ_{Se} −256). Although the reason for this up-field shift is ambiguous, the calculated ^{77}Se NMR chemical shift of **11** (δ_{Se} −524) is close to the experimental value [10–13].

So it is revealed that the narrow C_{aryl}—P—C_{aryl} angles in the 9-phosphatriptycene chalcogenides affect the hybridization of the phosphorus atoms significantly and the lone pair or the P—Ch σ bonds have large $3s$ character of the phosphorus atoms.

Reaction of 9-Phosphatriptycene Oxide with Lithium Naphthalenide

The cyclic voltammogram of **6** was shown in Fig. 3. The oxidation peak at 1.71 V may correspond to the

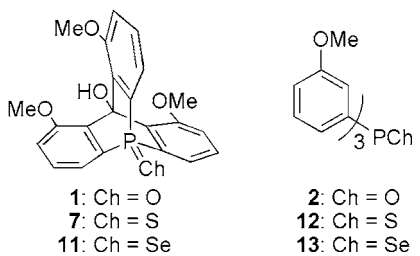


FIGURE 2 The 9-Phosphatriptycene Chalcogenides and Tris(3-methoxyphenyl)phosphine Chalcogenides.

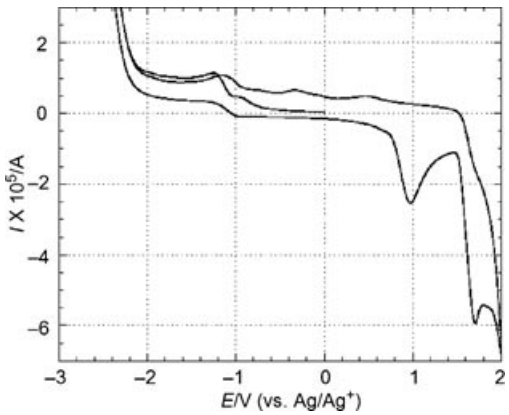


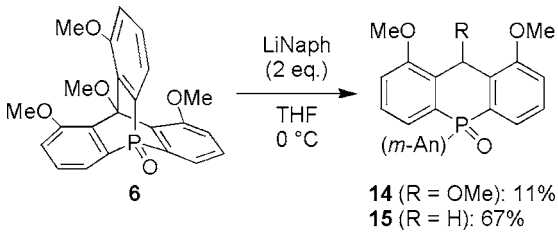
FIGURE 3 Cyclic voltammogram of **6**.

oxidation of aromatic π systems of **6**. On the other hand, the oxidation peak at 0.97 V should be attributed a new species generated by reduction of **6**, because this peak appeared not in the first anodic sweep but in the second sweep. So the chemical reduction with lithium naphthalenide (LiNaph) was examined in order to obtain information about the reduction process of **6**.

As shown in Scheme 6, the reaction of **6** with 2 equiv of LiNaph gave 9,10-dihydroacridophosphine oxides **14** and **15** that were obtained by the C10—C_{aryl} bond cleavage of **6**.

The plausible reaction mechanism was shown in Scheme 7. The anion radical generated by one-electron reduction of **6** undergoes the C10—C_{aryl} bond cleavage, and the 9,10-dihydroacridophosphine oxide anion radical **16** is generated. The anionic fragment in **16** is stabilized by the coordination of the phosphoryl group and methoxy group to the lithium atom, and the radical fragment is stabilized by the mesomeric effect of the two aryl groups. **16** abstracts hydrogen from the solvent successively to give the corresponding anion **17**. When **17** is quenched by proton sources, **14** is obtained. Alternatively, the further reduction of **17** causes the C10—OMe bond cleavage, which is the usual benzyl ether cleavage, and radical **18** is generated. **15** is obtained by hydrogen abstraction of **18** from the solvent followed by protonation.

In summary, we have reported the synthesis of the symmetrically multisubstituted 9-phosphatriptycene oxide. The advantages of this method are the decreased number of steps, the moderate yield, and the ease of the introduction of many substituents into the aromatic rings. The NMR data of the 9-phosphatriptycene chalcogenides indicated the large *s*-character of the P—Ch σ bond due to the narrow C—P—C angle, indicated by the X-ray



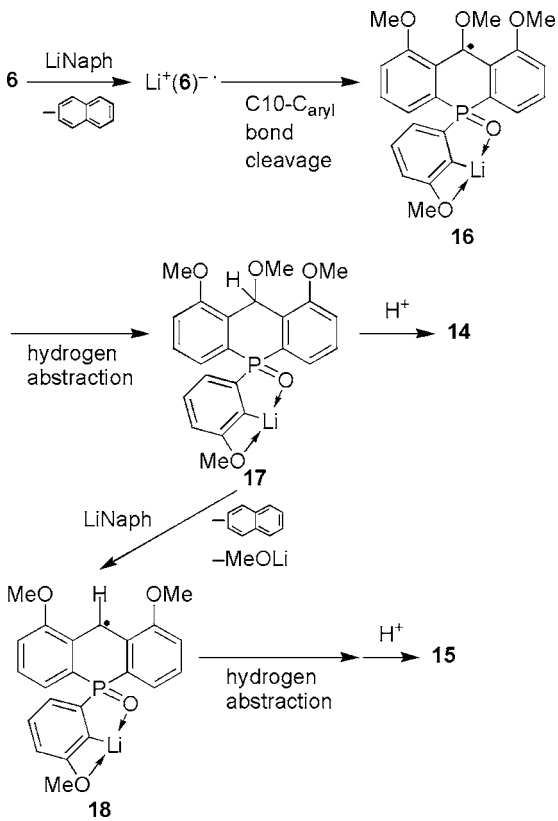
SCHEME 6

crystallographic analyses. The $C_{bridgehead}$—C_{aryl} bond cleavage occurred by the reduction of the 9-phosphatriptycene oxide.

EXPERIMENTAL

General Information

All melting points are uncorrected. Solvents were purified before use by reported methods. All reactions were carried out under dry argon atmosphere unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX500 and JEOL AL-400 spectrometers. ^{31}P NMR spectra were recorded on JEOL



SCHEME 7

Excalibur 270 and JEOL AL-400 spectrometers. ^{77}Se NMR spectra were recorded on a Bruker DRX500 spectrometer. All NMR spectra were recorded in $CDCl_3$ at 300 K, unless, otherwise mentioned. Chemical shifts are reported in δ value, downfield positive, and relative to tetramethylsilane for ^{1}H and ^{13}C NMR, 85% H_3PO_4 for ^{31}P NMR, or dimethylselenide for ^{77}Se NMR. High-performance liquid chromatography (HPLC) was performed by LC-918 and LC-908 C60 with JAIGEL 1H + 2H columns (Japan Analytical Industry) with chloroform as solvent. EI-MS and FAB-MS were recorded on Shimadzu QP-5000 and JEOL JMS-700P, respectively.

Tris(3-methoxyphenyl)phosphine, oxide **2**, and sulfide **12** were prepared according to the reported methods [14,15].

*Synthesis of Bis(3-methoxyphenyl)-2-phenoxycarbonylphenylphosphine Oxide (**3**)*

t-BuLi (2.65 M, pentane solution) (6.0 mL, 16 mmol) was added dropwise to a stirred solution of **2** (3.8 g, 10 mmol) in THF (300 mL) at −75°C and the reaction mixture was stirred for 2 h at −75°C. After the addition of a solution of $(PhO)_2CO$ (3.4 g, 16 mmol) in THF (30 mL), the reaction mixture was warmed to 0°C and stirred overnight. The mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to column chromatography on silica gel using 3:1 mixture of AcOEt/hexane as elutant to give a fraction containing **3**, which was further purified by recrystallization from AcOEt (1.54 g, 31%). **3** was also obtained in 60% yield by the use of $ClCO_2Me$ instead of $(PhO)_2CO$.

3: Colorless solids; mp 141–143°C; ^{1}H NMR (500 MHz, $CDCl_3$ δ 3.71 (s, 6H), 3.92 (s, 3H), 6.89 (ddd, J = 12.5, 7.5, 0.5 Hz, 1H), 7.03 (dt, J = 8.5, 1.3 Hz, 2H), 7.12–7.20 (m, 5H), 7.26–7.41 (m, 8H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.17 (s), 56.15 (s), 114.90 (s), 116.50 (d, J = 10.8 Hz), 118.17 (d, J = 2.1 Hz), 121.76 (s), 124.16 (d, J = 10.1 Hz), 124.47 (d, J = 10.0 Hz), 125.44 (s), 127.09 (d, J = 7.4 Hz), 128.93 (s), 129.38 (d, J = 14.6 Hz), 130.25 (d, J = 13.9 Hz), 131.21 (d, J = 100.1 Hz), 133.34 (d, J = 104.5 Hz), 150.81 (s), 157.21 (d, J = 12.6 Hz), 159.30 (d, J = 15.1 Hz), 164.63 (d, J = 4.8 Hz); ^{31}P{^{1}H} NMR (106 MHz, $CDCl_3$) δ 30.4; HRMS (FAB$^+$, *m*-NBA): *m*/*z* calcd for $C_{28}H_{26}O_6P$ 489.1467, found 489.1440 ([M + H$^+$]).

*Synthesis of 9-Phosphatriptycene Oxide (**1**)*

To a solution of **3** (39.9 mg, 82 μmol) in THF (1 mL) was added LDA (0.19 M, THF solution) (1.0 mL, 0.19 mmol) at −75°C, which was freshly prepared from ^{i}Pr$_2$NH (0.26 mL, 1.9 mmol) and *n*-BuLi (1.63 M, hexane solution) (1.2 mL, 1.9 mmol) in THF (10 mL), and the reaction mixture was stirred for 5 h at −75°C. The reaction mixture was gradually warmed to room temperature, and the mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to column chromatography on silica gel using AcOEt as elutant to give **1** as colorless solids (16.7 mg, 52%).

1: Colorless solids; mp 330–332°C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 9H), 6.18 (s, 1H), 6.95 (d, J = 7.8 Hz, 3H), 7.20 (td, J = 7.8, 3.4 Hz, 3H), 7.62 (dd, J = 12.3, 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 57.66 (s), 83.69 (d, J = 23.1 Hz), 117.11 (d, J = 1.9 Hz), 120.62 (d, J = 5.0 Hz), 127.69 (d, J = 14.1 Hz), 134.76 (d, J = 93.0 Hz), 137.75 (d, J = 7.3 Hz), 157.16 (d, J = 13.5 Hz); ^{31}P{^{1}H} NMR (109 MHz, $CDCl_3$) δ 2.0; HRMS (FAB$^+$, *m*-NBA): *m*/*z* calcd for $C_{22}H_{20}O_5P$ 395.1048, found 395.1031 ([M + H$^+$]).

*Synthesis of 9,10-Diphosphatriptycene Oxide (**5**)*

To a solution of **1** (492.0 mg, 1.3 mmol) in THF (100 mL) was added *t*-BuLi (2.65 M, pentane solution) (0.73 mL, 1.9 mmol) at −75°C, and the reaction mixture was stirred at −75°C for 2 h. After the addition of $(PhO)_3P$ (0.50 mL, 1.9 mL) to this mixture, the mixture was warmed to 0°C and stirred overnight at 0°C. After the generation of **4** was confirmed by ^{31}P NMR, the mixture was cooled to −75°C and LDA (0.39 M, THF solution) (10 mL, 3.9 mmol), which was freshly prepared from $(i\text{-Pr})_2$NH (0.54 mL, 3.9 mmol) and *n*-BuLi (1.63 M, hexane solution) (2.4 mL, 3.9 mmol) in THF (10 mL), was added. After the reaction mixture was warmed to room temperature gradually, the mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After the removal of the solvent, the residue was recrystallized from $CHCl_3$/EtOH to give **5** as colorless solids (28.6 mg, 6%).

5: Colorless solids; mp 368–370°C (dec.); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 9H), 6.87 (dd, J = 7.8, 5.2 Hz, 3H), 7.35 (td, J = 7.8, 4.0 Hz, 3H), 7.75 (dd, J = 10.7, 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 55.93 (s), 112.41 (s), 122.39 (d, J = 7.6 Hz), 129.56 (s), 130.10 (d, J = 13.6 Hz), 139.97 (d, J = 104.0 Hz), 161.74 (dd, J = 21.0, 13.1 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ −134.7 (d, J = 17.0 Hz), 7.6 (d, J = 17.0 Hz); HRMS (FAB$^+$, *m*-NBA): *m*/*z* calcd for $C_{21}H_{18}O_4P_2$ 396.0680, found 396.0688 (M$^+$).

H–D Exchange Reaction of **1**

In a 5-mm diameter NMR tube, D_2O or DCl/D_2O was added to a solution of **1** (5.0 mg, 13 μmol) in $CDCl_3$ (0.75 mL) at room temperature. The reaction was monitored by ^1H NMR spectroscopy.

*Synthesis of 9-Phosphatriptycene Oxide (***6***)*

A suspension of **1** (133 mg, 0.34 mmol) and NaH (60 wt % in mineral oil, 0.10 g, 2.5 mmol) in THF (20 mL) was stirred for 10 min at room temperature. To this mixture was added Me_2SO_4 (0.10 mL, 1.1 mmol), and the mixture was refluxed overnight. The mixture was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was subjected to HPLC to give **6** as colorless solids (130.4 mg, 94%).

6: Colorless solids; mp 318–322°C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 3.88 (s, 9H), 6.96 (d, $J = 7.7$ Hz, 3H), 7.21 (td, $J = 7.7$, 3.0 Hz, 3H), 7.65 (dd, $J = 12.5$, 7.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.12 (s), 58.70 (s), 87.90 (d, $J =$ 21.6 Hz), 119.09 (s), 121.24 (d, $J = 4.5$ Hz), 127.78 (d, $J = 14.3$ Hz), 135.55 (d, $J = 93.8$ Hz), 136.93 (d, $J = 6.8$ Hz), 156.55 (d, $J = 13.4$ Hz); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ 2.1; HRMS (FAB^+, *m*-NBA): *m/z* calcd for $C_{23}H_{21}O_5P$ 408.1127, found 408.1129 (M^+).

*Synthesis of 9-Phosphatriptycene Sulfide (***7***)*

A suspension of **1** (45.7 mg, 0.12 mmol) and Lawesson's reagent (234.5 mg, 0.58 mmol) in toluene (10 mL) was refluxed overnight. After removal of the solvent, the residue was subjected to HPLC to give a fraction containing **7**, which was further purified by recrystallization from $CHCl_3$/EtOH to give **7** as colorless solids (17.1 mg, 36%).

7: Colorless solids; mp 325–327°C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 9H), 6.26 (s, 1H), 6.97 (d, $J = 8.0$ Hz, 3H), 7.21 (td, $J = 8.0$, 3.7 Hz, 3H), 7.69 (dd, $J = 14.8$, 8.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.69 (s), 116.98 (s), 121.27 (d, $J = 8.8$ Hz), 127.43 (d, $J = 13.1$ Hz), 134.68 (d, $J =$ 75.9 Hz), 136.58 (d, $J = 4.3$ Hz), 157.00 (d, $J = 12.0$ Hz); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ 10.0; HRMS (FAB^+, *m*-NBA): *m/z* calcd for $C_{22}H_{20}O_4PS$ 411.0820, found 411.0808 ($M + H^+$).

The signal of the bridgehead carbon of **7** could not be observed because of the low solubility.

Desulfurization of **7**

In a 5-mm-diameter NMR tube, to a suspension of **7** (17.1 mg, 42 μmol) in toluene-d_8 (0.75 mL) was added $(n\text{-}Bu)_3P$ (50 μl, 0.20 mmol) at room temperature. After a few freeze-pump-thaw cycles, the tube was sealed in vacuo and the suspension was heated at 130°C for 5 d. After confirmation of disappearance of **7** by ^{31}P NMR spectroscopy, the sealed tube was opened and the solvent was removed under reduced pressure. The crude products were separated by HPLC to afford **8** as colorless solids (11.4 mg, 71%).

Reduction of **1** *with* $PhSiH_3$

A suspension of **1** (43.3 mg, 0.11 mmol) in $PhSiH_3$ (8.0 mL) was refluxed overnight, and the quantitative conversion of **1** to **8** was confirmed by ^{31}P NMR spectroscopy. The excess $PhSiH_3$ was removed under reduced pressure to give 8 as colorless solids (40.1 mg, 96%).

8: Colorless solids; mp 235–238°C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.89 (s), 6.33 (s, 1H), 6.86 (d, $J = 7.7$ Hz, 3H), 7.03 (td, $J = 7.7$, 2.3 Hz, 3H), 7.39 (dd, $J =$ 10.9, 7.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.88 (s), 88.65 (s), 116.26 (s), 125.73 (d, $J = 38.8$ Hz), 126.81 (d, $J = 14.6$ Hz), 128.49 (d, $J = 12.0$ Hz), 132.09 (d, $J = 9.9$ Hz), 157.43 (s); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ −68.7; HRMS (FAB^+, *m*-NBA): *m/z* calcd for $C_{22}H_{20}O_4P$ 379.1099, found 379.1088 ($[M+H^+]$).

Reduction of **1** *with* $HSiCl_3$

In a 5-mm-diameter NMR tube, to the suspension of **1** (19.2 mg, 49 μmol) in toluene-d_8 (1.0 mL) were added $HSiCl_3$ (0.20 mL, 2.0 mmol) and NEt_3 (0.30 mL, 2.2 mmol). After a few freeze-pump-thaw cycles, the tube was sealed in vacuo and the suspension was heated at 120°C for 2 d. After confirmation of disappearance of **1** by ^{31}P NMR spectroscopy, the sealed tube was opened. The mixture was treated with degassed ice-water and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give **10** as colorless solids (17.6 mg, 99%).

10: Colorless solids; mp 245–248°C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.91 (s, 6H), 6.73 (d, $J = 7.8$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 2H), 6.98 (td, $J = 7.8$, 1.8 Hz, 1H), 7.04 (td, $J = 7.7$, 1.7 Hz, 2H), 7.26 (ddd, $J = 10.6$, 7.8, 1.8 Hz, 1H), 7.39 (ddd, $J = 10.5$, 7.7, 1.7 Hz, 2H), 8.06 (s, 1H), 11.00 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.44 (s), 90.00 (d, $J =$ 1.9 Hz), 115.25 (s), 119.02 (s), 123.51 (d, $J = 37.9$ Hz), 126.05 (d, $J = 38.3$ Hz), 127.00 (d, $J = 14.1$ Hz), 127.49 (d, $J = 14.4$ Hz), 130.62 (d, $J = 2.8$ Hz), 136.50 (d, $J = 3.3$ Hz), 139.11 (d, $J = 5.8$ Hz), 142.20 (d, $J = 8.8$ Hz), 155.72 (s), 156.42 (s); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ −68.4; LRMS (EI): *m/z* 364 (M^+).

Synthesis of 9-Phosphatriptycene **9**

A suspension of **6** (530.4 mg, 1.3 mmol) in $PhSiH_3$ (2.0 mL) was refluxed overnight. After confirmation of quantitative conversion of **6** to **9** by ^{31}P NMR spectroscopy, the solvent was removed under reduced pressure. The residue was separated by HPLC to give **9** as colorless solids (169 mg, 33%).

9: Colorless solids; mp 218–220°C; ^1H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 9H), 3.89 (s, 3H), 6.86 (d, $J = 7.6$ Hz, 3H), 7.03 (td, $J = 7, 6, 2.0$ Hz, 3H), 7.41 (dd, $J = 11.1, 7.6$ Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 56.94 (s), 58.99 (s), 92.33 (s), 118.38 (s), 126.41 (d, $J = 39.3$ Hz), 126.76 (d, $J = 14.8$ Hz), 127.40 (d, $J = 15.8$ Hz), 131.48 (d, $J = 9.4$ Hz), 156.85 (s); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ −64.8; HRMS (FAB$^+$, *m*-NBA) *m/z* calcd for $C_{23}H_{21}O_4P$ 392.1177, found 392.1121 (M^+).

*Synthesis of 9-Phosphatriptycene Selenide (***11***)*

In a 5-mm-diameter NMR tube, to a suspension of **8** (11.3 mg, 30 μmol) in $CDCl_3$ (0.75 mL) was added elemental selenium (28.3 mg, 0.36 mmol). After a few freeze-pump-thaw cycles, the tube was sealed in vacuo and heated at 75°C for 5 h. After confirmation of disappearance of **8** by ^{31}P NMR, the sealed tube was opened. The residual elemental selenium was filtered off, and the solvent was removed under reduced pressure. The residue was subjected to HPLC to give **11** as colorless solids (4.9 mg, 33%).

11: Colorless solids; mp 336–338°C (dec.); ^1H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 9H), 6.30 (s, 1H), 6.98 (d, $J = 7.7$ Hz, 3H), 7.21 (tdd, $J = 7.7$, 4.0, 1.0 Hz, 3H), 7.71 (ddd, $J = 15.6, 7.7, 1.0$ Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 57.76 (s), 117.14 (s), 122.50 (d, $J = 10.4$ Hz), 127.37 (d, $J = 16.1$ Hz), 133.55 (d, $J = 67.8$ Hz), 136.31 (d, $J = 2.9$ Hz), 156.91 (d, $J = 11.3$ Hz); $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 4.7 (s, satellite, $^1J_{PSe} = 828$ Hz); $^{77}Se\{^1H\}$ NMR (95 MHz, $CDCl_3$) δ −601.3 (d, $^1J_{PSe} = 828$ Hz); HRMS (FAB$^+$, *m*-NBA): *m/z* calcd for $C_{22}H_{20}O_4P^{80}Se$ 459.0264, found 459.0277 ([M+H$^+$]).

The signal of the bridgehead carbon could not be observed because of the low solubility of **9**.

*Synthesis of Tris(3-methoxyphenyl)phosphine Selenide (***13***)*

A suspension of tris(3-methoxyphenyl)phosphine (213.0 mg, 0.61 mmol) and elemental selenium (180.0 mg, 2.3 mmol) in $CHCl_3$ (10 mL) was refluxed for 7 h. The residual elemental selenium was filtered off, and the solvent was removed under reduced pressure to give **11** as colorless solids (225.0 mg, 85%).

13: Colorless solids; mp 141–143°C. ^1H NMR (500 MHz, $CDCl_3$) δ 3.78 (s, 9H), 7.00 (dq, $J = 7.9$, 1.1 Hz, 3H), 7.16 (ddd, $J = 12.9, 7.9, 1.1$ Hz, 3H), 7.29–7.38 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.23 (s), 117.38 (s), 117.79 (d, $J = 13.0$ Hz), 124.47 (d, $J = 10.0$ Hz), 129.38 (d, $J = 14.5$ Hz), 132.73 (d, $J = 76.0$ Hz), 159.29 (d, $J = 15.8$ Hz); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ 38.1 (s, satellite, $^1J_{PSe} = 733$ Hz); $^{77}Se\{^1H\}$ NMR (95 MHz, $CDCl_3$) δ −256 (d, $^1J_{PSe} = 733$ Hz); HRMS (FAB$^+$, *m*-NBA): *m/z* calcd for $C_{21}H_{22}O_3P^{80}Se$ 433.0472, found 433.0459 ([M+H$^+$]).

Reduction of **6** *with Lithium Naphthalenide*

To a solution of **6** (67.5 mg, 0.17 mmol) in THF (10 mL) at −75°C was added LiNaph (1.0 M THF solution) (0.33 mL, 0.33 mmol), which was prepared according to the reported method [16], and the reaction mixture was warmed to 0°C. After the mixture was stirred at 0°C for 1 h, it was treated with aqueous NH_4Cl and extracted with $CHCl_3$. The extracts were dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was separated by HPLC and column chromatography on silica gel using AcOEt as elutant to give **14** (7.8 mg, 11%) and **15** (43.3 mg, 67%) as colorless solids.

14: Colorless solids; mp 194–196°C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.18 (s, 3H), 3.71 (s, 3H), 3.93 (s, 6H), 6.51 (s, 1H), 6.89 (dd, $J = 7.9$, 2.1 Hz, 1H), 7.11 (d, $J = 7.6$ Hz, 2H), 7.22 (td, $J = 7.9$, 3.9 Hz, 1H), 7.30–7.35 (m, 2H), 7.48 (td, $J = 7.6$, 3.0 Hz, 2H), 7.81 (dd, $J = 11.3$, 7.6 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 55.25 (s), 55.84 (s), 56.52 (s), 63.36 (d, $J = 10.8$ Hz), 114.10 (d, $J = 2.3$ Hz), 115.85 (d, $J = 12.4$ Hz), 117.45 (d, $J = 2.6$ Hz), 123.51 (d, $J = 5.6$ Hz), 123.61 (d, $J = 10.6$ Hz), 129.63 (d, $J = 9.6$ Hz), 129.25 (d, $J = 15.0$ Hz), 129.91 (d, $J = 13.1$ Hz), 132.59 (d, $J = 99.1$ Hz), 136.22 (d, $J = 107.6$ Hz), 157.20 (d, $J = 13.8$ Hz), 159.08 (d, $J = 15.9$ Hz); $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$) δ 11.6; HRMS (FAB$^+$, *m*-NBA): *m/z* calcd for $C_{23}H_{23}O_5P$ 410.1283, found 410.1265 (M^+).

15: Colorless solids; mp 250–254°C; ^1H NMR (500 MHz, $CDCl_3$) δ 3.58 (dd, $J = 22.0$, 3.3 Hz, 1H), 3.75 (s, 3H), 3.92 (s, 6H), 4.63 (dd, $J = 22.0$, 2.4 Hz, 1H), 6.89–6.96 (m, 2H), 7.03 (d, $J = 7.9$ Hz, 2H), 7.13 (dd, $J = 13.7$, 1.2 Hz, 1H), 7.20 (td, $J = 8.0$, 3.5 Hz, 1H), 7.39 (td, $J = 7.9$, 2.8 Hz, 2H), 7.60 (dd, $J = 11.6$, 7.9 Hz, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 22.72 (d, $J = 10.8$ Hz), 55.33 (s), 55.59 (s), 112.71 (s), 115.75 (d, $J = 11.3$ Hz), 117.15 (s), 122.42 (d, $J = 6.4$ Hz), 122.94 (d, $J = 10.4$ Hz), 127.89 (d, $J = 13.4$ Hz), 129.25 (d, $J = 10.5$ Hz), 129.611 (d, $J = 13.8$ Hz), 129.612 (d, $J = 102.0$ Hz), 136.20 (d, $J = 106.3$ Hz), 156.29 (d, $J = 13.9$ Hz), 159.37 (d, $J = 15.1$ Hz);

$^{31}P\{^{1}H\}$ NMR (109 MHz, $CDCl_3$) δ 11.2; HRMS (FAB^+, *m*-NBA): *m/z* calcd for $C_{22}H_{21}O_4P$ 380.1177, found 380.1171 (M^+).

Cyclic Voltammetry of **6**

The cyclic voltammetry of **6** was performed under dry argon atmosphere at room temperature using an ALS 617A voltammetric analyzer. Conditions: solvent, degassed CH_2Cl_2 with 0.1 M $(n\text{-Bu})_4NClO_4$as the supporting electrolyte; working electrode, glassy carbon; counter electrode, Pt wire; reference electrode, Ag/0.01 M $AgNO_3$/0.1 M $(n\text{-Bu})_4NClO_4/CH_3CN$; scan rate, 30 mVs^{-1}.

Crystallographic Studies of **6**

The intensities of reflection were collected at 120 K on a RIGAKU MSC Mercury CCD diffractometer with a graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) using CrystalClear (Rigaku Corp.). The data were corrected for Lorentz polarization effects. The crystallographic and experimental data are listed in Table 2. The structures were solved by the direct method (SIR 97) and expanded using Fourier techniques. The structures were refined by full-matrix least squares on F^2 (SHELXS-97) [17]. The nonhydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically.

Coordinates and other crystallographic information were deposited with Cambridge Crystallographic Database Centre as supplementary publication No. CCDC-237879. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

TABLE 2 Crystallographic Data of **6**

Formula	$C_{24}H_{25}O_5P$
Temperature	120 K
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.320(3)
b (Å)	10.071(3)
c (Å)	13.903(6)
α (degree)	70.146(12)
β (degree)	88.178(17)
γ (degree)	68.718(13)
V (Å^3)	1015.4(7)
Z	2
Calculated density	1.441 g cm^{-3}
Reflection collected	7630
Unique	4331
R_1 ($I > 2.00\ \sigma(I)$)	0.0349
wR_2 (all data)	0.0931
Goodness-of-Fit	1.065

Computational Methods

Structural optimizations were performed using the B3LYP functional theory with the 6-31G(d) basis set [10,11]. The NMR shielding tensors were computed with the GIAO methods at the B3LYP/6-31G(d) level of theory [12]. All calculations were performed using GAUSSIAN03 program package [13].

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