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Synthesis and reactions of a monosubstituted dithiirane 1-oxide, 3-(9-triptycyl)dithiirane 1-oxide

Akihiko Ishii,* Tetsuhiko Kawai, Mariko Noji and Juzo Nakayama

Department of Chemistry, Faculty of Science, Saitama University, Sakura-ku, Saitama 338-8570, Japan

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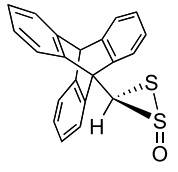
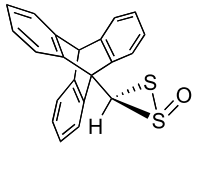
Abstract—A 3-monosubstituted dithiirane 1-oxide, 3-(9-triptycyl)dithiirane 1-oxide, was prepared for the first time, by the reaction of (9-triptycyl)diazomethane and S_8O. The dithiirane 1-oxide was obtained as *cis*- and *trans*-isomers, and the structure of the *trans*-isomer was verified by X-ray crystallography. The *cis*-isomer isomerized gradually to the *trans*-isomer in solution. The divalent sulfur atom of the *cis*- and *trans*-dithiirane 1-oxides were removed on treatment with triphenylphosphine to give the corresponding *Z*- and *E*-sulfines, respectively. The reaction of the *trans*-dithiirane 1-oxide with $(Ph_3P)_2Pt(C_2H_4)$ provided the (sulfenato-thiolato)Pt^{II} complex, and that with Lawesson's reagent yielded the 1,3,4,2-trithiaphospholane and 1,2,4,5,3-tetrathiaphosphorinane derivatives.

1. Introduction

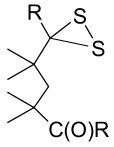
We report here, the synthesis of 3-(9-triptycyl)dithiirane 1-oxide **1**, the first, isolable 3-monosubstituted dithiirane 1-oxide, and its physical and chemical properties. While dithiiranes had been recognized as elusive intermediates,[1–7] we discovered the formation of isolable dithiiranes **2** and dithiirane 1-oxides **3** by oxidative hydrolysis of bicyclic 1,3-dithietanes **4** and **5**, respectively.[8–14] We have also disclosed two routes for dithiirane oxides **6**: one is the elimination of S_2O from tetrathiolane 2,3-dioxides[15,16] and the other is the reaction of diazoalkanes with S_8O.[17] Dithiirane 1-oxides **6** can be led to the corresponding dithiiranes **7** by treatment with Lawesson's reagent (LR).[18] On the other hand, Shimada and co-workers succeeded in the synthesis of dithiiranes **8** and **9** by the reaction of the corresponding thioketone *S*-oxides (sulfines) with LR.[19] Mloston and Maier reported the isolation of the parent dithiirane in the argon matrix at 10 K together with the parent thioformaldehyde *S*-sulfide (thiosulfine).[20] Thus, dithiiranes isolated so far at room temperature in air are limited to 3,3-dialkyl- and 3-alkyl-3-aryldithiirane derivatives. 3-Monosubstituted dithiiranes are of great interest not only for their physical and chemical properties but also from the viewpoint of to what extent the steric demand of the substituent can be reduced for the intrinsically unstable dithiirane ring. Previously, we reported that reactions of (2,4,6-trimethyl-



trans-**1**



cis-**1**



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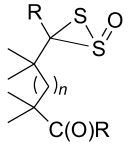
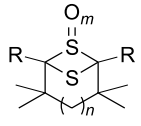
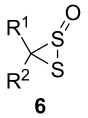


3: *n* = 0,1,2

R = aryl, *t*-Bu



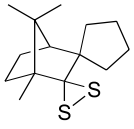
4: *n* = 1; *m* = 0
5: *n* = 0,1,2; *m* = 1



6

7

$R^1 = R^2$ = 1-adamantyl (1-Ad)
R^1 = 1-Ad; R^2 = *t*-Bu
R^1 = Ph; R^2 = *t*-Bu
R^1-R^2 = -$CMe_2CH_2CH_2CMe_2$-
R^1-R^2 = -CMe_2(*o*-C_6H_4)CMe_2-



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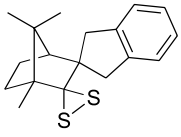

9

Keywords: Dithiirane oxide; Steric protection; 9-Triptycyl; Diazo compound; Octasulfur monoxide.
* Corresponding author. Tel.: +81 48 858 3394; fax: +81 48 858 3700; e-mail: ishiiaki@chem.saitama-u.ac.jp

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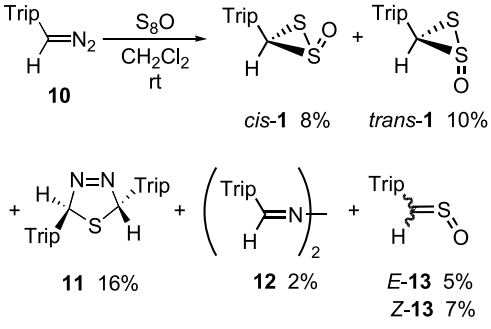
phenyl)- and (2,4,6-tri-*t*-butylphenyl)diazomathanes with S_8O failed to give the corresponding monosubstituted dithiirane 1-oxides.[17] Thus we next, employed 9-triptycyl as the substituent,[21] and the reaction of (9-triptycyl)diazomethane (**10**) with S_8O furnished the desired 3-monosubstituted dithiirane 1-oxide. Hereafter, the 9-triptycyl group is abbreviated to Trip for convenience.

2. Results and discussion

(9-Triptycyl)diazomethane (**10**), prepared by oxidation of the corresponding hydrazone ($TripCHNNH_2$), was treated with S_8O in dichloromethane at room temperature. After chromatographic purification, we obtained the desired *cis*-**1** [(1*R**,3*S**)-**1**] (8%) and *trans*-**1** [(1*S**,3*S**)-**1**] (10%) together with 1,3,4-thiadiazoline **11** (16%), azine **12** (2%), and sulfines *Z*-**13** (7%) and *E*-**13** (5%) (Eq. 1). The formation of **11** is explained by the reaction of **10** with TripCHS,[17,22] though TripCHS was not obtained in this reaction or in reactions reported later in this paper.[23] The stereochemistry of **11** was determined as *trans* by X-ray crystallography.[24] Azine **12** may be formed by the reaction of **10** with SO_2.[17,25–27] Sulfines **13** are the decomposition products of **1** on silica gel.



(1)

The structures of dithiirane 1-oxides, *cis*-**1** and *trans*-**1**, were elucidated by their spectroscopic data. In the ^1H NMR spectra (400 MHz) measured at 298 K, dithiirane ring protons of *cis*-**1** and *trans*-**1** appeared at δ 4.98 and 5.49, respectively. The low-field shift in *trans*-**1** is due to the anisotropic effect of the S=O group being *cis* to the proton.[28,29] At this temperature, three benzene rings of *cis*-**1** are not equivalent to each other, indicating that free rotation of the 9-triptycyl group in *cis*-**1** is slowed by the steric hindrance due to the *cis* oxygen atom.[30] In the ^{13}C NMR spectra, dithiirane ring carbons of *cis*-**1** and *trans*-**1** resonated at δ 66.7 and 66.9, respectively, and the ^1J (^{13}C–^1H) coupling constants determined with gated decoupling were 169 and 173 Hz, respectively. These ^1J (^{13}C–^1H) values are comparable to those of other three-membered cyclic compounds such as cyclopropane (161 Hz) and thiirane (171 Hz).[31] The stereochemistry of *trans*-**1** was verified by X-ray crystallography as depicted in Figure 1.

cis-**1** was not obtained in the pure form by chromatographic purification or recrystallization because of its gradual isomerization to *trans*-**1** in solution. The reverse isomerization from *trans*-**1** to *cis*-**1** was not observed under similar conditions. Standing a $CDCl_3$ solution of *cis*-**1** at room temperature in the dark for 3 months led to the complete

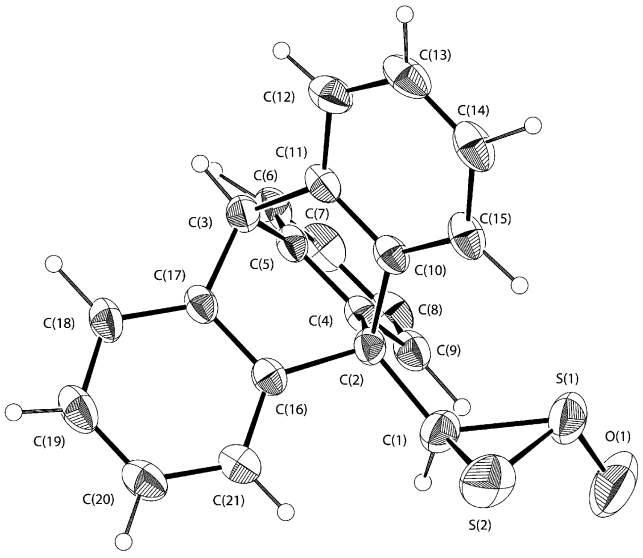
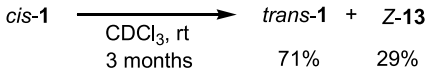


Figure 1. ORTEP drawing of *trans*-**1** (30% ellipsoidal probability). Relevant bond lengths (Å) and bond angles (deg) data: S1–O1 1.436(6), S1–C1 1.787(5), S1–S2 2.119(3), S2–C1 1.798(5), C2–C16 1.521(5), C2–C10 1.533(6), C2–C4 1.537(5), C2–C1 1.540(6), O1–S1–C1 113.2(3), O1–S1–S2 115.8(4), C1–S1–S2 54.01(18), C1–S2–S1 53.53(18), C16–C2–C10 105.7(3), C16–C2–C4 105.6(3), C10–C2–C4 105.9(3), C16–C2–C1 111.0(4), C10–C2–C1 119.7(4), C4–C2–C1 108.0(4), C2–C1–S1 123.4(4), C2–C1–S2 124.3(4), S1–C1–S2 72.5(2).

disappearance of *cis*-**1** to leave *trans*-**1** (71%) and *Z*-**13** (29%) (Eq. 2). This isomerization apparently obeyed the first-order kinetics ($k=4.0\times10^{-7}\ s^{-1}$, $r^2=0.966$). The presence of a small amount of a radical scavenger, 1,1-diphenyl-2-picryl hydrazyl (DPPH), led to substantial retardation of the isomerization ($k=0.81\times10^{-7}\ s^{-1}$, $r^2=0.913$); after 1 month, the isomerization proceeded up to 57% without DPPH and down to 31% in the presence of DPPH, suggesting the isomerization is caused by a radical contaminant. We have observed a similar retardation of the epimerization between dithiirane 1-oxides **2** (R=Ph) and **2′** (R=Ph) by DPPH (Eq. 3).[32]



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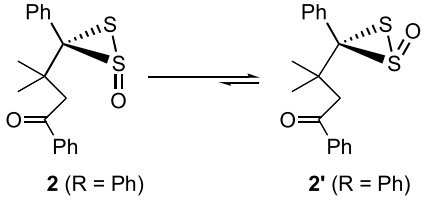
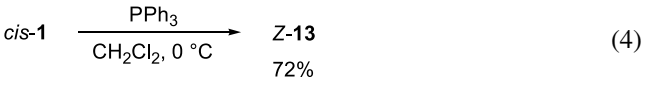


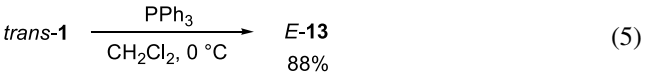
(3)

The divalent sulfur atom in a dithiirane 1-oxide is readily removed by treatment with tripheylphosphine to give the corresponding sulfine with retention of stereochemistry.[16] Treatment of *cis*-**1** and *trans*-**1** with triphenylphosphine gave *Z*-**13** and *E*-**13**, respectively, in high yields (Eqs. 4 and 5). The reaction of *trans*-**1** with $(Ph_3P)_2Pt(C_2H_4)$ yielded (sulfenato-thiolato)Pt^{II} complex **14** in 88% isolated yield.[33] When *cis*-**1** was allowed to react with $(Ph_3P)_2Pt(C_2H_4)$, the same complex was formed as the major product. A much low-field shift of the four-membered ring proton of **14** [δ 6.75 (d, $J=2.3$ Hz)] compared with the corresponding dithiirane protons of *cis*-**1** (δ 4.98) and *trans*-**1** (δ 5.49)

implies the *cis* configuration of the hydrogen to the S═O oxygen.



(4)



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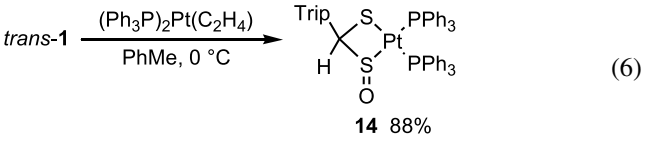
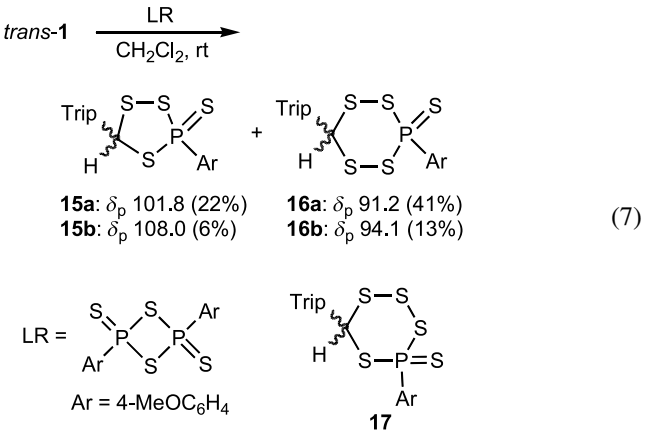


(6)

In the hope of obtaining the corresponding unoxidized dithiirane, *trans*-**1** was treated with LR in benzene at room temperature.[18] However, we obtained not the desired dithiirane but stereoisomers of 1,3,4,2-trithiaphospholanes **15a**,**b** and 1,2,4,5,3-tetrathiaphosphorinanes **16a**,**b**. The structures of **15a**,**b** and **16a**,**b** were elucidated by their ^{1}H, ^{13}C, and ^{31}P NMR data and mass spectroscopic data, though their stereochemistries were not determined. In the ^{1}H NMR of **15a**, the 1,3,4,2- trithiaphospholane ring proton appeared as a doublet with 2.7 Hz of the ^{3}J (^{1}H–^{31}P) coupling constant, and in the ^{13}C NMR, the ring carbon appeared as a doublet with 4.5 Hz of the ^{2}J (^{13}C–^{31}P) coupling constant. Similarly, the corresponding proton and carbon of **15b** resonated as a doublet. Such long-range couplings were not observed for **16a**,**b**, and their tetrathiaphosphorinane ring protons and the carbons appeared as a broad singlet. These observations would rule out 1,2,3,5,4-tetrathiaphosphorinane structures **17** for the six-membered compounds. Compounds **15a**,**b** formally correspond to adducts of $TripCHS_2$ with $ArPS_2$ (Ar=4-$MeOC_6H_4$), and **16a**,**b** correspond to those of $TripCHS_3$ with $ArPS_2$. Incidentally, we have recently, obtained adducts of thioketones with $ArPS_2$, which are 1,3,2-dithiaphosphetane derivatives.[34] Noteworthy is the formation of trithiaphospholanes **15a** and **15b** by the reaction of sulfine *Z*-**13** with LR in 31 and 17% yields, respectively. It has been reported that the reaction of a sulfine with LR gave the dithiirane.[19] At present, however, we do not have direct evidence of intervention of $TripCHS_2$ in these reactions.



(7)

3. Conclusion

3-Monosubstituted dithiirane 1-oxides *trans*-**1** and *cis*-**1** were successfully synthesized, for the first time, by taking advantage of a 9-triptycyl group as the steric-demanding group. The dithiirane 1-oxides **1** presented reactivities similar to those of 3,3-disubstituted dithiirane 1-oxides but the reaction with LR gave sulfur–phosphorus-containing heterocycles.

4. Experimental

4.1. General

The melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were determined on Bruker AM400 or DRX400 (400 and 100.6 MHz, respectively), AC300P (300 MHz for ^{1}H), or AC200 (200 and 50 MHz, respectively), spectrometers using $CDCl_3$ as the solvent at 25 °C, unless otherwise noted. ^{31}P NMR spectra were determined on Bruker AM400 or DRX400 (162 MHz) spectrometers using 85% H_3PO_4 as the external standard in $CDCl_3$ at 25 °C. IR spectra were taken on a Hitachi 270-50 spectrometer. Mass spectra were determined on a JEOL JMS-DX303 or a JEOL JMS-700AM spectrometers operating at 70 eV in the EI mode. FAB MS was measured with *m*-nitrobenzyl alcohol as the matrix. Elemental analysis was performed by the Chemical Analysis Center of Saitama University. Column chromatography was performed with silica gel (70–230 mesh), high-pressure liquid chromatography (HPLC) with a packed SiO_2 column (INERTSIL PREP-SIL: 10 mm i.d. or 20 mm i.d., GL Science Inc.), and gel permeation chromatography (GPC) on a Japan Analytical Industry LC-908; the eluent is shown in parentheses.

4.2. Preparation of (9-triptycyl)diazomethane (10)

4.2.1. Preparation of triptycene-9-carbaldehyde. Butyllithium (1.56 M in hexane, 5.6 mL, 8.74 mmol) was added to a solution of 9-bromotriptycene[35] (1.42 g, 4.25 mmol) in benzene (60 mL) and ether (95 mL) at −15 °C under argon, and the solution was stirred for 1 h at −15 °C. To the solution was added ethyl formate (5.6 mL, 69 mmol), and the mixture was warmed to room temperature. After stirring for 15 min, aqueous ammonium chloride and then ether were added to the mixture. The organic layer was washed with water, dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2/hexane 1:1) to give the aldehyde (825 mg, 69%).

Triptycene-9-carbaldehyde.[36] Colorless crystals. ^{1}H NMR (300 MHz) δ 5.40 (s, 1H), 6.98–7.05 (m, 6H), 7.40–7.44 (m, 3H), 7.59–7.63 (m, 3H), 11.22 (s, 1H).

4.2.2. Preparation of triptycene-9-carbaldehyde hydrazone. A solution of triptycene-9-carbaldehyde (1.40 g, 4.96 mmol) and hydrazine monohydrate (22 mL, 0.41 mol) in diethylene glycohol (50 mL) was refluxed for 0.5 h. The mixture was cooled to room temperature, diluted with water, and then extracted with dichloromethane. The

extract was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (CH_2Cl_2) to give the hydrazone (1.438 g, 98%).

Triptycene-9-carbaldehyde hydrazone. Colorless powder, mp >352 °C decomp. (EtOH–water). ^{1}H NMR (400 MHz) δ 5.39 (s, 1H), 5.93 (br s, 2H), 6.95–7.05 (m, 6H), 7.35–7.43 (m, 3H), 7.56–7.65 (m, 3H), 8.44 (s, 1H); ^{13}C NMR (100.6 MHz) δ 54.3 (CH), 54.6 (C), 123.0 (CH), 123.6 (CH), 124.9 (CH), 125.2 (CH), 141.1 (CH), 145.4 (C), 145.8 (C); IR (KBr) 3378 (NH_2), 1455, 754, 729 cm^{-1}. Anal. Found: C, 84.09; H, 5.53; N, 9.23. Calcd for $C_{21}H_{16}N_2\cdot 0.112C_2H_6O\cdot 0.213H_2O$: C, 83.48; H, 5.64; N, 9.17 (the ^{1}H NMR spectrum of the sample subjected to the elemental analysis showed that it contained 11.2 mol% of ethanol and 21.3 mol% of H_2O).

4.2.3. Preparation of (9-triptycyl)diazomethane (10). To a solution of triptycene-9-carbaldehyde hydrazone (221 mg, 0.745 mmol) in benzene was added 378 mg (1.54 g-atom of oxygen) of nickel peroxide (4.08×10^{-3} g-atom of oxygen/g).[37,38] The mixture was stirred for 1 h at room temperature. After filtration, the solvent was removed under reduced pressure to give (9-triptycyl)diazomethane (**10**). The diazomethane was used without further purification.

9-Triptycyl)diazomethane (**10**).[39] Orange oil. ^{1}H NMR (300 MHz) δ 5.07 (s, 1H), 5.42 (s, 1H), 7.01–7.09 (m, 6H), 7.38–7.43 (m, 6H); IR (neat) 2063, 1456, 748 cm^{-1}.

4.3. Reaction of (9-triptycyl)diazomethane (10) with S_8O

A mixture of S_8O[40] (415 mg, 1.53 mmol) and **10**, prepared above, in dichloromethane (45 mL) under argon was stirred for 1.5 h at room temperature. The solvent was evaporated to dryness, and the residue was passed through a short column of silica gel (dichloromethane). The fraction containing products was further subjected to HPLC (dichloromethane/hexane 60:40 and then 80:20 for *E*-**5**) to give a mixture of thiadiazoline **11** and azine **12**, *cis*-dithiirane 1-oxide *cis*-**1** (21.7 mg, 8%), *trans*-dithiirane 1-oxide *trans*-**1** (26.2 mg, 10%), *Z*-sulfine *Z*-**5** (16 mg, 7%), and *E*-sulfine *E*-**5** (11.8 mg, 5%) in this order. The mixture of **11** and **12** was subjected to GPC ($CHCl_3$) and again HPLC (dichloromethane/hexane 40:60) to give thiadiazoline **11** (36.5 mg, 16%) and azine **12** (4 mg, 2%).

4.3.1. *t*-3-(9-Triptycyl)dithiirane *r*-1-oxide (*trans*-1). Mp 186–187 °C (Et_2O–CH_2Cl_2). ^{1}H NMR (400 MHz): 300 K: δ 5.40 (s, 1H), 5.49 (s, 1H), 6.90 (br s, 1H), 7.09 (br s, 6H), 7.43 (br s, 3H), 7.83 (br s, 2H); 323 K: δ 5.36 (s, 1H), 5.47 (s, 1H), 6.80–8.06 (br s, 3H), 7.03 (br s, 6H), 7.38–7.41 (m, 3H); ^{13}C NMR (100.6 MHz, 323 K) δ 54.5 [CH, ^1J (^{13}C–^{1}H)=138 Hz], 55.0 (C), 66.9 [CH, ^1J (^{13}C–^{1}H)=173 Hz], 122.6 (br, CH), 124.0 (CH), 125.4 (CH), 126.0 (CH), 143.9 (br, C), 146.2 (C); IR (KBr) 1460, 1128 (S=O), 742 cm^{-1}. Anal. Calcd for $C_{21}H_{14}OS_2$: C, 72.80; H, 4.07. Found: C, 72.43; H, 3.93.

Crystallographic data for trans-**1**. $C_{21}H_{14}OS_2$, M_w=346.470, colorless plate, $0.20\times0.12\times0.06$ mm^3, monoclinic, $P2_1/c$, a=15.761(2) Å, b=8.1384(13) Å, c=13.756(2) Å, b=112.596(12)°, V=1629.0(5) Å^3, ρ_{calcd}=1.413 g cm^{-3}, Z=4, μ(Cu Kα)=2.981 cm^{-1}. Mac Science MXC3KHF diffractometer with graphite-monochromated Cu Kα radiation (λ=1.54178 Å), $\theta/2\theta$ scans method in the range $3°<2\theta<140°$ ($-19<h<17$, $0<k<9$, $0<l<16$), 2740 independent reflections. Absorption correction was done by the psi-can method.[41] The structure was solved with a direct method (SIR97[42]) and refined with full-matrix least-squares (SHELXL-97[43]) using all independent reflections, where nonhydrogen atoms were refined anisotropically and hydrogen atoms isotropically without the AFIX code except C(1)–*H*. $R1$=0.0894 ($I>2\sigma I$, 2485 reflections), w$R2$=0.2674 (for all), GOF=1.070, 271 parameters; max/min residual electron density=1.021/−0.542 e Å^{-3}. CCDC-268216 contains the supplementary crystallographic data. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223 336-033; E-mail: deposit@ccdc.cam.ac.uk].

4.3.2. *c*-3-(9-Triptycyl)dithiirane *r*-1-oxide (*cis*-1). ^{1}H NMR (400 MHz) δ 4.98 (s, 1H), 5.42 (s, 1H), 6.86 (td, J=7.7, 1.3 Hz, 1H), 6.94 (td, J=7.4, 0.9 Hz, 1H), 7.03–7.21 (m, 4H), 7.34 (dd, J=7.2, 1.1 Hz, 1H), 7.43–7.48 (m, 3H), 7.92 (d, J=8.6 Hz, 1H), 7.94 (d, J=8.5 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 54.5 [two carbons: CH with ^1J (^{13}C–^{1}H)=141 Hz and C], 59.9 [CH, ^1J (^{13}C–^{1}H)=169 Hz], 121.6 (CH), 121.9 (CH), 123.2 (CH), 123.78 (CH), 123.82 (CH), 124.0 (CH), 125.1 (CH), 125.3 (CH), 125.5 (CH), 126.0 (CH), 126.1 (CH), 128.0 (CH), 141.4 (C), 143.3 (C), 145.4 (C), 146.1 (C), 146.2 (C), 146.8 (C); IR (KBr) 1462, 1130, 1122 (S=O), 752 cm^{-1}.

4.3.3. 2,5-Di-(9-triptycyl)-1,3,4-thiadiazoline (11). Colorless crystals, mp 207–210 °C decomp. (hexane–CH_2Cl_2). ^{1}H NMR (300 MHz) δ 5.49 (s, 2H), 6.85 (d, J=7.7 Hz, 2H), 6.98–7.12 (m, 10H), 7.19 (td, J=7.7, 1.4 Hz, 2H), 7.45–7.53 (m, 6H), 7.59 (d, J=7.4 Hz, 2H), 8.10 (s, 2H), 8.54 (d, J=7.7 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 54.8 (CH), 59.0 (C), 102.6 (CH), 121.8 (CH), 122.7 (CH), 123.5 (CH), 123.8 (CH), 124.2 (CH), 124.6 (CH), 124.8 (CH), 125.1 (CH), 125.2 (CH), 125.5 (CH), 125.7 (CH), 126.0 (CH), 141.1 (C), 145.0 (C), 145.1 (C), 146.0 (C), 146.4 (C), 147.2 (C); IR (KBr) 1458, 744 cm^{-1}. Anal. Found: C, 81.31; H, 4.98; N, 4.27. Calcd for $C_{42}H_{28}N_2S\cdot 0.354CH_2Cl_2\cdot 0.261C_6H_{14}$: C, 81.74; H, 5.06; N, 4.34 (the ^{1}H NMR spectrum of the sample subjected to the elemental analysis showed that it contained 35.4 mol% of CH_2Cl_2 and 26.1 mol% of hexane).

4.3.4. Triptycene-9-carbaldehyde azine (12).[39] Colorless crystals, mp >352 °C decomp. ($CHCl_3$). ^{1}H NMR (400 MHz) δ 5.50 (s, 2H), 7.06–7.14 (m, 12H), 7.47–7.49 (m, 6H), 7.85–7.88 (m, 6H), 9.72 (s, 2H); ^{13}C NMR (100.6 MHz) δ 54.5 (CH), 55.4 (C), 123.1 (CH), 123.9 (CH), 125.2 (CH), 125.7 (CH), 144.5 (C), 145.9 (C), 164.4 (CH); IR (KBr) 1661, 1456, 758 cm^{-1}. Anal. Found: C, 88.79; H, 4.87; N, 4.92. Calcd for $C_{42}H_{28}N_2\cdot 0.0457CHCl_3$: C, 89.20; H, 4.99; N, 4.95 (the ^{1}H NMR spectrum, measured in CD_2Cl_2, of the sample subjected to the elemental analysis showed that it contained at least 4.57 mol% of $CHCl_3$).

4.3.5. (9-Triptycyl)methanethial (*E*)-*S*-oxide (*E*-13). Colorless crystals, mp 239–241 °C (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz) δ 5.45 (s, 1H), 7.02–7.09 (m, 6H), 7.40–7.46 (m, 6H), 10.15 (s, 1H); ^{13}C NMR (100.6 MHz) δ 54.1 (CH), 58.2 (C), 122.1 (CH), 124.1 (CH), 125.3 (CH), 126.1 (CH), 143.9 (C), 145.1 (C), 180.1 (CH); IR (KBr) 1457, 1103 (S=O), 743 cm^{-1}. MS (EI) *m/z* 314 (M^+). HRMS (EI): Calcd for $C_{21}H_{14}OS$: *M* 314.0765. Found: *m/z* 314.0792. Anal. Calcd for $C_{21}H_{14}OS$: C, 80.22; H, 4.49. Found: C, 79.53; H, 4.40.

4.3.6. (9-Triptycyl)methanethial (*Z*)-*S*-oxide (*Z*-13). Colorless crystals, mp 245–246 °C (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (s, 1H), 7.03–7.08 (m, 6H), 7.37–7.42 (m, 3H), 7.42–7.47 (m, 3H), 9.01 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 54.1 (CH), 60.5 (C), 121.8 (CH), 124.2 (CH), 125.1 (CH), 126.0 (CH), 141.0 (C), 144.7 (C), 165.5 (CH); IR (KBr) 1457, 1120 (S=O), 753 cm^{-1}; MS (EI) *m/z* 314 (M^+). HRMS (EI): Calcd for $C_{21}H_{14}OS$: *M* 314.0765. Found: *m/z* 314.0774. Anal. Calcd for $C_{21}H_{14}OS$: C, 80.22; H, 4.49. Found: C, 80.04; H, 4.41%.

4.4. Reaction of dithiirane 1-oxides *cis*-1 and *trans*-1 with triphenylphosphine

Dithiirane 1-oxide *cis*-**1** (7.0 mg, 0.02 mmol) and triphenylphosphine (5.6 mg, 0.021 mmol) were dissolved in dichloromethane (4 mL) under argon, and the solution was stirred at 0 °C for 5 min. The solvent was removed under reduced pressure, and the residue was subjected to HPLC (dichloromethane/hexane 65:35) to give sulfine *Z*-**13** (4.5 mg, 72%).

In a similar manner, *trans*-**1** (11 mg, 0.032 mmol) was treated with triphenylphosphine (8.6 mg, 0.033 mmol) in dichloromethane (3 mL) to yield *E*-**13** (8.9 mg, 88%).

4.5. Reaction of dithiirane 1-oxides *trans*-1 with $(Ph_3P)_2Pt(C_2H_4)$

To a solution of *trans*-**1** (15.8 mg, 0.456 mmol) in toluene (5 mL) under argon at 0 °C was added a solution of $(Ph_3P)_2Pt(C_2H_4)$ (34.1 mg, 0.456 mmol) in toluene (4 mL). The mixture was stirred for 1 h at 0 °C, and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (dichloromethane/ether 3:1) to give (sulfenato-thiolato)Pt^{II} complex **14** (42.5 mg, 88%).

4.5.1. [(9-Triptycyl)methanedithiolato(2-)-κ*S*,κ*S*′]bis(triphenylphosphine)platinum *S*-oxide (14). Yellow crystals, mp 192–193 °C decomp. (hexane–$CHCl_3$). ^{1}H NMR (400 MHz) δ 5.23 (s, 1H), 6.75 (d, J=2.3 Hz, 1H), 6.81–6.89 (m, 3H), 6.92 (td, J=7.5, 1.3 Hz, 1H), 7.05 (td, J=7.4, 0.7 Hz, 1H), 7.13 (td, J=7.5, 1.2 Hz, 1H), 7.17–7.21 (m, 13H), 7.23–7.32 (m, 6H), 7.36 (dd, J=7.3, 0.7 Hz, 1H), 7.44–7.53 (m, 13H), 7.82 (d, J=7.5 Hz, 1H), 8.14 (d, J=7.5 Hz, 1H), 8.55 (d, J=7.6 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 54.9 (CH), 64.4 (C), 75.4 (CH), 122.7 (CH), 123.0 (CH), 123.2 (CH), 123.3 (CH), 124.2 (CH), 124.36 (CH), 124.44 (CH), 124.5 (CH), 124.6 (2CH), 125.5 (CH), 127.0 (CH), 127.9 (CH, L), 128.0 (CH, L), 128.1 (CH, L), 128.2 (CH, L), 129.4 (C, L), 129.7 (C, L), 129.8 (C, L), 130.3 (C, L), 130.4 (*p*-CH, L), 134.2 (CH, L), 134.3 (CH, L), 134.5 (CH, L), 134.6 (CH, L), 143.4 (C), 144.1 (C), 144.8 (C), 146.6 (C), 146.7 (C), 147.0 (C) [L in the parentheses means that the signal is due to the Ph_3P ligand. Their J (^{13}C–^{31}P) coupling constants are not determined, and signals due to the Ph_3P ligands are listed as appeared]; ^{31}P NMR (162 MHz) δ 16.2 [d, ^2J (^{31}P–^{31}P)=25 Hz, ^1J (^{31}P–^{195}Pt)=2418 Hz], 17.7 [d, ^2J (^{31}P–^{31}P)=25 Hz, ^1J (^{31}P–^{195}Pt)=3189 Hz]; IR (KBr) 1484, 1460, 1438, 1096 (S=O), 1000, 982, 746, 692 cm^{-1}. Calcd for: $C_{57}H_{44}OP_2PtS_2\cdot CHCl_3$: C, 58.76; H, 3.83. Found: C, 58.28; H, 3.74.

4.6. Reaction of dithiirane 1-oxide *trans*-1 with Lawesson's reagent (LR)

A solution of dithiirane 1-oxide *trans*-**1** (31.4 mg, 0.091 mmol) and LR (76.2 mg, 0.188 mmol, Sigma-Aldrich Co.) in dichloromethane (15 mL) under argon was stirred for 4 h at room temperature. The solvent was removed under reduced pressure. Polar decomposition products of LR were removed by passing the residue through a short column of silica gel (dichloromethane), and a mixture containing the products thus obtained was subjected to HPLC (dichloromethane/hexane 45:55) to give tetrathiaphosphorinane **16a** (the major isomer) (20.8 mg, 41%), a 37:63 mixture of tetrathiaphosphorinane **16b** (the minor isomer) (13%) and trithiaphospholane **15a** (the major isomer) (22%), and trithiaphospholane **15b** (the minor isomer) (3.1 mg, 6%) in this order. A mixture of **16b** and **15a** could be separated with HPLC (dichloromethane/hexane 40:60) to give pure **16a** and **15a** in this order.

4.6.1. 1,2,4,5,3-Tetrathiaphosphorinane (16a). White powder, mp 219–221 °C decomp. (CH_2Cl_2–hexane). ^{1}H NMR (400 MHz) δ 3.94 (s, 3H), 5.34 (s, 1H), 6.19 (br s, 1H), 6.97–7.10 (m, 4H), 7.10–7.21 (m, 4H), 7.21–7.45 (m, 3H), 7.47 (dd, J=7.0, 1.0 Hz, 1H), 8.03 (br s, 1H), 8.31 (br s, 1H), 8.44 (dd, J=13.1, 8.8 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 54.6 (CH), 55.7 (CH_3), 59.5 (br s, CH), 61.6 (br s, C), 114.4 [d, J (^{13}C–^{31}P)=15 Hz, CH), 122.0 (br s, CH), 123.7 (br s, 2CH), 124.0 (br s, 2CH), 124.6 (2CH), 125.3 (CH), 125.6 (br s, 3CH), 126.3 (CH) 134.5 [d, J (^{13}C–^{31}P)=12 Hz, CH], 139.9 (C), 144.3 (2C), 145.0 (C), 146.4 (C), 147.3 (C), 164.4 [d, J (^{13}C–^{31}P)=3 Hz, C] (the quaternary carbon bonded to the P atom was not observed probably because of overlapping with signals due to CH carbons); ^{31}P NMR (162 MHz) δ 91.2; MS (FAB) *m/z* 565 ($M^+ + 1$). Anal. Calcd for $C_{28}H_{21}OPS_5$: C; 59.55%, H; 3.75%. Found: C; 59.53%, H; 3.63%.

4.6.2. 1,2,4,5,3-Tetrathiaphosphorinane (16b). Off-white powder, mp 172–177 °C decomp. (MeOH–MeCN). ^{1}H NMR (400 MHz) δ 3.93 (s, 3H), 5.34 (s, 1H), 6.32 (br s, 1H), 6.98–7.15 (m, 8H), 7.34–7.37 (m, 2H), 7.46–7.65 (m, 2H), 7.96 (br s, 1H), 8.09 (br s, 1H), 8.29 (dd, J=13.6, 8.8 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 54.5 (CH), 55.7 (CH_3), 61.3 (br s, CH and C), 114.5 [CH, J (^{13}C–^{31}P)=15 Hz], 122.5 (br s, CH), 123.8 (br s, 3CH), 124.1 (CH), 124.8 (3CH), 125.2 (br s, CH), 125.6 (br s, 2CH), 126.2 (CH), 133.5 [d, J (^{13}C–^{31}P)=13 Hz, CH), 140.1 (br s, C), 144.2 (2C), 145.3 (C), 145.4–147.3 (2C), 164.1 (C) (the quaternary carbon bonded to the P atom was not observed

probably because of overlapping with signals due to CH carbons); ^{31}P NMR (162 MHz) δ 94.1; MS (EI) *m/z* (rel. intensity) 564 (M^+, 3), 298 (100), 265 (74), 253 (67), 252 (65). The intensity ratio of *m/z* 564 (M^+)/565 ($M^+ + 1$)/566 ($M^+ + 2$) was 100/34.1/28.8, which is consistent with the calculated value of 100/35.8/28.6 for $C_{28}H_{21}OPS_5$.

4.6.3. 1,3,4,2-Trithiaphospholane (15a). White powder, mp 199–200 °C decomp. (MeOH–MeCN). ^{1}H NMR (400 MHz) δ 3.90 (s, 3H), 5.36 (s, 1H), 6.75 [d, *J* (^{1}H-^{31}P)=2.7 Hz, 1H], 6.95–7.13 (m, 7H), 7.19 (td, *J*=7.5, 1.1 Hz, 1H), 7.33–7.40 (m, 2H), 7.46 (d, *J*=7.0 Hz, 1H), 7.52–7.56 (m, 1H), 8.02 (d, *J*=7.5 Hz, 1H), 8.35 (dd, *J*=14.2, 8.8 Hz, 2H), 8.83 (d, *J*=7.5 Hz, 1H); ^{13}C NMR (100.6 MHz) δ 54.5 (CH), 55.7 (CH_3), 57.5 [d, *J* (^{13}C–^{31}P)=5 Hz, C), 74.4 [d, *J* (^{13}C–^{31}P)=6 Hz, CH], 114.5 [d, *J* (^{13}C–^{31}P)=15 Hz, CH], 122.2 [d, *J* (^{13}C–^{31}P)=11 Hz, CH], 122.7 [d, *J* (^{13}C–^{31}P)=85 Hz, C], 123.4 (CH), 123.6 (CH), 123.7 (CH), 123.8 (CH), 124.76 (CH), 124.80 (CH), 125.0 (CH), 125.7 (CH), 125.8 (CH), 126.0 (CH), 126.9 (CH), 134.9 [d, *J* (^{13}C–^{31}P)=14 Hz, CH], 139.5 (C), 144.0 (C), 145.0 (C), 145.5 (C), 146.3 (C), 147.2 (C), 163.9 [d, *J* (^{13}C–^{31}P)=3 Hz, C); ^{31}P NMR (162 MHz) δ 101.8; MS (EI) *m/z* (rel. intensity) 532 (M^+, 5), 298 (100), 265 (72), 252 (63). The intensity ratio of *m/z* 532 (M^+)/533 ($M^+ + 1$)/534 ($M^+ + 2$) was 100/33.8/25.4, which is consistent with the calculated value of 100/35.0/23.9 for $C_{28}H_{21}OPS_4$.

4.6.4. 1,3,4,2-Trithiaphospholane (15b). Off-white powder, mp 198–200 °C (MeOH–MeCN). ^{1}H NMR (400 MHz) δ 3.93 (s, 3H), 5.34 (s, 1H), 6.84–6.90 (m, 2H δ 6.86 [d, *J* (^{1}H-^{31}P)=5.9 Hz]), 6.98–7.10 (m, 7H), 7.34–7.38 (m, 2H), 7.46 (d, *J*=7.5 Hz, 1H), 7.81 (d, *J*=7.5 Hz, 1H), 7.92 (d, *J*=7.5 Hz, 1H), 8.06 (d, *J*=8.0 Hz, 1H), 8.18 (dd, *J*=15.0, 8.6 Hz, 2H); ^{13}C NMR (100.6 MHz) δ 54.5 (CH), 55.6 (CH_3), 57.8 [d, *J* (^{13}C–^{31}P)=5 Hz, C], 73.9 [d, *J* (^{13}C–^{31}P)=6 Hz, CH), 114.4 [d, *J* (^{13}C–^{31}P)=16 Hz, CH], 123.2 (CH), 123.3 (CH), 123.6 (CH), 123.8 (CH), 124.0 (CH), 124.3 (CH), 124.9 (CH), 125.1 (CH), 125.4 (CH), 125.7 (CH), 125.8 (CH), 126.2 (CH), 129.0 [d, *J* (^{13}C–^{31}P)=83 Hz, C], 133.1 [d, *J* (^{13}C–^{31}P)=14 Hz, CH], 139.9 (C), 143.8 (C), 145.0 (C), 145.5 (C), 146.1 (C), 147.0 (C), 163.3 [d, *J* (^{13}C–^{31}P)=4 Hz, C); ^{31}P NMR (162 MHz) δ 108.0; MS (EI) *m/z* (rel. intensity) 532 (M^+, 4), 298 (100), 265 (73), 252 (62). The intensity ratio of *m/z* 532 (M^+)/533 ($M^+ + 1$)/534 ($M^+ + 2$) was 100/35.4/24.0, which is consistent with the calculated value of 100/35.0/23.9 for $C_{28}H_{21}OPS_4$.

4.7. Reaction of sulfine *Z*-13 with LR

A mixture of *Z*-**13** (29 mg, 0.091 mmol) and LR (74.7 mg, 0.185 mmol) in dichloromethane was stirred under argon at room temperature for 7 h. The solvent was removed under reduced pressure, and the residue was subjected to a short column of silica gel (dichloromethane) to remove derivatives of LR. A mixture of **15a** and **15b** thus obtained was separated with HPLC (CH_2Cl_2/hexane 45:50) to give **15a** (15 mg, 31%) and **15b** (8.0 mg, 17%).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.05.017

References and notes

1. Nakayama, J.; Ishii, A. *Adv. Heterocycl. Chem.* **2000**, *77*, 221–284.
2. Fabian, J.; Senning, A. *Sulfur Rep.* **1998**, *21*, 1–42.
3. Murray, R. W.; Singh, M. Comprehensive Heterocyclic Chemistry II; Katritzky, A. R., Rees, C. W., Scrivan, E. E. V., Eds.; Pergamon: UK, 1996, Vol. 1A, pp 429–456.
4. Senning, A.; Hansen, H. C.; Abdel-Megeed, M. F.; Mazurkiewicz, W.; Jensen, B. *Tetrahedron* **1986**, *42*, 739–746.
5. Senning, A. *Sulfur Lett.* **1986**, *4*, 213–216.
6. Senning, A. *Sulfur Lett.* **1990**, *11*, 83–86.
7. Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 333–357.
8. Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4914–4915.
9. Ishii, A.; Akazawa, T.; Maruta, T.; Nakayama, J.; Hoshino, M.; Shiro, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 777–779.
10. Ishii, A.; Maruta, T.; Teramoto, K.; Nakayama, J. *Sulfur Lett.* **1995**, *18*, 237–242.
11. Ishii, A.; Jin, Y.-N.; Nagaya, H.; Hoshino, M.; Nakayama, J. *Tetrahedron Lett.* **1995**, *36*, 1867–1870.
12. Ishii, A.; Akazawa, T.; Ding, M.-X.; Honjo, T.; Maruta, T.; Nakamura, S.; Nagaya, H.; Ogura, M.; Teramoto, K.; Shiro, M.; Hoshino, M.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 509–529.
13. Ishii, A. *J. Synth. Org. Chem., Jpn.* **1997**, *55*, 897–906.
14. Ishii, A.; Umezawa, K.; Nakayama, J. *Tetrahedron Lett.* **1997**, *38*, 1431–1434.
15. Ishii, A.; Nakabayashi, M.; Nakayama, J. *J. Am. Chem. Soc.* **1999**, *121*, 7959–7960.
16. Ishii, A.; Nakabayashi, M.; Jin, Y.-N.; Nakayama, J. *J. Organomet. Chem.* **2000**, *611*, 127–135.
17. Ishii, A.; Kawai, T.; Tekura, K.; Oshida, H.; Nakayama, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1924–1926.
18. Ishii, A.; Yamashita, R.; Saito, M.; Nakayama, J. *J. Org. Chem.* **2003**, *68*, 1555–1558.
19. Shimada, K.; Kodaki, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C. *Chem. Lett.* **1999**, 695–696.
20. Mloston, G.; Romanski, J.; Reisenauer, H. P.; Maier, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 393–396.
21. Nakamura, N. *J. Am. Chem. Soc.* **1983**, *105*, 7172–7173.
22. Barton, D. H. R.; Guziec, F. S., Jr.; Shahak, I. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1794–1799 and references cited therein.
23. Okazaki, R.; Ishii, A.; Inamoto, N. Unpublished results: Reaction of TripLi with HC(=S)OEt and that of TripCH=NNH_2 with S_2Cl_2 failed to give TripCHS.
24. The *trans* stereochemistry of **11** was unambiguously determined by X-ray crystallography, though the positions of the sulfur atom and the –N=N– moiety in the thiadiazoline ring could not be determined because of disorder.
25. Opitz, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 107–123.
26. v. Vargha, L.; Kovács, E. *Ber.* **1942**, *75*, 794–802.
27. Tokura, N.; Nagai, T.; Matsumura, S. *J. Org. Chem.* **1966**, *31*, 349–350.

28. Sollman, P. B.; Nagarajan, R.; Dodson, R. M. *Chem. Commun.* **1967**, 552–554.
29. Wróbel, J. T.; Ruszkowska, J.; Bielawska, H. *Polish J. Chem.* **1979**, *53*, 39–48.
30. Oki, M. *Top. Stereochem.* **1983**, *14*, 1–81.
31. Kalinowski, H.-O.; Berger, S.; Braun, S. Carbon-13 NMR Spectroscopy; Wiley: Chichester, 1984; pp 495–501.
32. Ishii, A.; Nakamura, S.; Yamada, T.; Nakayama, J. *Tetrahedron* **1997**, *53*, 12203–12214.
33. Ishii, A.; Saito, M.; Murata, M.; Nakayama, J. *Eur. J. Org. Chem.* **2002**, 979–982.
34. Oshida, H.; Ishii, A.; Nakayama, J. *Tetrahedron Lett.* **2004**, *45*, 1331–1334.
35. Dence, J. B.; Roberts, J. D. *J. Org. Chem.* **1968**, *33*, 1251–1253.
36. Kornfeld, E. C.; Barney, P.; Blankley, J.; Faul, W. *J. Med. Chem.* **1965**, *8*, 342–347.
37. Nakagawa, K.; Onoue, H.; Minami, K. *Chem. Commun.* **1966**, 730–731.
38. Konaka, R. *J. Synth. Org. Jpn.* **1972**, *30*, 479–484.
39. Brunovlenskaya, I. I.; Gudasheva, T. A.; Skvarchenko, V. R. *Zh. Org. Khim.* **1974**, *10*, 1495–1497.
40. Steudel, R.; Latte, J. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 603–604.
41. North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr. Sect. A* **1968**, *A24*, 351–359.
42. Sheldrick, G. M. SHELXL-97: *Program for Crystal Structure Refinement*; Göttingen University, Germany, 1997.
43. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.