Synthetic Communications®, 43: 2305–2313, 2013

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2012.702290

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RING MODIFICATIONS IN CAMPHORIMINES PURELY ORGANIC OR PROMOTED BY Pt(II)

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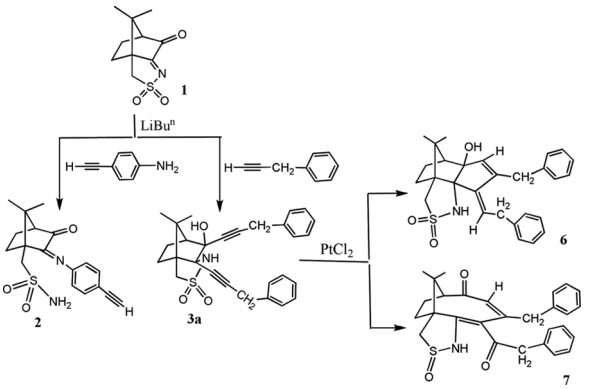
GRAPHICAL ABSTRACT



Abstract *The reactivity of 3-oxo-camphorsulfonylimine (**1**) was explored toward the formation of new organic species in processes strictly organic or catalyzed by platinum. Synthesis and characterization of (1*S*)-1-[7,7-dimethyl-2-(4-ethinylphenylimino)-3-oxo-bicyclo [2.2.1]heptanyl]-methanesulfonamide (**2**), (3a*S*,7*R*)-7-hydroxy-8,8-dimethyl-7-(*N*-methylamino-1-propynyl)-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (**4a**), (3a*S*,6a*R*,9a*R*)-8-benzyl-10,10-dimethyl-6a-hydroxy-9-(E-2-phenylethylidene)-3,3-a,4,5,6,7-hexahydro-1*H*,9*H*-3a,6-methano-indeno[3a,4c]isothiazole 2,2-dioxide (**6**), and (2*S*, 3a*S*,6*S*)-9-benzyl-5,6-dihydro-11,11-dimethyl-10-phenylacetyl-3*H*-3a,6-methano-1*H*-yclonon [c]isothiazol-7(4*H*)-one 2-oxide (**7**) are reported as well as the activation of (1a*S*,3a*S*,7*R*)-7-hydroxy-1a,7-bis(3-phenyl-1-propynyl)-8,8-dimethyl-1,1a,4,5,6,7-hexahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (**3a**) toward ring annulation or ring expansion by reaction with Pt(II) depending on the reaction conditions.*

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Keywords Cascade processes; catalysis; platinum; ring annulations; ring expansion

Received April 9, 2012.

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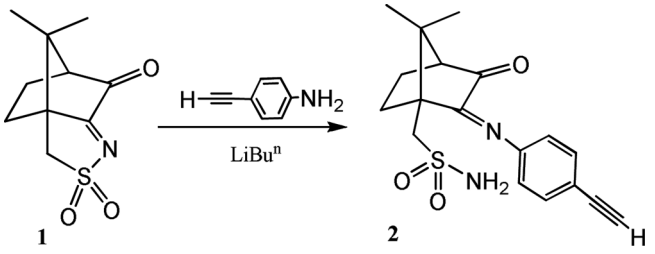


Scheme 1. Ring opening promoted by reaction of 4-aminophenylethyne with **1**.

INTRODUCTION

The stoichiometric addition of halogens or Brønsted acids (e.g., HCl) to dialkynes of type **3** (Scheme 1) starts a cascade reaction leading to annulation of a five-membered ring that forms from three of the triple-bond carbon atoms via cationic intermediates, combined with the reduction of sulfur(VI) to sulfur(IV) (oxygen transfer from sulfur to carbon).[1] This reactivity is possible because the two alkyne groups are kept in close vicinity by the rigid camphor skeleton.

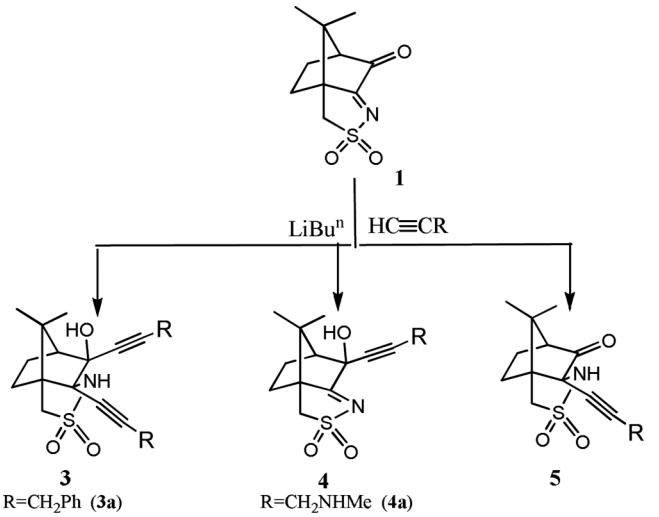
The catalytic isomerization with Pt(II) does not normally stop at the stage of ring annulation but continues the cascade with bond cleavage between the carbon atoms (C2, C3), which initially carried the alkynes, resulting in ring expansion to a tricyclic ring system with nine members.[2–5] We now report the isolation of the first product (**6**) of annulation of a five-membered ring to the camphor skeleton promoted by reaction of $PtCl_2$ with **3a** (R = benzyl).When $[PtCl_2(EtCN)_2]$ (a form of Pt(II) that is readily soluble in organic solvents) is used as catalystinstead of $PtCl_2$ for activation of **3a**, the product of ring expansion (**7**) is obtained, which resembles taxol with respect to the larger ring, the dimethylmethano bridge, and the points of attachment of the heterocyclic ring.

In contrast to ring annulation or ring expansion, the rupture of the sulfonylimine ring in **1** leads to **2** in a purely organic process.

RESULTS AND DISCUSSION

The rupture of the sulfonylimine ring in 3-oxo-camphorsulphonylimine (**1**) promoted by reaction with the lithium salt of 4-aminophenylethyne ($R=C_6H_4NH_2$) forming (1*S*)-1-[7,7-dimethyl-2-(4-ethinylphenylimino)-3-oxo-bicyclo[2.2.1]heptanyl]-methanesulfonamide (**2**) (Scheme 1) contrasts with the addition to the carbonyl group of the deprotonated N-methylpropargylamine ($R=CH_2NHMe$), forming (3a*S*,7*R*)-7-hydroxy-8,8-dimethyl-7-(*N*-methylamino-1-propynyl)-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-dioxide (CH_2NHMe, **4a**, Scheme 2). Ring rupture was unexpected because previous reactions involving 3-oxo-camphorsulfonylimine and lithiated alkynes underwent addition by nucleophilic attack to the carbonyl group (**4**), to the imine group (**5**), or to both groups (**3**) (Scheme 2), keeping intact the tricyclic structure of the camphorsulfonylimine.[6,7]

Ring rupture leading to **2** indicates that the NH_2 group instead of the terminal alkyne carbon atom is involved in attack to the imine group. The process is followed



Scheme 2. Reactivity trends in reaction of camphorsulfonylimine with lithiated alkynes.

by cleavage of the sulfonamide bond, leaving to a purely carbocyclic compound. It is not the presence of the NH groups as such that triggers this reactivity because *N*-methyl-propargylamine (*N*-methyl-prop-2-yn-1-amine, R=CH_2NHMe) reacts, as expected, with its terminal carbon atom.[2] To clarify the situation we studied by density functional theory (DFT) the influence of aliphatic vs. aromatic amino groups on the stability of the carbanions (both with and without Li^+ counterions) obtained by deprotonation of the respective alkynes at either the terminal carbon atom or the amino group (for details, see Supplemental Material). According to these calculations, carbanions (without counterions) are greatly stabilized by solvent effects (calculated for tetrahydrofuran, THF, as used in the experimental procedures). The effect is lower for the ion pairs with Li^+, but still exceeds that of the neutral amines. Thus we found that for 4-aminophenylethyne deprotonation at nitrogen is slightly preferred over deprotonation at the terminal carbon atom (e.g., 0.3 kcal/mol in THF solution with the Li^+ counterion), while for *N*-methylpropargylamine there is a considerable preference for deprotonation at the carbon atom (12.4 kcal/mol under the same conditions). Calculation and experiment are thus in good agreement with respect to formation of **2**.

In **2** (LH), there are several groups that can bind to transition metals. However, in CH_2Cl_2 no reaction occurs with Pt or Pd chlorides in the absence of base. Et_3N is essential to deprotonate the amine group and promote coordinationto $PdCl_2$, affording $[PdCl(L)Et_3N] \cdot Et_2O$ (**8**) (reaction 1).

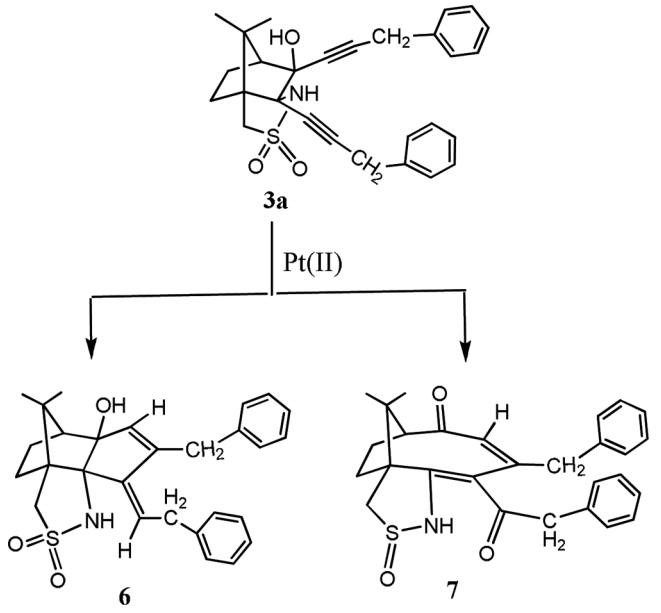
$$PdCl_2 + LH + 2Et_3N \rightarrow [PdCl(L)Et_3N] + Et_3NHCl \quad (1)$$

The structural characterization of **8** by x-rays was not possible (no suitable crystals were obtained) and its low solubility precluded NMR data. Nevertheless the infrared (IR) spectrum displays bands in the region of the uncoordinated CC

triple bonds (2203 cm^{-1}), SO_2 (1339, 1152 cm^{-1}), and a band in the NH region (3243 cm^{-1}), pointing tocoordination by the nitrogen atom of the amine group. Concomitant coordination by the imine group is supported by the considerable shift to greater values of the C=N stretch (1674 cm^{-1}) compared to that in **2** (1599 cm^{-1}).

In contrast to the formation of complex **8** by reaction of $PdCl_2$ with **2**, a cascade process is promoted in reaction of $PtCl_2$ with **3a** affording the organic compound **6** [(3a*S*,6a*R*,9a*R*)-8-benzyl-10,10-dimethyl-6a-hydroxy-9-(*E*-2-phenylethylidene)-3,3a,4,5,6,7-hexahydro-1*H*,9*H*-3a,6-methano-indeno[3a,4c]isothiazole 2,2-dioxide] (Scheme 3). Ring annulation in **6** contrasts with ring expansion promoted by $[PtCl_2(EtCN)_2]$ in **3a**, affording compound **7** [(2*S*,3a*S*,6*S*)-9-benzyl-5,6-dihydro-11,11-dimethyl-10-phenylacetyl-3*H*-3a,6-methano-1*H*-cyclonon[c]isothiazol-7(4*H*)-one 2-oxide] (Scheme 3). Discrimination in formation of **6** or **7** is attributedto the solubility of the Pt(II) species; that is, $[PtCl_2(EtCN)_2]$ is readily soluble in organic solvents whereas $PtCl_2$ is only sparingly soluble, which rends the reaction very slow and no ring expansion occurs.

Compound **6** is an unprecedented reduction product, formed in the ring annulation cascade promoted by Pt(II), which has basically the same structure as the addition products of dialkynes **3** with halogens[2] but with hydrogen atoms instead of the additional halogen atoms. The reduction is promoted by Pt(II), which is in turn oxidized to paramagnetic Pt(III) ill-defined complexes that could not be fully characterized. The hydrogen source may either be a trace of water or protons that result from oxidation reactions of **3a**. Because the yield of compound **6** is only 25% and no further products could be identified from the reaction mixture, we cannot decide this question. The action of $PtCl_2$ may even be stoichiometric rather than catalytic.



Scheme 3. Ring annulation and ring expansion promoted by reaction of **3a** with Pt(II).

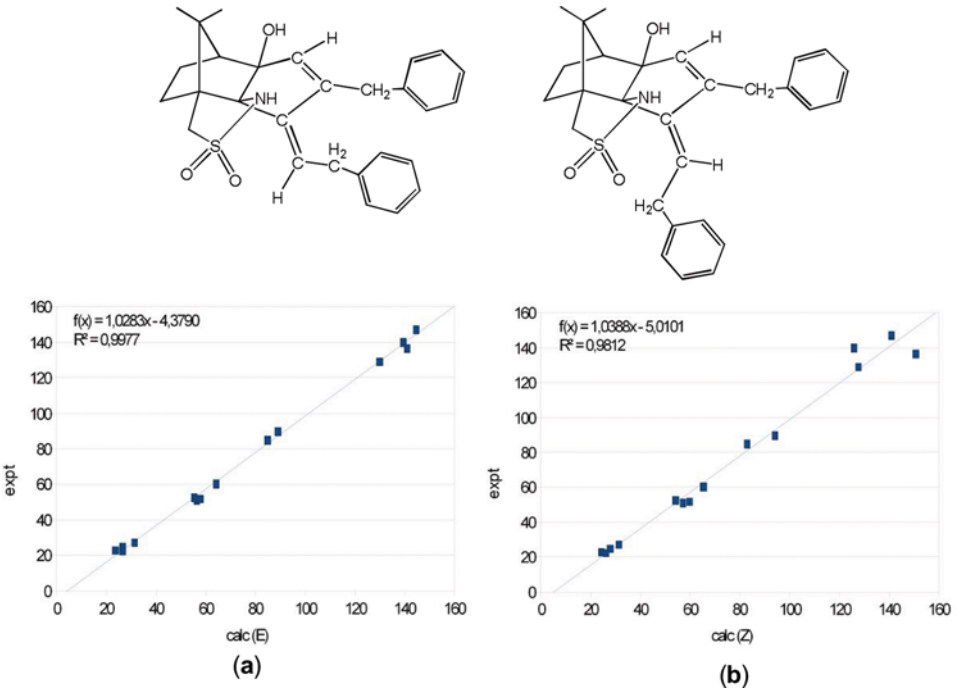


Figure 1. Correlation of experimental and calculated ^{13}C NMR data for *E* (a) and *Z* (b) isomer of compound **6**. (Figure is provided in color online.)

The basic structure of product **6** can readily be determined by NMR methods (see Supplemental Material). However, the decision between *E* or *Z* configuration at the exocyclic C=C double bond remains difficult on the basis of the NMR data because only one isomer was isolated and no camparison can be made. We therefore decided to calculate NMR data of both *E* and *Z* isomers and make the decision according to the best fit to the experimental data (for details, see Supplemental Material). As observed in similar cases[2] ^{13}C NMR data proved to be more reliable than ^{1}H. Figure 1 shows the comparison of experimental and calculated ^{13}C NMR chemical shifts. One can clearly see that the overall fit of the chemical shifts fits better to the *E* isomer. A detailed comparison of the chemical shifts of the double-bond carbon atoms confirms the attribution of the *E* configuration to compound **6** (see Supplemental Material for chemical shift data).

CONCLUSIONS

Two new types of compounds were obtained from 3-oxo-camphorsulphonylimine (**1**) in a purely organic process (**2**) or by catalysis with Pt(II) (**6**).

Compound **2** evidences the relevance of the substituent R-group of the aromatic moiety of the alkyne ($HC{\equiv}CC_6H_4NH_2$) in directing the deprotonation of the amine rather the alkyne group of 4-aminophenylethyne. Nucleophilic attack by the

deprotonate amine group is responsible for the rupture of the sulfonylimine ringin **1**, which contrasts with reactivitypromoted by nucleophilic attack by the deprotonated alkyne.

Compound **6** provides the experimental evidence for the annulation of a five-membered ring to the camphor skeleton during the process of ring expansion-from six to nine members catalyzed by Pt(II). This type of compound was proposed to form[2] in the ring enlargement process but had never been isolatedin Pt(II)-catalyzed processes. The isolation of compound **6** further reinforces the relevance of the experimental conditions in the cascade process that leads from the camphor dialkyne (**3a**) to compound **7**.

No modifications are observed in **2** by reaction with Pt(II) whereas [PdCl(L)Et_3N] forms by reaction with Pd(II).

EXPERIMENTAL

3-Oxo-camphorsulfonylimine (**1**),[8] the camphor dialkyne **3a**[7,6], and *trans*-[$PtCl_2(EtCN)_2$][9,10] were obtained by published methods. $PtCl_2$ was purchased from Sigma-Aldrich and the solvents from Panreac. All reactions were made under nitrogen atmosphere using the Schlenk technique. Infrared (IR) spectra were obtained in KBr pellets with a Jasco Fourier transform (FT)/IR 4100 spectrometer. NMR spectra [^{1}H, ^{13}C, distortionless enhancement by polarization transfer (DEPT), heteronuclear single quantum correlation (HSQC), heteronuclear multiple bond correlation (HMBC)] were obtained in $CDCl_3$ or dimethylsulfoxide (DMSO-d_6) using Bruker Avance II$^+$ Spectrometers (300 or 400 MHz). Tetramethylsilane (TMS) ($\delta = 0$ ppm) was used as internal reference.

(1*S*)-1-[7,7-Dimethyl-2-(4-ethinylphenylimino)-3-oxo-bicyclo[2.2.1] heptan-1-yl]-methane Sulfonamide (2)

Butyllithium (3.45 cm^3,1.6 M in n-hexane) was slowly added under nitrogen to a mixture of 3-oxo-camphorsulfonylimine (**1**, 0.50 g, 2.2 mmol) and 4-aminophenylethyne (**A**, 0.64 g, 5.5 mmol) in Et_2O (30 cm^3). The mixture was stirred at rt until complete consumption of **1**. The solid was filtered off and dissolved in H_2O (30 cm^3), and the solution extracted with CH_2Cl_2 (3×50 cm^3) and dried over $CaCl_2$ for a couple of hours. After filtration to separate the drying agent, the solution was evaporated to dryness, affording an orange compound (**2**, 0.45 g, 1.1 mmol, yield 50%). Elemental analysis (%) for $C_{18}H_{20}N_2O_3S \cdot Et_2O$: Found: C, 63.6; N, 6.9; H, 7.1; S, 7.6. Calculated: C, 63.2; N, 6.7; H, 7.2; S, 7.7. IR (cm^{-1}): 3365 (ν_{NH2}), 2109 ($\nu_{C\equiv C}$), 1752 (ν_{CO}), 1599, (ν_{CN}), 1339 ($\nu_{SO2asym}$), 1156 (ν_{SO2sym}). ^{1}H NMR ($CDCl_3$, δ ppm): 7.41 (d, $J_{HH} = 8.2$, 2H), 6.74 (d, $J_{HH} = 8.2$, 2H), 5.5 (s, 2H), 3.76, 3.38 (d, $J_{HH} = 15.1$, 2H), 3.04 (s, 1H), 2.55–1.50 (m, 4H), 2.48 (d, $J_{HH} = 5.0$, 1H), 1.09 (s, 3H), 1.08 (s, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 196.5 (C-2), 168.5 (C-3), 148.1, 132.7, 118.7 (C-Ph), 83.4, 79.0 (value obtained in DMSO-d_6) (C≡C), 58.6 (C-4), 55.9 (C-1), 54.7 (C-8), 46.1 (C-7), 29.1 (C-6), 22.2 (C-5); 20.7, 17.8 (C-9,10). For numbering of the carbon atoms, see Fig. 2.

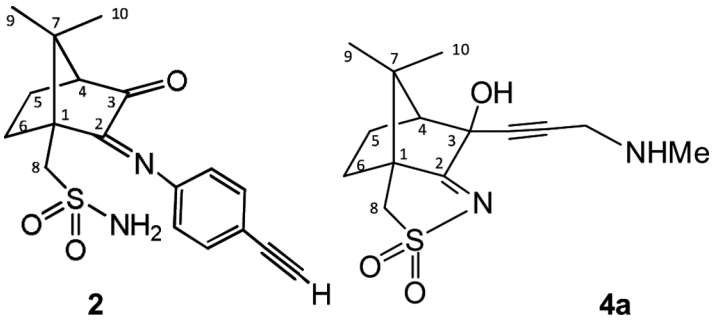


Figure 2. Numbering of carbon atoms for compounds **2** and **4a**.

(3a*S*,7*R*)-7-Hydroxy-8,8-dimethyl-7-(*N*-methylamino-1-propynyl)-4,5,6,7-tetrahydro-3*H*-3a,6-methano-2,1-benzisothiazole 2,2-Dioxide (4a)

Butyllithium (3.1 cm^3, 1.6 M in n-hexane) was added dropwise to a solution of *N*-methylprop-2-yn-1-amine (**B**, 0.38 cm^3, 4.5 mmol) in 10 ml of diethyl ether. The mixture was stirred for 1 day at rt. Then 3-oxo-camphorsulfonylimine (**1**, 0.50 g, 2.2 mmol) was added and after one more day the reaction was quenched with H_2O (2 cm^3). The aqueous layer was extracted with CH_2Cl_2 (3×40 cm^3), dried over $MgSO_4$, filtered to separate the drying agent, and taken to dryness, affording an orange powder (0.20 g, 0.68 mmol, yield, 15%). Elemental analysis (%) for $C_{14}H_{20}N_2O_3S \cdot CH_2Cl_2$: Found: C, 47.5; H, 5.9; N, 7.4; S, 8.4. Calculated: C, 47.1; H, 5.8; N, 7.3; S, 8.4. IR (cm^{-1}): 3399 (ν_{OH}), 2252 ($\nu_{C\equiv C}$), 1653 (ν_{CN}), 1337 ($\nu_{SO2asym}$), 1161 (ν_{SO2sym}). ^{1}H NMR ($CDCl_3$, δ ppm): 5.02 (br, 2H), 3.61–3.44 (m, 2H), 3.20, 3.08 (2d, $J_{HH} = 13.5$, 2H), 2.47 (d, $J_{HH} = 2.4$, 3H), 2.24–1.74 (m, 4H), 2.28 (d, $J_{HH} = 2.7$, 1H), 1.08 (s, 3H), 1.06 (s, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 195.1 (C-2), 85.6, 72.4 (C≡C), 64.2 (C-1), 56.0 (C-4), 50.0 (C-8), 47.4 (C-7), 39.1 (*C*H_2N-), 34.8 (-NH*C*H_3), 29.6 (C-3), 28.0 (C-6), 23.6 (C-5); 21.2, 21.0 (C-9,10). For numbering of the carbon atoms, see Fig. 2.

(3a*S*,6a*R*,9a*R*)-8-Benzyl-10,10-dimethyl-6a-hydroxy-9-(*E*-2-phenylethylidene)-3,3a,4,5,6,7-hexahydro-1*H*,9*H*-3a,6-methano-indeno[3a,4c]isothiazole 2,2-Dioxide (6)

Compound **3a** (0.38 g, 0.84 mmol) and **3a** (0.38 g, 0.84 mmol) and **3a** (0.38 g, 0.84 mmol) and $PtCl_2$(0.10 g, 0.38 mmol) were stirred in CH_2Cl_2 (55 cm^3) at rt for 7 days. The solvent was then evaporated, and the brownish oil was extracted with Et_2O (2×5 cm^3). Compound **6** precipitated upon partial evaporation of Et_2O as a pale yellow compound (0.10 g, 0.021 mmol), yield 25%. Elemental analysis (%) for ($C_{28}H_{31}NO_3S$) $1/8CH_2Cl_2$: Found: C, 71.3; N, 3.2; H, 7.1; S, 5.7. Calculated: C, 71.6; N, 3.0; H, 6.6; S, 6.8. IR (cm^{-1}): 3339 (ν_{OH}), 1660; 1601 (ν_{CC}), 1323 ($\nu_{SO2asym}$), 1097; 1061 (ν_{SO2sym}). ^{1}H NMR ($CDCl_3$, δ ppm): 7.3–7.1 (m, 8H), 7.04 (s, 1H), 7.02 (s, 1H), 6.97 (s, 1H), 5.54 (s, 1H), 3.5–3.4 (m, 4H), 3.31, 2.98 (2d, $J_{HH} = 13.2$, 2H),2.50 (s, 1H),2.00 (d, $J_{HH} = 4.2$, 1H), 1.75, 1.5 (m, 2H), 1.70, 1.38 (m, 2H), 1.36 (s, 3H), 0.91 (s, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 147.2 (C-11), 139.9 (C-13), 137.8 (C-23), 137.7 (C-17), 136.5 (C-14), 129.0 (C-12), 128.0–128.7 (C-18 to C-22), 126.6 (C-20), 126.5 (C-26), 89.7 (C-3), 84.8 (C-2) 60.2 (C-1), 52.5 (C-4), 51.8 (C-8), 51.1 (C-7), 38.5

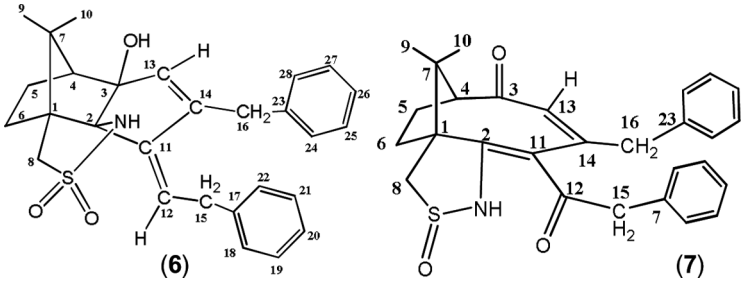


Figure 3. NMR labeling for compound **7**.

(C-16), 35.9 (C-15), 27.1 (C-6), 24.7 (C-5), 22.7 (C-9), 22.2 (C-10). For numbering of the carbon atoms, see Fig. 3.

(2*S*,3a*S*,6*S*)-9-Benzyl-5,6-dihydro-11,11-dimethyl-10-phenylacetyl-3*H*-3a,6-methano-1*H*-cyclonon[c]isothiazol-7(4*H*)-one 2-Oxide (7)

A solution of **3a** (0.19 g, 0.42 mmol) and $[PtCl_2(EtCN)_2]$ (0.070 g, 0.19 mmol) in toluene (15 cm^3) were stirred overnight. The solvent was then completely evaporated, and the dark red oily solid was extracted with Et_2O (15 cm^3). The solution was concentrated (ca. 5 cm^3), and n-pentane was added (15 cm^3). Compound **7** precipitated as a white solid (0.035 g; 0.073 mmol), yield 17%. Elemental analysis (%) for $(C_{28}H_{29}NO_3S) \cdot 5/4H_2O$: found: C, 68.9; N, 2.9; H, 6.4; S, 6.8. Calculated: C, 68.9; N, 2.9; H, 6.5; S, 6.6 (*m*/*z*, 460). IR (cm^{-1}): 1688 (ν_{CO}), 1624 ($\nu_{C=C}$), 1495 (ν_{ring}), 1057 (ν_{SO}). ^1H NMR (C_6D_6, δ ppm): 12.17 (s, 1H), 7.6–6.8 (m, 10 H), 5.77 (s, 1H), 4.02, 3.64 (d, 13.8, 2H), 3.28, 3.02 (d, 15.5, 2H), 2.53, 1.85 (d, 14.1, 2H), 2.19 (d, 6.5, 1H), 1.9-0.9 (m, 4H), 1.28 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (C_6D_6, δ ppm): 207.4 (C-3), 200.8 (C-12), 162.9 (C-2), 137.5 (C-14), 132.5 (C-13), 137.9, 135.9 (C7 and C23), 130.1–127.2 (*C*H, Ph), 108.1 (C-11), 66.8 (C-4), 61.3 (C-1), 59.2 (C-8), 47.7 (C-7), 47.1, 47.0 (C-15 and C-16), 34.2, 24.8 (C-5 and C-6), 28.5, 21.6 (C-9 and C-10). The numbering of the carbon atoms is shown in Fig. 3.

[PdCl(L)Et_3N] (8)

$PdCl_2$ (0.079 g; 0.44 mmol) *plus* compound **2** (0.32 g; 0.92 mmol) and Et_3N (0.26 cm^3, 1.8 mmol) were mixed in CH_2Cl_2 (40 cm^3) stirred for 9 days at rt. The dark precipitate formed was filtered off, washed with Et_2O, and dried under vacuum (0.20 g; 0.31 mmol, yield 70%). Elemental analysis (%) for $[PdCl(C_{18}H_{18}NO_3S)Et_3N] \cdot Et_2O$: Found: C, 51.3; N, 6.4; H, 5.5; S, 5.0. Calculated: C, 51.0; N, 6.4; H, 5.9; S, 4.9. IR (cm^{-1}): 3243 (ν_{NH}), 2203 (ν_{CC}), 1748 (ν_{CO}), 1674, (ν_{CN}), 1596 (ν_{CCring}), 1339 ($\nu_{SO2asym}$), 1152 (ν_{SO2sym}). NMR: not sufficiently soluble.

ACKNOWLEDGMENTS

FCT-Fundação para a Ciência e Tecnologia (PEst-OE/QUI/UI0100/2011) and the NMR Network are greatfully acknowledged for financial support and facilities access, respectively.

REFERENCES

1. Wagner, G.; Herrmann, R.; Schier, A. *J. Chem. Soc., Perkin Trans 1* **1997**, 701.
2. Lampropoulou, M.; Herrmann, R.; Wagner, G. *Tetrahedron* **2004**, *60*, 4635.
3. Carvalho, M. F. N. N.; Herrmann, R.; Pedersen, B.; Pombeiro, A. J. L.; Wagner, G. *Z. Naturforschung* **1999**, *54b*, 725.
4. Wagner, G.; Heiß, C.; Verführt, U.; Herrmann, R. *Z. Naturforsch.* **1996**, *51b*, 1655.
5. Wagner, G.; Pedersen, B.; Herrmann, R. *Electronic Conference on Trends in Organometallic Chemistry (ECTOC-3)*; H. Rzepa, C. Leach (Eds.); Royal Society of Chemistry, 1997. See also http://www.ch.ic.ac.uk/ectoc/ectoc-3/pub/042/.
6. Santos, A. M.; Carvalho, M. F. N. N.; Galvão, A. M.; Pombeiro, A. J. L. *Z. Naturforsch.* **2002**, *57b*, 691.
7. Carvalho, M. F. N. N.; Fernandes, T. A.; Ferreira, A. S. D.; Alves, L. G.; Herrmann, R. *J. Organometal. Chem.* **2008**, *693*, 2847.
8. Glahsl, G.; Herrmann, R. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1753.
9. Kukushkin, V. Y.; Oskarsson, Å.; Elding, L. I. *Inorg. Synth.* **1997**, *31*, 280.
10. Svensson, P.; Lovqvist, K.; Kukushkin, V. Y.; Oskarsson, Å. *Acta Chem. Scand.* **1995**, *49*, 72.