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COMMUNICATION

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Practical and theoretical aspects of Wacker oxidation of tolanophanes: Synthesis and characterization of novel diketonic cyclophanes

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Novel cyclophanes having 1,2-diketones **2a–c** were synthesized by Wacker oxidation of the corresponding tolanophanes **1a–c** having various alkyl chain lengths ($n = 2$–4). Among them, tolanophane **1a** with the shortest alkyl chain length ($n = 2$) having more strained alkyne shows the lowest product selectivity even lower than that of acyclic analogues at various reaction temperatures. In contrast, the oxidation of tolanophane **1b** ($n = 3$) is clean with the highest activity and selectivity of **2b**. Theoretical calculations confirm the experimental data. Based on *ab initio* calculations, the critical step of the reaction pathway is the interaction of oxygen atoms of **1** (in the absence of H_2O) with Pd ion of intermediate $[PdCl_3(\mathbf{1})]^-$ to give $[PdCl_2(\mathbf{1})]$ which keeps Pd ion close to the alkyne bond. This step is not observed computationally for **1a** because the positions of the oxygen atoms are outside of its central part. This is in good agreement with almost no activity of **1a** at room temperature to prove its rigid structure preventing the O…Pd interaction. Nevertheless, the alkyne…Pd interaction of **1b** is not detected by NMR measurements which may be due to its too slow interaction at room temperature (35% after 24 h); however, this confirms *ab initio* calculation data that the preferred coordinating site is oxygen in the reaction pathway. In contrast, cyclic voltammetry measurements distinguish a different behaviour for the palladium complexation of **1**. In general, it is found that the stereochemistry of tolanophanes rather than distortion of alkyne bond plays the critical role in the oxidation. The products are new and their structures were characterized.

KEYWORDS
complexation, tolanophanes, Wacker oxidation

1 | INTRODUCTION

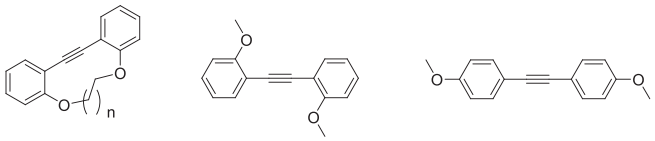
1,2-Diketones are fascinating building blocks in numerous biologically interesting products.[1–5] They are broadly utilized for the construction of elaborated compounds[1,6–10] and as photoinitiators for the free radical curing of polymer networks.[11,12]

Diphenylacetylenes (or tolans) are usually applied for larger systems which display interesting structural, electronic, nonlinear optical and luminescent properties.[13,14] Oxidation of substituted tolans by Wacker reaction is one of the most useful methods for the synthesis of 1,2-diketones.[15,16] Although several methods have been reported for the oxidation of alkynes, these reactions still suffer from drawbacks such as

harsh conditions, narrow substrate scope and low yield and/or chemoselectivity.[17–35]

Concerning Wacker oxidation, we recently designed some stilbenes (diphenylethylenes) to provide a better understanding of the structure–function relationships of various substituent groups within the molecule. It was found that *ortho* arrangement of methoxy and alkene substitutions on linear stilbenes plays a critical role in the complexation with $PdCl_2$.[36] Furthermore, a careful study of Wacker oxidation of stilbenophanes revealed the critical role of host–guest chemistry in the oxidation rate of substrates.[37]

In the work reported here, the Wacker oxidation of cyclic and acyclic tolans **1** was investigated in detail. The objective was to understand which factor, stereochemistry or distortion of alkyne bonds of **1**, plays a major role in their Wacker oxidation. Therefore, we investigated the practical and theoretical aspects of the reaction in detail. It is clear that development of Wacker oxidation of tolans **1** would not only expand the scope of the Wacker reaction but also pose an interesting mechanistic question.



2 | EXPERIMENTAL

2.1 | Materials and methods

^{1}H NMR and ^{13}C NMR spectra of **2b** and **2c** were recorded in $CDCl_3$ with a Bruker-500. Mass spectra were obtained with a Fisons instrument. Tolanophanes **1a–c** were synthesized from the corresponding stilbenophanes.[38–40] UV–visible spectra were recorded with an Agilent 8453. The cyclic voltammetry system was a Metrohm Autolab BV trace analyser. The auxiliary electrode was a Pt wire. The reference electrode was Ag/AgCl. The measurements were performed in dimethylformamide containing 0.3 M $(butyl)_4N(BF_4)$ under nitrogen atmosphere. Conductivity was measured using a Philips PW 9526 digital conductivity meter. A Fisons gas chromatograph 8000 equipped with a mass detector (Trio 1000) at 70 eV was used. A 60 m × 0.25 mm column packed with WCOT fused silica CP-sil 5 CB was employed. Carrier gas was helium and inlet pressure was 14 psi.

2.2 | General procedure for Wacker reaction of Tolanophanes 1

A 5 ml, two-necked, round-bottomed flask was fitted with a magnetic stirrer. The flask was charged with a mixture of tolan **1** (0.1 mmol), palladium chloride (2 mol%) and copper chloride (10 mol%) and dioxane–H_2O (4:1) as solvent. The reaction was heated at 100 °C for 24 h under oxygen atmosphere. After completion of the reaction (monitored by TLC), CH_2Cl_2 was added to the reaction mixture and the catalyst was recovered by filtration. The organic medium was removed with a rotary evaporator under reduced pressure to give the corresponding product **2**. The crude products **2b** and **2c** were purified by column chromatography using ethyl acetate–hexane (1:2) to afford pure products for analytical measurements.

2.3 | Selected spectroscopic data

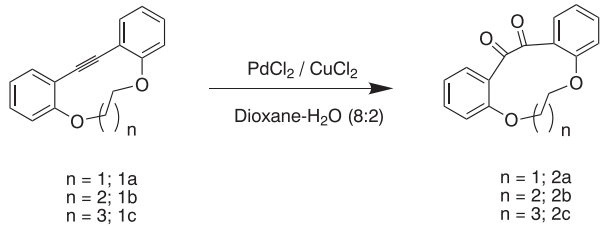
2b: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.88 (dd, J = 1.3, 7.7 Hz, 2H), 7.55 (m, J = 1.4, 7.8 Hz, 2H), 7.13 (t, J = 7.5 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 4.37 (t, J = 4.88 Hz, 4H), 1.85 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 193.3, 159.1, 135.5, 130.6, 127.4, 122.4, 116.9, 72.8, 27.7. IR (KBr, ν, cm^{-1}): 2956, 2926, 1729, 1670, 1596, 1451, 1269, 766. MS-ESI: m/z 282 (M^+, 100%), 197 (45%), 121 (92%), 92 (73%).

2c: ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.99 (dd, J = 1.5, 7.5 Hz, 2H), 7.57 (m, J = 1.8 Hz, 2H), 7.11 (t, J = 7.2 Hz, 2H), 6.99 (d, J = 8.1 Hz, 2H), 4.18 (t, J = 4.88 Hz, 4H), 1.82 (t, J = 4.88 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 193.1, 157.6, 135, 131.3, 125.5, 121.4, 113.8, 68.7, 26.2. IR (KBr, ν, cm^{-1}): 2956, 2926, 1729, 1658, 1594, 1480, 1281, 761. MS-ESI: m/z 296 (M^+, 22%), 197 (35%), 147 (31%), 121 (100%), 92 (50%).

3 | RESULTS AND DISCUSSION

Based on the reported ^{13}C NMR data, the sp carbon atoms of **1a** (95.4 ppm[39]) resonate strongly at lower field than those of **1b** (92.2 ppm[38]), **1c** (91.9 ppm[39]) and acyclic **1d** (89.7 ppm[40]), which is consistent with the increased ring strain in **1a** as a consequence of its decreased ring size.

The Wacker oxidation of **1a–c** is shown in Scheme 1. To gain more information on the reaction mechanism, two acyclic analogues **1d** and **1e** were also subjected to Wacker oxidation. All the reactions of tolans **1a–e** were carried out with catalytic amount of $PdCl_2/CuCl_2$ (5% $PdCl_2$ and 10% $CuCl_2$) in dioxane–water (8:2). All reactions were carried out for 24 h at various reaction temperatures under 1 atm of air and the results are summarized in Table 1. Substrates **1b–e** are oxidized to the corresponding 1,2-diketones in excellent yields at 100 and 60 °C. In contrast, although **1a** shows the same activity as **1b** and **1c**, the reaction is not clean and mostly leads to the formation of unknown by-product (Figure S1).



SCHEME 1 Wacker oxidation of **1a–c** with $PdCl_2$ in dioxane–H_2O (8:2)

Therefore, to evaluate which structural elements of these alkynes are more responsible for their activity and selectivity, the reactions were carried out at room temperature. As evident from Table 1, although the reaction rate is very slow, a clear difference in their activity is found in the order: **1b** > > **1c** > > **1d** ≈ **1e** > > **1a**. Surprisingly, **1a** having the most strained alkyne bond shows almost no activity, even lower than those of acyclic analogues.

The low by-product formation, except for **1a**, helped us to separate products rapidly in useful yields by column chromatography. Mass spectral analysis confirmed the molecular mass of products (Figures S2–S4). The NMR spectra of cyclophanes **2b** and **2c** are in accord with the symmetry of these molecules (Figures S5 and S8). The aromatic protons appear as two doublets and two triplets, while non-aromatic protons of **2b** and **2c** appear in different patterns, because of the different chain length of the etheric oxygen.

In the ^{13}C NMR spectra, nine signals are observed, which is in agreement with a time-averaged C2v symmetry in solution (Figures S6 and S9). The carbonyl signal is observed as a singlet at about 195 ppm. The formation of carbonyl bond was also confirmed using FT-IR spectrophotometry (Figures S7 and S10). The progress of the reactions determined using UV–visible spectrophotometry is easy because products show a blue shift of absorption maximum of materials (Figure S11).

With the aforementioned reaction conditions in hand, we examined the influence of the reaction time, the proportions of $PdCl_2$ to substrate, and the reaction atmosphere to optimize the reaction conditions for **1b** (Table 2). Conducting the reaction for 24 h stirring at 100 °C and 1 atm of oxygen atmosphere gave **2b** in 99% yield (Table 2, entry 1). It should be noted that using air in place of oxygen could also give good yield of product (Table 2, entry 2). Nevertheless, the preference for oxygen over air in terms of the reaction rate is evident when the reaction is conducted at lower temperature (Table 2, entries 3 and 4) or lower catalyst loading (Table 2, entries 5 and 6) or decreased reaction time (Table 2, entries 7 and 8). Decreasing the loading of the catalyst from 5 to 2 mol% gave almost acceptable yield of product (Table 2, entries 4 and 6).

Isotopic labelling experiments using $H_2{}^{18}O$ revealed that both oxygen atoms of the 1,2-diketone **2b** originated from water rather than molecular oxygen as analysed using mass spectrometry (Figure S12).

To obtain more information on the oxidation rate of **1a–c**, we performed density functional theory (DFT) calculations (Cam-B3LYP functional coupled with the def2-TZVP basis set for Pd and 6–311++G(d,p) for H, C, O and Cl elements) to investigate some important intermediate complexes of the early steps of the mechanism of the Wacker process. In the Wacker mechanism, two more possible active intermediates

TABLE 2 Optimization of reaction conditions for **1b**

Entry	$PdCl_2$ (%)	Reaction time (h)/atmosphere	Reaction temperature (°C)	Yield (%)
1	5	24/O_2	100	99
2	5	24/air	100	91
3	5	24/O_2	60	93
4	5	24/air	60	88
5	2	24/air	100	85
6	2	24/O_2	100	93
7	2	8/air	100	65
8	2	8/O_2	100	72

TABLE 1 Various reaction conditions for **1a–e** in the presence of $PdCl_2$ (5%) and $CuCl_2$ (10%)

	100 °C/24 h/air		60 °C/24 h/air		25 °C/24 h/air	
Substrates	**Conversion (%)**	**Product yield (%)**	**Conversion (%)**	**Product yield (%)**	**Conversion (%)**	**Product yield (%)**
1a	100[b]	32	100[b]	28	3	0.5[b]
1b	100	91	100	88	35[a]	35
1c	100	85	100	81	25[a]	25
1d	95[a]	81	77[a]	77	12[a]	12
1e	100	85	80[a]	80	13[a]	13

[a]The remaining percentage is starting materials.

[b]The starting material is mostly converted to unknown by-products.

for the alkene bonds, $[PdCl_3(C{=}C)]^-$ and $[PdCl_2(C{=}C)(H_2O)]$, have been proposed.[41–45] We considered these types of intermediates in the complexation of tolanophanes **1a–c** (Figures 1 and 2). Accordingly, the first chloride atom from the coordination sphere of ($[PdCl_4]^{2-}$) is removed to form the first intermediate $[PdCl_3(\mathbf{1})]^-$ as shown in Figure 1. The optimized geometries of this intermediate complex indicated that Pd ion is kept near the acetylene carbon atoms through the interactions between chloride atoms and hydrogen atoms of methylene unit and aromatic rings. The topological analysis of the electron density within QTAIM framework also demonstrate the existence of the weak bonding interactions between the chlorine atoms of $[PdCl_3]^-$ with hydrogen atoms of rings and CH_2 fragments. Thus, it seems reasonable to suppose that this hydrogen-bonding network is responsible for stabilizing the intermediate complex structure. The existence of an additional short intramolecular hydrogen bond between O…CH_2 in **1c** (2.37 Å) is expected to weaken the interaction of O…Pd. This is the reason why **1c** shows lower activity than **1b**.

A further chloride atom of intermediate $[PdCl_3(\mathbf{1})]^-$ is then removed by the oxygen atom, generating a complex with the oxygen and acetylene carbon of **1** (Figure 2). The oxygen source may be that of water or those of **1**, giving rise to $[PdCl_2(\mathbf{1})(H_2O)]$ or $[PdCl_2(\mathbf{1})]$ complex formation, respectively. This critical step of the reaction mechanism, however, was not observed computationally for **1a** because the positions of the oxygen atoms are outside of the central part of

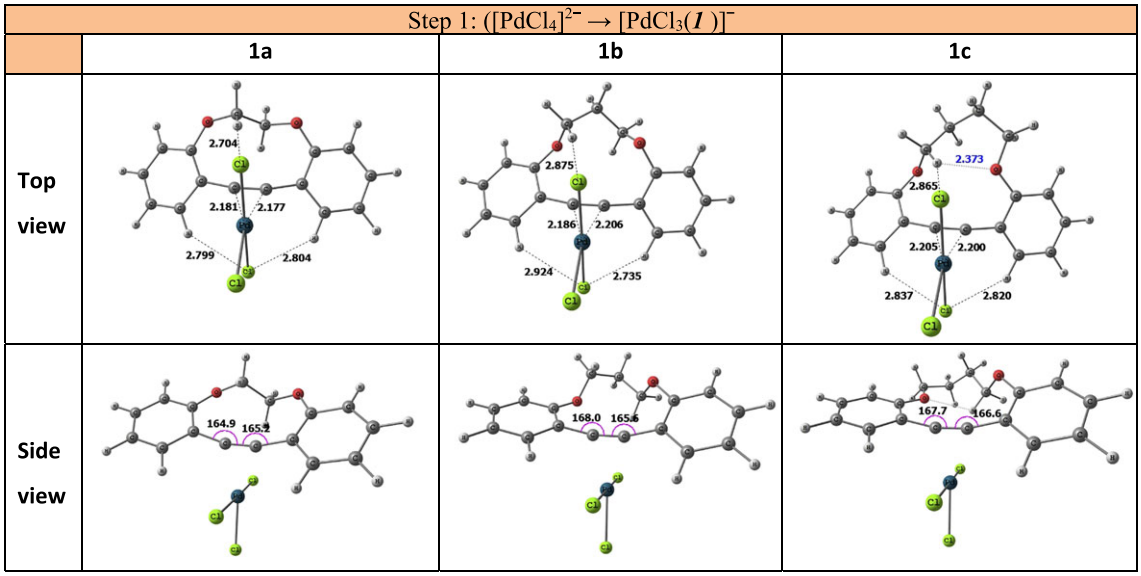


FIGURE 1 DFT-optimized geometries of the first step of intermediate formation. Distances in angstroms and angles in degrees

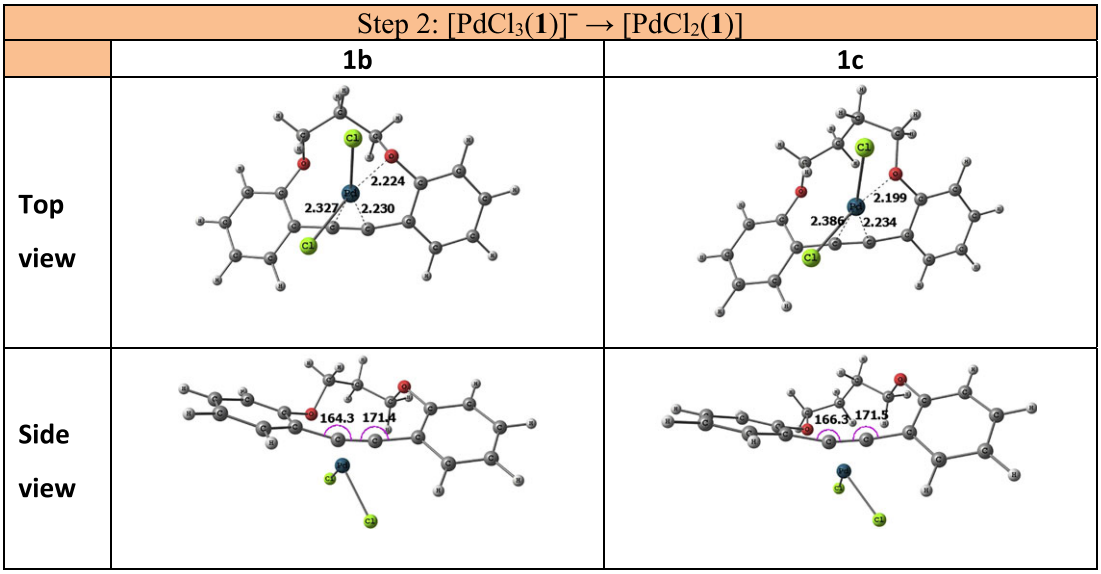


FIGURE 2 DFT-optimized geometries of the second step of intermediate formation. Distances in angstroms and angles in degrees

1a. Therefore, this process is not possible for **1a** because the oxygens of **1a** cannot move easily to construct this intermediate complex. This is in good agreement with our previous *ab initio* calculation for **1a** which showed its rigid structure due to a short distance (2.5 Å) between C─H (alkyl) and π-system (alkyne).[46] On the basis of these results one concludes that activity and product selectivity of **1a–c** are strongly dependent on structure and configuration.

As **1b** showed the best activity and selectivity, we measured its ^{1}H NMR and ^{13}C NMR complexation with equivalent amount of $PdCl_2$ in both DMSO-d_6 and $CDCl_3$. However, the complexation was not detected using NMR measurements which may be due to its too slow interaction at room temperature (Figures S13–S16). These data confirmed the *ab initio* calculation findings in which the preferred coordinating site is oxygen in the reaction pathway.

In contrast, cyclic voltammetry analysis of $PdCl_2$ with **1b** and **1c** showed that the current intensity of reduction and oxidation peaks becomes higher than for **1a** indicating better electron transfer between $PdCl_2$ and alkyne group (Table 3 and Figure 3). Moreover, new reduction and oxidation peaks at −1.4 and −1.6 eV for **1b**, unlike **1c**, appeared showing better interaction between $PdCl_2$ and alkyne group.

In this study, we considered tolanophanes **1a–c** with various alkyl chain lengths (n = 2–4) to investigate the progress of Wacker oxidation at a variety of reaction temperatures. The products are new and their structures were characterized. In general, tolanophane **1a** having the highest strain and rigidity showed the lowest activity and selectivity compared to **1b** and **1c**. Moreover, it showed lower activity than acyclic analogues at room temperature. On the other hand, **1b** showed a clean reaction with the highest activity and selectivity. This means that **1b** has sufficient alkyl chain length to make the best stereochemistry for hosting Pd ion. *Ab initio* calculations showed that Pd ion is kept closer to alkyne bonds of **1b**, unlike **1a**, through its interaction with oxygen atom of **1b** to confirm the difference in reaction rates of **1**. However, this complexation was not detected using NMR measurements which may be due to its slow reaction at room temperature. In contrast, cyclic voltammetry measurements showed a different behaviour for the complexation of **1a** and **1b** with palladium ion, confirming the experimental and theoretical data. In general, it was found that the stereochemistry of **1b** is more suitable for enhancing the reaction rate.

Further investigation of various tolanophanes is currently under way in our laboratory. The separation and characterization of by-products, especial those of **1a**, are also being investigated.

TABLE 3 Current intensity of reduction and oxidation peaks of tolans **1b** and **c** from cyclic voltammetry analysis

Material	I_{ox} (eV)	I_{red} (eV)	I_{ox} (eV)	I_{red} (eV)
$PdCl_2$	−0.91	−0.69	—	—
1b + Pd	−0.9	−0.68	−1.60	−1.40
1b	−0.91	−0.70	—	—
1c + Pd	−0.90	−0.69	—	—
1c	−0.87	−0.68	—	—

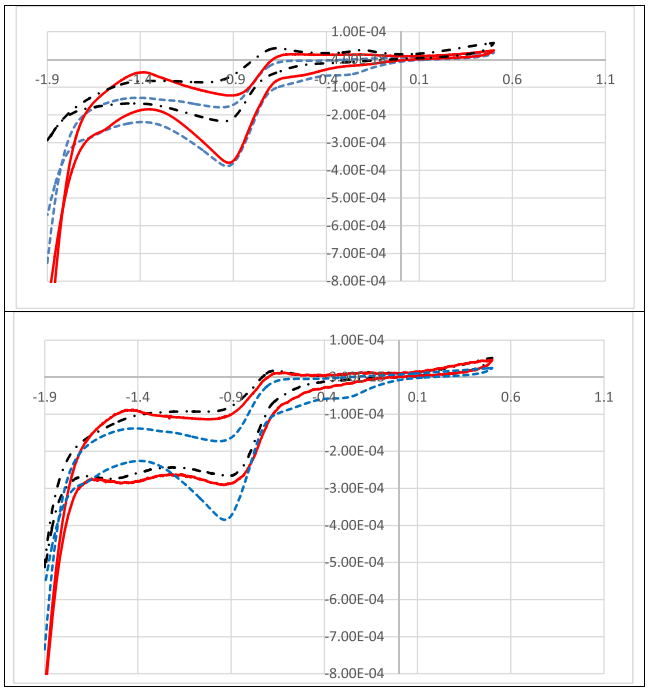


FIGURE 3 Top: cyclic voltammograms of **1b** (dash-dotted black line); $PdCl_2$ (dashed blue line); Pd complex of **1b** (solid red line). Bottom: cyclic voltammograms of **1c** (dash-dotted black line); $PdCl_2$ (dashed blue line); Pd complex of **1c** (solid red line)

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REFERENCES

[1] M. D. Rozwadowska, M. Chrzanowska, *Tetrahedron* **1985**, *41*, 2885.

[2] R. Maurya, R. Singh, M. Deepak, S. S. Handa, P. P. Yadav, P. K. Mishra, *Phytochemistry* **2004**, *65*, 915.

[3] W. Mahabusarakam, S. Deachathai, S. Phongpaichit, C. Jansakul, W. C. Taylor, *Phytochemistry* **2004**, *65*, 1185.

[4] R. M. Wadkins, J. L. Hyatt, X. Wei, K. J. P. Yoon, M. Wierdl, C. C. Edwards, C. L. Morton, J. C. Obenauer, K. Damodaran, P. Beroza, M. K. Danks, P. M. Potter, *J. Med. Chem.* **2005**, *48*, 2906.

[5] T. Harada, Y. Nakagawa, R. M. Wadkins, P. M. Potter, C. E. Wheelock, *Bioorg. Med. Chem.* **2009**, *17*, 149.

[6] M. Friedman, *J. Org. Chem.* **1965**, *30*, 859.

[7] M. Mazik, R. Boese, R. Sustmann, *Tetrahedron* **1996**, *52*, 3939.

[8] G. G. Muccioli, D. Martin, G. K. E. Scriba, W. Poppitz, J. H. Poupaert, J. Wouters, D. M. Lambert, *J. Med. Chem.* **2005**, *48*, 2509.

[9] W. D. Shipe, F. Yang, Z. Zhao, S. E. Wolkenberg, M. B. Nolt, C. W. Lindsley, *Heterocycles* **2006**, *70*, 655.

[10] D. P. Singh, R. Kumar, J. Singh, *Eur. J. Med. Chem.* **2009**, *44*, 1731.

[11] F. Catalina, C. Peinado, M. Blanco, A. Alonso, N. S. Allen, *J. Photochem. Photobiol. A* **2000**, *131*, 141.

[12] Z. Szablan, T. M. Lovestead, T. P. Davis, M. H. Stenzel, C. Barner-Kowollik, *Macromolecules* **2007**, *40*, 26.

[13] D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537.

[14] U. H. F. Bunz, *Chem. Rev.* **2000**, *100*, 1605.

[15] W. Ren, Y. Xia, S.-J. Ji, Y. Zhang, X. Wan, J. Zhao, *Org. Lett.* **2009**, *11*, 1841.

[16] S. Chandrasekhar, N. K. Reddy, V. P. Kumar, *Tetrahedron Lett.* **2010**, *51*, 3623.

[17] G. Gebeyehu, E. McNelis, *J. Org. Chem.* **1980**, *45*, 4280.

[18] Z. Zhu, J. H. Espenson, *J. Org. Chem.* **1995**, *60*, 7728.

[19] V. O. Rogatchov, V. D. Filimonov, M. S. Yusubov, *Synthesis* **2001**, 1001.

[20] J. Chu, Y. Chen, M. Wu, *Synthesis* **2009**, 2155.

[21] S. Dayan, I. Ben-David, S. Rozen, *J. Org. Chem.* **2000**, *65*, 8816.

[22] Z. Wan, C. D. Jones, D. Mitchell, J. Y. Pu, T. Y. Zhang, *J. Org. Chem.* **2006**, *71*, 826.

[23] M. S. Yusubov, G. A. Zholobova, S. F. Vasilevsky, E. V. Tretyakov, D. W. Knight, *Tetrahedron* **2002**, *58*, 1607.

[24] R. W. Murray, M. Singh, *J. Org. Chem.* **1993**, *58*, 5076.

[25] S. Wolfe, C. F. Ingold, *J. Am. Chem. Soc.* **1983**, *105*, 7755.

[26] A. Giraud, O. Provot, J. F. Peyrat, M. Alami, J. D. Brion, *Tetrahedron* **2006**, *62*, 7667.

[27] X. Deng, N. S. Mani, *Org. Lett.* **2006**, *8*, 269.

[28] D. Lee, V. S. Chang, *Synthesis* **1978**, 462.

[29] P. Li, F. H. Cheong, L. C. F. Chao, Y. H. Lin, I. D. Williams, *J. Mol. Catal. A* **1999**, *145*, 111.

[30] C. Mousset, O. Provot, A. Hamze, J. Bignon, J. D. Brion, M. Alami, *Tetrahedron* **2008**, *64*, 4287.

[31] C. Sheu, S. A. Richert, P. Cofre, B. Ross, A. Sobkowiak, D. T. Sawyer, J. R. Kanofsky, *J. Am. Chem. Soc.* **1990**, *112*, 1936.

[32] M. S. Yusubov, V. D. Filimonov, *Synthesis* **1991**, 131.

[33] M. S. Yusubov, E. A. Krasnokutskaya, V. P. Vasilyeva, V. D. Filimonov, K. W. Chi, *Bull. Korean Chem. Soc.* **1995**, *16*, 86.

[34] K. W. Chi, M. S. Yusubov, V. D. Filimonov, *Synth. Commun.* **1994**, *24*, 2119.

[35] C. M. Che, W. Y. Yu, P. M. Chan, W. C. Cheng, S. M. Peng, K. C. Lau, W. K. Li, *J. Am. Chem. Soc.* **2000**, *122*, 11380.

[36] H. R. Darabi, M. Mirzakhani, K. Aghapoor, L. Faraji, N. Sakhaee, K. Jadidi, *J. Organomet. Chem.* **2013**, *740*, 131.

[37] H. R. Darabi, M. Mirzakhani, K. Aghapoor, *J. Organomet. Chem.* **2015**, *786*, 10.

[38] G. T. Crisp, T. P. Bubner, *Tetrahedron* **1997**, *53*, 11881.

[39] H. R. Darabi, K. Jadidi, A. R. Mohebbi, L. Faraji, M. Azimzadeh, K. Aghapoor, S. Shahbazian, S. M. Nasseri, *Supramol. Chem.* **2008**, *20*, 327.

[40] G. Brizius, U. H. F. Bunz, *Org. Lett.* **2002**, *4*, 2829.

[41] V. Imandi, S. Kunnikuruvan, N. N. Nair, *Chem. – Eur. J.* **2013**, *19*, 4724.

[42] N. N. Nair, *J. Phys. Chem. B* **2011**, *115*, 2312.

[43] A. Comas-Vives, A. Stirling, A. Lledós, G. Ujaque, *Chem. – Eur. J.* **2010**, *16*, 8738.

[44] J. A. Keith, P. M. Henry, *Angew. Chem. Int. Ed.* **2009**, *48*, 9038.

[45] J. A. Keith, R. J. Nielsen, J. Oxgaard, W. A. Goddard, *J. Am. Chem. Soc.* **2007**, *129*, 12342.

[46] H. R. Darabi, M. Azimzadeh Arani, M. Tafazzoli, M. Ghiasi, *Monatsch. Chem.* **2008**, *139*, 1185.

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