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PII: S0040-4039(16)30122-8
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.02.012
Reference: TETL 47285

To appear in: *Tetrahedron Letters*

Received Date: 25 November 2015
Revised Date: 29 January 2016
Accepted Date: 3 February 2016

Please cite this article as: Chen, Y., Chen, B., Luo, D., Cai, Y., Wei, Y., Han, Y., A Facile Naphthalene-Based Fluorescent "Turn-On" Chemodosimeter for Palladium Ions in Aqueous Solution, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.02.012

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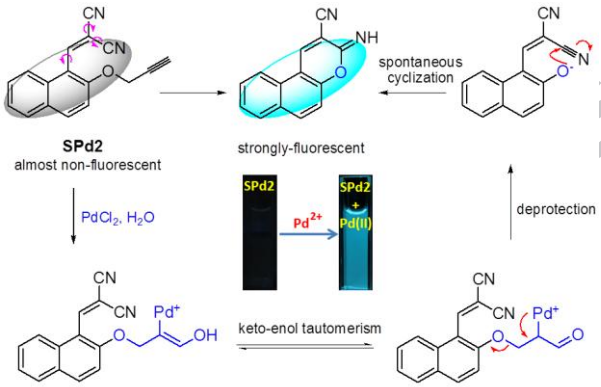

Tetrahedron Letters
journal homepage: www.elsevier.com

A Facile Naphthalene-Based Fluorescent "Turn-On" Chemodosimeter for Palladium Ions in Aqueous Solution

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Fluorescent probe
Chemodosimeter
Palladium ion
Reaction-based
Depropargylation-triggered

ABSTRACT

A novel and simple depropargylation-triggered spontaneous cyclization reaction based fluorescent turn-on chemodosimeter for the detection of Pd^{2+} has been reasonably designed and developed. Based on the specific reactivity of palladium ion-promoted hydrolysis reaction, the probe exhibited a high selectivity and sensitivity for Pd^{2+} with a low detection limit (53 nM, 5.7 μg/L) under physiological conditions in neutral PBS (only containing 1% organic cosolvent) without any additional reagents.

1. Introduction

Palladium, which is widely distributed in the environment duo to its use in alloys, fuel cells, chemical catalysts and especially in automobile catalytic converters, is one of the most ubiquitous and poisonous heavy metals.[1] Palladium ions are not biodegradable, and hence can be concentrated through the food chain, which may cause serious health problems. Excess palladium accumulation may result in the degradation of cell mitochondria and DNA, and also enzyme inhibition.[2] Thus, the governmental regulation on the proposed maximum dietary intake of palladium is less than 1.5-15 μg per person per day.[3] Therefore, the development of convenient and effective methods for palladium analysis is crucial both to the monitoring of environmental pollution and to the diagnosis of clinical disorders.

Conventional techniques used for quantification of palladium species, such as atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, and solid-phase microextraction high-performance liquid chromatography, often need the complicated sample preparation and the expensive and sophisticated instrumentation, and are therefore not suitable for real-time and in situ analysis.[4] Thus, current research has been focused on fluorescent probe techniques because of their ease of application in solution as well as their high sensitivity and selectivity for trace analytes.[5]

Recently, considerable efforts have been made to develop fluorescent probe for Pd^{2+} based on Pd^{2+} catalyzed depropargylation and deallylation reaction, Pd^{2+} catalyzed oxidative cyclization reaction, Pd^{2+} catalyzed ring-opening reaction, Pd^{2+} catalyzed C-I cleavage reaction, and the coordination of Pd^{2+} to heteroatom-based ligands (Fig. 1).[6]

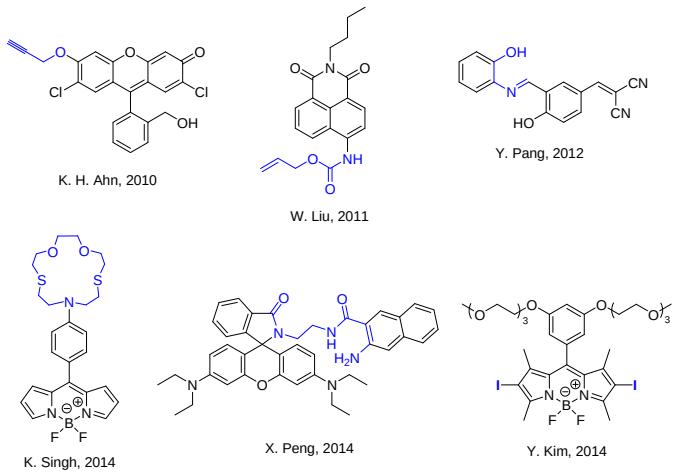
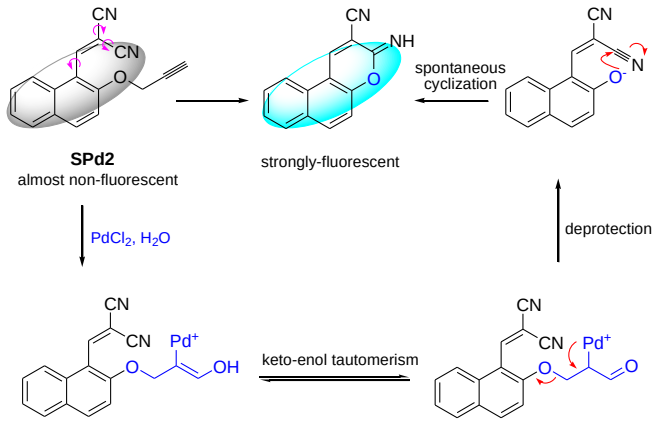


Figure 1. Structures of some reported palladium probes.

However, many of them still have limitations such as interference from other coexisting metal ions, only work in organic solvents and/or water-organic cosolvents, need additional reagents, and laborious synthesis processes expensive chemicals. Furthermore, among the few available Pd^{2+} chemodosimeters reported, most employ the pH-sensitive fluorescein or rhodamine as the fluorophore and their pH-dependence may pose detection errors to the results. It is therefore strongly desirable to develop novel and simple yet specific fluorescent chemodosimeters for the detection of Pd^{2+}.

Our research group is actively engaged in the development of novel specific fluorescent probes for heavy metal ions.[7] Herein, we report a novel yet simple depropargylation-triggered



Scheme 1. The "deprotection-cyclization" strategy for the design of **SPd2**.

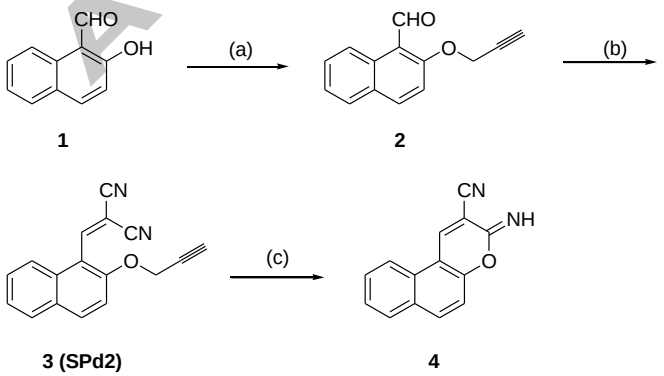
spontaneous cyclization based fluorescent chemodosimeter (**SPd2**) that shows high selectivity and sensitivity for Pd^{2+}. It should be mentioned that **SPd2** could be used to detect Pd^{2+} under physiological condition (at 37 ^{o}C in PBS, pH 7.4, only containing 1% organic cosolvent) without any additional reagents.

It is well known that the terminal propargyl ether can be specifically cleaved by palladium-catalyzed hydrolysis reaction to generate the corresponding free hydroxyl group.[6d, 6m] We envisioned that the fluorescent intensity of the **SPd2** might greatly reduce due to the effect of intramolecular rotation. On the other hand, the deprotection of the propargyl ether group of **SPd2** by Pd^{2+}-promoted hydrolysis reaction would releases the hydroxy intermediate, which wills spontaneous cyclize to form a highly fluorescent chemodosimeter (Scheme 1).

2. Results and discussions

As shown in Scheme 2, **SPd2** can be readily prepared in two convenient steps under facile conditions with high yield starting with commercially available 2-hydroxy-1-naphthaldehyde. The product (**SPd2**) was well characterized by ^{1}H, ^{13}C NMR, and HR-MS (ESI†).

We firstly assessed the UV-vis spectroscopic properties of **SPd2** in PBS buffer solution (10 mM, pH 7.4, containing 1.0% EtOH) (Fig. 2a). **SPd2** (20.0 μM) displayed a moderate UV-vis absorption around 390 nm. Upon the addition of Pd^{2+} (20.0 μM), the maximum absorption peak seems, underwent a blue-shift to 325 nm. But the absorption spectra of compound **4** were clearly shown that the absorption band at 325 nm belongs to the Pd^{2+}



Scheme 2. Synthesis of **SPd2**: (a) 3-bromopropyne/K_2CO_3, acetone, reflux, 4 h, 77%; (b) malononitrile, piperidine, EtOH, rt, 4 h, 98%; (c) $PdCl_2$, EtOH, rt, 4 h, 88%.

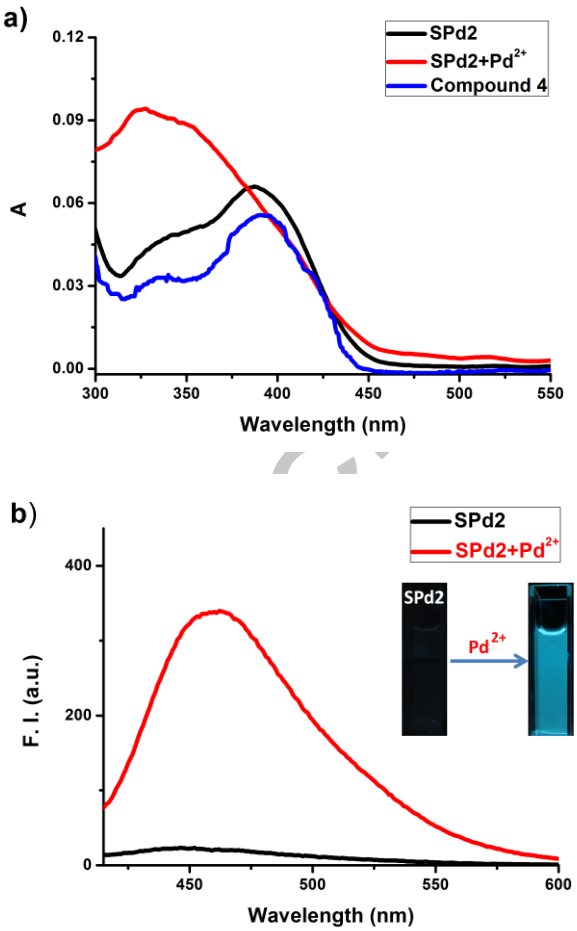


Figure 2. (a) UV-vis absorption spectra of **SPd2** (20.0 μM) in the absence and presence of Pd^{2+} (20.0 μM), and compound **4**. (b) Fluorescence spectra of **SPd2** (10.0 μM) in the absence and presence of Pd^{2+} (100.0 μM). Inset: Fluorescence changes excited by UV lamp (365 nm) in the absence and presence of Pd^{2+}. All spectra were acquired 1 h after Pd^{2+} addition at 37 °C in PBS buffer solutions (10 mM, pH 7.4, containing 1.0% EtOH). λ_{ex} = 395 nm.

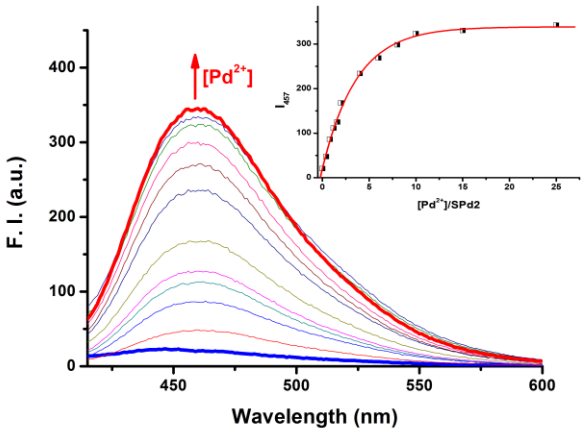


Figure 3. Fluorescence spectra of **SPd2** (10.0 μM) in PBS buffer solution (10 mM, pH 7.4, containing 1.0% EtOH) in the presence of different concentrations of Pd^{2+} (0-250.0 μM) (λ_{ex} = 395 nm). Inset: Fluorescence intensity (at 457 nm) changes of **SPd2** as a function of Pd^{2+} concentration.

(Fig. 2a, and S1, ESI). On the other hand, in the presence of Pd^{2+} (100.0 μM), **SPd2** (10.0 μM) showed a dramatic increase in cyan fluorescence emission at 457 nm (in PBS buffer solution, 10 mM, pH 7.4, containing 1.0% EtOH) (Fig. 2b).

The speculative mechanism of the Pd^{2+} induced fluorescence response is shown in Scheme 1. Efforts were then made to explore the nature of the palladium ion induced response. To this end, a comparison of fluorescent spectra between the **SPd2**-Pd^{2+} system and compound **4** was made to confirm the generation of **4** after treatment with Pd^{2+} (Fig. S2, ESI†). The ^{1}H- and ^{13}C- NMR spectra of the isolated product of the **SPd2**-Pd^{2+} solution were also measured to support the depropargylation-triggered spontaneous cyclization of **SPd2** (see ESI†).

Next, the emission spectra of **SPd2** and its fluorescent titration with Pd^{2+} were recorded in PBS buffer solution (10 mM, pH 7.4, containing 1.0% EtOH) (Fig. 3). As expected, **SPd2** alone is almost non-fluorescent (λ_{ex} = 395 nm, Φ = 0.08%, Table S1, ESI†) duo to the effect of intramolecular rotation (Scheme 1). However, with progressive addition of Pd^{2+}, the emission band at 457 nm rapidly increased (Fig. 3), which was attributed to the cleavage of propargyl ether group by palladium ion-promoted hydrolysis followed by spontaneous cyclization reaction to form the highly fluorescent cyclic compound **4** (Scheme 1). Furthermore, the fluorescence titration curve revealed that the fluorescence intensity at 457 nm increased linearly with increasing concentration of Pd^{2+} (Fig. S3, ESI†) and further smoothly increased until a maximum was reached up to 100.0 μM Pd^{2+} (λ_{ex} = 395 nm, Φ = 0.103, Table S1, ESI†). Owing to the specific reactivity of palladium ion-promoted hydrolysis reaction, **SPd2** displayed a high sensitivity toward Pd^{2+}.

Subsequently, the time-dependence of fluorescence was also evaluated in the presence of Pd^{2+} in PBS buffer solution (10 mM, pH 7.4, containing 1.0% EtOH) (Fig. 4 and Fig. S4, ESI†). The result shows that the fluorescence of the tested solutions remarkably increased to the maximum value within 100 minutes. Accordingly, the observed rate constant (k_{obs}) for the formation of compound **4** has been calculated to be 2.7 × 10^{-2} min^{-1} (Fig. S5, ESI†).[8]

Further, the fluorescence titration of **SPd2** with various metal ions was then conducted to examine the selectivity (Fig. 5, and S6, ESI†). Much to our delight, the turn-on response of **SPd2** is highly specific for Pd^{2+} and no obvious change of fluorescent emission was observed when it is treated with Al^{3+}, Ca^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, and Pb^{2+}. It should be mentioned that **SPd2** still responded to Pd^{2+} sensitively even in the presence of other relevant competing ions (Fig. 5, and S7, ESI†). Therefore, these results suggest that **SPd2** displays high selectivity toward Pd^{2+} in neutral aqueous solution.

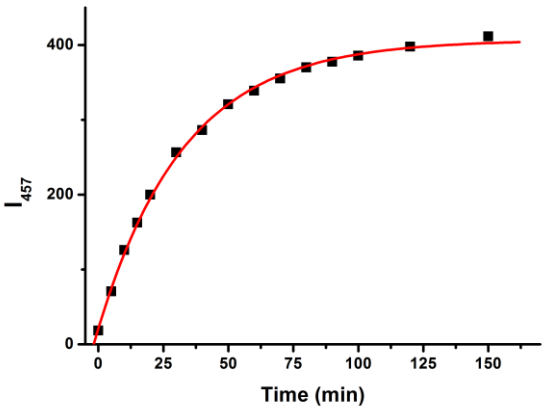


Figure 4. Time-dependent fluorescence intensity (at 457 nm) changes of **SPd2** (10.0 μM) upon addition of Pd^{2+} (10.0 equiv.) in PBS buffer solution (10 mM, pH 7.4, containing 1.0% EtOH) (λ_{ex} = 395 nm).

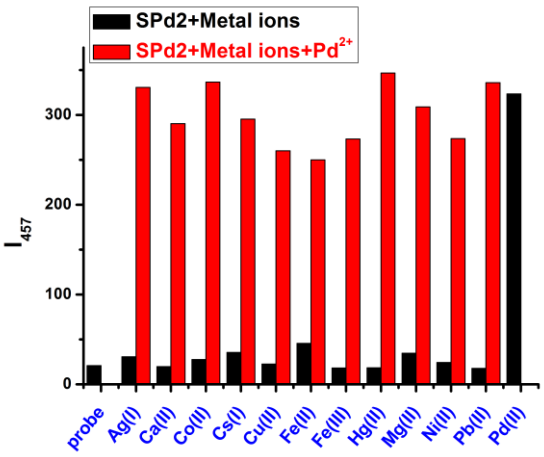


Figure 5. Fluorescence responses of **SPd2** to various metal ions (including Al^{3+}, Ca^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, and Pd^{2+}). Black bars represent the addition of 10.0 equiv. of the appropriate metal ion to a 10.0 μM solution of **SPd2** (in PBS buffer solution, 10 mM, pH 7.4, containing 1.0% EtOH). Red bars represent the addition of 10.0 equiv. of Pd^{2+} to the solutions containing **SPd2** (10.0 μM) and the appropriated metals (100.0 μM) (λ_{ex} = 395 nm).

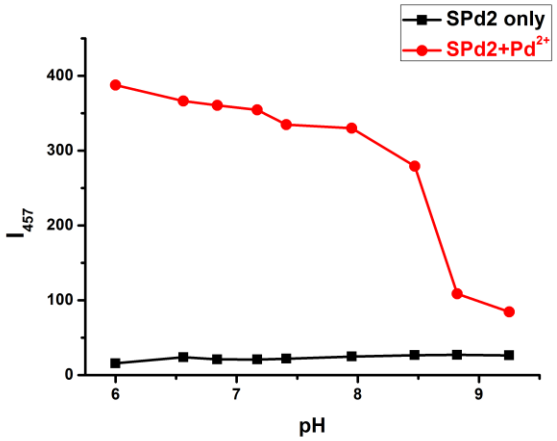


Figure 6. Effect of the pH on the fluorescence emission of **SPd2** (10.0 μM) alone and **SPd2** (10.0 μM) reacted with Pd^{2+} (10.0 equiv.).

Moreover, the Pd^{2+}-sensing ability of **SPd2** at a wide range of pH values was investigated. As depicted in Fig. 6, **SPd2** alone was inert to pH in the range of 6.0-9.3. On the other hand, it readily reacted with Pd^{2+} within the biologically relevant pH rang (6.0-8.5). These results indicate that **SPd2** could be used in neutral natural systems, or a mildly acidic or basic environment.

For practical purposes, the detection limit of **SPd2** for the analysis of Pd^{2+} was also an important parameter. The fluorescence titration curve revealed that the fluorescence intensity of **SPd2** at 457 nm increased linearly with the amount of Pd^{2+} in the range of 0-20.0 μM (R^2 = 0.994) (Fig. S8, ESI†). Thus, the detection limit of **SPd2** for Pd^{2+} was calculated to be 5.3 × 10^{-8} M (Pd^{2+} content = 5.7 μg/L),[9] which indicated that **SPd2** could be a sensitive fluorescent chemodosimeter for quantitative detection of Pd^{2+}.

3. Conclusions

In conclusion, we have successfully developed a novel and simple depropargylation-triggered spontaneous cyclization based fluorescent chemodosimeter for the detection of palladium ions under physiological conditions in neutral PBS (only containing 1% organic cosolvent) without any additional reagents. The probe has the unique advantage of easy-preparation, good water solubility, and excellent selectivity and sensitivity response towards Pd^{2+}, with a low detection limit (53 nM, 5.7 μg/L). We anticipate that the experimental results of this study will inspire the future design of metal-ion sensors in water for a variety of chemical and biological applications.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20902082), the Project Grants 521 Talents Cultivation of Zhejiang Sci-Tech University, and the Program for Innovative Research Team of Zhejiang Sci-Tech University (13060052-Y).

References and notes

1. (a) Zeni, G.; Larock, R. C. *Chem. Rev*., **2004**, *104*, 2285-2310. (b) Lyons, T. W.; Sanford, M. S. *Chem. Rev*., **2010**, *110*, 1147-1169. (c) Ravindra, K.; Bencs, L.; Grieken, R. V. *Sci. Total Environ*., **2004**, *318*, 1-43. (d) Zereini, F.; Wiseman, C.; Puttmann, W. *Environ. Sci. Technol*., **2007**, *41*, 451-456.
2. (a) Hensten-Pettersen, A. *Adv. Dent. Res*., **1992**, *6*, 38-43. (b) Wataha J. C.; Hanks, C. T. *J. Oral Rehabil*., **1996**, *23*, 309-320. (b) Kielhorn, J.; Melber, C.; Keller D.; Mangelsdorf, I. *Int. J. Hyg. Environ. Health*, **2002**, *205*, 417-432. (c) *International Programme on Chemical Safety. Palladium*, Environmental Health Criteria Series 226, World Health Organization: Geneva, 2002.
3. Garrett, C. E.; Prasad, K. *Adv. Synth. Catal*., **2004**, *346*, 889-900.
4. (a) Dimitrova, B.; Benkhedda, K.; Ivanova, E.; Adams, F. *J. Anal. At. Spectrom*., **2004**, *19*, 1394-1396, (b) Locatelli, C.; Melucci, D.; Torsi, G. *Anal. Bioanal. Chem*., **2005**, *382*, 1567-1573. (c) Van Meel, K.; Smekens, A.; Behets, M.; Kazandjian, P.; Van Grieken, R. *Anal. Chem*., **2007**, *79*, 6383-6389.
5. (a) Yin, J.; Hu, Y.; Yoon, J. *Chem. Soc. Rev*., **2015**, *44*, 4619-4644. (b) Zhu, L.; Yuan, Z.; Simmons, J. T.; Sreenath, K. *RSC Adv*., **2014**, *4*, 20398-20440. (c) Zhu, L.; Younes, A. H.; Yuan, Z.; Clark, R. J. *Journal of Photochemistry and Photobiology A: Chemistry*, **2015**, *311*, 1-15. (d) Ding, Y.; Tang, Y.; Zhu, W.; Xie, Y. *Chem. Soc. Rev*., **2015**, *44*, 1101-1112. (e) Yuan, Z.; Younes, A. H.; Allen, J. R.; Davidson, M. W.; Zhu, L. *J. Org. Chem*., **2015**, *80*, 5600-5610. (f) Carter, K. P.; Young, A. M.; Palmer, A. E. *Chem. Rev*., **2014**, *114*, 4564-4601. (g) Sreenath, K.; Yuan, Z.; Allen, J. R.; Davidson, M. W.; Zhu, L. *Chem. Eur. J*., **2015**, *21*, 867-874.
6. (a) Garner, A. L.; Koide, K. *J. Am. Chem. Soc*., **2008**, *130*, 16472-16473. (b) Garner, A. L.; Song, F.; Koide, K. *J. Am. Chem. Soc*., **2009**, *131*, 5163-5171. (c) Jun, M. E.; Ahn, K. H. *Org. Lett*., **2010**, *12*, 2790-2793. (d) Santra, M.; Ko, S.-K.; Shin, I.; Ahn, K. H. *Chem. Commun*., **2010**, *46*, 3964-3966. (e) Jiang, J.; Jiang, H.; Liu, W.; Tang, X.; Zhou, X.; Liu, W.; Liu, R. *Org. Lett*., **2011**, *13*, 4922-4925. (f) Chen, W.; Wright, B. D.; Pang, Y. *Chem. Commun*., **2012**, *48*, 3824-3826. (g) Li, H.; Fan, J.; Peng, X. *Chem. Soc. Rev*., **2013**, *42*, 7943-7962. (h) Keum, D.; Kim, S.; Kim, Y. *Chem. Commun*., **2014**, *50*, 1268-1270. (i) Kaur, P.; Kaur, N.; Kaur, M.; Dhuna, V.; Singh, J.; Singh, K. *RSC Adv*., **2014**, *4*, 16104-16108. (j) Sun, S.; Qiao, B.; Jiang, N.; Wang, J.; Zhang, S.; Peng, X. *Org. Lett*., **2014**, *16*, 1132-1135. (k) Wang, X.; Guo, Z.; Zhu, S.; Tian, H.; Zhu, W. *Chem. Commun*., **2014**, *50*, 13525-13528. (l) Liu, W.; Jiang, J.; Chen, C.; Tang, X.; Shi, J.; Zhang, P.; Zhang, K.; Li, Z.; Dou, W.; Yang, L.; Liu, W. *Inorg. Chem*., **2014**, *53*, 12590-12594. (m) Mahapatra, A. K.; Manna, S. K.; Maiti, K.; Mondal, S.; Maji, R.; Mandal, D.; Mandal, S.; Uddin, M. R.; Goswami, S.; Quah, C. K.; Fun, H.-K. *Analyst*, **2015**, *140*, 1229-1236. (n) Wang, M.; Liu, X.; Lu, H.; Wang, H.; Qin, Z. *ACS Appl. Mater. Interfaces*, **2015**, *7*, 1284-1289. (o) Reddy G, U.; Ali, F.; Taye, N.; Chattopadhyay, S.; Das, A. *Chem. Commun*., **2015**, *51*, 3649-3652. (p) Zhou, L.; Wang, Q.; Zhang, X.-B.; Tan, W. *Anal. Chem*., **2015**, *87*, 4503-4507. (q) Lim, C. S.; Cho, B. R. *Tetrahedron*, **2015**, *71*, 8219-8249. (r) Chen, X.; Li, H.; Jin, L.; Yin, B. *Tetrahedron Letters*, **2014**, *55*, 2537-2540. (s) Wang, P.; Xia, J.; Gu, Y. *Tetrahedron Letters*, **2015**, *56*, 6491-6494. (t) Wang, K.; Lai, G.; Li. Z.; Liu, M.; Shen, Y.; Wang, C. *Tetrahedron*, **2015**, *71*, 7874-7878.
7. (a) Chen, Y.; Yang, C.; Yu, Z.; Chen, B.; Han, Y. *RSC Adv*., **2015**, *5*, 82531-82534. (b) Yang, C.; Chen, Y.; Wu, K.; Wei, T.; Wang, J.; Zhang, S.; Han, Y. ***Anal. Methods***, **2015**, *7*, 3327-3330. (c) Wei, T.; Wang, J.; Chen, Y.; Han, Y. *RSC Adv*., **2015**, *5*, 57141-57146. (d) Wu, K.; Gao, Y.; Yu, Z.; Jiang, J.; Guo, J, Han, Y. *Anal. Methods*, **2014**, *6*, 3560-3563. (e) Liu, J.; Wu, K.; Li, S.; Song, T.; Han, Y.; Li, X. *Dalton Trans*., **2013**, *42*, 3854-3859. (f) Liu, J.; Wu, K.; Li, X.; Han, Y.; Xia, M. *RSC Adv*., **2013**, *3*, 8924-8928.
8. Jo, J.; Lee, H. Y.; Liu, W.; Olasz, A.; Chen, C.-H.; Lee, D. *J. Am. Chem. Soc*., **2012**, *134*, 16000-16007.
9. Joshi, B. P.; Lohani, C. R.; Lee, K. H. *Org. Biomol. Chem*., **2010**, *8*, 3220-3226.

Supplementary Material

Supplementary data (additional spectroscopic of SPd2) associated with this article - copies of ^{1}H and ^{13}C NMR Spectra can be found, in the online version, at http://dx.doi.org.