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Ratiometric fluorescent probe for determining Pd^{2+} ions based on coordination reaction

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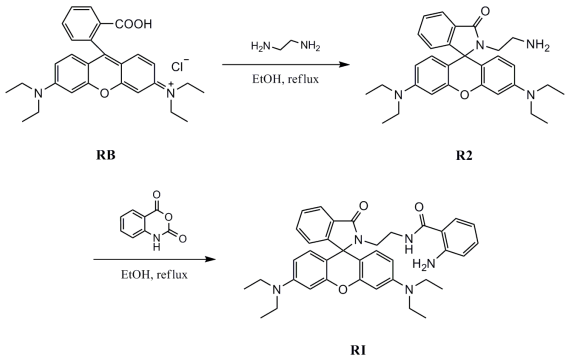
An aniline-rhodamine-based ratiometric fluorescent probe (RI) was designed and synthesized. RI, the metal coordinating chromophoric ligand, exhibited high selectivity and sensitivity for Pd^{2+} ions with a detection limit of 73.8 nM. This method of Pd^{2+} detection had a 10 min response time.

Palladium is widely used as a catalyst in synthesis because of its excellent catalytic ability.[1–6] Pd-catalyzed reactions are efficient and used in the synthesis of drug molecules.[7–10] However, high quantities of palladium can sometimes remain in the final product,[11–17] which can be consumed along with the drug. Palladium is also utilized in automobile catalytic converters to reduce emissions.[18–21] Unfortunately, such use leads to discharge of palladium into the environment, increasing its environmental content and consequently, increases the risk of palladium transport into human body. It has been shown that palladium can coordinate with DNA, thiol-containing amino acids, proteins, and vitamin B6, and disturb several cellular processes, thereby leading to health problems.[22–26] Thus, the threshold for palladium in drugs is set at 5 ppm to 10 ppm, and the proposed maximum dietary intake of palladium is <1.5 μg to 15 μg per person per day.[10,27] Consequently, effective methods to detect trace palladium are necessary.

Compared with traditional analytical methods (atomic absorption spectrometry, plasma emission spectroscopy, solid-phase microextraction–high-performance liquid chromatography, and X-ray fluorescence),[28–30] fluorescence methods are convenient, involve lower costs, easy to operate, highly sensitivity, and have excellent selectivity, thereby garnering the attention of several researchers.[31–36] Pd^{2+} ions can coordinate with the ligands, which contain N, O, S, or P and lead to a change in the color or fluorescence of the ligand.[37–41] On the basis of this concept, Mukherjee and co-workers have developed a tridentate N-containing fluorescence-quenched probe, which can selectively detect and extract the Pd^{2+} ions.[42] The spirolactam of rhodamine is an ideal chemical moiety suited for the development of a fluorescence probe.[43–47] In its spirolactam form, rhodamine is non-fluorescent, and when the spirolactam ring is opened, it emits distinct fluorescence. Peng and co-workers have modified the spirolactam moiety with suitable ligands to develop fluorescence-enhanced palladium probes, which have satisfactory sensitivity, selectivity, and response time.[48–50] However, these on–off or off–on sensors can be seriously affected by the excitation power and detector sensitivity in quantitative detection.[51,52] To solve this problem, several ratiometric fluorescence probes have been developed. The ratio of two absorption or emission peaks makes the detection more accurate and sensitive, and may also minimize the background signal.[53–55] Nearly all published ratiometric fluorescence probes of palladium are based on the Pd-catalyzed cleavage reactions and can recognize palladium with high sensitivity and excellent selectivity.[56–60] Unfortunately, the reaction conditions are relatively strict and have a long response time.[56,59]

Considering these limitations, a Pd^{2+}-selective ratiometric fluorescent probe (**RI**, Scheme 1) based on the coordination reaction is developed. The probe consists of the rhodamine and an anthraniloyl moiety. In the absence of Pd^{2+} ions, **RI** exhibits blue fluorescence (from the anthraniloyl moiety). On coordination with Pd^{2+} ions, the blue fluorescence is quenched; meanwhile, the spirolactam ring of rhodamine is opened, which leads to the strong red fluorescence, thereby allowing the ratiometric measurement of Pd^{2+} concentration. **RI** displays excellent selectivity for Pd^{2+} ions over other metal ions and can coordinate with Pd^{2+} ions at room temperature with the response time of 10 min.



Scheme 1 Synthesis of **RI**.

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† Electronic Supplementary Information (ESI) available: Reagents and instruments, synthesis procedures, additional spectroscopic data, ^{1}H NMR, ^{13}C NMR, MS. See DOI: 10.1039/b000000x/

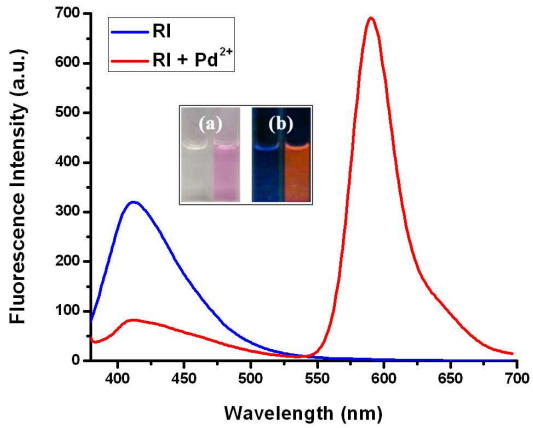


Fig. 1 Changes in fluorescence spectral of **RI** (10 μM) upon treatment with $PdCl_2$ (20 μM) in EtOH/H_2O (1:1, v/v) at room temperature. λ_{ex} = 360 nm. Inset: Photos show changes in the (a) visible color and (b) fluorescence color upon addition of $PdCl_2$.

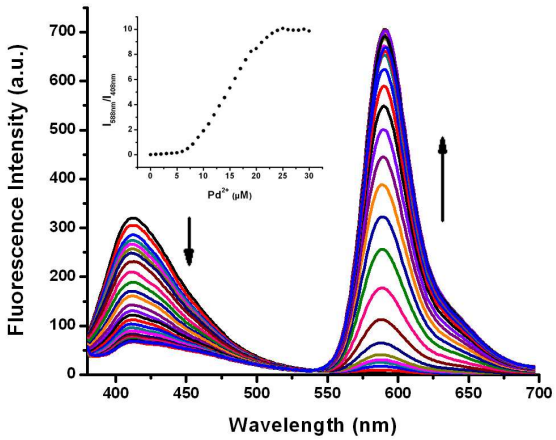
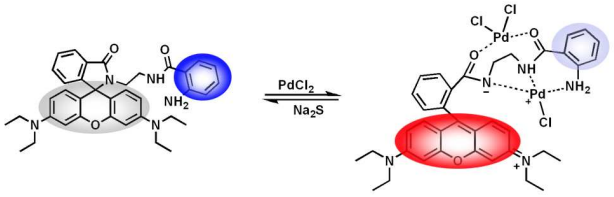


Fig. 2 Fluorescence spectra of **RI** (10 μM) upon titration with $PdCl_2$ (30 μM) in EtOH/H_2O (1:1, v/v) at room temperature. All spectra were recorded 10 min after the addition of Pd^{2+} ions. λ_{ex} = 360 nm. Inset: Changes in fluorescent intensities ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) in the presence of different concentrations of $PdCl_2$ (0 μM to 30 μM).

RI was synthesized according to procedures described in the literature.[61–63] The synthetic route is shown in Scheme 1. In solid state, the probe **RI** was a white powder with blue fluorescence, while in EtOH/H_2O (1:1, v/v), it formed a colorless solution and emitted blue fluorescence with the maxima at 408 nM. These observations indicate the ring-closed form of the rhodamine moiety, and the blue fluorescence can be ascribed to the anthraniloyl moiety. Addition of Pd^{2+} ions to the **RI** solution quenched the blue fluorescence, while a strong red fluorescence due to the opening of the spirolactam ring is observed, and the solution turned brilliant pink. The addition of Pd^{2+} ions shifted the fluorescence maxima from 408 nm to 588 nm. As shown in Fig. 1, the probe **RI** can detect Pd^{2+} ions through both fluorescence and colorimetric methods.

Changes in the fluorescence intensity ratio (I_{588nm}/I_{408nm}) of **RI** on treatment with $PdCl_2$ were monitored over time (Fig. S1). It was evident that the ratio rapidly increased for the initial 5 min and leveled off after 10 min. Therefore, all the subsequent tests were carried out after allowing for a 10 min equilibration time.



Scheme 2 Proposed mechanism for the complexation of Pd^{2+} with **RI**.

The changes in the fluorescence spectra of **RI** upon titration with Pd^{2+} ions are shown in Fig. 2. It is apparent that with increasing Pd^{2+} ion concentration, fluorescence intensity of **RI** at 408 nm decreased while a new emission peak at 588 nm appeared and increased. The fluorescence intensity ratios (I_{588nm}/I_{408nm}) linearly varied with the concentrations of Pd^{2+} ions in the range of 0 μM to 4 μM (Fig. S2), and the detection limit for Pd^{2+} ions with **RI** was 73.8 nM.[64] The fluorescence intensity ratio of **RI** (10 μM) reached the maximum (700-fold enhancement) when the concentration of Pd^{2+} ions was 25 μM, and the intensity of absorption at 566 nm also reached saturation (Fig. S3). This observation indicated that the two Pd^{2+} ions are coordinated to each **RI** molecule, which was substantiated by the results from the Job plot (Fig. S4). The 1:2 complexation of **RI**/Pd^{2+} was further confirmed by electrospray ionization mass spectrometry (ESI MS) analysis (Fig. S5); $m/z_{observed}$ = 920.16, $m/z_{calculated}$ for $[\mathbf{RI}+2Pd^{2+}+3Cl^-]^+$ = 920.03. In addition, the ion corresponding to a 1:1 complex of Pd^{2+} and RI was also identified; $m/z_{observed}$ = 744.25, $m/z_{calculated}$ for $[\mathbf{RI}+Pd^{2+}+Cl^-]^+$ = 744.19.

The coordination reaction between **RI** and Pd^{2+} ions was further probed by titration of the complex with sulfide (S^{2-}) (Fig. S6). Concurrent with the addition of Na_2S, the fluorescence intensity at 588 nm decreased, while the intensity of the peak at 408 nm increased. Addition of an excess amount of Na_2S completely quenched the fluorescence at 588 nm. Reaction with sulphide removed the coordinated Pd^{2+} ions from the complex, thereby, liberating **RI** (and its chromophoric features). These observations indicate that the coordination of the ligand with Pd^{2+} ions lead to the observed changes in the chromophoric characteristics of the probe. Considering the observations, a mechanism for the recognition of Pd^{2+} ions by **RI** is proposed (Scheme 2).

The probe **RI** recognized Pd^{2+} ions with high selectivity when compared with other common metal ions (Na^+, K^+, Ag^+, Hg^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+}, Fe^{3+}, Fe^{2+}, Co^{3+}, Zn^{2+}, Mn^{2+}, Ca^{2+}, Al^{3+}, Mg^{2+}, and La^{3+}) and platinum-group (Ru^{3+}, Rh^{3+}, Pt^{2+}) metal ions (Fig. 3). A large increase in the fluorescence intensity ratio (I_{588nm}/I_{408nm}) was induced only by Pd^{2+} ions, while other metal ions caused insignificant increases in the ratio. Interference experiments (determining Pd^{2+} ions in the presence of other ions) were also performed (Fig. 4). Most of the metal ions caused only tiny variations in the fluorescence intensity ratio when compared with the ratio obtained in the absence of any interference ions, and no obvious reduction of the fluorescence intensity ratio was observed.

The spirolactam ring of the rhodamine moiety in **RI** is susceptible to changes in pH; at strongly acidic pH, the ring opens, making the non-fluorescent rhodamine moiety emit red fluorescence. Such behavior can interfere with the detection of

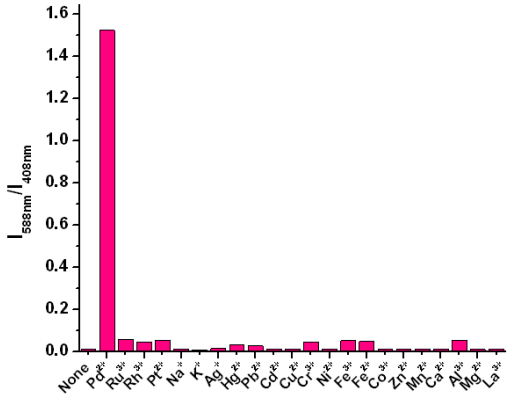


Fig. 3 Fluorescence intensity ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) in the presence of metal ions (10 μM for Pd^{2+} ions and 20 μM for other metals) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

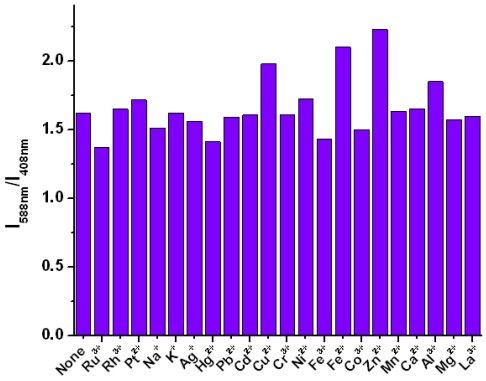


Fig. 4 Fluorescence intensity ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) after addition of $PdCl_2$ (10 μM) in the presence of other metal ions (20 μM) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

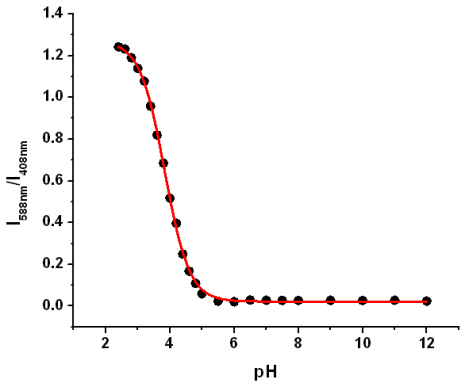


Fig. 5 Plot depicting the pH (2.4–12)-dependent variation in fluorescence intensity ratio (I_{588nm}/I_{408nm}) of **RI** (10 μM) in EtOH/H_2O (1:1, v/v). λ_{ex} = 360 nm.

Pd^{2+} ions. Therefore, we evaluated the fluorescence properties of **RI** in solutions with different pH values (2.4–12, Fig. 5). The fluorescence intensity ratio (I_{588nm}/I_{408nm}) of the probe remained stable in the pH 5.5–12 range. When the pH value was ≤5, an increase in the intensity of flourescence at 588 nm due to the rhodamine moiety is observed, while the fluorescence intensity at 408 nm remained almost unchanged (Fig. S8). The analysis of the pH curve determined the pK_a of **RI** to be 3.84 ± 0.01.

In summary, a highly selective and sensitive ratiometric fluorescent probe for Pd^{2+} ions is reported. The probe **RI** exhibits both fluorometric and colorimetric responses to Pd^{2+} ions, thus providing a method for visual detection of Pd^{2+} ions. Different from the reported ratiometric Pd^{2+} probes, the change in the fluorescence of **RI** is induced by complexation with Pd^{2+} ion, thereby providing a new approach of developing ratiometric probe for palladium.

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Notes and references

1 G. Zeni and R. C. Larock, *Chem. Rev.*, 2004, **104**, 2285.
2 L. F. Tietze, H. Ila and H. P. Bell, Chem. Rev., 2004, 104, 3453.
3 T. W. Lyons and M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147.
4 T. Iwasawa, M. Tokunaga, Y. Obora and Y. Tsuji, *J. Am. Chem. Soc.*, 2004, **126**, 6554.
5 M. Lafrance and K. Fagnou, *J. Am. Chem. Soc.*, 2006, **128**, 16496.
6 *Handbook of Organopalladium Chemistry for Organic Synthesis*, ed. E. Negishi and A. de Meijere, Wiley, New York, 2002.
7 J. Magano and J. R. Dunetz, *Chem. Rev.*, 2011, **111**, 2177.
8 K. C. Nicolaou, P. G. Bulger and D. Sarlah, *Angew. Chem. Int. Ed.*, 2005, **44**, 4442.
9 S. L. Buchwald, C. Mauger, G. Mignani and U. Scholz, *Adv. Synth. Catal.*, 2006, **348**, 23.
10 J. S. Carey, D. Laffan, C. Thomson and M. T. Williams, *Org. Biomol. Chem.*, 2006, **4**, 2337.
11 J. P, Huang, X. X. Chen, S. X.Gu, L.Zhao, W. X.Chen and F. E. Chen, *Org. Process Res. Dev.*, 2010, **14**, 939.
12 G. Reginato, P. Sadler and R. D. Wilkes, *Org. Process Res. Dev.*, 2011, **15**, 1396.
13 L. Wang, L. Green, Z. Li, J. McCabe Dunn, X. Bu, C. J. Welch, C. Li, T. Wang, Q. Tu, E. Bekos, D. Richardson, J. Eckert and J. Cui, *Org. Process Res. Dev.*, 2011, **15**, 1371.
14 B. Li, R. A. Buzon and Z. Zhang, *Org. Process Res. Dev.*, 2007, **11**, 951.
15 K. M. Bullock, M. B. Mitchell and J. F. Toczko, *Org. Process Res. Dev.*, 2008, **12**, 896.
16 A. L. Garner, F. Song and K. Koide, *J. Am. Chem. Soc.*, 2009, **131**, 5163.
17 J. T. Bien, G. C. Lane and M. R. Oberholzer, *Top. Organomet. Chem.*, 2004, **6**, 263.
18 K. Ravindra, L. Bencs and R. Van Grieken, *Sci. Total Environ.*, 2004, **318**, 1.
19 J. C. Ely, C. R. Neal, C. F. Kulpa, M. A. Schneegurt, J. A. Seidler and J. C. Jain, *Environ. Sci. Technol.*, 2001, **35**, 3816.
20 S. Rauch, H. F. Hemond, C. Barbante, M. Owari, G. M. Morrison, B. Peucker-Ehrenbrink and U. Wass, *Environ. Sci. Technol.*, 2005, **39**, 8156.
21 F. Zereini, C. Wiseman and W. Puttmann, *Environ. Sci. Technol.*, 2007, **41**, 451.
22 J. C. Wataha and C. T. Hanks, *J. Oral Rehabil.*, 1996, **23**, 309.
23 C. L. S. Wiseman and F. Zereini, *Sci. Tot. Env.*, 2009, **407**, 2493.
24 T. Gebel, H. Lantzsch, K. Plebow and H. Dunkelberg, *Mut. Res.-Gen. Toxicol. Env.*, 1997, **389**, 183.
25 International Programme on Chemical Safety. Palladium, Environmental Health Criteria Series 226; World Health Organization,Geneva, 2002.
26 J. Kielhorn, C. Melber, D. Keller and I. Mangelsdorf, *Int. J. Hyg. Env. Health*, 2002, **205**, 417.

27 C. E. Garrett and K. Prasad, *Adv. Synth. Catal.*, 2004, **346**, 889.
28 K. Van Meel, A. Smekens, M. Behets, P. Kazandjian and R. Van Grieken, *Anal. Chem.*, 2007, **79**, 6383.
29 C. Locatelli, D. Melucci and G. Torsi, *Anal. Bioanal. Chem.*, 2005, **382**, 1567.
30 B. Dimitrova, K. Benkhedda, E. Ivanova and F. Adams, *J. Anal. At. Spectrom.*, 2004, **19**, 1394.
31 H. Li, J. Fan and X. Peng, *Chem. Soc. Rev.*, 2013, **42**, 7943.
32 J. Du, M. Hu, J. Fan and X. Peng, *Chem. Soc. Rev.*, 2012, **41**, 4511.
33 M. E. Jun, B. Roy and K. H. Ahn, *Chem. Commun.*, 2011, **47**, 7583.
34 J. Zhang, Y. Zhou, J. Yoon and J. S. Kim, *Chem. Soc. Rev.*, 2011, **40**, 3416.
35 D. T. Quang and J. S. Kim, *Chem. Rev.*, 2010, **110**, 6280.
36 R. M. Duke, E. B. Veale, F. M. Pfeffer, P. E. Krugerc and T. Gunnlaugsson, *Chem. Soc. Rev.*, 2010, **39**, 3936.
37 A. Tamayo, L. Escriche, J. Casabo, B. Covelo and C. Lodeiro, *Eur. J. Inorg. Chem.*, 2006, 2997.
38 T. Schwarze, H. Muller, C. Dosche, T. Klamroth, W. Mickler, A. Kelling, H. G. Lohmannsroben, P. Saalfrank and H. J. Holdt, *Angew. Chem. Int. Ed.*, 2007, **46**, 1671.
39 R. J. T. Houk, K. J. Wallace, H. S. Hewage and E. V. Anslyn, *Tetrahedron*, 2008, **64**, 8271.
40 S. Fu, Z. Liu, S. Liu, J. Liu and A. Yi, *Anal. Chim. Acta.*, 2007, **599**, 271.
41 V. Madhu and S. K. Das, *Eur. J. Inorg. Chem.*, 2006, 1505.
42 S. Mukherjee, S. Chowdhury, A. K. Paul and R. Banerjee, *J. Lumin.*, 2011, **131**, 2342.
43 H. N. Kim, M. H. Lee, H. J. Kim, J. S. Kim and J. Y. Yoon, *Chem. Soc. Rev.*, 2008, **37**, 1465.
44 Z. Q. Hu, C. S. Lin, X. M. Wang, L. Ding, C. L. Cui, S. F. Liu and H. Y. Lu, *Chem. Commun.*, 2010, **46**, 3765.
45 X. Chen, T. Pradhan, F. Wang, J. S. Kim and J. Yoon, *Chem. Rev.*, 2012, **112**, 1910.
46 O. A. Egorova, H. Seo, A. Chatterjee and K. H. Ahn, *Org. Lett.*, 2010, **12**, 401.
47 J. Du, J. Fan, X. Peng, P. Sun, J. Wang, H. Li and S. Sun, *Org. Lett.*, 2010, **12**, 476.
48 H. Li, J. Fan, J. Du, K. Guo, S. Sun, X. Liu and X. Peng, *Chem. Commun.*, 2010, **46**, 1079.
49 H. Li, J. Fan, F. Song, H. Zhu, J. Du, S. Sun and X. Peng, *Chem. Eur. J.*, 2010, **16**, 12349.
50 H. Li, J. Fan, M. Hu, G. Cheng, D. Zhou, T. Wu, F. Song, S. Sun, C. Duan and X. Peng, *Chem. Eur. J.*, 2012, **18**, 12242.
51 K. Komatsu, Y. Urano, H. Kojima and T. Nagano, *J. Am. Chem. Soc.*, 2007, **129**, 13447.
52 D. Srikun, E. W. Miller, D. W. Domaille and C. J. Chang, *J. Am. Chem. Soc.*, 2008, **130**, 4596.
53 A. Ajayaghosh, P. Carol and S. Sreejith, *J. Am. Chem. Soc.*, 2005, **127**, 14962.
54 Z. Xu, K. H. Baek, H. N. Kim, J. Cui, X. Qian, D. R. Spring, I. Shin and J. Yoon, *J. Am. Chem. Soc.*, 2010, **132**, 601.
55 D. W. Domaille, L. Zeng and C. J. Chang, *J. Am. Chem. Soc.*, 2010, **132**, 1194.
56 B. Zhu, C. Gao, Y. Zhao, C. Liu, Y. Li, Q. Wei, Z. Ma, B. Du and X. Zhang, *Chem. Commun.*, 2011, **47**, 8656.
57 J. Jiang, H. Jiang, W. Liu, X. Tang, X. Zhou, W. Liu and R. Liu, *Org. Lett.*, 2011, **13**, 4922.
58 J. Wang, F. Song, J. Wang and X. Peng, *Analyst*, 2013, **138**, 3667.
59 B. Liu, H. Wang, T. Wang, Y. Bao, F. Du, J. Tian, Q. Li and R. Bai, *Chem. Commun.*, 2012, **48**, 2867.
60 H. Chen, W. Lin and L. Yuan, *Org. biomol. chem.*, 2013, **11**, 1938.
61 J. H. Soh, K. Swamy, S. K. Kim, S. Kim, S. H. Lee and J. Yoon, *Tetrahedron Lett.*, 2007, **48**, 5966.
62 C. Kaewtong, B. Wanno, Y. Uppa, N. Morakot, B. Pulpokac and T. Tuntulani, *Dalton Trans.*, 2011, **40**, 12578.
63 N. Hunter and K. Vaughan, *J. Heterocyclic Chem.*, 2006, **43**, 731.
64 M. Shortreed, R. Kopelman, M. Kuhn and B. Hoyland, *Anal. Chem.*, 1996, **68**, 1414.

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