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A simple and effective fluorescent chemosensor for the cascade recognition of Zn^{2+} and $H_2PO_4^-$ ions in protic media

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ABSTRACT

The chiral Schiff base *N*-(2-hydroxy-1-naphthyl)methylidene-(*S*)-α-phenylethylamine (**1**) was designed and synthesized as a fluorescent chemosensor based on the photoinduced electron transfer (PET) and C═N isomerization mechanisms. The receptor exhibited a highly selective switch-on fluorescence response toward Zn^{2+} and especially avoided the interference of Cd^{2+} when the detection was conducted in unbuffered methanol solution. Furthermore, the in situ generated **1**·Zn^{II}-complex could be employed for the specific recognition of $H_2PO_4^-$ by fluorescence turn-off signaling through a ligand displacement process.

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1. Introduction

Ions are ubiquitous and play pivotal roles in biological and environmental processes.[1] For example, zinc ions are involved in gene transcription, regulation of metalloenzymes, neural signal transmission, and apoptosis in living systems,[2] while pollution from inorganic phosphate anions and phosphorylated compounds are in part responsible for the eutrophication of natural water sources.[3] Accordingly, a considerable effort has been devoted to develop efficient and selective methods to detect Zn^{2+} or phosphate ions using fluorescence probes.[4,5] Although numerous chemosensors for a single species have been developed, there are very few reports on the sensing systems that allow the differential response to multiple analytes.[6] Recently, Yamato and co-workers described a new type of fluorescent sensor based on a pyrene-linked triazole-modified homooxacalix-[3]arene, which displayed ratiometric selectivity for Zn^{2+} and $H_2PO_4^-$ ions in neutral solution.[7] Bhalla et al. synthesized a fluorescent probe utilizing terphenylphenanthroline based macrocycle as a scaffold. The probe molecule showed high selectivity for zinc ions in THF; the addition of $H_2PO_4^-$ to the probe solution containing Zn^{2+} produced a blue-shifted emission band.[8] Undoubtedly, such chemosensors with multiple analyte recognition capability are cost effective and would be highly desirable from the viewpoint of practical applications.

Extensive research suggests that the rational use of nitrogen-containing fragments as a receptor unit is an efficient strategy in the design of fluorescent chemosensors for Zn^{2+}. Typical receptors to construct Zn^{2+} chemosensors include di-2-picolylamine, quinoline, bipyridine, acyclic and cyclic polyamines, triazole, and so on.[4,7,8] The nitrogen of a Schiff base is known to have high affinity for zinc. Therefore several fluorescent chemosensors with Schiff base (imine) structures have been developed for detecting zinc ions based on different signaling mechanisms, such as the photoinduced electron transfer (PET), C═N bond isomerization, and excited-state intramolecular proton transfer (ESIPT).[9] On the other hand, zinc also exhibit higher affinity toward phosphate functionality. Certain zinc(II) complexes of cresolic, polyammonium macrocycle, or porphyrin derivatives have been successfully used to achieve selective recognition of phosphate anions as the result of dative coordinative interaction between the metal center and a negatively charged oxygen atom present on the guest species.[10] These facts motivated us to explore the possibility of using a simple receptor molecule for monitoring both zinc ion and phosphate anions of interest.

In the present work, we designed and synthesized a chiral Schiff base *N*-(2-hydroxy-1-naphthyl)methylidene-(*S*)-α-phenyl-ethylamine (**1**) (Scheme 1). The Schiff base is fluorescently silent in the free-state owing to the PET from the imino nitrogen to the naphthalene fluorophore core and/or the C═N bond isomerization in

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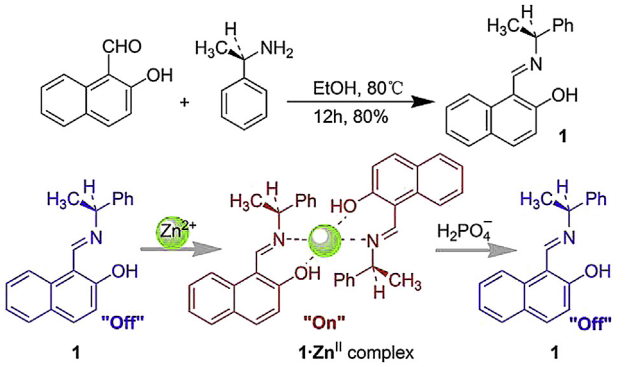
the excited states.[11] It can be expected that the formation of a metal complex would suppress both the PET and the conformational transition and thereby provoke fluorescence emission. In addition, the chiral feature of the receptor **1** allows the exploration of the possible host–guest interactions through circular dichroism spectroscopy. The results of our investigation show that **1** is highly selective to Zn^{2+} ion in switching-on-type fluorescence responses in unbuffered methanol solution. Moreover, the emission of **1** induced with Zn^{2+} ion could be selectively quenched by $H_2PO_4^-$. As a result, this simple Schiff base **1** serves as an efficient fluorescence probe for successively detecting Zn^{2+} and $H_2PO_4^-$ ions. To the best of our knowledge, similar examples are fairly limited in literature.[6–8,12]



Scheme 1. The synthetic procedure for receptor **1** and schematic representative of fluorescent sensing toward Zn^{2+} and $H_2PO_4^-$ ions.

2. Results and discussion

2.1. The interaction of receptor 1 with various cations

The binding behavior of receptor **1** toward various metal ions was examined by means of fluorescence in unbuffered methanol. The free receptor **1** (50 μM) showed a weak band with emission maxima positioned around 451 nm on excitation at 400 nm (Fig. 1). Upon addition of 0.5 equiv of Zn^{2+}, receptor **1** exhibited a remarkable enhancement in emission accompanied by a slight blue shift from 451 to 448 nm. The ratio of the emission intensity at 448 and 451 nm (I_{448}/I_{451}) reached 13.6. In contrast to what was seen with Zn^{2+}, much smaller fluorescence increase was observed with other metal ions. For example, the I_{448}/I_{451} values were 3.1 and 2.0 for Al^{3+} and Fe^{3+}, respectively. Little increase or a slight quenching in the emission intensity was detected upon the addition of Ag^+, Mg^{2+}, Cd^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, and Ca^{2+} into the methanol solution of **1**.

The expected preference for Zn^{2+} was observed, as inferred from competitive experiments (Fig. 2). It is noteworthy that the receptor **1** displayed a considerable ability to distinguish Zn^{2+} from Cd^{2+} in a common solution, which is usually difficult because both ions have similar chemical properties.[9j,13] The receptor binds Zn^{2+} more effectively than Cd^{2+} when acetonitrile was used as the solvent. However, in both cases this assay was subject to a severe interference from Cu^{2+} and Fe^{3+} ions. In general, Cu^{2+} can be considered as a fluorescence quencher, like other heavy metals with partially filled d-shells.[4d,f;14] As for the interference of Fe^{3+}, it may be attributed the possibility that the ligand was preferentially ligated by ferric ion due to its stronger complexing ability compared with Zn^{2+}.

Fluorescence titration spectra of **1** with Zn^{2+} are shown in Fig. 3. In the titration experiments employing **1** of 50 μM, the blue emission intensity around 448 nm increased with the ion concentration. Minimum 2.5 μM concentration of Zn^{2+} can be easily

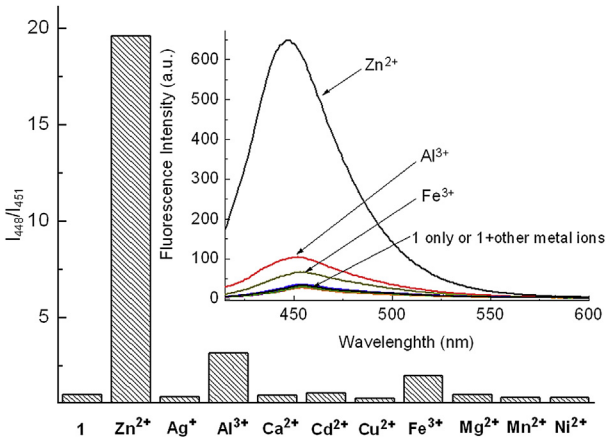


Fig. 1. Fluorescence responses of **1** (50 μM, λ_{ex}=400 nm) to various metal ions (25 μM) in methanol. I_{451} is the fluorescence emission intensity at 451 nm for the free **1**, and I_{448} is the fluorescence intensity at 448 nm after adding metal ions. Inset: the corresponding fluorescence spectra of **1** in the absence and presence of respective metal ions.

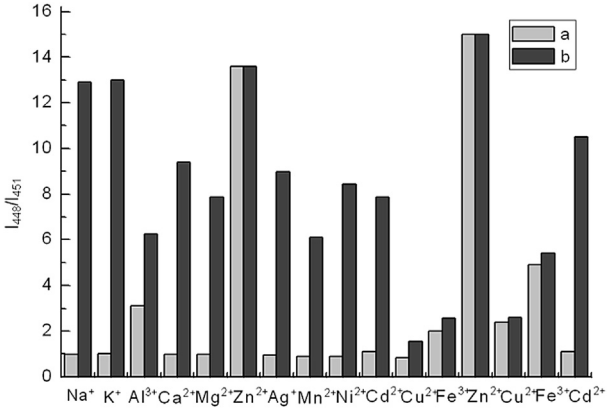


Fig. 2. Series (a) showing fluorescence response of **1** (50 μM) upon addition of various metal ions (0.5 equiv) and series (b) showing competitive selectivity of **1** towards Zn^{2+} in the presence of other metal ions (1 equiv) in methanol solution. Last four sets of data are from the competition experiments conducted in CH_3CN. λ_{ex}=400 nm.

detected by a threefold enhancement in the fluorescence intensity. Such a low detection limit might fully meet the requirements in biosensing. The fluorescence increase was saturated with 0.5 equiv of Zn^{2+}, indicating a 2:1 stoichiometry of the host–guest

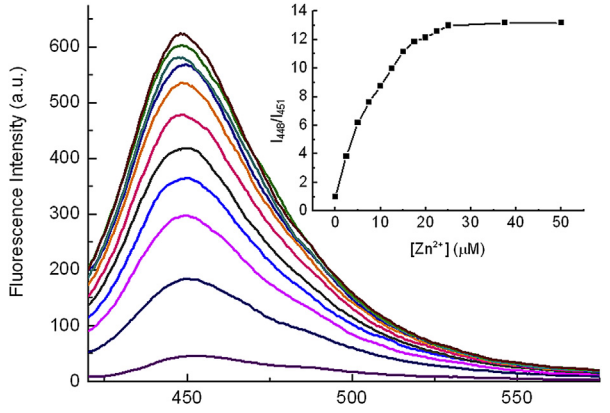


Fig. 3. Fluorescence titration profiles of **1** (50 μM) with $Zn(NO_3)_2$ (0–25 μM) in methanol (λ_{ex}=400 nm). Inset shows plots of the relative emission intensity (I_{448}/I_{451}) as a function of Zn^{2+} concentration (0–50 μM).

interactions. This binding stoichiometry in solution was further confirmed by the Job's plot of **1** with Zn^{2+} (Fig. S1). From the spectral titration data, the association constant (log K_{ass}) was determined to be 3.58.

Fig. 4 displays the UV–vis titration spectra of **1** with Zn^{2+} in methanol. The free ligand in solution exhibits characteristic absorption bands due to the $\pi \rightarrow \pi^*$ transitions of the intramolecularly hydrogen-bonded naphthaldimine chromophore at about 310 and 238 nm as well as two peaks around 400 and 418 nm, which resulted from the C=N isomerization.[9i] Upon addition of Zn^{2+} the two long wavelength peaks gradually merged to one, which indicates the imine cis–trans isomerization was interrupted. Although similar changes in absorption also happened with Cu^{2+} or Fe^{3+} (Fig. S2), only Zn^{2+} can lead to a large fluorescence enhancement (see: Fig. 1). Interestingly, the addition of Zn^{2+} ions did not seem to produce a substantial change in the CD spectra of **1** (the inset of Fig. 4).[15]

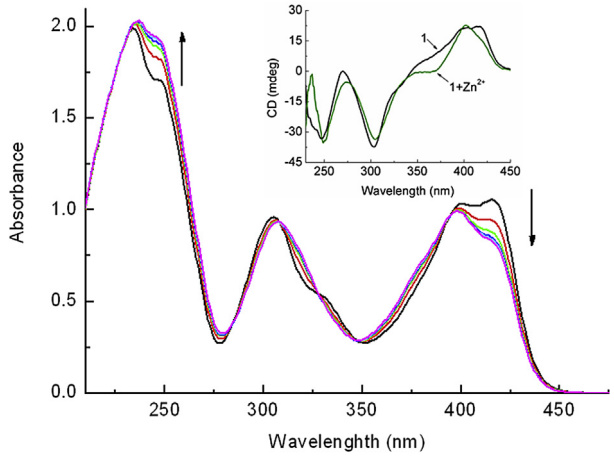


Fig. 4. UV–vis spectral changes of **1** (100 μM) upon successive addition of Zn^{2+} in methanol solution, [Zn^{2+}]=0, 10, 20, 30, 40, 50 μM. Inset: the corresponding CD change upon addition of 0.5 equiv of Zn^{2+}.

On the basis of above observations, the selective recognition of receptor **1** for Zn^{2+} over a variety of other cations is probably attributed to the fact that the chiral Schiff base as a bidentate chelate better satisfy the geometrical requirements of tetrahedral or pseudo-tetrahedral zinc(II) complexes.[16a] As depicted in the geometry optimized structure according to the density functional theory using B3LYP/6-31G(d) (Fig. 5), the in situ generated **1**·Zn^{II}-complex with two *N*,*O*-donor ligands coordinating to Zn^{2+} center is very similar to the closely related bis(salicylideneiminato)zinc(II) complexes.[16] The computed results show that there is a small conformational difference for the ligand before and after coordinating to Zn^{2+} ion. For the bound receptor, the lone pair of the imine nitrogen is engaged, electron transfer to the excited naphthalene fluorophore, i.e., the PET effect, does not take place. This may be responsible for the observed enhancement on luminescence response for receptor **1** on binding to Zn^{2+}. In addition, the formation of **1**·Zn^{II}-complex could inhibit the C=N isomerization, which is also expected to contribute to the observed switched-on emission. That is, the emission enhancement in the 1:2 Zn^{2+}·**1** complex is probably due to a combination of the retardation of PET and imine isomerization by chelation of both imine nitrogen atom and phenolic hydroxyl to metal ions.

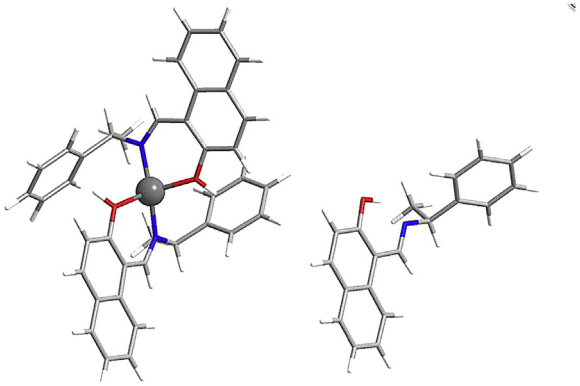


Fig. 5. Calculated energy-minimized structure for the in situ formed **1**·Zn^{II}-complex (left) and receptor 1 (right).

To gain a better understanding of the binding mode of Zn^{2+} to **1**, we also performed ^{1}H NMR titration (Fig. S3). The results showed that the proton signals of phenolic hydroxyl and imino groups were observable throughout the titration. This means that the complexation process of **1** with Zn^{2+} does not involve the deprotonation.

2.2. The sensing behavior of 1·Zn^{II}-complex toward anions

It is conceivable that the Zn^{2+}-containing complex of **1** is labile and thus an anion binding to the metal center would displace the neutral ligand and thereby change or recover its spectroscopic behavior. This coordination complex-based displacement approach has been used for detection of certain anionic species including phosphate anions.[7,8,10] In accord with the expectation, a dramatic decrease at the 448 nm emission was observed upon the addition of 0.15 equiv of NaH_2PO_4 into the solution of **1**·Zn^{II} (Fig. 6a). Both acetate and chloride induced a small increase for the fluorescence, whereas other anions (F^-, Br^-, I^-, NO_2^-, SO_4^{2-}, HPO_4^{2-}, PO_4^{3-}, or $P_2O_7^{4-}$) caused a slight fluorescence reduction. Compared with the sensing systems making using of hydrogen-bonding interaction,[5d,f,h] the in situ generated sensor appears to be attractive owing to the simplicity and particularly providing an effective discrimination of $H_2PO_4^-$ from AcO^- and F^- anions in protic media. Additionally, fluorescence titration results indicate that submillimolar concentrations of dihydrogen phosphate could be sensitively detected, and the relative emission intensity exhibited a good linear response to the change of $H_2PO_4^-$ concentrations in the 0.5–4.5 μM range (Fig. 6b).

Competition experiments were conducted for examining the selectivity of **1**·Zn^{II}-complex toward the detection of $H_2PO_4^-$. As shown in Fig. 7, little interference was observed in the presence of the other tested anions, even when certain anionic species were added at a threefold excess relative to $H_2PO_4^-$. Interestingly, comparison of spectral responses of **1**·Zn^{II}-complex and of its pre-synthesized analog bis{1-[1-phenylethyliminomethyl]-2-naphtholato-*N*,*O*}zinc(II) (**2**)[17] toward $H_2PO_4^-$ revealed that the former is a more sensitive sensor for the target anion under identical conditions (Figs. S4, S5). Both zinc(II)-complexes have almost the same fluorescence properties. Upon addition of 0.15 equiv of $H_2PO_4^-$ the emission of **2** was approximately quenched by 30%, whereas for the in situ formed **1**·Zn^{II}-complex its fluorescence was almost completely quenched. A set of comparable experiments without Zn^{2+} ions showed that almost no distinct spectral variations could be observed with the free ligand **1** (Fig. S6) upon addition of anions, suggesting that the formation of zinc(II) complex is indispensable for the anion detection. Nevertheless, the anion recognition effect of the metal complex decreases strongly in aqueous media (Fig. S7), which is related to its lower association constant (log K_{ass}=3.58).

3. Conclusions

In the present studies, we demonstrated that the chiral Schiff base **1** displays a highly selective fluorescence enhancement

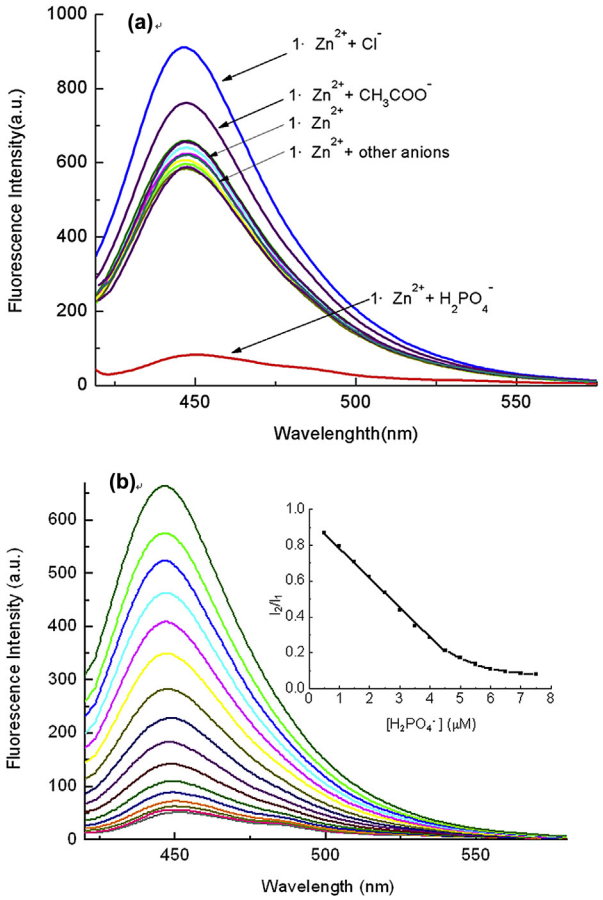


Fig. 6. (a) Fluorescence spectra of **1** (50 μM) in the presence of Zn^{2+} (0.5 equiv) in methanol upon addition of 0.15 equiv various anions (F^-, Cl^-, Br^-, I^-, NO_2^-, AcO^-, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, or $P_2O_7^{4-}$). λ_{ex}=400 nm. (b) Fluorescence titration spectra of **1** (50.0 μM) in the presence of Zn^{2+} (0.5 equiv) upon successive addition of $H_2PO_4^-$ in methanol solution (λ_{ex}=400 nm). Inset: relative emission intensity (I_2/I_1) versus $H_2PO_4^-$ concentration (0–7.5 μM). I_1 and I_2 represent the emission intensity of the solution of **1**·Zn^{II} before and after adding NaH_2PO_4, respectively.

toward Zn^{2+} over other metal ions of interest including Cd^{2+} in unbuffered methanol. Moreover, the in situ generated Zn^{II}-complex can be used as a probe for specifically detecting $H_2PO_4^-$ by fluorescence 'turn-off' signaling based on a ligand displacement mechanism. Thus, the cascade recognition of both ions was achieved by using the simple Schiff base derivative. This research suggests that the rational use of dynamical metal coordinative interaction may be a practicable strategy in the design of sensing systems for multiple analytes.

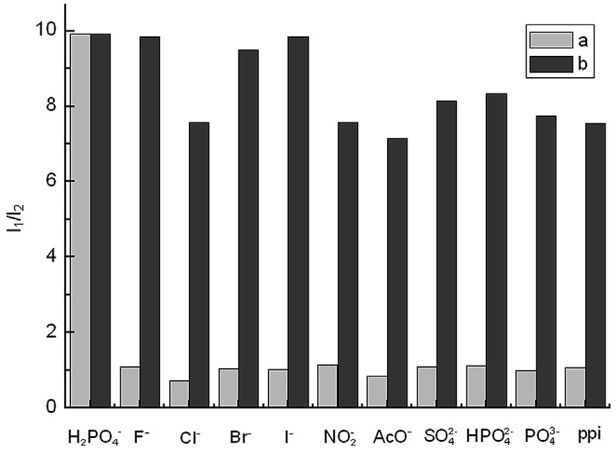


Fig. 7. Series (a) showing fluorescence response of **1**·Zn^{II}-complex (50 μM) toward various anions (0.15 equiv) and series (b) showing the competitive selectivity toward $H_2PO_4^-$ in the presence of different anions in methanol. λ_{ex}=400 nm.

4. Experimental

4.1. Reagents, instruments, and methods

2-Hydroxyl-1-naphthaldehyde, (*S*)-α-phenylethylamine, and all of the nitrate and sodium salts as analytes were purchased from Aladdin Shanghai Reagent Company. Methanol were strictly dehydrated and distilled before use. Other reagents were all used without any further purification.

^{1}H NMR and ^{13}C NMR spectra were recorded on a BruAvance AMX-400 or 500 NMR instrument. High-resolution mass spectrum (HRMS) was measured on a TripleTOF 4600 system with a Duo-Spray ion source. Steady-state fluorescence spectra were recorded on a Perkin–Elmer LS-55 fluorescence spectrometer in the right-angle geometry (90° collecting optics, λ_{ex}=400 nm). UV–vis spectra were obtained in methanol at 20 °C using a quartz cell of 1 cm on MOS-450 (Biologic Company, France).

The spectral analyses were accomplished in unbuffered methanol solution at room temperature. The concentration of **1** for fluorescence measurement was 50 μM and for UV–vis measurement was 100 μM. All the nitrate and sodium salts were prepared in aqueous solutions. UV–vis and fluorescence spectrophotometric titration were conducted directly in 2 mL cuvette by successive addition of corresponding chemical reagent using a microliter syringe. Upon addition of every aliquot, the solution was well mixed then the spectrum was measured.

4.2. Synthesis and characterization of receptor 1

To a solution of 2-hydroxyl-1-naphthaldehyde (1.72 g, 10.0 mmol) in ethanol (50 mL) was added (*S*)-α-phenylethylamine (1.21 g, 10.0 mmol). After refluxing at 80 °C for 12 h, the solvent was removed under reduced pressure to give the crude product. The product was recrystallized from *n*-hexane to give a yellow solid in 80% yield (2.45 g). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.96 (1H, m, $C_{10}H_6OH$), 9.33 (1H, d, *J* 8.2 Hz, *H*C=N), 8.14 (1H, d, *J* 8.4 Hz, $C_{10}H_aH_5$), 7.77 (1H, d, *J* 9.2 Hz, $C_{10}H_fH_5$), 7.67(1H, d, *J* 8.0 Hz, $C_{10}H_dH_5$), 7.38–7.48 (m, 5H, C_6H_5), 7.31 (m, 1H, $C_{10}H_bH_5$), 7.23 (m, 1H, $C_{10}H_cH_5$), 6.80 (1H, d, *J* 9.2 Hz, $C_{10}H_jH_5$), 5.01 (m, 1H, C*H*Me), 1.67 (3H, d, *J* 6.8 Hz, *Me*), see: Fig. S8; ^{13}C NMR (125 MHz, DMSO-d_6) δ 175.4, 158.2, 143.3, 137.3, 134.4, 129.4, 129.3, 128.4, 128.1, 126.7, 126.1, 124.9, 123.0, 119.4, 106.7, 61.4, 23.7; HRMS (TOF): MH^+, found 276.1371. $C_{19}H_{18}NO$ requires 276.1383. $[\alpha]_D^{20}$ +202.7 (*c* 0.5 g/dL, MeOH).

4.3. Computations

Geometry optimizations and zero-point energies of the compounds were performed in gas phase by the density functional theory (DFT) calculations at the B3LYP level[18] with a 6-31G(d) basis set using 'Gaussian program'.[19] Vibration frequencies were used to confirm intermediates (number of imaginary frequencies=0).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.10.099.

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