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A naphthalene benzimidazole-based chemosensor for the colorimetric and on-off fluorescent detection of fluoride ion

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ABSTRACT

A novel naphthalene benzimidazole (NBI)-based chemosensor (**D2**) was developed for fluoride ion (F^-) detection. The absorption spectrum of **D2** changed dramatically from yellow to blue in the visible region accompanied with a 225 nm red shift of its absorption maximum upon the addition of F^- in DMSO. **D2** also exhibited a fluorescence turn-off response towards the fluoride ion. The emission intensity of **D2** decreased drastically along the increasing F^- concentration and the detection limit for F^- was as low as 3.2×10^{-9} mol/L. ^1H NMR and HRMS-ESI results indicated that the formation of NBI-O^- through the desilylation reaction of F^- with NBI-OSi was responsible for the spectral changes. Overall, this kind of NBI-type molecules represent a new type chemosensor for the spectral detection of fluoride ion in solution.

1. Introduction

Anions play an important role in a wide range of chemical and biological processes [1–4]. Fluoride anion (F^-), as the smallest anion, holds a unique position among all the essential anions [5,6]. F^- is best known for its wide utilization in toothpaste, even though it is also frequently included in various pharmaceutical reagents for the treatment of osteoporosis and the prevention of dental cares and enamel demineralization [7–10]. However, high dose intake of F^- is harmful as it will cause fluorosis and nephrotoxic changes in both humans and animals [11–13]. Consequently, it is highly desirable to develop chemosensors with excellent selectivity and high sensitivity for the detection of F^-, preferably in solution phase [14,15]. Up to now, a large number of fluorescent sensors have been reported for F^- detection, most of which contain acceptors based on hydrogen bonding interaction or Lewis-acidic boron moieties, etc. [16]. As one of those most promising sensing strategies, fluorescence dosimetric detection of F^- based on irreversible chemical reaction has attracted increasing attention because of their high selectivity and stability [17]. Indeed, a series of F^- sensors based on F^--triggered Si—O bond cleavage and incidental release of fluorophores have been reported recently [18–26].

Naphthalene benzimidazole (NBI), a special class of environmentally sensitive fluorophore, exhibits excellent light-fastness and robust chemical and heat stability [27–29]. Several fluorescent sensors based on NBI have been developed to detect selectively ions, such as Cu^{2+} [30,31], Fe^{3+} [32], Cd^{2+} [33], OH^- [34], and Hg^{2+} [35,36]. However, to the best of our knowledge, there is no report of NBI-based chemosensors for F^- detection. Herein, we report a novel fluorescent sensor of 12-((*tert*-butyldiphenylsilyl)oxy)-8a,13a-dihydro-7H-benzo[*de*]benzo [4,5]imidazo[2,1-*a*]-isoquinolin-7-one (**D2**) for F^- detection, whose action is triggered by a desilylation and intramolecular charge-transfer mechanism. Our experimental results demonstrated that **D2** exhibited excellent selectivity and sensitivity for F^- detection in DMSO with a detection limit approaching 3.2×10^{-9} mol/L.

2. Results and Discussion

2.1. The Synthesis of Chemosensor D2

Our chemosensor **D2** was synthesized (Scheme 1) by two steps starting from 1,8-naphthalic anhydride, 2,3-diaminophenoland tert-butyl(chloro)diphenylsilane. The ^1H NMR spectra of the intermediate **D1** (3-((*tert*-butyldiphenylsilyl)oxy)benzene- 1,2-diamine) and **D2**, and the ^{13}C NMR and HRMS-ESI results of **D2** were included in Fig. S1–S4, respectively.

2.2. Colorimetric Analysis of D2 in the Presence of F^-

Fig. 1 showed the photo images of **D2** in DMSO without (blank) and with various anions such as F^-, Cl^-, Br^-, I^-, HSO_4^-, AcO^-, $H_2PO_4^-$, and ClO_4^- (as TBA^+ salts). It was visually apparent that a color change from yellow to blue occurred only in the presence of F^- (Fig. 1, top).

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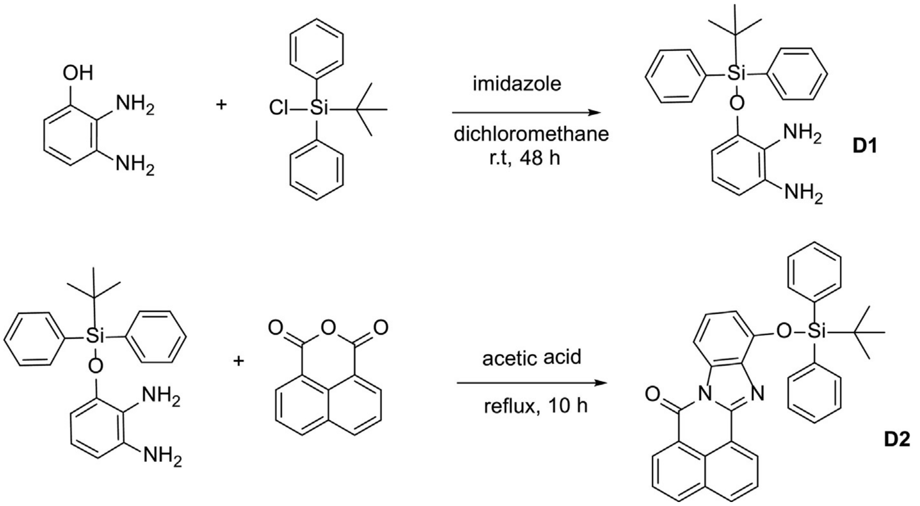


Scheme 1. Synthetic route of **D2**.

Under a UV lamp, strong fluorescence was observed from **D2** with the addition of other anions but F^- (Fig. 1, bottom).

2.3. Spectral Response of D2 Upon the Addition of F^-

The above color changes could also be verified by spectral methods. The absorption and fluorescence emission spectra of **D2** in the presence of anions (F^-, Cl^-, Br^-, I^-, HSO_4^-, AcO^-, $H_2PO_4^-$, ClO_4^-) were shown in Fig. 2. It could be seen from Fig. 2a that the absorption maximum of **D2** in DMSO was 395 nm. When 30 equiv. of F^- were added into the solution of **D2**, a red-shift from 395 to 620 nm ($\Delta\lambda = 225$ nm) was observed. However, other anions of equal concentrations caused insignificant changes on absorption spectra. The results indicated that **D2** could selectively detect F^- in DMSO. On the other hand, free **D2** exhibited a strong fluorescence emission centered at 530 nm (Fig. 2b). When 3 equiv. of anions were added into the DMSO solution of **D2** respectively, only F^- caused the fluorescence quenching remarkably, while other anions caused tiny changes. Therefore, according to the fluorescence and absorption results, **D2** was a highly efficient sensor for F^-. Meanwhile, the response of **D2** for F^- was also very fast (Fig. S5).

2.4. The Control Experiments With Other Common Anions

The selectivity of **D2** towards F^- was also studied by anion-competitive experiments (Fig. 3). The diagram displayed that the fluorescence intensities of **D2** after adding 3 equiv. F^- were almost unaffected by other common anions. In other words, **D2** could maintain its sensing response to F^- in the presence of other relevant anions. These results indicated that **D2** could serve as a chemosensor for F^- with high selectivity and strong anti-interference ability.

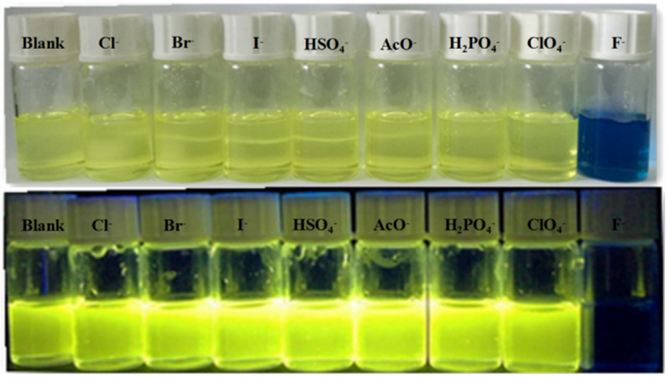


Fig. 1. Color changes induced by adding excess equivalents of various anions (TBA^+ salts) to **D2** (1×10^{-4} M) in DMSO under day lighting (top) and UV lamp (bottom).

2.5. The Absorption and Fluorescent Titration Curves of D2 Upon the Addition of F^-

In order to investigate the quantitative analysis of **D2** for F^-, the absorption titration curves were plotted in Fig. 4a. The absorption maximum of **D2** in DMSO was 395 nm, while the peak shifted to 620 nm upon addition of F^-. As far as we know, such a red shift of 225 nm in absorption was uncommon as to F^- sensors. The ratios of absorption intensities at 620 nm to those at 395 nm ($A_{620\ nm}/A_{395\ nm}$) fitted linear relation to F^- concentration in DMSO (Fig. 4b), which indicated that the **D2** could detect F^- quantitatively in DMSO with the UV–vis absorption method.

As mentioned above, **D2** also showed fluorescence turn-off property beside absorption change. To gain an insight into the fluorescence response of **D2** for F^- in DMSO, the fluorescence titration experiments were conducted and the results were depicted in Fig. 5a. When F^- were added to the DMSO solution of **D2**, the fluorescence intensities of **D2** at 530 nm decreased gradually until almost completely quenched when 30 equiv. of F^- were added [quenching efficiency $(I_0 - I)/I_0 \times 100\% = 98.5\%$, where I and I_0 were the fluorescence signal in the presence and absence of F^-, respectively]. The fluorescence intensities were not only highly sensitive, but also linearly corrected to F^- concentration. We obtained the slope as 411 for **D2** from the linear equation of fluorescence intensity to F^- concentration (Fig. 5b). The limit of detection (LOD) of **D2** for F^- was 3.2×10^{-9} M based on LOD $= 3\sigma/s$, where σ was the standard deviation of blank measurements and s was the slope. These data demonstrated that **D2** showed a potential to quantitatively detect F^- in DMSO with the fluorescence method.

2.6. The Sensing Mechanism of D2 for the Detection of F^-

Both the changes of absorption and fluorescence indicated that the structure of **D2** might broke and a new species was formed. To elucidate the mechanism of interaction between **D2** and F^-, the reaction process was monitored by ^1H NMR and HRMS-ESI. The systematic changes in ^1H NMR signals of **D2** upon addition of increasing amounts of F^- were shown in Fig. 6a. When F^- selectively attacked the silicon atom of the silyl ether group, the increased negative charge on the phenolate oxygen atom induced release of NBI-O^- (Scheme 2) [37–39]. The change of chemical structure accounted for the change of color and spectra.

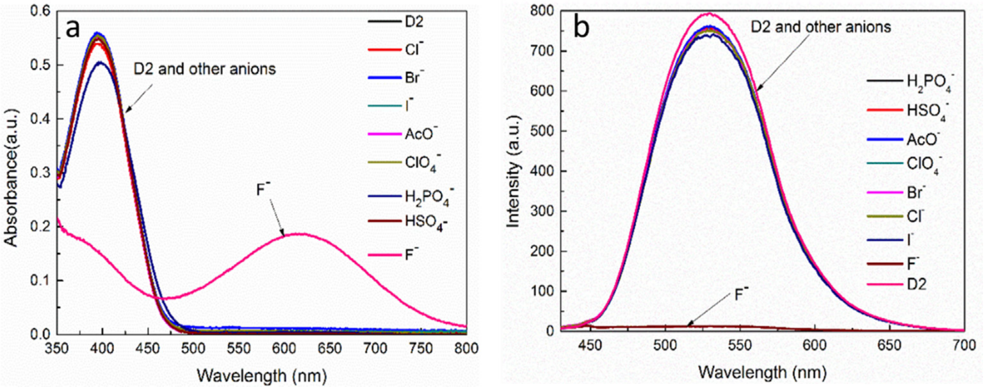


Fig. 2. (a) Absorption spectra of **D2** (1×10^{-5} M) in the presence of 30 equiv. of different anions in DMSO. (b) Fluorescent emission spectra of **D2** (1×10^{-5} M) in DMSO ($\lambda_{ex} = 395$ nm) after adding 3 equiv. of different anions.

After addition of F$^-$, the chemical shifts of protons on aromatic ring moiety shifted to up field respectively. On the other hand, to gain insight into the sensing mechanism, mass spectra were carried out and the changes in HRMS-ESI signals of sensor **D2** upon addition of F$^-$ were shown in Fig. 6b. **D2** gave a m/e peak of $[M + H]^+$ at 525.2001. After adding F$^-$, Si—O bond broken and promoted deprotection of **D2** to give NBI-O$^-$, and in HRMS-ESI a m/e peak of $[M]^-$ at 285.0670 occurred corresponding to that of NBI-O$^-$. These observations confirmed that the deprotection proceeded with the addition of F$^-$, and accordingly resulted in the spectral changes.

3. Conclusions

An efficient chemosensor **D2** was designed for the colorimetric detection of F$^-$. The chemical structure of **D2** was confirmed by ^{1}H NMR, ^{13}C NMR, and HRMS-ESI. **D2** showed excellent specificity towards F$^-$ based on F$^-$-triggered Si—O bond cleavage, which gave rise to a visible color change accompanied by a large red shift (225 nm) in absorption maximum and fluorescence quenching. Our results suggested that NBI could serve as a chromophore moiety for the design of chemosensors for the colorimetric detection of F$^-$.

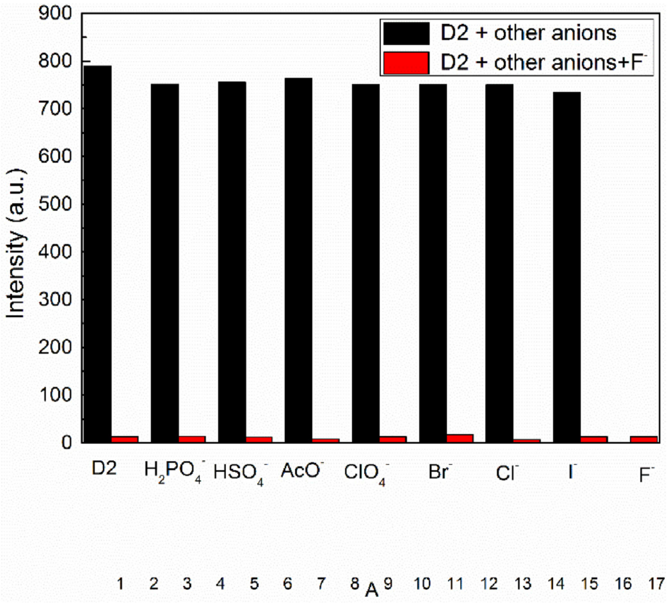


Fig. 3. Anion selectivity of **D2** towards F$^-$. Black bars: fluorescence intensities of **D2** (1×10^{-5} M) or **D2** and different anions (3×10^{-5} M) in DMSO. Red bars: fluorescence intensities of **D2** (1×10^{-5} M) after addition of F$^-$ (3×10^{-5} M) in the presence of different anions (3×10^{-5} M). Excitation wavelength was 395 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4. Experimental

4.1. Materials

All of the tetrabutylammonium (TBA$^+$) salts and other chemical reagents were purchased from Aladdin Shanghai Reagent Company. Organic solvents were purchased from commercial suppliers and used without further purification. All reactions were monitored by thin layer chromatography (TLC) analysis. Flash chromatography separations were carried out using silica gel (200–300 mesh).

4.2. Measurements and Instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV III 400 MHz NMR spectrometer with tetramethysilane (TMS) as the internal standard. HRMS-ESI data were obtained on an Agilent 6510 equipped with an electrospray source. UV–vis spectra were collected on a UV-2550 spectrophotometer. Fluorescent spectra were recorded on an RF-5301PC fluorescence spectrophotometer.

4.3. Calculation of Quantum Yield

The quantum yield was calculated according to the following Formula (1):

$$\Phi_u = \Phi_s \frac{F_u A_s {n_u}^2}{F_s A_u {n_s}^2} \tag{1}$$

where Φ is fluorescence quantum yield; F is the integrated area under the corrected emission spectra; A is the absorbance at the excitation wavelength; n is the refractive index of the solution; the subscripts u and s refer to the unknown and the standard samples, respectively. The quantum yield is 0.97 when Rhodamine B in ethanol solution was used as the standard.

4.4. Synthesis of D2

D2 was synthesized from *tert*-butyl(chloro)diphenylsilane according to the reported method [40].

4.4.1. Synthesis of 3-((tert-butyldiphenylsilyl)oxy)benzene-1,2-diamine (D1)

2,3-diaminophenol (0.44 g, 3.6 mmol) and imidazole (0.5 g, 7.3 mmol) were added into 40 mL of dry dichloromethane, and then *tert*-butyl(chloro)diphenylsilane (0.96 mL, 3.6 mmol) was added. The

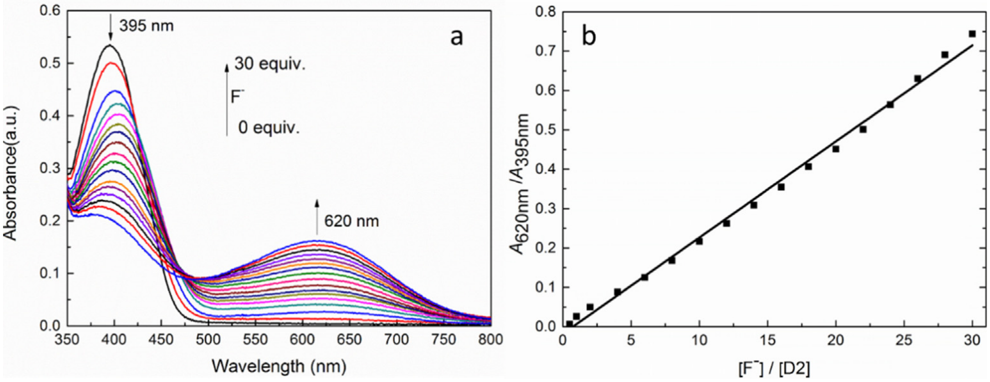


Fig. 4. Absorption spectra of **D2** (1×10^{-5} M) in the presence of F^- (0–30 equiv.) in DMSO (left), and the corresponding linear ability of (A_{620} nm/A_{395} nm) versus the F^- concentration in DMSO (right).

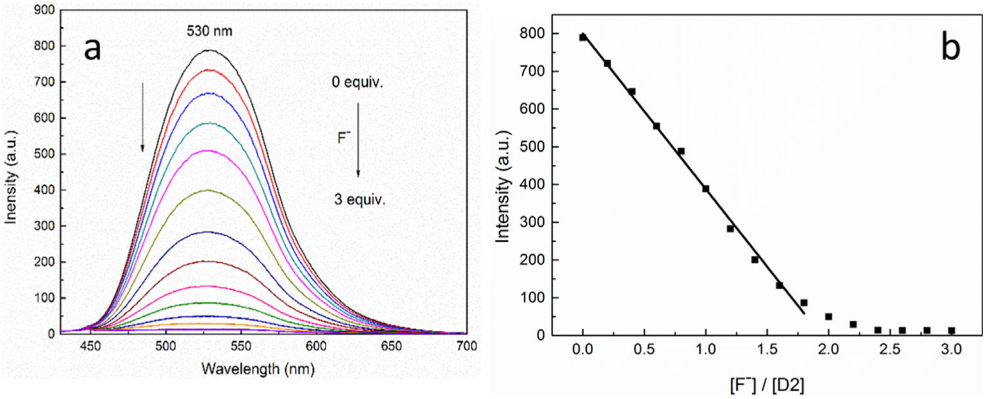


Fig. 5. (a) Fluorescence titration spectra of **D2** (1×10^{-5} M) in the presence of F^- ($0–3 \times 10^{-5}$ M) in DMSO (excited at 395 nm). (b) Plot of the emission intensities of **D2** versus concentration of F^- in DMSO.

mixture was stirred at room temperature for 48 h. Subsequently, the mixture was concentrated and purified by preparative thin-layer chromatography (PTLC) using dichloromethane/methanol (30:1, v/v) as the eluent to produce compound **D1**. Yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 6.5$ Hz, 4H), 7.44–7.51 (m, 6H), 6.34–6.38 (m, 2H), 6.10 (dd, $J = 5.8$, 3.6 Hz, 1H), 3.64 (s, 4H), 1.23 (s, 9H).

4.4.2. Synthesis of 12-((tert-butyldiphenylsilyl)oxy)-8a,13a-dihydro-7H-benzo[de]ben-zo[4,5]imidazo[2,1-a]isoquinolin-7-one (D2)

D1 (0.79 g, 2.2 mmol) and 1,8-naphthalic anhydride (0.39 g, 2.0 mmol) were mixed in 10 mL of glacial acetic acid. The mixture was heated to 118 °C for 10 h. Then the reaction mixture was cooled to room temperature. The obtained yellow solid precipitation was

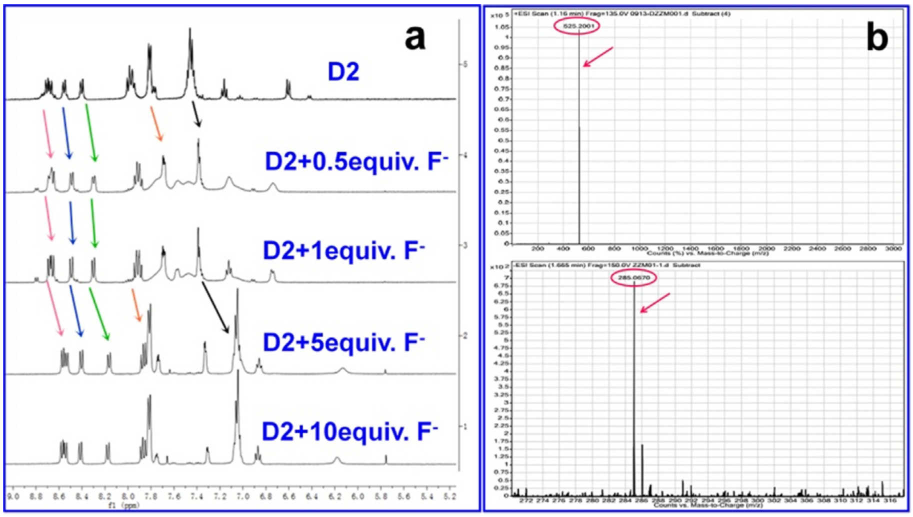
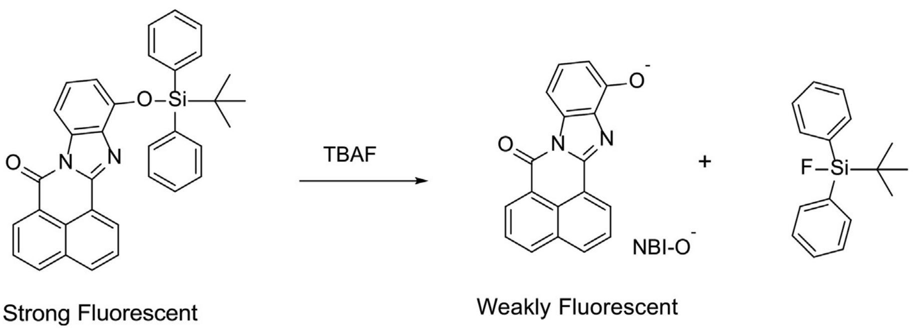


Fig. 6. (a) Partial ^{1}H NMR spectra of **D2** (1.3×10^{-5} M) in the presence of 0, 0.5, 1, 5 and 10 equiv. of TBAF in DMSO-d_6. (b) HRMS-ESI spectra of **D2** (top), and **D2** in the presence of F^- (bottom) in DMSO.



Scheme 2. F^- promoted release of NBI-O^-.

filtered and washed three times with glacial acetic acid to yield the final product **D2**. Yield: 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.78 (d, $J = 7.3$ Hz, 1H), 8.29 (d, $J = 8.2$ Hz, 1H), 8.15 (d, $J = 8.1$ Hz, 1H), 8.11 (d, $J = 8.0$ Hz, 1H), 7.93–7.86 (m, 4H), 7.83 (t, $J = 7.6$ Hz, 2H), 7.38–7.46 (m, 6H), 7.11 (t, $J = 8.1$ Hz, 1H), 6.67 (d, $J = 8.0$ Hz, 1H), 1.27 (d, $J = 15.8$ Hz, 9H)·^{13}C NMR (100 MHz, $CDCl_3$) δ 160.78, 147.77, 147.51, 136.07, 135.73, 135.08, 133.59, 133.20, 132.17, 131.32, 129.86, 127.83, 127.67, 127.30, 127.11, 126.99, 126.73, 125.86, 123.33, 121.01, 116.02, 109.05, 26.84, 19.95. HRMS (ESI) calculated: $C_{34}H_{28}N_2O_2Si$. $[M + H]^+ = 525.1998$, found: 525.2001.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.saa.2017.05.053.

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