Synthesis of ester-substituted dihydroacridine derivatives and their spectroscopic properties†

Ryota Suzuki, Reiki Tada, Takumi Hosoda, Youhei Miura and Naoki Yoshioka*

Three dihydroacridine derivatives, 2,7-bis(4-methoxycarbonylphenyl)-9,9-diphenyl-9,10-dihydroacridine (1), 2,8-bis(4-methoxycarbonylphenyl)-10,10-diphenyl-5,10-dihydrophenazasiline (2), and 2,7,9,9-tetraphenyl-9,10-dihydroacridine (3), were prepared and their spectroscopic properties were investigated. These compounds exhibited relatively high quantum yields in a range of solvents. The emission spectra of 1 and 2 displayed large solvatochromic shifts, while the fluorescence solvatochromic behavior was not observed in 3. The intramolecular charge transfer (CT) process from the electron donating moiety at the NH site to the electron withdrawing ester moiety occurs in the excited states of 1 and 2. The increase in the dipole moment induced by the CT process was determined to cause the positive fluorescence solvatochromism. The differences between the excited and ground state dipole moments based on the Lippert–Mataga expression were estimated. The effect of the push–pull substitution in the dihydroacridine π-conjugated system was also discussed using a computational method.

Introduction

Environment-sensitive fluorescent dyes are an interesting class of molecules exhibiting unique spectroscopic properties depending on the properties of their surroundings such as solvent polarity.1 Typical examples of these solvatochromic fluorophores are 4-dimethylamino phthalimide (4-DMAP),2 2-propionyl-6-dimethylaminonaphthalene (PRODAN),3 4-amino-1,8-naphthalimide (4-DN),4 and 6-N,N-dimethylamino-2,3-naphthalimide (6-DN)5 having a push–pull substituted π-conjugated system.6 It is also known that bridging an aromatic ring by a Si atom influences the spectroscopic property due to the hyperconjugation and perturbation of the electronic structure that often enhances the fluorescence intensity.7

During the course of the study on the synthesis and physicochemical properties of aromatic nitrooxide derivatives having rigid 1,2-dihydroquinone8 and 9,10-dihydroacridine9 backbones, we observed the fluorescence of phenyl substituted 9,10-dihydroacridine, which prompted us to investigate the structure–function relationship in 9,10-dihydroacridine derivatives because they have a planar backbone due to the cross-linked diphenylamine whose rigid structure is suitable for fluorescent molecules. In the present paper, we describe the synthesis of ester substituted derivatives, 2,7-bis(4-methoxycarbonylphenyl)-9,9-diphenyl-9,10-dihydroacridine (1) and its silicon containing analogue 2,8-bis(4-methoxycarbonylphenyl)-10,10-diphenyl-5,10-dihydrophenazasiline (2), and their spectroscopic properties in comparison with that of 2,7,9,9-tetraphenyl-9,10-dihydroacridine (3) (Fig. 1).

Results
Synthesis

The dihydroacridines, 1 and 3, were prepared in four steps from 9,9-diphenyl-9,10-dihydroacridine (4)10 according to Scheme S1 (ESI†). The aromatic substituent groups were introduced by the Suzuki–Miyaura cross-coupling reaction with good yields between the 2,7-dibromo-9,9-diphenyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester (6) with the 4-methoxycarbonylphenylboronic acid pinacol ester and the phenylboronic acid. 2,7-Dibromo-9,9-diphenyl-9,10-dihydroacridine (5) was protected with the tert-butoxycarbonyl group to enhance the reactivity. The synthetic scheme of the 2,8-diaryldihydrophenazasiline derivative, 2, is outlined in Scheme S2 (ESI†). 2 was prepared in six steps from 2,2′,4,4′-tetrabromodiphenylamine (9).11

Fig. 1 Chemical structures of 1, 2, and 3.
skeleton was constructed by the reaction between the o-dilithiodiphenylamine derivative and SiPh₂Cl₂ while the p-methoxybenzyl group was used as the protecting group for the NH site. The electron withdrawing group could be introduced by the Suzuki–Miyaura cross-coupling reaction via the same Scheme S1 (ESI†). The deprotection reaction of the BOC group was conducted using sulfuric acid in MeOH because the deprotection reaction using HCl in AcOEt did not provide a good yield.

### X-ray structural determinations

Block-shaped single crystals of 1 and 2 were obtained by slow evaporation from an acetonitrile solution. Their crystal structures were successfully determined by an X-ray crystallographic analysis (Table S1, ESI†). The ORTEP drawing is depicted in Fig. 2. 2 was crystallized with one molecule of acetonitrile and existed as two crystallographically independent structures (denoted as 2A and 2B). The bond lengths between the carbon atoms adjacent to the bridge atoms (C, Si) were 1: 1.539(3) Å, 1.543(3) Å, 2A: 1.837(5) Å, 1.848(6) Å, and 2B: 1.846(5) Å, 1.856(5) Å. The Si–C bond lengths are almost the same as the reported Si–C distance values which are 1.846 Å and 1.847 Å.¹³ The angles between the carbon atoms adjacent to the bridge atoms (C, Si) were 1: 108.66(15)°, 2A: 102.6(3)°, and 2B: 102.7(3)°. These angles depend on the atomic radius, and 1 has the larger angle. The long axes of the molecules were 1: 22.101 Å, 2A: 22.844 Å, and 2B: 22.860 Å. The dihedral angles between the dihydroacridine units and the 4-methoxycarbonyl units were 1: 23°, 32°, 2A: 24°, 30°, and 2B: 20°, 27°.

### Spectroscopic properties

The UV-vis and the fluorescence spectra of 1, 2, and 3 in various solvents are summarized in Table 1. The maximum absorption wavelengths of 1, 2, and 3 in MeOH were 370, 376, and 336 nm, respectively. Based on the UV-vis measurements, introduction of the ester group prompted a red-shift in the maximum absorption wavelength (Fig. S1, ESI†). While the wavelengths of the maximum absorptions of 1 and 2 were almost the same, the molar extinction coefficients of 2 were larger than those of 1 in all solvents. 1 and 2 exhibited a fluorescence solvatochromism and the emission spectra were also shifted along with a change in the solvent polarities, while 3 did not exhibit a fluorescence solvatochromism (Fig. 3). Shorter wavelength emission in an apolar solvent and longer wavelength emission in a polar solvent were observed for 1 and 2. The wavelength of the maximum emission of 1 was red-shifted by 98 nm from toluene to MeOH, while it was shifted 77 nm for 2 and 14 nm for 3. The Stokes shifts in toluene were 53 nm for 1, 41 nm for 2, and 48 nm for 3. Those in MeOH were 142 nm for 1, 108 nm for 2, and 58 nm for 3.

The CV measurements of 1, 2, and 3 were carried out to evaluate their electronic states. They have one reversible oxidation wave, and the half-wave potentials of 1, 2, and 3 were 0.50, 0.53 and 0.43 V (versus FeC/Fe⁷⁺), respectively (Fig. S2, ESI†). The oxidation potentials of 1 and 2 were higher than that of 3, which is explained by the introduction of the electron withdrawing ester group.

A DFT calculation with B3LYP/6-31G* was conducted to study the electronic structure (Fig. 4). Focusing on the molecular orbitals of the HOMO and LUMO, the HOMO distributes over the electron donating moiety and the LUMO is spread all over the electron withdrawing ester group. The energy gaps of 1, 2, and 3 have almost the same HOMO and LUMO energy levels, which are lower than those of 3. The energy gaps of 1, 2, and 3 are 3.78, 3.73 and 4.25 eV, respectively. The energy gaps of 1 and 2 are

### Table 1

Spectroscopic data of 1, 2, and 3 in various solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$E_c$(30)</th>
<th>$f (e)$</th>
<th>$\lambda_{abs,\text{max}}$ [nm]</th>
<th>$\varepsilon$ $\left[ 10^4 \text{M}^{-1} \text{cm}^{-1} \right]$</th>
<th>$\lambda_{em,\text{max}}$ [nm]</th>
<th>$\Phi_F$ [%]</th>
<th>$\varepsilon \times \Phi_F$ $\left[ 10^4 \text{M}^{-1} \text{cm}^{-1} \right]$</th>
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<tr>
<td>Toluene</td>
<td>33.9</td>
<td>0.24</td>
<td>361 366 332 3.9 5.5 3.2</td>
<td>414 407 380 65 69 63 2.5 3.8 2.0</td>
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<tr>
<td>THF</td>
<td>37.4</td>
<td>0.41</td>
<td>371 375 329 4.2 5.8 3.5</td>
<td>441 433 391 68 72 58 2.9 4.2 2.0</td>
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<tr>
<td>CH₂Cl₂</td>
<td>40.7</td>
<td>0.42</td>
<td>360 367 332 3.9 5.7 3.6</td>
<td>449 439 386 64 67 49 2.5 3.8 1.8</td>
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<td></td>
</tr>
<tr>
<td>DMF</td>
<td>43.2</td>
<td>0.48</td>
<td>376 381 338 4.1 5.7 3.4</td>
<td>472 462 399 60 62 69 2.3 3.5 2.3</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>MeCN</td>
<td>45.6</td>
<td>0.48</td>
<td>363 370 341 4.1 4.4 3.3</td>
<td>466 458 393 54 56 58 2.2 2.5 1.9</td>
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<tr>
<td>n-BuOH</td>
<td>49.7</td>
<td>0.46</td>
<td>378 382 339 3.8 5.6 3.3</td>
<td>472 461 392 53 53 63 2.0 3.0 2.1</td>
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<tr>
<td>EtOH</td>
<td>51.9</td>
<td>0.47</td>
<td>375 379 338 4.1 4.8 3.5</td>
<td>478 467 391 45 50 62 1.8 2.4 2.2</td>
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<tr>
<td>MeOH</td>
<td>55.4</td>
<td>0.48</td>
<td>370 376 336 4.2 5.7 3.5</td>
<td>512 484 394 17 25 57 0.7 1.4 2.0</td>
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smaller than that of 3. These calculations agree with the experimental results of the CV, UV-vis, and fluorescence spectra.

Discussion

We studied the correlation between the emission maxima and the solvent polarity index, $E_{T}(30)$ (Fig. 5). Good correlation was found in various solvents and linear fits were used to determine the slopes, i.e., 1: 240 cm$^{-1}$, 2: 241 cm$^{-1}$, 3: 78 cm$^{-1}$. These values of 1 and 2 are comparable to that of PRODAN (220 cm$^{-1}$)$^{15}$ and almost the same solvatochromic properties of PRODAN could be achieved using the dihydroacridine-based novel fluorophore.

The data plots in the protic solvents deviate up. For a further understanding, we studied the correlation as a function of the dielectric constant $f(e)$ which only accounts for the general dipolar interaction.$^{14}$ A high linearity was also observed in the aprotic solvents. On the other hand, the data plots in the protic solvents deviate low in 1 and 2 though a high linearity was observed in all solvents in 3. Though similar phenomena were reported in 3-hydroxyflavone$^{16}$ and 3-methoxychromone,$^{17}$ they could be assigned to the hydrogen bonding effects between the carbonyl group and solvents. To further study the fluorescence solvatochromic behaviors of 1 and 2, the difference between the ground and excited state dipole moments ($\mu_{E} - \mu_{G}$) was estimated by the Lippert–Mataga equation (eqn (1)),$^{18}$

$$\nu_{A} - \nu_{E} = \frac{2 \Delta \mu (\mu_{E} - \mu_{G})^{2}}{h c a^{3}}, \quad \Delta \mu = \frac{\varepsilon - 1}{2 \varepsilon + 1} - \frac{n^{2} - 1}{2 n^{2} - 1} \quad (1)$$

in which $\nu_{A}$ is the wavenumber of the absorption, $\nu_{E}$ is the wavenumber of the emission, $h$ is Planck’s constant, $c$ is the speed of light, $a$ is the cavity radius and $\Delta \mu$ is the orientation polarizability where $\Delta \mu$ is defined by the dielectric constant $\varepsilon$ and the refractive index $n$. The correlation between the Stokes shift and the orientation polarizability is shown in Fig. 6. Linear plots were obtained in various solvents and the slopes were 9959 cm$^{-1}$ ($R^{2} = 0.673$) for 1 and 9038 cm$^{-1}$ ($R^{2} = 0.805$) for 2.

The change in the dipole moments $\mu_{E} - \mu_{G}$ was estimated as 11.0 D for 1 and 10.5 D for 2 when 50% of the donor–acceptor
distance was used for the cavity radius17 and as 26.1 D for 1 and 26.2 D for 2 when 40% of the long axes of the molecular structure19 obtained by X-ray analysis was used for the cavity radius. These values of 1 and 2 are higher than the change in the dipole moments $\mu_R - \mu_G$ of the representative fluorescence solvatochromic dyes, Nile Red (6.8 D)20 and PRODAN (7.9 D).15

Although the quantum yields of 1 and 2 in MeOH were slightly low, the quantum yields of 1 and 2 were almost over 40% in other solvents. The quantum yields of 2 were higher than those of 1 in all solvents except for $n$-BuOH though their energy gaps between the HOMO and LUMO are almost the same. We assume that this observation is due to the introduction of the Si atom. The quantum yield is affected by radiation and non-radiation processes. The radiation process was accelerated in the Si atom substituted naphthalene derivatives.21 The Si atom might influence radiation and non-radiation processes. The higher molar extinction coefficients of 2 compared to those of 1 might be attributed to the acceleration of the radiation process. It is known that the quantum yield depends on the type of solvent and there are a few dyes which fulfill the noticeable solvatochromism and the high quantum yield in both polar and apolar media at the same time. The quantum yield often decreases in a polar or an apolar solvent although exhibiting the properties of fluorescence solvatochromism with a high quantum yield in both polar and apolar solvents is important for use as a fluorescent probe. The fluorescence spectra of 1 and 2 showed a broad peak in MeOH whereas that of 3 was sharp. The experimental results might be due to the reorganization of the dihydroacridine and ester-substituted phenyl units into a twisted charge transfer excited state conformation22 or aggregation induced in polar solvents.15 It might cause the decrease of the quantum yields in MeOH. On the other hand, the quantum yields of 3 were high in all solvents including MeOH. A TD-DFT calculation (B3LYP/6-31G*) for 1 was performed to estimate the optimized geometry at the excited state in toluene and MeOH (Fig. S3, ESI†). However, obvious difference was not observed between them. The fluorescence spectra of 3 showed a sharp peak in all solvents. The conformaion change at the excited state might not occur in 3. 3,8-Dibutyl-6-(piperidin-1-yl)pyrene-1-carbaldehyde (PA) and 1-(3,8-dibutyl-6-(piperidin-1-yl)pyren-1-yl)butan-1-one (PK) are known as the dyes which combine these two properties.15

PRODAN, 7-diethylamino-9,9-dimethyl-9H-fluorene-2-carbaldehyde (F0),23 1-(7-diethylamino-9,9-dimethyl-9H-fluoren-2-yl)-nonan-1-one (F8),23 7-diethylamino-9,9-dimethyl-9H-fluorene-2-carbaldehyde (F9),23 7-dimethylamino-9,10-dihydrophenanthrene-2-carbaldehyde (9Phen),23 and 1,3-diphenyl-2-[4-(N,N-diphenylamino)phenyl]-benzo[b]phosphole-P-oxide15 have been reported to show these two properties. Our spectroscopic data indicate that 1 and 2 also exhibit a fluorescence solvatochromism with high quantum yields in both polar and apolar solvents.

Conclusions

Spectroscopic properties of three dihydroacridine derivatives, 2,7-bis(4-methoxycarbonylphenyl)-9,9-diphenyl-10,10-dihydroacridine (1), 2,8-bis(4-methoxycarbonylphenyl)-10,10-diphenyl-5,10-dihydrophenazasiline (2), and 2,7,9-tetraphenyl-9,10-dihydroacridine (3), were investigated. These compounds exhibited relatively high quantum yields in a range of solvents (1: 17–68%, 2: 25–72%, 3: 49–69%). To evaluate their fluorescence behavior, the correlations between the fluorescence maxima and the empirical polarity parameter, $E_T$ (30), were studied. Linear correlations were obtained and the slopes for 1, 2, and 3 were 240, 241, and 78 cm$^{-1}$, respectively. The differences between the excited and the ground state dipole moments based on the Lippert–Mataga expression were higher than those of the representative fluorescence solvatochromic dyes, Nile Red and PRODAN. The effect of the push–pull substitution in the dihydroacridine $\pi$-conjugated system was discussed. Based on the MO calculation, the CT processes from the electron donating NH moiety to the electron withdrawing ester moiety are ascribed to causing the positive fluorescence solvatochromism in 1 and 2.

Experimental section

The reactions were performed under N$_2$ with the exception of the hydrogenation reaction. UV-vis and fluorescence spectra were recorded using JASCO V-650 and JASCO FP-777W, respectively. The quantum yields were determined by the absolute measurement using a Shimadzu RF-6000 attached integrating sphere unit. The CV measurements were performed in a CH$_2$Cl$_2$ solution with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte (298 K, 100 mV s$^{-1}$ scan rate). The observed redox potentials were corrected against the ferrocene/ferrofenium (Fc/Fc$^+$) couple. The X-ray diffraction data were collected by a Bruker D8 VENTURE diffractometer and refined by using SHELX-2014. Gaussian 03 programs were applied for the DFT calculations and Gaussian 09 programs were for the TD-DFT calculations.

2,7-Dibromo-9,9-diphenyl-10,10-dihydroacridine (5)

NBS (7.8 g, 4.4 eq.) dissolved in 20 ml of DMF was added to a solution of 9,9-diphenyl-10,10-dihydroacridine (1.7 g) in 10 ml of DMF. The reaction mixture was stirred at room temperature for 10 h. An aqueous solution of K$_2$CO$_3$ was then added to the mixture. The organic phase was extracted with AcOEt and dried over Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography.
(CH₂Cl₂/n-hexane = 1/2). The collected material was further purified by recrystallization from CH₂Cl₂/n-hexane to give a white solid (2.4 g, 95%). Mp 280–283 °C; ¹H NMR (300 MHz, acetone-d₆): δ = 8.63 (s, 1H), 7.35–7.27 (m, 8H), 6.96–6.92 (m, 6H), 6.86 (d, J = 2.4 Hz, 2H) ppm; ¹³C NMR (75 MHz, acetone-d₆): δ = 146.0, 140.2, 133.1, 131.1, 130.8, 129.9, 128.9, 127.7, 116.7, 112.5, 57.5 ppm; IR (KBr): 3389, 2360, 1665, 1598, 1472 cm⁻¹; MS (MALDI, matrix: SA): 490 [M + H]+; E.A. (%): found: C 61.01, H 3.33, N 2.87, calcd for C₂₅H₁₅Br₂N: C 61.13, H 3.31, N 2.87.

2,7-Dibromo-9,9-diphenyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester (6)

A solution of 2,7-dibromo-9,9-diphenyl-9,10-dihydroacridine (1.67 g, 3.4 mmol) and 4-dimethylaminopyridine (145 mg, 1.2 mmol) in dry THF, 2-(4-methoxyphenyl)acetic acid tert-butyl dicarbonate (1.13 g, 5.1 mmol, 1.5 eq.) in THF, and the reaction mixture was then poured into water and extracted with ethyl acetate. The organic extracts were washed with brine and dried (Na₂SO₄), concentrated, butyl dicarbonate (1.13 g, 5.1 mmol, 1.5 eq.) in THF, and the reaction mixture was refluxed for 24 h under nitrogen. The residue was poured into water and extracted with ethyl acetate. The organic extracts were washed with brine and dried with Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (ethyl acetate/n-hexane = 1/1). The collected material was further purified by recrystallization from CH₂Cl₂/n-hexane to give 6 as a white solid (1.86 g, 92%). Mp 204–209 °C; ¹H NMR (300 MHz, acetone-d₆): δ = 7.85 (s, 1H), 7.41–7.30 (m, 12H), 7.14 (d, J = 2.7 Hz, 2H), 6.98–6.96 (m, 4H), 1.22 (s, 9H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ = 167.0, 145.5, 145.3, 139.5, 132.1, 130.2, 130.1, 129.2, 128.4, 128.0, 127.9, 126.7, 126.3, 126.1, 114.3, 57.0, 52.0 ppm; IR (KBr): 3342, 2947, 1820, 1602, 1481, 1434, 1284, 1186, 1114 cm⁻¹; LRMS (EI): m/z (%): 524 (100) [M – C₆H₅]⁺, 601 (28) [M⁺]; HRMS (EI, quadrupole): m/z calcd for C₄₆H₃₉NO₆: 601.2253, found: 601.2268.

2,7,9,9-Tetraphenyl-9,10-dihydroacridine-10(9H)-carboxylic acid tert-butyl ester (8)

was obtained by a method similar to 7 and was obtained as a white solid (yield: 77%). Mp 242–246 °C; ¹H NMR (300 MHz, acetone-d₆): δ = 7.75 (d, J = 7.5 Hz, 2H), 7.63 (dd, J = 7.7 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 7.41–7.30 (m, 12H), 7.14 (d, J = 2.7 Hz, 2H), 6.98–6.96 (m, 4H), 1.22 (s, 9H) ppm; ¹³C NMR (75 MHz, CDCl₃): δ = 151.7, 143.8, 141.7, 140.7, 138.3, 137.3, 130.3, 128.7, 127.8, 127.1, 127.0, 126.9, 126.5, 125.0, 81.4, 58.6, 27.8 ppm; IR (KBr): 3392, 3056, 1602, 1474 cm⁻¹; LRMS (EI): m/z (%): 408 (100) [M – C₆H₅O₂⁺]², 484 (36) [M – Boc⁺]², 583.3 (18) [M⁺]; HRMS (EI, quadrupole): m/z calcd for C₄₁H₃₉N⁺: 407.1674, found: 407.1683.
6.82 (d, \( J \) = 8.4 Hz, 2H), 7.36 (d, \( J \) = 8.4 Hz, 2H), 7.26 (dd, \( J \) = 8.9 Hz, 2.3 Hz, 2H), 6.79 (d, \( J \) = 8.4 Hz, 4H), 4.68 (s, 2H), 3.75 (s, 3H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \( \delta \) = 158.7, 145.8, 138.6, 136.6, 130.9, 128.7, 128.6, 126.4, 121.9, 117.2, 113.8, 56.0, 55.1 ppm; IR (KBr): 2930, 2874, 1719, 1479, 1464, 1240, 1175 cm\(^{-1}\); LRMS (MALDI, matrix: SA): 605 [M\(^+\)]; E.A. (%): found: C 57.12, H 4.20, N 2.13, calcd for C\(_{24}\)H\(_{32}\)BrNO\(_2\)Si: C 57.34, H 4.15, N 2.31.

**2,8-Dibromo-10,10-diphenyl-5,10-dihydrophenazasiline-5(10H)-carboxylic acid tert-butyl ester (13)**

14 was prepared by a method similar to 7 and was obtained as a white solid. Yield: 51%; \( ^{1}H\) NMR (300 MHz, acetone-\( \text{d}_{6}\)): \( \delta \) = 8.04 (d, \( J \) = 8.7 Hz, 4H), 7.84–7.83 (m, 4H), 7.74–7.71 (m, 6H), 7.66–7.63 (m, 4H), 7.52–7.45 (m, 6H), 3.88 (s, 6H), 1.26 (s, 9H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \( \delta \) = 166.9, 153.3, 148.5, 145.6, 137.8, 137.0, 133.1, 131.4, 131.5, 131.0, 130.9, 129.9, 129.4, 129.3, 129.2, 127.8, 81.6, 52.3, 28.1 ppm; IR (KBr): 2976, 2950, 1719, 1609, 1597, 1489, 1457, 1321, 1278, 1161, 1110 cm\(^{-1}\); LRMS (EI): \( m/z \) (%): 540 (20) [M – 177], 617 (80) [M – 100], 662 (100) [M – 55], 717 (11) [M]; HRMS (ESI\(^{+}\), quadrupole): \( m/z \) calcd for C\(_{43}\)H\(_{39}\)NO\(_6\)Si [M + Na\(^+\)]: 740.2439, found: 740.2446.

**2,8-Dibromo-10,10-diphenyl-5,10-dihydrophenazasiline (12)**

Pd black (15 mg) and 11 (44 mg, 0.09 mmol) were placed in a one-necked flask and dichloromethane was then added. Nitrogen displacement was then conducted. The mixture was stirred for 15 h after the H\(_2\) displacement. Nitrogen was again displaced. The mixture was then filtered through Celite. Dichloromethane was added to carry out a conventional separation treatment. The organic extracts were washed with brine and dried with Na\(_2\)SO\(_4\). After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (CH\(_2\)Cl\(_2\)/n-hexane = 1/3). The collected material was further purified by recrystallization from CH\(_2\)Cl\(_2\)/n-hexane to give 12 as a white solid (25 mg, 63%). \( ^{1}H\) NMR (300 MHz, acetone-\( \text{d}_{6}\)): \( \delta \) = 9.01 (s, 1H), 7.60–7.57 (m, 6H), 7.51–7.44 (m, 8H), 7.09 (d, \( J \) = 9.0 Hz, 2H) ppm; \(^{13}C\) NMR (75 MHz, CDCl\(_3\)): \( \delta \) = 144.8, 137.8, 135.8, 133.9, 133.8, 130.1, 128.2, 117.4, 115.9, 112.8 ppm; IR (KBr): 3403, 1595, 1457, 1370, 1327, 1231 cm\(^{-1}\); LRMS (MALDI, matrix: SA): 505 [M\(^+\)]; E.A. (%): found: C 56.61, H 3.41, N 2.64, calcd for C\(_{24}\)H\(_{27}\)BrNSi: C 56.82, H 3.38, N 2.76.

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References


