

# A Palladium-Catalyzed Borylation/Silica Gel Promoted Hydrolysis Sequence for the Synthesis of Hydroquinine-6'-Boric Acid and Its Applications

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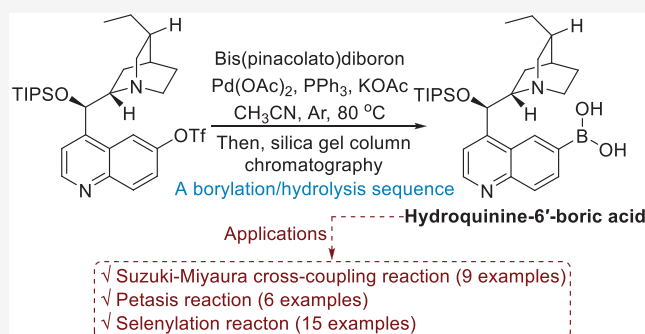
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**ABSTRACT:** Hydroquinine-6'-boric acid was first synthesized via a palladium-catalyzed borylation/silica gel promoted hydrolysis sequence of hydroquinine-derived triflate and bis(pinacolato)-diboron. The newly designed chiral building block was subjected to the Suzuki–Miyaura cross-coupling reaction, Petasis reaction, and selenylation reaction, respectively, and all these reactions worked well to afford the corresponding 6'-functionalized hydroquinines with satisfactory results, demonstrating its extraordinary application potency.



## INTRODUCTION

Arylboronic acids are highly active molecules that serve as the most essential building blocks in organic synthesis.<sup>1</sup> In the past decades, arylboronic acids participated in several significant types of coupling reaction, such as Suzuki–Miyaura cross-coupling reaction,<sup>2</sup> Chan–Lam reaction,<sup>3</sup> Liebeskind–Srogl reaction,<sup>4</sup> Petasis reaction,<sup>5</sup> *P*-arylation,<sup>6</sup> and selenylation,<sup>7</sup> leading to the construction of numerous valuable compounds—medicines, catalysts, natural products, and pesticides.<sup>8</sup>

Cinchona alkaloids, extracted from the bark of *Cinchona officinalis*, represent the most well-known natural products with quinine as a prominent member.<sup>9</sup> As early as the 17th century, cinchona alkaloids had been widely utilized for the treatment of malaria.<sup>10</sup> Additionally, they were recognized to exhibit a diverse spectrum of bioactivities like antineoplastic,<sup>11</sup> antimicrobial,<sup>12</sup> anti-inflammatory,<sup>13</sup> and analgesic<sup>14</sup> behaviors. On the other hand, a myriad of chiral organocatalysts have been created to facilitate the asymmetric synthesis of truly precious, optically pure molecules over the course of the past two decades, with cinchona alkaloids and their derivatives standing out as the most important members amidst them.<sup>15</sup> Currently, the structural transformations of cinchona alkaloids primarily include three aspects (Figure 1): (i) quinclidine isomerization,<sup>16</sup> terminal olefin conversion,<sup>17</sup> and quaternization;<sup>18</sup> (ii) conversions of secondary hydroxyl group at C-9 position comprising halogenation,<sup>19</sup> arylation,<sup>20</sup> amination,<sup>21</sup> hydroxyl protection,<sup>22</sup> and oxidation;<sup>23</sup> and (iii) structural modification of the quinoline-ring system at C-2', 5', 6', 7', and 8' positions.<sup>24</sup> It is noteworthy that the functionalization of the C-6' position is crucial, as the group at this position

often interacts with the quinclidine moiety, greatly affecting the biological activity or catalytic performance of cinchona alkaloids. Several studies focused on quinine or its derivatives to realize alkylation,<sup>25</sup> amination,<sup>26</sup> fluorination,<sup>27</sup> sulfonation,<sup>28</sup> and etherification<sup>29</sup> at the C-6' position for catalytic or pharmaceutical applications, predominantly due to the presence of convenient handles and the relatively lower cost compared to other cinchona alkaloids. Despite the seminal functionalization presented, it is still necessary to further adorn quinine and its derivatives at their C-6' position, thus accessing molecular diversity to meet the exuberant demand from drug discovery and asymmetric catalysis.

In this work, hydroquinine-6'-boric acid was first synthesized via a palladium-catalyzed borylation/silica gel promoted hydrolysis sequence of hydroquinine-derived triflate<sup>30</sup> and bis(pinacolato)diboron. The successful introduction of the boric acid group to the C-6' position of the quinoline ring bestowed infinite possibilities on the functionalization of hydroquinine. To demonstrate its application potency, hydroquinine-6'-boric acid was involved in a Suzuki–Miyaura cross-coupling with aryl bromides, achieving the decoration of hydroquinine effectively. Multicomponent reactions were widely used as complexity-generating tactics to rapidly

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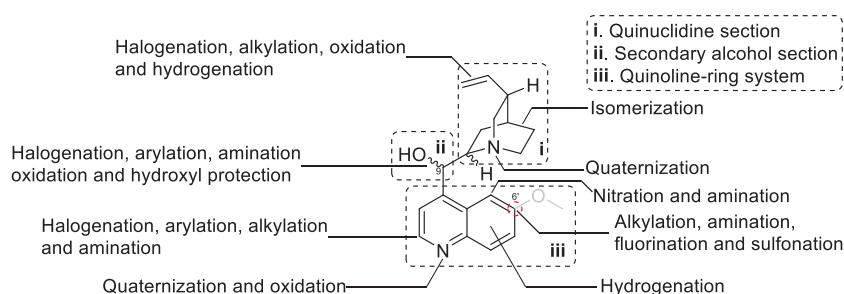
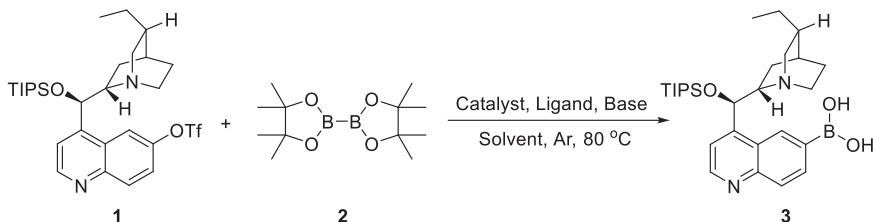


Figure 1. Structural modification of cinchona alkaloids.

Table 1. Optimization of Reaction Conditions<sup>a</sup>

Entry	Catalyst (mol %)	Ligand (mol %)	Solvent	Time (h)	Yield <sup>b</sup> (%)
1 <sup>c</sup>	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	1,4-Dioxane	8	N. R. <sup>j</sup>
2 <sup>d</sup>	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	1,4-Dioxane	8	N. R. <sup>j</sup>
3	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	1,4-Dioxane	4	30
4	PdCl <sub>2</sub> (5)	PPh <sub>3</sub> (20)	1,4-Dioxane	7	21
5	Pd(OAc) <sub>2</sub> (5)	DPPF (20)	1,4-Dioxane	8	10
6	NiCl <sub>2</sub> (5)	DPPP (5)	1,4-Dioxane	12	N. R. <sup>j</sup>
7	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	Toluene	24	11
8	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	DCE <sup>i</sup>	8	41
9	Pd(OAc) <sub>2</sub> (5)	PPh <sub>3</sub> (20)	CH <sub>3</sub> CN	4	85
10	Pd(OAc) <sub>2</sub> (3)	PPh <sub>3</sub> (12)	CH <sub>3</sub> CN	8	88
11	Pd(OAc) <sub>2</sub> (1)	PPh <sub>3</sub> (4)	CH <sub>3</sub> CN	8	5
12 <sup>e</sup>	Pd(OAc) <sub>2</sub> (3)	PPh <sub>3</sub> (12)	CH <sub>3</sub> CN	8	66
13 <sup>f</sup>	Pd(OAc) <sub>2</sub> (3)	PPh <sub>3</sub> (12)	CH <sub>3</sub> CN	8	79
14 <sup>g</sup>	Pd(OAc) <sub>2</sub> (3)	PPh <sub>3</sub> (12)	CH <sub>3</sub> CN	8	76
15 <sup>h</sup>	Pd(OAc) <sub>2</sub> (3)	PPh <sub>3</sub> (12)	CH <sub>3</sub> CN	12	86

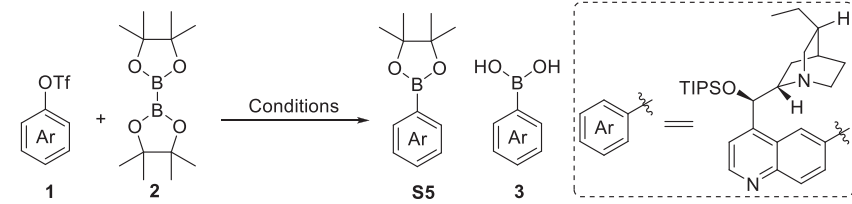
<sup>a</sup>Unless noted, the reaction was performed with **1** (600.8 mg, 1.0 mmol), **2** (380.9 mg, 1.5 mmol), and KOAc (294.4 mg, 3.0 mmol) in 10 mL of solvent at 80 °C under argon ambient; the solvent used was analytically pure but not ultradry; TIPS = triisopropylsilyl; Tf = triflyl. <sup>b</sup>Isolated yield after the purification by column chromatography on silica gel. <sup>c</sup>3.0 mmol of Cs<sub>2</sub>CO<sub>3</sub> were used. <sup>d</sup>3.0 mmol of NaOAc were used. <sup>e</sup>2.0 mmol of KOAc were used. <sup>f</sup>1.2 mmol of **2** was used. <sup>g</sup>1.0 mmol of **2** was used. <sup>h</sup>The reaction was performed on a 10.0 mmol scale. <sup>i</sup>1,2-Dichloroethane. <sup>j</sup>No reaction.

fabricate diverse frameworks of interests in synthetic and biological fields.<sup>31</sup> A catalyst-free Petasis reaction of hydroquinine-6'-boric acid, piperidine, and salicylaldehyde was then investigated, which afforded a set of hydroquinines equipped with aminoarylmethine motifs. Organoselenium compounds are a pivotal class of entities owing to their multitudinous applications in the realm of catalysis, pharmaceuticals, and agrochemicals.<sup>32</sup> Accordingly, we explored a CuO nanoparticles catalyzed coupling reaction of hydroquinine-6'-boric acid and dialkyl diselenides, and this reaction granted a series of distinctive hydroquinine-selenides.

## RESULTS AND DISCUSSION

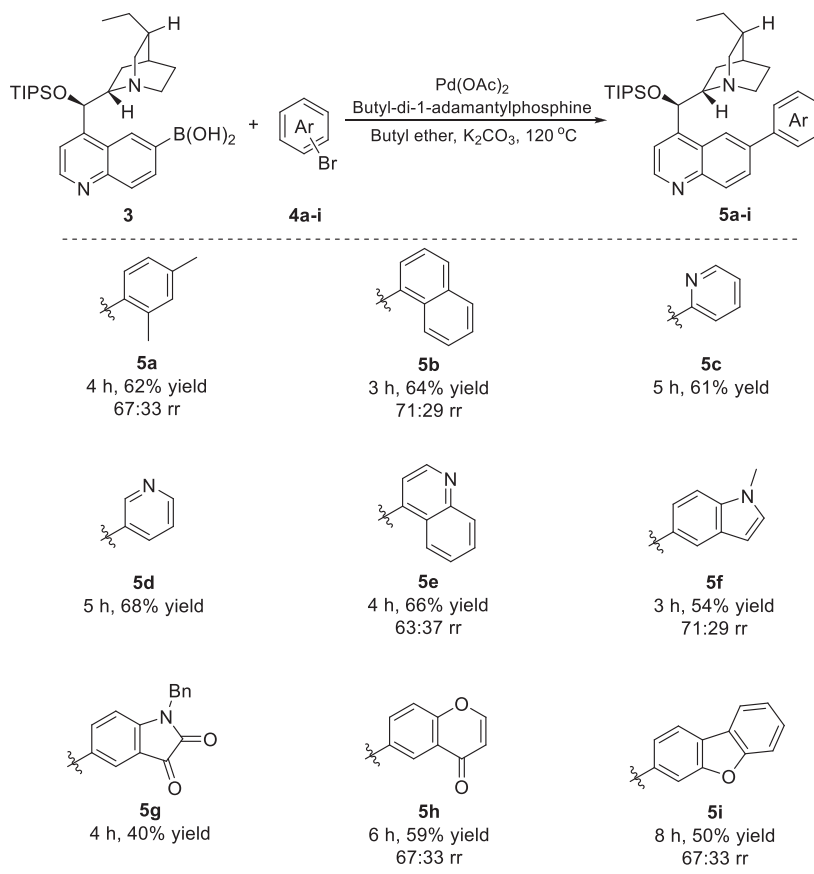
Initially, the palladium-catalyzed borylation reaction of hydroquinine-derived triflate **1** and bis(pinacolato)diboron **2** was conducted in the presence of Pd(OAc)<sub>2</sub> with triphenylphosphine (PPh<sub>3</sub>) as a ligand and Cs<sub>2</sub>CO<sub>3</sub> as a base in 1,4-dioxane (moisture content = 0.15%) under argon ambient, but no reaction was observed after being stirred at 80 °C for 8 h

(Table 1, entry 1). The same result was obtained when the inorganic base was replaced with NaOAc (entry 2). Fortunately, the reaction occurred smoothly to generate a new compound in 4 h, employing KOAc as the base (entry 3). However, the polarity of the compound was much larger than that of **1**, making us doubt whether the compound was hydroquinine-6'-borate. The structural characterization determined that the compound gained was hydroquinine-6'-boric acid **3** (30% yield). PdCl<sub>2</sub> exhibited lower catalytic activity, and only a 21% yield of product was obtained after 7 h (entry 4). Another ligand led to a worse result, as shown by the application of 1,1'-bis(diphenylphosphino)ferrocene (DPPF) (entry 5). The catalytic activity of NiCl<sub>2</sub> combined with 1,3-bis(diphenylphosphino)propane (DPPP) was tested, but it could not drive the reaction (entry 6). The solvents were screened, including toluene, 1,2-dichloroethane (DCE), and acetonitrile (entries 7–9). The use of acetonitrile (moisture content = 0.04%) as the solvent not only shortened the reaction time but also greatly increased the yield of product

Table 2. Controlled Experiments<sup>a</sup>


Entry	Conditions	Yield (%) of S5	Yield (%) of 3
1	Dry CH <sub>3</sub> CN. <sup>b</sup> Then, silica gel column chromatography	—	85 <sup>e</sup>
2	Dry CH <sub>3</sub> CN. <sup>b</sup> Then, filtered and concentrated	144 <sup>d</sup>	N. D. <sup>f</sup>
3	CH <sub>3</sub> CN. <sup>c</sup> Then, filtered and concentrated	147 <sup>d</sup>	N. D. <sup>f</sup>

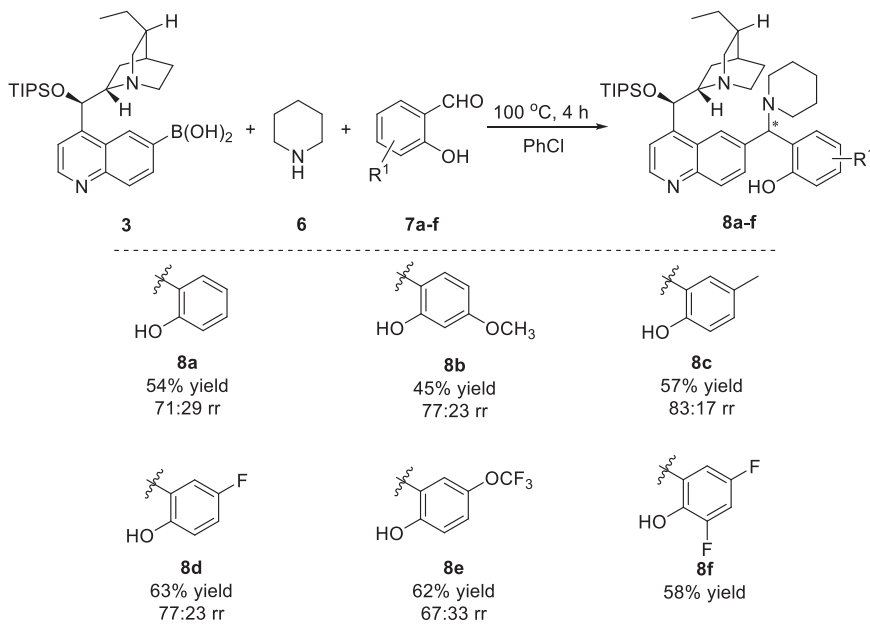
<sup>a</sup>The reaction was performed with **1** (120.2 mg, 0.2 mmol), **2** (76.2 mg, 0.3 mmol), Pd(OAc)<sub>2</sub> (1.35 mg, 3 mol %), PPh<sub>3</sub> (6.29 mg, 12 mol %), and KOAc (58.9 mg, 0.6 mmol) in 2 mL of solvent at 80 °C for 8 h under argon ambient. <sup>b</sup>Moisture content ≤10 ppm. <sup>c</sup>Moisture content = 0.04% (400 ppm). <sup>d</sup>Yield of crude product S5. <sup>e</sup>Isolated yield after the purification by column chromatography on silica gel. <sup>f</sup>Not detected in the crude product S5 by HRMS.

Table 3. Palladium-Catalyzed Suzuki–Miyaura Cross-Coupling Reaction of Hydroquinine-6'-Boric Acid and Aryl Bromides<sup>a,b,c</sup>

<sup>a</sup>Reaction conditions: **3** (49.7 mg, 0.1 mmol), **4a-i** (0.1 mmol), Pd(OAc)<sub>2</sub> (1.1 mg, 5 mol %), butyl-di-1-adamantylphosphine (7.2 mg, 20 mol %), and K<sub>2</sub>CO<sub>3</sub> (41.5 mg, 0.3 mmol) in butyl ether (2 mL), 120 °C. <sup>b</sup>Yield was determined after the product was purified by column chromatography on silica gel. <sup>c</sup>The rr value was determined by <sup>1</sup>H NMR analysis of the product.

(entry 9). Subsequently, we estimated the effect of the loading amount of catalyst and ligand on the reaction. It was found that 3 mol % of Pd(OAc)<sub>2</sub> together with 12 mol % of PPh<sub>3</sub> could still promote the reaction, affording the product in a slightly higher yield albeit with a prolonged reaction time (entry 10 vs entry 9). However, the catalytic efficiency dropped sharply using 1 mol % of Pd(OAc)<sub>2</sub> (entry 11). Reducing the amount of inorganic base was also detrimental to the reaction (entry

12). Finally, we checked the impact of the stoichiometry of the substrates on the reaction. Decreasing the amount of bis(pinacolato)diboron **2** resulted in slight erosion of the yield (entries 13 and 14 vs entry 10). To show the synthetic potential of this protocol, a preparative-scale synthesis of **3** was executed. Up to 10.0 mmol of **1** reacted with **2** smoothly under the optimized reaction conditions to provide the desired product **3** in maintained yield (entry 15). A single cuboid

Table 4. Petasis Reaction of Hydroquinine-6'-Boric Acid, Piperidine, and Salicylaldehydes<sup>a,b,c</sup>

<sup>a</sup>Reaction conditions: **3** (49.7 mg, 0.1 mmol), piperidine **6** (10.2 mg, 0.12 mmol), **7a-f** (0.1 mmol) in chlorobenzene (2 mL), 100 °C, 4 h. <sup>b</sup>Yield was determined after the product was purified by column chromatography on silica gel. <sup>c</sup>The rr value was determined by <sup>1</sup>H NMR analysis of the product.

crystal of triflate monohydrate of hydroquinine-6'-boric acid **3** was obtained by recrystallization from a petroleum ether/ethyl acetate system, and the absolute configuration of **3** was established by X-ray crystallographic analysis (CCDC number: 2141376).<sup>33</sup>

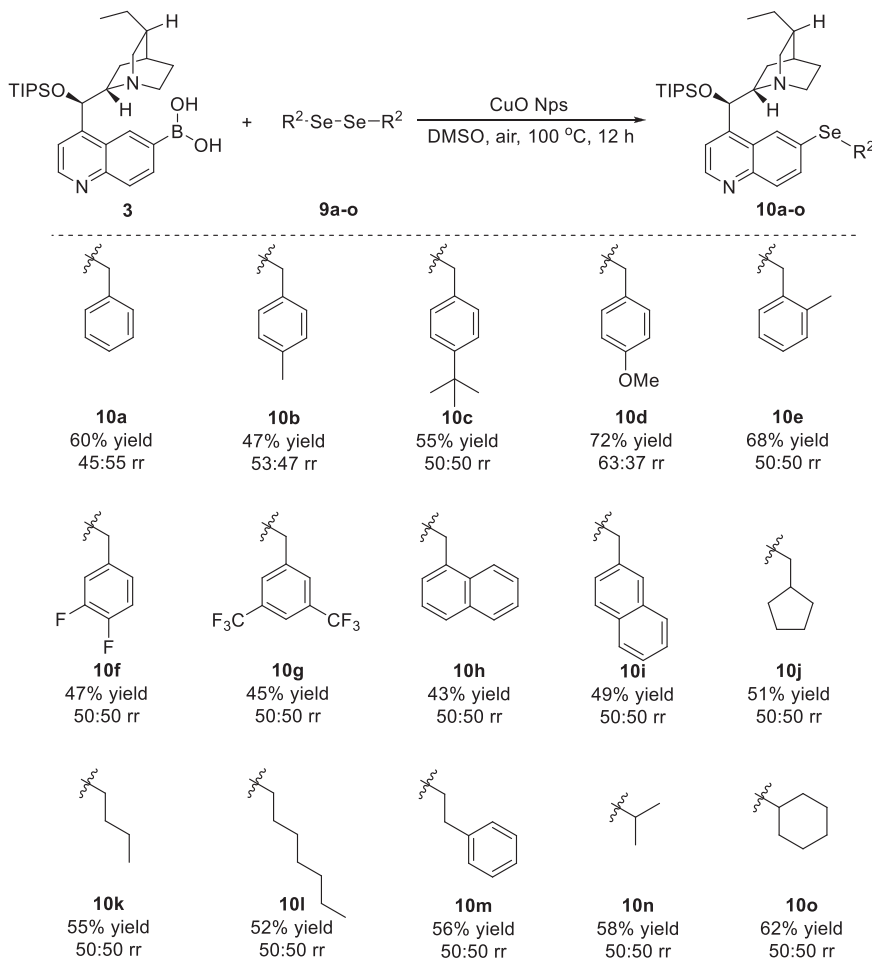
To probe the reaction mechanism, a borylation reaction which experienced anhydrous, moist, and silica gel-containing stages sequentially was monitored by high-resolution mass spectrometry (HRMS) (see SI for details). The spectra of HRMS implied that (i) the hydroquinine-6'-borate hardly underwent in situ hydrolysis in the borylation process, even if there was a high moisture content in the reaction system; and (ii) silica gel was able to promote the hydrolysis of hydroquinine-6'-borate to generate hydroquinine-6'-boric acid. The results of the subsequent controlled experiments (Table 2) further substantiated the hydrolysis of hydroquinine-6'-borate during the purification process through column chromatography on silica gel. Another vital piece of evidence was that hydroquinine-6'-borate was not observed at all on the silica gel plate when monitoring the reaction by thin-layer chromatography. Thus, it was a palladium-catalyzed borylation/silica gel promoted hydrolysis sequence that realized the construction of hydroquinine-6'-boric acid.

With hydroquinine-6'-boric acid **3** in hand, we first examined the palladium-catalyzed Suzuki–Miyaura cross-coupling reaction of **3** with 1-bromo-2,4-dimethylbenzene **4a** under the conditions we established previously (Table 3).<sup>34</sup> The reaction proceeded smoothly to produce the desired product **5a** as a mixture of rotamers with a 62% yield and a 67:33 rotameric ratio (rr) within 4 h. Without further optimization of reaction conditions, we sought to assess the scope and generality of the reaction with respect to multifarious aryl bromides. Polyaromatic bromine (**4b**) was tolerated to forge **5b** with an acceptable yield and rr value. Nitrogen-containing heterocycles as the basic scaffolds are

present in more than half of all marketed drugs.<sup>35</sup> Thus, heteroaryl bromides with pyridine-2-yl (**4c**), pyridine-3-yl (**4d**), quinoline-4-yl (**4e**), and indole-5-yl (**4f**) groups were evaluated. Substrates **4c** and **4d** appeared to be a little sluggish, taking more time to deliver the coupling products **5c** and **5d** in moderate yields. Note that the rotamers of **5c** and **5d** were not observed. Importantly, quinoline-4-yl (**4e**) and indole-5-yl (**4f**) groups could be introduced to the C-6' position of hydroquinine with satisfactory results (**5e** and **5f**). 5-Bromo isatin **4g** was an appropriate substrate to furnish the target product **5g** in 40% yield without a rotamer. Attempts to expand this catalytic chemistry to the oxygen-containing heteroaromatic bromides, such as 6-bromo-4*H*-chromen-4-one **4h** and 3-bromodibenzo[*b,d*]furan **4i**, were also successful.

Afterward, hydroquinine-6'-boric acid **3** was subjected to the Petasis reaction with piperidine **6** and salicylaldehyde **7a** as the partners. Without the catalyst, the reaction could proceed at 100 °C to unveil the coupling product **8a** with a 54% yield and 71:29 rr (Table 4). We then examined the scope of the reaction regarding a range of salicylaldehydes under the original conditions. This reaction was compatible with 4-methoxy substitution (**7b**), resulting in the generation of desired product **8b** with a 45% yield and 77:23 rr. The salicylaldehydes **7c–e** bearing electron-donating (–CH<sub>3</sub>) or electron-withdrawing (–F and –OCF<sub>3</sub>) groups at the C-5 position of the benzene ring were all competent in the reaction to deliver the corresponding products **8c–e** with modest results (57–63% yield and 67:33–83:17 rr). Equally impressively, this coupling process also tolerated difluorinated salicylaldehyde **7f**, as observed in the assembly of **8f**.

Inspired by a previous work on the formation of a C(sp<sup>2</sup>)–Se bond,<sup>36</sup> we initiated studies on the CuO nanoparticles (CuO NPs) catalyzed coupling reaction of hydroquinine-6'-boric acid and dibenzyl diselenides. Having established the optimized reaction conditions wherein hydroquinine-selenide

Table 5. CuO NPs Catalyzed Coupling Reaction of Hydroquinine-6'-Boric Acid and Dialkyl Diselenides<sup>a,b,c</sup>

<sup>a</sup>Reaction conditions: 3 (49.7 mg, 0.1 mmol), 9a–o (0.15 mmol), CuO Nps (0.24 mg, 3 mol %, 40 nm) in DMSO (2 mL), air, 100 °C, 12 h.

<sup>b</sup>Yield was determined after the product was purified by column chromatography on silica gel as a mixture of rotamers. <sup>c</sup>The rr value was determined by <sup>1</sup>H NMR analysis of the product.

10a was obtained with a 60% yield and 45:55 rr (see SI for details), we went on to assess the generality of the coupling reaction pertaining to an armory of dialkyl diselenides (Table 5). All the reactions proceeded smoothly to install alkylselenenyl groups (9b–o) onto the C-6' position, affording a variety of hydroquinine-selenides 10b–o with 43–72% yields and 50:50–63:37 rr within 12 h. Diselenides with electron-donating substituents including methyl (9b), *tert*-butyl (9c), and methoxy (9d) groups at the *para*-position of the benzene ring for the benzyl group could give rise to the products 10b–d. Among them, 10d was gained in a higher yield of 72%, suggesting the strong electron-donating group (9d) is beneficial to the current reaction. The *ortho*-substitution (9e) was tolerated, as displayed by the formation of 10e. It was revealed that the diselenides equipped by disubstituted phenyl groups (9f and 9g) on the  $\alpha$ -carbon were both suitable for the transformation (10f and 10g). The method was also compatible with fused aromatic substituents at the  $\alpha$ -position, such as naphthalene-1-yl (9h) and naphthalene-2-yl (9i) groups. 1,2-Bis(cyclopentylmethyl)diselenide (9j) was converted to the desired product (10j) smoothly in moderate yield. Furthermore, the linear chain alkyl diselenides, including *n*-butyl (9k), and *n*-heptyl (9l) groups, were tested. The results

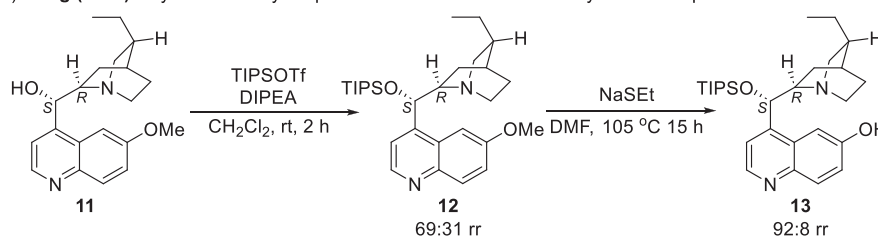
showed that the length of the alkyl group could influence the yield of the product, with a longer chain leading to a lower yield (10k vs 10l). The substitution could be extended to the phenylethyl group (9m), and the target product (10m) was gained in 56% yield and with 50:50 rr. The effect of steric hindrance was not observed when diselenides bearing *i*-propyl (9n) and cyclohexyl (9o) groups were used as the substrates. Hydroquinine-selenides 10a–o newly synthesized might be potent catalysts for the cross-oxidative coupling reaction of nucleophiles and olefins according to the previous reports,<sup>37</sup> which would give an entry to various allyl C–H functionalized compounds.

In 2011, Deng and coauthors reported a hydroquinidine-derived catalyst 13 bearing a TIPS-ether<sup>38</sup> (Scheme 1-1). When the TIPS group was installed on the hydroxyl group of hydroquinidine 11 at the C-9 position, the rotamers of intermediate 12 appeared (69:31 rr). Even if the adjacent methyl group was removed subsequently, the rotamers of 13 still existed (92:8 rr). These results indicated that the presence of the bulky TIPS group created a highly congested molecular space, thereby causing the occurrence of rotational isomerism. Similarly, the phenomenon was observed on the TIPS-protected hydroquinine 14 (75:25 rr), the demethylation

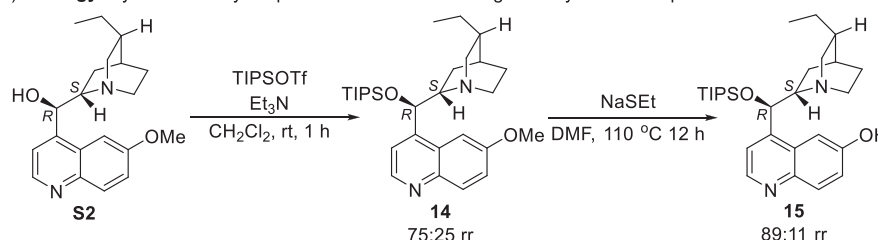


## Scheme 1. Investigations on the Rotational Isomerism

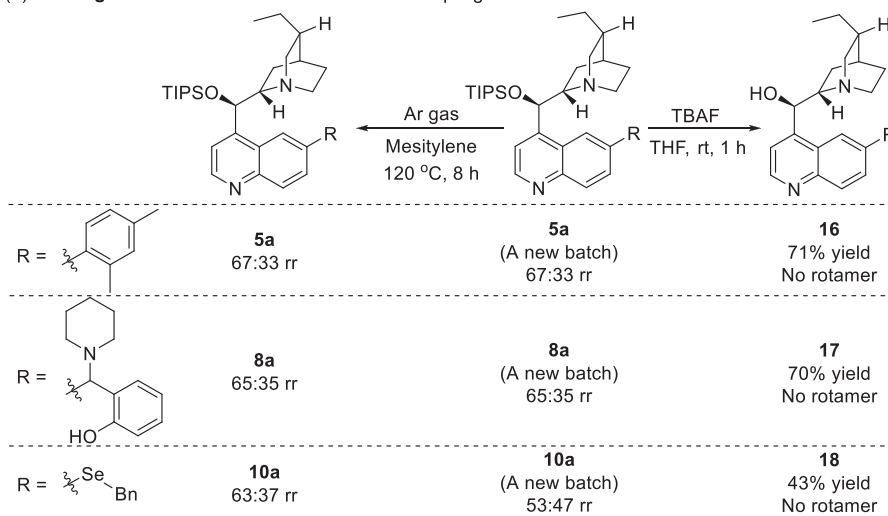
(1) Deng (2011): Synthesis of Hydroquinidine Derivatives with A Bulky TIPS Group



(2) Analogy: Synthesis of Hydroquinine Derivatives Bearing A Bulky TIPS Group



(3) Investigation: Rotational Isomerism for the Coupling Products



product **15** (89:11 rr) (Scheme 1-2), and most of the coupling products. To further confirm the existence of rotamers, the representative coupling products **5a**, **8a**, and **10a** were selected to remove the bulky TIPS group (Scheme 1-3). As expected, the corresponding derivatives **16**, **17**, and **18** were obtained without rotamers after the deprotection reaction. In addition, the stability of the rotamers of the coupling products was examined (Scheme 1-3). The rr values of the coupling products **5a** and **8a** remained unchanged after subjecting them to high temperature for 8 h, while the rr value of **10a** only displayed a slight increase. These findings strongly suggested that these rotamers possess considerable energy barriers that prevent interconversion.

## CONCLUSION

In summary, arylboronic acids are essential substrates in organic chemistry, playing a central role in a wide range of coupling reactions. Taking this truth into account, we designed and synthesized hydroquinine-6'-boric acid *via* a palladium-catalyzed borylation/silica gel promoted hydrolysis sequence, which granted infinite possibilities on the functionalization of hydroquinine. To illustrate the possibilities, hydroquinine-6'-boric acid was involved in the Suzuki–Miyaura cross-coupling

reaction, Petasis reaction, and selenylation reaction, respectively. All these reactions proceeded smoothly to access the corresponding valuable 6'-functionalized hydroquinines with satisfactory results. We believe that hydroquinine-6'-boric acid would be a promising versatile building block for drug discovery and catalytic chemistry. Further derivatizations of hydroquinine-6'-boric acid and evaluating the catalytic performance of hydroquinines with aminoarylmethine motifs and hydroquinine-selenides are underway in our laboratory.

## EXPERIMENTAL SECTION

**General Information.**  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker 400 MHz instrument (400 MHz for  $^1\text{H}$  NMR, 101 MHz for  $^{13}\text{C}$  NMR and 377 MHz for  $^{19}\text{F}$  NMR) with  $\text{CDCl}_3$  as a solvent.  $^1\text{H}$  NMR spectra were internally referenced to tetramethyl silane ( $\delta$  0).  $^{13}\text{C}$  NMR spectra were internally referenced to  $\text{CDCl}_3$  ( $\delta$  77.23). The data of high-resolution mass spectrometry (HRMS) were recorded on a Bruker Q-FT-MS Solarix 7T mass spectrometer or a Waters Xevo G2-S QToF mass spectrometer. The specific rotation was measured on a Shanghai Shengguang WZZ-2S automatic polarimeter. Melting points were determined on a Shanghai Shengguang WRS-2A melting point apparatus. Single crystal X-ray diffraction (XRD) data were collected on a Rigaku Oxford Diffraction SuperNova diffractometer using  $K\alpha$  radiation of Cu ( $\lambda = 1.54184$ ) at 149.99 K.

Unless otherwise noted, all reagents were purchased from commercial suppliers (Chron, Macklin, Micxy, Bidepharm, 9dingchem, and Aladdin) and used without further purification. The dry CH<sub>3</sub>CN (moisture content  $\leq 10$  ppm) was bought from J&K Scientific. The moisture content of solvent was determined by Karl Fischer moisture meter, 1,4-dioxane (moisture content = 0.15%) and acetonitrile (moisture content = 0.04%). Reactions were monitored by TLC using Huanghai HSGF254 silica gel plates. Column chromatography was conducted on Haiyang silica gel G (300–400 mesh). Dialkyl diselenides were synthesized in accordance with literature procedure.<sup>39</sup>

### Procedure for the Synthesis of Hydroquinine-6'-Boric Acid

**3.** Hydroquinine-derived triflate **1** (0.6008 g, 1.0 mmol), bis-(pinacolato)diboron **2** (0.3809 g, 1.5 mmol), potassium acetate powder (0.2944 g, 3.0 mmol), and acetonitrile (5 mL) were added sequentially to a glass flask, followed by the addition of Pd(OAc)<sub>2</sub> (0.0067 g, 3 mmol %) and PPh<sub>3</sub> (0.0315 g, 12 mol %) in acetonitrile (5 mL). The resulting mixture was heated to 80 °C in the oil bath, stirred for 8 h under argon ambient, and cooled to room temperature. Then, the mixture was concentrated under reduced pressure, and the residue was subjected to the silica gel column for purification (gradient elution, EtOAc:MeOH:Et<sub>3</sub>N = 100:1:1–100:5:1–100:20:1), which furnished hydroquinine-6'-boric acid **3**.

**Hydroquinine-6'-Boric Acid 3.** Grayish white solid; 0.4385 g, 88% yield; MP: 210.9–211.3 °C;  $[\alpha]_D^{20} = -37.5$  ( $c = 1.0$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  9.09 (s, 1H), 8.95 (s, 1H), 8.36 (d,  $J = 6.8$  Hz, 1H), 8.18–8.05 (m, 1H), 7.63 (d,  $J = 4.4$  Hz, 1H), 6.58 (s, 1H), 4.13 (d,  $J = 5.5$  Hz, 1H), 3.49–3.25 (m, 3H), 2.98 (d,  $J = 12.6$  Hz, 1H), 2.89 (d,  $J = 36.8$  Hz, 1H), 2.36–2.20 (m, 2H), 2.19–2.02 (m, 5H), 1.95–1.74 (m, 3H), 1.27–1.19 (m, 2H), 1.09 (s, 10H), 0.98 (s, 8H), 0.79 (t,  $J = 7.2$  Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  179.7, 162.7, 150.0, 146.4, 135.5, 128.9, 123.7, 121.7, 118.7, 77.4, 69.9, 60.3, 56.5, 42.9, 35.6, 27.3, 25.3, 24.5, 23.4, 18.1, 18.0, 13.1, 11.6. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>28</sub>H<sub>46</sub>BN<sub>2</sub>O<sub>3</sub>Si 497.3365; Found 497.3365.

**Procedure for the Suzuki–Miyaura Cross-Coupling Reaction.** To 2 mL of butyl ether were added hydroquinine-6'-boric acid **3** (49.7 mg, 0.1 mmol), aryl bromide **4** (0.1 mmol), Pd(OAc)<sub>2</sub> (1.1 mg, 5 mol %), butyl-di-1-adamantylphosphine (7.2 mg, 20 mol %), and K<sub>2</sub>CO<sub>3</sub> (41.5 mg, 0.3 mmol) sequentially. The resulting mixture was heated to 120 °C in the oil bath, stirred, and monitored by TLC. After the disappearance of the starting materials was confirmed, the mixture was cooled to room temperature. Then, the mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the coupling product **5**.

**Compound 5a.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); colorless oil; 34.7 mg, 62% yield;  $[\alpha]_D^{20} = -17.6$  ( $c = 1.0$ , CHCl<sub>3</sub>); 67:33 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals { $\delta_{\text{major}} = 5.79$  ppm (d),  $\delta_{\text{minor}} = 4.97$  ppm (d)}.

**Major Rotamer of 5a.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.91 (d,  $J = 4.5$  Hz, 1H), 8.14 (d,  $J = 8.6$  Hz, 1H), 7.90 (s, 1H), 7.67–7.56 (m, 2H), 7.20–7.10 (m, 3H), 5.79 (d,  $J = 4.7$  Hz, 1H), 3.41–3.28 (m, 1H), 2.90 (m, 2H), 2.57 (dd,  $J = 17.3, 6.6$  Hz, 1H), 2.41 (d,  $J = 9.1$  Hz, 3H), 2.27 (d,  $J = 13.7$  Hz, 3H), 2.10–2.03 (m, 1H), 1.85–1.56 (m, 4H), 1.56–1.46 (m, 1H), 1.39–1.32 (m, 2H), 1.24–1.18 (m, 1H), 1.00–0.93 (m, 18H), 0.80 (dd,  $J = 15.3, 7.9$  Hz, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  149.8, 149.5, 147.1, 140.3, 138.7, 137.4, 135.3, 131.2, 131.0, 130.1, 129.9, 126.6, 125.6, 122.5, 119.1, 80.5, 72.7, 62.8, 58.7, 43.4, 37.9, 28.9, 27.9, 25.6, 21.1, 20.4, 18.1, 18.1, 12.9, 12.2. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>53</sub>N<sub>2</sub>O<sub>3</sub>Si 557.3922; Found 557.3962.

**Minor Rotamer of 5a.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.78 (d,  $J = 4.3$  Hz, 0.5H), 8.50 (d,  $J = 1.4$  Hz, 0.5H), 8.10 (d,  $J = 8.7$  Hz, 0.5H), 7.67–7.56 (m, 1H), 7.20–7.10 (m, 1.5H), 4.97 (d,  $J = 9.8$  Hz, 0.5H), 3.59 (dd,  $J = 17.4, 9.3$  Hz, 0.5H), 2.90 (m, 1H), 2.57 (dd,  $J = 17.3, 6.6$  Hz, 0.5H), 2.41 (d,  $J = 9.1$  Hz, 1.5H), 2.27 (d,  $J = 13.7$  Hz, 1.5H), 2.10–2.03 (m, 0.5H), 1.85–1.56 (m, 2H), 1.56–1.46 (m, 0.5H), 1.39–1.32 (m, 1H), 1.24–1.18 (m, 0.5H), 1.00–0.93 (m, 9H), 0.80 (dd,  $J = 15.3, 7.9$  Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$

150.7, 149.3, 148.4, 139.1, 139.1, 137.0, 135.2, 131.1, 130.9, 130.1, 129.8, 126.5, 126.1, 121.3, 118.7, 80.4, 72.6, 61.7, 58.1, 41.4, 37.6, 29.0, 27.7, 27.0, 22.7, 20.5, 18.1, 17.9, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>36</sub>H<sub>53</sub>N<sub>2</sub>O<sub>3</sub>Si 557.3922; Found 557.3962.

**Compound 5b.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); colorless oil; 37.1 mg, 64% yield;  $[\alpha]_D^{20} = -24.3$  ( $c = 1.0$ , CHCl<sub>3</sub>); 71:29 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals { $\delta_{\text{major}} = 5.79$  ppm (d),  $\delta_{\text{minor}} = 4.99$  ppm (d)}.

**Major Rotamer of 5b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.97 (d,  $J = 4.6$  Hz, 1H), 8.24 (d,  $J = 8.6$  Hz, 1H), 8.10 (s, 1H), 7.97–7.81 (m, 4H), 7.70 (d,  $J = 4.5$  Hz, 1H), 7.60–7.50 (m, 2H), 7.49–7.47 (m, 1H), 7.42–7.38 (m, 1H), 5.79 (d,  $J = 4.7$  Hz, 1H), 3.36–3.23 (m, 1H), 2.93 (m, 2H), 2.59–2.50 (m, 1H), 2.29 (d,  $J = 13.5$  Hz, 1H), 1.81–1.71 (m, 2H), 1.69–1.56 (m, 2H), 1.36–1.22 (m, 4H), 1.03–0.93 (m, 18H), 0.83–0.73 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  150.1, 149.8, 147.5, 139.7, 139.1, 133.8, 131.8, 131.6, 130.3, 128.4, 128.1, 127.4, 127.4, 126.3, 126.0, 125.9, 125.5, 123.4, 119.3, 80.5, 72.5, 63.0, 58.8, 43.3, 37.9, 28.8, 27.9, 25.5, 18.2, 18.1, 12.9, 12.3. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>51</sub>N<sub>2</sub>O<sub>3</sub>Si 579.3765; Found 579.3769.

**Minor Rotamer of 5b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.84 (d,  $J = 4.3$  Hz, 0.4H), 8.70 (d,  $J = 0.8$  Hz, 0.4H), 8.20 (d,  $J = 8.6$  Hz, 0.4H), 7.97–7.81 (m, 1.6H), 7.79 (dd,  $J = 8.6, 1.4$  Hz, 0.4H), 7.60–7.50 (m, 0.8H), 7.49–7.47 (m, 0.4H), 7.24 (d,  $J = 4.3$  Hz, 0.4H), 4.99 (d,  $J = 9.7$  Hz, 0.4H), 3.58 (dd,  $J = 17.0, 9.0$  Hz, 0.4H), 2.93 (m, 0.8H), 2.59–2.50 (m, 0.4H), 2.14 (d,  $J = 13.4$  Hz, 0.4H), 1.81–1.71 (m, 0.8H), 1.69–1.56 (m, 0.8H), 1.36–1.22 (m, 1.6H), 1.03–0.93 (m, 7.2H), 0.83–0.73 (m, 2.4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  151.0, 149.5, 148.7, 140.2, 138.0, 133.8, 131.8, 131.4, 130.0, 128.3, 127.8, 127.6, 127.2, 126.1, 126.0, 125.8, 125.4, 123.4, 121.4, 80.5, 72.5, 61.8, 58.3, 41.4, 37.6, 27.8, 26.8, 22.8, 18.1, 17.9, 12.5, 12.3. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>38</sub>H<sub>51</sub>N<sub>2</sub>O<sub>3</sub>Si 579.3765; Found 579.3769.

**Compound 5c.** Purified by column chromatography on silica gel (EtOAc:MeOH:Et<sub>3</sub>N = 100:5:1); colorless oil; 32.2 mg, 61% yield;  $[\alpha]_D^{20} = -13.7$  ( $c = 1.0$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.98 (t,  $J = 4.1$  Hz, 1H), 8.80–8.76 (m, 1H), 8.74–8.67 (m, 2H), 8.37 (d,  $J = 8.0$  Hz, 1H), 8.32 (d,  $J = 8.8$  Hz, 1H), 8.06 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.66 (d,  $J = 4.5$  Hz, 1H), 7.40 (dd,  $J = 7.3, 5.1$  Hz, 1H), 6.60 (s, 1H), 4.25–4.13 (m, 1H), 3.74–3.64 (m, 1H), 3.52–3.40 (m, 1H), 3.33 (t,  $J = 9.3$  Hz, 1H), 2.98 (dd,  $J = 9.4, 4.3$  Hz, 1H), 2.92–2.72 (m, 1H), 2.51–2.42 (m, 1H), 2.21 (s, 1H), 2.13 (m, 1H), 1.96–1.85 (m, 2H), 1.68–1.59 (m, 1H), 1.28 (dd,  $J = 14.4, 4.9$  Hz, 4H), 1.10 (s, 10H), 1.01 (d,  $J = 5.8$  Hz, 8H), 0.83 (t,  $J = 7.3$  Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  154.8, 149.8, 148.9, 148.7, 145.9, 138.9, 138.5, 131.3, 129.2, 124.2, 123.5, 122.6, 119.5, 119.2, 69.1, 61.6, 57.2, 43.6, 35.5, 27.1, 25.0, 24.2, 18.1, 18.0, 13.1, 11.5. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>48</sub>N<sub>3</sub>O<sub>3</sub>Si 530.3561; Found 530.3561.

**Compound 5d.** Purified by column chromatography on silica gel (EtOAc:MeOH:Et<sub>3</sub>N = 100:5:1); colorless oil; 36.0 mg, 68% yield;  $[\alpha]_D^{20} = -15.8$  ( $c = 1.0$ , CHCl<sub>3</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.99 (dd,  $J = 16.9, 3.2$  Hz, 2H), 8.65 (d,  $J = 4.6$  Hz, 1H), 8.44 (d,  $J = 7.8$  Hz, 2H), 8.31 (d,  $J = 8.8$  Hz, 1H), 8.17 (d,  $J = 8.7$  Hz, 1H), 7.67 (d,  $J = 4.5$  Hz, 1H), 7.60 (dd,  $J = 7.9, 4.8$  Hz, 1H), 6.56 (s, 1H), 4.26–4.13 (m, 1H), 3.77–3.60 (m, 1H), 3.40 (td,  $J = 11.9, 3.6$  Hz, 1H), 3.27 (t,  $J = 9.4$  Hz, 1H), 2.92 (d,  $J = 13.7$  Hz, 1H), 2.45 (dd,  $J = 13.0, 9.2$  Hz, 1H), 2.25–2.07 (m, 3H), 1.98–1.83 (m, 2H), 1.70–1.57 (m, 1H), 1.34–1.21 (m, 4H), 1.09 (s, 10H), 1.00 (d,  $J = 5.1$  Hz, 8H), 0.83 (t,  $J = 7.3$  Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  149.6, 149.3, 148.0, 148.0, 145.3, 138.0, 136.0, 134.6, 131.6, 129.0, 124.8, 124.7, 119.5, 119.5, 69.0, 61.5, 58.4, 57.2, 43.7, 35.4, 27.2, 24.9, 24.1, 18.1, 18.0, 13.1, 11.5. HRMS (ESI-TOF)  $m/z$ : [M + H]<sup>+</sup> Calcd for C<sub>33</sub>H<sub>48</sub>N<sub>3</sub>O<sub>3</sub>Si 530.3561; Found 530.3567.

**Compound 5e.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); colorless oil; 38.4 mg, 66% yield;  $[\alpha]_D^{20} = -27.2$  ( $c = 1.0$ , CHCl<sub>3</sub>); 63:37 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals { $\delta_{\text{major}} = 5.78$  ppm (d),  $\delta_{\text{minor}} = 5.01$  ppm (d)}.

**Major Rotamer of 5e.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.02 (d,  $J$  = 4.3 Hz, 1H), 9.00 (d,  $J$  = 2.2 Hz, 1H), 8.31–8.21 (m, 2H), 8.13 (s, 1H), 7.96–7.70 (m, 4H), 7.50 (t,  $J$  = 7.6 Hz, 1H), 7.41 (t,  $J$  = 5.4 Hz, 1H), 5.78 (d,  $J$  = 4.9 Hz, 1H), 3.34–3.22 (m, 1H), 3.10–2.86 (m, 2H), 2.56 (t,  $J$  = 12.1 Hz, 1H), 2.48–2.33 (m, 1H), 2.28 (d,  $J$  = 13.6 Hz, 1H), 1.83–1.50 (m, 4H), 1.41–1.23 (m, 4H), 1.00–0.95 (m, 13H), 0.88–0.83 (m, 5H), 0.80 (d,  $J$  = 7.1 Hz, 2H), 0.74 (d,  $J$  = 6.8 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.4, 150.7, 150.0, 149.7, 148.7, 147.8, 136.2, 130.9, 130.4, 130.0, 129.5, 127.7, 126.9, 126.8, 125.8, 125.7, 121.7, 119.6, 80.4, 72.3, 63.2, 58.7, 43.3, 37.8, 28.7, 27.9, 25.4, 18.1, 18.1, 12.9, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{50}\text{N}_3\text{O}_3\text{Si}$  580.3718; Found 580.3722.

**Minor Rotamer of 5e.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.02 (d,  $J$  = 4.3 Hz, 0.6H), 8.88 (d,  $J$  = 4.3 Hz, 0.6H), 8.75 (s, 0.6H), 8.31–8.21 (m, 1.2H), 7.96–7.70 (m, 2.4H), 7.50 (t,  $J$  = 7.6 Hz, 0.6H), 7.41 (t,  $J$  = 5.4 Hz, 0.6H), 5.01 (d,  $J$  = 9.7 Hz, 0.6H), 3.55 (dd,  $J$  = 17.3, 9.1 Hz, 0.6H), 3.10–2.86 (m, 1.2H), 2.56 (t,  $J$  = 12.1 Hz, 0.6H), 2.13 (d,  $J$  = 13.5 Hz, 0.6H), 2.00 (m, 0.6H), 1.83–1.50 (m, 2.4H), 1.41–1.23 (m, 2.4H), 1.00–0.95 (m, 7.8H), 0.88–0.83 (m, 3H), 0.80 (d,  $J$  = 7.1 Hz, 1.2H), 0.74 (d,  $J$  = 6.8 Hz, 2.4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.4, 150.4, 150.0, 149.0, 148.5, 148.0, 135.1, 130.6, 130.2, 129.9, 129.4, 126.9, 126.9, 126.1, 125.8, 125.7, 123.5, 121.5, 80.4, 72.3, 62.1, 58.3, 41.4, 37.6, 28.8, 26.8, 22.9, 18.0, 17.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{50}\text{N}_3\text{O}_3\text{Si}$  580.3718; Found 580.3722.

**Compound 5f.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); light yellow oil; 31.4 mg, 54% yield;  $[\alpha]_{\text{D}}^{20}$  = –24.7 ( $c$  = 1.0,  $\text{CHCl}_3$ ); 71:29 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 6.02$  ppm (s),  $\delta_{\text{minor}} = 5.02$  ppm (d)}.

**Major Rotamer of 5f.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.88 (d,  $J$  = 4.5 Hz, 1H), 8.23 (d,  $J$  = 1.5 Hz, 1H), 8.19 (d,  $J$  = 8.8 Hz, 1H), 8.07 (dd,  $J$  = 8.8, 1.7 Hz, 1H), 7.97 (dd,  $J$  = 9.8, 1.3 Hz, 1H), 7.65–7.61 (m, 2H), 7.47 (d,  $J$  = 8.5 Hz, 1H), 7.11 (d,  $J$  = 3.1 Hz, 1H), 6.59 (dd,  $J$  = 3.0, 0.4 Hz, 1H), 6.02 (s, 1H), 3.84 (s, 3H), 3.57 (d,  $J$  = 7.4 Hz, 1H), 3.11–3.01 (m, 2H), 2.82–2.70 (m, 1H), 2.50–2.40 (m, 1H), 2.16–2.03 (m, 1H), 1.93–1.76 (m, 3H), 1.73–1.56 (m, 2H), 1.28–1.12 (m, 3H), 1.01–0.98 (m, 18H), 0.87 (d,  $J$  = 6.8 Hz, 3H), 0.83–0.76 (m, 5H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.2, 149.1, 147.3, 141.1, 136.6, 132.6, 130.7, 129.7, 129.6, 126.0, 124.0, 121.7, 120.0, 119.2, 109.9, 101.6, 80.2, 72.0, 62.6, 58.6, 43.5, 37.7, 33.0, 27.8, 27.7, 25.4, 18.2, 18.1, 12.9, 12.1. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{52}\text{N}_3\text{O}_3\text{Si}$  582.3874; Found 582.3879.

**Minor Rotamer of 5f.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.91 (d,  $J$  = 4.5 Hz, 0.4H), 8.85 (d,  $J$  = 1.9 Hz, 0.4H), 8.75 (d,  $J$  = 4.3 Hz, 0.4H), 8.07 (dd,  $J$  = 8.8, 1.7 Hz, 0.4H), 7.97 (dd,  $J$  = 9.8, 1.3 Hz, 0.4H), 7.65–7.61 (m, 0.8H), 7.43 (d,  $J$  = 8.6 Hz, 0.4H), 7.19 (d,  $J$  = 4.4 Hz, 0.4H), 6.55 (d,  $J$  = 2.9 Hz, 0.4H), 5.02 (d,  $J$  = 9.7 Hz, 0.4H), 3.84 (s, 1.2H), 3.57 (d,  $J$  = 7.4 Hz, 0.4H), 3.11–3.01 (m, 0.8H), 2.82–2.70 (m, 0.4H), 2.50–2.40 (m, 0.4H), 2.16–2.03 (m, 0.4H), 1.93–1.76 (m, 1.2H), 1.73–1.56 (m, 0.8H), 1.28–1.12 (m, 1.2H), 1.01–0.98 (m, 7.2H), 0.87 (d,  $J$  = 6.8 Hz, 1.2H), 0.83–0.76 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.2, 148.4, 148.2, 139.3, 136.4, 132.0, 130.5, 130.4, 129.1, 126.6, 122.5, 121.5, 121.3, 119.9, 119.5, 118.7, 109.6, 101.4, 80.1, 72.0, 61.7, 58.1, 41.4, 37.5, 33.0, 28.9, 26.6, 25.6, 18.2, 18.0, 12.6, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{52}\text{N}_3\text{O}_3\text{Si}$  582.3874; Found 582.3879.

**Compound 5g.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); yellow oil; 27.6 mg, 40% yield;  $[\alpha]_{\text{D}}^{20}$  = –14.6 ( $c$  = 1.0,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (d,  $J$  = 4.5 Hz, 1H), 8.38–8.32 (m, 2H), 8.23 (dd,  $J$  = 8.8, 4.7 Hz, 1H), 8.01 (dd,  $J$  = 8.9, 1.8 Hz, 1H), 7.93 (d,  $J$  = 1.9 Hz, 1H), 7.62 (d,  $J$  = 4.5 Hz, 1H), 7.47–7.42 (m, 2H), 7.39–7.33 (m, 2H), 7.30 (dt,  $J$  = 5.0, 1.9 Hz, 1H), 7.25 (d,  $J$  = 8.4 Hz, 1H), 6.51 (s, 1H), 5.00 (d,  $J$  = 15.3 Hz, 1H), 4.88 (d,  $J$  = 15.3 Hz, 1H), 4.20 (m, 1H), 3.62 (dd,  $J$  = 13.0, 11.1 Hz, 1H), 3.44–3.33 (m, 1H), 3.26 (dd,  $J$  = 15.8, 6.7 Hz, 1H), 2.97–2.86 (m, 1H), 2.44 (dd,  $J$  = 13.2, 8.9 Hz, 1H), 2.20 (s, 2H), 2.02 (d,  $J$  = 4.0 Hz, 4H), 1.67–1.58 (m, 2H), 1.27–1.21 (m, 2H), 1.07 (d,  $J$  = 2.0 Hz, 10H), 0.98 (d,  $J$  = 6.0 Hz, 8H), 0.80 (t,  $J$  = 7.3 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  183.5, 158.5, 150.6, 149.3, 145.5, 139.0,

138.9, 134.8, 134.7, 131.5, 129.0, 128.8, 128.2, 125.3, 124.6, 123.5, 119.5, 118.7, 118.4, 117.9, 113.0, 78.5, 69.0, 61.5, 57.4, 44.3, 43.7, 35.5, 31.6, 29.7, 27.2, 25.0, 24.1, 18.1, 18.0, 13.1, 11.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{43}\text{H}_{54}\text{N}_3\text{O}_3\text{Si}$  688.3929; Found 688.3935.

**Compound 5h.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); colorless oil; 35.1 mg, 59% yield;  $[\alpha]_{\text{D}}^{20}$  = –16.0 ( $c$  = 1.0,  $\text{CHCl}_3$ ); 67:33 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.94$  ppm (d),  $\delta_{\text{minor}} = 5.02$  ppm (d)}.

**Major Rotamer of 5h.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.93 (d,  $J$  = 4.5 Hz, 1H), 8.54 (dd,  $J$  = 5.5, 2.1 Hz, 1H), 8.27 (s, 1H), 8.20 (dd,  $J$  = 12.9, 8.8 Hz, 1H), 8.03 (d,  $J$  = 5.3 Hz, 1H), 8.02–7.97 (m, 1H), 7.89 (dd,  $J$  = 6.0, 2.9 Hz, 1H), 7.69 (d,  $J$  = 4.5 Hz, 1H), 7.60 (t,  $J$  = 8.2 Hz, 1H), 6.38 (d,  $J$  = 6.0 Hz, 1H), 5.94 (d,  $J$  = 1.1 Hz, 1H), 3.52–3.39 (m, 1H), 3.15–2.94 (m, 2H), 2.72 (dd,  $J$  = 16.0, 5.7 Hz, 1H), 2.37 (d,  $J$  = 13.3 Hz, 1H), 2.12 (m, 1H), 1.67 (m, 2H), 1.40 (m, 3H), 1.30–1.18 (m, 2H), 0.98 (dd,  $J$  = 11.9, 6.9 Hz, 18H), 0.84–0.76 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  177.6, 156.2, 155.4, 150.2, 150.0, 147.7, 137.8, 137.7, 133.0, 131.2, 128.6, 126.0, 125.1, 124.5, 120.8, 119.1, 113.1, 80.1, 72.2, 62.8, 58.5, 43.3, 37.6, 28.9, 27.8, 25.4, 18.1, 17.9, 12.9, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{49}\text{N}_2\text{O}_3\text{Si}$  597.3507; Found 597.3501.

**Minor Rotamer of 5h.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (d,  $J$  = 1.0 Hz, 0.5H), 8.80 (d,  $J$  = 4.3 Hz, 0.5H), 8.54 (dd,  $J$  = 5.5, 2.1 Hz, 0.5H), 8.20 (dd,  $J$  = 12.9, 8.8 Hz, 0.5H), 8.03 (d,  $J$  = 5.3 Hz, 0.5H), 8.02–7.97 (m, 0.5H), 7.89 (dd,  $J$  = 6.0, 2.9 Hz, 0.5H), 7.60 (t,  $J$  = 8.2 Hz, 0.5H), 7.23 (d,  $J$  = 4.3 Hz, 0.5H), 6.38 (d,  $J$  = 6.0 Hz, 0.5H), 5.02 (d,  $J$  = 9.7 Hz, 0.5H), 3.59 (dd,  $J$  = 17.4, 9.1 Hz, 0.5H), 3.15–2.94 (m, 1H), 2.89 (dd,  $J$  = 13.5, 8.9 Hz, 0.5H), 2.60–2.52 (m, 0.5H), 1.78 (m, 0.5H), 1.67 (m, 1H), 1.40 (m, 1.5H), 1.30–1.18 (m, 1H), 0.98 (dd,  $J$  = 11.9, 6.9 Hz, 9H), 0.84–0.76 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  177.5, 156.0, 155.3, 150.8, 149.6, 148.9, 138.2, 136.1, 132.7, 131.1, 128.2, 126.4, 124.8, 124.1, 121.5, 119.4, 113.1, 80.1, 72.2, 62.0, 58.2, 41.4, 37.7, 28.6, 26.6, 25.5, 18.1, 17.9, 12.5, 12.3. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{49}\text{N}_2\text{O}_3\text{Si}$  597.3507; Found 597.3501.

**Compound 5i.** Purified by column chromatography on silica gel (EtOAc:Et<sub>3</sub>N = 100:1); colorless oil; 30.9 mg, 50% yield;  $[\alpha]_{\text{D}}^{20}$  = –7.0 ( $c$  = 1.0,  $\text{CHCl}_3$ ); 67:33 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.92$  ppm (d),  $\delta_{\text{minor}} = 5.01$  ppm (d)}.

**Major Rotamer of 5i.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.90 (m, 1H), 8.31–8.24 (m, 1H), 8.24–8.12 (m, 1H), 8.09–7.99 (m, 2H), 7.98–7.87 (m, 2H), 7.68 (dd,  $J$  = 9.4, 4.6 Hz, 1H), 7.66–7.54 (m, 1H), 7.50–7.39 (m, 2H), 7.39–7.33 (m, 1H), 5.92 (d,  $J$  = 4.9 Hz, 1H), 3.51–3.40 (m, 1H), 3.04–2.99 (m, 1H), 2.99–2.94 (m, 1H), 2.68 (dd,  $J$  = 14.9, 5.0 Hz, 1H), 2.35 (d,  $J$  = 13.5 Hz, 1H), 2.27–1.98 (m, 1H), 1.76–1.56 (m, 2H), 1.53–1.37 (m, 2H), 1.35 (dd,  $J$  = 8.5, 5.6 Hz, 1H), 1.31–1.15 (m, 2H), 1.03–0.94 (m, 18H), 0.81 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.8, 150.0, 147.6, 140.2, 139.3, 130.9, 129.1, 128.9, 127.6, 127.4, 126.2, 124.0, 123.8, 123.0, 122.7, 121.1, 120.8, 120.7, 119.4, 111.8, 110.7, 80.2, 72.3, 63.0, 58.7, 43.4, 37.8, 28.9, 27.9, 25.5, 18.2, 18.0, 12.9, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{40}\text{H}_{51}\text{N}_2\text{O}_2\text{Si}$  619.3714; Found 619.3719.

**Minor Rotamer of 5i.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.90 (m, 0.5H), 8.79 (dd,  $J$  = 8.4, 4.3 Hz, 0.5H), 8.24–8.12 (m, 0.5H), 8.09–7.99 (m, 1H), 7.72 (dd,  $J$  = 8.1, 1.4 Hz, 0.5H), 7.68 (dd,  $J$  = 9.4, 4.6 Hz, 0.5H), 7.66–7.54 (m, 0.5H), 7.52 (dd,  $J$  = 8.1, 2.4 Hz, 0.5H), 7.50–7.39 (m, 1H), 7.21 (dd,  $J$  = 9.0, 4.4 Hz, 0.5H), 5.01 (d,  $J$  = 9.6 Hz, 0.5H), 3.64 (dd,  $J$  = 17.6, 9.3 Hz, 0.5H), 3.09 (m, 1H), 2.92–2.86 (m, 0.5H), 2.61–2.54 (m, 0.5H), 2.35 (d,  $J$  = 13.5 Hz, 0.5H), 2.27–1.98 (m, 0.5H), 1.76–1.56 (m, 1H), 1.53–1.37 (m, 1H), 1.35 (dd,  $J$  = 8.5, 5.6 Hz, 0.5H), 1.31–1.15 (m, 1H), 1.03–0.94 (m, 9H), 0.81 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.8, 149.8, 147.6, 140.5, 137.7, 131.1, 130.9, 128.6, 127.8, 127.3, 124.8, 124.1, 123.6, 122.9, 122.4, 121.5, 120.9, 120.7, 119.3, 111.8, 110.4, 80.2, 72.4, 61.9, 58.2, 41.4, 37.7, 28.8, 27.8, 25.6, 18.1, 18.0, 12.6, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{40}\text{H}_{51}\text{N}_2\text{O}_2\text{Si}$  619.3714; Found 619.3719.



**Procedure for the Petasis Reaction.** To 2 mL of chlorobenzene were added hydroquinine-6'-boric acid **3** (49.7 mg, 0.1 mmol), piperidine **6** (10.2 mg, 0.12 mmol), and salicylaldehyde **7** (0.1 mmol) sequentially. The resulting mixture was heated to 100 °C in the oil bath and stirred for 4 h. Then, the mixture was cooled to room temperature, and concentrated under reduced pressure. The residue was purified on silica gel column to afford the desired product **8**.

**Compound 8a.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 34.5 mg, 54% yield;  $[\alpha]_{\text{D}}^{20} = -19.7$  ( $c = 1.0$ , CHCl<sub>3</sub>); 71:29 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.72$  ppm (d),  $\delta_{\text{minor}} = 4.92$  ppm (d)}.

**Major Rotamer of 8a.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.48 (s, 1H), 8.87 (d,  $J = 4.5$  Hz, 1H), 8.10 (s, 1H), 8.06 (d,  $J = 8.7$  Hz, 1H), 7.80–7.68 (m, 1H), 7.59 (d,  $J = 4.5$  Hz, 1H), 7.10–7.05 (m, 1H), 6.92–6.82 (m, 3H), 5.72 (d,  $J = 2.9$  Hz, 1H), 4.65 (s, 1H), 3.01 (m, 1H), 2.95–2.78 (m, 2H), 2.55–2.37 (m, 2H), 2.21 (m, 2H), 2.09–1.94 (m, 1H), 1.93–1.83 (m, 1H), 1.78 (s, 1H), 1.65 (s, 6H), 1.58–1.46 (m, 2H), 1.45–1.39 (m, 2H), 1.36 (dd,  $J = 7.1$ , 4.0 Hz, 1H), 1.34–1.30 (m, 1H), 1.27 (d,  $J = 10.5$  Hz, 2H), 1.21 (dd,  $J = 11.4$ , 4.5 Hz, 1H), 0.99 (s, 7H), 0.97–0.89 (m, 11H), 0.85–0.79 (m, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  156.9, 150.2, 149.3, 147.7, 138.2, 131.1, 131.0, 129.2, 128.4, 126.0, 125.4, 121.3, 119.3, 119.1, 117.1, 80.0, 76.6, 61.7, 58.5, 37.8, 31.7, 29.7, 28.8, 27.9, 26.1, 25.6, 24.1, 18.1, 18.0, 12.8, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>40</sub>H<sub>60</sub>N<sub>3</sub>O<sub>2</sub>Si 642.4449; Found 642.4455.

**Minor Rotamer of 8a.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.37 (s, 0.4H), 8.73 (d,  $J = 4.3$  Hz, 0.4H), 8.53 (s, 0.4H), 8.03 (d,  $J = 8.9$  Hz, 0.4H), 7.88–7.80 (m, 0.4H), 7.13 (d,  $J = 4.4$  Hz, 0.4H), 7.10–7.05 (m, 0.4H), 6.91–6.82 (m, 0.9H), 6.69–6.64 (m, 0.4H), 4.92 (d,  $J = 9.6$  Hz, 0.4H), 4.57 (s, 0.4H), 3.63–3.56 (m, 0.4H), 2.95–2.78 (m, 1H), 2.55–2.37 (m, 1H), 2.21 (m, 1H), 2.09–1.94 (m, 0.4H), 1.93–1.83 (m, 0.4H), 1.78 (s, 0.4H), 1.65 (s, 3H), 1.58–1.46 (m, 1H), 1.45–1.39 (m, 1H), 1.36 (dd,  $J = 7.1$ , 4.0 Hz, 0.4H), 1.34–1.30 (m, 0.4H), 1.27 (d,  $J = 10.5$  Hz, 1H), 1.21 (dd,  $J = 11.4$ , 4.5 Hz, 0.4H), 0.99 (s, 5H), 0.97–0.89 (m, 7H), 0.85–0.79 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  156.7, 149.7, 148.9, 147.6, 138.1, 131.2, 131.0, 129.1, 128.4, 126.3, 125.4, 122.3, 119.2, 119.2, 117.1, 80.0, 76.6, 63.5, 58.0, 41.3, 29.7, 28.9, 28.1, 26.9, 26.2, 25.6, 24.2, 18.1, 18.0, 12.3, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>40</sub>H<sub>60</sub>N<sub>3</sub>O<sub>2</sub>Si 642.4449; Found 642.4455.

**Compound 8b.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 30.4 mg, 45% yield;  $[\alpha]_{\text{D}}^{20} = -30.5$  ( $c = 1.0$ , CHCl<sub>3</sub>); 77:23 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 6.07$ –5.47 ppm (m),  $\delta_{\text{minor}} = 4.93$  ppm (d)}.

**Major Rotamer of 8b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.60 (s,  $J = 51.3$  Hz, 1H), 8.87 (d,  $J = 4.5$  Hz, 1H), 8.20–8.07 (m, 1H), 8.04 (d,  $J = 3.9$  Hz, 1H), 7.94–7.61 (m, 1H), 7.59 (d,  $J = 4.5$  Hz, 1H), 6.89–6.67 (m, 1H), 6.43 (d,  $J = 2.4$  Hz, 1H), 6.28–6.24 (m, 1H), 6.07–5.47 (m, 1H), 4.66 (d,  $J = 11.4$  Hz, 1H), 3.73 (d,  $J = 2.5$  Hz, 3H), 3.14–2.90 (m, 2H), 2.90–2.77 (m, 1H), 2.61–2.35 (m, 3H), 2.35–2.08 (m, 2H), 2.08–1.94 (m, 1H), 1.94–1.76 (m, 2H), 1.64 (s, 6H), 1.54–1.49 (m, 1H), 1.48–1.35 (m, 3H), 1.31–1.21 (m, 3H), 0.99 (s, 9H), 0.95 (d,  $J = 16.1$  Hz, 9H), 0.82 (dt,  $J = 9.9$ , 7.6 Hz, 5H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  160.1, 158.1, 149.7, 148.9, 147.7, 131.0, 129.9, 129.7, 125.9, 121.3, 119.0, 117.8, 105.6, 105.2, 102.2, 80.0, 75.7, 61.7, 58.0, 55.2, 52.9, 41.3, 28.8, 28.1, 27.7, 26.1, 25.6, 24.1, 18.1, 18.1, 12.9, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>41</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>Si 672.4555; Found 672.4549.

**Minor Rotamer of 8b.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.60 (s,  $J = 51.3$  Hz, 0.3H), 8.73 (d,  $J = 4.3$  Hz, 0.3H), 8.55–8.46 (m, 0.3H), 8.02–7.99 (m, 0.3H), 7.94–7.61 (m, 0.3H), 7.15 (t,  $J = 4.2$  Hz, 0.3H), 6.89–6.67 (m, 0.3H), 6.48–6.44 (m, 0.3H), 6.22 (d,  $J = 2.5$  Hz, 0.3H), 4.93 (d,  $J = 9.7$  Hz, 0.3H), 4.55 (s, 0.3H), 3.73 (d,  $J = 2.5$  Hz, 0.9H), 3.14–2.90 (m, 0.6H), 2.90–2.77 (m, 0.3H), 2.61–2.35 (m, 0.9H), 2.35–2.08 (m, 0.6H), 2.08–1.94 (m, 0.3H), 1.94–1.76 (m, 0.6H), 1.64 (s, 1.8H), 1.54–1.49 (m, 0.3H), 1.48–1.35 (m, 0.9H), 1.31–1.21 (m, 0.9H), 0.99 (s, 2.7H), 0.95 (d,  $J = 16.1$  Hz,

2.7H), 0.82 (dt,  $J = 9.9$ , 7.6 Hz, 1.5H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  160.1, 158.2, 149.9, 149.2, 147.8, 131.1, 130.0, 129.8, 124.8, 122.0, 119.0, 117.9, 105.7, 105.5, 102.2, 80.0, 75.7, 61.8, 58.2, 55.1, 52.1, 37.7, 29.7, 26.8, 26.2, 25.5, 24.2, 18.2, 18.0, 12.9, 12.3. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>41</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>Si 672.4555; Found 672.4549.

**Compound 8c.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 37.4 mg, 57% yield;  $[\alpha]_{\text{D}}^{20} = -10.8$  ( $c = 1.0$ , CHCl<sub>3</sub>); 83:17 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 6.90$ –6.85 ppm (m),  $\delta_{\text{minor}} = 4.97$  ppm (d)}.

**Major Rotamer of 8c.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.09 (s, 0.3H), 8.86 (d,  $J = 4.5$  Hz, 1H), 8.21 (s, 1H), 8.05 (dd,  $J = 8.7$ , 3.6 Hz, 1H), 8.02–7.71 (m, 1H), 7.59 (t,  $J = 6.2$  Hz, 1H), 6.90–6.85 (m, 1H), 6.84–6.61 (m, 2H), 6.38–5.85 (m, 1H), 4.90–4.58 (m, 1H), 3.27–2.99 (m, 2H), 2.96–2.76 (m, 1H), 2.74–2.49 (m, 2H), 2.48–2.27 (m, 2H), 2.12 (d,  $J = 5.6$  Hz, 3H), 2.03–1.86 (m, 2H), 1.75–1.49 (m, 8H), 1.49–1.33 (m, 2H), 1.28–1.22 (m, 2H), 1.09–0.94 (m, 18H), 0.90 (dd,  $J = 12.7$ , 5.5 Hz, 2H), 0.82 (t,  $J = 7.3$  Hz, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  154.1, 149.7, 149.0, 147.8, 131.3, 129.8, 128.9, 128.4, 125.9, 125.4, 125.0, 121.4, 119.0, 116.8, 116.7, 80.0, 76.3, 70.5, 61.8, 57.7, 43.0, 37.6, 28.0, 27.5, 26.0, 24.9, 24.1, 20.4, 18.1, 18.0, 13.0, 11.9. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>41</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>Si 656.4606; Found 656.4613.

**Minor Rotamer of 8c.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.09 (s, 0.2H), 8.74 (d,  $J = 4.2$  Hz, 0.2H), 8.52 (d,  $J = 21.5$  Hz, 0.2H), 8.05 (dd,  $J = 8.7$ , 3.6 Hz, 0.2H), 8.02–7.71 (m, 0.2H), 7.17 (t,  $J = 4.5$  Hz, 0.2H), 6.90–6.85 (m, 0.2H), 6.84–6.61 (m, 0.4H), 4.97 (d,  $J = 9.3$  Hz, 0.2H), 4.49 (d,  $J = 13.8$  Hz, 0.2H), 3.27–2.99 (m, 0.4H), 2.96–2.76 (m, 0.2H), 2.74–2.49 (m, 0.4H), 2.48–2.27 (m, 0.4H), 2.12 (d,  $J = 5.6$  Hz, 0.6H), 2.03–1.86 (m, 0.4H), 1.75–1.49 (m, 1.6H), 1.49–1.33 (m, 0.4H), 1.28–1.22 (m, 0.4H), 1.09–0.94 (m, 3.6H), 0.90 (dd,  $J = 12.7$ , 5.5 Hz, 0.4H), 0.82 (t,  $J = 7.3$  Hz, 0.6H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  154.4, 154.1, 149.7, 149.6, 149.0, 148.9, 147.9, 147.8, 131.4, 131.3, 129.8, 129.7, 129.0, 128.9, 128.4, 128.3, 126.3, 125.9, 125.4, 125.2, 125.2, 125.0, 121.4, 121.4, 119.0, 118.8, 117.0, 116.8, 116.7, 116.6, 80.0, 76.2, 70.2, 62.4, 58.2, 41.3, 36.6, 29.7, 27.5, 26.2, 24.2, 23.4, 20.5, 18.2, 18.0, 12.4, 12.3. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>41</sub>H<sub>62</sub>N<sub>3</sub>O<sub>3</sub>Si 656.4606; Found 656.4613.

**Compound 8d.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 41.3 mg, 63% yield;  $[\alpha]_{\text{D}}^{20} = -24.1$  ( $c = 1.0$ , CHCl<sub>3</sub>); 77:23 rr, determined by <sup>1</sup>H NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 6.21$ –5.46 ppm (m),  $\delta_{\text{minor}} = 4.94$  ppm (d)}.

**Major Rotamer of 8d.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.28 (s,  $J = 68.7$  Hz, 1H), 8.89 (d,  $J = 4.5$  Hz, 1H), 8.30–8.10 (m, 1H), 8.08 (d,  $J = 8.7$  Hz, 1H), 7.94–7.66 (m, 1H), 7.60 (d,  $J = 4.5$  Hz, 1H), 6.81–6.74 (m, 2H), 6.72–6.61 (m, 1H), 6.21–5.46 (m, 1H), 4.88–4.58 (m, 1H), 3.53–3.45 (m, 1H), 3.33–3.27 (m, 1H), 3.19–2.92 (m, 2H), 2.59–2.35 (m, 3H), 2.28–2.11 (m, 1H), 2.11–1.98 (m, 1H), 1.97–1.78 (m, 2H), 1.73–1.67 (m, 2H), 1.67–1.65 (m, 2H), 1.65–1.62 (m, 2H), 1.61–1.49 (m, 4H), 1.49–1.38 (m, 2H), 1.30–21.22 (m, 2H), 0.96 (d,  $J = 25.4$  Hz, 18H), 0.81 (t,  $J = 7.1$  Hz, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  160.8, 154.8, 150.1 (d,  $J = 3.0$  Hz), 149.9, 147.8, 131.3, 126.1, 122.0, 121.5, 119.1, 117.9, 117.7, 115.6, 115.3, 114.9, 80.1, 75.9, 61.8, 58.1, 46.9, 41.3, 28.1, 27.7, 26.6, 26.0, 25.1, 24.0, 18.1, 18.0, 12.9, 12.4. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>):  $\delta$  -77.94. HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for C<sub>40</sub>H<sub>59</sub>FN<sub>3</sub>O<sub>2</sub>Si 660.4355; Found 660.4364.

**Minor Rotamer of 8d.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  12.28 (d,  $J = 68.7$  Hz, 0.3H), 8.75 (d,  $J = 4.3$  Hz, 0.3H), 8.58–8.48 (m, 0.3H), 8.05 (d,  $J = 8.8$  Hz, 0.3H), 8.00 (s, 0.3H), 7.16 (d,  $J = 4.3$  Hz, 0.3H), 6.81–6.74 (m, 0.6H), 6.59 (dd,  $J = 8.4$ , 1.5 Hz, 0.3H), 4.94 (d,  $J = 9.5$  Hz, 0.3H), 4.52 (s, 0.3H), 3.53–3.45 (m, 0.3H), 3.33–3.27 (m, 0.3H), 3.19–2.92 (m, 0.6H), 2.59–2.35 (m, 0.2H), 2.28–2.11 (m, 0.3H), 2.11–1.98 (m, 0.3H), 1.97–1.78 (m, 0.6H), 1.73–1.67 (m, 0.6H), 1.67–1.65 (m, 0.6H), 1.65–1.62 (m, 0.6H), 1.61–1.49 (m, 1.2H), 1.49–1.38 (m, 0.6H), 1.30–1.22 (m, 0.6H), 0.96 (d,  $J = 25.4$  Hz, 5.4H), 0.81 (t,  $J = 7.1$  Hz, 1.2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz,

$\text{CDCl}_3$ ):  $\delta$  157.2, 152.8, 150.1 (d,  $J = 2.0$  Hz), 149.2, 149.0 131.3, 126.3, 122.0, 121.4, 118.6, 117.8, 117.6, 115.4, 115.1, 114.7, 80.2, 75.8, 61.6, 58.1, 40.7, 37.7, 28.8, 26.8, 26.2, 25.5, 24.7, 24.1, 18.1, 18.0, 12.2, 12.0.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -77.94. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{40}\text{H}_{59}\text{FN}_3\text{O}_2\text{Si}$  660.4355; Found 660.4364.

**Compound 8e.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 45.2 mg, 62% yield;  $[\alpha]_{\text{D}}^{20} = -10.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 67:33 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.99\text{--}5.55$  ppm (d),  $\delta_{\text{minor}} = 4.94$  ppm (dd)}.

**Major Rotamer of 8e.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.69 (d,  $J = 26.7$  Hz, 1H), 8.90 (t,  $J = 5.1$  Hz, 1H), 8.12 (dd,  $J = 15.1$ , 5.6 Hz, 1H), 8.08–7.99 (m, 1H), 7.89–7.46 (m, 2H), 7.02–6.95 (m, 1H), 6.90–6.84 (m, 1H), 6.84–6.63 (m, 1H), 5.99–5.55 (m, 1H), 4.84–4.50 (m, 1H), 3.67–3.02 (m, 2H), 3.01–2.82 (m, 2H), 2.72–2.46 (m, 2H), 2.46–2.27 (m, 2H), 2.24–2.09 (m, 1H), 1.79 (dd,  $J = 14.3$ , 10.5 Hz, 2H), 1.73–1.53 (m, 6H), 1.53–1.32 (m, 4H), 1.25 (dd,  $J = 13.0$ , 7.7 Hz, 2H), 0.99 (dd,  $J = 9.2$ , 6.9 Hz, 8H), 0.96–0.87 (m, 10H), 0.87–0.77 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.7, 150.1, 149.4, 147.8, 141.3, 131.4, 131.2, 130.5, 129.0, 126.1, 122.4 (q,  $J = 9.1$  Hz), 122.1, 119.2, 118.7, 117.9, 117.8, 80.2, 76.5, 62.5, 58.6, 58.1, 43.2, 37.6, 28.8, 27.8, 26.0, 24.0, 18.1, 18.0, 12.8, 12.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -58.37. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{41}\text{H}_{59}\text{F}_3\text{N}_3\text{O}_3\text{Si}$  726.4272; Found 726.4275.

**Minor Rotamer of 8e.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  12.69 (d,  $J = 26.7$  Hz, 0.5H), 8.77 (dd,  $J = 7.2$ , 4.3 Hz, 0.5H), 8.64–8.52 (m, 0.5H), 8.08–7.99 (m, 0.5H), 7.89–7.46 (m, 1H), 7.17 (t,  $J = 4.3$  Hz, 0.5H), 6.94 (d,  $J = 2.8$  Hz, 0.5H), 4.94 (dd,  $J = 9.6$ , 4.4 Hz, 0.5H), 4.84–4.50 (m, 0.5H), 3.67–3.02 (m, 1H), 3.01–2.82 (m, 1H), 2.72–2.46 (m, 1H), 2.46–2.27 (m, 1H), 2.24–2.09 (m, 0.5H), 1.79 (dd,  $J = 14.3$ , 10.5 Hz, 1H), 1.73–1.53 (m, 3H), 1.53–1.32 (m, 2H), 1.25 (dd,  $J = 13.0$ , 7.7 Hz, 1H), 0.99 (dd,  $J = 9.2$ , 6.9 Hz, 4H), 0.96–0.87 (m, 5H), 0.87–0.77 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.6, 150.0, 149.9, 149.1, 141.2, 131.3, 131.2, 131.0, 128.8, 126.2, 121.8, 121.4 (q,  $J = 9.4$  Hz), 119.2, 118.7, 117.9, 117.7, 80.3, 76.1, 62.5, 61.8, 58.4, 58.3, 43.4, 41.2, 29.7, 27.0, 25.6, 25.4, 18.1, 18.0, 12.5, 12.4.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -77.97. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{41}\text{H}_{59}\text{F}_3\text{N}_3\text{O}_3\text{Si}$  726.4272; Found 726.4275.

**Compound 8f.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 100:100:1); colorless oil; 39.1 mg, 58% yield;  $[\alpha]_{\text{D}}^{20} = -33.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  13.11 (s, 0.3H), 8.90 (d,  $J = 4.5$  Hz, 1H), 8.30 (s, 1H), 8.11 (d,  $J = 8.8$  Hz, 1H), 8.00 (s, 1H), 7.59 (d,  $J = 4.5$  Hz, 1H), 6.69–6.58 (m, 2H), 6.52–6.39 (m, 1H), 5.13–4.88 (m, 1H), 4.29–4.02 (m, 1H), 3.63 (m, 1H), 3.50–3.46 (m, 1H), 3.33–3.28 (m, 2H), 3.08–2.95 (m, 1H), 2.66–2.28 (m, 4H), 2.14 (m, 2H), 1.98–1.83 (m, 2H), 1.72–1.69 (m, 1H), 1.69 (s, 1H), 1.67–1.66 (m, 1H), 1.66–1.63 (m, 1H), 1.62–1.55 (m, 3H), 1.53 (dd,  $J = 11.6$ , 5.8 Hz, 2H), 1.33–1.19 (m, 3H), 1.08 (d,  $J = 6.4$  Hz, 8H), 0.99 (d,  $J = 5.3$  Hz, 10H), 0.84 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.9, 149.6 (d,  $J = 9.1$  Hz), 148.1 (d,  $J = 4.0$  Hz), 132.2, 132.1, 131.9, 131.9, 128.6, 128.5, 124.1, 121.9, 119.1, 119.0, 118.8, 103.3, 75.1, 69.2, 61.7, 57.5, 46.9, 43.7, 40.7, 35.5, 27.2, 26.6, 25.1, 23.8, 18.1, 18.0, 13.1, 11.5.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -77.89, -125.22. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{40}\text{H}_{58}\text{F}_2\text{N}_3\text{O}_2\text{Si}$  678.4261; Found 678.4272.

**Procedure for the Selenylation Reaction.** To 2 mL of DMSO were added hydroquinine-6'-boric acid 3 (49.7 mg, 0.1 mmol), dialkyl diselenide 9 (0.15 mmol) and CuO Nps (0.24 mg, 3 mol %, 40 nm) sequentially. The resulting mixture was heated to 100 °C on the oil bath and stirred for 12 h under air ambient. Then, the mixture was cooled to room temperature, and directly subjected onto the silica gel column for purification, which furnished the product 10.

**Compound 10a.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 37.3 mg, 60% yield;  $[\alpha]_{\text{D}}^{20} = -19.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 45:55 rr, determined

by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.77\text{--}5.66$  ppm (m),  $\delta_{\text{minor}} = 5.01\text{--}4.93$  ppm (m)}.

**Minor Rotamer of 10a.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.95–8.54 (m, 2H), 8.20–8.03 (m, 1H), 8.02–7.91 (m, 1H), 7.71 (m, 1H), 7.66–7.61 (m, 1H), 7.61–7.41 (m, 1H), 7.24 (d,  $J = 5.9$  Hz, 1H), 7.19 (dd,  $J = 8.5$ , 4.0 Hz, 2H), 5.01–4.93 (m, 1H), 4.24 (d,  $J = 8.4$  Hz, 1H), 4.19 (d,  $J = 5.5$  Hz, 1H), 3.63–3.35 (m, 1H), 3.34–2.97 (m, 1H), 2.97–2.91 (m, 1H), 2.88 (dd,  $J = 12.3$ , 7.8 Hz, 1H), 2.62 (m, 1H), 2.53–2.28 (m, 1H), 2.11 (dt,  $J = 28.7$ , 16.0 Hz, 1H), 1.80 (t,  $J = 22.1$  Hz, 2H), 1.73–1.59 (m, 2H), 1.58–1.46 (m, 1H), 1.40 (dd,  $J = 17.6$ , 11.3 Hz, 2H), 1.34–1.23 (m, 2H), 1.19 (dd,  $J = 13.8$ , 6.5 Hz, 1H), 0.98 (d,  $J = 2.5$  Hz, 11H), 0.96 (d,  $J = 5.4$  Hz, 24H), 0.84 (s, 6H), 0.78 (dd,  $J = 14.5$ , 7.3 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 149.9, 148.2, 138.3, 133.9, 132.1, 130.7, 129.7, 128.7, 128.5, 127.0, 122.5, 119.3, 80.1, 72.8, 62.9, 58.6, 43.2, 37.9, 32.7, 28.9, 26.7, 22.9, 18.1, 18.1, 12.9, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{35}\text{H}_{51}\text{N}_2\text{OSeSi}$  623.2930; Found 623.2932.

**Major Rotamer of 10a.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.95–8.54 (m, 2H), 8.20–8.03 (m, 1.2H), 8.02–7.91 (m, 1.2H), 7.71 (m, 1.3H), 7.66–7.61 (m, 1.2H), 7.61–7.41 (m, 1.2H), 7.24 (d,  $J = 5.9$  Hz, 1.2H), 7.19 (dd,  $J = 8.5$ , 4.0 Hz, 2.4H), 5.77–5.66 (m, 1.2H), 4.24 (d,  $J = 8.4$  Hz, 1H), 4.19 (d,  $J = 5.5$  Hz, 1H), 3.63–3.35 (m, 1.2H), 3.34–2.97 (m, 1.3H), 2.97–2.91 (m, 1.2H), 2.88 (dd,  $J = 12.3$ , 7.8 Hz, 1.2H), 2.62 (m, 1.2H), 2.53–2.28 (m, 1.2H), 2.11 (dt,  $J = 28.7$ , 16.0 Hz, 1.2H), 1.80 (t,  $J = 22.1$  Hz, 2.4H), 1.73–1.59 (m, 2.4H), 1.58–1.46 (m, 1.2H), 1.40 (dd,  $J = 17.6$ , 11.3 Hz, 2.4H), 1.34–1.23 (m, 2.4H), 1.19 (dd,  $J = 13.8$ , 6.5 Hz, 1.2H), 0.98 (d,  $J = 2.5$  Hz, 11H), 0.96 (d,  $J = 5.4$  Hz, 24H), 0.84 (s, 6H), 0.78 (dd,  $J = 14.5$ , 7.3 Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.6, 147.3, 138.2, 133.2, 132.0, 130.3, 129.4, 128.7, 128.5, 126.7, 121.4, 118.7, 80.0, 72.3, 61.8, 58.1, 41.3, 37.6, 32.2, 27.8, 25.5, 22.1, 18.0, 17.9, 12.8, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{35}\text{H}_{51}\text{N}_2\text{OSeSi}$  623.2930; Found 623.2932.

**Compound 10b.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 29.9 mg, 47% yield;  $[\alpha]_{\text{D}}^{20} = -14.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 53:47 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 4.96$  ppm (t),  $\delta_{\text{minor}} = 5.72$  ppm (d)}.

**Major Rotamer of 10b.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.99–8.69 (m, 2H), 8.21–8.08 (m, 1H), 8.03–7.93 (m, 1H), 7.74–7.67 (m, 1H), 7.64 (t,  $J = 7.0$  Hz, 1H), 7.15 (dd,  $J = 10.9$ , 6.5 Hz, 2H), 7.03 (t,  $J = 6.8$  Hz, 1H), 4.96 (t,  $J = 9.0$  Hz, 1H), 4.27–4.12 (m, 2H), 3.53–3.31 (m, 1H), 3.09–2.95 (m, 1H), 2.95–2.82 (m, 2H), 2.73–2.43 (m, 2H), 2.30 (d,  $J = 5.0$  Hz, 2H), 2.28–2.26 (m, 1H), 2.16–2.01 (m, 1H), 1.83 (d,  $J = 22.4$  Hz, 2H), 1.76–1.63 (m, 2H), 1.62–1.46 (m, 2H), 1.46–1.36 (m, 2H), 1.36–1.27 (m, 2H), 1.27–1.16 (m, 2H), 0.98 (d,  $J = 2.6$  Hz, 10H), 0.97–0.94 (m, 24H), 0.84 (d,  $J = 5.4$  Hz, 5H), 0.81–0.77 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.6, 147.2, 136.6, 133.8, 130.5, 130.0, 129.3, 128.6, 126.7, 125.7, 122.5, 119.3, 80.0, 72.3, 63.0, 61.8, 58.6, 43.4, 37.7, 32.5, 27.8, 25.5, 21.1, 18.1, 18.1, 12.8, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{OSeSi}$  637.3087; Found 637.3105.

**Minor Rotamer of 10b.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.99–8.69 (m, 1.6H), 8.21–8.08 (m, 0.9H), 8.03–7.93 (m, 1.1H), 7.74–7.67 (m, 0.9H), 7.64 (t,  $J = 7.0$  Hz, 1.2H), 7.15 (dd,  $J = 10.9$ , 6.5 Hz, 1.8H), 7.03 (t,  $J = 6.8$  Hz, 1.3H), 5.72 (d,  $J = 4.6$  Hz, 0.9H), 4.27–4.12 (m, 1.3H), 3.53–3.31 (m, 1H), 3.09–2.95 (m, 1H), 2.95–2.82 (m, 1.8H), 2.73–2.43 (m, 1H), 2.30 (d,  $J = 5.0$  Hz, 1.9H), 2.28–2.26 (m, 1H), 2.16–2.01 (m, 1.1H), 1.83 (d,  $J = 22.4$  Hz, 1.9H), 1.76–1.63 (m, 1.8H), 1.62–1.46 (m, 1.8H), 1.46–1.36 (m, 1.8H), 1.36–1.27 (m, 1.8H), 1.27–1.16 (m, 2.2H), 0.98 (d,  $J = 2.6$  Hz, 9H), 0.97–0.94 (m, 24H), 0.84 (d,  $J = 5.4$  Hz, 5H), 0.81–0.77 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.26, 148.55, 148.2, 135.2, 133.1, 130.7, 130.3, 128.9, 128.7, 126.5, 125.5, 121.4, 118.7, 80.1, 72.9, 62.6, 61.6, 58.1, 41.4, 37.9, 31.9, 29.0, 25.5, 23.0, 18.0, 17.9, 12.9, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{OSeSi}$  637.3087; Found 637.3105.

**Compound 10c.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 37.3 mg, 55% yield;  $[\alpha]_{\text{D}}^{20} = -16.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined

by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.74$  ppm (d),  $\delta = 4.96$  ppm (d) $\}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.87 (d,  $J = 4.5$  Hz, 1H), 8.74 (d,  $J = 4.3$  Hz, 1H), 7.98–7.91 (m, 2H), 7.75–7.58 (m, 4H), 7.34–7.26 (m, 4H), 7.25–7.14 (m, 6H), 5.74 (d,  $J = 4.3$  Hz, 1H), 4.96 (d,  $J = 9.7$  Hz, 1H), 4.23 (t,  $J = 5.9$  Hz, 4H), 3.61–3.48 (m, 1H), 3.40–3.28 (m, 1H), 3.11–2.99 (m, 1H), 2.95 (d,  $J = 11.0$  Hz, 1H), 2.92–2.86 (m, 2H), 2.57–2.30 (m, 2H), 2.29–2.09 (m, 2H), 2.08–1.81 (m, 4H), 1.74 (dd,  $J = 27.9, 17.7$  Hz, 4H), 1.61 (m, 4H), 1.55–1.34 (m, 6H), 1.30 (d,  $J = 1.2$  Hz, 10H), 1.29–1.19 (m, 18H), 0.98 (s, 20H), 0.96 (d,  $J = 3.7$  Hz, 24H), 0.86–0.82 (m, 10H), 0.82–0.75 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 150.0, 149.9, 149.6, 148.5, 147.2, 135.1, 134.9, 133.6, 132.9, 131.8, 131.4, 130.7, 130.5, 130.2, 129.7, 129.2, 128.7, 128.5, 128.4, 126.5, 126.3, 125.6, 125.4, 121.4, 119.3, 80.1, 80.0, 72.4, 72.3, 63.0, 61.8, 58.6, 58.1, 43.2, 41.4, 37.9, 37.7, 34.5, 32.3, 31.7, 31.3, 28.9, 27.9, 26.7, 25.5, 18.2, 18.1, 18.0, 12.9, 12.8, 12.5, 12.5, 12.3, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{39}\text{H}_{59}\text{N}_2\text{OSeSi}$  679.3556; Found 679.3582.

**Compound 10d.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 46.9 mg, 72% yield;  $[\alpha]_{\text{D}}^{20} = -13.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 63:37 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 4.96$  ppm (t),  $\delta_{\text{minor}} = 5.73$  ppm (t) $\}$ .

**Major Rotamer of 10d.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94–8.56 (m, 2H), 8.18–7.92 (m, 2H), 7.66 (m, 2H), 7.17 (m, 2H), 6.81–6.73 (m, 1H), 4.96 (t,  $J = 8.6$  Hz, 1H), 4.31–4.10 (m, 2H), 3.84–3.68 (m, 3H), 3.54–3.31 (m, 1H), 3.02–2.87 (m, 2H), 2.63–2.30 (m, 2H), 2.12 (m, 2H), 1.78 (t,  $J = 15.1$  Hz, 2H), 1.67 (dd,  $J = 19.4, 7.7$  Hz, 2H), 1.61–1.52 (m, 1H), 1.43–1.35 (m, 2H), 1.32 (dd,  $J = 9.5, 7.8$  Hz, 1H), 1.26–1.16 (m, 2H), 0.98 (s, 10H), 0.96 (d,  $J = 5.2$  Hz, 24H), 0.88–0.71 (m, 10H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 150.0, 147.2, 133.9, 130.5, 130.2, 130.1, 129.8, 128.9, 126.7, 122.5, 119.3, 114.0, 80.0, 72.3, 63.0, 58.7, 55.2, 43.4, 37.9, 32.2, 28.9, 27.8, 25.5, 18.1, 17.9, 12.8, 12.5. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{O}_2\text{SeSi}$  653.3036; Found 653.3048.

**Minor Rotamer of 10d.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.9–8.56 (m, 1.2H), 8.18–7.92 (m, 1.4H), 7.66 (m, 1.3H), 7.17 (m, 1.4H), 6.81–6.73 (m, 1H), 5.73 (t,  $J = 6.5$  Hz, 0.6H), 4.31–4.10 (m, 0.6H), 3.84–3.68 (m, 1.2H), 3.54–3.31 (m, 0.7H), 3.02–2.87 (m, 1.4H), 2.63–2.30 (m, 1.4H), 2.12 (m, 1.4H), 1.78 (t,  $J = 15.1$  Hz, 1.2H), 1.67 (dd,  $J = 19.4, 7.7$  Hz, 1.3H), 1.61–1.52 (m, 0.6H), 1.43–1.35 (m, 1.3H), 1.32 (dd,  $J = 9.5, 7.8$  Hz, 1H), 1.26–1.16 (m, 1.3H), 0.98 (s, 6H), 0.96 (d,  $J = 5.2$  Hz, 24H), 0.88–0.71 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.7, 149.6, 148.1, 133.2, 130.7, 130.3, 130.2, 129.9, 128.8, 126.5, 121.4, 118.7, 114.0, 80.1, 72.9, 62.6, 58.1, 55.2, 41.4, 37.7, 31.7, 28.8, 27.9, 25.5, 18.0, 17.9, 12.9, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{O}_2\text{SeSi}$  653.3036; Found 653.3048.

**Compound 10e.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 43.2 mg, 68% yield;  $[\alpha]_{\text{D}}^{20} = -7.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.75$  ppm (d),  $\delta = 4.97$  ppm (t) $\}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.88 (d,  $J = 4.5$  Hz, 1H), 8.75 (d,  $J = 4.2$  Hz, 1H), 8.20 (d,  $J = 4.5$  Hz, 1H), 7.98–7.95 (m, 1H), 7.64 (m, 4H), 7.20–7.11 (m, 6H), 7.11–6.97 (m, 4H), 5.75 (d,  $J = 3.3$  Hz, 1H), 4.97 (t,  $J = 7.8$  Hz, 1H), 4.28–4.18 (m, 4H), 3.62–3.19 (m, 3H), 3.15–2.91 (m, 3H), 2.89 (dd,  $J = 12.8, 7.3$  Hz, 2H), 2.69–2.43 (m, 3H), 2.39 (d,  $J = 18.2$  Hz, 6H), 2.31 (dd,  $J = 17.1, 9.4$  Hz, 3H), 2.11 (dt,  $J = 22.8, 11.2$  Hz, 2H), 1.90–1.74 (m, 4H), 1.74–1.60 (m, 4H), 1.60–1.50 (m, 2H), 1.50–1.38 (m, 4H), 1.37–1.28 (m, 4H), 1.27–1.17 (m, 4H), 0.98 (s, 20H), 0.96 (s, 24H), 0.84 (s, 10H), 0.79 (dd,  $J = 15.1, 7.7$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.2, 150.0, 149.7, 148.6, 148.4, 147.2, 136.5, 136.4, 135.9, 135.7, 134.2, 133.3, 130.7, 130.6, 130.1, 129.7, 129.5, 129.0, 127.5, 127.4, 127.1, 126.9, 126.8, 126.4, 126.2, 126.1, 122.5, 121.4, 119.3, 118.7, 79.9, 72.2, 62.9, 61.8, 58.6, 58.1, 43.2, 41.4, 37.8, 37.6, 31.0, 30.4, 28.9, 28.7, 27.9, 26.7, 25.5, 22.8, 19.3, 19.2, 18.2, 18.1, 18.0, 17.9, 12.9, 12.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{OSeSi}$  637.3087; Found 637.3103.

**Compound 10f.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 30.9 mg, 47% yield;  $[\alpha]_{\text{D}}^{20} = -7.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.70$  ppm (d),  $\delta = 4.96$  ppm (t) $\}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (dd,  $J = 7.8, 4.6$  Hz, 1H), 8.81–8.75 (m, 1H), 8.17–8.04 (m, 2H), 8.03–7.95 (m, 2H), 7.74–7.61 (m, 4H), 7.19–6.82 (m, 6H), 5.70 (d,  $J = 4.7$  Hz, 1H), 4.96 (t,  $J = 8.8$  Hz, 1H), 4.14 (dd,  $J = 12.5, 7.2$  Hz, 3H), 3.48–3.28 (m, 2H), 3.01–2.84 (m, 4H), 2.57 (m, 2H), 2.40–2.14 (m, 2H), 2.13–1.97 (m, 4H), 1.86–1.74 (m, 4H), 1.66 (m, 4H), 1.59–1.42 (m, 4H), 1.41–1.29 (m, 6H), 1.28–1.10 (m, 6H), 0.97 (s, 20H), 0.95 (s, 24H), 0.83 (d,  $J = 3.5$  Hz, 10H), 0.78 (dd,  $J = 13.2, 7.3$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.5 (d,  $J = 18.2$  Hz), 150.3, 149.9, 149.5 (d,  $J = 18.2$  Hz), 148.6 (d,  $J = 21.2$  Hz), 148.1 (d,  $J = 21.2$  Hz), 147.3, 147.3, 134.0, 133.2, 131.0, 130.8, 130.5, 130.2, 128.9, 128.4, 127.5, 126.7, 124.6, 124.6, 122.5, 121.5, 119.4, 118.7, 117.6, 117.5, 117.3, 117.2, 117.1, 117.0, 80.1, 80.0, 72.9, 72.3, 63.0, 61.9, 58.7, 58.2, 43.2, 41.3, 37.8, 37.6, 31.5, 31.0, 28.8, 27.8, 26.7, 25.5, 25.4, 22.7, 18.1, 18.1, 17.9, 12.9, 12.9, 12.5, 12.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -137.22 (d,  $J = 24.1$  Hz), -137.30 (d,  $J = 7.5$  Hz), -139.78 (d,  $J = 33.7$  Hz), -139.81 (d,  $J = 20.2$  Hz). HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{35}\text{H}_{49}\text{F}_2\text{N}_2\text{OSeSi}$  659.2742; Found 659.2759.

**Compound 10g.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 34.1 mg, 45% yield;  $[\alpha]_{\text{D}}^{20} = -20.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.72$  ppm (d),  $\delta = 4.97$  ppm (d) $\}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.95–8.87 (m, 2H), 8.25–8.06 (m, 2H), 8.06–7.94 (m, 2H), 7.75–7.64 (m, 4H), 7.64–7.55 (m, 4H), 7.50 (dd,  $J = 13.5, 5.7$  Hz, 1H), 7.18 (dd,  $J = 7.6, 4.3$  Hz, 1H), 5.72 (d,  $J = 4.8$  Hz, 1H), 4.97 (d,  $J = 9.6$  Hz, 1H), 4.33–4.16 (m, 3.4H), 3.50–3.31 (m, 2H), 3.12–2.94 (m, 2H), 2.92–2.82 (m, 3H), 2.69–2.46 (m, 3H), 2.39–2.18 (m, 2H), 2.09 (dt,  $J = 35.2, 9.4$  Hz, 4H), 1.87–1.75 (m, 4H), 1.75–1.60 (m, 4H), 1.60–1.48 (m, 2H), 1.48–1.37 (m, 4H), 1.37–1.29 (m, 4H), 1.27–1.18 (m, 4H), 0.98 (s, 20H), 0.97 (s, 24H), 0.83 (s, 10H), 0.78 (dt,  $J = 7.6, 4.2$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 150.2, 149.9, 149.6, 148.1, 147.4, 141.2, 141.2, 134.2, 133.5, 132.0, 131.1, 130.5, 130.2, 128.7 (q,  $J = 4.0$  Hz), 128.7 (q,  $J = 4.0$  Hz), 127.4, 126.7, 125.7, 124.4, 122.5, 121.6, 121.0, 120.8, 119.5, 118.7, 80.1, 80.0, 72.9, 72.2, 62.5, 63.2, 58.6, 58.2, 43.3, 41.3, 37.8, 37.6, 31.5, 31.1, 28.8, 27.8, 26.7, 25.5, 22.7, 22.0, 18.1, 18.1, 17.9, 17.9, 12.9, 12.8, 12.5, 12.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.95, -62.98. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{37}\text{H}_{49}\text{F}_2\text{N}_2\text{OSeSi}$  759.2678; Found 759.2704.

**Compound 10h.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 28.9 mg, 43% yield;  $[\alpha]_{\text{D}}^{20} = -16.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.69$  ppm (d),  $\delta = 4.96$  ppm (t) $\}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.94–8.83 (m, 2H), 8.76 (dd,  $J = 11.6, 4.2$  Hz, 1H), 8.20 (s, 1H), 8.18–7.95 (m, 2H), 7.93 (d,  $J = 6.3$  Hz, 1H), 7.77 (d,  $J = 2.9$  Hz, 1H), 7.76–7.72 (m, 2H), 7.72–7.65 (m, 4H), 7.65–7.54 (m, 4H), 7.46–7.40 (m, 4H), 7.38 (s, 1H), 7.16 (d,  $J = 4.2$  Hz, 1H), 5.69 (d,  $J = 4.9$  Hz, 1H), 4.96 (t,  $J = 8.4$  Hz, 1H), 4.37 (d,  $J = 7.2$  Hz, 4H), 3.77–3.36 (m, 2H), 3.34–3.02 (m, 2H), 2.99–2.83 (m, 6H), 2.68–2.50 (m, 2H), 2.50–2.25 (m, 2H), 2.23–1.99 (m, 4H), 1.87–1.71 (m, 4H), 1.64 (m, 4H), 1.59–1.45 (m, 2H), 1.45–1.33 (m, 4H), 1.27 (dd,  $J = 13.4, 5.6$  Hz, 4H), 1.23–1.19 (m, 2H), 0.98 (d,  $J = 2.6$  Hz, 20H), 0.93 (d,  $J = 11.1$  Hz, 24H), 0.81 (d,  $J = 7.6$  Hz, 10H), 0.80–0.74 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.4, 150.1, 149.9, 149.7, 148.7, 148.4, 148.1, 147.2, 135.7, 135.6, 133.9, 133.3, 132.5, 130.8, 130.6, 130.5, 130.2, 129.5, 129.0, 128.8, 128.6, 128.4, 128.1, 127.7, 127.6, 127.2, 127.1, 127.1, 127.0, 126.7, 126.5, 126.2, 125.8, 122.5, 121.4, 119.3, 118.7, 80.1, 80.0, 72.9, 72.2, 63.1, 61.8, 58.6, 58.1, 43.4, 43.2, 42.7, 41.4, 37.8, 37.6, 33.2, 32.7, 28.8, 27.8, 26.7, 25.4, 18.1, 18.1, 17.9, 17.9, 12.9, 12.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{39}\text{H}_{53}\text{N}_2\text{OSeSi}$  673.3087; Found 673.3111.

**Compound 10i.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 32.9



mg, 49% yield;  $[\alpha]_D^{20} = -12.2$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.72$  ppm (d),  $\delta = 5.95$  ppm (t).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (dd,  $J = 11.2, 6.7$  Hz, 2H), 8.76 (d,  $J = 4.3$  Hz, 1H), 8.22 (s, 1H), 8.13 (dd,  $J = 15.5, 8.0$  Hz, 2H), 7.97 (d,  $J = 8.7$  Hz, 2H), 7.94–7.82 (m, 2H), 7.72 (m, 4H), 7.67–7.58 (m, 2H), 7.53 (m, 4H), 7.33–7.31 (m, 1H), 7.26 (d,  $J = 2.2$  Hz, 1H), 7.24–7.15 (m, 2H), 5.72 (d,  $J = 3.4$  Hz, 1H), 4.95 (t,  $J = 9.5$  Hz, 1H), 4.75–4.62 (m, 4H), 3.74–3.43 (m, 2H), 3.37–3.22 (m, 1H), 3.11–2.99 (m, 1H), 2.99–2.82 (m, 4H), 2.70–2.54 (m, 2H), 2.53–2.25 (m, 2H), 2.24–1.97 (m, 4H), 1.86–1.72 (m, 4H), 1.71–1.47 (m, 6H), 1.46–1.35 (m, 4H), 1.34–1.26 (m, 4H), 1.26–1.18 (m, 4H), 0.97 (s, 20H), 0.96 (d,  $J = 1.9$  Hz, 24H), 0.86–0.81 (m, 10H), 0.81–0.72 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.4, 150.1, 149.9, 149.7, 148.7, 148.4, 148.1, 147.2, 134.1, 134.0, 133.8, 133.7, 133.2, 133.2, 131.3, 131.2, 130.7, 130.6, 130.2, 130.0, 129.2, 128.9, 128.2, 128.1, 127.1, 126.9, 126.8, 126.5, 126.2, 125.9, 125.4, 125.3, 123.9, 123.9, 121.5, 121.5, 119.3, 118.7, 80.1, 80.0, 72.3, 72.2, 63.0, 61.8, 58.6, 58.3, 43.2, 41.4, 37.8, 37.6, 30.6, 30.0, 28.9, 28.8, 27.9, 27.8, 26.7, 25.5, 18.2, 18.1, 17.9, 17.9, 12.9, 12.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{39}\text{H}_{53}\text{N}_2\text{OSeSi}$  673.3087; Found 673.3109.

**Compound 10j.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 31.3 mg, 51% yield;  $[\alpha]_D^{20} = -14.8$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.75$  ppm (d),  $\delta = 4.95$  ppm (t).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.85 (d,  $J = 4.5$  Hz, 1H), 8.72 (t,  $J = 5.2$  Hz, 1H), 8.67 (d,  $J = 1.6$  Hz, 1H), 8.12 (s, 1H), 7.96 (dd,  $J = 15.1, 8.7$  Hz, 2H), 7.75 (m, 2H), 7.61 (d,  $J = 4.6$  Hz, 1H), 7.14 (d,  $J = 4.3$  Hz, 1H), 5.75 (d,  $J = 5.0$  Hz, 1H), 4.95 (t,  $J = 7.8$  Hz, 1H), 3.61–3.47 (m, 1H), 3.40–3.32 (m, 1H), 3.12–3.03 (m, 4H), 3.03–2.95 (m, 2H), 2.92–2.86 (m, 2H), 2.65–2.50 (m, 2H), 2.27 (dd,  $J = 21.2, 10.6$  Hz, 2H), 2.21–2.01 (m, 4H), 1.89–1.85 (m, 2H), 1.83 (d,  $J = 4.2$  Hz, 2H), 1.81–1.74 (m, 6H), 1.66 (dd,  $J = 9.0, 5.4$  Hz, 4H), 1.64–1.56 (m, 6H), 1.52 (m, 4H), 1.45–1.41 (m, 2H), 1.37 (m, 4H), 1.31 (d,  $J = 2.3$  Hz, 2H), 1.29–1.28 (m, 2H), 1.26 (s, 4H), 1.21 (dd,  $J = 14.8, 7.3$  Hz, 4H), 0.98 (s, 20H), 0.92 (dd,  $J = 28.2, 5.9$  Hz, 24H), 0.87–0.82 (m, 10H), 0.80 (t,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.7, 149.3, 148.2, 148.1, 147.0, 133.3, 132.5, 130.7, 130.4, 130.1, 129.2, 128.4, 126.8, 126.5, 125.5, 121.4, 119.3, 80.0, 80.0, 72.4, 72.3, 62.9, 61.7, 58.7, 58.2, 43.3, 41.3, 40.5, 40.3, 37.9, 37.6, 35.0, 34.5, 33.3, 33.2, 33.2, 32.9, 28.9, 27.9, 26.8, 25.5, 25.3, 23.0, 18.1, 18.1, 17.9, 17.9, 12.9, 12.5, 12.3, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{55}\text{N}_2\text{OSeSi}$  615.3243; Found 615.3262.

**Compound 10k.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 32.3 mg, 55% yield;  $[\alpha]_D^{20} = -16.5$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.87$  ppm (d),  $\delta = 4.96$  ppm (t).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.91 (d,  $J = 4.5$  Hz, 1H), 8.76 (dd,  $J = 21.9, 4.2$  Hz, 1H), 8.12 (dd,  $J = 14.3, 8.8$  Hz, 2H), 8.06–7.94 (m, 2H), 7.65 (dd,  $J = 11.6, 6.2$  Hz, 2H), 7.54–7.45 (m, 1H), 7.16 (dd,  $J = 9.1, 4.2$  Hz, 1H), 5.87 (d,  $J = 4.0$  Hz, 1H), 4.96 (t,  $J = 10.4$  Hz, 1H), 3.64–3.48 (m, 1H), 3.46–3.37 (m, 1H), 3.10–2.96 (m, 4H), 2.95–2.82 (m, 4H), 2.72–2.43 (m, 4H), 2.41–2.27 (m, 2H), 2.10 (dd,  $J = 29.3, 12.1$  Hz, 2H), 1.88–1.79 (m, 4H), 1.74 (dd,  $J = 15.7, 7.6$  Hz, 4H), 1.70–1.56 (m, 4H), 1.56–1.44 (m, 4H), 1.44–1.37 (m, 4H), 1.37–1.29 (m, 4H), 1.22 (m, 4H), 0.98 (d,  $J = 3.7$  Hz, 24H), 0.96 (d,  $J = 4.5$  Hz, 24H), 0.92–0.79 (m, 18H), 0.76 (d,  $J = 7.3$  Hz, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 149.9, 149.6, 149.3, 148.2, 147.1, 133.2, 132.5, 130.7, 130.5, 128.9, 128.7, 126.6, 125.7, 122.5, 121.0, 119.2, 118.7, 80.1, 80.0, 72.9, 72.3, 63.0, 62.6, 61.7, 61.6, 58.7, 58.1, 43.4, 41.3, 37.9, 37.7, 32.3, 32.1, 28.9, 28.8, 27.9, 27.8, 26.8, 25.6, 22.9, 22.1, 18.1, 18.1, 17.9, 17.9, 13.9, 12.9, 12.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{33}\text{H}_{53}\text{N}_2\text{OSeSi}$  589.3087; Found 589.3102.

**Compound 10l.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 32.8 mg, 52% yield;  $[\alpha]_D^{20} = -7.3$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.75$  ppm (d),  $\delta = 4.94$  ppm (d).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.85 (d,

$J = 4.5$  Hz, 1H), 8.72 (d,  $J = 4.3$  Hz, 1H), 8.67 (d,  $J = 1.3$  Hz, 1H), 8.10 (s, 1H), 7.97 (dd,  $J = 13.8, 8.8$  Hz, 2H), 7.77 (dd,  $J = 8.7, 1.5$  Hz, 1H), 7.71 (dd,  $J = 8.7, 1.6$  Hz, 1H), 7.61 (d,  $J = 4.5$  Hz, 1H), 7.14 (d,  $J = 4.3$  Hz, 1H), 5.75 (d,  $J = 4.7$  Hz, 1H), 4.94 (d,  $J = 9.8$  Hz, 1H), 3.58–3.32 (m, 2H), 3.04 (m, 6H), 2.96–2.84 (m, 4H), 2.66–2.51 (m, 2H), 2.28 (t,  $J = 11.5$  Hz, 1H), 2.16–2.08 (m, 1H), 2.08–1.92 (m, 4H), 1.82 (dd,  $J = 20.5, 9.5$  Hz, 4H), 1.76–1.71 (m, 4H), 1.71–1.61 (m, 4H), 1.59 (dd,  $J = 9.6, 5.8$  Hz, 2H), 1.43 (d,  $J = 2.5$  Hz, 4H), 1.39 (dd,  $J = 12.7, 5.0$  Hz, 6H), 1.33 (d,  $J = 11.8$  Hz, 4H), 1.29 (s, 4H), 1.24 (d,  $J = 12.8$  Hz, 14H), 0.98 (s, 18H), 0.96 (d,  $J = 2.9$  Hz, 24H), 0.87 (d,  $J = 4.8$  Hz, 8H), 0.84 (d,  $J = 4.8$  Hz, 8H), 0.81 (d,  $J = 7.4$  Hz, 4H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.0, 149.7, 149.3, 148.3, 148.2, 147.0, 133.2, 132.5, 130.7, 130.5, 129.8, 128.8, 128.7, 126.8, 126.5, 125.4, 121.4, 119.3, 80.0, 72.3, 62.9, 61.7, 58.7, 58.2, 43.3, 41.3, 37.9, 37.6, 31.8, 31.7, 30.3, 30.2, 30.1, 29.9, 29.8, 29.7, 28.9, 28.9, 28.8, 28.4, 27.9, 26.7, 25.5, 25.5, 23.0, 22.6, 18.1, 18.1, 18.1, 17.9, 14.1, 14.1, 12.9, 12.5, 12.3, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{35}\text{H}_{59}\text{N}_2\text{OSeSi}$  631.3556; Found 631.3574.

**Compound 10m.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 35.6 mg, 56% yield;  $[\alpha]_D^{20} = -19.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.87$  ppm (d),  $\delta = 5.01$ –4.92 ppm (m).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.89 (dd,  $J = 12.5, 4.5$  Hz, 2H), 8.76 (dd,  $J = 14.3, 4.2$  Hz, 1H), 8.16 (d,  $J = 12.5$  Hz, 1H), 8.05 (m, 3H), 7.82–7.65 (m, 3H), 7.63 (d,  $J = 4.3$  Hz, 2H), 7.52 (dt,  $J = 27.0, 7.4$  Hz, 2H), 7.30–7.25 (m, 2H), 7.22–7.14 (m, 4H), 5.87 (d,  $J = 4.1$  Hz, 1H), 5.01–4.92 (m, 1H), 3.60–3.39 (m, 2H), 3.24 (m, 2H), 3.01 (m, 4H), 2.96–2.81 (m, 4H), 2.62 (dd,  $J = 15.7, 8.4$  Hz, 2H), 2.31 (dd,  $J = 21.7, 13.7$  Hz, 2H), 2.17–1.98 (m, 2H), 1.89–1.78 (m, 4H), 1.77–1.62 (m, 4H), 1.62–1.54 (m, 2H), 1.54–1.44 (m, 2H), 1.40 (dd,  $J = 14.4, 4.9$  Hz, 4H), 1.34–1.25 (m, 4H), 1.20 (dt,  $J = 10.9, 7.6$  Hz, 4H), 0.98 (s, 24H), 0.96 (d,  $J = 4.5$  Hz, 24H), 0.86–0.80 (m, 10H), 0.77 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 149.9, 149.6, 149.3, 148.2, 147.2, 140.8, 140.7, 133.3, 132.7, 130.9, 130.5, 129.7, 128.9, 128.5, 128.4, 126.7, 126.5, 125.7, 125.5, 122.5, 122.5, 121.4, 121.0, 119.3, 118.7, 80.1, 80.1, 72.9, 72.4, 63.0, 62.6, 61.8, 61.6, 58.7, 58.1, 43.4, 41.4, 37.8, 36.6, 29.2, 28.9, 28.8, 27.8, 26.8, 25.5, 22.9, 22.0, 18.1, 18.1, 17.9, 17.9, 12.9, 12.9, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{36}\text{H}_{53}\text{N}_2\text{OSeSi}$  637.3087; Found 637.3097.

**Compound 10n.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 33.3 mg, 58% yield;  $[\alpha]_D^{20} = -18.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.87$  ppm (d),  $\delta = 4.97$  ppm (t).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.92–8.89 (m, 1H), 8.80–8.74 (m, 1H), 8.12 (dd,  $J = 14.8, 8.4$  Hz, 2H), 8.05–7.96 (m, 2H), 7.64 (t,  $J = 4.3$  Hz, 2H), 7.51 (dd,  $J = 17.7, 10.0$  Hz, 1H), 7.16 (t,  $J = 4.2$  Hz, 1H), 5.87 (d,  $J = 4.1$  Hz, 1H), 4.97 (t,  $J = 9.5$  Hz, 1H), 3.67–3.26 (m, 4H), 3.14–2.79 (m, 6H), 2.73–2.47 (m, 4H), 2.32 (t,  $J = 14.3$  Hz, 2H), 2.20–2.01 (m, 2H), 1.87–1.77 (m, 4H), 1.77–1.60 (m, 4H), 1.60–1.51 (m, 2H), 1.51–1.44 (m, 4H), 1.42 (s, 4H), 1.39–1.32 (m, 4H), 1.29 (dd,  $J = 14.2, 6.9$  Hz, 2H), 1.25–1.11 (m, 4H), 0.98 (d,  $J = 3.7$  Hz, 24H), 0.96 (d,  $J = 5.6$  Hz, 24H), 0.82 (t,  $J = 7.5$  Hz, 12H), 0.78 (dd,  $J = 9.7, 4.8$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.6, 150.1, 149.9, 149.6, 148.2, 147.3, 135.4, 134.6, 131.8, 130.5, 128.9, 128.7, 126.6, 125.8, 122.5, 121.0, 119.2, 118.7, 80.2, 80.1, 72.9, 72.4, 62.9, 62.6, 61.7, 61.6, 58.7, 58.1, 43.4, 41.3, 37.9, 37.7, 34.3, 33.9, 28.8, 27.8, 26.8, 25.6, 24.4, 24.1, 23.1, 22.1, 18.1, 18.1, 17.9, 17.9, 12.9, 12.8, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{51}\text{N}_2\text{OSeSi}$  575.2930; Found 575.2939.

**Compound 10o.** Purified by column chromatography on silica gel (Petroleum ether:EtOAc:Et<sub>3</sub>N = 150:100:1); light yellow oil; 38.1 mg, 62% yield;  $[\alpha]_D^{20} = -9.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 50:50 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta = 5.77$  ppm (d),  $\delta = 4.95$  ppm (d).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.88 (d,  $J = 4.5$  Hz, 1H), 8.75 (d,  $J = 1.3$  Hz, 1H), 8.74 (d,  $J = 4.3$  Hz, 1H), 8.20 (s, 1H), 7.99 (d,  $J = 8.7$  Hz, 1H), 7.95 (d,  $J = 8.7$  Hz, 1H), 7.83 (dd,  $J = 8.7, 1.5$  Hz, 1H), 7.76 (dd,  $J = 8.7, 1.6$  Hz, 1H), 7.63 (d,  $J =$



4.5 Hz, 1H), 7.15 (d,  $J = 4.3$  Hz, 1H), 5.77 (d,  $J = 5.1$  Hz, 1H), 4.95 (d,  $J = 9.8$  Hz, 1H), 3.53 (dd,  $J = 17.4$ , 9.2 Hz, 1H), 3.46–3.28 (m, 4H), 3.03 (m, 1H), 2.98–2.83 (m, 4H), 2.63–2.51 (m, 2H), 2.27 (dd,  $J = 23.5$ , 10.0 Hz, 2H), 2.19–2.07 (m, 4H), 2.04 (d,  $J = 13.5$  Hz, 4H), 1.84–1.77 (m, 4H), 1.76–1.69 (m, 6H), 1.62 (s, 4H), 1.59 (d,  $J = 7.5$  Hz, 4H), 1.43 (d,  $J = 4.0$  Hz, 2H), 1.38–1.32 (m, 6H), 1.30 (dd,  $J = 8.1$ , 2.8 Hz, 4H), 1.25 (d,  $J = 6.3$  Hz, 4H), 1.23–1.16 (m, 2H), 0.98 (d,  $J = 2.3$  Hz, 20H), 0.97–0.92 (m, 24H), 0.85 (t,  $J = 6.8$  Hz, 12H), 0.79 (t,  $J = 7.3$  Hz, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.3, 150.0, 149.5, 148.5, 148.4, 147.3, 135.5, 134.4, 131.1, 130.6, 130.4, 128.6, 128.1, 127.5, 126.7, 126.3, 121.3, 119.2, 80.1, 72.3, 62.9, 61.7, 58.7, 58.2, 43.7, 43.3, 43.2, 41.3, 37.8, 37.6, 34.5, 34.2, 28.8, 27.9, 26.9, 26.8, 25.7, 25.5, 23.0, 23.0, 18.1, 18.1, 18.1, 17.9, 12.9, 12.9, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{34}\text{H}_{55}\text{N}_2\text{OSeSi}$  615.3243; Found 615.3248.

**Procedure for the Synthesis of Compound 14.** Compound S2 (1.00 g, 3.1 mmol) and  $\text{Et}_3\text{N}$  (0.93 g, 9.2 mmol) were added to dichloromethane (25 mL), followed by the addition of TIPSOTf (1.02 g, 3.3 mmol). The resulting mixture was stirred at room temperature for 1 h, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ( $\text{EtOAc}:\text{Et}_3\text{N} = 100:1$ ) to afford compound 14.

**Compound 14.** Colorless oil; 1.26 g, 85% yield;  $[\alpha]_{\text{D}}^{20} = -27.1$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 75:25 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 5.99$  ppm (d),  $\delta_{\text{minor}} = 4.97$  ppm (d)}.

**Major Rotamer of 14.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (t,  $J = 5.7$  Hz, 1H), 8.03 (d,  $J = 9.2$  Hz, 1H), 7.59 (d,  $J = 4.5$  Hz, 1H), 7.38 (dd,  $J = 9.2$ , 2.6 Hz, 1H), 7.28 (d,  $J = 2.6$  Hz, 1H), 5.99 (d,  $J = 44.9$  Hz, 1H), 3.99 (s, 3H), 3.76 (dd,  $J = 29.8$ , 11.7 Hz, 1H), 3.49–3.12 (m, 1H), 3.11–2.83 (m, 2H), 2.70–2.44 (m, 1H), 2.09 (dd,  $J = 13.3$ , 2.9 Hz, 1H), 1.89 (dd,  $J = 22.1$ , 11.3 Hz, 1H), 1.73–1.49 (m, 3H), 1.48–1.33 (m, 1H), 1.33–1.18 (m, 2H), 1.07–0.94 (m, 18H), 0.89–0.75 (m, 6H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 147.2, 147.0, 144.4, 131.9, 126.1, 122.4, 119.0, 99.8, 79.8, 71.1, 61.9, 58.0, 56.1, 43.4, 37.6, 27.9, 27.5, 24.8, 18.1, 18.0, 12.9, 11.8. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{29}\text{H}_{47}\text{N}_2\text{O}_2\text{Si}$  483.3401; Found 483.3397.

**Minor Rotamer of 14.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.65 (t,  $J = 3.3$  Hz, 0.3H), 7.99 (d,  $J = 9.2$  Hz, 0.3H), 7.90 (d,  $J = 2.8$  Hz, 0.3H), 7.32 (dd,  $J = 9.2$ , 2.8 Hz, 0.3H), 7.14 (d,  $J = 4.4$  Hz, 0.3H), 4.97 (d,  $J = 9.6$  Hz, 0.3H), 3.92 (s, 1H), 3.62 (dd,  $J = 17.8$ , 9.2 Hz, 0.3H), 3.49–3.12 (m, 0.3H), 3.11–2.83 (m, 0.6H), 2.70–2.44 (m, 0.3H), 2.09 (dd,  $J = 13.3$ , 2.9 Hz, 0.3H), 1.89 (dd,  $J = 22.1$ , 11.3 Hz, 0.3H), 1.73–1.49 (m, 1H), 1.48–1.33 (m, 0.3H), 1.33–1.18 (m, 0.6H), 1.07–0.94 (m, 5.4H), 0.89–0.75 (m, 1.8H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.5, 147.5, 147.2, 145.4, 131.5, 127.1, 121.4, 121.3, 104.5, 79.8, 71.1, 60.9, 58.0, 55.3, 41.3, 36.7, 28.8, 26.5, 25.4, 18.0, 17.9, 12.4, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{29}\text{H}_{47}\text{N}_2\text{O}_2\text{Si}$  483.3401; Found 483.3397.

**Procedure for the Synthesis of Compound 15.** Compound 14 (1.00 g, 2.1 mmol) and sodium ethanethiol (0.70 g, 8.3 mmol) were added to dimethylformamide (10 mL). The reaction mixture was heated to 110 °C in the oil bath and stirred for 12 h under argon ambient. The mixture was cooled to room temperature, and aq. saturated  $\text{NH}_4\text{Cl}$  (30 mL) was added. The aqueous layer was extracted with  $\text{EtOAc}$  ( $3 \times 40$  mL). The combined organic layers were washed with aq. saturated  $\text{NaCl}$  ( $2 \times 20$  mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrate under reduced pressure. The residue was purified by column chromatography on silica gel ( $\text{EtOAc}:\text{MeOH}:\text{Et}_3\text{N} = 100:5:1$ ) to furnish the compound 15.

**Compound 15.** Light yellow solid; 0.85 g, 88% yield; MP: 115.3–117.1 °C;  $[\alpha]_{\text{D}}^{20} = -17.9$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ); 89:11 rr, determined by  $^1\text{H}$  NMR integration of the set of C-9 proton signals  $\{\delta_{\text{major}} = 6.08$  ppm (s),  $\delta_{\text{minor}} = 4.92$  ppm (d)}.

**Major Rotamer of 15.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J = 4.5$  Hz, 1H), 8.00 (t,  $J = 5.9$  Hz, 2H), 7.53 (d,  $J = 4.5$  Hz, 1H), 7.30–7.27 (m, 1H), 6.08 (s, 1H), 3.67 (m, 1H), 3.08 (dd,  $J = 13.4$ , 10.2 Hz, 1H), 2.96–2.74 (m, 2H), 2.33 (d,  $J = 13.7$  Hz, 1H), 2.07 (dd,  $J = 12.8$ , 8.5 Hz, 1H), 1.89–1.73 (m, 2H), 1.41 (m, 3H), 1.18–1.06 (m, 2H), 1.05–0.94 (m, 20H), 0.88 (s, 1H), 0.72 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.0, 147.8, 146.1, 143.3, 131.0, 1267.0, 123.1, 118.7, 106.2, 72.2, 60.9, 58.2, 43.1, 37.3, 28.0, 27.6, 25.2, 19.6, 18.2, 18.1, 13.0, 12.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{45}\text{N}_2\text{O}_2\text{Si}$  469.3245; Found 469.3241.

**Minor Rotamer of 15.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (d,  $J = 4.3$  Hz, 0.1H), 7.92 (t,  $J = 5.8$  Hz, 0.2H), 7.53 (d,  $J = 4.5$  Hz, 0.1H), 7.10 (d,  $J = 4.4$  Hz, 0.1H), 4.92 (d,  $J = 9.9$  Hz, 0.1H), 3.67 (m, 0.1H), 3.08 (dd,  $J = 13.4$ , 10.2 Hz, 0.1H), 2.96–2.74 (m, 0.2H), 2.33 (d,  $J = 13.7$  Hz, 0.1H), 2.07 (dd,  $J = 12.8$ , 8.5 Hz, 0.1H), 1.89–1.73 (m, 0.2H), 1.41 (m, 0.3H), 1.18–1.06 (m, 0.2H), 1.05–0.94 (m, 2H), 0.88 (s, 0.1H), 0.72 (t,  $J = 7.3$  Hz, 0.3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.1, 147.9, 146.1, 143.3, 131.3, 127.0, 123.1, 118.7, 106.2, 72.2, 60.9, 58.2, 43.1, 37.5, 28.0, 27.7, 25.7, 19.7, 18.1, 17.9, 12.5, 12.2. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{28}\text{H}_{45}\text{N}_2\text{O}_2\text{Si}$  469.3245; Found 469.3241.

**Procedure for the Synthesis of Compound 16.** To a glass tube were added 5a (111.4 mg, 0.2 mmol), TBAF trihydrate (189.3 mg, 0.6 mmol), and THF (4 mL) successively. The resulting mixture was stirred at room temperature for 1 h, and concentrated under vacuum to remove THF. The residue was dissolved in  $\text{EtOAc}$  (20 mL), washed with water ( $2 \times 10$  mL) and brine (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrate under reduced pressure. The crude product was purified by column chromatography on silica gel ( $\text{EtOAc}:\text{MeOH}:\text{Et}_3\text{N} = 100:5:1$ ) to furnish the product 16.

**Compound 16.** Colorless oil; 56.8 mg, 71% yield;  $[\alpha]_{\text{D}}^{20} = -13.6$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.57 (d,  $J = 4.5$  Hz, 1H), 8.02–7.96 (m, 2H), 7.56 (dd,  $J = 8.8$ , 1.6 Hz, 1H), 7.44 (d,  $J = 4.6$  Hz, 1H), 7.10 (d,  $J = 7.6$  Hz, 2H), 7.04 (d,  $J = 7.7$  Hz, 1H), 5.52 (d,  $J = 4.2$  Hz, 1H), 3.38–3.27 (m, 1H), 3.02 (dd,  $J = 14.3$ , 6.7 Hz, 1H), 2.88 (dd,  $J = 13.4$ , 9.9 Hz, 1H), 2.47–2.35 (m, 4H), 2.30–2.20 (m, 4H), 1.70–1.53 (m, 3H), 1.36–1.25 (m, 3H), 1.18 (m, 2H), 0.77 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1, 149.6, 146.8, 140.1, 138.4, 137.3, 135.1, 131.3, 131.0, 129.9, 129.5, 126.7, 125.4, 123.1, 118.8, 71.4, 60.3, 58.5, 43.2, 37.4, 28.1, 27.6, 25.4, 21.3, 21.1, 20.5, 12.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{27}\text{H}_{33}\text{N}_2\text{O}$  401.2587; Found 401.2584.

**Procedure for the Synthesis of Compound 17.** To a glass tube was added 8a (128.4 mg, 0.2 mmol), TBAF trihydrate (189.3 mg, 0.6 mmol), and THF (4 mL) successively. The resulting mixture was stirred at room temperature for 1 h, and concentrated under vacuum to remove THF. The residue was dissolved in  $\text{EtOAc}$  (20 mL), washed with water ( $2 \times 10$  mL) and brine (10 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrate under reduced pressure. The crude product was purified by column chromatography on silica gel ( $\text{EtOAc}:\text{MeOH}:\text{Et}_3\text{N} = 100:5:1$ ) to furnish the product 17.

**Compound 17.** Colorless oil; 68.2 mg, 70% yield;  $[\alpha]_{\text{D}}^{20} = -11.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.77 (dd,  $J = 4.5$ , 2.0 Hz, 1H), 8.09–7.93 (m, 2H), 7.87–7.66 (m, 1H), 7.61 (dd,  $J = 9.8$ , 4.5 Hz, 1H), 7.11–6.94 (m, 1H), 6.92–6.83 (m, 1H), 6.77 (d,  $J = 8.0$  Hz, 1H), 6.60 (t,  $J = 7.4$  Hz, 1H), 5.80 (d,  $J = 2.7$  Hz, 1H), 4.55 (d,  $J = 1.9$  Hz, 1H), 3.69–3.49 (m, 1H), 3.20–3.01 (m, 2H), 2.75–2.62 (m, 1H), 2.61–2.19 (m, 4H), 1.87–1.69 (m, 3H), 1.62–1.39 (m, 7H), 1.37–1.24 (m, 2H), 1.22–1.11 (m, 2H), 0.83–0.74 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.7, 150.2, 150.1, 147.7, 147.6, 131.0, 129.3, 129.0, 128.5, 128.5, 125.4, 122.6, 119.2, 118.6, 117.0, 76.3, 60.4, 58.5, 43.4, 37.2, 27.8, 27.7, 27.6, 26.0, 25.9, 25.3, 24.0, 12.0, 12.0. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{31}\text{H}_{40}\text{N}_2\text{O}$  486.3115; Found 486.3112.

**Procedure for the Synthesis of Compound 18.** To a glass tube were added 10a (124.4 mg, 0.2 mmol), TBAF trihydrate (189.3 mg, 0.6 mmol), and THF (4 mL) successively. The resulting mixture was stirred at room temperature for 1 h, and concentrated under vacuum to remove THF. The residue was purified by column chromatography on silica gel ( $\text{EtOAc}:\text{MeOH}:\text{Et}_3\text{N} = 100:5:1$ ) to furnish the product 18.

**Compound 18.** Light yellow oil; 40.3 mg, 43% yield;  $[\alpha]_{\text{D}}^{20} = -13.7$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.56 (d,  $J = 4.5$  Hz, 1H), 8.16 (d,  $J = 1.3$  Hz, 1H), 7.82 (d,  $J = 8.7$  Hz, 1H), 7.62 (dd,  $J = 8.7$ , 1.5 Hz, 1H), 7.47 (d,  $J = 4.5$  Hz, 1H), 7.23–7.12 (m, 5H), 5.43 (d,  $J = 4.6$  Hz, 1H), 4.19 (s, 2H), 3.30 (dd,  $J = 11.8$ , 9.5 Hz, 1H),

3.04–2.91 (m, 2H), 2.57–2.47 (m, 1H), 2.28 (d,  $J = 13.4$  Hz, 1H), 1.73 (s, 1H), 1.69–1.65 (m, 1H), 1.53–1.44 (m, 1H), 1.36 (d,  $J = 2.7$  Hz, 2H), 1.22 (dd,  $J = 7.3, 3.7$  Hz, 1H), 0.95 (d,  $J = 8.4$  Hz, 2H), 0.79 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.9, 149.3, 146.9, 138.2, 133.4, 130.2, 129.8, 128.8, 128.5, 127.0, 126.9, 126.4, 119.0, 71.3, 60.3, 58.5, 43.1, 37.5, 32.3, 28.3, 27.7, 25.4, 22.0, 18.1, 12.1. HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{26}\text{H}_{31}\text{N}_2\text{OSe}$  467.1596; Found 467.1592.

## ■ ASSOCIATED CONTENT

### Data Availability Statement

The data underlying this study are available in the published article and its [Supporting Information](#).

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.3c00774>.

General information, synthetic procedures, crystallographic data for triflate monohydrate of **3**, and NMR spectra (PDF)

### Accession Codes

CCDC 2141376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

The authors declare no competing financial interest.

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