

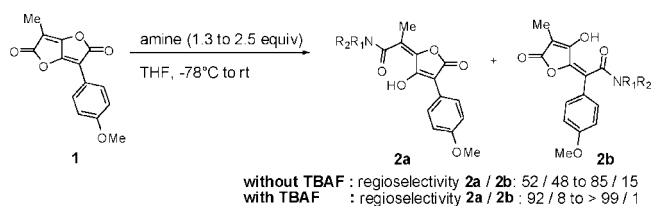
# Synthesis of Pulvinic Derivatives via TBAF-Mediated Regioselective Opening of an Unsymmetrical Monoaromatic Pulvinic Dilactone

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The synthesis of the monoaromatic pulvinic dilactone **1** from a tetronic acid derivative is reported. The reaction of **1** with various amines was found to provide the two pulvinamides regioisomers **2a** and **2b**. Using tetrabutylammonium fluoride (TBAF) as an activator, pulvinamides **2a** could be obtained with excellent regioselectivities and good yields. Additions of alcohols to **1** are also studied, leading to similar observations.

Pulvinic acids (Figure 1) constitute a family of fungi pigments containing a  $\gamma$ -alkylidene butenolide ring system.<sup>1</sup> Members differ by the aryl groups, often hydroxylated or methoxylated. Studies in our group demonstrated the antioxidant properties of several pulvinic derivatives.<sup>2</sup> The preparation of simplified analogues, bearing only one aromatic substituent, could help us elucidate the origin of the activity. For this purpose, the preparation of derivatives of types I and II was investigated (Figure 2b). To the best of our knowledge, one example of type I product has been described in the literature with very poor yields,<sup>3</sup> and no example of type II product has been reported.

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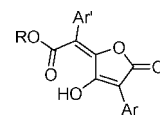


FIGURE 1. Structure of pulvinic (R = H) and vulpinic (R = Me) acids.

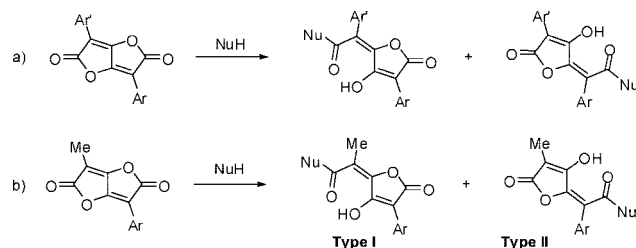
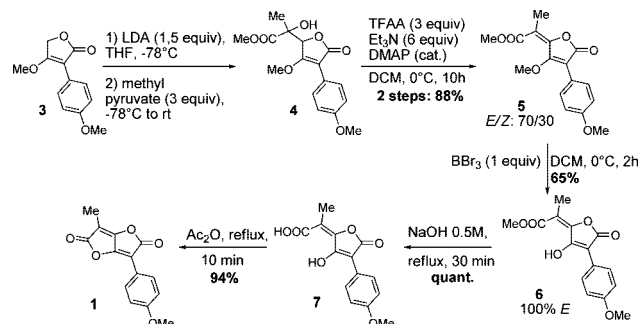


FIGURE 2. Reactivity of (a) diaromatic and (b) monoaromatic dilactones toward nucleophiles (NuH = H<sub>2</sub>O, ROH, RR'<sub>2</sub>NH<sub>2</sub>).

## SCHEME 1. Synthesis of Monoaromatic Dilactone 1



The syntheses of symmetrical (Ar = Ar') and unsymmetrical (Ar  $\neq$  Ar') pulvinic acids were recently the focus of a review article.<sup>4</sup> The pioneering work of Volhardt in 1894 allowed the preparation of symmetrical pulvinic acids by hydrolysis or methanolysis of a diaromatic dilactone (Figure 2a, Ar = Ar').<sup>5</sup> This methodology was improved and extended to the synthesis of unsymmetrical pulvinic acids by hydrolysis of diaromatic dilactones (Figure 2a, Ar  $\neq$  Ar').<sup>6</sup> Nevertheless, the formation of two pulvinic isomers is unavoidable, due to the similar reactivity of the two carbonyls of dilactones used.

Toward the synthesis of monoaromatic type I and type II compounds we thought of using a monoaromatic dilactone (Figure 2b) as a highly advanced intermediate which could lead in one step to both types of simplified pulvinic derivatives. Moreover, we found that the reaction of nucleophiles on such monophenyl dilactone can be tuned toward the selective formation of type I adducts.

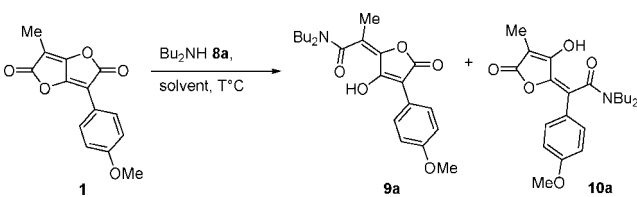
The synthesis of the selected dilactone **1** was achieved as follows (Scheme 1). A condensation reaction between the methoxy-protected 4-methoxyphenyl tetronic acid **3**<sup>7</sup> and methyl pyruvate provided **4** as a mixture of diastereomers (*syn/anti*:

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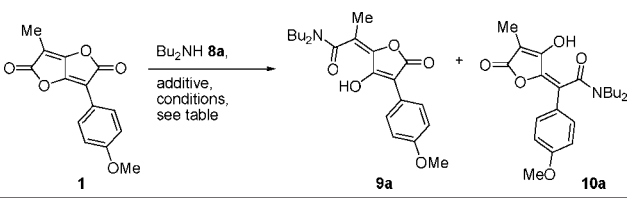
**TABLE 1.** Effect of Solvent and Temperature on the **9a/10a** Ratio<sup>a</sup>


entry	solvent	<i>T</i> (°C)	<b>9a/10a</b> ratio <sup>b</sup>
1	DCM	rt	55/45
2	DCM	−35	62/38
3	THF	−35	66/34
4	THF	−78	65/35
5	Et <sub>2</sub> O	−35	59/41
6	acetone	−35	67/33
7	DMF	−35	59/41
8	EtOH	−35	61/39
9	MeCN	−35	69/31
10	hexane	−35	
11 <sup>c</sup>		rt	70/30
12	H <sub>2</sub> O	5	63/37
13 <sup>d</sup>	[BMIM][BF <sub>4</sub> ]	rt	70/30
14	MeCN	85	67/33
15	MeCN	rt	66/34
16 <sup>e</sup>	MeCN	rt	64/36

<sup>a</sup> Addition of **1** to a solution of **8a** (1.3 equiv), 15 min of stirring at the specified temperature, unless otherwise specified. <sup>b</sup> Determined by integration in <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup> 20 equiv of **8a** was used. <sup>d</sup> 2.5 equiv of **8a** and 48 h stirring were required to reach completion. <sup>e</sup> Slow addition of a solution of **8a** on **1**.

1/1 by <sup>1</sup>H NMR). Crude compound **4** was dehydrated<sup>8</sup> to yield alkene **5** as a 70/30 mixture of *E* and *Z* isomers (attributed by NOESY experiments), which could be separated by chromatography, but were typically engaged as a mixture in the next step. Deprotection of the methyl enol ether of **5** using 1 equiv of BBr<sub>3</sub> was performed at 0 °C for 2 h.<sup>9</sup> Some starting material was recovered after this step, but longer reaction time led to the partial deprotection of the aromatic methoxy group. Noteworthy, both *E* and *Z* isomers led to a unique isomer of the monoaromatic vulpinic acid derivative **6** (see the Supporting Information). The corresponding acid derivative **7** was then obtained in a quantitative yield by saponification. Finally, treatment of **7** by acetic anhydride yielded the monoaromatic dilactone **1**. Incidentally, **6** and **7** were the first monoaromatic type I adducts that we synthesized (Figure 2b). Activation of acid **7** in the purpose of synthesizing other type I esters or amides was found to lead exclusively to dilactone **1**.

First, the reaction of **1** with dibutylamine **8a** was studied in different solvents and at different temperatures (Table 1). In DCM at rt, **1** was consumed after 15 min and a mixture of type I **9a** and type II **10a** adducts was obtained in a 55/45 ratio in favor of type I. The two products could be separated by chromatography on silica gel with a 86% global yield. Both products show significant differences in aspect (**9a** being a striking yellow solid, as usual pulvinic derivatives while **10a** is a pale yellow oil) and in <sup>1</sup>H NMR spectra (see the Supporting Information, aromatic protons).<sup>10</sup>

**TABLE 2.** Effect of Additives on the **9a/10a** Ratio


entry	additive (equiv)	solvent, <i>T</i> (°C)	<b>9a/10a</b> ratio <sup>a</sup>
1	PPh <sub>3</sub> (0.2)	MeCN, rt	67/33
2	NaCN (0.2)	MeCN, rt	67/33
3	DABCO (0.2)	MeCN, rt	66/34
4	HMPA (0.2)	DCM, rt	62/38
5	TMSOTf (0.2)	MeCN, rt	62/38
6	Ti(OiPr) <sub>4</sub> (0.2)	MeCN, rt	69/31
7	Al(OtBu) <sub>3</sub> (0.2)	MeCN, rt	69/31
8	Al(OtBu) <sub>3</sub> (0.2)	DCM, rt	62/38
9	Al(OtBu) <sub>3</sub> (0.2)	DMF, rt	64/46
10	Al(OtBu) <sub>3</sub> (0.2)	MeCN, −78	68/32
11	TBAF (2)	THF, rt	/ <sup>b</sup>
12	TBAF (0.2)	THF, −78	73/27
13	TBAF (1)	THF, −78	84/16
14	TBAF (2)	THF, −78	86/14
15	TBAF (1)	THF, −35	87/13
16	TBAF (2)	THF, −35 to −78	98/2
17	TBACl (2)	THF, −35 to −78	76/24
18	TBACN (2)	THF, −35 to −78	75/25
19	TBAI (2)	THF, −35 to −78	70/30
20	TMAF (2)	THF, −35 to −78	68/32
21	KF (2)	THF, −35 to −78	68/32
22	CsF (2)	THF, −35 to −78	64/36

<sup>a</sup> Determined from the crude reaction mixture on <sup>1</sup>H NMR spectrum. <sup>b</sup> No trace of the desired products was observed.

This interesting first result prompted us to optimize the reaction conditions in the aim to improve the regioselectivity of the nucleophilic attack. Decreasing of the temperature to −35 °C in DCM (Table 1, entry 2) slightly improved the **9a/10a** ratio. At low temperature, the screening of solvent showed only minor changes in the ratio (Table 1, entries 2–9). Only hexane did not allow the reaction (Table 1, entry 10). Neat (Table 1, entry 11, rt) or aqueous conditions (Table 1, entry 12, 5 °C) did not improve significantly the **9a/10a** ratio, neither did the use of ionic liquid (Table 1, entry 13, rt). Higher temperatures (Table 1, entries 14 and 15) or inversion of the addition order of reactants (Table 1, entry 16) have no effect. Nevertheless, clean and total conversion of **1** was always observed after 15 min as shown by TLC and <sup>1</sup>H NMR.

Then we considered the use of activators. For all reactions compiled in Table 2, the additive was mixed with the dilactone **1** and dibutylamine **8a** (1.3 equiv) was added dropwise. After 15 min at the specified temperature, **1** was always consumed (by TLC), and reactions were worked up and analyzed by NMR. The use of 0.2 equiv of various Lewis bases (Table 2, entries 1–4) or Lewis acids (Table 2, entries 5–7) had no effect on the regioselectivity of the addition of **8a** to **1**.

Using Al(*O-t*-Bu)<sub>3</sub>, the change of solvent (Table 2, entries 8–10) or the reduction of the temperature (Table 2, entry 10) did not affect the **9a/10a** ratio. In the next assay, we found that the use of 2 equiv of TBAF in THF (Table 2, entry 11) did not provide the expected amides, but the type I monoaromatic pulvinic acid derivative **7** instead in a quantitative yield. We hypothesized that water (5%) present in the TBAF–THF


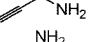

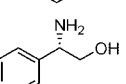

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TABLE 3. Formation of Amides **9** and **10** from Dilactone **1**

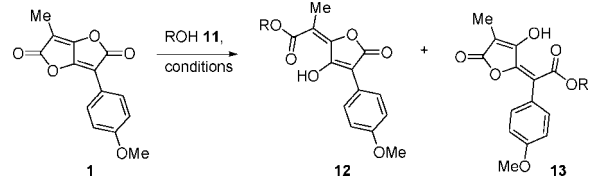
entry	amine		9 / 10 ratio		product yield (%) <sup>c</sup>
			without TBAF <sup>a</sup>	with TBAF <sup>b</sup>	
1	Bu <sub>2</sub> NH	<b>8a</b>	65 / 35	98 / 2	<b>9a</b> , 94
2	BuNH <sub>2</sub>	<b>8b</b> <sup>h</sup>	55 / 45	92 / 8	<b>9b</b> , 83
3	(C <sub>12</sub> H <sub>25</sub> ) <sub>2</sub> NH	<b>8c</b> <sup>h</sup>	64 / 36	> 99 / 1	<b>9c</b> , 80
4	C <sub>12</sub> H <sub>25</sub> NH <sub>2</sub>	<b>8d</b> <sup>h</sup>	52 / 48	92 / 8	<b>9d</b> , 88
5		<b>8e</b> <sup>h</sup>	52 / 48	> 99 / 1	<b>9e</b> , 96
6		<b>8f</b>	58 / 42	> 99 / 1	<b>9f</b> , 96
7		<b>8g</b>	85 / 15	> 99 / 1	<b>9g</b> , 25 <sup>d</sup>
8		<b>8h</b>	67 / 33	95 / 5	<b>9h</b> , 92
9		<b>8i</b> <sup>h</sup>	69 / 31	> 99 / 1	<b>9i</b> , 98



<sup>a</sup> Addition of **8** (1.3 equiv) to **1** at  $-78^{\circ}\text{C}$ , 15 min. <sup>b</sup> Addition of TBAF (2 equiv) to **1** at  $-35^{\circ}\text{C}$ , then addition of **8** (1.3 equiv) at  $-78^{\circ}\text{C}$ , 15 min. <sup>c</sup> Isolated yield, using TBAF. <sup>d</sup> 2.5 equiv of amine was used.

solution was responsible for the hydrolysis of the dilactone **1**. This hydrolysis reaction is triggered by TBAF (not observed in pure water, Table 1, entry 11) and regioselective. Since the preparation of anhydrous TBAF is not straightforward (see below; dried TBAF is reported to decompose by E2 elimination at rt),<sup>11</sup> for the ease of the procedure and to avoid the hydrolysis side reaction we considered the use of a smaller quantity of the commercially available TBAF–THF solution and/or lower temperature. The addition of 0.2 equiv of TBAF to **1** at  $-78^{\circ}\text{C}$  prior to the addition of **8a** yielded the expected amides in a 73/27 ratio (Table 2, entry 12) and prevented the hydrolysis of **1**. An increase to 1 or 2 equiv of TBAF at  $-78^{\circ}\text{C}$  allowed the ratio to raise to 85/15 approximately (Table 2, entries 13 and 14); a comparable ratio was obtained when the reaction was performed at  $-35^{\circ}\text{C}$  (Table 2, entry 15). In each case, low temperature avoided the hydrolysis of **1**. Finally, using 2 equiv of TBAF slowly added to dilactone **1** in THF at  $-35^{\circ}\text{C}$ , followed by the addition of dibutylamine **8a** at  $-78^{\circ}\text{C}$  and stirring for 15 min (Table 3, entry 16), regioisomer **9a** was obtained almost exclusively. Entries 17–22 of Table 2 are discussed at the end of this paper.

The optimized reaction conditions (Table 2, entry 16) were then applied to various amines and compared to reactions conducted in the absence of TBAF (Table 3). All experiments were completed after 15 min at  $-78^{\circ}\text{C}$ , but great improvements of the **9/10** ratio were observed when TBAF was used, affording products **9** in good to excellent isolated yields. Secondary amines showed slightly higher selectivity than the corresponding primary amines (Table 3, entries 1 and 3 versus 2 and 4). Morpholine (Table 3, entry 5) and propargylamine (Table 3, entry 6) reacted with total regioselectivity and almost quantitative yield. In the presence of TBAF, aniline reacted as well regioselectively (Table 3, entry 7), but only 25% of amide **9g** could be isolated since the hydrolysis adduct **7** was the major

TABLE 4. Formation of Esters **12** and **13** from Dilactone **1**



entry	alcohol	conditions (equiv) <sup>a</sup>	<b>12</b> / <b>13</b> / <b>7</b> ratio <sup>b</sup>	Product yield (%)
1	<i>i</i> -PrOH <b>11a</b>	<i>i</i> -PrOH <sup>d</sup> , reflux, overnight	59 / 41 / 0	<b>12a</b> , 53
2	<i>i</i> -PrOH <b>11a</b>	i) TBAF (1) ii) <b>11a</b> (1), $-35^{\circ}\text{C}$	65 / 5 / 30	/ <sup>e</sup>
3	<i>i</i> -PrOH <b>11a</b>	i) TBAF (2) ii) <b>11a</b> (1), $-35^{\circ}\text{C}$	51 / 0 / 49	/ <sup>e</sup>
4	<i>i</i> -PrOH <b>11a</b>	i) TBAF (2) ii) <b>11a</b> (5 eq), $-35^{\circ}\text{C}$	79 / 2 / 19	/ <sup>e</sup>
5	<i>i</i> -PrOH <b>11a</b>	i) TBAF (2), 4Å MS ii) <b>11a</b> (5 eq), $-35^{\circ}\text{C}$	70 / 0 / 30	/ <sup>e</sup>
6	<i>i</i> -PrOH <b>11a</b>	i) TBAF (2) ii) <b>11a</b> (10), $-78^{\circ}\text{C}$	83 / 0 / 17	<b>12a</b> , 83
7	<i>i</i> -PrOH <b>11a</b>	i) TBAF* (2) ii) <b>11a</b> (2.5), $-78^{\circ}\text{C}$	95 / 5 / 0	<b>12a</b> , 69
8	BnOH <b>11b</b>	i) TBAF* (2) ii) <b>11b</b> (2.5), $-78^{\circ}\text{C}$	85 / 15 / 0	<b>12b</b> , 83
9	 <b>11c</b>	i) TBAF* (2) ii) <b>11c</b> (2.5), $-78^{\circ}\text{C}$	85 / 15 / 0	<b>12c</b> , 65
10	 <b>11d</b>	i) TBAF* (2) ii) <b>11d</b> (2.5), $-78^{\circ}\text{C}$	87 / 13 / 0	<b>12d</b> , 58

<sup>a</sup> Except for entry 1, TBAF (or TBAF\*) was added to a solution of **1** in THF at  $-35^{\circ}\text{C}$ , then addition of **11**, 15 min. <sup>b</sup> Determined by integration in <sup>1</sup>H NMR of the crude reaction mixture. <sup>c</sup> Isolated yield. <sup>d</sup> *i*-PrOH was used as solvent. <sup>e</sup> Product not isolated.

product of the reaction. As a weaker nucleophile, aniline probably could not compete with water (contained in the TBAF–THF solution) as efficiently as previous alkylamines. Surprisingly, without TBAF, aniline afforded a fairly good **9/10** ratio, and **9g** could be isolated in 78% yield. Finally, only amides were obtained when amino alcohols were used, demonstrating the chemoselectivity of the reaction (Table 3, entries 8 and 9).

Then the additions of alcohols to **1** were studied. In the absence of activating agent isopropyl alcohol **11a**, even used as the solvent, did not react with **1** at room temperature. Refluxing **1** in **11a** overnight resulted in quantitative lactone opening with low type I/type II selectivity (Table 4, entry 1).

Using TBAF with **11a**, the lactone opening was found to be very regioselective since only type I, ester **12** or acid **7**, adducts were obtained (Table 4, entries 2–6). With 1 equiv of **11a** and TBAF at  $-35^{\circ}\text{C}$ , the lactone-opening reaction was complete after 15 min and very regioselective, but the hydrolysis product **7** was formed in the reaction mixture (Table 4, entry 2). As hypothesized earlier, formation of **7** could be due to a side reaction with water contained in the TBAF–THF solution; indeed the use of 2 equiv of the activator solution increased the proportion of **7** (Table 4, entry 3), whereas the use of an excess of alcohol **11a** reduced it (Table 4, entry 4). Addition of activated molecular sieves did not avoid the formation of **7** (Table 4, entry 5). Using the commercially available TBAF–THF solution, our best result was obtained by adding the activator (2 equiv) at  $-35^{\circ}\text{C}$  and then **11a** (10 equiv) at  $-78^{\circ}\text{C}$  for 15 min: specific formation of ester **12a**, isolated in 83% yield (Table 4, entry 6). Excess of *i*-PrOH was evaporated, but this protocol is not convenient for less volatile alcohols.

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To design an alternative protocol that could prevent the hydrolysis side reaction anhydrous TBAF was prepared. The recently reported procedure by DiMagno et al. was applied to produce anhydrous TBAF (noted TBAF\*).<sup>12</sup> Using this activator and the optimized reaction conditions for amines, the addition of *i*-PrOH **11a** was found to be slightly less selective since 5% of type II ester **13a** was detected by NMR (Table 4, entry 7), but the ester **12a** could be isolated with a good yield (69%) and the formation of **7** was avoided. The same protocol was applied to benzyl alcohol **11b**, dodecyl alcohol **11c** and solketal **11d** which showed comparable reactivity and furnished the corresponding esters **12b–d** in good yields (Table 4, entries 8–10). In each case, the use of anhydrous TBAF\* prevented the hydrolysis side reaction leading to **7**.

In regard of the mechanism of the reaction with TBAF, we first envisaged the formation of an acid fluoride intermediate by the regioselective addition of a fluoride anion on **1**. With the goal to detect such an intermediate, 1 equiv of **1** was mixed with 2 equiv of TBAF in THF-*d*<sub>8</sub> at –35 °C, and the resulting solution was analyzed by <sup>19</sup>F NMR (200 MHz) at low temperature (–20, –35, and –78 °C); unfortunately, no peak was observed that could be related to an acid fluoride (characteristic chemical shift in the range 20–50 ppm).<sup>13</sup> Thus, if an acid fluoride is formed, this intermediate is probably unstable, has a short lifetime, and reverts to the dilactone **1** in the absence of a nucleophile. Interestingly, variations of the anion or the cation of the activator alter a lot the regioselectivity of the reaction. The larger and more polarizable the anion is, the lower is the regioselectivity for the addition of **8a** on **1** (Table 2, entries 16–19). On the other hand, changing tetrabutylammonium for a smaller and more coordinating cation alters as well the nucleophile addition regioselectivity (Table 2, entries 20–22). It is noteworthy that in all experiments the total conversion of **1** into pulvinamides **9a** and **10a** was observed. It appears that a high reactivity of the activator system leads to a high regioselectivity. This observation, as well as our NMR experiment, does not provide a clear explanation for the striking jump in regioselectivity observed. Nevertheless, two hypotheses seem to prevail: the direct reaction of fluoride on **1** that would lead preferentially to a very reactive type I acid fluoride or the activation of the nucleophile by fluoride acting as a strong H-bond acceptor and able to modulate the outcome of the reaction. The Table 4 results showing a variation in the selectivity according to the alcohol used (entries 6–10) would support the second hypothesis, whereas the Table 3 results showing small selectivity variation when diverse amines were used support either the first hypothesis or second hypothesis if the H-bond acceptor effect is very high and equivalent for all substrates.

In conclusion, the preparation of a monoaromatic pulvinic dilactone **1** was described. It was found that TBAF was an efficient activator for the regioselective ring opening of **1** by amines and alcohols. Our methodology allowed the preparation of 13 unsymmetrical and monoaromatic pulvinic acid derivatives that are currently tested for their antioxidant capacities. The study of the addition of other nucleophiles on **1** and the preparation of type II monoaromatic derivatives (Figure 2b) are in progress and will be reported in due course.

## Experimental Section

**General Procedure for the Regioselective Ring Opening of Dilactone **1** with Amines.** To a solution of dilactone **1** (1 equiv) in 1.5 mL of THF was slowly added a solution of TBAF (1 M solution in THF, 2 equiv) at –35 °C. The mixture was stirred for 15 min and then cooled to –78 °C. A solution of amine (1.3–2.5 equiv) in 1 mL of THF was added. After 15 min of stirring at –78 °C, the reaction was completed and the mixture was allowed to warm to room temperature. After concentration in vacuo, the crude residue was purified by chromatography on silica gel. **Data for 9a:** prepared from **1** (19.7 mg, 0.08 mmol) and **8a** (9.7 μL, 0.10 mmol) and purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH: 95/5) as a yellow solid (31.0 mg, 94%); mp 86–87 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.3 (brs, 1H), 8.04 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.82 (s, 3H), 3.38 (t, *J* = 7.6 Hz, 4H), 2.13 (s, 3H), 1.68–1.53 (m, 4H), 1.38–1.24 (m, 4H), 0.94 (t, *J* = 7.1 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 172.1, 167.2, 162.0, 159.2, 159.1, 148.6, 129.1; 122.1, 114.3, 113.9, 104.2, 55.3, 47.6, 29.9, 20.1, 16.2, 13.8; IR 2959, 2932, 2871, 2837, 1759, 1604, 1537, 1432, 1249, 1094, 1072, 827 cm<sup>–1</sup>; HRMS (ES, pos) calcd for C<sub>22</sub>H<sub>30</sub>NO<sub>5</sub> [M + H]<sup>+</sup> 388.2118, found 388.2144. **Data for 9c:** prepared from **1** (20.2 mg, 0.08 mmol) and **8c** (70 mg, 0.19 mmol) and purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O: 90/10) as a yellow solid (38.2 mg, 80%); mp 48–49 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 11.26 (s, 1H), 8.05 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 3.38 (t, *J* = 9.0 Hz, 4H), 2.17 (s, 3H), 1.62–1.60 (m, 4H), 1.29–1.24 (m, 36H), 0.88 (t, *J* = 6.0 Hz, 6H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 172.2, 167.2, 159.2, 159.1, 148.8, 129.1, 122.2, 114.3, 113.9, 104.2, 55.4, 47.9, 32.0, 29.8, 29.7, 29.5, 29.4, 27.9, 26.9, 22.8, 16.3, 14.3; IR 2921, 2850, 1769, 1468, 1454, 1250, 1182, 1079, 828 cm<sup>–1</sup>; HRMS (ES, pos) calcd for C<sub>38</sub>H<sub>62</sub>NO<sub>5</sub> [M + H]<sup>+</sup> 612.4623, found 612.4631.

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**Supporting Information Available:** General information, analytical data, and <sup>1</sup>H and <sup>13</sup>C NMR spectra of all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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