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Beyond the Aza-Morita–Baylis–Hillman Reaction: Lewis Base-Catalyzed Reactions of *N*-Boc-imines with Ethyl 2,3-Butadienoate

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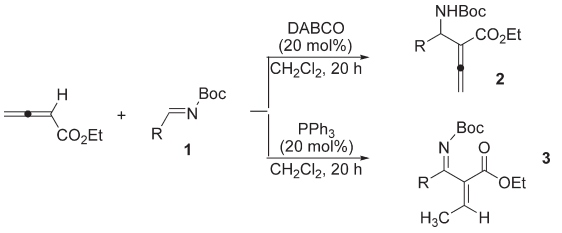

Lewis base catalyzed reactions of *N*-Boc-imines and ethyl 2,3-butadienoate were investigated systematically. The normal aza-Morita–Bylis–Hillman products were obtained in good to excellent yields catalyzed by DABCO. When PPh_3 was used as the catalyst, novel rearrangement product (*E*)-ethyl 2-((*Z*)-(*tert*-butoxycarbonylimino)-(aryl)methyl)but-2-enoates could be formed in moderate yields.

The use of imines as electrophiles in the Morita–Baylis–Hillman reactions,[1] commonly referred to as the aza-Morita–Baylis–Hillman (aza-MBH) reaction,[2] is extremely fascinating because of the great potential of its products for further transformation and its superior mild reaction conditions.[3] An extension of the aza-MBH reaction comes through variation in the structure of the α,β-unsaturated carbonyl compounds such as allenoates. However, there are very few reports about the aza-MBH reactions of imines with allenoates[4] providing densely functionalized allenes because many kinds of imines and 2,3-butadienoates are easy to obtain via cycloaddition reactions under different Lewis bases.[5–7] For instance, the reactions of *N*-tosylated imines and 2,3-butadienoates catalyzed by phosphine to give five-membered pyrrolidine derivatives (Scheme 1, eq 1) have been reported by Lu.[5] For the same reaction, we previously reported that different heterocyclic products such as azetidine or dihydropyridine derivatives could be formed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) or *N*,*N*-4-dimethylaminopyridine (DMAP), respectively (Scheme 1, eqs 2 and 3).[7]

Lu has also reported that the normal aza-MBH adducts could be formed in moderate yield in the PPh_3-catalyzed reaction between methyl 2,3-butadienoate and *N*-(ethoxycarbonyl)benzaldimine instead of *N*-sulfonylimines (Scheme 2, eq 1).[5b] Our DABCO-catalyzed reactions of *N*-tosylated imines with ethyl 2,3-butadienoate only afford trace normal aza-MBH adducts (Scheme 2, eq 2).[7b] These results showed that the reactivities of both imines and catalysts influence the final products from the same starting materials.

In this paper, we report the different reactivity patterns shown by nitrogen- and phosphorus-containing Lewis bases as catalysts in the reactions of *N*-Boc-imines with ethyl 2,3-butadienoate, which are different from the previous observations in the normal aza-MBH reactions of other imines and beyond the scope of the aza-MBH reactions.

The potential of several commonly used nitrogen-containing Lewis bases as catalysts has been assessed for the aza-MBH reaction of ethyl 2,3-butadienoate with *N*-Boc-imine **1a**. The results are summarized in Table 1. Notably, DABCO and pyridine are more efficient than other nitrogen-containing Lewis bases for catalysis of this reaction. As can be seen in Table 1, DABCO shows an excellent catalytic activity for the reaction of **1a** with ethyl 2,3-butadienoate in tetrahydrofuran (THF), affording product **2a** in 95% yield. Pyridine also proved as a good catalyst, forming **2a** in 66% yield (Table 1, entry 2). However, other nitrogen-containing Lewis bases *N*,*N*-4-dimethylaminopyridine (DMAP) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) gave poor yields,

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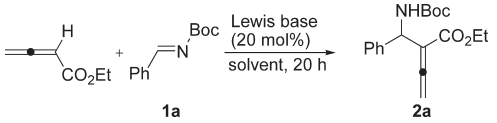
TABLE 1. Catalyst and Solvent Screen for the DABCO-Catalyzed Reactions of Ethyl 2,3-Butadienoate and *N*-Boc-imine 1a

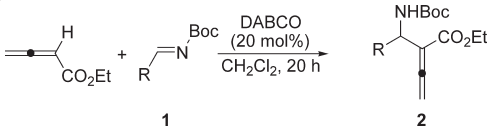


1a **2a**

entry[a]	Lewis base	solvent	yield[b] (%)
1	DABCO	THF	95
2	pyridine	THF	66
3	DMAP	THF	13
4	DBU	THF	16
5	NEt_3	THF	trace
6	imidazole	THF	trace
7	DABCO	CH_2Cl_2	99
8	DABCO	DMF	trace
9	DABCO	toluene	86
10	DABCO	CH_3CN	trace

[a]All reactions were carried out with **1a** (0.2 mmol) and ethyl 2,3-butadienoate (0.24 mmol) in the presence of Lewis base in solvent (1.0 mL) at room temperature. [b]Isolated yields.

TABLE 2. Scope of DABCO-Catalyzed Reactions of *N*-Boc-imines 1 and Ethyl 2,3-Butadienoate

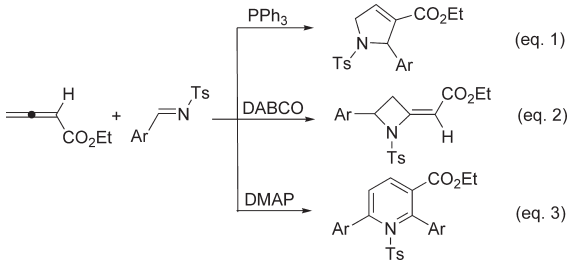


1 **2**

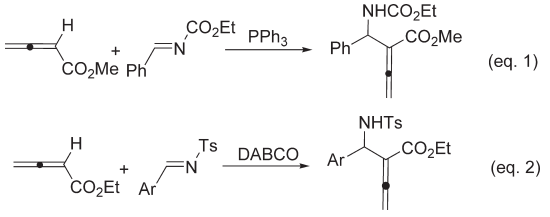
entry[a]	R	yield[b] (%)
1	*p*-$MeOC_6H_4$, **1b**	**2b**, 89
2	*p*-MeC_6H_4, **1c**	**2c**, 94
3	*p*-$CF_3C_6H_4$, **1d**	**2d**, 77
4	*p*-FC_6H_4, **1e**	**2e**, 76
5	*m*-MeC_6H_4, **1f**	**2f**, 98
6	*m*-ClC_6H_4, **1g**	**2g**, 84
7	*m,m,p*-$(MeO)_3C_6H_2$, **1h**	**2h**, 91
8	*o*-$MeOC_6H_4$, **1i**	**2i**, 79
9	*o*-ClC_6H_4, **1j**	**2j**, 87
10	2-furyl, **1k**	**2k**, 98
11	cyclohexyl, **1l**	complex

[a]All reactions were carried out with **1** (0.2 mmol) and ethyl 2,3-butadienoate (0.24 mmol) in the presence of DABCO in CH_2Cl_2 (1.0 mL) at room temperature. [b]Isolated yields.

SCHEME 1. Reaction of *N*-Tosylated Imines with Ethyl 2,3-Butadienoate Catalyzed by Different Lewis Bases



SCHEME 2. Normal Aza-Morita–Baylis–Hillman Reaction of Imines with 2,3-Butadienoates Catalyzed by PPh_3 or DABCO

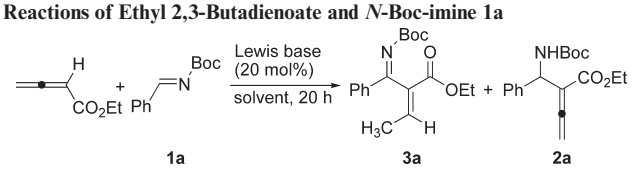


and triethylamine (NEt_3) and imidazole could not catalyze this type of reaction (Table 1, entries 3–6). Solvent effects were also examined. The results listed in Table 1 indicated that solvent effects had a dramatic influence on the reaction. The moderately polar solvents dichloromethane and toluene were suitable for the reaction to give **2a** in excellent yields (Table 1, entries 7 and 9). However, the more polar solvents acetonitrile and *N*,*N*-dimethylformamide (DMF) retarded this reaction and led to trace products (Table 1, entries 8 and 10).

Having the identified optimal reaction conditions, we next set out to examine the scope and limitations of this reaction using various *N*-Boc-imines **1** with different substituents on the benzene rings, and the results are summarized in Table 2. As shown in Table 2, whether electron-withdrawing or electron-donating group at the *ortho*-, *meta*-, or *para*-position of the benzene ring of *N*-Boc-imines **1** or the furfural *N*-(*tert*-butoxycarbonyl)imine **1k** were employed, the reactions proceeded smoothly to give **2** in good to excellent yields (Table 2, entries 1–10). Unfortunately, this reaction was not suitable for alkyl *N*-Boc imine **1l** (Table 2, entry 11), yielding complexes.

In addition to nitrogen-containing Lewis bases, the catalytic potential of readily available phosphines was also explored for this reaction. The results are listed in Table 3. Interestingly, replacing DABCO by PPh_3 led to the rearrangement product **3a** of normal aza-MBH adducts isolated in 63% yield with trace normal adduct **2a** (Table 3, entry 1). The structure of **3a** was determined by ^1H NMR, ^{13}C NMR, and NOESY spectra (see the Supporting Information). We also tested several stronger nucleophilic phosphines such as tributylphosphine (PBu_3), methyldiphenylphosphine (PPh_2Me), and dimethyl(phenyl)phosphine ($PPhMe_2$) and found that they could not catalyze this reaction (Table 3, entries 2–4). This implied that the nucleophilicities of phosphines had significant influence on the reaction; thus, we subsequently explored the influence of nucleophilicities of phosphines further. Three phosphines with different electronic-nature substituents on the benzene rings were chosen as catalysts to test in this reaction. We found that increasing the nucleophilicities of phosphines led to the decreased yield of **3a**. The least nucleophilic phosphine tris(4-fluorophenyl)phosphine ($P(p\text{-}FC_6H_4)_3$) could catalyze the reaction to give product **3a** in the highest yield among these three phosphines; however, the most nucleophilic tris(4-methoxyphenyl)phosphine ($P(p\text{-}MeOC_6H_4)_3$) just generated **3a** in 8% yield (Table 3, entries 5 and 7). The solvent effects were examined again using PPh_3 as the catalyst. Similar observations were obtained as the nitrogen base-catalyzed reactions. Dichloromethane and toluene were also optimal solvents to give **3a** in 66% and 62% yield, respectively, with **2a** as a byproduct (Table 3, entries 8 and 9), and the reaction could not occur in acetonitrile either (Table 3, entry 10). In order to maximize the yield of product **3a**, we attempted to vary some reaction conditions. Increasing the amount of ethyl 2,3-butadienoate

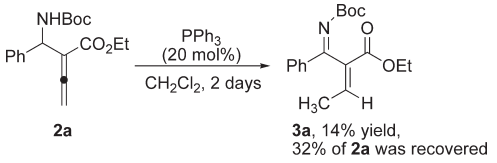
TABLE 3. Catalyst and Solvent Screen for the PPh_3-Catalyzed the Reactions of Ethyl 2,3-Butadienoate and *N*-Boc-imine 1a



entry[a]	Lewis base	solvent	yield of **3a**[b] (%)	yield of **2a**[b] (%)
1	PPh_3	THF	63	trace
2	PBu_3	THF	[c]	[c]
3	PPh_2Me	THF	[c]	[c]
4	$PPhMe_2$	THF	[c]	[c]
5	$P(p\text{-}MeOC_6H_4)_3$	THF	8	trace
6	$P(p\text{-}MeC_6H_4)_3$	THF	19	trace
7	$P(p\text{-}MeC_6H_4)_3$	THF	49	30
8	PPh_3	CH_2Cl_2	66	5
9	PPh_3	toluene	62	11
10	PPh_3	CH_3CN	trace	trace
11[d]	PPh_3	CH_2Cl_2	39	41
12[e]	PPh_3	CH_2Cl_2	19	49
13[f]	PPh_3	CH_2Cl_2	22	55
14[g]	PPh_3	CH_2Cl_2	21	9

[a]All reactions were carried out with **1a** (0.2 mmol) and ethyl 2,3-butadienoate (0.24 mmol) in the presence of Lewis base in solvent (1.0 mL) at room temperature. [b]Isolated yields. [c]These reactions gave complex product mixtures. [d]Ethyl 2,3-butadienoate (0.24 mmol) in CH_2Cl_2 (3.0 mL) was added with a syringe pump for 5 h. [e]The reaction was carried out in 2.0 mL of CH_2Cl_2. [f]The reaction was carried out in 4.0 mL of CH_2Cl_2. [g]The reaction was carried out with **1a** (0.3 mmol) and ethyl 2,3-butadienoate (0.2 mmol) in 1.0 mL of CH_2Cl_2.

SCHEME 3. Control Experiment



up to 3 equiv did not improve the yield.[8] Based on Lu's research[9] and our observations, we found that ethyl 2,3-butadienoate could undergo self-cycloaddition in the presence of PPh_3. In order to avoid its self-cycloaddition, we tried adding the diluted ethyl 2,3-butadienoate slowly by syringe pump, and the result showed that the yield of **3a** decreased while **2a** became the major product and the total yield of **2a** and **3a** increased (Table 3, entry 11). Interestingly, decreasing the concentration of ethyl 2,3-butadienoate also resulted in **2a** becoming the major product (Table 3, entries 12 and 13). Was the formation of **3a** due to the rearrangement of **2a** catalyzed by PPh_3? Next, we did the control experiment in which **2a** was stirred in CH_2Cl_2 in the presence of 20 mol % of PPh_3 for 2 days. Compound **3a** was isolated only in 14% yield with 32% of **2a** being recovered (Scheme 3), and the residues were difficult to identify. It indicated that the formation of **3a** was not through

(8) The yield using 3.0 equiv of ethyl 2,3-butadienoate is almost same as that using 1.0 equiv of ethyl 2,3-butadienoate.

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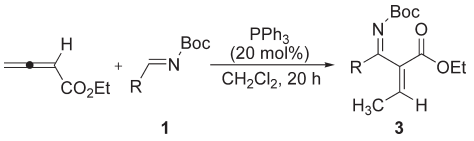
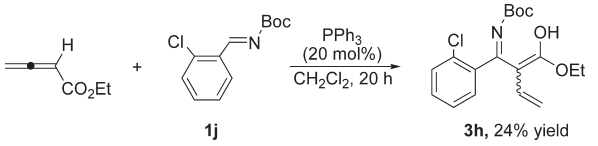
TABLE 4. Scope of the PPh_3-Catalyzed Reactions of *N*-Boc-imines 1 and Ethyl 2,3-Butadienoate



entry[a]	R	Yield (%)[b,c]
1	$p\text{-}MeOC_6H_4$, **1b**	**3b**, 49
2	$p\text{-}CF_6C_6H_4$, **1d**	**3c,** 48
3	$p\text{-}FC_3H_4$, **1e**	**3d**, 61
4	$p\text{-}MeC_6H_4$, **1f**	**3e**, 66
5	$m\text{-}ClC_6H_4$, **1g**	**3f**, 48
6	$m\text{-}MeOC_6H_4$, **1i**	complex
7	2-furyl, **1k**	**3g,** 94
8	cyclohexyl, **1 L**	complex

[a]All reactions were carried out with **1** (0.2 mmol) and ethyl 2,3-butadienoate (0.24 mmol) in the presence of PPh_3 in CH_2Cl_2 (1.0 mL) at room temperature. [b]Isolated yields. [c]Trace of **2** was also produced without isolation.

SCHEME 4. Reaction of *N*-Boc-imine 1j with Ethyl 2,3-Butadienoate Catalyzed by PPh_3



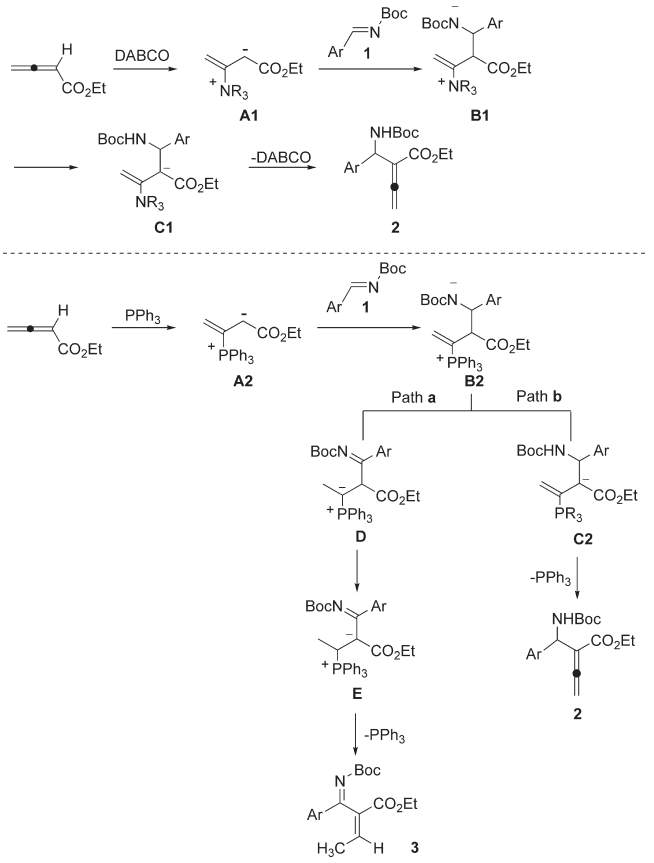
rearrangement of normal aza-MBH product **2a** under the reaction conditions.

Although the yield of **3a** was not improved by variation of reaction conditions, we were still interested in the scope and limitations of the reaction catalyzed by PPh_3 (Table 4) with respect to various substrates. The reactions proceeded smoothly to afford **3** in moderate yields, using the *N*-Boc-imines **1** with either electron-withdrawing or electron-donating substituent at the *meta*- or *para*-position of the benzene ring (Table 4, entries 1−5). In particular, the furfural *N*-(*tert*-butoxycarbonyl)imine **1k** could give **3g** in 94% yield (Table 4, entry 7). However, the *o*-methoxybenzaldehyde *N*-Boc-imine **1i** and alkyl *N*-Boc-imine **1l** were not suitable substrates (Table 4, entries 6 and 8). We also found that the PPh_3-catalyzed reaction of *o*-chlorobenzaldehyde *N*-Boc-imine **1j** and ethyl 2,3-butadienoate produced an uncommon product **3h** in 24% yield, and its structure was also determined by ^1H NMR, ^{13}C NMR, and NOESY spectra (Scheme 4).

On the basis of the above results and previous literature,[5] a plausible mechanism for the DABCO- or PPh_3-catalyzed reaction between ethyl 2,3-butadienoate and *N*-Boc-imines **1** is proposed in Scheme 5. The Lewis base DABCO or PPh_3 as a nucleophile reacts with ethyl 2,3-butadienoate to produce the zwitterionic intermediate **A1** or **A2**, which subsequently generates the intermediate **B1** or **B2** through nucleophilic addition of the *N*-Boc-imines **1**. In the case of DABCO, **B1** transforms to **C1** through a proton transfer. The elimination of DABCO from **C1** affords the product **2** and regenerates DABCO.

At the stage of the intermediate **B2**, the reaction diverges into two paths. In path **a**, the stable ylide intermediate **D** can

SCHEME 5. Plausible Reaction Mechanism



be formed through proton transfer and will undergo a hydrogen shift to form **E** when the concentration of intermediate **B2** is high. Then, the elimination of PPh_3 furnishes product **3** and regenerates the catalyst. Path **b** in which the intermediate **B2** follows the similar reaction path as the DABCO-catalyzed reaction to generate normal *aza*-MBH product **2** as the byproduct via the intermediate **C2** can compete with path **a** and even become dominant when the concentration of **B2** is low. The nature of the imine *N*-substituent also affects the reaction pathway. *N*-Acylimines with an ethoxycarbonyl substituent rather take path **b** to give normal aza-MBH product **2** in the presence of PPh_3 as a catalyst.[4] In contrast, *N*-Boc-imines mainly provide product **3**. Presumably, the steric hindrance of Boc group makes the proton transfer difficult to occur for formation of intermediate **C2**; thus, path **a** is more favorable with respect to *N*-Boc-imines.

In summary, we have presented that nitrogen- and phosphorus-containing Lewis bases show different catalytic patterns in the reactions of *N*-Boc-imines with ethyl 2,3-butadienoate. In particular, phosphorus-containing Lewis bases display a novel catalytic pattern resulting in uncommon products. Efforts are in progress to better understand the difference of the catalytic reactivity of phosphine- or nitrogen-containing Lewis bases in these reactions. Moreover, the asymmetric version of this type of reaction is in progress in our laboratory.

Experimental Section

General Procedure for the Reaction of Ethyl 2,3-Butadienoate and *N*-Boc-imines. To a solution of *N*-Boc-imine **1** (41 mg, 0.2 mmol) and DABCO (5.5 mg, 0.04 mmol) in CH_2Cl_2 (1.0 mL) was added ethyl 2,3-butadienoate (27 mg, 0.24 mmol) in one portion. After the reaction mixture was stirred at room temperature for 20 h, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/petroleum ether = 1/10) to yield the corresponding product **2** (63 mg, 99%) as a colorless oil.

Compound 2a:. colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.19 (t, 3H, J = 7.2 Hz, CH_3), 1.44 (s, 9H, CH_3), 4.12 (q, 2H, J = 7.2 Hz, CH_2), 5.37 (s, 2H, =CH_2), 5.49 (d, 1H, J = 8.7 Hz, NH), 5.65 (d, 1H, J = 8.7 Hz, CH), 7.22−7.36 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 28.2, 53.5, 61.1, 79.6, 81.3, 102.3, 126.6, 127.4, 128.4, 140.4, 154.7, 165.4, 212.9; IR (CH_2Cl_2) ν 3438, 3359, 2979, 2933, 1965, 1725, 1492, 1367, 1248, 1107, 1077, 1044, 1022, 886, 700 cm^{-1}; MS (ESI) m/z 340.0 (M + Na^+, 100); HRMS (ESI) calcd for $C_{18}H_{23}N_1Na_1O_4$ (M + Na^+) requires 340.15193, found 340.15176.

Compound 3a:. colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.16 (t, 3H, J = 7.2 Hz, CH_3), 1.47 (s, 9H, CH_3), 1.80 (d, 3H, J = 7.5 Hz, CH_3), 4.17 (brs, 2H, CH_2), 7.28 (q, 1H, J = 7.5 Hz, =CH), 7.39−7.51 (m, 3H, Ar), 7.85 (d, 2H, J = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.0, 16.0, 27.8, 61.1, 82.1, 128.2, 128.5, 130.7, 132.1, 135.5, 143.3, 161.4, 164.1, 166.2; IR (CH_2Cl_2) ν 2979, 2933, 1723, 1625, 1578, 1449, 1368, 1253, 1233, 1151, 1064, 1034, 929, 853, 776, 693 cm^{-1}; MS (ESI) m/z 340.0 (M + Na^+, 30); HRMS (ESI) calcd for $C_{18}H_{23}N_1Na_1O_4$ (M + Na^+) requires 340.15193, found 340.15159.

Compound 3h:. colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.33 (s, 9H, CH_3), 1.38 (t, 3H, J = 7.2 Hz, CH_3), 4.33 (qd, 2H, J_1 = 7.2 Hz, J_2 = 2.0 Hz, CH_2), 4.90 (dd, 1H, J_1 = 12.0 Hz, J_2 = 2.0 Hz, =CH), 5.23 (dd, 1H, J_1 = 17.6 Hz, J_2 = 2.0 Hz, =CH), 5.86 (dd, 1H, J_1 = 17.6 Hz, J_2 = 12.0 Hz, =CH), 7.18−7.21 (m, 1H, Ar), 7.27−7.34 (m, 2H, Ar), 7.38−7.41 (m, 1H, Ar), 10.6 (s, 1H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 27.9, 60.9, 81.1, 107.8, 116.8, 126.5, 129.2, 129.79, 129.84, 130.2, 132.8, 134.2, 148.5, 150.9, 169.1; IR (CH_2Cl_2) ν 3234, 2980, 2933, 1748, 1720, 1671, 1601, 1577, 1477, 1454, 1394, 1369, 1243, 1144, 1061, 1027, 1005, 915, 861, 802, 752 cm^{-1}; MS (ESI) m/z 374.0 (M + Na^+, 100); HRMS (MALDI) calcd for $C_{18}H_{22}Cl_1N_1Na_1O_4$ (M + Na^+) requires 374.11296, found 374.1144.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectroscopic and analytic data of compounds **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.