

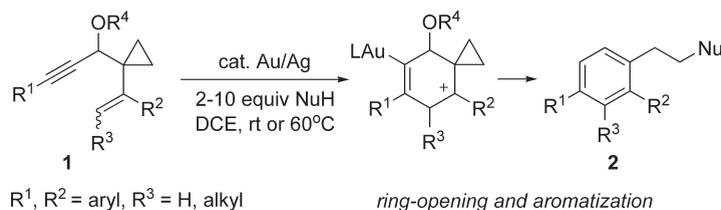
## Gold-Catalyzed Benzannulation of 3-Alkoxy-1,5-enynes: Access to Functionalized Benzenes

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A cationic Au(I) complex catalyzed benzannulation of 3-alkoxy-1,5-enynes bridged by a cyclopropyl ring with a variety of nucleophiles is described. The reaction occurs selectively through a 6-endo-dig pathway to provide tri- and tetrasubstituted benzenes efficiently under mild reaction conditions.

### Introduction

Transition metal-catalyzed 1,5- or 1,6-enyne cycloisomerizations provide rapid and highly efficient access to a variety of carbo- and heterocyclic structural motifs, which can find a wide range of synthetic applications.<sup>1</sup> Research of recent years demonstrates that gold complexes and its salts are emerging as powerful catalysts for enyne cyclization reactions due to their superior chemoselectivities and activities.<sup>2,3</sup> The resulting products strongly depended on the substitution pattern of enynes and the nature of the metallic species used. Although much progress has been achieved in this field, most of the studies

concentrated on the cyclopropanation reactions with or without skeletal rearrangement, while the gold-catalyzed benzannulation has received less attention.<sup>4</sup> These include cyclization of aromatic enynes to naphthalenes,<sup>4a,b</sup> cycloisomerization of enyne allene intermediates generated by gold-catalyzed 1,3-acyloxy migration of propargyl acetates to naphthyl ketones,<sup>4c</sup> cyclization of 7,7-disubstituted *cis*-4,6-dien-1-yn-3-ols,<sup>4d,e</sup> cyclization of 3,5-dien-1-ynes via a [1,7]-hydrogen shift,<sup>4f</sup> gold-catalyzed benzannulation of 3-hydroxy-1,5-enynes to substituted tetrahydronaphthalenes,<sup>4g,h</sup> and tandem allylation/cyclization reactions of alkynals via the intermediacy of 3-hydroxy- or alkoxy-1,5-enynes.<sup>4i</sup> Due to the importance of aromatic compounds, the regioselective construction of benzene derivatives is still highly desirable. On the other hand, cyclopropylmethyl cation has been proved to be a good precursor for ring-expansion or ring-opening reactions because of its ring strain energy.<sup>5</sup> During our ongoing

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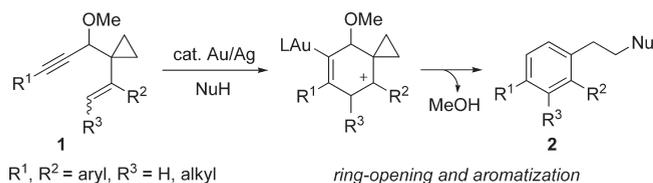
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## SCHEME 1



$R^1, R^2 = \text{aryl}, R^3 = \text{H, alkyl}$

studies on gold-catalyzed transformations,<sup>6</sup> we envisioned that the incorporation of a cyclopropyl ring into an enyne skeleton would greatly increase the versatility of the enyne cyclization reactions.<sup>7</sup> Herein, we would like to report our recent achievement on the cycloisomerizations of 3-alkoxy-1,5-enynes bridged by a cyclopropyl moiety like **1** assisted by the attack of nucleophiles to form tri- or tetrasubstituted benzenes (Scheme 1).

## Results and Discussion

To probe the feasibility of the enyne transformations, we initially investigated the cyclization reaction of (3-methoxy-3-(1-(1-phenylvinyl)cyclopropyl)prop-1-ynyl)benzene (**1a**; Table 1), which was easily prepared by three steps from commercially available cyclopropyl phenyl ketone.<sup>8</sup> To our disappointment, no reaction or trace product formation was observed when  $\text{PPh}_3\text{-AuCl}$ ,  $\text{AgBF}_4$ ,  $\text{PPh}_3\text{AuCl/AgOTf}$ , or  $\text{PPh}_3\text{AuCl/AgSbF}_6$  were used as catalysts in dichloromethane (entries 1–4).  $\text{PPh}_3\text{AuNTf}_2$  and  $\text{AuCl}_3$  also showed negative results even prolonged the reaction time to 20 h (entries 5 and 6). Surprisingly, we found that in the presence of 5 mol % of  $\text{PPh}_3\text{AuCl/AgBF}_4$ , **1a** could be consumed in 2 h to afford 4-methoxyethyl-1,3-diphenylbenzene (**2a**) in 54% yield (entry 7). The presence of the methoxy unit on the ethyl terminus in **2a** indicated that the ring-opening and alkoxylation by methanol formed in situ occurred during the process. We then added 5 equiv of MeOH to the reaction mixture; to our delight, the yield of the desired benzene **2a** increased dramatically to 78% (entry 8). Among various solvents we examined, 1,2-dichloroethane was found to be the best solvent, which afforded **2a** in 77–83% yields (entries 14 and 16–17). When 2 equiv of  $\text{H}_2\text{O}$  was added to the mixture, **2a** was still formed in 69% yield, together with 15% 2-(1,1',3',1'')-terphenyl-4'-yl-ethanol (entry 18).

With the optimized reaction conditions in hand, we proceeded to examine the reaction scope with a wide range of nucleophiles and the substrates of 3-alkoxy-1,5-enynes. We first investigated the scope of nucleophiles (Table 2). It was found that in addition to methanol, a variety of alcohols could be used as effective nucleophiles for this reaction. The use of 2 equiv of nucleophile such as ethanol resulted in the formation of a mixture of methyl and ethyl ether (Table 2, entry 1). In the presence of a large excess of ethanol (10 equiv), the desired ethyl ether **2b** was obtained in 69% yield, while only a trace amount of

TABLE 1. Optimization Studies on the Reaction Conditions

entry	catalyst	solvent	additive	time (h)	yield <sup>a</sup>
1	$\text{AuClPPh}_3$	$\text{CH}_2\text{Cl}_2$		20	NR <sup>b</sup>
2	$\text{AgBF}_4$	$\text{CH}_2\text{Cl}_2$		3	NR <sup>b</sup>
3	$\text{AuClPPh}_3/\text{AgOTf}$	$\text{CH}_2\text{Cl}_2$		4	trace
4	$\text{AuClPPh}_3/\text{AgSbF}_6$	$\text{CH}_2\text{Cl}_2$		4	trace
5	$\text{Ph}_3\text{PAuN}(\text{Tf})_2$	$\text{CH}_2\text{Cl}_2$		20	— <sup>c</sup>
6	$\text{AuCl}_3$	$\text{CH}_2\text{Cl}_2$		20	— <sup>c</sup>
7	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{CH}_2\text{Cl}_2$		2	54%
8	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{CH}_2\text{Cl}_2$	5.0 MeOH	2	78%
9	$\text{AuClPPh}_3/\text{AgBF}_4$	THF	5.0 MeOH	12	3% <sup>d</sup>
10	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{Et}_2\text{O}$	5.0 MeOH	20	18% <sup>e</sup>
11	$\text{AuClPPh}_3/\text{AgBF}_4$	toluene	5.0 MeOH	10	62%
12	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{CH}_3\text{CN}$	5.0 MeOH	8	trace
13	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{CH}_3\text{NO}_2$	5.0 MeOH	20	42% <sup>f</sup>
14	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	5.0 MeOH	2.5	81%
15	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{ClCH}_2\text{CH}_2\text{Cl}$		4	49%
16	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2.0 MeOH	2	83%
17	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	10.0 MeOH	10	77%
18	$\text{AuClPPh}_3/\text{AgBF}_4$	$\text{ClCH}_2\text{CH}_2\text{Cl}$	2.0 $\text{H}_2\text{O}$	1.5	69% <sup>g</sup>

<sup>a</sup>Isolated yield. <sup>b</sup>No reaction. <sup>c</sup>**2a** was not observed according to <sup>1</sup>H NMR of the crude mixture. <sup>d</sup>65% **1a** was recovered. <sup>e</sup>47% **1a** was recovered. <sup>f</sup>NMR yield. <sup>g</sup>The product of 2-(1,1',3',1'')-terphenyl-4'-yl-ethanol derived through ring-opening reaction by  $\text{H}_2\text{O}$  was also obtained in 15% yield.

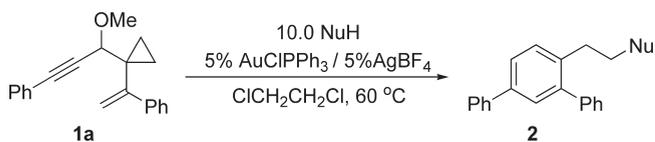
**2a** was observed (entry 2). Treatment of **1a** with a secondary alcohol such as 2-butanol afforded the corresponding alkoxy-cyclization<sup>9</sup> product **2c** in 77% yield (entry 3). Alcohols containing alkene or alkyne moieties were well tolerated in this  $\text{Au}^{\text{I}}$ -catalyzed transformation, furnishing **2d–h** in 54–91% yields (entries 4–8). Benzylic alcohol with a halide functionality such as (2-bromophenyl)methanol underwent the cyclization reaction smoothly to generate the desired **2i** in 75% yield (entry 9). The enantiomerically pure alcohols such as (–)-menthol and (–)-borneol were also successfully employed as nucleophiles for this cyclization, and the corresponding alkoxyated benzenes **2j** and **2k** were formed in 66% and 72% yields, respectively (entries 10 and 11). However, when 2-hydroxy-1,2-diphenylethanol or  $\text{TsNH}_2$  were used, only low yields of the desired products were obtained, which might be due to the lower nucleophilicity of these nucleophiles (entries 12 and 13). When the cyclopropane ring in enyne skeleton was replaced by a cyclobutane ring (for example, the enyne of (3-methoxy-3-(1-(1-phenylvinyl)cyclobutyl)prop-1-ynyl)benzene, **3a**) or dimethyl group at C-4 (for example, the enyne of (3-methoxy-4,4-dimethylhex-5-en-1-yne-1,5-diyl)dibenzene, **3b**), only a complicated reaction mixture was

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**TABLE 2.** Gold-Catalyzed Benzannulation of Enyne **1a** with Various Nucleophiles

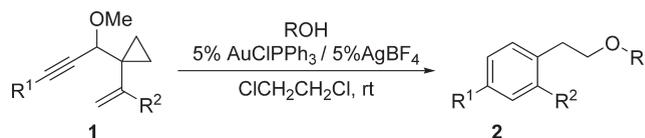
entry	NuH	time	product	yield <sup>a</sup>
1 <sup>b</sup>		5	<b>2a+2b</b>	94% <sup>c</sup>
2 <sup>b</sup>		5	<b>2b</b>	69%
3		12	<b>2c</b>	77%
4 <sup>b</sup>		2.5	<b>2d</b>	84%
5		1	<b>2e</b>	91%
6		1	<b>2f</b>	90%
7 <sup>b</sup>		5	<b>2g</b>	54%
8		2	<b>2h</b>	61%
9		5	<b>2i</b>	75%
10		4	<b>2j</b>	66%
11		2	<b>2k</b>	72%
12		1.5	<b>2l</b>	33% <sup>d</sup>
13	TsNH <sub>2</sub>	2	<b>2m</b>	23% <sup>d,e</sup>

<sup>a</sup>Isolated yield. <sup>b</sup>The reaction was carried out at room temperature. <sup>c</sup>2.0 equiv of EtOH was used, the ratio of **2a/2b** is 1:3.2. <sup>d</sup>Enyne was consumed; however, the reaction was not clean. <sup>e</sup>The reaction was carried out at 50 °C, and 5.0 equiv of TsNH<sub>2</sub> was used.

observed. It is clear that the existence of the cyclopropyl ring is crucial for the clean transformations.

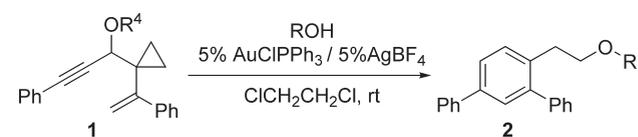
Next, we studied the scope of the enyne substrates (Table 3). It was found that the aromatic rings of R<sup>1</sup> at the alkyne terminus bearing an electron-donating or an electron-withdrawing group were all compatible under the reaction conditions, leading to the corresponding benzenes **2n–r** in 77–91% yields at room temperature in 0.5–3 h (Table 3, entries 1–5). A thienyl group of R<sup>1</sup> was also suitable for this reaction, and high yields of **2s** and **2t** could be achieved through the reactions with either MeOH or allylic alcohol (entries 6 and 7). A bulky aromatic ring such as 2-(6-methoxy)naphthyl group was well accommodated to yield the product **2u** in 96% yield (entry 8). Enyne **1g** with a substituted aryl group such as *p*-MeOC<sub>6</sub>H<sub>4</sub> present at the alkene double bond (R<sup>2</sup> group) was smoothly converted into the benzene derivatives **2v–w** in 67–75% yields (entries 9 and 10).

Enynes with a different protection group at the propargylic position (R<sup>4</sup>) have also been investigated. The

**TABLE 3.** Scope of the Gold-Catalyzed Benzannulation Reactions

entry	R <sup>1</sup>	R <sup>2</sup>	enyne	ROH (equiv)	product	yield <sup>a</sup>
1	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	<b>1b</b>	MeOH (2)	<b>2n</b>	91%
2	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Ph	<b>1c</b>	MeOH (5)	<b>2o</b>	88%
3			<b>1c</b>	(10)	<b>2p</b>	86%
4	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Ph	<b>1d</b>	MeOH (5)	<b>2q</b>	84%
5			<b>1d</b>	(10)	<b>2r</b>	77%
6	2-thienyl	Ph	<b>1e</b>	MeOH (5)	<b>2s</b>	91%
7			<b>1e</b>	(10)	<b>2t</b>	81%
8		Ph	<b>1f</b>	MeOH (5)	<b>2u</b>	96%
9	Ph	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<b>1g</b>	MeOH (5)	<b>2v</b>	75%
10			<b>1g</b>	(10)	<b>2w</b>	67%

<sup>a</sup>Isolated yield. All the reactions were carried out for 0.5–3 h.

**SCHEME 2**

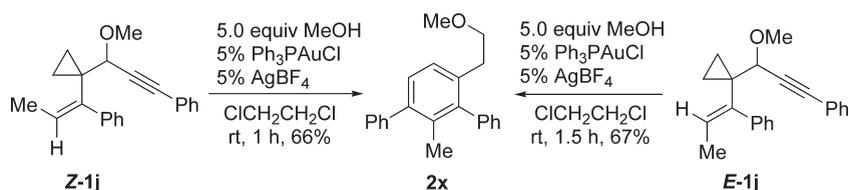
R <sup>4</sup> = Et ( <b>1h</b> )	2 equiv EtOH, 2.5 h	R = Et, <b>2b</b> , 82%
R <sup>4</sup> = Et ( <b>1h</b> )	10 equiv MeOH, 5 h	R = Me, <b>2a</b> , 63%
R <sup>4</sup> = allyl ( <b>1i</b> )	5 equiv prop-2-en-1-ol, 1 h	R = allyl, <b>2d</b> , 99%
R <sup>4</sup> = allyl ( <b>1i</b> )	10 equiv EtOH, 3 h	<b>2b+2d</b> (95%, 100:8)

results indicated that both the ethyl and allyl groups were compatible with the catalytic system, especially, a quantitative yield of **2d** was obtained within 1 h in the latter case with allylic alcohol as the nucleophile (Scheme 2).

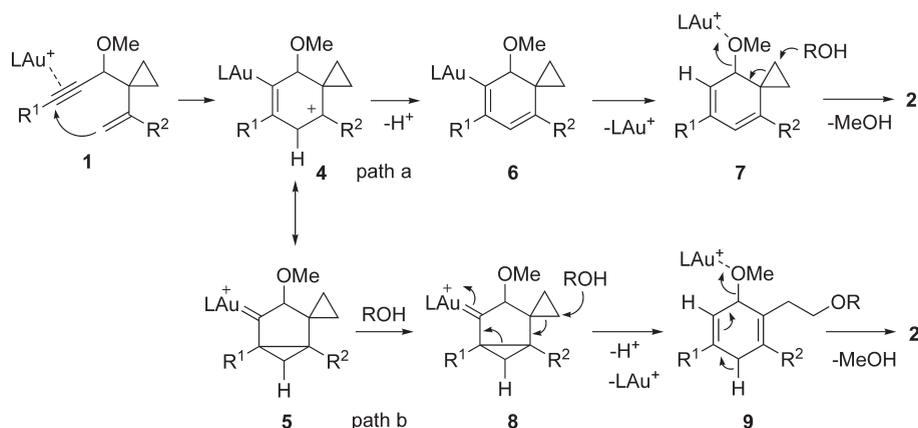
The reaction is also extendible to trisubstituted alkene **1j**. We prepared both *Z*- and *E*-isomers of this substrate, and their stereochemistry has been confirmed by NOESY spectra. Both isomers worked very well to afford the same tetrasubstituted benzene **2x** in good yields within a short time (Scheme 3). The results indicated that the geometry of the double bond in 1,5-enyne had a little influence on the cyclization reaction. The structure of **2x** has been confirmed by X-ray crystallographic analysis.<sup>8</sup>

We propose the following mechanism for this reaction. In the first step, the coordination of the triple bond of 1,5-enyne **1** to PPh<sub>3</sub>Au<sup>+</sup> enhances the electrophilicity of the alkyne, and the subsequent 6-*endo*-dig ring closure occurs to afford the cyclopropylmethyl cationic intermediate **4**, which is also represented by the resonance of carbenoid intermediate **5**. Two pathways might be involved in the following

## SCHEME 3



## SCHEME 4



transformations: in path a, deprotonation of **4** leads to cyclohexadienyl gold **6**, then deauration followed by nucleophilic attack of ROH to cyclopropyl ring furnishes the ring-opening and aromatized product **2** (Scheme 4).<sup>10</sup> Alternatively, in path b, direct attack of nucleophile to the cyclopropyl ring in **5** followed by protodemetalation and elimination of MeOH leads to the same product **2**.<sup>9a</sup> In addition, ring-opening by ROH from intermediate **4** to **9** also cannot be excluded.

## Conclusion

In summary, we have developed a gold-catalyzed benzannulation of 3-alkoxy-1,5-enynes bridged by a cyclopropyl ring with various nucleophiles under mild reaction conditions, which provided an efficient route to tri- and tetrasubstituted benzenes with a wide range of substituents. The existence of the cyclopropyl ring is proved to be crucial for the clean transformations. Further research to explore the new synthetic utility of this gold-catalyzed cascade reaction is currently underway.

## Experimental Section

**General Procedure for Au(I)-Catalyzed Benzannulation of 3-Alkoxy-1,5-enynes.** To a solution of 1,5-enyne **1** (0.3 mmol) and alcohol (2–10 equiv) in ClCH<sub>2</sub>CH<sub>2</sub>Cl (6 mL) was added Ph<sub>3</sub>PAuCl (0.015 mmol, 7.4 mg) and AgBF<sub>4</sub> (0.015 mmol, 300 μL, used as a 0.05 M solution in toluene). The resulting solution was stirred at room temperature or 60 °C until the reaction was complete as monitored by thin-layer chromatography. The solvent was evaporated under reduced pressure and

the residue was purified by chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the benzene derivatives **2**.

**2a:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the title compound **2a** as a brown sticky liquid in 83% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 300 MHz) δ 2.91 (t, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 3.47 (t, *J* = 7.2 Hz, 2H), 7.28–7.47 (m, 10H), 7.54 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.60–7.62 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 75 MHz) δ 32.8, 58.5, 73.0, 126.0, 127.0 (3C), 127.2, 128.1 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.1, 135.2, 139.0, 140.6, 141.5, 142.7; IR (KBr) 3057, 3027, 2976, 2925, 2871, 2824, 1600, 1479, 1443, 1383, 1180, 1113, 1027, 1012, 1000, 968, 895, 833, 762, 700 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>21</sub>H<sub>20</sub>O 288.1514, found 288.1513.

**2b:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2b** as a light yellow sticky liquid in 69% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 300 MHz) δ 1.13 (t, *J* = 7.2 Hz, 3H), 2.91 (t, *J* = 6.9 Hz, 2H), 3.38 (q, *J* = 7.2 Hz, 2H), 3.51 (t, *J* = 7.2 Hz, 2H), 7.28–7.42 (m, 10H), 7.52–7.55 (m, 1H), 7.59 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 75 MHz) δ 15.1, 33.0, 66.0, 71.0, 125.9, 126.95, 126.97 (2C), 127.1, 128.1 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.2, 135.3, 138.9, 140.6, 141.5, 142.7; IR (KBr) 3058, 3027, 2971, 2865, 1600, 1479, 1442, 1376, 1354, 1261, 1106, 1075, 1025, 894, 800, 762, 700 cm<sup>-1</sup>; HRMS (EI) calcd for C<sub>22</sub>H<sub>22</sub>O 302.1671, found 302.1674.

**2c:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the title compound **2c** as a light yellow sticky liquid in 77% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 300 MHz) δ 0.81 (t, *J* = 7.2 Hz, 3H), 1.02 (d, *J* = 6.0 Hz, 3H), 1.26–1.50 (m, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 3.16–3.23 (m, 1H), 3.40–3.48 (m, 1H), 3.51–3.59 (m, 1H), 7.28–7.47 (m, 10H), 7.53 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.58–7.62 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, Me<sub>4</sub>Si, 75 MHz) δ 9.7, 19.1, 29.0, 33.5, 68.7, 76.6, 125.9, 126.9, 127.0 (2C), 127.1, 128.1 (2C), 128.69 (2C), 128.74, 129.2 (2C), 130.3, 135.5, 138.9, 140.7, 141.6, 142.7; IR (KBr) 3058, 3028, 2966, 2931, 2873, 1600, 1479, 1464, 1443, 1373, 1340, 1261, 1172, 1139, 1113, 1083, 1026, 1012,

(10) As shown in Table 1, entry 7, the product of **2a** could be obtained in 54% yield without addition of any nucleophile. We suggested that in this case, a trace amount of H<sub>2</sub>O presented in the reaction mixture might induce the ring-opening reaction to release the MeOH, then the reaction could proceed.

895, 830, 762, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{26}\text{O}$  330.1984, found 330.1981.

**2d:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:1) afforded the title compound **2d** as a light yellow sticky liquid in 84% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.93 (t,  $J$  = 7.2 Hz, 2H), 3.52 (t,  $J$  = 7.2 Hz, 2H), 3.87 (dd,  $J$  = 5.1, 0.9 Hz, 2H), 5.11 (d,  $J$  = 10.5 Hz, 1H), 5.18 (d,  $J$  = 17.4 Hz, 1H), 5.76–5.89 (m, 1H), 7.28–7.46 (m, 10H), 7.53 (d,  $J$  = 7.8 Hz, 1H), 7.59 (d,  $J$  = 8.1 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.9, 70.6, 71.6, 116.7, 125.9, 127.0 (3C), 127.2, 128.1 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.2, 134.7, 135.2, 139.0, 140.6, 141.5, 142.7; IR (KBr) 3058, 3027, 2963, 2856, 1600, 1479, 1443, 1261, 1097, 1025, 923, 895, 800, 762, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{22}\text{O}$  314.1671, found 314.1667.

**2e:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2e** as a colorless sticky liquid in 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.26 (qt,  $J$  = 6.9, 1.5 Hz, 2H), 2.91 (t,  $J$  = 7.5 Hz, 2H), 3.36 (t,  $J$  = 6.6 Hz, 2H), 3.52 (t,  $J$  = 7.2 Hz, 2H), 4.98–5.07 (m, 2H), 5.69–5.82 (m, 1H), 7.27–7.46 (m, 10H), 7.53 (dd,  $J$  = 7.8, 1.5 Hz, 1H), 7.57–7.61 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.9, 34.1, 70.0, 71.3, 116.2, 125.9, 127.0 (3C), 127.1, 128.1 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.2, 135.2, 135.3, 138.9, 140.6, 141.5, 142.6; IR (KBr) 3059, 3027, 2931, 2859, 1641, 1600, 1479, 1442, 1391, 1362, 1260, 1108, 1026, 1012, 996, 914, 831, 762, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{24}\text{O}$  328.1827, found 328.1828.

**2f:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2f** as a colorless sticky liquid in 90% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  1.25–1.43 (m, 12H), 1.47–1.59 (m, 2H), 1.99–2.06 (m, 2H), 2.91 (t,  $J$  = 7.2, Hz, 2H), 3.30 (t,  $J$  = 6.6 Hz, 2H), 3.50 (t,  $J$  = 7.2 Hz, 2H), 4.90–5.02 (m, 2H), 5.73–5.86 (m, 1H), 7.27–7.46 (m, 10H), 7.53 (dd,  $J$  = 8.1, 1.5 Hz, 1H), 7.58–7.61 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  26.1, 28.9, 29.1, 29.4 (2C), 29.5, 29.6, 33.0, 33.8, 70.8, 71.2, 114.1, 125.9, 126.9, 127.0 (2C), 127.1, 128.1 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.2, 135.4, 138.9, 139.2, 140.7, 141.6, 142.6; IR (KBr) 3060, 3028, 2926, 2854, 1640, 1600, 1479, 1465, 1442, 1366, 1111, 1027, 1012, 994, 910, 831, 761, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{31}\text{H}_{38}\text{O}$  426.2923, found 426.2926.

**2g:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2g** as a light yellow sticky liquid in 54% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.38 (s, 1H), 2.94 (t,  $J$  = 7.2 Hz, 2H), 3.63 (t,  $J$  = 7.2 Hz, 2H), 4.05 (s, 2H), 7.30–7.47 (m, 10H), 7.50 (d,  $J$  = 7.5 Hz, 1H), 7.61 (d,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.7, 57.9, 70.3, 74.3, 79.7, 126.0, 127.0 (2C), 127.2, 128.2 (2C), 128.7 (2C), 128.9, 129.2 (2C), 130.2, 134.8, 139.1, 140.6, 141.4, 142.7. One carbon overlapped with other signals; IR (KBr) 3291, 3057, 3027, 2936, 2861, 2114, 1599, 1479, 1442, 1389, 1356, 1267, 1138, 1356, 1267, 1097, 1026, 1011, 896, 834, 762, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{20}\text{O}$  312.1514, found 312.1525.

**2h:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 10:1) afforded the title compound **2h** as a light yellow sticky liquid in 61% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  1.95 (t,  $J$  = 2.4 Hz, 1H), 2.38 (td,  $J$  = 6.9, 2.4 Hz, 2H), 2.92 (t,  $J$  = 7.5 Hz, 2H), 3.45 (t,  $J$  = 6.9 Hz, 2H), 3.56 (t,  $J$  = 7.5 Hz, 2H), 7.29–7.47 (m, 10H), 7.54 (dd,  $J$  = 8.1, 1.8 Hz, 1H), 7.60 (d,  $J$  = 7.5 Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  19.7, 32.8, 68.6, 69.2, 71.4, 81.3, 126.0, 127.0 (3C), 127.2, 128.2 (2C), 128.7 (2C), 128.8, 129.2 (2C), 130.2, 135.1, 139.0, 140.6, 141.5, 142.7; IR (KBr) 3296, 3057, 3027, 2916, 2865, 2116, 1599, 1479, 1442, 1391, 1364,

1110, 1075, 1026, 1012, 895, 832, 762, 700, 638  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{22}\text{O}$  326.1671, found 326.1672.

**2i:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2i** as a light yellow sticky liquid in 75% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.99 (t,  $J$  = 6.9 Hz, 2H), 3.62 (t,  $J$  = 7.5 Hz, 2H), 4.45 (s, 2H), 7.06 (td,  $J$  = 7.2, 1.5 Hz, 1H), 7.18–7.23 (m, 1H), 7.28–7.43 (m, 10H), 7.45–7.48 (m, 2H), 7.53 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 7.57–7.60 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  33.0, 71.2, 71.9, 122.4, 125.9, 126.96 (2C), 126.98, 127.2, 127.2, 128.1 (2C), 128.65, 128.69 (2C), 128.8, 129.2 (2C), 130.3, 132.3, 135.1, 137.6, 139.0, 140.6, 141.4, 142.7. One carbon overlapped with other signals; IR (KBr) 3057, 3027, 2926, 2862, 1599, 1568, 1479, 1441, 1390, 1357, 1263, 1205, 1122, 1101, 1027, 895, 832, 751, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{23}\text{OBr}$  442.0932, found 442.0940.

**2j:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2j** as a brown sticky liquid in 66% yield.  $[\alpha]_{\text{D}}^{20}$  –37.7 (*c* 1.22,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  0.63 (d,  $J$  = 6.9 Hz, 3H), 0.69–0.94 (m, 9H), 1.10–1.28 (m, 2H), 1.52–1.61 (m, 2H), 1.90 (d,  $J$  = 9.3 Hz, 1H), 2.02–2.08 (m, 1H), 2.82–2.93 (m, 3H), 3.29–3.37 (m, 1H), 3.64–3.72 (m, 1H), 7.27–7.46 (m, 10H), 7.51 (dd,  $J$  = 7.8, 2.1 Hz, 1H), 7.59 (d,  $J$  = 7.2, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 100 MHz)  $\delta$  16.1, 20.9, 22.3, 23.3, 25.4, 31.5, 33.7, 34.5, 40.4, 48.1, 68.9, 79.2, 125.9, 126.9, 127.0 (2C), 127.1, 128.1 (2C), 128.68 (2C), 128.74, 129.2 (2C), 130.3, 135.4, 139.0, 140.7, 141.6, 142.6; IR (KBr) 3058, 3027, 2955, 2922, 2867, 1599, 1479, 1453, 1384, 1369, 1343, 1262, 1179, 1107, 1089, 1013, 895, 831, 761, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{36}\text{O}$  412.2766, found 412.2762.

**2k:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2k** as a brown sticky liquid in 72% yield.  $[\alpha]_{\text{D}}^{20}$  –25.4 (*c* 0.674,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 400 MHz)  $\delta$  0.77–0.88 (m, 10H), 1.10–1.17 (m, 2H), 1.43–1.57 (m, 1H), 1.61–1.66 (m, 1H), 1.87–2.00 (m, 2H), 2.86–2.91 (m, 2H), 3.39–3.55 (m, 3H), 7.29–7.46 (m, 10H), 7.53 (dd,  $J$  = 7.6, 2.0 Hz, 1H), 7.59–7.62 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 100 MHz)  $\delta$  14.0, 18.8, 19.8, 26.6, 28.2, 33.4, 36.2, 44.9, 47.7, 49.1, 70.4, 84.6, 125.8, 126.9, 127.0 (2C), 127.1, 128.1 (2C), 128.7 (3C), 129.3 (2C), 130.5, 135.8, 138.8, 140.8, 141.7, 142.6; IR (KBr) 3058, 3027, 2949, 2873, 1600, 1479, 1452, 1387, 1369, 1358, 1232, 1139, 1117, 1094, 1076, 1026, 1013, 895, 830, 761, 700  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{34}\text{O}$  410.2610, found 410.2609.

**2l:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 25:1) afforded the title compound **2l** as a brown sticky liquid in 33% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 400 MHz)  $\delta$  2.98–3.02 (m, 2H), 3.60–3.64 (m, 2H), 5.40 (s, 1H), 7.22–7.46 (m, 18H), 7.50 (dd,  $J$  = 8.0, 0.8 Hz, 1H), 7.59–7.61 (m, 2H), 7.87–7.89 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  33.0, 70.2, 85.5, 125.9, 126.95 (3C), 127.12 (2C), 127.19, 128.1 (2C), 128.2, 128.3 (2C), 128.6 (2C), 128.7 (2C), 128.8, 129.1 (4C), 130.5, 133.1, 134.6, 134.9, 136.2, 139.1, 140.6, 141.3, 142.6, 197.4; IR (KBr) 3059, 3027, 2928, 2866, 1694, 1677, 1597, 1578, 1479, 1448, 1391, 1308, 1275, 1239, 1214, 1180, 1107, 1075, 1027, 968, 895, 831, 762, 697  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{34}\text{H}_{28}\text{O}_2$  468.2089, found 468.2093.

**2m:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5:1) afforded the title compound **2m** as a brown sticky liquid in 23% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.40 (s, 3H), 2.81 (t,  $J$  = 6.9 Hz, 2H), 3.00 (q,  $J$  = 6.9 Hz, 2H), 4.23 (t,  $J$  = 6.0 Hz, 1H), 7.20–7.23 (m, 5H), 7.25–7.46 (m, 7H), 7.51 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 7.58 (d,  $J$  = 7.5 Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  21.5, 32.7, 43.4, 126.2, 126.96 (2C), 127.00 (2C),

127.2, 127.4, 128.3 (2C), 128.8 (2C), 129.0 (2C), 129.1, 129.6 (2C), 130.1, 134.0, 136.7, 139.6, 140.3, 141.0, 142.6, 143.2; IR (KBr) 3285, 3058, 3028, 2926, 2872, 1710, 1598, 1479, 1443, 1328, 1159, 1093, 1076, 896, 814, 762, 701, 662, 550  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{27}\text{H}_{25}\text{NO}_2\text{S}$  427.1606, found 427.1603.

**2n:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound **2n** as a light brown sticky liquid in 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.90 (t,  $J$  = 7.2 Hz, 2H), 3.23 (s, 3H), 3.46 (t,  $J$  = 7.2 Hz, 2H), 3.79 (s, 3H), 6.92–6.96 (m, 2H), 7.34–7.43 (m, 7H), 7.47–7.54 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.7, 55.2, 58.4, 73.0, 114.1 (2C), 125.5, 126.9, 127.9 (2C), 128.1 (2C), 128.3, 129.2 (2C), 130.1, 133.1, 134.4, 138.6, 141.6, 142.6, 159.0; IR (KBr) 3053, 3024, 2930, 2894, 2834, 2808, 1609, 1580, 1519, 1499, 1484, 1463, 1442, 1384, 1287, 1249, 1179, 1112, 1041, 1029, 967, 896, 823, 773, 704  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_2$  318.1620, found 318.1618.

**2o:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound **2o** as a light brown sticky liquid in 88% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.35 (s, 3H), 2.90 (t,  $J$  = 7.2 Hz, 2H), 3.22 (s, 3H), 3.46 (t,  $J$  = 7.2 Hz, 2H), 7.20 (t,  $J$  = 7.8 Hz, 2H), 7.31–7.53 (m, 10H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  21.0, 32.7, 58.4, 73.0, 125.8, 126.8 (2C), 126.9, 128.1 (2C), 128.6, 129.2 (2C), 129.4 (2C), 130.1, 134.8, 136.9, 137.7, 138.9, 141.6, 142.6; IR (KBr) 3052, 3024, 2976, 2922, 2870, 2824, 1600, 1518, 1484, 1444, 1383, 1185, 1113, 1021, 1011, 967, 897, 811, 772, 703  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{22}\text{O}$  302.1671, found 302.1662.

**2p:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2p** as a light yellow sticky liquid in 86% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.36 (s, 3H), 2.92 (t,  $J$  = 7.5 Hz, 2H), 3.52 (t,  $J$  = 7.5 Hz, 2H), 3.85–3.88 (m, 2H), 5.09–5.21 (m, 2H), 5.76–5.89 (m, 1H), 7.21 (d,  $J$  = 7.8 Hz, 2H), 7.31–7.38 (m, 7H), 7.40–7.53 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  21.0, 32.9, 70.6, 71.6, 116.7, 125.7, 126.8 (2C), 126.9, 128.1 (2C), 128.56, 129.2 (2C), 129.4 (2C), 130.2, 134.7, 134.8, 136.9, 137.7, 138.9, 141.6, 142.6; IR (KBr) 3054, 3023, 2921, 2858, 1600, 1518, 1498, 1484, 1443, 1385, 1347, 1249, 1138, 1099, 991, 922, 811, 772, 703  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{24}\text{O}$  328.1827, found 328.1824.

**2q:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) afforded the title compound **2q** as a light yellow sticky liquid in 84% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.91 (t,  $J$  = 7.2 Hz, 2H), 3.24 (s, 3H), 3.47 (t,  $J$  = 7.2 Hz, 2H), 7.34–7.45 (m, 9H), 7.48–7.53 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.7, 58.4, 72.9, 125.7, 127.1, 128.2 (4C), 128.6, 128.8 (2C), 129.1 (2C), 130.2, 133.2, 135.6, 137.7, 139.0, 141.3, 142.8; IR (KBr) 3056, 3026, 2977, 2925, 2871, 2825, 1599, 1575, 1556, 1479, 1444, 1179, 1113, 1093, 1010, 968, 898, 816, 771, 752, 734, 703  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{OCl}$  322.1124, found 322.1121.

**2r:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2r** as a colorless sticky liquid in 77% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.92 (t,  $J$  = 7.2 Hz, 2H), 3.52 (t,  $J$  = 7.2 Hz, 2H), 3.88 (dt,  $J$  = 5.4, 1.2 Hz, 2H), 5.10–5.22 (m, 2H), 5.77–5.90 (m, 1H), 7.33–7.45 (m, 9H), 7.48–7.54 (m, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  33.0, 70.6, 71.6, 116.8, 125.8, 127.1, 128.2 (4C), 128.6, 128.9 (2C), 129.2 (2C), 130.4, 133.2, 134.7, 135.7, 137.7, 139.1, 141.3, 142.9; IR (KBr) 3058, 3025, 2927, 2856, 1599, 1479, 1443, 1381, 1348, 1137, 1094, 1015, 1000, 924, 817, 771, 703  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{23}\text{H}_{21}\text{OCl}$  348.1281, found 348.1285.

**2s:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1)

afforded the title compound **2s** as a brown black sticky liquid in 91% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.86 (t,  $J$  = 7.2 Hz, 2H), 3.21 (s, 3H), 3.43 (t,  $J$  = 7.5 Hz, 2H), 7.02 (t,  $J$  = 5.1 Hz, 1H), 7.20 (d,  $J$  = 5.1 Hz, 1H), 7.27 (d,  $J$  = 3.6 Hz, 1H), 7.31–7.43 (m, 6H), 7.47 (d,  $J$  = 1.8 Hz, 1H), 7.53 (dd,  $J$  = 7.8, 1.8 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.8, 58.4, 72.9, 122.9, 124.5, 124.8, 127.0, 127.5, 127.9, 128.1 (2C), 129.1 (2C), 130.2, 132.3, 135.4, 141.1, 142.7, 143.9; IR (KBr) 3104, 3059, 2923, 2868, 1599, 1560, 1483, 1442, 1401, 1380, 1188, 1110, 1024, 962, 889, 856, 817, 779, 748, 702  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{18}\text{OS}$  294.1078, found 294.1079.

**2t:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1) afforded the title compound **2t** as a light yellow sticky liquid in 81% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.89 (t,  $J$  = 7.2 Hz, 2H), 3.49 (t,  $J$  = 7.2 Hz, 2H), 3.84–3.87 (m, 2H), 5.09–5.20 (m, 2H), 5.76–5.88 (m, 1H), 7.04 (dd,  $J$  = 5.1, 3.6 Hz, 1H), 7.23 (dd,  $J$  = 5.1, 0.9 Hz, 1H), 7.28 (dd,  $J$  = 3.9, 0.6 Hz, 1H), 7.33–7.45 (m, 6H), 7.47 (d,  $J$  = 1.8 Hz, 1H), 7.54 (dd,  $J$  = 7.8, 2.1 Hz, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  33.0, 70.5, 71.6, 116.7, 122.9, 124.6, 124.8, 127.1, 127.5, 127.9, 128.1 (2C), 129.2 (2C), 130.3, 132.3, 134.7, 135.5, 141.2, 142.8, 144.0; IR (KBr) 3071, 3023, 2918, 2856, 1601, 1485, 1442, 1434, 1401, 1347, 1267, 1240, 1209, 1136, 1097, 990, 924, 891, 854, 818, 771, 701  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{20}\text{OS}$  320.1235, found 320.1237.

**2u:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) afforded the title compound **2u** as a white solid in 96% yield. Mp 94–95  $^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.93 (t,  $J$  = 7.5 Hz, 2H), 3.25 (s, 3H), 3.48 (t,  $J$  = 7.2 Hz, 2H), 3.89 (s, 3H), 7.13–7.16 (m, 2H), 7.36–7.46 (m, 6H), 7.58 (s, 1H), 7.64 (d,  $J$  = 7.8 Hz, 1H), 7.70–7.78 (m, 3H), 7.98 (s, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.8, 55.2, 58.4, 73.0, 105.4, 119.1, 125.3, 125.8, 126.0, 127.0, 127.2, 128.1 (2C), 128.8, 129.1, 129.2 (2C), 129.6, 130.2, 133.7, 134.9, 135.7, 138.9, 141.5, 142.7, 157.6; IR (KBr) 3052, 2993, 2954, 2920, 2871, 2817, 2807, 1626, 1606, 1490, 1388, 1239, 1201, 1168, 1114, 1029, 1016, 969, 893, 859, 837, 821, 775, 703  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{26}\text{H}_{24}\text{O}_2$  368.1776, found 368.1777.

**2v:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 40:1) afforded the title compound **2v** as a colorless sticky liquid in 75% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.92 (t,  $J$  = 7.5 Hz, 2H), 3.25 (s, 3H), 3.48 (t,  $J$  = 7.2 Hz, 2H), 3.83 (s, 3H), 6.93–6.97 (m, 2H), 7.26–7.33 (m, 3H), 7.37–7.46 (m, 4H), 7.51 (dd,  $J$  = 7.8, 2.4 Hz, 1H), 7.58–7.61 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  32.8, 55.2, 58.5, 73.0, 113.5 (2C), 125.7, 127.0 (2C), 127.1, 128.7 (2C), 129.0, 130.1, 130.2 (2C), 133.8, 135.3, 139.0, 140.7, 142.3, 158.6; IR (KBr) 3056, 3030, 2930, 2871, 2834, 1610, 1574, 1514, 1481, 1463, 1384, 1290, 1248, 1177, 1112, 1030, 835, 763, 699, 579  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_2$  318.1620, found 318.1622.

**2w:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50:1) afforded the title compound **2w** as a colorless sticky liquid in 67% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  2.94 (t,  $J$  = 7.5 Hz, 2H), 3.53 (t,  $J$  = 7.5 Hz, 2H), 3.84 (s, 3H), 3.89 (dt,  $J$  = 4.2, 1.2 Hz, 2H), 5.10–5.23 (m, 2H), 5.78–5.89 (m, 1H), 6.94–6.98 (m, 2H), 7.27–7.34 (m, 3H), 7.38–7.45 (m, 4H), 7.52 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 7.58–7.61 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 75 MHz)  $\delta$  33.0, 55.3, 70.7, 71.6, 113.5 (2C), 116.7, 125.7, 127.0 (2C), 127.1, 128.7 (2C), 129.0, 130.2, 130.3 (2C), 133.9, 134.7, 135.4, 139.0, 140.7, 142.3, 158.6; IR (KBr) 3058, 3030, 2955, 2932, 2907, 2854, 2830, 1610, 1574, 1515, 1481, 1463, 1290, 1245, 1177, 1097, 1030, 924, 834, 762, 698  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{24}\text{O}_2$  344.1776, found 344.1778.

**2x:** Purification of the crude product by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:1 to 50:1) afforded the title compound **2x** as a white solid in 66% (from **Z-1j**) or 67% (from **E-1j**) yield. Mp 60–62 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 300 MHz)  $\delta$  1.88 (s, 3H), 2.66 (t,  $J = 7.2$  Hz, 2H), 3.22 (s, 3H), 3.43 (t,  $J = 7.2$  Hz, 2H), 7.18–7.23 (m, 4H), 7.31–7.42 (m, 8H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ , 100 MHz)  $\delta$  18.9, 33.7, 58.3, 73.0, 126.5, 126.6, 126.8, 128.0 (2C), 128.4 (2C), 128.9, 129.3 (2C), 129.4 (2C), 133.7, 135.6, 140.4, 140.9, 142.4, 142.6; IR (KBr) 3060, 3022, 2970, 2958, 2928, 2864, 2827, 1600, 1469, 1442, 1405, 1382, 1184, 1111, 1101, 1070, 1023, 1003, 970, 925, 833, 763, 702  $\text{cm}^{-1}$ ; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{22}\text{O}$  302.1671, found 302.1669.

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**Supporting Information Available:** Experimental details, spectroscopic characterization of all new compounds, and X-ray crystallography of compound **2x**. This material is available free of charge via the Internet at <http://pubs.acs.org>.