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Lewis-Acid-Catalyzed Reactions of Bis(4-alkoxyphenyl)methanol with (Diarylmethylene)- and (Dialkylmethylene)cyclopropanes

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Bis(4-methoxyphenyl)methanol (**2a**) can be transformed by BF_3·OEt_2-catalyzed reactions of (arylmethylene)cyclopropanes **1** to the corresponding polysubstituted cyclopentenes **3** as the major products along with methylenecyclobutanes and dienes as minor products. The reaction conditions are mild, yields are moderate to good. In the reactions of aliphatic methylenecyclopropanes with bis(4-methoxyphenyl)methanol (**2a**), cyclopentenes **3o**–**q** were produced in good yields under the standard conditions. Interesting results were obtained from the reactions of 1-[cyclopropylidene(4-methoxyphenyl)methyl]-4-methoxybenzene (**1e**) with bis(4-alkoxyphenyl)methanols **2**: polysubstituted cyclopentene derivatives **5** were obtained in good yields under mild reaction conditions. Plausible reaction mechanisms based on the deuterium-labeling and control experiments are proposed.

Introduction

Methylenecyclopropanes (MCPs) are highly strained but readily accessible molecules, which can serve as useful building blocks in organic synthesis.[1] Their most interesting aspect is that MCPs can undergo a variety of ring-opening and cycloaddition reactions to give interesting products in the presence of transition metals or Lewis acids. Indeed, the relief of ring strain can provide a powerful thermodynamic driving force.[2,3] Thus far, a number of interesting cycloadditions and ring enlargements of MCPs have been explored. For example, Yamamoto et al. reported cycloaddition reactions of MCPs with aldehydes and imines using a palladium catalyst, affording the corresponding tetrahydrofuran (THF) and pyrrolidine skeletons in good yields.[4] In addition, we as well as other groups have developed a number of heterocycle-forming reactions starting from MCPs and aldehydes or imines as well as ring enlargements of MCPs in the presence of Lewis or Brønsted acids.[5,6] Recently, we have been investigating the Lewis-acid-mediated ring-opening reactions of MCPs **1** with a number of electrophiles such as phenylsulfenyl chloride and phenylselenyl chloride as well as 3-methoxy-1,3,3-triarylprop-1-yne or 1,1,3-triarylprop-2-yn-1-ol under mild conditions.[7] A variety of novel products could be obtained in good yields by a simple one-step reaction. Herein, we report an interesting Lewis-acid-catalyzed reaction of MCPs **1** with bis(4-alkoxyphenyl)methanols **2** to produce cyclopentenes **3** as the major products along with methylenecyclobutanes and diene derivatives **4a**–**c** as the minor products. We could also prepare novel polysubstituted cyclopentenes **5** in moderate to good yields under mild conditions.

Results and Discussion

We performed initial examinations with (diphenylmethylene)cyclopropane **1a** (0.2 mmol) and bis(4-methoxyphenyl)methanol **2a** (0.24 mmol) as substrates in the presence of various Lewis acids (10 mol-%) in 1,2-dichloroethane (DCE) to determine the best catalyst for this intermolecular reaction. The results of these experiments are summarized in Table 1. Except in THF or using $Yb(OTf)_3$ as the Lewis acid, the reactions proceeded smoothly with various Lewis acids in a variety of solvents at room temperature (20 °C), giving cyclopentene **3a** and methylenecyclobutane **4aa** along with ring-opened diene products **4ab** and **4ac** as (*E*/*Z*) mixtures in 63–84% total yields, respectively (Table 1, Entries 1–7 and 10–12). Using BF_3·OEt_2 as the catalyst afforded **3a** in the highest yield, perhaps due to its mild catalytic ability in the above reaction compared with that of $M(OTf)_n$ (n = 3 or 4, Table 1, Entry 1). Further increasing or decreasing the amount of BF_3·OEt_2 provided no improvement in the total yield (Table 1, Entries 8 and 9). In view of the total yield of this reaction, we used 10 mol-% of BF_3·OEt_2 as our optimal catalyst loading. We obtained the best result by using BF_3·OEt_2 (10 mol-%) as the catalyst in DCE at room temperature (20 °C), which afforded **3a** in 52% yield and a 72% total yield including **4aa**–**ac** (Table 1, Entry 1).

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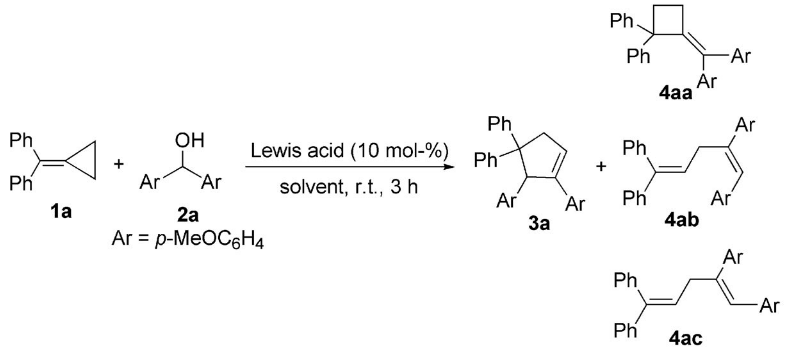
Table 1. Optimization of the reaction conditions.

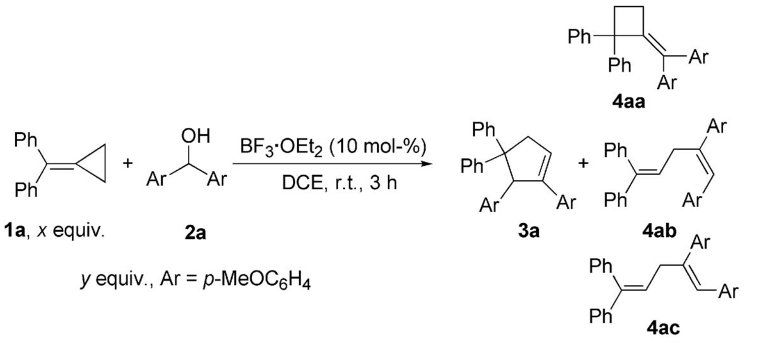


Entry[a]	Lewis acid	Solvent	% Yield[b] 3a	% Yield[b] 4[c,d]
1	**$BF_3 \cdot OEt_2$**	**DCE**	**52**	**20** (78:13:9)
2	$Nd(OTf)_3$	DCE	15	69 (18:68:14)
3	$In(OTf)_3$	DCE	10	67 (20:62:18)
4	$Zr(OTf)_4$	DCE	30	40 (22:63:15)
5	TfOH	DCE	48	20 (21:60:19)
6	$Yb(OTf)_3$[e]	DCE	trace	trace
7	$Sc(OTf)_3$	DCE	15	51 (29:51:20)
8	$BF_3 \cdot OEt_2$[f]	DCE	52	7 (81:7:12)
9	$BF_3 \cdot OEt_2$[g]	DCE	54	14 (79:12:9)
10	$BF_3 \cdot OEt_2$	toluene	35	40 (75:12:13)
11	$BF_3 \cdot OEt_2$	DCM	49	14 (76:14:10)
12	$BF_3 \cdot OEt_2$	THF	–	–

[a] All reactions were carried out with **1a** (0.2 mmol), **2a** (0.24 mmol) and Lewis acid (10 mol-%) in various solvents (2.0 mL) at room temperature. [b] Isolated yields. [c] Total yields of **4aa**–**ac** in which the (*E*) configuration of **4ab** has been determined by NOE spectroscopy (see the Supporting Information). [d] The ratios of **4aa**/**4ab**/**4ac** were determined by ^1H NMR spectroscopy. [e] The reaction mixtures were stirred for 24 h. [f] 20 mol-% of $BF_3 \cdot OEt_2$ was used. [g] 5 mol-% of $BF_3 \cdot OEt_2$ was used.

Next, we attempted to improve the yield of **3a** by adjusting the ratios of **1a** and **2a**. The results of these experiments are shown in Table 2. We found that using 1.0 equiv. of **1a** and 1.5 equiv. of **2a** produced **3a** in 45% yield and a mixture of **4aa**–**ac** in 13% total yield, respectively (Table 2, Entry 1). Increasing the amount of **1a** to 2.0 equiv. or 2.5 equiv. to react with **2a** (1.0 equiv.) afforded **3a** in 67 and 73% yields along with a mixture of **4aa**–**ac** in 28% and 14%

Table 2. Further optimization of the reaction conditions.

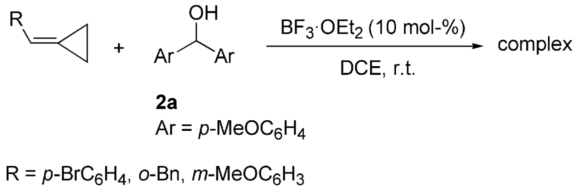


Entry	*x* **1a**	*y* **2a**	% Yield[a] 3a	% Yield[a] 4[b,c]
1	1	1.5	45	13 (90:5:5)
2	2	1	67	28 (71:13:16)
3	**2.5**	**1**	**73**	***14*** *(73:14:13)*
4	3	1	66	23 (66:16:18)

[a] Isolated yields. [b] Total yield of **4aa**–**ac**. [c] The ratios of **4aa**/**4ab**/**4ac** were determined by ^1H NMR spectroscopy.

total yields, respectively (Table 2, Entries 2 and 3). Further increases of the amount of **1a** provided no improvement in the yield (Table 2, Entry 4).

With these optimized reaction conditions in hand, we next turned our interest to the screening of the substrates. The results of these experiments are summarized in Table 3. We obtained the corresponding cyclopentene derivatives **3** in 25–78% yields along with the minor products **4** in 8–32% total yields. These studies highlighted the fact that substituents on the aromatic rings of **1** did not significantly affect the reaction outcomes (Table 3, Entries 1–7). Various strongly electron-donating alkoxy groups on the aromatic rings of **2** had little influence on the yields of **3** (Table 3, Entries 9–13). MCP **1i**−having an *ortho*-chloro atom on the aromatic ring−produced the corresponding cyclopentene **3i** in only 25% yield, presumably due to steric hindrance. We note that the strongly electron-donating group on the aromatic ring of **2** is essential in the reaction because when using diphenylmethanol or bis(4-chlorophenyl)methanol as the reactant, no reaction occurred under identical conditions. Moreover, it is noteworthy that, using triphenylmethanol as the substrate to react with **1**, no reaction occurred under identical conditions perhaps due to a steric effect. Furthermore, using monosubstituted MCPs to react with **2a** under identical conditions, complex product mixtures formed (Scheme 1). Thus, these studies outlined the fact that the reaction is determined by the substituted pattern of **1** and the electronic nature and the steric effect of **2**.

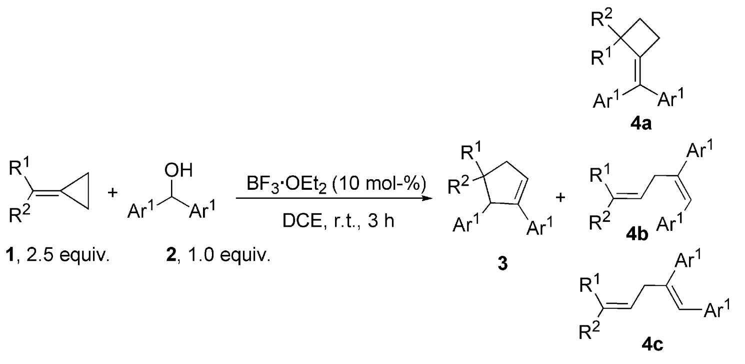


Scheme 1. Reaction of monosubstituted MCPs with **2a**.

We determined product structures by ^{1}H and ^{13}C NMR spectroscopy and HRMS or microanalyses. We determined the crystal structure of **3a** by X-ray diffraction (Figure 1), and its CIF data were deposited in a data base.[9] Moreover, we determined the (*E*) configuration of **4ab** by NOE studies (Figure 2, see the details in the Supporting Information).[8]

Furthermore, we observed an interesting phenomenon on the basis of ^{1}H NMR spectroscopic data; when it was stored at –18 °C for two weeks, the diene product **4ab** could be completely transformed into another diene **4aB** by allylic isomerization (Scheme 2). We unambiguously determined the structure of **4aB** by X-ray diffraction, and the ORTEP drawing is depicted in Figure 3.[9]

Table 3. Reactions of MCPs **1** with **2**, catalyzed by $BF_3 \cdot OEt_2$, under the optimized conditions.



Entry	1 (R^1/R^2)	2 (Ar^1)	% Yield[a] 3	% Yield[a] 4[c,d]
1	**1b** (p-MeC$_6$H$_4$/p-MeC$_6$H$_4$)	**2a**	**3b**, 61	**4ba**, **4bb**, **4bc** –
2	**1c** (p-FC$_6$H$_4$/p-FC$_6$H$_4$)	**2a**	**3c**, 62	**4ca**, **4cb**, **4cc** 19 (76:12:12)
3	**1d** (p-ClC$_6$H$_4$/p-ClC$_6$H$_4$)	**2a**	**3d**, 55	**4da**, **4db**, **4dc** 10 (63:22:15)
4	**1e** (p-MeOC$_6$H$_4$/p-MeOC$_6$H$_4$)	**2a**	**3e**, 57	**4ea**, **4eb**, **4ec** 32 (78:0:22)
5	**1f** (p-BrC$_6$H$_4$/p-BrC$_6$H$_4$)	**2a**	**3f**, 68	**4fa**, **4fb**, **4fc** 31 (79:9:12)
6	**1g** (p-ClC$_6$H$_4$/C$_6$H$_5$)	**2a**	**3g**, 64[b]	**4ga**, **4gb**, **4gc** –
7	**1h** (p-FC$_6$H$_4$/C$_6$H$_5$)	**2a**	**3h**, 78[b]	**4ha**, **4hb**, **4hc** 22 (80:12:8)[e]
8	**1i** (p-ClC$_6$H$_4$/o-ClC$_6$H$_4$)	**2a**	**3i**, 25	**4ia**, **4ib**, **4ic** –
9	**1a**	**2b** (p-EtOC$_6$H$_4$)	**3j**, 60	**4ja**, **4jb**, **4jc** –
10	**1a**	**2c** [p-CH$_3$(CH$_2$)$_5$OC$_6$H$_4$]	**3k**, 60	**4ka**, **4kb**, **4kc** 8 (88:12:0)
11	**1a**	**2d** (p-CH$_2$=CHCH$_2$OC$_6$H$_4$)	**3l**, 55	**4la**, **4lb**, **4lc** –
12	**1a**	**2e** (p-MOMC$_6$H$_4$)	**3m**, 45	**4ma**, **4mb**, **4mc** –
13	**1a**	**2f** (p-CH≡CCH$_2$OC$_6$H$_4$)	**3n**, 57	**4na**, **4nb**, **4nc** –

[a] Isolated yields. [b] For unsymmetrical substrates, diastereomers in a 1:1 ratio were obtained on the basis of ^{1}H NMR spectroscopy. [c] The total yields of **4a**–**c**. [d] The ratios of **4a**/**4b**/**4c** were determined by ^{1}H NMR spectroscopy. [e] For unsymmetrical substrates, the *E*/*Z* or *Z*/*E* ratio was 1:1.

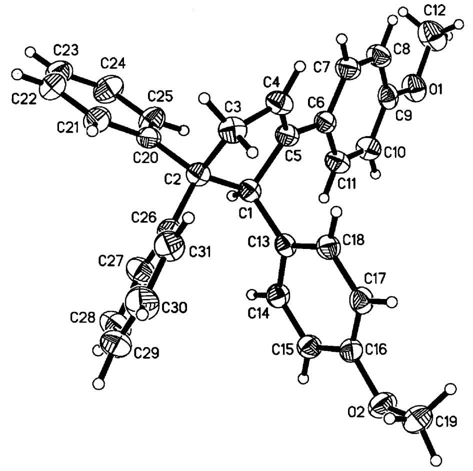


Figure 1. ORTEP drawing of **3a**.

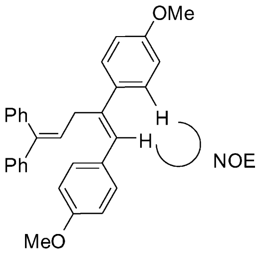
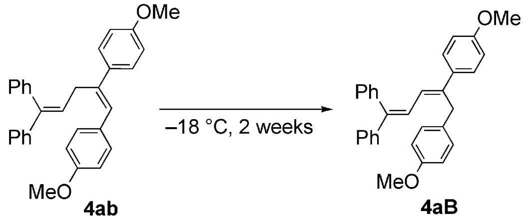


Figure 2. NOE studies on **4ab**.



Scheme 2. Transformation of **4ab** to **4aB**.

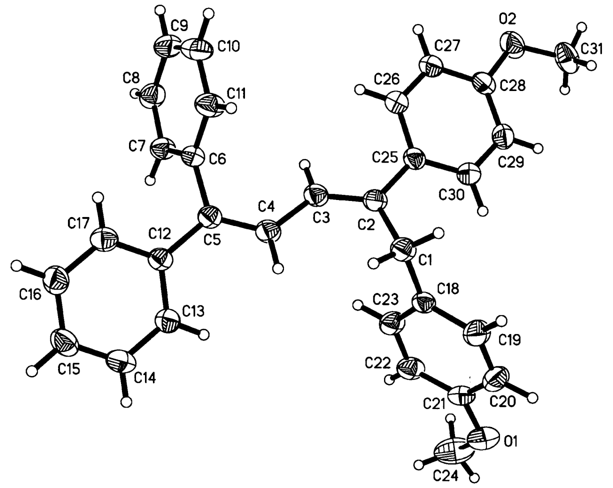
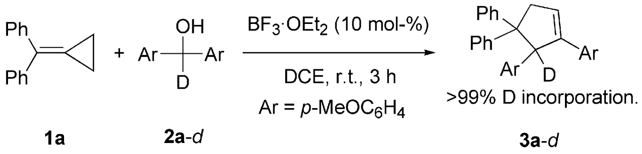


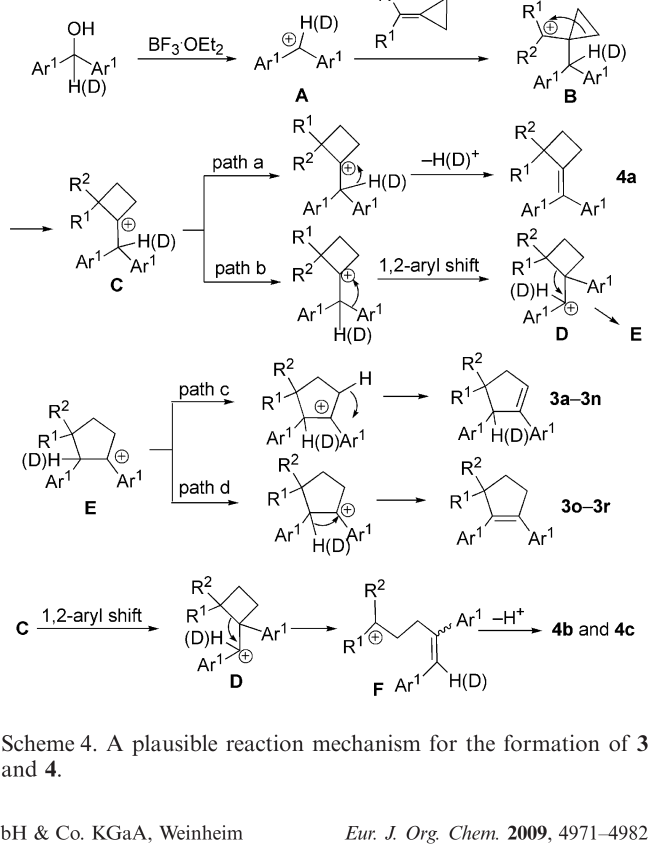
Figure 3. ORTEP drawing of **4aB**.

In order to have a better understanding of the reaction mechanism, we next carried out a deuterium-labeling experiment with **2a-*d*** as the substrate under the optimized conditions and found that the corresponding **3a-*d*** was formed in 66% yield with >99% D incorporation, suggesting that only aryl migration takes place in this reaction (Scheme 3).



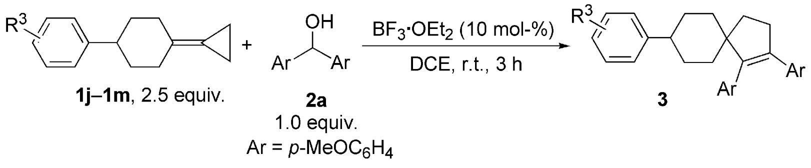
Scheme 3. Deuterium-labeling experiment of the reaction.

On the basis of deuterium-labeling experiment, we outlined a plausible reaction mechanism as shown in Scheme 4. In the presence of $BF_3{\cdot}OEt_2$, **2a** produces cationic intermediate **A**, which reacts with MCP **1** to afford cationic intermediate **B**. Intermediate **B** undergoes a ring expansion to give cationic intermediate **C**, which can proceed through two different reaction pathways. The deprotonation of **C** gives the minor product **4a** (path a). A 1,2-aryl shift produces intermediate **D**.[10] Intermediate **D** undergoes a 1,2-alkyl shift to intermediate **E**, which undergoes deprotonation to produce the major products **3a–n** (paths b and c). As for the products **4b** and **4c**, cationic intermediate **C** undergoes a 1,2-aryl shift to furnish cationic intermediate **D**, which undergoes a ring-opening process to afford cationic intermediate **F**. The deprotonation of intermediate **F** produces the products **4b** and **4c**.



Scheme 4. A plausible reaction mechanism for the formation of **3** and **4**.

Table 4. The reactions of aliphatic MCPs **1j**–**m** with **2a** in the presence of $BF_3{\cdot}OEt_2$.



Entry	R^3	% Yield of **3**[a]
1	H, **1j**	**3o**, 52
2	*p*-C_6H_5, **1k**	**3p**, 65
3	*o*,*p*-$2CH_3$, **1l**	**3q**, 67
4	*m*-Cl, **1m**	**3r**, 61

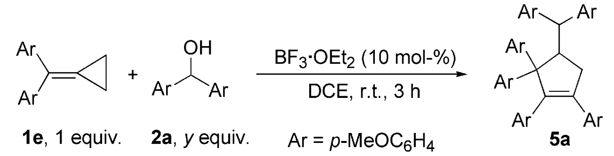
[a] Isolated yields.

Furthermore, we found that in the case of aliphatic MCP **1j**, product **3o** formed in 52% yield rather than the desired cyclopentene derivative of **3a**–**n**, presumably because the deprotonation in this particular case proceeded through path d (Table 4, Entry 1 and Scheme 4). Moreover, we also examined aliphatic MCPs **1k**–**m** in this reaction, and the results of these experiments are summarized in Table 4. The reactions proceeded smoothly to deliver the corresponding cyclopentene derivatives **3p**–**r** in good yields varying from 61–67% under the standard conditions, suggesting that the substituents on the aromatic rings have little influence on the reaction outcome.

Interestingly, we found that using 1.0 equiv. of MCP **1e**, having a strongly electron-donating methoxy group on the benzene ring, to react with 1.2 equiv. of **2a** afforded a new product **5a** in 55% yield under the standard conditions (Table 5, Entry 1). We also unambiguously determined the structure of **5a** by X-ray diffraction, and the ORTEP drawing is depicted in Figure 4.[9] Next, we attempted to improve the yield of **5a** by adjusting the ratios of **1e** and **2a** similarly. The results are shown in Table 5. When we used 1.0 equiv. of **1e** and 2.0 equiv. of **2a**, **5a** formed in 59% yield. Increasing the amount of **2a** to 2.5 equiv. and 3.0 equiv. improved the isolated yields of **5a** to 63% and 68%, respectively (Table 5, Entries 3 and 4). Further increasing the amount of **2a** (4.0 equiv.) furnished no improvement in the yield.

Thus, the optimized reaction conditions constitute a reaction in DCE at room temperature (20 °C) with 1.0 equiv. of **1e** and 3.0 equiv. of **2a** in the presence of $BF_3{\cdot}OEt_2$ (10 mol-%) for 3 h. Under these optimized conditions, we next examined the generality of this reaction using a variety of starting materials **2**, and the results are outlined in Table 6. The corresponding cyclopentene derivatives **5** formed in 50–57% yields (Table 6, Entries 1–4). Substituents on the aromatic rings of **2** have little influence on the reaction outcome. Moreover, we also determined the structure of **5b** by X-ray diffraction, and the ORTEP drawing is depicted in Figure 5.[9] More interestingly, on the basis of crystal data, the similar products **5a** and **5b** have different space groups ($P2_1/c$ and *P*-1, respectively).

Table 5. Optimization of the reaction conditions.



Entry	*y* **2a**	% Yield of **5a**[a]
1	1.2	55
2	2	59
3	2.5	63
4	**3**	**68**
5	4	54

[a] Isolated yields.

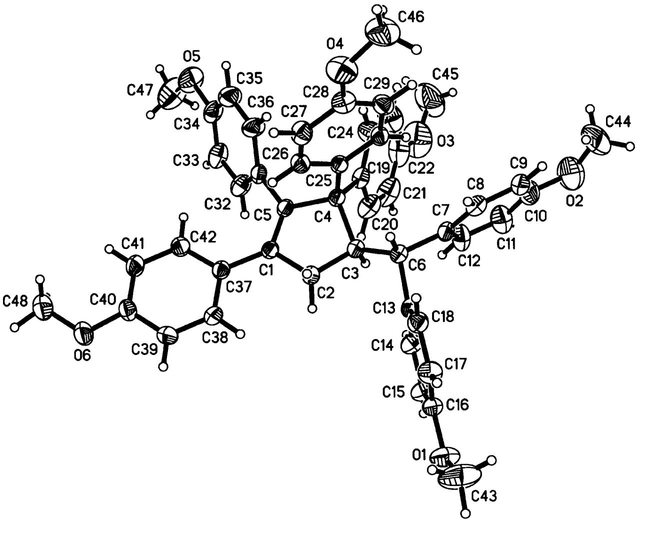
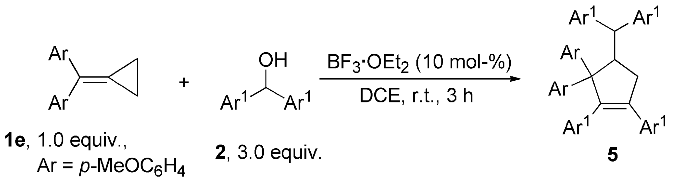


Figure 4. ORTEP drawing of **5a**.

In order to clarify the reaction route for the formation of **5**, we performed two control experiments (Scheme 5). We found that the reaction of **4eb** and **4ec** [(*E*/*Z*) mixtures, 0.1 mmol] with **2a** (0.2 mmol) under standard conditions

Table 6. Reactions of **1e** with **2b**–**f** under the optimized reaction conditions.



Entry	**2** (Ar^1)	% Yield of **5**[a]
1	**2b** (p-$EtOC_6H_4$)	**5b**, 50
2	**2c** [p-$CH_3(CH_2)_5OC_6H_4$]	**5c**, 50
3	**2d** (p-$CH_2{=}CHCH_2OC_6H_4$)	**5d**, 53
4	**2f** (p-$CH{\equiv}CCH_2OC_6H_4$)	**5e**, 57

[a] Isolated yields.

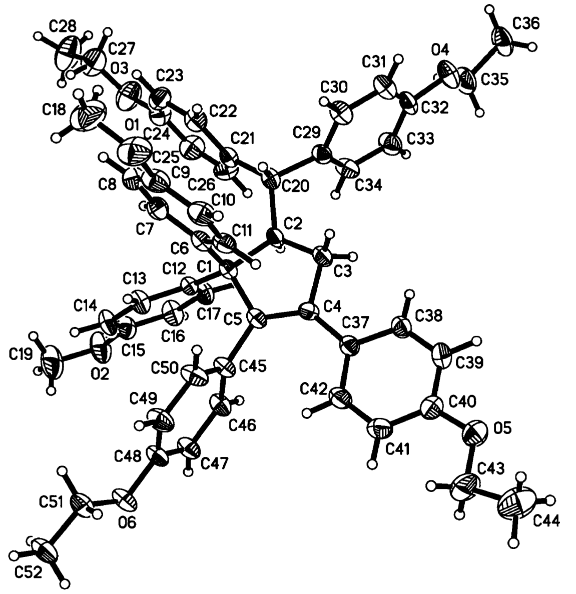
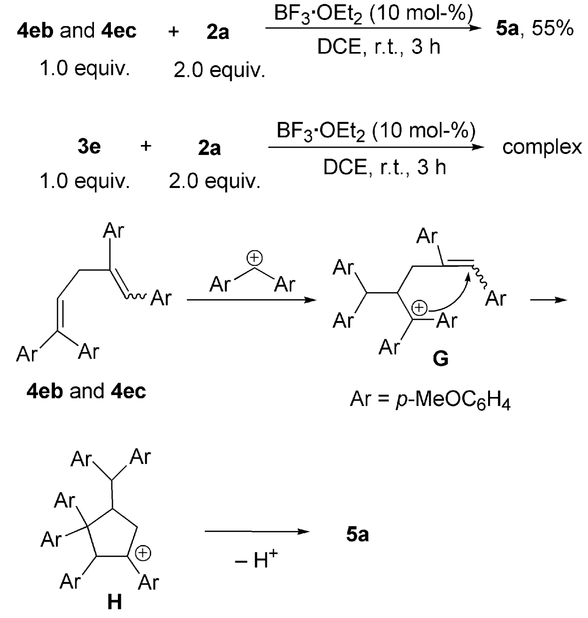


Figure 5. ORTEP drawing of **5b**.



Scheme 5. A control experiment and plausible reaction mechanism for the formation of **5**.

delivered the desired product **5a** in 55% yield (Scheme 5). Moreover, the reaction of **3e** (0.1 mmol) with **2a** (0.2 mmol) under the standard conditions afforded a complex product mixture rather than the desired product **5a** (Scheme 5). On the basis of these above results, a plausible reaction mechanism to account for the formation of **5** is shown in Scheme 4. The addition of cationic intermediate **A** (Scheme 5) to **4eb** and **4ec** produces intermediate **G**, which undergoes an intramolecular electrophilic addition to give the cationic intermediate **H**. The deprotonation of intermediate **H** affords the corresponding cyclopentene **5a**.

In conclusion, we have found an interesting procedure wherein diaryl or aliphatic MCPs can react with bis(alkoxyphenyl)methanols to provide cyclopentenes as the major products along with cyclobutanes and diene derivatives as the minor products under mild conditions. In the presence of $BF_3 \cdot OEt_2$, MCP **1e**, with a strongly electron-donating methoxy group, reacts with bis(alkoxyphenyl)methanol to produce novel polysubstituted cyclopentene derivatives in good yields. Plausible reaction mechanisms based on the deuterium-labeling and control experiments have been proposed. Further studies regarding the mechanistic details and scope of this process are in progress.

Experimental Section

Typical Procedure for the Reaction of MCPs 1 with Bis(4-alkoxyphenyl)methanol 2: MCP **1a** (0.25 mmol, 52 mg) and bis(4-methoxyphenyl)methanol **2a** (0.1 mmol, 24 mg) were dissolved in DCE (2.0 mL), and $BF_3 \cdot OEt_2$ (10 mol-%) was added. The mixture was stirred for 3.0 h at room temperature (25 °C). The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc (40:1) as an eluent to afford a white solid **3a** (32 mg, 73%) and the mixture of **4aa**–**4ac** (6 mg, 14%). Since these reaction products, having electron-rich substituents on the aromatic rings, are quite labile during purification and recrystallization (the solid product will become an oily product along with some decomposed byproducts during recrystallization), we could not send all of them for elemental analyses.

MCP **1e** (0.2 mmol, 53 mg) and bis(4-methoxyphenyl)methanol (**2a**) (0.6 mmol, 146 mg) were dissolved in DCE (2.0 mL), and $BF_3·OEt_2$ (10 mol-%) was added at room temperature. The mixture was stirred for 3 h. The solvent was removed in vacuo, and the residue was purified by flash column chromatography on silica gel with petroleum ether/EtOAc (10:1) as an eluent to give a white solid **5a** (98 mg, 68%).

3a: A white solid (32 mg, 73%), m.p. 151–153 °C. ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.70 (dd, *J* = 3.0, 16.2 Hz, 1 H, CH_2), 3.61 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.77 (d, *J* = 16.2 Hz, 1 H, CH_2), 4.79 (s, 1 H, CH), 6.19 (s, 1 H, =CH), 6.51 (d, *J* = 8.1 Hz, 2 H, Ar), 6.79 (d, *J* = 8.1 Hz, 2 H, Ar), 6.86 (d, *J* = 8.7 Hz, 2 H, Ar), 6.94–7.04 (m, 5 H, Ar), 7.13–7.22 (m, 5 H, Ar), 7.37 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.8, 54.9, 55.1, 59.9, 61.6, 113.1, 113.7, 122.1, 125.3, 125.5, 127.2, 127.3, 127.5, 128.1, 128.2, 128.8, 130.0, 131.2, 145.3, 145.6, 151.9, 157.7, 158.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3054, 3000, 2932, 2906, 2835, 2045, 1946, 1875, 1607, 1581, 1511, 1493, 1463, 1443, 1302, 1256, 1178, 1111, 1035, 830, 807, 789, 773, 756, 744, 700, 600, 531 cm^{-1}. MS (%): *m*/*z* = 432 (100) $[M]^+$, 91 (7), 121 (12), 165 (9), 239 (9), 265 (24), 311 (27), 324 (8), 341 (8), 433 (35). $C_{31}H_{28}O_2$ (432.2089): calcd. C 86.08, H 6.52; found C 86.23, H 6.74. HRMS (EI): calcd. for $C_{31}H_{28}O_2$ 432.2089; found 432.2104.

3b: A colorless oil (28 mg, 61%). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.16 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.67 (dd, *J* = 3.3, 16.2 Hz, 1 H, CH_2), 3.61 (s, 3 H, OCH_3), 3.71 (d, *J* = 16.2 Hz, 1 H, CH_2), 3.73 (s, 3 H, OCH_3), 4.75 (s, 1 H, CH), 6.18 (s, 1 H, =CH), 6.51 (d, *J* = 8.7 Hz, 2 H, Ar), 6.76–6.88 (m, 8 H, Ar), 6.98 (d, *J* = 8.1 Hz, 2 H, Ar), 7.09 (d, *J* = 8.1 Hz, 2 H, Ar), 7.35 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 20.8, 20.9, 44.0, 54.9, 55.1, 59.9, 60.9, 113.1, 113.7, 122.2, 127.3, 127.8, 127.9, 128.2, 128.3, 128.6, 130.0, 131.4, 134.5, 134.9, 142.4, 145.7, 149.2, 157.6, 158.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3050, 2998, 2922, 2835, 2045, 1891, 1607, 1582, 1573, 1512, 1463, 1442, 1302, 1246, 1177, 1111, 1036, 1003, 892, 864, 836, 808, 786, 750, 737, 702, 611, 575, 534 cm^{-1}. MS (%): *m*/*z* = 460 (100) $[M]^+$, 105 (12), 121 (26), 239 (12), 265 (15), 339 (48), 355 (15), 461 (37). HRMS (EI): calcd. for $C_{33}H_{32}O_2$ 460.2402; found 460.2396.

3c: A colorless oil (29 mg, 62%). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.64 (dd, *J* = 3.3, 16.5 Hz, 1 H, CH_2), 3.63 (s, 3 H, OCH_3), 3.70 (d, *J* = 16.5 Hz, 1 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.68 (s, 1 H, CH), 6.17 (s, 1 H, =CH), 6.53 (d, *J* = 8.4 Hz, 2 H, Ar), 6.69 (d, *J* = 8.7 Hz, 1 H, Ar), 6.72 (d, *J* = 8.7 Hz, 1 H, Ar), 6.79 (d, *J* = 8.7 Hz, 2 H, Ar), 6.82–6.93 (m, 6 H, Ar), 7.12 (dd, *J* = 5.4, 8.7 Hz, 2 H, Ar), 7.35 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 44.1, 54.9, 55.1, 60.3, 60.6, 113.3, 113.8, 114.0 (d, $J_{C,F}$ = 20.6 Hz), 114.3 (d, $J_{C,F}$ = 20.6 Hz), 121.8, 127.3, 127.8, 129.4 (d, $J_{C,F}$ = 7.4 Hz), 129.8, 130.2 (d, $J_{C,F}$ = 8.0 Hz), 130.7, 140.9, 141.0, 145.5, 147.3, 157.9, 158.9, 160.7 (d, *J* = 242.7 Hz), 160.9 (d, *J* = 243.9 Hz) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3058, 3000, 2933, 2907, 2836, 2043, 1962, 1885, 1757, 1607, 1583, 1573, 1514, 1463, 1442, 1418, 1406, 1305, 1261, 1163, 1140, 1108, 1035, 1015, 893, 865, 834, 787, 756, 737, 718, 701, 624, 610, 589, 573, 535, 508 cm^{-1}. MS (%): *m*/*z* = 468 (100) $[M]^+$, 109 (15), 121 (36), 133 (11), 239 (16), 265 (27), 347 (24), 360 (12). HRMS (EI): calcd. for $C_{31}H_{26}O_2F_2$ 468.1901; found 468.1900.

3d: A colorless oil (28 mg, 55%). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.63 (dd, *J* = 3.3, 16.5 Hz, 1 H, CH_2), 3.64 (s, 3 H, OCH_3), 3.69 (d, *J* = 16.5 Hz, 1 H, CH_2), 3.75 (s, 3 H, OCH_3), 4.67 (s, 1 H, CH), 6.16 (s, 1 H, =CH), 6.54 (d, *J* = 8.4 Hz, 2 H, Ar), 6.77–6.89 (m, 6 H, Ar), 7.00 (d, *J* = 8.4 Hz, 2 H, Ar), 7.08 (d, *J* = 8.7 Hz, 2 H, Ar), 7.14 (d, *J* = 8.7 Hz, 2 H, Ar), 7.34 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.8, 55.0, 55.2, 60.0, 60.8, 113.4, 113.8, 121.7, 127.3, 127.5, 127.70, 127.73, 129.4, 129.8, 130.1, 130.4, 131.3, 131.6, 143.5, 145.5, 149.8, 157.9, 158.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3052, 3000, 2932, 2907, 2836, 2288, 2043, 1893, 1607, 1582, 1573, 1510, 1491, 1464, 1442, 1420, 1398, 1303, 1258, 1177, 1142, 1112, 1093, 1035, 1013, 1003, 972, 892, 864, 814, 787, 767, 737, 705, 673, 622, 607, 561, 535 cm^{-1}. MS (%): *m*/*z* = 500 (100) $[M]^+$, 121 (40), 165 (15), 237 (15), 239 (21), 252 (37), 265 (61), 379 (22), 501 (34), 502 (67). HRMS (EI): calcd. for $C_{31}H_{26}O_2Cl_2$ 500.1310; found 500.1295.

3e: A colorless oil (28 mg, 57%). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.65 (dd, *J* = 2.4, 16.2 Hz, 1 H, CH_2), 3.64 (s, 3 H, OCH_3), 3.66 (s, 3 H, OCH_3), 3.68 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.78 (d, *J* = 16.2 Hz, 1 H, CH_2), 4.70 (s, 1 H, CH), 6.19 (s, 1 H, =CH), 6.53 (d, *J* = 8.4 Hz, 2 H, Ar), 6.56 (d, *J* = 8.4 Hz, 2 H, Ar), 6.72 (d, *J* = 8.4 Hz, 2 H, Ar), 6.79 (d, *J* = 8.4 Hz, 2 H, Ar), 6.85–6.89 (m, 4 H, Ar), 7.11 (d, *J* = 8.4 Hz, 2 H, Ar), 7.37 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 44.2, 54.9, 55.0, 55.1, 55.2, 60.2, 60.3, 112.5, 112.8, 113.2, 113.4, 113.5, 113.7, 122.2, 127.3, 128.3, 128.4, 128.9, 129.8, 130.0, 131.5, 137.8, 144.3, 145.7, 157.0, 157.3, 157.7, 158.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3035, 2999, 2932, 2906, 2835, 2058, 1607, 1581, 1510, 1463, 1441, 1301, 1249, 1178, 1111, 1036, 909, 822, 787, 754, 732, 611, 598, 579, 543 cm^{-1}. MS (%): *m*/*z* = 492 (100) $[M]^+$, 121 (73), 371 (70), 227 (60), 253 (56), 252 (46), 493 (37), 385 (31). HRMS (EI): calcd. for $C_{33}H_{32}O_4$ 492.2300; found 492.2301.

3f: A colorless oil (40 mg, 68%). ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.63 (dd, *J* = 3.6, 16.5 Hz, 1 H, CH_2), 3.66 (s, 3 H, OCH_3), 3.68 (d, *J* = 16.5 Hz, 1 H, CH_2), 3.76 (s, 3 H, OCH_3), 4.66 (s, 1 H, CH), 6.16 (s, 1 H, =CH), 6.54 (d, *J* = 8.4 Hz, 2 H, Ar), 6.77–6.85 (m, 6 H, Ar), 7.02 (d, *J* = 8.4 Hz, 2 H, Ar), 7.15 (d, *J* = 8.4 Hz, 2 H, Ar), 7.30 (d, *J* = 8.4 Hz, 2 H, Ar), 7.33 (d, *J* = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.8, 55.0, 55.2, 59.9, 61.0, 113.5, 113.8, 119.6, 119.8, 121.7, 127.3, 127.7, 129.8, 129.9, 130.38, 130.43, 130.5, 130.7, 143.9, 145.6, 150.3, 158.0, 159.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2929, 2835, 2359, 2342, 1683, 1652, 1606, 1558, 1509, 1488, 1472, 1457, 1437, 1418, 1394, 1302, 1256, 1177, 1111, 1075, 1035, 1009, 835, 808, 786, 763, 529 cm^{-1}. MS (%): *m*/*z* = 588 (51) $[M]^+$, 121 (52), 239 (22), 265 (55), 388 (26), 390 (25), 589 (20), 590 (100). HRMS (EI): calcd. for $C_{31}H_{26}O_2Br_2$ 588.0297; found 588.0300.

3g: A colorless oil (30 mg, 64%); (*syn* or *anti* isomer) ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.66 (dd, *J* = 3.3, 16.5 Hz, 1 H, CH_2), 3.61 (s, 3 H, OCH_3), 3.71 (d, *J* = 16.5 Hz, 1 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.70 (s, 1 H, CH), 6.17 (s, 1 H, =CH), 6.51 (d, *J* = 8.7 Hz, 2 H, Ar), 6.77–7.02 (m, 8 H, Ar), 7.12–7.22 (m, 4 H, Ar), 7.35 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. (*anti* or *syn* isomer) ^1H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.70 (dd, *J* = 3.3, 16.5 Hz, 1 H, CH_2), 3.63 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 3.76 (d, *J* = 16.5 Hz, 1 H, CH_2), 4.76 (s, 1 H, CH), 6.18 (s, 1 H, =CH), 6.54 (d, *J* = 8.7 Hz, 2 H, Ar), 6.77–7.02 (m, 8 H, Ar), 7.12–7.22 (m, 4 H, Ar), 7.35 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. (*syn* or *anti* isomer) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.6, 54.9, 55.0, 59.8, 61.1, 113.2, 113.75, 121.9, 125.6, 127.3, 127.4, 127.6, 128.0, 128.7, 129.5, 130.2, 130.7, 131.0, 144.1, 145.5, 150.4, 157.8, 158.8 ppm. (*anti* or *syn* isomer) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 44.0, 55.0, 55.1, 60.0, 61.3, 113.3, 113.8, 121.9, 125.7, 127.3, 127.6, 127.9, 128.7, 129.5, 129.9, 130.7, 130.8, 131.3, 144.7, 145.5, 151.3, 157.8, 158.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3054, 2932, 2906, 2835, 1607, 1574, 1510, 1492, 1463, 1443, 1398, 1303, 1256, 1177, 1111, 1093, 1035, 1013, 832, 813, 787, 754, 737, 700, 605, 560, 534 cm^{-1}. MS (%): *m*/*z* = 466 (100) $[M]^+$, 121 (46), 165 (20), 237 (13), 252 (26), 265

(45), 310 (16), 344 (12), 345 (28), 467 (36), 468 (41). HRMS (EI): calcd. for $C_{31}H_{27}O_2Cl$ 466.1700; found 466.1707.

3h: A colorless oil (35 mg, 78%); (*syn* or *anti* isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.66 (dd, J = 3.3, 16.5 Hz, 1 H, CH_2), 3.61 (s, 3 H, OCH_3), 3.71 (d, J = 16.5 Hz, 1 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.70 (s, 1 H, CH), 6.17 (s, 1 H, =CH), 6.51 (d, J = 8.7 Hz, 2 H, Ar), 6.77–7.02 (m, 8 H, Ar), 7.12–7.22 (m, 4 H, Ar), 7.35 (d, J = 8.7 Hz, 2 H, Ar) ppm. (*anti* or *syn* isomer) ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.70 (dd, J = 3.3, 16.5 Hz, 1 H, CH_2), 3.63 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.76 (d, J = 16.5 Hz, 1 H, CH_2), 4.76 (s, 1 H, CH), 6.18 (s, 1 H, =CH), 6.54 (d, J = 8.7 Hz, 2 H, Ar), 6.77–7.02 (m, 8 H, Ar), 7.12–7.22 (m, 4 H, Ar), 7.35 (d, J = 8.7 Hz, 2 H, Ar) ppm. (*syn* or *anti* isomer) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.8, 54.9, 55.1, 60.0, 61.0, 113.1, 113.3, 113.9 (d, J = 22.6 Hz), 122.0, 125.5, 125.7, 127.3, 127.6, 128.0, 128.7, 129.5 (d, J = 7.6 Hz), 129.9, 130.9, 131.0, 141.2, 145.0, 145.5, 145.6, 147.58, 151.5, 157.7, 158.79, 160.6 (d, J = 243.1 Hz) ppm. (*anti* or *syn* isomer) ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 44.1, 54.9, 55.1, 60.3, 61.1, 113.3, 113.7, 114.2 (d, J = 20.9 Hz), 122.0, 125.5, 125.7, 127.3, 127.6, 128.0, 128.7, 129.9, 130.2 (d, J = 7.4 Hz), 130.9, 131.0, 141.2, 145.0, 145.6, 147.6, 151.5, 157.8, 158.83, 160.8 (d, J = 242.9 Hz) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 3000, 2933, 2907, 2836, 2043, 1884, 1607, 1582, 1510, 1463, 1443, 1418, 1303, 1258, 1177, 1141, 1110, 1035, 1015, 909, 891, 864, 835, 787, 771, 752, 736, 700, 648, 628, 610, 578, 537 cm^{-1}. MS (%): m/z = 450 (100) $[M]^+$, 121 (43), 265 (37), 451 (34), 329 (33), 252 (25), 165 (25), 239 (23). HRMS (EI): calcd. for $C_{31}H_{27}O_2F$ 450.1994; found 450.1995.

3i: A colorless oil (13 mg, 25%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.99 (dd, J = 3.0, 16.8 Hz, 1 H, CH_2), 3.65 (d, J = 16.8 Hz, 1 H, CH_2), 3.67 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.61 (s, 1 H, CH), 6.21 (s, 1 H, =CH), 6.53 (d, J = 8.7 Hz, 2 H, Ar), 6.67–6.70 (m, 4 H, Ar), 6.74 (d, J = 8.7 Hz, 2 H, Ar), 6.92 (d, J = 8.7 Hz, 2 H, Ar), 7.17–7.54 (m, 6 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 40.0, 55.1, 55.2, 61.1, 61.3, 113.4, 113.8, 123.2, 126.0, 127.2, 127.7, 127.8, 128.6, 128.9, 129.6, 130.7, 131.9, 134.7, 142.8, 143.7, 146.0, 158.1, 158.9 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3052, 3000, 2954, 2932, 2835, 1887, 1607, 1583, 1573, 1510, 1492, 1465, 1441, 1399, 1303, 1256, 1177, 1111, 1093, 1035, 1013, 863, 837, 815, 786, 753, 738, 681, 626, 607, 539 cm^{-1}. MS (%): m/z = 500 (100) $[M]^+$, 121 (62), 125 (13), 165 (26), 227 (20), 239 (24), 252 (31), 265 (86), 501 (36), 502 (69), 503 (23). HRMS (EI): calcd. for $C_{31}H_{26}O_2Cl_2$ 500.1310; found 500.1303.

3j: A colorless oil (28 mg, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.27 (t, J = 6.9 Hz, 3 H, CH_3), 1.36 (t, J = 6.9 Hz, 3 H, CH_3), 2.69 (dd, J = 2.7, 16.9 Hz, 1 H, CH_2), 3.76 (d, J = 16.9 Hz, 1 H, CH_2), 3.82 (q, J = 6.9 Hz, 2 H, OCH_2), 3.96 (q, J = 6.9 Hz, 2 H, OCH_2), 4.77 (s, 1 H, CH), 6.17 (s, 1 H, =CH), 6.49 (d, J = 8.4 Hz, 2 H, Ar), 6.76 (d, J = 8.4 Hz, 2 H, Ar), 6.84 (d, J = 8.4 Hz, 2 H, Ar), 6.93–7.03 (m, 5 H, Ar), 7.11–7.22 (m, 5 H, Ar), 7.35 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.7, 14.8, 43.8, 59.9, 61.6, 63.0, 63.3, 113.7, 114.2, 122.0, 125.3, 125.5, 127.2, 127.3, 127.5, 128.1, 128.9, 130.0, 131.1, 145.4, 145.6, 151.9, 157.1, 158.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3054, 2979, 2927, 2903, 2848, 1943, 1882, 1607, 1580, 1509, 1493, 1477, 1443, 1392, 1302, 1244, 1177, 1116, 1090, 1047, 1002, 923, 863, 828, 803, 778, 756, 744, 699, 669, 648, 619, 548, 531 cm^{-1}. MS (%): m/z = 460 (100) $[M]^+$, 107 (15), 165 (15), 293 (20), 325 (25), 461 (35). HRMS (EI): calcd. for $C_{33}H_{32}O_2$ 460.2402; found 460.2410.

3k: A colorless oil (34 mg, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.92–0.94 (m, 6 H, CH_3), 1.33–1.54 (m, 12 H, CH_2), 1.67–1.80 (m, 4 H, CH_2), 2.74 (dd, J = 3.0, 16.2 Hz, 1 H, CH_2), 3.80 (d, J = 16.2 Hz, 1 H, CH_2), 3.81 (t, J = 6.6 Hz, 2 H, OCH_2), 3.93 (t, J = 6.6 Hz, 2 H, OCH_2), 4.82 (s, 1 H, CH), 6.22 (s, 1 H, =CH), 6.54 (d, J = 8.4 Hz, 2 H, Ar), 6.81 (d, J = 8.4 Hz, 2 H, Ar), 6.88 (d, J = 8.4 Hz, 2 H, Ar), 6.98–7.08 (m, 5 H, Ar), 7.16–7.26 (m, 5 H, Ar), 7.40 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.0, 22.6, 25.7, 29.2, 31.5, 31.6, 43.8, 59.9, 61.6, 67.6, 67.8, 113.8, 114.2, 121.9, 125.3, 125.5, 127.2, 127.3, 127.5, 127.9, 128.1, 128.9, 129.9, 131.0, 145.4, 145.7, 151.9, 157.2, 158.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 2957, 2855, 1939, 1881, 1607, 1580, 1509, 1493, 1469, 1444, 1390, 1302, 1243, 1176, 1112, 1033, 937, 907, 888, 864, 831, 780, 756, 744, 699, 670, 649, 620, 556, 531 cm^{-1}. MS (%): m/z = 572 (100) $[M]^+$, 43 (60), 91 (11), 167 (10), 381 (13), 573 (48), 574 (11). HRMS (EI): calcd. for $C_{41}H_{48}O_2$ 572.3654; found 572.3666.

3l: A colorless oil (27 mg, 55%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.69 (dd, J = 3.0, 16.5 Hz, 1 H, CH_2), 3.75 (d, J = 16.5 Hz, 1 H, CH_2), 4.31 (d, J = 4.8 Hz, 2 H, OCH_2), 4.46 (d, J = 4.8 Hz, 2 H, OCH_2), 4.77 (s, 1 H, CH), 5.18 (dd, J = 1.5, 10.5 Hz, 1 H, $=CH_2$), 5.24 (dd, J = 1.5, 10.5 Hz, 1 H, $=CH_2$), 5.27 (dd, J = 1.5, 17.1 Hz, 1 H, $=CH_2$), 5.34 (dd, J = 1.5, 17.1 Hz, 1 H, $=CH_2$), 5.87–6.05 (m, 2 H, =CH), 6.18 (s, 1 H, =CH), 6.51 (d, J = 8.4 Hz, 2 H, Ar), 6.79 (d, J = 8.4 Hz, 2 H, Ar), 6.84 (d, J = 8.4 Hz, 2 H, Ar), 6.91–7.03 (m, 5 H, Ar), 7.10–7.22 (m, 5 H, Ar), 7.34 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.7, 59.9, 61.6, 68.4, 68.6, 113.9, 114.5, 117.3, 117.6, 122.2, 125.3, 125.5, 127.2, 127.3, 127.5, 128.1, 128.3, 128.8, 129.9, 131.3, 133.2, 133.3, 145.3, 145.5, 151.8, 156.7, 157.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 2957, 2855, 1939, 1881, 1607, 1580, 1509, 1493, 1469, 1444, 1390, 1302, 1243, 1176, 1112, 1033, 937, 907, 888, 864, 831, 780, 756, 744, 699, 670, 649, 620, 556, 531 cm^{-1}. MS (%): m/z = 484 (100) $[M]^+$, 41 (98), 91 (31), 115 (21), 147 (11), 165 (21), 167 (42), 191 (36), 309 (14), 485 (39). HRMS (EI): calcd. for $C_{35}H_{32}O_2$ 484.2402; found 484.2407.

3m: A colorless oil (22 mg, 45%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.70 (dd, J = 3.0, 16.2 Hz, 1 H, CH_2), 3.37 (s, 3 H, OCH_3), 3.45 (s, 3 H, OCH_3), 3.77 (d, J = 16.2 Hz, 1 H, CH_2), 4.78 (s, 1 H, CH), 5.00 (s, 2 H, OCH_2), 5.14 (s, 2 H, OCH_2), 6.22 (s, 1 H, =CH), 6.63 (d, J = 8.4 Hz, 2 H, Ar), 6.85 (d, J = 8.4 Hz, 2 H, Ar), 6.92–7.01 (m, 7 H, Ar), 7.1–7.20 (m, 5 H, Ar), 7.38 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.8, 55.9, 56.0, 59.9, 61.6, 94.3, 94.4, 115.5, 116.0, 122.7, 125.3, 125.5, 127.2, 127.3, 127.5, 128.1, 128.8, 129.3, 130.0, 132.4, 145.2, 145.4, 151.8, 155.5, 156.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3054, 2997, 2928, 2848, 2824, 2786, 1994, 1947, 1888, 1727, 1606, 1578, 1510, 1443, 1406, 1312, 1240, 1200, 1150, 1111, 1077, 1000, 921, 888, 864, 808, 789, 772, 757, 744, 699, 669, 656, 631, 619, 594, 555, 531 cm^{-1}. MS (%): m/z = 492 (100) $[M]^+$, 167 (86), 169 (63), 91 (53), 115 (42), 101 (40), 191 (40), 69 (38). HRMS (EI): calcd. for $C_{33}H_{32}O_4$ 492.2301; found 492.2309.

3n: A colorless oil (27 mg, 57%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.42 (t, J = 2.4 Hz, 1 H, CH), 2.47 (t, J = 2.4 Hz, 1 H, CH), 2.70 (dd, J = 3.0, 16.2 Hz, 1 H, CH_2), 3.75 (d, J = 16.2 Hz, 1 H, CH_2), 4.47 (d, J = 2.4 Hz, 2 H, OCH_2), 4.62 (d, J = 2.4 Hz, 2 H, OCH_2), 4.78 (s, 1 H, CH), 6.21 (s, 1 H, =CH), 6.56 (d, J = 8.4 Hz, 2 H, Ar), 6.86 (d, J = 8.4 Hz, 4 H, Ar), 6.91–7.03 (m, 5 H, Ar), 7.11–7.22 (m, 5 H, Ar), 7.37 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 43.7, 55.6, 59.8, 61.6, 75.2, 75.6, 78.5, 78.6, 114.1, 114.6, 122.7, 125.3, 125.5, 127.2, 127.3, 127.5, 128.0, 128.8, 128.9, 129.9, 132.0, 145.1, 145.2, 151.7, 155.8, 156.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3290, 3053, 2924, 2850, 2121, 1878, 1605, 1509, 1493, 1444, 1375, 1304, 1266, 1219, 1178, 1114, 1030, 925, 864, 832, 783, 757, 744, 700, 644, 553, 530 cm^{-1}. MS (%): m/z

= 480 (76) [M]$^+$, 191 (100), 167 (95), 91 (89), 115 (89), 165 (89), 178 (53), 192 (43). HRMS (EI): calcd. for $C_{35}H_{28}O_2$ 480.2089; found 480.2093.

3o: A colorless oil (22 mg, 52%). ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 1.46–1.82 (m, 8 H, CH$_2$), 2.06 (t, J = 7.2 Hz, 2 H, CH$_2$), 2.27–2.34 (m, 1 H, CH), 2.82 (t, J = 7.2 Hz, 2 H, CH$_2$), 3.72 (s, 3 H, OCH$_3$), 3.86 (s, 3 H, OCH$_3$), 6.64 (d, J = 8.7 Hz, 2 H, Ar), 6.89 (d, J = 8.7 Hz, 2 H, Ar), 6.98 (d, J = 8.7 Hz, 2 H, Ar), 7.01 (d, J = 8.7 Hz, 2 H, Ar), 7.14–7.30 (m, 5 H, Ar) ppm. ^{13}C NMR (CDCl$_3$, 75 MHz, TMS): δ = 30.9, 33.0, 33.3, 35.0, 43.6, 52.7, 55.0, 55.1, 113.0, 113.6, 125.8, 126.7, 128.2, 128.8, 130.1, 130.7, 131.1, 135.3, 145.5, 147.7, 157.8, 158.2 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3058, 3027, 2999, 2926, 2850, 2063, 1884, 1605, 1570, 1513, 1441, 1338, 1284, 1248, 1178, 1106, 1053, 1035, 895, 830, 802, 788, 757, 700, 626, 586, 570, 540 cm^{-1}. MS (%): m/z = 424 (71) [M]$^+$, 91 (16), 121 (27), 171 (48), 292 (21), 305 (100), 306 (25), 425 (25). HRMS (EI): calcd. for $C_{30}H_{32}O_2$ 424.2402; found 424.2403.

3p: A white solid (32 mg, 65%), m.p. 188–190 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, TMS): δ = 1.52–1.57 (m, 2 H, CH$_2$), 1.64–1.71 (m, 4 H, CH$_2$), 1.81–1.85 (m, 2 H, CH$_2$), 2.07 (t, J = 7.2 Hz, 2 H, CH$_2$), 2.31–2.39 (m, 1 H, CH), 2.83 (t, J = 7.2 Hz, 2 H, CH$_2$), 3.71 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 6.64–6.66 (m, 2 H, Ar), 6.89–6.91 (m, 2 H, Ar), 6.98–7.03 (m, 4 H, Ar), 7.24–7.33 (m, 3 H, Ar), 7.39–7.43 (m, 2 H, Ar), 7.49–7.55 (m, 2 H, Ar), 7.56–7.58 (m, 2 H, Ar) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz, TMS): δ = 30.9, 33.1, 33.3, 35.0, 43.2, 52.8, 55.06, 55.12, 113.1, 113.7, 126.93, 126.97, 127.01, 127.2, 128.7, 128.8, 130.1, 130.8, 131.1, 135.4, 138.8, 141.1, 145.5, 146.8, 157.8, 158.3 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3026, 2924, 2848, 1882, 1605, 1571, 1510, 1485, 1461, 1439, 1409, 1287, 1240, 1173, 1106, 1054, 1028, 908, 827, 788, 765, 736, 698, 586, 562, 545, 511 cm^{-1}. MS (%): m/z = 500 (55) [M]$^+$, 305 (100), 171 (47), 292 (31), 306 (24), 501 (23), 121 (22), 180 (10). $C_{36}H_{36}O_2$ (500.2715): calcd. C 86.36, H 7.25; found C 86.68, H 7.23. HRMS (EI): calcd. for $C_{30}H_{36}O_2$ 500.2715; found 500.2717.

3q: A white solid (30 mg, 67%), m.p. 163–165 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, TMS): δ = 1.47–1.55 (m, 2 H, CH$_2$), 1.63–1.69 (m, 5 H, CH$_2$), 2.07 (t, J = 7.2 Hz, 2 H, CH$_2$), 2.21 (s, 3 H, CH$_3$), 2.27 (s, 3 H, CH$_3$), 2.43–2.50 (m, 1 H, CH), 2.82 (t, J = 7.2 Hz, 2 H, CH$_2$), 3.72 (s, 3 H, OCH$_3$), 3.84 (s, 3 H, OCH$_3$), 6.64–6.66 (m, 2 H, Ar), 6.89–6.93 (m, 3 H, Ar), 6.96–7.02 (m, 5 H, Ar), 7.14 (d, J = 8.0 Hz, 1 H, Ar) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz, TMS): δ = 19.3, 20.8, 30.1, 33.1, 33.3, 35.2, 38.7, 52.9, 55.06, 55.10, 113.0, 113.7, 125.2, 126.7, 128.8, 130.1, 130.8, 131.0, 131.1, 134.9, 135.1, 135.4, 142.5, 145.6, 157.8, 158.3 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3032, 2999, 2926, 2849, 1605, 1570, 1442, 1283, 1246, 1178, 1105, 1053, 1035, 909, 829, 788, 733, 591, 568, 539 cm^{-1}. MS (%): m/z = 452 (65) [M]$^+$, 305 (100), 132 (46), 171 (46), 119 (31), 292 (27), 121 (27), 453 (25). $C_{32}H_{36}O_2$ (452.2715): calcd. C 84.91, H 8.02; found C 85.37, H 7.83. HRMS (EI): calcd. for $C_{32}H_{36}O_2$ 452.2715; found 452.2714.

3r: A colorless oil (28 mg, 61%). ^{1}H NMR (CDCl$_3$, 400 MHz, TMS): δ = 1.11–1.26 (m, 3 H, CH$_2$), 1.55–1.67 (m, 3 H, CH$_2$), 1.74–1.77 (m, 2 H, CH$_2$), 2.04–2.08 (m, 2 H, CH$_2$), 2.66–2.74 (m, 1 H, CH), 2.81 (t, J = 7.2 Hz, 1 H, CH$_2$), 3.70 (s, 3 H, OCH$_3$), 3.81 (s, 3 H, OCH$_3$), 6.62–6.64 (m, 2 H, Ar), 6.85–6.90 (m, 2 H, Ar), 6.93–6.96 (m, 4 H, Ar), 7.06–7.10 (m, 2 H, Ar), 7.21–7.24 (m, 2 H, Ar) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz, TMS): δ = 23.3, 33.1, 33.40, 33.43, 33.9, 40.4, 42.9, 53.9, 55.0, 55.1, 113.0, 113.7, 128.2, 128.3, 128.8, 129.8, 130.0, 130.5, 131.1, 131.3, 135.6, 145.2, 146.0, 157.9, 158.3 ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3032, 2997, 2927, 2849, 1882, 1605, 1511, 1493, 1463, 1442, 1283, 1247, 1178, 1091, 1035, 1013, 908, 828, 732, 572, 530 cm^{-1}. MS (%): m/z = 458 (100) [M]$^+$, 415 (75), 460 (36), 459 (34), 291 (34), 121 (30), 171 (29), 417 (28). HRMS (EI): calcd. for $C_{30}H_{31}O_2Cl$: 458.2013; found 458.2014.

4aa and 4ac: A colorless oil (6 mg, 14%); **4aa**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 2.72–2.83 (m, 4 H, CH$_2$), 3.67 (s, 3 H, OCH$_3$), 3.76 (s, 3 H, OCH$_3$), 6.50 (d, J = 8.7 Hz, 2 H, Ar), 6.67 (d, J = 8.7 Hz, 2 H, Ar), 7.12–7.26 (m, 8 H, Ar), 7.32–7.35 (m, 4 H, Ar) ppm. **4ac**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.55 (d, J = 6.9 Hz, 2 H, CH$_2$), 3.80 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 6.04 (t, J = 6.9 Hz, 1 H, =CH), 6.49–7.35 (m, 19 H, Ar) ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3043, 2996, 2955, 2836, 2359, 2342, 1788, 1686, 1664, 1602, 1572, 1506, 1463, 1442, 1409, 1289, 1248, 1178, 1166, 1109, 1032, 1014, 830, 795, 766, 616, 576, 540 cm^{-1}. MS (%): m/z = 432 (100) [M]$^+$, 121 (29), 239 (20), 265 (34), 311 (38), 433 (36). HRMS (EI): calcd. for $C_{31}H_{28}O_2$ 432.2091; found 432.2089.

4ca, 4cb and 4cc: A colorless oil (9 mg, 19%); **4ca**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 2.66–2.70 (m, 2 H, CH$_2$), 2.76–2.82 (m, 2 H, CH$_2$), 3.69 (s, 3 H, OCH$_3$), 3.76 (s, 3 H, OCH$_3$), 6.53 (d, J = 8.7 Hz, 2 H, Ar), 6.64 (d, J = 8.7 Hz, 2 H, Ar), 6.73 (d, J = 8.7 Hz, 2 H, Ar), 6.90 (d, J = 8.7 Hz, 2 H, Ar), 6.93 (d, J = 8.7 Hz, 2 H, Ar), 7.12 (d, J = 8.7 Hz, 2 H, Ar), 7.23 (d, J = 8.7 Hz, 4 H, Ar) ppm. **4cb**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.19 (d, J = 7.2 Hz, 2 H, CH$_2$), 3.72 (s, 3 H, OCH$_3$), 3.80 (s, 3 H, OCH$_3$), 6.10 (t, J = 7.2 Hz, 1 H, =CH), 6.33 (s, 1 H, =CH), 6.53–7.23 (m, 16 H, Ar) ppm. **4cc**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.52 (d, J = 6.9 Hz, 2 H, CH$_2$), 3.79 (s, 3 H, OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 5.95 (t, J = 6.9 Hz, 1 H, =CH), 6.53–7.23 (m, 17 H, Ar) ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3041, 2999, 2955, 2836, 2359, 2342, 1782, 1683, 1662, 1602, 1572, 1506, 1463, 1442, 1409, 1289, 1248, 1178, 1161, 1106, 1032, 1014, 830, 795, 766, 616, 576, 540 cm^{-1}. MS (%): m/z = 468 (97) [M]$^+$, 109 (20), 121 (34), 265 (16), 361 (21), 373 (100), 374 (28), 469 (35). HRMS (EI): calcd. for $C_{31}H_{26}O_2F_2$: 468.1893; found 468.1901.

4da, 4db and 4dc: A colorless oil (5 mg, 10%); **4da**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 2.65–2.69 (m, 2 H, CH$_2$), 2.77–2.81 (m, 2 H, CH$_2$), 3.69 (s, 3 H, OCH$_3$), 3.76 (s, 3 H, OCH$_3$), 6.54 (d, J = 8.7 Hz, 2 H, Ar), 6.65 (d, J = 8.7 Hz, 2 H, Ar), 6.73 (d, J = 8.7 Hz, 2 H, 2 H, Ar), 7.12 (d, J = 8.7 Hz, 2 H, Ar), 7.21 (s, 8 H, Ar) ppm. **4db**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.19 (d, J = 7.5 Hz, 2 H, CH$_2$), 3.77 (s, 3 H, OCH$_3$), 3.81 (s, 3 H, OCH$_3$), 6.15 (t, J = 7.5 Hz, 1 H, =CH), 6.32 (s, 1 H, =CH) 6.54–7.21 (m, 16 H, Ar) ppm. **4dc**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.52 (d, J = 6.3 Hz, 2 H, CH$_2$), 3.73 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 6.00 (t, J = 6.3 Hz, 1 H, =CH) 6.54–7.21 (m, 17 H, Ar) ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3032, 3000, 2955, 2933, 2835, 2360, 2342, 1683, 1604, 1575, 1508, 1463, 1441, 1419, 1398, 1287, 1248, 1176, 1091, 1033, 1013, 830, 756, 738, 519 cm^{-1}. MS (%): m/z = 500 (100) [M]$^+$, 121 (62), 135 (17), 165 (21), 239 (36), 252 (21), 253 (22), 265 (54), 389 (49), 501 (38), 502 (73) 503 (25). HRMS (EI): calcd. for $C_{31}H_{26}O_2Cl_2$ 500.1309; found 500.1310.

4ea and 4ec: A colorless oil (16 mg, 32%); **4ea**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 2.65–2.69 (m, 2 H, CH$_2$), 2.74–2.79 (m, 2 H, CH$_2$), 3.68 (s, 3 H, OCH$_3$), 3.76 (s, 3 H, OCH$_3$), 3.78 (s, 6 H, 2 OCH$_3$), 6.52 (d, J = 8.7 Hz, 2 H, Ar), 6.65–6.78 (m, 8 H, Ar), 7.12 (d, J = 8.7 Hz, 2 H, Ar), 7.22 (d, J = 8.7 Hz, 2 H, Ar), 7.25 (d, J = 8.7 Hz, 2 H, Ar) ppm. **4ec**: ^{1}H NMR (CDCl$_3$, 300 MHz, TMS): δ = 3.54 (d, J = 6.6 Hz, 2 H, CH$_2$), 3.78 (s, 3 H, OCH$_3$), 3.79 (s, 3 H, OCH$_3$), 3.82 (s, 3 H, OCH$_3$), 3.83 (s, 3 H, OCH$_3$), 5.89 (t, J = 6.6 Hz, 1 H, =CH), 652–7.25 (m, 17 H, Ar) ppm. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 3033, 2997, 2953, 2928, 2835, 2359, 2342, 1605, 1575, 1507, 1463, 1441, 1289, 1248, 1178, 1112, 1036, 829, 802 cm^{-1}. MS (%): m/z = 492 (83) [M]$^+$, 121 (27), 227 (11), 253 (12), 371 (14), 384 (11), 385

(100), 386 (29), 493 (30). HRMS (EI): calcd. for $C_{33}H_{32}O_4$: 492.2300; found 492.2301.

4fa, 4fb and 4fc: A colorless oil (18 mg, 31%); **4fa**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.64–2.68 (m, 2 H, CH_2), 2.77–2.81 (m, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 6.54 (d, *J* = 8.7 Hz, 2 H, Ar), 6.64 (d, *J* = 8.7 Hz, 2 H, Ar), 6.72 (d, *J* = 8.7 Hz, 2 H, Ar), 7.11 (d, *J* = 8.7 Hz, 2 H, Ar), 7.15 (d, *J* = 8.7 Hz, 4 H, Ar), 7.35 (d, *J* = 8.7 Hz, 4 H, Ar) ppm. **4fb**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.18 (d, *J* = 6.6 Hz, 2 H, CH_2), 3.73 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 6.15 (t, *J* = 6.6 Hz, 1 H, =CH), 6.32 (s, 1 H, =CH), 6.54–7.35 (m, 16 H, Ar) ppm. **4fc**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.51 (d, *J* = 6.9 Hz, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.01 (t, *J* = 6.9 Hz, 1 H, =CH), 6.54–7.35 (m, 17 H, Ar) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 2953, 2927, 2835, 2360, 1653, 1604, 1570, 1558, 1507, 1487, 1458, 1439, 1289, 1248, 1177, 1076, 1034, 1008, 829, 796 cm^{-1}. MS (%): *m/z* = 588 (48) [M]$^+$, 121 (47), 265 (22), 433 (81), 434 (25), 435 (77), 436 (22), 589 (18), 590 (100), 591 (34), 592 (54), 593 (17). HRMS (EI): calcd. for $C_{31}H_{26}O_2Br_2$ 588.0302; found 588.0300.

4ha, 4hb and 4hc: A colorless oil (10 mg, 22%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.68–2.73 (m, 2 H, CH_2), 2.76–2.81 (m, 2 H, CH_2), 3.68 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 6.52 (d, *J* = 8.7 Hz, 2 H, Ar), 6.66 (d, *J* = 8.7 Hz, 2 H, Ar), 6.72 (d, *J* = 8.7 Hz, 2 H, Ar), 6.90 (t, *J* = 8.7 Hz, 2 H, Ar), 7.13 (d, *J* = 8.7 Hz, 2 H, Ar), 7.24–7.28 (m, 5 H, Ar) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 2999, 2954, 2836, 2538, 2358, 2048, 1888, 1683, 1662, 1602, 1574, 1506, 1463, 1443, 1289, 1248, 1177, 1161, 1033, 831, 812, 797, 765, 702, 576, 557, 539 cm^{-1}. MS (%): *m/z* = 450 (100) [M]$^+$, 121 (34), 343 (18), 355 (34), 373 (63), 374 (19), 451 (37). HRMS (EI): calcd. for $C_{31}H_{27}O_2F$: 450.1991; found 450.1995.

4ka and 4kb: A colorless oil (5 mg, 8%); **4ka**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.83–0.90 (m, 6 H, CH_3), 1.27–1.45 (m, 12 H, CH_2), 1.66–1.77 (m, 4 H, CH_2), 2.72–2.80 (m, 4 H, 2 CH_2), 3.79 (t, *J* = 6.6 Hz, 2 H, OCH_2), 3.90 (t, *J* = 6.6 Hz, 2 H, OCH_2), 6.49 (d, *J* = 8.7 Hz, 2 H, Ar), 6.65 (d, *J* = 8.7 Hz, 2 H, Ar), 6.71 (d, *J* = 8.7 Hz, 2 H, Ar), 7.10–7.23 (m, 8 H, Ar), 7.33 (d, *J* = 8.7 Hz, 4 H, Ar) ppm. **4kb**: ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.22 (d, *J* = 7.5 Hz, 2 H, CH_2), 6.19 (t, *J* = 7.5 Hz, 1 H, =CH), 6.35 (s, 1 H, =CH), 6.49–7.33 (m, 18 H, Ar) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3057, 2930, 2858, 2357, 2054, 1653, 1604, 1575, 1506, 1469, 1446, 1285, 1245, 1177, 1031, 830, 760, 701 cm^{-1}. MS (%): *m/z* = 572 (100) [M]$^+$, 43 (73), 107 (18), 495 (70), 496 (28), 573 (46), 574 (11). HRMS (EI): calcd. for $C_{41}H_{48}O_2$ 572.3652; found 572.3654.

4ab: A white solid (1 mg, 1%), m.p. 90–92 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.22 (d, *J* = 7.8 Hz, 2 H, CH_2), 3.71 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 6.18 (t, *J* = 7.8 Hz, 1 H, =CH), 6.35 (s, 1 H, =CH), 6.64 (d, *J* = 8.4 Hz, 2 H, Ar), 6.81 (d, *J* = 8.4 Hz, 2 H, Ar), 6.89 (d, *J* = 8.4 Hz, 2 H, Ar), 7.03 (d, *J* = 8.4 Hz, 2 H, Ar), 7.12–7.37 (m, 10 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 40.6, 55.06, 55.12, 113.2, 113.8, 125.8, 126.7, 126.96, 127.01, 127.3, 128.0, 128.1, 129.6, 129.8, 130.09, 130.14, 133.6, 139.6, 139.8, 142.6, 142.9, 157.8, 158.4 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3028, 2926, 2853, 2834, 1608, 1510, 1461, 1442, 1287, 1247, 1178, 1074, 1035, 900, 830, 805, 766, 745, 701, 600 cm^{-1}. MS (%): *m/z* = 432 (100) [M]$^+$, 121 (48), 433 (37), 311 (35), 265 (24), 165 (19), 310 (18), 91 (17). HRMS (EI): calcd. for $C_{31}H_{28}O_2$: 432.2091; found 432.2089.

4aB: A white solid (25 mg, 98%), m.p. 94–96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 3.73 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 4.06 (s, 2 H, CH_2), 6.72 (d, *J* = 11.4 Hz, 1 H, =CH), 6.74 (d, *J* = 8.7 Hz, 2 H, Ar), 6.81 (d, *J* = 8.7 Hz, 2 H, Ar), 7.09 (d, *J* = 11.4 Hz, 1 H, =CH), 7.17 (d, *J* = 8.7 Hz, 2 H, Ar), 7.23–7.44 (m, 12 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 34.9, 55.19, 55.21, 113.7, 113.9, 124.6, 125.2, 127.27, 127.32, 127.4, 127.7, 128.2, 129.0, 130.7, 131.8, 134.6, 139.5, 139.9, 142.8, 143.3, 157.9, 158.8 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3028, 2932, 2834, 1608, 1510, 1442, 1284, 1247, 1178, 1111, 1074, 1036, 898, 829, 804, 766, 746, 701, 600 cm^{-1}. MS (%): *m/z* = 432 (100) [M]$^+$, 121 (48), 433 (37), 311 (35), 265 (24), 165 (19), 310 (18), 91 (17). HRMS (EI): calcd. for $C_{31}H_{28}O_2$ 432.2091; found 432.2089.

5a: A white solid (98 mg, 68%), m.p. 244–246 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.39 (dd, *J* = 10.2, 16.2 Hz, 1 H, CH_2), 2.56 (dd, *J* = 7.8, 16.2 Hz, 1 H, CH_2), 3.21 (d, *J* = 10.5 Hz, 1 H, CH), 3.63 (s, 3 H, OCH_3), 3.67 (s, 3 H, OCH_3), 3.72 (s, 9 H, 3 OCH_3), 3.87 (s, 3 H, OCH_3), 4.23–4.32 (m, 1 H, CH), 6.41 (d, *J* = 8.7 Hz, 2 H, Ar), 6.44 (d, *J* = 8.7 Hz, 2 H, Ar), 6.52 (d, *J* = 8.7 Hz, 2 H, Ar), 6.57 (d, *J* = 8.7 Hz, 2 H, Ar), 6.65 (d, *J* = 8.7 Hz, 2 H, Ar), 6.68 (d, *J* = 8.7 Hz, 2 H, Ar), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar), 6.91 (d, *J* = 8.7 Hz, 2 H, Ar), 6.97 (d, *J* = 8.7 Hz, 2 H, Ar), 7.00 (d, *J* = 8.7 Hz, 2 H, Ar), 7.12 (d, *J* = 8.7 Hz, 2 H, Ar), 7.17 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 41.6, 52.1, 53.0, 54.8, 55.0, 55.1, 55.2, 68.1, 112.0, 112.5, 112.7, 112.8, 113.1, 113.6, 128.7, 129.5, 129.6, 129.8, 130.1, 130.7, 131.1, 131.3, 132.1, 135.9, 136.6, 136.8, 138.3, 143.9, 157.1, 157.2, 157.4, 157.6, 158.0, 158.2 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3033, 3000, 2933, 2905, 2834, 2532, 2054, 1890, 1606, 1581, 1514, 1461, 1441, 1419, 1336, 1290, 1254, 1177, 1115, 1035, 831, 788, 773, 738, 704, 684, 653, 642, 632, 617, 599, 584, 566, 543, 517 cm^{-1}. MS (%): *m/z* = 718 (2) [M]$^+$, 227 (100), 478 (37), 357 (29), 121 (26), 240 (18), 228 (18), 491 (16), 238 (15). $C_{48}H_{46}O_6$ (718.89): calcd. C 80.20, H 6.45; found C 80.25, H 6.61. HRMS (EI): calcd. for $C_{48}H_{46}O_6$ 718.3294; found 718.3306.

5b: A white solid (77 mg, 50%), m.p. 197–199 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.26–1.36 (m, 12 H, 4 CH_3), 2.38 (dd, *J* = 10.5, 15.9 Hz, 1 H, CH_2), 2.56 (dd, *J* = 7.5, 15.9 Hz, 1 H, CH_2), 3.19 (d, *J* = 10.5 Hz, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.78–3.98 (m, 11 H, CH_2 and OCH_3), 4.22–4.32 (m, 1 H, CH), 6.40 (d, *J* = 9.3 Hz, 2 H, Ar), 6.44 (d, *J* = 9.3 Hz, 2 H, Ar), 6.50–6.73 (m, 8 H, Ar), 6.81–7.00 (m, 8 H, Ar), 7.12 (d, *J* = 8.7 Hz, 2 H, Ar), 7.18 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.76, 14.84, 41.6, 52.2, 53.1, 55.1, 55.2, 62.9, 63.1, 63.2, 68.1, 112.0, 112.5, 113.2, 113.4, 113.7, 113.9, 114.1, 128.7, 129.5, 129.9, 130.0, 130.7, 131.1, 131.3, 132.1, 135.8, 136.6, 136.8, 138.2, 143.9, 156.6, 156.8, 157.0, 157.1, 157.5, 158.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3035, 2979, 2932, 2904, 2835, 1606, 1581, 1509, 1478, 1463, 1442, 1392, 1298, 1251, 1178, 1116, 1045, 923, 828, 808, 739, 611, 549, 518 cm^{-1}. MS (%): *m/z* = 774 (18) [M]$^+$, 506 (100), 255 (75), 519 (47), 227 (35), 268 (20), 371 (18). $C_{52}H_{54}O_6$ (775.00): calcd. C 80.59, H 7.02; found C 80.57, H 7.28. HRMS (EI): calcd. for $C_{52}H_{54}O_6$ 774.3929; found 774.3920.

5c: A colorless oil (102 mg, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 0.86–0.90 (m, 12 H, CH_3), 1.27–1.38 (m, 24 H, CH_2), 1.57–1.75 (m, 8 H, CH_2), 2.38 (dd, *J* = 7.8, 15.9 Hz, 1 H, CH_2), 2.57 (dd, *J* = 7.5, 15.9 Hz, 1 H, CH_2), 3.20 (d, *J* = 10.8 Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.74–3.98 (m, 11 H, CH_2 and CH_3), 4.20–4.32 (m, 1 H, CH), 6.40 (d, *J* = 9.3 Hz, 2 H, Ar), 6.43 (d, *J* = 9.3 Hz, 2 H, Ar), 6.50–6.72 (m, 8 H, Ar), 6.77–7.00 (m, 8 H, Ar), 7.12 (d, *J* = 9.3 Hz, 2 H, Ar), 7.19 (d, *J* = 9.3 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 14.0, 22.6, 25.65, 25.70, 29.2, 29.3, 31.5, 41.6, 52.1, 53.1, 55.1, 55.2, 67.5, 67.7, 68.1, 112.0, 112.5, 113.3, 113.4, 113.7, 113.8, 113.9, 114.1, 128.7, 129.4, 129.5, 129.8, 129.9, 130.7, 131.1, 131.4, 132.0, 132.1, 135.8, 136.7, 136.8, 138.2, 143.8, 156.8, 157.0, 157.1, 157.2, 157.7, 158.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3035, 2931, 2859, 1606, 1581, 1509, 1468, 1390, 1285, 1244, 1178, 1114, 1036, 938, 830, 787, 728, 614, 552 cm^{-1}. ESI-MS (%): m/z = 1021 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{68}H_{86}O_6$ 1021.6324; found 1021.6317.

5d: A white solid (90 mg, 53%), m.p. 182–184 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 2.39 (dd, J = 10.8, 16.2 Hz, 1 H, CH_2), 2.56 (dd, J = 7.2, 16.2 Hz, 1 H, CH_2), 3.20 (d, J = 10.5 Hz, 1 H, CH), 3.70 (s, 3 H, OCH_3), 3.85 (s, 3 H, OCH_3), 4.22–4.51 (m, 9 H, CH_2 and CH), 5.17–5.38 (m, 8 H, =CH_2), 5.88–6.06 (m, 4 H, =CH), 6.43 (s, 3 H, Ar), 6.54 (d, J = 8.4 Hz, 2 H, Ar), 6.56 (d, J = 8.4 Hz, 2 H, Ar), 6.65 (d, J = 8.4 Hz, 2 H, Ar), 6.70 (d, J = 8.4 Hz, 2 H, Ar), 6.82–7.01 (m, 9 H, Ar), 7.12 (d, J = 8.4 Hz, 2 H, Ar), 7.17 (d, J = 8.4 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, TMS): δ = 41.5, 52.1, 53.0, 55.0, 55.2, 68.1, 68.3, 68.5, 68.7, 112.0, 112.5, 113.5, 113.6, 113.9, 114.3, 117.4, 117.5, 117.6, 128.7, 129.5, 129.7, 129.9, 130.2, 130.7, 131.0, 131.2, 132.1, 133.1, 133.2, 133.3, 133.4, 136.0, 136.5, 136.7, 138.4, 143.9, 156.3, 156.5, 156.7, 157.1, 157.2, 158.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3034, 2995, 2932, 2835, 2533, 2051, 1884, 1648, 1606, 1581, 1508, 1461, 1442, 1424, 1361, 1294, 1247, 1179, 1115, 1032, 997, 926, 830, 787, 740, 623, 568, 546 cm^{-1}. $C_{56}H_{54}O_6$ (823.04): calcd. C 81.72, H 6.61; found C 81.47, H 6.66. ESI-MS (%): m/z = 822 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{55}H_{54}O_6Na^+$ 845.3801; found 845.3813.

5e: A white solid (95 mg, 57%), m.p. 188–190 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ = 2.39 (dd, J = 10.4, 16.0 Hz, 1 H, CH_2), 2.43–2.49 (m, 4 H, CH), 2.56 (dd, J = 7.6, 16.0 Hz, 1 H, CH_2), 3.22 (d, J = 10.4 Hz, 1 H, CH), 3.71 (s, 3 H, OCH_3), 3.87 (s, 3 H, OCH_3), 4.24–4.31 (m, 1 H, CH), 4.49 (d, J = 2.8 Hz, 2 H, CH_2), 4.54 (d, J = 2.8 Hz, 2 H, CH_2), 4.59 (d J = 2.8 Hz, 2 H, CH_2), 4.60 (d, J = 2.8 Hz, 2 H, CH_2), 6.43–6.50 (m, 4 H, Ar), 6.56 (d, J = 8.8 Hz, 2 H, Ar), 6.59 (d, J = 8.8 Hz, 2 H, Ar), 6.72 (d, J = 8.8 Hz, 2 H, Ar), 6.76 (d, J = 8.8 Hz, 2 H, Ar), 6.83 (d, J = 8.8 Hz, 2 H, Ar), 6.92 (d, J = 8.8 Hz, 2 H, Ar), 6.98 (d, J = 8.8 Hz, 2 H, Ar), 7.01 (d, J = 8.8 Hz, 2 H, Ar), 7.09 (d, J = 8.8 Hz, 2 H, Ar), 7.15 (d, J = 8.8 Hz, 2 H, Ar) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ = 41.6, 52.1, 53.1, 55.1, 55.2, 55.6, 55.7, 55.8, 58.4, 68.2, 75.2, 75.30, 75.33, 75.5, 78.5, 78.60, 78.67, 78.72, 112.1, 112.6, 113.8, 113.9, 114.2, 114.6, 128.8, 129.5, 129.9, 130.4, 130.7, 130.9, 131.06, 131.11, 132.1, 136.3, 136.6, 136.8, 139.0, 144.1, 155.4, 155.6, 155.9, 156.2, 157.2, 158.1 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3291, 3036, 2999, 2931, 2864, 2836, 2121, 2048, 1888, 1605, 1584, 1510, 1455, 1418, 1373, 1216, 1178, 1115, 1075, 1028, 925, 832, 739, 680, 643, 586, 543 cm^{-1}. $3(C_{56}H_{46}O_6)\cdot CH_2Cl_2$ (2526.9417): calcd. C 80.24, H 5.58; found C 80.14, H 5.70. ESI-MS (%): m/z = 837 [M + Na]$^+$. HRMS (ESI): calcd. for $C_{56}H_{46}O_6Na^+$ 837.3168; found 837.3187.

Supporting Information (see also the footnote on the first page of this article): The spectroscopic data (^{1}H and ^{13}C spectroscopic data), HRMS of the compounds shown in Tables 1–5 and Schemes 1–5, the X-ray crystal structures of **3a**, **4aB**, **5a** and **5b** along with the detailed description of experimental procedures are included in the Supporting Information.

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[1] For recent reviews, see: a) I. Nakamura, Y. Yamamoto, *Adv. Synth. Catal.* **2002**, *344*, 111–129; b) A. Brandi, S. Cicchi, F. M. Cordero, A. Goti, *Chem. Rev.* **2003**, *103*, 1213–1270; c) E. Nakamura, S. Yamago, *Acc. Chem. Res.* **2002**, *35*, 867–877; d) For the synthesis of MCPs, see: A. Brandi, A. Goti, *Chem. Rev.* **1998**, *98*, 589–636.

[2] Selected recent articles about transition-metal-catalyzed reactions of MCPs: a) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *J. Org. Chem.* **2001**, *66*, 270–275; b) M. Lautens, C. Meyer, A. Lorenz, *J. Am. Chem. Soc.* **1996**, *118*, 10676–10677; c) M. Lautens, Y. Ren, *J. Am. Chem. Soc.* **1996**, *118*, 9597–9605; d) S. Saito, M. Masuda, S. Komagawa, *J. Am. Chem. Soc.* **2004**, *126*, 10540–10541; e) M. Shi, B.-Y. Wang, J.-W. Huang, *J. Org. Chem.* **2005**, *70*, 5606–5610; f) I. Nakamura, H. Itagaki, Y. Yamamoto, *J. Org. Chem.* **1998**, *63*, 6458–6459; g) N. Tsukada, A. Hibuya, I. Nakamura, Y. Yamamoto, *J. Am. Chem. Soc.* **1997**, *119*, 8123–8124; h) M. Suginome, T. Matsuda, Y. Ito, *J. Am. Chem. Soc.* **2000**, *122*, 11015–11016; i) M. E. Scott, Y. Bethuel, M. Lautens, *J. Am. Chem. Soc.* **2007**, *129*, 1482–1483.

[3] Selected recent articles about Lewis-acid-mediated reactions of MCPs: a) M. Shi, B. Xu, *Org. Lett.* **2002**, *4*, 2145–2148; b) B. Xu, M. Shi, *Org. Lett.* **2003**, *5*, 1415–1418; c) X. Huang, H.-W. Zhou, *Org. Lett.* **2002**, *4*, 4419–4422; d) J.-W. Huang, M. Shi, *Tetrahedron Lett.* **2003**, *44*, 9343–9347; e) L.-F. Yao, M. Shi, *Org. Lett.* **2007**, *9*, 5187–5190 and references cited herein.

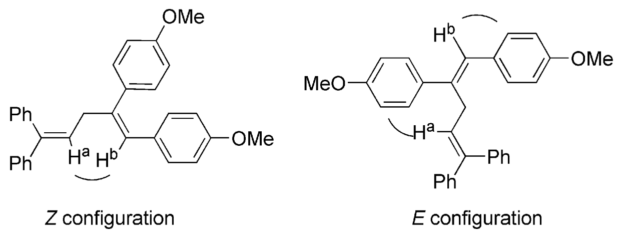
[4] a) D. H. Camacho, I. Nakamura, S. Saito, Y. Yamamoto, *Angew. Chem. Int. Ed.* **1999**, *38*, 3365–3367; b) I. Nakamura, B. H. Oh, S. Saito, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2001**, *40*, 1298–1300; c) B. H. Oh, I. Nakamura, S. Saito, Y. Yamamoto, *Tetrahedron Lett.* **2001**, *42*, 6203–6205; d) B. H. Oh, I. Nakamura, S. Saito, Y. Yamamoto, *Heterocycles* **2003**, *61*, 247–257; e) S. Braese, A. de Meijere, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2545–2547; f) I. Nakamura, T. Nemoto, Y. Yamamoto, A. de Meijere, *Angew. Chem. Int. Ed.* **2006**, *45*, 5176–5179.

[5] a) M. Shi, B. Xu, J.-W. Huang, *Org. Lett.* **2004**, *6*, 1175–1178; b) M. Shi, L.-X. Shao, B. Xu, *Org. Lett.* **2003**, *5*, 579–582; c) L.-X. Shao, B. Xu, J.-W. Huang, M. Shi, *Chem. Eur. J.* **2006**, *12*, 510–517; d) J.-W. Huang, M. Shi, *Synlett* **2004**, 2343–2346; e) L. Patient, M. B. Berry, J. D. Kilburn, *Tetrahedron Lett.* **2003**, *44*, 1015–1017.

[6] a) S.-M. Ma, J.-L. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 12386–12387; b) M. Lautens, W. Han, *J. Am. Chem. Soc.* **2002**, *124*, 6312–6316; c) M. Lautens, W. Han, J. H.-C. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 4028–4029; d) M. E. Scott, W. Han, M. Lautens, *Org. Lett.* **2004**, *6*, 3309–3312; e) M. E. Scott, M. Lautens, *Org. Lett.* **2005**, *7*, 3045–3047. Ring enlargement of MCPs; f) M. Shi, L. P. Liu, J. Tang, *J. Am. Chem. Soc.* **2006**, *128*, 7430–7431; g) A. Furstner, C. Aissa, *J. Am. Chem. Soc.* **2006**, *128*, 6306–6307.

[7] a) L. P. Liu, M. Shi, *J. Org. Chem.* **2004**, *69*, 2805–2808; b) L. F. Yao, M. Shi, *Org. Lett.* **2007**, *9*, 5187–5189; c) M. Shi, M. Jiang, L.-P. Liu, *Org. Biomol. Chem.* **2007**, *5*, 438–440.

[8] Compound **4ab** was determined to be (E)-configured based on the following two reasons: 1) no interaction between H^a and H^b was detected from the NOE spectroscopy and 2) the interactions between H^a and the aromatic ring and between H^b and the aromatic ring could be recognized by NOE spectroscopy.



Z configuration

E configuration

[9] CCDC-675136 (for **3a**), -712669 (for **4aB**), -684691 (for **5a**), -720536 (for **5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[10] a) A. W. Schrecker, L. Y. Greenberg, L. L. Hartwell, *J. Am. Chem. Soc.* **1952**, *74*, 5669–5671; b) E. L. Jackson, L. Pastiut, *J. Am. Chem. Soc.* **1928**, *50*, 2249–2260; c) D. J. Cram, *J. Am. Chem. Soc.* **1949**, *71*, 3863–3870; d) D. J. Cram, *J. Am. Chem. Soc.* **1952**, *74*, 2129–2137.

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