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$BF_3 \cdot OEt_2$-catalyzed intermolecular reactions of arylmethylenecyclopropanes with (*E*)-1,1,3-triarylprop-2-en-1-ols

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ABSTRACT

$BF_3 \cdot OEt_2$-catalyzed intermolecular reactions of arylmethylenecyclopropanes with (*E*)-1,1,3-triarylprop-2-en-1-ols produced the corresponding triene compounds, alcoholic derivatives or cyclobutane derivatives in moderate to excellent yields under mild conditions.

1. Introduction

Methylenecyclopropanes (MCPs) are highly strained but readily accessible molecules that have been serving as useful building blocks in organic synthesis for a long time.[1] For example, in the presence of transition metals or Lewis acids, MCPs can undergo a variety of ring-opening/cycloaddition reactions because the relief of ring strain provides a powerful thermodynamic driving force.[2,3] Thus far, a number of interesting cycloadditions and ring enlargements/openings of MCPs have been explored. For example, Yamamoto et al. reported cycloaddition reactions of MCPs with aldehydes and imines, using a palladium catalyst, that afforded the corresponding tetrahydrofuran and pyrrolidine skeletons in good yields.[4] In addition, we and others have developed a number of heterocycle-forming reactions from MCPs and aldehydes or imines as well as ring enlargements of MCPs in the presence of Lewis or Brønsted acids.[5,6] In our previous work, we have recently reported Lewis acid-catalyzed cascade reactions of MCPs as well as vinylidenecyclopropanes (VDCPs) with 1,1,3-triarylprop-2-yn-1-ols or their methyl ethers or 1,6-diynes and 1,6-enynes to produce functionalized methylenecyclobutene, cyclobutane, and cyclopropane derivatives or 4-dihydro-1*H*-cyclopenta[*b*]naphthalene derivatives and 1,2,3,8-tetrahydrocyclopenta[*a*]indene derivatives, respectively, in good to high yields depending on the substituents on the cyclopropane under mild conditions.[7] On the basis of the above results, herein, we wish to report a new intermolecular reaction of MCPs **1** with (*E*)-1,1,3-triarylprop-2-en-1-ols **2** catalyzed by Lewis acids to produce a variety of different products depending on the electronic nature of the substrates in good to excellent total yields under mild conditions.

2. Results and discussion

Initial examinations using diphenylmethylenecyclopropane (**1a**, 0.2 mmol) and (*E*)-1,1,3-triphenylprop-2-en-1-ol (**2a**, 0.2 mmol) as the substrates in the presence of various Lewis acids (10 mol %) were aimed at determining the best reaction conditions for this interesting intermolecular reaction and the results of these experiments are summarized in Table 1. We found that in the presence of $BF_3 \cdot OEt_2$ (10 mol %), this intermolecular reaction could complete with 5 min at room temperature in dichloromethane (DCM), giving the triene compound **3aa** in nearly quantitative yield as cis- and trans-isomeric mixtures because of the position of the two phenyl rings on the newly-formed double bond (Table 1, entry 1). Either no reaction occurred or complex product mixtures were obtained when other Lewis acids, such as $Yb(OTf)_3$, $Fe(OTf)_2$, $In(OTf)_3$, and $Zr(OTf)_4$ were utilized as the catalysts (Table 1, entries 2–5). Even in the presence of a Brønsted acid, such as trifluoromethanesulfonic acid CF_3SO_3H (TfOH) (50 mol %), **3aa** could also be produced in 97% yield (Table 1, entry 6). Solvent effects have been examined with BF3·OEt2 (10 mol %) at room temperature in 1,2-dichloroethane

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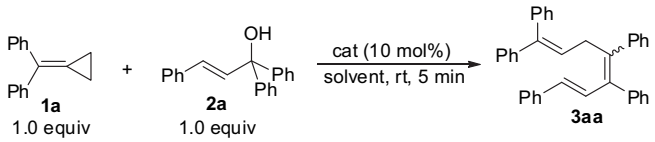
Table 1
Optimization of the reaction conditions[a]

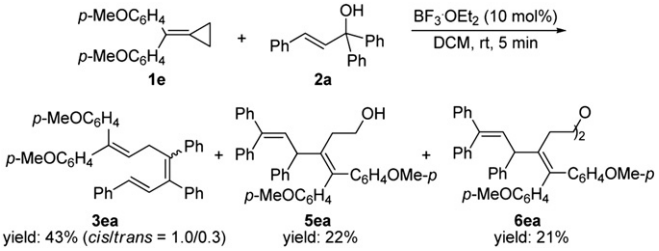


Entry	Cat (10 mol %)	Solvent	Yield[b] (%) (cis/trans)[c]
1	$BF_3{\cdot}OEt_2$	DCM	97 (1.0/0.5)
2	$Yb(OTf)_3$	DCM	nr
3	$In(OTf)_3$	DCM	Complex mixtures
4	$Zr(OTf)_4$	DCM	Complex mixtures
5	$Fe(OTf)_2{\cdot}2CH_3CN$	DCM	nr
6	HOTf (50 mo l%)	DCM	90 (1.0/0.5)
7	$BF_3{\cdot}OEt_2$	DCE	94 (1.0/0.5)
8	$BF_3{\cdot}OEt_2$	THF	Complex mixtures
9	$BF_3{\cdot}OEt_2$	Toluene	87 (1.0/0.5)

[a] All reactions were conducted with MCP **1a** (0.2 mmol, 1.0 equiv), (*E*)-1,1,3-triphenylprop-2-en-1-o1 **2a** (0.2 mmol, 1.0 equiv), and the catalyst (10 mol %) in the solvent (2.0 mL) at room temperature within 5 min otherwise specified.
[b] Isolated yield.
[c] Ratio of cis, trans-isomers determined by ^{1}H NMR spectroscopic data.

(DCE), tetrahydrofuran (THF), and toluene. It was found that in THF, complex product mixtures were formed and in DCE and toluene, the desired product **3aa** could also be obtained in good yields (Table 1, entries 7–9). Therefore, the optimized reaction conditions are considered to carry out the reaction in DCE or DCM using MCPs **1** (1.0 equiv) and (*E*)-1,1,3-triarylprop-2-en-1-ols **2** (1.0 equiv) as the substrates in the presence of $BF_3{\cdot}OEt_2$ (10 mol %) at room temperature.

Under these optimal reaction conditions, we next examined the generality of this interesting triene compound-forming reaction using a variety of starting materials MCPs **1** and (*E*)-1,1,3-triarylprop-2-en-1-ols **2** as the substrates and the results are shown in Table 2. As can be seen from Table 2, the corresponding triene compounds **3** were obtained in good to excellent yields in most cases. Using MCP **1a** as the substrate, the electronic nature of the aromatic rings in (*E*)-1,1,3-triarylprop-2-en-1-ols **2** has little influence on the reaction outcomes (Table 2, entries 1–4). However, the substituents on the aromatic rings of MCPs have significant effect on the reaction outcomes. As for MCPs **1b** and **1c** bearing electron-withdrawing substituents, such as Cl atom and Br atom on the aromatic rings, the corresponding triene products **3ba** and **3ca** were produced in good yields along with the formation of alcoholic compounds **4ba** and **4ca** in moderate yields (Table 2, entries 5 and 6). As for MCP **1d** bearing moderately electron-donating substituents Me group on the aromatic rings, the corresponding triene compound **3da** was also obtained in nearly quantitative yield (Table 2, entry 7). On the basis of ^{1}H NMR NOESY spectroscopic data, the major isomeric product in **3da** was identified as *cis*-configuration with the two Ar^3 rings at the same side of the double bond (See the Supplementary data for more details). But in the case of MCP **1e** having strongly electron-donating substituents MeO group on the aromatic rings, besides the triene compound **3ea** another type of alcoholic product **5ea** and its dimeric ether **6ea** were also obtained in excellent total yield under the standard conditions (Scheme 1).

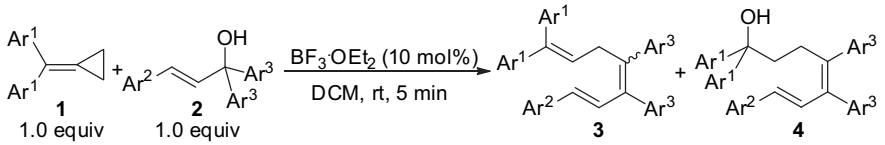


Scheme 1. $BF_3{\cdot}OEt_2$-catalyzed intermolecular reaction of **1e** with **2a**.

Furthermore, the structure of compound **5ea** was unambiguously determined by X-ray diffraction of its single-crystals. The ORTEP drawing of **5ea** is shown in Fig. 1 and its CIF data are presented in the Supplementary data.[8]

Moreover, we also examined the reactions of other MCPs having one methyl group and one aromatic ring with (*E*)-1,1,3-triarylprop-2-en-1-ols under the standard conditions and the results of these experiments are summarized in Table 3. As for MCP **1f** in which Ar^1 is a phenyl group, methylenecyclobutane **7fa** was formed in 78% yield along with the formation of **8fa** in 14% yield (Table 3, entry 1). Using MCP **1g** having an electron-withdrawing substituent Br atom on the aromatic ring as substrate afforded the major product **7ga** in 62% yield

Table 2
$BF_3{\cdot}OEt_2$-catalyzed intermolecular reactions of MCPs **1** with (*E*)-1,1,3-triarylprop-2-en-1-ols **2** under the optimal reaction conditions[a]



Entry	Ar^1		Ar^2		Ar^3	Yield of product[b] (%)	
						3 (cis/trans)[c]	**4**
1	**1a**	Ph	**2b**	p-MeC_6H_4	Ph	**3ab**, 90 (1 .0/0.5)	
2	**1a**	Ph	**2c**	p-ClC_6H_4	Ph	**3ac**, 85 (1.0/0.5)	
3	**1a**	Ph	**2d**	Ph	p-MeC_6H_4	**3ad**, 96 (1 .0/0.4)	
4	**1a**	Ph	**2e**	Ph	p-BrC_6H_4	**3ae**, 92 (1.0/0.6)	
5	**1b**	p-ClC_6H_4	**2a**	Ph	Ph	**3ba**, 63 (1.0/0.6)	**4ba**, 32
6	**1c**	p-BrC_6H_4	**2a**	Ph	Ph	**3ca**, 68 (1.0/0.5)	**4ca**, 29
7	**1d**	p-MeC_6H_4	**2a**	Ph	Ph	**3da**, 98 (1.0/0.5)	

[a] All reactions were conducted with MCP1 (0.2 mmol, 1.0 equiv), (*E*)-1,1,3-triarylprop-2-en-1-ol **2** (0.2 mmol, 1.0 equiv), and $BF_3{\cdot}OEt_2$(10 mol %) in DCM (2.0 mL) at room temperature within 5 min otherwise specified.
[b] Isolated yield.
[c] Ratios of cis, trans-isomers were determined by ^{1}H NMR spectroscopic data.

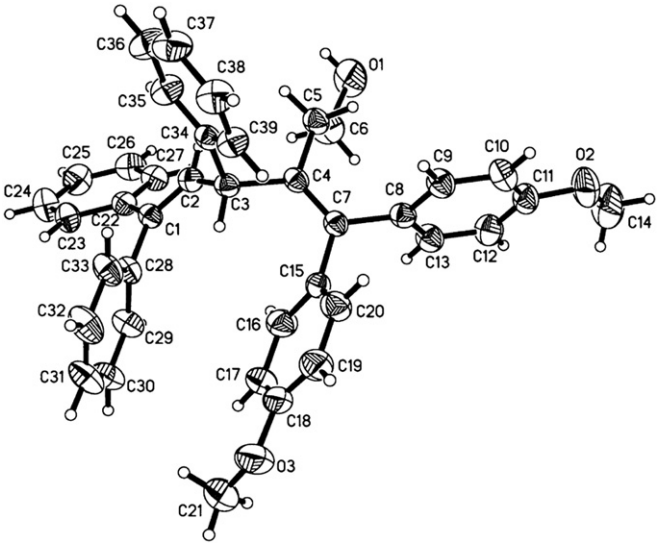
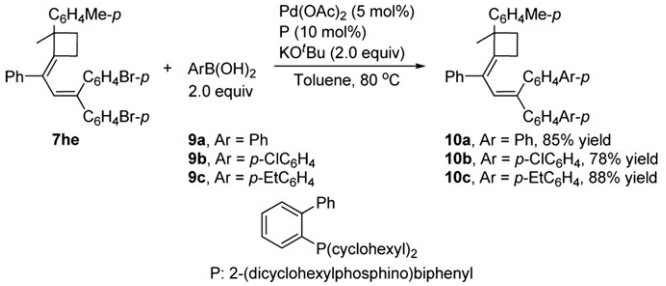
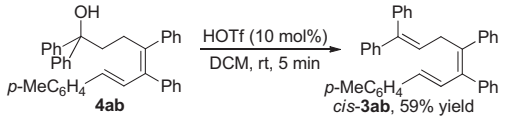


Fig. 1. ORTEP drawing of **5ea**.



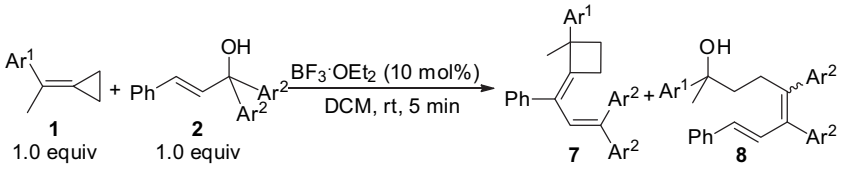
Scheme 2. Transformation of **7he** to **10** via Suzuki coupling reaction.

To investigate the reaction mechanism, a control experiment as shown in Scheme 3 was conducted. With the addition of HOTf (10 mol %), product **4ab** could be transformed to the major isomer *cis*-**3ab** in DCM in 59% yield, suggesting that triene compounds **3** might be derived from the corresponding alcohol products **4** with the elimination of H_2O during the reaction process.



Scheme 3. HOTf-Mediated transformation of **4ab** to *cis*-**3ab**.

Table 3
$BF_3 \cdot OEt_2$-catalyzed intermolecular reactions of MCPs **1** with (*E*)-1,1,3-triarylprop-2-en-1-ols **2** under the optimal reaction conditions[a]



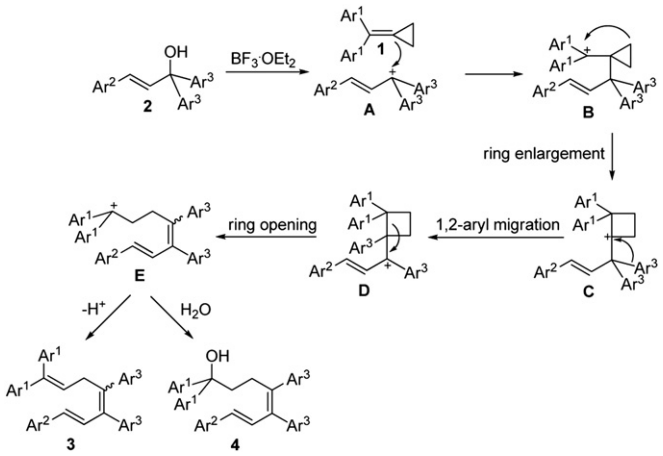
Entry	**1**, Ar^1	**2**, Ar^2	Yield of the product[b] (%)	
			7	**8** (cis/trans)[c]
1	**1f**, Ph	**2a**, Ph	**7fa**, 78	**8fa**, 14 (2.8:1.0)
2	**1g**, *p*-BrC_6H_4	**2a**, Ph	**7ga**, 62	**8ga**, 35 (4.6:1.0)
3	**1h**, *p*-MeC_6H_4	**2a**, Ph	**7ha**, 86	—
4	**1h**, *p*-MeC_6H_4	**2e**, *p*-BrC_6H_4	**7he**, 90	—

[a] All reactions were conducted with MCPs **1** (0.2 mmol, 1.0 equiv), (*E*)-1,1,3-triarylprop-2-en-1-ols **2** (0.2 m mol, 1.0 equiv), and $BF_3 \cdot OEt_2$ (10 mol %) in DCM (2.0 mL) at room temperature within 5 min otherwise specified.
[b] Isolated yield.
[c] Ratio of cis, trans-isomers was determined by ^1H NMR spectroscopic data.

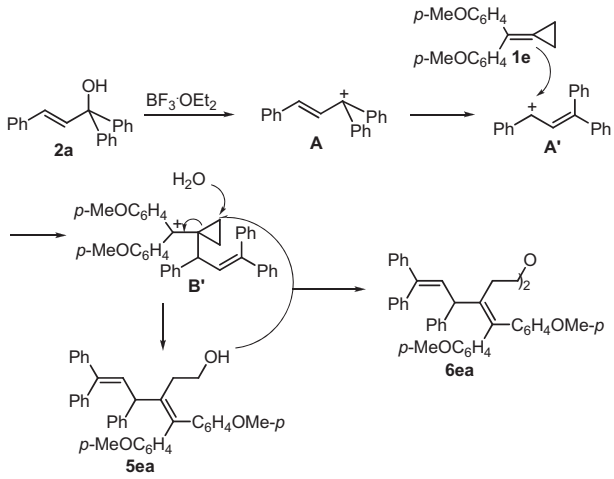
along with the minor product **8ga** in 35% yield (Table 3, entry 2). But under the standard reaction conditions, using MCP **1h** bearing an electron-rich aromatic ring as substrate mainly gave the corresponding methylenecyclobutane **7ha** in 86% yield (Table 3, entry 3). Even in the reaction of MCP **1h** with electron-deficient (*E*)-1,1,3-triarylprop-2-en-1-ol **2e**, the corresponding methylenecyclobutane product **7he** was exclusively obtained in 90% yield, further suggesting that the electronic property of MCPs can significantly affect the reaction outcome in this reaction (Table 3, entry 4). The structure of methylenecyclobutane **7** and its *Z*-configuration of the double bond were determined by the 2-D NMR spectroscopic data (HMQC, HMBC, DEPT, and NOESY spectra) of compound **7he** (see the Supplementary data for the details).

In addition, compound **7he** could also be transformed to the corresponding biaryl compounds **10** via Suzuki coupling reaction with various arylboronic acids **9** in good yields using 2-(dicyclohexylphosphino)biphenyl (P) (10 mol %) as a ligand and $Pd(OAc)_2$ (5 mol %) as a catalyst in the presence of KO^tBu in toluene at 80 °C (Scheme 2).

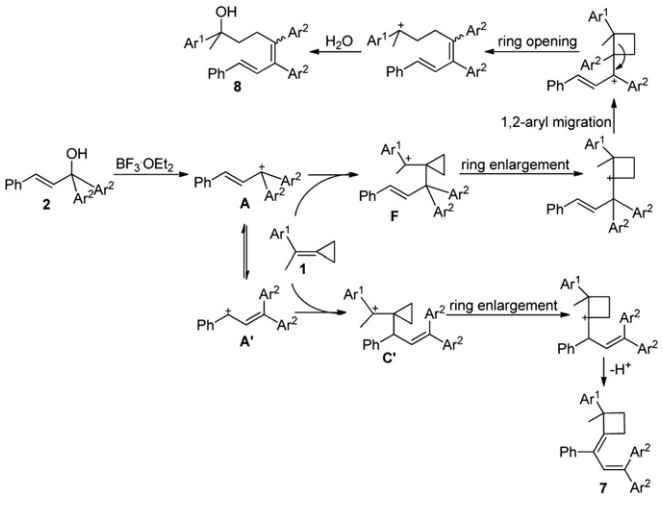
On the basis of the above results, plausible reaction mechanisms for the formation of the products **3**, **4**, **5**, **6**, **7**, and **8** are outlined in Schemes 4–6, respectively. All of the reactions are initiated by the cationic intermediate **A** derived from **2** in the presence of $BF_3 \cdot OEt_2$. As can be seen in Scheme 4, intermediate **A** reacts with MCP **1** to afford intermediate **B**, which is stabilized by two aromatic rings and one cyclopropane group,[9] giving intermediate **C** via a ring enlargement process. The subsequent 1,2-aryl migration of intermediate **C** furnishes a more stable cationic intermediate **D**, which is followed by a ring opening process to produce intermediate **E**. Elimination of a proton from intermediate **E** gives triene product **3** and the reaction of intermediate **E** with H_2O affords product **4**. As can be seen from the control experiment presented in Scheme 3, product **4** could be transformed to the corresponding triene compound **3** by elimination of H_2O. We assumed that the corresponding intermediate **E** exists as a mixture of cis- and trans-isomers and the cis-isomer may be liable to be attacked by H_2O, giving *cis*-product **4** exclusively.



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



Scheme 5. A plausible mechanism for the formation **5ae** and **6ae**.



Scheme 6. A plausible mechanism for the formation **7** and **8**.

As for the formation of **5ea** and **6ea** in the reaction of MCP **1e** with **2a**, a plausible mechanism is proposed in Scheme 5. Similarly, the reaction is initiated by the formation of cationic intermediate **A**, which tautomerizes to a less hindered cationic intermediate **A′** via an allylic rearrangement. The reaction of intermediate **A′** with **1e** affords intermediate **B′**, which is then attacked by H_2O along with the cyclopropane ring opening process to furnish the corresponding product **5ea**. At the same time, intermediate **B′** can also be attacked by product **5ea** to give the corresponding dimeric ether product **6ea**. In this case, the strongly electron-rich aromatic ring in MCP **1e** can significantly stabilize the sterically less hindered cationic intermediate **B′**, which can subsequently produce different products **5ea** and **6ea** through the reaction with H_2O and **5ea**, respectively rather than the ring enlargement as that mentioned in Scheme 4.

As shown in Scheme 6, we can also see that the initial intermediate **A** reacts with MCP **1** to afford intermediate **F**, which undergoes the similar cascade processes of ring enlargement, 1,2-aryl migration and ring opening, and then reacts with H_2O to give the corresponding product **8**. However, when the resonance-stabilized intermediate **A′** reacts with MCP **1**, product **7** is formed through a ring enlargement and a direct proton elimination pathway from intermediate **C′**.

As can be seen from the above reaction mechanisms, the electronic property of the substrates on MCPs **1** mainly dominated the reaction pathway to afford different kinds of products. The driving force of each different reaction process is the generation of the corresponding more stabilized cationic intermediates.

3. Conclusion

In conclusion, we have disclosed a $BF_3{\cdot}OEt_2$-catalyzed intermolecular reaction of MCPs with (*E*)-1,1,3-triarylprop-2-en-1-ols to afford a variety of different products effected by the electronic property of the substituents on MCPs in excellent total yields under mild conditions. The corresponding triene compounds, alcoholic derivatives or cyclobutane derivatives were obtained in moderate to good yields and the plausible reaction mechanisms for the formation of the corresponding products have been proposed based on the control experiment and previous literature. Efforts are underway to further elucidate the reaction mechanism and to understand the scope and limitations of this interesting process.

4. Experimental section

4.1. General remarks

Melting points are uncorrected. ^1H and ^{13}C NMR were recorded at 400 and 100 MHz, respectively. Mass spectra were recorded by EI or MALDI and HRMS was measured by EI or MALDI method. Organic solvents used were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC. Flash column chromatography was carried out using 300–400 mesh silica gel under increased pressure.

4.2. General procedure

Under an argon atmosphere, MCP **1** (0.20 mmol), (*E*)-1,1,3-triarylprop-2-en-1-ol **2** (0.20 mmol, 1.0 equiv), and DCM (2.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at room temperature (20 °C), and then $BF_3{\cdot}OEt_2$ (10 mol %) was added. The reaction completed after 5 min monitored by TLC. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography to give the desired product **3**–**8**.

Under an argon atmosphere, Compound **7he** (0.20 mmol), arylboronic acid **9** (0.40 mmol, 2.0 equiv) $Pd(OAc)_2$ (5 mol %), 2-(dicyclohexylphosphino)biphenyl (10 mol %), KO^{t}Bu (0.40 mmol, 2.0 equiv), and toluene (5.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 80 °C monitored by TLC. The solvent was removed under reduced pressure and the residue was

purified by a flash column chromatography to give the desired product **10**.

*4.2.1. Product **3aa** (1.0:0.5 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.19 (*trans*-, d, J=7.6 Hz, 1H, CH_2), 3.61 (*cis*-, d, J=7.6 Hz, 2H, CH_2), 5.97 (*trans*-, t, J=7.6 Hz, 0.5H, CH), 6.07 (*cis*-, t, J=7.6 Hz, 1H, CH), 6.28 (*trans*-, d, J=11.6 Hz, 0.5H, CH=), 6.56 (*cis*-, d, J=11.6 Hz, 1H, CH=), 6.59 (*trans*-, d, J=11.6 Hz, 0.5H, CH=), 6.85 (*cis*-, d, J=11.6 Hz, 1H, CH=), 7.00–7.37 (*cis*- and *trans*-, m, 38.5H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 31.1, 38.9, 122.0, 124.2, 128.1, 125.5, 125.7, 126.1, 126.5, 126.6, 127.0, 127.1, 129.3, 127.5, 127.66, 127.75, 127.8, 128.1, 128.27, 128.32, 128.7, 129.3, 129.8, 130.0, 130.5, 130.6, 130.8, 136.3, 136.6, 139.68, 139.74, 139.8, 140.0, 140.6, 141.9, 142.2, 142.3, 142.5, 142.6, 142.8, 142.9, 143.4, 143.7, 143.8, 146.9. IR (CH_2Cl_2) ν 3055, 3026, 2928, 1597, 193, 1443, 1265, 1074, 1030, 763, 699, 638, 608 cm^{-1}. MS (%) m/z 474 (M^+, 100), 307 (51), 281 (40), 215 (24), 191 (32), 167 (52), 115 (28), 91 (66), 77 (16), 57 (14). HRMS (EI) calcd for $C_{37}H_{30}$: 474.2348, found: 474.2344.

*4.2.2. Product **3ab** (1.00:0.5 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.34 (*cis*- and *trans*-, s, 4.5H, CH_3), 3.18 (*trans*-, d, J=7.6 Hz, 1H, CH_2), 3.59 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.97 (*trans*-, t, J=7.2 Hz, 0.5H, CH), 6.07 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.25 (*trans*-, d, J=11.2 Hz, 0.5H, CH), 6.54 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.78 (*trans*-, d, J=11.2 Hz, 0.5H, CH), 6.84 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.86–7.39 (*cis*- and *trans*-, m, 36H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.2, 21.3, 31.1, 36.1, 121.1, 124.20, 124.25, 124.3, 124.4, 125.0, 125.4, 125.5, 126.0, 126.1, 126.6, 126.8, 127.0, 127.2, 127.3, 127.6, 127.7, 127.8, 128.08, 128.11, 128.3, 128.6, 128.8, 129.0, 129.1, 129.3, 129.8, 130.0, 130.3, 130.6, 130.8, 130.9, 133.4, 133.9, 136.3, 136.4, 136.9, 137.1, 139.0, 139.8, 139.9, 140.5, 141.6, 142.3, 142.9, 143.2, 143.7, 146.0, 146.9, 150.2. IR (CH_2Cl_2) ν 3055, 3024, 2924, 1597, 1493, 1443, 1265, 1031, 817, 764, 699 cm^{-1}. MS (%) m/z 488 (M^+, 100), 321 (36), 294 (22), 215 (15), 191 (18), 165 (16), 115 (18), 91 (20). HRMS (EI) calcd for $C_{38}H_{32}$: 488.2504, found: 488.2510.

*4.2.3. Product cis-**3ab**.* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.30 (s, 3H, CH_3), 3.59 (d, J=6.8 Hz, 2H, CH_2), 6.06 (t, J=6.8 Hz, 1H, CH), 6.52 (d, J=11.6 Hz, 1H, CH), 6.83 (d, J=11.6 Hz, 1H, CH), 7.05 (d, J=8.0 Hz, 2H, Ar), 7.16–7.20 (m, 11H, Ar), 7.23–7.27 (m, 6H, Ar), 7.34–7.38 (m, 5H, Ar).

*4.2.4. Product **3ac** (1.00:0.5 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.15 (*trans*-, d, J=7.2 Hz, 0.5H, CH_2), 3.57 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.93 (*trans*-, t, J=7.2 Hz, 0.5H, CH), 6.02 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.28 (*trans*-, d, J=11.2 Hz, 0.5H, CH), 6.51 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.68 (*trans*-, d, J=11.2 Hz, 0.5H, CH), 6.84 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.99–7.38 (*cis*- and *trans*-, m, 36H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 30.9, 38.7, 123.9, 124.6, 126.1, 126.8, 127.0, 127.3, 127.4, 127.50, 127.53, 127.8, 128.0, 128.08, 128.10, 128.13, 128.2, 128.4, 129.7, 130.0, 130.1, 130.5, 130.6, 132.8, 132.9, 139.0, 139.2, 139.6, 139.7, 139.8, 140.3, 141.8, 142.2, 142.4, 142.6, 143.0, 143.2, 144.3. IR (CH_2Cl_2) ν 3078, 3055, 3026, 2958, 2926, 1489, 1443, 1093, 828, 766, 700 cm^{-1}. MS (%) m/z 508 (M+, 100), 341 (65), 328 (29), 314 (39), 303 (41), 279 (24), 215 (30), 191 (50), 167 (93), 115 (48), 91 (51). HRMS (EI) calcd for $C_{37}H_{29}Cl$: 508.1958, found: 508.1594.

*4.2.5. Product **3ad** (1.0:0.4 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.25 (*trans*-, s, 1.2H, CH_3), 2.28 (*trans*-, s, 1.2H, CH_3), 2.32 (*cis*-, s, 3H, CH_3), 2.35 (*cis*-, s, 3H, CH_3), 3.19 (*trans*-, d, J=7.2 Hz, 0.8H, CH_2), 3.60 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.99 (*trans*-, t, J=7.2 Hz, 0.4H, CH), 6.08 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.30 (*trans*-, d, J=11.6 Hz, 0.4H, CH), 6.58 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.70 (*trans*-, d, J=11.6 Hz, 0.4H, CH), 6.81 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.97–7.37 (*cis*- and *trans*-, m, 32.2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.10, 21.13, 21.3, 31.1, 38.8, 122.4, 123.26, 123.34, 124.2, 124.3, 126.0, 126.1, 126.4, 126.6, 126.9, 127.2, 127.3, 127.5, 127.67, 127.73, 127.8, 127.9, 128.0, 128.1, 128.2, 128.3, 128.8, 129.3, 129.8, 130.0, 130.3, 130.5, 130.6, 130.7, 135.5, 136.8, 139.9, 137.0, 137.1, 137.2, 139.80, 139.85, 140.0, 142.10, 142.15, 142.3, 143.68, 143.72, 146.9. IR (CH_2Cl_2) ν 3054, 3023, 2920, 2866, 1598, 1511, 1493, 1443, 820, 759, 700 cm^{-1}. MS (%) m/z 502 (M^+, 100), 335 (16), 308 (26), 229 (9), 215 (12), 205 (14), 195 (18), 167 (14), 115 (12), 105 (13), 91 (15). HRMS (EI) calcd for $C_{39}H_{34}$: 502.2661, found: 502.2665.

*4.2.6. Product **3ae** (1.0:0.6 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.20 (*trans*-, d, J=7.2 Hz, 1.2H, CH_2), 3.60 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.96 (*trans*-, t, J=7.2 Hz, 0.6H, CH), 6.04 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.21 (*trans*-, d, J=11.6 Hz, 0.6H, CH=), 6.46 (*cis*-, d, J=11.6 Hz, 1H, CH=), 6.70 (*trans*-, d, J=11.6 Hz, 0.6H, CH=), 6.77 (*cis*-, d, J=11.6 Hz, 1H, CH=), 6.93–7.37 (*cis*- and *trans*-, m, 33.7H, Ar), 7.47–7.51 (*cis*- and *trans*-, m, 3.1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 31.2, 38.9, 121.3, 121.6, 121.8, 124.8, 125.0, 125.99, 126.03, 126.1, 126.8, 127.0, 127.1, 127.3, 127.39, 127.44, 127.9, 128.0, 128.1, 128.2, 128., 128.4, 128.6, 128.9, 129.19, 129.26, 129.7, 130.0, 131.3, 131.5, 132.18, 132.222, 132.4, 138.1, 138.3, 139.6, 139.67, 139.70, 140.3, 140.8, 140.90, 140.94, 141.6, 142.1, 142.2, 142.35, 142.45, 143.2, 144.9, 146.7. IR (CH_2Cl_2) ν 3055, 3025, 1488, 1443, 1398, 1072, 1010, 827, 758, 700 cm^{-1}. MS (%) m/z 632 (M+2$^+$, 100), 630 (M^+, 48), 465 (22), 438 (9), 384 (11), 358 (11), 325 (14), 307 (53), 281 (39), 229 (20), 215 (35), 203 (31), 191 (34), 167 (39), 115 (36), 91 (35). HRMS (EI) calcd for $C_{37}H_{28}Br_2$: 630.0558, found: 630.0555.

*4.2.7. Product **3ba** (1.0:0.6 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.16 (*trans*-, dd, J=7.6, 0.8 Hz, 1.2H, CH_2), 3.58 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.95 (*trans*-, t, J=7.6 Hz, 0.6H, CH), 6.04 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.21 (*trans*-, d, J=11.6 Hz, 0.6H, CH), 6.54 (*cis*-, d, J=11.6 Hz, 1H, CH), 6.72 (*trans*-, d, J=11.6 Hz, 0.6H, CH), 6.73 (*trans*-, d, J=11.6 Hz, 0.6H, CH), 6.76 (*cis*-, d, J=11.6 Hz, 1H, CH), 6.85 (*cis*-, d, J=11.6 Hz, 1H, CH), 6.89–6.93 (*cis*- and *trans*-, m, 4.8H, Ar), 7.00–7.04 (*cis*- and *trans*-, m, 3.0H, Ar), 7.10–7.45 (*cis*- and *trans*-, m, 27.4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 31.1, 38.8, 122.6, 123.9, 124.0, 124.6, 124.9, 125.6, 126.0, 126.1, 126.7, 127.1, 127.2, 127.46, 127.55, 127.7, 128.14, 128.16, 128.18, 128.2, 128.35, 128.44, 128.7, 129.8, 130.6, 130.8, 131.1, 131.3, 132.3, 132.97, 133.06, 133.1, 133.4, 135.4, 136.6, 137.6, 137.7, 139.6, 139.7, 139.9, 140.0, 140.4, 140.6, 140.7, 141.7, 142.2, 142.2, 142.4, 142.7, 143.3, 144.1, 144.9. IR (CH_2Cl_2) ν 3057, 3027, 2925, 1490, 1444, 1091, 1014, 826, 766, 699 cm^{-1}. MS (%) m/z 542 (M^+, 10), 502 (43), 307 (28), 277 (25), 215 (35), 191 (40), 167 (47), 115 (42), 105 (52), 91 (100), 77 (54), 57 (43). HRMS (EI) calcd for $C_{37}H_{28}Cl_2$: 542.1568, found: 542.1566.

*4.2.8. Product **4ba**.* A white solid, mp: 136–139 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.18 (s, 1H, OH), 2.36–2.40 (m, 2H, CH_2), 2.71–2.75 (m, 2H, CH_2), 6.49 (d, J=11.6 Hz, 1H, CH=), 6.77 (d, J=11.6 Hz, 1H, CH=), 7.10–7.42 (m, 23H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.3, 41.0, 77.7, 123.6, 125.5, 126.0, 127.3, 127.38, 127.45, 127.6, 128.2, 128.3, 128.5, 130.6, 133.0, 139.6, 141.6, 141.8, 142.4, 143.8, 144.8. IR (CH_2Cl_2) ν 3552, 3056, 3028, 1489, 1442, 1400, 1093, 1013, 907, 822, 766, 733, 700 cm^{-1}. MS (%) m/z 560 (M^+, 12), 367 (27), 307 (15), 251 (16), 215 (31), 202 (32), 191 (38), 139 (99.5), 105 (52), 91 (100.0), 77 (38). HRMS (EI) calcd for $C_{37}H_{30}Cl_2O$: 560.1674, found: 560.1661.

*4.2.9. Product **3ca** (1.0:0.5 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.15 (*trans*-, d, J=7.6 Hz, 1.0H, CH_2), 3.57 (*cis*-, d, J=7.2 Hz, 2H, CH_2), 5.96 (*trans*-, t, J=7.6 Hz, 0.5H, CH), 6.05 (*cis*-, t, J=7.2 Hz, 1H, CH), 6.21 (*trans*-, d,

J=11.6 Hz, 0.5H, CH), 6.54 (*cis*-, d, *J*=11.6 Hz, 1H, CH), 6.72 (*trans*-, d, *J*=11.6 Hz, 0.5H, CH), 6.76 (*cis*-, d, *J*=11.6 Hz, 1H, CH), 6.82–6.87 (*cis*- and *trans*-, m, 5H, Ar), 6.96 (*cis*-, d, *J*=8.8 Hz, 2H, Ar), 7.05 (*cis*-, d, *J*=8.8 Hz, 2H, Ar), 7.18–7.41 (*cis*- and *trans*-, m, 23.5H, Ar), 7.47 (*cis*-, d, *J*=8.8 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 31.1, 38.8, 120.5, 121.3, 121.6, 122.6, 123.90, 123.94, 124.6, 125.7, 126.0, 126.1, 126.7, 127.1, 127.2, 127.4, 127.5, 127.6, 127.7, 128.16, 128.20, 128.3, 128.7, 128.9, 129.9, 130.5, 130.6, 130.8, 131.0, 131.1, 131.2, 131.4, 131.6, 131.7, 135.3, 136.6, 138.1, 139.6, 139.8, 140.1, 140.7, 141.7, 142.4, 142.5, 142.7, 143.4, 144.1, 145.4. IR (CH_2Cl_2) ν 3056, 3026, 2926, 1488, 1443, 1393, 1073, 1009, 821, 767, 699 cm^{-1}. MS (%) *m*/*z* 632 ($M+2^+$, 100), 630 (M^+, 48), 465 (17), 384 (14), 358 (15), 325 (17), 307 (53), 280 (67), 215 (40), 202 (44), 191 (67), 167 (57), 115 (41), 91 (74), 77 (18). HRMS (EI) calcd for $C_{37}H_{28}Br_2$: 630.0558, found: 630.0550.

4.2.10. Product ***4ca****.* A white solid, mp: 145–148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.18 (s, 1H, OH), 2.35–2.39 (m, 2H, CH_2), 2.71–2.75 (m, 2H, CH_2), 6.50 (d, *J*=11.6 Hz, 1H, CH=), 6.78 (d, *J*=11.6 Hz, 1H, CH=), 7.09–7.39 (m, 23H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 24.3, 40.9, 77.8, 123.6, 125.5, 126.0, 127.3, 127.4, 127.5, 127.6, 127.7, 128.1, 128.2, 128.3, 128.4, 128.8, 130.5, 131.3, 131.4, 139.6, 141.6, 141.7, 142.3, 143.8, 145.2. IR (CH_2Cl_2) ν 3557, 3055, 3027, 2926, 1487, 1442, 1396, 1074, 1009, 907, 817, 766, 733, 700 cm^{-1}. MS (%) *m*/*z* 650 ($M+2^+$, 16), 648 (M^+, 8), 457 (34), 307 (19), 279 (20), 215 (38), 202 (37), 183 (63), 167 (43), 115 (43), 105 (67), 91 (100), 77 (43), 57 (35). HRMS (EI) calcd for $C_{37}H_{30}OBr_2$: 648.0663, found: 648.0651.

4.2.11. Product ***3da*** *(1.0:0.5 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.28 (*cis*-, s, 3H, CH_3), 2.30 (*trans*-, s, 1.5H, CH_3), 2.34 (*trans*-, s, 1.5H, CH_3), 2.36 (*cis*-, s, 3H, CH_3), 3.19 (*trans*-, d, *J*=9.6 Hz, 1H, CH_2), 3.60 (*cis*-, d, *J*=9.2 Hz, 2H, CH_2), 5.90 (*trans*-, t, *J*=9.6 Hz, 0.5H, CH), 6.00 (*cis*-, t, *J*=9.2 Hz, 1H, CH), 6.27 (*trans*-, d, *J*=15.2 Hz, 0.5H, CH), 6.54 (*cis*-, d, *J*=15.2 Hz, 1H, CH), 6.74 (*trans*-, d, *J*=15.2 Hz, 0.5H, CH), 6.86 (*cis*-, d, *J*=15.2 Hz, 1H, CH), 6.90–6.94 (*cis*- and *trans*-, m, 2.4H, Ar), 7.00–7.46 (*cis*- and *trans*-, m, 31.4H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 21.1, 21.2, 22.6, 31.1, 38.9, 124.3, 125.3, 125.6, 126.1, 126.2, 127.0, 127.2, 127.28, 127.34, 127.4, 127.7, 128.0, 128.1, 128.2, 128.7, 128.9, 129.3, 129.6, 129.9, 130.5, 130.6, 136.4, 136.5, 136.6, 136.7, 136.9, 139.7, 139.8, 140.0, 140.1, 140.7, 140.8, 141.96, 142.00, 142.1, 142.4, 142.5, 142.6, 143.5, 143.7. IR (CH_2Cl_2) ν 3053, 3024, 2955, 2923, 2855, 1509, 1491, 1442, 1110, 1074, 765, 698, 502 cm^{-1}. MS (%) *m*/*z* 502 (M^+, 85), 335 (47), 307 (37), 279 (26), 265 (18), 229 (25), 215 (41), 202 (45), 195 (71), 178 (42), 167 (55), 129 (38), 115 (50), 105 (79), 91 (100), 77 (50). HRMS (EI) calcd for $C_{39}H_{34}$: 502.2661, found: 502.2660.

4.2.12. Product cis- ***3da****.* A white solid, mp: 135–136 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.28 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.59 (d, *J*=9.2 Hz, 2H, CH_2), 5.99 (t, *J*=9.2 Hz, 1H, CH), 6.52 (d, *J*=15.2 Hz, 1H, CH), 6.85 (d, *J*=15.2 Hz, 1H, CH), 7.00–7.06 (m, 4H, Ar), 7.11–7.40 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.3, 31.1, 124.3, 125.6, 126.17, 126.25, 127.0, 127.2, 127.3, 127.4, 127.7, 128.07, 128.14, 128.2, 128.7, 129.0, 129.9, 130.6, 136.66, 136.72, 137.0, 139.76, 139.80, 140.8, 141.97, 142.05, 142.6, 143.5.

4.2.13. Product ***3ea*** *(1.0:0.3 mixture of cis- and trans-isomers).* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.19 (*trans*-, d, *J*=6.8 Hz, 0.6H, CH_2), 3.60 (*cis*-, d, *J*=6.8 Hz, 2H, CH_2), 3.75 (*cis*-, s, 3H, OCH_3), 3.78 (*trans*-, s, 0.9H, OCH_3), 3.808 (*cis*-, s, 3H, OCH_3), 3.814 (*trans*-, s, 0.9H, OCH_3), 5.82 (*trans*-, t, *J*=6.8 Hz, 0.3H, CH), 5.92 (*cis*-, t, *J*=6.8 Hz, 1H, CH), 6.26 (*trans*-, d, *J*=11.2 Hz, 0.3H, CH), 6.53 (*cis*-, d, *J*=11.2 Hz, 1H, CH), 6.73–6.98 (*cis*- and *trans*-, m, 8.7H, Ar), 7.08 (*cis*-, d, *J*=8.8 Hz, 2H, Ar), 7.14–7.29 (*cis*- and *trans*-, m, 16.8H, Ar), 7.33–7.40 (*cis*- and *trans*-, m, 4.7H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ (*cis*- and *trans*-) 31.1, 38.9, 55.17, 55.20, 55.4, 113.2, 113.36, 113.43, 113.6, 114.0, 124.3, 124.6, 125.22, 125.26, 125.3, 125.5, 126.1, 127.0, 127.2, 127.3, 127.4, 127.7, 128.08, 128.11, 128.2, 128.5, 128.7, 129.98, 130.03, 130.56, 130.63, 130.7, 130.9, 131.2, 132.2, 132.4, 135.4, 139.8, 140.9, 141.2, 142.0, 142.5, 143.5, 143.8, 158.6, 158.7, 162.8. IR (CH_2Cl_2) ν 3056, 3029, 2932, 1603, 1510, 1445, 1253, 1168, 1031, 834, 769, 701 cm^{-1}. MS (%) *m*/*z* 534 (M^+, 23), 367 (19), 354 (9), 277 (13), 253 (30), 242 (24), 227 (100), 135 (90), 105 (61), 91 (44), 77 (84). HRMS (EI) calcd for $C_{39}H_{34}O_2$: 534.2559, found: 534.2552.

4.2.14. Product ***5ea****.* A white solid, mp: 155–158 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.36–2.44 (m, 1H, CH), 2.54–2.62 (m, 1H, CH), 3.29–3.35 (m, 1H, CH), 3.46–3.53 (m, 1H, CH), 3.67 (s, 3H, OCH_3), 3.76 (s, 3H, CH_3), 4.95 (d, *J*=10.4 Hz, 1H, OH), 6.40 (d, *J*=8.8 Hz, 2H, Ar), 6.46 (d, *J*=10.4 Hz, 1H, CH), 6.74 (d, *J*=8.8 Hz, 2H, Ar), 6.82 (d, *J*=8.8 Hz, 2H, Ar), 6.96 (dd, *J*=8.8, 1.2 Hz, 2H, Ar), 7.10–7.32 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 33.9, 47.6,55.0, 55.1, 62.3, 113.3, 113.8, 126.3, 127.0, 127.2, 127.78, 127.83, 128.0, 128.18, 128.24, 128.4, 129.5, 129.6, 130.0, 134.7, 134.8, 135.6, 139.4, 141.8, 142.9, 143.2, 143.8, 157.7, 158.1. IR (CH_2Cl_2) ν 3456, 3026, 2930, 1605, 1508, 1283, 1243, 1173, 1033, 832, 701 cm^{-1}. MS (%) *m*/*z* 552 (M^+, 24), 367 (54), 341 (13), 321 (11), 269 (30), 227 (34), 191 (57), 165 (33), 121 (49), 91 (100), 57 (27). HRMS (EI) calcd for $C_{39}H_{36}O_3$: 552.2264, found: 552.2685.

4.2.15. Product ***6ea****.* A white solid, mp: 176–180 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.16–2.23 (m, 1H, CH), 2.34–2.48 (m, 1H, CH), 2.68–2.78 (m, 1H, CH), 2.98–3.12 (m, 1H, CH), 3.67 (s, 3H, OCH_3), 3.72 (s, 3H, CH_3), 4.85 (dd, *J*=10.4, 4.0 Hz, 1H, OH), 6.35 (dd, *J*=10.0, 2.0 Hz, 1H, CH), 6.40 (dd, *J*=8.8, 3.6 Hz, 2H, CH), 6.70 (dd, *J*=8.8, 6.0 Hz, 2H, Ar), 6.76 (d, *J*=8.4 Hz, 2H, Ar), 6.92 (t, *J*=6.8 Hz, 2H, Ar), 6.99 (dd, *J*=8.4, 1.2 Hz, 2H, Ar), 7.10–7.26 (m, 14H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 30.4, 47.7, 47.8, 55.0, 55.1, 69.5, 69.6, 113.2, 113.6, 126.1, 126.9, 127.2, 127.77, 127.84, 128.0, 128.1, 128.3, 129.6, 130.0, 134.9, 135.0, 135.6, 139.4, 141.2, 142.4, 143.2, 143.8, 157.6, 158.0. IR (CH_2Cl_2) ν 3055, 3026, 2930, 1605, 1508, 1443, 1244, 1172, 1034, 832, 767, 738, 701 cm^{-1}. MS (%) *m*/*z* 552 ($M-C_{39}H_{34}O_2^+$, 2), 502 (4), 367 (4), 341 (4), 277 (21), 191 (16), 155 (18), 115 (21), 91 (59), 77 (39), 57 (63), 43 (100). HRMS (EI) calcd for $C_{78}H_{70}O_5$: 1086.5223, found: 552.2665.

4.2.16. Product ***7fa****.* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.69 (s, 3H, CH_3), 1.89–1.96 (m, 1H, CH), 2.18–2.24 (m, 1H, CH), 2.51–2.59 (m, 1H, CH), 2.74–2.81 (m, 1H, CH), 6.80 (d, *J*=12.0 Hz, 1H, Ar), 6.99 (d, *J*=11.2 Hz, 1H, Ar), 7.05–7.42 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.6, 29.4, 39.0, 43.0, 120.5, 121.5, 124.1, 124.2, 125.7, 126.3, 127.17, 127.25, 127.4, 127.6, 127.9, 128.1, 128.6, 130.8, 136.1, 137.2, 139.9, 142.8, 144.4, 149.2. IR (CH_2Cl_2) ν 3057, 3026, 2962, 1493, 1443, 1029, 761, 699, 530 cm^{-1}. MS (%) *m*/*z* 412 (M^+, 35), 291 (6), 248 (10), 191 (25), 178 (16), 165 (19), 115 (6), 91 (100), 71 (26), 57 (41). HRMS (EI) calcd for $C_{32}H_{28}$: 412.2191, found: 412.2195.

4.2.17. Product ***8fa*** *(1.0:0.4 mixture of cis- and trans-isomers).* A white solid, mp: 121–126 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.46 (*trans*-, s, 1.2H, CH_3), 1.59 (*cis*-, s, 3H, CH_3), 1.94–2.03 (*cis*- and *trans*-, m, 2.8H, CH_2), 2.23–2.30 (*trans*-, m, 0.4H, CH_2), 2.34–2.41 (*trans*-, m, 0.4H, CH_2), 2.50–2.57 (*cis*-, m, 1H, CH_2), 2.73–2.81 (*cis*-, m, 1H, CH_2), 6.16 (*trans*-, d, *J*=11.2 Hz, 0.4H, CH), 6.44 (*cis*-, d, *J*=11.2 Hz, 1H, CH), 6.66 (*trans*-, d, *J*=11.2 Hz, 0.4H, CH), 6.82 (*cis*-, d, *J*=11.2 Hz, 1H, CH), 7.09–7.22 (*cis*- and *trans*-, m, 0.9H, Ar), 7.29–7.42 (*cis*- and *trans*-, m, 25.1H, Ar), 7.46–7.48 (*cis*- and *trans*-, m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ (*cis*- and *trans*-) 24.7, 30.8, 43.5, 74.9, 123.9, 124.7, 124.8, 125.1, 126.0, 127.69, 127.05, 127.3, 127.6, 128.1, 128.30, 128.32, 128.8, 130.6, 139.8, 141.9, 142.3, 142.5, 143.2, 147.2. IR (CH_2Cl_2) ν 2956, 2925, 2853, 1445, 974, 763, 699 cm^{-1}. MS (%) *m*/*z* 430 (M^+, 17), 412 (5), 307 (18), 215 (15), 202 (15), 191 (13), 121 (22),

105 (27), 91 (49), 77 (18), 57 (20). HRMS (EI) calcd for $C_{32}H_{30}O$: 430.2297, found: 430.2289.

4.2.18. Product ***7ga****.* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.66 (s, 3H, CH_3), 1.88–1.95 (m, 1H, CH), 2.13–2.19 (m, 1H, CH), 2.50–2.56 (m, 1H, CH), 2.75–2.79 (m, 1H, CH), 6.78 (d, J=11.2 Hz, 1H, Ar), 6.91 (d, J=8.4 Hz, 2H, Ar), 6.97 (d, J=11.2 Hz, 1H, Ar), 7.02–7.41 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 23.5, 29.3, 38.7, 42.7, 119.6, 121.7, 124.1, 124.2, 126.5, 127.3, 127.4, 127.6, 127.9, 128.1, 129.0, 130.7, 131.0, 136.1, 136.6, 139.8, 142.8, 143.0, 143.7, 148.3. IR (CH_2Cl_2) ν 3057, 2961, 2927, 1487, 1443, 1080, 1008, 760, 700, 520 cm^{-1}. MS (%) m/z 492 (M+2$^+$, 100), 490 (M$^+$, 100), 319 (10), 294 (27), 243 (18), 229 (17), 215 (29), 191 (48), 167 (32), 142 (22), 115 (40), 91 (44). HRMS (EI) calcd for $C_{32}H_{27}Br$: 490.1296, found: 490.1299.

4.2.19. Product ***8ga*** *(1.0:0.3 mixture of cis- and trans-isomers).* A white solid, mp: 119–123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.41 (*trans*-, s, 0.9H, CH_3), 1.53 (*cis*-, s, 3H, CH_3), 1.94–1.98 (*cis*- and *trans*-, m, 2.6H, CH_2), 2.18–2.26 (*trans*-, m, 0.3H, CH_2), 2.32–2.40 (*trans*-, m, 0.3H, CH_2), 2.46–2.54 (*cis*-, m, 1H, CH_2), 2.72–2.80 (*cis*-, m, 1H, CH_2), 6.14 (*trans*-, d, J=11.2 Hz, 0.3H, CH), 6.44 (*cis*-, d, J=11.2 Hz, 1H, CH), 6.66 (*trans*-, d, J=11.2 Hz, 0.3H, CH), 6.79 (*cis*-, d, J=11.2 Hz, 1H, CH), 7.09–7.44 (*cis*- and *trans*-, m, 24.7H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ (*cis*- and *trans*-) 24.6, 30.6, 30.9, 33.8, 42.2, 43.3, 74.5, 74.6, 120.6, 123.8, 125.2, 125.9, 126.7, 126.8, 127.1, 127.38, 127.45, 127.5, 128.0, 128.1, 128.3, 128.4, 128.8, 130.6, 131.1, 131.3, 139.7, 141.8, 142.0, 142.4, 143.4, 146.2. IR (CH_2Cl_2) ν 3054, 2956, 2925, 1489, 1442, 1078, 1008, 827, 765, 699, 530 cm^{-1}. MS (%) m/z 510 (M+2$^+$, 7), 508 (M$^+$, 6), 307 (10), 215 (12), 202 (13), 191 (13), 165 (10), 115 (18), 91 (44), 57 (40). HRMS (EI) calcd for $C_{32}H_{29}BrO$: 508.1402, found: 508.1400.

4.2.20. Product ***7ha****.* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.70 (s, 3H, CH_3), 1.90–1.97 (m, 1H, CH), 2.19–2.25 (m, 1H, CH), 2.28 (s, 3H, CH_3), 2.54–2.60 (m, 1H, CH), 2.76–2.81 (m, 1H, CH), 6.78 (d, J=11.2 Hz, 1H, Ar), 6.96–7.42 (m, 19H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.8, 23.7, 29.5, 39.0, 42.6, 121.4, 124.1, 124.3, 126.2, 127.1, 127.2, 127.4, 127.6, 128.1, 128.6, 130.8, 135.1, 136.1, 137.3, 139.9, 142.7, 142.9, 144.7, 146.3. IR (CH_2Cl_2) ν 3054, 6024, 2925, 1493, 1443, 1376, 1018, 815, 760, 699 cm^{-1}. MS (%) m/z 426 (M$^+$, 25), 233 (11), 215 (12), 191 (24), 165 (18), 115 (28), 105 (31), 91 (39), 71 (55), 57 (95). HRMS (EI) calcd for $C_{33}H_{30}$: 426.2348, found: 426.2353.

4.2.21. Product ***7he****.* A yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.72 (s, 3H, CH_3), 1.91–1.98 (m, 1H, CH), 2.20–2.26 (m, 1H, CH), 2.30 (s, 3H, CH_3), 2.50–2.58 (m, 1H, CH), 2.74–2.82 (m, 1H, CH), 6.68 (d, J=11.2 Hz, 1H, Ar), 6.95–6.98 (m, 3H, Ar), 7.05 (d, J=8.0 Hz, 2H, Ar), 7.10–7.19 (m, 7H, Ar), 7.40 (d, J=8.0 Hz, 2H, Ar), 7.41–7.43 (m, 1H, Ar), 7.55 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.9, 23.8, 29.0, 8.8, 42.6, 120.6, 124.1, 125.1, 126.4, 127.1, 127.6, 128.2, 128.6, 129.1, 131.3, 131.5, 132.4, 135.2, 135.8, 138.3, 138.8, 140.0, 141.3, 144.8, 146.1. IR (CH_2Cl_2) ν 2962, 2925, 1507, 1340, 1094, 1018, 806, 744 cm^{-1}. MS (MALDI) m/z 584.1 (M$^+$). HRMS (MALDI) calcd for $C_{33}H_{28}Br_2$: 582.0545, found: 582.0552.

4.2.22. Product ***10a****.* A yellow solid, mp: 144–146 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.72 (s, 3H, CH_3), 1.94–2.00 (m, 1H, CH), 2.22–2.28 (m, 1H, CH), 2.30 (s, 3H, CH_3), 2.57–2.64 (m, 1H, CH), 2.81–2.87 (m, 1H, CH), 6.87 (d, J=11.6 Hz, 1H, Ar), 6.99 (d, J=8.0 Hz, 2H, Ar), 7.06 (d, J=8.0 Hz, 2H, Ar), 7.09–7.15 (m, 3H, Ar), 7.31–7.54 (m, 14H, Ar), 7.60 (d, J=8.0 Hz, 2H, Ar), 7.68 (d, J=8.0 Hz, 2H, Ar), 7.70 (d, J=8.0 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 23.8, 29.5, 39.0, 42.7, 121.4, 124.1, 124.5, 126.3, 126.8, 126.88, 126.92, 127.0, 127.1, 127.27, 127.32, 127.4, 128.16, 128.21, 128.7, 128.76, 128.84, 131.3, 135.2, 136.1, 137.6, 138.8, 140.0, 140.1, 140.6, 141.9, 144.7, 146.3. IR (CH_2Cl_2) ν 2962, 2924, 2852, 1487, 1262, 1093, 1020, 802, 704 cm^{-1}. MS (MALDI) m/z 578.3 (M$^+$). HRMS (MALDI) calcd for $C_{45}H_{38}$: 578.2960, found: 578.2968.

4.2.23. Product ***10b****.* A yellow solid, mp: 152–156 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.73 (s, 3H, CH_3), 1.94–2.01 (m, 1H, CH), 2.22–2.28 (m, 1H, CH), 2.30 (s, 3H, CH_3), 2.58–2.64 (m, 1H, CH), 2.80–2.86 (m, 1H, CH), 6.84 (d, J=11.2 Hz, 1H, Ar), 6.98 (d, J=8.4 Hz, 2H, Ar), 7.05–7.16 (m, 6H, Ar), 7.37–7.41 (m, 6H, Ar), 7.44–7.53 (m, 7H, Ar), 7.62 (d, J=8.4 Hz, 2H, Ar), 7.64 (d, J=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 23.8, 29.7, 39.0, 42.7, 121.2, 124.1, 124.8, 126.3, 126.7, 126.8, 127.1, 128.1, 128.2, 128.7, 128.9, 129.0, 131.4, 133.4, 133.5, 135.2, 136.0, 138.0, 138.8, 138.9, 139.0, 139.1, 141.4, 142.1, 144.8, 146.3. IR (CH_2Cl_2) ν 2957, 2925, 2854, 1484, 1263, 1094, 1059, 1019, 819, 744 cm^{-1}. MS (MALDI) m/z 646.2 (M$^+$). HRMS (MALDI) calcd for $C_{45}H_{36}Cl_2$: 646.2182, found: 646.2187.

4.2.24. Product ***10c****.* A yellow solid, mp: 149–151 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25–1.30 (m, 6H, $2CH_3$), 1.72 (s, 3H, CH_3), 1.93–1.99 (m, 1H, CH), 2.21–2.30 (m, 1H, CH), 2.30 (s, 3H, CH_3), 2.56–2.75 (m, 5H, CH and $2CH_2$), 2.80–2.86 (m, 1H, CH), 6.86 (d, J=11.2 Hz, 1H, Ar), 6.98 (d, J=8.4 Hz, 2H, Ar), 7.04–7.14 (m, 6H, Ar), 7.26 (d, J=8.4 Hz, 2H, Ar), 7.31 (d, J=8.4 Hz, 2H, Ar), 7.36–7.40 (m, 4H, Ar), 7.45–7.47 (m, 1H, Ar), 7.51–7.53 (m, 4H, Ar), 7.63 (d, J=8.4 Hz, 2H, Ar), 7.66 (d, J=8.4 Hz, 2H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 15.6, 20.9, 23.7, 28.5, 29.4, 39.0, 42.7, 121.5, 124.1, 124.3, 126.3, 126.6, 126.7, 126.8, 126.9, 127.1, 128.1, 128.2, 128.3, 128.4, 128.6, 131.3, 135.2, 136.1, 137.4, 138.0, 138.1, 138.5, 140.0, 141.6, 142.0, 143.4, 143.5, 144.7, 146.4. IR (CH_2Cl_2) ν 3026, 2961, 2924, 2856, 1461, 1261, 1091, 1019, 822, 749, 730 cm^{-1}. MS (MALDI) m/z 634.4 (M$^+$). HRMS (MALDI) calcd for $C_{49}H_{46}$: 634.3587, found: 634.3594.

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Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.06.009.

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