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Note

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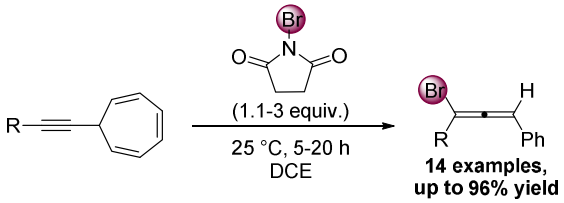
Synthesis of 3-Substituted 3-Bromo-1-phenylallenes from Alkynylcycloheptatrienes.

Marie Vayer, Régis Guillot, Christophe Bour,* and Vincent Gandon*

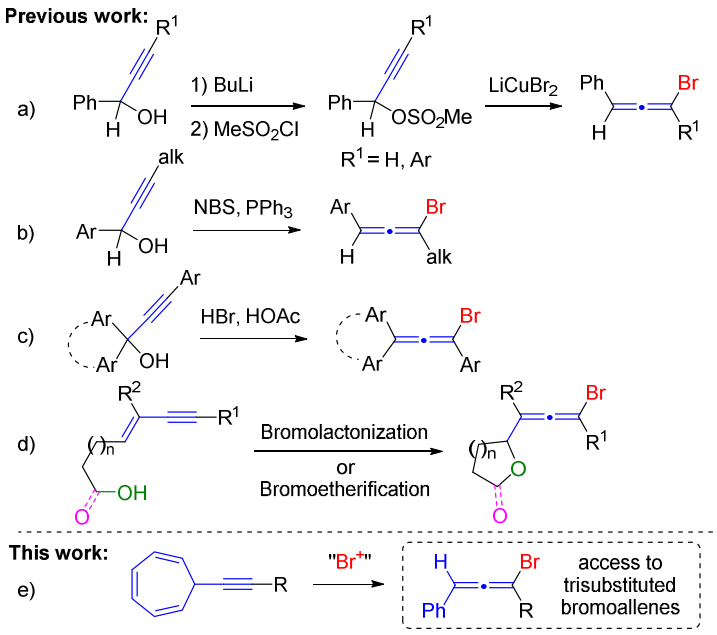
Institut de Chimie Moléculaire et des Matériaux d'Orsay, CNRS UMR 8182, Université Paris-Sud, Université Paris-Saclay, Bâtiment 420, 91405 Orsay cedex, France.

Abstract: A new method has been developed for the preparation of 3-bromo-1-phenylallenes from 7-alkynylcycloheptatrienes and *N*-bromosuccinimide. Trisubstituted bromoallenes were obtained at room temperature in moderate to excellent yields. Functionalization of the carbon-bromine bond *via* Pd- or Cu-catalyzed cross-coupling reactions easily provided substituted allenes.



Bromoallenes constitute an important class of compounds. Their framework can be found in a variety of biologically active molecules.[1] Besides, they have been used on many occasions as key intermediates in organic synthesis.[2] However, only a few methods to synthesize bromoallenes have been reported. For instance, bromopropadiene can be prepared by isomerization of 3-bromopropyne in the presence of copper(I) bromide.[3,4] It can also be obtained by flash vacuum pyrolysis (400 °C) of 1-bromocyclopropene.[5] Substituted bromoallenes have been synthesized by S_N2' reaction[6] of propargyl methanesulfonates with a bromocuprate (Scheme 1a).[7,8]

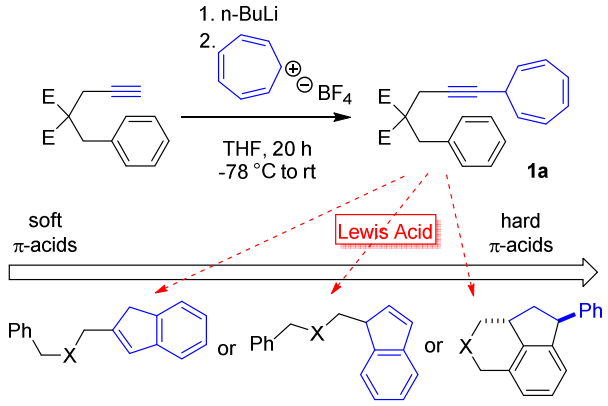
Scheme 1. Synthesis of Bromoallenes



Bromination of aryl propargyl alcohols using *N*-bromosuccinimide (NBS) or HBr has been reported (Scheme 1b-c).[9,10] Finally, bromoallenes can also be reached by bromolactonization of conjugated enynes,[11,12] or bromoetherification of enynes (Scheme 1d),[13,14] an approach used for the total synthesis of (±)-panacene.[15,16]

Our approach to bromoallenes is very different and complementary to the existing ones (Scheme 1e). In our case, starting materials are based on the 7-alkynylcycloheptatriene moiety. Such compounds have been used previously as substrates in gold-catalyzed transformations for the synthesis of indenes,[17] barbaralones and bullvalenes,[18] as precursors of cumulenes and barbaralanes,[19] and of arylallenes or endoperoxides.[20] They are stable and can be easily synthesized in one operational steps from an alkyne and the commercially available tropylium tetrafluoroborate salt. We have used 7-alkynylcycloheptatriene derivatives as tools to reveal the π-acidity of Lewis acids (Scheme 2).[21] For instance, depending on the softness or hardness of the Lewis acid catalysts used, compound **1a** may transform into distinct cycloisomerization products.

Scheme 2. Divergent Reaction Pathways in the Lewis Acid-Catalyzed Skeletal Reorganization of **1a** (E = CO_2Me)

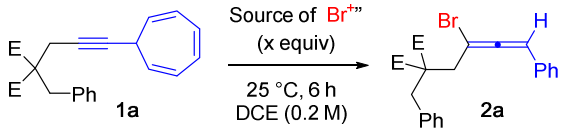


We have found that the reaction of these species with electrophilic bromination agents yields 3-substituted 3-bromo-1-phenylallenes (Scheme 1d). In addition to being a new way of making such compounds, this transformation is appealing because it forms trisubstituted bromoallenes which have been rarely synthesized.[7,9,11,12,14] Because of the lack of availability of substituted tropylium cations,[22] the reaction is so far limited to 3-bromo-1-phenylallenes, yet phenylallenes are themselves key reagents in a number of important transformations.[23]

Based on our experience with 7-alkynylcycloheptatrienes derived from arenynes,[21] we began our investigations with compound **1a** (Table 1). Treatment with 1.1 equiv of NBS in $MeNO_2$ resulted in a complex mixture of products. In toluene, a low conversion was obtained. In 1,2-dichloroethane (DCE), bromoallene **2a** could be isolated in 56% yield (Entry 1). Full conversion was reached with at least 3 equiv of NBS, allowing to isolate **2a** in 68% yield after removal of unidentified side products by silica gel chromatography (Entry 2). Other sources of electrophilic bromine were also tested. When employing 1.1 equiv of Br_2, pyridinium tribromide, 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) [24] or 2,4,4,6-tetrabromo-2,5-cyclohexadien-1-one

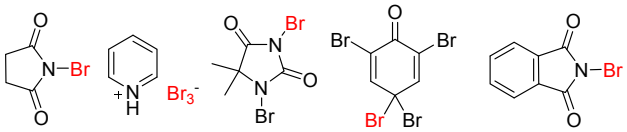
(TBCD),[24] only complex mixtures or low conversions were observed. On the other hand, *N*-bromophthalimide led to **2a** in 60% yield (Entry 3). Increasing the amount of *N*-bromophthalimide to 3 equiv resulted in the formation of side-products (Entry 4).

Table 1. Optimization of the Reaction Conditions (E = CO_2Me)



Entry	[Br^+] source	x	Yield of **2a**[a]
1	NBS	1.1	56 (83)
2	NBS	3	68 (100)
3	*N*-bromophthalimide	1.1	60 (100)
4	*N*-bromophthalimide	3	- (100)[c]

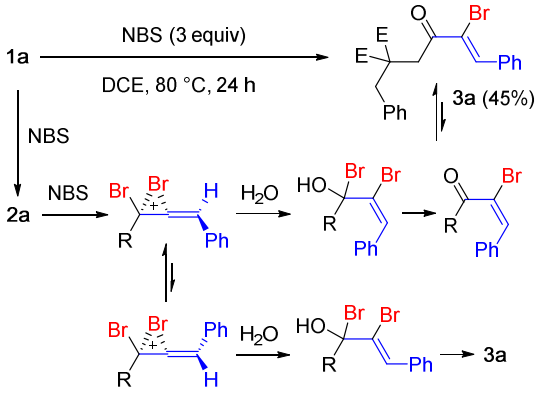
[a] Isolated yield after flash chromatography, conversion indicated in parentheses. [b] Complex mixture. [c] **2a** observed but contaminated by a large amount of side-products.



When the reaction of **1a** was carried out during an extended reaction time of 24 h (instead of 6 h) and at a higher temperature of 80 °C (instead of 25 °C), the bromoallene **2a** was not isolated (Scheme 3). We observed instead the formation of the brominated enone **3a**. Its structure was

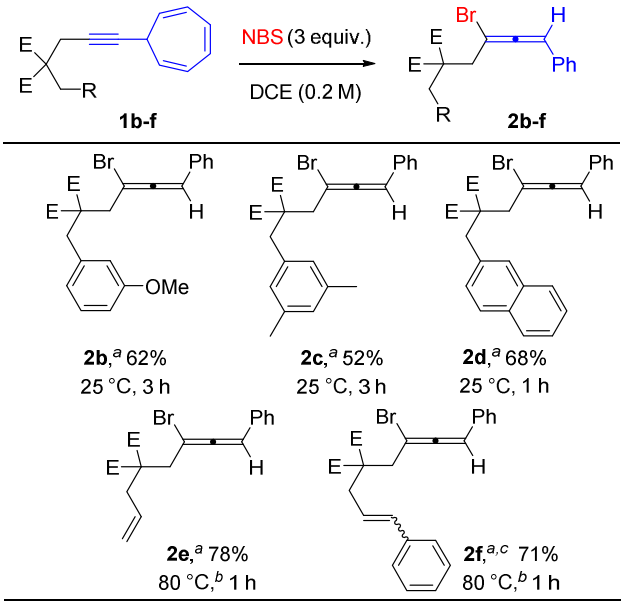
ascertained by X-ray crystallography (see the Supporting Information). It presumably arises from the reaction of **2a** with NBS to give a bromonium intermediate which is trapped by adventitious water. From the less hindered bromonium ion, this results in the formation of a *E* bromoenone which isomerizes into the thermodynamic *Z* product **3a**.[25] Alternatively, opening of the bromonium ion, rotation of the vinyl cation and bromonium reformation leads, through the most hindered isomer, to the *Z* olefin directly.

Scheme 3. Formation of the *Z* bromoenone **3a**



In spite of this possible side reaction, we decided to use 3 equiv of NBS with other malonates (Scheme 4). With a *meta* methoxyphenyl (**1b**) or a 3,5-dimethylphenyl group (**1c**), the reaction were faster than with **1a** (3 h instead of 6 h), with still full conversion. The rate was even higher when the phenyl group was replaced by naphthalene, which gave rise to **2d** in 68% yield in only 1 h. The presence of an alkene instead of a phenyl group proved also compatible with our conditions. However, the transformations of **1e** and **1f** were slower at 25 °C (~ 40% conversion after 6 h). The yields could be markedly increased to 78% and 71% for **2e** and **2f** respectively at 80 °C in 1 h, without enone formation.

Scheme 4. Substrate Scope with Dimethyl Malonates (E = CO_2Me)

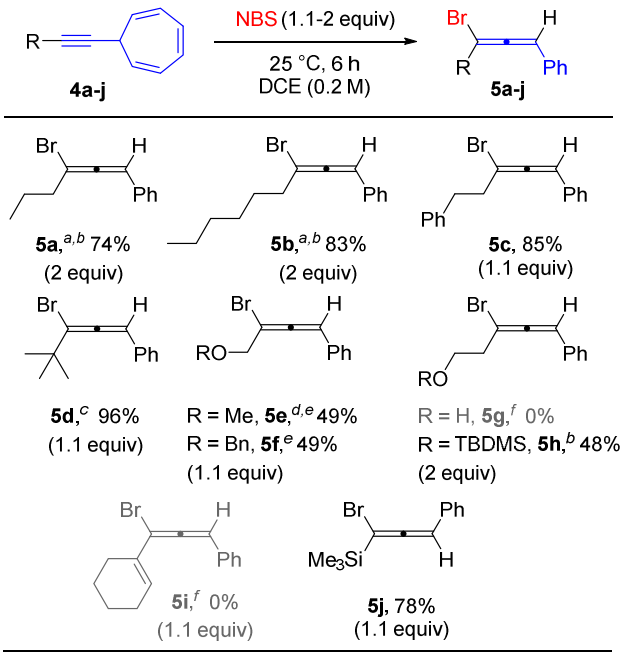


[a] 100% conversion (NMR), yields of isolated products are given. [b] Full conversion was not observed at 25 °C. [c] *E*/*Z* 80:20.

We then studied the formation of bromoallenes with substrates synthesized from simple commercially available alkynes (Scheme 5). With these, the amount of NBS could be decreased to 2 or even 1.1 equiv to reach full conversion. Substrates displaying *n*-propyl and *n*-hexyl groups were first tested, leading to **5a** and **5b** as major products with 2 equiv of NBS, although some impurities could not be eliminated from these non-polar products. With a phenethyl substituent and only 1.1 equiv of NBS, the desired bromoallene **5c** was isolated in 85% yield by simple filtration on silica gel. Bromoallene **5d** exhibiting a *t*-butyl group was obtained with an excellent 96% yield. This reaction was scaled up to 1 g of substrate, with still a very good yield of 88%. With alkoxy groups in the alkyl chain, the products were isolated in yields around 50% (**5e**, **5f**, **5h**). On the other hand, using a free alcohol as in **4g** resulted in decomposition. The same phenomenon was observed with substrate **4i** bearing a conjugated alkene group. The reason for the instability of **4g** and **4i** under the reaction conditions could not be rationalized. Of particular in-

terest, a silylated alkyne could be efficiently converted into a bromosilylallene in 78% yield (**5j**). Such compounds are not easily prepared by conventional methods and have yet proven to be useful intermediates.[2a,26]

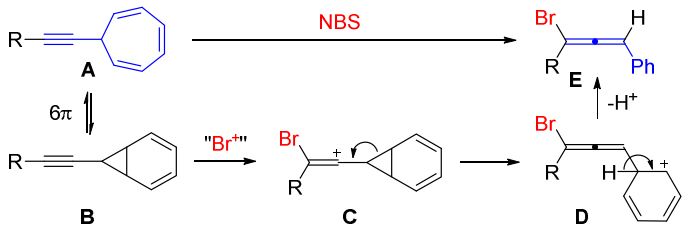
Scheme 5. Substrate Scope with Simple 7-Alkynylcycloheptatrienes



[a] Presence of impurities, the yield corresponds to a maximum. [b] ~ 40-70% conversion with 1.1 equiv. [c] 88% yield on a 1 g scale. [d] 87% conversion. [e] After flash chromatography. [f] Decomposition.

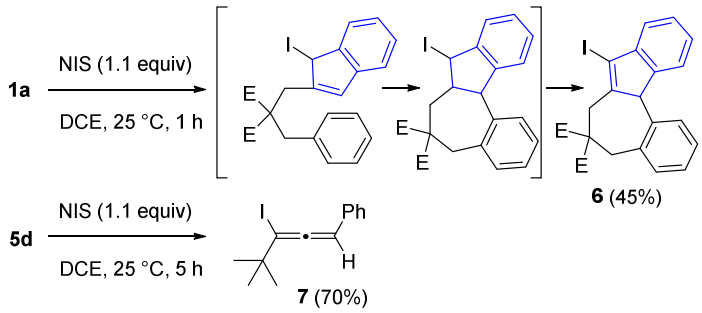
A mechanistic rationale is shown in Scheme 6.[20a,c] The substrate **A** is in equilibrium with the norcaradiene form **B** after 6π electrocyclization.[27] Bromination of the alkyne moiety of **B** gives rise to the vinyl carbocation **C**. The allene framework is then formed by ring opening of the cyclopropane to give **D**. Proton elimination finally leads to the bromoallene **E**.

Scheme 6. Postulated Mechanism



Of note, no reaction took place when NCS was used instead of NBS. With NIS, in sharp contrast with NBS, compound **1a** transformed into **6** (Scheme 7). This product presumably arises from the hydroarylation and oxidation of an iodoindene intermediate. As mentioned above, 7-alkynylcycloheptatrienes can be readily isomerized into indenes under gold catalysis.[17] The soft I^+ cation behaves in this case as a soft Au^+ ion and triggers a non-classical carbocation pathway.[28] However, this takes place only because the intermediate iodoindene can be trapped by hydroarylation. With the simple substrate **5d**, the expected iodoallene **7** could be isolated in 70% yield.

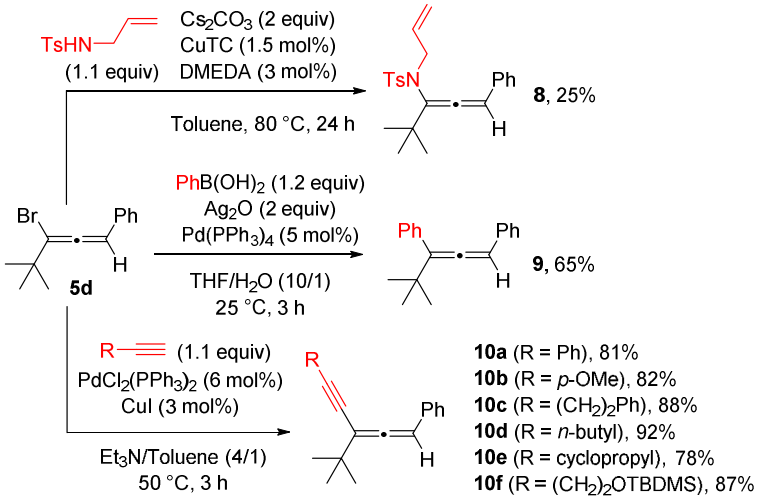
Scheme 7. Reactions with NIS (E = CO_2Me)



To illustrate the utility of our methodology, we carried out functionalizations of bromoallene **5d** (Scheme 8). A copper-catalyzed C-N coupling[2f] involving *N*-allyl-4-methylbenzenesulfonamide enabled the formation of **8** with an uncompleted conversion and a moderate yield of 25%. A Suzuki-Miyaura cross-coupling[2g] was also performed and proved more efficient, as compound **9** could be isolated in 65% yield. Finally, the Sonogashira cross-coupling[2l] was studied and provided the 1,3-allenynes **10a-f** with a large tolerance on the alkyne moiety and

excellent yields without purification by column chromatography.[29] As above, the products were simply isolated by filtration on silica gel. The conjugated allenyne scaffold is actually commonly found in natural products and is a useful building block in organic synthesis.[1,30]

Scheme 8. Derivatization of Bromoallene **5d**



In conclusion, an efficient and straightforward procedure for the synthesis of trisubstituted 3-bromo-1-phenylallenes from 7-alkynylcycloheptatrienes and NBS has been developed. The products can then be used to easily introduce allene moiety by cross-coupling reactions.

EXPERIMENTAL SECTION

General Information. All reactions were performed in oven-dried flasks. Unless otherwise stated, products were purified by flash chromatography on silica gel. Reactions in overheated solvent were performed in 10 mL reaction tubes sealed with a Teflon-coated Rodaviss® stopper and immersed in a pre-heated oil bath when necessary. Reactions were monitored using thin-layer chromatography (TLC) on silica gel plates (0.25 mm) pre-coated with a fluorescent indicator. The spots were visualized with ultraviolet light and/or *p*-anisaldehyde stain with heat as revealing

agent. Flash column chromatography was performed on CombiFlash System with silica gel. NMR characterization data was collected at 296 K on a AM 250, AV 300, AV 360 Bruker spectrometers, operating at 250, 300, and 360 MHz respectively for ^{1}H NMR. ^{1}H NMR chemical shifts are reported in ppm using residual solvent peak as reference ($CHCl_3$: δ = 7.27 ppm). Data for ^{1}H NMR are presented as follows: chemical shift δ (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constant J (Hz) and integration; ^{13}C NMR spectra were recorded at 296 K on AM 250, AV 300, AV 360 Bruker spectrometers, operating at 63, 75, and 90 MHz respectively, using broadband proton decoupling. Chemical shifts are reported in ppm using residual solvent peaks as reference ($CHCl_3$: δ = 77.16 ppm). Melting points were determined using a Reichert melting point apparatus. IR characterization data were recorded on a FT-IR spectrometer (Perkin-Elmer). HRMS was performed on a MicrOTOFq Bruker spectrometer (ESI) or on a Q-TOF Agilent (APPI). Deprotonated molecular ions $[M - H]^-$, protonated molecular ions $[M + H]^+$, or sodium adducts $[M + Na]^+$ were used for empirical formula confirmation. Compounds **4f, 5b**, **5h**, **10d** and **10f** proved too apolar and too sensitive to allow mass-spectroscopy analysis.

Materials. Reagents were purchased from commercially suppliers (Alfa Aesar, Sigma Aldrich or Strem) and used as received, unless stated otherwise. Solvents were dried by distillation under argon from the followings: tetrahydrofuran (sodium/benzophenone); toluene (sodium); 1,2-dichloroethane (calcium hydride). Organic extracts were, in general, dried over anhydrous magnesium sulfate ($MgSO_4$). 1,6-Arenynes **S1a-d,**[31a-d] 1,6-enynes **S1e-f,**[32,] 1,6-arenyne **S4f**, [31c] and compounds **1a**,[21] **1f**,[17a] **4c**,[17a] **4j**,[17a] were synthetized according to the literature.

Procedure for the synthesis of the 7-alkynylcycloheptatrienes.

The alkyne (1 equiv) was placed in an oven-dried 250 mL screw-cap tube fitted with a septum under a nitrogen atmosphere. Dry THF (0.1 M) was added and the resulting solution was cooled to -78 ºC before adding *n*-BuLi (1.5 equiv) and stirred for 1 h at this temperature. Tropylium tetrafluoroborate (1.2 equiv) was added, and then, the cooling bath was removed. After stirring the mixture at RT for 20 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl (30 mL) and the aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography on silica gel (80 g of silica, Cy/AcOEt, 100:0 to 97:3) to afford the desired product.

Compound 1b. Following the general procedure, **1b** was obtained from **S1b** (1.39 g, 4.8 mmol, 1 equiv) as a colorless oil (0.9 g, 2.4 mmol, 49%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.19 (t, J = 8.0 Hz, 1H), 6.80-6.77 (m, 1H), 6.76-6.72 (m, 2H), 6.66 (dd, J = 3.7, 2.7 Hz, 2H), 6.18 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.34 (dd, J = 8.8, 5.5 Hz, 2H), 3.76 (s, 6H), 3.40 (s, 2H), 2.73 (d, J = 2.4 Hz, 2H), 2.57-2.51 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4 (2 C=O), 159.7 (C), 137.3 (C), 131.2 (2 CH), 129.5 (CH), 124.9 (2 CH), 123.8 (2 CH), 122.3 (CH), 115.8 (CH), 112.6 (CH), 85.9 (C), 75.4 (C), 58.7 (C), 55.2 (CH_3), 52.8 (2 CH_3), 37.7 (CH_2), 31.8 (CH), 22.7 (CH_2). FT-IR (neat, cm^{-1}): 3024, 2956, 1737, 1641, 1610, 1490, 1434, 1304, 1282, 1263, 1242, 1208, 1180, 1053. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{24}O_5Na$ 403.1516; Found 403.1502.

Compound 1c. Following the general procedure, **1c** was obtained from **S1c** (1.3 g, 4.5 mmol) as a yellow oil (0.82 g, 2.2 mmol, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.87 (s, 1H), 6.76 (s, 2H), 6.67 (dd, J = 3.7, 2.7 Hz, 2H), 6.19 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.35 (dd, J = 8.8, 5.5 Hz, 2H), 3.75 (s, 6H), 3.34 (s, 2H), 2.71 (d, J = 2.4 Hz, 2H), 2.58-2.52 (m, 1H), 2.27 (s, 6H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 170.5 (2 C=O), 137.9 (2 C), 135.6 (C), 131.2 (2 CH), 128.9 (CH),

127.8 (2 CH), 124.9 (2 CH), 123.8 (2 CH), 85.7 (C), 75.5 (C), 58.8 (C), 52.7 (2 CH_3), 37.6 (CH_2), 31.8 (CH), 22.6 (CH_2), 21.5 (2 CH_3). FT-IR (neat, cm^{-1}): 3026, 2952, 1738, 1642, 1606, 1435, 1334, 1296, 1275, 1241, 1206, 1067, 1051. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{26}O_4Na$ 401.1723; Found 401.1723.

Compound 1d. Following the general procedure, **1d** was obtained from **S1d** (1.8 g, 5.8 mmol) as a yellow oil (1.2 g, 3.0 mmol, 52%). ^1H NMR (360 MHz, $CDCl_3$): δ 7.83-7.74 (m, 3H), 7.65 (s, 1H), 7.47-7.43 (m, 2H), 7.28 (dd, J = 8.1 Hz, J = 2.0 Hz, 1H), 6.69 (dd, J = 3.7, 2.7 Hz, 2H), 6.22 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.39 (dd, J = 8.8, 5.5 Hz, 2H), 3.77 (s, 6H), 3.59 (s, 2H), 2.75 (d, J = 2.4 Hz, 2H), 2.62-2.57 (m, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.5 (2 C=O), 133.5 (C), 133.3 (C), 132.7 (C), 131.2 (2 CH), 128.9 (CH), 128.2 (CH), 128.0 (CH), 127.8 (CH), 127.8 (CH), 126.2 (CH), 125.9 (CH), 125.0 (2 CH), 123.8 (2 CH), 85.9 (C), 75.4 (C), 58.9 (C), 52.9 (2 CH_3), 37.9 (CH_2), 31.8 (CH), 22.7 (CH_2). FT-IR (neat, cm^{-1}): 3025, 2652, 1738, 1601, 1436, 1330, 1288, 1243, 1204, 1065, 1050. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{24}O_4Na$ 423.1567; Found 423.1547.

Compound 1e. Following the general procedure, **1e** was obtained from **S1e** (1.0 g, 4.8 mmol, 1 equiv) as a pale yellow oil (0.77 g, 2.6 mmol, 54%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.64 (dd, J = 3.7, 2.3 Hz, 2H), 6.19-6.11 (m, 2H), 5.65 (ddt, J = 17.0, 10.0, 7.4 Hz, 1H), 5.26 (dd, J = 9.3, 5.7 Hz, 2H), 5.22-5.10 (m, 2H), 3.74 (s, 6H), 2.85-2.81 (m, 4H), 2.48-2.41 (m, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 170.5 (2 C=O), 132.0 (CH), 131.1 (2 CH), 124.8 (2 CH), 123.9 (2 CH), 119.9 (CH_2), 85.1 (C), 74.9 (C), 57.4 (C), 52.9 (2 CH_3), 36.8 (CH_2), 31.8 (CH), 23.1 (CH_2). FT-IR (neat, cm^{-1}): 2953, 1739, 1437, 1327, 1291, 1250, 1218, 1141. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{20}O_4Na$ 323.1254; Found 323.1248.

Compound 4a. Following the general procedure, **4a** was obtained from 1-pentyne (1.0 ml, 10.1 mmol, 1 equiv) as a yellow oil (1.5 g, 9.5 mmol, 94%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.65 (dd, J = 3.7, 2.7 Hz, 2H), 6.16 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.33 (dd, J = 8.8, 5.5 Hz, 2H), 2.48-2.42 (m, 1H), 2.21 (td, J = 7.2, 2.4 Hz, 2H), 1.61-1.51 (m, 2H), 1.01 (t, J = 7.2 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 131.1 (2 CH), 124.5 (4 CH), 81.8 (C), 80.6 (C), 31.9 (CH), 22.5 (CH_2), 20.9 (CH_2), 13.6 (CH_3). FT-IR (neat, cm^{-1}): 3014, 2963, 1933, 1873, 1635, 1453, 1390, 1329, 1281. HRMS (APPI) *m/z*: $[M - H]^-$ Calcd for $C_{12}H_{13}$ 157.1023; Found 157.1012.

Compound 4b. Following the general procedure, **4b** was obtained from 1-octyne (1.0 ml, 6.7 mmol, 1 equiv) as a yellow oil (1.18 g, 5.9 mmol, 88%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.64 (dd, J = 3.7, 2.7 Hz, 2H), 6.15 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.32 (dd, J = 8.8, 5.5 Hz, 2H), 2.47-2.41 (m, 1H), 2.22 (td, J = 7.2, 2.4 Hz, 2H), 1.58-1.48 (m, 2H), 1.46-1.38 (m, 2H), 1.35-1.26 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 131.1 (2 CH), 124.5 (4 CH), 81.6 (C), 80.8 (C), 32.0 (CH), 31.5 (CH_2), 29.1 (CH_2), 28.7 (CH_2), 22.8 (CH_2), 18.9 (CH_2), 14.2 (CH_3). FT-IR (neat, cm^{-1}): 3052, 3023, 3013, 2954, 2932, 2856, 1466, 1390, 1279. HRMS (APPI) *m/z*: $[M]^+$ Calcd for $C_{15}H_{21}$ 201.1643; Found 201.1640.

Compound 4d. Following the general procedure, **4d** was obtained from 3,3-dimethyl-1-butyne (1.0 ml, 8.0 mmol, 1 equiv) as a yellow oil (1.22 g, 7.1 mmol, 88%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.64 (dd, J = 3.7, 2.7 Hz, 2H), 6.14 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.31 (dd, J = 8.8, 5.5 Hz, 2H), 2.39-2.43 (m, 1H), 1.25 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 131.0 (2 CH), 124.8 (2 CH), 124.4 (2 CH), 89.3 (C), 80.0 (C), 31.9 (CH), 31.4 (3 CH_3), 27.5 (C). FT-IR (neat, cm^{-1}): 3027, 2968, 2867, 1698, 1601, 1475, 1457, 1390, 1361, 1284, 1204, 1094. HRMS (APPI) *m/z*: $[M - H]^-$ Calcd for $C_{13}H_{15}$ 171.1168; Found 171.1168.

Compound 4e. Following the general procedure, **4e** was obtained from 3-methoxyprop-1-yne (0.7 g, 10.0 mmol, 1 equiv) as a yellow oil (1.17 g, 7.3 mmol, 73%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.65 (dd, J = 3.7, 2.7 Hz, 2H), 6.17 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.34 (dd, J = 8.8, 5.5 Hz, 2H), 4.16 (d, J = 2.0 Hz, 2H), 3.41 (s, 3H), 2.57-2.51 (m, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 131.1 (2 CH), 124.7 (2 CH), 123.2 (2 CH), 88.2 (C), 76.1 (C), 60.2 (CH_2), 57.6 (CH_3), 31.8 (CH). FT-IR (neat, cm^{-1}): 3027, 2934, 2820, 2236, 1699, 1602, 1464, 1449, 1391, 1377, 1357, 1278, 1187, 1142, 1099. MS (IE) *m/z*: $[M]^+$ Calcd for $C_{11}H_{12}O$ 160.09; Found 160.00.

Compound 4f. Following the general procedure, **4f** was obtained from **S4f** (2.0 g, 13.7 mmol) as a dark yellow oil (2.5 g, 10.6 mmol, 77%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.40-7.34 (m, 4H), 7.33-7.28 (m, 1H), 6.67 (dd, J = 3.7, 2.2 Hz, 2H), 6.21-6.15 (m, 2H), 5.35 (dd, J = 9.0, 5.5 Hz, 2H), 4.63 (s, 2H), 4.24 (d, J = 2.2 Hz, 2H), 2.60-2.54 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.7 (C), 131.1 (2 CH), 128.6 (2 CH), 128.3 (2 CH), 128.0 (CH), 124.9 (2 CH), 123.2 (2 CH), 88.3 (C), 76.2 (C), 71.6 (CH_2), 57.8 (CH_2), 31.9 (CH). FT-IR (neat, cm^{-1}): 3028, 2853, 1698, 1603, 1593, 1495, 1454, 1390, 1354, 1260. HRMS (ESI) *m/z*: $[M + Na]^+$ $C_{17}H_{16}ONa$ 259.1093; Found 259.1094.

Compound 4h. Following the general procedure, **4h** was obtained from (but-3-yn-1-yloxy)(tert-butyl)dimethylsilane[33] (2.0 g, 10.9 mmol, 1 equiv) as a yellow oil (1.2 g, 4.4 mmol, 41%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.64 (dd, J = 3.7, 2.7 Hz, 2H), 6.15 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.31 (dd, J = 8.8, 5.5 Hz, 2H), 3.75 (t, J = 7.1 Hz, 2H), 2.48-2.41 (m, 3H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 131.1 (2 CH), 124.6 (2 CH), 124.2 (2 CH), 82.8 (C), 77.4 (C), 62.4 (CH_2), 31.9 (CH), 36.1 (3 CH_3), 23.3 (CH_2), 18.5 (C), -5.1 (2 CH_3). FT-IR (neat, cm^{-1}): 3029, 2955, 2929, 2857, 1471, 1463, 1390, 1255, 1105, 1058. HRMS (ESI) *m/z*: $[M + Na]^+$ $C_{17}H_{26}OSiNa$ 297.1645; Found 297.1642.

Compound 4i. Following the general procedure, **4i** was obtained from 1-(prop-2-yn-1-yl)cyclohex-1-ene (1.0 g, 8.3 mmol, 1 equiv) as a yellow oil (1.69 g, 8.3 mmol, 97%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.68 (dd, J = 3.7, 2.7 Hz, 2H), 6.17 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 6.11 (tt, J = 4.1, 2.0 Hz, 1H), 5.34 (dd, J = 8.8, 5.5 Hz, 2H), 2.58 (tt, J = 5.6, 1.5 Hz, 1H), 2.17-2.12 (m, 2H), 2.12-2.06 (m, 2H), 1.68-1.54 (m, 5H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 134.3 (CH), 131.1 (2 CH), 124.6 (2 CH), 123.9 (2 CH), 120.8 (C), 88.3 (C), 82.5 (C), 32.3 (CH), 29.6 (CH_2), 25.7 (CH_2), 22.5 (CH_2), 21.7 (CH_2). FT-IR (neat, cm^{-1}): 3026, 2929, 2858, 2835, 1697, 1633, 1601, 1447, 1435, 1390, 1347, 1285, 1266, 1136, 1076, 1051. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{16}$ 197.1330; Found 197.1322.

Synthesis of 7-alkynylcycloheptatriene 4g. In a 100 mL round bottom flask, **4h** (1.4 g, 5.1 mmol, 1 equiv) and THF (20 mL) was introduced. Tetrabutylammonium fluoride solution (5.1 mL, 5.1 mmol, 1 M in THF) was added slowly and the resulting solution was stirred at RT during 1 hour. Then, H_2O was added and the mixture was stirred for 30 min. The aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic extracts were washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude reaction mixture was purified by chromatography on silica gel (80 g of silica, Cy/AcOEt, 100:0 to 80:20) to afford **4g** (0.67 g, 4.2 mmol, 82%) as a yellow liquid. ^{1}H NMR (360 MHz, $CDCl_3$): δ 6.65 (dd, J = 3.7, 2.7 Hz, 2H), 6.16 (dddd, J = 8.8, 3.7, 2.7, 1.5 Hz, 2H), 5.31 (dd, J = 8.8, 5.5 Hz, 2H), 3.77-3.70 (m, 2H), 2.53-2.48 (m, 3H), 1.90 (brs, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 131.1 (2 CH), 124.8 (2 CH), 123.7 (2 CH), 83.9 (C), 76.9 (C), 61.4 (CH_2), 31.7 (CH), 23.3 (CH_3). FT-IR (neat, cm^{-1}): 3344, 3026, 2938, 1391, 1282, 1182. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{11}H_{12}ONa$ 183.0776; Found 183.0780.

Procedure for the Formation of Compounds 2a-f. In air, substrate **1b-f** (1 equiv), NBS (3 equiv) and dry DCE (0.2 M) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The tube was sealed with a plastic stopper and the mixture was stirred at the indicated temperature during the indicating time with TLC reaction progress monitoring. Then, the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_4$ (5 mL) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (12 g of SiO_2 previously treated by 5% of Et_3N, Cy/EtOAc, 100:0 to 95:5) to afford bromoallene **2b-f**.

Compound 2a. The general procedure was followed with **1a** (30 mg, 0.09 mmol) to afford **2a** as a colorless oil (24.5 mg, 0.06 mmol, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (s, 2H), 7.38-7.37 (m, 2H), 7.32-7.24 (m, 4H), 7.15-7.11 (m, 2H), 6.34 (dd, J = 3.2, 3.2 Hz, 1H), 3.69 (s, 3H), 3.55 (s, 3H), 3.38 (s, 2H), 3.25 (dd, J = 16.6, 3.2 Hz, 1H), 3.08 (dd, J = 16.6, 3.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.7 (C), 170.1 (C=O), 170.0 (C=O), 135.7 (C), 132.1 (C), 130.0 (2 CH), 129.0 (2 CH), 128.8 (CH), 128.5 (2 CH), 128.3 (2 CH), 127.3 (CH), 102.3 (CH), 89.8 (C), 58.8 (C), 52.8 (2 CH_3), 39.5 (CH_2), 37.5 (CH_2). FT-IR (neat, cm^{-1}): 2949, 2620, 1952, 1736, 1603, 1437, 1335, 1273, 1239, 1215, 1065. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}O_4BrNa$ 451.0515; Found 451.0497.

Compound 2b. The general procedure was followed with **1b** (40 mg, 0.11 mmol) to afford **2b** as a colorless oil (30.0 mg, 0.07 mmol, 62%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.38-7.35 (m, 4H), 7.32-7.26 (m, 1H), 7.17 (t, J = 8.1 Hz, 1H), 6.77 (dd, J = 8.1, 2.6 Hz, 1H), 6.69-6.65 (m, 2H), 6.32 (dd, J = 3.2, 3.2 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.54 (s, 3H), 3.33 (s, 2H), 3.24 (dd, J = 16.6, 3.2 Hz, 1H), 3.07 (dd, J = 16.6, 3.2 Hz, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 200.8 (C),

170.2 (C=O), 170.0 (C=O), 159.7 (C), 137.2 (C), 132.2 (C), 129.5 (CH), 129.1 (2 CH), 128.9 (CH), 128.3 (2 CH), 122.3 (CH), 115.5 (CH), 113.1 (CH), 102.3 (CH), 89.9 (C), 58.8 (C), 55.3 (CH_3), 52.9 (CH_3), 52.8 (CH_3), 39.5 (CH_2), 37.5 (CH_2). FT-IR (neat, cm^{-1}): 2952, 2836, 1950, 1738, 1600, 1584, 1489, 1452, 1434, 1282, 1263, 1203, 1181, 1054, 1043. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{23}H_{23}O_5BrNa$ 481.0621; Found 481.0621.

Compound 2c. The general procedure was followed with **1c** (40 mg, 0.11 mmol) to afford **2c** as a colorless oil (25.1 mg, 0.05 mmol, 52%). ^1H NMR (360 MHz, $CDCl_3$): δ 7.39-7.35 (m, 4H), 7.32-7.28 (m, 1H), 6.85 (s, 1H), 6.70 (s, 2H), 6.32 (dd, J = 3.2, 3.2 Hz, 1H), 3.69 (s, 3H), 3.54 (s, 3H), 3.28 (s, 2H), 3.21 (dd, J = 16.6, 3.2 Hz, 1H), 3.04 (dd, J = 16.6, 3.2 Hz, 1H), 2.23 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 201.0 (C), 170.3 (C=O), 170.2 (C=O), 137.8 (2 C), 135.3 (C), 132.2 (C), 128.9 (2 CH), 128.8 (CH), 128.7 (CH), 128.2 (2 CH), 127.7 (2 CH), 102.1 (CH), 89.8 (C), 58.7 (C), 52.6 (CH_3), 52.6 (CH_3), 39.3 (CH_2), 37.3 (CH_2), 21.3 (2 CH_3). FT-IR (neat, cm^{-1}): 2951, 2621, 1950, 1739, 1605, 1434, 1333, 1275, 1236, 1212, 1068. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{25}O_4BrNa$ 479.0828; Found 479.0826.

Compound 2d. The general procedure was followed with **1d** (50 mg, 0.12 mmol) to afford **2d** as a colorless oil (40.7 mg, 0.08 mmol, 68%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (dd, J = 6.0, 3.3 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.69 (dd, J = 6.0, 3.3 Hz, 1H), 7.59 (s, 1H), 7.46-7.42 (m, 2H), 7.41-7.34 (m, 4H), 7.33-7.29 (m, 1H), 7.21 (dd, J = 8.5, 1.8 Hz, 1H), 6.37 (dd, J = 3.2, 3.2 Hz, 1H), 3.69 (s, 3H), 3.55 (s, 3H), 3.53 (s, 2H), 3.26 (dd, J = 16.6, 3.2 Hz, 1H), 3.09 (dd, J = 16.6, 3.2 Hz, 1H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 201.1 (C), 170.2 (C=O), 170.1 (C=O), 133.5 (C), 133.3 (C), 132.6 (C), 132.3 (C), 129.2 (CH), 129.1 (2 CH), 128.9 (CH), 128.4 (2 CH), 128.1 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 126.3 (CH), 125.9 (CH), 102.3 (CH), 89.8 (C), 59.0 (C), 52.9 (2 CH_3), 39.7 (CH_2), 37.8 (CH_2). FT-IR (neat, cm^{-1}): 2951, 1949, 1738, 1434, 1332,

1286, 1215, 1068. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{23}O_4BrNa$ 501.0672; Found 501.0682.

Compound 2e.The general procedure was followed with **1e** (50 mg, 0.17 mmol) to afford **2e** as a colorless oil (49.2 mg, 0.13 mmol, 78%). ^1H NMR (360 MHz, $CDCl_3$): δ 7.39-7.35 (m, 1H), 7.34-7.32 (m, 2H), 7.31-7.27 (m, 2H), 6.21 (dd, J = 3.2, 3.2 Hz, 1H), 5.70-5.58 (m, 1H), 5.12-5.05 (m, 2H), 3.69 (s, 3H), 3.60 (s, 3H), 3.24 (dd, J = 16.6, 3.2 Hz, 1H), 3.16 (dd, J = 16.6, 3.2 Hz, 1H), 2.99 (d, J = 7.6 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 201.4 (C), 170.4 (C=O), 170.3 (C=O), 132.2 (C), 132.1 (CH), 129.0 (2 CH), 128.8 (CH), 128.3 (2 CH), 119.9 (CH_2), 101.4 (CH), 89.0 (C), 57.7 (C), 52.8 (2 CH_3), 40.3 (CH_2), 36.5 (CH_2). FT-IR (neat, cm^{-1}): 3029, 2972, 2950, 2868, 1950, 1738, 1604, 1494, 1430, 1382, 1254, 1205, 1116, 1074. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{18}H_{19}O_4BrNa$ 401.0364; Found 401.0355.

Compound 2f. The general procedure was followed with **1f** (50 mg, 0.13 mmol) to afford **2f** as a colorless oil (43.0 mg, 0.09 mmol, 71%, mixture of isomers, *E*/*Z* : 80/20). ^1H NMR (300 MHz, $CDCl_3$, major isomer): δ 7.25-7.18 (m, 4H), 7.17-7.10 (m, 6H), 6.30 (d, J = 15.7 Hz, 1H), 6.16 (dd, J = 3.2, 3.2 Hz, 1H), 5.97-5.82 (m, 1H), 3.68 (s, 3H), 3.61 (s, 3H), 3.27 (dd, J = 16.6, 2.6 Hz, 1H), 3.19 (dd, J = 16.6, 2.6 Hz, 1H), 2.80 (d, J = 7.2 Hz, 2H). ^{13}C NMR (90 MHz, $CDCl_3$, major isomer): δ 201.5 (C), 170.4 (C=O), 170.3 (C=O), 137.0 (C), 134.7 (CH), 132.2 (C), 129.0 (2 CH), 128.8 (CH), 128.6 (2 CH), 128.3 (2 CH), 126.4 (CH), 126.3 (2 CH), 123.4 (CH), 101.3 (CH), 88.9 (C), 57.9 (C), 52.9 (2 CH_3), 40.5 (CH_2), 35.8 (CH_2). FT-IR (neat, cm^{-1}): 3029, 2971, 2951, 2870, 1948, 1738, 1601, 1492, 1433, 1382, 1254, 1205, 1116, 1076. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{24}H_{23}O_4BrNa$ 477.0672; Found 477.0637.

Procedure for formation of compounds 5a-j (Scheme 5). In air, substrate **5a-j** (1 equiv), NBS (1.1-2 equiv) and dry DCE (0.2 M) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The tube was sealed with a plastic stopper and the mixture was stirred at RT during 6 h. Then, the crude mixture was filtrated over a pad of silica previously treated by 5% of Et_3N (unless otherwise stated) and rinsed with cyclohexane to afford bromoallene **5a-j** after evaporation.

Compound 5a. The general procedure was followed with **4a** (50 mg, 0.32 mmol) to afford **5a** as a colorless oil (55.7 mg, 0.24 mmol, 74%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H), 7.31-7.27 (m, 1H), 6.22 (dd, J = 2.7, 2.7 Hz, 1H), 2.53 (td, J = 7.2, 2.4 Hz, 2H), 1.72-1.56 (m, 2H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 200.0 (C), 133.1 (C), 128.9 (2 CH), 128.3 (CH), 127.9 (2 CH), 100.5 (CH), 96.0 (C), 40.2 (CH_2), 21.5 (CH_2), 13.4 (CH_3). FT-IR (neat, cm^{-1}): 2960, 2930, 2870, 1949, 1494, 1459, 1380, 1233, 1195, 1103, 1073. HRMS (APPI): *m/z*: $[M - H]^-$ Calcd for $C_{12}H_{12}Br$ 235.0112; Found 235.0116.

Compound 5b. The general procedure was followed with **4b** (50 mg, 0.25 mmol) to afford **5b** as a colorless oil (57.8 mg, 0.21 mmol, 83%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.38-7.34 (m, 4H), 7.31-7.26 (m, 1H), 6.23 (dd, J = 2.7, 2.7 Hz, 1H), 2.56 (td, J = 7.2, 2.4 Hz, 2H), 1.68-1.56 (m, 2H), 1.43-1.28 (m, 6H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 199.9 (C), 133.1 (C), 128.9 (2 CH), 128.3 (CH), 127.9 (2 CH), 100.5 (CH), 96.3 (C), 38.2 (CH_2), 31.6 (CH_2), 28.4 (CH_2), 28.1 (CH_2), 22.7 (CH_2), 14.2 (CH_3). FT-IR (neat, cm^{-1}): 2959, 2932, 2872, 1952, 1496, 1457, 1379, 1235, 1193, 1101, 1072.

Compound 5c. The general procedure was followed with **4c** (50 mg, 0.23 mmol) to afford **5c** as a colorless oil (57.7 mg, 0.19 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.25 (m, 8H),

7.15-7.11 (m, 2H), 6.18 (dd, J = 2.7, 2.7 Hz, 1H), 3.01-2.95 (m, 2H), 2.92-2.85 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 200.3 (C), 140.4 (C), 132.8 (C), 128.8 (3 CH), 128.6 (2 CH), 128.3 (CH), 128.0 (2 CH), 126.3 (CH), 100.8 (CH), 95.0 (C), 39.8 (CH_2), 34.2 (CH_2). FT-IR (neat, cm^{-1}): 3587, 3567, 3423, 3057, 3027, 2919, 1948, 1601, 1494, 1453, 1194, 1075, 1027, 1015. HRMS (APPI): *m/z*: $[M]^+$ Calcd for $C_{17}H_{15}Br$ 298.0357; Found 298.0349.

Compound 5d. The general procedure was followed with **4d** (50 mg, 0.29 mmol) to afford **5d** as a colorless oil (69.4 mg, 0.28 mmol, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.32 (m, 4H), 7.31-7.24 (m, 1H), 6.22 (s, 1H), 1.29 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5 (C), 133.3 (C), 128.9 (2 CH), 128.2 (CH), 127.7 (2 CH), 108.5 (C), 100.4 (CH), 37.8 (C), 29.3 (3 CH_3). FT-IR (neat, cm-1): 2967, 2928, 1947, 1474, 1457, 1362, 1242, 1143, 1025. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{15}Br$ 251.0435; Found 251.0429.

Compound 5e. The general procedure was followed with **4e** (50 mg, 0.31 mmol) to afford **5e** as a colorless oil (36.7 mg, 0.15 mmol, 49%). ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.37-7.34 (m, 4H), 7.37-7.34 (m, 1H), 6.36 (dd, J = 2.7, 2.7 Hz, 1H), 4.24 (d, J = 2.4 Hz, 2H), 3.42 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 200.9 (C), 132.1 (C), 128.9 (2 CH), 128.6 (CH), 128.1 (2 CH), 101.8 (CH), 91.7 (C), 74.5 (CH_2), 57.9 (CH_3). FT-IR (neat, cm^{-1}): 2968, 2930 1948, 1651, 1494, 1459, 1352, 1193, 1105, 1026. HRMS (ESI) *m/z*: $[2M + Na]^+$ Calcd for $C_{22}H_{22}O_2Br_2Na$ 498.9879; Found 498.9869.

Compound 5f. The general procedure was followed with **4f** (40 mg, 0.17 mmol) to afford **5f** as a colorless oil (55.5 mg, 0.08 mmol, 49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.32 (m, 8H), 7.31-7.27 (m, 2H), 6.37 (dd, J = 2.4, 2.4 Hz, 1H), 4.61 (d, J = 4.0 Hz, 2H), 4.33 (d, J = 2.4 Hz, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 201.2 (C), 137.6 (C), 132.2 (C), 129.1 (2 CH), 128.8 (CH),

128.6 (2 CH), 128.2 (4 CH), 128.0 (CH), 102.0 (CH), 92.0 (C), 72.2 (CH_2), 72.1 (CH_2). FT-IR (neat, cm^{-1}): 2968, 2930 1948, 1651, 1494, 1459, 1352, 1193, 1105, 1026. HRMS (ESI) *m/z*: [M + Na]$^+$ Calcd for $C_{17}H_{15}OBrNa$ 337.0198; Found 337.0190.

Compound 5h. The general procedure was followed with **4h** (100 mg, 0.36 mmol) to afford **5h** as a colorless oil (62 mg, 0.18 mmol, 48%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.30 (m, 4H), 7.29-7.26 (m, 1H), 6.19 (dd, J = 2.7, 2.7 Hz, 1H), 3.83 (td, J = 6.3, 2.7 Hz, 2H), 2.72 (dt, J = 6.3, 2.7 Hz, 2H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.9 (C), 132.9 (C), 128.9 (2 CH), 128.4 (CH), 128.1 (2 CH), 100.4 (CH), 92.7 (C), 61.0 (CH_2), 41.4 (CH_2), 26.1 (3 CH_3), 18.5 (C), -5.1 (CH_3), -5.2 (CH_3). FT-IR (neat, cm^{-1}): 2950, 2929, 2859, 1949, 1651, 1472, 1462, 1255, 1106, 1076.

Compound 5j.The general procedure was followed with **4j** (50 mg, 0.27 mmol) to afford **5j** as a colorless oil (55.3 mg, 0.21 mmol, 78%). 1H NMR (360 MHz, CDCl3): δ 7.36-7.32 (m, 4H), 7.29-7.26 (m, 1H), 6.10 (s, 1H), 0.27 (s, 9H). 13C NMR (90 MHz, CDCl3): δ 204.7 (C), 132.8 (C), 129.0 (2 CH), 128.1 (CH), 127.5 (2 CH), 98.0 (CH), 89.9 (C), -1.5 (3 CH3). FT-IR (neat, cm-1): 3061, 3330, 2960, 1941, 1495, 1456, 1250, 1185, 1046, 1027. HRMS (APPI): *m/z*: [M – Br]$^+$ Calcd for $C_{12}H_{15}Si$ 187.0943; Found 187.0939.

Compound 3a (Scheme 3). In air, substrate **1a** (50 mg, 0.14 mmol, 1 equiv), NBS (76.2 mg, 0.064 mmol, 3 equiv) and DCE (0.7 mL) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The tube was sealed with a plastic stopper and the mixture was stirred at 80 °C during 24 h. Then, the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_4$ (5 mL) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pres-

sure. The crude product was purified by flash chromatography (12 g of SiO_2 previously treated by 5% of Et_3N, Cy/EtOAc, 100:0 to 95:5) to afford the bromoenone **3a** (28.6 mg, 0.06 mmol, 45%) as a yellow oil. The structure was confirmed by X-ray diffraction of crystals of **3a** (see Supporting Information).^{1}H NMR (360 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.91-7.83 (m, 2H), 7.46-7.43 (m, 2H), 7.34 (dd, J = 5.3, 2.1 Hz, 1H), 7.24 (dd, J = 2.1, 1.2 Hz, 2H), 7.19 (dd, J = 5.3, 2.8 Hz, 1H), 6.96 (dd, J = 7.5, 2.0 Hz, 2H), 3.79 (s, 6H), 3.71 (s, 2H), 3.48 (d, J = 2.8 Hz, 2H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 192.7 (C=O), 170.7 (2 C=O), 140.2 (CH), 140.0 (C), 136.1 (C), 130.8 (3 CH), 130.2 (2 CH), 128.7 (2 CH), 128.6 (2 CH), 127.4 (CH), 122.2 (C), 57.1 (C), 53.1 (2 CH_3), 41.2 (CH_2), 38.6 (CH_2). FT-IR (neat, cm^{-1}): 2952, 2097, 1736, 1642, 1494, 1446, 1434, 1277, 1242, 1179, 1152, 1080, 1057. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{21}O_5BrNa$ 467.0470; Found 467.0443.

Compound 6 (Scheme 7). In air, substrate **1a** (50 mg, 0.14 mmol, 1 equiv), NIS (35.3 mg, 0.16 mmol, 1.1 equiv) and DCE (0.7 mL) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The tube was sealed with a plastic stopper and the mixture was stirred at RT during 1 hour. Then, the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_4$ (5 mL) and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (12 g of SiO_2, Cy/EtOAc, 100:0 to 95:5) to afford **6** (30.4 mg, 0.06 mmol, 45%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30-7.26 (m, 3H), 7.08-7.03 (m, 2H), 7.02-6.97 (m, 3H), 4.59 (dd, J = 2.3, 2.3 Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 3.45 (dd, J = 16.0, 3.6 Hz, 1H), 3.39 (dd, J = 16.0, 3.6 Hz, 1H), 3.19 (dd, J = 16.4, 2.3 Hz, 1H), 3.09 (dd, J = 16.4, 2.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2 (C=O), 171.0 (C=O), 147.3 (C), 143.3 (C), 140.1 (C), 138.4 (C), 128.9 (2 CH), 128.5 (2 CH), 127.5

(CH), 126.6 (CH), 125.4 (CH), 122.2 (CH), 99.0 (C), 63.7 (CH), 55.7 (C), 53.2 (CH_3), 53.1 (CH_3), 33.9 (CH_2), 33.4 (CH_2). FT-IR (neat, cm^{-1}): 3030, 2952, 2917, 2849, 1737, 1685, 1599, 1493, 1447, 1433, 1396, 1279, 1245, 1202, 1183, 1158, 1080, 1061, 1035. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{22}H_{19}O_4INa$ 497.0226; Found 497.0230.

Compound 7 (Scheme 7). In air, substrate **1d** (40 mg, 0.23 mmol, 1 equiv), NIS (58 mg, 0.26 mmol, 1.1 equiv) and dry DCE (1.1 mL) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The tube was sealed with a plastic stopper and the mixture was stirred at RT during 5 h. Then, the reaction was filtrated over a pad of silica (unless otherwise stated) previously treated by 5% of Et_3N and rinsed with cyclohexane to afford iodoallene **7** (48.2 mg, 0.16 mmol, 70%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40-7.25 (m, 5H), 5.96 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 201.0 (C), 133.3 (C), 129.0 (2 CH), 127.9 (CH), 127.6 (2 CH), 96.0 (CH), 83.2 (C), 38.0 (C), 29.9 (3 CH_3). FT-IR (neat, cm^{-1}): 2968, 2931, 2868, 2211, 1685, 1648, 1599, 1492, 1476, 1453, 1393, 1363, 1271, 1071. HRMS (APPI): *m/z*: $[M - I]^+$ Calcd for $C_{13}H_{15}$ 171.1174; Found 171.1174.

Compound 8 (Scheme 8). Following the procedure reported by Bäckvall,[2q] *N*-allyl-4-methylbenzenesulfonamide (33.7 mg, 0.16 mmol, 1.0 equiv), copper(I) thiophene-2-carboxylate (CuTC) (4.6 mg, 0.02 mmol, 0.15 equiv), Cs_2CO_3 (104 mg, 0.32 mmol, 2.0 equiv) and dry toluene (0.9 mL) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. The resulting mixtures was stirred for 2-3 minutes and then *N*,*N*'-dimethylethylenediamine (DMEDA) (4.2 mg, 0.05 mmol, 0.30 equiv) and bromoallene **5d** (100 mg, 0.40 mmol, 2.5 equiv) were added. The tube was sealed, wrapped in aluminum foil and stirred at 80 °C for 24 h. The reaction was cooled to RT, filtrated over a pad of celite and rinsed with Et_2O. The resulting mixture was then purified by flash chromatography (12 g of SiO_2 previously treated by 5% of Et_3N,

Cy/EtOAc, 100:0 to 95:5) to afford coupling product **8** (15.0 mg, 0.04 mmol, 25%) as a yellow oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.67 (dd, J = 8.3, 1.4 Hz, 2H), 7.56 (tt, J = 7.3, 1.3 Hz, 1H), 7.48-7.41 (m, 4H), 6.96 (s, 1H), 6.84 (d, J = 8.3 Hz, 2H), 6.17 (dddd, J = 17.2, 10.1, 7.6, 6.1 Hz, 1H), 5.25-5.16 (m, 2H), 4.43 (ddt, J = 15.3, 6.1, 1.5 Hz, 1H), 4.12 (ddt, J = 15.3, 7.6, 1.5 Hz, 1H), 2.18 (s, 3H), 1.36 (s, 9H) . ^{13}C NMR (90 MHz, $CDCl_3$): δ 189.5 (C), 161.0 (C), 143.0 (C), 137.8 (C), 137.1 (C), 135.4 (CH), 133.2 (CH), 129.3 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 127.9 (2 CH), 126.4 (CH), 118.5 (CH_2), 57.8 (CH_2), 39.4 (C), 31.4 (3 CH_3), 21.5 (CH_3). FT-IR (neat, cm^{-1}): 2962, 1914, 1669, 1601, 1506, 1448, 1344, 1249, 1222, 1159, 1090, 1053. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{27}NO_2SNa$ 404.1655; Found 404.1632.

Compound 9 (Scheme 8). Following a modified procedure reported by Burke,[2r] in air, $PhB(OH)_2$ (31.6 mg, 0.26 mmol, 1.0 equiv), Ag_2O (120.0 mg, 0.52 mmol, 2.0 equiv), bromo-allene **5d** (65 mg, 0.26 mmol, 1.0 equiv), THF (1.2 mL) and distillated water (0.12 mL) were charged in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. Argon was bubbled into the mixture during 10 min and $Pd(PPh_3)_4$ (15 mg, 0.01 mmol, 0.05 equiv) was added. The tube was sealed with a plastic stopper and the mixture was stirred at RT during 2 h. Then, the reaction was filtrated over a pad of celite and rinsed with Et_2O. The resulting mixture was purified by flash chromatography (12 g of SiO_2 previously treated by 5% of Et_3N, Cy/EtOAc, 100:0 to 95:5) to afford coupling product **9** (42.0 mg, 0.17 mmol, 65%) as a colorless oil. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.41-7.35 (m, 5H), 7.35 (s, 2H), 7.33-7.27 (m, 2H), 7.22 (tt, J = 6.9, 1.7 Hz, 1H), 6.28 (s, 1H), 1.27 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 203.2 (C), 137.4 (C), 135.6 (C), 129.4 (2 CH), 128.7 (2 CH), 128.0 (2 CH), 127.0 (CH), 126.7 (CH), 126.5 (2 CH), 119.9 (C), 95.3 (CH), 35.4 (C), 30.1 (3 CH_3). FT-IR (neat, cm^{-1}): 3060, 2963, 2900, 1944, 1597, 1491, 1475,

1457, 1391, 1361, 1230, 1130, 1071, 1026. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{19}H_{20}$ 249.1643; Found 249.1635.

Procedure for Sonogashira cross-coupling reactions. In air, bromoallene **5d** (1.0 equiv) was dissolved in a 3:1 mixture of triethylamine and toluene (0.2 M) in a 10 mL tube equipped with a Teflon-coated magnetic stir bar. $PdCl_2(Ph_3)_2$ (0.06 equiv), CuI (0.03 equiv) and the alkyne (1.1 equiv) was added. The tube was sealed with a plastic stopper and the mixture was stirred at 50 °C during 3 h. Then, the reaction was filtrated over a pad of silica (previously treated by 5% of Et_3N in Et_2O) and rinsed with cyclohexane to afford coupling product **10a-f**.

Compound 10a. The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10a** as a yellow solid (43.7 mg, 0.16 mmol, 81%). m.p. (°C): 83-85. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.53-7.48 (m, 2H), 7.39-7.36 (m, 4H), 7.36-7.32 (m, 3H), 7.31-7.24 (m, 1H), 6.50 (s, 1H), 1.33 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 209.8 (C), 134.0 (C), 131.6 (2 CH), 128.9 (2 CH), 128.4 (2 CH), 128.2 (CH), 127.4 (CH), 127.2 (2 CH), 123.7 (C), 105.2 (C), 97.6 (CH), 93.2 (C), 83.1 (C), 35.8 (C), 29.5 (3 CH_3). FT-IR (neat, cm^{-1}): 2967, 2929, 1929, 1729, 1669, 1598, 1489, 1456, 1392, 1362, 1234, 1072. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}$ 273.1631; Found 273.1638.

Compound 10b.The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10b** as a yellow solid (49.1 mg, 0.16 mmol, 82%). m.p. (°C): 81-83. ^{1}H NMR (360 MHz, $CDCl_3$): δ 7.44 (d, J = 8.7 Hz, 2H), 7.38 (s, 2H), 7.36 (s, 2H), 7.30-7.24 (m, 1H), 6.88 (d, J = 8.7 Hz, 2H), 6.48 (s, 1H), 3.84 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (60 MHz, $CDCl_3$): δ 209.7 (C), 159.6 (C), 134.2 (C), 133.0 (2 CH), 128.8 (2 CH), 127.4 (CH), 127.2 (2 CH), 115.9 (C), 114.4 (2 CH), 105.4 (C), 97.5 (CH), 93.2 (C), 81.6 (C), 55.4 (CH_3), 35.8 (C), 29.5 (3 CH_3). FT-IR (neat, cm^{-1}):

3030, 2962, 2931, 2902, 2206, 1929, 1604, 1509, 1457, 1441, 1362, 1288, 1247, 1173, 1148, 1057, 1030. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{22}H_{22}O$ 303.1749; Found 303.1749.

Compound 10c. The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10c** as a yellow oil (52.6 mg, 0.18 mmol, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 7.29-7.20 (m, 5H), 6.37 (s, 1H), 2.90 (t, J = 7.4, 2H), 2.67 (t, J = 7.4, 2H), 1.17 (s, 9H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 209.5 (C), 140.8 (C), 134.3 (C), 128.8 (2 CH), 128.6 (2 CH), 128.5 (2 CH), 127.2 (CH), 127.1 (2 CH), 126.4 (CH), 105.2 (C), 97.1 (CH), 97.4 (C), 74.5 (C), 35.4 (C), 35.3 (CH_2), 29.3 (3 CH_3), 22.0 (CH_2). FT-IR (neat, cm^{-1}): 3028, 2959, 2948, 2215, 1936, 1600, 1495, 1473, 1454, 1361, 1203, 1114, 1074, 1026. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{23}H_{24}$ 301.1951; Found 301.1945.

Compound 10d. The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10d** as a yellow oil (46.0 mg, 0.18 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.27 (m, 4H), 7.23-7.16 (m, 1H), 6.34 (s, 1H), 2.35 (t, J = 7.1, 2H), 1.58-1.37 (m, 4H), 1.18 (s, 9H), 0.92 (t, J = 7.1, 3H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 209.4 (C), 134.4 (C), 128.8 (2 CH), 127.2 (CH), 127.1 (2 CH), 105.4 (C), 97.1 (CH), 94.4 (C), 73.7 (C), 35.5 (C), 31.1 (CH_2), 29.3 (3 CH_3), 22.2 (CH_2), 19.5 (CH_2), 13.8 (CH_3). FT-IR (neat, cm^{-1}): 3029, 2960, 2929, 2869, 1936, 1600, 1495, 1474, 1457, 1362, 1246, 1202, 1116.

Compound 10e.The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10e** as a yellow oil (36.9 mg, 0.16 mmol, 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.32 (m, 1H), 7.32-7.27 (m, 3H), 7.26-7.18 (m, 1H), 6.36 (s, 1H), 1.45-1.67 (m, 1H), 1.20 (s, 9H), 0.83-0.73 (m, 4H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 209.7 (C), 134.4 (C), 128.8 (2 CH), 127.2 (CH), 127.1 (2 CH), 105.3 (C), 97.4 (C), 97.1 (CH), 68.8 (C), 35.5 (C), 29.3 (3 CH_3), 8.8 (2 CH_2), 0.57 (CH).

FT-IR (neat, cm^{-1}): 3030, 2961, 2930, 2869, 1932, 1603, 1493, 1473, 1457, 1361, 1247, 1202, 1114. HRMS (APPI): *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{20}$ 237.1643; Found 237.1641.

Compound 10f. The general procedure was followed with **5d** (50 mg, 0.20 mmol) to afford **10f** as a yellow oil (61.7 mg, 0.17 mmol, 87%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.27 (m, 4H), 7.23-7.17 (m, 1H), 6.34 (s, 1H), 3.75 (t, J = 7.1, 2H), 2.57 (td, J = 7.1, 0.9 Hz, 2H), 1.18 (s, 9H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (90 MHz, $CDCl_3$): δ 209.6 (C), 134.3 (C), 128.8 (2 CH), 127.2 (CH), 127.1 (2 CH), 105.2 (C), 97.2 (CH), 91.1 (C), 74.8 (C), 62.1 (CH_2), 35.5 (C), 29.3 (3 CH_3), 26.0 (3 CH_3), 24.2 (CH_2), 18.4 (C), -5.1 (2 CH_3). FT-IR (neat, cm^{-1}): 3028, 2958, 2928, 2858, 1936, 1600, 1495, 1472, 1460, 1361, 1254, 1106, 1056.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on ACS Publications website at DOI: XXXX

X-ray diffraction analysis of compound **3a**. Copies of ^1H NMR and ^{13}C NMR spectra of the products.

AUTHOR INFORMATION

Corresponding Author

* vincent.gandon@u-psud.fr; christophe.bour@u-psud.fr.

ORCID

Vincent Gandon: 0000-0003-1108-9410

Christophe Bour: 0000-0001-6733-5284

Notes

The authors declare no competing financial interest.

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