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Unsaturated Four-Membered Rings: Efficient Strategies for the Construction of Cyclobutenes and Alkylidenecyclobutanes.

Michael Eisold,[a] Andreas N. Baumann,[a] Gabriel M. Kiefl,[a] Sebastian T. Emmerling,[a] and Dorian Didier*[a]

Abstract: Our recent advances on diastereo- and enantioselective formation of strained alkylidenecycloalkanes drove us to investigate more thoroughly the formation of four-membered rings, for which only few efficient methods are described. We first developed a strategy for the diversification of the saturated part of four-membered rings and applied it to a highly diastereoselective synthesis of more elaborated alkylidenecyclobutanes, completing our precedent studies. In parallel, cyclobutene ring structures were built employing classical and simple methods of organometallic chemistry and further functionalized to give a wide and diverse range of new patterns, enriching consequently the pool of cyclobutene-based building blocks.

Introduction

Cyclobutenes (CBs) and alkylidenecyclobutanes (ACBs) are interesting patterns driving a continuous interest among the organic chemistry community.

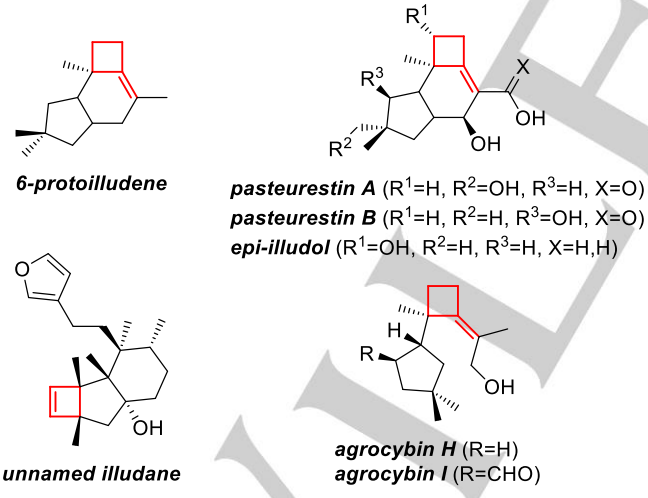

Figure 1. Naturally occurring CB- and ACB-containing substances.

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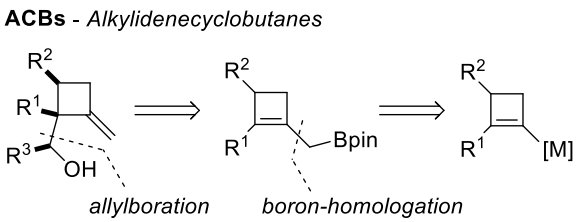
While cyclobutenes are rarely observed in natural architectures,[1] alkylidenecyclobutanes can be found as core patterns in a number of them, as depicted in Figure 1.[2] Besides their natural occurrence, CBs and ACBs have thrilled curiosity for their particular ability to undergo subsequent transformations such as ring expansions[3] and rearrangements.[4] However and despite growing interest, four-membered ring systems have been scarcely studied, mainly due to the difficulty of accessing their core structure. Generally obtained *via* [2+2] cycloadditions[5] or metal-catalyzed processes,[6] CBs and ACBs remain a synthetic challenge in organic chemistry. Developing simple and straightforward strategies for the generation of strained building blocks[7] undoubtedly opens a new area of interest for further explorations, as the limitation of the scope is a consequence of the lack of diversified and available methodologies.

Results and Discussion

Synthetic routes towards alkylidenecyclobutanes (ACBs)

We recently reported an efficient method for the diastereo- and enantioselective preparation of alkylidenecyclopropanes[8] and –butanes.[9] Our general approach is based on a combination of boron-homologation and boron-allylation sequences in a single-pot operation. Starting from a pre-formed cyclobutenylmetal species, installation of the allylic boron moiety is done by boron-homologation which was assembled following the very useful and pioneering work of Matteson,[10] and ACBs are finally formed by simple allylboration of aldehydes (Scheme 1).



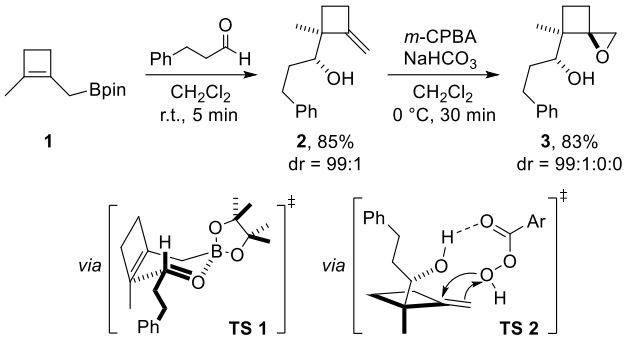
Scheme 1. Retrosynthetic approach to ACBs.

As a representative example, the cyclobutenylmethylboronate **1** afforded the methylenecyclobutane **2** after addition of dihydrocinnamaldehyde in 85% yield and with a perfect control of the diastereoselectivity (dr = 99:1) in remarkably short time and at ambient temperature. A subsequent oxidation could furnish the

10.1002/chem.201604585

FULL PAPER

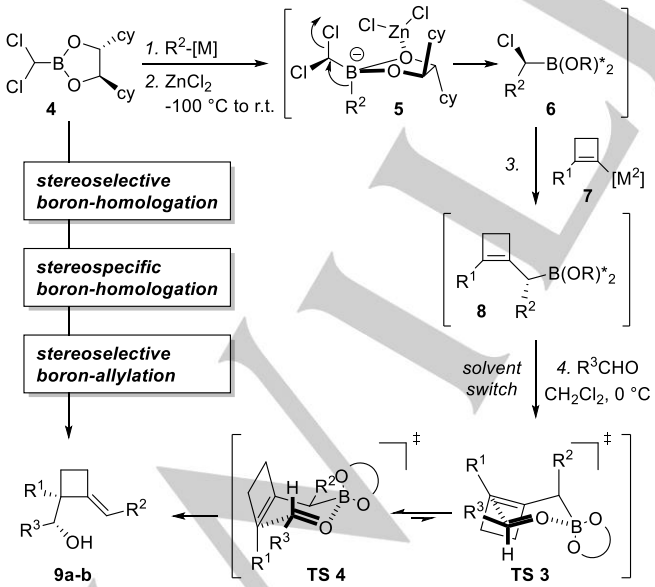
diastereoisomerically pure oxaspirohexane **3** in 83% yield (scheme **2**). We proposed to explain the high diastereoisomeric ratio observed for the formation of **2** by a Zimmermann-Traxler transition state, in which the lateral chain of the aldehyde adopts the pseudo-equatorial position, as postulated initially by Hoffmann for allylboration reactions (**TS 1**).[11] We also proposed that the epoxidation of the alkylidene moiety takes place on the side of the secondary alcohol, preferred in this case – in the absence of protic solvent - by H-bonding with the *m*-chloroperbenzoic acid (**TS 2**).



Scheme 2. ACB formation and application to synthesis of oxaspirohexane **3**.

This new method to easily generate ACBs proved to be quite general and was broadly examplified by the use of a wide range of aromatic, heteroaromatic and aliphatic aldehydes, receiving chiral adducts with high diastereomeric ratios.

In a second time, we developed an asymmetric version of the one-pot sequence by using chiral diols as ligands of the boron, allowing for the preparation of enantiomerically enriched ACBs.[9b]



Scheme 3. One-pot stereoselective synthesis of ACBs **9a-b**.

In this single-pot sequence, dichloromethylboronic ester **4** reacts with an organometallic nucleophile to promote the stereoselective formation of a α-chiral chloromethylboronic ester **6** *via* a 1,2-metallate rearrangement controlled by the chiral diol ligand, relayed by the presence of zinc chloride (through the intermediate boronate **5**).[12] Addition of a cyclobutenylmetal species **7** undergoes a second stereospecific boron-homologation leading to the α-chiral cyclobutenylmethylboronic ester **8**. Allylation reaction was finally performed by introducing an aldehyde. Diastereoselectivity of the transformation was controlled by a Zimmerman-Traxler transition state in which both R^2 and R^3 groups adopt pseudo-equatorial positions (**TS 4**).

A wide variety of novel ACBs (**9a-b**) were generated through this diastereoselective and enantioselective procedure. In Figure 2, we show representative examples of such molecules obtained in each case with excellent diastereo- and enantiomeric excesses. Aromatic (**9a**) and aliphatic aldehydes (**9b**) gave the desired ACBs in 55 to 79% yield.

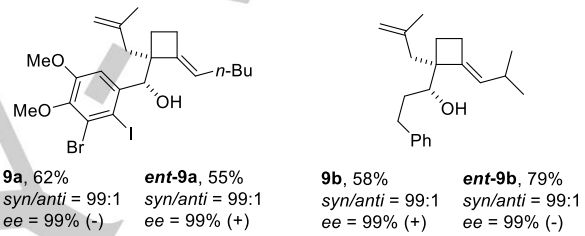
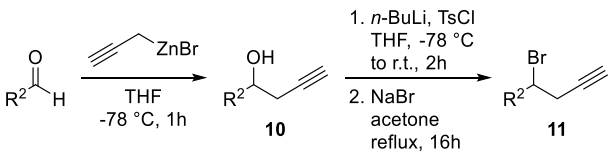


Figure 2. Representative examples of enantiomerically enriched ACBs.

Alternatively, we envisioned that the diastereoselectivity could come from the cyclobutene itself. In this case, starting propargyl bromides had to be adequately prepared in order to install the lateral chain R^2 (scheme 4). Trying to avoid the use of expensive propargylation reagents,[13] we chose to employ readily available aldehydes in the presence of an *ex-situ* prepared and storable propargylzinc reagent to undergo the formation of substituted homopropargylic alcohol precursors **10**. Maintaining the temperature at -78 °C allowed for the selective formation of the expected alkyne, containing only traces of the competitive allenylation compound. Subsequent tosylation of the resulting secondary alcohol followed by a nucleophilic substitution afforded the corresponding homopropargylic bromides **11**. Worthy of note, employing PBr_3 or Appel's conditions for the direct synthesis of substituted propargyl bromides from corresponding alcohols only yielded traces of the desired products, the major adduct resulting from an elimination reaction.

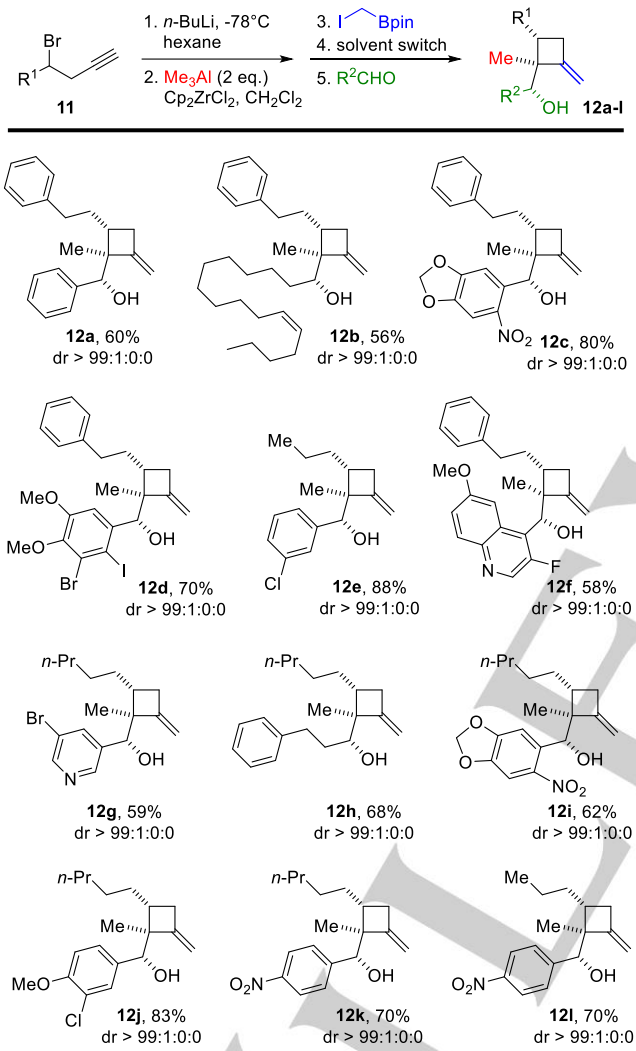


Scheme 4. Synthesis of homopropargylic bromides **11**.

10.1002/chem.201604585

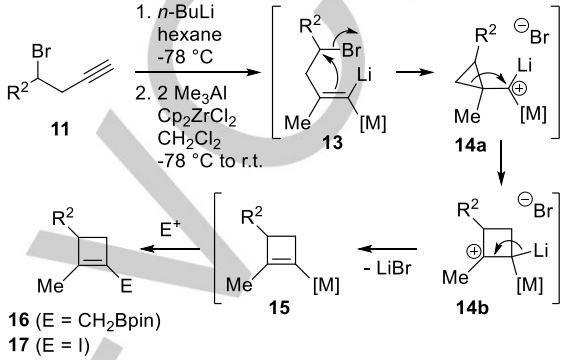
FULL PAPER

In a one-pot sequence – for which the cyclization mechanism is discussed hereafter – boron-homologation and allylboration reactions were merged, leading to obtain ACBs **12a-l** with excellent diastereoisomeric ratios (in all cases dr > 99:1:0:0). Employing simple propargyl bromides **11**, the strategy was largely exemplified with the use of aromatic, heteroaromatic and aliphatic aldehydes, furnishing expected compounds containing three consecutive stereocenters, one being quaternary, in good yields up to 88% (Scheme 5).



Scheme 5. One-pot diastereoselective synthesis of ACBs containing a side-chain.

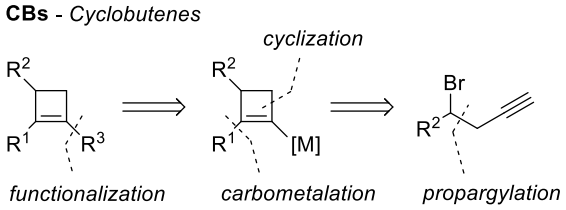
Initiated by an alkyne deprotonation with *n*-butyllithium, the sequence was realized by addition of a mixture of dichlorozirconocene and trimethylaluminium in dichloromethane in order to undergo a carboalumination reaction (**13**). Following the mechanism proposed by Negishi, a π-cyclization takes place furnishing intermediary a *gem*-bismetalated cyclopropyl-methylium **14a**. Subsequent migration of the methylene gives the cyclobutenylium **14b** through a C-C bond cleavage, leading to the cyclobutenyl-metal species **15** with the shown substitution pattern by elimination of lithium bromide. Regiochemistry of the overall cyclization process was clarified by NMR experiments.[14] Introduction of the appropriate electrophile finally gave the cyclobutenylmethylboronic ester **16** (scheme 6) used for the allylation sequence with an aldehyde, or the iodocyclobutene **17** useful for cyclobutene functionalization.



Scheme 6. Proposed mechanism for the formation of cyclobutene iodides.

Synthetic routes towards cyclobutenes (CBs)

We envisioned that functionalization of cyclobutenes can be made in a late-stage of the sequence, having previously generated a cyclobutenyl-metal species bearing a pre-installed R^2 moiety, following afore mentioned cyclization strategies. Derivatization of the unsaturated part of cyclobutene rings was consequently undertaken by intermediary generating cyclobutenylmetal species (scheme 7).



Scheme 7. Retrosynthetic approach to CBs.

With a range of propargyl bromides in hands, the synthesis of cyclobutene iodides (**17**) was simply conducted by addition of iodine to *in-situ* generated cyclobutenyl metal species **15**.
A first derivatization was undertaken by cross-coupling reactions of **17** with different zinc species in the presence of $Pd(dba)_2$ and TFP (tri-2-furylphosphane). Results are depicted in Scheme 8.

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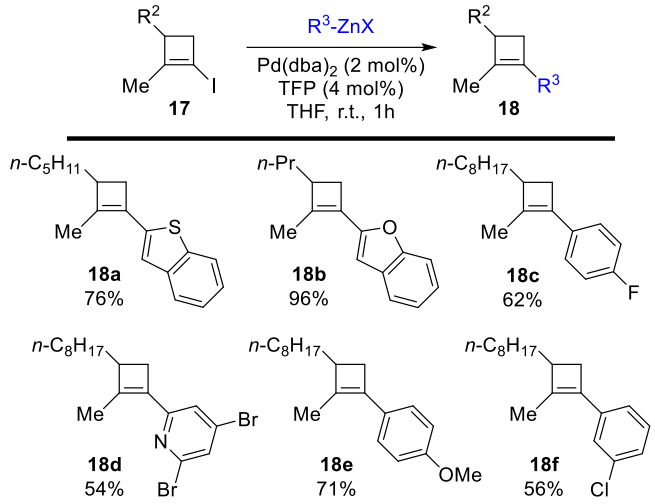
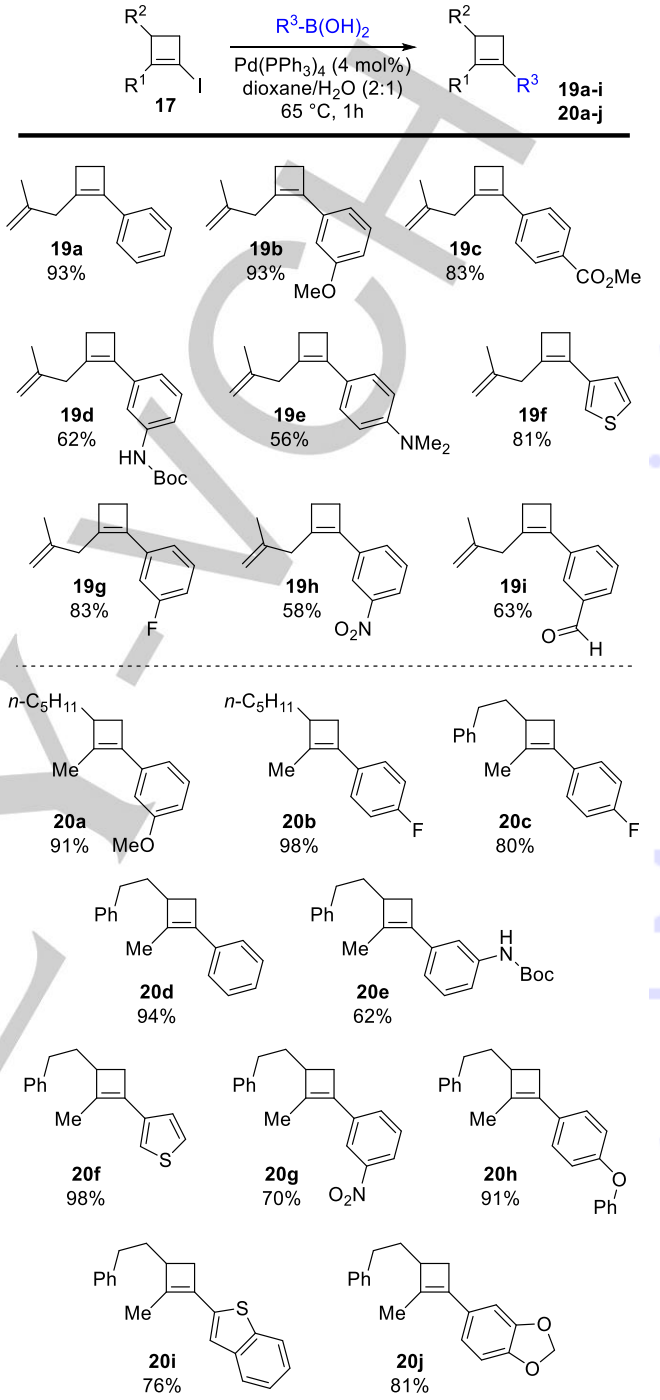


Scheme 8. Derivatization of cyclobutenes *via* Negishi cross-coupling reactions.

Aromatic and heteroaromatic substrates were easily introduced, furnishing substituted cyclobutenes **18a-f** in good to excellent yields.

On the strength of these successful first results, we took a step further by envisaging boronic acids as cross-coupling partners. A wide range of commercially available boronic acids was used in the Suzuki cross-coupling of cyclobutene iodides **17** in the presence of tetrakis(triphenylphosphine)palladium (4 mol%), demonstrating exceptional efficiency and tolerance towards the presence of a broad variety of functional groups, as shown in Scheme 9.[15] Halogen, ether and NO_2- substituted aromatics were introduced very efficiently, as well as Boc-protected aromatic amines (**19d**, **20e**) or the even more challenging *m*-formyl phenyl group (**19i**). Functionalized four-membered rings were obtained with very good yields (up to 98%) and we were able to show the high tolerance of the system to undergo cross-coupling reactions with a wide range of functional groups (**19a-i** and **20a-j**). Unfortunately, aliphatic residues could not be introduced through the Suzuki cross-coupling by employing alkylboronic acids and starting cyclobutene iodides were recovered.

Alternatively, cyclobutenyl-metal can be generated and used *in-situ* by employing allylzinc species for which the formation of metallic reagents was performed following conditions described by Villiéras et. al., by simple insertion of zinc into the carbon-halogen bond (Scheme 10).



Scheme 9. Derivatization of cyclobutenes *via* Suzuki cross-coupling reactions.

Allylzinc reagents were then added to *in-situ* metalated 4-bromobutyne to perform a carbometallation / cyclization sequence leading to a new cyclobutenyl-zinc species. In the first case, aromatic and heteroaromatic iodides were added in the presence of $Pd(dba)_2$ and TFP to undergo a cross-coupling reaction and furnish substituted cyclobutenes **19a** and **21a-k** in good yields (up to 87%). In the second case, furoyl chloride was

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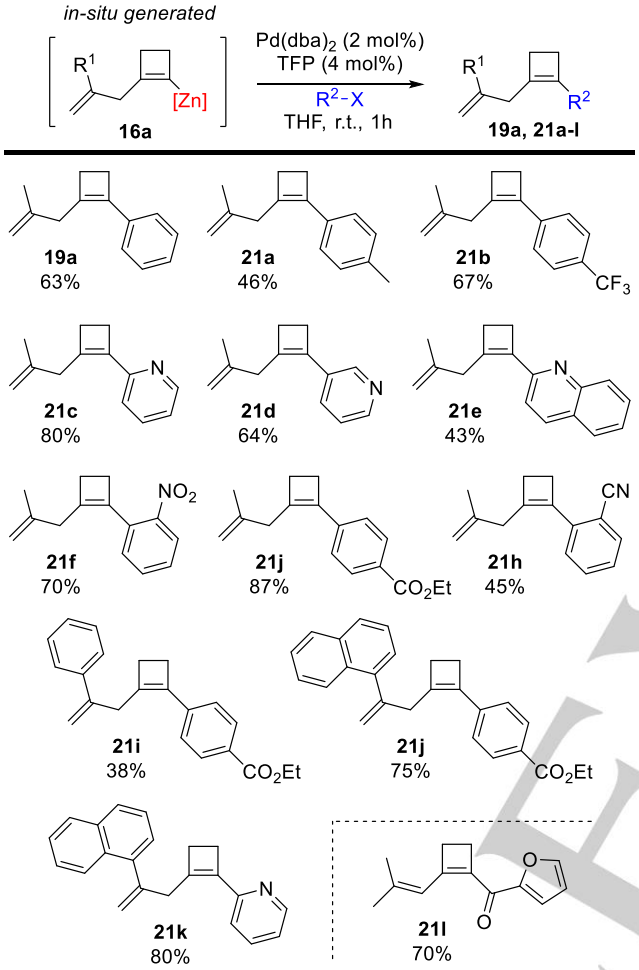
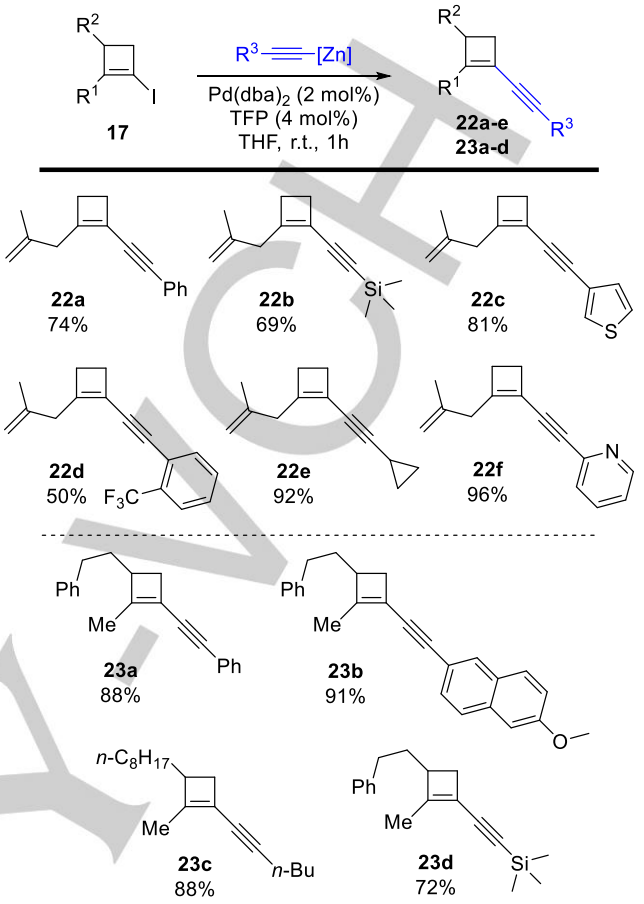
introduced to give the conjugated cyclobutenylketone **21l**. Surprisingly, isomerization of the allylic double bond was observed, leading to the more stable 6-π electron conjugated system as sole product of the reaction.



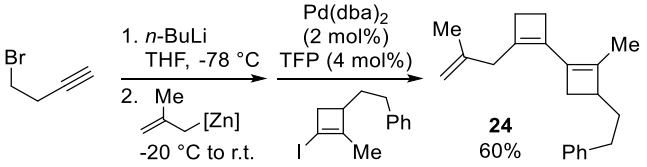
Scheme 10. Derivatization of in-situ generated cyclobutenylzinc species.

Taking into account the importance of 1,3-enyne systems to undergo further interesting transformations,[16] we envisaged that cyclobutenyl-ynes could be highly valuable substrates for further studies. Alkynyl-zinc reagents prepared by deprotonation of the corresponding terminal alkyne and subsequent transmetallation with $ZnCl_2$ were able to undergo a fast cross-coupling reaction with diverse allylcyclobutene iodides to obtain conjugated cyclobutenyl acetylene **22a-f** and **23a-d** in good yields (50-96%), showing the potential of this methodology to diversify the pool of previously described cyclobutenes (Scheme 11). The Sonogashira-type cross-coupling reaction of a cyclobutene iodide was previously described by Okamura et al..[17] The resulting cyclobutenyl acetylene was applied to a concise synthesis of (+)-Sterpurene.



Scheme 11. Cross-coupling reactions of allylcyclobutene iodides.

Finally, we were able to apply this straightforward methodology to the synthesis the bicyclobutene **24**. A similar one-pot sequence was employed to generate the allylcyclobutenyl metal species, followed by a cross-coupling reaction involving a cyclobutene iodide. **24** was obtained in 60% yield.



Scheme 12. Synthetic approach to bicyclobutene **24**.

Conclusions

Through the use of simple organometallic methodologies, we thoroughly assembled efficient routes to access substituted four-membered ring patterns. On the one hand, unprecedented single-pot sequences led us to develop a highly diastereoselective synthesis of alkylidenecyclobutanes possessing three

consecutive stereocenters, one being quaternary. On the other hand, valuable aryl-, alkynyl- and acyl-cyclobutenes were generated by merging an efficient preparation of cyclobutenyl derivatives with cross-coupling reactions. It makes no doubt that such easily accessible routes for producing unsaturated four-membered ring architectures is of great interest for further investigations, as these structures are usually difficult to access.

Experimental Section

General Procedure A: Preparation of propargyl alcohols **10**: To a suspension of zinc dust (3.8 eq.) and lithium chloride (2.0 eq) were added a few drops of 1,2-dibromoethane to activate the zinc. A solution of propargyl bromide (1.0 eq.) in THF was slowly added while keeping the reaction slightly above room temperature (~ 30-40 °C). Upon full addition, the mixture was stirred for another 90 mins at room temperature. The suspension was cooled to −78 °C and the according aldehyde was slowly added neat. The mixture was allowed to react for 30 mins at aforesaid temperature and was quenched by adding conc. hydrochloric acid (2.0 eq). The mixture was allowed to reach room temperature overnight and then extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with saturated aqueous sodium hydrogencarbonate solution (50 mL) and Brine (50 mL). The washed solution was dried over magnesium sulfate, filtrated and concentrated under reduced pressure (careful, as some products **10** are quite volatile). The crude alcohol was purified by flash column chromatography over silica, using the appropriate mixture of ethyl acetate in hexanes.

General Procedure B: Synthesis of propargyl bromides **11:** To a solution of alcohol **10** in THF (0.5 M) was dropwise added a solution of *n*-BuLi in hexane (1.0 eq.) at −78 °C. The solution was allowed to react for 30 mins at aforesaid temperature and then warmed to room temperature. A solution of 4-methylbenzene-1-sulfonyl chloride in THF (1.0 M) was added. The reaction mixture was stirred at room temperature for another 30 mins. The mixture was poured onto water (50 mL) and extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with Brine (50 mL), dried over magnesium sulfate, filtrated and concentrated under reduced pressure. The crude tosylate **25** was used without further purification. For analysis, a sample was purified by flash column chromatography over silica, using the appropriate mixture of ethyl acetate in hexanes. The crude tosylate **25** was dissolved in acetone (0.3 M) and lithium bromide (5.0 eq) was added. The reaction mixture was stirred at reflux for 10 h, upon which full consumption of the tosylate was observed. (Alternatively the reaction can be performed in a pressure vessel at 65 C for 10 h). After cooling to room temperature, the reaction mixture was poured onto water and consequently extracted with hexanes (3 × 50 mL). The combined organic phases were washed with Brine (50 mL), dried over magnesium sulfate, filtrated and concentrated under reduced pressure (careful, as some products **11** are quite volatile). The crude bromide was purified by flash column chromatography over silica using hexanes as an eluent.

General Procedure C: Synthesis of iodocyclobutenes **17a-d**: To a solution of 4-bromobutyne **11** in hexane (0.5 M), was added dropwise a solution of *n*-butyllithium (1.0 eq.) in hexane at −78 °C and stirred for 30 minutes. A second flask was charged with Cp_2ZrCl_2 (1.0 eq.) in CH_2Cl_2 (0.5 M) and a solution of trimethylaluminium (2.0 eq.) in hexane was added at room temperature and stirred for 30 minutes. The second solution was transferred to the first one at −78 °C *via* cannula. The resulting mixture was the allowed to stir at room temperature for 2 hours to form the metallated cyclobutenyl derivative **16**. The suspension was cooled to 0 °C and a solution of iodine in THF (1.5 eq.) was added slowly. After stirring for 30 mins at aforesaid temperature, the mixture was slowly poured onto ice-cold hydrochloric acid (10 eq.,~0.5 M HCl), while stirring vigorously. The aqueous phase was extracted with hexanes (3 × 50 mL). The combinded organic phases were washed with saturated aqueous sodium hydrogencarbonate solution (50 mL) and Brine (50 mL). The washed solution was dried over magnesium sulfate, filtrated and concentrated under reduced pressure (careful, as some products xx are quite volatile). The crude cyclobutyl iodide **17a-d** was purified by flash column chromatography over silica using hexanes as an eluent.

General Procedure D: Synthesis of alkylidenecyclobutylcarbinols **12**: To a solution of 4-bromobutyne **11** in hexane (0.5 M), was added dropwise a solution of *n*-butyllithium (1.0 eq.) in hexane at −78 °C and stirred for 30 minutes. A second flask was charged with Cp_2ZrCl_2 (1.0 eq.) in CH_2Cl_2 (0.5 M) and a solution of trimethylaluminium (2.0 eq.) in hexane was added at room temperature and stirred for 30 minutes. The second solution was transferred to the first one at −78 °C *via* cannula. The resulting mixture was the allowed to stir at room temperature for 2 hours to form the metallated cyclobutenyl derivative **15**. The reaction mixture was cooled back to −78 °C and 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in THF (1.0 eq., 0.5 M) was added. The solution was warmed to room temperature over 2 hours. Excess organometallic species were quenched through addition of water (very carefully) and the boronic ester **16** was extracted with diethyl ether (3 × 20 mL). The combined organic layers were washed with Brine (20 mL), dried over magnesium sulfate, filtrated and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (0.5 M) and cooled to 0 °C. The liquid and solid aldehydes (0.5 eq.) were added neat and dissolved in CH_2Cl_2, respectively. Upon full consumption of the boronate intermediate **16**, saturated ammonium chloride solution and diethyl ether were added and the mixture was stirred vigorously. The aqueous phase was extracted with diethyl ether (3 × 20 mL) and the combined organic layers washed with aqueous sodium metabisulfite (20 mL). The washed solution was dried over magnesium sulfate, filtrated and concentrated under reduced pressure. The crude alcohol was purified by flash-column chromatography on silica gel with ethyl acetate in hexanes and diethyl ether in hexanes, respectively to afford the pure alkylidenecyclobutylcarbinols **12**.

General procedure E: Suzuki-cross-coupling of arlyboronic acids with cyclobutene-iodides: To a stirred solution of cyclobutene-iodide (**17**) (1 eq.) in dioxane/H_2O (2:1) (0.05 M) was added arylboronic acid (1.33 eq.) and K_2CO_3 (2.7 eq) at room temperature. The reaction mixture was stirred for 10 min before adding the $Pd(PPh_3)_4$ (4 mol%). The cross-coupling was performed at 50 °C for 1 h. The color of the reaction mixture turned after completion to red or black. At last the reaction was treated with a small amount of water, extracted three times with diethyl ether and dried over dry magnesium sulfate. The solvent was removed under reduced pressure and the crude was purified by column chromatography or preparative-layer plates with appropriate solvent mixture to obtain aryl-cyclobutene derivatives (**19**/**20**).

General Procedure F: *In-situ* Negishi-cross-coupling of aryl iodides with cyclobutene derivatives: To a stirred solution of 4-bromobut-1-yne (1 eq.) in THF (0.2 M) was added dropwise *n*-BuLi (1 eq.) at -78 °C. After 15 min the cooling bath was exchanged to an -30 °C one. This temperature was held for 5 min before adding dropwise the allyl-zinc-species (1 eq.). After 10 min the cooling bath was removed and the colorless solution was warmed to room temperature over 1 h. The color changed from colorless to pale yellowish. During this time, $Pd(dba)_2$ (4 mol%) and TFP (8 mol%) was dissolved in THF in a second flask. After 10-20 min the red solution turned to yellow. The aryl-iodide (0.95 eq.) was added in THF (0.15 M) to the yellow solution of the catalytic-system and stirred for 10 min. Finally the cyclobutenyl-zinc-species (**15a-c**) was quickly added to the second flask with the aryl-iodide and stirred for 1 h. After quenching with water the crude mixture was extracted three times with diethyl ether and dried over dry magnesium sulfate. The solvent was removed under reduced pressure

and the crude was purified by column chromatography or preparative-layer plates with appropriate solvent mixture to obtain aryl-cyclobutene derivatives (**21**).

General procedure G: Negishi-cross-coupling of alkynes with cyclobutene-iodides: To a stirred solution of alkynes (1 eq.) in THF (0.15 M) was added dropwise *n*-BuLi (1 eq.) at -78 °C. After 30 min the reaction mixture was treated dropwise with $ZnCl_2$ solution (1 M in THF) (1.33 eq) at the same temperature. The reaction mixture was again stirred for 30 min at -78 °C. At least the cooling bath was removed and the system was allowed to reach room temperature. During this time, $Pd(dba)_2$ (4 mol%) and TFP (8 mol%) was dissolved in THF in a second flask. After 10-20 min the red solution turned to yellow. The cyclobutene-iodide (0.95 eq.) (**17**) was added in THF (0.15 M) to the yellow solution of the catalytic-system and stirred for 10 min. Finally the alkenyl-zinc-species was quickly added to the second flask with the cyclobutene-iodide and stirred for 1 h. After quenching with water the crude mixture was extracted three times with diethyl ether and dried over dry magnesium sulfate. The solvent was removed under reduced pressure and the crude was purified by column chromatography or preparative-layer plates with appropriate solvent mixture to obtain alkyne-cyclobutene derivatives (**22/23**).

Hept-1-yn-4-yl 4-methylbenzenesulfonate (25a): Using alcohol **10a** according to general procedure **B** provided **25a** (4.21 g, quantitative) as a colorless oil. R_f = 0.35 (9:1 hexane:EtOAc, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 2H), 4.63 – 4.50 (m, 1H), 2.55 – 2.50 (m, 2H), 2.45 (s, 3H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.70 (td, *J* = 8.1, 6.4 Hz, 2H), 1.39 – 1.13 (m, 2H), 0.83 ppm (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 144.9, 134.1, 129.9, 128.0, 80.2, 78,6, 71.3, 35.5, 24.8, 21.8, 18.0, 13.7 ppm. HRMS (EI) : calcd for $C_{14}H_{18}O_3S^+$: 266.0977, found 266.0980. IR (ν, cm^{-1}) 3289 (w), 2962 (w), 2936 (w), 2876 (vw), 1599 (w), 1496 (vw), 1460 (w), 1356 (m), 1308 (w), 1292 (w), 1188 (m), 1174 (vs), 1097 (m).

Non-1-yn-4-yl 4-methylbenzenesulfonate (25b): Using alcohol **10b** according to general procedure **B** provided **25b** (5.79 g, quantitative) as a colorless oil. R_f = 0.45 (9:1 hexane:EtOAc, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.81 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 4.55 (tt, *J* = 6.8, 5.2 Hz, 1H), 2.56 – 2.51 (m, 2H), 2.45 (s, 3H), 1.96 (t, *J* = 2.7 Hz, 1H), 1.71 (dddd, *J* = 8.9, 7.1, 5.3, 3.0 Hz, 2H), 1.28 – 1.07 (m, 6H), 0.82 ppm (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 144.9, 134.1, 129.9, 128.0, 80.5, 78.7, 71.3, 33.4, 31.4, 24.9, 24.4, 22.5, 21.8, 14.0 ppm. HRMS (ESI) : calcd for $C_{16}H_{22}O_3S^+$: 294.1290, found: 294.1274. IR (ν, cm^{-1}) 3291 (w), 2956 (w), 2929 (w), 2862 (w), 1598 (w), 1496 (w), 1466 (w), 1458 (w), 1359 (m), 1307 (w), 1292 (w), 1188 (s), 1174 (vs), 1097 (m), 1020 (w).

Dodec-1-yn-4-yl 4-methylbenzenesulfonate (25c): Using alcohol **10c** according to general procedure **B** provided **25c** (4.58 g, quantitative) as a colorless oil. R_f = 0.33 (99:1 hexane:EtOAc, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.78 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 4.59 – 4.46 (m, 1H), 2.54 – 2.49 (m, 2H), 2.42 (s, 3H), 1.95 (t, *J* = 2.7 Hz, 1H), 1.75 – 162 (m, 2H), 1.34 – 1.03 (m, 12H), 0.86 ppm (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 144.8, 134.0, 129.8, 127.9, 80.4, 78.6, 71.3, 33.3, 31.9, 29.4, 29.2, 29.1, 24.8, 24.6, 22.7, 21.7, 14.2 ppm.

1-Phenylhex-5-yn-3-yl 4-methylbenzenesulfonate (25d): Using alcohol **10d** according to general procedure **B** provided **25d** (5.04 g, quantitative) as a colorless oil., R_f = 0.30 (9:1 hexane:EtOAc, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.82 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 6.8 Hz, 2H), 4.61 (dt, *J* = 12.1, 5.9 Hz, 1H), 2.69 – 2.60 (m, 1H), 2.58 (dd, *J* = 5.9, 2.7 Hz, 2H), 2.54 – 2.47 (m, 1H), 2.46 (s, 3H), 2.10 – 2.01 (m, 2H), 1.99 ppm (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 145.0, 140.7, 134.0, 130.0, 128.6, 128.4, 128.0, 126.3, 79.7, 78.4, 71.6, 35.1, 31.0, 24.8, 21.8 ppm. HRMS (EI): calcd for $C_{19}H_{20}O_3S^+$: 328.1133, found 328.1147. IR (ν, cm^{-1}) 3292 (w), 3063 (vw), 3028 (vw), 2925 (vw), 2862 (vw), 1599 (w), 1496 (w), 1455 (w), 1361 (m), 1307 (w), 1293 (w), 1212 (vw), 1189 (m), 1175 (vs), 1120 (vw), 1097 (w), 1018 (w).

4-Bromohept-1-yne (11a): Using tosylate **25a** according to general procedure B provided 11a (1.10 g, 40%) as a colorless oil. R_f = 0.41 (hexane, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 4.07 (dtd, *J* = 8.8, 6.3, 4.5 Hz, 1H), 2.87 – 2.72 (m, 2H), 2.12 (t, *J* = 2.6 Hz, 1H), 2.01 – 1.78 (m, 2H), 1.69 – 1.50 (m, 1H), 1.44 (dddd, *J* = 13.4, 9.6, 7.4, 6.3 Hz, 1H), 0.95 ppm (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 80.7, 71.1, 52.3, 39.9, 29.4, 20.8, 13.5 ppm. HRMS (EI) : calcd for $C_7H_{11}{}^{79}Br^+$: 174.0044, found 174.0101.

4-Bromonon-1-yne (11b): Using tosylate **25b** according to general procedure **B** provided **11b** (2.33 g, 46%) as a colorless oil. R_f = 0.50 (hexane, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.99 (dtd, *J* = 8.8, 6.3, 4.5 Hz, 1H), 2.82 – 2.65 (m, 2H), 2.06 (t, *J* = 2.6 Hz, 1H), 1.96 – 1.72 (m, 2H), 1.54 – 1.42 (m, 1H), 1.40 – 1.31 (m, 1H), 1.31 – 1.17 (m, 4H), 0.84 ppm (t, *J* = 6.95 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 80.7, 71.1, 52.7, 37.8, 31.2, 29.4, 27.2, 22.6, 14.1 ppm. HRMS (EI): calcd for $C_7H_{10}{}^{79}Br^+$ ($[M–C_2H_5]^+$): 172.9966, found 172.9965. IR (ν, cm^{-1}) 3063 (w), 3027 (w), 2932 (w), 1603 (w), 1496 (m), 1469 (vw).

4-Bromododec-1-yne (11c): Using tosylate **25c** according to general procedure **B** provided **10c** (2.47 g, 84%) as a colorless oil. R_f = 0.78 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 4.05 (dtd, *J* = 8.8, 6.3, 4.5 Hz, 1H), 2.82 (ddd, *J* = 17.2, 5.9, 2.6 Hz, 1H), 2.76 (ddd, *J* = 17.2, 6.5, 2.6 Hz, 1H), 2.12 (t, *J* = 2.6 Hz, 1H), 2.01 – 1.79 (m, 2H), 1.61 – 1.46 (m 1H), 1.46 – 1.19 (m, 11H), 0.88 ppm (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 80.7, 71.0, 52.6, 37.9, 32.0, 29.5, 29.4, 29.3, 29.0, 27.5, 22.8, 14.2 ppm. IR (ν, cm^{-1}) 3311 (w), 2956 (m), 2924 (vs), 2855 (s), 1465 (m), 1430 (w), 1378 (w), 1303 (w), 1255 (w), 1178 (w).

(3-Bromohex-5-yn-1-yl)benzene (11d): Using tosylate **25d** according to general procedure **B** provided **11d** (2.77 g, 88%) as a yellow oil. R_f = 0.23 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.4 – 7.3 (m, 2H), 7.2 – 7.2 (m, 3H), 4.1 – 4.0 (m, 1H), 3.0 – 2.9 (m, 1H), 2.8 (ddd, *J* = 9.2, 6.3, 2.7 Hz, 2H), 2.8 – 2.7 (m, 1H), 2.3 – 2.1 (m, 2H), 2.1 ppm (t, *J* = 2.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 140.7, 128.7 (2 ^{13}C signals overlapping), 126.4, 80.4, 71.3, 51.5, 39.4, 33.7, 29.5 ppm. HRMS (EI): calcd for $C_{12}H_{13}{}^{79}Br^+$: 236.0201, found 236.0183. IR (ν, cm^{-1}) 3295 (m) 3086 (w) 3063 (w) 3027 (w) 2932 (w) 2860 (w) 1603 (w) 1496 (m) 1454 (m) 1429 (w) 1419 (w) 1331 (w) 1285 (w) 1195 (w) 1180 (w) 1031 (w).

1-Iodo-2-methyl-3-propylcyclobut-1-ene (17a): Using bromide **11a** according to general procedure **C** provided **17a** (260 mg, 59%) as a colorless oil. R_f = 0.87 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.97 – 2.81 (m, 2H), 2.38 – 2.29 (m, 1H), 1.58 (td, *J* = 2.3, 1.1 Hz, 4H), 1.41 – 1.22 (m, 3H), 0.90 ppm (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.3, 83.0, 48.6, 43.4, 35.0, 20.7, 14.9, 14.3 ppm. HRMS (EI) : calcd for $C_8H_{13}I^{+}$: 236.0062, found 236.0059. IR (ν, cm^{-1}) 2958 (vs), 2931 (s), 2872 (s), 1710 (vs), 1462 (s), 1379 (s), 1211 (s), 1166 (s), 1088 (s).

1-Iodo-2-methyl-3-pentylcyclobut-1-ene (17b): Using bromide **11b** according to general procedure **C** provided **17b** (348 mg, 59%) as a colorless oil. R_f = 0.90 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.86 – 2.75 (m, 2H), 2.32 – 2.22 (m, 1H), 1.51 (td, *J* = 2.3, 1.0 Hz, 4H), 1.30 – 1.14 (m, 7H), 0.81 ppm (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.3, 83.1, 48.8, 43.4, 32.8, 32.1, 27.1, 22.7, 14.9, 14.2 ppm. HRMS (EI) : calcd for $C_{10}H_{17}I^{+}$: 264.0375, found 264.0375. IR (ν, cm^{-1}) 2956 (s), 2924 (vs), 2872 (m), 2853 (m), 1712 (w), 1649 (w), 1466 (w), 1456 (w), 1438 (w), 1372 (w), 1242 (m), 1182 (w), 1094 (w), 1059 (w), 1006 (m).

1-Iodo-2-methyl-3-octylcyclobut-1-ene (17c): Using bromide **11c** according to general procedure **C** provided **17c** (2.54 g, 79%) as a colorless oil. R_f = 0.93 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 2.93 – 2.30 (m, 2H), 2.37 – 2.30 (m, 1H), 1.60 – 1.56 (m, 4H), 1.40 – 1.18 (m, 13H), 0.88 ppm (t, *J* = 6.9 Hz. 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.3, 83.1, 48.9, 43.4, 32.8, 32.0, 29.9, 29.7, 29.4, 27.5, 22.8, 14.9, 14.3 ppm. HRMS (EI) : calcd for $C_{13}H_{23}I^+$: 306.0844, found 306.0833. IR (ν, cm^{-1}) 2954 (m), 2922 (vs), 2852 (m), 2361 (vw), 1648 (vw), 1465 (w), 1456 (w), 1437 (w), 1371 (w), 1240 (w), 1094 (vw).

(2-(3-Iodo-2-methylcyclobut-2-en-1-yl)ethyl)benzene (17d): Using bromide **11d** according to general procedure **C** provided **17d** (3.38 g, 62%) as a colorless oil. R_f = 0.58 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.31 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 2.96 (dtt, *J* = 9.2, 4.7, 1.4 Hz, 1H), 2.87 (ddq, *J* = 12.3, 4.5, 2.3 Hz, 1H), 2.64 (dd, *J* = 8.8, 6.9 Hz, 2H), 2.42 – 2.32 (m, 1H), 1.95 (dddd, *J* = 13.3, 8.4, 7.3, 4.9 Hz, 1H), 1.73 – 1.62 (m, 1H), 1.59 ppm (td, *J* = 2.3, 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 157.9, 142.2, 128.5 (2 ^{13}C signals overlapping), 126.0, 83.3, 48.3, 43.1, 34.6, 33.8, 14.9 ppm. HRMS (EI): calcd for $C_{13}H_{15}I^+$: 298:0218, found 298:0214. IR (ν, cm^{-1}) 3085 (vw), 3062 (vw), 3026 (w), 2923 (m), 2847 (w), 1648 (w), 1603 (w), 1496 (m), 1453 (m), 1436 (w), 1371 (w), 1319 (vw), 1239 (m), 1181 (w), 1094 (w), 1057 (w), 1029 (w), 1022 (w), 1002 (w).

1-Iodo-2-(2-methylallyl)cyclobut-1-ene (17e): To a stirred solution of 4-bromobut-1-yne (1 eq.) in THF (0.2 M) was added dropwise *n*-BuLi (1 eq.) at -78 °C. After 15 min the cooling bath was exchanged to an -30 °C one. This temperature was held for 5 min before adding dropwise the (2-methylallyl)zinc bromide (1 eq.). After 10 min the cooling bath was removed and the colorless solution was warmed to room temperature over 1 h. The color changed from colorless to pale yellowish. The reaction mixture was treated with iodine (1 eq) followed by a small amount of water. The crude mixture was extracted three times with diethyl ether and dried over dry magnesium sulfate. The solvent was removed under reduced pressure at 0 °C. The crude was purified by column chromatography with hexanes in the dark to obtain **17e** (945 mg, 40%) as a colorless oil. R_f = 0.9 (hexane, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$) δ 4.80 – 4.77 (m, 1H), 4.75 – 4.72 (m, 1H), 2.78 – 2.74 (m, 2H), 2.73 – 2.70 (m, 2H), 2.69 – 2.66 (m, 2H), 1.72 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 141.5, 112.3, 84.5, 39.5, 36.4, 34.7, 22.7 ppm. HRMS (EI): calcd for $C_8H_{11}I^+$: 233.9905, found 233.9906.

1-Bromo-2-(2-methylallyl)cyclobut-1-ene (17f): Following the procedure employed for the preparation of **17e**, NBS (1 eq.) was employed as the electrophile, furnishing **17f** (299 mg, 32%). Colorless oil, *R*f = 0.79 (hexane, UV, KMnO4, PAA). ^1H NMR (400 MHz, $CDCl_3$) δ 4.80 – 4.77 (m, 1H), 4.75 – 4.73 (m, 1H), 2.77 – 2.74 (m, 2H), 2.74 – 2.71 (m, 2H), 2.49 (ddd, J = 4.1, 2.2, 1.0 Hz, 2H), 1.73 ppm (t, J = 1.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 141.6, 112.2, 109.8, 37.5, 35.2, 31.0, 22.7 ppm. LRMS (DEP/EI): m/z (%): 188.0 (11) $[M]^+$, 186.0 (11) [M]+, 171.0 (6), 107.1 (35), 91.1 (100), 79.1 (61), 65.1 (34), 51.0 (22). HRMS (EI): calcd for $C_8H_{11}{}^{79}Br^+$: 186.0044, found 188.0034. IR (ν, cm^{-1}) 2963 (s), 2948 (s), 2930 (vs), 2854 (m), 2362 (m), 2334 (m), 1735 (m), 1700 (m), 1653 (s), 1456 (m), 1438 (m), 1375 (m), 1261 (m), 1094 (s), 1031 (s), 1021 (s).

(*R,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-phenethylcyclobutyl) (phenyl)methanol (12a)**: Using bromide **11d** and benzaldehyde as aldehyde according to general procedure **D** afforded **12a** (88 mg, 60%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.24 (95:5 hexane:EtOAc, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.29 – 7.21 (m, 7H), 7.19 – 7.11 (m, 1H), 7.08 – 7.03 (m, 2H), 5.02 (t, *J* = 2.6 Hz, 1H), 4.84 (t, *J* = 2.1 Hz, 1H), 4.67 (d, *J* = 2.9 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.48 (ddd, *J* = 14.3, 9.4, 5.3 Hz, 1H), 2.35 – 2.18 (m, 3H), 2.11 (d, *J* = 2.9 Hz, 1H, OH), 1.54 – 1.31 (m, 2H), 1.00 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 155.6, 142.4, 141.0, 128.5, 128.4, 127.9, 127.5, 127.2, 125.8, 106.0, 79.2, 54.1, 36.3, 33.8, 33.8, 32.3, 14.3 ppm. HRMS (EI): calcd for $C_{14}H_{18}{}^+$ $[M\text{-}C_7H_7O]^+$: 186.1403, found 186.1397. IR (ν, cm^{-1}) 3568 (vw), 3454 (vw), 3084 (vw), 3062 (vw), 3027 (w), 2963 (w), 2932 (w), 2856 (w), 1668 (w), 1603 (w), 1494 (w), 1452 (m), 1371 (w), 1296 (w), 1188 (w), 1155 (w), 1081 (w), 1034 (m), 1022 (m).

(*R,*Z*,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-phenethylcyclobutyl) hexadec-11-en-1-ol (12b)**: Using bromide **11d** and (*Z*)-hexadec-11-enal as aldehyde according to general procedure **D** afforded **12b** (120 mg, 56%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.16 (98:2 hexane:EtOAc, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.30 – 7.26 (m, 2H), 7.20 – 7.16 (m, 3H), 5.41 – 5.30 (m, 2H), 4.89 (t, *J* = 2.7 Hz, 1H), 4.81 (t, *J* = 2.1 Hz, 1H), 3.49 – 3.42 (m, 1H), 2.80 (ddt, *J* = 16.0, 9.0, 2.5 Hz, 1H), 2.55 (dddd, *J* = 40.8, 13.7, 10.1, 5.8 Hz, 2H), 2.22 (ddt, *J* = 15.9, 5.0, 2.4 Hz, 1H), 2.07 – 1.96 (m, 5H), 1.85 – 1.75 (m, 1H), 1.72 – 1.69 (m, 1H), 1.68 – 1.59 (m, 1H), 1.59 – 1.52 (m, 1H), 1.32 – 1.26 (m, 19H), 1.01 (s, 3H), 0.91 – 0.88 ppm (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 156.1, 142.5, 130.0, 130.0, 128.5, 128.5, 125.9, 105.7, 77.0, 54.1, 36.8, 34.2, 33.8, 33.0, 32.1, 31.3, 29.9, 29.9, 29.8, 29.8, 29.7, 29.5, 27.4, 27.3, 27.1, 22.5, 14.2, 13.4 ppm. HRMS (EI): calcd for $C_{30}H_{48}O^+$: 424.3705, found 424.3690. IR (ν, cm^{-1}) 2924 (vs), 2854 (s), 1774 (w), 1668 (w), 1604 (w), 1496 (w), 1454 (m), 1375 (w), 1058 (w), 1030 (w).

(*S,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-phenethylcyclobutyl)(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methanol (12c)**: Using bromide **11d** and 6-nitrobenzo[*d*][1,3]dioxole-5-carbaldehyde as aldehyde according to general procedure **D** afforded **12c** (153 mg, 80%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.39 (80:20 hexane:EtOAc, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.35 (s, 1H), 7.31 – 7.22 (m, 3H), 7.21 – 7.10 (m, 3H), 6.09 (s, 2H), 5.78 (d, *J* = 4.2 Hz, 1H), 4.90 (t, *J* = 2.6 Hz, 1H), 4.83 (t, *J* = 2.1 Hz, 1H), 2.58 (ddt, *J* = 15.4, 9.0, 2.5 Hz, 1H), 2.54 – 2.34 (m, 3H), 2.23 (tt, *J* = 8.9, 6.0 Hz, 1H), 2.14 (ddt, *J* = 15.4, 6.1, 2.4 Hz, 1H), 1.56 – 1.48 (m, 2H), 1.05 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 153.8, 151.2, 147.0, 142.9, 142.5, 133.6, 128.4, 128.4, 125.8, 108.3, 107.1, 105.3 102.9, 72.2, 54.8, 36.2, 34.3, 34.1, 33.1, 15.9 ppm. IR (ν, cm^{-1}) 3552 (vw), 3026 (vw), 2914 (w), 2856 (vw), 1668 (w), 1618 (w), 1520 (s), 1504 (s), 1480 (s), 1454 (m), 1418 (m), 1394 (m), 1370 (m), 1332 (s), 1250 (vs), 1162 (w), 1120 (w), 1034 (vs).

(*S,1'*S**,4'*R**)-(3-Bromo-2-iodo-4,5-dimethoxyphenyl)(1'-methyl-2'-methylene-4'-phenethylcyclobutyl)methanol (12d)**: Using bromide **11d** and 3-bromo-2-iodo-4,5-dimethoxybenzaldehyde as aldehyde according to general procedure **D** afforded **12d** (194 mg, 70%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.24 (90:10 hexane:EtOAc, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.34 – 7.28 (m, 3H), 7.25 – 7.19 (m, 1H), 7.18 – 7.14 (m, 2H), 5.32 (d, *J* = 3.5 Hz, 1H), 5.03 (t, *J* = 2.6 Hz, 1H), 4.96 (t, *J* = 2.1 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 2.97 (ddt, *J* = 15.4, 9.3, 2.4 Hz, 1H), 2.69 (ddt, *J* = 9.1, 7.6, 5.9 Hz, 1H), 2.58 (dt, *J* = 13.6, 7.7 Hz, 1H), 2.46 (dt, *J* = 13.7, 8.0 Hz, 1H), 2.39 (d, *J* = 3.5 Hz, 1H), 2.28 (ddt, *J* = 15.6, 5.8, 2.3 Hz, 1H), 1.69 – 1.55 (m, 2H), 1.16 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 155.0, 153.1, 146.6, 142.6, 142.4, 128.5, 128.4, 126.4, 125.8, 112.1, 106.9, 96.6, 82.8, 60.5, 56.1, 55.3, 36.6, 34.6, 34.0, 32.7, 15.3 ppm. HRMS (EI): calcd for $C_{23}H_{26}{}^{79}BrIO_3{}^+$: 556.0110, found 556.0105. IR (ν, cm^{-1}) 3482 (w), 2962 (m), 2934 (m), 2854 (w), 2360 (w), 2342 (vw), 1668 (w), 1602 (w), 1578 (w), 1542 (m), 1496 (w), 1462 (vs), 1420 (vs), 1368 (s), 1334 (m), 1280 (m), 1246 (m), 1214 (m), 1190 (m), 1158 (m), 1058 (vs), 1030 (m), 1002 (s).

(*R,1'*S**,4'*R**)-(3-Chlorophenyl)(1'-methyl-2'-methylene-4'-propylcyclobutyl)methanol (12e)**: Using bromide **11a** and 3-chlorobenzaldehyde as aldehyde according to general procedure **D** afforded **12e** (110 mg, 83%) as a colorless oil in 99:1:0:0 *dr.* R_f= 0.48 (9:1 hexane:Et_2O, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.39 (br, 1H), 7.24 (d, *J* = 1.4, 3H), 5.01 (t, *J* = 2.7, 1H), 4.87 (t, *J* = 2.1, 1H), 4.69 (s, 1H), 2.79-2.71 (m, 1H), 2.30–2.16 (m, 2H), 1.31 – 1.00 (m, 4H), 0.97 (s, 3H), 0.94–0.87 (m, 1H), 0.83 ppm (t, *J*= 6.9, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$): δ: 155.6, 143.2, 133.9, 129.1, 127.6, 127.4, 125.4, 106.3, 78.6, 54.3, 36.8, 34.0, 32.7, 20.8, 14.3, 14.3 ppm. HRMS (EI): calcd for $C_{16}H_{21}ClO^+$: 264.1281; found: 264.1280. IR (ν, cm^{-1}) 3463 (w), 2958 (s), 2928 (s), 2872 (m), 1710 (w), 1668 (m), 1596 (m), 1573 (m), 1465 (m), 1428 (m), 1378 (m), 1283 (m), 1193 (m), 1079 (m).

(*S,1'*S**,4'*R**)-(3-Fluoro-6-methoxyquinolin-4-yl)(1'-methyl-2'-methylene-4'-phenethylcyclobutyl)methanol (12f)**: Using bromide **11d** and 3-fluoro-6-methoxyquinoline-4-carbaldehyde as aldehyde according to general procedure **D** afforded **12f** (110 mg, 58%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.08. (9:1 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.27 – 8.13 (m, 2H), 8.08 (d, *J* = 9.2 Hz, 1H), 7.31 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.25 – 7.12 (m, 3H), 6.99 – 6.94 (m, 2H), 5.63 (s, 1H), 5.04 (t, *J* = 2.6 Hz, 1H), 4.85 (t, *J* = 2.1 Hz, 1H), 3.91 (s, 3H), 2.78 (ddt, *J* = 15.3, 9.0, 2.3 Hz, 1H), 2.50 – 2.35 (m, 2H), 2.32 – 2.20 (m, 2H), 1.58 – 1.44 (m, 1H), 1.34 – 1.21 (m, 2H), 1.18 ppm (d, *J* = 1.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.5, 154.1, 153.8 (d, *J* = 250.1 Hz), 141.9, 129.9, 128.5, 128.5, 128.4, 128.4, 126.0, 123.4, 123.3, 107.0, 106.6, 106.5, 73.8, 55.8, 55.2, 36.0, 34.1, 33.6, 32.6, 16.6 ppm. HRMS (EI): calcd for $C_{25}H_{26}O_2NF^+$: 391.1948; found 391.1935. IR (ν, cm^{-1}) 3316 (m), 2935 (m), 2021 (w), 1670 (w), 1621 (m), 1602 (w), 1550 (w), 1509 (m) 1453 (m), 1422 (m), 1352 (m), 1307 (m), 1242 (s), 1249 (vs), 1144 (m), 1085 (w) 1027 (m).

(*S,1'*S**,4'*R**)-(5-Bromopyridin-3-yl)(1'-methyl-2'-methylene-4'-pentylcyclobutyl)methanol (12g)**: Using bromide **11b** and 5-bromonicotinealdehyde as aldehyde according to general procedure **D** afforded **12g** (79 mg, 59%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.23 (9:1 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.55 (s, 1H), 8.51(s, 1H), 8.00 (s, 1H), 4.96 (s, 1H), 4.87 (s, 1H), 4.74 (s, 1H), 2.70-2.62 (m, 1H), 1.20-2.13 (m, 2H), 1.30-1.15 (m, 8H), 1.06–1.02 (m, 1H), 0.97 (s, 3H), 0.82 ppm (t,*J* = 7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 154.5, 147.9, 145.1, 139.7, 139.1, 120.6, 107.0, 76.0, 54.0, 36.6, 33.9, 31.9, 30.4, 27.2, 22.6, 14.5, 14.1 ppm. HRMS (EI): *m/z* calcd for $C_{17}H_{24}{}^{79}BrNO^+$: 337.1041; found: 337.1039. IR (ν, cm^{-1}) 3282 (w), 2956 (m), 2925 (s), 2854 (m), 1669 (w), 1421 (m), 1098 (w), 1042 (m), 1021 (m).

(*R,1'*S**,4'*R**)-1-(1'-Methyl-2'-methylene-4'-pentylcyclobutyl)-3-phenylpropan-1-ol (12h)**: Using bromide **11b** and hydrocinnamaldehyde as aldehyde according to general procedure **D** afforded **12h** (93 mg, 68%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.15. (97:3 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.31–6.95 (m, 5H), 4.80 (t, *J* = 2.7, 1H), 4.72 (t, *J* = 2.2, 1H), 3.42 (dd, *J* = 7.0, 5.2, 1H), 2.96–2.82 (m, 1H), 2.70–2.49 (m, 2H), 2.07 (ddt, *J* = 16.0, 5.0, 2.3, 1H), 1.78 (ddt, *J* = 10.3, 9.0, 5.1, 1H), 1.65 – 1.57 (m, 2H), 1.34 (dtd, *J* = 13.5, 7.5, 6.0, 3.8, 1H), 1.26 – 1.04 (m, 8H), 0.92 (s, 3H), 0.81 ppm (t, *J* = 6.8, 3H). ^{13}C NMR (100 MHz, CDCl3): δ: 156.3, 142.5, 128.5, 128.4, 125.8, 105.5, 76.3, 53.8, 37.0, 33.7, 33.4, 33.0, 32.0, 30.7, 27.4, 22.7, 14.1, 13.1 ppm. HRMS (EI): *m/z* calcd for $C_{20}H_{30}O^+$: 286.2297; found: 286.2297. IR (ν, cm^{-1}) 3427 (w), 2954 (m), 2923 (s), 2855 (m), 1667 (w), 1604 (w), 1496 (m), 1454 (m), 1376 (m), 1260 (w) 1053 (m).

(*S,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-pentylcyclobutyl)(6-nitrobenzo[*d*][1,3]dioxol-5-yl)methanol (12i)**: Using bromide **11b** and 6-nitrobenzo[*d*][1,3]dioxole-5-carbaldehyde as aldehyde according to general procedure **D** afforded **12i** (108 mg, 62%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.10 (95:5 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.33 (s, 1H), 7.27 (s, 1H), 6.10 (s, 2H), 5.75 (s, 1H), 4.87 (t, *J* = 2.6, 1H),4.79 (t, *J* = 2.1, 1H), 2.58–2.51 (m, 1H), 2.34 (br, s, 1H, OH), 2.16 – 2.03 (m, 2H), 1.24–1.16 (m, 8H), 1.01 (s, 3H), 0.84 ppm (t, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 154.1, 151.0, 146.8, 142.8, 133.5, 108.3, 106.8, 105.2, 102.8, 72.1, 54.7, 36.2, 34.2, 31.9, 30.6, 27.2, 22.6, 15.7, 14.0 ppm. IR (ν, cm^{-1}) 3535 (vw), 2956 (w), 2923 (m), 2854 (w), 1669 (vw), 1617 (w), 1522 (m), 1504 (m), 1481 (s), 1332 (m), 1250 (s), 1120 (w).

(*R,1'*S**,4'*R**)-(3-Chloro-4-methoxyphenyl)(1'-methyl-2'-methylene-4'-pentylcyclobutyl)methanol (12j)**: Using bromide **11b** and 3-chloro-4-methoxybenzaldehyde as aldehyde according to general procedure **D** afforded **12j** (135 mg, 83%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.35 (9:1 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.38 (d, *J* = 2.1, 1H), 7.20 (dd, *J* = 8.5, 2.2, 1H), 6.85 (d, *J* = 8.5, 1H), 4.97 (t, *J* = 2.5, 1H), 4.83 (t, *J* = 2.0, 1H), 4.62 (s, 1H), 3.88 (s, 3H), 2.71 (dtd, *J* = 10.7, 8.1, 2.6, 1H), 2.27–2.10 (m, 2H), 1.33–1.06 (m, 9H), 0.95 (s, 3H), 0.82 ppm (t, *J* = 7.0, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 155.7, 154.3, 134.4, 129.1, 126.5, 121.9, 111.4, 106.1, 78.3, 56.3, 54.4, 37.0, 34.0, 32.0, 30.4, 27.3, 22.8, 14.2, 14.2 ppm. HRMS (EI): calcd for $C_{19}H_{27}O_2N^+$: 322.1700; found: 322.1674. IR (ν, cm^{-1}) 3431 (w), 2956 (m), 2927 (s), 2854 (m), 2362 (w), 1669 (w), 1604 (w), 1502 (s), 1462 (m), 1441 (w), 1377 (w), 1284 (m), 1235 (s), 1193 (w), 1064 (s), 1025 (m).

(*R,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-pentylcyclobutyl)(4-nitrophenyl)methanol (12k)**: Using bromide **11b** and 4-nitrobenzaldehyde as aldehyde according to general procedure **D** afforded **12k** (106 mg, 70%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.12 (95:5 hexane:EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.19 (d, *J* = 8.7, 2H), 7.58 (d, *J* = 8.7, 2H), 5.03 (s, 1H), 4.91 (s, 1H), 4.83 (s, 1H), 2.84–2.66 (m, 1H), 2.35-2.11 (m, 2H) 2.24 (s, 1H, OH), 1.34–1.09 (m, 7H), 1.06–0.99 (m, 1H), 0.98 (s, 3H), 0.86 ppm (t, *J* = 6.9, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 155.1, 148.7, 147.3, 128.1, 123.0, 106.8, 78.3, 54.3, 37.0, 34.0, 31.9, 30.4, 27.3, 22.7, 14.4, 14.1 ppm. HRMS (EI): calcd for $C_{18}H_{25}NO_3^+$: 303.1834; found: 303.1858. IR (ν, cm^{-1}) 3556 (vw), 2974 (w), 2927 (m), 1708 (w), 1669 (w), 1520 (m), 1345 (s), 1198 (w), 1108 (w), 1042 (w).

(*R,1'*S**,4'*R**)-(1'-Methyl-2'-methylene-4'-propylcyclobutyl)(4-nitrophenyl)methanol (12l)**: Using bromide **11a** and 4-nitrobenzaldehyde as aldehyde according to general procedure **D** afforded **12l** (96 mg, 70%) as a colorless oil in 99:1:0:0 *dr*. R_f = 0.10 (97:3 hexane:EtOAc, UV, $KMnO_4$ PAA). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 8.15 (d, *J* = 8.8, 2H), 7.53 (d, *J* = 9.6, 2H), 4.99 (t, *J* = 2.7, 1H), 4.87 (t, *J* = 2.2, 1H), 4.80 (s, 1H), 2.72 (ddt, *J* = 15.6, 8.8, 2.5, 1H), 2.32 – 2.12 (m, 2H), 2.28 (s, 1H, OH), 1.23 – 0.98 (m, 4H), 0.93 (s, 3H), 0.81 ppm (t, *J* = 6.9, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 155.1, 148.7, 147.3, 128.1, 123.1, 106.8, 78.3, 54.3, 36.8, 34.0, 32.7, 20.8, 14.4, 14.3 ppm. HRMS (EI): calcd for $C_{16}H_{20}NO_2^+$; $[M–OH]^+$: 258.1494; found: 258.1476. IR (ν, cm^{-1}) 3541 (w), 3075 (vw), 2957 (w), 2928 (w), 2871 (w), 1668 (w), 1604 (w), 1516 (s), 1458 (w), 1344 (s), 1253 (w), 1179 (w), 1109 (w), 1039 (m), 1013 (w).

2-(2-Methyl-3-pentylcyclobut-1-en-1-yl)benzo[*b*] thiophene (18a): To a solution of benzo[*b*]thiophene in THF (0.25 M) was dropwise added at room temperature a freshly titrated solution of TMPMgCl·LiCl in THF (1.1 eq, 1.1 M). The mixture was stirred at aforesaid temperature for 2 hours, until iodolysis of a sample indicated completed metallation. A solution of zinc chloride in THF (1.1 eq, 1.0 M) was dropwise added and the mixture stirred for another 30 mins at room temperature to allow full transmetallation. In a second reaction tube $Pd(dba)_2$ (2 mol%) and TFP (4 mol%) were dissolved in THF and stirred for 5 mins, to allow ligand exchange. Iodide **17b** was added (0.3 M) and the reaction mixture was stirred for another 5 mins before the previously obtained zinc species (1.5 eq) was added at once. The reaction mixture was stirred at room temperature for 2 hours and then quenched by addition of saturated aqueous ammonium chloride solution. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with Brine and dried over magnesium sulfate. The dried organic phase was filtrated and concentrated under reduced pressure and the product was obtained by flash column chromatography using hexanes as an eluent. The title compound **18a** was obtained as a colorless oil (61 mg, 76%). R_f = 0.67 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.77 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.30 (ddd, 2H), 7.04 (s, 1H), 2.84 (ddt, *J* = 11.4, 4.3, 2.2 Hz, 1H), 2.77 – 2.65 (m, 1H), 2.28 (dp, *J* = 11.9, 2.1

Hz, 1H), 1.98 (q, *J* = 2.0 Hz, 3H), 1.79 – 1.62 (m, 1H), 1.46 – 1.24 (m, 7H), 0.92 ppm (t, *J* = 6.8 Hz, 3H. ^{13}C NMR (101 MHz, $CDCl_3$): δ: 144.8, 139.8, 139.6, 139.2, 130.9, 124.4, 124.0, 123.3, 122.3, 119.0, 42.8, 33.8, 33.0, 32.3, 27.4, 22.8, 14.3, 14.3 ppm. HRMS (EI): calcd for $C_{18}H_{22}S^+$: 270.1442, found 270.1446. IR (ν, cm^{-1}) 3057 (vw), 2955 (m), 2920 (m), 2853 (m), 1713 (w), 1695 (w), 1667 (w), 1593 (vw), 1562 (vw), 1516 (w), 1456 (m), 1435 (m), 1372 (m), 1354 (w), 1330 (w), 1302 (m), 1250 (w), 1227 (w), 1182 (w), 1155 (m), 1130 (w), 1066 (w), 1016 (w).

2-(2-Methyl-3-propylcyclobut-1-en-1-yl)benzofuran (18b): The same procedure as for **18a** was used, but iodide **17a** was employed. (As the metallation of benzofurane with TMPMgCl·LiCl was not completed after 3 h at room temperature, the concentration of metallated benzofurane was determined through iodolysis and GC-analysis. Excess of zinc chloride solution was used to grant full transmetallation of the metallated benzofurane.) The title compound **18b** was obtained as a colorless oil (48 mg, 96%). R_f = 0.71 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.50 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.28 – 7.14 (m, 2H), 6.46 (s, 1H), 2.83 – 2.70 (m, 2H), 2.23 (dq, *J* = 11.7, 2.0 Hz, 1H), 2.05 (q, *J* = 2.0 Hz, 3H), 1.76 – 1.65 (m, 1H), 1.48 – 1.30 (m, 3H), 0.99 – 0.91 ppm (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 154.7, 153.6, 146.5, 128.9, 126.7, 123.9, 122.7, 120.7, 111.0, 101.6, 43.2, 35.2, 32.2, 20.9, 14.7, 14.5 ppm. IR (ν, cm^{-1}) 2957 (w), 2920 (m), 2871 (w), 2844 (w), 2359 (vw), 2337 (vw), 1713 (w), 1708 (w), 1699 (w), 1683 (m), 1614 (w), 1559 (w), 1464 (w), 1451 (s), 1374 (w), 1356 (w), 1301 (m), 1256 (m), 1184 (m), 1156 (m), 1140 (m), 1108 (w), 1086 (w), 1025 (w), 1005 (m).

1-Fluoro-4-(2-methyl-3-octylcyclobut-1-en-1-yl) benzene (18c): To a solution of 1-fluoro-4-iodobenzene in THF (0.5 M) was dropwise added a solution of *n*-BuLi at −78 °C. The solution was stirred for 30 mins at aforesaid temperature, to allow full halogen metal exchange. A solution of zinc chloride (1.1 eq, 1.0 M) was added dropwise and the solution was warmed to room temperature. After stirring for 30 mins at room temperature, the amount of metallated species was determined through iodolysis and GC-analysis. In a second reaction tube $Pd(dba)_2$ (2 mol%) and TFP (4 mol%) were dissolved in THF and stirred for 5 mins, to allow ligand exchange. Iodide **17c** was added (0.3 M) and the reaction mixture was stirred for another 5 mins before the previously obtained zinc species (1.5 eq) was added at once. The reaction mixture was stirred at room temperature for 2 hours and then quenched by addition of saturated aqueous ammonium chloride solution. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with Brine and dried over magnesium sulfate. The dried organic phase was filtrated and concentrated under reduced pressure and the product was obtained by flash column chromatography using hexanes as an eluent. The title compound **18c** was obtained as a colorless oil (51 mg, 62%). R_f = 0.85 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.34 – 7.26 (m, 2H), 7.06 – 6.99 (m, 2H), 2.75 (ddq, *J* = 12.0, 4.3, 2.1 Hz, 1H), 2.62 (dd, *J* = 8.7, 4.8 Hz, 1H), 2.17 (dp, *J* = 12.1, 2.2 Hz, 1H), 1.96 (q, *J* = 2.0 Hz, 3H), 1.73 – 1.65 (m, 1H), 1.44 – 1.22 (m, 13H), 0.94 – 0.86 ppm (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 161.5 (d, *J* = 245.6 Hz), 142.3 (d, *J* = 2.2 Hz), 134.8, 132.8 (d, *J* = 3.2 Hz), 127.1 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.4 Hz), 41.9, 33.1, 32.9, 32.1, 30.1, 29.8, 29.5, 27.7, 22.9, 14.3, 14.2 ppm. IR (ν, cm^{-1}) 2956 (m), 2923 (s), 2853 (m), 1716 (vw), 1690 (w), 1655 (vw), 1601 (w), 1508 (vs), 1466 (w), 1410 (w), 1376 (w), 1354 (w), 1324 (w), 1294 (w), 1230 (s), 1155 (m), 1104 (w), 1070 (vw), 1013 (vw).

2,4-Dibromo-6-(2-methyl-3-octylcyclobut-1-en-1-yl)Pyridine (18d): The same procedure as for **18a** was used, but iodide **17c** was employed. (full metallation of 2,4-dibromopyridine was achieved at –25 °C after 3 h) The title compound **18d** was obtained as a slightly yellow oil (67 mg, 54%). R_f = 0.33 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.42 – 7.40 (m, 1H), 7.17 (d, *J* = 1.4 Hz, 1H), 2.83 – 2.70 (m, 1H), 2.70 – 2.59 (m, 1H), 2.24 – 2.14 (m, 1H), 2.11 (q, *J* = 1.9 Hz, 3H), 1.74 – 1.61 (m, 1H), 1.44 – 1.16 (m, 13H), 0.88 ppm (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 156.2, 154.1, 141.9, 133.6, 133.6, 127.1, 121.8, 42.6, 32.5, 32.4, 31.9, 29.9, 29.6, 29.3, 27.5, 22.7, 14.6, 14.2 ppm. HRMS (EI): calcd for $C_{18}H_{25}{}^{79}Br_2N^+$: 413.0345, found 413.0345. IR (ν, cm^{-1}) 3098 (vw), 2954 (w), 2921 (m), 2852 (m), 1654 (m), 1554 (vs), 1520 (s), 1465 (w), 1430 (w), 1380 (w), 1368 (m), 1352 (m), 1300 (w), 1240 (vw), 1184 (w), 1151 (s), 1122 (w), 1081 (m).

1-Methoxy-4-(2-methyl-3-octylcyclobut-1-en-1-yl) benzene (18e): To a freshly titrated solution of (4-methoxyphenyl)magnesium bromide in THF (0.55 M) was added a solution of zinc chloride in THF (1.0 M) and stirred for 30 minutes at room temperature. In a second reaction tube $Pd(dba)_2$ (2 mol%) and TFP (4 mol%) were dissolved in THF and stirred for 5 mins, to allow ligand exchange. Iodide **17c** was added (0.3 M) and the reaction mixture was stirred for another 5 mins before the previously obtained zinc species (1.5 eq) was added at once. The reaction mixture was stirred at room temperature for 2 hours and then quenched by addition of saturated aqueous ammonium chloride solution. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were washed with Brine and dried over magnesium sulfate. The dried organic phase was filtrated and concentrated under reduced pressure and the product was obtained by flash column chromatography using hexanes as an eluent. The title compound **18e** was obtained as a colorless oil (61 mg, 71%). R_f = 0.1 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.30 –7.24 (m, 2H), 6.90 – 6.85 (m, 2h), 3.81 (s, 3H), 2.73 (m, 1H), 2.62 – 2.55 (m, 1H), 2.15 (dt, *J* = 12.1 , 2.1 Hz, 1H), 1.95 – 1.92 (m, 3H), 1.74 – 1.62 (m, 1H), 1.44 – 1.22 (m, 13H), 0.90 ppm (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.3, 140.4, 135.2, 129.7, 126.8, 113.9, 55.4, 41.8, 33.2, 32.9, 32.1, 30.2, 29.8, 29.5, 27.8, 22.9, 14.3, 14.2 ppm. HRMS (EI): calcd for $C_{20}H_{30}O^+$: 286.2297, found 286.2304. IR (ν, cm^{-1}) 2955 (w), 2922 (s), 2852 (m), 1606 (m), 1673 (w), 1510 (s), 1464 (m), 1442 (w), 1418 (w) 1375 (w), 1330 (w), 1301 (w), 1391 (m), 1344 (vs), 1172 (m), 1114 (w), 1072 (w), 1038 (m).

1-Chloro-3-(2-methyl-3-octylcyclobut-1-en-1-yl) benzene (18f): **18f** was obtained like **18c**, using 1-chloro-3-iodobenzene. The title compound **18f** was obtained as a colorless oil (56 mg, 56%). R_f = 0.95 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.32 – 7.14 (m, 4H), 2.75 (ddq, *J* = 12.1, 4.4, 2.2 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.18 (dp, *J* = 12.1, 2.2 Hz, 1H), 1.98 (q, *J* = 2.0 Hz, 3H), 1.74 – 1.64 (m, 1H), 1.44 – 1.21 (m, 13H), 0.94 – 0.86 ppm (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 145.0, 138.2, 134.7, 134.4, 129.7, 126.4, 125.6, 123.7, 42.0, 32.9, 32.8, 32.1, 30.1, 29.8, 29.5, 27.7, 22.9, 14.4, 14.3 ppm. IR (ν, cm^{-1}) 2956 (m), 2924 (vs), 2853 (m), 2361 (vw), 2339 (vw), 1716 (vw), 1693 (w), 1652 (w), 1593 (m), 1562 (w), 1468 (w), 1425 (w), 1374 (w), 1325 (w), 1260 (vw), 1233 (vw), 1182 (vw), 1110 (vw), 1080 (w).

(2-(2-Methylallyl)cyclobut-1-en-1-yl)benzene (19a): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and phenylboronic acid according to general procedure **E** provided **19a** (43 mg, 93%) as pale yellow oil. R_f = 0.8 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 4H), 7.24 – 7.18 (m, 1H), 4.83 – 4.79 (m, 2H), 3.11 – 3.07 (m, 2H), 2.69 – 2.63 (m, 2H), 2.47 – 2.43 (m, 2H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.7, 140.4, 139.3, 136.1, 128.5, 126.8, 125.7, 111.6, 39.1 28.4, 26.1, 23.1 ppm. HRMS (EI): calcd for $C_{14}H_{16}^+$: 184.1252, found 184.1247. IR (ν, cm^{-1}) 3079 (w), 3061 (w), 3027 (w), 2914 (m), 2836 (w), 1720 (w), 1714 (w), 1688 (s), 1656 (w), 1650 (m), 1644 (w), 1598 (m), 1493 (m), 1448 (m), 1426 (w), 1414 (w), 1374 (m), 1358 (w), 1335 (w), 1323 (m), 1301 (w), 1263 (m), 1245 (m), 1221 (w), 1212 (m), 1179 (w), 1107 (w), 1082 (w), 1066 (m), 1052 (w), 1020 (m), 1002 (w).

1-Methoxy-3-(2-(2-methylallyl)cyclobut-1-en-1-yl)benzene (19b): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (3-methoxyphenyl)boronic acid according to general procedure **E** provided **19b** (50 mg, 93%) as colorless oil. R_f = 0.4 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.9 Hz, 1H), 6.92 (d, *J* =

7.6, 1.2 Hz, 1H), 6.86 – 6.84 (m, 1H), 6.75 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.82 – 4.77 (m, 2H), 3.79 (s, 3H), 3.08 – 3.05 (m, 2H), 2.65 – 2.61 (m, 2H), 2.44 – 2.40 (m, 2H), 1.76 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.7, 142.7, 140.8, 139.2, 137.4, 129.4, 118.4, 112.4, 111.7, 111.2, 55.3, 39.1, 28.4, 26.2, 23.0 ppm. HRMS (EI): calcd for $C_{15}H_{18}O^+$: 214.1358, found 214.1350. IR (ν, cm^{-1}) 3075 (w), 2939 (m), 2913 (m), 2833 (w), 1689 (w), 1650 (w), 1598 (m), 1576 (s), 1486 (m), 1482 (m), 1464 (m), 1452 (m), 1428 (m), 1374 (w), 1334 (m), 1285 (m), 1262 (s), 1220 (s), 1195 (m), 1175 (m), 1166 (s), 1092 (w), 1043 (s).

Methyl 4-(2-(2-methylallyl)cyclobut-1-en-1-yl)benzoate (19c): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (4-(methoxycarbonyl)phenyl)-boronic acid according to general procedure **E** provided **19c** (50 mg, 83%) as colorless oil. R_f = 0.6 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.39 – 7.34 (m, 2H), 4.84 – 4.79 (m, 2H), 3.90 (s, 3H), 3.13 – 3.09 (m, 2H), 2.70 – 2.65 (m, 2H), 2.50 – 2.44 (m, 2H), 1.78 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 144.1, 142.1, 140.1, 138.6, 129.8, 128.0, 125.5, 111.9, 52.2, 39.2, 28.7, 26.1, 23.1 ppm. HRMS (EI): calcd for $C_{16}H_{18}O_2^+$: 242.1307, found 242.1302. IR (ν, cm^{-1}) 2949 (w), 2918 (m), 2850 (w), 1721 (s), 1640 (w), 1606 (m), 1435 (m), 1310 (w), 1276 (vs), 1194 (w), 1177 (w), 1110 (m), 1016 (w).

***tert*-Butyl(3-(2-(2-methylallyl)cyclobut-1-en-1-yl)phenyl) carbamate (19d)**: Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (3-((tert-butoxycarbonyl) amino)-phenyl)boronic acid according to general procedure **E** provided **19d** (35 mg, 62%) as pale yellow oil. R_f = 0.5 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.25 – 7.20 (m, 3H), 7.04 – 7.00 (m, 1H), 6.43 (s, 1H), 4.81 – 4.78 (m, 2H), 3.09 – 3.06 (m, 2H), 2.65 – 2.60 (m, 2H), 2.44 – 2.38 (m, 2H), 1.77 (s, 3H), 1.51 ppm (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 152.8, 142.7, 140.9, 139.0, 138.5, 136.8, 129.1, 120.6, 117.0, 115.7, 111.7, 80.6, 39.1, 28.5, 28.3, 26.2, 23.1 ppm. HRMS (EI): calcd for $C_{19}H_{25}NO_2^+$: 299.1885, found 299.1880. IR (ν, cm^{-1}) 3332 (w), 3075 (vw), 2977 (w), 2916 (m), 2835 (w), 1729 (m), 1703 (m), 1606 (m), 1586 (m), 1544 (m), 1536 (m), 1530 (m), 1486 (m), 1442 (m), 1425 (m), 1404 (w), 1392 (w), 1367 (m), 1282 (w), 1236 (m), 1160 (vs), 1054 (m).

***N*,*N*-Dimethyl-4-(2-(2-methylallyl)cyclobut-1-en-1-yl)aniline (19e)**: Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (4-(dimethylamino)phenyl)-boronic acid according to general procedure **E** provided **19e** (32 mg, 56%) as yellow oil. R_f = 0.7 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.21 (m, 2H), 6.71 – 6.66 (m, 2H), 4.79 – 4.76 (m, 2H), 3.05 – 3.02 (m, 2H), 2.93 (s, 6H), 2.62 – 2.57 (m, 2H), 2.42 – 2.38 (m, 2H), 1.76 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 143.2, 139.1, 135.6, 126.7, 125.2, 112.5, 111.2, 40.7, 39.1, 28.2, 26.1, 23.0 ppm. HRMS (EI): calcd for $C_{16}H_{21}N^+$: 227.1674, found 227.1660. IR (ν, cm^{-1}) 3075 (w), 2966 (w), 2911 (m), 2835 (m), 1609 (s), 1520 (vs), 1480 (w), 1461 (w), 1444 (m), 1428 (w), 1353 (s), 1265 (w), 1224 (m), 1194 (m), 1167 (m), 1128 (w), 1061 (w).

3-(2-(2-Methylallyl)cyclobut-1-en-1-yl)thiophene (19f): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and thiophen-3-ylboronic acid according to general procedure **E** provided **19f** (46 mg, 81%) as orange oil. R_f = 0.8 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.18 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.15 – 7.12 (m, 1H), 4.86 – 4.80 (m, 2H), 3.06 – 3.00 (m, 2H), 2.68 – 2.62 (m, 2H), 2.51 – 2.44 (m, 2H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 138.1, 138.1, 134.9, 125.8, 125.6, 120.3, 111.6, 39.0, 28.8, 26.8, 22.9 ppm. HRMS (EI): calcd for $C_{12}H_{14}S^+$: 190.0816, found 190.0814. IR (ν, cm^{-1}) 3101 (vw), 3075 (w), 2969 (w), 2940 (m), 2913 (m), 2835 (w), 1656 (w), 1650 (w), 1644 (w), 1442 (w), 1426 (w), 1412 (w), 1373 (w), 1302 (w), 1268 (w), 1207 (w), 1182 (w), 1082 (w), 1066 (w).

1-Fluoro-3-(2-(2-methylallyl)cyclobut-1-en-1-yl)benzene (19g): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (3-fluorophenyl)boronic acid according to general procedure **E** provided **19g** (50 mg, 83%) as pale yellow oil. R_f = 0.9 (hexane, UV, $KMnO_4$, PAA). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (td, *J* = 8.0, 6.0 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.05 – 7.00 (m, 1H), 6.91 (td, *J* = 8.5, 2.6, 0.9 Hz, 1H), 4.86 – 4.80 (m, 2H), 3.10 – 3.08 (m, 2H), 2.67 – 2.63 (m, 2H), 2.49 – 2.45 (m, 2H), 1.80 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.11 (d, *J* = 245.0 Hz), 142.3, 142.1, 138.32 (d, *J* = 2.4 Hz), 138.14 (d, *J* = 7.7 Hz), 129.89 (d, *J* = 8.4 Hz), 121.42 (d, *J* = 2.8 Hz), 113.59 (d, *J* = 21.4 Hz), 112.41 (d, *J* = 21.4 Hz), 111.8, 39.0, 28.5, 26.2, 23.1 ppm. HRMS (EI): calcd for $C_{14}H_{15}F^+$: 202.1158, found 202.1153. IR (ν, cm^{-1}) 2964 (w), 2933 (w), 2915 (m), 2832 (w), 1650 (w), 1643 (w), 1610 (s), 1580 (s), 1483 (m), 1445 (s), 1375 (w), 1334 (m), 1264 (m), 1210 (w), 1181 (m), 1174 (m), 1154 (m).

1-(2-(2-Methylallyl)cyclobut-1-en-1-yl)-3-nitrobenzene (19h): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (3-nitrophenyl)boronic acid according to general procedure **E** provided **19h** (40 mg, 58%) as yellow oil. R_f = 0.8 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 2.0 Hz, 1H), 8.06 – 8.01 (m, 1H), 7.63 – 7.59 (m, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 4.87 – 4.82 (m, 2H), 3.14 – 3.10 (m, 2H), 2.72 – 2.69 (m, 2H), 2.53 – 2.50 (m, 2H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 144.3, 141.9, 137.4, 137.3, 131.4, 129.3, 121.3, 120.4, 112.2, 39.1, 28.9, 26.2, 23.0 ppm. HRMS (EI): calcd for $C_{14}H_{15}NO_2^+$: 229.1103, found 229.1091. IR (ν, cm^{-1}) 3077 (vw), 2916 (w), 2829 (w), 1642 (w), 1525 (vs), 1478 (w), 1442 (w), 1423 (w), 1374 (w), 1348 (vs), 1306 (w), 1264 (w), 1222 (w), 1201 (w), 1178 (w), 1099 (w).

3-(2-(2-Methylallyl)cyclobut-1-en-1-yl)benzaldehyde (19i): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and (3-formylphenyl)boronic acid according to general procedure **E** provided **19i** (40 mg, 63%) as pale yellow oil. R_f = 0.6 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.81 – 7.78 (m, 1H), 7.71 (dt, *J* = 7.4, 1.5 Hz, 1H), 7.59 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 4.86 – 4.80 (m, 2H), 3.12 (s, 2H), 2.73 – 2.67 (m, 2H), 2.53 – 2.46 (m, 2H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 142.7, 142.2, 138.1, 136.8, 136.6, 131.6, 129.1, 128.0, 126.7, 112.0, 39.1, 28.7, 26.2, 23.0 ppm. HRMS (EI): calcd for $C_{15}H_{16}O^+$: 212.1201, found 212.1179. IR (ν, cm^{-1}) 3076 (w), 2968 (w), 2937 (w), 2915 (m), 2830 (w), 2726 (w), 1698 (vs), 1650 (w), 1642 (w), 1597 (w), 1580 (w), 1442 (w), 1434 (w), 1377 (w), 1262 (w), 1205 (w), 1174 (m), 1162 (m).

1-Methoxy-3-(2-methyl-3-pentylcyclobut-1-en-1-yl)benzene (20a): Using **17b** as iodide and (3-methoxyphenyl)boronic acid according to general procedure **E** provided **20a** (49 mg, 91%) as a colorless oil. R_f = 0.62 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.23 (d, *J* = 7.9 Hz, 1H), 6.94 (ddd, *J* = 7.5, 1.2 Hz, 1H), 6.85 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.75 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.74 (ddt, *J* = 12.0, 4.3, 2.1 Hz, 1H), 2.65 – 2.56 (m, 1H), 2.17 (dt, *J* = 12.1, 2.1 Hz, 1H), 1.96 (q, *J* = 2.0 Hz, 3H), 1.73 – 1.62 (m, 1H), 1.44 – 1.23 (m, 7H), 0.95 – 0.86 ppm (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 159.7, 143.6, 137.9, 135.7, 129.4, 118.3, 112.0, 111.1, 55.3, 41.9, 33.0, 32.9, 32.3, 27.4, 22.9, 14.3, 14.3 ppm. HRMS (EI): calcd for $C_{17}H_{24}O^+$ 244.1827, found 244.1816. IR (ν, cm^{-1}) 2955 (m), 2922 (vs), 2870 (m), 2854 (m), 1653 (w), 1604 (s), 1599 (s), 1577 (s), 1487 (m), 1465 (m), 1454 (m), 1432 (m), 1376 (w), 1372 (w), 1332 (m), 1323 (m), 1285 (s), 1250 (s), 1230 (w), 1212 (m), 1176 (m), 1167 (m), 1047 (s).

1-Fluoro-4-(2-methyl-3-pentylcyclobut-1-en-1-yl)benzene (20b): Using **17b** as iodide and (4-fluorophenyl)boronic acid according to general procedure **E** provided **20b** (51 mg, 98%) as a colorless oil. R_f = 0.88 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.33 – 7.26 (m, 2H), 7.07 – 6.98 (m, 2H), 2.75 (ddq, *J* = 12.0, 4.4, 2.1 Hz, 1H), 2.65 – 2.57 (m, 1H), 2.17 (dp, *J* = 12.1, 2.2 Hz, 1H), 1.96 (q, *J* = 2.0 Hz, 3H), 1.75 – 1.65 (m, 1H), 1.45 – 1.27 (m, 7H), 0.92 ppm (m, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$): δ: 161.5 (d, *J* = 245.5 Hz), 142.3 (d, *J* = 2.3 Hz), 134.8, 132.8 (d, *J* = 3.2 Hz), 127.1 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.4 Hz), 41.9, 33.0, 32.9, 32.3, 27.4, 22.9, 14.3, 14.2. ppm. HRMS (EI): calcd for $C_{16}H_{21}F^+$: 232.1627, found 232.1624. IR (ν, cm^{-1}) 2957 (m), 2923 (m), 2855 (m), 1655 (vw), 1601 (w), 1507 (vs), 1467 (w), 1408 (vw), 1376 (w), 1324 (w), 1294 (w), 1230 (s), 1182 (vw), 1155 (m), 1104 (w), 1069 (vw), 1012 (vw).

1-Fluoro-4-(2-methyl-3-phenethylcyclobut-1-en-1-yl) benzene (20c): Using **17d** as iodide and (4-fluorophenyl)boronic acid according to general procedure **E** provided **20c** (71 mg, 80%) as a colorless oil. R_f = 0.51 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.29 (ddd, *J* = 7.8, 4.7, 2.0 Hz, 4H), 7.23 – 7.16 (m, 3H), 7.05 – 6.96 (m, 2H), 2.79 – 2.63 (m, 4H), 2.20 (dp, *J* = 12.1, 2.0 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.93 (q, *J* = 2.0 Hz, 3H), 1.72 – 1.58 ppm (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 161.6 (d, *J* = 245.7 Hz), 142.8, 141.8 (d, *J* = 2.2 Hz), 135.0, 132.6 (d, *J* = 3.3 Hz), 128.6, 128.4, 127.2 (d, *J* = 7.8 Hz), 125.8, 115.3 (d, *J* = 21.4 Hz), 41.4, 35.0, 34.1, 32.8, 14.2 ppm. HRMS (EI): calcd for $C_{19}H_{19}F^+$: 266.1371, found 266.1461. IR (ν, cm^{-1}) 3027 (w), 2911 (m), 2851 (w), 2363 (vw), 2338 (vw), 1654 (w), 1601 (w), 1507 (vs), 1455 (w), 1437 (w), 1374 (w), 1323 (w), 1229 (m), 1156 (m), 1105 (vw), 1070 (vw).

(2-Methyl-3-phenethylcyclobut-1-en-1-yl)benzene (20d): Using **17d** as iodide and phenylboronic acid according to general procedure **E** provided **20d** (78 mg, 94%) as a colorless oil. R_f = 0.71 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.36 – 7.27 (m, 6H), 7.24 – 7.16 (m, 4H), 2.79 (ddt, *J* = 11.7, 4.0, 1.9 Hz, 1H), 2.75 – 2.64 (m, 3H), 2.24 (dp, *J* = 12.1, 2.2 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.98 – 1.95 (m, 3H), 1.66 ppm (dtd, *J* = 13.4, 9.5, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 142.9, 142.6, 136.3, 136.1, 128.6, 128.4, 126.6, 125.8, 125.7, 41.4, 35.0, 34.1, 32.6, 14.3 ppm. (2 aromatic ^{13}C signals overlapping) HRMS (EI): calcd for $C_{19}H_{20}^+$: 248.1565, found 248.1544. IR (ν, cm^{-1}) 3061 (w), 3026 (w), 2911 (m), 2851 (w), 2363 (vw), 2338 (vw), 1688 (vw), 1656 (vw), 1651 (vw), 1601 (w), 1494 (m), 1453 (w), 1446 (m), 1374 (w), 1322 (w), 1181 (w), 1056 (w), 1030 (w).

***tert*-Butyl (3-(2-methyl-3-phenethylcyclobut-1-en-1-yl)phenyl) carbamate (20e)**: Using **17d** as iodide and (3-((tert-butoxycarbonyl)amino)phenyl)boronic acid according to general procedure **E** provided **20e** (76 mg, 62%) as a colorless oil. R_f = 0.50 (95:5 hexane:EtOAc, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.33 – 7.14 (m, 8H), 7.02 (dt, *J* = 6.8, 1.7 Hz, 1H), 6.44 (s, 1H), 2.77 (ddd, *J* = 12.2, 4.5, 2.2 Hz, 1H), 2.73 – 2.61 (m, 3H), 2.22 (dt, *J* = 12.1, 2.1 Hz, 1H), 2.09 – 1.97 (m, 1H), 2.00 – 1.93 (m, 3H), 1.64 (dtd, *J* = 13.3, 9.5, 6.0 Hz, 1H), 1.52 ppm (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 156.2, 143.1, 142.9, 138.5, 137.1, 135.9, 129.0, 128.6, 128.4, 125.8, 120.5, 118.3, 116.8, 80.6, 41.4, 34.9, 34.1, 32.7, 28.5, 14.3 ppm. HRMS (EI): calcd for $C_{24}H_{29}NO_2^+$: 363.2198, found 363.2198. IR (ν, cm^{-1}) 3331 (w), 2978 (w), 2927 (w), 2856 (w), 2363 (vw), 2339 (vw), 1728 (m), 1700 (m), 1654 (w), 1606 (m), 1586 (m), 1539 (m), 1493 (m), 1454 (m), 1439 (m), 1421 (w), 1392 (w), 1367 (m), 1285 (m), 1236 (m), 1158 (vs), 1055 (w), 1029 (w).

3-(2-Methyl-3-phenethylcyclobut-1-en-1-yl)thiophene (20f): Using **17d** as iodide and thiophen-3-ylboronic acid according to general procedure **E** provided **20f** (90 mg, 98%) as a colorless oil. R_f = 0.38 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.29 (td, *J* = 6.5, 5.6, 3.5 Hz, 3H), 7.24 – 7.16 (m, 4H), 7.09 (d, *J* = 2.5 Hz, 1H), 2.81 – 2.67 (m, 4H), 2.22 (dp, *J* = 11.9, 2.1 Hz, 1H), 2.02 (dddd, *J* = 13.9, 9.5, 6.6, 4.7 Hz, 1H), 1.90 (q, *J* = 2.0 Hz, 3H), 1.67 ppm (dtd, *J* = 13.3, 9.3, 6.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 142.9, 140.3, 138.3, 131.9, 128.6, 128.4, 125.8, 125.7, 119.9, 42.0, 35.1, 34.1, 33.3, 14.0 ppm. (2 aromatic ^{13}C signals overlapping) HRMS (EI): calcd for $C_{17}H_{18}S^+$: 254.1129, found 254.1122. IR (ν, cm^{-1}) 3104 (vw), 3084 (vw), 3062 (vw), 3026 (w), 2909 (m), 2850 (w), 1690 (w), 1603 (w), 1496 (m), 1453 (m), 1413 (w), 1371 (w), 1298 (w), 1234 (w), 1202 (w), 1180 (w), 1085 (w), 1076 (w), 1030 (w).

1-(2-Methyl-3-phenethylcyclobut-1-en-1-yl)-3-nitrobenzene (20g): Using **17d** as iodide and (3-nitrophenyl)boronic acid according to general procedure **E** provided **20g** (69 mg, 70%) as a colorless oil. R_f = 0.67 (95:5 hexane:EtOAc, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 8.11 (t, *J* = 2.0 Hz, 1H), 8.03 (ddd, *J* = 8.2, 2.3, 1.0 Hz, 1H), 7.61 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.23 – 7.18 (m, 3H), 2.83 (ddd, *J* = 12.1, 4.5, 2.2 Hz, 1H), 2.72 (dt, *J* = 9.0, 6.7 Hz, 3H), 2.28 (dt, *J* = 12.1, 2.1 Hz, 1H), 2.11 – 2.03 (m, 1H), 2.02 (d, *J* = 1.7 Hz, 3H), 1.67 ppm (dtd, *J* = 13.4, 9.4, 6.1 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$): δ: 148.6, 146.5, 142.5, 137.8, 134.2, 131.4, 129.3, 128.6, 128.5, 125.9, 121.1, 120.2, 41.7, 34.7, 34.0, 32.7, 14.4 ppm. HRMS (EI): calcd for $C_{19}H_{19}NO_2^+$: 293.1416, found 293.1409. IR (ν, cm^{-1}) 3085 (vw), 3062 (vw), 3026 (w), 2914 (w), 2855 (w), 1700 (w), 1696 (w), 1684 (w), 1653 (w), 1603 (w), 1527 (vs), 1496 (m), 1454 (w), 1438 (w), 1349 (vs), 1181 (w), 1079 (w).

1-(2-Methyl-3-phenethylcyclobut-1-en-1-yl)-4-phenoxybenzene (20h): Using **17d** as iodide and (4-phenoxyphenyl)boronic acid according to general procedure **E** provided **20h** (104 mg, 91%) as a colorless oil. R_f = 0.15 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.38 – 7.27 (m, 6H), 7.25 – 7.18 (m, 3H), 7.13 – 7.08 (m, 1H), 7.01 (td, *J* = 7.7, 7.0, 1.6 Hz, 4H), 2.78 (ddq, *J* = 11.7, 5.1, 2.3 Hz, 1H), 2.70 (ddt, *J* = 11.0, 9.4, 4.7 Hz, 3H), 2.23 (dp, *J* = 12.1, 2.2 Hz, 1H), 2.05 (dddd, *J* = 14.1, 9.6, 6.6, 4.7 Hz, 1H), 1.96 (q, *J* = 2.0 Hz, 3H), 1.67 ppm (dtd, *J* = 13.3, 9.5, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 157.5, 155.7, 142.9, 141.3, 135.3, 131.9, 129.8 128.6, 128.4, 127.0, 125.8, 123.2, 119.1, 118.8, 41.4, 35.0, 34.1, 32.7, 14.2. ppm. HRMS (EI): calcd for $C_{25}H_{24}O^+$: 340.1827, found 340.1813. IR (ν, cm^{-1}) 3061 (vw), 3027 (w), 2909 (w), 2850 (w), 1654 (vw), 1588 (m), 1503 (s), 1488 (vs), 1454 (m), 1374 (w), 1325 (w), 1231 (vs), 1201 (m), 1164 (m), 1111 (w), 1071 (w), 1023 (w).

2-(2-Methyl-3-phenethylcyclobut-1-en-1-yl)benzo[*b*] thiophene (20i): Using **17d** as iodide and benzo[*b*]thiophen-2-ylboronic acid according to general procedure **E** provided **20i** (77 mg, 76%) as a colorless oil. R_f = 0.28 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.77 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.35 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.04 (s, 1H), 2.86 (ddt, *J* = 11.6, 4.2, 2.1 Hz, 1H), 2.80 – 2.65 (m, 3H), 2.32 (dt, *J* = 11.9, 2.1 Hz, 1H), 2.04 (dddd, *J* = 13.9, 9.3, 6.7, 4.9 Hz, 1H), 1.97 (q, *J* = 2.0 Hz, 3H), 1.71 ppm (dtd, *J* = 13.4, 9.3, 6.3 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$): δ: 144.2, 142.7, 139.8, 139.7, 139.0, 131.1, 128.6, 128.5, 125.9, 124.5, 124.1, 123.4, 122.3, 119.2, 42.3, 34.9, 34.0, 33.6, 14.3 ppm. HRMS (EI): calcd for $C_{21}H_{20}S^+$: 304.1286, found 304.1278. IR (ν, cm^{-1}) 3060 (w), 3025 (w), 2913 (m), 2851 (w), 1655 (w), 1603 (w), 1496 (m), 1455 (m), 1436 (m), 1372 (w), 1330 (w), 1303 (m), 1250 (w), 1155 (w), 1066 (w), 1030 (w), 1016 (w).

5-(2-Methyl-3-phenethylcyclobut-1-en-1-yl)benzo[*d*] [1,3] dioxole (20j): Using **17d** as iodide and benzo[*d*][1,3]dioxol-5-ylboronic acid according to general procedure **E** provided **20j** (80 mg, 81%) as a colorless oil. R_f = 0.33 (hexane, UV, $KMnO_4$). ^1H NMR (400 MHz, $CDCl_3$): δ: 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 6.86 – 6.83 (m, 1H), 6.78 (s, 2H), 5.94 (s, 2H), 2.77 – 2.60 (m, 4H), 2.18 (dt, *J* = 12.1, 2.1 Hz, 1H), 2.08 – 1.96 (m, 1H), 1.92 (q, *J* = 1.9 Hz, 3H), 1.63 ppm (dtd, *J* = 13.3, 9.4, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 147.7, 146.3, 142.9, 140.5, 135.6, 131.0, 128.6 128.4, 125.8, 119.2, 108.4, 106.1, 101.0, 41.2, 35.0, 34.1, 32.9, 14.1 ppm. HRMS (EI): calcd for $C_{20}H_{20}O_2^+$: 292.1463, found 292.1458. IR (ν, cm^{-1}) 3062 (vw), 3026 (w), 2908 (m), 2855 (w), 2778 (vw), 1700 (w), 1684 (w), 1676 (w), 1654 (w), 1604 (w), 1503 (s), 1485 (s), 1443 (s), 1373 (w), 1355 (m), 1308 (w), 1243 (vs), 1217 (s), 1102 (w), 1070 (w), 1038 (vs).

1-Methyl-4-(2-(2-methylallyl)cyclobut-1-en-1-yl)benzene (21a): Using (2-methylallyl)zinc bromide and 1-iodo-4-methylbenzene according to general procedure **F** provided **21a** (56 mg, 46%) as pale yellow oil. R_f = 0.8 (hexane, UV, $KMnO_4$, PAA). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 7.17 – 7.12 (m, 2H), 4.83 – 4.79 (m, 2H), 3.10 – 3.07 (m, 2H), 2.68 – 2.63 (m, 2H), 2.47 – 2.42 (m, 2H), 2.35 (s, 3H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 139.2, 139.1, 136.5, 133.4, 129.1,

125.7, 111.5, 39.1, 28.3, 26.2, 23.1, 21.4 ppm. HRMS (EI): calcd for $C_{15}H_{18}^+$: 198.1409, found 198.1410. IR (ν, cm^{-1}) 3077 (w), 3024 (w), 2969 (m), 2939 (s), 2914 (vs), 2872 (m), 2836 (m), 2361 (w), 2331 (vw), 1652 (m), 1511 (s), 1443 (m), 1374 (m), 1328 (w), 1112 (w).

1-(2-(2-Methylallyl)cyclobut-1-en-1-yl)-4-(trifluoromethyl)benzene (21b): Using (2-methylallyl)zinc bromide and 1-iodo-4-(trifluoromethyl)benzene according to general procedure **F** provided **21b**(100 mg, 67%) as yellowish oil. R_f = 0.8 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 4.86 – 4.78 (m, 2H), 3.12 – 3.08 (m, 2H), 2.70 – 2.67 (m, 2H), 2.51 – 2.48 (m, 2H), 1.79 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 142.1, 139.2 (q, *J* = 2 Hz), 138.2, 128.44 (q, *J* = 32.3 Hz), 125.8, 125.43 (q, *J* = 3.9 Hz), 124.4 (q, *J* = 272.7 Hz) 112.0, 39.1, 28.7, 26.1, 23.1 ppm. HRMS (EI): calcd for $C_{15}H_{15}F_3^+$: 252.1126, found 252.1112. IR (ν, cm^{-1}) 3079 (vw), 2918 (w), 2840 (vw), 1650 (vw), 1616 (w), 1411 (w), 1325 (vs), 1165 (m), 1124 (m), 1112 (m), 1070 (m), 1015 (w).

2-(2-(2-Methylallyl)cyclobut-1-en-1-yl)pyridine (21c): Using (2-methylallyl)zinc bromide and 2-iodopyridine according to general procedure **F** provided **21c** (88 mg, 80%) as orange oil. R_f = 0.4 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 – 8.54 (m, 1H), 7.60 (td, *J* = 7.7, 1.8 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 1H), 7.06 (dd, *J* = 7.4, 5.8 Hz, 1H), 4.81 – 4.78 (m, 2H), 3.27 (s, 2H), 2.77 – 2.70 (m, 2H), 2.49 – 2.45 (m, 2H), 1.77 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3, 149.6, 146.0, 142.7, 139.3, 136.0, 121.3, 120.6, 111.7, 39.1, 28.5, 26.0, 23.0 ppm. HRMS (EI): calcd for $C_{13}H_{15}N^+$: 185.1204, found 185.1199. IR (ν, cm^{-1}) 3076 (w), 3008 (vw), 2914 (m), 2840 (w), 2827 (w), 2220 (vw), 1700 (vw), 1645 (m), 1583 (s), 1560 (m), 1474 (m), 1467 (m), 1435 (m), 1426 (m), 1374 (w), 1338 (w), 1200 (w), 1148 (m), 1067 (w).

3-(2-(2-Methylallyl)cyclobut-1-en-1-yl)pyridine (21d): Using (2-methylallyl)zinc bromide and 3-iodopyridine according to general procedure **F** provided **21d** (70 mg, 64%) as orange oil. R_f = 0.2 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59-8.58 (d, *J* = 2.1 Hz, 1H), 8.41-8.40 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.58-7.55 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.23-7.20 (ddd, *J* = 7.9, 4.9, 0.9 Hz, 1H), 4.83 – 4.76 (m, 2H), 3.06 (s, 2H), 2.69 – 2.62 (m, 2H), 2.53 – 2.42 (m, 2H), 1.76 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 147.2, 143.2, 142.0, 136.3, 132.6, 131.4, 123.4, 111.9, 39.1, 29.0, 25.8, 22.9 ppm. HRMS (EI): calcd for $C_{13}H_{15}N^+$: 185.1204, found 185.1203. IR (ν, cm^{-1}) 3078 (vw), 2963 (w), 2915 (m), 2838 (w), 1717 (w), 1696 (w), 1685 (w), 1670 (w), 1653 (w), 1647 (w), 1636 (w), 1617 (w), 1586 (w), 1560 (w), 1474 (w), 1456 (w), 1437 (w), 1419 (m), 1408 (m), 1374 (w), 1363 (w), 1312 (w), 1267 (w), 1251 (w), 1222 (w), 1188 (w), 1124 (w), 1101 (w), 1064 (w), 1043 (w), 1023 (m), 1004 (w).

2-(2-(2-Methylallyl)cyclobut-1-en-1-yl)quinolone (21e): Using (2-methylallyl)zinc bromide and ethyl 2-iodoquinoline according to general procedure **F** provided **21e** (60 mg, 43%) as pale yellow oil. R_f = 0.5 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.7 Hz, 1H), 8.33 (d, *J* = 8.5, 1.1 Hz, 1H), 7.79 (d, *J* = 8.2, 1.2 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.55 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.50 (d, *J* = 5.6 Hz, 1H), 4.83 – 4.81 (m, 2H), 3.18 – 3.16 (m, 2H), 3.13 – 3.08 (m, 2H), 2.65 – 2.60 (m, 2H), 1.73 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 148.4, 142.9, 142.5, 139.1, 136.7, 129.9, 127.0, 126.9, 126.7, 126.6, 119.3, 112.0, 39.4, 29.8, 29.4, 23.1 ppm. HRMS (EI): calcd for $C_{17}H_{17}N^+$: 235.1361, found 235.1261. IR (ν, cm^{-1}) 2961 (m), 2918 (m), 1734 (m), 1717 (s), 1700 (s), 1684 (s), 1670 (m), 1654 (vs), 1647 (s), 1636 (s), 1624 (s), 1618 (m), 1576 (m), 1559 (vs), 1550 (m), 1541 (s), 1522 (m), 1507 (s), 1498 (m), 1473 (m), 1457 (s), 1437 (m), 1419 (m), 1261 (m), 1092 (m), 1020 (m).

1-(2-(2-Methylallyl)cyclobut-1-en-1-yl)-2-nitrobenzene (21f): Using (2-methylallyl)zinc bromide and 1-iodo-2-nitrobenzene according to general procedure **F** provided **21f** (95 mg, 70%) as orange oil. R_f = 0.7 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.51 (td, *J* = 7.6, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.34 (td, *J* = 7.7, 1.5 Hz, 1H), 4.81 (s, 1H), 4.78 – 4.74 (m, 1H), 2.90 (s, 2H), 2.68 – 2.60 (m, 2H), 2.48 (dd, *J* = 4.1, 2.4 Hz, 2H), 1.73 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2, 145.5, 142.3, 136.1, 132.3, 130.5, 130.3, 127.6, 124.1, 112.1, 38.4, 29.4, 28.1, 23.0 ppm. HRMS (EI): calcd for $C_{14}H_{15}NO_2^+$: 229.1103, found 229.1107. IR (ν, cm^{-1}) 3076 (vw), 2965 (w), 2918 (w), 2843 (vw), 2363 (vw), 1717 (w), 1651 (w), 1648 (w), 1605 (w), 1569 (w), 1523 (vs), 1477 (w), 1442 (w), 1349 (s), 1293 (w), 1257 (w), 1223 (w), 1201 (w), 1179 (w), 1163 (w), 1088 (w), 1067 (w), 1006 (w).

Ethyl 4-(2-(2-methylallyl)cyclobut-1-en-1-yl)benzoate (21g): Using (2-methylallyl)zinc bromide and ethyl 4-iodobenzoate according to general procedure **F** provided **21g** (132 mg, 87%) as pale yellow oil. R_f = 0.6 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.82 (d, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.11 (s, 2H), 2.74 – 2.64 (m, 2H), 2.53 – 2.40 (m, 2H), 1.78 (s, 3H), 1.39 ppm (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.9, 142.2, 140.1, 138.7, 129.8, 128.4, 125.5, 111.9, 61.0, 39.3, 28.7, 26.1, 23.1, 14.5 ppm. HRMS (EI): calcd for $C_{17}H_{20}O_2^+$: 256.1463, found 256.1463. IR (ν, cm^{-1}) 3077 (vw), 2980 (w), 2914 (w), 2874 (vw), 2838 (vw) 1712 (s), 1652 (w), 1646 (w), 1636 (w), 1606 (m), 1560 (w), 1473 (w), 1457 (w), 1445 (w), 1408 (w), 1389 (w), 1367 (m), 1326 (w), 1310 (w), 1268 (vs), 1198 (w), 1174 (m), 1101 (s), 1058 (w), 1018 (m).

2-(2-(2-Methylallyl)cyclobut-1-en-1-yl)benzonitrile (21h): Using (2-methylallyl)zinc bromide and 2-iodobenzonitrile according to general procedure **F** provided **21h** (56 mg, 45%) as pale yellow oil. R_f = 0.5 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 1H), 7.51 (td, *J* = 7.7, 1.4 Hz, 1H), 7.46 – 7.41 (m, 1H), 7.31 – 7.24 (m, 1H), 4.85 – 4.81 (m, 1H), 4.80 – 4.77 (m, 1H), 3.04 (s, 2H), 3.00 (dq, *J* = 5.3, 1.7 Hz, 2H), 2.53 – 2.47 (m, 2H), 1.75 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 142.0, 139.2, 137.2, 133.9, 132.4, 128.2, 126.9 119.2, 112.2, 109.3, 39.1, 29.5, 28.7, 23.1 ppm. HRMS (EI): calcd for $C_{15}H_{15}N^+$: 209.1204, found 209.1154. IR (ν, cm^{-1}) 3076 (w), 2968 (w), 2917 (m), 2828 (w), 2362 (vw), 2223 (m), 1653 (m), 1648 (w), 1636 (w), 1624 (w), 1594 (w), 1559 (w), 1479 (m), 1457 (w), 1446 (m), 1438 (m), 1421 (w), 1374 (w), 1260 (w), 1222 (w), 1181 (w), 1164 (w), 1136 (w), 1068 (w), 1012 (w).

Ethyl 4-(2-(2-phenylallyl)cyclobut-1-en-1-yl)benzoate (21i): Using (2-phenylallyl)zinc bromide and ethyl 4-iodobenzoate according to general procedure **F** provided **21i** (35 mg, 38%) as yellow oil. R_f = 0.5 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.48 – 7.44 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 5.47 (s, 1H), 5.18 (d, *J* = 1.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 2H), 2.66 – 2.61 (m, 2H), 2.41 – 2.37 (m, 2H), 1.40 ppm (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.0, 143.7, 141.0, 140.0, 138.7, 129.9, 128.5, 127.8, 126.3, 126.0, 125.5, 114.0, 61.0, 36.7, 28.7, 26.1, 14.5 ppm. HRMS (EI): calcd for $C_{22}H_{22}O_2^+$: 318.1620, found 318.1614. IR (ν, cm^{-1}) 2982 (w), 2930 (w), 1716 (s), 1692 (m), 1623 (w), 1607 (w), 1574 (w), 1448 (w), 1408 (w), 1368 (w), 1309 (w), 1275 (vs), 1176 (w), 1106 (m), 1062 (w), 1019 (m).

Ethyl 4-(2-(2-(naphthalen-1-yl)allyl)cyclobut-1-en-1-yl)benzoate (21j): Using (2-(naphthalen-1-yl)allyl)zinc bromide and ethyl 4-iodobenzoate according to general procedure **F** provided **21j** (80 mg, 75%) as yellow oil. R_f = 0.5 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 7.95 – 7.91 (m, 2H), 7.87 – 7.83 (m, 1H), 7.78 – 7.73 (m, 1H), 7.52 – 7.46 (m, 1H), 7.45 – 7.36 (m, 1H), 7.33 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.53 (d, *J* = 1.7 Hz, 1H), 5.25 – 5.21 (m, 1H), 4.40 – 4.32 (m, 2H), 3.61 – 3.59 (m, 2H), 2.65 – 2.62 (m, 2H), 2.45 – 2.41 (m, 2H), 1.39 ppm (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 166.6, 144.5, 142.9, 141.0, 139.9, 139.3, 133.8, 131.2, 129.7, 128.5, 128.4, 127.6, 126.0, 125.8, 125.6, 125.4, 125.2, 117.0, 61.0, 39.7, 28.8, 26.3, 14.5 ppm. HRMS (EI): calcd for $C_{26}H_{24}O_2^+$: 368.1776, found 368.1774. IR (ν, cm^{-1}) 3058 (vw), 3045 (vw), 2980 (w), 2916 (w), 2850 (vw), 2363 (vw), 2341 (vw), 2254 (vw), 1711 (s), 1676 (w), 1653 (w), 1636 (w), 1606 (m), 1591 (w), 1577 (w), 1560 (w), 1541 (w), 1534 (vw), 1522 (vw), 1507 (w), 1490 (vw), 1474 (w), 1464 (w), 1458 (w), 1437 (w), 1420 (w), 1407 (w), 1388 (w), 1366 (m), 1309 (w), 1269 (vs), 1203 (w), 1174 (m), 1102 (s), 1062 (w), 1052 (w), 1018 (m), 1007 (w).

2-(2-(2-(Naphthalen-1-yl)allyl)cyclobut-1-en-1-yl)pyridine (21k): Using (2-(naphthalen-1-yl)allyl)zinc bromide and 2-iodopyridine according to general procedure **F** provided **21k** (63 mg, 73%) as orange oil. R_f = 0.3 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.4 Hz, 1H), 8.20 – 8.14 (m, 1H), 7.87 – 7.82 (m, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.45 (m, 3H), 7.43 – 7.34 (m, 2H), 7.10 – 7.01 (m, 2H), 5.53 (d, 1H), 5.22 (s, 1H), 3.79 (s, 2H), 2.74 – 2.68 (m, 2H), 2.48 – 2.43 ppm (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 149.6, 145.2, 145.1, 141.3, 139.8, 135.9, 133.8, 131.3, 128.4, 127.4, 125.9, 125.7, 125.3, 125.2, 121.3, 120.4, 116.9, 39.4, 28.8, 26.2 ppm. HRMS (EI): calcd for $C_{22}H_{19}N^+$: 297.1517, found 297.1503. IR (ν, cm^{-1}) 3076 (vw), 3056 (w), 3044 (w), 3006 (vw), 2913 (w), 2837 (vw), 2826 (vw), 1936 (vw), 1734 (vw), 1700 (vw), 1652 (w), 1636 (w), 1582 (m), 1560 (m), 1507 (w), 1473 (m), 1466 (w), 1426 (m), 1388 (w), 1337 (w), 1287 (w), 1270 (w), 1243 (w), 1205 (w), 1190 (w), 1176 (w), 1148 (w), 1133 (w), 1107 (w), 1066 (w), 1043 (w), 1024 (w), 1005 (w).

Furan-2-yl(2-(2-methylprop-1-en-1-yl)cyclobut-1-en-1-yl)methanone (21l): Using (2-methylallyl)zinc bromide and furan-2-carbonyl chloride according to general procedure **F** provided **21l** (40 mg, 68%) as colorless oil. R_f = 0.3 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.15 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.90 (d, *J* = 1.4 Hz, 1H), 6.52 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.01 – 2.98 (m, 2H), 2.93 – 2.89 (m, 2H), 1.93 (s, 3H), 1.91 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 157.9, 153.8, 147.8, 146.2, 133.1, 120.9, 117.1, 112.1, 31.6, 29.3, 27.7, 20.1 ppm. HRMS (EI): calcd for $C_{13}H_{14}O_2^+$: 202.0994, found 202.0986. IR (ν, cm^{-1}) 3145 (w), 3100 (w), 2966 (m), 2917 (m), 2853 (w), 1654 (m), 1635 (s), 1610 (s), 1569 (vs), 1560 (s), 1541 (m), 1507 (m), 1463 (vs), 1448 (m), 1437 (m), 1394 (m), 1377 (m), 1370 (m), 1343 (m), 1288 (m), 1276 (m), 1188 (m), 1151 (m), 1040 (m), 1014 (m).

((2-(2-Methylallyl)cyclobut-1-en-1-yl)ethynyl)benzene (22a): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and ethynylbenzene according to general procedure **G** provided **22a** (45 mg, 74%) as pale yellowish oil. R_f = 0.7 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.34 – 7.27 (m, 3H), 4.82 – 4.76 (m, 2H), 2.96 – 2.91 (m, 2H), 2.63 – 2.59 (m, 2H), 2.43 – 2.39 (m, 2H), 1.78 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 142.5, 131.6, 128.4, 128.1, 123.6, 121.3, 112.2, 91.1, 84.5, 39.8, 30.1, 29.8, 22.9 ppm. HRMS (EI): calcd for $C_{16}H_{16}^+$: 208.1252, found 208.1253. IR (ν, cm^{-1}) 3078 (w), 2959 (w), 2916 (w), 2870 (w), 2842 (w), 1650 (w), 1594 (w), 1488 (m), 1443 (m), 1374 (w), 1322 (w), 1260 (w), 1224 (w), 1202 (w), 1178 (w), 1069 (w), 1027 (w).

Trimethyl((2-(2-methylallyl)cyclobut-1-en-1-yl)ethynyl)silane (22b): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and ethynyltrimethylsilane according to general procedure **G** provided **22b** (41 mg, 69%) as pale yellow oil. R_f = 0.6 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 – 4.72 (m, 2H), 2.90 – 2.85 (m, 2H), 2.55 – 2.49 (m, 2H), 2.37 – 2.31 (m, 2H), 1.74 (s, 3H), 0.19 ppm (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9, 142.3, 121.4, 112.2, 99.8, 96.4, 39.8, 30.0, 29.6, 22.8, 0.2 ppm. HRMS (EI): calcd for $C_{13}H_{20}Si^{+\cdot}$: 204.1334, found 204.1330. IR (ν, cm^{-1}) 2962 (w), 2929 (w), 2254 (vw), 2140 (vw), 1722 (w), 1713 (w), 1698 (w), 1679 (w), 1631 (w), 1620 (w), 1613 (w), 1422 (w), 1410 (w), 1392 (w), 1378 (w), 1366 (w), 1360 (w), 1252 (m), 1174 (w), 1112 (w).

2-((2-(2-Methylallyl)cyclobut-1-en-1-yl)ethynyl)thiophene (22c): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and 3-ethynylthiophene according to general procedure **G** provided **22c** (50 mg, 81%) as orange oil. R_f = 0.6 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 3.0, 1.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.11 (dd, *J* = 5.0, 1.2 Hz, 1H), 4.82 – 4.75 (m, 2H), 2.94 – 2.90 (m, 2H), 2.62 – 2.58 (m, 2H), 2.42 – 2.38 (m, 2H), 1.77 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 142.5, 130.0, 128.3, 125.4, 122.6, 121.2, 112.1, 86.2, 83.9, 39.7, 30.0, 29.8, 22.8 ppm. HRMS (EI): calcd for $C_{14}H_{14}S^{+\cdot}$: 214.0816, found 214.0821. IR (ν, cm^{-1}) 3107 (w), 2959 (m), 2925 (m), 2855 (w), 2198 (m), 1705 (vs), 1667 (s), 1650 (m), 1644 (m), 1632 (m), 1621 (m), 1414 (m), 1360 (s), 1258 (m), 1244 (m), 1222 (m), 1189 (m), 1094 (s), 1076 (s).

1-((2-(2-Methylallyl)cyclobut-1-en-1-yl)ethynyl)-2-(trifluoromethyl)benzene (22d): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and 1-ethynyl-2-(trifluoromethyl) benzene according to general procedure **G** provided **22d** (40 mg, 50%) as pale yellow oil. R_f = 0.7 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6, 1.1 Hz, 1H), 4.83 – 4.75 (m, 2H), 2.98 – 2.93 (m, 2H), 2.66 – 2.59 (m, 2H), 2.46 – 2.39 (m, 2H), 1.77 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 142.3, 133.7, 131.4, 131.39 (q, *J* = 30.2 Hz), 127.7, 125.95 (q, *J* = 5.1 Hz), 123.69 (q, *J* = 273.3 Hz), 121.92 (q, *J* = 2.2 Hz) 121.1, 112.2, 90.0, 87.0, 39.8, 30.0, 29.8, 22.6 ppm. HRMS (EI): calcd for $C_{17}H_{15}F_3^{+\cdot}$: 276.1126, found 276.1132. IR (ν, cm^{-1}) 3076 (vw), 2953 (w), 2918 (m), 2849 (w), 2208 (vw), 1727 (w), 1679 (w), 1601 (w), 1573 (w), 1490 (w), 1464 (w), 1451 (w), 1376 (w), 1316 (s), 1260 (m), 1171 (m), 1131 (s), 1110 (s), 1057 (m), 1032 (s).

1-(Cyclopropylethynyl)-2-(2-methylallyl)cyclobut-1-ene (22e): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and ethynylcyclopropane according to general procedure **G** provided **22e** (46 mg, 92%) as pale yellow oil. R_f = 0.5 (hexane, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 – 4.69 (m, 2H), 2.86 – 2.80 (m, 2H), 2.48 – 2.43 (m, 2H), 2.33 – 2.27 (m, 2H), 1.74 – 1.71 (m, 3H), 1.37 (q, 1H), 0.84 – 0.78 (m, 2H), 0.74 – 0.69 ppm (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 142.7, 121.8, 111.8, 95.4, 71.0, 39.4, 30.1, 29.3, 22.8, 8.9, 0.4 ppm. HRMS (EI): calcd for $C_{13}H_{16}^+$: 172.1252, found 172.1246. IR (ν, cm^{-1}) 3076 (w), 3012 (w), 2956 (m), 2924 (s), 2918 (s), 2872 (w), 2842 (w), 2215 (w), 1656 (w), 1651 (w), 1442 (m), 1426 (m), 1374 (m), 1364 (m), 1265 (w), 1197 (m), 1176 (w), 1082 (w), 1052 (m), 1028 (m).

2-((2-(2-Methylallyl)cyclobut-1-en-1-yl)ethynyl)pyridine (22f): Using 1-iodo-2-(2-methylallyl)cyclobut-1-ene (**17e**) and 2-ethynylpyridine according to general procedure **G** provided **22f** (22 mg, 96%) as pale yellowish oil. R_f = 0.3 (9:1 hexane/EtOAc, UV, $KMnO_4$, PAA). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (ddd, *J* = 4.9, 1.8, 0.9 Hz, 1H), 7.63 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.19 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 4.83 – 4.79 (m, 1H), 4.78 – 4.75 (m, 1H), 2.98 – 2.94 (m, 2H), 2.64 – 2.60 (m, 2H), 2.44 – 2.40 (m, 2H), 1.76 ppm (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 150.1, 143.8, 142.2, 136.2, 127.2, 122.6, 120.8, 112.3, 90.4, 84.3, 39.8, 30.0, 29.9, 22.8 ppm. HRMS (EI): calcd for $C_{15}H_{15}N^+$: 209.1204, found 209.1187. IR (ν, cm^{-1}) 3076 (w), 3051 (w), 2963 (w), 2925 (m), 2918 (m), 2842 (w), 2200 (m), 1651 (w), 1579 (s), 1562 (m), 1462 (vs), 1440 (w), 1427 (s), 1375 (w), 1326 (w), 1276 (w), 1262 (w), 1150 (w), 1071 (w), 1044 (w).

(2-(2-Methyl-3-(phenylethynyl) cyclobut-2-en-1-yl) ethyl)benzene (23a): Using **17d** as iodide and ethynylbenzene according to general procedure **G** provided **23a** (83 mg, 88%) as a colorless oil. R_f = 0.33 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.47 – 7.41 (m, 2H), 7.33 – 7.26 (m, 5H), 7.22 – 7.15 (m, 3H), 2.77 – 2.70 (m, 1H), 2.70 – 2.63 (m, 3H), 2.25 – 2.18 (m, 1H), 2.02 – 1.91 (m, 1H), 1.83 (q, *J* = 2.0 Hz, 3H), 1.72 – 1.60 ppm (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 156.3, 142.5, 133.2, 131.6, 128.5, 128.5, 128.1, 125.9, 123.6, 119.0, 91.4, 84.4, 43.1,

36.5, 34.6, 34.0, 14.7 ppm. HRMS (EI): calcd for $C_{21}H_{20}^+$: 272.1565, found 272.1598. IR (ν, cm^{-1}) 3413 (w), 3062 (w), 3028 (w), 2936 (w), 2863 (w), 2366 (w), 2335 (vw), 2201 (m), 1754 (m), 1710 (s), 1703 (vs), 1672 (s), 1644 (m), 1620 (w), 1599 (m), 1582 (w), 1493 (m), 1452 (m), 1436 (w), 1434 (m), 1416 (m), 1358 (m), 1315 (m), 1266 (s), 1175 (m), 1160 (m), 1142 (m), 1100 (m), 1071 (m), 1029 (m), 1000 (m).

2-Methoxy-6-((2-methyl-3-phenethylcyclobut-1-en-1-yl) ethynyl)naphthalene (23b): Using **17d** as iodide and 2-ethynyl-6-methoxynaphthalene according to general procedure **G** provided **23b** (107 mg, 91%) as a colorless oil. R_f = 0.20 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.88 (t, *J* = 1.1 Hz, 1H), 7.67 (t, *J* = 8.7 Hz, 2H), 7.46 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.30 (ddd, *J* = 7.6, 6.4, 1.9 Hz, 2H), 7.22 – 7.18 (m, 3H), 7.14 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 3.92 (s, 3H), 2.76 (ddd, *J* = 12.0, 4.5, 2.2 Hz, 1H), 2.72 – 2.64 (m, 3H), 2.23 (dt, *J* = 11.9, 2.1 Hz, 1H), 2.06 – 1.93 (m, 1H), 1.86 (d, *J* = 2.0 Hz, 3H), 1.74 – 1.61 ppm (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 158.3, 156.0, 142.6, 134.1, 131.2, 129.4, 129.2, 128.6, 128.6, 128.5, 126.9, 125.9, 119.5, 119.1, 118.5, 105.9, 92.0, 84.1, 55.5, 43.2, 36.5, 34.6, 34.1, 14.8 ppm. HRMS (EI): calcd for $C_{26}H_{24}O^+$: 352.1827, found 352.1822. IR (ν, cm^{-1}) 3060 (w), 3026 (w), 2920 (m), 2843 (w), 2363 (w), 2340 (vw), 1717 (m), 1706 (w), 1700 (m), 1684 (w), 1653 (m), 1646 (m), 1625 (s), 1600 (vs), 1559 (m), 1540 (w), 1506 (m), 1498 (s), 1482 (s), 1456 (s), 1438 (m), 1419 (w), 1411 (m), 1391 (s), 1368 (w), 1364 (w), 1336 (w), 1266 (vs), 1250 (s), 1226 (m), 1207 (vs), 1164 (s), 1135 (m), 1069 (w), 1031 (s).

1-(Hex-1-yn-1-yl)-2-methyl-3-octylcyclobut-1-ene (23c): Using **17c** as iodide and 1-hexyne according to general procedure **G** provided **23c** (96 mg, 88%) as a light orange oil. R_f = 0.90 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.61 – 2.54 (m, 1H), 2.54 – 2.47 (m, 1H), 2.34 (t, *J* = 7.0 Hz, 2H), 2.08 – 1.98 (m, 1H), 1.75 – 1.71 (m, 3H), 1.60 – 1.18 (m, 18H), 0.90 ppm (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 154.4, 119.1, 92.4., 75.8, 43.2, 36.7, 32.7, 32,1, 31.3, 30.0, 29,7, 29.5, 27.7, 22.8, 22.1, 19.4, 14.4, 14.3, 13.8 ppm. HRMS (EI): calcd for $C_{19}H_{32}^+$: 260.2504, found 260.2495.

Trimethyl((2-methyl-3-phenethylcyclobut-1-en-1-yl) ethynyl) silane (23d): Using **17d** as iodide and trimethylacetylene according to general procedure **G** provided **23d** (67 mg, 72%) as a colorless oil. R_f = 0.48 (hexane, UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$): δ: 7.06 – 7.00 (m, 2H), 6.97 – 6.90 (m, 3H), 2.46 – 2.31 (m, 4H), 1.92 – 1.82 (m, 1H), 1.74 – 1.61 (m, 1H), 1.53 (q, 3H), 1.44 – 1.29 (m, 1H), -0.05 ppm (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 157.6, 142.5, 128.5, 128.5, 125.9, 119.1, 99.9, 96.5, 42.9, 36.4, 34.4, 34.0, 14.8, 0.2 ppm. IR (ν, cm^{-1}) 3027 (vw), 2958 (w), 2922 (w), 2852 (vw), 2139 (w), 1715 (w), 1678 (w), 1604 (vw), 1496 (w), 1454 (w), 1372 (w), 1355 (w), 1249 (m), 1203 (w), 1186 (w), 1154 (w), 1115 (w), 1069 (w), 1053 (w), 1030 (w).

2-Methyl-2'-(2-methylallyl)-3-phenethyl-[1,1'-bi(cyclobutane)]-1,1'-diene (24): Using (2-methylallyl)zinc bromide and (2-(3-iodo-2-methylcyclobut-2-en-1-yl)ethyl)-benzene (instead of an aryl-iodide) according to general procedure **F** provided **24** (45 mg, 60%) as a colorless oil. R_f = 0.51 (hexane, UV, $KMnO_4$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ: 7.34 (tt, *J* = 7.1, 2.4 Hz, 2H), 7.28 – 7.20 (m, 3H), 4.82 – 4.79 (m, 1H), 4.78 (q, *J* = 1.5 Hz, 1H), 2.89 (s, 1H), 2.75 – 2.66 (m, 4H), 2.60 – 2.56 (m, 2H), 2.47 – 2.43 (m, 2H), 2.19 – 2.13 (m, 1H), 2.04 – 1.96 (m, 1H), 1.81 – 1.77 (m, 6H), 1.72 – 1.61 ppm (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ: 143.5, 142.9, 142.6, 139.6, 136.0, 132.8, 128.5, 128.4, 125.7, 111.3, 43.2, 38.8, 35.2, 34.1, 33.8, 29.8, 27.2, 22.8, 13.7 ppm. HRMS (EI): calcd for $C_{21}H_{26}^+$: 278.2035, found 278.2042. IR (ν, cm^{-1}) 3026 (w), 2912 (m), 2855 (w), 1712 (w), 1694 (w), 1651 (w), 1604 (w), 1496 (w), 1453 (m), 1440 (m), 1374 (m), 1355 (w), 1261 (w), 1198 (w), 1177 (w), 1065 (w), 1030 (w).

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Keywords: cyclobutenes • alkylidenecyclobutanes • cross-couling • boron-homologation • allylboration

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[14] See Supplementary material for assignments by 2D NMR experiments.

[15] Cyclobutenebromide **17f** was synthesized by reaction of the corresponding cyclobutenylzinc species with *N*-bromosuccinimide (see supporting information). Suzuki cross-coupling of **17f** with $PhB(OH)_2$ in the same conditions than those of scheme 11 furnished the phenylcyclobutene **19a** in 76% yield.

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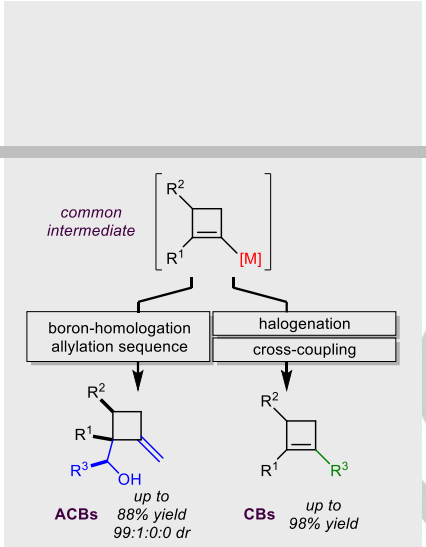
Entry for the Table of Contents

FULL PAPER

Taking advantage of an easy and straightforward preparation of cyclobutenylmetal species, unsaturated four-membered ring systems possessing an endocyclic (cyclobutenes) or exocyclic double bond (alkylidenecyclobutanes) were generated through one-pot sequences.



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Page No. – Page No.

Unsaturated Four-Membered Rings: Efficient Strategies for the Construction of Cyclobutenes and Alkylidenecyclobutanes