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FULL PAPER

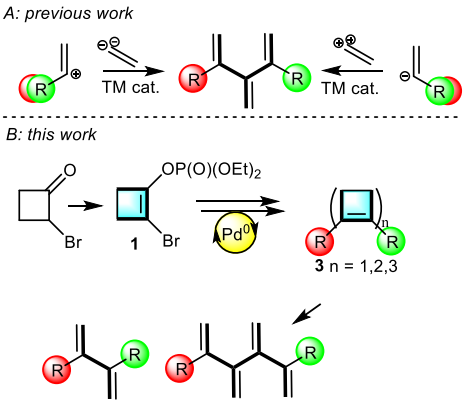
Novel approach to only terminally substituted [n]dendralenes

Peter Polák[a] Tomáš Tobrman[a]*

Abstract: Dendralenes are simple alkenes with cross-conjugated double bonds that are frequently synthesized due to being potentially valuable building blocks for the synthesis of more complex structures. The synthetic approaches to dendralenes are based on the cross-coupling reactions of electrophilic and nucleophilic synthones derived from geminally substituted ethylene. Our novel methodology for the synthesis of only terminally substituted [3]- and [4]dendralenes, as well as 2,3-disubstituted buta-1,3-dienes, involves the preparation of 1,2-disubstituted cyclobutenes from readily available 2-bromocyclobutanone and the subsequent thermal ring-opening reactions.

Introduction

The acyclic molecules with cross-conjugated double bonds known as dendralenes form a significant group of compounds that have been intensively studied with respect to their properties, reactivity, and preparation.[1] Among all the polysubstituted [n]dendralenes, the synthesis of unsubstituted and terminally substituted [n]dendralenes remains the most difficult task since [3]-, [5]-, and [7]dendralenes are unstable exhibiting half-lifes of 10, 25, and 63 hours affording the Diels-Alder dimerization products.[2] In the case of [4]-, [6]-, [8]dendralenes the docomposition was slower but still observable.[2] The unsubstituted or only terminally substituted [n]dendralenes with five or more cross-conjugated ethylene units are usually prepared by means of cross-couplings between nucleophilic and electrophilic ethylene templates (Scheme 1, route A).[2,3] From a synthetic point of view, dendralenes with four cross-conjugated double bonds are synthesized by the Suzuki reaction,[4] Stille coupling,[5] addition reactions,[6] cycloaddition,[7] isomerization processes,[8] and other reactions.[9] The preparation of [3]dendralenes with terminal substitution can be achieved via carbopalladation[10] or isomerization reactions.[11] The two double bonds system with cross-conjugated carbon-substituents is represented by the 2,3-disubstituted buta-1,3-dienes scaffold. These substances can be prepared by means of allene carbopalladation,[10] palladium-catalyzed allylic substitution,[12] the Suzuki[13] and Kumada[14] reactions, oxidative cross-coupling reactions,[15] elimination reactions,[16] samarium-catalyzed dimerization of acetophenones,[17] and other reactions.[18]. However, based on our previous investigations of the application of bromoenol phosphates[19] in organic synthesis, we envisioned that our novel approach to the synthesis of [n]dendralenes could use 2-bromocyclobutanone as the starting compound. In the first step, the 2-bromocyclobutanone is converted to the phosphate **1**, then disubstituted cyclobutenes **3** is prepared and, finally, cross-conjugated double bonds are obtained by the electrocyclic ring-opening reaction of cyclobutene (Scheme 1, route B). The designed synthetic route possesses several interesting features from practical point of view. 2-Bromocyclobutanone,[20] and 2,2-dibromocyclobutanone[21] are easily preparable from commercially available cyclobutanone. The synthesis of 1,2-diarylcyclobut-1-enes includes the McMurry reaction,[22] inter-[23] and intramolecular[24] nucleophilic substitution, ring contraction,[25] and isomerization,[26] although readily available 2-bromocyclobutenyl phosphates have not previously been used for their synthesis. The cyclobutene derivatives **3** should have better stability, compared to some unsubstituted dendralenes, allowing to use them as bench-stable precursors for the dendralene synthesis. Electrocyclic ring-opening reactions is a well known concept that has been extensively reviewed.[27] The electrocyclic ring-opening reaction of cyclobutenes was intensively studied[28] and used[29] mainly for the preparation of mono- or oligosubstituted 1,3-butadienes. Besides of the other disubstituted butadienes available by the cyclobutene ring opening reaction, 2,3-disubstituted buta-1,3-dienes are rarely prepared by this reaction. The reported examples count only compounds with substituents connected via a heteroatom spacer.[30] Moreover, only a limited number of papers on the synthesis of unsubstituted[31] and trisubstituted [3]dendralenes[29e] via electrocyclic ring-opening reaction of cyclobutene were published. However, to the best of our knowledge no report on a general method for the synthesis of only terminally disubstituted 2,3-disubustituted buta-1,3-dienes [3]-, [4]dendralenes bearing carbon substituents, starting from readily available cyclobutanone and using the electrocyclic ring-opening reaction have been published. Therefore, we decided to explore the synthetic potential of designed procedure.



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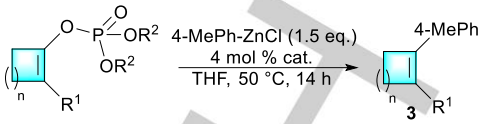
Supporting information for this article is given via a link at the end of the document.

Scheme 1. Synthetic approaches to dendralenes.

Results and Discussion

The synthesis of the phosphate **1** began with 2-bromocyclobutanone, which was transformed into 2,2-dibromocyclobutanone, before the Perkow reaction gave phosphate **1**. Based on our previous work,[19a] we expected that the introduction of the first substituents by means of the bromine replacement could be performed with the Suzuki reaction using either boronic acids or boronates. Indeed, it was found that the reported conditions[19a] were sufficient for the introduction of the aryl substituents (Table 2). Thus, we focused our attention on the optimization of the Negishi reaction involving phosphates **2** (Table 1). Despite the tremendous progress that has been made in relation to the cross-coupling reactions of aryl and alkenyl phosphates,[32] the Negishi reaction involving cyclobutenyl phosphates has not previously been reported. At the beginning of our work, we considered only diethyl phosphate, since it exhibits better atom economy when compared to diphenyl phosphate. However, it soon became clear that the phosphate **2a** does not couple with 4-methylphenylzinc chloride using palladium and nickel catalysts in dry tetrahydrofuran (THF) at 75 °C (Table 1, entries 1 and 2). The addition of 1.0 equiv. of aluminum chloride increased the rate of conversion of the phosphate **2a** into the product **3aa** to 93%. The product **3aa** was isolated at a 89% yield, while the nickel catalysts remained unfruitful (Table 1, entries 3–5). The complete conversion of **2a** was achieved using 4 mol % of DPPF and the RuPhos ligand, although the isolated yields of **3aa** were low (Table 1, entries 6 and 7). $PdCl_2$(DPEPhos) gave the best yield of cyclobutene **3aa** (Table 1, entry 8). The use of 2 mol % of the catalyst resulted in the complete conversion of the phosphate **2a**, although the isolated yield of **3aa** decreased to 83% (Table 1, entry 9). At this point, we briefly explored the reactivity of the other unsubstituted cyclic phosphates **2b**–**d** under the developed conditions. The cyclobutenyl phosphate **2b** showed complete conversion into **3ba**, but the isolated yield was only 67% (Table 1, entry 10). The cyclopentenyl phosphate **2c** exhibited poor conversion into the product **3ca** with 4-tolylzinc chloride in the presence of $AlCl_3$ and a $PdCl_2$DPEPhos catalyst (Table 1, entry 11), while the reaction using $PdCl_2$DPPF resulted in the 90% conversion of **2c** (Table 1, entry 12). The ring enlargement made to the cyclohexenyl phosphate **2d** along with the optimized conditions afforded the product **3da** in an 80% isolated yield (Table 1, entry 13). No superior results were obtained during the $AlCl_3$-free Negishi reaction with other catalysts, including $PdCl_2(SPhos)_2$, $PdCl_2$DPPF, $PdCl_2$DPEPhos, $NiCl_2$DPPP, and $NiCl_2(PCy_3)_2$ (Table 1, note d). The observed reactivity is in good agreement with our previous results,[19c] which prompted us to propose that $AlCl_3$ coordinates with the phosphate moiety, thereby enhancing its reactivity during the Negishi reaction. In some cases, the large differences observed between the rate of conversion and the isolated yield (Table 1, entries 4, 5, 7, and 10) were attributed to the McKenna-type degradation[33] of the starting phosphates.

Table 1. The Negishi reaction of phosphates **2** with 4-tolylzinc chloride.



2a, n = 1, R^1 = 4-MeOPh, R^2 = Et
2b, n = 1, R^1 = H, R^2 = Et
2c, n = 2, R^1 = H, R^2 = Et
2d, n = 3, R^1 = H, R^2 = Et

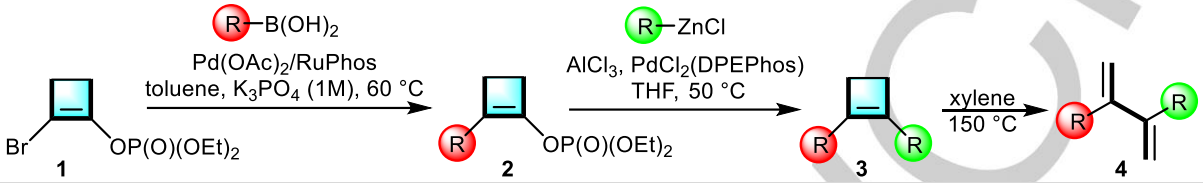
Entry	2	Catalyst	Conversion (%)[a]
1	**2a**,	$PdCl_2(SPhos)_2$[b]	**3aa**, <5
2	**2a**	$NiCl_2(PCy_3)_2$[b]	**3aa**, <5
3	**2a**	$PdCl_2(SPhos)_2/AlCl_3$	**3aa**, 93 (89[e])
4	**2a**	$NiCl_2(PCy_3)_2/AlCl_3$	**3aa**, 100 (0[e])
5	**2a**	$NiCl_2$DPPP/$AlCl_3$	**3aa**, 100 (0[e])
6	**2a**	$PdCl_2(RuPhos)_2/AlCl_3$	**3aa**, 100 (82[e])
7	**2a**	$PdCl_2$DPPF/$AlCl_3$	**3aa**, 100 (65[e])
8	**2a**	$PdCl_2$DPEPhos/$AlCl_3$	**3aa**, 100 (92[e])
9	**2a**	$PdCl_2$DPEPhos/$AlCl_3$[c]	**3aa**, 100 (83[e])
10	**2b**	$PdCl_2$DPEPhos/$AlCl_3$[d]	**3ba**, 100 (67[e])
11	**2c**	$PdCl_2$DPEPhos/$AlCl_3$[d]	**3ca**, 50 (38[e])
12	**2c**	$PdCl_2$DPPF/$AlCl_3$[d]	**3ca**, 90 (55[e])
13	**2d**	$PdCl_2$DPEPhos/$AlCl_3$[d]	**3da**, 100 (80[e])

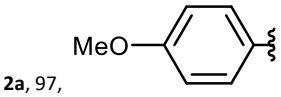
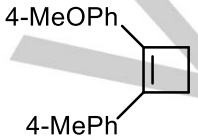
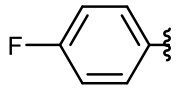
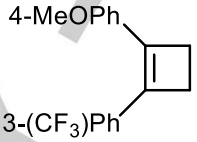
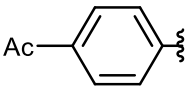
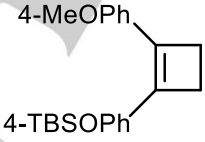
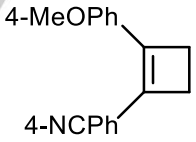
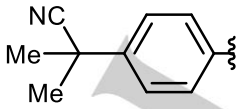
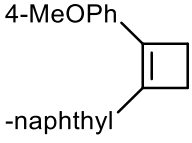
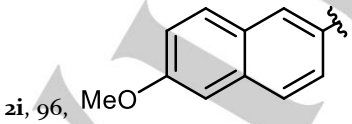
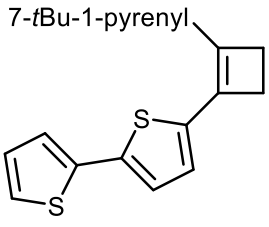
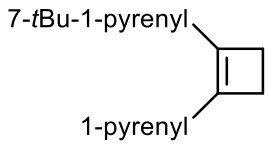
[a] The reactions were performed on a 0.30 mmol scale, and the conversion was determined by means of ^{1}H NMR. [b] The reaction was stirred for 24 h at 75 °C. [c] A 2 mol % catalyst loading was used. [d] The Negishi reaction was also performed with the following catalysts, $PdCl_2(SPhos)_2$, $PdCl_2$DPPF, $PdCl_2$DPEPhos, $NiCl_2$DPPP, and $NiCl_2(PCy_3)_2$, without $AlCl_3$ in dry THF at 75 °C, although no superior results were obtained. [e] Isolated yield.

The optimized reaction conditions for the substitution of the phosphate moiety were used to verify the feasibility of the proposed methodology (Table 2). Thus, the bromoenol phosphate **1** was treated with arylboronic acids, and the arylated cyclobutenyl phosphates were prepared in almost quantitative yields (Table 2, entries 1–7). The Suzuki reaction proceeded with the electron rich and poor acids with the same results, and the sensitive functional groups, for instance, the keto or nitrile groups, were tolerated (Table 2, entries 3 and 5). It is worth noting that the 2-thienyl and 1-pyrenyl substituents were also introduced in high yields (Table 2, entries 4 and 7). The prepared phosphates **2a**,**e–j** were mixed with arylzinc chlorides and the aluminum chloride promoted the Negishi reaction, which was performed with outstanding results (Table 2, entries 1–5). In two cases, the introduction of bithiophenyl **3jf** and the pyrenyl ring **3jg** was performed, which afforded π-conjugated molecules in high isolated yields (Table 2, entries 6 and 7). Finally, the obtained cyclobutenes **3aa–af**,**jg** were used for the thermal ring-opening reactions. The ring-opening reactions were performed in xylene

at 150°C, and quantitative conversion was obtained within several hours. A lower reaction temperature led to the incomplete conversion of the starting cyclobutenes **3aa–af**,**jg**. When the ring-opening reaction was performed in decalin at 200 °C the yield of the compound **4aa** significantly dropped due to side reactions (Table 2, entry 1). On the other hand, The 2,3-disubstituted buta-1,3-dienes **4aa**–**ae** were isolated in almost quantitative yields (Table 2, entries 1–5). Surprisingly, the cyclobutene with a bithiophene substituent failed to give the expected product, and the formation of a complex reaction mixture was observed (Table 2, entry 6). Yet, the cyclobutene **3jg** smoothly opened to give buta-1,3-diene with cross-conjugated pyrene units **4jg** (Table 2, entry 7).

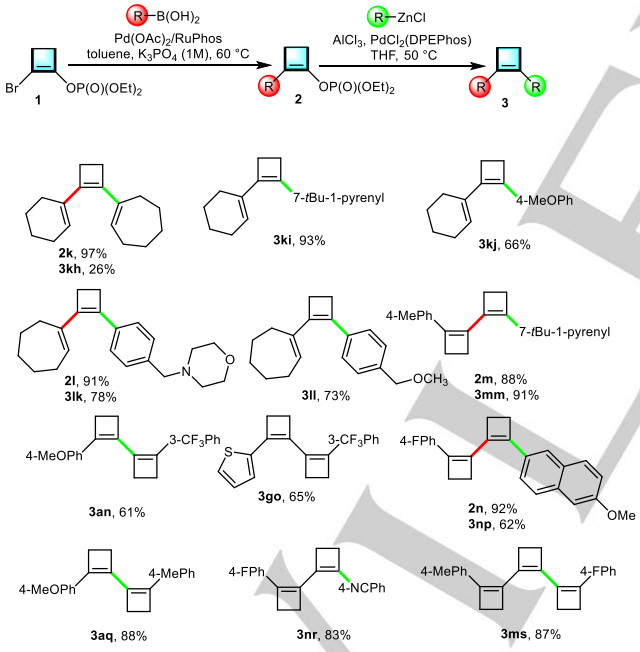
Table 2. The preparation of cross-conjugated systems with two double bonds.



Entry	**2**, Yield[a] (%), R	**3**, Isolated yield (%)	**4** Isolated yield (%)
1	 **2a**, 97,	 **3aa**, 92,	**4aa**, 92 (43[b])
2	 **2e**, 95,	 **3ab**, 93,	**4ab**, 92
3	 **2f**,96,	 **3ac**, 94,	**4ac**, 98
4	 **2g**, 94,	 **3ad**, 96,	**4ad**, 93
5	 **2h**, 95,	 **3ae**, 95,	**4ae**, 95
6	 **2i**, 96,	 **3jf**, 90,	—[a]
7	 **2j**, 91,	 **3jg**, 84,	**4jg**, 81

[a] Decomposition of the starting compound was observed. [b] The reaction was performed in decalin at 200 °C.

Encouraged by the obtained results, we expected to extend the developed methodology to the regioselective synthesis of [3]- and [4]dendralenes (Scheme 2). In this case, the introduction of the alkenyl or cyclobutenyl moiety would be a crucial step. We were pleased to observe that the Suzuki reaction involving the alkenyl fragment **2k**,**l** proceeded with high isolated yields. Surprisingly, the Suzuki reaction involving the vinylboronic acid neopentylglycol ester proceeded well, although the formed 2-vinylcyclobutenyl phosphate was unstable and decomposed during the isolation by flash chromatography. Additionally, the cyclobutenyl boronates were smoothly coupled with the enol phosphate **1**, as can be seen from the prepared compounds **2m**,**n**. The Negishi reaction involving the substituted enol phosphates turned out to be difficult in the case of the cycloalkenylzinc chlorides **3kh**. Aromatic as well as cyclobutenyl substituents were introduced in high isolated yields. The methodology hence allows access to the substituted cyclobutenes with a heteroaromatic ring **3go** and the tricyclobutene **3ms**. The prepared compounds **3aq**,**ms** were chosen in order to illustrate the stability of the cyclobutenes. We were pleased to discover that the tested compounds were sufficiently stable that they could be stored at room temperature under an air atmosphere for several months.



Scheme 2. The preparation of the alkenyl cyclobutenes.

With the cyclobutene **3** in our hands (Scheme 2), we selected illustrative examples and tested their behavior during the thermal ring-opening reaction (Scheme 3). The cyclobutenes with alkenyl fragments were transformed to the [3]dendralenes **4ki**,**kj**,**lk**,**ll** in high isolated yields. The biscyclobutenes were also opened, thereby affording the [4]dendralenes **4mm**,**an**,**np**,**aq**,**nr** substituted at the terminal positions in moderate isolated yields. It is worth noting that the tricyclobutene **3ms** failed to give the expected product and a complex reaction mixture was instead formed under the tested conditions. We expect that the formed [6]dendralene is unstable under the tested conditions and hence undergoes thermally induced side reactions. The same reactivity was observed in the case of the cyclobutene **3kh**, where decomposition was found to be the main reaction pathway.

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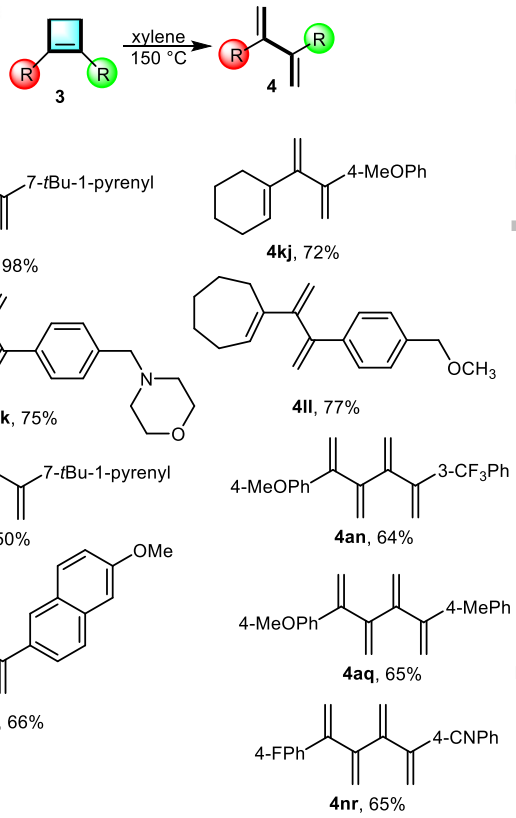
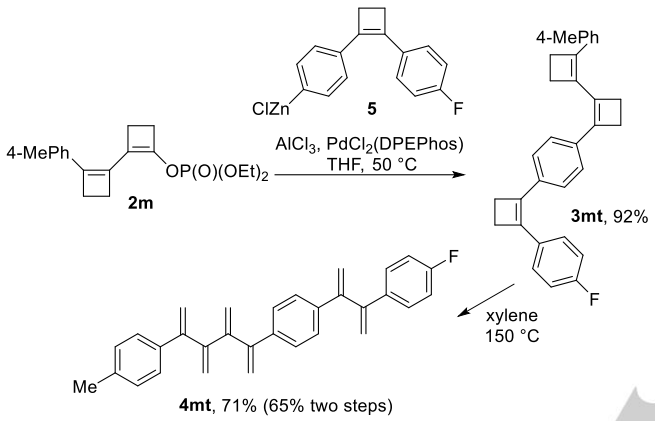


Scheme 3. Thermal cyclobutene-opening reaction of the substituted cyclobutenes.

In principle, the developed methodology is not limited to the synthesis of simple disubstituted cyclobutenes. In order to demonstrate the modularity and versatility of our methodology, we have chosen the representative example of molecule **4mt** with two cross-conjugated parts connected via a spacer (Scheme 4). To achieve the synthesis of compound **4mt**, the previously prepared phosphate **2m** was treated with organozinc reagent **5**, thereby affording cyclobutene **3mt** in a 92% isolated yield. The prepared compound **3mt** was heated to 150 °C in dry xylene, and the formed dendralene **4mt** bearing two cross-conjugated parts connected by a 1,4-phenylene spacer was obtained in a 65% isolated yield in two steps from the phosphate **2m**.



Scheme 4. The preparation of the cross-conjugated fragments connected via a 1,4-phenylene spacer.

Conclusions

To summarize, we have developed a novel methodology for the synthesis of [3]- and [4]dendralenes, as well as 2,3-disubstituted buta-1,3-dienes, which utilizes readily available 2-bromocyclobutanone that is transformed into diethyl bromoenol phosphates. The subsequent Suzuki reaction along with the aluminum chloride-promoted Negishi reaction was used to change the bromine and phosphate moieties. The prepared cyclobutenes showed excellent stability and no signs of their decomposition were observed within 6 months. The cyclobutenes were opened in dry xylene at 150 °C, thereby affording 2,3-disubstituted buta-1,3-dienes as well as terminally disubstituted [3]- and [4]dendralenes. The attempts to prepare [6]dendralenes were unsuccessful. The methodology is also suitable for the preparation of alkenes with cross-conjugated substituents connected via a spacer. Further studies involving the application of the developed methodology to the synthesis of higher dendralenes are ongoing in our laboratory.

Experimental Section

All reactions were performed under an argon atmosphere. NMR spectra were measured on a Varian Gemini 300 (^{1}H, 300.07 MHz; ^{13}C, 75.46 MHz), or a Bruker DRX 500 Avance (^{1}H, 500.13 MHz) spectrometer at 298 K. Mass spectra were measured on ZAB-SEQ (VG Analytical). The dry and degassed solvents were prepared by PureSolv MD7; silica gel (Merck, Silica Gel 60, 40-63 μm) was used for column chromatography. Cyclopentenyl diethyl phosphate (**2c**) and cyclohexenyl diethyl phosphate (**2d**) were prepared following the literature procedure.[34] BuLi (2.5 M solution in hexane) and other compounds were purchased. Concentration of BuLi was determined by titration using menthol and 1,10-phenanthroline before use. Concentration of organozinc reagents was determined by titration using iodine.

General procedure for the preparation of diethyl 2-substituted cyclobutenyl phosphates 2

Toluene (4 mL/mmol) was added to a mixture of diethyl 2-bromocyclobuten-1-yl phosphate (1.0 equiv.) (**1**), boronic acid or boronic ester (1.3 equiv.), palladium acetate (1 mol %) and RuPhos (2 mol %). The reaction mixture was stirred for 1 min at ambient temperature, and then 1M K_3PO_4 (3 equiv.) was added at once. The reaction mixture was stirred for 18 h at 60 °C. The reaction mixture was diluted with ether, washed with 1M KOH, water and brine then dried over $MgSO_4$. Column chromatography (silica gel) afforded pure products.

Diethyl 2-(4-methoxyphenyl)-cyclobuten-1-yl phosphate (2a): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (2.85 g, 10 mmol), 4-methoxyphenylboronic acid (1.98 g, 13 mmol), $Pd(OAc_2)$ (22.5 mg, 1 mol.%), RuPhos (93.3 mg, 2 mol%), 1M K_3PO_4 (30 mL), hexane/EtOAc (3:1→ 2:1, R_f = 0.2), 97% yield (3.03 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.31 (m, 2H), 6.89–6.82 (m, 2H), 4.28–4.15 (m, 4H), 3.81 (s, 3H), 2.91–2.87 (m, 2H), 2.40–2.36 (m, 2H), 1.37 (td, *J* = 7.1, 1.1 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ 158.5, 132.9 (d, *J* = 7.9 Hz), 127.3, 125.9 (d, *J* = 1.3 Hz), 120.7 (d, *J* = 10.8 Hz), 113.7, 64.4 (d, *J* = 6.0 Hz), 55.2, 31.0 (d, *J* = 2.7 Hz), 20.9, 16.1 (d, *J* = 6.7 Hz). HRMS (ESI) $[M+H]^+$ calcd for $C_{15}H_{21}O_5P$: 313.11994, found: 313.11946.

Diethyl 2-(4-fluorophenyl)-cyclobuten-1-yl phosphate (2e): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.570 g, 2 mmol), 4-fluorophenylboronic acid (0.364 g, 2.6 mmol), $Pd(OAc)_2$ (4.5 mg, 1 mol %), RuPhos (18.7 mg, 2 mol %), 1M K_3PO_4 (6 mL), hexane/EtOAc (3:1→2:1, R_f = 0.3), 95% yield (0.570 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.33 (m, 2H), 7.05–6.96 (m, 2H), 4.29–4.14 (m, 4H), 2.93–2.89 (m, 2H), 2.41–2.36 (m, 2H), 1.38 (td, *J* = 7.1, 0.9 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 161.6 (d, *J* = 246.9 Hz), 134.5 (dd, *J* = 7.4, 2.6 Hz), 129.1 (dd, *J* = 3.3, 1.3 Hz), 127.6 (d, *J* = 7.9 Hz), 120.0 (d, *J* = 11.0 Hz), 115.3 (d, *J* = 21.7 Hz), 64.5 (d, *J* = 5.6 Hz), 31.1 (d, *J* = 2.5 Hz), 20.9, 16.1 (d, *J* = 6.5 Hz). ^{19}F NMR ($CDCl_3$): δ = -114.59 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{14}H_{18}FO_4P$: 301.09995, found: 301.10013.

Diethyl 2-(4-acetylphenyl)-cyclobuten-1-yl phosphate (2f): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.285 g, 1 mmol), 2-(4-acetylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.302 g, 1.3 mmol), $Pd(OAc)_2$ (2.25 mg, 1 mol %), RuPhos (9.33 mg, 2 mol %), 1M K_3PO_4 (3 mL), hexane/EtOAc (3:1 → 2:1, R_f = 0.3), 96% yield (0.311 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.93–7.87 (d, *J* = 8.4 Hz, 2H), 7.47–7.42 (d, *J* = 8.4 Hz, 2H), 4.29–4.16 (m, 4H), 2.97–2.91 (m, 2H), 2.57 (s, 3H), 2.46–2.41 (m, 2H), 1.38 (td, *J* = 7.1, 1.1 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 197.4, 138.3 (d, *J* = 8.0 Hz), 137.2, 135.1, 128.5, 125.9, 120.0 (d, *J* = 10.4 Hz), 64.7 (d, *J* = 5.8 Hz), 31.4 (d, *J* = 2.5 Hz), 26.5, 20.8, 16.1 (d, *J* = 5.8 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{16}H_{21}O_5P$: 325.11994, found: 325.12013.

Diethyl 2-(2-thienyl)-cyclobuten-1-yl phosphate (2g): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.285 g, 1 mmol), 5,5-

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dimethyl-2-(thiophen-2-yl)-1,3,2-dioxaborinane (0.255 g, 1.3 mmol), $Pd(OAc)_2$ (2.25 mg, 1 mol %), RuPhos (9.33 mg, 2 mol %), 1M K_3PO_4 (3 mL), hexane/EtOAc (3:1, R_f = 0.35), 94% yield (0.271 g), brownish viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22–7.18 (m, 1H), 6.99–6.94 (m, 2H), 4.28–4.14 (m, 4H), 2.97–2.90 (m, 2H), 2.46–2.39 (m, 2H), 1.37 (td, *J* = 7.1, 1.0 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 135.2 (d, *J* = 1.7 Hz), 132.9 (d, *J* = 7.7 Hz), 126.8, 124.6, 123.7, 115.4 (d, *J* = 11.0 Hz), 64.6 (d, *J* = 6.0 Hz), 31.8 (d, *J* = 2.6 Hz), 22.0, 16.1 (d, *J* = 6.7 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{12}H_{17}O_4PS$: 289.06579, found: 289.06581.

Diethyl 2-[4-(2-cyanoprop-2-yl)phenyl]-cyclobuten-1-yl phosphate (2h): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.285 g, 1 mmol), [4-(1-cyano-1-methylethyl)phenyl]boronic acid (0.246 g, 1.3 mmol), $Pd(OAc)_2$ (2.25 mg, 1 mol %), RuPhos (9.33 mg, 2 mol %), 1M K_3PO_4 (3 mL), Hexane:EtOAc (3:1 → 2:1, R_f = 0.2), 95% yield (0.332 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41 (s, 4H), 4.28–4.15 (m, 4H), 2.94–2.89 (m, 2H), 2.43–2.37 (m, 2H), 1.70 (s, 6H), 1.38 (td, *J* = 7.2, 1.0 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 139.8, 135.9 (d, *J* = 7.9 Hz), 132.4, 126.5, 125.1, 124.4, 120.1 (d, *J* = 10.7 Hz), 64.6 (d, *J* = 6.1 Hz), 37.0, 31.2 (d, *J* = 2.6 Hz), 29.0, 20.8, 16.1 (d, *J* = 6.6 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{24}NO_4P$: 350.15157, found: 350.15170.

Diethyl 2-(6-methoxynapht-2-yl)-cyclobuten-1-yl phosphate (2i): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.285 g, 1 mmol), 2-(6-methoxynaphthalen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (0.351 g, 1.3 mmol), $Pd(OAc)_2$ (2.25 mg, 1 mol %), RuPhos (9.33 mg, 2 mol %), 1M K_3PO_4 (3 mL), hexane:EtOAc (3:1, R_f = 0.3), 96% yield (0.348 g), yellow crystalline solid, m.p. 59–61 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.59 (m, 4H), 7.16–7.06 (m, 2H), 4.32–4.18 (m, 4H), 3.91 (s, 3H), 2.99–2.93 (m, 2H), 2.52–2.46 (m, 2H), 1.39 (td, *J* = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 157.7, 154.7 (d, *J* = 7.8 Hz), 133.6, 129.4, 128.7, 128.4 (d, *J* = 1.5 Hz), 126.8, 125.2, 124.1, 121.3 (d, *J* = 10.7 Hz), 119.0, 105.9, 64.5 (d, *J* = 5.9 Hz), 55.3, 31.2 (d, *J* = 2.5 Hz), 20.9, 16.1 (d, *J* = 6.5 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{19}H_{23}O_5P$: 363.13559, found: 363.13546.

Diethyl 2-(7-*tert*-butylpyrene-1-yl)-cyclobuten-1-yl phosphate (2j): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (1.43 g, 5 mmol), 7-*tert*-butylpyren-1-yl boronic acid (1.97 g, 6.5 mmol), $Pd(OAc)_2$ (11.3 mg, 1 mol %), RuPhos (46.7 mg, 2 mol %), 1M K_3PO_4 (15 mL), hexane/DCM (9:1→ hexane:EtOAc 3:1 → 2:1, R_f = 0.3), 91% yield (2.10 g), dark-yellow solid, m.p. 80–83 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.57 (d, *J* = 8.4 Hz, 1H), 8.21 (s, 2H), 8.11–7.97 (m, 5H), 4.29–4.15 (m, 4H), 3.16–3.10 (m, 2H), 3.94–3.89 (m, 2H), 1.59 (s, 9H), 1.35 (td, *J* = 7.1, 1.0 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 149.0, 135.8 (d, *J* = 7.4 Hz), 131.3, 130.7, 130.3, 127.8, 127.7 (d, *J* = 1.2 Hz), 127.5, 127.3, 127.2, 125.6, 124.90, 124.88, 124.5, 123.1, 122.4, 122.1, 121.0 (d, *J* = 10.8 Hz), 64.6 (d, *J* = 6.1 Hz), 35.1, 31.9, 34.4 (d, *J* = 2.5 Hz), 24.5, 16.1 (d, *J* = 6.6 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{28}H_{31}O_4P$: 463.20327, found: 463.20359.

Diethyl 2-(cyclohexen-1-yl)-cyclobuten-1-yl phosphate (2k): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.855 g, 3 mmol), 1-cyclohexenyl-5,5-dimethyl-1,3,2-dioxaborinane (0.741 g, 3.9 mmol), $Pd(OAc_2)$ (6.8 mg, 1 mol %), RuPhos (28.0 mg, 2 mol %), 1M K_3PO_4 (9 mL), hexane:EtOAc (3:1, R_f = 0.35), 97% yield (0.834 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.61 (brs, 1H), 4.17 (quint, *J* = 7.5 Hz, 4H), 2.73 (brs, 2H), 2.34–2.36 (m, 2H), 2.15–2.04 (m, 4H), 1.68–1.52 (m, 4H), 1.36 (tt, *J* = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ =132.2 (d, *J* = 8.4 Hz), 131.3 (d, *J* = 1.5 Hz), 124.4 (d, *J* = 1.0 Hz), 123.9 (d, *J* = 10.4 Hz), 64.3 (d, *J* = 6.0 Hz), 30.3 (d, *J* = 2.3 Hz), 26.2, 25.2, 22.3, 22.2, 20.3, 16.1 (d, *J* = 6.5 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{14}H_{23}O_4P$: 287.14067, found: 287.14055.

Diethyl 2-(cycloheptene-1-yl)-cyclobuten-1-yl phosphate (2l): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (1.71 g, 6 mmol), 1-cycloheptenyl-5,5-dimethyl-1,3,2-dioxaborinane (1.62 g, 7.8 mmol), $Pd(OAc)_2$ (13.5 mg, 1 mol %), RuPhos (56 mg, 2 mol %), 1M K_3PO_4 (18 mL), hexane:EtOAc (3:1, R_f = 0.35), 91% yield (1.64 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.74 (t, *J* = 6.8 Hz, 1H), 4.15 (quint, *J* = 7.5 Hz, 4H), 2.70 (brs, 2H), 2.49–2.41 (m, 2H), 2.19–2.04 (m, 4H), 1.75–1.65 (m, 2H), 1.54–1.40 (m, 4H), 1.33 (tt, *J* = 7.2, 1.0 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 138.1 (d, *J* = 1.5 Hz), 132.0 (d, *J* = 8.2 Hz), 129.9 (d, *J* = 1.3 Hz), 124.9 (d, *J* = 10.3 Hz), 64.2 (d, *J* = 5.8 Hz), 32.4, 30.0 (d, *J* = 2.5 Hz), 29.7, 28.3, 26.9, 26.6, 21.0, 16.0 (d, *J* = 6.6 Hz). HRMS (APCI) $[M+H]^+$ calcd for $C_{15}H_{25}O_4P$: 301.15632, found: 301.15631.

Diethyl 2-(2-(4-tolyl)cyclobutene-1-yl)cyclobutene-1-yl phosphate (2m): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.855 g, 3 mmol), 2-(2-(4-methylphenyl)cyclobutenyl)-5,5-dimethyl-1,3,2-dioxaborinane (0.999 g, 3.9 mmol), $Pd(OAc)_2$ (6.8 mg, 1 mol %), RuPhos (28 mg, 2 mol %), 1M K_3PO_4 (9 mL), hexane:EtOAc (3:1, R_f = 0.2), 88% yield (0.920 g), yellow solid, the product partially decomposed upon storage in a refrigerator for 1 week. However, it can be stored in a freezer at -20 °C for several weeks without decomposition, m.p. 46–48 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.18 (p, *J* = 7.4 Hz, 4H), 2.87 (brs, 2H), 2.74–2.63 (m, 4H), 2.49 (q, *J* = 2.4 Hz, 2H), 2.33 (s, 3H), 1.37 (tt, *J* = 7.1, 0.8 Hz, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 138.3 (d, *J* = 1.2 Hz), 136.88, 136.84 (d, *J* = 8.0 Hz), 132.9, 129.8 (d, *J* = 1.8 Hz), 128.9, 125.9, 118.3 (d, *J* = 10.8 Hz), 64.5 (d, *J* = 6.0 Hz), 32.1 (d, *J* = 2.8 Hz), 27.5, 27.0, 23.8, 21.3, 16.1 (d, *J* = 6.7 Hz). HRMS (ESI) $[M+H]^+$ calcd for $C_{19}H_{25}O_4P$: 349.15632, found: 349.15560.

Diethyl 2-(2-(4-fluorophenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (2n): Prepared from diethyl 2-bromocyclobuten-1-yl phosphate (**1**) (0.855 g, 3 mmol), 2-(2-(4-fluorophenyl)cyclobutenyl)-5,5-dimethyl-1,3,2-dioxaborinane (1.02 g, 3.9 mmol), $Pd(OAc)_2$ (6.8 mg, 1 mol %), RuPhos (28 mg, 2 mol %), 1M K_3PO_4 (9 mL), hexane:EtOAc (3:1, R_f = 0.2), 92% yield (0.971 g), yellow viscous liquid, product partially decomposed upon storage in refrigerator for 1 week. However it can be stored at -20 °C for several weeks without decomposition. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 2H), 7.03–6.94 (m, 2H), 4.24–4.11 (m, 4H), 2.88 (brs, 2H), 2.73–2.61 (m, 4H), 2.49–2.42 (m, 2H), 1.37 (td, *J* = 7.1, 1.0, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 161.8 (d, *J* = 247.2 Hz), 137.3 (dd, *J* = 8.1, 0.6 Hz), 137.0 (d, *J* = 1.2 Hz), 131.9 (d, *J* = 3.3 Hz), 130.3 (t, *J* = 2.0 Hz), 127.5 (d, *J* = 7.8 Hz), 117.9 (d, *J* = 10.8 Hz), 115.1 (d, *J* = 21.8 Hz), 64.5 (d, *J* = 6.2 Hz), 32.1 (d, *J* = 2.5 Hz), 27.6, 26.9, 23.7, 16.1 (d, *J* = 6.6 Hz). ^{19}F NMR ($CDCl_3$): δ = -114.85 (m). HRMS (ESI) $[M+Na]^+$ calcd for $C_{18}H_{22}FO_4P$: 375.11320, found: 375.11352.

General procedure for the preparation of 1,2-disubstituted cyclobutenes 3

A solution of freshly prepared and titrated arylzinc chloride·LiCl reagent (1.5 equiv.) was added to a mixture of 2-arylcyclobutene-1-yl phosphate **2**, $PdCl_2$DPEPhos complex (4 mol %). Then a solution of $AlCl_3$ in dry THF (0.5M) was added. The reaction mixture was stirred for indicated time period at 50 °C. Then the reaction mixture was diluted with ether (40 mL) and quenched with 1M solution of tartaric acid or Rochelle salt in water (10 mL). The mixture was stirred for 20 minutes then the organic phase was washed with brine and dried over $MgSO_4$. Column chromatography (silicagel) afforded the final products.

1-(4-Methoxyphenyl)-2-(4-methylphenyl)cyclobutene (**3aa**): Prepared from diethyl 2-(4-methoxyphenyl)-cyclobuten-1-yl phosphate (**2a**) (0.625 g, 2 mmol), 4-methylphenylzinc chloride•lithium chloride (6.67 mL, 3.0 mmol, 0.45M), $PdCl_2$DPEPhos (57.3 mg, 4 mol %), $AlCl_3$ (4 mL, 2.0 mmol, 0.5M), the reaction mixture was stirred for 14 h, hexane→hexane/DCM

(9:1)→hexane/EtOAc (20:1, R_f = 0.4), 92% yield (0.461 g), white crystalline solid, m.p. 74–75 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.38 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.89–6.82 (m, 2H), 3.82 (s, 3H), 2.74 (s, 4H), 2.35 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 158.8, 137.4, 136.9, 136.6, 133.7, 129.2, 129.0, 127.3, 125.9, 113.6, 55.2, 26.7, 26.6, 21.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{18}O$: 251.14304, found: 251.14297.

1-(3-Trifluoromethylphenyl)-2-(4-methoxyphenyl)cyclobutene (3ab): Prepared from diethyl 2-(4-methoxyphenyl)-cyclobuten-1-yl phosphate (**2a**) (0.234 g, 0.75 mmol), 3-trifluoromethylphenylzinc chloride•lithium chloride (1.13 mmol, 2.56 mL, 0.44M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 15 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.6), 93% yield (0.213 g), white crystalline solid, m.p. 41–43 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74–7.66 (m, 2H), 7.50–7.38 (m, 4H), 6.91–6.84 (m, 2H), 3.83 (s, 3H), 2.77 (s, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.4, 140.5, 137.1, 134.8, 130.8 (q, *J* = 32.2 Hz), 128.9 (q, *J* = 1.2 Hz), 128.7, 128.5, 127.4, 124.2 (q, *J* = 272.5 Hz), 123.6 (q, *J* = 3.8 Hz), 122.6 (q, *J* = 3.8 Hz), 113.8, 55.3, 27.0, 26.5. ^{19}F NMR ($CDCl_3$): δ = -63.29 (s). HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{15}F_3O$: 305.11478, found: 305.11510.

1-(4-Methoxyphenyl)-2-(4-*tert*-butyldimethylsilyloxyphenyl)cyclobutene (3ac): Prepared from diethyl 2-(4-methoxyphenyl)cyclobuten-1-yl phosphate (**2a**) (0.234 g, 0.75 mmol), 4-(*tert*-butyldimethylsilyloxy)phenylzinc chloride•lithium chloride (2.74 mL, 1.12 mmol, 0.41M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 15 h, hexane→hexane/DCM (9:1)→Hexane/EtOAc (20:1, R_f = 0.5), 94% yield (0.237 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.43 (m, 2H), 7.42–7.36 (m, 2H), 6.89–6.82 (m, 2H), 6.81–6.75 (m, 2H), 3.82 (s, 3H), 2.71 (s, 4H), 0.98 (s, 9H), 0.21 (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 158.7, 154.9, 136.35, 136.31, 129.8, 129.4, 127.3, 127.1, 119.8, 113.6, 55.3, 26.7, 26.6, 25.7, 18.2, 4.4. HRMS (APCI) $[M+H]^+$ calcd for $C_{23}H_{30}O_2Si$: 367.20878, found: 367.20961.

1-(4-Methoxyphenyl)-2-(4-cyanophenyl)cyclobutene (3ad): Prepared from diethyl 2-(4-methoxyphenyl)-cyclobuten-1-yl phosphate (**2a**) (0.469 g, 1.5 mmol), 4-cyanophenylzinc chloride•lithium chloride (4.50 mL, 2.25 mmol, 0.50M), $PdCl_2$DPEPhos (43.0 mg, 4 mol %), $AlCl_3$ (3.0 mL, 1.5 mmol, 0.5M), the reaction mixture was stirred for 13 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.5), 96% yield (0.377 g), white crystalline solid, m.p. 106–107 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (s, 4H), 7.46–7.40 (m, 2H), 6.91–6.85 (m, 2H), 3.84 (s, 3H), 2.81–2.73 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.6, 143.0, 140.5, 134.5, 132.2, 128.3, 127.6, 126.2, 119.2, 113.9, 110.0, 55.3, 27.3, 26.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{15}NO$: 262.12264, found: 262.12263.

1-(4-Methoxyphenyl)-2-(1-naphtyl)cyclobutene (3ae): Prepared from diethyl 2-(4-methoxyphenyl)cyclobuten-1-yl phosphate (**2a**) (0.234 g, 0.75 mmol), 1-naphtylzinc chloride•lithium chloride (2.54 mL, 1.12 mmol, 0.44M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M) the reaction mixture was stirred for 16.5 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.3), 95% yield (0.204 g), white crystalline solid, m.p. 83–85 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.57-7.45 (m, 3H), 7.44–7.36 (m, 1H), 7.16–7.09 (m, 2H), 6.74–6.68 (m, 2H), 3.75 (s, 3H), 3.02–2.91 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 158.9, 140.2, 135.7, 135.5, 133.7, 130.3, 128.3, 127.6, 127.4, 126.5, 125.9, 125.8, 125.5, 125.4, 113.4, 55.2, 30.3, 26.6. HRMS (APCI) $[M+H]^+$ calcd for $C_{21}H_{18}O$: 287.14304, found: 287.14327.

1-(5-(2,2'-Bithienyl))-2-(7-*tert*-butyl-1-pyrenyl)cyclobutene (3jf): Prepared from diethyl 2-(7-*tert*-butylpyrene-1-yl)cyclobuten-1-yl phosphate (**2j**) (0.347 g, 0.75 mmol), 5-(2,2'-bithienyl)zinc chloride•lithium chloride (2.3 mL, 1.13 mmol, 0.49M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 18.5 h, hexane→hexane/DCM (9:1, R_f = 0.5), 90% yield (0.320 g), bright yellow crystalline solid, m.p. 82 °C decomp. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27–8.20 (m, 3H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.08–8.01 (m, 4H), 7.12 (dq, *J* = 5.2, 1.1 Hz, 1H), 6.99–6.95 (m, 2H), 6.90 (dd, *J* = 5.2, 3.7 Hz, 1H), 6.77 (d, *J* = 3.8 Hz, 1H), 3.25–3.19 (m, 2H), 3.07–3.01 (m, 2H), 1.59 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 149.1, 137.5, 137.4, 137.2, 136.5, 134.5, 131.5, 131.2, 130.9, 130.7, 127.74, 127.73, 127.67, 127.5, 127.3, 125.8, 125.7, 125.4, 124.9, 124.5, 124.2, 123.7, 123.6, 123.1, 122.44, 122.39, 35.2, 31.9, 31.1, 27.8. HRMS (APCI) $[M+H]^+$ calcd for $C_{32}H_{26}S_2$: 475.15487, found: 475.15522.

1-(1-Pyrenyl)-2-(7-*tert*-butyl-1-pyrenyl)cyclobutene (3jg): Prepared from diethyl 2-(7-*tert*-butylpyrene-1-yl)-cyclobuten-1-yl phosphate (**2j**) (0.925 g, 2.0 mmol), 1-pyrenylzinc chloride•lithium chloride (6.52 mL, 3.0 mmol, 0.46M,), $PdCl_2$DPEPhos (57.3 mg, 4 mol %), $AlCl_3$ (4.0 Ml, 2.0 mmol, 0.5M), the reaction mixture was stirred for 19 h, hexane→hexane/DCM (9:1, R_f = 0.5), 84% yield (0.858 g), bright yellow crystalline solid, m.p. 168–172 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 9.8 Hz, 1H), 8.29 (d, *J* = 9.2 Hz, 1H), 8.21–2.17 (m, 1H), 8.13 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.07–7.87 (m, 11H), 7.70 (d, *J* = 9.3 Hz, 1H), 7.68 (d, *J* = 9.4 Hz, 1H), 3.45 (s, 4H), 1.54 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 148.9, 141.7, 141.4, 131.8, 131.5, 131.3, 131.2, 130.8, 130.7, 130.6, 128.0, 127.8, 127.5, 127.41, 127.37, 127.3, 127.23, 127.18, 126.1, 125.8, 125.7, 125.3, 125.1, 125.0, 124.91, 124.88, 124.83, 124.7, 124.5, 123.1, 122.3, 122.2, 35.1, 31.8, 31.2, 31.1. HRMS (APCI) $[M+H]^+$ calcd for $C_{40}H_{30}$: 511.24203, found: 511.24220.

1-(1-Cycloheptenyl)-2-(1-cyclohexenyl)cyclobutene (3kh): Prepared from diethyl 2-(cyclohexen-1-yl)-cyclobuten-1-yl phosphate (**2k**) (0.215 g, 0.75 mmol), cycloheptene-1-ylzinc chloride•lithium chloride (2.39 mL, 1.12 mmol, 0.47M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 18 h, hexane (R_f = 0.9), 26% yield (0.045 g), clear oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85 (t, *J* = 6.7 Hz, 1H), 5.70–5.65 (m, 1H), 2.38–2.31 (m, 6H), 2.24–2.08 (m, 6H), 1.80–1.71 (m, 2H), 1.67–1.42 (m, 8H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 141.8, 139.7, 138.7, 134.4, 130.4, 125.5, 32.7, 30.4, 28.7, 27.2, 27.0, 26.9, 26.1, 25.6, 25.5, 22.8, 22.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{17}H_{24}$: 229.19508, found: 229.19520.

1-(Cyclohexen-1-yl)-2-(7-*tert*-butylpyren-1-yl)cyclobutene (3ki): Prepared from diethyl 2-(cyclohexene-1-yl)cyclobuten-1-yl phosphate (**2k**) (0.287 g, 1.0 mmol), 7-*tert*-butylpyrene-1-ylzinc chloride•lithium chloride (3.0 mL, 1.5 mmol, 0.50M), $PdCl_2$DPEPhos (28.7 mg, 4 mol %), $AlCl_3$ (2.0 mL, 1.0 mmol, 0.50M), the reaction mixture was stirred for 12.5 h, hexane, (R_f = 0.55) 93% yield (0.364 g), yellow foam. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 9.4 Hz, 1H), 8.21 (d, *J* = 7.7 Hz, 2H), 8.04 (d, *J* = 10.7 Hz, 4H), 7.86 (d, *J* = 7.7 Hz, 1H), 5.91–5.85 (m, 1H), 2.95 (s, 2H), 2.81–2.74 (m, 2H), 2.19–2.09 (m, 2H), 1.81–1.70 (m, 2H), 1.59 (s, 9H), 1.54–1.45 (m, 2H), 1.37–1.23 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 149.0, 143.9, 136.1, 134.6, 133.8, 131.3, 131.0, 130.1, 127.5, 127.26, 127.22, 127.18, 125.85, 125.80, 125.75, 124.7, 124.2, 123.1, 122.2, 122.0, 35.2, 31.9, 30.5, 26.2, 25.8, 25.6, 22.3, 22.2. HRMS (APCI) $[M+H]^+$ calcd for $C_{30}H_{30}$: 391.24203, found: 391.24220.

1-(1-Cyclohexenyl)-2-(4-methoxyphenyl)cyclobutene (3kj): Prepared from diethyl 2-(cyclohexen-1-yl)cyclobuten-1-yl phosphate (**2k**) (0.430 g, 1.5 mmol), 4-methoxyphenylzinc chloride•lithium chloride (5.0 mL, 2.25 mmol, 0.45M), $PdCl_2$DPEPhos (43.0 mg, 4 mol %), $AlCl_3$ (3.0 mL, 1.5 mmol, 0.5M), the reaction mixture was stirred for 14 h, hexane→hexane/DCM (9:1, R_f = 0.45), 66% yield (0.238 g), clear oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 2H), 6.88–6.81 (m, 2H), 5.88–5.82 (m, 1H), 3.81 (s, 3H), 2.63–2.57 (m, 2H), 2.52–2.47 (m, 2H),

2.25–2.12 (m, 4H), 1.66–1.58 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 158.4, 139.4, 135.8, 134.3, 129.9, 128.3, 125.5, 113.4, 55.2, 27.1, 26.7, 25.6, 22.7, 22.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{17}H_{20}O$: 241.15869, found: 241.15888.

1-Cycloheptenyl-2-(4-(morpholin-4-ylmethyl)phenyl)cyclobutene (3lk): Prepared from diethyl 2-(cyclohepten-1-yl)-cyclobuten-1-yl phosphate (**2l**) (0.601 g, 2 mmol), 4-(morpholin-4-ylmethyl)phenylzinc chloride•lithium chloride (10.0 mL, 3.0 mmol, 0.30M), $PdCl_2$DPEPhos (57.3 mg, 4 mol %), $AlCl_3$ (4.0 mL, 2.0 mmol, 0.5M), the reaction mixture was stirred for 16 h, hexane/EtOAc (3:1→2:1, R_f = 0.50), 78% yield (0.505 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (s, 4H, overlapping with $CHCl_3$), 6.02 (t, *J* = 6.8 Hz, 1H), 3.74–3.67 (m, 4H), 3.48 (s, 2H), 2.62–2.58 (m, 2H), 2.53–2.48 (m, 2H), 2.47–2.41 (m, 4H), 2.39–2.33 (m, 2H), 2.24 (q, *J* = 4.1 Hz, 2H), 1.82–1.73 (m, 2H), 1.58–1.48 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 141.7, 141.5, 136.1, 135.7, 135.6, 131.3, 128.7, 126.9, 67.0, 63.2, 53.6, 32.6, 29.8, 28.7, 26.9, 26.8, 26.3, 26.1. HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{29}NO$: 324.23219, found: 324.23258.

1-Cycloheptenyl-2-(4-(methoxymethyl)phenyl)cyclobutene (3ll): Prepared from diethyl 2-(cyclohepten-1-yl)-cyclobuten-1-yl phosphate (**2l**) (0.601 g, 2.0 mmol), 4-(methoxymethyl)phenylzinc chloride•lithium chloride (6.10 mL, 2.99 mmol, 0.49M), $PdCl_2$DPEPhos (57.3 mg, 4 mol %), $AlCl_3$ (4.0 mL, 2.0 mmol, 0.5M), the reaction mixture was stirred for 17 h, hexane→hexane/DCM (9:1, R_f = 0.30), 73% yield of a mixture with 15 mol % of 4,4'-bis(methoxymethyl)biphenyl (0.451 g), yellow liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.27 (m, 4H), 6.02 (t, *J* = 6.6 Hz, 1H), 4.44 (s, 2H), 3.40 (s, 3H), 2.63–2.58 (m, 2H), 2.53–2.48 (m, 2H), 2.38–2.32 (m, 2H), 2.28–2.20 (m, 2H), 1.82–1.73 (m, 2H), 1.57–1.47 (m, 4H). HRMS (APCI) $[M+H]^+$ calcd for $C_{19}H_{24}O$: 269.18999, found: 269.18998.

1-(2-(4-Methoxyphenyl)cyclobuten-1-y)-2-(3-(trifluoromethyl)phenyl) cyclobutene (3an): Prepared from diethyl 2-(4-methoxyphenyl)cyclobuten-1-yl phosphate (**2a**) (0.394 g, 1.26 mmol), 2-(3-(trifluoromethyl)phenyl)cyclobuten-1-ylzinc chloride•lithium chloride (5.4 mL,1.89 mmol, 0.35M), $PdCl_2$DPEPhos (36.0 mg, 4 mol %), $AlCl_3$ (2.5 mL, 1.25 mmol, 0.5M), the reaction mixture was stirred for 16 h, hexane→hexane/DCM (9:1, R_f = 0.20), 61% (0.274 g), greenish crystalline solid, m.p. 109–111 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.44–7.31 (m, 2H), 7.30–7.24 (m, 2H), 6.82–6.77 (m, 2H), 3.79 (s, 3H), 2.78 (s, 4H), 2.77–2.72 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.1, 142.0, 138.1, 137.0, 136.4, 131.9, 130.4 (q, *J* = 32.1 Hz), 129.4 (q, *J* = 1.2 Hz), 128.7, 128.4, 128.0, 124.2 (q, *J* = 272.3 Hz), 123.2 (p, *J* = 4.0 Hz), 113.5, 55.3, 28.4, 27.9, 27.2, 26.9. ^{19}F NMR ($CDCl_3$): δ = -63.36 (s). HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{19}F_3O$: 357.14608, found: 357.14643.

1-(4-Methoxyphenyl)-2-(2-(4-methylphenyl)cyclobuten-1-yl)cyclobutene (3aq): Prepared from diethyl 2-(4-methoxyphenyl)cyclobuten-1-yl phosphate (**2a**) (0.422 g, 1.35 mmol), 2-(4-methylphenyl)cyclobuten-1-ylzinc chloride•lithium chloride (4.58 mL, 2.43 mmol, 0.53M), $PdCl_2$DPEPhos (38.7 mg, 4 mol %), $AlCl_3$ (2.7 mL, 1.35 mmol, 0.5M), the reaction mixture was stirred for 12.5 h, hexane→hexane/DCM (9:1, R_f = 0.30), 88% yield (0.360 g), white crystalline solid, m.p. 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 4H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.85–6.78 (m, 2H), 3.80 (s, 3H), 2.75–2.71 (m, 8H), 2.33 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 158.8, 140.27, 140.25, 136.8, 134.0, 133.2, 132.8, 129.0, 128.7, 127.9, 126.5, 113.5, 55.2, 28.3, 28.2, 27.11, 27.06, 21.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{22}O$: 303.17434, found: 303.17453.

1-(2-Thienylcyclobutene-1-y)-2-(3-(trifluoromethyl)phenyl)cyclobutene (3go): Prepared from diethyl 2-(2-thienyl)cyclobuten-1-yl phosphate (**2g**) (0.216 g, 0.75 mmol), 2-(3-trifluoromethylphenyl)cyclobutene-1-ylzinc chloride•lithium chloride (3.88 mL, 1.13 mmol, 0.29M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 18 h, hexane (R_f = 0.60), 65% yield (0.162 g), greenish crystalline solid, m.p. 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.55 (d, *J* = 7.1 Hz, 1H), 7.48–7.37 (m, 2H), 7.25 (dd, *J* = 4.4, 1.2 Hz, 1H), 7.03–6.97 (m, 2H), 2.98–2.92 (m, 2H), 2.86–2.75 (m, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 139.2, 138.5, 136.4, 136.1, 135.2, 131.4, 130.5 (q, *J* = 32.1 Hz), 129.4 (q, *J* = 1.1 Hz), 128.6, 127.2, 125.8, 125.7, 124.2 (q, *J* = 272.5 Hz), 123.5 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 4.0 Hz), 28.9, 28.4, 27.4. ^{19}F NMR ($CDCl_3$): δ = -63.32 (s). HRMS (APCI) $[M+H]^+$ calcd for $C_{19}H_{15}F_3S$: 333.09193, found: 333.09197.

1-(2-(4-Methylphenyl)cyclobutene-1-yl)-2-(7-*tert*-butylpyren-1-yl)cyclobutene (3mm): Prepared from diethyl 2-(2-(4-methylphenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (**2m**) (0.385 g, 1.0 mmol), 7-*tert*-butylpyren-1-ylzinc chloride•lithium chloride (3.0 mL, 1.5 mmol, 0.50M), $PdCl_2$DPEPhos (28.6 mg, 4 mol %), $AlCl_3$ (2.0 mL, 1.0 mmol, 0.5M), the reaction mixture was stirred for 12.5 h, hexane→hexane/DCM (9:1, R_f = 0.35), 91% yield (0.412 g), bright yellow crystalline solid, m.p. 150–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (d, *J* = 9.3 Hz, 1H), 8.20 (s, 2H), 8.12–8.00 (m, 4H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 3.15 (brs, 2H), 3.11–3.04 (m, 2H), 2.60 (brs, 2H), 2.31 (s, 3H), 2.21 (brs, 2H), 1.59 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 149.0, 141.7, 140.7, 138.1, 137.0, 134.0, 133.1, 132.3, 131.3, 130.9, 130.3, 128.8, 128.3, 127.4, 127.2, 126.2, 125.7, 125.6, 124.8, 124.1, 123.1, 122.2, 122.0, 35.2, 31.9, 31.5, 29.7, 27.4, 27.1, 21.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{35}H_{32}$: 453.25768, found: 453.25799.

1-(2-(4-Fluorophenyl)cyclobuten-1-yl)-2-(6-methoxynaphth-2-yl)cyclobutene (3np): Prepared from diethyl 2-(2-(4-fluorophenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (**2n**) (0.265 g, 0.75 mmol), 6-methoxynaphthylzinc chloride•lithium chloride (2.81 mL, 1.12 mmol, 0.40M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 18 h, hexane→hexane/DCM (9:1→hexane:EtOAc 20:1, R_f = 0.45), 62% yield (0.166 g), greenish crystalline solid, m.p. 173–175 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.56 (m, 3H), 7.51–7.46 (m, 1H), 7.37–7.29 (m, 2H), 7.13–7.06 (m, 2H), 6.96–6.88 (m, 2H), 3.91 (s, 3H), 2.89–2.74 (m, 8H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 161.8 (d, *J* = 247.1 Hz), 157.8, 141.0, 139.4 (d, *J* = 0.6 Hz), 134.6 (d, *J* = 2.2 Hz), 134.2, 133.8, 132.2 (d, *J* = 3.4 Hz), 131.3, 129.6, 128.6, 128.2 (d, *J* = 7.9 Hz), 126.3, 125.4 (d, *J* = 0.8 Hz), 118.9, 115.1, 114.8, 105.8, 55.3, 28.3, 28.2, 27.15, 27.10. ^{19}F NMR ($CDCl_3$): δ = -114.65 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{21}FO$: 357.16492, found: 357.16525.

1-(4-Cyanophenyl)-2-(2-(4-fluorophenyl)cyclobuten-1-yl)cyclobutene (3nr): Prepared from diethyl 2-(2-(4-fluorophenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (**2n**) (0.352 g, 1.0 mmol), 4-cyanophenylzinc chloride•lithium chloride (2.88 mL, 1.50 mmol, 0.52M), $PdCl_2$DPEPhos (28.6 mg, 4 mol %), $AlCl_3$ (2.0 mL, 1.0 mmol, 0.5M), the reaction mixture was stirred for 13 h, hexane→hexane/DCM (9:1→hexane:EtOAc 20:1, R_f = 0.55), 83% yield (0.250 g), greenish crystalline solid, m.p. 119–122 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.28 (dd, *J* = 7.6, 6.0 Hz, 2H), 6.95 (t, *J* = 8.4 Hz, 2H), 2.80–2.71 (m, 8H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 162.2 (d, *J* = 247.5 Hz), 141.9 (d, *J* = 0.9 Hz), 139.6, 138.9, 138.5, 133.5 (d, *J* = 2.2 Hz), 131.83, 131.76 (d, *J* = 3.4 Hz), 128.4 (d, *J* = 8.1 Hz), 126.7, 119.1, 115.1 (d, *J* = 21.6 Hz), 110.0, 28.5, 28.0, 27.3, 26.8. ^{19}F NMR ($CDCl_3$): δ = -113.42 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{21}H_{16}FN$: 302.13395, found: 302.13397.

1-(2-(4-Fluorophenyl)cyclobuten-1-yl)-2-(2-(4-methylphenyl)cyclobuten-1-yl)cyclobutene (3ms): Prepared from 2-(2-

(4-methylphenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (**2m**) (0.289 g, 0.75 mmol), 2-(4-fluorophenyl)cyclobuten-1-ylzinc chloride•lithium chloride (3.55 mL, 1.35 mmol, 0.38M), $PdCl_2$DPEPhos (21.5 mg, 4 mol %), $AlCl_3$ (1.5 mL, 0.75 mmol, 0.5M), the reaction mixture was stirred for 13 h, hexane (R_f = 0.65), 87% yield (0.223 g), bright yellow crystalline solid, m.p. 146–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.33 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 7.03–6.94 (m, 2H), 2.81–2.72 (m, 4H), 2.69 (m, 8H), 2.34 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 161.8 (d, *J* = 247.7 Hz), 141.5, 139.7 (d, *J* = 0.8 Hz), 137.3, 137.1, 136.2, 134.3 (d, *J* = 2.2 Hz), 133.6, 133.2, 132.3 (d, *J* = 3.5 Hz), 128.8, 128.1 (d, *J* = 8.0 Hz), 126.5, 115.0 (d, *J* = 21.4 Hz), 29.7, 29.6, 28.20, 28.17, 27.44, 27.41, 21.3. ^{19}F NMR ($CDCl_3$): δ = -114.78 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{23}F$: 343.18566, found: 343.18582.

1-{4-[2-(4-Fluorophenyl)cyclobutenyl]phenyl}-2-[2-(4-methylphenyl) cyclobutenyl]cyclobutene(**3mt**): Prepared from 2-(2-(4-methylphenyl)cyclobuten-1-yl)cyclobuten-1-yl phosphate (**2m**) (0.385 g, 1.0 mmol), 4-(2-(4-(fluorophenyl)cyclobuten-1-yl)phenyl)zinc chloride•lithium chloride (3.0 mL, 1.5 mmol, 0.50M), $PdCl_2$DPEPhos (28.6 mg, 4 mol %), $AlCl_3$ (2.0 mL, 1.0 mmol, 0.5M), the reaction mixture was stirred for 14 h, hexane (R_f = 0.25), 92% yield (0.386 g), bright yellow crystalline solid, m.p. 176–180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.24 (m, 8H), 7.09 (d, *J* = 7.9 Hz, 2H), 7.03–6.95 (m, 2H), 2.76 (s, 8H), 2.75 (s, 4H), 2.33 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 162.0 (d, *J* = 247.2 Hz), 141.4, 140.1, 138.3 (d, *J* = 1.8 Hz), 137.6, 137.1, 135.4, 135.1, 134.6, 133.9, 133.2, 132.5 (d, *J* = 3.4 Hz), 128.7, 127.8 (d, *J* = 8.0 Hz), 126.6, 126.5, 125.6, 115.2 (d, *J* = 21.3 Hz), 28.4, 28.3, 27.2, 27.0, 26.6, 21.4. ^{19}F NMR ($CDCl_3$): δ = -114.23 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{31}H_{27}F$: 419.21696, found: 419.21708.

General procedure for the synthesis of alkenes 4 by opening of the cyclobutene ring.

A solution of 1,2-disubstituted cyclobutene **3** in xylene (10 mL/mmol) was stirred at 150 °C. After the reaction was complete, the majority of xylene was evaporated and the resultant mixture was subjected to column chromatography (silica gel) affording the final product **4**.

2-(4-Methoxyphenyl)-3-(4-methylphenyl)buta-1,3-diene (4aa): Prepared from 1-(4-methoxyphenyl)-2-(4-methylphenyl)cyclobutene (**3aa**) (0.250 g, 1.0 mmol), the reaction mixture was stirred for 14 h, hexane→hexane/DCM (9:1→hexane:EtOAc 20:1, R_f = 0.4), 92% yield (0.230 g), white crystalline solid, m.p. 36–38 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.25 (m, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.83–6.76 (m, 2H), 5.52 (d, *J* = 1.8 Hz, 1H), 5.47 (d, *J* = 1.7 Hz, 1H), 5.28 (d, *J* = 1.8 Hz, 1H), 5.24 (d, *J* = 1.7 Hz, 1H), 3.77 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.0, 149.8, 149.3, 137.24, 137.19, 132.7, 128.9, 128.5, 127.2, 115.2, 114.5, 113.5, 55.2, 21.1. HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{18}O$: 251.14304, found: 251.14319.

2-(4-Methoxyphenyl)-3-(3-trifluoromethylphenyl)buta-1,3-diene (4ab): Prepared from 1-(3-trifluoromethylphenyl)-2-(4-methoxyphenyl)cyclobutene (**3ab**) (0.152 g, 0.5 mmol), the reaction mixture was stirred for 15 h, hexane→hexane/DCM (9:1, R_f = 0.35), 92% yield (0.140 g), clear viscous liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.66 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.32–7.28 (m, 2H), 6.83–6.79 (m, 2H), 5.58 (d, *J* = 1.2 Hz, 1H), 5.50 (d, *J* = 1.5 Hz, 1H), 5.41 (d, *J* = 1.2 Hz, 1H), 5.23 (d, *J* = 1.7 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.3, 148.9, 148.6, 141.0, 132.2, 130.8 (q, *J* = 1.4 Hz), 130.6 (q, *J* = 32.4 Hz), 128.6, 124.17 (q, *J* = 3.8 Hz), 124.12 (q, *J* = 270.8 Hz), 124.17 (q, *J* = 3.9 Hz), 124.07 (q, *J* = 3.9 Hz), 117.4, 115.5, 113.7, 55.2. ^{19}F NMR ($CDCl_3$): δ = -63.14 (s). HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{15}F_3O$: 305.11478, found: 305.11525.

2-(4-Methoxyphenyl)-3-(4-*tert*-butyldimethylsilyloxyphenyl)buta-1,3-diene (4ac): Prepared from 1-(4-methoxyphenyl)-2-(4-*tert*-butyldimethylsilyloxyphenyl) cyclobutene (**3ac**) (0.168 g, 0.5 mmol), the reaction mixture was stirred for 14 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.5), 98% yield (0.165 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.22 (m, 4H), 6.82–6.69 (m, 4H), 5.74 (d, *J* = 1.8 Hz, 2H), 5.22 (d, *J* = 1.7 Hz, 2H), 3.77 (s, 3H), 0.96 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.0, 155.2, 149.5, 149.4, 133.2, 132.7, 128.51, 128.47, 119.6, 114.4, 114.3, 113.5, 55.2, 25.6, 18.2, -4.4. HRMS (APCI) $[M+H]^+$ calcd for $C_{23}H_{30}O_2Si$: 367.20878, found: 367.20895.

2-(4-Cyanophenyl)-3-(4-methoxyphenyl)buta-1,3-diene (4ad): Prepared from 1-(4-methoxyphenyl)-2-(4-cyanophenyl)cyclobutene (**3ad**) (0.131 g, 0.5 mmol), the reaction mixture was stirred for 14 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.35), 93% yield (0.122 g), white crystalline solid, m.p. 57–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.30–7.24 (m, 2H), 6.83–6.76 (m, 2H), 5.64 (d, *J* = 1.1 Hz, 1H), 5.53 (d, *J* = 1.5 Hz, 1H), 5.50 (d, *J* = 1.1 Hz, 1H), 5.25 (d, *J* = 1.4 Hz, 1H), 3.77 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.3, 148.6, 148.1, 144.6, 132.0, 131.7, 128.4, 127.9, 118.8, 118.5, 115.4, 113.7, 111.0, 55.2. HRMS (APCI) $[M+H]^+$ calcd for $C_{18}H_{15}NO$: 262.12264, found: 262.12276.

2-(4-Methoxyphenyl)-3-(1-naphthyl)buta-1,3-diene (4ae): Prepared from 1-(4-methoxyphenyl)-2-(1-naphthyl)cyclobutene (**3ae**) (0.143 g, 0.5 mmol), the reaction mixture was stirred for 18 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f = 0.4), 95% yield (0.136 g), white crystalline solid, m.p. 75–76 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11–8.04 (m, 1H), 7.89–7.78 (m, 2H), 7.52–7.40 (m, 6H), 6.96–6.88 (m, 2H), 5.50 (d, *J* = 1.8 Hz, 1H), 5.41–5.38 (m, 1H), 5.19–5.17 (m, 1H), 4.81 (d, *J* = 1.4 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.1, 149.9, 148.8, 139.7, 133.60, 133.55, 131.9, 129.8, 128.2, 127.7, 126.9, 126.1, 125.8, 125.6, 125.3, 120.2, 117.7, 113.5, 55.3. HRMS (APCI) $[M+H]^+$ calcd for $C_{21}H_{18}O$: 287.14304, found: 287.14329.

2-(1-Pyrenyl)-3-(7-*tert*-butyl-1-pyrenyl)buta-1,3-diene (4jg): Prepared from 1-(1-pyrenyl)-2-(7-*tert*-butyl-1-pyrenyl)cyclobutene (**3jg**) (0.255 g, 0.5 mmol), the reaction mixture was stirred for 20 h. After the reaction mixture was cooled to ambient temperature, about half of xylene was evaporated on vacuum and the mixture was diluted with hexane. The pure product precipitated immediately and filtration afforded 0.206 g (81%) of the pure product as a white crystalline solid, m.p. 264 °C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.49 (d, *J* = 9.1 Hz, 1H), 8.45 (d, *J* = 9.1 Hz, 1H), 8.34–8.09 (m, 14H), 8.04 (t, *J* = 7.7 Hz, 1H), 5.43–5.38 (m, 2H), 5.22–5.17 (m, 2H), 1.61 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 149.4, 149.3, 136.7, 136.5, 131.4, 131.3, 131.1, 130.9, 130.7, 130.5, 129.4, 129.2, 127.71, 127.65, 127.58, 127.53, 127.45, 127.43, 127.38, 127.29, 127.26, 126.0, 125.6, 125.4, 125.2, 125.0, 124.91, 124.88, 124.80, 124.6, 124.4, 123.1, 122.4, 122.3, 122.03, 121.97, 35.3, 32.0. HRMS (APCI) $[M+H]^+$ calcd for $C_{40}H_{30}$: 511.24203, found: 511.24215.

2-Cyclohexene-1-yl-3-(7-*tert*-butylpyrene-1-yl)buta-1,3-diene (4ki): Prepared from 1-(cyclohexene-1-yl)-2-(7-*tert*-butylpyren-1-yl)cyclobutene (**3ki**) (0.195 g, 0.5 mmol), the reaction mixture was stirred for 16 h, hexane (R_f=0.45), 98% yield (0.191 g), yellow viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.34 (d, *J* = 9.2 Hz, 1H), 8.22–8.17 (m, 2H), 8.11–7.99 (m, 4H), 7.84 (d, *J* = 8.0 Hz, 1H), 5.95–5.89 (m, 1H), 5.78 (d, *J* = 2.1 Hz, 1H), 5.44 (d, *J* = 1.9 Hz, 1H), 5.13 (d, *J* = 1.5 Hz, 1H), 4.76 (d, *J* = 1.8 Hz, 1H), 2.38–2.29 (m, 2H), 2.10–2.01 (m, 2H), 1.74–1.52 (m, 13H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 153.3, 149.0, 148.3, 137.4, 137.3, 131.2, 130.8, 130.2, 128.5, 127.31, 127.26, 127.20, 126.7, 125.4, 124.9, 124.2, 123.1, 122.2, 122.0, 119.6, 114.4, 35.2, 32.0, 28.0, 25.6, 22.9, 22.2. HRMS (APCI) $[M+H]^+$ calcd for $C_{30}H_{30}$: 391.24203, found: 391.24234.

2-(1-Cyclohexenyl)-3-(4-methoxyphenyl)buta-1,3-diene (4kj): Prepared from 1-(1-cycohexenyl)-2-(4-methoxyphenyl)cyclobutene (**3kj**) (0.120 g, 0.5 mmol), the reaction mixture was stirred for 17 h, hexane→hexane/DCM (9:1, R_f=0.55), 72% yield (0.087 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 2H), 6.86–6.79 (m, 2H), 5.74–5.69 (m, 1H), 5.44 (d, *J* = 1.8 Hz, 1H), 5.22–5.20 (m, 1H), 5.09 (d, *J* = 1.8 Hz, 1H), 5.02–5.00 (m, 1H), 3.80 (s, 3H), 2.26–2.18 (m, 2H), 2.04–1.95 (m, 2H), 1.71–1.60 (m, 2H), 1.58–1.47 (m, 2H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.0, 151.3, 149.3, 135.3, 133.0, 128.8, 127.5, 113.4, 112.5, 111.6, 55.2, 25.8, 22.8, 22.1. HRMS (APCI) $[M+H]^+$ calcd for $C_{17}H_{20}O$: 241.15869, found: 241.15878.

2-(1-Cycloheptenyl)-3-(4-(morpholin-4-ylmethyl)phenyl)buta-1,3-diene (4lk): Prepared from 1-cycloheptenyl-2-(4-(morpholin-4-ylmethyl)phenyl)cyclobutene (**3lk**) (0.187 g, 0.578 mmol), the reaction mixture was stirred for 21 h, hexane:EtOAc (3:1)→(2:1, R_f=0.60), 75% yield (0.140 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 5.90 (t, *J* = 6.7 Hz, 1H), 5.43 (d, *J* = 1.8 Hz, 1H), 5.21–5.19 (m, 2H), 4.98 (d, *J* = 1.9 Hz, 1H), 3.73–3.68 (m, 4H), 3.48 (s, 2H), 2.47–2.40 (m, 4H), 2.36–2.29 (m, 2H), 2.14–2.05 (m, 2H), 1.75–1.65 (m, 2H), 1.46–1.34 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 152.8, 149.6, 143.8, 139.5, 136.8, 132.4, 128.8, 127.0, 114.5, 112.8, 67.0, 63.2, 53.6, 32.5, 30.5, 28.6, 26.6, 26.4. HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{29}NO$: 324.23219, found: 324.23261.

2-(1-Cycloheptenyl)-3-(4-(methoxmethyl)phenyl)buta-1,3-diene (4ll): Prepared from of 1-cycloheptenyl-2-(4-(morpholin-4-ylmethyl)phenyl)cyclobutene (**3ll**) (0.20 g, 0.64 mmol containing approximately 15 mol.% of 4,4'-bis(methoxymethyl)biphenyl), the reaction mixture was stirred for 22 h, hexane→hexane/DCM (9:1→4:1, R_f=0.20), 77% yield (0.133 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 5.88 (t, *J* = 6.7 Hz, 1H), 5.43 (d, *J* = 1.8 Hz, 1H), 5.22 (d, *J* = 1.8 Hz, 1H), 5.20 (d, *J* = 1.9 Hz, 1H), 4.99 (d, *J* = 1.8 Hz, 1H), 4.44 (s, 2H), 3.39 (s, 3H), 2.36–2.28 (m, 2H), 2.13–2.04 (m, 2H), 1.75–1.64 (m, 2H), 1.48–1.33 (m, 4H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 152.7, 149.6, 143.7, 140.1, 137.2, 132.4, 127.4, 127.1, 114.7, 112.8, 74.5, 58.1, 32.4, 30.5, 28.6, 26.6, 26.4. HRMS (APCI) $[M+H]^+$ calcd for $C_{19}H_{24}O$: 269.18999, found: 269.19001.

2-(7-*tert*-Butylpyrenyl)-3,4-dimethylene-5-(4-tolyl)hexa-1,5-diene (4mm): Prepared from 1-(2-(4-methylphenyl)cyclobuten-1-yl)-2-(7-*tert*-butylpyrene-1-yl)cyclobutene (**3mm**) (0.226 g, 0.5 mmol), the reaction mixture was stirred for 24 h, hexane (R_f=0.50), 50% yield (0.113 g), yellowish wax. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26–8.20 (m, 2H), 8.11 (d, *J* = 7.7 Hz, 1H), 8.07 (s, 2H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 9.3 Hz, 1H), 7.74 (d, *J* = 7.8 Hz, 1H), 5.98 (d, *J* = 1.7 Hz, 1H), 5.55 (d, *J* = 1.7 Hz, 1H), 5.44 (brs, 1H), 5.40 (d, *J* = 1.4 Hz, 1H), 5.33–5.29 (m, 2H), 4.90 (d, *J* = 1.8 Hz, 1H), 2.44 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 150.2, 149.5, 149.0, 147.6, 137.9, 137.1, 136.7, 131.2, 130.8, 130.3, 128.9, 128.7, 128.2, 127.4, 127.3, 127.2, 127.1, 125.4, 124.6, 124.1, 123.0, 122.2, 122.1, 120.0, 119.8, 118.8, 115.7, 35.2, 31.9, 21.2. HRMS (APCI) $[M+H]^+$ calcd for $C_{35}H_{32}$: 453.25768, found: 453.25801.

2-(4-Methoxyphenyl)-3,4-dimethylene-5-(3-(trifluoromethyl)phenyl)hexa-1,5-diene (4an): Prepared from 1-(2-(4-methoxyphenyl)cyclobutene-1-y)-2-(3-(trifluoromethyl)phenyl)cyclobutene (**3an**) (0.179 g, 0.5 mmol), the reaction mixture was stirred for 23 h, hexane→hexane/DCM (9:1, R_f=0.35), 64% yield (0.114 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.38 (m, 4H), 7.25–7.20 (m, 2H), 6.88–6.81 (m, 2H), 5.44 (d, *J* = 1.4 Hz, 1H), 5.38 (d, *J* = 1.4 Hz, 1H), 5.35–5.32 (m, 2H), 5.25 (d, *J* = 1.9 Hz, 1H), 5.22 (d, *J* = 1.8 Hz, 1H), 5.21 (d, *J* = 1.8 Hz, 1H), 5.16 (d, *J* = 1.5 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.3, 148.8, 148.5, 148.2, 148.0, 141.4, 132.8, 130.6 (q, *J* = 1.2 Hz), 130.5 (q, *J* = 32.1 Hz), 128.6, 128.4, 124.18 (q, *J* = 272.2 Hz), 124.14 (two overlapping quartets), 119.7, 119.0, 117.3, 114.5, 113.5, 55.2. ^{19}F NMR ($CDCl_3$): δ = -63.04 (s). HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{19}F_3O$: 357.14608, found: 357.14660.

2-(4-Fluorophenyl)-3,4-dimethylene-5-(6-methoxynaphthyl)hexa-1,5-diene (4np): Prepared from 1-(2-(4-fluorophenyl)cyclobuten-1-yl)-2-(6-methoxynaphth-2-yl)cyclobutene (**3np**) (0.178 g, 0.5 mmol), the reaction mixture was stirred for 24 h, hexane→hexane/DCM (9:1, R_f=0.40), 66% yield (0.118 g), yellow crystalline solid, m.p. 91–94 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 2.8 Hz, 1H), 7.65 (d, *J* = 3.0 Hz, 1H), 7.61 (d, *J* = 1.3 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.32–7.25 (m, 2H), 7.18–7.11 (m, 2H), 7.03–6.94 (m, 2H), 5.50 (d, *J* = 1.7 Hz, 1H), 5.36 (d, *J* = 1.5 Hz, 1H), 5.34–5.29 (m, 4H), 5.23 (d, *J* = 1.7 Hz, 1H), 5.17 (d, *J* = 1.6 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 162.4 (d, *J* = 246.2 Hz), 157.8, 149.0, 148.70, 148.66, 148.3, 136.6 (d, *J* = 3.2 Hz), 135.7, 134.0, 129.6, 129.0 (d, *J* = 8.2 Hz), 128.7, 126.5, 126.1, 126.0, 119.20, 119.15, 118.9, 115.70 (d, *J* = 1.1 Hz), 115.65, 114.9 (d, *J* = 21.4 Hz), 105.7, 55.3. ^{19}F NMR ($CDCl_3$): δ = -115.59 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{25}H_{21}FO$: 357.16492, found: 357.16548.

2-(4-Methoxyphenyl)-3,4-dimethylene-5-(4-tolyl)hexa-1,5-diene (4aq): Prepared from 1-(4-methoxyphenyl)-2-(2-(4-methylphenyl)cyclobuten-1-yl)cyclobutene (**3aq**) (0.151 g, 0.5 mmol), the reaction mixture was stirred for 23 h, hexane→hexane/DCM (9:1, R_f=0.40), 65% yield (0.098 g), clear viscous liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.19 (m, 4H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.87–6.81 (m, 2H), 5.37 (d, *J* = 1.8 Hz, 1H), 5.33 (d, *J* = 1.8 Hz, 1H), 5.27–5.23 (m, 3H), 5.21 (d, *J* = 1.8 Hz, 1H), 5.17–5.15 (m, 2H), 3.82 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 159.2, 149.1, 149.0, 148.9, 148.7, 137.8, 137.2, 133.2, 128.8, 128.5, 127.2, 118.9, 118.8, 115.0, 114.3, 113.4, 55.3, 21.2. HRMS (APCI) $[M+H]^+$ calcd for $C_{22}H_{22}O$: 303.17434, found: 303.17462.

2-(4-Cyanophenyl)-3,4-dimethylene-5-(4-fluorophenyl)hexa-1,5-diene (**4nr**): Prepared from 1-(4-cyanophenyl)-2-(2-(4-fluorophenyl)cyclobuten-1-yl)cycobutene (**3nr**) (0.151 g, 0.5 mmol), the reaction mixture was stirred for 24 h, hexane→hexane/DCM (9:1)→hexane/EtOAc (20:1, R_f=0.50), 65% yield (0.098 g), yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.56 (m, 2H), 7.37–7.31 (m, 2H), 7.24–7.18 (m, 2H), 7.03–6.94 (m, 2H), 5.44 (d, *J* = 1.2 Hz, 1H), 5.39 (d, *J* = 1.2 Hz, 1H), 5.35–5.31 (m, 2H), 5.27–5.24 (m, 2H), 5.19 (d, *J* = 1.8 Hz, 1H), 5.16 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 162.5 (d, *J* = 247.1 Hz), 148.4, 147.94, 147.85, 147.7, 145.1, 136.3 (d, *J* = 3.5 Hz), 132.0, 129.0 (d, *J* = 8.0 Hz), 128.0, 119.8, 119.4, 118.8, 118.4, 116.1 (d, *J* = 1.0 Hz), 115.0 (d, *J* = 21.3 Hz), 111.2. ^{19}F NMR ($CDCl_3$): δ = -115.16 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{21}H_{16}FN$: 302.13395, found: 302.13399.

2-{4-[2-(4-fluorophenyl)-1-methyleneprop-2-enyl]phenyl}-3,4-dimethylene-5-(4-methylphenyl)hexa-1,5-diene(4mt): Prepared from alkene **3mt** (0.222 g, 0.53 mmol), the reaction mixture was stirred for 24 h, hexane (R_f=0.30), 72% yield (0.160 g), slightly yellow wax. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 4H), 7.27–7.15 (m, 4H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.01–6.91 (m, 2H), 5.58 (d, *J* = 1.5 Hz, 1H), 5.51 (d, *J* = 1.5 Hz, 1H), 5.39 (d, *J* = 1.6 Hz, 1H), 5.36 (d, *J* = 1.6 Hz, 1H), 5.32 (d, *J* = 1.4 Hz, 1H), 5.31 (d, *J* = 1.6 Hz, 1H), 5.30–5.24 (m, 3H), 5.23 (d, *J* = 1.7 Hz, 1H), 5.15–5.13 (m, 2H), 2.35 (s, 3H). ^{13}C NMR (75MHz, $CDCl_3$): δ = 162.4 (d, *J* = 246.6 Hz), 149.3, 149.0, 148.9, 148.81, 148.80, 148.76, 139.9, 139.0, 137.7, 137.2, 136.2 (d, *J* = 3.4 Hz), 129.1 (d, *J* = 8.0 Hz), 128.8, 127.27, 127.25, 127.1, 118.9, 116.21, 116.15, 116.14, 115.7, 115.13, 115.06 (d, *J* = 21.4 Hz), 21.1. ^{19}F NMR ($CDCl_3$): δ = -115.42 (m). HRMS (APCI) $[M+H]^+$ calcd for $C_{31}H_{27}F$: 419.21696, found: 419.21713.

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Keywords: alkenes • cross-coupling • aluminum • C-C bond formation • electrocyclic reactions

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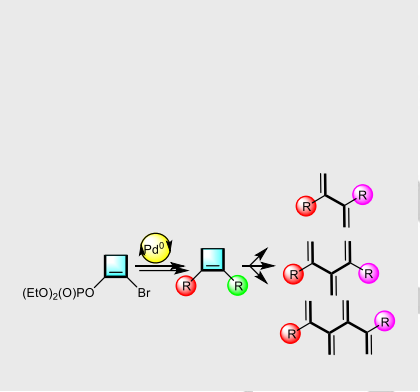

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