Suzuki-Miyaura Coupling Enabled by Aryl to Vinyl 1,4-Palladium Migration

- >90 successful examples with up to 99% yield
- Efficient transformation with excellent regio- and stereoselectivity
- Excellent compatibility toward functional groups and heteroaryl rings
- Versatile transformations for the synthesis of potential material molecules

HIGHLIGHTS
Suzuki-Miyaura coupling via controllable aryl to vinyl 1,4-palladium migration
Synthesis of multisubstituted olefins and 1,3-dienes in stereospecific way
Wide substrate scope and excellent functional-group tolerance
A powerful tool for the studies on geometric isomers in material science

DATA AND CODE AVAILABILITY
www.ccdc.cam.ac.uk/data_request/cif

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Suzuki-Miyaura Coupling Enabled by Aryl to Vinyl 1,4-Palladium Migration

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SUMMARY

The Suzuki-Miyaura coupling is a fundamentally important transformation in modern organic synthesis. The development of new reaction modes for new chemical accessibility and higher synthetic efficiency is still the consistent pursuance in this field. An efficient Suzuki-Miyaura coupling enabled by a controllable 1,4-palladium migration was realized to afford stereodefined multisubstituted olefins and 1,3-dienes. The reaction exhibits remarkable broad substrate scope, excellent functional-group tolerance, versatile conversion with obtained products, and easy scalability. The practicality of this method is highlighted by the aggregation-induced emission feature of the produced olefins and 1,3-dienes, as well as the capability of affording geometric isomer pairs with a marked difference on photoluminescent quantum yield values.

INTRODUCTION

Since the introduction of the Suzuki-Miyaura coupling in 1979 (Miyaura et al., 1979), this Nobel Prize winning chemistry has developed into one of the most synthetically valuable processes for the construction of carbon-carbon bonds and been widely applied in both academia and industry (Beletskaya et al., 2019; MaLuenda and Navarro, 2015; Miyaura and Suzuki, 1995). For example, according to statistics, over 60% of the carbon-carbon bond-forming processes in medicinal chemistry now are accomplished through this reaction (Schneider et al., 2016). Despite brilliant achievements, the continuing efforts for broader reaction scope and higher efficiency have never ceased.

Mechanistically, this reaction is initiated by the generation of a key organopalladium(II) intermediate, normally a result of direct oxidative addition of palladium(0) to a carbon-heteroatom bond. Later, direct C-H bond activation by palladium(II) becomes a second important route (Chen et al., 2006; Giri et al., 2007; Shi et al., 2007; Wang et al., 2008; Yang et al., 2008). Compared with these direct generation modes, the organopalladium(II) intermediate can also be produced via an indirect manner, which has been far less developed and mainly focused on the generation via a migratory insertion of organopalladium to olefins (Grigg et al., 1997; Schempp et al., 2017; Zhang et al., 2019) or alkynes (Couty et al., 2004; Monks and Cook, 2012) (Figure 1A).

Palladium migration, which can relay the palladium from the original place to a remote position, is a novel strategy for the indirect generation of the desired palladium(II) intermediate and has been applied in several efficient organic transformations (Ma and Gu, 2005; Shi and Larock, 2010; Rahim et al., 2019). Early attempts to execute Suzuki-Miyaura coupling via palladium migration were made, but only limited success has been achieved.

Buchwald and co-workers realized a Suzuki-Miyaura coupling through a complete aryl to alkyl 1,4-palladium migration (Barder et al., 2005). However, only a single arylbromide with two neighboring positions blocked by tert-butyl groups was tested. Later, Larock and co-workers tried Suzuki-Miyaura coupling via aryl to aryl 1,4-palladium migration and found it was hard to control this migration process efficiently (Campos et al., 2007). Usually, a significant amount of non-migrated product was generated. Therefore, Suzuki-Miyaura coupling enabled by controllable palladium migration, further expanding this important transformation and affording new chemical accessibility, is highly desirable. As a continuing effort on developing reactions via palladium migration (Hu et al., 2016, 2018), herein we present the first Suzuki-Miyaura coupling enabled by aryl to vinyl 1,4-palladium migration (Figure 1B), which offered an efficient way to synthesize stereodefined, multisubstituted olefins (Gao et al., 2010; Wang, 2012; Wencel-Delord et al., 2012; Zhang et al., 2016a; Li et al., 2017; Li and Duan, 2018; Lin et al., 2019) and 1,3-dienes (Besset et al., 2011; Boutiladakis-Arapinis et al., 2014; De Paolis et al., 2012; Hu et
al., 2015; Liang et al., 2017; Liu et al., 2019; Siu, 2019). Notably, multiaryl substituted olefins and 1,3-di-enes may display interesting electronic and photonic properties owing to their π-extended systems and have been widely applied in many diverse fields, such as chemical or biological sensors, stimuli response material, and fluorescent materials (Kong et al., 2018; Yang et al., 2014; He et al., 2019). Despite the fact that the geometry of double bonds in these molecules has great influence on the material performance, effective synthetic approaches toward these structures remain to be limited, in which the application of symmetric starting material or a homo-coupling reaction is often necessary to overcome the geometric problem (Xie and Li, 2019; Zhang et al., 2016b).

Figure 1. Suzuki-Miyaura Coupling Enabled by Aryl to Vinyl 1,4-Palladium Migration
(A) Two Suzuki-Miyaura coupling modes.
(B) Aryl to vinyl 1,4-palladium migration/Suzuki-Miyaura coupling sequence.
(C) Possible applications in material science.
RESULTS AND DISCUSSION
Reaction Conditions Development

We began our investigation by studying the coupling of ortho-vinyl bromobenzene 1a and various phenylboron reagents 2a, and some representative results are listed in Scheme 1. With phenylboronic acid 2a1 as the coupling partner, the expected triphenyl substituted olefin 3aa was obtained in 56% reaction yield, but a significant amount of the direct coupling product 4aa was formed, along with some side products from the dimerization of 1a (entry 1). Screening of ligands, solvents, or bases failed to improve the migration efficiency. We speculated

| Entry | Ligand | Base | Phenylboron | Yield of 3aa (%) | Ratio of 3aa/4aa |
|-------|--------|------|-------------|-----------------|-----------------|
| 1     | L1     | CsOAc | 2a1         | 56              | 62:38           |
| 2     | L1     | CsOAc | 2a2         | 55              | 56:42           |
| 3     | L1     | CsOAc | 2a3         | 8               | nd              |
| 4     | L1     | CsOAc | 2a4         | 29              | 97:3            |
| 5     | L1     | CsOAc | 2a5         | 64              | 94:6            |
| 6     | L1     | CsOAc | 2a6         | 79              | 93:7            |
| 7     | L1     | CsOAc | 2a7         | 28              | 33:67           |
| 8     | L1     | CsOAc | 2a8         | 69              | 91:9            |
| 9     | L1     | CsOAc | 2a9         | 66              | 50:10           |
| 10    | L2     | CsOAc | 2a5         | 33              | 60:40           |
| 11    | L3     | CsOAc | 2a6         | 15              | nd              |
| 12    | L4     | CsOAc | 2a6         | 35              | 50:50           |
| 13    | L5     | CsOAc | 2a6         | 56              | 67:33           |
| 14    | L6     | CsOAc | 2a6         | 56              | 94:6            |
| 15    | L7     | CsOAc | 2a6         | 37              | 50:50           |
| 16    | L8     | CsOAc | 2a6         | 32              | 60:40           |
| 17    | L1     | KOAc  | 2a6         | 41              | 89:11           |
| 18    | L1     | CsOAc | 2a6         | 94              | 95:5            |

*All reactions were conducted with 1a (1.0 equiv, 0.2 mmol), phenylboron 2 (3.0 equiv, 0.6 mmol), Pd(OAc)2 (5 mol %), L1-L6 (10 mol %), or L7-L8 (5 mol %) and base (2.0 equiv, 0.4 mmol) in THF (2.0 mL) at 110°C for 3 h. Determined by GC analysis using dodecane as an internal standard.

RESULTS AND DISCUSSION
Reaction Conditions Development

We began our investigation by studying the coupling of ortho-vinyl bromobenzene 1a and various phenylboron reagents 2a, and some representative results are listed in Scheme 1. With phenylboronic acid 2a1 as the coupling partner, the expected triphenyl substituted olefin 3aa was obtained in 56% reaction yield, but a significant amount of the direct coupling product 4aa was formed, along with some side products from the dimerization of 1a (entry 1). Screening of ligands, solvents, or bases failed to improve the migration efficiency. We speculated
that the arylboron reagent should have its reactivity in a reasonable zone (Lennox and Lloyd-Jones, 2014; Tobisu and Chatani, 2009), allowing for the completion of the palladium migration process prior to the subsequent coupling step, meantime keeping a faster Suzuki-Miyaura coupling with the generated alkenylpalladium species over the self-Heck reaction. Therefore, a variety of other organoboron types were evaluated (entries 2–9), including triphenylboroxine (2a9), potassium trifluoroborate salt (2a9), and different boronate esters (2a2–2a9). Triphenylboroxine 2a2 gave a comparable result, but the coupling reaction was almost shut down with potassium trifluoroborate 2a3 where the dimethenization of 1a became the major reaction pathway. Pinacol boronate ester 2a4 gave excellent regioselectivity (3aa/4aa = 97:3) albeit in a low reaction yield, possibly due to its low reactivity. Slightly more reactive boronate esters with less sterically hindered protection could improve reaction yields with maintained high regioselectivities. However, catechol boronate ester 2a7 was too reactive, thus affording the direct coupling product 4aa as the major product. Six-membered boronate esters (2a8 and 2a9) could also give product 3aa in moderate yields and with high regioselectivities but failed to offer better results compared with the best five-membered one 2a6.

With boronate ester 2a6 as the coupling partner, further screening of different ligands (entries 10–16, and Table S1 for details) was carried out. Slight modifications by removing o-MeO substituents (L2), replacing them with Me substituents (L3), or moving them to the other positions (L4 and L5) led to a severe loss of catalyst activity, as well as the capability to control regioselectivity, further demonstrating the important beneficial effect enabled by the hemilabile o-MeO coordination (Wakioka et al., 2014). Other types of ligands could not improve this transformation, either. Bulky electron-rich dialkylbiaryl phosphine L6 gave a higher regioselectivity but a reduced yield of 3aa. The open-chain bisphosphine ligands (L7 and L8) afforded low yield of 3aa and poor regioselectivity. Base also played an important role in this reaction. Both yield of 3aa and regioselectivity were further enhanced by switching CsOAc to CsOPiv (entry 18, and Table S2 for details). A more thorough list of variable screening is given in the Supplemental Information (Tables S1–S3).

**Substrate Scope**

**Synthesis of Trisubstituted Olefins**

With the optimal reaction conditions identified, the generality of this reaction was then investigated. First, the coupling of various ortho-vinyl aromatic bromides 1 with aryl boronate esters 2a was carried out (Scheme 2). In general, very good reaction yields were observed for the substrates bearing substituents with different electronic and steric properties at the phenyl ring A. Replacement of the phenyl ring with a naphthyl (3ia) or pyridyl (3ja) group was also well accommodated. It is worth mentioning that the possible coordination of pyridine moiety with palladium catalyst did not affect this catalytic process, and an excellent reaction yield of 3ja (91%) was achieved.

Variation of the phenyl ring B was also examined. Methyl substitution at different positions of the phenyl ring was tested to explore the spatial effect on this reaction. Ortho-methyl substitution gave the best reaction yield, suggesting the steric hindrance from this methyl group prohibited the potential dimerization of 1. Electronic effect at this phenyl ring B was also evaluated with different substitutions installed to its para-position, and the electron-withdrawing groups showed a beneficial effect on the reaction. When the phenyl ring B was replaced by naphthyl group, sterically more hindered 1-naphthyl (3ta) substitution showed a higher reaction yield than 2-naphthyl (3sa) one, which was consistent with the above observations. Switching the phenyl group to heteroaromatic rings, like substituted pyridyl (3ua) and 2-thienyl (3va) groups, was also compatible for this reaction, giving 92% and 67% reaction yields, respectively. The aryl ring can also be replaced by alkyl (3wa and 3xa), cyano (3ya), and ester (3za) groups, affording the products in high reaction yields.

Next, the scope of arylboronates was examined. When ortho-methyl phenylboronate ester was applied, the reaction yield decreased a little to 60% due to steric effect (3ab). However, more sterically congested 2,6-dimethyl one could still offer a decent yield of 3ac (44%). Good to excellent reaction yields were obtained with boronate esters bearing an electron-withdrawing or electron-donating substitution at its para-position of the phenyl ring. Chemically reactive functional groups, such as aldehyde (3al), ketone (3am), and ester (3an), were well tolerated. Free amino group (3ao) and thioether (3ap), which can frequently deactivate palladium catalyst owing to their strong coordination with palladium, were also compatible. In search for wide application of our palladium-catalyzed transformation in material science, the examples with Cl (3aq) and TMS (3ar) substitutions offered useful handles for their future incorporation to functional material molecules (Siamaki et al., 2011; Carsten et al., 2011).
The introduction of polycyclic aromatic moiety to a molecule can quickly expand the existing π-extended system, which is often of great importance for enhanced electronic and photonic performance (Itami et al., 2005). Therefore, a variety of aryl boronate esters bearing commonly used polycyclic aromatic rings (Scheme 3), including naphthyl (6aa, 6ab), phenanthryl (6ac), anthryl (6ad), triphenylenyl (6ae), and pyrenyl (6af) groups, were examined in the coupling with ortho-vinyl bromobenzene 1a. All reactions proceeded quite well with good to excellent isolated yields. The structure of 6af was further confirmed by X-ray crystallography.

Heteroaromatic rings are another family of substructures with wide existence in material molecules (Li et al., 2010). Although the coupling with heteroarylboron reagents is a straightforward way to install these important subunits, the strong coordinating capability of hetero atoms to palladium center may raise potential

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**Scheme 2. Coupling of ortho-Vinyl Aromatic Bromides with Aryl Boronate Esters**

All reactions were conducted with substrate 1 (1.0 equiv, 0.3 mmol), phenylboronate ester 2a (3.0 equiv, 0.9 mmol), Pd(OAc)$_2$ (5 mol%), L1 (10 mol%), and CsOPiv (2.0 equiv, 0.6 mmol) in THF (3 mL) at 110°C for 3 h.
concerns (Billingsley et al., 2006; Billingsley and Buchwald, 2007). To our delight, a wide range of heteroaromatic rings (Scheme 3), including furyl (6ag), benzofuryl (6ah), thienyl (6ai, 6aj), benzothiophenyl (6ak), thieno[3,2-b]thienyl (6al), pyridyl (6am), pyrazolyl (6an), quinolyl (6ao), indolyl (6ap), pyrimidyl (6aq), and carbazolyl (6ar), were successfully assembled in good to excellent yields, further demonstrating the potential of this method for material science.

**Synthesis of Multisubstituted 1,3-Dienes**

Encouraged by the above success in preparing trisubstituted olefins, we envision that the coupling reaction with arylethenyl boron reagents would lead to the generation of stereodefined multisubstituted 1,3-dienes. A number of arylethenyl boron reagents are commercially available, and several stereoselective synthetic methods were developed, which laid a firm base for this strategy (Yoshii et al., 2019). The optimized conditions used in the above coupling with arylboronate esters were also suitable for the arylethenyl boron esters. Further screening of the reaction conditions led to the use of boronate pinacol ester as the best choice. In addition, the reaction could go to completion with a decreased catalyst loading (2.5 mol %), a lower reaction temperature (70°C), and a shorter reaction time (1 h).

By employing the above newly optimized reactions, the reaction scope was examined (Scheme 4). Unlike the reactions with arylboronate esters, variation on ortho-vinyl arylbromides 1 showed marginal effect on the couplings with phenylethenyl boronate pinacol ester. Excellent yields were achieved in all cases when substitutions with different steric and electronic profiles were introduced to either phenyl ring A or B. Replacement of phenyl ring B with 1-naphthenyl (8ta), 2-naphthenyl (8sa), or 2-thienyl (8va) group still maintained high reaction yield.

**Scheme 3. Coupling of ortho-Vinyl Bromobenzene 1a with Polycyclic Aromatic and Heteroaryl Boronate Esters**

All reactions were conducted with substrate 1a (1.0 equiv, 0.3 mmol), (hetero)arylboronate 5 (3.0 equiv, 0.9 mmol), Pd(OAc)2 (5 mol %), P(2-MeO-Ph)3 (10 mol %), and CsOPiv (2.0 equiv, 0.6 mmol) in THF (3 mL) at 110°C for 3 h (unless otherwise noted). *Pinacol esters were used instead of glycol ester.
A variety of E-arylethenyl boronates with different substitutions at the para-position of the phenyl ring were evaluated. Both electron-withdrawing and -donating groups gave the desired (E)-1,3-dienes in excellent yields (8ab–8af). (Z)-phenylethenyl boronate pinacol ester led to (Z)-1,3-diene as the predominant product (8ag), along with some (E)-1,3-diene due to the partial isomerization of its double bond during the reaction process. Aryl substitutions can also be replaced by various alkyl groups (8ah and 8ai), and slightly lower yields were observed with sterically more hindered cyclic alkenyl boronates (8aj-8al). The use of b,b-diaryl-substituted vinyl boronates can potentially generate stereodefined tetra-aryl substituted 1,3-dienes. Therefore, several stereodefined vinyl boronates, which were prepared according to our previous results (Hu et al., 2016), were applied in this transformation. Despite slightly decreased yields, likely due to the increased steric hindrance, the desired tetra-aryl substituted 1,3-dienes were produced in geometrically pure form (8qm, 8em, 8qn, and 8en), overcoming the synthetic challenges in the preparation of such single stereoisomers by traditional methods. The stereochemistry of the obtained products was further confirmed by the X-ray crystallography of diene 8ka.

Scheme 4. Coupling of ortho-Vinyl Aromatic Bromides with Alkenylboronate Esters
All reactions were conducted with substrate 1 (1.0 equiv, 0.3 mmol), arylethenyl boronate ester 7 (2.0 equiv, 0.6 mmol), Pd(OAc)2 (2.5 mol %), L1 (5 mol %), and CsOPiv (2.0 equiv, 0.6 mmol) in THF (3 mL) at 70°C.
Transformation of the Products and Gram Scale Synthesis

To demonstrate the practicality of this method, we illustrated some chemical transformations of the produced trisubstituted olefins, providing potentials to embody these subunits to the designed material molecules (Scheme 5A). The chloride in olefin 3aq offered a handle for versatile derivatization using palladium-catalyzed coupling reactions, like Miyaura borylation with (Bpin)$_2$ and Suzuki-Miyaura coupling with aryl- or alkenylboronates, which are widely used transformations in material science (Yu et al., 2017; Li et al., 2018; Wang et al., 2020). The CHO group also offers potential use in versatile functionalization. The aldehyde could be converted to diaminomaleonitrile-modified olefin 9d (Huang et al., 2017). Such a special imine derivative displayed photo- and mechano-responsive properties, further expanding the application of this method in the field of multi-responsive material. In addition, the compounds 9e and 9f with triphenylethylene skeleton, a kind of donor-π-acceptor fluorophores with color-tunable aggregation-induced

Scheme 5. Practicality Demonstrations
(A) Transformations of the obtained products.
(B) Gram-scale reactions.
emission (AIE) behaviors (Wen et al., 2016), were prepared from aldehyde 3al through Knoevenagel condensation and HWE olefination reaction, respectively. All these high-yielding transformations provide infinite potentials in commercial application for full-color displays.

The scalability of the reaction was also investigated with two representative examples (Scheme 5B). The coupling of ortho-vinyl bromobenzene 1a with arylboronate 2j produced the desired olefin 3ak in excellent yield (92%), similar to the small trial. It is also the case for the coupling of ortho-vinyl bromobenzene 1A with phenylethenylboronate 7a.

Proposed Reaction Mechanism
Although the mechanism of this reaction is not clear at this stage, a tentative catalytic cycle is proposed in Scheme 6. Initial oxidative addition of arylbromide to palladium(0) generates the intermediate II (step A), which may exchange its bromide anion with PivO⁻ (step B) to facilitate the following C-H activation step (step C). Instead of a second oxidative addition to form a palladium(IV) species, theoretical studies have revealed that a concerted metalation-deprotonation (CMD) mechanism would be energetically favored, in which carboxylates were often needed to act as an inner base (Cheng et al., 2014; Gorelsky et al., 2008). The generated five-membered palladacycle IV undergoes a formal proton transfer to render a net 1,4-palladium shift from the aryl to alkenyl position (step D) and then proceeds through the following Suzuki coupling sequences to afford the desired product VII (step E and F).

Application in Aggregation-Induced Emission Materials
AIE Characteristics
To shed light on the potential application of our methodology in material science, some obtained products with rotatable aryl rings were subjected to the AIE properties test according to the restriction of intramolecular motion (Mei et al., 2014, 2015). Since the first report by Tang and co-workers in 2001, AIE concept and phenomenon have attracted considerable research attention and created a variety of potential applications in various fields (Luo et al., 2001; An et al., 2002). Several AIE systems have been elaborately
designed and well studied, where multi-aryl-substituted olefins and 1,3-dienes represent two of the most effective structures (Kong et al., 2018; Yang et al., 2014; He et al., 2019).

Some of the obtained products exhibited a distinct AIE effect. Non-emission was observed in dilute solutions, whereas the solid states gave strong emission. To further confirm the AIE feature of these compounds, the photoluminescence (PL) was studied in THF and THF/water mixtures with varying water fractions ($f_w$). As shown in Figure 2, olefin 6af was negligibly emissive in dilute THF solution. However, the PL intensity was greatly enhanced in THF/water mixtures with $f_w > 70\%$, probably due to the formation of nanoaggregate, exhibiting typical AIE characteristics. Notably, the luminescence intensity achieved a maximum at 469 nm when water fraction reached 90\%. 1,3-Dienes also showed similar AIE behavior. The fluorescence intensity of 8na was about 5.0-fold higher in THF/water mixtures with $f_w > 90\%$ than in pure THF.
It is well known that structurally similar geometric isomers may exhibit different AIE properties. However, the accessibility of all corresponding isomers in pure form restricted such systematic studies. Our new method allowed for the convenient generation of various pure geometric isomers, and several pairs of multi-aryl substituted olefins and 1,3-dienes were prepared. Figure 3 listed the PL quantum yields (PLQY, $\Phi_F$) of these geometric isomers in solid states (for further details, see Table S4). $E$-TriPE-F (3na) and $E$-TriPE-Me (3ma) showed higher $\Phi_F$ (12.0% and 20.8%, respectively) than those of $Z$-TriPE-F (3ga, $\Phi_F = 0.1\%$) and $Z$-TriPE-Me (3ca, $\Phi_F = 0.1\%$). These results suggest that rigidification of the $E$-isomers is higher than that of $Z$-ones (Mei et al., 2014). Similar phenomena were also observed for 1,3-dienes. Compared with 3Z-TPBDE (8ag, $\Phi_F = 3.1\%$) and 1Z-TPBDE-F (8ga, $\Phi_F = 12.0\%$), 3E-TPBDE (8aa, $\Phi_F = 23.0\%$) and 1E-TPBDE-F (8na, $\Phi_F = 41.5\%$) exhibited significantly enhanced $\Phi_F$. These results indicated that the geometry of double bond significantly affects the photophysical properties in solid state. Therefore, our synthetic methodology provided a powerful tool for the discovery of advanced material through precise control of the double bond geometry.

**Conclusion**

We have developed an efficient Suzuki-Miyaura coupling through a controllable 1,4-palladium migration process for the stereospecific synthesis of multisubstituted olefins and 1,3-dienes. A precise reactivity balance of the used organoboronates played a vital role in this process. The practicality of this method was demonstrated by the excellent capability and flexibility in stereochemical control, broad substrate scope, excellent functional
group tolerance, as well as versatile conversion with obtained products and easy scalability. The power of this method is also highlighted by the AIE feature studies of some obtained products. Several pairs of pure geometrical isomers were prepared and showed significant differences in photoluminescent quantum yield values.

Limitations of the Study
All ortho-vinyl aromatic bromides used in the current 1,4-palladium migration/Suzuki-Miyaura coupling sequence were terminal alkenes. Effort to use trisubstituted olefins as starting material is unsuccessful, and only a trace amount of desired product can be observed.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

DATA AND CODE AVAILABILITY
The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under accession number CCDC: 1965806 (6af) and 1965885 (8ka). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100966.

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AUTHOR CONTRIBUTIONS
M.-Y.L. and T.-J.H. performed the reaction optimization. M.-Y.L. investigated the scope of the substrate. P.H. invested the AIE behavior of the obtained products. D.W. and G.Z. prepared some starting materials. A.Q. and B.Z.T. directed the AIE studies. G.-Q.L. and C.-G.F. directed the project and wrote the manuscript with input from all authors. All authors analyzed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

Suzuki-Miyaura Coupling Enabled
by Aryl to Vinyl 1,4-Palladium Migration

Meng-Yao Li, Pengbo Han, Tian-Jiao Hu, Dong Wei, Ge Zhang, Anjun Qin, Chen-Guo Feng, Ben Zhong Tang, and Guo-Qiang Lin
More reaction condition optimization details:

Table S1. The effect of ligand, related to Scheme 1.

| Entry | Ligand | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> | Entry | Ligand | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> |
|-------|--------|-----------------------------|-----------------------------|-------|--------|-----------------------------|-----------------------------|
| 1     | L1     | 45                          | 60:40                       | 10    | L7     | 39                          | 90:10                       |
| 2     | L2     | 35                          | 60:40                       | 11    | L8     | 40                          | 50:50                       |
| 3     | L3     | 25                          | 50:50                       | 12    | L9     | 36                          | 50:50                       |
| 4     | L4     | 65                          | 93:7                        | 13    | L10    | 29                          | 50:50                       |
| 5     | L5     | 27                          | 96:4                        | 14    | L11    | 79                          | 75:25                       |
| 6     | L6     | 75                          | 84:16                       | 15    | L12    | 54                          | 83:17                       |

<sup>a</sup> Reactions conditions: 1a (1.0 equiv, 0.2 mmol), phenylboron 2a<sub>6</sub> (3.0 equiv, 0.6 mmol) Pd(OAc)<sub>2</sub> (5 mol %), L1-L7 (10 mol %) or L8-L12 (5 mol %), and CsOAc (2.0 equiv, 0.4 mmol) in THF (2.0 mL) at 110 °C for 3 h. <sup>b,c</sup> Determined by GC analysis using dodecane as an internal standard.
Table S2. The effect of solvent, related to Scheme 1.

| Entry<sup>a</sup> | Solvent | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> | Entry<sup>a</sup> | Solvent | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> |
|-------------------|---------|-----------------------------|-----------------------------|-------------------|---------|-----------------------------|-----------------------------|
| 1                 | THF     | 79                          | 93.7                        | 8                 | DMF     | 46                          | 92.8                        |
| 2                 | 2-Me-THF| 40                          | 89:11                       | 9                 | CH₃CN   | 66                          | 88:14                       |
| 3                 | Dioxane | 45                          | 90:10                       | 10                | DCE     | 21                          | 75:25                       |
| 4                 | DME     | 14                          | 66:34                       | 11                | EA      | 66                          | 90:10                       |
| 5                 | TBME    | 51                          | 50:50                       | 12                | Toluene | 14                          | 80:20                       |
| 6                 | PhOMe   | 47                          | 50:50                       | 13                | Hexane  | 45                          | 80:20                       |
| 7                 | Et₂O    | 67                          | 80:20                       | 14                | EtOH    | 31                          | 83:17                       |

<sup>a</sup> Reactions conditions: 1a (1.0 equiv, 0.2 mmol), phenylboron 2a₈ (3.0 equiv, 0.6 mmol), Pd(OAc)<sub>2</sub> (5 mol %), P(2-MeO-C₆H₄)₃ (10 mol %) and CsOAc (2.0 equiv, 0.4 mmol) in solvent (2.0 mL) at 110 °C for 3 h unless otherwise noted.<sup>b,c</sup> Determined by GC analysis using dodecane as an internal standard.

Table S3. The effect of base, related to Scheme 1.

| Entry<sup>a</sup> | Base   | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> | Entry<sup>a</sup> | Base   | Yield of 3aa (%)<sup>b</sup> | Ratio of 3aa/4aa<sup>c</sup> |
|-------------------|--------|-----------------------------|-----------------------------|-------------------|--------|-----------------------------|-----------------------------|
| 1                 | LiOAc  | 3                           | nd                          | 10                | KF     | 38                          | 66:34                       |
| 2                 | NH₄OAc | 3                           | nd                          | 11                | Na₂CO₃ | 20                          | 66:34                       |
| 3                 | KOAc   | 41                          | 89:11                       | 12                | K₂CO₃  | 30                          | 50:50                       |
| 4                 | CsOAc  | 79                          | 93:7                        | 13                | BaCO₃  | Trace                       | nd                          |
| 5                 | AgOAc  | Trace                       | nd                          | 14                | NaHCO₃ | 3                           | nd                          |
| 6                 | Cs₂CO₃| Trace                       | nd                          | 15                | KOH    | Trace                       | nd                          |
| 7                 | CsF    | 32                          | 50:50                       | 16                | KO'Bu  | Trace                       | nd                          |
| 8                 | CsOPiv | 94                          | 95:5                        | 17                | K₃PO₄ | 6                           | 14:86                       |
| 9                 | CF₃COOCs| Trace                     | nd                          | 18                | LiOH   | 14                          | 17:83                       |

<sup>a</sup> Reactions conditions: 1a (1.0 equiv, 0.2 mmol), phenylboron 2a₈ (3.0 equiv, 0.6 mmol), Pd(OAc)<sub>2</sub> (5 mol %), P(2-MeO-C₆H₄)₃ (10 mol %) and base (2.0 equiv, 0.4 mmol) in THF (2.0 mL) at 110 °C for 3 h unless otherwise noted.<sup>b,c</sup> Determined by GC analysis using dodecane as an internal standard.
Supplemental Figures for NMR spectrums:

Figure S1. $^1$H NMR spectrum of substrate 1f, related to Scheme 2.

Figure S2. $^{13}$C NMR spectrum of substrate 1f, related to Scheme 2.
**Figure S3.** $^1$H NMR spectrum of substrate 1A, related to Scheme 2.

**Figure S4.** $^{13}$C NMR spectrum of substrate 1A, related to Scheme 2.
Figure S5. $^{19}$F NMR spectrum of substrate 1A, related to Scheme 2.

Figure S6. $^1$H NMR spectrum of substrate 1B, related to Scheme 2.
Figure S7. $^{13}$C NMR spectrum of substrate 1B, related to Scheme 2.

Figure S8. $^{19}$F NMR spectrum of substrate 1B, related to Scheme 2.
Figure S9. $^1$H NMR spectrum of substrate 2i, related to Scheme 2.

Figure S10. $^{13}$C NMR spectrum of substrate 2i, related to Scheme 2.
Figure S11. $^1$H NMR spectrum of substrate 2j, related to Scheme 2.

Figure S12. $^{13}$C NMR spectrum of substrate 2j, related to Scheme 2.
Figure S13. $^1$H NMR spectrum of substrate 2k, related to Scheme 2.

Figure S14. $^{13}$C NMR spectrum of substrate 2k, related to Scheme 2.
Figure S15. $^1$H NMR spectrum of substrate 2m, related to Scheme 2.

Figure S16. $^{13}$C NMR spectrum of substrate 2m, related to Scheme 2.
Figure S17. $^1$H NMR spectrum of substrate 2p, related to Scheme 2.

Figure S18. $^{13}$C NMR spectrum of substrate 2p, related to Scheme 2.
Figure S19. $^1$H NMR spectrum of substrate $2r$, related to Scheme 2.

Figure S20. $^{13}$C NMR spectrum of substrate $2r$, related to Scheme 2.
Figure S21. $^1H$ NMR spectrum of substrate 5d, related to Scheme 2.

Figure S22. $^{13}C$ NMR spectrum of substrate 5d, related to Scheme 2.
Figure S23. $^1$H NMR spectrum of substrate 5e, related to Scheme 2.

Figure S24. $^{13}$C NMR spectrum of substrate 5e, related to Scheme 2.
Figure S25. $^1$H NMR spectrum of substrate 5f, related to Scheme 2.

Figure S26. $^{13}$C NMR spectrum of substrate 5f, related to Scheme 2.
Figure S27. $^1$H NMR spectrum of substrate 5i, related to Scheme 2.

Figure S28. $^{13}$C NMR spectrum of substrate 5i, related to Scheme 2.
Figure S29. $^1$H NMR spectrum of substrate 5k, related to Scheme 2.

Figure S30. $^{13}$C NMR spectrum of substrate 5k, related to Scheme 2.
Figure S31. $^1$H NMR spectrum of substrate 5I, related to Scheme 2.

Figure S32. $^{13}$C NMR spectrum of substrate 5I, related to Scheme 2.
Figure S33. $^1$H NMR spectrum of product 3aa, related to Scheme 2.

Figure S34. $^1$H NMR spectrum of product 4aa, related to Scheme 2.
Figure S35. $^1$H NMR spectrum of product 3ba, related to Scheme 2.

Figure S36. $^1$H NMR spectrum of product 3ca, related to Scheme 2.
Figure S37. $^1$H NMR spectrum of product 3da, related to Scheme 2.

Figure S38. $^1$H NMR spectrum of product 3ea, related to Scheme 2.
Figure S39. $^1$H NMR spectrum of product 3fa, related to Scheme 2.

Figure S40. $^{13}$C NMR spectrum of product 3fa, related to Scheme 2.
Figure S41. $^1$H NMR spectrum of product 3ga, related to Scheme 2.

Figure S42. $^1$H NMR spectrum of product 3ha, related to Scheme 2.
Figure S43. $^1$H NMR spectrum of product 3ia, related to Scheme 2.

Figure S44. $^{13}$C NMR spectrum of product 3ia, related to Scheme 2.
Figure S45. $^1$H NMR spectrum of product 3ja, related to Scheme 2.

Figure S46. $^{13}$C NMR spectrum of product 3ja, related to Scheme 2.
Figure S47. $^1$H NMR spectrum of product 3ka, related to Scheme 2.

Figure S48. $^1$H NMR spectrum of product 3la, related to Scheme 2.
Figure S49. $^1$H NMR spectrum of product 3ma, related to Scheme 2.

Figure S50. $^1$H NMR spectrum of product 3na, related to Scheme 2.
Figure S51. $^1$H NMR spectrum of product 3oa, related to Scheme 2.

Figure S52. $^1$H NMR spectrum of product 3pa, related to Scheme 2.
**Figure S53.** $^1$H NMR spectrum of product 3qa, related to Scheme 2.

**Figure S54.** $^1$H NMR spectrum of product 3ra, related to Scheme 2.
Figure S55. $^{13}$C NMR spectrum of product 3ra, related to Scheme 2.

Figure S56. $^1$H NMR spectrum of product 3sa, related to Scheme 2.
Figure S57. $^{13}$C NMR spectrum of product 3sa, related to Scheme 2.

Figure S58. $^1$H NMR spectrum of product 3ta, related to Scheme 2.
Figure S59. $^1$H NMR spectrum of product 3ua, related to Scheme 2.

Figure S60. $^{13}$C NMR spectrum of product 3ua, related to Scheme 2.
Figure S61. $^1$H NMR spectrum of product 3va, related to Scheme 2.

Figure S62. $^{13}$C NMR spectrum of product 3va, related to Scheme 2.
Figure S63. $^1$H NMR spectrum of product 3wa, related to Scheme 2.

Figure S64. $^{13}$C NMR spectrum of product 3wa, related to Scheme 2.
Figure S65. $^1$H NMR spectrum of product 3xa, related to Scheme 2.

Figure S66. $^{13}$C NMR spectrum of product 3xa, related to Scheme 2.
Figure S67. $^1$H NMR spectrum of product 3ya, related to Scheme 2.

Figure S68. $^1$H NMR spectrum of product 3za, related to Scheme 2.
Figure S69. $^1$H NMR spectrum of product 3ab, related to Scheme 2.

Figure S70. $^1$H NMR spectrum of product 3ac, related to Scheme 2.
Figure S71. $^{13}$C NMR spectrum of product 3ac, related to Scheme 2.

Figure S72. $^1$H NMR spectrum of product 3ad, related to Scheme 2.
Figure S73. $^1$H NMR spectrum of product 3ae, related to Scheme 2.

Figure S74. $^1$H NMR spectrum of product 3af, related to Scheme 2.
Figure S74. $^1$H NMR spectrum of product 3ag, related to Scheme 2.

Figure S76. $^1$H NMR spectrum of product 3ah, related to Scheme 2.
Figure S77. $^1$H NMR spectrum of product 3ai, related to Scheme 2.

Figure S78. $^1$H NMR spectrum of product 3aj, related to Scheme 2.
Figure S79. $^{13}$C NMR spectrum of product 3aj, related to Scheme 2.

Figure S80. $^1$H NMR spectrum of product 3ak, related to Scheme 2.
Figure S81. $^{13}$C NMR spectrum of product 3ak, related to Scheme 2.

Figure S82. $^1$H NMR spectrum of product 3al, related to Scheme 2.
Figure S83. $^{13}$C NMR spectrum of product 3al, related to Scheme 2.

Figure S84. $^1$H NMR spectrum of product 3am, related to Scheme 2.
Figure S85. $^{13}$C NMR spectrum of product 3am, related to Scheme 2.

Figure S86. $^1$H NMR spectrum of product 3an, related to Scheme 2.
Figure S87. $^{13}$C NMR spectrum of product 3an, related to Scheme 2.

Figure S88. $^1$H NMR spectrum of product 3ao, related to Scheme 2.
Figure S89. $^1$H NMR spectrum of product 3ap, related to Scheme 2.

Figure S90. $^1$H NMR spectrum of product 3aq, related to Scheme 2.
Figure S91. $^1$H NMR spectrum of product 3ar, related to Scheme 2.

Figure S92. $^{13}$C NMR spectrum of product 3ar, related to Scheme 2.
Figure S93. $^1$H NMR spectrum of product 6aa, related to Scheme 3.

Figure S94. $^1$H NMR spectrum of product 6ab, related to Scheme 3.
Figure S95. $^1$H NMR spectrum of product 6ac, related to Scheme 3.

Figure S96. $^{13}$C NMR spectrum of product 6ac, related to Scheme 3.
Figure S97. $^1$H NMR spectrum of product 6ad, related to Scheme 3.

Figure S98. $^{13}$C NMR spectrum of product 6ad, related to Scheme 3.
Figure S99. $^1$H NMR spectrum of product 6ae, related to Scheme 3.

Figure S100. $^{13}$C NMR spectrum of product 6ae, related to Scheme 3.
Figure S101. $^1$H NMR spectrum of product 6af, related to Scheme 3.

Figure S102. $^{13}$C NMR spectrum of product 6af, related to Scheme 3.
Figure S103. $^1$H NMR spectrum of product 6ag, related to Scheme 3.

Figure S104. $^{13}$C NMR spectrum of product 6ag, related to Scheme 3.
Figure S105. $^1$H NMR spectrum of product 6ah, related to Scheme 3.

Figure S106. $^{13}$C NMR spectrum of product 6ah, related to Scheme 3.
Figure S107. $^1$H NMR spectrum of product 6ai, related to Scheme 3.

Figure S108. $^{13}$C NMR spectrum of product 6ai, related to Scheme 3.
Figure S109. $^1$H NMR spectrum of product 6aj, related to Scheme 3.

Figure S110. $^{13}$C NMR spectrum of product 6aj, related to Scheme 3.
Figure S111. $^1$H NMR spectrum of product 6ak, related to Scheme 3.

Figure S112. $^{13}$C NMR spectrum of product 6ak, related to Scheme 3.
Figure S113. $^1$H NMR spectrum of product 6al, related to Scheme 3.

Figure S114. $^{13}$C NMR spectrum of product 6al, related to Scheme 3.
Figure S115. $^1$H NMR spectrum of product 6am, related to Scheme 3.

Figure S116. $^1$H NMR spectrum of product 6an, related to Scheme 3.
Figure S117. $^{13}$C NMR spectrum of product 6an, related to Scheme 3.

Figure S118. $^1$H NMR spectrum of product 6ao, related to Scheme 3.
Figure S119. $^1$H NMR spectrum of product 6ap, related to Scheme 3.

Figure S120. $^{13}$C NMR spectrum of product 6ap, related to Scheme 3.
Figure S121. \(^1\)H NMR spectrum of product 6aq, related to Scheme 3.

Figure S122. \(^{13}\)C NMR spectrum of product 6aq, related to Scheme 3.
Figure S123. $^1$H NMR spectrum of product 6ar, related to Scheme 3.

Figure S124. $^{13}$C NMR spectrum of product 6ar, related to Scheme 3.
Figure S125. $^1$H NMR spectrum of product 8aa, related to Scheme 4.

Figure S126. $^1$H NMR spectrum of product 8ba, related to Scheme 4.
Figure S127. $^{13}$C NMR spectrum of product 8ba, related to Scheme 4.

Figure S128. $^1$H NMR spectrum of product 8ca, related to Scheme 4.
Figure S129. $^{13}$C NMR spectrum of product 8ca, related to Scheme 4.

Figure S130. $^1$H NMR spectrum of product 8da, related to Scheme 4.
Figure S131. $^{13}$C NMR spectrum of product 8da, related to Scheme 4.

Figure S132. $^{19}$F NMR spectrum of product 8da, related to Scheme 4.
Figure S133. $^1$H NMR spectrum of product 8ea, related to Scheme 4.

Figure S134. $^{13}$C NMR spectrum of product 8ea, related to Scheme 4.
Figure S135. $^1$H NMR spectrum of product 8ga, related to Scheme 4.

Figure S136. $^{13}$C NMR spectrum of product 8ga, related to Scheme 4.
Figure S137. $^{19}$F NMR spectrum of product 8ga, related to Scheme 4.

Figure S138. $^1$H NMR spectrum of product 8ha, related to Scheme 4.
Figure S139. $^{13}$C NMR spectrum of product 8ha, related to Scheme 4.

Figure S140. $^1$H NMR spectrum of product 8ka, related to Scheme 4.
**Figure S141.** $^{13}$C NMR spectrum of product 8ka, related to Scheme 4.

**Figure S142.** $^1$H NMR spectrum of product 8la, related to Scheme 4.
Figure S143. $^{13}$C NMR spectrum of product 8la, related to Scheme 4.

Figure S144. $^1$H NMR spectrum of product 8ma, related to Scheme 4.
Figure S145. $^{13}$C NMR spectrum of product 8ma, related to Scheme 4.

Figure S146. $^1$H NMR spectrum of product 8na, related to Scheme 4.
Figure S147. $^{13}$C NMR spectrum of product 8na, related to Scheme 4.

Figure S148. $^{19}$F NMR spectrum of product 8na, related to Scheme 4.
Figure S149. $^1$H NMR spectrum of product 8oa, related to Scheme 4.

Figure S150. $^{13}$C NMR spectrum of product 8oa, related to Scheme 4.
Figure S151. $^1$H NMR spectrum of product 8pa, related to Scheme 4.

Figure S152. $^{13}$C NMR spectrum of product 8pa, related to Scheme 4.
Figure S153. $^{19}$F NMR spectrum of product 8pa, related to Scheme 4.

Figure S154. $^1$H NMR spectrum of product 8qa, related to Scheme 4.
**Figure S155.** $^{13}$C NMR spectrum of product 8qa, related to Scheme 4.

**Figure S156.** $^1$H NMR spectrum of product 8sa, related to Scheme 4.
Figure S157. $^{13}$C NMR spectrum of product 8sa, related to Scheme 4.

Figure S158. $^1$H NMR spectrum of product 8ta, related to Scheme 4.
Figure S159. $^{13}$C NMR spectrum of product 8ta, related to Scheme 4.

Figure S160. $^1$H NMR spectrum of product 8va, related to Scheme 4.
Figure S161. $^{13}$C NMR spectrum of product 8va, related to Scheme 4.

Figure S162. $^1$H NMR spectrum of product 8Aa, related to Scheme 4.
Figure S163. $^{13}$C NMR spectrum of product 8Aa, related to Scheme 4.

Figure S164. $^{19}$F NMR spectrum of product 8Aa, related to Scheme 4.
Figure S165. $^1$H NMR spectrum of product 8Ba, related to Scheme 4.

Figure S166. $^{13}$C NMR spectrum of product 8Ba, related to Scheme 4.
Figure S167. $^{19}$F NMR spectrum of product 8Ba, related to Scheme 4.

Figure S168. $^1$H NMR spectrum of product 8Ca, related to Scheme 4.
Figure S169. $^{13}$C NMR spectrum of product 8Ca, related to Scheme 4.

Figure S170. $^{19}$F NMR spectrum of product 8Ca, related to Scheme 4.
Figure S171. $^1$H NMR spectrum of product 8ab, related to Scheme 4.

Figure S172. $^{13}$C NMR spectrum of product 8ab, related to Scheme 4.
Figure S173. $^1$H NMR spectrum of product 8ac, related to Scheme 4.

Figure S174. $^{13}$C NMR spectrum of product 8ac, related to Scheme 4.
Figure S175. $^1$H NMR spectrum of product 8ad, related to Scheme 4.

Figure S176. $^{13}$C NMR spectrum of product 8ad, related to Scheme 4.
Figure S177. $^{19}$F NMR spectrum of product 8ad, related to Scheme 4.

Figure S178. $^1$H NMR spectrum of product 8ae, related to Scheme 4.
Figure S179. $^{13}$C NMR spectrum of product 8ae, related to Scheme 4.

Figure S180. $^{19}$F NMR spectrum of product 8ae, related to Scheme 4.
Figure S181. $^1$H NMR spectrum of product 8af, related to Scheme 4.

Figure S182. $^{13}$C NMR spectrum of product 8af, related to Scheme 4.
Figure S183. $^1$H NMR spectrum of product 8ag, related to Scheme 4.

Figure S184. $^{13}$C NMR spectrum of product 8ag, related to Scheme 4.
Figure S185. $^1$H NMR spectrum of product 8ah, related to Scheme 4.

Figure S186. $^{13}$C NMR spectrum of product 8ah, related to Scheme 4.
**Figure S187.** $^1$H NMR spectrum of product 8ai, related to Scheme 4.

**Figure S188.** $^{13}$C NMR spectrum of product 8ai, related to Scheme 4.
Figure S189. $^1$H NMR spectrum of product 8aj, related to Scheme 4.

Figure S190. $^{13}$C NMR spectrum of product 8aj, related to Scheme 4.
Figure S191. $^1$H NMR spectrum of product 8ak, related to Scheme 4.

Figure S192. $^{13}$C NMR spectrum of product 8ak, related to Scheme 4.
Figure S193. $^1$H NMR spectrum of product 8al, related to Scheme 4.

Figure S194. $^{13}$C NMR spectrum of product 8al, related to Scheme 4.
Figure S195. $^1$H NMR spectrum of product 8qm, related to Scheme 4.

Figure S196. $^{13}$C NMR spectrum of product 8qm, related to Scheme 4.
Figure S197. $^{19}$F NMR spectrum of product 8qm, related to Scheme 4.

Figure S198. $^1$H NMR spectrum of product 8em, related to Scheme 4.
Figure S199. $^{13}$C NMR spectrum of product 8em, related to Scheme 4.

Figure S200. $^{19}$F NMR spectrum of product 8em, related to Scheme 4.
**Figure S201.** $^1$H NMR spectrum of product 8qn, related to Scheme 4.

**Figure S202.** $^{13}$C NMR spectrum of product 8qn, related to Scheme 4.
Figure S203. $^{19}$F NMR spectrum of product 8qn, related to Scheme 4.

Figure S204. $^1$H NMR spectrum of product 8en, related to Scheme 4.
Figure S205. $^{13}$C NMR spectrum of product 8en, related to Scheme 4.

Figure S206. $^{19}$F NMR spectrum of product 8en, related to Scheme 4.
Figure S207. $^1$H NMR spectrum of product 9a, related to Scheme 5.

Figure S208. $^{13}$C NMR spectrum of product 9a, related to Scheme 5.
Figure S209. $^1$H NMR spectrum of product 9b, related to Scheme 5.

Figure S210. $^1$H NMR spectrum of product 9c, related to Scheme 5.
Figure S211. $^{13}$C NMR spectrum of product 9c, related to Scheme 5.

Figure S212. $^1$H NMR spectrum of product 9d, related to Scheme 5.
Figure S213. $^{13}$C NMR spectrum of product 9d, related to Scheme 5.

Figure S214. $^1$H NMR spectrum of product 9e, related to Scheme 5.
Figure S215. $^1$H NMR spectrum of product 9f, related to Scheme 5.
Transparent Methods

1. General information

All reactions were carried out with standard Schlenk techniques under argon atmosphere. All the solvents were dried using standard procedure and distilled before use. All commercially available chemical resources were used as received, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) supplied by Yantai Jiangyou Silicon Material Company (China). Visualization was accomplished with UV light or basic aqueous potassium permanganate (KMnO$_4$). Chromatography was achieved using forced flow (flash chromatography) of the indicated solvent system on 300-400 mesh silica gel (Silicycle flash F60) unless otherwise noted. Nuclear Magnetic Resonance (NMR) spectra were acquired on Agilent 400 or Bruker 400 instrument operating at 400, 100 and 376 MHz for $^1$H, $^{13}$C and $^{19}$F, respectively. Chemical shifts are reported in δ ppm referenced to an internal SiMe$_4$ standard (TMS: δ 0.000 ppm) for $^1$H NMR, chloroform-d (δ 77.16) for $^{13}$C NMR unless otherwise noted. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quintet = quint, heptet = hept, m = multiplet, br = broad resonance. High-resolution mass spectra (HRMS) and Low resolution mass spectra (LRMS) were acquired through the National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry (CAS) and determined on a Waters Micromass GCT Premie spectrometer. Solid state luminescent quantum yield measurements for olefins and 1,3-dienes were performed with Hamamatsu absolute PL quantum yield spectrometer C11347 Quantaurus_QY. UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrophotometer and photoluminescence spectra were recorded on a Horiba Fluoromax-4 spectrofluorometer.

The ortho-vinyl arylbromides (1a-1e, 1g-1v, 1B) (Wei et al., 2019; Wei et al., 2018; Ryutaro Hayashi, 2018; Hu et al., 2018; Shen et al., 2017; Rossi et al., 2001), (hetero)aryl boronate esters (2a-2h, 2l-2o, 2q, 5a-5c, 5j, 5r) (Zhang et al., 2018; Carreira-Barral et al., 2018; Zhou et al., 2017; Ranjani and Nagarajan, 2017; Bello and Schmidt-Leithoff, 2012; Yu et al., 2010; Gómez-Blanco et al., 2009; Iwai et al., 2008; Stephen J. Baker, 2006; Burstein et al., 2005; Wong et al., 2002), diaryl-vinyl boronate esters (7h, 7i) (Hu et al., 2016) were prepared according to the literatures. Heteroaryl boronate esters (5g-5h, 5m-5q) and vinyl boronate esters (7a-7g) were purchased and used directly from commercial sources.

2. Synthesis of substrates

2.1. Preparation of ortho-vinyl arylbromides 1

Scheme S1. Synthesis of ortho-vinyl arylbromides 1, related to Scheme 2 and Scheme 4.

To a stirred mixture of triphenyl phosphonium salt (5.5 mmol) in THF (20 mL) was added $^t$BuLi (2 mL, 2.5 N...
in hexane, 5.0 mmol) dropwise at 0 °C under argon atmosphere. After 30 min, a solution of ortho-carbonyl arylbromides S1 (4.0 mmol) in THF (4 mL) was added to the yellowish mixture dropwise at the same temperature. After being stirred at room temperature for further 8 h, the reaction was quenched by adding H2O and ethyl acetate. The organic layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The residue was purified by chromatography on silica gel to afford product 1.

1-bromo-4,5-dimethoxy-2-(1-phenylvinyl)benzene (1f), white solid (92% yield). 1H NMR (400 MHz, CDCl3) δ 7.34-7.23 (m, 5H), 7.07 (s, 1H), 6.80 (s, 1H), 5.83 (d, J = 1.3 Hz, 1H), 5.27 (d, J = 1.1 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 149.01, 148.79, 148.34, 139.78, 134.84, 128.47, 127.88, 126.69, 116.20, 115.74, 114.24, 113.46, 56.33, 56.23 ppm; EI-MS m/z (%): 318 (M+); HRMS (EI): m/z Exact mass calcd for C16H15O2Br [M]+: 318.0255, found: 318.0264.

1-bromo-4-fluoro-2-(1-phenylvinyl)benzene (1A), colorless oil (95% yield). 1H NMR (400 MHz, CDCl3) δ 7.54 (dd, J = 8.8, 5.3 Hz, 1H), 7.39-7.20 (m, 5H), 7.06 (dd, J = 8.9, 3.0 Hz, 1H), 6.95 (td, J = 8.4, 3.1 Hz, 1H), 5.85 (s, 1H), 5.28 (s, 1H) ppm; 13C NMR (100 MHz, CDCl3) δ 161.94 (d, J = 247.6 Hz), 148.24 (d, J = 1.5 Hz), 144.57 (d, J = 8.0 Hz), 139.04, 134.29 (d, J = 8.0 Hz), 128.57, 128.11, 126.63, 118.73 (d, J = 22.5 Hz), 117.66 (d, J = 3.1 Hz), 116.70, 116.28 (d, J = 22.5 Hz) ppm; 19F NMR (376 MHz, CDCl3) δ -115.31 ppm; EI-MS m/z (%): 276 (M+); HRMS (EI): m/z Exact mass calcd for C14H9FBr [M]+: 275.9950, found: 275.9952.

1-bromo-4,5-difluoro-2-(1-phenylvinyl)benzene (1B), white solid (89% yield). 1H NMR (400 MHz, CDCl3) δ 7.43 (dd, J = 9.7, 7.5 Hz, 1H), 7.36-7.28 (m, 3H), 7.28-7.20 (m, 2H), 7.16 (dd, J = 10.5, 8.3 Hz, 1H), 5.85 (s, 1H), 5.27 (s, 1H) ppm; 13C NMR (100 MHz, CDCl3) δ 150.81 (dd, J = 12.8, 8.6 Hz), 148.30 (dd, J = 12.8, 5.9 Hz), 147.47, 139.53 (dd, J = 5.7, 4.2 Hz), 138.91, 128.62, 128.22, 126.59, 121.93 (d, J = 19.8 Hz), 120.00 (d, J = 17.5 Hz), 117.14, 117.07 (d, J = 3.4, 3.8 Hz) ppm; 19F NMR (376 MHz, CDCl3) δ -138.69, -136.47 ppm; EI-MS m/z (%): 294 (M+); HRMS (EI): m/z Exact mass calcd for C14H9F2Br [M]+: 293.9856, found: 293.9862.
2. Preparation of (hetero)aryl boronate esters 2

Scheme S2. Synthesis of (hetero)aryl boronic acid glycol ester substrates 2, related to Scheme 2.

To the stirring suspension of arylboronic acid S2 (40 mmol) and MgSO₄ (60 mmol) in CH₂Cl₂ (80 mL) was added glycol (44 mmol) at room temperature dropwise. Then the resulting mixture was allowed to stir at room temperature for further 4 h. The white solid was filtered through a pad of Celite and the filtrate was concentrated under reduced pressure to afford the crude product as a solid. The crude was recrystallized with CH₂Cl₂-hexane mixed-solvent system to afford the pure product.

2-(4-nitrophenyl)-1,3,2-dioxaborolane (2i), pale yellow solid (87% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, J = 8.6 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 4.44 (s, 4H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 150.10, 135.90, 122.70, 66.53 ppm; EI-MS m/z (%): 193 (M⁺); HRMS (EI): m/z Exact mass calcd for C₈H₆NO₂BO₄ [M⁺]: 192.0583, found: 192.0591.

4-(1,3,2-dioxaborolan-2-yl)-N,N-dimethylbenzamide (2j), white solid (92% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.95-7.67 (m, 2H), 7.56-7.33 (m, 2H), 4.40 (s, 4H), 3.04 (br, 6H) ppm; EI-MS m/z (%): 218 (M⁺); HRMS (EI): m/z Exact mass calcd for C₁₁H₁₃NO₂BO₃ [M⁺]: 217.1025, found: 217.1032.

2-(4-(methylsulfonyl)phenyl)-1,3,2-dioxaborolane (2k), white solid (95% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.28-7.60 (m, 4H), 4.43 (s, 4H), 3.07 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 142.90, 135.74, 126.49, 66.43, 44.43 ppm; EI-MS m/z (%): 226 (M⁺); HRMS (EI): m/z Exact mass calcd for C₉H₁₁NO₂SO₂BO₃ [M⁺]: 225.0507, found: 225.0513.

1-(4-(1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one (2m), white solid (88% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.92 (ddd, J = 13.4, 7.8, 3.6 Hz, 4H), 4.40 (s, 4H), 2.62 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 198.40, 139.17, 135.04, 127.42, 66.23, 26.77 ppm; EI-MS m/z (%): 190 (M⁺); HRMS (EI): m/z Exact mass calcd for C₁₀H₁₀NO₂BO₃ [M⁺]: 189.0838, found: 189.0836.
2-(4-(methylthio)phenyl)-1,3,2-dioxaborolane (2p), white solid (78% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.71 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 4.37 (s, 4H), 2.50 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.06, 135.27, 125.12, 66.15, 15.05 ppm; EI-MS m/z (%): 194 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_9$H$_{11}$BO$_2$S [M]+: 193.0609, found: 193.0611.

(4-(1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane (2r), colorless oil (97% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.9$ Hz, 2H), 7.55 (d, $J = 7.9$ Hz, 2H), 4.37 (s, 3H), 0.27 (s, 9H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.67, 134.04, 132.87, 66.15, -1.12 ppm; EI-MS m/z (%): 220 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{11}$H$_{17}$BO$_2$Si [M]+: 219.1127, found: 219.1136.

(4-(1,3,2-dioxaborolan-2-yl)phenyl)trimethylsilane (2r), colorless oil (97% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.78 (d, $J = 7.9$ Hz, 2H), 7.55 (d, $J = 7.9$ Hz, 2H), 4.37 (s, 3H), 0.27 (s, 9H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.67, 134.04, 132.87, 66.15, -1.12 ppm; EI-MS m/z (%): 220 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{11}$H$_{17}$BO$_2$Si [M]+: 219.1127, found: 219.1136.

2-(anthracen-9-yl)-1,3,2-dioxaborolane (5d), pale yellow solid (85% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.50 (s, 1H), 8.44 (d, $J = 8.6$ Hz, 2H), 8.00 (d, $J = 7.8$ Hz, 2H), 7.52-7.42 (m, 4H), 4.63 (s, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.18, 131.27, 130.04, 128.94, 128.73, 125.99, 125.12, 66.27 ppm; EI-MS m/z (%): 248 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{16}$H$_{13}$BO$_2$ [M]+: 247.1045, found: 247.1041.

2-(triphenylen-2-yl)-1,3,2-dioxaborolane (5e), white solid (90% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.15 (d, $J = 9.1$ Hz, 1H), 8.81-8.73 (m, 1H), 8.71-8.60 (m, 4H), 8.05 (dd, $J = 8.3, 1.3$ Hz, 1H), 7.66 (qd, $J = 4.1, 2.1$ Hz, 4H), 4.47 (s, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.79, 132.26, 130.79, 130.43, 129.91, 129.79, 129.64, 129.11, 128.70, 127.37, 127.32, 127.29, 127.59, 123.39, 123.31, 122.71, 66.29 ppm; EI-MS m/z (%): 298 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{20}$H$_{15}$BO$_2$ [M]+: 297.1201, found: 297.1200.

2-(pyren-1-yl)-1,3,2-dioxaborolane (5f), brown solid (80% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.05 (d, $J = 9.2$ Hz, 1H), 8.56 (d, $J = 7.7$ Hz, 1H), 8.27-8.10 (m, 5H), 8.07 (d, $J = 8.9$ Hz, 1H), 8.01 (t, $J = 7.6$ Hz, 1H), 4.56 (s, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.63, 134.24, 133.81, 131.23, 130.85, 128.87, 128.07, 127.96, 127.59, 125.92, 125.62, 125.48, 124.70, 124.55, 124.30, 66.21 ppm; EI-MS m/z (%): 272 (M$^+$); HRMS (EI):
m/z Exact mass calcd for C_{16}H_{18}BO_{2} [M]^{+}: 271.1045, found: 271.1046.

2-(thiophen-2-yl)-1,3,2-dioxaborolane (5i), white solid (80% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.67 (t, J = 4.4 Hz, 2H), 7.21 (dd, J = 4.5, 3.6 Hz, 1H), 4.38 (s, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 137.64, 132.86, 128.49, 66.29 ppm; EI-MS m/z (%): 154 (M\(^+\)); HRMS (EI): m/z Exact mass calcd for C_{6}H_{7}BO_{2}S [M]^{+}: 153.0296, found: 153.0289.

2-(benzo[b]thiophen-2-yl)-1,3,2-dioxaborolane (5k), white solid (90% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.94-7.84 (m, 3H), 7.43-7.30 (m, 2H), 4.42 (s, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.88, 140.51, 134.96, 125.61, 124.62, 124.32, 122.67, 66.43 ppm; EI-MS m/z (%): 204 (M\(^+\)); HRMS (EI): m/z Exact mass calcd for C_{10}H_{9}BO_{2}S [M]^{+}: 203.0453, found: 203.0455.

2-(thieno[3,2-b]thiophen-2-yl)-1,3,2-dioxaborolane (5l), gray solid (70% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (s, 1H), 7.51 (d, J = 5.3 Hz, 1H), 7.29 (d, J = 5.3 Hz, 1H), 4.40 (s, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 145.87, 140.96, 130.43, 129.39, 119.57, 66.34 ppm; EI-MS m/z (%): 210 (M\(^+\)); HRMS (EI): m/z Exact mass calcd for C_{8}H_{7}BO_{2}S [M]^{+}: 209.0017, found: 209.0012.

3. General procedure for synthesis tri-aryl substituted olefins 3 and 6

3.1. Synthesis of compounds 3aa-3za, 3ab-3ar, 6aa-6af, 6ai-6al, 6ar

Scheme S3. Synthesis of compounds 3aa-3za, 3ab-3ar, 6aa-6af, 6ai-6al, 6ar, related to Scheme 2 and Scheme 3

To the suspension of ortho-vinyl arylbromides 1 (0.30 mmol), (hetero)arylboronates esters 2 (0.90 mmol), Pd(OAc)\(_2\) (5 mol %), P(2-MeO-Ph)\(_3\) (10 mol %) and CsO\(_2\)Piv (0.60 mmol) was added THF (3.0 mL) under argon atmosphere. The mixture was stirred at 110 °C for 3 h. After being cooled down to room temperature, the reaction was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford pure product 3.
3.2. Synthesis of compounds 6ag-6ah, 6am-6aq

Scheme S4. Synthesis of compounds 6ag-6ah, 6am-6aq, related to Scheme 3

To the suspension of ortho-vinyl arylbromides 1 (0.30 mmol), (hetero)arylboron esters 5 (0.90 mmol), Pd(OAc)$_2$ (5 mol %), P(2-MeO-Ph)$_3$ (10 mol %) and CsOPiv (0.60 mmol) was added THF (3.0 mL) under argon atmosphere. The mixture was stirred at 110 °C for 3 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 6.

3.3. Characterization data of Compounds 3aa-3za, 3ab-3ar, 6aa-6ar, 4aa

ethene-1,1,2-triyltribenzene (3aa), white solid (88% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.25 (m, 8H), 7.23-7.18 (m, 2H), 7.16-7.07 (m, 3H), 7.05-6.99 (m, 2H), 6.96 (s, 1H) ppm; EI-MS m/z (%): 256 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

2-(1-phenylvinyl)-1,1'-biphenyl (4aa), Colorless oil; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.29 (m, 4H), 7.27-7.18 (m, 2H), 7.18-7.01 (m, 8H), 5.56 (d, $J = 1.3$ Hz, 1H), 5.18 (d, $J = 1.2$ Hz, 1H) ppm; EI-MS m/z (%): 256 (M$^+$). The data is consistent with the literature (Wang et al., 2017).
(Z)-(1-(m-tolyl)ethene-1,2-diyl)dibenzene (3ba), colorless oil (74% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.26 (m, 5H), 7.24-7.19 (m, 1H), 7.17-7.09 (m, 4H), 7.06-7.98 (m, 4H), 6.94 (s, 1H), 2.30 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Wen et al., 2017).

(Z)-(1-(p-tolyl)ethene-1,2-diyl)dibenzene (3ca), white solid (72% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.26 (m, 5H), 7.17-7.02 (m, 9H), 6.92 (s, 1H), 2.38 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Wen et al., 2017).

(Z)-(1-(4-(trifluoromethyl)phenyl)ethene-1,2-diyl)dibenzene (3da), white solid (78% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 8.1 Hz, 2H), 7.38-7.30 (m, 5H), 7.30-7.26 (m, 2H), 7.19-7.12 (m, 3H), 7.05-6.97 (m, 3H) ppm; EI-MS m/z (%): 324 (M$^+$). The data is consistent with the literature (Robbins and Hartwig, 2011).

(Z)-(1-(4-methoxyphenyl)ethene-1,2-diyl)dibenzene (3ea), white solid (77% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.27 (m, 5H), 7.19-7.09 (m, 5H), 7.08-7.04 (m, 2H), 6.90 (s, 1H), 6.89-6.86 (m, 1H), 6.86-6.83 (m, 1H), 3.83 (s, 3H) ppm; EI-MS m/z (%): 286 (M$^+$). The data is consistent with the literature (Wen et al., 2017).
(Z)-1-(3,4-dimethoxyphenyl)ethene-1,2-diyldibenzene (3fa), white solid (70% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39-7.26 (m, 5H), 7.21-7.09 (m, 3H), 7.07 (dd, $J = 5.2, 3.1$ Hz, 2H), 6.92 (s, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.75 (dd, $J = 8.2, 1.9$ Hz, 1H), 6.71 (d, $J = 2.0$ Hz, 1H), 3.91 (s, 3H), 3.68 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.05, 148.49, 143.67, 142.46, 137.72, 132.85, 129.63, 128.32, 128.13, 128.03, 127.81, 127.67, 126.82, 123.02, 113.68, 111.29, 55.94 ppm; EI-MS m/z (%): 316 (M$^+$). HRMS (EI): m/z Exact mass calcd for C$_{22}$H$_{20}$O$_2$ [M$^+$]: 316.1463, found: 316.1467.

(Z)-1-(4-fluorophenyl)ethene-1,2-diyldibenzene (3ga), white solid (85% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.28 (m, 5H), 7.19-7.11 (m, 5H), 7.05-6.99 (m, 4H), 6.96 (s, 1H) ppm; EI-MS m/z (%): 274 (M$^+$). The data is consistent with the literature (Wen et al., 2017).

(Z)-1-(4-chlorophenyl)ethene-1,2-diyldibenzene (3ha), white solid (85% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.26 (m, 7H), 7.20-7.10 (m, 5H), 7.07-7.01 (m, 2H), 6.96 (s, 1H) ppm; EI-MS m/z (%): 290 (M$^+$). The data is consistent with the literature (Robbins and Hartwig, 2011).

(Z)-2-(1,2-diphenylnvinyl)naphthalene (3ia), white solid (40% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 7.7$ Hz, 1H), 7.79 (d, $J = 8.4$ Hz, 1H), 7.75-7.66 (m, 2H), 7.52-7.42 (m, 2H), 7.38-7.27 (m, 6H), 7.12-7.02 (m, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.78, 142.56, 138.10, 137.43, 133.77, 132.86, 129.72, 129.47, 128.83, 128.75, 128.37, 128.29, 128.24, 128.17, 127.95, 127.86, 127.71, 126.97, 126.16, 126.12 ppm; EI-MS m/z (%): 306 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{24}$H$_{18}$ [M$^+$]: 306.1409, found: 306.1417.
(Z)-4-(1,2-diphenylinyl)pyridine (3ja), white solid (91% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.57 (d, J = 5.9 Hz, 2H), 7.33 (t, J = 5.7 Hz, 3H), 7.30-7.23 (m, 2H), 7.20-7.12 (m, 5H), 7.06-7.02 (m, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.35, 148.84, 142.06, 140.15, 136.55, 130.09, 129.65, 128.61, 128.38, 128.16, 127.74, 127.57, 125.65 ppm; EI-MS m/z (%): 257 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{19}$H$_{16}$N [M+H]$^+$: 258.1277, found: 258.1277.

(E)-(1-(o-tolyl)ethene-1,2-diyl)dibenzene (3ka), white solid (97% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.28 (dd, J = 6.8, 2.0 Hz, 1H), 7.25-7.09 (m, 13H), 6.61 (s, 1H), 2.11 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(E)-(1-(m-tolyl)ethene-1,2-diyl)dibenzene (3la), colorless oil (69% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34 (dd, J = 5.0, 1.7 Hz, 3H), 7.25-7.19 (m, 3H), 7.18-7.09 (m, 6H), 7.06-7.00 (m, 2H), 6.96 (s, 1H), 2.35 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Kumar et al., 2016).

(E)-(1-(p-tolyl)ethene-1,2-diyl)dibenzene (3ma), white solid (60% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.28 (m, 3H), 7.24-7.16 (m, 4H), 7.12-7.08 (m, 5H), 7.04-6.98 (m, 2H), 6.93 (s, 1H), 2.34 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Rao et al., 2018).
(E)-(1-(4-fluorophenyl)ethene-1,2-diyl)dibenzene (3na), white solid (68% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.22 (m, 5H), 7.21-7.08 (m, 5H), 7.07-6.94 (m, 4H), 6.90 (s, 1H) ppm; EI-MS m/z (%): 274 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(E)-(1-(4-chlorophenyl)ethene-1,2-diyl)dibenzene (3oa), white solid (84% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.30 (m, 3H), 7.29-7.21 (m, 4H), 7.20-7.16 (m, 2H), 7.15-7.08 (m, 3H), 7.04-6.99 (m, 2H), 6.94 (s, 1H) ppm; EI-MS m/z (%): 290 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(E)-(1-(4-(trifluoromethyl)phenyl)ethene-1,2-diyl)dibenzene (3pa), white solid (89% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 7.38-7.32 (m, 3H), 7.21-7.18 (m, 2H), 7.16-7.11 (m, 3H), 7.06-7.02 (m, 2H), 7.01 (s, 1H) ppm; EI-MS m/z (%): 324 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(E)-(1-(4-methoxyphenyl)ethene-1,2-diyl)dibenzene (3qa), colorless oil (70% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36-7.29 (m, 3H), 7.29-7.23 (m, 2H), 7.23-7.17 (m, 2H), 7.15-7.06 (m, 3H), 7.04-6.97 (m, 2H), 6.89 (s, 1H), 6.87-6.82 (m, 2H), 3.81 (s, 3H) ppm; EI-MS m/z (%): 286 (M$^+$). The data is consistent with the literature (Wu et al., 2001).
(E)-(1-(3,4-dimethoxyphenyl)ethene-1,2-diyl)dibenzene (3ra), white solid (60% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35-7.28 (m, 3H), 7.23-7.19 (m, 2H), 7.16-7.07 (m, 3H), 7.05-6.97 (m, 2H), 6.90 (s, 2H), 6.86-6.77 (m, 2H), 3.89 (s, 3H), 3.83 (s, 3H) ppm;
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.92, 148.75, 142.49, 140.52, 137.64, 136.57, 130.57, 129.59, 128.71, 128.09, 127.57, 126.92, 126.67, 120.68, 110.85, 110.83, 56.08, 56.00 ppm; EI-MS m/z (%): 316 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{22}$H$_{20}$O$_2$ [M$^+$]: 316.1463, found: 316.1474.

(E)-2-(1,2-diphenylvinyl)naphthalene (3sa), white solid (71% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86-7.72 (m, 3H), 7.70 (s, 1H), 7.52 (dd, J = 8.6, 1.8 Hz, 1H), 7.48-7.41 (m, 2H), 7.39-7.33 (m, 3H), 7.30-7.22 (m, 3H), 7.18-7.09 (m, 4H), 7.09-7.02 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.69, 140.92, 140.44, 137.53, 133.43, 132.95, 130.63, 129.73, 128.84, 128.39, 128.13, 127.85, 127.67, 126.66, 126.98, 126.94, 126.30, 126.11, 125.74 ppm; EI-MS m/z (%): 306 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{24}$H$_{18}$ [M$^+$]: 306.1409, found: 306.1402.

(E)-1-(1,2-diphenylvinyl)naphthalene (3ta), white solid (94% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.10 (d, J = 8.4 Hz, 1H), 7.83 (dd, J = 16.2, 7.9 Hz, 2H), 7.49-7.40 (m, 3H), 7.41-7.33 (m, 1H), 7.29-7.13 (m, 10H), 6.80 (s, 1H) ppm; EI-MS m/z (%): 306 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(E)-5-(1,2-diphenylvinyl)-2-ethoxypyridine (3ua), colorless oil (92% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 2.5 Hz, 1H), 7.41 (dd, J = 8.7, 2.5 Hz, 1H), 7.29-7.20 (m, 3H), 7.15-7.09 (m, 2H), 7.09-6.98 (m, 3H), 6.98-6.89 (m, 2H), 6.80 (s, 1H), 6.58 (d, J = 8.7 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 163.43, 145.80, 139.79, 139.45, 137.86, 137.24, 132.48, 130.33, 129.61, 128.90, 128.13, 127.76, 127.28, 126.95, 110.50, 62.00, 14.83 ppm; EI-MS m/z (%): 301 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{24}$H$_{18}$O [M$^+$]: 301.1327, found: 301.1329.
mass calcd for C_{19}H_{19}NO [M]^{+}: 301.1467, found: 301.1460.

\[ 
\text{(E)-2-(1,2-diphenylvinyl)thiophene (3va), colorless oil (67% yield); } \]
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.40-7.35 (m, 3H), 7.33-7.28 (m, 2H), 7.21 (d, } J = 5.1 \text{ Hz, 1H), 7.09 (t, } J = 5.8 \text{ Hz, 3H), 7.05 (s, 1H), 6.99-6.90 (m, 3H), 6.72 (d, } J = 3.5 \text{ Hz, 1H ppm; } \text{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) } \delta \text{ 148.05, 139.54, 136.74, 136.37, 130.02, 129.56, } \\
\text{128.92, 128.12, 127.97, 127.60, 126.95, 126.46, 126.23, 124.86 ppm; EI-MS m/z (%): 262 (M\textsuperscript{+}); HRMS (EI): m/z Exact mass calcd for C_{18}H_{14}S [M]^{+}: 262.0816, found: 262.0821.}
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\[ 
\text{(Z)-but-1-ene-1,2-diyl)benzene (3wa), colorless oil (78% yield); } \]
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.33-7.21 (m, 3H), 7.18-7.12 (m, 2H), 7.11-7.01 (m, 3H), 6.94-6.88 (m, 2H), 6.42 (s, 1H), 2.51 (qd, } J = 7.4, 1.1 \text{ Hz, 2H), 1.07 (t, } J = 7.4 \text{ Hz, 3H); } \text{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) } \delta \text{ 145.09, 141.62, 137.67, 129.11, 128.67, 128.60, 127.92, } \\
\text{126.93, 126.15, 125.18, 33.68, 13.04. EI-MS m/z (%): 208 (M\textsuperscript{+}); HRMS (EI): m/z Exact mass calcd for C_{16}H_{16} [M]^{+}: 208.1252, found: 208.1253.}
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\text{(Z)-(3-methylbut-1-ene-1,2-diyl)dibenzene (3xa), colorless oil (88% yield); } \]
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.39-7.21 (m, 4H), 7.16-7.08 (m, 2H), 7.08-6.98 (m, 3H), 6.85 (d, } J = 6.5 \text{ Hz, 2H), 6.40 (s, 1H), 3.12-2.44 (m, 1H), 1.11 (d, } J = 6.8 \text{ Hz, 6H); } \text{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) } \delta \text{ 149.56, 141.36, 137.74, 129.12, 128.49, 127.89, } \\
\text{126.82, 126.11, 124.30, 37.52, 21.92; EI-MS m/z (%): 222 (M\textsuperscript{+}); HRMS (EI): m/z Exact mass calcd for C_{17}H_{18} [M]^{+}: 222.1409, found: 222.1413.}
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\[ 
\text{(E)-2,3-diphenylacrylonitrile (3ya), colorless oil (88% yield); } \]
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.41-7.32 (m, 6H), 7.31-7.19 (m, 3H), 7.16 (d, } J = 7.3 \text{ Hz, 2H); EI-MS m/z (%): 205 (M\textsuperscript{+}). The data is consistent with the literature (Wang et al., 2019).}
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\text{methyl (E)-2,3-diphenylacrylate (3za), colorless oil (81% yield); } \]
\[ \text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) } \delta \text{ 7.85 (s, 1H), 7.41-7.34 (m, 3H), 7.24-7.10 (m, 5H), 7.03 (d, } J = 7.2 \text{ Hz, 2H), 3.79 (s, 3H); EI-MS m/z (%): 238 (M\textsuperscript{+}). The} \]
Data is consistent with the literature (Tsoi et al., 2010).

(2-(o-tolyl)ethene-1,1-diyl)dibenzene (3ab), white solid (60% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.28 (m, 5H), 7.23-7.18 (m, 3H), 7.15-7.07 (m, 3H), 7.06-7.00 (m, 1H), 6.97 (s, 1H), 6.90-6.79 (m, 2H), 2.33 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Shimasaki et al., 2009).

(2-(2,6-dimethylphenyl)ethene-1,1-diyl)dibenzene (3ac), white solid (44% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.31 (m, 5H), 7.18-7.08 (m, 3H), 7.07-6.99 (m, 1H), 6.99-6.90 (m, 4H), 6.83 (s, 1H), 2.12 (s, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.47, 143.57, 140.36, 137.01, 136.28, 129.90, 128.56, 128.28, 127.81, 127.65, 127.55, 127.35, 127.31, 126.84, 20.70 ppm; EI-MS m/z (%): 284 (M$^+$); HRMS (El): m/z Exact mass calcd for C$_{22}$H$_{20}$ [M]$^+$: 284.1565, found: 284.1572.

(2-(4-fluorophenyl)ethene-1,1-diyl)dibenzene (3ad), white solid (81% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.26 (m, 8H), 7.21-7.16 (m, 2H), 7.00-6.94 (m, 2H), 6.92 (s, 1H), 6.85-6.78 (m, 2H) ppm; EI-MS m/z (%): 274 (M$^+$). The data is consistent with the literature (Berthiol et al., 2003).

(2-(4-(trifluoromethyl)phenyl)ethene-1,1-diyl)dibenzene (3ae), white solid (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (s, 1H), 7.37-7.28 (m, 9H), 7.21-7.15 (m, 2H), 7.10 (d, $J$ = 8.2 Hz, 2H), 6.97 (s, 1H) ppm; EI-MS m/z (%): 324 (M$^+$). The data is consistent with the literature (Berthiol et al., 2003).
(2-(4-methoxyphenyl)ethene-1,1-diyldibenzene (3af), white solid (72% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.27 (m, 7H), 7.25-7.20 (m, 3H), 6.97-6.93 (m, 2H), 6.91 (s, 1H), 6.68-6.64 (m, 2H), 3.74 (s, 3H) ppm; EI-MS m/z (%): 286 (M$^+$). The data is consistent with the literature (Shimasaki et al., 2009).

(2-(p-toly)ethene-1,1-diyldibenzene (3ag), white solid (79% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.26 (m, 8H), 7.23-7.18 (m, 2H), 6.97-6.88 (m, 5H), 2.26 (s, 3H) ppm; EI-MS m/z (%): 270 (M$^+$). The data is consistent with the literature (Shimasaki et al., 2009).

4-(2,2-diphenylvinyl)benzonitrile (3ah), white solid (83% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39 (d, $J = 8.3$ Hz, 2H), 7.37-7.30 (m, 8H), 7.17 (s, 2H), 7.08 (d, $J = 8.4$ Hz, 2H), 6.94 (s, 1H) ppm; EI-MS m/z (%): 281 (M$^+$). The data is consistent with the literature (Rao et al., 2018).

(2-(4-nitrophenyl)ethene-1,1-diyldibenzene (3ai), yellow solid (74% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, $J = 8.8$ Hz, 2H), 7.40-7.30 (m, 8H), 7.20-7.15 (m, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.00 (s, 1H) ppm; EI-MS m/z (%): 301 (M$^+$). The data is consistent with the literature (Rao et al., 2018).
4-(2,2-diphenylvinyl)-N,N-dimethylbenzamide (3aj), colorless oil (74% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36-7.28 (m, 8H), 7.22-7.16 (m, 4H), 7.04 (d, $J = 8.1$ Hz, 2H), 6.95 (s, 1H), 3.01 (s, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.57, 144.01, 143.26, 140.11, 138.93, 134.29, 130.45, 129.49, 128.86, 128.38, 127.90, 127.80, 127.77, 127.36, 127.09 ppm; EI-MS m/z (%): 327 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{23}$H$_{21}$NO [M$^+$]: 327.1623, found: 327.1621.

(2-(4-(methylsulfonyl)phenyl)ethene-1,1-diyl)dibenzene (3ak), white solid (99% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 (d, $J = 8.5$ Hz, 2H), 7.40-7.31 (m, 8H), 7.21-7.13 (m, 4H), 6.98 (s, 1H), 3.01 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.43, 143.15, 142.54, 139.41, 137.94, 130.20, 130.19, 129.00, 128.43, 128.39, 128.18, 127.85, 127.08, 125.99, 44.51 ppm; EI-MS m/z (%): 334 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{21}$H$_{18}$O$_2$S [M$^+$]: 334.1028, found: 334.1033.

4-(2,2-diphenylvinyl)benzaldehyde (3al), white solid (77% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 9.89 (s, 1H), 7.64 (d, $J = 8.2$ Hz, 2H), 7.40-7.29 (m, 8H), 7.22-7.10 (m, 4H), 7.00 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.83, 146.06, 143.95, 142.87, 139.79, 134.48, 130.37, 130.10, 129.57, 128.95, 128.46, 128.32, 128.11, 127.94, 126.96 ppm; EI-MS m/z (%): 284 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{21}$H$_{16}$O [M$^+$]: 284.1201, found: 284.1207.

1-(4-(2,2-diphenylvinyl)phenyl)ethan-1-one (3am), white solid (84% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, $J = 8.4$ Hz, 2H), 7.38-7.29 (m, 8H), 7.22-7.16 (m, 2H), 7.12-7.06 (m, 2H), 6.99 (s, 1H), 2.53 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.73, 145.36, 142.98, 142.47, 139.94, 135.11, 130.38, 129.70, 128.92, 128.43, 128.21, 128.18, 127.98, 127.88, 127.08, 26.69 ppm; EI-MS m/z (%): 298 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{22}$H$_{18}$O [M$^+$]: 298.1358, found: 298.1364.
methyl 4-(2,2-diphenylvinyl)benzoate (3an), white solid (65% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $J$ = 8.4 Hz, 2H), 7.36-7.28 (m, 8H), 7.20-7.16 (m, 2H), 7.07 (d, $J$ = 8.3 Hz, 2H), 6.98 (s, 1H), 3.86 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.02, 145.15, 143.04, 142.27, 139.93, 130.40, 129.52, 129.37, 128.87, 128.42, 128.11, 128.07, 127.93, 127.88, 127.19, 52.14 ppm; EI-MS m/z (%): 314 (M$^+$); HRMS (EI): m/z Exact mass calcld for C$_{22}$H$_{18}$O$_2$ [M$^+$]: 314.1307, found: 314.1310.

3-(2,2-diphenylvinyl)aniline (3ao), yellow oil (63% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.27 (m, 8H), 7.23-7.19 (m, 2H), 6.93 (t, $J$ = 7.8 Hz, 1H), 6.88 (s, 1H), 6.45 (d, $J$ = 7.8 Hz, 2H), 6.33 (s, 1H), 3.43 (br, 2H) ppm; EI-MS m/z (%): 271 (M$^+$). The data is consistent with the literature.

(4-(2,2-diphenylvinyl)phenyl)(methyl)sulfane (3ap), white solid (81% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.26 (m, 8H), 7.22-7.18 (m, 2H), 7.02-6.98 (m, 2H), 6.96-6.88 (m, 3H), 2.41 (s, 3H) ppm; EI-MS m/z (%): 302 (M$^+$). The data is consistent with the literature (Dai et al., 2014).

(2-(4-chlorophenyl)ethene-1,1-diyl)dibenzene (3aq), white solid (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.27 (m, 8H), 7.18 (dd, $J$ = 6.6, 3.0 Hz, 2H), 7.10-7.07 (m, 2H), 6.95 (s, 1H), 6.92 (s, 1H), 6.90 (s, 1H) ppm; EI-MS m/z (%): 290 (M$^+$). The data is consistent with the literature (Wu et al., 2011).
(4-(2,2-diphenylvinyl)phenyl)trimethylsilane (3ar), colorless oil (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38-7.25 (m, 10H), 7.25-7.19 (m, 2H), 7.00 (d, $J = 7.9$ Hz, 2H), 6.95 (s, 1H), 0.21 (s, 9H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.56, 142.81, 140.59, 139.19, 137.77, 133.16, 130.42, 128.90, 128.85, 128.33, 128.29, 127.70, 127.64, 127.57, -1.01 ppm; EI-MS m/z (%): 328 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{23}$H$_{24}$Si [M$^+$]: 328.1647, found: 328.1654.

1-(2,2-diphenylvinyl)naphthalene (6aa), white solid (93% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20-8.11 (m, 1H), 7.85-7.77 (m, 1H), 7.64 (d, $J = 8.1$ Hz, 1H), 7.51-7.44 (m, 3H), 7.44-7.30 (m, 3H), 7.19-7.11 (m, 4H), 7.10-7.06 (m, 1H) ppm; EI-MS m/z (%): 306 (M$^+$). The data is consistent with the literature (Shimasaki et al., 2009).

2-(2,2-diphenylvinyl)naphthalene (6ab), white solid (53% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 (dd, $J = 6.0$, 3.4 Hz, 1H), 7.63 (dd, $J = 6.0$, 3.3 Hz, 1H), 7.57 (s, 1H), 7.53 (d, $J = 8.6$ Hz, 1H), 7.44-7.40 (m, 2H), 7.39-7.30 (m, 3H), 7.19-7.11 (m, 4H), 7.10-7.06 (m, 1H) ppm; EI-MS m/z (%): 306 (M$^+$). The data is consistent with the literature (Xiao et al., 2009).

9-(2,2-diphenylvinyl)phenanthrene (6ac), white solid (79% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 8.0$ Hz, 1H), 8.62 (d, $J = 8.3$ Hz, 1H), 8.23 (d, $J = 7.5$ Hz, 1H), 7.71-7.64 (m, 1H), 7.64-7.59 (m, 1H), 7.58-7.53 (m, 1H), 7.53-7.49 (m, 1H), 7.49-7.43 (m, 4H), 7.41-7.34 (m, 3H), 7.32 (s, 1H), 7.18-7.08 (m, 5H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.22, 143.46, 140.22, 133.91, 131.87, 131.73, 130.59, 130.42, 129.81, 128.75, 128.62, 128.44, 128.32, 128.24, 127.88, 127.28, 126.77, 126.62, 126.60, 125.54, 123.12, 122.48 ppm; EI-MS m/z (%): 356 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{28}$H$_{20}$ [M$^+$]: 356.1565, found: 356.1561.
9-(2,2-diphenylvinyl)anthracene (6ad), canary solid (67% yield); $^1$H NMR (400 MHz, Tol) δ 8.27-8.17 (m, 2H), 7.75-7.66 (m, 2H), 7.52-7.43 (m, 3H), 7.26-7.13 (m, 7H), 6.97-6.89 (m, 2H), 6.63-6.52 (m, 3H) ppm; $^{13}$C NMR (100 MHz, Tol) δ 147.72, 143.44, 140.33, 133.02, 131.91, 130.06, 129.97, 129.03, 128.81, 128.64, 128.10, 127.85, 127.35, 126.98, 126.67, 125.65, 125.29, 125.26 ppm; EI-MS m/z (%): 356 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{28}$H$_{20}$ [M$^+$]: 356.1565, found: 356.1567.

![Structure of 9-(2,2-diphenylvinyl)anthracene (6ad)](image)

2-(2,2-diphenylvinyl)triphenylene (6ae), white solid (85% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.63-8.56 (m, 2H), 8.55-8.50 (m, 1H), 8.39 (d, J = 8.6 Hz, 1H), 8.31 (s, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.65-7.56 (m, 3H), 7.55-7.49 (m, 1H), 7.46-7.39 (m, 5H), 7.38-7.28 (m, 6H), 7.23 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.33, 140.79, 136.10, 130.51, 129.95, 129.90, 129.85, 129.72, 129.44, 129.15, 128.94, 128.53, 128.44, 128.10, 127.80, 127.73, 127.31, 127.23, 127.17, 124.52, 123.43, 123.39, 123.35, 123.30, 123.03 ppm; EI-MS m/z (%): 406 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{32}$H$_{22}$ [M$^+$]: 406.1722, found: 406.1724.

![Structure of 2-(2,2-diphenylvinyl)triphenylene (6ae)](image)

1-(2,2-diphenylvinyl)pyrene (6af), golden yellow solid (72% yield); $^1$H NMR (400 MHz, Tol) δ 8.22 (d, J = 9.2 Hz, 1H), 7.94-7.82 (m, 3H), 7.76-7.68 (m, 3H), 7.64 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.0 Hz, 1H), 7.45 (dd, J = 7.9, 1.6 Hz, 2H), 7.22-7.16 (m, 3H), 7.15-7.11 (m, 2H), 6.95-6.85 (m, 3H) ppm; $^{13}$C NMR (100 MHz, Tol) δ 145.52, 144.11, 140.77, 133.32, 131.91, 131.61, 131.50, 130.81, 130.26, 128.77, 128.52, 128.06, 127.86, 127.59, 127.46, 127.16, 126.04, 125.51, 125.47, 124.72, 124.49 ppm; EI-MS m/z (%): 380 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{30}$H$_{20}$ [M$^+$]: 380.1565, found: 380.1562.

![Structure of 1-(2,2-diphenylvinyl)pyrene (6af)](image)

2-(2,2-diphenylvinyl)furan (6ag), red oil (66% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.38 (m, 3H), 7.34-7.28 (m, 4H), 7.28-7.23 (m, 3H), 7.16-7.13 (m, 2H), 6.88 (s, 1H), 5.61 (d, J = 1.1 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.61, 142.56, 142.31, 141.01, 140.76, 130.04, 128.97, 128.36, 127.71, 127.34, 126.98, 123.56, 117.69, 110.18 ppm; EI-MS m/z (%): 246 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{18}$H$_{14}$O [M$^+$]: 246.1045, found: 246.1047.

![Structure of 2-(2,2-diphenylvinyl)furan (6ag)](image)
2-(2,2-diphenylvinyl)benzofuran (6ah), red oil (63% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.45 (m, 3H), 7.40-7.36 (m, 2H), 7.35-7.28 (m, 7H), 7.21-7.16 (m, 1H), 7.14-7.08 (m, 1H), 7.07 (s, 1H), 5.80 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.96, 154.10, 144.13, 141.57, 140.11, 129.68, 129.09, 129.05, 128.51, 128.16, 128.08, 127.31, 124.40, 122.83, 120.95, 116.29, 110.93, 105.36 ppm; EI-MS m/z (%): 296 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{17}$O [M+H]$^+$: 297.1274, found: 297.1274.

2-(2,2-diphenylvinyl)thiophene (6ai), colorless oil (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.51-7.44 (m, 3H), 7.37-7.27 (m, 6H), 7.27-7.23 (m, 2H), 7.04 (d, $J = 5.0$ Hz, 1H), 6.93 (d, $J = 3.2$ Hz, 1H), 6.87 (dd, $J = 5.0$, 3.7 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.88, 141.46, 139.85, 139.54, 130.47, 129.45, 129.11, 128.43, 128.20, 127.49, 126.87, 126.41, 126.32, 121.01 ppm; EI-MS m/z (%): 262 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{18}$H$_{14}$S [M]$^+$: 262.0816, found: 262.0822.

3-(2,2-diphenylvinyl)thiophene (6aj), colorless oil (67% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45-7.36 (m, 3H), 7.35-7.21 (m, 7H), 7.06-7.00 (m, 2H), 6.87-6.81 (m, 1H), 6.53-6.47 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.75, 141.13, 140.81, 139.13, 130.19, 129.01, 128.39, 128.36, 127.70, 127.46, 127.27, 124.68, 124.62, 122.05 ppm; EI-MS m/z (%): 262 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{18}$H$_{14}$S [M]$^+$: 262.0816, found: 262.0822.

2-(2,2-diphenylvinyl)benzo[b]thiophene (6ak), white solid (78% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 7.5$ Hz, 1H), 7.56 (d, $J = 7.9$ Hz, 1H), 7.52-7.46 (m, 3H), 7.39-7.15 (m, 11H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.34, 141.88, 141.52, 140.81, 139.83, 138.93, 138.87, 130.73, 129.22, 128.51, 128.48, 127.88, 127.20, 126.08, 124.57, 124.30, 123.28, 122.05, 121.63 ppm; EI-MS m/z (%): 312 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{22}$H$_{16}$S [M]$^+$: 312.0973, found: 312.0976.
2-(2,2-diphenylvinyl)thieno[3,2-b]thiophene (6al), white solid (73% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (dd, $J$ = 4.9, 1.7 Hz, 3H), 7.31 (m, 7H), 7.26-7.20 (m, 2H), 7.08 (s, 1H), 6.99 (d, $J$ = 5.2 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.81, 141.77, 140.50, 140.19, 139.15, 138.48, 130.59, 129.41, 128.44, 128.40, 127.60, 127.50, 126.91, 121.68, 121.05, 119.57 ppm; EI-MS m/z (%): 318 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{20}$H$_{14}$S$_2$ [M$^+$]: 318.0537, found: 318.0530.

3-(2,2-diphenylvinyl)pyridine (6am), white solid (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.36 (d, $J$ = 1.8 Hz, 1H), 8.32 (dd, $J$ = 4.7, 1.3 Hz, 1H), 7.39-7.29 (m, 8H), 7.21-7.14 (m, 3H), 7.01 (dd, $J$ = 7.9, 4.8 Hz, 1H), 6.93 (s, 1H) ppm; EI-MS m/z (%): 257 (M$^+$). The data is consistent with the literature (Shigeno et al., 2019).

4-(2,2-diphenylvinyl)-1-methyl-1H-pyrazole (6an), red oil (65% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54-7.37 (m, 3H), 7.37-7.15 (m, 7H), 7.02 (s, 1H), 6.89 (s, 1H), 6.57 (s, 1H), 3.72 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.14, 141.18, 139.76, 139.32, 129.78, 129.33, 129.24, 128.34, 127.68, 127.08, 126.63, 120.00, 117.68, 38.95 ppm; EI-MS m/z (%): 260 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{18}$H$_{17}$N$_2$ [M+H]$^+$: 261.1386, found: 261.1386.

3-(2,2-diphenylvinyl)quinolone (6ao), white solid (97% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.59 (d, $J$ = 2.1 Hz, 1H), 8.03 (d, $J$ = 8.4 Hz, 1H), 7.69 (d, $J$ = 1.9 Hz, 1H), 7.65-7.60 (m, 1H), 7.54 (d, $J$ = 8.1 Hz, 1H), 7.50-7.42 (m, 1H), 7.41-7.30 (m, 7H), 7.28-7.19 (m, 3H), 7.10 (s, 1H) ppm; EI-MS m/z (%): 307 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{23}$H$_{18}$N [M+H]$^+$: 308.1434, found: 308.1433.
**tert-butyl 3-(2,2-diphenylvinyl)-1H-indole-1-carboxylate (6ap),** white solid (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 (d, $J = 7.8$ Hz, 1H), 7.66 (d, $J = 7.7$ Hz, 1H), 7.49-7.37 (m, 5H), 7.37-7.22 (m, 7H), 7.20 (s, 1H), 6.48 (s, 1H), 1.53 (s, 9H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.41, 142.27, 141.97, 141.97, 134.89, 130.58, 129.71, 129.31, 128.45, 127.47, 127.00, 124.64, 124.18, 122.79, 118.73, 117.23, 116.99, 115.19, 83.50, 28.20 ppm; ESI-MS (m/z): 396 [M+H]$^+$; HRMS (ESI): m/z Exact mass calcd for C$_{27}$H$_{26}$O$_2$N [M+H]$^+$: 396.1958, found: 396.1958.

**5-(2,2-diphenylvinyl)pyrimidine (6aq),** white solid (87% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.90 (s, 1H), 8.32 (s, 2H), 7.42-7.30 (m, 8H), 7.18 (dd, $J = 6.5$, 3.0 Hz, 2H), 6.83 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.77, 156.04, 147.42, 141.90, 138.89, 131.57, 129.92, 129.33, 128.61, 128.52, 128.50, 127.71, 120.24 ppm; EI-MS m/z (%): 258 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{18}$H$_{14}$N$_2$ [M]$^+$: 258.1157, found: 258.1154.

**9-(4-(2,2-diphenylvinyl)phenyl)-9H-carbazole (6ar),** white solid (83% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, $J = 7.7$ Hz, 2H), 7.46-7.12 (m, 20H), 7.03 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.45, 143.28, 140.73, 140.26, 136.52, 136.06, 130.95, 130.42, 128.97, 128.41, 127.85, 127.83, 127.74, 127.20, 126.40, 125.98, 123.49, 120.37, 120.05, 109.96 ppm; EI-MS m/z (%): 421 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{32}$H$_{23}$N [M]$^+$: 421.1830, found: 421.1840.

4. General procedure for synthesis multi-aryl substituted 1,3-dienes 8

4.1. Synthesis of 1,3-dienes 8
Scheme S5. Synthesis of 1,3-dienes 8, related to Scheme 4

To the suspension of ortho-vinyl arylbromides 1 (0.30 mmol), vinylboronate ester 7 (0.60 mmol), Pd(OAc)$_2$ (2.5 mol %), P(2-MeO-Ph)$_3$ (5.0 mol %) and CsOPiv (0.60 mmol) was added THF (3.0 mL) under argon atmosphere. The mixture was stirred at 70 °C for 1 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 8.

4.2. Characterization data of 1,3-dienes 8

(E)-buta-1,3-diene-1,1,4-triyltribenzene (8aa), white solid (95% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47-7.37 (m, 3H), 7.34-7.23 (m, 11H), 7.21-7.15 (m, 1H), 6.95-6.83 (m, 2H), 6.80-6.70 (m, 1H) ppm; EI-MS m/z (%): 282 (M$^+$). The data is consistent with the literature (Yang et al., 2013).

(((1Z,3E)-1-(m-tolyl)buta-1,3-diene-1,4-diyl)dibenzene (8ba)), white solid (98% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34-7.14 (m, 14H), 6.94 (dd, $J = 15.3, 10.9$ Hz, 1H), 6.84 (d, $J = 11.0$ Hz, 1H), 6.72 (d, $J = 15.3$ Hz, 1H), 6.70 (d, $J = 11.0$ Hz, 1H), 6.67 (d, $J = 15.3$ Hz, 1H), 2.38 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.46, 142.50, 139.83, 137.98, 137.69, 133.81, 131.26, 128.70, 128.38, 128.34, 128.29, 128.22, 127.92, 127.73, 127.59, 127.55, 127.40, 126.60, 21.63 ppm; EI-MS m/z (%): 296 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{23}$H$_{21}$[M+H]$^+$: 297.1638, found: 297.1638.

(((1Z,3E)-1-(p-tolyl)buta-1,3-diene-1,4-diyl)dibenzene (8ca)), white solid (99% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.34-7.14 (m, 14H), 6.94 (dd, $J = 15.3, 10.9$ Hz, 1H), 6.84 (d, $J = 11.0$ Hz, 1H), 6.72 (d, $J = 15.3$ Hz, 1H), 6.70 (d, $J = 11.0$ Hz, 1H), 6.67 (d, $J = 15.3$ Hz, 1H), 2.38 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.46, 142.50, 139.83, 137.98, 137.69, 133.81, 131.26, 128.70, 128.38, 128.34, 128.29, 128.22, 127.92, 127.73, 127.59, 127.55, 127.40, 126.60, 21.63 ppm; EI-MS m/z (%): 296 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{23}$H$_{21}$[M+H]$^+$: 297.1638, found: 297.1638.
1H), 2.43 (s, 3H) ppm; 13C NMR (100 MHz, CDCl₃) δ 143.35, 142.70, 137.73, 137.35, 136.91, 133.74, 130.70, 129.07, 128.69, 128.31, 128.23, 127.83, 127.54, 127.45, 126.58, 21.47 ppm; EI-MS m/z (%): 296 (M⁺); HRMS (ESI): m/z Exact mass calcd for C₂₃H₂₁ [M+H]⁺: 297.1638, found: 297.1638.

((1Z,3E)-1-(4-(trifluoromethyl)phenyl)buta-1,3-diene-1,4-diyl)dibenzene (8da), white solid (88% yield); 1H NMR (400 MHz, CDCl₃) δ 7.69 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 7.36-7.24 (m, 10H), 7.24-7.16 (m, 1H), 6.93 (dd, J = 7.8, 2.6 Hz, 1H), 6.84-6.74 (m, 2H) ppm; 13C NMR (100 MHz, CDCl₃) δ 143.76, 141.71, 141.55, 137.27, 135.30, 131.12, 129.73 (q, J = 270.7 Hz), 129.38, 128.80, 128.55, 128.01, 127.92, 127.66, 126.71, 126.29, 125.42 (q, J = 3.8 Hz), 124.39 (q, J = 32.2 Hz) ppm; 19F NMR (376 MHz, CDCl₃) δ -62.43 ppm; EI-MS m/z (%): 350(M⁺); HRMS (EI): m/z Exact mass calcd for C₂₃H₁₇F₃ [M⁺]: 350.1282, found: 350.1273.

((1Z,3E)-1-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl)dibenzene (8ea), white solid (90% yield); 1H NMR (400 MHz, CDCl₃) δ 7.35-7.23 (m, 9H), 7.23-7.15 (m, 3H), 6.99-6.89 (m, 3H), 6.82 (d, J = 11.0 Hz, 1H), 6.72 (d, J = 15.4 Hz, 1H), 3.87 (s, 3H) ppm; 13C NMR (100 MHz, CDCl₃) δ 159.15, 143.05, 142.81, 137.75, 133.59, 132.23, 132.01, 128.70, 128.32, 128.10, 127.87, 127.57, 127.49, 126.54, 113.75, 55.42 ppm; EI-MS m/z (%): 312(M⁺); HRMS (EI): m/z Exact mass calcd for C₂₃H₂₀O [M⁺]: 312.1514, found: 312.1509.

((1Z,3E)-1-(4-fluorophenyl)buta-1,3-diene-1,4-diyl)dibenzene (8ga), white solid (99% yield); 1H NMR (400 MHz, CDCl₃) δ 7.34-7.16 (m, 12H), 7.15-7.08 (m, 2H), 6.90-6.80 (m, 2H), 6.79-6.71 (m, 1H) ppm; 13C NMR (100 MHz, CDCl₃) δ 162.37 (d, J = 246.7 Hz), 142.25, 142.11, 137.51, 135.81 (d, J = 3.4 Hz), 134.33, 132.41 (d, J = 7.9 Hz), 128.76, 128.67, 128.44, 127.78, 127.75, 127.67, 126.90, 126.60, 115.41 (d, J = 21.3 Hz) ppm; 19F NMR (376 MHz, CDCl₃) δ -114.49 ppm; EI-MS m/z (%): 300 (M⁺); HRMS (ESI): m/z Exact mass calcd for C₂₃H₁₈F [M+H]⁺: 301.1387, found: 301.1387.
((1Z,3E)-1-(4-chlorophenyl)buta-1,3-diene-1,4-diyl)dibenzene (8ha), white solid (90% yield); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 (d, \(J = 8.4\) Hz, 2H), 7.34-7.24 (m, 9H), 7.21 (dd, \(J = 11.9, 5.3\) Hz, 3H), 6.90-6.80 (m, 2H), 6.80-6.70 (m, 1H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.01, 141.88, 138.38, 137.43, 134.63, 133.55, 132.14, 128.85, 128.77, 128.68, 128.46, 127.85, 127.80, 127.69, 126.71, 126.64 ppm; EI-MS m/z (%): 316 (M\(^{+}\)); HRMS (ESI): m/z Exact mass calcd for C\(_{22}\)H\(_{18}\)Cl [M+H]\(^{+}\): 317.1092, found: 317.1090.

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((1E,3E)-1-(o-tolyl)buta-1,3-diene-1,4-diyl)dibenzene (8ka), white solid (91% yield); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38-7.33 (m, 4H), 7.34-7.25 (m, 6H), 7.25-7.19 (m, 4H), 7.16-7.12 (m, 1H), 6.72 (d, \(J = 15.6\) Hz, 1H), 6.50 (d, \(J = 11.1\) Hz, 1H), 2.05 (s, 3H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.71, 143.53, 140.42, 137.65, 136.64, 134.24, 130.64, 130.56, 130.37, 130.04, 128.74, 128.26, 127.64, 127.62, 127.36, 126.63, 126.61, 125.75, 20.78 ppm; EI-MS m/z (%): 296 (M\(^{+}\)); HRMS (EI): m/z Exact mass calcd for C\(_{23}\)H\(_{20}\) [M]\(^{+}\): 297.1565, found: 297.1567.

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((1E,3E)-1-(m-tolyl)buta-1,3-diene-1,4-diyl)dibenzene (8la), white solid (86% yield); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.34 (m, 3H), 7.33-7.23 (m, 6H), 7.22-7.15 (m, 2H), 7.14 (s, 1H), 7.11-7.04 (m, 2H), 6.94-6.82 (m, 2H), 6.78-6.67 (m, 1H), 2.32 (s, 3H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.42, 142.44, 140.00, 137.90, 137.67, 133.84, 130.78, 128.70, 128.43, 128.37, 128.33, 128.31, 128.25, 127.59, 127.58, 127.31, 126.57, 125.03, 21.63 ppm; EI-MS m/z (%): 296 (M\(^{+}\)); HRMS (ESI): m/z Exact mass calcd for C\(_{23}\)H\(_{20}\) [M+H]\(^{+}\): 297.1638, found: 297.1637.

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((1E,3E)-1-(p-tolyl)buta-1,3-diene-1,4-diyl)dibenzene (8ma), white solid (97% yield); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45-7.33 (m, 3H), 7.33-7.23 (m, 6H), 7.22-7.15 (m, 2H), 7.14 (s, 1H), 7.11 (d, \(J = 8.0\) Hz, 2H), 6.94-6.80 (m, 2H), 6.76-6.66 (m, 1H), 2.34 (s, 3H) ppm; \(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.25, 142.44, 140.00, 137.90, 137.67, 133.84, 130.78, 128.70, 128.43, 128.37, 128.33, 128.31, 128.25, 127.59, 127.58, 127.31, 126.57, 125.03, 21.63 ppm; EI-MS m/z (%): 296 (M\(^{+}\)); HRMS (ESI): m/z Exact mass calcd for C\(_{23}\)H\(_{21}\) [M+H]\(^{+}\): 297.1638, found: 297.1638.
((1E,3E)-1-(4-fluorophenyl)buta-1,3-diene-1,4-diyldibenzene (8na), white solid (87% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.35 (m, 3H), 7.33-7.22 (m, 8H), 7.21-7.15 (m, 1H), 7.02-6.95 (m, 2H), 6.88 (dd, $J$ = 15.1, 10.8 Hz, 1H), 6.80 (d, $J$ = 10.8 Hz, 1H), 6.73 (d, $J$ = 15.1 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.48 (d, $J$ = 247.3 Hz), 142.18, 139.74, 138.62 (d, $J$ = 3.3 Hz), 137.55, 134.08, 130.53, 129.17 (d, $J$ = 8.0 Hz), 128.56, 128.31, 128.06 (d, $J$ = 1.5 Hz), 127.62, 127.69, 127.09, 126.59, 115.25 (d, $J$ = 21.5 Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -114.82 ppm; EI-MS m/z (%): 300 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{18}$F$^+[M+H]^+$: 301.1387, found: 301.1387.

((1E,3E)-1-(4-chlorophenyl)buta-1,3-diene-1,4-diyldibenzene (8oa), white solid (89% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.38 (m, 3H), 7.34-7.17 (m, 11H), 6.92-6.81 (m, 2H), 6.80-6.72 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.00, 140.92, 139.46, 137.48, 134.53, 133.39, 130.69, 128.94, 128.74, 128.52, 127.85, 127.80, 126.98, 126.65 ppm; EI-MS m/z (%): 316 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{17}$Cl$^+[M]^+$: 316.1013, found: 316.1013.

((1E,3E)-1-(4-(trifluoromethyl)phenyl)buta-1,3-diene-1,4-diyldibenzene (8pa), white solid (99% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, $J$ = 8.3 Hz, 2H), 7.49-7.36 (m, 5H), 7.36-7.24 (m, 6H), 7.23-7.18 (t, $J$ = 7.0 Hz, 1H), 6.96-6.85 (m, 2H), 6.85-6.74 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.91, 141.75, 139.17, 137.30, 135.46, 130.68, 130.17, 129.30 (q, $J$ = 30.1 Hz), 128.78, 128.62, 128.02, 127.99, 127.86, 126.76, 126.74, 125.31 (q, $J$ = 3.8 Hz), 124.39 (q, $J$ = 270.6 Hz) ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.47 ppm; EI-MS m/z (%): 350 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{23}$H$_{16}$F$_3$ [M+H]$^+$: 351.1355, found: 351.1355.
((1E,3E)-1-(4-methoxyphenyl)buta-1,3-diene-1,4-diyldibenzene (8qa), white solid (88% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46-7.36 (m, 3H), 7.33-7.21 (m, 8H), 7.20-7.14 (m, 1H), 6.92-6.78 (m, 4H), 6.70 (d, $J$ = 14.8 Hz, 1H), 3.81 (s, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$159.35, 142.91, 140.12, 137.79, 135.08, 133.09, 130.75, 128.91, 128.68, 128.34, 127.58, 127.46, 127.44, 126.82, 126.48, 113.78, 55.46 ppm; EI-MS m/z (%): 312 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{23}$H$_{21}$O [M+H]$^+$: 313.1587, found: 313.1587.

2-((1E,3E)-1,4-diphenylbuta-1,3-dien-1-yl)naphthalene (8sa), white solid (91% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83-7.70 (m, 3H), 7.65 (s, 1H), 7.54 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.49-7.37 (m, 5H), 7.36-7.24 (m, 6H), 7.22-7.16 (m, 1H), 7.03 (d, $J$ = 10.9 Hz, 1H), 6.94 (dd, $J$ = 15.1, 10.9 Hz, 1H), 6.79 (d, $J$ = 15.1 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.23, 139.88, 139.76, 137.63, 134.19, 133.48, 132.93, 130.87, 128.94, 128.73, 128.46, 128.39, 127.88, 127.73, 127.69, 127.66, 127.30, 127.10, 126.63, 126.32, 126.11, 125.56 ppm; EI-MS m/z (%): 332(M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{26}$H$_{20}$ [M$^+$]: 332.1565, found: 332.1569.

1-((1E,3E)-1,4-diphenylbuta-1,3-dien-1-yl)naphthalene (8ta), white solid (98% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J$ = 8.5 Hz, 1H), 7.83 (dd, $J$ = 13.6, 8.1 Hz, 2H), 7.52-7.17 (m, 15H), 6.78-6.64 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.09, 141.77, 141.06, 137.61, 134.19, 134.09, 132.12, 132.03, 129.99, 128.77, 128.39, 128.06, 127.79, 127.75, 127.54, 126.68, 126.62, 126.42, 126.08, 125.76, 125.41 ppm; EI-MS m/z (%): 332 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{26}$H$_{21}$ [M+H]$^+$: 333.1638, found: 333.1638.
2-((1E,3E)-1,4-diphenylbuta-1,3-dien-1-yl)thiophene (8va), white solid (88% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47-7.39 (m, 3H), 7.38-7.34 (m, 2H), 7.31-7.22 (m, 4H), 7.21-7.14 (m, 2H), 6.96-6.87 (m, 2H), 6.79-6.67 (m, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 147.11, 138.86, 137.57, 137.11, 133.70, 130.34, 128.70, 128.43, 128.01, 127.71, 127.64, 127.10, 126.57, 126.55, 126.27, 124.89 ppm; EI-MS m/z (%): 288 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{20}$H$_{17}$S [M+H]$^+$: 289.1045, found: 289.1045.

((1Z,3E)-1-(3-fluorophenyl)buta-1,3-diene-1,4-diyl)dibenzene (8Aa), white solid (97% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.41-7.35 (m, 1H), 7.34-7.16 (m, 10H), 7.11-7.04 (m, 2H), 7.02-6.97 (m, 1H), 6.90-6.81 (m, 2H), 6.80-6.71 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.90 (d, $J$ = 246.4 Hz), 142.17 (d, $J$ = 7.6 Hz), 141.80, 141.78, 137.41, 134.65, 129.89 (d, $J$ = 8.4 Hz), 128.92, 128.75, 128.47, 127.86, 127.79, 127.61, 126.67, 126.56 (d, $J$ = 2.9 Hz), 117.56 (d, $J$ = 21.2 Hz), 114.61 (d, $J$ = 21.0 Hz) ppm; F NMR (376 MHz, CDCl$_3$) $\delta$ -113.22 ppm; EI-MS m/z (%): 300 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{18}$F [M+H]$^+$: 301.1387, found: 301.1387.

((1Z,3E)-1-(3,4-difluorophenyl)buta-1,3-diene-1,4-diyl)dibenzene (8Ba), white solid (91% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.17 (m, 11H), 7.14-7.05 (m, 1H), 7.05-6.99 (m, 1H), 6.91-6.72 (m, 2H), 6.80-6.71 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.22 (dd, $J$ = 247,5, 40.0 Hz), 150.10 (dd, $J$ = 248.0, 40.0 Hz), 141.67, 140.88, 137.30, 136.83 (dd, $J$ = 5.7, 4.0 Hz), 135.07, 129.18, 128.81, 128.54, 127.99, 127.94, 127.59, 127.00 (dd, $J$ = 6.1, 3.5 Hz), 126.68, 126.34, 119.59 (d, $J$ = 16.9 Hz), 117.29 (d, $J$ = 17.1 Hz) ppm; F NMR (376 MHz, CDCl$_3$) $\delta$ -137.72, -139.02 ppm; EI-MS m/z (%): 318(M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{16}$F$_2$ [M$^+$]: 318.1220, found: 318.1226.

((1E,3E)-1-(3-fluorophenyl)buta-1,3-diene-1,4-diyl)dibenzene (8Ca), white solid (96% yield); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48-7.36 (m, 3H), 7.34-7.23 (m, 7H), 7.23-7.16 (m, 1H), 7.08 (d, $J$ = 7.8 Hz, 1H), 7.03-6.91 (m, 2H), 6.91-6.82 (m, 2H), 6.80-6.71 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.99 (d, $J$ = 245.0 Hz), 144.73 (d, $J$ = 7.6 Hz), 142.00, 139.32, 137.43, 134.83, 130.69, 129.70 (d, $J$ = 8.4 Hz), 129.26, 128.74, 128.52, 127.86, 126.88, 126.69, 123.32 (d, $J$ = 2.7 Hz), 114.48 (d, $J$ = 10.7 Hz), 114.27 (d, $J$ = 9.9 Hz) ppm; F NMR (376 MHz, CDCl$_3$) $\delta$ -113.63 ppm; EI-MS m/z (%): 300 (M$^+$); HRMS (ESI): m/z Exact mass calcd for C$_{22}$H$_{16}$F$_2$ [M$^+$]: 300.1314, found: 300.1318.
(E)-(4-(p-toly)buta-1,3-diene-1,1-diyl)dibenzene (8ab), white solid (95% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45-7.34 (m, 3H), 7.33-7.23 (m, 7H), 7.22-7.18 (m, 2H), 7.07 (d, \(J = 8.0\) Hz, 2H), 6.90-6.80 (m, 2H), 6.76-6.66 (m, 1H), 2.31 (s, 3H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.67, 142.53, 140.01, 137.59, 134.86, 134.06, 130.80, 129.43, 128.60, 128.35, 128.34, 127.71, 127.55, 127.48, 126.53, 126.33, 21.40 ppm; EI-MS m/z (%): 296(M\(^+\)); HRMS (EI): m/z Exact mass calcd for C\(_{23}\)H\(_{20}\) [M\(^+\)]: 296.1565, found: 296.1566.

(4-(4-chlorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (8ac), white solid (96% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.35 (m, 3H), 7.33-7.17 (m, 11H), 6.93-6.80 (m, 2H), 6.72-6.62 (m, 1H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 143.89, 142.28, 139.79, 136.14, 133.11, 132.55, 130.73, 128.86, 128.42, 128.39, 128.06, 127.79, 127.76, 127.74, 127.71 ppm; EI-MS m/z (%): 316 (M\(^+\)); HRMS (ESI): m/z Exact mass calcd for C\(_{22}\)H\(_{18}\)Cl [M+H\(^+\)]: 317.1092, found: 317.1091.

(4-(4-fluorophenyl)buta-1,3-diene-1,1-diyl)dibenzene (8ad), white solid (99% yield); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.46-7.35 (m, 3H), 7.32-7.23 (m, 9H), 6.98-6.90 (m, 2H), 6.88-6.75 (m, 2H), 6.69 (d, \(J = 14.6\) Hz, 1H) ppm; \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 162.36 (d, \(J = 247.5\) Hz), 143.33 (d, \(J = 1.3\) Hz), 142.36, 139.88, 133.83 (d, \(J = 3.4\) Hz), 132.69, 130.74, 128.41, 128.38, 128.18, 128.10, 128.02, 127.72, 127.65 (d, \(J = 2.5\) Hz), 126.98 (d, \(J = 2.4\) Hz), 115.67 (d, \(J = 21.7\) Hz) ppm; \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -114.17 ppm; EI-MS m/z (%): 300 (M\(^+\)); HRMS (ESI): m/z Exact mass calcd for C\(_{22}\)H\(_{18}\)F [M+H\(^+\)]: 301.1387, found: 301.1388.

(4-(4-(trifluoromethyl)phenyl)buta-1,3-diene-1,1-diyl)dibenzene (8ae), white solid (96% yield); \(^1\)H NMR
(400 MHz, CDCl₃) δ 7.50 (d, J = 8.2 Hz, 2H), 7.47-7.35 (m, 5H), 7.34-7.24 (m, 7H), 6.96 (dd, J = 15.1, 11.0 Hz, 1H), 6.88 (d, J = 11.0 Hz, 1H), 6.74 (d, J = 15.1 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.10, 142.13, 141.10, 139.63, 132.15, 130.73, 129.65, 129.12 (q, J = 32.3 Hz), 128.46, 128.43, 127.97, 127.91, 127.86, 127.76, 127.05 (q, J = 270.4 Hz), 128.46, 127.59, 125.64 (q, J = 3.8 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.51 ppm; EI-MS m/z (%): 350 (M⁺); HRMS (ESI): m/z Exact mass calcd for C₂₃H₁₇F₃[M⁺]: 350.1277, found: 350.1277.

(E)-(4-(4-methoxyphenyl)buta-1,3-diene-1,1-diyl)dibenzene (8af), white solid (99% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.46-7.34 (m, 3H), 7.32-7.22 (m, 9H), 6.89-6.64 (m, 5H), 3.79 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.34, 142.56, 142.07, 140.07, 133.64, 130.80, 130.47, 128.67, 128.36, 128.33, 127.85, 127.64, 127.49, 127.39, 125.26, 114.17, 55.43 ppm; EI-MS m/z (%): 312 (M⁺); HRMS (EI): m/z Exact mass calcd for C₂₃H₂₀O [M⁺]: 312.1514, found: 312.1516.

(Z)-buta-1,3-diene-1,1,4-triyltribenzene (8ag), white solid (73% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.30 (m, 3H), 7.30-7.18 (m, 8H), 7.17 (d, J = 11.4 Hz, 1H), 6.47 (d, J = 11.6 Hz, 1H), 6.31 (t, J = 11.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 145.22, 142.45, 139.76, 137.76, 131.24, 130.76, 129.27, 128.47, 128.34, 128.27, 128.02, 127.73, 127.69, 127.23, 124.40 ppm; EI-MS m/z (%): 282(M⁺); HRMS (EI): m/z Exact mass calcd for C₂₂H₁₈O [M⁺]: 282.1409, found: 282.1406.

(E)-hepta-1,3-diene-1,1,diyl dibenzene (8ah), colorless oil (83% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.30 (m, 3H), 7.30-7.18 (m, 7H), 6.67 (d, J = 11.0 Hz, 1H), 6.14 (dd, J = 15.1, 10.9 Hz, 1H), 5.96-5.84 (m, 1H), 2.04 (dd, J = 14.1, 7.0 Hz, 2H), 1.39 (dq, J = 14.7, 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.70, 140.28, 140.17, 137.30, 130.63, 128.56, 128.55, 128.27, 128.25, 128.27, 127.52, 127.23, 127.14, 35.23, 22.72, 13.87; EI-MS m/z (%): 248 (M⁺); HRMS (EI): m/z Exact mass calcd for C₁₉H₂₀ [M⁺]: 248.1565, found: 248.1557.
(4-methylpenta-1,3-diene-1,1-diyl)dibenzene (8ai), colorless oil (85% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42-7.35 (m, 2H), 7.35-7.30 (m, 1H), 7.30-7.24 (m, 4H), 7.24-7.18 (m, 3H), 6.87 (d, $J = 11.4$ Hz, 1H), 5.92 (d, $J = 11.4$ Hz, 1H), 1.89 (s, 3H), 1.76 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.23, 140.32, 139.82, 137.90, 130.71, 128.25, 128.23, 127.56, 127.14, 127.03, 124.63, 123.28, 26.65, 18.78; EI-MS m/z (%): 234 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{18}$H$_{18}$ [M$^+$]: 234.1409, found: 234.1402.

(2-(cyclopent-1-en-1-yl)ethene-1,1-diyl)dibenzene (8aj), colorless oil (49% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.30 (m, 3H), 7.29-7.22 (m, 4H), 7.22-7.16 (m, 3H), 6.88 (s, 1H), 5.86 (s, 1H), 2.35-2.25 (m, 2H), 1.85-1.74 (m, 2H), 1.74-1.65 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.18, 142.83, 140.98, 140.00, 135.50, 130.72, 128.21, 127.81, 127.27, 127.23, 127.05, 125.42, 33.55, 32.22, 24.44; EI-MS m/z (%): 246 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{19}$H$_{18}$ [M$^+$]: 246.1409, found: 246.1414.

(2-(cyclohex-1-en-1-yl)ethene-1,1-diyl)dibenzene (8ak), colorless oil (53% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35-7.28 (m, 3H), 7.28-7.17 (m, 7H), 6.55 (s, 1H), 5.85-5.76 (m, 1H), 2.14-2.06 (m, 2H), 1.70-1.60 (m, 2H), 1.52-1.46 (m, 2H), 1.45-1.39 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.08, 141.44, 138.66, 136.53, 132.38, 132.27, 130.64, 128.14, 127.91, 127.51, 127.06, 126.89, 28.25, 26.36, 23.10, 22.19; EI-MS m/z (%): 260 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{20}$H$_{20}$ [M$^+$]: 260.1565, found: 260.1555.

4-(2,2-diphenylvinyl)-3,6-dihydro-2H-pyran (8al), colorless oil (76% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (m, 3H), 7.31-6.98 (m, 7H), 6.56 (s, 1H), 5.76 (s, 1H), 4.25-4.15 (br, 2H), 3.56 (t, $J = 5.3$ Hz, 2H), 1.78-1.70 (br, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.42, 140.80, 140.30, 134.10, 130.54, 130.00, 129.15, 128.23, 128.11, 127.52, 127.46, 127.31, 66.13, 64.38, 28.43; EI-MS m/z (%): 262 (M$^+$); HRMS (EI): m/z Exact
mass calcd for C₁₉H₁₈O [M⁺]: 262.1358, found: 262.1351.

(1E,3E)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl)dibenzene (8qm), white solid (82% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.45-7.33 (m, 6H), 7.33-7.27 (m, 4H), 7.15-7.05 (m, 4H), 6.94-6.86 (m, 2H), 6.76 (d, J = 8.9 Hz, 2H), 6.68 (s, br, 2H), 3.77 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 162.31 (d, J = 247.1 Hz), 159.31, 143.87, 142.11, 140.17, 139.98, 138.90 (d, J = 3.3 Hz), 135.18, 130.78, 129.32 (d, J = 7.9 Hz), 129.01, 128.45, 128.37, 127.68, 127.64, 126.13, 126.11, 124.41, 115.12 (d, J = 21.4 Hz), 113.70, 55.42 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.18 ppm; EI-MS m/z (%): 406 (M⁺); HRMS (EI): m/z Exact mass calcd for C₂₉H₂₃OF [M⁺]: 406.1733, found: 406.1739.

(1E,3Z)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl)dibenzene (8em), white solid (87% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.34 (m, 3H), 7.33-7.26 (m, 4H), 7.19-7.10 (m, 4H), 6.98-6.88 (m, 4H), 6.71 (dd, J = 11.4 Hz, 2H), 3.87 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 162.38 (d, J = 247.3 Hz), 159.17, 144.04, 142.94, 142.64, 139.92, 138.88 (d, J = 3.1 Hz), 132.29, 132.09, 130.74, 129.40 (d, J = 7.9 Hz), 128.45, 128.25, 128.00, 127.73, 127.53, 126.24, 125.71, 115.15 (d, J = 21.4 Hz), 113.75, 55.43 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -115.06 ppm; EI-MS m/z (%): 406 (M⁺); HRMS (EI): m/z Exact mass calcd for C₂₉H₂₃OF [M⁺]: 406.1733, found: 406.1740.

(1E,3E)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl)dibenzene (8qn), white solid (78% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.34 (m, 3H), 7.33-7.26 (m, 4H), 7.16-7.07 (m, 6H), 6.81-6.76 (m, 2H), 6.74 (d, J = 11.5 Hz, 1H), 6.65 (d, J = 11.4 Hz, 1H), 3.78 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 162.30 (d, J = 246.5 Hz), 159.39, 144.16, 142.55, 142.04, 140.11, 136.05 (d, J = 3.4 Hz), 135.15,
132.50 (d, J = 8.0 Hz), 130.77, 129.01, 128.37, 128.33, 127.70, 127.47, 126.62, 124.26, 115.38 (d, J = 21.3 Hz), 113.76, 55.43 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -114.65 ppm; EI-MS m/z (%): 406 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{29}$H$_{23}$OF [M$^+$]: 406.1733, found: 406.1731.

$\text{[(1Z,3Z)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)buta-1,3-diene-1,4-diyl]}$dibenzenzene (8en), white solid (75% yield); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32-7.20 (m, 10H), 7.20-7.14 (m, 4H), 7.13-7.05 (m, 2H), 6.96-6.91 (m, 2H), 6.81 (d, J = 11.4 Hz, 1H), 6.66 (d, J = 11.4 Hz, 1H), 3.86 (s, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.32 (d, J = 246.6 Hz), 159.21, 144.33, 142.93, 142.58, 142.55, 136.01 (d, J = 3.4 Hz), 132.47 (d, J = 7.9 Hz), 132.24, 132.08, 128.35, 128.29, 127.99, 127.77, 127.61, 125.76, 125.56, 115.38 (d, J = 21.2 Hz), 113.77, 55.42 ppm; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -114.56 ppm; EI-MS m/z (%): 406 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{29}$H$_{23}$OF [M$^+$]: 406.1733, found: 406.1744.

5. Gram-scale reactions

To the suspension of ortho-vinyl bromobenzene 1a (1.30 g, 5.0 mmol), arylboronate ester 2k (3.39 g, 15.0 mmol), Pd(OAc)$_2$ (56.0 mg, 0.25 mmol), P(2-MeO-Ph)$_3$ (176.2 mg, 0.50 mmol) and CsOPiv (2.34 g, 10.0 mmol) was added THF (100 mL) under argon atmosphere. The mixture was stirred at 110 °C for 3 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 3ak with 92% yield.

Scheme S6. Gram-scale reactions of 3ak, related to Scheme 5

Scheme S7. Gram-scale reactions of 8Aa, related to Scheme 5
To the suspension of ortho-vinyl bromobenzene 1A (1.38 g, 5.0 mmol), vinylboronate ester 7a (2.30 g, 10.0 mmol), Pd(OAc)$_2$ (28.0 mg, 0.125 mmol), P(2-MeO-Ph)$_3$ (88.1 mg, 0.25 mmol) and CsOPiv (2.34 g, 10.0 mmol) was added THF (100 mL) under argon atmosphere. The mixture was stirred at 70 °C for 1 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 8Aa with 92% yield.

6. Transformation of obtained products

**Scheme S8. Transformation of 3aq, related to Scheme 5**

2-(4-(2,2-diphenylvinyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9a) To the suspension of 3aq (87 mg, 0.3 mmol), Pd(PCy$_3$)$_2$Cl$_2$ (11.1 mg, 5 mol %), KOAc (59 mg, 0.6 mmol) and B$_2$pin$_2$ (152.4 mg, 0.6 mmol) was added dioxane (3 mL) under argon atmosphere. The mixture was stirred at 90 °C for 5 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 9a with 63% yield as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.1$ Hz, 2H), 7.36-7.26 (m, 8H), 7.22-7.15 (m, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 6.97 (s, 1H), 1.31 (s, 12H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.65, 143.41, 140.35, 140.33, 134.50, 130.48, 128.96, 128.76, 128.33, 128.26, 127.80, 127.76, 127.59, 83.82, 25.01 ppm; EI-MS m/z (%): 382 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{26}$H$_{27}$O$_2$B [M$^+$]: 381.2140, found: 381.2143.

**Scheme S9. Transformation of 3aq, related to Scheme 5**

4-(2,2-diphenylvinyl)-1,1'-biphenyl (9b) To the suspension of 3aq (87 mg, 0.3 mmol), Pd$_2$(dba)$_3$ (6.9 mg, 2.5 mol %), Cs$_2$CO$_3$ (196 mg, 0.6 mmol), phenylboronic acid (110.0 mg, 0.9 mmol) and P(t-Bu)$_3$ (6.1 mg, 10 mol %) was added dioxane (3 mL) under argon atmosphere. The mixture was stirred at 120 °C for 6 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 9b with 92% yield as a while solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.58-7.51 (m, 2H), 7.43-7.21 (m, 15H), 7.09 (d, $J = 8.2$ Hz, 2H), 7.00 (s, 1H) ppm; EI-MS m/z (%): 332 (M$^+$); The data is consistent with the literature (Doni et al., 2015).
Scheme S10. Transformation of 3aq, related to Scheme 5

(E)-(2-(4-styrylphenyl)ethene-1,1-diyldibenzene (9c) To the suspension of 3aq (87 mg, 0.3 mmol), Pd$_2$(dba)$_3$ (6.9 mg, 2.5 mol %), Cs$_2$CO$_3$ (196 mg, 0.6 mmol), trans-β-styrylboronic acid pinacol ester (207.0 mg, 0.9 mmol) and P$_t$Bu$_3$ (6.1 mg, 10 mol %) was added dioxane (3 mL) under argon atmosphere. The mixture was stirred at 120 °C for 6 h. After being cooled down to room temperature, it was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel to afford pure product 9b with 92% yield as a white solid.  $^1$H NMR (400 MHz, CDCl$_3$) δ 7.51-7.41 (m, 2H), 7.38-7.14 (m, 15H), 7.09-6.89 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.51, 142.76, 140.58, 137.49, 136.98, 135.87, 130.52, 130.02, 128.87, 128.81, 128.66, 128.41, 128.36, 127.94, 127.72, 127.67, 127.64, 126.60, 126.27 ppm; EI-MS m/z (%): 358 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{28}$H$_{22}$ [M]$: 358.1722, found: 358.1729.

Scheme S11. Transformation of 3al, related to Scheme 5

2-amino-3-(((E)-4-(2,2-diphenylyvinyl)benzylidene)amino)maleonitrile (9d) A mixture of 3al (85 mg, 0.3 mmol), 2,3-diaminomaleonitrile (35 mg, 0.3 mmol), AcOH (0.1 mL) in ethyl alcohol (1 mL) was heated at 85 °C for 8 h. After cooling down to the room temperature, the mixture was concentrated under reduced pressure. The residue was purified by recrystallization (CH$_2$Cl$_2$-hexane mixed-solvent system) to afford 9d with 89% yield as a pale brown solid.  $^1$H NMR (400 MHz, CD$_2$Cl$_2$) δ 8.30 (s, 1H), 7.60 (d, $J$ = 8.4 Hz, 2H), 7.42-7.26 (m, 7H), 7.24-7.16 (m, 2H), 7.10 (d, $J$ = 8.4 Hz, 2H), 7.01 (s, 1H), 5.32-5.30 (m, 1H), 5.24 (br, 2H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ 158.58, 145.49, 143.28, 142.24, 140.41, 133.51, 130.61, 130.41, 129.18, 129.14, 128.66, 128.39, 128.19, 128.05, 127.49, 124.90, 114.13, 112.76, 108.68 ppm; EI-MS m/z (%): 374 (M$^+$); HRMS (EI): m/z Exact mass calcd for C$_{25}$H$_{18}$N$_4$ [M]$^+$: 374.1531, found: 374.1533.
Scheme S12. Transformation of 3al, related to Scheme 5

(Z)-3-(4-(2,2-diphenylnvinyl)phenyl)-2-phenylacrylonitrile (9e) A mixture of 3al (85 mg, 0.3 mmol), benzyl cyanide (39 mg, 0.33 mmol), MeONa (3.3 mg, 0.06 mmol) in ethyl alcohol (10 mL) was stirred at 25 °C for 8 h. The mixture was quenched with water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane-ethyl acetate mixed-solvent system) to afford 9e with 96% yield as a golden yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.71-7.66 (m, 2H), 7.66-7.60 (m, 2H), 7.48-7.28 (m, 12H), 7.24-7.19 (m, 2H), 7.13-7.05 (m, 2H), 6.98 (s, 1H) ppm; EI-MS m/z (%): 383 (M$^+$); The data is consistent with the literature (Wen et al., 2016).

Scheme S13. Transformation of 3al, related to Scheme 5

(E)-4-(4-(2,2-diphenylnvinyl)styryl)benzonitrile (9f) A mixture of 3al (85 mg, 0.3 mmol), diethyl (4-cyanobenzyl)phosphonate (114 mg, 0.45 mmol), $^1$BuOK (67 mg, 0.6 mmol) in THF (6 mL) was stirred at 25 °C for 8 h. The mixture was quenched with water and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over MgSO$_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (hexane-ethyl acetate mixed-solvent system) to afford 9f with 83% yield as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.61 (d, $J$ = 8.4 Hz, 2H), 7.57-7.49 (m, 2H), 7.38-7.27 (m, 10H), 7.25-7.19 (m, 2H), 7.15-6.95 (m, 5H) ppm; EI-MS m/z (%): 383 (M$^+$); The data is consistent with the literature (Wen et al., 2016).

7. Photophysical propertied of the prepared olefins and 1,3-dienes

| Entry | Compounds | Geometry of double bonds | $\lambda_{abs}$ (nm) | Solution (THF) | Solid |
|-------|-----------|--------------------------|----------------------|----------------|-------|
|       |           |                          | $\lambda_{em}$ (nm) | $\Phi_f$ (%)   | $\lambda_{em}$ (nm) | $\Phi_f$ (%) |
| 1     | 3nh       | $E$                       | 289                  | 357, 374       | 1.3   | 431   | 12  |
| 2     | 3ga       | $Z$                       | 298                  | 361, 374       | 0.9   | 430   | 0.1 |
| 3     | 3ma       | $E$                       | 298                  | 359, 374       | 0.7   | 433   | 20.8 |
| 4     | 3ca       | $Z$                       | 306                  | 359, 375       | 1.4   | 423   | 0.1 |
| 5     | 8aa       | $3E$                      | 337                  | 406            | 0.6   | 419   | 23.0 |
| 6     | 8ag       | $3Z$                      | 324                  | 397            | 0.3   | 423   | 3.1 |
| 7     | 8na       | $1E$                      | 337                  | 397            | 1.0   | 417   | 41.5 |
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