JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.8b02279 • Publication Date (Web): 29 Oct 2018

Nickel-Catalyzed Benzylation of Aryl Alkenes with Benzylamines via C-N Bond Activation

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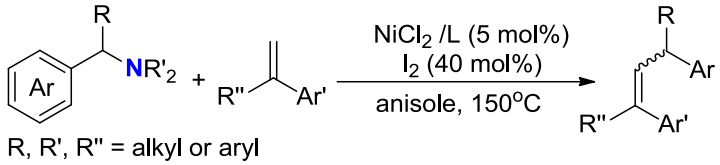


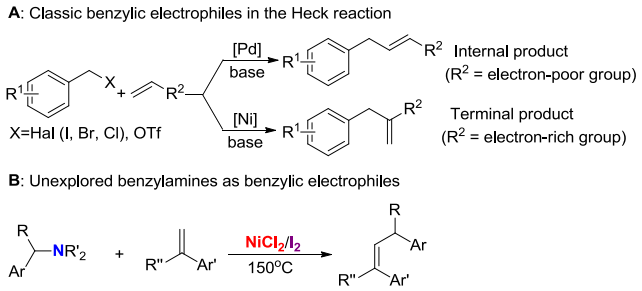
ABSTRACT: We have developed the first example of nickel-catalyzed Heck-type benzylation of aryl olefins with various benzylamines as benzyl electrophiles, and the benzylic C-N bond cleavage was efficiently promoted by amine-I_2 charge transfer complex (CT-complex). The combination of low-cost $NiCl_2$ and I_2 has been found to facilitate Heck reaction of tertiary benzylamines and alkenes into various benzyl-substituted alkenes in good to excellent yields. This unconventional Heck reaction is proposed to go through initially the formation of a benzylic radical via oxidative addition of C-N bond with Ni(0), then captured by aryl alkene via radical addition, followed by single-electron transfer redox and proton abstraction without oxidant and external base.

INTRODUCTION

The Heck reaction has become one of the most powerful strategies for the construction of C-C bonds since its discovery in 1972.[1] The classic Heck reaction delivers functionalized alkenes that are essential structural motifs for the synthesis of pharmaceuticals, organic materials, agrochemicals, and complex natural products in both academic and industrial settings.[2] Although tremendous effort has been devoted to the development of this synthetically useful reaction, compared with significant advances on the field of alkyl halides, vinyl or aryl halides cross coupling,[3] comparatively little progress has been achieved in the Heck reaction of non-halogen-containing alkyl electrophiles such as amines.

As one of the most ample chemical bonds, C-N bond exists widespreadly in organic molecules and bioactive molecules.[4] On account of the high C-N bond dissociation energy and good nucleophilicity of the amine group, amines are more commonly acted as nucleophiles in organic transformations. As for utilizing as Heck-reaction coupling partners, amines were usually transformed into the corresponding energetically favored compounds such as diazonium salts,[5,6] or ammonium salts.[7] Such kind of strategies usually produce lots of wastes, thus, cannot fit for the idea of sustainable development. Heck-type benzylation of alkenes is a useful method for synthesis of allylic compounds. The traditional benzyl electrophiles for such a reaction were toxic benzyl halides or related derivatives,[8] delivering two kinds of products (Internal and Terminal products) according to the property of olefins, and limiting the development of alkene benzylation reaction (Scheme 1A). Compared with benzyl halides, to the best of our knowledge, no simple amine has been directly used as electrophile precursors in Heck reaction, which is in largely due to the deficiency of effective strategies for cleavage of inert C-N bonds.

Scheme 1. Classic and Unexplored Benzyl Electrophiles in the Heck reaction.



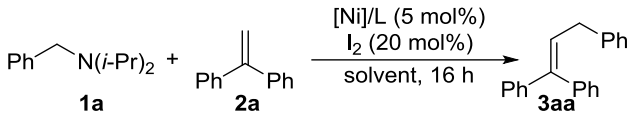
Our group has recently been focusing on developing efficient strategies for activation of inert C-N bond of simple amines merging transition-metal catalysis. Several useful strategies have been developed and successfully employed in a series of C-C and C-N bond construction reactions.[9,10] The key to the success of those competent strategies is to enhance the oxidation state of the amines by lowering the electron-density of the nitrogen atom. Such kind of strategies could not only facilitate the C-N bond to form σ-complex with a transition metal, but also improve the π-back bonding capability between metal center and C-N bond, and ultimately realize C-N bond activation by oxidative addition with low valence transition metal. One strategy with great promise for amine-I_2 CT-

complex promoted benzylic C-N bond activation has been realized and applied in the nickel-catalyzed direct carbonylation of benzylamines and alkylarylation of activated alkenes successfully.[10] Mechanistic studies have disclosed that the formation of amine-I_2 complex leads to reinforcement of π-back bonding capability between metal center and C-N bond, thus prompts C-N bond experiencing single electron oxidative addition with Ni^0 to deliver a benzylic radical without external oxidant. In this context, it would be reasonable that benzylic radicals generated from the benzylamines by CT-complex induced C-N bond cleavage could be applied to nickel catalyzed Heck-type benzylation reaction. Herein, we develop a nickel-catalyzed Heck-type benzylation reaction of aryl alkenes with benzylamines as benzyl electrophile precursors in the absence of external bases via C-N bond activation (Scheme 1B).

RESULTS AND DISCUSSION

Our initial effort was made to achieve the successful cross coupling of readily available N-benzyl-N-isopropylpropan-2-amine (**1a**) and 1,1-diphenylethylene (**2a**) (Table 1). After

Table 1. Screening of Reaction Conditions [a]



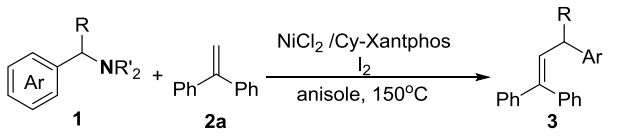
1a **2a** **3aa**

entry	[Ni]	ligand	solvent	yield (%)
1	$NiCl_2$	Xantphos	anisole	47
2	$NiBr_2$	Xantphos	anisole	45
3	NiI_2	Xantphos	anisole	45
4	$Ni(cod)_2$	Xantphos	anisole	40
5	$NiCl_2$	PCy_3	anisole	25
6	$NiCl_2$	DPPF	anisole	32
7	$NiCl_2$	DPPOct	anisole	31
8	$NiCl_2$	Cy-Xantphos	anisole	54
9	$NiCl_2$	Cy-Xantphos	CH_3CN	6
10	$NiCl_2$	Cy-Xantphos	DMF	22
11	$NiCl_2$	Cy-Xantphos	DME	15
12	$NiCl_2$	Cy-Xantphos	toluene	23
13[b]	$NiCl_2$	Cy-Xantphos	anisole	93(90)
14[c]	$NiCl_2$	Cy-Xantphos	anisole	0
15[b]	-	Cy-Xantphos	anisole	17
16[b]	$NiCl_2$	-	anisole	57

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (0.5 mmol), [Ni] (0.025 mmol), ligand (monodentate ligand : 0.06 mmol; bidentate ligand : 0.03 mmol), I_2 (0.1 mmol), solvent (2 mL), 150 °C, 16 h. GC yield determined by using *n*-dodecane as an internal standard and isolated yields were given within parentheses; [b]I_2 (0.2 mmol); [c]Without I_2.

extensive and systematic study, gratifyingly, the cross-coupled adduct **3aa** was obtained in 47% GC yield at 150 °C when simple catalytic system $NiCl_2$/Xantphos was combined with catalytic amount of I_2 (Table 1, entry 1). Further screening of other representative nickel catalysts proved that both Ni(0) and Ni(II) could catalyze this Heck reaction to produce **3aa** and various nickel precursor did not greatly influence the transformation (Table 1, entries 2-4). Inspired by this positive lead, we next sought to improve the efficiency of the reaction. The impact of various phosphine ligands was then screened with low-cost $NiCl_2$ as the ideal catalyst, and the corresponding

Table 2. Substrate Scope of Benzylamines [a]



1 **2a** **3**

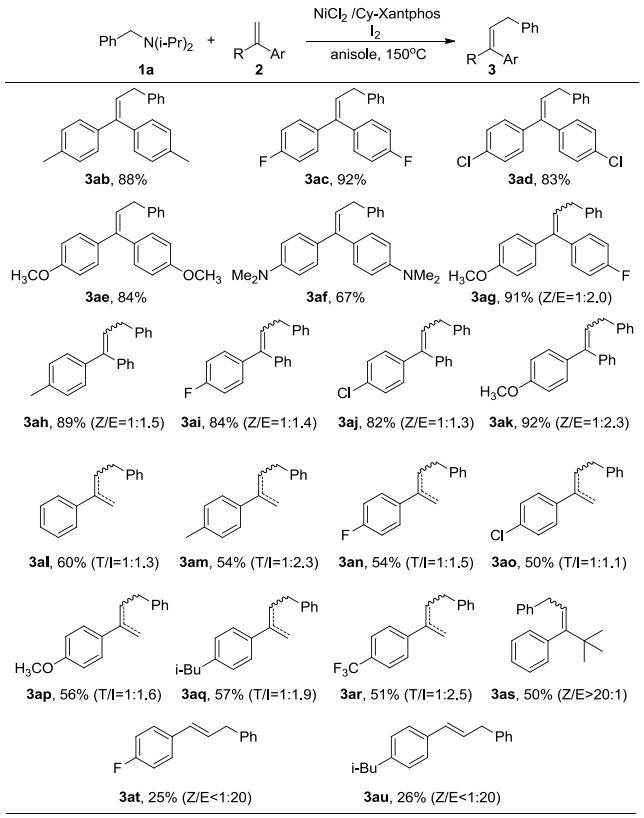
entry	Ar	R	R'	product	yield (%)[b]
1	Ph	H	H	**3aa**	0
2	Ph	H	Me	**3aa**	14
3	Ph	H	Et	**3aa**	34
4	Ph	H	*n*-Pr	**3aa**	39
5	Ph	H	*i*-Pr	**3aa**	90
6	Ph	H	*n*-Bu	**3aa**	36
7	Ph	H	allyl	**3aa**	37
8	Ph	H	Ph	**3aa**	5
9	Ph	H	Cy	**3aa**	80
10	Ph	H	Bn	**3aa**	77
11	2-$CH_3C_6H_4$	H	*i*-Pr	**3ba**	95
12	3-$CH_3C_6H_4$	H	*i*-Pr	**3ca**	86
13	4-$CH_3C_6H_4$	H	*i*-Pr	**3da**	90
14	2-ClC_6H_4	H	*i*-Pr	**3ea**	76
15	3-ClC_6H_4	H	*i*-Pr	**3fa**	66
16	4-ClC_6H_4	H	*i*-Pr	**3ga**	83
17	2,6-di-ClC_6H_4	H	*i*-Pr	**3ha**	94
18	4-FC_6H_4	H	*i*-Pr	**3ia**	73
19	4-CNC_6H_4	H	*i*-Pr	**3ja**	76
20	4-$MeOC_6H_4$	H	*i*-Pr	**3ka**	94
21	4-AcC_6H_4	H	*i*-Pr	**3la**	80
22	4-$MeOC(O)C_6H_4$	H	*i*-Pr	**3ma**	64
23	1-naphthyl	H	*i*-Pr	**3na**	93
24	2-naphthyl	H	*i*-Pr	**3oa**	88
25	2-thienyl	H	*i*-Pr	**3pa**	86
26	Ph	CH_3	*i*-Pr	**3qa**	76
27	Ph	Ph	*i*-Pr	**3ra**	73

[a]Reaction conditions: **1** (1.0 mmol), **2a** (0.5 mmol), $NiCl_2$ (0.025 mmol), Cy-Xantphos (0.03 mmol), I_2 (0.2 mmol), anisole (2 mL), 150 °C, 16 h. [b]Isolated yield.

results indicated that the commercialized Cy-Xantphos was the best ligand for Heck reaction to deliver the benzylated alkene **3aa** in 54% GC yield (Table 1, entry 8). As shown in entries 9-12, some common organic solvents such as CH_3CN, DMF, DME and toluene were also evaluated, however, they afforded unsatisfying yields of **3aa**. To our great delight, further increasing the catalyst loading of I_2 to 40 mol%, the benzylated adduct **3aa** was isolated in 90% yield under other iden-

tical reaction conditions (Table 1, entry 13). As we expected, control experiments demonstrated that no desired adduct could be detected when the Heck reaction was dealt without I_2 and adduct **3aa** was isolated in only 17% yield under metal-free conditions, in addition, some additives such as AcOH and MeOTf instead of iodine were not effective for this transformation (See the Supporting Information), and the above results indicated iodine and nickel catalyst are crucial for the Heck reaction to proceed smoothly (Table 1, entries 14 and 15). While this reaction was conducted in the absence of Cy-Xantphos, the desired adduct **3aa** was still isolated in 57% yield (Table 1, entry 16), which revealed that the ligand is not necessary for this Heck-type benzylation.

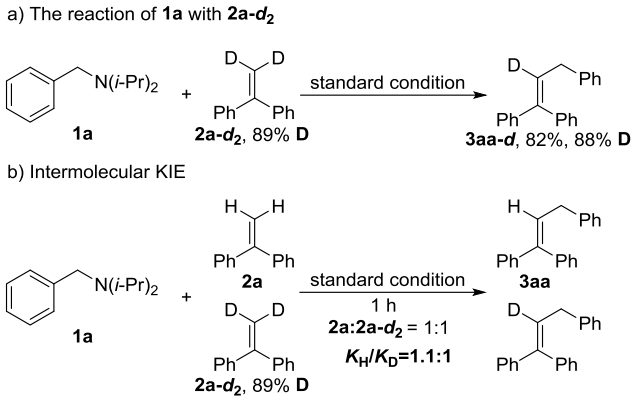
Scheme 2. Substrate Scope of alkenes [a,b]



[a]Reaction conditions: **1a** (1.0 mmol), **2** (0.5 mmol), $NiCl_2$ (0.025 mmol), Cy-Xantphos (0.03 mmol), I_2 (0.2 mmol), anisole (2 mL), 150 oC, 16 h. [b]Isolated yield, the ratio of Z/E and T/I (terminal/internal) was determined by GC-MS analysis of the crude product.

After establishing the optimum reaction conditions, we next examined the substrate scope of benzylamines. Considering different substituents linked to nitrogen atom may have a remarkable influence on the reactivity, benzylic amines with different leaving groups (NR'_2) were firstly screened under optimized reaction conditions. As we expected, the substrates with different substituents R' on the N atom delivered the desired cross-coupled product **3aa** in distinctly different yields (Table 2, entries 1-10). When the substrates with different leaving groups, such as -N(*i*-Pr)$_2$, -NCy$_2$ and -NBn$_2$ were conducted in this reaction, the desired alkene **3aa** was obtained in 77-90% yields under the optimal reaction conditions (Table 2, entries 5, 9 and 10). For the benzylamines with H, methyl (Me), ethyl (Et), *n*-propyl (*n*-Pr), *n*-butyl (*n*-Bu), allyl and phenyl (Ph) as substituents, however, the yield of product **3aa** was dramatically decreased under the same reaction conditions. The relatively higher activity of the substrate with isopropyl (*i*-Pr) might be attributed to the combined effect of electrical property and steric hindrance. Taking the significantly different reactivity of benzylamines with diverse substituents into consideration, we focused our attention on the various benzylamines with leaving group -N(*i*-Pr)$_2$ to study its substrate scope and generality, and the results are summarized in Table 2. Various benzylamines bearing different functional groups such as alkyl and halogen on the phenyl ring can be applied to this unconventional Heck reaction, affording different benzylated adducts **3ba**-**3ma** in 64-95% yields (Table 2, entries 11-22). Apart from common benzyl-substituted amines, as shown in entries 23 and 24, naphthyl substituted amines were also applicable to this transformation, delivering the benzylated alkenes **3na** and **3oa** in excellent yields. We were also glad to see that 2-thienyl-substituted amine **1p** is also compatible with this Heck reaction and proceed efficiently to afford the benzylated alkenes **3pa** in 86% isolated yield (Table 2, entry 25). Moreover, benzylamines with *α*-substituted group **1q** and **1r** were also applicable to this transformation, providing corresponding adducts **3qa** and **3ra** in 76% and 73% yield, respectively (Table 2, entries 26 and 27).

Scheme 3. Deuterium-Labeled Experiments



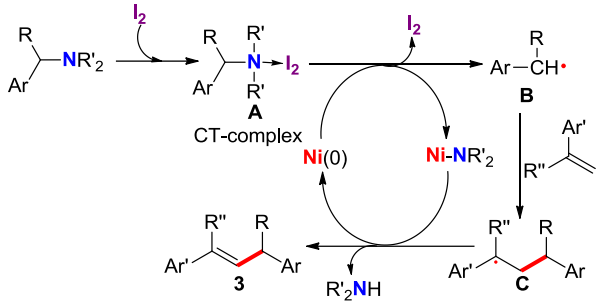
Next, the scope of aryl alkenes **2** was investigated under the optimal reaction conditions. As shown in Scheme 2, both electron donating group and electron withdrawing group on the phenyl ring of symmetrical diarylalkenes were well tolerated, providing the cross-coupling products **3ab**-**3af** in 67-92% isolated yields. In addition to symmetrical arenes, asymmetrical diarylalkenes were also compatible with this transformation, generating the corresponding mixed adducts **3ag**-**3ak** in 82-92% isolated yields but lower selectivity, which may partly attribute to high reaction temperature. Furthermore, *α*-methyl substituted styrene **2l**-**2r** underwent the benzylation reaction in moderate yields, affording the corresponding products as a mixture of terminal and internal according to the different position of carbon-carbon double bond. It is worth noting that when *α*-*tert*-butyl styrene **2s** was submitted to this Heck reaction, the adduct **3as** was obtained in 50% isolated yield and with excellent *Z*-selectivity because of steric hindrance. Unfortunately, only low yields but good *E*-selectivity were obtained for the 4-fluorostyrene **2t** and 4-isobutylstyrene **2u**, besides, other types of alkenes such as acrylate are not compatible with this transformation (For more details see the Supporting Information).

To gain some mechanistic insights into the reaction pathway, a few control experiments were carried out. It is found that the desired adduct **3aa** could not be detected in the presence of

radical scavenger TEMPO (see the supporting information), which indicates that a radical pathway proceeding through a single-electron transfer process is highly possible in this transformation. In addition, when **2a-*d*$_2$** instead of **2a** was added into this system, the benzylated alkene **3aa-*d*** was isolated in 82% yield with 88% **D** (Scheme 3a). The result K_H/K_D = 1.1 of an intermolecular competition KIE experiment indicates that C-H bond cleavage is not involved in the rate-determining step of the Heck-type benzylation process (Scheme 3b).

On the basis of our previous work[10]and mechanistic studies, the most plausible mechanism is illustrated in Figure 1. Initially, an active Ni(0) center which may be generated by the reduction of Ni(II) with phosphine ligand or benzylamine underwent oxidative addition with the amine-I_2 CT complex **A** to form the benzylic radical **B**, then this radical could be captured by the alkene through radical addition process to deliver the radical intermediate **C**, followed by the reduction of Ni^I to Ni^0 with intermediate **C** via single-electron transfer (SET). In the same time, the proton included in the oxidized intermediate **C** was removed by the inner base R'_2N^- to afford the desired product **3** with the release of R'_2NH.

Figure 1. Plausible Reaction Mechanism



CONCLUSION

In summary, we have described a novel nickel-catalyzed Heck type benzylation of aryl alkenes with benzylamines via benzylic C-N bond cleavage, in which the cheap and easily accessible benzylamines were used as benzyl electrophile. Compared with traditional benzyl electrophiles, our reaction avoids the use of base and toxic benzyl halides, providing a practical and efficient approach to obtain various benzylated alkenes. Further application of this strategy is in progress.

EXPERIMENTAL SECTION

General Information. All non-aqueous reactions and manipulations were operated under argon atmosphere. All solvents were dried and distilled before use. TLC was performed on a silica gel-coated plates. NMR spectra were recorded on BRUKER Avence III 400 MHz spectrometers (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C{^{1}H} NMR and 376 MHz for ^{19}F NMR). Chemical shifts were expressed in parts per million (ppm), and coupling constants (*J*) given in Hz. High resolution mass spectra (HRMS) were performed using ESI or EI. GC analysis were performed on Agilent 7890 with OV-225 column or Hp-5 column, and GS-MS analysis performed with Agilent 7890A/5975C GC-MS system. All of the benzylamines and alkenes are known compounds and synthesized according to the reported methods.[11]

General Procedure. A mixture of $NiCl_2$ (3.2 mg, 0.025 mmol), Cy-Xantphos (18.1 mg, 0.03 mmol), *N*,*N*-diisopropylbenzylamine (**1a**) (191 mg, 1.0 mmol), **2a** (90 mg, 0.5 mmol), I_2 (50.8 mg, 0.2 mmol) and anisole (2 mL) was added to a 25 mL flame-dried Young-type tube under argon atmosphere. The mixture was stirred at 150°C for 16 hours. After the reaction finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel and eluted with ethyl acetate/petroleum ether (1/200-1/50) to afford the desired product **3aa**.

Spectroscopic Data of the Products. *Prop-1-ene-1,1,3-triyltribenzene (**3aa**)*. Colorless oil (122 mg, 90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.40 (m, 15H), 6.27 (t, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 142.6, 142.6, 141.1, 139.9, 130.1, 128.6, 128.5, 128.4, 128.2, 127.9, 127.5, 127.3, 127.2, 126.1, 36.1; HRMS (ESI) calcd. for $C_{21}H_{17}$ [M-H]$^-$: 269.1335, found: 269.1317.

*(3-(o-Tolyl)prop-1-ene-1,1-diyl)dibenzene (**3ba**)*. Colorless oil (135 mg, 95 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.40 (m, 3H), 7.11-7.25 (m, 11H), 6.19 (t, *J* = 7.2 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 142.6, 140.0, 139.4, 136.4, 130.2, 130.0, 128.8, 128.4, 128.2, 127.5, 127.3, 127.2, 126.3, 126.2, 33.9, 19.6; HRMS (ESI) calcd. for $C_{22}H_{19}$ [M-H]$^-$: 283.1491, found: 283.1472.

*(3-(m-Tolyl)prop-1-ene-1,1-diyl)dibenzene (**3ca**)*. Colorless oil (122 mg, 86 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.40 (m, 3H), 7.15-7.25 (m, 8H), 6.98-7.01 (m, 3H), 6.26 (t, *J* = 7.6 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 142.6, 142.5, 141.0, 140.0, 138.2, 130.1, 129.3, 128.5. 128.4, 128.2, 128.0, 127.5, 127.2, 127.2, 126.9, 125.6, 36.0, 21.6; HRMS (ESI) calcd. for $C_{22}H_{19}$ [M-H]$^-$: 283.1491, found: 283.1473.

*(3-(p-Tolyl)prop-1-ene-1,1-diyl)dibenzene (**3da**)*. Colorless oil (128 mg, 90 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.39 (m, 3H), 7.16-7.24 (m, 7H), 7.06-7.11 (m, 4H), 6.25 (t, *J* = 7.6 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 142.6, 142.4, 140.0, 138.0, 135.6, 130.1, 129.3, 128.4, 128.2, 128.2, 127.5, 127.2, 127.1, 35.6, 21.1; HRMS (ESI) calcd. for $C_{22}H_{19}$ [M-H]$^-$: 283.1491, found: 283.1472.

*(3-(2-Chlorophenyl)prop-1-ene-1,1-diyl)dibenzene (**3ea**)*. Colorless oil (116 mg, 76 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.40 (m, 4H), 7.10-7.25 (m, 10H), 6.23 (t, *J* = 7.6 Hz, 1H), 3.55 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 143.4, 142.5, 139.8, 138.7, 134.1, 130.3, 130.0, 129.6, 128.5, 128.3, 127.6, 127.5, 127.4, 127.3, 127.0, 126.1, 33.9; HRMS (ESI) calcd. for $C_{21}H_{17}ClNa$ [M+Na]$^+$: 327.0911, found: 327.0906.

*(3-(3-Chlorophenyl)prop-1-ene-1,1-diyl)dibenzene (**3fa**)*. Colorless oil (100 mg, 66 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.40 (m, 3H), 7.14-7.28 (m, 10H), 7.04-7.06 (m, 1H), 6.21 (t, *J* = 8.0 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 143.3, 143.1, 142.3, 139.7, 134.4, 130.0, 129.8, 128.6, 128.5, 128.3, 127.5, 127.4, 127.4, 126.7, 126.7, 126.3, 35.7; HRMS (ESI) calcd. for $C_{21}H_{17}ClNa$ [M+Na]$^+$: 327.0911, found: 327.0908.

*(3-(4-Chlorophenyl)prop-1-ene-1,1-diyl)dibenzene (**3ga**)*. Colorless oil (126 mg, 83 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.40 (m, 3H), 7.20-7.27 (m, 9H), 7.08-7.11 (m, 2H), 6.20 (t, *J* = 7.6 Hz, 1H), 3.41 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 143.1, 142.3, 139.8, 139.5, 131.9, 130.0, 129.8, 128.7, 128.5, 128.3, 127.5, 127.4, 127.3,

127.1, 35.4; HRMS (ESI) calcd. for $C_{21}H_{17}ClNa$ $[M+Na]^+$: 327.0911, found: 327.0910.

(3-(2,6-Dichlorophenyl)prop-1-ene-1,1-diyl)dibenzene ***(3ha)***. Colorless oil (159 mg, 94 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17-7.43 (m, 12H), 7.03-7.07 (m, 1H), 5.97 (t, *J* = 6.8 Hz, 1H), 3.76 (d, *J* = 6.8 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 143.4, 142.4, 140.0, 136.9, 135.7, 130.1, 128.3, 128.3, 128.2, 128.0, 127.5, 127.3, 127.2, 124.6, 32.3; HRMS (ESI) calcd. for $C_{21}H_{17}Cl_2$ $[M+H]^+$: 339.0702, found: 339.0697.

(3-(4-Fluorophenyl)prop-1-ene-1,1-diyl)dibenzene ***(3ia)***. Colorless oil (105 mg, 73 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.19-7.40 (m, 10H), 7.11-7.14 (m, 2H), 6.93-6.99 (m, 2H), 6.22 (t, *J* = 7.6 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 160.3 (d, *J* = 242.4 Hz), 142.8, 142.4, 139.8, 136.7 (d, *J* = 3.1 Hz), 130.0, 129.8 (d, *J* = 7.9 Hz), 128.5, 128.3, 127.6, 127.5, 127.4, 127.3, 115.2 (d, *J* = 21.1 Hz), 35.2; ^{19}F NMR (376 MHz $CDCl_3$) δ -117.3; HRMS (ESI) calcd. for $C_{21}H_{17}FNa$ $[M+Na]^+$: 311.1206, found: 311.1196.

4-(3,3-Diphenylallyl)benzonitrile ***(3ja)***. Colorless oil (112 mg, 76 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.48 (m, 2H), 7.22-7.32 (m, 3H), 7.09-7.19 (m, 9H), 6.10 (t, *J* = 7.6 Hz, 1H), 3.41 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 146.7, 144.0, 142.0, 139.5, 132.4, 129.8, 129.2, 128.5, 128.3, 127.5, 127.4, 125.6, 119.1, 110.0, 36.1; HRMS (ESI) calcd. for $C_{22}H_{17}NNa$ $[M+Na]^+$: 318.1253, found: 318.1247.

(3-(4-Methoxyphenyl)prop-1-ene-1,1-diyl)dibenzene ***(3ka)***. Colorless oil (141 mg, 94 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.39 (m, 3H), 7.18-7.25 (m, 7H), 7.09-7.11 (m, 2H), 6.81-6.85 (m, 2H), 6.24 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.39 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 158.1, 142.6, 142.3, 140.0, 133.1, 130.1, 129.4, 128.4, 128.3, 128.2, 127.5, 127.2, 127.1, 114.0, 55.4, 35.2; HRMS (EI) calcd. for $C_{22}H_{20}O$ $[M]^+$: 300.1509, found: 300.1505.

1-(4-(3,3-Diphenylallyl)phenyl)ethanone ***(3la)***. Colorless oil (125 mg, 80 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.88-7.90 (m, 2H), 7.31-7.41 (m, 3H), 7.20-7.28 (m, 9H), 6.23 (t, *J* = 7.6 Hz, 1H), 3.51 (d, *J* = 7.6 Hz, 2H), 2.57 (s, 3H),; ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 197.9, 146.8, 143.5, 142.2, 139.6, 135.3, 129.9, 128.8, 128.7, 128.5, 128.3, 127.4, 127.4, 126.4, 36.0, 26.7; HRMS (ESI) Calcd for $C_{23}H_{20}NaO$ $[M+Na]^+$: 335.1406, Found:335.1395.

Methyl 4-(3,3-Diphenylallyl)benzoate ***(3ma)***. Colorless oil (105 mg, 64 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.97 (m, 2H), 7.30-7.40 (m, 3H), 7.20-7.28 (m, 9H), 6.24 (t, *J* = 7.6 Hz, 1H), 3.89 (s, 3H), 3.50 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 167.2, 146.6, 143.4, 142.3, 139.7, 129.9, 129.9, 128.5, 128.5, 128.3,128.1, 127.4, 127.4, 127.4, 126.6, 52.1, 36.1; HRMS (ESI) calcd. for $C_{23}H_{20}NaO_2$ $[M+Na]^+$: 351.1356, found: 351.1349.

1-(3,3-Diphenylallyl)naphthalene ***(3na)***. Colorless oil (149 mg, 93 % yield). ^1H NMR (400 MHz, Acetone-d_6) δ 7.87-7.92 (m, 2H), 7.75-7.77 (m, 1H), 7.30-7.49 (m, 9H), 7.17-7.25 (m, 5H), 6.34 (t, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, Acetone-d_6) δ 143.5, 143.3, 140.8, 137.9, 135.0, 132.9, 130.7, 129.6, 129.4, 129.1, 128.5, 128.3, 128.1, 128.0, 127.8, 126.8, 126.7, 126.6, 126.5, 124.7, 34.0; HRMS (ESI) calcd. for $C_{25}H_{19}$ $[M-H]^-$: 319.1491, found: 319.1464.

2-(3,3-Diphenylallyl)naphthalene ***(3oa)***. Colorless oil (141 mg, 88 % yield). ^1H NMR (400 MHz, Acetone-d_6) δ 7.81-7.85 (m, 3H), 7.70 (s, 1H), 7.35-7.48 (m, 6H), 7.21-7.31 (m, 7H), 6.40 (t, *J* = 7.6 Hz, 1H), 3.60 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, Acetone-d_6) δ 143.6, 143.3, 140.8, 139.4, 134.8, 133.2, 130.7, 129.3, 129.1, 129.0, 128.5, 128.4, 128.4, 128.2, 128.1, 128.1, 128.0, 127.1, 126.9, 126.2, 36.7; HRMS (ESI) calcd. for $C_{25}H_{19}$ $[M-H]^-$: 319.1491, found: 319.1467.

2-(3,3-Diphenylallyl)thiophene ***(3pa)***. Colorless oil (119 mg, 86 % yield). ^1H NMR (400 MHz, Acetone-d_6) δ 7.41-7.45 (m, 2H), 7.34-7.38 (m, 1H), 7.21-7.31 (m, 8H), 6.93-6.95 (m, 1H), 6.86-6.87 (m, 1H), 6.31 (t, *J* = 7.6 Hz, 1H), 3.61 (dd, J_1 = 0.8 Hz, J_2 = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, Acetone-d_6) δ 144.3, 143.6, 143.1, 140.4, 130.6, 129.3, 129.1, 128.3, 128.2, 128.1, 127.8, 127.6, 125.3, 124.5, 30.8; HRMS (ESI) Calcd for $C_{19}H_{16}NaS$ $[M+Na]^+$: 299.0865, Found: 299.0868.

But-1-ene-1,1,3-triyltribenzene ***(3qa)***. Colorless oil (108 mg, 76 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.39 (m, 15H), 6.20 (d, *J* = 10.4 Hz, 1H), 3.56-3.64 (m, 1H), 1.37 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 146.3, 142.5, 140.3, 140.2, 134.3, 129.9, 128.6, 128.4, 128.2, 127.4, 127.2, 127.1, 127.1, 126.1, 39.4, 22.5; HRMS (ESI) calcd. for $C_{22}H_{19}$ $[M-H]^-$: 283.1491, found: 283.1469.

Prop-1-ene-1,1,3,3-tetrayltetrabenzene ***(3ra)***. Colorless oil (126 mg, 73 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.14-7.38 (m, 20H), 6.53 (d, *J* = 10.4 Hz, 1H), 4.80 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 144.6, 142.4, 141.7, 139.8, 131.1, 129.9, 128.6, 128.5, 128.4, 128.3, 127.6, 127.4, 127.4, 126.4, 50.7; HRMS (EI) calcd. for $C_{27}H_{22}$ $[M]^+$: 346.1717; found: 346.1713.

4,4'-(3-Phenylprop-1-ene-1,1-diyl)bis(methylbenzene) ***(3ab)***. Colorless oil (131mg, 88 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.26-7.30 (m, 2H), 7.11-7.20 (m, 9H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.19 (t, *J* = 7.6 Hz, 1H), 3.46 (d, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 2.31 (s, 3H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 142.4, 141.3, 140.0, 137.1, 136.9, 136.8, 130.0, 129.1, 128.9, 128.6, 128.6, 127.4, 126.8, 126.0, 36.1, 21.4, 21.2; HRMS (ESI) calcd. for $C_{23}H_{21}$ $[M-H]^-$: 297.1648, found: 297.1625.

4,4'-(3-Phenylprop-1-ene-1,1-diyl)bis(fluorobenzene) ***(3ac)***. Colorless oil (141 mg, 92 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.31 (m, 2H), 7.16-7.22 (m, 7H), 7.05-7.10 (m, 2H), 6.92-6.97 (m, 2H), 6.20 (t, *J* = 7.6 Hz, 1H), 3.43 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 245.2 Hz), 161.0 (d, *J* = 244.9 Hz), 140.8, 140.6, 138.6 (d, *J* = 3.2 Hz), 135.6 (d, *J* = 3.5 Hz), 131.6 (d, *J* = 7.9 Hz), 129.0 (d, *J* = 7.8 Hz), 128.7, 128.5, 128.1, 126.3, 115.4 (d, *J* = 21.2 Hz), 115.0 (d, *J* = 21.2 Hz), 36.0; ^{19}F NMR (376 MHz $CDCl_3$) δ -114.7, -115.3; HRMS (EI) calcd. for $C_{21}H_{16}F_2$ $[M]^+$: 306.1215; Found: 306.1217.

4,4'-(3-Phenylprop-1-ene-1,1-diyl)bis(chlorobenzene) ***(3ad)***. Colorless oil (140 mg, 83 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34-7.37 (m, 2H), 7.27-7.31 (m, 2H), 7.11-7.23 (m, 9H), 6.24 (t, *J* = 7.6 Hz, 1H), 3.43 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 140.6, 140.5, 140.4, 137.8, 133.5, 133.3, 131.4, 129.0, 128.8, 128.7, 128.7, 128.5, 128.4, 126.3, 36.0; HRMS (EI) Calcd for $C_{21}H_{16}Cl_2$ $[M]^+$: 338.0624, Found: 338.0626.

4,4'-(3-Phenylprop-1-ene-1,1-diyl)bis(methoxybenzene) ***(3ae)***. Colorless oil (139 mg, 84 % yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.17-7.21 (m, 2H), 7.05-7.11 (m, 7H), 6.80-6.84 (m, 2H), 6.68-6.72 (m, 2H), 6.04 (t, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 3.37 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR $\{^1H\}$ (100 MHz, $CDCl_3$) δ 158.9, 158.8, 141.6, 141.4, 135.7, 132.4,

131.2, 128.6, 128.6, 128.5, 126.0, 125.9, 113.7, 113.6, 55.4, 55.3, 36.1; HRMS (ESI) calcd. for $C_{23}H_{22}NaO_2$ $[M+Na]^+$: 353.1512, found: 353.1510.

*4,4'-(3-Phenylprop-1-ene-1,1-diyl)bis(N,N-dimethylaniline) (**3af**)*. Yellow oil (119 mg, 67 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.29 (m, 9H), 6.71 (d, *J* = 7.6 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 6.02-6.06 (m, 1H), 3.50 (d, *J* = 7.6 Hz, 2H), 2.95 (s, 6H), 2.90 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 149.8, 149.5, 142.4, 142.1, 131.9, 130.9, 128.6, 128.5, 128.4, 125.8, 123.7, 112.2, 112.1, 40.7, 40.7, 36.1; HRMS (ESI) calcd. for $C_{25}H_{29}N_2$ $[M+H]^+$: 357.2325, found: 357.2318.

*1-Fluoro-4-(1-(4-methoxyphenyl)-3-phenylprop-1-en-1-yl)-benzene (**3ag**, E/Z = 2.0:1)*. Colorless oil (145 mg, 91 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.30 (m, 11H), 6.77-6.95 (m, 2H), 6.12-6.19 (m, 1H), 3.82 (s, 0.68H), 3.76 (s, 2.33H), 3.47 (d, *J* = 7.6 Hz, 0.47H), 3.42 (d, *J* = 7.6 Hz, 1.63H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 244.7 Hz), 160.9 (d, *J* = 244.4 Hz), 159.1, 158.9, 141.1, 139.1 (d, *J* = 3.0 Hz), 136.0 (d, *J* = 3.3 Hz), 135.1, 132.0, 131.6 (d, *J* = 7.9 Hz), 131.1, 129.1 (d, *J* = 7.8 Hz), 128.6, 128.5, 128.5, 127.5, 126.5, 126.2, 115.2 (d, *J* = 21.1 Hz), 114.9 (d, *J* = 21.1 Hz), 113.9, 113.7, 55.4, 55.4, 36.1, 36.0; ^{19}F NMR (376 MHz $CDCl_3$) δ -115.1, -115.7; HRMS (ESI) calcd. for $C_{22}H_{19}FNaO$ $[M+Na]^+$: 341.1312, found: 341.1314.

*(1-(p-Tolyl)prop-1-ene-1,3-diyl)dibenzene (**3ah**, E/Z = 1.5:1)*. Colorless oil (126 mg, 89 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.39 (m, 13H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.23 (t, *J* = 7.6 Hz, 1H), 3.47 (d, *J* = 7.6 Hz, 0.9H), 3.44 (d, *J* = 7.6 Hz, 1.1H), 2.37 (s, 1.3H), 2.31 (s, 1.7H); ^{13}C NMR {^{1}H} (100 MHz, CDCl3) δ 142.8, 142.5, 142.5, 141.2, 141.2, 140.1, 139.8, 137.0, 136.9, 130.1, 130.0, 129.1, 129.0, 128.6, 128.6, 128.4, 128.2, 127.7, 127.5, 127.4, 127.2, 127.1, 127.0, 126.1, 36.1, 36.0, 21.4, 21.2; HRMS (ESI) calcd. for $C_{22}H_{19}$ $[M-H]^-$: 283.1491, found: 283.1470.

*(1-(4-Fluorophenyl)prop-1-ene-1,3-diyl)dibenzene (**3ai**, E/Z = 1.4:1)*. Colorless oil (121 mg, 84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.40 (m, 12H), 7.05-7.09 (m, 0.88H), 6.91-6.96 (m, 1.19H), 6.27 (t, *J* = 8.0 Hz, 0.43H), 6.19 (t, *J* = 7.6 Hz, 0.59H), 3.44 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 244.8 Hz), 160.9 (d, *J* = 244.4 Hz), 142.4, 141.7, 141.6, 141.0, 140.9, 139.8, 138.7 (d, *J* = 3.3 Hz), 135.8 (d, *J* = 3.4 Hz), 131.6 (d, *J* = 7.9 Hz), 130.0, 129.0 (d, *J* = 7.9 Hz), 128.7, 128.7, 128.5, 128.5, 128.3, 128.2, 127.8, 127.8, 127.4, 127.3, 126.2, 126.2, 115.3 (d, *J* = 21.1 Hz), 114.9 (d, *J* = 21.2 Hz), 36.1, 36.0; ^{19}F NMR (376 MHz $CDCl_3$) δ -115.0, -115.6; HRMS (ESI) calcd. for $C_{21}H_{17}FNa$ $[M+Na]^+$: 311.1206, found: 311.1202.

*(1-(4-Chlorophenyl)prop-1-ene-1,3-diyl)dibenzene (**3aj**, E/Z = 1.3:1)*. Colorless oil (125 mg, 82 % yield). ^{1}H NMR (400 MHz, CDCl3) δ 7.15-7.41 (m, 14H), 6.28 (t, *J* = 7.6 Hz, 0.45H), 6.24 (t, *J* = 8.0 Hz, 0.53H), 3.45 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 142.1, 141.5, 141.1, 140.8, 140.7, 139.5, 138.4, 133.2, 133.0, 131.5, 130.0, 128.7, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.4, 128.4, 127.5, 127.5, 127.4, 126.3, 126.2, 36.1, 36.0; HRMS (ESI) calcd. for $C_{21}H_{17}ClNa$ $[M+Na]^+$: 327.0911, found: 327.0904.

*(1-(4-Methoxyphenyl)prop-1-ene-1,3-diyl)dibenzene (**3ak**, E/Z = 2.3:1)*. Colorless oil (138 mg, 92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.39 (m, 12H), 6.77-6.93 (m, 2H), 6.22 (t, *J* = 7.6 Hz, 0.28H), 6.17 (t, *J* = 7.6 Hz, 0.70H), 3.81 (s, 0.83H), 3.76 (s, 2.22H), 3.48 (d, *J* = 7.6 Hz, 0.55H), 3.43 (d, *J* = 7.6 Hz, 1.46H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 159.0, 158.8, 143.0, 142.2, 142.0, 141.3, 141.2, 140.2, 135.3, 132.2, 131.2, 130.0, 128.6, 128.5, 128.5, 128.4, 128.2, 127.6, 127.6, 127.2, 127.1, 126.2, 126.1, 126.1, 113.8, 113.6, 55.4, 55.3, 36.1, 36.0; HRMS (ESI) calcd. for $C_{22}H_{20}NaO$ $[M+Na]^+$: 323.1406, found: 323.1398.

***3al**. A mixture of but-2-ene-1,3-diyldibenzene (Internal product) and but-3-ene-1,3-diyldibenzene (Terminal product)*. Colorless oil (62 mg, 60 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.44 (m, 27.54H), 5.95-5.99 (m, 1.73H), 5.29 (d, *J* = 1.2 Hz, 1H), 5.05 (d, *J* = 1.2 Hz, 1H), 3.55 (d, *J* = 7.6 Hz, 3.64H), 2.79-2.83 (m, 2H), 2.73-2.77 (m, 2H), 2.13 (s, 2.82H), 2.13 (s, 2.45H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 147.9, 143.7, 142.1, 141.2, 141.1, 135.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 127.6, 126.9, 126.9, 126.3, 126.1, 126.0, 125.9, 112.8, 37.4, 35.1, 34.9, 16.1; HRMS (ESI) calcd. for $C_{16}H_{15}$ $[M-H]^-$: 207.1178, found: 207.1160.

***3am**. A mixture of 1-methyl-4-(4-phenylbut-2-en-2-yl)benzene (Internal product) and 1-methyl-4-(4-phenylbut-1-en-2-yl)benzene (Terminal product)*. Colorless oil (60 mg, 54 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.34 (m, 27H), 5.94-5.96 (m, 1H), 5.92-5.94 (m, 1H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.00 (d, *J* = 0.8 Hz, 1H), 3.53 (d, *J* = 7.6 Hz, 4H), 2.76-2.81 (m, 2H), 2.72-2.76 (m, 2H), 2.34 (s, 3H), 2.31 (s, 6H), 2.11 (s, 3H), 2.11 (s, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 147.7, 142.2, 141.3, 140.9, 138.3, 137.3, 136.5, 135.6, 129.2, 129.0, 128.6, 128.6, 128.5, 128.4, 126.1, 126.0, 126.0, 126.0, 125.7, 112.0, 37.4, 35.1, 34.9, 21.2, 21.1, 16.1; HRMS (ESI) calcd. for $C_{17}H_{17}$ $[M-H]^-$: 221.1335, found: 221.1315.

***3an**. A mixture of 1-fluoro-4-(4-phenylbut-2-en-2-yl)benzene (Internal product) and 1-fluoro-4-(4-phenylbut-1-en-2-yl)benzene (Terminal product)*. Colorless oil (61 mg, 54 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.39 (m, 18H), 6.95-7.04 (m, 5H), 5.90-5.92 (m, 0.79H), 5.88-5.90 (m, 0.78H), 5.23 (d, *J* = 0.8 Hz, 1H), 5.04 (d, *J* = 0.8 Hz, 1H), 3.54 (d, *J* = 7.6 Hz, 3.31H), 2.76-2.80 (m, 2H), 2.71-2.76 (m, 2H), 2.11 (s, 2.35H), 2.11(s, 2.46H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 161.1 (d, *J* = 244.7 Hz), 160.7 (d, *J* = 244.0 Hz), 146.8, 141.8, 141.0, 139.7 (d, *J* = 3.1 Hz), 137.2, 134.7, 128.6, 128.5, 128.4, 128.4, 127.7 (d, *J* = 7.7 Hz), 127.2 (d, *J* = 7.8 Hz), 126.7, 126.1, 126.0, 115.1 (d, *J* = 21.2 Hz), 114.8 (d, *J* = 21.1 Hz), 112.7, 37.4, 35.0, 34.7, 16.1; ^{19}F NMR (376 MHz $CDCl_3$) δ -115.2, -116.3; HRMS (ESI) calcd. for $C_{16}H_{16}F$ $[M+H]^+$: 227.1231, found: 227.1227.

***3ao**. A mixture of 1-chloro-4-(4-phenylbut-2-en-2-yl)benzene (Internal product) and 1-chloro-4-(4-phenylbut-1-en-2-yl)benzene (Terminal product)*. Colorless oil (61 mg, 50 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.35 (m, 16H), 5.94-5.97 (m, 0.40H), 5.92-5.94 (m, 0.40H), 5.26 (d, *J* = 0.8 Hz, 1H), 5.06 (d, *J* = 0.8 Hz, 1H), 3.53 (d, *J* = 7.6 Hz, 1.66H), 2.75-2.79 (m, 2H), 2.71-2.75 (m, 2H), 2.10 (s, 1.32H), 2.10 (s, 1.15H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 146.8, 142.1, 141.8, 140.9, 139.6, 134.7, 133.3, 132.6, 128.7, 128.6, 128.5, 128.5, 128.5, 128.4, 127.6, 127.4, 127.1, 126.2, 126.1, 113.4, 37.3, 35.1, 34.7, 16.0; HRMS (ESI) calcd. for $C_{16}H_{16}Cl$ $[M+H]^+$: 243.0936, found: 243.0930.

***3ap**. A mixture of 1-methoxy-4-(4-phenylbut-2-en-2-yl)benzene (Internal product) and 1-methoxy-4-(4-phenylbut-1-en-2-yl)benzene (Terminal product)*. Colorless oil (67 mg, 56 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): internal isomer: δ 7.19-7.35 (m, 7H), 6.83-6.85 (m, 2H), 5.90-5.91 (m, 0.51H), 5.87-5.89 (m, 0.49H), 3.78 (s, 3H), 3.54 (d, *J* = 7.2 Hz, 2H), 2.11 (s, 1.62H), 2.11 (s, 1.43H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 158.7, 141.4, 136.3, 135.1, 128.6, 128.6, 126.9,

126.0, 125.3, 113.7, 55.4, 35.1, 16.1; HRMS (ESI) calcd. for $C_{17}H_{19}O$ $[M+H]^+$: 239.1430, found: 239.1426.

3aq. *A mixture of 1-isobutyl-4-(4-phenylbut-2-en-2-yl)benzene (Internal product) and 1-isobutyl-4-(4-phenylbut-1-en-2-yl)benzene (Terminal product)*. Colorless oil (75 mg, 57 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.36 (m, 21H), 7.06-7.12 (m, 6H), 5.96-5.98 (m, 1H), 5.94-5.96 (m, 1H), 5.28 (d, *J* = 1.2 Hz, 1H), 5.01 (d, *J* = 0.8 Hz, 1H), 3.54 (d, *J* = 7.6 Hz, 4H), 2.75-2.81 (m, 4H), 2.46 (d, *J* = 7.2 Hz, 2H), 2.43 (d, *J* = 7.2 Hz, 4H), 2.12 (s, 3H), 2.12 (s, 3H), 1.79-1.90 (m, 3H), 0.90 (d, *J* = 6.8 Hz, 12H), 0.88 (s, 6H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 147.7, 142.2, 141.3, 141.1, 141.0, 140.4, 138.4, 135.6, 129.2, 129.1, 128.6, 128.5, 128.4, 126.0, 126.0, 125.9, 125.9, 125.5, 111.9, 45.2, 45.2, 37.4, 35.1, 35.0, 30.4, 22.5, 16.0; HRMS (ESI) calcd. for $C_{20}H_{23}$ $[M-H]^-$: 263.1804, found: 263.1783.

3ar. *A mixture of 1-(4-phenylbut-2-en-2-yl)-4-(trifluoromethyl)benzene (Internal product) and 1-(4-phenylbut-1-en-2-yl)-4-(trifluoromethyl)benzene (Terminal product)*. Colorless oil (70 mg, 51 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.59 (m, 12H), 7.14-7.32 (m, 15H), 6.03-6.05 (m, 1H), 6.01-6.03 (m, 1H), 5.34 (s, 1H), 5.15 (d, *J* = 1.2 Hz, 1H), 3.56 (d, *J* = 7.2 Hz, 4H), 2.79-2.83 (m, 2H), 2.72-2.76 (m, 2H), 2.14 (s, 3H), 2.14 (s, 3H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 147.2, 146.9, 144.9, 141.6, 140.6, 134.8, 129.1, 129.0, 128.7 (q, *J* = 3.5 Hz), 126.6, 126.3, 126.2, 126.1, 125.8, 125.8, 125.5 (q, *J* = 3.7 Hz), 125.3 (q, *J* = 3.7 Hz), 123.1, 123.1, 114.8, 37.2, 35.2, 34.7, 16.0; ^{19}F NMR (376 MHz $CDCl_3$) δ -62.3, -62.4; HRMS (ESI) calcd. for $C_{17}H_{15}F_3Na$ $[M+Na]^+$: 299.1018, found: 299.1014.

*(4,4-Dimethylpent-2-ene-1,3-diyl)dibenzene (**3as**, Z/E > 20:1)*. Colorless oil (63 mg, 50 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.33 (m, 2H), 7.22-7.26 (m, 3H), 7.12-7.17 (m, 1H), 7.06-7.09 (m, 4H), 5.70 (t, *J* = 7.2 Hz, 1H), 2.97 (d, *J* = 7.2 Hz, 2H), 1.08 (s, 9H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 151.4, 141.9, 140.5, 130.0, 128.5, 128.4, 127.8, 126.3, 125.8, 122.9, 36.2, 35.7, 29.9; HRMS (EI) calcd for $C_{19}H_{22}[M]^+$: 250.1717, found: 250.1734.

*1-Fluoro-4-(3-phenylprop-1-en-1-yl)benzene (**3at**, E/Z > 20:1)*. Colorless oil (27 mg, 25 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.33 (m, 7H), 6.94-6.99 (m, 2H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.22-6.30 (m, 1H), 3.52 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 160.9 (d, *J* = 244.5 Hz), 140.1, 133.6 (d, *J* = 3.1 Hz), 129.9, 129.1 (double peak), 128.7, 128.6, 127.6 (d, *J* = 7.7 Hz), 126.3, 115.3 (d, *J* = 21.3 Hz), 39.3; ^{19}F NMR (376 MHz $CDCl_3$) δ -115.3; HRMS (ESI) calcd for $C_{15}H_{12}F$ $[M-H]^-$: 211.0928; found, 211.0920.

*1-Isobutyl-4-(3-phenylprop-1-en-1-yl)benzene (**3au**, E/Z > 20:1)*. Colorless oil (33 mg, 26 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.31 (m, 7H), 7.05-7.07 (m, 2H), 6.41 (d, *J* = 15.6 Hz, 1H), 6.26-6.34 (m, 1H), 3.51 (d, *J* = 6.8 Hz, 2H), 2.42 (d, *J* = 7.2 Hz, 2H), 1.78-1.88 (m, 1H), 0.87 (d, *J* = 6.4 Hz, 6H) ; ^{13}C NMR {^{1}H} (100 MHz, $CDCl_3$) δ 140.9, 140.5, 135.1, 131.1, 129.4, 128.8, 128.6, 128.3, 126.3, 126.0, 45.3, 39.5, 30.4, 22.5; HRMS (EI) calcd for $C_{19}H_{22}[M]^+$: 250.1717, found: 250.1728.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at http://pubs.acs.org.

Reaction optimization, mechanistic studies and copies for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR of the products (PDF).

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The authors declare no competing financial interest.

ACKNOWLEDGMENT

This research was supported by the National Natural Science Foundation of China (21672199 and 21790333), the CAS Interdisciplinary Innovation Team, the Anhui provincial Natural Science Foundation (1708085MB28), and the Fundamental Research Funds for the Central Universities.

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