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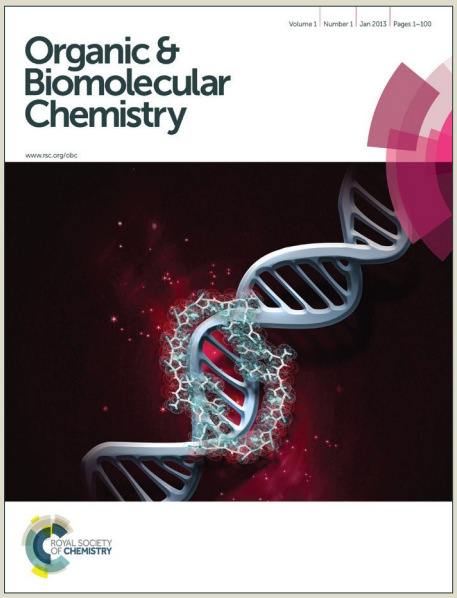

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ARTICLE

Pd(0)-Catalyzed cross-coupling of allyl halides with α–diazocarbonyl compounds or *N*-mesylhydrazones: synthesis of 1,3-diene compounds

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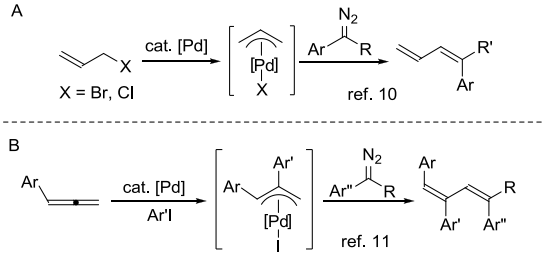
With palladium catalysis, allyl bromides or chlorides react with α-diazocarbonyl compounds or *N*-mesylhydrazones to afford 1,3-diene derivatives. The reaction represents a novel and efficient method for the synthesis of 1,3-butadiene derivatives. Mechanistically, the reaction is proposed to follow a pathway involving the formation of π-allylic palladium carbene complex and subsequent migratory insertion.

Introduction

Conjugated 1,3-dienes are basic and ubiquitous structure units existing in natural products and functional materials.[1] They are also important intermediates in organic synthesis.[2] Due to the intensive applications of substrates with 1,3-diene motifs in various transformations, great efforts have been devoted to the preparation of 1,3-diene products.[3] Among the many traditional methods, the Wittig reaction or its variant olefination methods represent convenient approaches toward conjugated dienes from ketones or aldehydes.[4] Recently, the coupling reaction of two vinyl substrates[5] and the hydrovinylation of alkynes[6] have been significantly developed which allows for the direct and stereo-selective preparation of 1,3-dienes. Moreover, palladium-catalyzed coupling reaction of vinyl halides with structurally defined organometallic alkenes and Mizoroki-Heck reaction of olefins with vinyl halides represents alternative approaches toward 1,3-dienes.[7] Despite the various well-established methods, the synthesis of conjugated dienes, especially those with different substitution patterns, is still highly demanded.

On the other hand, the transition-metal-catalyzed transformations involving metal carbene migratory insertion process have been established as a powerful strategy for carbon carbon bond formations, especially for the C=C double bond constructions.[8,9] Both stable diazo compounds and non-stabilized diazo compounds generated in situ from *N*-tosylhydrazones have been explored extensively in recent years as versatile carbene precursors in these reactions. The cross-coupling reaction involving carbene migratory insertion can also be applied to the synthesis of 1,3-diene formations. In 2008, we have communicated the Pd-catalyzed reaction of allyl halides with α-diazocarbonyl compounds to form 1,3-diene products (Scheme 1A).[10] The reaction is proposed to involve π-allylic palladium complexes and palladium carbene migratory insertions. Late we reported a palladium-catalyzed three-component reaction of allenes, aryl iodides and diazo compounds. The reaction mechanism involves similar π-allylic palladium complexes and migratory insertion of allyl group (Scheme 1B).[11] More recently, we have further expanded this type of cross-coupling reactions to the non-stabilized diazo compounds, which are generated *in situ* from the corresponding *N*-mesylhydrazones. In this article we report the details of these studies.



Scheme 1 1,3-Diene synthesis through Pd-catalyzed reaction of π-allylic palladium complexes with diazo compounds

Results and discussion

The investigation started with the Pd-catalyzed reaction of allyl bromide **1a** with methyl phenyldiazoacetate **2a**. Through extensive optimization of the reaction conditions, it was concluded that the 1,3-diene product **3a** could be isolated in 77% yield with $Pd(OAc)_2$ (5 mol%) as the catalyst, Et_3N as the base, MeCN as the solvent at 25 °C for 12 h (eq 1).[12] It is worth

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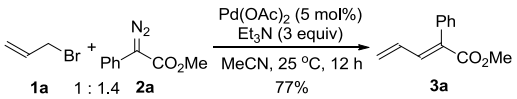
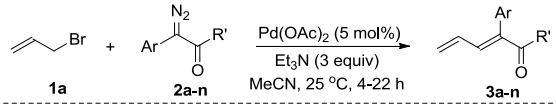
mentioning that in the absence of palladium catalyst no reaction occurred under the otherwise identical conditions.



(1)

With the optimized reaction conditions, the substrate scope of the reaction was studied with allyl bromide and a series of aryldiazoacetates and aryldiazoacetones **2a-n** (Table 2). The reaction tolerates various substitutions on the aromatic ring and moderate to good yields of the 1,3-butadiene products **3a-n** could be obtained with high stereoselectivity. It is worth mentioning that the reaction under identical conditions with ethyl diazoacetate (EDA) resulted in complex mixture.

Table 2 Scope of diazocarbonyl compounds for the $Pd(OAc)_2$-catalyzed reaction with allyl bromide[a]



3a, Ar = Ph, 12 h, 77% (*E*:*Z* >20:1)
3b, Ar = *p*-MeC_6H_4, 12 h, 77% (*E*:*Z* = 5:1)
3c, Ar = *p*-$MeOC_6H_4$, 4 h, 53% (*E*:*Z* >20:1)
3d, Ar = *m*-$MeOC_6H_4$, 17 h, 71% (*E*:*Z* = 5:1)
3e, Ar = *o*-ClC_6H_4, 7 h, 61% (*E*:*Z* = 10:1)
3f, Ar = *p*-ClC_6H_4, 12 h, 73% (*E*:*Z* = 10:1)
3g, Ar = *m*, *p*-$Cl_2C_6H_3$, 22 h, 50% (*E*:*Z* = 10:1)

3h, Ar = Ph, 8 h, 55% (*E*:*Z* >20:1)[b]
3i, Ar = *p*-ClC_6H_4, 20 h, 68% (*E*:*Z* >20:1)[b]
3j, Ar = *m*-ClC_6H_4, 4 h, 70% (*E*:*Z* >20:1)[b,c]
3k, Ar = *p*-BrC_6H_4, 4 h, 63% (*E*:*Z* >20:1)[b,c]
3l, Ar = *m*,*p*-$Cl_2C_6H_3$, 4 h, 60% (*E*:*Z* >20:1)[b,c]

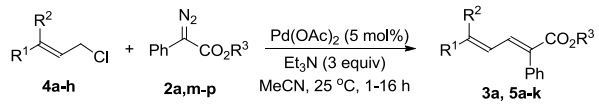
3m, 4 h, 77% (*E*:*Z* >20:1)

3n, 5 h, 69% (*E*:*Z* >20:1)

[a] Unless otherwise noted, the reaction was carried out with 0.3 mmol of **1a**, 0.42 mmol of **2a-n**, and 0.9 mmol of Et_3N in 5 mL MeCN. All the yields refer to the isolated products after silica gel column chromatography. The product ratio was determined by GC-MS or 1H NMR of the crude product. [b] The reaction was carried out with 1 equiv of diazo substrate and 3 equiv of allyl bromide. [c] The reaction was carried out at 60 °C.

The scope of allyl substrates was next investigated. Under the identical reaction conditions, the reaction of methyl phenyldiazoacetate **2a** with substituted allyl bromide resulted in low yield of the expected diene products. Gratifyingly, the reaction with substituted allyl chloride afforded the 1,3-diene product smoothly under the same reaction conditions. As summarized in Table 3, a series of substituted allyl chlorides **4a-h** were submitted to the reaction with methyl phenyldiazoacetate **2a** under the same reaction conditions. The corresponding 1,3-diene products were obtained in moderately good yields and high selectivity. It is worth mentioning that both alkyl and aryl substituted allyl chlorides are suitable substrates under the current reaction conditions.

Table 3 Scope of the $Pd(OAc)_2$-catalyzed reaction with allyl chlorides[a]



3a, $R^1 = R^2$ = H, 12 h, 74% (*E*:*Z* >20:1)
5a, R^1 = Me, R^2 = H, 11 h, 63% (*E*:*Z* = 10:1)
5b, R^1 = Me, R^2 = Me, 1 h, 72% (*E*:*Z* >20:1)
5c, $R^1 = R^2$ = -C_5H_{10}-, 2 h, 71% (*E*:*Z* >20:1)
5d, R^1 = Ph, R^2 = H, 4 h, 66% (*E*:*Z* >20:1)
5e, R^1 = *p*-MeC_6H_4, R^2 = H, 14 h, 57% (*E*:*Z* >20:1)
5f, R^1 = *p*-ClC_6H_4, R^2 = H, 3 h, 65% (*E*:*Z* >20:1)
5g, R^1 = Ph, R^2 = Ph, 15 h, 65% (*E*:*Z* >20:1)

5h,16 h, 70% (*E*:*Z* >20:1)

5i,16 h, 60% (*E*:*Z* >20:1)

5j,7 h, 58% (*E*:*Z* >20:1)

5k,3 h, 51% (*E*:*Z* >20:1)

[a] The reaction follows the general procedure as described in Table 2.

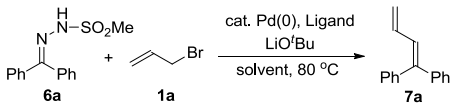
Encouraged by the above $Pd(OAc)_2$-catalyzed coupling reaction with α-diazocarbonyl compounds, we further proceeded to expand the reaction to the *N*-tosylhydrazones, which have been extensively explored as cross-coupling partners in transition-metal-catalyzed reactions in recent years.[8,13] However, the transition-metal-catalyzed cross coupling of *N*-tosylhydrazones with allyl halides has not been reported.

In the initial studies, we found that instead of producing dienes products, *N*-allylated product of *N*-tosylhydrazone were found as the main products. Those products could be formed *via* nucleophilic attack of *N*-anion of *N*-tosylhydrazone to allyl halide after deprotonation. We reasoned that these *N*-allylated products might be avoided by reducing the nucleophilicity of the nitrogen. Since $MeSO_2$ (mesyl) group has stronger electron-withdrawing ability than its tosyl counterpart,[14] we thus focused our efforts on *N*-mesylhydrazones for the coupling reaction with allyl halides.

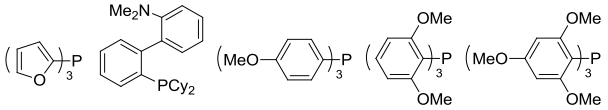
At the outset of the investigation, we chose diphenyl *N*-mesylhydrazone as the carbene precursor and allyl bromide as the coupling partner to optimize the reaction conditions. Thus, *N*-mesylhydrazone **6a** (0.2 mmol) and allyl bromide **1a** (0.2 mmol) were treated with $Pd_2(dba)_3$ (2.5 mol%), tris(2-furyl)phosphine **L1** (20 mol%) and LiO^tBu (2 equiv) in dioxane at 80 °C for 5 h (Table 4). Gratifyingly, the diene product **7a** was isolated in 20 % yield under the initial conditions (Table 4, entry 1). We then optimized the amount of LiO^tBu (entries 2, 3 and 7) and found that 5 equiv of LiO^tBu was optimal, affording the product in 47 % yield. Further screening of the solvent suggested that THF was the most effective one while toluene gave poorest result (entries 4-6 and 8). Through increasing the amount of allyl bromide from 1 equiv to 1.5 equiv and adding the *N*-mesylhydrazone dropwise into the reaction mixture, we

could isolate the product in 64 % (entry 9). Finally, the effect of ligands was investigated (entries 10-13), showing that tris(2,6-dimethoxyphenyl)phosphine **L4** afforded the best results to give the diene product in 73% yield, while the ligands **L2**, **L3** and **L5** were less effective.

Table 4 Optimization of the Reaction Conditions[a]



Entry	**1a** (equiv)	Pd(0) /L	solvent (mL)	LiO^{t}Bu (equiv)	yield[b] (%)
1	1.0	$Pd_2(dba)_3$/**L1**	dioxane (2)	2	20
2	1.0	$Pd_2(dba)_3$/**L1**	dioxane (2)	3	27
3	1.0	$Pd_2(dba)_3$/**L1**	dioxane (2)	4	42
4	1.0	$Pd_2(dba)_3$/**L1**	dioxane (2)	4	13
5	1.0	$Pd_2(dba)_3$/**L1**	DCE (2)	4	42
6	1.0	$Pd_2(dba)_3$/**L1**	THF (2)	4	48
7	1.0	$Pd_2(dba)_3$/**L1**	dioxane (2)	5	47
8	1.0	$Pd_2(dba)_3$/**L1**	THF (2)	5	53
9	1.5	$Pd_2(dba)_3$/**L1**	THF (5)	5	64
10[c]	2.0	$Pd_2(dba)_3$/**L1**	THF (5)	5	46
11[c]	1.2	$Pd_2(dba)_3$/**L1**	THF (5)	5	36
12[c]	1.5	$Pd_2(dba)_3$/**L2**	THF (5)	5	32
13[c]	1.5	$Pd_2(dba)_3$/**L3**	THF (5)	5	58
14[c]	1.5	$Pd_2(dba)_3$/**L4**	THF (5)	5	73
15[c]	1.5	$Pd_2(dba)_3$/**L5**	THF (5)	5	70

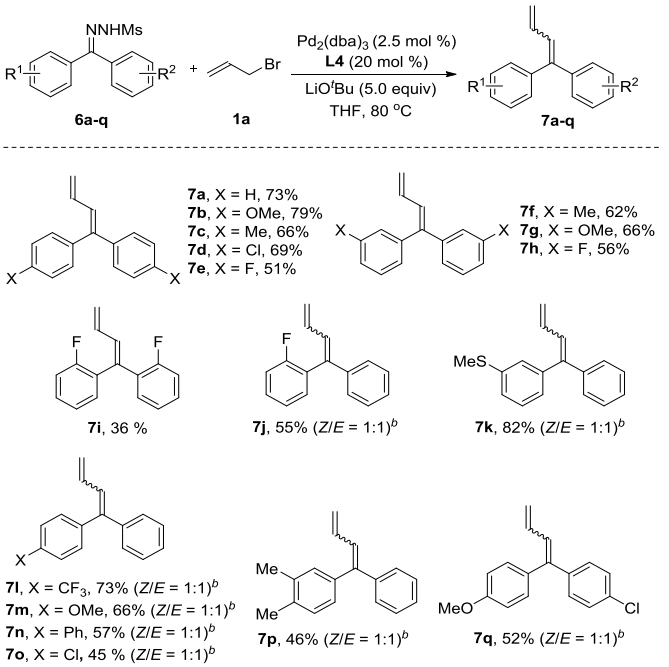


[a] If not otherwise noted, reaction conditions are as follows: **6a** (0.20 mmol), **1a** (0.20 mmol), $Pd_2(dba)_3$ (5 mol%), ligand (20 mol%) and LiO^{t}Bu in a solvent stirred at 80 °C for 5 h. [b] Isolated product with silica gel column chromatography. [c] 1a was added dropwise into the reaction system.

With the optimized reaction conditions (Table 4, entry 14), the scope of the *N*-mesylhydrazones was first examined (Table 5). Symmetrical diaryl *N*-mesylhydrazones with *para*- and *meta*-substituents **6a-i** worked well to give 1,1-diaryl butadienes in moderate to good yields regardless of their electronic properties. The *N*-mesylhydrazone which bears two *ortho* fluorine-substituents was a poor substrate for this reaction which gave the corresponding product **7i** in only 36% yield probably due to its steric hindrance. The unsymmetrical diaryl *N*-mesylhydrazones **6j-q** which have two different substituted aryl rings could also be compatible by reacting with allyl bromides, both electronic-donating and electronic-withdrawing groups were well tolerated.

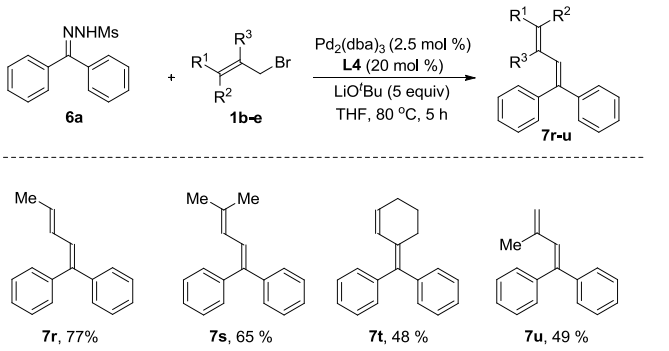
Next, the scope of allyl halides was examined under the same reaction conditions (Table 6). Allyl bromides with different substitution patterns **1b-e** could be well tolerated. For example, *trans*-crotyl bromide, prenyl bromide and 3-bromo-2-methylpropene all gave the corresponding 1,3-butadienes **7r-s**, **7u** in moderate to good yields. 3-Bromo-1-cyclohexene **1d** could also be compatible with the reaction to give the product in 48 % yields

Table 5 Scope of *N*-mesylhydrazone[a]



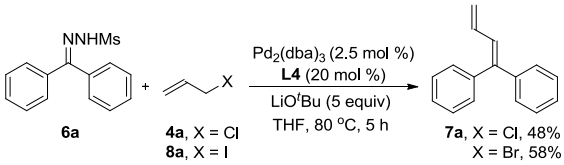
[a] Reaction conditions: **6a-q** (0.20 mmol), **1a** (0.30 mmol), $Pd_2(dba)_3$ (2.5 mol%), **L4** (20 mol%) and LiO^{t}Bu (5 equiv) in THF (5 mL) stirred at 80 ℃ for 5 h. All the yields refer to isolated products with silica gel column chromatography. [b] The *Z*/*E* ratio was determined by ^{1}H NMR.

Table 6 Scope of Allyl Bromides[a]



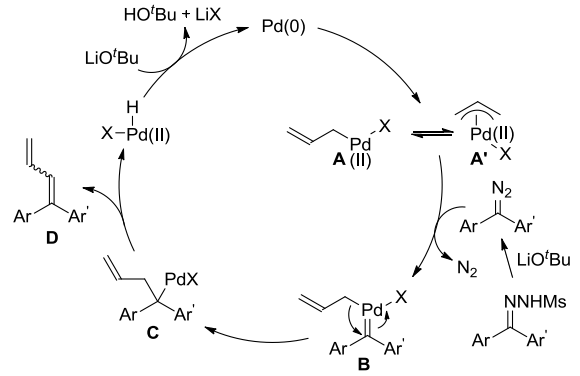
[a] Reaction conditions: **6a** (0.20 mmol), **1b-e** (0.30 mmol), $Pd_2(dba)_3$ (2.5 mol%), **L4** (20 mol%) and LiO^{t}Bu (5 equiv) in THF (5 mL) stirred at 80 ℃ for 5 h.

Finally, both allyl chloride **4a** and allyl iodide **8a** reacted with *N*-mesylhydrazones to give 1,3-butadiene **7a** in good yields (Scheme 2).



Scheme 2 Reaction of allyl chloride and iodide

As illustrated in Scheme 3, a plausible reaction mechanism is proposed according to our understanding on the palladium-catalyzed carbene-based cross-coupling reactions.[8] First, oxidative addition of Pd(0) to allyl halide generates η^1-allylpalladium complex **A**, which is in equilibrium with η^3-allylpalladium complex **A'**. In the case of coupling with *N*-mesylhydrazone, the diazo compound is generated in situ from *N*-mesylhydrazone in the presence of LiO^{t}Bu. Reaction of the diazo compound with π-allyllic palladium complex leads to the formation of palladium carbene complex **B**.[8,15] Migratory insertion of the allyl group of **B** to the carbenic carbon produces species **C**, from which β-H elimination occurs to generate 1,3-butadiene product and regenerate Pd(0) catalyst.



Scheme 3 Proposed reaction mechanism

Conclusion

In conclusion, we have developed a new route towards 1,3-diene compounds through palladium-catalyzed coupling reaction of allyl halides with α-diazocarbonyl compounds or *N*-mesylhydrazones.[16] Mechanistically, the reaction may involve a π-allylic migratory insertion of palladium carbene intermediate. Further studies on the development of transition-metal-catalyzed carbene-based coupling reaction are currently underway in our laboratory and the results will be reported in due course.

Experimental

General methods.

All reactions were performed under a nitrogen atmosphere in oven-dried reaction flasks. All solvents were freshly distilled and degassed according to the handbook *Purification of Laboratory Chemicals* (4th Edition, B. Heinemann, W. L. F. Armarego and D. D. Perrin). The boiling point of petroleum ether was between 60 and 70 °C. For chromatography, 200-300 mesh silica gel was employed. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C{^{1}H}NMR spectra are reported relative to the chemical shift of tetramethylsilane (TMS): chemical shifts (δ) were reported in ppm, and coupling constants (J) are in Hertz (Hz). IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. PE: petroleum either; EA: ethyl acetate. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General Procedure for the Pd(OAc)$_2$-catalyzed reaction of allylic halides with diazo compounds.

To a solution of allylic halide (0.3 mmol) in anhydrous CH_3CN (5 mL) was added Et_3N (0.9 mmol) and $Pd(OAc)_2$ (0.015 mmol) at room temperature. After 5 minutes, diazo compound (0.42 mmol) was added and the mixture was stirred for several hours at 25 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, solvent was removed under vacuum, and the crude product was purified by column chromatography.

*(E)-Methyl 2-phenylpenta-2,4-dienoate (**3a**).*[17] Yield 77% (44 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 5.42 (ddd, J = 0.6, 1.5, 10.8 Hz, 1H), 5.66 (ddd, J = 0.6, 1.5, 16.8 Hz, 1H), 6.39 (ddd, J = 10.2, 11.4, 16.8 Hz, 1H), 7.21-7.26 (m, 2H), 7.32-7.42 (m, 3H), 7.46 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 125.7, 127.7, 127.9, 128.2, 130.1, 133.1, 134.8, 140.7, 167.8.

*(E)-Methyl 2-p-tolylpenta-2,4-dienoate (**3b**).* Yield 77% (47 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1718, 1514, 1435, 1245 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 3.76 (s, 3H), 5.40 (ddd, J = 0.6, 1.5, 9.9 Hz, 1H), 5.65 (ddd, J = 0.6, 1.5, 16.8 Hz, 1H), 6.41 (ddd, J = 10.2, 11.4, 16.8 Hz, 1H), 7.11-7.28 (M, 5H), 7.45 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 52.1, 125.4, 128.7, 130.0, 131.9, 133.2, 133.3，137.5, 140.4, 168.0; EI-MS (*m/z*, relative intensity): 202 (M^+, 30), 143 (100). HRMS (EI) calcd for $C_{13}H_{14}O_2^+$ $[M]^+$: 202.0994; Found: 202.0992.

*(E)-Methyl 2-(4-methoxyphenyl)penta-2,4-dienoate (**3c**).* Yield 53% (35 mg, purified by silica gel column chromatography using PE:EA = 20:1 as eluent, R_f = 0.35); colorless oil; IR (neat) 1736, 1613, 1513, 1247 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.84 (s, 3H), 5.41 (ddd, J = 0.6, 1.8, 10.2 Hz, 1H), 5.66 (ddd, J = 0.6, 1.8, 16.5 Hz, 1H), 6.43 (ddd, J = 10.2, 11.4, 16.5 Hz, 1H), 6.90-6.95 (m, 2H), 7.14-7.19 (m, 2H), 7.43 (d, J = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 55.2, 113.4, 125.3, 127.0, 131.3, 132.7, 133.3, 140.3, 159.1, 168.1; EI-MS (*m/z*, relative intensity): 218 (M^+, 20), 159 (48), 121(100). HRMS (EI) calcd for $C_{13}H_{14}O_3^+$ $[M]^+$: 218.0943; Found: 218.0943.

*(E)-Methyl 2-(3-methoxyphenyl)penta-2,4-dienoate (**3d**).* Yield 71% (47 mg, purified by silica gel column chromatography using PE:EA = 20:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1713,

1601, 1585, 1246 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.82 (s, 3H), 5.42 (ddd, *J* = 1.2, 1.8, 10.2 Hz, 1H), 5.66 (ddd, *J* = 0.9, 1.8, 16.8 Hz, 1H), 6.40 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 6.76-6.82 (m, 2H), 6.88-6.91 (m, 1H), 7.27-7.33 (m, 1H), 7.45 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 55.2, 113.2, 115.7, 122.5, 125.8, 129.0, 133.0, 133.1, 136.1, 140.8, 159.1, 167.7; EI-MS (*m/z*, relative intensity): 218 (M^+, 50), 159 (100). HRMS (EI) calcd for $C_{13}H_{14}O_3^+$ $[M]^+$: 218.0943; Found: 218.0944.

*(E)-Methyl 2-(2-chlorophenyl)penta-2,4-dienoate (**3e**).* Yield 61% (41 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); colorless oil; IR (neat) 1715, 1629, 1434, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.46 (dd, *J* = 1.5, 9.9 Hz, 1H), 5.70 (dd, *J* = 1.5, 16.8 Hz, 1H), 6.17 (ddd, *J* = 10.2, 11.4, 17.1 Hz, 1H), 7.17-7.46 (m, 4H), 7.51 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 126.5, 126.6, 129.3, 129.4, 131.0, 131.7, 132.5, 134.0, 134.1, 141.8, 167.0; EI-MS (*m/z*, relative intensity): 222 (M^+, 17), 187 (59), 128 (100). HRMS (EI) calcd for $C_{12}H_{11}O_2Cl^+$ $[M]^+$: 222.0448; Found: 222.0444.

*(E)-Methyl 2-(4-chlorophenyl)penta-2,4-dienoate (**3f**).* Yield 73% (49 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); colorless oil; IR (neat) 1713, 1624, 1493, 1420, 1242 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.78 (s, 3H), 5.46 (dd, *J* = 1.2, 10.2 Hz, 1H), 5.69 (dd, *J* = 0.9, 16.8 Hz, 1H), 6.36 (ddd, *J* = 10.2, 11.4, 16.8 Hz, 1H), 7.15-7.19 (m, 2H), 7.35-7.38 (m, 2H), 7.47 (d, *J* = 11.4 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.3, 126.4, 128.2, 131.5, 131.6, 131.9, 132.7, 133.1, 141.2, 167.4; EI-MS (*m/z*, relative intensity): 222 (M^+, 28), 128 (100). HRMS (EI) calcd for $C_{12}H_{11}O_2Cl^+$ $[M]^+$: 222.0448; Found: 222.0449.

*(E)-Methyl 2-(3,4-dichlorophenyl)penta-2,4-dienoate (**3g**).* Yield 50 % (39 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); yellow oil; IR (neat) 1714, 1580, 1475, 1244 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.52 (d, *J* = 10.5 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.34 (ddd, *J* = 10.5, 11.4, 16.8 Hz, 1H), 7.07 (dd, *J* = 1.8, 8.4 Hz, 1H), 7.27-7.34 (m, 1H), 7.45-7.51 (m, 2H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.4, 127.3, 128.0, 129.6, 130.0, 130.7, 132.0, 132.2, 132.4, 134.7, 141.8, 167.0; EI-MS (*m/z*, relative intensity): 256 (M^+, 23), 162 (100). HRMS (EI) calcd for $C_{12}H_{10}O_2Cl_2^+$ $[M]^+$: 256.0058; Found: 256.0065.

*(E)-3-Phenylhexa-3,5-dien-2-one (**3h**).* Yield 55% (28 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1665, 1615, 1249, 1226 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 3H), 5.45 (d, *J* = 9.9 Hz, 1H), 5.70 (d, *J* = 16.8 Hz, 1H), 6.34 (td, *J* = 10.5, 16.8 Hz, 1H), 7.14-7.43 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.6, 126.1, 127.7, 128.2, 129.9, 133.5, 135.5, 139.4, 141.8, 198.8; EI-MS (*m/z*, relative intensity): 172 (M^+, 36), 129 (100). HRMS (EI) calcd for $C_{12}H_{12}O^+$ $[M]^+$: 172.0888; Found: 172.0884.

*(E)-3-(4-Chlorophenyl)hexa-3,5-dien-2-one (**3i**).* Yield 68% (42 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1668, 1619, 1491, 1250, 1090 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 3H), 5.49 (d, *J* = 10.2 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.2, 16.8 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.26-7.29 (m, 1H), 7.38 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 126.8, 128.4, 131.3, 133.2, 133.7, 133.8, 140.3, 140.7, 198.3; EI-MS (*m/z*, relative intensity): 206 (M^+, 45), 128 (75), 43 (100). HRMS (EI) calcd for $C_{12}H_{11}OCl^+$ $[M]^+$: 206.0498; Found: 206.0496.

*(E)-3-(3-Chlorophenyl)hexa-3,5-dien-2-one (**3j**).* Yield 70% (44 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1668, 1621, 1423, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.51 (d, *J* = 10.2 Hz, 1H), 5.74 (d, *J* = 16.8 Hz, 1H), 6.32 (td, *J* = 10.8, 16.8 Hz, 1H), 7.02-7.05 (m, 1H), 7.15 (s, 1H), 7.26–7.35 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.2, 127.0, 127.9, 128.2, 129.5, 129.9, 133.2, 134.1, 137.2, 140.4, 140.5, 198.1; EI-MS (*m/z*, relative intensity): 206 (M^+, 22), 128 (49), 43 (100). HRMS (EI) calcd for $C_{12}H_{11}OCl^+$ $[M]^+$: 206.0498; Found: 206.0494.

*(E)-3-(4-Bromophenyl)hexa-3,5-dien-2-one (**3k**).* Yield 63% (48 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); colorless oil; IR (neat) 1667, 1615, 1487, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 5.49 (d, *J* = 9.9 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.8, 16.8 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 11.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 27.1, 122.0, 126.8, 131.3, 131.6, 133.2, 134.1, 140.3, 140.7, 198.2; EI-MS (*m/z*, relative intensity): 252 (M^+, 19), 128 (75), 43 (100). HRMS (EI) calcd for $C_{12}H_{11}OBr^+$ $[M]^+$: 249.9993; Found: 249.9981.

*(E)-3-(3,4-Dichlorophenyl)hexa-3,5-dien-2-one (**3l**).* Yield 60% (44 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.35); yellow oil; IR (neat) 1666, 1621, 1473, 1250 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.40 (s, 3H), 5.54 (d, *J* = 10.2 Hz, 1H), 5.77 (d, *J* = 16.8 Hz, 1H), 6.33 (td, *J* = 10.8, 16.8 Hz, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 7.26-7.31 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.9, 127.5, 129.5, 130.2, 131.8, 132.1, 132.3, 132.9, 135.1, 139.5, 141.0, 197.8; EI-MS (*m/z*, relative intensity): 240 (M^+, 81), 162 (100). HRMS (EI) calcd for $C_{12}H_{10}OCl_2^+$ $[M]^+$: 240.0109; Found: 240.0099.

*(E)-2-(Allyloxy)phenyl 2-phenylpenta-2,4-dienoate (**3m**).* Yield 77% (67 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1730, 1604, 1498, 1183, 1157 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.55 (dt, *J* = 1.5, 5.1 Hz, 2H), 5.25 (dt, *J* = 1.5, 10.8 Hz, 1H), 5.40 (ddd, *J* = 1.8, 3.3, 17.4 Hz, 1H), 5.49 (d, *J* = 9.9 Hz, 1H), 5.73 (d, *J* = 16.8 Hz, 1H), 6.01 (m, 1H), 6.51 (m, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 7.05-7.19 (m, 2H), 7.30-7.38 (m, 5H), 7.67 (d, *J* = 11.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 113.8, 117.3, 121.0, 122.9, 126.4, 126.6, 127.8, 127.9, 130.3, 132.5, 132.9, 133.1, 134.6, 140.4, 141.9, 150.0, 165.5; EI-MS (*m/z*, relative intensity): 306 (M^+, 12), 157 (89), 129 (100). HRMS (EI) calcd for $C_{20}H_{18}O_3^+$ $[M]^+$: 306.1256; Found: 306.1265.

*(E)-Benzhydryl 2-phenylpenta-2,4-dienoate (**3n**).* Yield 69% (71 mg, purified by silica gel column chromatography using PE:EA =

30:1 as eluent, R_f = 0.40); white solid; IR (neat) 1711, 1495, 1232, 1175 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.41 (dd, *J* = 0.6, 10.5 Hz, 1H), 5.66 (d, *J* = 17.1 Hz, 1H), 6.41 (ddd, *J* = 10.2, 11.1, 17.1, Hz, 1H), 6.97 (s, 1H), 7.23-7.44 (m, 5H), 7.54 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.3, 125.9, 126.9, 127.1, 127.4, 127.7, 127.9, 128.2, 128.4, 128.6, 129.3, 130.1, 133.1, 134.7, 140.3, 140.9, 166.1; EI-MS (*m/z*, relative intensity): 340 (M^+, 17), 167 (100). HRMS (EI) calcd for $C_{24}H_{20}O_2^+$ $[M]^+$: 340.1463; Found: 340.1464.

*(2E,4E)-Methyl 2-phenylhexa-2,4-dienoate (**5a**).*[18] Yield 63% (38 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 1710, 1637, 1434, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.78 (d, *J* = 6.6 Hz, 3H), 3.75 (s, 3H), 6.06-6.26 (m, 2H), 7.22-7.26 (m, 2H), 7.32-7.42 (m, 3H), 7.46 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.9, 52.1, 127.4, 127.9, 128.1, 130.1, 135.0, 135.2, 139.9, 141.1, 168.1; EI-MS (*m/z*, relative intensity): 202 (M^+, 23), 143 (100). HRMS (EI) calcd for $C_{13}H_{14}O_2^+$ $[M]^+$: 202.0994; Found: 202.0995.

*(E)-Methyl 5-methyl-2-phenylhexa-2,4-dienoate (**5b**).*[19] Yield 72% (47 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.79 (s, 3H), 1.95 (s, 3H), 3.76 (s, 3H), 5.87 (d, *J* = 12.0 Hz, 1H), 7.20-7.23 (m, 2H), 7.29-7.42 (m, 3H), 7.77 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.1, 26.9, 52.0, 121.9, 127.3, 127.9, 129.4, 130.2, 135.5, 136.9, 146.8, 168.5.

*(E)-Methyl 4-cyclohexylidene-2-phenylbut-2-enoate (**5c**).* Yield 71 % (61 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); colorless oil; IR (neat) 2931, 1710, 1627, 1434, 1242 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.59~1.60 (br, m, 6H), 2.11~2.13 (br, m, 2H), 2.45~2.47 (br, m, 2H), 3.75 (s, 3H), 5.83 (d, *J* = 12.0 Hz, 1H), 7.21-7.27 (m, 2H), 7.33-7.40 (m, 3H), 7.84 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.5, 27.9, 28.5, 29.9, 38.0, 52.0, 118.7, 127.3, 127.9, 129.6, 130.3, 135.5, 136.1, 154.9, 168.5; EI-MS (*m/z*, relative intensity): 256 (M^+, 100), 197 (98). HRMS (EI) calcd for $C_{17}H_{20}O_2^+$ $[M]^+$: 256.1463; Found: 256.1459.

*(2E,4E)-Methyl 2,5-diphenylpenta-2,4-dienoate (**5d**).* Yield 66% (53 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); white solid; IR (neat) 1707, 1616, 1434, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.81 (dd, *J* = 11.4, 15.6 Hz, 1H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.25-7.44 (m, 10H), 7.66 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 124.7, 127.2, 127.7, 128.0, 128.7, 128.9, 130.3, 132.2, 135.1, 136.2, 140.6, 140.7, 167.9; EI-MS (*m/z*, relative intensity): 264 (M^+, 57), 205 (100). HRMS (EI) calcd for $C_{18}H_{16}O_2^+$ $[M]^+$: 264.1150; Found: 264.1142.

*(2E,4E)-Methyl 2-phenyl-5-p-tolylpenta-2,4-dienoate (**5e**).* Yield 57% (48 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.35); white solid; IR (neat) 1708, 1603, 1434, 1233 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32 (s, 3H), 3.79 (s, 3H), 6.76 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.95 (d, *J* = 15.6 Hz, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 7.23-7.31 (m, 4H), 7.36-7.45 (m, 3H), 7.65 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 52.1, 123.8, 127.2, 127.7, 128.0, 129.4, 130.4, 131.7, 133.5, 135.2, 139.1, 140.7, 141.0, 168.0. EI-MS (*m/z*, relative intensity): 278 (M^+, 60), 219 (100). HRMS (EI) calcd for $C_{19}H_{18}O_2^+$ $[M]^+$: 278.1307; Found: 278.1305.

*(2E,4E)-Methyl 5-(4-chlorophenyl)-2-phenylpenta-2,4-dienoate (**5f**).* Yield 65% (58 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); white solid; IR (neat) 1708, 1616, 1490, 1232 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.76 (dd, *J* = 11.1, 15.6 Hz, 1H), 6.91 (d, *J* = 15.6 Hz, 1H), 7.26-7.30 (m, 6H), 7.39-7.47 (m, 3H), 7.63 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.2, 125.2, 127.8, 128.1, 128.3, 128.9, 130.3, 132.8, 134.5, 134.7, 135.0, 139.0, 140.3, 167.8; EI-MS (*m/z*, relative intensity): 298 (M^+, 64), 204 (100). HRMS (EI) calcd for $C_{18}H_{15}O_2Cl^+$ $[M]^+$: 298.0761; Found: 298.0760.

*(E)-Methyl 2,5,5-triphenylpenta-2,4-dienoate (**5g**).* Yield 65% (66 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); white solid; IR (neat) 1707, 1604, 1434, 1262, 1234 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.69 (s, 3H), 6.70 (d, *J* = 11.7 Hz, 1H), 7.17~7.43 (m, 15H), 7.57 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.1, 123.7, 127.7, 128.0, 128.2, 128.3, 128.4, 130.3, 130.5, 133.1, 135.2, 138.1, 138.8, 141.6, 150.8, 168.0; EI-MS (*m/z*, relative intensity): 340 (M^+, 93), 281 (100). HRMS (EI) calcd for $C_{24}H_{20}O_2^+$ $[M]^+$: 340.1463; Found: 340.1469.

*(2E,4E)-2-(Allyloxy)phenyl 2,5-diphenylpenta-2,4-dienoate (**5h**).* Yield 70% (78 mg, purified by silica gel column chromatography using PE:EA = 20:1 as eluent, R_f = 0.35); white solid; IR (neat) 1724, 1614, 1497, 1183 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.56 (d, *J* = 4.8 Hz, 2H), 5.26 (dd, *J* = 1.2, 10.5 Hz, 1H), 5.41 (dd, *J* = 1.5, 17.4 Hz, 1H), 6.02 (ddd, *J* = 5.4, 10.5, 12.0 Hz, 1H), 6.88-7.45 (m, 16H), 7.86 (d, *J* = 10.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 69.3, 113.8, 117.2, 121.0, 123.0, 124.7, 126.5, 127.3, 127.8, 128.0, 128.7, 129.0, 130.5, 131.5, 132.9, 134.9, 136.2, 140.6, 141.3, 142.0, 150.1, 165.6; EI-MS (*m/z*, relative intensity): 382 (M^+, 6), 233 (100). HRMS (EI) calcd for $C_{26}H_{22}O_3^+$ $[M]^+$: 382.1569; Found: 382.1558.

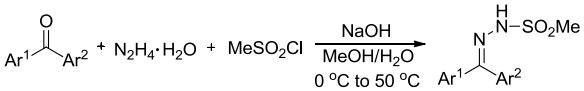
*(2E,4E)-Benzhydryl 2,5-diphenylpenta-2,4-dienoate (**5i**).* Yield 60% (75 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); white solid; IR (neat) 1706, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.97-7.02 (m, 2H), 7.24 -7.44 (m, 20H), 7.73 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 77.3, 124.7, 126.9, 127.2, 127.7, 128.0, 128.4, 128.7, 128.9, 130.4, 132.4, 135.0, 136.2, 140.4, 140.8, 140.9, 166.2; EI-MS (*m/z*, relative intensity): 416 (M^+, 3), 167 (100). HRMS (EI) calcd for $C_{30}H_{24}O_2^+$ $[M]^+$: 416.1776; Found: 416.1762.

*(2E,4E)-Cinnamyl 2,5-diphenylpenta-2,4-dienoate (**5j**).* Yield 58% (64 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.40); white solid; IR (neat) 1703, 1223 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.87 (d, *J* = 6.0 Hz, 2H), 6.34 (td, *J* = 6.0, 15.9 Hz, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.83 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 7.26-7.47 (m, 15H), 7.69 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 123.3, 124.7, 126.6, 127.2, 127.8, 128.0, 128.1, 128.6, 128.7, 128.9, 130.4, 132.3,

133.8, 135.0, 136.2, 140.7, 140.8, 167.1; EI-MS (*m/z*, relative intensity): 366 (M^+, 3), 117 (100). HRMS (EI) calcd for $C_{26}H_{22}O_2^+$ $[M]^+$: 366.1620; Found: 366.1628.

*(2E,4E)-allyl 2,5-diphenylpenta-2,4-dienoate (**5k**).* Yield 51% (45 mg, purified by silica gel column chromatography using PE:EA = 30:1 as eluent, R_f = 0.45); white solid; IR (neat) 1707, 1224 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71 (d, *J* = 5.4 Hz, 2H), 5.23 (dd, *J* = 0.9, 10.5 Hz, 1H), 5.30 (dd, *J* = 1.2, 17.1 Hz, 1H), 5.97 (ddd, *J* = 5.4, 10.8, 15.9 Hz, 1H), 6.83 (dd, *J* = 11.4, 15.6 Hz, 1H), 6.99 (d, *J* = 15.6 Hz, 1H), 7.26–7.46 (m, 10H), 7.68 (d, *J* = 11.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 65.5, 117.9, 124.7, 127.2, 127.7, 128.0, 128.7, 128.9, 130.4, 132.2, 135.0, 136.2, 140.7, 140.8, 167.0; EI-MS (*m/z*, relative intensity): 290 (M^+, 55), 205 (100). HRMS (EI) calcd for $C_{20}H_{18}O_2^+$ $[M]^+$: 290.1307; Found: 290.1318.

General procedure for the preparation of *N*-mesylhydrazones.



Methanesulfonyl chloride (1.15 g, 10 mmol) was added slowly to a stirred ice-cold solution of hydrazine hydrate (0.5 g, 10 mmol) in water (1.5 mL), followed by 2 M NaOH (aq, 5 mL), such that the temperature did not exceed 8 °C. On completion, the mixture was added into a solution of ketone (10 mmol) in a minimum amount of MeOH. The reaction mixture was heated at 50 °C and monitored by TLC analysis. After completion of the reaction, the product was collected by filtration and washed thoroughly with cold Et_2O or recrystallized with EtOH (10 mL).

*N-(Diphenylmethylene)methanesulfonohydrazide (**6a**).* Yield 64 % (1.73 g); white solid; mp: 207-208 °C; IR (film): 3203, 1396, 1337, 1160, 990, 882, 785, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.26-7.29 (m, 2H), 7.32-7.8 (m, 3H), 7.44 (broad, 1H), 7.54-7.58 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 127.7, 128.3, 128.4, 129.9, 130.1, 130.3, 131.1, 136.3, 154.2; HRMS (ESI) calcd for $C_{14}H_{15}N_2O_2S^+$ $(M+H)^+$: 275.0854; Found: 275.0854; Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21. Found: C, 61.29; H, 5.12; N, 10.35.

*N-(Bis(4-methoxyphenyl)methylene)methanesulfonohydrazide (**6b**).* Yield 38 % (1.28 g); white solid; mp: 103-105 °C; IR (film): 3208, 1609, 1512, 1318, 1159, 1030, 983, 839 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.17 (s, 3H), 3.82 (s, 3H), 3.89 (s, 3H), 6.84-6.87 (m, 2H), 7.04-7.07 (m, 2H), 7.19-7.23 (m, 2H), 7.38 (broad, 1H), 7.40-7.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.9, 55.4, 55.5, 113.7, 115.1, 123.1, 129.3, 129.4, 130.0, 154.2, 160.8, 161.2; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_4S^+$ $(M+H)^+$: 335.1066; Found: 335.1064.

*N-(Di-p-tolylmethylene)methanesulfonohydrazide (**6c**).* Yield 32 % (1.12 g); white solid; mp: 151-152 °C; IR (film): 3200, 1392, 1340, 1160, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.44 (s, 3H), 3.17 (s, 3H), 7.12-7.16 (m, 4H), 7.34-7.36 (m, 2H), 7.41 (broad, 1H), 7.45-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 39.0, 127.7, 128.1, 128.3, 129.0, 130.4, 133.7, 140.3, 140.4, 154.6; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S^+$ $(M+H)^+$: 303.1167; Found: 303.1160; Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.49; H, 6.08; N, 9.25.

*N-(Bis(4-chlorophenyl)methylene)methanesulfonohydrazide (**6d**).* Yield 46 % (1.53 g); white solid; mp: 145-146 °C; IR (film): 3198, 1386, 1159, 984, 829 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.22-7.24 (m, 2H), 7.30-7.33 (m, 2H), 7.41 (broad, 1H), 7.45-7.49 (m, 2H), 7.56-7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 128.7, 128.8, 128.9, 129.8, 130.4, 134.4, 136.5, 136.8, 151.8; HRMS (ESI) calcd for $C_{14}H_{13}Cl_2N_2O_2S^+$ $(M+H)^+$: 343.0075; Found: 343.0048; Anal. Calcd for $C_{14}H_{12}Cl_2N_2O_2S$: C, 48.99; H, 3.52; N, 8.16. Found: C, 48.59; H, 3.47; N, 8.25.

*N-(Bis(4-fluorophenyl)methylene)methanesulfonohydrazide (**6e**).* Yield 44 % (1.37 g); white solid; mp: 141-142 °C; IR (film): 3190, 1606, 1507, 1392, 1312, 1224, 1165, 1063, 987, 842, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 3H), 7.01-7.05 (m, 2H), 7.26-7.29 (m, 4H), 7.40 (broad, 1H), 7.51-7.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 115.6, 117.2, 126.7, 129.6, 130.6, 132.4, 152.2, 162.8, 165.3; HRMS (ESI) calcd for $C_{14}H_{13}F_2N_2O_2S^+$ $(M+H)^+$: 311.0666; Found: 311.0654; Anal. Calcd for $C_{14}H_{12}F_2N_2O_2S$: C, 54.19; H, 3.90; N, 9.03. Found: C, 54.26; H, 3.87; N, 9.07.

*N-(Di-m-tolylmethylene)methanesulfonohydrazide (**6f**).* Yield 25 % (0.73 g); white solid; mp: 160-161 °C; IR (film): 3209, 1585, 1380, 1340, 1316, 1163, 1062, 969, 873 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.42 (s, 3H), 3.16 (s, 3H), 7.04-7.05 (m, 2H), 7.18-7.23 (m, 2H), 7.28-7.30 (m, 1H), 7.32-7.33 (m, NH), 7.42-7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 39.1, 125.1, 125.2, 127.9, 128.2, 128.6, 129.7, 130.9, 130.9, 131.2, 136.3, 138.1, 139.9, 154.7; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S^+$ $(M+H)^+$: 303.1167; Found: 303.1160; Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.47; H, 6.03; N, 9.23.

*N-(Bis(3-methoxyphenyl)methylene)methanesulfonohydrazide (**6g**).* Yield 25 % (0.84 g); white solid; mp: 100-101 °C; IR (film): 3195, 1577, 1464, 1310, 1173, 1002, 969, 871, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 3H), 3.80 (s, 3H), 3.83 (s, 3H), 6.75-6.83 (m, 2H), 6.92-6.94 (m, 1H), 7.03-7.05 (m, 1H), 7.10-7.12 (m, 1H), 7.18 (broad, 1H), 7.25-7.26 (m, 1H), 7.45-7.49 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 55.4, 55.5, 113.0, 113.6, 115.6, 115.8, 120.1, 120.5, 129.3, 131.1, 132.3, 137.5, 153.8, 159.6, 160.6; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_4S^+$ $(M+H)^+$: 335.1066; Found: 335.1063.

*N-(Bis(3-fluorophenyl)methylene)methanesulfonohydrazide (**6h**).* Yield 35 % (1.06 g); white solid; mp: 165-167 °C; IR (film): 3202, 1583, 1442, 1340, 1271, 1176, 1016, 977, 893 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 6.98-7.01 (m, 1H), 7.07-7.12 (m, 2H), 7.26-7.34 (m, 4H), 7.48 (broad, 1H), 7.56-7.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 114.3, 115.7, 117.4, 117.9, 123.4, 124.1, 130.0, 132.0, 132.5, 138.0, 151.2, 162.2, 164.7; HRMS (ESI) calcd for $C_{14}H_{13}F_2N_2O_2S^+$ $(M+H)^+$: 311.0666; Found: 311.0652.

*N-(Bis(2-fluorophenyl)methylene)methanesulfonohydrazide (**6i**).* Yield 36 % (1.12 g); white solid; mp: 201-202 °C; IR (film): 3206, 1614, 1488, 1451, 1319, 1220, 1108, 990, 764 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.20 (s, 3H), 7.00-7.05 (m, 1H), 7.16-7.32 (m, 4H),

7.37-7.41 (m, 1H), 7.50-7.55 (m, 1H), 7.62 (broad, 1H), 7.64-7.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 116.6, 117.0, 124.2, 124.6, 125.5, 129.6, 130.2, 131.8, 132.6, 145.3, 157.4, 159.9, 162.0; HRMS (ESI) calcd for $C_{14}H_{13}F_2N_2O_2S^+$ $(M+H)^+$: 311.0666; Found: 311.0662.

N-((2-Fluorophenyl)(phenyl)methylene)methanesulfonohydrazide ***(6j)***. Yield 91 % (2.65 g); white solid; mp: 196-198 °C; IR (film): 2926, 2351, 1590, 1519, 1317, 1159, 982, 836 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.26-7.46 (m, 4H), 7.51-7.41 (m, 4H), 7.67-7.69 (m, 1H), 7.84-7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 117.0, 118.6, 125.7, 127.2, 127.9, 128.5, 129.7, 130.3, 131.5, 132.7, 135.6, 148.9; HRMS (ESI) calcd for $C_{14}H_{14}FN_2O_2S^+$ $(M+H)^+$: 293.0760; Found: 293.0758.

N-((3-(Methylthio)phenyl)(phenyl)methylene)methanesulfonohydrazide ***(6k)***. Yield 59 % (1.35 g); white solid; mp: 168-170 °C; IR (film): 3211, 1335, 1319, 1159, 785, 705 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (m, 3H), 3.19 (s, 3H), 7.27 (m, 5H), 7.45 (s, NH), 7.48 (s, 1H), 7.56-7.57 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 39.1, 124.6, 125.6, 127.9, 128.3, 128.8, 129.9, 130.4, 130.8, 136.9, 139.0, 153.6; HRMS (ESI) calcd for $C_{15}H_{17}N_2O_2S_2^+$ $(M+H)^+$: 321.0731; Found: 321.0726.

N-(Phenyl(4-(trifluoromethyl)phenyl)methylene)methanesulfonohydrazide ***(6l)***. Yield 67 % (1.67 g); white solid; mp: 129-131 °C; IR (film): 3195, 1612, 1409, 1312, 1162, 1067, 983, 849, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (m, 3H), 7.26-7.61 (m, 8H), 7.67-7.69 (m, 1H), 7.84-7.86 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 39.2, 122.2, 122.5, 124.9, 125.3, 125.3, 125.3, 126.9, 126.9, 127.5, 127.9, 128.3, 128.5, 129.1, 130.1, 130.3, 130.5, 130.6, 131.5, 131.8, 132.2, 132.6, 134.9, 134.9, 135.6, 139.6, 152.4, 152.6; HRMS (ESI) calcd for $C_{15}H_{14}F_3N_2O_2S^+$ $(M+H)^+$: 343.0728; Found: 343.0715; Anal. Calcd for $C_{15}H_{13}F_3N_2O_2S$: C, 52.63; H, 3.83; N, 8.18. Found: C, 52.45; H, 3.83; N, 8.22.

N-((4-Methoxyphenyl)(phenyl)methylene)methanesulfonohydrazide ***(6m)***. Yield 31 % (0.94 g); white solid; mp: 173-175 °C; IR (film): 3189, 2357, 1609, 1511, 1317, 1251, 1140, 1029, 989 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (s, 3H), 3.82 (s, 3H), 6.84-6.86 (m, 2H), 7.25-7.28 (m, 2H), 7.31 (broad, 1H), 7.49-7.58(m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.0, 55.4, 113.7, 128.3, 129.0, 129.2, 129.8, 130.2, 131.3, 154.2, 161.2; HRMS (ESI) calcd for $C_{15}H_{17}N_2O_3S^+$ $(M+H)^+$: 305.0960; Found: 305.0959; Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30; N, 9.20. Found: C, 59.23; H, 5.24; N, 9.37.

N-([1,1'-Biphenyl]-4-yl(phenyl)methylene)methanesulfonohydrazide ***(6n)***. Yield 12 % (0.36 g); white solid; mp: 204-205 °C; IR (film): 3198, 2926, 1606, 1485, 1385, 1318, 1162, 983, 844, 769 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.21 (s, 3H), 7.26 (broad, 1H), 7.30-7.39 (m, 3H), 7.43-7.47(m, 3H), 7.56-7.85 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 127.0, 127.1, 127.8, 128.1, 128.3, 128.9, 129.9, 130.3, 131.1, 135.2, 140.2, 142.8, 153.9; HRMS (ESI) calcd for $C_{20}H_{19}N_2O_2S^+$ $(M+H)^+$: 351.1167; Found: 351.1158.

N-((4-chlorophenyl)(phenyl)methylene)methanesulfonohydrazide ***(6o)***. Yield 41 % (1.27 mg); white solid; mp: 180-183 °C; IR (film): 3200, 2363, 1485, 1393, 1335, 1314, 1145, 1092, 990, 830 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.19 (s, 3H), 7.25-7.32 (m, 4H), 7.46 (broad, 1H), 7.49-7.51(m, 2H), 7.56-7.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 128.3, 128.6, 128.9, 130.0, 130.5, 130.6, 134.7, 136.2, 153.0; HRMS (ESI) calcd for $C_{14}H_{14}ClN_2O_2S^+$ $(M+H)^+$: 309.0465; Found: 309.0451; Anal. Calcd for $C_{14}H_{13}ClN_2O_2S$: C, 54.46; H, 4.24; N, 9.07. Found: C, 54.54; H, 4.22; N, 9.19.

N-((3,4-dimethylphenyl)(phenyl)methylene)methanesulfonohydrazide ***(6p)***. Yield 25 % (0.73 g); white solid; mp: 193-195 °C; IR (film): 3200, 1354, 1442, 1396, 1338, 1311, 1145, 1029, 989, 910, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.27 (s, 3H), 3.18 (s, 3H), 7.07-7.09 (m, 1H), 7.19-7.21 (dd, *J* = 7.9 Hz, 1.8 Hz, 1H), 7.24-7.35 (m, 3H), 7.40 (broad, 1H), 7.52-7.57(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 19.8, 39.0, 125.5, 128.3, 128.4, 129.6, 129.8, 130.1, 131.3, 133.9, 136.7, 139.2, 154.6; HRMS (ESI) calcd for $C_{16}H_{19}N_2O_2S^+$ $(M+H)^+$: 303.1167; Found: 303.1154; Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 6.00; N, 9.26. Found: C, 63.50; H, 5.99; N, 9.31.

N-((4-Chlorophenyl)(4-methoxyphenyl)methylene)methanesulfonohydrazide ***(6q)***. Yield 25 % (0.85 g); white solid; mp: 144-145 °C; IR (film): 3208, 1609, 1485, 1381, 1340, 1316, 1159, 1091, 983, 824 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37-2.47 (m, 3H), 3.18 (s, 3H), 7.14-7.16 (m, 2H), 7.22-7.26 (m. 2H), 7.29-7.32 (m, 2H), 7.41-7.43 (m, NH), 7.49-7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 39.0, 39.1, 127.5, 127.6, 128.2, 128.6, 128.9, 129.2, 129.5, 129.9, 130.2, 130.6, 133.2, 135.0, 136.1, 136.5, 140.7, 140.7, 153.2, 153,2; HRMS (ESI) calcd for $C_{15}H_{16}ClN_2O_3S^+$ $(M+H)^+$: 339.0570; Found: 339.0556.

General procedure for the synthesis of 1,1'-diaryl butadienes from *N*-mesylhydrazones and allyl bromides.

A 10 mL Schlenk tube was charged with $Pd_2(dba)_3$ (4.6 mg, 2.5 mol%), tris(2,6-dimethoxyphenyl)phosphine (17.7 mg, 20 mol%) and LiO^tBu (80.0 mg, 5.0 equiv). After degassed and filled with N_2 for 4 times, the tube was charged with 1 mL of THF. The allyl halides (1.5 equiv) was then added into the mixture. After that, the *N*-mesylhydrazone was dissolved in THF (4 mL) and the solution was added dropwise to the reaction *via* peristaltic pump at 80 °C for 1 h. The reaction mixture was stirred at 80 °C for another 4 h. Then the mixture was filtrated through a pad of silica gel and washed with Et_2O. Solvent was evaporated under reduced pressure to leave a crude mixture, which is purified by silica gel column chromatography to afford the product.

Buta-1,3-diene-1,1-diyldibenzene ***(7a)***.[20] Yield 73% (30 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.75); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.12 (dd, *J* = 1.8, 10.1 Hz, 1H), 5.41 (dd, *J* = 1.8, 16.8 Hz, 1H), 6.44 (ddd, *J* = 16.9, 10.2, 10.8 Hz, 1H), 6.72 (d, *J* = 11.0 Hz, 1H), 7.21-7.40 (m ,10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.6, 127.4, 127.5, 127.6, 128.2, 128.2, 128.5, 130.4, 135.0, 139.7, 142.1, 143.2.

*4,4'-(Buta-1,3-diene-1,1-diyl)bis(methoxybenzene) (**7b**).*[20] Yield 79 % (42 mg, purified by silica gel column chromatography using PE:EA = 10:1 as eluent, R_f = 0.38); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.85 (s, 3H), 5.07 (dd, *J* = 1.6, 9.9 Hz, 1H), 5.34 (dd, *J* = 1.6, 16.6 Hz, 1H), 6.45 (ddd, *J* = 16.7, 10.8, 10.1 Hz, 1H), 6.69 (d, *J* = 11.0 Hz, 1H), 6.81-6.83 (m, 2H), 6.90-6.92 (m, 2H), 7.13-7.15 (m, 2H), 7.20-7.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 113.5, 113.6, 117.3, 126.7, 128.9, 131.6, 132.2, 135.1, 135.3, 142.4, 158.9, 159.2.

*4,4'-(Buta-1,3-diene-1,1-diyl)bis(methylbenzene) (**7c**).*[21] Yield 66 % (31 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.70); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.39 (s, 3H), 5.08 (dd, *J* = 1.5, 10.1 Hz, 1H), 5.33 (dd, *J* = 1.9, 17.3 Hz, 1H), 6.45 (ddd, *J* = 16.8, 10.9, 10.1 Hz, 1H), 6.65 (d, *J* = 11.0 Hz, 1H), 7.07-7.14 (m, 4H), 7.16-7.24 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.3, 117.8, 127.5, 127.6, 128.8, 128.9, 130.3, 135.2, 136.8, 137.0, 137.3, 139.5, 143.1.

*4,4'-(Buta-1,3-diene-1,1-diyl)bis(chlorobenzene) (**7d**).*[20] Yield 69 % (38 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.61); yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (dd, *J* = 1.1, 10.1 Hz, 1H), 5.42 (dd, *J* = 1.0, 16.7 Hz, 1H), 6.37 (ddd, *J* = 16.8, 10.9, 10.2 Hz, 1H), 6.67 (d, *J* = 11.0 Hz, 1H), 7.11-7.19 (m, 4H), 7.23-7.26 (m, 2H), 7.34-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.9, 128.5, 128.6, 128.8, 129.3, 131.7, 133.6, 133.6, 134.2, 137.6, 140.2, 140.7.

*4,4'-(Buta-1,3-diene-1,1-diyl)bis(fluorobenzene) (**7e**).*[21] Yield 51 % (25 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.65); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (dd, *J* = 1.2, 10.0 Hz, 1H), 5.40 (dd, *J* = 1.1, 16.8 Hz, 1H), 6.38 (ddd, *J* = 16.8, 10.9, 10.2 Hz, 1H), 6.63 (d, *J* = 11.0 Hz, 1H), 6.95-7.02 (m, 2H), 7.05-7.10 (m, 2H), 7.14-7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.1, 115.3, 119.1, 128.7, 129.2, 132.0, 134.5, 135.3, 138.1, 141.1, 161.2, 163.7.

*3,3'-(Buta-1,3-diene-1,1-diyl)bis(methylbenzene) (**7f**).* Yield 62 % (29 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.68); colorless oil; IR (film): 1604, 1510, 1463, 1285, 1246, 1173, 1035 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.35 (s, 3H), 5.10 (dd, *J* = 1.9, 10.1 Hz, 1H), 5.37 (dd, *J* = 1.8, 16.8 Hz, 1H), 6.45 (ddd, *J* = 16.8, 11.0, 10.1 Hz, 1H), 6.67 (d, *J* = 11.0 Hz, 1H), 7.01-7.29 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 118.2, 124.9, 127.5, 128.0, 128.1, 128.1, 128.2, 128.3, 130.9, 135.1, 137.1, 139.7, 132.2, 143.4; HRMS (ESI) calcd for $C_{18}H_{19}^+$ $(M+H)^+$: 235.1487; Found: 235.1481.

*3,3'-(Buta-1,3-diene-1,1-diyl)bis(methoxybenzene) (**7g**).* Yield 66 % (35 mg, purified by silica gel column chromatography using PE:EA = 10:1 as eluent, R_f = 0.35); yellow oil; IR (film): 1596, 1576, 1486, 1463, 1432, 1285, 1159 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (s, 3H), 3.79 (s, 3H), 5.13 (dd, *J* = 1.6, 10.1 Hz, 1H), 5.39 (dd, *J* = 1.5, 16.8 Hz, 1H), 6.45 (ddd, *J* = 16.9, 10.8, 10.2 Hz, 1H), 6.70 (d, *J* = 11.0 Hz, 1H), 6.75-6.89 (m, 6H), 7.18-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 112.9, 113.1, 115.8, 118.8, 120.2, 122.9, 128.7, 129.1, 129.2, 134.9, 140.9, 142.8, 143.3, 159.4, 159.5; HRMS (ESI) calcd for $C_{18}H_{19}O_2^+$ $(M+H)^+$: 267.1385; Found: 267.1379.

*3,3'-(Buta-1,3-diene-1,1-diyl)bis(fluorobenzene) (**7h**).*[22] Yield 56 % (27 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.66); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (dd, *J* = 1.1, 10.1 Hz, 1H), 5.45 (dd, *J* = 0.9, 16.8 Hz, 1H), 6.40 (ddd, *J* = 16.8, 10.8, 10.3 Hz, 1H), 6.72 (d, *J* = 11.0 Hz, 1H), 6.96-7.09 (m, 6H), 7.22-7.28 (m, 1H), 7.34-7.39 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 114.1, 117.1, 120.2, 123.0, 126.1, 129.8, 134.1, 140.5, 141.1, 143.7, 161.5, 161.6, 163.9, 164.0.

*2,2'-(Buta-1,3-diene-1,1-diyl)bis(fluorobenzene) (**7i**).* Yield 36 % (18 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.55); yellow oil; IR (film): 1488, 1453, 1248, 1224, 1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (dd, *J* = 1.2, 10.1 Hz, 1H), 5.44 (dd, *J* = 1.1, 16.9 Hz, 1H), 6.34 (ddd, *J* = 16.9, 10.8, 10.3 Hz, 1H), 6.78 (d, *J* = 11.0 Hz, 1H), 7.00-7.25 (m, 7H), 7.29-7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.7, 115.9, 115.9, 116.1, 120.3, 123.9, 123.9, 123.9, 126.9, 127.0, 128.9, 129.0, 129.5, 129.5, 130.5, 130.5, 131.3, 132.0, 132.1, 134.2, 134.2, 134.3, 158.7, 159.0, 161.2, 161.5; HRMS (ESI) calcd for $C_{16}H_{19}F_2^+$ $(M+H)^+$: 243.0985; found: 243.0979.

*(Z/E)-1-Fluoro-2-(1-phenylbuta-1,3-dien-1-yl)benzene (**7j**).* Yield 55 % (25 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.60); yellow oil; IR (film): 1487, 1448, 1222, 996, 907 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (dd, *J* = 1.1, 10.1 Hz, 1H), 5.43 (dd, *J* = 1.0, 16.9 Hz, 1H), 6.22-6.32 (m, 1H), 6.84 (d, *J* = 11.0 Hz, 1H), 7.10-7.38 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.7, 116.0, 119.4, 124.0, 124.0, 126.6, 126.7, 126.9, 127.7, 128.4, 129.5, 129.6, 130.0, 132.5, 132.5, 134.5, 136.6, 140.6, 158.9, 161.4; HRMS (ESI) calcd for $C_{16}H_{14}F^+$ $(M+H)^+$: 225.1080; Found: 225.1074.

*(Z/E)-Methyl(3-(1-phenylbuta-1,3-dien-1-yl)phenyl)sulfane (**7k**).* Yield 82 % (41 mg, purified by silica gel column chromatography using PE:EA = 20:1 as eluent, R_f = 0.60); yellow oil; *Z*/*E* = 50:50, two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 and 2.46 (s each, 3:3H), 5.14 and 5.40 (d each, *J* = 10.1 and 16.9 Hz, 1:1H), 6.43 (m, 2H), 6.70 (m, 2H), 6.97-7.02 (m, 2H), 7.10-7.23 (m, 8H), 7.28-7.40 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 15.9, 119.0, 119.0, 124.7, 125.4, 125.6, 125.8, 127.2, 127.5, 127.6, 128.1, 128.2, 128.3, 128.6, 128.8, 129.0, 130.3, 134.8, 134.8, 138.4, 138.5, 139.3, 140.3, 141.76, 142.6, 142.7, 142.8; HRMS (ESI) calcd for $C_{17}H_{17}S^+$ $(M+H)^+$: 253.1051; Found: 253.1045.

*(Z/E)-1-(1-Phenylbuta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (**7l**).* Yield 73 % (40 mg, purified by silica gel column chromatography using PE:EA = 40:1 as eluent, R_f = 0.70); yellow oil; IR (film): 1326, 1167, 1127, 1068, 1017, 911, 842 cm^{-1}; *Z*/*E* = 51:49, Two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 (m, 2H), 5.43 and 5.47 (dd each, *J* = 1.0 and 5.9 Hz, 1:1H), 6.32-6.50 (m, 2H), 6.74 and 6.77 (d each, *J* = 11.1 Hz, 1:1H), 7.19-7.66 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.9, 120.1, 125.1, 125.2, 125.2, 125.2, 127.5, 127.8, 127.9, 128.4, 129.1, 129.4, 129.7, 130.3, 130.3, 130.8, 134.2, 134.6, 138.9, 141.3, 141.6, 141.8, 143.5, 145.6; HRMS (ESI) calcd for $C_{17}H_{14}F_3^+$ $(M+H)^+$: 275.1048; Found: 275.1042.

(Z/E)-1-Methoxy-4-(1-phenylbuta-1,3-dien-1-yl)benzene ***(7m)***.[20] Yield 66 % (31 mg, purified by silica gel column chromatography using PE:EA = 20:1 as eluent, R_f = 0.70); yellow oil; *Z*/*E* = 51:49, Two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 and 2.47 (s each, 3:3H), 5.13 and 5.16 (m each, 2H), 5.38 and 5.42 (m each, 2H), 6.38-6.48 (m, 2H), 6.68 and 6.73 (d each, *J* = 11.0 Hz, 1:1H), 6.97-7.40 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 113.5, 113.6, 117.6, 118.2, 126.9, 127.3 127.5, 127.7, 128.2, 128.3, 128.7, 120.4, 131.7, 131.9, 135.1, 139.9, 142.5, 142.8, 158.9; HRMS (ESI) calcd for $C_{17}H_{17}O^+$ $(M+H)^+$: 237.1279; Found: 237.1274.

(Z/E)-4-(1-Phenylbuta-1,3-dien-1-yl)-1,1'-biphenyl ***(7n)***.[21] Yield 57 % (32 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.66); white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (m, 1H), 5.42 (m, 1H), 6.40-6.58 (m, 1H), 6.72-6.80 (m, 1H), 7.25-7.66 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.7, 118.8, 126.9, 126.9, 127.0, 127.1, 127.4, 127.4, 127.5, 127.6, 128.4, 128.7, 128.7, 127.8, 128.0, 128.3, 128.5, 128.8, 128.9, 130.5, 130.9, 135.0, 138.7, 139.6, 140.2, 140.3, 140.7, 140.8, 141.0, 142.2, 142.7, 142.8.

(Z/E)-1-Chloro-4-(1-phenylbuta-1,3-dien-1-yl)benzene ***(7o)***.[23] Yield 45 % (22 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.68); yellow oil; *Z*/*E* = 50:50, Two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14-5.18 (m, 2H), 5.39 and 5.43 (m each,1:1H), 6.36-6.47 (m, 2H), 6.67-6.72 (m, 2H), 7.14-7.41 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.2, 119.3, 127.6, 127.6, 127.7, 128.2, 128.3, 128.4, 128.5, 128.8, 128.8, 129.0, 130.4, 131.8, 133.3, 133.4, 134.5, 134.8, 138.1, 139.2, 140.6, 141.7, 141.8, 141.9.

(Z/E)-1,2-Dimethyl-4-(1-phenylbuta-1,3-dien-1-yl)benzene ***(7p)***.[21] Yield 46 % (22 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.75); colorless oil; *Z*/*E* = 51:50, Two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22-2.25 (s each, 3:3H), 2.26-2.30 (s each, 3:3H), 5.11 (m, 2H), 5.35 and 5.38 (m each, 1:1H), 6.37-6.52 (m, 2H), 6.67-6.68 (d each, *J* = 11.0 Hz, 1:1H), 6.95-7.00 (m, 3H), 7.04-7.22 (m, 6H), 7.28-7.40 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.6, 19.8, 19.9, 118.0, 118,1, 125.2, 127.3, 127.7, 127.9, 128.1, 128.2, 128.7, 129.5, 129.5, 130.4, 131.5, 135.1, 135.3, 135.8, 136.2, 136.3, 137.1, 139.7, 139.9, 142.4, 143.2, 143.3.

(Z/E)-1-Chloro-4-(1-(4-methoxyphenyl)buta-1,3-dien-1-yl)benzene ***(7q)***. Yield 52 % (28 mg, purified by silica gel column chromatography using PE:EA = 10:1 as eluent, R_f = 0.36); yellow oil; IR (film): 1511, 1489, 1419, 1394, 1090, 1015, 909 cm^{-1}; *Z*/*E* = 50:50, Two sets of resonance signals were observed for the (*Z*/*E*)-isomers in the NMR spectra. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 and 2.39 (s each, 3:3H), 5.12 and 5.15 (s each, 1:1H), 5.37 and 5.41 (s each, 1:1H), 6.37-6.49 (m, 2H), 6.84-6.70 (m, 2H), 7.07-7.16 (m, 8H), 7.19-7.26 (m, 6H), 7.34-7.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 118.8, 118.9, 127.4, 128.1, 128.2, 128.3, 128.4, 128.7, 128.9, 129.0, 129.0, 129.6, 130.3, 131.8, 133.3, 134.6, 134.9, 136.2, 137.4, 137.7, 138.2, 138.8, 140.8, 141.8, 142.0; HRMS (ESI) calcd for $C_{17}H_{16}ClO^+$ $(M+H)^+$: 271.0890; Found: 271.0884.

(E)-Penta-1,3-diene-1,1-diyldibenzene ***(7r)***.[24] Yield 77 % (34 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.68); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (d, *J* = 6.8 Hz, 3H), 5.86-5.95 (m, 1H), 6.12-6.18 (m, 1H), 6.67 (d, *J* = 10.9 Hz, 1H), 7.21-7.28 (m, 8H), 7.33-7.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.5, 127.0, 127.1, 127.4, 128.1, 128.2, 128.3, 129.7, 130.5, 131.7, 140.0, 140.0, 142.5.

(4-Methylpenta-1,3-diene-1,1-diyl)dibenzene ***(7s)***.[20] Yield 65% (30 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.70); colorless oil; IR (film): 1602, 1485, 997, 787, 773 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 3H), 1.89 (s, 3H), 5.90 (d, *J* = 11.4 Hz, 1H), 6.87 (d, *J* = 11.4 Hz, 1H), 7.21-7.40 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.7, 26.6, 123.2, 124.5, 126.9, 127.0, 127.5, 128.1, 128.2, 130.6, 137.8, 139.7, 140.2, 143.1; HRMS (ESI) calcd for $C_{19}H_{19}^+$ $(M+H)^+$: 247.1487; Found: 247.1481.

(Cyclohex-2-en-1-ylidenemethylene)dibenzene ***(7t)***. Yield 48% (24 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.60); yellow oil; IR (film): 1490, 1442, 1074, 1030, 761, 680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (q, *J* = 6.1 Hz, 2H), 2.18 (m, 2H), 2.46 (t, *J* = 6.2 Hz, 2H), 5.83 (dt, *J* = 10.1, 4.1 Hz, 1H), 6.25 (dt, *J* = 10.1, 2.1 Hz, 1H), 7.13-7.30 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 26.0, 29.1, 126.4, 126.5, 127.7, 127.8, 130.3, 130.6, 130.9, 133.0, 136.9, 142.2, 142.4.

(3-Methylbuta-1,3-diene-1,1-diyl)dibenzene ***(7u)***.[24] Yield 49% (22 mg, purified by silica gel column chromatography using PE as eluent, R_f = 0.65); white oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (s, 3H), 4.97 (s, 1H), 5.19 (m, 1H), 6.86 (s, 1H), 7.19-7.26 (m, 6H), 7.31-7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 114.3, 119.1, 127.2, 127.5, 128.0, 128.1, 130.3, 130.8, 140.7, 141.5, 142.5, 143.3.

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