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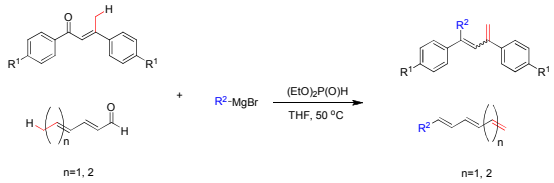
A convenient one-pot protocol involving the transfer of carbon-carbon double bonds to obtain conjugated dienes and polyenes has been developed.



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ARTICLE TYPE

Synthesis of Conjugated Dienes and Polyenes via Diethyl Phosphite Promoted Carbonyl Olefination

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A protocol has been developed for the synthesis of conjugated dienes and polyenes from unsaturated carbonyl compounds and Grignard reagents in the presence of diethyl phosphite. This reaction was conveniently carried out under mild conditions in a one-pot fashion with moderate to good yields.

Introduction

Alkenes represent one of the most widely occurring and important classes of organic compounds due to their versatility as building skeleton or starting substrates in organic synthesis. Especially conjugated alkenes not only play an important role in the synthesis of many compounds, but also are found in the structure of numerous natural products and pharmaceutical agents (Figure 1).[1] Accordingly, the practical and efficient synthesis of conjugated alkenes has provided major challenges to synthetic organic chemists. Carbonyl olefination has been considered as a well-established approach for the construction of olefins. In particular, Wittig reaction,[2] Julia reaction[3] and Peterson reaction,[4] as well as their variants[5] have been applied as the most powerful tools of modern organic chemistry. Whereas, the need of ylides which were generated by a stepwise procedure under basic condition could not be avoided in these reactions. Then,

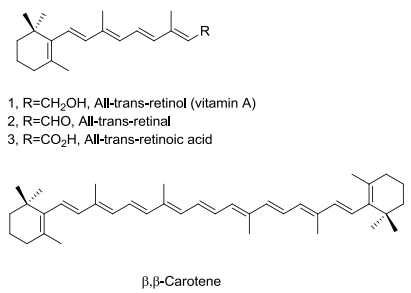

Figure 1 General structure and numbering of retinoid and carotenoid.

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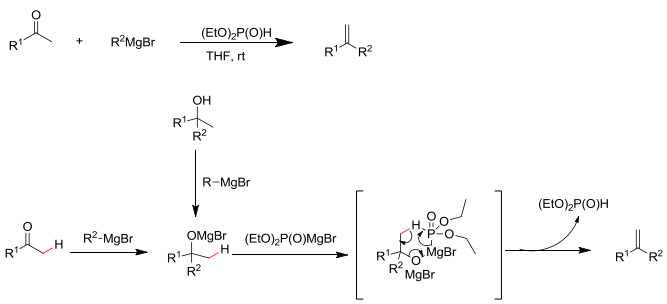
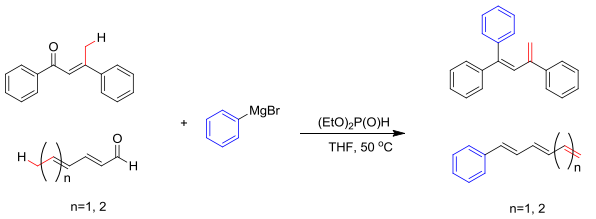
Wong[6] and Hopf[7] investigated that utilizing elimination reaction affords conjugated diene under the condition of strong base. Moreover, several reactions employing Ni,[8] Pd,[9] Ru[10] complexes to synthesize conjugated alkene have been researched, this strategy is useful but becomes less practical with precious metal.

The above widely used methods still suffer from several drawbacks. More recently, our attentions have been focused on the concise and elegant synthesis of olefins by the application of organometallic reagents. Several findings involving allylsamarium bromide,[11] Grignard reagents[12] or organozinc reagents[13] have been presented (Scheme 1).



Scheme 1 Olefination of carbonyl compounds with Grignard reagents.

These works prompted us to explore the possibility of developing a one-pot synthesis method for the preparation of conjugated dienes and polyenes through unsaturated carbonyl compounds and Grignard reagents (Scheme 2). Herein, we report a convenient one-pot protocol involving the transfer of carbon-carbon double bonds to obtain conjugated dienes and polyenes in the presence of diethyl phosphite.

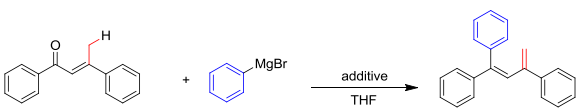


Scheme 2 Olefination of unsaturated carbonyl compounds with Grignard reagents.

Results and Discussion

Initially, α,β-unsaturated ketone **1a** and phenyl magnesium bromide **2a** were selected as a model reaction to optimize reaction conditions (Table 1, entries 1-13). Firstly, kinds of organophosphorus additives were examined at room temperature with THF as the solvent and the results were summarized in Table 1. The reaction was dramatically influenced by the additives. With Ph_3P, $(EtO)_3P$, $(EtO)_3PO$ and $(EtO)_2P(O)CH_2COOEt$ as additives, no product was obtained (Table 1, entries 1-4). However, with $(EtO)_2P(O)H$ as an additive, product **3a** could be obtained in good yield (Table 1, entry 5). Subsequently, the molar ratio of **1a**/additive/**2a** was also investigated (Table 1, entries 6-10). In the presence of 1.2 equiv of $(EtO)_2P(O)H$ and 3 equiv of Grignard reagent, a gratifying yield was obtained. To our delight, the yield could be further improved through increasing the temperature from room temperature to 50 °C (Table 1, entries 11-13). Thus, $(EtO)_2P(O)H$ as an additive and 50 °C as the reaction temperature with a 1/1.2/3 molar ratio of **1a**/additive/**2a** were proved to be the optimal reaction conditions for the reaction.

Table 1 Optimization of reaction conditions[a]



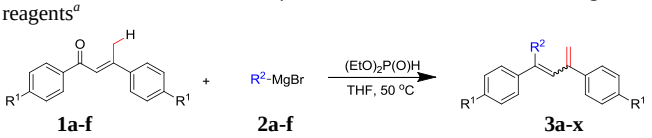
1a **2a** **3a**

Entry	Additive (equiv.)	**2a** (equiv.)	Time (h)	Temp. (°C)	Yield(%)[b]
1	Ph_3P (1.2)	3	12	r.t.	None
2	$(EtO)_3P$ (1.2)	3	12	r.t.	None
3	$(EtO)_3PO$ (1.2)	3	12	r.t.	None
4	$(EtO)_2P(O)CH_2COEt$ (1.2)	3	12	r.t.	None
5	$(EtO)_2P(O)H$ (1.2)	3	12	r.t.	75
6	$(EtO)_2P(O)H$ (1.5)	3	12	r.t.	59
7	$(EtO)_2P(O)H$ (1.0)	3	12	r.t.	63
8	$(EtO)_2P(O)H$ (0.8)	3	12	r.t.	60
9	$(EtO)_2P(O)H$ (1.2)	4	12	r.t.	66
10	$(EtO)_2P(O)H$ (1.2)	2	12	r.t.	43
11	$(EtO)_2P(O)H$ (1.2)	3	12	50	95
12	$(EtO)_2P(O)H$ (1.2)	3	6	50	47
13	$(EtO)_2P(O)H$ (1.2)	3	18	50	85

[a] Unless noted, to a solution of **1a** (0.5 mmol) in THF (3 mL) was added **2a** (X mmol) in THF under a nitrogen atmosphere at room temperature, the mixture was stirred for 4 h, then the additive (Y mmol) was added to this mixture and stirred at corresponding temperature. [b] Isolated yield based on **1a** after silica gel chromatography.

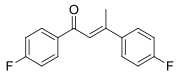
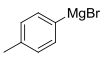
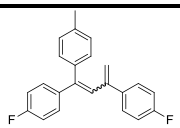
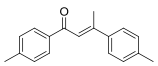
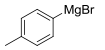
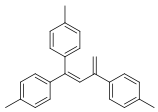
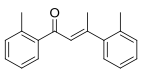
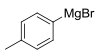
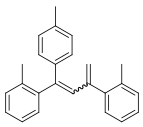
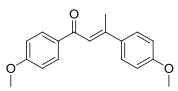
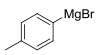
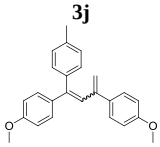
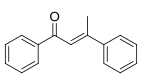
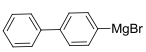
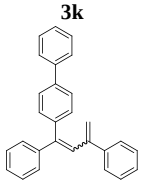
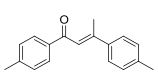
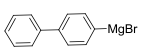
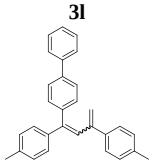
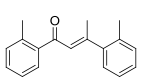
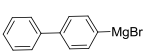
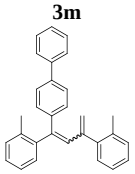
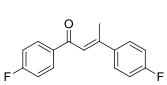
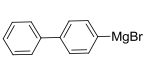
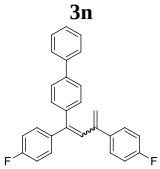
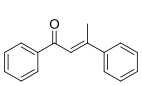
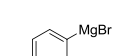
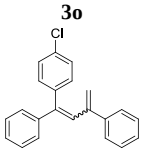
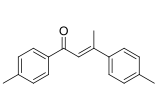
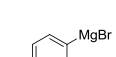
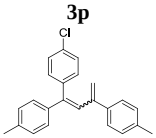
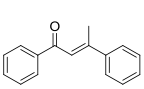
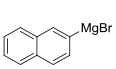
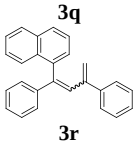
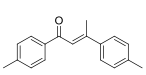
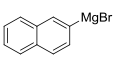
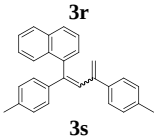
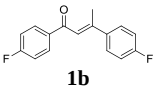
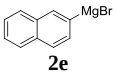
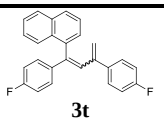
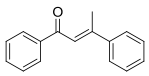
In order to investigate the generality of this reaction, the scope of the substrate with different Grignard reagent was subsequently explored and the results were summarized in Table 2. We found that α,β-unsaturated ketones were treated with phenyl magnesium bromide under the conditions listed in Table 2 to obtain the corresponding conjugated dienes in good to excellent yields (Table 2, entries 1-6). Good yields were also afforded with other kinds of Grignard reagents, such as 4-methyl phenyl magnesium bromide, 4-chloride phenyl magnesium, 4-phenyl phenyl magnesium bromide, 3,5-dimethyl phenyl magnesium bromide, 2-naphthyl magnesium bromide (Table 2, entries 7-24). The above results clearly showed that the yields were not received significant impact with α,β-unsaturated ketones bearing electron-donating groups or electron-withdrawing groups. When the aryl groups of α,β-unsaturated ketones and the group of Grignard reagents were not the same, the mixture of E/Z isomers were obtained. The ratio of E/Z (or Z/E) could be determined from ^1H NMR spectra (Table 2, entries 5, 10, 14, 23).

Table 2 Olefination of α,β-unsaturated ketones with Grignard reagents[a]



1a-f **2a-f** **3a-x**

Entry	Substrate	Magnesium reagent	Product	Yield (%)[b]
1	**1a**	**2a**	**3a**	95
2	**1b**	**2a**	**3b**	80[c]
3	**1c**	**2a**	**3c**	65[c]
4	**1d**	**2a**	**3d**	77[c]
5	**1e**	**2a**	**3e**	65 (3:1)
6	**1f**	**2a**	**3f**	55[c]
7	**1a**	**2b**	**3g**	90[c]

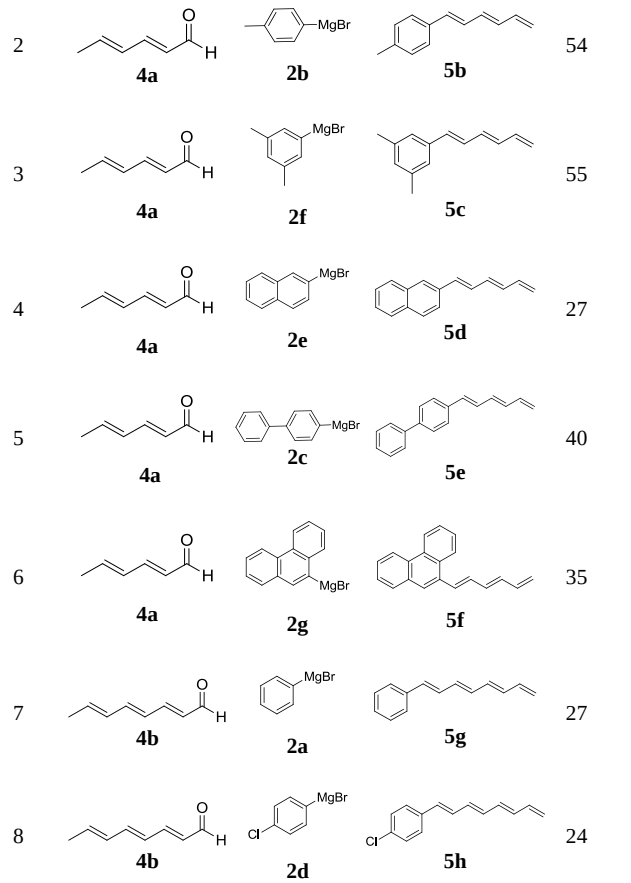
8	 **1b**	 **2b**	 **3h**	80[c]
9	 **1d**	 **2b**	 **3i**	45
10	 **1e**	 **2b**	 **3j**	47 (5:1)
11	 **1f**	 **2b**	 **3k**	43[c]
12	 **1a**	 **2c**	 **3l**	77[c]
13	 **1d**	 **2c**	 **3m**	82[c]
14	 **1e**	 **2c**	 **3n**	40 (6:1)
15	 **1b**	 **2c**	 **3o**	89[c]
16	 **1a**	 **2d**	 **3p**	45[c]
17	 **1d**	 **2d**	 **3q**	74[c]
18	 **1a**	 **2e**	 **3r**	50[c]
19	 **1d**	 **2e**	 **3s**	83[c]
20	 **1b**	 **2e**	 **3t**	71[c]
21	 **1a**	**2f**	**3u**	66[c]
22	**1d**	**2f**	**3v**	61[c]
23	**1e**	**2f**	**3w**	55 (10:1)
24	**1b**	**2f**	**3x**	64[c]

[a] Unless noted, to a solution of α,β-unsaturated ketone (0.5 mmol) in THF (3 mL) was added Grignard reagent (1.5 mmol) in THF under a nitrogen atmosphere at room temperature. The mixture was stirred for 4 h, and then diethyl phosphite (0.6 mmol) was added to this mixture and stirred at 50 °C for 12 h. [b] Isolated yield based on α,β-unsaturated ketones after silica gel chromatography. [c] The ratio of E/Z can not be determined by ^{1}H NMR.

Experiments to further explore the scope of this method were then conducted, a number of unsaturated aldehydes were subjected to this reaction and the results were summarized in Table 3. As we can see, when (2E,4E)-hexa-2,4-dienal was applied with phenyl magnesium bromide, 4-methyl phenyl magnesium bromide or 3,5-dimethyl phenyl magnesium bromide, the reaction could occur smoothly to afford the desired products with moderate yields (Table 3, entries 1-3). When, (2E,4E)-hexa-2,4-dienal was treated with 2-naphthyl magnesium bromide, 4-phenyl phenyl magnesium bromide or 9-phenanthryl magnesium bromide, corresponding conjugated-trienes were obtained at an acceptable yields (Table 3, entries 4-6). Additionally, when (2E,4E,6E)-octa-2,4,6-trienal was applied, slightly lower yields were obtained (Table 3, entries 7-8). Fortunately, we were pleased to find that this type of reaction has high stereoselectivity, only (E)-selective alkene isomerization could be obtained.

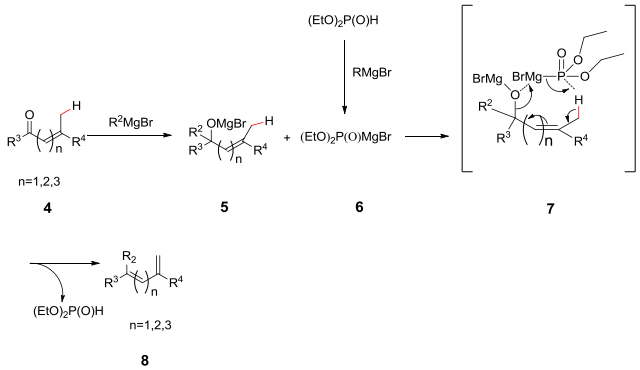
Table 3 Olefination of unsaturated aldehydes with Grignard reagents[a]

Entry	Substrate	Magnesium reagent	Product	Yield (%)[b]
1	**4a**	**2a**	**5a**	63



[a] Unless noted, to a solution of unsaturated aldehyde (0.5 mmol) in THF (3 mL) was added Grignard reagent (1.0 mmol) in THF under a nitrogen atmosphere at room temperature. The mixture was stirred for 4 h, and then diethyl phosphite (0.6 mmol) was added to this mixture and stirred at 50 °C for 12 h. [b] Isolated yield based on unsaturated aldehydes after silica gel chromatography.

According to our previous work,[11-13] a similar mechanism was proposed (Scheme 3). First, unsaturated carbonyl compound **4** transforms into intermediate **5** through nucleophilic addition. Then the P anion of **6** abstracts the H of the methyl group of intermediate **5** with –MgBr of **6** as the assistant in the cyclic transition state **7**. Then elimination of phosphate gives conjugated alkene **8** and corresponding magnesium salts.



Scheme 3 Proposed mechanism for olefination of carbonyl.

Conclusions

In summary, we have documented a promising one-pot synthetic protocol for the preparation of conjugated dienes and polyenes from unsaturated carbonyl compounds and Grignard reagents in the presence of diethyl phosphite. This strategy provides a broad scope and moderate to good yields of the products. Efforts are in progress to elucidate the mechanistic details of this reaction.

Experimental section

General Methods and Materials

THF was distilled from sodium benzophenone under nitrogen. All reactions were conducted under a nitrogen atmosphere. Metallic magnesium and all solvents were purchased from commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300–400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian-Inova-400 spectrometer. Solvent for NMR is $CDCl_3$ or DMSO-d_6, unless the otherwise noted. Chemical shifts are reported in delta (δ) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on 100 MHz. Chemical shifts are reported in parts per million relative to the central line of the multiplet at 77.5 ppm for $CDCl_3$, 40.5 ppm for DMSO. High-resolution mass spectra were obtained with a GCT-TOF instrument.

All chemicals were purchased from Aldrich, Alfa or Acros chemical company and used thus, without further purification. Petroleum ether (PE) used refers to the 60–90°C boiling point fraction of petroleum.

General procedure for synthesis of Grignard reagents. Aryl bromide (**2a**, **2b**, **2d** and **2f**, 1.6 mmol) and Mg powder (0.0365 g, 1.5 mmol) in dry THF (3 mL) under a nitrogen atmosphere at room temperature (5% I_2 was added to trigger the reaction.). The mixture was stirred for about 1 h.

Mg powder (0.0243 g, 1.1 mmol) in dry THF (3 mL) was treated dropwise with a solution of aryl bromide (**2c** and **2e**, 1.0 mmol) in dry THF (3 mL) under a nitrogen atmosphere at ice-bath (5% I_2 was added to trigger the reaction.), and the reaction mixture was allowed to warm to room temperature. Stirring was continued for 1 h.

Synthesis of conjugated dienes. To a solution of α,β-unsaturated ketone (0.5 mmol) in dry THF (3 mL) was added Grignard reagent (1.5 mmol) in dry THF under a nitrogen atmosphere at room temperature. The mixture was stirred for about 4 h. Then diethyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred at 50 °C and then was quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300–400 mesh, petroleum ether as eluent).

Synthesis of conjugated polyenes. To a solution of unsaturated aldehyde (0.5 mmol) in dry THF (3 mL) was added Grignard reagent (1.0 mmol) in dry THF under a nitrogen atmosphere at room temperature. The mixture was stirred for about 4 h. Then diethyl phosphite (0.6 mmol) was added (the reaction was monitored by TLC). The reaction mixture was stirred at 50 °C and then was quenched with dilute hydrochloric acid. The resulting mixture was extracted with diethyl ether (3×10 mL), and dried over anhydydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded olefins (300–400 mesh, petroleum ether as eluent).

Buta-1,3-diene-1,1,3-triyltribenzene (3a). The title compound was obtained according to the general procedure. Colourless oil; Yield: 95%; IR (KBr): 3080, 3055, 3025, 2952, 2929, 2855, 1660, 1597, 1491, 1444, 905, 734, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, *J* = 6.8 Hz, 2H), 7.31-7.28 (m, 5H), 7.22-7.15 (m, 8H), 6.73 (s, 1H), 5.38 (s, 1H), 5.03 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 145.2, 143.6, 141.1, 140.5, 130.6, 128.8, 128.6, 128.6, 128.4, 128.4, 128.1, 127.9, 127.5, 127.1, 117.8. HRMS (EI^+): calcd. for $C_{22}H_{18}$ $[M+1]^+$: 283.1481, found: 283.1489.

4,4'-(1-phenylbuta-1,3-diene-1,3-diyl)bis(fluorobenzene) (3b). The title compound was obtained according to the general procedure. Colourless oil; Yield: 80%; IR (KBr): 3055, 3023, 2958, 2926, 2844, 1660, 1506, 1445, 1402, 835, 766, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.26 (m, 6H), 7.15 (s, 1H), 7.06-7.02 (m, 2H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.88-6.81 (m, 3H), 6.74-6.66 (m, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 5.08 (d, *J* = 11.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 163.9, 163.7, 161.8, 161.5, 161.2, 145.1, 145.0, 144.3, 144.2, 143.3, 140.2, 139.6, 139.6, 137.2, 137.1, 137.1, 137.0, 136.3, 136.2, 132.3, 132.2, 130.5, 130.1, 130.0, 128.9, 128.9, 128.9, 128.8, 128.8, 128.7, 128.4, 128.3, 127.8, 118.3, 118.1, 115.6, 115.4, 115.4, 115.4, 115.2, 115.2, 115.2. HRMS (EI^+): calcd. for $C_{22}H_{16}F_2$ $[M+1]^+$: 319.1293, found: 319.1295.

4,4'-(1-phenylbuta-1,3-diene-1,3-diyl)bis(chlorobenzene) (3c). The title compound was obtained according to the general procedure. Colourless oil; Yield: 65%; IR (KBr): 3058, 3030, 2925, 2852, 1659, 1593, 1489, 1445, 907, 759, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30-7.28 (m, 3H), 7.26-7.22 (m, 4H), 7.16 (t, *J* = 11.6 Hz, 4H), 7.03 (t, *J* = 12.8 Hz, 2H), 6.70 (d, *J* = 11.6 Hz, 1H), 5.38 (d, *J* = 9.2 Hz, 1H), 5.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 144.7, 144.4, 142.9, 141.9, 139.8, 139.4, 139.3, 138.8, 134.1, 133.8, 133.6, 131.9, 130.5, 129.7, 128.8, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 127.9, 118.9, 118.8. HRMS (EI^+): calcd. for $C_{22}H_{16}Cl_2$ $[M+1]^+$: 351.0702, found: 351.0698.

4,4'-(1-phenylbuta-1,3-diene-1,3-diyl)bis(methylbenzene) (3d). The title compound was obtained according to the general procedure. Colourless oil; Yield: 77%; IR (KBr): 3079, 3050, 3023, 2922, 2855, 1606, 1510, 1492, 1445, 895, 820, 764, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.32-7.30 (m, 3H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.07-7.05 (m, 3H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.99 (m, 13H), 6.67 (d, *J* = 6.4 Hz, 1H), 5.35 (d, *J* = 8.8 Hz, 1H), 4.95 (d, *J* = 13.2 Hz, 1H), 2.34-2.30 (m, 3H), 2.30-2.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 144.9, 143.8, 140.8, 138.4, 137.8, 137.6, 137.1, 130.5, 130.4, 129.4, 129.3, 129.1, 128.7, 128.6, 128.4, 128.4, 128.3, 128.2, 127.9, 127.4, 126.9, 116.6, 30.2, 21.7, 21.6. HRMS (EI^+): calcd. for $C_{24}H_{22}$ $[M+1]^+$: 311.1794, found: 311.1795.

2,2'-(1-phenylbuta-1,3-diene-1,3-diyl)bis(methylbenzene) (3e). The title compound was obtained according to the general procedure. Colourless oil; Yield: 65%; IR (KBr): 3059, 3018, 2952, 2924, 2854, 1600, 1489, 1457, 1378, 902, 762, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.27-7.09 (m, 5H), 7.04-6.99 (m, 1H), 6.97-6.91 (m, 5H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.88-6.85 (m, 1H), 5.22 (s, 1H), 5.01 (d, *J* = 1.6 Hz, 1H), 2.25 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.7, 143.7, 142.7, 142.5, 142.3, 141.4, 139.6, 139.3, 136.8, 136.7, 135.3, 135.1, 131.6, 130.9, 130.5, 130.3, 130.2, 130.2, 130.1, 130.0, 129.9, 129.5, 129.1, 128.8, 127.8, 127.7, 127.4, 127.3, 127.1, 127.0, 126.0, 125.8, 125.6, 125.6, 122.2, 120.3, 21.0, 20.8, 20.2. HRMS (EI^+): calcd. for $C_{24}H_{22}$ $[M+1]^+$: 311.1794, found: 311.1802.

4,4'-(1-phenylbuta-1,3-diene-1,3-diyl)bis(methoxybenzene) (3f). The title compound was obtained according to the general procedure. Colourless oil; Yield: 55%; IR (KBr): 3031, 3000, 2956, 2931, 2835, 1713, 1605, 1509, 1461, 1416, 891, 823, 740, 700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33 (d, *J* = 8.4 Hz, 3H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.19-7.14 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 5.6 Hz, 1H), 5.32-5.27 (m, 1H), 4.96-4.89 (m, 1H), 3.80-3.75 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 159.5, 159.1, 145.3, 145.1, 144.6, 144.5, 144.0, 140.8, 136.2, 134.4, 134.0, 133.8, 132.9, 131.8, 130.5, 129.9, 129.6, 129.2, 128.6, 128.6, 128.5, 128.3, 128.2, 128.2, 128.0, 127.7, 127.6, 127.5, 127.4, 115.8, 115.7, 114.0, 113.9, 113.8, 55.7, 55.6. HRMS (EI^+): calcd. for $C_{24}H_{22}O_2$ $[M+1]^+$: 343.1693, found: 343.1700.

(1-(p-tolyl)buta-1,3-diene-1,3-diyl)dibenzene (3g). The title compound was obtained according to the general procedure. Colourless oil; Yield: 90%; IR (KBr): 3079, 3054, 3024; 2921, 2866, 1714, 1660, 1598, 1492, 1444, 907, 818, 758, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 (t, *J* = 6.8 Hz, 2H), 7.32-7.31 (m, 1H), 7.26 (d, *J* = 6.0 Hz, 1H), 7.21-7.20 (m, 4H), 7.14 (s, 3H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.37 (d, *J* = 8.0 Hz, 1H), 5.01 (d, *J* = 7.6 Hz, 1H), 2.33-2.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 145.2, 145.0, 143.8, 141.3, 140.8, 140.7, 137.9, 137.6, 137.1, 130.6, 130.5, 129.4, 129.1, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.3, 128.0, 127.8, 127.4, 127.1, 127.1, 117.6, 117.5, 21.7, 21.6. HRMS (EI^+): calcd. for $C_{23}H_{20}$ $[M+1]^+$: 297.1638, found: 297.1635.

4,4'-(1-(p-tolyl)buta-1,3-diene-1,3-diyl)bis(fluorobenzene) (3h). The title compound was obtained according to the general procedure. Colourless oil; Yield: 80%; IR (KBr): 3045, 3026, 2952, 2922, 2867, 1688, 1657, 1601, 1507, 1451, 1409, 908, 835,

733, 606 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26 (s, 3H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.03-7.02 (m, 1H), 6.96 (s, 3H), 6.86-6.80 (m, 3H), 6.70-6.61 (m, 1H), 5.32 (s, 1H), 5.06 (s, 1H), 2.34-2.27 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 145.0, 144.1, 140.5, 138.2, 137.5, 137.2, 132.3, 132.2, 130.4, 130.1, 129.5, 129.1, 128.9, 128.8, 128.8, 128.3, 128.1, 128.1, 118.1, 117.8, 115.6, 115.4, 115.1, 21.7, 21.6. HRMS (EI^+): calcd. for $C_{23}H_{18}F_2$ $[M+1]^+$: 333.1449, found: 333.1452.

4,4',4''-(buta-1,3-diene-1,1,3-triyl)tris(methylbenzene) (3i). The title compound was obtained according to the general procedure. Colourless oil; Yield: 45%; IR (KBr): 3083, 3040, 3022, 2944, 2919, 2864, 1607, 1510, 1448, 1407, 895, 785, 732 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 8.4, *J* = 2.4 Hz, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 5.34 (d, *J* = 1.6 Hz, 1H), 4.93 (s, 1H), 2.34 (s, 3H), 2.30 (d, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 144.9, 141.0, 138.5, 137.8, 137.6, 137.0, 130.4, 129.3, 129.3, 129.1, 128.3, 127.9, 126.9, 116.4, 21.7, 21.6, 21.6. HRMS (EI^+): calcd. for $C_{25}H_{24}$ $[M+1]^+$: 325.1951, found: 325.1959.

(E)-2,2'-(1-(p-tolyl)buta-1,3-diene-1,3-diyl)bis(methylbenzene) (3j). The title compound was obtained according to the general procedure. Colourless oil; Yield: 47%; IR (KBr): 3058, 3018, 2949, 2921, 2861, 1734, 1601, 1509, 1453, 1381, 903, 820, 761, 701 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.10 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.02-7.00 (m, 1H), 6.96-6.93 (m, 4H), 6.88-6.87 (m, 1H), 6.85 (s, 1H), 6.83-6.72 (m, 1H), 5.19 (s, 1H), 4.98 (d, *J* = 1.6 Hz, 1H), 2.30 (s, 3H), 2.24 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 144.8, 143.6, 142.6, 142.5, 141.6, 139.5, 139.5, 137.6, 136.8, 136.7, 136.6, 135.3, 135.1, 131.2, 130.8, 130.5, 130.2, 130.1, 130.1, 130.0, 129.7, 129.5, 129.1, 128.6, 128.2, 127.7, 127.6, 127.0, 127.0, 125.9, 125.8, 125.6, 125.5, 121.7, 119.9, 30.2, 21.6, 21.0, 20.8, 20.2. HRMS (EI^+): calcd. for $C_{25}H_{24}$ $[M+1]^+$: 325.1951, found: 325.1949.

4,4'-(1-(p-tolyl)buta-1,3-diene-1,3-diyl)bis(methoxybenzene) (3k). The title compound was obtained according to the general procedure. Colourless oil; Yield: 43%; IR (KBr): 3034, 2999, 2953, 2931, 2835, 1606, 1510, 1461, 1413, 1380,1359, 891, 831, 726 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.33 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 9.6 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.06-7.03(m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.78-6.75 (m, 2H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.29 (d, *J* = 11.2 Hz, 1H), 4.91 (d, *J* = 18.8 Hz, 1H), 3.76 (t, *J* = 10.6 Hz, 6H), 3.37-3.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 159.5, 159.5, 159.1, 145.3, 145.2, 144.4, 141.2, 137.8, 137.8, 137.0, 136.4, 134.0, 133.9, 133.0, 131.7, 130.4, 129.6, 129.3, 129.1, 128.4, 128.2, 128.2, 127.8, 127.2, 115.6, 115.5, 113.9, 113.9, 113.7, 55.7, 55.6, 21.7, 21.6. HRMS (EI^+): calcd. for $C_{25}H_{24}O_2$ $[M+1]^+$: 357.1849, found: 357.1848.

4-(1,3-diphenylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3l). The title compound was obtained according to the general procedure. Colourless oil; Yield: 77%; IR (KBr): 3077, 3055, 3027, 2958, 2929, 1754, 1599, 1488, 1444, 1403, 905, 839, 765, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43-7.38 (m, 3H), 7.24 (s, 7H), 7.14 (s, 3H), 7.05 (s, 6H), 6.65 (d, *J* = 14.0 Hz, 1H), 5.27 (s, 1H), 4.99-4.92 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 145.7, 144.7, 143.6, 142.5, 141.3, 141.2, 141.1, 140.8, 140.4, 140.2, 139.5, 131.1, 130.6, 129.2, 129.2, 129.1, 128.8, 128.7, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.6, 127.5, 127.4, 127.4, 127.3, 127.2, 127.1, 127.0, 118.1, 117.9. HRMS (EI^+): calcd. for $C_{28}H_{22}$ $[M+1]^+$: 359.1794, found: 359.1793.

4-(1,3-di-p-tolylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3m). The title compound was obtained according to the general procedure. Colourless oil; Yield: 82%; IR (KBr): 3057, 3026, 2923, 2854, 1654, 1602, 1510, 1485, 1450, 1404, 1380, 895, 821, 763, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 6.4 Hz, 2H), 7.38-7.35 (m, 4H), 7.32-7.23 (m, 4H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 15.6, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 6.0 Hz, 2H), 5.36 (s, 1H), 5.02-4.97 (m, 1H), 2.28 (t, *J* = 15.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.6, 145.4, 144.5, 144.5, 142.7, 141.3, 141.1, 140.8, 140.7, 140.1, 139.8, 138.4, 138.3, 137.9, 137.6, 137.5, 137.1, 131.0, 130.4, 129.4, 129.3, 129.2, 129.2, 129.2, 129.1, 128.8, 128.7, 128.5, 128.4, 127.7, 127.6, 127.4, 127.4, 127.3, 127.1, 126.9, 117.1, 116.7, 21.6. HRMS (EI^+): calcd. for $C_{30}H_{26}$ $[M+1]^+$: 387.2107, found: 387.2109.

4-(1,3-di-o-tolylbuta-1,3-dien-1-yl)-1,1'-biphenyl (3n). The title compound was obtained according to the general procedure. Colourless oil; Yield: 40%; IR (KBr): 3058, 3026, 2951, 2921, 2858, 1731, 1666, 1599, 1486, 1452, 1380, 905, 840, 764, 730, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.19-7.09 (m, 1H), 7.05-7.00 (m, 1H), 6.98 (d, *J* = 4.4 Hz, 2H), 6.94 (d, *J* = 4.4 Hz, 2H), 6.92-6.89 (m, 2H), 6.88-6.74 (m, 1H), 5.23 (s, 1H), 5.02 (d, *J* = 1.2 Hz, 1H), 2.26 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.0, 142.7, 142.6, 139.7, 139.3, 136.9, 135.1, 133.9, 133.2, 130.4, 130.3, 130.0, 130.0, 129.2, 128.8, 128.3, 128.0, 127.8, 127.1, 126.5, 126.4, 126.3, 126.3, 125.9, 125.6, 125.0, 120.4, 20.9, 20.3. HRMS (EI^+): calcd. for $C_{30}H_{26}$ $[M+1]^+$: 387.2107, found: 387.2114.

4-(1,3-bis(4-fluorophenyl)buta-1,3-dien-1-yl)-1,1'-biphenyl (3o). The title compound was obtained according to the general procedure. Colourless oil; Yield: 89%; IR (KBr): 3080, 3048, 3030, 2960, 2929, 2847, 1652, 1600, 1506, 1486, 1404, 907, 877, 733, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.58 (d, *J* = 6.8 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 2H), 7.40-7.34 (m, 4H), 7.32-7.26 (m, 3H), 7.12-7.05 (m, 2H), 7.00 (t, *J* = 11.2 Hz, 1H), 6.86-6.79 (m, 4H), 6.68 (s, 1H), 5.34 (s, 1H), 5.12 (d, *J* = 12.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 161.5, 145.1, 143.9, 143.8, 142.2, 141.2, 141.1, 141.0, 140.6, 139.6, 139.1, 137.1, 136.2, 132.3, 132.3, 131.0, 130.2, 130.1, 129.3, 129.2, 129.0, 128.9, 128.9, 128.8, 128.7, 127.9, 127.8, 127.4, 127.1, 118.4, 115.7, 115.5, 115.4, 115.2, 115.2. HRMS (EI^+): calcd. for $C_{28}H_{20}F_2$ $[M+1]^+$: 395.1606, found: 395.1600.

(1-(4-chlorophenyl)buta-1,3-diene-1,3-diyl)dibenzene (3p). The title compound was obtained according to the general procedure. Colourless oil; Yield: 45%; IR (KBr): 3080, 3048, 3030, 2960, 2929, 2847, 1652, 1600, 1506, 1486, 1404, 907, 877,

733, 696 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.36-7.33 (m, 2H), 7.29 (s, 3H), 7.24 (d, *J* = 4.0 Hz, 2H), 7.22-7.19 (m, 3H), 7.17 (dd, *J* = 4.4, *J* = 1.2 Hz, 1H), 7.13-7.10 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.73 (d, *J* = 16.8 Hz, 1H), 5.40 (d, *J* = 8.8 Hz, 1H), 5.04 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 145.6, 144.0, 143.9, 143.1, 142.1, 141.0, 140.9, 140.1, 139.0, 133.9, 133.4, 132.0, 130.5, 129.7, 129.5, 129.2, 128.8, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.1, 127.1, 118.3, 118.2. HRMS (EI^+): calcd. for $C_{22}H_{17}Cl$ $[M+1]^+$: 317.1092, found: 317.1093.

4,4'-(1-(4-chlorophenyl)buta-1,3-diene-1,3-diyl)bis(methylbenzene) (3q). The title compound was obtained according to the general procedure. Colourless oil; Yield: 74%; IR (KBr): 3084, 3051, 3024, 2949, 2920, 2865, 1654, 1608, 1510, 1487, 1449, 1400, 906, 822, 766, 731 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29-7.22 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.10 (t, *J* = 8.4 Hz, 3H), 7.05 (d, *J* = 9.2 Hz, 2H), 7.01-6.99 (m, 2H), 6.69-6.62 (m, 1H), 5.35 (s, 1H), 4.96 (s, 1H), 2.33-2.27 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 145.3, 143.8, 143.6, 142.3, 140.4, 139.2, 138.2, 138.1, 138.0, 137.8, 137.7, 137.4, 137.2, 133.8, 133.3, 131.9, 130.4, 129.7, 129.4, 129.3, 129.2, 129.0, 128.9, 128.7, 128.5, 128.3, 127.0, 126.9, 117.1, 116.9, 21.7, 21.6, 21.6. HRMS (EI^+): calcd. for $C_{24}H_{21}Cl$ $[M+1]^+$: 345.1405, found: 345.1402.

1-(1,3-diphenylbuta-1,3-dien-1-yl)naphthalene (3r). The title compound was obtained according to the general procedure. Colourless oil; Yield: 50%; IR (KBr): 3080, 3054, 3024, 2960, 2926, 2847, 1597, 1573, 1492, 1443, 1383, 904, 857, 748, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.62 (m, 2H), 7.51 (d, *J* = 10.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 7.28 (s, 5H), 7.16 (d, *J* = 5.6 Hz, 2H), 7.12-6.99 (m, 6H), 6.70-6.60 (m,1H), 4.95 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.8, 145.7, 145.2, 145.1, 143.6, 141.2, 141.0, 140.5, 138.1, 133.8, 133.6, 133.4, 133.0, 130.7, 129.7, 129.4, 129.3, 128.8, 128.7, 128.6, 128.5, 128.5, 128.2, 128.0, 127.9, 127.8, 127.6, 127.2, 127.1, 126.6, 126.5, 126.4, 126.3, 118.2, 118.0. HRMS (EI^+): calcd. for $C_{26}H_{20}$ $[M+1]^+$: 333.1638, found: 333.1635.

1-(1,3-di-p-tolylbuta-1,3-dien-1-yl)naphthalene (3s). The title compound was obtained according to the general procedure. Colourless oil; Yield: 83%; IR (KBr): 3053, 3023, 2955, 2923, 2853, 1606, 1510, 1461, 1377, 895, 854, 818, 745, 723 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.68 (m, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 8.4, *J* = 1.6 Hz, 1H), 7.38-7.29 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.01 (td, *J* = 15.6, *J* = 8.0 Hz, 4H), 6.78 (d, *J* = 16.4 Hz, 1H), 5.38-5.30 (m, 1H), 4.98 (m, 1H), 2.31-2.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 145.4, 145.0, 144.8, 141.2, 140.9, 138.4, 138.4, 138.3, 137.9, 137.6, 137.6, 137.6, 137.2, 133.8, 133.7, 133.3, 133.0, 130.5, 129.6, 129.4, 129.3, 129.3, 129.3, 129.2, 128.9, 128.7, 128.7, 128.5, 128.4, 128.1, 128.0, 127.8, 127.6, 127.0, 126.9, 126.6, 126.5, 126.4, 126.2, 117.1, 116.7, 21.7, 21.6, 21.6, 21.5. HRMS (EI^+): calcd. for $C_{28}H_{24}$ $[M+1]^+$: 361.1951, found: 361.1950.

1-(1,3-bis(4-fluorophenyl)buta-1,3-dien-1-yl)naphthalene (3t). The title compound was obtained according to the general procedure. Colourless oil; Yield: 71%; IR (KBr): 3054, 3020, 2955, 2925, 2854, 1771, 1600, 1506, 1440, 900, 837, 748. cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.74 (m, 2H), 7.69-7.62 (m, 1H), 7.54 (s, 1H), 7.46-7.40 (m, 2H), 7.31-7.27 (m, 3H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.10-7.07 (m, 1H), 6.99 (t, *J* = 8.4 Hz, 1H), 6.89-6.84 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.78-6.73 (m, 1H), 5.38-5.30 (m, 1H), 5.14-5.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 163.9, 163.8, 163.7, 161.8, 161.5, 161.4, 161.3, 145.1, 144.7, 144.2, 144.2, 140.6, 139.6, 139.5, 137.7, 137.1, 137.1, 137.0, 137.0, 136.2, 136.2, 133.7, 133.5, 133.4, 133.0, 132.4, 132.3, 130.2, 130.1, 129.8, 129.5, 128.9, 128.8, 128.7, 128.7, 128.7, 128.5, 128.3, 128.3, 128.0, 127.7, 126.8, 126.7, 126.5, 126.4, 126.3, 126.3, 118.4, 118.4, 115.7, 115.5, 115.4, 115.4, 115.3, 115.2, 115.1. HRMS (EI^+): calcd. for $C_{26}H_{19}F_2$ $[M+1]^+$: 369.1449, found: 369.1456.

(1-(3,5-dimethylphenyl)buta-1,3-diene-1,3-diyl)dibenzene (3u). The title compound was obtained according to the general procedure. Colourless oil; Yield: 66%; IR (KBr): 3078, 3054, 3025, 2949, 2917, 2861, 1751, 1598, 1492, 1440, 1382, 900, 848, 772, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.37 (d, *J* = 6.8 Hz, 1H), 7.32 (d, *J* = 7.2 Hz, 2H), 7.26 (d, *J* = 10.4 Hz, 1H), 7.21-7.15 (m, 6H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.75-6.72 (m, 1H), 6.70 (d, *J* = 10.4 Hz, 1H), 5.36 (s, 1H), 5.09-5.00 (m, 1H), 2.26 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 145.8, 145.4, 143.8, 143.7, 141.3, 140.3, 138.1, 137.6, 130.6, 129.8, 129.0, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.6, 127.4, 127.2, 127.2, 126.4, 118.1, 117.6, 21.8, 21.6. HRMS (EI^+): calcd. for $C_{24}H_{22}$ $[M+1]^+$: 311.1794, found: 311.1797

4,4'-(1-(3,5-dimethylphenyl)buta-1,3-diene-1,3-diyl)bis(methylbenzene) (3v). The title compound was obtained according to the general procedure. Colourless oil; Yield: 61%; IR (KBr): 3083, 3022, 2949, 2921, 2856, 1788, 1652, 1600, 1510, 1455, 1378, 895, 820, 731, 708 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.23 (q, *J* = 7.6 Hz, 2H), 7.09-6.91 (m, 7H), 6.75 (d, *J* = 12.4 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 1H), 5.31 (d, *J* = 12.8 Hz, 1H), 4.98-4.92 (m, 1H), 2.31 (d, *J* = 12.4 Hz, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 145.5, 145.2, 145.0, 143.9, 141.1, 140.5, 138.8, 138.5, 138.0, 137.8, 137.7, 137.6, 137.3, 137.0, 130.4, 129.7, 129.3, 129.3, 129.1, 129.1, 128.9, 128.5, 128.3, 128.3, 127.8, 127.0, 126.9, 126.4, 116.8, 116.3, 30.2, 21.8, 21.6. HRMS (EI^+): calcd. for $C_{26}H_{27}$ $[M+1]^+$: 339.2107, found: 339.2111.

2,2'-(1-(3,5-dimethylphenyl)buta-1,3-diene-1,3-diyl)bis(methylbenzene) (3w). The title compound was obtained according to the general procedure. Colourless oil; Yield: 55%; IR (KBr): 3063, 3016, 2955, 2918, 2861, 1597, 1486, 1453, 1380, 904, 848, 763, 730, 702, 658 cm-1; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.15-7.00 (m, 2H), 6.94 (d, *J* = 7.6 Hz, 4H), 6.86 (d, *J* = 15.2 Hz, 5H), 6.75-6.41 (m, 1H), 5.17 (s, 1H), 4.98 (s, 1H), 2.25 (s, 3H), 2.22 (s, 6H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 142.9, 142.7, 142.5, 139.5, 138.1, 136.8, 135.1, 130.2, 130.1, 130.0, 129.6, 129.3, 129.1, 127.5, 127.0, 125.8, 125.5, 125.0, 120.0, 21.8, 20.9, 20.3. HRMS (EI^+): calcd. for $C_{26}H_{26}$ $[M+1]^+$: 339.2107, found: 339.2105.

4,4'-(1-(3,5-dimethylphenyl)buta-1,3-diene-1,3-diyl)bis(fluorobenzene) (3x). The title compound was obtained according to the general procedure. Colourless oil; Yield: 64%; IR (KBr): 3041, 3009, 2955, 2923, 2855, 1649, 1601, 1507, 1462, 1380, 1228, 901, 838, 734, 707 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.19 (m, 3H), 7.05-7.01 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 12.4 Hz, 2H), 6.84-6.79 (m, 3H), 6.72 (d, *J* = 14.4 Hz, 1H), 6.63 (d, *J* = 3.2 Hz, 1H), 5.30 (d, *J* = 12.4 Hz, 1H), 5.13-5.06 (m, 1H), 2.27 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 163.9, 163.7, 163.6, 161.7, 161.4, 161.3, 161.2, 145.4, 145.1, 144.5, 144.3, 143.4, 139.9, 138.2, 137.7, 137.4, 137.3, 137.1, 137.1, 136.5, 136.4, 132.3, 132.2, 130.1, 130.1, 130.0, 129.3, 128.9, 128.9, 128.8, 128.8, 128.7, 128.4, 128.1, 126.4, 124.6, 118.4, 118.0, 115.5, 115.4, 115.3, 115.3, 115.2, 115.1, 115.0, 114.8, 21.8. HRMS (EI^+): calcd. for $C_{24}H_{20}F_2$ $[M+1]^+$: 347.1606, found: 347.1606.

(1E,3E)-hexa-1,3,5-trien-1-ylbenzene (5a). The title compound was obtained according to the general procedure. White solid; Yield: 63%; IR (KBr): 3060, 3025, 2918, 1675, 1618, 1492, 1449, 989, 750, 693 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 (d, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.20 (t, *J* = 7.2 Hz, 1H), 6.80 (dd, *J* = 15.6, *J* = 9.6 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.47-6.31 (m, 3H), 5.26 (dd, *J* = 16.8, *J* = 1.2 Hz, 1H), 5.13-5.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 137.5, 134.2, 133.9, 133.4, 129.3, 129.1, 128.0, 126.9, 118.0. HRMS (EI^+): calcd. for $C_{12}H_{12}$ $[M+1]^+$:157.1012, found:157.1021.

1-((1E,3E)-hexa-1,3,5-trien-1-yl)-4-methylbenzene (5b). The title compound was obtained according to the general procedure. White solid; Yield: 54%; IR (KBr): 3021, 2918, 2861, 1725, 1679, 1606, 1511, 1450, 1383, 987, 802, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 15.2, *J* = 9.6 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.47-6.29 (m, 3H), 5.24 (dd, *J* = 16.8, *J* = 1.6 Hz, 1H), 5.10 (dd, *J* = 10.0, *J* = 1.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 138.0, 137.6, 135.0, 134.1, 133.7, 133.4, 129.8, 128.4, 126.8, 117.6, 21.7. HRMS (EI^+): calcd. for $C_{13}H_{14}$ $[M+1]^+$:171.1168, found: 171.1170.

1-((1E,3E)-hexa-1,3,5-trien-1-yl)-3,5-dimethylbenzene (5c). The title compound was obtained according to the general procedure. White solid; Yield: 55%; IR (KBr): 3014, 2914, 2855, 1805, 1720, 1671, 1597, 1458, 1380, 976, 898, 824, 689 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.01 (s, 2H), 6.86 (s, 1H), 6.78 (dd, *J* = 15.6, *J* = 9.6 Hz, 1H), 6.50 (d, *J* = 15.2 Hz, 1H), 6.46-6.32 (m, 3H), 5.25 (d, *J* = 16.4 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 2.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 137.7, 137.6, 134.2, 133.9, 133.7, 129.9, 129.0, 124.8, 117.7, 21.7. HRMS (EI^+): calcd. for $C_{14}H_{16}$ $[M+1]^+$: 185.1325, found: 185.1328.

1-((1E,3E)-hexa-1,3,5-trien-1-yl)naphthalene (5d). The title compound was obtained according to the general procedure. White solid; Yield: 27%; IR (KBr): 3060, 3025, 2918, 1720, 1675, 1618, 1492, 1449, 989, 910, 748, 693 cm^{-1}; ^1H NMR (DMSO, 400 MHz): δ 7.87 (d, *J* = 8.8 Hz, 4H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.51-7.45 (m, 2H), 7.15-7.09 (m, 1H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.53-6.45 (m, 3H), 5.32 (d, *J* = 15.6 Hz, 1H), 5.17 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ 138.2, 135.6, 135.0, 134.8, 134.3, 133.9, 133.6, 130.5, 129.2, 128.9, 128.6, 127.5, 127.3, 127.1, 124.5, 119.1. HRMS (EI^+): calcd. for $C_{14}H_{16}$ $[M+1]^+$: 185.1325, found: 185.1328.

4-((1E,3E)-hexa-1,3,5-trien-1-yl)-1,1'-biphenyl (5e). The title compound was obtained according to the general procedure. White solid; Yield: 40%; IR (KBr): 3060, 3025, 2918, 1720, 1675, 1618, 1492, 1449, 989, 910, 748, 693 cm^{-1}; ^1H NMR (DMSO, 400 MHz): δ 7.67 (dd, *J* = 10.8, *J* = 7.6 Hz, 4H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.06-7.00 (m, 1H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.54-6.44 (m, 2H), 5.31 (d, *J* = 15.2 Hz, 1H), 5.16 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ 140.5, 140.2, 138.1, 137.1, 134.9, 134.7, 133.3, 130.05, 129.9, 128.5, 127.9, 127.9, 127.4, 119.0. HRMS (EI^+): calcd. for $C_{14}H_{16}$ $[M+1]^+$: 185.1325, found: 185.1328.

9-((1E,3E)-hexa-1,3,5-trien-1-yl)phenanthrene (5f). The title compound was obtained according to the general procedure. White solid; Yield: 35%; IR (KBr): 3025, 2923, 2858, 1720, 1677, 1615, 1493, 1449, 1383, 990, 905, 748, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.71 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.89-7.86 (m, 2H), 7.69-7.55 (m, 4H), 7.36-7.24 (m, 1H), 6.96 (dd, *J* = 15.2, *J* = 10.8 Hz, 1H), 6.61-6.41 (m, 3H), 5.32 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 9.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 134.7, 134.1, 134.0, 132.5, 132.2, 130.9, 130.7, 130.5, 129.2, 127.3, 127.1, 127.0, 127.0, 124.9, 124.7, 123.6, 123.0, 118.4. HRMS (EI^+): calcd. for $C_{20}H_{16}$ $[M+1]^+$: 257.1325, found: 257.1319.

(1E,3E,5E)-octa-1,3,5,7-tetraen-1-ylbenzene (5g). The title compound was obtained according to the general procedure. White solid; Yield: 27%; IR (KBr): 3023, 2923, 2852, 1720, 1675, 1595, 1444, 1383, 989, 904, 748, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.22 (dd, *J* = 15.2, *J* = 8.0 Hz, 1H), 6.84 (dd, *J* = 15.6, *J* = 10.0 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 6.46-6.28 (m, 5H), 5.25 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 137.6, 134.2, 134.2, 133.9, 133.6, 133.2, 129.5, 129.1, 128.0, 126.8, 118.0. HRMS (EI^+): calcd. for $C_{14}H_{14}$ $[M+1]^+$: 183.1168, found: 183.1166.

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