


 Cite this: *RSC Adv.*, 2024, 14, 22076

 Received 3rd April 2024
 Accepted 6th July 2024

DOI: 10.1039/d4ra02525c

rsc.li/rsc-advances

Synthesis of 1-aryl-2,3-diaroyl cyclopropanes from 1,3,5-triaryl-1,5-diketones and their transformation into *E,E*-1,4-diaryl-1,3-butadienes†

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A new method for the synthesis of 1-aryl-2,3-diaroyl cyclopropanes has been developed by iodine/DBU-mediated cyclization of 1,3,5-triaryl-1,5-diketones. The alcohols derived by the reduction of these cyclopropanes, when treated with conc. HCl, afforded a series of 1,3-dienes through cyclopropyl ring-opening and subsequent fragmentation. Overall, the synthetic sequence represents a new non-Wittig methodology for the synthesis of 1,3-dienes from 1,5-diketones.

Introduction

Cyclopropanes, especially those having electron donating and withdrawing groups in the vicinal position continue to receive a major focus in organic synthesis owing to their enormous synthetic potential.¹ The inherent angle and torsional strains in the three-carbon ring system coupled with the presence of push-pull groups in adjacent positions bestow them with high reactivity. Such cyclopropanes undergo various transformations such as annulation,² rearrangement³ and ring-opening⁴ reactions upon exposure to suitable reagents to yield a diverse range of products. Most of the methods used for the synthesis of donor-acceptor cyclopropanes fall into two major categories: (1) [2 + 1] cycloaddition of carbenes generated from diazo compounds or iodonium ylides to alkenes and (2) Michael-initiated ring closure strategy involving addition of nucleophiles to electrophilic alkenes followed by cyclization. Both methods have been extensively used for the access of various types of donor-acceptor cyclopropanes in both racemic and chiral forms.⁵

1,3,5-Triaryl-1,5-diketones are important building blocks for the synthesis of various heterocyclic compounds such as pyridines,⁶ thiophenes⁷ and pyrylium compounds.⁸ These 1,5-diketones could be easily prepared by the base-mediated Michael addition of aryl methyl ketones to chalcones in a one-pot or stepwise manner.⁹ However, the application of these 1,5-diketones for synthesis of carbocycles such as cyclopropanes has been scarcely investigated in the literature. To the best of our knowledge, there is only one report to effect the

transformation using iodobenzene diacetate and the reaction yields cyclopropanes only in low yields with three other by-products.¹⁰ Our research group prepared aryl/nitro substituted donor-acceptor cyclopropanes **2** by iodine/DBU mediated oxidative cyclization of Michael adducts of chalcones/nitrostyrenes with malonates **1** (Scheme 1, eqn. (1)).¹¹ Noticing the presence of acidic protons in suitable positions in 1,3,5-triaryl-1,5-diketones **3** as well, we envisaged that they could be also subjected to a similar oxidative cyclization using iodine/DBU to obtain 1-aryl-2,3-diaroyl cyclopropanes **4/5** (Scheme 1, eqn. (2)). We herein present the results along with further transformation of the cyclopropanes into *E,E*-1,4-diaryl-1,3-dienes. It may be noted that this type of donor-acceptor cyclopropane has been mostly synthesized by employing sulphur ylides in the literature.¹²

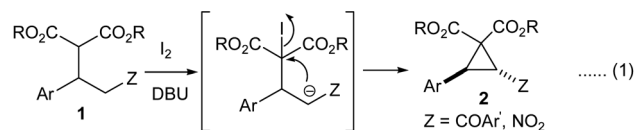
Result and discussion

We began the study by identifying suitable reaction conditions for iodine-mediated oxidative cyclization of 1,3,5-triaryl-1,5-

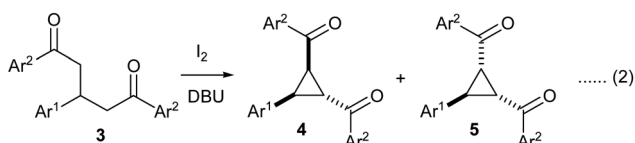
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† Electronic supplementary information (ESI) available: Copies of ¹H and ¹³C NMR spectra of all products and X-ray structural information of **8h**. CCDC 2338084. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4ra02525c>

Our previous work:



This work:

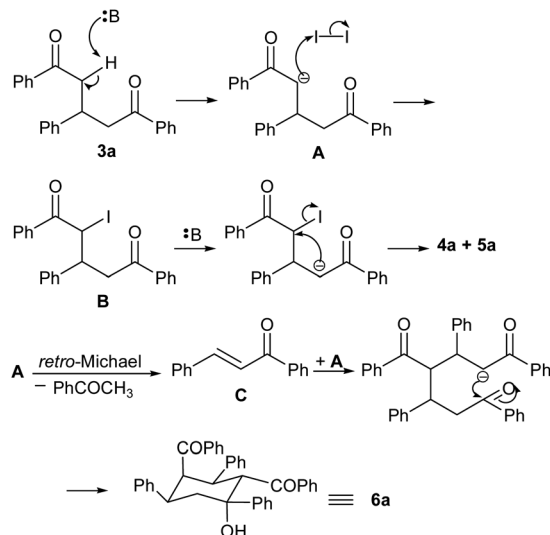


Scheme 1 Comparison of the present work with our previous work.



diketones **3**, which were prepared as per literature reports.⁹ We selected diketone **3a** as a model substrate and treated with iodine in the presence of two equiv. of DBU in DCM, as per our reported methods for the cyclization of Michael adducts of chalcones/nitrostyrenes.¹¹ Pleasingly, it underwent the expected oxidative cyclization to afford two diastereomeric cyclopropanes **4a** and **5a** along with a cyclohexanol derivative **6a**¹³ in 43, 37 and 7% yields, respectively (entry 1). With a view to synthesize one of the cyclopropane products in a better yield, we employed different bases such as Et₃N, piperidine and DABCO in the reaction (entries 2–4). However, we could not see better outcomes with these bases as compared to DBU. Next, we examined the use of different solvents in the reaction (entries 5–10). We found better results with MeCN (entry 8) and hence it was selected as the solvent of choice for other reactions. In Table 1, it is interesting to note that the yield of **4a** (in which the two aryl groups are *trans* to each other) is always higher than that of **5a** (in which the aryl groups are *cis*) and hence we attribute the observed diastereoselectivity to the repulsion between the two aryl groups.

A plausible mechanism for the formation of different products in the transformation is outlined in Scheme 2. The base (DBU) removes one of the acidic protons in diketone **3a** and the resulting carbanion **A** attacks iodine to give mono-iodinated intermediate **B**. Next, the base removes the remaining acidic proton in **B** and the anion so formed attacks the iodine-containing carbon in an intermolecular S_N2 fashion to give diastereomeric cyclopropane products **4a** and **5a**. The

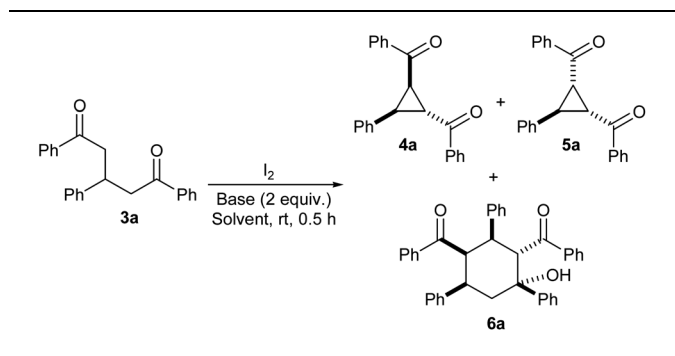
Scheme 2 Mechanism for the formation of products **4a**, **5a** and **6a**.

carbanion **A** produced in the first step may also undergo retro-Michael reaction to give chalcone **C** via elimination of acetophenone. A subsequent tandem Michael addition/aldol reaction between **A** and **C** gives cyclohexanol **6a**.

While investigating the reactivity of the major cyclopropane products **4** (discussed later), we found that the minor cyclopropane products **5** also give the same result. So, we next focused our attention only on synthesizing various derivatives of **4** (and not **5**) and the results are summarized in Table 2. Initially, we employed diketones having different electron-donating, electron-withdrawing and halogen substituents on Ar¹ and Ar² (entries 1–13). Pleasingly, all the diketones afforded the respective cyclopropanes **4a–m** in 56–68% yields. The reaction also tolerated the use of bulky 1-naphthyl and heteroaromatic, 2-thienyl as Ar¹ or Ar² and the corresponding cyclopropanes **4n–s** are produced in 60–67% yields (entries 14–19).

Next, we investigated the ring-opening reactions of cyclopropanes **4** with various Lewis acids such as AlCl₃, SnCl₄, TiCl₄, BF₃·OEt₂, FeCl₃, SnCl₂, Cu(OTf)₂, In(OTf)₃, Sc(OTf)₃, and Yb(OTf)₃ and Brønsted acids such as *p*-TsOH, TFA and con. HCl to identify the mode of cleavage of the cyclopropane ring. Unfortunately, none of the reagents could bring any change to cyclopropanes **4**. So, we decided to reduce their keto group into alcoholic group and then attempt their ring-opening reactions.¹⁴ Accordingly, cyclopropanes **4** were subjected to reduction using NaBH₄ in MeOH and the resulting diastereomeric mixtures of alcohols **7**, after work-up, were treated as such without further purification with different Lewis/Brønsted acids. We found that the treatment of **7** with a few drops of con. HCl in 1,2-DCE yielded a series of 1,3-dienes **8** (Table 3; the structure of **8h** was confirmed by X-ray crystallographic analysis¹⁵). The conversion could also be achieved by using one equiv. of AlCl₃, Sc(OTf)₃, Yb(OTf)₃ or TFA with similar yields.¹⁶ It may be noted that in case of **8f**, the strong electron withdrawing aryl group would destabilize the respective carbocation **B** (Scheme 3) and hence its formation would have been sluggish

Table 1 Optimisation of reaction conditions

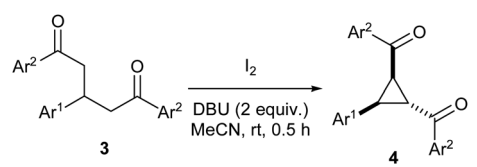


S. no.	Reaction conditions	Yield ^a (%)		
		4a	5a	6a
1	DBU, DCM	43	37	7
2	Et ₃ N, DCM	52	10	13
3	Piperidine, DCM	62	9	14
4	DABCO, DCM	48	6	8
5	DBU, CHCl ₃	35	7	5
6	DBU, 1,2-DCE	51	9	11
7	DBU, toluene	31	30	10
8	DBU, ^b MeCN	65	11	12
9	DBU, THF	61	9	10
10	DBU, EtOH	37	35	20

^a Isolated yield. ^b When 1 equiv. of DBU was used, the yields of **4a**, **5a** and **6a** were 52, 13 and 7%, respectively.



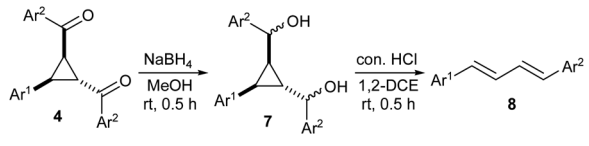
Table 2 Scope of formation of Cyclopropanes



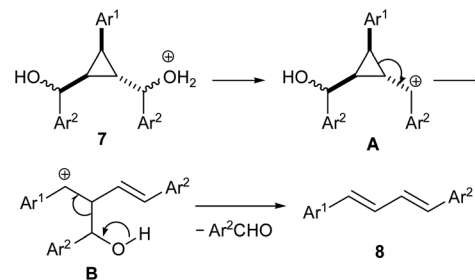
S. no.	Ar ¹ , Ar ² (3)	Yield of 4 ^a (%)
1	Ph, Ph (3a)	65 (4a)
2	Ph, 4-MeC ₆ H ₄ (3b)	59 (4b)
3	Ph, 4-MeOC ₆ H ₄ (3c)	63 (4c)
4	Ph, 4-BrC ₆ H ₄ (3d)	56 (4d)
5	4-MeC ₆ H ₄ , Ph (3e)	60 (4e)
6	4-F ₃ CC ₆ H ₄ , Ph (3f)	57 (4f)
7	2-MeC ₆ H ₄ , 4-MeC ₆ H ₄ (3g)	67 (4g)
8	4-MeC ₆ H ₄ , 4-MeC ₆ H ₄ (3h)	68 (4h)
9	4- ^t BuC ₆ H ₄ , 4-MeC ₆ H ₄ (3i)	67 (4i)
10	4-ClC ₆ H ₄ , 4-MeC ₆ H ₄ (3j)	60 (4j)
11	4-FC ₆ H ₄ , 4-MeC ₆ H ₄ (3k)	61 (4k)
12	4-MeC ₆ H ₄ , 4-BrC ₆ H ₄ (3l)	58 (4l)
13	4-MeC ₆ H ₄ , 4-ClC ₆ H ₄ (3m)	60 (4m)
14	1-Naphthyl, Ph (3n)	62 (4n)
15	1-Naphthyl, 4-MeC ₆ H ₄ (3o)	67 (4o)
16	Ph, 2-thienyl (3p)	61 (4p)
17	4-MeC ₆ H ₄ , 2-thienyl (3q)	60 (4q)
18	2-Thienyl, Ph (3r)	65 (4r)
19	2-Thienyl, 4-MeC ₆ H ₄ (3s)	63 (4s)

^a Isolated yield.

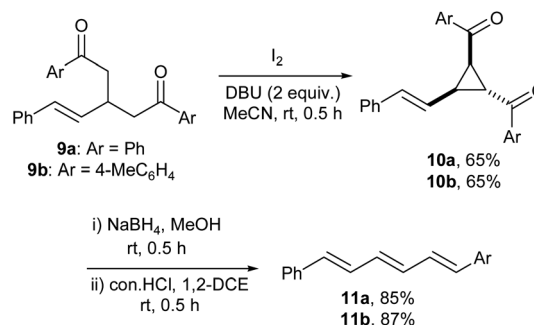
Table 3 Scope of formation of 1,3-dienes



S. no.	Ar ¹ , Ar ² (4)	Yield of 8 ^a (%)
1	Ph, Ph (4a)	89 (8a) ^b
2	Ph, 4-MeC ₆ H ₄ (4b)	79 (8b)
3	Ph, 4-MeOC ₆ H ₄ (4c)	80 (8c)
4	Ph, 4-BrC ₆ H ₄ (4d)	75 (8d)
5	4-MeC ₆ H ₄ , Ph (4e)	82 (8e)
6	4-F ₃ CC ₆ H ₄ , Ph (4f)	Trace (8f)
7	2-MeC ₆ H ₄ , 4-MeC ₆ H ₄ (4g)	87 (8g)
8	4-MeC ₆ H ₄ , 4-MeC ₆ H ₄ (4h)	88 (8h)
9	4- ^t BuC ₆ H ₄ , 4-MeC ₆ H ₄ (4i)	81 (8i)
10	4-ClC ₆ H ₄ , 4-MeC ₆ H ₄ (4j)	80 (8j)
11	4-FC ₆ H ₄ , 4-MeC ₆ H ₄ (4k)	83 (8k)
12	4-MeC ₆ H ₄ , 4-BrC ₆ H ₄ (4l)	72 (8l)
13	4-MeC ₆ H ₄ , 4-ClC ₆ H ₄ (4m)	82 (8m)
14	1-Naphthyl, Ph (4n)	87 (8n)
15	1-Naphthyl, 4-MeC ₆ H ₄ (4o)	85 (8o)
16	Ph, 2-thienyl (4p)	Trace (8p)
17	4-MeC ₆ H ₄ , 2-thienyl (4q)	84 (8q)
18	2-Thienyl, Ph (4r)	80 (8r)
19	2-Thienyl, 4-MeC ₆ H ₄ (4s)	87 (8s)

^a Isolated yield. ^b The diastereomeric cyclopropane, 5a also gave 8a in 86% yield.

Scheme 3 Plausible mechanism for the formation of 1,3-dienes.



Scheme 4 Synthesis of trienes from styryl-substituted cyclopropanes.

resulting in trace amount of the final product. We also observed that one of the diastereomeric cyclopropanes, 5a also produced the same 1,3-diene 8a in 86% yield when treated with con. HCl.

Mechanistically, the ring-opening reaction of cyclopropane alcohols 7 may take place as shown in Scheme 3. The protonation of hydroxyl group of alcohols 7 leads to the elimination of the hydroxyl group with formation of carbocation A. This triggers cyclopropane ring-opening to generate a new carbocation B, which undergoes fragmentation to yield 1,3-diene 8 with loss of arylaldehyde. We have previously observed such fragmentation with aryl-substituted donor-acceptor cyclopropanes.^{11b}

Finally, we extended the scope of the three-step transformation for diketones 9 having a styryl group with a view to obtain the respective trienes (Scheme 4). Pleasingly, diketones 9 gave the respective styryl cyclopropanes 10 when treated with iodine/DBU and the cyclopropanes furnished the corresponding trienes 11 when subjected to reduction followed by treatment with con. HCl.

1,3-Dienes are usually synthesized by (i) the Wittig and related reactions, (ii) cross-coupling reactions, (iii) olefin metathesis and (iv) rearrangement/isomerisation reactions.¹⁷ Among them, the Wittig strategy is one of the most commonly employed methods. The present work represents a new non-Wittig strategy for the synthesis of 1,3-dienes and 1,3,5-trienes from 1,5-diketones.

Conclusions

In conclusion, we have synthesized a series of 1-aryl-2,3-diaroyl cyclopropanes by iodine/DBU-mediated cyclization of 1,3,5-triaryl-1,5-diketones. The cyclopropanes when subjected to



reduction followed by treatment with con. HCl afforded *E,E*-1,5-diaryl-1,3-butadienes, through the formation of the respective alcohols, followed by cyclopropyl ring-opening promoted by elimination of a hydroxyl group and subsequent fragmentation. It was also possible to obtain few trienes by employing styryl-substituted cyclopropanes.

Experimental section

General remarks. Melting points were determined by the open capillary tube method and are uncorrected. The IR spectra were recorded on an FT-IR spectrometer using ATR. The ^1H and ^{13}C NMR spectra were recorded on a 400 MHz NMR spectrometer. High resolution mass spectra (ESI) were recorded on a Q-TOF mass spectrometer. X-ray crystallographic data were collected on a CCD diffractometer using graphite-monochromated Mo- $K\alpha$ radiation. Thin layer chromatography (TLC) was performed on pre-coated alumina sheets and detected under UV light. Silica gel (100–200 mesh) was used for column chromatography. 1,5-Diketones **3a–s** and **9a–b** were prepared as per a reported literature procedure^{9d} and among the diketones, **3a**, **3c–f**, **3h**, **3j**, **3k**, **3l**, **3n**, **3q** and **9a** are known compounds.¹⁸ Among the new compounds **3b**, **3p** and **3r** had about 15–25% inseparable impurities and hence were taken as such to the next step.

3-*o*-Tolyl-1,5-di-*p*-tolyl-pentane-1,5-dione (3g)

White solid. Yield: 2.83 g (70%); M. p. 90–92 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, J = 8.0 Hz, 4H), 7.32–7.27 (m, 5H), 7.21–7.11 (m, 3H), 4.37 (dd, J_1 = 6.8 Hz, J_2 = 11.0 Hz, 1H), 3.48 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H), 3.36 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H) 2.44 (s, 6H), 2.42 (s, 3H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 198.4, 143.9, 142.3, 136.0, 134.5, 131.9, 130.7, 130.3, 129.3, 128.3, 126.3, 126.2, 125.7, 44.6, 32.2, 21.7, 19.8 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{O}_2$, 371.2006; found: 371.2010.

3-(4-*tert*-Butyl-phenyl)-1,5-di-*p*-tolyl-pentane-1,5-dione (3i)

White solid. Yield: 1.52 g (71%); M. p. 102–104 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, J = 8.4 Hz, 4H), 7.20–7.17 (m, 2H), 7.13 (t, J = 8.2 Hz, 6H), 3.35 (dd, J_1 = 7.2 Hz, J_2 = 16.4 Hz, 2H), 3.23 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H) 2.31 (s, 6H), 1.19 (s, 9H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 198.5, 149.2, 143.8, 141.0, 134.5, 129.2, 128.3, 127.1, 125.5, 44.9, 36.8, 34.4, 31.4, 21.7 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{32}\text{O}_2$, 413.2475; found: 413.2477.

1,5-Bis-(4-chloro-phenyl)-3-*p*-tolyl-pentane-1,5-dione (3m)

White solid. Yield: 2.89 g (75%); M. p. 73–75 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.80 (d, J = 8.4 Hz, 4H), 7.33 (d, J = 8.4 Hz, 4H), 7.03 (dd, J_1 = 7.8 Hz, J_2 = 22.2 Hz, 4H), 3.90 (t, J = 7.0 Hz, 1H), 3.36 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H), 3.20 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H), 2.21 (s, 3H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 197.5, 140.4, 139.6, 136.5, 135.2, 129.6, 129.4, 128.9, 127.2, 45.0, 36.9, 21.0 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_2$, 411.0913; found: 411.0918.

3-Naphthalen-1-yl-1,5-di-*p*-tolyl-pentane-1,5-dione (3o)

White solid. Yield: 2.73 g (71%); M. p. 107–109 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.33 (d, J = 8.4 Hz, 1H), 7.93–7.90 (m, 5H), 7.77 (d, J = 8.0 Hz, 1H), 7.60–7.51 (m, 3H), 7.46 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 8.0 Hz, 4H), 5.11 (t, J = 6.6 Hz, 1H), 3.66 (dd, J_1 = 7.2 Hz, J_2 = 16.8 Hz, 2H), 3.57 (dd, J_1 = 6.0 Hz, J_2 = 17.0 Hz, 2H), 2.44 (s, 6H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 198.4, 143.9, 140.3, 134.6, 134.2, 131.4, 129.3, 129.0, 128.3, 127.2, 126.3, 125.6, 125.4, 123.3, 44.4, 21.7 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{26}\text{O}_2$, 407.2006; found: 407.2013.

3-Thiophen-2-yl-1,5-di-*p*-tolyl-pentane-1,5-dione (3s)

White solid. Yield: 2.43 g (71%); M. p. 97–99 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, J = 8.0 Hz, 4H), 7.16 (d, J = 8.0 Hz, 4H), 7.01 (d, J = 4.4 Hz, 1H), 6.79 (d, J = 4.8 Hz, 2H), 4.33 (t, J = 6.8 Hz, 1H), 3.40 (dd, J_1 = 6.8 Hz, J_2 = 16.8 Hz, 2H), 3.30 (dd, J_1 = 7.0 Hz, J_2 = 16.6 Hz, 2H), 2.32 (s, 6H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 197.8, 147.7, 144.0, 134.4, 129.3, 128.3, 126.7, 124.2, 123.3, 45.6, 32.6, 21.7 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}$, 363.1413; found: 363.1420.

3-Styryl-1,5-di-*p*-tolyl-pentane-1,5-dione (9b)

Yellow solid. Yield: 2.79 g (78%); M. p. 70–72 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, J = 8.0 Hz, 3H), 7.22–7.15 (m, 9H), 7.13–7.08 (m, 1H), 6.34 (d, J = 16.0 Hz, 1H), 6.20 (dd, J_1 = 8.2 Hz, J_2 = 15.6 Hz, 1H), 3.52 (dd, J_1 = 7.0 Hz, J_2 = 13.8 Hz, 1H), 3.24 (dd, J_1 = 6.6 Hz, J_2 = 16.2 Hz, 2H), 3.08 (dd, J_1 = 6.8 Hz, J_2 = 16.0 Hz, 2H), 2.33 (s, 6H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 198.6, 143.9, 137.2, 134.6, 132.1, 130.3, 129.3, 128.4, 128.3, 127.2, 126.3, 43.4, 35.2, 21.7 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{26}\text{O}_2$, 383.2006; found: 383.2008.

General procedure for the synthesis of donor–acceptor cyclopropanes **4a–s** and **10a–b**

To a solution of 1,5-diketones **3** (3.0 mmol) in acetonitrile was added DBU (6.0 mmol) followed by iodine (3.0 mmol) and stirred for 0.5 h. The reaction mixture was quenched by aq. $\text{Na}_2\text{S}_2\text{O}_3$ solution, diluted with water and extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using EtOAc/hexane (1 : 19, v/v) to afford the pure cyclopropanes **4a–s** and **10a–b**.

((1*R**,2*S**,3*S**)-3-phenylcyclopropane-1,2-diyl) bis(phenylmethanone) (**4a**):^{12c}

White solid. Yield: 644 mg (65%); M. p. 120–122 °C; IR (KBr): ν 1652, 1587, 1289, 1208, 1013, 733, 693 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.21 (d, J = 7.6 Hz, 2H), 8.04 (d, J = 7.6 Hz, 2H), 7.68 (t, J = 7.2 Hz, 1H), 7.61–7.56 (m, 3H), 7.51–7.48 (m, 2H), 7.32–7.20 (m, 5H), 4.31 (t, J = 5.6 Hz, 1H), 3.84 (dd, J_1 = 4.8 Hz, J_2 = 10.0 Hz, 1H), 3.62 (dd, J_1 = 6.2 Hz, J_2 = 10.2 Hz, 1H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 197.5, 193.8, 137.5, 137.1, 134.4, 133.6, 133.3, 128.83, 128.78, 128.7, 128.5, 128.4, 128.3, 127.3, 38.1, 37.5, 29.8 ppm.



((1R*,2S*,3S*)-3-phenylcyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4b)

White solid. Yield: 632 mg (59%); M. p. 126–128 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18–7.14 (m, 6H), 7.12–7.08 (m, 1H), 4.14 (t, *J* = 5.4 Hz, 1H), 3.67 (dd, *J*₁ = 4.8 Hz, *J*₂ = 10.0 Hz, 1H), 3.45 (dd, *J*₁ = 6.0 Hz, *J*₂ = 10.0 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.1, 193.4, 144.5, 144.1, 135.1, 134.64, 134.61, 129.5, 129.3, 128.8, 128.6, 128.5, 128.2, 127.2, 37.8, 37.3, 29.6, 21.8, 21.7 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₅H₂₃O₂, 355.1693; found: 355.1706.

((1R*,2S*,3S*)-3-phenylcyclopropane-1,2-diyl)bis((4-methoxy)phenylmethanone) (4c)

White solid. Yield: 731 mg (63%); M. p. 110–112 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.97–7.89 (m, 3H), 7.35 (d, *J* = 4.8 Hz, 1H), 7.14 (d, *J* = 6.8 Hz, 3H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.11–4.08 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.63 (dd, *J*₁ = 4.8 Hz, *J*₂ = 10.0 Hz, 1H), 3.42 (dd, *J*₁ = 6.2 Hz, *J*₂ = 9.8 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 195.9, 192.3, 163.9, 163.6, 134.8, 132.3, 130.8, 130.75, 130.67, 130.2, 128.8, 128.5, 128.2, 127.1, 114.0, 113.8, 113.7, 55.6, 55.5, 37.5, 37.0, 29.4 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₅H₂₃O₄, 387.1591; found: 387.1599.

((1R*,2S*,3S*)-3-phenylcyclopropane-1,2-diyl)bis((4-bromophenyl)methanone) (4d)

White solid. Yield: 810 mg (56%); M. p. 146–148 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.30–7.23 (m, 5H), 4.22 (t, *J* = 5.4 Hz, 1H), 3.76 (dd, *J*₁ = 4.0 Hz, *J*₂ = 10.2 Hz, 1H), 3.59 (dd, *J*₁ = 6.0 Hz, *J*₂ = 10.0 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.2, 192.6, 136.0, 135.7, 133.9, 132.2, 130.0, 129.8, 129.0, 128.7, 128.6, 128.4, 127.5, 38.2, 37.4, 29.6 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₁₇Br₂O₂, 482.9590; found: 482.9590.

((1R*,2S*,3S*)-3-(*p*-tolyl)cyclopropane-1,2-diyl)bis(phenylmethanone) (4e):^{12c}

White solid. Yield: 620 mg (60%); M. p. 139–141 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.61–7.55 (m, 3H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.30 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 4.27 (t, *J* = 5.6 Hz, 1H), 3.81 (dd, *J*₁ = 4.8 Hz, *J*₂ = 10.0 Hz, 1H), 3.57 (dd, *J*₁ = 6.2 Hz, *J*₂ = 9.8 Hz, 1H), 2.29 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.5, 193.9, 137.6, 137.1, 136.9, 133.5, 133.2, 131.3, 129.0, 128.8, 128.63, 128.61, 128.5, 128.4, 38.0, 37.5, 30.0, 21.1 ppm.

((1R*,2S*,3S*)-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,2-diyl)bis(phenylmethanone) (4f)

White solid. Yield: 673 mg (57%); M. p. 110–112 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.21 (d, *J* = 7.6 Hz, 2H), 8.04 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.63–7.57 (m, 3H), 7.55–7.49 (m, 4H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.33 (t, *J* = 5.4 Hz, 1H), 3.87 (dd, *J*₁

= 4.8 Hz, *J*₂ = 10.0 Hz, 1H), 3.65 (dd, *J*₁ = 6.2 Hz, *J*₂ = 9.8 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.8, 193.4, 138.6, 137.3, 136.9, 133.8, 133.6, 129.3, 129.2, 128.9, 128.8, 128.5, 128.4, 125.33, 125.29, 125.25, 125.22, 37.3, 37.1, 29.9 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₅H₁₈F₃O₂, 395.1253; found: 395.1263.

((1R*,2S*,3S*)-3-(*o*-tolyl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4g)

White solid. Yield: 747 mg (67%); M. p. 130–132 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19–7.16 (m, 3H), 7.08–7.02 (m, 2H), 6.98–6.96 (m, 1H), 4.14 (dd, *J*₁ = 4.8 Hz, *J*₂ = 6.0 Hz, 1H), 3.80 (dd, *J*₁ = 4.6 Hz, *J*₂ = 9.4 Hz, 1H), 3.37 (dd, *J*₁ = 6.4 Hz, *J*₂ = 9.6 Hz, 1H), 2.36 (s, 3H), 2.32 (s, 3H), 2.15 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.2, 193.2, 144.5, 144.1, 137.7, 134.8, 134.6, 132.7, 129.9, 129.5, 129.3, 128.9, 128.6, 128.5, 127.3, 125.6, 37.2, 36.0, 30.6, 21.8, 21.7, 19.8 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₆H₂₅O₂, 369.1849; found: 369.1868.

((1R*,2S*,3S*)-3-(*p*-tolyl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4h)

White solid. Yield: 750 mg (68%); M. p. 131–133 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 4.18–4.09 (m, 1H), 3.64 (dd, *J*₁ = 4.8 Hz, *J*₂ = 10.0 Hz, 1H), 3.40 (dd, *J*₁ = 6.2 Hz, *J*₂ = 9.8 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.2, 193.5, 144.4, 144.0, 136.8, 135.2, 134.7, 131.5, 129.5, 129.3, 129.0, 128.64, 128.62, 128.5, 37.7, 37.3, 34.7, 31.6, 29.8, 22.7, 21.8, 21.7, 21.1 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₆H₂₅O₂, 369.1849; found: 369.1853.

((1R*,2S*,3S*)-3-(4-(*tert*-butyl)phenyl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4i)

White solid. Yield: 832 mg (67%); M. p. 126–128 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.16–7.14 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 4.13–4.10 (m, 1H), 3.66 (dd, *J*₁ = 5.0 Hz, *J*₂ = 9.8 Hz, 1H), 3.39 (dd, *J*₁ = 6.0 Hz, *J*₂ = 10.0 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 1.16 (s, 9H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.2, 193.6, 149.9, 144.4, 144.0, 135.3, 134.7, 129.5, 129.3, 128.6, 128.5, 128.4, 125.2, 37.9, 37.4, 34.4, 31.3, 31.0, 30.0, 21.8, 21.7 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₉H₃₁O₂, 411.2319; found: 411.2320.

((1R*,2S*,3S*)-3-(4-chlorophenyl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4j)

White solid. Yield: 700 mg (60%); M. p. 137–139 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 2H), 7.10 (s, 4H), 4.09 (dd, *J*₁ = 4.8 Hz, *J*₂ = 6.0 Hz, 1H), 3.67–3.64 (m, 1H), 3.40 (dd, *J*₁ = 6.0 Hz, *J*₂ = 10.0 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H) ppm. ¹³C {¹H}



NMR (100 MHz, CDCl₃): δ 196.7, 193.1, 144.6, 144.3, 135.0, 134.5, 133.2, 133.0, 130.1, 129.5, 129.4, 128.6, 128.5, 128.45, 128.42, 37.1, 36.8, 29.7, 21.73, 21.68 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₅H₂₂ClO₂, 389.1303; found: 389.1316.

((1R*,2S*,3S*)-3-(4-fluorophenyl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4k)

White solid. Yield: 680 mg (61%); M. p. 115–117 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.97 (d, J = 8.0 Hz, 2H), 7.87–7.80 (m, 2H), 7.25 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.14–7.10 (m, 2H), 6.82 (t, J = 8.6 Hz, 2H), 4.10 (t, J = 5.4 Hz, 1H), 3.64 (dd, J_1 = 4.6 Hz, J_2 = 9.8 Hz, 1H), 3.41 (dd, J_1 = 6.2 Hz, J_2 = 9.8 Hz, 1H), 2.37 (d, J = 4.4 Hz, 3H), 2.31 (d, J = 7.2 Hz, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.8, 193.3, 163.1, 160.7, 144.6, 144.3, 135.1, 134.6, 130.4, 130.3, 130.1, 129.5, 129.4, 129.2, 128.6, 128.5, 128.4, 115.3, 115.1, 37.1, 36.8, 29.9, 21.73, 21.68 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₅H₂₂FO₂; 373.1598; found: 373.1606.

((1R*,2S*,3S*)-3-(*p*-tolyl)cyclopropane-1,2-diyl)bis((4-bromophenyl)methanone) (4l)

White solid. Yield: 861 mg (58%); M. p. 157–159 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.92 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 4.06 (t, J = 5.4 Hz, 1H), 3.62 (dd, J_1 = 4.8 Hz, J_2 = 10.0 Hz, 1H), 3.42 (dd, J_1 = 6.2 Hz, J_2 = 9.8 Hz, 1H), 2.18 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.3, 192.7, 137.2, 136.1, 135.8, 132.1, 132.0, 130.8, 130.0, 129.9, 129.1, 128.9, 128.6, 128.4, 38.1, 37.5, 29.7, 21.1 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₄H₁₉Br₂O₂, 496.9746; found: 496.9748.

((1R*,2S*,3S*)-3-(*p*-tolyl)cyclopropane-1,2-diyl)bis((4-chlorophenyl)methanone) (4m)

White solid. Yield: 735 mg (60%); M. p. 136–138 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.13 (d, J = 8.4 Hz, 2H), 7.97 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 4.21–4.18 (m, 1H), 3.75 (dd, J_1 = 4.8 Hz, J_2 = 10.0 Hz, 1H), 3.55 (dd, J_1 = 6.0 Hz, J_2 = 10.0 Hz, 1H), 2.30 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.1, 192.5, 140.1, 139.8, 137.2, 135.7, 135.4, 130.8, 129.9, 129.8, 129.2, 129.1, 129.0, 128.5, 38.1, 37.5, 29.7, 21.1 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₄H₁₉Cl₂O₂, 409.0757; found: 409.0765.

((1R*,2S*,3S*)-3-(naphthalene-1-yl)cyclopropane-1,2 diyl)bis(phenylmethanone) (4n):^{12c}

White solid. Yield: 707 mg (62%); M. p. 121–122 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.16–8.14 (m, 2H), 8.01 (d, J = 8.0 Hz, 1H), 7.89–7.87 (m, 2H), 7.72–7.65 (m, 2H), 7.60–7.56 (m, 1H), 7.51–7.39 (m, 4H), 7.36–7.30 (m, 4H), 7.29–7.24 (m, 1H), 4.31 (dd, J_1 = 4.6 Hz, J_2 = 6.2 Hz, 1H), 4.00 (dd, J_1 = 4.8 Hz, J_2 = 9.6 Hz, 1H), 3.89 (dd, J_1 = 6.4 Hz, J_2 = 9.6 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.5, 193.6, 137.3, 137.1, 133.7, 133.5, 133.1,

132.7, 130.2, 128.9, 128.7, 128.6, 128.5, 128.4, 128.1, 126.9, 126.1, 125.7, 125.1, 123.7, 36.54, 36.50, 30.8 ppm.

((1R*,2S*,3S*)-3-(naphthalene-1-yl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4o)

White solid. Yield: 821 mg (67%); M. p. 128–130 °C; ¹H NMR (400 MHz, CDCl₃): 8.09–8.03 (m, 3H), 7.79 (d, J = 8.0 Hz, 2H), 7.70–7.68 (m, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.38–7.25 (m, 6H), 7.11 (d, J = 8.0 Hz, 2H), 4.27 (dd, J_1 = 4.6 Hz, J_2 = 6.2 Hz, 1H), 3.95 (dd, J_1 = 4.8 Hz, J_2 = 9.6 Hz, 1H), 3.82 (m, 1H), 2.37 (s, 3H), 2.28 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 197.1, 193.2, 144.6, 144.0, 135.0, 134.7, 133.6, 132.8, 130.5, 129.6, 129.2, 128.8, 128.7, 128.5, 128.1, 126.9, 126.1, 125.7, 125.1, 123.8, 36.4, 36.3, 30.7, 21.8, 21.7 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₉H₂₅O₂, 405.1849; found: 405.1857.

((1R*,2S*,3S*)-3-phenylcyclopropane-1,2-diyl)bis(thiophen-2-ylmethanone) (4p)

White solid. Yield: 620 mg (61%); M. p. 146–148 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, J = 3.6 Hz, 1H), 7.93 (d, J = 3.6 Hz, 1H), 7.78 (d, J = 4.8 Hz, 1H), 7.67 (d, J = 4.8 Hz, 1H), 7.29 (d, J = 4.4 Hz, 4H), 7.27–7.24 (m, 2H), 7.20–7.18 (m, 1H), 4.08 (t, J = 5.4 Hz, 1H), 3.75 (dd, J_1 = 4.6 Hz, J_2 = 9.8 Hz, 1H), 3.54 (dd, J_1 = 6.4 Hz, J_2 = 10.0 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 189.6, 186.0, 144.7, 144.2, 134.7, 134.12, 134.10, 130.0, 132.9, 128.6, 128.3, 127.4, 37.6, 36.8, 30.9 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₉H₁₅O₂S₂, 339.0508; found: 339.0517.

((1R*,2S*,3S*)-3-(*p*-tolyl)cyclopropane-1,2-diyl)bis(thiophen-2-ylmethanone) (4q)

White solid. Yield: 635 mg (60%); M. p. 156–158 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 3.6 Hz, 1H), 7.92 (d, J = 3.6 Hz, 1H), 7.77 (d, J = 4.8 Hz, 1H), 7.66 (d, J = 5.2 Hz, 1H), 7.27–7.24 (m, 1H), 7.19–7.17 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 4.05 (t, J = 5.4 Hz, 1H), 3.73 (dd, J_1 = 4.8 Hz, J_2 = 9.6 Hz, 1H), 3.51 (dd, J_1 = 6.2 Hz, J_2 = 9.8 Hz, 1H), 2.32 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 189.7, 186.2, 144.8, 144.2, 137.0, 134.7, 134.0, 133.0, 132.5, 131.0, 129.0, 128.8, 128.5, 128.3, 37.5, 36.8, 31.0, 21.2 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₀H₁₇O₂S₂, 353.0664; found: 353.0673.

((1R*,2S*,3R*)-3-(thiophene-2-yl)cyclopropane-1,2-diyl)bis(phenylmethanone) (4r)

White solid. Yield: 655 mg (65%); M. p. 116–118 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.06 (d, J = 7.2 Hz, 2H), 7.94 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 7.6 Hz, 1H), 7.45 (dd, J_1 = 7.2 Hz, J_2 = 14.8 Hz, 3H), 7.38 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 5.2 Hz, 1H), 6.81 (d, J = 3.2 Hz, 1H), 6.78–6.76 (m, 1H), 4.13 (t, J = 5.4 Hz, 1H), 3.69 (dd, J_1 = 5.2 Hz, J_2 = 9.6 Hz, 1H), 3.53 (dd, J_1 = 6.0 Hz, J_2 = 9.6 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.7, 193.2, 137.4, 137.3, 136.9, 133.7, 133.4, 128.8, 128.7, 128.5, 128.4, 126.8, 126.5, 124.7, 37.7, 32.2, 31.5 ppm. HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₂₁H₁₆O₂SNa, 355.0763; found: 355.0766.



((1R*,2S*,3R*)-3-(thiophene-2-yl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (4s)

White solid. Yield: 687 mg (63%); M. p. 140–142 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.31–7.30 (m, 2H), 7.11 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.2 Hz, 1H), 6.93–6.87 (m, 2H), 4.21 (t, *J* = 5.6 Hz, 1H), 3.77 (dd, *J*₁ = 5.2 Hz, *J*₂ = 9.6 Hz, 1H), 3.64–3.59 (m, 1H), 2.49 (s, 3H), 2.45 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.3, 192.8, 144.6, 144.2, 137.7, 134.9, 134.5, 129.5, 129.4, 128.7, 128.6, 126.8, 126.4, 124.6, 37.5, 31.9, 31.3, 21.8, 21.7 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₃H₂₁O₂S, 361.1257; found: 361.1256.

((1R*,2S*,3R*)-3-((*E*)-styryl)cyclopropane-1,2-diyl)(bis-phenylmethanone) (10a)

Yellow oil. Yield: 686 mg (65%); IR (KBr): ν 1658, 1589, 1331, 1215, 1011, 749, 692, 644 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.07 (t, *J* = 7.4 Hz, 4H), 7.61–7.55 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 3H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.27–7.23 (m, 2H), 7.19 (d, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 15.6 Hz, 1H), 6.24 (dd, *J*₁ = 9.6 Hz, *J*₂ = 15.6 Hz, 1H), 3.92 (t, *J* = 5.2 Hz, 1H), 3.85–3.81 (m, 1H), 3.06–3.00 (m, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.7, 195.3, 137.5, 137.1, 136.6, 133.9, 133.54, 133.47, 128.8, 128.7, 128.6, 128.5, 127.7, 126.2, 123.8, 37.9, 35.7, 33.0 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₅H₂₁O₂, 353.1536; found: 353.1547.

((1R*,2S*,3S*)-3-((*E*)-styryl)cyclopropane-1,2-diyl)bis(*p*-tolylmethanone) (10b)

Yellow oil. Yield: 748 mg (65%); ¹H NMR (400 MHz, CDCl₃): δ 8.03 (t, *J* = 7.8 Hz, 4H), 7.37–7.29 (m, 8H), 7.25–7.21 (m, 1H), 6.72 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J*₁ = 9.6 Hz, *J*₂ = 15.6 Hz, 1H), 3.95 (t, *J* = 5.2 Hz, 1H), 3.85 (dd, *J*₁ = 5.2 Hz, *J*₂ = 9.2 Hz, 1H), 3.09–3.03 (m, 1H), 2.46 (d, *J* = 7.2 Hz, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 196.4, 194.9, 144.4, 144.3, 136.7, 135.1, 134.6, 133.6, 129.43, 129.40, 128.6, 128.5, 127.5, 126.2, 124.1, 37.6, 35.5, 32.8, 21.73, 21.71 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₂₇H₂₅O₂, 381.1849; found: 381.1866.

((1R*,2R*,3S*)-3-phenylcyclopropane-1,2-diyl)bis(phenylmethanone) (5a)^{12c}

White solid. Yield: 108 mg (11%); M. p. 148–150 °C; IR (KBr): ν 1678, 1588, 1211, 990, 750, 689 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.05–8.03 (m, 4H), 7.60–7.56 (m, 2H), 7.49–7.41 (m, 6H), 7.36 (d, *J* = 7.2 Hz, 3H), 3.60 (t, *J* = 6.0 Hz, 1H), 3.44 (d, *J* = 6.0 Hz, 2H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 194.3, 138.5, 137.2, 133.2, 128.9, 128.7, 128.6, 128.4, 127.3, 126.6, 36.94, 36.89, 31.3 ppm.

((1S*,2S*,3R*,4S*,6S*)-4-hydroxy-2,4,6-triphenylcyclohexane-1,3-diyl)bis(phenylmethanone) (6a)

White solid. Yield: 117 mg (12%); M. p. 188–194 °C; IR (KBr): ν 1653, 1588, 1290, 1209, 1013, 732, 693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.61–7.47 (m, 3H), 7.34–7.30 (m, 3H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.23 (d, *J*

= 7.6 Hz, 1H), 7.17–7.09 (m, 8H), 7.05–7.01 (m, 3H), 6.87 (d, *J* = 7.2 Hz, 2H), 5.78 (d, *J* = 12.0 Hz, 1H), 5.28 (s, 1H), 4.43 (t, *J* = 4.4 Hz, 1H), 4.27–4.19 (m, 2H), 3.58–3.38 (m, 1H), 2.11 (dd, *J*₁ = 3.2 Hz, *J*₂ = 13.6 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 208.3, 206.9, 146.9, 143.9, 141.7, 140.2, 139.3, 138.3, 137.0, 133.1, 132.9, 132.0, 128.8, 128.7, 128.6, 128.4, 128.3, 128.20, 128.19, 128.1, 127.83, 127.76, 127.7, 127.5, 127.4, 127.0, 126.7, 126.6, 125.2, 52.8, 50.2, 48.1, 44.9, 42.3, 38.4, 37.2 ppm. HRMS (ESI-TOF) *m/z*: [M + Na]⁺ calcd for C₃₈H₃₂O₃Na, 559.2244; found: 559.2242.

General procedure for the synthesis of 1,3-dienes 8a–s and 1,3,5-trienes 11a–b

To a solution of cyclopropane 4 (0.9 mmol) in MeOH (10 mL), was added NaBH₄ (1.8 mmol) and the reaction mixture was stirred at room temperature for 0.5 h. After removal of the solvent under reduced pressure, the reaction mixture was extracted with ethyl acetate and the combined organic layers were washed with brine solution and dried over anhydrous Na₂SO₄. The removal of solvent under reduced pressure provided the crude cyclopropane alcohol as a mixture of diastereomers. The crude product (0.6 mmol) was then treated with con. HCl (five drops) in 1,2-DCE at room temperature for 0.5 h. The reaction mixture was extracted with DCM. The combined organic layers were washed with water and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by column chromatography using EtOAc/hexane (1:19 v/v) to afford 1,3-dienes 8a–s and 1,3,5-trienes 11a–b.

((1E,3E)-1, 4-diphenylbuta-1, 3-diene (8a)¹⁹

White solid. Yield: 176 mg (89%); M. p. 150–151 °C; IR (KBr, cm⁻¹): ν 1659, 1589, 1446, 1331, 1214, 1012, 747, 694, 645 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 7.6 Hz, 4H), 7.25 (t, *J* = 7.8 Hz, 4H), 7.17–7.14 (m, 2H), 6.92–6.84 (m, 2H), 6.63–6.56 (m, 2H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): 137.4, 132.9, 129.3, 128.7, 127.6, 126.4, ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₆H₁₅, 207.1168; found: 207.1167 (The minor cyclopropane products 5 also give the same result).

1-Methyl-4-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)benzene (8b)

White solid. Yield: 169 mg (79%); M. p. 152–154 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.26 (t, *J* = 8.6 Hz, 4H), 7.16 (q, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.91–6.80 (m, 2H), 6.61–6.55 (m, 2H), 2.27 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.5, 134.6, 132.9, 132.3, 129.5, 129.4, 128.7, 128.4, 127.5, 126.3, 21.3 ppm. HRMS (ESI-TOF) *m/z*: [M + H]⁺ calcd for C₁₇H₁₇, 221.1325; found: 221.1317.

1-Methoxy-4-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)benzene (8c)

White solid. Yield: 187 mg (80%); M. p. 164–165 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.17–7.12 (m, 1H), 6.86 (dd, *J*₁ = 10.4 Hz, *J*₂ = 15.2 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.76–6.72 (m, 1H), 6.54 (d, *J* = 15.2 Hz, 2H), 3.73 (s, 3H) ppm. ¹³C {¹H} NMR



(100 MHz, CDCl₃): δ 159.3, 137.6, 132.5, 131.7, 130.2, 129.6, 128.7, 127.7, 127.4, 127.3, 126.3, 114.2, 55.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₇H₁₇O, 237.1274; found: 237.1269. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₇H₁₇O, 237.1274; found: 237.1269.

1-Bromo-4-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)benzene (8d):¹⁹

White solid. Yield: 218 mg (75%); M. p. 188–190 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, J = 8.4 Hz, 4H), 7.26–7.15 (m, 5H), 6.87–6.80 (m, 2H), 6.63–6.45 (m, 2H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.2, 136.3, 133.6, 131.8, 131.5, 130.0, 128.9, 128.8, 127.9, 127.8, 126.5, 121.3 ppm.

1-Methyl-4-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)benzene (8e)

White solid. Yield: 169 mg (82%); M. p. 152–154 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, J = 7.6 Hz, 2H), 7.27–7.23 (m, 4H), 7.17–7.15 (m, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.91–6.80 (m, 2H), 6.57 (d, J = 14.8 Hz, 1H), 2.27 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.54, 137.51, 134.6, 132.9, 132.3, 129.5, 129.4, 129.7, 128.7, 128.3, 127.5, 126.3, 21.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₇H₁₇, 221.1325; found: 221.1321.

1-Methyl-2-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8g):²⁰

White solid. Yield: 194 mg (87%); M. p. 105–106 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 7.6 Hz, 1H), 7.40–7.37 (m, 3H), 7.21–7.18 (m, 5H), 6.92–6.90 (m, 2H), 6.69 (d, J = 14.8 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.5, 136.3, 135.5, 134.6, 132.7, 130.51, 130.48, 129.4, 128.7, 127.4, 126.33, 126.27, 126.1, 125.0, 21.3, 19.9 ppm.

(1E,3E)-1, 4-di-*p*-tolylbuta-1,3-diene (8h)

White solid. Yield: 198 mg (88%); M. p. 107–109 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, J = 8.0 Hz, 4H), 7.18 (d, J = 8.0 Hz, 4H), 6.99–6.91 (m, 2H), 6.70–6.63 (m, 2H), 2.39 (s, 6H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.4, 134.7, 132.3, 129.4, 128.5, 126.3, 21.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₈H₁₉, 235.1481; found: 235.1486.

1-(*tert*-butyl)-4-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8i)

White solid. Yield: 201 mg (81%); M. p. 137–139 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.24 (m, 6H), 7.05 (d, J = 8.0 Hz, 2H), 6.85–6.81 (m, 2H), 6.57–6.53 (m, 2H), 2.26 (s, 3H), 1.25 (s, 9H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 150.7, 137.4, 134.8, 132.3, 132.2, 129.4, 129.2, 128.8, 128.6, 126.3, 126.1, 126.0, 125.6, 34.7, 31.3, 21.3 ppm. HRMS (ESI-TOF) m/z : [M-Me + H]⁺ calcd for C₂₁H₂₅, 263.1794; found: 263.1794.

1-Chloro-4-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8j)

White solid. Yield: 188 mg (80%); M. p. 198–200 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.29–7.26 (m, 4H), 7.23–7.20 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.87–6.78 (m, 2H), 6.62–6.48 (m, 2H), 2.28 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.7, 136.0, 134.5, 133.5, 132.9, 130.8, 130.0, 129.4, 128.8, 128.0, 127.4, 126.4,

21.3 ppm. HRMS (ESI-TOF) m/z : [M]⁺ calcd for C₁₇H₁₅Cl, 254.0862; found: 254.0891.

1-Fluoro-4-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8k)

White solid. Yield: 187 mg (83%); M. p. 201–203 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.32 (dd, J_1 = 5.6 Hz, J_2 = 8.8 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 8.6 Hz, 2H), 6.86–6.75 (m, 2H), 6.60–6.49 (m, 2H), 2.28 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.6, 134.5, 132.9, 130.9, 129.4, 129.2, 128.5, 128.1, 127.8, 127.7, 126.33, 126.26, 115.7, 115.5, 21.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₇H₁₆F, 239.1231; found: 239.1214.

1-Bromo-4-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8l)

White solid. Yield: 217 mg (72%); M. p. 197–199 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.35–7.31 (m, 2H), 7.19 (d, J = 7.6 Hz, 2H), 7.01–6.90 (m, 2H), 6.73–6.59 (m, 2H), 2.40 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.8, 136.5, 134.4, 133.6, 131.8, 130.8, 130.2, 129.4, 128.0, 127.8, 126.4, 121.1, 21.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₇H₁₆Br, 298.0357; found: 298.0343.

1-Chloro-4-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)benzene (8m)

White solid. Yield: 203 mg (82%); M. p. 198–200 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.29–7.25 (m, 4H), 7.22–7.18 (m, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.87–6.78 (m, 2H), 6.60–6.49 (m, 2H), 2.27 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.7, 136.0, 134.4, 133.5, 132.9, 130.8, 130.0, 129.4, 128.8, 128.0, 127.5, 126.4, 21.3 ppm. HRMS (ESI-TOF) m/z : [M]⁺ calcd for C₁₇H₁₅Cl, 254.0862; found: 254.0848.

2-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)naphthalene (8n)

White solid. Yield: 199 mg (87%); M. p. 155–157 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.12 (d, J = 8.4 Hz, 1H), 7.80–7.77 (m, 1H), 7.71 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.2 Hz, 1H), 7.49–7.38 (m, 7H), 7.30–7.27 (m, 2H), 7.08–6.93 (m, 2H), 6.66 (d, J = 15.2 Hz, 1H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 133.8, 133.1, 132.0, 129.55, 129.46, 128.7, 128.6, 128.0, 127.7, 126.5, 126.1, 125.7, 123.6, 123.3 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₀H₁₇, 257.1325; found: 257.1309.

2-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)naphthalene (8o)

White solid. Yield: 208 mg (85%); M. p. 158–160 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.08 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.42–7.33 (m, 4H), 7.28 (t, J = 7.6 Hz, 2H), 7.05 (d, J = 7.6 Hz, 2H), 6.96–6.87 (m, 2H), 6.58 (d, J = 14.4 Hz, 1H), 2.25 (s, 3H) ppm. ¹³C {¹H} NMR (100 MHz, CDCl₃): δ 137.7, 134.8, 134.7, 133.9, 133.2, 132.2, 131.2, 129.5, 128.9, 128.72, 128.69, 128.0, 126.5, 126.1, 125.9, 125.8, 123.7, 123.3, 21.4 ppm. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₂₁H₁₉, 271.1481; found: 271.1471.

2-((1E,3E)-4-(*p*-tolyl)buta-1, 3-dien-1-yl)thiophene (8q)

White solid. Yield: 179 mg (84%); M. p. 166–168 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.39 (d, J = 8.0 Hz, 2H), 7.22 (t, J = 8.0 Hz,



3H), 7.05 (d, $J = 4.8$ Hz, 2H), 6.93–6.82 (m, 3H), 6.68 (d, $J = 14.8$ Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 143.1, 137.6, 134.6, 132.7, 129.5, 129.3, 127.8, 127.7, 126.4, 125.8, 125.1, 124.3, 21.3 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{S}$, 227.0889; found: 227.0889.

2-((1E,3E)-4-phenylbuta-1, 3-dien-1-yl)thiophene (8r)

White solid. Yield: 161 mg (80%); M. p. 161–163 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.34 (d, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 7.6$ Hz, 2H), 7.19–7.13 (m, 2H), 7.09 (d, $J = 4.8$ Hz, 1H), 6.93–6.89 (m, 2H), 6.84–6.78 (m, 1H), 6.71 (s, 1H), 6.56 (d, $J = 15.2$ Hz, 1H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 142.9, 137.4, 132.7, 129.1, 128.73, 128.70, 127.7, 127.6, 126.4, 125.9, 125.7, 124.5 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{13}\text{S}$, 213.0732; found: 213.0723.

2-((1E,3E)-4-(p-tolyl)buta-1, 3-dien-1-yl)thiophene (8s)

White solid. Yield: 189 mg (87%); M. p. 162–164 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 8.0$ Hz, 2H), 7.10–7.05 (m, 3H), 6.91–6.89 (m, 2H), 6.80–6.74 (m, 1H), 6.69 (d, $J = 7.6$ Hz, 2H), 6.54 (d, $J = 14.8$ Hz, 1H), 2.27 (s, 3H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 143.1, 137.6, 132.7, 129.4, 129.3, 127.8, 127.7, 126.3, 125.7, 125.1, 124.3, 21.3 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{15}\text{S}$, 227.0889; found: 227.0885.

1-Phenyl-4-((1E,3E,5E)-6-phenylhexa-1, 3, 5-trien-1-yl)benzene (11a)²¹

Yellow solid. Yield: 182 mg (85%); M. p. 196–198 °C; IR (KBr): ν 1655, 1588, 1289, 1209, 1006, 738, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, $J = 7.6$ Hz, 4H), 7.38 (t, $J = 7.6$ Hz, 5H), 7.31–7.27 (m, 2H), 7.04–6.92 (m, 2H), 6.66 (d, $J = 15.6$ Hz, 2H), 6.58 (dd, $J_1 = 2.8$ Hz, $J_2 = 7.2$ Hz, 1H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 137.4, 133.6, 132.9, 132.7, 130.13, 129.8, 129.3, 129.2, 128.7, 127.8, 127.6, 126.6, 126.4, 124.3 ppm.

1-Methyl-4-((1E,3E,5E)-6-phenylhexa-1, 3, 5-trien-1-yl)benzene (11b)

White solid. Yield: 201 mg (87%); M. p. 186–188 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (d, $J = 7.6$ Hz, 2H), 7.39–7.35 (m, 4H), 7.27 (t, $J = 7.4$ Hz, 1H), 7.18 (d, $J = 8.0$ Hz, 2H), 6.97–6.86 (m, 2H), 6.65 (d, $J = 3.2$ Hz, 1H), 6.61 (d, $J = 3.2$ Hz, 1H), 6.56 (dd, $J_1 = 4.2$ Hz, $J_2 = 4.6$ Hz, 2H), 2.40 (s, 3H) ppm. ^{13}C { ^1H } NMR (100 MHz, CDCl_3): δ 137.53, 137.50, 134.7, 133.8, 133.1, 132.8, 132.4, 129.4, 129.3, 128.7, 128.2, 127.5, 126.4, 126.3, 21.3 ppm. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}$, 246.1409; found: 246.1412.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors thank Science and Engineering Research Board (SERB) and MoE-RUSA 2.0, India for financial support and DST-FIST for instrumentation facilities at School of Chemistry, Bharathidasan University.

Notes and references

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