PAPER

Monoallylation and benzylation of dicarbonyl compounds with alcohols catalysed by a cationic cobalt(III) compound†

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Monoallylation and monoalkylation of diketones and β-keto esters with allylic and benzylic alcohols catalysed by [Cp*Co(CH$_3$CN)$_3$][SbF$_6$]$_2$ (I) are reported. The method does not require any additive and affords regioselective products. The mechanistic investigations were done by *in situ* ^{1}H NMR spectroscopy as well as control experiments. It has been shown that reactions proceed *via* η^3-allyl complex formation or ally ether intermediate. The alkylation takes place *via* only ether intermediate. The resulting allylated and alkylated products have been used for the synthesis of eleven new trisubstituted pyrazoles and one pyrazolone.
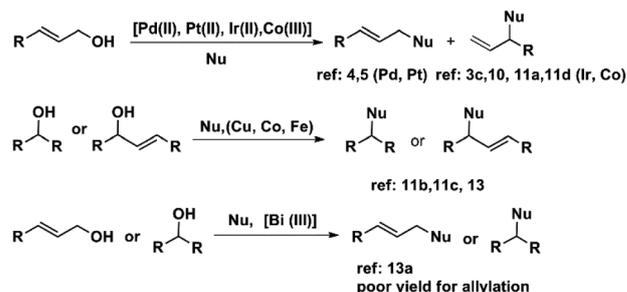
Introduction

Allylation and alkylation of active methylene compounds are essential in synthetic organic chemistry. Usually, allyl halides and alkyl halides are used for allylation in the presence of a base. However, these reactions are not atom economical or green, as a large amount of salts is generated. Allylation and alkylation using the corresponding alcohol are attractive. The reaction is green as only water is produced as the side product.[1] The selective mono-allylated diketones are used as a precursor for synthesising natural and unnatural bioactive molecules.[2]

The hydroxyl group is a weak leaving group. Usually, the alcohols are converted into acetate, carbonate, or halide for smooth allylation and alkylation reactions.[3] In addition to the Pd-catalysed Tsuji–Trost reaction,[1a,1b] which proceeds through palladium π-allyl intermediate, complexes of palladium,[4] platinum,[5] ruthenium,[6] indium,[1c] molybdenum,[7] gold,[8] and rhodium[9] have been used as catalysts for this kind of allylation reaction. The palladium-based catalysts predominantly afford the linear allylated products, although some diallyl products are also obtained. When complexes of iridium,[3c,10] and rhodium, are used as catalysts, branched allylation products were found to be the primary products. Recently, Ohshima *et al.* reported selective monoallylation of active methylene compound using 2 mol% [Pt(cod)Cl$_2$] 2 mol% xantphos as the ligand along with 10 mol% each, of pyrrolidine, and acetic acid as co-catalysts. However, this catalytic system is useful for only allylic alcohols.[5b] Cobalt compounds have been used as catalysts for allylation reaction.[11] For example, cobalt carbonyl compounds,

[(crotyl)Co(CO)$_3$], and Na[Co(CO)$_4$] have been shown to catalyse allylation using ally formate, chloride, and acetate. However, the conversions were found to be low.[11a] Similarly, cobalt(III) DMG (DMG = dimethylglyoxime) complex was used as a catalyst for the allylation using allyl alcohol.[11b] But the conversions were low, and the catalyst loading was comparatively higher (5 mol%), and acetic acid was used as the reaction medium. Ackermann and coworkers have reported cobalt(III) catalysed allylative C–H and C–F functionalisation.[11e] It may be pointed out that most of the reported methods either require additives or are not regioselective. Some of the methods afford a mixture of diallylated and monoallylated products (Scheme 1). Therefore, the development of an additive-free strategy for regioselective allylic substitution is highly desirable.

Recently a high valent cobalt complex, Cp*Co(CO)$_2$[12] has been used as a precatalyst for dehydrogenation of alcohols.[12] High valent cationic cobalt complex has been shown to catalyse directed C–H bond activation.[13]

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Scheme 1 Reported reactions catalysed various metal compounds.
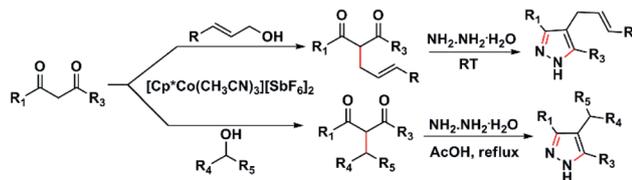
Scheme 2 Reactions reported here.

Lewis acids or Brønsted acids,[14] including InCl$_3$,[1c] Bi(OTf)$_3$,[15a] FeCl$_3$,[15b] carbon-supported iron – ionic liquid,[15c] and PTSA,[16] have been used for the benzylation of active methylene compounds by benzylic alcohols. To the best of our knowledge, there is only one report on the benzylation and allylation of β-keto carbonyl compounds using the same catalyst. It has been reported that Bi(OTf)$_3$ can catalyse both allylation and alkylation of active methylene compounds.[14] The yields of benzylated products were found to be excellent. Allylation reactions were found to be useful only for cinnamyl alcohol, and the products were obtained in moderate yield. The selective allylation and alkylation reaction with cobalt complexes as catalysts are preferable because its compounds are comparatively inexpensive than those of rhodium, iridium, and palladium.

Recently we have shown that [Cp*Co(CH$_3$CN)$_3$][SbF$_6$]$_2$ (**I**) is an efficient catalyst for the Nakamura reaction.[17] In continuation of our studies on the catalytic activity of [Cp*Co(CH$_3$CN)$_3$][SbF$_6$]$_2$ (**I**), herein, we report the monoallylation and benzylation of diketones and β-keto esters using allylic alcohols and secondary benzyl alcohols, respectively. Eleven new pyrazoles and one pyrazolone have been synthesized from the allylated and alkylated products (Scheme 2).

Results and discussion

The optimization of the allylation reaction was done using 1-phenyl-butane-1,3-dione (**1b**) and cinnamyl alcohol (**2a**) as model substrates. In the preliminary stage, we did a blank reaction with 1-benzoyl acetone (**1b**) and cinnamyl alcohol (**2a**) at different temperatures (room temperature to 110 °C) in toluene for 24 hours. However, we did not get any desired product (entry 1, Table 1). When we added the catalyst (1 mol%) and heated the reaction solution to 90 °C for 12 hours, the product was isolated in 49% yield (entry 2, Table 1). Next, the reaction solution was heated at 110 °C for 12 hours, and the desired product, (**3b**), was isolated in 58% yield (entry 3, Table 1). It was anticipated that the addition of base to the reaction mixture would enhance the reaction rate as a base can deprotonate the active methylene –CH$_2$ protons and enolisation of the β-dicarbonyl compounds may happen faster. Thus, we carried out the reaction in the presence of inorganic bases, K$_2$CO$_3$, and Na$_2$CO$_3$, but the yield decreased unexpectedly (entries 4 and 5, Table 1). When we added the base, the yield of the reaction drastically reduced. The reduction in the yield could be due to the catalyst degradation upon addition of the base. When the base was added, the reaction mixture's colour changed, and within a few minutes, the solution became hazy. Then we carried out the reaction in the

Table 1 Optimization table for diketone addition to cinnamyl alcohol[a]

Entry	**I** (mol%)	Temperature (°C)	Time (h)	Solvent	Yield[b] (%)
1	—	90/110	24	Toluene	—
2	**1**	90	12	Toluene	49
3	1	110	12	Toluene	58
4	1	110	12	Toluene	19[c]
5	1	110	12	Toluene	13[d]
6	1	110	8	Toluene	72[e]
7	1	110	8	DCE	65[e]
8	1	100	8	CH$_3$CN	—[e]
9	1.5	110	8	Toluene	76[e]
10	2	110	8	Toluene	81[e]
11	1.5	110	8	Toluene	80[f]
12	1.7	**110**	8	Toluene	**83[f]**

[a] **1b** (0.2 mmol), **2a** (0.2 mmol), **I** (1 mol%, 0.0015 g), toluene (2 mL). [b] Isolated yield. [c] In the presence of K$_2$CO$_3$ (1 equivalent). [d] In the presence of Na$_2$CO$_3$ (1 equivalent). [e] **1b** (0.2 mmol), **2a** (0.3 mmol). [f] **1b** (0.2 mmol), **2a** (0.34 mmol).

presence of 1 mol% **I** in toluene, using **1b** and **2a** in the 1 : 1.5 ratio. The yield was found to be 72% (entry 6, Table 1). The reaction carried out in dichloroethane (DCE) afforded the product in moderate yields (entry 7, Table 1). We could not detect any product formation when CH$_3$CN was used as a solvent (entry 8, Table 1). When 1.5 mol% of **I** was used, maintaining the **1b** : **2a** ratio at 1 : 1.5, the product was obtained in 76% yield in eight hours (entry 9, Table 1). Similarly, when the catalyst loading was 2 mol%, the product was isolated in 81% yield in eight hours (entry 10, Table 1). When the reactants, **1b** and **2a** were used in 1 : 1.7 ratio, in the presence of 1.5 mol% of **I**, the product was isolated in 80% yield (entry 11, Table 1). On increasing the catalyst loading to 1.7 mol%, the product was isolated in 83% yield (entry 12, Table 1).

After optimizing the time, temperature, solvent, and catalyst loading, we studied the effect of the leaving group. When cinnamyl chloride was used, the product was isolated in a 91%

Table 2 Effect of leaving group on conversion to the product[a]

Entry	Leaving group (X)	Time (h)	Yield (%)
1	Cl	6	91
2	OAc	8	59
3	OCO$_2$–CH$_2$^{i}Pr	6	79

[a] **1b** (0.3 mmol), **2a** (0.51 mmol), **I** (0.0040 g, 1.7 mol%), toluene (2 mL), 110–115 °C.

yield in six hours (entry 1, Table 2). The yield decreased drastically to 59% in eight hours, when cinnamyl acetate was used as the reactant (entry 2, Table 2). However, when carbonic acid isobutyl easter-3-phenyl-ally ester was used, the product was isolated in 79% in six hours (entry 3, Table 2). Although the conversion to the product was higher in the case of chloride leaving group, we preferred to use allylic alcohols as the method is green.

After the optimization of the reaction condition, we proceeded to investigate the scope of the reaction. Reactions were carried out between various diketones and β-keto esters with different allylic alcohols. Pentane-2,4-dione (**1a**), 1-phenyl
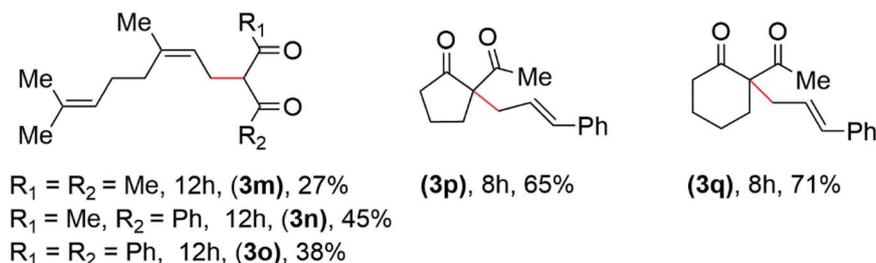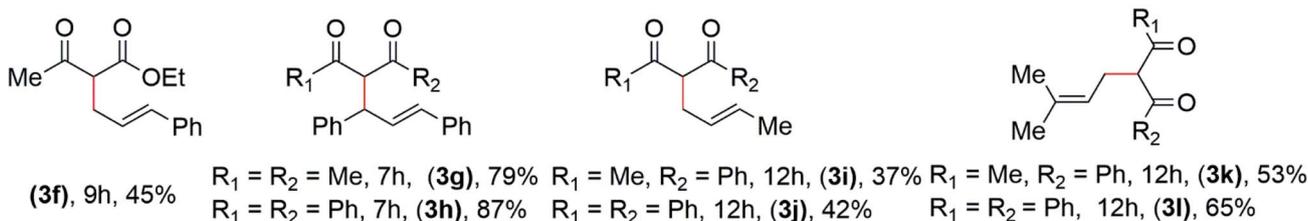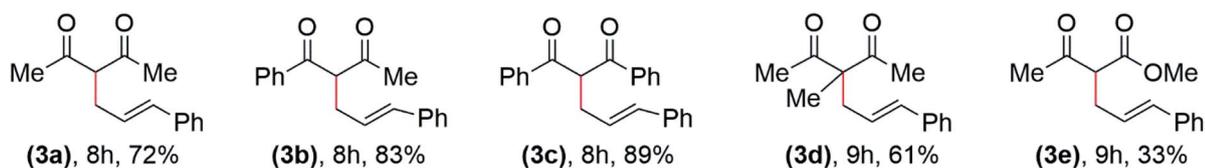
butane-1,3-dione (**1b**), 1,3-diphenyl propane-1,3-dione (**1c**), and 3-methyl pentane-2,4-dione (**1d**) on reaction with cinnamyl alcohol (**2a**) afforded the monoallylated products **3a**, **3b**, **3c**, and **3d** in 72%, 83%, 89% in eight hours, and 61% in nine hours, respectively (Table 3). 3-Oxo-butyric acid-methyl ester (**1e**) and 3-oxo-butyric acid-ethyl ester (**1f**) on reaction with cinnamyl alcohol (**2a**) afford the products, **3e** and **3f** in 33% and 45% yield, respectively in nine hours (Table 3). The products, 3(1,3-diphenyl-ally)-pentane-2,4-dione (**3g**) and 2-(1,3-diphenyl-allyl)-1-phenyl-butane-1,3-dione (**3h**) were isolated in 79% and 87% yield, respectively in seven hours form the reaction of (*E*)-1,3-diphenyl-prop-2-en-1-ol (**2b**) with **1a** and **1c** (Table 3). Similarly,

Table 3 Regioselective monallylation reaction between different β-keto compounds with cinnamyl alcohol[a,b]
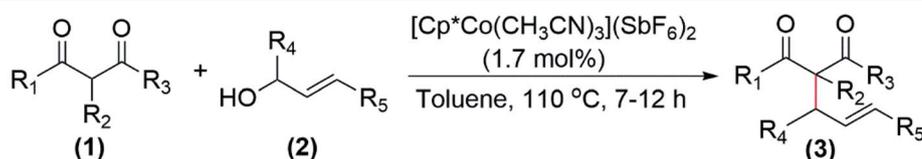
$R_1 = R_3 = Me$, $R_2 = H$ (**1a**); $R_1 = Ph$, $R_3 = Me$, $R_2 = H$ (**1b**); $R_1 = R_3 = Ph$, $R_2 = H$ (**1c**); $R_1 = R_3 = Me$, $R_2 = Me$ (**1d**); $R_1 = Me$, $R_3 = OMe$, $R_2 = H$ (**1e**); $R_1 = Me$, $R_3 = OEt$, $R_2 = H$ (**1f**); 2-acetyl cylopentan-1-one (**1g**), 2-acetyl cyclohexan-1-one (**1h**)

$R_4 = H$, $R_5 = Ph$ (**2a**); $R_4 = R_5 = Ph$ (**2b**); $R_4 = H$, $R_5 = Me$ (**2c**); $R_4 = H$, $R_5 = C(Me)_2$ (**2d**); $R_4 = H$, $R_5 = C(Me)CH_2CH_2CHC(Me)_2$ (**2e**)

(**3a**), 8h, 72% (**3b**), 8h, 83% (**3c**), 8h, 89% (**3d**), 9h, 61% (**3e**), 9h, 33%

(**3f**), 9h, 45%

$R_1 = R_2 = Me$, 7h, (**3g**), 79% $R_1 = Me$, $R_2 = Ph$, 12h, (**3i**), 37% $R_1 = Me$, $R_2 = Ph$, 12h, (**3k**), 53%
$R_1 = R_2 = Ph$, 7h, (**3h**), 87% $R_1 = R_2 = Ph$, 12h, (**3j**), 42% $R_1 = R_2 = Ph$, 12h, (**3l**), 65%

$R_1 = R_2 = Me$, 12h, (**3m**), 27% (**3p**), 8h, 65% (**3q**), 8h, 71%
$R_1 = Me$, $R_2 = Ph$, 12h, (**3n**), 45%
$R_1 = R_2 = Ph$, 12h, (**3o**), 38%

[a] **1** (0.2 mmol), **2** (0.34 mmol), **I** (1.7 mol%). [b] All yields are isolated yield.

(E)-but-2-en-1-ol (**2c**) on reaction with **1b** and 1,4-diphenyl-2,3-butanedione (**1c**) afforded the product **3i** and **3j** in 37% and 42% yield, respectively, in twelve hours (Table 3). 3-Methyl-2-buten-1-ol (**2d**), when reacted with **1b**, and **1c**, the products, **3k** and **3l** were isolated in 53%, and 65% yield, respectively in 12 hours. 3,6-Dimethyl-2,6-octadiene-1-ol (**2e**) on reaction with **1a**, **1b**, and **1c** afforded the corresponding products, **3m**, **3n**, and **3o**, in twelve hours, in 27%, 45%, and 38%, respectively.

Thus, it was observed that in the cases of aliphatic allylic alcohols, comparatively lower yields of the products were obtained (Table 3). 2-Acetylcyclopentan-1-one (**1g**) and 2-acetylcyclohexan-1-one (**1h**) on reaction with **2a**, afforded the products, **3p**, and **3q** in 65 and 71% yield, respectively.

We then proceeded to study the alkylation of diketones using secondary aromatic alcohols. There is only one report on both allylation and alkylation of β-keto carbonyl compounds, catalysed by the same catalyst.[15] Thus, **1a** on reaction with 1-phenyl-ethan-1-ol (**4a**) and substituted 1-phenyl-ethan-ols {p-Me (**4b**), p-

OMe (**4c**), p-Cl (**4d**), and p-F (**4e**)} afforded the alkylated products **5a** to **5e** in excellent yields within four to five hours. However, in the case of 1-(4-triflouromethylphenyl)-ethan-1-ol (**4f**), the conversion to the product **5f** was found to be negligible, even after ten hours of the reaction time. Interestingly, when **1a** was reacted with diphenylmethanol (**4g**) the product, **5g** was isolated in almost quantitative yield (98%) in four hours. Similarly, **1b** on reaction with **4a**, **4b**, and **4g** afforded the products **5h**, **5i**, and **5j**, respectively, in excellent yields in 3.5 to 5 hours (Table 4). When **1c** was reacted with **4a** and **4g**, the products, **5k**, and **5l** were obtained in quantitative yields in 3.5 and 2.5 hours, respectively. 3-Methylpentane-2,4-dione (**1d**) on reaction with **4g** afforded the product, **5m** in 53% yield in nine hours. Cyclic diketones, **1g**, and **1h** on reaction with **4g** afforded the product, **5n**, and **5o** in 91% and 78%, respectively, in 5 hours.
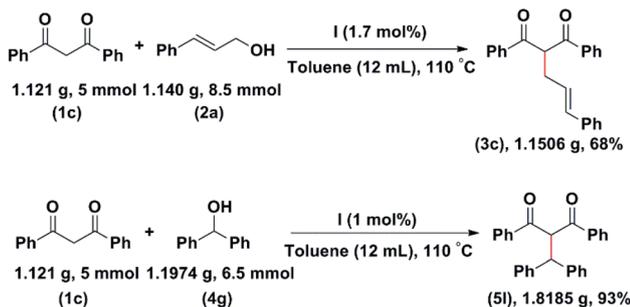
The β-ketoester, **1e**, was found to react with **4a** and **4g** to afford the corresponding products in 62% and 97% in 8 and 5 hours, respectively. The β-Ketoester, **1f** on reaction with **4a** and

Table 4 Reaction of β-keto compounds with secondary alcohols[a,b]
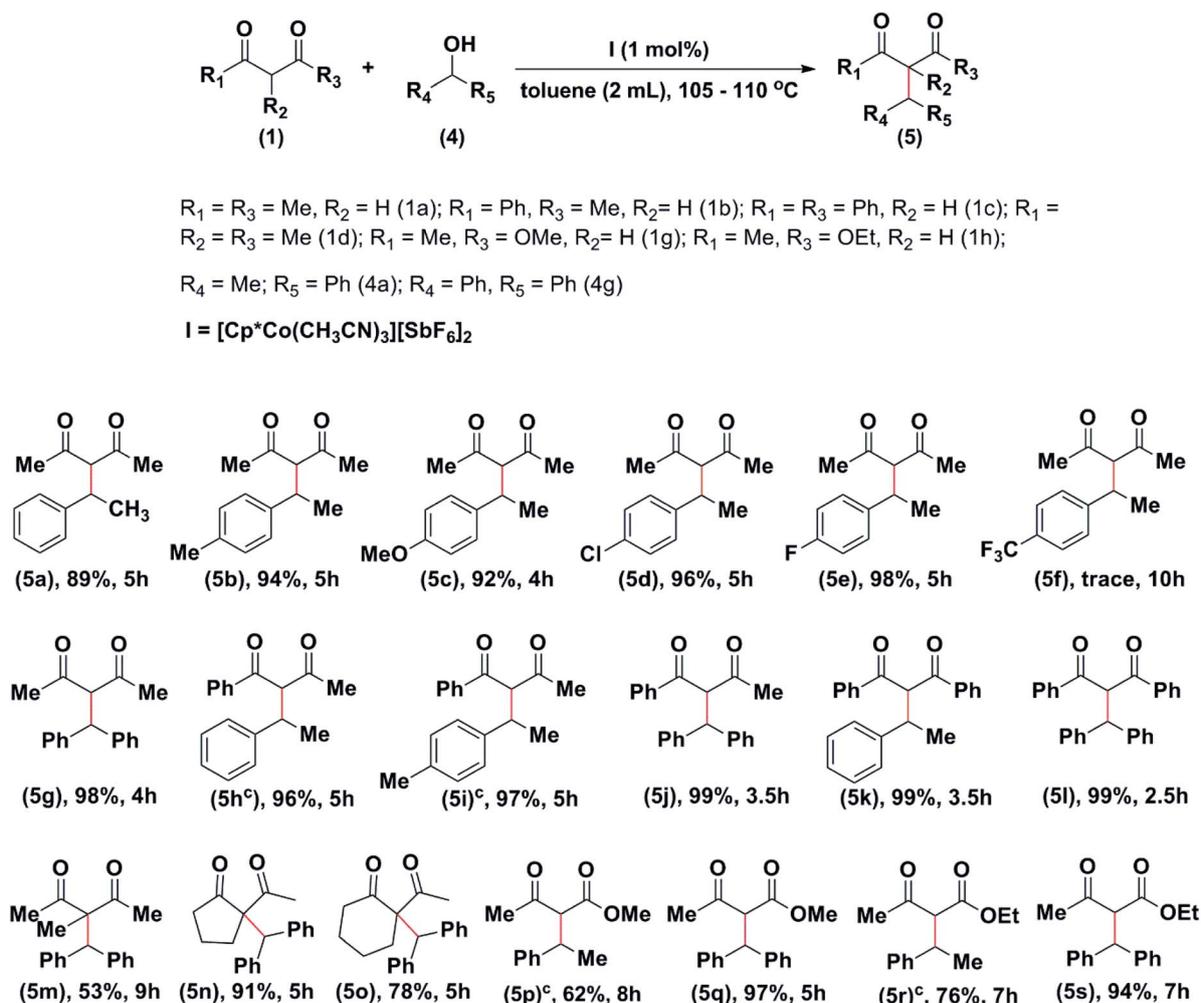
[a] Nucleophile (**1**) (0.2 mmol), alcohol (**4**) (0.26 mmol), **I** (1.5 mg, 1 mol%), 110 °C. [b] All yields are isolated yields. [c] 1 : 1 diastereomeric mixture.

Scheme 3 Gram scale reactions.

4g afforded the products **5r**, and **5s** in 76% and 94% yield, respectively, in 7 hours (Table 4). It may be noted that no product could be isolated from the reaction of **1c** with 2-propanol and 1-(thiophen-2-yl)ethan-1-ol. From the data, it is clear that the highest rate of conversion was found for the reactions of diphenylmethanol (**4g**) with β-keto compounds. Similarly, the highest conversion rate was observed in the reactions of 1-phenyl-butane-1,3-dione (**1b**).

There are two possible pathways for allylation of 1,3-diketone by allylic alcohol. One path is through activation of alcohol by the metal centre *via* the formation of ether, followed by addition. The second pathway is η^3-allyl metal complex formation.[1c]

We have carried out reactions between 1,3-diphenyl propane-1,3-dione (**1c**) with cinnamyl alcohol (**2a**) and diphenylmethanol (**4g**) on a gram scale to check the scalability of the reaction. The allylation product **3c** has been obtained in 68% yield. The alkylation product **5l** has been isolated in 93% yield (Scheme 3).

In a recent publication for this laboratory, we have shown that when acetylacetone is added to the solution of [Cp*Co(CH$_3$CN)$_3$][SbF$_6$]$_2$ (**I**), it forms [Cp*Co(acac)]$^+$ ($m/z = 293.1$) in LCMS of the reaction mixture.[17]

The mechanism was studied by ^{1}H NMR spectroscopy. The solution of cinnamyl alcohol and **I** (1 mol%) was heated at 100 °C for 18 hours, and the ^{1}H NMR spectrum (Fig. S3, ESI†) was recorded. The NMR spectrum shows a signal at 4.21 ppm (doublet, $J = 6$ Hz), which can be assigned to the –CH$_2$ protons of the ether (Scheme 3).

Similarly, the ^{1}H NMR spectrum (Fig. S4, ESI†) of the solution of diphenylmethanol and **I** (1 mol%) was recorded after heating the reaction solution at 110 °C. The NMR spectrum shows a singlet at 5.43 ppm along with the signals of aromatic protons. This signal is due to the –CH proton of the ether.
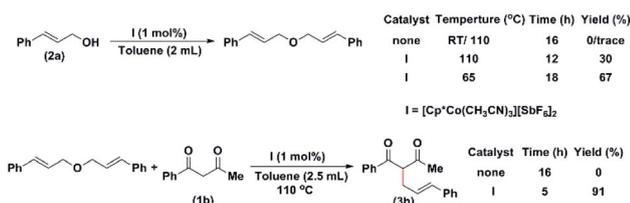
**Scheme 4** Control experiments of allylation.
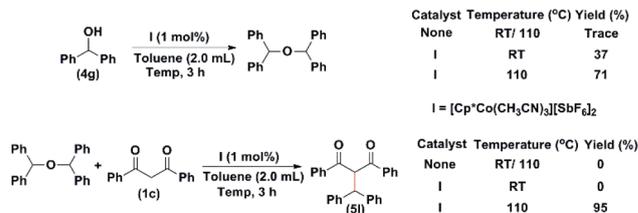
Scheme 5 Control experiments of alkylation.

Similarly, when diphenylmethanol (**4g**) was mixed with **I** and stirred at room temperature. The corresponding ether was isolated in a 37% yield in three hours. When the reaction was conducted at 110 °C, the ether was isolated in a 71% yield in three hours (Scheme 4). The ether was isolated and was reacted with **1c**. In the absence of **I**, no product formation was detected. Therefore, to investigate the reaction mechanism, we performed two control experiments (Scheme 4). First, cinnamyl alcohol was heated to different temperatures in the absence and in the presence (1 mol%) of the catalyst. In the absence of the catalyst, we could detect the formation of a trace amount of ether (Scheme 4). In the presence of the catalyst, at 65 °C, the ether was isolated in a 67% yield. At 110 °C, the observed yield of the ether decreased to 30%. We then carried out a reaction between the isolated ether and 1b. In the absence of **I**, no product could be isolated. However, in the presence of the catalyst, the product was isolated in 91% yield in 5 hours (Scheme 4).

However, in the presence **I**, the product was isolated in 95% yield in 3 hours (Scheme 5).

Yasuda *et al.* reported InCl$_3$ mediated alkylation of diketones. They suggested that the reaction of alcohols proceed through indium mediated ether formation and subsequent alkylation.[1c] They have also suggested a direct activation of alcohol for the alkylation. It may be mentioned that Fe(OTf)$_3$ has been shown to catalyse dehydration of alcohols to ether.[18]
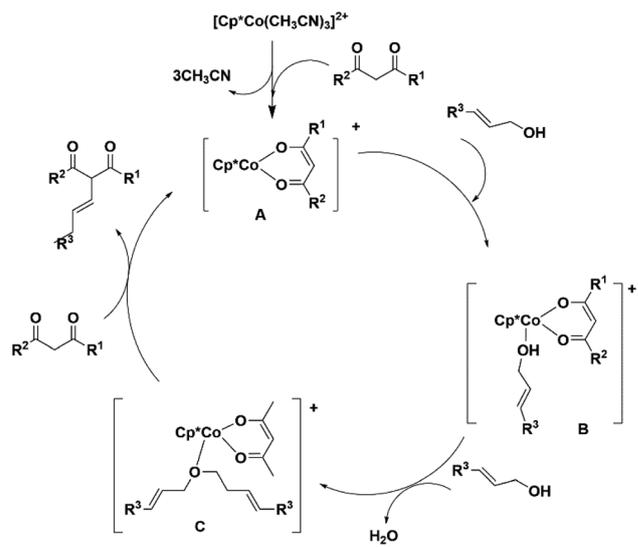
Scheme 6 Plausible mechanisms of allylation and alkylation of the diketones.
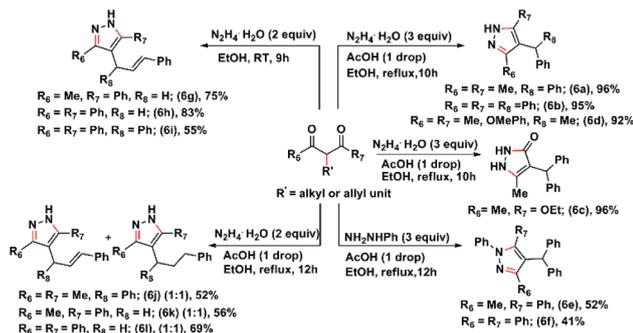
Scheme 7 Synthesis of substituted pyrazoles and 4-benzhydryl-5-methyl-1,2-dihydro-pyrazole-3-one.

Based on the report from this laboratory[17] and other reports, it is proposed that first, the diketone forms the intermediate **A**. Which reacts with allyl alcohol to produce the intermediate **B**. The intermediate **B** on reaction with another molecule of allylic alcohol forms the ether, which is coordinated to the cobalt centre (**C**). In the next step, the nucleophilic addition to the enolized diketones occurs, followed by the release of the product by proton transfer from another molecule of diketone to produce the intermediate **A** (Scheme 6). We believe that the alkylation also takes place *via* the same mechanism.

After the synthesis of substituted diketones, we thought of using these for the synthesis of pyrazoles. Pyrazoles and pyrazolones are an important class of compounds having potential medicinal use.[19] Thus, we carried out the reaction of the substituted diketones, **5c**, **5g**, and **5k** with hydrazine in ethanol, in the presence of acetic acid. The resulting pyrazoles were isolated in excellent yields (Scheme 7). Similarly, ethyl-2-benzhydryl-3-oxobutanoate (**5s**) on reaction with hydrazine under the same condition, afforded 4-benzhydryl-5-methyl-1,2-dihydro-pyrazole-3-one (**6c**) in 96% yield. Corresponding pyrazoles, **6e**, and **6f** were isolated from the reaction of phenylhydrazine with the diketones, **5j** & **5l** (Scheme 7). The pyrazoles, **6g**, **6h**, and **6i**, were isolated in excellent yield form the reaction of **3b**, **3c**, and **3h** with hydrazine hydrate in ethanol at room temperature (Scheme 7). Interestingly, when the reaction of diketones, **3g**, **3b**, and **3c** with hydrazine hydrate were carried out in the presence of one drop of acetic acid in ethanol for 12 hours, a 1 : 1 mixture of 4-(1,3-diphenyl-propyl)-3,5-dimethyl-pyrazole and 4-(1,3-diphenyl-allyl)-3,5-dimethyl-pyrazole (**6j**)

was obtained. The reaction of **3b** and **3c** with hydrazine hydrate under the same reaction condition afforded the 1 : 1 mixture of the allylated and alkylated pyrazoles **6k** and **6l**, respectively (Scheme 7).

We have carried one-pot sequential reactions for the synthesis of pyrazoles. For example, 1,3-diphenyl propane-1,3-dione (**1c**) was first reacted with cinnamyl alcohol (**2a**) and **4g** under optimized condition. Upon completion of the reaction a few millilitre EtOH hydrazine hydrate was added, and the corresponding product was isolated (Scheme 8).

Conclusion

In summary, allylation and alkylation of active methylene compounds using the corresponding alcohol are reported. The reaction is regioselective. Also, the method affords only mono-allylated and monoalkylated products, unlike most of the reported methods.

The reactions have been carried out under aerobic conditions in toluene. These allylated and alkylated diketones and a β-keto ester have been used for the synthesis of eleven new pyrazoles and a new pyrazolone.

## Experimental section

General methods and materials

All the reactions are performed in the air without further purification of commercially available reagents and solvents. The catalyst $[Cp*Co(CH_3CN)_3][SbF_6]_2$ was synthesized from the literature procedure.[16] The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in $CDCl_3$. The LCMS data of the reaction mixture were recorded with a TOF mass spectrometer in ESI$^+$ mode in MeOH and acetonitrile solvent. The HRMS data of newly synthesized compounds were recorded with a TOF mass spectrometer in ESI$^+$ mode in acetonitrile/water mixture. Flash column chromatography was done in silica gel (60–120 mesh) for purification of product from the crude reaction mixture.

General procedure for the reaction of allylic alcohols with diketones and β-keto esters

The catalyst (0.0027 g, 1.7 mol%), toluene (2 mL), the β-keto compound (0.2 mmol), and allylic alcohol (0.34 mmol, 1.7 equivalent) were taken in a screw-cap reaction tube. The reaction tube was placed in an oil-bath at a temperature of 110 °C and continuously stirred for 8–12 hours. The reaction was monitored by TLC. The solvent was removed *in vacuo*, and the products were purified by silica gel (60–120 mesh) column chromatography using hexane-ethyl acetate (1–5%) as eluent.

Synthesis of pyrazoles

The alkylated diketones, **5c**, **5g**, **5k**, and **5s** (0.2 mmol) were dissolved in ethanol, and one drop of acetic acid was added to this. The reaction solution was refluxed for 12 hours. The solvent was removed *in vacuo*, and the products were purified by
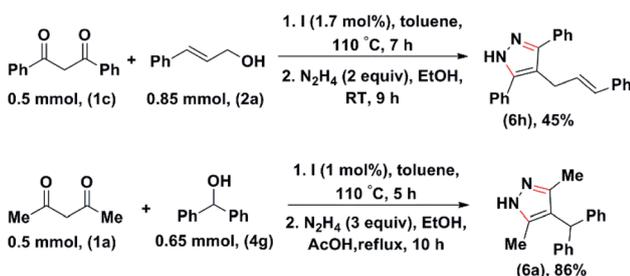
Scheme 8 One pot synthesis of substituted pyrazoles 6h and 6a.

silica gel (60–120 mesh) column chromatography using hexane-ethyl acetate (1–5%) as eluent.

The newly synthesized allylated compounds, **3b**, **3c**, and **3h** (0.2 mmol) and hydrazine hydrate (0.4 mmol) were dissolved in ethanol, and the reaction solution was stirred for 9 hours at room temperature. The solvent was removed *in vacuo*, and the products were purified by silica gel (60–120 mesh) column chromatography using hexane-ethyl acetate (1–5%) as eluent. In another set of reactions, the reaction solutions were stirred for 12 hours in the presence of one drop of acetic acid.

3-(3-Phenyl-allyl)-pentane-2,4,done (3a).[5b,15a] Colourless liquid; yield 0.0311 g, 72%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 (t, J = 6.2 Hz, 2.7H), 7.31–7.27 (m, 5H), 7.24–7.20 (m, 2H), 6.45 (d, J = 15.6 Hz, 1H), 6.35 (d, J = 16.0 Hz, 0.8H), 6.22 (dt, J = 16.0, 5.2 Hz, 0.8H), 6.07 (dt, J = 15.6, 7.2 Hz, 1H), 3.80 (t, J = 7.4 Hz, 1H), 3.16 (dd, J = 5.2, 1.2 Hz, 1.7H), 2.75 (t, J = 7.0 Hz, 2H), 2.21 (s, 6H), 2.16 (s, 5H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.6, 191.6, 137.1, 136.8, 132.8, 130.1, 128.6, 128.5, 127.6, 127.5, 127.3, 126.2, 126.1, 125.4, 107.4, 68.4, 31.6, 30.5, 29.4, 23.1.

2-Phenyl-2-(phenyl-allyl)-butane-1,3-dione (3b).[5b,15a] Colourless liquid; yield 0.0463 g, 83%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.98 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.27–7.23 (m, 4H), 7.19–7.17 (m, 1H), 6.44 (d, J = 16.0 Hz, 1H), 6.15–6.07 (m, 1H), 4.59 (t, J = 7.0 Hz, 1H), 2.94–2.82 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 203.5, 195.8, 136.9, 136.4, 133.8, 132.7, 128.9, 128.8, 128.5, 127.4, 126.2, 125.9, 63.2, 32.4, 28.3.

1,3-Diphenyl-2-(3-phenyl-ally)-propane-1,3-dione (3c).[5b,15a] Off white liquid; yield 0.0607 g, 89%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (d, J = 7.6 Hz, 4H), 7.57 (t, J = 7.2 Hz, 2H), 7.46 (t, J = 7.8 Hz, 4H), 7.30–7.19 (m, 5H), 6.47 (d, J = 15.6 Hz, 1H), 6.30–6.22 (m, 1H), 5.37 (t, J = 6.6 Hz, 1H), 3.04 (t, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.6, 137.0, 135.9, 133.6, 132.5, 128.9, 128.6, 128.5, 127.4, 126.8, 126.2, 57.2, 33.0.

3-Methyl-3-(3-phenyl-allyl)-pentane-2,4-dione (3d).[20] Colourless liquid; yield 0.0281 g, 61%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32–7.29 (m, 4H), 7.24–7.20 (m, 1H), 6.44 (d, J = 15.6 Hz, 1H), 6.01–5.93 (m, 1H), 2.75 (d, J = 7.2 Hz, 2H), 2.15 (s, 6H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.7, 136.9, 134.1, 128.5, 127.5, 126.2, 123.9, 66.7, 38.1, 29.7, 26.7, 18.3.

2-Acetyl-5-phenyl-pent-4-enoic acid methyl ester (3e).[21] Colourless liquid; yield 0.0155 g, 33%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33–7.32 (m, 1H), 7.31–7.30 (m, 2H), 7.29–7.28 (m, 1H), 7.23–7.21 (m, 1H), 6.46 (d, J = 16.0 Hz, 1H), 6.11 (dt, J = 15.7, 7.3 Hz, 1H), 3.75 (s, 3H), 3.61 (t, J = 7.4 Hz, 1H), 2.75 (t, J = 7.2 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 202.3, 169.7, 137.0, 132.8, 128.5, 127.4, 126.2, 125.6, 59.4, 52.5, 31.6, 29.7 (grease), 29.3.

2-Acetyl-5-phenyl-pent-4-enoic acid ethyl ester (3f).[5b] Light yellow liquid; yield 0.0223 g, 45%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32–7.27 (m, 4H), 7.23–7.19 (m, 1H), 6.46 (d, J = 15.6 Hz, 1H), 6.15–6.08 (m, 1H), 4.21 (q, J = 7.2 Hz, 2H), 3.59 (t, J = 7.4 Hz, 1H), 2.75 (t, J = 7.2 Hz, 2H), 2.26 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.4, 169.2, 137.0, 132.7, 128.5, 127.4, 126.2, 125.7, 61.5, 59.6, 31.5, 29.7 (grease), 29.2, 14.1.

3-(1,3-Diphenyl-allyl)-pentane-2,4-dione (3g).[1c] Light yellow liquid; yield 0.0462 g, 79%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34–7.20 (m, 10H), 6.43 (d, J = 15.6 Hz, 1H), 6.20 (ddd, J = 15.8, 5.6, 2.2 Hz, 1H), 4.37–4.30 (m, 2H), 2.25 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 202.9, 202.7, 140.1, 136.5, 131.7, 129.2, 129.0, 128.5, 127.9, 127.7, 127.3, 126.4, 74.5, 49.2, 30.1, 29.7.

2-(1,3-Diphenyl-allyl)-1,3-diphenyl-propane-1,3-dione (3h).[22] Pale yellow liquid; yield 0.0724 g, 87%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 (d, J = 8.5 Hz, 2H), 7.82 (d, J = 8.5 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.48–7.43 (m, 3H), 7.36–7.31 (m, 4H), 7.23 (t, J = 7.7 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.14–7.12 (m, 2H), 7.09 (d, J = 8.0 Hz 2H), 6.36–6.28 (m, 2H), 5.97 (d, J = 10.5 Hz, 1H), 4.81 (dd, J = 10.5, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.4, 193.8, 140.9, 137.3, 136.9, 133.4, 133.2, 131.9, 129.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.3, 126.8, 126.2, 62.6, 50.0.

2-But-2-enyl-1-phenyl-butane-1,3-dione (3i). Liquid; yield 0.0160 g, 37%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 5.56–5.49 (m, 1H), 5.39–5.33 (m, 1H), 4.48 (t, J = 7.0 Hz, 1H), 2.68–2.65 (m, 2H), 2.14 (s, 3H), 1.60 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 203.9, 196.0, 136.5, 133.6, 128.8, 128.7, 128.2, 126.8, 63.5, 32.1, 28.0, 17.8. HRMS (ESI-TOF) m/z: [C$_{14}$H$_{16}$O$_2$ + H]$^+$ calcd for C$_{14}$H$_{17}$O$_2$ 217.1224; found 217.1229.

2-But-2-enyl-1,3-diphenyl-propane-1,3-dione (3j). Light yellow liquid; yield 0.0235 g, 42%; ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.95 (d, J = 8.4 Hz, 4H), 7.56 (t, J = 7.2 Hz, 2H), 7.45 (t, J = 7.2 Hz, 4H), 5.52–5.48 (m, 2H), 5.25–5.23 (m, 1H), 2.80 (t, J = 6.3 Hz, 2H), 1.59 (d, J = 5.4 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 195.8, 136.1, 133.5, 128.9, 128.7, 128.1, 127.7, 57.5, 32.6, 17.9. Calc. [M + H]$^+$ = 279.1380, found [M + H]$^+$ = 279.1386.

2-(3-Methyl-but-2-enyl)-1-phenylbutane-1,3-dione (3k).[23] Light yellow liquid; yield 0.0244 g, 53%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, J = 7.2 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 5.03 (td, J = 6.6, 1.2 Hz, 1H), 4.44 (t, J = 7.4 Hz, 1H), 2.68 (t, J = 7.2 Hz, 2H), 2.14 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 204.2, 196.3, 136.5, 134.7, 133.6, 128.8, 128.7, 120.0, 63.4, 29.7 (grease), 28.0, 27.8, 25.7, 17.8. HRMS (ESI-TOF) m/z: [C$_{15}$H$_{18}$O$_2$ + H]$^+$ calcd for C$_{15}$H$_{19}$O$_2$ 231.1380; found 231.1383.

2-(3-Methylbut-2-enyl)-1,3-diphenylpropane-1,3-dione (3l). Colourless liquid; yield 0.0381 g, 65%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 7.2 Hz, 4H), 7.56 (t, J = 7.4 Hz, 2H), 7.44 (t, J = 7.6 Hz, 4H), 5.20 (t, J = 6.8 Hz, 1H), 5.16–5.14 (m, 1H), 2.81 (t, J = 7.0 Hz, 2H), 1.61 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 196.0, 136.2, 134.4, 133.4, 128.8, 128.6, 120.9, 57.5, 28.3, 25.6, 17.8. HRMS (ESI-TOF) m/z: [C$_{20}$H$_{20}$O$_2$ +H]$^+$ Calcd for C$_{20}$H$_{21}$O$_2$ 293.1537; found 293.1543.

2-(3,7-Dimethyl-octa-2,6-dienyl)-pentane-2,4-dione (3m). Light yellow liquid; yield 0.0128 g, 27%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 5.09–4.93 (m, 3H; geraniol vinyl proton keto substrate 2H and enol form 1H), 3.64 (t, J = 7.4 Hz, 1H; keto compound methylene proton), 2.90 (d, J = 6.0 Hz, 1H; enol form geraniol CH$_2$), 2.54 (t, J = 7.2 Hz, 2H; ketone form geraniol CH$_2$), 2.17 (s, 6H, ketone form acetylacetone Me), 2.10 (s, 3H; enol form acetylacetone Me), 2.06–2.02 (m, 4H; ketone form geraniol CH$_2$), 1.99–1.95 (m, 2H; enol form geraniol CH$_2$), 1.66 (s, 6H; ketone form geraniol Me), 1.62 (s, 3H; enol form geraniol Me), 1.59 (s,

5H; ketone and enol form geraniol Me); ^{13}C NMR (100 MHz, CDCl$_3$) δ 204.3, 191.0, 138.5, 135.7, 131.7, 131.6, 124.0, 123.9, 123.0, 119.6, 109.8, 68.6, 39.6, 39.5, 29.3, 27.1, 26.5, 26.4, 26.2, 25.7, 25.6, 23.0, 17.6, 16.1. HRMS (ESI-TOF) *m/z*: [C$_{15}$H$_{24}$O$_2$ + H]$^+$ Calcd for C$_{15}$H$_{25}$O$_2$ 237.1850; found 237.1853.

2-(3,7-Dimethylocta-2,6-dienyl)-1-phenyl-butane-1,3-dione (3n).[24] Light yellow liquid; yield 0.0268 g, 45%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.05 (t, *J* = 7.0 Hz, 1H), 5.00 (t, *J* = 6.6 Hz, 1H), 4.46 (t, *J* = 7.2 Hz, 1H), 2.70 (t, *J* = 7.2 Hz, 2H), 2.14 (s, 3H), 1.97–1.93 (m, 4H), 1.63 (s, 3H), 1.61 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 204.1, 196.4, 138.3, 136.6, 133.6, 131.5, 128.8, 128.7, 123.9, 119.9, 63.3, 39.6, 29.7 (grease), 28.1, 27.8, 26.4, 25.6, 17.6, 16.1.

2-(3,7-Dimethyl-octa-2,6-dienyl)-1,3-diphenyl-propane-1,3-dione (3o).[24] Light yellow liquid; yield 0.0274 g, 38%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, *J* = 7.2 Hz, 4H), 7.55 (t, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 4H), 5.20 (dt, *J* = 15.4, 7.0 Hz, 2H), 5.00 (t, *J* = 6.0 Hz, 1H), 2.83 (t, *J* = 7.0 Hz, 2H), 1.95–1.87 (m, 4H), 1.61 (s, 3H), 1.58 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 195.9, 138.0, 136.3, 133.4, 128.8, 128.6, 127.5, 124.0, 120.7, 57.3, 39.6, 28.3, 26.5, 25.6, 17.6, 16.1.

2-Acetyl-2-(3-phenyl-allyl)-cyclopentanone (3p).[24] Colourless liquid; yield 0.0315 g, 65%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32–7.27 (m, 4H), 7.24–7.19 (m, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 5.99–5.90 (m, 1H), 2.85–2.79 (m, 1H), 2.68–2.57 (m, 2H), 2.34–2.27 (m, 2H), 2.25 (s, 3H), 1.91–1.83 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 215.6, 203.9, 136.7, 134.1, 128.5, 127.6, 126.2, 123.8, 68.7, 38.6, 38.3, 30.3, 26.2, 19.3.

2-Acetyl-2-(3-phenyl-allyl)-cyclohexanone (3q).[24] Pale yellow liquid; yield 0.0364 g, 71%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32–7.27 (m, 4H), 7.22–7.18 (m, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.06–5.98 (m, 1H), 2.75–2.69 (m, 1H), 2.63–2.57 (m, 1H), 2.53–2.47 (m, 2H), 2.34–2.26 (m, 1H), 2.13 (s, 3H), 2.02–1.97 (m, 1H), 1.78–1.65 (m, 3H), 1.58–1.50 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 209.6, 206.1, 137.0, 133.5, 128.5, 127.4, 126.2, 124.4, 67.9, 41.8, 37.9, 34.1, 27.1, 26.4, 22.2.

3-(1-Phenyl-ethyl)-pentane-2,4-dione (5a).[15a,22] Light yellow liquid; yield 0.0362 g, 89%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30–7.26 (m, 2H), 7.22–7.16 (m, 3H), 4.03 (d, *J* = 11.2 Hz, 1H), 3.58 (dt, *J* = 13.6, 6.8 Hz, 1H), 2.26 (s, 3H), 1.82 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.7, 203.6, 143.2, 129.0, 127.5, 127.2, 76.9, 40.6, 30.0, 29.9, 21.1.

3-(1-(p-Tolyl-ethyl))pentane-2,4-dione (5b).[22] Off white solid; yield 0.0411 g, 94%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13–7.05 (m, 4H), 4.01 (d, *J* = 11.2 Hz, 1H), 3.55 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.84 (s, 3H), 1.18 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.7, 203.6, 139.9, 136.5, 129.5, 127.1, 76.82, 40.1, 29.8, 29.7, 20.9.

3-[1-(4-Methoxyphenyl-ethyl]-)pentane-2,4-dione (5c).[22] Off white solid; yield 0.0431 g, 92%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.98 (d, *J* = 11.6 Hz, 1H), 3.76 (s, 3H), 3.54 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.25 (s, 3H), 1.83 (s, 3H), 1.18 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.7, 203.6, 158.4, 135.0, 128.2, 114.1, 76.9, 55.2, 39.7, 29.8, 29.7, 20.9.

3-[1-(4-Chlorophenyl-ethyl)]-pentane-2,4-dione (5d).[22] Colourless liquid; yield 0.0457 g, 96%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 3.98 (d, *J* = 11.6 Hz, 1H), 3.57 (dq, *J* = 13.7, 6.8 Hz, 1H), 2.24 (s, 3H), 1.85 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.1, 203.0, 141.6, 132.6, 128.9, 128.6, 76.6, 39.6, 29.8, 29.6, 20.7.

3-[1-(4-Fluorophenyl-ethyl)]-pentane-2,4-dione (5e).[22] Colourless liquid; yield 0.0436 g, 98%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.95 (t, *J* = 8.6 Hz, 2H), 3.97 (d, *J* = 11.2 Hz, 1H), 3.57 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.23 (s, 3H), 1.82 (s, 3H), 1.16 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.2, 203.1, 161.6 (d, *J* = 244 Hz), 138.7 (d, *J* = 3 Hz), 128.8 (d, *J* = 8 Hz), 115.6 (d, *J* = 22 Hz), 76.8, 39.6, 29.8, 29.6, 20.8.

3-Benzhydry-lpentane-2,4-dione (5g).[15c] White solid; yield 0.0522 g, 98%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 (d, *J* = 4.8 Hz, 8H), 7.20–7.14 (m, 2H), 4.82 (d, *J* = 12.4 Hz, 1H), 4.75 (d, *J* = 12.4 Hz, 1H), 2.00 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.0, 141.3, 128.9, 127.7, 127.1, 74.5, 51.2, 29.7.

1-Phenyl-2-(1-pheny-ethyl)-butane-1,3-dione (diastereomer with low polarity, 5ha).[13a] White solid; total yield of **5h** 0.0513 g, 96%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 9.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22–7.14 (m, 4H), 7.10–7.05 (m, 1H), 4.82 (d, *J* = 11.2 Hz, 1H), 3.85 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.25 (s, 3H), 1.31 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.7, 195.3, 143.4, 137.0, 133.4, 128.6, 128.5, 127.4, 126.6, 71.5, 40.3, 27.5, 20.3.

1-Phenyl-2-(1-phenyl-ethyl)butane-1,3-dione (diastereomer with high polarity, 5hb).[13a,22] White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.34–7.18 (m, 5H), 4.91 (d, *J* = 11.2 Hz, 1H), 3.88 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.89 (s, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.2, 195.2, 143.2, 137.2, 133.8, 128.9, 128.8, 127.5, 127.0, 70.9, 40.9, 27.9, 21.6.

1-Phenyl-2-[1-(p-tolyl-ethyl)]-butane-1,3-dione (diastereomer with low polarity, 5ia).[25a] White solid; total yield of **5i** 0.0544 g, 97%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.0 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 11.2 Hz, 1H), 3.84 (dq, *J* = 13.6, 6.8 Hz, 1H), 2.31 (s, 3H), 1.91 (s, 3H), 1.19 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.4, 195.3, 140.1, 137.3, 136.6, 133.8, 129.5, 128.9, 128.8, 127.3, 71.0, 40.6, 27.8, 21.7, 21.0.

1-Phenyl-2-(1-(p-tolyl-ethyl))-butane-1,3-dione (diastereomer with high polarity, 5ib).[25a] White solid; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.6 Hz, 2H), 7.49 (dd, *J* = 13.2, 7.2 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 10.8 Hz, 1H), 3.82 (dq, *J* = 14.2, 6.8 Hz, 1H), 2.23 (s, 3H), 2.20 (s, 3H), 1.28 (d, *J* = 7.0 Hz, 5H), 1.28 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.8, 195.3, 140.5, 137.1, 136.1, 133.4, 129.1, 128.6, 128.5, 127.2, 71.6, 39.9, 27.4, 20.9, 20.4.

2-Benzhydryl-1-phenyl-butane-1,3-dione (5j).[25b] White solid; yield 0.0647 g, 99%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 13.3, 7.3 Hz, 4H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.28–7.19 (m, 3H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 5.64 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* =

12.0 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.0, 194.3, 141.7, 141.2, 136.9, 133.7, 129.0, 128.7, 128.7, 128.1, 127.7, 127.1, 126.7, 68.9, 51.5, 27.9.

1,3-Diphenyl-2-(1-phenyl-ethyl)-propane-1,3-dione (5k).[22] White solid; yield 0.0650 g, 99%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.47–7.39 (m, 3H), 7.30–7.26 (m, 4H), 7.18 (t, J = 7.6 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H), 5.63 (d, J = 10.0 Hz, 1H), 4.10 (dq, J = 14.0, 7.2 Hz, 1H), 1.36 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.0, 194.6, 143.8, 137.2, 136.9, 133.6, 133.1, 128.9, 128.8, 128.5, 128.4, 128.4, 127.7, 126.6, 64.8, 41.2, 20.2.

2-Benzhydryl-1,3-diphenyl-propane-1,3-dione (5l).[22] White solid; yield 0.0771 g, 99%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 (d, J = 7.6 Hz, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.33 (t, J = 7.6 Hz, 4H), 7.25 (d, J = 7.2 Hz, 4H), 7.15 (t, J = 7.4 Hz, 4H), 7.05 (t, J = 7.2 Hz, 2H), 6.36 (d, J = 11.6 Hz, 1H), 5.33 (d, J = 11.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.1, 141.7, 136.9, 133.3, 128.7, 128.6, 128.5, 128.3, 126.6, 62.3, 52.4.

3-Benzhydryl-3-methyl-pentane-2,4-dione (5m).[25c] Colourless liquid; yield 0.0297 g, 53%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.25–7.21 (m, 4H), 7.18–7.16 (m, 6H), 5.64 (s, 1H), 1.95 (s, 6H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 206.2, 141.1, 129.7, 128.4, 126.7, 72.9, 52.3, 26.9, 16.8.

2-Acetyl-2-benzhydryl-cyclopentanone (5n).[15c] White solid; yield 0.0530 g, 91%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, J = 7.2 Hz, 2H), 7.23–7.14 (m, 6H), 7.01 (d, J = 7.2 Hz, 2H), 5.34 (s, 1H), 3.18–3.12 (m, 1H), 2.20–2.072 (m, 2H), 2.05 (s, 3H), 1.80–1.65 (m, 2H), 1.40–1.33 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 215.2, 202.6, 140.5, 140.4, 129.9, 129.0, 128.8, 128.4, 127.0, 126.9, 74.4, 55.2, 38.9, 27.5, 26.0, 19.6.

2-Acetyl-2-benzhydryl-cyclohexanone (5o).[25d] White solid; yield 0.0478 g, 78%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29–7.24 (m, 5H), 7.22–7.19 (m, 4H), 7.17–7.12 (m, 1H), 5.46 (s, 1H), 2.78 (dd, J = 13.4, 2.6 Hz, 1H), 2.51 (d, J = 15.2 Hz, 1H), 2.22–2.14 (m, 1H), 1.93–1.88 (m, 2H), 1.85 (s, 3H), 1.73–1.66 (m, 2H), 1.53–1.41 (m, 1H); ^{13}C NMR (150 MHz, CDCl$_3$) δ 208.6, 204.4, 140.8, 140.2, 130.4, 130.2, 128.4, 128.1, 126.9, 126.4, 73.5, 53.3, 42.3, 31.2, 26.9, 25.2, 22.8. HRMS (ESI-TOF) m/z: [C$_{21}$H$_{22}$O$_2$ + Na]$^+$ Calcd for C$_{21}$H$_{22}$O$_2$Na 329.1512; found 329.1519.

3-Oxo-2-(1-phenyl-ethyl)-butyric acid methyl ester (5p).[15c] Colourless liquid; yield 0.0274 g, 62%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30–7.26 (m, 4H), 7.22–7.18 (m, 6H), 3.81 (d, J = 10.8 Hz, 1H), 3.76 (m, 3H), 3.75 (d, J = 10.8 Hz, 1H), 3.58–3.49 (m, 2H), 3.43 (s, 3H), 2.29 (s, 3H), 1.91 (s, 3H), 1.29 (d, J = 6.8 Hz, 3H), 1.24 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.3, 202.3, 169.1, 168.6, 143.2, 143.0, 128.7, 128.5, 127.4, 127.3, 127.0, 126.8, 67.4, 66.8, 52.4, 52.1, 40.1, 39.8, 29.9, 29.6, 20.6, 20.1.

2-Benzhydryl-3-oxo-butyric acid methyl ester (5q).[15c] White solid; yield 0.0548 g, 97%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31–7.24 (m, 8H), 7.20–7.15 (m, 2H), 4.80 (d, J = 12.4 Hz, 1H), 4.57 (d, J = 12.0 Hz, 1H), 3.53 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.7, 168.2, 141.6, 141.1, 128.9, 128.7, 127.9, 127.6, 127.0, 126.9, 65.0, 52.5, 50.9, 30.1.

3-Oxo-2-(1-phentyl-ethyl)-butyric acid ethyl ester (5r).[16b] Colourless liquid; yield 0.0356 g, 76%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31–7.25 (m, 4H), 7.22–7.18 (m, 6H), 4.22 (q, J = 7.2 Hz, 2H), 3.87 (q, J = 7.1 Hz, 2H), 3.79 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.2 Hz, 1H), 3.58–3.49 (m, 2H), 2.30 (s, 3H), 1.93 (s, 3H), 1.29 (d, J = 6.8 Hz, 6H), 1.23 (t, J = 6.8 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.4, 168.6, 168.2, 143.2, 143.1, 128.7, 128.4, 127.4, 127.3, 126.9, 126.8, 67.6, 67.0, 61.5, 61.1, 40.0, 39.8, 29.9, 29.5, 20.5, 20.3, 14.1, 13.7.

2-Benzhydryl-3-oxo-butyric acid ethyl ester (5s).[25b] White solid; yield 0.0558 g, 94%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.23–7.14 (m, 8H), 7.09–7.05 (m, 2H), 4.69 (d, J = 12.5 Hz, 1H), 4.45 (dd, J = 12.2, 1.2 Hz, 1H), 3.91–3.87 (m, 2H), 2.01 (s, 3H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.6, 166.6, 140.6, 140.3, 127.8, 127.6, 126.8, 126.7, 125.9, 125.8, 64.2, 60.4, 49.9, 28.9, 12.7.

4-Benzhydryl-3,5-dimethyl-1H-pyrazole (6a). Off white solid; yield 0.0252 g, 96%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (t, J = 7.2 Hz, 4H), 7.22 (d, J = 7.1 Hz, 2H), 7.10 (d, J = 7.4 Hz, 4H), 5.45 (s, 1H), 1.89 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.1, 129.1, 128.2, 126.2, 117.3, 46.5, 11.6. HRMS (ESI-TOF) m/z: [C$_{18}$H$_{18}$N$_2$ + H]$^+$ calcd for C$_{18}$H$_{19}$N$_2$ 263.1543; found 263.1547.

3,5-Diphenyl-4-(1-phenyl-ethyl)-1H-pyrazole (6b). Off white solid; yield 0.0308 g, 95%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37–7.20 (m, 15H), 4.44 (q, J = 7.3 Hz, 1H), 1.46 (d, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 146.2, 132.5, 128.8, 128.3, 128.2, 128.0, 127.4, 125.7, 117.2, 33.6, 20.0. HRMS (ESI-TOF) m/z: [C$_{23}$H$_{20}$N$_2$ + H]$^+$ calcd for C$_{23}$H$_{21}$N$_2$ 325.1700; found 325.1702.

4-Benzhydryl-5-methyl-1H-pyrazol-3(2H)-one (6c). Off white solid; yield 0.0254 g, 96%; ^{1}H NMR (500 MHz, CD$_3$OD) δ 7.25 (t, J = 7.5 Hz, 4H), 7.17 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 8.0 Hz, 4H), 6.62 (s, 0.6H; NH), 5.42 (s, 1H), 1.73 (s, 3H); ^{13}C NMR (125 MHz, MeOD) δ 163.1, 151.3, 144.8, 142.8, 130.2, 129.2, 127.2, 116.9, 46.2, 11.5. HRMS (ESI-TOF) m/z: [C$_{17}$H$_{16}$N$_2$O + H]$^+$ calcd for C$_{17}$H$_{17}$N$_2$O 265.1336; found 265.1337.

4-[1-((4-Methoxy-phenyl)ethy)]-3,5-dimethyl-1H-pyrazole (6d). Off white solid; yield 0.0211 g, 92%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.12 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.71 (s, 0.7H; NH), 4.04 (q, J = 7.2 Hz, 1H), 3.78 (s, 3H), 2.10 (s, 6H), 1.56 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.6, 149.8, 141.8, 137.5, 128.1, 119.7, 116.3, 113.5, 55.2, 33.2, 20.4, 11.6. HRMS (ESI-TOF) m/z: [C$_{14}$H$_{18}$N$_2$O + H]$^+$ calcd for C$_{14}$H$_{19}$N$_2$O 231.1492; found 231.1496.

4-Benzhydryl-3-methyl-1,5-diphenyl-1H-pyrazole (6e). Off white liquid; yield 0.0209 g, 52%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, J = 6.8 Hz, 4H), 7.26 (bs, 4H), 7.25–7.20 (m, 6H), 7.10 (d, J = 8.0 Hz, 4H), 7.02 (d, J = 7.6 Hz, 2H), 5.41 (s, 1H), 1.92 (s, 3H); ^{13}C NMR (125 MHz, CDCl3) δ 148.7, 143.1, 141.4, 140.1, 130.7, 130.2, 129.2, 128.6, 128.4, 128.3, 128.2, 126.4, 126.2, 124.4, 121.2, 46.4, 29.7 (grease), 13.9. HRMS (ESI-TOF) m/z: [C$_{29}$H$_{24}$N$_2$ + H]$^+$ calcd for C$_{29}$H$_{25}$N$_2$ 401.2013; found 401.2013.

4-Benzhydryl-1,3,5-triphenyl-1H-pyrazole (6f). Off white solid; yield 0.0190 g, 41%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (dd, J = 7.2, 2.4 Hz, 2H), 7.28–7.26 (m, 3H), 7.24–7.22 (m, 3H), 7.21–7.15 (m, 4H), 7.14–7.05 (m, 7H), 7.00 (dd, J = 7.6, 2.8 Hz, 4H), 6.86 (d, J = 7.2 Hz, 2H), 5.66 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 143.2, 130.6, 129.5, 129.1, 128.5, 128.0, 127.8, 127.6, 126.7, 125.9, 124.8, 120.9, 46.9, 29.7 (grease). HRMS (ESI-TOF) m/z: [C$_{34}$H$_{26}$N$_2$ + H]$^+$ calcd for C$_{34}$H$_{27}$N$_2$ 463.2169; found 463.2173.

4-Cinnamyl-3-methyl-5-phenyl-1H-pyrazole (6g). White solid; yield 0.0206 g, 75%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.35–7.30 (m, 3H), 7.29 (bs, 1H), 7.26 (d, J = 3.6 Hz, 1H), 7.20 (t, J = 7.0 Hz, 1H), 6.36–6.28 (m, 2H), 3.45 (d, J = 4.4 Hz, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 146.2, 143.9, 137.5, 132.0, 130.2, 128.8, 128.6, 128.5, 127.9, 127.6, 127.0, 126.1, 112.6, 26.7, 10.8. HRMS (ESI-TOF) m/z: [C$_{19}$H$_{18}$N$_2$ + H]$^+$ calcd for C$_{19}$H$_{19}$N$_2$ 275.1543; found 275.1546.

4-Cinnamyl-3,5-diphenyl-1H-pyrazole (6h). White solid; yield 0.0281 g, 83%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, J = 6.8 Hz, 4H), 7.42–7.33 (m, 6H), 7.31–7.21 (m, 4H), 7.21 (t, J = 6.8 Hz, 1H), 6.50 (dt, J = 16.0, 4.8 Hz, 2H), 6.36 (d, J = 16.0 Hz, 4H), 3.60–3.59 (m, 2H).; ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.3, 137.5, 131.7, 131.2, 129.7, 128.7, 128.5, 128.1, 127.6, 127.1, 126.1, 112.4, 29.7 (grease), 27.2. HRMS (ESI-TOF) m/z: [C$_{24}$H$_{20}$N$_2$ + H]$^+$ calcd for C$_{24}$H$_{21}$N$_2$ 337.1700; found 337.1707.

4-(1,3-Diphenylallyl)-3,5-diphenyl-1H-pyrazole (6i). White solid; yield 0.0226 g, 55%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.39–7.37 (m, 4H), 7.31 (d, J = 6.8 Hz, 6H), 7.24–7.16 (m, 8H), 7.09 (d, J = 7.2 Hz, 2H), 6.45–6.34 (m, 2H), 5.09 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 147.3, 143.6, 137.2, 132.1, 131.6, 131.5, 128.8, 128.5, 128.4, 128.2, 128.2, 128.1, 127.2, 126.2, 117.3, 43.8, 29.7 (grease). HRMS (ESI-TOF) m/z: [C$_{30}$H$_{24}$N$_2$ + H]$^+$ calcd for C$_{30}$H$_{25}$N$_2$ 413.2013; found 413.2017.

4-(1,3-Diphenylallyl)-3,5-dimethyl-1H-pyrazole & 4-(1,3-diphenyl-propyl)-3,5-dimethyl-1H-pyrazole (6j) (1.2 : 1). Off white liquid; yield 0.0149 g, 52% w.r.t **6j1**; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.37 (d, J = 7.5 Hz, 1H), 7.32–7.27 (m, 3H), 7.25–7.21 (m, 2H), 7.19 (d, J = 7.0 Hz, 1.4H), 7.17 (d, J = 7.0 Hz, 0.5H), 7.14 (d, J = 7.0 Hz, 1H), 6.62 (dd, J = 15.5, 7.0 Hz, 0.67H), 6.32 (d, J = 16 Hz, 0.64H), 4.84 (d, J = 7.0 Hz, 0.65H), 3.88 (dd, J = 10, 6.3 Hz, 0.53H), 2.65 (ddt, J = 13.8, 9.4, 5.5 Hz, 1H), 2.45–2.39 (m, 0.55H), 2.35–2.27 (m, 0.62H), 2.15 (s, 2.3H), 2.11 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.4, 142.7, 141.9, 137.3, 131.2, 130.8, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.5, 127.3, 126.3, 126.2, 125.9, 125.8, 43.6, 39.8, 35.5, 34.2, 11.8, 11.7; **DEPT** ^{13}C NMR (125 MHz, CDCl$_3$) δ 131.2, 130.8, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 127.5, 127.3, 126.3, 126.2, 125.9, 125.8, 43.6, 39.8, 35.5, 34.2, 11.8, 11.7. HRMS (ESI-TOF) m/z: [C$_{20}$H$_{20}$N$_2$ + H]$^+$ & [C$_{20}$H$_{22}$N$_2$ + H]$^+$ calcd for C$_{20}$H$_{21}$N$_2$ & C$_{20}$H$_{23}$N$_2$ 289.1700 & 291.1856; found 289.1681 & 291.1857.

4-Cinnamyl-3-methyl-5-phenyl-1H-pyrazole & 3-methyl-5-phenyl-4-(3-phenylpropyl)-1H-pyrazole (6k) (1 : 1). Off white solid; yield 0.0154 g, 56% w.r.t **6k1**; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (d, J = 7.5 Hz, 2H), 7.45 (d, J = 7.0 Hz, 2H), 7.41–7.27 (m, 10H), 7.24 (bs, 1H), 7.21–7.16 (m, 2H), 7.12 (d, J = 7.5 Hz, 2H), 6.39–6.29 (m, 2H), 3.45 (d, J = 4.5 Hz, 2H), 2.62–2.55 (m, 4H), 2.24 (s, 3H), 2.21 (s, 3H), 1.82 (dt, J = 15.4, 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 142.0, 137.5, 130.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 127.0, 126.1, 125.7, 35.6, 32.0, 26.7, 22.8, 10.9. HRMS (ESI-TOF) m/z: [C$_{19}$H$_{18}$N$_2$ + H]$^+$ & [C$_{19}$H$_{20}$N$_2$ + H]$^+$ calcd for C$_{19}$H$_{19}$N$_2$ & C$_{19}$H$_{21}$N$_2$ 275.1543 & 277.1700; found 275.1504 & 277.1700.

4-Cinnamyl-3,5-diphenyl-1H-pyrazole & 3,5-diphenyl-4-(3-phenyl-propyl)-1H-pyrazole (6l) (1.2 : 1). Off white solid; yield 0.0233 g, 69% w.r.t **6l1**; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, J = 7.5 Hz, 3H), 7.52 (d, J = 7.5 Hz, 2H), 7.41–7.35 (m, 7H), 7.33–7.28 (m, 3H), 7.23–7.20 (m, 1.6H), 7.17–7.14 (t, J = 7.3 Hz, 0.5H), 7.01 (d, J = 7.0 Hz, 1H), 6.49 (dt, J = 16.0, 5.0 Hz, 1H), 6.36 (d, J = 16.0 Hz, 1H), 3.60 (dd, J = 4.5, 2.0 Hz, 1H), 2.76 (t, J = 8.0 Hz, 1H), 2.52 (t, J = 7.5 Hz, 1H), 1.77 (dt, J = 15.5, 7.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 141.8, 137.5, 131.2, 129.7, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 126.2, 125.7, 115.7, 112.4, 35.5, 31.8, 27.2, 22.9; **DEPT** ^{13}C NMR (125 MHz, CDCl$_3$) δ 131.2, 129.7, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 126.2, 125.7, 35.5, 31.8, 27.2, 22.9. HRMS (ESI-TOF) m/z: [C$_{24}$H$_{20}$N$_2$ + H]$^+$ & [C$_{24}$H$_{22}$N$_2$ + H]$^+$ calcd for C$_{24}$H$_{21}$N$_2$ & C$_{24}$H$_{23}$N$_2$ 337.1700 & 339.1856; found 337.1784 & 339.1857.

Oxybis(methanetriyl)tetrabenzene.[16] Colourless semi-liquid; yield 0.0994 g, 71%; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (d, J = 7.6 Hz, 8H), 7.34 (t, J = 7.6 Hz, 4H), 7.30–7.26 (m, 4H), 5.44 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.2, 128.4, 127.4, 127.3, 80.1.

((1E,1′E)-Oxybis(prop-1-ene-3,1-diyl))dibenzene.[16] Off white liquid; yield 0.0673 g, 67%; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.43 (d, J = 7.5 Hz, 4H), 7.35 (dd, J = 10.3, 4.8 Hz, 4H), 7.32–7.26 (m, 2H), 6.68 (d, J = 16.0 Hz, 2H), 6.36 (dt, J = 15.9, 6.0 Hz, 2H), 4.24 (dd, J = 6.0, 1.5 Hz, 4H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 136.7, 132.6, 128.6, 127.7, 126.5, 126.1, 70.8.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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