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# Rhodium catalyzed reaction of internal alkynes with organoborons under CO atmosphere: a product tunable reaction

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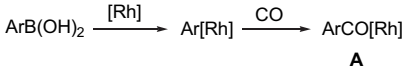
ABSTRACT

Alkynes react with organoborons under a CO atmosphere in the presence of a rhodium(I) catalyst to afford mainly 5-aryl-2(5*H*)-furanones, α,β-unsaturated ketones, and indanones. The product selectivity can be tuned by modifying the reaction conditions.



## 1. Introduction

Intra- and intermolecular carbonylative arylations of unsaturated systems by in-situ formed acyl metal species under a CO atmosphere are powerful methods for the synthesis of compounds with carbonyl moieties, as well as a range of heterocycles.[1,2] Palladium catalyzed carbonylation of aryl halides is a frequently applied method to create acyl palladium species, which having a considerable electrophilic character, are capable of reacting with nucleophilic sites.[1] However, it has been recently shown that arylboronic reagents can also be carbonylated by rhodium catalysis to give acyl rhodium species **A** (Scheme 1), which are amenable to add unsaturated C–C bonds.[2] These methods can be respected as complementary to each other and the latter method providing possible alternative routes as compared to their Pd catalyzed counterparts.




**Scheme 1.** Formation of aroylrhodium species from arylboronic reagents.

In this context, we disclosed recently that the rhodium catalyzed carbonylation of an internal alkyne and arylboronic acid mixture could yield the 5-aryl-2(5*H*)-furanone (**3**), α,β-unsaturated ketone (**4**), indenone (**5**), and indanone (**6**) products (Scheme 2) and aimed at the selective synthesis of each product by a suitable modification of the reaction conditions.[2b,f]

We have shown in our preliminary studies that product selectivity of the method could be made tunable by varying the experimental conditions to favor formation of structures **3** or **4**.[2b,f] In this report we present additional scope and limitations of this method and provide more insight into the reaction pathways.

## 2. Results and discussion

### 2.1. Synthesis of 5-aryl-2(5*H*)-furanones

The $[Rh(cod)Cl]_2$ complex was the catalyst precursor of choice in the synthesis of **3** in our preliminary study.[2b] Further exploration of rhodium complexes for the carbonylation of the diphenylacetylene and phenylboronic acid mixture at 80 °C, in toluene and under 20 atm of CO pressure led us to attain somewhat better and more reproducible results specifically with the $[Rh(cod)OH]_2$ complex, producing the corresponding furanone in an isolated yield of 86% (Table 1, entries 1–6).

The effect of CO pressure was also investigated with the use of $[Rh(cod)OH]_2$. It was observed that lower CO pressures resulted in proportionally lower product yield (entries 7 and 8).

The methodology was particularly applicable with *m*- and *p*-substituted phenylboronic acids, which tolerated both electron-donating or withdrawing groups and afforded excellent yields when reacted with diphenylacetylene under optimum reaction conditions (Table 2). For instance, a carbonylative reaction of

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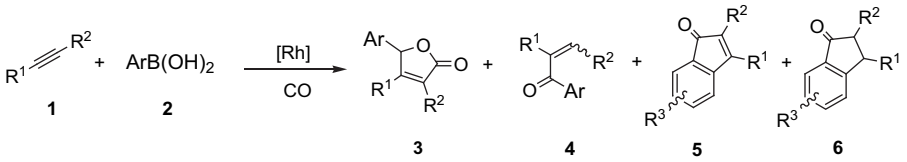
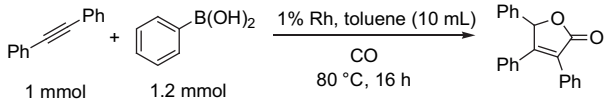



**Scheme 2.** Rhodium catalyzed carbonylative reaction of alkynes with arylboronic acids.

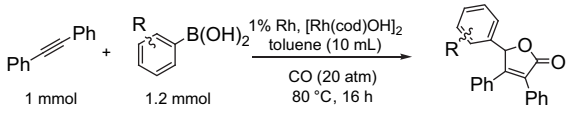
**Table 1**
Effect of rhodium complex and CO pressure on the formation of 3,4,5-triphenylfuran-2(5*H*)-one




| Entry | Complex | *P* (atm) | Conversion % | Yield[a] % |
|---|---|---|---|---|
| 1 | $[Rh(cod)Cl]_2$ | 20 | 100 | 89 (78) |
| 2 | $[Rh(cod)OH]_2$ | 20 | 100 | 93 (86) |
| 3 | $[Rh(C_2H_4)_2Cl]_2$ | 20 | 100 | 35 |
| 4 | $[Rh(C_2H_4)_2acac]_2$ | 20 | 87 | 63 |
| 5 | $Rh(cod)_2BF_4$ | 20 | 100 | 84 |
| 6 | $[Rh(CO)_2Cl]_2$ | 20 | 100 | 88 |
| 7 | $[Rh(cod)OH]_2$ | 10 | 100 | 76 |
| 8 | $[Rh(cod)OH]_2$ | 5 | 100 | 65 |

[a] Determined by GC. Isolated yields are given in parentheses.

**Table 2**
Carbonylative reaction of diphenylacetylene with arylboronic acids, leading to 5-aryl-2(5*H*)-furanones



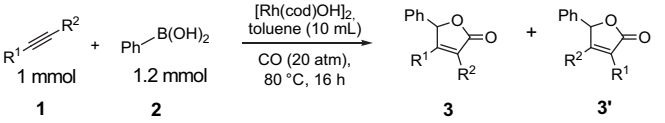

| Entry | R | Isolated yield % |
|---|---|---|
| 1 | H | 86 (**3aa**) |
| 2 | *p*-$CH_3$ | 88 (**3ab**) |
| 3 | *m*-$CH_3$ | 90 (**3ac**) |
| 4 | *p*-$OCH_3$ | 90 (**3ad**) |
| 5 | *p*-$COCH_3$ | 88 (**3ae**) |
| 6[a] | *p*-$CF_3$ | 82 (**3af**) |
| 7[a] | *o*-$CH_3$ | 41 (**3ag**) |

[a] 3% Rh.

electron poor *p*-acetylphenylboronic acid with diphenylacetylene resulted in an isolated yield of 88% of **3ae** in the presence of 1% rhodium (entry 5). In contrast, the reaction of 4-(trifluoromethyl)-phenylboronic acid with diphenylacetylene required a higher Rh concentration (3%) to afford a high yield of the corresponding furanone (**3af**) (entry 6). A modest furanone product (**3ag**) can also be recovered with sterically hindered *o*-tolylboronic acid (entry 7). It must be noted, however, that *o*-tolylboronic acid had failed to undergo carbonylative addition to diphenylacetylene when using $[Rh(cod)Cl]_2$ as shown in our previous study[2b] and that in general better yields were also realized by using $[Rh(cod)OH]_2$ instead of $[Rh(cod)Cl]_2$.

High yields of furanone products were also achieved by the carbonylative reaction of 4-octyne and a number of non-symmetric alkynes with phenylboronic acid in the presence of 0.88–3% Rh (Table 3). GC and GC–MS analyses of the crude product recovered from the reaction of 4-octyne and phenylboronic acid showed the presence of the corresponding 2(5*H*)-furanone (**3ba**) product together with a regioisomer. The regioisomer readily underwent isomerization to form **3ba** during column separation, which is tentatively recognized to be 5-phenyl-3,4-dipropylfuran-2(3*H*)-one by NMR spectroscopic analyses of the crude product. The product **3ba** was isolated at a yield of 60% when the reaction was performed with 0.88% rhodium (entry 1); however, it increased to a yield of 76% yield with the use of 2.63% rhodium (entry 2).

**Table 3**
The synthesis of 5-aryl-2(5*H*)-furanones by the rhodium catalyzed carbonylative reaction of phenylboronic acid with various alkynes

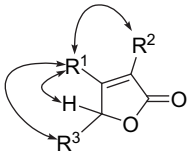



| Entry | $R^1$ | $R^2$ | Rh% | Isolated yield % | |
|---|---|---|---|---|---|
| | | | | **3** | **3′** |
| 1 | *n*-$C_3H_7$ | *n*-$C_3H_7$ | 0.88 | 60 (**3ba**) | — |
| 2 | *n*-$C_3H_7$ | *n*-$C_3H_7$ | 2.63 | 76 (**3ba**) | — |
| 3 | Ph | *n*-$C_3H_7$ | 2.63 | 35 (**3ca**)[a] | 47 (**3ca′**)[a] |
| 4 | Ph | $CH_3$ | 2.63 | 32 (**3da**) | 32 (**3da′**) |
| 5 | *p*-$CH_3COC_6H_4$ | *n*-$C_4H_9$ | 0.88 | 24 (**3ea**) | 42 (**3ea′**) |
| 6 | *p*-$CH_3OC_6H_4$ | *n*-$C_4H_9$ | 1 | 36 (**3fa**) | 44 (**3fa′**) |
| 7 | *o*-$CH_3OC_6H_4$ | *n*-$C_4H_9$ | 3 | 11 (**3ga**) | 48 (**3ga′**) |
| 8 | *p*-$CH_3COC_6H_4$ | Ph | 0.88 | 45 (**3ha**) | 36 (**3ha′**) |
| 9 | *p*-$CH_3OC_6H_4$ | Ph | 0.88 | 29 (**3ia**) | 48 (**3ia′**) |
| 10 | *o*-$CH_3C_6H_4$ | Ph | 1 | 30 (**3ja**) | 42 (**3ja′**) |
| 11 | *o*-$CH_3OC_6H_4$ | Ph | 1 | 26 (**3ka**) | 68 (**3ka′**) |
| 12 | *o*-$CH_3OC_6H_4$ | *p*-$CH_3COC_6H_4$ | 1 | 23 (**3la**)[a] | 63 (**3la′**)[a] |

[a] Isomeric ratio was determined by $^1H$ NMR spectroscopy.

In the case of non-symmetric alkynes, the methodology was moderately regioselective. The relative formation of isomeric products was influenced by electronic and steric variations on the alkyne substrate. It can be deduced on the basis of the product distribution that the aroylation step relatively favored the alkyl substituted, more electrophilic, and less sterically congested alkynyl carbon. Nevertheless, the method was not successful with ester functionalized alkynes, yielding a complex mixture after the reaction.

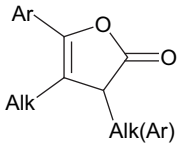
Regioisomeric 2(5*H*)-furanones could be separated in most cases by column chromatography. The isomers of **3la** and **3la′** could not be separated and the relative proportions of **3ca** and **3ca′** could only be enriched by column chromatography. The regioisomeric structures of furanones were elucidated via NOE measurements, while that of **3ca** was identified by comparison with the literature.[3]




Eventually, the $^1H$ NMR spectra of the 2(5*H*)-furanones synthesized in this study and those from the literature demonstrate the existence of a correlation between the chemical shift values of the 5*H* signals and diamagnetic field induced by the substituent at position 4 of the ring. When both positions 4 and 5 of the ring were occupied by aryl groups, a 5*H* resonance signal appeared at field

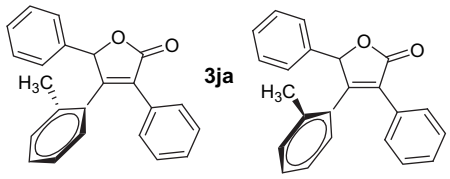
strengths lower than 6 ppm (typically in the range of 6.0–6.5 ppm). The corresponding signal shifted to higher fields, giving a resonance signal in the range of 5.3–6.0 ppm, when position 4 on the furanone ring was occupied with an alkyl group.[1d,2b,3,4]

A third isomer was also detected by GC and GC–MS analyses of the crude products of the reactions performed with alkynes substituted with both alkyl and aryl groups on the alkynyl carbons (entries 3–7), which converted to isomer **3′** during purification work-up and their structures were tentatively assigned to be 4-alkyl-2(3*H*)-furanone as determined by $^1$H NMR spectroscopic analysis of the crude products.

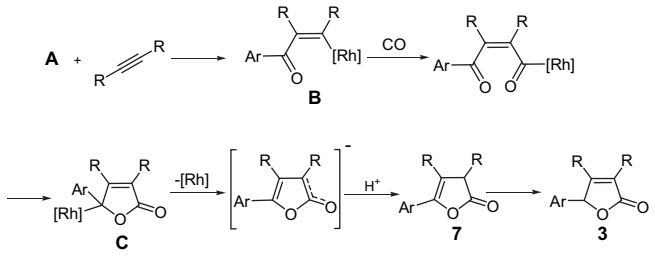



No traces of 4-aryl-2(3*H*)-furanone isomeric forms were detected from the reactions of alkyl-aryl or diaryl substituted acetylene reagents. Probably, more extended π electron conjugation of 4-aryl-2(5*H*)-furanones as compared to 4-alkyl-2(5*H*)-furanones facilitated the isomerization of 4-aryl-2(3*H*)-furanones to structure **3**.

The $^1$H NMR spectrum of the product **3ja** revealed the existence of two methyl hydrogen singlets at 2.02 and 2.39 ppm in a respective ratio of 1:2 and an enlarged 5*H* signal. 2-D NMR studies indicated that furanone **3ja** exists as an atropisomeric mixture (entry 10).



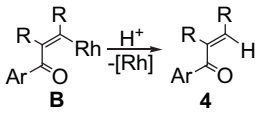

In light of the findings given above, the formed aroylrhodium(I) species **A** should subsequently undergo 1,2-addition to the carbon–carbon triple bond (Scheme 3). Insertion of CO into the resulting β-aroyl alkenylrhodium(I) complex (**B**) followed by a ring closure could form a σ-furanoyl complex (**C**). Displacement of Rh from the cyclic complex and subsequent protonation leads to a 5-aryl-2(3*H*)-furanone molecule (**7**), which then should undergo isomerization to a more stable structure, 5-aryl-2(5*H*)-furanone molecule (**3**).




**Scheme 3.** The proposed mechanisms for the formation of 2(5*H*)-furanone (**3**).

## 2.2. Synthesis of α,β-unsaturated ketones

A prompt protodemetalation of the alkenylrhodium intermediate (**B**), before the insertion of CO, which leads to the product **3** should be responsible for the formation of the α,β-unsaturated ketone (**4**), and hence, we have considered that the presence of an acidic additive and a protic solvent medium would promote the protodemetalation step provided that the catalyst retains its activity.




Under the established optimum conditions, the reaction of diphenylacetylene (1.5 mmol, **1a**) with several arylboronic acids (3 mmol) in the presence of $[Rh(C_2H_4)_2Cl]_2$ complex (3% Rh), $CF_3COOH$ (2 mmol), and water (0.1 mL) as additives in methanol (9.9 mL) solvent, yielded mixtures of both *Z*- and *E*-isomers of the corresponding enones (**4a**), which can be isolated separately by flash chromatography on silica gel along with the following by-products: furanones (**3a**), indenones (**5a**), indanones (**6a**), and a methoxycarbonylated product of diphenylacetylene, methyl 2,3-diphenylacrylate (**8a**) (Table 4).

Isomers of **4a** were identified or estimated by comparing with IR carbonyl frequencies and melting points from the literature. It has been reported that existence of steric inhibition of the enone resonance in *Z*-enones results in the appearance of their carbonyl absorption bands at relatively higher wavenumbers than those of the *E*-isomers.[5]

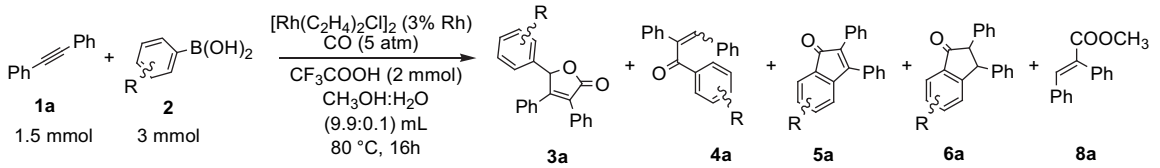
The reaction of arylboronic acid **2a** with alkyne **1a** afforded the isolated products *E*- and *Z*-**4aa** in overall yield of 58% and produced by-products at 30% yield (entry 1). Arylboronic acids, **2b** and **2d**, which have methyl and methoxy groups, respectively, at the *p*-position of the phenyl ring, gave the corresponding hydroacylation products in yields of 70% yields for both the *E*- and *Z*-**4ab** and 76% for both the *E*- and *Z*-**4ad** isomers (entries 2 and 3). Lower amounts of by-products (16 and 11%, respectively) were generated when using these arylboronic acids. Furthermore, a partial deboronylation was also observed with electron-rich boronic acids. The reaction with *m*-tolylboronic acid, **2c**, proceeded to give the corresponding enones (*E*- and *Z*-**4ac**) in an overall yield of 61%, along with formation of the by-products at a yield of 24% (entry 4).

The hydroacylation reaction could also be realized with a moderately electron poor *p*-chlorophenylboronic acid, giving rise to the corresponding enones (*E*- and *Z*-**4ah**) in modest yield (entry 5). However, the reactions involving *o*-tolylboronic or *p*-(trifluoromethyl)phenylboronic acids with alkyne **1a** resulted in correspondingly low enone yields, a marked increase in the amount of side products, and even yielded significant amounts of the corresponding hydroarylation products, triarylacetylene structures. These results indicate that enone formation is responsive to the steric and electronic nature of arylboronic acids. Low reactivity of these reagents should be due to a decreased ability of the corresponding electron poor arylrhodium species to undergo CO insertion at lower CO pressures, because these boronic reagents were shown to successfully yield the furanones when a higher CO pressure was applied under optimum conditions, albeit requiring a higher Rh concentration (see Section 2.1).

As determined by NOE studies,[2f] hydroaroylation proceeded exclusively with *syn*-selectivity for other alkynes, which have only one aryl substituent or none, yielding only the *E*-isomer of the corresponding enones (Table 5).

The carbonylative reaction of 4-octyne (**1b**) with **2a** proceeded with a relatively low isolated yield of *E*-**4ba** (30%) (entry 1). Better yields of *E*-**4bb** and *E*-**4bd** were obtained via the reaction of **1b** with the arylboronic acids **2b** and **2d** at yields of 53% and 57%, respectively (entries 2 and 3). Reactions were also regioselective for those alkynes that had been activated with an ester functionality. The aroyl group was introduced selectively at the β-position with respect to the electron-withdrawing group (entries 4–6). High regioselectivity was also observed with 1-phenylpropyne (**1d**), the aroyl group primarily introduced at the methyl substituted acetylenic carbon (entries 7–9). However, the presence of

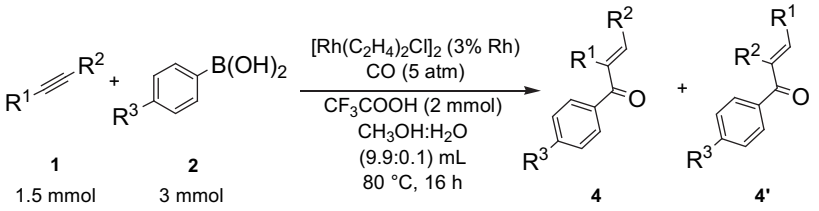
**Table 4**
The synthesis of enones (**4a**) by carbonylative addition of various arylboronic acids (**2**) to alkyne **1a**




| Entry | R | Yield (%) | | | | |
|---|---|---|---|---|---|---|
| | | **4aa**[a] | **3ab**[b] | **5ab**[b] | **6ab**[b] | **8ab**[b] |
| 1 | H | **4aa** (33 *Z*, 25 *E*) | **3aa** (11) | **5aa** (3) | **6aa** (12) | (4) |
| 2 | *p*-$CH_3$ | **4ab** (55 *Z*, 16 *E*) | **3ab** (8) | **5ab** (<1) | **6ab** (5) | (2) |
| 3 | *p*-$OCH_3$ | **4ad** (45 *Z*, 31 *E*) | **3ad** (5) | **5ad** (2) | **6ad** (1) | (3) |
| 4 | *m*-$CH_3$ | **4ac** (29 *Z*, 32 *E*) | **3ac** (7) | **5ac** (3) | **6ac** (9) | (5) |
| 5 | *p*-Cl | **4ah** (20 *Z*, 17 *E*) | **3ah** (4) | **5ah** (3) | **6ah** (5) | (14) |

[a] Isolated yield.
[b] Determined by GC.

**Table 5**
The synthesis of enones (**4**) by carbonylative addition of various arylboronic acids (**2**) to alkynes (**1**)




**1b:** $R^1 = R^2 = n\text{-}C_3H_7$
**1c:** $R^1 = n\text{-}C_3H_7$, $R^2$ = Ph
**1d:** $R^1 = CH_3$, $R^2$ = Ph
**1g:** $R^1 = n\text{-}C_4H_9$, $R^2 = o\text{-}CH_3OC_6H_4$
**1m:** $R^1 = n\text{-}C_4H_9$, $R^2 = CO_2CH_3$
**1n:** $R^1 = CH_3$, $R^2 = CO_2CH_3$
**1o:** $R^1 = n\text{-}C_4H_9$, $R^2$ = 2-$C_5H_5N$
**1p:** $R^1 = n\text{-}C_4H_9$, $R^2$ = 2-thienyl

**2a:** $R^3$ = H
**2b** $R^3 = CH_3$
**2d:** $R^3 = OCH_3$

| Entry | Yield (%) | | | |
|---|---|---|---|---|
| | **1** | **2** | **4**[a] | **4′** |
| 1 | **1b** | **2a** | **4ba** (30) | — |
| 2 | **1b** | **2b** | **4bb** (53) | — |
| 3 | **1b** | **2d** | **4bd** (57) | — |
| 4 | **1m** | **2b** | **4mb** (52) | (2)[b] |
| 5 | **1m** | **2d** | **4md** (64) | (<1)[b] |
| 6 | **1n** | **2d** | **4nd** (54) | (2)[b] |
| 7 | **1d** | **2a** | **4da** (42) | (3)[b] |
| 8 | **1d** | **2b** | **4db** (75) | (2)[b] |
| 9 | **1d** | **2d** | **4dd** (74) | (6)[b] |
| 10 | **1c** | **2d** | **4cd** (41) | (13)[a] |
| 11 | **1g** | **2b** | **4gb** (39) | (7)[b] |
| 12 | **1o** | **2d** | **4od** (16)[c] | (16)[c] |
| 13 | **1p** | **2d** | **4pd** (42) | (10)[b] |

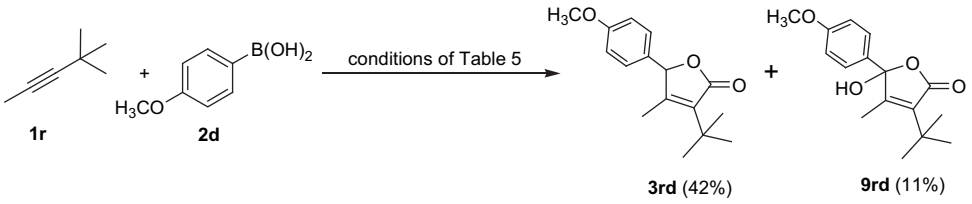
[a] Isolated yield.
[b] Determined by GC.
[c] Isomeric ratio was determined by $^1H$ NMR spectroscopy.

a larger alkyl group on the alkynyl carbon somewhat reduced its regioselectivity, probably due to increased steric hindrance (entry 10). The presence of an electron-donating methoxy group on the *o*-position of 1-phenylpentyne had a modest effect on regioselectivity (entry 11). The overall yield of by-products was nearly 30% for the reaction of **1b** with **2a**, whereas it was less than 10% for other reactions as determined by GC.

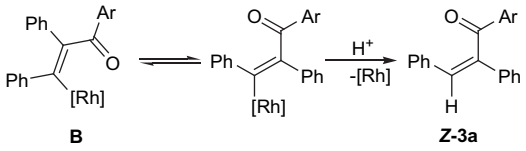
Hydroaroylation reactions were also performed with heteroaryl substituted alkynes. A complex mixture of products was obtained for the reaction of 2-(pent-1-ynyl)pyridine (entry 12). The corresponding enone products were isolated as a 1:1 ratio of regio-isomers, whereas a higher yield and better regioselectivity could be attained when using 2-(pent-1-ynyl)thiophene (entry 13).

Surprisingly, a 2(5*H*)-furanone product (**3rd**) and its hydrated compound **9rd** were isolated from the carbonylative reaction of 4,4-dimethylpent-2-yne (**1r**) with **2d** under the general conditions applied for enone synthesis. The latter product was formed by conversion of an isomer of **3rd** (its structure hitherto not assigned) during silica gel column chromatography and determined by GC–MS. The factors that led alkyne **1r** to its being converted to the furanone structures rather than the expected enone products are not known currently. It must also be noted that the alkyne **1r** had failed to yield furanones under the typical conditions applied for synthesis of the 2(5*H*)-furanones.

Demetalation of vinylrhodium via protonation should play a role in the formation of *E*-enones. A control reaction performed using the pure *E*-isomer of **4ad** under the general reaction




protocols but in the absence of arylboronic acid brought about its isomerization to the *Z*-configuration in a yield of approximately 25%. Although this result shows that *E*-enones formed from diphenylacetylene can isomerize partly during the course of the carbonylative arylation reactions, it cannot account for the *Z*:*E* ratios given in Table 4. Probably the intermediate **B** can also undergo isomerization, which is facilitated by extended conjugation when the alkenyl carbons are substituted with two aryl groups (Scheme 4).




**Scheme 4.** Isomerization of β-aroyl alkenylrhodium(I) complex.

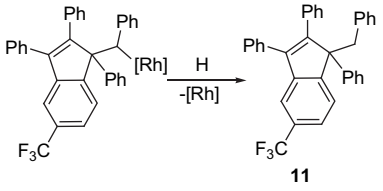
## 2.3. Synthesis of inda(e)nones

The next stage of our efforts in the reactions of alkynes and organoborons under a CO atmosphere was to promote the selective formation of indenone (**5**) and indanone (**6**) (inda(e)nones) products since they are also reagents of high value.

First, optimum conditions were established by thoroughly studying the effect of many variables, such as Rh complexes, solvents, additives, organoboron types, CO pressure, and temperature. Then the scope of the method was examined for a number of alkynes and organoborons. To this end, alkynes (1 mmol), and arylboroxines (1 mmol) were reacted in 10 mL of methanol in the presence of 1.5% of $Rh(cod)_2BF_4$ under 1 atm of CO pressure, and at 120 °C. The results are given in Table 6.

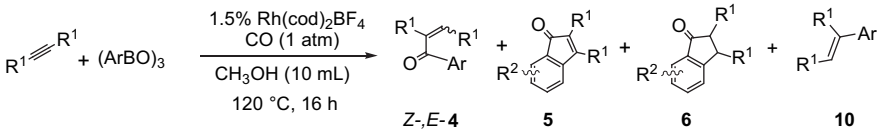
2-enone) were obtained as by-products at an overall yield of 20%.

Lower amounts of inda(e)none products were formed when using either *m*- or *p*-methoxy substituted phenylboroxine reagents. However, nearly 50% of overall inda(e)none products could be achieved with *m*- or *p*-tolylboroxine reagents (entries 2 and 5). The reaction of diphenylacetylene with *p*-$CF_3$ substituted phenylboroxine produced the corresponding indenone and indanone products only at an overall yield of 20% (entry 6). The reaction, however, yielded a significant amount of an indene product **11** (42% yield). The formation of this type of indene structure was shown and well discussed for the rhodium catalyzed reaction of 4-octyne and phenylboroxine by Hayashi et al. previously.[6] However, the reaction conditions and the use of diphenylacetylene in our case led to the hydrodemetalation of a cyclic alkylrhodium intermediate instead of α-hydrogen elimination during the last step of the reaction cycle.




AM1 calculations indicated that the dihedral angles of the ring hydrogens in the *cis*- and *trans*-**6aa** isomers are <1° and ≈124°, respectively. On the basis of coupling constants of the ring hydrogens in the $^1$H NMR spectra, the indanones produced should be in *trans*-isomeric form.

**Table 6**
The synthesis of inda(e)nones by rhodium catalyzed reactions of alkynes with arylboroxines under CO atmosphere[a]

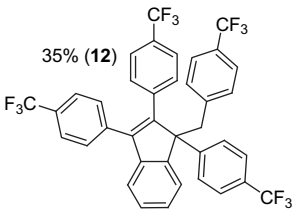



| Entry | $R^1$ | Arylboroxine | Yield (%) | | | |
|---|---|---|---|---|---|---|
| | | | **4**[b] | **5**[b] | **6**[a] | **10**[b] |
| 1 | Ph | $(PhBO)_3$ | **4aa** (10) | **5aa** (7) | **6aa** (43) | **10aa** (9) |
| 2 | Ph | $(p\text{-}OCH_3C_6H_4BO)_3$ | **4ad** (15) | **5ad** (7)[a] | **6ad** (26) | **10ad** (3) |
| 3 | Ph | $(p\text{-}CH_3C_6H_4BO)_3$ | **4ab** (25) | **5ab** (8) | **6ab** (41) | **10ab** (7) |
| 4 | Ph | $(m\text{-}CH_3C_6H_4BO)_3$ | **4ac** (6) | **5ac** (4) | **6ac** (43) | **10ac** (15) |
| 5 | Ph | $(m\text{-}OCH_3C_6H_4BO)_3$ | **4ai** (<1) | **5ai** (<1) | **6ai** (24) | **10ai** (13) |
| 6 | Ph | $(p\text{-}CF_3C_6H_4BO)_3$ | **4af** (2) | **5af** (7) | **6af** (13) | **10af** (7) |
| 7 | *p*-$CH_3O$ | $(PhBO)_3$ | **4sa** (18) | **5sa** (15) | **6sa** (26) | **10sa** (20)[a] |
| 8 | *p*-$CF_3$ | $(PhBO)_3$ | **4ta** (3) | **5ta** (6) | **6ta** (30) | **10ta** (9)[a] |

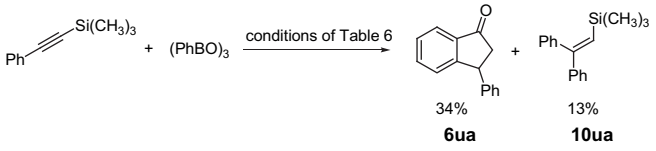
[a] Isolated yield.
[b] GC yield.

The reaction of diphenylacetylene with $(PhBO)_3$ yielded 43% of indanone **6aa** and 7% of indenone **5aa** as isolated products (entry 1). The corresponding *Z*- and *E*-enones, a hydroarylation product (1,1,2-triphenylacetylene), and an intermolecular Pauson Khand reaction product (2,3,4,5-tetraphenylcyclopent-

The presence of an electron-donating methoxy group at the *p*-position on both of the phenyl groups of the alkyne led to an increased amount of indenone product (entry 7). *p*-$CF_3$ substitution on both ends of the diphenylacetylene substrate, however, also rendered the indene (**12**) formation in significant quantity (entry 8).

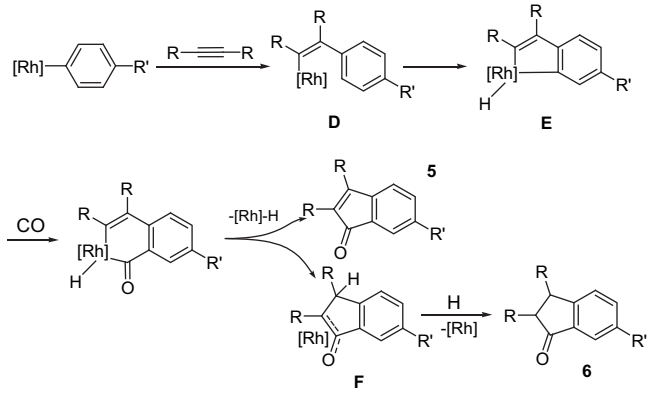



The reaction with trimethyl(2-phenylethynyl)silane proceeded in a regioselective manner, affording a desilylated indanone product (**6ua**) together with a hydrophenylated product (**10ua**).




Under the general conditions of inda(e)none synthesis, the reactions of alkyl or ester functionalized alkynes produced low amounts of inda(e)nones and increased amounts of by-products.

The regioisomeric structures of products **5** and **6** imply that the reaction mechanisms involve a rhodoarylation step, analogous to the carbonylative reaction of *o*-halo arylboronic acids with alkynes, which gives rise to indenones as was reported by Chatani et al.[7] This is unlike the reactions yielding furanones and enones, in which rhodoaroylation of the alkyne is the key step. The reaction mechanisms should involve the formation of an alkenylrhodium intermediate (**D**), which undergoes oxidative addition to a C–H bond on the *o*-position of the aryl ring that is contributed by the arylboroxine reagent to generate the Rh(III) species (**E**) (Scheme 5). The insertion of CO followed by reductive elimination produces **5**. Indanone should form through protonation of intermediate (**F**). The notion that hydrogenation of **5** to **6** was invalidated since a control experiment conducted using the rhodium catalyst in the presence of a preformed indenone produced no hydrogenation product and the starting material was recovered in high yield.




**Scheme 5.** The mechanisms of indenone and indanone formation.

## 3. Conclusions

In summary, we have shown here that internal alkynes and organoborons react under a CO atmosphere in the presence of a rhodium complex to yield 5-aryl-2(5*H*)-furanone, an α,β-unsaturated ketone, and inda(e)none products mainly. The insertion of an in-situ generated aroylrhodium complex to an alkyne was a key step in formation of the former two products, while indanone or indenone formation involved a rhodoarylation step. The product selectivity can be controlled by modifying the experimental conditions.

## 4. Experimental section

### 4.1. General

The alkynes **1e–l**,**o**,**p** were synthesized by the Sonogashira method.[8] The alkynes **1s**,**t** were synthesized as described elsewhere.[9] Arylboroxines were synthesized by azeotropic removal of water from the refluxing benzene solution of arylboronic acids.[10] The products were analyzed by GC and GC–MS (Varian Star 3400CX/Saturn 2000 or HP 6890/5973N) and isolated by column chromatography. High-resolution mass spectral analyses were performed at Dortmund University of Technology Mass Spectrometry Laboratory on a Thermo Electron system. $^{1}$H, $^{13}$C, and $^{19}$F NMR spectra were recorded on a Varian VnmrJ 400 spectrometer. $^{19}$F NMR spectra were recorded in the presence of $CF_3COOH$ as standard. $^{19}$F signal of the acid was set to −76.55 ppm. Melting points were determined using an Electrothermal Melting Point Apparatus 9200. Infrared spectra were obtained using Perkin–Elmer Spectrum 100 by ATR or KBr pellet methods.

### 4.2. Carbonylation reactions

Reaction conditions for the synthesis of **3** and **4** are given elsewhere.[2b,f] Typical reaction conditions for the synthesis of **5** and **6**: a mixture of alkyne (1 mmol), arylboroxine (0.5 mmol), $Rh(cod)_2BF_4$ (1.5 mol% Rh), and 10 mL of degassed $CH_3OH$ (predried over Mg turnings and stored on molecular sieve 4 Å) was added to a 50 mL stainless steel autoclave containing a glass insert tube. Then, the sealed autoclave was evacuated and purged with 5 atm CO twice, successively. Subsequently, the reactor was pressurized to 1 atm with CO and the mixture was stirred magnetically in an oil bath preheated at 120 °C. After cooling, the reaction mixture was recovered with ethyl acetate. Physical and spectrometric characteristics of the samples are reported or given elsewhere.[2b,f]

*4.2.1. 3,4-Diphenyl-5-m-tolylfuran-2(5H)-one (**3ac**).* Hexane/ethyl acetate; yellow paste; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.21 (s, 3H), 6.13 (s, 1H), 6.98–7.41 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 20.3, 82.7, 123.8, 125.7, 127.1, 127.3, 127.5, 127.6, 127.7, 127.8, 128.4, 128.5, 128.8, 129.1, 130.1, 133.6, 137.7, 158.3, 171.5; MS (EI, *m*/*z*): 326 (61, $M^+$), 207 (54), 179 (100), 119 (100); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1746; HRMS (*m*/*z*, $M^+$): 326.1327 (calculated), 326.1303 (found).

*4.2.2. 5-(4-Acetylphenyl)-3,4-diphenylfuran-2(5H)-one (**3ae**).* Hexane/ethyl acetate; yellow paste; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.25 (s, 3H), 6.34 (s, 1H), 7.00–7.90 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 26.9, 83.1, 126.7, 127.1, 127.9 (2C), 128.5 (2C), 128.7, 128.9, 129.1, 129.1, 129.3, 129.6, 130.4, 131.0, 137.9, 159.5, 172.6, 197.9; MS (EI, *m*/*z*): 354 (22, $M^+$), 281 (29), 207 (100), 179 (91); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1748; HRMS (*m*/*z*, $M^+$): 354.1256 (calculated), 354.1241 (found).

*4.2.3. 3,4-Diphenyl-5-o-tolylfuran-2(5H)-one (**3ag**).* Hexane/ethyl acetate; light yellow solid; mp: 140.7–142.6 °C; $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.5 (s, 3H), 6.5 (s, 1H), 7.08–7.5 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 19.5, 81.0, 126.8, 127.8, 127.9, 128.4, 128.8, 129.0, 129.1, 129.5, 129.6, 130.1, 130.3, 131.3, 131.6, 133.1, 137.7, 159.3, 172.7; MS (EI, *m*/*z*): 326 (68, $M^+$), 207 (68), 179 (100), 119 (52), 91 (16); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1741; calculated for $C_{23}H_{18}O_2$: C, 84.6; H, 5.6; found: C, 84.2; H, 5.7.

*4.2.4. 4,5-Diphenyl-3-propylfuran-2(5H)-one (**3ca**) and 3,5-diphenyl-4-propylfuran-2(5H)-one (**3ca′**).* Hexane/ethyl acetate, only the isomer **3ca′** could be enriched by column chromatography; (**3ca**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.97 (t, $J$=7.4 Hz, 3H), 1.61–1.75

(m, 2H), 2.44–2.51 (m, 2H), 6.13 (s, 1H), 7.0–7.39 (m, 10H); MS (EI, *m*/*z*): 278 (58, $M^+$), 260 (46), 25 (33), 173 (82), 105 (100); HRMS (*m*/*z*, $M^+$): 278.1301 (calculated), 278.1300 (found); (**3ca′**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.87 (t, *J*=7.4 Hz, 3H), 1.29–1.52 (m, 2H), 2.08 (ddd, *J*=14.4, 9.5, 5.4 Hz, 1H), 2.58 (ddd, *J*=14.4, 9.6, 6.8 Hz, 1H), 5.85 (s, 1H), 7.17–7.49 (m, 10H); MS (EI, *m*/*z*): 278 (47, $M^+$), 235 (100), 105 (23); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1749; HRMS (*m*/*z*, $M^+$): 278.1301 (calculated), 278.1302 (found).

*4.2.5. 3-Methyl-4,5-diphenylfuran-2(5H)-one (**3da**) and 4-methyl-3,5-diphenylfuran-2(5H)-one (**3da′**).* Hexane/dichloromethane; (**3da**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.15 (d, *J*=1.6, 3H), 6.18 (d, *J*=2.0, 1H), 7.20–7.40 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 10.5, 77.6, 77.3, 76.9, 83.9, 124.4, 127.7, 128.3, 128.9, 129.0, 129.4, 129.9, 131.7, 135.3, 158.6, 174.7; MS (EI, *m*/*z*): 250 (61, $M^+$), 235 (5), 222 (19), 145 (100), 115 (88); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1747; HRMS (*m*/*z*, $M^+$): 250.0994 (calculated), 250.0995 (found); (**3da′**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.00 (s, 3H), 5.74 (s, 1H), 7.25–7.56 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.6, 76.97, 77.3, 77.6, 85.1, 126.7, 127.2, 128.77, 128.83, 129.1, 129.2, 129.3, 129.7, 130.1, 135.01, 160.6, 173.0; MS (EI, *m*/*z*): 250 (69, $M^+$), 235 (23), 207 (38), 145 (41), 117 (100), 115 (86); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1748; HRMS (*m*/*z*, $M^+$): 250.0994 (calculated), 250.0983 (found).

*4.2.6. 4-(4-Acetylphenyl)-3-butyl-5-phenylfuran-2(5H)-one (**3ea**) and 3-(4-acetylphenyl)-4-butyl-5-phenylfuran-2(5H)-one (**3ea′**).* Hexane/dichloromethane; (**3ea**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.91 (t, *J*=7.3, 3H), 7.17 (m, 2H), 6.15 (s, 1H), 2.53 (s, 3H), 2.50 (m, 2H), 1.63 (m, 2H), 1.38 (sext, 2H), 7.28 (m, 5H), 7.92 (d, *J*=8.8, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.0, 22.9, 24.5, 26.8, 31.0, 83.9, 127.5, 128.3, 128.9, 129.2, 129.6, 130.5, 134.8, 136.3, 137.7, 157.9, 173.8, 197.4; MS (EI, *m*/*z*): 334 (20, $M^+$), 289 (31), 247 (13), 185 (14), 105 (33), 43 (100); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1747; HRMS (*m*/*z*, $M^+$): 334.1569 (calculated), 334.1559 (found); (**3ea′**): colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.80 (t, *J*=7.2, 3H), 1.45–1.49 (m, 1H), 1.34–1.38 (m, 1H), 1.21–1.29 (m, 2H), 2.13 (ddd, *J*=5.6, 9.8, 14.4, 1H), 2.56–2.62 (m, 1H), 2.63 (s, 1H), 5.89 (s, 1H), 7.29 (m, 3H), 7.43 (m, 4H), 7.52 (dd, *J*=3.0, 6.8, 1H), 7.61 (m, 3H), 8.03 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.8, 22.8, 26.9, 27.2, 30.2, 84.1, 126.1, 127.3, 128.7, 128.72, 129.5, 129.9, 134.6, 135.0, 137.1, 166.6, 172.6, 197.9; MS (EI, *m*/*z*): 334 (16, $M^+$), 289 (31), 247 (13), 185 (15), 145 (12), 105 (34), 43 (100); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1750; HRMS (*m*/*z*, $M^+$): 334.1569 (calculated), 334.1559 (found).

*4.2.7. 3-Butyl-4-(4-methoxyphenyl)-5-phenylfuran-2(5H)-one (**3fa**) and 4-butyl-3-(4-methoxyphenyl)-5-phenylfuran-2(5H)-one (**3fa′**).* Hexane/ethyl acetate; (**3fa**): white solid; mp: 66.7–70.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.94 (t, *J*=7.4 Hz, 3H), 1.42 (sext, *J*=7.4 Hz, 2H), 1.54–1.73 (m, 2H), 2.51–2.56 (m, 2H), 3.77 (s, 3H), 6.12 (s, 1H), 6.85 (d, *J*=8.8 Hz, 2H), 7.17–7.20 (m, 4H), 7.26–7.29 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 23.1, 24.6, 30.6, 55.5, 83.7, 114.5, 124.0, 127.4, 127.7, 129.0, 129.3, 129.6, 135.7, 158.3, 160.7, 174.7; MS (EI, *m*/*z*): 322 (22, $M^+$), 255 (100), 105 (31); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1726; HRMS (*m*/*z*, $M^+$): 322.1563 (calculated), 322.1567 (found); (**3fa′**): light yellow, solid; mp: 84.1–86.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.83 (t, *J*=7.2 Hz, 3H), 1.20–1.50 (m, 4H), 2.08 (ddd, *J*=14.0, 9.6, 5.4 Hz, 1H), 2.61 (ddd, *J*=15.2, 9.0, 6.2 Hz, 1H), 3.84 (s, 3H), 5.83 (s, 1H), 6.98 (d, *J*=8.8 Hz, 2H), 7.26–7.30 (m, 2H), 7.38–7.42 (m, 3H), 7.46 (d, *J*=8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.9, 22.9, 27.1, 30.2, 55.6, 88.8, 114.2, 122.4, 126.3, 127.4, 129.3, 129.6, 130.5, 135.2, 160.0, 163.6, 173.5; MS (EI, *m*/*z*): 322 (100, $M^+$), 217 (60), 105 (70); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1732; calculated for $C_{21}H_{22}O_3$: C, 78.2; H, 6.0; found: C, 77.8, H, 6.2; HRMS (*m*/*z*, $M^+$): 322.1563 (calculated), 322.1553 (found).

*4.2.8. 3-Butyl-4-(2-methoxyphenyl)-5-phenylfuran-2(5H)-one (**3ga**) and 4-butyl-3-(2-methoxyphenyl)-5-phenylfuran-2(5H)-one (**3ga′**).* Hexane/ethyl acetate; (**3ga**): light yellow solid; mp: 141.5–145.2 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.85 (t, *J*=7.2 Hz, 3H), 1.29 (sext, *J*=7.6 Hz, 2H), 1.45–1.64 (m, 2H), 2.39 (t, *J*=7.6 Hz, 2H), 3.81 (s, 3H), 6.36 (s, 1H), 6.80–7.30 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.9, 22.8, 24.5, 30.2, 55.6, 83.9, 111.2, 120.8, 120.9, 126.9, 128.7, 128.8, 129.2, 130.1, 130.9, 135.7, 155.6, 159.3, 174.6; MS (EI, *m*/*z*): 322 (14, $M^+$), 251 (15), 217 (100), 121 (30); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1746; HRMS (*m*/*z*, $M^+$): 322.1600 (calculated), 322.1600 (found); (**3ga′**): yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.74 (t, *J*=7.2 Hz, 3H), 1.0–1.4 (m, 4H), 1.98 (ddd, *J*=14.5, 9.1, 6 Hz, 1H), 2.31 (ddd, *J*=15.6, 9.2, 6.8 Hz, 1H), 3.85 (s, 3H), 5.9 (s, 1H), 6.9–7.4 (m, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.9, 22.7, 27.6, 30.2, 55.8, 84.3, 111.4, 119.4, 120.8, 125.1, 127.6, 129.2, 129.6, 130.4, 131.2, 135.3, 157.5, 164.4, 173.2; MS (EI, *m*/*z*): 322 (70, $M^+$), 265 (90), 121 (100); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1750; HRMS (*m*/*z*, $M^+$): 322.1600 (calculated), 322.1559 (found).

*4.2.9. 4-(4-Acetylphenyl)-3,5-diphenylfuran-2(5H)-one (**3ha**) and 3-(4-acetylphenyl)-4,5-diphenylfuran-2(5H)-one (**3ha′**).* Hexane/dichloromethane; (**3ha**): light yellow solid; mp: 78.9–80.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.51 (s, 3H), 6.28 (s, 1H), 7.29 (d, *J*=8.8 Hz, 2H), 7.33–7.47 (m, 10H), 7.79 (d, *J*=8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 26.9, 83.8, 127.8, 128.5, 128.8, 128.9, 129.3, 129.5, 129.6, 129.8, 158.3, 172.3, 197.5; MS (EI, *m*/*z*): 354 (71, $M^+$), 281 (29), 249 (51), 207 (77), 176 (27), 105 (57); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1749; calculated for $C_{24}H_{18}O_3$ C, 81.3; H, 5.1; found: C, 81.0; H, 5.3; HRMS (*m*/*z*, $M^+$): 354.1256 (calculated), 354.1241 (found); (**3ha′**): pale yellow solid; mp: 105.2–108.7; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.60 (s, 3H), 6.29 (s, 1H), 7.08 (d, *J*=8.4 Hz, 2H), 7.20–7.34 (m, 8H), 7.59 (d, *J*=8.8 Hz, 2H), 7.93 (d, *J*=8.8 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 26.9, 84.1, 126.1, 128.8, 128.7, 129.1, 129.2, 129.7, 129.9, 130.5, 130.9, 134.6, 134.9, 137.2, 161.1, 172.1, 197.9; MS (EI, *m*/*z*): 354 (69, $M^+$), 281 (46), 249 (60), 221 (100), 207 (97), 105 (52); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1751; calculated for $C_{24}H_{18}O_3$: C, 81.3, H, 5.1, found: C, 80.8; H, 5.4; HRMS: 354.1256 (calculated), 354.1240 (found).

*4.2.10. 4-(4-Methoxyphenyl)-3,5-diphenylfuran-2(5H)-one (**3ia**) and 3-(4-methoxyphenyl)-4,5-diphenylfuran-2(5H)-one (**3ia′**).* Hexane/ethyl acetate; (**3ia**): light yellow solid; mp: 139.3–142.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.73 (s, 3H), 6.24 (s, 1H), 6.70 (d, *J*=4.8 Hz, 2H), 7.09 (d, *J*=8.8 Hz, 2H), 7.30–7.51 (m, 10H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.4, 83.7, 114.3, 123.4, 125.7, 128.0, 128.88, 128.96, 129.34, 129.6, 129.7, 130.3, 130.7, 135.5, 158.8, 161.0, 172.9; MS (EI, *m*/*z*): 342 (100), 237 (60); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1741; HRMS: 342.1247 (calculated), 342.1250 (found); (**3ia′**): light yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.74 (s, 3H), 6.14 (s, 1H), 6.80 (d, *J*=8.8 Hz, 2H), 7.02–7.05 (m, 2H), 7.12–7.25 (m, 8H), 7.37 (d, *J*=9.2, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.5, 83.9, 114.2, 122.2, 126.5, 127.9, 128.5, 128.9, 129.1, 129.5, 129.9, 131.0, 131.7, 135.1, 158.1, 160.2, 173.0; FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1751; MS (EI, *m*/*z*): 342 (100, $M^+$), 237 (22), 165 (24), 105 (35); calculated for $C_{23}H_{18}O_3$: C, 80.7; H, 5.3, found C, 80.0; H, 5.4; HRMS (*m*/*z*, $M^+$): 342.1247 (calculated), 342.1254 (found).

*4.2.11. 3,5-Diphenyl-4-o-tolylfuran-2(5H)-one (**3ja**) and 4,5-diphenyl-3-o-tolylfuran-2(5H)-one (**3ja′**).* Hexane/ethyl acetate; (**3ja**): light yellow solid; mp: 138.0–141.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.02 and 2.39 (s, in a ratio of 1:2, 3H), 6.41 (br s, 1H), 7.10–7.40 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 19.9 ($CH_3$), 20.0 ($CH_3$), 83.9, 126.6, 128.0, 128.5, 128.9, 129.3, 129.7, 130.4, 130.9, 135.6, 159.2; MS (EI, *m*/*z*): 326 (60, $M^+$), 282 (100), 236 (33), 105 (22); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1750; HRMS (*m*/*z*, $M^+$): 326.1301 (calculated), 326.1304 (found); (**3ja′**): yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.70 (s, 3H), 6.11 (s, 1H), 6.9–7.46 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 19.3, 84.3, 126.0, 126.3, 126.4, 128.0, 128.3, 128.36, 128.39, 128.4, 128.6, 128.8, 129.96, 129.06, 129.13, 129.2, 129.6, 129.9, 130.7, 131.0, 134.2, 135.4, 161.6, 172.4; MS (EI, *m*/*z*): 326 (70, $M^+$), 194 (100), 105

(65); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1752; HRMS ($m/z$, $M^+$): 326.1301 (calculated), 326.1295 (found).

*4.2.12. 4-(2-Methoxyphenyl)-3,5-diphenylfuran-2(5H)-one (**3ka**) and 3-(2-methoxyphenyl)-4,5-diphenylfuran-2(5H)-one (**3ka′**).* Hexane/ethyl acetate; (**3ka**): light yellow solid; mp: 67.7–69.1 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.68 (s, 3H), 6.49 (s, 1H), 6.72 (t, $J$=7.6 Hz, 1H), 6.78–6.84 (m, 2H), 7.18–7.30 (m, 9H), 7.44–7.47 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.5, 83.9, 111.5, 120.8, 121.0, 127.2, 127.3, 128.4, 128.7, 128.8, 129.1, 129.2, 130.46, 130.50, 131.3, 135.3, 156.8, 159.5, 172.9; MS (EI, $m/z$): 342 (86, $M^+$), 237 (50), 209 (53), 91 (86); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1744; calculated for $C_{23}H_{18}O_3$: C, 80.7; H, 5.3; found: C, 80.4; H, 5.4; (**3ka′**): light yellow solid; mp: 142.0–145.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.61 (s, 3H), 6.34 (s, 1H), 6.94 (d, $J$=8.4 Hz, 1H), 7.02 (t, $J$=7.6 Hz, 1H), 7.1–7.4 (m, 12H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.6, 83.9, 111.7, 120.0, 121.2, 125.2, 128.08, 128.12, 128.6, 129.2, 129.5, 130.0, 130.6, 131.2, 131.9, 135.8, 157.5, 159.5, 172.8; MS (EI, $m/z$): 342 (100, $M^+$), 297 (14), 237 (29), 105 (13); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1745; calculated for $C_{23}H_{18}O_3$: C, 80.7; H, 5.3; found: C, 80.0; H, 5.2; HRMS ($m/z$, $M^+$): 342.1256 (calculated), 342.1242 (found).

*4.2.13. 4-(4-Acetylphenyl)-3-(2-methoxyphenyl)-5-phenylfuran-2(5H)-one (**3la′**).* Hexane/ethyl acetate; this isomer was isolated in part from the isomeric mixture; yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.60 (s, 3H), 2.48 (m, 3H), 6.36 (s, 1H), 6.92–7.40 (m, 11H), 7.36 (m, 7H), 7.73 (d, $J$=8.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 26.5, 55.3, 83.6, 111.4, 119.1, 121.1, 126.5, 127.8, 128.0, 128.1, 128.2, 129.1, 129.5, 130.8, 130.9, 135.0, 136.2, 137.4, 157.1, 158.0, 172.1, 198.2; MS (EI, $m/z$): 385 (68, $M^+$), 280 (100), 237 (40), 105 (74); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1748; HRMS ($m/z$, $M^+$): 384.1356 (calculated), 384.1355 (found).

*4.2.14. 3-tert-Butyl-5-(4-methoxyphenyl)-4-methylfuran-2(5H)-one (**3rd**) and 3-tert-butyl-5-hydroxy-5-(4-methoxyphenyl)-4-methylfuran-2(5H)-one (**9rd**).* Hexane/ethyl acetate; (**3rd**): beige solid; mp: 97–102 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.39 (s, 9H), 1.91 (s, 3H), 3.81 (s, 3H), 5.37 (s, 1H), 6.89 (d, $J$=9.2, 2H), 7.11 (d, $J$=9.2, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.1, 29.3, 33.3, 55.3, 84.2, 114.3, 127.1, 128.5, 156.2, 160.3, 173.3; MS (EI, $m/z$): 260 (72, $M^+$), 245 (30), 135 (100), 108 (71); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1740; HRMS ($m/z$, $M^+$): 260.1407 (calculated), 260.1412 (found); (**9rd**): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 1.34 (s, 9H), 1.95 (s, 3H), 3.56 (s, 1H), 3.81 (s, 3H), 6.89 (d, $J$=8.8, 2H), 7.34 (d, $J$=8.8, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$:12.3, 29.3, 33.2, 55.3, 104.3, 113.9, 127.1, 129.2, 133.1, 156.8, 160.2, 171.4; MS (EI, $m/z$): 276 (76, $M^+$), 258 (9), 243 (17), 231 (100), 220 (26); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1763; HRMS ($m/z$, $M^+$): 276.13656 (calculated), 276.1351 (found).

*4.2.15. (E,Z)-1-(4-Chlorophenyl)-2,3-diphenylprop-2-en-1-one (**4ah**).* Hexane/ethyl acetate; (*E*-**4ah**): yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.05–7.45 (m, 13H), 7.78 (d, $J$=8.4, 2H); MS (EI, $m/z$): 318 (100, $M^+$), 283 (27), 178 (55), 139 (52), 111 (25), 75 (13), 50 (10); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1645; HRMS ($m/z$, $M^+$): 318.0806 (calculated), 318.0804 (found); (*Z*-**4ah**): yellow paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.14–7.45 (m, 13H), 7.91 (d, $J$=10.4, 2H); MS (EI, $m/z$): 318 (100, $M^+$), 283 (48), 178 (75), 139 (82), 111 (51), 75 (35), 50 (25); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1665; HRMS ($m/z$, $M^+$): 318.0806 (calculated), 318.0805 (found).

*4.2.16. (E)-2-Methyl-3-phenyl-1-p-tolylprop-2-en-1-one (**4db**).* Hexane/ethyl acetate; yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.26 (d, $J$=1.6 Hz, 3H), 2.42 (s, 3H), 7.15 (d, $J$=1.6 Hz, 1H), 7.27 (d, $J$=8.0 Hz, 2H), 7.30–7.42 (m, 5H), 7.68 (d, $J$=8.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.6, 21.6, 128.5, 128.9, 129.7, 129.8, 135.6, 135.9, 137.0, 141.3, 142.4, 199.2; MS (EI, $m/z$): 236 (100, $M^+$), 219 (12), 119 (25); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1642; HRMS ($m/z$, $M^+$): 236.1196 (calculated), 236.1194 (found).

*4.2.17. (E)-2-(2-Methoxybenzylidene)-1-p-tolylhexan-1-one (**4gb**).* Hexane/ethyl acetate; yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.87 (t, $J$=7.2 Hz, 3H), 1.35 (sext, $J$=7.6 Hz, 2H), 1.49 (pent, $J$=7.6 Hz, 2 H), 2.40 (s, 3H), 2.65 (t, $J$=7.2 Hz, 2H), 3.76 (s, 3H), 6.87 (d, $J$=8.0 Hz, 1H), 6.98 (t, $J$=7.6 Hz, 1H), 7.18 (s, 1H), 7.24 (d, $J$=8.0 Hz, 2H), 7.30 (t, $J$=7.6 Hz, 1H), 7.36 (d, $J$=7.6 Hz, 1H), 7.78 (d, $J$=8.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.9, 21.6, 22.9, 27.8, 30.9, 55.4, 110.5, 120.2, 125.1, 128.8, 129.5, 129.6, 130.1, 135.9, 136.0, 141.9, 142.6, 157.3, 199.0; MS (EI, $m/z$): 308 (57, $M^+$), 277 (100), 119 (75); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1656; HRMS ($m/z$, $M^+$): 308.1771 (calculated), 308.1775 (found).

*4.2.18. (E)-Methyl 4-(4-p-tolyl)-3-butyl-4-oxobut-2-enoate (**4mb**).* Hexane/ethyl acetate, yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.9 (t, $J$=7.4 Hz, 3H), 1.36–1.51 (m, 4H), 2.40 (s, 3H), 2.98 (t, $J$=7.8 Hz, 2H), 3.76 (s, 3H), 6.0 (s, 1H), 7.27 (d, $J$=8.0 Hz, 2H), (d, $J$=8.0 Hz, 2H), 7.73 (d, $J$=8.0 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 13.8, 21.7, 22.9, 28.9, 30.5, 51.5, 122.9, 129.3, 130.0, 133.5, 144.3, 157.5, 166.1, 197.6; MS (EI, $m/z$): 260 (25, $M^+$), 245 (29), 229 (65), 214 (46), 119 (100); FTIR (ATR) $\nu$ ($cm^{-1}$): 1659 (CO), 1724 ($COOCH_3$); HRMS ($m/z$, $M^+$): 260.1407 (calculated), 260.1406 (found).

*4.2.19. (E)-1-(4-Methoxyphenyl)-2-((thiophen-2-yl)methylene)-hexan-1-one (**4pd**).* Hexane/ethyl acetate; yellow oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 0.96 (t, $J$=7.2 Hz, 3H), 1.48 (pent, $J$=6.8 Hz, 2H), 1.53–1.61 (m, 2H), 2.86 (t, $J$=7.2 Hz, 2H), 3.88 (s, 3H), 6.95 (d, $J$=9.2 Hz, 2H), 7.08 (dd, $J$=3.6, 5.2 Hz 1H), 7.15 (d, $J$=3.6 Hz, 1H), 7.19 (s, 1H), 7.47 (d, $J$=5.2 Hz, 1H), 7.75 (d, $J$=9.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 14.0, 23.2, 28.6, 30.4, 55.4, 113.6, 127.3, 128.9, 131.6, 131.8, 138.6, 139.2, 162.7, 197.8; MS (EI, $m/z$): 300 (62, $M^+$), 269 (19), 135 (100), 203 (16); FTIR (ATR) $\nu$ ($cm^{-1}$): 1636; HRMS ($m/z$, $M^+$): 300.1179 (calculated), 300.1178 (found).

*4.2.20. 2,3-Dihydro-2,3-diphenylinden-1-one (**6aa**).* Hexane/ethyl acetate; orange paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.81 (d, $J$=4.8 Hz, 1H), 4.57 (d, $J$=4.8 Hz, 1H), 7.07–7.13 (m, 4H), 7.23–7.82 (m, 7H), 7.48 (t, $J$=7.4 Hz, 1H), 7.64 (dt, $J$=1.0, 7.6 Hz, 1H), 7.89 (d, $J$=8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.1, 64.9, 124.3, 126.9, 127.4, 127.4, 128.1, 128.5, 128.6, 129.1, 129.2, 135.7, 136.4, 138.8, 142.8 156.4, 205.5; MS (EI, $m/z$): 284 (100, $M^+$), 206 (20), 178 (25); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1711; HRMS ($m/z$, $M^+$): 284.1196 (calculated), 284.1206 (found).

*4.2.21. 2,3-Dihydro-6-methoxy-2,3-diphenylinden-1-one (**6ad**) and 6-methoxy-2,3-diphenyl-1H-inden-1-one (**5ad**).* Hexane/ethyl acetate; (**6ad**): white solid; mp: 137.1–146.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.80 (d, $J$=4.4 Hz, 1H), 3.88 (s, 3H), 4.5 (d, $J$=4.4 Hz, 1H), 7.06–7.34 (m, 14H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 54.5, 56.0, 65.6, 105.2, 125.1, 127.36, 127.43, 127.7. 128.0, 128.6, 129.1, 129.1, 137.7, 138.9, 143.0, 149.3, 160.3, 205.5; MS (EI, $m/z$): 314 (100, $M^+$), 223 (10); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1698; HRMS ($m/z$, $M^+$): 314.1301 (calculated), 314.1290 (found); (**5ad**): red paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.85 (s, 3H), 6.80 (dd, $J$=2.2 Hz, $J$=8.0 Hz, 1H), 7.04 (d, $J$=8.0, 1H), 7.17–7.26 (m, 6H), 7.34–7.43 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.8, 110.6, 116.3, 122.2, 127.5, 128.0, 128.4, 128.7, 129.3, 129.8, 131.0, 131.4, 133.0, 136.9, 156.4, 161.1, 196.2; MS (EI, $m/z$): 312 ($M^+$); 270.

*4.2.22. 2,3-Dihydro-6-methyl-2,3-diphenylinden-1-one (**6ab**).* Hexane/ethyl acetate; white solid; mp: 67.4–74.8 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.46 (s, 3H), 3.79 (d, $J$=4.8 Hz, 1H), 4.53 (d, $J$=4.8 Hz, 1H), 7.05–7.11 (m, 4H), 7.19 (d, $J$=7.6 Hz, 1H), 7.23–7.33 (m, 6H), 7.46 (dd, $J$=1.4 Hz, $J$=7.8, 1H), 7.69 (s, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 21.4,

54.8, 65.2, 124.2, 126.6, 127.3, 127.4, 128.1, 128.6, 129.02, 129.06, 136.6, 136.9, 138.6, 139.0, 143.0, 153.9, 205.6; MS (EI, *m*/*z*): 298 (100, $M^+$), 208 (10); HRMS (*m*/*z*, $M^+$): 298.1352 (calculated), 298.1341 (found).

*4.2.23. 2,3-Dihydro-5-methyl-2,3-diphenylinden-1-one (**6ac**).* Hexane/ethyl acetate; pale yellow solid; mp: 113.9–117.5 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.40 (s, 3H), 3.79 (d, *J*=4.8 Hz, 1H), 4.51 (d, *J*=4.8 Hz, 1H), 7.06–7.12 (m, 5H), 7.2–7.34 (m, 7H), 7.78 (d, *J*=7.6 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 22.2, 54.8, 64.7, 123.9, 126.9, 127.1, 127.9, 123.0, 128.8, 128.9 129.6, 134.0, 138.8, 142.7, 146.8, 156.7; MS (EI, *m*/*z*): 298 (100, $M^+$), 221 (40), 178 (23); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1696; HRMS (*m*/*z*, $M^+$): 298.1352 (calculated), 298.1340 (found).

*4.2.24. 2,3-Dihydro-5-methoxy-2,3-diphenylinden-1-one (**6ai**).* Hexane/ethyl acetate; white solid; mp: 139–142 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.78 (d, *J*=4.8 Hz, 1H), 3.80 (s, 3H), 4.49 (d, *J*=4.8 Hz, 1H), 6.69 (d, *J*=1.2 Hz, 1H), 7.0 (dd, *J*=8.4, 2.4 Hz, 1H), 7.09 (d, *J*=7.6 Hz, 4H), 7.22–7.34 (m, 6H), 7.82 (d, *J*=8.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.0, 55.8, 64.8, 109.6, 116.5, 125.8, 127.1, 127.2, 127.9, 128.3, 128.8, 128.9, 129.6, 139.0, 142.6, 159.2, 165.9, 203.4; MS (EI, *m*/*z*): 314 (100, $M^+$), 238 (30), 165 (20); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1702; HRMS (*m*/*z*, $M^+$): 314.1301 (calculated), 314.1287 (found).

*4.2.25. 2,3-Dihydro-2,3-bis(4-methoxyphenyl)inden-1-one (**6sa**) and 2,3-bis(4-methoxyphenyl)-1H-inden-1-one (**5sa**).* Hexane/ethyl acetate; (**6sa**): orange-red solid; mp: 115.0–118.9; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.71 (d, *J*=4.8 Hz, 1H), 3.78 (s, 3H), 3.79 (s, 3H), 4.47 (d, *J*=4.8 Hz, 1H), 6.83 (d, *J*=2.0 Hz, 2H), 6.86 (d, *J*=2.8 Hz, 2H), 7.0 (d, *J*=4.8 Hz, 2H), 7.02 (d, *J*=4.4 Hz, 2H), 7.29 (d, *J*=8.0 Hz, 1H), 7.46 (t, *J*=7.4 Hz, 1H), 7.62 (t, *J*=7.4 Hz, 1H), 7.86 (d, *J*=7.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 54.3, 55.3, 114.3, 123.9, 126.6, 128.2, 128.9, 129.4, 134.5, 135.3, 136.1; 156.2, 158.7, 205.7; FTIR (KBr) $\nu$ ($cm^{-1}$) CO: 1709; MS (EI, *m*/*z*): 344 (97, $M^+$), 237 (100), 208 (40), 166 (40), 122 (35), 73 (63); HRMS (*m*/*z*, $M^+$): 344.1407 (calculated), 344.1406 (found); (**5sa**): red paste; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.79 (s, 3H), 3.85 (s, 3H), 6.82 (d, *J*=9.2 Hz, 2H), 6.94 (d, *J*=8.8 Hz, 2H), 7.16 (d, *J*=7.2 Hz, 1H), 7.21–7.28 (m, 3H), 7.31–7.37 (m, 3H), 7.55 (d, *J*=6.8 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 55.1, 55.2, 113.7, 114.2, 120.9, 122.7, 123.4, 125.1, 128.6, 130.2, 131.0, 131.2, 133.2, 134.9, 145.5, 153.8, 159.1, 160.3, 196.9; MS (EI, *m*/*z*): 342 (100, $M^+$); HRMS (*m*/*z*, $M^+$): 342.1250 (calculated), 342.1244 (found).

*4.2.26. 6-(Trifluoromethyl)-2,3-dihydro-2,3-diphenylinden-1-one (**6af**) and 1-benzyl-5-(trifluoromethyl)-1,2,3-triphenyl-1H-indene (**11**).* Hexane; (**6af**) pale yellow solid; mp: 81.6–83.3 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.89 (d, *J*=5.2 Hz, 1H), 4.62 (d, *J*=5.2 Hz, 1H), 7.06–7.11 (m, 4H), 7.28–7.37 (m, 6H), 7.45 (d, *J*=7.6 Hz, 1H), 7.80 (d, *J*=8.0 Hz, 1H), 8.16 (s, 1H); FTIR (KBr) $\nu$ ($cm^{-1}$) CO: 1725; MS (EI, *m*/*z*): 352 (100, $M^+$), 274 (28), 246 (12), 205 (14); HRMS (*m*/*z*, $M^+$): 352.1075 (calculated), 352.1070 (found); $^{19}$F NMR (375.9 MHz, $CDCl_3$) $\delta$: −63.5; (**11**): white solid; mp: 138–140 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.57 (d, *J*=12.4 Hz, 1H), 3.96 (d, *J*=12.4 Hz, 1H), 6.35 (d, *J*=7.2 Hz, 2H), 6.74 (d, *J*=8.4 Hz, 2H), 6.89 (t, *J*=7.6 Hz, 2H), 6.98–7.05 (m, 6H), 7.2 (s, 1H), 7.28–7.46 (10H); MS (EI, *m*/*z*): 502 (4, $M^+$), 483 (6), 411 (100), 334 (25), 91 (27); HRMS (*m*/*z*, $M^+$): 502.1908 (calculated), 502.1890 (found). $^{19}$F NMR (375.9 MHz, $CDCl_3$) $\delta$: −63.4.

*4.2.27. 2,3-Bis(4-(trifluoromethyl)phenyl)-2,3-dihydroinden-1-one (**6ta**) and 1-(4-(trifluoromethyl)benzyl)-1,2,3-tris(4-(trifluoromethyl)phenyl)-1H-indene (**12**).* Hexane/ethyl acetate; (**6ta**): light yellow solid; mp: 135.6–136.9 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 3.84 (d, *J*=5.6 Hz, 1H), 4.63 (d, *J*=5.6 Hz, 1H), 7.20–7.33 (m, 5H), 7.52–7.72 (m, 6H), 7.93 (d, *J*=7.6 Hz, 1H); MS (EI, *m*/*z*): 420 (100, $M^+$), 401 (15), 351 (10), 275 (30), 261 (18); FTIR (KBr) $\nu$ ($cm^{-1}$) CO: 1705; HRMS (*m*/*z*, $M^+$): 420.0943 (calculated), 420.0934 (found); $^{19}$F NMR (375.9 MHz, $CDCl_3$) $\delta$: −63.7, −63.5; (**12**): white solid; mp: 229–234 °C; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$: 3.56 (d, *J*=12.4 Hz, 1H), 3.98 (d, *J*=12.8 Hz, 1H), 6.36 (d, *J*=7.6 Hz, 2H), 6.69 (d, *J*=8.0 Hz, 2H), 6.90–6.94 (m, 1H), 7.00 (d, *J*=8.0 Hz, 2H), 7.10 (d, *J*=8.0 Hz, 2H), 7.17–7.27 (m, 5H), 7.45–7.60 (m, 6H); MS (EI, *m*/*z*): 706 (8, $M^+$), 687 (5), 547 (100), 401 (12); HRMS (*m*/*z*, $M^+$): 706.153 (calculated), 706.143 (found). $^{19}$F NMR (375.9 MHz, $CD_2Cl_2$) $\delta$: −63.5, −63.3, −63.2, −63.17.

*4.2.28. 2,3-Dihydro-3-phenylinden-1-one (**6ua**).* Hexane/ethyl acetate; yellow solid; mp: 72.8–75.7 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 2.69 (dd, *J*=19.2, 4.0 Hz, 1H), 3.23 (dd, *J*=19.2, 8.0 Hz, 1H), 5.57 (dd, *J*=8.0, 3.6 Hz, 1H), 7.10–7.14 (m, 2H), 7.20–7.33 (m, 4H), 7.41 (t, *J*=7.4 Hz, 1H), 7.81 (d, *J*=8.0 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 44.4, 46.8, 123.4, 126.9, 127.0, 127.6, 127.9, 128.9, 135.1, 136.7, 143.7, 158.0, 206.1; MS (EI, *m*/*z*): 208 (100, $M^+$), 193 (13), 178 (25), 165 (20), 130 (10); FTIR (ATR) $\nu$ ($cm^{-1}$) CO: 1705; HRMS (*m*/*z*, $M^+$): 208.0883 (calculated), 208.0874 (found).

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