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An Aqueous Mediated Approach for One-pot Regioselective Synthesis of Indenones via Palladium Catalyzed Annulation

Karu Ramesh and Gedu Satyanarayana*

Abstract: A one-pot synthesis of indenones, was presented. The reaction involved palladium catalyzed annulation of *ortho*-halobenzaldehydes with internal alkynes. Notably, this process was successful in water as the sole green solvent. Significantly, unlike earlier reports, this protocol showed excellent regioselectivity with unsymmetrical alkylarylacetylenes. Further, the strategy was extended to a one-pot synthesis of neo-lignan.

Introduction

Sustainable chemical transformations are desirable in organic synthesis.[1] In particular, use of less toxic solvents, to some extent, could contribute to the green chemistry.[2] Therefore, the development of one-pot synthetic strategies with the generation of little waste and under non-hazardous conditions are vital.[3] In this context, water is an ideal green solvent on the earth,[4] as it is most abundant, renewable, non-flammable and non-toxic.

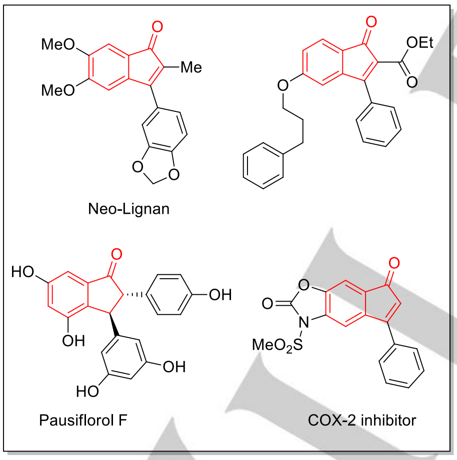

Figure 1: Compounds containing an indenone skeleton.

Indenones are important carbocycles that constitute natural products and drugs. Also, they have been found to have useful applications in pharmacology and material chemistry.[5] As a result, much attention was drawn from the synthetic community and led to the development of notable synthetic processes for their preparation.[6] Most of the classical approaches established were mainly based on intramolecular Friedel-Crafts acylation and Grignard addition followed by dehydration sequence of 2-substituted-1,3-indandiones.[7] Primarily, annulations of alkynes with *ortho*-functionalized arenes under transition metal catalysis have been turned out to be the most efficient strategies leading to indenones.[8] Recently, functional group assisting transition-metal-catalyzed *ortho*-C−H activations, provided, a direct access to indenones with alkynes.[9] An intramolecular addition[10] and radically initiated cyclizations[11] have also been established for the construction of various indenone motifs. However, these developed methods often made use of expensive reagents, toxic organic solvents, and toxic CO gas as carbonylating agent.[12] Therefore, still, there is a room to explore and to develop chemical strategies to furnish indenones, particularly, using simple catalytic systems and non-toxic solvent(s).

With this background, we envisioned that it would be feasible to accomplish indenones using water as the green solvent, in the presence of simple palladium catalyst and with the support of phase transfer catalyst. In continuation of our interests on transition-metal catalyzed domino transformations,[13] very recently, we have reported a domino one-pot synthesis of indenones using [Pd]-catalyzed direct acylation and intramolecular aldol condensation sequence.[14] Inspired by these results, herein, we describe [Pd]-catalyzed one-pot synthesis of indenones using water as the sole green solvent. Gratifyingly, unlike most of the earlier reports, present strategy showed excellent regioselectivity, particularly, with unsymmetrical alkylarylacetylenes. Siginificantly, the synthetic utility of this protocol was established by a one-pot synthesis of natural product neo-lignan.

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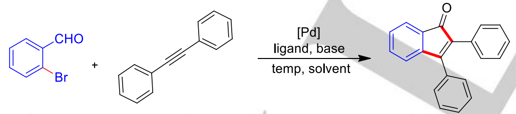
Results and Discussion

To begin with, *ortho*-bromobenzaldehyde **1a** was chosen to study the annulation with diphenylacetylene **2a**, in the presence of a [Pd]-catalyst and water as a solvent. Thus, the reaction was performed with $Pd(OAc)_2$ (5 mol%), L-proline (20 mol%), base Na_2CO_3 (4 equiv) and additive TBAI (1 equiv) at 100 °C for 36 h. As anticipated, the desired indenone **3aa** was obtained, albeit in moderate yield (Table 1, entry 1). When the temperature raised to 140 °C, yield was improved to 60% (Table 1, entry 2). With the base K_2CO_3 (4 equiv) and at 100 °C for 36 h, furnished the product **3aa**, in moderate yield (Table 1, entry 3). Gratifyingly, the reaction at elevated temperature 140 °C, afforded **3aa**, in very good yield (Table 1, entry 4). While in the presence of other additives, like tetrabutylammonium chloride (TBAC) and tetrabutylammonium bromide (TBAB), indenone **3aa** was formed in 29% and 64% yields, respectively (Table 1, entries 5 & 6). Whereas the reaction either without additive/base (Table 1, entry 7) and without additive and with base (Table 1, entry 8), gave poor yields of **3aa**. Thus, reveals the importance of both additive (phase transfer catalyst) and base to drive the reaction. On the other hand, in the presence of bases, such as $NaHCO_3$ and Li_2CO_3, no progress was observed (Table 1, entries 9 & 10). However, the reaction with 1,10-phenanthroline ligand and the base K_2CO_3 (4 equiv) at 140 and 120 °C, gave the product **3aa**, in 20% and 18% yields, respectively (Table 1, entries 11 & 12). Almost no progress was noticed with the ligand PCy_3 (Table 1, entry 13). While the reaction without the ligand L-proline, gave only 28% of **3aa** (Table 1, entry 14), hence, ascertain the need of ligand.

Table 1. Optimization studies for the formation of 2,3-diarylindenones **3aa**[a,b,c,d,e]



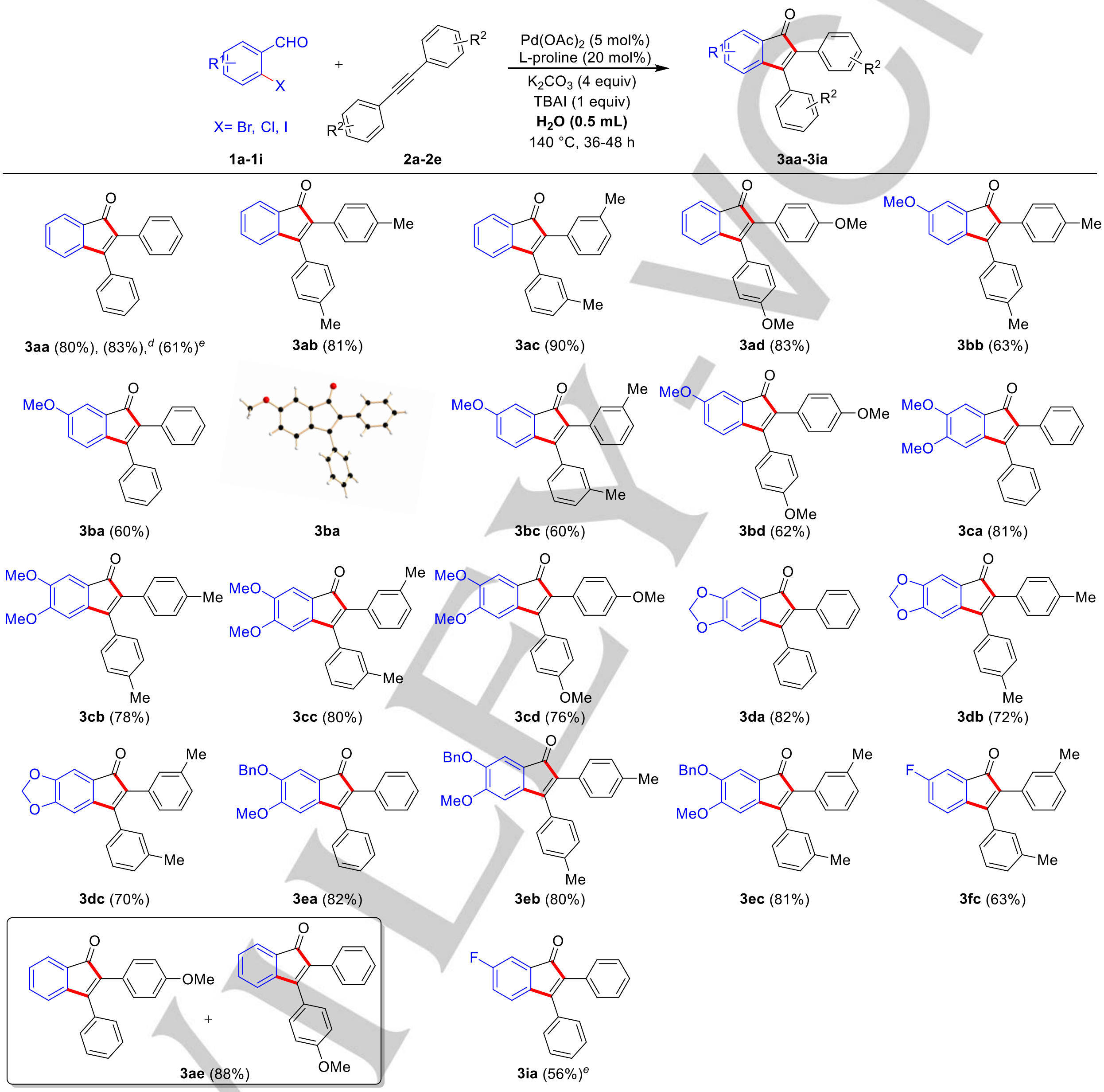
entry	ligand	additive	base	temp (°C)	time (h)	yield **3aa**[b] (%)
1	L-proline	TBAI	Na_2CO_3	100	36	40
2	L-proline	TBAI	Na_2CO_3	140	36	60
3	L-Proline	TBAI	K_2CO_3	100	72	40 + --[c]
4	**L-Proline**	**TBAI**	$\mathbf{K_2CO_3}$	**140**	**36**	**80**
5	L-Proline	TBACMH	K_2CO_3	140	36	29
6	L-Proline	TBAB	K_2CO_3	140	36	64
7	L-proline	--	--	100	42	trace
8	L-proline	--	K_2CO_3	140	72	35
9	L-Proline	TBAI	$NaHCO_3$	100	42	--[c]
10	L-Proline	TBAI	Li_2CO_3	100	48	--[c]
11	1,10-phen	TBAI	K_2CO_3	140	36	20
12	1,10-phen	TBAI	K_2CO_3	120	36	18
13	$P(Cy)_3$	TBAI	K_2CO_3	100	36	trace
14	--	TBAI	K_2CO_3	140	72	28

[a]Reaction conditions: By using 46.2 mg (0.25 mmol) of *ortho*-halobenzaldehyde **1a**, 111.2 mg (0.62 mmol) of 1,2-diphenylethyne **2a**, base (1 mmol, 4 equiv), $Pd(OAc)_2$ (5 mol%), ligand (20 mol%), additive (1 equiv) and solvent (0.5 mL). [b]Yields in the parentheses are isolated yields of product **3aa** with respect to the *ortho*-bromobenzaldehyde **1a**. [c]Starting material recovered. [d]Tetrabutylammonium chloride (TBAC); tetrabutylammonium bromide (TBAB); tetrabutylammonium iodide (TBAI).

With the above optimized conditions [i.e. **1a** (1.0 equiv), **2a** (2.5 equiv), $Pd(OAc)_2$ (5 mol %)/L-proline (20 mol%), TBAI (1 equiv) and K_2CO_3 (4 equiv) at 140 °C for 36 h (Table 1, entry 3)], to check the scope and compatibility of the strategy, annulation reaction was performed between different *ortho*-bromobenzldehydes **1a-1i** and diarylacetylenes **2a-2e**. To our delight, the reaction showed good substrate scope and furnished the indenone products **3aa-3ia**, in fair to excellent yields (Table 2). The reaction was amenable to various functional groups ranging from simple to electron donating substituents on the aromatic ring of *ortho*-bromobenzaldehydes **3aa-3ia**. Also, amenable with electron deactivating F group on the benzaldehyde **1f** (Table 2, **3fc**). In addition, the reaction was compatible with simple phenyl, tolyl and anisyl moieties of symmetric internal acetylenes. Notably, the reaction was smooth with *ortho*-iodo-/chloro-benzaldehyde (**1g** & **1h**) and afforded the indenone **3aa**, in 83% and 61% yields, respectively (Table 2). The reaction with other *ortho*-chlorobenzaldehyde (i.e. 2-chloro-5-fluorobenzaldehyde **1i**) was also feasible and delivered the expected product **3ia** in 56% yield. While the reaction with unsymmetrical biaryl acetylenes gave almost 1:1 regioisomeric mixture of indenones **3ae**. Further, to the spectroscopic evidence, the chemical structure of the indenones has been further confirmed by the single crystal X-ray diffraction analysis of **3ba** (Table 2) (see; supporting information for X-ray data [CCDC 1820880]).

To further demonstrate the utility of this protocol, next, it was planned for the synthesis of indenones with unsymmetrical alkylaryl acetylenes. Therefore, the reaction was conducted between *ortho*-bromobenzaldehydes **1a** and unsymmetrical alkylaryl acetylenes **2f**, under standard conditions (Table 3, entry 1). However, the reaction was not smooth, i.e., neither recovered the starting material nor the product was obtained. Then, the reaction was performed at a lower temperature (100 °C) instead of 140 °C (Table 3, entry 2). Significantly, furnished a single regioisomeric indenone **3fa**, in good yield. Further, to improve the yield as well as to understand the reason for regioselectivity, the reaction was attempted under different conditions. With other ligands, PPh_3 and BINAP gave single regioisomeric product **3fa** in 10% and 48% yields, respectively (Table 3, entries 3 & 4). While all other variants turned out to be inferior (Table 3, entries 5 to 8).

Table 2. Synthesis of diarylindenones **3aa-3ia** with substituted *ortho*-halobenzaldehyde **1a-1i** and aromatic acetylenes **2a-2e**. [a,b,c,d,e]



1a-1i **2a-2e** **3aa-3ia**

3aa (80%), (83%),[d] (61%)[e] **3ab** (81%) **3ac** (90%) **3ad** (83%) **3bb** (63%)

3ba (60%) **3ba** **3bc** (60%) **3bd** (62%) **3ca** (81%)

3cb (78%) **3cc** (80%) **3cd** (76%) **3da** (82%) **3db** (72%)

3dc (70%) **3ea** (82%) **3eb** (80%) **3ec** (81%) **3fc** (63%)

3ae (88%) **3ia** (56%)[e]

[a] Reaction conditions: substituted *ortho*-halobenzaldehydes **1a-1i** (0.25 mmol), diaryl acetylenes **2a-2e** (0.62 mmol), of $Pd(OAc)_2$ (5 mol%), L-proline (20 mol%), TBAI (1 equiv), K_2CO_3 (4 equiv), H_2O (0.5 mL), 140 °C, 24 to 36 h. [b] Yields in the parentheses are isolated yields products **3aa-3ia** with respect to the *ortho*-bromobenzaldehydes **1a-1i**. [c] The first alphabet of products **3aa-3ia** refers to the *ortho*-halobenzaldehydes, while the second letter indicates the alkynes. [d] Yield of the product **3aa** when *ortho*-iodobenzaldehyde used. [e] Yield of the product **3aa** when *ortho*-chlorobenzaldehydes **1a** and **1i** were used.

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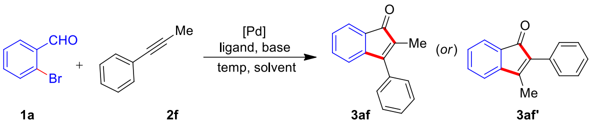
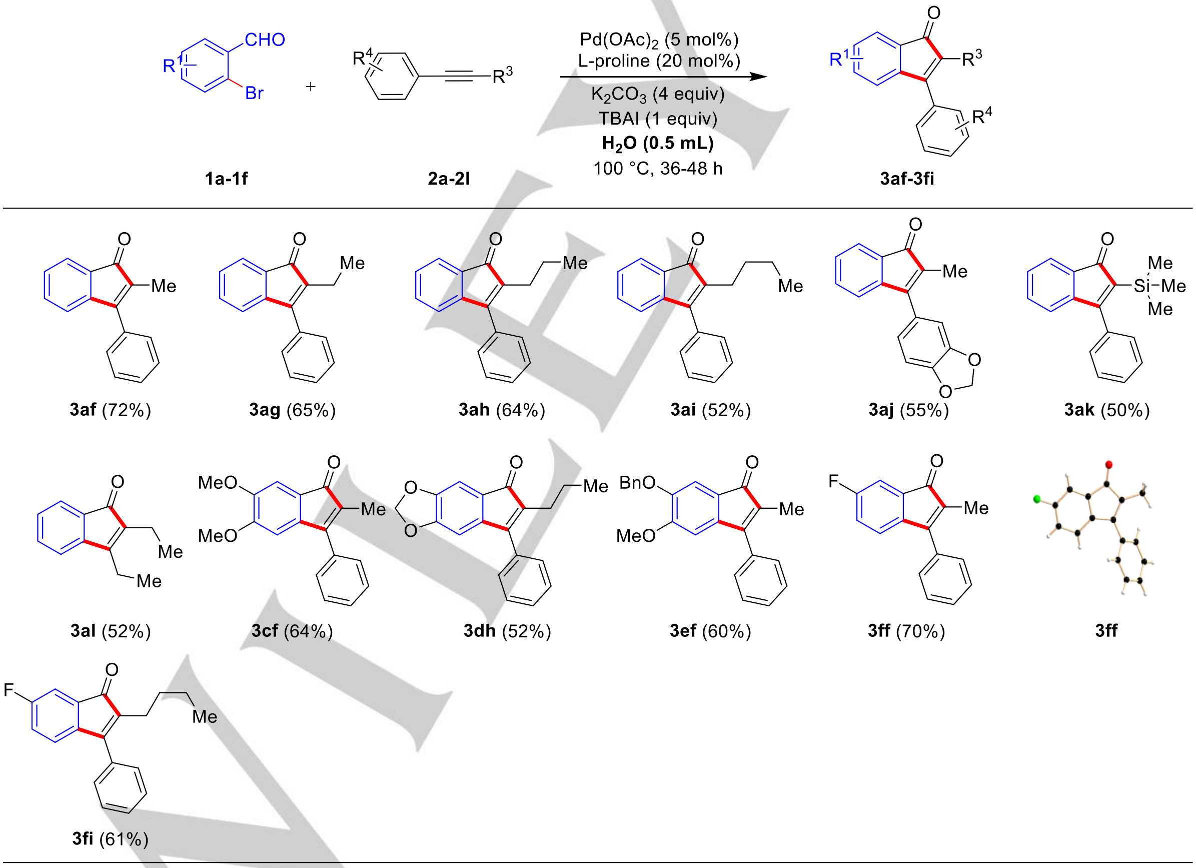
Table 3. Optimization studies for the formation of alkylarylindenones **3af**.[a,b,c,d,e]



entry	catalyst	ligand	additive	base	solvent	temp	yield 3af:3af'[b] (%)
1	$Pd(OAc)_2$	L-Proline	TBAI	K_2CO_3	H_2O	140	--[c]
2	**$Pd(OAc)_2$**	**L-Proline**	**TBAI**	**K_2CO_3**	**H_2O**	**100**	**72 : 0**
3	$Pd(OAc)_2$	PPh_3	TBAI	K_2CO_3	H_2O	100	48 : 0
4	$Pd(OAc)_2$	BINAP	TBAI	K_2CO_3	H_2O	100	30 : 0
5	$Pd(OAc)_2$	Glycine	TBAI	K_2CO_3	H_2O	100	10 : 0 + --[d]
6	$Pd(OAc)_2$	L-Proline	BTEAC	K_2CO_3	H_2O	100	20 : 0 + --[d]
7	$Pd(OAc)_2$	L-Proline	TBAI	K_2CO_3	DMF	100	15 : 0
8	$Pd(OAc)_2$	L-Proline	TBAI	K_2CO_3	Toluene	100	12 : 0

[a] Reaction conditions: By using 46.2 mg (0.25 mmol) of *ortho*-bromobenzaldehyde **1a**, 111.2 mg (0.62 mmol) of prop-1-yn-1-ylbenzene **2f**, base (1 mmol, 4 equiv), catalyst (5 mol%), ligand (20 mol%), additive (1 equiv) and solvent (0.5 mL). [b] Yields in the parentheses are isolated yields of product **3aa** with respect to the *ortho*-bromobenzaldehyde **1a**. [c] Starting material recovered. [d] Neither the starting material nor the product was isolated. [e] Benzyltriethylammonium chloride (BTEAC); Tetrabutylammonium iodide (TBAI).

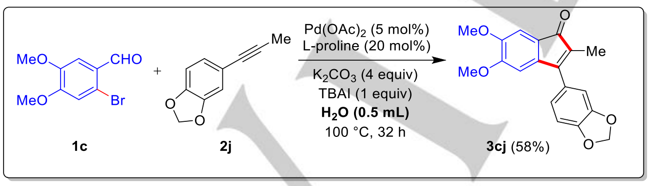
Table 4. Synthesis of arylalkylindenones **3af-3fi** with substituted *ortho*-bromobenzaldehyde **1a-1f** and alkylaryl acetylenes **2a-2l**.[a,b,c]



[a] Reaction conditions: substituted *ortho*-bromobenzaldehydes **1a-1f** (0.25 mmol), alkylaryl acetylenes **2a-2l** (0.62 mmol), of $Pd(OAc)_2$ (5 mol%), L-proline (20 mol%), TBAI (1 equiv), K_2CO_3 (4 equiv), H_2O (0.5 mL), 100 °C, 36 to 48 h. [b] Yields in the parentheses are isolated yields products **3af-3fi** with respect to the *ortho*-bromobenzaldehydes **1a-f**. [c] The first alphabet of products **3af-3fi** refers to the *ortho*-bromobenzaldehydes, while the second letter indicates the alkynes.

Further, to demonstrate the feasibility of the strategy, the reaction was conducted between *ortho*-bromobenzaldehydes **1a-1f** and unsymmetrical alkylaryl acetylenes **2a-2l**, under standard conditions (Table 3, entry 2). Gratifyingly, unlike most of the earlier reports, the present strategy showed excellent regioselectivity and delivered exclusively a single regioisomeric indenones **3af-3fi**, in moderate to very good yields (Table 4). In all cases, the alkyl group of each internal acetylene is situated at the C-2 position of indenones **3**, as confirmed by the single crystal X-ray diffraction analysis of **3ff** (Table 4) (see; supporting information for X-ray data [CCDC 1820879]). Significantly, the reaction was smooth with phenyltrimethylsilyl acetylene **2k** as well and furnished a single regioisomeric indenone **3ak**, wherein silyl group is also situated at the C-2 position of indenone (Table 4, **3ak**).[17] The regioselectivity in the formation of indenones **3af-3fi** (except for **3al**) may be attributed to the steric hindrance.[2a,12e] Further, the strategy was also successful with symmetrical 3-hexyne **3l** (Table 4, **3al**). Thus, reveals the efficacy and utility of the present strategy.

The natural product neo-lignan was isolated from the fruits of Virola Sebifera, in 1984 by Otto R. Gottlieb.[15] Subsequently, in the year 1998, Davi C. Harrowven et al. revised its structure as neo-lignan **3cj** based on their synthetic, physical and spectroscopic analysis (see; Figure 1).[16] Furthermore, to illustrate the synthetic application of the present methodology, next, it was aimed for one-pot synthesis of neo-lignan **3cj**. Thus, the annulation reaction was carried out between *ortho*-bromobenzaldehyde **1c** and unsymmetrical acetylene **2j**, under established conditions. To our delight, the natural product neo-lignan **3cj** was obtained in 58% yield, in one-pot (Scheme 1).



Scheme 1: Synthesis of Neo-lignan **3cj** from 2-bromo-4,5-dimethoxybenzaldehyde **1c** and 5-(prop-1-yn-1-yl)benzo[d][1,3]dioxole **2j**.

Conclusions

In conclusion, we have developed an efficient one-pot process for the synthesis of indenones. Significantly, this strategy was successful using water as the sole solvent. Notably, unlike most of the earlier reports, this protocol showed excellent regioselectivity with unsymmetrical alkylaryl acetylenes. Gratifyingly, this one-pot strategy was also successfully applied to the synthesis of neo-lignan.

Experimental Section

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in CDCl$_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) (δ_H =0.00 ppm) or CHCl$_3$ (δ_H = 7.25 ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at RT in CDCl$_3$; chemical shifts (δ ppm) are reported relative to CDCl$_3$ [δ_C = 77.00 ppm (central line of the triplet)]. In the ^{13}C NMR, the nature of carbons (C, CH, CH$_2$ and CH$_3$) was determined by recording the DEPT-135 spectra, and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH$_2$) and q = quartet (for CH$_3$). In the ^{1}H-NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui =quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, ^{13}C CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale dry reactions were carried out using screw cap reaction vials under nitrogen inert atmosphere. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Palladium acetate, L-proline, and TBAI (tetrabutylammonium iodide) were purchased from Sigma-Aldrich and used as received. K$_2$CO$_3$ was purchased from Sigma-Aldrich. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude material). It is worth noting that these sort of experimental procedures have already been published elsewhere.[13b,13e,13f]

GP (General procedure for the making of indenones): To a hot oven dried Screwcap vial was equipped with a magnetic stir bar, were added Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), *ortho*-bromobenzaldehyde **1** (45.7-80 mg, 0.25 mmol) and biaryl acetylenes **2** (50.8-147.1 mg, 0.62 mmol), under nitrogen inert atmosphere and finally the solvent water (0.5 mL) was added via syringe. After the addition of solvent the reaction mixture was allowed to stir at 140 °C for diarylacetylenes, and 100 °C for alkylarylacetylenes for 36 to 46 h. Progress of the reaction was monitored by TLC till the reaction is completed. Then, the reaction mixture was cooled to room temperature, quenched by the addition of aqueous NaHCO$_3$ solution and extracted by using ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (with Na_2SO_4) and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), gave the indenones **3** (50–90%) as semi-solid/solid.

2,3-Diphenyl-1*H*-inden-1-one (3aa): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3aa** (56.3 mg, 80%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2a**)=0.8, R_f(**3aa**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1708, 1606, 1457, 1347, 1182, 756, 698, 513 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.58 (d, 1H, *J*=6.84 Hz, Ar-H), 7.41-7.34 (m, 6H, Ar-H), 7.30–7.24 (m, 6H, Ar-H), 7.14 (d, 1H, *J*=7.33 Hz, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.5 (s, C=O), 155.3 (s, Ar-C), 145.2 (s, Ar-C), 133.5 (d, Ar-CH), 132.7 (s, Ar-C), 132.2 (s, Ar-C), 130.6 (s, Ar-C), 130.0 (d, 2 × Ar-CH), 129.3 (d, Ar-CH), 129.0 (d, Ar-CH), 128.8 (d, 3C, 3 × Ar-CH), 128.5 (d, 2C, 2 × Ar-CH), 128.1 (d, 2C, 2 × Ar-CH), 127.8 (d, Ar-CH), 123.0 (d, Ar-CH), 121.3 (d, Ar-CH) ppm. HR-MS (ESI+) m/z calculated for $[C_{21}H_{15}O]^+$=$[M+H]^+$: 283.1117; found 282.1112.

2,3-Bis(4-methylphenyl)-1*H*-inden-1-one (3ab): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 1-methyl-4-[(4-methylphenyl)ethynyl]benzene **2b** (127.7 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ab** (62.6 mg, 81%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2b**)=0.7, R_f(**3ab**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2851, 1710, 1607, 1459, 1344, 1182, 1071, 809, 730 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.54 (d, 1H, *J*=7.3 Hz, Ar-H), 7.33 (t, 1H, *J*=7.3 Hz, Ar-H), 7.31–7.09 (m, 8H, Ar-H), 7.06 (d, 2H, *J*=7.8 Hz, Ar-H), 2.38 (s, 3H, Ar-CH_3), 2.30 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.7 (s, C=O), 154.7 (s, Ar-C), 145.4 (s, Ar-C), 139.3 (s, Ar-C), 137.5 (s, Ar-C), 133.2 (d, Ar-CH), 132.0 (s, Ar-C), 130.9 (s, Ar-C), 129.9 (s, Ar-C), 129.8 (d, 2C, 2 × Ar-CH), 129.4 (d, 2C, 2 × Ar-CH), 128.8 (d, 2C, 2 × Ar-CH), 128.7 (d, Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.0 (s, Ar-C), 122.7 (d, Ar-CH), 121.1 (d, Ar-CH), 21.4 (q, 3H, Ar-CH_3), 21.3 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{19}O]^+$=$[M+H]^+$: 310.1358; found 310.1431.

2,3-Bis(3-methylphenyl)-1*H*-inden-1-one (3ac): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ac** (69.6 mg, 90%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2c**)=0.7, R_f(**3ac**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2930, 2852, 1711, 1610, 1462, 1346, 1187, 1074, 802, 734 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.57 (d, 1H, *J*=6.85 Hz, Ar-H), 7.36 (dt, 1H, *J*=1.4 Hz, *J*=7.3 Hz Ar-H), 7.25–7.30 (m, 2H, Ar-H), 7.21 (d, 2H, Ar-H), 7.14–7.10 (m, 4H, Ar-H), 7.05 (d, 1H, Ar-H), 7.00 (d, 1H, Ar-H), 2.35 (s, 3H, Ar-CH_3), 2.28 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.7 (s, C=O), 155.4 (s, Ar-C), 145.4 (s, Ar-C), 138.3 (s, Ar-C), 137.5 (s, Ar-C), 133.4 (d, Ar-CH), 132.7 (s, Ar-C), 132.7 (s, Ar-C), 132.3 (s, Ar-C), 130.8 (s, Ar-C), 130.5 (d, Ar-CH), 130.0 (d, Ar-CH), 128.9 (d, Ar-CH), 128.8 (d, Ar-CH), 128.7 (d, Ar-CH), 128.5 (d, Ar-CH), 127.9 (d, Ar-CH), 127.0 (d, Ar-CH), 125.7 (d, Ar-CH), 122.9 (d, Ar-CH), 121.3 (d, Ar-CH), 21.5 (q, 3H, Ar-CH_3), 21.4 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{19}O]^+$=$[M+H]^+$: 310.1430; found 310.1431.

2,3-Bis(4-methoxyphenyl)-1*H*-inden-1-one (3ad): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 1-methoxy-4-[(4-methoxyphenyl)ethynyl]benzene **2d** (147.5 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ad** (70.8 mg, 83%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2d**)=0.5, R_f(**3ad**)=0.4, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.54 (d, 1H, *J*=6.3 Hz, Ar-H), 7.37-7.33 (m, 3H, Ar-H), 7.27–7.22 (m, 3H, Ar-H), 7.16 (d, 1H, *J*=6.85 Hz, Ar-H), 6.93 (d, 2H, J=8.81 Hz, Ar-H), 6.82 (d, 2H, J=9.29 Hz, Ar-H) 3.85 (s, 3H, Ar-CH_3) 3.79 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.9 (s, C=O), 160.2 (s, Ar-C), 159.0 (s, Ar-C), 153.7 (s, Ar-C), 145.4 (s, Ar-C), 133.2 (d, Ar-CH), 131.3 (d, 2C, 2 × Ar-CH), 131.2 (s, Ar-C), 131.0 (s, Ar-C), 130.2 (d, 2C, 2 × Ar-CH), 128.6 (d, Ar-CH), 125.0 (s, Ar-C), 123.4 (s, Ar-C), 122.7 (d, Ar-CH), 120.1 (d, Ar-CH), 114.2 (d, 2C, 2 × Ar-CH), 113.7 (d, 2C, 2 × Ar-CH), 55.3 (q, 3H, Ar-CH_3), 55.2 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{19}O_3]^+$=$[M+H]^+$: 343.1256; found 343.1321.

6-Methoxy-2,3-diphenyl-1*H*-inden-1-one (3ba): GP was carried out with 2-bromo-5-methoxybenzaldehyde **1b** (53.7 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ba** (46.7 mg, 60%) as a light brown solid compound, recrystallized the solid with dichloromethane/hexane, m. p. 199-201 °C [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**2a**)=0.8, R_f(**3ba**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2931, 2862, 1712, 1616, 1467, 1357, 1183, 757, 699, 523 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.41-7.36 (m, 5H, Ar-H), 7.25-7.21 (m, 5H, Ar-H), 7.19 (d, 1H, *J*=2.45 Hz, Ar-H), 7.04 (d, 1H, *J*=7.83 Hz, Ar-H), 6.80 (dt, 1H, *J*=2.44 Hz, Ar-H), 3.85 (s, 3H, Ar-OCH_3), ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.2 (s, C=O), 161.0 (s, Ar-C), 156.3 (s, Ar-C), 136.9 (s, Ar-C), 133.0 (s, Ar-C), 132.9 (s, Ar-C), 131.4 (s, Ar-C), 131.0 (s, Ar-C), 129.8 (d, 2 × Ar-CH), 129.3 (d, Ar-CH), 128.7 (d, 2 × Ar-CH), 128.4 (d, 2 × Ar-CH), 128.0 (d, 2C, 2 × Ar-CH), 127.5 (d, Ar-CH), 122.2 (s, Ar-C), 116.3 (d, Ar-CH), 110.6 (d, Ar-

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CH), 55.8 (q, 3H, Ar-OCH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{17}O_2]^+$=[M+H]$^+$: 313.1223; found 313.1223.

6-Methoxy-2,3-bis(4-methylphenyl)-1*H*-inden-1-one (3bb): GP was carried out with 2-bromo-5-methoxybenzaldehyde **1b** (53.7 mg, 0.25 mmol), 1-methyl-4-[(4-methylphenyl)ethynyl]benzene **2b** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) gave the indene **3bb** (53.4 mg, 63%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2b**)=0.8, R_f(**3bb**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2926, 2850, 1704, 1614, 1506, 1458, 1293, 1259, 1187, 1031, 834 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.29-7.25 (m, 2H, Ar-H), 7.20 (m, 2H, Ar-H), 7.16 (m, 2H, Ar-H), 7.13 (s, 1H, Ar-H), 7.07 (s, 1H, Ar-H), 7.04 (m, 2H, Ar-H), 6.78 (dd, 1H, *J*=7.83 Hz, Ar-H), 3.84 (s, 3H, Ar-OCH$_3$), 2.39 (s, 3H, Ar-CH$_3$) 2.31 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.4 (s, C=O), 160.8 (s, Ar-C), 155.8 (s, Ar-C), 139.3 (s, Ar-C), 137.2 (s, Ar-C), 137.1 (s, Ar-C), 133.1 (s, Ar-C), 131.0 (s, Ar-C), 130.0 (s, Ar-C), 129.6 (d, 2C, 2 × Ar-CH), 129.4 (d, 2C, 2 × Ar-CH), 128.8 (d, 2C, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.1 (s, Ar-C), 122.1 (d, Ar-CH), 116.1 (d, Ar-CH), 110.4 (d, Ar-CH), 55.8 (q, 3H, Ar-OCH$_3$), 21.5 (q, 3H, Ar-CH$_3$), 21.3 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{21}O_2]^+$=[M+H]$^+$: 341.1536; found 341.1533.

6-Methoxy-2,3-bis(3-methylphenyl)-1*H*-inden-1-one (3bc): GP was carried out with 2-bromo-5-methoxybenzaldehyde **1b** (53.7 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) gave the indene **3bc** (50.9 mg, 60%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2c**)=0.8, R_f(**3bc**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2934, 2851, 1704, 1608, 1525, 1459, 1294, 1259, 1187, 1030, 834 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.25 (t, 1H, *J*=5.38 Hz, Ar-H), 7.20-7.17 (m, 3H, Ar-H), 7.14-7.09 (m, 3H, Ar-H), 7.04-6.97 (m, 3H, Ar-H), 6.79 (dd, 1H, *J*=7.83 Hz, Ar-H), 3.85 (s, 3H, Ar-OCH$_3$), 2.34 (s, 3H, Ar-CH$_3$), 2.30 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.3 (s, C=O), 160.9 (s, Ar-C), 156.4 (s, Ar-C), 138.3 (s, Ar-C), 137.4 (s, Ar-C), 137.1 (s, Ar-C), 133.0 (s, Ar-C), 132.9 (s, Ar-C), 131.4 (s, Ar-C), 130.9 (s, Ar-C), 130.4 (d, Ar-CH), 130.0 (d, Ar-CH), 128.7 (d, Ar-CH), 128.5 (d, Ar-CH), 128.2 (d, Ar-CH), 127.8 (d, Ar-CH), 126.8 (d, Ar-CH), 125.6 (d, Ar-CH), 122.2 (d, Ar-CH), 116.2 (d, Ar-CH), 110.5 (d, Ar-CH), 55.8 (q, 3H, Ar-OCH$_3$), 21.4 (2 × q, 6H, 2 × Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{21}O_2]^+$=[M+H]$^+$: 341.1536; found 341.1533.

6-Methoxy-2,3-bis(4-methoxyphenyl)-1*H*-inden-1-one (3bd): GP was carried out with 2-bromo-5-methoxybenzaldehyde **1b** (92.3 mg, 0.25 mmol), 1-methoxy-4-[(4-methoxyphenyl)ethynyl]benzene **2d** (147.5 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (56.7 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) gave the indene **3bd** (57.5 mg, 62%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 96:4), R_f(**2d**)=0.9, R_f(**3bd**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2931, 2851, 1704, 1605, 1506, 1457, 1223, 1232, 1123, 1045, 832 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.35 (d, 1H, *J*=2.45 Hz, Ar-H), 7.32 (d, 1H, *J*=2.44 Hz, Ar-H), 7.20 (d, 1H, *J*=1.96 Hz, Ar-H), 7.18 (d, 1H, *J*=1.96 Hz, Ar-H), 7.15 (d, 1H, *J*=2.44 Hz, Ar-H), 7.05 (d, 1H, J=7.82 Hz, Ar-H), 6.92 (d, 1H, *J*=1.96 Hz, Ar-H), 6.90 (d, 1H, *J*=1.96 Hz, Ar-H), 6.81 (d, 1H, *J*=1.96 Hz, Ar-H), 6.79 (m, 1H, Ar-H), 6.76 (d, 1H, *J*=2.44 Hz, Ar-H), 3.84 (2 × s, 6H, 2 × Ar-OCH$_3$), 3.78 (s, 3H, Ar-OCH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.6 (s, C=O), 160.7 (s, Ar-C), 160.3 (s, Ar-C), 158.8 (s, Ar-C), 154.9 (s, Ar-C), 137.1 (s, Ar-C), 133.2 (s, Ar-C), 131.1 (d, 2C, 2 × Ar-CH), 130.1 (d, 2C, 2 × Ar-CH), 130.2 (s, Ar-C), 125.3 (s, Ar-C), 123.6 (s, Ar-C), 121.9 (d, Ar-CH), 116.1 (d, Ar-CH), 114.1 (d, 2C, 2 × Ar-CH), 113.6 (d, 2C, 2 × Ar-CH), 110.3 (d, Ar-CH), 55.8 (q, 3H, Ar-OCH$_3$), 55.3 (q, 3H, Ar-OCH$_3$), 55.1 (q, 3H, Ar-OCH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{21}O_4]^+$=[M+H]$^+$: 373.1434; found 373.1364.

5,6-Dimethoxy-2,3-diphenyl-1*H*-inden-1-one (3ca): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) gave the indene **3ca** (68.9 mg, 81%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2a**)=0.9, R_f(**3ca**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2855, 1712, 1612, 1458, 1327, 1184, 732, 702, 515 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.42-7.35 (m, 5H, Ar-H), 7.25-7.21 (m, 6H, Ar-H), 6.68 (s, 1H, Ar-H), 3.93 (s, 3H, Ar-OCH$_3$), 3.87 (s, 3H, Ar-OCH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=195.9 (s, C=O), 154.0 (s, Ar-C), 152.8 (s, Ar-C), 149.2 (s, Ar-C), 139.7 (s, Ar-C), 132.9 (s, Ar-C), 131.3 (s, Ar-C), 130.9 (s, Ar-C), 129.8 (d, 2 × Ar-CH), 129.1 (d, Ar-CH), 128.8 (d, 2 × Ar-CH), 128.3 (d, 2 × Ar-CH), 128.0 (d, 2C, 2 × Ar-CH), 127.4 (d, Ar-CH), 123.0 (s, Ar-C), 107.7 (d, Ar-CH), 106.0 (d, Ar-CH), 56.4 (q, 3H, Ar-CH$_3$), 56.3 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{23}H_{19}O_3]^+$=[M+H]$^+$: 343.1329; found 343.1325.

5,6-Dimethoxy-2,3-bis(4-methylphenyl)-1*H*-inden-1-one (3cb): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), 1-methyl-4-[(4-methylphenyl)ethynyl]benzene **2b** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) gave the indene **3cb** (71.6 mg, 78%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**2b**)=0.9, R_f(**3cb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 2856, 1704, 1614, 1505, 1468, 1283, 1249, 1177, 1031, 799 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.28-7.25 (m, 2H, Ar-H), 7.22-7.19 (m, 3H, Ar-H), 7.14 (d, 2H, *J*=8.31 Hz Ar-H), 7.05 (d, 2H, *J*=8.32 Hz, Ar-H), 6.69 (s, 1H, Ar-H), 3.92 (s, 3H, Ar-OCH$_3$) 3.87 (s, 3H, Ar-OCH$_3$), 2.40 (s, 3H, Ar-CH$_3$) 2.30 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.2 (s, C=O), 153.4 (s, Ar-C), 152.6 (s, Ar-C), 149.0 (s, Ar-C), 139.9 (s, Ar-C), 139.1 (s, Ar-C), 137.1 (s, Ar-C), 131.0 (s, Ar-C), 130.0 (s, Ar-C), 129.6 (d, 2C, 2 × Ar-CH), 129.5 (d, 2C, 2 × Ar-CH), 128.7 (d, 2C, 2 × Ar-CH), 128.3 (d, 2C, 2 × Ar-CH), 128.2 (s, Ar-C), 123.2 (s, Ar-C), 107.5 (d, Ar-CH), 105.9 (d, Ar-CH), 56.4 (q, Ar-CH$_3$), 56.3 (q, Ar-

CH_3), 21.4 (q, Ar-CH_3), 21.2 (q, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{23}O_3]^+$=$[M+H]^+$: 371.1642; found 371.1634.

5,6-Dimethoxy-2,3-bis(3-methylphenyl)-1*H*-inden-1-one (3cc): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) gave the indene **3cc** (71.8 mg, 80%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**2c**)=0.9, R_f(**3cc**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 2854, 1705, 1605, 1506, 1459, 1294, 1259, 1157, 1040, 838 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.30 (t, 1H, *J*=7.34 Hz, Ar-H), 7.22-7.14 (m, 4H, Ar-H), 7.12-7.08 (m, 2H, Ar-H), 7.02 (d, 1H, *J*=7.82 Hz, Ar-H), 6.96 (d, 1H, *J*=8.32 Hz, Ar-H), 6.67 (s, 1H, Ar-H), 3.93 (s, 3H, Ar-OCH_3) 3.87 (s, 3H, Ar-OCH_3), 2.34 (s, 3H, Ar-CH_3) 2.26 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.2 (s, C=O), 154.0 (s, Ar-C), 152.6 (s, Ar-C), 149.0 (s, Ar-C), 139.8 (s, Ar-C), 138.5 (s, Ar-C), 137.4 (s, Ar-C), 132.9 (s, Ar-C), 131.3 (s, Ar-C), 130.9 (s, Ar-C), 130.4 (d, Ar-CH), 130.0 (d, Ar-CH), 128.8 (d, Ar-CH), 128.7 (d, Ar-CH), 128.2 (d, Ar-CH), 127.8 (d, Ar-CH), 126.8 (d, Ar-CH), 125.5 (d, Ar-CH), 123.0 (s, Ar-C), 107.5 (d, Ar-CH), 105.9 (d, Ar-CH), 56.4 (q, Ar-CH_3), 56.3 (q, Ar-CH_3), 21.5 (q, 3H, Ar-CH_3), 21.4 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{21}O_3]^+$=$[M+H]^+$: 371.1642; found 371.1634.

5,6-Dimethoxy-2,3-bis(4-methoxyphenyl)-1*H*-inden-1-one (3cd): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), 1-methoxy-4-[(4-methoxyphenyl)ethynyl]benzene **2d** (147.5 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) gave the indene **3cd** (76 mg, 76%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**2d**)=0.5, R_f(**3cd**)=0.4, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.32 (d, 2H, *J*=8.80 Hz, Ar-H), 7.21 (s, 1H, Ar-H), 7.18 (d, 2H, *J*=2.44 Hz, Ar-H), 6.94 (d, 2H, *J*=8.81 Hz, Ar-H), 6.79 (d, 2H, J=8.80 Hz, Ar-H), 6.70 (s, 1H, Ar-H) 3.92 (s, 3H, Ar-OCH_3) 3.90 (s, 3H, Ar-OCH_3), 3.85 (s, 3H, Ar-OCH_3) 3.80 (s, 3H, Ar-OCH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.5 (s, C=O), 160.2 (s, Ar-C), 158.9 (s, Ar-C), 152.6 (s, Ar-C), 152.4 (s, Ar-C), 148.8 (s, Ar-C), 139.9 (s, Ar-C), 131.0 (d, 2C, 2 × Ar-CH), 130.2 (s, Ar-C), 130.0 (d, 2C, 2 × Ar-CH), 125.3 (s, Ar-C), 123.7 (s, Ar-C), 123.3 (s, Ar-C), 114.3 (d, 2C, 2 × Ar-CH), 113.6 (d, 2C, 2 × Ar-CH), 107.5 (d, Ar-CH), 105.8 (d, Ar-CH), 55.4 (q, 3H, Ar-CH_3), 55.4 (q, 3H, Ar-CH_3), 55.3 (q, 3H, Ar-CH_3), 55.1 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{25}H_{23}O_5]^+$=$[M+H]^+$: 403.1540; found 403.1545.

6,7-Diphenyl-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (3da): GP was carried out with 2-bromo-1,3-benzodioxole-5-carbaldehyde **1d** (57 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) gave the indene **3da** (64.4 mg, 82%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2a**)=0.9, R_f(**3da**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1708, 1606, 1457, 1347, 1182, 756, 698, 513 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.40-7.38 (m, 3H, Ar-H), 7.34-7.31 (m, 2H, Ar-H), 7.24-7.21 (m, 5H, Ar-H), 7.07 (s, 1H, Ar-H), 6.83 (s, 1H, Ar-H), 6.00 (s, 2H, O-CH_2-O) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=195.0 (s, C=O), 153.6 (s, Ar-C), 151.5 (s, Ar-C), 147.6 (s, Ar-C), 141.8 (s, Ar-C), 132.7 (s, Ar-C), 131.3 (s, Ar-C), 130.7 (s, Ar-C), 129.8 (d, 2C, 2 × Ar-CH), 129.2 (d, Ar-CH), 128.8 (d, 2 × Ar-CH), 128.3 (d, 2 × Ar-CH), 128.0 (d, 2C, 2 × Ar-CH), 127.5 (d, Ar-CH), 124.6 (s, Ar-C), 105.2 (d, Ar-CH), 103.9 (d, Ar-CH), 102.0 (t, O-CH_2 -O), ppm. HR-MS (ESI+) m/z calculated for $[C_{22}H_{15}O_3]^+$=$[M+H]^+$: 327.1016; found 327.1018.

6,7-Bis(4-methylphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (3db): GP was carried out with 2-bromo-1,3-benzodioxole-5-carbaldehyde **1d** (57 mg, 0.25 mmol), 1-methyl-4-[(4-methylphenyl)ethynyl]benzene **2b** (127.7 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) gave the indene **3db** (63.4 mg, 72%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2b**)=0.8, R_f(**3db**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.25-7.18 (m, 4H, Ar-H), 7.15-7.11 (m, 2H, Ar-H), 7.09-7.04 (m, 3H, Ar-H), 6.64 (s, 1H, Ar-H), 6.00 (s, 2H, O-CH_2-O), 2.40 (s, 3H, Ar-CH_3) 2.30 (s, 3H, Ar-CH_3) ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ=196.0 (s, C=O), 153.1 (s, Ar-C), 151.5 (s, Ar-C), 147.5 (s, Ar-C), 142.0 (s, Ar-C), 139.2 (s, Ar-C), 137.4 (s, Ar-C), 137.3 (s, Ar-C), 131.0 (s, Ar-C), 130.2 (s, Ar-C), 129.8 (s, Ar-C), 129.6 (d, Ar-CH), 129.5 (d, Ar-CH), 128.7 (d, 2C, 2 × Ar-CH), 128.3 (d, Ar-CH), 128.0 (s, Ar-C), 127.4 (s, Ar-C), 124.8 (s, Ar-C), 105.1 (d, Ar-CH), 103.9 (d, Ar-CH), 102.0 (t, O-CH_2-O), 21.5 (q, 3H, Ar-CH_3), 21.3 (q, 3H, Ar-CH_3) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{19}O_3]^+$=$[M+H]^+$: 355.1329; found 355.1328.

6,7-Bis(3-methylphenyl)-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (3dc): GP was carried out with 2-bromo-1,3-benzodioxole-5-carbaldehyde **1d** (57 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), $Pd(OAc)_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K_2CO_3 (138.6 mg, 1 mmol), and H_2O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 98:2) gave the indene **3dc** (61.6 mg, 70%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**2c**)=0.8, R_f(**3dc**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ=7.25 (t, 1H, *J*=7.83 Hz, Ar-H), 7.19-7.14 (m, 2H, Ar-H), 7.10-7.05 (m, 4H, Ar-H), 7.01 (d, 1H, *J*=7.83 Hz, Ar-H), 6.95 (d, 1H, *J*=7.82 Hz, Ar-H), 6.61 (s, 1H, Ar-H), 6.00 (s, 2H, O-CH_2-O), 2.32 (s, 3H, Ar-CH_3) 2.24 (s, 3H, Ar-CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ=195.3 (s, C=O), 153.7 (s, Ar-C), 151.5 (s, Ar-C), 147.5 (s, Ar-C), 142.0 (s, Ar-C), 138.4 (s, Ar-C), 137.4 (s, Ar-C), 132.7 (s, Ar-C), 131.3 (s, Ar-C), 130.7 (s, Ar-C), 130.4 (d, Ar-CH), 129.9 (d, Ar-CH), 128.6 (d, 2C, 2 × Ar-CH), 128.3 (d, Ar-CH), 127.8 (d, Ar-CH), 126.8

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(d, Ar-CH), 125.5 (d, Ar-CH), 124.7 (s, Ar-C), 105.1 (d, Ar-CH), 103.9 (d, Ar-CH), 102.0 (t, O-CH$_2$-O), 21.4 (q, 3H, Ar-CH$_3$), 21.4 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{24}$H$_{19}$O$_3$]$^+$=[M+H]$^+$: 355.1329; found 355.1325.

6-(Benzyloxy)-5-methoxy-2,3-diphenyl-1*H*-inden-1-one (3ea): GP was carried out with 5-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **1e** (80 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 92:8) gave the indene **3ea** (85.3 mg, 82%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**2a**)=0.9, R_f(**3ea**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2921, 2851, 1708, 1606, 1457, 1347, 1182, 756, 698, 513 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.45-7.30 (m, 10H, Ar-H), 7.24-7.22 (m, 6H, Ar-H), 6.69 (s, 1H, Ar-H), 5.17 (s, 2H, O-CH$_2$-Ar), 3.86 (s, 3H, Ar-OCH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=195.7 (s, C=O), 153.9 (s, Ar-C), 153.6 (s, Ar-C), 148.2 (s, Ar-C), 140.1 (s, Ar-C), 136.5 (s, Ar-C), 132.9 (s, Ar-C), 131.6 (s, Ar-C), 130.9 (s, Ar-C), 129.8 (d, 2 × Ar-CH), 129.1 (d, Ar-CH), 128.8 (d, 2 × Ar-CH), 128.6 (d, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.0 (d, Ar-CH), 127.9 (d, 2 × Ar-CH), 127.4 (d, Ar-CH), 127.3 (d, 2 × Ar-CH), 123.0 (s, Ar-C), 110.3 (d, Ar-CH), 106.5 (d, Ar-CH), 71.4 (t, -O-CH$_2$-Ar), 56.4 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{29}$H$_{23}$O$_3$]$^+$=[M+H]$^+$: 419.1642; found 419.1634.

6-(Benzyloxy)-5-methoxy-2,3-bis(4-methylphenyl)-1*H*-inden-1-one (3eb): GP was carried out with 5-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **1e** (80 mg, 0.25 mmol), 1-methyl-4-[(4-methylphenyl)ethynyl]benzene **2b** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 92:8) gave the indene **3eb** (88.8 mg, 80%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**2b**)=0.9, R_f(**3eb**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.44 (d, 2H, J=6.85 Hz, Ar-H), 7.38 (t, 2H, J=8.31 Hz, Ar-H), 7.32 (d, 1H, J=6.84 Hz, Ar-H), 7.27 (d, 3H, J=8.31 Hz, Ar-H), 7.22 (d, 3H, J=6.36 Hz, Ar-H), 7.13 (d, 2H, J=8.32 Hz, Ar-H), 7.05 (d, 2H, J=8.31 Hz, Ar-H), 6.71 (s, 1H, Ar-H), 5.18 (s, 2H, Ar-O-CH$_2$-), 3.88 (s, 3H, Ar-OCH$_3$), 2.40 (s, 3H, Ar-CH$_3$) 2.30 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.1 (s, C=O), 153.4 (s, Ar-C), 153.3 (s, Ar-C), 147.9 (s, Ar-C), 140.3 (s, Ar-C), 139.2 (s, Ar-C), 137.2 (s, Ar-C), 136.6 (s, Ar-C), 131.2 (s, Ar-C), 130.0 (s, Ar-C), 129.7 (d, 2C, 2 × Ar-CH), 129.5 (d, 2C, 2 × Ar-CH), 128.8 (d, 2C, 2 × Ar-CH), 128.6 (d, 2C, 2 × Ar-CH), 128.3 (s, 2C, 2 × Ar-CH), 128.1(s, Ar-C), 128.0 (d, Ar-CH), 127.4 (s, 2C, 2 × Ar-CH), 123.2 (s, Ar-C), 110.1 (d, Ar-CH), 106.3 (d, Ar-CH), 71.4 (t, Ar-CH$_2$-O-), 56.4 (q, 3H, Ar-OCH$_3$), 21.5 (q, 3H, Ar-CH$_3$), 21.3 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{31}$H$_{27}$O$_3$]$^+$=[M+H]$^+$: 447.1955; found 447.1950.

6-(Benzyloxy)-5-methoxy-2,3-bis(3-methylphenyl)-1*H*-inden-1-one (3ec): GP was carried out with 5-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **1e** (80 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 92:8) gave the indene **3ec** (89.9 mg, 81%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**2c**)=0.9, R_f(**3ec**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.45 (d, 2H, J=7.34 Hz, Ar-H), 7.38 (t, 2H, J=7.83 Hz, Ar-H) 7.33-7.28 (m, 2H, Ar-H), 7.21 (d, 2H, J=6.85 Hz, Ar-H), 7.15 (t, 2H, J=7.83 Hz, Ar-H), 7.10 (t, 2H, J=7.83 Hz, Ar-H), 7.02 (d, 1H, J=7.34 Hz, Ar-H), 6.96 (d, 1H, J=7.33 Hz, Ar-H), 6.69 (s, 1H, Ar-H), 5.18 (s, 2H, Ar-H), 3.87 (s, 3H, 1 × Ar-OCH$_3$), 2.34 (s, 3H, Ar-CH$_3$) 2.26 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.0 (s, C=O), 153.9 (s, Ar-C), 153.4 (s, Ar-C), 148.0 (s, Ar-C), 140.3 (s, Ar-C), 138.4 (s, Ar-C), 137.4 (s, Ar-C), 136.5 (s, Ar-C), 132.9 (s, Ar-C), 131.5 (s, Ar-C), 130.8 (s, Ar-C), 130.4 (d, Ar-CH), 129.9 (d, Ar-CH), 128.8 (d, Ar-CH), 128.7 (d, Ar-CH), 128.6 (d, 2 × Ar-CH), 128.3 (d, Ar-CH), 128.1 (d, Ar-CH), 127.8 (d, Ar-CH), 127.4 (d, 2 × Ar-CH), 126.9 (d, Ar-CH), 125.5 (d, Ar-CH), 123.0 (s, Ar-C), 110.1 (d, Ar-CH), 106.5 (d, Ar-CH), 71.4 (t, -O-CH$_2$-Ar), 56.5 (q, 3H, Ar-OCH$_3$), 21.5 (q, 3H, Ar-CH$_3$), 21.4 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{31}$H$_{27}$O$_3$]$^+$=[M+H]$^+$: 447.1955; found 447.1950.

6-Fluoro-2,3-bis(3-methylphenyl)-1*H*-inden-1-one (3fc): GP was carried out with 2-bromo-5-fluorobenzaldehyde **1f** (50.7 mg, 0.25 mmol), 1-methyl-3-[(3-methylphenyl)ethynyl]benzene **2c** (127.7 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3fc** (51.5 mg, 63%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2c**)=0.9, R_f(**3fc**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2920, 2851, 1710, 1607, 1459, 1344, 1182, 1071, 809, 730 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.29-7.25 (m, 3H, Ar-H), 7.20 (m, 2H, Ar-H), 7.13–7.09 (m, 3H, Ar-H), 7.08-7.03 (m, 2H, Ar-H), 7.01–6.96 (m, 2H, Ar-H), 2.34 (s, 3H, Ar-CH$_3$), 2.27 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=195.0 (s, C=O), 164.8 (s, Ar-C), 162.3 (s, Ar-C), 155.5 (s, Ar-C), 140.8 (s, Ar-C), 138.5 (s, Ar-C), 137.6 (s, Ar-C), 133.3,133.2 (d, Ar-C), 132.7,132.6 (d, Ar-C), 132.5 (s, Ar-C), 130.5 (d, Ar-CH), 130.3 (d, Ar-CH), 128.7 (d, 2 × Ar-CH), 128.6 (d, Ar-CH), 127.9 (d, Ar-CH), 126.9 (d, Ar-CH), 125.6 (d, Ar-CH), 122.4,122.3 (d, Ar-CH), 118.6,118.4 (d, Ar-CH), 111.6,111.3 (d, Ar-CH), 21.5 (q, 3H, Ar-CH$_3$), 21.4 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{23}$H$_{18}$FO]$^+$=[M+H]$^+$: 329.1336; found 329.1333.

3-(4-Methoxyphenyl)-2-phenyl-1*H*-inden-1-one And 2-(4-methoxyphenyl)-3-phenyl-1*H*-inden-1-one (3ae): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 1-methoxy-4-(phenylethynyl)benzene **2e** (128.9 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 95:5) gave the indene **3ae** (68.2 mg, 88%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**2e**)=0.7,

R_f(**3ae**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2924, 2850, 1704, 1604, 1505, 1458, 1293, 1249, 1177, 1030, 824 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.54 (t, 2H, *J*=6.36 Hz, Ar-H), 7.38-7.36 (m, 5H, Ar-H), 7.34–7.30 (m, 4H, Ar-H), 7.26-7.16 (m, 11H, Ar-H), 7.06 (d, 1H, *J*=6.85 Hz, Ar-H), 6.91-6.88 (d, 2H, J=8.81 Hz, Ar-H), 6.77 (d, 2H, J=8.81 Hz, Ar-H), 3.81 (s, 3H, Ar-CH$_3$), 3.75 (s, 3H, Ar-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.9 (s, C=O), 196.4 (s, C=O), 160.4 (s, Ar-C), 159.1 (s, Ar-C), 155.1 (s, Ar-C), 153.7 (s, Ar-C), 145.5 (s, Ar-C), 145.1 (s, Ar-C), 133.4 (d, Ar-CH), 133.2 (d, Ar-CH), 132.9 (s, Ar-C), 131.8 (s, Ar-C), 131.6 (s, Ar-CH), 131.2 (d, 2C, 2 × Ar-CH), 131.1 (s, Ar-C), 131.0 (s, Ar-C), 130.6 (s, Ar-C), 130.2 (d, 2C, 2 × Ar-CH), 129.9 (d, 2C, 2 × Ar-CH), 129.1 (d, Ar-CH), 128.8 (d, Ar-CH), 128.7 (d, 2C, 2 × Ar-CH), 128.6 (d, Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.0 (d, 2C, 2 × Ar-CH), 127.5 (d, Ar-CH), 124.7 (s, Ar-C), 123.0 (s, Ar-C), 122.8 (d, Ar-CH), 122.7 (d, Ar-CH), 121.2 (d, Ar-CH), 120.9 (d, Ar-CH), 114.1 (d, 2C, 2 × Ar-CH), 113.6 (d, 2C, 2 × Ar-CH), 55.2 (q, 3H, Ar-CH$_3$), 55.1 (q, 3H, Ar-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{22}$H$_{17}$O$_2$]$^+$=[M+H]$^+$: 313.1223; found 313.1152.

6-Fluoro-2,3-diphenyl-1*H*-inden-1-one (3ia): GP was carried out with 2-chloro-5-fluorobenzaldehyde **1i** (39.5 mg, 0.25 mmol), 1,2-diphenylethyne **2a** (111.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ia** (42 mg, 56%) as a light yellow oily compound [TLC control (petroleum ether/ethyl acetate 100:2), R_f(**2a**)=0.8, R_f(**3ia**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2939, 2822, 1722, 1636, 1465, 1337, 1283, 857, 799, 623 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.42-7.40 (m, 3H, Ar-H), 7.37-7.35 (m, 2H, Ar-H), 7.29 (dd, 1H, *J*=6.84 Hz, 2.45 Hz, Ar-H), 7.27-7.23 (m, 5H, Ar-H), 7.12 (dd, 1H, *J*=8.31 Hz, 4.40 Hz, Ar-H), 7.04-6.99 (dt, 1H, *J*=16.6 Hz, 8.81 Hz, 2.45 Hz, Ar-H) ppm.^{13}C NMR (CDCl$_3$, 100 MHz): δ=194.9 (s, C=O), 164.9 (d, Ar-C), 155.3 (s, Ar-C), 140.6 (d, Ar-C), 133.2 (d, Ar-C), 132.6 (d, Ar-C), 132.4 (s, Ar-C), 130.5 (s, Ar-C), 129.8 (d, 2C, 2 × Ar-CH), 129.5 (d, Ar-CH), 128.9 (d, 2C, 2 × Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 128.1 (d, 2C, 2 × Ar-CH), 127.8 (d, Ar-CH), 122.4 (d, Ar-C), 118.7 (d, Ar-CH), 111.7 (d, Ar-CH) ppm. HR-MS (ESI+) m/z calculated for [C$_{21}$H$_{14}$FO]$^+$=[M+H]$^+$: 300.0953; found 300.0958.

2-Methyl-3-phenyl-1*H*-inden-1-one (3af): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), prop-1-ynylbenzene **2f** (71.9 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3af** (39.3 mg, 72%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2f**)=0.9, R_f(**3af**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2922, 2852, 1709, 1616, 1467, 1341, 1195, 756, 702, 700, 523 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53-7.43 (m, 6H, Ar-H), 7.29 (t, 1H, *J*=8.80 Hz, Ar-H), 7.18 (t, 1H, *J*=7.83 Hz, Ar-H), 7.06 (d, 1H, *J*=7.34 Hz, Ar-H), 1.92 (s, 3H, O=C-C-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=198.3 (s, C=O), 154.7 (s, Ar-C), 145.7 (s, Ar-C), 133.1 (d, Ar-CH), 132.7 (s, Ar-C), 131.1 (s, Ar-C), 131.0 (s, Ar-C), 128.7 (d, 2 × Ar-CH), 128.1 (d, Ar-CH), 128.0 (d, 2C, 2 × Ar-CH), 122.5 (d, Ar-CH), 120.4 (d, Ar-CH), 8.6 (q, 3H, O=C-C-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{16}$H$_{12}$NaO]$^+$=[M+Na]$^+$: 243.0780; found 243.0780.

2-Ethyl-3-phenyl-1*H*-inden-1-one (3ag): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), but-1-ynylbenzene **2g** (80.6 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ag** (37.7 mg, 65%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2g**)=0.9, R_f(**3ag**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2931, 2851, 1718, 1656, 1465, 1386, 1181, 757, 699, 566 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53-7.44 (m, 6H, Ar-H), 7.30-7.25 (m, 1H, Ar-H), 7.21-7.17 (d, 1H, *J*=7.34 Hz, Ar-H), 2.39-2.33 (q, 2H, *J*=7.34 Hz, O=C-C-*CH$_2$-*), 1.11 (t, 3H, *J*=7.34 Hz, O=C-C-CH$_2$-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=198.2 (s, C=O), 154.6 (s, Ar-C), 145.9 (s, Ar-C), 136.7 (s, Ar-C), 133.1 (d, Ar-CH), 132.8 (s, Ar-C), 131.1 (s, Ar-C), 129.1 (d, Ar-CH), 128.7 (d, 2 × Ar-CH), 128.2 (d, Ar-CH), 127.8 (d, 2 × Ar-CH), 122.4 (d, Ar-CH), 120.5 (d, Ar-CH), 16.7 (t, 2H, O=C-C-*CH$_2$-*), 13.9 (q, 3H, O=C-C-CH$_2$-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{17}$H$_{15}$O]$^+$=[M+H]$^+$: 235.1117; found 235.1117.

3-Phenyl-2-propyl-1*H*-inden-1-one (3ah): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), pent-1-ynylbenzene **2h** (89.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ah** (39.9 mg, 64%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2h**)=0.9, R_f(**3ah**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2932, 2852, 1858, 1726, 1452, 1447, 1162, 756, 688, 583 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.52-7.49 (m, 2H, Ar-H), 7.47-7.42 (m, 4H, Ar-H), 7.30-7.25 (m, 1H, Ar-H), 7.20-7.17 (m, 1H, Ar-H), 6.98 (d, 1H, *J*=7.33 Hz, Ar-H), 2.31 (t, 2H, *J*=7.34 Hz, O=C-C-*CH$_2$-*), 1.56-1.46 (m, 2H, O=C-C-CH$_2$-*CH$_2$-*), 0.87 (t, 3H, *J*=7.34 Hz, O=C-C-CH$_2$-CH$_2$-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=198.4 (s, C=O), 155.2 (s, Ar-C), 145.9 (s, Ar-C), 135.3 (s, Ar-C), 133.1 (d, Ar-CH), 132.9 (s, Ar-C), 130.1 (s, Ar-C), 129.0 (d, Ar-CH), 128.7 (d, 2 × Ar-CH), 128.1 (d, Ar-CH), 127.8 (d, 2 × Ar-CH), 122.4 (d, Ar-CH), 120.5 (d, Ar-CH), 25.3 (t, O=C-C-*CH$_2$-*), 22.6 (t, 2H, O=C-C-CH$_2$-*CH$_2$-*), 14.2 (q, 3H, O=C-C-CH$_2$-CH$_2$-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{28}$H$_{17}$O]$^+$=[M+H]$^+$: 249.1274; found 249.1276.

2-Butyl-3-phenyl-1*H*-inden-1-one (3ai): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), hex-1-ynylbenzene **2i** (97.5 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ai** (33.8 mg, 52%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2i**)=0.9, R_f(**3ai**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2930, 2862, 1888, 1676, 1457, 1357, 1182, 796, 708, 633 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53-7.43 (m, 6H, Ar-H), 7.30-7.25 (m, 1H, Ar-H), 7.20-7.16 (m, 1H, Ar-H), 6.98 (d, 1H, *J*=7.34 Hz, Ar-H), 2.33 (t, 2H, *J*=7.83 Hz, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 1.51-1.43

(t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 1.34-1.24 (m, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 0.84 (t, 3H, *J*=7.34 Hz, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=198.3 (s, C=O), 155.0 (s, Ar-C), 145.9 (s, Ar-C), 135.5 (s, Ar-C), 133.1 (d, Ar-CH), 132.9 (s, Ar-C), 131.0 (s, Ar-C), 129.0 (d, Ar-CH), 128.7 (d, 2 × Ar-CH), 128.1 (d, Ar-CH), 127.7 (d, 2 × Ar-CH), 122.4 (d, Ar-CH), 120.4 (d, Ar-CH), 31.4 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 23.0 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 22.7 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 13.7 (q, 3H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{19}$H$_{19}$O]$^+$=[M+H]$^+$: 263.1430; found 263.1340.

3-(1,3-Benzodioxol-5-yl)-2-methyl-1*H*-inden-1-one (3aj): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), 5-prop-1-ynyl-1,3-benzodioxole **2j** (99.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) gave the indene **3aj** (36.0 mg, 55%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 97:3), *R$_f$*(**2j**)=0.8, *R$_f$*(**3aj**)=0.7, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2933, 2862, 1778, 1676, 1477, 1367, 1172, 776, 668, 573 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.45 (s, 1H, *J*=6.85 Hz, Ar-H), 7.29 (t, 1H, *J*=7.83 Hz, Ar-H), 7.18 (t, 1H, *J*=7.33 Hz, Ar-H), 7.08 (d, 1H, *J*=7.34 Hz, Ar-H), 7.01-6.93 (m, 3H, Ar-H), 6.04 (s, 2H, O-CH$_2$-O), 1.92 (s, 3H, O=C-C-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=198.2 (s, C=O), 154.4 (s, Ar-C), 148.3 (s, Ar-C), 147.9 (s, Ar-C), 145.5 (s, Ar-C), 133.0 (d, Ar-CH), 131.2 (s, Ar-C), 130.4 (s, Ar-C), 128.1 (d, Ar-CH), 126.4 (s, Ar-C), 122.4 (s, Ar-C), 122.3 (d, Ar-CH), 120.3 (d, Ar-CH), 108.7 (d, Ar-CH), 108.4 (d, Ar-CH), 101.4 (t, 2H, O-CH$_2$-O), 8.7 (q, 3H, O=C-C-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{17}$H$_{13}$O$_3$]$^+$=[M+H]$^+$: 265.0859; found 265.0789.

3-Phenyl-2-(trimethylsilyl)-1*H*-inden-1-one (3ak): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), trimethyl(phenylethynyl)silane **2k** (107.8 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ak** (34.5 mg, 50%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R$_f$*(**2k**)=0.9, *R$_f$*(**3ak**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2986, 2882, 1788, 1656, 1497, 1397, 1192, 796, 628, 503 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.45-7.40 (m, 3H, Ar-H), 7.35-7.30 (m, 2H, Ar-H), 7.26-7.18 (m, 3H, Ar-H), 6.83 (d, 1H, *J*=6.85 Hz, Ar-H), 0.00 (s, 9H, O=C-C-Si(*CH$_3$)$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=201.8 (s, C=O), 170.7 (s, Ar-C), 160.0 (d, Ar-CH), 147.2 (s, Ar-C), 135.0 (s, Ar-C), 134.7 (s, Ar-C), 133.0 (d, Ar-CH), 132.3 (s, Ar-C), 129.1 (d, Ar-CH), 128.4 (d, 2C, 2 × Ar-CH), 127.7 (d, 2C, 2 × Ar-CH), 122.3 (d, Ar-CH), 120.8 (d, Ar-CH), -0.20 (q, 3H, O=C-C-Si(*CH$_3$)$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{18}$H$_{19}$OSi]$^+$=[M+H]$^+$: 279.1200; found 279.1200.

2,3-Diethyl-1*H*-inden-1-one (3al): GP was carried out with 2-bromobenzaldehyde **1a** (45.7 mg, 0.25 mmol), hex-3-yne **2l** (50.8 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3al** (24.0 mg, 52%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), *R$_f$*(**2l**)=0.9, *R$_f$*(**3al**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2941, 2841, 1748, 1676, 1557, 1247, 1172, 756, 726, 623 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.71-7.69 (d, 1H, *J*=7.83 Hz, Ar-H), 7.60-7.56 (m, 1H, Ar-H), 7.47-7.45 (m, 1H, Ar-H), 7.37-7.33 (m, *J*=15.17, 7.83 Hz, 1H, Ar-H), 3.07-3.04 (m, 1H, Ar-H), 2.37-2.33 (m, 1H, Ar-H), 1.81-1.71 (m, 2H, Ar-H), 1.61-1.51 (m, 2H), 1.48-1.34 (m, 6H), 0.96-0.90 (t, 6H) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=209.3 (s, C=O), 158.0 (s, Ar-C), 136.2 (s, Ar-C), 134.6 (d, Ar-CH), 127.4 (d, Ar-CH), 125.7 (d, Ar-CH), 123.7 (d, Ar-CH), 53.6 (s, -C), 44.7 (d, -C), 38.6 (t, -CH$_2$), 34.4 (t, -CH$_2$), 20.5 (t, -CH$_2$), 14.3 (q, -CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{13}$H$_{15}$O]$^+$=[M+H]$^+$: 187.1117; found 187.1050.

5,6-Dimethoxy-2-methyl-3-phenyl-1*H*-inden-1-one (3cf): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), prop-1-ynylbenzene **2f** (71.9 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 94:6) gave the indene **3cf** (44.6 mg, 64%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 93:7), *R$_f$*(**2f**)=0.7, *R$_f$*(**3cf**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2941, 2862, 1752, 1608, 1467, 1357, 1192, 786, 688, 533 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.54-7.50 (m, 2H, Ar-H), 7.45 (m, 3H, Ar-H), 7.12 (s, 1H, Ar-H), 6.62 (s, 1H, Ar-H), 3.89 (s, 3H, Ar-OCH$_3$), 3.85 (s, 3H, Ar-OCH$_3$), 1.87 (s, 3H, O=C-C-CH$_3$) ppm.^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=197.8 (s, C=O), 153.1 (s, Ar-C), 152.4 (s, Ar-C), 148.3 (s, Ar-C), 140.3 (s, Ar-C), 132.9 (s, Ar-C), 129.9 (s, Ar-C), 129.0 (d, Ar-CH), 123.3 (s, Ar-C), 128.8 (d, 2 × Ar-CH), 127.9 (d, 2 × Ar-CH), 107.5 (d, Ar-CH), 105.4 (d, Ar-CH), 56.4 (q, 3H, Ar-OCH$_3$), 56.3 (q, 3H, Ar-OCH$_3$), 8.6 (q, 3H, O=C-C-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for [C$_{18}$H$_{17}$O$_3$]$^+$=[M+H]$^+$: 281.1172; found 281.1100.

7-Phenyl-6-propyl-5*H*-indeno[5,6-*d*][1,3]dioxol-5-one (3dh): GP was carried out with 2-bromo-1,3-benzodioxole-5-carbaldehyde **1d** (57 mg, 0.25 mmol), pent-1-ynylbenzene **2h** (89.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) gave the indene **3dh** (37.8 mg, 52%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 97:3), *R$_f$*(**2h**)=0.6, *R$_f$*(**3dh**)=0.5, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2986, 2850, 1705, 1607, 1458, 1349, 1186, 757, 628, 553 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ*=7.51-7.47 (m, 2H, Ar-H), 7.44-7.38 (m, 3H, Ar-H), 6.98 (s, 1H, Ar-H), 6.51 (s, 1H, Ar-H), 5.97 (s, 2H, O-CH$_2$-O), 2.26-2.22 (t, 2H, *J*=7.33 Hz, O=C-C-*CH$_2$*-CH$_2$-CH$_3$), 1.52-1.43 (m, 2H, O=C-C-CH$_2$-*CH$_2$*-CH$_3$), 0.85 (t, 3H, *J*=7.34 Hz, O=C-C-CH$_2$-CH$_2$-*CH$_3$*) ppm.^{13}C NMR (CDCl$_3$, 100 MHz): *δ*=197.0 (s, C=O), 153.3 (s, Ar-C), 151.3 (s, Ar-C), 147.0 (s, Ar-C), 142.5 (s, Ar-C), 134.3 (s, Ar-C), 132.8 (s, Ar-C), 129.0 (d, Ar-CH), 128.8 (d, 2C, 2 × Ar-CH), 127.7 (d, 2 × Ar-CH), 124.8 (s, Ar-C), 105.0 (d, Ar-CH), 103.5 (d, Ar-CH), 101.9 (t, O-CH$_2$ -O), 25.4 (t, 2H, O=C-C-CH$_2$-*CH$_2$*-CH$_3$), 22.7 (t, 2H, O=C-C-CH$_2$-*CH$_2$*-CH$_3$), 14.1 (q, 3H, O=C-C-CH$_2$-CH$_2$-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for [C$_{19}$H$_{17}$O$_3$]$^+$=[M+H]$^+$: 293.1172; found 293.1102.

6-(Benzyloxy)-5-methoxy-2-methyl-3-phenyl-1*H*-inden-1-one (3ef): GP was carried out with 5-(benzyloxy)-2-bromo-4-methoxybenzaldehyde **1e** (80 mg, 0.25 mmol), prop-1-ynylbenzene **2f** (71.9 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 97:3) gave the indene **3ef** (53.2 mg, 60%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**2f**)=0.9, R_f(**3ef**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2956, 2832, 1712, 1612, 1486, 1356, 1192, 786, 700, 666, 526 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53-7.50 (m, 2H, Ar-H), 7.46-7.42 (m, 5H, Ar-H), 7.36 (m, 2H, Ar-H), 7.30 (m, 1H, Ar-H), 7.14 (s, 1H, Ar-H), 6.63 (s, 1H, Ar-H), 5.14 (s, 2H, O-CH$_2$-Ar), 3.85 (s, 3H, Ar-OCH$_3$), 1.86 (s, 3H, O=C-C-CH$_3$) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=197.6 (s, C=O), 153.3 (s, Ar-C), 153.0 (s, Ar-C), 147.4 (s, Ar-C), 140.8 (s, Ar-C), 136.6 (s, Ar-C), 132.9 (s, Ar-C), 130.3 (s, Ar-C), 129.0 (d, Ar-CH), 128.8 (d, 2 × Ar-CH), 128.6 (d, 2 × Ar-CH), 128.0 (d, Ar-CH), 127.9 (d, 2 × Ar-CH), 127.4 (d, 2 × Ar-CH), 123.3 (s, Ar-C), 110.4 (d, Ar-CH), 106.0 (d, Ar-CH), 71.4 (t, -O-CH$_2$-Ar), 56.4 (q, 3H, Ar-CH$_3$), 8.6 (q, 3H, O=C-C-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{24}H_{21}O_3]^+$=$[M+H]^+$: 357.1485; found 357.1480.

6-Fluoro-2-methyl-3-phenyl-1*H*-inden-1-one (3ff): GP was carried out with 2-bromo-5-fluorobenzaldehyde **1f** (50.7 mg, 0.25 mmol), prop-1-ynylbenzene **2f** (71.9 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3ff** (41.3 mg, 70%) as a purple colored solid compound, recrystallized the solid with dichloromethane/hexane, m. p. 200–201 °C [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2f**)=0.9, R_f(**3ff**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2952, 2848, 1758, 1666, 1437, 1387, 1172, 796, 668, 553, 500 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.53-7.44 (m, 5H, Ar-H), 7.20-7.17 (dd, 1H, *J*=7.33 Hz, Ar-H), 7.00 (q, 1H, *J*=7.82 Hz, Ar-H), 6.98-6.91 (dt, 1H, *J*=7.81 Hz, Ar-H), 1.91 (s, 3H, O=C-C-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.6 (s, C=O), 164.4 (s, Ar-C), 162.0 (s, Ar-C), 154.8 (s, Ar-C), 141.0 (s, Ar-C), 133.6 (d, Ar-C), 132.5 (s, Ar-C), 131.2 (d, Ar-C), 129.4 (d, Ar-CH), 128.8 (d, Ar-CH), 127.9 (d, Ar-CH), 121.3 (d, Ar-CH), 118.2 (d, Ar-CH), 118.0 (d, Ar-CH), 111.4 (d, Ar-CH), 111.1 (d, Ar-CH), 8.7 (q, 3H, O=C-C-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for $[C_{16}H_{12}FO]^+$=$[M+H]^+$: 239.0867; found 239.0867.

2-Butyl-6-fluoro-3-phenyl-1*H*-inden-1-one (3fi): GP was carried out with 2-bromo-5-fluorobenzaldehyde **1f** (50.7 mg, 0.25 mmol), hex-1-ynylbenzene **2i** (97.5 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 99:1) gave the indene **3fi** (42.7 mg, 61%) as a light yellow jelly compound, [TLC control (petroleum ether/ethyl acetate 100:0), R_f(**2i**)=0.9, R_f(**3fi**)=0.8, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2942, 2891, 1788, 1688, 1499, 1447, 1282, 856, 658, 585, 524 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.52-7.49 (m, 2H, Ar-H), 7.47-7.44 (m, 1H, Ar-H), 7.43-7.41 (m, 2H, Ar-H), 6.93-6.92 (m, 2H, Ar-H), 2.31 (t, 2H, *J*=15.65, 7.82 Hz, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 1.49-1.41 (m, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 1.33-1.23 (m, 3H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 0.83 (t, 3H, *J*=14.18, 7.34 Hz, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*) ppm. ^{13}C NMR (CDCl$_3$, 100 MHz): δ=196.7 (s, C=O), 164.5 (s, Ar-C), 162.0 (s, Ar-C), 155.1 (s, Ar-C), 141.2 (s, Ar-C), 135.7 (d, Ar-C), 133.4 (d, Ar-C), 132.6 (s, Ar-C), 129.3 (d, Ar-CH), 128.8 (d, 2 × Ar-CH), 127.6 (d, 2 × Ar-CH), 121.4 (d, Ar-CH), 121.3 (d, Ar-CH), 118.2 (d, Ar-CH), 118.0 (d, Ar-CH), 111.2 (d, Ar-CH), 110.1 (d, Ar-CH), 31.3 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 23.1 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 22.7 (t, 2H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*), 13.7 (q, 3H, O=C-C-CH$_2$-CH$_2$-CH$_2$-*CH$_3$*) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{18}FO]^+$=$[M+H]^+$: 281.1336; found 281.1270.

3-(1,3-Benzodioxol-5-yl)-5,6-dimethoxy-2-methyl-1*H*-inden-1-one (3cj): GP was carried out with 2-bromo-4,5-dimethoxybenzaldehyde **1c** (61 mg, 0.25 mmol), 5-prop-1-ynyl-1,3-benzodioxole **2j** (99.2 mg, 0.62 mmol), Pd(OAc)$_2$ (2.8 mg, 5 mol%), L-Proline (5.7 mg, 20 mol%), TBAI (92.3 mg, 0.25 mmol), K$_2$CO$_3$ (138.6 mg, 1 mmol), and H$_2$O (0.5 mL). Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 100:0 to 90:10) gave the indene **3cj** (46.8 mg, 58%) as a red solid compound, recrystallized the solid with dichloromethane/hexane, m. p. 210–212 °C [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**2j**)=0.8, R_f(**3cj**)=0.6, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max}=2942, 2815, 1712, 1696, 1486, 1355, 1166, 799, 685, 545, 483 cm^{-1}. ^{1}H NMR (CDCl$_3$, 400 MHz): δ=7.11 (s, 1H, Ar-H), 6.96-6.93 (m, 3H, Ar-H), 6.64 (s, 1H, Ar-H), 6.05 (s, 2H, O-CH$_2$-O), 3.89 (s, 3H, Ar-OCH$_3$), 3.87 (s, 3H, Ar-OCH$_3$), 1.87 (s, 3H, O=C-C-CH$_3$) ppm.^{13}C NMR (CDCl$_3$, 100 MHz): δ=197.7 (s, C=O), 152.9 (s, Ar-C), 152.3 (s, Ar-C), 148.3 (s, Ar-C), 148.2 (s, Ar-C), 148.0 (s, Ar-C), 140.1 (s, Ar-C), 129.4 (s, Ar-C), 126.6 (s, Ar-C), 123.5 (s, Ar-C), 122.1 (d, Ar-CH), 108.8 (d, Ar-CH), 108.3 (d, Ar-CH), 107.5 (d, Ar-CH), 105.4 (d, Ar-CH), 101.5 (t, 2H, O-CH$_2$-O), 56.4 (2 × q, 2 × 3H, 2 × Ar-OCH$_3$), 8.8 (q, 3H, O=C-C-CH$_3$) ppm. HR-MS (ESI+) m/z calculated for $[C_{19}H_{17}O_5]^+$=$[M+H]^+$: 325.1071; found 325.1069.

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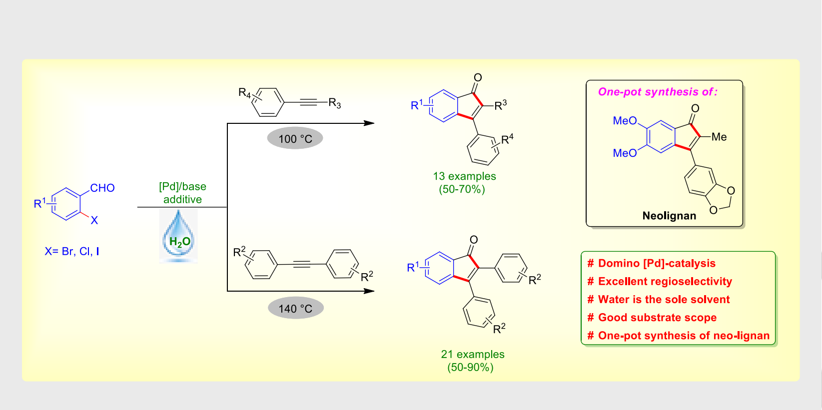

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An Aqueous Mediated Approach for One-pot Regioselective Synthesis of Indenones via Palladium Catalyzed Annulation

Domino [Pd]-catalyzed annulation of *ortho*-halobenzaldehydes with internal alkynes by using water as a sole green solvent, functionalized indenones were synthesized. This protocol showed excellent regioselectivity with unsymmetrical alkylarylacetylenes and the strategy was extended to the synthesis of a neo-lignan natural product.