

Synthesis of Substituted Indenes from Isovanillin via Claisen Rearrangement and Ring-closing Metathesis

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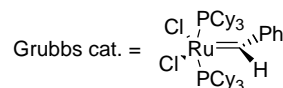
A new synthesis of substituted indenenes was studied. Based on Claisen rearrangement, Wittig reaction and ring-closing metathesis (RCM), a series of substituted indenenes was synthesized from isovanillin in good yields.

Keywords: Isovanillin; Claisen rearrangement; RCM; Indenes.

INTRODUCTION

Indenes, playing an important role as structural units or starting material for the construction of some important organic compounds, have been well recognized.¹ For example, sulindac is an anti-inflammatory drug which has an indene moiety in the structure.² Recently indenenes have been the subject of extensive studies due to their biological activities, which include antibacterial activity,^{3a} antiviral activity,^{3b} antifungal activity,^{3c} apoptosis activity,^{3d} and cytotoxicity to hepatic tumors.^{3e} However, only a few indenenes with functional substituents have been described. They include (i) a [1,5] H shift of isoindene;^{4a} (ii) a reaction of indanone tosylhydrazone with *n*-BuLi;^{4b} (iii) a flash vacuum thermolysis of 1,3,8-nonatriene;^{4c} (iv) a cocondensation of arc generated carbon vapor with cyclooctatetraene at 77 K;^{4d} and (v) a traditional method, by dehydration of corresponding indanol with acid.^{4e} Even though, there still exist some drawbacks such as tedious reaction conditions, commercially unavailable starting materials, and low yields.⁵ Thus, it is necessary to develop a more practical and efficient method for the preparation of substituted indenenes. Since 1995 Grubbs et al.⁶ discovered a novel ruthenium-benzylidene carbene complex (Grubbs cat.) catalyzed ring closing olefin metathesis (RCM), it has been widely and rapidly applied in organic synthesis in many aspects.⁷ Until the present no attention has been paid to apply this RCM reaction to indenenes chemistry.

Recently we reported a novel method for the synthesis of substituted naphthalenes.⁸ It turned out to be an efficient



method for introduction of functional substituents in naphthalenes. In continuation of studies, herein we would like to disclose a versatile and novel strategy for the synthesis of poly-substituted indenenes by the following protocols (Scheme 1).

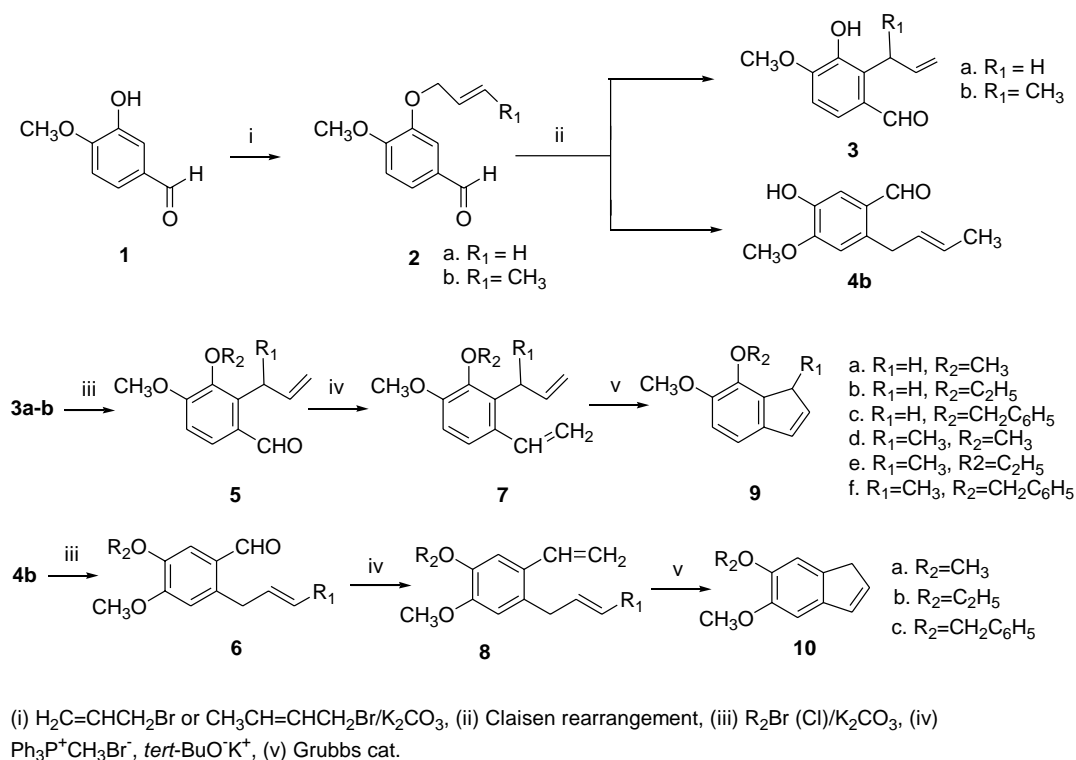
(i) various allylisovanillins (**2a-b**) prepared from *o*-alkylation of isovanillin with corresponding alkyl halide underwent [3,3] sigmatropic (Claisen) rearrangement to furnish *ortho* (**3a-b**) and (or) *para*-product (**4b**); (ii) followed by *o*-alkylation with various alkyl halides to give corresponding dialkoxyl derivatives as key intermediates (**5a-f**, **6a-e**); (iii) subsequently the key intermediates were allowed to react with methylene ylide, generated from triphenylphosphonium methyl bromide and potassium *tert*-butoxide *in situ* to lead a carbon carbon double bond selectively from the corresponding carbonyl compounds (**7a-f**, **8a-c**); (iv) and then by treating these allyl vinyl benzenes with Grubbs catalyst to undergo RCM, it successfully produced a series of substituted indenenes (**9a-f**, **10a-c**) in good overall yields.

RESULTS AND DISCUSSION

As in the general procedure and in our previous report,⁸ isovanillin (**1**) was alkylated with various allylic halides such

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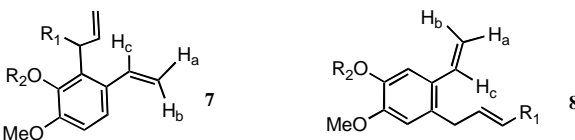
Scheme I



as allyl bromide and 1-bromo-2-butene in anhydrous acetone in the presence of potassium carbonate to give various allyl-isovanillins (**2a-b**) in yields of 88-92%, respectively. Followed by Claisen rearrangement of these allyl-isovanillins (**2a-b**), the different ratios of *ortho* and *para* products was given. Subsequently the products of Claisen rearrangement, **3a**, **3b**, and **4b**, were alkylated as in the general procedure with various alkyl halides such as methyl iodide, ethyl iodide, and benzyl bromide in anhydrous acetone in the presence of potassium carbonate to give **5a-f** and **6a-c** in yields of 80-98%, respectively. The structures of **5a-f**, and **6a-c** are supported by their ^1H and ^{13}C NMR spectra. Following treatment of **5a-f** and **6a-c** with methyl triphenylphosphorus bromide and potassium *tert*-butoxide to undergo Wittig reaction, the desired allyl vinylbenzenes **7a-f** and **8a-c** in yields of 76-90% were given. The chemical elucidation of **7a-f** and **8a-c** can be confirmed by examining the new formation of a vinyl group or the disappearance of a formyl group in ^1H -NMR or ^{13}C -NMR spectra compared with the starting materials **5a-f** and **6a-c**. For example, the vinyl group of **7a** can be easily verified by examining their proton signals in ^1H -NMR, which showed three doublet-doublet splits at δ 5.18, 5.54 and 6.85 with coupling constant, $J_{\text{cis-gem}}$ 11.0 Hz, and 1.5 Hz; $J_{\text{trans-gem}}$ 17.5 Hz, and 1.5 Hz; and $J_{\text{trans-cis}}$ 17.5 Hz, and 11.0 Hz, respectively. In addition, high-resolution mass spectro-

scopy showed the expected molecular ion of **7a** at m/z 204.1152 ($\text{C}_{13}\text{H}_{16}\text{O}_2$ requires M , 204.1150). The vinyl group characteristic protons of **7a-f** and **8a-c** are summarized in Table 1. Furthermore the signal corresponding to the typical carbonyl carbon of starting materials **5a-f** and **6a-c** around 189.6-191.5 ppm has disappeared in the ^{13}C -NMR spectra of **7a-f** and **8a-c**, indicating the work of a Wittig reaction.

Finally, treating these allyl vinylbenzenes **7a-f**, and **8a-c**, respectively, with 5% mole Grubbs catalyst in 0.05 M anhydrous CH_2Cl_2 to undergo RCM, successfully gave 7-alkoxy-6-methoxyindenes (**9a-c**), 7-alkoxy-6-methoxy-1-methylindenes (**9d-f**), and 5-alkoxy-6-methoxyindenes (**10a-c**) in yields of 92-96%. Grubbs catalyst is a highly active and functional group-tolerant catalyst for RCM reactions,⁹ and the presence of alkoxy groups also gave a satisfying results in our experimental cases. The structures of final products, indenes **9a-f** and **10a-c**, were assigned and confirmed by their ^1H and ^{13}C NMR. The ^1H NMR spectra of **9a-f** and **10a-c** show two new olefinic signals at 6.25-6.44 ppm and 6.60-6.79 ppm and loss of four olefinic protons compared to the starting materials; their ^1H -NMR spectra are summarized in Table 2. Further structural proof for the indenes substructure came from the 2D NMR spectroscopy. The NOESY spectrum of indenes **10c** shows the relatively strong intensity of (a) H-1 \leftrightarrow H-2, H-7; (b) OMe \leftrightarrow H-7; (c) OCH $_2$ Ph \leftrightarrow H-4,

Table 1. The Vinyl Protons of Allylvinylbenzenes **7a-f** and **8a-c** in $^1\text{H-NMR}$ Spectra


Entry	H _a (dd, $J = 11.0, 1.5$ Hz)	H _b (dd, $J = 17.5, 1.5$ Hz)	H _c (dd, $J = 17.5, 11.0$ Hz)
7a	5.18	5.54	6.85
7b	5.17	5.53	6.86
7c	5.18	5.54	6.85
7d	5.14	5.44	7.02
7e	5.11	5.44	7.03
7f	5.11	5.44	7.03
8a	5.19	5.54	6.91
8b	5.18	5.52	6.90
8c	5.14	5.41	6.86

Table 2. The Chemical Shifts of Substituted Indenes **9a-f** and **10a-c** in $^1\text{H-NMR}$ Spectra

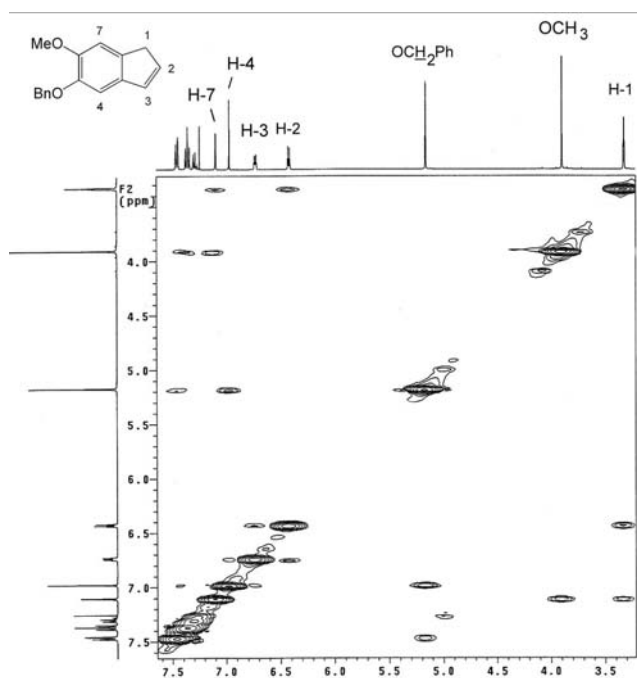
Entry	R ₁	R ₂	H-1	H-2	H-3	H-4	H-5	H-7
9a	H	Me	3.46 (dd, $J = 2.0, 0.8$ Hz)	6.43 (dt, $J = 5.5, 2.0$ Hz)	6.79 (dt, $J = 5.5, 0.8$ Hz)	7.06 (d, $J = 8.5$ Hz)	6.87 (d, $J = 8.5$ Hz)	—
9b	H	Et	3.42 (dd, $J = 2.0, 0.8$ Hz)	6.41 (dt, $J = 5.5, 2.0$ Hz)	6.77 (dt, $J = 5.5, 0.8$ Hz)	7.05 (d, $J = 8.1$ Hz)	6.85 (d, $J = 8.1$ Hz)	—
9c	H	Bn	3.25 (dd, $J = 2.0, 0.8$ Hz)	6.34 (dt, $J = 5.5, 2.0$ Hz)	6.73 (dt, $J = 5.5, 0.8$ Hz)	7.05 (d, $J = 8.0$ Hz)	6.86 (d, $J = 8.0$ Hz)	—
9d	Me	Me	3.66 (qdd, $J = 7.5, 2.0, 0.8$ Hz)	6.32 (dd, $J = 5.5, 2.0$ Hz)	6.64 (dd, $J = 5.5, 0.8$ Hz)	7.00 (d, $J = 8.1$ Hz)	6.83 (d, $J = 8.1$ Hz)	—
9e	Me	Et	3.61 (qdd, $J = 7.5, 2.0, 0.8$ Hz)	6.29 (dd, $J = 5.6, 2.0$ Hz)	6.61 (dd, $J = 5.5, 0.8$ Hz)	6.97 (d, $J = 8.0$ Hz)	6.80 (d, $J = 8.0$ Hz)	—
9f	Me	Bn	3.46 (qdd, $J = 7.5, 2.0, 0.8$ Hz)	6.25 (dt, $J = 5.5, 2.0$ Hz)	6.60 (dt, $J = 5.5, 0.8$ Hz)	6.98 (d, $J = 8.0$ Hz)	6.81 (d, $J = 8.0$ Hz)	—
10a	—	Me	3.33 (dd, $J = 2.0, 0.8$ Hz)	6.44 (dt, $J = 5.5, 2.0$ Hz)	6.79 (dt, $J = 5.5, 0.8$ Hz)	6.97 (s)	—	7.07 (s)
10b	—	Et	3.34 (dd, $J = 2.0, 0.8$ Hz)	6.44 (dt, $J = 5.5, 2.0$ Hz)	6.78 (dt, $J = 5.5, 0.8$ Hz)	6.97 (s)	—	7.08 (s)
10c	—	Bn	3.33 (dd, $J = 2.0, 0.8$ Hz)	6.43 (dd, $J = 5.5, 1.8$ Hz)	6.74 (dd, $J = 5.5, 1.8$ Hz)	7.01 (s)	—	7.26 (s)

$\text{OCH}_2\text{C}_6\text{H}_5$, cross-peaks point to a short distance between these proton (Fig. 1). The other NOESY spectrum of **9c** shows cross-peaks of (a) H-1 \leftrightarrow OCH_2Ph , H-2; (b) $\text{OMe} \leftrightarrow$ H-5. Thus, the indenenes structure **9a-f** and **10a-c** are character-

ized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and NOESY spectrum. Due to the fact only one set of signals in both $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra was found in the structures of indenenes **9a-f** and **10a-c**, it means no other isomer was found in our reaction condi-

tions. The results are compiled in Table 3.

In conclusion, based on Claisen rearrangement, Wittig reaction, and RCM, we have established a straightforward, versatile, and novel route to transform isovanillin into a number of potential substituted indenenes, and the overall yields range from 65% to 76%, calculated from compound **3** or **4** (Table 3). The sequence works well for substituted alkoxyindenes such as 7-alkoxy-6-methoxyindenes, 7-alkoxy-6-methoxy-1-methylindenes, and 5-alkoxy-6-methoxyindenes. Among these products, many have not been previously reported. The application of our synthetic strategy to some potential compounds is currently in progress in our laboratory.



EXPERIMENTAL

Melting points (Yanaco micro melting-point apparatus) are uncorrected. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were obtained on a Varian Gemini-300 or Varian Unity plus 400 or Varian Unity Inova 500 Spectrometer. Chemical shifts are measured in parts per million with respect to TMS. Mass spectra were recorded on a Chem/hp/middle instrument. The high-resolution mass spectra were performed on a JEOL JMS SX/SX 102A. Silica gel (230-400 mesh) for column chromatography and the precoated silica gel plate (60 F-254) for TLC were purchased from E. Merck Co. UV light (254 nm) was used to detect spots on TLC plates after development. 3-Hydroxy-4-methoxybenzaldehyde (isovanillin) (**1**) purchased from TCI (Tokyo Kasei Industry) was used directly without purification. Grubbs catalyst was purchased from Fluca Company.

General procedure for the preparation of vinylbenzenes (**7a-f**) and (**8a-c**)

To a stirred suspension of methyl triphosphonium bromide (2.0 g, 5.5 mmol) in dry THF (20 mL) at 0 °C, the powder of potassium *tert*-butoxide (0.6 g, 5.5 mmol) was added under dried nitrogen, in several portions over 5 minutes. After 10 min. of addition, the yellowish white suspension was formed, which was respectively added dropwise with aldehydes **5a-f** (5 mmol) or **6a-c** (5 mmol) in THF (20 mL). The suspension was continually stirred for 2-3 h until the aldehyde was consumed completely under TLC (EA/n-hexane = 1/6) monitoring, and then was concentrated under vacuum. The residue was added with water (20 mL), and extracted with ethyl acetate (15 mL \times 5). The organic layer was washed with brine, and then dried with anhydrous MgSO_4 , and then filtered. The filtrate was concentrated under vacuum to give a

pale yellow residue. Finally the given residue was subjected to chromatographic column (*n*-hexane/EA = 8/1) to afford pure *o*-allyl vinylbenzenes **7a-f** and **8a-c** in good yields.

2-Allyl-3,4-dimethoxy-1-vinylbenzenes (7a)

Pure **7a** (0.93 g, 83%) was obtained as pale yellow liquid, R_f 0.65 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 3.51 (ddd, $J = 6.0$ Hz, 1.8 Hz, 1.8 Hz, 2H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 3.80, 3.87 (each s, 3H, OCH_3), 4.92 (ddd, $J = 17.0$ Hz, 3.3 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 5.01 (ddd, $J = 10.3$ Hz, 3.3 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 5.18 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.54 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.97 (ddt, $J = 17.0$ Hz, 10.3 Hz, 6.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 6.80 (d, $J = 8.5$ Hz, 1H, ArH), 6.85 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.25 (d, $J = 8.5$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3 , 125 MHz) δ 30.15 ($\text{CH}_2=\text{CHCH}_2\text{Ar}$), 55.64, 60.81 (each, OCH_3), 110.40, 113.97, 115.18, 121.27, 130.72, 131.24, 134.34, 136.68, 146.92, 152.29; EI-MS (70 eV) m/z (rel. intensity, %): 204 (M^+ , 69.30), 189 (80.71), 176 (98.49), 174 (66.49), 173 (40.02), 161 (44.59), 159 (45.59), 158 (100), 131 (48.50), 129 (88.28), 128 (57.57), 115 (74.05), 91 (38.93); HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150. Found: 204.1152.

2-Allyl-3-ethoxy-4-methoxy-1-vinylbenzene (7b)

Pure **7b** (0.96 g, 80%) was obtained as pale yellow liquid; R_f 0.70 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.37 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 3.52 (ddd, $J = 5.9$ Hz, 1.8 Hz, 1.8 Hz, 2H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 3.84 (s, 3H, OCH_3), 3.98 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 4.91 (ddd, $J = 17.0$ Hz, 3.8 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 5.00 (ddd, $J = 10.3$ Hz, 3.8 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 5.17 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.53 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.95 (ddt, $J = 17.0$ Hz, 10.3 Hz, 5.9 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 6.79 (d, $J = 8.5$ Hz, 1H, ArH), 6.86 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.24 (d, $J = 8.5$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3 , 125 MHz) δ 15.65 (OCH_2CH_3), 30.32 ($\text{CH}_2=\text{CHCH}_2\text{Ar}$), 55.62 (OCH_3), 68.82 (OCH_2CH_3), 110.31, 113.80, 115.06, 121.06, 130.65, 131.35, 134.45, 136.70, 146.14, 152.40; EI-MS (70 eV) m/z (rel. intensity, %) 218 (M^+ , 50.53), 190 (59.28), 175 (28.36), 162 (26.06), 161 (23.86), 157 (32.35), 147 (31.94), 144 (20.85), 143 (100), 129 (71.96), 128 (38.55), 115 (80.41), 103 (21.52), 91 (30.24); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1307.

2-Allyl-3-benzyloxy-4-methoxy-1-vinylbenzene (7c)

Pure **7c** (1.39 g, 90%) was obtained as pale yellow liquid; R_f 0.70 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500

MHz) δ 3.51 (ddd, $J = 5.6$ Hz, 1.8 Hz, 1.8 Hz, 2H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 3.86 (s, 3H, OCH_3), 4.89 (ddd, $J = 17.0$ Hz, 3.5 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 4.96 (s, 2H, $\text{OCH}_2\text{C}_6\text{H}_5$), 4.99 (ddd, $J = 10.3$ Hz, 3.5 Hz, 1.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 5.18 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.54 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.92 (ddt, $J = 17.0$ Hz, 10.3 Hz, 5.6 Hz, 1H, $\text{CH}_2=\text{CHCH}_2\text{Ar}$), 6.82 (d, $J = 8.5$ Hz, 1H, ArH), 6.85 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.27 (d, $J = 8.5$ Hz, 1H, ArH), 7.31-7.47 (m, 5H, $\text{OCH}_2\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 30.32 ($\text{CH}_2=\text{CHCH}_2\text{Ar}$), 55.67 (OCH_3), 74.70 ($\text{OCH}_2\text{C}_6\text{H}_5$), 110.45, 113.91, 115.22, 121.41, 127.73, 127.92, 128.29, 130.73, 131.46, 134.35, 136.62, 137.93, 145.80, 152.38; EI-MS (70 eV) m/z (rel. intensity, %) 280 (M^+ , 5.13), 189 (26.14), 161 (8.10), 157 (7.02), 146 (5.41), 143 (12.30), 131 (8.31), 129 (13.46), 128 (8.92), 117 (6.49), 115 (10.93), 92 (8.20), 91 (100), 65 (8.26); HRMS calcd for $\text{C}_{19}\text{H}_{20}\text{O}_2$: 280.1463. Found: 280.1465.

3,4-Dimethoxy-2-(1-methyl-2-propenyl)-1-vinylbenzene (7d)

Pure **7d** (0.97 g, 81%) was obtained as pale yellow liquid; R_f 0.77 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.41 (d, $J = 7.5$ Hz, 3H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 3.79, 3.86 (each s, 3H, OCH_3), 4.13 (m, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.01 (dd, $J = 17.0$ Hz, 2.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.05 (dd, $J = 10.3$ Hz, 2.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.14 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.44 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 6.16 (ddd, $J = 17.0$ Hz, 10.3 Hz, 5.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 6.78 (d, $J = 8.5$ Hz, 1H, ArH), 7.02 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.18 (d, $J = 8.5$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3 , 125 MHz) δ 18.94 ($\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 35.32 ($\text{CH}_2=\text{CHCHAr}$), 55.64, 60.84 (each, OCH_3), 110.29, 112.89, 113.86, 122.52, 130.88, 135.80, 136.67, 142.83, 146.93, 152.48; EI-MS (70 eV) m/z (rel. intensity, %) 218 (M^+ , 44.73), 203 (66.16), 190 (35.80), 189 (100), 188 (76.70), 175 (39.85), 174 (51.61), 173 (55.78), 172 (88.06), 159 (45.18), 158 (44.36), 145 (47.87), 143 (52.31), 129 (47.51), 115 (91.24), 91 (35.00); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1307.

3-Ethoxy-4-methoxy-2-(1-methyl-2-propenyl)-1-vinylbenzene (7e)

Pure **7e** (0.98 g, 77%) was obtained as pale yellow liquid; R_f 0.78 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.38 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.41 (d, $J = 7.5$ Hz, 3H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 3.84 (s, 3H, OCH_3), 3.98 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 4.22 (m, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$),

5.01 (dd, $J = 17.0$ Hz, 2.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.04 (dd, $J = 10.3$ Hz, 2.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.11 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.44 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 6.15 (ddd, $J = 17.0$ Hz, 10.3 Hz, 5.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 6.77 (d, $J = 8.5$ Hz, 1H, ArH), 7.03 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.18 (d, $J = 8.5$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3 , 125 MHz) δ 15.56 (OCH_2CH_3), 18.80 ($\text{CH}_2=\text{CHCH}_3$), 34.90 ($\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 55.62 (OCH_3), 68.79 (OCH_2CH_3), 110.18, 112.83, 113.45, 122.36, 130.85, 135.93, 136.73, 142.82, 145.91, 152.53; EI-MS (70 eV) m/z (rel. intensity, %) 232 (M^+ , 45.35), 203 (47.03), 175 (34.06), 171 (29.38), 157 (91.16), 145 (27.65), 144 (25.66), 143 (100), 129 (56.41), 128 (56.06), 115 (64.87); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: 232.1463. Found: 232.1463.

3-Benzyloxy-4-methoxy-2-(1-methyl-2-propenyl)-1-vinylbenzene (7f)

Pure **7f** (1.33 g, 82%) was obtained as pale yellow liquid; R_f 0.77 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 400 MHz) δ 1.35 (d, $J = 7.2$ Hz, 3H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 3.86 (s, 3H, OCH_3), 4.24 (m, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 4.95 (s, 2H, $\text{OCH}_2\text{C}_6\text{H}_5$), 4.98 (dd, $J = 17.2$ Hz, 1.2 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.02 (dd, $J = 10.6$ Hz, 1.2 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 5.11 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.44 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 6.56 (ddd, $J = 17.2$ Hz, 10.6 Hz, 5.0 Hz, 1H, $\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 6.80 (d, $J = 8.8$ Hz, 1H, ArH), 7.03 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.21 (d, $J = 8.8$ Hz, 1H, ArH), 7.31-7.47 (m, 5H, $\text{OCH}_2\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 18.80 ($\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 34.93 ($\text{CH}_2=\text{CHCH}_3\text{CHAr}$), 55.68 (OCH_3), 74.74 ($\text{OCH}_2\text{C}_6\text{H}_5$), 110.38, 112.94, 113.51, 122.72, 127.77, 128.07, 128.33, 130.97, 135.92, 136.89, 137.86, 142.74, 145.58; EI-MS (70 eV) m/z (rel. intensity, %) 294 (M^+ , 4.10), 203 (25.11), 175 (8.12), 171 (9.23), 161 (10.90), 157 (11.91), 145 (7.54), 143 (14.90), 129 (8.78), 128 (14.74), 115 (17.14), 91 (98.20); HRMS calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$: 294.1620. Found: 294.1620.

2-(2-Butenyl)-4,5-dimethoxy-1-vinylbenzene (8a)

Pure **8a** (0.92 g, 77%) was obtained as pale yellow liquid, R_f 0.54 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.66 (dd, $J = 6.5$ Hz, 1.5 Hz, 3H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.32 (d, $J = 6.8$ Hz, 2H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.87, 3.89 (each s, 3H, OCH_3), 5.19 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CH}_2\text{Ar}$), 5.41 (dq, $J = 14.0$ Hz, 6.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 5.54 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CH}_2\text{Ar}$), 5.55 (dtd, $J = 14.0$ Hz, 6.8 Hz, 1.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 6.64, 7.03 (each s, 1H, ArH), 6.91 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.81 (CH_3), 35.78

($\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 55.80, 55.85 (each, OCH_3), 108.28, 112.52, 113.11, 126.04, 128.57, 129.65, 130.85, 134.09, 147.38, 148.76; EI-MS (70 eV) m/z (rel. intensity, %) 218 (M^+ , 88.71), 203 (90.21), 189 (100), 188 (68.90), 176 (46.40), 174 (43.09), 172 (40.73), 128 (47.51), 115 (60.36); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_2$: 218.1307. Found: 218.1307.

2-(2-Butenyl)-5-ethoxy-4-methoxy-1-vinylbenzene (8b)

Pure **8b** (1.03 g, 81%) was obtained as pale yellow liquid, R_f 0.63 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.46 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 1.66 (dd, $J = 6.5$ Hz, 1.5 Hz, 3H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.32 (d, $J = 6.5$ Hz, 2H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.86 (s, 3H, OCH_3), 4.12 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 5.18 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.41 (dq, $J = 14.0$ Hz, 6.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 5.52 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.56 (dtd, $J = 14.0$ Hz, 6.5 Hz, 1.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 6.64, 7.04 (each s, 1H, ArH), 6.90 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.83 (OCH_2CH_3), 17.86 ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 35.84 ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 55.91 (OCH_3), 64.40 (OCH_2CH_3), 109.98, 112.79, 113.06, 126.07, 128.60, 129.71, 130.92, 134.16, 146.70, 149.15; EI-MS (70 eV) m/z (rel. intensity, %) 232 (M^+ , 63.50), 203 (39.19), 190 (38.13), 189 (81.99), 175 (100), 174 (37.40), 160 (33.04), 143 (32.32), 131 (33.48), 129 (43.16), 128 (49.94), 115 (50.74), 91 (33.62); HRMS calcd for $\text{C}_{15}\text{H}_{20}\text{O}_2$: 232.1463. Found: 232.1463.

5-Benzyloxy-2-(2-butenyl)-4-methoxy-1-vinylbenzene (8c)

Pure **8c** (1.26 g, 78%) was obtained as pale yellow liquid; R_f 0.66 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.66 (dd, $J = 6.5$ Hz, 1.5 Hz, 3H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.31 (d, $J = 6.5$ Hz, 2H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 3.88 (s, 3H, OCH_3), 5.14 (dd, $J = 11.0$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.15 (s, 2H, $\text{OCH}_2\text{C}_6\text{H}_5$), 5.41 (dq, $J = 15.1$ Hz, 6.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 5.41 (dd, $J = 17.5$ Hz, 1.5 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 5.54 (dtd, $J = 15.1$ Hz, 6.5 Hz, 1.5 Hz, 1H, $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 6.66, 7.06 (each s, 1H, ArH), 6.86 (dd, $J = 17.5$ Hz, 11.0 Hz, 1H, $\text{CH}_2=\text{CHAr}$), 7.31-7.46 (m, 5H, $\text{OCH}_2\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 17.88 ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 35.87 ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{Ar}$), 56.00 (OCH_3), 71.30 ($\text{OCH}_2\text{C}_6\text{H}_5$), 111.44, 113.11, 113.21, 126.151, 127.40, 127.80, 128.50, 128.66, 129.64, 131.54, 133.99, 137.32, 146.63, 149.54; EI-MS (70 eV) m/z (rel. intensity, %) 294 (M^+ , 17.26), 203 (39.72), 175 (16.19), 143 (19.72), 133 (9.30), 1129 (9.80), 128 (21.41), 117 (9.24), 115 (15.52); HRMS calcd for $\text{C}_{20}\text{H}_{22}\text{O}_2$: 294.1620. Found: 294.1620.

General procedure for preparation of indenenes (9a-f) and (10a-c)

Compound **7a-f** or **8a-c** (1 mmol) dissolved in anhydrous CH_2Cl_2 (20 mL), was added with Grubbs catalyst (5% mol). The mixture was stirred for 2 h at ambient temperature under dry argon. Finally the solvent was removed under reduced pressure, and the residue was subjected to a silica gel column (5:1 hexane/MTBE) or to distill under vacuum to give **9a-f**, and **10a-c** respectively.

6,7-Dimethoxyindene (9a)^{10a}

Pure **9a** (0.17 g, 94%) was obtained as colorless liquid; R_f 0.63 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 3.46 (dd, $J = 2.0$ Hz, 0.8 Hz, 2H, H-1), 3.89, 3.95 (each s, 3H, OCH_3), 6.43 (dt, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.79 (dt, $J = 5.5$ Hz, 0.8 Hz, 1H, H-3), 6.87 (d, $J = 8.5$ Hz, 1H, H-4), 7.06 (d, $J = 8.5$ Hz, 1H, H-5); ^{13}C NMR (CDCl_3 , 125 MHz) δ 36.79 (C-1), 56.33, 60.00 (each OCH_3), 111.23, 115.80, 131.51, 132.38, 135.22, 139.59, 145.40, 150.10; EI-MS (70 eV) m/z (rel. intensity, %) 176 (M^+ , 100), 161 (70.16), 145 (16.69), 133 (44.40), 118 (41.05), 115 (33.71), 105 (37.56), 103 (20.12), 90 (17.35), 89 (26.05); HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: 176.0837. Found: 176.0831.

7-Ethoxy-6-methoxyindene (9b)

Pure **9b** (0.17 g, 92%) was obtained as colorless liquid, R_f 0.63 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 300 MHz) δ 1.38 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 3.42 (dd, $J = 2.0$ Hz, 0.8 Hz, 2H, H-1), 3.86 (s, 3H, OCH_3), 4.17 (q, $J = 7.0$ Hz, 2H, OCH_2CH_3), 6.41 (dt, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.77 (dt, $J = 5.5$ Hz, 0.8 Hz, 1H, H-3), 6.85 (d, $J = 8.1$ Hz, 1H, H-4), 7.05 (d, $J = 8.1$ Hz, 1H, H-5); ^{13}C NMR (CDCl_3 , 75 MHz) δ 15.67 (OCH_2CH_3), 36.87 (C-1), 56.35 (OCH_3), 68.06 (OCH_2CH_3), 111.36, 115.78, 131.49, 132.34, 136.28, 139.41, 144.37, 150.47; EI-MS (70 eV) m/z (rel. intensity, %) 190 (M^+ , 86.73), 162 (41.43), 161 (22.24), 147 (100), 133 (21.57), 130 (24.76), 119 (33.21), 118 (26.56), 115 (20.26), 105 (21.76), 102 (21.82), 91 (25.44), 89 (23.36); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.0994. Found: 190.0996.

7-Benzoyloxy-6-methoxyindene (9c)

Pure **9c** (0.23 g, 93%) was obtained as colorless liquid, R_f 0.51 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 3.25 (dd, $J = 2.0$ Hz, 0.8 Hz, 1H, H-1), 3.88 (s, 3H, OCH_3), 5.11 (s, 2H, $\text{OCH}_2\text{C}_6\text{H}_5$), 6.34 (dt, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.73 (dt, $J = 5.5$ Hz, 0.8 Hz, 1H, H-3), 6.86, 7.05 (each d, $J = 8.0$ Hz, 1H, H-4 and H-5), 7.29-7.43 (m, 5H, $\text{OCH}_2\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 36.78 (C-1), 56.39 (OCH_3),

74.30 ($\text{OCH}_2\text{C}_6\text{H}_5$), 111.50, 116.06, 127.81, 128.12, 128.30, 131.33, 132.45, 134.32, 136.59, 139.36, 144.21, 150.45; EI-MS (70 eV) m/z (rel. intensity, %) 252 (M^+ , 15.61), 161 (38.63), 133 (19.35), 118 (18.57), 105 (21.31), 92 (11.92), 91 (100), 90 (12.31), 89 (13.69); HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: 252.1150. Found: 252.1159.

6,7-Dimethoxy-1-methylindene (9d)

Pure **9d** (0.18 g, 92%) was obtained as colorless liquid; R_f 0.76 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.37 (d, $J = 7.5$ Hz, 3H, CH_3), 3.66 (qdd, $J = 7.5$ Hz, 2.0 Hz, 2.0 Hz, 1H, H-1), 3.87 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 6.32 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.64 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-3), 6.83 (d, $J = 8.0$ Hz, 1H, H-4), 7.00 (d, $J = 8.0$ Hz, 1H, H-5); ^{13}C NMR (CDCl_3 , 125 MHz) δ 15.22 (CH_3), 44.14 (C-1), 56.21 (OCH_3), 60.36 (OCH_3), 111.31 (C-2), 115.96 (C-3), 129.25, 138.55, 140.13, 140.88, 145.90, 150.80; EI-MS (70 eV) m/z (rel. intensity, %) 190 (M^+ , 84.79), 175 (76.40), 160 (19.15), 159 (33.80), 147 (19.57), 144 (14.43), 143 (25.28), 132 (26.14), 131 (21.37), 129 (14.86), 128 (13.63); 115 (100), 103 (18.01), 89 (14.08); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.0994. Found: 190.0995.

7-Ethoxy-6-methoxy-1-methylindene (9e)

Pure **9e** (0.19 g, 93%) was obtained as colorless liquid, R_f 0.78 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 400 MHz) δ 1.37 (d, $J = 7.5$ Hz, 3H, CH_3), 1.39 (t, $J = 7.0$ Hz, 3H, OCH_2CH_3), 3.61 (qdd, $J = 7.5$ Hz, 2.0 Hz, 2.0 Hz, 1H, H-1), 3.82 (s, 3H, OCH_3), 4.20 (q, $J = 7.0$ Hz, 1H, OCH_2CH_3), 6.29 (dd, $J = 5.6$ Hz, 2.0 Hz, 1H, H-2), 6.61 (dd, $J = 5.6$ Hz, 2.0 Hz, 1H, H-3), 6.80 (d, $J = 8.0$ Hz, 1H, H-4), 6.97 (d, $J = 8.0$ Hz, 1H, H-5); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.98 (OCH_2CH_3), 15.73 (CH_3), 44.20 (C-1), 56.06 (OCH_3), 68.09 (OCH_2CH_3), 111.23, 115.72, 129.16, 138.39, 139.94, 141.09, 144.82, 150.89; EI-MS (70 eV) m/z (rel. intensity, %) 204 (M^+ , 64.88), 176 (21.99), 175 (31.94), 161 (61.89), 160 (10.58), 144 (29.63), 143 (38.39), 132 (12.17), 131 (15.94), 128 (10.36), 116 (24.26), 115 (100), 103 (18.09); HRMS calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2$: 204.1150. Found: 204.1153.

7-Benzoyloxy-6-methoxy-1-methylindene (9f)

Pure **9f** (0.26 g, 96%) was obtained as colorless liquid; R_f 0.76 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 400 MHz) δ 1.33 (d, $J = 7.5$ Hz, 3H, CH_3), 3.46 (qdd, $J = 7.5$ Hz, 2.0 Hz, 2.0 Hz, 1H, H-1), 3.83 (s, 3H, OCH_3), 5.09 (m, 2H, $\text{OCH}_2\text{C}_6\text{H}_5$), 6.25 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.60 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-3), 6.81 (d, $J = 8.0$ Hz, 1H, H-4), 6.98 (d, $J = 8.0$ Hz, 1H, H-5), 7.29-7.47 (m, 5H, $\text{OCH}_2\text{C}_6\text{H}_5$);

^{13}C NMR (CDCl_3 , 100 MHz) δ 15.16 ($\underline{\text{C}}\text{H}_3$), 44.23 (C-1), 56.20 ($\text{O}\underline{\text{C}}\text{H}_3$), 74.36 ($\text{O}\underline{\text{C}}\text{H}_2\text{C}_6\text{H}_5$), 111.44, 116.08, 127.71, 127.93, 128.25, 129.12, 138.13, 138.48, 140.12, 141.38, 144.68, 150.88; EI-MS (70 eV) m/z (rel. intensity, %) 266 (M^+ , 13.47), 176 (11.17), 175 (97.37), 143 (27.16), 132 (10.06), 131 (13.23), 116 (13.30), 115 (91.23), 103 (14.34), 91 (100); HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: 266.1307. Found: 266.1301.

5,6-Dimethoxyindene (10a)^{10b}

Pure **10a** (0.16 g, 90%) was obtained as colorless crystals, mp 70-71 °C; R_f 0.53 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 400 MHz) δ 3.33 (dd, $J = 2.0$ Hz, 0.8 Hz, 2H, H-1), 3.89, 3.90 (each s, 3H, $\text{O}\underline{\text{C}}\text{H}_3$), 6.44 (dd, $J = 5.6$ Hz, 2.0 Hz, 1H, H-2), 6.79 (dd, $J = 5.6$ Hz, 0.8 Hz, 1H, H-3), 6.96, 7.07 (each s, 1H, H-7 and H-4); ^{13}C NMR (CDCl_3 , 100 MHz) δ 38.99 (C-1), 56.02, 56.15 (each $\text{O}\underline{\text{C}}\text{H}_3$), 104.49, 107.92, 131.61, 132.70, 136.04, 137.51, 147.10, 148.13; EI-MS (70 eV) m/z (rel. intensity, %): 176 (M^+ , 100), 161 (65.51), 133 (40.46), 118 (26.82), 115 (32.24), 105 (51.39), 103 (21.16), 90 (22.90), 89 (26.75); HRMS calcd for $\text{C}_{11}\text{H}_{12}\text{O}_2$: 176.0837. Found: 176.0834.

5-Ethoxy-6-methoxyindene (10b)^{10c}

Pure **10b** (0.17 g, 90%) was obtained as colorless crystals, mp 65-66 °C; R_f 0.62 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 1.48 (t, $J = 7.0$ Hz, 3H, $\text{O}\underline{\text{C}}\text{H}_2\text{C}\underline{\text{H}}_3$), 3.34 (dd, $J = 2.0$ Hz, 0.8 Hz, 2H, H-1), 3.89 (s, 3H, $\text{O}\underline{\text{C}}\text{H}_3$), 4.12 (q, $J = 7.0$ Hz, 2H, $\text{O}\underline{\text{C}}\text{H}_2\text{C}\underline{\text{H}}_3$), 6.44 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.78 (dd, $J = 5.5$ Hz, 0.8 Hz, 1H, H-3), 6.97, 7.08 (each s, 1H, H-7 and H-4); ^{13}C NMR (CDCl_3 , 125 MHz) δ 14.88 ($\text{O}\underline{\text{C}}\text{H}_2\text{C}\underline{\text{H}}_3$), 39.05 (C-1), 56.30 ($\text{O}\underline{\text{C}}\text{H}_3$), 64.56 ($\text{O}\underline{\text{C}}\text{H}_2\text{C}\underline{\text{H}}_3$), 106.14, 108.22, 131.67, 132.70, 136.16, 137.55, 147.37, 147.47; EI-MS (70 eV) m/z (rel. intensity, %) 190 (M^+ , 89.04), 162 (50.55), 161 (40.31), 147 (100), 133 (30.89), 130 (40.35), 119 (32.00), 118 (21.49), 115 (26.33), 105 (41.76), 102 (22.08), 91 (27.95), 90 (23.19), 89 (26.02); HRMS calcd for $\text{C}_{12}\text{H}_{14}\text{O}_2$: 190.0994. Found: 190.0992.

5-Benzoyloxy-6-methoxyindene (10c)^{10d}

Pure **10c** (0.23 g, 93%) was obtained as colorless crystals, mp 85-87 °C (lit. mp 83-85 °C); R_f 0.65 (EA/*n*-hexane = 1/7); ^1H NMR (CDCl_3 , 500 MHz) δ 3.33 (dd, $J = 2.0$ Hz, 0.8 Hz, 2H, H-1), 3.91 (s, 3H, $\text{O}\underline{\text{C}}\text{H}_3$), 5.17 (s, 2H, $\text{O}\underline{\text{C}}\text{H}_2\text{C}_6\text{H}_5$), 6.43 (dd, $J = 5.5$ Hz, 2.0 Hz, 1H, H-2), 6.74 (dd, $J = 5.5$ Hz, 0.8 Hz, 1H, H-3), 7.01, 7.26 (each s, 1H, H-7 and H-4), 7.30-7.46 (m, 5H, $\text{O}\underline{\text{C}}\text{H}_2\text{C}_6\text{H}_5$); ^{13}C NMR (CDCl_3 , 125 MHz) δ 39.07 (C-1), 56.51 ($\text{O}\underline{\text{C}}\text{H}_3$), 71.52 ($\text{O}\underline{\text{C}}\text{H}_2\text{C}_6\text{H}_5$), 107.66,

108.76, 127.26, 127.67, 128.48, 131.67, 132.74, 136.93, 137.54, 137.65, 147.44, 147.99; EI-MS (70 eV) m/z (rel. intensity, %): 252 (M^+ , 27.00), 161 (100), 133 (41.05), 118 (18.50), 115 (21.92), 105 (56.82), 103 (16.19), 91 (84.57), 90 (25.75), 89 (19.36); HRMS calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: 252.1150. Found: 252.1156.

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