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Ruthenium-Catalyzed Regioselective Cyclization of Aromatic Ketones with Alkynes: An Efficient Route to Indenols and Benzofulvenes

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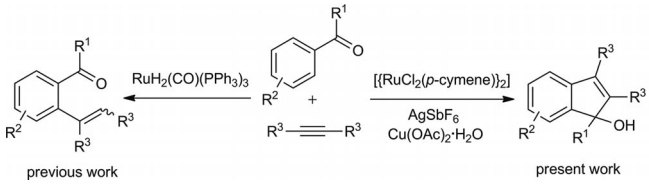
The reactions of substituted acetophenones with diphenylacetylene in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (8 mol-%), and $Cu(OAc)_2{\cdot}H_2O$ (25 mol-%) in 1,2-dichloroethane at 120 °C for 10 h provided substituted indenol derivatives in good-to-excellent yields. Under similar reaction conditions, unsymmetrical alkynes such as 1-phenyl-1-propyne, 1-phenyl-1-butyne, 1-phenyl-2-(trimethylsilyl)-acetylene, and a substituted enyne also reacted efficiently with substituted acetophenones to afford the corresponding indenol derivatives in a highly regioselective manner. The amount of silver salt plays a key role in the reaction. When the amount of silver salt exceeded more than 8 mol-% in the presence of 2 mol-% [{$RuCl_2$(*p*-cymene)}$_2$], a different type of dehydration product, namely a benzofulvene derivative, started to appear. In the presence of 20 mol-% $AgSbF_6$, substituted acetophenones readily reacted with alkynes in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%) to give benzofulvene derivatives in excellent yields. A plausible reaction mechanism is proposed to account for the cyclization reaction.

Introduction

The transition-metal-catalyzed carbocyclization reaction is one of the most efficient methods for constructing carbo- and heterocyclic compounds in one pot.[1] Several approaches have been reported in the literature for the synthesis of cyclic compounds in the presence of metal catalysts.[1] Of these approaches, the cyclization of *o*-haloaromatic carbonyls or imines with π components has been established as a powerful synthetic method.[2] More recently, the cyclization of *o*-acylphenylboronic acids with π components has been used to synthesize cyclic compounds.[3] In carbocyclization reactions, a preactivated coupling partner such as a C–X or C–M reagent is usually required as a starting material to construct the carbo- and heterocyclic compounds. However, if the cyclization could be carried out directly by C–H bond activation instead of with a preactivated species, it would be very useful because this would be highly atom economic as well as an environmentally friendly process.[4–6] In this regard, transition-metal chelation-assisted cyclization of the *ortho* aromatic C–H bond with π components is a very useful method for the construction of cyclic compounds.[6] In general, mostly rhodium complexes have previously been used as catalysts in this cyclization reaction[7,8] and the use of less-expensive ruthenium catalysts in carbocyclization processes is underexplored.[9,10] Very recently, Ackermann et al. reported a ruthenium-catalyzed oxidative cyclization of acrylamides with alkynes[11a,11b] as well as the cyclization of aromatic acids with alkenes.[11c]

In this paper we wish to report the cyclization of aromatic ketones with alkynes in the presence of a less expensive ruthenium catalyst. This method offers a general method for the highly regioselective synthesis of indenols and benzofulvenes in good-to-excellent yields. The reactions of aromatic ketones with alkynes in the presence of [$RuH_2(CO)(PPh_3)_3$] have been reported in the literature,[12a,12b] however, only addition products were observed (Scheme 1). Similar carbonyl-directed C–H activated alkenylation reactions with alkynes have also been studied by other research groups.[12c–12i] In contrast, in this work, cyclic products were exclusively observed for the reaction performed in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (Scheme 1).



Scheme 1.

Results and Discussion

In the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (8 mol-%), and $Cu(OAc)_2{\cdot}H_2O$ (25 mol-%), 4-bromoacetophenone (**1a**) reacted with diphenylacetylene (**2a**) in 1,2-dichloroethane (DCE) at 120 °C for 10 h to give ind-

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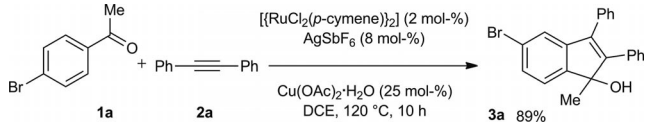
enol derivative **3a** in 89% isolated yield (Scheme 2). The reaction was completely atom economic. Interestingly, only a catalytic amount of oxidant $Cu(OAc)_2·H_2O$ (25 mol-%) was required, whereas in most rhodium-catalyzed reactions stoichiometric amounts of oxidant were used.[7,8] Control experiments revealed that no reaction occurred at all in the absence of $[\{RuCl_2(p\text{-cymene})\}_2]$, $AgSbF_6$, or $Cu(OAc)_2·H_2O$. Note that substituted indenol derivatives are known to show important biological properties such as analgesic, insecticidal, and myorelaxation activity.[13]

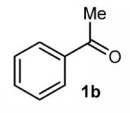
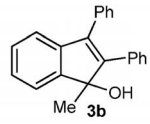
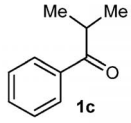
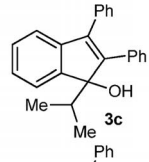
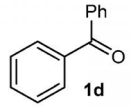
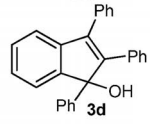
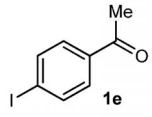
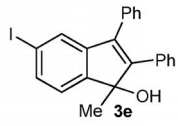
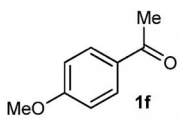
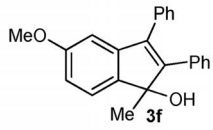
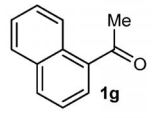
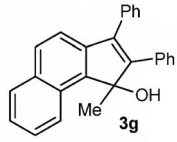
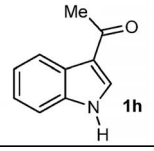
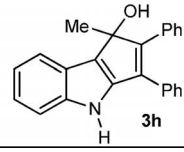


Scheme 2. Reaction of 4-bromoacetophenone (**1a**) with diphenylacetylene (**2a**) in the presence of ruthenium catalyst.

To optimize this ruthenium-catalyzed cyclization reaction, the reaction of **1a** with **2a** in the presence of $[\{RuCl_2(p\text{-cymene})\}_2]$ (2 mol-%) was examined with various solvents, additives (8 mol-%), and $Cu(OAc)_2·H_2O$ (25 mol-%). The reaction was first tested in various solvents. Of the solvents tested, 1,2-dichloromethane (DCE) was the most effective, affording **3a** in 96% yield. The yield of **3a** was determined by the ^1H NMR integration method using mesitylene as the internal standard. Toluene was also effective, providing **3a** in 55% yield. Other solvents such as THF and *tert*-amyl alcohol were less effective, giving **3a** in yields of 25 and 15%, respectively. Other solvents such as DMF, CH_3CN, and CH_3COOH were totally ineffective. Next, the effect of the silver salt (8 mol-%) was examined. A variety of silver salts such as $AgSbF_6$, AgOTf, $AgBF_4$, AgOAc, AgO_2CCF_3, and Ag_2O were tested. Of these, $AgSbF_6$ was very effective, giving **3a** in 96% yield. AgOTf and $AgBF_4$ were less effective, giving **3a** in yields of 40 and 21%, respectively. AgOAc, AgO_2CCF_3, and Ag_2O were totally ineffective.

This ruthenium-catalyzed cyclization reaction was successfully extended to different substituted aromatic ketones **1b**–**h** and substituted alkynes **2b**–**e** (Table 1 and Table 2). The reaction of acetophenone (**1b**) with diphenylacetylene (**2a**) under the optimized reaction conditions, that is, $[\{RuCl_2(p\text{-cymene})\}_2]$ (2 mol-%), $AgSbF_6$ (8 mol-%), and $Cu(OAc)_2·H_2O$ (25 mol-%) in 1,2-dichloroethane afforded product **3b** in 83% yield (Table 1, entry 1). Similarly, isobutyrophenone (**1c**) and benzophenone (**1d**) reacted with **1a** to give the corresponding cyclization products **3c** and **3d** in yields of 76 and 73%, respectively (entries 2 and 3). Under similar conditions, 4-iodoacetophenone (**1e**) and 4-methoxyacetophenone (**1f**) reacted well with **2a** to afford indenols **3e** and **3f** in yields of 88 and 85%, respectively (entries 4 and 5). The reaction of 1-naphthophenone (**1g**) with **2a** provided **3g** exclusively in 82% yield (entry 6) with the C–H bond activation taking place at the carbon adjacent to the acetyl group of **1g**. This catalytic reaction was also tested with a heteroaromatic compound: Treatment of indole-3-acetophenone (**1h**) with **2a** gave **3h** in 69% yield (entry 7). It is significant that this catalytic reaction tolerates a variety of sensitive functional groups such as I, Br, OMe, and NH on the aromatic and heteroaromatic rings of **1** (Scheme 2 and Table 1).

Table 1. Ruthenium-catalyzed cyclization reactions of substituted aromatic ketones **1b**–**h** with diphenylacetylene (**2a**).[a]

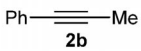
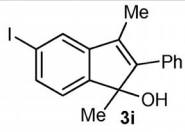
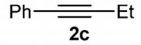
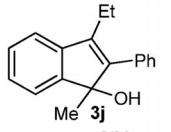
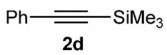
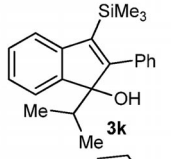
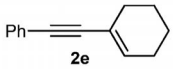
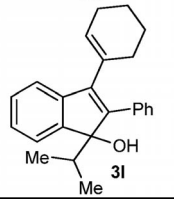
Entry	1	Product 3	Yield [%][b]
1			83
2			76
3			73
4			88
5			85
6			82
7			69

[a] All reactions were carried out with substituted aromatic ketones **1** (1.00 mmol), diphenylacetylene (**2a**) (1.20 mmol), $[\{RuCl_2(p\text{-cymene})\}_2]$ (2 mol-%), $AgSbF_6$ (8 mol-%), $Cu(OAc)_2·H_2O$ (25 mol-%), and 1,2-dichloroethane (3.0 mL) at 120 °C for 10 h. [b] Isolated yields.

Next we examined the reaction of various substituted unsymmetrical alkynes **2b**–**e** with substituted aromatic ketones **1** (Table 2). In all these reactions, complete regioselectivity was observed. Thus, 1-phenyl-1-propyne (**2b**) and 1-phenyl-1-butyne (**2c**) underwent cyclization with 4-iodoacetophenone (**1e**) or acetophenone (**1b**) to give products **3i** and **3j** in yields of 83 and 79%, respectively, in a highly regioselective manner (Table 2, entries 1 and 2). In the indenols **3i** and **3j**, the alkynic phenyl group is placed at the C-2 carbon next to the alcohol group and the alkyl group at the C-3 carbon. The regiochemistry of the reactions was established by NOESY experiments (see the Supporting Information). Similarly, in the reaction of 1-phenyl-2-(trimethylsilyl)-acetylene (**2d**) with **1c**, the silylated indenol derivative **3k** was obtained in 76% yield in a highly regioselective manner

with the Ph group attached to C-2 and the silyl group attached to C-3 (entry 3). It is significant that most metal-catalyzed chelation-assisted cyclization reactions of the *ortho* aromatic C–H bond with **2d** provide only desilylated compounds.[7d,14] The catalytic reaction was also tested with substituted unsymmetrical enyne **2e**, which reacted with **1c** to give a single regioisomeric product **3l** in 71% yield with the Ph group present at the C-2 carbon (entry 4).

Table 2. Ruthenium-catalyzed cyclization reactions of substituted aromatic ketones **1b**,**c**,**e** with unsymmetrical alkynes **2b**–**e**.[a]

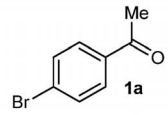
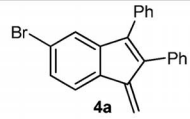
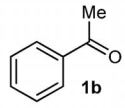
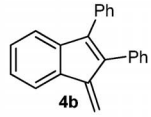
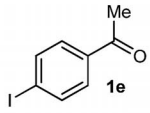
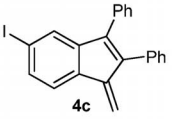
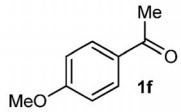
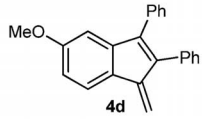
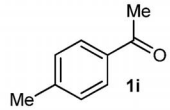
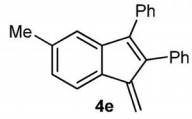
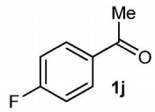
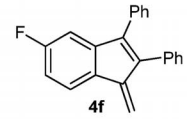
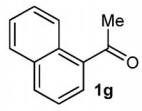
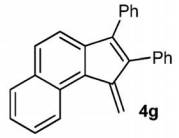
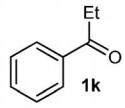
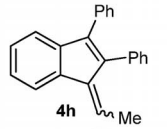
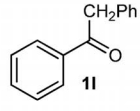
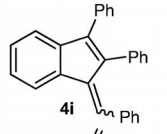
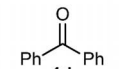
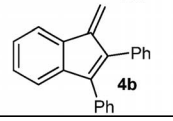
Entry	1	2	Product 3	Yield [%][b]
1	**1e**	 **2b**	 **3i**	83
2	**1b**	 **2c**	 **3j**	79
3	**1c**	 **2d**	 **3k**	76
4	**1c**	 **2e**	 **3l**	71

[a] All reactions were carried out with substituted aromatic ketones **1b**,**c**,**e** (1.00 mmol), alkynes **2** (1.20 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (8 mol-%), $Cu(OAc)_2 \cdot H_2O$ (25 mol-%), and 1,2-dichloroethane (3.0 mL) at 120 °C for 10 h. [b] Isolated yields.

In the cyclization reactions, the alkynic carbon atom bearing the less electron-donating substituent (Ph) connects to the keto group of **1** and the alkynic carbon atom with the more electron-donating substituent (Me, Et, and $SiMe_3$) attaches to the *ortho* carbon of the aryl ketone moiety. This regiochemistry exactly matches that observed for the cyclization reactions of *o*-halophenyl ketones with unsymmetrical alkynes in the presence of cobalt and nickel catalysts.[2a–2d] Although the exact reason for this is not clear, the Michael-type addition pattern dominates the product distribution and the trend in regiochemistry is as proposed by Cheng and co-workers.[2a–2d]

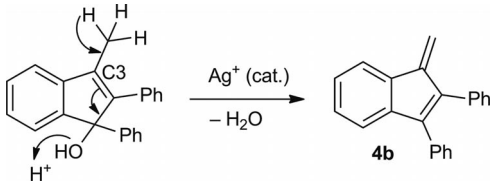
The amount of silver salt plays an important role in the reaction. When the amount of silver salt exceeded 8 mol-% in the presence of 2 mol-% of [{$RuCl_2$(*p*-cymene)}$_2$], a different type of dehydration product, namely a benzofulvene derivative, started to appear (see below). Thus, treatment of 4-bromoacetophenone (**1a**) with diphenylacetylene (**2a**) in the presence of [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (20 mol-%), and $Cu(OAc)_2 \cdot H_2O$ (25 mol-%) in 1,2-dichloroethane at 120 °C for 10 h afforded benzofulvene derivative **4a** in 93% isolated yield (Table 3, entry 1). Recently, Shibata and co-workers reported the synthesis of benzofulvene derivatives by the iridium-catalyzed *ortho* C–H bond alkenylation of aryl ketones with alkynes followed by cyclization and dehydration.[8g,9] It is significant that benzofulvene derivatives find versatile applications in materials science, organometallics, and medicinal chemistry.[15]

Table 3. Ruthenium-catalyzed synthesis of benzofulvene derivatives.[a]

Entry	1	2	Product 4	Yield [%][b]
1	 **1a**	**2a**	 **4a**	93
2	 **1b**	**2a**	 **4b**	89
3	 **1e**	**2a**	 **4c**	91
4	 **1f**	**2a**	 **4d**	86
5	 **1i**	**2a**	 **4e**	87
6	 **1j**	**2a**	 **4f**	92
7	 **1g**	**2a**	 **4g**	80
8	 **1k**	**2a**	 **4h**	85[c]
9	 **1l**	**2a**	 **4i**	82[c]
10	 **1d**	**2b**	 **4b**	75

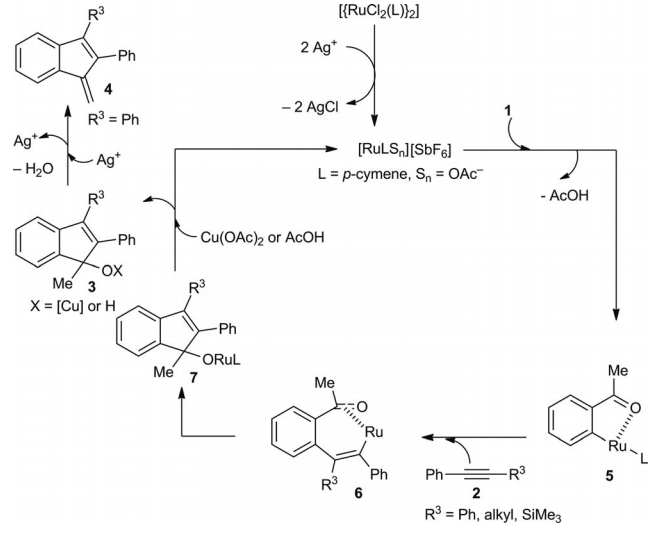
[a] All reactions were carried out with substituted acetophenones **1** (1.00 mmol), alkyne **2** (1.20 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (20 mol-%), $Cu(OAc)_2 \cdot H_2O$ (25 mol-%), and 1,2-dichloroethane (3.0 mL) at 120 °C for 10 h. [b] Isolated yields. [c] *E*:*Z* stereoisomeric ratio: **4h** 85:15, **4i** 98:2.

In the presence of an excess amount of silver salt (20 mol-%), acetophenone (**1b**), 4-iodoacetophenone (**1e**), 4-methoxyacetophenone (**1f**), 4-methylacetophenone (**1i**), and 4-fluoroacetophenone (**1j**) efficiently reacted with **2a** to provide benzofulvene derivatives **4b**–**f** in yields of 86–92% (Table 3, entries 2–6). Similarly, 1-napthophenone (**1g**) afforded **4g** exclusively in 80% yield (entry 7) with the C–H bond activation taking place at the carbon atom adjacent to the acetyl group. Likewise, propiophenone (**1k**) and 2-phenylacetophenone (**1l**) also reacted efficiently with **2a** to give benzofulvene derivatives **4h** and **4i** in yields of 85 and 82% with *E*/*Z* ratios of 85:15 and 98:2, respectively (entries 8 and 9). Interestingly, benzophenone (**1d**) reacted with the unsymmetrical 1-phenyl-1-propyne (**2b**) to give **4b** in 75% yield (entry 10). In this reaction, one of the hydrogen atoms of the methyl group of the C-3 carbon of the indenol moiety (intermediate) was involved in intramolecular dehydration [Reaction (1)]. Note that no dehydration product was observed in the reaction of isobutyrophenone (**1c**) with diphenylacetylene (**2a**), even in the presence of an excess amount of the silver salt (20 mol-%).



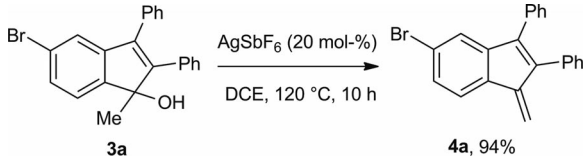
(1)

Based on the above observations and known metal-catalyzed C–H bond activation reactions,[4–10] a plausible reaction mechanism is proposed in Scheme 3. The first step likely starts with the removal of the chloride ligands from the [{$RuCl_2$(*p*-cymene)}$_2$] complex with the aid of the Ag^+ salt. Next, coordination of the carbonyl oxygen of **1** to the active ruthenium cationic species followed by *ortho* metalation provides intermediate **5**. Coordinative insertion of alkyne **2** into the Ru–C bond of intermediate **5** affords intermediate **6**. Intramolecular insertion of the C=O group into the Ru–alkenyl bond of **6** affords the five-membered ruthenium alkoxide intermediate **7**. Protonation of the intermediate **7** by means of $Cu(OAc)_2$ provided the final product **3** and regenerated the active ruthenium species for the next catalytic cycle. The exact role of the copper source in the reaction is not clear, but we propose that $Cu(OAc)_2$·H_2O provides the OAc^- source to the active ruthenium species to accelerate the *ortho*-metalation and also to replace the ruthenium species in intermediate **7** by transmetalation in the first catalytic cycle. In subsequent catalytic cycles, protonation of the intermediate **7** by AcOH provides the final product **3** and regenerates the active ruthenium species for the next catalytic cycle.



Scheme 3. Proposed mechanism for the cyclization reaction.

In this reaction the amount of silver salt added determines the nature of the product. The role of the silver salt, as stated above, is likely to remove chloride ligands from [{$RuCl_2$(*p*-cymene)}$_2$]. In the reaction, 2 mol-% of [{$RuCl_2$(*p*-cymene)}$_2$] was used and 8 mol-% of Ag salt is enough to remove all four chloride ligands. When the amount of silver salt exceeded 8 mol-%, the dehydration product benzofulvene was observed. The formation of this product can be explained by the coordination of the alcohol group of indenol **3** to the excess silver salt followed by subsequent dehydration. The proposed silver-catalyzed dehydration pathway is strongly supported by Reaction (2): Treatment of indenol **3a** (1.0 mmol) with $AgSbF_6$ (20 mol-%) in the presence of DCE at 120 °C for 10 h gave the product **4a** in 94% yield.



(2)

Conclusions

We have developed a highly regioselective ruthenium-catalyzed cyclization of substituted aromatic ketones with alkynes that occurs by C–H bond activation. This methodology offers a simple and mild method for the synthesis of indenols and benzofulvenes in a highly regioselective manner. The amount of silver salt used determined the nature of the product: In the presence of 2 mol-% of the ruthenium catalyst, 8 mol-% of the silver salt favored the formation of indenols whereas with 20 mol-% of the silver salt benzofulvenes were obtained. Extending the scope of these cyclization reactions to other π components is underway as well a detailed study of the reaction mechanism.

Experimental Section

General Procedure for the Cyclization of Aromatic Ketones 1 with Alkynes 2: A 15 mL pressure tube containing [{$RuCl_2$(*p*-cymene)}$_2$] (2 mol-%), $AgSbF_6$ (8 mol-%), and $Cu(OAc)_2$·H_2O (25 mol-%) was

evacuated and purged with nitrogen gas three times. Freshly distilled 1,2-dichloromethane (3.0 mL), aromatic ketones **1** (1.00 mmol) and alkynes **2** (1.20 mmol) were sequentially added to the system and the reaction mixture was stirred at 120 °C for 10 h. The mixture was filtered through a short Celite and silica gel pad and washed with dichloromethane several times. The filtrate was concentrated and the residue was purified on a silica gel column using hexanes/ethyl acetate as eluent to afford the cyclization products **3**. Products **4a**–**i** were also synthesized according to this procedure, but 20 mol-% of $AgSbF_6$ were required.

5-Bromo-1-methyl-2,3-diphenyl-1*H*-inden-1-ol (3a): Yellow solid; m.p. 127–129 °C; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3396, 2923, 1589, 1453, 1264, 1082 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.41–7.38 (m, 4 H), 7.34–7.30 (m, 4 H), 7.28–7.21 (m, 5 H), 2.02 (br. s, 1 H), 1.55 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.3, 148.2, 144.3, 137.8, 134.3, 134.0, 129.5, 129.3, 129.2, 128.8, 128.2, 127.9, 127.7, 124.0, 123.3, 122.6, 83.0, 24.0 ppm. GC–MS (70 eV, CI): *m*/*z* = 377 $[M + H]^+$, 201, 199, 119, 92. HRMS (EI): calcd. for $C_{22}H_{17}OBr$ 376.0463; found 376.0468.

1-Methyl-2,3-diphenyl-1*H*-inden-1-ol (3b): Pale-yellow solid; m.p. 123–125 °C; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3369, 2924, 1596, 1451, 1269 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (d, *J* = 8.0 Hz, 1 H), 7.44–7.41 (d, *J* = 8.0 Hz, 2 H), 7.34–7.29 (m, 5 H), 7.26–7.24 (m, 2 H), 7.23–7.20 (m, 4 H), 2.01 (br. s, 1 H), 1.59 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.6, 147.0, 142.3, 138.8, 134.8, 129.5, 129.3, 128.9, 128.6, 127.9, 127.4, 127.2, 127.2, 126.7, 122.0, 120.9, 83.4, 24.0 ppm. GC–MS (70 eV, CI): *m*/*z* = 298 $[M + H]^+$, 252, 123. HRMS (ESI): calcd. for $C_{22}H_{18}ONa$ $[M + Na]^+$ 321.1255; found 321.1263.

1-Isopropyl-2,3-diphenyl-1*H*-inden-1-ol (3c): Pale-yellow solid; m.p. 151–153 °C; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3439, 2925, 1596, 1456, 1026 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.51 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.0 Hz, 1 H), 7.34–7.29 (m, 3 H), 7.28–7.23 (m, 4 H), 7.22–7.18 (m, 5 H), 2.21–2.16 (m, 1 H), 2.14 (br. s, 1 H), 1.21 (d, *J* = 8.0 Hz, 3 H), 0.57 (d, *J* = 8.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.6, 146.4, 143.9, 140.4, 135.4, 134.8, 129.6, 129.4, 128.5, 128.4, 128.0, 127.5, 127.3, 126.1, 123.6, 120.7, 89.2, 34.0, 16.9, 16.8 ppm. GC–MS (70 eV, CI): *m*/*z* = 327 $[M + H]^+$, 315, 298, 221. HRMS (ESI): calcd. for $C_{24}H_{22}ONa$ $[M + Na]^+$ 349.1568; found 349.1568.

1,2,3-Triphenyl-1*H*-inden-1-ol (3d): Colorless solid; m.p. 206–208 °C; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3438, 2922, 1591, 1449, 1125 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (d, *J* = 8.0 Hz, 2 H), 7.53 (t, *J* = 8.0 Hz, 2 H), 7.49–7.45 (m, 3 H), 7.36–7.31 (m, 6 H), 7.27–7.23 (m, 3 H), 7.15–7.12 (m, 3 H), 2.91 (br. s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.2, 147.7, 142.9, 141.9, 140.8, 135.1, 133.9, 129.8, 129.2, 128.7, 128.5, 128.4, 127.8, 127.3, 127.1, 125.3, 123.1, 121.2, 87.2 ppm. GC–MS (70 eV, CI): *m*/*z* = 361 $[M + H]^+$, 294, 176, 142, 134. HRMS (ESI): calcd. for $C_{27}H_{20}ONa$ $[M + Na]^+$ 383.1412; found 383.1412.

5-Iodo-1-methyl-2,3-diphenyl-1*H*-inden-1-ol (3e): Pale-yellow solid; m.p. 151–153 °C; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3367, 2923, 1589, 1449, 1085 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.51 (d, *J* = 8.0 Hz, 1 H), 7.43 (s, 1 H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 2 H), 7.26–7.22 (m, 3 H), 7.19–7.16 (m, 2 H), 7.15–7.12 (m, 4 H), 1.57 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.1, 148.0, 144.5, 137.9, 135.5, 134.3, 134.1, 129.8, 129.5, 129.2, 128.9, 128.2, 127.9, 127.7, 123.8, 94.2, 83.2, 24.0 ppm. HRMS (EI): calcd. for $C_{22}H_{17}OI$ 424.0324; found 424.0331.

5-Methoxy-1-methyl-2,3-diphenyl-1*H*-inden-1-ol (3f): Pale-yellow solid; m.p. 142–144 °C; eluent: 15% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3356, 2924, 1591, 1474, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.39–7.36 (m, 3 H), 7.27–7.24 (m, 5 H), 7.14–7.13 (m, 3 H), 6.72 (s, 1 H), 6.70 (d, *J* = 8.0 Hz, 1 H), 3.71 (s, 3 H), 2.04 (br. s, 1 H), 1.50 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.5, 148.3, 143.9, 141.8, 138.4, 134.9, 134.7, 129.5, 129.4, 128.7, 128.1, 127.7, 127.4, 122.6, 111.1, 107.6, 82.9, 55.7, 24.2 ppm. HRMS (EI): calcd. for $C_{23}H_{20}O_2$ 328.1463; found 328.1460.

1-Methyl-2,3-diphenyl-1*H*-cyclopenta[*a*]naphthalen-1-ol (3g): Red semi-solid; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3417, 2922, 1589, 1127 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.29 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.43–7.37 (m, 3 H), 7.35–7.31 (m, 3 H), 7.26–7.20 (m, 5 H), 7.14–7.07 (m, 2 H), 2.21 (br. s, 1 H), 1.65 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.5, 143.2, 139.2, 138.6, 135.1, 134.8, 133.1, 129.7, 129.5, 129.2, 129.1, 128.7, 128.6, 128.1, 127.7, 127.4, 126.6, 125.0, 124.0, 119.6, 85.1, 25.1 ppm. GC–MS (70 eV, CI): *m*/*z* = 349 $[M + H]^+$, 346, 338, 328, 128. HRMS (EI): calcd. for $C_{26}H_{20}O$ 348.1514; found 348.1509.

1-Methyl-2,3-diphenyl-1,4-dihydrocyclopenta[*b*]indol-1-ol (3h): Red semi-solid; eluent: 35% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3372 (br., s), 2923, 1611, 1430, 1025 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.51 (dd, *J* = 8.0, 4.0 Hz, 2 H), 7.37–7.28 (m, 6 H), 7.16–7.11 (m, 3 H), 7.05–6.99 (m, 3 H), 1.26 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.0, 140.3, 135.6, 135.5, 133.1, 132.6, 129.8, 129.7, 117.0, 129.2, 129.1, 129.0, 128.7, 126.5, 123.9, 123.3, 122.9, 111.3, 90.3, 14.3 ppm. HRMS (ESI): calcd. for $C_{24}H_{20}NO$ $[M + H]^+$ 338.1545; found 338.1530.

5-Iodo-1,3-dimethyl-2-phenyl-1*H*-inden-1-ol (3i): Orange oil; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3345, 2923, 1447, 1081 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, *J* = 8.0, 4.0 Hz, 1 H), 7.56 (s, 1 H), 7.52–7.50 (m, 2 H), 7.43–7.40 (m, 2 H), 7.35 (t, *J* = 8.0 Hz, 1 H), 7.18 (d, *J* = 8.0 Hz, 1 H), 2.05 (s, 3 H), 1.92 (br. s, 1 H), 1.45 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.9, 147.8, 145.8, 135.3, 134.9, 133.6, 129.2, 128.8, 128.5, 127.8, 123.4, 94.2, 83.0, 23.8, 11.7 ppm. HRMS (ESI): calcd. for $C_{17}H_{16}IO$ $[M + H]^+$ 363.0246; found 363.0242.

3-Ethyl-1-methyl-2-phenyl-1*H*-inden-1-ol (3j): Orange semi-solid; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3349, 2969, 1597, 1457, 1363, 1088 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.45–7.42 (m, 2 H), 7.41–7.36 (m, 3 H), 7.33–7.28 (m, 2 H), 7.26–7.18 (m, 2 H), 2.46 (q, *J* = 8.0 Hz, 2 H), 1.88 (br. s, 1 H), 1.44 (s, 3 H), 1.17 (t, *J* = 8.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.6, 146.5, 142.3, 140.1, 135.4, 129.1, 128.5, 128.3, 127.5, 126.3, 121.8, 119.9, 83.1, 23.8, 19.3, 13.6 ppm. HRMS (EI): calcd. for $C_{18}H_{18}O$ 250.1358; found 250.1363.

1-Isopropyl-2-phenyl-3-(trimethylsilyl)-1*H*-inden-1-ol (3k): Orange oil; eluent: 4% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3402, 1580, 1128 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.45 (d, *J* = 8.0 Hz, 1 H), 7.38–7.31 (m, 4 H), 7.29–7.24 (m, 3 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 2.00–1.97 (m, 1 H), 1.95 (br. s, 1 H), 1.15 (d, *J* = 8.0 Hz, 3 H), 0.56 (d, *J* = 8.0 Hz, 3 H), 0.02 (s, 9 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.8, 146.1, 139.8, 137.6, 129.5, 128.5, 128.3, 128.0, 127.8, 125.1, 123.5, 122.6, 89.7, 33.2, 17.1, 16.4, 0.3 ppm. HRMS (EI): calcd. for $C_{21}H_{26}OSi$ 322.1753; found 322.1758.

3-(Cyclohex-1-en-1-yl)-1-isopropyl-2-phenyl-1*H*-inden-1-ol (3l): Orange oil; eluent: 10% ethyl acetate in hexanes. IR (ATR): $\tilde{\nu}$ = 3422, 2930, 1591, 1456, 1370, 1267, 1035 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, *J* = 8.0 Hz, 1 H), 7.39–7.31 (m, 4 H), 7.29–7.23 (m, 3 H), 7.10 (t, *J* = 8.0 Hz, 1 H), 5.77 (t, *J* = 4.0 Hz, 1 H), 2.31–2.25 (m, 1 H), 2.18–2.11 (m, 2 H), 2.09–2.01 (m, 1 H), 1.91–1.85 (m, 2 H), 1.79–1.61 (m, 3 H), 1.13 (d, *J* = 8.0 Hz, 3 H), 0.51

(d, J = 8.0 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.7, 143.7, 136.2, 135.9, 132.3, 129.1, 128.8, 128.2, 127.9, 127.2, 125.7, 123.4, 120.5, 88.9, 34.1, 28.0, 25.5, 22.9, 22.2, 16.9, 16.7 ppm. HRMS (EI): calcd. for $C_{24}H_{26}O$ 330.1984; found 330.1983.

5-Bromo-1-methylene-2,3-diphenyl-1*H*-indene (4a): Pale-yellow semi-solid; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.56 (d, J = 8.0 Hz, 1 H), 7.46 (s, 1 H), 7.40 (dd, J = 8.0, 4.0 Hz, 1 H), 7.35–7.29 (m, 4 H), 7.28–7.25 (m, 4 H), 7.19–7.17 (m, 2 H), 6.25 (s, 1 H), 5.77 (s, 1 H) ppm.^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.8, 144.7, 141.1, 138.7, 135.0, 134.2, 133.9, 130.7, 129.4, 128.5, 128.4, 128.2, 127.8, 127.3, 123.3, 122.4, 121.2, 115.4 ppm. GC–MS (70 eV, CI): m/z = 359 $[M + H]^+$, 338, 294, 272, 196.

1-Methylene-2,3-diphenyl-1*H*-indene (4b): Pale-yellow oil; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.71 (d, J = 8.0 Hz, 1 H), 7.34 (t, J = 8.0 Hz, 1 H), 7.30–7.25 (m, 10 H), 7.20–7.18 (m, 2 H), 6.25 (s, 1 H), 5.72 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.7, 142.8, 140.9, 137.5, 136.3, 134.7, 134.6, 130.8, 129.4, 128.6, 128.3, 128.1, 127.5, 127.0, 125.8, 120.2, 119.9, 114.2 ppm. GC–MS (70 eV, CI): m/z = 281 $[M + H]^+$, 265, 220.

5-Iodo-1-methylene-2,3-diphenyl-1*H*-indene (4c): Pale-yellow solid; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.67 (s, 1 H), 7.62 (dd, J = 8.0, 4.0 Hz, 1 H), 7.45 (d, J = 8.0 Hz, 1 H), 7.35–7.30 (m, 4 H), 7.29–7.25 (m, 4 H), 7.20–7.18 (m, 2 H), 6.28 (s, 1 H), 5.78 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.0, 144.9, 138.6, 135.8, 134.6, 134.3, 134.1, 130.9, 129.8, 129.6, 129.2, 128.7, 128.3, 127.9, 127.5, 121.7, 115.6, 94.1 ppm. GC–MS (70 eV, CI): m/z = 407 $[M + H]^+$, 330, 266, 225, 108.

5-Methoxy-1-methylene-2,3-diphenyl-1*H*-indene (4d): Orange semi-solid; eluent: 1% ethyl acetate in hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, J = 8.0 Hz, 1 H), 7.34–7.28 (m, 8 H), 7.25–7.22 (m, 2 H), 6.96 (s, 1 H), 6.83 (dd, J = 8.0, 4.0 Hz, 1 H), 6.15 (s, 1 H), 5.66 (s, 1 H), 3.84 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 160.6, 147.2, 144.5, 141.5, 138.9, 134.8, 134.6, 130.8, 129.6, 129.1, 128.4, 128.1, 127.6, 127.1, 120.9, 112.9, 110.8, 106.6, 55.7 ppm. GC–MS (70 eV, CI): m/z = 311 $[M + H]^+$, 179, 167, 119.

5-Methyl-1-methylene-2,3-diphenyl-1*H*-indene (4e): Pale-yellow oil; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.62 (d, J = 8.0 Hz, 1 H), 7.35–7.31 (m, 4 H), 7.30–7.27 (m, 4 H), 7.22–7.20 (m, 2 H), 7.17 (s, 1 H), 7.10 (d, J = 4.0 Hz, 1 H), 6.21 (s, 1 H), 5.70 (s, 1 H), 2.40 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 147.7, 143.2, 142.0, 138.5, 137.9, 134.9, 133.9, 130.9, 129.7, 128.5, 128.2, 127.6, 127.1, 126.5, 121.1, 119.9, 113.6, 22.0 ppm. GC–MS (70 eV, CI): m/z = 295 $[M + H]^+$, 181, 152, 129.

5-Fluoro-1-methylene-2,3-diphenyl-1*H*-indene (4f): Pale-yellow oil; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.52 (dd, J = 8.0, 4.0 Hz, 1 H), 7.22–7.15 (m, 8 H), 7.10–7.07 (m, 2 H), 6.95 (dd, J = 8.0, 4.0 Hz, 1 H), 6.86–6.81 (m, 1 H), 6.08 (s, 1 H), 5.61 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 164.9 and 162.4 (C-F coupling), 146.7, 144.9 and 144.8 (C-F coupling), 141.0, 139.2, 134.4, 134.1, 132.0, 130.8, 129.4, 128.5, 128.2, 127.8, 127.3, 121.0 and 120.9 (C-F coupling), 114.6, 112.3 and 112.1 (C-F coupling), 107.8 and 107.6 (C-F coupling) ppm. GC–MS (70 eV, CI): m/z = 299 $[M + H]^+$, 279, 221. HRMS (ESI): calcd. for $C_{22}H_{16}F$ $[M + H]^+$ 299.1236; found 299.1232.

1-Methylene-2,3-diphenyl-1*H*-cyclopenta[*a*]naphthalene (4g): Red semi-solid; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.52 (d, J = 8.0 Hz, 1 H), 7.86 (dd, J = 8.0, 4.0 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.58–7.52 (m, 2 H), 7.44–7.33 (m, 8 H), 7.30–7.23 (m, 3 H), 7.12 (s, 1 H), 6.88 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 148.1, 139.6, 138.9, 138.1, 134.5, 134.2, 132.6, 129.1, 128.9, 129.1, 128.7, 128.1, 128.2, 127.8, 127.2, 127.0, 126.1, 124.0, 123.6, 119.6, 110.9 ppm. GC–MS (70 eV, CI): m/z = 331 $[M + H]^+$, 281, 268, 209, 191. HRMS (ESI): calcd. for $C_{26}H_{19}$ $[M + H]^+$ 331.1487; found 331.1487.

(*E*)- and (*Z*)-1-Ethylidene-2,3-diphenyl-1*H*-indene (4h): Pale-yellow oil; eluent: hexanes. *E*/*Z* ratio 85:15. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.89 (d, J = 8.0 Hz, 1 H) (major isomer), 7.65 (d, J = 8.0 Hz, 1 H) (minor isomer), 7.42 (t, J = 8.0 Hz, 1 H), 7.33–7.22 (m, 10 H), 7.19–7.16 (m, 2 H), 6.90 (q, J = 8.0 Hz, 1 H) (minor isomer), 6.37 (q, J = 8.0 Hz, 1 H) (major isomer), 2.40 (d, J = 8.0 Hz, 3 H) (major isomer), 1.68 (d, J = 8.0 Hz, 1 H) (minor isomer) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.6, 141.7, 139.5, 138.7, 137.8, 135.4, 135.3, 135.0, 132.9, 131.2, 130.4, 129.7, 129.5, 128.2, 128.1, 127.9, 127.3, 127.1, 127.0, 126.9, 125.4, 125.3, 123.9, 120.3, 120.0, 118.4, 15.9, 15.6 ppm. GC–MS (70 eV, CI): m/z = 295 $[M + H]^+$, 278, 217, 145.

(*E*)-1-Benzylidene-2,3-diphenyl-1*H*-indene (4i): Pale-yellow semi-solid; eluent: hexanes. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.60–7.56 (m, 3 H), 7.45 (t, J = 8.0 Hz, 2 H), 7.39 (t, J = 8.0 Hz, 2 H), 7.35–7.26 (m, 11 H), 7.20 (s, 1 H), 7.05 (t, J = 8.0 Hz, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.0, 141.7, 140.7, 139.9, 137.3, 135.3, 134.9, 134.8, 134.7, 131.5, 130.4, 129.9, 129.8, 129.6, 128.7, 128.4, 128.3, 128.2, 127.5, 127.2, 125.5, 123.5, 120.3 ppm. GC–MS (70 eV, CI): m/z = 357 $[M + H]^+$, 325, 295, 217, 167.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR spectra of all compounds.

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[1] For selected reviews, see: a) E.-I. Negishi, C. Copret, S. Ma, S.-Y. Liou, F. Liu, *Chem. Rev.* **1996**, *96*, 365; b) I. Ojima, M. Tzamarioudaki, Z. Li, R. T. Donovan, *Chem. Rev.* **1996**, *96*, 635; c) I. Nakamura, Y. Yamamoto, *Chem. Rev.* **2004**, *104*, 2127; d) H. W. Fruhauf, *Chem. Rev.* **1997**, *97*, 523; e) G. Zeni, R. C. Larock, *Chem. Rev.* **2004**, *104*, 2285.

[2] For selected papers, see: a) D. K. Rayabarapu, C.-H. Cheng, *Chem. Commun.* **2002**, 942; b) K.-J. Chang, D. K. Rayabarapu, C.-H. Cheng, *Org. Lett.* **2003**, *5*, 3965; c) K.-J. Chang, D. K. Rayabarapu, C.-H. Cheng, *J. Org. Chem.* **2004**, *69*, 4781; d) D. K. Rayabarapu, P. Sukula, C.-H. Cheng, *Org. Lett.* **2003**, *5*, 4903; e) L. G. Quan, V. Gevorgyan, Y. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 3545; f) L. G. Quan, V. Gevorgyan, Y. Yamamoto, *J. Am. Chem. Soc.* **1999**, *121*, 9485; g) R. P. Korivi, C.-H. Cheng, *Org. Lett.* **2005**, *7*, 5179.

[3] For selected papers, see: a) T. Miura, M. Murakami, *Chem. Commun.* **2007**, 217; b) T. Matsuda, M. Makino, M. Murakami, *Chem. Lett.* **2005**, *34*, 1416; c) B. Gourdet, M. E. Rudkin, H. W. Lam, *Org. Lett.* **2010**, *12*, 2554.

[4] For reviews and a book, see: a) G. Dyker, *Angew. Chem.* **1999**, *111*, 1808; *Angew. Chem. Int. Ed.* **1999**, *38*, 1698; b) V. Ritleng, C. Sirlin, M. Pfeffer, *Chem. Rev.* **2002**, *102*, 1731; c) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211; d) G. Dyker (Ed.), *Handbook of C-H Transformations*, Wiley-VCH, Weinheim, **2005**; e) C. G. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633.

[5] For selected C–H bond activation by metal bases, see: a) M. C. Whisler, S. MacNeil, V. Snieckus, P. Beak, *Angew. Chem.* **2004**, *116*, 2256; *Angew. Chem. Int. Ed.* **2004**, *43*, 2206; b) A. Krasovskiy, V. Krasovskaya, P. Knochel, *Angew. Chem.* **2006**, *118*, 3024; *Angew. Chem. Int. Ed.* **2006**, *45*, 2958; c) S. H. Wunderlich, P. Knochel, *Angew. Chem.* **2007**, *119*, 7829; *Angew. Chem. Int. Ed.* **2007**, *46*, 7685; d) S. H. Wunderlich, M. Kienle, P. Knochel, *Angew. Chem.* **2009**, *121*, 7392; *Angew. Chem. Int.*

Ed. **2009**, *48*, 7256; e) S. H. Wunderlich, P. Knochel, *Chem. Eur. J.* **2010**, *16*, 3304.

[6] For recent reviews, see: a) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174; b) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074; c) M. C. Willis, *Chem. Rev.* **2010**, *110*, 725; d) O. Daugulis, *Top. Curr. Chem.* **2010**, *292*, 57; e) R. Giri, B.-F. Shi, K. M. Engle, N. Maugel, J.-Q. Yu, *Chem. Soc. Rev.* **2009**, *38*, 3242; f) B. Karimi, H. Behzadnia, D. Elhamifar, P. F. Akhavan, F. K. Esfahani, *Synthesis* **2010**, 1399; g) D. A. Colby, R. G. Bergman, J. A. Ellman, *Chem. Rev.* **2010**, *110*, 624; h) T. W. Lyons, M. S. Sanford, *Chem. Rev.* **2010**, *110*, 1147; i) J. F. Hartwig, *Chem. Soc. Rev.* **2011**, *40*, 1992; j) L. McMurray, F. O. Hara, M. J. Gaunt, *Chem. Soc. Rev.* **2011**, *40*, 1885; k) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; l) L. Ackermann, *Chem. Rev.* **2011**, *111*, 1315.

[7] For selected rhodium papers, see: a) C.-H. Jun, C. W. Moon, D.-Y. Lee, *Chem. Eur. J.* **2002**, *8*, 2423; b) S.-G. Lim, J.-A. Ahn, C.-H. Jun, *Org. Lett.* **2004**, *6*, 4687; c) N. Umeda, H. Tsurugi, T. Satoh, M. Miura, *Angew. Chem.* **2008**, *120*, 4083; *Angew. Chem. Int. Ed.* **2008**, *47*, 4019; d) K. Parthasarathy, M. Jeganmohan, C.-H. Cheng, *Org. Lett.* **2008**, *10*, 325; e) K. Parthasarathy, C.-H. Cheng, *J. Org. Chem.* **2009**, *74*, 9359; f) N. Guimond, C. Gouliaras, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 6908; g) T. K. Hyster, T. Rovis, *J. Am. Chem. Soc.* **2010**, *132*, 10565; h) M. P. Huestis, L. Chan, D. R. Stuart, K. Fagnou, *Angew. Chem. Int. Ed.* **2011**, *50*, 1338; i) Z.-M. Sun, S.-P. Chen, P. Zhao, *Chem. Eur. J.* **2010**, *16*, 2619; j) K. Morimoto, K. Hirano, T. Satoh, M. Miura, *Org. Lett.* **2010**, *12*, 2068; k) N. Guimond, K. Fagnou, *J. Am. Chem. Soc.* **2009**, *131*, 12050; l) S. H. Park, J. Y. Kim, S. Chang, *Org. Lett.* **2011**, *13*, 2372.

[8] Acetophenone-directed C–H activation reactions: for rhodium-catalyzed reactions, see: a) K. Tanaka, Y. Otake, A. Wada, K. Noguchi, M. Hirano, *Org. Lett.* **2007**, *9*, 2203; b) P. Gandeepan, K. Parthasarathy, C.-H. Cheng, *J. Am. Chem. Soc.* **2010**, *132*, 8569; c) K. K. Muralirajan, K. Parthasarathy, C.-H. Cheng, *Angew. Chem. Int. Ed.* **2011**, *50*, 4169; d) F. W. Patureau, T. Besset, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 1064; e) F. W. Patureau, T. Besset, N. Kuhl, F. Glorius, *J. Am. Chem. Soc.* **2011**, *133*, 2154; f) K. Tsuchikama, M. Kasagawa, Y.-K. Hashimoto, K. Endo, T. Shibata, *J. Organomet. Chem.* **2008**, *693*, 3939; for iridium-catalyzed reactions, see: g) ; K. Tsuchikama, M. Kasagawa, K. Endo, T. Shibata, *Synlett* **2010**, 97.

[9] The cost of 1 g of [{$RuCl_2$(*p*-cymene)}$_2$] is $36 from Alfa-Asear, whereas 1 g of [{Cp*$RhCl_2$}$_2$] costs $702 and 1 g of [Ir(cod)$_2$]$BF_4$ costs $571.

[10] For selected ruthenium-catalyzed addition reactions of acetophenones with alkenes, see: a) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, *366*, 529; b) T. Naota, H. Takaya, S.-I. Murahashi, *Chem. Rev.* **1998**, *98*, 2599; c) F. Kakiuchi, S. Murai, *Acc. Chem. Res.* **2002**, *35*, 826; d) R. Martinez, R. Chevalier, S. Darses, J.-P. Genet, *Angew. Chem.* **2006**, *118*, 8412; *Angew. Chem. Int. Ed.* **2006**, *45*, 8232; e) M.-O. Simon, J.-P. Genet, S. Darses, *Org. Lett.* **2010**, *12*, 3038; f) A. J. A. Watson, A. C. Maxwell, J. M. J. Williams, *Org. Lett.* **2010**, *12*, 3856; g) F. Kakiuchi, T. Kochi, E. Mizushima, S. Murai, *J. Am. Chem. Soc.* **2010**, *132*, 17741; h) L. Ackermann, R. Vicente, *Top. Curr. Chem.* **2010**, *292*, 211; i) K. Tanaka, Y. Otake, A. Wada, K. Noguchi, M. Hirano, *Org. Lett.* **2007**, *9*, 2203.

[11] For recent ruthenium-catalyzed cyclization reactions, see: a) L. Ackermann, A. V. Lygin, N. Hofmann, *Org. Lett.* **2011**, *13*, 3278; b) L. Ackermann, A. V. Lygin, N. Hofmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 6379; c) L. Ackermann, J. Pospech, *Org. Lett.* **2011**, *13*, 4153.

[12] For carbonyl-directed ruthenium-catalyzed C–H bond alkenylation reactions with alkynes, see: a) N. J. Clegg, S. Paruthiyil, D. C. Leitman, F. Kakiuchi, Y. Yamamoto, N. Chatani, S. Murai, *Chem. Lett.* **1995**, 681; b) F. Kakiuchi, T. Uetsuhara, Y. Tanaka, N. Chatani, S. Murai, *J. Mol. Catal. A* **2002**, *182*; F. Kakiuchi, T. Uetsuhara, Y. Tanaka, N. Chatani, S. Murai, *J. Mol. Catal. A* **2002**, 511; c) P. W. R. Harris, C. E. F. Rickard, P. D. Woodgate, *J. Organomet. Chem.* **1999**, *589*, 168; d) B. M. Trost, K. Imi, I. W. Davies, *J. Am. Chem. Soc.* **1995**, *117*, 5371; e) T. Mitsudo, S.-W. Zhang, M. Nagao, Y. Watanabe, *J. Chem. Soc., Chem. Commun.* **1991**, 598; f) M. Mori, Y. Kozawa, M. Nishida, M. Kanamaru, K. Onozuka, M. Takimoto, *Org. Lett.* **2000**, *2*, 3245; g) N. M. Neisius, B. Plietker, *Angew. Chem.* **2009**, *121*, 5863; *Angew. Chem. Int. Ed.* **2009**, *48*, 5752; for palladium-catalyzed reactions, see: A. T. Lindhardt, M. L. H. Mantel, T. Skrydstrup, *Angew. Chem.* **2008**, *120*, 2708; *Angew. Chem. Int. Ed.* **2008**, *47*, 2668; for rhodium-catalyzed reactions, see: h) Y. Shibata, M. Hirano, K. Tanaka, *Org. Lett.* **2008**, *10*, 2829; i) Y. Shibata, Y. Otake, M. Hirano, K. Tanaka, *Org. Lett.* **2009**, *11*, 689.

[13] a) Kurakay Co., Ltd. Jpn. Kokai Tokkyo Koho, JP 81,113,740 (C1. C07C69/017), Sept 7, **1981** (*Chem. Abstr.* **1982**, *96*, 68724b); b) K. Samula, B. Cichy, *Acta Pol. Pharm.* **1985**, *42*, 256 (*Chem. Abstr.* **1986**, *105*, 171931v); c) L. S. Liebeskind, J. R. Gasdaska, J. S. MaCallum, S. J. Tremont, *J. Org. Chem.* **1989**, *54*, 669; d) R. C. Cambie, M. R. Metzler, P. S. Rutledge, P. D. Woodgate, *J. Organomet. Chem.* **1990**, *381*, C26; e) K. Samula, B. Cichy, *Acta Pol. Pharm.* **1985**, *42*, 256 (*Chem. Abstr.* **1986**, *105*, 171931v).

[14] P. W. R. Harris, C. E. F. Rickard, P. D. Woodgate, *J. Organomet. Chem.* **1999**, *589*, 168.

[15] For selected references, see: a) E. D. Bergmann, *Chem. Rev.* **1968**, *68*, 41; b) C. S. Bryan, M. Lautens, *Org. Lett.* **2010**, *12*, 2754; c) M. Schmittel, C. Vavilala, *J. Org. Chem.* **2005**, *70*, 4865; d) S. Ye, K. Gao, H. Zhou, X. Yang, J. Wu, *Chem. Commun.* **2009**, 5406; e) S. M. Abdur Rahman, M. Sonoda, M. Ono, K. Miki, Y. Tobe, *Org. Lett.* **2006**, *8*, 1197; f) N. J. Clegg, S. Paruthiyil, D. C. Leitman, T. S. J. Scanlan, *J. Med. Chem.* **2005**, *48*, 5989; g) H. Gao, J. A. Katzenellenbogen, R. Garg, C. Hansch, *Chem. Rev.* **1999**, *99*, 723.

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