Rhodium-Catalyzed Coupling Reaction of Aroyl Chlorides with Alkenes

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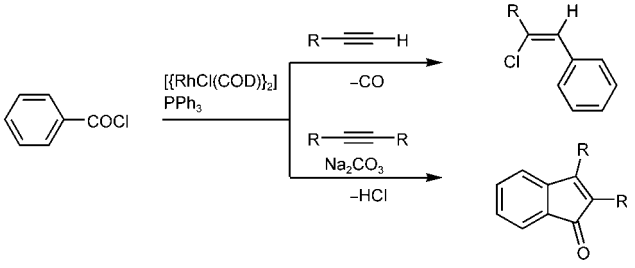
Abstract: Aroyl chlorides react with acyclic and cyclic alkenes in the presence of a rhodium catalyst to give Mizoroki–Heck type and cyclization products, respectively. A rhodium-ethylene complex, $[\{RhCl(C_2H_4)_2\}_2]$, showed excellent performance for these reactions. Notably, the reactions can be conducted effectively under base- and phosphane-free conditions.

Keywords: C-C coupling; cyclization; Heck reaction; homogeneous catalysis; rhodium

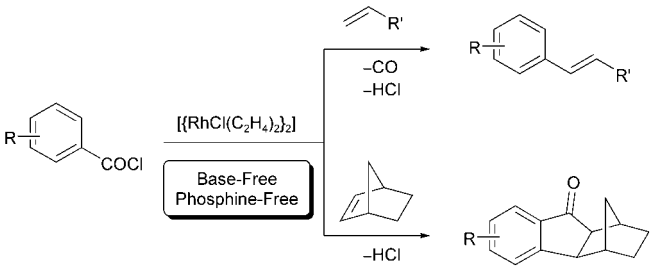
Introduction

Aroyl chlorides are known to smoothly react with low-valent transition metal species, including rhodium and palladium complexes, to form the corresponding aroylchlorometal complexes, which can undergo decarbonylation at somewhat elevated temperatures to afford arylchlorometal complexes.[1] Aroyl- and arylpalladium species are synthetically versatile, and indeed, catalytic aroylations of alkenes[2] and alkynes[3] as well as arylations of alkenes[4] and dienes[5] using aroyl chlorides have been successfully developed.

Meanwhile, we have reported that treatment of aroyl chlorides with alkynes in the presence of a rhodium catalyst system, $[\{RhCl(COD)\}_2]/PPh_3$, gives rise to different products than those under palladium catalysis. Thus, the reaction with terminal alkynes produces β-chlorostyrenes accompanied by decarbonylation, whereas that with internal alkynes affords indenone derivatives with the evolution of HCl (Scheme 1).[6] The reaction with alkenes under the same conditions, however, gave poor results.[7] During our further investigations, we observed that a rhodium-ethylene complex, $[\{RhCl(C_2H_4)_2\}_2]$, exhibits excellent activity as catalyst for the Mizoroki–Heck type coupling of aroyl chlorides with acyclic alkenes accompanied by decarbonylation to afford arylated alkenes (Scheme 2). In particular, the reaction efficiently proceeded even without the addition of bases as well as phosphane ligands. This contrasts markedly with the usual Mizoroki–Heck reaction using palladium catalysts.[8] Furthermore, the use of the rhodium-ethylene complex enabled the coupling of aroyl chlorides with cyclic alkenes such as norbornenes to produce indanone derivatives. We report herein the details of these reactions as well as other related reactions.[9]



Scheme 1. Rhodium-catalyzed coupling reaction of aroyl chlorides with alkynes.



Scheme 2. Rhodium-catalyzed coupling reaction of aroyl chlorides with alkenes.

Results and Discussion

First, benzoyl chloride (**1a**) was reacted with styrene (**2a**; 1 equiv.) in a batch reactor with an N_2 balloon. Under conditions similar to those employed for the reaction with internal alkynes, using $[\{RhCl(COD)\}_2]$ (COD = 1,5-cyclooctadiene, 1 mol %), PPh_3 (2 mol %), and Na_2CO_3 (1 equiv.) in refluxing *o*-xylene for 24 h,[6] (*E*)-stilbene (**3a**) was formed in a low yield, as described above (Table 1, entry 1). In contrast, the ethylene com-

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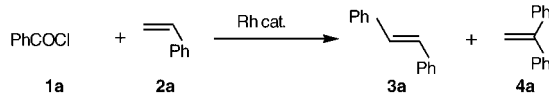
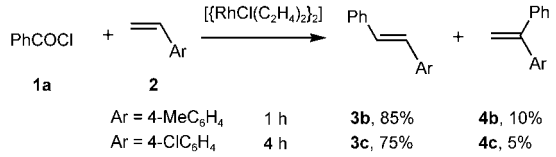
Table 1. Reaction of benzoyl chloride (**1a**) with styrene (**2a**).[a]



Entry	Rh catalyst (mol %)	Time [h]	Yield [%][b]	
			3a	**4a**
1[c]	$[\{RhCl(COD)\}_2]$ (1)/PPh_3 (2)	24	7	
2[c]	$[\{RhCl(C_2H_4)_2\}_2]$ (1)/PPh_3 (2)	23	69	8
3	$[\{RhCl(C_2H_4)_2\}_2]$ (1)/PPh_3 (2)	23	69	7
4	$[\{RhCl(C_2H_4)_2\}_2]$ (1)	4	82	8
5	$[Rh(acac)(COD)_2]$ (1)	26	36	3
6	$[\{RhCl(NBD)\}_2]$ (1)	4	33	2
7	$[\{RhCl(NBD)\}_2]$ (1)	18	88	6
8	$[\{RhCl(C_2H_4)_2\}_2]$ (0.25)	4	72	10
9[d]	$[\{RhCl(C_2H_4)_2\}_2]$ (0.25)	2	87	9
10[d, e]	$[\{RhCl(C_2H_4)_2\}_2]$ (0.25)	8	75	7

[a] Unless noted, the reaction of **1a** (1 mmol) with **2a** (1 mmol) was conducted in refluxing *o*-xylene (5 cm^3) under N_2.
[b] Yield determined by GC based on the amount of **1a** used.
[c] With Na_2CO_3 (1 mmol).
[d] **2a** (1.2 mmol) was used.
[e] With LiCl (0.04 mmol).



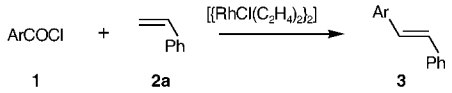
Scheme 3. Reaction of **1a** with **2**. Reaction conditions: **1** (1 mmol), **2** (1.2 mmol), $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol), *o*-xylene, reflux.

plex $[\{RhCl(C_2H_4)_2\}_2]$ catalyzed the reaction effectively to give **3a** in 69% yield; a minor amount of 1,1-diphenylethylene (**4a**) was detected, as was the case in the palladium-catalyzed Mizoroki–Heck reaction (entry 2).[8] Interestingly, the reaction proceeded much more smoothly by eliminating the phosphane ligand and base. As a result, **3a** was obtained in 82% yield within 4 h (entry 4). Under the same conditions, $[Rh(acac)(COD)_2]$ and $[\{RhCl(NBD)\}_2]$ (NBD = norbornadiene) showed lower activity (entries 5 and 6). In the latter case, however, prolonging the reaction time afforded a satisfactory product yield (entry 7). Although reducing the amount of $[\{RhCl(C_2H_4)_2\}_2]$ to 0.25 mol % resulted in a slight decrease in the product yield (entry 8), one of 87% was attained within 2 h by using 1.2 equivs. of **2a** (entry 9).

Substituted styrenes, 4-methyl- and 4-chlorostyrene, also underwent phenylation efficiently by treatment with **1a** to give the corresponding stilbenes **3b** and **3c** along with minor amounts of 1,1-diarylethylenes (Scheme 3).

One of the substantial problems in the palladium-catalyzed Mizoroki–Heck reaction comes from an acidic by-product, which requires the addition of stoichiometric amount of a base. Recently, use of aromatic carboxylic acid anhydrides[10] and aryl esters[11a] has been shown to allow one to conduct the reaction under base-free conditions. Although the methods are useful, additional work-up procedures such as fractional distillation and acid-base extraction are needed for obtaining pure coupling products due to the corresponding organic by-products. Gooßen and Paetzold have demonstrated that use of isopropenyl esters of benzoic acids is an excellent method in which only volatile by-products, CO and acetone, are evolved.[11b] Considering the stoichiometry of the present reaction, the by-products appear to be CO and HCl, which are also readily removable.[12]

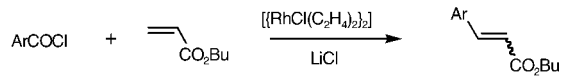
Table 2. Reaction of aroyl chlorides **1** with styrene (**2a**).[a]



Entry	**1**	Ar	**1/2** [mmol/mmol]	Time [h]	Product	Yield [%][b]
1	**a**	Ph	10/15	6	**3a**	86
2	**b**	4-MeC_6H_4	10/15	7	**3b**	79
3	**d**	4-$MeOC_6H_4$	1/1.2	4	**3d**	51
4	**e**	4-BrC_6H_4	10/15	6	**3e**	81
5	**f**	4-NCC_6H_4	1/1.5	6	**3f**	73
6	**g**	4-$O_2NC_6H_4$	10/15	10	**3g**	75
7	**h**	4-$MeO_2CC_6H_4$	1/1.5	24	**3h**	75
8	**i**	2-naphthyl	1/1.2	3	**3i**	83
9	**j**	2-AQ[c]	1/1.2	12	**3j**	69

[a] Unless noted, the reaction was carried out with $[\{RhCl(C_2H_4)_2\}_2]$ (2.5 μmol) in refluxing *o*-xylene (5 cm^3) under a slow stream of N_2.
[b] Yield of isolated product based on the amount of **1** used.
[c] 2-AQ-COCl = anthraquinone-2-carbonyl chloride.

Table 3. Reaction of aroyl chlorides **1** with *n*-butyl acrylate (**5**).[a]



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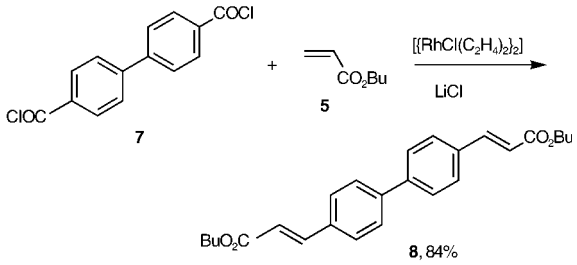
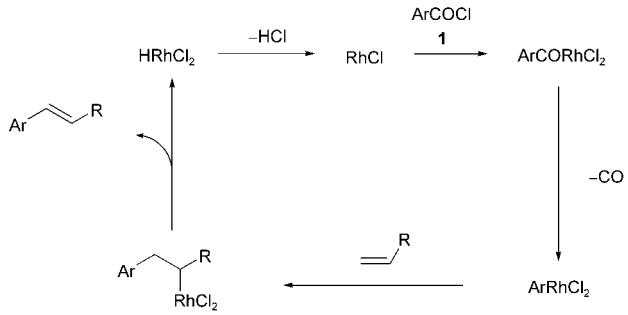
Entry	1	Ar	Time [h]	Product	Yield [%][b]	*E*/*Z*
1[c]	**a**	Ph	7	**6a**	73	95/5
2[d]	**a**	Ph	9	**6a**	81	93/7
3	**a**	Ph	9	**6a**	98	96/4
4[e]	**a**	Ph	48	**6a**	(72)	93/7
5	**b**	4-MeC_6H_4	5	**6b**	88 (85)	96/4
6	**c**	4-ClC_6H_4	12	**6c**	68 (64)	95/5
7	**d**	4-$MeOC_6H_4$	12	**6d**	68 (58)	98/2
8	**g**	4-$O_2NC_6H_4$	6	**6g**	70 (62)	94/6
9	**i**	2-naphthyl	5	**6i**	98 (90)	97/3

[a] Unless noted, the reaction of **1** (1 mmol) with **5** (1.2 mmol) was carried out using $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol) and LiCl (0.04 mmol) in refluxing *o*-xylene (5 cm^3) under N_2.
[b] GC yield based on the amount of **1** used. Value in parenthesis indicates isolated yield.
[c] Without LiCl.
[d] Using $Me(n\text{-}C_8H_{17})_3NCl$ (0.04 mmol) in place of LiCl.
[e] With **1** (10 mmol), **5** (12 mmol), and $[\{RhCl(C_2H_4)_2\}_2]$ (2.5 μmol).



Scheme 4. Reaction of **7** with **5**. Reaction conditions: **7** (1 mmol), **5** (3 mmol), $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol), LiCl (0.04 mmol), *o*-xylene, reflux, 23 h.



Scheme 5. A plausible mechanism for the reaction of **1** with acyclic alkenes.

Thus, treatment of various aroyl chlorides **1a**, **1b**, and **1d**–**j** with **2a** under a slow stream of N_2 gave simple reaction mixtures, from which essentially pure products **3a**, **3b**, and **3d**–**j** could be isolated with a simple work-up procedure: that is, only filtration, evaporation, and washing with an appropriate solvent such as methanol (Table 2). The removal of HCl by the N_2 flow enabled various functional groups to be tolerated.[13] It is noted that the reactions in entries 1, 2, 4, and 6 were carried out with use of 10 mmol of **1**. Even on a relatively larger scale with a higher substrate/catalyst ratio (**1**/Rh = 2000), the products were obtained with good yields after reasonable reaction times.

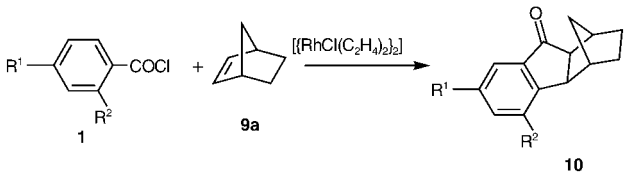
Under the present rhodium catalysis, butyl acrylate (**5**) was effectively arylated by treatment with a number of aroyl chlorides **1a**–**d**, **1g**, and **1i** to produce the corresponding cinnamates **6** (Table 3).[14] It was found that the addition of a chloride source such as an alkylammonium chloride or lithium chloride considerably improved the reaction efficiency (entries 2 and 3 *vs.* 1). The synthesis of cinnamate **6a** could also be carried out on a 10 mmol scale effectively (entry 4).

The reaction of a dicarbonyl chloride **7** with **5** was also examined in the presence of LiCl as cocatalyst (Scheme 4). Using these substrates in a 1:3 ratio gave the expected 1:2 coupling product **8** in 84% yield.

As illustrated in Scheme 5, the initial step of the present reaction appears to involve oxidative addition of **1** to Rh(I)Cl species to generate $ArCORh(III)Cl_2$. Then, the latter undergoes decarbonylation to give $ArRh(III)Cl_2$ as the key intermediate.[6,15] The subsequent insertion of alkene and β-hydride elimination as in the palladium-catalyzed Mizoroki–Heck reaction affords coupling product and $Rh(III)(H)Cl_2$. The latter may release HCl, regenerating Rh(I)Cl. Dienes such as COD and NBD on the catalyst precursors may retard the reaction by their stronger coordination ability relative to that of the alkene substrates. The success with the bromide **1d** seems to be due to the fact that oxidative addition of aryl halides under the present conditions takes place only with difficulty. While the precise role of added chloride salts in the reaction with **5** (Table 3) is not definitive at the present stage, the fact that a positive effect was not observed in the reaction with styrene (**2a**) (entry 10 in Table 1) implies that the enhancement is due to the generation of anionic rhodium species by the coordination of chloride. The electron-poor alkene may preferably interact with the metal center.

Next, the reaction of **1a** with 2-norbornene (**9a**; 2 equivs.) was examined (Table 4). Treatment of these substrates in the presence of $[\{RhCl(C_2H_4)_2\}_2]$ (1 mol %) in *o*-xylene at 120 °C for 20 h gave indanone **10a** as a single major product in 65% yield (entry 2). The analogous indenone construction was previously observed in the reaction of **1** with internal alkynes.[6] In the latter case, however, $[\{RhCl(COD)\}_2]$ was effective as the catalyst, but *not* in the present reaction with the alkene (entry 1). The reaction proceeded more effec-

Table 4. Reaction of aroyl chlorides **1** with 2-norbornene (**9a**).[a]



Entry	**1**	R^1	R^2	**9a** [mmol]	Temp. [°C]	Product	Yield [%][b]
1[c]	**a**	H	H	2	120	**10a**	tr.
2	**a**	H	H	2	120	**10a**	65
3	**a**	H	H	2	160	**10a**	77
4	**a**	H	H	5	160	**10a**	92 (84)
5	**b**	Me	H	5	160	**10b**	85 (75)
6	**e**	Br	H	5	160	**10e**	54 (42)
7	**k**	H	Me	5	160	**10k**	80 (69)

[a] Unless noted, the reaction of **1** (1 mmol) was carried out with $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol) in *o*-xylene (5 cm^3) under N_2 for 20 h.

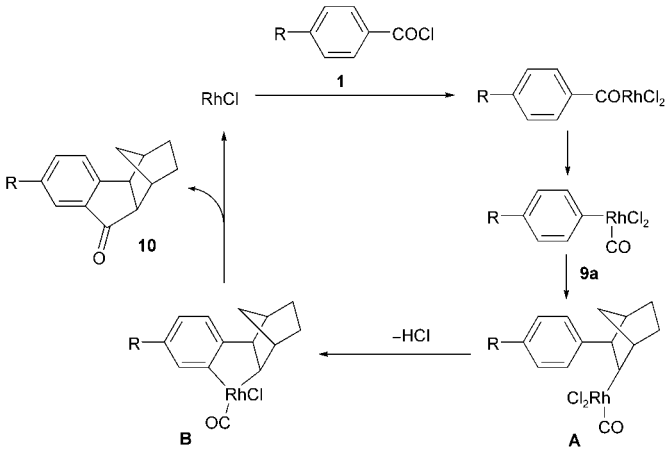
[b] GC yield based on the amount of **1** used. Value in parenthesis indicates isolated yield.

[c] With $[\{RhCl(COD)\}_2]$ (0.01 mmol) in place of $[\{RhCl(C_2H_4)_2\}_2]$.

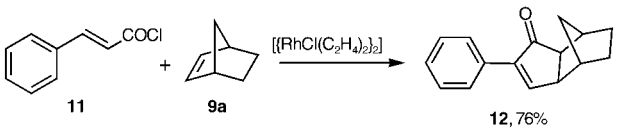
tively in the presence of $[\{RhCl(C_2H_4)_2\}_2]$ at 160 °C using 5 equivs. of **9a**, whereupon the yield of **10a** was improved to 92% (entry 4). 4-Methyl-, 4-bromo-, and 2-methylbenzoyl chlorides **1b**, **1e**, and **1k** also underwent the coupling reaction with **9a** to produce the corresponding indanones **10** (entries 5–7).

The present reaction of **1** with **9a** may proceed *via* a similar sequence to that for the reaction with internal alkynes (Scheme 6). Thus, oxidative addition of **1** to Rh(I)Cl generates $ArCORh(III)Cl_2$, which undergoes decarbonylation to give $ArRh(III)Cl_2$. The subsequent insertion of **9a** followed by cyclorhodation affords a five-membered rhodacycle intermediate **B**. Then, reinsertion of carbon monoxide coordinated to the metal center and reductive elimination may occur to release **10** and regenerate Rh(I)Cl. Although the alkene **9a** is known to be relatively reactive towards coordination-insertion on transition metals, the existence of COD on the catalyst precursor may retard such steps.

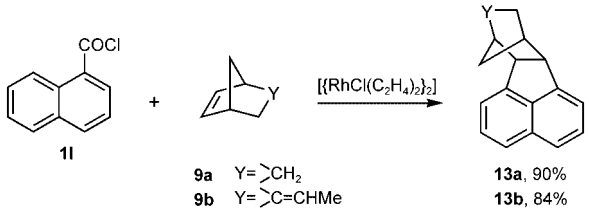
Acid chlorides other than benzoyl chlorides were also found to couple with norbornenes. Cinnamoyl chloride (**11**) underwent similar reaction with **9a** to produce cyclopentenone **12** in 76% yield (Scheme 7). On the other hand, treatment of 1-naphthoyl chloride (**1 l**) with **9a** led to a different type of coupling accompanied by decarbonylation to give rise to 6b,7,8,9,10,10a–hexahydro-7,10-methanofluoranthene (**13a**) in 90% yield (Scheme 8).[16] As shown in Scheme 9, after the insertion of **9a** to a naphthylrhodium(III) species, the cyclorhodation may occur *via* C–H bond cleavage at the *peri*-position to form a six-membered rhodacycle intermediate



Scheme 6. A plausible mechanism for the reaction of **1** with **9a**.



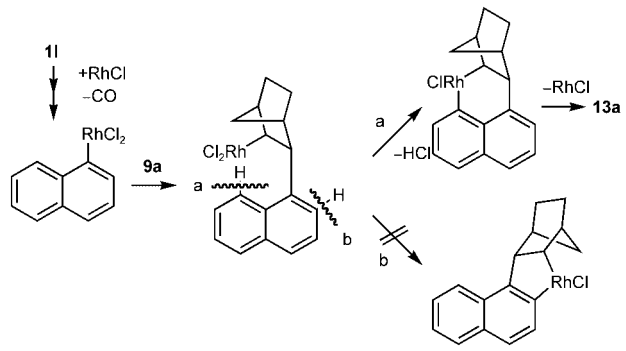
Scheme 7. Reaction of **11** with **9a**. Reaction conditions: **11** (1 mmol), **9a** (5 mmol), $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol), *o*-xylene, reflux, 20 h.



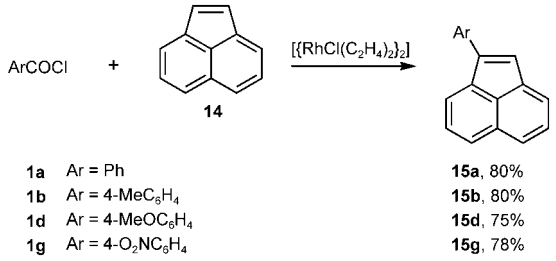
Scheme 8. Reaction of **1 l** with **9**. Reaction conditions: **1 l** (1 mmol), **9** (5 mmol), $[\{RhCl(C_2H_4)_2\}_2]$ (0.01 mmol), *o*-xylene, reflux, 5 h.

(path a) in preference to a five-membered one (path b). The six-membered rhodacycle appears to undergo reductive elimination readily without reinsertion of carbon monoxide. The acid chloride **1l** also reacted well with 5-ethylidene-2-norbornene (**9b**) to give fluoranthene **13b** in 84% yield.

Finally, the reaction of acid chlorides **1** with acenaphthylene (**14**), which possesses a reactive double bond, as well as **9**,[16,17] was examined (Scheme 10). Treatment of 4-substituted benzoyl chlorides **1a**, **1b**, **1d**, and **1 g** with **14** (2 equivs.) in the presence of $[\{RhCl(C_2H_4)_2\}_2]$ (1 mol %) in refluxing *o*-xylene for 5 h gave the Mizoroki–Heck-type products, the 1-arylacenaphthylenes **15a**, **15b**, **15d**, and **15 g** in 75–80% yields. In this case, insertion of **14** to $ArRh(III)Cl_2$ may be followed by elimination of $HRh(III)Cl_2$ to yield **15** prior to cyclorhodation. It is cited that a similar trend was observed in the palla-



Scheme 9. A plausible pathway toward **13a**.



Scheme 10. Reaction of **1** with **14**. Reaction conditions: **1** (1 mmol), **14** (2 mmol), [{RhCl(C_2H_4)$_2$}$_2$] (0.01 mmol), *o*-xylene, reflux, 5 h.

dium-catalyzed coupling of 2-iodobenzonitrile with alkenes.[17]

Conclusion

We have demonstrated that the Mizoroki–Heck-type arylation takes place upon treatment of acyclic alkenes such as styrene and butyl acrylate with aroyl chlorides in the presence of a rhodium catalyst. The reaction efficiently proceeds even without the addition of any phosphine ligand and base. Under similar conditions, cyclic alkenes such as norbornenes also react with aroyl chlorides accompanied by cyclization to afford indanone derivatives. Depending on the structure of the substrates, other types of reactions have also been shown to occur. Further investigations on related aroylative and arylative reactions are in progress.

Experimental Section

General Remarks

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX spectrometer at 400 and 100 MHz, respectively, for $CDCl_3$ solutions. *o*-Xylene was distilled from CaH_2. Aroyl chlorides were purified by bulb-to-bulb distillation before use. LiCl was dried at 150 °C under vacuum overnight.

Typical Experimental Procedure for the Reaction of 1 with 2

A mixture of **1a** (10 mmol, 1.41 g), **2a** (15 mmol, 1.56 g), and [RhCl(C_2H_4)$_2$]$_2$ (2.5 μmol, 1 mg) in refluxing *o*-xylene (5 mL) was stirred under a N_2 flow (*in a draft chamber*). The effluent gas was led to water during the reaction, so that HCl could be recovered as hydrochloric acid. After 6 h, the mixture was cooled to room temperature, Et_2O (30 mL) was added, and a small amount of insoluble material was removed by filtration using filter paper. After evaporation of the solvents under vacuum, MeOH (10 mL) was added, and then the resulting mixture was filtered to give white crystals of **3a**; yield: 1.54 g (86%).

Isolation and Characterization of 3

Methanol was used for the isolation of compounds **3** with the exception of that of **3f**, for which ethyl acetate was suitable. Due to the significantly different solubilities between the products and the minor isomers, essentially pure stilbenes could be obtained, which was checked by GC and NMR. In the case that the recovery was not sufficient, the mother liquor was concentrated and then a second crop was obtained. Characterization data of compounds **3** are given below.

(*E*)-Stilbene (3a): mp 123–125 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.03 (s, 2H), 7.15–7.19 (m, 2H), 7.25–7.30 (m, 4H), 7.42–7.45 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 126.50, 127.60, 128.66, 128.69, 137.33; MS: *m/z* = 180 (M^+).

(*E*)-4-Methylstilbene (3b): mp 118–120 °C (ref.[18] 118–119 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.36 (s, 3H), 7.05 (d, 1H, *J* = 16.5 Hz), 7.09 (d, 1H, *J* = 16.5 Hz), 7.16 (d, 2H, *J* = 8.4 Hz), 7.22–7.26 (m, 1H), 7.32–7.36 (m, 2H), 7.41 (d, 2H, *J* = 7.1 Hz), 7.50 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.23, 126.38, 126.41, 127.38, 127.69, 128.27, 128.64, 128.84, 129.38, 134.54, 137.50; MS: *m/z* = 194 (M^+).

(*E*)-4-Chlorostilbene (3c): mp 129–131 °C (ref.[19] 128 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.03 (d, 1H, *J* = 16.5 Hz), 7.08 (d, 1H, *J* = 16.5 Hz), 7.24–7.37 (m, 5H), 7.43 (d, 2H, *J* = 8.8 Hz), 7.49 (d, 2H, *J* = 7.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 126.53, 127.35, 127.64, 127.85, 128.72, 128.82, 129.31, 133.16, 135.84, 136.97; MS: *m/z* = 214, 216 (M^+).

(*E*)-4-Methoxystilbene (3d): mp 135–137 °C (ref.[19] 136 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.83 (s, 3H), 6.90 (d, 2H, *J* = 8.8 Hz), 6.97 (d, 1H, *J* = 16.5 Hz), 7.07 (d, 1H, *J* = 16.5 Hz), 7.23 (t, 1H, *J* = 7.7 Hz), 7.34 (t, 2H, *J* = 7.7 Hz), 7.45 (d, 2H, *J* = 8.8 Hz), 7.49 (d, 2H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 55.32, 114.13, 126.24, 126.62, 127.20, 127.70, 128.21, 128.63, 130.15, 137.65, 159.30; MS: *m/z* = 210 (M^+).

(*E*)-4-Bromostilbene (3e): mp 126–128 °C (ref.[20] 132–133 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.02 (d, 1H, *J* = 16.5 Hz), 7.09 (d, 1H, *J* = 16.5 Hz), 7.25–7.29 (m, 1H), 7.34–7.38 (m, 4H), 7.45–7.51 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 121.30, 126.55, 127.40, 127.89, 127.96, 128.73, 129.43, 131.77, 136.28, 136.95; MS: *m/z* = 258, 260 (M^+).

(*E*)-4-Cyanostilbene (3f): mp 115–118 °C (ref.[19] 115 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.09 (d, 1H, *J* = 16.5 Hz), 7.21 (d, 1H, *J* = 16.5 Hz), 7.32 (t, 1H, *J* = 7.7 Hz), 7.39 (t, 2H, *J* = 7.7 Hz), 7.53 (d, 2H, *J* = 7.7 Hz), 7.58 (d, 2H, *J* = 8.4 Hz), 7.63 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 110.58, 118.99, 126.71, 126.84, 126.89, 128.62, 128.84, 132.39, 132.47, 136.27, 141.82; MS: *m/z* = 205 (M^+).

(*E*)-4-Nitrostilbene (3g): mp 156–158 °C (ref.[18] 155–156 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.14 (d, 1H, *J* = 16.1 Hz), 7.27 (d, 1H, *J* = 16.1 Hz), 7.33 (t, 1H, *J* = 7.0 Hz), 7.40 (t, 2H, *J* = 7.0 Hz), 7.55 (d, 2H, *J* = 7.0 Hz), 7.62 (d, 2H, *J* = 8.8 Hz), 8.21 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 124.12, 126.27, 126.84, 127.00, 128.82, 128.88, 133.29, 136.17, 143.83, 146.76; MS: *m/z* = 225 (M^+).

Methyl 4-[(*E*)-2-phenylethenyl]benzoate (3h): mp 157–159 °C (ref.[21] 158–159 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): = 3.93 (s, 3H), 7.13 (d, 1H, *J* = 16.5 Hz), 7.22 (d, 1H, *J* = 16.5 Hz), 7.30 (t, 1H, *J* = 7.3 Hz), 7.38 (t, 2H, *J* = 7.3 Hz), 7.54 (d, 2H, *J* = 7.3 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 8.03 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 52.06, 126.30, 126.77, 127.57, 128.22, 128.77, 128.91, 130.02, 131.23, 136.75, 141.82, 166.88; MS: *m/z* = 238 (M^+).

2-[(*E*)-2-Phenylethenyl]naphthalene (3i): mp 146–147 °C (ref.[22] 148–149 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.24–7.30 (m, 2H), 7.36–7.40 (m, 2H), 7.42–7.49 (m, 2H), 7.56 (d, 2H, *J* = 7.6 Hz), 7.74 (dd, 1H, *J* = 1.8, 8.7 Hz), 7.78–7.85 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 123.51, 125.89, 126.33, 126.54, 126.61, 127.69, 127.98, 128.30, 128.37, 128.72, 128.77, 129.03, 133.04, 133.71, 134.82, 137.36; MS: *m/z* = 230 (M^+).

2-[(*E*)-2-Phenylethenyl]anthraquinone (3j):[23] mp 195–197 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21 (d, 1H, *J* = 16.5 Hz), 7.31–7.42 (m, 4H), 7.57 (d, 2H, *J* = 7.3 Hz), 7.78–7.82 (m, 2H), 7.87 (dd, 1H, *J* = 1.8, 8.1 Hz), 8.28–8.33 (m, 3H), 8.41 (d, 1H, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 124.75, 126.69, 127.04, 127.20, 127.23, 127.95, 128.72, 128.87, 131.55, 132.11, 133.04, 133.56, 133.72, 133.87, 133.94, 134.15, 136.31, 143.25, 182.58, 183.27; MS: *m/z* = 310 (M^+).

Reaction of Benzoyl Chloride (1a) with Butyl Acrylate (5)

A mixture of **1a** (10 mmol, 1.41 g), **5** (12 mmol, 1.54 g), $[RhCl(C_2H_4)_2]_2$ (2.5 μmol, 1 mg), and LiCl (0.04 mmol, 1.7 mg) was stirred in refluxing *o*-xylene (5 mL) under an N_2 flow. After 2 d, the mixture was cooled to room temperature, Et_2O (30 mL) was added, and a small amount of insoluble material was removed by filtration using filter paper. After evaporation of the solvents under vacuum, bulb-to-bulb distillation (*ca.* 120 °C/3 mmHg) of the residue afforded pure butyl cinnamate (**6a**, *E*:*Z* = 93:7) as an oil; yield: 1.46 g.

The cinnamates **6b–d**, **6g**, and **6i** were isolated by column chromatography on silica gel using hexane-ethyl acetate as eluent.

***n*-Butyl cinnamate (6a, *E*:*Z* = 93:7):**[22] oil; ^{1}H NMR ($CDCl_3$, 400 MHz): d = 0.90 (t, 3H, *J* = 7.3 Hz, *Z*), 0.97 (t, 3H, *J* = 7.3 Hz, *E*), 1.25–1.34 (m, 2H, *Z*), 1.40–1.47 (m, 2H, *E*), 1.55–1.62 (m, 2H, *Z*), 1.66–1.73 (m, 2H, *E*), 4.11 (t, 2H, *J* = 6.6 Hz, *Z*), 4.21 (t, 2H, *J* = 6.6 Hz, *E*), 5.95 (d, 1H, *J* = 12.5 Hz, *Z*), 6.44 (d, 1H, *J* = 16.1 Hz, *E*), 6.95 (d, 1H, *J* = 12.5 Hz, *Z*), 7.36–7.55 (m, 5H), 7.68 (d, 1H, *J* = 16.1 Hz, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.73, 19.19, 30.77, 64.42, 118.29, 128.03, 128.85, 130.18, 134.47, 144.54, 167.09; MS: *m/z* = 204 (M^+).

***n*-Butyl 3-(4-methylphenyl)-2-propenoate (6b, *E*:*Z* = 96:4):**[22] oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91 (t, 3H, *J* = 7.6 Hz, *Z*), 0.96 (t, 3H, *J* = 7.6 Hz, *E*), 1.29–1.49 (m, 2H), 1.56–1.72 (m, 2H), 2.37 (s, 3H, *E*), 2.45 (s, 3H, *Z*), 4.12 (t, 2H, *J* = 6.6 Hz, *Z*), 4.20 (t, 2H, *J* = 6.6 Hz, *E*), 5.89 (d, 1H, *J* = 12.7 Hz, *Z*), 6.39 (d, 1H, *J* = 16.0 Hz, *E*), 6.90 (d, 1H, *J* = 12.7 Hz, *Z*), 7.19 (d, 2H, *J* = 8.3 Hz), 7.42 (d, 2H, *J* = 8.3 Hz), 7.66 (d, 1H, *J* = 16.0 Hz, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.72, 19.19, 21.43, 30.79, 64.32, 117.20, 128.02, 129.58, 131.74, 140.58, 144.52, 167.27; MS: *m/z* = 218 (M^+).

***n*-Butyl 3-(4-chlorophenyl)-2-propenoate (6c, *E*:*Z* = 95:5):**[22] mp 30–32 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91 (t, 3H, *J* = 7.3 Hz, *Z*), 0.97 (t, 3H, *J* = 7.3 Hz, *E*), 1.30–1.48 (m, 2H), 1.56–1.73 (m, 2H), 4.11 (t, 2H, *J* = 6.6 Hz, *Z*), 4.21 (t, 2H, *J* = 6.6 Hz, *E*), 5.96 (d, 1H, *J* = 12.5 Hz, *Z*), 6.41 (d, 1H, *J* = 16.1 Hz, *E*), 6.88 (d, 1H, *J* = 12.5 Hz, *Z*), 7.35 (d, 2H, *J* = 8.4 Hz), 7.45 (d, 2H, *J* = 8.4 Hz), 7.62 (d, 1H, *J* = 16.1 Hz, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.72, 19.18, 30.75, 64.53, 118.90, 129.14, 129.18, 132.97, 136.10, 143.06, 166.81; MS: *m/z* = 238, 240 (M^+).

***n*-Butyl 3-(4-methoxyphenyl)-2-propenoate (6d, *E*:*Z* = 98:2):**[22] oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.81 (t, 3H, *J* = 7.3 Hz, *Z*), 0.96 (t, 3H, *J* = 7.3 Hz, *E*), 1.29–1.48 (m, 2H), 1.53–1.72 (m, 2H), 3.84 (s, 3H, *E*), 3.89 (s, 3H, *Z*), 4.01 (t, 2H, *J* = 6.6 Hz, *Z*), 4.20 (t, 2H, *J* = 6.6 Hz, *E*), 6.11 (d, 1H, *J* = 11.8 Hz, *Z*), 6.31 (d, 1H, *J* = 16.1 Hz, *E*), 6.51 (d, 1H, *J* = 11.8 Hz, *Z*), 6.90 (d, 2H, *J* = 8.8 Hz), 7.48 (d, 2H, *J* = 8.8 Hz), 7.64 (d, 1H, *J* = 16.1 Hz, *E*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.73, 19.20, 30.81, 55.34, 64.24, 114.29, 115.79, 127.22, 129.66, 144.17, 161.31, 167.41; MS: *m/z* = 234 (M^+).

***n*-Butyl 3-(4-nitrophenyl)-2-propenoate (6g, *E*:*Z* = 94:6):**[22] mp 64–65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 (t, 3H, *J* = 7.3 Hz, *Z*), 0.98 (t, 3H, *J* = 7.3 Hz, *E*), 1.28–1.49 (m, 2H), 1.54–1.74 (m, 2H), 4.11 (t, 2H, *J* = 6.9 Hz, *Z*), 4.24 (t, 2H, *J* = 6.9 Hz, *E*), 6.14 (d, 1H, *J* = 12.7 Hz, *Z*), 6.57 (d, 1H, *J* = 16.3 Hz, *E*), 7.01 (d, 1H, *J* = 12.7 Hz, *Z*), 7.68 (d, 2H, *J* = 8.3 Hz), 7.71 (d, 1H, *J* = 16.3 Hz, *E*), 8.25 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): d = 13.70, 19.16, 30.69, 64.89, 122.62, 124.15, 128.59, 140.64, 141.56, 148.48, 166.09; MS: *m/z* = 249 (M^+).

***n*-Butyl 3-(2-naphthyl)-2-propenoate (6i, *E*:*Z* = 97:3):**[22] mp 60–61 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.85 (t, 3H, *J* = 7.3 Hz, *Z*), 0.98 (t, 3H, *J* = 7.3 Hz, *E*), 1.24–1.51 (m, 2H), 1.54–1.75 (m, 2H), 4.13 (t, 2H, *J* = 6.6 Hz, *Z*), 4.24 (t, 2H, *J* = 6.6 Hz, *E*), 6.03 (d, 1H, *J* = 12.5 Hz, *Z*), 6.55 (d, 1H, *J* = 15.9 Hz, *E*), 7.10 (d, 1H, *J* = 12.5 Hz, *Z*), 7.48–7.53 (m, 2H), 7.65–7.73 (m, 1H), 7.81–7.83 (m, 3H), 7.84 (d, 1H, *J* = 15.9 Hz, *E*), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.75, 19.22, 30.80, 64.44, 118.46, 123.51, 126.67, 127.17, 127.75, 128.53, 128.64, 129.83, 131.98, 133.29, 134.19, 144.56, 167.14; MS: *m/z* = 254 (M^+).

Di-*n*-butyl 3,3′-[(1,1′-biphenyl)-4,4′-diyl]bis-2-propenoate [8, (2*E*,2′*E*):(2*E*,2′*Z*) = 97:3]: mp 90–92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.91 (t, 6H, *J* = 7.3 Hz, *EZ*), 0.98 (t, 6H, *J* = 7.3 Hz, *EE*), 1.28–1.50 (m, 4H), 1.58–1.74 (m, 4H), 4.14 (t, 4H, *J* = 6.6 Hz, *EZ*), 4.23 (t, 4H, *J* = 6.6 Hz, *EE*), 5.98 (d, 2H, *J* = 12.5 Hz, *EZ*), 6.48 (d, 2H, *J* = 15.8 Hz, *EE*), 6.97 (d, 2H, *J* = 12.5 Hz, *EZ*), 7.60–7.65 (m, 8H), 7.71 (d, 2H, *J* = 15.8 Hz, *EE*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.74, 19.20, 30.78, 64.48, 118.50, 127.40, 128.62, 133.98, 141.80, 143.81, 167.02; MS: *m/z* = 406 (M^+); anal. calcd. for $C_{26}H_{30}O_4$: C 76.82, H 7.44; found: C 76.95, H 7.51.

Typical Experimental Procedure for the Reaction of 1 with Cyclic Alkenes

A mixture of **1a** (1 mmol, 141 mg), **9a** (5 mmol, 470 mg), and $[RhCl(C_2H_4)_2]_2$ (0.01 mmol, 4 mg) in refluxing *o*-xylene (5 mL) was stirred under N_2 (1 atm). After 20 h, the mixture was cooled to room temperature. After evaporation of the solvents under vacuum, the product 1,2,3,4,4a,9a–hexahydro-1,4-methanofluoren-9-one (**10a**)[17] was isolated by column chromatography on silica gel using hexane-ethyl acetate as eluent; yield: 166 mg (84%); mp 51–53 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 (dt, 1H, *J* = 10.5, 1.8 Hz), 0.95 (dt, 1H, *J* = 10.5, 1.5 Hz), 1.35–1.50 (m, 2H), 1.60–1.76 (m, 2H), 2.41 (d, 1H, *J* = 4.0 Hz), 2.50 (d, 1H, *J* = 6.2 Hz), 2.60 (d, 1H, *J* = 4.0 Hz), 3.15 (d, 1H, *J* = 5.8 Hz), 7.35 (t, 1H, *J* = 7.6 Hz), 7.50 (dd, 1H, *J* = 0.7, 7.6 Hz), 7.61 (dt, 1H, *J* = 1.1, 7.6 Hz), 7.71 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.65, 28.86, 32.18, 40.36, 41.24, 48.01, 55.81, 123.14, 126.12, 127.35, 134.91, 139.04, 157.21, 208.85; MS: *m/z* = 198 (M^+); anal. calcd. for $C_{14}H_{14}O$: C 84.81, H 7.12; found: C 84.52, H, 7.25.

1,2,3,4,4a,9a-Hexahydro-7-methyl-1,4-methanofluoren-9-one (10b): mp 74–76 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 (dt, 1H, *J* = 10.5, 1.5 Hz), 0.93 (dt, 1H, *J* = 10.5, 1.5 Hz), 1.33–1.48 (m, 2H), 1.59–1.75 (m, 2H), 2.37–2.40 (m, 4H), 2.49 (d, 1H, *J* = 5.8 Hz), 2.58 (d, 1H, *J* = 4.4 Hz), 3.10 (d, 1H, *J* = 6.2 Hz), 7.37–7.44 (m, 2H), 7.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.06, 28.65, 28.82, 32.12, 40.28, 41.17, 47.66, 56.17, 123.07, 125.77, 136.20, 137.29, 139.21, 154.66, 208.94; MS: *m/z* = 212 (M^+); anal. calcd. for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 84.61, H 7.59.

7-Bromo-1,2,3,4,4a,9a–hexahydro-1,4-methanofluoren-9-one (10e): mp 84–85 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 (dt, 1H, *J* = 10.5, 1.8 Hz), 0.97 (dt, 1H, *J* = 10.5, 1.5 Hz), 1.33–1.49 (m, 2H), 1.60–1.77 (m, 2H), 2.39 (d, 1H, *J* = 4.4 Hz), 2.52 (d, 1H, *J* = 5.9 Hz), 2.60 (d, 1H, *J* = 4.4 Hz), 3.10 (d, 1H, *J* = 6.2 Hz), 7.38 (d, 1H, *J* = 8.1 Hz), 7.70 (dd, 1H, *J* = 1.8, 8.1 Hz), 7.83 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.55, 28.81, 32.24, 40.52, 41.17, 47.73, 56.19, 121.74, 126.17, 127.72, 137.68, 140.90, 155.69, 207.25; MS: *m/z* = 276, 278 (M^+); anal. calcd. for $C_{14}H_{13}BrO$: C 60.67, H 4.73, Br 28.83; found: C 60.38, H 4.74, Br 28.77.

1,2,3,4,4a,9a-Hexahydro-5-methyl-1,4-methanofluoren-9-one (10k): mp 68–72 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (dt, 1H, *J* = 10.6, 1.8 Hz), 0.95 (dt, 1H, *J* = 10.6, 1.5 Hz), 1.35–1.51 (m, 2H), 1.61–1.77 (m, 2H), 2.45 (s, 3H), 2.50 (d, 2H, *J* = 5.1 Hz), 2.63 (d, 1H, *J* = 4.0 Hz), 3.12 (d, 1H, *J* = 5.9 Hz), 7.27 (t, 1H, *J* = 7.7 Hz), 7.41 (d, 1H, *J* = 7.7 Hz), 7.56 (d, 1H, *J* = 7.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.05, 28.43, 29.19, 32.29, 38.92, 40.26, 47.26, 56.06, 120.71, 127.62, 135.78, 135.81, 139.06, 155.39, 209.22; MS: *m/z* = 212 (M^+); anal. calcd. for $C_{15}H_{16}O$: C 84.87, H 7.60; found: C 84.59, H 7.56.

3a,4,5,6,7,7a-Hexahydro-2-phenyl-4,7-methano-*1H*-inden-1-one (12): mp 95–97 °C (ref.[24] 95 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): d = 1.00 (dt, 1H, *J* = 10.5, 1.5 Hz), 1.12 (dt, 1H, *J* = 10.5, 2.2 Hz), 1.29–1.40 (m, 2H), 1.58–1.76 (m, 2H), 2.28 (d, 1H, *J* = 4.4 Hz), 2.37 (d, 1H, *J* = 5.4 Hz), 2.50 (d, 1H, *J* = 4.4 Hz), 2.69–2.71 (m, 1H), 7.30–7.40 (m, 3H), 7.64 (d, 1H, *J* = 3.3 Hz), 7.68–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 28.39, 29.15, 31.28, 38.36, 39.46, 47.73, 54.94, 127.04, 128.37, 128.39, 131.52, 146.12, 160.15, 208.98; MS: *m/z* = 224 (M^+); anal. calcd. for $C_{16}H_{16}O$: C 85.68, H 7.19; found: C 85.48, H 7.19.

6b,7,8,9,10,10a-Hexahydro-7,10-methanofluoranthene (13a):[16] mp 52–54 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.70 (d, 1H, *J* = 10.3 Hz), 0.87 (d, 1H, *J* = 10.3 Hz), 1.42–1.47 (m, 2H), 1.59–1.64 (m, 2H), 2.32–2.33 (m, 2H), 3.39 (s, 2H), 7.17 (d, 2H, *J* = 7.0 Hz), 7.37 (dd, 2H, *J* = 7.0, 8.3 Hz), 7.50 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 29.36, 32.64, 42.85, 53.46, 119.00, 122.37, 127.90, 131.03, 140.82, 148.29; MS: *m/z* = 220 (M^+).

8-Ethylidene-6b,7,8,9,10,10a–hexahydro-7,10-methanofluoranthene (13b, *major*:*minor* = *ca.* 3:1): oil; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.84 (d, 1H, *J* = 10.3 Hz), 1.08 (d, 1H, *J* = 10.3 Hz), 1.62 (d, 3H, *J* = 6.6 Hz, *major*), 1.81 (d, 3H, *J* = 6.6 Hz, *minor*), 2.11–2.36 (m, 2H), 2.48–2.49 (m, 1H, *minor*), 2.54–2.56 (m, 1H, *major*), 2.79 (s, 1H, *major*), 3.11 (s, 1H, *minor*), 3.53–3.60 (m, 2H), 5.20–5.25 (m, 1H, *minor*), 5.48–5.54 (m, 1H, *major*), 7.27–7.29 (m, 2H), 7.46 (dd, 2H, *J* = 7.0, 8.3 Hz), 7.59 (d, 2H, *J* = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 14.03, 14.63, 33.01, 33.28, 35.30, 38.29, 43.00, 43.02, 45.56, 51.06, 52.59, 52.76, 52.92, 53.44, 112.78, 113.40, 119.09, 119.13, 119.17, 119.21, 122.52, 122.56, 122.62, 127.93, 127.97, 131.08, 140.95, 144.30, 145.19, 146.96, 147.07, 147.92, 147.96; MS: *m/z* = 246 (M^+); anal. calcd. for $C_{19}H_{18}$: C 92.64, H 7.36; found: C 92.36, H 7.48.

1-Phenylacenaphthylene (15a): mp 52–54 °C (ref.[25] 56–58 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.17 (s, 1H), 7.38 (t, 1H, *J* = 7.3 Hz), 7.49 (t, 2H, *J* = 7.3 Hz), 7.55 (dd, 1H, *J* = 6.9, 8.3 Hz), 7.60 (dd, 1H, *J* = 6.9, 8.3 Hz), 7.69 (d, 1H, *J* = 6.9 Hz), 7.78–7.81 (m, 3H), 7.85 (d, 1H, *J* = 8.3 Hz), 7.94 (d, 1H, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 123.86, 124.42, 125.54, 127.00, 127.49, 127.58, 127.61, 127.93 (overlapped), 128.41, 128.76, 129.32, 136.17, 138.66, 139.11, 143.46; MS: *m/z* = 228 (M^+).

1-(4-Methylphenyl)acenaphthylene (15b): mp 64–66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): d = 2.43 (s, 3H), 7.13 (s, 1H), 7.30 (d, 2H, *J* = 8.1 Hz), 7.54 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.59 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.66 (d, 1H, *J* = 7.0 Hz), 7.69 (d, 2H, *J* = 8.1 Hz), 7.78 (d, 1H, *J* = 8.4 Hz), 7.84 (d, 1H, *J* = 8.1 Hz), 7.93 (d, 1H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 21.29, 123.61, 124.37, 124.91, 126.80, 127.46, 127.50, 127.80, 127.92, 128.38, 129.35, 129.49, 133.31, 137.49, 138.82, 139.25, 143.43; MS: *m/z* = 242 (M^+); anal. calcd. for $C_{19}H_{14}$: C 94.18, H 5.82; found: C 93.90, H 5.95.

1-(4-Methoxyphenyl)acenaphthylene (15d): mp 69–71 °C (ref.[26] 76.5–77.5 °C); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.88 (s, 3H), 7.03 (d, 2H, *J* = 8.8 Hz), 7.08 (s, 1H), 7.53 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.59 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.64 (d, 1H, *J* = 6.6 Hz), 7.73 (d, 2H, *J* = 8.8 Hz), 7.77 (d, 1H, *J* = 8.1 Hz), 7.84 (d, 1H, *J* = 8.1 Hz), 7.92 (d, 1H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 76.69, 114.27, 123.40, 124.19, 124.28, 126.62, 127.42, 127.50, 127.95, 128.37, 128.85, 129.06, 129.34, 138.91, 139.35, 143.09, 159.37; MS: *m/z* = 258 (M^+); anal. calcd for $C_{19}H_{14}O$: C 88.34, H 5.46; found: C 88.01, H, 5.59.

1-(4-Nitrophenyl)acenaphthylene (15g): mp 130–131 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35 (s, 1H), 7.61 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.64 (dd, 1H, *J* = 7.0, 8.1 Hz), 7.78 (d, 1H, *J* = 7.0 Hz), 7.88–7.95 (m, 5H), 8.33 (d, 2H, *J* = 9.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 124.16, 124.53, 125.17, 127.66, 128.20 (overlapped), 128.23, 128.27, 128.49, 128.58, 129.30, 137.56, 138.30, 140.90, 142.76, 146.89; MS: *m/z* = 273 (M^+); anal. calcd. for $C_{18}H_{11}NO_2$: C 79.11, H 4.06, N 5.13; found: C 79.38, H 4.18, N 5.02.

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