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Silver-Catalyzed Domino Reaction of ortho-Carbonylated Alkynyl-Substituted Arylaldehydes with Conjugated Dienes: Stereoselective Access to Indanone-Fused Cyclohexenes

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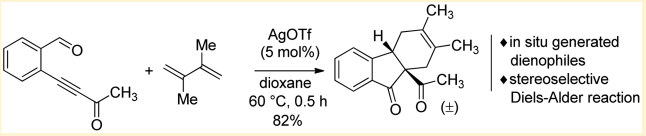
Supporting Information

ABSTRACT: A silver-catalyzed domino reaction of ortho-carbonylated alkynyl-substituted arylaldehydes with conjugated dienes is described here. Through this reaction, the synthesis of a variety of indanone-fused cyclohexene derivatives can be achieved efficiently. The formation of these tricyclic products could involve a key Diels–Alder reaction of *in situ* generated indanenone dienophiles with conjugated dienes. Particularly, the products can be accomplished in a high *endo*/*exo* selective way.



INTRODUCTION

Indanone-fused cyclohexanes are vitally important polycyclic skeletal structures, which can be found in many natural products and pharmaceutically active molecules such as compounds **1**–**5** (Figure 1).[1−5] For instance, exiguaquinol

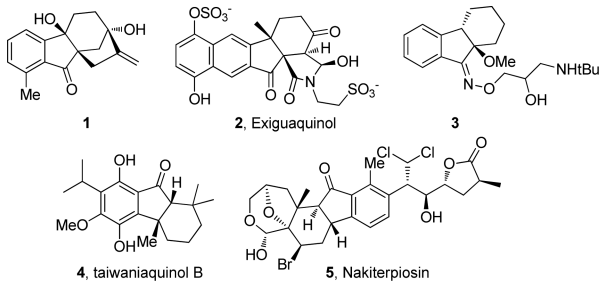


Figure 1. Representative bioactive compounds having indanone-fused cyclohexane skeleton.

(**2**),[2] isolated from the Australian sponge *Neopetrosia exigua*, can inhibit *Helicobacter pylori* glutamate racemase (Murl) with an IC_{50} of 4.4 μM. Compound **3** exhibits very high selective β_2-blocking properties.[3] And nakiterpiosin (**5**) is a marine sponge metabolite and exhibits potent cytotoxicity against the P388 murine leukemia cell line (GI_{50} = 10 ng/mL).[5] Therefore, the construction of the tricyclic skeleton has attracted the attention of synthetic chemists and various approaches have been developed.[6] However, efficient and simple routes in a step- and atom-economic fashion are still highly desired.

Ortho-alkynylarylaldehydes have become one of the most valuable building blocks in the field of synthetic organic chemistry since Yamamoto and co-workers reported the reaction of acetylenic aldehydes with alcohols produced 1*H*-isochromene derivatives.[7] By the design of substrates and the selection of reaction partners, it has made the construction of various structural skeletons acheivable over the past decade.[8,9] In particular, the employment of ortho-carbonylated alkynyl-substituted arylaldehyde substrates could provide a novel active form for diversity-oriented synthesis. And based on this class of versatile building blocks, some interesting products have been exploited. For instance, Zhu and co-workers reported the synthesis of polycyclic products with alkenes as a partner.[10] Recently, the same group developed $In(OTf)_3$-catalyzed reactions of enynals with propynol or alkynes for generation of tricyclic indanone products.[11] Han and Lu's group reported that the implementation of nucleophilic acetic acid and indoles can afford isobenzofuran and indanone derivatives,[12] respectively. Bull and Cao et al. reported independently a metal-free synthesis of isoindolinone and indenamine derivatives when amine compounds were employed.[13] In addition, conjugated dienes as a class of valuable partners have been used in the reaction of *ortho*-alkynylarylaldehydes. As shown in the eq 1 of Scheme 1, Zhu and co-workers reported the synthesis of the highly strained cyclopropane-fused polycyclic skeleton by a bioinspired intramolecular Diels–Alder reaction.[14] An efficient access to highly strained tetracyclic bridgehead olefins from similar starting materials was also discovered by Cao and co-workers (Scheme 1, eq 2).[15] Following our continuing interest in the transformation of *ortho*-alkynylarylaldehydes,[13b,15,16] herein we would like to describe a new transformation of enynals with conjugated dienes to access useful indanone-fused cyclohexene derivatives enabled by silver catalysis (Scheme 1, eq 3). To the best of our knowledge, the stereoselective construction of these types of cycles via the present reaction is not yet reported.[6]

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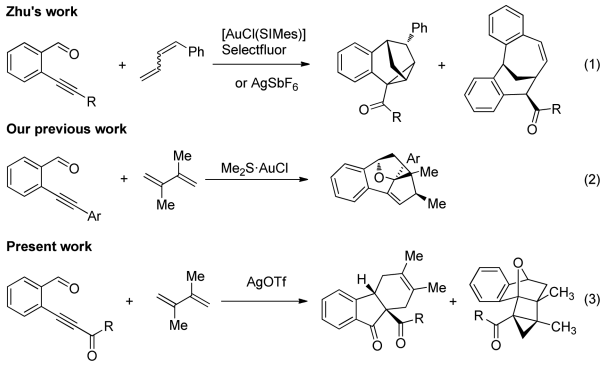
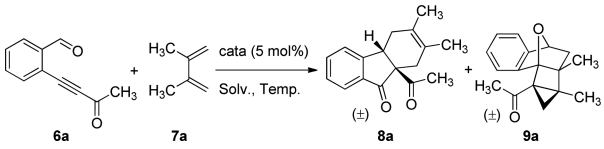
Scheme 1. Reactions of Enynals with Conjugated Dienes



RESULTS AND DISCUSSION

We commenced our investigation by studying the reaction of *o*-alkynylbenzaldehyde (**6a**) with conjugated diene (**7a**) to establish reaction conditions (Table 1). It can be found that

Table 1. Optimization of Reaction Conditions[a]



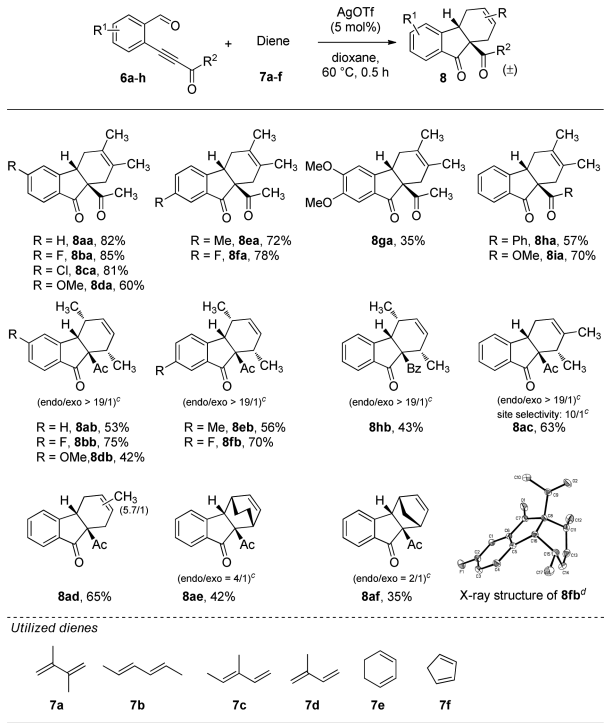
					Yield (%)[b]	
entry	catalyst (5 mol %)	solvent	temp (°C)	time (h)	**8a**	**9a**
1	$In(OTf)_3$	dioxane	60	12	50	0
2	TfOH	dioxane	60	12	70	0
3	$AgSbF_6$	dioxane	60	0.5	75	0
4	$AgBF_4$	dioxane	60	0.5	76	0
5	AgOTf	dioxane	60	0.5	82	0
6	$AgNTf_2$	dioxane	60	0.5	80	0
7	AgOTf	DCE	60	1	0	30
8	AgOTf	$CHCl_3$	60	1	0	26
9	AgOTf	CH_3CN	60	6	30	0
10	AgOTf	THF	60	2	24	0
11	AgOTf	toluene	60	12	0	0
12	AgOTf	dioxane	40	1	60	0

[a]All the reactions were carried out with **6a** (0.2 mmol), **7a** (5 equiv), and catalyst (5 mol %) in the indicated solvent (2.0 mL). [b]Yield of isolated products.

the use of several Lewis and Brønsted acids can promote the generation of tricyclic product **8a** with 1,4-dioxane as the solvent at 60 °C in acceptable yields (Table 1, entries 1−6).[17] The reaction time could be shortened greatly when the silver salts were selected (Table 1, entries 3−6), and the AgOTf catalyst gave product **8a** in a slightly high yield (Table 1, entry 5). Interestingly, changing the solvent to 1,2-dichloroethane or chloroform led to the formation of a new product (**9a**) in low yield (Table 1, entries 7−8). The product **9a** bears a strained pentacyclic skeleton. Efforts to address the improvement of yield of **9a** were inefficient.[18] Other solvents such as acetonitrile could not give a better yield of **8a** (Table 1, entries 9−11). The study of the reaction temperature showed a low yield of product **8a** was observed at 40 °C. Finally, the optimal conditions for the formation of **8a** were established involving the use of 5 mol % AgOTf with 1,4-dioxane as the solvent at 60 °C (Table 1, entry 5).

Under the optimal reaction conditions (Table 1, entry 5), we examined the scope of enynals and conjugated dienes for the formation of indanone-fused cyclohexene derivatives. It can be found that a variety of desired tricyclic products can be obtained in good yields (Table 2). The enynal substrates **6a−f**

Table 2. Synthesis of Tricyclic Cyclohexene Derivatives[a,b]



[a]All the reactions were carried out with **6** (0.3 mmol), 7 (5 equiv), and AgOTf (5 mol %) in dioxane (3.0 mL) at 60 °C for 0.5 h, unless otherwise noted. [b]Yield of isolated products. [c]The selectivity was determined by ^{1}H NMR analysis of the crude product. [d]Hydrogen atoms are omitted for clarity.

bearing both an electron-deficient and -donating group can react with diene **7a** to give the desired products **8aa−fa** in satisfactory yields (60−85%), whereas the reaction of substrate **6g** having two strong electron-donating groups (−OMe) with **7a** can only produce **8ga** in 35% yield. Substrates **6h** and **6i** with a benzoyl or an ester group attached to the alkyne motif were also suitable for the present reaction to afford the corresponding products **8ha** and **8ia** in acceptable yields. Subsequently, different diene compounds were investigated. The results exhibited the reactions of diene **7b** with several enynals can provide the desired cyclohexene derivatives with good efficiency (**8ab−bb**, **8db−fb**, and **8hb**). The structure of product **8fb** was confirmed unambiguously by the X-ray analysis of crystal structure,[19] and the relative configurations of other products were tentatively assigned by analogy with that of **8fb**. Notably, these products could be produced in high *endo*/*exo* selectivities (>19/1) based on ^{1}H NMR analysis of the crude product. Other asymmetrical dienes such as **7c** and **7d** were tolerated to achieve this transformation; thus, products **8ac** and **8ad** were obtained efficiently with good regio- and stereoselectivities. With regard to the examination of cyclic conjugated dienes such as 1,3-cyclohexadiene **7e** and cyclopentadiene **7f**, the bridged cyclic products **8ae** and **8af** could be also afforded albeit with more modest yields and *endo*/*exo* selectivities. Moreover, the reaction of (−)-perillaldehyde-

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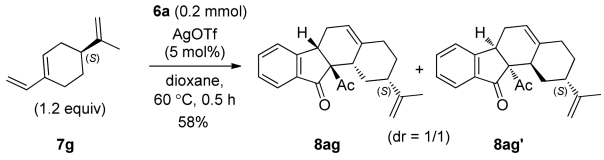
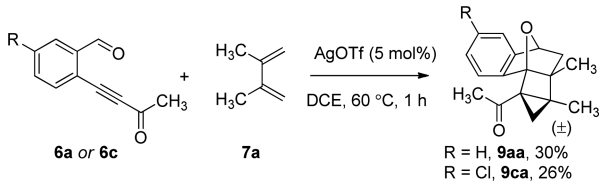
derived diene **7a** with **6a** was carried out, leading to the formation of the interesting tetracyclic products **8ag**/**8ag′** in 58% yield with the ratio 1/1 (Scheme 2). This shows the possibility of building structurally complex molecules by utilizing the present protocol.

Scheme 2. Reaction of (−)-Perillaldehyde-Derived Diene 7g with 6a



We also expand the reaction scope of silver-catalyzed enynals with dienes to give the strained pentacyclic products. Thus, the expected products **9aa** and **9ca** could be obtained albeit with low yields (Scheme 3). In these cases, an intramolecular tandem [3 + 2]/[2 + 1] cycloaddition was achieved to produce the fused polycyclic skeleton with respect to the previous reported procedure.[10]

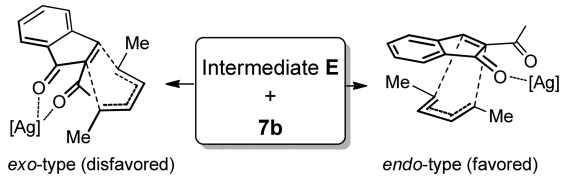
Scheme 3. Examples on the Formation of Strained Pentacyclic Products 9



A possible mechanism for the formation of **8a** and **9a** is provided in Scheme 4.[10−12] The coordination of the silver catalyst to the triple bond of substrate **6a** gives complex **A** which then undergoes a 5-*exo*-*dig* cyclization to produce the key intermediate **B**. The active oxonium ion **B** can be converted into *β*-diketone **C** via hydrolysis reaction in the presence of adventitious water (*path a*). With the silver salt, the equilibrium between **C** and **D** could occur. Subsequently, Knoevenagel condensation leads to the formation of indenone **E** that can afford the final tricyclic product **8a** via a [4 + 2] cycloaddition with diene **7a**.[20] With regard to the formation of strained compound **9a**, *path b* can be followed. As shown in Scheme 4 (right part), the dipole **F** with a silver carbene unit could be generated from intermediate **B**. Followed by the [3 + 2] cycloaddition of the dipole motif with diene to give bridged-ring **G**, the cyclopropanation of silver carbene with the unreacted alkene unit can achieve the construction of polycyclic skeleton **9a**, along with regeneration of the silver catalyst.

It should be noted that the high stereoselectivity of **8** can result from the Diels−Alder cycloaddition step.[21] In this step, the *endo*-type mode could be more preferred to the *exo*-type mode (Scheme 5, for one example).

Scheme 5. *exo*/*endo* Selectivity of Diels−Alder Reaction



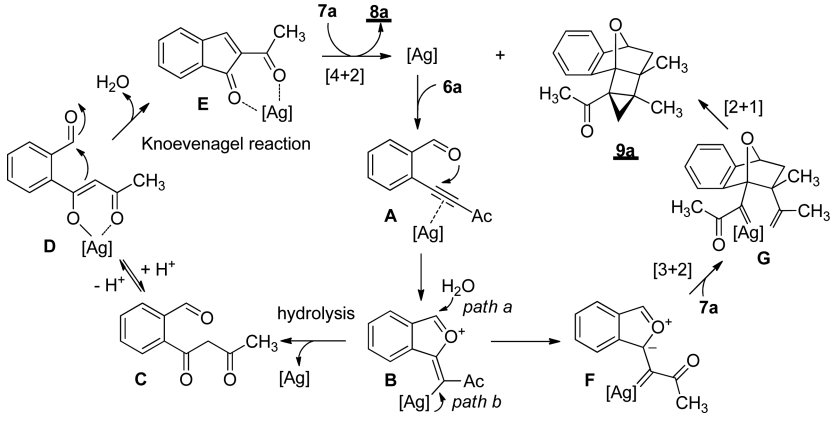
CONCLUSION

In summary, a silver-catalyzed domino reaction of ortho-carbonylated alkynyl-substituted arylaldehydes with conjugated dienes has been developed. This reaction provides an efficient method for the synthesis of indanone-fused cyclohexene derivatives in highly stereoselective way. The mechanism for the formation of this class of skeleton was proposed to be a domino hydrolysis/Knoevenagel condensation/Diels−Alder reaction. Interestingly, an intramolecular tandem [3 + 2]/[2 + 1] cycloaddition reaction can be achieved to access the highly strained polycyclic structure depending on the selection of reaction solvents. The present reaction features readily accessible starting materials, mild reaction conditions, and simple operation. Further works will focus on the detailed reaction mechanisms by DFT calculations and application of this methodology to achieve the synthesis of interesting molecules.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in air unless otherwise noted. Dioxane, THF, and toluene were distilled from sodium and benzophenone. DCE, chloroform, and acetonitrile were distilled from CaH_2. Unless noted, all commercial reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 500 and 125 MHz, respectively. ^1H NMR spectra were recorded

Scheme 4. Proposed Reaction Mechanism for the Formation of 8a and 9a



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with tetramethylsilane (δ = 0.00 ppm) or the solvent residual peak ($CDCl_3$, 7.26 ppm) as the internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as the internal reference. High-resolution mass spectra were performed on a mass spectrometer with an FT-ICR analyzer.

General Procedure for Preparation of Substrates 6. Under an argon atmosphere, to a stirred suspension of $PdCl_2(PPh_3)_2$ (3 mol %, 63.2 mg) and CuI (5 mol %, 28.6 mg) in dry THF (12 mL) were added *o*-bromoaldehyde (3 mmol, 1.0 equiv), alkynol (4.5 mmol, 1.5 equiv), and NEt_3 (6 mL) sequentially. The resulting mixture was stirred at 60 °C overnight. After completion which was monitored by TLC, the mixture was cooled and then filtered through a short silica gel column, and then volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petrol ether = 1/10) to give the alcohol intermediate. This compound was dissolved into EtOAc (6 mL) at room temperature, and then active MnO_2 (10 equiv) was added. The resulting mixture was stirred overnight. After completion, the mixture was filtered through a short silica gel column, and then the solvent was removed. The residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petrol ether = 1/20) to afford pure **6**.

Substrates **6a**−**e** and **6h**−**i** were known and prepared according to literature procedures.[10,13b] Substrates **6f** and **6g** were prepared according to the above procedure.

*4-Fluoro-2-(3-oxobutynyl)benzaldehyde (**6f**).* White solid, mp 68−69 °C; yield 211 mg, 37% over two steps; R_f = 0.47 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 10.39 (s, 1H), 8.01 (dd, J = 8.7, 5.7 Hz, 1H), 7.37 (dd, J = 8.5, 2.5 Hz, 1H), 7.29 (ddd, J = 8.3, 8.3, 2.6 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 188.5, 183.5, 165.3 (d, J = 258.7 Hz), 133.6 (d, J = 3.1 Hz), 130.9 (d, J = 10.0 Hz), 125.2 (d, J = 10.8 Hz), 121.0 (d, J = 24.3 Hz), 118.8 (d, J = 21.9 Hz), 93.7, 83.0 (d, J = 2.8 Hz), 32.7; HRMS (ESI) m/z calcd for $C_{11}H_8FO_2$ $(M + H)^+$ 191.0503, found 191.0503.

*4,5-Dimethoxy-2-(3-oxobutynyl)benzaldehyde (**6g**).* White solid, mp 107−109 °C; yield 83 mg, 12% over two steps; R_f = 0.45 (hexanes/EtOAc = 3/1); ^1H NMR (500 MHz, $CDCl_3$): δ 10.37 (s, 1H), 7.45 (s, 1H), 7.10 (s, 1H), 3.98 (s, 6H), 2.49 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 189.1, 183.9, 153.5, 151.6, 131.9, 117.0, 115.6, 108.8, 92.9, 85.5, 56.5, 56.3, 32.7; HRMS (ESI) m/z calcd for $C_{13}H_{13}O_4$ $(M + H)^+$ 233.0808, found 233.0811.

Typical Procedure for the AgOTf-Catalyzed Reaction. To a solution of **6a** (0.3 mmol, 1 equiv) and **7a** (1.5 mmol, 5 equiv) in 1,4-dioxane (3.0 mL, 0.1 M), AgOTf (5 mol %, 3.9 mg) was added. The resulting mixture was stirred at 60 °C for 0.5 h. After completion, volatiles were removed under reduced pressure, and the final product was purified by column chromatography (ethyl acetate/petrol ether =1/20).

*9a-Acetyl-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8aa**).* Colorless oil; yield 62.0 mg, 82%; R_f = 0.63 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 7.7 Hz, 1H), 7.62 (ddd, J = 7.7, 7.2, 1.1 Hz, 1H), 7.54 (dd, J = 7.8, 0.7 Hz, 1H), 7.36 (dd, J = 7.5, 7.4 Hz, 1H), 4.08 (dd, J = 6.5, 3.4 Hz, 1H), 2.64 (d, J = 14.3 Hz, 1H), 2.52 (dd, J = 14.6, 6.6 Hz, 1H), 2.47 (d, J = 14.3 Hz, 1H), 2.25 (dd, J = 14.7, 3.3 Hz, 1H), 2.20 (s, 3H), 1.61 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.3, 204.1, 157.6, 136.4, 135.5, 127.7, 126.9, 125.8, 125.3, 123.7, 69.9, 42.1, 36.2, 35.8, 26.6, 19.3, 19.1; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_2$ $(M + H)^+$ 255.1380, found 255.1380.

*9a-Acetyl-6-fluoro-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ba**).* White solid; mp 94−96 °C; yield 69.4 mg, 85%; R_f = 0.76 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.67 (dd, J = 8.5, 5.4 Hz, 1H), 7.18 (dd, J = 8.5, 1.9 Hz, 1H), 7.06 (ddd, J = 8.6, 8.6, 2.1 Hz, 1H), 4.11 (dd, J = 6.6, 3.3 Hz, 1H), 2.67 (d, J = 14.3 Hz, 1H), 2.52 (dd, J = 14.8, 6.3 Hz, 1H), 2.44 (d, J = 14.3 Hz, 1H), 2.26−2.19 (m, 1H), 2.24 (s, 3H), 1.62 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.0, 202.0, 167.7 (d, J = 257.9 Hz), 160.7 (d, J = 9.3 Hz), 132.7 (d, J = 1.5 Hz), 126.8, 126.1 (d, J = 10.7 Hz), 125.9, 116.2 (d, J = 23.9 Hz), 111.9 (d, J = 22.4 Hz), 70.2, 41.7 (d, J = 1.7 Hz), 36.3, 35.6, 26.6, 19.3, 19.1; HRMS (ESI) m/z calcd for $C_{17}H_{18}FO_2$ $(M + H)^+$ 273.1285, found 273.1289.

*9a-Acetyl-6-chloro-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9-(9aH)-one (**8ca**).* White solid; mp 128−130 °C; yield 70.1 mg, 81%; R_f = 0.79 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.2 Hz, 1H), 7.52 (d, J = 0.7 Hz, 1H), 7.34 (dd, J = 8.2, 1.3 Hz, 1H), 4.10 (dd, J = 6.7, 3.3 Hz, 1H), 2.67 (d, J = 14.3 Hz, 1H), 2.52 (dd, J = 14.7, 5.8 Hz, 1H), 2.44 (d, J = 14.3 Hz, 1H), 2.26−2.19 (m, 1H), 2.23 (s, 3H), 1.62 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.8, 202.5, 159.2, 142.0, 134.7, 128.6, 126.9, 125.9, 125.5, 124.9, 70.2, 41.7, 36.3, 35.6, 26.5, 19.4, 19.1; HRMS (ESI) m/z calcd for $C_{17}H_{18}ClO_2$ $(M + H)^+$ 289.0990, found 289.0991. Anal. Calcd for $C_{17}H_{17}ClO_2$: C, 70.71; H, 5.93. Found: C, 70.53; H, 5.88.

*9a-Acetyl-6-methoxy-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9-(9aH)-one (**8da**).* Colorless oil; yield 51.2 mg, 60%; R_f = 0.50 (hexanes/EtOAc = 4/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.89 (dd, J = 8.5, 2.0 Hz, 1H), 4.00 (dd, J = 6.5, 3.6 Hz, 1H), 3.89 (s, 3H), 2.62 (d, J = 14.3 Hz, 1H), 2.50 (dd, J = 14.6, 6.4 Hz, 1H), 2.45 (d, J = 14.3 Hz, 1H), 2.22 (dd, J = 14.6, 3.5 Hz, 1H), 2.20 (s, 3H), 1.62 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.7, 201.8, 165.9, 160.6, 129.7, 126.7, 126.0, 125.5, 115.7, 108.4, 70.1, 55.7, 41.9, 36.0, 35.8, 26.5, 19.4, 19.1; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $(M + H)^+$ 285.1485, found 285.1490.

*9a-Acetyl-2,3,7-trimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ea**).* Colorless oil; yield 57.6 mg, 72%; R_f = 0.76 (hexanes/EtOAc = 4/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.44 (dd, J = 8.0, 1.4 Hz, 1H), 7.41 (d, J = 7.9 Hz, 1H), 4.00 (dd, J = 6.5, 3.3 Hz, 1H), 2.61 (d, J = 14.2 Hz, 1H), 2.49 (dd, J = 14.6, 6.5 Hz, 1H), 2.46 (d, J = 14.2 Hz, 1H), 2.38 (s, 3H), 2.22 (dd, J = 14.7, 3.3 Hz, 1H), 2.17 (s, 3H), 1.60 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.4, 204.2, 155.0, 137.7, 136.8, 136.7, 126.8, 125.8, 124.9, 123.6, 70.1, 41.8, 36.0, 35.8, 26.6, 21.0, 19.3, 19.1; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_2$ $(M + H)^+$ 269.1536, found 269.1539.

*9a-Acetyl-7-fluoro-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8fa**).* White solid; mp 99−101 °C; yield 63.5 mg, 78%; R_f = 0.75 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, J = 8.4, 4.5 Hz, 1H), 7.33 (ddd, J = 8.5, 8.5, 2.6 Hz, 1H), 7.29 (dd, J = 7.5, 2.5 Hz, 1H), 4.07 (dd, J = 6.4, 3.1 Hz, 1H), 2.65 (d, J = 14.3 Hz, 1H), 2.51 (dd, J = 14.6, 6.1 Hz, 1H), 2.44 (d, J = 14.3 Hz, 1H), 2.22 (dd, J = 14.6, 3.2 Hz, 1H), 2.21 (s, 3H), 1.61 (s, 3H), 1.42 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.8, 203.1 (d, J = 3.2 Hz), 162.4 (d, J = 248.9 Hz), 153.1 (d, J = 1.8 Hz), 138.0 (d, J = 7.3 Hz), 126.9, 126.7 (d, J = 8.2 Hz), 125.8, 123.2 (d, J = 23.7 Hz), 109.4 (d, J = 21.8 Hz), 70.7, 41.5, 36.4, 35.8, 26.6, 19.4, 19.1; HRMS (ESI) m/z calcd for $C_{17}H_{18}FO_2$ $(M + H)^+$ 273.1285, found 273.1282.

*9a-Acetyl-6,7-dimethoxy-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ga**).* Colorless oil; yield 33.0 mg, 35%; R_f = 0.46 (hexanes/EtOAc = 3/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.08 (s, 1H), 6.91 (s, 1H), 3.99 (s, 3H), 3.95 (dd, J = 6.5, 3.5 Hz, 1H), 3.90 (s, 3H), 2.61 (d, J = 14.3 Hz, 1H), 2.50 (dd, J = 14.5, 6.2 Hz, 1H), 2.46 (d, J = 14.3 Hz, 1H), 2.20 (dd, J = 14.5, 3.4 Hz, 1H), 2.19 (s, 3H), 1.63 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.8, 202.2, 156.2, 153.0, 149.7, 129.3, 126.5, 126.0, 105.9, 104.0, 70.1, 56.3, 56.1, 41.9, 35.9, 35.8, 26.5, 19.4, 19.1; HRMS (ESI) m/z calcd for $C_{19}H_{23}O_4$ $(M + H)^+$ 315.1591, found 315.1594.

*9a-Benzoyl-2,3-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ha**).* Colorless oil; yield 54.0 mg, 57%; R_f = 0.74 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, J = 7.7 Hz, 1H), 7.68 (ddd, J = 7.6, 7.4, 1.0 Hz, 1H), 7.59−7.53 (m, 3H), 7.47−7.40 (m, 2H), 7.29−7.23 (m, 2H), 4.02 (dd, J = 5.8, 4.1 Hz, 1H), 2.94 (d, J = 14.8 Hz, 1H), 2.57 (dd, J = 14.9, 5.8 Hz, 1H), 2.48 (d, J = 14.8 Hz, 1H), 2.30 (dd, J = 14.9, 4.1 Hz, 1H), 1.62 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.5, 198.7, 156.9, 137.2, 136.3, 135.4, 132.3, 128.3, 128.1, 128.0, 126.5, 125.9, 125.4, 124.1, 68.3, 44.8, 36.8, 35.3, 19.3, 18.9; HRMS (ESI) m/z calcd for $C_{22}H_{21}O_2$ $(M + H)^+$ 317.1536, found 317.1539.

*Methyl 2,3-Dimethyl-9-oxo-4,4a,9,9a-tetrahydro-1H-fluorene-9a-carboxylate (**8ia**).* White solid; mp 99−100 °C; yield 57 mg, 70%; R_f = 0.71 (hexanes/EtOAc = 5/1); ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.7 Hz, 1H), 7.63 (ddd, J = 7.7, 7.2, 1.1 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.37 (dd, J = 7.5, 7.4 Hz, 1H), 3.92 (dd, J = 6.5, 3.9 Hz, 1H), 3.65 (s, 3H), 2.63 (d, J = 14.6 Hz, 1H), 2.58 (dd,

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J. Org. Chem. 2016, 81, 12401−12407

J = 14.7, 6.5 Hz, 1H), 2.53 (d, J = 14.5 Hz, 1H), 2.22 (dd, J = 14.6, 3.8 Hz, 1H), 1.62 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.1, 172.2, 157.3, 136.4, 135.3, 127.7, 126.5, 126.48, 125.1, 124.0, 61.6, 52.6, 44.7, 35.7, 35.2, 19.3, 18.9; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_3$ $(M + H)^+$ 271.1329, found 271.1329.

*9a-Acetyl-1,4-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ab**).* Colorless oil; yield 40.4 mg, 53%; R_f = 0.59 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (d, J = 7.7 Hz, 1H), 7.60−7.55 (m, 2H), 7.43−7.38 (m, 1H), 5.54 (ddd, J = 8.7, 3.4, 3.4 Hz, 1H), 5.29 (ddd, J = 8.8, 3.4, 3.4 Hz, 1H), 3.61 (d, J = 6.1 Hz, 1H), 3.09−3.01 (m, 1H), 2.72−2.63 (m, 1H), 2.05 (s, 3H), 1.42 (d, J = 7.4 Hz, 3H), 1.39 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.6, 204.8, 152.9, 139.4, 134.4, 134.2, 132.7, 128.0, 127.7, 123.6, 72.2, 51.6, 35.1, 33.2, 28.6, 17.9, 15.3; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_2$ $(M + H)^+$ 255.1380, found 255.1385.

*9a-Acetyl-6-fluoro-1,4-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8bb**).* White solid; mp 69−70 °C; yield 61.3 mg, 75%; R_f = 0.9 (hexanes/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73 (dd, J = 8.5, 5.5 Hz, 1H), 7.22 (dd, J = 9.1, 2.1 Hz, 1H), 7.10 (ddd, J = 8.6, 8.4, 1.9 Hz, 1H), 5.55 (ddd, J = 8.8, 3.7, 3.1 Hz, 1H), 5.32 (ddd, J = 8.8, 3.5, 3.4 Hz, 1H), 3.57 (d, J = 6.1 Hz, 1H), 3.07−2.98 (m, 1H), 2.73−2.64 (m, 1H), 2.06 (s, 3H), 1.42 (d, J = 7.4 Hz, 3H), 1.37 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.3, 202.8, 166.7 (d, J = 256.4 Hz), 155.7 (d, J = 9.4 Hz), 135.8 (d, J = 1.5 Hz), 134.3, 132.5, 125.8 (d, J = 10.5 Hz), 116.4 (d, J = 23.7 Hz), 114.3 (d, J = 22.8 Hz), 72.4, 51.2 (d, J = 2.0 Hz), 35.3, 33.1, 28.6, 17.7, 15.2; HRMS (ESI) m/z calcd for $C_{17}H_{18}FO_2$ $(M + H)^+$ 273.1285, found 273.1285. Anal. Calcd for $C_{17}H_{17}FO_2$: C, 74.98; H, 6.29. Found: C, 74.65; H, 6.36.

*9a-Acetyl-6-methoxy-1,4-dimethyl-4,4a-dihydro-1H-fluoren-9-(9aH)-one (**8db**).* White solid; mp 110−112 °C; yield 35.5 mg, 42%; R_f = 0.75 (hexanes/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (d, J = 8.6 Hz, 1H), 6.97 (d, J = 2.1 Hz, 1H), 6.94 (dd, J = 8.5, 2.2 Hz, 1H), 5.55 (ddd, J = 8.8, 3.6, 3.2 Hz, 1H), 5.31 (ddd, J = 8.6, 3.5, 3.5 Hz, 1H), 3.89 (s, 3H), 3.52 (d, J = 6.0 Hz, 1H), 3.07−2.99 (m, 1H), 2.71−2.61 (m, 1H), 2.05 (s, 3H), 1.43 (d, J = 7.4 Hz, 3H), 1.37 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 206.0, 202.7, 164.8, 155.6, 134.4, 133.0, 132.5, 125.3, 115.4, 111.5, 72.3, 55.7, 51.4, 35.0, 33.2, 28.5, 17.9, 15.4; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_3$ $(M + H)^+$ 285.1485, found 285.1484.

*9a-Acetyl-1,4,7-trimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8eb**).* Colorless oil; yield 45.0 mg, 56%; R_f = 0.87 (hexanes/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (s, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.39 (dd, J = 7.9, 1.3 Hz, 1H), 5.53 (ddd, J = 8.8, 3.4, 3.4 Hz, 1H), 5.28 (ddd, J = 8.7, 3.5, 3.4 Hz, 1H), 3.54 (d, J = 6.0 Hz, 1H), 3.08−3.01 (m, 1H), 2.69−2.60 (m, 1H), 2.40 (s, 3H), 2.03 (s, 3H), 1.41 (d, J = 7.4 Hz, 3H), 1.37 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.6, 204.8, 150.3, 139.7, 138.1, 135.7, 134.2, 132.7, 127.4, 123.5, 72.5, 51.2, 35.0, 33.2, 28.5, 21.0, 17.9, 15.3; HRMS (ESI) m/z calcd for $C_{18}H_{21}O_2$ $(M + H)^+$ 269.1536, found 269.1532.

*9a-Acetyl-7-fluoro-1,4-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8fb**).* White solid; mp 98−100 °C; yield 57.0 mg, 70%; R_f = 0.91 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (dd, J = 8.5, 4.5 Hz, 1H), 7.35 (dd, J = 7.4, 2.6 Hz, 1H), 7.29 (ddd, J = 8.5, 8.5, 2.6 Hz, 1H), 5.54 (ddd, J = 8.7, 3.6, 3.2 Hz, 1H), 5.28 (ddd, J = 8.8, 3.5, 3.4 Hz, 1H), 3.57 (d, J = 6.0 Hz, 1H), 3.07−2.99 (m, 1H), 2.71−2.61 (m, 1H), 2.05 (s, 3H), 1.39 (d, J = 7.4 Hz, 3H), 1.37 (d, J = 7.2 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.1, 203.8 (d, J = 3.0 Hz), 162.7 (d, J = 249.9 Hz), 148.3 (d, J = 1.9 Hz), 141.1 (d, J = 7.1 Hz), 134.2, 132.6, 129.1 (d, J = 7.9 Hz), 122.1 (d, J = 23.6 Hz), 109.3 (d, J = 21.5 Hz), 73.0, 51.0, 35.3, 33.1, 28.6, 17.8, 15.2; HRMS (ESI) m/z calcd for $C_{17}H_{18}FO_2$ $(M + H)^+$ 273.1285, found 273.1288.

*9a-Benzoyl-1,4-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8hb**).* Colorless oil; yield 41.0 mg, 43%; R_f = 0.82 (hexanes/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 7.7 Hz, 1H), 7.64−7.60 (m, 2H), 7.50 (dd, J = 8.3, 1.0 Hz, 2H), 7.47−7.40 (m, 2H), 7.28−7.22 (m, 2H), 5.53 (ddd, J = 8.8, 3.4, 3.2 Hz, 1H), 5.36 (ddd, J = 8.6, 3.5, 3.4 Hz, 1H), 3.90 (d, J = 5.1 Hz, 1H), 3.50−3.42 (m, 1H), 2.78−2.68 (m, 1H), 1.49 (d, J = 7.4 Hz, 3H), 1.33 (d, J = 7.1 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.8, 199.2, 152.6, 140.0, 136.4, 134.5, 133.9, 132.8, 132.5, 128.4, 128.14, 128.13, 127.6, 123.8, 71.1, 52.7, 35.4, 33.3, 18.1, 15.8; HRMS (ESI) m/z calcd for $C_{22}H_{21}O_2$ $(M + H)^+$ 317.1536, found 317.1539.

*9a-Acetyl-1,2-dimethyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ac**, Isomers Ratio 10/1).* Colorless oil; yield 48.0 mg, 63%; R_f = 0.53 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 7.7 Hz, 1H), 7.66 (ddd, J = 7.7, 7.2, 1.0 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.41 (dd, J = 7.5, 7.4 Hz, 1H), 5.49−5.44 (m, 1H), 3.88 (dd, J = 8.1, 8.1 Hz, 1H), 3.10 (q, J = 7.3 Hz, 1H), 2.80−2.72 (m, 1H), 2.32−2.23 (m, 1H), 2.16 (s, 3H), 1.78 (s, 3H), 0.89 (d, J = 7.3 Hz, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.9, 204.4, 158.4, 141.4, 136.9, 135.6, 127.9, 125.1, 123.8, 119.5, 72.7, 41.6, 39.0, 27.6, 27.1, 21.4, 12.8; HRMS (ESI) m/z calcd for $C_{17}H_{19}O_2$ $(M + H)^+$ 255.1380, found 255.1381.

*9a-Acetyl-3(or 4)-methyl-4,4a-dihydro-1H-fluoren-9(9aH)-one (**8ad**, Isomers Ratio 5.7/1).* Colorless oil; yield 46.9 mg, 65%; R_f = 0.74 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70−7.66 (m, 1H), 7.66−7.60 (m, 1H), 7.56−7.51 (m, 1H), 7.40−7.34 (m, 1H), 5.47−5.42 (m, 0.85H), 5.35−5.29 (m, 0.15H), 4.18 (dd, J = 6.8, 3.4 Hz, 0.85H), 4.07 (dd, J = 7.0, 3.3 Hz, 0.15H), 2.75 (dd, J = 14.9, 6.6 Hz, 0.85H), 2.67 (d, J = 14.7 Hz, 0.15H), 2.57−2.49 (m, 1H), 2.48−2.40 (m, 1H), 2.31 (dd, J = 14.9, 3.4 Hz, 1H), 2.24 (s, 2.55H), 2.19 (s, 0.45H), 1.68 (s, 0.45H), 1.50 (s, 2.55H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 204.3, 204.2, 157.5, 136.7, 136.3, 135.5, 127.8, 125.1, 123.8, 119.2, 69.3, 41.5, 33.8, 30.0, 26.6, 23.4; HRMS (ESI) m/z calcd for $C_{16}H_{17}O_2$ $(M + H)^+$ 241.1223, found 241.1223.

*9a-Acetyl-4,4a-dihydro-1H-1,4-ethanofluoren-9(9aH)-one (**8ae**, dr 4/1).* Colorless oil; yield 31.8 mg, 42%; R_f = 0.79 (hexanes/EtOAc = 3/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 7.7 Hz, 0.8H), 7.64 (ddd, J = 7.6, 7.4, 1.1 Hz, 0.8H), 7.60 (d, J = 8.1 Hz, 0.2H), 7.56 (d, J = 7.4 Hz, 0.2H), 7.50 (d, J = 7.7 Hz, 0.8H), 7.47 (d, J = 8.3 Hz, 0.2H), 7.40 (dd, J = 7.5, 7.4 Hz, 0.8H), 7.31 (dd, J = 7.6, 7.4 Hz, 0.2H), 6.47 (dd, J = 7.4, 7.3 Hz, 0.8H), 6.30 (dd, J = 7.3, 7.0 Hz, 0.8H), 6.07 (dd, J = 7.6, 7.5 Hz, 0.2H), 5.73 (dd, J = 7.4, 7.2 Hz, 0.2H), 4.12 (d, J = 2.9 Hz, 0.2H), 3.97 (d, J = 3.7 Hz, 0.8H), 3.53−3.50 (m, 0.2H), 3.50−3.45 (m, 0.8H), 3.04−2.98 (m, 1H), 2.42 (s, 0.6H), 2.27 (s, 2.4H), 1.81−1.74 (m, 0.2H), 1.54−1.47 (m, 0.2H), 1.47−1.38 (m, 1H), 1.32−1.26 (m, 0.2H), 1.20−1.12 (m, 0.8H), 1.04−0.93 (m, 1.6H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.9, 203.3, 203.2, 202.5, 157.0, 156.9, 136.7, 136.6, 136.2, 135.4, 135.2, 133.0, 131.7, 131.0, 128.1, 127.5, 125.9, 125.5, 124.5, 123.8, 73.8, 73.4, 46.7, 44.9, 38.0, 37.3, 36.1, 34.7, 26.7, 26.6, 24.2, 21.3, 20.9, 19.5; HRMS (ESI) m/z calcd for $C_{17}H_{17}O_2$ $(M + H)^+$ 253.1223, found 253.1227.

*9a-Acetyl-4,4a-dihydro-1H-1,4-methanofluoren-9(9aH)-one (**8af**, endo/exo = 2/1).* Colorless oil; yield 25.0 mg, 35%; R_f = 0.64 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 7.7 Hz, 1H), 7.62 (ddd, J = 7.6, 7.4, 1.0 Hz, 1H), 7.58 (d, J = 7.7 Hz, 0.5H), 7.55 (ddd, J = 7.5, 7.4, 1.0 Hz, 0.5H), 7.50 (dd, J = 7.7, 0.7 Hz, 1H), 7.43 (dd, J = 7.7, 0.6 Hz, 0.5H), 7.38 (dd, J = 7.5, 7.5 Hz, 1H), 7.33 (dd, J = 7.5, 7.5 Hz, 0.5H), 6.50 (dd, J = 5.6, 3.1 Hz, 1H), 6.18 (dd, J = 5.6, 2.8 Hz, 1H), 6.00 (dd, J = 5.5, 3.0 Hz, 0.5H), 5.54 (dd, J = 5.6, 3.0 Hz, 0.5H), 4.30 (d, J = 4.4 Hz, 0.5H), 3.80 (s, 1H), 3.55−3.52 (m, 0.5H), 3.48−3.43 (m, 1H), 3.24−3.19 (m, 0.5H), 2.90 (s, 1H), 2.35 (s, 3H), 2.34 (s, 1.5H), 1.82−1.76 (m, 1H), 1.51−1.48 (m, 0.5H), 1.48−1.46 (m, 0.5H), 1.22 (d, J = 9.5 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 203.5, 202.5, 202.4, 201.3, 155.6, 154.8, 140.8, 139.2, 138.3, 136.1, 135.5, 135.0, 134.6, 133.9, 128.0, 127.9, 125.84, 125.75, 124.2, 124.0, 78.3, 76.3, 51.4, 50.1, 49.8, 49.6, 48.8, 47.2, 46.0, 44.2, 27.9, 27.8; HRMS (ESI) m/z calcd for $C_{16}H_{15}O_2$ $(M + H)^+$ 239.1067, found 239.1060.

*11a-Acetyl-2-(prop-1-en-2-yl)-3,4,6,6a,11a,11b-hexahydro-1H-benzo[a]fluoren-11(2H)-one (**8ag**, dr 1/1).* Colorless oil; yield 55.7 mg, 58%; R_f = 0.67 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (dd, J = 7.7, 4.6 Hz, 1H), 7.26 (dd, J = 7.6, 7.4 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.37 (dd, J = 7.7, 7.2 Hz, 1H), 5.37−5.33 (m, 0.5H), 5.30−5.24 (m, 0.5H), 4.79 (d, J = 16.0 Hz, 1H), 4.61−4.56 (m, 1H), 3.82 (dd, J = 6.6, 3.0 Hz, 0.5H), 3.66 (d, J = 4.9 Hz, 0.5H), 3.15−3.08 (m, 0.5H), 2.89 (d, J = 11.8 Hz, 0.5H), 2.61−2.49 (m, 1.5H), 2.45−2.34 (m, 1H), 2.25−2.12 (m, 1H), 2.22 (s, 1.5H), 2.12−2.00 (m, 2H), 2.11 (s, 1.5H), 1.88−1.78 (m, 1H), 1.76 (s,

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1.5H), 1.74−1.66 (m, 1H), 1.63 (s, 1.5H), 1.43−1.32 (m, 0.5H), 1.27−1.18 (m, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.6, 205.4, 205.1, 204.4, 156.5, 156.2, 149.7, 149.4, 141.1, 139.8, 138.4, 137.4, 135.3, 135.2, 127.9, 127.8, 125.0, 124.4, 123.5, 123.3, 117.3, 116.5, 108.9, 108.7, 71.2, 70.7, 44.5, 44.4, 41.7, 40.2, 39.4, 36.4, 32.2, 32.1, 30.4, 29.6, 28.2, 27.9, 27.7, 27.5, 27.4, 26.4, 21.6, 20.5; HRMS (ESI) *m*/*z* calcd for $C_{22}H_{25}O_2$ $(M + H)^+$ 321.1849, found 321.1847.

*1-(6a,6b-Dimethyl-5,6,6a,6b,7,7a-hexahydro-5,7b-epoxycyclopropa[3,4]cyclobuta[1,2-a]naphthalen-7a-yl)ethanone (**9aa**).* Colorless oil; yield 23.0 mg, 30%; R_f = 0.8 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22−7.17 (m, 2H), 7.09 (ddd, *J* = 7.5, 7.5, 1.3 Hz, 1H), 6.91 (dd, *J* = 7.4, 1.3 Hz, 1H), 5.23 (d, *J* = 7.0 Hz, 1H), 2.27 (d, *J* = 6.7 Hz, 1H), 2.18 (d, *J* = 12.9 Hz, 1H), 2.14 (s, 3H), 1.85 (dd, *J* = 12.9, 7.0 Hz, 1H), 1.40 (d, *J* = 6.7 Hz, 1H), 1.13 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.9, 143.2, 133.2, 127.9, 125.1, 124.6, 123.1, 85.2, 79.1, 54.7, 38.2, 36.7, 27.6, 25.6, 21.9, 18.5, 12.4; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}O_2$ $(M + H)^+$ 255.1380, found 255.1386.

*1-(3-Chloro-6a,6b-dimethyl-5,6,6a,6b,7,7a-hexahydro-5,7b-epoxycyclopropa[3,4]cyclobuta[1,2-a]naphthalen-7a-yl)ethanone (**9ca**).* Colorless oil; yield 23.0 mg, 26%; R_f = 0.8 (hexanes/EtOAc = 5/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, *J* = 2.1 Hz, 1H), 7.17 (dd, *J* = 7.9, 2.2 Hz, 1H), 6.82 (d, *J* = 7.9 Hz, 1H), 5.17 (d, *J* = 7.0 Hz, 1H), 2.30 (d, *J* = 6.8 Hz, 1H), 2.17 (d, *J* = 13.0 Hz, 1H), 2.13 (s, 3H), 1.85 (dd, *J* = 13.0, 7.0 Hz, 1H), 1.39 (d, *J* = 7.1 Hz, 1H), 1.12 (s, 3H), 0.53 (s, 3H); ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 205.5, 144.8, 131.9, 130.2, 127.7, 125.6, 124.2, 85.1, 78.6, 54.8, 38.1, 36.3, 27.6, 25.9, 22.1, 18.4, 12.4; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{18}ClO_2$ $(M + H)^+$ 289.0990, found 289.0995.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02529.

Copies of ^{1}H and ^{13}C NMR spectra (PDF)

Crystallographic data for compound **8fb** (CIF)

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Notes

The authors declare no competing financial interest.

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(18) Other metal catalysts such as $AuCl_3$, $AuCl{\cdot}SMe_2$, and $Cu(OTf)_2$ proved to be insufficient.

(19) CCDC 1510146 (**8fb**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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