

Rhodium- and Iridium-Catalyzed Dehydrogenative Cyclization through Double C–H Bond Cleavages To Produce Fluorene Derivatives

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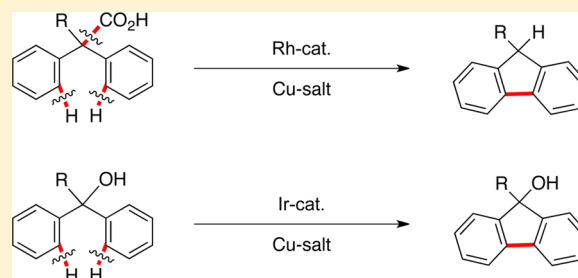
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Supporting Information

ABSTRACT: The rhodium-catalyzed cyclization of a series of 2,2-diaryllalkanoic acids in the presence of copper acetate as an oxidant smoothly proceeded through double C–H bond cleavages and subsequent decarboxylation to produce the corresponding fluorene derivatives. The direct cyclization of triarylmethanols also took place efficiently by using an iridium catalyst in place of the rhodium, while the hydroxy function was still intact.

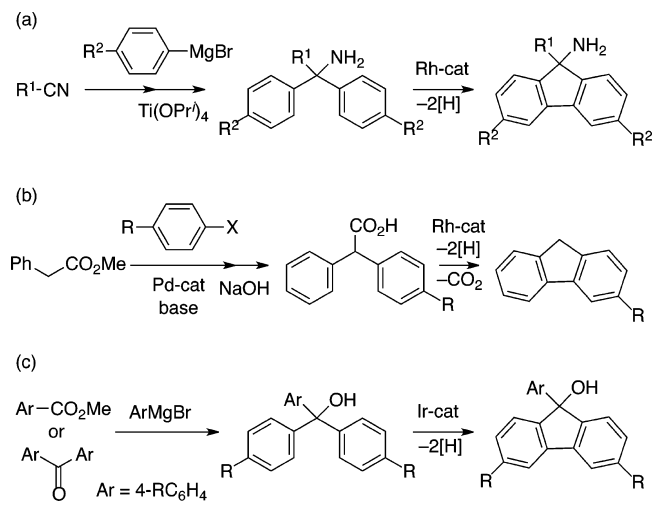


INTRODUCTION

The transition-metal-catalyzed aryl–aryl coupling between aryl halides and arylmetal reagents has been recognized as one of the most reliable methods for constructing biaryl frameworks, which can be ubiquitously seen in a wide range of fine chemicals including medicines and organic materials.¹ From atom- and step-economical points of view, the direct coupling of simple arenes through Ar–H bond cleavage has recently attracted much attention because waste(s) from the coupling event as well as the substrate preparation steps can be undoubtedly reduced.² In particular, the dehydrogenative coupling of two simple arenes involving double Ar–H bond cleavages has been regarded as a challenging goal in the field of cross-coupling.³ However, examples actually applied to precise organic synthesis are so far limited due to difficulties in controlling regioselectivity in the C–H bond activation steps and avoiding undesired homocouplings.

Meanwhile, the intramolecular version of the dehydrogenative aryl–aryl coupling may provide useful synthetic procedures for dibenzo-fused cyclic compounds.^{3b,4} This type of reaction has been undertaken only under palladium(II) catalysis, and therefore, the substrate scope is quite limited. Recently, various rhodium(III)-catalyzed dehydrogenative functionalization reactions of Ar–H bonds have been developed by us⁵ and others⁶ to demonstrate a wider range of applicability compared to that of palladium(II)-based catalyzes, and we succeeded in applying the Rh(III) catalysis to an intramolecular dehydrogenative cyclization. Thus, 1-amino-1,1-diaryllalkanes were found to be effectively transformed to 9-aminofluorenes (Scheme 1a).⁷ Since the starting amines can be readily prepared by 2-fold nucleophilic addition

Scheme 1. Fluorene Synthesis from Simple Building Blocks



of arylmagnesium reagents to nitriles,⁸ this reaction provides a simple and useful approach from the easily available substrates to the cyclized products. Notably, fluorene derivatives have been employed as important components in organic materials fields including light-emitting devices, organic field-effect transistors, and organic photovoltaic cells as well as biosensors.⁹

2,2-Diaryllacetic acids and triarylmethanols can also be readily prepared through the arylation reactions of phenylacetates and

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benzoates or benzophenones, respectively (Scheme 1b,c). It might be conceived that these substrates undergo similar dehydrogenative cyclization, as the oxygen-containing functionalities may act as good directing groups as well as amine- and imine-based ones to enable catalytic regioselective C–H bond functionalization. Indeed, we observed that 2,2-diphenylacetic acid as well as 2,2-diphenylpropanoic acid could undergo rhodium-catalyzed direct cyclization accompanied by decarboxylation.¹⁰ Consequently, the scope of the reactions with the acid derivatives has been investigated. On the other hand, triarylmethanols have been found to give rise to the corresponding fluorenes with the hydroxy function intact. It should be noted that 9-hydroxyfluorene structures have been utilized as the core of crystalline inclusion compounds¹¹ and luminescent materials¹² as well as the sources of stable 9-fluorenyl radicals and cations.¹³ Interestingly, the reaction of the alcohols is effectively catalyzed by iridium rather than rhodium. The detailed results for these oxygen-directed dehydrogenative cyclization reactions are described herein.

RESULTS AND DISCUSSION

Rhodium-catalyzed oxidative coupling reactions on arenes are commonly carried out by using $[\text{Cp}^*\text{RhCl}_2]_2$ as the catalyst precursor in combination with a Cu(II) or Ag(I) oxidant ($\text{Cp}^* = 1,2,3,4,5\text{-pentamethylcyclopentadienyl}$). We previously found that the oxidative cyclization of 2,2-diphenylpropanoic acid (**1a**) could be better catalyzed by $[\text{Cp}^{\text{E}}\text{RhCl}_2]_2$ ¹⁴ rather than $[\text{Cp}^*\text{RhCl}_2]_2$ ($\text{Cp}^{\text{E}} = 1,3\text{-bis(ethoxycarbonyl)-2,4,5-trimethylcyclopentadienyl}$).⁷ Thus, treatment of **1a** in the presence of $[\text{Cp}^{\text{E}}\text{RhCl}_2]_2$ (2 mol %), AgSbF_6 (8 mol %), $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2 equiv), and K_2CO_3 (1 equiv) in diglyme at 120 °C for 20 h afforded the expected fluorene **2a** in 65% GC yield (Table 1, entry 2 vs entry 1 with $[\text{Cp}^*\text{RhCl}_2]_2$). The yield was improved up to 73% (63% after isolation) by adding 2,6-dimethylbenzoic acid (0.5 equiv) as a promoter (entry 3).¹⁵ Under similar conditions, 2-methoxy-2,2-diphenylacetic acid (**1b**) also underwent the reaction efficiently to produce 9-methoxyfluorene (**2b**) selectively (entry 4). In the reaction of 2,2-diphenylacetic acid (**1c**), a slightly better result was obtained at 100 °C rather than at 120 °C (entry 5 vs entry 6). Thus, under the milder conditions, 9-unsubstituted fluorene (**2c**) was obtained in 56% yield. In this case, the addition of 2,6-dimethylbenzoic acid was not necessary (entry 7). Treatment of 2-(4-substituted phenyl)-2-phenylacetic acids **1d–g** under similar conditions gave the corresponding 3-substituted fluorenes **2d–g** in 43–56% yields (entries 8–11). In contrast to **1d–g**, treatment of substrates possessing electron-withdrawing groups including halogens gave only trace amounts of cyclization products. Most of the substrates were consumed by unidentified side reactions. Five-membered ring formation exclusively took place upon treatment of 2-(1-naphthyl)-2-phenylacetic acid (**1h**) to produce 11H-benzo[*a*]fluorene (**2h**) (entry 12): no six-membered cyclic product via C–H bond cleavage at the C8-position of the naphthyl moiety was detected. Similarly, 2-(2-naphthyl)-2-phenylacetic acid (**1i**) underwent the reaction to produce 11H-benzo[*b*]fluorene (**2i**) (entry 13). No regioisomer was detected by GC and GC–MS even in this case. Under the present conditions, 2-(2 or 3-thienyl)-2-phenylacetic acid remained almost completely intact. The construction of ladder-type indenofluorene structure was achieved through double cyclization of α,α' -diphenyl-1,4-benzenediacetic acid (**1j**), albeit with low efficiency (entry 14).

Table 1. Reaction of 2,2-Diarylalkanoic Acids **1**^a

entry	1	temp (°C)	time (h)	product, % yield
1 ^b	1a , R = Me	120	20	2a , R = Me, (45) ^c
2	1a , R = Me	120	20	2a , R = Me, (65) ^c
3 ^d	1a , R = Me	120	20	2a , R = Me, 63 (73) ^c
4 ^d	1b , R = OMe	120	20	2b , R = OMe, 62
5 ^d	1c , R = H	120	20	2c , R = H, (51) ^c
6 ^d	1c , R = H	100	48	2c , R = H, (56) ^c
7	1c , R = H	100	48	2c , R = H, 57 (57) ^c
8	1d , R = Me	100	48	2d , R = Me, 56
9	1e , R = Bu ^t	100	48	2e , R = Bu ^t , 53
10	1f , R = 4-Bu ^t C ₆ H ₄	100	48	2f , R = 4-Bu ^t C ₆ H ₄ , 45
11	1g , R = OMe	100	48	2g , R = OMe, 43
12	1h	100	48	2h , 50
13	1i	100	48	2i , 33
14	1j	100	48	2j , 14

^aReaction conditions: **1**: $[\text{Cp}^{\text{E}}\text{RhCl}_2]_2$: $[\text{AgSbF}_6]$: $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]$: $[\text{K}_2\text{CO}_3]$ = 0.5:0.01:0.04:1:0.5 (in mmol), in diglyme (3 mL) under N₂. ^b $[\text{Cp}^*\text{RhCl}_2]_2$ (0.01 mmol) was employed in place of $[\text{Cp}^{\text{E}}\text{RhCl}_2]_2$. ^cGC yield. ^d2,6-Me₂C₆H₃CO₂H (0.25 mmol) was added.

We next examined the cyclization of triphenylmethanol (**3a**). First, **3a** was treated under similar conditions to those for the reactions of 1-amino-1,1-diarylalkanes in Scheme 1a,⁷ using $[\text{Cp}^{\text{E}}\text{RhCl}_2]_2$ or $[\text{Cp}^*\text{RhCl}_2]_2$ (2 mol %) together with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (2 equiv) in *o*-xylene at 130 °C. However, no cyclized product was obtained at all (entries 1 and 2 in Table 2). When the reaction was conducted with the addition of K_2CO_3 (1 equiv) in diglyme at 120 °C, a small amount of 9-hydroxy-9-phenylfluorene was formed (entry 3). At 160 °C with the further addition of 2,6-Me₂C₆H₃CO₂H (0.5 equiv), as in the reactions of **1a** and **1b**, the yield of **3a** was improved to 12% (entry 5). Interestingly, $[\text{Cp}^*\text{IrCl}_2]_2$ was found to be more effective compared to $[\text{Cp}^*\text{RhCl}_2]_2$ (entry 6 vs entry 5). Furthermore, the Ir-catalyzed reaction proceeded more smoothly in less polar solvents (entries 7–10). Thus, dodecane was the solvent of choice (entry 10). A better result was obtained in the absence of K_2CO_3 and 2,6-Me₂C₆H₃CO₂H

Table 2. Reaction of Triphenylmethanol (3a)^a

entry	catalyst	solvent	temp (°C)	yield of 4a ^b (%)
1	[Cp ⁺ RhCl ₂] ₂	<i>o</i> -xylene	130	0
2	[Cp ⁺ RhCl ₂] ₂	<i>o</i> -xylene	130	0
3 ^c	[Cp ⁺ RhCl ₂] ₂	diglyme	120	2
4 ^c	[Cp ⁺ RhCl ₂] ₂	diglyme	160	4
5 ^{c,d}	[Cp ⁺ RhCl ₂] ₂	diglyme	160	12
6 ^{c,d}	[Cp ⁺ IrCl ₂] ₂	diglyme	160	16
7 ^{c,d}	[Cp ⁺ IrCl ₂] ₂	DMAc	160	4
8 ^{c,d}	[Cp ⁺ IrCl ₂] ₂	NMP	160	4
9 ^{c,d}	[Cp ⁺ IrCl ₂] ₂	mesitylene	160	28
10 ^{c,d}	[Cp ⁺ IrCl ₂] ₂	dodecane	160	33
11	[Cp ⁺ IrCl ₂] ₂	dodecane	160	62 (49)
12	[Cp ⁺ IrCl ₂] ₂	dodecane	170	82 (70)

^aReaction conditions: [3a]:[catalyst]:[Cu(OAc)₂·H₂O] = 0.5:0.01:1 (in mmol), in solvent (3 mL) for 6–10 h under N₂. ^bGC yield based on the amount of 3a used. Value in parentheses indicates yield after purification. ^cWith K₂CO₃ (0.5 mmol). ^dWith 2,6-Me₂C₆H₃CO₂H (0.25 mmol).

(entry 11). Finally, the reaction efficiency was considerably improved at 170 °C to produce 3a in 82% yield (entry 12).

Under the optimized conditions (entry 12 in Table 2), tris(4-substituted phenyl)methanols 3b–f underwent the dehydrogenative cyclization efficiently to produce the corresponding fluorenes 4b–f in 46–76% yields (entries 1–5 in Table 3). In contrast to the case with 2,2-diphenylacetic acids 1, the alcohols 3 possessing electron-donating groups such as 3f showed relatively poorer reactivities. Indeed, tris(4-methoxyphenyl)methanol was completely recovered under the present conditions. In the reaction of (2-methylphenyl)diphenylmethanol (3g), the cyclization took place selectively between two unsubstituted phenyl groups to afford 9-(2-phenyl)fluoren-9-ol (4g) (entry 6). The cyclization involving 2-methylphenyl moiety seems to be inhibited by steric factors. In contrast, no preference between unsubstituted and 4-substituted phenyl groups was observed in the reaction of (4-substituted phenyl)diphenylmethanols 3h and 3i: mixtures with statistic distributions were formed (entries 7 and 8). Tris(2-naphthyl)methanol (3j) also underwent the cyclization to give a mixture of two pentacyclic compounds 4j and 4j' (entry 9). In this case, a small amount of dehydrogenative cyclization/dehydroarylation¹¹ product 5 was also detected.

The rhodium-catalyzed cyclization of 2,2-diaryllacetic acids 1 appears to proceed through steps similar to those in the reaction of 1-amino-1,1-diaryllacetic acids, which was proposed in our previous communication.⁷ The mechanism for the cyclization of triarylmethanols 3 under iridium catalysis is also expected to be essentially similar. A plausible pathway from 3 to 4 is illustrated in Scheme 2. Initial coordination of the hydroxy oxygen of 3 to an iridium center gives a triarylmethoxyiridium species A. Then, hydroxy-directed metalation takes place to form a five-membered iridacycle intermediate B. Subsequently, the second cyclometallation to form a six-membered species C and reductive elimination may occur to produce 4. In the reaction of 3g, cyclometallation on the 2-methylphenyl ring appears to be suppressed due to the

Table 3. Reaction of Triarylmethanols 3^a

entry	3	product(s), % yield
1		
2	3b , R = Br	4b , R = Br, 76
3	3c , R = Cl	4c , R = Cl, 73
4	3d , R = F	4d , R = F, 70
5	3e , R = CF ₃	4e , R = CF ₃ , 76
6	3f , R = Me	4f , R = Me, 46
7		
8	3g	4g , 32
9		
10	3h , R = CF ₃	4h+4h' , R = CF ₃ , 65 (27:73)
11	3i , R = Me	4i+4i' , R = Me, 57 (38:62)
12		
13	3j	4j+4j' , 55 (43:57) ^b
14		
15		5

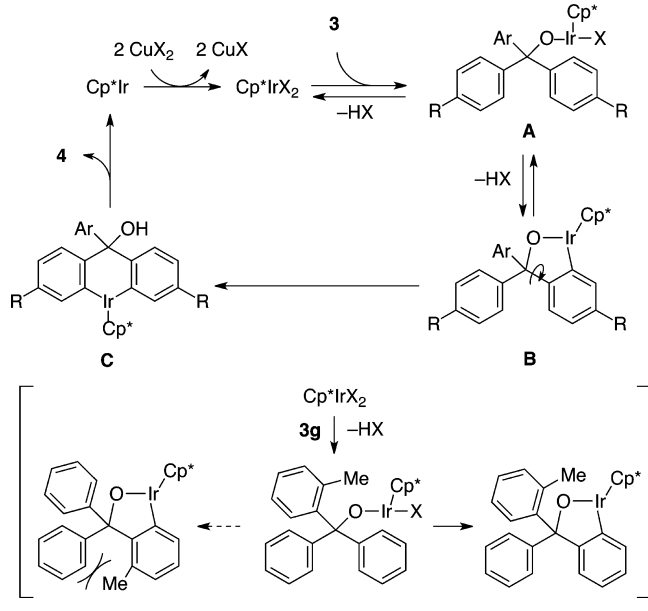
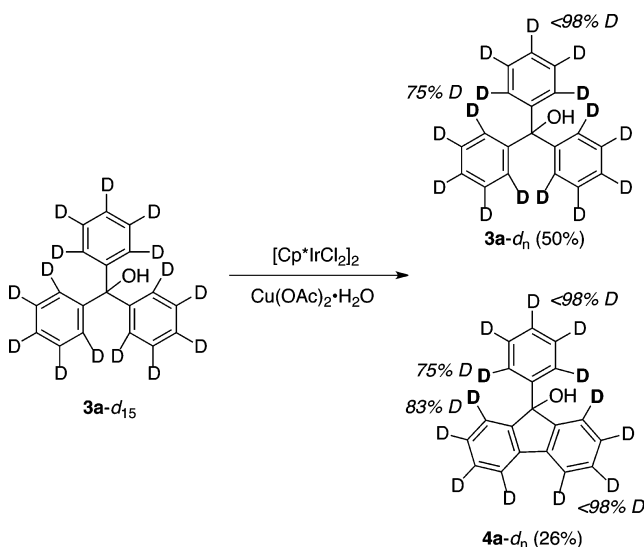
^aReaction conditions: [3]:[{Cp⁺IrCl₂]₂]:[Cu(OAc)₂·H₂O] = 0.5:0.01:1 (in mmol), in dodecane (3 mL) at 170 °C for 8 h under N₂. ^bA separable byproduct, 12H-dibenzo[b,h]fluoren-12-one (5), was also formed (7%).

steric repulsion between the methyl group and two phenyl groups.

For providing further mechanistic information, an isotope-labeled triphenylmethanol (3a-d₁₅) was subjected to the reaction conditions (Scheme 3). In the early stage, considerable hydrogen incorporations at the *ortho* positions of recovered 3a-d_n and at the 1- and/or 8-positions of the fluorene nucleus and *ortho* positions of the 9-phenyl moiety of produced 4a-d_n were observed. Note that a similar H–D exchange was also observed in the rhodium-catalyzed cyclization of 1-amino-1,1-diaryllacetic acids.⁷ This result indicates that at least the first cyclometallation step to form B seems to be partly reversible.

In summary, we have demonstrated that the dehydrogenative cyclization of 2,2-diphenylacetic acids and triarylmethanols can be performed effectively under rhodium and iridium catalyzes, respectively. These procedures provide simple synthetic pathways to fluorene derivatives from readily available substrates.

Scheme 2. Plausible Mechanism for the Reaction of 3

Scheme 3. Reaction of Isotope-Labeled 3a-d₁₅^a

^aReaction conditions: [3a-d₁₅]:[Cp*IrCl₂]₂: [Cu(OAc)₂·H₂O] = 0.5:0.01:1 (in mmol), in dodecane (3 mL) at 170 °C for 4 h under N₂.

EXPERIMENTAL SECTION

General Methods. ¹H and ¹³C NMR spectra were recorded at 400 and 100 MHz for CDCl₃ solutions. HRMS data were obtained by EI using a double-focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC–MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ¹H and ¹³C NMR with the aid of NOE, COSY, HMQC, and HMBC experiments.

[Cp*RhCl₂]₂,¹⁴ 2,2-diaryllalkanoic acids **1b**,^{16a} **1d–g**,^{16b} and **1h–j**,^{16c} and triarylmethanols **3b,e,h**,^{17a} and **3d,g,i**^{17b} were prepared according to published procedures. Other starting materials and reagents were commercially available.

General Procedure for Cyclization of 2,2-Diaryllalkanoic Acids. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added 2,2-diaryllalkanoic acid **1** (0.5 mmol), [Cp*RhCl₂]₂ (0.01 mmol, 8.5 mg), AgSbF₆ (0.04 mmol, 14 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg), K₂CO₃ (0.5 mmol, 69 mg),

(2,6-Me₂C₆H₃CO₂H (0.25 mmol, 38 mg)), 1-methylnaphthalene (ca. 40 mg) as internal standard, and diglyme (3 mL). The resulting mixture was stirred under nitrogen at 100–120 °C for 20–48 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed by water (100 mL, three times) and dried over Na₂SO₄. Product **2** was isolated by column chromatography on silica gel using hexane as eluant.

General Procedure for Cyclization of Triarylmethanols. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added triarylmethanol **3** (0.5 mmol), [Cp*IrCl₂]₂ (0.01 mmol, 8.0 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and dodecane (3 mL). The resulting mixture was stirred under nitrogen at 170 °C for 8 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed with water (100 mL, three times) and dried over Na₂SO₄. Purification by column chromatography on silica gel using hexane–ethyl acetate (10:1) as eluent and subsequent gel permeation chromatography gave product **4**.

Procedure for Cyclization of Deuterated Triphenylmethanol. To a 20 mL two-necked flask with a reflux condenser, a balloon, and a rubber cup were added triphenylmethanol-d₁₅ (**3a-d₁₅**) (0.5 mmol, 138 mg), [Cp*IrCl₂]₂ (0.01 mmol, 8.0 mg), Cu(OAc)₂·H₂O (1 mmol, 200 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and dodecane (3 mL). The resulting mixture was stirred under nitrogen at 170 °C for 4 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL) and ethylenediamine (2 mL). The organic layer was washed with water (100 mL, three times) and dried over Na₂SO₄. Purification by column chromatography on silica gel using hexane–ethyl acetate (10:1) as eluent and subsequent gel permeation chromatography gave product **4a-d_n** and recovered **3a-d_n**. Recovered **3a-d_n** (68.8 mg, 50%): ¹H NMR (400 MHz, CDCl₃) δ 2.80 (s, 1H), 7.27 (s, 1.5H). Produced **4a-d_n** (34.7 mg, 26%): ¹H NMR (400 MHz, CDCl₃) δ 2.44 (s, 1H), 7.31 (s, 0.34H), 7.37 (s, 0.50H), 7.66 (s, 0.043H).

9-Methyl-9H-fluorene (2a):⁷ mp 43–44 °C, 57 mg (63%); ¹H NMR (400 MHz, CDCl₃) δ 1.52 (d, J = 7.8 Hz, 3H), 3.94 (q, J = 7.8 Hz, 1H), 7.29–7.38 (m, 4H), 7.50 (d, J = 7.3 Hz, 2H), 7.75 (d, J = 6.9 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 18.2, 42.4, 119.8, 124.0, 126.90, 126.92, 140.5, 149.0; HRMS *m/z* calcd for C₁₄H₁₂ (M⁺) 180.0939, found 180.0938.

9-Methoxy-9H-fluorene (2b):¹⁸ mp 44–45 °C, 61 mg (62%); ¹H NMR (400 MHz, CDCl₃) δ 3.06 (s, 3H), 5.61 (s, 1H), 7.32 (t, J = 7.3 Hz, 2H), 7.40 (t, J = 7.3 Hz, 2H), 7.61 (d, J = 7.3 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 52.2, 81.3, 119.9, 125.5, 127.5, 129.0, 141.0, 142.5; HRMS *m/z* calcd for C₁₄H₁₂O (M⁺) 196.0888, found 196.0890.

9H-Fluorene (2c):⁷ mp 113–114 °C, 48 mg (57%); ¹H NMR (400 MHz, CDCl₃) δ 3.90 (s, 2H), 7.28–7.32 (m, 2H), 7.36–7.39 (m, 2H), 7.54 (d, J = 7.3 Hz, 2H), 7.79 (d, J = 7.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 36.9, 119.9, 125.0, 126.68, 126.70, 141.7, 143.2; HRMS *m/z* calcd for C₁₃H₁₀ (M⁺) 166.0783, found 166.0784.

3-Methyl-9H-fluorene (2d):¹⁹ mp 88–89 °C, 50 mg (56%); ¹H NMR (400 MHz, CDCl₃) δ 2.45 (s, 3H), 3.85 (s, 2H), 7.12 (d, J = 7.8 Hz, 1H), 7.26–7.30 (m, 1H), 7.34–7.38 (m, 1H), 7.42 (d, J = 7.8 Hz, 1H), 7.53 (d, J = 7.3 Hz, 1H), 7.60 (s, 1H), 7.76 (d, J = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 36.5, 119.7, 120.4, 124.7, 125.0, 126.5, 126.6, 127.6, 136.3, 140.3, 141.7, 141.8, 143.6; HRMS *m/z* calcd for C₁₄H₁₂ (M⁺) 180.0939, found 180.0940.

3-tert-Butyl-9H-fluorene (2e): mp 55–56 °C (lit.²⁰ mp 54–55 °C), 59 mg (53%); ¹H NMR (400 MHz, CDCl₃) δ 1.41 (s, 9H), 3.86 (s, 2H), 7.26–7.30 (m, 1H), 7.35–7.39 (m, 2H), 7.48 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.3 Hz, 1H), 7.80–7.82 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 31.6, 34.8, 36.5, 116.6, 119.7, 124.1, 124.5, 125.0, 126.5, 126.6, 140.4, 141.6, 141.9, 143.6, 149.9; HRMS *m/z* calcd for C₁₇H₁₈ (M⁺) 222.1409, found 222.1406.

3-(4-tert-Butylphenyl)-9H-fluorene (2f): mp 117–118 °C, 67 mg (45%); ¹H NMR (400 MHz, CDCl₃) δ 1.38 (s, 9H), 3.93 (s, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.3 Hz, 1H), 7.49–7.63 (m, 7H),

7.84 (d, $J = 7.3$ Hz, 1H), 7.99 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.4, 34.5, 36.7, 118.5, 119.9, 125.1, 125.2, 125.7, 125.8, 126.76, 126.80, 126.9, 138.7, 140.0, 141.6, 142.0, 142.2, 143.6, 150.2; HRMS m/z calcd for $\text{C}_{23}\text{H}_{22}$ (M^+) 298.1722, found 298.1724.

3-Methoxy-9H-fluorene (2g):¹⁹ mp 79–80 °C, 61 mg (62%); ^1H NMR (400 MHz, CDCl_3) δ 3.83 (s, 2H), 3.89 (s, 3H), 6.87 (dd, $J = 2.8, 8.2$ Hz, 1H), 7.28–7.32 (m, 2H), 7.37 (t, $J = 6.4, 7.3$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 1H), 7.53 (d, $J = 7.3$ Hz, 1H), 7.75 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 36.1, 55.5, 104.8, 113.2, 119.8, 125.0, 125.5, 126.6, 126.7, 135.3, 141.6, 143.0, 144.3, 159.1; HRMS m/z calcd for $\text{C}_{14}\text{H}_{12}\text{O}$ (M^+) 196.0888, found 196.0890.

11H-Benzo[a]fluorene (2h): mp 183–184 °C (lit.²¹ mp 177 °C), 54 mg (50%); ^1H NMR (400 MHz, CDCl_3) δ 4.13 (s, 2H), 7.28–7.32 (m, 1H), 7.39 (t, $J = 7.3$ Hz, 1H), 7.42–7.46 (m, 1H), 7.49–7.53 (m, 1H), 7.60 (d, $J = 7.3$ Hz, 1H), 7.83–7.90 (m, 4H), 7.97 (d, $J = 8.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.6, 118.7, 119.6, 124.1, 124.9, 125.3, 126.3, 126.4, 126.8, 127.8, 128.9, 130.7, 132.8, 138.9, 139.8, 142.6, 143.3; HRMS m/z calcd for $\text{C}_{17}\text{H}_{12}$ (M^+) 216.0939, found 216.0938.

11H-Benzo[b]fluorene (2i): mp 198–199 °C (lit.¹⁹ mp 207–208 °C), 36 mg (33%); ^1H NMR (400 MHz, CDCl_3) δ 4.05 (s, 2H), 7.32–7.36 (m, 1H), 7.38–7.48 (m, 3H), 7.55 (d, $J = 7.2$ Hz, 1H), 7.83–7.85 (m, 1H), 7.90–7.92 (m, 3H), 8.17 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 36.4, 117.8, 120.6, 123.3, 125.25, 125.30, 125.4, 126.9, 127.5, 127.8, 128.1, 133.0, 133.1, 140.5, 141.1, 141.2, 143.7; HRMS m/z calcd for $\text{C}_{17}\text{H}_{12}$ (M^+) 216.0939, found 216.0941.

3,9-Di-tert-butyl-6,12-dihydroindeno[1,2-b]fluorene (2j): mp 246–247 °C, 26 mg (14%); ^1H NMR (400 MHz, CDCl_3) δ 1.41 (s, 18H), 3.92 (s, 4H), 7.34 (dd, $J = 1.8, 7.7$ Hz, 2H), 7.48 (d, $J = 7.7$ Hz, 2H), 7.84 (d, $J = 1.3$ Hz, 2H), 7.95 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 31.7, 34.8, 36.3, 116.2, 116.3, 123.7, 124.5, 140.8, 140.9, 141.8, 142.7, 149.9; HRMS m/z calcd for $\text{C}_{28}\text{H}_{30}$ (M^+) 366.2348, found 366.2346.

9-Phenyl-9H-fluoren-9-ol (4a): mp 91–92 °C (lit.²² mp 90 °C), 90 mg (70%); ^1H NMR (400 MHz, CDCl_3) δ 2.48 (s, 1H), 7.18–7.37 (m, 11H), 7.65 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 83.6, 120.1, 124.8, 125.4, 127.2, 128.2, 128.4, 129.1, 139.5, 143.1, 150.4; HRMS m/z calcd for $\text{C}_{19}\text{H}_{14}\text{O}$ (M^+) 258.1045, found 258.1050.

3,6-Dibromo-9-(4-bromophenyl)-9H-fluoren-9-ol (4b): mp 126–127 °C, 189 mg (76%); ^1H NMR (400 MHz, CDCl_3) δ 2.51 (s, 1H), 7.11 (d, $J = 8.2$ Hz, 2H), 7.15–7.18 (m, 2H), 7.35–7.40 (m, 4H), 7.73 (d, $J = 1.4$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.6, 121.7, 123.6, 123.8, 126.2, 127.0, 131.5, 132.1, 140.2, 140.9, 148.8; HRMS m/z calcd for $\text{C}_{19}\text{H}_{11}\text{Br}_3\text{O}$ (M^+) 491.8360, found 491.8362.

3,6-Dichloro-9-(4-chlorophenyl)-9H-fluoren-9-ol (4c): mp 90–91 °C, 132 mg (73%); ^1H NMR (400 MHz, CDCl_3) δ 2.60 (s, 1H), 7.14 (d, $J = 7.8$ Hz, 2H), 7.21–7.23 (m, 6H), 7.56 (d, $J = 1.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.4, 120.8, 125.9, 126.7, 128.5, 129.1, 133.4, 135.5, 139.9, 140.5, 148.5; HRMS m/z calcd for $\text{C}_{19}\text{H}_{11}\text{Cl}_3\text{O}$ (M^+) 359.9875, found 359.9879.

3,6-Difluoro-9-(4-fluorophenyl)-9H-fluoren-9-ol (4d): mp 109–110 °C, 109 mg (70%); ^1H NMR (400 MHz, CDCl_3) δ 2.54 (s, 1H), 6.90–6.97 (m, 4H), 7.21 (dd, $J = 5.0, 8.2$ Hz, 2H), 7.24–7.32 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.2, 107.7 (d, $J = 24.0$ Hz), 115.2 (d, $J = 21.0$ Hz), 115.8 (d, $J = 23.0$ Hz), 126.1 (d, $J = 8.7$ Hz), 127.0 (d, $J = 8.6$ Hz), 138.2 (d, $J = 2.9$ Hz), 140.5 (dd, $J = 2.9, 8.6$ Hz), 146.4 (d, $J = 2.8$ Hz), 162.2 (d, $J = 246.3$ Hz), 163.8 (d, $J = 247.3$ Hz); HRMS m/z calcd for $\text{C}_{19}\text{H}_{11}\text{F}_3\text{O}$ (M^+) 312.0762, found 312.0766.

3,6-Bis(trifluoromethyl)-9-(4-(trifluoromethyl)phenyl)-9H-fluoren-9-ol (4e): mp 174–175 °C, 175 mg (76%); ^1H NMR (400 MHz, CDCl_3) δ 2.68 (s, 1H), 7.42 (d, $J = 7.8$ Hz, 2H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 7.98 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 83.0, 117.8 (q, $J = 3.8$ Hz), 123.8 (q, $J = 272.2$ Hz), 124.0 (q, $J = 272.2$ Hz), 125.4, 125.6 (q, $J = 3.8$ Hz), 125.7, 126.6 (q, $J = 3.8$ Hz), 130.2 (q, $J = 32.6$ Hz), 132.4 (q, $J = 32.6$ Hz), 139.0, 145.2, 153.2; HRMS m/z calcd for $\text{C}_{22}\text{H}_{11}\text{F}_9\text{O}$ (M^+) 462.0666, found 462.0663.

3,6-Dimethyl-9-(4-methylphenyl)-9H-fluoren-9-ol (4f): mp 109–110 °C, 69 mg (46%); ^1H NMR (400 MHz, CDCl_3) δ 2.28 (s, 3H), 2.33 (s, 1H), 2.40 (s, 6H), 7.02–7.06 (m, 4H), 7.17 (d, $J = 7.7$ Hz,

2H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.44 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 21.6, 83.0, 120.6, 124.4, 125.3, 128.8, 129.0, 136.6, 138.8, 139.7, 140.6, 148.2; HRMS m/z calcd for $\text{C}_{22}\text{H}_{20}\text{O}$ (M^+) 300.1514, found 300.1512.

9-(2-Methylphenyl)-9H-fluoren-9-ol (4g):²³ mp 117–118 °C, 43 mg (32%); ^1H NMR (400 MHz, CDCl_3) δ 1.31 (s, 3H), 2.33 (s, 1H), 6.95 (d, $J = 7.3$ Hz, 1H), 7.16–7.24 (m, 5H), 7.34–7.39 (m, 3H), 7.68 (d, $J = 7.8$ Hz, 2H), 8.32 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.4, 82.7, 120.2, 124.3, 125.7, 126.5, 127.5, 128.6, 129.1, 131.4, 135.1, 140.0, 140.2, 149.3; HRMS m/z calcd for $\text{C}_{20}\text{H}_{16}\text{O}$ (M^+) 272.1201, found 272.1199.

9-(4-(Trifluoromethyl)phenyl)-9H-fluoren-9-ol (4h)²⁴ + 9-phenyl-3-(trifluoromethyl)-9H-fluoren-9-ol (4h'): 106 mg (65%); ^1H NMR (400 MHz, CDCl_3) δ 2.71 (s, 1H), 7.18–7.48 (m, 10H), 7.64 (t, $J = 7.2$ Hz, 1.27H), 7.86 (s, 0.73H); ^{13}C NMR (100 MHz, CDCl_3) δ 83.27, 83.31, 117.0 (q, $J = 3.8$ Hz), 120.2, 120.5, 124.2 (q, $J = 272.8$ Hz), 124.7, 124.9, 125.09, 125.12, 125.16, 125.21, 125.3 (q, $J = 3.8$ Hz), 125.8, 127.5, 128.3, 128.6, 129.1, 129.3, 129.39, 129.42, 131.3 (q, $J = 32.4$ Hz), 138.1, 139.5, 140.2, 142.1, 147.3, 149.7, 150.3, 153.8; HRMS m/z calcd for $\text{C}_{20}\text{H}_{13}\text{F}_3\text{O}$ (M^+) 326.0918, found 326.0921.

9-(4-Methylphenyl)-9H-fluoren-9-ol (4i)²⁴ + 3-methyl-9-phenyl-9H-fluoren-9-ol (4i'):²⁵ 78 mg (57%); ^1H NMR (400 MHz, CDCl_3) δ 2.27 (s, 1H), 2.39–2.44 (m, 3H), 7.02–7.05 (m, 1.36H), 7.15–7.36 (m, 9H), 7.45 (s, 0.62H), 7.60–7.64 (m, 1.38H); ^{13}C NMR (100 MHz, CDCl_3) δ 21.0, 21.5, 83.3, 83.5, 119.9, 120.0, 120.7, 124.5, 124.68, 124.71, 125.25, 125.33, 127.1, 128.1, 128.3, 128.4, 128.88, 128.93, 129.0, 129.2, 136.8, 139.0, 139.5, 139.6, 139.7, 140.2, 143.3, 147.6, 150.5, 150.8; HRMS m/z calcd for $\text{C}_{20}\text{H}_{16}\text{O}$ (M^+) 272.1201, found 272.1205.

12-(Naphthalen-2-yl)-12H-dibenzo[b,h]fluoren-12-ol (4j) + 7-(naphthalen-2-yl)-7H-dibenzo[b,g]fluoren-7-ol (4j'): 112 mg (55%); ^1H NMR (400 MHz, CDCl_3) δ 2.70 (s, 0.43H), 2.82 (s, 0.57H), 7.06 (dd, $J = 1.8, 8.7$ Hz, 0.43H), 7.11 (dd, $J = 1.8, 8.7$ Hz, 0.43H), 7.35–7.94 (m, 15H), 8.21–8.22 (m, 1.21H), 8.28 (s, 0.86H), 8.60 (s, 0.43H), 8.86 (d, $J = 8.7$ Hz, 0.43H); ^{13}C NMR (100 MHz, CDCl_3) δ 82.91, 82.94, 119.2, 122.0, 122.3, 123.5, 123.9, 124.3, 124.35, 124.44, 124.6, 125.8, 125.9, 126.05, 126.09, 126.11, 126.2, 126.5, 126.6, 126.8, 127.4, 127.5, 127.8, 127.87, 127.91, 128.17, 128.22, 128.26, 128.29, 128.59, 128.62, 129.4, 129.5, 130.4, 131.8, 132.5, 132.6, 133.0, 133.1, 133.2, 133.9, 134.2, 134.37, 134.43, 134.7, 137.3, 138.8, 140.6, 141.9, 148.7, 149.3, 149.4; HRMS m/z calcd for $\text{C}_{31}\text{H}_{20}\text{O}$ (M^+) 408.1514, found 408.1512.

12H-Dibenzo[b,h]fluoren-12-one (5):²⁶ mp 281–282 °C, 10 mg (7%); ^1H NMR (400 MHz, CDCl_3) δ 7.46–7.50 (m, 2H), 7.54–7.58 (m, 2H), 7.86 (d, $J = 8.3$ Hz, 2H), 7.90 (d, $J = 7.8$ Hz, 2H), 8.07 (s, 2H), 8.25 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 119.6, 125.7, 126.9, 128.7, 129.0, 130.8, 133.6, 134.3, 137.2, 138.8, 192.8; HRMS m/z calcd for $\text{C}_{21}\text{H}_{12}\text{O}$ (M^+) 280.0888, found 280.0886.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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