Synthesis of Biaryls, Fluorenones, Cyclopenta[*def*]phenanthren-4-ones, and Benzophenones Based on Formal [3+3] Cyclocondensations of 1,3-Bis(silyloxy)buta-1,3-dienes with 3-(Silyloxy)-2-en-1-ones

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Abstract: Functionalized fluorenones were efficiently prepared in four steps. The [3+3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 3-(silyloxy)-2-en-1-ones afforded salicylates that were transformed into their enol triflates. The Suzuki cross-coupling reaction of the latter with arylboronic acids afforded 2-(methoxycarbonyl)biaryls that were subsequently transformed into the target molecules by intramolecular Friedel–Crafts acylation. In addition, 1-hydroxyfluorenones were prepared by cyclization of 3-aryl-3-(silyloxy)-2-en-1-ones with 1,3-bis(silyloxy)buta-1,3-dienes and subsequent intramolecular Friedel–Crafts acylation of the 6-arylsalicylates thus formed. In this context, the synthesis of novel cyclopenta[*def*]phenanthren-4-ones is reported. In addition, the synthesis of functionalized benzophenones is reported.

Key words: cyclizations, fluorenones, regioselectivity, silyl enol ethers

Fluorenones occur in a number of natural products. This includes various highly hydroxylated derivatives, such as dengibsin, dengibsinin, or dendroflorin (Figure 1).[1] The first two fluorenone natural products, dengibsin and dengibsinin, were isolated 1985 by Talapatra et al. from the orchid *Dendrobium gibsonii* Lindl.[1a] These products were first prepared by Sargent and co-workers.[1b] Fluorenones are of considerable pharmacological relevance.[2] They have been used as probes for the redox activity of DNA.[3] Amidofluorenone derivatives have been shown to be telomerase inhibitors, which are important for the development of anticancer agents.[4] In addition, fluorenones represent versatile synthetic intermediates. They have been used, for example, during the synthesis of the antibiotic kinamycin D.[5] Fluorenones are also important compounds in photochemistry.[6]

The most important synthetic approach to fluorenones includes intramolecular Friedel–Crafts acylations of appropriate biaryls.[7] Other syntheses rely on [4+2] cycloadditions of conjugated enynes[8] and on the oxidation of fluorenes.[9] Snieckus and co-workers reported the synthesis of fluorenones based on remote aromatic metalation.[10] Larock and co-workers reported the synthesis of fluorenones by palladium-catalyzed cyclocarbonylation of 2-halobiaryls.[2] Valesco and Yu reported the synthesis of fluorenones based on the reaction of malononitrile with aromatic aldehydes and methyl ketones.[11] Ciske and Jones prepared fluorenones by Suzuki reaction of boronic acids, generated in situ from benzoic acid amides, with aryl triflates and subsequent cyclization by remote metalation.[12] Fluorenones have been prepared by acid-mediated intramolecular Friedel–Crafts cyclization of 2-(methoxycarbonyl)biaryls. Recently, the synthesis of the latter by Suzuki reactions of salicylate-derived enol triflates has been reported.[13]

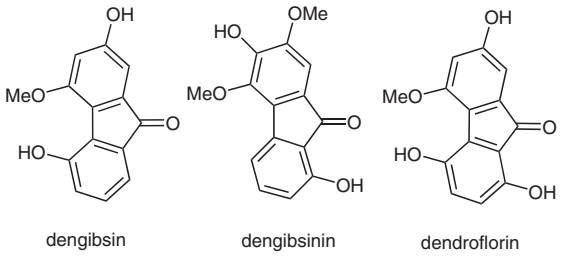

Figure 1 Fluorenone natural products

Salicylates are available by various synthetic strategies. An important approach to salicylates, first reported by Chan and co-workers,[14] relies on the formal [3+3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes[15] with 3-(silyloxy)-2-en-1-ones. In recent years, we have reported the application of this methodology to the synthesis of a variety of functionalized arenes.[16] Recently, we have reported[17] a convenient four-step synthesis of fluorenones: the [3+3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 3-(silyloxy)-2-en-1-ones afforded salicylates that were transformed into their enol triflates. The Suzuki cross-coupling reaction of the latter with arylboronic acids afforded 2-(methoxycarbonyl)biaryls that were subsequently transformed into the target molecules by intramolecular Friedel–Crafts acylation. Herein, we report full details of these studies. In addition, we report the synthesis of 1-hydroxyfluorenones by cyclization of 3-aryl-3-(silyloxy)-2-en-1-ones with 1,3-bis(silyloxy)buta-1,3-dienes and subsequent intramolecular Friedel–Crafts acylation of the 6-arylsalicylates thus formed.[18] In this context, the synthesis of novel cyclopenta[*def*]phenanthren-4-ones is reported. We also report the synthesis of

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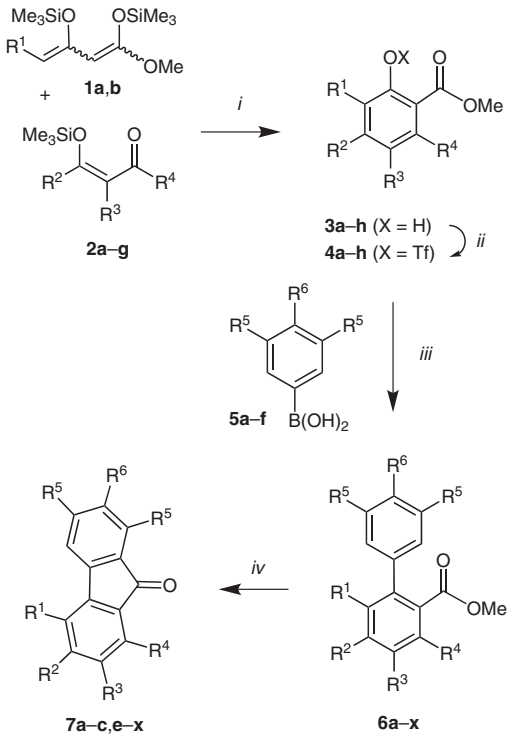
functionalized benzophenones based on formal [3+3] cyclocondensations. The advantage of the two synthetic strategies outlined herein relies on the fact that various substitution patterns are readily available based on a building-block strategy. The products are not readily available by other methods.

1,3-Bis(silyloxy)buta-1,3-dienes **1** and 3-(silyloxy)-2-en-1-ones **2** were prepared as previously reported.[6] The titanium(IV) chloride mediated [3+3] cyclocondensation of 1,3-bis(silyloxy)buta-1,3-diene **1a** with 3-methyl-4-(trimethylsilyloxy)pent-3-en-2-one (**2a**), following the procedure reported by Chan,[14] afforded salicylate **3a** (Scheme 1, Table 1). The cyclization presumably proceeds, following a mechanism suggested by Chan,[14] by titanium(IV) chloride mediated attack of the terminal carbon atom of **1a** on to the double bond of **2a**, cyclization via the central carbon atom of the 1,3-dicarbonyl moiety, and subsequent aromatization.

Salicylate **3a** was transformed into triflate **4a**. The Suzuki reaction of the latter with boronic acids **5a–c** afforded biaryls **6a–c**. Treatment of the latter with concentrated sulfuric acid afforded fluorenones **7a–c** in high yields (Scheme 1, Tables 1 and 2). Fluorenones **7e**,**f** were prepared based on the cyclization of **1a** with 1-phenyl-3-(trimethylsilyloxy)but-2-en-1-one (**2b**). Fluorenones **7g–i** were available starting with **1a** and 4-(trimethylsilyloxy)pent-3-en-2-one (**2c**). The tetracyclic fluorenones **7j–l** were prepared from 2-[1-(trimethylsilyloxy)ethylidene]cyclohexanone (**2d**). Fluorenones **7m–o** were obtained based on the cyclization of **1a** with 3-ethyl-4-(trimethylsilyloxy)pent-3-en-2-one (**2e**). Fluorenones **7p–s** were available based on the cyclization of **1a** with 5-(trimethylsilyloxy)hept-4-en-3-one (**2f**). The cyclization of **2a** with 1,3-bis(silyl enol ether) **1b**, prepared from methyl 3-oxohexanoate, afforded salicylate **3g**, which was transformed into fluorenone **7t**. The chlorinated fluorenones **7u–x** were prepared based on the cyclization of **1a** with 3-chloro-4-(trimethylsilyloxy)pent-3-en-2-one (**2g**). The Suzuki reactions proceeded in 44–95% yield. The formation of the fluorenones generally proceeded in very good yields.

The structures of all products were established by spectroscopic methods. The structure of **7b** was independently confirmed by X-ray crystal structure analysis (Figure 2).[19] The aryl moieties and the ester groups of **6e** and **6j** are twisted out of plane, presumably due to steric or crystal packing effects. The fluorenones are, as expected, flat molecules. The aliphatic six-membered ring of **6j** and **7l** is slightly twisted out of plane.

The reaction of 1,3-bis(silyl enol ethers) **1a**,**c–e** with 3-(silyloxy)-2-en-1-ones **2h–l**, prepared from aryl ketones, resulted in regioselective formation of salicylates **3i–r**, which were transformed into fluorenones **7y–ah** (Scheme 2, Table 3). The regioselective formation of **3i–r** can be explained by isomerization of **2h–l** into *iso*-**2h–l** and subsequent cyclization as described above.



Scheme 1 Synthesis of fluorenones **7a–x**. *Reagents and conditions*: (i) $TiCl_4$, CH_2Cl_2, –78 to 20 °C; (ii) Tf_2O, pyridine, –78 to –10 °C; (iii) $Pd(PPh_3)_4$ (3 mol%), K_3PO_4 (1.6 equiv), 1,4-dioxane, reflux, 4–20 h; (iv) concd H_2SO_4, 1 h.

Table 1 Synthesis of **3** and **4**

1	2	3,4	R^1	R^2	R^3	R^4	Isolated yield (%)	
							3	**4**
a	**a**	**a**	H	Me	Me	Me	51	96
a	**b**	**b**	H	Me	H	Ph	55	69
a	**c**	**c**	H	Me	H	Me	46	97
a	**d**	**d**	H	Me	$(CH_2)_4$		32	97
a	**e**	**e**	H	Me	Et	Me	45	89
a	**f**	**f**	H	Et	H	Et	44	89
b	**a**	**g**	Et	Me	Me	Me	50	94
a	**g**	**h**	H	Me	Cl	Me	62	98

The structures of all products were established by spectroscopic methods. The structure of **7ab** was independently confirmed by an X-ray crystal structure analysis (Figure 3).[19] The fluorenone is, as expected, a flat molecules. An intramolecular hydrogen bond is present.

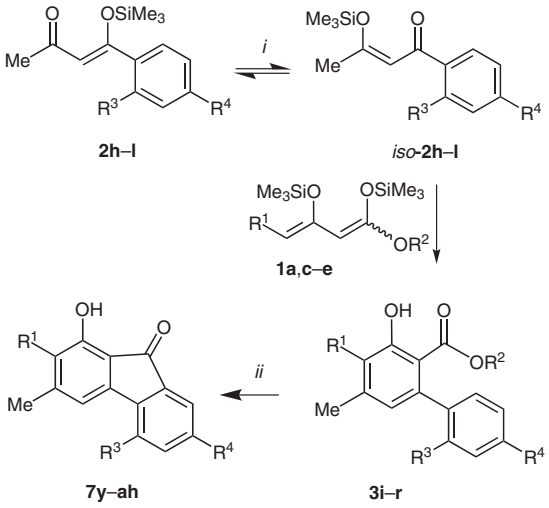
The reaction of 1,3-bis(silyl enol ether) **1a** with 3-(silyloxy)-2-en-1-one **8**, prepared from 2-acetyl-1-tetralone, resulted in regioselective formation of the known[6a] dihydrophenanthrene **9** (Scheme 3).

The regioselectivity can be again explained based on titanium(IV) chloride mediated isomerization of **8** into *iso*-**8**

Table 2 Synthesis of **6** and **7**

6,7	R^1	R^2	R^3	R^4	R^5	R^6	Yield[a] (%)	
							6	**7**
a	H	Me	Me	Me	H	OMe	79	85
b	H	Me	Me	Me	H	H	87	94
c	H	Me	Me	Me	H	Me	87	90
d	H	Me	H	Ph	H	OMe	84	–[b]
e	H	Me	H	Ph	H	H	79	92
f	H	Me	H	Ph	H	Me	75	80
g	H	Me	H	Me	H	OMe	95	91
h	H	Me	H	Me	H	H	91	85
i	H	Me	H	Me	H	Me	44	91
j	H	Me	$(CH_2)_4$		H	OMe	58	61
k	H	Me	$(CH_2)_4$		H	H	89	91
l	H	Me	$(CH_2)_4$		H	Me	83	89
m	H	Me	Et	Me	H	OMe	71	92
n	H	Me	Et	Me	H	H	46	91
o	H	Me	Et	Me	H	Me	75	89
p	H	Et	H	Et	H	H	88	92
q	H	Et	H	Et	H	Me	76	93
r	H	Et	H	Et	H	OMe	86	80
s	H	Et	H	Et	OMe	OMe	59	91
t	Et	Me	Me	Me	H	OMe	44	92
u	H	Me	Cl	Me	H	OMe	82	90
v	H	Me	Cl	Me	H	Cl	90	89
w	H	Me	Cl	Me	H	CF_3	88	99
x	H	Me	Cl	Me	H	H	59	99

[a] Yields of isolated products.
[b] Experiment was not performed.



Scheme 2 Synthesis of fluorenones **7y**–**ah**. *Reagents and conditions*: (i) $TiCl_4$, CH_2Cl_2, –78 to 20 °C; (ii) concd H_2SO_4, 1 h.

Table 3 Products and Yields

1	2	3	7	R^1	R^2	R^3	R^4	Yield[a] (%)	
								3	**7**
a	**h**	**i**	**y**	H	Me	Me	H	43	68
a	**i**	**j**	**z**	H	Me	H	Cl	40	83
c	**i**	**k**	**aa**	$(CH_2)_5Me$	Me	H	Cl	34	65
a	**j**	**l**	**ab**	H	Me	Cl	H	37	75
d	**j**	**m**	**ac**	Me	Me	Cl	H	32	80
e	**j**	**n**	**ad**	Et	Et	Cl	H	35	60
a	**k**	**o**	**ae**	H	Me	F	H	49	75
d	**k**	**p**	**af**	Me	Me	F	H	32	51
a	**l**	**q**	**ag**	H	Me	H	F	44	68
e	**l**	**r**	**ah**	Et	Et	H	F	44	76

[a] Yields of isolated products.

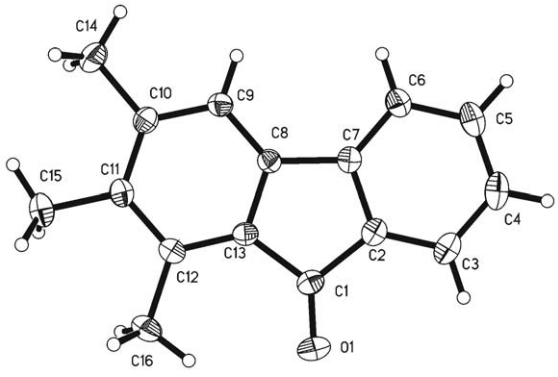


Figure 2 ORTEP plot of **7b** (50% probability level)

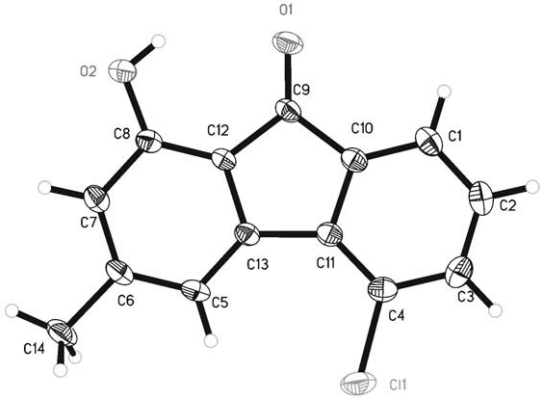
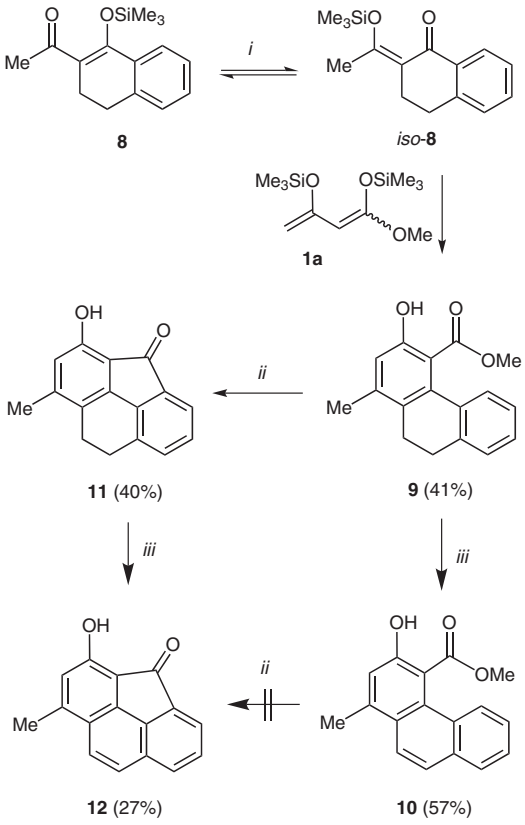


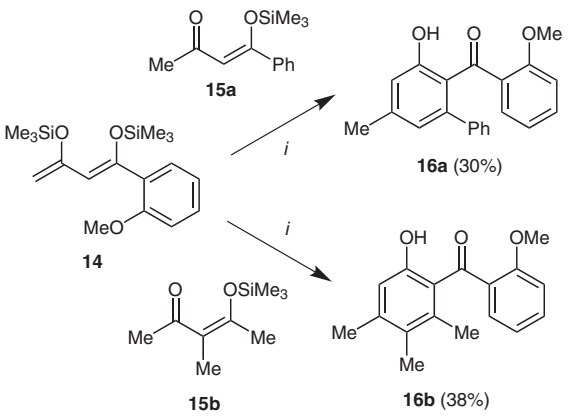
Figure 3 ORTEP plot of **7ab** (50% probability level)



Scheme 3 Synthesis of cyclopenta[*def*]phenanthren-4-one **12**. *Reagents and conditions*: (i) $TiCl_4$, CH_2Cl_2, –78 to 20 °C; (ii) H_2SO_4, 1 h; (iii) DDQ (2.0 equiv), 1,4-dioxane, reflux, 48 h.

and subsequent cyclization. Treatment of **9** with concentrated sulfuric acid afforded product **11**, which was transformed into cyclopenta[*def*]phenanthren-4-one **12** by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (Scheme 3).[16] The oxidation of **9** afforded the phenanthrene **10**. All attempts to transform **10** into **12** proved to be unsuccessful, presumably due to the rigid character of **10**.

To the best of our knowledge, the synthesis of functionalized benzophenones based on formal [3+3] cyclocondensations has not been reported to date. The reaction of the novel 1,3-bis(trimethylsilyloxy)buta-1,3-diene **14** with 3-(silyloxy)-2-en-1-ones **15a** and **15b** afforded the functionalized benzophenones **16a** and **16b**, respectively (Scheme 4).



Scheme 4 Synthesis of benzophenones **16a**,**b**. *Reagents and conditions*: (i) $TiCl_4$, CH_2Cl_2, –78 to 20 °C; (ii) concd H_2SO_4, 1 h.

In conclusion, two methods for the synthesis of functionalized fluorenones were developed. The first approach relies on the [3+3] cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 3-(silyloxy)-2-en-1-ones to give salicylates. Suzuki cross-coupling reactions of the salicylate-derived enol triflates afforded 2-(methoxycarbonyl)biaryls that were subsequently transformed into the target molecules by intramolecular Friedel–Crafts acylation. The second approach allows a convenient synthesis of 1-hydroxyfluorenones. The cyclization of 3-aryl-3-(silyloxy)-2-en-1-ones with 1,3-bis(silyloxy)buta-1,3-dienes afforded 6-arylsalicylates that were subsequently transformed into the products by intramolecular Friedel–Crafts acylation. In this context, the synthesis of novel cyclopenta[*def*]phenanthren-4-ones is reported. The synthesis of functionalized benzophenones has also been reported. The advantage of the synthetic strategies outlined herein relies on the fact that various substitution patterns are readily available based on a building-block strategy. The products are not readily available by other methods.

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^1H and ^{13}C NMR spectra the deuterated solvents indicated were used. MS data were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane), or electrospray ionization (ESI). For preparative scale chromatography silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used.

Salicylates 3 and 9; General Procedure

To a CH_2Cl_2 soln of 3-(silyloxy)-2-en-1-ones **2a**–**k** or **8** (1.0 equiv) and 1,3-bis(silyl enol ethers) **1a**–**c** (1.0 equiv) was added dropwise, at –78 °C, $TiCl_4$ (1.0 equiv) under an argon atmosphere. The mixture was stirred at –78 °C for 30 min and was then allowed to warm to 20 °C over 18 h. To the mixture was added aq 10% HCl, the organic layer was separated, and the aqueous layer was repeatedly extracted with CH_2Cl_2. The combined organic extracts were dried (Na_2SO_4) and filtered. The filtrate was concentrated in vacuo and the residue was purified by chromatography (silica gel, *n*-heptane–EtOAc) to give salicylates **3** or **9**.

Methyl 6-Hydroxy-2,3,4-trimethylbenzoate (3a)

Starting with **1a** (1.042 g, 4.0 mmol), **2a** (0.745 g, 4.0 mmol), and $TiCl_4$ (0.40 mL, 4.0 mmol) in CH_2Cl_2 (8 mL), **3a** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless solid; yield: 0.395 g (51%); mp 54–55 °C.

IR (Nujol): 1665 (s), 1598 (w), 1577 (w), 1346 (m), 1313 (s), 1234 (s), 1207 (s), 1155 (m), 1065 (w), 1006 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.94 (s, 3 H, OCH_3), 6.68 (s, 1 H, CH), 10.48 (s, 1 H, OH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.3, 19.0, 21.6 (CH_3), 51.9 (OCH_3), 111.4 (C), 116.2 (CH), 127.3, 138.2, 143.9 (C), 159.1 (COH), 172.0 (CO_2Me).

MS (CI, isobutane): *m*/*z* (%) = 195 ([M + 1]$^+$, 100).

Anal. Calcd for $C_{11}H_{14}O_3$ (194.23): C, 68.02; H, 7.27. Found: C, 67.95; H, 7.27.

Methyl 3-Hydroxy-5-methylbiphenyl-2-carboxylate (3b)
Starting with **1a** (2.605 g, 10.0 mmol), **2b** (2.344 g, 10.0 mmol), and $TiCl_4$ (1.10 mL, 10.0 mmol) in CH_2Cl_2 (20 mL), **3b** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless oil; yield: 1.333 g (55%). A small amount of starting material could not be separated.

IR (Nujol): 1657 (s), 1611 (s), 1572 (m), 1359 (s), 1325 (s), 1272 (s), 1217 (s), 1165 (m), 1142 (w), 1100 (m), 1030 (w), 1010 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 3.46 (s, 3 H, OCH_3), 6.61–6.62 (m, 1 H, CH), 6.81–6.82 (m, 1 H, CH), 7.19–7.22 (m, 2 H, CH), 7.29–7.35 (m, 3 H, CH), 10.76 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 51.5 (OCH_3), 109.3 (C), 116.9, 124.0, 126.7, 127.0, 127.5, 128.1, 128.6 (CH), 142.9, 144.7, 144.8 (C), 161.7 (COH), 171.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 242 (M^+, 29), 211 (15), 210 (100), 182 (35).

Methyl 2-Hydroxy-4,6-dimethylbenzoate (3c)
Starting with **1a** (2.605 g, 10.0 mmol), **2c** (1.723 g, 10.0 mmol), and $TiCl_4$ (1.10 mL, 10.0 mmol) in CH_2Cl_2 (20 mL), **3c** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless solid; yield: 0.825 g (46%); mp 41–43 °C.

IR (Nujol): 1664 (s), 1625 (w), 1573 (w), 1316 (m), 1262 (s), 1212 (s), 1165 (w), 1100 (m), 1062 (w), 1035 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 2.49 (s, 3 H, CH_3), 3.93 (s, 3 H, OCH_3), 6.53 (s, 1 H, CH), 6.65 (s, 1 H, CH), 11.32 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 23.9 (CH_3), 51.9 (OCH_3), 109.6 (C), 115.8, 124.2 (CH), 141.0, 145.3 (C), 163.0 (COH), 172.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 180 (M^+, 36), 149 (34), 148 (100), 120 (35), 91 (36).

Anal. Calcd for $C_{10}H_{12}O_3$ (180.20): C, 66.65; H, 6.71. Found: C, 66.49; H, 6.72.

Methyl 2-Hydroxy-4-methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (3d)
Starting with **1a** (1.302 g, 5.0 mmol), **2d** (1.062 g, 5.0 mmol), and $TiCl_4$ (0.60 mL, 5.0 mmol) in CH_2Cl_2 (10 mL), **3d** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless solid; yield: 0.352 g (32%).

IR (KBr): 3429 (m), 2929 (s), 1657 (s), 1608 (s), 1443 (s), 1318 (s), 1234 (s), 1075 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.66–1.80 (m, 4 H, CH_2), 2.19 (s, 3 H, CH_3), 2.57 (m, 2 H, CH_2), 2.98 (t, *J* = 6.3 Hz, 2 H, CH_2), 3.93 (s, 3 H, OCH_3), 6.69 (s, 1 H, CH), 10.84 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.4 (CH_3), 22.5, 23.1, 27.0, 30.2 [$(CH_2)_4$], 51.9 (OCH_3), 110.4 (C), 116.5 (CH), 127.7, 139.3, 144.7 (C), 159.9 (COH), 172.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 220 (M^+, 22), 189 (16), 188 (100), 160 (16), 132 (13), 28 (67).

Anal. Calcd for $C_{13}H_{16}O_3$ (220.26): C, 70.89; H, 7.32. Found: C, 70.87; H, 7.35.

Methyl 3-Ethyl-6-hydroxy-2,4-dimethylbenzoate (3e)
Starting with **1a** (0.521 g, 2.0 mmol), **2e** (0.401 g, 2.0 mmol), and $TiCl_4$ (0.20 mL, 2.0 mmol) in CH_2Cl_2 (4 mL), **3e** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless solid; yield: 0.186 g (45%).

IR (KBr): 3022 (m), 2969 (s), 1661 (s), 1445 (s), 1354 (s), 1228 (s), 1156 (s), 1074 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, *J* = 7.2 Hz, 3 H, CH_3), 2.47 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 2.63 (q, *J* = 7.1 Hz, 2 H, CH_2), 3.94 (s, 3 H, OCH_3), 6.68 (s, 1 H, CH), 10.54 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 18.1, 20.7 (CH_3), 22.3 (CH_2), 51.9 (OCH_3), 111.6 (C), 116.8 (CH), 133.3, 137.8, 143.6 (C), 159.3 (COH), 172.1 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 208 (M^+, 16), 176 (53), 161 (53), 28 (100).

Anal. Calcd for $C_{12}H_{16}O_3$ (208.25): C, 69.21; H, 7.74. Found: C, 68.9; H, 7.77.

Methyl 2,4-Diethyl-6-hydroxybenzoate (3f)
Starting with **1a** (2.605 g, 10.0 mmol), **2f** (2.004 g, 10.0 mmol), and $TiCl_4$ (1.10 mL, 10.0 mmol) in CH_2Cl_2 (20 mL), **3f** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a colorless oil; yield: 0.911 g (44%).

IR (neat): 3408 (br, w), 2969 (m), 2936 (m), 2877 (w), 1661 (s), 1617 (m), 1570 (m), 1438 (m), 1361 (m), 1323 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.18 (t, ^3J = 7.3 Hz, 3 H, CH_3), 1.21 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.57 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.90 (q, ^3J = 7.3 Hz, 2 H, CH_2), 3.94 (s, 3 H, OCH_3), 6.58 (d, ^4J = 1.8 Hz, 1 H, CH), 6.69 (d, ^4J = 1.8 Hz, 1 H, CH), 11.24 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6, 16.1 (CH_3), 28.8, 29.6 (CH_2), 51.9 (OCH_3), 114.5, 121.8 (CH), 109.1, 147.3, 151.5 (C), 162.9 (COH), 172.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 208 (M^+, 23), 177 (15), 176 (100), 133 (26).

Anal. Calcd for $C_{12}H_{16}O_3$ (208.25): C, 69.21; H, 7.74. Found: C, 68.93; H, 7.83.

Methyl 3-Ethyl-2-hydroxy-4,5,6-trimethylbenzoate (3g)
Starting with **1b** (2.885 g, 10.0 mmol), **2a** (1.863 g, 10.0 mmol), and $TiCl_4$ (1.10 mL, 10.0 mmol) in CH_2Cl_2 (20 mL), **3g** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 20:1) as a yellow oil; yield: 1.073 g (50%).

IR (Nujol): 1733 (w), 1718 (w), 1657 (s), 1599 (s), 1570 (m), 1355 (s), 1318 (s), 1273 (s), 1241 (m), 1203 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.15 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.73 (q, ^3J = 7.5 Hz, 2 H, CH_2), 3.93 (s, 3 H, OCH_3), 10.67 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 16.1, 16.6, 19.2 (CH_3), 19.8 (CH_2), 52.0 (OCH_3), 111.2, 127.1, 128.1, 134.8, 141.5 (C), 156.8 (COH), 172.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 222 (M^+, 36), 191 (21), 190 (90), 162 (100), 147 (24).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{18}O_3$: 222.12505; found: 222.12559.

Methyl 3-Chloro-6-hydroxy-2,4-dimethylbenzoate (3h)
Starting with **1a** (1.980 g, 7.6 mmol), **2g** (1.571 g, 7.6 mmol), and $TiCl_4$ (0.80 mL, 7.6 mmol) in CH_2Cl_2 (15 mL), **3h** was isolated as a colorless solid; yield: 1.010 g (62%); mp 59–60 °C.

IR (KBr): 3426 (w), 3000 (w), 2952 (s), 2874 (m), 1663 (s), 1603 (s), 1564 (s), 1449 (s), 1381 (m), 1358 (s), 1310 (s), 1229 (s), 1190 (s), 1104 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.60 (s, 3 H, CH_3), 3.96 (s, 3 H, OCH_3), 6.76 (s, 1 H, CH), 10.83 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9, 21.9 (CH_3), 52.3 (OCH_3), 111.9 (C), 117.4 (CH), 126.8, 137.9, 143.6 (C), 159.9 (COH), 171.3 (CO_2Me).

MS (EI, 70 eV): *m/z* (%) = 214 (M^+, ^{35}Cl, 88), 184 (100), 154 (60), 91 (64).

Anal. Calcd for $C_{10}H_{11}ClO_3$ (214.65): C, 55.96; H, 5.17. Found: C, 55.97; H, 5.17.

Methyl 3-Hydroxy-2′,5-dimethylbiphenyl-2-carboxylate (3i)
Starting with **1a** (0.287 g, 1.1 mmol), **2i** (0.273 g, 1.1 mmol), and $TiCl_4$ (0.10 mL, 1.1 mmol) in CH_2Cl_2 (2 mL), **3i** was isolated as a yellow oil; yield: 0.120 g (43%).

IR (neat): 3069 (w), 3015 (w), 2954 (m), 2853 (w), 1661 (s), 1612 (m), 1572 (m), 1438 (m), 1353 (m), 1259 (s), 1215 (s), 1123 (m), 1013 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.03 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.43 (s, 3 H, OCH_3), 6.50 (s, 1 H, CH), 6.82 (s, 1 H, CH), 6.99–7.02 (m, 1 H, CH), 7.15–7.20 (m, 3 H, CH), 11.11 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8, 20.6 (CH_3), 50.6 (OCH_3), 108.3 (C), 115.8, 122.5, 123.9, 125.7, 128.4, 132.3 (CH), 133.7, 141.7, 143.2, 144.2 (C), 161.0 (COH), 170.3 (CO_2Me).

MS (EI, 70 eV): *m/z* (%) = 256 (M^+, 28), 225 (19), 224 (100), 181 (19), 153 (26).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{16}O_3$: 256.10940; found: 256.110114.

Methyl 4′-Chloro-3-hydroxy-5-methylbiphenyl-2-carboxylate (3j)
Starting with **1a** (0.573 g, 2.2 mmol), **2i** (0.591 g, 2.2 mmol), and $TiCl_4$ (0.20 mL, 2.2 mmol) in CH_2Cl_2 (4 mL), **3j** was isolated as a colorless solid; yield: 0.242 g (40%); mp 94–96 °C.

IR (neat): 3060 (w), 3020 (w), 2960 (m), 2848 (w), 1664 (s), 1612 (m), 1572 (m), 1438 (m), 1353 (m), 1259 (s), 1215 (s), 1123 (m), 1013 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 3.50 (s, 3 H, OCH_3), 6.56 (br s, 1 H, CH), 6.82 (br s, 1 H, CH), 7.11–7.16 (m, 2 H, CH), 7.29–7.34 (m, 2 H, CH), 10.83 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 51.6 (OCH_3), 109.0 (C), 117.3, 123.9, 127.7, 129.4 (CH), 132.7, 141.4, 143.4, 145.0 (C), 161.9 (COH), 171.1 (CO_2Me).

MS (EI, 70 eV): *m/z* (%) = 276 (M^+, ^{35}Cl, 30), 244 (100), 216 (26), 152 (27).

HRMS (EI): *m/z* (M^+, ^{35}Cl) calcd for $C_{15}H_{13}ClO_3$: 276.05477; found: 276.05567.

Methyl 4′-Chloro-4-hexyl-3-hydroxy-5-methylbiphenyl-2-carboxylate (3k)
Starting with **1c** (0.758 g, 2.2 mmol), **2i** (0.591 g, 2.2 mmol), and $TiCl_4$ (0.20 mL, 2.2 mmol) in CH_2Cl_2 (4 mL), **3k** was isolated as a yellow oil; yield: 0.273 g (34%).

IR (neat): 3074 (w), 3022 (w), 2955 (m), 2860 (w), 1665 (s), 1617 (m), 1568 (m), 1429 (m), 1353 (m), 1259 (s), 1215 (s), 1123 (m), 1013 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 0.76–0.82 (m, 3 H, CH_3), 1.19 [m, 8 H, $(CH_2)_4$], 2.04 (s, 3 H, CH_3), 3.43 (m, 2 H, CH_2), 3.63 (s, 3 H, OCH_3), 6.72 (s, 1 H, CH), 7.34 (d, *J* = 8.6 Hz, 2 H, CH), 7.76 (d, *J* = 8.6 Hz, 2 H, CH), 11.00 (s, 1 H, OH).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.0, 17.6 (CH_3), 19.2, 27.3, 28.8, 31.7, 48.1 (CH_2), 52.3 (OCH_3), 124.2, 128.7, 128.9 (CH), 137.2, 139.1, 154.5, 166.9, 189.6 (C), 200.8 (CO_2Me).

MS (EI, 70 eV): *m/z* (%) = 360 (M^+, ^{35}Cl, 49), 311 (28), 257 (68), 223 (100), 165 (46).

HRMS (EI): *m/z* (M^+, ^{35}Cl) calcd for $C_{21}H_{25}ClO_3$: 360.14867; found: 360.147678.

Methyl 2′-Chloro-3-hydroxy-5-methylbiphenyl-2-carboxylate (3l)
Starting with **1a** (0.537 g, 2.2 mmol), **2j** (0.591 g, 2.2 mmol), and $TiCl_4$ (0.20 mL, 2.2 mmol) in CH_2Cl_2 (4 mL), **3l** was isolated as a colorless solid; yield: 0.226 g (37%).

IR (neat): 3070 (w), 3017 (w), 2952 (m), 2857 (w), 1660 (s), 1612 (m), 1572 (m), 1433 (m), 1353 (m), 1259 (s), 1215 (s), 1123 (m), 1013 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 3.39 (s, 3 H, OCH_3), 6.42 (s, 1 H, CH), 6.77 (s, 1 H, CH), 7.08–7.11 (m, 1 H, CH), 7.14–7.20 (m, 2 H, CH), 7.26–7.29 (m, 1 H, CH), 11.05 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.6 (CH_3), 50.8 (OCH_3), 108.4 (C), 116.7, 122.6, 125.8, 127.5, 128.9, 130.6 (CH), 134.5, 140.3, 140.7, 144.3 (C), 160.9 (COH), 169.9 (CO_2Me).

MS (EI, 70 eV): *m/z* (%) = 276 (M^+, ^{35}Cl, 30), 241 (100), 152 (21).

HRMS (EI): *m/z* (M^+, ^{35}Cl) calcd for $C_{15}H_{13}ClO_3$: 276.05477; found: 276.054962.

Methyl 2′-Chloro-3-hydroxy-4,5-dimethylbiphenyl-2-carboxylate (3m)
Starting with **1d** (0.603 g, 2.2 mmol), **2j** (0.535 g, 2.2 mmol), and $TiCl_4$ (0.417 g, 2.2 mmol) in CH_2Cl_2 (4 mL), **3m** was isolated; yield: 0.190 g (32%).

IR (KBr): 2958 (s), 2870 (m), 1655 (s), 1616 (m), 1503 (m), 1468 (m), 1415 (m), 1399 (m), 1246 (s), 1233 (s), 1097 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.20 (s, 3 H, CH_3), 3.38 (s, 3 H, OCH_3), 6.42 (s, 1 H, CH), 7.06–7.10 (m, 1 H, CH), 7.12–7.16 (m, 2 H, CH), 7.25–7.28 (m, 1 H, CH), 11.34 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.9, 20.9 (CH_3), 52.5 (OCH_3), 109.5 (C), 124.1 (CH), 125.1 (C), 126.6, 128.3, 128.9, 130.2 (CH), 133.1, 138.5, 142.4, 143.8 (C), 160.3 (COH), 171.9 (CO_2Me).

GC-MS (EI, 70 eV): *m/z* (%) = 290 (M^+, ^{35}Cl, 9), 255 (57), 240 (5), 223 (100), 195 (9), 165 (18), 152 (14), 128 (6).

HRMS (EI): *m/z* (M^+, ^{35}Cl) calcd for $C_{16}H_{15}ClO_3$: 290.07042; found: 290.07117.

Ethyl 2′-Chloro-4-ethyl-3-hydroxy-5-methylbiphenyl-2-carboxylate (3n)
Starting with **1e** (0.651 g, 2.2 mmol), **2j** (0.535 g, 2.2 mmol), and $TiCl_4$ (0.417 g, 2.2 mmol) in CH_2Cl_2 (4 mL), **3n** was isolated; yield: 0.224 g (35%).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.66 (t, ^3J = 7.5 Hz, 3 H, CH_2CH_3), 1.08 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_3), 2.23 (s, 3 H, CH_3), 2.58–2.79 (m, 2 H, CH_2CH_3), 3.81–3.91 (m, 2 H, OCH_2CH_3), 6.40 (s, 1 H, CH), 7.07–7.10 (m, 1 H, CH), 7.11–7.15 (m, 2 H, CH), 7.24–7.27 (m, 1 H, CH), 11.47 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0 (CH_2CH_3), 18.4 (OCH_2CH_3), 18.5 (CH_3), 18.6 (CH_2CH_3), 59.8 (OCH_2CH_3), 108.3 (C), 122.8, 126.7, 127.4, 128.8, 129.5 (CH), 131.9, 137.3, 141.4, 141.5 (C), 158.9 (COH), 170.0 (CO_2Et).

GC-MS (EI, 70 eV): *m/z* (%) = 318 (M^+, ^{35}Cl, 10), 283 (50), 272 (11), 255 (17), 237 (100), 165 (21), 152 (6).

HRMS (EI): *m/z* (M^+, ^{35}Cl) calcd for $C_{18}H_{19}ClO_3$: 318.10172; found: 318.102.

Methyl 2′-Fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (3o)

Starting with **1a** (0.286 g, 1.1 mmol), **2k** (0.252 g, 1.0 mmol), and $TiCl_4$ (0.120 mL, 1.1 mmol) in CH_2Cl_2 (2 mL), **3o** was isolated as a yellowish oil; yield: 0.127 g (49%).

IR (neat): 3060 (w), 3025 (w), 2960 (m), 2851 (w), 1653 (s), 1612 (m), 1572 (m), 1438 (m), 1353 (m), 1259 (s), 1215 (s), 1112 (m), 1013 (s), 848 (m), 722 (s), 697 (s), 626 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 3.43 (s, 3 H, OCH_3), 6.50 (s, 1 H, ArH), 6.76 (s, 1 H, ArH), 6.91–6.97 (m, 1 H, ArH), 7.03–7.21 (m, 3 H, ArH), 10.93 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 52.1 (OCH_3), 110.1 (C), 114.7, 118.2, 124.0, 124.6, 129.1, 130.4 (CH), 138.1, 145.6, 158.1, 161.3, 162.3 (C), 171.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 260 (M^+, 37), 229 (18), 228 (100), 200 (42), 171 (17), 151 (3).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{13}FO_3$: 260.08432; found: 260.083875.

Methyl 2′-Fluoro-3-hydroxy-4,5-dimethylbiphenyl-2-carboxylate (3p)

Starting with **1d** (0.452 g, 1.6 mmol), **2k** (0.412 g, 1.5 mmol), and $TiCl_4$ (0.313 g, 1.6 mmol) in CH_2Cl_2 (3 mL), **3p** was isolated as a yellow solid; yield: 0.150 g (32%).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 3.43 (s, 3 H, OCH_3), 6.51 (s, 1 H, CH), 6.90–6.96 (m, 1 H, CH), 7.04–7.07 (m, 1 H, CH), 7.11–7.22 (m, 2 H, CH), 11.27 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.5, 20.4 (CH_3), 51.7 (OCH_3), 109.3 (C), 114.4, 123.6, 124.3 (CH), 124.8 (C), 128.6, 130.1 (CH), 130.8, 134.4, 143.4 (C), 159.7 (d, ^1J = 240.9 Hz, CF), 159.9 (COH), 171.6 (CO_2Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 274 (M^+, 45), 242 (100), 227 (58), 213 (10), 199 (59), 183 (12), 170 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{15}FO_3$: 274.09997; found: 274.09978.

Methyl 4′-Fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (3q)

Starting with **1a** (0.378 g, 1.5 mmol), **2l** (0.429 g, 1.6 mmol), and $TiCl_4$ (0.312 g, 1.6 mmol) in CH_2Cl_2 (3 mL), **3q** was isolated as a colorless oil; yield: 0.168 g (44%).

IR (KBr): 2948 (s), 2895 (m), 1675 (s), 1616 (m), 1493 (m), 1458 (m), 1405 (m), 1399 (m), 1254 (s), 1219 (s), 1068 (m), 748 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 3.41 (s, 3 H, OCH_3), 6.49 (s, 1 H, CH), 6.74 (s, 1 H, CH), 6.92–9.98 (m, 2 H, CH), 6.83 (s, 2 H, CH), 10.74 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5 (CH_3), 50.5 (OCH_3), 108.2 (C), 113.4, 116.1, 123.0, 128.5 (CH), 137.8, 142.5, 143.9 (C), 160.9 (d, ^1J = 219.5 Hz, CF), 162.5 (COH), 170.2 (CO_2Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 260 (M^+, 34), 228 (100), 200 (46), 171 (21), 157 (6), 146 (4).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{13}FO_3$: 260.08432; found: 260.08383.

Ethyl 4-Ethyl-4′-fluoro-3-hydroxy-5-methylbiphenyl-2-carboxylate (3r)

Starting with **1e** (0.378 g, 1.5 mmol), **2l** (0.484 g, 1.6 mmol), and $TiCl_4$ (0.312 g, 1.6 mmol) in CH_2Cl_2 (3 mL), **3r** was isolated as a colorless oil; yield: 0.224 g (44%).

IR (KBr): 2958 (s), 2870 (m), 1655 (s), 1616 (m), 1503 (m), 1468 (m), 1415 (m), 1399 (m), 1246 (s), 1233 (s), 1097 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.73 (t, ^3J = 7.2 Hz, 3 H, CH_2CH_3), 1.09 (t, ^3J = 7.4 Hz, 3 H, OCH_2CH_3), 2.25 (s, 3 H, CH_3), 2.66 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 3.91 (q, ^3J = 7.3 Hz, 2 H, OCH_2CH_3), 6.49 (s, 1 H, CH_{Ar}), 6.91–6.97 (m, 2 H, CH_{Ar}), 7.08–7.11 (m, 2 H, CH_{Ar}), 11.14 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.0 (CH_2CH_3), 18.4 (OCH_2CH_3), 18.5 (CH_3), 28.6 (CH_2CH_3), 59.8 (OCH_2CH_3), 108.3 (C), 113.2, 123.2 (CH), 128.7 (C), 129.0 (CH), 136.6, 138.4, 141.1 (C), 158.7 (COH), 160.8 (d, ^1J = 244.0 Hz, CF), 170.3 (CO_2Et).

GC-MS (EI, 70 eV): *m*/*z* (%) = 302 (M^+, 53), 256 (73), 241 (100), 223 (10), 213 (57), 199 (8), 183 (29).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{19}FO_3$: 302.13127; found: 302.13190.

Methyl 3-Hydroxy-1-methyl-9,10-dihydrophenanthrene-4-carboxylate (9)

Starting with **1a** (2.605 g, 10.0 mmol), **8** (1.302 g, 5.0 mmol), and $TiCl_4$ (0.60 mL, 5.0 mmol) in CH_2Cl_2 (10 mL), **9** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 9:1) as a yellow oil; yield: 0.549 g (41%).

IR (neat): 3330 (w), 3278 (w), 3067 (w), 3021 (w), 2949 (m), 2896 (w), 2840 (w), 1731 (w), 1666 (s), 1605 (m), 1572 (s), 1492 (m), 1435 (s), 1317 (s), 1236 (s), 1209 (s), 1128 (m), 1066 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 2.57–2.62 (m, 2 H, CH_2), 2.78–2.83 (m, 2 H, CH_2), 3.64 (s, 3 H, OCH_3), 6.79 (s, 1 H, CH), 7.04–7.08 (m, 1 H, CH), 7.16–7.24 (m, 2 H, CH), 7.26–7.28 (m, 1 H, CH), 9.53 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (CH_3), 24.8, 29.1 (CH_2), 51.6 (OCH_3), 109.2 (C), 117.5, 125.4, 127.1, 127.3, 129.0 (CH), 130.6, 134.4, 136.6, 137.9, 141.9 (C), 158.1 (COH), 172.0 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 268 (M^+, 35), 237 (21), 236 (100), 208 (19), 165 (32).

Anal. Calcd for $C_{17}H_{16}O_3$ (268.31): C, 76.10; H, 6.01. Found: C, 76.36; H, 6.05.

Triflates 4; General Procedure

To a soln of **3a–h** (1.0 equiv) in CH_2Cl_2 (10 mL/mmol) was added pyridine (2.0 equiv) at –78 °C under an argon atmosphere. After 10 min, Tf_2O (1.2 equiv) was added at –78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 h. The products were isolated by column chromatography (silica gel; CH_2Cl_2).

Methyl 2,3,4-Trimethyl-6-(trifluoromethylsulfonyloxy)benzoate (4a)

Starting with **3a** (0.833 g, 4.3 mmol), pyridine (0.70 mL, 8.6 mmol), and Tf_2O (0.90 mL, 5.1 mmol) in CH_2Cl_2 (43 mL), **4a** was isolated as a colorless oil; yield: 1.342 g (96%).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 3.93 (s, 3 H, OCH_3), 6.96 (s, 1 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.5, 17.6, 21.0 (CH_3), 52.5 (OCH_3), 118.5 (q, $^1J_{C,F}$ = 320.5 Hz, CF_3), 120.0 (CH), 125.3, 136.4, 136.8, 140.4, 143.8 (C), 166.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 326 (M^+, 51), 295 (39), 193 (100), 162 (37), 161 (36), 133 (41).

Methyl 5-Methyl-3-(trifluoromethylsulfonyloxy)biphenyl-2-carboxylate (4b)

Starting with **3b** (0.700 g, 2.9 mmol), pyridine (0.50 mL, 5.8 mmol), and Tf_2O (0.60 mL, 3.5 mmol) in CH_2Cl_2 (29 mL), **4b** was isolated as a colorless solid; yield: 0.749 g (69%).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 3.66 (s, 3 H, OCH_3), 7.13 (s, 1 H, CH), 7.23 (m, 1 H, CH), 7.31–7.36 (m, 2 H, CH), 7.36–7.39 (m, 2 H, CH), 7.40–7.44 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4 (CH_3), 52.4 (OCH_3), 118.5 (q, $^1J_{C,F}$ = 320.4 Hz, CF_3), 120.7 (CH), 124.0 (C), 128.1, 128.2, 128.5, 130.6 (CH), 139.0, 142.3, 143.1, 146.4 (C), 165.4 (CO_2Me).

Methyl 2,4-Dimethyl-6-(trifluoromethylsulfonyloxy)benzoate (4c)

Starting with **3c** (0.773 g, 4.3 mmol), pyridine (0.70 mL, 8.6 mmol), and Tf_2O (0.90 mL, 5.2 mmol) in CH_2Cl_2 (43 mL), **4c** was isolated as colorless oil; yield: 1.302 g (97%).

IR (KBr): 2959 (m), 1736 (s), 1624 (s), 1568 (m), 1425 (s), 1278 (s), 1212 (s), 1143 (s), 1089 (s), 1023 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 3.92 (s, 3 H, OCH_3), 6.94 (s, 1 H, CH), 7.06 (s, 1 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 20.1, 21.2 (CH_3), 52.4 (OCH_3), 118.5 (q, $^1J_{C,F}$ = 320.4 Hz, CF_3), 119.6 (CH), 123.7 (C), 131.3 (CH), 139.7, 142.4, 146.9 (C), 165.4 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 312 (M^+, 42), 281 (50), 179 (100), 147 (44), 119 (33), 91 (37).

Methyl 4-Methyl-2-(trifluoromethylsulfonyloxy)-5,6,7,8-tetrahydronaphthalene-1-carboxylate (4d)

Starting with **3d** (0.269 g, 1.2 mmol), pyridine (0.20 mL, 2.4 mmol), and Tf_2O (0.20 mL, 1.5 mmol) in CH_2Cl_2 (12 mL), **4d** was isolated as a colorless solid; yield: 0.416 g (97%).

IR (KBr): 3443 (m), 2940 (m), 1735 (s), 1607 (m), 1423 (s), 1233 (s), 1214 (s), 1145 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74–1.85 (m, 4 H, CH_2), 2.26 (s, 3 H, CH_3), 2.61 (t, *J* = 6.1 Hz, 2 H, CH_2), 2.80 (t, *J* = 6.1 Hz, 2 H, CH_2), 3.92 (s, 3 H, OCH_3), 6.94 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.9 (CH_3), 21.9, 22.2, 26.8, 27.8 [$(CH_2)_4$], 52.4 (OCH_3), 116.3 (C), 119.6 (CH), 124.4, 136.7, 137.6, 140.9, 143.7 (C), 166.1 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 352 (M^+, 15), 219 (34), 187 (100).

Methyl 3-Ethyl-2,4-dimethyl-6-(trifluoromethylsulfonyloxy)benzoate (4e)

Starting with **3e** (0.739 g, 3.6 mmol), pyridine (0.60 mL, 7.1 mmol), and Tf_2O (0.70 mL, 4.3 mmol) in CH_2Cl_2 (36 mL), **4e** was isolated as colorless oil; yield: 1.070 g (89%).

IR (KBr): 2971 (s), 2884 (m), 1738 (s), 1607 (s), 1421 (s), 1278 (s), 1211 (s), 1147 (s), 1048 (s), 1012 cm^{-1} (s).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (t, *J* = 7.1 Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.66 (q, *J* = 6.9 Hz, 2 H, CH_2), 3.94 (s, 3 H, OCH_3), 6.96 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 17.0, 20.5 (CH_3), 22.6 (CH_2), 52.6 (OCH_3), 116.4 (C), 120.4 (CH), 120.8, 136.7, 140.4, 142.5, 144.2 (C), 166.3 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 340 (M^+, 58), 309 (42), 207 (100), 176 (39), 175 (75), 146.5 (23), 119 (30).

Anal. Calcd for $C_{13}H_{15}F_3O_5S$ (340.32): C, 45.88; H, 4.44. Found: C, 46.11; H, 4.52.

Methyl 2,4-Diethyl-6-(trifluoromethylsulfonyloxy)benzoate (4f)

Starting with **3f** (0.771 g, 3.7 mmol), pyridine (0.60 mL, 7.4 mmol), and Tf_2O (0.70 mL, 4.4 mmol) in CH_2Cl_2 (37 mL), **4f** was isolated as colorless liquid; yield: 1.119 g (89%); R_f = 0.90 (CH_2Cl_2).

IR (neat): 2973 (m), 2940 (m), 2880 (w), 1737 (s), 1621 (m), 1565 (m), 1424 (s), 1288 (m), 1220 (br, s), 1142 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.67 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.73 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.92 (s, 3 H, OCH_3), 6.96 (br s, 1 H, CH), 7.10 (br s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9, 15.5 (CH_3), 26.9, 28.6 (CH_2), 52.5 (OCH_3), 118.4, 128.5 (CH), 118.5 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3), 123.7, 145.6, 146.7, 148.7 (C), 165.6 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 340 (M^+, 27), 309 (36), 207 (62), 176 (29), 175 (100).

Anal. Calcd for $C_{13}H_{15}F_3O_5S$ (340.32): C, 45.88; H, 4.44. Found: C, 45.80; H, 4.49.

Methyl 3-Ethyl-4,5,6-trimethyl-2-(trifluoromethylsulfonyloxy)benzoate (4g)

Starting with **3g** (0.218 g, 1.0 mmol), pyridine (0.20 mL, 2.0 mmol), and Tf_2O (0.20 mL, 1.2 mmol) in CH_2Cl_2 (10 mL), **4g** was isolated as yellow solid; yield: 0.326 g (94%); mp 67–68 °C; R_f = 0.22 (*n*-heptane–EtOAc, 5:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.77 (q, ^3J = 7.5 Hz, 2 H, CH_2), 3.90 (s, 3 H, OCH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 16.5, 16.6, 17.8 (CH_3), 20.8 (CH_2), 52.5 (OCH_3), 118.4 (q, $^1J_{C,F}$ = 320.0 Hz, CF_3), 126.0, 133.5, 133.7, 137.0, 139.1, 141.0 (C), 166.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 354 (M^+, 35), 323 (27), 221 (40), 190 (29), 189 (100).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{17}F_3O_5S$: 354.07433; found: 354.07433.

Methyl 3-Chloro-2,4-dimethyl-6-(trifluoromethylsulfonyloxy)benzoate (4h)

Starting with **3h** (0.279 g, 1.3 mmol), pyridine (0.20 mL, 2.6 mmol), and Tf_2O (0.30 mL, 1.6 mmol) in CH_2Cl_2 (13 mL), **4h** was isolated as a colorless oil; yield: 0.440 g (98%).

IR (KBr): 2958 (w), 1740 (s), 1426 (s), 1272 (s), 1243 (s), 1214 (s), 1141 (s), 1023 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.95 (s, 3 H, OCH_3), 7.08 (s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.3, 21.3 (CH_3), 52.8 (OCH_3), 118.4 (q, $J_{C,F}$ = 318.2 Hz, CF_3), 120.9 (CH), 126.3, 135.3, 137.0, 140.4, 143.9 (C), 164.9 (CO_2Me).

GC-MS (EI, 70 eV): *m*/*z* (%) = 346 (M^+, ^{35}Cl, 20), 315 (27), 213 (100), 182 (44), 153 (51), 91 (57), 69 (64).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{10}ClF_3O_5S$: 345.9884; found: 345.9876.

Biaryls 6; General Procedure

A 1,4-dioxane soln of the arylboronic acid, K_3PO_4, $Pd(PPh_3)_4$, and triflate **4** was stirred at 110 °C for 4–20 h. After cooling to r.t., sat. aq NH_4Cl soln was added, the organic and the aqueous layer were separated, and the latter was extracted with Et_2O. The combined organic layers were dried (Na_2SO_4), and filtered and the filtrate was concentrated in vacuo. The residue was purified by chromatography.

Methyl 4′-Methoxy-3,4,5-trimethylbiphenyl-2-carboxylate (6a)

Starting with triflate **4a** (0.228 g, 0.7 mmol), 4-methoxyphenylboronic acid (0.138 g, 0.9 mmol), K_3PO_4 (0.238 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.024 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.8 mL), **6a** was isolated as a colorless oil; yield: 0.158 g (79%).

IR (neat): 3031 (w), 2997 (m), 2948 (m), 2865 (w), 2837 (m), 1725 (br s), 1610 (s), 1578 (w), 1516 (s), 1462 (s), 1435 (s), 1394 (m), 1321 (w), 1290 (s), 1260 (s), 1248 (s), 1180 (s), 1164 (s), 1129 (s), 1080 (m), 1043 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.28 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 3.62 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.88–6.94 (m, 2 H, CH), 7.02 (s, 1 H, CH), 7.26–7.32 (m, 2 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 15.4, 17.3, 20.7 (CH_3), 51.7, 55.2 (OCH_3), 113.6, 128.8, 129.3 (CH), 131.7, 133.1, 133.5, 134.2, 136.5, 137.7, 158.8 (C), 171.1 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 285 (18), 284 (M^+, 100), 253 (69), 252 (26), 238 (27).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{20}O_3$: 284.14070; found: 284.13999.

Methyl 3,4,5-Trimethylbiphenyl-2-carboxylate (6b)

Starting with triflate **4a** (0.228 g, 0.7 mmol), phenylboronic acid (0.111 g, 0.9 mmol), K_3PO_4 (0.238 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.024 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.8 mL), **6b** was isolated as a colorless solid; yield: 0.154 g (87%); mp 63–64 °C.

IR (KBr): 3452 (br m), 3411 (m), 3065 (w), 3036 (w), 2995 (w), 2946 (m), 2925 (w), 1714 (s), 1598 (w), 1558 (w), 1502 (w), 1458 (m), 1433 (s), 1395 (w), 1382 (w), 1319 (w), 1272 (s), 1262 (s), 1188 (s), 1166 (s), 1134 (m), 1078 (w), 1047 (s), 1009 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 3.56 (s, 3 H, OCH_3), 7.04 (s, 1 H, CH), 7.26–7.40 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 17.3, 20.8 (CH_3), 51.8 (OCH_3), 127.0, 128.1, 128.2, 128.8 (CH), 131.6, 133.2, 134.7, 136.9, 137.8, 141.0 (C), 171.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 255 (41), 254 (M^+, 100), 223 (100), 222 (83), 180 (77), 179 (76), 165 (82).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O_2$: 254.1301; found: 254.1295.

Methyl 3,4,4′,5-Tetramethylbiphenyl-2-carboxylate (6c)

Starting with triflate **4a** (0.300 g, 0.9 mmol), 4-methylphenylboronic acid (0.163 g, 1.2 mmol), K_3PO_4 (0.312 g, 1.5 mmol), $Pd(PPh_3)_4$ (0.032 g, 0.03 mmol, 3 mol%), and 1,4-dioxane (2.3 mL), **6c** was isolated as a colorless solid; yield: 0.215 g (87%); mp 67–68 °C.

IR (KBr): 3438 (w), 3026 (w), 2953 (m), 2922 (w), 2862 (w), 1734 (s), 1515 (w), 1460 (w), 1425 (m), 1383 (w), 1274 (s), 1260 (s), 1213 (w), 1184 (m), 1162 (m), 1126 (m), 1081 (w), 1043 (m), 1019 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.68 (s, 3 H, OCH_3), 7.12 (s, 1 H, CH), 7.23 (s, 1 H, CH), 7.32 (s, 1 H, CH), 7.36–7.43 (s, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$,): δ = 15.2, 17.2, 20.6, 20.9 (CH_3), 51.6 (OCH_3), 127.9, 128.7, 128.8 (CH), 131.5, 133.0 134.3, 136.5, 136.7, 137.6, 138.0 (C), 171.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 268 (M^+, 96), 237 (100), 236 (29), 221 (29), 194 (31), 179 (39).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{20}O_2$: 268.1458; found: 268.1457.

Methyl 4-Methoxy-5′-methyl-1,1′;3′,1″-terphenyl-2′-carboxylate (6d)

Starting with triflate **4b** (0.101 g, 0.27 mmol), 4-methoxyphenylboronic acid (0.053 g, 0.4 mmol), K_3PO_4 (0.091 g, 0.4 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.01 mmol, 3 mol%), and 1,4-dioxane (0.7 mL), **6d** was isolated as a colorless solid; yield: 0.075 g (84%); mp 82–83 °C.

IR (KBr): 3437 (br m), 3034 (w), 3002 (w), 2953 (w), 2837 (w), 1729 (s), 1611 (m), 1599 (w), 1514 (s), 1457 (w), 1441 (w), 1271 (s), 1247 (s), 1177 (m), 1103 (m), 1053 (m), 1030 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.43 (s, 3 H, CH_3), 3.38 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.89–6.95 (m, 2 H, CH), 7.16–7.17 (m, 2 H, CH), 7.29–7.31 (m, 1 H, CH), 7.32–7.35 (m, 2 H, CH), 7.36–7.38 (m, 3 H, CH), 7.39–7.40 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 51.7, 55.2 (OCH_3), 113.7, 127.3, 128.2, 128.3, 129.2, 129.4, 129.6 (CH), 130.0, 133.0, 139.2, 139.9, 140.3, 140.7, 159.0 (C), 170.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 333 (20), 332 (M^+, 85), 302 (22), 301 (100), 258 (14), 215 (25).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{20}O_3$: 332.14070; found: 332.14079.

Methyl 5′-Methyl-1,1′;3′,1″-terphenyl-2′-carboxylate (6e)

Starting with triflate **4b** (0.097 g, 0.26 mmol), phenylboronic acid (0.041 g, 0.3 mmol), K_3PO_4 (0.089 g, 0.4 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.01 mmol, 3 mol%), and 1,4-dioxane (0.7 mL), **6e** was isolated as a colorless solid; yield: 0.062 g (79%); mp 120–122 °C.

IR (KBr): 3437 (m), 3064 (w), 3028 (w), 2946 (w), 2918 (w), 1731 (s), 1600 (m), 1497 (w), 1450 (w), 1436 (w), 1259 (s), 1189 (m), 1104 (s), 1055 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.44 (s, 3 H, CH_3), 3.36 (s, 3 H, OCH_3), 7.19 (m, 2 H, CH), 7.30–7.40 (m, 10 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (CH_3), 51.6 (OCH_3), 127.4, 128.2, 128.3, 129.5, 130.1 (CH), 139.3, 140.4, 140.6 (C), 170.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 302 (M^+, 53), 272 (20), 271 (100), 228 (20), 165 (12).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{18}O_2$: 302.13013; found: 302.13015.

Methyl 4,5′-Dimethyl-1,1′;3′,1″-terphenyl-2′-carboxylate (6f)

Starting with triflate **4b** (0.101 g, 0.27 mol), 4-methylphenylboronic acid (0.048 g, 0.4 mmol), K_3PO_4 (0.091 g, 0.4 mmol), $Pd(PPh_3)_4$ (0.009 g, 0.01 mmol, 3 mol%), and 1,4-dioxane (0.7 mL), **6f** was isolated as a colorless oil; yield: 0.064 g (75%).

IR (neat): 3027 (m), 2947 (m), 2921 (m), 2865 (w), 1729 (br s), 1600 (s), 1574 (m), 1515 (s), 1441 (s), 1427 (s), 1262 (br s), 1190 (s), 1100 (s), 1052 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 3.39 (s, 3 H, OCH_3), 7.19 (m, 2 H, CH), 7.22 (s, 1 H, CH), 7.29 (s, 1 H, CH), 7.32 (s, 1 H, CH), 7.34–7.43 (m, 6 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 21.3 (CH_3), 51.7 (OCH_3), 127.4, 128.1, 128.2, 128.2, 128.3, 128.5, 129.0, 129.4, 129.6, 130.0 (CH), 137.1, 137.7, 139.0, 139.3, 140.4, 140.7, 142.3 (C), 170.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 316 (M^+, 46), 286 (23), 285 (100), 242 (22), 241 (23), 239 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{20}O_2$: 316.14578; found: 316.14543.

Methyl 4′-Methoxy-3,5-dimethylbiphenyl-2-carboxylate (6g)

Starting with triflate **4c** (0.219 g, 0.7 mmol), 4-methoxyphenylboronic acid (0.138 g, 0.9 mmol), K_3PO_4 (0.238 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.024 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.8 mL), **6g** was isolated as a colorless oil; yield: 0.180 g (95%).

IR (neat): 3033 (w), 2997 (w), 2950 (s), 2925 (s), 2854 (m), 1727 (br s), 1609 (s), 1576 (w), 1514 (s), 1457 (m), 1442 (m), 1379 (w), 1263 (s), 1250 (s), 1180 (s), 1128 (m), 1082 (s), 1035 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 6 H, CH_3), 3.59 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.87–6.89 (m, 1 H, CH), 6.91–6.93 (m, 1 H, CH), 6.99–7.00 (m, 2 H, CH), 7.24–7.26 (m, 1 H, CH), 7.28–7.30 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 21.2 (CH_3), 51.8, 55.2 (OCH_3), 113.7, 127.9, 129.2, 129.5 (CH), 130.3, 133.5, 135.4, 139.3, 139.8, 158.9 (C), 170.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 270 (M^+, 100), 239 (97), 238 (45), 223 (12), 196 (17).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O_3$: 270.12505; found: 270.12425.

Methyl 3,5-Dimethylbiphenyl-2-carboxylate (6h)

Starting with triflate **4c** (0.153 g, 0.5 mmol), phenylboronic acid (0.078 g, 0.6 mmol), K_3PO_4 (0.166 g, 0.8 mmol), $Pd(PPh_3)_4$ (0.017 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.2 mL), **6h** was isolated as a colorless oil; yield: 0.107 g (91%).

IR (neat): 3058 (w), 3030 (w), 2949 (m), 2924 (m), 2857 (w), 1727 (br s), 1606 (m), 1577 (w), 1497 (w), 1436 (m), 1380 (w), 1269 (s), 1189 (m), 1128 (m), 1084 (s), 1032 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 3.55 (s, 3 H, OCH_3), 7.03 (br s, 2 H, CH), 7.27–7.41 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 21.2 (CH_3), 51.7 (OCH_3), 127.2, 127.9, 128.1, 128.2, 129.9 (CH), 130.3, 135.5, 139.4, 140.3, 141.1 (C), 170.4 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 240 (M^+, 60), 210 (16), 209 (100), 208 (26), 166 (24), 165 (42).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}O_2$: 240.11448; found: 240.11519.

Methyl 3,4′,5-Trimethylbiphenyl-2-carboxylate (6i)

Starting with triflate **4c** (0.500 g, 1.6 mmol), 4-methylphenylboronic acid (0.283 g, 2.1 mmol), K_3PO_4 (0.543 g, 2.6 mmol), $Pd(PPh_3)_4$ (0.055 g, 0.05 mmol, 3 mol%), and 1,4-dioxane (4.0 mL), **6i** was isolated as a colorless oil; yield: 0.181 g (44%).

IR (neat): 3024 (m), 2993 (m), 2948 (m), 2923 (m), 2865 (m), 1726 (br s), 1605 (m), 1576 (w), 1515 (m), 1437 (m), 1269 (s), 1188 (m), 1181 (m), 1127 (m), 1082 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 6 H, CH_3), 2.37 (s, 3 H, CH_3), 3.59 (s, 3 H, OCH_3), 7.01 (m, 2 H, CH), 7.16–7.19 (m, 2 H, CH), 7.22–7.27 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.6, 21.1, 21.2 (CH_3), 51.7 (OCH_3), 128.0, 129.0, 129.7, (CH), 130.3, 135.4, 136.9, 138.1, 139.3, 140.2 (C), 170.6 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 254 (M^+, 68), 223 (100), 222 (36), 179 (27), 165 (42).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O_2$: 254.13013; found: 254.12981.

Methyl 2-(4-Methoxyphenyl)-4-methyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (6j)

Starting with triflate **4d** (0.250 g, 0.7 mmol), 4-methoxyphenylboronic acid (0.140 g, 0.9 mmol), K_3PO_4 (0.242 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.024 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.8 mL), **6j** was isolated as a colorless oil; yield: 0.128 g (58%); R_f = 0.53 (*n*-heptane–EtOAc, 15:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.72–1.90 (m, 4 H, CH_2), 2.25 (s, 3 H, CH_3), 2.66 (t, ^3J = 6.1 Hz, 2 H, CH_2), 2.77 (t, ^3J = 6.1 Hz, 2 H, CH_2), 3.59 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.86–6.95 (m, 2 H, CH), 7.01 (s, 1 H, CH), 7.24–7.32 (m, 2 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 19.7 (CH_3), 22.5, 22.8, 26.9, 27.5 [$(CH_2)_4$], 51.8, 55.2 (OCH_3), 113.7, 128.4, 129.3 (CH), 131.0, 133.4, 133.9, 134.7, 136.3, 138.1, 158.8 (C), 170.9 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 310 (M^+, 100), 279 (33), 278 (84), 263 (40), 247 (24).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{22}O_3$: 310.15635; found: 310.15590.

Methyl 4-Methyl-2-phenyl-5,6,7,8-tetrahydronaphthalene-1-carboxylate (6k)

Starting with triflate **4d** (0.201 g, 0.6 mmol), phenylboronic acid (0.090 g, 0.7 mmol), K_3PO_4 (0.193 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.020 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.4 mL), **6k** was isolated as a colorless solid; yield: 0.142 g (89%); mp 151 °C; R_f = 0.23 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2924 (m), 2863 (m), 1715 (s), 1635 (br, w), 1600 (w), 1557 (w), 1451 (m), 1432 (m), 1396 (w), 1252 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.71–1.92 (m, 4 H, CH_2), 2.26 (s, 3 H, CH_3), 2.67 (t, ^3J = 6.1 Hz, 2 H, CH_2), 2.78 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.55 (s, 3 H, OCH_3), 7.03 (br s, 1 H, CH), 7.26–7.41 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7 (CH_3), 22.5, 22.8, 26.9, 27.5 [$(CH_2)_4$], 51.7 (OCH_3), 127.1, 128.2, 128.2, 128.4 (CH), 131.0, 134.0, 135.1, 136.8, 138.2, 141.0 (C), 170.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 280 (M^+, 73), 248 (100), 249 (42), 233 (23), 205 (21).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}O_2$: 280.14578; found: 280.14552.

Methyl 4-Methyl-2-(4-tolyl)-5,6,7,8-tetrahydronaphthalene-1-carboxylate (6l)

Starting with triflate **4d** (0.201 g, 0.57 mmol), 4-methylphenylboronic acid (0.101 g, 0.7 mmol), K_3PO_4 (0.193 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol, 5 mol%), and 1,4-dioxane (1.4 mL), **6l** was isolated as a colorless solid; yield: 0.139 g (83%); mp 82 °C; R_f = 0.22 (*n*-heptane–EtOAc, 15:1).

IR (KBr): 2928 (m), 2860 (m), 1724 (s), 1596 (w), 1558 (w), 1518 (m), 1458 (m), 1434 (m), 1392 (w), 1252 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.70–1.91 (m, 4 H, CH_2), 2.25 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 2.66 (t, ^3J = 6.1 Hz, 2 H, CH_2), 2.77 (t, ^3J = 5.8 Hz, 2 H, CH_2), 3.58 (s, 3 H, OCH_3), 7.01 (s, 1 H, CH), 7.12–7.28 (m, 4 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7, 21.1 (CH_3), 22.5, 22.8, 26.9, 27.5 [$(CH_2)_4$], 51.7 (OCH_3), 126.8, 128.1, 128.4, 129.0, 129.4 (CH), 131.0, 133.9, 134.8, 136.7, 138.0, 138.2, 170.8 (C), 181.3 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 294 (M^+, 77), 263 (41), 262 (100), 247 (55), 219 (23).

Anal. Calcd for $C_{20}H_{22}O_2$ (294.39): C, 81.60; H, 7.53. Found: C, 81.22; H, 7.65.

Methyl 4-Ethyl-4′-methoxy-3,5-dimethylbiphenyl-2-carboxylate (6m)

Starting with triflate **4e** (0.201 g, 0.6 mmol), 4-methoxyphenylboronic acid (0.117 g, 0.8 mmol), K_3PO_4 (0.200 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.021 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.5 mL), **6m** was isolated as a colorless solid; yield: 0.125 g (71%); mp 61 °C; R_f = 0.14 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2996 (m), 2964 (m), 2952 (m), 2935 (m), 1725 (s), 1610 (m), 1595 (m), 1517 (s), 1465 (m), 1447 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.13 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.69 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.60 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.85–6.94 (m, 2 H, CH), 7.00 (s, 1 H, CH), 7.21–7.32 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 16.3, 19.9 (CH_3), 22.6 (CH_2), 51.8, 55.2 (OCH_3), 113.6, 129.3 (CH), 132.0, 132.5, 133.4, 136.5, 137.2, 140.0, 158.8 (C), 171.3 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 298 (M^+, 100), 283 (33), 267 (31), 251 (32), 239 (12).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{22}O_3$: 298.15635; found: 298.15567.

Methyl 4-Ethyl-3,5-dimethylbiphenyl-2-carboxylate (6n)

Starting with triflate **4e** (0.231 g, 0.7 mmol), phenylboronic acid (0.107 g, 0.9 mmol), K_3PO_4 (0.231 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.031 g, 0.03 mmol, 4 mol%), and 1,4-dioxane (1.7 mL), **6n** was isolated as a colorless solid; yield: 0.084 g (46%); mp 60 °C; R_f = 0.14 (*n*-heptane–EtOAc, 20:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.36 (br s, 3 H, CH_3), 2.71 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.56 (s, 3 H, OCH_3), 7.03 (s, 1 H, CH), 7.22–7.41 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.2, 16.3, 19.9 (CH_3), 22.6 (CH_2), 51.8 (OCH_3), 127.1, 128.2, 128.2, 129.3 (CH), 132.0, 132.7, 137.0, 137.3, 140.4, 141.0 (C), 171.1 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 268 (M^+, 100), 253 (40), 237 (71), 221 (31), 178 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{20}O_2$: 268.14578; found: 268.14558.

Methyl 4-Ethyl-3,4′,5-trimethylbiphenyl-2-carboxylate (6o)

Starting with triflate **4e** (0.201 g, 0.6 mmol), 4-methylphenylboronic acid (0.105 g, 0.8 mmol), K_3PO_4 (0.200 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.035 g, 0.03 mmol, 5 mol%), and 1,4-dioxane (1.5 mL), **6o** was isolated as a colorless oil; yield: 0.125 g (75%); R_f = 0.21 (*n*-heptane–EtOAc, 10:1).

IR (neat): 3023 (m), 2968 (s), 2948 (m), 2924 (m), 2872 (m), 1727 (s), 1596 (m), 1557 (w), 1517 (m), 1454 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.36 (br s, 6 H, CH_3), 2.71 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.60 (s, 3 H, OCH_3), 7.02 (s, 1 H, CH), 7.12–7.28 (m, 4 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.2, 16.3, 19.9, 21.1 (CH_3), 22.6 (CH_2), 51.8 (OCH_3), 128.0, 128.9, 129.3 (CH), 131.9, 132.5, 136.7, 136.9, 137.2, 138.0, 140.2 (C), 171.2 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 282 (M^+, 100), 267 (34), 251 (48), 235 (37), 182 (54).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{22}O_2$: 282.16143; found: 282.16140.

Methyl 3,5-Diethylbiphenyl-2-carboxylate (6p)

Starting with triflate **4f** (0.214 g, 0.63 mmol), phenylboronic acid (0.100 g, 0.8 mmol), K_3PO_4 (0.214 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.022 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.6 mL), **6p** was isolated as a colorless oil; yield: 0.149 g (88%); R_f = 0.17 (*n*-heptane–EtOAc, 20:1).

IR (neat): 3057 (m), 3028 (m), 2966 (s), 2874 (m), 1727 (s), 1603 (m), 1577 (m), 1459 (m), 1430 (m), 1279 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.26 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.68 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.70 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.54 (s, 3 H, OCH_3), 7.06 (d, ^4J = 1.7 Hz, 1 H, CH), 7.08 (d, ^4J = 1.7 Hz, 1 H, CH), 7.27–7.48 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 15.8 (CH_3), 26.8, 28.7 (CH_2), 51.7 (OCH_3), 126.9, 127.2, 127.3, 128.2, 128.7 (CH), 130.1, 140.3, 141.3, 141.8, 145.8 (C), 170.5 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 268 (M^+, 96), 237 (100), 236 (69), 207 (95), 165 (12).

Anal. Calcd for $C_{18}H_{20}O_2$ (268.35): C, 80.56; H, 7.51. Found: C, 80.56; H, 7.72.

Methyl 3,5-Diethyl-4′-methylbiphenyl-2-carboxylate (6q)

Starting with triflate **4f** (0.245 g, 0.7 mmol), 4-methylphenylboronic acid (0.128 g, 0.9 mmol), K_3PO_4 (0.244 g, 1.2 mmol), $Pd(PPh_3)_4$ (0.034 g, 0.03 mmol, 4 mol%), and 1,4-dioxane (1.8 mL), **6q** was isolated as a colorless oil; yield: 0.154 g (76%); R_f = 0.39 (*n*-heptane–EtOAc, 10:1).

IR (neat): 3024 (m), 2966 (s), 2874 (m), 1727 (s), 1603 (m), 1573 (m), 1516 (m), 1458 (m), 1430 (m), 1278 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.25 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.66 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.68 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.57 (s, 3 H, OCH_3), 7.01–7.08 (m, 2 H, CH), 7.14–7.29 (m, 4 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 15.8, 21.1 (CH_3), 26.8, 28.7 (CH_2), 51.7 (OCH_3), 126.9, 127.0, 128.1, 129.0 (CH), 130.1, 136.9, 138.3, 140.2, 141.7, 145.8 (C), 170.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 282 (M^+, 100), 251 (87), 250 (31), 235 (19), 2221 (89).

Anal. Calcd for $C_{19}H_{22}O_2$ (282.38): C, 80.82; H, 7.85. Found: C, 80.57; H, 7.99.

Methyl 3,5-Diethyl-4′-methoxybiphenyl-2-carboxylate (6r)

Starting with triflate **4f** (0.221 g, 0.65 mmol), 4-methoxyphenylboronic acid (0.129 g, 0.9 mmol), K_3PO_4 (0.221 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.030 g, 0.03 mmol, 4 mol%), and 1,4-dioxane (1.6 mL), **6r** was isolated as a yellow oil; yield: 0.167 g (86%); R_f = 0.52 (toluene–EtOAc, 30:1).

IR (neat): 2966 (s), 2936 (m), 2875 (m), 2836 (m), 1725 (s), 1609 (s), 1577 (m), 1515 (s), 1461 (s), 1430 cm^{-1} (s).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.25 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.67 (q, ^3J = 7.6 Hz, 2 H, CH_2), 2.68 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.58 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.86–8.96 (m, 2 H, CH), 6.99–7.08 (m, 2 H, CH), 7.23–7.34 (m, 2 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.4, 15.8 (CH_3), 26.8, 28.7 (CH_2), 51.7, 55.2 (OCH_3), 113.7, 126.9, 129.3 (CH), 130.1, 133.7, 139.8, 141.6, 145.7, 158.9 (C), 170.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 298 (M^+, 100), 267 (45), 266 (32), 237 (70), 235 (18).

Anal. Calcd for $C_{19}H_{22}O_3$ (298.38): C, 76.48; H, 7.43. Found: C, 76.47; H, 7.58.

Methyl 3,5-Diethyl-3′,4′,5′-trimethoxybiphenyl-2-carboxylate (6s)

Starting with triflate **4f** (0.180 g, 0.53 mmol), 3,4,5-trimethoxyphenylboronic acid (0.146 g, 0.7 mmol), K_3PO_4 (0.180 g, 0.9 mmol), $Pd(PPh_3)_4$ (0.018 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.3 mL), **6s** was isolated as a yellow solid; yield: 0.113 g (59%); mp 84–87 °C; R_f = 0.32 (toluene–EtOAc, 10:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.26 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.67 (q, ^3J = 7.6 Hz, 4 H, CH_2), 3.60 (s, 3 H, OCH_3), 3.86 (br s, 6 H, OCH_3), 3.87 (s, 3 H, OCH_3), 6.59 (s, 2 H, CH), 7.06 (d, ^4J = 1.7 Hz, 1 H, CH), 7.08 (d, ^4J = 1.7 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 15.7 (CH_3), 26.8, 28.7 (CH_2), 51.9, 56.1, 60.9 (OCH_3), 105.4, 126.6, 127.3 (CH), 130.2, 136.8, 137.2, 140.0, 141.7, 145.8, 153.0 (C), 170.6 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 358 (M^+, 100), 343 (53), 297 (14), 295 (31).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{21}H_{26}O_5$: 358.17748; found: 358.17676.

Methyl 6-Ethyl-4′-methoxy-3,4,5-trimethylbiphenyl-2-carboxylate (6t)

Starting with triflate **4g** (0.244 g, 0.7 mmol), 4-methoxyphenylboronic acid (0.137 g, 0.9 mmol), K_3PO_4 (0.233 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.032 g, 0.03 mmol, 4 mol%), and 1,4-dioxane (1.7 mL), **6t** was isolated as a yellow solid; yield: 0.096 g (44%); mp 89 °C; R_f = 0.37 (toluene–EtOAc, 50:1).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.92 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 2.44 (q, ^3J = 7.5 Hz, 2 H, CH_2), 3.41 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.83–6.93 (m, 2 H, CH), 7.07–7.17 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 16.2, 16.3, 17.6 (CH_3), 23.7 (CH_2), 51.5, 55.1 (OCH_3), 113.0, 130.8 (CH), 129.1, 132.1, 133.5, 135.2, 135.8, 135.9, 138.7, 158.4 (C), 171.0 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 312 (M^+, 100), 281 (21), 265 (36), 238 (17), 237 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{24}O_3$: 312.17200; found: 312.17130.

Methyl 4-Chloro-4′-methoxy-3,5-dimethylbiphenyl-2-carboxylate (6u)

Starting with triflate **4h** (0.257 g, 0.74 mmol), 4-methoxyphenylboronic acid (0.146 g, 1.0 mmol), K_3PO_4 (0.250 g, 1.2 mmol), Pd catalyst (0.025 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.9 mL), **6u** was isolated as a colorless oil; yield: 0.186 g (82%); R_f = 0.39 (toluene).

IR (neat): 3035 (m), 2998 (m), 2950 (m), 2837 (m), 1728 (s), 1610 (s), 1514 (s), 1456 (s), 1439 (s), 1383 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.34 (br s, 3 H, CH_3), 2.41 (br s, 3 H, CH_3), 3.61 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 6.87–6.94 (m, 2 H, CH), 7.05–7.12 (m, 1 H CH), 7.21–7.29 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 21.0 (CH_3), 52.1, 55.2 (OCH_3), 113.8, 129.3, 129.6 (CH), 132.4, 132.6, 133.2, 134.0, 137.4, 137.6, 159.1 (C), 169.9 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 304 (M^+, ^{35}Cl, 100), 272 (41), 238 (33).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{17}H_{17}ClO_3$: 304.08607; found: 304.08598.

Methyl 4,4′-Dichloro-3,5-dimethylbiphenyl-2-carboxylate (6v)

Starting with triflate **4h** (0.270 g, 0.8 mmol), 4-chlorophenylboronic acid (0.158 g, 1.0 mmol), K_3PO_4 (0.265 g, 1.3 mmol), $Pd(PPh_3)_4$ (0.027 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (2.0 mL), **6v** was isolated as a colorless solid; yield: 0.218 g (90%); mp 98–99 °C; R_f = 0.27 (*n*-heptane–EtOAc, 20:1).

IR (KBr): 2949 (m), 2922 (m), 2856 (m), 1722 (s), 1489 (m), 1436 (m), 1381 (m), 1274 (s), 1233 (m), 1105 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 2.42 (br s, 3 H, CH_3), 3.60 (s, 3 H, OCH_3), 7.07 (s, 1 H, CH), 7.21–7.29 (m, 2 H CH), 7.30–7.38 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0, 21.0 (CH_3), 52.1 (OCH_3), 128.5, 129.4, 129.5 (CH), 132.5, 133.6, 133.7, 134.8, 136.6, 137.9, 138.5 (C), 169.5 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 308 (M^+, ^{35}Cl, 86), 277 (100), 241 (39).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{16}H_{14}Cl_2O_2$: 308.03654; found: 308.03617.

Methyl 4-Chloro-3,5-dimethyl-4′-(trifluoromethyl)biphenyl-2-carboxylate (6w)

Starting with triflate **4h** (0.236 g, 0.68 mmol), 4-(trifluoromethyl)phenylboronic acid (0.167 g, 0.9 mmol), K_3PO_4 (0.231 g, 1.1 mmol), $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.7 mL), **6w** was isolated as a colorless solid; yield: 0.204 g (88%); mp 84–85 °C; R_f = 0.41 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2954 (m), 2928 (m), 1727 (s), 1617 (m), 1570 (m), 1438 (m), 1387 (m), 1326 (s), 1262 (s), 1232 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 3.59 (s, 3 H, OCH_3), 7.09 (s, 1 H, CH), 7.44 (d, ^3J = 8.1 Hz, 2 H, CH), 7.64 (d, ^3J = 8.1 Hz, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.0, 21.0 (CH_3), 52.2 (OCH_3), 124.1 (q, ^1J = 272.0 Hz, CF_3), 125.3 (q, ^3J = 3.8 Hz, CF_3CCH), 128.6, 129.4 (CH), 129.7 (q, ^2J = 32.5 Hz, CF_3C), 132.5, 133.8, 135.2, 136.4, 138.0, 143.7 (C), 169.3 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 342 (M^+, ^{35}Cl, 64), 311 (100), 248 (21).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{17}H_{14}ClF_3O_2$: 342.06289; found: 342.06222.

Methyl 4-Chloro-3,5-dimethylbiphenyl-2-carboxylate (6x)

Starting with triflate **4h** (0.208 g, 0.6 mmol), phenylboronic acid (0.095 g, 0.8 mmol), K_3PO_4 (0.204 g, 1.0 mmol), $Pd(PPh_3)_4$ (0.021 g, 0.02 mmol, 3 mol%), and 1,4-dioxane (1.5 mL), **6x** was isolated as a colorless solid; yield: 0.097 g (59%); mp 55 °C.

IR (KBr): 3428 (m), 2994 (w), 2946 (w), 1722 (s), 1466 (m), 1447 (m), 1433 (m), 1438 (m), 1252 (s), 1226 (m), 1094 (m), 1012 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 3.57 (s, 3 H, OCH_3), 7.12 (s, 1 H, CH), 7.25–7.38 (m, 5 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 21.0 (CH_3), 52.0 (OCH_3), 127.5, 128.1, 128.3, 129.5 (CH), 132.5, 133.3, 134.3, 137.6, 137.8, 140.0 (C), 169.7 (CO_2Me).

MS (EI, 70 eV): *m*/*z* (%) = 274 (M^+, ^{35}Cl, 93), 243 (100), 207 (21), 180 (37), 165 (43).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{16}H_{15}ClO_2$: 274.0755; found: 274.0750.

Fluorenones 7 and 11; General Procedure

Compound **6** was dissolved in concd H_2SO_4 and the mixture was stirred at 20 °C for 1 h. The mixture was poured into ice water and extracted with Et_2O (3 ×). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo to give **7**. Compounds **7a–i**,**x–z**,**aa–ah**, and **11** were purified by precipitation and washing with Et_2O. The other fluorenones were purified by chromatography.

7-Methoxy-1,2,3-trimethyl-9*H*-fluoren-9-one (7a)

Starting with **6a** (0.097 g, 0.34 mmol) and concd H_2SO_4 (4.1 mL), **7a** was isolated as a yellow solid; yield: 0.073 g (85%); mp 135–136 °C.

IR (KBr): 3437 (br, m), 2952 (w), 2937 (w), 2833 (w), 1696 (s), 1601 (s), 1482 (m), 1462 (s), 1433 (s), 1372 (w), 1289 (s), 1259 (m), 1222 (s), 1200 (w), 1192 (w), 1069 (w), 1031 cm^{-1} (w).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 6.91 (dd, ^3J = 8.2 Hz, ^4J = 2.5 Hz, 1 H, CH), 7.03 (s, 1 H, CH), 7.12 (d, ^4J = 2.5 Hz, 1 H, CH), 7.29 (d, ^3J = 8.2 Hz, 1 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.8, 14.6, 15.4 (CH_3), 55.7 (OCH_3), 108.9, 119.1, 119.7, 120.4 (CH), 129.3, 135.9, 136.3, 136.6, 138.7, 142.7, 143.2, 160.5 (C), 195.2 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 252 (M^+, 100), 237 (67), 165 (48).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{16}O_2$: 252.1145; found: 252.1143.

Anal. Calcd for $C_{17}H_{16}O_2$ (252.31): C, 80.93; H, 6.39. Found: C, 80.90; H, 6.51.

1,2,3-Trimethyl-9*H*-fluoren-9-one (7b)
Starting with **6b** (0.028 g, 0.11 mmol) and concd H_2SO_4 (1.3 mL), **7b** was isolated as a yellow solid; yield: 0.023 g (94%); mp 167–168 °C.

IR (KBr): 3439 (br, m), 3382 (m), 3058 (w), 3050 (w), 2977 (w), 2919 (m), 2856 (w), 1701 (s), 1612 (s), 1598 (s), 1468 (w), 1452 (m), 1416 (w), 1372 (m), 1297 (w), 1257 (w), 1199 (w), 1177 (m), 1132 (w), 1087 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 7.17 (br s, 1 H, CH), 7.20–7.24 (m, 1 H, CH), 7.40–7.43 (m, 2 H, CH), 7.56–7.60 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 14.8, 21.7 (CH_3), 119.4, 119.7, 123.7, 128.2 (CH), 129.1 (C), 134.0 (CH), 134.8, 137.3, 138.6, 142.3, 143.1, 143.7 (C), 195.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 222 (M^+, 100), 207 (66), 179 (52), 178 (58), 165 (23), 152 (22).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{14}O$: 222.1039; found: 222.1036.

Anal. Calcd for $C_{16}H_{14}O$ (222.28): C, 86.45; H, 6.35. Found: C, 86.19; H, 6.54.

1,2,3,7-Tetramethyl-9*H*-fluoren-9-one (7c)
Starting with **6c** (0.043 g, 0.16 mmol) and concd H_2SO_4 (1.9 mL), **7c** was isolated as a yellow solid; yield: 0.034 g (90%); mp 151–152 °C.

IR (KBr): 3456 (br, m), 3384 (m), 3034 (m), 2921 (m), 2861 (m), 1703 (s), 1604 (s), 1591 (m), 1486 (m), 1456 (m), 1427 (m), 1374 (m), 1277 (m), 1221 (m), 1200 (m), 1144 (m), 1099 (w), 1069 (w), 1007 cm^{-1} (w).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, CH_3), 2.32 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 7.11 (s, 1 H, CH), 7.21 (br d, ^3J = 7.5 Hz, 1 H, CH), 7.30 (d, ^3J = 7.5 Hz, 1 H, CH), 7.38 (br s, 1 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 13.8, 14.7, 21.3, 21.7 (CH_3), 119.2, 119.4, 124.4 (CH), 129.3 (C), 134.5 (CH), 135.2, 136.7, 138.4, 138.5, 141.1, 142.5, 143.0 (C), 195.7 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 237 (36), 236 (M^+, 100), 221 (88), 193 (47), 178 (34).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{16}O$: 236.1196; found: 236.1191.

3-Methyl-1-phenyl-9*H*-fluoren-9-one (7e)
Starting with **6e** (0.036 g, 0.12 mmol) and concd H_2SO_4 (1.5 mL), **7e** was isolated as a yellow solid; yield: 0.030 g (92%); mp 83–85 °C.

IR (KBr): 3437 (br, m), 3395 (m), 3056 (m), 3029 (m), 2921 (m), 1709 (s), 1613 (s), 1604 (s), 1573 (m), 1467 (m), 1456 (w), 1290 (w), 1275 (w), 1183 (m), 1127 (m), 1076 (w), 1030 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 7.00–7.01 (m, 1 H, CH), 7.27 (dt, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1 H, CH), 7.33–7.34 (m, 1 H, CH), 7.40–7.58 (m, 8 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.0 (CH_3), 119.8, 120.1, 123.9, 127.8, 128.1, 128.2, 128.3, 129.0, 132.0, 134.2, 134.8 (CH), 137.5, 139.3, 140.6, 142.2, 143.4, 145.2, 145.9 (C), 192.7 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 270 (M^+, 56), 269 (100), 239 (18), 134 (12), 120 (10).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{14}O$: 270.10392; found: 270.10329.

3,7-Dimethyl-1-phenyl-9*H*-fluoren-9-one (7f)
Starting with **6f** (0.035 g, 0.11 mmol) and concd H_2SO_4 (1.3 mL), **7f** was isolated as a orange oil; yield: 0.025 g (80%).

IR (KBr): 3436 (br, s), 3433 (s), 2923 (w), 1706 (s), 1607 (m), 1468 (w), 1428 (w), 1279 (w), 1219 (m), 1143 (m), 1091 (w), 1035 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 6.97 (br s, 1 H, CH), 7.28 (br s, 2 H, CH), 7.36 (br s, 1 H, CH), 7.39 (br s, 1 H, CH), 7.40–7.45 (m, 3 H, CH), 7.49–7.53 (m, 2 H, CH).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 21.4, 22.0 (CH_3), 119.6, 119.9, 124.6, 127.8, 128.1, 129.1, 131.6, 134.7 (CH), 134.8, 137.6, 140.8, 142.1, 143.7, 145.2, 146.1, 148.2 (C), 195.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 284 (M^+, 63), 283 (100), 239 (18), 141 (13), 134 (19).

HRMS (EI): *m*/*z* [M – H] calcd for $C_{21}H_{15}O$: 283.11174; found: 283.11180.

7-Methoxy-1,3-dimethyl-9*H*-fluoren-9-one (7g)
Starting with **6g** (0.049 g, 0.18 mmol) and concd H_2SO_4 (2.2 mL), **7g** was isolated as a yellow solid; yield: 0.039 g (91%); mp 113–114 °C.

IR (KBr): 3439 (br, m), 3391 (m), 2923 (m), 2853 (m), 1728 (w), 1703 (s), 1606 (m), 1590 (m), 1491 (m), 1471 (m), 1434 (m), 1373 (w), 1293 (s), 1268 (m), 1225 (m), 1199 (m), 1145 (w), 1091 (w), 1021 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.75–6.76 (m, 1 H, CH), 6.94 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1 H, CH), 7.05–7.06 (m, 1 H, CH), 7.15 (d, ^4J = 2.4 Hz, 1 H, CH), 7.35 (d, ^3J = 8.2 Hz, 1 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 17.7, 21.9 (CH_3), 55.7 (OCH_3), 108.8, 118.2, 119.6, 120.8, 131.1 (CH), 136.3, 139.4, 145.2, 148.0, 160.7, 183.2 (C), 194.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 238 (M^+, 100), 223 (48), 195 (11), 167 (12).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{14}O_2$: 238.0988; found: 238.0993.

1,3-Dimethyl-9*H*-fluoren-9-one (7h)
Starting with **6h** (0.031 g, 0.13 mmol) and concd H_2SO_4 (1.6 mL), **7h** was isolated as a yellow solid; yield: 0.023 g (85%); mp 108–109 °C.

IR (KBr): 3440 (br, m), 2918 (w), 1699 (s), 1616 (m), 1602 (m), 1592 (m), 1458 (w), 1375 (w), 1293 (w), 1173 (w), 1134 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 2.57 (s, 3 H, CH_3), 6.83–6.84 (m, 1 H, CH), 7.16 (m, 1 H, CH), 7.22–7.29 (m, 1 H, CH), 7.40–7.49 (m, 2 H, CH), 7.60 (dt, ^3J = 7.3 Hz, ^4J = 1.1 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.7, 21.9 (CH_3), 118.9, 119.8, 123.7, 128.8, 132.3, 134.0 (CH), 134.9, 139.4, 143.7, 145.0, 145.2, 181.3 (C), 194.7 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 208 (M^+, 100), 193 (14), 179 (10), 178 (13), 165 (30).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{12}O$: 208.0883; found: 208.0879.

1,3,7-Trimethyl-9*H*-fluoren-9-one (7i)
Starting with **6i** (0.086 g, 0.34 mmol) and concd H_2SO_4 (4.1 mL), **7i** was isolated as a yellow solid; yield: 0.069 g (91%); mp 121–122 °C.

IR (KBr): 3439 (br, w), 3383 (w), 3022 (w), 2919 (m), 2856 (w), 1699 (s), 1608 (s), 1592 (m), 1491 (w), 1456 (w), 1373 (w), 1283 (m), 1219 (w), 1187 (w), 1155 (m), 1115 (w), 1090 (w), 1035 cm^{-1} (w).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.34 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.55 (s, 3 H, CH_3), 6.79 (br s, 1 H, CH), 7.10 (br s, 1 H, CH), 7.22 (br d, ^3J = 7.5 Hz, 1 H, CH), 7.33 (d, ^3J = 7.5 Hz, 1 H, CH), 7.40 (br s, 1 H, CH).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.7, 21.3, 21.9 (CH_3), 118.6, 119.6, 124.3 (CH), 128.8 (C), 131.8, 134.4 (CH), 135.2, 138.9, 139.2, 141.1, 144.9, 145.4 (C), 194.9 (C=O).

MS (EI, 70 eV): *m/z* (%) = 223 (23), 222 (M^+, 100), 179 (34).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{16}H_{14}O$: 222.1039; found: 222.1035.

9-Methoxy-5-methyl-1,2,3,4-tetrahydro-11*H*-benzo[*a*]fluoren-11-one (7j)

Starting with **6j** (0.102 g, 0.33 mmol) and concd H_2SO_4 (4.0 mL), **7j** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.056 g (61%); mp 149–150 °C; R_f = 0.35 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2942 (m), 2924 (m), 2868 (m), 2833 (m), 1698 (s), 1598 (s), 1486 (m), 1460 (s), 1436 (s), 1286 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.67–1.89 (m, 4 H, CH_2), 2.23 (s, 3 H, CH_3), 2.57 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.15 (t, ^3J = 6.1 Hz, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 6.90 (dd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, 1 H, CH), 7.03 (s, 1 H, CH), 7.11 (d, ^4J = 2.4 Hz, 1 H, CH), 7.29 (d, ^3J = 8.1 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (CH_3), 22.0, 22.8, 26.1, 27.0 [$(CH_2)_4$], 55.7 (OCH_3), 108.9, 118.9, 119.4, 120.4 (CH), 128.6, 136.0, 136.4, 136.6, 139.4, 142.9, 143.8, 160.4 (C), 195.0 (C=O).

MS (EI, 70 eV): *m/z* (%) = 278 (M^+, 100), 279 (18), 263 (66), 235 (15), 189 (15).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{18}O_2$: 278.13013; found: 278.12967.

5-Methyl-1,2,3,4-tetrahydro-11*H*-benzo[*a*]fluoren-11-one (7k)

Starting with **6k** (0.081 g, 0.29 mmol) and concd H_2SO_4 (3.5 mL), **7k** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.066 g (91%); mp 95–97 °C; R_f = 0.47 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2938 (br, m), 2870 (m), 1696 (s), 1609 (m), 1598 (s), 1464 (m), 1451 (m), 1408 (m), 1383 (w), 1299 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.68–1.90 (m, 4 H, CH_2), 2.24 (s, 3 H, CH_3), 2.58 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.17 (t, ^3J = 6.0 Hz, 2 H, CH_2), 7.11 (br s, 1 H, CH), 7.14–7.27 (m, 1 H, CH), 7.33–7.44 (m, 2 H, CH), 7.50–7.59 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7 (CH_3), 21.9, 22.8, 26.1, 27.2 [$(CH_2)_4$], 119.4, 119.5, 123.5, 128.3 (CH), 128.4 (C), 133.9 (CH), 134.8, 137.3, 139.3, 142.4, 143.7, 143.9 (C), 195.2 (C=O).

MS (EI, 70 eV): *m/z* (%) = 248 (M^+, 91), 233 (100), 215 (24), 202 (22), 189 (22).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{16}O$: 248.11957; found: 248.11892.

5,9-Dimethyl-1,2,3,4-tetrahydro-11*H*-benzo[*a*]fluoren-11-one (7l)

Starting with **6l** (0.100 g, 0.34 mmol) and concd H_2SO_4 (4.1 mL), **7l** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.079 g (89%); mp 203–204 °C; R_f = 0.42 (*n*-heptane–EtOAc, 5:1).

IR (KBr): 2933 (s), 2857 (m), 1695 (s), 1616 (m), 1598 (s), 1487 (m), 1459 (m), 1438 (m), 1287 (m), 1203 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.68–1.89 (m, 4 H, CH_2), 2.24 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.58 (t, ^3J = 6.0 Hz, 2 H, CH_2), 3.16 (t, ^3J = 6.0 Hz, 2 H, CH_2), 7.08 (s, 1 H, CH), 7.14–7.39 (m, 3 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 21.3 (CH_3), 21.9, 22.8, 26.1, 27.1 [$(CH_2)_4$], 119.2, 119.2, 124.2, 134.2 (CH), 128.5, 135.1, 137.7, 138.4, 139.2, 141.2, 142.6, 143.6 (C), 195.5 (C=O).

MS (EI, 70 eV): *m/z* (%) = 262 (M^+, 91), 247 (66), 202 (9).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{19}H_{18}O$: 262.13522; found: 262.13506.

2-Ethyl-7-methoxy-1,3-dimethyl-9*H*-fluoren-9-one (7m)

Starting with **6m** (0.090 g, 0.3 mmol) and concd H_2SO_4 (3.6 mL), **7m** was isolated after column chromatography (silica gel, toluene) as an orange solid; yield: 0.074 g (92%); mp 133–134 °C; R_f = 0.68 (toluene–EtOAc, 10:1).

IR (KBr): 2964 (m), 2927 (m), 1868 (m), 1700 (s), 1602 (s), 1489 (m), 1457 (m), 1436 (m), 1377 (m), 1294 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.09 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.61 (s, 3 H, CH_3), 2.64 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.83 (s, 3 H, OCH_3), 6.91 (dd, ^3J = 8.2 Hz, ^4J = 2.5 Hz, 1 H, CH), 7.04 (s, 1 H, CH), 7.13 (d, ^4J = 2.5 Hz, 1 H, CH), 7.30 (d, ^3J = 8.2 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 13.3, 20.8 (CH_3), 21.7 (CH_2), 55.7 (OCH_3), 108.2, 119.6, 116.7, 120.4 (CH), 129.6, 136.2, 136.6, 138.2, 141.8, 142.8, 142.8, 160.4 (C), 195.2 (C=O).

MS (EI, 70 eV): *m/z* (%) = 266 (M^+, 52), 252 (18), 251 (100), 208 (13), 165 (11).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{18}H_{18}O_2$: 266.13013; found: 266.12994.

Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81. Found: C, 80.78; H, 6.79.

2-Ethyl-1,3-dimethyl-9*H*-fluoren-9-one (7n)

Starting with **6n** (0.070 g, 0.26 mmol) and concd H_2SO_4 (3.1 mL), **7n** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.056 g (91%); mp 112–113 °C; R_f = 0.44 (*n*-heptane–EtOAc, 5:1).

IR (Nujol): 1703 (s), 1611 (m), 1599 (m), 1292 (m), 1217 (w), 1177 (m), 1130 (m), 1083 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 2.63 (s, 3 H, CH_3), 2.66 (q, ^3J = 7.6 Hz, 2 H, CH_2), 7.15 (s, 1 H, CH), 7.16–7.12 (m, 1 H, CH), 7.35–7.45 (m, 2 H, CH), 7.52–7.62 (m, 1 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 13.1, 13.3, 20.8 (CH_3), 21.8 (CH_2), 119.4, 120.2, 123.7, 128.3, 134.0 (CH), 139.4, 134.8, 138.1, 142.4, 142.6, 143.1, 143.6 (C), 195.4 (C=O).

MS (EI, 70 eV): *m/z* (%) = 236 (M^+, 44), 222 (18), 221 (100), 178 (18).

HRMS (EI): *m/z* $[M]^+$ calcd for $C_{17}H_{16}O$: 236.11957; found: 236.11918.

2-Ethyl-1,3,7-trimethyl-9*H*-fluoren-9-one (7o)

Starting with **6o** (0.082 g, 0.29 mmol) and concd H_2SO_4 (3.5 mL), **7o** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.065 g (89%); mp 164–165 °C; R_f = 0.45 (*n*-heptane–EtOAc, 5:1).

IR (KBr): 2965 (m), 2923 (m), 2867 (m), 1700 (s), 1616 (m), 1605 (m), 1486 (m), 1460 (br, m), 1375 (m), 1280 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.62 (s, 3 H, CH_3), 2.65 (q, ^3J = 7.6 Hz, 2 H, CH_2), 7.10 (s, 1 H, CH), 7.16–7.41 (m, 3 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 13.3, 20.8, 21.3 (CH_3), 21.8 (CH_2), 119.2, 119.9, 124.4, 134.5 (CH), 129.5, 135.1, 138.0, 138.4, 141.0, 142.5, 142.6 (C), 195.6 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 250 (M^+, 38), 235 (100), 236 (17), 191 (10).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{18}O$: 250.13522; found: 250.13538.

1,3-Diethyl-9*H*-fluoren-9-one (7p)

Starting with **6p** (0.107 g, 0.4 mmol) and concd H_2SO_4 (4.8 mL), **7p** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 5:1) as a yellow solid; yield: 0.087 g (92%); mp 46–47 °C; R_f = 0.50 (*n*-heptane–EtOAc, 5:1).

IR (neat): 3052 (m), 2967 (m), 2932 (m), 2872 (m), 1704 (s), 1613 (s), 1603 (s), 1589 (s), 1469 (m), 1460 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.28 (t, ^3J = 7.5 Hz, 3 H, CH_3), 2.66 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.03 (q, ^3J = 7.5 Hz, 2 H, CH_2), 6.85–6.93 (m, 1 H, CH), 7.13–7.29 (m, 2 H, CH), 7.36–7.63 (m, 3 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 15.3 (CH_3), 24.7, 29.4 (CH_2), 117.7, 119.7, 123.7, 128.7, 129.5, 134.0 (CH), 128.3, 134.9, 143.8, 145.5, 146.1, 151.6 (C), 194.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 236 (M^+, 100), 221 (41), 207 (71), 178 (33), 165 (13).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{16}O$: 236.11957; found: 236.11902.

1,3-Diethyl-7-methyl-9*H*-fluoren-9-one (7q)

Starting with **6q** (0.110 g, 0.39 mmol) and concd H_2SO_4 (4.7 mL), **7q** was isolated after column chromatography (silica gel, toluene) as a orange solid; yield: 0.091 g (93%); mp 88–89 °C; R_f = 0.83 (toluene).

IR (Nujol): 1698 (m), 1607 (m), 1582 (m), 1281 (m), 1218 (w), 1185 (w), 1155 (m), 1088 (w), 1060 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 1.27 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.65 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.02 (q, ^3J = 7.6 Hz, 2 H, CH_2), 6.82–6.89 (m, 1 H, CH), 7.14 (br s, 1 H, CH), 7.19–7.27 (m, 1 H, CH), 7.30–7.42 (m, 2 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.8, 15.2, 21.4 (CH_3), 24.6, 29.3 (CH_2), 117.5, 119.6, 124.4, 129.1, 134.5 (CH), 128.4, 135.2, 138.9, 141.2, 145.7, 146.0, 151.5 (C), 194.8 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 250 (M^+, 100), 236 (22), 235 (26), 207 (14), 178 (22).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{18}O$: 250.13522; found: 250.13487.

1,3-Diethyl-7-methoxy-9*H*-fluoren-9-one (7r)

Starting with **6r** (0.140 g, 0.47 mmol) and concd H_2SO_4 (5.6 mL), **7r** was isolated after column chromatography (silica gel, toluene) as an orange solid; yield: 0.100 g (80%); mp 45–46 °C; R_f = 0.71 (toluene–EtOAc, 10:1).

IR (Nujol): 1709 (m), 1608 (m), 1589 (m), 1284 (m), 1274 (m), 1233 (m), 1190 (w), 1028 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.26 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.63 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.00 (q, ^3J = 7.5 Hz, 2 H, CH_2), 3.84 (s, 3 H, OCH_3), 6.81 (br s, 1 H, CH), 6.93 (dd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, 1 H, CH), 7.07 (br s, 1 H, CH), 7.14 (d, ^4J = 2.4 Hz, 1 H, CH), 7.35 (d, ^3J = 8.1 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.7, 15.1 (CH_3), 24.8, 29.4 (CH_2), 55.7 (OCH_3), 108.3, 117.1, 119.6, 120.8, 128.4 (CH), 128.4, 136.4, 136.7, 145.9, 146.2, 151.8, 160.7 (C), 194.3 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 266 (M^+, 100), 251 (36), 237 (25), 165 (16).

Anal. Calcd for $C_{18}H_{18}O_2$ (266.33): C, 81.17; H, 6.81. Found: C, 80.76; H, 6.89.

6,8-Diethyl-1,2,3-trimethoxy-9*H*-fluoren-9-one (7s)

Starting with **6s** (0.093 g, 0.26 mmol) and concd H_2SO_4 (3.1 mL), **7s** was isolated after column chromatography (silica gel, toluene–EtOAc, 4:1) as a yellow oil; yield: 0.077 g (91%); R_f = 0.50 (toluene–EtOAc, 2:1).

IR (Nujol): 1690 (m), 1596 (m), 1308 (m), 1240 (m), 1198 (w), 1124 (m), 1074 (w), 1045 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.5 Hz, 3 H, CH_3), 1.27 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.65 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.01 (q, ^3J = 7.5 Hz, 2 H, CH_2), 3.85 (s, 3 H, OCH_3), 3.98 (s, 3 H, OCH_3), 4.09 (s, 3 H, OCH_3), 6.81 (s, 1 H, CH), 6.85 (br s, 1 H, CH), 7.10 (br s, 1 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.9, 15.2 (CH_3), 24.5, 29.3 (CH_2), 56.4, 61.4, 62.0 (OCH_3), 99.5, 116.9, 129.5 (CH), 118.9, 128.9, 141.5, 142.0, 144.0, 145.4, 150.6, 153.1, 158.7 (C), 191.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 326 (M^+, 98), 311 (100), 293 (29), 283 (22), 253 (34).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{22}O_4$: 326.15126; found: 326.15071.

4-Ethyl-7-methoxy-1,2,3-trimethyl-9*H*-fluoren-9-one (7t)

Starting with **6t** (0.084 g, 0.27 mmol) and concd H_2SO_4 (3.2 mL), **7t** was isolated after column chromatography (silica gel, toluene–EtOAc, 50:1) as an orange solid; yield: 0.070 g (92%); mp 160–161 °C; R_f = 0.73 (toluene–EtOAc, 10:1).

IR (KBr): 2975 (m), 2956 (m), 2927 (m), 2836 (m), 1694 (s), 1622 (m), 1590 (m), 1574 (m), 1483 (s), 1438 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (t, ^3J = 7.6 Hz, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 2.90 (q, ^3J = 7.6 Hz, 2 H, CH_2), 3.84 (s, 3 H, OCH_3), 6.92 (dd, ^3J = 8.4 Hz, ^4J = 2.6 Hz, 1 H, CH), 7.17 (d, ^4J = 2.6 Hz, 1 H, CH), 7.48 (d, ^3J = 8.4 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.4, 13.9, 15.6, 16.0 (CH_3), 22.7 (CH_2), 55.6 (OCH_3), 108.8, 119.5, 123.7 (CH), 129.4, 135.4, 136.3, 136.5, 136.7, 137.3, 140.1, 142.0, 159.6 (C), 195.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 280 (M^+, 84), 266 (27), 265 (100), 222 (16), 178 (18).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{20}O_2$: 280.14578; found: 280.14588.

2-Chloro-7-methoxy-1,3-dimethyl-9*H*-fluoren-9-one (7u)

Starting with **6u** (0.146 g, 0.48 mmol) and concd H_2SO_4 (5.8 mL), **7u** was isolated after column chromatography (silica gel, toluene–EtOAc, 30:1) as a yellow solid; yield: 0.118 g (90%); mp 141–143 °C; R_f = 0.75 (toluene–EtOAc, 10:1).

IR (KBr): 2951 (m), 2925 (m), 1711 (s), 1603 (m), 1492 (m), 1455 (m), 1434 (m), 1380 (m), 1293 (m), 1261 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 2.65 (s, 3 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.94 (dd, ^3J = 8.2 Hz, ^4J = 2.4 Hz, 1 H, CH), 7.11 (br s, 1 H, CH), 7.13 (d, ^4J = 2.4 Hz, 1 H, CH), 7.31 (d, ^3J = 8.2 Hz, 1 H, CH).

^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.3, 21.9 (CH_3), 55.7 (OCH_3), 109.1, 119.5, 120.1, 120.9 (CH), 135.1, 135.5, 136.3, 138.0, 142.6, 143.1, 147.8, 160.8 (C), 193.8 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 272 (M^+, ^{35}Cl, 100), 257 (60), 201 (28), 165 (47).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{16}H_{13}ClO_2$: 272.05986; found: 272.05936.

2,7-Dichloro-1,3-dimethyl-9*H*-fluoren-9-one (7v)

Starting with **6v** (0.139 g, 0.45 mmol) and concd H_2SO_4 (5.4 mL), **7v** was isolated after column chromatography (silica gel, toluene) as a yellow solid; yield: 0.111 g (89%); mp 181–182 °C; R_f = 0.83 (toluene).

IR (KBr): 2955 (w), 2923 (w), 1705 (s), 1609 (m), 1598 (m), 1452 (m), 1430 (m), 1376 (m), 1245 (m), 1186 cm^{-1} (s).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.41 (br s, 3 H CH_3), 2.64 (s, 3 H, CH_3), 7.16 (br s, 1 H, CH), 7.28–7.43 (m, 2 H, CH), 7.48–7.54 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 21.9 (CH_3), 120.3, 120.9, 124.3, 133.9 (CH), 129.9, 135.0, 136.0, 136.6, 138.4, 141.0, 141.8, 143.0 (C), 192.3 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 276 (M^+, ^{35}Cl, 100), 241 (39), 176 (64).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{15}H_{10}Cl_2O$: 276.01032; found: 276.00990.

2-Chloro-1,3-dimethyl-7-(trifluoromethyl)-9*H*-fluoren-9-one (7w)

Starting with **6w** (0.075 g, 0.22 mmol) and concd H_2SO_4 (2.6 mL), **7w** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.068 g (99%); mp 171–172 °C; R_f = 0.66 (*n*-heptane–EtOAc, 10:1).

IR (KBr): 2987 (w), 2928 (w), 1657 (s), 1701 (s), 1623 (s), 1594 (m), 1455 (m), 1390 (m), 1327 (s), 1279 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.45 (s, 3 H, CH_3), 2.68 (s, 3 H, CH_3), 7.29 (s, 1 H, CH), 7.49–7.57 (m, 1 H, CH), 7.66–7.76 (m, 1 H, CH), 7.82 (br s, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.4, 22.0 (CH_3), 120.0, 120.9 (CH), 121.0 (q, ^3J = 3.8 Hz, C*C*H), 131.2 (q, ^2J = 33 Hz, *C*CF_3), 131.3 (q, ^3J = 3.8 Hz, C*C*H), 123.7 (q, ^1J = 272 Hz, CF_3), 130.2, 134.8, 137.6, 138.6, 141.2, 143.2, 145.9 (C), 192.8 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 310 (M^+, ^{35}Cl, 100), 275 (54), 247 (16), 91 (16).

Anal. Calcd for $C_{16}H_{10}ClF_3O$ (310.70): C, 61.85; H, 3.24. Found: C, 61.74; H, 3.18.

2-Chloro-1,3-dimethyl-9*H*-fluoren-9-one (7x)

Starting with **6x** (0.055 g, 0.2 mmol) and concd H_2SO_4 (2.5 mL), **7x** was isolated as a yellow solid; yield: 0.048 g (99%), mp 142 °C.

IR (KBr): 3381 (w), 2953 (w), 2920 (w), 2851 (w), 1703 (s), 1609 (m), 1597 (m), 1448 (m), 1186 (m), 1138 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, CH_3), 2.67 (s, 3 H, CH_3), 7.20 (s, 1 H, CH), 7.24–7.60 (m, 4 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.3, 21.9 (CH_3), 119.8, 120.1, 124.0, 128.9 (CH), 130.0 (C), 134.3 (CH), 134.5, 136.3, 138.0, 142.5, 142.6, 142.9 (C), 193.9 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 242 (M^+, ^{35}Cl, 100), 207 (42), 178 (23).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{15}H_{11}ClO$: 242.0493; found: 242.0490.

1-Hydroxy-3,5-dimethyl-9*H*-fluoren-9-one (7y)

Starting with **3i** (0.118 g, 0.46 mmol) and concd H_2SO_4 (5.7 mL), **7y** was isolated as a yellow solid; yield: 0.070 mg (68%), mp 140–145 °C.

IR (neat): 3339 (s), 2355 (m), 2923 (m), 1675 (s), 1627 (s), 1602 (s), 1587 (m), 1457 (m), 1334 (m), 1295 (m), 1238 (m), 1207 (m), 1172 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 6.54 (s, 1 H, CH), 6.89 (s, 1 H, CH), 7.13–7.23 (m, 2 H, CH), 7.46 (d, ^3J = 7.1 Hz, 1 H, CH), 8.60 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.1, 22.6 (CH_3), 115.5 (C), 117.5, 121.5, 128.7 (CH), 134.1, 135.1 (C), 137.0 (CH), 141.6, 144.7, 149.1 (C), 157.5 (COH), 196.1 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 224 (M^+, 100), 195 (17), 181 (37), 165 (16), 152 (20).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{12}O_2$: 224.08318; found: 224.083191.

7-Chloro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7z)

Starting with **3j** (0.199 g, 0.72 mmol) and concd H_2SO_4 (8.9 mL), **7z** was isolated as a yellow solid; yield: 0.146 g (83%), mp 165–167 °C.

IR (neat): 3402 (s), 2917 (w), 1680 (s), 1624 (s), 1604 (s), 1445 (m), 1391 (w), 1309 (s), 1257 (m), 1217 (m), 1190 (s), 1160 (m), 1098 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 3 H, CH_3), 6.58 (br s, 1 H, CH), 6.84 (br s, 1 H, CH), 7.40–7.41 (m, 2 H, CH), 7.56 (br s, 1 H, CH), 8.22 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.4 (CH_3), 114.4 (CH), 115.3 (C), 118.2, 121.7, 124.2, 133.8 (CH), 135.0, 136.4, 142.0, 143.0, 149.8 (C), 157.4 (COH), 194.0 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 244 (M^+, ^{35}Cl, 100), 181 (17), 152 (30).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{14}H_9ClO_2$: 244.02856; found: 244.028552.

7-Chloro-2-hexyl-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7aa)

Starting with **3k** (0.249 g, 0.7 mmol) and concd H_2SO_4 (8.5 mL), **7aa** was isolated as a yellowish solid; yield: 0.147 g (65%), mp 73–75 °C.

IR (neat): 3349 (w), 2949 (m), 2918 (s), 2851 (m), 1676 (s), 1624 (m), 1596 (m), 1451 (m), 1384 (w), 1298 (m), 1258 (m), 1168 (s), 1115 (m), 1094 (m), 1031 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 0.86–0.91 (m, 3 H, CH_3), 1.24–1.33 (m, 8 H, CH_2), 2.32 (s, 3 H, CH_3), 2.56–2.62 (m, 2 H, CH_2), 6.81 (s, 1 H, CH), 7.35–7.41 (m, 2 H, CH), 7.53 (dd, ^3J = 1.7 Hz, ^5J = 0.6 Hz, 1 H, CH), 8.49 (s, 1 H, OH).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 14.1, 20.5 (CH_3), 22.6, 25.4, 28.9, 29.5, 31.7 (CH_2), 115.4, 121.5, 124.2 (CH), 127.6, 131.1 (C), 133.7 (CH), 134.4, 136.4, 139.7, 142.4, 146.9 (C), 156.1 (COH), 194.8 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 328 (M^+, ^{35}Cl, 21), 258 (55), 257 (100), 165 (19).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{20}H_{21}ClO_2$: 328.12246; found: 328.122093.

5-Chloro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7ab)

Starting with **3l** (0.219 g, 0.8 mmol) and concd H_2SO_4 (9.7 mL), **7ab** was isolated as a colorless solid; yield: 0.145 g (75%), mp 145–150 °C.

IR (neat): 3345 (s), 2918 (m), 1694 (s), 1619 (s), 1592 (s), 1445 (m), 1412 (w), 1377 (w), 1316 (m), 1296 (s), 1239 (m), 1168 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 6.59 (s, 1 H, CH), 7.19 (t, ^3J = 7.6 Hz, 1 H, CH), 7.36–7.39 (m, 2 H, CH), 7.50 (d, ^3J = 7.6 Hz, 1 H, CH), 8.44 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.7 (CH_3), 115.2 (C), 118.3 (CH), 118.4 (C), 118.5, 122.1, 129.8, 135.7 (CH), 137.1, 140.1, 142.2, 149.7 (C), 157.5 (COH), 194.2 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 244 (M^+, ^{35}Cl, 100), 216 (17), 181 (32), 152 (31).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{14}H_9ClO_2$: 244.02856; found: 244.028810.

5-Chloro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (7ac)
Starting with **3m** (31 mg, 0.1 mmol) and concd H_2SO_4 (1.5 mL), **7ac** was isolated as a yellow solid; yield: 0.023 g (80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 7.05–7.11 (m, 1 H, CH), 7.26–7.29 (m, 2 H, CH), 7.41 (dd, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 1 H, CH), 8.65 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.6, 21.2 (CH_3), 115.0 (C), 118.8, 122.0 (CH), 126.3 (C), 129.3 (CH), 129.4 (C), 135.6 (CH), 136.9, 138.9, 140.4, 147.3 (C), 156.0 (COH), 194.8 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 258 (M^+, ^{35}Cl, 100), 243 (59), 215 (12), 195 (8), 176 (11), 165 (22), 152 (14).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{15}H_{11}ClO_2$: 258.04421; found: 258.04370.

5-Chloro-2-ethyl-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7ad)
Starting with **3n** (80 mg, 0.27 mmol) and concd H_2SO_4 (3.0 mL), **7ad** was isolated as a yellow solid; yield: 0.041 g (60%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, ^3J = 7.8 Hz, 3 H, CH_2CH_3), 2.25 (s, 3 H, CH_3), 2.54 (q, ^3J = 7.3 Hz, 2 H, CH_2CH_3), 7.02–7.08 (m, 1 H, CH), 7.22–7.26 (m, 2 H, CH), 7.38 (dd, ^3J = 8.0 Hz, ^4J = 0.9 Hz, 1 H, CH), 8.61 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1 (CH_2CH_3), 28.2 (CH_2CH_3), 20.1 (CH_3), 115.2 (C), 119.2, 121.9, 129.3 (CH), 129.5, 132.5 (C), 135.5 (CH), 137.0, 139.0, 140.2, 146.4 (C), 156.0 (COH), 194.8 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 272 (M^+, ^{35}Cl, 40), 257 (100), 229 (7), 189 (4), 165 (15).

HRMS (EI): *m*/*z* (M^+, ^{35}Cl) calcd for $C_{16}H_{13}ClO_2$: 272.05986; found: 272.05940.

5-Fluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7ae)
Starting with **3o** (0.120 g, 0.46 mmol) and concd H_2SO_4 (5.7 mL), **7ae** was isolated as a colorless solid; yield: 0.079 g (75%), mp 113–118 °C.

IR (neat): 3341 (s), 2923 (s), 2853 (m), 1649 (s), 1620 (s), 1585 (s), 1455 (m), 1305 (m), 1240 (s), 1199 (s), 1144 (s), 1113 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (s, 3 H, CH_3), 6.59 (s, 1 H, CH), 7.03 (s, 1 H, CH), 7.13–7.19 (m, 1 H, CH), 7.23–7.29 (m, 1 H, CH), 7.43 (d, ^3J = 7.2 Hz, 1 H, CH), 8.30 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (CH_3), 113.9 (C), 117.1, 118.8, 121.2 (CH), 128.3 (C), 129.7 (CH), 136.4, 139.7, 148.9, 155.2, 156.4, 158.5 (C), 193.3 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 228 (M^+, 100), 200 (15), 199 (41), 171 (12), 170 (22).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_9FO_2$: 228.05811; found: 228.0577962.

5-Fluoro-1-hydroxy-2,3-dimethyl-9*H*-fluoren-9-one (7af)
Starting with **3p** (111 mg, 0.4 mmol) and concd H_2SO_4 (4.8 mL), **7af** was isolated as a yellow solid; yield: 50 mg (51%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 3 H, CH_3), 2.21 (s, 3 H, CH_3), 6.88 (s, 1 H, CH), 7.00–7.18 (m, 2 H, CH), 7.29–7.32 (m, 1 H, CH), 8.51 (s, 1 H, OH).

^{13}C NMR (62 MHz, CDCl3): δ = 10.6, 21.0 (CH_3), 114.7 (C), 118.6, 119.7, 122.2 (CH), 125.9 (C), 129.7, 130.2 (CH), 137.3, 137.4, 147.5 (C), 155.9 (COH), 157.6 (d, ^1J = 253.5 Hz, CF), 195.0 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 242 (M^+, 100), 227 (81), 213 (9), 199 (22), 183 (12), 170 (16).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{11}FO_2$: 242.07376; found: 242.07375.

7-Fluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7ag)
Starting with **3q** (0.114 g, 0.44 mmol) and concd H_2SO_4 (2.3 mL), **7ag** was isolated as a yellow oil; yield: 0.067 g (68%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 6.45 (s, 1 H, CH), 6.74 (s, 1 H, CH), 7.01–7.09 (m, 1 H, CH), 7.21 (dd, ^3J = 7.4 Hz, ^4J = 3.0 Hz, 1 H, CH), 7.34 (dd, ^3J = 7.5 Hz, ^4J = 4.5 Hz, 1 H, CH), 8.15 (s, 1 H, OH).

^{13}C NMR (62 MHz, $CDCl_3$): δ = 22.5 (CH_3), 111.4, 114.1, 117.7, 120.4, 122.0 (CH), 129.4, 137.2, 139.6, 143.4, 149.9 (C), 157.5 (COH), 163.4 (d, ^1J = 247.4 Hz, CF), 194.0 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 228 (M^+, 100), 199 (36), 170 (26), 151 (3), 100 (5), 85 (9).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_9FO_2$: 228.05811; found: 228.057995.

2-Ethyl-7-fluoro-1-hydroxy-3-methyl-9*H*-fluoren-9-one (7ah)
Starting with **3r** (0.132 g, 0.44 mmol) and concd H_2SO_4 (2.3 mL), **7ah** was isolated as a yellow viscous oil; yield: 0.085 g (76%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, ^3J = 7.6 Hz, 3 H, CH_2CH_3), 2.26 (s, 3 H, CH_3), 2.56 (q, ^3J = 7.4 Hz, 2 H, CH_2CH_3), 6.57 (s, 1 H, CH), 7.03 (ddd, ^3J = 8.2 Hz, ^3J = 6.3 Hz, ^4J = 0.5 Hz, 1 H, CH), 7.19 (m, 1 H, CH), 7.29 (m, 1 H, CH), 8.42 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.2 (CH_2CH_3), 18.3 (CH_3), 28.2 (CH_2CH_3), 109.6 (CH), 111.9 (C), 113.1, 118.4, 119.7 (CH), 126.4, 129.7 (C), 135.0, 138.0, 144.7 (C), 154.0 (COH), 161.2 (d, ^1J = 245.5 Hz, CF), 192.7 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 256 (M^+, 42), 241 (100), 213 (8), 183 (12), 170 (7).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{13}FO_2$: 256.08941; found: 256.08976.

3-Hydroxy-1-methyl-8,9-dihydro-4*H*-cyclopenta[*def*]phenanthren-4-one (11)
Starting with **9** (0.164 g, 0.6 mmol) in concd H_2SO_4 (7.5 mL), **11** was isolated as a brownish solid; yield: 0.056 g (40%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.21 (s, 3 H, CH_3), 2.83–2.89 (m, 2 H, CH_2), 3.01–3.07 (m, 2 H, CH_2), 6.43 (s, 1 H, CH), 6.92 (s, 1 H, OH), 7.08–7.19 (m, 2 H, CH), 7.30–7.33 (m, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (CH_3), 22.3, 25.0 (CH_2), 113.3 (C), 118.6 (CH), 121.3 (C), 122.0, 129.4 (CH), 130.3, 132.2 (C), 132.3 (CH), 140.6, 141.6, 147.2 (C), 154.2 (COH), 195.0 (C=O).

DDQ-Mediated Dehydrogenation; General Procedure
To a soln of the substrate (1.0 equiv) in 1,4-dioxane (7 mL/mmol) was added DDQ (2.0 equiv) under an argon atmosphere at 20 °C. The mixture was heated under reflux for 48 h and then cooled to 20 °C and the solvent was removed in vacuo. To the residue was added Et_2O to give a precipitate, which was filtered off. The filtrate was concentrated in vacuo and the residue was purified by column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) to give the products.

Methyl 3-Hydroxy-1-methylphenanthrene-4-carboxylate (10)
Starting with **9** (0.140 g, 0.5 mmol) and DDQ (0.308 g, 1.0 mmol) in 1,4-dioxane (3.6 mL), **10** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow oil; yield: 0.078 g (57%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.71 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 7.12 (s, 1 H, CH), 7.42–7.49 (m, 1 H, CH), 7.52–7.58 (m, 1 H, CH), 7.68–7.71 (m, 1 H, CH), 7.81–7.94 (m, 3 H, CH), 9.76 (s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.3 (CH_3), 51.9 (OCH_3), 106.7 (C), 118.8, 121.9, 124.4, 125.3 (CH), 126.2 (C), 126.7, 127.9, 128.7 (CH), 129.1, 130.5, 133.1, 142.4 (C), 159.0 (COH), 172.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 266 (M^+, 40), 235 (24), 234 (100), 206 (27), 178 (61).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{14}O_3$: 266.09375; found: 266.09411.

3-Hydroxy-1-methyl-4*H*-cyclopenta[*def*]phenanthren-4-one (12)
Starting with **11** (0.015 g, 0.06 mmol) and DDQ (0.029 g, 0.13 mmol) in 1,4-dioxane (0.5 mL), **12** was isolated after column chromatography (silica gel, *n*-heptane–EtOAc, 10:1) as a yellow solid; yield: 0.004 g (27%).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.63 (s, 3 H, CH_3), 6.82 (s, 1 H, CH), 7.49–7.61 (m, 2 H, CH), 7.68–7.74 (m, 2 H, CH), 7.85 (d, ^3J = 7.9 Hz, 1 H, CH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.4 (CH_3), 112.5 (C), 120.3 (CH), 121.7 (C), 122.6, 122.7, 122.8 (CH), 127.7 (C), 129.0, 130.9 (CH), 133.9, 137.3, 139.4, 145.0 (C), 153.7 (COH), 194.0 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 234 (M^+, 100), 233 (11), 205 (12), 178 (11).

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{10}O_2$: 234.06753; found: 234.06716.

(3-Hydroxy-5-methylbiphenyl-2-yl)(2-methoxyphenyl)methanone (16a)
Starting with **15a** (0.468 g, 2.0 mmol), **14** (0.799 g, 2.2 mmol), and $TiCl_4$ (0.238 mL, 2.2 mmol), **16a** was isolated after chromatography (silica gel) as a colorless oil; yield: 0.190 g (30%).

IR (neat): 3427 (w), 3054 (w), 2922 (m), 1623 (s), 1490 (s), 1432 (m), 1279 (s), 1207 (s), 1162 (m), 1023 (m), 917 (s), 754 (s), 700 (m), 639 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26 (s, 3 H, CH_3), 3.52 (s, 3 H, OCH_3), 6.05 (s, 1 H, CH_{Ar}), 6.28 (d, ^3J = 7.3 Hz, 1 H, CH_{Ar}), 6.46–6.49 (m, 3 H, CH_{Ar}), 6.78 (s, 1 H, CH_{Ar}), 6.80–6.89 (m, 4 H, CH_{Ar}), 7.70–7.72 (d, ^3J = 7.5 Hz, 1 H, CH_{Ar}), 11.10 (br s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (CH_3), 55.3 (OCH_3), 110.9, 117.2, 119.4, 123.9, 127.2, 127.4, 127.6, 129.0, 129.6, 130.0 (CH_{Ar}), 130.9 (C), 132.3 (CH_{Ar}), 132.6, 141.4, 145.7, 146.1 (C), 156.6 (COH), 162.0 (C), 194.1 (CO).

GC-MS (EI, 70 eV): *m*/*z* (%) = 318 (M^+, 12), 317 (12), 303 (22), 287 (100), 210 (5), 182 (4), 165 (6), 135 (8), 77 (9).

Anal. Calcd for $C_{21}H_{18}O_3$: C 78.93, H 5.33; found: C 78.97, H 5.35.

(6-Hydroxy-2,3,4-trimethylphenyl)(2-methoxyphenyl)methanone (16b)
Starting with **15b** (0.371 g, 2.0 mmol), **14** (0.799 g, 2.2 mmol), and $TiCl_4$ (0.238 mL, 2.2 mmol), **16b** was isolated after chromatography (silica gel) as a colorless solidifying oil; yield: 0.205 g (38%); mp 127–130 °C.

IR (neat): 3333 (m), 1663 (s), 1596 (m), 1486 (m), 1442 (s), 1317 (m), 1244 (s), 1075 (w), 908 (w), 855 (w), 759 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.78 (s, 3 H, CH_3), 1.97 (s, 3 H, CH_3), 2.09 (s, 3 H, CH_3), 3.79 (s, 3 H, OCH_3), 6.64 (s, 1 H, CH_{Ar}), 6.92–6.95 (m, 2 H, CH_{Ar}), 7.06 (d, ^3J = 7.4 Hz, 1 H, CH_{Ar}), 7.19 (dd, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 1 H, CH_{Ar}), 11.46 (br s, 1 H, OH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 18.7, 20.5 (CH_3), 54.8 (OCH_3), 110.8, 115.3, 119.6 (CH_{Ar}), 120.5, 126.1 (C), 129.1 (CH_{Ar}), 130.6 (C), 131.5 (CH_{Ar}), 134.3, 144.3 (C), 157.3 (COH), 160.3 (C), 200.1 (CO).

GC-MS (EI, 70 eV): *m*/*z* (%) = 270 (M^+, 55), 255 (49), 239 (100), 224 (22), 209 (8), 162 (65), 119.1 (8), 91 (21), 77 (29), 65 (8), 51 (5), 39 (5).

HRMS (EI): *m*/*z* $[M]_+$ calcd for $C_{17}H_{18}O_3$: 270.12505; found: 270.12454.

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