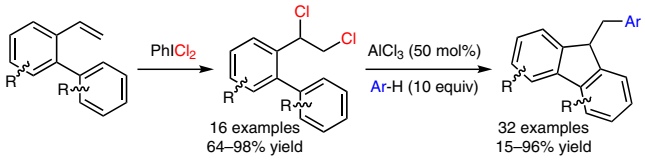
Synthesis Z. Zhao et al. Feature

Vicinal Dichlorination of *o*-Vinylbiphenyls and the Synthesis of 9-(Arylmethyl)fluorenes via Tandem Friedel–Crafts Alkylations

Zhensheng Zhao
Islam Jameel
Graham K. Murphy*

Department of Chemistry, University of Waterloo, 200 University Ave W, Waterloo, Ontario N2L3G1, Canada
graham.murphy@uwaterloo.ca



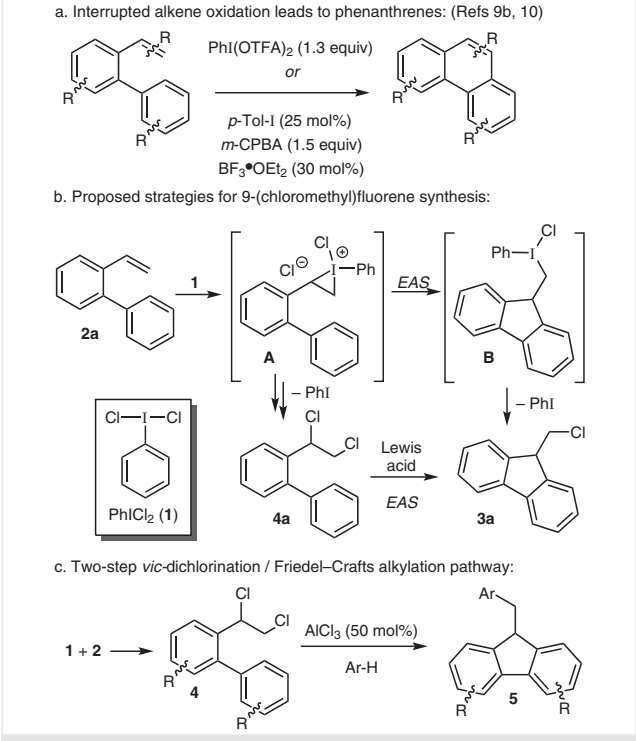
Received: 25.03.2019
Accepted after revision: 02.05.2019
Published online: 28.05.2019
DOI: 10.1055/s-0037-1611562; Art ID: ss-2019-z0195-fa

Abstract Reacting *ortho*-vinylbiphenyls with (dichloroiodo)benzene ($PhICl_2$) gives vicinal dichlorides, rapidly, and in excellent yield at room temperature. Treating the *vic*-dichlorides with 50 mol% $AlCl_3$ in the presence of arene nucleophiles results in sequential intramolecular and intermolecular Friedel–Crafts alkylations to generate 9-(arylmethyl)fluorene derivatives. The dichlorination and alkylation reactions are operationally simple and tolerant of a variety of functional groups and substitution patterns, and give the products in moderate to excellent yield.

Key words fluorene, 1-aryl-1,2-dichloroethane, chlorination, hypervalent iodine, Friedel–Crafts

(Dichloroiodo)benzene ($PhICl_2$, **1**) was the first known hypervalent iodine (HVI) reagent, prepared in 1886 by Willgerodt.[1] Given that alkyl chlorides are important and versatile intermediates and finished products, and given the mild and environmentally benign reaction conditions associated with HVI chemistry in general,[2] using **1** is widely appealing. The inherent value of $PhICl_2$ led to improved syntheses, in which chlorine gas[3] was replaced by readily available reagents such as sodium hypochlorite and HCl,[4] and also to recyclable[5] or solid-supported[6] derivatives.

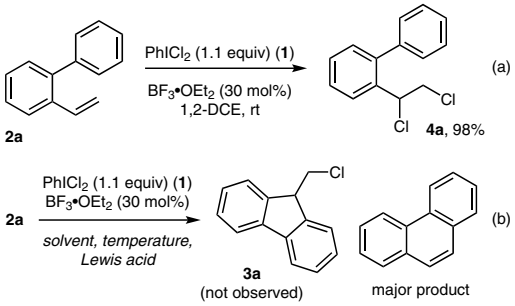
The reactivity of (dichloroiodo)arenes with alkenes is complex, as both ionic and radical mechanisms are both operative, and these can change depending on the reaction conditions.[2b,7] Generally, such (dichloroiodo)arenes are stable, solid alternatives to chlorine gas, and regardless of the reaction mechanism, their reactions with alkenes usually lead to vicinal dichloride products,[8] though molecular rearrangements can occur under polar conditions. Recently, we investigated the oxidative and halogenative chemistry between vinylarenes, allenylarenes, or *o*-vinylbiphenyls and HVI reagents.[9] For example, we developed a catalytic[9b] version of Breder's[10] oxidative alkene arylation, where a pendant arene intercepts an intermediate via electrophilic aromatic substitution to give phenanthrenes (Scheme 1a). We were interested to see if reacting *o*-vinylbiphenyls (e.g., **2a**) with $PhICl_2$ would also lead to phenanthrene, or whether it could instead give 9-(chloromethyl)fluorene **3a** (Scheme 1b).[11] We envisioned **3a** arising from an ionic reaction where iodiranium ion **A** undergoes attack by the pendant arene to give **B**, whose hypernucleofugal phenyliodonio



Scheme 1 Background, proposed strategy and final synthetic sequence

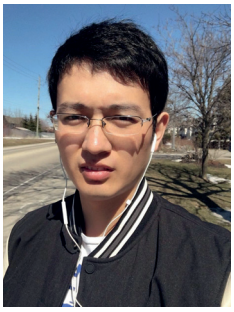
group is then displaced by chloride. If this interrupted chlorination sequence failed, we expected that chloride trapping of **A** would lead to **4a**. In this case, a two-step synthesis of **3a** might be achieved upon subsequent Lewis acid activation of the *vic*-dichloride **4a** (Scheme 1b). These routes would offer a versatile and convenient approach to functionalized derivatives of **3a** because of the modular synthesis of biphenyl **2a**.[12] In this study, we were unable to generate **3a** from either **2a** or **4a** as proposed; however, we found that **4a**, when treated with 50 mol% $AlCl_3$ and an arene nucleophile, undergoes sequential intra- and intermolecular Friedel–Crafts alkylations to give 9-(arylmethyl)fluorenes **5** (Scheme 1c).

We began this study by reacting **2a** with $PhICl_2$ and 30 mol% $BF_3{\cdot}OEt_2$, but only dichloride **4a** was observed in 98% yield (Scheme 2a). A variety of solvents, reaction conditions and other Lewis acidic additives failed to generate **3a**, and instead gave complex mixtures of products containing predominantly phenanthrene (Scheme 2b). The presence of phenanthrene suggests that **3a** may be generated, but that it undergoes a subsequent acid-catalyzed rearrangement.[13] More importantly, this confirms that the pendant arene is a viable nucleophile for intercepting an activated reaction intermediate.



Scheme 2 Initial study of the reaction of 2-vinylbiphenyl with $PhICl_2$ and $BF_3{\cdot}OEt_2$: (a) formation of the *vic*-dichloride, (b) modified reaction conditions to give phenanthrene

Biographical Sketches



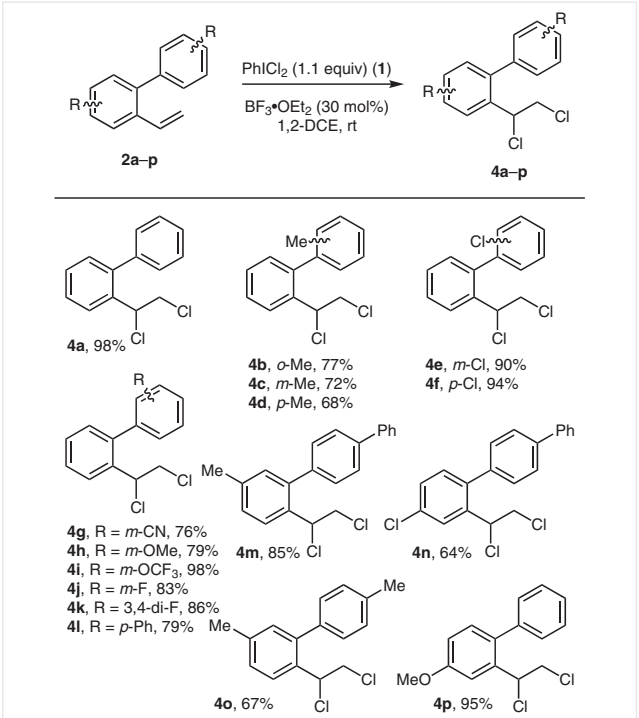
Zhensheng Zhao obtained his Ph.D. from the Institute of Chemistry, Chinese Academy of Sciences in 2016 under the supervision of Prof. Guoqiang Yang. In 2016, he moved to the University of Waterloo to join the group of Prof. Graham Murphy as a postdoctoral fellow. His research focused on developing novel reactions mediated by hypervalent iodine reagents. In 2018, he moved to the Scripps Research Institute (Florida), where he joined the lab of Prof. Alexander Adibekian.

Islam Jameel completed her Honours B.Sc. in Chemistry from the University of Waterloo in 2018. She is currently pursuing her M.Sc. in organic chemistry under the supervision of Prof. Graham Murphy. Her research focuses on developing novel HVI-mediated reactions, specifically involving iodonium ylides.

Graham Murphy received his Ph.D. from the University of Alberta in 2007 where he worked in the laboratory of Dr. F. G. West. He held a JSPS postdoctoral fellowship at Tohoku University with Dr. Masahiro Hirama, an NSERC postdoctoral fellowship at Colorado State University with Dr. J. L. Wood, and he was a postdoctoral fellow supported by the Biorefining Conversions Network at the University of Alberta. He began his independent career in 2011 at the University of Waterloo, Canada, and was promoted to Associate Professor with tenure in July 2017. His independent research program concerns developing novel reactions mediated by hypervalent iodine reagents.

To test the proposed two-step synthesis of **3a**, we applied these reaction conditions to other *o*-vinylbiaryl derivatives **2a–p**, and generated a series of *vic*-dichlorides **4a–p** possessing functional groups distributed about the appended arenes (Scheme 3). The reaction was successful with methyl (**4b–d**), chloro (**4e**,**f**), cyano (**4g**), methoxy (**4h**), OCF_3 (**4i**), mono- and difluoro (**4j**,**k**), and even phenyl (**4l**) functional groups, at either the *ortho*-, *meta*-, or *para*-positions, with the corresponding products being isolated in 68–98% yields (Scheme 3). Substitution on the vinyl-bearing arene was also possible, with substrates **2m–p** converted into the corresponding dichlorides **4m–p** in 64–95% yields. Our subsequent efforts to develop the two-step synthesis of **3a** failed (see Scheme 2b). Treating dichloride **4a** with $AlCl_3$ again led to phenanthrene, and we reasoned that even if **3a** is being generated, activation of its remaining chlorine must be facile.

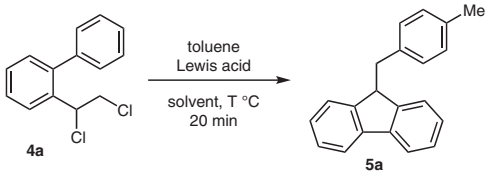
We presumed that this activated intermediate might be a competent electrophile in an intermolecular Friedel–Crafts alkylation, which would instead provide access to various 9-(arylmethyl)fluorene derivatives **5**, that are important biological agents,[14] ligands,[15] and organic materials.[16]



Scheme 3 Synthesis of *vic*-dichlorides

Treating dichloride **4a** with 50 mol% $AlCl_3$ in toluene at room temperature gave **5a** in 50% NMR yield (Table 1, entry 1).[17] Repeating the reaction in 1,2-DCE at room temperature with 10 equiv of toluene led to **5a** in 25% yield (entry 2), and decreasing the temperature to 0 °C gave **5a** in 45% yield (entry 3). Many other solvents were tested, and while MeCN or DMF inhibited the reaction, using CH_2Cl_2 gave **5a** in 94% NMR yield, and 89% isolated yield, as a single isomer (see entries 4–6 and the Supporting Information). Increasing the loading of $AlCl_3$ to 1 equiv gave a lower yield of **5a**, as did decreasing the loading, such that when 10 mol% of $AlCl_3$ was used, only a trace of **5a** was observed (entries 7–9). Among the other Lewis acids tested (see Supporting Information for full details), $FeBr_3$ and $InBr_3$ gave **5a** in 83% and 47% yield, respectively (entries 10 and 11). Finally, the loading of toluene was varied, and while increasing the loading had little impact, decreasing the loading also decreased the yield (entries 12–14).

Table 1 Optimization of the Synthesis of 9-(4-Methylbenzyl)-9*H*-fluorene



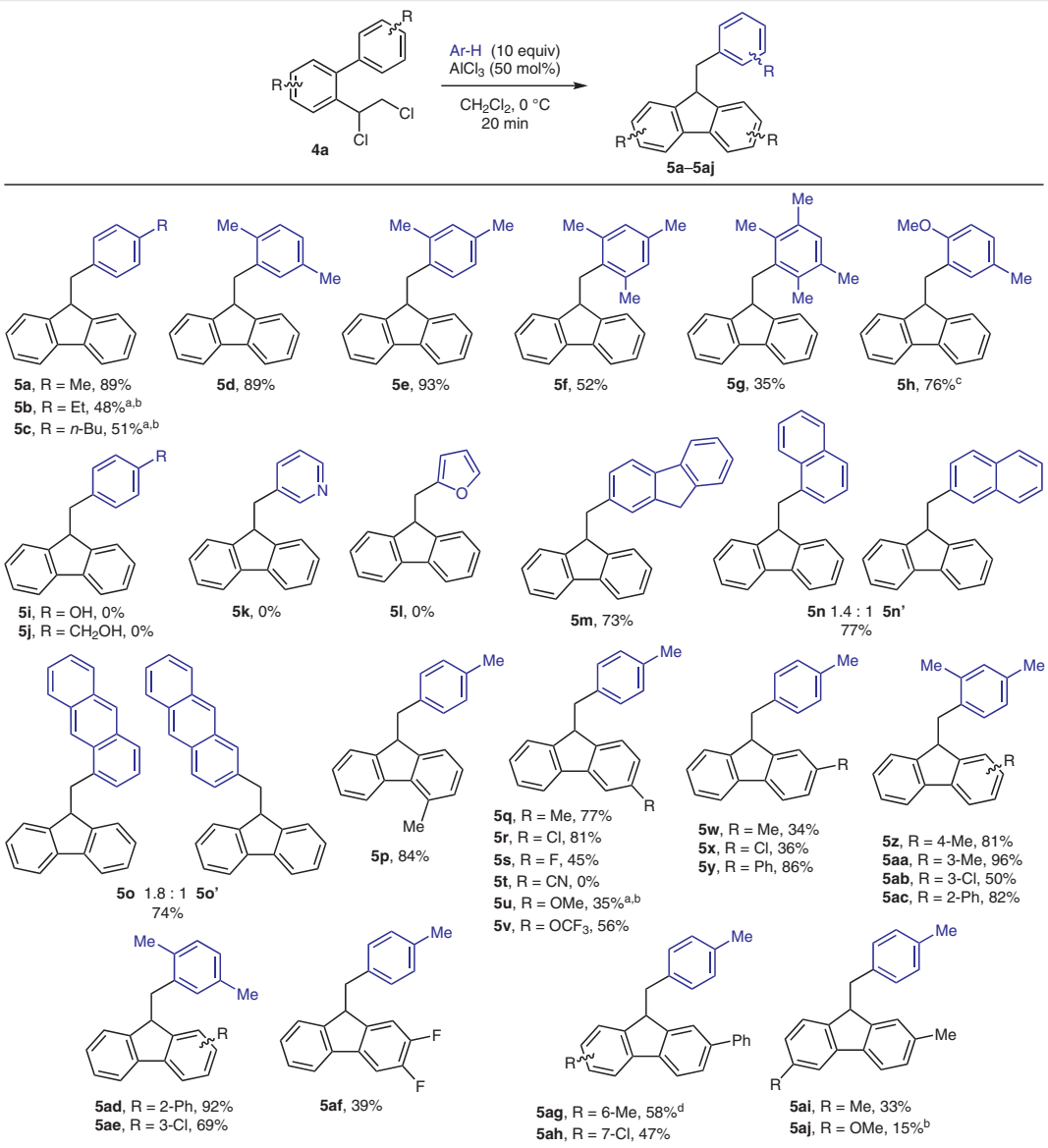
Entry	Solvent	T (°C)	Lewis acid (mol%)	Toluene (equiv)	Yield[a] (%)
1	toluene	rt	$AlCl_3$ (50)	–	50
2	1,2-DCE	rt	$AlCl_3$ (50)	10	25
3	1,2-DCE	0	$AlCl_3$ (50)	10	45
4	MeCN	0	$AlCl_3$ (50)	10	–
5	DMF	0	$AlCl_3$ (50)	10	–
6	CH_2Cl_2	0	$AlCl_3$ (50)	10	94 (89)[b]
7	CH_2Cl_2	0	$AlCl_3$ (100)	10	59
8	CH_2Cl_2	0	$AlCl_3$ (30)	10	68
9	CH_2Cl_2	0	$AlCl_3$ (10)	10	trace
10	CH_2Cl_2	0	$FeBr_3$ (50)	10	83
11	CH_2Cl_2	0	$InBr_3$ (50)	10	47
12	CH_2Cl_2	0	$AlCl_3$ (50)	1.5	28
13	CH_2Cl_2	0	$AlCl_3$ (50)	5	58
14	CH_2Cl_2	0	$AlCl_3$ (50)	12	93

[a] ^{1}H NMR yield using HMDSO (hexamethyldisiloxane) as internal standard.
[b] Isolated yield.

Having established effective reaction conditions, we tested various dichlorides in the reaction to investigate its scope (Scheme 4). Dichloride **4a** reacted with toluene to give **5a** in 89% yield, and when 2 equiv of either ethyl- or butylbenzene were used, **5b** and **5c** were observed in 48% and 51% yields, respectively. Dichloride **4a** was also reacted in the presence of *m*-xylene, *p*-xylene, mesitylene, and durene, all of which were effective, providing **5d–g** in 35–93% yields. 4-Methylanisole reacted at the activated position *ortho*- to the methoxy group, giving **5h** in 76% yield. When

the reaction was attempted using phenol, benzyl alcohol, pyridine, or furan as arene nucleophiles, none of the desired products **5i–l** were recovered. Other polycyclic aromatics were viable, with fluorene, naphthalene, and anthracene all giving the anticipated products in 73–77% yields, as mixtures of isomers for **5n** (1.4:1) and **5o** (1.8:1).

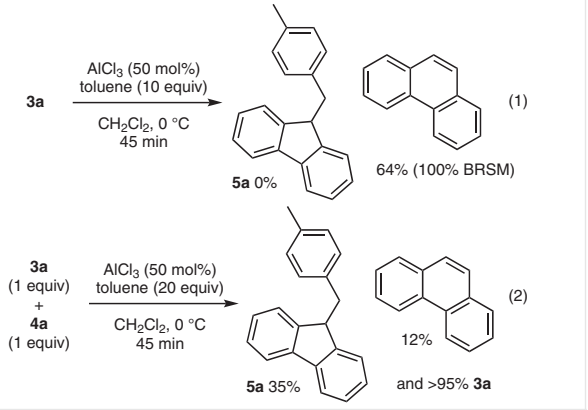
We next tested the substituted dichlorides in the reaction. First, **4b**, with an *ortho*-methyl group, was reacted in the presence of toluene to give **5p** in 84% yield. *meta*-Substituted derivatives were also reacted with toluene, and while the *m*-methyl **4c** and *m*-chloro **4e** derivatives gave the desired products in 77% (**5q**) and 81% (**5r**) yields, the *m*-cyano substrate **4g** failed. This likely occurred because a strongly electron-withdrawing group would deactivate the pendant arene, precluding the initial electrophilic aromatic substitution. The *m*-methoxy-bearing substrate **4h** worked, albeit in a lower yield than expected, possibly due to aryl methyl ether cleavage under the acidic reaction conditions. Dichloride **4i**, bearing a *m*-trifluoromethoxy substituent, gave **5v** in 56% yield. Substrates bearing either methyl or chloro substituents at the *para* position afforded products **5w** and **5x**, respectively, in 34–36% yields; however, with a phenyl group at this *para* position, the yield of product **5y** drastically increased to 86%. *m*-Xylene was again a suitable trapping agent, and gave the 2-, 3- or 4-substituted arylation products **5z–5ac** in 50–96% yields. Likewise, *p*-xylenes



Scheme 4 Synthesis of 9-(arylmethyl)fluorenes. [a] Arene nucleophile (2.0 equiv) was used. [b] ^{1}H NMR yield using HMDSO as internal standard. [c] $AlCl_3$ (2.0 equiv) was used. [d] Obtained as a mixture of *ortho*- and *para*-substitution products.

could be used to intercept the reaction of dichlorides *m*-chloro **4e** and *p*-phenyl **4l**, giving **5ae** and **5ad** in 69% and 92% yields. Several disubstituted derivatives were tested in the reaction, and while difluoride **4k** was intercepted with toluene to give **5af** in 39% yield, derivatives **4m** and **4n**, possessing both a phenyl and either a methyl or a chloro substituent, reacted with toluene to give the desired products **5ag** and **5ah**, respectively, in 58% and 47% yields. Finally, we tested 5-methyl **4o** and 4-methoxy **4p** in the reaction, and these gave the corresponding 9-(arylmethyl)fluorenes **5aj** and **5ai** in 33% and 15% yields.

To test the intermediacy of **3a** in the conversion of **4a** into **5a**, we subjected **3a** to the reaction conditions (Scheme 5). When treated with 50 mol% $AlCl_3$ in CH_2Cl_2 at 0 °C in the presence of 10 equiv of toluene, the reaction failed to provide **5a**, and instead gave phenanthrene in 64% yield (100% based on recovered **3a**) by ^1H NMR. Decreasing the loading of $AlCl_3$ to 10 mol% also gave phenanthrene, as did treating **3a** with anhydrous HCl (not shown). We believed it possible that the acidic byproducts formed during the conversion of **4a** into **5a** could be activating **3a**, if it actually is a reaction intermediate. To test this, we treated an equimolar mixture of **3a** and **4a** with 50 mol% $AlCl_3$ and 20 equiv of toluene, which led to a mixture of phenanthrene and **5a** (Scheme 5).

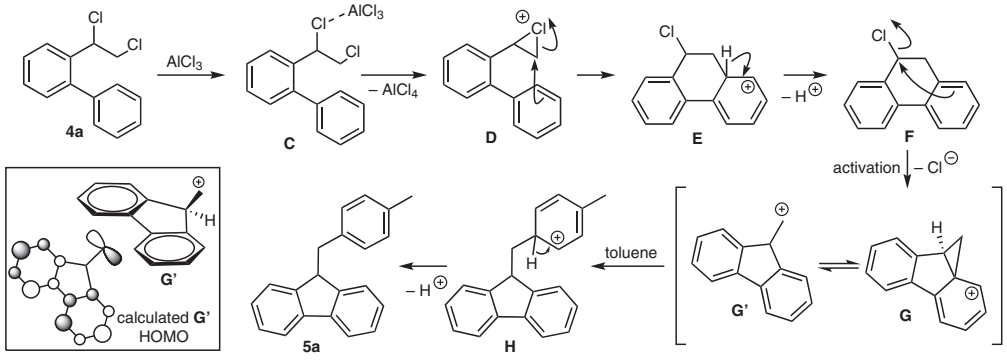


Scheme 5

While only a trace of **4a** remained in the resulting reaction mixture, chloride **3a** was untouched by the reaction conditions (as determined by ^1H NMR analysis). These results support the conclusion that the current process does not involve **3a** as a reaction intermediate, which is consistent with there being no reports (to our knowledge) of using **3a** as a reagent in Friedel–Crafts alkylations.

We propose the following mechanism for the synthesis of 9-(arylmethyl)fluorenes **5a** from dichloride **4a**, intentionally bypassing the formation of **3a** (Scheme 6). We expect the dichloride **4a** to be activated by $AlCl_3$ at the benzylic position, giving chloronium ion **D**, and if attack occurs at the terminus by the pendant arene, the resulting arenium ion **E** could rearomatize to give **F**.[18] Activation of the chlorine in **F** may form phenonium ion **G** or cation **G′**. While **G′** might be expected to undergo a 1,2-hydride shift to give the tertiary benzylic cation, this is not operative as it leads to an anti-aromatic product. Intermediate **G′** is in fact calculated to be stabilized by the proximal benzene rings via in-phase overlap of fluorene's HOMO and the lobes of the carbocation's *p*-orbital (Scheme 6, inset).[19] Intermediates **G**/**G′** would be susceptible to intermolecular attack by toluene to give **5a** via **H**, or if the nucleophile is not present, deprotonation of the activated intermediate **G** would lead to phenanthrene.[13a]

In conclusion, we intended to develop a $PhICl_2$-mediated synthesis of 9-(chloromethyl)fluorene derivatives using an intramolecular Friedel–Crafts alkylation reaction. Though this failed, we discovered that vicinal dichlorides **4** could be readily prepared in high yield, and that these could undergo sequential intra- and intermolecular Friedel–Crafts alkylations upon exposure to 50 mol% $AlCl_3$ and an arene nucleophile. The reactions were tolerant to a variety of functional groups and substitution patterns on the substrate and the arene nucleophile, giving the products in yields up to 96%. This reaction offers a new strategy for preparing valuable 9-(arylmethyl)fluorene derivatives, and as polycyclic aromatic hydrocarbons were shown to be viable as arene nucleophiles, this may prove useful for derivatizing organic materials.



Scheme 6 Proposed mechanism for the tandem Friedel–Crafts alkylation reaction

Reactions were carried out in oven-dried glassware under a N_2 atmosphere. Solvents were dried and purified using a JC Meyer solvent purification system, and were used without further purification. Transfer of anhyd solvents and reagents was accomplished with oven-dried syringes. TLC was performed on glass plates pre-coated with 0.25 mm Kieselgel 60 F254 (Silicycle). Flash chromatography columns were packed with 230–400 mesh silica gel (Silicycle). Radial chromatography was carried out on a Chromatotron 7924T (Harrison Research) equipped with 4-mm silica gel 60 F254 with gypsum binder (EM) thick-layer plates on glass rotors. Melting points were recorded on a MEL-TEMP II instrument and are uncorrected. Infrared spectra were recorded on a Perkin Elmer FT-IR Spectrum Two with ATR Two. ^{1}H NMR were recorded at 300 or 500 MHz, and are reported relative to the residual chloroform peak (δ = 7.26). ^{13}C NMR were recorded at 125 or 75 MHz and are reported relative to the center line of the triplet from $CDCl_3$ (δ = 77.16). ^{19}F NMR spectra were recorded at 282 MHz, and are reported relative to TFA. HRMS was performed on a Thermo Fisher Scientific Q-Exactive hybrid mass spectrometer equipped with an Agilent HPLC pump interfaced with the Q-Exactive's APCI and ESI source.

The alkenes **2** are known compounds and were prepared according to the literature.[9a]

Synthesis of *vic*-Dichlorides 4a–p; General Procedure A

To an oven-dried flask with a magnetic stirrer bar was added $PhICl_2$ (**1**; 0.22 mmol, 1.1 equiv) and anhyd 1,2-DCE (1 mL, 0.2 M), and to this was added the alkene **2** (0.2 mmol, 1.0 equiv), and the resulting mixture was placed under a N_2 atmosphere. The mixture was stirred at rt and $BF_3{\cdot}Et_2O$ (7.8 μL, 30 mol%) was added, after which the reaction was monitored by TLC analysis. Upon consumption of the alkene **2** (approx. 20 min), the mixture was concentrated under vacuum by rotary evaporation and the resulting crude mixture was purified by chromatography (silica gel).

2-(1,2-Dichloroethyl)biphenyl (4a)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.031 g (0.123 mmol, 98%); R_f = 0.35 (hexanes).

IR (ATR): 1598, 1479, 1438, 1203, 1009, 940, 919, 773, 749, 719, 700, 616, 596, 553 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 7.7 Hz, 1 H), 7.53–7.41 (m, 7 H), 7.33 (d, *J* = 7.2 Hz, 1 H), 5.25 (t, *J* = 7.5 Hz, 1 H), 3.99 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.3, 139.9, 135.6, 130.4, 129.3, 128.8, 128.6, 128.4, 127.7, 126.8, 57.8, 47.9.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{14}H_{12}Cl_2$: 250.0310; found: 250.0309.

2-(1,2-Dichloroethyl)-2′-methylbiphenyl (4b)

Mixture of atropisomers purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.095 g (0.358 mmol, 77%); R_f = 0.30 (hexanes).

IR (ATR): 1477, 1444, 1278, 755, 729, 692 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.67 (m, 1 H), 7.50 (q, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.36–7.14 (m, 5 H), 4.94–4.83 (m, 1 H), 4.07–3.84 (m, 2 H), 2.14 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.7, 141.4, 139.1, 138.9, 136.3, 136.1, 136.0, 135.7, 130.3, 130.3, 130.1, 130.0, 129.7, 129.6, 128.7, 128.6, 128.3, 128.2, 128.0, 126.7, 126.4, 125.6, 125.6, 57.7, 57.5, 48.0, 46.8, 20.3, 20.1.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{15}H_{14}Cl_2$: 264.0467; found: 264.0473.

2-(1,2-Dichloroethyl)-3′-methylbiphenyl (4c)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.157 g (0.592 mmol, 72%); R_f = 0.30 (hexanes).

IR (ATR): 1475, 1445, 1274, 1199, 941, 792, 756, 706, 693 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.9 Hz, 1 H), 7.49 (t, *J* = 7.7 Hz, 1 H), 7.42 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.33–7.28 (m, 1 H), 7.26 (d, *J* = 7.7 Hz, 1 H), 7.22–7.20 (m, 2 H), 5.23 (t, *J* = 7.5 Hz, 1 H), 3.98 (d, *J* = 7.6 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.3, 139.8, 138.2, 135.5, 130.3, 130.0, 128.7, 128.4, 128.3, 128.2, 126.6, 126.3, 57.8, 47.9, 21.5.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{15}H_{14}Cl_2$: 264.0467; found: 264.0473.

2-(1,2-Dichloroethyl)-4′-methylbiphenyl (4d)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.056 g (0.211 mmol, 68%); R_f = 0.30 (hexanes).

IR (ATR): 1736, 1478, 1445, 1236, 1050, 1007, 941, 921, 821, 758, 696, 553 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 7.8 Hz, 1 H), 7.47 (t, *J* = 7.7 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 7.29 (m, 5 H), 5.21 (t, *J* = 7.5 Hz, 1 H), 3.97 (d, *J* = 7.5 Hz, 2 H), 2.46 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.2, 137.4, 136.9, 135.6, 130.4, 129.2, 129.1, 128.7, 128.1, 126.6, 57.8, 47.8, 21.2.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{15}H_{14}Cl_2$: 264.0467; found: 264.0473.

3′-Chloro-2-(1,2-dichloroethyl)biphenyl (4e)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.180 g (0.630 mmol, 90%); R_f = 0.55 (hexanes/CH_2Cl_2 95:5).

IR (ATR): 1593, 1467, 1407, 1080, 1024, 941, 791, 755, 698 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.8 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 1 H), 7.45–7.40 (m, 4 H), 7.29 (t, *J* = 8.2 Hz, 2 H), 5.13 (t, *J* = 7.5 Hz, 1 H), 3.99 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.6, 140.7, 135.5, 134.4, 130.2, 129.7, 129.4, 128.9, 128.8, 127.9, 127.5, 126.7, 57.2, 47.5.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{14}H_{11}Cl_3$: 283.9920; found: 283.9917.

4′-Chloro-2-(1,2-dichloroethyl)biphenyl (4f)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.240 g (0.845 mmol, 94%); R_f = 0.55 (hexanes/CH_2Cl_2 95:5).

IR (ATR): 1477, 1089, 1006, 941, 832, 759, 696, 551 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.8 Hz, 1 H), 7.50 (t, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.34 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 7.4 Hz, 1 H), 5.12 (t, *J* = 7.6 Hz, 1 H), 3.98 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.0, 138.2, 135.6, 133.9, 130.6, 130.2, 128.9, 128.7, 128.7, 126.7, 57.3, 47.5.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{14}H_{11}Cl_3$: 283.9926; found: 283.9917.

2′-(1,2-Dichloroethyl)biphenyl-3-carbonitrile (4g)

Purified by column chromatography (silica gel, hexanes/EtOAc) to give a colorless liquid; yield: 0.080 mg (0.290 mmol, 76%); R_f = 0.45 (hexanes/EtOAc 90:10).

IR (ATR): 2230, 1474, 1446, 1412, 1194, 941, 904, 803, 757, 696, 497 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.7 Hz, 1 H), 7.70 (d, *J* = 6.3 Hz, 1 H), 7.67–7.65 (m, 2 H), 7.61 (t, *J* = 7.7 Hz, 1 H), 7.55 (t, *J* = 7.7 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 1 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 4.99 (t, *J* = 7.7 Hz, 1 H), 3.99 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.2, 139.9, 135.5, 133.7, 132.7, 131.4, 130.1, 129.4, 129.3, 129.1, 126.8, 118.5, 112.9, 56.8, 47.3.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{12}NCl_2$: 276.0341; found: 276.0340.

2-(1,2-Dichloroethyl)-3′-methoxybiphenyl (4h)

Purified by column chromatography (silica gel, hexanes/EtOAc) to give a colorless liquid; yield: 0.110 mg (0.391 mmol, 79%); R_f = 0.40 (hexanes/EtOAc 90:10).

IR (ATR): 1722, 1437, 1309, 1244, 1192, 1114, 1084, 749, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 7.6 Hz, 1 H), 8.09 (s, 1 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 7.61 (d, *J* = 7.8 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 8.6 Hz, 1 H), 5.10 (t, *J* = 7.5 Hz, 1 H), 4.01–3.93 (m, 5 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 166.8, 141.1, 140.1, 135.6, 133.6, 130.5, 130.3, 128.9 (2 C), 128.7, 128.6, 126.7, 57.4, 52.3, 47.6.

HRMS (APCI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}OCl_2$: 281.0494; found: 281.0493.

2-(1,2-Dichloroethyl)-3′-(trifluoromethoxy)biphenyl (4i)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.098 g (0.292 mmol, 98%); R_f = 0.45 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1608, 1585, 1475, 1248, 1214, 1156, 1002, 848, 798, 758, 699, 596 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.9 Hz, 1 H), 7.58–7.50 (m, 2 H), 7.46 (t, *J* = 7.5 Hz, 1 H), 7.36 (d, *J* = 7.7 Hz, 1 H), 7.31 (d, *J* = 6.6 Hz, 3 H), 5.12 (t, *J* = 7.6 Hz, 1 H), 4.00 (d, *J* = 7.6 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 149.2, 141.8, 140.6, 135.6, 130.2, 129.9, 128.9 (2 C), 127.7, 126.8, 121.9, 121.5 (q, *J* = 257.6 Hz), 120.1, 57.1, 47.5.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{15}H_{11}OCl_2F_3$: 334.0133; found: 334.0130.

2-(1,2-Dichloroethyl)-3′-fluorobiphenyl (4j)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.245 g (0.910 mmol, 83%); R_f = 0.40 (hexanes).

IR (ATR): 1584, 1475, 1334, 1198, 1178, 1129, 883, 791, 758, 699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.1 Hz, 1 H), 7.51 (t, *J* = 7.4 Hz, 1 H), 7.48–7.42 (m, 2 H), 7.29 (d, *J* = 6.7 Hz, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.16–7.11 (m, 2 H), 5.15 (t, *J* = 7.6 Hz, 1 H), 3.99 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.6 (d, *J* = 247.5 Hz), 141.9 (d, *J* = 7.7 Hz), 140.9 (d, *J* = 1.9 Hz), 135.5, 130.1, 130.0 (d, *J* = 8.4 Hz), 128.9, 128.8, 126.7, 125.1 (d, *J* = 2.7 Hz), 116.4 (d, *J* = 21.7 Hz), 114.6 (d, *J* = 21.0 Hz), 57.27, 47.57.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –112.7.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{14}H_{11}Cl_2F_2$: 268.0216; found: 268.0215.

2-(1,2-Dichloroethyl)-3′,4′-difluorobiphenyl (4k)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.229 g (0.797 mmol, 86%); R_f = 0.40 (hexanes).

IR (ATR): 1523, 1487, 1312, 1264, 1225, 1118, 824, 756, 700 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.9 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.31–7.22 (m, 3 H), 7.15–7.12 (m, 1 H), 5.10 (t, *J* = 7.6 Hz, 1 H), 4.00 (d, *J* = 7.7 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.0 (dd, *J* = 12.7, 2.9 Hz), 149.1 (dd, *J* = 12.6, 3.5 Hz), 140.1, 136.7 (d, *J* = 4.7 Hz), 135.6, 130.2, 128.9 (2 C), 126.7, 125.5 (q, *J* = 3.8 Hz), 118.5 (d, *J* = 17.4 Hz), 117.4 (d, *J* = 17.3 Hz), 57.01, 47.38.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –137.21 (d, *J* = 20.4 Hz), –139.33 (d, *J* = 20.8 Hz).

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{14}H_{10}Cl_2F_2$: 286.0122; found: 286.0109.

2-(1,2-Dichloroethyl)-1,1′:4′,1″-terphenyl (4l)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.220 g (0.672 mmol, 79%); R_f = 0.45 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1600, 1479, 1445, 1397, 1203, 1006, 941, 843, 754, 732, 695, 576 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 7.3 Hz, 2 H), 7.68 (d, *J* = 7.7 Hz, 1 H), 7.55–7.49 (m, 5 H), 7.38–7.42 (m, 2 H), 7.37 (d, *J* = 7.8 Hz, 1 H), 5.30 (t, *J* = 7.5 Hz, 1 H), 4.02 (d, *J* = 7.5 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.9, 140.6, 140.5, 138.8, 135.6, 130.4, 129.7, 128.9, 128.8, 128.4, 127.5, 127.2 (2 C), 126.7, 57.7, 47.8.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{20}H_{16}Cl_2$: 326.0623; found: 326.0616.

2-(1,2-Dichloroethyl)-5-methyl-1,1′:4′,1″-terphenyl (4m)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.100 g (0.293 mmol, 85%); R_f = 0.50 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1610, 1484, 1445, 1007, 843, 766, 696, 586 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71 (t, *J* = 8.3 Hz, 4 H), 7.55 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 2 H), 7.49 (d, *J* = 7.9 Hz, 2 H), 7.42 (t, *J* = 7.3 Hz, 1 H), 7.33 (d, *J* = 8.3 Hz, 1 H), 7.18 (s, 1 H), 5.25 (t, *J* = 7.6 Hz, 1 H), 4.01 (d, *J* = 7.5 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.7, 140.6, 140.4, 138.9, 138.8, 132.7, 131.0, 129.7, 129.2, 128.9, 127.5, 127.2, 127.1, 126.6, 57.8, 47.8, 21.3.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{21}H_{18}Cl_2$: 340.0780; found: 340.0771.

4-Chloro-2-(1,2-dichloroethyl)-1,1′:4′,1″-terphenyl (4n)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.120 g (0.332 mmol, 64%); R_f = 0.50 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1477, 1097, 1005, 846, 822, 765, 740, 696, 576 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.1 Hz, 2 H), 7.69 (d, *J* = 7.4 Hz, 2 H), 7.63 (d, *J* = 2.1 Hz, 1 H), 7.51 (t, *J* = 7.6 Hz, 2 H), 7.49–7.39 (m, 4 H), 7.31–7.25 (m, 1 H), 5.23–5.17 (m, 1 H), 3.97 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.9, 140.4, 140.3, 137.6, 137.5, 134.2, 131.7, 129.6, 129.1, 128.9, 127.6, 127.3, 127.1, 126.9, 56.8, 47.5.

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{20}H_{15}Cl_3$: 360.0221; found: 360.0221.

2-(1,2-Dichloroethyl)-4′,5-dimethylbiphenyl (4o)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.028 mg (0.100 mmol, 67%); R_f = 0.45 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2921, 1611, 1495, 821, 716, 689, 582, 551 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.0 Hz, 1 H), 7.29–7.28 (m, 5 H), 7.11 (s, 1 H), 5.18 (t, *J* = 7.5 Hz, 1 H), 3.96 (d, *J* = 7.6 Hz, 2 H), 2.45 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.1, 138.7, 137.2, 137.0, 132.7, 131.1, 129.1, 129.1, 128.9, 126.5, 57.9, 47.8, 21.2 (2 C).

HRMS (APCI): *m*/*z* [M$^+$] calcd for $C_{16}H_{16}Cl_2$: 278.0623; found: 278.0625.

2-(1,2-Dichloroethyl)-4-methoxybiphenyl (4p)

Purified by column chromatography (silica gel, hexanes/EtOAc) to give a colorless liquid; yield: 0.101 g (0.359 mmol, 95%); R_f = 0.40 (hexanes/EtOAc 90:10).

IR (ATR): 1611, 1509, 1484, 1286, 1233, 1053, 1007, 820, 767, 704 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (t, *J* = 7.4 Hz, 2 H), 7.42 (d, *J* = 7.3 Hz, 1 H), 7.37 (d, *J* = 7.4 Hz, 2 H), 7.24 (d, *J* = 8.5 Hz, 1 H), 7.14 (s, 1 H), 6.98 (d, *J* = 8.6 Hz, 1 H), 5.17 (t, *J* = 7.4 Hz, 1 H), 3.95 (d, *J* = 7.4 Hz, 2 H), 3.91 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.4, 139.6, 136.7, 134.7, 131.5, 129.5, 128.5, 127.4, 114.5, 111.9, 57.9, 55.5, 47.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}OCl_2$: 281.0494; found: 281.0493.

Synthesis of 9-(Arylmethyl)fluorenes 5a–aj; General Procedure B

To an oven-dried flask containing anhyd CH_2Cl_2 (2 mL, 0.1 M) and a magnetic stirrer bar was charged dichloride **4** (0.2 mmol, 1.0 equiv) and arene (2.0 mmol, 10 equiv), and the resulting solution was cooled to 0 °C under N_2. The mixture was stirred for 10 min and then $AlCl_3$ (50 mol%) was added. The reaction was monitored by TLC analysis, and upon consumption of dichloride **4** (approx. 20 min), water (15 mL) and CH_2Cl_2 (15 mL) were added. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were washed with sat. NaCl solution, dried (Na_2SO_4), and concentrated under reduced pressure. The crude product was purified by column chromatography to afford fluorene **5**.

9-(4-Methylbenzyl)-9*H*-fluorene (5a)[20]

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.033 g (0.128 mmol, 89%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15); mp 122–128 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.4 Hz, 2 H), 7.25 (t, *J* = 7.1 Hz, 2 H), 7.22 (d, *J* = 7.6 Hz, 2 H), 7.16 (n, 4 H), 4.25 (t, *J* = 7.6 Hz, 1 H), 3.11 (d, *J* = 7.6 Hz, 2 H), 2.40 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.0, 140.8, 136.7, 135.8, 129.4, 129.0, 127.1, 126.6, 124.9, 119.8, 48.8, 39.7, 21.1.

9-(2,5-Dimethylbenzyl)-9*H*-fluorene (5d)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.025 g (0.089 mmol, 89%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2920, 1476, 1448, 1377, 1032, 809, 739, 731, 621, 580, 518 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.6 Hz, 2 H), 7.40 (t, *J* = 7.5 Hz, 2 H), 7.24 (t, *J* = 7.4 Hz, 2 H), 7.15 (d, *J* = 7.2 Hz, 4 H), 7.08 (d, *J* = 7.7 Hz, 1 H), 4.22 (t, *J* = 8.1 Hz, 1 H), 3.04 (d, *J* = 8.1 Hz, 2 H), 2.39 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 140.7, 138.2, 135.3, 133.6, 131.1, 130.3, 127.2, 127.1, 126.7, 124.9, 119.8, 47.8, 37.6, 21.1, 19.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}$: 285.1637; found: 285.1635.

9-(2,4-Dimethylbenzyl)-9*H*-fluorene (5e)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.026 g (0.093 mmol, 93%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15); mp 68–70 °C.

IR (ATR): 1499, 1440, 1365, 1240, 1032, 750, 702 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 7.5 Hz, 2 H), 7.39 (t, *J* = 7.4 Hz, 2 H), 7.25 (t, *J* = 7.5 Hz, 2 H), 7.18 (t, *J* = 8.5 Hz, 3 H), 7.09 (s, 1 H), 7.07 (d, *J* = 7.7 Hz, 1 H), 4.21 (t, *J* = 8.0 Hz, 1 H), 3.05 (d, *J* = 8.0 Hz, 2 H), 2.41 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.2, 140.7, 136.5, 136.0, 135.3, 131.2, 130.3, 127.1, 126.7, 126.6, 124.9, 119.8, 47.7, 37.3, 21.1, 19.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}$: 285.1637; found: 285.1635.

9-(2,4,6-Trimethylbenzyl)-9*H*-fluorene (5f)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.015 g (0.052 mmol, 52%); R_f = 0.30 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1476, 1447, 1376, 1301, 751, 732, 594, 568 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 2 H), 7.39 (t, *J* = 7.5 Hz, 2 H), 7.23 (t, *J* = 7.4 Hz, 2 H), 7.09 (d, *J* = 7.6 Hz, 2 H), 6.94 (s, 2 H), 4.22 (t, *J* = 8.6 Hz, 1 H), 3.07 (d, *J* = 8.6 Hz, 2 H), 2.37 (s, 3 H), 2.19 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 140.7, 137.0, 135.7, 133.6, 129.1, 127.0, 126.7, 124.8, 119.8, 46.3, 33.9, 21.0, 20.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}$: 299.1794; found: 299.1794.

9-(2,3,5,6-Tetramethylbenzyl)-9*H*-fluorene (5g)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.011 g (0.035 mmol, 35%); R_f = 0.30 (hexanes/CH_2Cl_2 85:15); mp 136–140 °C.

IR (ATR): 1448, 1365, 1228, 1216, 755, 733, 527 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.5 Hz, 2 H), 7.20 (t, *J* = 7.5 Hz, 2 H), 7.05 (d, *J* = 7.6 Hz, 2 H), 7.00 (s, 1 H), 4.18 (t, *J* = 8.6 Hz, 1 H), 3.17 (d, *J* = 8.6 Hz, 2 H), 2.30 (s, 6 H), 2.09 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.0, 140.7, 136.4, 133.8, 133.0, 130.0, 127.0, 126.6, 124.9, 119.8, 46.7, 34.5, 20.8, 16.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{25}$: 313.1950; found: 313.1949.

9-(2-Methoxy-5-methylbenzyl)-9*H*-fluorene (5h)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.023 g (0.077 mmol, 76%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15); mp 105–110 °C.

IR (ATR): 1738, 1499, 1440, 1365, 1240, 1032, 750, 702, 515 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (t, *J* = 8.2 Hz, 1 H), 7.41–7.31 (m, 4 H), 7.26 (d, *J* = 7.6 Hz, 1 H), 7.21 (d, *J* = 6.9 Hz, 2 H), 7.00 (d, *J* = 8.2 Hz, 1 H), 6.88 (s, 1 H), 6.69 (d, *J* = 8.3 Hz, 1 H), 4.89 (t, *J* = 7.8 Hz, 1 H), 3.98–3.90 (m, 2 H), 3.58 (s, 3 H), 2.27 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.9, 143.1, 141.4, 138.3, 130.4, 129.4, 129.3 (2 C), 129.2, 128.2, 127.8 (2 C), 127.5, 127.3, 126.8, 126.5, 110.7, 55.3, 45.9, 43.0, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}O$: 301.1586; found: 301.1585.

2-(9*H*-Fluoren-9-ylmethyl)-9*H*-fluorene (5m)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a pale yellow liquid; yield: 0.025 g (0.073 mmol, 73%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 3016, 1738, 1448, 1365, 1216, 825, 762, 733, 527 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.6 Hz, 1 H), 7.78 (t, *J* = 7.7 Hz, 3 H), 7.59 (d, *J* = 7.4 Hz, 1 H), 7.47 (s, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 7.39 (t, *J* = 7.3 Hz, 2 H), 7.35 (t, *J* = 7.4 Hz, 1 H), 7.30 (d, *J* = 7.6 Hz, 1 H), 7.27–7.20 (m, 4 H), 4.33 (t, *J* = 7.7 Hz, 1 H), 3.93 (s, 2 H), 3.22 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.9, 143.5, 143.3, 141.7, 140.8, 140.0, 138.6, 128.2, 127.1, 126.8, 126.7, 126.5, 126.2, 125.1, 124.9, 119.8, 119.7 (2 C), 49.0, 40.4, 36.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{21}$: 345.1637; found: 345.1636.

9-(Naphthalen-1-ylmethyl)-9*H*-fluorene (5n) and 9-(Naphthalen-2-ylmethyl)-9*H*-fluorene (5n′)[20]

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a mixture of compounds as a white solid; yield: 0.023 g (0.077 mmol, 77%); ratio **5n**/**5n′** 1.4:1; R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.3 Hz, 1 H, **5n**), 8.00 (d, *J* = 8.0 Hz, 1 H, **5n**), 7.90 (d, *J* = 8.4 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 1 H, **5n′**), 7.84–7.78 (m, 6 H), 7.68 (s, 1 H), 7.64–7.54 (m, 3 H), 7.52–7.49 (m, 5 H), 7.42–7.37 (m, 5 H), 7.33 (d, *J* = 7.0 Hz, 2 H, **5n**), 7.25–7.21 (m, 7 H), 7.13 (d, *J* = 7.6 Hz, 3 H), 4.46 (t, *J* = 7.9 Hz, 1 H, **5n**), 4.39 (t, *J* = 7.7 Hz, 1 H, **5n′**), 3.53 (d, *J* = 7.9 Hz, 3 H, **5n**), 3.31 (d, *J* = 7.6 Hz, 2 H, **5n′**).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.1, 146.8, 140.8, 140.8, 137.4, 136.0, 134.1, 133.5, 132.3, 132.0, 129.1, 128.3, 128.0, 128.0, 127.9, 127.7, 127.5, 127.2, 126.7, 126.7, 126.1, 126.0, 125.7, 125.4, 125.3, 125.2, 124.9, 123.8, 119.9, 48.6, 47.6, 40.4, 38.1.

1-(9*H*-Fluoren-9-ylmethyl)anthracene (5o) and 2-(9*H*-Fluoren-9-ylmethyl)anthracene (5o′)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a mixture of compounds as a white solid; yield: 0.024 g (0.067 mmol, 74%); ratio **5o**/**5o′** 1.8:1; R_f = 0.15 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 3054, 1672, 1477, 1447, 1264, 875, 733, 703, 468 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42–8.32 (m, 2 H), 8.05–7.89 (m, 5 H), 7.82 (d, *J* = 7.2 Hz, 1 H), 7.66 (s, 1 H), 7.52–7.26 (m, 21 H), 7.17 (d, *J* = 9.0 Hz, 1 H), 5.46 (t, *J* = 7.6 Hz, 1 H, **5o**), 4.73 (t, *J* = 7.7 Hz, 1 H, **5o′**), 4.25 (d, *J* = 7.8 Hz, 2 H, **5o**), 4.16 (d, *J* = 7.7 Hz, 1 H, **5o′**).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 143.0, 142.5, 141.2, 141.1, 138.2, 136.9, 132.2, 131.9, 131.6, 131.5, 131.2, 130.8, 130.6, 130.6, 129.8, 129.4, 129.4, 128.5, 128.4, 128.2, 128.1, 128.1, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.2, 127.2, 127.0, 127.0, 126.9, 126.4, 126.4, 126.2, 125.9, 125.5, 125.3, 122.0, 49.2, 47.0, 46.5, 45.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{21}$: 357.1637; found: 357.1636.

4-Methyl-9-(4-methylbenzyl)-9*H*-fluorene (5p)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a yellow liquid; yield: 0.024 g (0.084 mmol, 84%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2921, 1738, 1454, 1365, 1228, 1216, 764, 726, 514 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.7 Hz, 1 H), 7.40 (t, *J* = 7.4 Hz, 1 H), 7.30–7.21 (m, 3 H), 7.17 (d, *J* = 6.3 Hz, 5 H), 7.12 (q, *J* = 4.5 Hz, 1 H), 4.23 (t, *J* = 7.5 Hz, 1 H), 3.10 (qd, *J* = 13.8, 7.7 Hz, 2 H), 2.75 (s, 3 H), 2.40 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4 (2 C), 141.8, 138.8, 136.8, 135.8, 132.9, 129.4 (2 C), 129.0, 127.0, 126.3, 125.9, 124.8, 123.1, 122.3, 48.6, 40.1, 21.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}$: 285.1637; found: 285.1635.

3-Methyl-9-(4-methylbenzyl)-9*H*-fluorene (5q)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.022 g (0.077 mmol, 77%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 3455, 2970, 1738, 1454, 1365, 1228, 1216, 736, 527 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.5 Hz, 1 H), 7.60 (s, 1 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.28–7.20 (m, 2 H), 7.17 (s, 4 H), 7.10–7.05 (m, 2 H), 4.20 (t, *J* = 7.6 Hz, 1 H), 3.08 (t, *J* = 7.5 Hz, 2 H), 2.47 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 144.2, 140.9, 140.8, 136.9, 136.7, 135.8, 129.4, 129.0, 127.6, 127.0, 126.5, 124.8, 124.6, 120.4, 119.7, 48.5, 39.8, 21.6, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}$: 285.1637; found: 285.1635.

3-Chloro-9-(4-methylbenzyl)-9*H*-fluorene (5r)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.025 g (0.082 mmol, 81%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1446, 1365, 1228, 1216, 1073, 822, 739, 527 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.70 (m, 2 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.32–7.26 (m, 2 H), 7.19 (d, *J* = 7.7 Hz, 1 H), 7.15 (d, *J* = 8.2 Hz, 2 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 7.06 (d, *J* = 8.1 Hz, 1 H), 4.20 (t, *J* = 7.5 Hz, 1 H), 3.15 (dd, *J* = 13.8, 7.3 Hz, 1 H), 3.00 (dd, *J* = 13.9, 8.0 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.4, 145.1, 142.7, 139.6, 136.3, 136.0, 133.1, 129.3, 129.0, 127.4, 127.3, 126.5, 126.0, 124.9, 120.0 (2 C), 48.5, 39.5, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}Cl$: 305.1091; found: 305.1094.

3-Fluoro-9-(4-methylbenzyl)-9*H*-fluorene (5s)

Purified by column chromatography (silica gel, hexanes) to give a colorless liquid; yield: 0.013 g (0.045 mmol, 45%); R_f = 0.20 (hexanes).

IR (ATR): 2970, 1738, 1487, 1449, 1365, 1228, 1216, 1162, 902, 809, 771, 737 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.5 Hz, 1 H), 7.42 (d, *J* = 9.1 Hz, 1 H), 7.39 (d, *J* = 7.6 Hz, 1 H), 7.30–7.26 (m, 2 H), 7.14 (s, 4 H), 7.11–7.05 (m, 1 H), 6.92 (t, *J* = 9.3 Hz, 1 H), 4.20 (t, *J* = 7.6 Hz, 1 H), 3.15 (dd, *J* = 13.8, 7.2 Hz, 1 H), 3.01 (dd, *J* = 13.9, 7.9 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.7 (d, *J* = 243.4 Hz), 147.8 (2 C), 142.8 (d, *J* = 8.8 Hz), 142.2, 139.9, 136.4, 135.9, 129.3, 129.0, 127.2 (d, *J* = 6.6 Hz), 125.9 (d, *J* = 9.0 Hz), 124.9, 120.0, 113.4 (d, *J* = 22.9 Hz), 106.7 (d, *J* = 22.8 Hz), 48.25, 39.65, 21.13.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –116.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}F$: 289.1387; found: 289.1385.

9-(4-Methylbenzyl)-3-(trifluoromethoxy)-9*H*-fluorene (5v)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.020 g (0.056 mmol, 56%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1738, 1449, 1365, 1256, 1227, 1217, 1166, 738, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 7.6 Hz, 1 H), 7.58 (s, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.29 (p, *J* = 7.3 Hz, 3 H), 7.17–7.12 (m, 4 H), 7.07 (d, *J* = 9.0 Hz, 1 H), 4.23 (t, *J* = 7.7 Hz, 1 H), 3.15 (dd, *J* = 13.8, 7.4 Hz, 1 H), 3.02 (dd, *J* = 13.9, 7.8 Hz, 1 H), 2.40 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.8, 147.6, 145.2, 142.7, 139.6, 136.3, 136.0, 129.3, 129.1, 127.5, 127.3, 125.8, 124.9, 122.6 (q, *J* = 256.5 Hz), 120.1, 119.1, 112.6, 48.4, 39.5, 21.1.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –58.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}OF_3$: 355.1304; found: 355.1304.

2-Methyl-9-(4-methylbenzyl)-9*H*-fluorene (5w)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a pale yellow liquid; yield: 9.8 mg (0.034 mmol, 34%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1738, 1449, 1365, 1228, 1216, 810, 774, 738, 588, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.73 (t, *J* = 7.7 Hz, 1 H), 7.65 (d, *J* = 7.7 Hz, 1 H), 7.34 (t, *J* = 7.5 Hz, 1 H), 7.20–7.15 (m, 6 H), 7.12 (d, *J* = 7.5 Hz, 1 H), 7.08 (s, 1 H), 4.18 (t, *J* = 7.5 Hz, 1 H), 3.17 (dd, *J* = 13.8, 7.2 Hz, 1 H), 2.99 (dd, *J* = 13.8, 8.0 Hz, 1 H), 2.40 (s, 3 H), 2.39 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.3, 146.8, 138.2, 137.1, 136.9, 136.5, 135.8, 129.4, 128.9, 127.9, 127.0, 126.1, 125.5, 124.9, 119.5, 119.4, 48.7, 39.8, 21.7, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{21}$: 285.1637; found: 285.1635.

2-Chloro-9-(4-methylbenzyl)-9*H*-fluorene (5x)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.011 g (0.036 mmol, 36%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15); mp 100–101 °C.

IR (ATR): 1738, 1444, 1365, 1228, 1216, 1075, 812, 771, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 7.7 Hz, 1 H), 7.66 (d, *J* = 8.1 Hz, 1 H), 7.41–7.33 (m, 2 H), 7.28 (d, *J* = 5.7 Hz, 1 H), 7.20 (t, *J* = 4.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.13 (d, *J* = 3.1 Hz, 2 H), 4.21 (t, *J* = 7.5 Hz, 1 H), 3.14–3.04 (m, 2 H), 2.40 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.6, 146.7, 139.8, 139.4, 136.1 (2 C), 132.3, 129.3, 129.1, 127.4, 127.3, 126.9, 125.2, 125.0, 120.7, 119.8, 48.8, 39.4, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{18}Cl$: 305.1091; found: 305.1094.

9-(4-Methylbenzyl)-2-phenyl-9*H*-fluorene (5y)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.030 g (0.087 mmol, 86%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15); mp 110–118 °C.

IR (ATR): 1738, 1454, 1365, 1228, 1216, 756, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.8 Hz, 1 H), 7.81 (d, *J* = 7.5 Hz, 1 H), 7.64 (d, *J* = 7.9 Hz, 1 H), 7.60 (d, *J* = 7.8 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.44–7.35 (m, 3 H), 7.33–7.25 (m, 2 H), 7.20 (s, 4 H), 4.30 (t, *J* = 7.8 Hz, 1 H), 3.21 (dd, *J* = 13.7, 7.7 Hz, 1 H), 3.12 (dd, *J* = 13.8, 7.9 Hz, 1 H), 2.43 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.5, 147.3, 141.4, 140.5, 140.1, 139.5, 136.8, 135.9, 129.5, 129.1, 128.7, 127.2, 127.1 (2 C), 126.7, 126.2, 124.9, 123.8, 120.0, 119.9, 49.0, 39.8, 21.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{23}$: 347.1794; found: 347.1793.

9-(2,4-Dimethylbenzyl)-4-methyl-9*H*-fluorene (5z)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.024 g (0.080 mmol, 81%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2920, 1701, 1514, 1453, 1303, 1235, 1112, 1033, 786, 733, 513 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 7.8 Hz, 1 H), 7.41 (t, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.4 Hz, 1 H), 7.17 (d, *J* = 7.0 Hz, 4 H), 7.08 (d, *J* = 6.6 Hz, 2 H), 7.06 (s, 1 H), 4.20 (t, *J* = 8.0 Hz, 1 H), 3.07 (dd, *J* = 13.9, 7.8 Hz, 1 H), 3.00 (dd, *J* = 13.9, 8.2 Hz, 1 H), 2.78 (s, 3 H), 2.41 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 147.6, 141.7, 138.7, 136.5, 136.0, 135.3, 133.0, 131.2, 130.4, 129.4, 127.0, 126.6, 126.4, 126.0, 124.8, 123.1, 122.3, 47.5, 37.8, 21.2, 21.1, 19.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}$: 299.1792; found: 299.1794.

9-(2,4-Dimethylbenzyl)-3-methyl-9*H*-fluorene (5aa)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.028 g (0.094 mmol, 96%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1449, 1365, 1228, 1216, 818, 741, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.7 Hz, 1 H), 7.64 (s, 1 H), 7.40 (t, *J* = 7.4 Hz, 1 H), 7.26 (t, *J* = 7.4 Hz, 1 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 7.19 (d, *J* = 7.6 Hz, 1 H), 7.11–7.08 (m, 4 H), 4.19 (t, *J* = 8.0 Hz, 1 H), 3.05 (d, *J* = 8.1 Hz, 2 H), 2.50 (s, 3 H), 2.43 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.6, 144.4, 140.9, 140.8, 136.7, 136.5, 136.0, 135.4, 131.2, 130.3, 127.6, 127.0, 126.6, 126.6, 124.9, 124.6, 120.4, 119.7, 47.4, 37.5, 21.6, 21.1, 19.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}$: 299.1791; found: 299.1794.

3-Chloro-9-(2,4-dimethylbenzyl)-9*H*-fluorene (5ab)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.016 g (0.050 mmol, 50%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 1503, 1473, 1443, 1376, 1216, 1075, 811, 730, 589 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.8 Hz, 2 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.33–7.25 (m, 1 H), 7.23 (d, *J* = 7.5 Hz, 1 H), 7.19–7.17 (m, 1 H), 7.15 (d, *J* = 7.6 Hz, 1 H), 7.08 (s, 1 H), 7.06 (d, *J* = 7.8 Hz, 1 H), 6.98 (d, *J* = 8.0 Hz, 1 H), 4.17 (t, *J* = 8.1 Hz, 1 H), 3.09 (dd, *J* = 13.9, 7.7 Hz, 1 H), 2.93 (dd, *J* = 13.9, 8.6 Hz, 1 H), 2.40 (s, 3 H), 2.26 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 145.3, 142.6, 139.5, 136.4, 136.2, 134.9, 133.1, 131.3, 130.2, 127.4, 127.3, 126.6, 126.5, 126.0, 124.9, 120.1, 47.4, 37.2, 21.1, 19.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}Cl$: 319.1248; found: 319.1244.

9-(2,4-Dimethylbenzyl)-2-phenyl-9*H*-fluorene (5ac)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a colorless liquid; yield: 0.029 g (0.080 mmol, 82%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1435, 1365, 1228, 1216, 899, 758, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.9 Hz, 1 H), 7.83 (d, *J* = 7.4 Hz, 1 H), 7.65 (d, *J* = 7.9 Hz, 1 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.42 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.4 Hz, 1 H), 7.32–7.23 (m, 3 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 7.13 (s, 1 H), 7.10 (d, *J* = 7.7 Hz, 1 H), 4.26 (t, *J* = 8.2 Hz, 1 H), 3.18 (dd, *J* = 13.7, 8.0 Hz, 1 H), 3.03 (dd, *J* = 13.7, 8.5 Hz, 1 H), 2.44 (s, 3 H), 2.30 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.6 (2 C), 141.4, 140.4, 140.0, 139.5, 136.6, 136.2, 135.4, 131.3, 130.5, 128.7, 127.2, 127.1 (2 C), 126.7, 126.6, 126.2, 124.9, 123.9, 120.0, 119.9, 47.8, 37.5, 21.1, 19.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}$: 361.1950; found: 361.1949.

9-(2,5-Dimethylbenzyl)-2-phenyl-9*H*-fluorene (5ad)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.033 g (0.092 mmol, 92%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1454, 1365, 1228, 1216, 757, 697 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 8.1 Hz, 1 H), 7.85 (d, *J* = 7.4 Hz, 1 H), 7.66 (d, *J* = 7.9 Hz, 1 H), 7.58 (d, *J* = 7.7 Hz, 2 H), 7.47 (t, *J* = 7.7 Hz, 2 H), 7.43 (d, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.28 (q, *J* = 9.0, 7.7 Hz, 3 H), 7.21 (d, *J* = 7.8 Hz, 1 H), 7.17 (s, 1 H), 7.13 (d, *J* = 7.9 Hz, 1 H), 4.27 (t, *J* = 8.2 Hz, 1 H), 3.22 (dd, *J* = 13.6, 7.7 Hz, 1 H), 2.99 (dd, *J* = 13.7, 8.8 Hz, 1 H), 2.41 (s, 3 H), 2.31 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.6, 147.5, 141.4, 140.4, 140.0, 139.5, 138.2, 135.3, 133.6, 131.4, 130.4, 128.7, 127.4, 127.2, 127.1 (2 C), 126.8, 126.2, 124.8, 124.0, 120.1, 119.9, 47.8, 37.9, 21.0, 19.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}$: 361.1950; found: 361.1949.

3-Chloro-9-(2,5-dimethylbenzyl)-9*H*-fluorene (5ae)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.022 g (0.069 mmol, 69%); R_f = 0.25 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1504, 1474, 1443, 1375, 1228, 1075, 771, 740, 729, 588 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2 H), 7.41 (t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 8.5 Hz, 1 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 7.17–7.15 (m, 2 H), 7.11 (s, 1 H), 7.08 (d, *J* = 7.8 Hz, 1 H), 6.95 (d, *J* = 8.0 Hz, 1 H), 4.18 (t, *J* = 8.2 Hz, 1 H), 3.09 (dd, *J* = 13.7, 7.7 Hz, 1 H), 2.92 (dd, *J* = 13.8, 8.7 Hz, 1 H), 2.38 (s, 3 H), 2.22 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.6, 145.2, 142.6, 139.5, 137.8, 135.4, 133.5, 133.1, 131.0, 130.4, 127.4, 127.3, 126.5, 126.0, 124.9, 120.1 (2 C), 47.5, 37.5, 21.0, 19.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{20}Cl$: 319.1248; found: 319.1244.

2,3-Difluoro-9-(4-methylbenzyl)-9*H*-fluorene (5af)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.012 g (0.039 mmol, 39%); R_f = 0.40 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1409, 1455, 1361, 1216, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 7.6 Hz, 1 H), 7.52–7.46 (m, 1 H), 7.41–7.37 (m, 1 H), 7.29–7.27 (m, 2 H), 7.15 (d, *J* = 7.9 Hz, 2 H), 7.11 (d, *J* = 7.8 Hz, 2 H), 6.92–6.85 (m, 1 H), 4.18 (t, *J* = 7.6 Hz, 1 H), 3.18 (dd, *J* = 13.8, 7.0 Hz, 1 H), 2.95 (dd, *J* = 13.9, 8.2 Hz, 1 H), 2.39 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 151.5, 149.8, 147.2, 142.6, 139.4, 137.1, 136.2, 135.9, 129.3, 129.1, 127.4, 126.9, 124.6, 119.7, 113.8 (d, *J* = 18.4 Hz), 108.3 (d, *J* = 18.3 Hz), 48.60, 39.46, 21.13.

^{19}F NMR (471 MHz, $CDCl_3$): δ = –139.64 (d, *J* = 19.9 Hz), –139.85 (d, *J* = 19.4 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{17}F_2$: 307.1928; found: 307.1924.

6-Methyl-9-(4-methylbenzyl)-2-phenyl-9*H*-fluorene (5ag)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.021 g (0.058 mmol, 58%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15); mp 129–138 °C.

IR (ATR): 1514, 1484, 1448, 1216, 812, 755, 697, 515 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.8 Hz, 1 H), 7.62 (d, *J* = 6.8 Hz, 2 H), 7.58 (d, *J* = 7.8 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.38–7.32 (m, 2 H), 7.29 (s, 1 H), 7.21–7.18 (m, 3 H), 7.12–7.06 (m, 2 H), 4.24 (t, *J* = 7.8 Hz, 1 H), 3.12 (qd, *J* = 13.7, 7.7 Hz, 2 H), 2.48 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.9, 144.5, 141.5, 140.6, 140.1, 139.4, 137.0, 136.8, 135.9, 129.5, 129.0, 128.7, 127.6, 127.1, 127.0, 126.1, 124.6, 123.7, 120.5, 119.9, 48.6, 40.0, 21.6, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}$: 361.1950; found: 361.1949.

2-Chloro-9-(4-methylbenzyl)-7-phenyl-9*H*-fluorene (5ah)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.019 g (0.050 mmol, 47%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15).

IR (ATR): 2970, 1738, 1447, 1365, 1228, 1216, 899, 527 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 7.9 Hz, 1 H), 7.68 (d, *J* = 8.1 Hz, 1 H), 7.62 (d, *J* = 8.1 Hz, 1 H), 7.56 (d, *J* = 7.8 Hz, 2 H), 7.46 (t, *J* = 7.6 Hz, 2 H), 7.39–7.34 (m, 2 H), 7.31 (s, 1 H), 7.29 (s, 2 H), 7.20–7.14 (m, 3 H), 4.25 (t, *J* = 7.7 Hz, 1 H), 3.18 (dd, *J* = 13.7, 7.5 Hz, 1 H), 3.07 (dd, *J* = 13.7, 7.7 Hz, 1 H), 2.41 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.9, 147.3, 141.2, 139.8, 139.1, 139.0, 136.2 (2 C), 132.4, 129.4, 129.1, 128.7, 127.5, 127.2, 127.1, 126.4, 125.3, 123.8, 120.8, 120.1, 49.0, 39.6, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{27}H_{22}Cl$: 381.1404; found: 381.1403.

2,7-Dimethyl-9-(4-methylbenzyl)-9*H*-fluorene (5ai)

Purified by column chromatography (silica gel, hexanes/CH_2Cl_2) to give a white solid; yield: 0.010 g (0.034 mmol, 33%); R_f = 0.20 (hexanes/CH_2Cl_2 85:15); mp 55–60 °C.

IR (ATR): 1738, 1365, 1264, 1216, 1009, 467 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.7 Hz, 1 H), 7.54 (s, 1 H), 7.19–7.14 (m, 5 H), 7.07 (s, 1 H), 7.00 (d, *J* = 7.7 Hz, 1 H), 6.97 (d, *J* = 7.8 Hz, 1 H), 4.14 (t, *J* = 7.6 Hz, 1 H), 3.15 (dd, *J* = 13.7, 7.1 Hz, 1 H), 2.95 (dd, *J* = 13.7, 8.3 Hz, 1 H), 2.44 (s, 3 H), 2.40 (s, 6 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 147.7, 144.0, 141.0, 138.2, 137.0, 136.6, 136.3, 135.7, 129.4, 128.9, 127.8, 127.0, 125.5, 124.6, 120.1, 119.4, 48.3, 39.9, 21.7, 21.5, 21.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{23}$: 299.1794; found: 299.1794.

Funding Information

This work was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council (NSERC) of Canada (Grant No. 418602-2013).

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611562.

References

(1) Willgerodt, C. *J. Prakt. Chem.* **1886**, *33*, 154.
(2) (a) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2008**, *108*, 5299. (b) Zhdankin, V. *Hypervalent Iodine Chemistry: Preparation, Structure, and Synthetic Applications of Polyvalent Iodine Compounds*; John Wiley & Sons: Chichester, **2014**. (c) Yoshimura, A.; Zhdankin, V. V. *Chem. Rev.* **2016**, *116*, 3328. (d) Wirth, T. *Hypervalent Iodine Chemistry*; Springer Verlag: Berlin, **2016**. (e) *The Chemistry of Hypervalent Halogen Compounds*, In *PATAI's Chemistry of Functional Groups*; Marek, I.; Olofsson, B.; Rappoport, Z., Ed.; Wiley: New York, **2019**.
(3) Lucas, H. J.; Kennedy, E. R. *Org. Synth.* **1942**, *22*, 69.
(4) Zhao, X. F.; Zhang, C. *Synthesis* **2007**, 551.
(5) (a) Montanari, V.; Resnati, G. *Tetrahedron Lett.* **1994**, *35*, 8015. (b) Bravo, P.; Montanari, V.; Resnati, G.; Desmarteau, D. D. *J. Org. Chem.* **1994**, *59*, 6093. (c) Yusubov, M. S.; Drygunova, L. A.; Zhdankin, V. V. *Synthesis* **2004**, 2289. (d) Podgorsek, A.; Jurisch, M.; Stavber, S.; Zupan, M.; Iskra, J.; Gladysz, J. A. *J. Org. Chem.* **2009**, *74*, 3133.
(6) (a) Yusubov, M. S.; Zhdankin, V. V. *Mendeleev Commun.* **2010**, *20*, 185. (b) Chen, J. M.; Zeng, X. M.; Middleton, K.; Zhdankin, V. V. *Tetrahedron Lett.* **2011**, *52*, 1952.
(7) (a) Varvoglis, A. *Synthesis* **1984**, 709. (b) Merkushev, E. B. *Russ. Chem. Rev.* **1987**, *56*, 826.
(8) Romero, R. M.; Wöste, T. H.; Muñiz, K. *Chem. Asian J.* **2014**, *9*, 972.
(9) (a) Zhao, Z.; Racicot, L.; Murphy, G. K. *Angew. Chem. Int. Ed.* **2017**, *56*, 11620. (b) Zhao, Z.; Britt, L. H.; Murphy, G. K. *Chem. Eur. J.* **2018**, *24*, 17002. (c) Zhao, Z.; Murphy, G. K. *Beilstein J. Org. Chem.* **2018**, *14*, 796.
(10) Depken, C.; Krätzschmar, F.; Breder, A. *Org. Chem. Front.* **2016**, *3*, 314.
(11) HVI-mediated reactions of styryl derivatives are prone to 1,2-phenyl shifts, which is also possible here; for further information see: (a) Singh, F. V.; Wirth, T. *Synthesis* **2013**, *45*, 2499. (b) Brown, M.; Kumar, R.; Rehbein, J.; Wirth, T. *Chem. Eur. J.* **2016**, *22*, 4030.
(12) (a) Ishibashi, Y.; Miyata, K.; Kitamura, M. *Eur. J. Org. Chem.* **2010**, *2010*, 4201. (b) Sakai, N.; Nakajima, T.; Yoneda, S.; Konakahara, T.; Ogiwara, Y. *J. Org. Chem.* **2014**, *79*, 10619. (c) Boo, B. H.; Lee, M.; Jeon, K.-S.; Kim, S.-J. *J. Phys. Chem. A* **2014**, *118*, 2269.
(13) (a) Greenhow, E. J.; McNeil, D.; White, E. N. *J. Chem. Soc.* **1952**, 986. (b) Gualtieri, F.; Teodori, E.; Bellucci, C.; Pesce, E.; Piacenza, G. *J. Med. Chem.* **1985**, *28*, 1621.
(14) (a) Claxton, G. P.; Grisar, J. M.; Roberts, E. M.; Fleming, R. W. *J. Med. Chem.* **1972**, *15*, 500. (b) Dow, R. L. WO9221660A1, **1992**. (c) Hamilton, G. S.; Mewshaw, R. E.; Bryant, C. M.; Feng, Y.; Endemann, G.; Madden, K. S.; Janczak, J. E.; Perumattam, J.; Stanton, L. W.; Yang, X. J.; Yin, Z. W.; Venkataramen, B.; Liu, D. Y. *J. Med. Chem.* **1995**, *38*, 1650. (d) Mahboobi, S.; Sellmer, A.; Pongratz, H.; Leonhardt, M.; Kraemer, O.; Boehmer, F.-D.; Kelter, G. WO2016020369A1, **2016**.
(15) (a) Fleckenstein, C. A.; Plenio, H. *Organometallics* **2008**, *27*, 3924. (b) Fleckenstein, C. A.; Kadyrov, R.; Plenio, H. *Org. Process Res. Dev.* **2008**, *12*, 475.
(16) (a) de Frutos, Ó.; Granier, T.; Gómez-Lor, B.; Jiménez-Barbero, J.; Monge, Á.; Gutiérrez-Puebla, E.; Echavarren, A. M. *Chem. Eur. J.* **2002**, *8*, 2879. (b) Kwag, G.; Park, E.; Lee, S. N. *J. Appl. Polym. Sci.* **2005**, *96*, 1335.
(17) Formation of 9-tolyl-9,10-dihydrophenanthrene was also considered. Given the symmetry elements found in the ^{13}C NMR spectrum of **5a**, and that the spectra matched previous reports (see ref. 20), we deemed its structure to be correct. For reference, the spectra of 9-tolyl-9,10-dihydrophenanthrene can be found here: Goerner, R. N.; Cote, P. N.; Vittimberga, B. M. *J. Org. Chem.* **1977**, *42*, 19.
(18) (a) Yamato, T.; Komine, M.; Matsuo, K. *J. Chem. Res., Synop.* **1997**, 82. (b) Yamato, T.; Komine, M.; Nagano, Y. *Org. Prep. Proced. Int.* **1997**, *29*, 300. (c) *Comprehensive Organic Synthesis, 1st ed*; Trost, B. M.; Fleming, I., Ed.; Pergamon: Oxford, **1991**. (d) Yamato, T.; Sakaue, N.; Shinoda, N.; Matsuo, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1193.
(19) Ohwada, T. *J. Am. Chem. Soc.* **1992**, *114*, 8818.
(20) Chen, J.; Li, Y.; Li, S.; Liu, J.; Zheng, F.; Zhang, Z.; Xu, Q. *Green Chem.* **2017**, *19*, 623.