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ARTICLE

Synthesis of Fluorenyl Alcohols *via* Cooperative Palladium/Norbornene Catalysis

Alessandra Casnati, Marco Fontana, Elena Motti* and Nicola Della Ca'*

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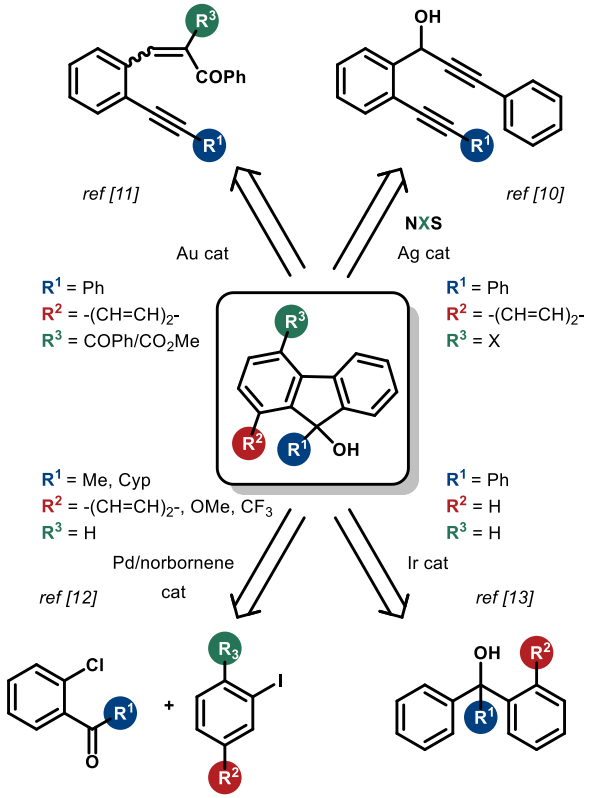
Herein we report a novel catalytic synthesis of substituted 9*H*-fluoren-9-ols starting from aryl iodides and secondary *ortho*-bromobenzyl alcohols in the presence of palladium/norbornene as catalytic system. The present protocol displays high functional group tolerance, mild reaction conditions and moderate to good yields. This transformation is based on two sequential pathways: i) the Pd(II)-mediated oxidation of the secondary alcohol to the corresponding ketone and ii) the Pd(0)/norbornene-catalyzed reaction of the *in situ* generated *ortho*-bromoacetophenone with the aryl iodide.

Introduction

The fluorene structural motif is prevalent in many pharmaceuticals, agrochemicals, and biologically active compounds.[1] Besides, they are widely used in the preparation of photoluminescent complexes, dyes and polymers,[2] optoelectronic materials,[3] and crystalline inclusion compounds.[4] Remarkably, 9-hydroxyfluorene derivatives were recently proposed as precursor for the preparation of new promising fluorene-derived compounds to be used as wakefulness enhancing agents in place of Modafinil-based drugs.[1a]

Traditionally, the 9-hydroxyfluorene core can be obtained through various oxidation strategies, such as a photocatalytic oxidation of the corresponding fluorene moiety by means of Pd/Bi/Sn-based nanocomposites[5] or $KMnO_4$ with a phase transfer oxidation protocol.[6] In both cases, the partial oxidation to fluorenol is difficult to achieve. Alternatively, 9-substituted-9*H*-fluorenol-9-ols may be obtained by reaction of the corresponding fluorenone with a Grignard type reagent.[7] Benzo[b]fluorenols can be synthesized under both thermal conditions,[8] or metal catalysed reactions.[9] The synthesis of benzo[a]fluorenols, bearing a substituent on the 9 position, may be achieved under catalytic reactions, using for example Ag[10] or Au[11] based catalysts (Scheme 1). Lautens and coworkers reported a straightforward synthesis of fluoren-9-ol derivatives, based on a palladium/norbornene catalyzed Catellani-type reaction, from aryl iodides and 2-chloroacetophenones.[12] More recently, Miura has reported a very efficient method to access 9-substituted-9H-fluoren-9-ols starting from 3-arylmethanols with Iridium-based catalysts.[13]



Scheme 1. Significative catalytic strategies to 9-substituted-9H-fluoren-9-ol derivatives.

In the framework of the C-H activation, Catellani reactions represent an outstanding tool for the one-pot *ortho* and *ipso* functionalization of aryl halides[14] and *ortho*-substituted boronic acids[15]. In the course of our research aimed at the development of new palladium/norbornene-based catalytic protocols for the synthesis of value-added compounds,[14e,16] we demonstrated that heterocycles containing the biaryl unit can be selectively synthesized by unsymmetrical coupling of an aryl iodide and a suitably *ortho*-substituted aryl bromide, followed by an intramolecular cyclization step.[17] In order to achieve this goal it

Department of Chemistry, Life Sciences and Environmental Sustainability and CIRCC, University of Parma, Parco Area delle Scienze 17/A, 43124 Parma, Italy. E-mail: elena.motti@unipr.it, nicola.dellaca@unipr.it

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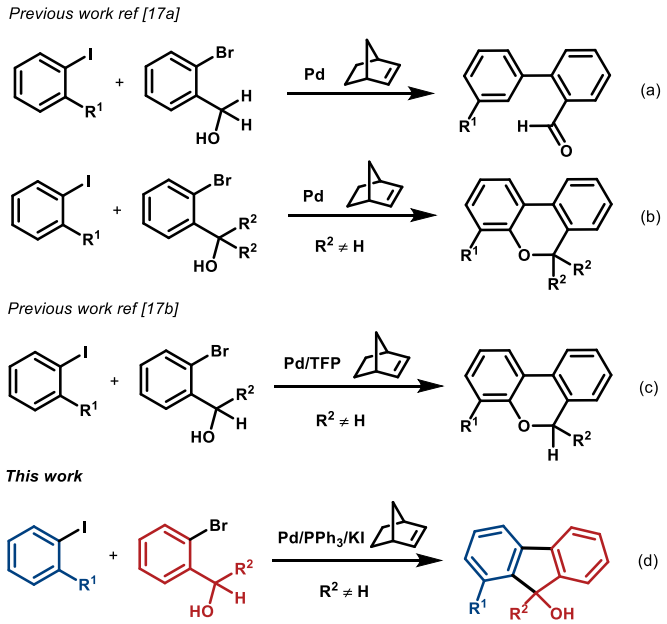
is essential to properly choose the two aryl halides, balancing their reactivity towards palladium(0) and palladium(II) species. It has been ascertained that *ortho*-substituted aryl iodides bearing electron-releasing groups and aryl bromides containing *ortho* chelating groups could be the winning combination for the selective construction of unsymmetrical heterocyclic biaryl derivatives.[14,16]

We have previously exploited the reactivity of 2-bromobenzyl alcohols with aryl iodides under Pd/norbornene catalysis, and we successfully obtained *ortho*-biaryl carbaldeydes (Scheme 2a) and 6H-dibenzopyrans (Scheme 2b) from primary and tertiary alcohols respectively with good to excellent yields in a one-pot procedure.[17a] The chemoselectivity of the reaction was essentially determined by the alcohol moiety: primary and tertiary alcohols led selectively to *ortho*-biaryl aldehydes and dibenzopyrans, respectively, while secondary alcohols generally afforded, under similar conditions, mixtures of *ortho*-biaryl ketones and dibenzopyrans. In continuation of this work, we have found that, adding TFP or analogous phosphine ligands to the reaction mixture, dibenzopyran derivatives were preferentially obtained from secondary benzyl alcohols (Scheme 2c).[17b] Among all the reported examples, the reaction of 2-iodotoluene and 1-(2-bromophenyl)-phenylmethanol gave 1-methyl-9-phenyl-9H-fluoren-9-ol in 11% yield as byproduct.[17a] Now we report a palladium/norbornene-based modified protocol for the selective synthesis of substituted 2-fluorenols from secondary *ortho*-bromobenzyl alcohols and *ortho*-substituted aryl iodides (Scheme 2d).

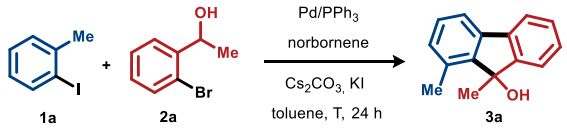


Scheme 2. Reactivity of 2-bromobenzyl alcohols in Catellani-type reactions.

Results and discussion

In the attempt to find appropriate conditions to make the reaction selective towards fluorenol derivatives, we cause to react 2-iodotoluene and 1-(2-bromophenyl)ethanol, using $Pd(OAc)_2/PPh_3$ as catalyst, toluene as solvent and Cs_2CO_3 as a base. Under these conditions, despite the low conversion of the aryl halides (<50%), the fluorenol product **3a** was obtained in 12% yield (Table 1, entry 1) together with the ketone derivative (3%) and the 6H-dibenzopyran (5%).

Table 1. Optimization study for the Pd/norbornene catalyzed synthesis of 9*H*-fluorenols.[a]



1a 2a 3a

Entry	Pd cat	PPh_3 (mol%)	KI (mol%)	T (°C)	Yield (%)[b] **3a**
1	$Pd(OAc)_2$	10	-	90	12
2	PdI_2	10	-	90	65
3	PdI_2	10	25	90	77
4	PdI_2	10	50	90	64
5	PdI_2	-	25	90	-
6	PdI_2	15	25	90	49
7	PdI_2	10	25	105	75
8	PdI_2	10	25	80	71
9	PdI_2	10	25	120	66
10	$PdCl_2$	10	25	120	63

[a] Reaction conditions: **1a** (0.34 mmol, 1.05 equiv), **2a** (0.32 mmol, 1.0 equiv), norbornene (0.16 mmol, 0.5 equiv), Pd cat (5 mol%), PPh_3, KI, Cs_2CO_3 (0.7 mmol, 2.2 equiv), in toluene (7 mL) under N_2, 24 h. [b] Determined by NMR analysis.

Surprisingly, PdI_2 in place of $Pd(OAc)_2$ gave 65% yield of **3a** (Table 1, entry 2). We found that a moderate addition of KI as an additive was beneficial to the reaction (Table 1, entry 3).[18] Doubling the amount of KI, the yield of **3a** slightly decreased to 64% (Table 1, entry 4). No conversion was obtained in the absence of a ligand (Table 1, entry 4), and among several triaryl phosphines, PPh_3 proved to be the best one, under these conditions. Moreover, the amount of the phosphine is critical to the outcome of the reaction and the best results were obtained with 10 mol% of PPh_3. In fact, when PPh_3 was increased up to 15 mol% the yield of **3a** dropped to 49% (Table 1, entry 6). The optimal reaction temperature was found to be 90 °C since at 105 °C a similar reaction outcome was observed (Table 1, entry 7), while higher or lower temperatures affected negatively the fluorenol formation (Table 1, entries 8 and 9). The use of $PdCl_2$ as catalyst gave results comparable to those obtained in the presence of PdI_2 (Table 1, entries 9 and 10).[19]

Under the optimized reaction conditions (Table 1, entry 3), the substrate scope was then examined (Scheme 3). First, *ortho*-substituted aryliodides were caused to react with 1-(2-bromophenyl)ethanol (**2a**). The increased steric hindrance of the *ortho* substituent (R^1) was well tolerated since the series Me, Et, *i*-Pr led respectively to 76, 71, 49% yield of the corresponding fluorenols (**3a-c**). High yield (79%) of benzo[*a*]fluorenol **3d** was obtained starting from the commercial 1-iodonaphtalene and substrate **2a**. Strongly electron donating (R^1 = OMe, OBn) groups gave satisfactory yields of the desired fluorenols (57-72%), while the reaction with 2-iodotrifluoromethylbenzene performed poorly (34%, **3h**). Double substituted aryl iodides in *ortho* and *para* positions were successfully converted into the corresponding tricyclic compounds **3e** and **3i** with 71 and 75% yield, respectively.

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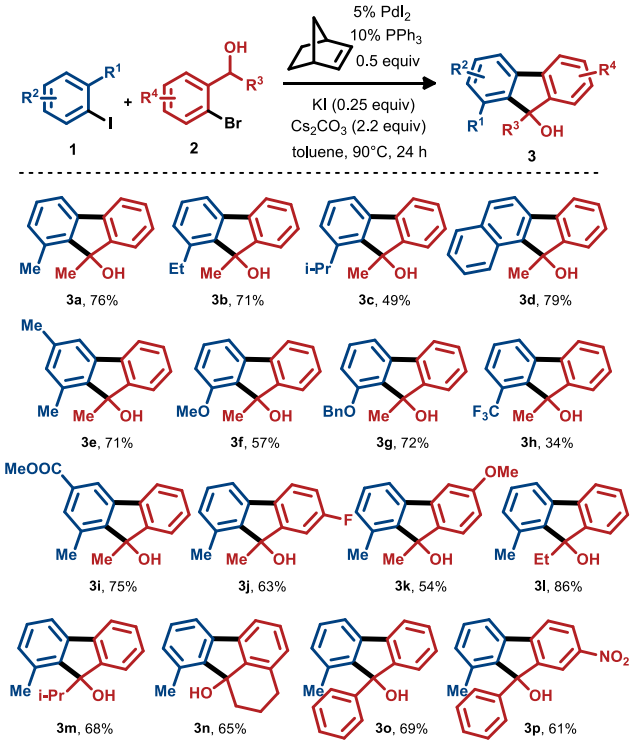
Differently substituted secondary bromobenzylalcohols were then considered. In particular, electron poor (R^4 = F) or electron rich (R^4 = OMe) bromoaryls were nicely tolerated in this transformation leading to synthetically useful yields of **3j** (63%), and **3k** (54%). The 2-chloro benzylalcohol **2p**, bearing a NO_2 group in *para* position to the Cl, readily afforded **3p** in 61% yield. Moreover, more sterically hindered secondary alcohols at the benzylic position (R^3) were converted with high efficacy. In fact, fluorenols **3l**, **3m** and **3o** bearing respectively Et, *i*-Pr and Ph in that position, were obtained in good to excellent yields. The fused tetracyclic compound **3n** was conveniently isolated in 65% yield. Curiously, starting from 1-iodo-2-methoxy-4-nitrobenzene and **2a**, dibenzopyran **4a** was obtained in 46% yield in place of the expected fluorenol. Primary alcohols in place of secondary ones led to very complex reaction mixture, with large amounts of norbornane-containing organic molecules coming mainly from aryl iodides, and small quantities of fluorenones in place of fluorenols.



Scheme 3. Reaction scope for the Pd/norbornene catalyzed synthesis of fluorenol **3**.

The formation of fluorenol **3** usually occurs with the total conversion of the aryl iodide, while the secondary bromobenzyl alcohol was often recovered at the end of the reaction (5-25%). Remarkably, not negligible amounts (see Experimental part for details) of 2-bromoacetophenones were frequently detected by GC-MS analysis of the final reaction mixture. The oxidation of secondary benzyl alcohols to the corresponding ketones can be readily performed by palladium species.[20] According to this consideration and taking advantage of our deep knowledge on Pd/norbornene catalyzed reactions involving 2-bromobenzyl alcohol derivatives and aryl iodides,[17a,b] a possible rational for the fluorenol formation is shown in Scheme 4.

At the beginning, the starting secondary alcohol could easily coordinate to the palladium(II) which is responsible for its oxidation to the corresponding ketone. After the formation of *ortho*-bromoacetophenone and Pd(0), the aryl iodide oxidatively adds to the metal forming the arylpalladium iodide **I**.[21] Norbornene readily coordinates and inserts into the arylpalladium bond of **I** affording intermediate **II**, displaying the metal and the aryl ring on the same side of the methylene bridge of the norbornyl ring. This *cis*,*exo* geometry allows a weak interaction through an η^2 coordination mode between the palladium atom and a double bond of the aromatic ring, in a sort of pre-organization favouring the ring closure to the arylalkylpalladacycle **III**, through C-H activation.[22] The resulting metallacycle **III** undergoes oxidative addition by the *in situ* formed *ortho*-bromoacetophenone, giving the Pd(IV) complex **IV**. A Csp^2–Csp^2 coupling by reductive elimination readily occurs to generate intermediate **V**, containing the biaryl unit. This intermediate, due to the steric hindrance around the metal center, undergoes a C–C cleavage with norbornene deinsertion yielding complex **VI**. Palladium is now in proper position to attack the carbonyl moiety, leading to intermediate **VII** which, after protonolysis, affords fluorenol **3** and liberates palladium in the oxidation state +2. By oxidation of a new alcohol molecule, *ortho*-bromoacetophenone is formed and palladium is reduced to the oxidation state 0, ready to start a new catalytic cycle. As we have previously observed in other Catellani-type reactions,[23] the presence of iodide anions coming from PdI_2 and KI exerts a positive effect to the reaction outcome.

According to the proposed redox process, 2-bromoacetophenone is formed at the beginning in a stoichiometric amount and is present in solution in very low concentration. The palladium(0) species resulting from the redox process is ready to start the palladium/norbornene cycle by the oxidative addition of the aryl iodide, leading after a few

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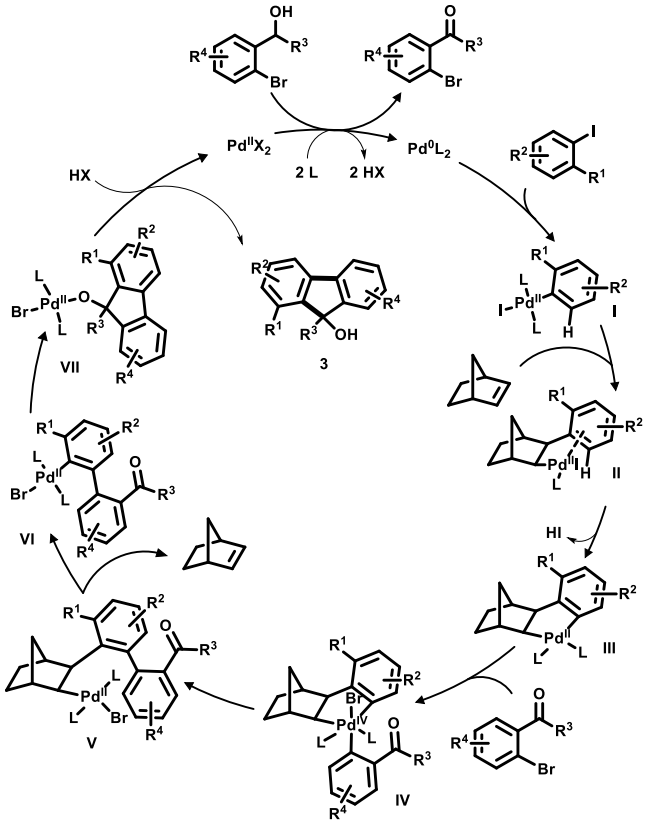


Scheme 4. Proposed reaction mechanism for the Pd/norbornene catalyzed synthesis of fluorenol **3**.

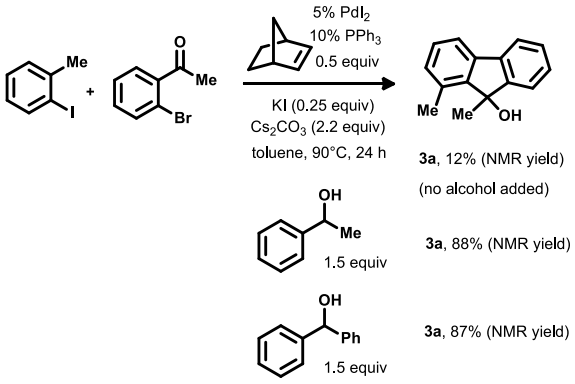
steps to the palladacycle, which selectively reacts with o-bromoacetophenone in spite of the its lower concentration with respect to those of the starting *o*-bromobenzyl alcohol.

The electron withdrawing character of the carbonyl substituent is essential to favor the oxidative addition step (from **III** to **IV**). At the end of the process Pd(II) is released in solution and another benzyl alcohol molecule can be oxidized to *o*-bromoacetophenone.

Thus, this catalytic cycle consists of two complementary processes (scheme 4): the former starts from a Pd(II) species and leads to the formation of Pd(0) involving the OH group of the *o*-bromobenzyl alcohol; the latter begins with the oxidative addition of the Pd(0) species by the aryl iodide, and ends up with the release of the metal in the oxidation state +2. The combination of the two stoichiometric reactions makes the entire process catalytic. *o*-Bromoacetophenone, coming from the first redox reaction, becomes substrate for the subsequent palladium-mediated synthesis of the fluorenyl alcohol.

To the best of our knowledge, this is a rare example of catalytic process in which two different oxidation states of the same metal (Pd(0) and Pd(II)) are employed and work synergistically in two different reactions.[24] In our case, we succeeded to efficiently synchronize two reactions and combine them in a single process where the "spent" catalyst at the end of a reaction is regenerated by the other one, and vice versa.

To take advantage from these results, we performed the reaction under the usual conditions with 2-iodotoluene as iodide, but using 2-bromoacetophenone in place of the secondary benzyl alcohol and in the presence of an excess of a readily oxidizable alcohol, such as 1-phenylethan-1-ol and diphenylmethanol (Scheme 5). Fluoren-9-ol **3a** was obtained in high yields (88 and 87%, respectively), comparable with the amount of acetophenone and diphenylketone, that were respectively obtained by oxidation of the starting sacrificial alcohol employed. When we tried the reaction of 2-iodotoluene and 2-bromoacetophenone in the absence of the alcohol, a very little amount of fluorenol derivative was instead observed (ca. 12%). Under our optimized reaction conditions, the formation of fluorenol derivatives from aryl iodides and 2-bromoacetophenones can be successfully performed in the presence of a readily oxidizable alcohol, providing a valid alternative to Lautens' protocol.[25]



Scheme 5. Reaction of **1a** and 2-bromoacetophenone in the presence of a stoichiometric amount of a sacrificial secondary alcohol.

Conclusions

In conclusion, we have developed a catalytic method to obtain fluorenol derivatives from aryl iodides and secondary 2-bromobenzylalcohols in the presence of the palladium/norbornene catalytic system. Fluorenols are formed in fair to good yields making this new Catellani-type transformation a viable synthetic method complementary to existing transition-metal catalyzed alternatives. The reaction proceeds through two independent stoichiometric reactions: 1) the Pd(II)-mediated oxidation of the secondary alcohol to the corresponding ketone and 2) the Pd(0)/norbornene-catalyzed reaction of the *in situ* generated *ortho*-bromoacetophenone with the aryl iodide. Notably, the reaction proceeds well starting from an aryl iodide and 2-bromoacetophenone in the presence of a stoichiometric amount of a sacrificial secondary alcohol.

Experimental

General methods

All chemicals were purchased from commercial sources and used as received, unless otherwise indicated. Toluene, THF and all other solvents were dried and stored over molecular sieves previously activated in oven at 300 °C overnight. Catalytic

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reactions were carried out under nitrogen using standard Schlenk technique. GC analyses were performed with an Agilent Technologies 7820A equipped with a FID detector and a 30 m capillary column. GC-MS analyses (m/z, relative intensity %) were performed with an Agilent Technologies 6890N gas chromatograph coupled to an 5973N mass selective detector (Agilent Technologies) working at 70 eV ionizing voltage. The conversion of the starting materials has been calculated via GC analyses using dodecane as internal standard. NMR spectra were recorded at 298 K, in $CDCl_3$ on Bruker AV300 and Bruker 400 MHz using the solvent as internal standard (7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR). The terms m, s, d, t, q, and quint represent multiplet, singlet, doublet, triplet, quadruplet, and quintuplet, respectively, and the term br means a broad signal. MS-ESI analyses were recorded on an Infusion Water Acquity Ultra Performance LC HO6UPS-823 M instrument (electrospray source, quadrupole analyzer). IR spectra were run on a Nicolet FT-IR 5700 spectrophotometer paired with a Diamond Smart Orbit accessory. Melting points were measured with an Electrothermal apparatus and are uncorrected. Elemental analyses were performed with a Carlo Erba EA 1108-Elemental Analyzer.

Preparation of secondary 2-bromobenzylalcohols

General procedure A: Grignard addition to 2-bromo benzaldehydes

In a flame dried 50 mL Schlenk tube, the required Grignard reagent (1.1 equiv.) was added dropwise to a solution of aldehyde (5 mmol, 1.0 equiv.) in anhydrous THF (0.35 M) at 0 °C under an atmosphere of N_2. The resulting mixture was stirred at 0 °C for 30 min and then at rt for 4 hours. The reaction was quenched with sat. NH_4Cl and the organic layer was separated. The aqueous layer was extracted with EtOAc (3×20mL). The combined organic layers were washed with brine (3×30mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residual was either purified by silica-gel column chromatography (hexane/EtOAc) or used without further purification.

General Procedure B: Reduction of 2-haloketones

Sodium borohydride (2.0 equiv.) was added portionwise to a solution of the required 2-aloketone (1.0 equiv.) dissolved in methanol (0.5 M) at 0 °C. The mixture was stirred at 0 °C until complete conversion was detected by TLC analysis. The mixture was concentrated under reduced pressure before being diluted with CH_2Cl_2, washed with water and brine and then dried over $MgSO_4$ to afford the product used without further purification.

Synthesis and characterization of 2j, 2k, 2l, 2m, 2p

1-(2-Bromo-5-fluorophenyl)ethanol (2j). 1-(2-Bromo-5-fluorophenyl)ethanol (**2j**) was synthesized according to the general procedure A without further purification. **2j** was obtained as a colorless oil (870 mg, Yield 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.27 (dd, *J* = 9.7, 3.1 Hz, 1H), 6.88 – 6.76 (m, 1H), 5.11 (q, *J* = 6.3 Hz, 1H), 3.00 (bs, 1H), 1.40 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.9 Hz), 147.1 (d, *J* = 6.7 Hz), 133.9 (d, *J* = 7.8 Hz), 115.9 (d, *J* = 22.8 Hz), 115.3 (d, *J* = 3.1 Hz), 114.0 (d, *J* = 23.9 Hz), 69.1, 23.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.49. Anal. Calcd for C_8H_8BrFO: C, 43.87; H, 3.68; Br, 36.48; F, 8.67; O, 7.30. Found: C 43.89, H 3.63.

1-(2-Bromo-4-methoxyphenyl)ethanol (2k). Acetyl chloride (1.2 equiv., 6 mmol, 430 µL) is added dropwise to a stirred suspension of 3-bromoanisole (1 equiv., 5 mmol, 630 µL) and $AlCl_3$ (6 mmol, 800 mg) in anhydrous CH_2Cl_2 (5 mL) at 0°C under an N_2 atmosphere in a flame dried 25 mL Schlenk tube. The resulting mixture was stirred at 0 °C for 1 hour and then at room temperature for 2 hours. The reaction was then diluted with 10 mL of H_2O and 5 mL of 2 N HCl, and extracted with CH_2Cl_2 (3×20mL). The combined organics were washed with brine and dried over $MgSO_4$. The reaction crude was purified by silica-gel column chromatography (hexane/EtOAc 90:10) to afford 1-(2-bromo-4-methoxyphenyl)ethanone (**2'k**) as a colorless oil (1.5 mmol, 350 mg, 30%). The spectroscopic data of **2'k** were consistent with literature values.[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.79 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.76 (s, 3H), 2.54 (s, 3H).

1-(2-Bromo-4-methoxyphenyl)ethanone **2'k** (1.5 mmol, 350 mg) was employed as starting material in the general procedure B to afford 1-(2-bromo-4-methoxyphenyl)ethanol **2k** as a colorless oil (333 mg, Yield 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.7 Hz, 1H), 7.00 (d, *J* = 2.6 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.5 Hz, 1H), 5.10 (q, *J* = 6.4 Hz, 1H), 3.74 (s, 3H), 3.15 (bs, 1H), 1.38 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.9, 136.8, 127.2, 121.8, 117.6, 113.8, 68.5, 55.5, 23.7. Anal. Calcd for $C_9H_{11}BrO_2$: C, 46.78; H, 4.80; Br, 34.58; O, 13.85. Found: C 46.84, H 4.78.

1-(2-Bromophenyl)propan-1-ol (2l). 1-(2-Bromophenyl)propan-1-ol (**2l**) was synthesized according to the general procedure A. The reaction crude was purified by silica-gel column chromatography (hexane/EtOAc 90:10) to afford **2l** as a colorless oil (467 mg, Yield 51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9, 1.3 Hz, 2H), 7.30 (td, *J* = 7.7, 0.9 Hz, 1H), 7.09 (td, *J* = 7.7, 1.7 Hz, 1H), 4.97 (dd, *J* = 7.7, 4.7 Hz, 1H), 2.77 (bs, 1H), 1.90 – 1.55 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 132.6, 128.7, 127.7, 127.5, 122.1, 74.1, 30.6, 10.1. Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.15; Br, 37.15; O, 7.44. Found: C 50.29, H 5.11.

1-(2-Bromophenyl)-2-methylpropan-1-ol (2m). 1-(2-Bromophenyl)-2-methylpropan-1-ol (**2m**) was synthesized according to the general procedure A. The reaction crude was purified by silica-gel column chromatography (hexane/EtOAc 90:10) to afford **2m** as a yellowish oil (228 mg, Yield 20%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (td, *J* = 7.8, 1.5 Hz, 2H), 7.37 – 7.28 (m, 1H), 7.16 – 7.07 (m, 1H), 4.86 (d, *J* = 5.8 Hz, 1H), 2.15 – 1.96 (m, 1H (bs, OH) and 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.94 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0, 132.7, 128.8, 128.4, 127.5, 122.8, 77.6, 34.1, 19.6, 16.9. Anal. Calcd for $C_{10}H_{13}BrO$: C, 52.42; H, 5.72; Br, 34.88; O, 6.98. Found: C 52.48, H 5.69.

(2-Chloro-5-nitrophenyl)(phenyl)methanol (2p). (2-Chloro-5-nitrophenyl)(phenyl)methanol (**2p**) was synthesized according to the general procedure B. Compound **2p** was obtained as dark yellow oil (301 mg, Yield 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61

(d, *J* = 2.7 Hz, 1H), 8.04 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.45 (d, *J* = 8.7 Hz, 1H), 7.39 – 7.24 (m, 5H), 6.12 (s, 1H), 3.13 (bs, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 143.0, 140.8, 139.0, 130.5, 128.8, 128.5, 127.2, 123.4, 122.9, 72.4. Anal. Calcd for $C_{13}H_{10}ClNO_3$: C, 59.22; H, 3.82; Cl, 13.45; N, 5.31; O, 18.20. Found: C 59.26, H 3.80, N 5.37.

General procedure for the catalytic synthesis of fluorenols 3

Cesium carbonate (229 mg, 0.70 mmol, 2.2 equiv) is heated at 110 °C under vacuum in a Schlenk type tube for 1.5 h. After cooling to room temperature the tube is filled with nitrogen, evacuated and back-filled with nitrogen three times. A toluene solution (7 ml) of the aryl iodide (0.34 mmol), aryl bromide (0.32 mmol) and norbornene (15.6 mg, 0.16 mmol) is added to the Schlenk, followed by PdI_2 (6.0 mg, 0.016 mmol), PPh_3 (8.8 mg, 0.033 mmol) and KI (13.8 mg, 0.08 mmol) as solids. The reaction flask is stirred under nitrogen at r.t. for 10 minutes and then heated into an oil bath at 90 °C for 24 h. After cooling to room temperature, the mixture is diluted with ethyl acetate (50 ml), transferred into a separating funnel and washed twice with brine (50 ml). The resulting solution is dried over Na_2SO_4 and the solvent was removed under vacuum. The crude mixture is purified by flash column chromatography on silica gel using a mixture of n-hexane/EtOAc.

Characterization of fluorenols 3

1,9-Dimethyl-9H-fluoren-9-ol (3a). 1,9-Dimethyl-9H-fluoren-9-ol (**3a**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3a** (51 mg, 76%) as a white solid; m.p. (hexane) 176.2 – 177.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 2.60 (s, 3H), 2.21 (bs, 1H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 146.6, 139.1, 138.6, 135.5, 130.4, 128.9, 128.8, 128.0, 123.0, 119.9, 117.6, 81.0, 24.6, 17.9. MS (ESI) calcd for $C_{15}H_{13}^+$ $(M\text{-}OH)^+$ 193.10, found 193.16. IR (neat) 3293, 2972, 1453, 1093, 1075, 765, 758, 741 cm^{-1}. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71; O, 7.61. Found: C 85.72, H 6.70.

1-Ethyl-9-methyl-9H-fluoren-9-ol (3b). 1-Ethyl-9-methyl-9H-fluoren-9-ol (**3b**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3b** (51 mg, 71%) as a white solid; m.p. (hexane) 181.3 – 182.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.53 – 7.48 (m, 1H), 7.46 (d, further splitting, *J* = 7.4, 1H), 7.37 – 7.27 (m, 3H), 7.15 (d, *J* = 7.7 Hz, 1H), 3.02 (dq, *J* = 7.5, 1.7 Hz, 2H), 2.03 (bs, 1H), 1.79 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 146.0, 142.0, 139.1, 138.6, 129.1, 128.9, 128.6, 128.0, 123.0, 119.9, 117.5, 81.2, 26.0, 23.9, 15.9. MS (ESI) calcd for $C_{16}H_{15}^+$ $(M\text{-}OH)^+$ 207.12, found 207.20. IR (neat) 3276, 2970, 1431, 1088, 1074, 765, 750, 746 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C 85.60, H 7.23.

1-Isopropyl-9-methyl-9H-fluoren-9-ol (3c). 1-Isopropyl-9-methyl-9H-fluoren-9-ol (**3c**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3c** (37 mg, 49%) as a white solid; m.p. (hexane) 188.3 – 189.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.1 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.45 (d, further splitting, *J* = 7.3, 1H), 7.38 – 7.22 (m, 4H), 3.81 (dt, *J* = 13.7, 6.9 Hz, 1H), 2.06 (bs, 1H), 1.79 (s, 3H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.31 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 147.2, 145.2, 138.9, 138.6, 129.3, 128.8, 128.0, 125.8, 123.0, 119.9, 117.5, 81.2, 28.1, 26.6, 24.5, 24.4. MS (ESI) calcd for $C_{17}H_{17}^+$ $(M\text{-}OH)^+$ 221.13, found 221.23. IR (neat) 3279, 3056, 2978, 1409, 1074, 1067, 769, 756, 740 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.62; O, 6.71. Found: C 85.70, H 7.56.

11-Methyl-11H-benzo[a]fluoren-11-ol (3d). 11-Methyl-11H-benzo[a]fluoren-11-ol (**3d**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3d** (62 mg, 79%) as a light yellow solid; m.p. (hexane) 176.0 – 177.4 °C. The spectroscopic data of **3d** were consistent with literature values.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.95 – 7.85 (m, 2H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.51 – 7.45 (m, 1H), 7.43 – 7.30 (m, 2H), 2.47 (bs, 1H), 1.90 (s, 3H). MS (ESI) calcd for $C_{18}H_{13}^+$ $(M\text{-}OH)^+$ 229.10, found 229.16. IR (neat) 3205, 3053, 2973, 2925, 1607,1091, 1080, 750, 643 cm^{-1}.

1,3,9-Trimethyl-9H-fluoren-9-ol (3e). 1,3,9-Trimethyl-9H-fluoren-9-ol (**3e**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3e** (51 mg, 71%) as a white solid; m.p. (hexane) 179.7 – 180.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.2 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.25 (s, 1H), 6.87 (s, 1H), 2.52 (s, 3H), 2.37 (s, 3H), 1.97 (bs, 1H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 143.8, 139.3, 138.7, 138.6, 135.2, 131.2, 128.7, 127.9, 122.9, 119.8, 118.3, 80.7, 24.7, 21.4, 17.8. MS (ESI) calcd for $C_{16}H_{15}^+$ $(M\text{-}OH)^+$ 207.12, found 207.19. IR (neat) 3271, 2978, 1413, 1097, 760, 751, 743 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C 85.73, H 7.18.

1-Methoxy-9-methyl-9H-fluoren-9-ol (3f). 1-Methoxy-9-methyl-9H-fluoren-9-ol (**3f**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (90:10) plus 1% of Et_3N as eluent to give **3f** (41 mg, 57%) as a yellow solid; m.p. (hexane) 98.6 – 100.1 °C. The spectroscopic data of **3f** were consistent with literature values.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.62 – 7.56 (m, 1H), 7.42 – 7.32 (m, 3H), 7.31 – 7.27 (m, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 3.97 (s, 3H), 2.91 (bs, 1H), 1.89 (s, 3H). MS (ESI) calcd for $C_{15}H_{13}O^+$ $(M\text{-}OH)^+$ 209.26, found 209.22. IR (neat) 3336, 2995, 1602, 1259, 1128, 1075, 750, 582 cm^{-1}.

1-(Benzyloxy)-9-methyl-9H-fluoren-9-ol (3g). 1-(Benzyloxy)-9-methyl-9H-fluoren-9-ol (**3g**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (90:10) plus 1% of Et_3N as eluent to give **3g** (70 mg, 72%) as a light yellow solid; m.p. (hexane) 127.6 – 128.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 15.1, 6.5 Hz, 2H), 7.50 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.25 (m, 5H), 6.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 5.23

(s, 2H), 2.75 (bs, 1H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 149.8, 141.0, 138.9, 136.9, 135.8, 130.4, 128.80, 128.77, 128.2, 128.1, 127.3, 123.2, 120.3, 113.2, 111.6, 80.4, 70.0, 25.6. MS (ESI) calcd for $C_{21}H_{17}O^+$ $(M\text{-}OH)^+$ 285.13, found 285.22. IR (neat) 3280, 3021, 2920, 1612, 1470, 1311, 1211, 1139, 1070, 830, 601 cm^{-1}. Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00; O, 10.58. Found: C 83.40, H 6.01.

9-Methyl-1-(trifluoromethyl)-9H-fluoren-9-ol (3h). 9-Methyl-1-(trifluoromethyl)-9H-fluoren-9-ol (**3h**) was obtained following the general procedure. The conversion of 1-(2-bromophenyl)ethanol was 79%. 1-(2-Bromophenyl)ethanone was detected by GC-MS analysis (42%). The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3h** (29 mg, 34%) as a white solid; m.p. (hexane) 116.4 – 118.6 °C. The spectroscopic data of **3h** were consistent with literature values.[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.1 Hz, 1H), 7.67 – 7.63 (m, 1H), 7.61 – 7.55 (m, 2H), 7.51 – 7.47 (m, *J* = 11.9, 4.3 Hz, 1H), 7.42 – 7.36 (m, 2H), 1.86 (s, 3H), 1.69 (bs, 1H). MS (ESI) calcd for $C_{15}H_{10}F_3^+$ $(M\text{-}OH)^+$ 247.07, found 247.12. IR (neat) 3334, 2923, 1314, 1138, 767 cm^{-1}.

Methyl 9-hydroxy-1,9-dimethyl-9H-fluorene-3-carboxylate (3i). Methyl 9-hydroxy-1,9-dimethyl-9H-fluorene-3-carboxylate (**3i**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (85:15) plus 1% of Et_3N as eluent to give **3i** (64 mg, 75%) as a white solid; m.p. (hexane) 192.3 – 194.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 0.9 Hz, 1H), 7.66 (dd, *J* = 1.4, 0.7 Hz, 1H), 7.64 – 7.60 (m, 1H), 7.55 – 7.51 (m, 1H), 7.40 – 7.30 (m, 2H), 3.83 (s, 3H), 2.61 (s, 3H), 2.10 (bs, 1H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 151.3, 150.6, 139.5, 137.8, 135.5, 131.9, 130.5, 129.2, 128.6, 123.1, 120.3, 118.7, 80.9, 52.2, 24.7, 17.9. MS (ESI) calcd for $C_{17}H_{15}O_2^+$ $(M\text{-}OH)^+$ 251.11, found 251.22. IR (neat) 3381, 2987, 2943, 2385, 1619, 1608, 1479, 1210, 1132, 1098, 833, 603 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; O, 17.89. Found: C 76.04, H 6.03.

7-Fluoro-1,9-dimethyl-9H-fluoren-9-ol (3j). 7-Fluoro-1,9-dimethyl-9H-fluoren-9-ol (**3j**) was obtained following the general procedure. The conversion of 1-(2-bromo-5-fluorophenyl)ethanol was complete. 1-(2-Bromo-5-fluorophenyl)ethanone was detected by GC-MS analysis (35%). The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3j** (46 mg, 63%) as a white solid; m.p. (hexane) 159.1 – 160.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.3, 4.9 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.08 – 6.99 (m, *J* = 9.2, 8.3, 2.4 Hz, 2H), 2.58 (s, 3H), 1.86 (bs, 1H), 1.77 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (d, *J* = 246.6 Hz), 152.9 (d, *J* = 7.2 Hz), 146.4, 138.4, 135.6, 134.5 (d, *J* = 2.5 Hz), 121.2 (d, *J* = 8.6 Hz), 130.2, 129.1, 117.3, 115.9 (d, *J* = 23.1 Hz), 110.7 (d, *J* = 23.0 Hz), 80.9, 24.7, 17.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.47. MS (ESI) calcd for $C_{15}H_{12}F^+$ $(M\text{-}OH)^+$ 211.09, found 211.14. IR (neat) 3297, 2928, 1612, 1466, 1489, 1302, 1120, 806, 601 cm^{-1}. Anal. Calcd for $C_{15}H_{13}FO$: C, 78.93; H, 5.74; F, 8.32; O, 7.01. Found: C 78.85, H 5.80.

6-Methoxy-1,9-dimethyl-9H-fluoren-9-ol (3k). 6-Methoxy-1,9-dimethyl-9H-fluoren-9-ol (**3k**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (85:15) plus 1% of Et_3N as eluent to give **3k** (41 mg, 54%) as a dark yellow solid; m.p. (hexane) 88.3 – 89.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, *J* = 7.9, 4.4 Hz, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.02 (m, 2H), 6.79 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.81 (s, 3H), 2.57 (s, 3H), 2.17 (bs, 1H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6, 147.4, 142.9, 140.1, 138.9, 135.5, 130.6, 128.7, 123.7, 117.5, 113.5, 105.4, 80.5, 55.6, 24.7, 17.9. MS (ESI) calcd for $C_{16}H_{15}O^+$ $(M\text{-}OH)^+$ 223.11, found 223.14. IR (neat) 3275, 2926, 2385, 1608, 1472, 1311, 1215, 1134, 1075, 837, 607 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71; O, 13.32. Found: C 79.87, H 6.70.

9-Ethyl-1-methyl-9H-fluoren-9-ol (3l). 9-Ethyl-1-methyl-9H-fluoren-9-ol (**3l**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3l** (62 mg, 86%) as a white solid; m.p. (hexane) 116.9 – 117.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 1H), 7.46 – 7.41 (m, 2H), 7.36 – 7.26 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 2.53 (s, 3H), 2.45-2.19 (m, 2H), 2.12 (bs, 1H), 0.38 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 144.8, 140.2, 140.0, 135.7, 130.3, 128.9, 128.8, 127.9, 123.1, 119.7, 117.4, 84.9, 30.4, 17.9, 8.4. MS (ESI) calcd for $C_{16}H_{15}^+$ $(M\text{-}OH)^+$ 207.12, found 207.24. IR (neat) 3301, 2969, 1454, 1015, 765, 802, 746 cm^{-1}. Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19; O, 7.13. Found: C 85.60, H 7.21.

9-Isopropyl-1-methyl-9H-fluoren-9-ol (3m). 9-Isopropyl-1-methyl-9H-fluoren-9-ol (**3m**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3m** (48 mg, 68%) as a pale yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 2.84-2.76 (m, 1H), 2.57 (s, 3H), 2.01 (bs, 1H), 1.31 (d, *J* = 6.8 Hz, 3H), 0.29 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 146.7, 140.6, 140.1, 135.0, 130.6, 128.8, 128.6, 127.1, 125.2, 119.7, 117.2, 87.3, 34.3, 18.1, 17.7, 17.2. MS (ESI) calcd for $C_{17}H_{17}^+$ $(M\text{-}OH)^+$ 221.13, found 221.16. IR (neat) 3279, 3051, 2978, 1400, 1067, 761, 752, 729 cm^{-1}. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61; O, 6.71. Found: C 85.60, H 7.57.

7-Methyl-4,5,6,6a-tetrahydrofluoranthen-6a-ol (3n). 7-Methyl-4,5,6,6a-tetrahydrofluoranthen-6a-ol (**3n**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3n** (46 mg, 65%) as a viscous transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.13 – 7.05 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 4.96 (dd, *J* = 10.4, 5.5 Hz, 1H), 2.94 – 2.78 (m, 2H), 2.57 – 2.47 (m, 1H), 2.29 (s, 3H), 2.15 – 1.96 (m, 2H), 1.88 – 1.74 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.2, 135.6, 131.0, 130.75, 130.7, 128.0, 127.9, 126.6, 123.4, 121.4, 121.3, 120.1, 74.0, 29.4, 28.7, 21.0, 16.0. MS (ESI) calcd for $C_{17}H_{15}^+$ $(M\text{-}OH)^+$ 219.12, found 219.16. IR (neat) 3288, 3033, 2967, 1432, 1232, 1075, 762, 750, 746 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82; O, 6.77. Found: C 86.37, H 6.89.

1-Methyl-9-phenyl-9H-fluoren-9-ol (3o). 1-Methyl-9-phenyl-9H-fluoren-9-ol (**3o**) was obtained following the general procedure. The crude was purified by flash column chromatography using hexane/ethyl acetate (95:5) plus 1% of Et_3N as eluent to give **3o** (60 mg, 69%) as a white solid; m.p. (hexane) 137.5 – 138.7 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.39 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.17 (m, 5H), 7.05 (d, *J* = 7.5 Hz, 1H), 2.28 (bs, 1H), 2.12 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.3, 147.4, 142.3, 140.3, 139.2, 136.3, 130.6, 129.5, 129.0, 128.4, 128.3, 127.0, 125.2, 124.5, 120.1, 117.6, 84.2, 18.0. MS (ESI) calcd for $C_{20}H_{15}^+$ $(M\text{-}OH)^+$ 255.12, found 255.20. IR (neat) 3544, 2922, 2360, 1445, 1066, 765, 746, 693 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92; O, 5.87. Found: C 88.18, H 5.97.

1-Methyl-7-nitro-9-phenyl-9H-fluoren-9-ol (3p). 1-Methyl-7-nitro-9-phenyl-9H-fluoren-9-ol (**3p**) was obtained following the general procedure. The conversion of (2-chloro-5-nitrophenyl)(phenyl)methanol was 70%. (2-Chloro-5-nitrophenyl)(phenyl)methanone was detected by GC-MS analysis (5%). The crude was purified by flash column chromatography using hexane/ethyl acetate (90:10) plus 1% of Et_3N as eluent to give **3p** (62 mg, 61%) as a white solid; m.p. (hexane) 199.8 – 202.0 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.35 – 7.26 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 2.55 (bs, 1H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 148.6, 148.0, 145.6, 140.6, 138.0, 137.0, 132.7, 130.1, 128.7, 127.7, 125.2, 125.1, 120.4, 120.2, 119.0, 83.9, 17.9. MS (ESI) calcd for $C_{20}H_{14}NO_2^+$ $(M\text{-}OH)^+$ 300.10, found 300.12. IR (neat) 3528, 3462, 2924, 1596, 1508, 1325, 770, 761, 667 cm^{-1}. Anal. Calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41; O, 15.13. Found: C 75.61, H 4.80, N 4.35.

4-Methoxy-6-methyl-2-nitro-6*H*-dibenzopyran (4a). 4-Methoxy-6-methyl-2-nitro-6*H*-dibenzopyran (**4a**) was obtained following the general procedure at 105 °C. The crude was purified by flash column chromatography using hexane/ethyl acetate (80:20) plus 1% of Et_3N as eluent to give **4a** (40 mg, 46%) as a dark yellow solid; m.p. (hexane) 172.3 – 174.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 2.3 Hz, 1H), 7.81 – 7.73 (m, *J* = 11.7, 4.9 Hz, 2H), 7.47 – 7.36 (m, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 5.51 (q, *J* = 6.6 Hz, 1H), 4.00 (s, 3H), 1.66 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.2, 142.2, 135.0, 129.4, 128.8, 127.2, 124.5, 122.9, 122.7, 111.8, 106.5, 75.3, 56.6, 21.1. MS (ESI) calcd for $C_{15}H_{14}NO_4^+$ $(M+H)^+$ 272.09, found 272.11. Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16; O, 23.59. Found: C 66.47, H 4.80, N 5.28.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

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