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Ligand-Free Ru-Catalyzed Direct sp^3 C-H Alkylation of Fluorene Using Alcohols

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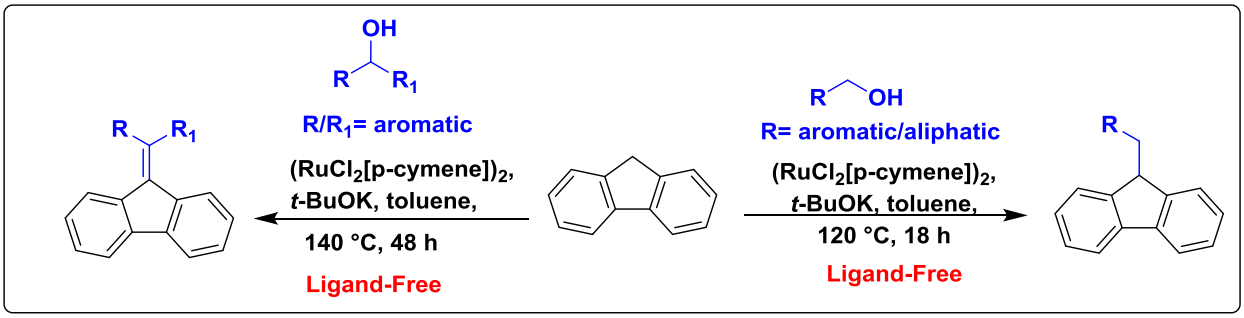


ABSTRACT: The sp^3 C-H alkylation of 9*H*-fluorene using alcohol and Ru-catalyst via borrowing hydrogen concept has been described. This reaction was catalyzed by [Ru(p-cymene)Cl_2]$_2$ complex (3 mol%) and exhibited a broad reaction scope with different alcohols, allowing primary and secondary alcohols to be employed as non-hazardous and greener alkylating agents with the formation of environmentally benign water as a by-product. A variety of 9*H*-fluorene underwent selective and exclusive mono-C9-alkylation with primary alcohols in good to excellent isolated yield (26 examples, 50–92% yield). Whereas this reaction with

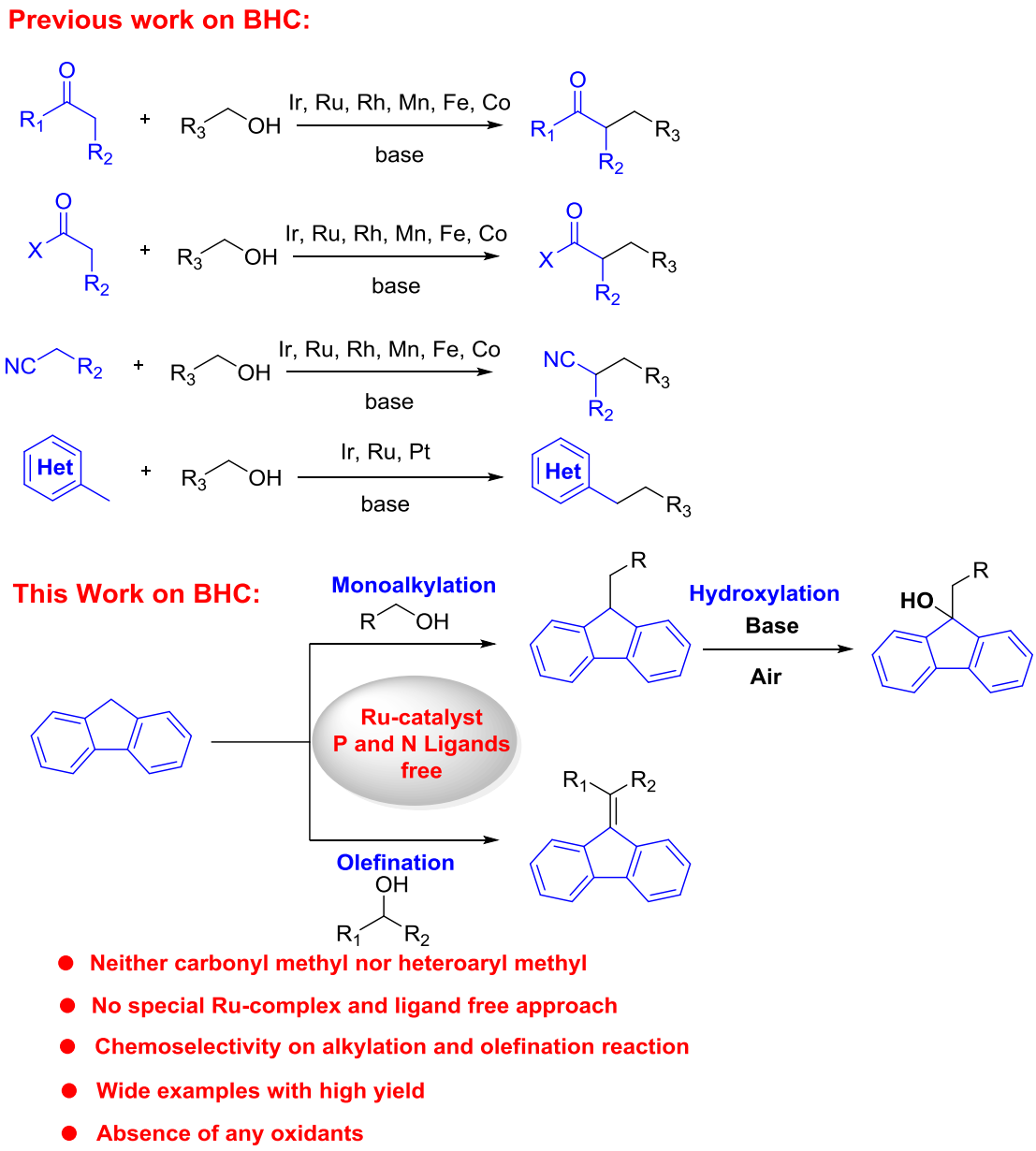
secondary alcohols in the absence of any external oxidants furnished the tetrasubstituted alkene as major product. Further, a base mediated C-H hydroxylation of the synthesized 9*H*-fluorene derivatives afforded 9*H*-hydroxy functionalized quaternary fluorene derivatives in excellent yield.

INTRODUCTION

Transition-metal catalyzed borrowing hydrogen (BH) or hydrogen auto-transfer methodology is an attractive and greener approach for the formation of a C−C bond in modern synthetic methods.[1] In the BH process, multiple transformations occur sequentially in one step *via* a domino manner. Typically, this methodology involves the abstraction of hydrogen from alcohol by transition-metals to generate respective carbonyl compounds *in situ*, which then subsequently undergoes Aldol or Knoevenegal type condensation reaction with nucleophilic enolate to form C=C bond. In the end, metal-catalyzed saturation of the C=C by the addition of "borrowed" hydrogen to form the desired α-branched carbonyl compounds. As a result, metal promotes the concomitant redox process in the BH process to afford the product with the formation of environmentally benign H_2O as a sole by-product. Due to increasing demand for environmentally benign chemical procedures, the direct substitution of alcohol through a BH strategy has recently received noteworthy interest and it is considered one of the key green chemistry research approaches by pharmaceutical manufacturers.[2] An atom economy and efficiency have been increased by using renewable, and inexpensive alcohol as an alkylating agent, which avoids the use of mutagenic alkyl halides and sulfonate esters as alkylating agents, resulting in water as the sole by-product.[1] The α-alkylation of carbonyl compounds using various primary and secondary alcohols catalyzed by transition metal-catalyst has been well studied. In literature, homogeneous metal catalysts such as Ru[3] and Ir[4] complexes were known to be

effective catalysts for this reaction. Other metal complexes such as Rh,[5] Au,[6] Cu,[7] Ni,[8] Fe,[9] Mn,[10] Pd,[11] and Os[12] were also reported as the alternative catalysts (Scheme 1).

Scheme 1. State of art for the borrowing hydrogen concept



Furthermore, this transformation uses a limited group of compounds containing activated methylene groups adjacent to electron-withdrawing substituents. For example, amides[13] and

nitriles[14] were alkylated at the α-position using various alcohols in the presence of a metal catalyst to afford the corresponding α-branched derivatives. Seminal reports on the catalytic alkylation of methyl heteroarenes system with various alcohols by Ru, Ir, Ni, and Pt have been reported (Scheme 1).[15]

From the survey of the BH strategy, it is known that a selective group of compounds *viz* ketone, ester, amide, nitrile, and heteroarene possessing methylene or methyl were frequently used as the synthetic starting material for alkylation reaction using alcohols. The majority of the reported BH method has been catalyzed by the specially made metal complexes or *in situ* generations of the metal complexes by the reaction of the metal precursor with the ligands. In this regard, the development of the ligand-free BH approach for the alkylation reaction using alcohol is highly desirable. In this concept, Lang and co-workers reported the ligand-free Ru-catalyzed alkylation of methylazarenes with alcohols.[15c] Besides, developing a BH strategy to other substrates possessing methylene functionality is also challenging in this area. Thus, we envisioned from the literature that the alkylation of the methylene group of the fluorene is not studied for the BH concept. A specific interest of our research group relay on methylene alkylation of fluorene is due to the widespread application in pharmaceutical and materials.[16] In the last few decades, the synthesis of 9-monoalkylated and 9,9-dialkylated fluorene monomers have attracted more attention by chemist as they are key starting material for poly(alkylfluorene)s due to their chemical, physical, and photoelectric properties.[17] In literature, many methods are available for the synthesis of 9,9-dialkylated fluorene by using excess alkyl halides in the presence of a strong base such as *n*-BuLi[18] or NaOH[19]. But there are only a few methods available for selective 9-monoalkylation. A method for selective 9-monoalkylation of fluorene was carried out with excess use of alkyl halides in the presence of *n*-BuLi,[18] having very harsh reaction conditions

with poor yield. In another method dehydrative alkylation of fluorene was carried out by using only benzyl alcohol as an alkylating reagent under microwave condition at elevated temperature[20]. However, this method is unsuccessful with aliphatic alcohols. Very recently, Qing Xu reported CsOH mediated selective synthesis of 9-monoalkylated fluorene by dehydrative C-alkylation with primary and secondary alcohols, which is catalyzed by aldehyde or ketone.[21]

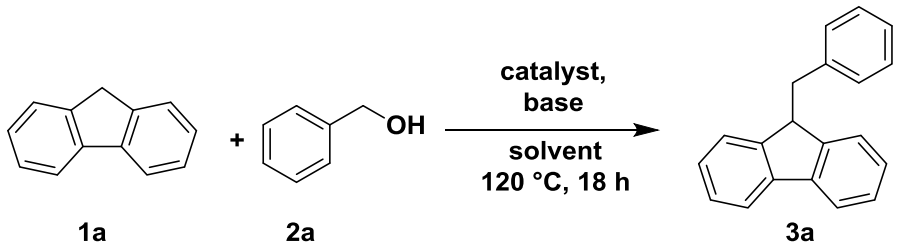
Although several other transformations are known for 9-monoalkylation/alkenylation of fluorenes, Ruthenium-catalyzed alkylation of 9*H*-fluorene with primary and secondary alcohols for the synthesis of 9-substituted products under ligand-free condition has not been developed. Herein, we report the first example of the base-metal-catalyzed practical route to the synthesis of 9-monosubstituted fluorene by using aliphatic or aromatic alcohols under ligand-free conditions. Moreover, C-H hydroxylation of fluorene derivatives promoted by the base is also described in this work.

RESULT AND DISCUSSIONS

Initially, the reaction optimization for the 9-alkylation reaction of 9*H*-Fluorene **1a** with benzyl alcohol **2a** using Ru-catalyst was performed by varying the concentrations of the catalyst, base, and solvent (Table 1). A control experiment was performed for this reaction using 1.5 equivalent of *t*-BuOK in absence of a catalyst showed 45% of 9-benzyl-9*H*-fluorene **3a** in isolated yield (Table 1, entry 1). In another control experiment, a solution of 0.3 mmol of 9*H*-Fluorene, 0.45 mmol of benzyl alcohol and 3 mol% of $[Ru(p\text{-cymene})Cl_2]_2$] of catalyst were heated at 120 °C in the absence of base, and we found that there is no product formation (Table 1, entry 2). The absence of 9-benzyl-9*H*-fluorene **3a**, emphasizes the importance of the *t*-BuOK as a base for this reaction (Table 1, entry 2). An excess of the base (> 3 eq.) under the above reaction condition results in a complicated reaction mixture. The best optimized condition was

obtained by heating the reaction mixture of 9*H*-Fluorene **1a** and benzyl alcohol **2a**, in the presence of 1.5 equivalent of *t*-BuOK and 3 mol% of [[Ru(p-cymene)Cl_2]$_2$] catalyst at 120 °C for 18 hrs, which afford 9-

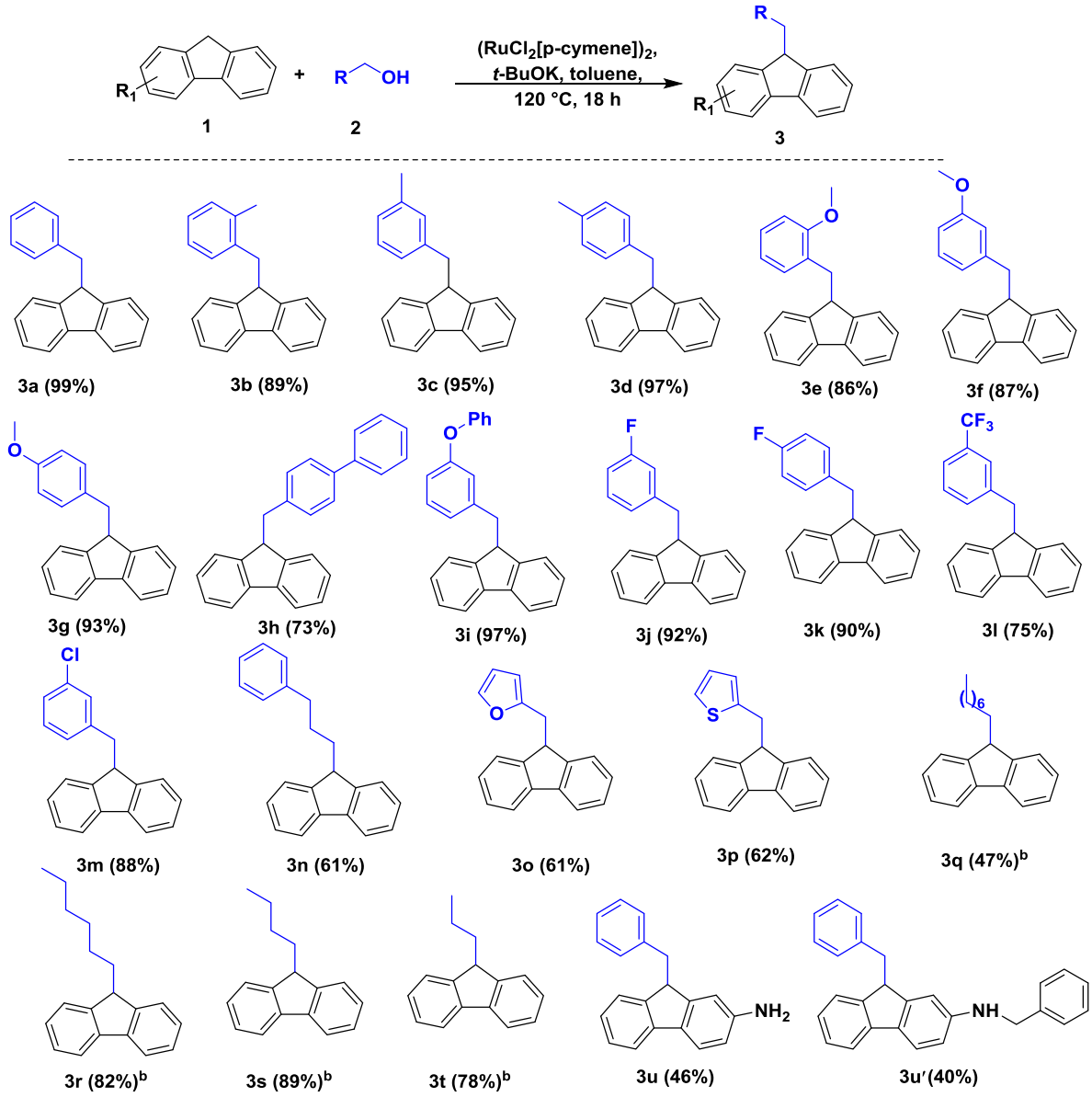
Table 1. Optimization for the 9-alkylation reaction of 9*H*-Fluorene[a]



Entry	catalyst (3 mol%)	base (1.5 eq.)	solvent	temp (°C)	yield of **3a** (%)
1	-	*t*-BuOK[b]	Toluene	120	45
2	[Ru(p-cymene)Cl_2]$_2$	-	Toluene	120	no reaction
3	**[Ru(p-cymene)Cl_2]$_2$**	***t*-BuOK**	**Toluene**	**120**	**99**
4	[Ru(p-cymene)Cl_2]$_2$	KOH	Toluene	120	57
5	[Ru(p-cymene)Cl_2]$_2$	NaOH	Toluene	120	Traces
6	[Ru(p-cymene)Cl_2]$_2$	K_2CO_3	Toluene	120	no reaction
7	[Ru(p-cymene)Cl_2]$_2$	Cs_2CO_3	Toluene	120	no reaction
8	[Ru(p-cymene)Cl_2]$_2$	Na_2CO_3	Toluene	120	no reaction
9	$RuCl_3.XH_2O$	*t*-BuOK	Toluene	120	90
10	$RuHClCO(PPh_3)$	*t*-BuOK	Toluene	120	83
11	$RuH_2CO(PPh_3)_3$	*t*-BuOK	Toluene	120	92
12	$RuH_2(PPh_3)_4$	*t*-BuOK	Toluene	120	93
13	Ru-MACHO	*t*-BuOK	Toluene	120	23
14	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	1,4-Dioxane	120	50
15	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	DCE	120	no reaction
16	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	DMF	120	no reaction
17	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	DMSO	120	no reaction
18	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	Toluene	80	Traces
19	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	Toluene	100	49
20[c]	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	Toluene	120	no reaction
21[d]	[Ru(p-cymene)Cl_2]$_2$	*t*-BuOK	Toluene	120	58

Reaction Conditions: [a] 9*H*-fluorene **1a** (0.3 mmol), benzyl alcohol **2a** (0.45 mmol), catalyst (3 mol%), base (1.5 equiv.) were stirred at 120 °C for 18 hrs under nitrogen atmosphere. [b] excess of base results complicated reaction mixture. [c] base (0.5 equiv.). [d] base (1 equiv.)

Scheme 2. Ruthenium-catalyzed 9-alkylation reaction of 9*H*-fluorene with substituted aromatic alcohols and aliphatic alcohols



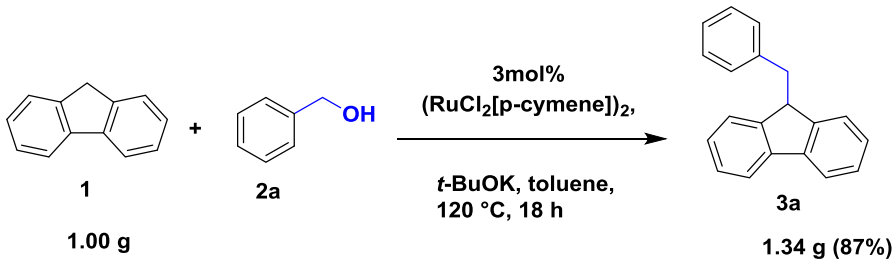
Reaction conditions: [a]9*H*-fluorene (0.3 mmol), alcohol (0.45 mmol), catalyst (3 mol%), and *t*-BuOK (1.5 equiv.) were heated at 120 °C under nitrogen atmosphere for 18 hrs. [b]9*H*-fluorene (0.3 mmol), alcohol (0.45 mmol), catalyst (3 mol %), and *t*-BuOK (2 equiv.) were heated at 140 °C under nitrogen atmosphere for 48 hrs. Yields corresponds to isolated pure compounds.

benzyl-9*H*- fluorene **3a** in 99% yield (Table 1, entry 3). In contrast, KOH gave only moderate yield of **3a** under the present conditions (Table 1, entry 4). Other bases such as NaOH, K_2CO_3, Cs_2CO_3, Na_2CO_3 are failed to deliver 9-benzyl-9H-fluorene **3a** under similar reaction conditions (Table 1, entries 5-8). Other Ru-catalysts such as $RuCl_3.XH_2O$, $RuHClCO(PPh_3)_3$, $RuH_2CO(PPh_3)_3$, $RuH_2(PPh_3)_4$ also afforded 83-92% yield of 9-benzyl-9*H*-fluorene **3a** under the same reaction condition (Table 1, entries 9-12). Using the optimized reaction condition, a wide range of primary alcohols were subjected to ruthenium-catalyzed 9-alkylation of 9*H*-fluorene (Scheme 2).

In general, benzyl alcohols bearing electron-donating and withdrawing substituents such as methyl, methoxy, chloro, phenyl, fluoro, and trifluoromethyl afforded the corresponding 9-alkylated 9*H*-fluorene in good to excellent yields. Electron-rich benzyl alcohols having methyl group on ortho, meta and para position were converted into **3b, 3c** and **3d** in 89% 95% and 97% yields, respectively. The 9-alkylation of 9*H*-fluorene with 2-methoxy, 3-methoxy, 4-methoxy benzyl alcohols afforded the corresponding products **3e-3g** in 86%, 87%, and 93% yield, respectively. Notably, under standard experimental condition, 4-phenyl substituted benzyl alcohols provided good to excellent yields of corresponding products **3h** and **3i** in 73% and 97% respectively. The presence of an electron-withdrawing substituent such as 3-fluoro, 4-fluoro, 4-trifluoromethyl, and 3-chloro on the aryl ring of benzyl alcohol provided 9-alkylated products **3j-3m** in excellent yield. Gratifyingly, heteroaryl methanols were tolerated under this catalytic 9-alkylation reaction of 9*H*-fluorene. Furfuryl alcohol and 2-thiophenemethanol provided 9-alkylated products **3o** and **3p** in good yields. Further, the scope of the reaction was evaluated with aliphatic primary alcohols. When long-chain 1-octanol was subjected for alkylation reaction under standard optimized condition, the 9-alkylated product was isolated in poor yield (35%). An

increasing base loading to 2 equivalents afforded the product **3q** in 47% in 48 hrs. Due to less reactivity of aliphatic primary alcohols, the reaction required longer reaction time (48 hrs) to provide 9-alkylated 9*H*-fluorene (**3q-3t**) in very good yield. Interestingly, 9*H*-fluoren-2-amine was also successfully alkylated to afford 9-benzyl-9*H*-fluoren-2-amine **3u** in 46% yield along with the *N*-alkylated product **3u'** in 40% yield. A gram scale reaction was performed with fluorene **1** and benzylalcohol under the standard condition to afford 1.34 g (87%) of the product **3a** after column purification (Scheme 3).

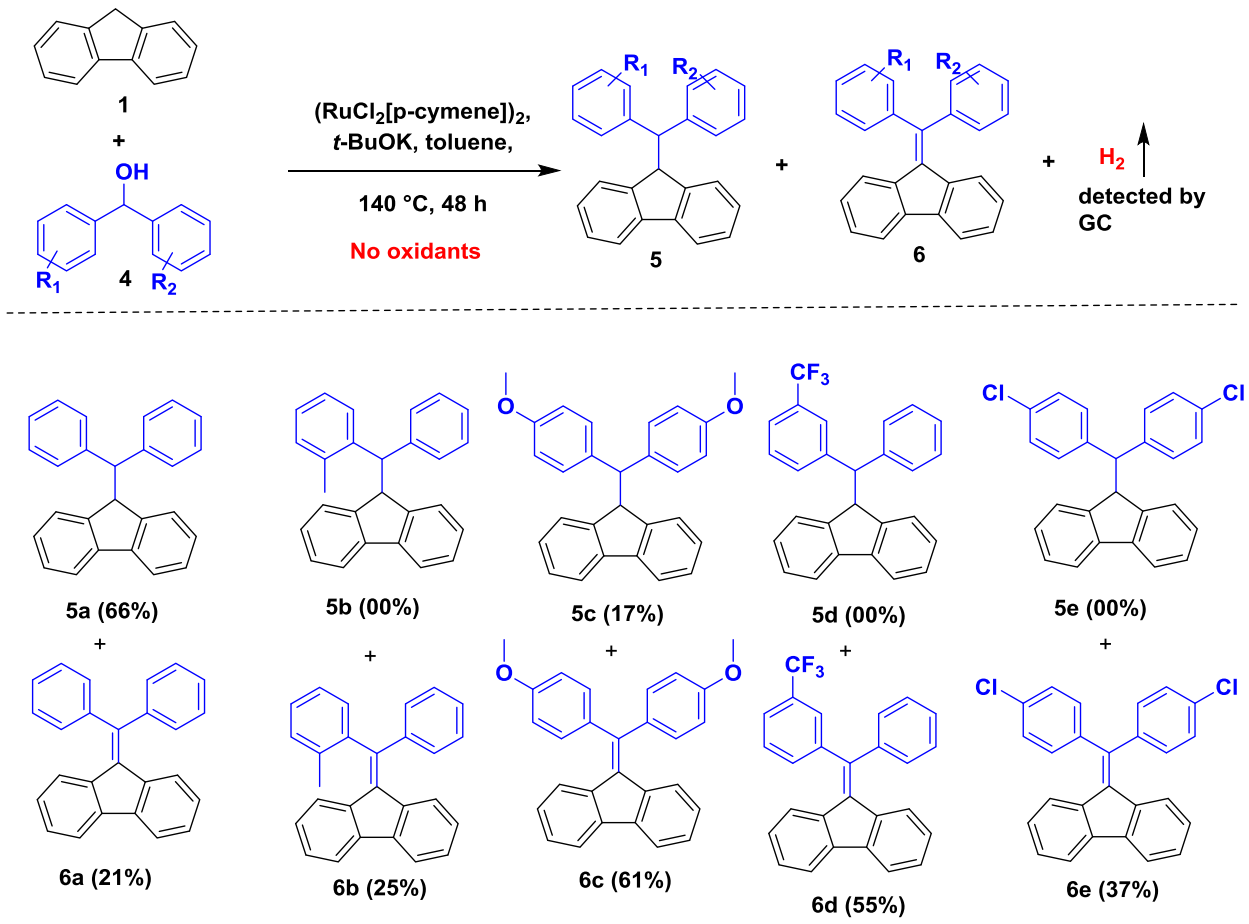
Scheme 3. Gram scale reaction



We further checked the generality of this reaction for the alkylation of 9*H*-fluorene by using secondary alcohols (Scheme 4). A reaction of 9*H*-fluorene with diphenylmethanol under the above optimized reaction condition by using 3 mol% of [Ru(p-cymene)Cl_2]$_2$ and *t*-BuOK (1.5 equivalent) for 18 hrs failed to deliver 9-sec-alkyl fluorene **5a**. Hence, we have re-optimized the reaction condition to obtain 9-sec-alkyl fluorene. Upon heating the reaction mixture containing 9*H*-fluorene (0.3 mmol) and diphenyl methanol (0.6 mmol) in the presence of 5 mol% of [Ru(p-cymene)Cl_2]$_2$ and 2 equivalent of *t*-BuOK at 140 °C, affording 9-benzhydryl-9*H*-fluorene **5a** in 66% yield and 9-(diphenylmethylene)-9*H*-fluorene **6a** in 21% yield. Furthermore, we set out the substrate scope of this reaction by using substituted secondary alcohol. Thus the reaction of the 9*H*-fluorene **1** with various substituted benzhydrazol such as methyl-, methoxy-, trifluoromethyl-, and chloro in the presence of 5 mol% [Ru(p-cymene)Cl_2]$_2$ and 2 equivalents of *t*-BuOK at 140

°C, afforded the respective alkene products **6b-e** as the exclusive isomer in good yield. Interestingly, in the case of secondary alcohols, higher selectivity for the formation of alkene was observed which might be due to sterically hindered alkene difficult to coordinate with the Ru-catalyst for further hydrogenation reaction.

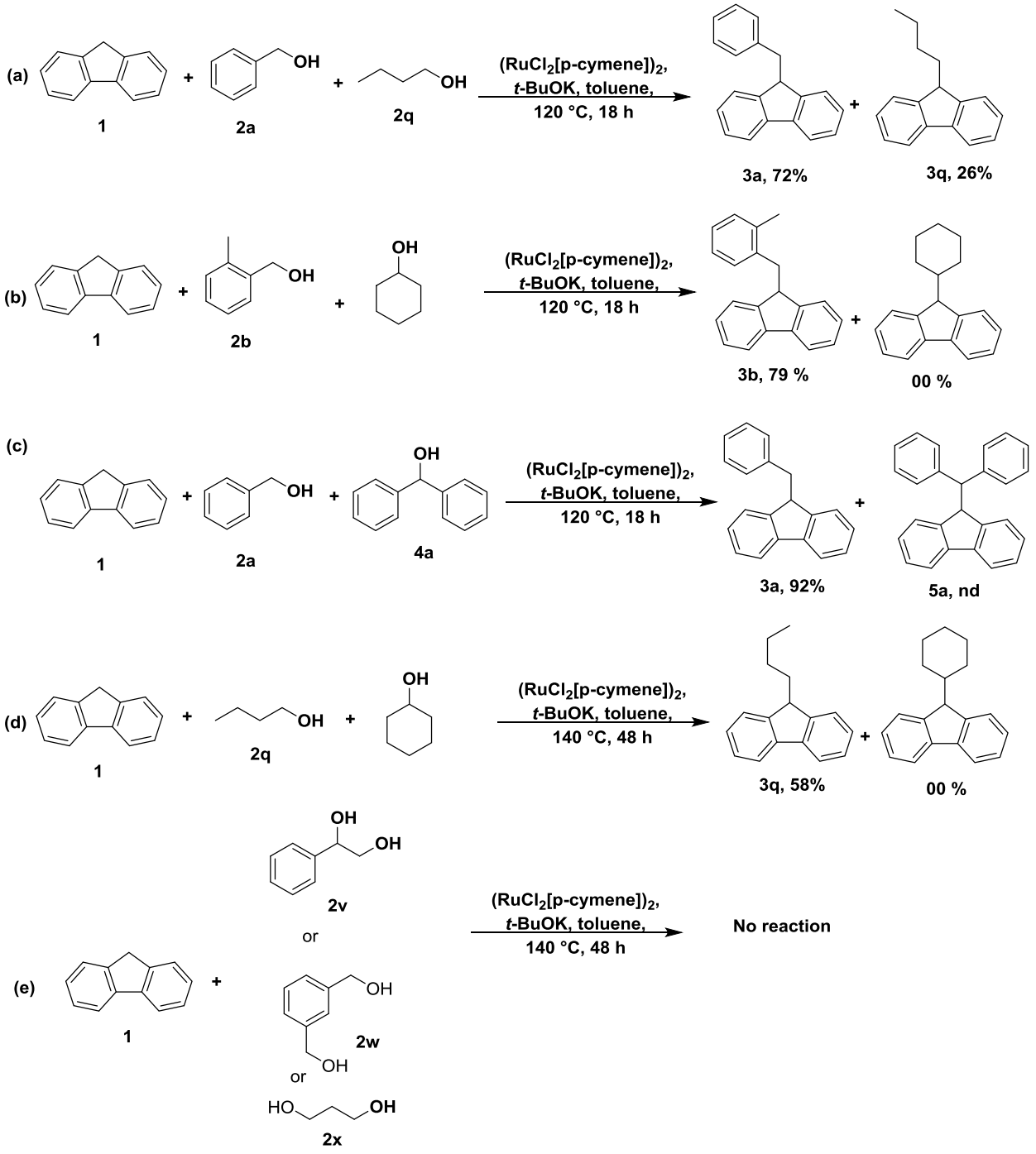
Scheme 4. Ruthenium-catalyzed 9-alkylation/alkenylation reaction of 9*H*-fluorene with substituted aromatic secondary alcohols[a]



Reaction conditions:[a]9*H*-fluorene (0.3 mmol), alcohol (0.6 mmol), catalyst (5 mol%), and *t*-BuOK (2 equiv.) were heated at 140 °C under nitrogen atmosphere for 48 hrs. Yields corresponds to isolated pure compounds.

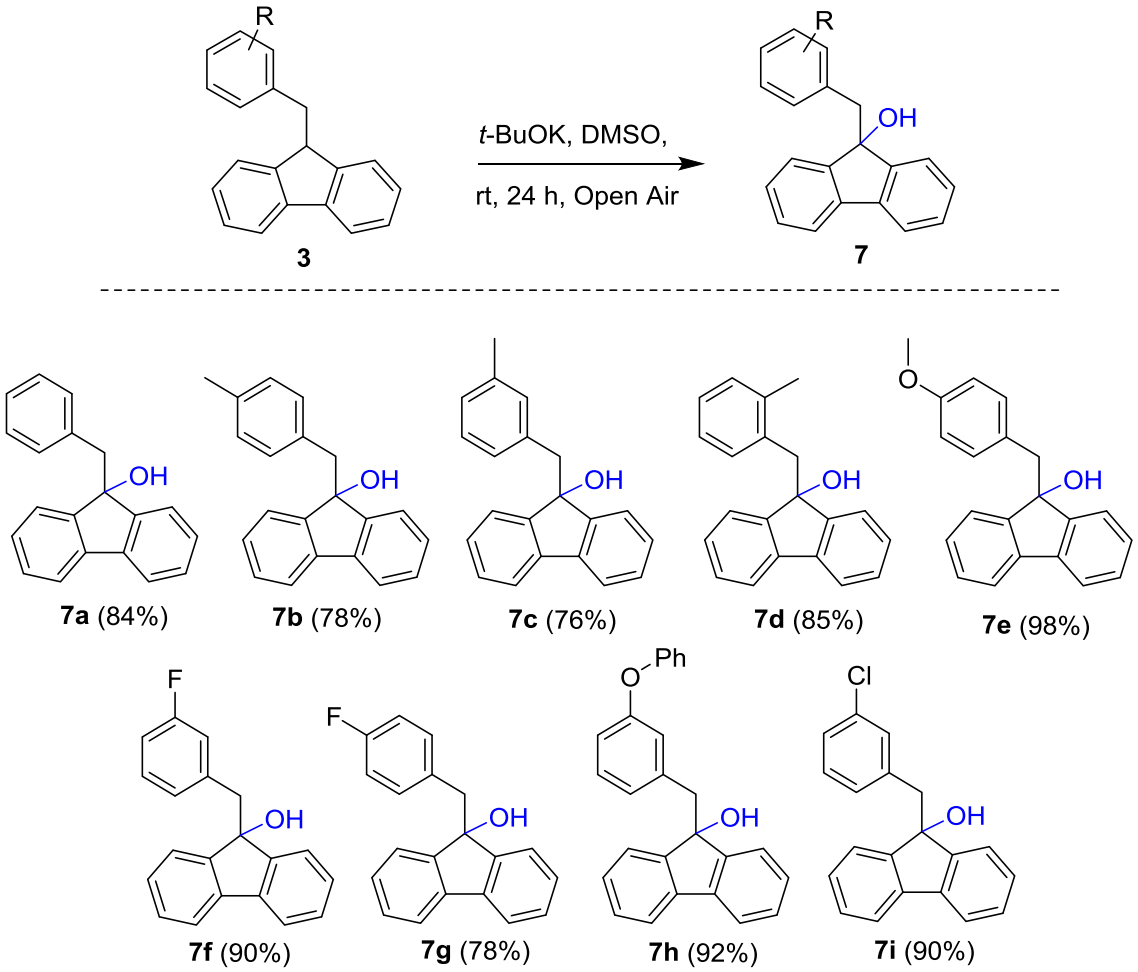
Next, selectivity on the alkylation of 9*H*-Fluorene with primary alcohols over secondary alcohols was investigated under an optimized reaction condition using $[Ru(p\text{-cymene})Cl_2]_2$ (3 mol%) and *t*-BuOK (1.5 equivalent) (Scheme 4). Hence, a reaction of 9*H*-fluorene (0.3 mmol) with equimolar amount of benzyl alcohol and 1-butanol (each 0.45 mmol) under optimized reaction condition afforded 9-benzyl-9*H*-fluorene (**3a**, 72% isolated yield, Scheme 5a), and 9-butyl-9*H*-fluorene (**3q**, 26% isolated yield, Scheme 5a), which proves that aromatic alcohols are more reactive and selective than aliphatic alcohols for this transformation. A similar experiment using 2-methyl benzyl alcohol and 1-cyclohexanol was quantitatively converted to the 9-(2-methylbenzyl)-9*H*-fluorene (**3b**, Scheme 5b) in 79% isolated yield, which confirms that benzyl alcohol reacts faster than secondary alcohols. Remarkably, when 9*H*-fluorene (0.3 mmol) was reacted with benzyl alcohol (0.45 mmol) and diphenylmethanol (0.45 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (3 mol %) and *t*-BuOK (1.5 equivalent), quantitative conversion of 9-benzyl-9*H*-fluorene (**3a**, 92% isolated yield, Scheme 5c) was observed. In another experiment using 1- butanol and 1-cyclohexanol provided exclusively 9-alkylated **3q** (58%, isolated yield, Scheme 5d). These experimental results demonstrate that these reactions afforded high chemoselectivity with aromatic primary alcohols. Moreover, secondary alcohols were either non-reactive or less yield in these competitive experiments. High chemoselectivity was achieved with the aliphatic primary alcohols over the aliphatic secondary alcohols, which might be due to the steric effect present in the secondary alcohols. These reaction were also performed with various diols such as 1,3-benzenedimethanol, 1-phenyl-1,2-ehanediol, 1,2-butandiol and 1,3-propandiol under the standard condition as well as heated up to 160 °C. But this reaction was not successful to afford the desired products (Scheme 5e).

Scheme 5. Chemoselectivity of primary alcohols over secondary alcohols on the alkylation of 9*H*-Fluorene



To study the hydroxylation reaction,[22] 9-alkylation of 9*H*-fluorene was exposed to air under basic condition (Scheme 6). A solution of compound **3a** and *t*-BuOK in DMSO was allowed to stir at room temperature in an atmospheric air for 24 hrs. It was noted that the compound **3a** undergoes hydroxylation to afford the quaternary 9-hydroxy functionalized fluorene **7a** in 84% yield (Scheme 6). Similarly, other derivatives of compound **3** were incorporated for the C-H hydroxylation reaction to afford the respective quaternary 9-hydroxy functionalized fluorene derivative **7b-i** in excellent yield (Scheme 6).

Scheme 6. *t*-BuOK mediated C-H hydroxylation of 9-alkylated 9*H*-fluorene[a]

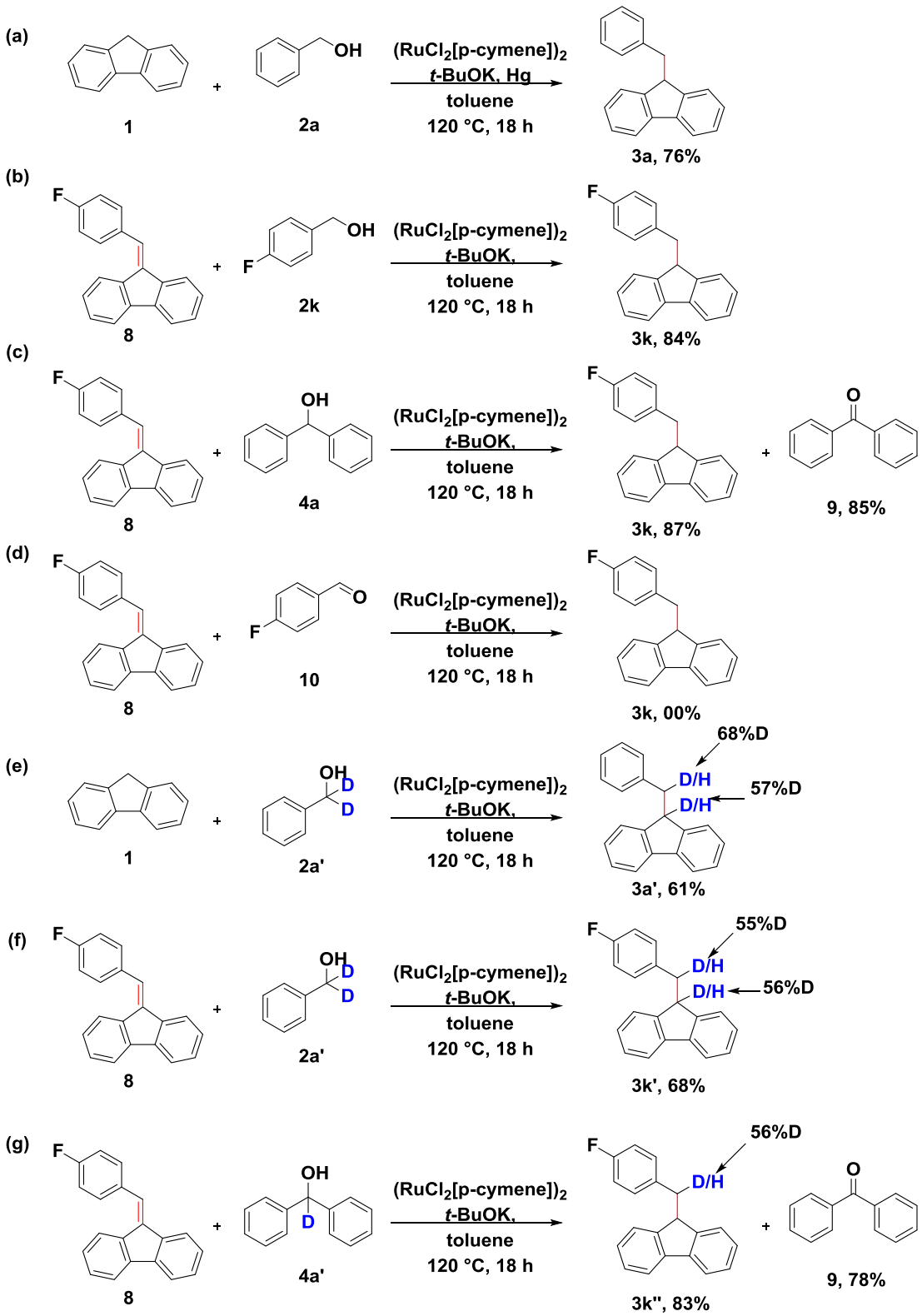


Reaction conditions: [a]9-alkyl-9*H*-fluorene (0.3 mmol), *t*-BuOK (1 equiv.) at room temperature in an open-air atmosphere for 24 hrs. Yields corresponds to isolated pure compounds.

A mercury-poisoning experiment[23] was performed to examine the involvement of any heterogeneous catalyst formed from the ruthenium catalyst under experimental reaction conditions. The catalytic reaction of 9*H*-fluorene with benzyl alcohol was carried out in the presence of mercury (10 equiv., relative to substrate **1a**), which provided the corresponding alkylated 9*H*-fluorene **3a** in 76% isolated yield (against the 99% yield in the absence of mercury, see Scheme 7), indicating that the reaction proceeds under homogeneous condition (Scheme 7a).

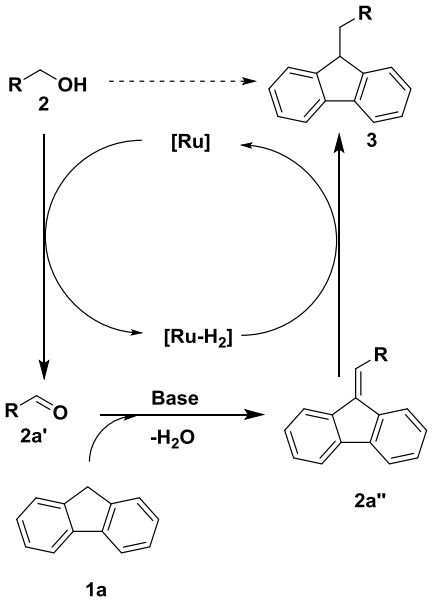
To probe hydrogen source for reduction of unsaturated intermediate, a reaction of 9-(4-fluorobenzylidene)- 9*H*-fluorene **8** with 4-fluorobenzyl alcohol in the standard condition was performed, resulted in the formation of desired product **3k** in 84% yield (Scheme 7b). Further, a reaction of 9-(4-fluorobenzylidene)- 9*H*-fluorene **8** with 4-fluorobenzyl alcohol under standard reaction condition led to product **3k** in 87% yield with the formation of benzophenone **9** as a by-product. This indicates that alcohol is necessary to generate hydride species which is required for the reduction of the condensed product. To exclude the other possibility for the formation of **3k**, a reaction of **8** with 4-fluoro benzaldehyde **10** was performed and reveals no reaction. Deuterium labeling experiment with deuterated benzyl alcohol **2a'** shows 57% (α) and 68% (β) D incorporation (Scheme 7e). Moreover, a reaction of 9-(4-fluorobenzylidene)- 9*H*-fluorene **8** with deuterated benzyl alcohol **2a'** afforded the product **3k'** with 56% (α) and 55% (β) D incorporation (Scheme 7f). From the above experiments, deuteride transfer to Fluorene derivative occurs from a Ru-deuteride intermediate. Besides, a similar reaction with deuterated diphenyl methanol **4a'** shows the product **3k"** with 56% (β) deuterium incorporation (Scheme 7g), which confirms deuteride transfer occurs at the β-position of Fluorene derivative from a Ru-deuteride intermediate.

Scheme 7. Mechanistic studies for the 9-alkylation of 9*H*-fluorene



From the experimental observations and literature precedents, we have proposed a mechanistic pathway for the alkylation reaction (Scheme 8).[3,5] The ruthenium catalyst reacts with alcohol **2** to generate aldehyde **2a'** and Ru-H_2 species. Moreover, the formation of a hydride signal was confirmed by ^{1}H-NMR analysis and the liberation of H_2 gas was confirmed by GC analysis (Figure 85, ESI). Subsequently, the condensation of an aldehyde with 9*H*-fluorene in the presence of base afforded desired 9-benzylidene-9*H*-fluorene (**2a''**). Further, condensed product **2a''** undergoes catalytic hydrogenation to lead 9-benzyl-9*H*-fluorene **3** by the Ru-H_2 complex.

Scheme 8. A plausible mechanism for the alkylation of 9*H*-fluorene



CONCLUSIONS

In conclusion, we have developed a novel, highly efficient and chemoselective catalytic method for the alkylation/alkenylation of 9*H*-fluorene by using various primary and secondary alcohols in absence of any external oxidants to afford the 9-monosubstituted-9*H*-fluorene in high yield. This transformation was carried out by using inexpensive, highly air-stable $[Ru(p\text{-cymene})Cl_2]_2$

complex in the absence of ligand. This methodology developed an environmentally benign conditions for the alkylation of fluorene by using greener and non-hazardous alkylating reagents with the formation of water as a by-product. Moreover, an efficient C-H hydroxylation of 9*H*-fluorene derivatives using inexpensive *t*-BuOK was demonstrated under simple reaction conditions in the absence of any oxidants. A plausible mechanism for this transformation was proposed with the experimental observation includes hydride detection and hydrogen liberation.

EXPERIMENTAL SECTION

General information and data collection:

All the chemicals were purchased from Sigma Aldrich or Alfa-Aesar. All stoichiometric reactions were performed under nitrogen atmosphere. Dry solvents were prepared according to standard procedures. Column chromatographic separations performed over 100−200 Silica-gel. Visualization was accomplished with UV light and phosphomolybdic acid (PMA), Ceric ammonium molybdate (CAM) stain followed by heating. Deuterated solvents were used as received. ^{1}H, $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm downfield from tetramethylsilane. Multiplicity is abbreviated as: s, singlet; d, doublet; dd, doublet of doublets; dt, doublet of triplets; t, triplet; q, quartet; dq, doublet of quartets; td, triplet of doublets; m, multiplet; br, broad. High-resolution mass spectra were recorded with Waters-synapt G2 using electrospray ionization (ESI-TOF). The quantitative analysis of molecular hydrogen gas was carried out by using gas chromatograph (GC) equipped with a TCD detector (Agilent 7890), column type carbosieve and mesh range-100, max temp 225 ^{o}C with flow rate for other gases 14 mL/min and hydrogen 4 mL/min. The temperature gradient of the detector and oven were 200 ^{o}C, 60 ^{o}C respectively. The temperature of the injector was 150 ^{o}C during the experiment.

A) General experimental procedure for the 9-alkylation of 9*H*-fluorene with primary alcohol (Method A): $[Ru(p\text{-cymene})Cl_2]_2$ (3 mol%), *t*-BuOK (1.5 equiv.), 9*H*-fluorene (0.3 mmol), alcohol (0.45 mmol), and toluene (2 mL) were added to an oven-dried 20 mL resealable pressure tube (equipped with rubber septum) under a N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 120 °C for 18 h on a preheated oil bath. The reaction mixture was cooled to room temperature and concentrated under vacuum. DCM was added to the reaction mixture and passed through a plug of celite. The filtrate was concentrated under reduced pressure and the residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:99) to afford the pure product of 9-alkylated 9*H*-fluorene **3**. (In the case of aliphatic alcohols, 5 mol% of $[Ru(p\text{-cymene})Cl_2]_2$ catalyst *t*-BuOK (2 equiv.) was used and kept for 48 h).

B) General experimental procedure for the 9-alkylation of 9*H*-fluorene with secondary alcohol (Method B): $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol%), *t*-BuOK (2 equiv.), 9*H*-fluorene (0.3 mmol), alcohol (0.60 mmol), and toluene (2 mL) were added to an oven-dried 20 mL resealable pressure tube (equipped with rubber septum) under a N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 140 °C for 48 h on a preheated oil bath. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. DCM was added to the reaction mixture and passed through a plug of celite. The filtrate was concentrated under reduced pressure and the residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:99) to afford the pure product of 9-alkylated 9*H*-fluorene.

C) Experimental procedure for control experiment in the absence of catalyst: *t*-BuOK (1.5 equiv.), 9*H*-fluorene (0.3 mmol), benzyl alcohol (0.45 mmol), and toluene (2 mL) were added to

an oven-dried 20 mL resealable pressure tube (equipped with rubber septum) under N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 120 °C for 24 h on a preheated oil bath. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. DCM was added to the reaction mixture and passed through a plug of celite. The filtrate was concentrated under reduced pressure and the residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:99) to afford the 9-benzyl-9*H*-fluorene **3a** in 45% yield.

D) Experimental procedure for control experiment in the absence of base: [Ru(p-cymene)Cl_2]$_2$ (3 mol%), 9*H*-fluorene (0.3 mmol), benzyl alcohol (0.45 mmol), and toluene (2 mL) were added to an oven-dried 20 mL resealable pressure tube (equipped with rubber septum) under a N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 120 °C for 18 h on a preheated oil bath. This showed no reaction.

E) General experimental procedure for C-H hydroxylation of 9-alkyl-9*H*-fluorene: 9-Alkyl-9*H*-fluorene (1 eq), *t*-BuOK (1 equiv.) and DMSO (2 mL) were added to a 20 mL tube with a magnetic bar and then the mixture was stirred at room temperature in open air for 24 h. The solution was then diluted with dichloromethane (10 mL), washed with water (5 x 3) and brine (5x 5 mL), dried over anhydrous Na_2SO_4, filtered, and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (ethyl acetate/petroleum ether 05:95).

F) Experimental procedure for the detection of H_2 gas using GC analysis: To an oven-dried 20 mL resealable pressure tube (equipped with a rubber septum), [Ru(*p*-cymene)Cl_2]$_2$ (3 mol%), *t*-BuOK (1.5 equi.), 9*H*-fluorene (0.3 mmol), benzyl alcohol (0.45 mmol), and toluene (2 mL)

were added under N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 120 °C for 6 h on a preheated oil bath. The gas phase of the reaction mixture was taken out by a gas tight glass syringe and immediately injected into the injector of the GC instrument. The liberation of H_2 was detected by GC analysis.

G) Experimental procedure for hydride detection in the reaction mixture: In a dry NMR tube, charged with $[Ru(p\text{-cymene})Cl_2]_2$ (20 mol%), *t*-BuOK (0.1 mmol), 9*H*-fluorene (0.1 mmol), and 4-methyl benzyl alcohol (0.1 mmol) in benzene-d_6. The NMR tube was then kept in a preheated oil bath at 80 °C for 30 min. Subsequently, the sample was analyzed by ^{1}H NMR spectroscopy, hydride signals were detected at the δ -17.12 and -17.19 ppm (see ESI). The same sample was then heated at 100 ^{0}C for 1 h and recorded ^{1}H-NMR analysis. There was no chemical shift change for the hydride signals. These experimental evidence support the formation of Ru-H intermediate in the reaction mixture.

H) Experimental procedure for gram scale reaction: $[Ru(p\text{-cymene})Cl_2]_2$ (74 mg, 2 mol%), *t*-BuOK (1.011 g, 9.03 mmol), 9*H*-fluorene **1** (1.0 g, 6.02 mmol), benzyl alcohol **2a** (975 mg, 9.03 mmol), and toluene (6 mL) were added to an oven-dried 30 mL resealable pressure tube (equipped with rubber septum) under a N_2 atmosphere. The tube was purged with N_2 and sealed with a cap using a crimper. The reaction mixture was stirred at 120 °C for 18 h on a preheated oil bath. The reaction mixture was cooled to room temperature and concentrated under vacuum. DCM was added to the reaction mixture and passed through a plug of celite. The filtrate was concentrated under reduced pressure and the residue was purified by 100-200 mesh silica-gel column chromatography using ethyl acetate/petroleum ether (1:99) to afford the pure 9-benzyl-9*H*-fluorene **3a** (1.34 g 87%).

I) Analytical data for the product:

9-Benzyl-9*H*-fluorene (**3a**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), benzyl alcohol (65 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-benzyl-9*H*-fluorene **3a** (76 mg, 99 %) as a white solid. Melting point: 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.38 – 7.13 (m, 11H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.12 (d, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.9, 140.9, 139.9, 129.6, 128.4, 127.2, 126.7, 126.5, 124.9, 119.9, 48.8, 40.2. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{20}H_{17}$ 257.1330; Found 257.1335.

9-(2-Methylbenzyl)-9*H*-fluorene (**3b**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 2-methylbenzyl alcohol (73 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(2-methylbenzyl)-9*H*-fluorene **3b** (73 mg, 89 %) as a white solid. Melting point: 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.21 (m, 6H), 7.15 (d, *J* = 7.5 Hz, 2H), 4.24 (t, *J* = 8.0 Hz, 1H), 3.09 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.2, 140.8, 138.5, 136.8, 130.6, 130.5, 127.2, 126.8, 126.7, 126.0, 124.9, 119.9, 47.7, 37.8, 19.8. HRMS (ESI-TOF) *m/z*: [M+Na]+ Calcd for $C_{21}H_{18}Na$ 293.1306; Found 293.1305.

9-(3-Methylbenzyl)-9*H*-fluorene (**3c**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-methylbenzyl alcohol (54 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-methylbenzyl)-9*H*-fluorene **3c** (77 mg, 95 %) as a white solid. Melting

point: 114−116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.21 (td, *J* = 7.3, 0.9 Hz, 3H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.06 (m, 3H), 4.22 (t, *J* = 7.7 Hz, 1H), 3.06 (d, *J* = 7.7 Hz, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 140.9, 139.9, 138.0, 130.4, 128.3, 127.3, 127.2, 126.7, 126.6, 119.9, 48.8, 40.2, 21.6. HRMS (ESI-TOF) *m/z*: [M+Na]+ Calcd for $C_{21}H_{18}Na$ 293.1306; Found 293.1314.

9-(4-Methylbenzyl)-9*H*-fluorene (**3d**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 4-methyl benzyl alcohol (54 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(4-methylbenzyl)-9*H*-fluorene **3d** (78 mg, 97 %) as a white solid. Melting point: 134−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.14 (d, *J* = 1.4 Hz, 4H), 4.23 (t, *J* = 7.6 Hz, 1H), 3.09 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.0, 140.9, 136.8, 135.9, 129.5, 129.1, 127.1, 126.7, 125.0, 119.9, 48.9, 39.7, 21.2. HRMS (ESI-TOF) *m/z*: [M+Na]+ Calcd for $C_{21}H_{18}Na$ 293.1306; Found 293.1309.

9-(2-Methoxybenzyl)-9*H*-fluorene (**3e**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol 2-methoxybenzyl alcohol (62 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(2-methoxybenzyl)-9*H*-fluorene **3e** (74 mg, 86 %) as a sticky yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.41 – 7.31 (m, 3H), 7.28 – 7.20 (m, 4H), 7.10 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.96 (m, 2H), 4.41 (t, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 3.11 (d, *J* = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.1, 147.8, 140.8, 131.7, 128.7, 127.9, 126.9, 126.6, 125.1, 120.2, 119.8, 110.4, 55.4, 46.8, 35.7. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{21}H_{19}O$ 287.1436; Found 287.1443.

9-(3-Methoxybenzyl)-9*H*-fluorene (**3f**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-methoxybenzyl alcohol (62 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-methoxybenzyl)-9*H*-fluorene **3f** (75 mg, 87 %) as a white solid. Melting point: 80−82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.33 (m, 2H), 7.23 (dt, *J* = 6.8, 3.0 Hz, 5H), 6.86 – 6.75 (m, 3H), 4.24 (t, *J* = 7.5 Hz, 1H), 3.77 (s, 3H), 3.09 (d, *J* =7.5, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.6, 146.9, 141.5, 140.9, 129.4, 127.6, 126.9, 125.1, 122.1, 119.9, 115.0, 112.1, 55.3, 48.6, 40.1. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{21}H_{19}O$ 287.1436; Found 287.1449.

9-(4-Methoxybenzyl)-9*H*-fluorene (**3g**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 4-methoxybenzyl alcohol (62 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(4-methoxybenzyl)-9*H*-fluorene **3g** (80 mg, 93 %) as a white solid. Melting point: 109−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.20 (t, *J* = 7.5 Hz, 1H), 3.83 (s, 3H), 3.07 (d, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 147.0, 140.9, 131.9, 130.5, 127.1, 126.7, 124.9, 119.9, 113.7, 55.2, 48.9, 39.1. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{21}H_{19}O$ 287.1436; Found 287.1450.

9-([1,1'-Biphenyl]-4-methyl)-9*H*-fluorene (**3h**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), ([1,1'-biphenyl]-4-methyl) alcohol (77 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-([1,1'-biphenyl]-4-methyl)-9*H*-fluorene **3h** (73 mg, 73 %) as a white solid. Melting point: 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J*

= 7.8 Hz, 2H), 7.71 (m, 1H), 7.66 – 7.62 (m, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.34 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.22 (m, 4H), 4.27 (t, *J* = 7.5 Hz, 1H), 3.16 (d, *J* = 7.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 146.9, 140.9, 139.2, 139.0, 130.0, 128.9, 127.2, 127.1, 127.0, 126.8, 124.9, 119.9, 48.8, 39.8. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{26}H_{21}$ 333.1638; Found 333.1643.

9-(3-Phenoxybenzyl)-9*H*-fluorene (**3i**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-phenoxybenzyl alcohol (90 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-phenoxybenzyl)-9*H*-fluorene **3i** (102 mg, 97 %) as a white solid. Melting point: 96−98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 2H), 7.40 – 7.31 (m, 4H), 7.29 – 7.22 (m, 5H), 7.13 – 7.08 (m, 1H), 6.99 – 6.86 (m, 5H), 4.23 (t, *J* = 7.4 Hz, 1H), 3.13 (d, *J* = 7.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 157.5, 157.0, 146.6, 141.7, 140.9, 129.8, 129.6, 127.2, 126.8, 124.9, 124.7, 123.1, 120.3, 119.9, 118.7, 117.3, 48.6, 39.9. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{26}H_{21}O$ 349.1592; Found 349.1588.

9-(3-Fluorobenzyl)-9*H*-fluorene (**3j**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-fluorobenzyl alcohol (57 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-fluorobenzyl)-9*H*-fluorene **3j** (76 mg, 92 %) as a white solid. Melting point: 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.30 – 7.20 (m, 5H), 6.98 (m, 3H), 4.25 (t, *J* = 7.4 Hz, 1H), 3.15 (d, *J* = 7.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 162.88 (d, *J* = 243.8 Hz), 146.5, 142.4 (d, *J* = 7.1 Hz), 140.9, 129.8 (d, *J* = 8.2 Hz), 127.3, 126.8, 125.34 (d, *J* = 2.7 Hz), 124.8, 120.0, 116.4 (d, *J* = 20.8 Hz), 113.4 (d, *J* =

20.8 Hz), 48.5, 39.8. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{20}H_{16}F$ 275.1236; Found 275.1238.

9-(4-Fluorobenzyl)-9*H*-fluorene (**3k**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 4-fluorobenzyl alcohol (57 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(4-fluorobenzyl)-9*H*-fluorene **3k** (74 mg, 90 %) as a white solid. Melting point: 136−138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.27-7.20 (m, 4H), 7.15 (m, 2H), 6.98 (t, *J* = 8.6 Hz, 2H), 4.22 (t, *J* = 7.4 Hz, 1H), 3.14 (d, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7 (d, *J* = 242.5 Hz), 146.6, 141.0, 135.3 (d, *J* = 3.2 Hz), 131.00 (d, J = 7.8 Hz), 127.3, 126.8, 124.8, 120.0, 115.1 (d, J = 20.9 Hz), 48.8, 39.2. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{20}H_{16}F$ 275.1236; Found 275.1223.

9-(3-Trifluorobenzyl)-9*H*-fluorene (**3l)**: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-trifluorobenzyl alcohol (79 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-trifluorobenzyl)-9*H*-fluorene **3l** (74 mg, 75 %) as a white solid. Melting point: 92−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.41 (s, 1H), 7.39 – 7.29 (m, 4H), 7.25 – 7.18 (m, 4H), 4.25 (t, *J* = 7.2 Hz, 1H), 3.21 (d, *J* = 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.2, 141.0, 140.4, 133.0, 130.5 (q, *J* = 31.7 Hz), 128.6, 127.4, 126.8, 126.4 (q, *J* = 3.5 Hz), 124.8, 124.3 (q, *J* = 270 Hz), 123.3 (q, *J* = 3.7 Hz), 120.0, 48.4, 39.8. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{21}H_{16}F_3$ 325.1204; Found 325.1195.

9-(3-Chlorobenzyl)-9*H*-fluorene (**3m**)[21]: [Ru(p-cymene)Cl_2]$_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-chlorobenzyl alcohol (64 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-chlorobenzyl)-9*H*-fluorene **3m** (78 mg, 88 %) as a white solid. Melting point: 118−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.31 – 7.22 (m, 7H), 7.11 (d, *J* = 6.2 Hz, 1H), 4.26 (t, *J* = 7.5 Hz, 1H), 3.14 (d, *J* = 7.5 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.4, 141.8, 140.9, 134.1, 129.7, 129.6, 127.8, 127.4, 126.9, 126.7, 124.8, 120.0, 48.5, 39.8.

9-(3-Phenylpropyl)-9*H*-fluorene (**3n**): [Ru(p-cymene)Cl_2]$_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), 3-phenylpropyl alcohol (62 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-(3-phenylpropyl)-9*H*-fluorene **3n** (53 mg, 61 %) as a white solid. Melting point: 68−70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.32 (td, *J* = 7.3, 1.2 Hz, 2H), 7.26 (*v*t, *J* = 6.8 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 2H), 4.02 (t, *J* = 5.8 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.09 (m, 2H), 1.58 – 1.48 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.4, 142.3, 141.2, 128.5, 128.3, 127.0, 126.9, 125.8, 124.4, 119.9, 47.4, 36.2, 32.6, 27.3. HRMS (ESI-TOF) *m/z*: [M]+ Calcd for $C_{22}H_{20}$ 284.1565; Found 284.1562.

2-(9*H*-Fluoren-9-yl)methylfuran (**3o**)[21]: [Ru(p-cymene)Cl_2]$_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), furan-2-methanol (41 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 2-(9*H*-Fluoren-9-yl)methylfuran **3o** (45 mg, 61 %) as a white solid. Melting point: 62−64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 1.5 Hz, 1H), 7.37

(t, J = 7.4 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.19 (dd, J = 7.3, 0.6 Hz, 2H), 6.35 (dd, J = 3.1, 1.9 Hz, 1H), 5.98 (dd, J = 3.2, 0.7 Hz, 1H), 4.33 (t, J = 7.6 Hz, 1H), 3.10 (d, J = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.8, 146.6, 141.2, 140.9, 127.3, 127.0, 124.7, 119.9, 110.5, 107.2, 46.3, 32.4. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{18}H_{15}O$ 247.1123; Found 247.1122.

2-(9*H*-Fluoren-9-yl)methylthiophene (**3p**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), thiophene-2-methanol (52 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 2-(9*H*-fluoren-9-yl)methylthiophene **3p** (49 mg, 62 %) as a white solid. Melting point: 95−97 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.12 (dt, J = 5.0, 1.2 Hz, 1H), 6.88 (ddd, J = 5.2, 3.5, 1.8 Hz, 1H), 6.72 – 6.69 (m, 1H), 4.23 (t, J = 7.0 Hz, 1H), 3.39 (d, J = 6.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.2, 142.1, 141.0, 127.4, 126.9, 126.6, 126.0, 124.7, 123.8, 119.9, 49.0, 34.0. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{18}H_{15}S$ 263.0894; Found 263.0892.

9-Octyl-9*H*-fluorene (**3q**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), octanol (78 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-octyl-9*H*-fluorene **3q** (39 mg, 47 %) as sticky yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 7.1 Hz, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.39 – 7.28 (m, 4H), 3.98 (t, J = 5.9 Hz, 1H), 2.00 (m, 2H), 1.24 (m, 12H), 0.86 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 147.7, 141.2, 127.0, 126.9, 124.4, 119.8, 47.6, 33.2, 31.9, 30.1, 29.5, 29.4, 25.8, 22.7, 14.2.

9-Hexyl-9*H*-fluorene (**3r**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), hexanol (62 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were

allowed to react in 20 mL resealable pressure tube according to method A to afford 9-hexyl-9*H*-fluorene **3r** (62 mg, 82 %) as sticky yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.1 Hz, 2H), 7.54 (dd, *J* = 7.5, 0.9 Hz, 2H), 7.38 (m, 2H), 7.33 (td, *J* = 7.4, 1.3 Hz, 2H), 4.00 (d, *J* = 5.9 Hz, 1H), 2.02 (m, 2H), 1.24 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 141.2, 126.94, 126.9, 124.4, 119.8, 47.5, 33.1, 31.6, 29.6, 25.7, 22.6, 14.1.

9-Butyl-9*H*-fluorene (**3s**)[20]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), butanol (45 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-butyl-9*H*-fluorene **3s** (60 mg, 89 %) as sticky yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 2H), 7.31 (td, *J* = 7.4, 1.1 Hz, 2H), 3.98 (t, *J* = 5.9 Hz, 1H), 2.04 – 1.97 (m, 2H), 1.32 – 1.23 (m, 2H), 1.17 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 141.2, 126.96, 126.90, 124.4, 119.9, 47.6, 32.9, 27.9, 23.1, 14.0.

9-Propyl-9*H*-fluorene (**3t**)[16d]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), propanol (36 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-propyl-9*H*-fluorene **3t** (48 mg, 78 %) as sticky yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.35 (m, 4H), 4.00 (d, *J* = 5.4 Hz, 1H), 2.00 (m, 2H), 1.34 – 1.20 (m, 2H), 0.94 – 0.86 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 141.2, 127.0, 126.9, 124.4, 119.9, 47.5, 35.5, 19.1, 14.5.

9-Benzyl-9*H*-fluoren-2-amine (**3u**)[17c]: $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), benzyl alcohol (48.73 mg, 0.45 mmol), 2-aminofluorene (54 mg, 0.30

mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford 9-benzyl-9*H*-fluoren-2-amine **3u** (35 mg, 46 %) as a brownish solid. Melting point: 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.27 – 7.14 (m, 6H), 7.00 – 6.95 (m, 2H), 6.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.35 (d, *J* = 1.7 Hz, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 2.97 (d, *J* = 8.7 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.8, 146.0, 145.6, 141.3, 140.1, 132.1, 129.6, 128.4, 127.1, 126.4, 125.1, 124.6, 120.7, 118.6, 114.3, 111.8, 48.6, 40.3. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{20}H_{18}N$ 272.1439; Found 272.1440.

N,9-Dibenzyl-9*H*-fluoren-2-amine (**3u´**): $[Ru(p\text{-cymene})Cl_2]_2$ (5.4 mg, 0.009 mmol), *t*-BuOK (50.50 mg, 0.45 mmol), benzyl alcohol (48.73 mg, 0.45 mmol), 2-aminofluorene (54 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method A to afford *N*,9-dibenzyl-9*H*-fluoren-2-amine **3u´** (40 mg, 40 %) as a brownish solid. Melting point: 75−77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.25 (d, *J* = 2.0 Hz, 4H), 7.19 – 7.09 (m, 7H), 6.99 (s, 2H), 6.51 (dd, *J* = 8.1 Hz 1H), 6.28 (s, 1H), 4.17 (s, 2H), 4.01 (t, *J* = 7.5 Hz, 1H), 3.03 (dd, *J* = 13.5, 7.5 Hz 1H), 2.91 (dd, *J* = 13.5, 8.0 Hz 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 148.6, 147.3, 145.8, 141.4, 140.0, 139.3, 129.6, 128.6, 128.2, 127.5, 127.2, 127.0, 126.2, 124.7, 124.4, 120.5, 118.3, 112.3, 109.2, 48.6, 48.4, 40.4. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{27}H_{24}N$ 362.1909; Found 362.1913.

9-Benzhydryl-9*H*-fluorene (**5a**)[21]: $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67mg, 0.60 mmol), benzhydrazol (110 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-benzhydryl-9*H*-fluorene **5a** (66 mg, 66 %) as a white solid. Melting point: 218−220 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.19 (m, 12H), 6.99 (t, *J* = 7.5 Hz, 2H),

6.59 (d, *J* = 7.7 Hz, 2H), 4.82 (d, *J* = 9.3 Hz, 1H), 4.16 (d, *J* = 9.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.7, 143.2, 141.3, 129.0, 128.5, 127.2, 126.8, 126.4, 125.8, 119.6, 55.9, 51.7.

9-(Diphenylmethylene)-9*H*-fluorene (**6a**)[24]: $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67 mg, 0.60 mmol), benzhydrazol (110 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(diphenylmethylene)-9*H*-fluorene **6a** (23 mg, 21 %) as a white solid. Melting point: 223−225 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.45 – 7.36 (m, 10H), 7.25 – 7.18 (m, 2H), 6.94 – 6.88 (m, 2H), 6.61 (d, *J* = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 145.6, 143.1, 140.6, 138.8, 134.3, 129.8, 128.9, 128.3, 127.7, 126.5, 125.0, 119.4.

9-(Phenyl(o-toyl)methylene)-9*H*-fluorene (**6b**)[25]: $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67mg, 0.60 mmol), 2-methyl benzhydrazol (110 mg, 0.45 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(phenyl(o-tolyl)methylene)-9*H*-fluorene **6b** (27 mg, 25 %) as a white solid. Melting point: 176−178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.6, 2.3 Hz, 2H), 7.44 – 7.37 (m, 4H), 7.36 – 7.22 (m, 7H), 6.98 – 6.89 (m, 2H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.31 (d, *J* = 7.9 Hz, 1H), 2.23 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 144.4, 142.4, 141.9, 140.4, 140.4, 138.9, 138.3, 135.8, 130.9, 129.2, 128.2, 128.1, 127.86, 127.81, 127.0, 126.8, 126.5, 125.1, 124.4, 119.4, 119.3, 20.0.

9-(Bis(4-methoxyphenyl)methyl)-9*H*-fluorene (**5c**): $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67mg, 0.60 mmol), 4,4'-dimethoxybenzhydrazol (146 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(bis(4-methoxyphenyl)methyl)-9*H*-fluorene **5c** (20 mg, 17%)

as a white solid. Melting point: 204−206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz 2H), 7.17 (m, 4H), 7.02 (td, *J* = 7.5, 1.1 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 4H), 6.66 (d, *J* = 7.6 Hz, 2H), 4.75 (d, *J* = 9.1 Hz, 1H), 4.12 (d, *J* = 9.1 Hz, 1H), 3.79 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 145.9, 141.3, 135.8, 129.8, 127.1, 126.4, 125.9, 119.6, 113.8, 55.3, 54.1, 52.1. HRMS (ESI-TOF) *m/z*: [M+Na]+ Calcd for $C_{28}H_{24}O_2Na$ 415.1678; Found 415.1678.

9-(Bis(4-methoxyphenyl)methylene)-9*H*-fluorene (**6c**)[24]: $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67 mg, 0.60 mmol), 4,4'-dimethoxybenzhydrazol (146 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(bis(4-methoxyphenyl)methylene)-9*H*-fluorene **6c** (72 mg, 61 %) as a yellow solid. Melting point: 145−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.33 – 7.24 (m, 6H), 6.96 (m, 6H), 6.83 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.0, 145.6, 140.3, 139.3, 135.7, 133.3, 132.0, 127.3, 126.3, 124.6, 119.3, 114.1, 55.4. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{28}H_{23}O_2$ 391.1698; Found 391.1695.

9-(Phenyl(3-(trifluoromethyl)phenyl)methylene)-9*H*-fluorene (**6d**): $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67 mg, 0.60 mmol), 3-trifloromethyl benzhydrazol (150 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(phenyl(3-(trifluoromethyl)phenyl)methylene)-9*H*-fluorene **6d** (66 mg, 55 %) as an orange solid. Melting point: 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.7 Hz, 1H), 7.56 (s, 3H), 7.49 – 7.39 (m, 2H), 7.35 – 7.30 (m, 3H), 7.26 (s, 2H), 7.17 – 7.11 (m, 2H), 6.85 – 6.79 (m, 2H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) 143.7, 143.2,

142.3, 140.9, 140.7, 138.5, 138.2, 135.4, 133.3, 131.4 (q, J = 32.2 Hz), 129.86, 129.78, 129.5, 129.21,129.17, 128.6, 128.25, 128.22, 126.74, 126.71, 125.1, 125.0 (q, J = 3.7 Hz), 124.7, 124.1 (q, J = 270 Hz), 119.6, 119.4. HRMS (ESI-TOF) *m/z*: [M+H]+ Calcd for $C_{27}H_{18}F_3$ 399.1355; Found 399.1363.

9-(Bis(4-chlorophenyl)methylene)-9*H*-fluorene (**6e**)[24]: $[Ru(p\text{-cymene})Cl_2]_2$ (9.1 mg, 0.015 mmol), *t*-BuOK (67 mg, 0.60 mmol), 4,4'-dimethoxybenzhydrazol (150 mg, 0.60 mmol), 9*H*-fluorene (50 mg, 0.30 mmol) and toluene (2 mL) were allowed to react in 20 mL resealable pressure tube according to method B to afford 9-(bis(4-chlorophenyl)methylene)-9*H*-fluorene **6e** (44 mg, 37 %) as an yellow solid. Melting point: 185−187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.5 Hz, 2H), 7.40 (dt, J = 8.8, 2.0 Hz, 4H), 7.32 – 7.24 (m, 6H), 7.00 – 6.95 (m, 2H), 6.71 (d, J = 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.3, 141.1, 140.8, 138.3, 135.3, 134.7, 131.5, 129.3, 128.2, 126.7, 124.9, 119.5.

9-Benzyl-9*H*-fluoren-9-ol (**7a**)[26]: The reaction of 9-benzyl-9*H*-fluorene **3a** (40 mg, 0.17 mmol) and *t*-BuOK (20 mg, 0.17 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-benzyl-9*H*-fluoren-9-ol **7a** (36 mg, 84%) of as a white solid. Melting point: 138−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.4 Hz, 2H), 7.35 – 7.22 (m, 6H), 7.18-7.10 (m, 3H), 6.98 (dd, J = 7.5, 2.0 2H), 3.30 (s, 2H), 2.17 (bs, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 139.4, 136.4, 130.9, 129.0, 127.7, 127.6, 126.6, 124.4, 120.0, 82.4, 45.9. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{20}H_{15}$ 255.1168; Found 255.1179.

9-(2-Methylbenzyl)-9*H*-fluoren-9-ol (**7b**): The reaction of 9-(2-methylbenzyl)-9*H*-fluorene **3b** (40 mg, 0.15 mmol) and *t*-BuOK (17 mg, 0.15 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(2-methylbenzyl)-9*H*-fluoren-9-ol **7b** (36 mg, 85%) of as a

white solid. Melting point: 94−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 0.8 Hz, 2H), 7.39 – 7.33 (m, 3H), 7.22 – 7.17 (m, 4H), 7.46 (m, 3H), 3.21 (s, 2H), 2.13 (bs, 1H), 1.82 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.8, 138.9, 137.9, 135.3, 131.4, 130.1, 128.9, 127.6, 126.8, 125.3, 124.1, 119.9, 82.2, 42.1, 19.8. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{21}H_{17}$ 269.1325; Found 269.1337.

9-(3-Methylbenzyl)-9*H*-fluoren-9-ol (**7c**): The reaction of 9-(3-methylbenzyl)-9*H*-fluorene **3c** (40 mg, 0.15 mmol) and *t*-BuOK (17 mg, 0.15 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(3-methylbenzyl)-9*H*-fluoren-9-ol **7c** (32 mg, 76%) of as a white solid. Melting point: 147−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.5 Hz, 0.7 Hz, 2H), 7.36 (td, *J* = 7.2 Hz, 1.6 Hz, 2H), 7.31 – 7.25 (m, 4H), 7.08 – 6.99 (m, 2H), 6.86 (s, 1H), 6.82 (d, *J* = 7.4 Hz, 1H), 3.27 (s, 2H), 2.25 (s, 3H), 2.22 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.4, 139.4, 137.1, 136.3, 131.8, 129.0, 127.9, 127.6, 126.5, 127.3, 124.4, 120.0, 82.3, 45.9, 21.4. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{21}H_{17}$ 269.1325; Found 269.1336.

9-(4-Methylbenzyl)-9*H*-fluoren-9-ol (**7d**): The reaction of 9-(4-methylbenzyl)-9*H*-fluorene **3d** (40 mg, 0.15 mmol) and *t*-BuOK (17 mg, 0.15 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(4-methylbenzyl)-9*H*-fluoren-9-ol **7d** (33 mg, 78%) of as a white solid. Melting point: 139−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.4 Hz, 2H), 7.35 - 7.23 (m, 6H), 6.95 (d, *J* = 7.9Hz 2H), 6.88 (d, *J* = 7.9 Hz, 2H), 3.25 (s, 2H), 3.09 (s, 3H), 2.18 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.4, 139.4, 136.1, 133.2, 130.7, 129.0, 128.4, 127.6, 124.4, 120.0, 82.4, 45.5, 21.2. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{21}H_{17}$ 269.1325; Found 269.1335.

9-(4-Methoxylbenzyl)-9*H*-fluoren-9-ol (**7e**) [26]: The reaction of 9-(4-methoxybenzyl)-9*H*-fluorene **3g** (40 mg, 0.14 mmol) and *t*-BuOK (16 mg, 0.14 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(4-methoxylbenzyl)-9*H*-fluoren-9-ol **7e** (41 mg, 98%) of as a white solid. Melting point: 104−106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 2H), 7.26 – 7.19 (m, 4H), 7.17 – 7.14 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 3.65 (s, 3H), 3.15 (s, 2H), 2.10 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 148.4, 139.4, 131.8, 129.0, 128.5, 127.6, 124.3, 120.0, 113.1, 82.5, 55.2, 45.0. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{21}H_{17}O$ 285.1274; Found 285.1285.

9-(3-Fluorobenzyl)-9*H*-fluoren-9-ol (**7f**): The reaction of 9-(3-fluorobenzyl)-9*H*-fluorene **3j** (40 mg, 0.14 mmol) and *t*-BuOK (17 mg, 0.14 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(3-fluorobenzyl)-9*H*-fluoren-9-ol **7f** (37 mg, 90%) of as a white solid Melting point: 127−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.4 Hz, 2H), 7.39 – 7.26 (m, 6H), 7.13 – 7.05 (m, 1H), 6.90 – 6.83 (m, 1H), 6.73 (vt, *J* = 9.2 Hz, 2H), 3.31 (s, 2H), 2.20 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3 (d, *J* = 243 Hz), 148.0, 139.4, 139.0 (d, *J* = 7.5 Hz), 129.2, 128.8 (d, *J* = 8.3 Hz), 127.8, 126.5 (d, *J* = 2.8 Hz), 124.2, 120.1, 117.6 (d, *J* = 21 Hz), 113.4 (d, *J* = 21 Hz), 82.3, 45.61 (d, *J* = 1.6 Hz). HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{20}H_{14}F$ 273.1074; Found 273.1087.

9-(4-Fluorobenzyl)-9*H*-fluoren-9-ol (**7g**): The reaction of 9-(4-fluorobenzyl)-9*H*-fluorene **3k** (40 mg, 0.14 mmol) and *t*-BuOK (17 mg, 0.14 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(4-fluorobenzyl)-9*H*-fluoren-9-ol **7g** (33 mg, 78%) of as a white solid. Melting point: 107−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.4 Hz, 2H), 7.35 – 7.23 (m, 6H), 6.91 – 6.86 (m, 2H), 6.81 – 6.75 (m, 2H), 3.27 (s, 2H), 2.16 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.3 (d, *J* = 242 Hz), 148.1, 139.4, 132.2 (d, *J* = 7.9 Hz), 132.1 (d, *J*

= 3.2 Hz),129.1, 127.7, 124.2, 120.0, 114.3 (d, J = 21 Hz), 82.5, 45.1. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{20}H_{14}F$ 273.1074; Found 273.1081.

9-(3-Phenoxylbenzyl)-9*H*-fluoren-9-ol (**7h**): The reaction of 9-(3-phenoxybenzyl)-9*H*-fluorene **3i** (40 mg, 0.12 mmol) and *t*-BuOK (13 mg, 0.12 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(3-phenoxylbenzyl)-9*H*-fluoren-9-ol **7h** (38 mg, 92%) of as a white solid. Melting point: 106−108 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 7.4 Hz, 2H), 7.28 – 7.24 (m, 3H), 7.22 (dd, J = 7.9, 1.7 Hz, 1H), 7.20 – 7.14 (m, 4H), 6.97 (m, 2H), 6.74 – 6.67 (m, 3H), 6.60 (d, J = 7.6 Hz, 1H), 6.51 – 6.48 (m, 1H), 3.22 (s, 2H), 2.09 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.5, 156.2, 148.1, 139.5, 138.3, 129.7, 129.1, 128.8, 127.8, 125.9, 124.2, 122.8, 121.7, 120.0, 118.4, 117.6, 82.5, 45.7. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{26}H_{19}O$ 347.1430; Found 347.1434.

9-(3-Chlorobenzyl)-9*H*-fluoren-9-ol (**7i**): The reaction of 9-(3-chlorobenzyl)-9*H*-fluorene **3m** (40 mg, 0.14 mmol) and *t*-BuOK (16 mg, 0.14 mmol) in DMSO (2.0 mL) at room temperature under open air for 24 h afforded 9-(3-chlorobenzyl)-9*H*-fluoren-9-ol **7i** (38 mg, 90%) of as a white solid. Melting point: 138−140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.5 Hz, 2H), 7.39 – 7.26 (m, 6H), 7.15 (ddd, J = 8.0, 2.0, 1.1 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 7.01 (t, J = 1.6 Hz, 1H), 6.85 (d, J = 7.6 Hz, 1H), 3.28 (s, 2H), 2.17 (bs, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.0, 139.3, 138.5, 133.3, 130.9, 129.2, 129.0, 128.7, 127.8, 126.7, 124.2, 120.1, 82.3, 45.5. HRMS (ESI-TOF) *m/z*: [M+H-H_2O]+ Calcd for $C_{20}H_{14}Cl$ 289.0779; Found 289.0793.

9-(4-Fluorobenzylidene)-9*H*-fluorene (**8**)[27]: The reaction 9*H*-fluorene (200 mg, 1.2 mmol), 4-fluorobenzaldehyde (224 mg, 1.8 mmol) and KOH (100 mg, 1.8 mmol) heated at 120 °C 4 h afforded 9-(4-fluorobenzylidene)-9*H*-fluorene **8** (274 mg, 83%) of as a yellow solid. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.63 (s, 1H), 7.58 – 7.50 (m, 3H), 7.39 (ddd, *J* = 7.7, 4.5, 1.3 Hz, 1H), 7.34 (ddt, *J* = 8.7, 4.9, 1.2 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.11 – 7.06 (m, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246 Hz), 141.4, 139.4, 139.2, 136.8, 136.4, 132.9 (d, *J* = 4.0 Hz), 131.19 (d, *J* = 7.9 Hz), 128.7, 128.4, 127.1, 126.8, 126.1, 124.3, 120.3, 119.9, 119.7, 115.7 (d, *J* = 21.6 Hz).

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website.

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

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Notes

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