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PAPER

Highly efficient synthesis of 9-fluorenones from 9*H*-fluorenes by air oxidation

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9-Fluorenones substituted with nitro, halogen, or alkyl groups can be easily obtained in high yield and purity by aerobic oxidation of 9*H*-fluorenes under ambient conditions in the presence of KOH in THF.

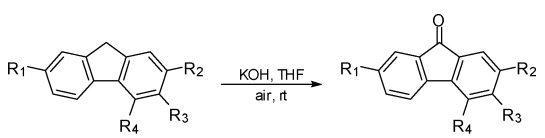
Introduction

9-Fluorenones are important building blocks and intermediates in organic synthesis and materials chemistry, ranging from the synthesis of medicinal and pharmaceutical agents, organic dyes, plastic additives, to the preparation of the organic light-emitting materials (OLEDs).[1] At present, 9-fluorenones are synthesized mainly from 9*H*-fluorenes by oxidation. Owing to their importance in various areas, there is a continuous interest in developing simple, practical and green oxidation methods that would produce the desirable 9-fluorenones in high yields.

Traditionally, stoichiometric, and even over-stoichiometric, amounts of metal oxides or metal salts, especially chromium(VI) reagents, are used as oxidizing reagents.[2] These procedures, which generate copious quantities of heavy metal wastes, are incompatible with environmental regulations. This has led to research interests in alternative procedures using catalytic amounts of transition metal, and a benign stoichiometric oxidants, such as $FeCl_3$/*t*-BuOOH,[3] CrO_3/*t*-BuOOH,[4] $MgCl_2$/NHPI/O_2,[5] NiAl-hydrotalcite/O_2,[6] CuCl/NHTPPI/O_2,[7] Ru-porphyrin complexes/N_2O,[8] $Co(Ac)_2$/PEG-1000/O_2,[9] and others.[10] However, a common difficulty associated with these reported homogeneous procedures is the separation step required for the removal of the catalyst, which cannot easily be recovered and reused. In comparison with homogeneous catalysts, heterogeneous systems present many advantages such as easy separation and recovery of the catalyst from the reaction media, higher stability of the catalytic species and catalyst protection against destruction. Therefore, many oxidation methods which use immobilized metal oxidants or metal catalysts on various solid supports have been developed.[11] Representative examples include $KMnO_4$ supported on $MnSO_4$,[12] MnO_2,[13] $CuSO_4$,[14] and montmorillonite K10;[15] manganese Schiff base complexes[16] or manganese(III) porphyrins[17] immobilized on various solid supports, both using sodium periodate as oxidant.

The above oxidation catalysts all still contain expensive and toxic transition metals, which limit their use in some areas such as the pharmaceutical industry. Recently, metal-free organic catalysts have been used in the preparation of 9-fluorenones by oxidation because of their stability and nontoxicity compared to the traditional metallic sources. These oxidizing systems include NHPI/$NaClO_2$,[18] NaOCl/*t*-BuOOH,[19] Triton B/O_2,[20] Bu_4NOH/O_2,[21] *t*-BuOOH under microwave irradiation,[22] and others.[23] Other oxidation methods—such as using ionic liquids as solvents[24] or using an activated carbon-oxygen system[25]—have also been explored.

All the above-mentioned methods have their drawbacks, making them not so "green" when scaled up into production, either due to the involvement of difficult procedures or toxic reagents. Increasing environmental awareness and economic concern have led to the consideration of highly efficient and green synthesis of 9-fluorenones from 9*H*-fluorenes. Here we report a new oxidation method using air as the oxidant and potassium hydroxide as the catalyst. The new protocol is more cost-effective, easier to handle, more environmentally benign and with higher yield than the current methods (Scheme 1). Furthermore, the newly developed method has the advantage of potential industrial application.



(R_1, R_2, R_3, R_4 = H, F, Cl, Br, NO_2, Me)

Scheme 1 Aerobic oxidation from 9*H*-fluorenes to 9-fluorenones.

Results and discussion

Initially, 2,7-dibromofluorene was chosen as a typical substrate for the optimization of reaction conditions. We first examined

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Table 1 Effect of different bases and solvents on the yield for the aerobic oxidation of 2,7-dibromofluorene[a]

Entry	Base (mmol)	Solvent (mL)	Yield (%)
1	K_2CO_3 (5)	THF (15)	< 10
2	NaOH (5)	THF (15)	70
3	KOH (5)	THF (15)	99
4	*t*-BuOK (5)	THF (15)	99
5	KOH (5)	Toluene (15)	45
6	KOH (5)	Benzene (15)	40
7	KOH (5)	CH_2Cl_2 (15)	30
8	KOH (5)	DMSO (15)	96
9[b]	KOH (5)	H_2O (15)	0
10[b]	KOH (5)	H_2O/THF(9 : 1, v/v)(15)	< 5
11[b]	KOH (5)	H_2O/THF(7 : 3, v/v)(15)	< 20
12[b]	KOH (5)	H_2O/THF(5 : 5, v/v)(15)	50

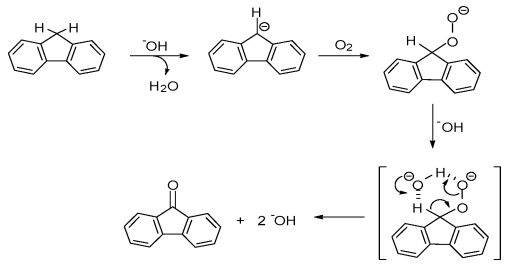
[a] Reaction conditions: the reactions were performed with 5 mmol (1.62 g) of 2,7-dibromofluorene in the presence of the base and the solvent as indicated for 8 h at rt under air. [b] $N(n\text{-}Bu)_4^+Br^-$ (5 mmol%) was used as the phase transfer catalyst.

the effect of different bases using THF as the solvent. As shown in Table 1 (entries 1–4), KOH and *t*-BuOK were found to be better catalysts to promote the oxidation and the reaction essentially gave quantitative yield of 2,7-dibromofluorenone. Because of its low cost and straightforward recycling procedure, KOH was selected as the catalyst. We next examined the effect of a variety of organic solvents (entries 5–8, Table 1). THF and DMSO were found to be suitable solvents. Because of the lower boiling point of THF and hence the readiness of its recycling through ordinary distillation as compared to that of DMSO, the former was considered as the solvent of choice for this aerobic oxidation. Furthermore, workup was extremely straightforward when THF was used as the solvent and simply involves filtration to remove KOH and concentration to obtain the crude reaction product. This workup procedure also allows for the recycling and reuse of both the base and the solvent. To pursue a greener methodology, we also tried water and mixtures of water and THF as the solvent in the presence of tetra-*n*-butylammonium bromide (TBAB) as phase transfer catalyst. Unfortunately, the yields were undesirably low (entries 9–12, Table 1). It is noteworthy to point out that, although higher temperature can accelerate the reaction, it would also cause the loss of solvent and consume more energy, and as such, the reaction was performed at room temperature.

We also found that reactions performed under oxygen flow went to completion much faster (within 5 h) whereas under an argon atmosphere no product could be detected. This proves the oxidation function of dioxygen for this reaction. From an economic view, we selected air rather than pure oxygen as the oxidant.

The mechanism[26] for the formation of 9-fluorenones from reaction of the fluorenyl anion with molecular oxygen presumably involves abstraction of a proton from the benzylic site of the fluorenylperoxy anion intermediate by ^-OH, leading to the cleavage of the peroxy bond and the formation of a carbonyl group (Scheme 2).

Considering the wide application and large demand of 2,7-dibromofluorenone in many fields, especially as a raw material for making OLEDs,[27] we conducted a scale-up preparation study based on the above optimized conditions. The reaction



Scheme 2 Proposed mechanisms for the formation of 9-fluorenones.

conditions and relevant processing parameters of 5.00 kg of 2,7-dibromofluorene in a 50 L volume glass reactor were optimized and the final yield reached 98%. It should be noted that the purity[28] of crude product was higher than 98% without any purification by organic solvents, demonstrating the practical advantages of this oxidation method for large scale synthesis of 9-fluorenones.

We also monitored the environmental pollution during and after the preparation, and the result showed there is almost no solid or gas pollution. Analysis of waste water showed that it has little pollution and is in accordance with the emission standard of relevant environment regulations.[29]

In order to expand the scope of this newly-developed oxidation method, we explored the oxidation of other common 9*H*-fluorenes. As can be seen from the results shown in Table 2, all reactions that were tested gave the corresponding 9-fluorenones in > 90% yield.

Conclusions

In conclusion, we have developed a new oxidation method to obtain 9-fluorenones from 9*H*-fluorenes that uses the cheapest and most environmentally friendly oxidant, the air, along with an inexpensive base KOH as the catalyst and THF as the solvent. The oxidation reaction proceeded smoothly under mild conditions with high yields and purity. The new synthesis involves very simple workup procedures, and the solvent THF and the catalyst KOH can be recycled and reused. The scale-up preparation study employing this method was also conducted and showed its advantages of being both cost-effective and environmentally friendly. Further study of industrial synthesis of 9-fluorenones by this newly-developed method is underway.

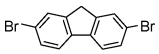
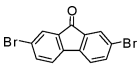
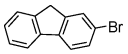
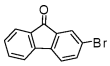
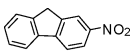
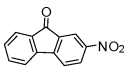
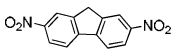
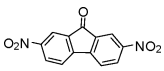
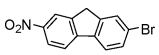
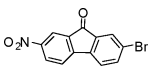
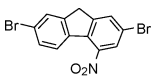
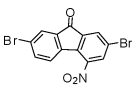
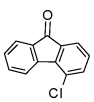
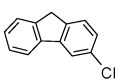
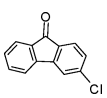
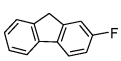
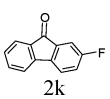
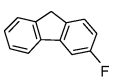
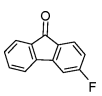
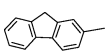
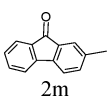
Experimental

Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C NMR) spectra were recorded on a 300 MHz NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration.

General procedures for synthesis of 9-fluorenones

Into a 100 mL, two-necked flask equipped with a electromagnetic stirrer and an air condenser were charged 9*H*-fluorenes, KOH and THF, and stirred at room temperature. The reaction

Table 2 Air oxidation of 9*H*-fluorenes **1a–1n**[a]

Entry	Substrate	Time/h	Product	Yield/%	m.p./°C	Lit./°C
1	 1a	8	 2a	99	203–205	204–205[30]
2	 1b	14	 2b	98	146–148	145–147[30]
3	 1c	24	 2c	92	83–85	83–84[31]
4	 1d	12	 2d	95	222–223	222–224[32]
5	 1e	8	 2e	93	293–295	296[33]
6	 1f	8	 2f	95	228–230	230–231[34]
7	 1g	8	 2g	94	194–196	196–197[35]
8	 1h	12	 2h	94	174–176	172.5–173[36]
9	 1i	14	 2i	95	145–147	147–148[37]
10	 1j	16	 2j	92	158–160	157[38]
11	 1k	10	 2k	95	115–117	113–115[31]
12	 1l	14	 2l	93	123–125	128.5–129[39]
13	 1m	24	 2m	90	91–92	90–92[31]
14	 1n	24	 2n	91	67–69	65–67[31]

[a] Reaction conditions: 9*H*-fluorenes (5 mmol), THF (15 mL) and KOH (5 mmol) were used for the reactions of entries 1, 2, 4-12; the reactions of entries 3, 13, 14 were carried out with 7.5 mmol of KOH at rt.

mixture was filtered to remove KOH and the filtrate was concentrated to obtain the crude product. The crude product was washed with water (3 × 100 mL), dried and purified by recrystallization from ethanol to give the final product. KOH and THF were recycled.

Synthesis of 2,7-dibromo-9-fluorenone (2a)

Application of the above procedure (without recrystallization in ethanol) to 2,7-dibromo-9-fluorene (**1a**) (1.620 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2a** (1.673 g, 99%) as a yellow solid: mp 203–205°. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 1.8 Hz, 2H), 7.52 (dd, J = 7.9 Hz, 1.8 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 191.1, 142.4, 137.7, 135.4, 128.0, 123.5, 122.0. Analysis calculated for (%) $C_{13}H_6Br_2O$: C, 46.20; H, 1.79. Found C, 46.44; H, 1.81.

Synthesis of 2-bromo-9-fluorenone (2b)

Application of the above procedure (without recrystallization in ethanol) to 2-bromofluorene (**1b**) (1.226 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2b** (1.264 g, 98%) as a yellow solid: mp 146–148°. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (s, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.62 (d, J = 7.8 Hz, 1H), 7.52–7.53 (m, 2H), 7.41 (d, J = 7.8 Hz, 1H), 7.34–7.35 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.3, 143.6, 142.9, 137.0, 135.7, 135.0, 133.6, 129.3, 127.5, 124.5, 122.8, 121.6, 120.3. Analysis calculated for (%) $C_{13}H_7BrO$: C, 60.26; H, 2.72. Found C, 60.41; H, 2.74.

Synthesis of 9-fluorenone (2c)

Application of the above procedure to fluorene (**1c**) (0.832 g, 5 mmol), KOH (0.420 g, 7.5 mmol) and THF (15 mL) afforded compound **2c** (0.831 g, 92%) as a yellow solid: mp 83–85°. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 7.2 Hz, 2H), 7.45–7.48 (m, 4H), 7.28 (d, J = 7.0 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 193.6, 144.3, 134.5, 134.0, 128.9, 124.0, 120.2. Analysis calculated for (%) $C_{13}H_8O$: C, 86.65; H, 4.47. Found C, 86.74; H, 4.48.

Synthesis of 2-nitro-9-fluorenone (2d)

Application of the above procedure to 2-nitro-9-fluorene (**1d**) (1.056 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2d** (1.068 g, 95%) as a yellow solid: mp 222–223 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, J = 1.9 Hz, 1H), 8.43 (dd, J = 1.9 Hz, 8.2 Hz, 1H), 7.77 (d, J = 7.3 Hz, 1H), 7.72–7.67 (m, 2H), 7.62 (t, 1H), 7.46 (t, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 191.2, 150.0, 149.0, 142.5, 135.7, 135.5, 135.3, 131.3, 130.2, 125.4, 122.1, 121.0, 119.8. Analysis calculated for (%) $C_{13}H_7NO_3$: C, 69.33; H, 3.13; N, 6.22. Found C, 69.21; H, 3.11; N, 6.25.

Synthesis of 2,7-dinitro-9-fluorenone (2e)

Application of the above procedure to 2,7-dinitro-9-fluorene (**1e**) (1.282 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2e** (1.256 g, 93%) as a yellow solid: mp 293–295 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.62 (d, J = 1.8 Hz, 2H), 8.58 (dd, J = 8.5 Hz, 1.8 Hz, 2H), 7.91 (d, J = 8.5 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 190.8, 150.0, 147.9, 136.0, 131.5, 124.7, 119.6. Analysis calculated for (%) $C_{13}H_6N_2O_5$: C, 57.79; H, 2.24; N, 10.37. Found C, 57.96; H, 2.26; N, 10.41.

Synthesis of 2-nitro-7-bromo-9-fluorenone (2f)

Application of the above procedure to 2-nitro-7-bromo-9-fluorene (**1f**) (1.450 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2f** (1.445 g, 95%) as a yellow solid: mp 228–230 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (d, J = 1.8 Hz, 1H), 8.48 (dd, J = 1.8 Hz, 8.2 Hz, 1H), 7.93 (d, J = 1.8 Hz, 1H), 7.78 (dd, J = 1.8 Hz, 8.0 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 188.5, 144.9, 138.5, 137.3, 135.6, 135.2, 132.7, 131.9, 128.3, 127.7, 125.9, 123.5. Analysis calculated for (%) $C_{13}H_6BrNO_3$: C, 51.35; H, 1.99; N, 4.61. Found C, 51.21; H, 1.98; N, 4.59.

Synthesis of 2,7-dibromo-4-nitro-9-fluorenone (2g)

Application of the above procedure to 2,7-dibromo-4-nitro-9-fluorene (1 g) (1.845 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound 2 g (1.801 g, 94%) as a yellow solid: mp 194–196 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, J = 1.8 Hz, 1H), 8.06 (d, J = 1.8 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.74 (dd, J = 8.3 Hz, 2.0 Hz, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): d 190.3, 149.4, 141.9, 139.2, 137.1, 134.8, 131.7, 128.2, 125.8, 125.4, 123.5, 119.7. Analysis calculated for (%) $C_{13}H_5Br_2NO_3$: C, 40.77; H, 1.32; N, 3.66. Found C, 40.86; H, 1.33; N, 3.64.

Synthesis of 4-nitro-9-fluorenone (2h)

Application of the above procedure to 4-nitro-9-fluorene (**1h**) (1.056 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2h** (1.058 g, 94%) as a yellow solid: mp 174–176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (t, 2H), 7.96 (d, J = 7.6 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.62 (t, 1H), 7.46–7.49 (m, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 191.2, 145.0, 140.5, 137.2, 136.5, 135.8, 134.3, 130.2, 129.9, 129.8, 128.5, 126.0, 124.9. Analysis calculated for (%)$C_{13}H_7NO_3$: C, 69.33; H, 3.13; N, 6.22. Found C, 69.49; H, 3.15; N, 6.25.

Synthesis of 4-chlorofluorenone (2i)

Application of the above procedure to 4-chlorofluorene (**1i**) (1.003 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2i** (1.020 g, 95%) as a yellow solid: mp 145–147 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 7.6 Hz, 1H), 7.73 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 7.2 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.3 Hz, 1H), 7.38 (t, 1H), 7.26 (t, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.6, 143.0, 140.7, 136.4, 136.2, 134.8, 134.0, 129.8, 129.4, 129.3, 124.3, 124.0, 122.5. Analysis calculated for (%) $C_{13}H_7ClO$: C, 72.74; H, 3.29. Found C, 72.49; H, 3.31.

Synthesis of 3-chlorofluorenone (2j)

Application of the above procedure to 3-chlorofluorene (**1j**) (1.003 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2j** (0.987 g, 92%) as a yellow solid: mp

158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.33 (t, 1H), 7.25 (t, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.6, 146.2, 143.1, 141.5, 135.2, 134.5, 132.5, 130.2, 129.2, 125.5, 124.8, 121.3, 120.6. Analysis calculated for (%) $C_{13}H_7ClO$: C, 72.74; H, 3.29. Found C, 72.91; H, 3.31.

Synthesis of 2-fluorofluorenone (2k)

Application of the above procedure to 2-fluorofluorene (**1k**) (0.921 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2k** (0.941 g, 95%) as a yellow solid: mp 115–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66–7.69 (m, 1H), 7.45–7.49 (m, 3H), 7.33–7.36 (m, 1H), 7.27–7.31 (m, 1H), 7.14–7.18 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.4, 165.9, 161.1, 143.8, 140.1, 140.0, 136.3, 136.2, 135.0, 134.3, 128.7, 124.5, 121.8, 121.7, 121.2, 120.8, 120.1, 112.1, 111.9. Analysis calculated for (%) $C_{13}H_7FO$: C, 78.78; H, 3.56. Found C, 78.59; H, 3.54.

Synthesis of 3-fluorofluorenone (2l)

Application of the above procedure to 3-fluorofluorene (**1l**) (0.921 g, 5 mmol), KOH (0.280 g, 5 mmol) and THF (15 mL) afforded compound **2l** (0.924 g, 93%) as a yellow solid: mp 123–125 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (t, 2H), 7.50–7.53 (m, 2H), 7.33–7.37 (m, 1H), 7.22 (d, J = 5.5 Hz, 1H), 6.94–6.98 (m, 1H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 192.2, 168.5, 166.4, 147.8, 147.7, 142.9, 134.9, 134.8, 130.5, 130.0, 126.8, 126.7, 124.5, 120.5, 116.0, 115.9, 108.8, 108.6. Analysis calculated for (%) $C_{13}H_7FO$: C, 78.78; H, 3.56. Found C, 78.61; H, 3.55.

Synthesis of 2-methylfluorenone (2m)

Application of the above procedure to 2-methylfluorene (**1m**) (0.901 g, 5 mmol), KOH (0.420 g, 7.5 mmol) and THF (15 mL) afforded compound **2m** (0.874 g, 90%) as a yellow solid: mp 91–92 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J = 7.2 Hz, 1H), 7.44–7.47 (m, 3H), 7.38 (d, J = 7.6 Hz, 1H), 7.23–7.28 (m, 2H), 2.36 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.1, 144.3, 141.3, 138.8, 135.0, 134.4, 134.1, 134.0, 128.5, 124.7, 123.9, 121.8, 119.5, 21.1. Analysis calculated for (%) $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found C, 86.69; H, 5.20.

Synthesis of 3-methylfluorenone (2n)

Application of the above procedure to 3-methylfluorene (**1n**) (0.901 g, 5 mmol), KOH (0.420 g, 7.5 mmol) and THF (15 mL) afforded compound **2n** (0.884 g, 91%) as a yellow solid: mp 67–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.46–7.51 (m, 2H), 7.35 (s, 1H), 7.28–7.30 (m, 1H), 7.10 (d, J = 8.0 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 194.0, 146.3, 145.3, 144.8, 135.2, 135.1, 132.4, 130.0, 129.5, 124.7, 124.6, 121.7, 120.5, 22.1. Analysis calculated for (%) $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found C, 86.74; H, 5.21.

Pilot-scale study for synthesis of 2,7-dibromofluorenone

Into a 50 L four-necked flask equipped with a mechanical stirrer, a snorkel and an air condenser were charged 2,7-dibromo-9-fluorene (**1a**) (5.00 Kg, 15.43 mol), KOH (0.87 Kg, 15.43 mol) and THF (25 L). The reaction mixture was stirred at room temperature while the solution was kept lower than the snorkel, and air was introduced for 5 min every 30 min to ensure there was sufficient oxygen with minimal loss of solvent. At the completion of the reaction, the reaction mixture was filtered to remove KOH and the filtrate was concentrated to obtain the crude product. The crude product was washed with water (3 × 50 L), dried to give 5.11 Kg of 2,7-dibromofluorenone, yield: 98%. KOH (0.65 Kg, 75%) and THF (20 L, 75%) were recycled.

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