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Ken Okamoto, Fengniu Lu, and Takashi Nakanishi*

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Posttreatment Technique for S_N2 Alkylation of Aromatics with Alkyl Halides: Aiming Toward Large-Scale Synthesis of Building Blocks for Soft π-Molecular Materials

Ken Okamoto,[1,2] Fengniu Lu,[1] and Takashi Nakanishi*[1]

[1]Frontier Molecules Group, International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

[2]Department of Engineering for Future Innovation, Division of Chemical Engineering and Biotechnology, National Institute of Technology, Ichinoseki College, Takanashi, Hagisho, Ichinoseki 021-8511, Japan

E-mail: NAKANISHI.Takashi@nims.go.jp

Takashi Nakanishi
Takashi Nakanishi received PH.D. Degree in shorter period from Nagasaki University in 2000. Thereafter, he did JSPS postdoctoral researches at Houston University (USA), and at Oxford University (UK) and joined the National Institute for Materials Science (NIMS), Japan, in 2004. Since 2016, he is being the current position as a group leader at WPI-MANA, NIMS. In 2007-2010, he was also a group leader at the Max Planck Institute of Colloids and Interfaces (Germany). He also has several visiting professor experiences at Warsaw University of Technology (Poland), Institute for Molecular Science (Japan), Shenzhen University (China), and Hokkaido University (Japan). His research focuses about functional soft materials with precisely controlled self-assembly, in particular optoelectronically-functional molecular liquids.

Abstract

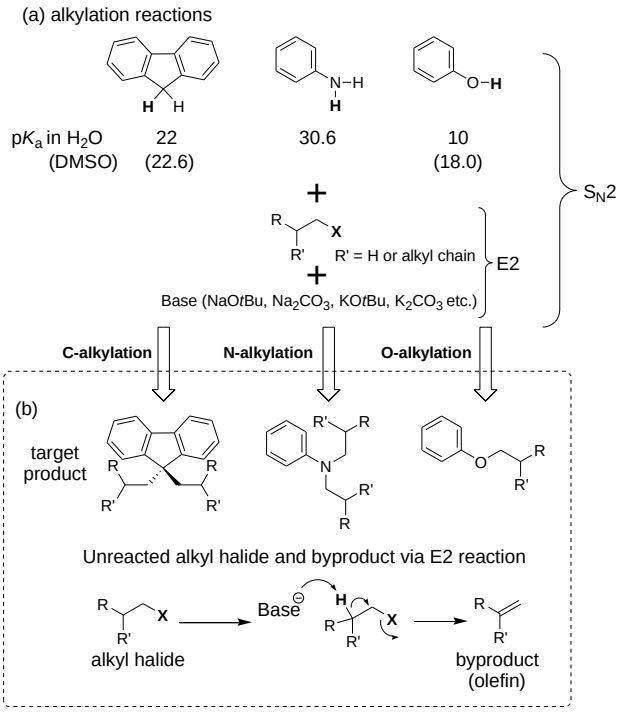
Unreacted alkyl halide and byproduct olefin contaminants in products of S_N2 alkylation reactions of aromatic compounds can be efficiently removed by sequential posttreatments with a base and a boron compound (sodium borohydride or 9-borabicyclo[3.3.1]nonane), followed by column chromatography on silica gel. These treatments permit large-scale purification of various alkylated aromatics, thereby assisting in the development of soft π-conjugated materials, such as monomers for semiconducting polymers or alkylated π-functional liquids.

1. Introduction

The self-assembly controlled spatial arrangement of π-conjugated moieties plays a decisive role in the optoelectronic properties of organic soft materials such as liquid crystals, gels, as well as nanoarchitectonics typified by layer-by-layer (LbL).[1–6] It has been recently found that the installation of alkyl[7–13] or siloxy groups[14–18] onto π-conjugated molecular soft materials can often tailor their physical properties such as physical state (e.g. solid-liquid or crystal-liquid phase transformation), assembled morphology, and molecular orientation, which significantly influence their optoelectronic applications.[7–9] In particular, the effects of alkyl substituents on aromatics or rigid metal complexes, such as the odd–even effect[19,20] or the fastener effect,[21,22] have become widely known for liquid crystals. On the other hand, recent insights into the role of alkyl chains attached to π-conjugated materials have resulted in the development of 'side-chain engineering' or 'alkyl-chain engineering' strategies.[7–12] There are many reports in the literature that describe the significant effects of alkyl chains on controlling the assembly and orientation of optoelectronically active π-conjugated molecules. For instance, Takimiya and Osaka and their co-workers reported that well-controlled substitution of branched alkyl groups can modify the photovoltaic performance of organic donor–acceptor-type polymers by changing the orientation of the polymers on the relevant devices.[23] In addition, several recent perspective papers have emphasized that alkyl chains on aromatics have a far greater role than merely increasing the solubility and improving the wet-processability of these organic materials.[8,9,12] As other attractive and relatively new examples, highly luminescent, light- and heat-stable, solvent-free, π-conjugated molecules that are liquid at room temperature have been developed by attaching multiple long branched alkyl chains to a π-unit.[24–33] To provide those versatile alkylated π-conjugated molecules, processes for the alkylation of the corresponding aromatic substrates on a large scale are in high demand.

In general, fluorenes, anilines, and phenols, which contain highly acidic (or low-pK_a) protons, are the most commonly used substrates (Scheme 1a) to be functionalized to form π-conjugated molecules. To introduce the alkyl chains, a bimolecular nucleophilic substitution (S_N2) reaction is normally employed for C-alkylation at cross-linking sites of fluorene, N-alkylation of anilines, or Williamson ether synthesis from phenols; these reactions will be referred to subsequently as C-, N-, and O-alkylation, respectively. However, the S_N2 reaction is intrinsically accompanied by a bimolecular elimination (E2) reaction of the starting alkyl halide. Consequently, the resulting mixtures potentially include the target products, unreacted chemicals, and olefins resulting from the E2 reaction (Scheme 1b). Although yields of alkylation with linear chains are moderately good,[34] the yields of alkylation with branched chains tend to be lower,[35] possibly due to more stabilized intermediates of the E2 reaction by the branched alkyl chains.[36] Because of the similar polarities of the target compound and byproduct, the purification through conventional column chromatography becomes bottleneck for the large-scale synthesis. Furthermore, the difficulty in crystallization of compounds with long linear or branched alkyl chains often requires other more work-intensive purification processes. Actually, with some of our previously reported liquid π-conjugated molecules, we had no choice but to use high-performance liquid chromatography (HPLC) as a purification process, which does not allow large-scale

purification because of the limited volume of HPLC systems.[30]



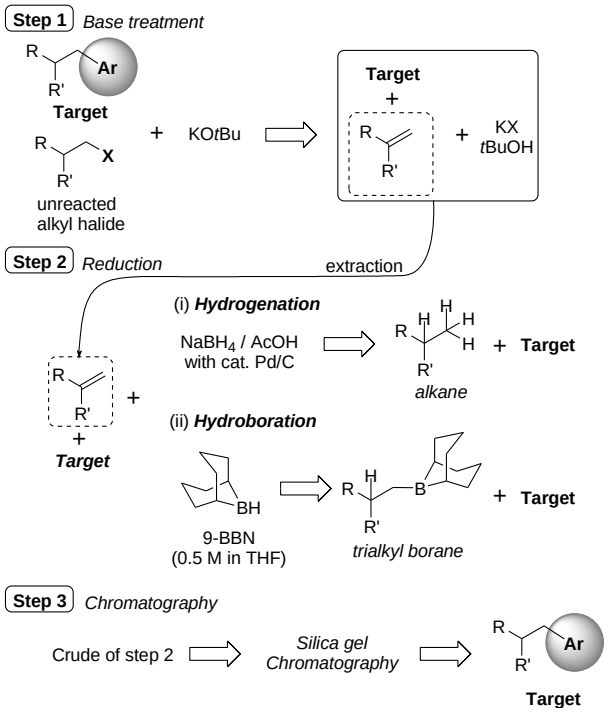
Scheme 1. (a) Typical alkylation reactions of aromatics and (b) possible mixtures resulting from alkylation reactions.

In this study, we describe a series of posttreatments for the purification of alkylated aromatics by using common chemicals to remove unreacted alkyl halides and byproduct olefins from the reaction mixtures (Scheme 2). The first posttreatment involves the transformation of unreacted alkyl halides into olefins with potassium tert-butoxide (KO*t*Bu). The second posttreatment is either (a) a mild hydrogenation of the olefins with sodium borohydride ($NaBH_4$) in acetic acid in the presence of Pd/C or (b) hydroboration of the olefins with a 0.5 M solution of 9-borabicyclo[3.3.1]nonane (9-BBN) in tetrahydrofuran (THF). In case (a), the resulting compound is a saturated alkane that is not as reactive as the original olefin. In case (b), the olefin is converted into an alkyl boron compound that can be readily removed by column chromatography on silica gel. As a result of these treatments, the target alkylated aromatic compounds could be collected as the first fraction from column chromatography on silica gel (the third posttreatment). Notably, even products produced on gram-scale could be purified by one short-column after the first and second posttreatments.

2. Experimental

2.1 Instrumentation and Materials. ^{1}H NMR and ^{13}C NMR spectra were obtained on JEOL ECS-400 spectrometers using $CDCl_3$ as a solvent (peak position δ^1H = 7.26 ppm) and tetramethylsilane was used as an internal standard for ^{1}H NMR spectra (0.00 ppm). For thin-layer chromatography (TLC) analyses in this work, EMD/Merck^{TM} KGaA precoated TLC plates (silica-gel 60 Al F_{254}) were used.

All reactions were carried out under an argon atmosphere using a standard 2-neck flask with a three-way stopcock and a rubber septum. Aniline, 2-hexyl-1-decanol, and KO*t*Bu were purchased form Sigma-Aldrich Company.



Scheme 2. Proposed three-step treatment.

2-Bromo-9*H*-fluorene, 1-bromododecane, 1-bromo-3,5-dimethoxybenzene, 1-bromobutane, 2-ethylhexylbromide, potassium borohydride ($NaBH_4$) were purchased from TCI Japan. Fluorene and 2-dimethylaminoethanol were purchased from Wako chemicals. Ammonium chloride (NH_4Cl), dry THF, *n*-hexane, ethy acetate (EtOAc), dichloromethane (DCM), I_2 (for TLC stain) were purchased from Kanto Chemical. All Chemical were used without further purification. The branched alkylhalide (so-called swallowtail-type alkyl chain): 2-hexyldecanbromide and 5-bromobenzene-1,3-diol were synthesized according to the literature procedures.[37,38]

2.2 General Procedure of Alkylation: Fluorenes. The general procedure for the alkylation of fluorene (C-alkylation) is as follows. A two-neck flask with a three-way stopcock and a rubber septum was charged with fluorene (4 mmol, 0.664 g) and dry THF (20 mL). KO*t*Bu (12 mmol, 1.346 g) was added to the flask at room temperature, then the mixture was heated at reflux for 20 min. The flask was allowed to reach room temperature with stirring for 30 min. 1-Bromododecane (8.8 mmol, 2.20 g) was slowly added to the reaction mixture at 0 °C, then again the flask was allowed to reach room temperature with stirring for overnight.

2.2.1 The First Posttreatment. After checking of TLC and ^{1}H NMR spectrum, the reaction mixture refluxed for one hour. The reaction was quenched by the addition of sat. NH_4Cl aqueous solution, extracted into *n*-hexane (50 × 3 mL), washed successively with water, brine, dried (anhydrous Na_2SO_4) and concentrated by rotary evaporator to afford the reaction mixture (including the target dialkylated fluorene and olefin,).

2.2.2 The Second Posttreatment. 2-(a): To a mixture of the crude mixture of the first posttreatment, 5wt% Pd/C (0.100 g) and acetic acid (AcOH, 4 mmol) in THF (10 mL) were slowly added portionwise $NaBH_4$ (4 mmol, 0.151 g), and the resulting mixture was stirred at room temperature for 12 hours. Thereafter, the mixture was filtered and the precipitate was washed with hexane and concentrated by rotary evaporator for NMR measurement.

2-(b): Since the alkylation was an almost quantitative

reaction, the expected amount of olefin in the mixture was equal to the excess amount of starting alkyl halide (0.8 mmol in the above case). It could be assumed that 0.8 mmol of olefin should be treated with the small excess of 9-BBN (1.2 mmol, 1.5 eq vs olefin). A two neck flask with a three-way stopcock and a rubber septum was charged with the above reaction mixture and dry THF (20 mL). 0.5 M 9-BBN in THF (1.2 mmol, 2.4 mL) was added to the flask at 0 °C and then the flask was allowed to warm to room temperature and stirred for one hour. To quench the remaining 9-BBN in the reaction, aminoalchol (2-dimethylaminoethanol, 0.5 mmol, 0.045 g) was added to the flask and stirred for another one hour.[39] The final reaction mixture was quenched by the addition of water (5 mL), extracted into EtOAc (50 × 3 mL), washed successively with water, brine, dried (anhydrous Na_2SO_4) and concentrated by rotary evaporator to afford the crude mixture.

2.2.3 The Third Posttreatment: The crude product was purified on short silica-gel [5 cm (diameter of column) × 10 cm (length of deposition of silica-gel) was enough for this scale] with *n*-hexane as eluent to give the dialkylated fluorene.

3. Results and Discussion

Our investigation began with the alkylation of 9*H*-fluorene with 1-bromododecane as a representative linear long-chain alkyl halide. The crude ^{1}H NMR spectrum showed an almost quantitative reaction, with no residual fluorene (Figure 1; the peak at δ = 3.89 ppm corresponding to protons in the 9-position of fluorene is absent). However, the signals of small amounts of unreacted 1-bromodecane and byproduct dec-1-ene were observed in the ^{1}H NMR spectrum.

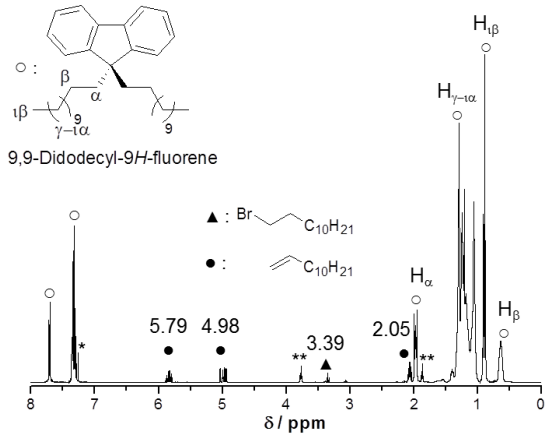


Figure 1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of crude 9,9-didodecyl-9*H*-fluorene without purification or further treatment. Notations: ○ : 9,9-didodecyl-9*H*-fluorene, ▲: 1-bromodecane, ●: dec-1-ene, *: $CHCl_3$, **: THF.

Despite the quantitative nature of this reaction, previously reported yields of this type of alkylation of a fluorene unit are about 80–85%,[32] possibly as a result of unavoidable losses during purification. Both the unreacted alkyl halides and olefins can be active partners for subsequent cross-coupling reactions, such as the Kumada–Tamao–Corriu coupling[40,41] or Mizoroki–Heck reaction,[42,43] or further polymerizations to give π-conjugated polymers. For reliability and ease of purification, the unreacted alkyl halide was transformed into the corresponding olefin by refluxing the reaction mixture with residual KO*t*Bu in the same flask for one hour, as the E2 reaction does not proceed smoothly at room temperature. After this first treatment, the ^{1}H NMR of the reaction mixture showed the presence of dec-1-ene as the sole byproduct, and no signals for unreacted 1-bromodecane were observed (Figure 2).

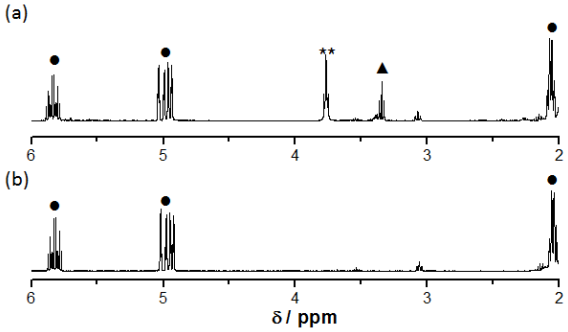


Figure 2. Expanded ^{1}H NMR spectra (400 MHz, $CDCl_3$, room temperature) of crude 9,9-didodecyl-9*H*-fluorene (a) before and (b) after refluxing for one hour with residual KO*t*Bu, without purification by silica-gel column chromatography. Notations: ▲: 1-bromodecane, ●: dec-1-ene, **: THF.

Removal of the resulting olefin is highly dependent on its chain length. If the alkyl halide has six carbon atoms or less, the resultant olefins (e.g., hex-1-ene) can be removed by rotary evaporation, because the boiling points of short-chain alkyl halides and their corresponding olefins are sufficiently low, even under atmospheric pressure (Table 1). For instance, when the alkylation of fluorene with 1-bromobutane was examined, 1-bromobutane and but-1-ene were not observed after evaporation (in practice, by using a rotary evaporator) and subsequent filtration through a short column of silica gel, without any other posttreatment (see Figure S1 in supporting information). In the case of alkylation of fluorene with 2-ethylhexyl bromide, neither the alkyl bromide nor its corresponding olefin (2-ethylhex-1-ene) were detected after the first posttreatment (see Figure S2 in supporting information). Therefore, depending on the boiling points of short-chain alkyl bromides and their corresponding olefins, the first posttreatment plus evaporation using a conventional rotary evaporator might be sufficient to eliminate these impurities.

However, for long-chain linear or branched olefins, which have much higher boiling points, evaporative removal is an uncertain method unless it is checked by a qualitative test. To establish a versatile and universal method for the transformation of impurities by using common chemicals, we attempted to convert the byproduct olefins into alkanes or alkyl boranes, as shown in Scheme 2.

First, we attempted to treat the crude product in a second posttreatment procedure by using the conditions reported by Cordes and co-workers.[44,45] A mixture of 9,9-didodecylfluorene and dodec-1-ene was treated with $NaBH_4$ in AcOH in the presence of Pd/C at room temperature. After 12 hours, no dodec-1-ene was observed in the ^{1}H NMR spectrum (Figure 3a; compare with Figure 2). As an alternative second posttreatment step, we treated the reaction mixture with a 0.5 M THF solution of 9-BBN, a highly reactive hydroboration agent. After hydroboration at 0 °C for 30 minutes then at room temperature for one hour, none of the olefin was detected in the ^{1}H NMR spectrum (Figure 3b). We then subjected the mixture to chromatography on a short silica gel column, which gave the target 9,9-didodecyl-9*H*-fluorene in an excellent 95% yield (Figure 3c).

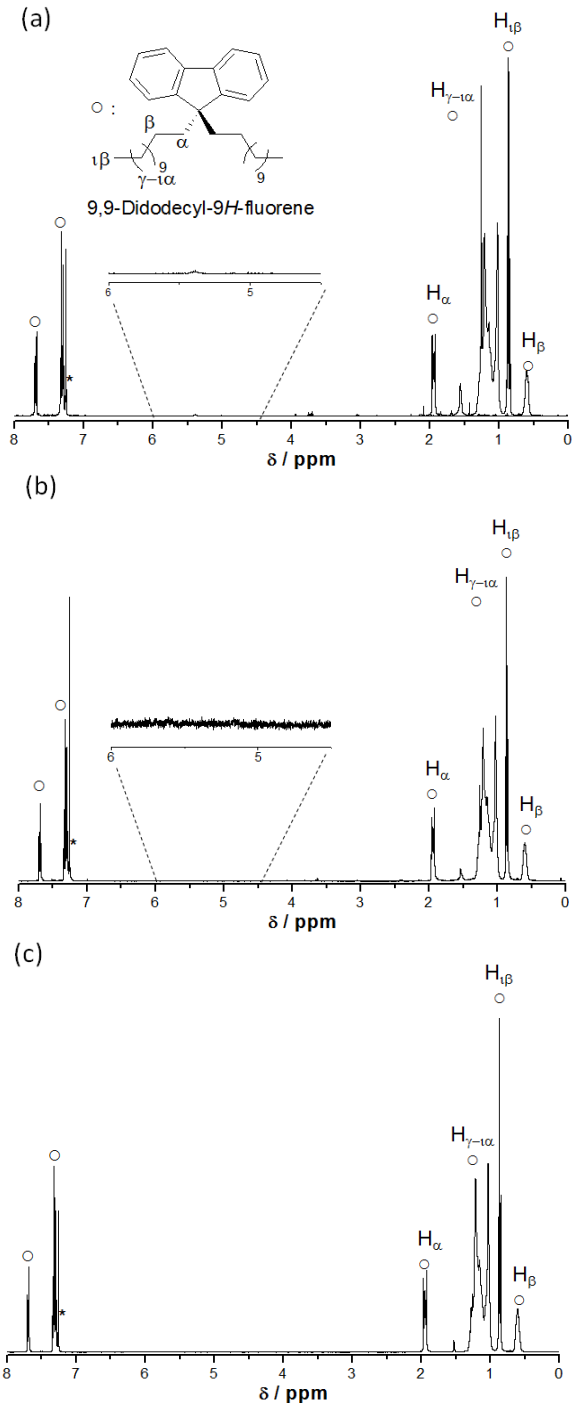


Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) of 9,9-didodecyl-9*H*-fluorene (a) after the treatment with $NaBH_4$ without purification by silica-gel column chromatography, (b) after the treatment with 9-BBN without purification by silica-gel column chromatography, and (c) after silica-gel column chromatography of the crude product treated with 9-BBN.

To examine the scope of application of the treatment, reaction mixtures from other aromatic building blocks for developing optoelectronically active materials [2-bromo-9*H*-fluorene, aniline, and 5-bromobenzene-1,3-diol] were subjected to our three-step posttreatment, mainly using 9-BBN (Scheme 2 and Table 1), because the target alkylated aromatics can be collected as first fractions from column chromatography. As shown in Table 1, even when we used hexane, a nonpolar solvent, as the eluent for thin-layer

Table 1. Summary of alkylation reactions and retention factors in TLC

Entry	Aromatic (R_{f0})[a]	**R**Br (R_{f1}/bp)[a,b] / **O**lefin (R_{f2}/bp)[a,b]	Target alkylated compound (R_{f3})[a]	$\Delta R_{f1} = R_{f1} - R_{f3}$ / $\Delta R_{f2} = R_{f2} - R_{f3}$
1	(0.42)	nC$_{12}$H$_{25}$Br: **R$_1$**Br (0.77/276)	(0.64)	0.13
		nC$_{10}$H$_{21}$: **O1** (0.83[c]/213[47])		0.19
2		: **R$_2$**Br (0.68/93–98)		0.01
		: **O2** (0.76[c]/120,[48] 66–70 at 120 Torr[49])	(0.67)	0.09
3	(0.51)	**R$_1$**Br (0.77)	(0.67)	0.10
		O1 (0.83[c])		0.16
4		: **R$_3$**Br (0.78/114–118 at 0.5 Torr[50])	(0.77)	0.01
		: **O3** (0.84[c]/165 at 9 Torr[51])		0.07
5	(<0.1)[c]	**R$_1$**Br (0.77)	(0.82)	0.05
		O1 (0.83[c])		0.01
6	(0.0)	**R$_3$**Br (0.78)	(0.69)	0.09
		O3 (0.84[c])		0.15

[a] TLC silica gel 60 Al plates (5 cm × 1.5 cm) were used in determining the retention factors (R_f), The values of R_{f1} and R_{f2} were determined by using pure chemicals and R_{f3} was determined by using the crude mixture. The R_f values were calculated from the averages of two or three TLC tests. All TLC tests were carried out by using hexane as an eluent at room temperature. [b] Boiling point/°C at 760 Torr are reported unless otherwise noted. [c] With short tailing.

chromatography (TLC) tests, the retention factors (R_f) of the byproduct olefins were only slightly higher than those of the target alkylated aromatics. For this reason, it is difficult to separate the target from the unreacted alkyl halide and byproduct olefin through chromatography on a short column of silica gel. The values of the differences in retention factor between the alkyl halide and the target alkylated compound (ΔR_{f1}) and between the alkene and the target alkylated compound (ΔR_{f2}) tended to be small for fluorenes bearing halo groups and/or alkyl chains (Table 1, entries 1 and 2, 3 and 4). Alternatively, other alkylation reagent such as alkyl tosylates that have higher polarities than alkyl halides can be used. However, the risk of the E2 reaction with alkyl tosylates is similar to that with alkyl halides.[46] Although linear alkyl halides rarely undergo E2 reactions with weak bases such as potassium carbonate (K_2CO_3), small amounts of olefin were detected in the ^{1}H NMR spectrum (entry 5, see Figure S3 in supporting information). We therefore added additional KO*t*Bu to the resulting mixture for entry 5 to transform any unreacted linear alkyl halide into the corresponding olefin. In the case of entry 6, the excess branched alkyl halide was completely converted into the corresponding olefin by the E2 reaction with K_2CO_3 (see Figure S4 in supporting information). The second and third posttreatments were highly effective in the purification in the cases of entries 5 and 6, and no impurity was observed in the final ^{1}H NMR spectra (see Figures S5 and S6 in supporting information). In addition, we tested the above treatment for a gram-scale synthesis of *N*,*N*-didodecylaniline (entry 5) and we obtained this compound in a very high yield of 91%.

From the results shown in Table 1, we suggest the flow chart shown in Figure 4 as a versatile and universal method for the purification of C-, N-, and O-alkylation reactions. Regardless of the alkylating reagent used, we obtained the target product readily and with a consistent quality, as judged from NMR measurements.

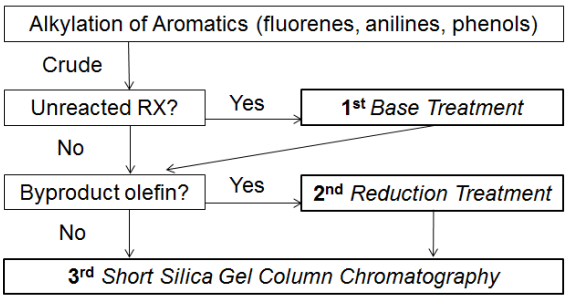


Figure 4. Flow chart of the three-step posttreatment method.

4. Conclusion

In summary, a three-step posttreatment procedure following C-alkylation of fluorenes, N-alkylation of anilines, or O-alkylation of phenols is remarkably effective in removing unreacted alkyl halides and the corresponding olefin byproducts from the reaction mixture. This posttreatment technique should significantly facilitate the development of various functional π-conjugated building blocks and future optoelectronic soft materials based on alkyl-chain engineering.

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