Perfluorinated sulfonic acid resin (Nafion-H) catalysed *trans*-*t*-butylation of 7-*t*-butyl-1,3-disubstituted pyrenes; a new route for the preparation of 1,3-disubstituted pyrenes

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The perfluorinated sulfonic acid resin (Nafion-H) catalyst is found to be effective in promoting the *trans*-*t*-butylation of 7-*t*-butyl-1,3-dialkylpyrenes to afford the corresponding 1,3-dialkylpyrenes in good yields.

Keywords: solid superacid, Nafion-H, *trans*-*t*-butylation, pyrenes

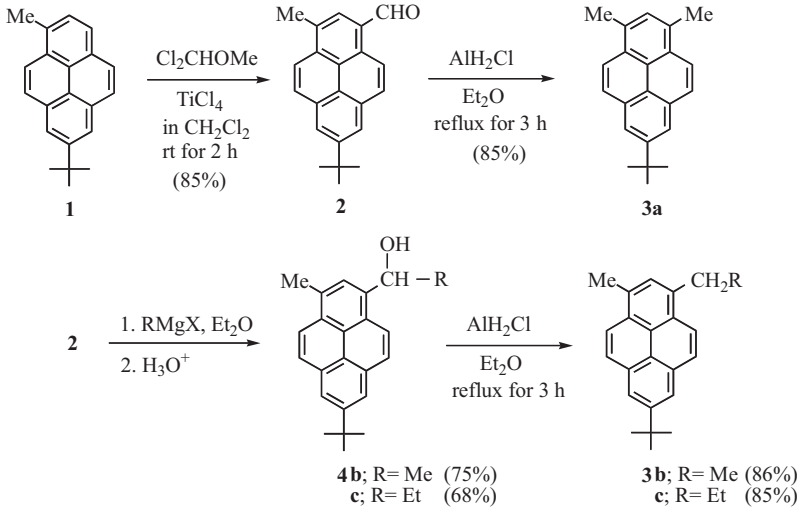
Pyrenes and their derivatives, which belong to the class of polycyclic aromatic hydrocarbons, are reported to cause cancer or mutations in living organisms,[1] thus making pyrenes the largest class of chemical carcinogens known today. Pyrenes are formed when organic materials are burnt or strongly heated. They are produced in larger amounts under inefficient combustion conditions. Analysis of the complicated mixtures of polycyclic aromatic compounds in the environment is possible only when pure and well-characterised reference materials are available.[2] Reference materials are essential also for the study of the biological effects of polycyclic aromatic compounds and for the establishment of structure-activity relationships.

Electrophilic substitution of pyrene occurs at 1, 3, 6, and 8 positions, but not at the other positions (2, 4, 5, 7, 9, and 10).[3–7] Therefore, pyrenes substituted at the latter positions must be prepared in ways other than direct electrophilic substitution of pyrene itself.[8] For example, Hempenius *et al.*[6] reported the introduction of methyl groups at 1, 2, and 3 positions, starting from 1*H*-phenalene to construct a pyrene ring. There is substantial interest in investigating the selective introduction of substituents at positions 1, 2 and 3 in ways other than by direct electrophilic substitution of pyrene.

We previously reported a convenient preparative route for 7-*t*-butyl-1-methylpyrene (**1**) from pyrene in three steps, which involves formylation of pyrene and Wolff-Kishner reduction to afford 1-methylpyrene followed by *t*-butylation with *t*-butyl chloride.[9] This compound can afford a convenient starting material to prepare a series of 1,3-disubstituted pyrenes by electrophilic substitution because one of the active positions of pyrene is protected by the *t*-butyl group. On the other hand, we reported that $AlCl_3$–$MeNO_2$ catalysed *trans*-*t*-butylation of *t*-butyl-substituted pyrenes in benzene did not afford any product.[9] This result seems to indicate that the pyrenes are easily complexed with Lewis acids decreasing their reactivity for the *trans*-*t*-butylation. We have also found the convenient and efficient method of Nafion-H (a solid perfluorinated sulfonic acid resin) catalysed *trans*-*t*-butylation of *t*-butylphenols, *t*-butyldiphenylalkanes, and *t*-butylcarbazoles.[10,11] We now report Nafion-H catalysed *trans*-*t*-butylation of 7-*t*-butyl-1,3-disubstituted pyrenes to give the corresponding 1,3-disubstituted pyrenes.

Results and discussion

The preparation of 7-*t*-butyl-1-methylpyrene (**1**) was carried out according to the reported procedure.[9] Formylation of 7-*t*-butyl-1-methylpyrene (**1**) with dichloromethylmethyl ether in the presence of titanium tetrachloride occurred selectively at the 3-position to afford the corresponding 3-formyl derivative **2** in 85% yield. This was converted into 7-*t*-butyl-1,3-dimethylpyrene (**3a**) in 85% yield by chlorohydroalane (AlH_2Cl) reduction.[12] 7-*t*-Butyl-1-ethyl-3-methylpyrene (**3b**) and 7-butyl-1-methyl-3-propylpyrene (**3c**) were obtained by Grignard reaction of **2** with alkyl magnesium halides to afford the alcohol derivatives **4b** and **4c,** respectively, followed by chlorohydroalane reduction (Scheme 1).



Scheme 1

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Table 1 Nafion-H catslysed *trans*-*t*-butylation of 7-*t*-butyl-1,3-disubstituted pyrenes[a]

Run	substrate	R	ArH	Reaction time/h	Product yields/%	Recovery/%
1	**3a**	Me	Toluene	1	**10a** (90)[80][b]	**3a** (10)
2	**3a**	Me	*o*-xylene	1	**10a** (98)[87][b]	**3a** (2)
3	**3b**	Et	*o*-xylene	1	**10b** (92)[85][b]	**3b** (8)
4	**3c**	Pr	*o*-xylene	1	**10c** (88)[82][b]	**3c** (12)
5	**5**	Br	*o*-xylene	1	**10d** (0)[c]	**5** (0)
6	**6**	OMe	*o*-xylene	1	**10e** (0)[c]	**6** (0)
7	**7**	NO_2	*o*-xylene	12	**10f** (0)	**7** (100)

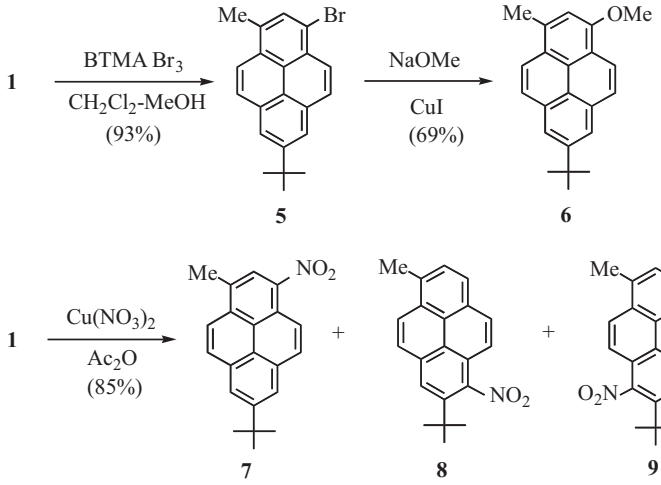
[a]Yields are determined by GLC analyses, [b]Isolated yields are shown in square parentheses. [c]An intractable mixture of products was obtained.

The same regioselectivity was observed in bromination of **1** with BTMA Br_3[13] to afford 1-bromo-7-*t*-butyl-3-methylpyrene (**5**) in 93% yields. The relatively facile electrophilic substitution at the 3-position instead of *ortho* to a *t*-butyl group (6- or 8-position) on the pyrene ring is attributed to the steric bulk of the *t*-butyl group inhibiting the substitution at the 6 and 8 positions on the pyrene ring. No substitution at 4, 5, 9 and 10 positions was observed. This results attributable to the high reactivity of the 1, 3, 6 and 8-positions. On the other hand, when nitration of **1** with cuprous nitrate in acetic anhydride was carried out at room temperature, the 3-nitro derivative **7** was obtained in 53% yield along with a mixture of products **8** and **9** derived from nitration at the 6- or 8-positions of the pyrene ring, in 20% yield. The nitronium ion attack on the pyrene ring occurred due to the higher π-basicity of the pyrene ring as compared to a benzene ring even in the relatively mild reaction conditions. The present lower positional selectivity may be governed by the stabilities of π-complex transition states proposed in the normal aromatic nitration being different from those of the σ-complex transition states in the bromination or formylation.[14] 7-*t*-Butyl-1-methoxy-3-methylpyrene (**6**) was prepared from (**5**) by reaction with NaOMe in the presence of CuI in 69% yield.

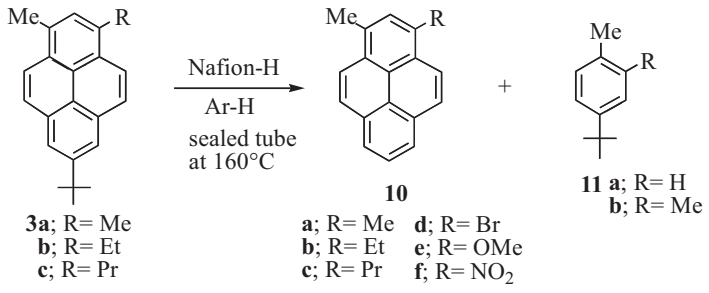
When 7-*t*-butyl-1,3-dimethylpyrene (**3a**) was treated with perfluorinated sulfonic acid resin (Nafion-H) (100 wt%) in boiling toluene for 12 h, the desired 1,3-dimethyl-pyrene (**10a**) was obtained in 78% yield along with 4-*t*-butyltoluene (**11a**) (See Table 1). The higher temperature in toluene or in *o*-xylene at 160°C in sealed tube reduced the reaction time to 1 h to complete the reaction. This method provides good yields, easy isolation of the products, and no concomitant demethylation was observed under the reaction conditions.

Similar *trans*-*t*-butylation of ethyl derivative **3b** and propyl derivative **3c** in the presence of Nafion-H as a catalyst, was carried out in *o*-xylene in the sealed tube to afford the desired ethyl (**10b**) and propyl (**10c**) derivatives in good yields, respectively, along with 4-*t*-butyl-*o*-xylene (**11b**).

Nafion-H-catalysed *trans*-*t*-butylation reaction of 1-bromo-7-*t*-butyl-3-methylpyrene (**5**) and 7-*t*-butyl-1-methoxy-3-methylpyrene (**6**) was attempted to afford the corresponding **10d** and **10e** resulted only in a mixture of intractable products. Thus, we have not succeeded in the selective removal of the *t*-butyl groups of **5** and **6** due to the concomitant Nafion-H



Scheme 2



Scheme 3

induced side reactions such as debromination or demethylation of the methoxy group under the reaction conditions used. Similar treatment of 7-*t*-butyl-1-methyl-3-nitropyrene (**6**) under *o*-xylene at 160°C failed. Only the starting compound was recovered.

Conclusions

We conclude that the electrophilic substitutions of 7-*t*-butyl-1-methylpyrene lead to the first-reported direct introduction of one substituent at the 3-position. The preparative route of **1** → **2** → **3** → **10** should be useful for the preparation of 1,3-dialkyl-substituted pyrenes. Further application of the present method is currently under study in our laboratory.

Experimental

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with Me_4Si as an internal reference. IR spectra were measured as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed on a Yanaco MT-5 instrument.

Materials

The preparation of 7-*tert*-butyl-1-methylpyrene (**1**) has previously been described.[9]

Preparation of 7-t-butyl-3-methylpyrene-1-carboaldehyde (**2**): To a stirred solution of **1** (60.0 g, 220 mmol) and dichloromethyl methyl ether (50.0 g, 440 mmol) in CH_2Cl_2 (600 cm^3) was added at 0°C a solution of titanium tetrachloride (24 cm^3, 218.9 mmol) in CH_2Cl_2 (50 cm^3). This mixture was stirred for 2 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (250 cm^3 × 2). The organic layer was washed with water (300 cm^3 × 2), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed over silica gel (Wako, C-300; 500 g) with a benzene as eluent to give a yellow solid, which was recrystallised from hexane–$CHCl_3$ (1 : 1) to afford **2** (54.0 g, 82%) as pale yellow prisms, m.p. 238–238°C; ν_{max}(KBr)/cm^{-1} : 3050, 2950, 1670, 1570, 1470; δ_H ($CDCl_3$) : 1.60 (9H, s, *t*Bu), 3.00 (3H, s, *Me*), 8.22 (1H, d, *J* = 9.3 Hz, Ar–*H*), 8.24 (1H, d, *J* = 9.3 Hz, Ar–*H*), 8.25 (1 H, d, *J* = 9.3 Hz, Ar–*H*), 8.26 (1H, s, Ar–*H*), 8.33 (2H, s, Ar–*H*), 9.33 (1H, d, *J* = 9.3 Hz), 10.77 (1H, s, C*H*O); *m*/*z*: 300 (M$^+$). Anal. calcd. for $C_{22}H_{20}O$ (300.4): C, 87.96; H, 6.71. Found: C, 88.0; H, 6.8.

Bromination of 7-t-butyl-1-methylpyrene (**1**): To a solution of **1** (1.73 g, 6.36 mmol) in a mixture of CH_2Cl_2 (75 cm^3) and MeOH (25 cm^3) was added a solution of BTMA Br_3 (2.5 g, 6.36 mmol) at 0°C. After the reaction mixture was stirred for 2 h at room temperature, it was poured into water (100 cm^3). The organic layer was extracted with CH_2Cl_2 (50 cm^3 × 2). The extract was washed with 10% aqueous sodium thiosulfate (50 cm^3) and water (50 cm^3), dried (Na_2SO_4), and concentrated. The residue was column chromatographed over silica gel (Wako, C-300; 200 g) with hexane as an eluent to afford colourless solid. Recrystallisation from hexane–benzene (1 : 1) afforded **5** (2.08 g, 93%) as colourless plates, m.p. 256–258°C; ν_{max}(KBr)/cm^{-1}: 2980, 1600, 1500, 1480, 1380, 1230, 1160, 990, 870; δ_H ($CDCl_3$): 1.58 (9H, s, *t*Bu), 2.91 (3H, s, *Me*), 8.06 (1H, s, Ar*H*), 8.07 (1H, d, *J* = 9.2 Hz, Ar–*H*), 8.09 (1H, d, *J* = 9.2 Hz, Ar–*H*), 8.12 (1H, d, *J* = 9.2 Hz, Ar–*H*), 8.22 (2H, s, Ar–*H*), 8.33 (1H, d, *J* = 9.2 Hz, Ar–*H*); *m*/*z*: 350, 352 (M$^+$). Anal. calcd. for $C_{21}H_{19}Br$ (351.29): C, 71.80; H, 5.45. Found: C, 71.5; H, 5.45.

Nitration of 7-t-butyl-1-methylpyrene (**1**): To a solution of **1** (173 mg, 0.636 mmol) in acetic anhydride (50 cm^3) was added cuprous nitrate (184.4 mg, 0.763 mmol) at room temperature. After the reaction mixture was stirred for 1 h at room temperature, it was poured into a large amount of ice water (200 cm^3) and extracted with CH_2Cl_2 (50 cm^3 × 2). The CH_2Cl_2 extract was washed with water and dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give as a pale yellow solid a mixture of **7** and (**8** + **9**) (171 mg, 85%) in the ratio 80 : 20 (NMR spectrum). Recrystallisation from benzene afforded 7-*t*-butyl-1-methyl-3-nitropyrene (**7**) (107 mg, 53%) as pale orange prisms, m.p. 240–241°C; ν_{max}(KBr)/cm^{-1}: 2950, 1590, 1530, 1500, 1320, 1310, 1230, 910, 880; δ_H ($CDCl_3$): 1.61 (9H, s, *t*Bu), 2.95 (3H, s, *Me*), 8.19 (1H, d, *J* = 9.5 Hz, Ar–*H*), 8.23 (1H, d, *J* = 9.5 Hz, Ar–*H*), 8.26 (1H, d, *J* = 9.5 Hz, Ar–*H*), 8.33 (1H, d, *J* = 1.5 Hz, Ar–*H*), 8.34 (1H, d, *J* = 1.5 Hz, Ar–*H*), 8.47 (1H, s, Ar–*H*), 8.83 (1H, d, *J* = 9.5 Hz, Ar–*H*); *m*/*z*: 317 (M$^+$). Anal. calcd. for $C_{21}H_{19}NO_2$ (317.39): C, 79.47; H, 6.03; N, 4.41. Found: C, 79.9; H, 6.0; N, 4.4.

Preparation of 7-t-butyl-1-methoxy-3-methylpyrene (**6**): To methanol (18 cm^3) was added sodium (580 mg, 25.2 mmol) and then a mixture of CuI (177 mg, 0.93 mmol) and **5** (447.0 mg, 1.27 mmol) in DMF (5 cm^3). After the reaction mixture was refluxed for 36 h, it was poured into ice-water (100 cm^3 × 2) and extracted with CH_2Cl_2 (70 cm^3 × 2). The extract was washed with water (40 cm^3 × 2), dried (Na_2SO_4), and concentrated. The residue was column chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to afford a colourless solid. Recrystallisation from hexane afforded the *title compound* **6** (264.6 mg, 69%) as colourless prisms, m.p. 160–162°C; ν_{max}(KBr)/cm^{-1}: 3050, 2980, 1600, 1550, 1520, 1350, 1270, 1220, 1110, 880, 840; δ_H ($CDCl_3$): 1.56 (9H, s, *t*Bu), 2.92 (3H, s, *Me*), 4.12 (3H, s), 7.34 (1H, s, Ar–*H*), 7.88 (1H, d, *J* = 9.2 Hz, Ar–*H*), 7.94 (1H, d, *J* = 9.2 Hz, Ar–*H*), 8.07 (1H, d, *J* = 9.2 Hz, Ar–*H*), 8.09 (2H, s, Ar–*H*), 8.36 (1H, d, *J* = 9.2 Hz, Ar–*H*); *m*/*z*: 302 (M$^+$). Anal. calcd. for $C_{22}H_{22}O$ (302.42): C, 87.37; H, 7.33. Found: C, 87.3; H, 7.5.

Preparation of 1-(7-t-butyl-3-methylpyren-1-yl)propan-1-ol (**4c**): To a solution of EtMgBr (prepared from ethyl bromide (872 mg, 8 mmol) and magnesium (122 mg, 5 mmol) in diethyl ether (25 cm^3) was gradually added a room temperature solution of 7-*t*-butyl-3-methylpyrene-1-carboaldehyde (**2**) (300 mg, 1 mmol) and diethyl ether (15 cm^3) dropwise at such a rate as to allow the mixture to reflex gently. After the addition the mixture was refluxed for an additional 12 h and the reaction mixture was quenched with 10% ammonium chloride and extracted with CH_2Cl_2 (50 cm^3). The organic layer was washed with water, dried by Na_2SO_4, and then concentrated. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give a colourless solid, which was recrystallised from hexane to afford **4c** (224 mg, 68%) as pale yellow prisms, m.p. 140–142°C; δ_H ($CDCl_3$): 1.05–1.08 (3H, t, *J* = 7.4 Hz, –CH_2CH_3), 1.58 (9H, s, *t*Bu), 2.04–2.10 (3H, m, CH_2, –*OH*), 2.97 (3H, s, *Me*), 5.66–5.70 (1H, m, –*CH*), 7.25 (1H, s, Ar–*H*), 7.98–8.27 (6H, m, Ar–*H*); *m*/*z*: 330 (M$^+$). Anal. calcd. for $C_{24}H_{26}O$ (330.27): C, 87.23; H, 7.93. Found: C, 87.0; H, 7.9.

Similarly, compound **4b** was prepared by the reaction of **2** with MeMgI in 75% yield.

1-(7-*t*-Butyl-3-methylpyren-1-yl)ethan-1-ol (**4b**) was obtained as pale yellow prisms (hexane), m.p.196–198°C; δ_H ($CDCl_3$): 1.58 (9H, s, *t*Bu), 1.77 (3H, d, *J* = 6.3 Hz, CH_3), 2.04 (1H, s, –*OH*), 2.99 (3H, s, *Me*), 5.99 (1H, d, *J* = 6.3 Hz), 8.01–8.30 (7H, m, Ar–*H*); *m*/*z*: 316 (M$^+$). Anal. calcd. for $C_{23}H_{24}$ (316.24): C, 87.30; H, 7.64. Found: C, 87.3; H, 7.75.

Preparation of 7-t-butyl-1,3-dimethylpyrene (**3a**): To a solution of AlH_2Cl [prepared from $AlCl_3$ (1.33 g, 1 mmol) and $LiAlH_4$ (380 mg, 1 mmol) in diethyl ether (25 cm^3) was gradually added a solution of 7-*tert*-butyl-3-methylpyrene-1-carboaldehyde (**2**) (600 mg, 2 mmol) in diethyl ether (50 cm^3) while stirring at room temperature. After the reaction mixture had been refluxed for an additional 3 h, it was quenched by adding to a large excess of ice-water and the reaction mixture was extracted with ethyl acetate. The organic layer was washed with water, dried by Na_2SO_4 and concentrated. The residue was chromatographed over silica gel (Wako, C-300; 300 g) with hexane as eluent to give a colourless solid, which was recrystallised from hexane to afford **3a** (486 mg, 85%) as colourless prisms, m.p. 221–221.5°C; ν_{max}(KBr)/cm^{-1}: 2950, 1600, 1450, 1380; δ_H ($CDCl_3$): 1.51 (9H, s, *t*Bu), 2.86 (6H, s, *Me*), 7.63 (1H, s, Ar*H*), 7.98 (2H, d, *J* = 10.1 Hz, Ar–*H*), 8.10 (2H, s, Ar–*H*), 8.12 (2H, d, *J* = 10.1 Hz, Ar–*H*); *m*/*z*: 286 (M$^+$). Anal. calcd. for $C_{22}H_{22}$ (286.18): C, 92.26; H, 7.74. Found: C, 92.5; H, 7.6.

Similarly, compounds **3b** and **3c** were prepared by the chlorohydroalane reduction of **4b** and **4c** in 86 and 85% yields, respectively.

7-*t*-Butyl-1-ethyl-3-methylpyrene (**3b**) was obtained as colourless prisms (hexane), m.p. 204–206°C; δ_H ($CDCl_3$): 1.39 (3H, t, *J* = 7.4 Hz CH_2CH_3), 1.51 (9H, s, *t*Bu), 2.88 (3H, s, *Me*), 3.26 (2H, q, *J* = 7.4 Hz, CH_2CH_3), 7.64 (1H, s, Ar–*H*), 7.89–8.16 (6H, m, Ar–*H*); *m*/*z*: 300 (M$^+$). Anal. calcd. for $C_{23}H_{24}$ (300.30): C, 91.95; H, 8.05. Found: C, 91.8; H, 7.9.

7-*t*-Butyl-1-methyl-3-propylpyrene (**3c**) was obtained as colourless prisms (hexane), m.p. 144–146°C; δ_H ($CDCl_3$): 1.07 (3H, t, *J* = 7.4 Hz, CH_2CH_3), 1.58 (9H, s, *t*Bu), 1.84–1.91 (2H, m, $CH_2CH_2CH_3$), 2.86 (3H, s, *Me*), 3.2–3.29 (2H, m, CH_2CH_3), 7.69 (1H, s, Ar–*H*), 7.97–8.22 (6H, m, Ar–*H*); *m*/*z*: 314 (M$^+$). Anal. calcd. for $C_{24}H_{26}$ (314.28): C, 91.67; H, 8.33. Found: C, 91.4; H, 8.3.

Preparation of 1,3-dimethylpyrene (**10a**): A solution of **3a** (200 mg, 0.70 mmol) in *o*-xylene (5 cm^3) and Nafion-H (200 mg) was heated at 160°C in a sealed tube under nitrogen for 1 h. After the reaction mixture was cooled to room temperature, it was filtered and the filtrate was concentrated. The residue was chromatographed over silica gel (Wako, C-300; 50 g) with hexane as eluent to give a colourless solid, which was recrystallised from hexane to afford **10a** (140 mg, 87%) as colourless prisms, m.p. 142–143°C; ν_{max}(KBr)/cm^{-1}: 3050, 2950, 1600, 1450, 1370, 1260, 1180, 1060; δ_H ($CDCl_3$): 2.93 (6H, s, *Me*), 7.72 (1H, s, Ar–*H*), 7.95 (1H, t, *J* = 7.7 Hz, Ar–*H*), 8.02 (2H, d, *J* = 9.2 Hz, Ar–*H*), 8.13 (2H, d, *J* = 7.7 Hz, Ar–*H*), 8.20 (2H, d, *J* = 9.2 Hz, Ar–*H*); *m*/*z*: 230 (M^+). Anal. calcd. for $C_{18}H_{14}$ (230.30): C, 93.87; H, 6.13. Found: C, 93.8; H, 6.5.

The formation of 4-*t*-butyl-*o*-xylene (**11b**) was confirmed by GLC (conditions: Shimadzu gas chromatography, GC-14A, Silicone OV-1, 2 m, programmed temperature rise 12°C/min; carrier gas nitrogen 25 cm^3/min).

Similarly, compounds **10b** and **10c** were prepared in 85 and 82% yields, respectively.

1-Ethyl-3-methylpyrene (**10b**) was obtained as colourless prisms (hexane), m.p. 210–212°C; δ_H ($CDCl_3$): 1.48 (3H, t, *J* = 7.4 Hz, CH_2CH_3), 2.97 (3H, s, *Me*), 3.35 (2H, q, *J* = 7.4 Hz, CH_2CH_3), 7.76 (1H, s, Ar-*H*), 7.93–8.27 (7H, m, Ar–*H*); *m*/*z*: 244 (M^+). Anal. calcd. for $C_{18}H_{16}$ (244.33): C, 93.40; H, 6.60. Found: C, 93.4; H, 6.6.

1-Methy-3-propylpyrene (**10c**) was obtained as a colourless oil; δ_H ($CDCl_3$): 1.08 (3H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 1.84–1.92 (2H, m, $CH_2CH_2CH_3$), 2.95 (3H, s, *Me*), 3.28 (2H, t, *J* = 7.4 Hz, $CH_2CH_2CH_3$), 7.73 (1H, s, Ar-*H*), 7.85–8.23 (7H, m, Ar-*H*); *m*/*z*: 258 (M^+). Anal. calcd. for $C_{20}H_{18}$ (258.36): C, 92.98; H, 7.02. Found: C, 92.7; H, 7.0.

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