Metacyclophanes and Related Compounds. Part 16. Preparation of 8-Fluoro-t-butyl[2.2]metacyclophanes and their Treatment with Aluminium Chloride–Nitromethane in Benzene[1]

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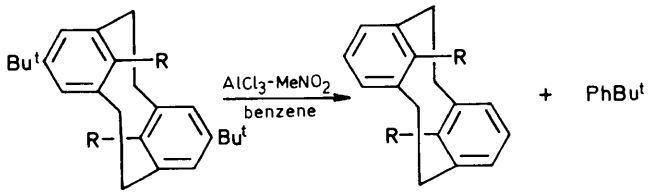
The preparation of 8-fluoro-t-butyl[2.2]metacyclophanes (**5**) are described. Dithia[3.3]metacyclophane (**3**) and [3.3]metacyclophane bis(sulphones) (**4**) were obtained as a mixture of *transoid* and *cisoid* conformers, but [2.2]metacyclophanes (**5**) were exclusively obtained as the *transoid* conformer after pyrolysis of the sulphones (**4**). $AlCl_3$–$MeNO_2$-Catalyzed *trans*-t-butylation of 8-fluoro-16-methyl-5,13-di-t-butyl[2.2]metacyclophane (**5a**) in benzene under a variety of conditions failed to give 8-fluoro-16-methyl[2.2]metacyclophane (**32**) but, instead, the tetrahydropyrenes (**33**) and/or (**34**) were obtained depending upon the conditions used. Internally substituted [2.2]metacyclophanes were isomerized to the strainless [2.2]metacyclophanes and these were then oxidized to the tetrahydropyrene (**33**).

Recently we found that 8,16-dimethyl-[2], 8,16-dihydroxy-,[3] and 8,16-difluoro-[2.2]metacyclophanes[4] can be prepared by $AlCl_3$–$MeNO_2$-catalyzed *trans*-t-butylation of the corresponding t-butyl derivative. These results suggest that 16-substituted 8-fluoro[2.2]metacyclophanes might be prepared from the corresponding t-butyl derivatives by the similar manner.[2] We report here the preparation of the title compounds and their treatment with $AlCl_3$–$MeNO_2$ catalyst in a benzene solution.



Scheme 1.

Results and Discussion

Preparation.—A preparative route to the title compounds is summarized in Scheme 2.

The preparations of (**1a**)[5] and (**2a—b**)[2] have already been described in earlier papers. Since, however, the chloromethylation of t-butylfluorobenzene afforded (**1a**) only in low yield, the preparation of 2,6-bis(bromomethyl)-4-t-butylfluorobenzene (**15**) was, instead, attempted.

1-Fluoro-2,6-dimethyl-4-t-butylbenzene (**10**), prepared in four steps from *m*-xylene, on bromination with 2.2 equivalents of NBS gave a mixture of mono- (**14**), di- (**15**), and tri-bromides (**16**); with 4.1 equiv. of NBS the tetrabromide (**17**) was obtained in 54% yield. Compound (**12**) was prepared from (**10**) by $AlCl_3$–$MeNO_2$-catalyzed *trans*-t-butylation in the presence of biphenyl (**11**) as an acceptor.[6] In contrast to that of (**10**), bromination of (**12**) with 2.2 equiv. of NBS afforded a good yield of the desired compounds (**1b**).

The preparative route to compound (**2c**) is shown in Scheme 4. Direct preparation of (**19**) from (**18**) by bromination afforded a mixture of (**19**) and its isomer (**20**). The molar ratio of (**19**):(**20**) is 1:1, as estimated from n.m.r. spectral results.

Table 1. Chemical shifts (δ) of internal methyl protons of dithia[3.3]metacyclophanes (**3**), [3.3]metacyclophane bis(sulphones) (**4**), and [2.2]metacyclophanes (**5**).

	Chemical shifts (p.p.m.) of methyl protons		Ratio of *transoid* and *cisoid* methyl protons	
Compound	*transoid*	*cisoid*	*transoid*	*cisoid*
(**3a**)	1.47	2.40	3	2
(**3b**)	1.53	2.40	1.6	1
(**3d**)	1.56	2.40	1	2
(**4a**)	1.37	2.50	3	2
(**4b**)	1.34	2.55	1.6	1
(**4d**)	1.24	2.50	1	2
(**5a**)	0.63		1	0
(**5b**)	0.59		1	0
(**5d**)	0.63		1	0

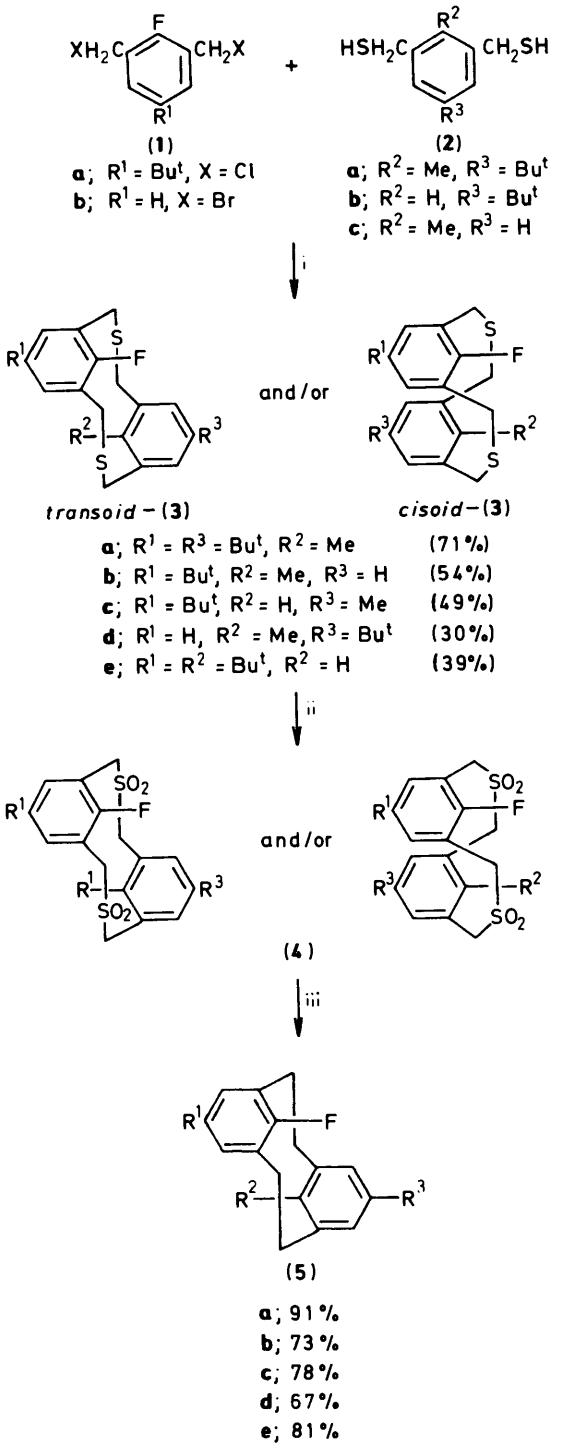
Table 2. The $AlCl_3$–$MeNO_2$ catalyzed reaction of 8-fluoro-16-methyl-5,15-di-t-butyl[2.2]metacyclophane (**5a**) in benzene[a]

Run	Catalyst/(**5a**) (mol/mol)	Time (h)	Product (%)[b]
1	1.3	2	(**33**) (82)
2	2.0	2.5	(**33**) (80), (**34**) (6)
3	2.6	3	(**34**) (97)
4	4.0	1.5	(**34**) (96)
5[c]	1.3	0.25	(**34**) (90)

[a] The reaction temperature was 25 °C. [b] The isolated yields are shown. [c] $AlCl_3$ is used as a catalyst.

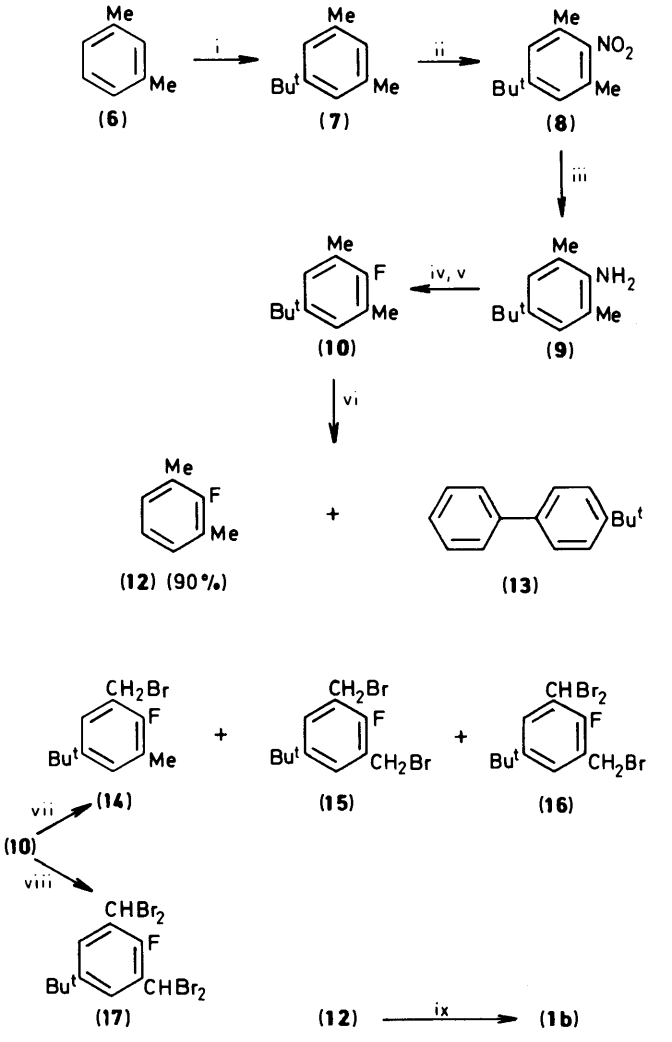
Therefore, (**19**) was prepared by the alternative route shown in Scheme 4. The trans-t-butylation of (**23**) in the presence of $AlCl_3$, $AlBr_3$, and AlI_3 or de-t-butylation in boiling 85% H_3PO_4 failed to give the expected compound (**24**). However, the trans-t-butylation of (**19**), which was prepared from (**22**), gave (**25**) in good yield.

Mitchell and Boekelheide[7] reported that reaction of 2,6-bis(chloromethyl)toluene (**27**) and (**2c**) afforded a mixture of the *transoid* and *cisoid* conformers (**28**) and (**29**) respectively. In contrast we found that[2] reaction of 2,6-bis(chloromethyl)-4-t-butyltoluene (**30**) and (**2a**) afforded exclusively the *transoid* conformer (**31**). The n.m.r. spectra of (**3**) and (**4**) prepared in the



Scheme 2. *Reagents and conditions:* i, KOH–EtOH, high dilution; ii, *m*-CPBA, $CHCl_3$ (*ca.* 100%); iii, 500 °C, 3 mmHg

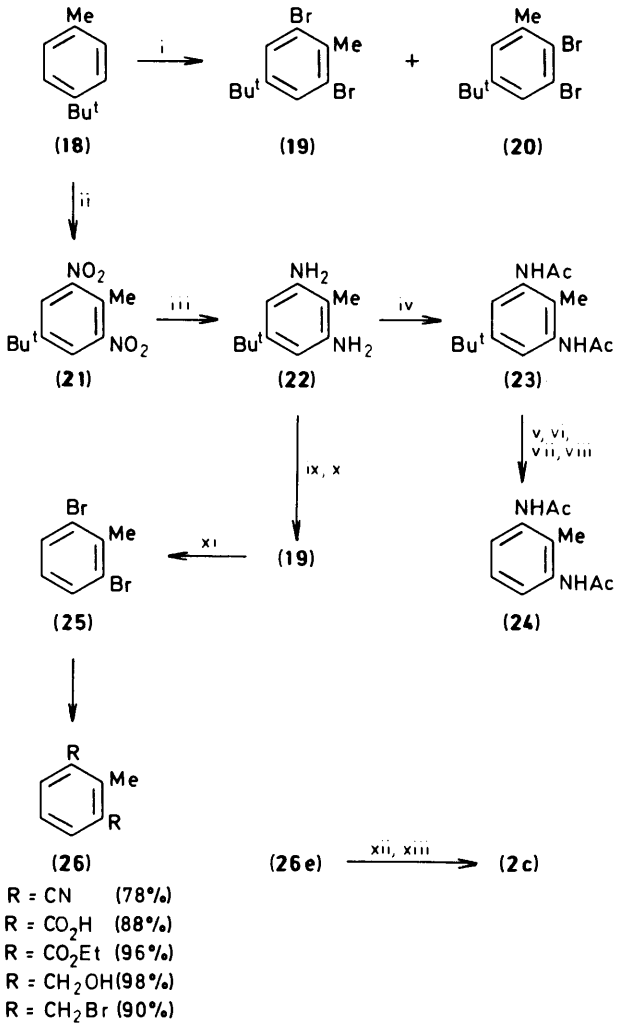
present work show that they are a mixture of *transoid* and *cisoid* conformers, the molar ratio of which seems dependent upon the 5- and 13-substituents (see Table 1). The data show that the molar ratios of the *transoid* and *cisoid* conformers of (**3**) and (**4**) are almost equivalent, an indication that there is no exchange between the two during the oxidation of (**3**) to (**4**). On pyrolysis, compound (**4**) gave the less strained *transoid* conformer of (**5**) exclusively, the *syn* conformer not being detected by n.m.r. spectroscopy. $AlCl_3$–$MeNO_2$-catalyzed *trans*-t-butylation of



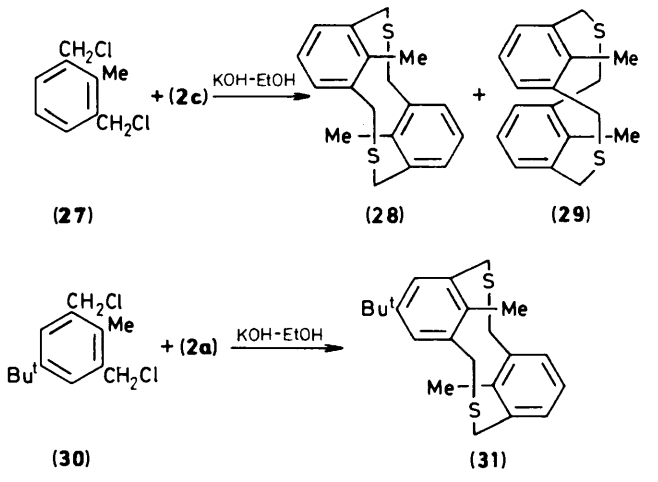
Scheme 3. *Reagents and conditions:* i, 4-methyl-2,6-di-t-butylphenol, $AlCl_3$–$MeNO_2$ (quart); ii, HNO_3 (75%); iii, Fe–HCl (89%); iv, $NaNO_2$, HBF_4; v, heat (47%); vi, $AlCl_3$, CS_2, Ph–Ph (**11**); vii, NBS (2.2 equiv.), CCl_4; viii, NBS (4.1 equiv.), CCl_4 (54%); ix, NBS (2.2 equiv.), CCl_4 (80%).

(**5a**) in benzene under a variety of conditions failed to give the expected compound 8-fluoro-16-methyl[2.2]metacyclophane (**32**),[2-4] 4-t-butylbenzene (**35**) and the tetrahydropyrenes (**33**) and/or (**34**) being formed instead (see Scheme 6 and Table 2). Mild conditions gave compound (**33**) as the sole product whilst more severe gave compound (**34**) a result which suggests that (**33**) might be an intermediate in the formation of (**34**). Indeed, (**34**) was also obtained in good yield when (**33**) was treated with $AlCl_3$–$MeNO_2$; oxidation of (**34**) with DDQ in benzene led to 2-methylpyrene (**36**).[8]

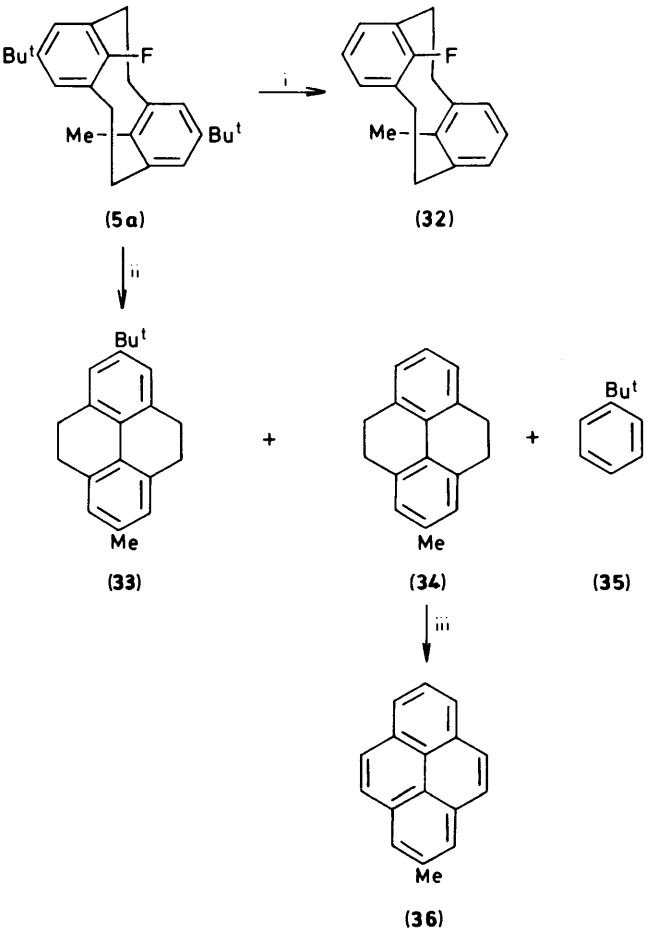
Similar catalytic treatment of (**5b**) also afforded (**33**) (79%) while (**5d**) gave only (**34**) (84%) $AlCl_3$–$MeNO_2$ Catalyzed reaction of (**5b**) and (**5d**) also afforded (**33**) and (**34**), and a schematic representation of the path for this set of reactions is shown in Scheme 7. Although two routes, a and b (see Scheme 7) may be envisaged for the formation of (**34**) from (**5a**), route b may be ruled out because (i) the $AlCl_3$–$MeNO_2$ catalyzed reaction of (**5a**) under mild conditions afforded (**33**) exclusively and (ii) isomerization of (**5b**) to give strainless (**5c**) is more likely than a route *via* (**5d**) and the strained compound (**37**). Indeed, catalytic treatment of (**5c**) in benzene gave compound (**33**) (86%) as expected on the basis of earlier reported observations.[2] A mechanism for the formation of (**33**) from (**5c**) is tentatively



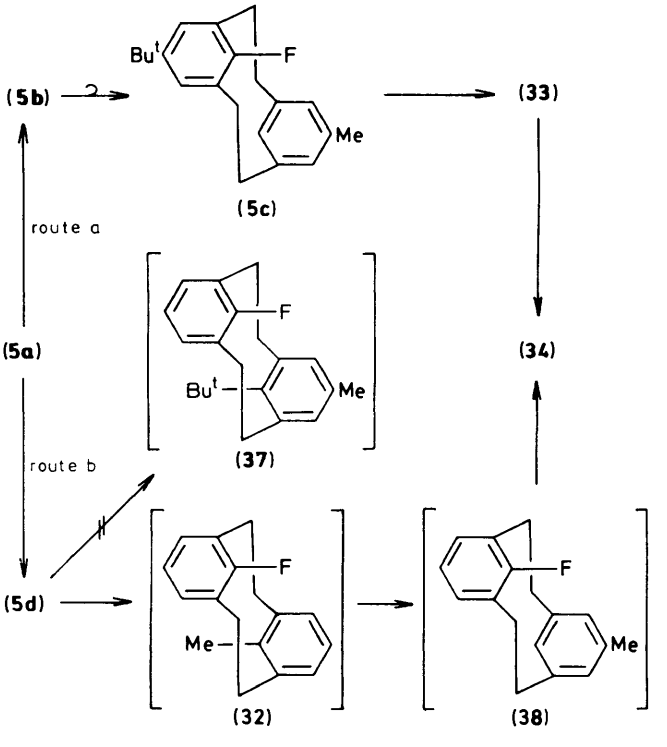
Scheme 4. *Reagents and conditions:* i, Br_2, Fe; ii, HNO_3, H_2SO_4 (77%); iii, Fe–HCl (60%); iv, Ac_2O, AcOH (98%); v, $AlCl_3$; vi, $AlBr_3$; vii, AlI_3; viii, H_3PO_4, heat; ix, $NaNO_2$; x, CuBr, HBr (62%); xi, $AlCl_3$, benzene (83%); xii, thiourea; xiii, NaOH (92%).



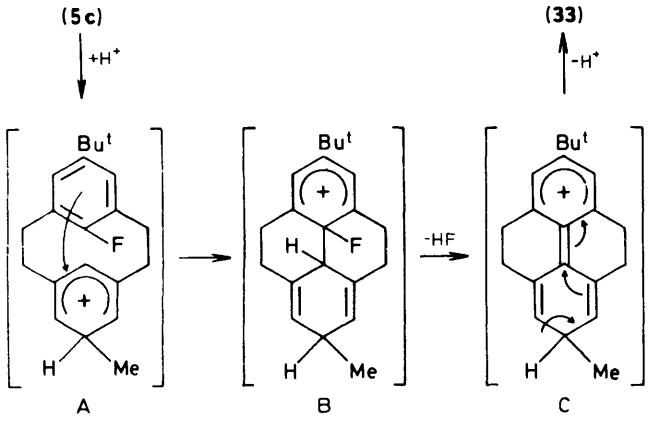
Scheme 5.



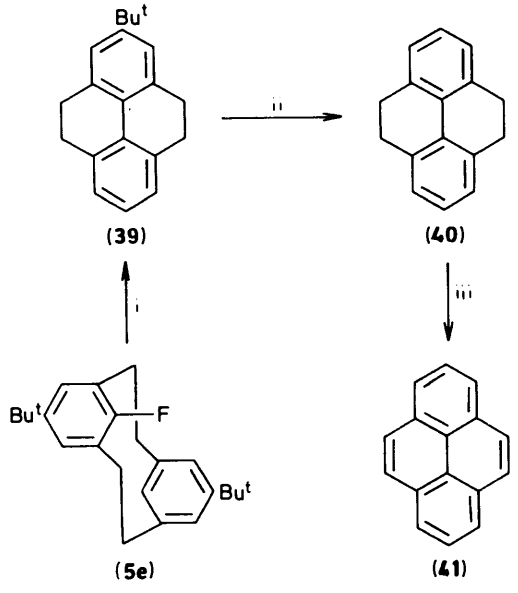
Scheme 6. *Reagents and conditions:* i, $AlCl_3$–$MeNO_2$, benzene



Scheme 7.



Scheme 8.



Scheme 9. *Reagents and conditions:* i, $AlCl_3$–$MeNO_2$, benzene (73%); ii, $AlCl_3$–$MeNO_2$, benzene (83%); iii, DDQ, benzene (80%).

proposed in Scheme 8. On the basis of above results it was expected that (**5e**) might give the corresponding tetrahydropyrenes (**39**) and (**40**) and indeed this occurred. Thus (**5e**) with $AlCl_3$–$MeNO_2$ in benzene at 25 °C for 1 h gave (**39**) (73%) and this upon further treatment (13 h) gave compound (**40**) in good yield. Oxidation with DDQ of (**40**) in boiling benzene afforded pyrene (**41**) itself (see Scheme 9).

Formation of (**39**) from (**5e**) appears to support the proposed reaction pathways described above.

Experimental

All m.p.s and b.p.s are uncorrected. N.m.r. spectra were determined at 100 MHz with a Nippon Denshi JEOL FT-100 n.m.r. spectrometer with $SiMe_4$ as an internal reference, and i.r. spectra were measured as KBr pellets or a liquid film on NaCl plates in a Nippon Bunko IR-A-102 spectrophotometer. Mass spectra were obtained on a Nippon Denshi JMS-01SA-2 spectrometer at 75 eV using a direct inlet system through g.c.

Preparation of 1,3-*Dimethyl*-2-*nitro*-5-*t*-*butylbenzene* (**8**).—To a solution of compound (**7**)[8] (117 g, 0.72 mol) in acetic anhydride (130 g) was added gradually at 25 °C a mixture of nitric acid (68 g), acetic acid (43 g) and acetic anhydride (43 g). After this addition, the reaction mixture was poured into a large amount of ice–water and extracted with benzene. The benzene solution was washed with 10% aqueous NaOH and water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was recrystallized from ethanol to give (**8**) (112 g, 75%) as pale yellow prisms, m.p. 85–86 °C (lit.,[9] m.p. 85 °C).

Preparation of 2,6-*Dimethyl*-4-*t*-*butylaniline* (**9**).—A mixture of compound (**8**) (86.7 g, 0.42 mol), iron powder (81 g), concentrated HCl (30 ml), ethanol (40 ml), and water (250 ml) was stirred and heated under reflux for 28 h after which time the iron powder was filtered off. The filtrate was extracted with benzene and the extract washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was distilled under reduced pressure to give (**9**) (65.8 g, 89%) as colourless oil, b.p. 89—91 °C at 1 mmHg; $\nu_{max.}$(NaCl) 3 450, 3 375, 3 000, 2 950, 2 840, 1 615, 1 515, 1 488, 1 350, 1 210, 1 120, 1 025, 860, and 725 cm^{-1}; $\delta_H(CDCl_3)$ 1.26 (9 H, s), 2.12 (6 H, s), 3.34 (2 H, br s, exchanged by D_2O), 6.92 (2 H, s); *m*/*z* 177 (M^+) (Found: C, 81.2; H, 11.2. $C_{12}H_{19}N$ requires C, 81.30; H, 10.80%).

Preparation of 1-*Fluoro*-2,6-*dimethyl*-4-*t*-*butylbenzene* (**10**).—To a solution of the amine (**9**) (50.1 g, 0.28 mol) in tetrahydrofuran (95 ml) cooled in an ice–NaCl bath was added first HBF_4 (42%) (447 ml) and then saturated aqueous $NaNO_2$ (11 g). The resulting crystalline precipitated was filtered off, washed with 5% HBF_4 solution and methanol, and dried *in vacuo*. Subsequently it was heated under reflux in toluene for 5 h, to afford after evaporation under reduced pressure of the solvent a residue which was distilled under reduced pressure to give (**10**) as pale yellow oil (24.2 g, 48%), b.p. 70–71 °C at 4 mmHg; $\nu_{max.}$(NaCl) 2 980, 2 890, 1 490, 1 365, 1 320, 1 195, 1 120, 870, 815, and 725 cm^{-1}; $\delta_H(CDCl_3)$ 1.26 (9 H, s), 2.22 (6 H, d, *J* 2 Hz), and 6.94 (2 H, d, *J* 2 Hz); *m*/*z* 179 (M^+) (Found: C, 80.1; H, 9.6. $C_{12}H_{17}F$ requires C, 79.96; H, 9.51%).

Bromination of Compound (**10**) *with NBS: Typical Procedure*.—A solution of compound (**10**) (2.0 g, 11.1 mmol), NBS (8.1 g, 45.5 mmol), and benzoyl peroxide (500 mg) in CCl_4 (300 ml) was heated under reflux for 4 h after which the mixture was cooled to room temperature. The precipitated succinimide was filtered off and the filtrate evaporated under reduced pressure to leave a residue which was recrystallized from hexane to give (**17**) (2.89 g, 54%) as pale yellow prisms, m.p. 132—133 °C; $\nu_{max.}$(KBr) 2 970, 2 870, 1 660, 1 470, 1 360, 1 275, 1 210, 1 150, 1 090, 975, 880, 815, 750, 695, and 660 cm^{-1}; $\delta_H(CDCl_3)$ 1.37 (9 H, s), 6.85 (2 H, s), and 7.76 (2 H, d, *J* 7 Hz); *m*/*z* 491, 493, 495, 497, and 499 (M^+) (Found: C, 29.15; H, 2.75. $C_{12}H_{13}FBr_4$ requires C, 29.07; H, 2.64%).

When bromination of (**10**) with 2.1 equiv. of NBS was carried out under similar conditions to those described above, a mixture of (**10**), (**14**), (**15**), and (**16**) was obtained as described in the text. The molar ratios of the products was estimated by n.m.r. spectral analysis of the mixture.

Preparation of 1-*Fluoro*-2,6-*dimethylbenzene* (**12**).—To a solution of compound (**10**) (2.0 g, 11.1 mmol) and biphenyl (8.55 g, 5.55 mmol) in CS_2 (15 ml) was added $AlCl_3$ (0.5 g, 3.75 mmol). The mixture was then stirred at room temperature for 1.5 h after which it was poured into a large amount of ice–water and extracted with methylene chloride; the extract was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was distilled under reduced pressure to give (**12**) (1.24 g, 89.9%) as a colourless oil, b.p. 165—167 °C at 760 mmHg (lit.,[10] b.p. 85 °C at 115 mmHg).

Preparation of 1,3-*Bis(bromomethyl)*-2-*fluorobenzene* (**1b**).—A solution of compound (**12**) (3.0 g, 24.2 mmol), NBS (9.48 g, 532 mmol), and benzoyl peroxide (500 mg) in CCl_4 (300 ml) was treated and worked up as described above, to afford (**1b**) (5.46 g, 80%) as colourless prisms (from hexane), m.p. 90—91 °C (lit.,[11] m.p. 90—91.5 °C).

Bromination of 4-*t-Butyltoluene* (**18**) *with Bromine*.—Although bromination of (**18**) with bromine under the reported conditions[12] afforded the desired 2-bromo-4-t-butyltoluene in good yield, similar bromination of (**18**) with 2 mol equiv. of bromine gave a mixture of (**19**) and (**20**), which were inseparable by distillation and column chromatography (silica gel). The molar ratio and the determination of the structures of both products were carried out by n.m.r. spectral analysis.

Preparation of 2,6-*Diamino*-4-*t-butyltoluene* (**22**).—A mixture of compound (**21**)[13] (30 g, 126 mmol), iron powder (4.88 g), concentrated HCl (18.1 ml), and water (200 ml) was treated and worked up as described in the reduction of compound (**8**), to afford (**22**) (13.5 g, 60%) as colourless plates (from hexane), m.p. 96—97 °C; $\nu_{max.}$(KBr) 3 430, 3 380, 3 310, 3 200, 2 950, 2 850, 1 570, 1 510, 1 450, 1 425, 1 355, 1 330, 1 270, 1 200, 1 160, 1 135, 1 070, 940, 840, 820, 780, 710, and 660 cm^{-1}; $\delta_H(CDCl_3)$ 1.22 (9 H, s), 1.93 (3 H, s), 3.30 (4 H, br s, disappeared with D_2O), and 6.20 (2 H, s); *m/z* 177 (M^+) (Found: C, 74.25; H, 10.5; N, 15.5. $C_{11}H_{18}N_2$ requires C, 74.11; H, 10.18; N, 15.71%).

Preparation of 2,6-*Diacetamido*-4-*t-butyltoluene* (**23**).—A solution of compound (**22**) (10 g, 56 mmol) in acetic acid (15 ml) and acetic anhydride (150 ml) was stirred for 15 min at room temperature and then heated for 30 min on water-bath, before it was poured into a large amount of ice–water. The precipitated crystals were filtered off, washed with water, and recrystallized from ethanol to give (**23**) (14.4 g, 98%) as colourless prisms, m.p. > 300 °C; $\nu_{max.}$(KBr) 3 230, 3 040, 2 960, 2 870, 1 650, 1 610, 1 530, 1 475, 1 425, 1 400, 1 365, 1 290, 1 270, 1 230, 1 110, 1 035, 970, 930, 870, 815, 730, and 700 cm^{-1}; $\delta_H(Me_2SO)$ 1.21 (9 H, s), 1.94 (3 H, s), 2.01 (6 H, s), 7.11 (2 H, s), and 9.30 (2 H, s, exchangeable with D_2O); *m/z* 261 (M^+) (Found: C, 68.85; H, 8.6; N, 10.55. $C_{15}H_{22}N_2O_2$ requires C, 68.67; H, 8.45; N, 10.68%).

Preparation of 2,6-*Dibromo*-4-*t-butyltoluene* (**19**) *from compound* (**22**).—To concentrated H_2SO_4 (75 ml) was added first $NaNO_2$ (7.5 g) at 70 °C and then a solution of compound (**22**) (8.2 g, 46 mmol) in acetic anhydride (45 ml). This solution was then added gradually to a solution of CuBr (6.7 g, 46.5 mmol) in concentrated hydrobromic acid (140 ml) <40 °C. After cessation of N_2 evolution the reaction mixture, was poured into water, steam distilled, and the distillate extracted with benzene. The extract was washed with 10% aqueous NaOH and water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was distilled under reduced pressure to give (**19**) (8.73 g, 62%) as a colourless oil, b.p. 100—112 °C at 2.5 mmHg; $\nu_{max.}$(NaCl) 2 960, 2 870, 1 590, 1 530, 1 450, 1 380, 995, 870, 730, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 1.27 (9 H, s), 2.51 (3 H, s), and 7.46 (2 H, s); *m/z* 304, 306, and 308 (M^+) (Found: C, 42.6; H, 4.4. $C_{11}H_{14}Br_2$ requires C, 42.93; H, 4.61%).

Preparation of 2,6-*Dibromotoluene* (**25**).—A mixture of compound (**19**) (5.0 g, 16.3 mmol) and $AlCl_3$ (2.2 g, 16.5 mmol) in benzene (40 ml) was stirred at room temperature for 6 h after which the mixture was poured into a large volume of water and extracted with ether. The ether solution was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a residue which was distilled under reduced pressure to give (**25**) (3.38 g, 83%) as a colourless oil, b.p. 123—125 °C at 23 mmHg (lit.,[14] 122 °C at 23 mmHg). t-Butylbenzene formation was detected by g.c. analysis of the reaction mixture.

Preparation of the Toluene Derivatives (**26a—e**).—Compounds (**26a—e**) were prepared according to the reported method:[15] (**26a**), colourless prisms (from ethanol), m.p. 133—134 °C (lit.,[15] m.p. 134—135 °C); (**26b**), colourless prisms (from benzene), m.p. 227—229 °C (lit.,[16] m.p. 228—230 °C); (**26c**), colourless oil, b.p. 141—143 °C at 1 mmHg (lit.,[15] b.p. 143 °C at 1 mmHg); (**26d**), colourless prisms (from water), m.p. 124—125 °C (lit.,[15] m.p. 123—124 °C); (**26e**), colourless prisms (from hexane), m.p. 93—94 °C (lit.,[15] m.p. 94—95 °C).

Preparation of 2,6-*Bismercaptomethyltoluene* (**2c**).—This compound, prepared from (**26e**) according to the reported procedure, formed colourless needles (from hexane and benzene); m.p. 39.5—40 °C (lit.,[7] m.p. 40—41 °C).

Preparation of 2-*Methyl*-7-*t-butyl*- (**33**) *and/or* 2-*Methyl*-4,5,9,10-*tetrahydropyrene* (**34**) *from* (**5a**) *with* $AlCl_3$–$MeNO_2$: *Typical Procedure*.—To a solution of compound (**5a**) (100 mg, 0.284 mmol) in benzene (20 ml) was added a solution of $AlCl_3$ (50 mg, 0.364 mmol) in CH_3NO_2 (0.5 ml). After the reaction mixture had been stirred for 2 h at 25 °C, it was poured into ice–water and extracted with ether. The ether solution was dried (Na_2SO_4) and evaporated under reduced pressure to leave a residue, which was recrystallized from MeOH to give (**33**) (64.4 mg, 82%) as colourless prisms, m.p. 117—118 °C; $\nu_{max.}$(KBr) 3 040, 2 960, 2 950, 2 900, 2 850, 1 610, 1 470, 1 460, 1 360, 1 240, 870, 860, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.32 (9 H, s), 2.30 (3 H, s), 2.84 (8 H, s), 6.83 (2 H, s), and 7.04 (2 H, s); *m/z* 276 (M^+) (Found: C, 91.0; H, 8.8. $C_{21}H_{24}$ requires C, 91.25; H, 8.75%).

Compound (**34**), also obtained from (**5a**) under alternative conditions (see Table 2), formed colourless prisms (from MeOH), m.p. 96—98 °C; $\nu_{max.}$(KBr) 3 040, 2 950, 2 850, 1 605, 1 450, 1 240, 860, 820, 760, 740, and 720 cm^{-1}; $\delta_H(CDCl_3)$ 2.31 (3 H, s), 2.83 (8 H, s), 6.86 (2 H, s), and 7.02 (3 H, s); *m/z* 220 (M^+) (Found: C, 92.9; H, 7.25. $C_{17}H_{16}$ requires C, 92.68; H, 7.32%).

DDQ Oxidation of the Tetrahydropyrene (**34**) *to give* 2-*Methylpyrene* (**36**).—To a solution of (**34**) (66.1 mg, 0.30 mmol) in dry benzene (30 ml) was added DDQ (90%) (167 mg) at room temperature under a nitrogen atmosphere. After 2 days at room temperature the mixture was filtered and concentrated and the residue purified by column chromatography (silica gel) with a hexane–benzene (1:1) as eluant. The crystals isolated from the eluate were recrystallized from EtOH to give (**3b**) (53.2 mg, 82%) as colourless prisms, m.p. 144—145 °C (lit.,[17] m.p. 143—143.5 °C).

Preparation of 2-*t-Butyl*-4,5,9,10-*tetrahydropyrene* (**39**) *from the Metacyclophane* (**5e**) *with* $AlCl_3$–Me_3NO_2.—To a solution of (**5e**) (15 mg, 0.044 mmol) in benzene (4 ml) was added a solution of $AlCl_3$ (7.7 mg, 0.058 mmol) in $MeNO_2$ (0.10 ml). The reaction mixture was worked up as described above, to afford (**39**) 8.5 mg, 73%) as colourless prisms (from MeOH), m.p. 109—110 °C; $\nu_{max.}$(KBr) 3 030, 2 940, 2 850, 1 590, 1 470, 1 450, 1 430, 1 410, 1 370, 1 350, 1 220, 1 200, 1 170, 870, 750, and 710 cm^{-1}; $\delta_H(CDCl_3)$ 1.34 (9 H, s), 2.86 (8 H, s), and 7.02—7.06 (5 H, m); *m/z* 262 (M^+) (Found: C, 91.1; H, 8.4. $C_{20}H_{22}$ requires C, 91.55; H, 8.45%).

Preparation of 4,5,9,10-*Tetrahydropyrene* (**40**).—To a solution of (**39**) (250 mg, 1.5 mmol) in benzene (10 ml) was added a solution of $AlCl_3$ (15 mg, 0.11 mmol) in $MeNO_2$ (0.5 ml). The reaction mixture was worked up as usual, to afford (**40**) (161 mg, 83%) as colourless prisms (from hexane), m.p. 136—138 °C (lit.,[18] m.p. 137—138 °C).

DDQ Oxidation of the Tetrahydropyrene (**40**) *to give Pyrene* (**41**).—To a solution of (**40**) (80 mg, 0.39 mmol) in dry benzene

(35 ml) was added DDQ (90%) (200 mg) at room temperature under a nitrogen atmosphere. After 2 days, the mixture was worked up, to afford (**41**) (63 mg, 80%) as colourless prisms (from EtOH), m.p. 148—149 °C (lit.,[19] m.p. 149—150 °C).

Preparation of Trisubstituted 8-*Fluoro*[2.2]*metacyclophanes* (**5**) *from* (**3**).—The preparation of compounds (**3**), (**4**), and (**5**) were described in a previous report.[2] The yields are summarized in Scheme 2.

6,15,18-*Trisubstituted* 9-*Fluoro*-2,11-*dithia*[3.3]*metacyclophanes* (**3**).—Compound (**3a**), colourless prisms (from hexane), m.p. 152.5—153 °C; $\nu_{max.}$(KBr) 2 950, 1 600, 1 480, 1 460, 1 390, 1 360, 1 260, 1 230, 1 190, 1 170, 1 090, 880, and 760 cm^{-1}; $\delta_H(CDCl_3)$ 1.11, 1.16 (s, 7.2 H, *cisoid*-Bu^t), 1.30, 1.36 (s, 10.8 H, *transoid*-Bu^t), 1.47 (s, 1.8 H, *transoid*-Me), 2.40 (d, 1.2 H, *cisoid*-Me, *J* 4 Hz), 3.12—4.37 (m, 8 H, CH_2), and 6.78—7.30 (m, 4 H, ArH); *m/z* 416 (M^+) (Found: C, 72.25; H, 8.05. $C_{25}H_{33}FS_2$ requires, C, 72.07; H, 7.98%).

Compound (**3b**), colourless prisms (from hexane), m.p. 109—110 °C; $\nu_{max.}$(KBr) 2 950, 2 875, 1 485, 1 460, 1 415, 1 360, 1 260, 1 225, 1 200, 1 095, 910, 870, 780, 755, and 735 cm^{-1}; $\delta_H(CDCl_3)$ 1.20 (s, 5.5 H, *transoid*-Bu^t), 1.31 (s, 3.5 H, *cisoid*-Bu^t), 1.53 (s, 1.85 H, *transoid*-Me), 2.40 (d, 1.15 H, *cisoid*-Me, *J* 4 Hz), 3.16—4.47 (m, 8 H, CH_2), and 6.60—7.37 (m, 5 H, ArH); *m/z* 360 (M^+) (Found: C, 70.1; H, 7.05. $C_{21}H_{25}FS_2$ requires C, 69.96; H, 6.99%).

Compound (**3c**), colourless prisms (from hexane), m.p. 94—95 °C; $\nu_{max.}$(KBr) 3 020, 2 950, 2 900, 1 600, 1 475, 1 420, 1 385, 1 350, 1 220, 1 185, 1 165, 1 085, 880, 860, 850, 750, 735, and 710 cm^{-1}; $\delta_H(CDCl_3)$ 1.13 (s, 9 H, Bu^t), 2.10 (s, 3 H, Me), 3.41, 4.16 (4 H, AB pattern, J_{AB} 15 Hz), 3.71 (s, 4 H, CH_2), 6.68 (br s, 2 H, ArH), 6.68 (d, 2 H, ArH, *J* 6 Hz), and 6.88 (br s, 2 H, ArH); *m/z* 360 (M^+) (Found: C, 69.8; H, 6.9. $C_{21}H_{25}FS_2$ requires C, 69.95; H, 6.99%).

Compound (**3d**), colourless prisms (from hexane), m.p. 145—147 °C; $\nu_{max.}$(KBr) 2 950, 2 850, 1 600, 1 470, 1 450, 1 420, 1 350, 1 290, 1 250, 1 225, 1 185, 1 050, 895, 865, 810, 780, 740, and 730 cm^{-1}; $\delta_H(CDCl_3)$ 1.14 (s, 6 H, *cisoid*-Bu^t), 1.37 (s, 3 H, *transoid*-Bu^t), 1.56 (s, 1 H, *transoid*-Me), 2.40 (d, 2 H, *cisoid*-Me_3, *J* 4 Hz), 3.16—4.40 (m, 8 H, CH_2), and 6.52—7.31 (m, 5 H, ArH); *m/z* 360 (M^+) (Found: C, 69.95; H, 7.25. $C_{21}H_{25}FS_2$ requires C, 69.95; H, 6.99%).

Compound (**3e**), colourless oil; $\nu_{max.}$(NaCl) 2 950, 2 920, 2 860, 1 595, 1 475, 1 455, 1 410, 1 390, 1 360, 1 250, 1 220, 1 195, 1 090, 920, 875, 750, 730, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.11 (s, 9 H, Bu^t), 1.17 (s, 9 H, Bu^t), 3.32—4.51 (m, 8 H, CH_2), 6.60 (s, 1 H, ArH), 6.88 (d, 2 H, ArH, *J* 6 Hz), and 6.91 (s, 2 H, ArH); *m/z* 402 (M^+).

Since crystallization of (**3e**) was incomplete, the identification was carried out by the spectral data of (**4e**) which was obtained from (**3e**) by oxidation.

6,15,18-*Trisubstituted* 9-*Fluoro*-2,11-*dithia*[3.3]*metacyclophane* 2,2,11,11-*Tetraoxide* (**4**).—(**4a**), pale orange solid, m.p. 270—300 °C; $\nu_{max.}$(KBr) 2 950, 1 600, 1 480, 1 400, 1 350, 1 300, 1 260, 1 230, 1 160, 1 140, 1 100, 940, 920, 890, 810, 760, 720, and 700 cm^{-1}; $\delta_H(CDCl_3)$ 1.13, 1.19 (s, 7.2 H, *cisoid*-Bu^t), 1.37, 1.38 (s, 10.8 H, *transoid*-Bu^t), 1.37 (s, 1.8 H, *transoid*-Me_3), 2.50 (d, 1.2 H, *cisoid*-Me, *J* 4 Hz), 3.80—4.91 (m, 8 H, CH_2), and 7.16—7.68 (m, 4 H, ArH); *m/z* 480 (M^+) (Found: C, 62.35; H, 6.85. $C_{25}H_{33}FO_4S_2$ requires C, 62.47; H, 6.92%).

Compound (**4b**), colourless prisms, m.p. > 300 °C; $\nu_{max.}$(KBr) 2 950, 2 900, 1 490, 1 450, 1 400, 1 360, 1 305, 1 260, 1 210, 1 170, 1 100, 1 020, 940, 890, 860, 810, 725, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 1.22 (s, 9 H, Bu^t), 1.34 (s, 1.85 H, *transoid*-Me), 2.55 (d, 1.15 H, *cisoid*-Me), *J* 4 Hz), 3.72—4.92 (m, 8 H, CH_2), and 6.67—7.72 (m, 5 H, ArH); *m/z* 424 (M^+) (Found: C, 59.3; H, 6.0. $C_{21}H_{25}O_4FS_2$ requires C, 59.41; H, 5.94%).

Compound (**4c**), colourless prisms, m.p. > 300 °C; $\nu_{max.}$(KBr) 3 020, 2 970, 2 920, 1 600, 1 480, 1 460, 1 405, 1 330, 1 300, 1 260, 1 200, 1 175, 1 115, 915, 890, and 880 cm^{-1}; $\delta_H(CDCl_3)$ 1.17 (s, 9 H, Bu^t), 2.15 (s, 3 H, Me), 3.80—4.22 (m, 4 H, CH_2), 4.34, 4.76 (4 H, AB pattern, J_{AB} 14 Hz), 7.09 (br s, 2 H, ArH), 7.12 (br s, 1 H, ArH), and 7.27 (d, 2 H, ArH, *J* 6 Hz); *m/z* 424 (M^+) (Found: C, 59.3; H, 5.9. $C_{21}H_{25}FO_4S_2$ requires C, 59.41; H, 5.94%).

Compound (**4d**), colourless prisms, m.p. > 300 °C; $\nu_{max.}$(KBr) 2 960, 2 910, 1 610, 1 470, 1 405, 1 360, 1 310, 1 270, 1 255, 1 210, 1 175, 1 110, 890, 855, 800, 750, 730, and 695 cm^{-1}; $\delta_H(CDCl_3)$ 1.15 (s, 6 H, *cisoid*-Bu^t), 1.24 (s, 1 H, *transoid*-Me), 1.38 (s, 3 H, *transoid*-Bu^t), 2.50 (d, 2 H, *cisoid*-Me, *J* 4 Hz), 3.68—4.89 (m, 8 H, CH_2), 6.68—6.89, and 7.12—7.76 (m, 5 H, ArH); *m/z* 424 (M^+) (Found: C, 59.7; H, 6.2. $C_{21}H_{25}FS_2O_4$ requires C, 59.41; H, 5.94%).

Compound (**4e**), colourless prisms, m.p. > 300 °C; $\nu_{max.}$(KBr) 2 950, 2 860, 1 550, 1 480, 1 415, 1 350, 1 305, 1 255, 1 170, 1 110, 1 030, 1 000, 880, 840, 810, 750, and 710 cm^{-1}; $\delta_H(CDCl_3)$ 1.16 (s, 9 H, Bu^t), 1.18 (s, 9 H, Bu^t), 3.72—4.96 (m, 8 H, CH_2), and 7.08—7.72 (m, 4 H, ArH); *m/z* 466 (M^+) (Found: C, 61.9; H, 6.6. $C_{24}H_{31}FS_2O_4$ requires C, 61.78; H, 6.70%).

5,13,16-*Trisubstituted* 8-*Fluoro*[2.2]*metacyclophane* (**5**).—Compound (**5a**), colourless prisms (from hexane), m.p. 188—189 °C; $\nu_{max.}$(KBr) 2 950, 2 880, 1 480, 1 360, 1 295, 1 280, 1 210, 1 190, 1 090, 885, 860, 805, 745, and 720 cm^{-1}; $\delta_H(CDCl_3)$ 0.63 (s, 3 H), 1.27 (s, 9 H), 1.31 (s, 9 H), 2.48—3.04 (m, 8 H), 7.03 (s, 2 H), and 7.06 (d, 2 H, *J* 6 Hz); *m/z* 352 (M^+) (Found: C, 85.2; H, 9.65. $C_{25}H_{33}F$ requires C, 85.18; H, 9.43%).

Compound (**5b**), colourless prisms (from hexane), m.p. 192—194 °C; $\nu_{max.}$(KBr) 2 970, 2 870, 1 590, 1 480, 1 460, 1 435, 1 360, 1 295, 1 200, 1 185, 1 115, 895, 870, 810, 780, 740, and 715 cm^{-1}; $\delta_H(CDCl_3)$ 0.59 (d, 3 H, *J* 2 Hz), 1.22 (s, 9 H), 2.40—3.72 (m, 8 H), and 6.88—7.24 (m, 5 H); *m/z* 296 (M^+) (Found: C, 85.2; H, 8.45. $C_{21}H_{25}F$ requires C, 85.09; H, 8.50%).

Compound (**5c**), colourless prisms (from MeOH), m.p. 44—45 °C; $\nu_{max.}$(KBr) 3 020, 2 950, 2 850, 1 595, 1 475, 1 460, 1 435, 1 360, 1 280, 1 200, 1 180, 860, 840, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 1.35 (s, 9 H), 1.95—3.06 (m, 8 H), 2.32 (s, 3 H), 4.09 (br s, 1 H), 6.87 (br s, 2 H), and 7.02 (d, 2 H, *J* 6 Hz); *m/z* 296 (M^+) (Found: C, 85.45; H, 8.62. $C_{21}H_{25}F$ requires C, 85.09; H, 8.50%).

Compound (**5d**), colourless prisms (from hexane), m.p. 142—143 °C; $\nu_{max.}$(KBr) 3 050, 2 970, 2 860, 1 480, 1 455, 1 430, 1 360, 1 296, 1 250, 1 185, 1 060, 1 020, 1 005, 875, 860, 805, 780, and 740 cm^{-1}; $\delta_H(CDCl_3)$ 0.63 (d, 3 H, *J* 2 Hz), 1.31 (s, 9 H), 2.48—3.00 (m, 8 H), and 6.72—7.32 (m, 5 H); *m/z* 296 (M^+) (Found: C, 85.1; H, 8.2. $C_{21}H_{25}F$ requires C, 85.09; H, 8.50%).

Compound (**5e**), colourless prisms (from hexane), m.p. 157—158 °C; $\nu_{max.}$(KBr) 2 960, 2 850, 1 590, 1 565, 1 470, 1 420, 1 390, 1 360, 1 280, 1 240, 1 200, 1 090, 1 070, 1 020, 880, 800, 780, 750, 735, and 710 cm^{-1}; $\delta_H(CDCl_3)$ 1.31 (s, 9 H), 1.35 (s, 9 H), 2.50—3.36 (m, 8 H), 5.28 (s, 1 H), and 6.96—7.66 (m, 4 H); *m/z* 338 (M^+) (Found: C, 74.0; H, 8.2. $C_{24}H_{31}F$ requires C, 74.20; H, 8.04%).

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