

Polymer supported magnesium anthracene: application in the synthesis of benzylic Grignard reagents [☆]

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Abstract

Reactions of polystyrene supported magnesium anthracene containing radical anion and dianion sites, **7**, **7'**, with benzylic chlorides or bromides, affords Grignard reagents, RMgX, in modest to high yields, in THF at -10°C to 20°C . Novel benzylic-type Grignard reagents prepared in high yield include those of 2,6-(dichloromethyl)pyridine, 2,6-(dibromomethyl)pyridine, 2,2',2''-trispyridylmethylchloride, 2-methoxy-3-methyl-1-benzylchloride, 2,4-dimethoxy-5-methyl-1-benzylchloride, 3,5-dimethoxy-4-methyl-1-benzylchloride, 2,4,6-trimethoxy-3-methyl-1-benzylchloride, and 2,5-dimethoxybenzylchloride. Selected allylic halides similarly yield Grignard reagents.

Keywords: Polymer; Magnesium; Anthracene; Grignard Reagent; Benzylic halide; Styrene

1. Introduction

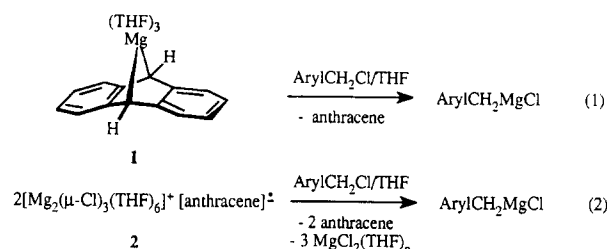
Anthracene and a variety of substituted anthracenes react with magnesium in THF yielding species based on the doubly reduced anthracene [1–11], for example $[\text{Mg}(\text{anthracene})(\text{THF})_3]$, **1** (THF = tetrahydrofuran), or species based on the radical anion of anthracene, especially if magnesium halide is present, e.g. in the formation of $[\text{Mg}_2(\mu\text{-Cl})_3(\text{THF})_6]^+[\text{anthracene}]^{\bullet-}$, **2** [5,8,9,12,13]. Compound **1** is a remarkably versatile reagent highlighted by (i) its use in the formation of anthracene derivatives of other metals [8,9,14–16], (ii) its ability to act as a potent reducing agent [2,9] for example, in forming $\text{Mg}(\text{COT})(\text{THF})_{2.5}$ and anthracene when treated with COT (= cyclooctatetraene) [2], (iii) its decomposition in solvents other than THF to a synthetically useful activated form of magnesium [6,9,17], like Rieke's magnesium [18], condensed magnesium [19], and magnesium derived from the equilibration of bulk metal with a catalytic amount of anthracene in THF [11]; in some cases decomposition is via the

bis-tetrahydrofuran analogue, $[\text{Mg}(\text{anthracene})(\text{THF})_2]$ [2,7,20], and is accelerated by graphite [20], (iv) undergoing ethylene insertion into one Mg–C bond [23], (v) it simply acting as a dinucleophile [3,5,7,9,12,17], and (vi) the formation of Grignard reagents in high yield when treated with benzylic halides [1,2,15,22–29]. For the latter, compound **1** acts as a soluble source of magnesium, although the complex itself, and derived radical anion complexes, are involved in the reaction via electron transfer processes [2]. Other organic halides and **1** can give (a) addition compounds, viz. an example of **1** acting as a dinucleophile [2,9,30], (b) a mixture of Grignard reagents and addition compounds for allylic halides [2], or (c) RH involving a single electron transfer to the halide RX [9,30]. The only other non-benzylic halide to yield a Grignard reagent is $\text{ClC}(\text{SiMe}_3)_3$ [2]. The cyclooctatetraene compound $\text{Mg}(\text{COT})(\text{THF})_{2.5}$ also acts a source of magnesium with benzylic halides; however, Wurtz coupling dominates [31].

Grignard reagents of benzylic halides are often difficult to prepare or inaccessible using the classical method involving bulk magnesium [32], and even using condensed or Rieke's magnesium [2,22]. The ability of **1** to afford such Grignard reagents in high yield has led to the development of a new synthesis of naturally occurring anthraquinones, where the key step is condensation of previously inaccessible, highly substituted Grignard

[☆] Dedicated to Professor Dr. Henri Brunner on the occasion of his 60th birthday.

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reagents, e.g. 1-ClMgCH₂-2,5-(MeO)₂-3-MeC₆H₂, with *o*-(methoxy)aryloxazolines [24,25]. In addition, benzylic ethers can be cleaved, e.g. *o*- and *p*-MeOCH₂C₆H₄-CH₂Cl yield the 'di-Grignard reagents' even with one equivalent of **1**, and the *m*-isomer affords the expected mono-Grignard reagent. The insertion of magnesium into C–O bonds normally requires rather forcing conditions and the use of highly activated magnesium. The only other magnesium–arene compound to cleave carbon heteroatom bonds is Mg(naphthalene)₂ in the ring opening of epoxides [16].

Compound **2** can also yield Grignard reagents when treated with benzylic halides, however, this has synthetic limitations since the compound is more difficult to prepare than **1**, and related compounds [8], and two equivalents of the reducing agent are required. Moreover, like compound **1** the solutions of the Grignard reagents are loaded with anthracene. To overcome this practical inconvenience a polymer supported magnesium anthracene has been developed whereby the spent polymer containing the anthracene unit can be separated by filtration. Results of our endeavours are reported herein, along with comparative studies of a model compound. This work is an extension of a preliminary account of the synthesis of a low loading polymer supported magnesium(anthracene) material and its reactions with benzyl chloride [22], and relates to our recent report on a silica supported analogue [1].

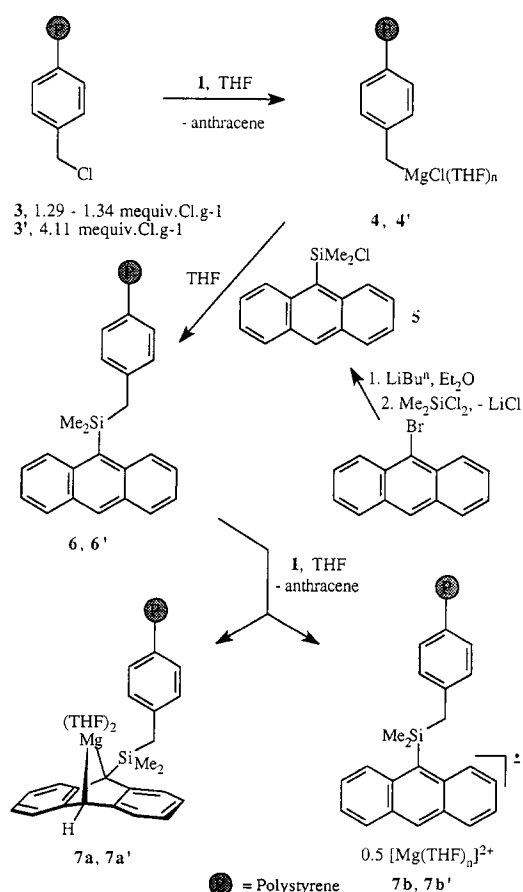
2. Results and discussion

2.1. Polymer supported magnesium anthracene

Microporous chloromethylated polystyrene (cross-linked by 1% divinylbenzene) at a low loading, 1.20–1.34 mmol g^{−1} Cl, **3**, and high loading, 4.11–4.15 mmol g^{−1} Cl **3'**, is a benzylic halide and therefore is likely to be converted to the corresponding Grignard reagent by compound **1**. Indeed, addition of **1** to a THF slurry of **3** or **3'** afforded the corresponding Grignard reagent in high yield, > 95%, **4**, and > 75% **4'**, respectively (Scheme 1). Addition in the reverse order was equally effective, although swelling of polystyrene resins

is recommended before chemical modification of crosslinked polystyrene.

For the different loadings the reaction was characterised by the appearance of deep green solutions containing paramagnetic species (*g*_{av} = 2.0030, 2.0033 respectively), as has been observed in the reactions of **1** with benzylic and allylic halides [12]. Here the colour discharges if the reaction is quantitative or with the addition of more organic halide if some Wurtz coupling occurs. The radical species are based on anthracene and arise from equilibration of unreacted **1**, anthracene and magnesium halide [12,13], or are generated directly from **1** via a single electron transfer reaction. The presence of residual radicals in the reactions involving stoichiometric quantities of the two reactants suggests that increased crosslinking of the polymers occurs during Grignard reagent formation through intra-resin Wurtz coupling. The need for close to stoichiometric quantities of **4** indicates that the extent of Wurtz coupling is minimal for the lower loading. For the higher loading the amount of **1** consumed is significantly less than stoichiometric, 80%, with the yield of the Grignard reagent (based on weight gain) lower, 78%, **4'**, cf. 99%, **4**. The lower yield of the Grignard reagent for the



Scheme 1.

higher loading is consistent with the higher probability of an intramacromolecular encounter of a preformed Grignard centre with a chloromethyl group. The ability to prepare supported Grignard reagents stems from the source of the magnesium being soluble in THF and thus mobilised in the polymer.

Contemporary investigations by Frechet et al. [33] on the reaction of chloromethylated polystyrene, 1.35 mequiv. Cl g^{-1} , with an excess of **1** established a 90% yield of the Grignard, with ca. 3% increase in crosslinkage. Prior to this work, there were many unsuccessful attempts at direct formation of Grignard reagents of insoluble halogenated polystyrene resins, including chloromethylated polystyrene [34]. This is due to the lack of encounter of the functional group and/or its immediate surroundings with the metal. However, with the recent availability of the lithium reagent of the same polymer [35] the corresponding Grignard reagent is available, in principle, by treating this reagent with magnesium halides. This method has been successfully employed for the formation of the Grignard reagent of bromopolystyrene [36], and other reagents that are inaccessible using the classical method of Grignard reagent formation [37].

Treatment of a THF slurry of **4**; **4'** with an excess of 9-(chlorodimethylsilyl)anthracene, **5**, yielded the anthracene functionalised polymer, **6**; **6'** (Scheme 1), in greater than 95% yield, based on weight increase (assuming two THF molecules attached to each metal centre), IR studies and analysis for residual chlorine content. Compound **5** was prepared by quenching 9-lithioanthracene with excess dichlorodimethylsilane.

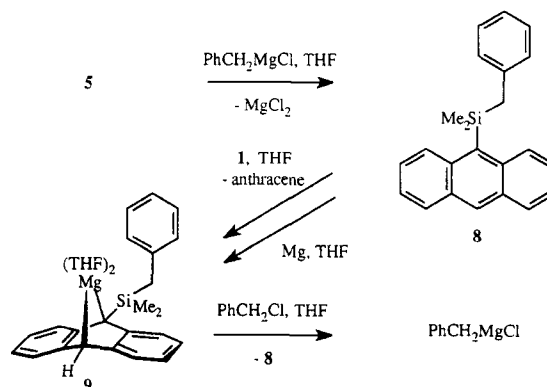
Reactions involving modification of crosslinked chloromethylated polystyrene **3**; **3'**, were monitored by (i) changes in $\nu_{\text{C-H}}$ bending mode of the methylene group [38], displaced from 1265 cm^{-1} to 1252 cm^{-1} on converting the chloride to the silane, and (ii) the appearance of characteristic absorption bands at 1248 and 843 cm^{-1} (shoulder), attributed to Si–C stretching and Si–Me deformations respectively [38].

Compound **1** was added to a THF slurry of **6**; **6'** until an excess of the former was visible in the reaction mixture. The new polymer was collected and washed with THF to remove anthracene and excess **1**, yielding a deep green paramagnetic solid ($g_{\text{av}} = 2.0030, 2.0030$) containing both dianion, **7a**, **7a'**, and radical anion moieties **7b**, **7b'**; Scheme 1. The presence of radical centres in the polymer most likely arises from two anthracene units being in close proximity to a single magnesium cation, such as the well known $[\text{Mg}(\text{THF})_6]^{2+}$ [39]. This may occur as a result either of space limitations within the polymer matrix, or of electrostatic constraints in building up two negative charges per anthracene within a confined volume, viz. communication effects between anthracene units. In this context we note that silica supported magnesium anthracene

which is similarly prepared and based on a 9-dimethylsilyl substituted anthracene gives exclusively anthracene dianion sites [1]. Here the functional groups are exposed directly to the solvent and any space limitations for uptake of magnesium would be minimal as would charge limitations associated with anthracene groups spread out on a surface.

Polymers **7** and **7'** contain radical anion centres and dianion centres, relative ratio ca. 1:1 based on the uptake of magnesium when reacted with **1** and the reactivity of the polymer towards benzylic halides, further supported by the paramagnetic character of the material. The successful preparation of **7a**, **7b**; **7a'**, **7b'**, and also **4**; **4'**, stems from **1** being a soluble source of metal (ca. 3 g l^{-1} in THF) allowing intimate contact between the magnesium reagent and the polymer. Metathetical exchange of magnesium involving **6** and **6'** in the presence of **1** relates to the ability of silicon to stabilise charge by polarisation [40], and that silylated anthracenes are more readily reduced than anthracene [10]. It is also noteworthy that magnesium complexes based on 9,10-silyl substituted anthracene [2] are inherently more stable with respect to decomposition to their constituents than compound **1**.

The compound 9-(benzyl dimethylsilyl)anthracene, **8**, was prepared by the treatment of benzyl magnesium chloride with **5** in diethyl ether, in an attempt to model reaction of the functionalised polymer **6**, **6'** with magnesium sources. Reaction of **8** with **1** yielded a diamagnetic solid $\text{Mg}(\text{9-(benzyl dimethylsilyl)anthracene})_2(\text{THF})_2$, **9**, based exclusively on dianions rather than a mixture of radical anions and dianions (Scheme 2). This complex was also prepared by treatment of magnesium with **8** in THF, the reaction proceeding to completion after 48 h at room temperature. Presumably **9** has a similar structure to **1** [23], and the related complexes [2,8,10], viz. magnesium bound to the $\text{C}_{9,10}$ atoms of the substituted anthracene, and bound to two THF molecules (ratio of THF/anthracene based on ^1H NMR data of decomposition product). The IR absorption bands due to methyl rocking and C–H bending in **8** are well



Scheme 2.

resolved appearing at 1250 and 1260 cm^{-1} respectively.

Surprisingly, THF solutions containing **8**, magnesium

and magnesium bromide did not afford highly coloured radical species, of the type found in the synthesis of **1** and substituted magnesium anthracene complexes [2].

Table 1

Comparison of the yield of benzylic Grignard reagents (and some allylic Grignard reagents) using $[\text{Mg}(\text{anthracene})(\text{THF})_3]$, **1**, and polymer supported magnesium-anthracene derived from 1.34 (or 1.29) and 4.11 mequiv g^{-1} , ca. 1.0% cross-linked ^a

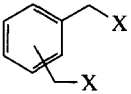
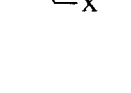
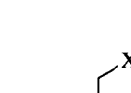
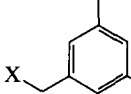
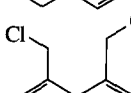
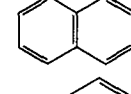
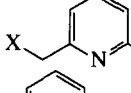
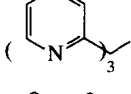
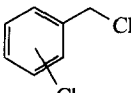
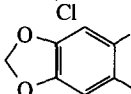
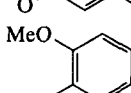
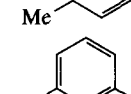
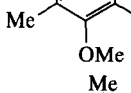
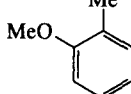
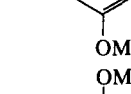
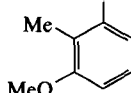
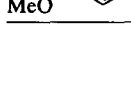
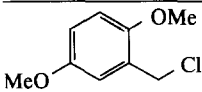
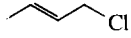
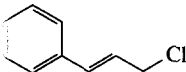
Organic halide	Compound 1	1.34 mequiv g^{-1}	4.11 mequiv g^{-1}
Benzyl chloride 14	95 ⁱ	95	95
Benzyl bromide ^{b,c} 15	85 ⁱ	95	90
9-(Chloromethyl)anthracene ^d 16	90 ⁱ	90	95
 1,2- X = Cl ^{e,f} 17	90 ⁱ	95	90
 1,3- X = Cl ^e 18a	95 ⁱ	95	95
 1,3- X = Br ^e 18b	90 ⁱ	95	90
 1,4- X = Cl ^e 19	90 ⁱ	90	90
 X = Cl ^b 20a,b	85 ⁱ	90	85
 X = Br ^b 20a,b	85 ⁱ	90	90
 21	95 ⁱ	95	85
 X = Cl ^g 22a,b	80	85	85
 X = Br ^g 22a,b	85	90	85
 23	—	80	80
 <i>o</i> - 24a	95 ^j	90	85
 <i>m</i> - b	95 ^j	95	90
 <i>p</i> - c	95 ^j	95	95
 25	95 ^j	85	90
 26	85	85	85
 27	90	90	90
 28	90	95	90
 29	85	85	85

Table 1 (continued)

Organic halide	Compound 1	1.34 mequiv g ⁻¹	4.11 mequiv g ⁻¹
 30	90	95	90
 32	85	90	90
 33	85	90	90

^a For chloromethyl- or bromomethyl-aromatic species (**17–22**), the yields are for the poly-Grignard reagent, and for benzylic halides bearing a chloro group attached to the aromatic ring (**24** and **25**), the yields are for the conversion of the chloromethyl group to the corresponding Grignard functionality. Reactions are in THF at 20°C unless stated.

^b Reaction at 0°C.

^c < 5% coupled product.

^d Acid quenched yield, < 5% 9-methylanthracene.

^e Reaction at < -10°C.

^f < 5% coupled di-Grignard.

^g Isolated yield of ClSiMe₃ derivative.

^h D₂O quenched to establish yield.

Ref. [12].

Ref. [28].

2.2. Grignard reagents

Examples of novel benzylic Grignard reagents **14–30** prepared using polymers **7a**, **7b**; **7a'**, **7b'** and comparisons with the use of **1** are presented in Table 1, along with some allylic Grignard reagents **31**, **32**. In all cases target concentrations of the Grignard reagents were close to 0.1 M and yields were high and comparable to those obtained using **1**. In a typical experiment the organic halide was added slowly as a THF solution to a THF slurry of the polymer. This resulted in dissipation of the deep green colour and formation of the corresponding anthracene-free Grignard reagent in ca. 90% yield; Eq. (3). Unlike reactions involving **1** there was no evidence of radical species during Grignard reagent formation (as indicated by pale yellow solutions and ESR studies), although this does not preclude a radical pathway. Alternatively, passing a THF solution of the halide through a column packed with the polymer results in elution of a solution of pure Grignard reagent.



For the new polymers **6**; **6'**, the initial uptake of magnesium was ca. 75%. Assuming that within the polymer matrix two radical anion centres are associated with a single magnesium cation, this corresponds to a ratio between **7a** and **7b**, and **7a'** and **7b'**, of ca. 1:1. Dissipation of the deep green colour during the addition of benzylic halides (and allylic halides) and formation of the corresponding Grignard reagent in high yield indicates that the dianion and radical anion sites are both effective in reducing the organic halide. This is in accordance with the ability of the known radical anion complex **2** to afford benzylic Grignards in high yields.

Indeed, the dianion sites are likely to form radical anion sites in undergoing a single electron transfer with the organic halide, as demonstrated by our earlier studies on the reactions of **1** with benzylic halides [12]. Single electron transfer reactions would also be consistent with the generally accepted mechanism of the formation of Grignard reagents using bulk metal [41].

The ability to form Grignard reagents of allylic halides in high yield is noteworthy. Like Grignard reagents of benzylic halides, allylic Grignard reagents are difficult to prepare using the classical method of Grignard reagent formation involving the use of bulk metal. Reaction of **1** with allylic halides yields 50–70% of the target Grignard reagent, the competing reaction being addition to anthracene, yielding on work up a 9-substituted dihydroanthracene [12]. Polymers **7** and **7'** give high yield of the allylic Grignard reagents of **32**, **33**, with minimal addition to the polymer matrix as a competing reaction. Solutions of the Grignard reagents are free of coupled product normally associated with the classical method, and addition product associated with using compound **1**. The improved yield of the Grignard reagent using the polymer versus **1** relates to the polymer matrix delivering sequential electrons to the halide as opposed to intimate contact of a dianion site, **7a**, **7a'**, required to afford the addition product. Preformed allylic Grignard reagents do not appreciably add to anthracene and silylsubstituted anthracenes [12].

Other important features include the use of the polymers **7** and **7'** to form Grignard reagents of highly substituted benzylic halides, **25–30**, all formed in > 85% yield, with no evidence of coupled or addition products, the formation of Grignard reagents of heterocyclic compounds **22**, **23**, and the formation of poly-Grignard reagents of **17–22**. Another important aspect

Table 2

Uptake of $[\text{Mg}(\text{anthracene})(\text{THF})_3]$, **1**, by anthracene functionalised polymer **6**, **6'**, and yield of the Grignard from the subsequent reaction with benzyl chloride in THF at ca. 25°C, entry 1, and recycling of the recovered polymers, entry 2, and then repeating this process and recycling the recovered polymer, entry 3, etc.

Cycle	Addition of 1 (% theoretical)		% Grignard reagent ^a formation	
	6	6'	6	6' ^b
1.	74–76	74–76	92–97	90–96
2.	65–67	64–67	90–93	84–86
3.	60–62	54–56	88–92	81–83
4.	57–60	48–51	87–91	80–83

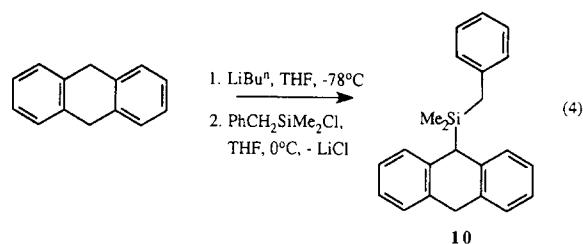
^a Range over three separate runs. ^b Reactions carried out < 0°C, for maximum yield.

of the use of the polymer over the use of magnesium anthracene is reduced reaction times (e.g. **16** requires times in excess of 36 h using **1** [12], compared with 12 h using **7** or **7'**) and reduction in coupling products (e.g. **17** 10% coupled di-Grignard reagent using **1** [12], compared to < 5% coupled di-Grignard using **7** or **7'**).

2.3. Polymer recycling

In the case of generating the Grignard reagent of benzyl chloride using **7a**, **7b**; **7a'**, **7b'** the spent polymer was tested for its ability to be recycled. After quenching with benzyl chloride the polymer was collected and washed with THF and then loaded with magnesium using **1** as before yielding a deep green polymer (see above). This was treated with benzyl chloride and the procedure repeated, etc. Results of this study as measured by the amount of compound **1** consumed and the yield of the Grignard reagents are given in Table 2. Overall, the uptake of magnesium by the spent polymer diminished significantly for successive cycles, but the yield of derived Grignard reagent based on the amount of **1** consumed is unchanged.

The inability of the recovered polymers to consume the same amount of **1** as polymers in earlier cycles is due to 'poisoning' of the active sites within the polymer matrix through formation of 9,10-dihydroanthracene moieties. This could arise from proton abstraction by the dianion and/or radical anion centres from the solvent during washings to remove anthracene and excess **1**. Similar reactions have been identified for the naphthalene radical anion [42] and complex **2**. Reaction with trace amounts of water in the solvent would give similar results. To establish the presence of 9,10-dihydroanthracene moieties in the recovered polymers, a second model compound, 9-(benzyl dimethylsilyl)-9,10-dihydroanthracene, **10**, was prepared for spectral comparison. This involved the treatment of 9-lithio-9,10-dihydroanthracene with benzyl dimethylchlorosilane; Eq. (4).



Similarly the dihydroanthracene polymer **12** and **12'** was prepared by the treatment of a THF slurry of **4** and **4'** with 9-(chlorodimethylsilyl)-9,10-dihydroanthracene, **11**, in greater than 95% yield based on weight gain (Scheme 3). Compound **11** was prepared by quenching 9-lithio-9,10-dihydroanthracene with dichlorodimethylsilane. In addition, hydrolysis of **7** and **7'** by the addition of moist THF yields mainly the dihydroanthracene polymer, **12**, **12'**. Comparison of ²⁹Si CP MAS NMR data of this material, with those of **8**, **10**, new and recycled **6** and **6'**, **12** and **12'**, in part presented in Fig. 1, supports the presence of 9,10-dihydroanthracene sites being formed in recycled **4** and **4'**.

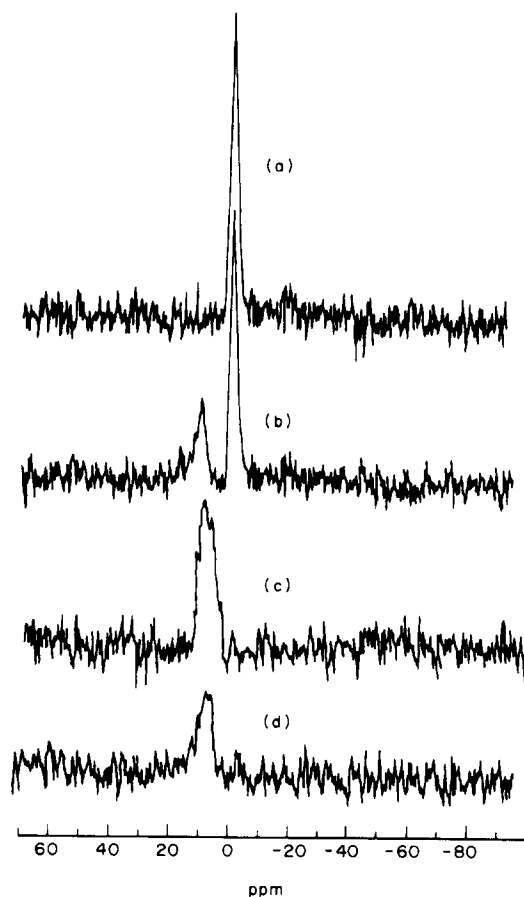
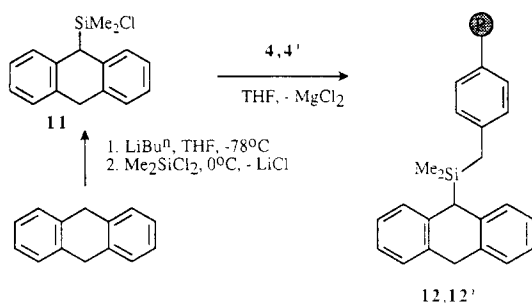


Fig. 1. CP MAS ²⁹Si NMR spectra (59.61 MHz) of (i) the anthracene functionalised polymer **6'**, (ii) polymer **6'** after being recycled three times, and (iii) 9,10-dihydroanthracene functionalised polymer **12'**, and (iv) hydrolysed polymer **13'**.



Scheme 3.

The cleavage of functional groups from the support was discounted as a possible cause of diminished uptake of **1**, since there was negligible weight difference between cycles of the polymers. Functional groups were also absent in the ^1H NMR analysis of the washings. The addition of preformed Grignard reagent across the $\text{C}_{9,10}$ positions of anthracene moieties within the polymer was also a potential source of reduced consumption of **1**, given the slow reaction of some benzylic Grignard reagents with 9-trimethylsilylanthracene [12]. However, treatment of **7a**, **7b** with one equivalent of a 0.1 M THF solution of benzylmagnesium chloride resulted in only a ca. 2% reduction in the activity of the mother liquor after stirring at room temperature for 24 h. Considering the limited contact time between solutions of the Grignard reagent and the polymer, it is unlikely that a reaction of this type contributes significantly to the 'poisoning' of functional groups within the polymer. There was no discernible difference in IR spectra of **6** and **6'**, and its recycled material which is consistent with the low degree of functionalisation of the polymer and the similarity in the spectra of the model compounds **8** and **10**.

The ^{29}Si CP MAS NMR spectra of the anthracene functionalised polymers **6'** and the third recycled material are shown in Fig. 1. Whereas **6'** exhibits a single resonance at $\delta -5.0$ ppm, a second broader peak centred at $\delta +6$ ppm is subsequently observed. Comparison of the spectra obtained for **6'** and the model compound **8**, which exhibits a single resonance at $\delta -5.5$ ppm, indicates that spectral correlation between free and polymer supported systems are valid. A sharp singlet at $\delta -4.46$ ppm observed in the ^{29}Si NMR spectra of **10** in C_6D_6 suggests that comparison of chemical shift values between solution and solid state spectra for such compounds is less accurate. Thus, the solid state ^{29}Si NMR spectrum of **10**, which shows a sharp singlet at $\delta +5.5$ ppm and **12'**, which shows a singlet at $\delta +6.1$ ppm, provide evidence for the presence of 9,10-dihydroanthracene moieties in the recycled polymers. The solid state ^{29}Si NMR spectrum of the reaction product of **7'** and water, **13'**, shows a singlet at $\delta +6.0$ ppm.

2.4. Conclusion

Grignard reagents of benzylic and allylic halides are accessible in high yield using polymer supported magnesium anthracene, many of them being inaccessible using classical techniques involving bulk metal, or even using highly activated metal. While some 'poisoning' of the polymer occurs in recycling studies, the ability to generate some of these reagents coupled with the simplicity of using a column of the polymer offers new directions in the application of Grignard reagents, and also the application of the polymer as a potent reducing reagent without the resulting solutions being loaded with anthracene.

3. Experimental section

3.1. General

Techniques and procedures for drying solvents are described in earlier papers [2,12]. NMR spectra were recorded on Bruker WP-80, Bruker AM-300, Varian Gemini-200 or Varian Unity-400 spectrometers. ESR were recorded on a Bruker ER-100 or Bruker ER 200 D spectrometer. Mass spectra were recorded on a Varian CH7 mass spectrometer (70 eV), Hewlett Packard 5986 GC/MS or VG Platform 2 (electrospray) spectrometer. Infra-red spectra were recorded as thin films or nujol mulls on a Perkin-Elmer 283, Matson Sirius 100 FT or a Perkin-Elmer 1725 X FT infra-red spectrometer. Elemental analyses were performed by the Micro Analytical Services Pty. Ltd., Melbourne. Chloromethylated polystyrenes (1.20–1.34, and 4.11–4.15 mmol g^{-1} Cl) were purchased from BIO-RAD. Benzyldimethylchlorosilane [43], 9-chlorodimethylsilylanthracene [44] and compound **1** were prepared using literature procedures. Li^nBu was obtained from Metallgesellschaft (AG) West Germany as a hexane solution, typically 1.60 M, and was standardised before use. Reaction of **7a**, **7b** and **9** with benzylic halides is typified by the formation of the Grignard reagent of benzyl chloride.

3.2. Synthesis of the Grignard reagent of chloromethylated polystyrene, **4, 4'**

THF (75 ml) was added to chloromethylated polystyrene [(a) 5.0 g, 1.34 mmol g^{-1} , 6.7 mmol; (b) 5.0 g, 4.11 mmol g^{-1} , 20.6 mmol] and the resulting slurry was stirred for 12 h at room temperature. The THF was removed, replaced with fresh solvent (75 ml) and **1** [(a) 2.82 g, 6.7 mmol; (b) 6.89 g, 16.5 mmol] added portionwise. After the addition of ca. one quarter of **1**, the THF solution turned a deep green colour which dissipated after stirring for 2 min at room temperature. The remaining solid was added over a period of 1 h.

The resulting polymer was then filtered, washed with THF (3×75 ml), and dried in vacuo at 60 °C for 6 h to afford the Grignard reagent of chloromethylated polystyrene as a fine, light green powder [(a) 6.04 g, 99% based on weight gained; (b) 6.60 g, 78% based on weight gained], ESR: g_{av} (a) 2.0030, (b) 2.0033. To a THF slurry of the Grignard reagent of chloromethylated polystyrene [(a) 2.0 g, 2.3 mmol; (b) 3.2 g, 8.4 mmol] in THF was added excess ClSiMe_3 , and the resulting mixture was stirred for 12 h at room temperature. The polymer was then filtered, washed with THF, (3×75 ml) and dried in vacuo at 60 °C for 6 h, affording a pale yellow solid [(a) 2.2 g, 99% based on weight gained; (b) 2.9 g, 78% based on weight gained]. (Found for **4a**: C and H, 97.03; Cl, 0.31%; **4a** requires; C and H 96.42; Cl, 0%) (Found for **4a'**: C, 84.36; H, 6.72 Cl, < 0.2%; **4a'** requires; C and H, 89.9; Cl, 0%). IR(KBr disk): ν_{CH} (methylene) 1252, 1250 cm^{-1} , ν_{SiC} 848, 837 cm^{-1} .

3.3. Synthesis of 9-(chlorodimethylsilyl)anthracene 5

To an ice-cold slurry of 9-bromoanthracene (10.0 g, 39 mmol) in Et_2O (100 ml) was added a hexane solution of Li^nBu (27 ml, 1.6 M, 47 mmol) over 5 min. The resulting deep orange solution was stirred for 1 h at room temperature during which an orange precipitate formed. The mixture was then added to a solution of dichlorodimethylsilane (10 ml, 82 mmol) in Et_2O (50 ml) over 15 min and the reaction mixture was stirred for 12 h at room temperature. Volatiles were then removed in vacuo and the residue was taken up in hexane (100 ml), filtered to remove lithium chloride and the solution concentrated under reduced pressure to ca. 40 ml. Cooling this solution to –30 °C yielded a bright yellow solid which was collected, washed with ice-cold hexane (2×20 ml) and dried in vacuo to afford **5** (8.5 g, 80%), m.p. 62–64 °C (Found: C, 70.91; H, 5.66; Cl, 12.88%; $\text{C}_{16}\text{H}_{15}\text{SiCl}$ requires; C, 70.96; H, 5.58; Cl, 13.09%). ^1H NMR (80.0 MHz, C_6D_6), δ 0.87 (6H, s, $\text{Si}(\text{CH}_3)_3$), 7.14–7.35 (4H, m, $\text{CH}_{2,3,6,7}$), 7.64–7.76 (2H, m, $\text{CH}_{4,5}$), 8.55–8.67 (2H, m, $\text{CH}_{1,8}$), 8.12 (1H, s, CH_{10}); ^{13}C NMR (20.1 MHz, C_6D_6), δ 8.1 ($\text{Si}(\text{CH}_3)_3$), 124.9 ($\text{CH}_{4,5}$), 125.9 ($\text{CH}_{3,6}$), 128.4 ($\text{CH}_{2,7}$), 129.8 ($\text{CH}_{1,8}$), 130.2 (CH_9), 131.7 (CH_{10}), 132.3 ($\text{C}_{4a,10a}$), 137.3 ($\text{C}_{5a,8a}$); ^{29}Si NMR (59.61 MHz, C_6D_6), δ +17.4 ppm. M/e (relative intensity): 235 (41%, $\text{M}^+ - \text{Cl}$), 221 (13%, $\text{M}^+ - \text{Cl}$, Me), 178 (100%, $\text{M}^+ - \text{SiMe}_2\text{Cl}$).

3.4. Synthesis of anthracene functionalised polymers, **6**, **6'**

To an ice-cold slurry of the Grignard reagent of chloromethylated polystyrene [(a) 6.0 g, 1.34 mmol g^{-1} , 6.56 mmol; (b) 6.40 g, 4.11 mmol g^{-1} , 15.55 mmol] in THF (100 ml) was added a solution of 9-

(chlorodimethylsilyl)anthracene, [(a) 1.78 g, 6.57 mmol; (b) 4.3 g, 15.88 mmol] in THF and the reaction mixture was stirred for 12 h at room temperature. The resulting polymer was filtered, washed with THF (3×75 ml) and dried in vacuo for 6 h at 60 °C to afford compound as a white solid [(a) 6.2 g, 99% based on weight gain; (b) 7.0 g, 100% based on weight gain]. (Found for **6**: C, 87.79; H, 7.95; Cl, 0.23%, **6** requires; C and H 97.10, Cl 0%). (Found for **6'**: C, 87.54; H, 7.34; Cl < 0.1%, **6'** requires; C and H 93.6; Cl, 0%). CP MAS ^{29}Si NMR (59.61 MHz), δ –5.2, –5.0 ppm. IR (KBr disk): ν_{CH} (methylene) 1252, 1255 cm^{-1} , ν_{SiC} 843, 837 cm^{-1} .

3.5. Synthesis of magnesium anthracene functionalised polymers, **7a**, **7b**; **7a'**, **7b'**

THF (75, 50 ml) was added to the silylanthracene functionalised polymer **6**, **6'** (5.02 g, 5.4 mmol; 2.0 g, 4.6 mmol) and the resulting slurry was stirred for 12 h at room temperature. Solid **1** (1.7 g, 4.1 mmol; 1.4 g, 3.3 mmol) was added portionwise to the swollen polymer, affording a deep green solid, containing a small amount of unreacted **1**. The filtrate was removed and the polymer washed with THF (4×50 ml) and dried in vacuo for 6 h at 30 °C to afford compound **7a**, **7a'**; **7b**, **7b'** as a dark green solid (5.80 g; 2.1 g). ESR: g_{av} = 2.0030, 2.0030.

3.6. Synthesis of 9-(benzyl dimethylsilyl)anthracene, **8**

To an ice-cold solution of 9-chlorodimethylsilylanthracene, **5** (4.67g, 17 mmol) in Et_2O (50 ml) was added an ethereal solution of benzyl magnesium chloride (26 ml, 0.77 M, 20 mmol) and the reaction mixture was stirred for 12 h at room temperature. Volatiles were removed in vacuo and the residue taken up in hexane (100 ml), washed with water (2×25 ml) and the organic layer separated and dried over anhydrous magnesium sulphate. Removal of the solvent in vacuo yielded a yellow oil which crystallised from hexane (10 ml) upon cooling to –30 °C. Recrystallisation from hexane afforded compound **8** as pale yellow crystals (4.20 g, 74.5%), m.p. 56–58 °C (Found: C, 84.42; H, 6.92%. $\text{C}_{23}\text{H}_{22}\text{Si}$ requires; C, 84.60; H, 6.79%). ^1H NMR (300 MHz, C_6D_6), δ 0.78 (6H, s, $\text{Si}(\text{CH}_3)_3$), 2.88 (2H, s, CH_2), 7.21 (5H, m, $\text{C}_{\text{aromatic}}\text{H}$), 7.54 (4H, m, $\text{CH}_{2,3,6,7}$), 8.08 (2H, m, $\text{CH}_{4,5}$), 8.44 (2H, m, $\text{CH}_{1,8}$), 8.54 (1H, s, CH_{10}); ^{13}C NMR (75.47 MHz, C_6D_6) δ 3.2 ($\text{Si}(\text{CH}_3)_3$), 28.3 (CH_2), 124.2 ($\text{CH}_{4,5}$), 124.4 ($\text{CH}_{3,6}$), 124.8 ($\text{CH}_{2,7}$), 128.2 ($\text{CH}_{1,8}$), 128.3 ($\text{C}_{\text{aromatic}}\text{H}$), 130.2 (CH_{10}), 131.2 (CH_9), 133.9 ($\text{C}_{4a,10a}$), 137.2 ($\text{C}_{8a,9a}$); ^{29}Si (59.61 MHz, C_6D_6), δ –4.46 ppm; CP MAS ^{29}Si NMR (59.61 MHz), δ –5.5 ppm. M/e, relative intensity: 235 (38%, $\text{M}^+ - \text{CH}_2\text{Ph}$), 178 (100%, $\text{M}^+ - \text{SiMe}_2\text{CH}_2\text{Ph}$).

3.7. Synthesis of Mg(9-(benzyltrimethylsilyl)anthracene)(THF)₂, **9**

Method A: To a stirred suspension of magnesium powder (0.20 g, 8.2 mmol) in THF (5 ml) was added 1,2-dibromoethane (3 drops). After the evolution of ethene had ceased 9-(benzyltrimethylsilyl)anthracene **8** (4.85 g, 15 mmol) and more THF (50 ml) were added and the reaction mixture was stirred at room temperature for 48 h after which time all of the magnesium had been consumed and a yellow solid precipitated from solution. The solid was filtered, washed with THF (3 × 20 ml) and dried in vacuo to afford compound **9** (3.81 g, 93%), m.p. 70 °C (dec.) Found: C, 73.89; H, 7.42; Mg, 4.64%. C₃₁H₃₈O₂MgSi requires; C, 75.21; H, 7.74; Mg, 4.91%. Ratio of **8**: THF, 1:2 (as determined by ¹H NMR of CCl₄ decomposition mixture). **Method B:** To a stirred suspension of **1** (3.61 g, 8.6 mmol) in THF (30 ml) was added **8** (3.0 g, 9.2 mmol). A yellow solid formed immediately which was filtered, washed with THF (2 × 25 ml) and dried in vacuo to afford compound **9** (4.1 g, 96%).

3.8. Synthesis of 9-(benzyltrimethylsilyl)-9,10-dihydroanthracene, **10**

To a stirred solution of 9,10-dihydroanthracene (3.6 g, 20 mmol) in THF (100 ml) cooled to –30 °C, was added LiⁿBu (14 ml, 1.6 M, 23 mmol). The resulting deep brown solution was stirred for 30 min, the temperature was lowered to –78 °C and a THF solution of benzyltrimethylchlorosilane (5.5 g, 20 mmol in 20 ml of THF) was added over a period of 10 min. The reaction mixture was allowed to warm to room temperature and stirring was continued for another 2 h. Volatiles were removed in vacuo and the residue was taken up in hexane (100 ml), washed with water (2 × 25 ml) and the organic layer separated and dried over anhydrous magnesium sulphate. Removal of the solvent in vacuo yielded a white solid which was recrystallised from hexane as white needles of **10** (5.7 g, 87%) m.p. 126–128 °C. (Found: C, 84.22; H, 7.29%. C₂₃H₂₄Si requires; C, 84.09; H 7.36%). ¹H NMR (300 MHz, C₆D₆), δ –0.2 (6H, s, Si(CH₃)₃), 1.97 (2H, s, CH₂), 3.59 (2H, m, 2 × CH₁₀), 3.90 (1H, m, CH₉), 7.08 (13H, m, C_{aromatic}H); ¹³C NMR (75.47 MHz, C₆D₆), δ –4.3 (Si(CH₃)₃), 24.4 (CH₂Si), 36.6 (CH₂), 41.5 (CHSi), 124.5 (CH_{4,5}), 125.4 (CH_{3,6}), 126.1 (CH_{2,7}), 127.5 (CH_{1,8}), 128.3–128.6 (C_{aromatic}H), 134.3 (C_{4a,10a}), 138.5 (C_{8a,9a}); ²⁹Si NMR (59.61 MHz, C₆D₆), δ +6.26 ppm; CP MAS ²⁹Si NMR (59.61 MHz), δ 5.5 ppm. M/e (relative intensity): 179 (100%, M⁺ – SiMe₂CH₂Ph).

3.9. Synthesis of 9-chlorodimethylsilyl-9,10-dihydroanthracene **11**

To a slurry of dihydroanthracene (3.24 g, 18.0 mmol) in THF (50 ml) at –30 °C was added LiⁿBu (13 ml,

2.0 mmol) over 5 min. The resulting orange/brown solution was stirred for 30 min at room temperature. To the solution was then added to a solution of dichlorodimethylsilane (3.9 g, 30.0 mmol) in THF (20 ml) over 15 min and the reaction mixture was stirred for 3 h at room temperature. Volatiles were then removed in vacuo and the residue was taken up in hexane (75 ml), filtered to remove lithium chloride and the solution concentrated and on cooling to –30 °C afforded a pale yellow solid (4.2 g, 85%). Found: C, 74.06; H, 6.28%. C₁₆H₁₇SiCl requires; C, 70.43; H, 7.4%. ¹H NMR (200 MHz, C₆D₆), δ 0.33 (6H, s, Si(CH₃)₂), 3.6–4.2 (3H, m, 2 × C₁₀, C₉) 7.14–7.5 (8H, m, C_{aromatic}H); ¹³C NMR (53.1 MHz, C₆D₆), δ 1.0 (Si(CH₃)₂), 36.3 (CH₂), 43.4 (SiCH) 125.8, 126.1 (CH_{4,5}), 127.9, 128.1 (CH_{3,6}), 133.3, 134.4 (CH_{2,7}), 135.6, 135.6 (CH_{1,8}); ²⁹Si NMR (59.61 MHz, C₆D₆), δ +25.9 ppm.

3.10. Synthesis of dihydroanthracene functionalised polymers, **12**, **12'**

To a slurry of the Grignard reagent of chloromethylated polystyrene [(a) 1.1 g, 1.20 mmol g^{–1}, 1.28 mmol; (b) 1.2 g, 4.15 mmol g^{–1}, 4.53 mmol] in THF (40 ml) was added a solution of 9-chlorodimethylsilyl-9,10-dihydroanthracene, [(a) 0.35 g, 1.28 mmol; (b) 1.19 g, 4.36 mmol] in THF giving a brown solution, and the reaction mixture was stirred for 12 h at room temperature. The resulting polymer was filtered, washed with THF (3 × 25 ml) and dried in vacuo for 6 h at 60 °C to afford compound **12**, **12'** as a pale yellow solid [(a) 1.30 g, 95% based on weight gain; (b) 1.38 g, 96% based on weight gain]. Found C, 88.04; H, 7.70%, **12** requires; C and H 97.40%. Found for **12**: C, 81.46; H, 7.45%, **12'** requires; C and H 93.6%. CP MAS ²⁹Si NMR (59.61 MHz), δ +7.6, +6.1 ppm. IR (KBr disk): ν_{CH} (methylene) 1256, 1257 cm^{–1}, ν_{SiC} 840, 837 cm^{–1}.

3.11. Hydrolysis of magnesium anthracene functionalised polymers, **13**, **13'**

THF (75 ml) was added to polymer **7** (5.70 g) derived from reaction of **6** (5.0 g, 5.4 mmol) with **1** (2.30 g, 5.5 mmol) and the reaction mixture was stirred for 2 h at room temperature. A THF solution of H₂O (0.20 M) was added to the resulting dark green slurry, yielding a colourless solution and pale yellow solid. CP MAS ²⁹Si NMR (59.61 MHz), δ +7.5, +6.0 ppm.

3.12. Reaction of benzyl chloride and polymer, **7a**, **7b**

THF (75 ml) was added to polymer **7a**, **7b** (5.70 g) derived from reaction of **6** (5.0 g, 5.4 mmol) with **1** (2.30 g, 5.5 mmol) and the reaction mixture was stirred for 12 h at room temperature. A THF solution of benzyl

chloride (0.20 M) was added to the resulting dark green slurry, yielding a colourless solution and pale yellow solid after the addition of 11.5 ml (2.3 mmol) of the halide solution. Quenching of aliquots as above indicated that the solution was 0.024 M of the Grignard reagent (91%). The filtrate was removed via a cannula and the polymer was washed with THF (2 × 50 ml). Chlorotrimethylsilane (2 ml, 16 mmol) was added to the combined filtrate and washings and after stirring for 12 h at room temperature the resulting solution was extracted in the usual manner to afford a colourless liquid which was shown by ^1H NMR and GC/MS analysis to be pure benzyltrimethylsilane. The recovered polymer was dried in vacuo for 12 h at 40 °C to afford compound **6'** (1st cycle) (5.1 g, 100% recovery).

3.13. Reaction of benzyl chloride with Mg(9-(benzyltrimethylsilyl)anthracene)(THF)₂, **9**

A THF solution of benzyl chloride (0.71 g, 5.6 mmol in 20 ml of THF) was added over a period of 30 min to a stirred slurry of **9** (2.76 g, 5.6 mmol) in THF (35 ml). After addition was complete the reaction mixture was stirred for 1 h at room temperature, yielding a turbid, pale yellow solution. Quenching of 2 × 2 ml aliquots with 0.1 M aqueous HCl and back titration with 0.1 M NaOH indicated that the solution was 0.098 M of the Grignard reagent (96%). Chlorotrimethylsilane (2 ml, 16 mmol) was added to the remainder of the Grignard reagent solution and after stirring for 12 h at room temperature the resulting solution was extracted in the usual manner to afford a pale yellow solid which was shown by ^1H NMR and GC/MS analysis to be a mixture of benzyltrimethylsilane and **8**.

3.14. Synthesis of 2,4-dimethoxy-5-methylphenylmethanol

A solution of sodium borohydride (0.26 g, 6.87 mmol) in aqueous sodium hydroxide was added dropwise at 0 °C to a stirred solution of the 2,4-dimethoxy-5-methylbenzaldehyde (1.2 g, 6.66 mmol) in THF. The solution was stirred at room temperature for 0.5 h, and then poured into an excess of dilute hydrochloric acid at 0 °C. The crude product was isolated by extraction from Et₂O and the alcohol crystallised from Et₂O as needles (1.2 g, 99%), m.p. 88 °C. (Found: C, 65.97; H, 7.72%. C₁₀H₁₄O₃ requires; C, 65.92; H, 7.74%). ^1H NMR (200 MHz, CDCl₃), δ 1.63 (1H, s, CH₂OH), 2.15 (3H, s, CH₃), 3.85 (3H, s, OCH₃), 3.87 (3H, s, OCH₃), 4.60 (2H, d, CH₂OH), 6.45 (1H, s, C_{aromatic}H), 7.01 (1H, s, C_{aromatic}H); ^{13}C NMR (50.3 MHz, CDCl₃), δ 15.24 (CH₃), 55.62 (OCH₃), 55.65 (OCH₃), 61.70 (CH₂OH), 118.08 (C_{aromatic}), 120.62 (C_{aromatic}), 131.25 (2 × C_{aromatic}H), 156.70 (C_{aromatic}), 158.19 (C_{aromatic}); M/e (relative intensity): 205.2 (100%, M⁺ + K).

3.15. Synthesis of 2,4-dimethoxy-5-methyl-1-chloromethylbenzene, **29**

Freshly distilled thionyl chloride (1.8 g, 15.13 mmol) was added to a solution of the foregoing alcohol (1.0 g, 5.49 mmol) in benzene containing pyridine and the solution was heated under reflux for 3 h. It was then cooled, diluted with ethyl acetate, and washed in turn with water, saturated aqueous sodium hydrogen carbonate, and finally with saturated brine. Crystallisation in Et₂O gave the chloride (1.0 g, 91%) m.p. 40 °C dec (Found: C, 62.82; H, 7.43%; C₁₀H₁₃O₂Cl requires; C, 59.86; H, 6.53%); ^1H NMR (200 MHz, CDCl₃), δ 2.05 (2H, s, CH₃), 3.79 (3H, s, OCH₃), 3.82 (3H, s, OCH₃), 4.60 (2H, d, CH₂Cl), 6.42 (1H, s, C_{aromatic}H), 6.73 (1H, s, C_{aromatic}H); ^{13}C NMR (50.3 MHz, CDCl₃), δ 15.27 (CH₃), 55.56 (OCH₃), 55.89 (OCH₃), 117.80 (C_{aromatic}), 121.10 (C_{aromatic}), 131.05 (2 × C_{aromatic}H), 156.23 (C_{aromatic}), 156.45 (C_{aromatic}).

3.16. Synthesis of 2,4-dimethoxy-5-methyl-1-trimethylsilylmethylbenzene, **29a**

Method A: A solution of 2,4-dimethoxy-5-methyl-1-chloromethylbenzene (0.13 g, 0.65 mmol), in THF (25 ml) was added dropwise to a stirred slurry of magnesium anthracene (0.30 g, 0.71 mmol). The orange suspension disappeared with the formation of a deep green solution, on addition of final drops of halide, the solution turned pale yellow. The concentration of the Grignard reagent was established by quenching an aliquot of the solution with 0.1 M HCl (10 ml) and back-titrating with 0.1 M NaOH, and was found to be > 95%. Chlorotrimethylsilane was added to the solution and stirred for 2 h; the resulting solution was extracted in the usual manner to afford an oily solid, which was shown by GC and ^1H NMR analysis to be a mixture of the title compound and anthracene. Method B: THF (35 ml) was added to polymer **7'b**, **7'b** derived from reaction of **6'** (0.50 g, 1.1 mmol) with **1** (0.35 g, 0.84 mmol) and the reaction mixture was stirred for 12 h at room temperature. A solution of 2,4-dimethoxy-5-methyl-1-chloromethylbenzene (0.10 g, 0.50 mmol), in THF (25 ml) was added dropwise to the resulting green slurry, yielding a colourless solution and a pale yellow solid. The concentration of the Grignard reagent was established as above and was found to be > 95%. Chlorotrimethylsilane was added to the combined filtrate and washings and stirred for 2 h, the resulting solution was extracted in the usual manner to afford a colourless liquid which was shown by GC and ^1H NMR analysis to be pure 2,4-dimethoxy-5-methyl-1-trimethylsilylmethylbenzene (0.11g, 93%); ^1H NMR (200 MHz, C₆D₆, CDCl₃), δ 0.07 (9H, s, Si(CH₃)₃), 2.06 (2H, s, CH₃), 3.79 (6H, s, OCH₃), 4.56 (2H, s, CH₂SiMe₃), 6.50 (1H, s, C_{aromatic}H), 6.82 (1H, s, C_{aromatic}H); M/e

(relative intensity): 277.32 (60%, $M^+ + K$), 165.32 (100%, $M^+ - CH_2SiMe_3$)

3.17. Synthesis of 2,4,6-trimethoxy-3-methylbenzene-methanol

A solution of 2,4,6-trimethoxy-3-methylbenzoate (1.5 g, 6.24 mmol) in anhydrous OEt_2 was added dropwise with stirring to lithium aluminium hydride in Et_2O at $0^\circ C$. The mixture was stirred at room temperature for 1 h then cooled to $0^\circ C$ and treated with sodium sulphate until coagulation occurred. The mixture was filtered through celite then washed with water followed by saturated brine. Removal of the solvent gave the alcohol which crystallised from Et_2O as needles (1.25 g, 94%), m.p. $110^\circ C$ (Found: C, 61.98; H, 7.76%; $C_{11}H_{16}O_4$ requires; C, 62.25; H, 7.6%), NMR: 1H (200 MHz, $CDCl_3$), δ 1.66 (1H, s, CH_2OH), 2.09 (3H, s, CH_3), 3.76 (3H, s, OCH_3), 3.84 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 4.70 (2H, d, CH_2OH), 6.29 (1H, s, $C_{aromatic}H$); ^{13}C (50.3 MHz, $CDCl_3$), δ 8.52 (CH_3), 55.41 (OCH_3), 55.74 (OCH_3), 55.78 (OCH_3), 61.79 (CH_2OH), 111.79 ($C_{aromatic}$), 114.65 ($C_{aromatic}$), 157.14 ($C_{aromatic}$), 158.08 ($C_{aromatic}$), 158.78 ($C_{aromatic}$).

3.18. Synthesis of 2,4,6-trimethoxy-3-methyl-1-chloromethylbenzene

The foregoing alcohol (1.0 g, 4.71 mmol) was converted into the chloride by a method similar to that described for **29**, (1.0 g, 92%), m.p. $> 30^\circ C$ dec, (Found: C, 60.92; H, 7.60%; $C_{11}H_{13}O_3Cl$ requires; C, 67.67; H, 7.74%), 1H NMR (200 MHz, $CDCl_3$); 2.07 (2H, s, CH_3), 3.84 (3H, s, OCH_3), 3.86 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 5.97 (2H, s, CH_2Cl), 6.25 (1H, s, $C_{aromatic}H$), ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 8.95 (CH_3), 55.75 ($2 \times OCH_3$), 56.3 (OCH_3), 62.2 (CH_2Cl).

3.19. Synthesis of 2,4,6-trimethoxy-3-methyl-1-trimethylsilylmethylbenzene

The foregoing chloride was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a pale yellow oil, pure by GC/MS, M/e (relative intensity): 291 (52%, $M^+ + Na$).

3.20. Synthesis of 2-methoxy-3-methyl-1-trimethylsilylmethylbenzene

2-Methoxy-3-methyl-1-chloromethylbenzene was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a pale yellow oil, pure by GC, 1H NMR (200 MHz, $CDCl_3$), δ 0.11 (9H, s, $Si(CH_3)_3$), 2.32 (3H, s, CH_3), 3.75 (3H, s,

OCH_3), 3.97 (2H, d, CH_2SiMe_3), 7.0 (1H, m, $C_{aromatic}H$), 7.25–7.35 (2H, m, $C_{aromatic}H$).

3.21. Synthesis of 3,5-dimethoxy-4-methyl-1-trimethylsilylmethylbenzene

3,5-Dimethoxy-4-methyl-1-chloromethylbenzene was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a clear oil, pure by GC, NMR: 1H (200 MHz, $CDCl_3$), δ 0.15 (9H, s, $Si(CH_3)_3$), 2.15 (2H, s, CH_2SiMe_3), 3.95 (6H, s, OCH_3), 4.73 (3H, d, CH_3), 6.57 (1H, s, $C_{aromatic}H$); M/e (relative intensity): 238 (100%, $M^+ + K$).

3.22. Synthesis of 2,5-dimethoxy-1-trimethylsilylmethylbenzene

2,5-Dimethoxy-1-chloromethylbenzene was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a clear oil (95%) pure by GC, 1H NMR (200 MHz, $CDCl_3$), δ 0.01 (9H, s, $Si(CH_3)_3$), 2.15 (2H, s, CH_2SiMe_3), 3.75 (3H, s, OCH_3), 3.76 (3H, d, OCH_3), 6.57–6.61 (2H, m, $C_{aromatic}H$), 6.70 (1H, s, $C_{aromatic}H$); ^{13}C NMR (50.3 MHz, $CDCl_3$), δ 1.48 ($SiCH_3$), 20.8 (CH_2Si), 55.4, 55.6 ($2 \times OCH_3$), 108.8, 110.5, 115.8, 150.9, 153.2 ($C_{aromatic}$); M/e (relative intensity): 225 (72%, $M^+ + 1$).

3.23. Synthesis of 2,6-(bistrimethylsilylmethyl)pyridine

2,6-(Dichloromethyl)-pyridine (or 2,6-(dibromomethyl)pyridine) was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a clear oil, pure by GC/MS, M/e (relative intensity): 236 (100%, M^+), and 1H NMR as for literature values [45].

3.24. Synthesis of D-2,2',2''-trispyridylmethane

2,2',2''-Trispyridylmethylchloride was converted to the trimethylsilyl derivative by a method similar to that described for **29a**, affording a clear oil, pure by GC/MS, M/e (relative intensity): 271 (100%, $M^+ + Na$).

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