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General Ambient Temperature Benzylic Metalations Using Mixed-Metal Li/K-TMP Amide

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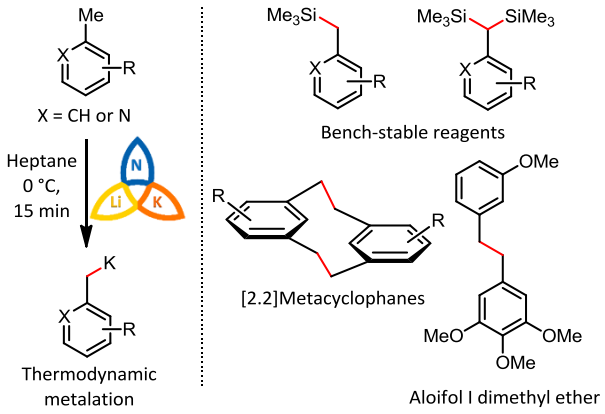


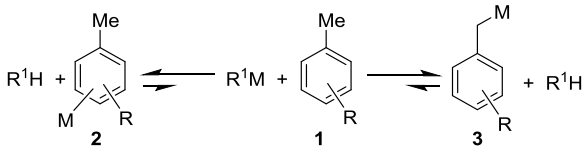
ABSTRACT

Highly regioselective benzylic metalations in hydrocarbon solvent have been achieved at rt and 0 °C using a mixed-metal Li/K-TMP amide comprised of KO*t*Bu, BuLi and 2,2,6,6,-tetramethylpiperidine (TMP(H)). Mixing of KO*t*Bu, BuLi and TMP(H) in heptane gave a solution of the base mixture which when used in deuterium labelling experiments confirmed the requirement of the three reagent components for both reactivity and selectivity. The reaction protocol is operationally straightforward and found to be applicable to a broad range of substrates. Upon generation of the metalated products they be reacted in heptane at ambient temperature in a variety of synthetically useful ways. Illustrated examples include generation of the benzyltrimethylsilanes and α,α-bis(trimethylsilyl)toluenes reagents, which are bench-stable surrogates of benzyl anions and α-silyl carbanions utilized for nucleophilic addition and Peterson olefination reactions. Direct C-C couplings mediated by 1,2-dibromoethane provided entries into bibenzyls and [2.2]metacyclophanes. Comparison of reaction outcomes with the same reactions carried out in THF at -78 °C showed no negative effects for conducting the reactions under these milder more user friendly conditions.

INTRODUCTION

The founding principles for the predictive use of organometallic bases for selective kinetic proton abstraction were established in the work of Curtin, Gilman and Wittig[1-3] and expanded to the breadth of organic synthesis by the immense contributions of Schlosser,[4] Beak,[5] Snieckus[5] and many others. The use of thermodynamic metalating conditions is often thought of as less challenging technically, but does also pose significant selectivity challenges. For example, substituted toluenes **1** are one group of substrates for which differentiation between kinetic and thermodynamic metalation sites is often a challenging issue depending upon the nature and position of the R substituent(s) on the aryl ring. Specifically, one or more directed *ortho* metalation product(s) **2** can exist, restricting attainment of the benzylic metalated product **3** with high selectivity (Scheme 1).[6] Numerous reports of lateral metalations (defined as deprotonation of a benzylic position that is lateral, or flanked by, a heteroatom containing substituent) have shown that they are highly substrate dependent leading to a myriad of conditions used with high selectivities often unachievable.[7]

Scheme 1. Competing Metalation Sites (M = metal)



In previously reported work we have shown that, in THF at -78 °C, the use of the triad of reagents BuLi/KO*t*Bu/TMP(H) was a general method to achieve benzylic metalations with excellent selectivity, irrespective of whether the benzylic position is lateral (*ortho*) to a heteroatom containing substituent or not (i.e. *meta* or *para*) (Scheme 2).[8] This can be attributed

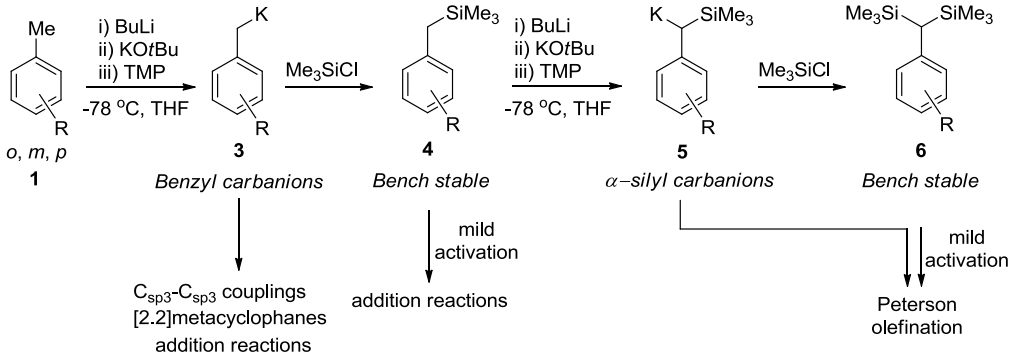
to the enhanced reactivity of the *in situ* formed mixed Li/K metal TMP amide over LiTMP alone and the ability of the TMP(H) to facilitate an anion migration from kinetic aryl to thermodynamic benzylic position.[8b] The term LiNK was coined to describe the synergetic combination of the mixed metal amide containing lithium (Li), nitrogen (N) from the TMP and potassium (K). For simplicity the benzylic species generated from the LiNK metalation are presented only as the K species based on the recent characterization of the PhLi/PhK/*t*BuOLi mediated metalation of toluene as benzylpotassium, though it should be understood that the exact nature of these organometallics could be substrate dependant and may be mixed metal species.[9]

The synthetic uses of these benzylic organometallics have included electrophile reactions,[8b] direct C_{sp3}-C_{sp3} coupling for bibenzyl,[10] and [2.2]metacyclophane[11] synthesis and further transmetalation to Si by reaction with chlorotrimethylsilane providing access to the bench stable benzyltrimethylsilane class **4** (Scheme 2).[12] Alternative procedures for the synthesis of benzyltrimethylsilanes require Pd or Ni catalyzed cross-coupling of the organo-lithium or -magnesium substrates MCH_2SiMe_3, (M = Li or Mg) with aryl-halides, -methylethers or -methylthioethers.[13] The synthetic advantage of silanes **4** lies in the fact that they can act as surrogates of benzyl anions and participated in nucleophilic addition reactions with mild silyloxide or fluoride activation (Scheme 2).[14]

Additionally, the utility of LiNK metalation (in THF at -78 °C) has been extended to include the regioselective benzylic metalation of substituted benzyltrimethylsilanes **4** generating the α-silyl carbanions **5**, which upon chlorotrimethylsilane quench yields the α,α-bis(trimethylsilyl)toluenes **6**.[15] The literature precedents for synthesis of reagents **6** using organometallic deprotonation as the key step are few.[16] Recently, the transition-metal catalyzed cross-couplings of $(Me_3Si)_2MgBr.LiCl$ or $(Me_3Si)_2ZnCl.MgBrCl.LiCl$ with aryl halides has been

reported as an additional route to this reagent class.[17] The synthetic value of reagents **6** lie in their bench stability, yet under mild activation conditions they can react as equivalents of the α-silyl carbanions **5** in Peterson olefination reactions.[15,17,18] The utility of reagents **6** for *E*-selective Peterson olefination from *N*-phenyl imines has recently been reported.[15]

Scheme 2. Selective Benzylic Metalation and Bench Stable Equivalents



The ability of LiNK to favour the thermodynamic over kinetic metalation product at –78 °C in THF raised the possibility that this low temperature may not always be necessary to achieve selective metalation. Recognising the instability of THF to strong bases at ambient temperature, we chose to investigate the reactivity and selectivity in hydrocarbon solvents with the key goals being to make the use of the base mixture as operationally straightforward as possible and facilitate the generation of important silicon reagents.

Extensive studies of *o*-metalations in hydrocarbon solvents have been reported by Slocum and co-workers, yet the literature precedents on thermodynamic benzylic metalation in hydrocarbons are considerably less prevalent with poor selectivity and limited substrate scope often obtained.[19] The kinetic *versus* thermodynamic *o*- and benzylic deprotonation of *p*-tolylsulfonamide, *p*-tolylsulfonate and *p*-toluamide have previously been investigated in the literature.[20] Arguably, a

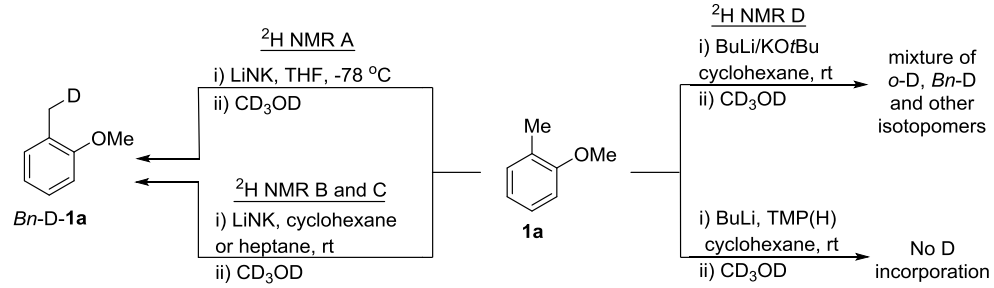
general ambient temperature method for benzylic metalation and electrophile reaction is desirable due to the broad synthetic potential of this reaction as outlined above.

RESULTS AND DISCUSSION

At the outset of our investigation into ambient temperature LiNK metalations in hydrocarbon solvents, 2-methylanisole **1a** was chosen as a model substrate. Previous reports have shown that selective benzylic lithiation of **1a** in hydrocarbons was challenging, for example BuLi/cyclohexane (reflux, 10 h) gave bn/*o* ratio of 67/33,[21a] BuLi/TMEDA/cyclohexane (rt, 10 h) gave a 25/75 bn/*o* mixture,[21b] BuLi/KO*t*Bu/heptane (reflux, 4.5 h) gave 49/25 for bn/*o* product ratio with the remainding being rearrangement products,[21b] while LDA/KO*t*Bu/hexane (25 °C, 10 h) provided 100/0: bn/*o*.[21c]

To gain a comparative understanding about the reactivity and selectivity of LiNK metalation of **1a** the following five reactions were carried out: (a) as per the previously established LiNK conditions with the three reagents BuLi, KO*t*Bu, TMP(H) at -78 °C in THF, (b) with BuLi, KO*t*Bu, TMP(H) at rt in cyclohexane (c) with BuLi, KO*t*Bu, TMP(H) at rt in heptane (d) with BuLi, KO*t*Bu at rt in cyclohexane and (e) with BuLi/TMP(H) in cyclohexane at rt (Scheme 3). Each reaction was stirred for 15 min and the resulting metalated mixture treated with CD_3OD and the deuterated products analyzed by ^1H and ^2H NMR. As anticipated, conditions (a) gave *Bn*-D-**1a** exclusively as product with good deuterium incorporation (>80%) (Figure 1, NMR A) and gratifyingly, a similar exclusively benzylic deuterated product was observed for both hydrocarbon reactions (b) and (c) at rt (>65% *Bn*-D) with no detectable *o*-D incorporation (Figure 1, NMRs B and C). In contrast, when only the two components BuLi, KO*t*Bu were used, as in reaction (d), a complex mixture of deuterated isotopomers was obtained showing complete loss of selectivity (Figure 1, NMR D).

Scheme 3. Metalation of 2-Methylanisole Under Various Conditions[a]



[a]All reaction times of 15 min, 1.2 equiv. of each reagent used.

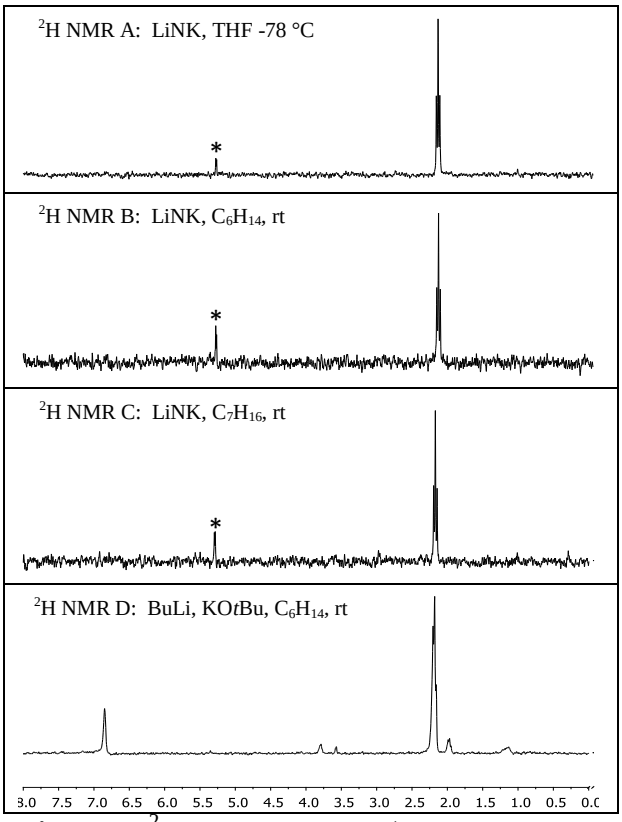
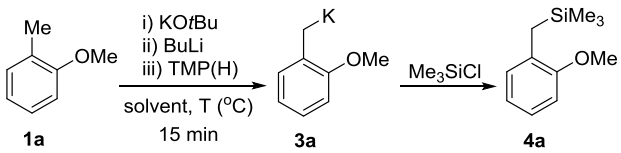


Figure 1. ^{2}H NMR spectra. (*CD_2Cl_2)

When the alternative two reagents BuLi and TMP(H) were used as in conditions (e), no deuterium incorporation was detected showing that if LiTMP formed *in situ*[22] it had insufficient basic strength to deprotonate under these conditions. Taken together these experiments highlight the significance of each component of the reagent mixture in delivering sufficient base strength yet maintaining a high degree of selectivity for benzylic metalation.

A further optimization was next conducted using TMSCl as electrophile. When conducting these experiments, it was found easiest to first sequentially add the three LiNK reagents (KO*t*Bu, BuLi, and TMP(H)) to the flask and then subsequently add the substrate **1a**, followed by the electrophile. Reactions in both cyclohexane and heptane at rt gave the expected TMS product **4a** in 65% and 69% yields respectively (Scheme 4, entries 1, 2). Lowering the reaction temperature to 0 °C gave a marginal improvement in the yields (entries 3 and 4), though starting material was recovered after workup. Increasing the LiNK mixture to 2 equiv. in heptane at 0 °C gave complete conversion, with the best yield of 86% (entry 5). Collectively, these results suggest that 2.0 equiv. of the preformed base mix KO*t*Bu/BuLi/TMP(H) in heptane at 0 °C followed by addition of substrate would be the optimal general procedure.

Scheme 4: Screening of Hydrocarbon Solvents[a]

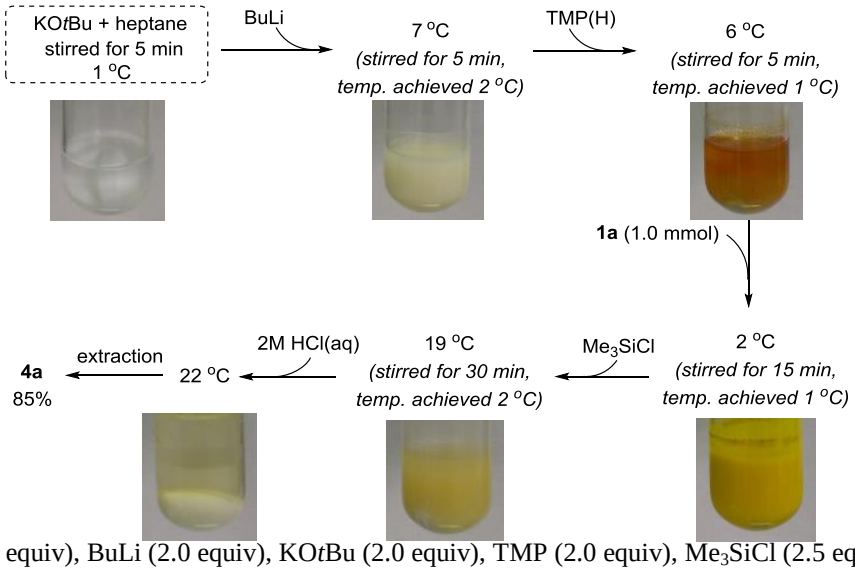


Entry	Solvent	T (°C)	Yield (%)
1	cyclohexane	rt	65
2	heptane	rt	69
3	cyclohexane	0	70
4	heptane	0	73
5	[b]heptane	0	86
6	[b]heptane	rt	86

Conditions: [a] **1a** (1.0 mmol), BuLi (1.2 mmol), KO*t*Bu (1.2 mmol), TMP(H) (1.2 mmol), solvent (2.5 mL) Me_3SiCl (2.5 mmol). [b] **1a** (1.0 mmol), BuLi (2.0 mmol), KO*t*Bu (2.0 mmol), TMP(H) (2.0 mmol), solvent (2.5 mL), TMSCl (2.5 mmol).

Prior to exploring the generality of this method, a temperature profile analysis of the formation and reaction of LiNK was undertaken (Figure 2). A stirred colorless suspension of KO*t*Bu in heptane was cooled in an ice-bath to 1 °C, and BuLi added dropwise giving a suspension of the

Lochmann-Schlosser base with a 7 °C temperature rise.[23] Upon the addition of TMP(H) a temperature rise of 4 °C occurred with the formation of an orange-brown solution from which a trace of precipitate formed over the 5 min time period before it was used. These results showed that no large exotherm was associated with the formation of a 0.6 M solution of the LiNK reagent generated for these experiments. Upon addition of the substrate **1a** (1.0 mmol) no change in temperature was detected and an immediate yellow suspension of **3a** formed. Next, upon addition of chlorotrimethylsilane electrophile a significant rise in temperature of 18 °C was observed. Once the reaction mixture had cooled back to 2 °C (30 mins), 2M HCl was added which also gave a significant temperature rise of 20 °C. Consequently, the electrophile quench and reaction workup steps are critical in term of exotherms, confirming that it is advisable to conduct these reactions at 0 °C for temperature control. Similar incremental increases in temperature profile were observed when the reaction was carried out at rt (Figure S1, SI).

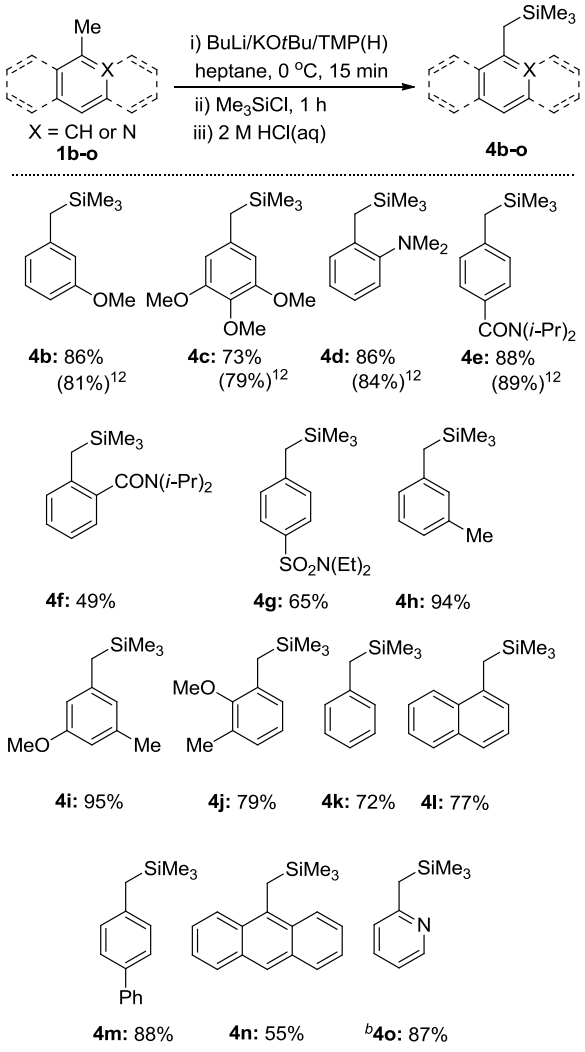


[a]Condition: **1a** (1.0 equiv), BuLi (2.0 equiv), KO*t*Bu (2.0 equiv), TMP (2.0 equiv), Me_3SiCl (2.5 equiv).

Figure 2. Temperature profile of benzylic metalation, TMSCl reaction and workup[a]

As there is a growing interest in the use of bench stable organosilicon reagents as carbanion equivalents, their synthesis was explored for a range of substrates using this approach.[12,13,14] Encouragingly, electron-rich toluenes such as 3-methylanisole **1b**, 3,4,5-trimethoxyanisole **1c** and 2-*N*,*N*-trimethylaniline **1d** each gave their corresponding benzyltrimethylsilanes **4b-d** with high yields 88%, 73%, 92% respectively (Scheme 5).

Scheme 5. Synthesis of substituted benzyltrimethylsilane reagents[a]



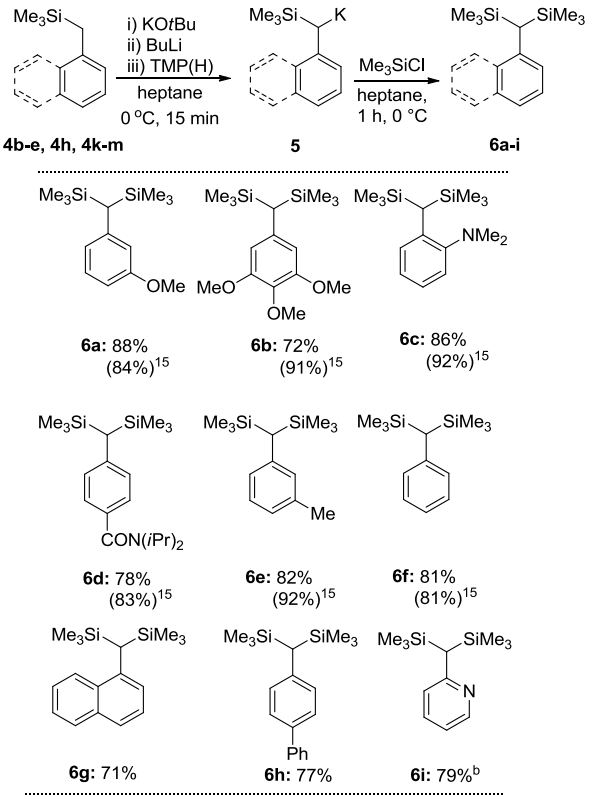
[a]Condition: Substrate (1.0 equiv), BuLi (2.0 equiv), KO*t*Bu (2.0 equiv), TMP(H) (2.0 equiv) and Me_3SiCl (2.5 equiv).[b]1.2 equiv of each BuLi/KO*t*Bu/TMP(H) used. [12] Reference for literature reported yields in THF at -78 °C.

Comparison of the results for **4b**-**e** with those previously reported in THF at -78 °C showed yields to be within small experimental error differences (Scheme 5, yields given in brackets).[12] The electron deficient *o*/*p* amido and sulfonamido substituted toluenes were successfully converted to their corresponding silanes **4e-g** in 49-91% yields. For substrates containing more than one methyl group such as *m*-xylene **1h**, 3,5-dimethylanisole **1i**, and 2,6-dimethylanisole **1j** the procedure was equally successful with yields for **4h**-**j** ranging from 79 to 95% (Scheme 5). Next, the set of aromatic hydrocarbons **1k**-**n** was screened and found to be convertible to their corresponding benzyltrimethylsilanes **4k**-**n** in good yields, illustrating that heteroatom substituent is not an essential factor. The heterocycle, α-picoline **1o**, also reacted under the established conditions with product **4o** obtained in 87% yield. One substrate limitation encountered was for halogenated toluenes, which were found to be incompatible with the metalation conditions, leading to complex product mixtures.

To further expand the repertoire of silicon reagents, the synthesis of $\alpha,\alpha,$-bis(trimethylsilyl)toluenes from benzyltrimethylsilanes was next addressed using **4b** as the test substrate. Pleasingly, following a 15 min LiNK metalation in heptane to form the α-silylcarbanion **5** and treatment with TMSCl the bis(silane) product **6a** was selectively obtained in a 88% yield (Scheme 6). Substrates **4c**-**e** containing trimethoxy, *o*-dimethylamino and *p*-amido substituents were also successfully converted to their corresponding di-TMS products **6b-d** in good to excellent yields (72-86%) which compared favorably with those previously reported in THF at -78 °C.[15] Notably, the presence of a competing methyl group in **4h** did not interfere with metalation regioselectivity, as product **6e** was obtained in a 82% yield. Trimethylsilanes **4k-m**, which contain no heteroatom substituent, were also converted to products **6f**, **6g** and **6h** with

81%, 71% and 77% yields, respectively. Conveniently, a one-pot conversion of 2-picoline **1o** into bis-trimethylsilane **6i** was directly achieved with 2.2 equiv of the LiNK reagent (Scheme 6). Overall, a two-fold LiNK metalation / TMSCl quench procedure at ambient temperature appears to be a routine general method for access to this class of Peterson olefination reagent.[15]

Scheme 6: Synthesis of Peterson olefination reagents

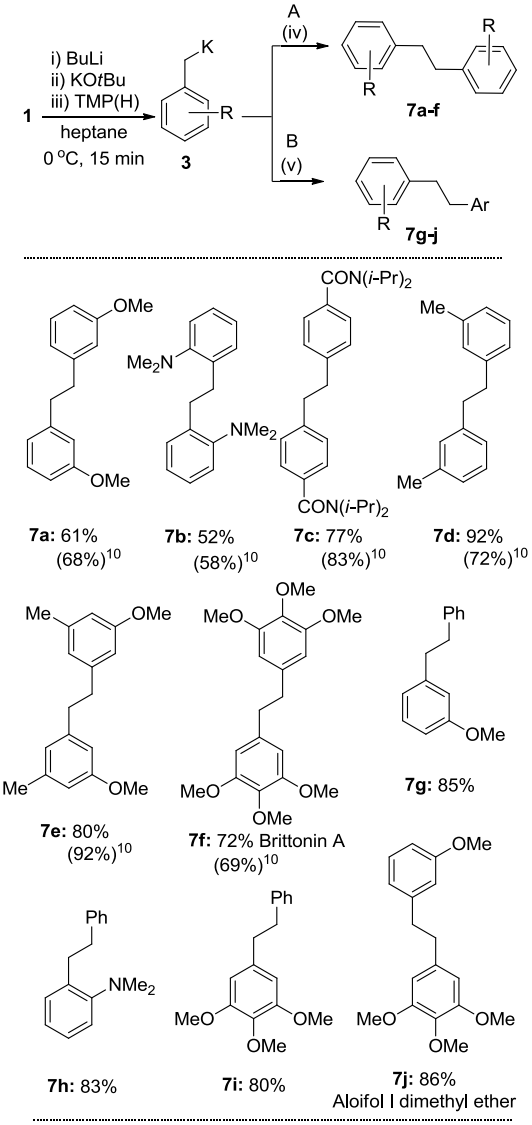


[a]Condition: Substrate (1.0 equiv), BuLi (2.0 equiv), KO*t*Bu (2.0 equiv), TMP(H) (2.0 equiv) and Me_3SiCl (2.5 equiv). [b] **1o** used as starting substrate with BuLi (2.2 equiv), KO*t*Bu (2.2 equiv), TMP(H) (2.2 equiv) and Me_3SiCl (2.5 equiv). [15]Reference for literature reported yields in THF at -78 °C.

Transition-metal free coupling of two carbon nucleophiles generated by direct deprotonation is an atom-economical method for C-C bond formation.[24] In a previous report it was shown that LiNK metalation of toluenes in THF at -78 °C and treatment with 1,2-dibromoethane was an effective method to produce 1,2-diarylethanes.[10] As such, it was of

interest to determine if this coupling was also achievable under ambient temperature heptane conditions. Generality of the reaction sequence was established with toluene substrates **1b**, **c**, **d**, **e**, **h**, and **i** which were metalated and treated with 1,2-dibromoethane to provide the coupled products **7a-e** in moderate to excellent yields of 52 to 92% (Scheme 7, route A).

Scheme 7: C_{sp3}-C_{sp3} couplings and benzylbromide reactions[a]

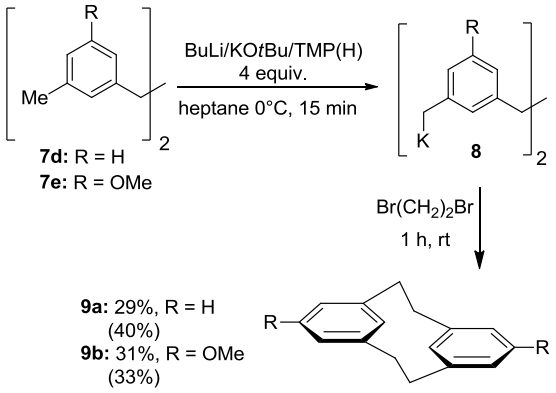


[a]Conditions: **1** (1.0 equiv), BuLi (2.0 equiv), KO*t*Bu (2.0 equiv), TMP(H) (2.0 equiv). (iv) 1,2-dibromoethane (4.0 equiv), (v) $ArCH_2Br$ (4.0 equiv). [10]Reference for literature reported yields in THF at -78 °C.

Comparison with previously reported results in -78 °C THF showed some marginally higher and some lower yields but with only one example, **7d**, showing a substantial difference.[10] Notably, the natural product Brittonin A, **7f**, was accessible with this approach in a single-step showing that conducting these C-C bond forming reactions in hydrocarbon solvent had no negative effect. Efficient synthesis of bibenzyls with two differing aryl rings is also appealing and could be addressed by using substituted benzylbromides electrophiles (Scheme 7, route B). As examples, 3-methoxytoluene **1b**, 3,4,5-trimethoxytoluene **1c** and 2-*N*,*N*-trimethylaniline **1d** were metalated with subsequent benzylbromide reaction to afford **7g-i** in excellent yields (80-85%) and dimethyl ether derivative of Aloifol I natural product **7j** in 86%.

Finally, the ambient temperature metalation approach was applied to the synthesis of [2.2]metacylcyclophanes.[11] A double LiNK metalation of bibenzyls **7d**, **e** generated di-metalated species **8** which upon treatment with dibromoethane effectively ring closed to produce metacyclophanes **9a**, and **b** in 29% and 31% yields, respectively (Scheme 8). This repetitive two step synthesis of [2.2]metacyclophanes offers a straightforward entry into this strained cyclic system.

Scheme 8: Synthesis of [2.2]metacyclophanes.



CONCLUSION

In summary, regioselective benzylic metalations of substituted toluenes, xylenes and benzylsilanes can be successfully accomplished in hydrocarbon reaction media at 0 °C using the LiNK reagent triad. Subsequent reaction of the generated metalated species with TMSCl gave the corresponding benzyltrimethylsilanes and α,α-bis(trimethylsilyl)toluenes which are bench-stable pro-nucleophiles for addition and Peterson olefination reactions. This new approach provides routine access to these important Si-reagents which should find widespread use in organic chemistry. Direct C-C couplings also allowed for atom efficient synthesis of bibenzyl derivatives and [2.2]metacyclophane. Further synthetic and mechanistic studies involving the LiNK reagent are ongoing.

EXPERIMENTAL SECTION

General information. All of the reactions involving air-sensitive reagents were performed under nitrogen either in oven- or flame-dried glassware using syringe-septum cap technique. All of the solvents were purified and degassed before use. 2,2,6,6-Tetramethylpiperidine, TMP(H), was distilled from CaH_2 prior to use. Heptane and cyclohexane were purified under nitrogen from CaH_2. THF was purified on Na/benzophenone. BuLi was purchased as a 2.5 M solution in hexanes. The exact concentration of the BuLi was determined by titration with diphenylacetic acid in THF prior to use. KO*t*Bu was sublimed prior to use. Chlorotrimethylsilane and CD_3OD was used as received. Chromatographic separations were carried out under pressure on Merck silica gel 60 or aluminium oxide 60 using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates with

UV light (254 nm) as the visualizing agent. ^{1}H and ^{13}C NMR spectra were recorded at room-temperature on a 400 and 600 MHz spectrometer. TOF mass analyzers were used for HRMS measurements. The yields are after column chromatography.

Metalation of 2-methylanisole under various conditions (Scheme 3)

Reaction (i): A solution of 2-methylanisole **1a** (124 µL, 1.0 mmol) in THF (2.5 mL) at -78 °C was treated with KO*t*Bu (135 mg, 1.2 equiv). Subsequently, BuLi (512 µL, 2.35 M in hexanes, 1.2 equiv) and TMP(H) (202 µL, 1.2 equiv) was slowly added. The resulting solution was stirred for 15 min at -78 °C. Methanol-d_4 (203 µL, 5.0 equiv) was added and warmed it to rt and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness gave crude 1-methoxy-2-deuteriomethylbenzene *Bn*-D-**1a**[8b]. ^{1}H NMR (600 MHz, CH_2Cl_2): δ 7.17–7.10 (m, 2.55 H), 6.86–6.81 (m, 2.20H), 3.81 (s, 3H), 2.21–2.17 (m, 2.64H). ^{2}H NMR (92.07 MHz, CH_2Cl_2): 2.18 (t, 3H). (>75 % D incorporation).

Reaction (ii) and (iii): A solution of 2-methylanisole **1a** (124 µL, 1.0 mmol) in heptane or cyclohexane (2.5 mL) at rt was treated KO*t*Bu (135 mg, 1.2 equiv). BuLi (512 µL, 2.35 M in hexanes, 1.2 equiv) and TMP(H) (202 µL, 1.2 equiv) was slowly added. The resulting suspension was stirred for 15 min at rt. Methanol-d_4 (203 µL, 5.0 equiv) was added and stirred it for 1 h and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness gave crude 1-methoxy-2-deuteriomethylbenzene *Bn*-D-**1a**[8b]. ^{1}H NMR (600 MHz, CH_2Cl_2): δ 7.16–7.09 (m, 3.18H), 6.87–6.81 (m, 2.55H), 3.81

(s, 3H), 2.20–2.15 (m, 2.90H). ^{2}H NMR (92.07 MHz, CH_2Cl_2): 2.18 (t, 3H). (>65 % D incorporation).

Reaction (iv): A mixture of 2-methylanisole **1a** (124 µL, 1.0 mmol) and KO*t*Bu (135 mg, 1.2 equiv) in heptane (2.5 mL) at rt was treated with BuLi (512 µL, 2.35 M in hexanes, 1.2 equiv). The resulting suspension was stirred for 15 min at rt. Methanol-d_4 (203 µL, 5.0 equiv) was added and stirred it for 1 h at rt and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness gave crude products. See the complex ^{1}H NMR in SI. ^{2}H NMR (92.07 MHz, CH_2Cl_2): δ 6.95–6.77 (m, 0.70H), 3.85–3.75 (m, 0.15H), 3.63–3.50 (m, 0.05H), 2.30–2.10 (m, 3H), 2.05–1.87 (m, 0.30H), 1.30–1.11 (m, 0.25H).

Reaction (v): 2-Methylanisole **1a** (124 µL, 1.0 mmol) in heptane (2.5 mL) was treated with TMP(H) (202 µL, 1.2 equiv) and BuLi (512 µL, 2.35 M in hexanes, 1.2 equiv) and was slowly added. The resulting reaction mixture was stirred at rt for 15 min. Methanol-d_4 (203 µL, 5.0 equiv) was added and stirred it for 1 h at rt and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness gave crude product. ^{1}H NMR (600 MHz, CH_2Cl_2): δ 7.21–7.12 (m, 2H), 6.90–6.82 (m, 2H), 3.83 (s, 3H), 2.24 (s, 2H). ^{2}H NMR (92.07 MHz, CH_2Cl_2): No signals observed.

Screening of hydrocarbon solvents (Scheme 4)

Entries 1-3: A mixture of 2-methylanisole **1a** (124 µL, 1.0 mmol) and sublimed KO*t*Bu (135 mg, 1.2 equiv) in the corresponding solvent (2.5 mL) was treated with BuLi (512 µL, 1.2 equiv, 2.35 M in hexanes) at specified temperature in Scheme 4. TMP(H) (202 µL, 1.2 equiv) was added

dropwise and it was stirred for 15 min. Chlorotrimethylsilane (317 µL, 2.5 equiv) was added and stirred it for 1 h and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (2 × 20 mL) and organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4a** as colorless oil. The product yields are depicted in Scheme 4.

Entry 4: Sublimed KO*t*Bu (135 mg, 1.2 equiv) in heptane (2.5 mL) was treated with BuLi (512 µL, 1.2 equiv, 2.35 M in hexanes) at 0 °C. TMP(H) (202 µL, 1.2 equiv) was added dropwise and the resulting suspension was stirred for 5 min. A solution of 2-methylanisole **1a** (124 µL, 1.0 mmol) in heptane (0.5 mL) was added dropwise and the reaction mixture was stirred for 15 min. Chlorotrimethylsilane (317 µL, 2.5 equiv) was added and stirred it for 1 h and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (2 × 20 mL) and organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4a**[12] (142 mg, 73%) as a colorless oil.

Entries 5 and 6: Sublimed KO*t*Bu (224 mg, 2.0 equiv) in heptane (2.5 mL) was treated with BuLi (851 µL, 2.0 equiv, 2.35 M in hexanes) at rt. TMP(H) (338 µL, 2.0 equiv) was added dropwise and the resulting suspension was stirred for 5 min. A solution of 2-methylanisole **1a** (124 µL, 1.0 mmol) in heptane (0.5 mL) was added dropwise and the reaction mixture was stirred for 15 min. Chlorotrimethylsilane (317 µL, 2.5 equiv) was added, stirred for 1 h and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (2 × 20 mL) and organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4a**[12]

as a colorless oil. The product yields are depicted in Scheme 4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10–7.04 (m, 1H), 7.05–6.96 (m, 1H), 6.87–6.78 (m, 2H), 3.79 (s, 3H), 2.10 (s, 2H), -0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 129.4, 129.2, 124.9, 120.2, 109.8, 54.8, 20.5, -1.6. HRMS–EI $[M]^+$: 194.1125, $C_{11}H_{18}OSi$ requires 194.1127.

Exothermicity analysis in benzylic metalation of 1a (Figure 2)

Sublimed KO*t*Bu (224 mg, 2.0 equiv) in heptane (2.5 mL) was cooled at 1 °C. BuLi (832 µL, 2.0 equiv, 2.4 M in hexanes) was added dropwise with internal temperature monitored with a Hanna thermometer. The temperature of the reaction was increased from 1 °C to 7 °C. The reaction was stirred for 5 min and cooled to 2 °C. TMP(H) (338 µL, 2.0 equiv) was added dropwise and the temperature of the reaction was increased up to 6 °C. The reaction was stirred for 5 min and cooled to 1 °C. A solution of 2-methylanisole **1a** (124 µL, 1.0 mmol) in heptane (0.5 mL) was added dropwise. The temperature was increased from 1 °C to 2 °C. The resulting precipitates was stirred for 15 min and cooled to 1 °C. Chlorotrimethylsilane (317 µL, 2.5 equiv) was added slowly and the temperature of the reaction was increased from 1 °C to 19 °C. The reaction mass was stirred for 1 h and cooled to 2 °C. 2 M HCl (10 mL) was slowly added and the temperature of the reaction was increased from 2 °C to 22 °C. The residue was extracted with diethyl ether (2 × 20 mL) and organic layers were combined, washed with brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4a** (173 mg, 85%) as a colorless oil.

(3-Methoxybenzyl)trimethylsilane, 4b[12]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution

of 3-methylanisole **1b** (378 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred it for 1 h at rt and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4b** (502 mg, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.10 (m, 1H), 6.67–6.52 (m, 3H), 3.78 (s, 3H), 2.06 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 142.2, 129.0, 120.7, 113.8, 109.1, 55.0, 27.2, -1.9 ppm. MS–EI $[M]^+$: 194.6, $C_{11}H_{18}OSi$ requires 194.3.

3,4,5-(Trimethoxybenzyl)trimethylsilane, 4c[12]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 3,4,5-trimethoxytoluene **1c** (505 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred it for 1 h at rt and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with petroleum ether/ethylacetate (1/1) yielded **4c** (560 mg, 73%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.20 (s, 2H), 3.82 (s, 6H), 3.81 (s, 3H), 2.02 (s, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 138.1, 136.7, 106.8, 62.7, 57.8, 29.2, -0.00 ppm. HRMS–ESI $[M+H]^+$: 255.1411, $C_{13}H_{23}O_3Si$ requires 255.1416.

***N,N*-Dimethyl-2-[(trimethylsilyl)methyl]aniline, 4d**[12]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 2-*N*,*N*-trimethylaniline **1d** (437 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified on alumina eluting with cyclohexane/ethyl acetate (95/5) yielded **4d** (540 mg, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.05 (m, 2H), 7.02–6.98 (m, 1H), 6.96–6.91 (m, 1H), 2.62 (s, 6H), 2.17 (s, 2H), -0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 136.2, 129.7, 124.8, 123.3, 119.6, 44.8, 22.1, -1.2 ppm. MS–EI $[M]^+$: 207.7, $C_{12}H_{21}NSi$ requires 207.4.

***N*,*N*-Diisopropyl-4-[(trimethylsilyl)methyl]benzamide, 4e**[12]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of *N*,*N*-diisopropyl-4-methylbenzamide **1e** (660 mg, 3.0 mmol) in heptane (3.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with ethyl acetate (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (9/1) yielded **4e** (772 mg, 88%) as a colorless solid, m.p. 53–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.17 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 4.25–3.25 (m, 2H), 2.08 (s, 2H), 1.75–0.75 (m, 12H), -0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 141.4, 134.5, 127.8, 125.8, 27.1, 20.8, -2.0 ppm. MS–EI $[M]^+$: 291.3, $C_{17}H_{29}NOSi$ requires 291.2.

***N*,*N*-Diisopropyl-2-[(trimethylsilyl)methyl]benzamide, 4f**[25]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of *N*,*N*-diisopropyl-2-methylbenzamide **1f** (660 mg, 3.0 mmol) in heptane (3.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with ethyl acetate (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (8/2) yielded **4f** (429 mg, 49%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.16 (m, 1H), 7.09–7.03 (m, 3H), 3.68 (m, 1H), 3.58 (m, 1H), 2.05 (s, 2H), 1.57–1.55 (m, 6H), 1.12 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 137.3, 136.8, 128.8, 127.7, 125.2, 124.1, 50.6, 45.5, 23.8, 20.9, 20.8, 20.6, 20.4, -1.10 ppm. MS–EI $[M]^+$: 291.7, $C_{17}H_{29}NOSi$ requires 291.2.

***N*,*N*-Diethyl-4-[(trimethylsilyl)methyl]benzenesulfonamide, 4g**[20a]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of *N*,*N*-diethyl-4-methylbenzenesulfonamide **1g** (682 mg, 3.0 mmol) in heptane (3.0

mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with ethyl acetate (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (8/2) yielded **4g** (584 mg, 65%) as a colorless solid. m.p. 45–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.23 (q, 4H), 2.16 (s, 2H), 1.10 (t, 6H), -0.02 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 135.8, 128.2, 127.0, 41.9, 27.7, 14.0, -2.0 ppm. MS–EI $[M]^+$: 299.2, $C_{14}H_{25}NO_2SSi$ requires 299.5.

Trimethyl(3-methylbenzyl)silane, 4h[26]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of *m*-xylene **1h** (367 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4h** (502 mg, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13–7.08 (m, 1H), 6.91–6.86 (m, 1H), 6.84–6.78 (m, 2H), 2.30 (s, 3H), 2.04 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 137.5, 128.9, 128.0, 125.1, 124.6, 26.9, 21.4, -1.9 ppm. HRMS–EI $[M]^+$: 178.1179, $C_{11}H_{18}Si$ requires 178.1178.

(3-Methoxy-5-methylbenzyl)trimethylsilane, 4i

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 3,5-dimethylanisole **1i** (424 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added and stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (95/5) yielded **4i** (625 mg, 95%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.60–6.40 (m, 2H), 6.39–6.27 (m, 1H), 3.76 (s, 3H), 2.28 (s, 3H), 2.02 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 141.9, 138.9, 121.6, 110.8, 110.1, 55.0, 27.1, 21.6, -1.8 ppm. HRMS–EI $[M]^+$: 208.1289, $C_{12}H_{20}OSi$ requires 208.1283.

(2-Methoxy-3-methylbenzyl)trimethylsilane, 4j

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 2,6-dimethylanisole **1j** (425 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (99/1) yielded **4j** (495 mg, 79%) as a

colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92–6.84 (m, 3H), 3.69 (s, 3H), 2.29 (s, 3H), 2.08 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 133.5, 130.8, 127.6, 127.2, 123.5, 59.5, 20.4, 16.3, -1.4 ppm. HRMS–EI $[M]^+$: 208.1290, $C_{12}H_{20}OSi$ requires 208.1283.

Benzyltrimethylsilane, 4k[12]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of toluene **1k** (320 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4k** (351 mg, 72%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.20 (m, 2H), 7.07 (m, 1H), 7.03–6.98 (m, 2H), 2.08 (s, 2H), -0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 128.1, 128.0, 123.8, 27.0, -1.9 ppm. MS–EI $[M]^+$: 164.6, $C_{10}H_{16}$ requires 164.3.

Trimethyl(naphthalen-1-ylmethyl)silane, 4l[27]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 1-methylnapthalene **1l** (426 µL, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 ×

20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4l** (494 mg, 77%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96–7.93 (m, 1H), 7.85–7.82 (m, 1H), 7.64–7.51 (m, 1H), 7.50–7.42 (m, 2H), 7.40–7.32 (m, 1H), 7.18–7.14 (m, 1H), 2.58 (s, 2H), 0.00 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 133.9, 131.7, 128.6, 125.5, 125.3, 125.2, 125.0, 124.8, 124.6, 23.4, -1.2 ppm. MS–EI $[M]^+$: 214.6, $C_{14}H_{18}Si$ requires 214.4.

[(1,1'-Biphenyl)]-4-ylmethyl]trimethylsilane, 4m[28]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 4-phenyltoluene **1m** (505 mg, 3.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4m** (633 mg, 88%) as a colorless solid, m.p. 42–44 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65–7.61 (m, 2H), 7.51 (d, J = 7.6 Hz, 2H), 7.48–7.43 (m, 2H), 7.37–7.32 (m, 1H), 7.11 (d, J = 7.6 Hz, 2H), 2.17 (s, 2H), 0.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 139.7, 136.7, 128.7, 128.4, 126.8, 126.8, 126.7, 26.7, -1.9 ppm. MS–EI $[M]^+$: 240.6, $C_{16}H_{20}$ requires 240.4.

(Anthracen-9-ylmethyl)trimethylsilane, 4n[29]

Under inert atmosphere, a mixture of KO*t*Bu (673 mg, 6.0 mmol) in heptane (7.5 mL) at 0 °C was treated with BuLi (2.55 mL, 2.35 M in hexanes, 6.0 mmol), followed by TMP(H) (1.0 mL, 6.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 9-methylantracene **1n** (576 mg, 3.0 mmol) in heptane (3.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (952 µL, 7.5 mmol) was added, stirred it for 1 h at 0 °C and 2 M HCl (20 mL) was slowly added. The residue was extracted with diethyl ether (3 × 20 mL) and organic layers were combined, washed with water (2 × 20 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4n** (434 mg, 55%) as a yellow solid, m.p. 45–47 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.22–8.19 (m, 2H), 8.02–8.00 (m, 2H), 7.51–7.45 (m, 4H), 3.20 (s, 2H), 0.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 132.1, 129.5, 129.4, 125.8, 125.1, 124.9, 124.0, 19.3, 0.0 ppm. MS–EI $[M]^+$: 264.5, $C_{18}H_{20}$ requires 264.4.

2-[(Trimethylsilyl)methyl]pyridine, 4o[30]

Under inert atmosphere, a mixture of KO*t*Bu (135 mg, 1.2 mmol), in heptane (2.5 mL) at 0 °C was treated with BuLi (501 µL, 2.4 M in hexanes, 1.20 mmol), followed by TMP(H) (203 µL, 1.2 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of *α*-picoline **1o** (99 µL, 1.0 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (317 µL, 2.50 mmol) was added, stirred for 1 h at 0 °C and NH_4Cl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **4o** (143 mg, 87%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40–8.30 (m, 1H), 7.53–7.45 (m, 1H), 7.00–6.90 (m, 2H), 2.33 (s, 2H),

0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 148.9, 135.7, 122.1, 119.1, 30.2, -1.8 ppm. MS–EI $[M]^+$: 165.8, $C_9H_{15}NSi$ requires 165.3.

[(3-Methoxyphenylmethylene)bis(trimethylsilane)], 6a[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of (3-methoxybenzyl)trimethylsilane **4b** (49 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **6a** (59 mg, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (t, 1H), 6.60–6.56 (m, 1H), 6.53–6.48 (m, 2H), 3.77 (s, 3H), 1.47 (s, 1H), 0.03 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 144.7, 128.9, 121.5, 114.6, 108.3, 54.9, 29.8, 0.02 ppm. HRMS–EI $[M]^+$: 266.1533, $C_{14}H_{26}OSi_2$ requires 266.1522.

{[(3,4,5-Trimethoxyphenyl)methylene]bis(trimethylsilane)}, 6b[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of trimethyl-(3,4,5-trimethoxybenzyl)silane **4c** (64 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was added. The residue was extracted with ethyl acetate (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and

brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (8/2) yielded **6b** (59 mg, 72%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.13 (s, 2H), 3.81 (s, 3H), 3.80 (s, 6H), 1.40 (s, 1H), 0.04 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 138.9, 134.4, 105.7, 61.0, 55.9, 29.9, 0.2 ppm. MS–EI $[M]^+$: 326.7, $C_{16}H_{30}O_3Si_2$ requires 326.6.

2-[Bis(Trimethylsilyl)methyl]-*N*,*N*-dimethylaniline, 6c[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of *N*,*N*-dimethyl-2-[(trimethylsilyl)methyl]aniline **4d** (52 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified on alumina eluting with cyclohexane yielded **6c** (60 mg, 86%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (m, 1H), 7.06–6.92 (m, 3H), 2.58 (s, 6H), 2.49 (s, 1H), 0.03 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 139.2, 129.0, 123.8, 123.4, 120.3, 45.1, 20.1, 0.4 ppm. MS–EI $[M]^+$: 279.3, $C_{15}H_{29}NSi_2$ requires 279.8.

4-[Bis(trimethylsilyl)methyl]-*N*,*N*-diisopropylbenzamide, 6d[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of *N*,*N*-diisopropyl-4-[(trimethylsilyl)methyl] benzamide **4e** (73 mg, 0.25 mmol) in

heptane (2.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane/ethyl acetate (8/2) yielded **6d** (71mg, 78%) as a colorless solid, m.p. 55–56°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 3.70 (br, 2H), 1.53 (s, 1H), 1.33 (br, 12H), 0.02 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 144.4, 133.7, 128.4, 125.9, 31.0, 29.8, 20.9, 0.1 ppm. MS–EI $[M]^+$: 364.4, $C_{20}H_{37}NOSi_2$ requires 364.2.

[(*m*-Tolylmethylene)bis(trimethylsilane)], 6e[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of (3-methylbenzyl)trimethylsilane **4h** (45 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **6e** (64 mg, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08–7.04 (m, 1H), 6.83 (m, 1H), 6.73–6.72 (m, 2H), 2.28 (s, 3H), 1.45 (s, 1H), 0.02 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 137.3, 129.6, 127.8, 125.7, 124.0, 29.3, 21.6, 0.2 ppm. MS–EI $[M]^+$: 250.2, $C_{14}H_{28}Si_2$ requires 250.5.

[(Phenylmethylene)bis(trimethylsilane)], 6f[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of benzyltrimethylsilanes **4k** (41 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred it for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **6f** (48 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.14 (m, 2H), 7.06–7.00 (m, 1H), 6.92 (d, J = 7.0 Hz, 2H), 1.49 (s, 1H), 0.03 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 128.7, 127.9, 123.2, 29.5, 0.2 ppm. HRMS–EI $[M]^+$: 236.1411, $C_{13}H_{24}Si_2$ requires 236.1417.

(Naphthalen-1-ylmethylene)bis(trimethylsilane), 6g[15]

Under inert atmosphere, a suspension of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting mixture was stirred for 5 min at 0 °C. A solution of trimethyl(naphthalen-1-ylmethyl)silane **4l** (54 mg, 0.25 mmol) in heptane (0.5 mL) was added dropwise and the reaction mixture was stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **6g** (51 mg, 71%) as a green oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05–8.00 (m, 1H), 7.85–7.78 (m,

1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.50–7.41 (m, 2H), 7.40–7.33 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 1H), 0.04 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 134.3, 132.3, 128.9, 125.1, 125.1, 124.9, 124.6, 123.9, 22.1, 0.4 ppm. MS–EI $[M]^+$: 286.9, $C_{17}H_{26}Si_2$ requires 286.6.

[(1,1'-Biphenyl)-4-ylmethylene]bis(trimethylsilane), 6h[15]

Under inert atmosphere, a mixture of KO*t*Bu (56 mg, 0.50 mmol), in heptane (1.0 mL) at 0 °C was treated with BuLi (213 µL, 2.35 M in hexanes, 0.50 mmol) followed by TMP(H) (84 µL, 0.50 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of [(1,1'-biphenyl)-4-ylmethyl]trimethylsilane **4m** (60 mg, 0.25 mmol) in heptane (2.0 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (79 µL, 0.63 mmol) was added, stirred for 1 h at 0 °C and 2 M HCl (5 mL) was slowly added. The residue was extracted with diethyl ether (2 × 15 mL) and organic layers were combined, washed with water (2 × 5 mL) and brine (5 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **6h** (60 mg, 77%) as a colorless solid, m.p. 52–54 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.58 (m, 2H), 7.47–7.38 (m, 4H), 7.32–7.27 (m, 1H), 7.00 (d, *J* = 8.1 Hz, 2H), 1.56 (s, 1H), 0.06 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 141.2, 136.0, 129.3, 128.8, 126.8, 126.7, 29.4, 0.3 ppm. MS–EI $[M]^+$: 312.4, $C_{19}H_{28}Si_2$ requires 312.6.

2-[Bis(trimethylsilyl)methyl]pyridine, 6i[31]

Under inert atmosphere, a mixture of KO*t*Bu (247 mg, 2.20 mmol), in heptane (2.5 mL) at 0 °C was treated with BuLi (917 µL, 2.35 M in hexanes, 2.20 mmol) followed by TMP(H) (371 µL, 2.20 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of *α*-picoline **1o** (99 µL, 1.0 mmol) in heptane (0.5 mL) was added dropwise and stirred for 15 min at 0 °C. Chlorotrimethylsilane (381 µL, 3.0 mmol) was added, stirred for 1 h at 0 °C and

NH_4Cl (10 mL) was slowly added. The residue was extracted with diethyl ether (3 × 15 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica gel column chromatography eluting with cyclohexane yielded **6i** (187 mg, 79%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42–8.38 (m, 1H), 7.48–7.38 (m, 1H), 6.94–6.83 (m, 2H), 1.88 (s, 1H), 0.03 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 149.0, 135.4, 122.6, 118.3, 33.3, 0.1 ppm. MS–EI $[M]^+$: 237.3, $C_{12}H_{23}NSi_2$ requires 237.5.

1,2-Bis(3-methoxyphenyl)ethane, 7a[10]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol), in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 3-methylanisole **1b** (244 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1 h 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **7a** (148 mg, 61%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, J = 8.0 Hz, 2H), 6.80–6.73 (m, 6H), 3.77 (s, 6H), 2.90 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 143.3, 129.3, 120.8, 114.1, 111.2, 55.1, 37.8 ppm. MS-ESI $[M + H]^+$: 243.5, $C_{16}H_{18}O_2$ requires 243.3.

2,2'-[(Ethane-1,2-diyl)bis(*N*,*N*-dimethylaniline)], 7b[10]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol), in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL,

4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 2-*N*,*N*-trimethylaniline **1d** (271 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1 h 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **7b** (139 mg, 52%) as a colorless solid, m.p. 54–56 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 3.03 (d, 12H), 2.69 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 137.3, 129.7, 126.5, 123.3, 119.5, 45.2, 31.8 ppm. MS-EI $[M]^+$: 268.6, $C_{18}H_{24}N_2$ requires, 268.4.

4,4-[(Ethane-1,2-diyl)bis(*N*, *N*-diisopropylbenzamide)], 7c[10]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol), in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of *N*,*N*-diisopropyl-4-methylbenzamide **1e** (438 mg, 2.0 mmol) in heptane (5.0 mL) was added slowly and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **7c** (337 mg, 77%) as a colorless solid, m.p. 143–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 3.68 (br, 4H), 1.32 (br, 24H). ^{13}C NMR (100 MHz,

$CDCl_3$): δ 171.0, 141.9, 136.5, 128.3, 125.6, 50.1, 45.8, 37.3, 20.6 ppm. MS-ESI $[M + H]^+$: 437.5, $C_{28}H_{41}N_2O_2$ requires, 437.3.

1,2-Di-*m*-tolylethane, 7d[11a]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of *m*-xylene **1h** (244 µL, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1 h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with diethyl ether (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **7d** (190 mg, 92%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.19 (m, 2H), 7.09–6.99 (m, 6H), 2.91 (s, 4H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 137.9, 129.2, 128.2, 126.6, 125.4, 38.0, 21.4 ppm. MS-EI $[M]^+$: 210.5, $C_{16}H_{18}$ requires 210.2.

1,2-Bis(3-methoxy-5-methylphenyl)ethane, 7e[11a]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 1-methoxy-3,5-dimethylbenzene **1i** (272 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1 h 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10

mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane yielded **7e** (214 mg, 80%) as a colorless solid, m.p. 81–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 7.4 Hz, 2H), 6.80–6.65 (m, 4H), 3.82 (s, 6H), 2.91 (s, 4H), 2.22 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.6, 140.7, 130.4, 124.0, 120.1, 110.4, 55.2, 38.1, 15.8 ppm. MS-ESI $[M + Na]^+$: 293.5, $C_{18}H_{22}O_2Na$ requires 293.1.

1,2-Bis(3,4,5-trimethoxyphenyl)ethane, 7f[11a]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol), in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A solution of 3,4,5-trimethoxytoluene **1c** (364 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (689 µL, 8.0 mmol) was added, the reaction stirred for 1h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (95/5) yielded **7f** (262 mg, 72%) as a colorless solid, m.p. 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.36 (s, 4H), 3.82 (s, 18H), 2.84 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 137.4, 136.1, 105.4, 60.9, 56.0, 38.5 ppm. MS–ESI $[M + Na]^+$: 385.2, $C_{20}H_{26}O_6Na$ requires 385.5.

1-Methoxy-3-phenethylbenzene, 7g[11a]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. 3-

Methylanisole **1b** (248 µL, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Benzyl bromide (594 µL, 5.0 mmol) was added, the reaction stirred for 1h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (95/5) yielded **7g** (360 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 2H), 7.24–7.18 (m, 4H), 6.83–6.79 (m, 1H), 6.78–6.73 (m, 2H), 3.80 (m, 3H), 2.97–2.89 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.6, 143.4, 141.7, 129.3, 128.4, 128.3, 125.9, 120.9, 114.2, 111.3, 55.1, 38.0, 37.8 ppm. MS–EI $[M]^+$: 212.5, $C_{15}H_{16}O$ requires 212.3.

***N,N*-Dimethyl-2-phenethylaniline, 7h**[6]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. 2-*N*,*N*-trimethylaniline **1d** (290 µL, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Benzyl bromide (594 µL, 5.0 mmol) was added, the reaction stirred for 1h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (95/5) yielded **7h** (372 mg, 83%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.15 (m, 7H), 7.13–7.11 (m, 1H), 7.05–6.99 (m, 1H), 3.05–2.91 (m, 4H), 2.67 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 142.5, 136.7,

129.6, 128.4, 128.3, 126.7, 125.7, 123.3, 119.6, 45.2, 36.8, 32.9 ppm. MS–EI $[M]^+$: 225.7, $C_{16}H_{11}N$ requires 225.3.

1,2,3-Trimethoxy-5-phenethylbenzene, 7i[10]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. 3,4,5-Trimethoxytoluene **1c** (364 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. Benzyl bromide (594 µL, 5.0 mmol) was added, the reaction stirred for 1 h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (90/10) yielded **7i** (440 mg, 80%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.17 (m, 2H), 7.15–7.07 (m, 3H), 6.28 (s, 2H), 3.75 (s, 3H), 3.73 (s, 6H), 2.86–2.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 141.5, 137.4, 136.1, 128.5, 128.3, 125.9, 105.3, 60.8, 55.9, 38.3, 37.9 ppm. MS–EI $[M]^+$: 272.7, $C_{17}H_{20}O_3$ requires 272.3.

1,2,3-Trimethoxy-5-(3-methoxyphenethyl)benzene, 7j[10]

Under inert atmosphere, a mixture of KO*t*Bu (449 mg, 4.0 mmol) in heptane (5.0 mL) at 0 °C was treated with BuLi (1.70 mL, 2.35 M in hexanes, 4.0 mmol) followed by TMP(H) (675 µL, 4.0 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. 3,4,5-Trimethoxytoluene **1c** (364 mg, 2.0 mmol) in heptane (1.0 mL) was added dropwise and stirred for 15 min at 0 °C. 3-Methoxybenzyl bromide (700 µL, 2.5 mmol) was added, the reaction stirred for 1 h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with

ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (70/30) yielded **7j** (520 mg, 86%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, *J* = 8.0 Hz, 1H), 6.82–6.72 (m, 3H), 6.38 (s, 2H), 3.84 (s, 3H), 3.83 (s, 6H), 3.79 (s, 3H), 2.93–2.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 152.0, 142.2, 136.4, 135.1, 128.3, 119.9, 113.2, 110.3, 104.4, 59.8, 55.0, 54.1, 37.2, 37.0 ppm. MS–EI $[M]^+$: 302.6, $C_{18}H_{22}O_4$ requires 302.4.

[2.2]Metacyclophane, 9a[11a]

Under inert atmosphere, a mixture of KO*t*Bu (216 mg, 1.92 mmol), in heptane (3.0 mL) at 0 °C was treated with BuLi (824 µL, 2.35 M in hexanes, 1.92 mmol), followed by TMP(H) (324 µL, 1.92 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of 1,2-di-*m*-tolylethane **7d** (100 mg, 0.48 mmol) in heptane (3.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (331 µL, 3.84 mmol) was added, the reaction stirred for 1 h at 0 °C and 2 M HCl (10 mL) was added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (98/2) yielded **9a** (29 mg, 29%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.27 (m, 2H), 7.11–7.05 (m, 4H), 4.29 (s, 2H), 3.17–3.05 (m, 4H), 2.17–2.04 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 136.5, 128.8, 125.4, 40.9 ppm. MS–EI $[M]^+$: 208.5, $C_{16}H_{16}$ requires 208.2.

5,13-Dimethoxy[2.2]metacylcophane, 9b[11b]

Under inert atmosphere, a mixture of KO*t*Bu (332 mg, 2.96 mmol) in heptane (3.0 mL) at 0 °C was treated with BuLi (1.24 mL, 2.35 M in hexanes, 2.96 mmol), followed by TMP(H) (500 µL,

2.96 mmol) was slowly added. The resulting suspension was stirred for 5 min at 0 °C. A suspension of 1,2-bis-(3-methoxy-5-methylphenyl)ethane **7e** (200 mg, 0.74 mmol) in heptane (3.0 mL) was added dropwise and stirred for 15 min at 0 °C. 1,2-Dibromoethane (510 µL, 5.92 mmol) was added and the reaction stirred for 1h at 0 °C and 2 M HCl (10 mL) was slowly added. The residue was extracted with ethyl acetate (2 × 25 mL) and organic layers were combined, washed with water (2 × 10 mL) and brine (10 mL), dried over Na_2SO_4, and concentrated to dryness. The product was purified by silica-gel column chromatography eluting with cyclohexane/ethyl acetate (95/5) yielded **9b** (62 mg, 31%) as a colorless solid, m.p. 170–171 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (s, 4H), 4.09 (s, 2H), 3.84 (s, 6H), 3.06–2.96 (m, 4H), 2.17–2.10 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 140.4, 129.5, 110.8, 55.3, 41.0 ppm. MS–EI $[M]^+$: 268.7, $C_{18}H_{20}O_2$ requires 268.3.

ASSOCIATED CONTENTS

Supporting information: ^{1}H and ^{13}C spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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