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ARTICLE

Structural and metal-halogen exchange reactivity studies of sodium magnesiate biphenolate complexes

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Bimetallic sodium magnesiates have been employed in metal-halogen exchange for the first time. Utilising the racemic phenoxide ligand 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol [(*rac*)-BIPHEN-H₂], the dialkyl sodium magnesiates [(*rac*)-BIPHEN]Na₂MgBu₂(TMEDA)₂ **3** and [(*rac*)-BIPHEN]Na₂MgBu₂(PMDETA)₂ **4** have been synthesised. Both **3** and **4** can be easily prepared through co-complexation of di-*n*-butylmagnesium with the sodiated (*rac*)-BIPHEN precursor which can be prepared *in situ* in hydrocarbon solvent. Prior to the main investigation, synthesis of the sodiated precursor [BIPHEN]₂Na₄(THF)₄ **1** was explored in order to better understand the formation of sodium magnesiates utilising the dianionic (*rac*)-BIPHEN ligand as the parent ligand. In addition, a BIPHEN-rich sodium magnesiate [BIPHEN]₂Na₂Mg(THF)₄ **2** was prepared and characterised, and its formation was rationalised. Complex **1** and **4** have also been fully characterised in both solid and solution state. In terms of onward reactivity, **3** and **4** have been tested as potential exchange reagents with aryl and heteroaryl iodides to produce aryl and heteroaryl magnesium phenoxides utilising toluene as a non-polar hydrocarbon solvent. Complex **3** reacted smoothly to give a range of aryl and heteroaryl magnesium phenoxides, whilst **4**'s reactivity is more sluggish.

Introduction

Metal-halogen exchange involving aromatic halides is a powerful transformation in synthetic chemistry. It allows the facile conversion of aromatic halides to useful functionalised arenes via metal aryl intermediates. Traditionally this exchange has been carried out utilising monometallic lithium- and magnesium-based reagents. Organolithium reagents typically require the use of cryogenic conditions and exhibit a poor functional group tolerance, whilst organomagnesiums often display a greater functional group tolerance but are generally less reactive. However, the reactivity of organomagnesium reagents can be increased by combining them with an alkali metal one to generate an alkali metal magnesiate.¹ As structure is inextricably linked to reactivity in organomagnesium chemistry, and much like monometallic Grignard reagents whose solution-state structure is dictated by the Schlenk equilibrium, alkali metal magnesiates also show a structural complexity which might not be immediately evident or expected.^{2,3} The synergic behaviour arising from the

combination of two metal centres within a complex gives these reagents unique and often enhanced reactivity, allowing them to perform transformations that would otherwise be unachievable using their monometallic parent complexes.^{1,4,5} Not only do these bimetallic reagents allow for reactions to be carried out under milder conditions⁶ (*i.e.*, carried out at temperatures at or close to ambient temperature), they also exhibit a much greater functional group tolerance compared to monometallic bases.⁷ Consequently, bimetallic magnesiates have attracted much attention for use in metal-halogen exchange reactions. Trialkylmagnesiates are also used extensively.⁸ The enhanced reactivity of these species can, in some cases, enable exchange to occur using sub-stoichiometric quantities of magnesiate.⁹ Despite their reactivity, it has been shown that exchange does not always occur with full consumption of all the alkyl ligands leading to undesired side reactions.¹⁰

Replacement of unreactive alkyl ligands with alkoxides is therefore an attractive principle for tuning the chemoselectivity of magnesiate complexes. Knochel and co-workers have recently utilised 2-ethylhexanol to synthesise alkylmagnesium alkoxides ^tBuMgOR·LiOR and ^tBu₂Mg·2LiOR (where R = 2-ethylhexyl).¹¹ These reagents undergo magnesium-halogen exchange with a range of aryl and hetero-aryl substrates at ambient temperatures in non-polar solvents. Furthermore, the inclusion of alkoxide ligands also provides facile access to the realm of asymmetric synthesis.^{12–16} Noyori has reported the efficient enantioselective alkylation of aldehydes using a lithium magnesiate containing the chiral BINOL alkoxide ligand.¹⁷

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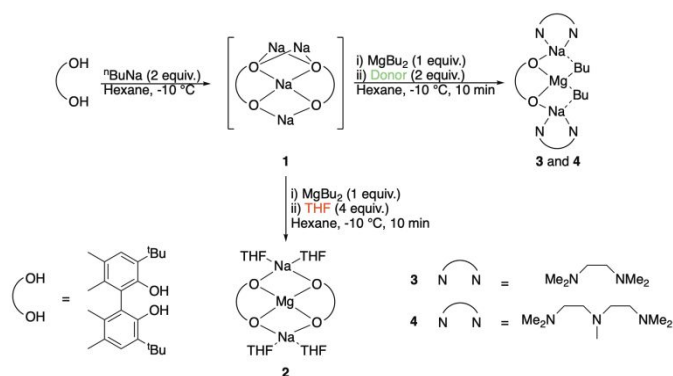
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† Dedicated to Professor Robert E. Mulvey, a fantastic mentor and colleague, on the occasion of his 60th birthday.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Furthermore, the groups of Gros and Mongin have utilised lithium magnesiate containing the chiral diols (*R,R*)-TADDOL and (*R*)-BIPHEN [(*R,R*)-TADDOL is (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl]bis(bis(4-*tert*-butyl)phenyl)methanol and (*R*)-BIPHEN is 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol] as alkoxide ligands in metal-halogen exchange reactions to access a range of chiral alcohols.^{18,19} A well-defined and robust organometallic complex with complete saturation of the metal coordination sites is essential in order to limit excess aggregation and subsequent loss of enantioselectivity. Our group has successfully characterised a series of dilithium dialkylmagnesiate containing the (*rac*)-BIPHEN ligand and demonstrated their reactivity in metal-halogen exchange.²⁰ Using the enantiomerically pure form of the ligand, (*S*)-BIPHEN, Gros and co-workers have synthesised a range of chiral 3-substituted isobenzofuranones with good enantiomeric ratios and yields from reaction of the monoalkyl lithium magnesiate (*S*)-BIPHENⁿBuMgLi with ethyl-2-iodobenzoate and subsequent electrophilic quenching with a range of aldehydes.²¹

Despite the wealth of knowledge relating to the structure of lithium magnesiate and their reactivity in metal-halogen exchange, the same cannot be said for sodium magnesiate, particularly those bearing alkoxide ligands. Sodium magnesiate have primarily been employed as powerful bases in deprotonation chemistry^{22,23} and as efficient catalysts for a range of transformations.^{24–28} To the best of our knowledge there are no examples of metal-halogen exchange involving sodium magnesiate. Herein, we report the synthesis of two new disodium dialkylmagnesiate containing the (*rac*)-BIPHEN ligand (Scheme 1) and discuss their preliminary reactivity in metal-halogen exchange.



Scheme 1: Preparation of sodium dialkylmagnesiate.

Results and Discussion

Syntheses of Sodium Magnesiate from (*rac*)-BIPHEN

Prior to preparing the desired sodium magnesiate, synthesis of the homometallic sodium precursor was initiated starting from the (*rac*)-BIPHEN ligand. The parent (*rac*)-BIPHEN-H₂ ligand was doubly deprotonated using ⁿBuNa (two molar equivalents) in hexane solution. To aid crystallisation, the majority of the hexane was removed *in vacuo* and replaced with THF. Cooling

the resultant solution to -18 °C generated the desired disodium phenoxide

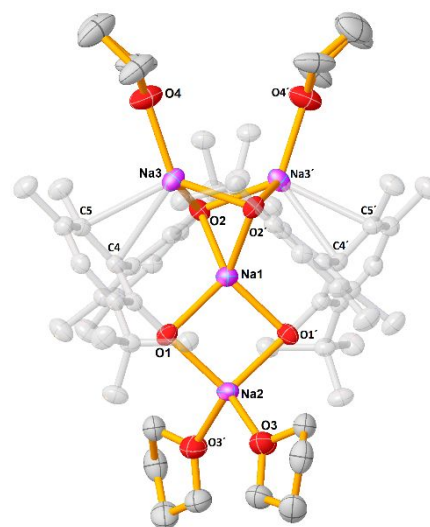


Figure 1: Solid state structure of [BIPHEN]₂Na₄(THF)₄.0.4(THF) **1**. Hydrogen atoms and disorder in THF molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Key bond distances (Å) and bond angles (°): Na(1)-O(1), 2.217(2); Na(1)-O(1'), 2.217(2); Na(1)-O(2), 2.313(2); Na(1)-O(2'), 2.313(2); Na(2)-O(1), 2.199(2); Na(2)-O(1'), 2.199(2); Na(2)-O(3), 2.308(3); Na(2)-O(3'), 2.308(3); Na(3)-O(2), 2.265(2); Na(3)-O(2'), 2.298(2); Na(3)-O(4), 2.298(3); Na(3)-C(4), 2.878(3); Na(3)-C(5), 2.808(3); Na(3')-O(2), 2.298(2); Na(3')-O(2'), 2.265(2); Na(3')-O(4'), 2.298(3); O(1)-Na(1)-O(1'), 92.49(11); O(1)-Na(1)-O(2), 110.87(7); O(2)-Na(1)-O(2'), 78.01(10); O(1)-Na(2)-O(1'), 93.45(12); O(3)-Na(2)-O(3'), 103.62(14); O(2)-Na(3)-O(2'), 79.27(8); O(2)-Na(3')-O(2'), 79.27(8).

[BIPHEN]₂Na₄(THF)₄ **1** (unoptimised 26% crystalline yield). In an attempt to prepare the desired magnesiate, a hexane solution of the sodium reagent was generated *in-situ* as described herein, followed by co-complexation with ⁿBu₂Mg (one molar equivalent). THF was added and the mixture heated gently to ensure complete dissolution. After cooling to -18 °C, X-ray quality colourless crystals were isolated and were determined to be the ⁿBu-free [BIPHEN rich] complex [BIPHEN]₂MgNa₂(THF)₄ **2** (37% crystalline yield. Maximum yield of 50% based on metals). In an attempt to prepare heteroleptic (mixed alkyl/phenoxide) magnesiate, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *N,N,N',N',N''*-pentamethylethylenetriamine (PMDETA) were utilised as chelating donor ligands. To emphasise, instead of using THF in the aforementioned reaction, TMEDA and PMDETA (two molar equivalents) were utilised. Using this slightly modified synthetic methodology, the higher order magnesiate [(*rac*)-BIPHEN]₂Na₂MgⁿBu₂(TMEDA)₂ **3** (56 % yield) and [(*rac*)-BIPHEN]₂Na₂MgⁿBu₂(PMDETA)₂ **4** (55 % yield) were synthesised.

X-ray crystallographic studies

The structure of the disodium phenoxide, which crystallised as a dimeric THF solvate, was revealed to be the tetranuclear complex [BIPHEN]₂Na₄(THF)₄ **1**. Each molecule has crystallographically imposed 2-fold symmetry, and as two of the Na centres sit on the twofold axis, there are three chemically distinct sodium environments (Figure 1). Despite using the racemic form of the BIPHEN ligand during synthesis, the crystal

of **1** measured was enantiopure, chiral space group $P4_12_12$, with one crystallographically unique BIPHEN ligand per asymmetric unit [Flack parameter, 0.018(14)]. Spontaneous resolution upon crystallisation is thought to occur for approximately 5 to 10% of all racemic compounds. This forms conglomerates, or physical mixtures, of separate *R*- and *S*-crystals.^{29,30} In the absence of any driver to enantiopurity, this is presumably the case here.

Analysis of the organometallic framework of **1** shows the central sodium atom Na1 is four coordinate with a distorted tetrahedral geometry (sum of bond angles 664.1°) and is bound to all four oxygen atoms of both BIPHEN ligands [range of Na-O bond distances, 2.215(3) - 2.315(3) Å]. Na2 is also four coordinate with a distorted tetrahedral geometry (sum of bond angles, 661.1°) and is bound to one oxygen atom from each BIPHEN ligand [Na2-O1 2.200(3) Å]. The coordination sphere of Na2 is complete by coordination to two molecules of THF [Na2-O3 2.310(4) Å]. The other sodium sites Na3/Na3' each make short contacts with 5 atoms. Each such Na centre coordinates to three O atoms [one from each BIPHEN ligand and one from a THF molecule]. The remaining contacts are η^2 - π -interactions to an adjacent phenyl group [Na3-C4 and Na3-C5 bond distances, 2.878(3) and 2.808(3) Å respectively]. Comparison of the key bond lengths and bond angles of **1** with its related tetranuclear lithium complex (BIPHEN)₂Li₄(THF)₄ reported in our previous work,²⁰ revealed an enhanced puckering of the four membered ring at the top of the structure (Na3-O2-Na3'-O2' ring in Figure 1). For a comparison see the Supporting Information.

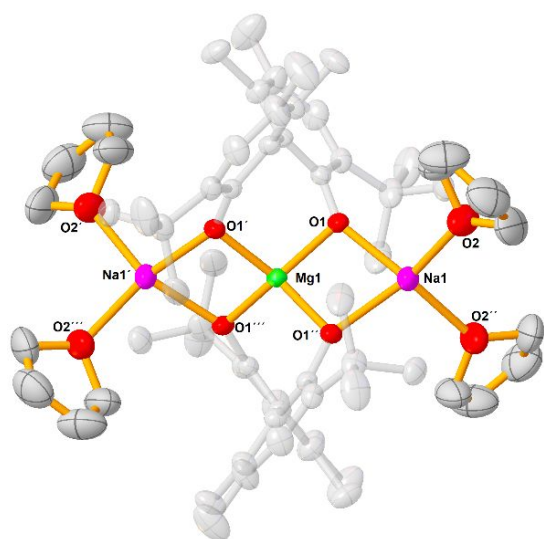


Figure 2: Solid-state structure of [BIPHEN]₂MgNa₂(THF)₄. Hydrogen atoms and disorder in THF molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 1.960(16); Mg(1)-Na(1), 3.0914(14); Mg(1)-Na(1'), 3.0913(14); Na(1)-O(1), 2.2372(19); Na(1)-O(2), 2.270(7); O(1)-Mg(1)-O(1'), 102.72(9); O(1)-Mg(1)-O(1''), 92.32(9); O(1)-Mg(1)-O(1'''), 137.67(10); Na(1)-Mg(1)-Na(1'), 180; O(1)-Na(1)-O(1''), 78.38(38); O(2)-Na(1)-O(2''), 101.5(2).

Turning to the BIPHEN-rich **2** which also crystallised with crystallographically imposed symmetry. The central magnesium centre Mg1 sits on three twofold axes and is four coordinate with a distorted tetrahedral geometry (sum of bond angles

665.6°). The Mg-O bond length is 1.962(3) Å and this is in good agreement with its homometallic analogue.³¹ The related sodium atom sites Na1/Na1' are situated on a twofold axis and are also four coordinate, again adopting a distorted tetrahedral geometry (sum of bond angles 662.1°). They are bound to a single oxygen atom of each of the BIPHEN ligands [Na1-O1 bond distance, 2.229(4) Å] and their coordination spheres are completed by two molecules of THF [Na1-O2 bond distance, 2.273(5) Å]. Similar to the situation observed with **1**, the single crystal of **2** examined was determined to be chiral, crystallising in the chiral space group I222 [Flack parameter, -0.16(17)].

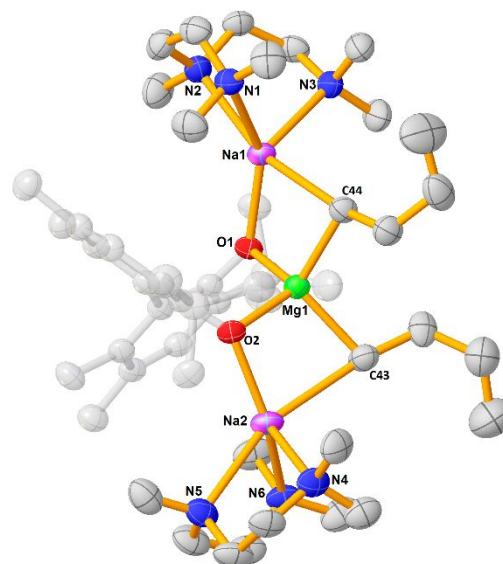


Figure 3: Solid state structure of [(*rac*)-BIPHEN]Na₂MgBu₂(PMDETA)₂. Hydrogen atoms and disorder in PMDETA molecules are omitted for clarity. Thermal ellipsoids are set to 50 % probability level. Key bond distances (Å) and bond angles (°): Mg(1)-O(1), 2.011(3); Mg(1)-O(2), 2.009(3); Mg(1)-C(43), 2.203(6); Mg(1)-C(44), 2.204(5); Na(1)-O(1), 2.279(3); Na(1)-N(1), 2.614(4); Na(1)-N(2), 2.558(4); Na(1)-N(3), 2.520(4); Na(2)-O(2), 2.267(3); Na(2)-N(4), 2.492(5); Na(2)-N(6), 2.618(4); Na(1)-C(44), 2.690(5); Na(2)-C(43), 2.688(6); O(1)-Mg(1)-O(2), 99.35(13); C(43)-Mg(1)-C(44), 107.7(2); Na(1)-C(44)-Mg(1), 79.3(2); Na(2)-C(43)-Mg(1), 79.1(2); O(1)-Na(1)-C(44), 82.0(1); O(2)-Na(2)-C(43), 91.9(3).

Introduction of the tridentate donor PMDETA lead to isolation of [(*rac*)-BIPHEN]Na₂MgBu₂(PMDETA)₂. Interestingly, complex **4** crystallised in the P_n space group indicating the racemic form of the BIPHEN ligand is retained. In keeping with the other magnesiates prepared in this work, the central magnesium atom of **4** was found to be four coordinate with a distorted tetrahedral geometry (sum of bond angles 658.6°). It is bound to the (*rac*)-BIPHEN ligand in a chelating fashion and to two butyl ligands. The Mg-O bond lengths were found to be identical within experimental error [Mg1-O1 2.011(3) Å and Mg1-O2 2.009(3) Å] as were the Mg-C bond lengths [Mg1-C42 2.203(6) Å and Mg1-C44 2.204(3) Å] making the bonding symmetrical in each case. Sodium atoms Na1 and Na2 are five coordinate, each forming a bond to the oxygen atoms of the (*rac*)-BIPHEN ligand (Na1-O1 2.279(3) Å and Na2-O2 2.267(3) Å) and an interaction with the terminal methylene group, the α -carbon, of the butyl chains. The sodium to alkyl carbon bond distances were 2.690(5) Å (Na1-C44) and 2.688(6) Å (Na2-C43). Each sodium is capped by a tridentate PMDETA ligand [Na1-N1, 2.614(4) Å;

Na1-N2, 2.558(4) Å; Na1-N3, 2.520(4) Å; Na2-N4, 2.492(5) Å; Na2-N5, 2.514(5) Å; and, Na2-N6, 2.618(4) Å].

Solution studies

The isolation of the BIPHEN-rich complex **2** is perhaps surprising considering the stoichiometry of starting reagents used in the reaction. It can be attributed to the disproportionation (ligand reorganisation) of the expected disodium dialkyl magnesiate product, [(*rac*)-BIPHEN]MgNa₂Bu₂(THF)₄ (Scheme 2). This type of reorganisation is a common pathway to generally undesired compounds in related bimetallic chemistry.^{32,33} It is possible that the formation of **2** may be due to thermal decomposition; however, no other products from this Schlenk-like equilibrium



Scheme 2: Simplified Schlenk equilibrium demonstrating the formation of **2**.

were isolated from the reaction (Scheme 2). The reaction was subsequently repeated using the bulkier dialkylmagnesium reagent Mg(CH₂SiMe₃)₂. Co-complexation of Mg(CH₂SiMe₃)₂ with **1** again produced the BIPHEN-rich **2** as the only isolable reaction product and not the desired magnesiate [(*rac*)-BIPHEN]Na₂MgR₂(THF)₄. Despite multiple attempts at preparing both dialkylmagnesiate, their solid-state structure could not be determined – the only isolable product on each occasion was **2**.

In an attempt to preclude the aforementioned Schlenk-like equilibrium, the bidentate donor TMEDA was employed. It was expected that the strong chelation of the diamine with the Na centre may inhibit further reaction to form undesired **2**. This was indeed the case and the formation and isolation of [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ **3** was facile. As noted previously, by employing PMDETA, the related complex **4** was prepared. The excellent solubilities of **3** and **4** in arene solvents has allowed them to be characterised by ¹H and ¹³C NMR spectroscopy (Tables 2 and 3). The CH₂-Mg methylene hydrogen atoms for **3** appear at δ -0.31 and -0.78 ppm as two broad multiplets rather than a single resonance due to the diastereotopic nature of these hydrogen atoms. The corresponding CH₂-Mg was located at 8.84 ppm in the ¹³C NMR spectrum. Comparison of the ¹H and ¹³C NMR spectra of **3** with those of **4** showed a good level of agreement with the exception of the resonance

Table 1: Key ¹H NMR chemical shifts for **3** and **4** in C₆D₆ at 300K.

	¹ H Chemical Shift (ppm)	
	3	4
Ar	7.18	7.14
^t Bu	1.70	1.77
Me	1.80, 2.23	1.90, 2.31
Mg-CH ₂	-0.78, -0.31	-0.75
TMEDA	1.79, 1.86	-
PMDETA	-	1.82, 1.86, 1.93

associated with the Mg-CH₂ H atoms which appear as one broad multiplet at -0.75 ppm, instead of two distinct multiplets. A low temperature NMR spectroscopic study failed to separate this multiplet (see Supporting Information). The data for **3** and **4** are consistent with values reported in literature for the related lithium magnesiate.²⁰

To further investigate the role in which TMEDA and PMDETA play in suppressing disproportionation, C₆D₆ and d₈-THF solutions of complexes **3** and **4** were prepared. Immediate displacement of TMEDA and PMDETA by THF was observed for both **3** and **4** in d₈-THF. Monitoring the solutions by ¹H NMR spectroscopy showed no disproportion occurred in either solution of **3** or **4** at 300 K. Heating these solutions to 50°C for a further 12 hours showed no change in ¹H NMR spectra of **3** or **4** in C₆D₆. In d₈-THF however, complex **3** showed multiple new resonances in the aliphatic and aromatic regions of the ¹H NMR spectrum which was accompanied by a colour change in the solution from colourless to yellow. Surprisingly, the ¹H NMR spectrum of **4** in d₈-THF showed comparatively little decomposition compared to that of complex **3** under the same conditions and suggests the parent magnesiate **4** remains intact *i.e.*, no ligand rearrangement occurs after heating in d₈-THF (see Supporting Information).

Table 2: Key ¹³C NMR chemical shifts for **3** and **4** in C₆D₆ at 300K.

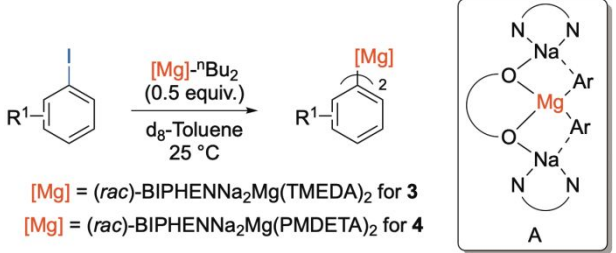
	¹³ C Chemical Shift (ppm)	
	3	4
Ar	119.6, 127.2, 132.1, 132.7, 135.9, 162.7	119.8, 126.5, 132.6, 134.1, 134.8, 163.0
^t Bu	31.7, 35.3	32.2, 35.4
Me	17.4, 20.7	17.9, 20.8
Mg-CH ₂	8.8	8.7
TMEDA	45.5, 56.9	-
PMDETA	-	44.1, 45.5, 54.0, 57.1

Metal-halogen exchange studies













The reactivity of **3** and **4** were investigated to assess their potential in metal-halogen exchange reactions ultimately generating of aryl and heteroaryl magnesium reagents (**5-10**, Table 3). Investigations into Mg-I exchange were performed using a 2:1 ratio of organic substrate to exchange reagent (**3** or **4**) in order to achieve high efficiency double Mg-I exchange. Initially examining the reactivity of substrates bearing electron donating functionalities, the reaction of **3** and **4** with 2-iodoanisole produced **5** in a 60 and 30% yield respectively after 15 minutes. Concomitant formation of 4-iodobutane was observed as evidenced by resonances at δ 2.76, 1.43, 1.13 and 0.69 ppm in the associated ¹H NMR spectra in both cases. Formation of an additional product [29% yield for **3** and (41%) for **4**, δ 3.33 ppm] was tentatively assigned to be the intermediate monoalkyl-monoaryl-magnesium species resulting from exchange of a single alkyl ligand. Continued monitoring of the reactions over a further 12 hours showed an increase in the yield of **5** to 90% with full consumption of **3**,

while a maximum yield of 77% was achievable using **4**. Furthermore, no changes were observed in the ^1H NMR spectra after full consumption of **3** and **4** which indicates no subsequent reaction between the newly formed diaryl magnesiate and the iodobutane generated *in situ*.

Table 3: Metal-halogen exchange of aryl iodides using **3 and **4**.**



$[\text{Mg}] = (\text{rac})\text{-BIPHENNa}_2\text{Mg}(\text{TMEDA})_2$ for **3**
 $[\text{Mg}] = (\text{rac})\text{-BIPHENNa}_2\text{Mg}(\text{PMDETA})_2$ for **4**

Product	Substrate	Metal-Halogen Exchange Product	Yield using 3	Yield using 4
5			90 % ^[a]	77 % ^[a]
6			91 % ^[a]	65 % ^[b]
7			79 % ^[b]	20 % ^[b]
8			90 % ^[a]	57 % ^{[b][c]}
9			87 % ^[d]	84 % ^[a]
10			78 % ^[d]	80 % ^[d]

Reactions were performed in a Young's cap NMR tube using 0.0377 mmol of magnesiate and 0.0754 mmol of Iodoarene. Unless otherwise stated yields were calculated from ^1H NMR spectroscopic data by integration against an internal standard of 1,2,3,4-tetraphenylnaphthalene. ^[a] Full consumption of magnesiate observed within 18 hours. ^[b] Incomplete conversion of magnesiate after 18 hours. ^[c] Calculated from ^1H NMR spectroscopic data by integration against an internal standard of hexamethylcyclotrisiloxane. ^[d] Full consumption of magnesiate observed within 15 minutes.

Having demonstrated the ability of **3** and **4** to perform magnesium-halogen exchange reactions, the scope was expanded to investigate the tolerance of both magnesiates towards *meta*- and *para*-substituted electron rich substrates. Reaction with 3- and 4-iodoanisole produced **6** and **7** in considerably diminished yields of 14% and 6% respectively after 15 minutes using **3** while no appreciable reactivity was observed using **4**. This significantly decreased reactivity is likely due to the more remote nature of the Lewis basic MeO-group with respect to the site of metal-halogen exchange *c.f.*, Directed *ortho*-Metallation (*DoM*) chemistry.³⁴ After 1 hour an increase in the yields of **6** and **7** to 41% and 20% respectively were observed using **3** whilst with **4**, **6** was obtained in only a 6% yield and no

formation of **7** was observed. In all cases there were significant quantities of the starting material 4-iodoanisole remaining. Continued monitoring of the reaction gave a maximum yield of 91% for **6** accompanied by full consumption of **3** whilst a maximum conversion of 79% was observed for **7** without complete consumption of the parent magnesiate after an additional 12 hours. In the case of **4**, full consumption of the magnesiate was not observed in either case and gave **6** and **7** in yields of 65% and 20% respectively. Complexes **3** and **4** were next tested with iodobenzene and furnished **8** in a low yield of 10% after 15 minutes using **3** whilst **4** again showed no reaction. After 1 hour, **8** was obtained in a 28% yield using **3**; however, no increase in the yield was observed in the case of **4**. Full conversion of **3** to **8** was observed after prolonged monitoring to give a maximum yield of 90% whilst **4** remained only partially consumed giving **8** in a moderate yield of 57%.

Turning to substrates containing electron withdrawing functionalities, the reactivity of **3** and **4** were investigated using 4-iodobenzotrifluoride. Complex **3** produced **9** in an 87% yield after less than 15 minutes with no observable increase in the yield after 1 hour. Complex **4** reacted slower producing **9** in yields of 24% and 56% after 15 minutes and 1 hour respectively. Conversion of **4** to **9** reached a maximum yield of 84% after a further 12 hours of reaction time. The tolerance of heteroaromatic substrates was next examined. Thus, complexes **3** and **4** were reacted with 2-iodopyridine to give **10** in yields of 78% and 80% respectively within 15 minutes. Despite the sluggish reactivity of **4** compared to **3** for the majority of substrates, reaction with the electron deficient 2-iodopyridine gave a comparable yield. No increase in the yield of **5f** was observed over time using **3** or **4**. Perhaps counterintuitively, **3/4** appear to react slower than their THF-solvated lithium analogues in metal-halogen exchange reaction.²⁰ This comparison has to be taken tentatively due to the difference in Lewis bases solvating the different metal centres. Intriguingly, a lower reactivity could potentially benefit selectivity/enantioselectivity which will be studied in due course.

Conclusions

Four novel organometallic complexes starting from the (*rac*)-BIPHEN ligand have been characterised in both solid (**1**, **2** and **4**) and solution-state (**1-4**). The heterobimetallic sodium magnesiates **3** and **4** been prepared and utilised in metal-halogen exchange reactions using a range of electron rich and electron poor substrates. Magnesiate **3** generally possesses high levels of reactivity in non-polar solvents particularly with electron deficient substrates; whereas, **4** is largely less reactive. It is possible that this difference in reactivity may be exploited in the future as it is likely that **4** will display higher levels of selectivity due to its lower reactivity. To the best of our knowledge these reactions represent the first examples of metal-halogen exchange utilising sodium magnesiates. Building on these results, the next stage in our research will utilise the enantiomerically pure ligands and apply the resulting magnesiates in asymmetric synthesis.

Conflicts of interest

There are no conflicts to declare.

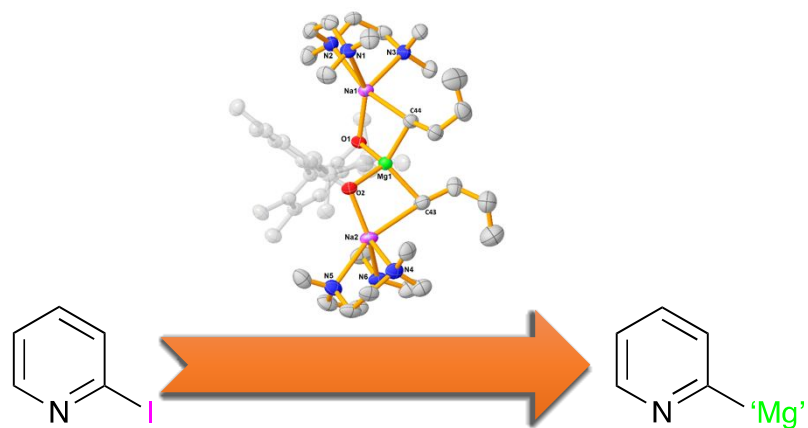
Acknowledgements

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Sodium magnesiate incorporating the (*rac*)-BIPHEN ligand have been prepared and characterised and subsequently used in metal-halogen exchange reactions.



**Structural and metal-halogen exchange reactivity studies of sodium
magnesiato biphenolate complexes**

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Ross McLellan,^a Antonio J. Martínez-Martínez^c and Charles T. O'Hara*^a

General Consideration

All reactions were carried out under a protective atmosphere of argon using standard Schlenk techniques. Non-deuterated solvents were dried by refluxing over sodium in the presence of benzophenone under a nitrogen environment. Deuterated solvents were degassed using the freeze, pump, thaw method and stored over 4 Å molecular sieves. (*rac*)-BIPHEN-H₂, ⁿBuLi and MgⁿBu₂ were purchased from Sigma-Aldrich and used without any further purification. TMEDA and PMDETA were purchased from Alfa Aesar, dried by refluxing over CaH₂ and stored over 4 Å molecular sieves under a protective atmosphere of nitrogen. Iodobenzene, 4-iodobenzotrifluoride, 2, 3 and 4-iodoanisole were obtained from Sigma-Aldrich; and 2-iodopyridine from Fluorchem. All substrates were stored over 4 Å molecular sieves and used without any further purification. NMR Spectra were recorded on a Bruker AVIII 400 MHz spectrometer operating at 400.1 MHz for ¹H and 100.6 MHz for ¹³C. Single-crystal X-ray diffraction data were collected at 123 K using an Oxford Diffraction Gemini and Xcalibur diffractometers with monochromated Cu ($\lambda = 1.5418 \text{ \AA}$) and Mo ($\lambda = 0.71 \text{ \AA}$) radiation. The structures were solved by direct methods and refined to convergence on F^2 and against all independent reflections by full-matrix least squares and ShelXL programs.

General Synthesis of ⁿBuNa

NaOⁿBu (3.84g, 40 mmol) was suspended in hexane in an argon filled schlenk and cooled to 0 °C. Commercial ⁿBuLi (25 ml, 40 mmol, 1.6 M solution) was added dropwise to give a white suspension. The suspension was allowed to warm to ambient temperature and was stirred for 12 hours. The reaction was then filtered under argon and the white solid washed with hexane (3 x 20 ml). The solid was then dried in vacuo and stored in an argon filled glovebox (typical yield 2.7 g, 84 %).

General Synthesis of MgR₂ (where R = CH₂SiMe₃)

Mg turnings (4g) were added to a round bottom flask along with 100 ml of ether. A solution of Me₃SiCH₂Cl (19 ml) in ether (50ml) was then added dropwise to the Mg turnings. The solution was then heated to reflux and stirred for 1 hour. A solution of dioxane (10 ml) in ether (80 ml) was then added dropwise to the Grignard solution to give a viscous grey suspension. The suspension was stirred for 12 hours at ambient temperature. The suspension

was then filtered through Celite and glasswool and washed with ether (20 ml). The solvent was removed *in vacuo* and the resulting solid was purified by sublimation under reduced pressure at 160 °C to give the final product as a white microcrystalline powder. The powder was stored in an argon filled glovebox. All magnesiates were prepared and isolated prior to use in metal-halogen exchange reactions.

Synthesis of [BIPHEN]₂Na₄(THF)₄

[BIPHEN]₂Na₄(THF)₄ was prepared by the addition of a solution of (*rac*)-BIPHEN-H2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at -10 °C. The suspension was stirred for 1 hour with slow warming to room temperature. The solvent was removed *in vacuo* and THF (3 ml) was added to give a colourless solution. The solution was subsequently stored at -33 °C to yield colourless crystals of [BIPHEN]₂Na₄(THF)₄ (yield 0.145 g, 26 %). ¹H NMR (400.13 MHz, 298 K, d₈-THF): δ 1.30 (36H, bs, C(CH₃)₃), 1.56 (12H, bs, CH₃), 1.73 (10H, m, OCH₂CH₂, THF), 2.07 (12H, bs, CH₃), 3.58 (10H, m, OCH₂CH₂, THF), 6.69 (4H, s, Ph). ¹³C NMR (100.62 MHz, 298 K, d₈-THF): δ 16.71 (CH₃), 20.34 (CH₃), 26.15 (THF), 30.27 (C(CH₃)₃), 34.75 (C(CH₃)₃), 68.00 (THF), 116.19, 125.91, 132.40, 133.12, 133.70, 165.12 (Ph)

Synthesis of [BIPHEN]₂Na₂Mg(THF)₄

[BIPHEN]₂Na₂Mg(THF)₄ was prepared by the addition of a solution of (*rac*)-BIPHEN-H2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at -10 °C. The suspension was stirred for 30 minutes after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to create a white suspension. The suspension was allowed to warm to ambient temperature and THF was added dropwise to give a pale yellow solution. The solution was concentrated *in vacuo* and the solution stored at -33 °C to give [BIPHEN]₂Na₂Mg(THF)₄ as colourless crystals (yield 0.197 g, 37%). [BIPHEN]₂Na₂Mg(THF)₄ can also be prepared by using Mg(CH₂SiMe₃) as a replacement for MgBu₂. ¹H NMR (400.13 MHz, 298 K, d₈-THF): δ 1.15 (36H, bs, C(CH₃)₃), 1.45 (12H, s, CH₃), 1.77 (14H, m, OCH₂CH₂, THF), 2.04 (12H, s, CH₃), 3.61 (10H, m, OCH₂CH₂, THF), 6.72 (4H, s, Ph). ¹³C NMR (100.62 MHz, 298 K, d₈-THF): δ 16.90 (CH₃), 20.43 (CH₃), 26.18 (THF), 31.05 (C(CH₃)₃), 34.62 (C(CH₃)₃), 68.02 (THF), 120.70, 125.82, 132.69, 132.89, 134.21, 161.31 (Ph)

Synthesis of [(rac)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂

[(rac)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ was prepared by the addition of a solution of (rac)-BIPHEN-H2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at -10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to create a white suspension. The suspension was stirred at -10 °C for 5 minutes after which time TMEDA (0.15 ml, 1 mmol) was added to give a pale yellow solution. The solution was concentrated in vacuo and the solution stored at -33 °C. After storage at sub-ambient temperature the solution was filtered to yield [(rac)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ as a microcrystalline powder (yield 0.216 g, 56 %). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ -0.79 (2H, m, MgCH₂), -0.314 (2H, m, MgCH₂), 1.25 (6H, t, CH₃), 1.69 (9H, bs, C(CH₃)₃), 1.79 (8H, bs, CH₂, TMEDA), 1.80 (6H, s, CH₃), 1.85 (33H, bs, CH₃ TMEDA and C(CH₃)₃), 2.22 (6H, s, CH₃), 7.18 (2H, s, Ph). ¹³C NMR (100.62 MHz, 298 K, C₆D₆): δ 8.84 (2 x MgCH₂), 14.90 (2 x CH₃, Butyl), 17.48 (2 x CH₃, (rac)-BIPHEN), 20.77 (2 x CH₃, (rac)-BIPHEN), 31.70 (C(CH₃)₃, (rac)-BIPHEN), 32.81-33.74 (CH₂, Butyl), 35.34 (C(CH₃)₃, (rac)-BIPHEN), 45.53 (TMEDA), 56.99 (TMEDA), 119.61, 127.26, 132.10, 132.74, 135.90, 162.71 (Ph).

Synthesis of [(rac)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂

[(rac)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ was prepared by the addition of a solution of (rac)-BIPHEN-H2 (0.177g, 0.5 mmol) in hexane (2 ml) to a suspension of freshly prepared ⁿBuNa (0.08 g, 1 mmol) in hexane (5 ml) at -10 °C. The suspension was stirred until a colourless solution was formed after which commercial MgⁿBu₂ (0.5 ml, 0.5 mmol, 1 M solution) was added to create a white suspension. The suspension was stirred at -10 °C for 5 minutes after which time PMDETA (0.21 ml, 1 mmol) was added to give a white suspension. The suspension was concentrated *in vacuo* then heated gently to give a colourless solution. The solution was then allowed to cool slowly to ambient temperature to give colourless crystals of [(rac)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (yield 0.245 g, 56 %). ¹H NMR (400.13 MHz, 298 K, C₆D₆): δ -0.75 (4H, m, MgCH₂), 1.26 (6H, t, CH₃), 1.77 (18H, bs, C(CH₃)₃), 1.82 (16H, bs, CH₂, PMDETA), 1.86 (6H, s, CH₃, PMDETA), 1.90 (6H, s, CH₃), 1.93 (24H, bs, CH₃, PMDETA), 2.31 (6H, s, CH₃), 7.14 (2H, s, Ph). ¹³C NMR (100.62 MHz, 298 K, C₆D₆): δ 8.78 (2 x MgCH₂), 14.87 (2 x CH₃, Butyl), 17.95 (2 x CH₃, (rac)-BIPHEN), 20.81 (2 x CH₃, (rac)-BIPHEN), 32.25 (C(CH₃)₃, (rac)-BIPHEN),

33.53 (CH₂, Butyl), 34.00 (CH₂, Butyl), 35.45 (C(CH₃)₃, (*rac*)-BIPHEN), 44.16 (PMDETA), 45.59 (PMDETA), 54.09 (PMDETA), 57.12 (PMDETA), 119.85, 126.58, 132.62, 134.11, 134.80, 163.06 (Ph).

General Procedure for NMR Scale Metal-Halogen Exchange Reactions using 3

All reactions were carried out on an NMR scale using a 2:1 ratio of substrate to magnesiate. [(*rac*)-BIPHEN]Na₂MgⁿBu₂(TMEDA)₂ (0.029 g, 0.0377 mmol) was combined with tetraphenylnaphthalene (0.010 g, 0.025 mmol) as an internal standard and 0.5 ml of d₈-toluene in a J Young's NMR tube. The desired substrate (0.0754 mmol) was then added and the reaction monitored at regular intervals by ¹H NMR spectroscopy and yields obtained were calculated from NMR spectroscopic integrals relative to the internal standard.

General Procedure for NMR Scale Metal-Halogen Exchange Reactions using 4

All reactions were carried out on an NMR scale using a 2:1 ratio of substrate to magnesiate. [(*rac*)-BIPHEN]Na₂MgⁿBu₂(PMDETA)₂ (0.033 g, 0.0377 mmol) was combined with tetraphenylnaphthalene (0.010 g, 0.025 mmol) (5a-c, e and f) or hexamethylcyclotrisiloxane (0.011 g, 0.050 mmol) (5d) as internal standards and 0.5 ml of d₈-toluene in a J Young's NMR tube. The desired substrate (0.0754 mmol) was then added and the reaction monitored at regular intervals by ¹H NMR spectroscopy and yields obtained were calculated from NMR spectroscopic integrals relative to the internal standard.

Crystallographic and Refinement data for Compounds 1, 2 and 4

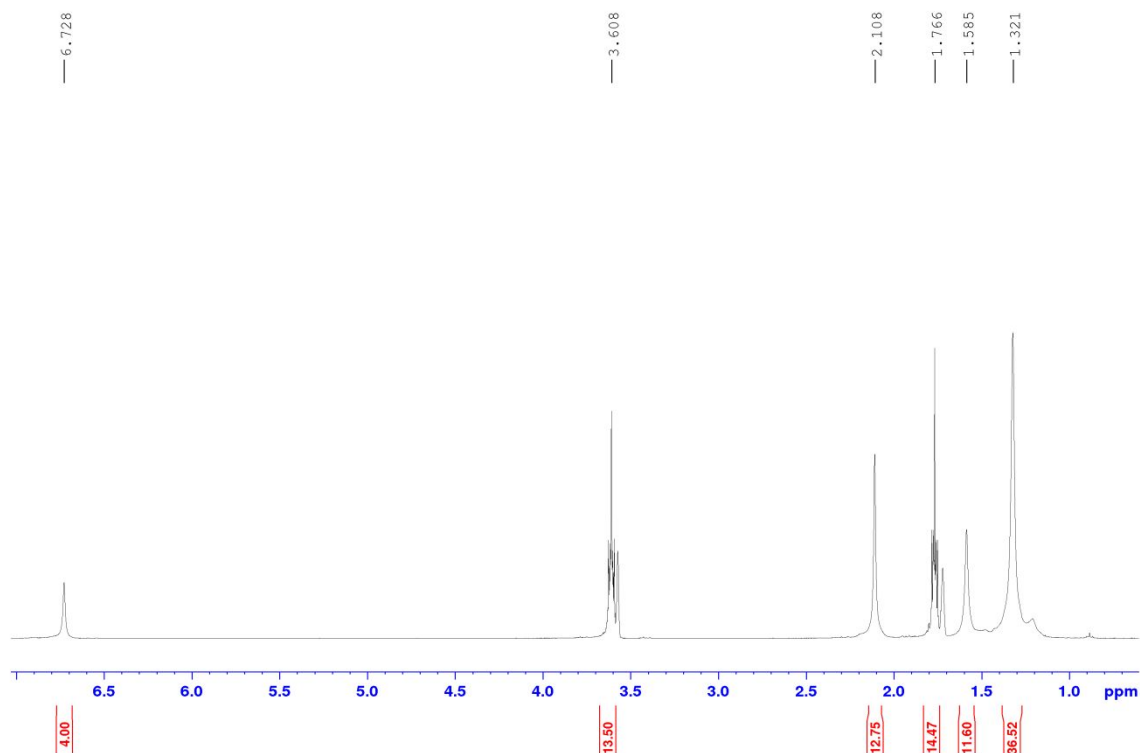
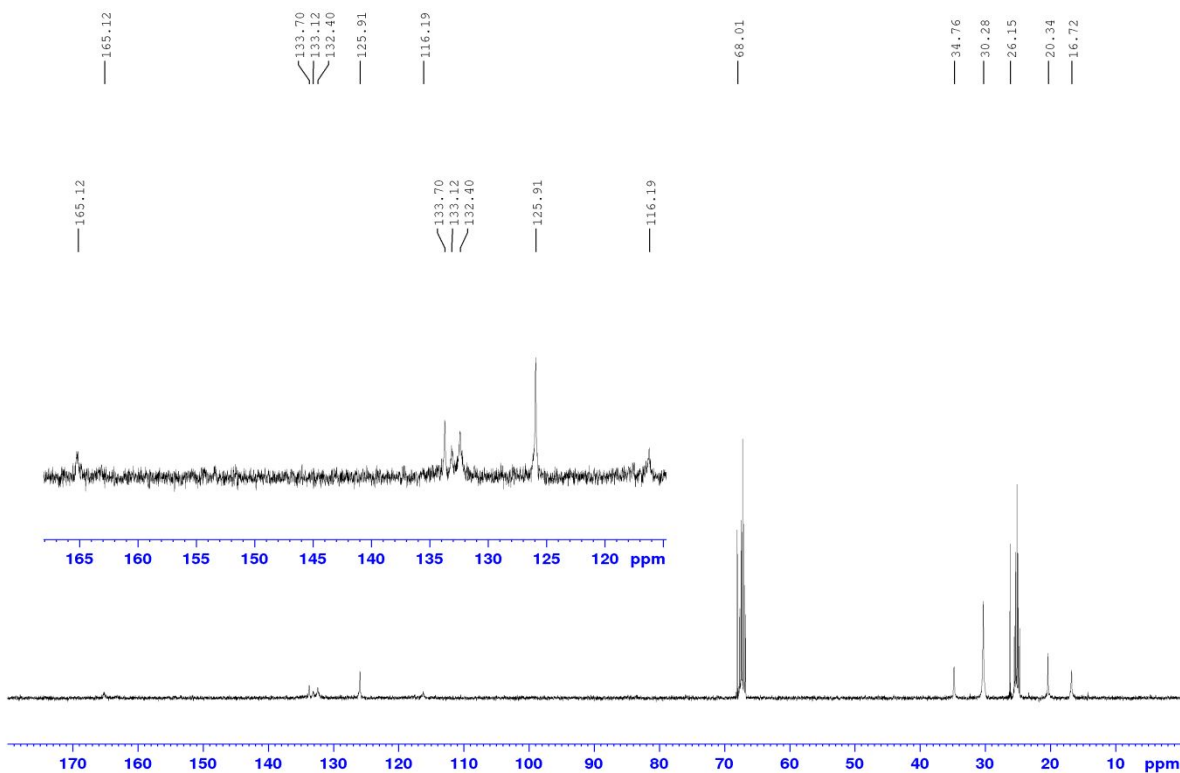
Data for all compounds were measured at low temperature using Oxford Diffraction instruments. Refinement was to convergence and against F^2 using all unique reflections.¹ Structure **2** contained a region of disordered solvent that could not be adequately modelled. The contribution of this feature to the structure was removed using the SQUEEZE routine within the PLATON program suite.² A total of 79 electron equivalents was removed from approximately 248 Å³ of space. This corresponds to approximately 2 THF molecules per unit cell. All three structures include moieties that have been modelled as disordered over two sites. For **1** and **2** some THF ligands have been treated in this way and for **3** one butyl group is disordered. Selected structural and refinement data are tabulated below and full details are available in cif format via the CCDC, deposition numbers 1988061 to 1988063.

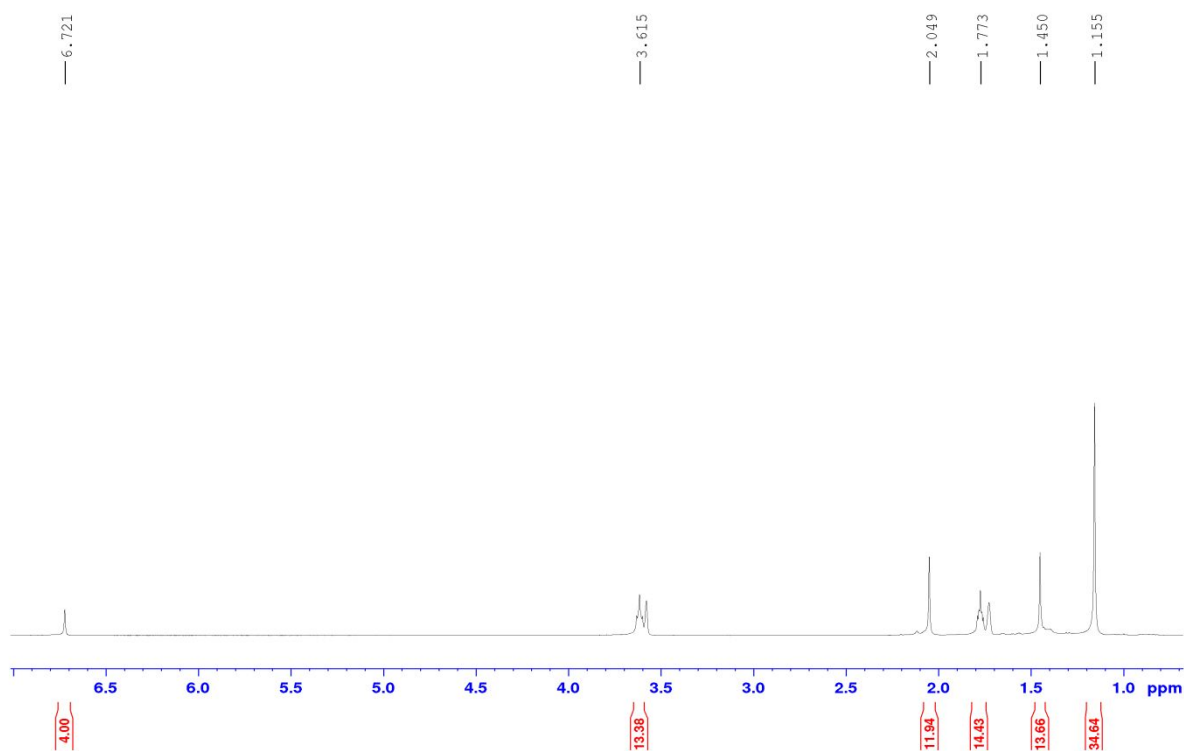
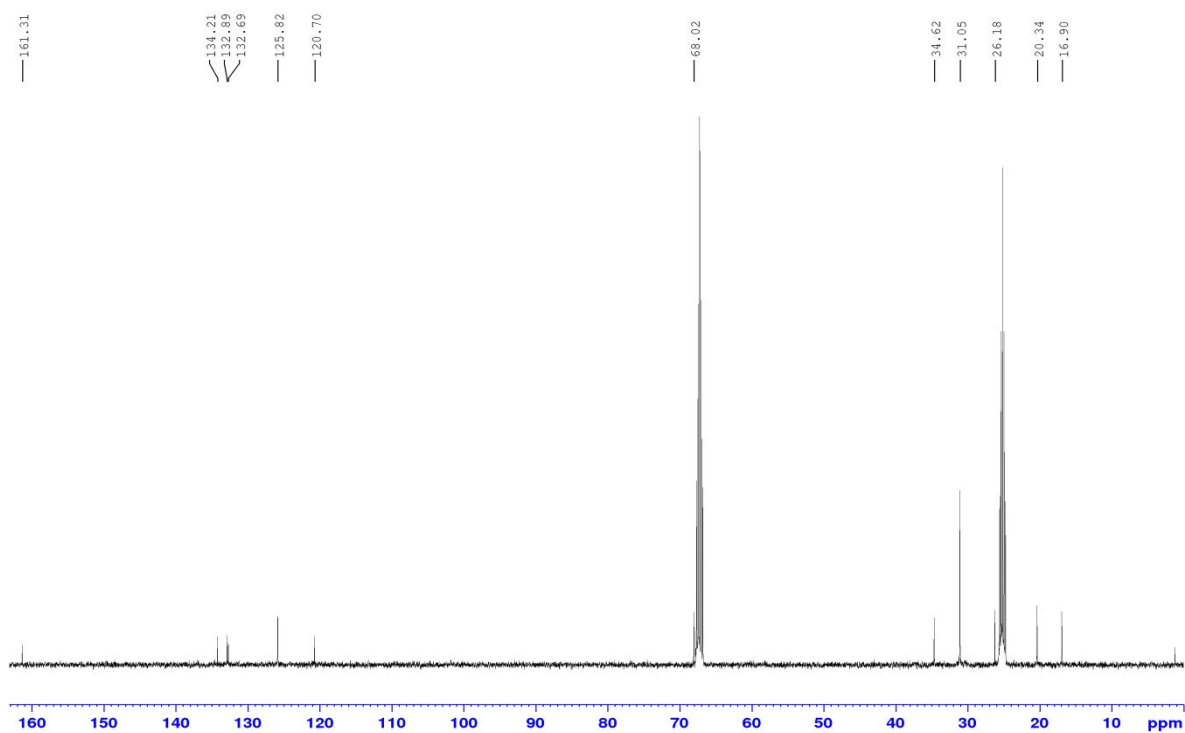
Compound	1	2	4
Formula	C _{65.6} H ₉₉ .Na ₄ O _{8.4}	C ₆₄ H ₉₆ MgNa ₂ O ₈	C ₅₀ H ₉₆ MgN ₆ Na ₂ O ₂
FW	1114.20	1063.69	883.61
Crystal System	Tetragonal	Orthorhombic	Monoclinic
Space Group	P4 ₁ 2 ₁ 2	I222	P _n
Wavelength/Å	1.54184	0.71073	1.54184
a/Å	13.33310(10)	11.3684(11)	12.9924(3)
b/Å	13.33310(10)	15.6863(16)	14.0108(3)
c/Å	37.0015(5)	18.5667(12)	15.4464(5)
β/°	90	90	100.040(3)
Volume/Å³	6577.81(13)	3311.0(5)	2768.71(13)
Z	4	2	2
Temperature/K	123(2)	156(2)	123(2)
Reflections Collected	25584	7323	27167
Reflections Unique	6448	3269	8631
Reflections Observed	6182	2829	7768

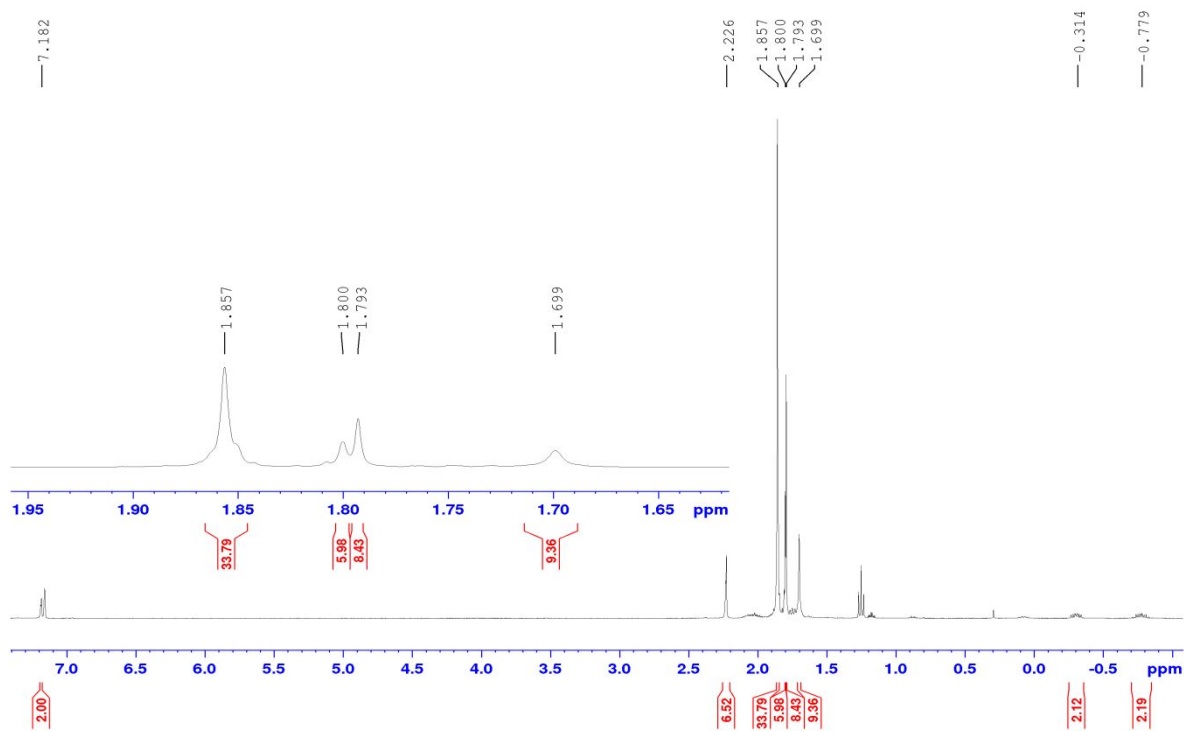
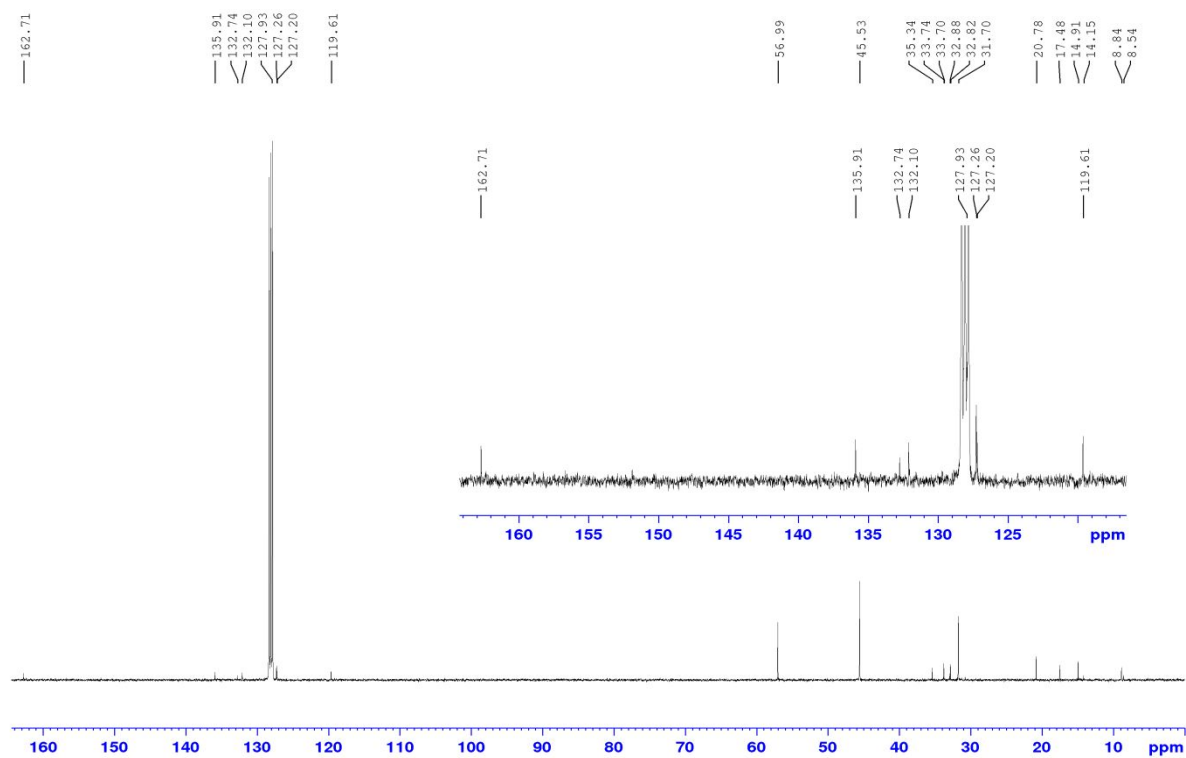
No.	404	192	583
Parameters			
2θmax	146.36	54.00	146.41
Rint	0.0202	0.0234	0.0506
Goodness of Fit	1.074	1.043	1.038
R[on F, obs refs only]	0.0453	0.0426	0.0713
wR (on F², all data)	0.1365	0.1128	0.1896
Largest diff. peak/hole / e \AA^{-3}	0.52/-0.27	0.21/-0.19	1.09/-0.28
Flack Parameter	0.018(14)	-0.16(17)	0.07(4)

Table S1: Comparison of key bond lengths and bond angles between **(1)** and $(\text{BIPHEN})_2\text{Li}_4(\text{THF})_4$ [where Am = Na for **1** and Am = Li for $(\text{BIPHEN})_2\text{Li}_4(\text{THF})_4$].

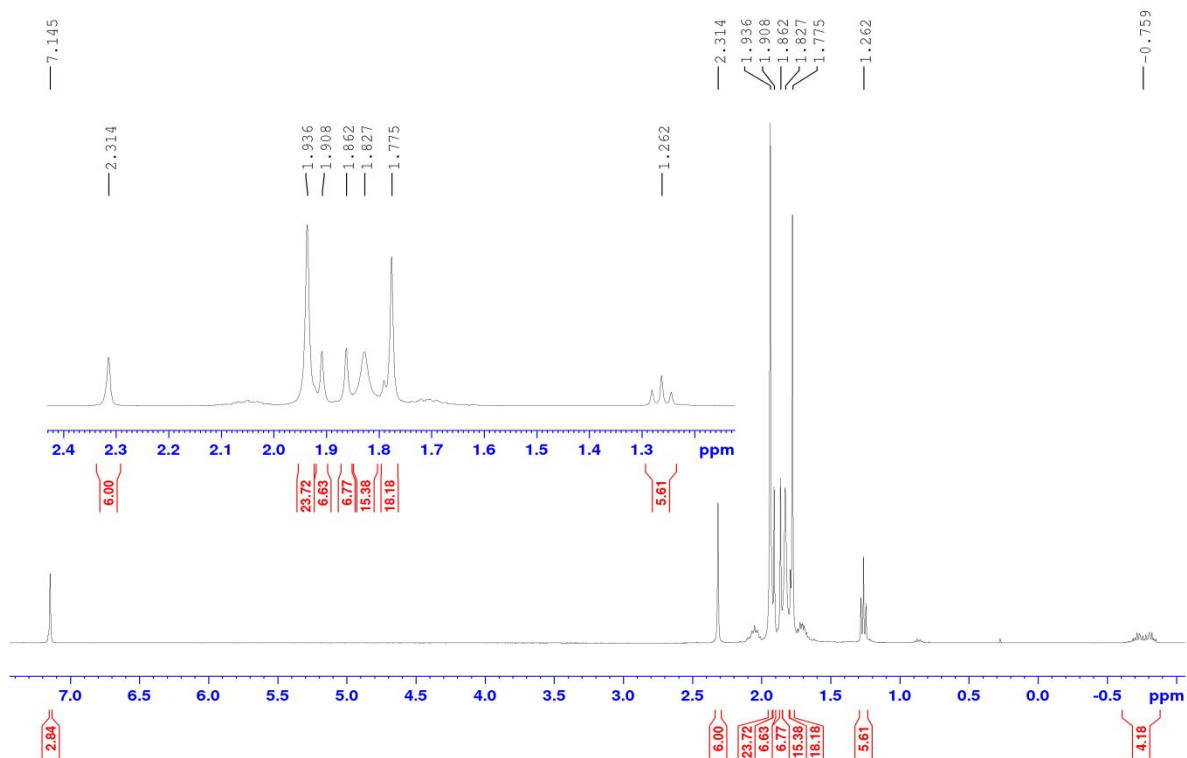
	$(\text{BIPHEN})_2\text{Na}_4(\text{THF})_4$	$(\text{BIPHEN})_2\text{Li}_4(\text{THF})_4$
Bond Lengths (Å)		
AM(1)-O(1)	2.217(2)	1.879(3)
AM(1)-O(2)	2.313(2)	2.070(3)
AM(2)-O(1)	2.199(2)	1.875(3)
AM(3)-O(2)	2.265(2)	1.901(3)
Bond Angles (°)		
O(1)-AM(1)-O(2)	110.87(7)	133.04(5)
O(1)-AM(1)-O(1')	92.49(11)	92.27(17)
O(2)-AM(1)-O(2')	78.01(10)	76.46(13)
O(1)-AM(2)-O(1')	93.45(12)	92.50(18)
O(2)-AM(3)-O(2')	79.27(8)	84.53(12)

Solution-State data for Complexes 1-4**[BIPHEN]₂Na₄(THF)₄ (1)**S1: ¹H NMR Spectrum of [BIPHEN]₂Na₄(THF)₄ in d₈-THF at 300 KS2: ¹³C NMR Spectrum of [BIPHEN]₂Na₄(THF)₄ in d₈-THF at 300 K

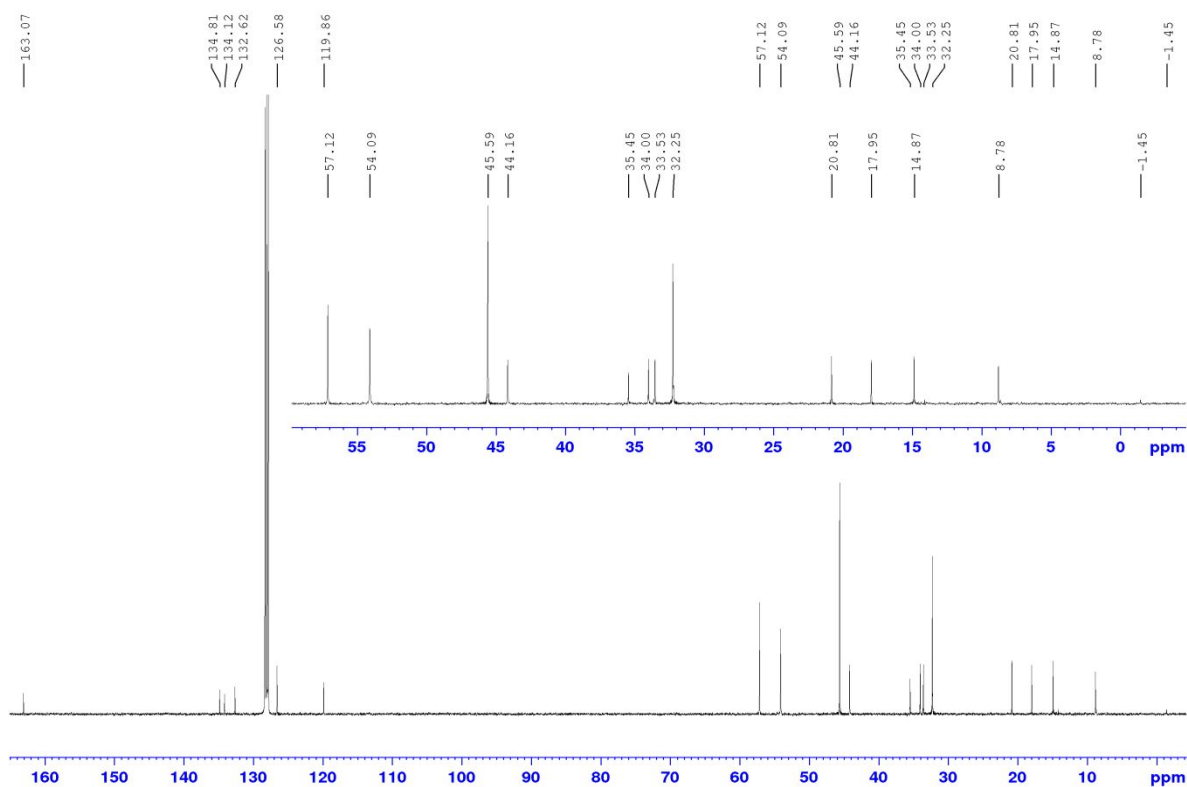
[BIPHEN]₂Na₂Mg(THF)₄ (2)S3: ¹H NMR Spectrum of [BIPHEN]₂Na₂Mg(THF)₄ in d₈-THF at 300 KS4: ¹³C NMR Spectrum of [BIPHEN]₂Na₂Mg(THF)₄ in d₈-THF at 300 K

[(rac)-BIPHEN]Na₂MgBu₂(TMEDA)₂ (3)S5: ¹H NMR Spectrum of [(rac)-BIPHEN]Na₂MgBu₂(TMEDA)₂ in C₆D₆ at 300 KS6: ¹³C NMR Spectrum of [(rac)-BIPHEN]Na₂MgBu₂(TMEDA)₂ in C₆D₆ at 300 K

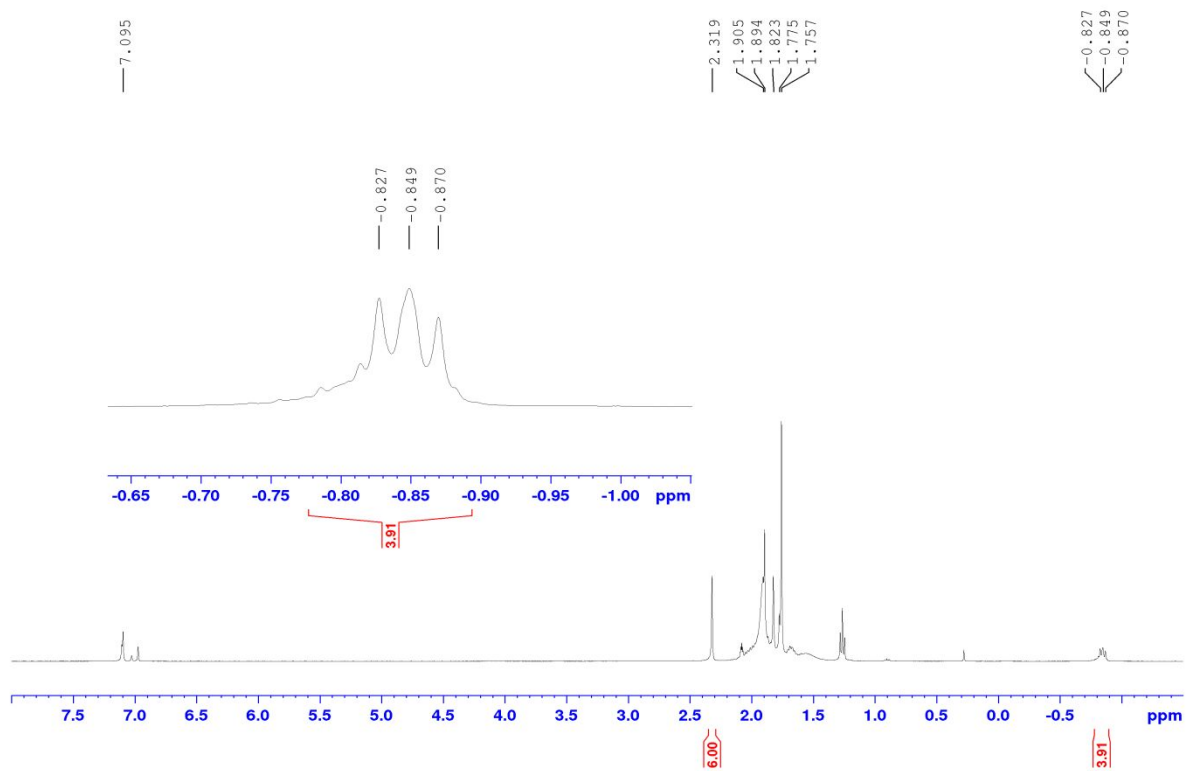
[(rac)-BIPHEN]Na₂MgR₂(PMDETA)₂ (4)



S7: ¹H NMR Spectrum of [(rac)-BIPHEN]Na₂MgR₂(PMDETA)₂ in C₆D₆ at 300 K

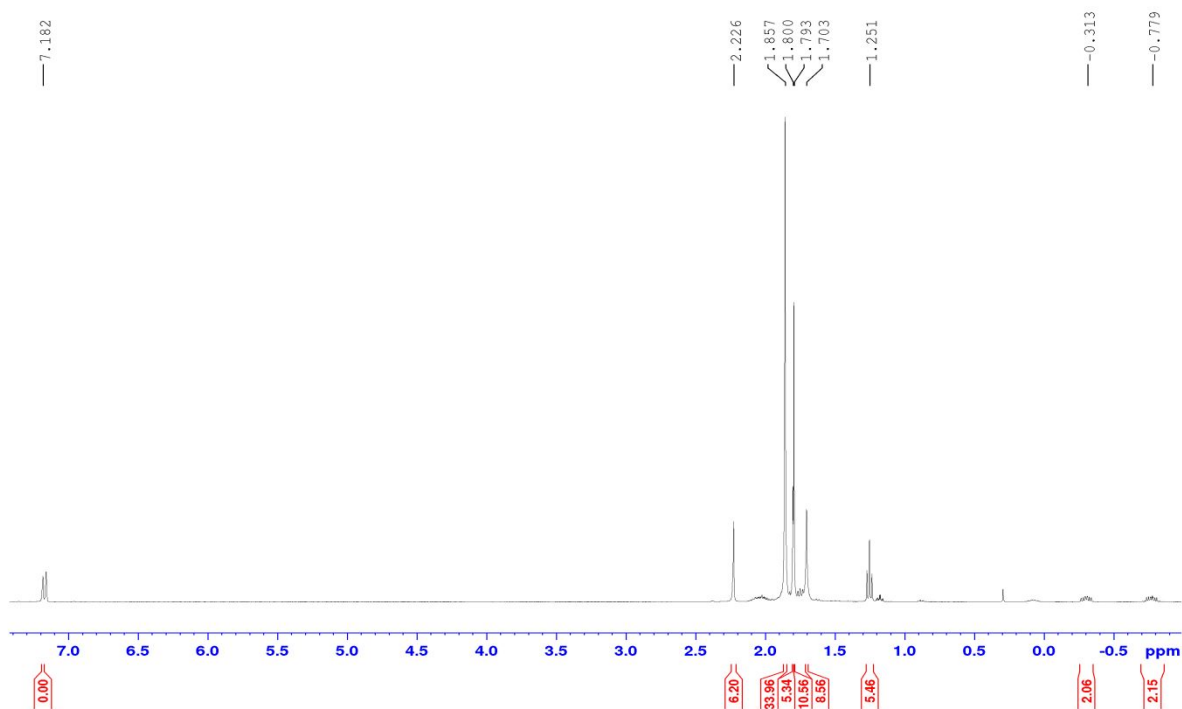


S8: ¹³C NMR Spectrum of [(rac)-BIPHEN]Na₂MgR₂(PMDETA)₂ in C₆D₆ at 300 K

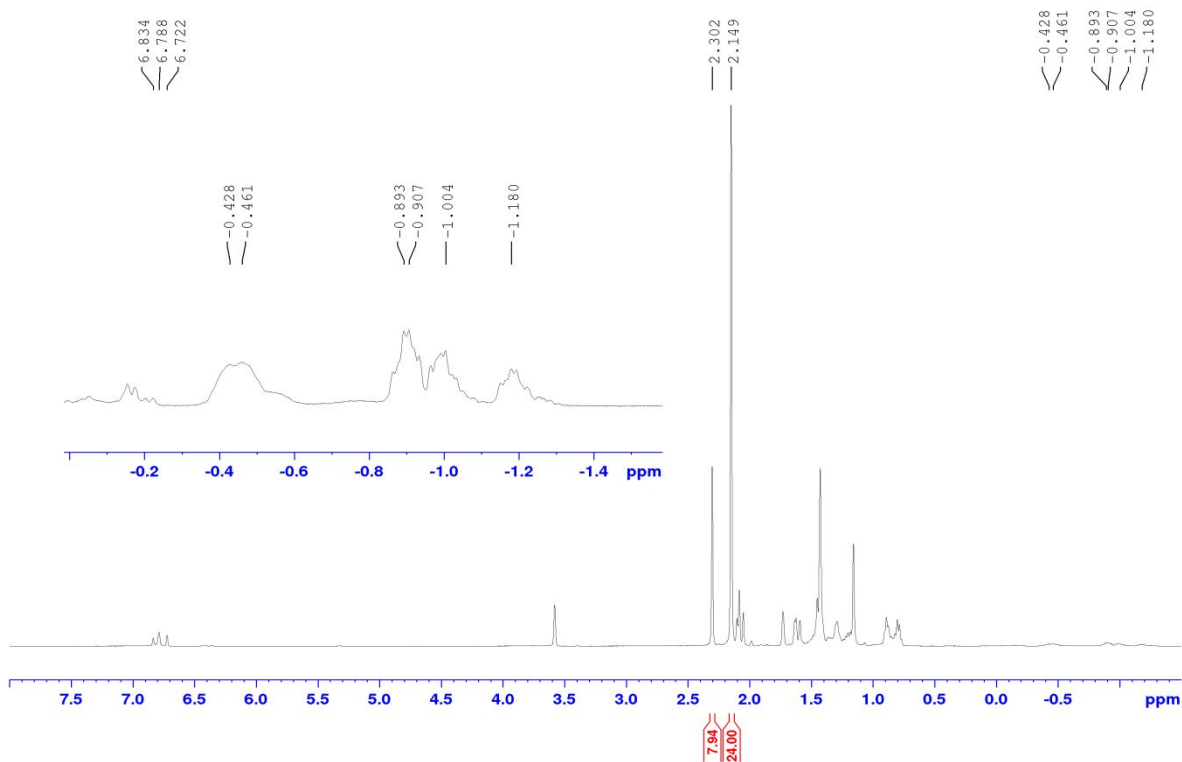


S9: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgR}_2(\text{PMDETA})_2$ in $d_8\text{-Tol}$ at 263 K.

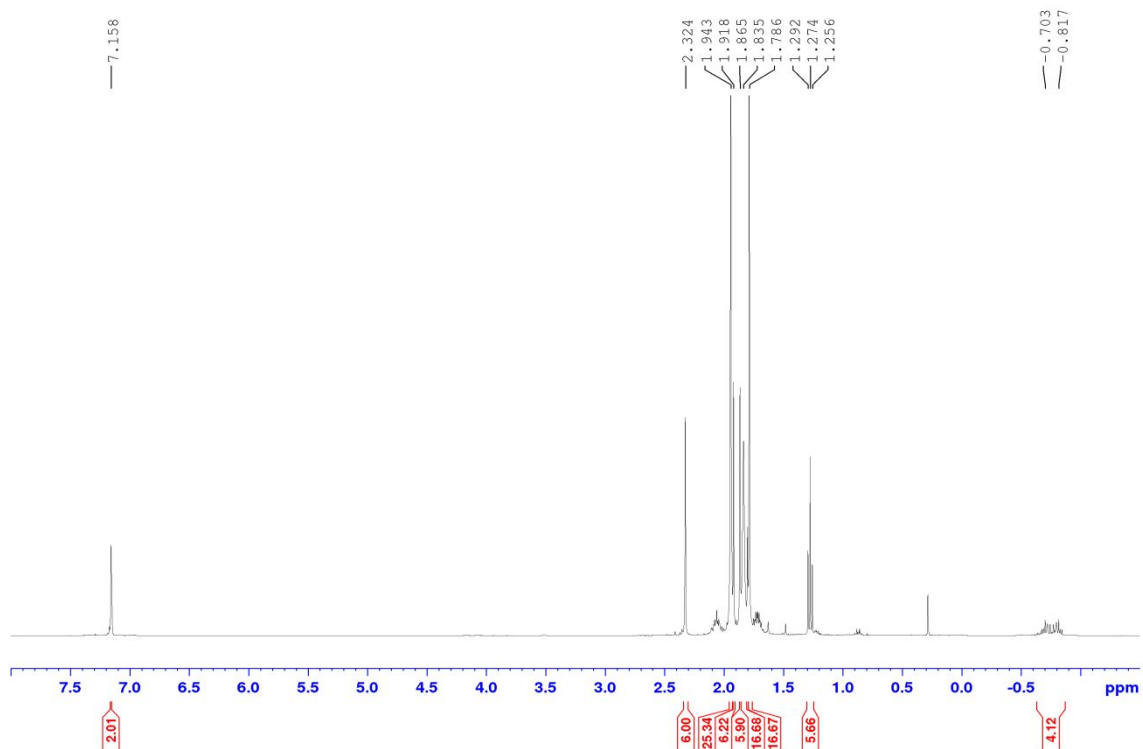
Variable Temperature Stability Studies of 3 and 4



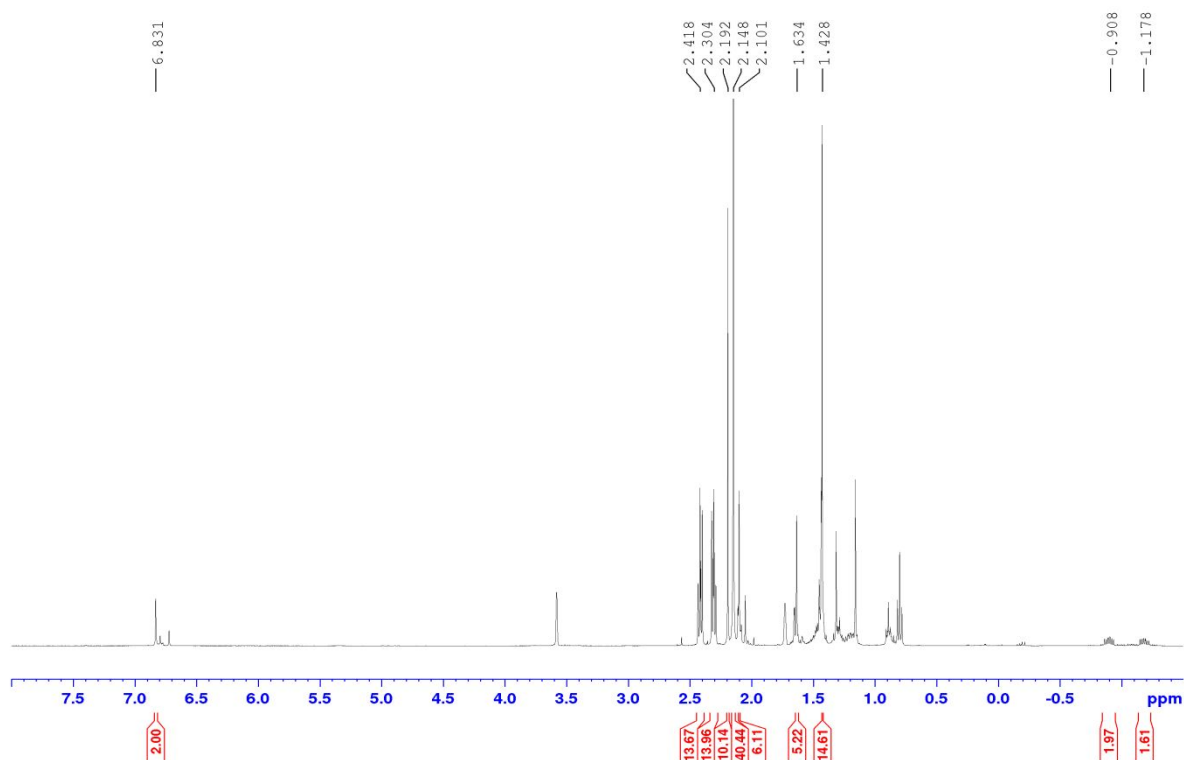
S10: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgBu}_2(\text{TMEDA})_2$ in C_6D_6 after heating to $50\text{ }^\circ\text{C}$ for 12 hours



S11: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgBu}_2(\text{TMEDA})_2$ in $\text{d}_8\text{-THF}$ after heating to $50\text{ }^\circ\text{C}$ for 12 hours



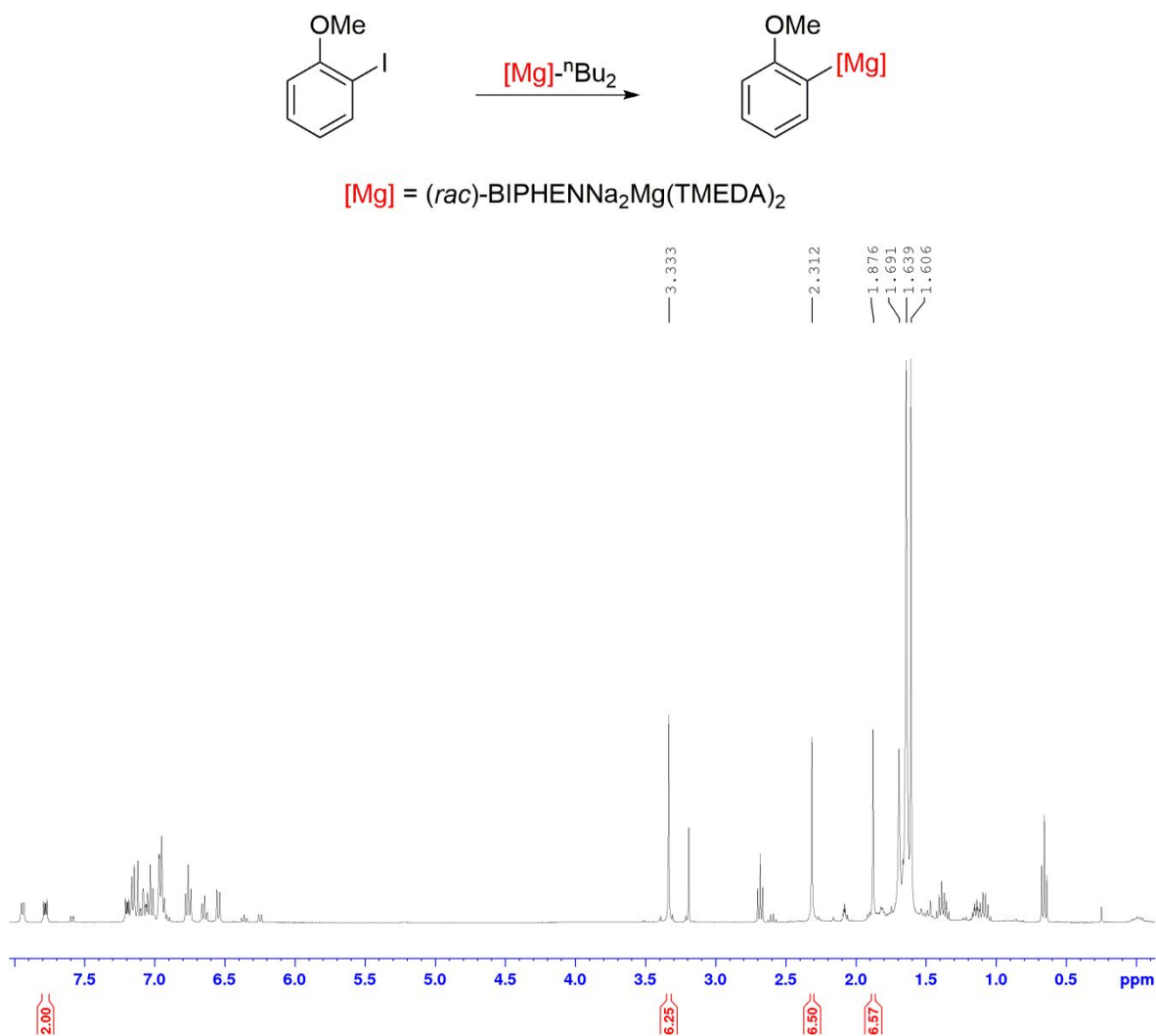
S12: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgBu}_2(\text{PMDETA})_2$ in C_6D_6 after heating to $50\text{ }^\circ\text{C}$ for 12 hours



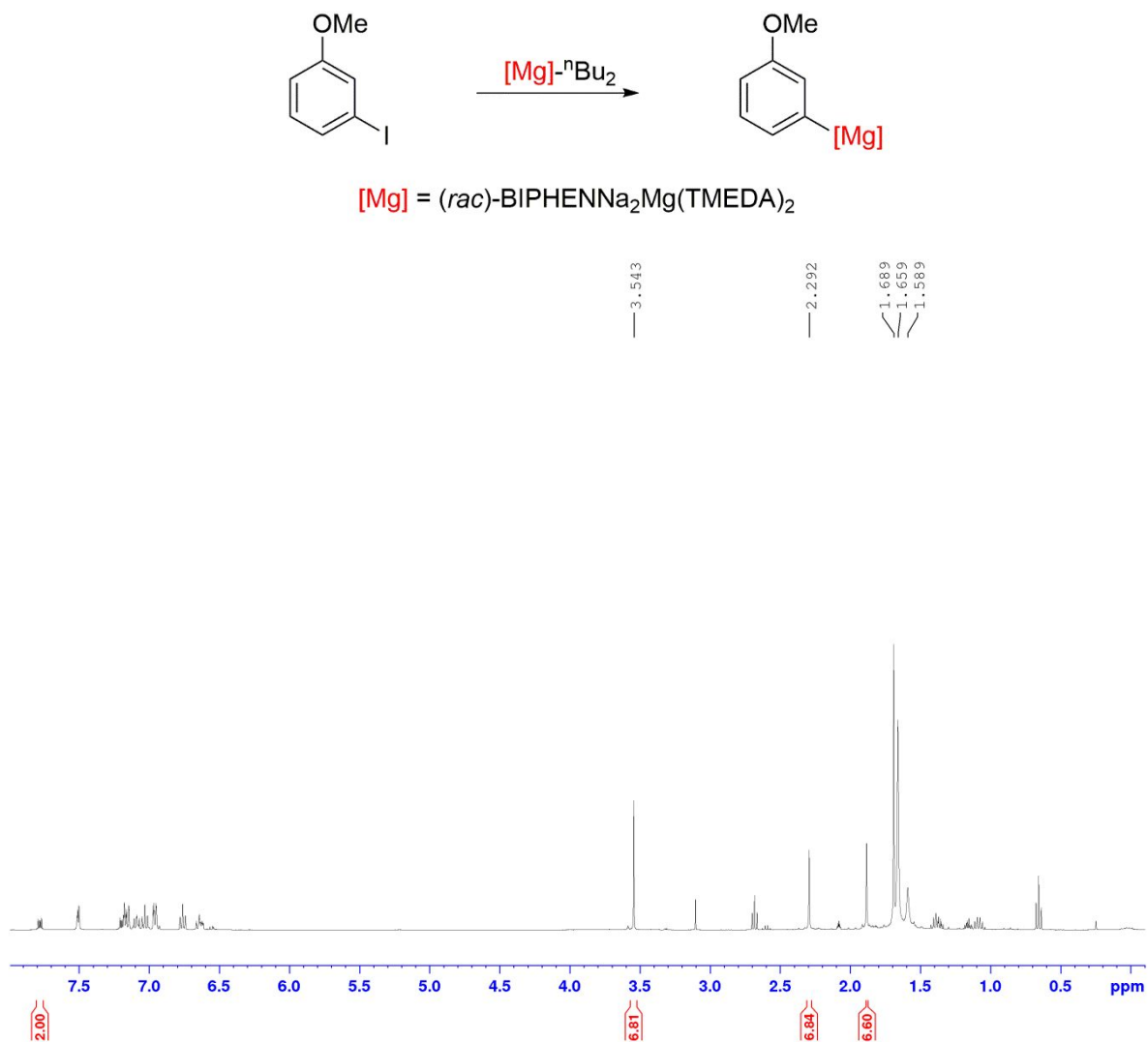
S13: ^1H NMR Spectrum of $[(rac)\text{-BIPHEN}]\text{Na}_2\text{MgBu}_2(\text{PMDETA})_2$ in $d_8\text{-THF}$ after heating to $50\text{ }^\circ\text{C}$ for 12 hours

Metal-Halogen Exchange reactions

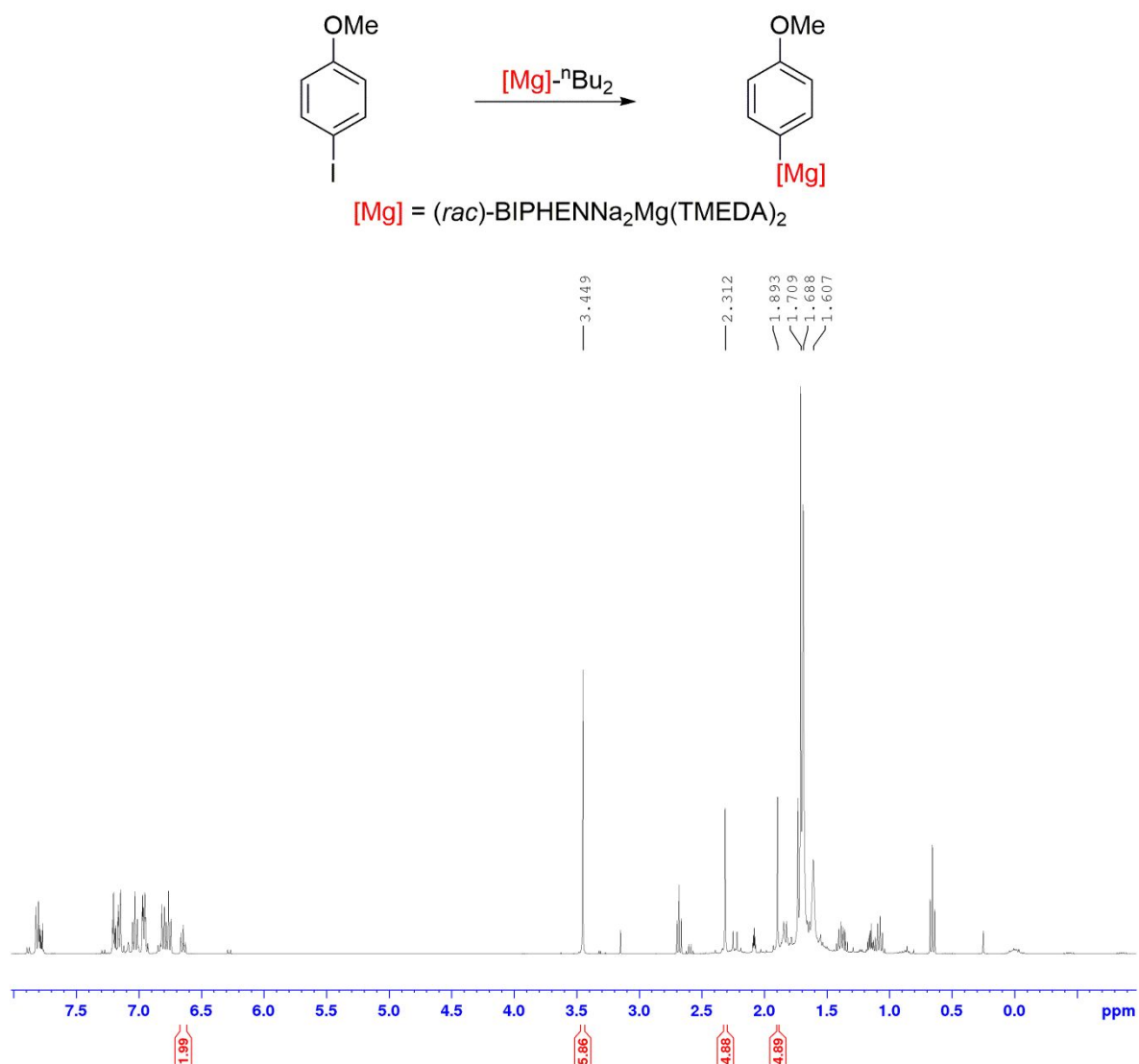
Table 3, product **5** using **3**



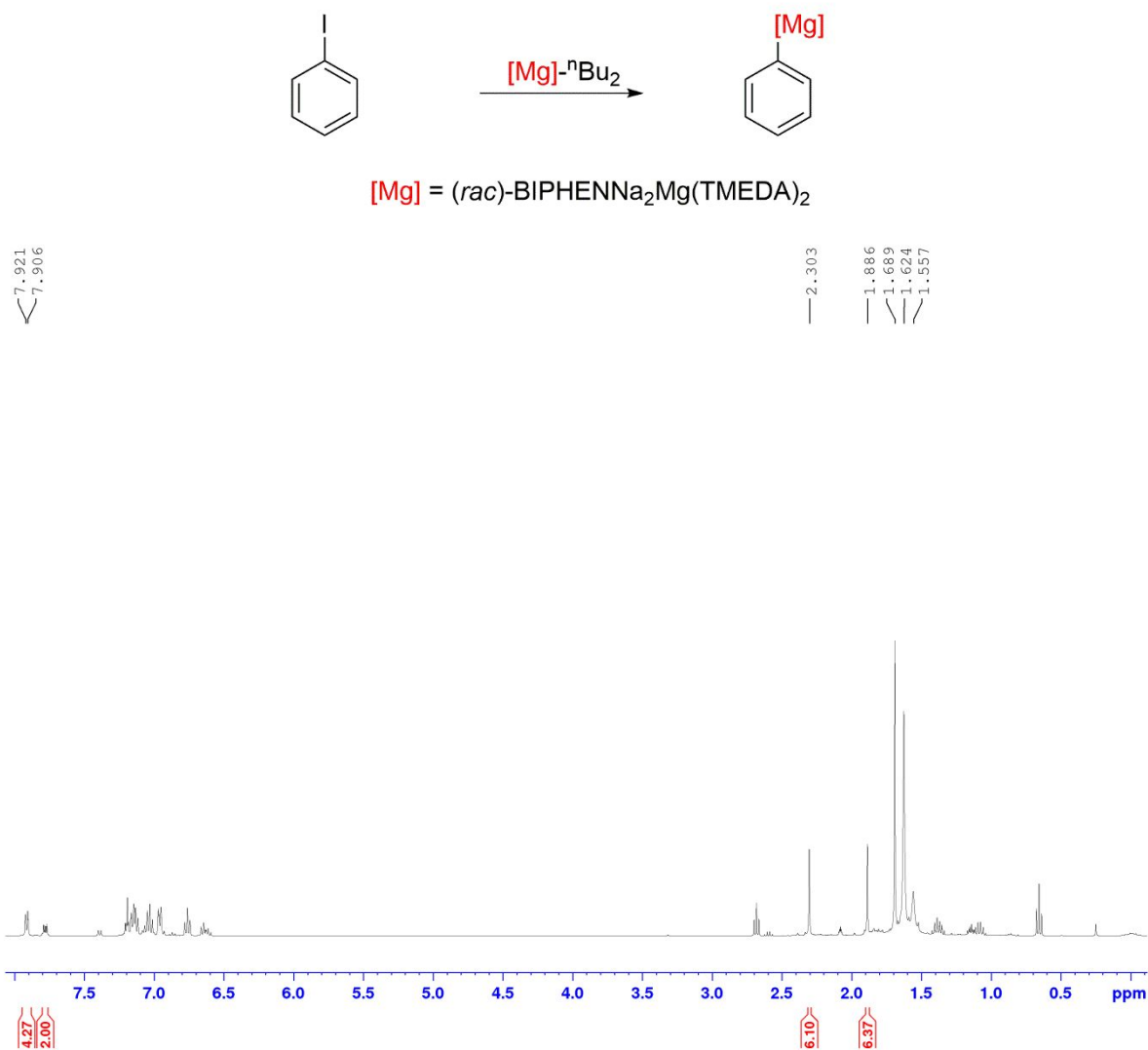
S14: Product **5** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 90% (25 °C, 18 h)

Table 3, product **6** using **3**

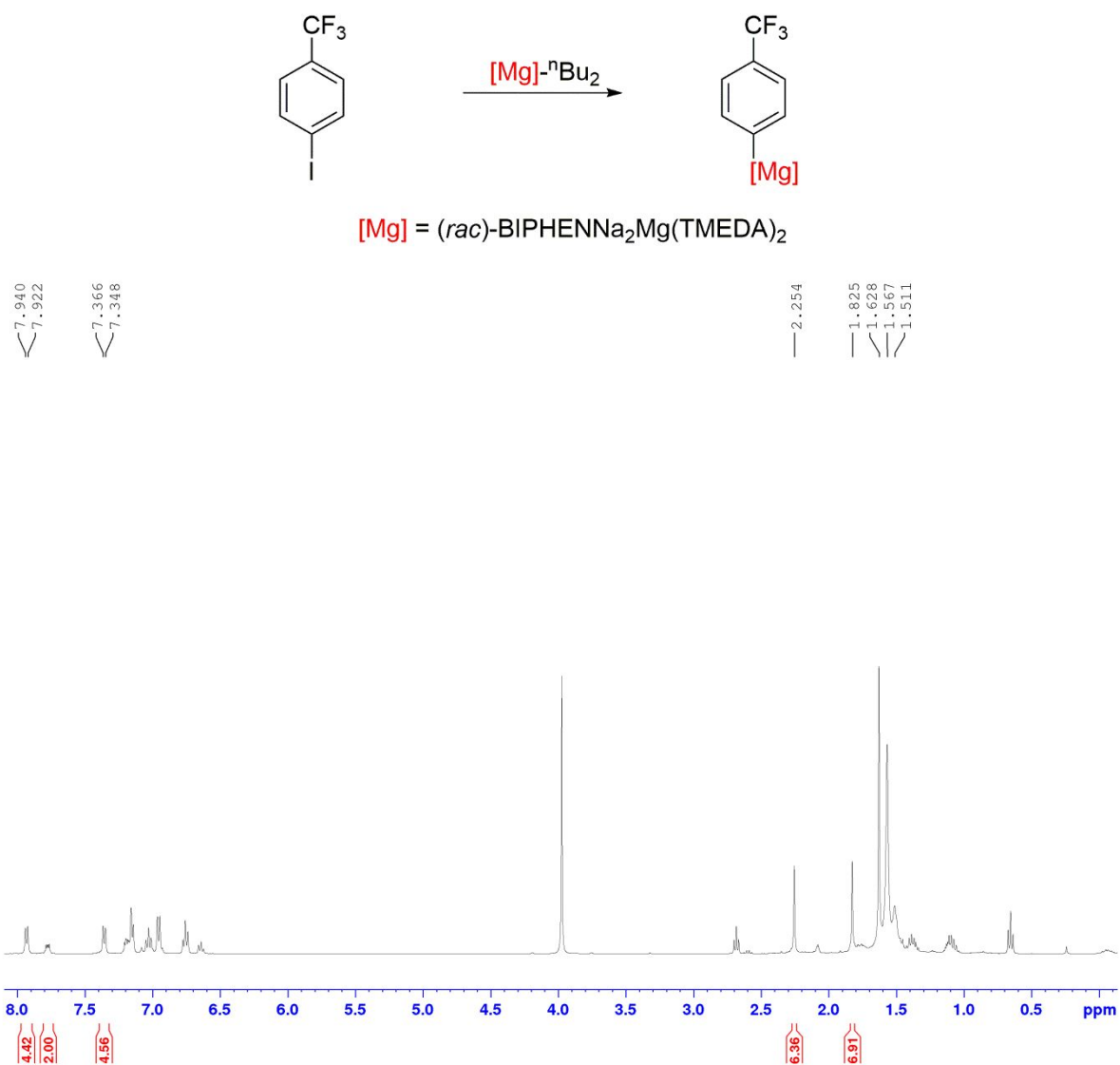
S15: Product **6** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 91% (25 °C, 18 h)

Table 3, product **7** using **3**

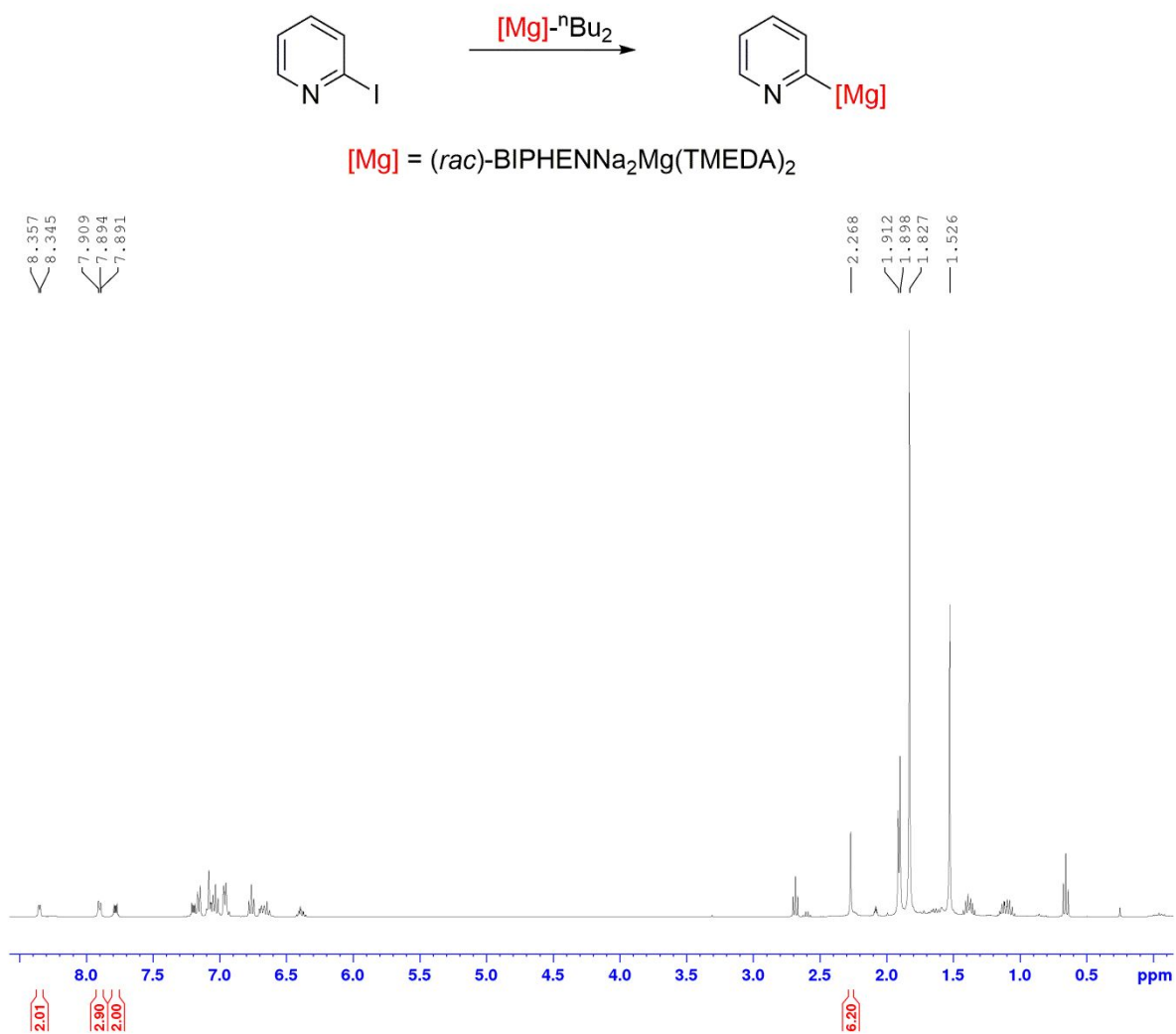
S16: Product **7** in d_8 -Tol with 1,2,3,4-Tetraphenyl-naphthalene as internal standard, yield 79% (25 °C, 18 h)

Table 3, product **8** using **3**

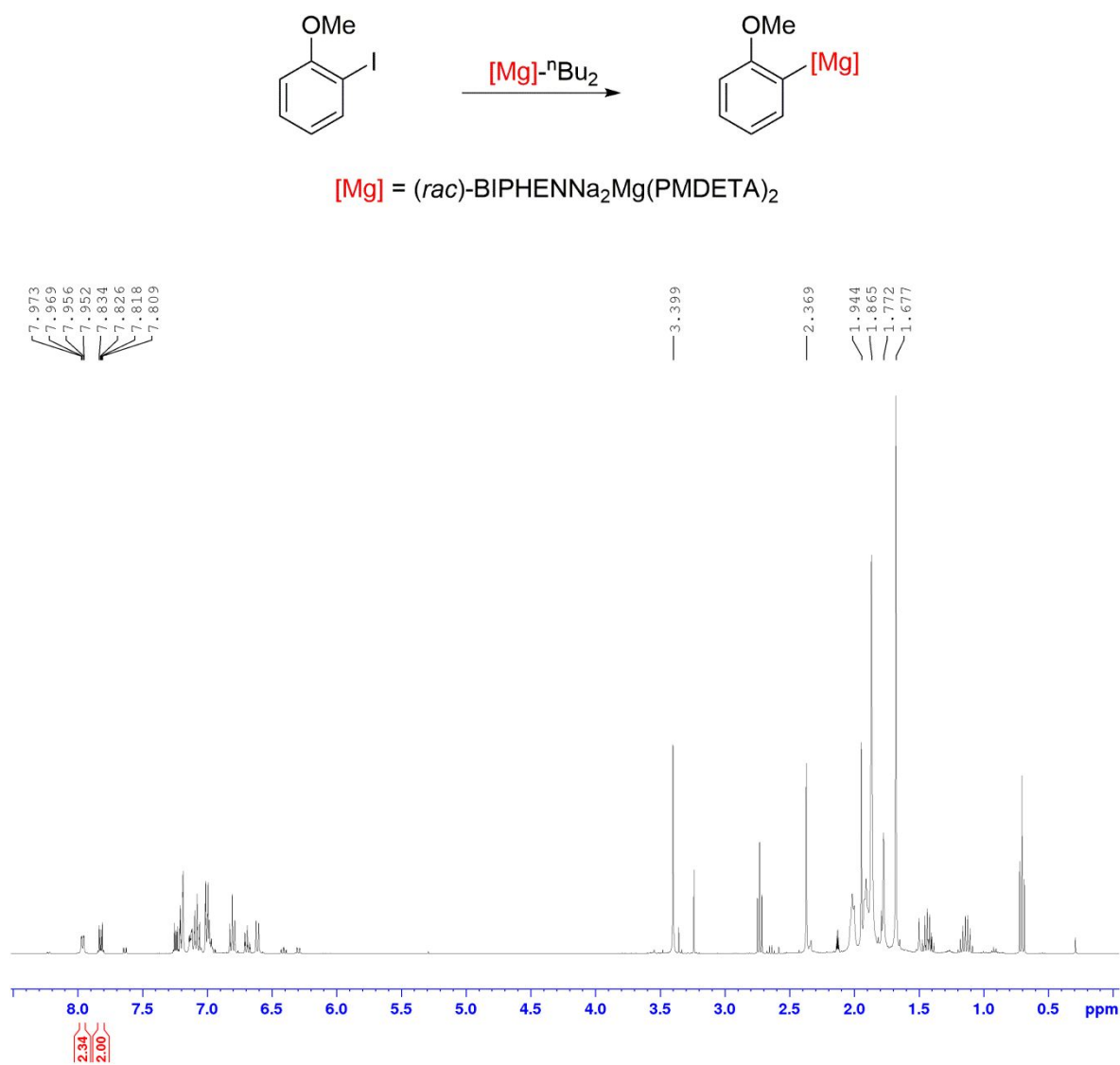
S17: Product **8** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 90% (25 °C, 18 h)

Table 3, product **9** using **3**

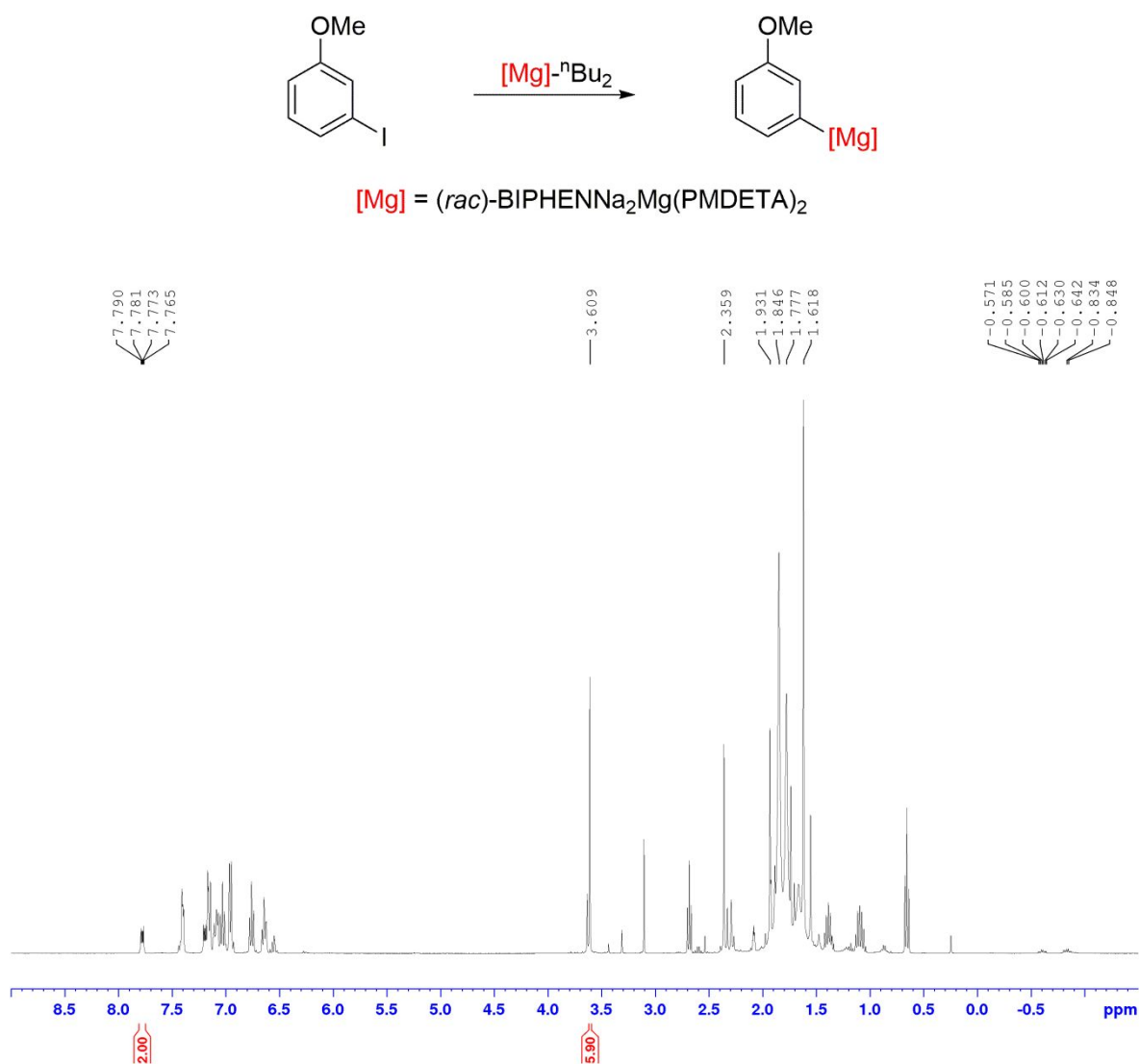
S18: Product **9** in d₈-Tol with 1,2,3,4-Tetraphenylnaphthalene and ferrocene as internal standard, yield 87% (25 °C, 15 min)

Table 3, product **10** using **3**

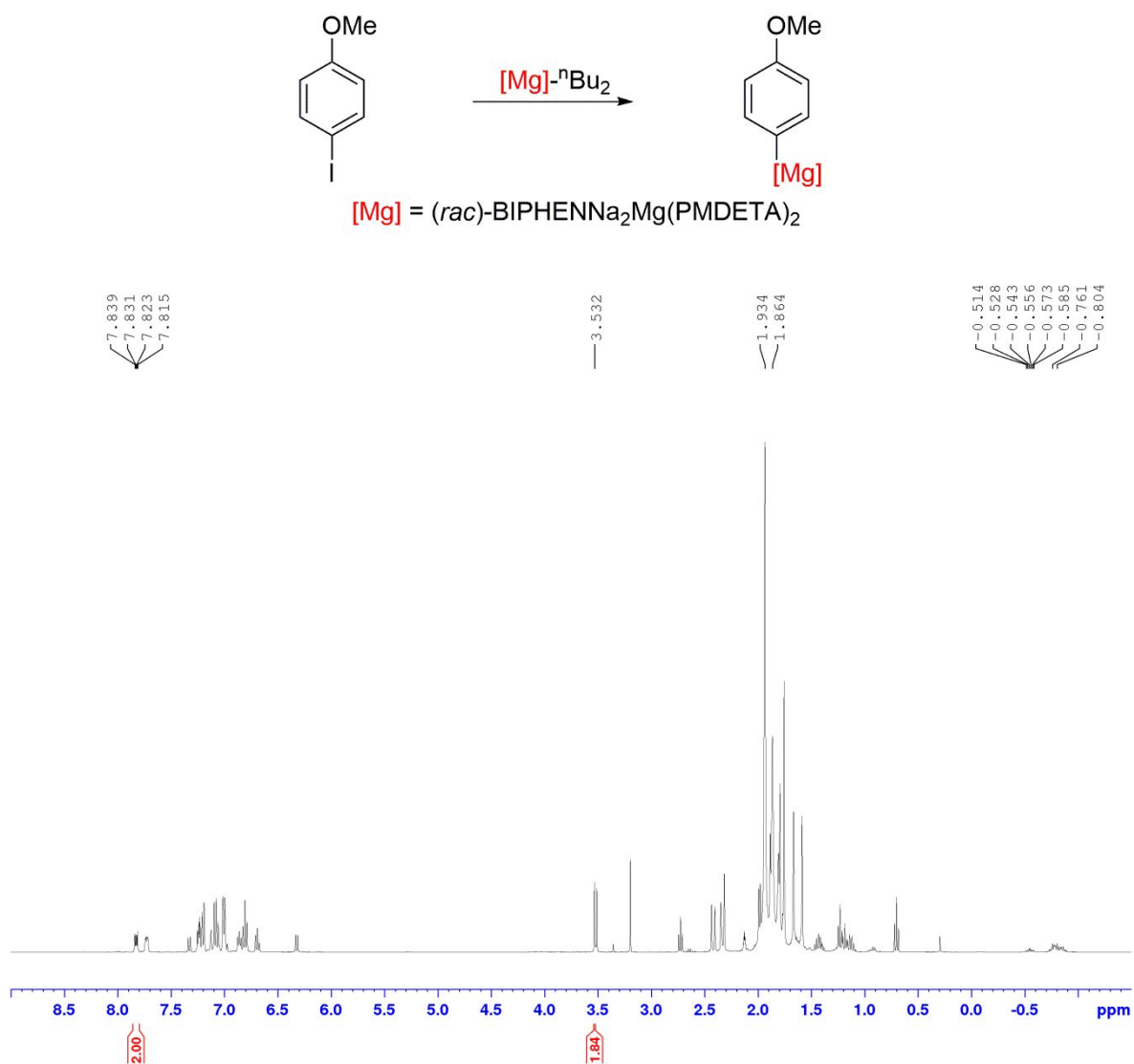
S19: Product **10** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 78% (25 °C, 15 min)

Table 3, product **5** using **4**

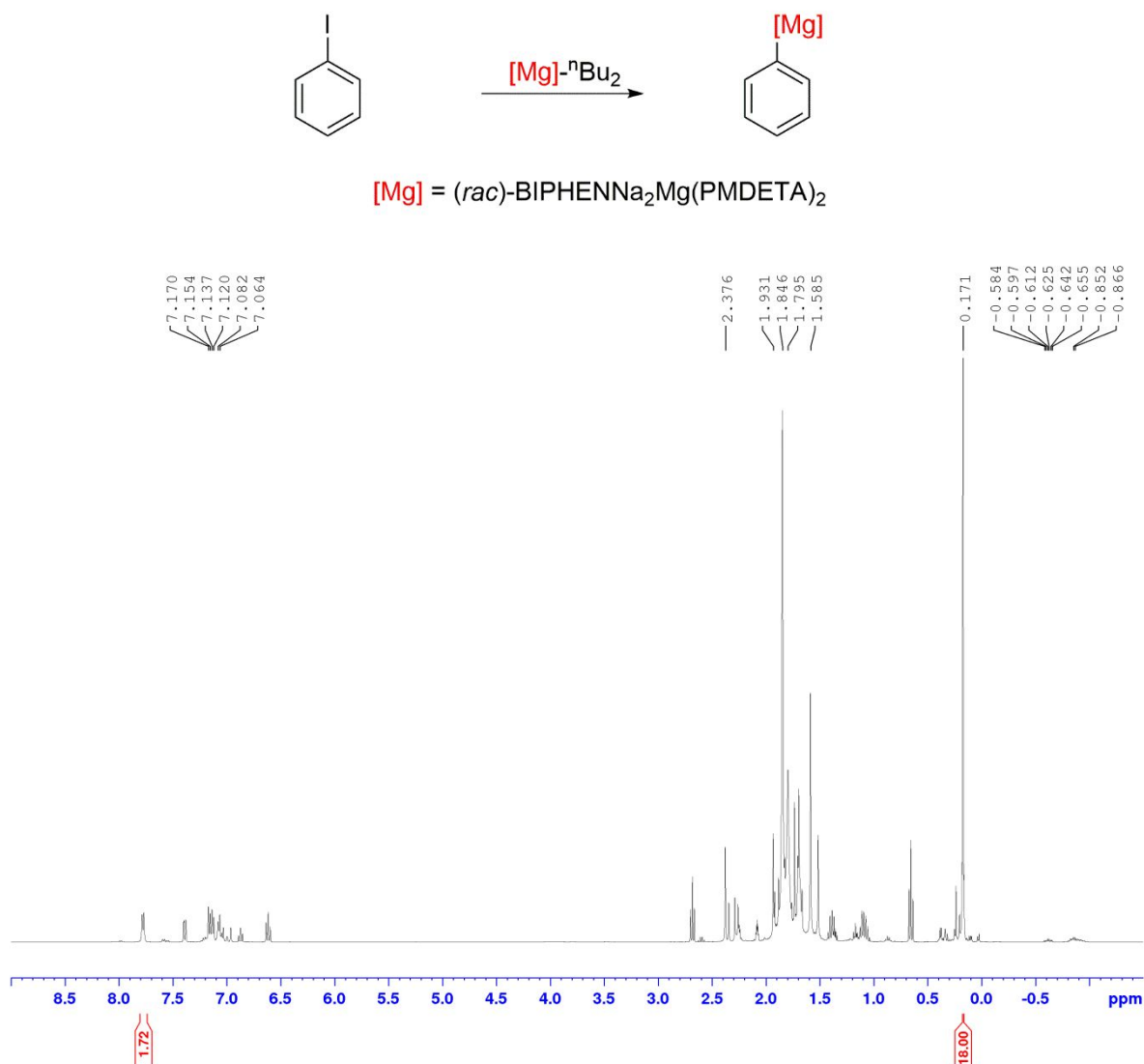
S20: Product **5** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 77% (25 °C, 18 h)

Table 3, product **6** using **4**

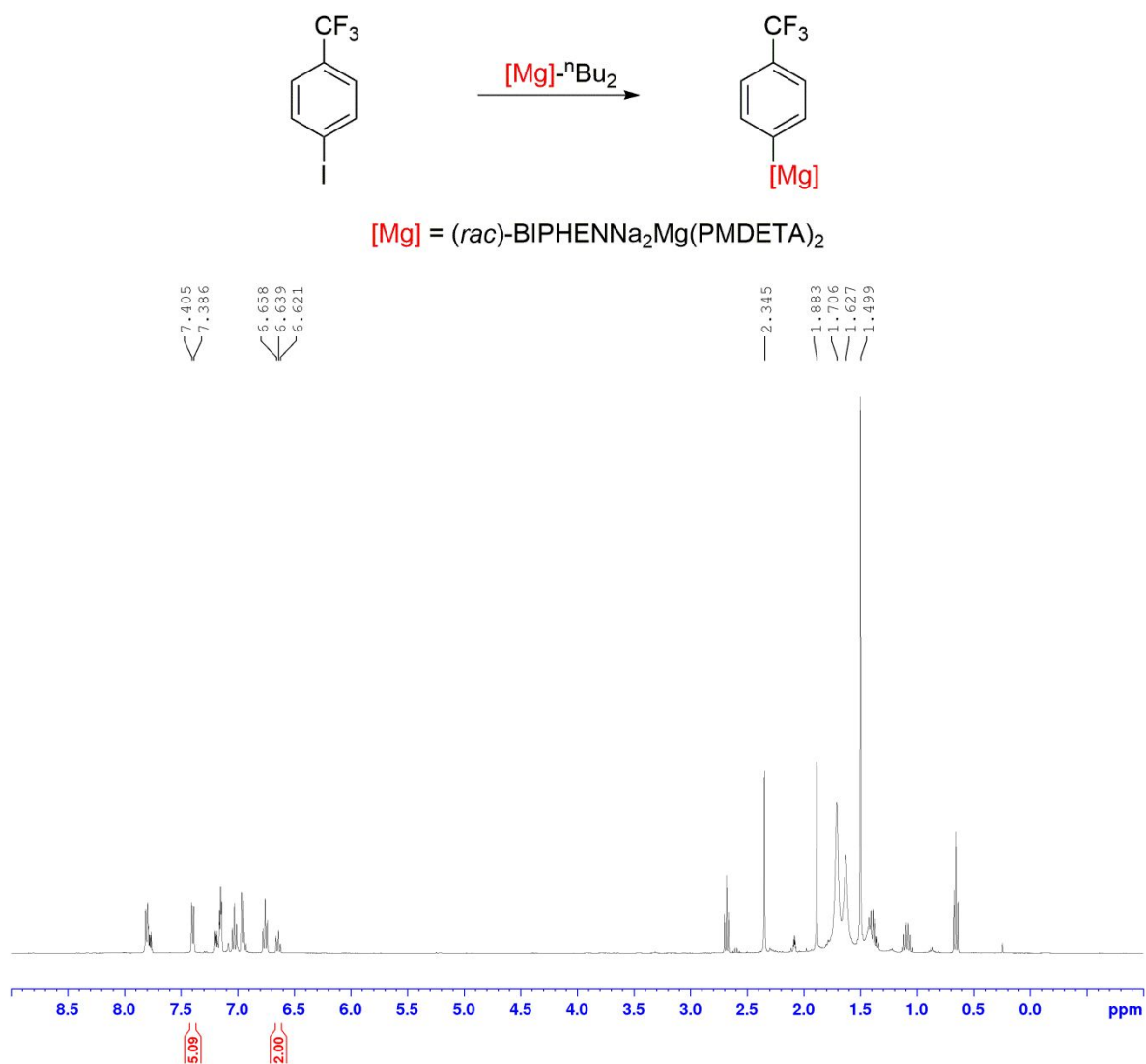
S21: Product **6** in d_8 -Tol with 1,2,3,4-Tetraphenyl-naphthalene as internal standard, yield 65% (25 °C, 18 h)

Table 3, product **7** using **4**

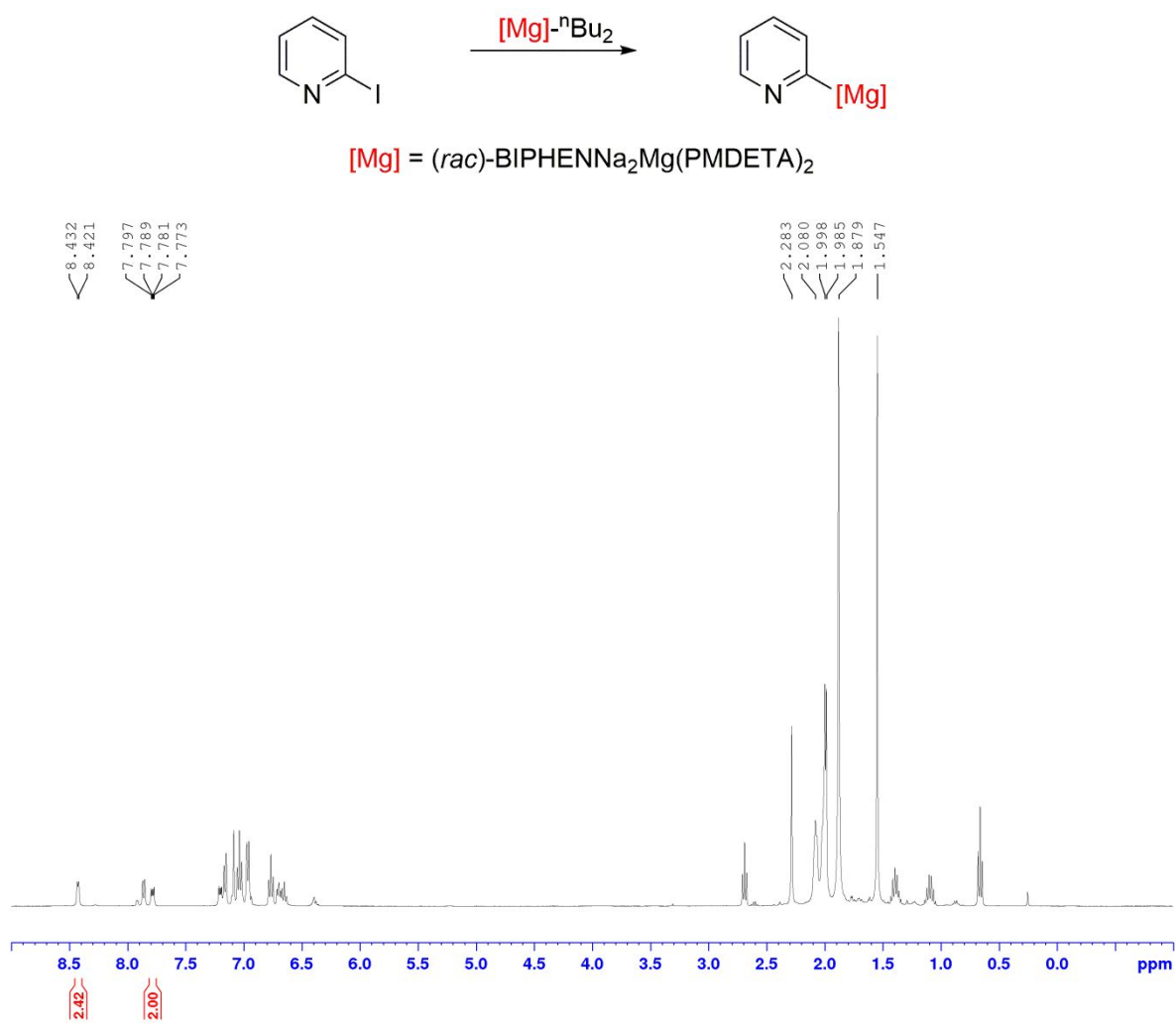
S22: Product **7** in d_8 -Tol with 1,2,3,4-Tetraphenyl-naphthalene as internal standard, yield 20% (25 °C, 18 h)

Table 3, product **8** using **4**

S23: Product **8** in d_8 -Tol with hexamethylcyclotrisiloxane as internal standard, yield 57% (25 °C, 18 h)

Table 3, product **9** using **4**

S24: Product **9** in d_8 -Tol with 1,2,3,4-Tetraphenylnaphthalene as internal standard, yield 84% (25 °C, 18 h)

Table 3, product **10** using **4**

S25: Product **10** in d_8 -Tol with 1,2,3,4-Tetraphenyl-naphthalene as internal standard, yield 80% (25 °C, 15 min)

References

1. G.M. Sheldrick, *Acta Cryst.*, **2015**, C71, 3-8.
2. A. L. Spek, **2015**, *Acta Cryst.* C71, 9-18.