*Electronic Supplementary Information*

# Isomeric and chemical consequences of the direct magnesiation of 1,3-benzoazoles using β-diketiminate-stabilized magnesium bases

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## Experimental Section

**General procedures**. All experiments were carried out using standard Schlenk and glove box techniques under an inert atmosphere of argon. Solvents (THF and hexane) were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for $^{1}$H, and 100.62 MHz for $^{13}$C{$^{1}$H}. $^{n}$BuLi in the form of (a 1.6 M solution in hexane) and dibutylmagnesium (a 1.0 M solution in heptane) were purchased from Sigma Aldrich Chemicals and used as received. $H_2$NDipp was dried with $CaH_2$ and distilled under argon at reduced pressure prior to use. The β-diketiminate ligand precursor [ArNC(Me)CHC(Me)NHAr] (Ar = 2,6-di-iso-propylphenyl) was synthesised according to literature method.[1] Satisfactory elemental analysis of compounds **1**-**5** and **7**-**8** could not be obtained due to their highly air and moisture sensitive nature.

**X-ray crystallography.** Data for samples **1**, **2**, **7** and **8** were measured with Oxford Diffraction Gemini S or Xcalibur E instruments with graphite-monochromated Mo (λ = 0.71073 Å) radiation.[2] Data for samples **3**, **4** and **5** were measured at Station I19 of the DIAMOND synchrotron radiation source using 0.6889 Å radiation and a Crystal Logics diffractometers with Rigaku Saturn 724+ CCD detector; data collection and processing used Rigaku and Bruker software.[2] All structures were solved and refined to convergence on $F^2$ using programs from the SHELX family.[2] All examined samples of **7** diffracted very weakly. Note that, despite the near 90° value found for β, orthorhombic Laue symmetry was not present. Many attempts were made to refine the model as a twin (e.g. during initial data processing and

1 M. Stender, R. J. Wright, B. E. Eichler, J. Prust, M. M. Olmstead, H. W. Roesky, P. P. Power, *J. Chem. Soc. Dalton Trans.* **2001**, 3465.
2 (a) *CrysAlisPro*, Oxford Diffraction Ltd, Oxford, UK, 2008. (b) G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112

during final refinement, and assuming both pseudo-merohedral or non-merohedral twinning) but none of these treatments were convincing and none improved the final model. Compound **3** was subjected to the PLATON/SQUEEZE procedure,[3] to treat disordered solvent in the structure; this indicated a total contribution of approximately 140 electrons in the unit cell. Selected crystallographic data are presented in Table S1 in the Supporting Information and full details in cif format are available from the CCDC (CCDC916806 – 916812).

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}Mg(Bu)(THF)] (1).** A Schlenk tube was charged with THF (10 mL) and $Bu_2Mg$ (4 mL of a 1M solution of $Bu_2Mg$ in hexane, 4 mmol) followed by the addition of 1.66 g of NacnacH (4 mmol) and the resulting pale yellow solution was stirred for 1 hour at room temperature. The solution was concentrated *in vacuo* and left to stand at -30$^{o}$C in the freezer. After 24 hours, a crop of colorless crystals of **1** was obtained (1.23 g, 54%). $^{1}$H NMR ($C_6D_6$, 298K ) δ7.17 [s, 6H, Ar*], 4.80 [s, 1H, C*H*], 3.57 [m, 4H, OC$H_2$, THF], 3.30 [m, 4H, C*H*, $^{i}$Pr, Ar*], 1.66 [s, 6H, C$H_3$], 1.47 [m, 2H, C$H_2$, Bu], 1.36 [m, 2H, C$H_2$, Bu], 1.30 [m, 4H, C$H_2$, THF], 1.30 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 1.23 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 0.92 [t, 3H, C$H_3$, Bu], -0.35 [m, 2H, Mg-C$H_2$, Bu]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) δ167.15 [CH*C*(Me)], 145.28 [*C*, Ar*], 141.60 [*C*, Ar*], 124.33 [*CH*, Ar*], 122.98 [*CH*, Ar*], 93.83 [*C*HC(Me)], 68.48 [O*C*$H_2$,THF], 31.88 [*C*$H_2$, THF], 31.17 [*C*$H_2$, Bu], 27.40 [*C*H, $^{i}$Pr, Ar*], 24.55 [*C*$H_2$, Bu], 24.32 [*C*$H_3$, $^{i}$Pr, Ar*], 23.68[*C*$H_3$, $^{i}$Pr, Ar*], 23.29 [*C*$H_3$], 13.90 [*C*$H_3$, Bu], 4.99 [Mg-*C*$H_2$, Bu].

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}Mg(TMP)] (2)** $Mg(TMP)_2$ was prepared *in situ* by refluxing over 1 hour a mixture of $Bu_2Mg$ (4mL of 1M solution in hexane, 4 mmol) and TMP(H) (1.36 mL, 8 mmol) in hexane. NacnacH (1.66 g, 4 mmol) was then added and the resulting yellow solution was stirred for one hour at 60$^{o}$C. Overnight storage of the solution in the freezer provided a batch of colorless crystals of **2** (1.15 g, 52%). $^{1}$H NMR ($C_6D_6$, 298K ) δ7.13 [s, 6H, Ar*], 4.86 [s, 1H, C*H*], 3.22 [m, 4H, C*H*, $^{i}$Pr, Ar*], 1.69 [s, 6H, C$H_3$], 1.66 [m, 2H, C$H_2$, γ-TMP], 1.38 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 1.18 [m, 2H, C$H_2$, β-TMP], 1.17 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 0.95 [s, 12H, C$H_3$, TMP]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) δ169.07 [CH*C*(Me)], 144.14 [*C*, Ar*], 141.48 [*CH*, Ar*], 124.96 [*C*, Ar*], 123.31 [*CH**, Ar], 94.65 [*C*HC(Me)], 49.88 [*C*, *α*-TMP], 38.28 [*C*$H_2$, β-TMP], 34.81 [C(*C*$H_3$)$_2$, TMP], 28.09 [*C*H, $^{i}$Pr, Ar*], 24.10 [*C*$H_3$, $^{i}$Pr, Ar*], 23.87 [*C*$H_3$, $^{i}$Pr, Ar*], 23.79 [*C*$H_2$, γ-TMP], 19.00 [*C*$H_3$].

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}Mg{O(*o*-$C_6H_4$)NC}(THF)] (3)** Isolated crystals of **2** (0.56 g, 1 mmol) were placed in a Schlenk tube and dissolved in THF (5 mL). Benzoxazole (0.1 mL, 1 mmol) was then added and the solution stirred for 2 hours. During this time the solution changed from light yellow to orange in color. Hexane (4 mL) was introduced and, after storage in the freezer for 24

3 A. L. Spek, *J. Appl. Cryst*. **2003**, *36*, 7.

hours, the solution deposited red crystals (0.31 g, 55%). Similar yields were observed when the reaction was carried out under identical conditions using butyl derivative **1** instead of **2** as the base. $^{1}$H NMR ($d_8$-THF, 298K, 298K ) δ7.11 [m, 6H, Ar*], 7.01 [m, 2H, $C_6H_4NC$], 6.50 [d, 1H, $C_6H_4NC$], 6.36 [t, 1H, $C_6H_4NC$], 5.00 [s, 1H, C*H*], 3.61 [m, 4H, OC$H_2$, THF], 3.22 [m, 4H, C*H*, $^{i}$Pr, Ar*], 1.77 [m, 10H, C$H_2$, THF and C$H_3$], 1.10 [d, 12H, $CH_3$, $^{i}$Pr, Ar*], 1.01 [d, 12H, $CH_3$, $^{i}$Pr, Ar*]. $^{13}$C NMR{$^{1}$H} ($d_8$-THF, 298K, 298K) δ169.80 [*C*, CH*C*(Me)], 165.71 [*C*, $C_{isocyanide}$ ], 162.15 [*C*, $C_{\alpha\text{-phenolate}}$], 145.42 [*C*, Ar*], 143.38 [*C*, Ar*], 130.31 [*C*H, $C_6H_4NC$], 127.05 [*C*H, $C_6H_4NC$], 125.91 [*C*H, Ar*], 124.48 [*C*H, Ar*], 122.06 [*C*H, $C_6H_4NC$], 113.92 [*C*H, $C_6H_4NC$, $C_{\beta\text{-phenolate}}$], 94.62 [*C*H], 28.63 [*C*H, $^{i}$Pr, Ar*], 26.40 [*C*$H_2$,THF], 24.70 [*C*$H_3$, $^{i}$Pr, Ar* ], 24.61 [*C*$H_3$, $^{i}$Pr, Ar* ], 23.50 [*C*$H_3$ ].

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${btz*}$_2$] (4)** Isolated crystals of **2** (0.56 g, 1 mmol) were added to a Schlenk tube and dissolved in THF (5 mL). Benzothiazole was then introduced (0.11 mL, 1 mmol) and the solution was stirred for 2 hours. The solution turned blue instantaneously then gradually became green and finally red in color. Hexane (4 mL) was added and, after storage in the freezer for 24 hours, the solution deposited a crop of red crystals (0.24 g, 43%). $^{1}$H NMR ($C_6D_6$, 298K ) δ8.71 [d, 1H, btz*], 7.66 [d, 2H, btz*], 7.34 [t, 2H, btz*], 7.04-6.98 [m, 2H, btz* and 6H , Ar*], 6.76 [d, 4H, Ar*], 5.24 [s, 2H, C*H*], 4.01 [m, 4H, C*H*, $^{i}$Pr, Ar*], 2.54 [m, 4H, C*H*, $^{i}$Pr, Ar*], 1.67 [s, 12H, C$H_3$], 1.63 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 1.42 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], 0.62 [d, 12H, C$H_3$, $^{i}$Pr, Ar*], -0.68 [d, 12H, C$H_3$, $^{i}$Pr, Ar*]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) δ216.27 [$C_\alpha$, Btz*], 169.71 [CH*C*(Me)], 155.24, 146.20, 142.99, 142.00, 136.41, 135.86, [*C*, Ar* and btz*], 125.20 [*C*H, Ar*], 124.86 [*C*H, btz*], 124.26 [*C*H, Ar*], 123.73 [*C*H, btz*], 123.44 [*C*H, Ar*], 121.22 [*C*H, btz*], 120.99 [*C*H, btz*], 95.43 [*C*H], 29.83 [*C*H, $^{i}$Pr, Ar*], 27.27 [*C*H, $^{i}$Pr, Ar*], 25.18 [*C*$H_3$, $^{i}$Pr, Ar*], 24.93 [*C*$H_3$], 24.80 [*C*$H_3$, $^{i}$Pr, Ar*], 24.12 [*C*$H_3$, $^{i}$Pr, Ar*], 22.81 [*C*$H_3$, $^{i}$Pr, Ar*].

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}Mg{(btz*)C(H)=N(*o*-$C_6H_4$)S)}] (5)** Isolated crystals of compound **1** (0.57 g, 1 mmol) were added to a Schlenk tube and dissolved in THF ( 4 mL). Benzothiazole was then added (0.22 mL, 2 mmol). The resulting solution mixture turned blue immediately and it was stirred at room temperature for 1 hour. Addition of hexane (3 mL) and overnight storage of the resulting solution in the freezer resulted in the formation of blue crystals (0.47 g, 58%). $^{1}$H NMR ($C_6D_6$, 298K ) δ9.03 [d, 1H, btz*], 7.58 [d, 1H, N(*o*-$C_6H_4$)S], 7.28 [m, 2H, btz*], 7.18 [m, 2H, Ar*], 7.05 [m, 2H, Ar*], 6.98 [m, 2H, 1H of btz* and 1H of C(*H*)=N], 6.92 [d, 2H, Ar*], 6.72 [t, 1H, N(*o*-$C_6H_4$)S], 6.35 [t, 1H, N(*o*-$C_6H_4$)S], 6.09 [d, 1H, N(*o*-$C_6H_4$)S], 5.15 [s, 1H, C*H*], 3.89 [m, 2H, C*H*, $^{i}$Pr, Ar*], 2.89 [m, 2H, C*H*, $^{i}$Pr, Ar*], 1.80 [s, 6H, C$H_3$], 1.73 [d, 6H, C$H_3$, $^{i}$Pr, Ar*], 1.35 [d, 6H, C$H_3$, $^{i}$Pr, Ar*], 0.71 [d, 6H, C$H_3$, $^{i}$Pr, Ar*], 0.58 [d, 6H, C$H_3$, $^{i}$Pr, Ar*]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) δ168.21[CH*C*(Me)], 164.68, 154.56, 151.40, 146.07, 145.18 [*C*, Ar*, N(*o*-$C_6H_4$)S and Btz*], 145.01 [*C*H, *C*(H)=N], 143.38, 141.58 [*C*, Ar*], 135.04 [*C*H, N(*o*-$C_6H_4$)S], 129.98 [*C*H, N(*o*-$C_6H_4$)S],

128.45, 127.26, 125.55 [*C*H's, btz*], 125.01, 124.33, 122.77 [*C*H's, Ar*], 122.24 [*C*H, btz*], 120.04, 116.59 [*C*H's, N(*o*-$C_6H_4$)S], 94.89 [*C*H], 29.04[*C*H, $^{i}$Pr, Ar*], 27.41 [*C*H, $^{i}$Pr, Ar*], 25.66 [*C*$H_3$, $^{i}$Pr, Ar*], 25.10 [*C*$H_3$, $^{i}$Pr, Ar*], 24.89 [*C*$H_3$, $^{i}$Pr, Ar*], 24.60 [*C*$H_3$, $^{i}$Pr, Ar*].

**Synthesis of 2,2'-bisbenzothiazole (6).** A solution of **5** (prepared *in situ* by reacting **1** (1.14 g, 2 mmol) with two molar equivalents of benzothiazole (0.45 mL, 4 mmol) over 1 hour) in THF (10 mL). was quenched with a saturated aq $NH_4Cl$ solution (5 mL). The product was extracted with ethyl acetate (3 x 15 mL) and the combined organic phases dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was then dissolved in toluene (20 mL) and treated with TEMPO (0.98 g, 6 mmol). The reaction mixture was allow to stir at room temperature for 8 hours to afford **6** as a white solid which was filtered and washed with toluene (0.38 g, 72%). $^{1}$H NMR ($CDCl_3$, 298K ) δ8.15 [d, 2H,], 7.97 [d, 2H,], 7.56 [t, 2H,], 7.49 [t, 3H]. $^{13}$C NMR{$^{1}$H} ($CDCl_3$, 298K) δ 160.42, 151.86, 136.58 [*C*] 126.08, 125.17, 123.86, 121,92 [*C*H]. These spectroscopic data is in agreement with that previously reported in the literature.[4]

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${bIm$^{Me}$*}$_2$] (7)** Compound **2** (0.56 g, 1 mmol) was dissolved in THF (5 ml). After the addition of *N*-methylbenzimidazole (0.13 g, 1 mmol) the pale yellow solution was stirred for 2 hours, resulting in a green solution. Storage for 24 hours in the freezer yielded colorless crystals (0.32 g, 57%). $^{1}$H NMR ($C_6D_6$, 298K ) δ8.23 [d, 2H, bIm$^{Me}$*], 7.26 [d, 2H, bIm$^{Me}$*], 7.11 [t, 2H, bIm$^{Me}$*], 7.03 [m, 8H, Ar*], 6.85 [m, 6H, 4H Ar* and 2H bIm$^{Me}$*], 5.24 [s, 2H, C*H*], 3.75 [s, 6H, C*H*$_3$, bIm$^{Me}$*], 3.57 [m, 12H, 4H C*H*, $^{i}$Pr, Ar* and 8H OC*H*2, THF], 2.64 [m, 4H, C*H*, $^{i}$Pr, Ar*], 1.68 [m, 8H, C*H*$_2$, THF], 1.71 [s, 12H, C*H*$_3$], 1.24 [d, 12H, C*H*$_3$, $^{i}$Pr, Ar*], 1.12 [d, 12H, C*H*$_3$, $^{i}$Pr, Ar*], 0.65 [d, 12H, C*H*$_3$, $^{i}$Pr, Ar*], -0.31 [d, 12H, C*H*$_3$, $^{i}$Pr, Ar*]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) δ192.93 [*C*$_\alpha$, bIm$^{Me}$*], 169.52 [CH*C*(Me)], 147.00, 144.75, 143.40, 143.19, 141.62, 135.93 [*C*, Ar* and bIm$^{Me}$*], 124.30, 123.90, 123.61 [*C*H, Ar*], 121.17, 120.99, 118.45, 117.91 [*C*H, bIm$^{Me}$*], 95.89 [*C*H], 67.82 [O*C*H$_2$, THF], 34.47 [*C*H$_3$, bIm$^{Me}$*], 28.69 [*C*H, $^{i}$Pr, Ar*], 27.06 [*C*H, $^{i}$Pr, Ar*], 25.64 [O*C*H$_2$, THF], 25.43 [*C*H$_3$, $^{i}$Pr, Ar*], 25.39 [*C*H$_3$], 24.48 [*C*H$_3$, $^{i}$Pr, Ar*], 23.57 [*C*H$_3$, $^{i}$Pr, Ar*], 22.84 [*C*H$_3$, $^{i}$Pr, Ar*].

**Synthesis of [{Ar*NC(Me)CHC(Me)NAr*}Mg(Bu)(bIm$^{Me}$)] (8).** Isolated crystals of **1** (0.57 g, 1 mmol) were added to a Schlenk tube and dissolved in THF (5 ml). *N*-Methylbenzimidazole (0.13 g, 1 mmol) was added and the pale yellow solution stirred for 2 hours. After storage in the freezer overnight, a crop of colorless crystals was produced (0.28 g, 43 %). $^{1}$H NMR ($C_6D_6$, 298K ) δ8.48 [d, 1H, bIm$^{Me}$], 7.92 [s, 1H, N=C*H*NMe, bIm$^{Me}$], 7.31-7.11 [m, 6H, 4H of Ar* and 2H of MeBIm], 7.07 [d, 2H, Ar*], 6.90 [d, 1H, bIm$^{Me}$], 5.21 [s, 1H, C*H*], 3.83 [m, 2H, C*H*, $^{i}$Pr, Ar*], 2.95 [m, 2H, C*H*, $^{i}$Pr,

4 M. Zhu, K. Fujita, R. Yamaguchi, *Chem. Comm.* **2011**, *47*, 12876.

Ar*], 2.63 [s, 3H, C*H*$_3$, bIm$^{Me}$], 1.86 [s, 6H, C*H*$_3$], 1.69 [d, 6H, C*H*$_3$, $^{i}$Pr, Ar*], 1.49 [m, 2H, C*H*$_2$, Bu], 1.42 [d, 6H, C*H*$_3$, $^{i}$Pr, Ar*], 1.32 [m, 2H, C*H*$_2$, Bu], 1.06 [m, 3H, CH$_3$, Bu], 0.97 [d, 6H, C*H*$_3$, $^{i}$Pr, Ar*] ], 0.26 [d, 6H, C*H*$_3$, $^{i}$Pr, Ar*], -0.10 [m, 2H, Mg-C*H*$_2$, Bu]. $^{13}$C NMR{$^{1}$H} ($C_6D_6$, 298K) 167.59 [CH*C*(Me)], 146.25 [*C*, Ar*], 145.23 [N=*C*HNMe, bIm$^{Me}$], 142.75, 142.30, 140.98, 134.04 [*C*, Ar* and bIm$^{Me}$], 124.84, 124.01, 123.83, 123.71, 123.28, 120.64, 109.59 [*C*H, Ar* and bIm$^{Me}$], 93.87 [*C*H], 33.08, 32.14 [*C*H$_2$, Bu], 30.03 [*C*H$_3$, bIm$^{Me}$], 28.92 [*C*H, $^{i}$Pr, Ar*], 27.19 [*C*H, $^{i}$Pr, Ar*], 25.59 [*C*H$_3$, $^{i}$Pr, Ar*], 24.75 [*C*H$_3$, $^{i}$Pr, Ar*], 24.40 [*C*H$_3$, $^{i}$Pr, Ar*], 24.02 [*C*H$_3$], 22.89 [*C*H$_3$, $^{i}$Pr, Ar*], 14.43 [*C*H$_3$, Bu], 6.83 [*C*H$_2$, Mg-Bu].

**Table S1.** Selected crystallographic and refinement parameters.

| **Compound** | **1** | **2** | **3** | **4** | **5** | **7** | **8** |
|---|---|---|---|---|---|---|---|
| formula | $C_{37}H_{58}MgN_2O$ | $C_{38}H_{59}MgN_3$ | $C_{40}H_{53}MgN_3O_2$ | $C_{78}H_{104}Mg_2N_6S_2$ | $C_{48}H_{60}MgN_4O_{1.25}S_2$ | $C_{80}H_{110}Mg_2N_8$ | $C_{42.5}H_{61.5}MgN_4$ |
| F. weight | 571.16 | 582.19 | 632.16 | 1238.1 | 801.43 | 1232.38 | 652.77 |
| Cryst syst. | triclinic | monoclinic | trigonal | monoclinic | monoclinic | monoclinic | monoclinic |
| sp. gr. | P-1 | $P2_1/n$ | R3m | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ | $P2_1/n$ |
| *a* Å | 9.1792(4) | 9.0121(2) | 32.394(6) | 13.5757(17) | 18.964(5) | 12.703(3) | 14.0179(4) |
| *b* Å | 12.1190(4) | 20.1333(5) | 32.394(6) | 14.4034(18) | 12.505(3) | 21.654(5) | 13.5976(3) |
| *c* Å | 15.8077(6) | 19.8758(4) | 11.017(2) | 18.932(2) | 38.624(10) | 13.282(3) | 21.7756(6) |
| $\alpha$ ° | 85.527(3) | 90 | 90 | 90 | 90 | 90 | 90 |
| $\beta$ ° | 77.912(3) | 91.504(2) | 90 | 92.2137(13) | 96.385(3) | 90.01(2) | 96.842(3) |
| $\gamma$ ° | 87.404(3) | 90 | 120 | 90 | 90 | 90 | 90 |
| V Å$^3$ | 1713.51(11) | 3605.09(14) | 10012(3) | 3699.1(8) | 9103 | 3653.5(15) | 4121.08(19) |
| T K | 123 | 123 | 150 | 150 | 120 | 123 | 123 |
| Z | 2 | 4 | 9 | 2 | 8 | 2 | 4 |
| λ Å | 0.71073 | 0.71073 | 0.6889 | 0.6889 | 0.6889 | 0.71073 | 0.71073 |
| μ mm$^{-1}$ | 0.082 | 0.077 | 0.069 | 0.126 | 0.159 | 0.081 | 0.075 |
| 2θmax ° | 58.0 | 54 | 48.0 | 48.4 | 48.4 | 50 | 52 |
| refls. coll. | 20725 | 20209 | 23375 | 26382 | 69167 | 9900 | 21699 |
| refls. uniq. | 8803 | 7869 | 1967 | 6415 | 16016 | 5404 | 8074 |
| refls. obs. | 5110 | 6088 | 1919 | 5418 | 11598 | 1931 | 5016 |
| Rint | 0.0449 | 0.0299 | 0.0588 | 0.0865 | 0.0683 | 0.1131 | 0.0380 |
| GoF | 0.900 | 1.054 | 1.112 | 1.157 | 1.037 | 1.026 | 0.978 |
| R[I>2σ(I)][a] | 0.0513 | 0.0478 | 0.0751 | 0.0830 | 0.0746 | 0.0995 | 0.0640 |
| Rw2[b] | 0.1217 | 0.1216 | 0.1877 | 0.2099 | 0.1956 | 0.2343 | 0.1953 |

[a] Based on *F* and observed reflections only.
[b] Based on $F^2$ and all unique reflections.

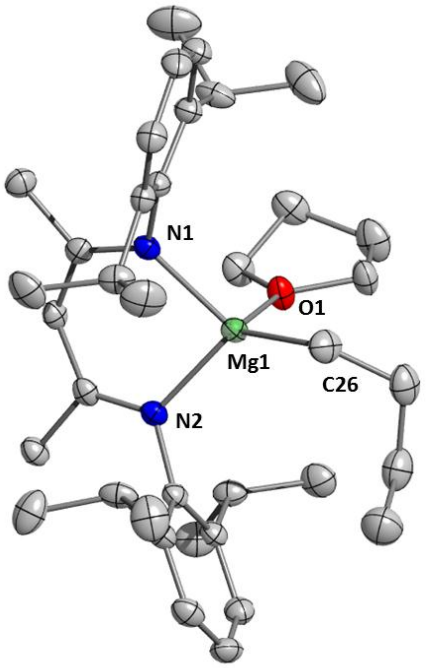


**Figure S1.** Molecular structure of **1** with 50% probability displacement ellipsoids.[5] Hydrogen atoms are omitted for clarity. Selected geometrical parameters for **1** (distances in Å and angles in deg): Mg(1)-N(1) 2.0657(14), Mg(1)-N(2) 2.0594(14), Mg(1)-O(1) 2.0544(12), Mg(1)-(C26) 2.1268(16), N(1)-Mg(1)-N(2) 92.96(5), O(1)-Mg(1)-N(1) 102.70(5), O(1)-Mg(1)-N(2) 101.10(5), N(1)-Mg(1)-C(26) 118.96(6), N(2)-Mg(1)-C(26) 126.35(7), O(1)-Mg(1)-C(26) 110.94(6)

[5] A structural determination of **1** using X-ray crystallography has also been recently reported by Chisholm *et al*, see: M. H. Chisholm, K. Choojun, J. C. Galluci, P. M. Wambua, *Chem. Sci*. **2012**, *2*, 3445.

## NMR spectra

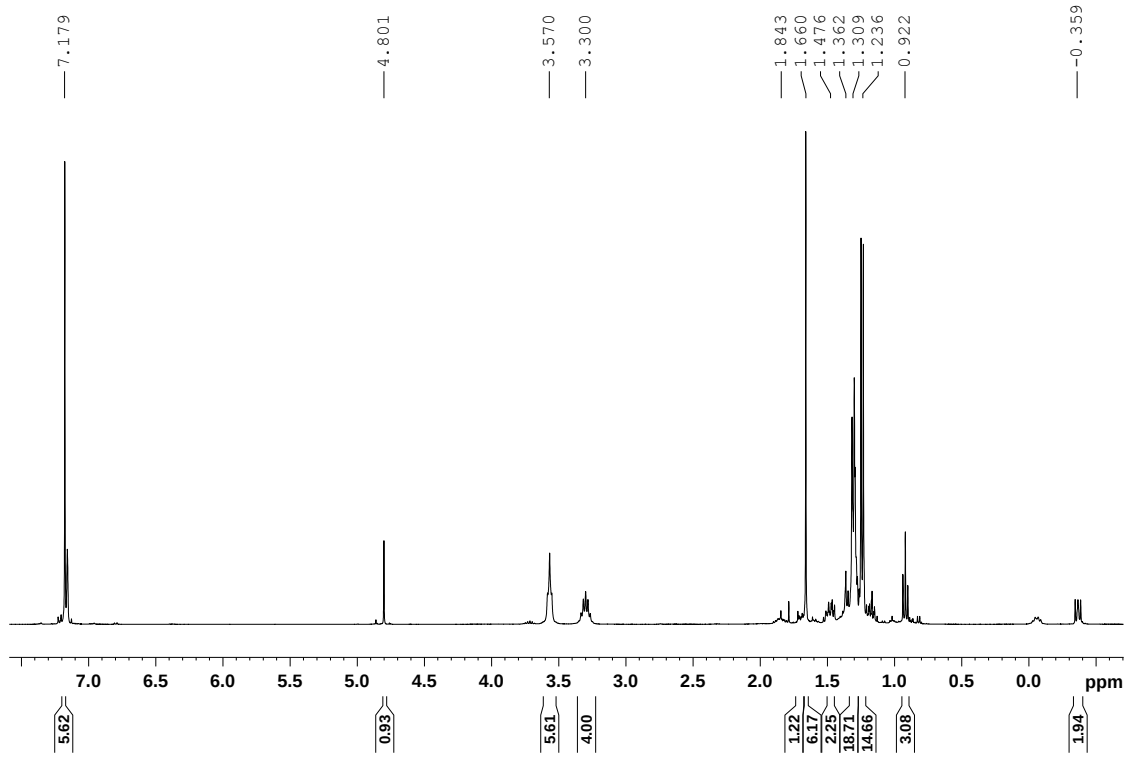


**Figure S2**: $^{1}$H NMR of [($^{Dipp}$Nacnac)Mg(Bu)(THF)] **1** in $C_6D_6$ solution

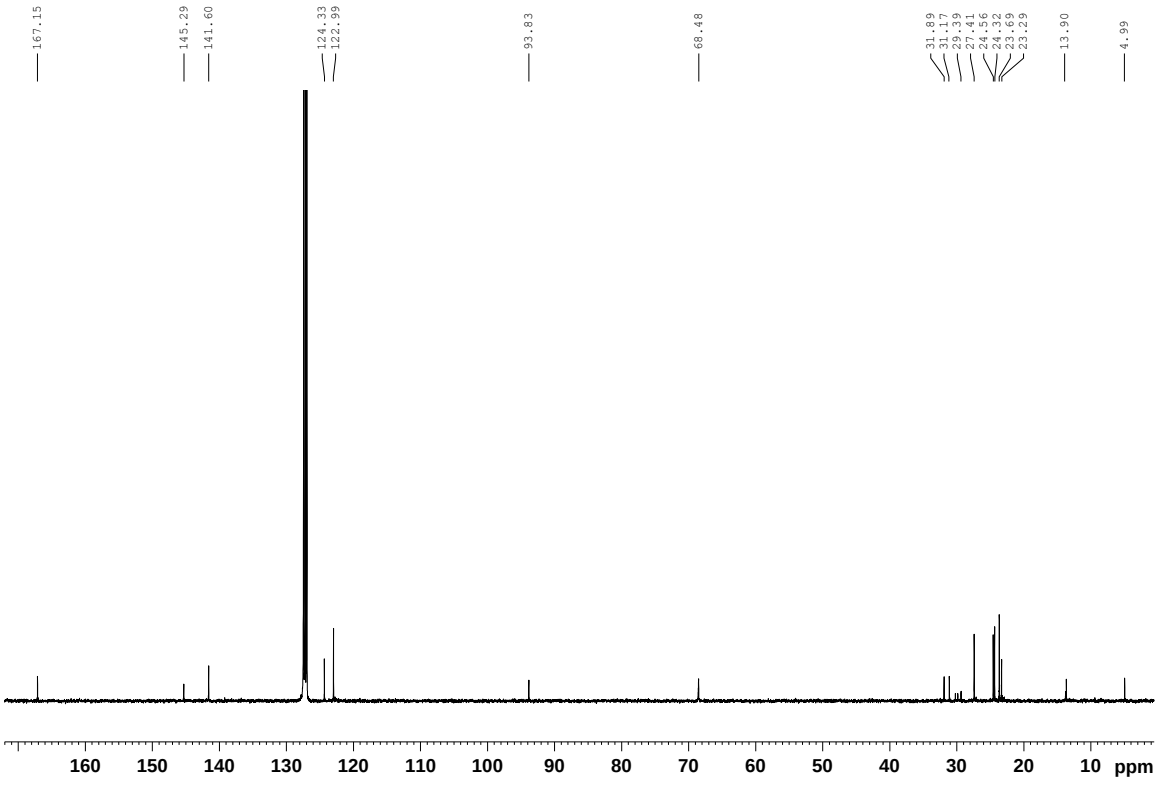


**Figure S3**: $^{13}$C{$^{1}$H} NMR of [($^{Dipp}$Nacnac)Mg(Bu)(THF)] **1** in $C_6D_6$ solution

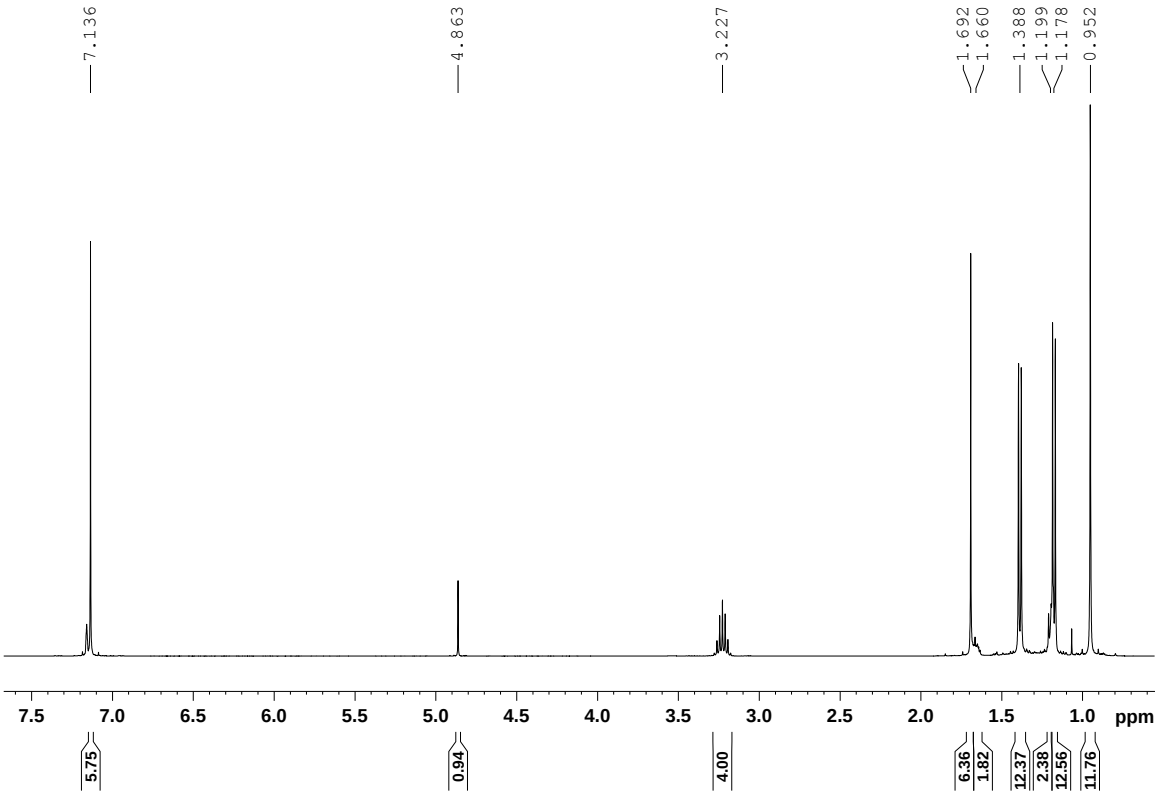


**Figure S4**: $^{1}$H NMR of [($^{Dipp}$Nacnac)Mg(TMP)] **2** in $C_6D_6$ solution

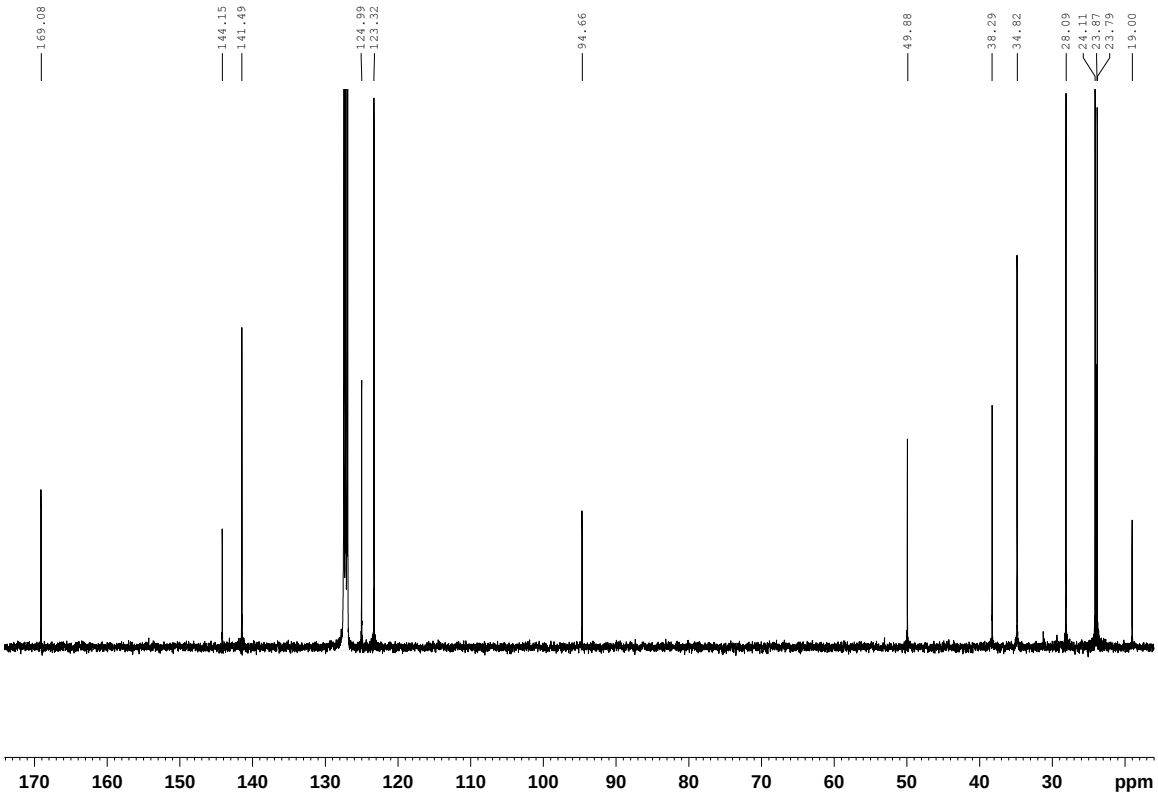


**Figure S5**: $^{13}$C{$^{1}$H} NMR of [($^{Dipp}$Nacnac)Mg(TMP)] **2** in $C_6D_6$ solution

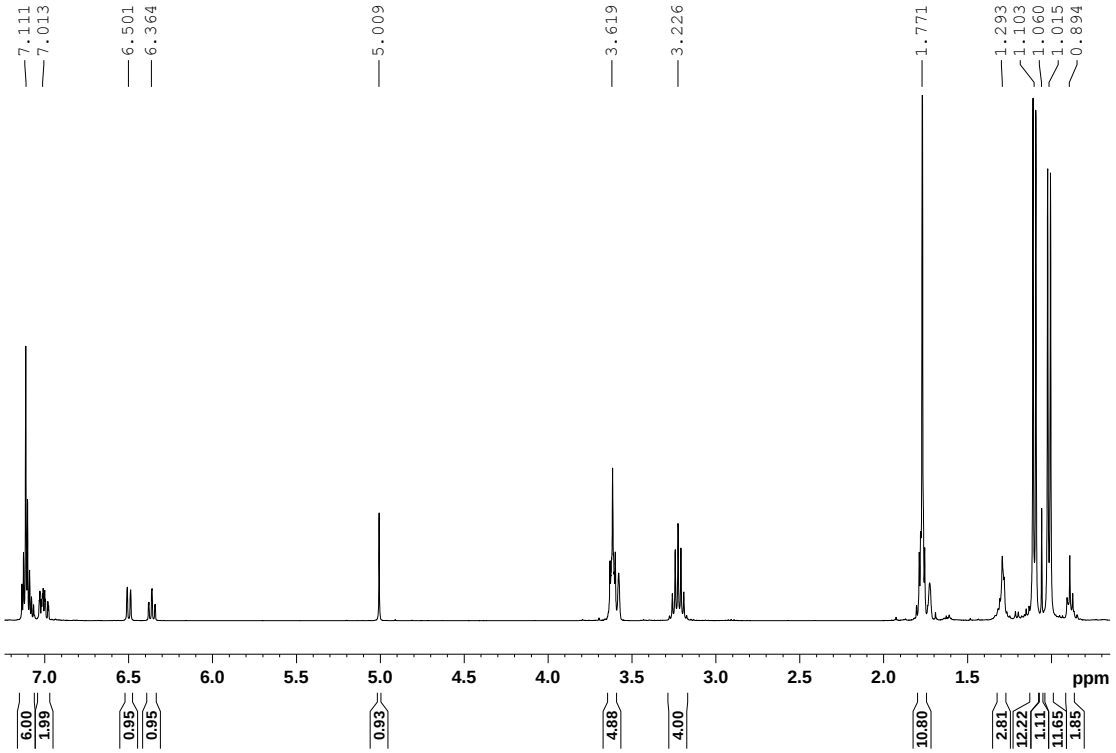


**Figure S6**: $^{1}$H NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg{O(o-$C_6H_4$)NC}(THF)] **3** in $d_8$-THF solution

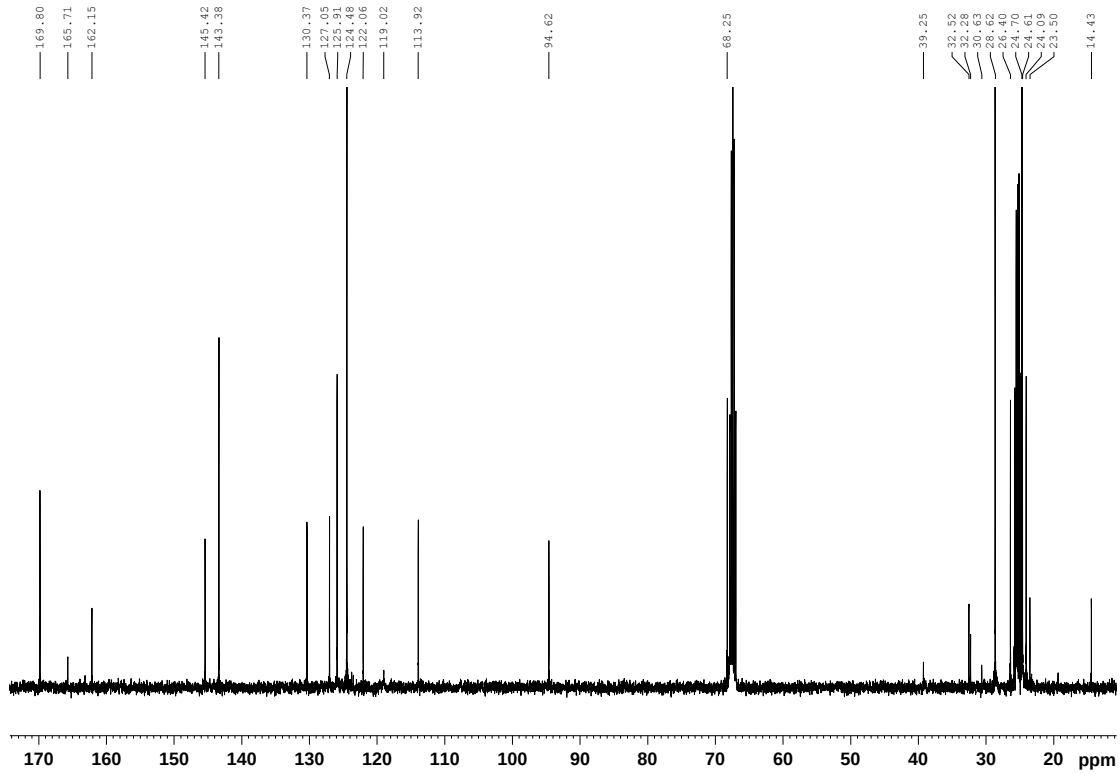


**Figure S7**: $^{13}$C{$^{1}$H} NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg{O(o-$C_6H_4$)NC}(THF)] **3** in $d_8$-THF solution

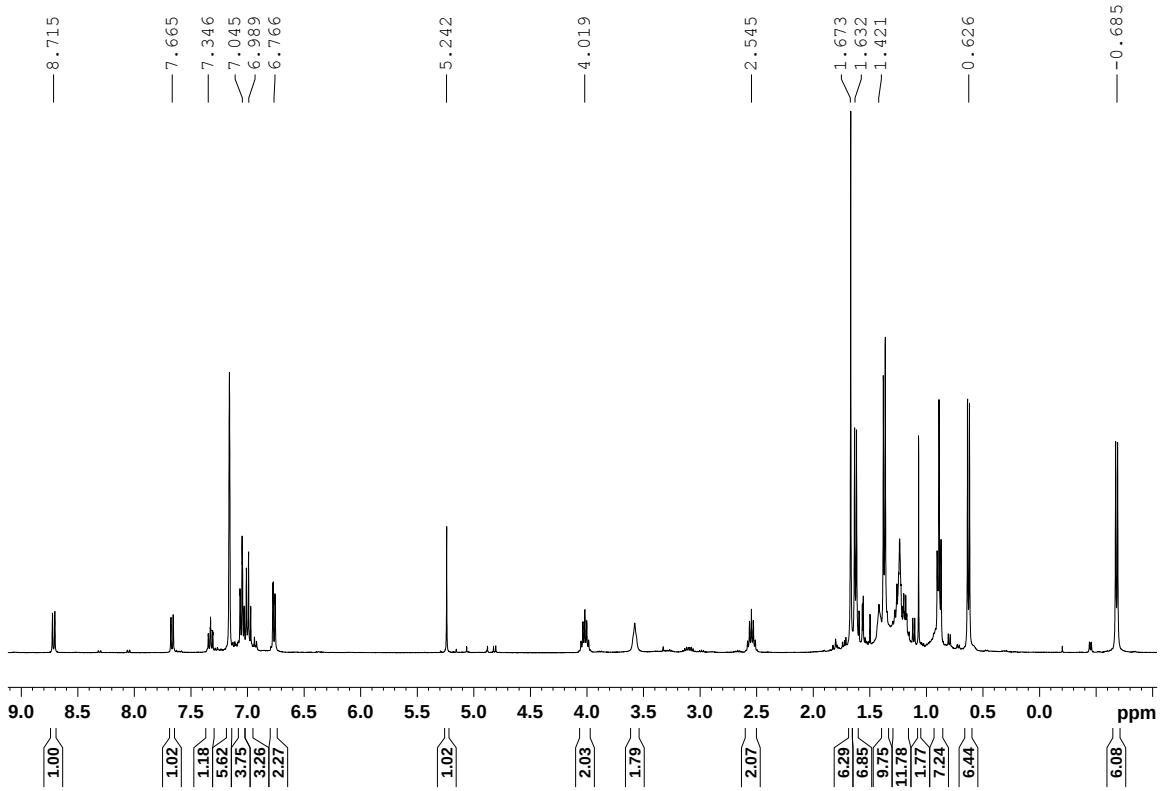


**Figure S8**: $^{1}$H NMR of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${btz*}$_2$] **4** in $C_6D_6$ solution

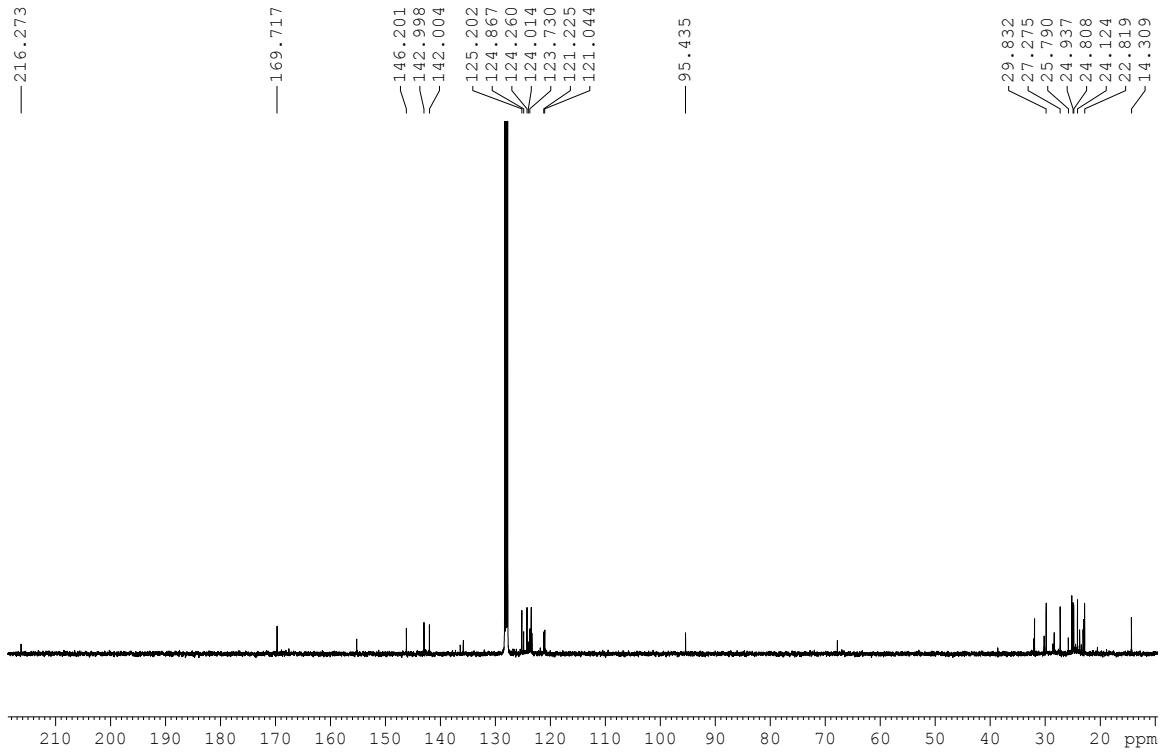


**Figure S9**: $^{13}$C{$^{1}$H} NMR of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${btz*}$_2$] **4** in $C_6D_6$ solution

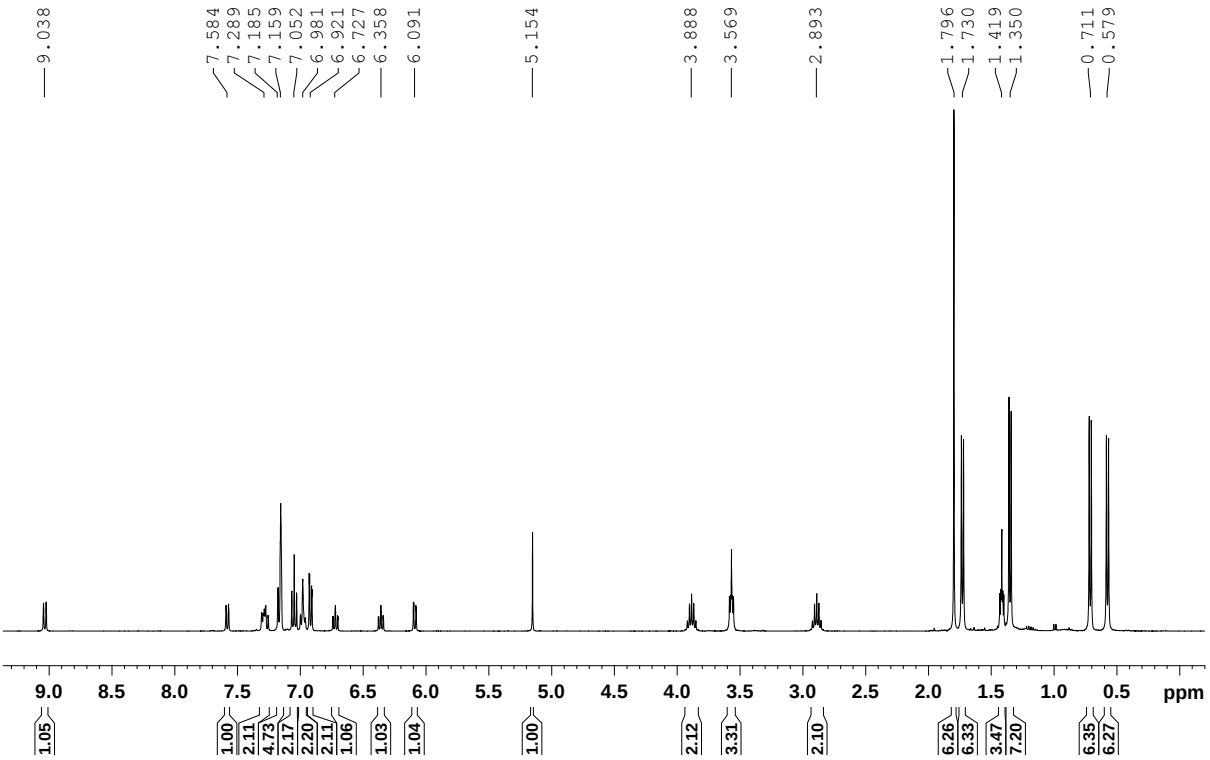


**Figure S10**: $^{1}$H NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg{(btz*)C(H)=N(*o*-$C_6H_4$)S)}] **5** in $C_6D_6$ solution

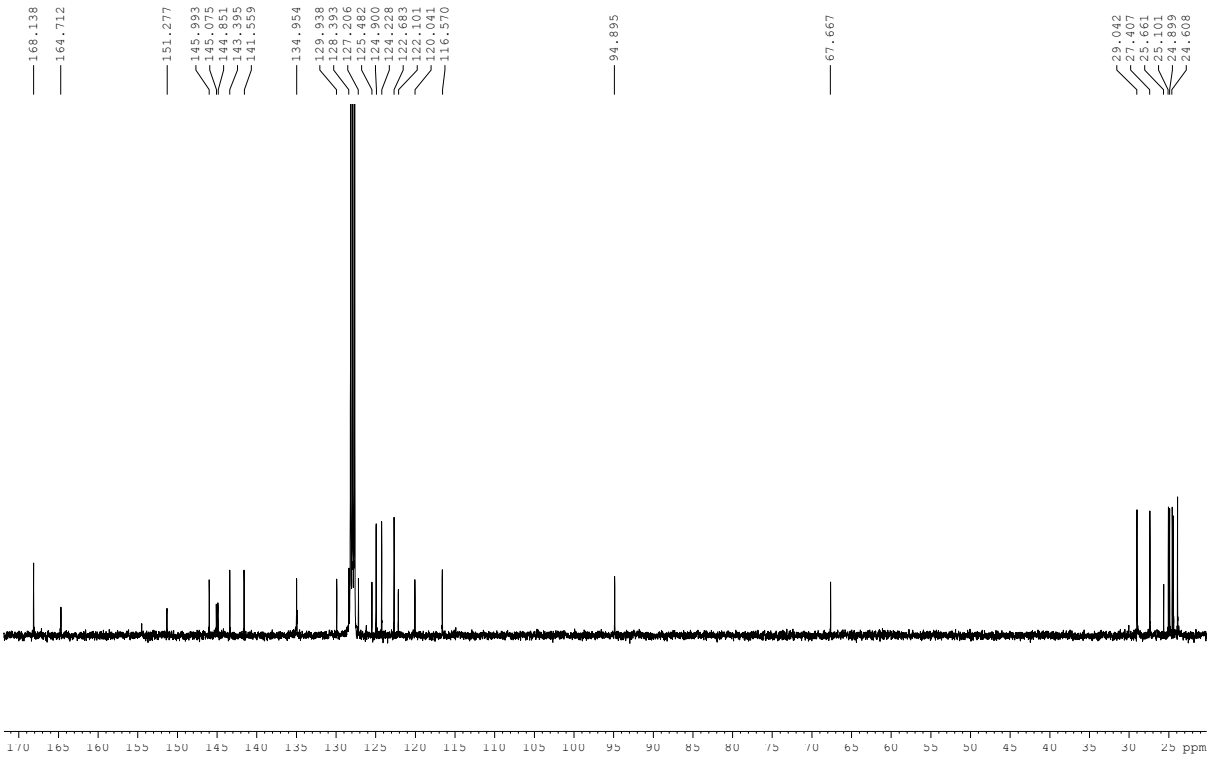


**Figure S11**: $^{13}$C{$^{1}$H} NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg{(btz*)C(H)=N(*o*-$C_6H_4$)S)}] **5** in $C_6D_6$ solution

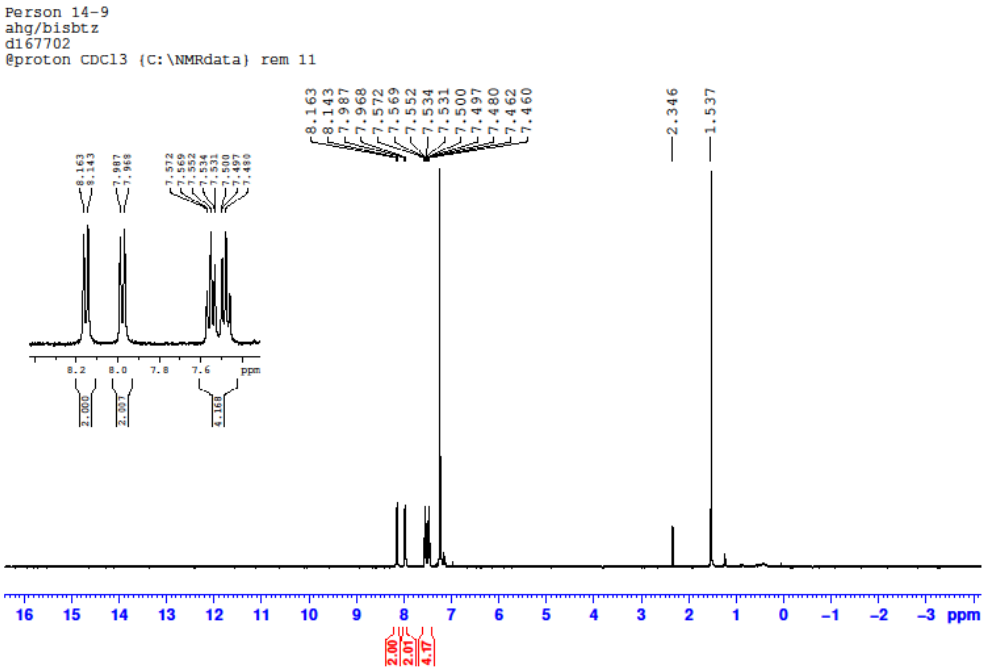


**Figure S12**: $^{1}$H NMR of **6** in $CDCl_3$ solution

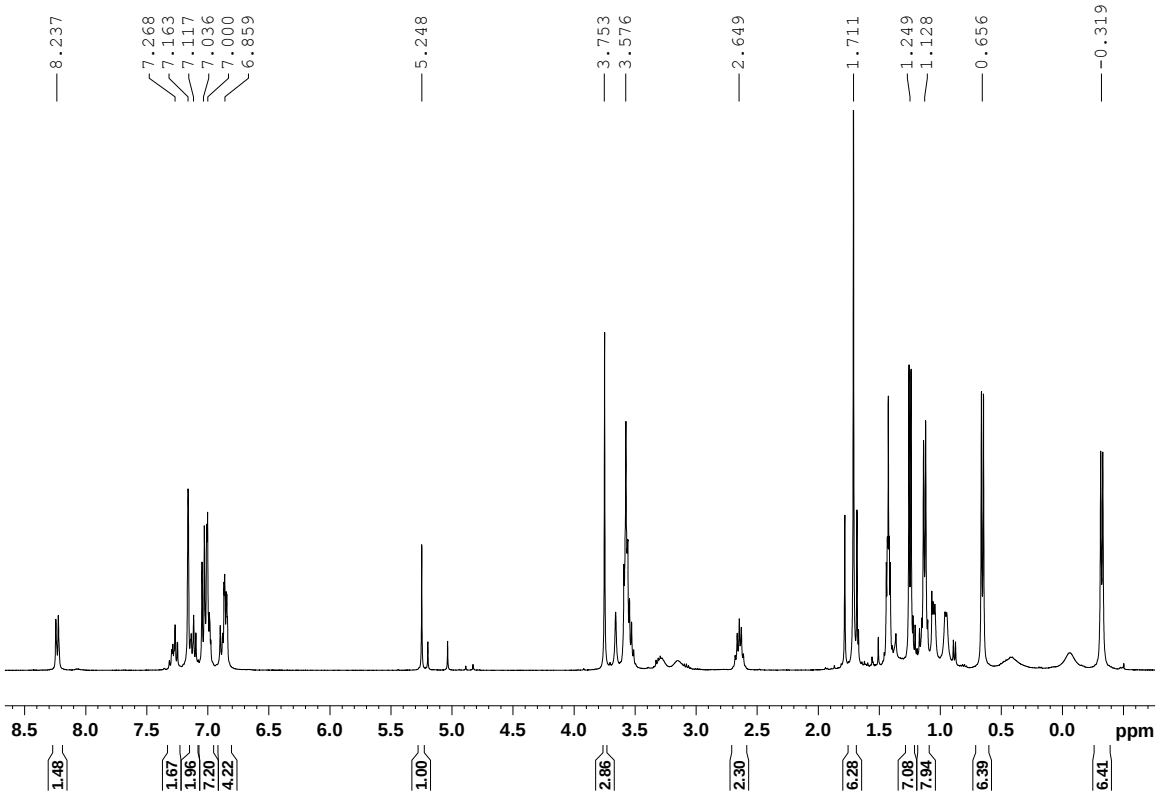


**Figure S13**: $^{1}$H NMR of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${bIm$^{Me}$*}$_2$] **7** in $C_6D_6$ solution

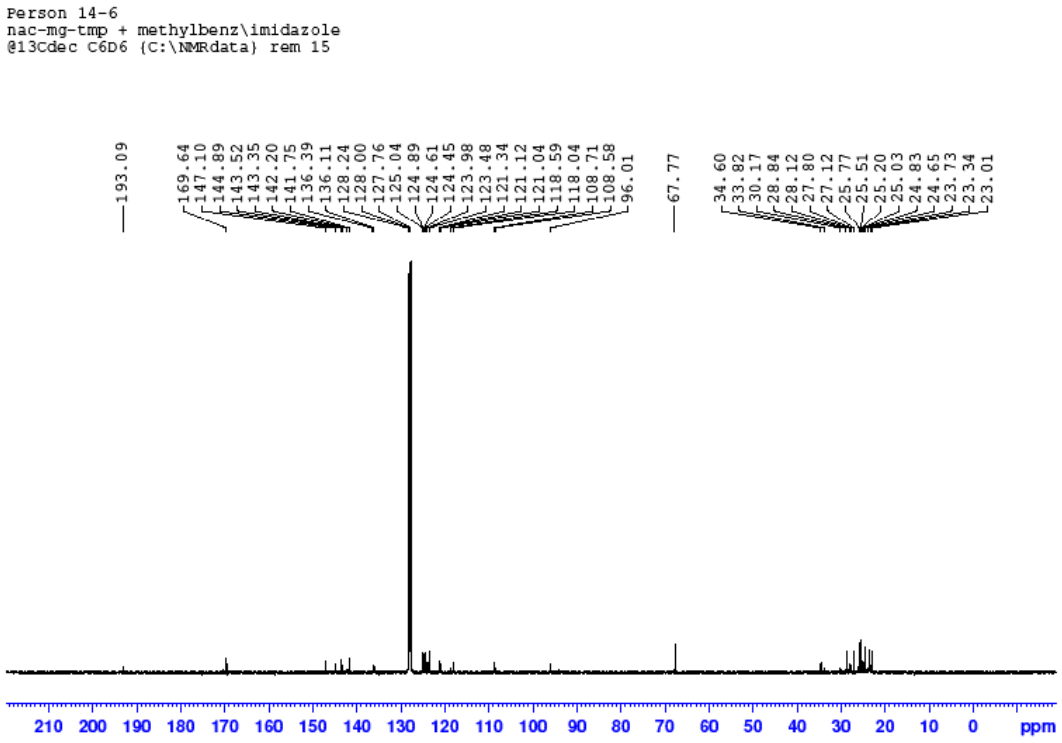


**Figure S14**: $^{13}C\{^{1}H\}$ NMR of [{Ar*NC(Me)CHC(Me)NAr*}$_2$Mg$_2${bIm$^{Me}$*}$_2$] **7** in $C_6D_6$ solution

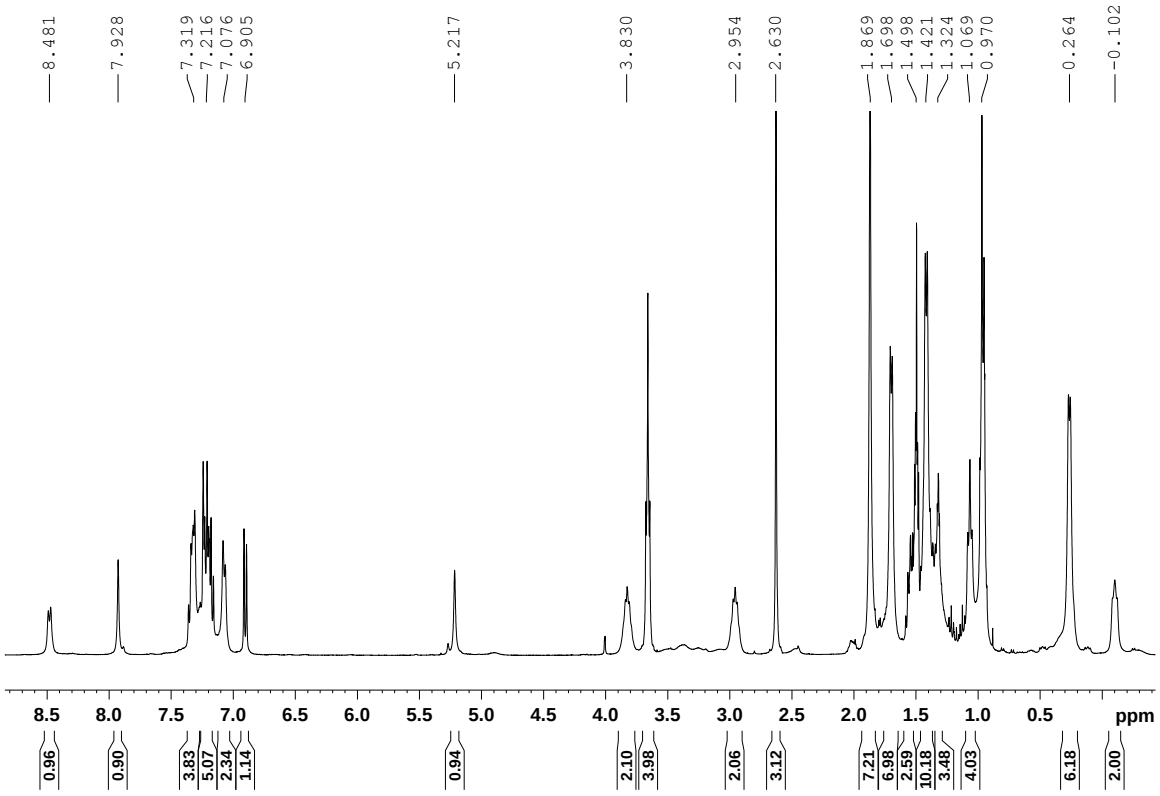

**Figure S15**: $^{1}$H NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg(Bu)(bIm$^{Me}$)] **8** in $C_6D_6$ solution

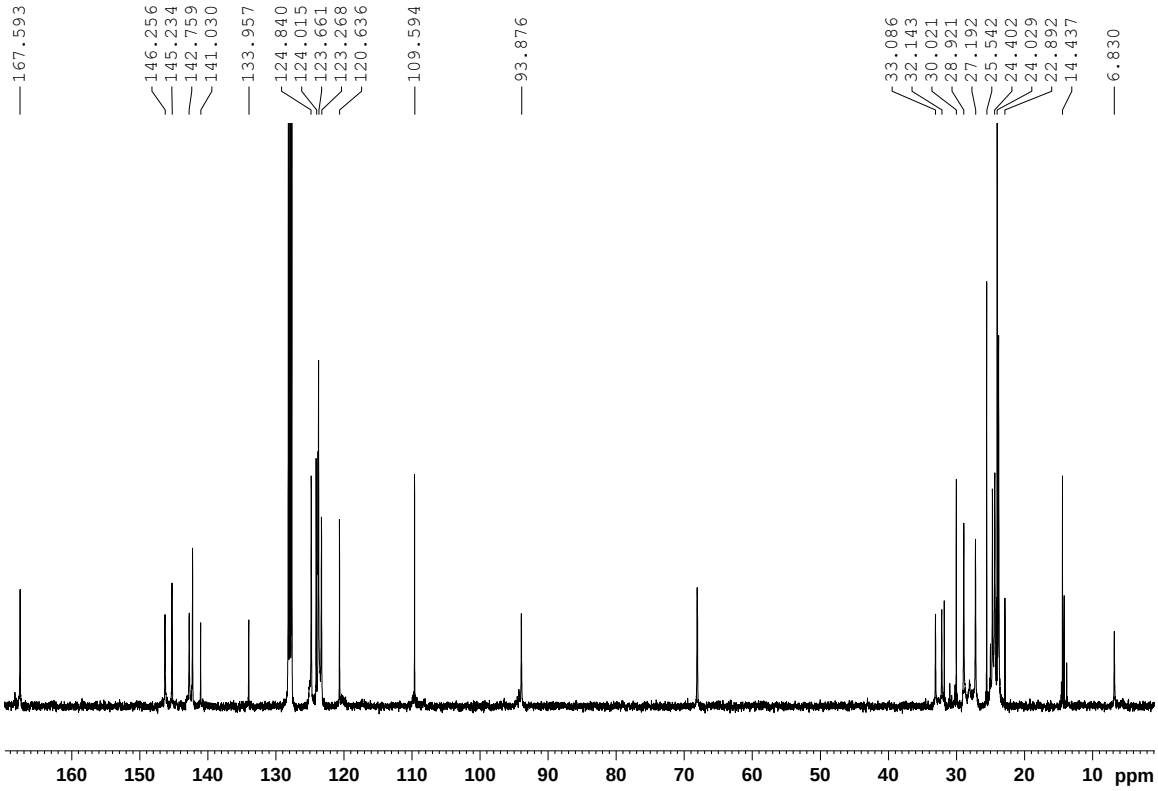


**Figure S16**: $^{13}$C{$^{1}$H} NMR of [{Ar*NC(Me)CHC(Me)NAr*}Mg(Bu)(bIm$^{Me}$)] **8** in $C_6D_6$ solution

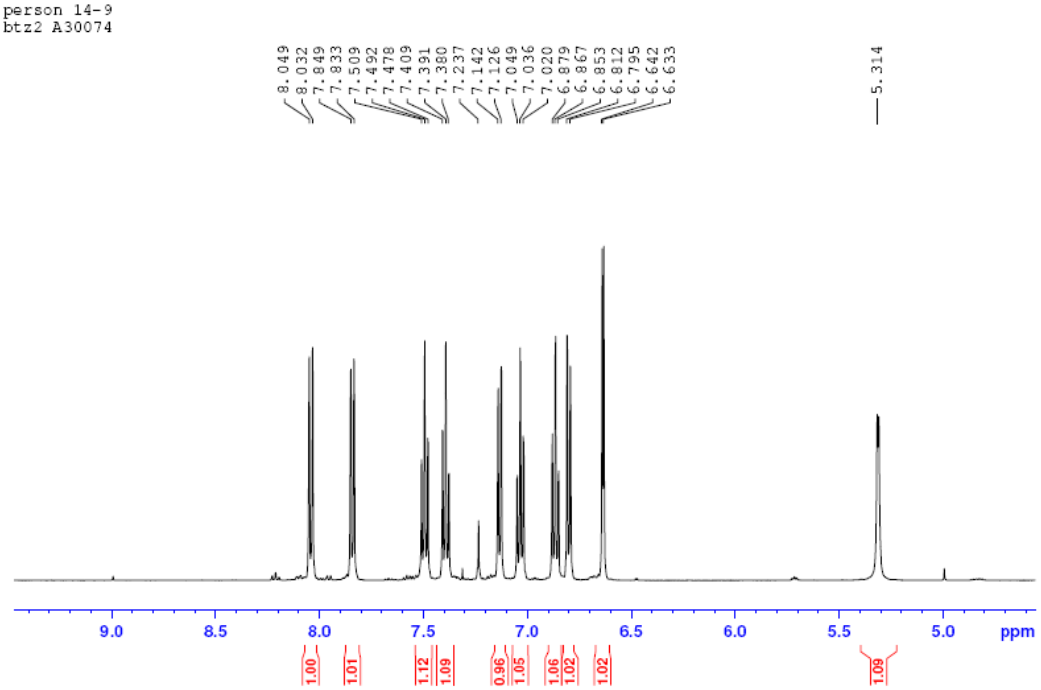


**Figure S17**: $^{1}$H NMR of 2,3-dihydro-2,2'-bis(benzothiazole) in $C_6D_6$ solution

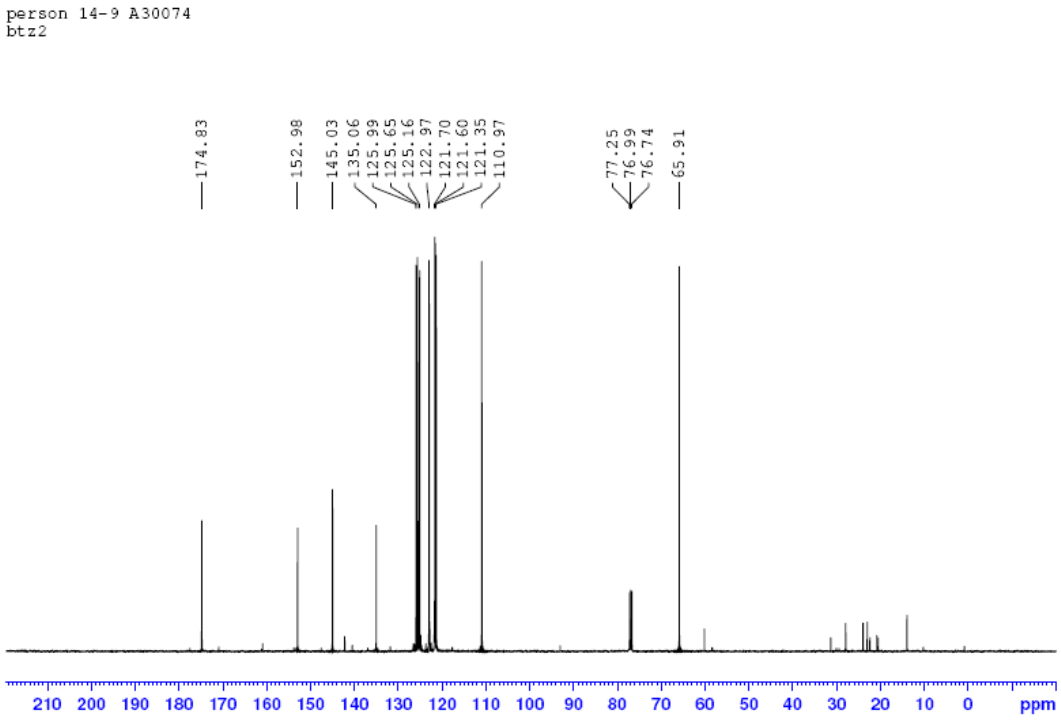


**Figure S18**: $^{13}$C{$^{1}$H} NMR of 2,3-dihydro-2,2'-bis(benzothiazole) in $C_6D_6$ solution