Supporting Information

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SI Text

General Conditions. All reactions were performed under a protective argon atmosphere by using standard Schlenk techniques. Hexane and THF were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use. $^t\mathrm{Bu_2Zn}$[1] was prepared according to literature methods. 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.

Synthesis of $[(\mathrm{THF})_4\mathrm{Mg}(\mu\text{-Cl})_2\mathrm{Zn}(^t\mathrm{Bu})(\mathrm{Cl})]$ (1). A solution of *tert*-butylmagnesium chloride (2 mL of a 1 M solution in THF, 2 mmol) in THF (10 mL) was cooled to 0 °C, and zinc chloride (2 mL of a 1 M solution in diethyl ether, 2 mmol) was added dropwise, resulting in the formation of a white precipitate. After stirring for 1 h at 0 °C, the solid was removed by filtration. The filtrate was concentrated in vacuo (to approx. 3 mL), and then hexane (2 mL) was added. The resulting colorless solution was then transferred to the freezer (−30 °C) and after 48 h a crop of colorless crystals of **1** were isolated (average isolated yield = 0.11g, 10%). The isolated yield of **1** could be improved to ~95% by reacting ^{t}BuZnCl (2 mmol) with $\mathrm{MgCl_2}$ (2 mmol) in THF. ^{1}H NMR (400.13 MHz, 298 K, d_8-THF) δ 3.63 [16 H, m, $\mathrm{OCH_2}$, THF], 1.77 [16 H, m, $\mathrm{CH_2}$, THF], 0.99 [9 H, s, $\mathrm{C(CH_3)_3}$]. No changes in the ^{1}H spectrum of **1** were observed when low temperature NMR studies were carried out at −40 °C, suggesting that even at subambient temperatures, **1** retains its bimetallic constitution. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, 298 K, d_8-THF) δ 68.5 [$\mathrm{OCH_2}$, THF], 33.6 [$\mathrm{C(CH_3)_3}$], 26.5 [$\mathrm{CH_2}$, THF], 21.9 [$\mathrm{C(CH_3)_3}$].

Synthesis of $[\{\mathrm{Mg_2Cl_3(THF)_6}\}^+\{\mathrm{Zn}^t\mathrm{Bu_3}\}^-]$ (4). A solution of *tert*-butylmagnesium chloride (6 mL of a 1 M solution in THF, 6 mmol) in THF (10 mL) was cooled to 0 °C, and zinc chloride (2 mL of a 1 M solution in diethyl ether, 2 mmol) was added dropwise. The resulting colorless solution was stirred for 1 h at 0 °C, concentrated in vacuo (to approx. 3 mL) and then transferred to the freezer (−30 °C). After 24 h a crop of colorless crystals of $[\mathrm{(THF)_4MgCl_2}]$ were isolated (0.54 g, 1.4 mmol). To the filtrate was added hexane (2 mL) and the resulting solution returned to the freezer for 48 h. A batch of colorless crystals of **4** were isolated (average crystalline yield = 0.39 g, 38%). Compound **4** could also be prepared by using an alternative co-complexation route by reacting ^{t}BuMgCl with $^t\mathrm{Bu_2Zn}$. ^{1}H NMR (400.13 MHz, 298K, d_8-THF) δ 3.63 [24 H, m, $\mathrm{OCH_2}$, THF], 1.77 [24 H, m, $\mathrm{CH_2}$, THF], 0.97 [1.91 H, s, $\mathrm{C(CH_3)_3}$, $^t\mathrm{Bu_2Zn}$], 0.91 [23.4 H, s, $\mathrm{C(CH_3)_3}$, $\mathrm{Zn}^t\mathrm{Bu}_3^-$], 0.89 [0.59 H, s, $\mathrm{C(CH_3)_3}$, ^{t}BuMgCl], 0.87 [0.42 H, s, $\mathrm{C(CH_3)_3}$,^{t}BuMgCl]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, 298 K, d_8-THF) δ 68.5 [$\mathrm{OCH_2}$, THF], 36.8 [$\mathrm{C(CH_3)_3}$, $\mathrm{Zn}^t\mathrm{Bu}_3^-$], 35.9 [$\mathrm{C(CH_3)_3}$, [^{t}BuMgCl], 35.2 [$\mathrm{C(CH_3)_3}$, ^{t}BuMgCl], 33.1 [$\mathrm{C(CH_3)_3}$, $^t\mathrm{Bu_2Zn}$], 26.5 [$\mathrm{CH_2}$, THF], 25.4 [$\mathrm{C(CH_3)_3}$, $^t\mathrm{Bu_2Zn}$], 24.2 [$\mathrm{C(CH_3)_3}$, $\mathrm{Zn}^t\mathrm{Bu}_3^-$], 15.8 [$\mathrm{C(CH_3)_3}$,^{t}BuMgCl], 15.2 [$\mathrm{C(CH_3)_3}$,^{t}BuMgCl].

Synthesis of $[\{\mathrm{Mg_2Cl_3(THF)_6}\}^+\{\mathrm{Zn}(p\text{-Tol})_3\}^-]$ (5). Compound **4** was generated in situ by adding $\mathrm{Zn}^t\mathrm{Bu_2}$ (0.36 g, 2 mmol in 10 ml THF) to a solution of *tert*-butylmagnesium chloride (1 M solution in THF, 2 ml, 2 mmol) in THF (10 ml). 4-iodotoluene (1.308 g, 6 mmol) was then introduced and the resulting yellow solution stirred for 30 min at room temperature. The volatiles (including ^{t}BuI) were then removed in vacuo, then THF (20 mL) was added and the solution stirred at room temperature for 1 h. The solution was concentrated in vacuo, and then transferred to the freezer for 48 h. A batch of colourless crystals of **5** were isolated (average crystalline yield = 0.994 g, 60%). Compound **5** can also be obtained when compound **4** is prepared by using the metathetical approach (3 M equivalents of ^{t}BuMgCl and $\mathrm{ZnCl_2}$) however the resulting crystalline samples of **5** proved to be contaminated by co-crystallisation of $[\mathrm{(THF)_4MgCl_2}]$. ^{1}H NMR (400.13 MHz, 298 K, d_8-THF) δ 7.67 [6 H, d, $\mathrm{CH_{ortho}}$], 6.87 [6 H, d, $\mathrm{CH_{meta}}$], 3.61 [24 H, m, $\mathrm{OCH_2}$, THF], 2.21 [9 H, s, $\mathrm{CH_3}$], 1.77 [24 H, m, $\mathrm{OCH_2}$, THF]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, 298 K, d_8-THF) δ 162.8 [$\mathrm{Zn\text{-}C_{ipso}}$], 141.3 [$\mathrm{C_{ortho}}$], 133.0 [$\mathrm{C_{para}}$], 127.5 [$\mathrm{C_{meta}}$], 68.5 [$\mathrm{OCH_2}$, THF], 26.6 [$\mathrm{CH_2}$, THF], 22.0 [$\mathrm{CH_3}$].

Cross-Coupling of 4-Iodotoluene with Iodobenzene. Following the procedure described above, tris(aryl) magnesium zincate **5** (1 mmol) was prepared by reaction of tris(alkyl) magnesium zincate **4** (1 mmol) and 3 M equivalents of 4-iodotoluene (0.654 g, 3 mmol) in THF at room temperature. A solution of $\mathrm{PdCl_2(dppf)_2}$ (0.054 g, 2.5 mol%) and Iodobenzene (0.34 mL, 3 mmol) in THF (10 mL),was added, affording a yellow suspension that was stirred at room temperature for 48 h. The reaction was quenched with a solution of saturated $\mathrm{NH_4Cl}$, extracted with $\mathrm{Et_2O}$ (3 × 15 mL) and dried over $\mathrm{MgSO_4}$. The solvent was removed in vacuo, and the crude product purified by column chromatography ($\mathrm{SiO_2}$, hexane). The product (0.334 g, 66%) was obtained as a white solid. When this reaction was carried out using isolated crystals of **5** the yield of the cross-coupling rection was improved to 98%. ^{1}H NMR (400.13 MHz, 298 K, $\mathrm{CDCl_3}$) δ 7.58 [2 H, d, $\mathrm{H_c}$], 7.50 [2 H, d, $\mathrm{H_b}$], 7.43 [2 H, t, $\mathrm{H_d}$], 7.33 [1 H, t, $\mathrm{H_e}$], 7.26 [2 H, d, $\mathrm{H_a}$], 2.41 [3 H, s, $\mathrm{CH_3}$]. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (100.62 MHz, 298 K, $\mathrm{CDCl_3}$) δ 141.2 [$\mathrm{C_f}$], 138.4 [$\mathrm{C_g}$], 136.9 [$\mathrm{C_h}$], 129.5 [$\mathrm{C_a}$], 128.7 [$\mathrm{C_d}$], 126.9 [$\mathrm{C_b}$ and $\mathrm{C_c}$], 126.8 [$\mathrm{C_e}$], 21.0 [$\mathrm{CH_3}$].

Crystal Data for 1: $\mathrm{C_{20}H_{41}Cl_3MgO_4Zn}$; A colorless crystal fragment gave monoclinic space group $P2_1/c$, $a = 12.1266(3)$ $b = 10.5782(2)$ $c = 20.7697(5)$ Å, $\beta = 100.848(2)°$, $V = 2616.68(10)$ Å^3, $T = 123$ K, $Z = 4$, $\rho_{\mathrm{calc}} = 1.375$ Mg m^{-3}, $2\theta_{\max} = 56.3°$, MoK_α $\lambda = 0.71073$ Å. All structures were solved and refined to convergence on F^2 (SHELXS and SHELXL-97; G. M. Sheldrick, University of Göttingen, Germany). $R1 = 0.0374$ (for 3781 reflections with $I > 2\sigma(\mathrm{I})$) $wR2 = 0.0691$ and $S = 0.917$ for 283 parameters and 5614 unique reflections. Minimum/maximum residual electron density −0.311/0.446 eÅ^{-3}. Crystallographic data (excluding structure factors) for the compounds reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC 741906–741908 and 753728. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk). **Crystal Data for 3**: $\mathrm{C_{24}H_{48}Cl_6MgO_6Zn_2}$; A colorless crystal prism gave monoclinic space group $P2_1/n$, $a = 10.2436(2)$ $b = 13.7110(3)$ $c = 12.1826(2)$ Å, $\beta = 97.188(2)°$, $V = 1697.60(6)$ Å^3, $T = 123$ K, $Z = 2$, $\rho_{\mathrm{calc}} = 1.566$ Mg m^{-3}, $2\theta_{\max} = 51.96°$, MoK_α $\lambda = 0.71073$ Å. $R1 = 0.0277$ (for 2381 reflections with $I > 2\sigma(\mathrm{I})$) $wR2 = 0.0582$ and $S = 0.944$ for 187 parameters and 3329 unique reflections. Minimum/maximum residual electron density −0.218/0.313 eÅ^{-3}. **Crystal Data for 4:** $\mathrm{C_{40}H_{83}Cl_3Mg_2O_7Zn}$; A colorless crystal fragment gave orthorhombic space group $P2_12_12_1$, $a = 13.5244(2)$ $b = 18.7865(3)$ $c = 19.3262(3)$ Å, $V = 4910.33(13)$ Å^3, $T = 123$ K, $Z = 4$, $\rho_{\mathrm{calc}} = 1.213$ Mg m^{-3}, $2\theta_{\max} = 123.34°$, CuK_α $\lambda = 1.54185$ Å. $R1 = 0.0382$ (for 4416 reflections with $I > 2\sigma(\mathrm{I})$) $wR2 = 0.0751$ and $S = 0.877$ for 486 parameters and 6591 unique reflections. Minimum/maximum residual electron density −0.224/0.579 eÅ^{-3}. **Crystal Data for 5**: $C_{45}H_{69}Cl_3Mg_2O_6Zn$; A colorless fragment gave monoclinic space group $P2_1/c$, $a = 14.6632(14)$ $b = 21.3537(19)$ $c = 15.8903(16)$ Å, $\beta = 107.164(10)°$, $V = 4753.9(8)$ Å^3, $T = 123$ K, $Z = 4$, $\rho_{\text{calc}} = 1.294$ Mg m^{-3}, $2\theta_{\max} = 47°$, MoK$_\alpha$ $\lambda = 0.71073$ Å. $R1 = 0.0498$ (for 2783 reflections with $I > 2\sigma(\text{I})$) $wR2 = 0.0785$ and $S = 0.706$ for 509 parameters and 6,899 unique reflections. Minimum/maximum residual electron density −0.393/ 0.595 eÅ^{-3}.

Zn-I Exchange Reactivity Studies. Reaction of [(THF)$_4$Mg(μ-Cl)$_2$Zn(^{t}Bu)(Cl)] (1) with 4-Iodotoluene. Isolated crystals of **1** (0.135 g, 0.25 mmol) were dissolved in d_8-THF (0.5 mL), and analyzed by ^{1}H NMR spectroscopy. A solution of 4-iodotoluene (0.055 g, 0.25 mmol) in d_8-THF (0.2 mL) was then injected into the NMR tube, and the resulting solution was analyzed by ^{1}H NMR spectroscopy. After 24 h the ^{1}H NMR spectrum showed that no reaction had taken place, and only the starting materials were present.^{1}H NMR (400.13 MHz, 298 K, d_8-THF) δ 7.53 [2 H, d, H$_{\text{ortho}}$, 4-iodotoluene], 6.93 [2 H, d, H$_{\text{meta}}$, 4-iodotoluene], 3.62 [16 H, m, OCH_2, THF, **1**], 2.25 [3 H, s, CH_3, 4-iodotoluene], 1.76 [16 H, m, OCH_2, THF, **1**], 0.98 [9 H, s, $C(CH_3)_3$, **1**].

1. P. C. Andrikopoulos, D. R. Armstrong, H. R. L. Barley, W. Clegg, S. H. Dale, E. Hevia, G. W. Honeyman, A. R. Kennedy, R. E. Mulvey, *J Am Chem Soc.* 2005, 127, 6184.

Reaction of [{$Mg_2Cl_3(THF)_6$}$^+${Zn^{t}Bu$_3$}$^-$] (4) with 4-Iodotoluene. Following the same protocol as for **1**, isolated crystals of **4** (0.165 g, 0.20 mmol) were dissolved in d_8-THF (0.5 mL), placed in an NMR tube and analyzed by ^{1}H NMR spectroscopy. A solution of 4-iodotoluene (0.132 g, 0.60 mmol) in d_8-THF (0.2 mL) was then introduced, and the resulting pale yellow solution was analyzed by ^{1}H NMR spectroscopy. A ^{1}H NMR spectrum recorded 30 min after the addition revealed that 83% of zincate (**4**) have reacted to form the new zincate species [{$Mg_2Cl_3(THF)_6$}$^+${$ZnAr_3$}$^-$] (Ar = C_6H_4-Me) along with *tert*-butyliodide. ^{1}H NMR (400.13 MHz, 298 K, d_8-THF) δ 7.67 [6 H, d, CH,*p*Tol, **5**], 7.54 [1 H, d, CH, 4-iodotoluene], 6.93 [1 H, d, CH, 4-iodotoluene], 6.87 [6 H, d, CH,*p*Tol, **5**], 3.61 [24 H, m, OCH_2, THF], 2.25 (1.5 H, s, CH_3, 4-iodotoluene), 2.21 [9 H, s, CH_3,*p*Tol, **5**], 1.91 (6 H, s, $C(CH_3)_3$, ^{t}BuI), 1.77 [24 H, m, OCH_2, THF], 1.01 [3.8H, s, $C(CH_3)_3$, Zn^{t}Bu$_3$, **4**].

After 4 h s at room temperature, traces of a new arylzinc species and 4-*tert*-butyl-toluene can be observed (Fig. S2*B* and *C*).

NMR spectra data.

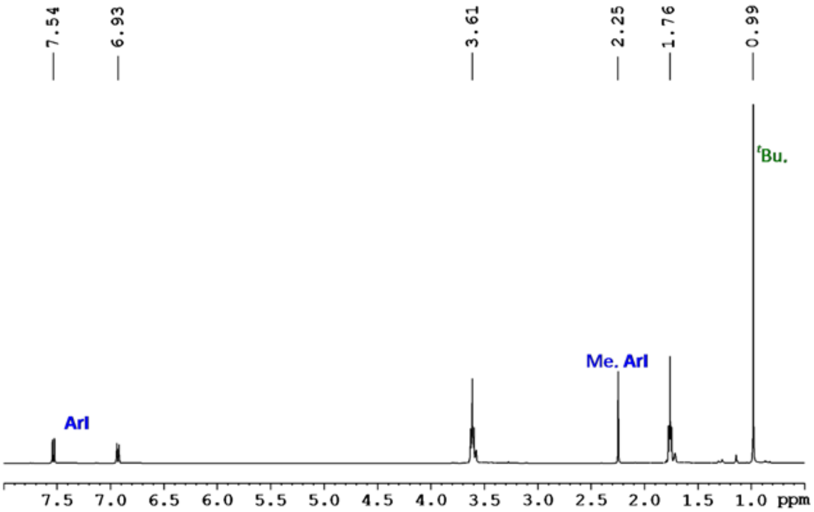

Fig. S1. ^{1}H NMR of reaction mixture of **1** with one equivalent of ArI in d_8-THF solution after 24 h.

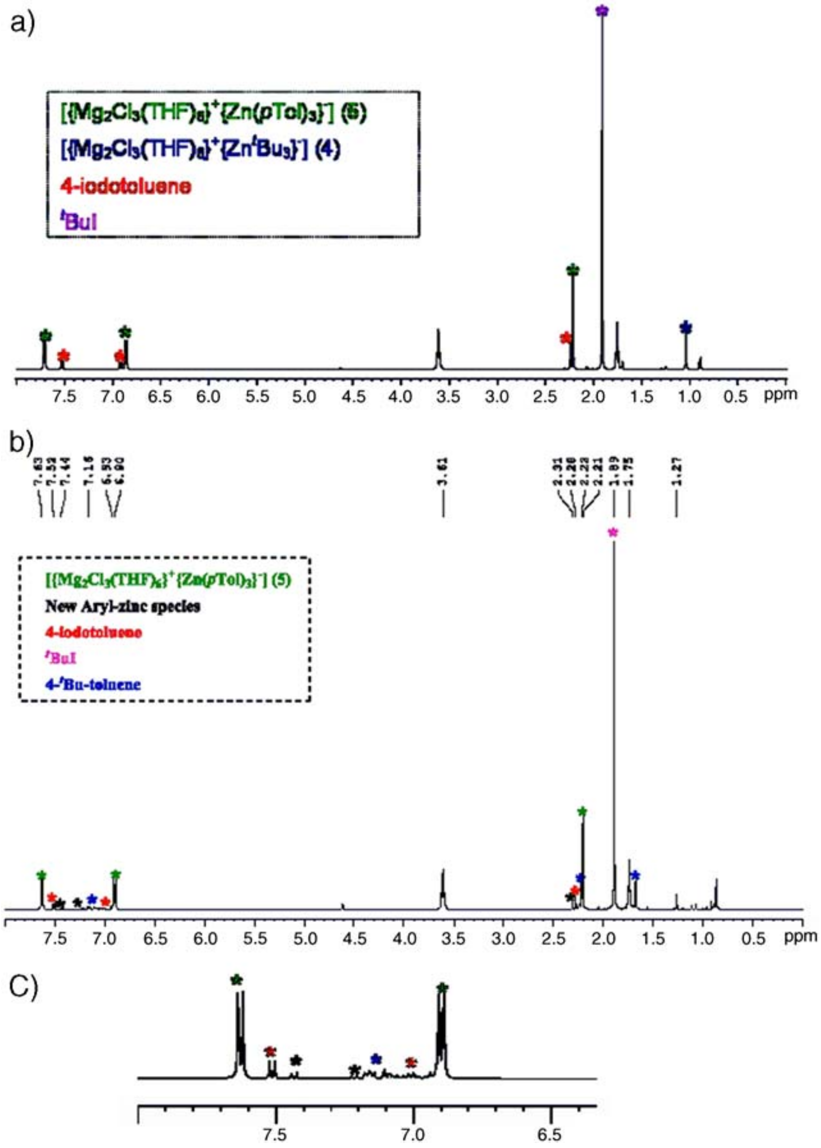

Fig. S2. *A*) ^{1}H NMR spectrum of [$\{Mg_2Cl_3(THF)_6\}^+\{Zn^tBu_3\}^-$] (**4**) in deuterated thf solution on the addition of 3 M equivalents of 4-iodotoluene after 30 min at room temperature. *B*) ^{1}H NMR spectrum of [$\{Mg_2Cl_3(THF)_6\}^+\{Zn^tBu_3\}^-$] (**4**) in deuterated thf solution on the addition of 3 M equivalents of 4-iodotoluene after 4 h at room temperature. *C*) Expansion of the aromatic region of ^{1}H NMR spectrum of [$\{Mg_2Cl_3(THF)_6\}^+\{Zn^tBu_3\}^-$] (**4**) in deuterated thf solution on the addition of 3 M equivalents of 4-iodotoluene after 4 h at room temperature.

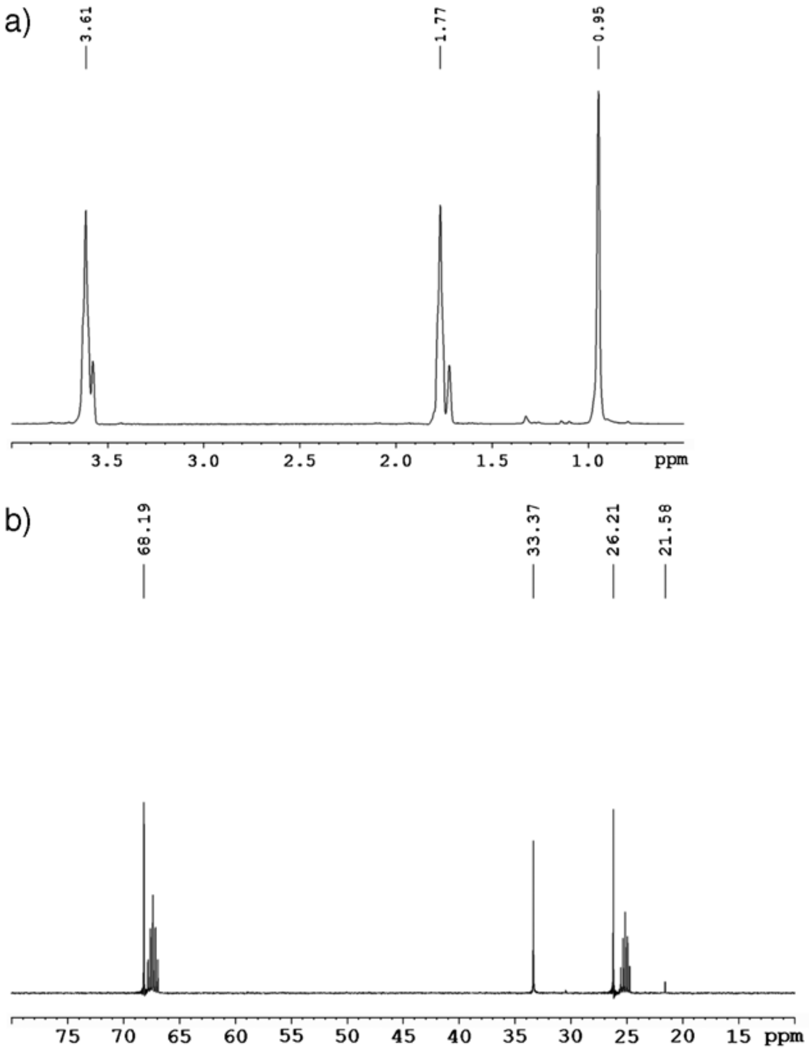

Fig. S3. *A*) ^{1}H NMR of **1** in d_8-THF solution at −50 °C. *B*) ^{13}C{^{1}H} NMR of **1** in d_8-THF solution at room temperature.

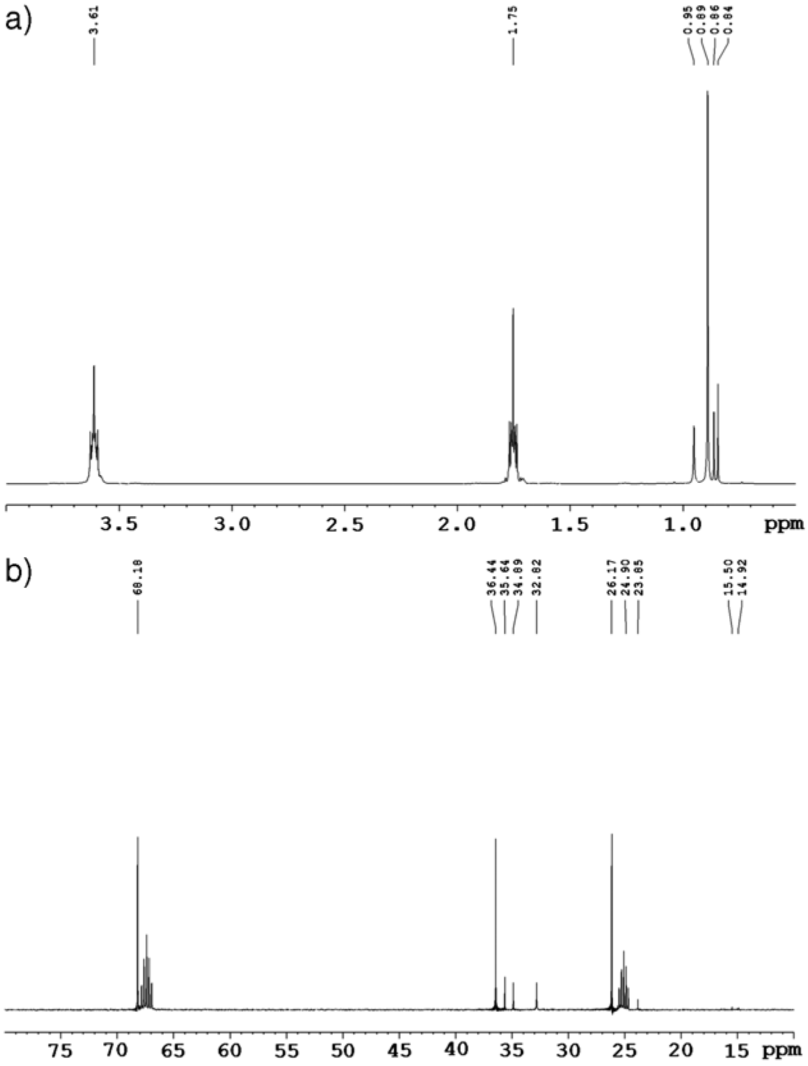

Fig. S4. *A*) ^{1}H NMR of **4** in d_8-THF solution at room temperature. *B*) ^{13}C{^{1}H} NMR of **4** in d_8-THF solution at room temperature.

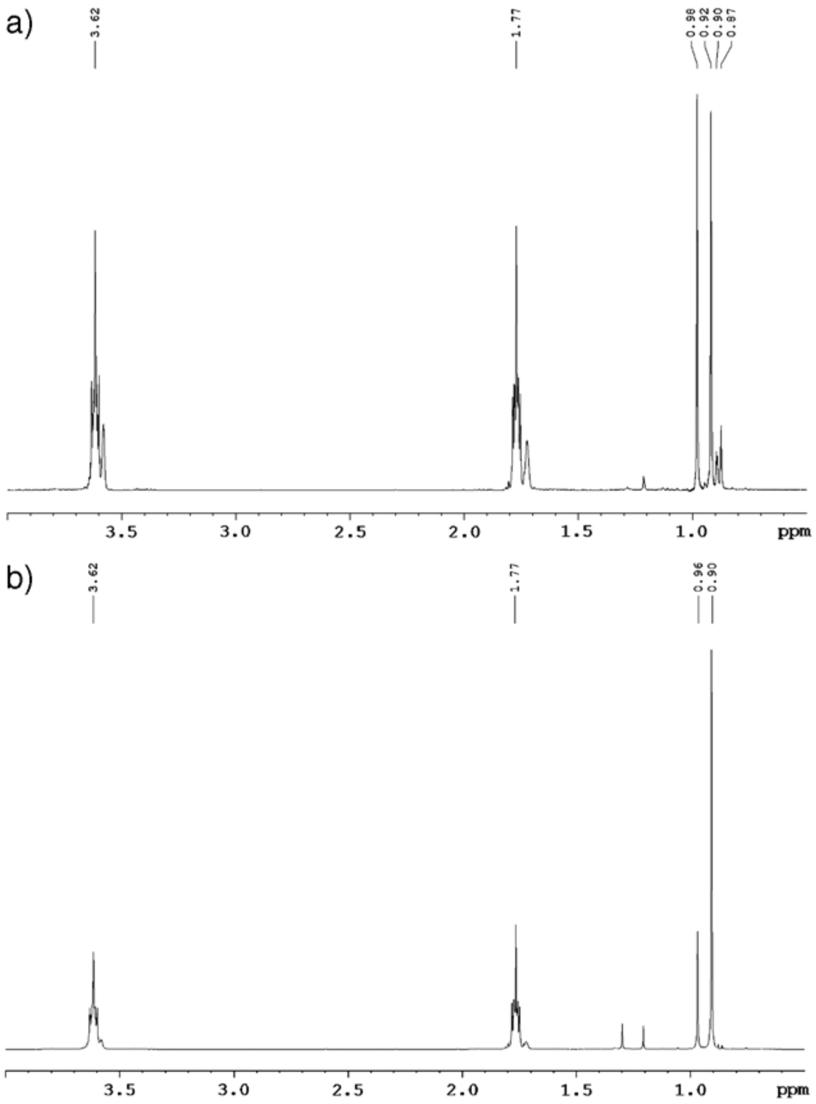

Fig. S5. *A*) ^{1}H NMR of **4** in d_8-THF solution at room temperature (low concentration). *B*) ^{1}H NMR of **4** in d_8-THF solution at room temperature (high concentration).

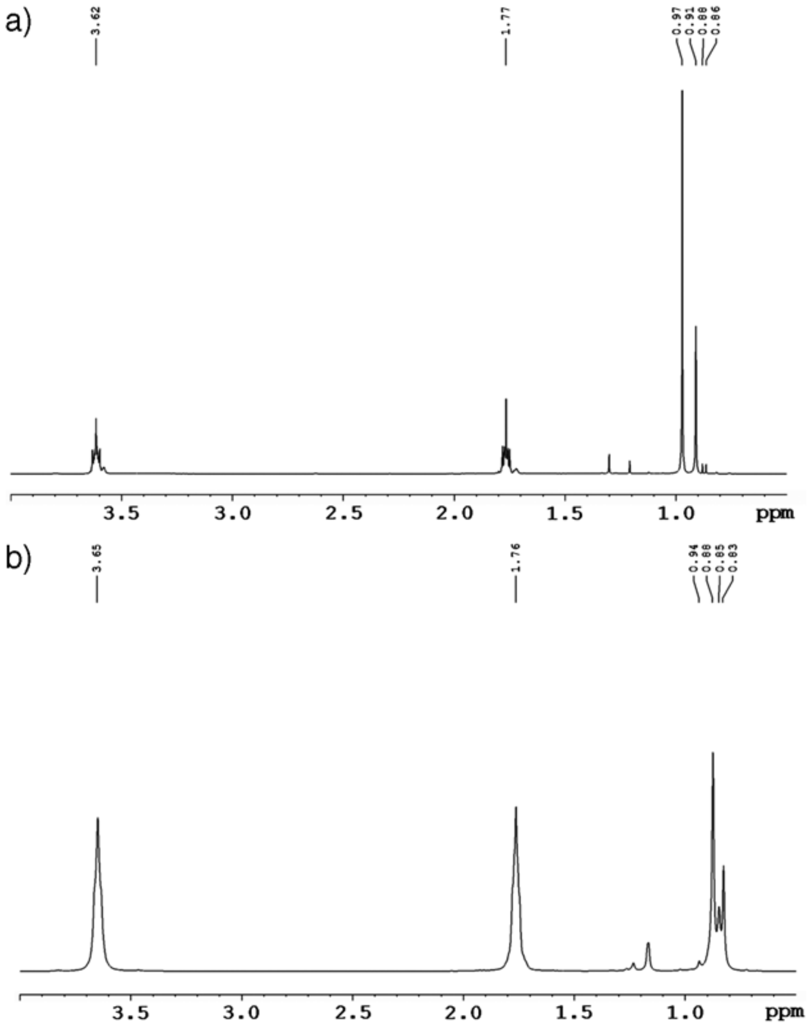

Fig. S6. *A*) ^{1}H NMR of **4** on the addition of an excess of ^{t}Bu$_2$Zn in d_8-THF solution at room temperature. *B*) ^{1}H NMR of **4** on the addition of an excess of ^{t}BuMgCl in d_8-THF solution at room temperature.

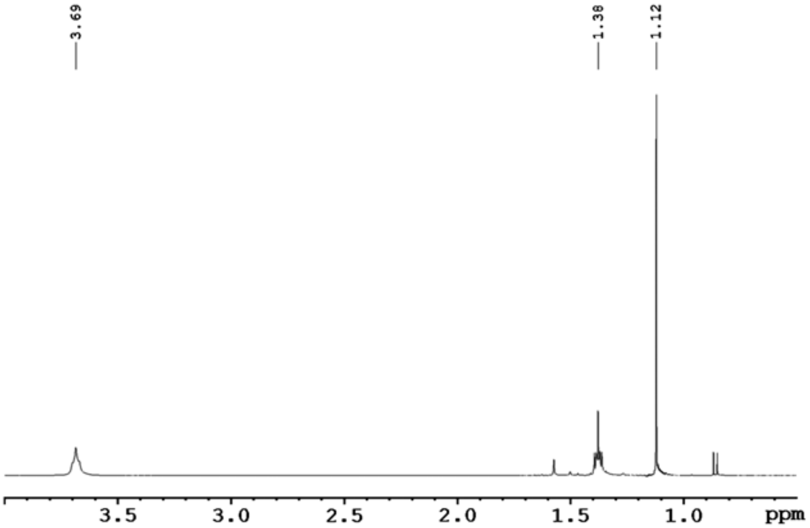

Fig. S7. ^{1}H NMR of **4** in d_6-benzene solution at room temperature: No disproportionation into monometallic components is observed.

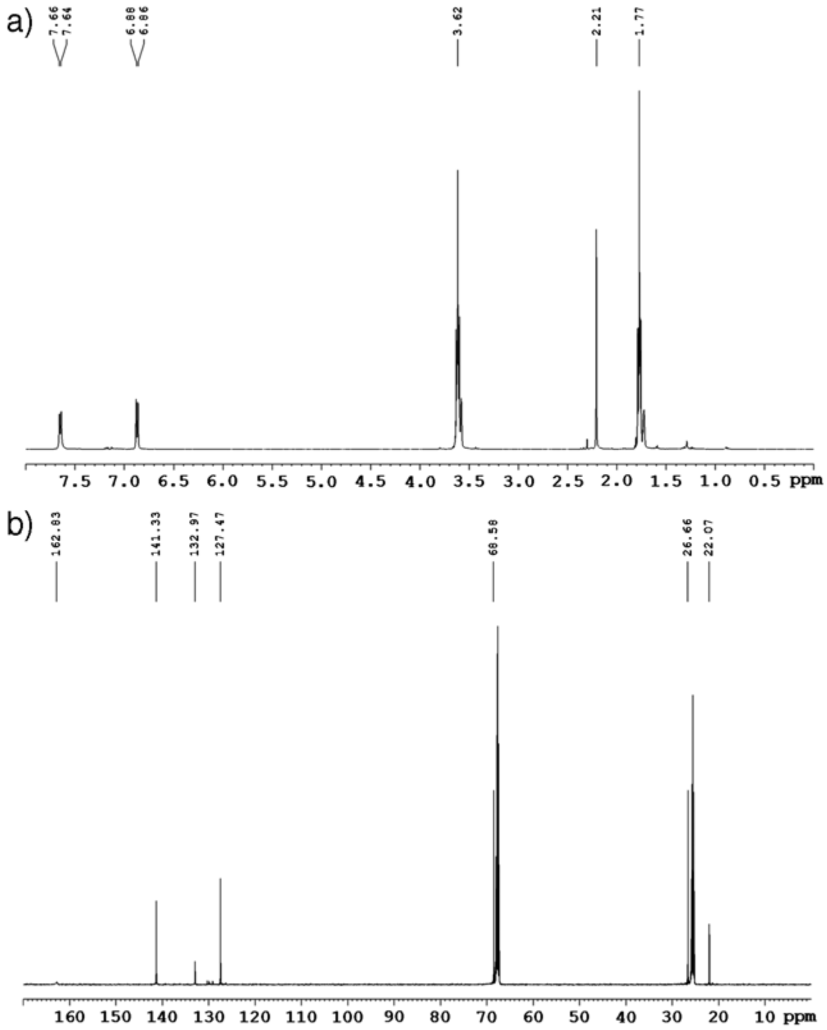

Fig. S8. *A*) ^{1}H NMR of **5** in d_8-THF solution at room temperature. *B*) ^{13}C{^{1}H} NMR of **5** in d_8-THF solution at room temperature

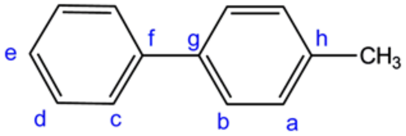

Chart 1. Labelling Scheme for **6**.

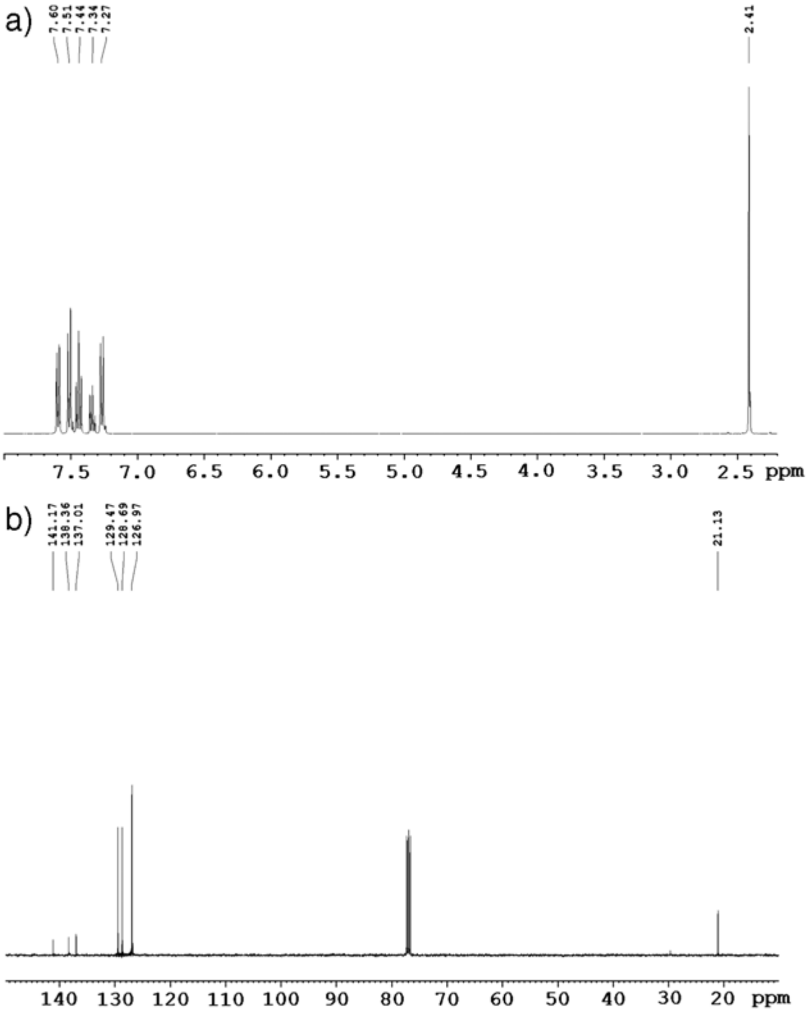

Fig. S9. *A*) ^{1}H NMR of 4-methylbiphenyl in $CDCl_3$ solution at room temperature. *B*) $^{13}C\{^1H\}$ NMR of 4-methylbiphenyl in $CDCl_3$ solution at room temperature