SUPPORTING INFORMATION

Structural Studies of (*rac*)-BIPHEN Organomagnesiates and Intermediates in the Halogen-metal Exchange of 2-Bromopyridine

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General Methods

All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane and THF were obtained from Aldrich and freshly distilled from sodium/benzophenone prior to use. $(CH_2SiMe_3)_2Mg$ and $(CH_2CMe_3)_2Mg$ were prepared from the Grignard reagent $(CH_2SiMe_3)MgCl$ and $(CH_2CMe_3)MgCl$ by manipulation of the Schlenk equilibrium via the dioxane precipitation method. The resultant off-white solid was purified via sublimation at 175 °C (10^{-2}Torr) to furnish pure $(CH_2SiMe_3)_2Mg$ and $(CH_2CMe_3)_2Mg$. Other chemicals were obtained from Aldrich or Strem Chemicals and were used as supplied. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer. All ^{13}C NMR spectra were proton decoupled. Elemental analyses were attempted using a Perkin-Elmer 2400 elemental analyzer; however, due to the extreme air sensitivity of the compounds satisfactory analyses could not be obtained.

Synthesis of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$·(THF)] (1). (*rac*)-BIPHEN (0.35 g, 1 mmol) was dissolved in THF (5 mL) and cooled to 0 °C for 15 minutes. At this stage ^{n}BuLi (1.4 mL, 2 mmol) was added. After stirring for 1 hour, the solvent was removed *in vacuo* resulting in a pale yellow solid. The resulting solid was recrystallized from 15 mL of hot hexane. To aid the crystallization the resulting colourless solution was placed in the freezer at −35 °C, deposited a crop of colorless crystals (0.24 g, yield 47%). ^1H NMR (400.13 MHz, 298 K, d_8-THF): 1.33 (36H, s, C(CH_3)$_3$), 1.61 (12H, s, CH_3), 1.81-1.85 (16H, m, OCH$_2$CH_2, THF), 2.15 (12H, s, CH_3,), 3.65-3.68 (16H, m, OCH_2CH$_2$, THF), 6.76 (4H, s, Ph). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, d_8-THF): 16.61 (*C*H$_3$), 19.75 (*C*H$_3$), 25.42 (OCH$_2$*C*H$_2$, THF), 30.40 (C(*C*H$_3$)$_3$), 34.04 (*C*(CH$_3$)$_3$), 67.27 (O*C*H$_2$CH$_2$, THF), 118.33, 125.59, 131.32, 132.31, 133.75, 161.95 (Ph). ^{7}Li NMR (155.50 MHz, 298 K, d_8-THF): δ -0.27.

Synthesis of [(*rac*)-BIPHEN]Li$_2$MgBu$_2$(THF)$_3$ (2). (*rac*)- BIPHEN (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C for 15 minutes. At this stage ^{n}BuLi (1.4 mL, 2 mmol) was added and stirred for 1 hour. (^{n}Bu)$_2$Mg (1 mL of a 1M solution in heptane, 1 mmol) was added at this point, and the resulting suspension was heated gently, affording a clear solution. Addition of THF (0.24 mL, 3 mmol) and slow cooling to -28 °C resulted in the formation of clear colorless crystals (0.46 g, yield 65%). ^1H NMR (400.13 MHz, 298 K, d_8-THF): -1.73- -1.16 (2H, m, MgCH_2), -0.90 - -0.83 (2H, m, MgCH_2), 0.75-0.80 (6H, m, Bu), 1.11-1.39 (8H, s, Bu), 1.42 (18H, s, C(CH_3)$_3$), 1.51 (6H, s, CH_3), 1.77-1.79 (12H, m, OCH$_2$CH_2, THF), 2.08 (6H, s, CH_3), 3.60-3.63 (12H, m, OCH_2CH$_2$, THF), 6.80 (4H, s, Ph). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, d_8-THF): 9.01 (MgCH$_2$), 15.10 (*C*H$_3$), 18.06 (*C*H$_3$), 21.43 (*C*H$_3$), 27.27 (2 x *C*H$_2$), 32.27(C(*C*H$_3$)$_3$), 34.09 (OCH$_2$*C*H$_2$, THF), 36.20 (*C*(CH$_3$)$_3$), 69.15 (O*C*H$_2$CH$_2$, THF), 122.26, 127.09, 134.34, 134.64, 136.26, 161.97 (Ph). ^{7}Li NMR (155.50 MHz, 298 K, d_8-THF): δ 1.41.

Synthesis of [(*rac*)-BIPHEN]Li$_2$Mg(CH$_2$SiMe$_3$)$_2$(THF)$_3$ (3). (*rac*)- BIPHEN (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C for 15 minutes. At this stage ^{n}BuLi (1.4 mL, 2 mmol) was added and stirred for 1 hour. $(CH_2SiMe_3)_2Mg$ (0.2 g, 1 mmol) was added at this point, and the resulting suspension was heated gently, affording a clear solution. Addition of THF (0.24 mL, 3 mmol) and slow cooling resulted in the formation of clear colorless crystals (0.64 g, yield 82%). ^1H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): -2.31 (2H, m, MgCH_2Si(CH$_3$)$_3$), -1.65 (2H, m, MgCH_2Si(CH$_3$)$_3$), -0.02 (18H, s, Si(CH$_3$)$_3$), 1.45 (18H, s, C(CH_3)$_3$), 1.61 (6H, s, CH_3), 1.72-1.76 (12H, m, OCH$_2$CH_2, THF), 2.14 (6H, s, CH_3), 3.50-3.54 (12H, m, OCH_2CH$_2$, THF), 6.92 (2H, s, Ph). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): -9.74 (Si*C*H$_2$), 3.04 (Si(*C*H$_3$)$_3$), 16.04 (*C*H$_3$), 19.53 (*C*H$_3$), 25.16 (OCH$_2$*C*H$_2$, THF), 30.39 (C(*C*H$_3$)$_3$), 34.39(*C*(CH$_3$)$_3$), 67.63 (O*C*H$_2$CH$_2$, THF), 121.42, 126.07, 131.32, 132.29, 135.33, 158.97 (Ph). ^{7}Li NMR (155.50 MHz, 298 K, *cyc*-C_6D_{12}): δ -0.18.

Synthesis of [(*rac*)-BIPHEN]Li$_2$Mg(^{neo}Pe)$_2$(THF)$_2$ (4). (*rac*)- BIPHEN (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C for 15 minutes. At this stage ^{n}BuLi (1.4 mL, 2 mmol) were added and stirred for 1 hour. (^{neo}Pe)$_2$Mg (0.16 g, 1 mmol) was added at this point, and the resulting suspension was heated gently, affording a clear solution. Addition of THF (0.16 mL, 2 mmol) and slow cooling resulted in the formation of clear colorless crystals (0.25 g, yield 36%). ^1H NMR (400.13 MHz, 298 K, *cyc*-C_6D_{12}): -1.10 (2H, d, $^3J_{HH}$ = 15Hz, MgCH_2), -0.13 (2H, d, $^3J_{HH}$ = 15Hz, MgCH_2), 1.03 (18H, s, C(CH_3)$_3$), 1.44 (18H, s, C(CH_3)$_3$), 1.61 (6H, s, CH_3), 1.73-1.76 (12H,

m, OCH_2CH_2, THF), 2.13 (6H, s, CH_3), 3.50-3.54 (12H, m, OCH_2CH_2, THF), 6.91 (4H, s, Ph). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, *cyc*-C_6D_{12}): 16.12 (CH_3), 19.53 (CH_3), 25.17 (OCH_2CH_2, THF), 25.51 (2 x $MgCH_2$), 30.14($C(CH_3)_3$), 32.34 ($C(CH_3)_3$), 34.49 ($C(CH_3)_3$), 67.53 (OCH_2CH_2, THF), 121.01, 126.18, 130.97, 132.43, 135.55, 159.34 (Ph). ^{7}Li NMR (155.50 MHz, 298 K, *cyc*-C_6D_{12}): δ 0.07.

Synthesis of [(*rac*)-BIPHEN]$Li_2Mg(2\text{-pyridine})_2(THF)_2$ (5). (*rac*)- BIPHEN (0.35 g, 1 mmol) was dissolved in hexane (10 mL) and cooled to 0 °C for 15 minutes. At this stage ^{n}BuLi (1.4 mL, 2 mmol) was added and stirred for 1 hour. $(^n Bu)_2Mg$ (1 mL of a 1M solution in heptane, 1 mmol) was added at this point. The solution was cooled to -60 °C, and then 2-bromopyridine (0.095 mL, 1 mmol) was added, and the resulting suspension was allowed to reach ambient temperature slowly. Addition of THF (0.16 mL, 2 mmol), gently heating and slow cooling resulted in the formation of clear colorless crystals (0.32 g, yield 47%; 94% based on 2-bromopyridine). An alternative stoichiometric synthesis could be achieved by reacting isolated crystals of [(*rac*)-BIPHEN]$Li_2Mg(CH_2SiMe_3)_2(THF)_3$ (**3**) (0.78 g, 1 mmol) with 2-bromopyridine (0.19 mL, 2 mmol) at -60 °C. After reaching ambient temperature, THF (0.16 mL, 2 mmol) was added, obtaining a white suspension that transforms into a deep orange solution after vigorous heating. To aid crystallization, the resulting solution was placed in the freezer at −35 °C, and deposited a crop of yellow crystals (0.46 g, yield 66%). ^{1}H NMR (400.13 MHz, 298 K, d_8-THF): 1.26 (18H, s, $C(CH_3)_3$), 1.76 (6H, s, CH_3), 1.79-1.82 (8H, m, OCH_2CH_2, THF), 2.16 (6H, s, CH_3), 3.63-3.67 (8H, m, OCH_2CH_2, THF), 6.69-6.73 (2H, m, Ar), 6.79 (2H, s, Ph), 7.06-7.10 (2H, m, Ar), 7.57 (2H, d, $^3J_{HH}$ = 7.6 Hz, Ar), 8.24 (2H, d, $^3J_{HH}$ = 5.2 Hz, Ar). $^{13}C\{^1H\}$ NMR (100.62 MHz, 298 K, d_8-THF): 16.02 (CH_3), 19.24 (CH_3), 25.00 (OCH_2CH_2, THF), 30.33 ($C(CH_3)_3$), 33.88 ($C(CH_3)_3$), 66.86 (OCH_2CH_2, THF), 117.06 (Ar), 120.49, 125.52, 128.45 (Ph), 131.79 (Ar), 132.05, 134.50 (Ph), 135.23, 145.99 (Ar), 159.57 (Ph), 214.7 (Ar). ^{7}Li NMR (155.50 MHz, 298 K, d_8-THF): δ 0.65.

Table S1: Key crystallographic and refinement parameters for compounds **1-5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{68}H_{104}Li_4O_9$	$C_{44}H_{74}Li_2MgO_5$	$C_{44}H_{78}Li_2MgO_5Si_2$	$C_{42}H_{70}Li_2MgO_4$	$C_{42}H_{56}Li_2MgN_2O_4$
M_r	1093.27	721.22	781.43	677.17	691.08
Cryst syst	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	C 2/c	P -1	P -1	C 2/ c	C 2/ c
a (Å)	15.9337(4)	11.3150(5)	11.1354(3)	11.7525(4)	16.4177(14)
b (Å)	21.4472(6)	11.6395(5)	12.7861(3)	17.2189(5)	12.3325(8)
c (Å)	18.7634(4)	18.4418(8)	17.7097(6)	21.5342(7)	20.0058(15)
α (deg)		88.063(3)	91.832(2)		
β (deg)	91.798(2)	81.313(4)	98.917(3)	100.468(3)	103.285(8)
γ (deg)		69.075(4)	105.629(2)		
V (Å^3)	6408.9(3)	2242.06(17)	2391.69(12)	4285.2(2)	3942.2(5)
Z	4	2	2	4	4
μ (mm^{-1})	0.072	0.637	0.126	0.077	0.087
T **(K)**	123	123	123	123	123
Reflections collected	21498	22999	20870	13998	10804
Reflections unique	7361	8791	8851	4936	4441
Reflections observed	5316	6636	6106	3735	3200
R_{int}	0.0333	0.0252	0.0311	0.0288	0.0385
No. Parameters	413	504	540	275	236
(*GOF*)	1.018	1.054	1.034	1.029	1.032
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0526	R1 = 0.0640,	R1 = 0.0786	R1 = 0.0491	R1 = 0.0606
***R* indices (all data)**	wR2 = 0.1292	wR2 = 0.1883	wR2 = 0.2336	wR2 = 0.1228	wR2 = 0.1679
Largest diff. peak and hole (e Å^{-3})	0.294 and -0.218	0.504 and -0.301	1.382 and -0.963	0.268 and -0.201	0.578 and -0.271

Figure S1. ^{1}H NMR of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in d$_8$-THF

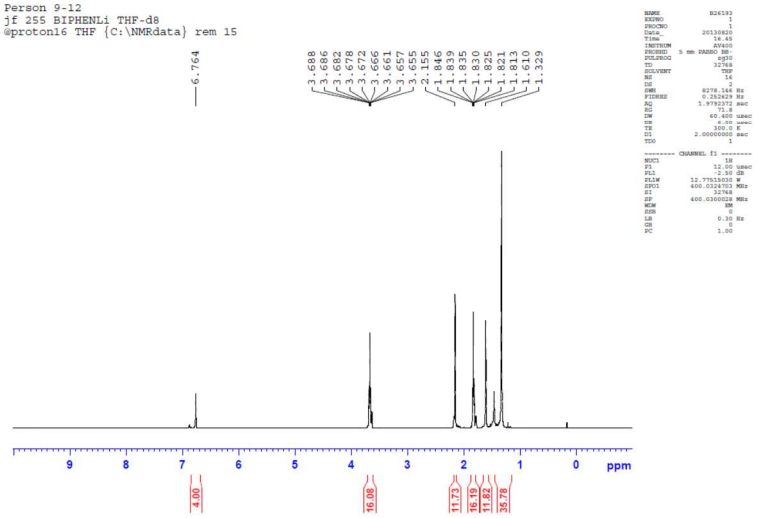


Figure S2. ^{7}Li NMR of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in d$_8$-THF

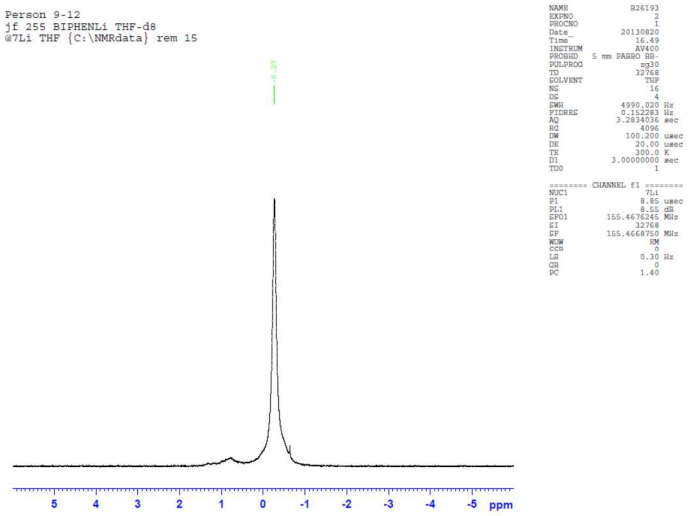


Figure S2b. ^{7}Li NMR of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in *cyc*-C$_6$D$_{12}$

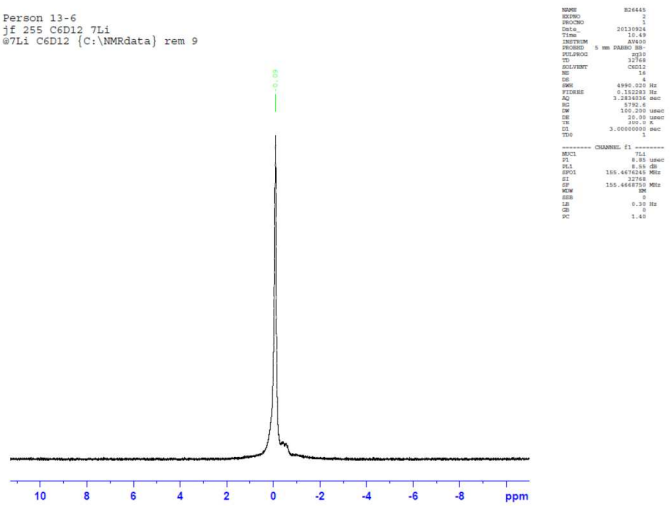


Figure S3. ^{13}C NMR of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in d$_8$-THF

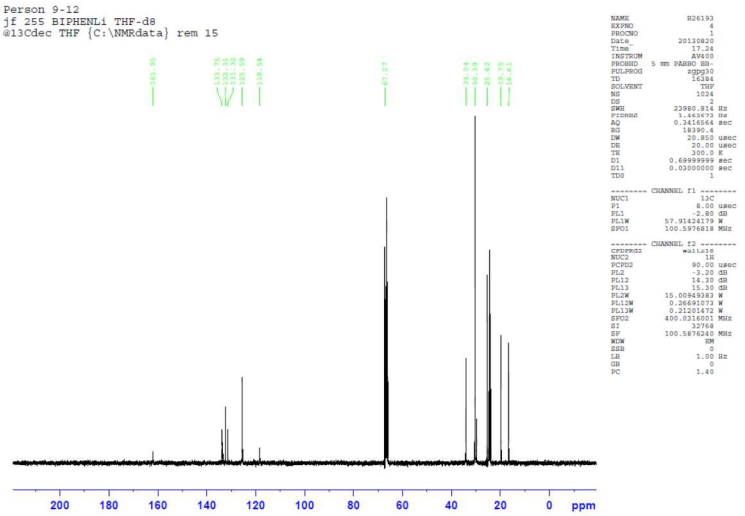


Figure S4. ^{1}H NMR of [(*rac*)-BIPHENate]Li$_2$Mg(^{n}Bu)$_2$(THF)$_3$ (2) in d$_8$-THF. The resonance at approximately −0.5 ppm is an uncharacterized soluble alkyl-containing impurity that appears to be present in the commercially sourced ^{n}Bu$_2$Mg. Note that the commercial reagent contains a significant quantity of Et$_3$Al.

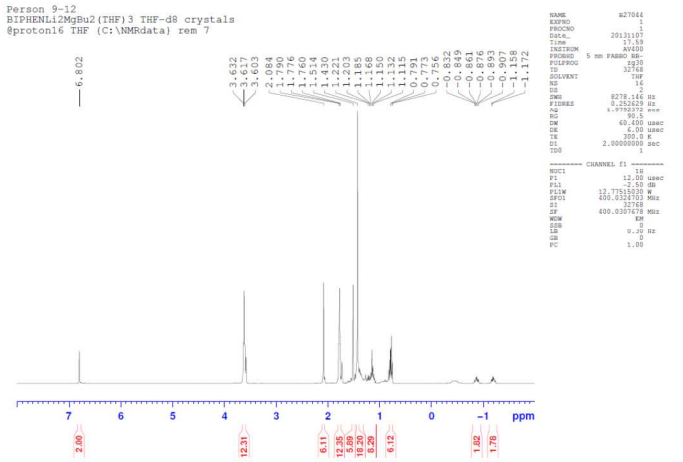


Figure S5. ^{7}Li NMR of [(*rac*)-BIPHEN]Li$_2$Mg(^{n}Bu)$_2$(THF)$_3$ (2) in d$_8$-THF

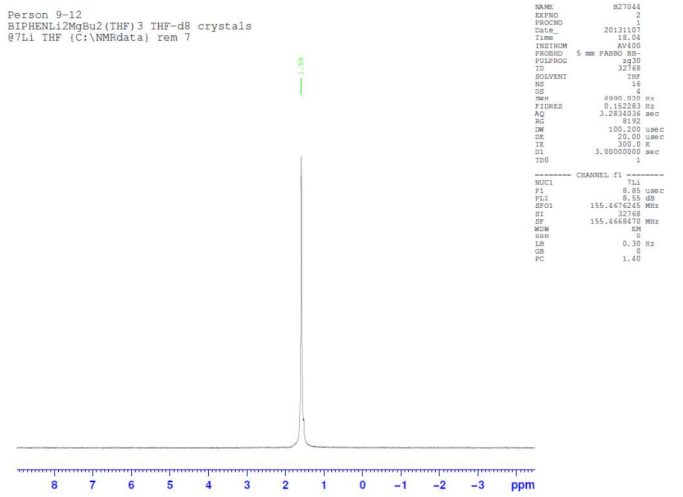


Figure S6. ^{13}C NMR of [(*rac*)-BIPHEN]$Li_2Mg(^nBu)_2(THF)_3$ (2) in d_8-THF

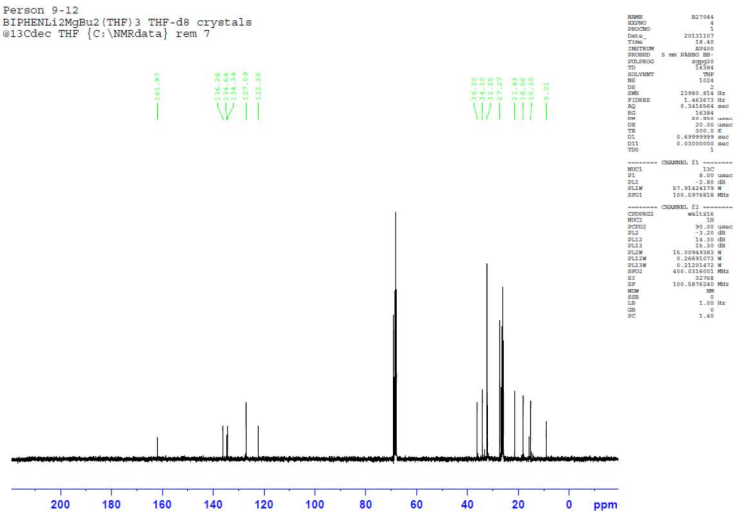


Figure S7. ^{1}H NMR of [(*rac*)-BIPHEN]$_2Li_2Mg(THF)_4$ (2b) in *cyc*-C_6D_{12}

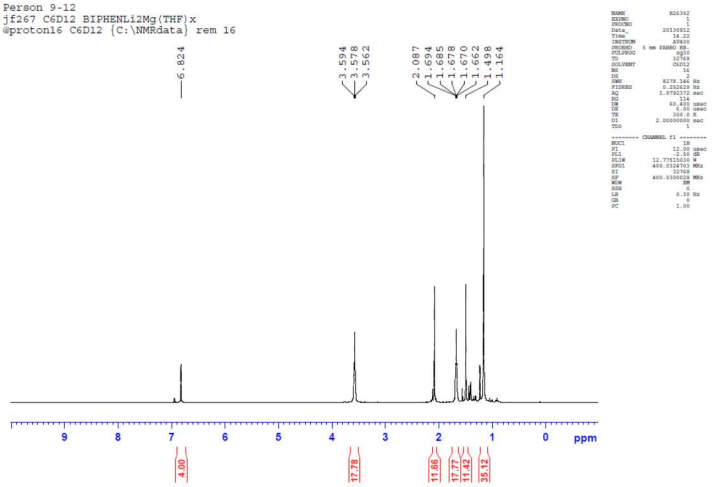


Figure S8. ^{1}H NMR of [(*rac*)-BIPHEN]$Li_2Mg(CH_2SiMe_3)_2(THF)_3$ (3) in *cyc*-C_6D_{12}

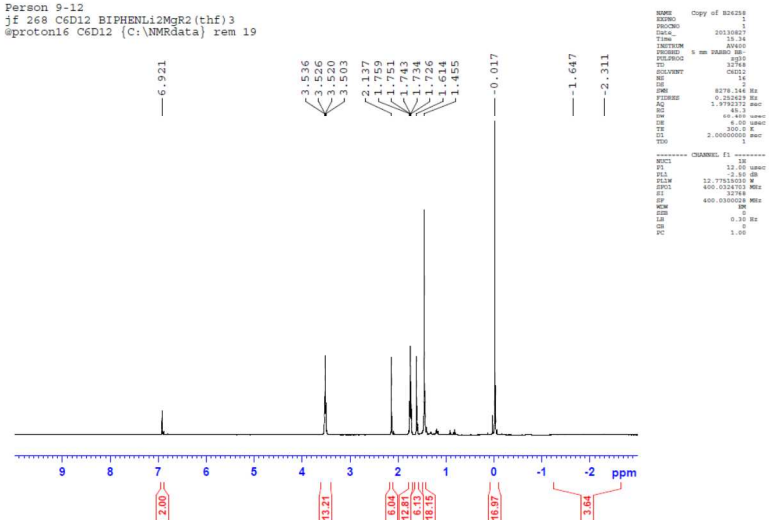


Figure S9. ^{7}Li NMR of [(*rac*)-BIPHEN]$Li_2Mg(CH_2SiMe_3)_2(THF)_3$ (3) in *cyc*-C_6D_{12}

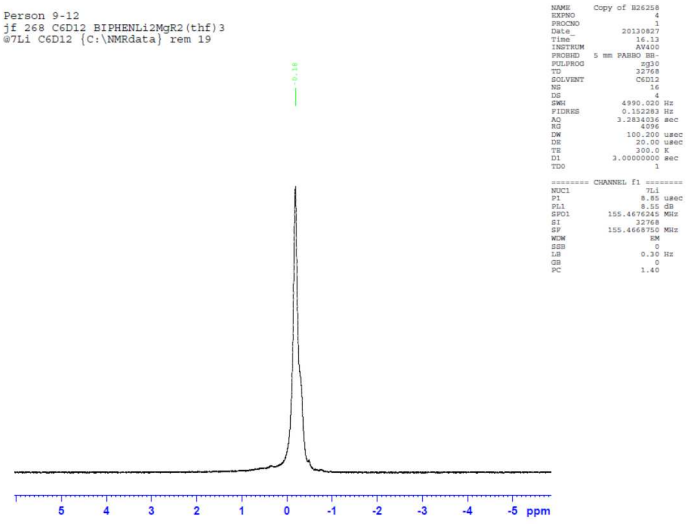


Figure S10. ^{13}C NMR of [(*rac*)-BIPHEN]$Li_2Mg(CH_2SiMe_3)_2(THF)_3$ (3) in *cyc*-C_6D_{12}

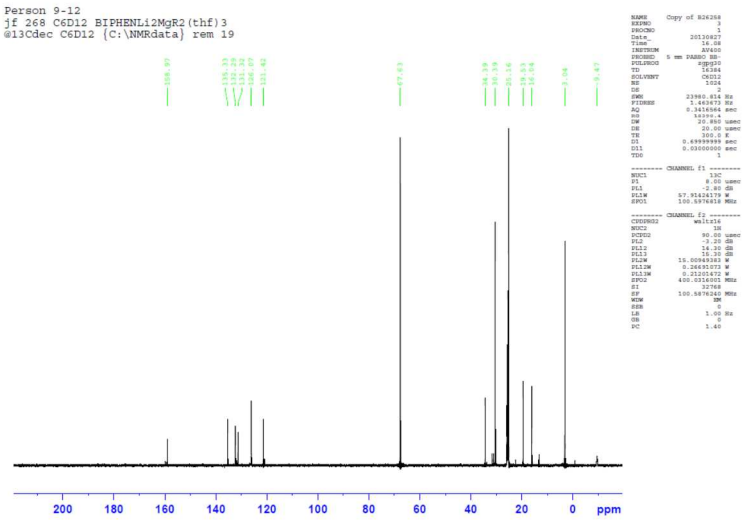


Figure S11. ^{1}H NMR of [(*rac*)-BIPHEN]$Li_2Mg(^{neo}Pe)_2(THF)_2$ (4) in *cyc*-C_6D_{12}

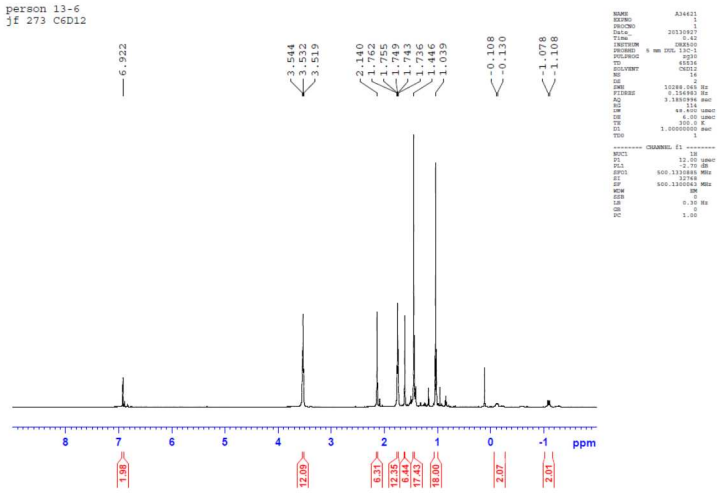


Figure S12. ^{7}Li NMR of [(*rac*)-BIPHEN]$Li_2Mg(^{neo}Pe)_2(THF)_2$ (4) in *cyc*-C_6D_{12}

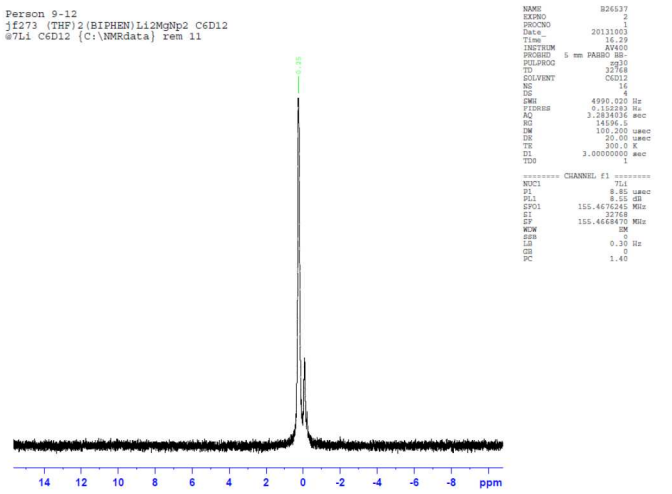


Figure S13. ^{13}C NMR of [(*rac*)-BIPHEN]Li$_2$Mg(^{neo}Pe)$_2$(THF)$_2$ (4) in *cyc*-C$_6$D$_{12}$

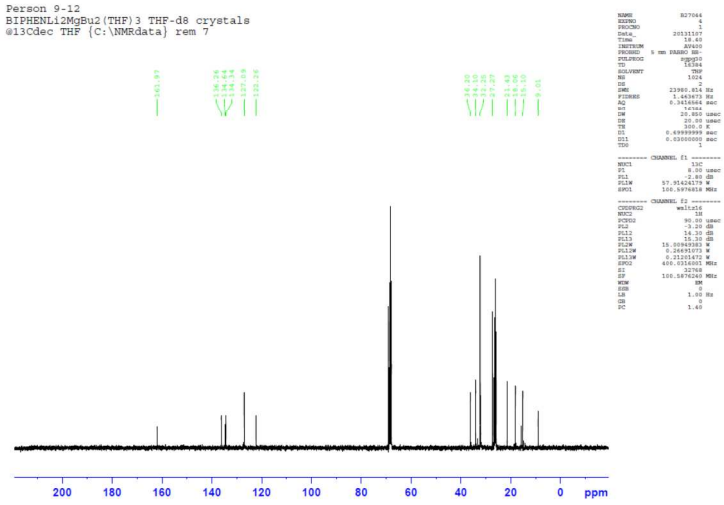


Figure S14. ^{1}H NMR of [(*rac*)-BIPHEN]Li$_2$Mg(2-pyridyl)$_2$(THF)$_2$ (5) in d$_8$-THF

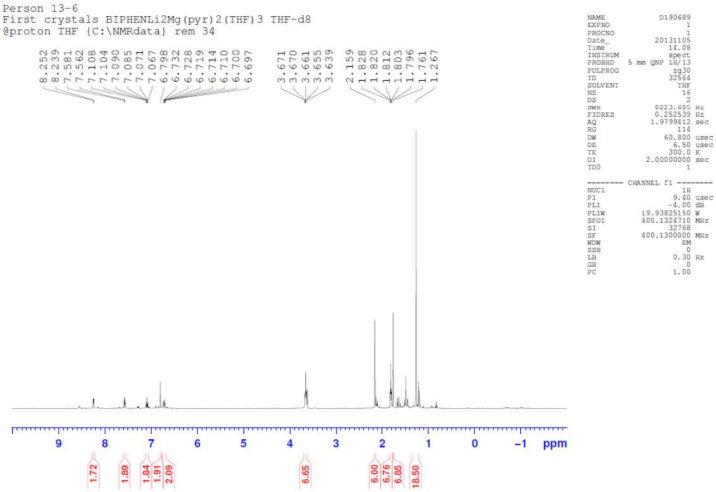


Figure S15. ^{7}Li NMR of [(*rac*)-BIPHEN]Li$_2$Mg(2-pyridyl)$_2$(THF)$_2$ (5) in d$_8$-THF

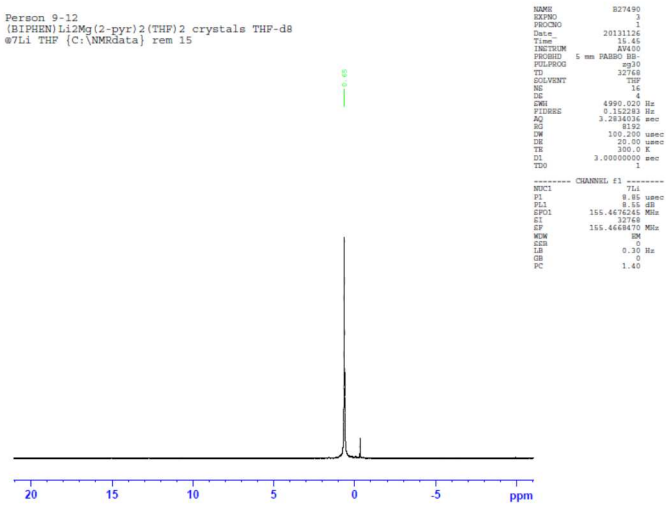
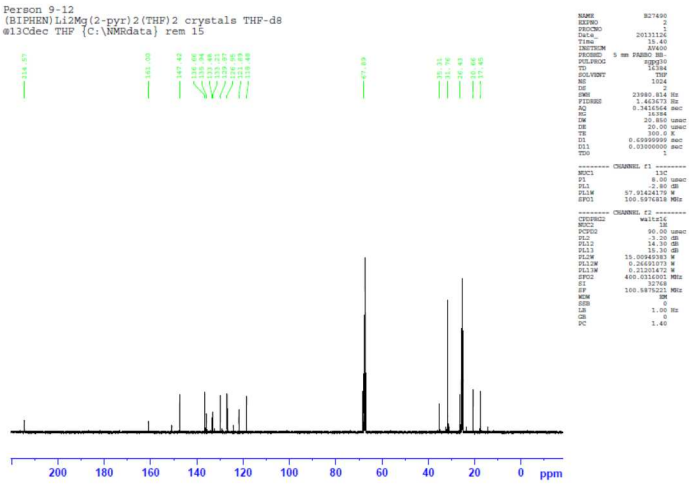


Figure S16. ^{13}C NMR of [(*rac*)-BIPHEN]$Li_2Mg(2\text{-pyridyl})_2(THF)_2$ (5) in d_8-THF



Solution studies of starting materials.

Figure S17. ^{1}H NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + ^{n}BuMgCl in d$_8$-THF

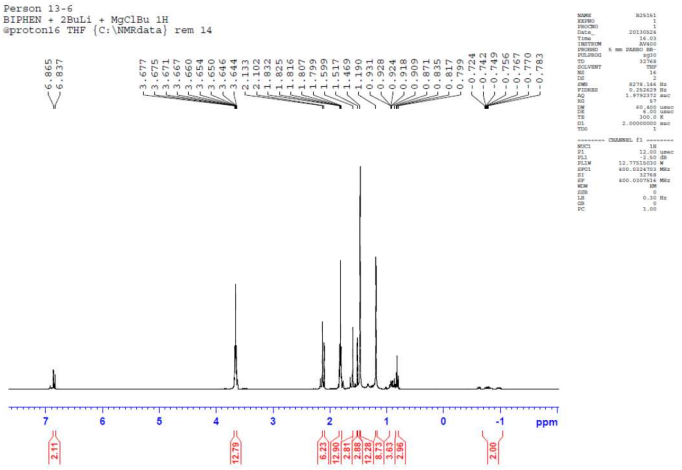


Figure S18. ^{7}Li NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + ^{n}BuMgCl in d$_8$-THF

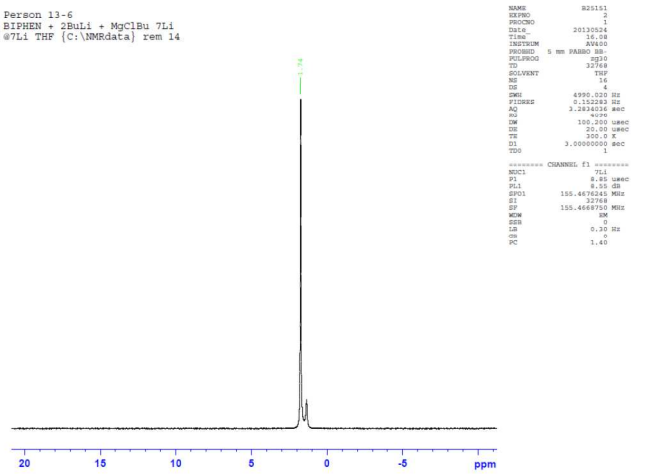


Figure S19. ^{1}H NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + ^{n}BuMgCl + ^{n}BuLi in d$_8$-THF

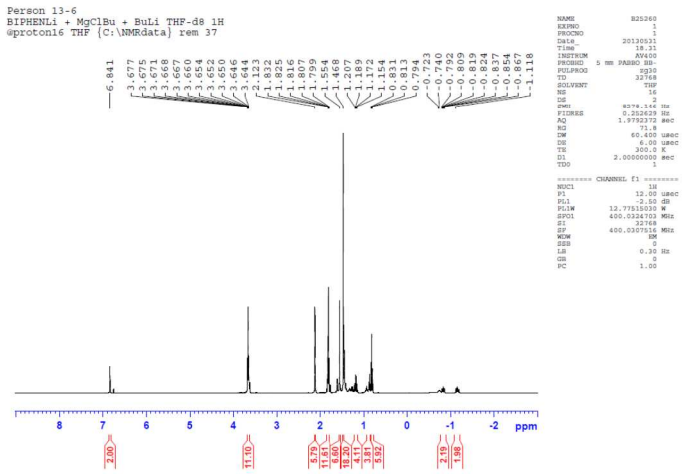


Figure S20. ^{7}Li NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + ^{n}BuMgCl + ^{n}BuLi in d$_8$-THF

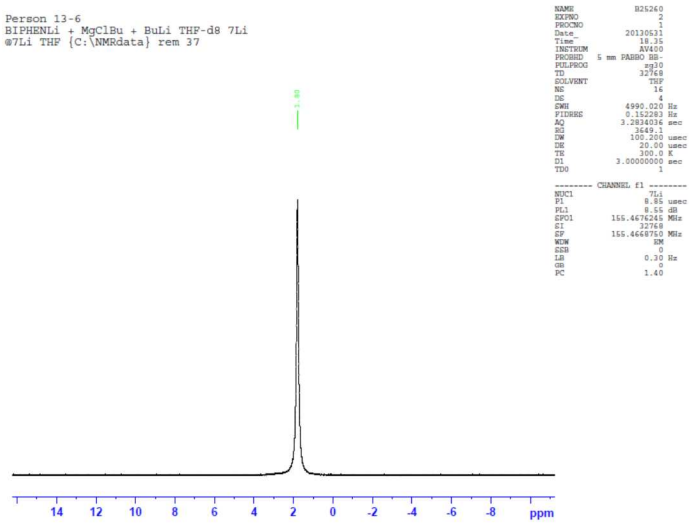


Figure S21. ^{1}H NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + (^{n}Bu)$_2$Mg in d$_8$-THF

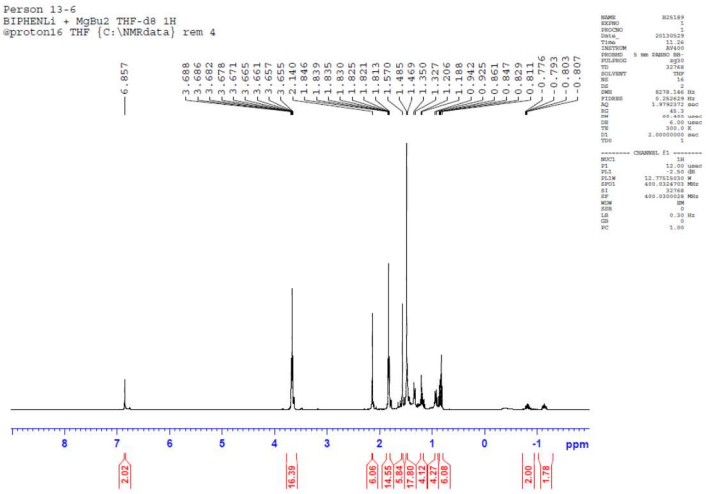


Figure S22. ^{7}Li NMR of a *in situ* mixture (*rac*)-BIPHEN-H$_2$ + 2 ^{n}BuLi + (^{n}Bu)$_2$Mg in d$_8$-THF

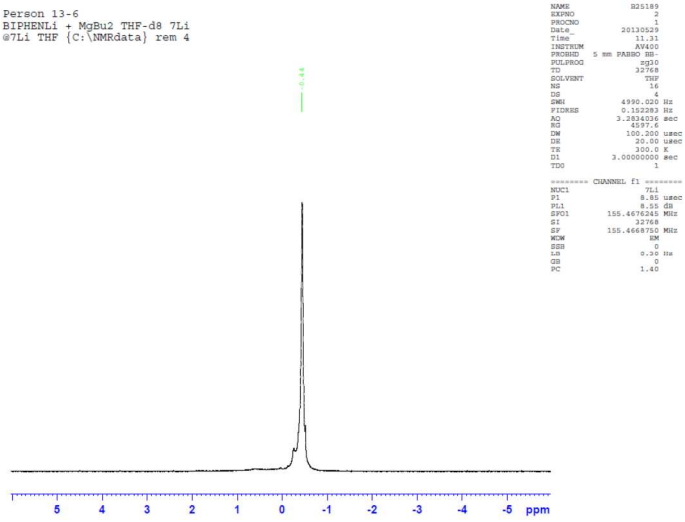


Figure S23. ^{1}H NMR comparison of Routes A & B in d$_8$-THF

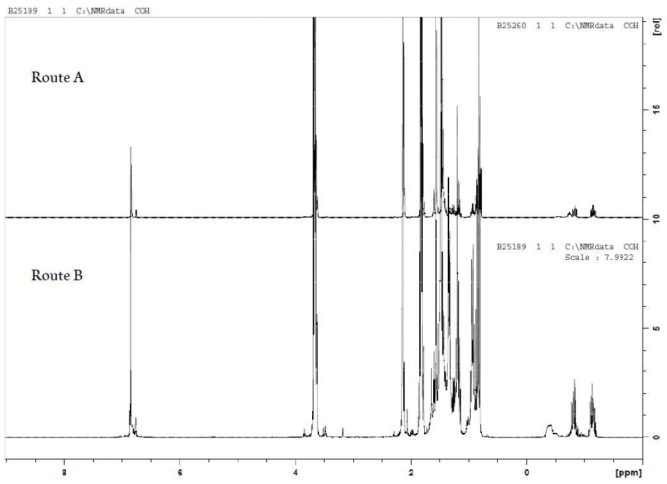


Figure S24. ^{1}H NMR of a mixture BIPHEN + 2BuLi + $MgBu_2$ after reflux.

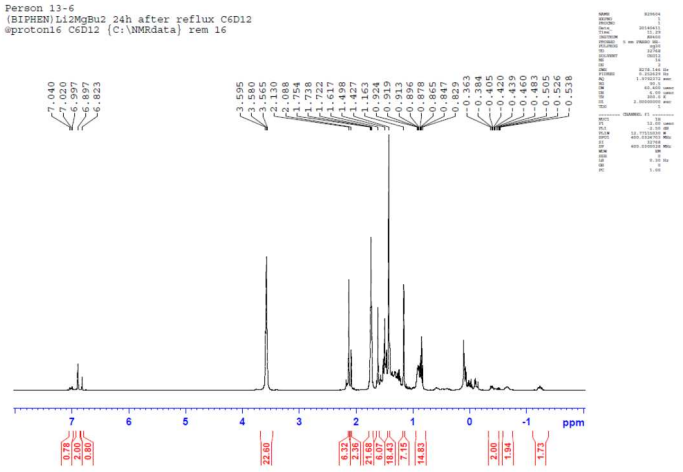


Figure S25. ^{7}Li NMR of a mixture BIPHEN + 2BuLi + $MgBu_2$ after reflux.

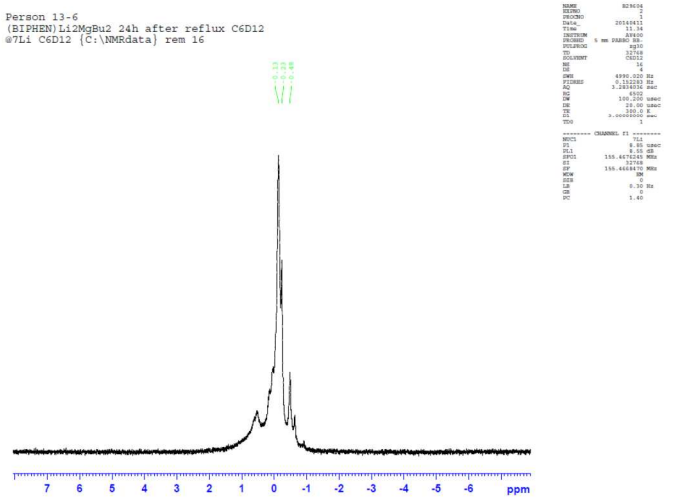


Figure S26. ^{1}H NMR of a mixture BIPHEN + 2BuLi + $MgBu_2$ after reflux. t = 2 days.

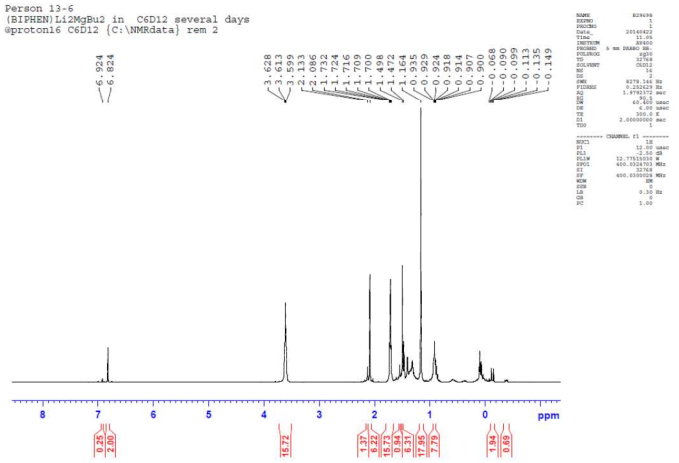
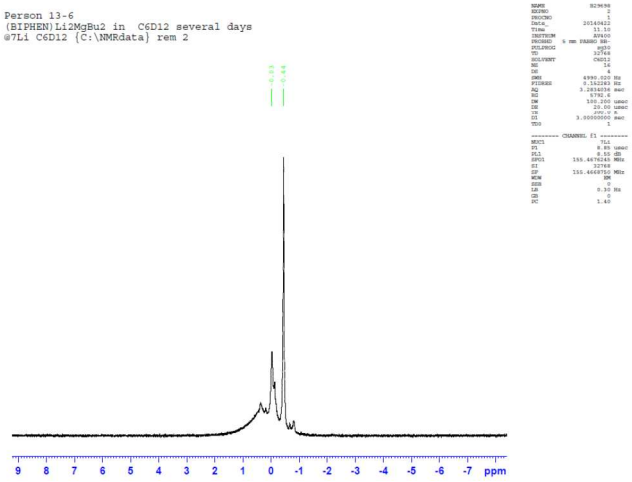
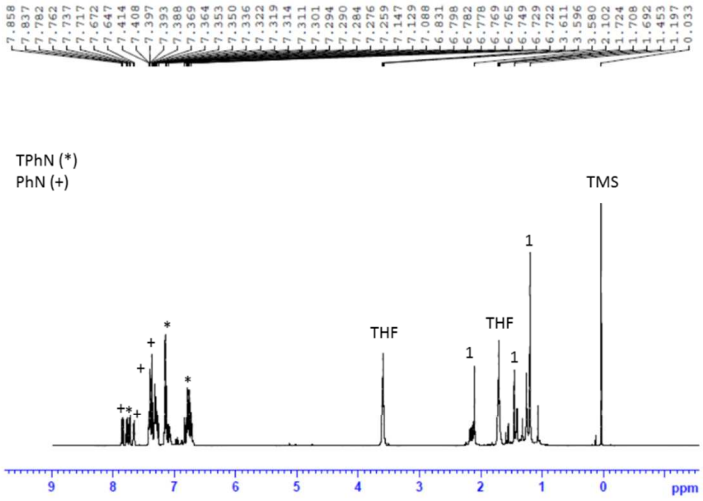


Figure S27. ^{7}Li NMR of a mixture BIPHEN + 2BuLi + $MgBu_2$ after reflux. t = 2 days.

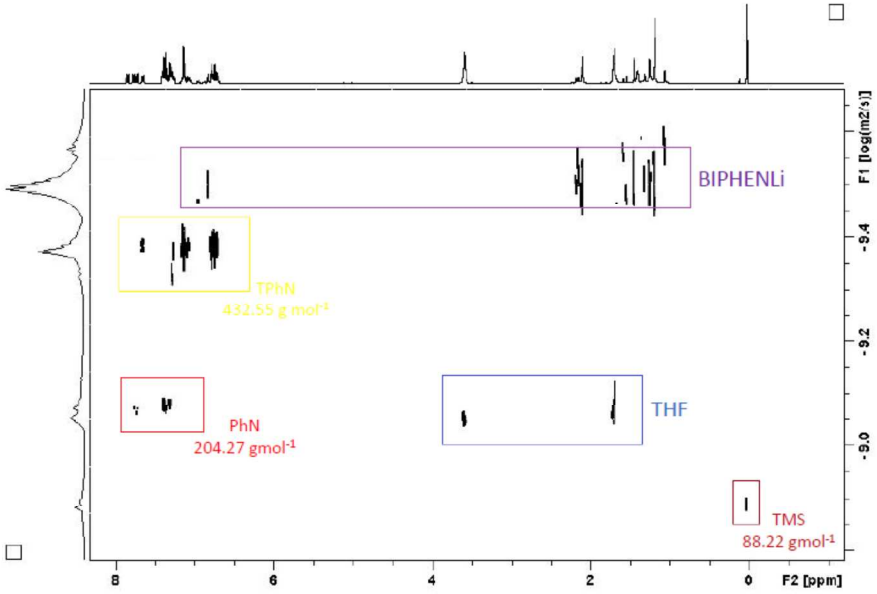


DOSY EXPERIMENTS

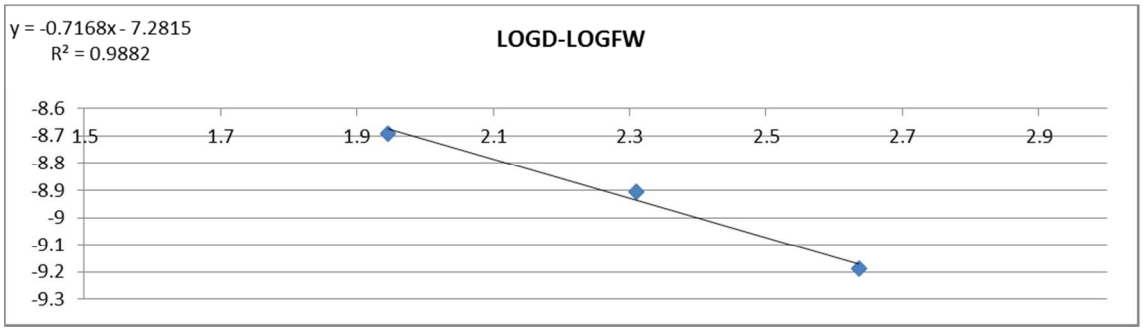
^{1}H NMR spectrum of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1), TPhN, PhN and TMS at 25 °C in *cyc*-C$_6$D$_{12}$ (traces of grease are also observed).



^{1}H-DOSY NMR spectrum of 1 and the standards TPhN, PhN and TMS in *cyc*-C$_6$D$_{12}$ at 298 K (some traces of grease are also observed).



log *D* – log FW representation from the ^{1}H-DOSY data obtained for the mixture of 1, TPhN, PhN and TMS in *cyc*-C$_6$D$_{12}$



Possible species of [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in *cyc*-C$_6$D$_{12}$ with errors (in brackets) respect to the FW value predicted through the DOSY study.

FW predicted for [(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ · (THF) (1) in cyc-C$_6$D$_{12}$ = 667.4 gmol^{-1}	
A	[(*rac*)-BIPHEN]$_2$Li$_4$(THF)$_4$ $C_{64}H_{96}Li_4O_8$ = 1020.77 gmol^{-1} (36%)
B	[(*rac*)-BIPHEN]$_2$Li$_4$ $C_{48}H_{64}Li_4O_4$ = 732.5 gmol^{-1} (9%)
C	[(*rac*)-BIPHEN]Li$_2$ $C_{24}H_{32}Li_2O_2$ = 366.4 gmol^{-1} (-82%)
D	[(*rac*)-BIPHEN]Li$_2$(THF)$_4$ = 654.86 gmol^{-1} (-1.9%)

^{1}H-DOSY NMR spectrum of 2 in *cyc*-C$_6$D$_{12}$ at 298 K.