Electronic Supplementary Material (ESI) for Dalton Transactions.

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

Callum Yeardley,[a] Alan R. Kennedy,[a] Philippe C. Gros,[b] Sabrina Touchet,[b], Michael Fairley[a] 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 stabdard Schlenk techniques. Non-deuterated solvents were dried by refluxing over sodium in the presence of benzophenone under a nitrogen enviroment. Deuterated solvents were degassed using the freeze, pump, thaw method and stored over 4 Å molecular sieves. (*rac*)-BIPHEN-H_2, ^{n}BuLi and $Mg^{n}Bu_2$ were purchased from Sigma-Aldrich and used without any further purification. TMEDA and PMDETA were purchased from Alfa Aesar, dried by refluxing over CaH_2 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 substrtes were stored over 4 Å molecular sieves and used without any further purification. NMR Spectra were recordeded on a Bruker AVIII 400 MHz spectrometer operating at 400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C. Single-crystal X-ray diffraction data were collected at 123 K using an Oxford Diffraction Gemini and Xcalibur diffractometers with monochromated Cu (λ= 1.5418 Å) and Mo (λ= 0.71 Å) radition. The structures were solved by direct methods and refined to convegence on F^2 and against all independent reflections by full-matrix least squares and ShelXl programs.

Gerenal Synthesis of ^{n}BuNa

$NaO^{t}Bu$ (3.84g, 40 mmol) was suspended in hexane in an argon filled schlenk and cooled to 0 °C. Commercial ^{n}BuLi (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 MgR_2 (where R = CH_2SiMe_3)

Mg turnings (4g) were added to a round bottom flask along with 100 ml of ether. A solution of Me_3SiCH_2Cl (19 ml) in ether (50ml) was then added dropwise to the Mg turnings. The solution was then heated to reflux and 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 vicous 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 microcrystaline 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 $[BIPHEN]_2Na_4(THF)_4$

$[BIPHEN]_2Na_4(THF)_4$ 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 ^{n}BuNa (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 $[BIPHEN]_2Na_4(THF)_4$ (yield 0.145 g, 26 %). ^{1}H NMR (400.13 MHz, 298 K, d_8-THF): δ 1.30 (36H, bs, $C(CH_3)_3$), 1.56 (12H, bs, CH_3), 1.73 (10H, m, OCH_2CH_2, THF), 2.07 (12H, bs, CH_3), 3.58 (10H, m, OCH_2CH_2, THF), 6.69 (4H, s, Ph). ^{13}C NMR (100.62 MHz, 298 K, d_8-THF): δ 16.71 (CH_3), 20.34 (CH_3), 26.15 (THF), 30.27 ($C(CH_3)_3$), 34.75 ($C(CH_3)_3$), 68.00 (THF), 116.19, 125.91, 132.40, 133.12, 133.70, 165.12 (Ph)

Synthesis of $[BIPHEN]_2Na_2Mg(THF)_4$

$[BIPHEN]_2Na_2Mg(THF)_4$ 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 ^{n}BuNa (0.08 g, 1 mmol) in hexane (5 ml) at -10 °C. The suspension was stirred for 30 minutes after which commercial Mg^nBu_2 (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 $[BIPHEN]_2Na_2Mg(THF)_4$ as colourless crystals (yield 0.197 g, 37%). $[BIPHEN]_2Na_2Mg(THF)_4$ can also be prepared by using $Mg(CH_2SiMe_3)$ as a replacement for $MgBu_2$. ^{1}H NMR (400.13 MHz, 298 K, d_8-THF): δ 1.15 (36H, bs, $C(CH_3)_3$), 1.45 (12H, s, CH_3), 1.77 (14H, m, OCH_2CH_2, THF), 2.04 (12H, s, CH_3), 3.61 (10H, m, OCH_2CH_2, THF), 6.72 (4H, s, Ph). ^{13}C NMR (100.62 MHz, 298 K, d_8-THF): δ 16.90 (CH_3), 20.43 (CH_3), 26.18 (THF), 31.05 ($C(CH_3)_3$), 34.62 ($C(CH_3)_3$), 68.02 (THF), 120.70, 125.82, 132.69, 132.89, 134.21, 161.31 (Ph)

Synthesis of [(*rac*)-BIPHEN]$Na_2Mg^nBu_2(TMEDA)_2$

[(*rac*)-BIPHEN]$Na_2Mg^nBu_2(TMEDA)_2$ 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 ^{n}BuNa (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 Mg^nBu_2 (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. Affter storage at sub-ambient temperature the soluton was filtered to yield [(*rac*)-BIPHEN]$Na_2Mg^nBu_2(TMEDA)_2$ as a microcrystaline powder (yield 0.216 g, 56 %). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ -0.79 (2H, m, $MgCH_2$), -0.314 (2H, m, $MgCH_2$), 1.25 (6H, t, CH_3), 1.69 (9H, bs, $C(CH_3)_3$), 1.79 (8H, bs, CH_2, TMEDA), 1.80 (6H, s, CH_3), 1.85 (33H, bs, CH_3 TMEDA and $C(CH_3)_3$), 2.22 (6H, s, CH_3), 7.18 (2H, s, Ph). ^{13}C NMR (100.62 MHz, 298 K, C_6D_6): δ 8.84 (2 x $MgCH_2$), 14.90 (2 x CH_3, Butyl), 17.48 (2 x CH_3, (*rac*)-BIPHEN), 20.77 (2 x CH_3, (*rac*)-BIPHEN), 31.70 ($C(CH_3)_3$, (*rac*)-BIPHEN), 32.81-33.74 (CH_2, Butyl), 35.34 ($C(CH_3)_3$, (*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]$Na_2Mg^nBu_2(PMDETA)_2$

[(*rac*)-BIPHEN]$Na_2Mg^nBu_2(PMDETA)_2$ 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 ^{n}BuNa (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 Mg^nBu_2 (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 colouless crystals of [(*rac*)-BIPHEN]$Na_2Mg^nBu_2(PMDETA)_2$ (yield 0.245 g, 56 %). ^{1}H NMR (400.13 MHz, 298 K, C_6D_6): δ -0.75 (4H, m, $MgCH_2$), 1.26 (6H, t, CH_3), 1.77 (18H, bs, $C(CH_3)_3$), 1.82 (16H, bs, CH_2, PMDETA), 1.86 (6H, s, CH_3, PMDETA), 1.90 (6H, s, CH_3), 1.93 (24H, bs, CH_3, PMDETA), 2.31 (6H, s, CH_3), 7.14 (2H, s, Ph). ^{13}C NMR (100.62 MHz, 298 K, C_6D_6): δ 8.78 (2 x $MgCH_2$), 14.87 (2 x CH_3, Butyl), 17.95 (2 x CH_3, (*rac*)-BIPHEN), 20.81 (2 x CH_3, (*rac*)-BIPHEN), 32.25 ($C(CH_3)_3$, (*rac*)-BIPHEN),

33.53 (CH_2, Butyl), 34.00 (CH_2, Butyl), 35.45 ($C(CH_3)_3$, (*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]$Na_2Mg^nBu_2(TMEDA)_2$ (0.029 g, 0.0377 mmol) was combined with tetraphenylnapthalene (0.010 g, 0.025 mmol) as an internal standard and 0.5 ml of d_8-toluene in a J Young's NMR tube. The desired substrate (0.0754 mmol) was then added and the reation monitored at regular intervals by ^{1}H 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]$Na_2Mg^nBu_2(PMDETA)_2$ (0.033 g, 0.0377 mmol) was combined with tetraphenylnapthalene (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 d_8-toluene in a J Young's NMR tube. The desired substrate (0.0754 mmol) was then added and the reation monitored at regular intervals by ^{1}H NMR spectroscopy and yields obtained were calculated from NMR spectroscopic integrals relative to the internal standard.

Crystalographic 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 thatcould 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 form approximately 248 $Å^3$ 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	$C_{65.6}H_{99.}Na_4O_{8.4}$	$C_{64}H_{96}MgNa_2O_8$	$C_{50}H_{96}MgN_6Na_2O_2$
FW	1114.20	1063.69	883.61
Crystal System	Tetragonal	Orthorhombic	Monoclinic
Space Group	$P4_12_12$	I222	P_n
Wavelengh/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

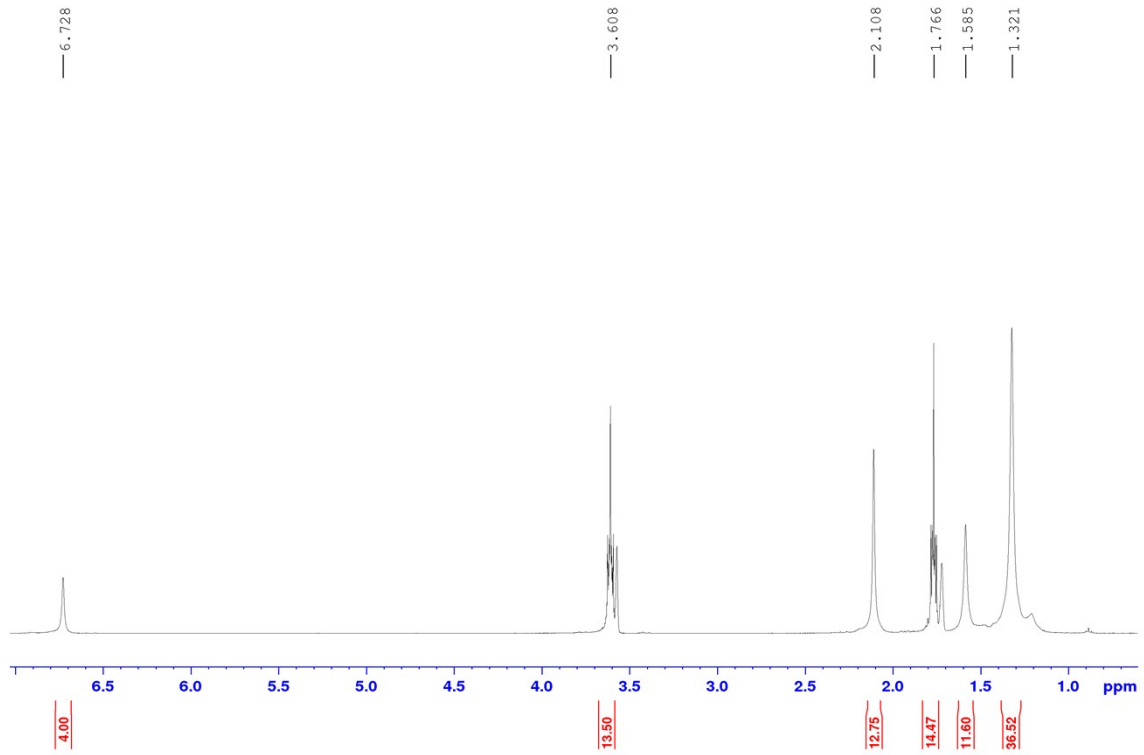
Parameters			
2θmax	146.36	54.00	146.41
Rint	0.0202	0.0234	0.0506
Goodness of Fit	1.074	1.043	1.038
R[on F, obs refs only]	0.0453	0.0426	0.0713
wR (on F^2, all data)	0.1365	0.1128	0.1896
Largest diff. peak/hole / e $Å^{-3}$	0.52/−0.27	0.21/−0.19	1.09/−0.28
Flack Parameter	0.018(14)	−0.16(17)	0.07(4)

Table S1: Comparison of key bond lengths and bond angles between (**1**) and $(BIPHEN)_2Li_4(THF)_4$ [where Am = Na for **1** and Am = Li for $(BIPHEN)_2Li_4(THF)_4$].

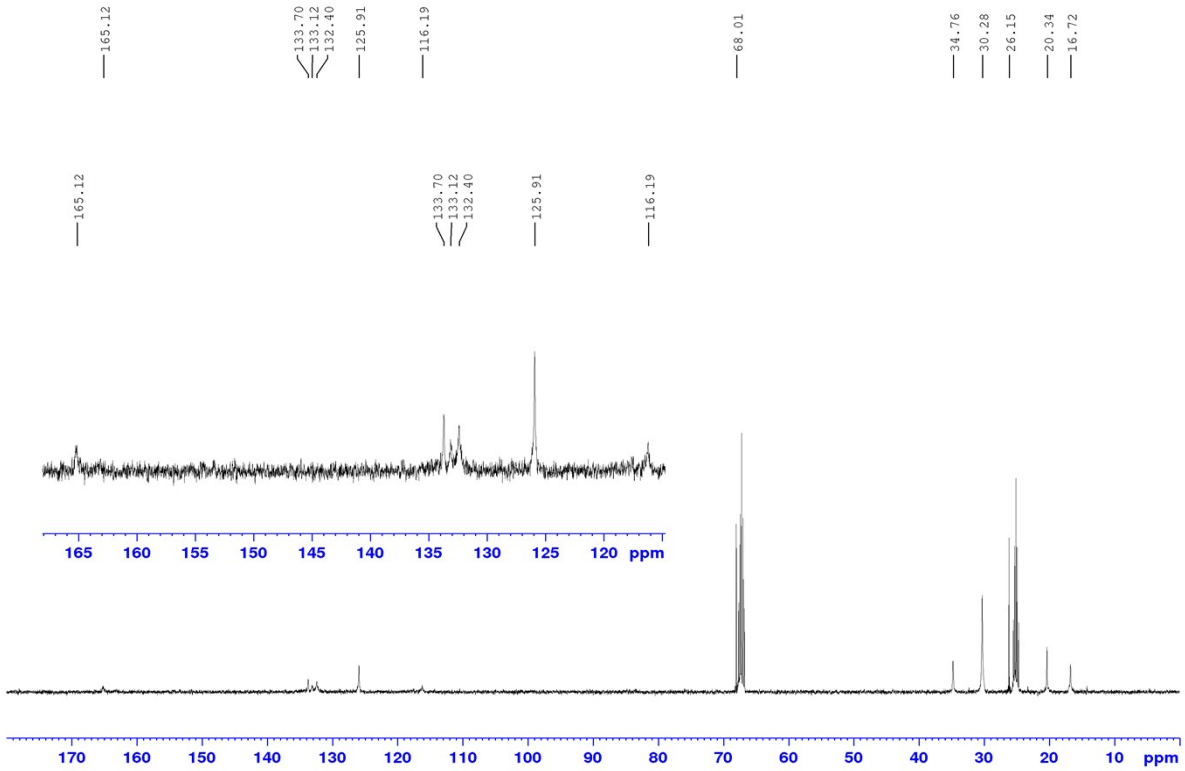
	$(BIPHEN)_2Na_4(THF)_4$	$(BIPHEN)_2Li_4(THF)_4$
Bond Lengths (Å)		
AM(1)-O(1)	2.217(2)	1.879(3)
AM(1)-O(2)	2.313(2)	2.070(3)
AM(2)-O(1)	2.199(2)	1.875(3)
AM(3)-O(2)	2.265(2)	1.901(3)
Bond Angles (°)		
O(1)-AM(1)-O(2)	110.87(7)	133.04(5)
O(1)-AM(1)-O(1´)	92.49(11)	92.27(17)
O(2)-AM(1)-O(2´)	78.01(10)	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

$[BIPHEN]_2Na_4(THF)_4$ (1)

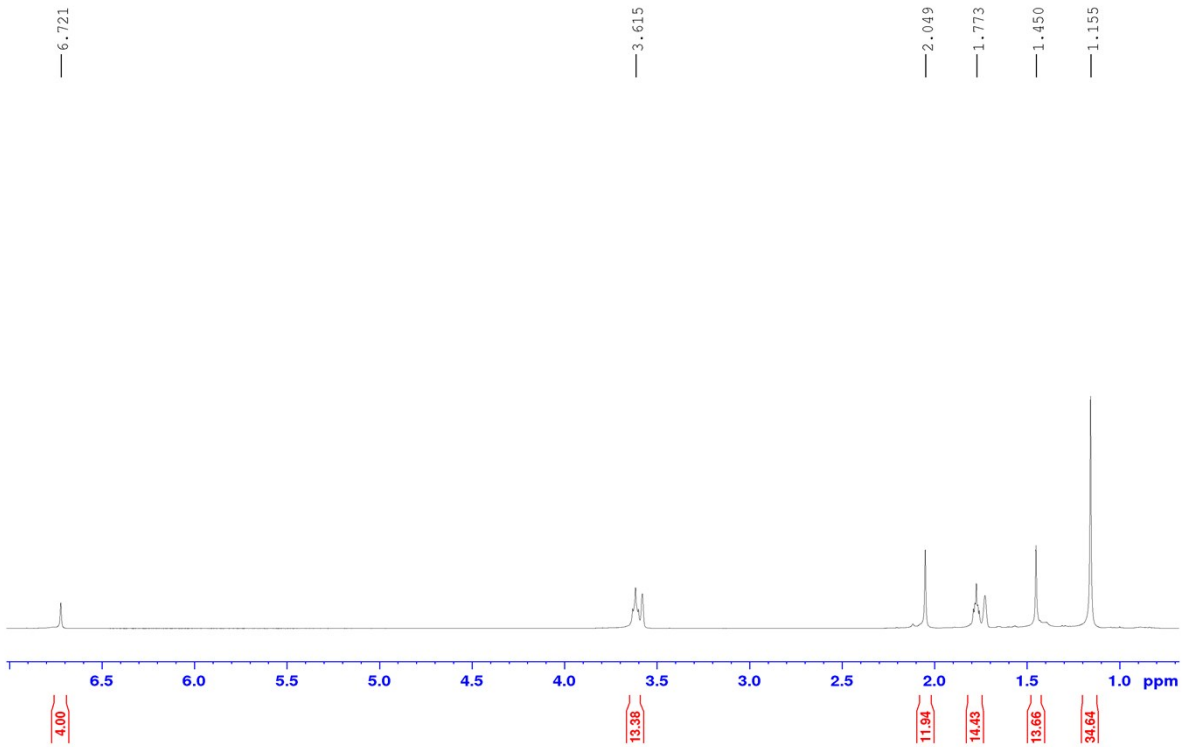


S1: ^1H NMR Spectrum of $[BIPHEN]_2Na_4(THF)_4$ in d_8-THF at 300 K

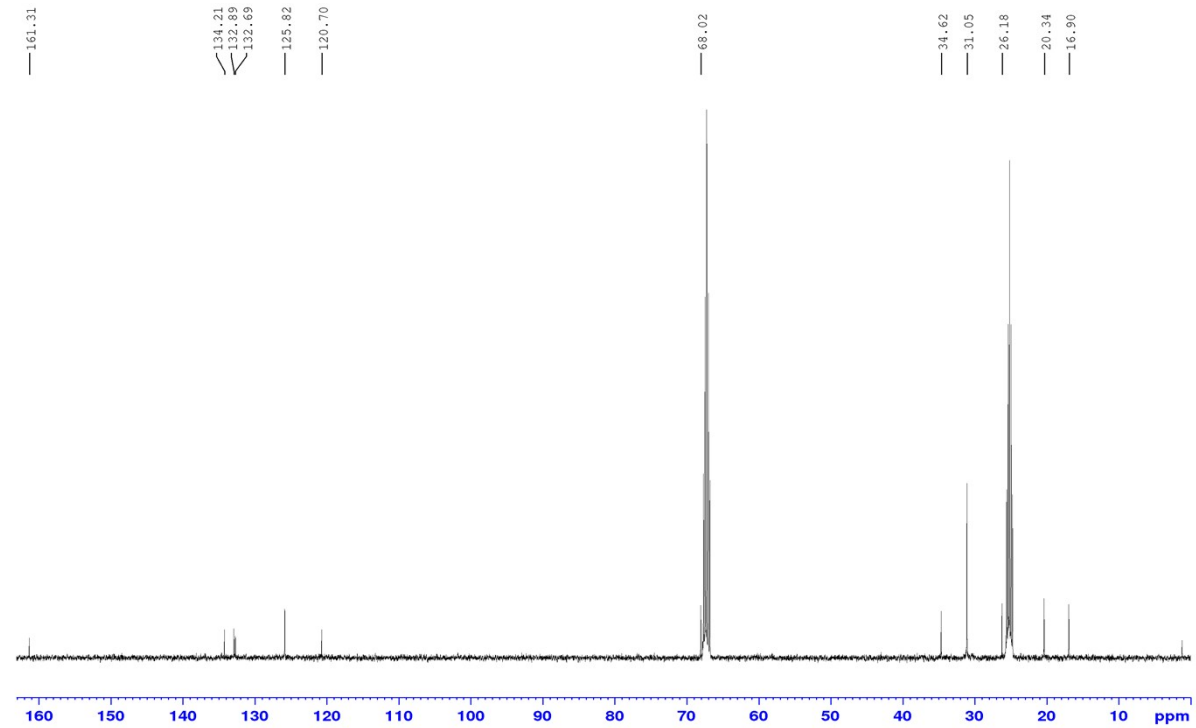


S2: ^{13}C NMR Spectrum of $[BIPHEN]_2Na_4(THF)_4$ in d_8-THF at 300 K

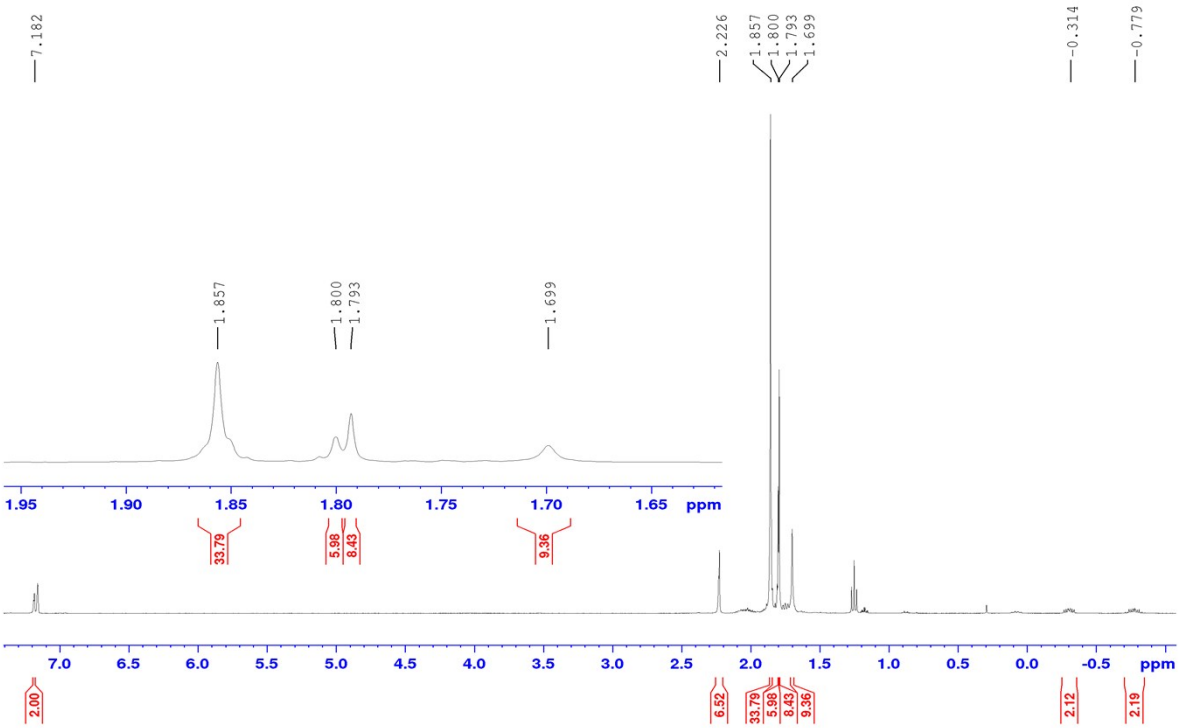
[BIPHEN]$_2$Na$_2$Mg(THF)$_4$ (2)



S3: ^{1}H NMR Spectrum of [BIPHEN]$_2$Na$_2$Mg(THF)$_4$ in d_8-THF at 300 K

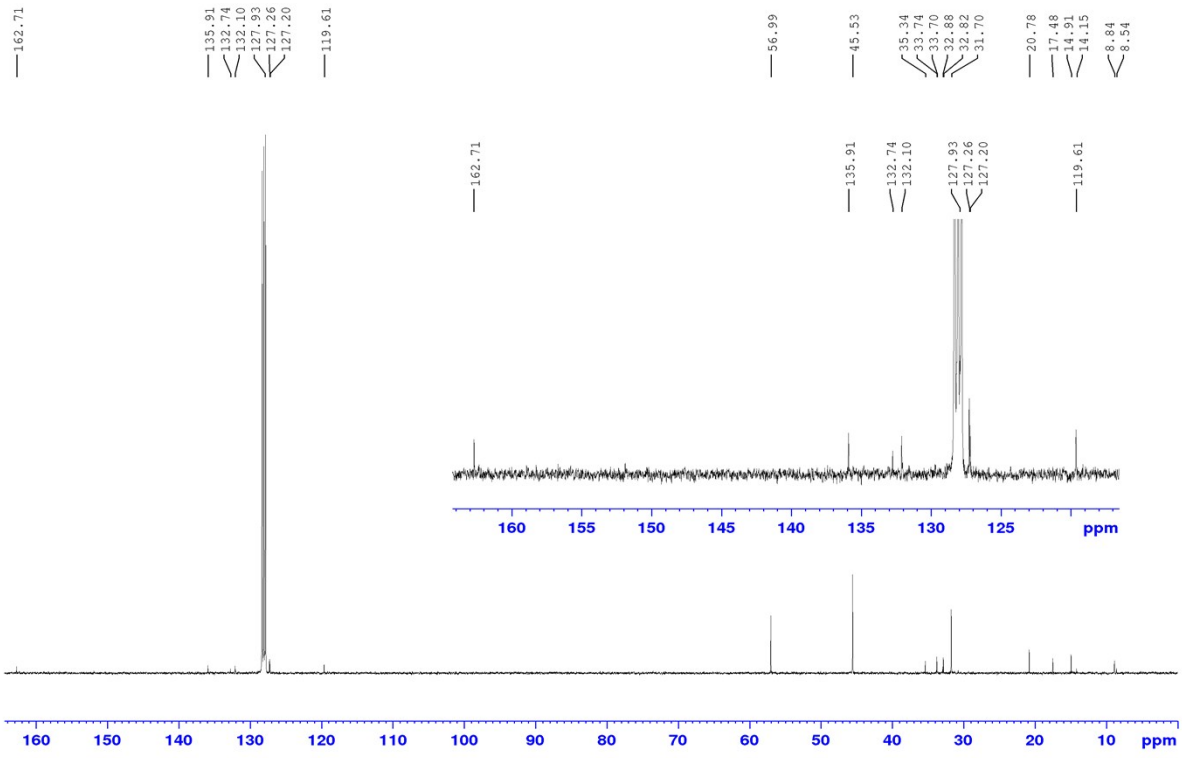


S4: ^{13}C NMR Spectrum of [BIPHEN]$_2$Na$_2$Mg(THF)$_4$ in d_8-THF at 300 K



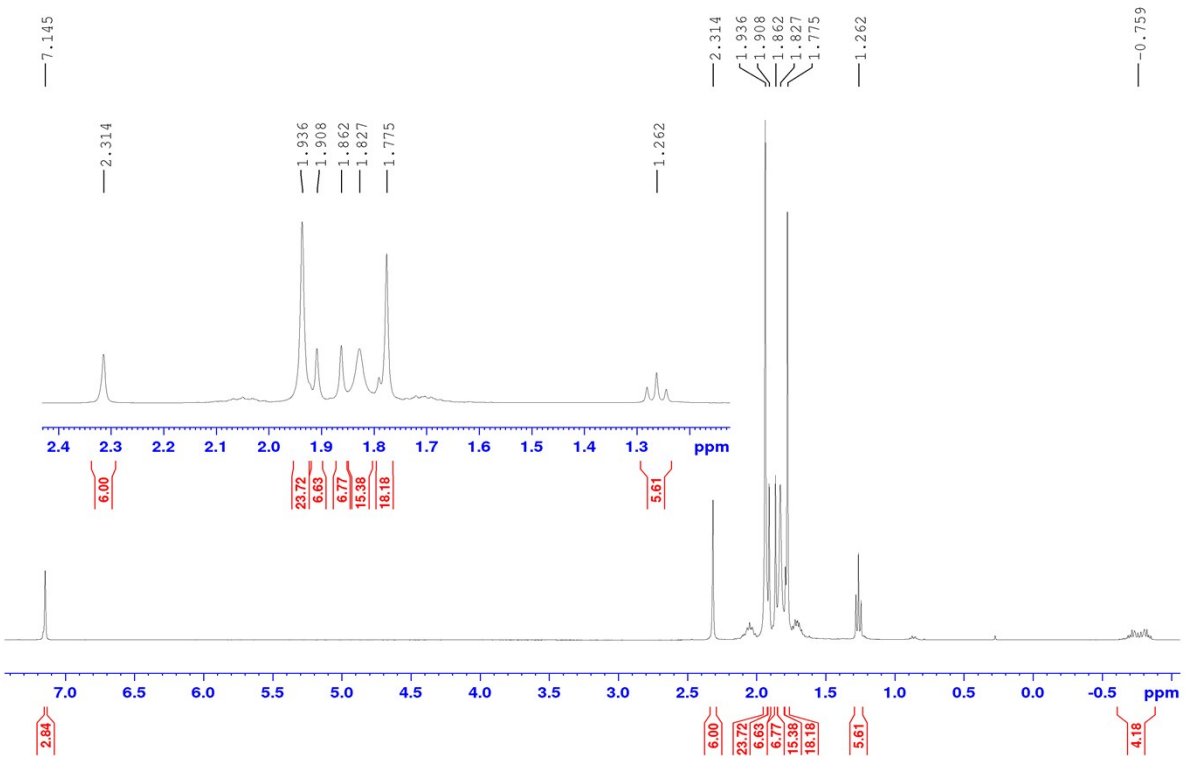
[(*rac*)-BIPHEN]$Na_2MgBu_2(TMEDA)_2$ (3)

S5: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(TMEDA)_2$ in C_6D_6 at 300 K

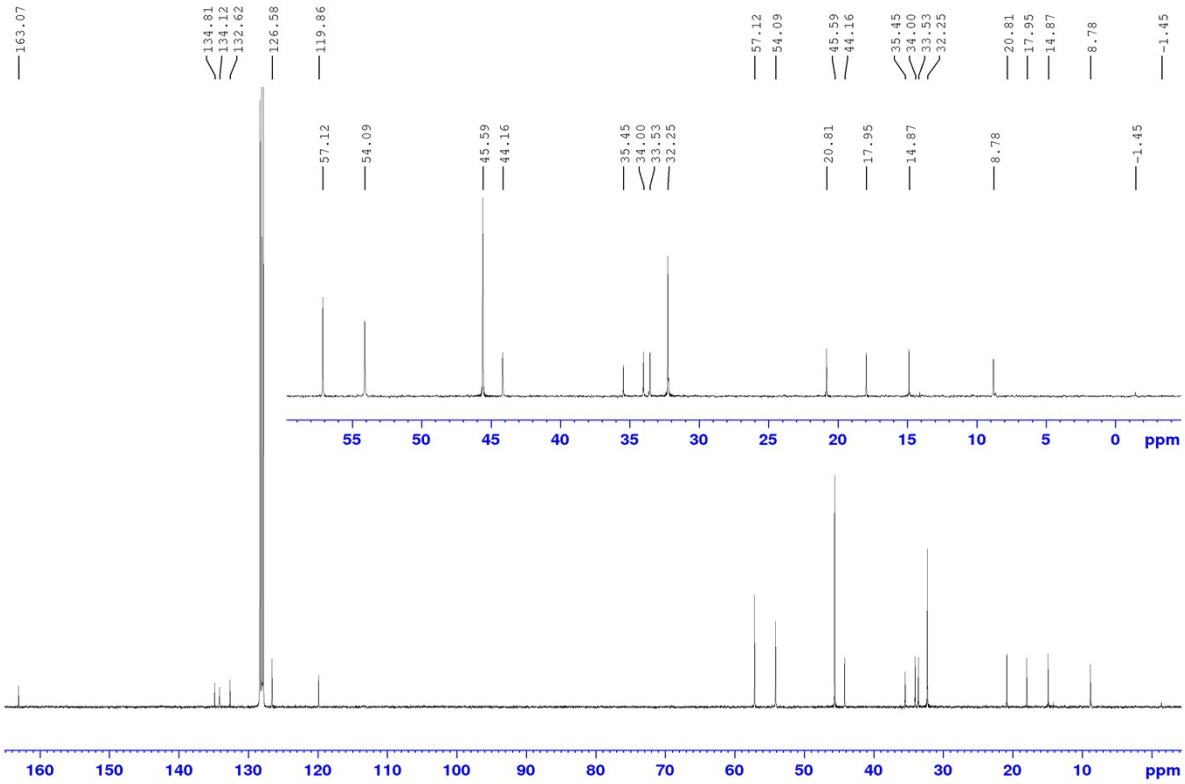


S6: ^{13}C NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(TMEDA)_2$ in C_6D_6 at 300 K

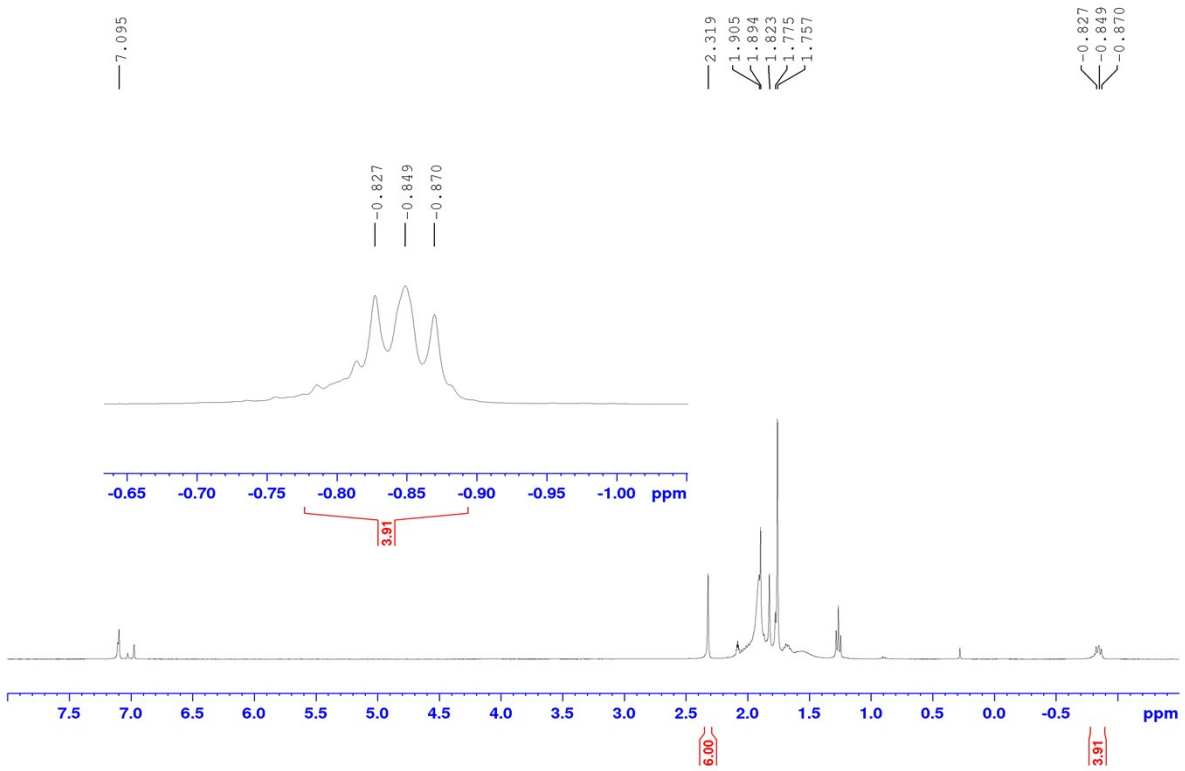
[(*rac*)-BIPHEN]$Na_2MgR_2(PMDETA)_2$ (4)



S7: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgR_2(PMDETA)_2$ in C_6D_6 at 300 K

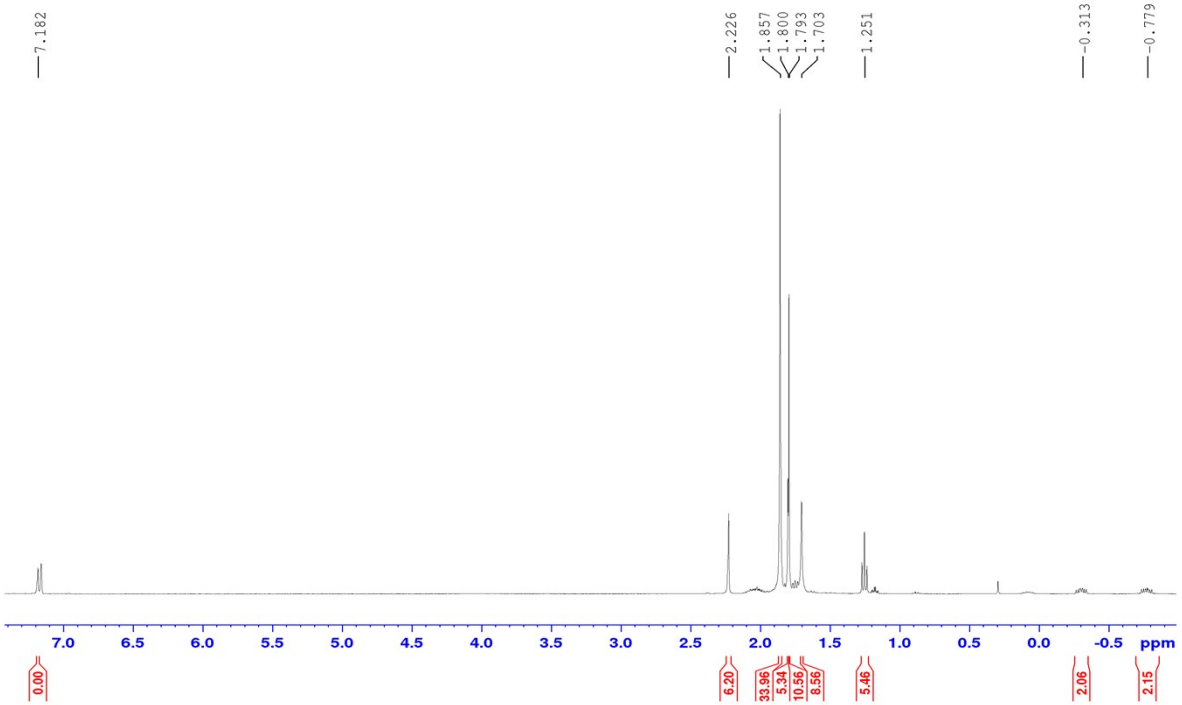


S8: ^{13}C NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgR_2(PMDETA)_2$ in C_6D_6 at 300 K

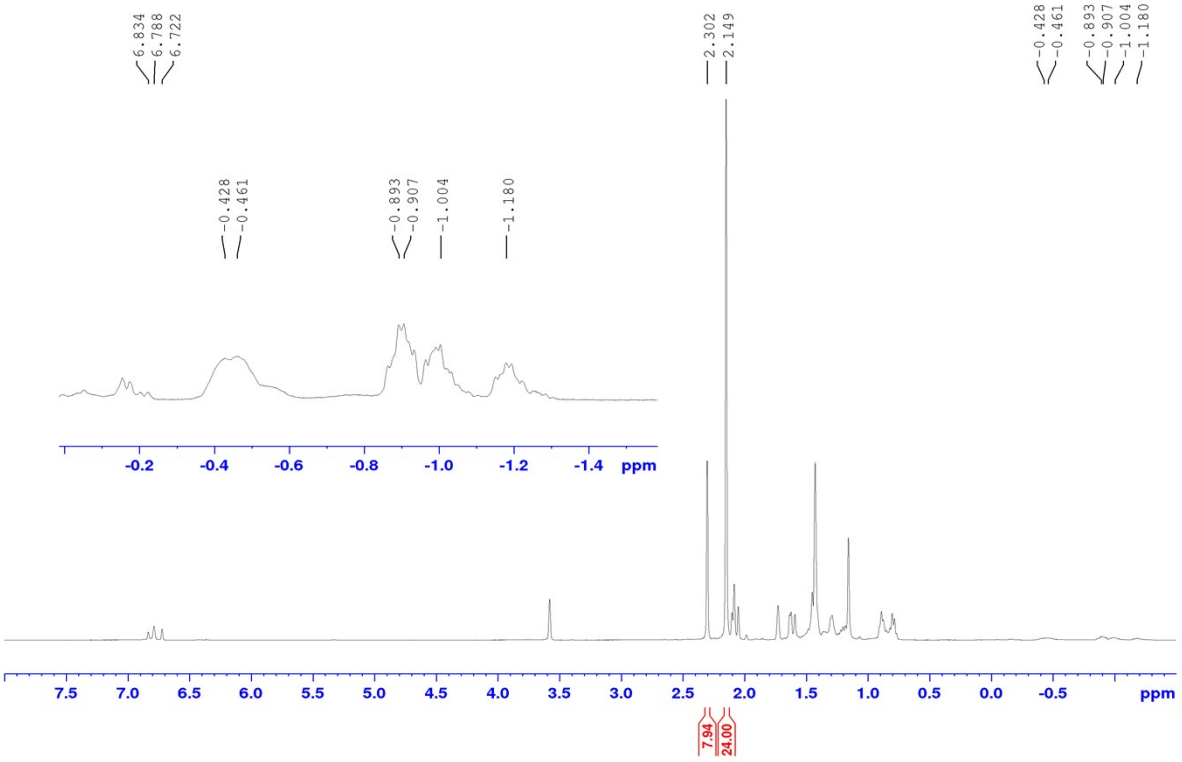


S9: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgR_2(PMDETA)_2$ in d_8-Tol at 263 K.

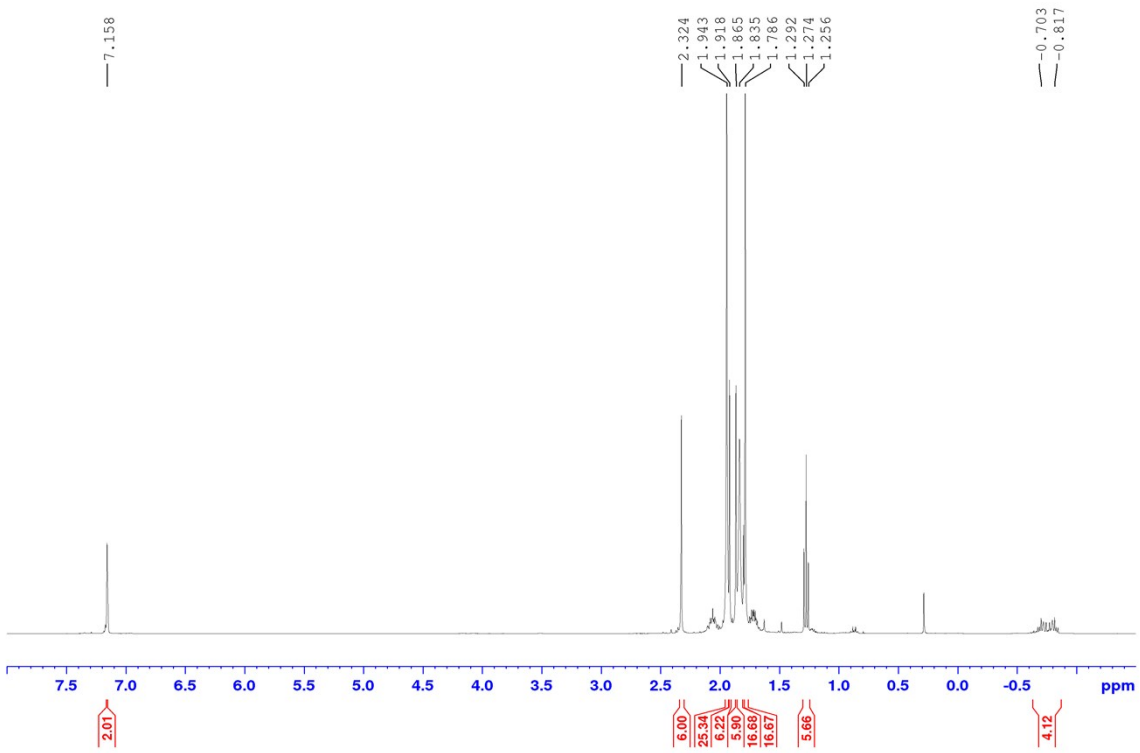
Variable Temperature Stability Studies of 3 and 4



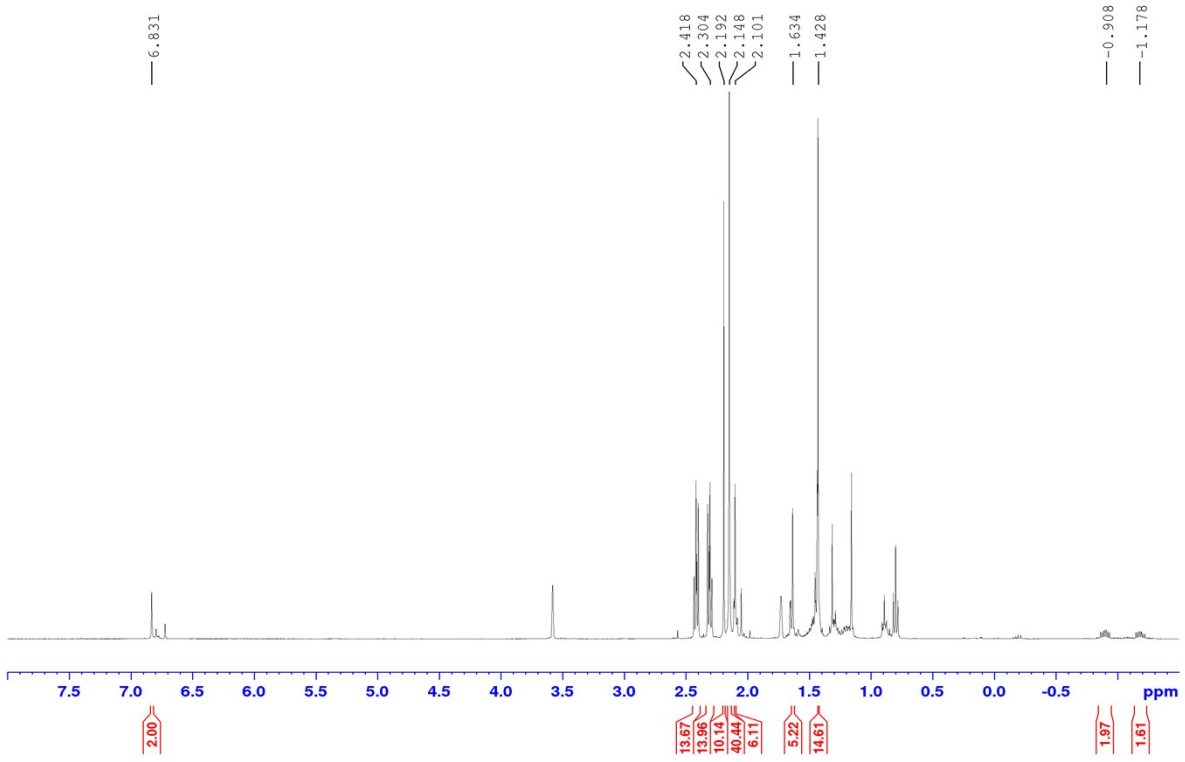
S10: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(TMEDA)_2$ in C_6D_6 after heating to 50 °C for 12 hours



S11: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(TMEDA)_2$ in d_8-THF after heating to 50 °C for 12 hours

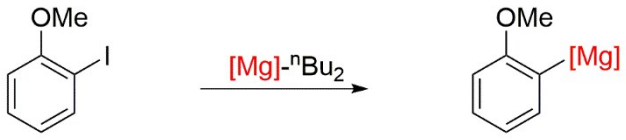


S12: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(PMDETA)_2$ in C_6D_6 after heating to 50 °C for 12 hours



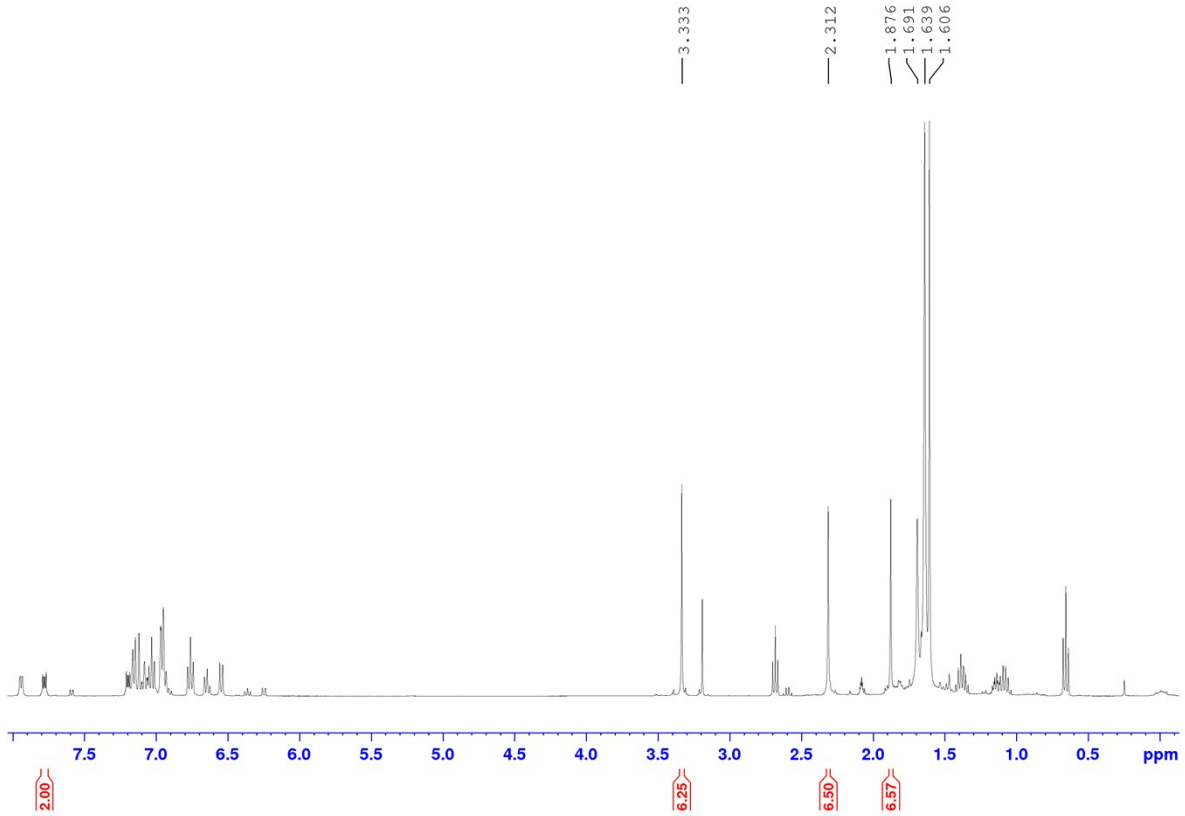
S13: ^{1}H NMR Spectrum of [(*rac*)-BIPHEN]$Na_2MgBu_2(PMDETA)_2$ in d_8-THF after heating to 50 °C for 12 hours

Metal-Halogen Exchange reactions



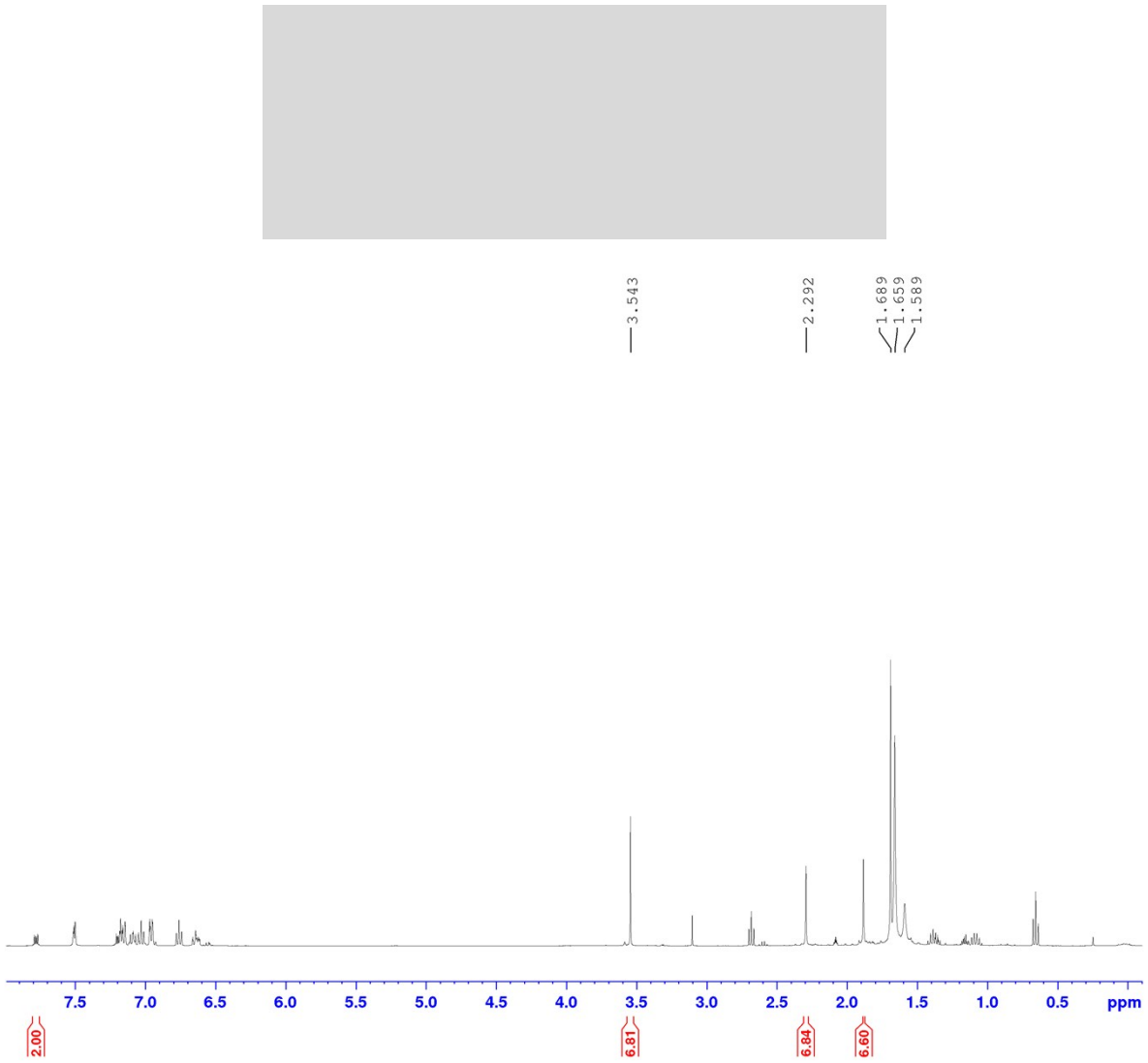
[Mg] = (*rac*)-BIPHENNa$_2$Mg(TMEDA)$_2$

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



S14: Product **5** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene 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-Tetraphenylnapthalene as internal standard, yield 91% (25 °C, 18 h)

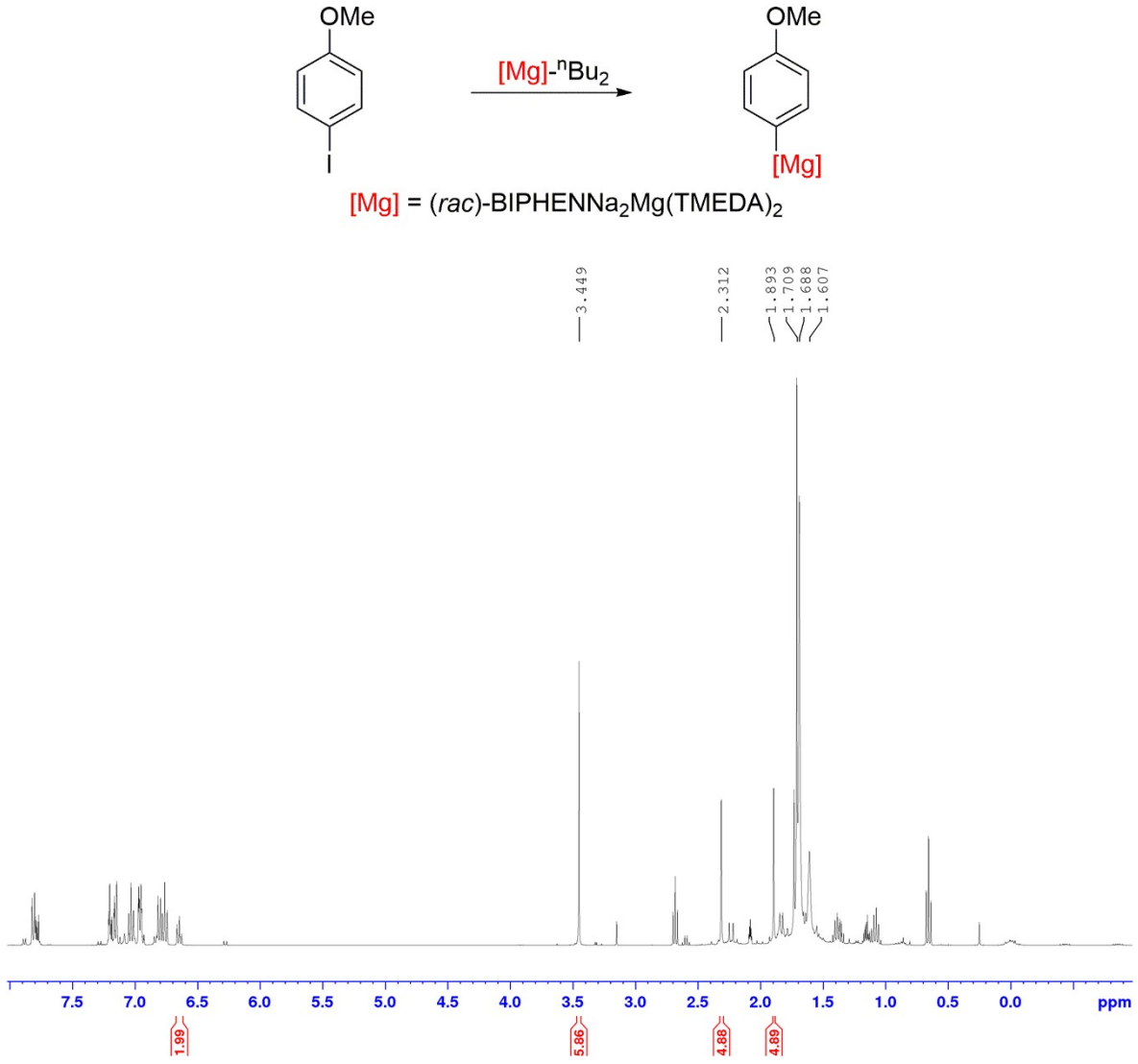
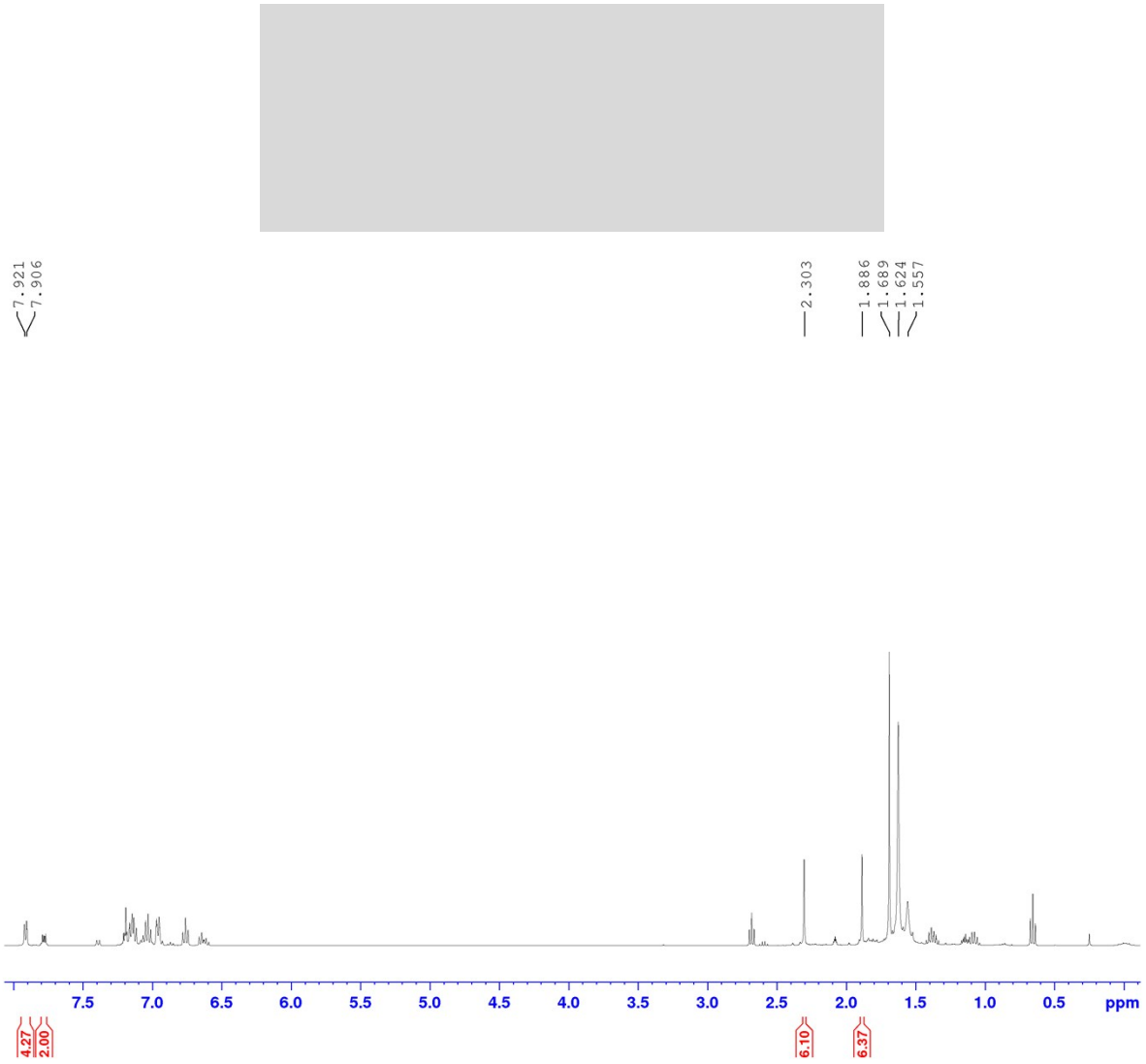


Table 3, product **7** using **3**

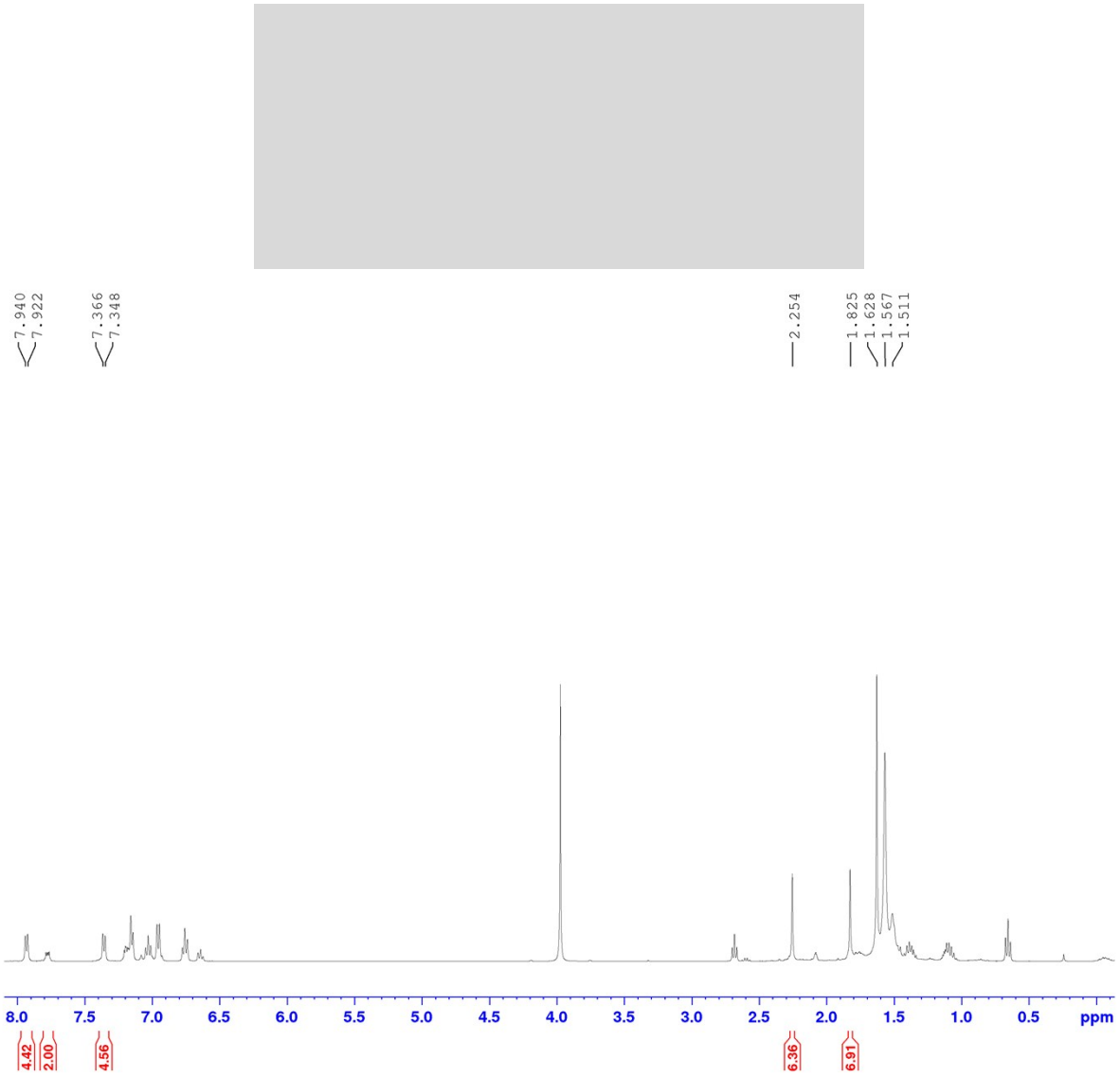
S16: Product **7** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene as internal standard, yield 79% (25 °C, 18 h)

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



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

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



S18: Product **9** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene and ferrocene as internal standard, yield 87% (25 °C, 15 min)

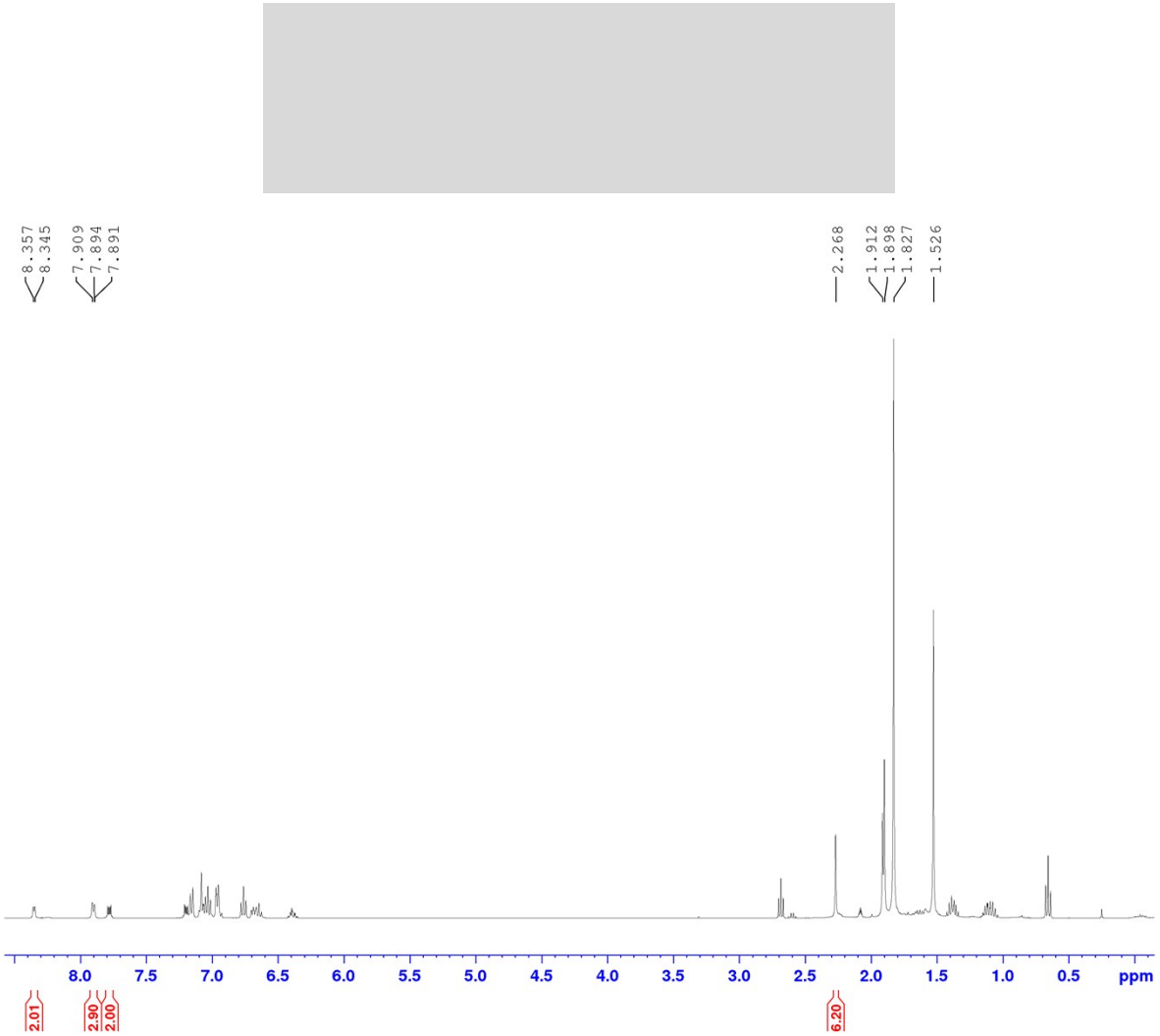
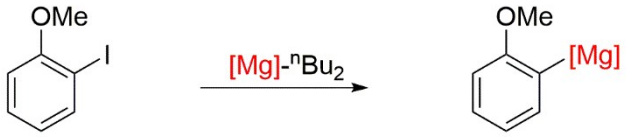


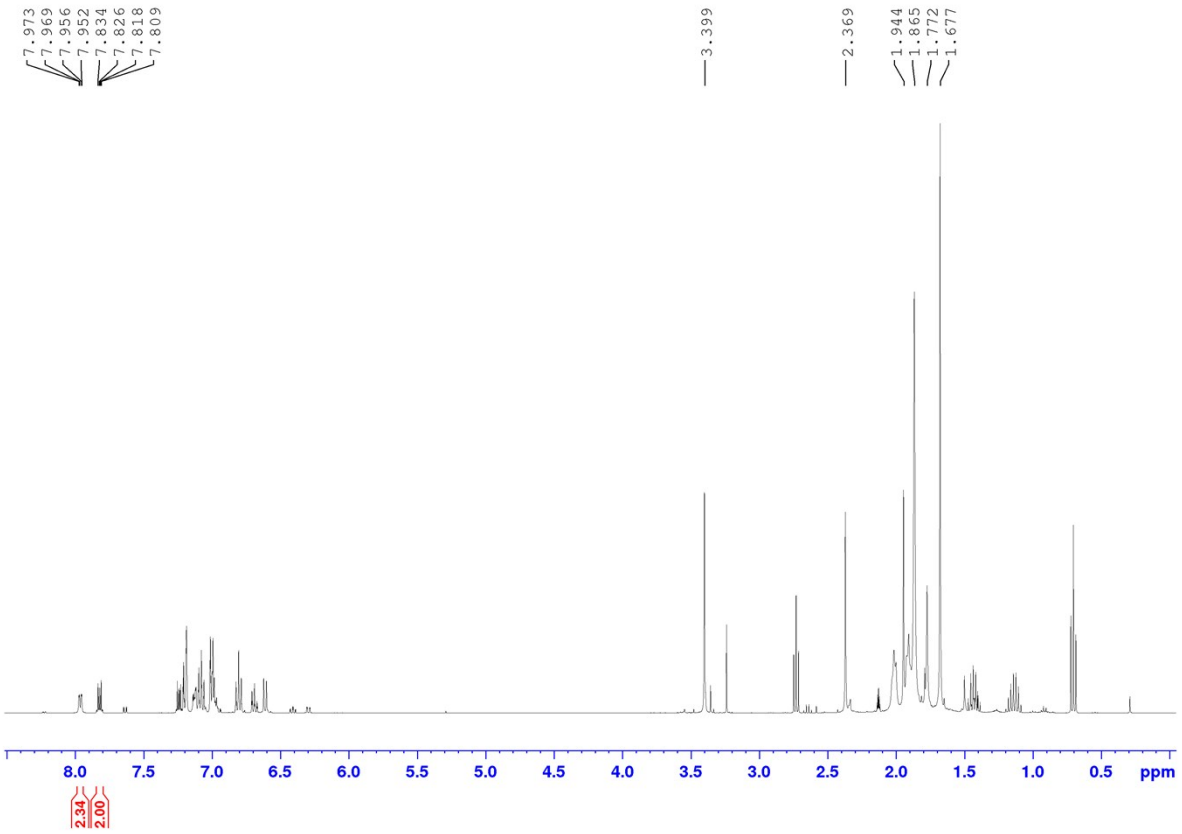
Table 3, product **10** using **3**

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

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

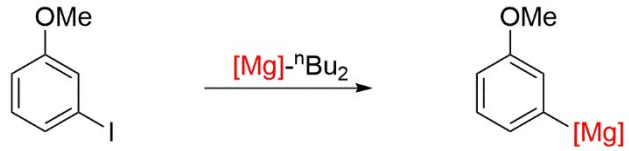


[Mg] = (*rac*)-BIPHENNa$_2$Mg(PMDETA)$_2$

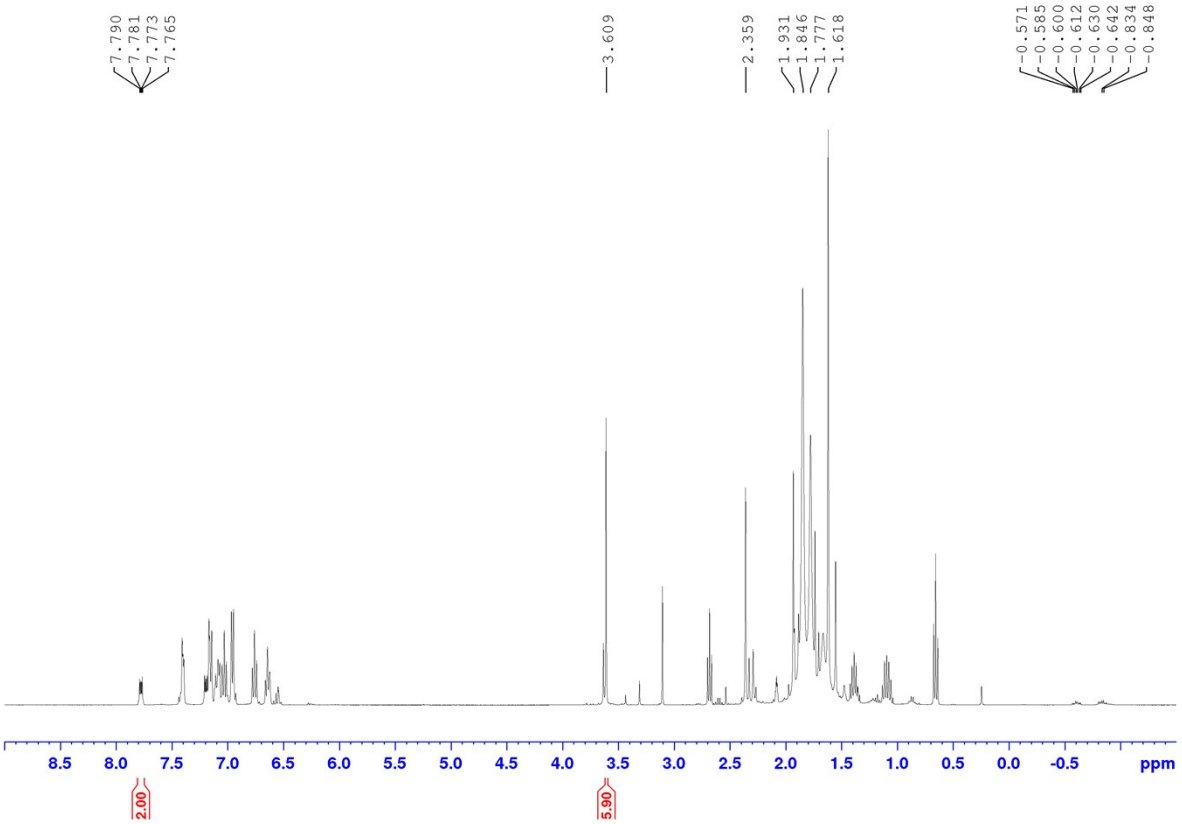


S20: Product **5** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene as internal standard, yield 77% (25 °C, 18 h)

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

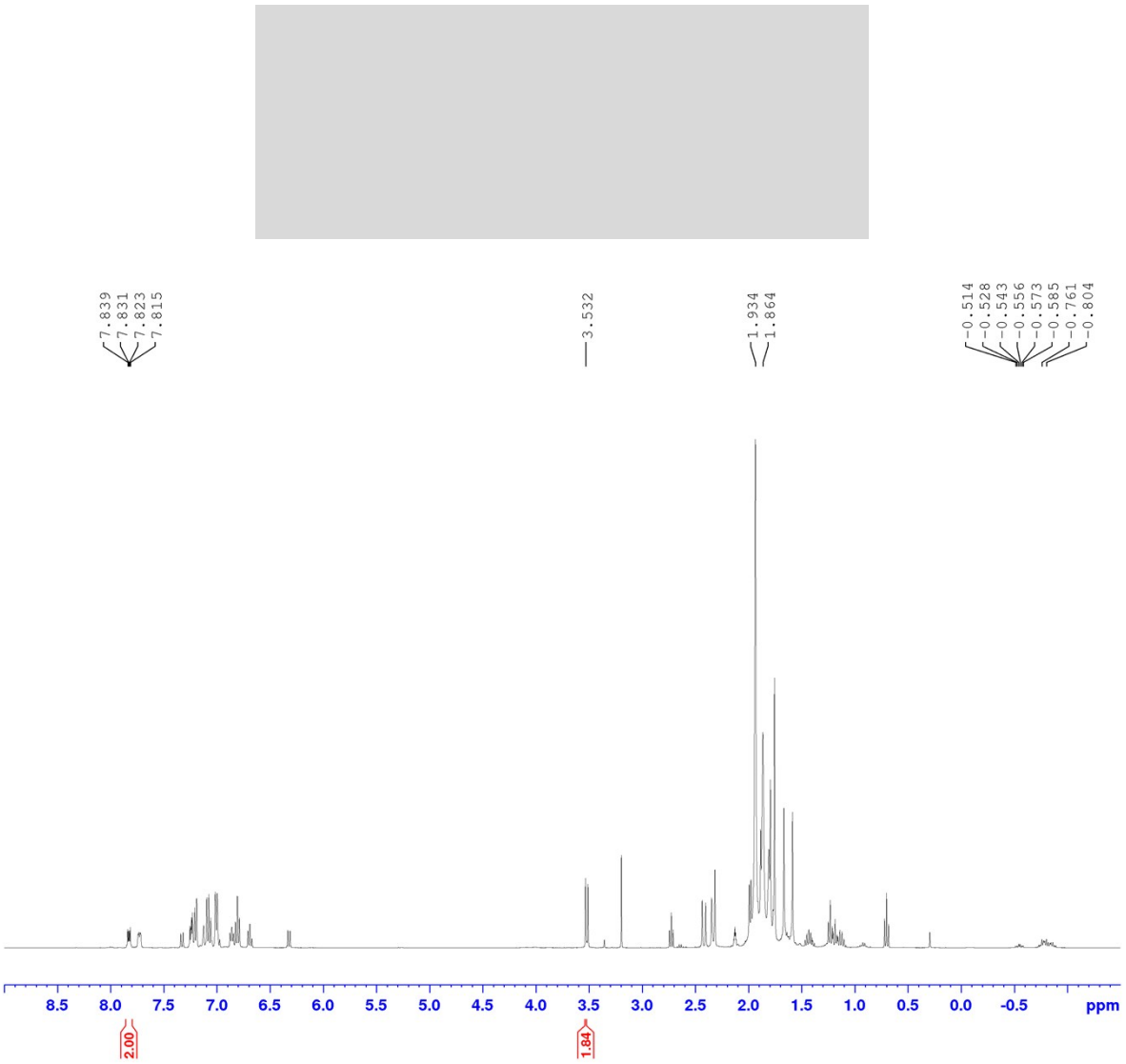


[Mg] = (*rac*)-BIPHENNa$_2$Mg(PMDETA)$_2$



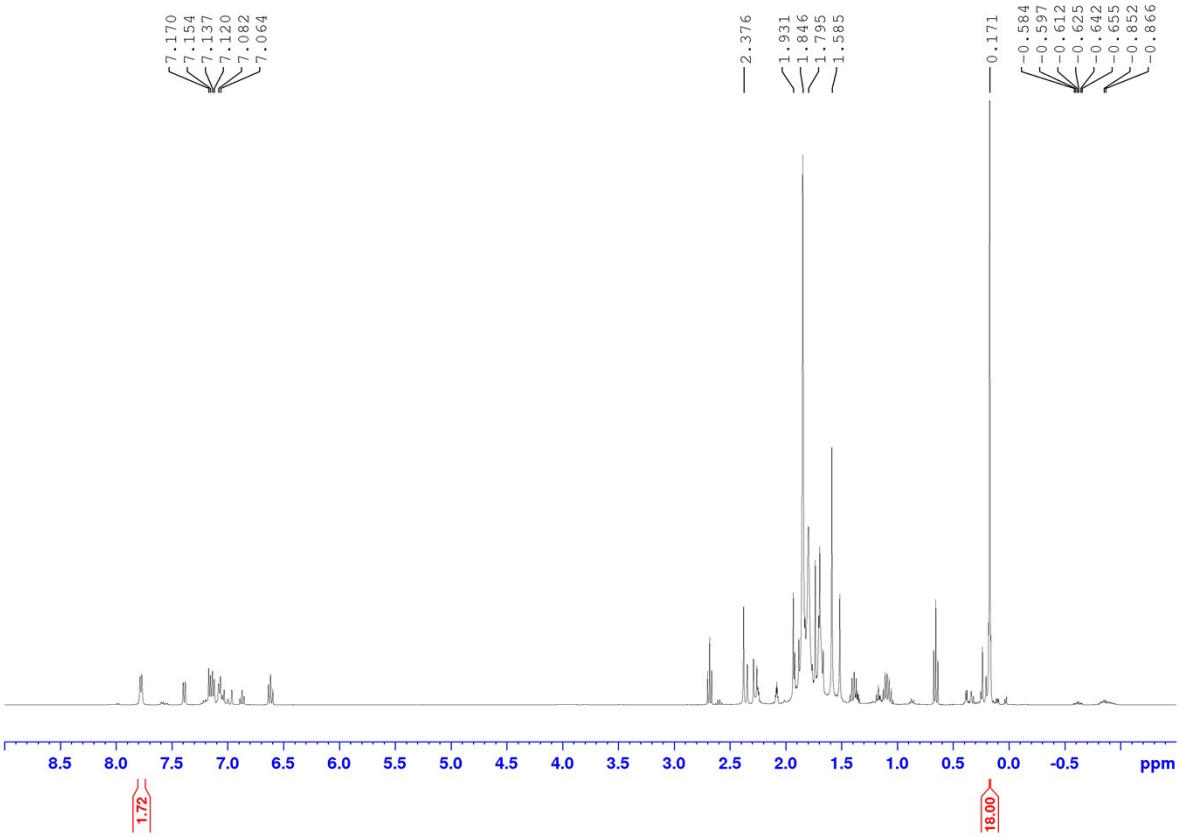
S21: Product **6** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene as internal standard, yield 65% (25 °C, 18 h)

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



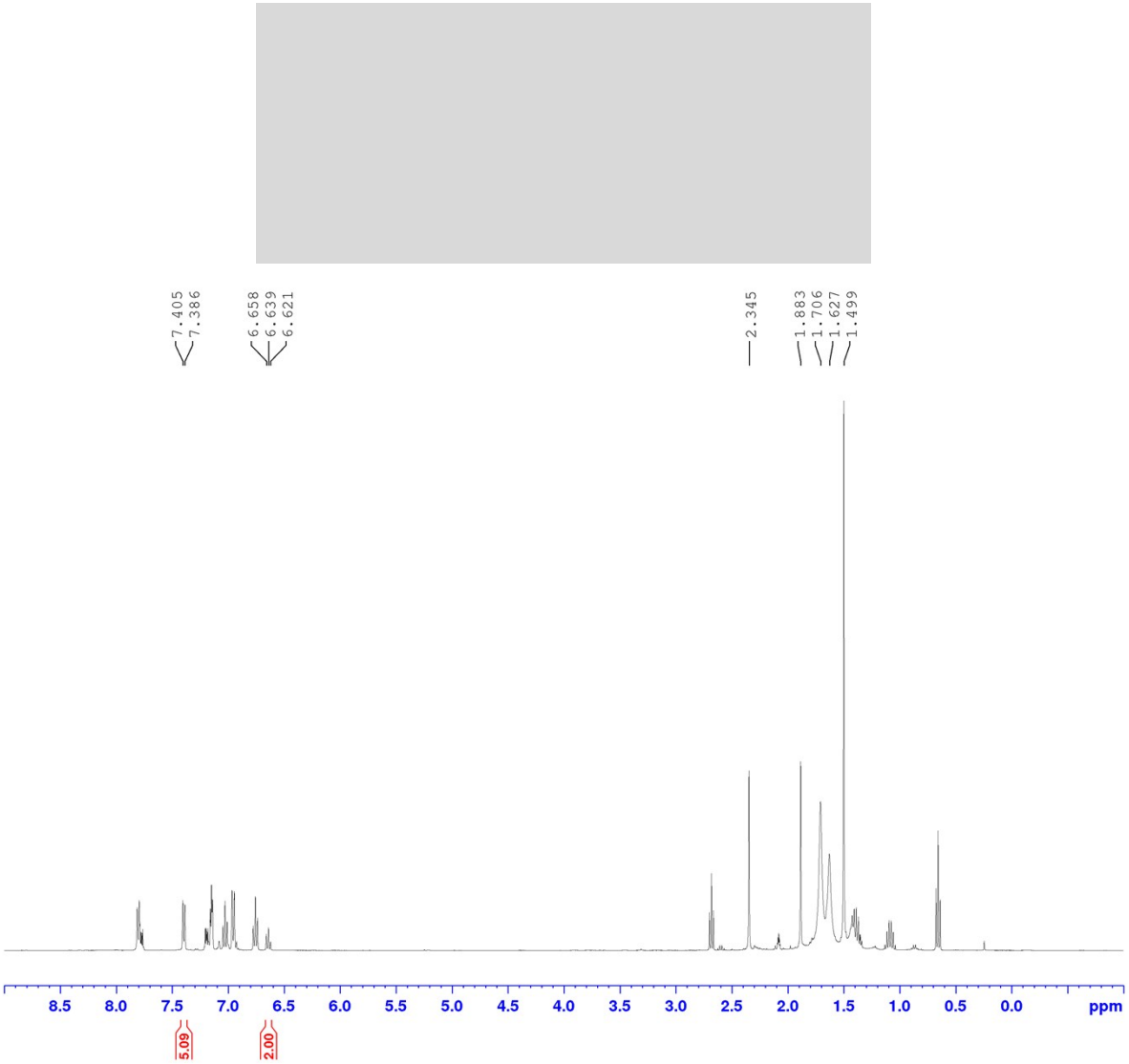
S22: Product **7** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene as internal standard, yield 20% (25 °C, 18 h)

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



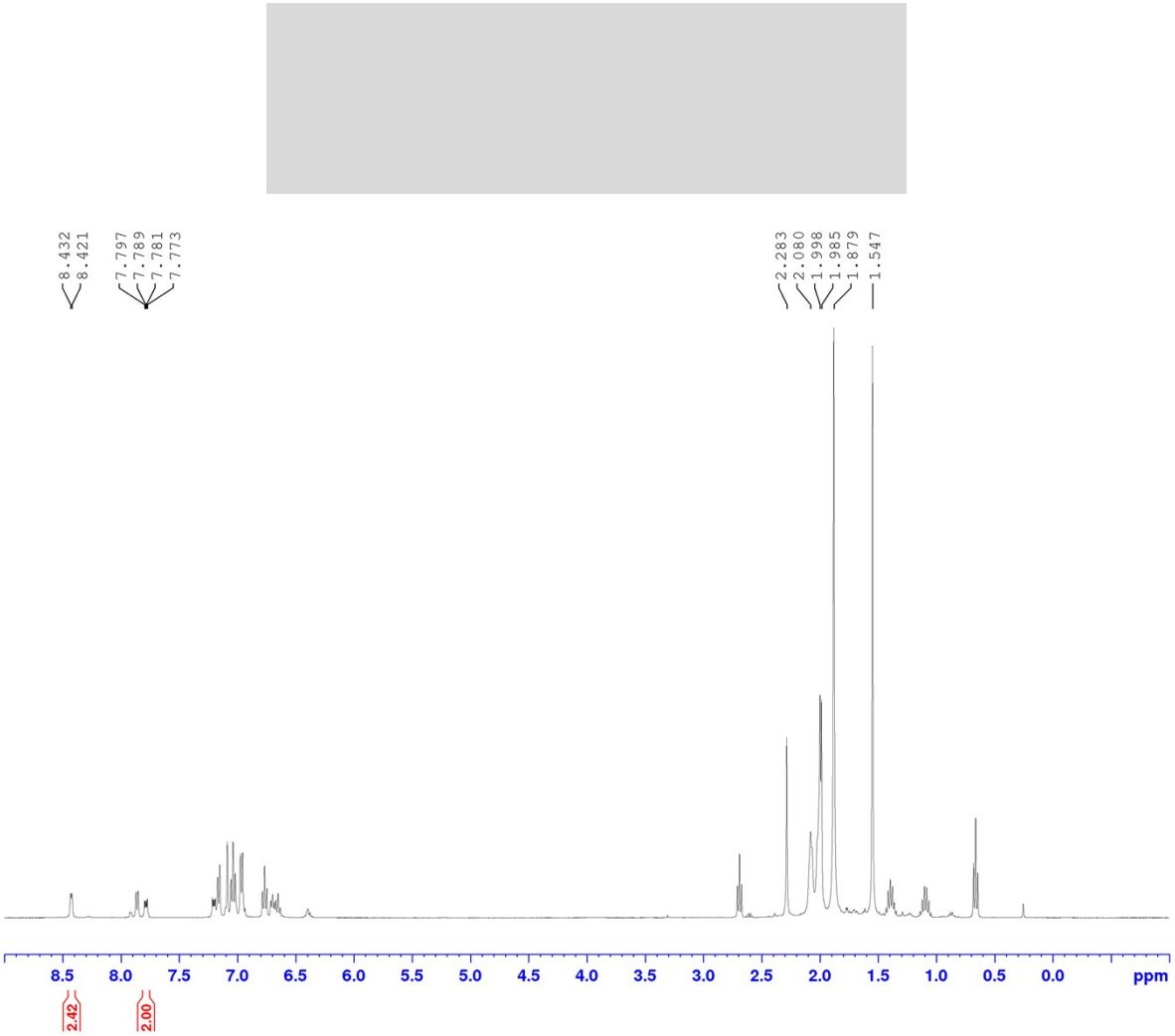
S23: Product **8** in d_8-Tol with hexamethylcyclotrisiloxane as internal standard, yield 57% (25 °C, 18 h)

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



S24: Product **9** in d_8-Tol with 1,2,3,4-Tetraphenylnapthalene 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-Tetraphenylnapthalene 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.