Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Lithium phenolates with a hexagonal-prismatic Li_6O_6 core isolated via a cage-shaped tripodal ligands system: crystal structures and their behavior in solution

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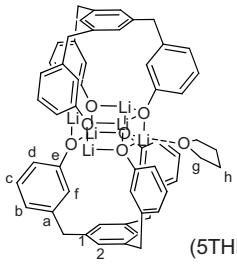
General. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 spectrophotometer. ^{1}H and ^{13}C spectra were obtained with a 400 and 100 MHz spectrometer, respectively, with TMS as internal standard. ^{19}F NMR spectra were obtained with a 372 MHz spectrometer with $BF_3{\cdot}OEt_2$ in $CDCl_3$ as external standard. ^{7}Li NMR spectra were obtained with a 154 MHz spectrometer with LiCl in D_2O as external standard. ^{19}F NMR spectra were obtained with a 372 MHz spectrometer with $BF_3{\cdot}OEt_2$ in $CDCl_3$ as external standard. Mass spectra were recorded on a JEOL JMS-DS303. All reactions were carried out under nitrogen. Synthesis of lithium complexes was performed in nitrogen-filled glove box.

Materials. Dehydrated dichloromethane, THF, and hexane were purchased and used as obtained. The compounds **1a-d**H_3 were prepared according to our previous report.[1] All other reagents are commercially available.

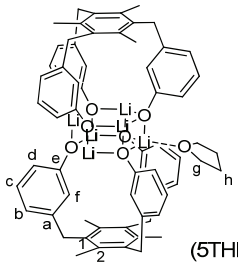
(**1a**Li_3)$_2$·(THF)$_6$



(5THFs is omitted)

In a glove box, to a mixture of 1,3,5-tris(3-hydroxybenzyl)benzene (0.1 mmol = 39.8 mg) in THF (5 mL) was added *n*-BuLi in hexane (0.318 mmol, 0.2 mL, 1.59 M) at -30 °C with stirring. The stirring was kept for 2 h with warming up to rt. Evaporation of volatiles gave a white solid. The obtained crude materials were washed with hexane and evaporated to give the product quantitatively. The product was recrystallized from dichloromethane/hexane(2/1) for X-ray analysis. ^{1}H NMR: (400 MHz, $CDCl_3$) 6.88 (m, 12H, c-H and 2-H), 6.49 (d, J = 7.6 Hz, 6H, b-H), 6.23 (dd, J = 7.6, 1.8 Hz, 6H, d-H), 5.86 (s, 6H, f-H), 3.91 (s, 12H, 1-CH_2), 3.19 (br, 24H, g-H_2), 1.47 (br, 24H, h-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 166.0 (s, C-e), 143.7 (s, C-a), 141.7 (s, C-1), 130.0 (d, C-2), 128.6 (d, C-c), 121.2 (d, C-f), 116.7 (d, C-d), 115.2 (d, C-b), 67.6 (t, C-g), 40.6 (t, 1-CH_2), 25.1 (t, C-h); ^{7}Li NMR: (153.7 MHz, $CDCl_3$) 0.08.

(**1b**Li_3)$_2$·(THF)$_6$

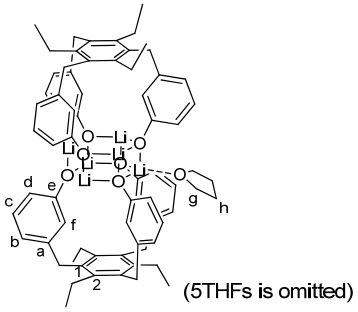


(5THFs is omitted)

In a glove box, to a mixture of 1,3,5-tris(3-hydroxybenzyl)-2,4,6-trimethylbenzene (0.1 mmol = 43.8 mg) in THF (5 mL) was added *n*-BuLi in hexane (0.318 mmol, 0.2 mL, 1.59 M) at -30 °C with stirring. The stirring was kept for 2 h with warming up to rt. Evaporation of volatiles gave a

white solid. The obtained crude materials were washed with hexane and evaporated to give the product quantitatively. The product was recrystallized from dichloromethane/hexane(2/1) for X-ray analysis. ^{1}H NMR: (400 MHz, $CDCl_3$) 6.90 (dd, *J* =8.0, 7.8 Hz, 6H, c-H), 6.58 (d, *J* = 7.8 Hz, 6H, b-H), 6.20 (dd, *J* = 8.0, 1.8 Hz, 6H, d-H), 5.91 (s, 6H, f-H), 4.13 (s, 12H, 1-CH_2), 3.13 (br, 24H, g-H_2), 2.08 (s, 18H, 2-CH_3), 1.51 (br, 24H, h-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 165.9 (s, C-e), 141.8 (s, C-a), 135.5 (s, C-2), 134.5 (s, C-1), 128.7 (d, C-c), 119.4 (d, C-f), 116.5 (d, C-d), 116.1 (d, C-b), 67.6 (t, C-g), 34.8 (t, 1-CH_2), 25.3 (t, C-h), 16.3 (q, 2-CH_3); ^{7}Li NMR: (153.7 MHz, $CDCl_3$) 0.06.

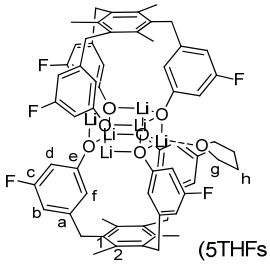
(**1c**Li_3)$_2$·$(THF)_6$



In a glove box, to a mixture of 1,3,5-tris(3-hydroxybenzyl)-2,4,6-triethylbenzene (0.1 mmol = 48.3 mg) in THF (5 mL) was added *n*-BuLi in hexane (0.318 mmol, 0.2 mL, 1.59 M) at -30 °C with stirring. The stirring was kept for 2 h with warming up to rt. Evaporation of volatiles gave a white solid. The obtained crude materials were washed with hexane and evaporated to give the product quantitatively. The product was recrystallized from dichloromethane/hexane(2/1) for X-ray analysis. ^{1}H NMR: (400 MHz, $CDCl_3$) 6.88 (dd, *J* = 7.8, 7.8 Hz, 6H, c-H), 6.57 (d, *J* = 7.8 Hz, 6H, b-H), 6.20 (d, *J* = 7.8, 1.6 Hz, 6H, d-H), 5.92 (s, 6H, f-H), 4.04 (s, 12H, 1-CH_2), 3.07 (t, *J* = 6.5 Hz, 24H, g-H_2), 2.30 (q, *J* = 7.4 Hz, 12H, 2-CH_2), 1.47 (t, *J* = 6.5 Hz, 24H, h-H_2), 1.22 (t, *J* = 7.4 Hz, 18H, 2-$CH_2C\mathit{H_3}$); ^{13}C NMR: (100 MHz, $CDCl_3$) 166.3 (s, C-e), 142.3 (s, C-a), 141.5 (s, C-2), 134.4 (s, C-1), 128.5 (d, C-c), 120.0 (d, C-f), 116.6 (d, C-d), 115.6 (d, C-b), 67.5 (t, C-

g), 33.6 (t, 1-CH_2), 25.3 (t, C-h), 23.5 (t, 2-CH_2), 16.0 (q, 2-CH_2CH_3); ^{7}Li NMR: (153.7 MHz, $CDCl_3$) -0.01.

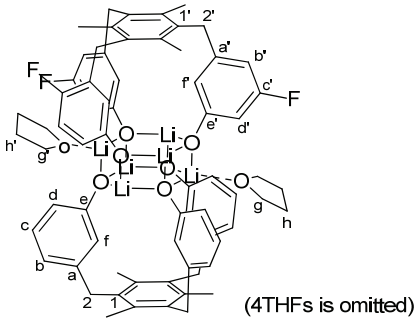
(**1d**Li_3)$_2$·$(THF)_6$



(5THFs is omitted)

In a glove box, to a mixture of 1,3,5-tris(3-fluoro-5-hydroxybenzyl)-2,4,6-trimethylbenzene (0.1 mmol = 49.2 mg) in THF (5 mL) was added *n*-BuLi in hexane (0.318 mmol, 0.2 mL, 1.59 M) at -30 °C with stirring. The stirring was kept for 2 h with warming up to rt. Evaporation of volatiles gave a white solid. The obtained crude materials were washed with hexane and evaporated to give the product quantitatively. The product was recrystallized from dichloromethane/hexane(2/1) for X-ray analysis. ^{1}H NMR: (400 MHz, $CDCl_3$) 6.31 (d, $^3J_{FH}$ = 9.4 Hz, 6H, b-H), 5.90 (dd, $^3J_{FH}$ = 12.0, 1.6 Hz, 6H, d-H), 5.62 (s, 6H, f-H), 4.07 (s, 12H, 1-CH_2), 3.14 (br, 24H, g-H_2), 2.04 (s, 18H, 2-CH_3), 1.56 (br, 24H, h-H_2); ^{13}C NMR: (100 MHz, $CDCl_3$) 167.6 (s, d by $^3J_{CF}$ = 11.5 Hz, C-e), 164.3 (s, d by $^1J_{CF}$ = 243.6 Hz, C-c), 142.7 (s, d by $^3J_{CF}$ = 10.3 Hz, C-a), 135.1 (s, C-1 or C-2), 134.7 (s, C-1 or C-2), 115.1 (d, C-f), 103.5 (d, d by $^2J_{CF}$ = 19.7 Hz, C-d), 102.5 (d, d by $^2J_{CF}$ = 21.4 Hz, C-b), 67.8 (t, C-g), 34.9 (t, 1-CH_2), 25.3 (t, C-h), 16.3 (q, 2-CH_3); ^{7}Li NMR: (153.7 MHz, $CDCl_3$) -0.18; ^{19}F NMR: (372.35 MHz, $CDCl_3$) 37.38 (dd, $^3J_{FH}$ = 10.7, 10.7 Hz)

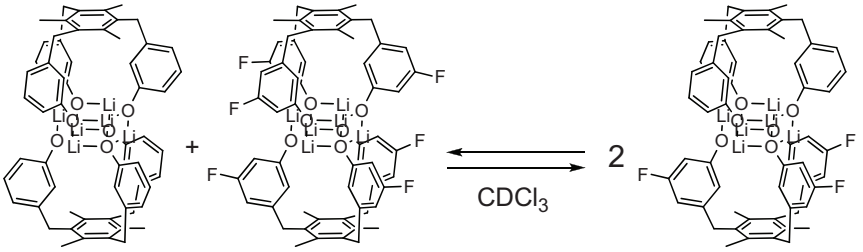
(**1b**Li_3)(**1d**Li_3)·$(THF)_6$



Each compound (**1b**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_6$ was dissolved in $CDCl_3$ to prepare 0.01 M solutions. They were mixed with ratios of 1/1 at room temperature. In the resulting mixture, (**1b**Li_3)(**1d**Li_3)·$(THF)_6$ was observed accompanied with the starting homoaggregated species (**1b**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_6$. Selected signals for (**1d**Li_3)(**1d**Li_3)·$(THF)_6$ are shown. ^{1}H NMR: (400 MHz, $CDCl_3$) 6.90 (m, 3H, c-H), 6.58 (m, 3H, b-H), 6.31 (m, 3H, b'-H), 6.18 (m, 3H, d-H), 5.90 (m, 6H, f-H and d'-H), 5.62 (s, 3H, f'-H), 4.13 (s, 6H, 1-CH_2), 4.07 (s, 6H, 1'-CH_2), 3.13 (br, 24H, g-H_2 and g'-H_2), 2.07 (s, 9H, 2-CH_3), 2.05 (s, 9H, 2'-CH_3), 1.57 (br, 24H, h-H_2 and h'-H_2); ^{7}Li NMR: (153.7 MHz, $CDCl_3$) -0.05; ^{19}F NMR: (372.35 MHz, $CDCl_3$) 37.22 (dd, $^3J_{FH}$ = 10.7, 10.7 Hz)

Method of Continuous Variation (Figure 2)

A ligand exchange between lithium phenolates (**1b**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_6$ is described below.



(**1b**Li_3)$_2$·$(THF)_6$ (**1d**Li_3)$_2$·$(THF)_6$ (**1b**Li_3)(**1d**Li_3)·$(THF)_6$

	(**1b**Li_3)$_2$·$(THF)_6$	(**1d**Li_3)$_2$·$(THF)_6$	(**1b**Li_3)(**1d**Li_3)·$(THF)_6$
molar ratios at an initial state	1	r	0
molar ratios at an equilibrium state	1-α	r-α	2α

Molar ratio *s* of (**1d**Li_3)$_2$·$(THF)_6$ to (**1b**Li_3)(**1d**Li_3)·$(THF)_6$ was measured by ^{19}F NMR integration.

$$s = \frac{[(\mathbf{1d}Li_3)_2\cdot(THF)_6]}{[(\mathbf{1b}Li_3)(\mathbf{1d}Li_3)\cdot(THF)_6]}$$

Molar ratios of formed lithium phenolates under an equibrium state were expressed by following equation.

$$s = \frac{r-\alpha}{2\alpha}$$

$$\alpha = \frac{r}{2s+1}$$

$$\text{molar ratio of } (\mathbf{1b}Li_3)_2\cdot(THF)_6 = \frac{1-\alpha}{1+r} \quad (1)$$

$$\text{molar ratio of } (\mathbf{1d}Li_3)_2\cdot(THF)_6 = \frac{r-\alpha}{1+r} \quad (2)$$

$$\text{molar ratio of } (\mathbf{1b}Li_3)(\mathbf{1d}Li_3)\cdot(THF)_6 = \frac{2\alpha}{1+r} \quad (3)$$

Each compound (**1b**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_6$ was dissolved in $CDCl_3$ to prepare 0.01 M solutions. They were mixed with ratios of 1/4, 2/3, 1/1, 3/2, and 4/1 (χ = 0.2, 0.4, 0.5, 0.6, and 0.8) at room temperature. Molar ratios of formed species were estimated by equations 1-3 described above.

Rate of Lignad-Exchange (Table 2)

Each compound (**1b**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_6$ was dissolved in $CDCl_3$ to prepare 0.01 M solutions. The pre-mixed solvents were prepared from $CDCl_3$ and THF at various ratios ($CDCl_3$:THF = 50/50, 80/20, 90/10, 100/0). To the pre-mixed solvents (0.1 mL), the solutions of (**1b**Li_3)$_2$·THF (0.25 mL) and (**1d**Li_3)$_2$·THF (0.25 mL) were added at room temperature. Molar ratios of (**1b**Li_3)(**1d**Li_3)·$(THF)_6$ were estimated by equation 3 described above.

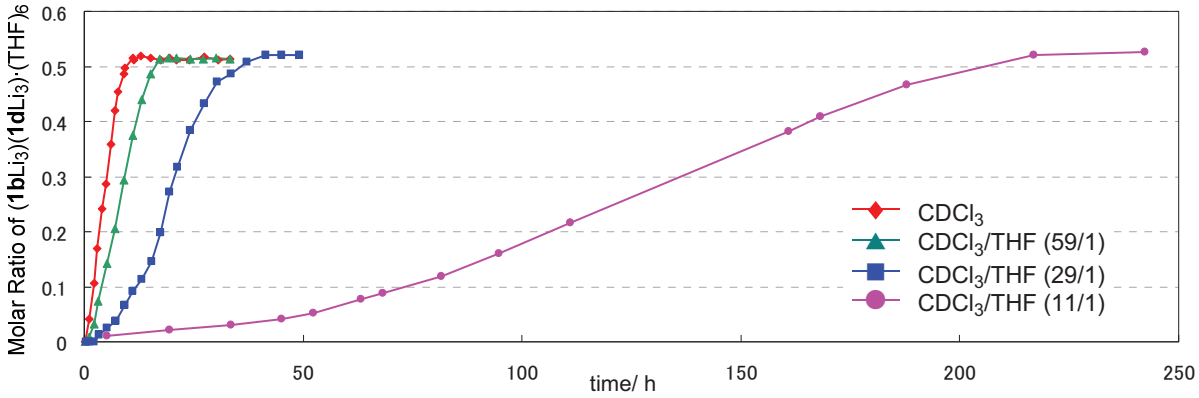


Figure S1. Effect of solvent systems on relationship between formed amount of (**1b**Li_3)(**1d**Li_3)·$(THF)_6$ and reaction time.

Crystal Structure Determination

The single-crystal structure data of complexes (**1a**$Li_3)_2\cdot(THF)_6$, (**1b**$Li_3)_2\cdot(THF)_6$, (**1c**$Li_3)_2\cdot(THF)_6$, and (**1b**$Li_3)_2\cdot(THF)_4$ were determined by a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα (l = 0.71075 Å) radiation at 273 (2) K. The single-crystal structure data of complexes (**1d**$Li_3)_2\cdot(THF)_6$ was determined by a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα (l = 0.71075 Å) radiation at 253 (2) K.

Following shelxl restrains were used for (**1a**$Li_3)_2\cdot(THF)_6$;

DELU C10 > C17

SIMU 0.04 0.08 C10 > C17

SAME C14 > C17

SAME C13 < C10

Following shelxl restrains were used for (**1c**$Li_3)_2\cdot(THF)_6\cdot0.5(C_6H_6)$;

DFIX 1.39 0.02 C46 C49 C49 C47 C47 C46_$1

DANG 2.42 0.04 C46 C47 C49 C46_$1 C49 C47_$1

Table S1. X-ray data for all crystallographically characterized complexes.

	(**1a**Li_3)$_2$·(THF)$_6$	(**1b**Li_3)$_2$·(THF)$_6$	(**1c**Li_3)$_2$·(THF)$_6$·0.5(C_6H_6)	(**1d**Li_3)$_2$·(THF)$_6$·0.25(C_6H_6)	(**1b**Li_3)$_2$·(THF)$_4$·3(C_6H_6)
chemical formula	$C_{78}H_{90}Li_6O_{12}$	$C_{84}H_{102}Li_6O_{12}$	$C_{93}H_{113}Li_6O_{12}$	$C_{171}H_{195}F_{12}Li_{12}O_{24}$	$C_{94}H_{104}Li_6O_{10}$
formula weight	1261.21	1345.37	1468.51	2945.68	1435.50
space group	*P*a-3	*P*a-3	$P2_1/n$	*P*cca	*P*-1
μ(Mo-K) (mm^{-1})	0.076	0.077	0.072	0.086	0.073
a(Å)	19.2239(12)	19.5449(6)	12.3152(5)	31.5198(6)	12.9238(13)
b(Å)	-	-	15.6985(7)	16.6893(3)	13.6966(15)
c(Å)	-	-	22.3318(8)	31.2344(6)	14.6695(15)
α(deg)	-	-	-	-	67.099(2)
β(deg)	-	-	94.310(1)	-	64.141(2)
γ(deg)	-	-	-	-	64.306(2)
V_c ($Å^3$)	7104.3(8)	7466.2(4)	4305.2(3)	16430.6(5)	2040.5(4)
Z	4	4	2	4	1
*R*1	0.1069	0.0845	0.0737	0.0784	0.0946
*wR*2	0.2860	0.2687	0.2325	0.2628	0.2804

Table S2. Selected bond lengths [Å] and angles [degree] for (**1a-c**$Li_3)_2$·$(THF)_6$.

		(**1a**$Li_3)_2$·$(THF)_6$		(**1b**$Li_3)_2$·$(THF)_6$		(**1c**$Li_3)_2$·$(THF)_6$·0.5(C_6H_6)	
Length (Å)	$Li\text{-}O_{Ar}$ (six-member ring)	1.966(8)	1.964(8)	1.985(5)	1.953(5)	1.983(4) 1.990(4) 1.975(4)	1.959(4) 1.974(4) 1.984(5)
	$Li\text{-}O_{Ar}$ (vertical)	1.964(8)		1.969(5)		1.944(5) 1.958(5)	1.996(4)
	Li-O(THF)	2.039(8)		2.041(5)		2.004(4) 2.053(5)	1.976(4)
	Li-Li (six-member ring)	3.38(1)		3.364(6)		3.347(5) 3.393(6)	3.459(6)
	Li-Li (four-member ring)	2.65(1)		2.653(6)		2.627(6) 2.639(6)	2.644(5)
	O-O (six-member ring)	3.400(4)		3.432(2)		3.422(2) 3.451(2)	3.359(2)
	O-O (four-member ring)	2.904(4)		2.910(2)		2.948(2) 2.912(2)	2.937(2)
angle (degree)	$Li\text{-}O_{Ar}\text{-}Li$ (six-member ring)	118.6(3)		117.4(2)		115.5(2) 119.2(2)	121.0(2) 1.990(4)
	$Li\text{-}O_{Ar}\text{-}Li$ (four-member ring)	84.7(3)	84.6(3)	84.3(2)	85.2(2)	84.9(2) 84.3(2) 84.2(2)	82.6(2) 83.1(2) 84.4(2)
	$O_{Ar}\text{-}Li\text{-}O_{Ar}$ (six-member ring)	119.8(4)		121.3(2)		119.2(2) 122.7(2)	115.9(2)
	$O_{Ar}\text{-}Li\text{-}O_{Ar}$ (four-member ring)	95.3(4)	95.4(4)	95.8(2)	94.7(2)	96.4(2) 95.3(2) 96.6(2)	96.8(2) 96.0(2) 95.4(2)
	$C\text{-}C_{methylene}\text{-}C$	114.3(7)		114.2(3)		113.5(2) 113.2(2)	113.2(2)

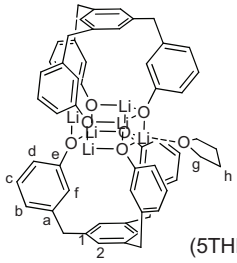
Table S3. Selected bond lengths [Å] and angles [degree] for (**1d**Li_3)$_2$·$(THF)_6$ and (**1d**Li_3)$_2$·$(THF)_4$.

		(**1d**Li_3)$_2$·$(THF)_6$·0.25(C_6H_6)				(**1b**Li_3)$_2$·$(THF)_4$·3(C_6H_6)	
		Part 1		Part 2			
Length (Å)	Li-O_{Ar} (six-member ring)	1.969(5)	1.979(4)	1.978(5)	1.975(5)	1.904(8)	1.919(9)
		1.986(5)	1.990(4)	1.963(5)	1.986(5)	1.976(8)	1.971(9)
		1.952(5)	1.974(5)	1.976(5)	1.968(5)	1.94(1)	1.95(1)
	Li-O_{Ar} (vertical)	1.963(5)	1.984(5)	1.941(5)	1.969(4)	1.887(8)	1.967(7)
		1.941(4)		1.946(5)		1.950(8)	
	Li-O(THF)	1.990(5)	2.004(5)	2.014(5)	2.016(5)	1.945(8)	2.001(9)
		1.987(5)		1.989(4)			
	Li-Li (six-member ring)	3.435(6)	3.356(6)	3.402(6)	3.373(6)	3.561(9)	3.22(2)
		3.434(6)		3.410(6)		3.15(2)	
	Li-Li (four-member ring)	2.664(6)	2.668(6)	2.664(6)	2.648(6)	2.58(1)	2.56(1)
		2.685(6)		2.655(6)		2.62(1)	
	O-O (six-member ring)	3.342(2)	3.418(2)	3.429(2)	3.407(2)	3.523(3)	3.252(6)
		3.452(2)		3.426(2)		3.312(6)	
	O-O (four-member ring)	2.890(2)	2.855(2)	2.891(2)	2.907(2)	2.889(5)	2.881(4)
		2.922(2)		2.878(2)		2.885(4)	
angle (degree)	Li-O_{Ar}-Li (six-member ring)	118.8(2)	119.2(2)	117.2(2)	120.6(2)	128.9(4)	109.3(4)
		117.8(2)		120.1(2)		113.2(4)	
	Li-O_{Ar}-Li (four-member ring)	84.1(2)	85.3(2)	86.5(2)	84.3(2)	83.9(4)	83.3(4)
		85.7(2)	85.5(2)	84.6(2)	84.8(2)	83.2(4)	83.0(4)
		85.2(2)	85.0(2)	83.3(2)	83.3(2)	84.6(4)	84.4(4)
	O_{Ar}-Li-O_{Ar} (six-member ring)	120.5(3)	119.0(3)	120.4(3)	115.9(3)	134.3(5)	115.8(5)
		120.8(3)		120.8(2)		111.8(4)	
	O_{Ar}-Li-O_{Ar} (four-member ring)	95.3(2)	95.3(2)	94.6(2)	94.5(2)	94.6(4)	98.9(5)
		94.7(2)	94.6(2)	94.8(2)	95.8(2)	98.6(5)	94.0(4)
		95.1(2)	94.2(2)	96.6(2)	96.6(2)	95.0(4)	95.9(4)
	C-$C_{methylene}$-C	113.6(3)	113.1(3)	113.6(3)	112.9(3)	113.3(4)	113.2(5)
		113.7(3)		113.4(3)		112.7(4)	

References

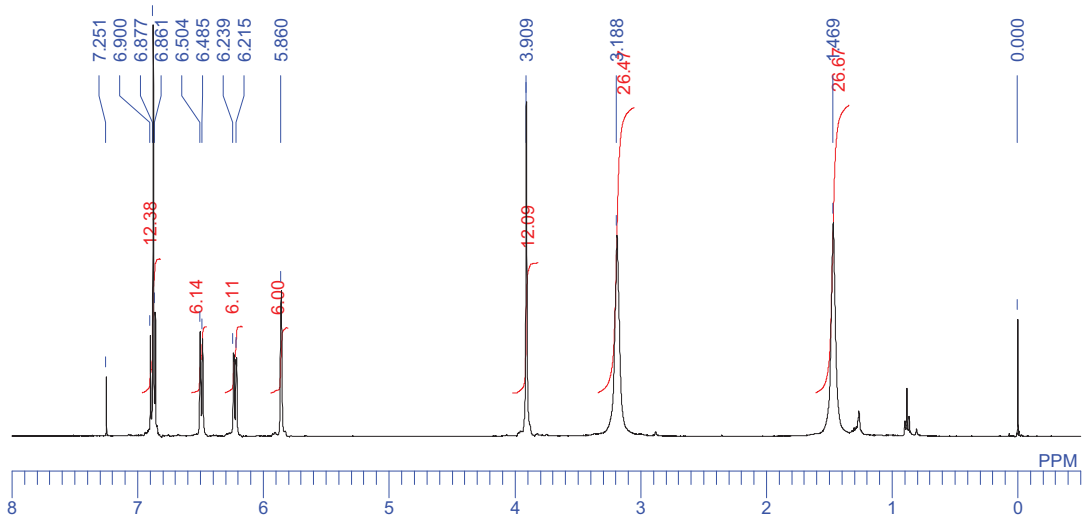
1. H. Nakajima, M. Yasuda, K. Chiba, A. Baba, *Chem. Commun.* 2010, **46**, 4794-4796.

$(\mathbf{1a}Li_3)_2\cdot(THF)_6$

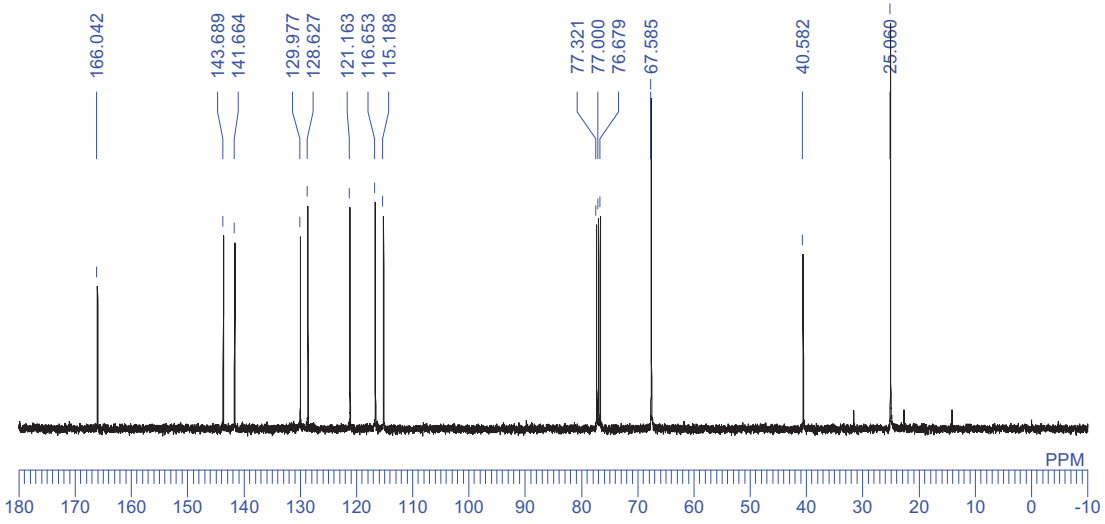


(5THFs is omitted)

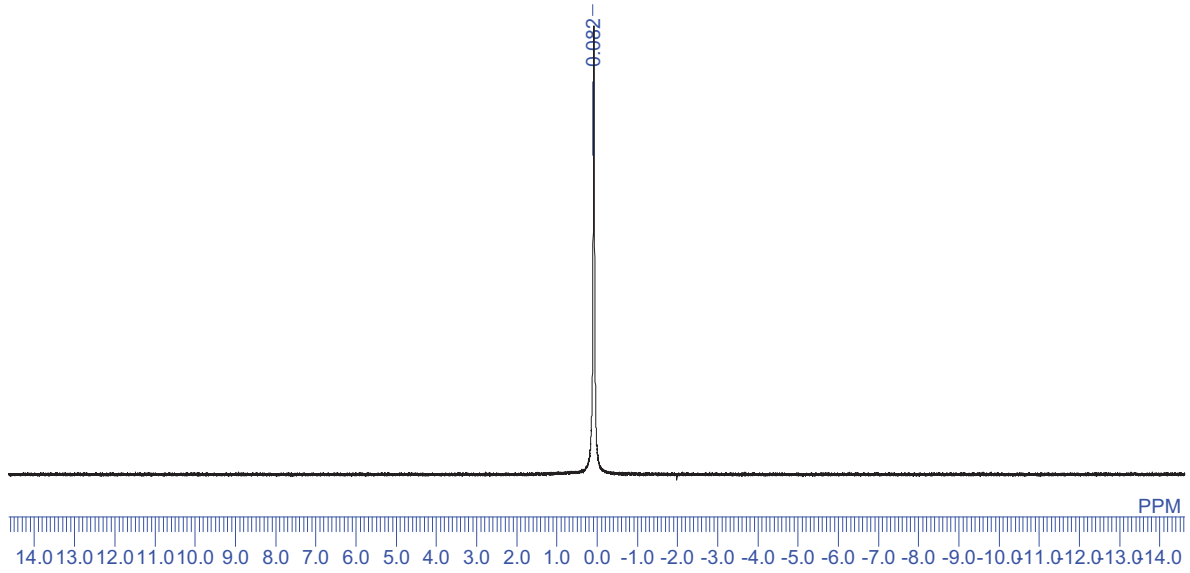
^{1}H NMR



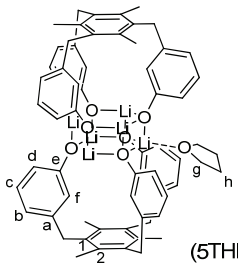
^{13}C NMR



^{7}Li NMR

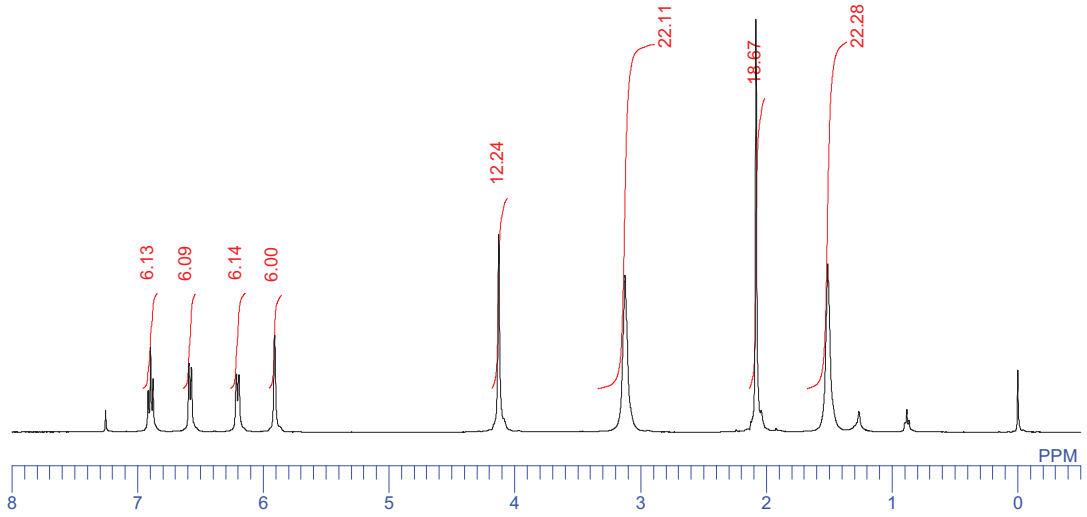

0.082
PPM
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0 -4.0 -5.0 -6.0 -7.0 -8.0 -9.0 -10.0 -11.0 -12.0 -13.0 -14.0

$(\mathbf{1b}Li_3)_2\cdot(THF)_6$

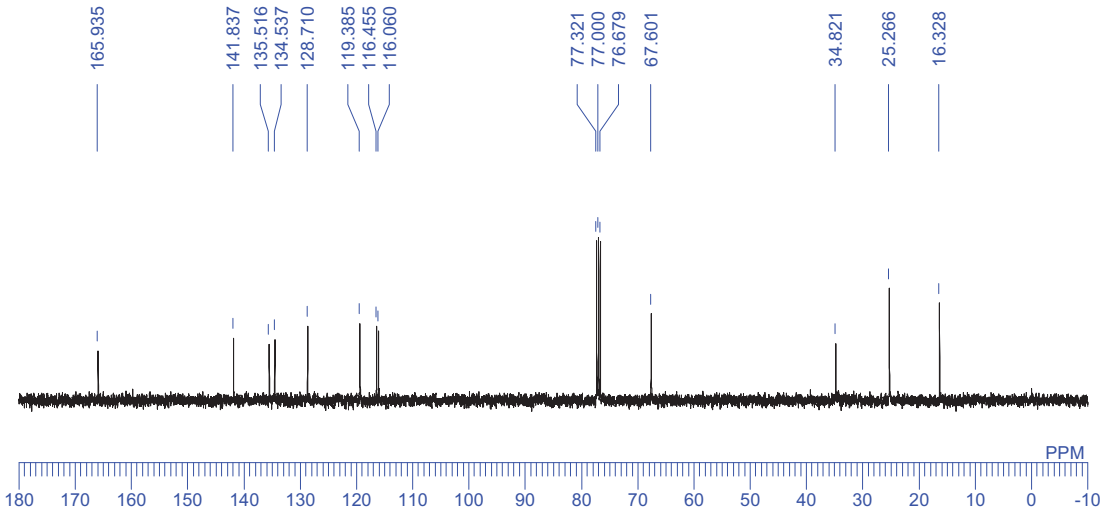


(5THFs is omitted)

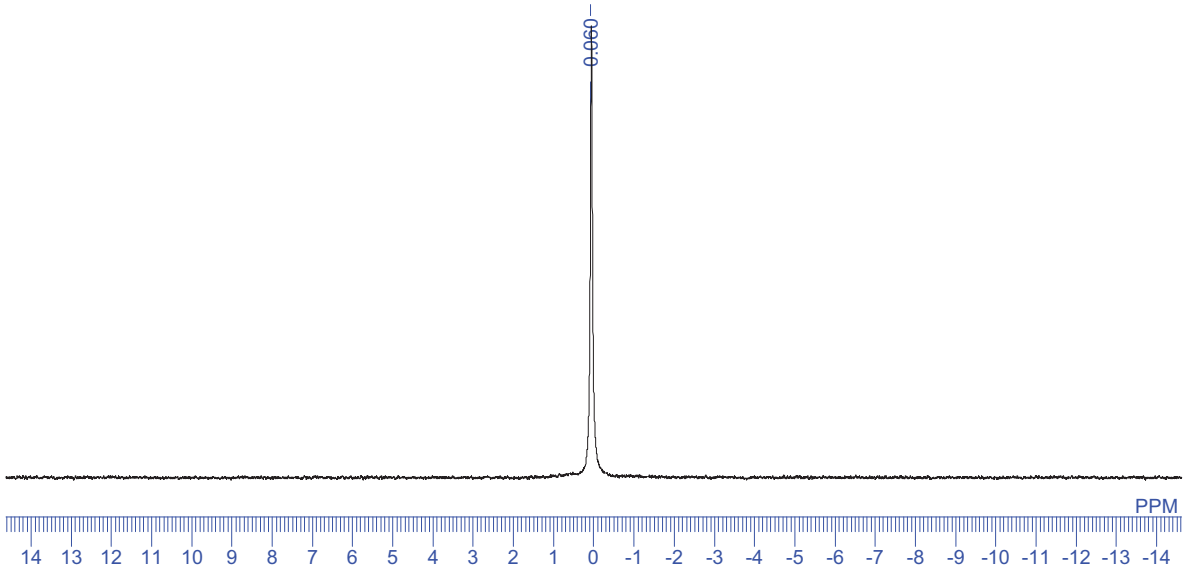
^{1}H NMR



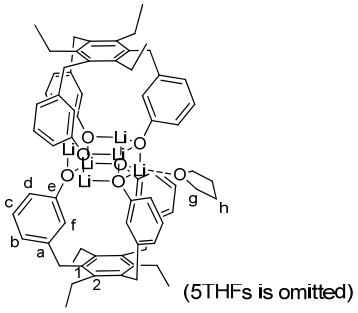
^{13}C NMR



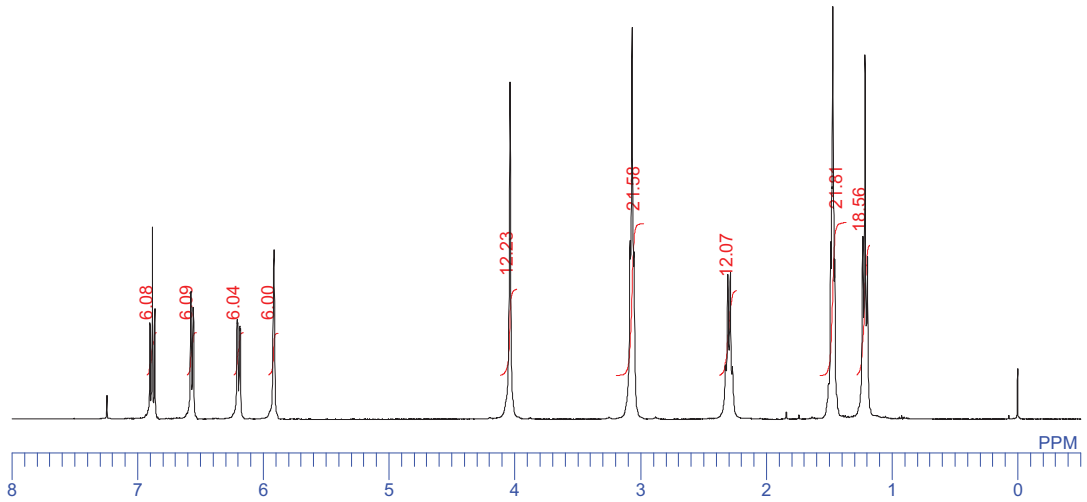
^{7}Li NMR



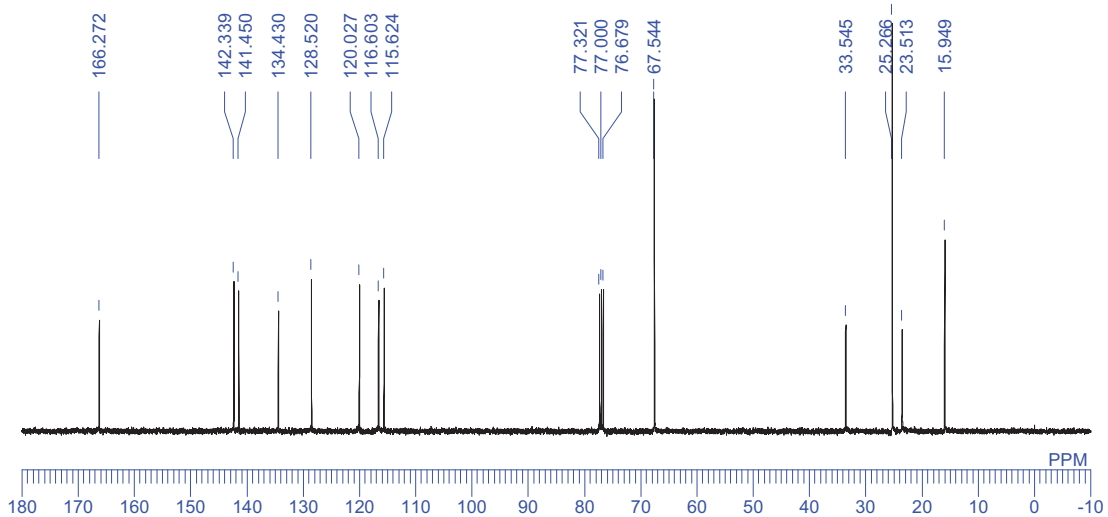
$(\mathbf{1c}Li_3)_2\cdot(THF)_6$



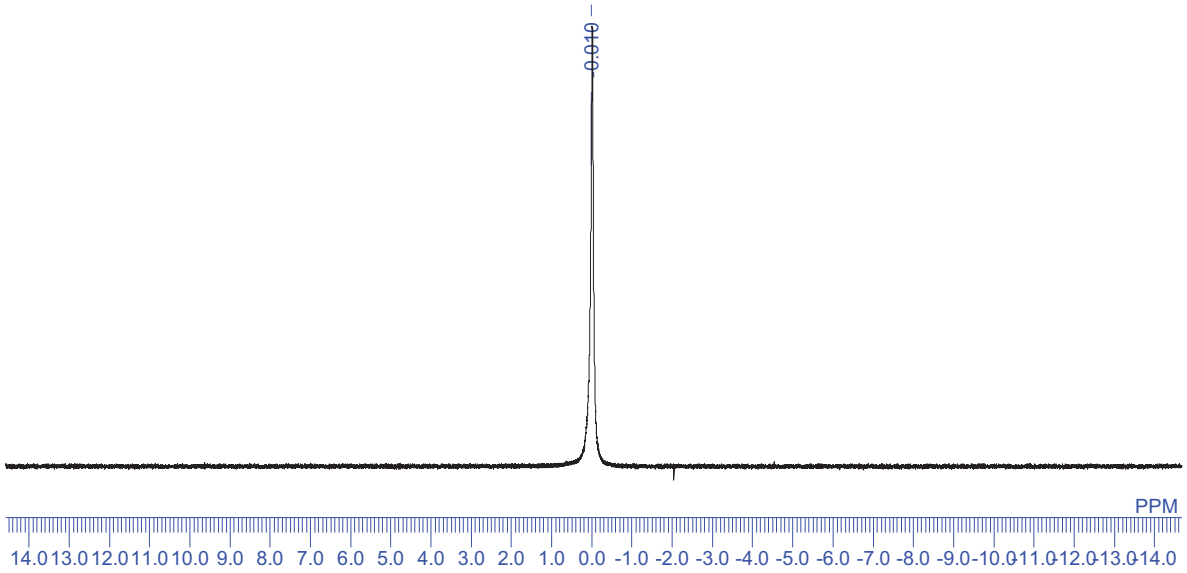
^{1}H NMR



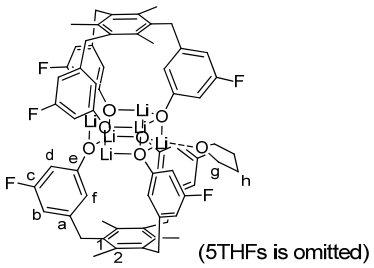
^{13}C NMR



^{7}Li NMR

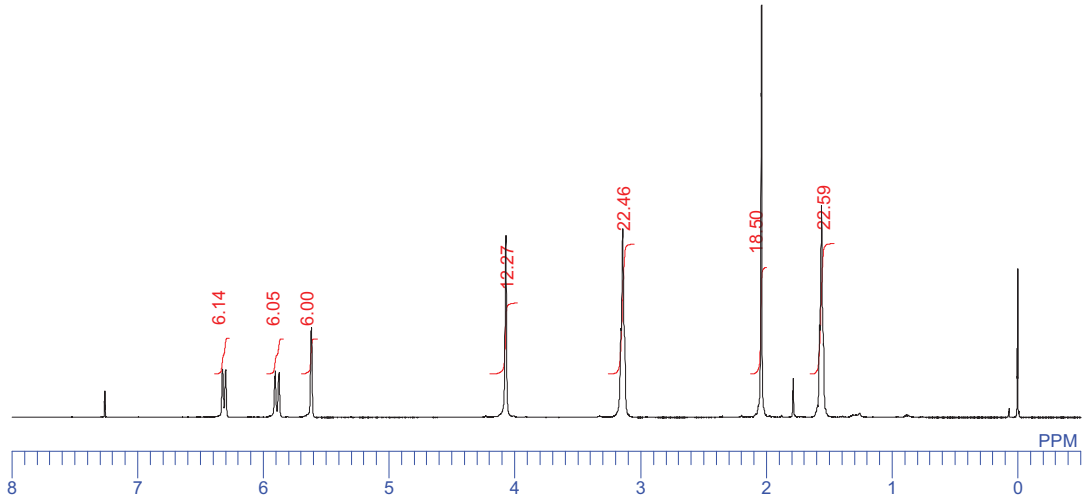

0.010
PPM
14.0 13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0 -3.0 -4.0 -5.0 -6.0 -7.0 -8.0 -9.0 -10.0 -11.0 -12.0 -13.0 -14.0

$(\mathbf{1d}Li_3)_2\cdot(THF)_6$

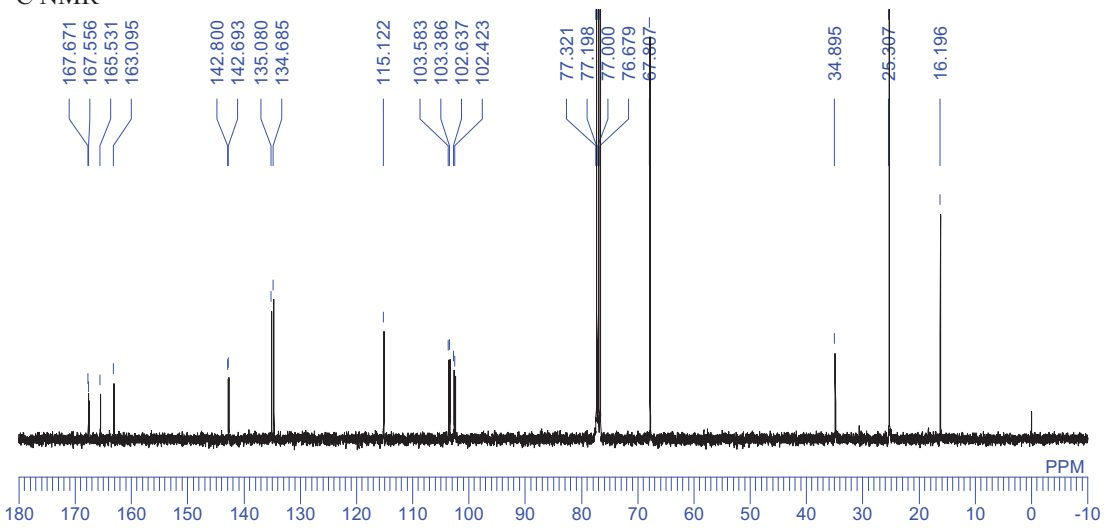


(5THFs is omitted)

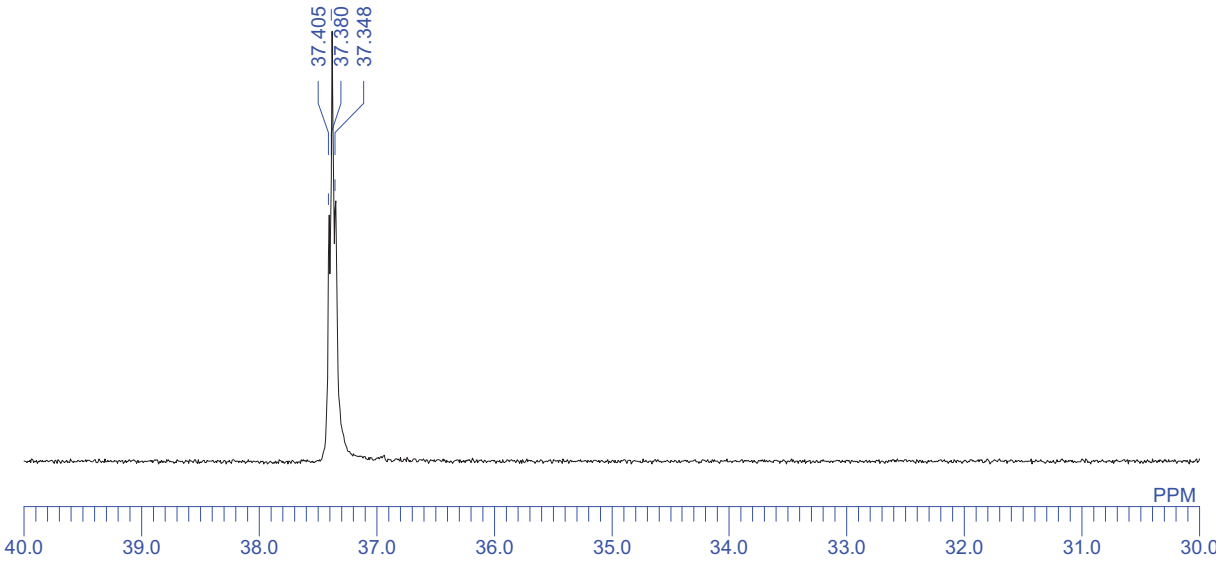
^{1}H NMR



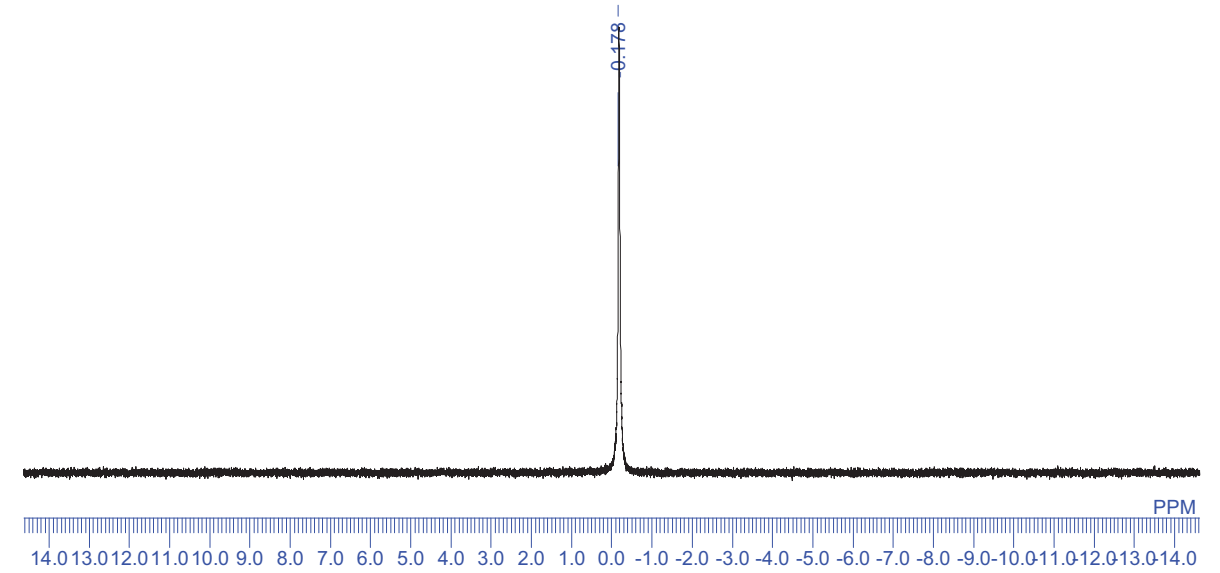
^{13}C NMR

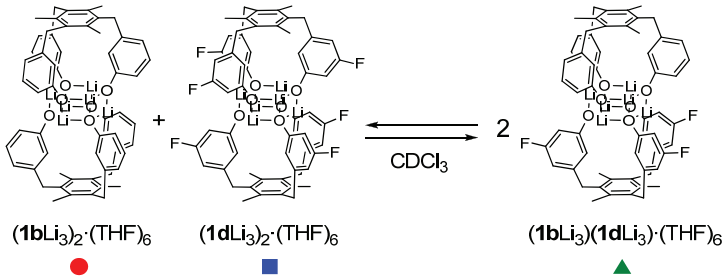


^{19}F NMR

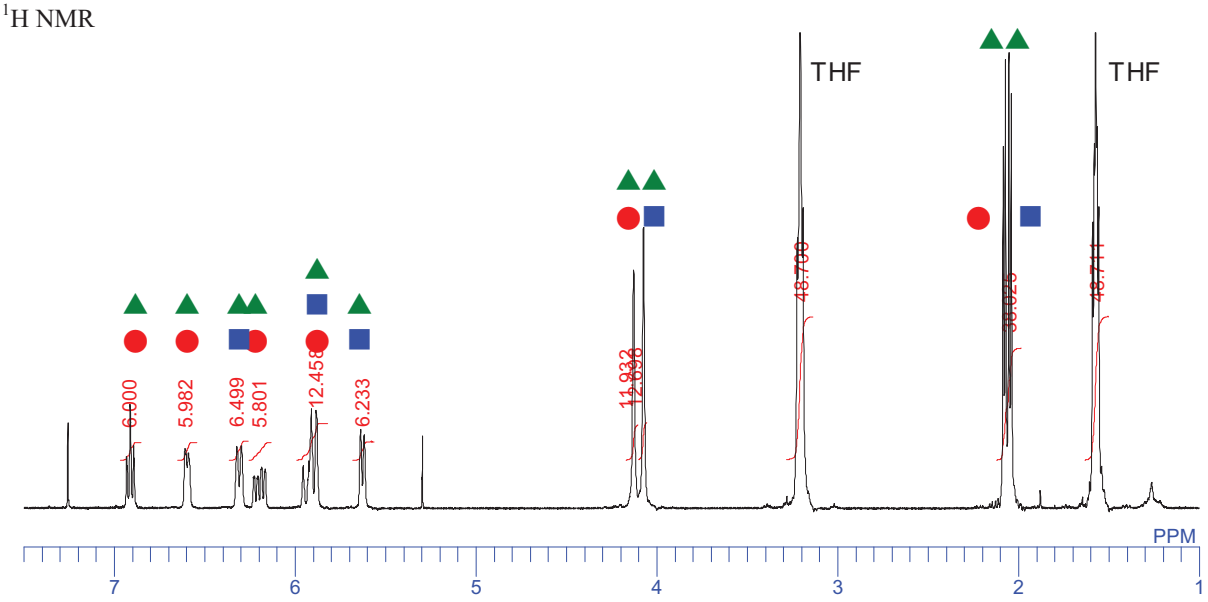


^{7}Li NMR

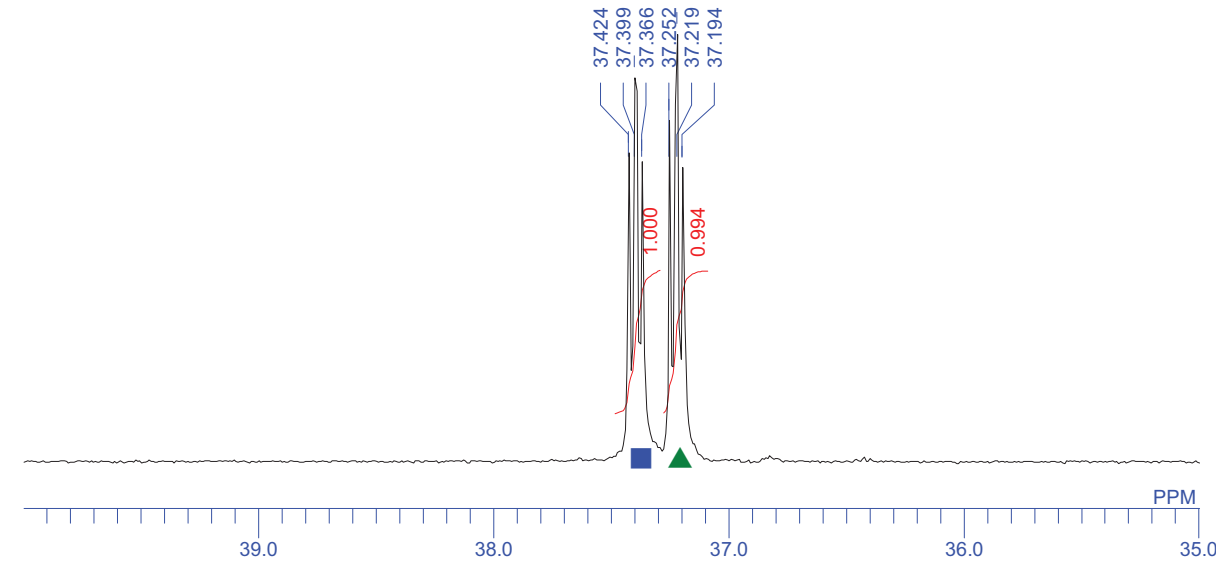




^{1}H NMR



^{19}F NMR



^{7}Li NMR