Electronic supplementary information

for

Lithium complexes derived of benzylphosphines: Synthesis, characterization and evaluation in the ROP of *rac*-lactide and ε-caprolactone

Ernesto Rufino-Felipe, Miguel A. Muñoz-Hernández and Virginia Montiel-Palma*

Centro de Investigaciones Químicas, Instituto de Investigación en Ciencias Básicas y Aplicadas, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, Cuernavaca, Morelos 62209 México. Tel.:+ 52 777 3297997

E-mail: vmontielp@uaem.mx

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1. NMR spectroscopic data for all lithium complexes

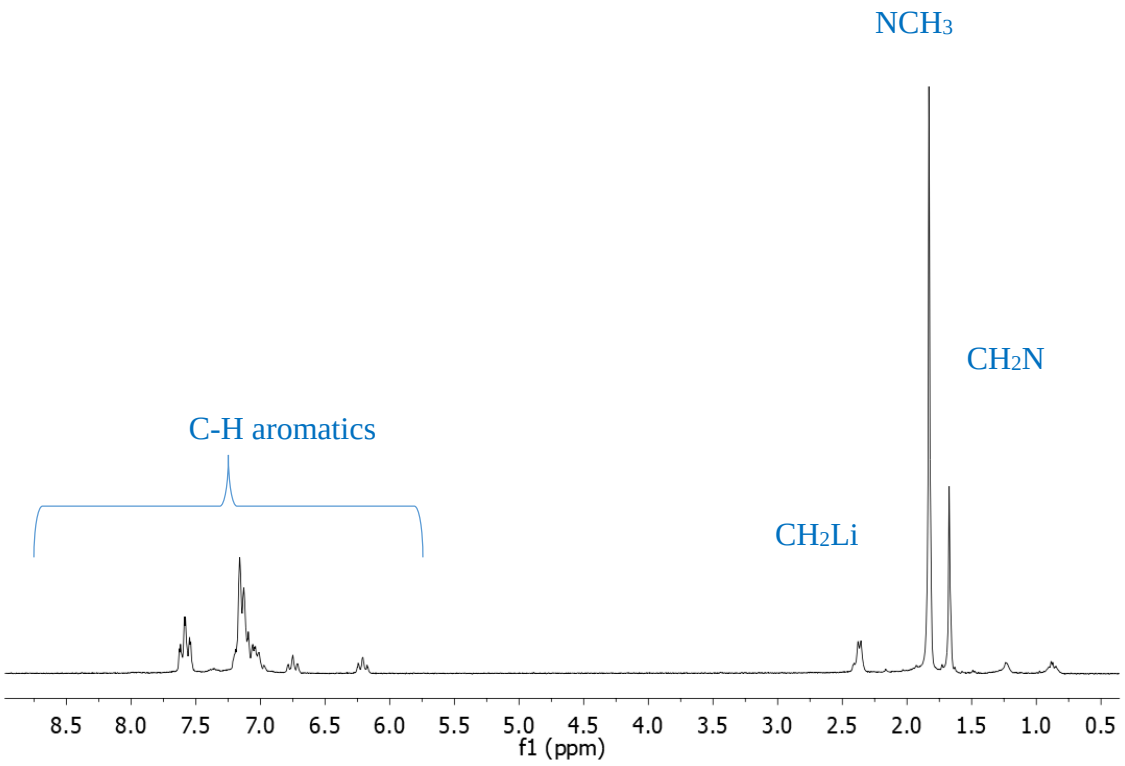


Figure S1. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of complex **1-Li**.

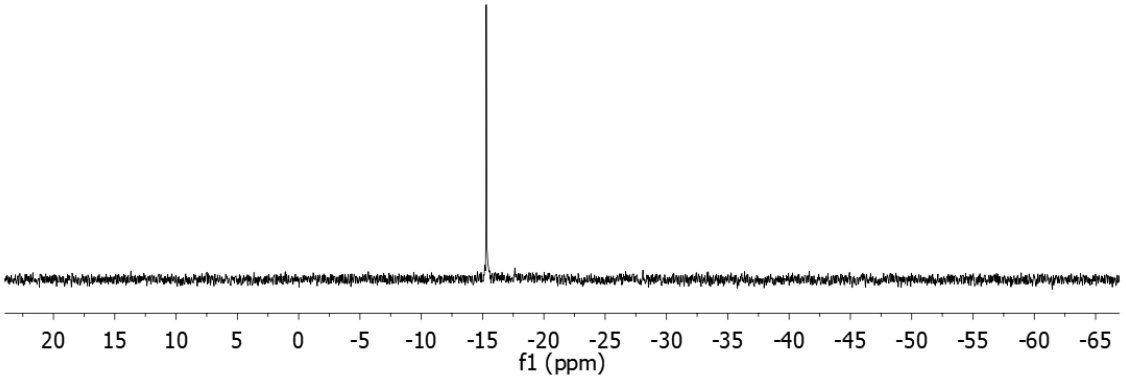


Figure S2. $^{31}P\{^{1}H\}$ NMR spectrum (161.92 MHz, C_6D_6, 298 K) of complex **1-Li**.

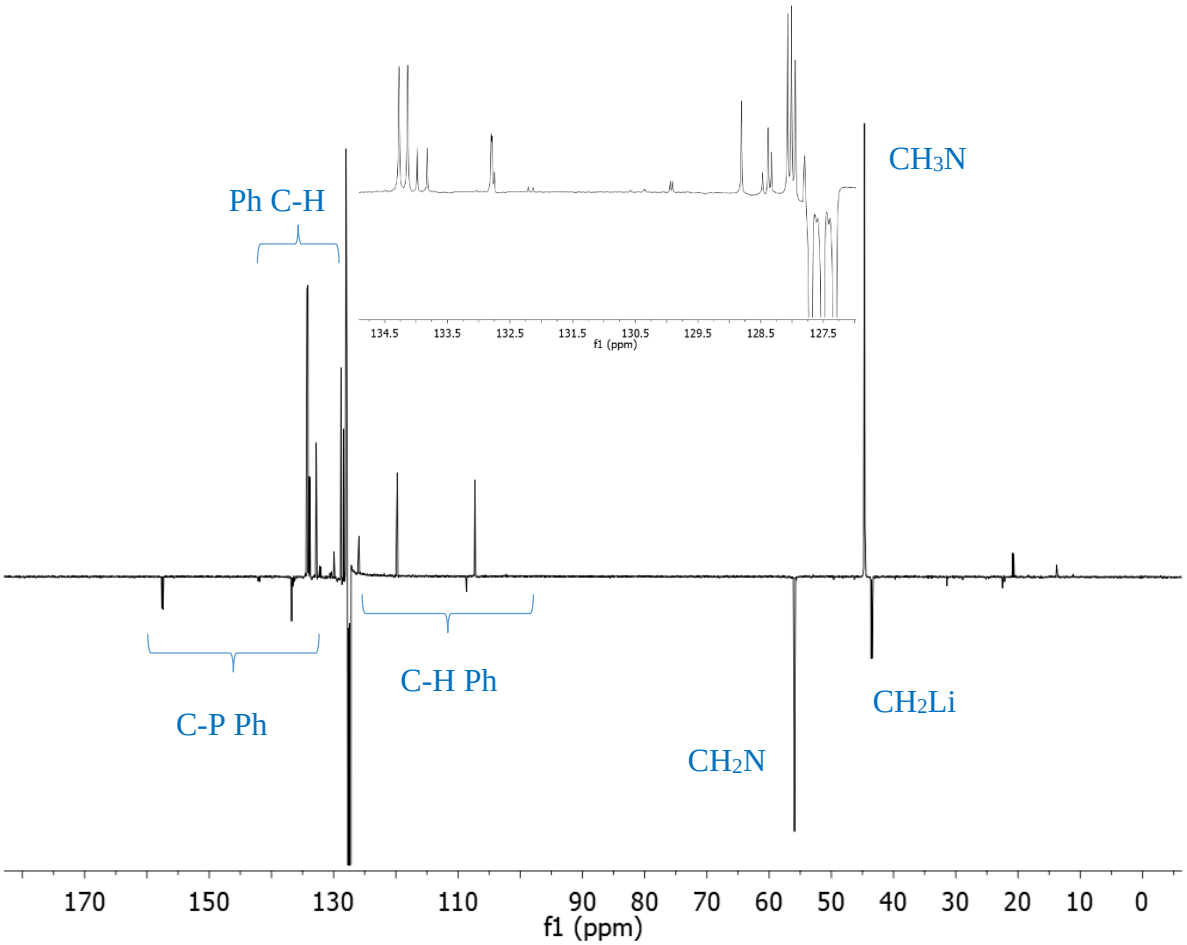


Figure S3. DEPTQ NMR spectrum (100.68 MHz, C_6D_6, 298 K) of complex **1-Li**.

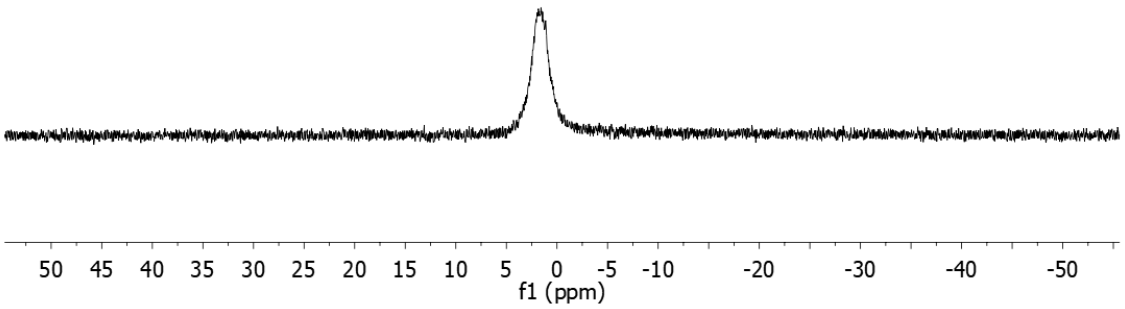


Figure S4. ^{7}Li NMR spectrum (155.45 MHz, C_6D_6, 298 K) of complex **1-Li**.

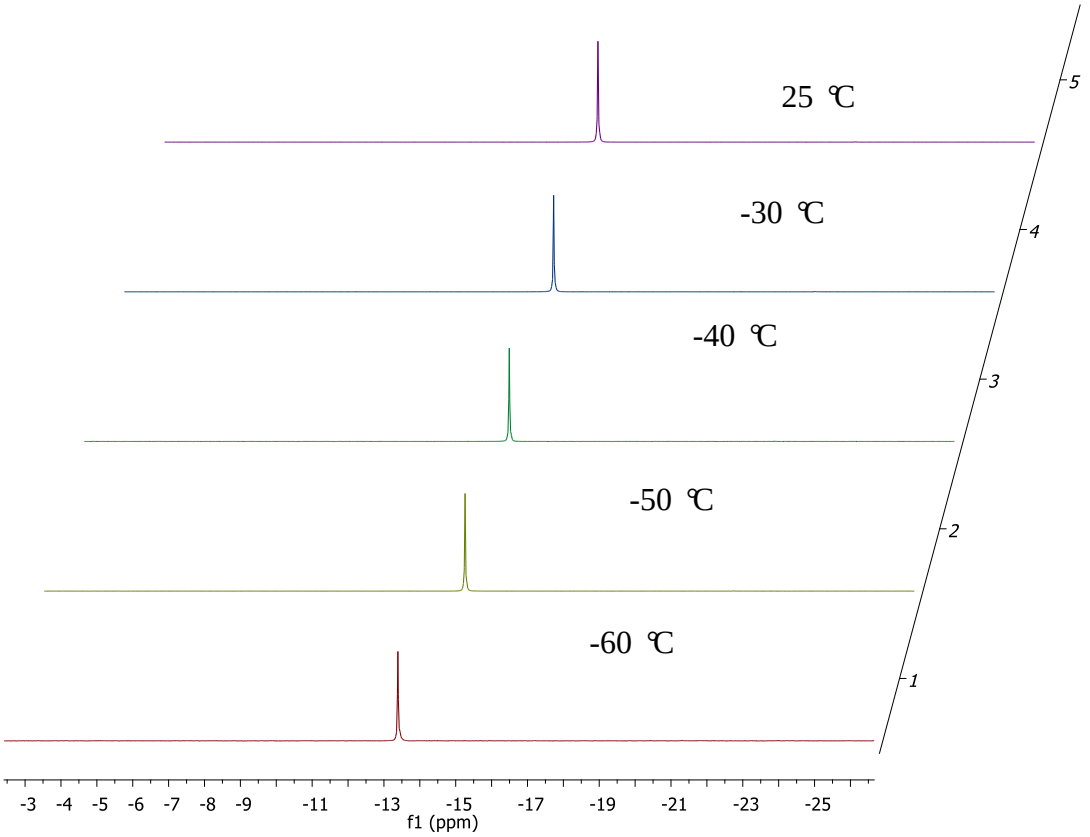
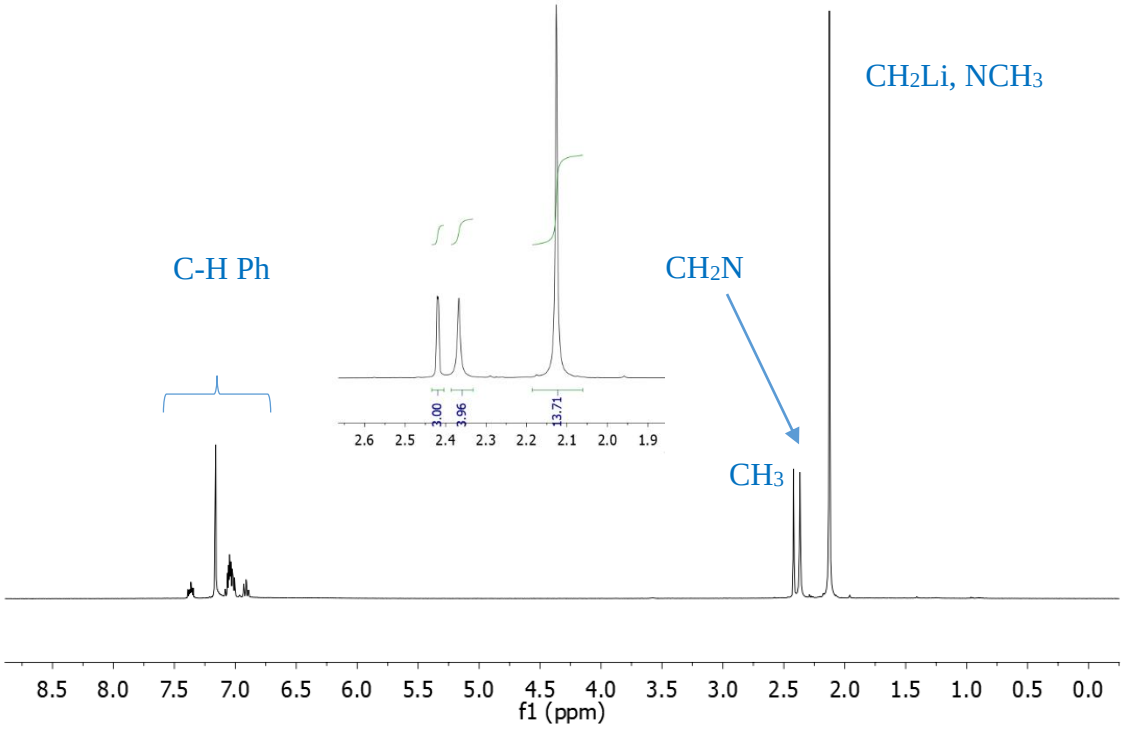


Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum (202.40 MHz, C_7D_8) at variable temperatures of complex **1-Li**.



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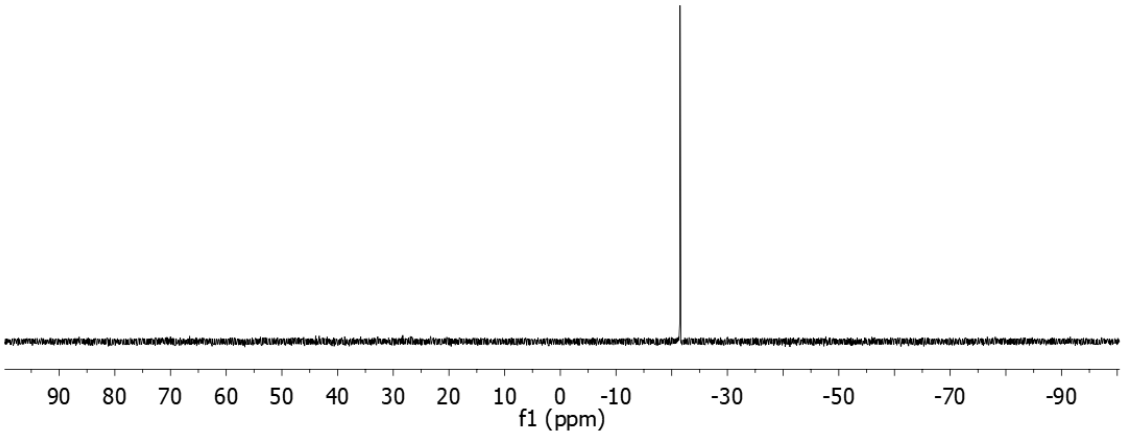


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum (161.92 MHz, C_6D_6, 298 K) of complex **2-Li**.

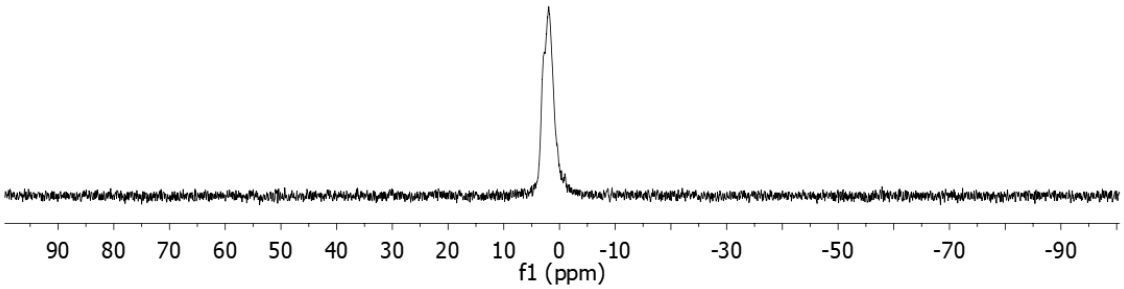


Figure S8. ^{7}Li NMR spectrum (155.45 MHz, C_6D_6, 298 K) of complex **2-Li**.

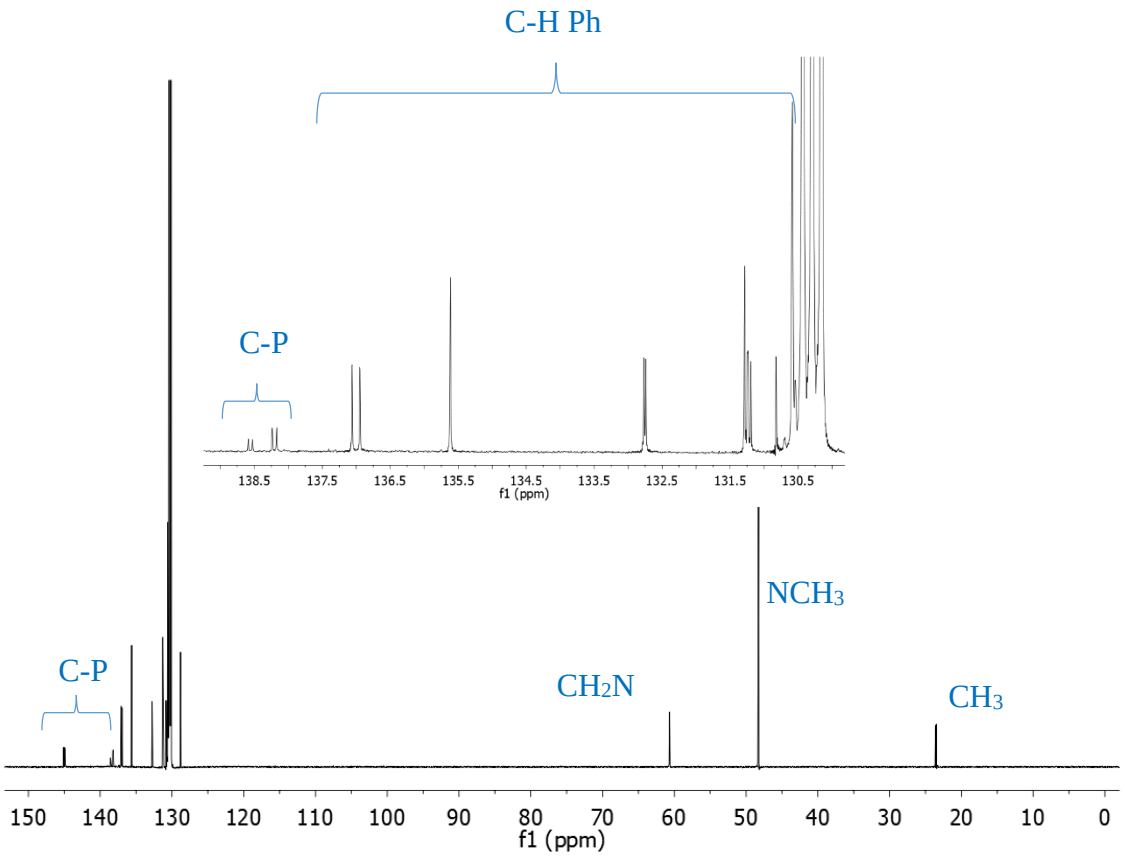


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum (700 MHz, C_6D_6, 298 K) of complex **2-Li**.

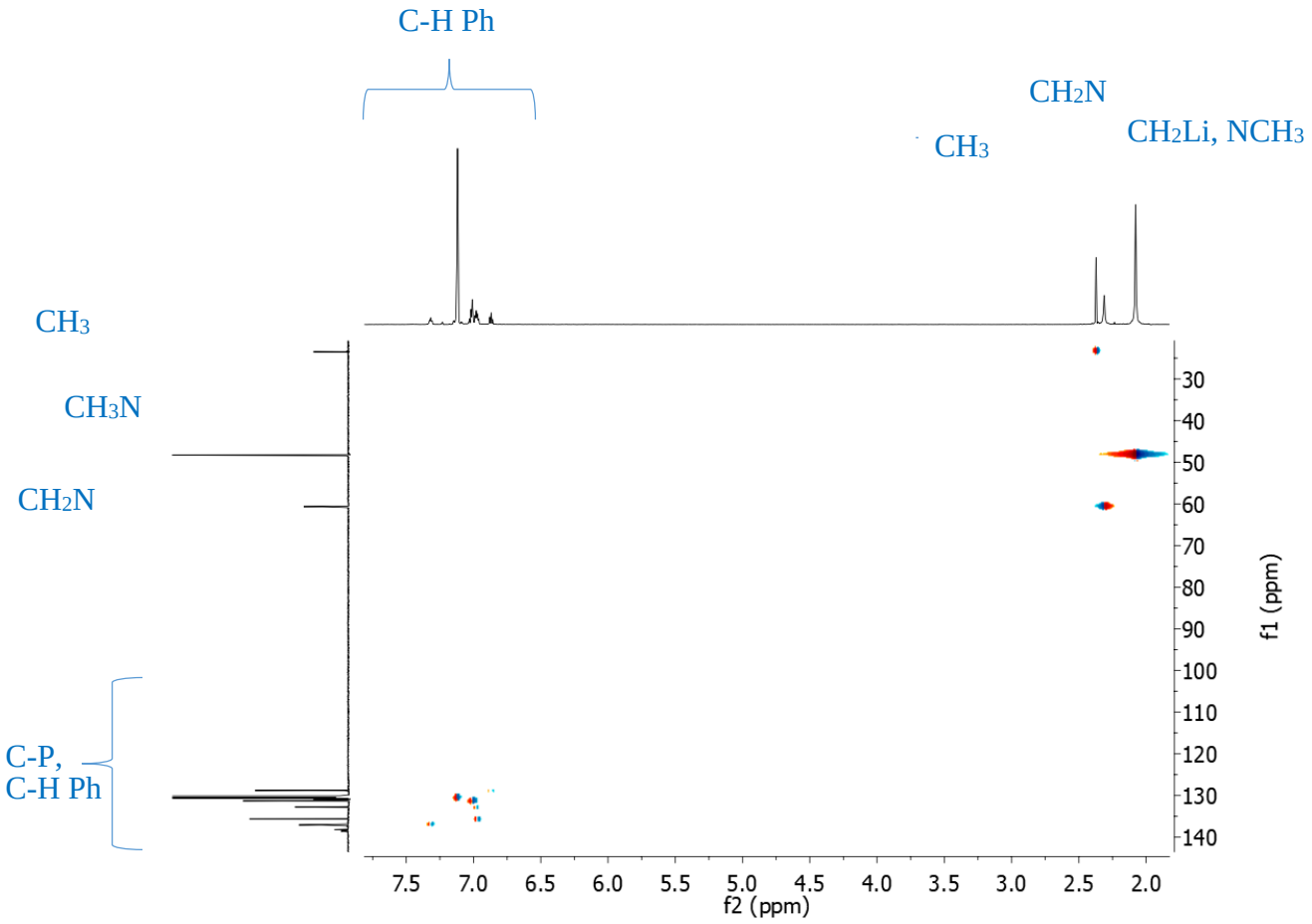


Figure S10. HSQC ^{1}H-^{13}C NMR spectrum (700 MHz, C_6D_6, 298 K) of complex **2-Li.**

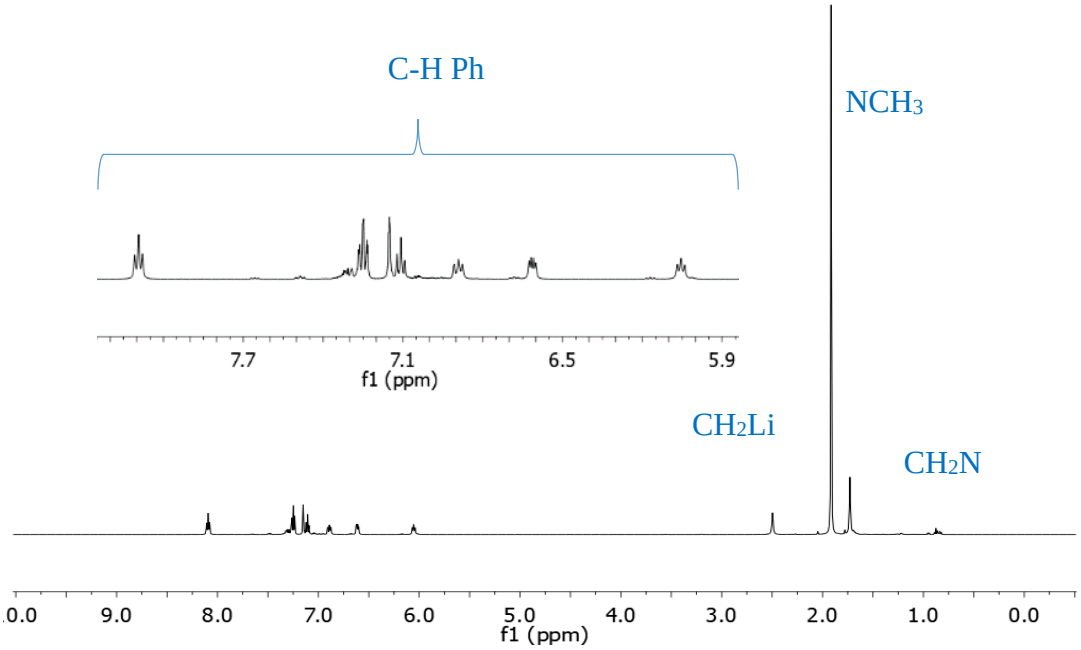


Figure S11. ^{1}H NMR spectrum (400 MHz, C_6D_6, 298 K) of complex **2-Li$_2$**.

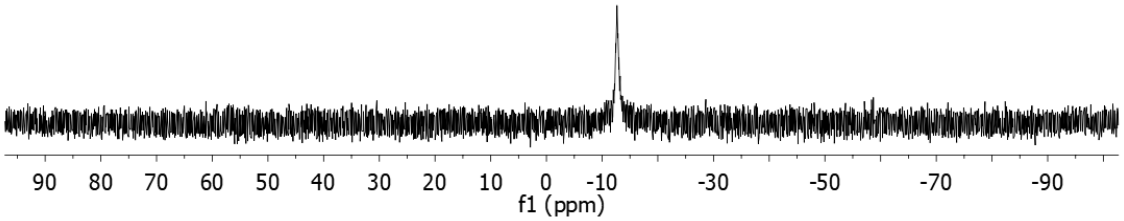


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum (161.92 MHz, C_6D_6, 298 K) of complex **2-Li$_2$**.

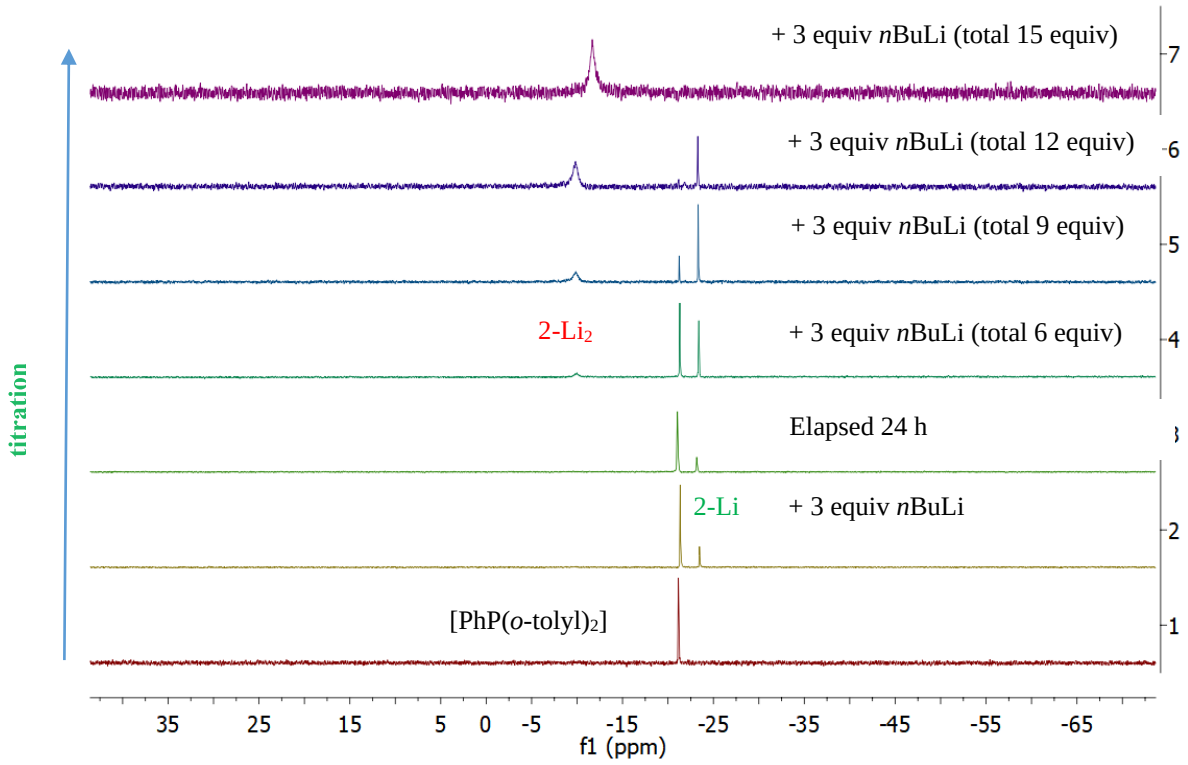


Figure S13. $^{31}P\{^{1}H\}$ NMR spectra for the titration of [PhP(o-tolyl)2] with excess *n*BuLi, evidencing the formation of complexes **2Li** and **2-Li$_2$** (161.92 MHz, C_6D_6, 25 °C).

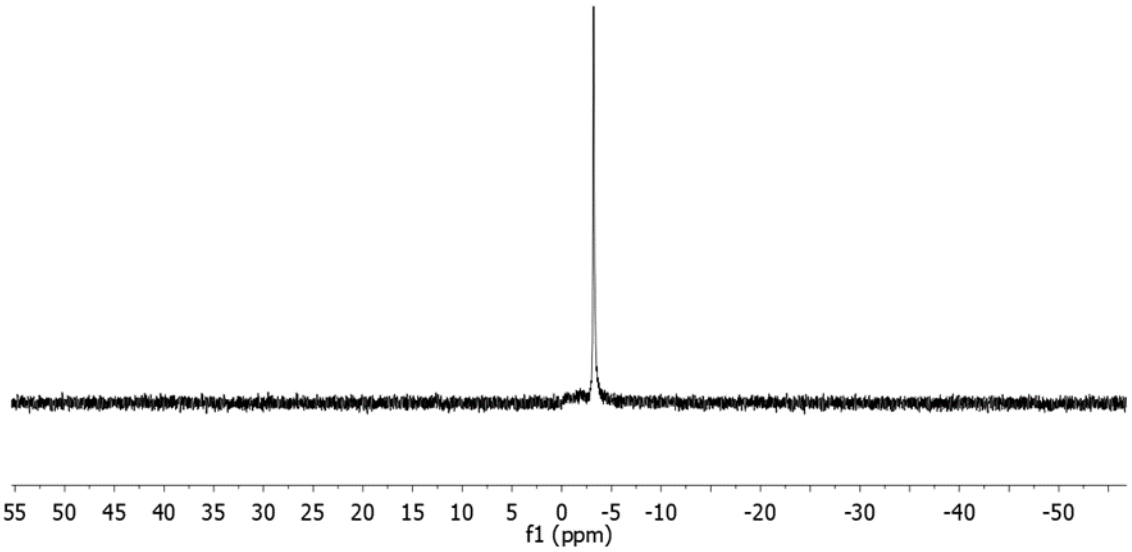


Figure S14. ^{7}Li NMR spectrum (155.45 MHz, C_6D_6, 298 K) of complex **2-Li$_2$**.

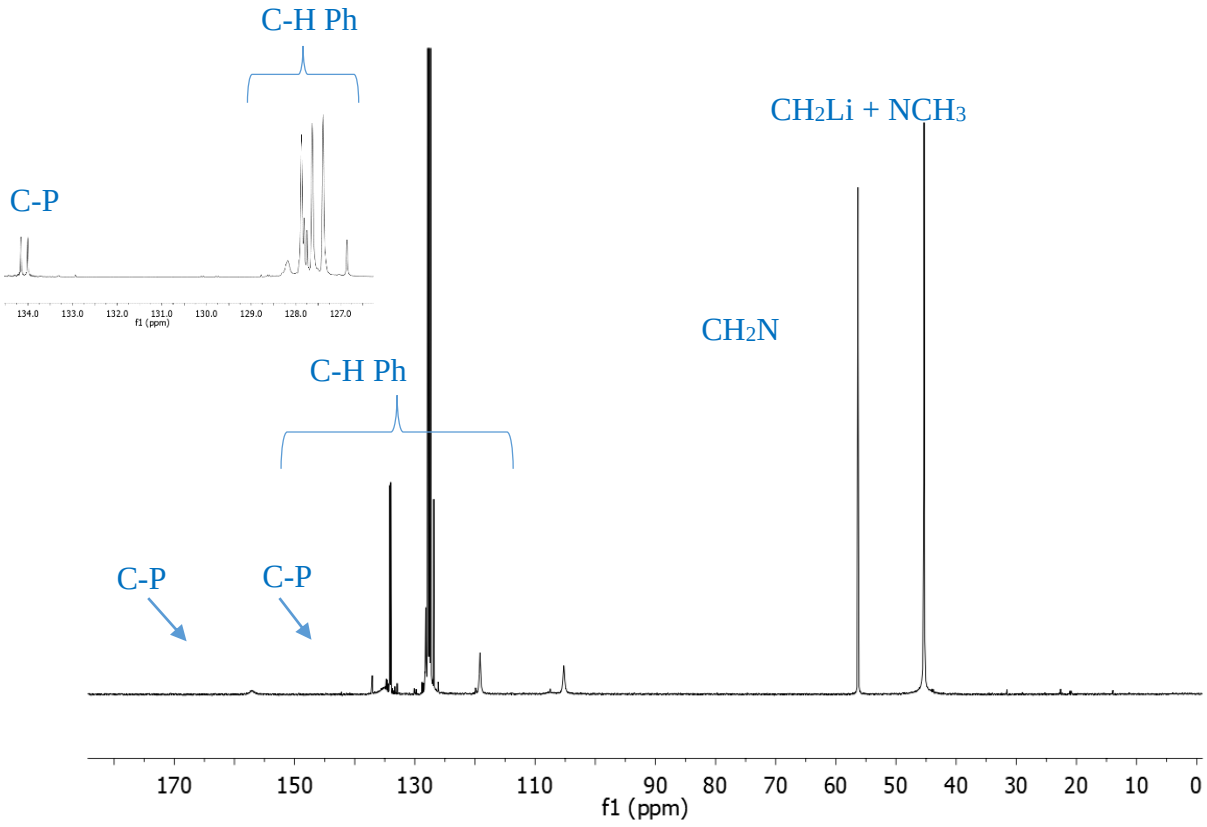


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (125.72 MHz, C_6D_6, 25°C) of complex **2-Li$_2$**.

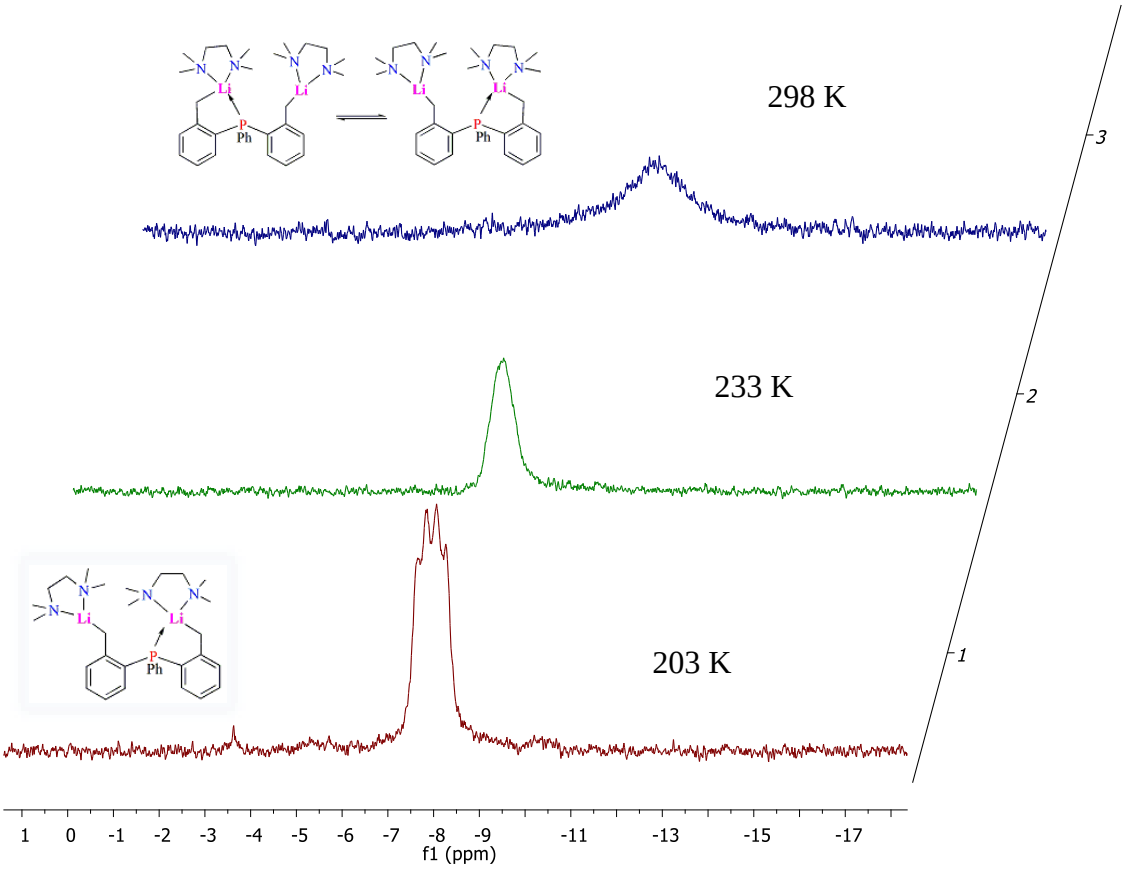


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum (202.40, toluene-d_8) of complex **2-Li$_2$** at given temperatures.

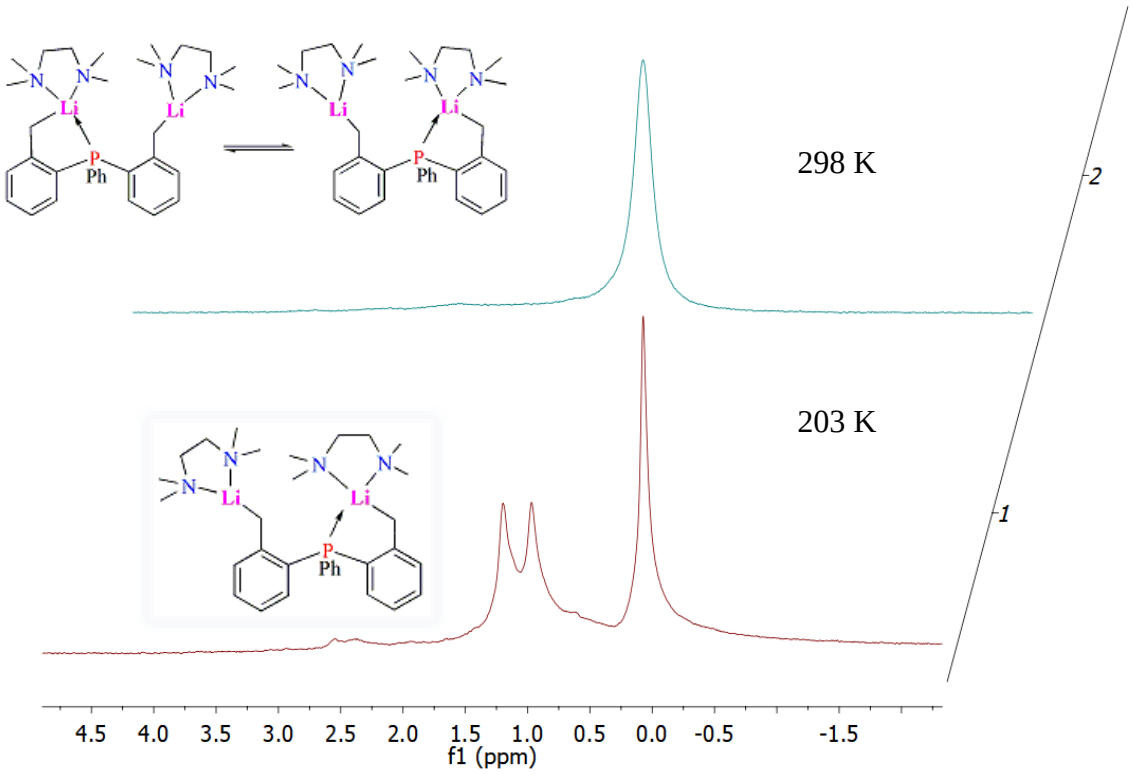


Figure S17. ^{7}Li NMR spectrum at 298 K and 203 K (194.32 MHz, C_7D_8) of complex **2-Li$_2$**

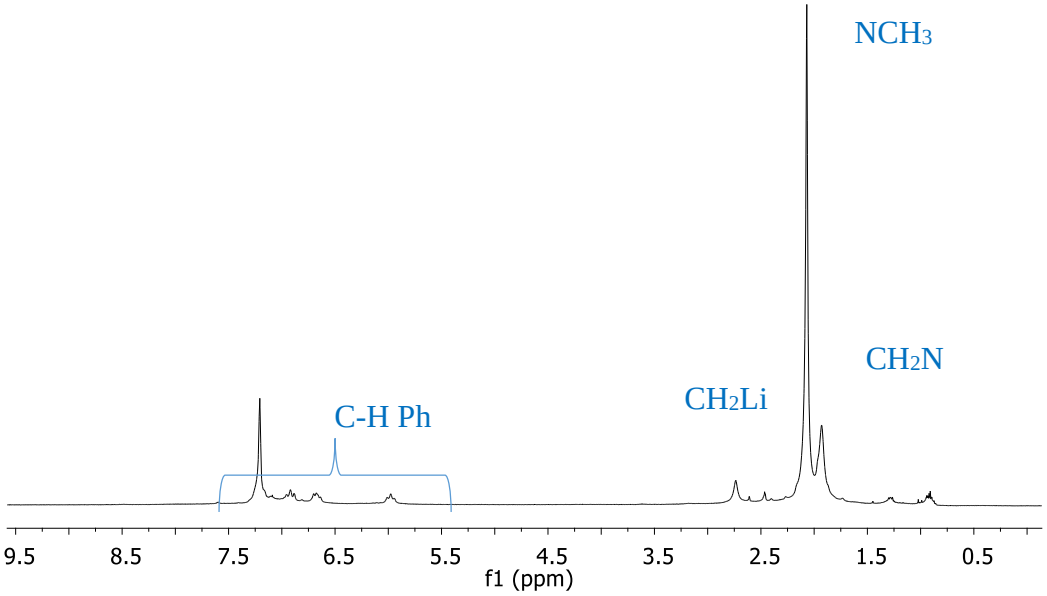


Figure S18. ^{1}H NMR spectrum (400 MHz, C_6D_6, 25 °C) of complex **3-Li$_3$**

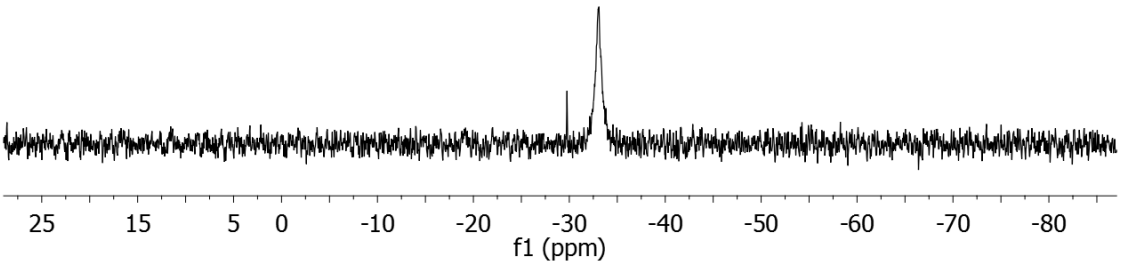


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum (161.92 MHz, C_6D_6, 298 K) of complex **3-Li$_3$**.

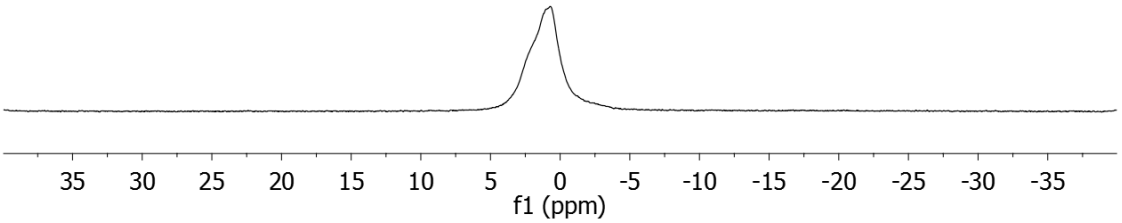


Figure S20. ^{7}Li NMR spectrum (194.32 MHz, C_6D_6, 298 K) of complex **3-Li$_3$**.

2. FT IR spectra

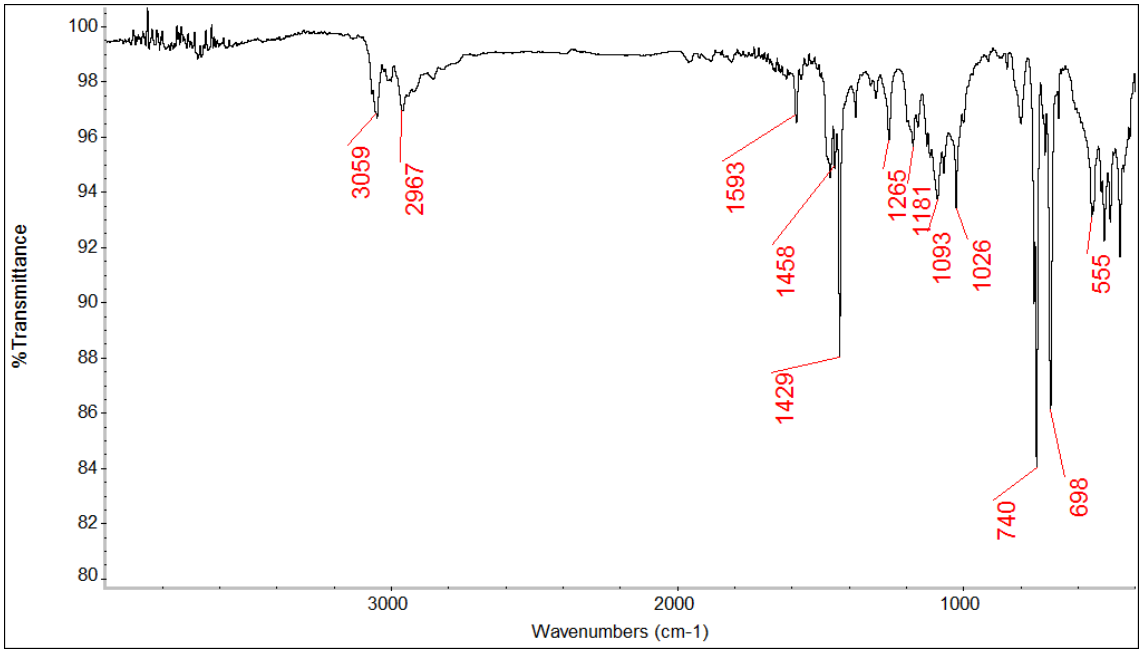


Figure S21. Infrared spectrum of **1-Li** (KBr disc)

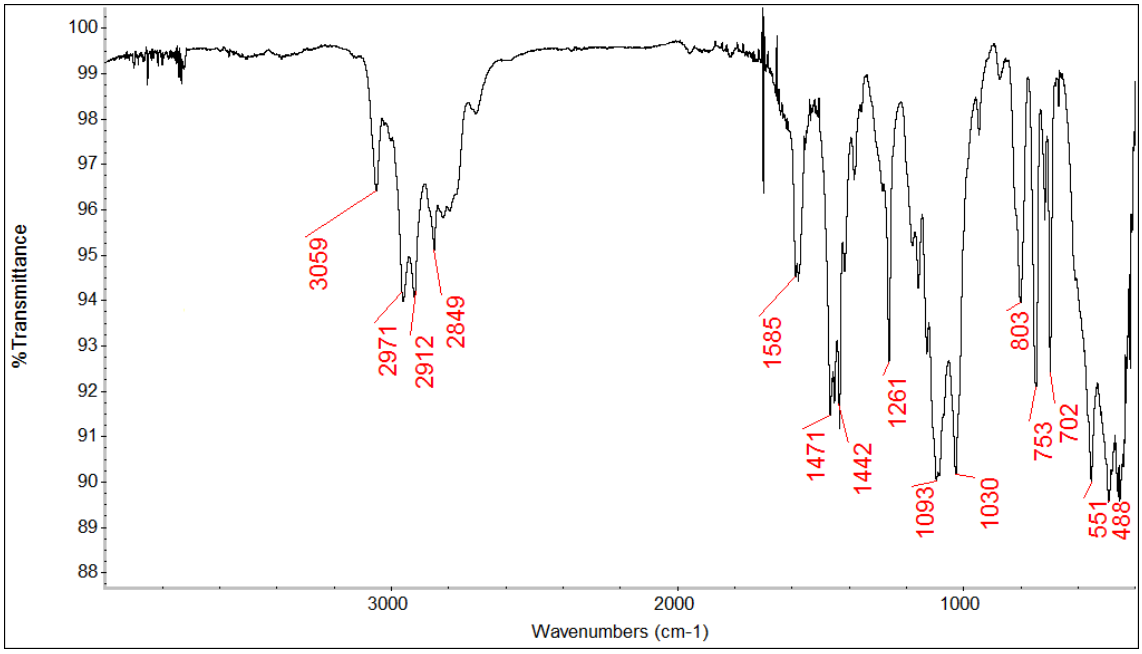


Figure S22. Infrared spectrum of 2-Li (KBr disc)

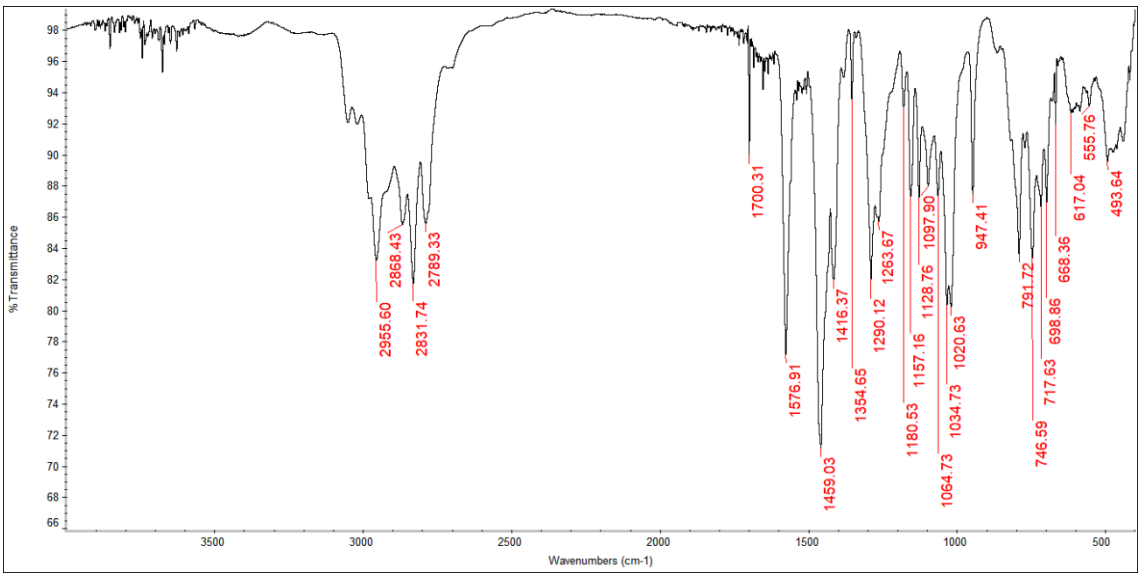


Figure S23. Infrared spectrum of **2-Li$_2$** (KBr disc).

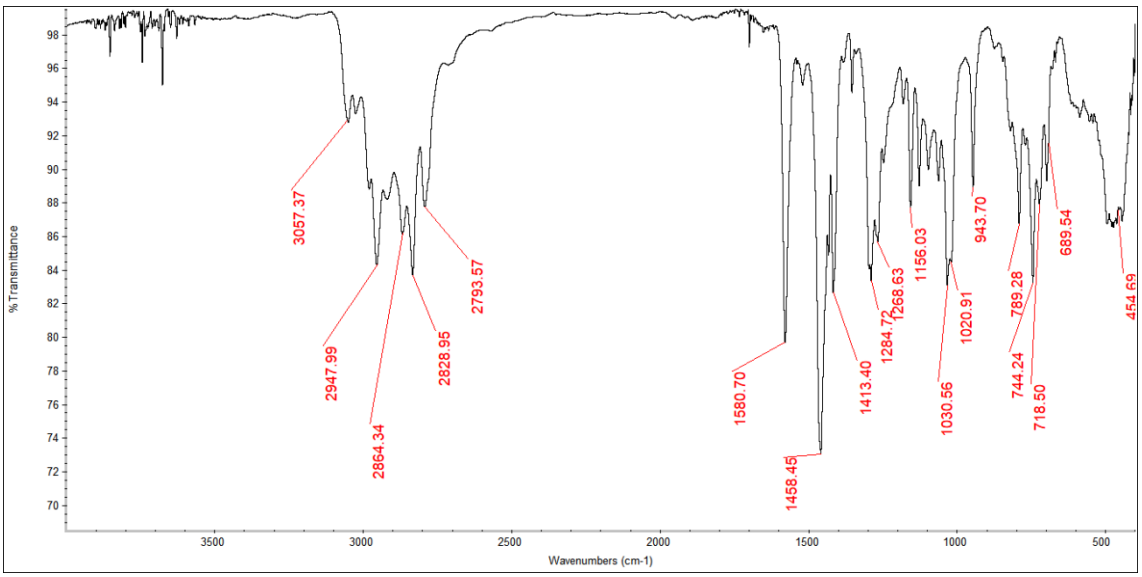


Figure S24. Infrared spectrum of **2-Li$_3$** (KBr disc).

3. X-ray diffraction data

3.1 X-ray diffraction data of complex 1-Li

Table S 1. Crystal data and structure refinement for 1-Li.

Identification code MM89a
Empirical formula $C_{25}H_{32}LiN_2P$
Formula weight 398.43
Temperature/K 113(18)
Crystal system monoclinic
Space group C2/c
a/Å 17.0285(9)
b/Å 14.1666(7)
c/Å 19.4268(10)
α/° 90
β/° 96.613(5)
γ/° 90
Volume/Å^3 4655.3(4)
Z 8
ρ_{calc}g/cm^3 1.137
μ/mm^{-1} 1.117
F(000) 1712.0
Crystal size/mm^3 0.21 × 0.18 × 0.08
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 8.14 to 145.162
Index ranges -13 ≤ h ≤ 20, -15 ≤ k ≤ 17, -23 ≤ l ≤ 20
Reflections collected 8275
Independent reflections 4529 [R_{int} = 0.0294, R_{sigma} = 0.0353]
Data/restraints/parameters 4529/0/261
Goodness-of-fit on F^2 1.047
Final R indexes [I>=2σ (I)] R_1 = 0.0514, wR_2 = 0.1362
Final R indexes [all data] R_1 = 0.0566, wR_2 = 0.1424
Largest diff. peak/hole / e Å^{-3} 0.53/-0.43

Table S 2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 1-Li.

Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
P1	3265.5(2)	4468.8(3)	6618.6(2)	20.68(14)
C3	1266.4(10)	5659.8(12)	5562.8(9)	26.9(4)
C1	2269.9(9)	4669.2(12)	6205.3(8)	21.1(3)
C8	3839.8(9)	5474.2(12)	6356.7(8)	23.7(3)
N1	1809.5(8)	5389.5(10)	7960.9(7)	25.6(3)
C2	2055(1)	5442.7(12)	5779.5(8)	24.1(3)
C5	875.6(9)	4332.2(12)	6229.2(9)	24.7(3)

C19 4345.9(9) 3043.0(12) 6416.9(8) 23.4(3)
C20 2264.5(11) 5648.2(14) 8628.8(9) 32.1(4)
C17 4335.9(10) 2075.1(12) 5399.7(9) 26.0(3)
C13 4225.7(10) 5483.3(12) 5760.8(9) 26.9(4)
C23 1708.9(11) 6213.4(13) 7500.6(9) 31.1(4)
N2 2975.9(9) 4120.5(12) 8648.5(7) 31.8(3)
C18 4681.6(9) 2336.0(12) 6054.0(9) 26.4(4)
C15 3315.8(9) 3236.9(11) 5469.5(8) 22.3(3)
C16 3652.5(9) 2528.8(12) 5107.1(8) 24.4(3)
C14 3661.3(9) 3509.6(11) 6127.5(8) 21.1(3)
C7 1869.4(9) 3241.1(12) 6843.7(8) 24.7(3)
C6 1677.2(9) 4042.9(11) 6428.9(8) 21.7(3)
C4 683.9(9) 5094.3(12) 5808.2(8) 26.6(4)
C25 3788.9(11) 4456.4(17) 8631.4(10) 43.4(5)
C22 1023.9(10) 5019.8(15) 8066.6(10) 34.7(4)
C11 4727.8(12) 7037.7(15) 6031.2(10) 39.3(5)
C21 2534.6(11) 4782.1(14) 9046.9(9) 33.2(4)
C12 4664.7(11) 6259.2(14) 5602.8(9) 32.3(4)
C10 4342.7(14) 7043.6(15) 6623.2(11) 44.3(5)
C9 3912.9(11) 6265.3(14) 6788(1) 35.4(4)
C24 2991.2(16) 3178.5(16) 8958.3(12) 52.4(6)
Li1 2403.6(17) 4221(2) 7648.2(15) 28.2(6)

Table S 3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1-Li.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$. Atom U_{11} U_{22} U_{33} U_{23} U_{13} U_{12}

P1 16.8(2) 22.6(2) 23.1(2) -1.15(14) 4.36(15) -0.20(13)
C3 26.6(8) 27.8(9) 26.4(8) 2.0(6) 2.7(6) 7.2(7)
C1 18.3(7) 22.9(8) 22.7(7) -2.9(6) 4.8(5) 1.7(6)
C8 18.8(7) 24.5(8) 27.9(8) -0.3(6) 3.7(6) -1.7(6)
N1 20.5(7) 29.0(8) 27.8(7) -4.6(6) 4.5(5) -0.4(5)
C2 22.2(8) 25.2(8) 26.1(8) -1.5(6) 7.2(6) 1.0(6)
C5 18.1(7) 26.2(8) 30.1(8) -6.7(6) 4.4(6) -1.2(6)
C19 18.6(7) 25.4(8) 26.3(7) 2.0(6) 3.3(6) -0.8(6)
C20 30.6(9) 36.2(10) 29.4(9) -11.3(7) 2.5(7) 2.3(7)
C17 23.7(8) 23.6(8) 32.8(8) 0.9(6) 12.1(6) 0.9(6)
C13 24.2(8) 27.6(9) 29.2(8) -3.1(6) 4.8(6) -3.4(6)
C23 30.3(9) 28.8(9) 34.7(9) -3.8(7) 6.0(7) 5.3(7)
N2 31.5(8) 34.2(9) 29.0(7) -1.8(6) 0.8(6) 3.7(6)
C18 18.5(7) 26.1(9) 35.2(8) 4.5(7) 5.5(6) 2.7(6)
C15 16.1(7) 24.1(8) 27.3(7) 0.5(6) 4.5(5) 0.1(6)
C16 22.5(8) 25.9(8) 25.9(7) -2.1(6) 6.8(6) -3.2(6)
C14 16.0(7) 21.6(8) 26.9(7) 0.8(6) 6.8(5) -1.1(6)
C7 21.0(7) 24.0(8) 29.7(8) -2.0(6) 6.0(6) -1.0(6)

C6 20.3(7) 21.9(8) 23.4(7) -6.2(6) 4.6(5) -0.2(6)
C4 20.1(7) 30.0(9) 29.3(8) -6.2(7) 0.6(6) 5.7(6)
C25 26.6(10) 67.0(16) 35.9(10) -1.3(9) 0.3(8) 8.4(9)
C22 21.6(8) 41.6(11) 42.3(10) -7.1(8) 10.1(7) -1.1(7)
C11 45.0(11) 34(1) 40.4(10) -3.3(8) 11.4(8) -18.4(9)
C21 32.0(9) 43.0(11) 25.2(8) -4.0(7) 4.9(7) 0.7(8)
C12 31.9(9) 35.3(10) 31.3(8) -1.9(7) 10.9(7) -8.5(7)
C10 57.9(13) 34.2(11) 43.6(11) -13.7(9) 17.6(9) -16.2(9)
C9 39.9(10) 33.9(10) 34.7(9) -7.3(7) 14.2(7) -8.7(8)
C24 66.1(15) 40.0(12) 47.2(12) 5.0(9) -11.0(11) 3.9(11)

Table S 4. Bond Lengths for 1-Li.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	C1	1.8128(16)	C19	C14	1.400(2)
P1	C8	1.8325(17)	C20	C21	1.513(3)
P1	C14	1.8328(16)	C17	C18	1.388(2)
P1	Li1	2.637(3)	C17	C16	1.392(2)
C3	C2	1.395(2)	C13	C12	1.383(2)
C3	C4	1.401(3)	N2	C25	1.468(3)
C1	C2	1.396(2)	N2	C21	1.475(2)
C1	C6	1.447(2)	N2	C24	1.463(3)
C8	C13	1.395(2)	N2	Li1	2.076(3)
C8	C9	1.396(2)	C15	C16	1.387(2)
N1	C20	1.479(2)	C15	C14	1.399(2)
N1	C23	1.468(2)	C7	C6	1.409(2)
N1	C22	1.473(2)	C7	Li1	2.206(3)
N1	Li1	2.068(3)	C6	Li1	2.555(3)
C5	C6	1.435(2)	C11	C12	1.378(3)
C5	C4	1.371(2)	C11	C10	1.388(3)
C19	C18	1.386(2)	C10	C9	1.381(3)

Table S 5. Bond Angles for 1-Li.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P1	C8	104.90(7)	C24	N2	Li1	115.58(15)
C1	P1	C14	105.48(7)	C19	C18	C17	120.14(15)
C1	P1	Li1	77.46(8)	C16	C15	C14	120.58(14)
C8	P1	C14	101.06(7)	C15	C16	C17	120.11(15)
C8	P1	Li1	132.50(9)	C19	C14	P1	118.69(12)
C14	P1	Li1	124.48(8)	C15	C14	P1	122.64(12)
C2	C3	C4	117.79(15)	C15	C14	C19	118.66(14)
C2	C1	P1	123.59(12)	C6	C7	Li1	87.00(12)
C2	C1	C6	120.97(14)	C1	C6	Li1	86.44(11)
C6	C1	P1	114.83(12)	C5	C6	C1	114.72(14)
C13	C8	P1	123.71(13)	C5	C6	Li1	124.49(12)
C13	C8	C9	118.18(15)	C7	C6	C1	122.80(14)

C9 C8 P1 118.08(13) C7 C6 C5 122.39(15)
C20 N1 Li1 103.40(13) C7 C6 Li1 59.57(11)
C23 N1 C20 110.48(14) C5 C4 C3 121.61(15)
C23 N1 C22 108.87(14) C12 C11 C10 119.58(18)
C23 N1 Li1 118.96(13) N2 C21 C20 112.04(14)
C22 N1 C20 111.00(14) C11 C12 C13 120.55(17)
C22 N1 Li1 103.84(14) C9 C10 C11 120.05(18)
C3 C2 C1 121.97(15) C10 C9 C8 120.98(17)
C4 C5 C6 122.67(15) N1 Li1 P1 116.74(13)
C18 C19 C14 120.67(15) N1 Li1 N2 88.42(12)
N1 C20 C21 111.48(15) N1 Li1 C7 122.41(15)
C18 C17 C16 119.83(15) N1 Li1 C6 98.64(12)
C12 C13 C8 120.64(16) N2 Li1 P1 118.48(13)
C25 N2 C21 110.16(15) N2 Li1 C7 136.95(16)
C25 N2 Li1 107.39(14) N2 Li1 C6 170.37(16)
C21 N2 Li1 103.60(13) C7 Li1 P1 76.51(10)
C24 N2 C25 109.45(17) C7 Li1 C6 33.42(7)
C24 N2 C21 110.47(17) C6 Li1 P1 64.04(7)

Table S 6. Torsion Angles for MM89a.

A B C D Angle/° A B C D Angle/°
P1 C1 C2 C3 -169.24
(13) C14 P1 C1 C6 83.47(12)
P1 C1 C6 C5 166.25(11) C14 P1 C8 C13 19.87(15)
P1 C1 C6 C7 -10.3(2) C14 P1 C8 C9 -158.29
(14)
P1 C1 C6 Li1 39.66(12) C14 C19 C18 C17 -0.7(2)
P1 C8 C13 C12 -178.49
(14) C14 C15 C16 C17 0.6(2)
P1 C8 C9 C10 179.50(17) C6 C1 C2 C3 1.4(2)
C1 P1 C8 C13 -89.60(15) C6 C5 C4 C3 -2.0(2)
C1 P1 C8 C9 92.24(15) C4 C3 C2 C1 2.4(2)
C1 P1 C14 C19 -164.97
(12) C4 C5 C6 C1 5.5(2)
C1 P1 C14 C15 16.30(15) C4 C5 C6 C7 -177.93
(15)
C8 P1 C1 C2 0.85(15) C4 C5 C6 Li1 109.03(18)
C8 P1 C1 C6 -170.30
(11) C25 N2 C21 C20 78.39(18)
C8 P1 C14 C19 86.01(13) C22 N1 C20 C21 71.93(19)
C8 P1 C14 C15 -92.71(14) C11 C10 C9 C8 -1.7(3)
C8 C13 C12 C11 -0.1(3) C12 C11 C10 C9 1.3(3)
N1 C20 C21 N2 53.9(2) C10 C11 C12 C13 -0.4(3)
C2 C3 C4 C5 -2.1(2) C9 C8 C13 C12 -0.3(3)
C2 C1 C6 C5 -5.1(2) C24 N2 C21 C20 -160.58
(16)

C2 C1 C6 C7 178.33(14) Li1 P1 C1 C2 131.92(15)
C2 C1 C6 Li1 -131.73
(15) Li1 P1 C1 C6 -39.22(12)
C13 C8 C9 C10 1.2(3) Li1 P1 C8 C13 -176.11
(14)
C23 N1 C20 C21 -167.19
(14) Li1 P1 C8 C9 5.7(2)
C18 C19 C14 P1 -177.73
(12) Li1 P1 C14 C19 -79.73(15)
C18 C19 C14 C15 1.1(2) Li1 P1 C14 C15 101.54(15)
C18 C17 C16 C15 -0.3(2) Li1 N1 C20 C21 -38.85(18)
C16 C17 C18 C19 0.3(2) Li1 N2 C21 C20 -36.22(19)
C16 C15 C14 P1 177.71(12) Li1 C7 C6 C1 62.36(17)
C16 C15 C14 C19 -1.0(2) Li1 C7 C6 C5 -113.90
(16)
C14 P1 C1 C2 -105.39
(14)

Crystal structure determination of [MM89a]

Crystal Data for $C_{25}H_{32}LiN_2P$ (M =398.43 g/mol): monoclinic, space group C2/c (no. 15), a = 17.0285(9) Å, b = 14.1666(7) Å, c = 19.4268(10) Å, β = 96.613(5)°, V = 4655.3(4) Å^3, Z = 8, T = 113(18) K, μ(CuKα) = 1.117 mm^{-1},

Table S 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1-Li.

Atom x y z U(eq)
H3 1132 6163 5265 32
H2 2450 5825 5636 29
H5 470 3989 6392 30
H19 4577 3209 6857 28
H20A 1938 6035 8894 39
H20B 2722 6018 8542 39
H17 4560 1598 5157 31
H13 4188 4963 5467 32
H23A 1418 6693 7711 47
H23B 1424 6031 7066 47
H23C 2218 6455 7424 47
H18 5140 2036 6249 32
H15 2856 3533 5273 27
H16 3421 2357 4668 29
H7A 2245 2819 6663 30
H7B 1414 2899 6972 30
H4 154 5239 5682 32
H25A 3779 5084 8445 65
H25B 4060 4045 8345 65
H25C 4060 4460 9093 65
H22A 1084 4479 8366 52
H22B 746 4840 7628 52

H22C 730 5499 8274 52
H11 5026 7556 5924 47
H21A 2869 4976 9461 40
H21B 2077 4462 9191 40
H12 4919 6255 5204 39
H10 4374 7572 6909 53
H9 3669 6268 7192 43
H24A 3276 2755 8691 79
H24B 2460 2954 8963 79
H24C 3248 3208 9424 79

Dcalc = 1.137 g/cm3, 8275 reflections measured (8.14° ≤ 2Θ ≤ 145.162°), 4529 unique (R_{int} = 0.0294, R_{sigma} = 0.0353)which were used in all calculations. The final R_1 was 0.0514 (I > 2σ(I)) and wR_2 was 0.1424 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups
2.a Secondary CH2 refined with riding coordinates:
C20(H20A,H20B), C7(H7A,H7B), C21(H21A,H21B)
2.b Aromatic/amide H refined with riding coordinates:
C3(H3), C2(H2), C5(H5), C19(H19), C17(H17), C13(H13), C18(H18), C15(H15),
C16(H16), C4(H4), C11(H11), C12(H12), C10(H10), C9(H9)
2.c Idealised Me refined as rotating group:
C23(H23A,H23B,H23C), C25(H25A,H25B,H25C), C22(H22A,H22B,H22C), C24(H24A,H24B,
H24C)

3.2 X-ray diffraction data of complex 2-Li

Table S 8. Crystal data and structure refinement for 2-Li.

Identification code MM122
Empirical formula $C_{26}H_{34}LiN_2P$
Formula weight 412.46
Temperature/K 100.0(3)
Crystal system monoclinic
Space group $P2_1/n$
a/Å 10.90505(11)
b/Å 18.17218(18)
c/Å 12.49103(13)
α/° 90
β/° 103.7696(10)
γ/° 90
Volume/Å^3 2404.19(4)
Z 4
ρ_{calc}g/cm^3 1.140
μ/mm^{-1} 1.097
F(000) 888.0
Crystal size/mm^3 0.21 × 0.16 × 0.12
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 8.764 to 145.202
Index ranges $-12 \le h \le 13$, $-22 \le k \le 18$, $-15 \le l \le 11$
Reflections collected 8793
Independent reflections 4677 [R_{int} = 0.0109, R_{sigma} = 0.0153]
Data/restraints/parameters 4677/0/282
Goodness-of-fit on F^2 1.042
Final R indexes [I>=2σ (I)] R_1 = 0.0685, wR_2 = 0.1834
Final R indexes [all data] R_1 = 0.0704, wR_2 = 0.1851
Largest diff. peak/hole / e Å^{-3} 1.70/-0.64
MM122

Table S 9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for MM122.

U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
P7	1904.8(5)	1260.4(3)	7728.4(5)	19.44(19)
C1	2642(2)	1248.7(13)	9218.2(19)	21.8(5)
C4	3803(3)	1245.2(18)	11461(2)	38.7(7)
C9	-714(2)	1220.3(13)	6981(2)	25.4(5)
C20	4528(2)	1328.8(13)	7310(2)	23.0(5)
C8	319(2)	922.3(12)	7732.6(18)	20.2(5)

N26 1998(2) 1601.0(12) 4581.7(17) 29.4(5)
N23 2786(2) 2975.3(12) 5686.6(19) 32.9(5)
C19 3872(2) 670.8(13) 6964.7(18) 20.6(5)
C2 2395(2) 1824.6(13) 9891(2) 27.1(5)
C12 -1110(2) 145.6(13) 8438.0(19) 24.8(5)
C18 4343(2) 127.9(13) 6333.7(19) 23.6(5)
C6 3448(2) 676.2(15) 9690(2) 29.2(5)
C3 2987(3) 1813.1(16) 11007(2) 34.6(6)
C13 104(2) 385.2(13) 8465.2(19) 23.0(5)
C10 -1931(2) 983.2(15) 6960(2) 29.5(5)
C15 2013(2) -143.2(14) 6773(2) 28.5(5)
C17 3697(2) -505.6(14) 5965(2) 27.7(5)
Li30 2918(4) 1887(2) 6193(3) 25.3(8)
C11 -2130(2) 448.6(14) 7688(2) 26.3(5)
C14 2645(2) 509.0(13) 7163.2(18) 21.9(5)
C21 1487(3) 2435.8(15) 9418(2) 39.4(7)
C5 4021(3) 670.3(18) 10808(2) 37.1(6)
C16 2522(2) -654.9(15) 6182(2) 32.4(6)
C24 2371(4) 2918.9(19) 4474(3) 57.6(10)
C25 1567(4) 2287.9(18) 4062(3) 54.2(9)
C27 3008(4) 1300(2) 4098(3) 56.1(10)
C28 1035(4) 1016(2) 4402(3) 57.9(10)
C22 1736(4) 3310(2) 6066(4) 70.3(12)
C29 3929(4) 3397(2) 5974(4) 69.4(12)

Table S 10. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2-Li.

The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom U_{11} U_{22} U_{33} U_{23} U_{13} U_{12}

P7 19.0(3) 20.5(3) 19.5(3) 0.2(2) 6.0(2) 0.4(2)
C1 21.1(11) 24.9(12) 20.9(11) -0.6(8) 7.8(9) -3.4(9)
C4 33.3(14) 61.2(19) 21.1(12) 0.0(12) 5.8(11) -5.6(13)
C9 24.9(12) 29.6(12) 22.3(11) 5.5(9) 6.7(9) 4.1(9)
C20 17.3(11) 26.9(12) 24.2(12) -0.9(9) 4.1(9) 0.8(9)
C8 20.4(10) 21.8(11) 19.4(10) -2.1(8) 6.7(8) 1.6(8)
N26 30.5(11) 36.9(12) 20.4(10) -1.0(8) 4.9(8) -8.0(9)
N23 40.9(13) 23.7(10) 33.2(12) 2.1(9) 7.3(10) 3.4(9)
C19 18.4(10) 25.2(11) 17.2(10) 2.3(8) 2.3(8) 3.1(9)
C2 32.5(13) 23.6(12) 27.1(12) -2.8(9) 11(1) -6.2(10)
C12 27.3(12) 25.3(12) 23.4(11) 0.1(9) 8.9(9) -2.5(9)
C18 17.9(10) 31.5(12) 21.5(11) 0.0(9) 4.9(9) 3.8(9)
C6 24.8(12) 38.2(14) 26.0(12) 1.5(10) 8.5(10) 6.4(10)
C3 41.8(15) 37.7(14) 26.4(13) -7.5(11) 12.4(11) -9.6(12)
C13 21.8(11) 24.3(11) 22.0(11) 2.0(9) 3.2(9) 2.2(9)
C10 21.1(11) 37.9(14) 27.8(12) 4.4(11) 2.5(9) 4.8(10)
C15 24.3(12) 29.0(13) 34.5(13) -7.6(10) 12(1) -3.8(10)

C17 26.6(12) 30.4(13) 26.8(12) -6.5(10) 7.5(10) 5(1)
Li30 25.5(19) 28(2) 21.6(19) 0.4(16) 3.5(15) 1.5(16)
C11 20.6(11) 31.8(13) 27.3(12) -3.8(10) 7.3(9) -2.1(9)
C14 20.6(11) 24.6(11) 20.8(11) -1.6(9) 5.6(8) 0.8(9)
C21 59.2(19) 24.7(13) 36.6(15) -2.1(11) 16.2(13) 6.1(12)
C5 27.5(13) 55.2(18) 28.6(13) 10.4(12) 6.9(11) 9.4(12)
C16 29.9(13) 28.7(13) 40.1(14) -12.3(11) 11.4(11) -5.2(10)
C24 71(2) 44.4(18) 43.9(18) 21.4(15) -12.1(16) -15.6(17)
C25 77(2) 46.5(18) 28.0(14) 0.4(13) -9.7(15) 23.2(17)
C27 79(3) 56(2) 35.3(17) -1.4(14) 18.0(17) 21.5(18)
C28 60(2) 67(2) 42.7(18) -0.4(17) 2.8(16) -23.6(18)
C22 79(3) 49(2) 88(3) -4(2) 30(2) 20(2)
C29 71(3) 52(2) 70(3) 9.3(19) -12(2) -30.0(19)

Table S 11. Bond Lengths for 2-Li.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P7	C1	1.843(2)	N23	C24	1.477(4)
P7	C8	1.836(2)	N23	C22	1.471(4)
P7	Li30	2.684(4)	N23	C29	1.434(4)
P7	C14	1.813(2)	C19	C18	1.432(3)
C1	C2	1.408(3)	C19	Li30	2.533(5)
C1	C6	1.399(3)	C19	C14	1.448(3)
C4	C3	1.392(4)	C2	C3	1.391(4)
C4	C5	1.381(4)	C2	C21	1.511(4)
C9	C8	1.393(3)	C12	C13	1.386(3)
C9	C10	1.389(3)	C12	C11	1.387(3)
C20	C19	1.407(3)	C18	C17	1.371(4)
C20	Li30	2.211(5)	C6	C5	1.388(4)
C8	C13	1.395(3)	C10	C11	1.383(4)
N26	Li30	2.090(4)	C15	C14	1.399(3)
N26	C25	1.434(4)	C15	C16	1.383(4)
N26	C27	1.481(4)	C17	C16	1.398(4)
N26	C28	1.473(4)	C24	C25	1.461(5)
N23	Li30	2.071(5)			

Table S 12. Bond Angles for 2-Li.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	P7	Li30	124.86(11)	C18	C19	C14	114.9(2)
C8	P7	C1	100.25(10)	C14	C19	Li30	85.97(16)
C8	P7	Li30	133.79(11)	C1	C2	C21	120.9(2)
C14	P7	C1	104.89(11)	C3	C2	C1	118.5(2)
C14	P7	C8	104.84(10)	C3	C2	C21	120.5(2)
C14	P7	Li30	75.16(12)	C13	C12	C11	120.0(2)
C2	C1	P7	119.63(18)	C17	C18	C19	122.7(2)

C6 C1 P7 120.87(18) C5 C6 C1 121.1(2)
C6 C1 C2 119.5(2) C2 C3 C4 121.3(3)
C5 C4 C3 120.2(2) C12 C13 C8 120.8(2)
C10 C9 C8 120.5(2) C11 C10 C9 120.3(2)
C19 C20 Li30 85.82(17) C16 C15 C14 121.9(2)
C9 C8 P7 118.65(18) C18 C17 C16 121.3(2)
C9 C8 C13 118.6(2) C20 Li30 P7 75.81(13)
C13 C8 P7 122.78(17) C20 Li30 C19 33.65(10)
C25 N26 Li30 104.5(2) N26 Li30 P7 113.45(18)
C25 N26 C27 109.4(3) N26 Li30 C20 128.4(2)
C25 N26 C28 114.5(3) N26 Li30 C19 102.08(18)
C27 N26 Li30 104.6(2) N23 Li30 P7 127.79(19)
C28 N26 Li30 119.2(2) N23 Li30 C20 128.1(2)
C28 N26 C27 104.2(3) N23 Li30 N26 87.74(17)
C24 N23 Li30 103.2(2) N23 Li30 C19 160.3(2)
C22 N23 Li30 107.5(2) C19 Li30 P7 63.88(11)
C22 N23 C24 106.7(3) C10 C11 C12 119.8(2)
C29 N23 Li30 116.1(2) C19 C14 P7 115.42(17)
C29 N23 C24 109.3(3) C15 C14 P7 123.07(18)
C29 N23 C22 113.2(3) C15 C14 C19 120.7(2)
C20 C19 C18 122.1(2) C4 C5 C6 119.3(3)
C20 C19 Li30 60.53(15) C15 C16 C17 118.4(2)
C20 C19 C14 122.9(2) C25 C24 N23 115.3(3)
C18 C19 Li30 124.06(18) N26 C25 C24 114.8(3)

Table S 13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2-Li.

Atom	x	y	z	U(eq)
H4	4203	1253	12207	46
H9	-589	1581	6490	30
H20A	5360(30)	1397(17)	7170(30)	34
H20B	4370(30)	1604(18)	7930(30)	34
H12	-1240	-218	8923	30
H18	5119	209	6167	28
H6	3603	293	9246	35
H3	2836	2192	11459	42
H13	784	186	8978	28
H10	-2614	1185	6454	35
H15	1229	-236	6916	34
H17	4048	-843	5563	33
H11	-2946	293	7675	32
H21A	1778	2683	8846	59
H21B	1442	2780	9990	59
H21C	665	2232	9118	59
H5	4546	283	11114	44
H16	2093	-1088	5934	39

H24A 1917 3365 4195 69
H24B 3115 2895 4176 69
H25A 726 2385 4161 65
H25B 1503 2241 3277 65
H27A 2673 1204 3328 84
H27B 3324 851 4467 84
H27C 3682 1652 4184 84
H28A 318 1180 4659 87
H28B 1383 583 4801 87
H28C 776 904 3630 87
H22A 1485 3759 5668 105
H22B 2004 3415 6840 105
H22C 1035 2976 5937 105
H29A 4585 3144 5729 104
H29B 4175 3458 6760 104
H29C 3792 3871 5627 104

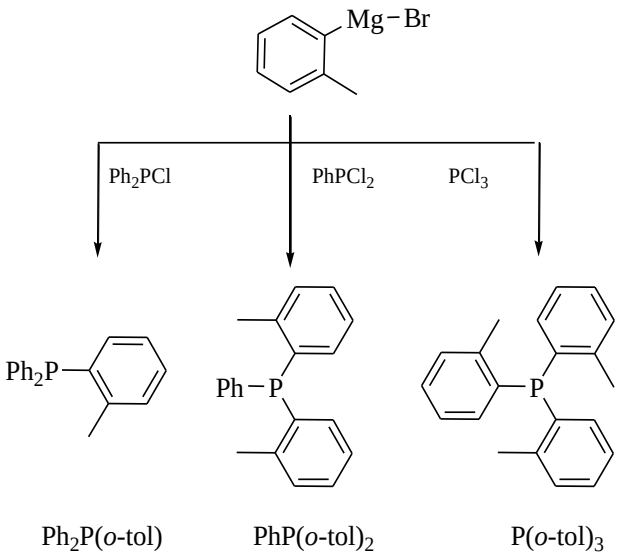
Crystal Data for $C_{26}H_{34}LiN_2P$ (M =412.46 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.90505 (11) Å, b = 18.17218(18) Å, c = 12.49103(13) Å, β = 103.7696(10)°, V = 2404.19(4) $Å^3$, Z = 4, T = 100.0(3) K, μ (CuKα) = 1.097 mm^{-1}, Dcalc = 1.140 g/cm^3, 8793 reflections measured (8.764° ≤ 2Θ ≤ 145.202°), 4677 unique (R_{int} = 0.0109, R_{sigma} = 0.0153) which were used in all calculations. The final R_1 was 0.0685 ($I > 2\sigma(I)$) and wR_2 was 0.1851 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
At 1.2 times of:
All C(H) groups, {H24A,H24B} of C24, {H25A,H25B} of C25
At 1.5 times of:
All C(H,H,H) groups, {H20A,H20B} of C20
2.a Secondary CH2 refined with riding coordinates:
C24(H24A,H24B), C25(H25A,H25B)
2.b Aromatic/amide H refined with riding coordinates:
C4(H4), C9(H9), C12(H12), C18(H18), C6(H6), C3(H3), C13(H13), C10(H10),
C15(H15), C17(H17), C11(H11), C5(H5), C16(H16)
2.c Idealised Me refined as rotating group:
C21(H21A,H21B,H21C), C27(H27A,H27B,H27C), C28(H28A,H28B,H28C), C22(H22A,H22B,
H22C), C29(H29A,H29B,H29C)



Scheme S1. Synthesis of benzylphosphines ligands 1, 2 and 3.

4. DFT computations for 1a-Li.

4.1 Cartesian coordinates

15	-0.767531001	-0.186762034	-0.211395927
6	0.047497975	2.083229169	3.114919325
1	-0.155486079	3.085122237	3.477974357
6	-0.280896983	0.344032025	1.455019202
6	-1.528860114	1.307938053	-0.954943982
7	3.161594271	0.615218178	0.121095098
6	-0.523289051	1.628805112	1.941516237
1	-1.159831125	2.301551138	1.370454196
6	1.138855142	-0.054152951	3.370020346
1	1.782146216	-0.716706977	3.947285392
6	-2.771636090	-1.889623243	-1.113166995
1	-2.311150059	-1.727476211	-2.087039070
6	3.770125316	0.587240196	-1.205843003
1	4.730165370	1.136772280	-1.214968003
1	3.099647243	1.123665215	-1.888980054
6	-4.471358176	-2.910847384	0.236447107
1	-5.343720233	-3.551107468	0.325490114
6	-2.836066230	1.713213032	-0.699257965
1	-3.463006256	1.116945961	-0.040569914
6	2.689549184	1.958852263	0.436581122
1	3.518073218	2.688577350	0.422282121
1	2.223651146	1.969013245	1.426007197
1	1.933394112	2.269991256	-0.290492934
7	2.765825327	-1.618835010	-1.683951038
6	-3.887609142	-2.700913344	-1.004705990
1	-4.303168157	-3.174543397	-1.889311054
6	-2.822139105	-1.485820213	1.250511182
1	-2.400116095	-1.006721160	2.130953252
6	-3.934537163	-2.307091317	1.361690195

1	-4.385291190	-2.474285345	2.335461266
6	-2.235833071	-1.265322171	0.010596090
6	0.847008190	-1.882180100	1.724540219
1	0.076127150	-2.428020172	1.179990180
1	1.410780254	-2.512910130	2.411101275
6	0.546907116	-0.576816013	2.184732255
6	0.894855074	1.219757136	3.817792380
1	1.359985096	1.556414183	4.741613453
6	1.924227249	-1.321775017	-2.835852130
1	1.650335186	-0.263506948	-2.855358127
1	0.994956201	-1.894310097	-2.770617122
1	2.434618298	-1.573852018	-3.782005202
6	4.094286355	0.175820180	1.152165178
1	4.402047419	-0.861190887	0.988715164
1	3.598344316	0.225739165	2.125802251
1	4.997169403	0.811504260	1.176656178
6	-2.540115281	3.643035192	-2.100865069
1	-2.935274349	4.551465245	-2.545196107
6	3.995498387	-0.825358898	-1.705701043
1	4.431423418	-0.797091880	-2.720230119
1	4.732157463	-1.327435911	-1.069288993
6	-3.337855312	2.871996100	-1.268794007
1	-4.358159405	3.178401084	-1.058377993
6	-1.239607167	3.247590210	-2.368395094
1	-0.613046144	3.843095281	-3.025618140
6	-0.743786088	2.083760140	-1.802704048
1	0.273188005	1.764215156	-2.028212065
6	3.063763400	-3.043123106	-1.647484037
1	2.130324351	-3.610984186	-1.603926034
1	3.644151455	-3.280395104	-0.751000970
1	3.632062459	-3.367378111	-2.536789105
3	1.746874219	-0.947092997	0.038740092

5. Polymerization reactions

5.1 NMR spectra of selected polymers before purification to determine conversion values

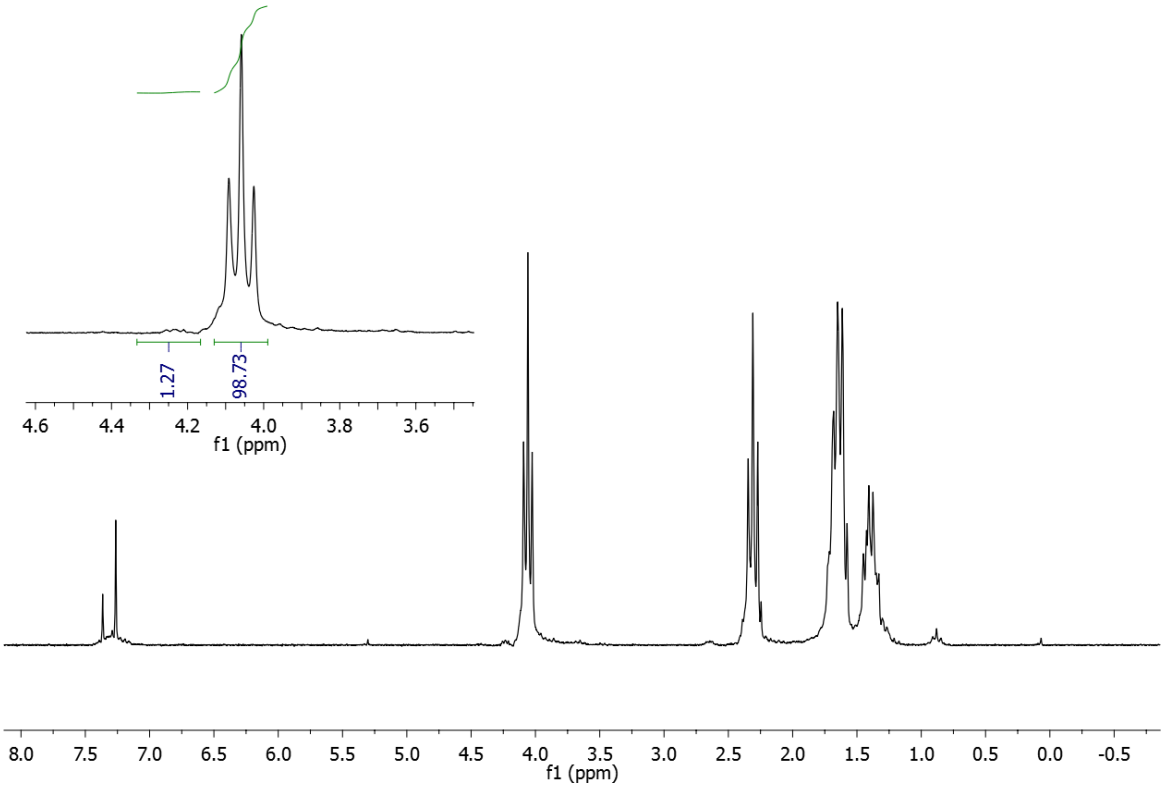


Figure S25. ^{1}H NMR spectrum of PCL obtained with catalyst **1-Li** (Table 1, entry 1).

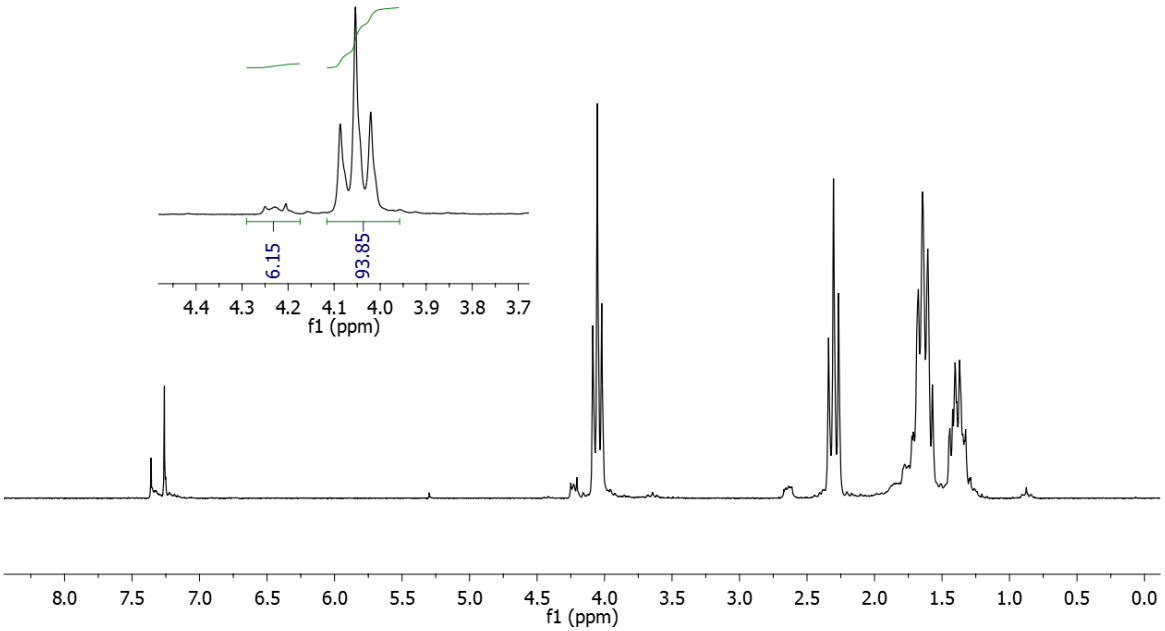


Figure S26. ^{1}H NMR spectrum of PCL obtained with catalyst **2-Li** (Table 1, entry 2).

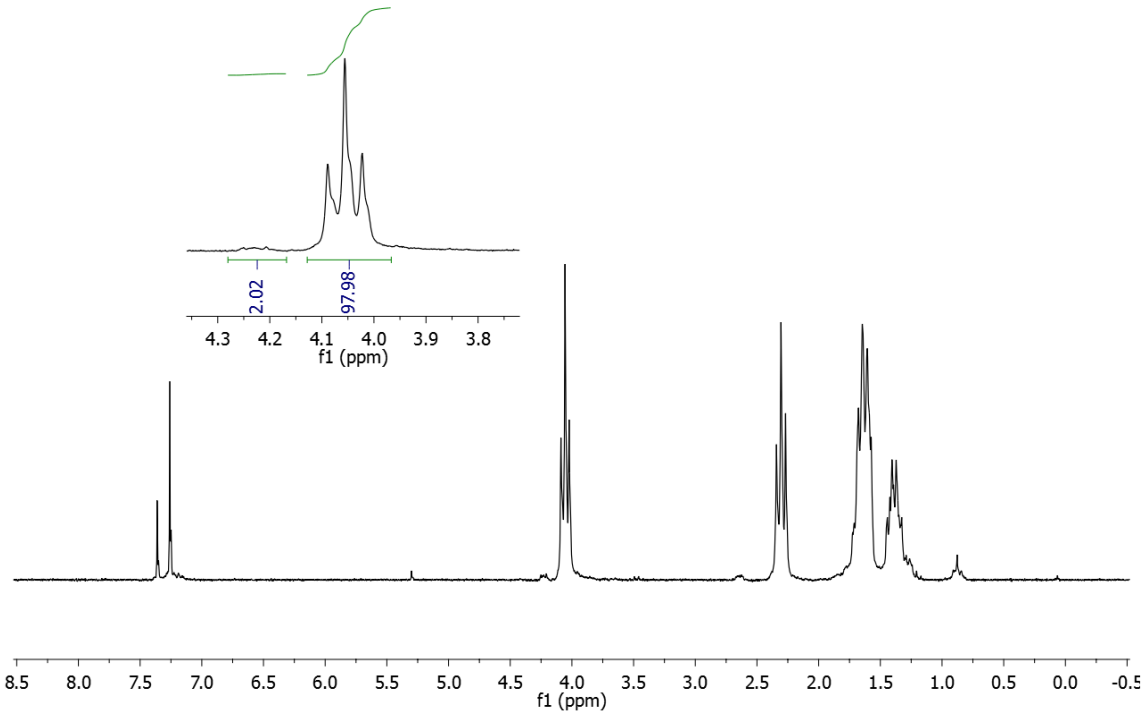


Figure S27. ^{1}H NMR spectrum of PCL obtained with catalyst **2-Li$_2$** (Table 1, entry 3).

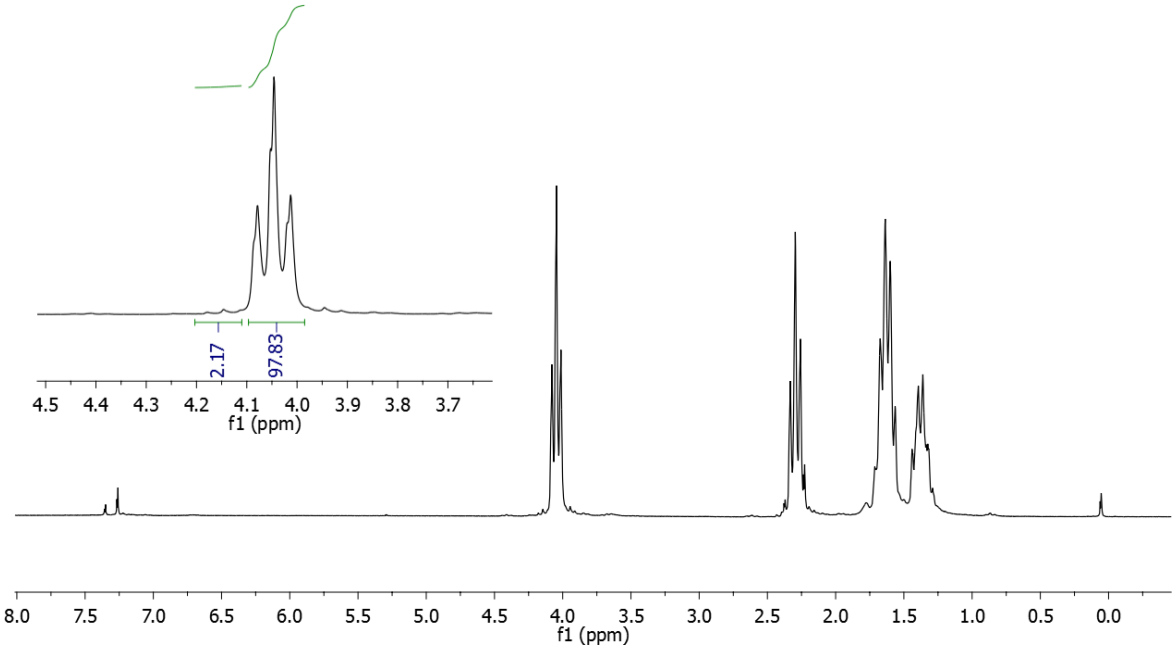


Figure S28. ^{1}H NMR spectrum of PCL obtained with catalyst **3-Li$_3$** (Table 1, entry 4)

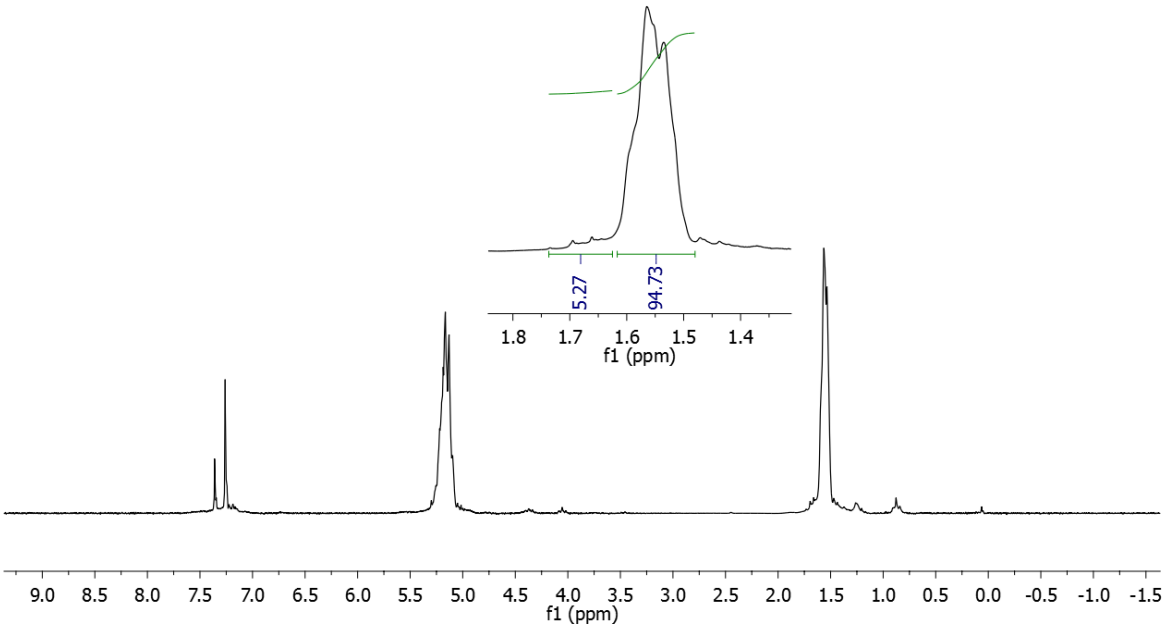


Figure S29. ^{1}H NMR spectrum of PLA obtained with catalyst **2-Li** (200 MHz, Table 2, entry 2).

5.2 NMR spectra of selected polymers following purification

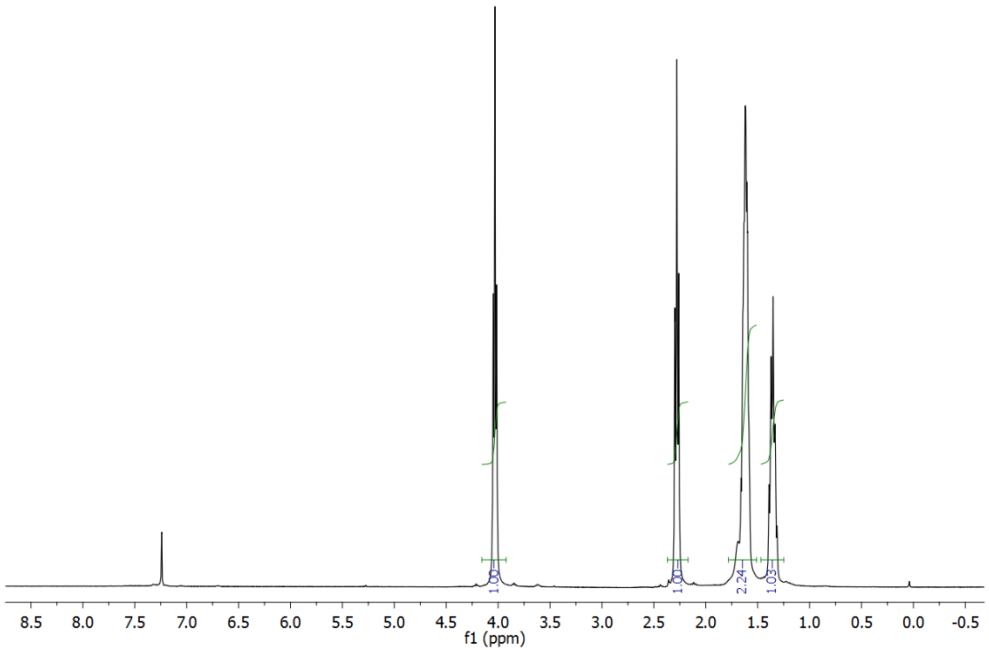


Figure S30. ^{1}H NMR spectrum of PCL obtained with catalyst **2-Li** (Table 1, entry 2).

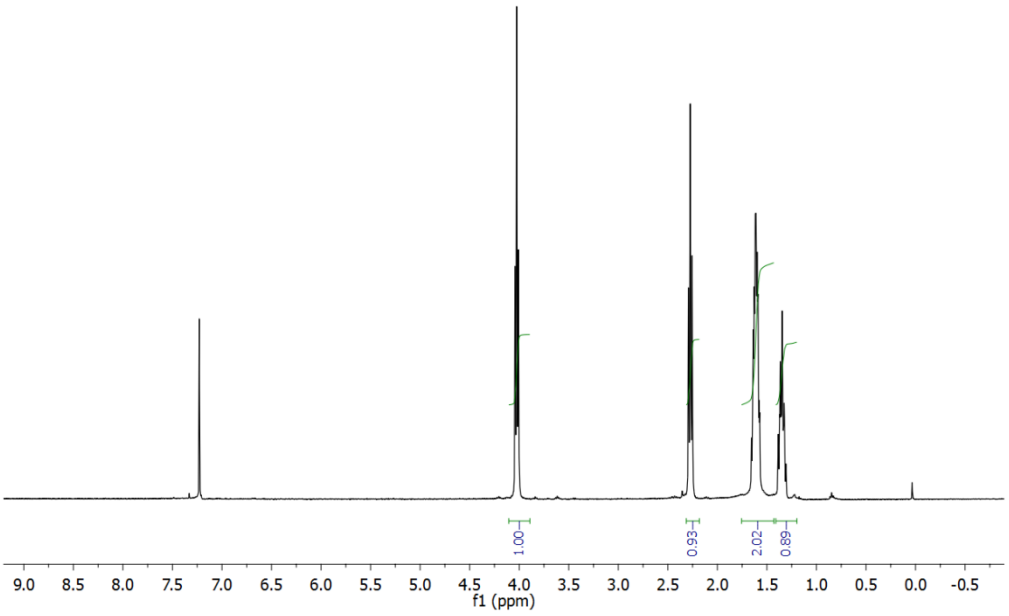


Figure S31. ^{1}H NMR spectrum of PCL obtained with catalyst **3-Li$_3$** (Table 1, entry 4).

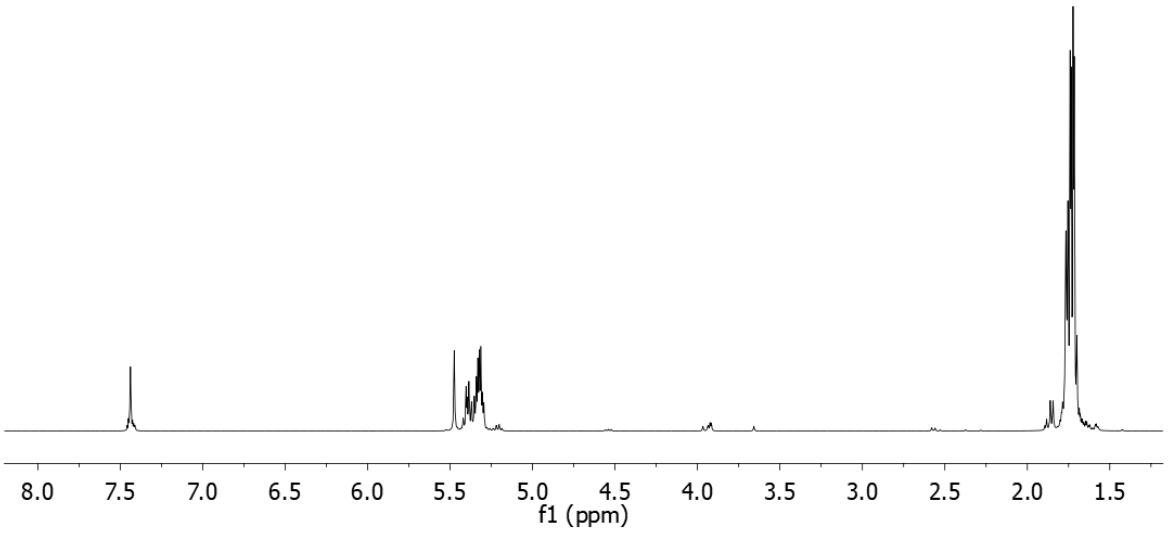


Figure S32. ^{1}H NMR of PLA obtained with catalyst **2-Li** (500 MHz, Table 2, entry 2).

5.3 Calculation procedure for determining the isotactic probability of the polylactides from the methine region of their ^{1}H NMR spectra giving rise to the values shown in Table 2.

The calculation procedure for the determination of the isotactic probability of the polymers was based on the methods reported in the references below:

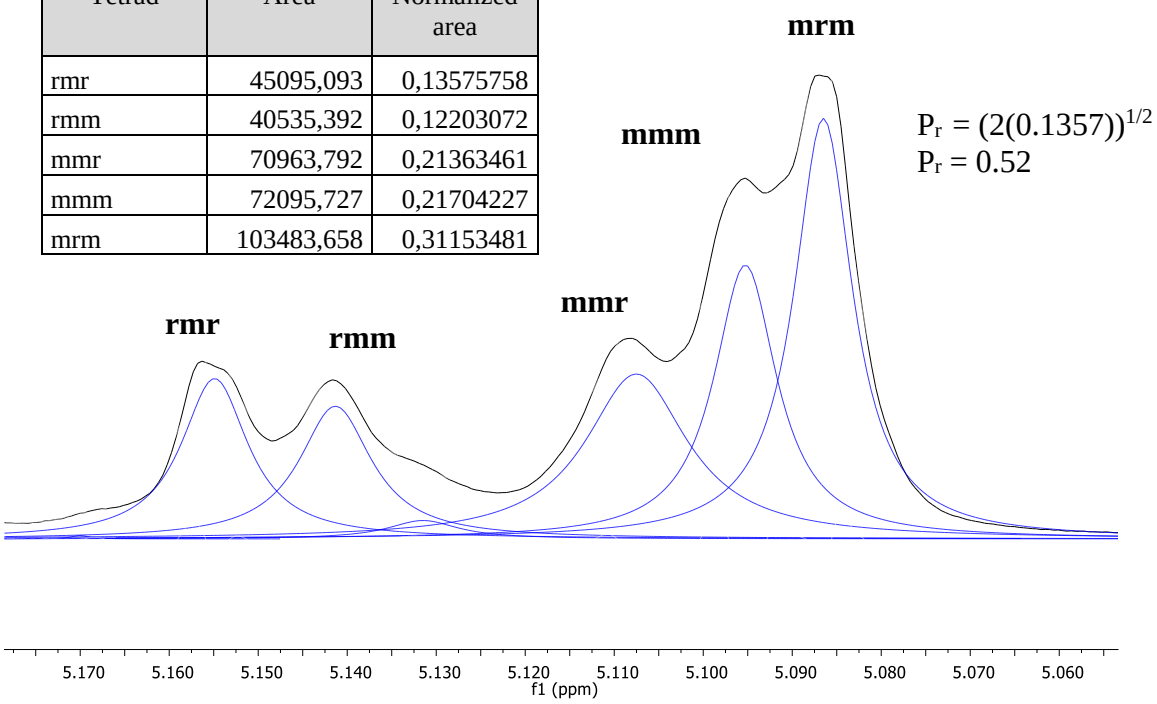
- Coudane, J., et al. (1997). "More about the stereodependence of DD and LL pair linkages during the ring-opening polymerization of racemic lactide." Journal of Polymer Science Part A: Polymer Chemistry **35**(9): 1651-1658.

- Chamberlain, B. M., et al. (2001). "Polymerization of Lactide with Zinc and Magnesium β-Diiminate Complexes: Stereocontrol and Mechanism." Journal of the American Chemical Society **123**(14): 3229-3238.

- Xiong, J., et al. (2015). "Iso-Selective Ring-Opening Polymerization of rac-Lactide Catalyzed by Crown Ether Complexes of Sodium and Potassium Naphthalenolates." Inorganic Chemistry **54**(4): 1737-1743.

Herein, we show a representative example of the methine region of one of our polymers and of the calculations giving rise to the results presented in Table 2 of the manuscript.

Tetrad	Area	Normalized area
rmr	45095,093	0,13575758
rmm	40535,392	0,12203072
mmr	70963,792	0,21363461
mmm	72095,727	0,21704227
mrm	103483,658	0,31153481



$P_r = (2(0.1357))^{1/2}$

$P_r = 0.52$

Figure S 33. Deconvolution of the methine region of the homonuclear-decoupled ^{1}H NMR spectrum of PLA using 2-Li (Table 2, entry 2).

5.4 Yields of isolated polymers

Table S 14. Polymerization of ε-CL by lithium complexes at 25°C including observed conversion and yields of isolated polymers. Modified from Table 1 in main text. Cat = catalyst.

Entry	Cat	$[\varepsilon\text{-CL}]_0/[\text{Cat}]_0$	Conversion [a] (%)	Yield [b] (%)
1	**1-Li**	100	99	77
2	**2-Li**	100	94	80
3	**2-Li$_2$**	100	98	90
4	**3-Li$_3$**	100	98	92

[a] Conversion was determined by ^{1}H NMR of $CDCl_3$ solutions of the polymers formed after the reaction times indicated in Table 1 and according to the description in the Experimental Part of the main text. [b] The yield was determined from gravimetric analysis of the isolated polymer after purification as described in the Experimental Part.

Table S 15. Polymerization of *rac*-LA by lithium complexes at 140°C including yields of isolated polymers. Modified from Table 2 in main text. Cat= catalyst.

Entry	Cat.	$[rac\text{-LA}]_0/[\text{Cat}]_0$	Conversion [a] (%)	Yield[b] (%)
1	**1-Li**	100	93	92
2	**2-Li**	100	95	89
3	**2-Li$_2$**	100	97	90
4	**3-Li$_3$**	100	98	95

[a] Conversion was determined by ^{1}H NMR of $CDCl_3$ solutions of the polymers formed after the reaction times indicated in Table 2 and according to the description in the Experimental Part of the main text. [b] The yield was determined from gravimetric analysis of the isolated polymer after purification as described in the Experimental Part.