Direct Lateral Metallation using Alkali-Metal Mediated Zincation (AMM*Zn*): SiC-H vs Si-O Bond Cleavage

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General: All reactions were performed under a protective argon atmosphere using standard Schlenk techniques. Hexane, THF and toluene were dried by heating to reflux over sodium benzophenone ketyl and distilled under nitrogen prior to use.. $^{t}Bu_2Zn$[1] was prepared according to literature methods. NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer, operating at 400.13 MHz for ^{1}H 150.32 MHz for ^{7}Li and 100.62 MHz for ^{13}C. Satisfactory elemental analysis of compounds **3** and **4** could not be obtained due to their highly air and moisture sensitive nature.

X-ray crystallography

Single-crystal diffraction data were recorded at 150 K on Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation (λ= 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares against F^2 using SHELXTL. Crystal data for **3**: $C_{26}H_{48}LiNO_2SiZn$, M_r = 507.05, triclinic, space group P $\bar{1}$, a = 11.2813(5), b= 11.3700(6), c= 13.0987(6) Å, α = 79.264(4), β = 79.106(4), γ = 61.575(5)°, V = 1441.91(12) Å^3, Z = 2, λ = 0.71073 Å, μ = 0.913 mm^{-1}, T = 123 K; 20418 reflections, 7908 unique, R_{int} 0.0326; final refinement to convergence on F^2 gave R = 0.0314 (F, 6081 obs. data only) and R_w = 0.0725 (F^2, all data), GOF = 0.967. Crystal data for **4**: $C_{31}H_{54}LiNO_2Si_2Zn$, M_r = 601.23, monoclinic, space group $P2_1/c$, a = 12.4930(3), b= 12.8910(3), c= 20.8841(5) Å, β = 92.494(2)°, V = 3360.14(14) Å^3, Z = 4, λ = 0.71073 Å, μ = 0.828 mm^{-1}, T = 123 K; 55721 reflections, 9627 unique, R_{int} 0.04263; final refinement to convergence

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

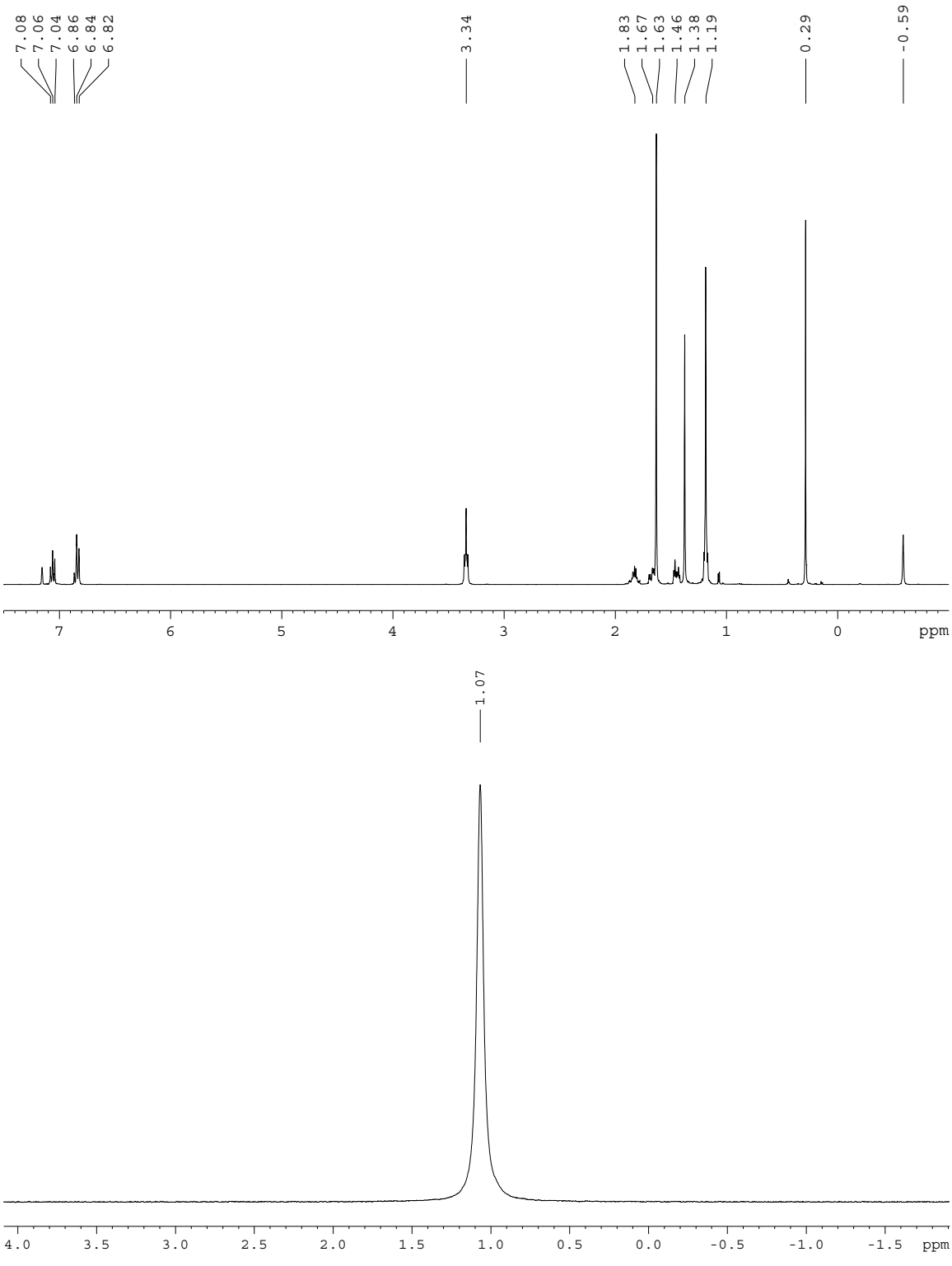
on F^2 gave R = 0.0352 (F, 7223 obs. data only) and R_w = 0.0742 (F^2, all data), GOF = 0.997. CCDC reference numbers ??????. See http://www.rsc.org/suppdata/cc????????? for crystallographic data in CIF or other electronic format.

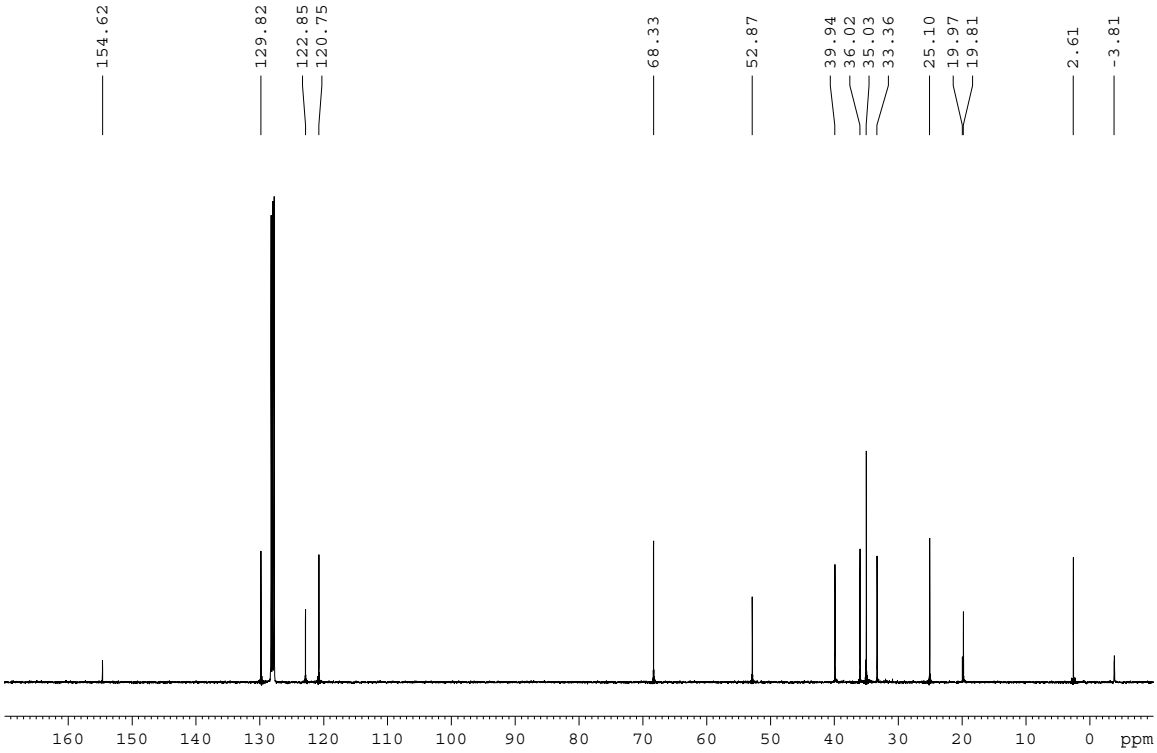
Synthesis of [(THF)Li(TMP)Zn($C_6H_5OSi(CH_2)Me_2$)^{t}Bu]. To a solution of hexane (10ml) and TMPH (0.34ml, 2mmol) was added ^{n}BuLi (1.6M in hexane, 1.25ml, 2mmol), and the resulting colourless solution was stirred for 1 hour at room temperature. A solution of ^{t}Bu$_2$Zn (0.36g, 2mmol in 10ml of hexane) was added via canula, followed by THF (0.18ml, 2mmol) to give a colourless solution. Phenoxy(trimethylsialne) was then added (0.36ml, 2mmol) and after stirring for 1 hour the solution was concentrated in vacuo, then placed in the freezer (-30^{o}C) for 4 days. Large colourless crystals were isolated (0.518g, yield 52%). ^{1}H NMR (400.13 MHz, 298K, C_6D_6) δ 7.06 (2H, t, H_{meta}), 6.86 (1H, t, H_{para}), 6.83 (2H, d, H_{ortho}), 3.34 (4H, m, OCH_2, THF), 1.83 (2H, m, H_γ, TMP), 1.68 (2H, m, H_β, TMP), 1.63 (9H, s, CH_3, ^{t}Bu), 1.45 (2H, m, H_β, TMP), 1.38 (6H, s, α-CH_3, TMP), 1.19 (6H, s, α-CH_3, TMP), 1.19 (4H, m, CH_2, THF), 0.29 (6H, s, OSi(CH_3)$_2$), -0.59 (2H, s, OSiCH_2). ^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6) δ 154.6 (C_{ipso}), 129.8 (C_{ortho}), 122.8 (C_{para}), 120.7 (C_{meta}), 68.3 (OCH_2, THF), 52.8 (C_α, TMP), 39.9 (C_β, TMP), 36.1 (α-CH_3, TMP), 35.0 (CH_3, ^{t}Bu), 33.3 (α-CH_3, TMP), 25.0 (CH_2, THF), 20.0 ($C(CH_3)_3$, ^{t}Bu), 19.8 (C_γ, TMP), 2.6 (OSi(CH_3)$_2$), -3.9 (OSiCH_2). ^{7}Li NMR (298K, d^8-THF, reference LiCl in D_2O at 0.00 ppm): δ 1.07.

Synthesis of [($C_6H_5OSiMe_3$)Li(TMP)Zn($C_6H_5OSi(CH_2)Me_2$)^{t}Bu]. To a solution of hexane (10ml) and TMPH (0.34ml, 2mmol) was added ^{n}BuLi (1.6M in hexane, 1.25ml, 2mmol), and the resulting colourless solution was stirred for 1 hour at room temperature. A solution of ^{t}Bu$_2$Zn (0.36g, 2mmol in 10ml of hexane) was added via canula, followed by Phenoxy(trimethylsialne) (0.36ml, 2mmol) and after stirring for 1 hour the solution was concentrated in vacuo, then placed in the freezer (-30^{o}C) for 7 days. A batch of large colourless crystals were isolated (0.194g, yield 16%). ^{1}H NMR (400.13 MHz, 298K, C_6D_6) δ 7.10 (2H, t, H_{meta} (co-ord.)), 7.03 (2H, t, H_{meta}, (met.)), 6.89-6.84 (4H, m, H_{para} (met. & co-ord.) & H_{ortho} (co-ord.)), 6.76 (2H, d, H_{ortho}(met.)), 1.72 (2H, m, H_γ, TMP), 1.60 (2H, m, H_β, TMP), 1.53 (9H, s, CH_3, ^{t}Bu), 1.48 (2H, m, H_β, TMP), 1.25 (6H, s, α-CH_3, TMP), 1.04 (6H, s, α-CH_3, TMP), 0.22 (6H, s,

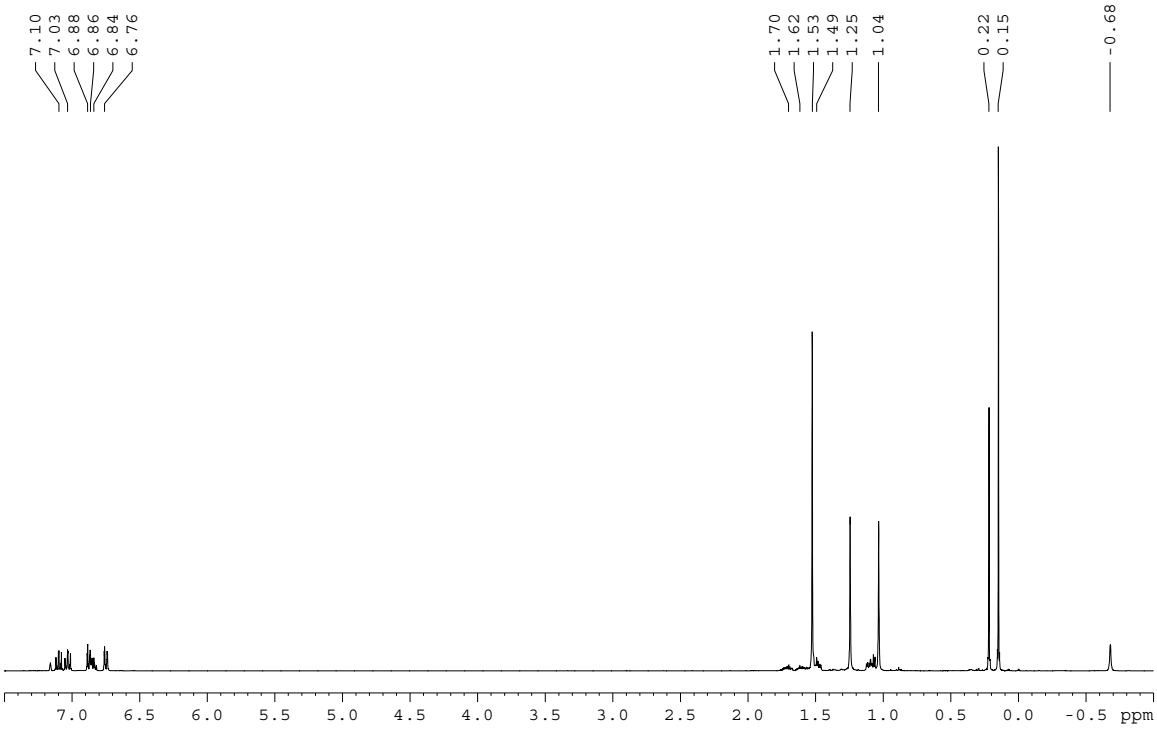
OSi(CH_3)$_2$), 0.15 (9H, s, OSi(CH_3)$_3$), -0.68 (2H, s, OSiCH_2). ^{13}C{^{1}H} NMR (100.62 MHz, 298K, C_6D_6) δ 155.7 (C_{ipso} (co-ord.)), 153.7 (C_{ipso} (met.)), 130.2 (C_{ortho} (met.)), 129.8 (C_{ortho} (co-ord.)), 123.5 (C_{para} (met.)), 121.8 (C_{para} (co-ord.)), 120.4 (C_{meta} (co-ord.)), 119.9 (C_{meta} (met.)), 52.7 ($C_α$, TMP), 40.6 (α-CH$_3$, TMP), 35.8 (α-CH$_3$, TMP), 34.2 (CH$_3$, ^{t}Bu), 34.1 ($C_β$, TMP), 20.6 (C(CH$_3$)$_3$, ^{t}Bu), 19.5 ($C_γ$, TMP), 2.2 (OSi(CH$_3$)$_2$), 0.2 (OSi(CH$_3$)$_3$), -4.2 (OSiCH$_2$). ^{7}Li NMR (298K, d^8-THF, reference LiCl in D_2O at 0.00 ppm): δ 1.89.

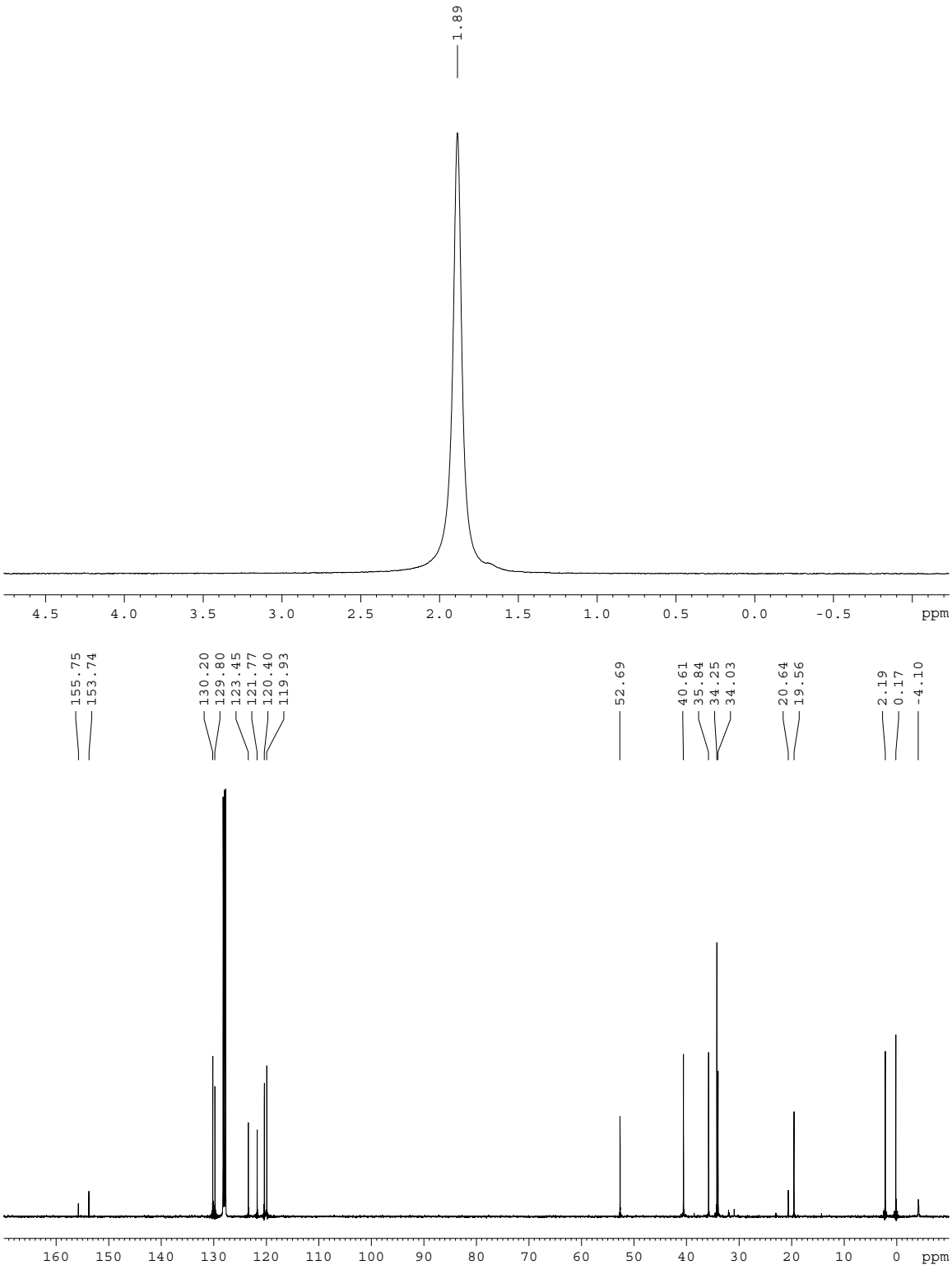
[(THF)Li(TMP)($C_6H_5OSiMe_2CH_2$)Zn^{t}Bu] (3)





$[(C_6H_5OSiMe_3)Li(TMP)(C_6H_5OSiMe_2CH_2)Zn^tBu]$ (4)

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120
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100
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80
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50
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30
20
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0
ppm

[$C_6H_5OLi(THF)$]