Supporting Information for

Homoleptic Tris(*α,ω*-alkanediyl)yttriates of the Type [{Li(dme)}$_3${Y(CH$_2$-X-CH$_2$)$_3$}] (X = C_2H_4, C_3H_6, $Si(CH_3)_2$)

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Table of Contents

NMR Spectra

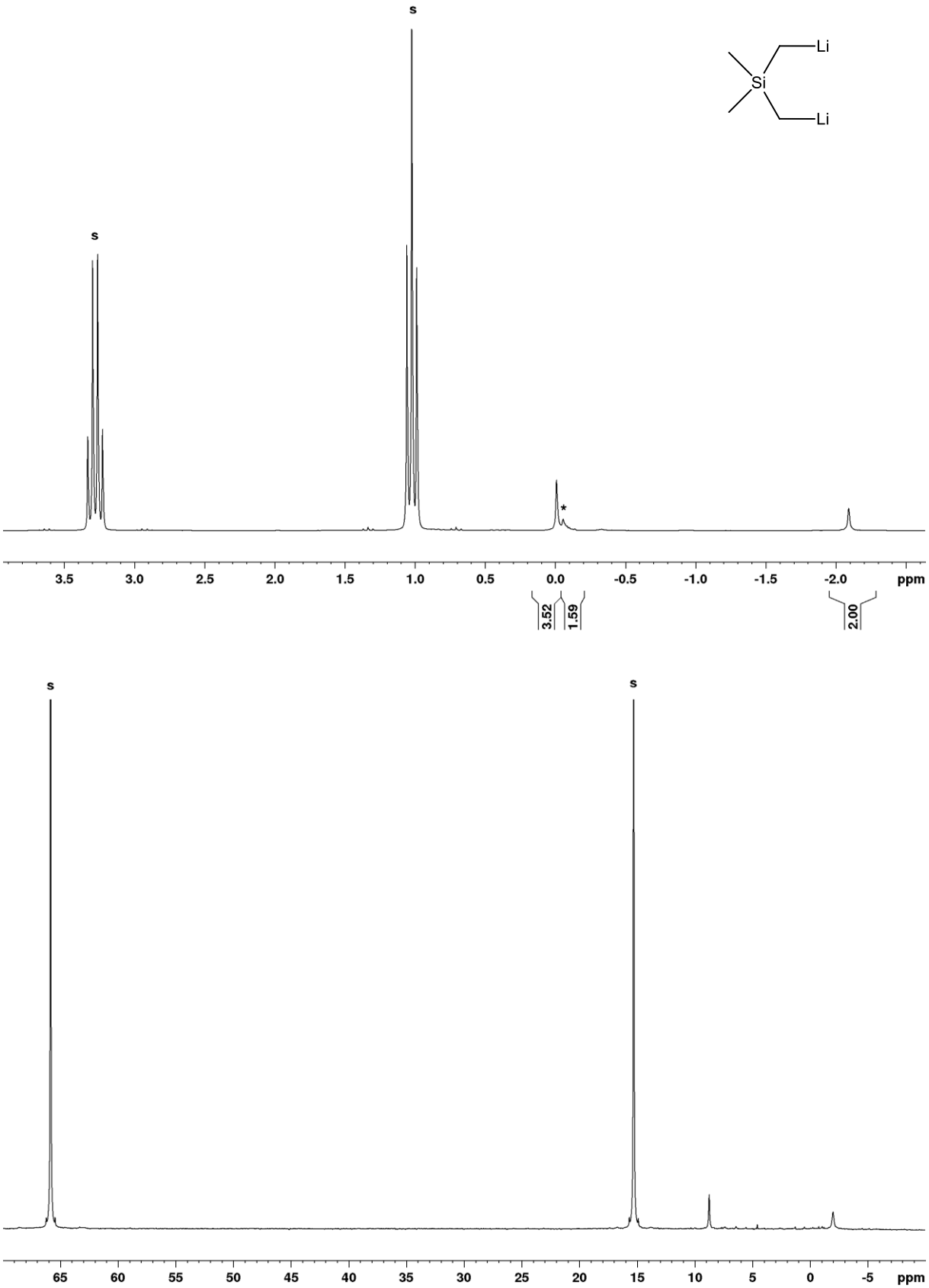

Figure S1. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of $[(Et_2O)_4\{(LiCH_2)_2Si(CH_3)_2\}_3(LiCl)]_2$ (**1**), measured at 200 MHz, and at 50.3 MHz, respectively, in benzene-d_6/diethyl ether (1:3) at 25 °C (* = degradation products; s = diethyl ether).

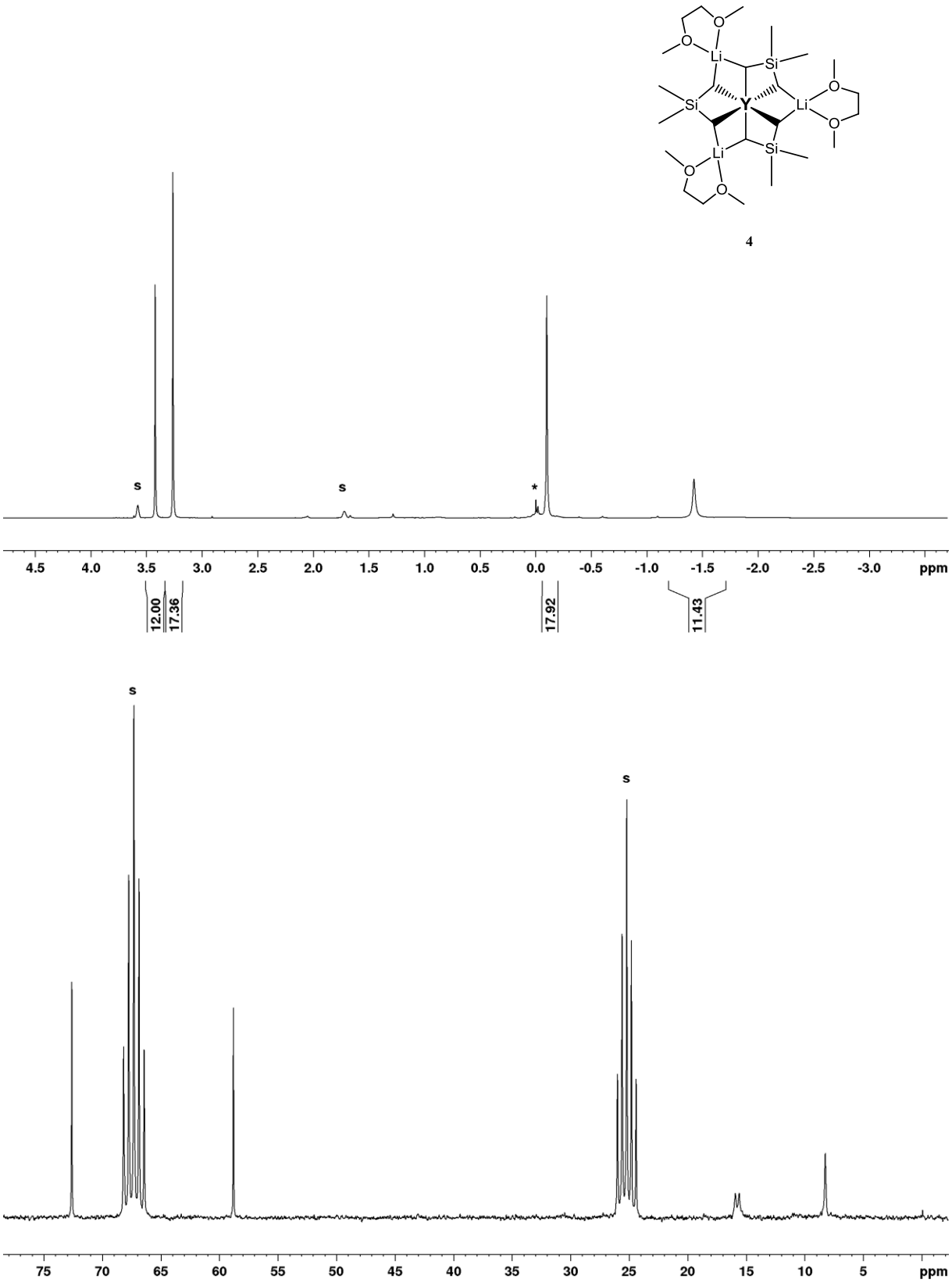

Figure S2. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of [{Li(dme)}$_3$(Y{$CH_2Si(CH_3)_2CH_2$}$_3$)] (**4**), measured at 200 MHz, and at 50.3 MHz, respectively, in THF-d_8 at 25 °C (* = degradation products; s = (residual) signal of THF-d_8).

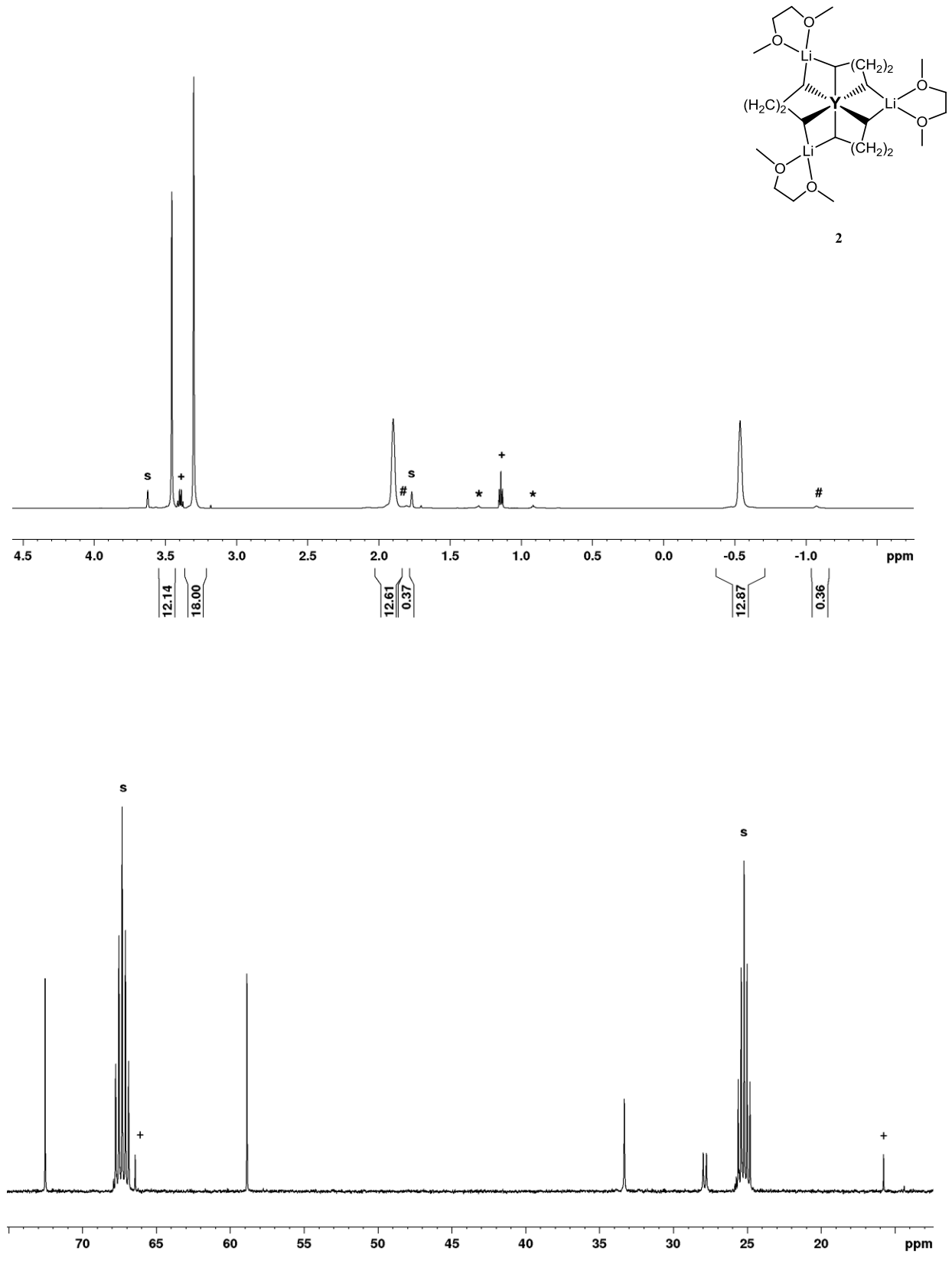

Figure S3. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of [{Li(dme)}$_3${Y(C_4H_8)$_3$}] (**2**), measured at 400 MHz, and at 100.6 MHz, respectively, in THF-d_8 at -40 °C (+ = diethyl ether; * = *n*-butane, # = dissociation product probably 1,4-dilithiobutane; s= (residual) signal of THF-d_8).

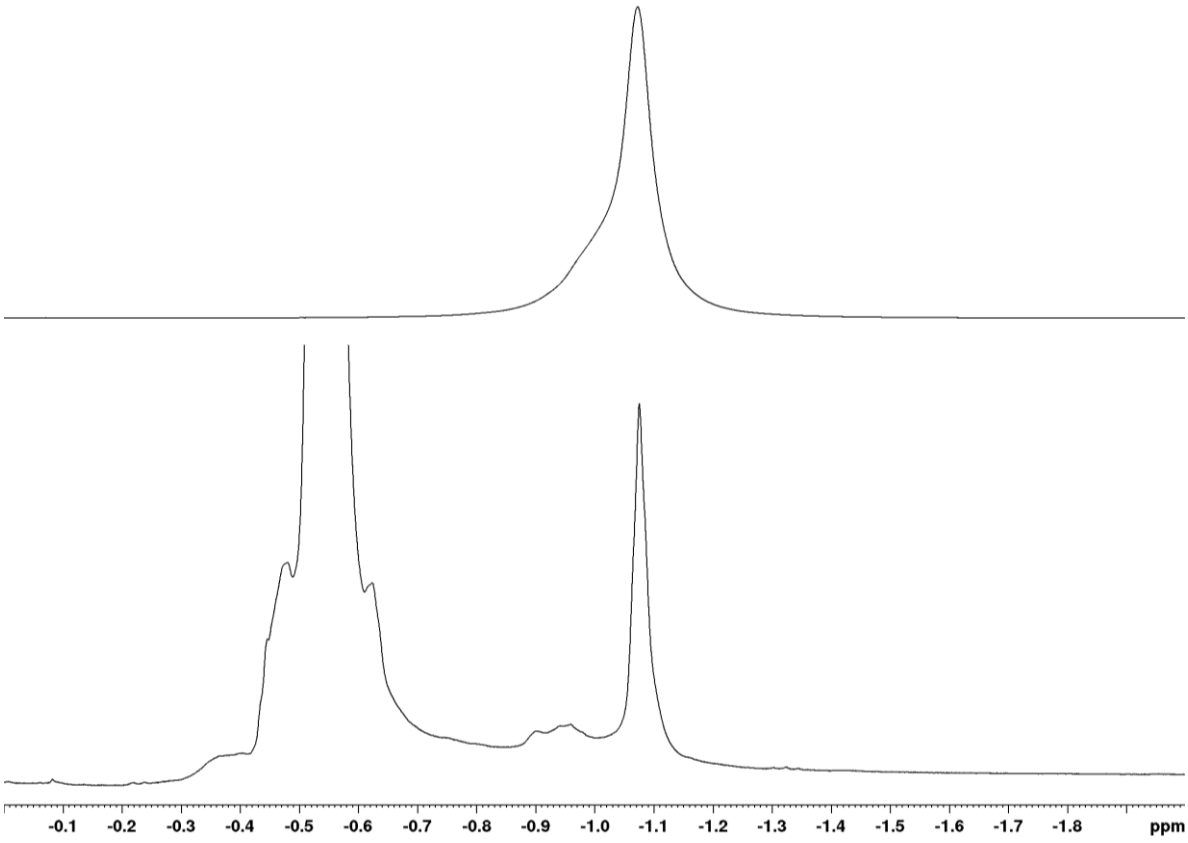

Figure S4. Part of the ^{1}H NMR of [{Li(dme)}$_3${Y(C_4H_8)$_3$}] (**2**) (bottom) and 1,4-dilithiobutane (top), measured at 400 MHz, in THF-d_8 at -40 °C.

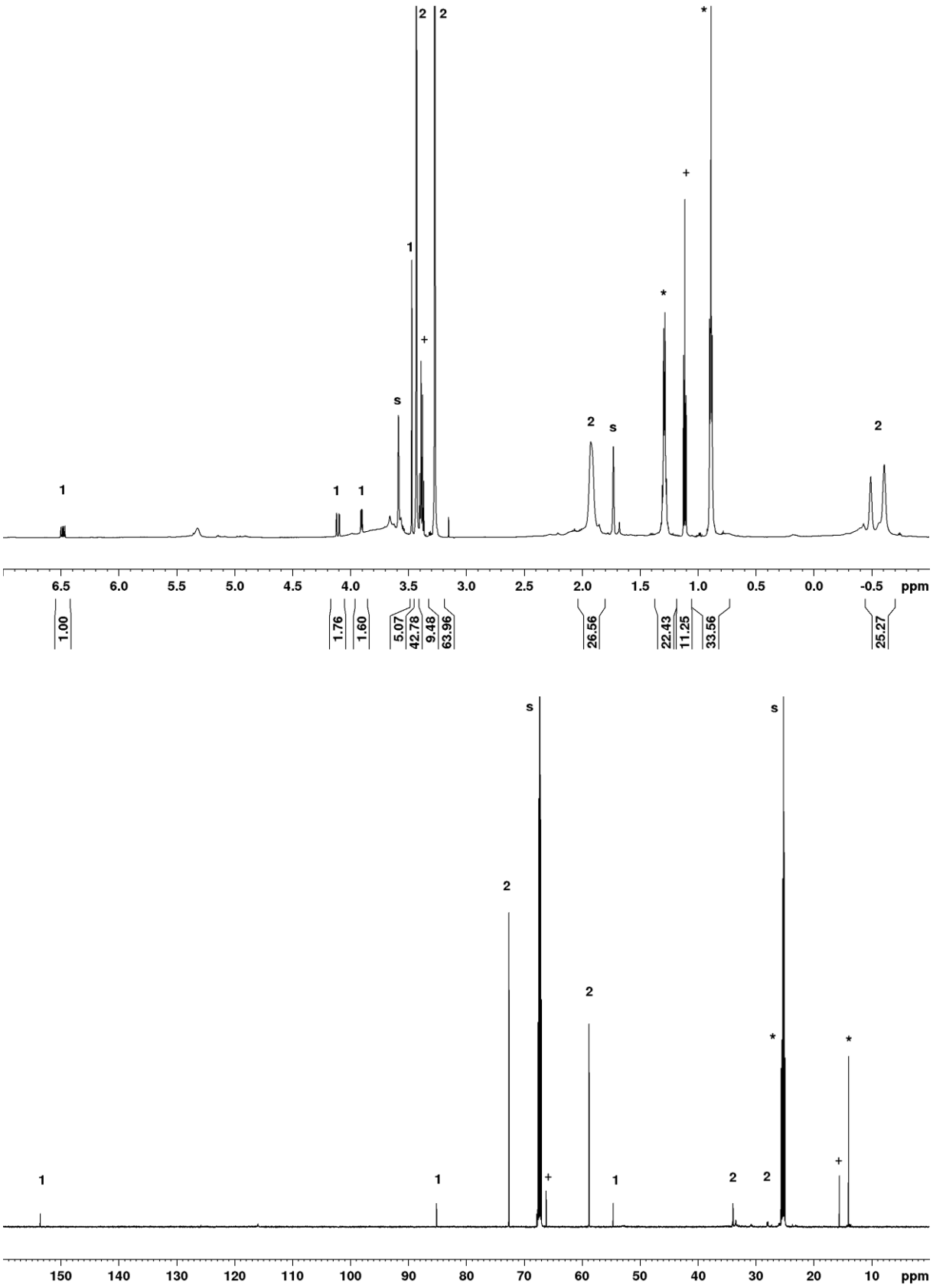

Figure S5. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of degradation of [{Li(dme)}$_3${Y(C_4H_8)$_3$}] (**2**), measured at 600 MHz, and at 150.9 MHz, respectively, in THF-d_8, after storing 24 h at 25 °C (1 = methyl vinyl ether; 2 = residual organoyttrium species; + = diethyl ether; * = *n*-butane; s = (residual) signal of THF-d_8).

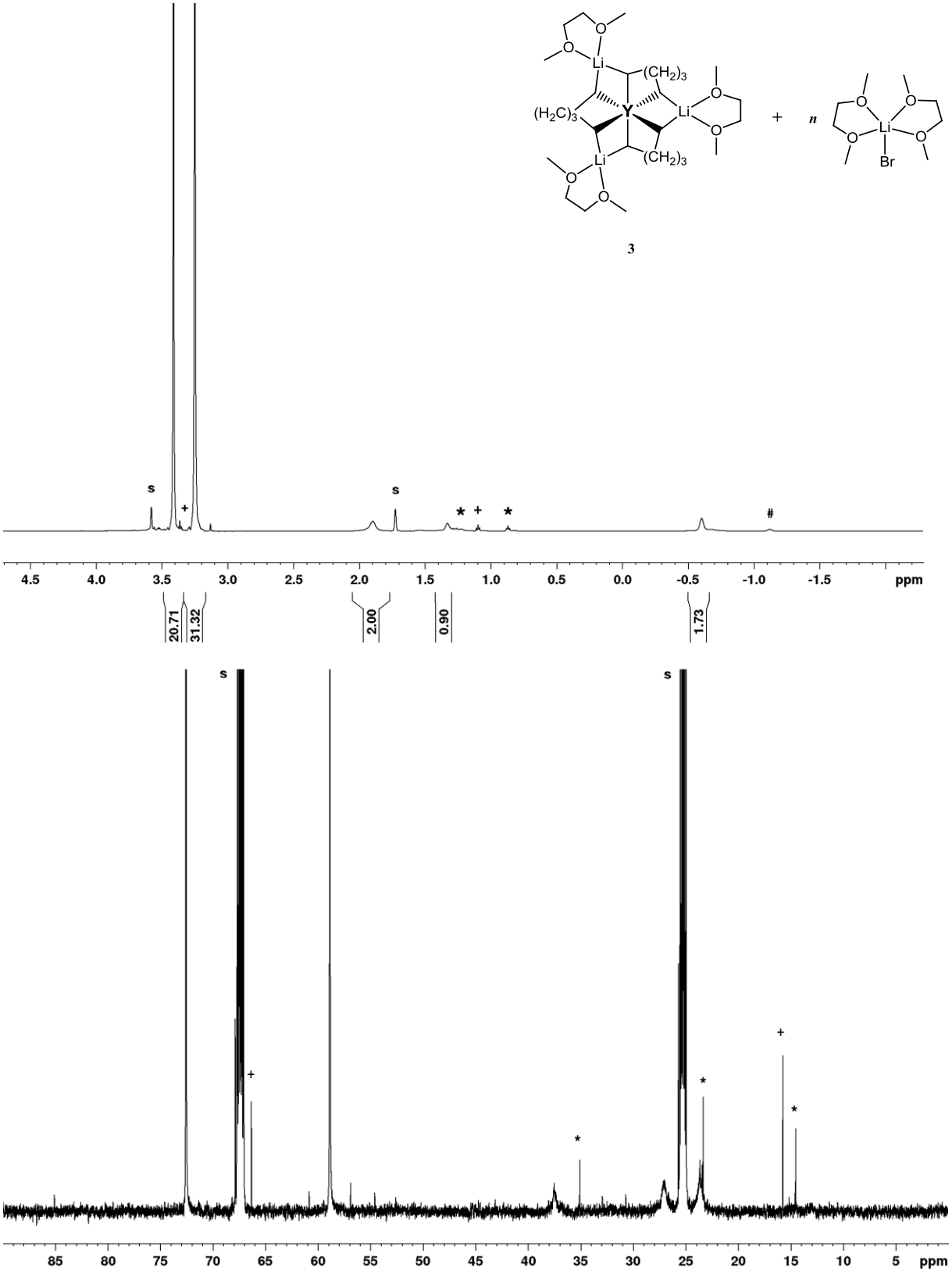

Figure S6. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of [{Li(dme)}$_3${Y(C_5H_{10})$_3$}] (**3**), measured at 600 MHz, and at 150.9 MHz, respectively, in THF-d_8 at -20 °C (+ = diethyl ether; * = *n*-pentane; # = dissociation product; s = (residual) signal of THF-d_8).

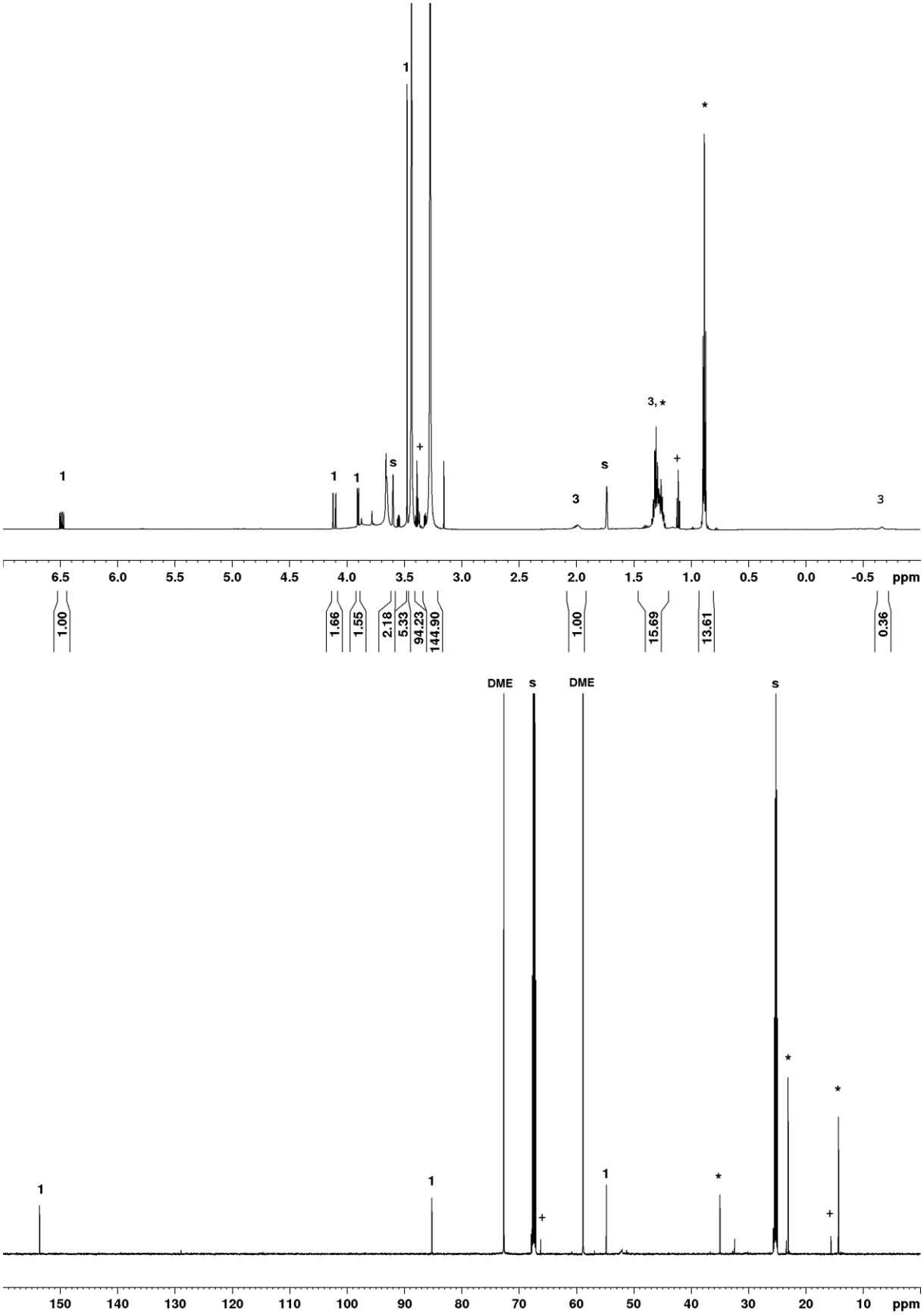

Figure S7. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of degradation of [{Li(dme)}$_3${Y(C_5H_{10})$_3$}] (**3**), measured at 600 MHz, and at 150.9 MHz, respectively, in THF-d_8, after storing 24 h at 25 °C (1 = methyl vinyl ether; 3 = residual organoyttrium species; + = diethyl ether; * = *n*-pentane; s = (residual) signal of THF-d_8).

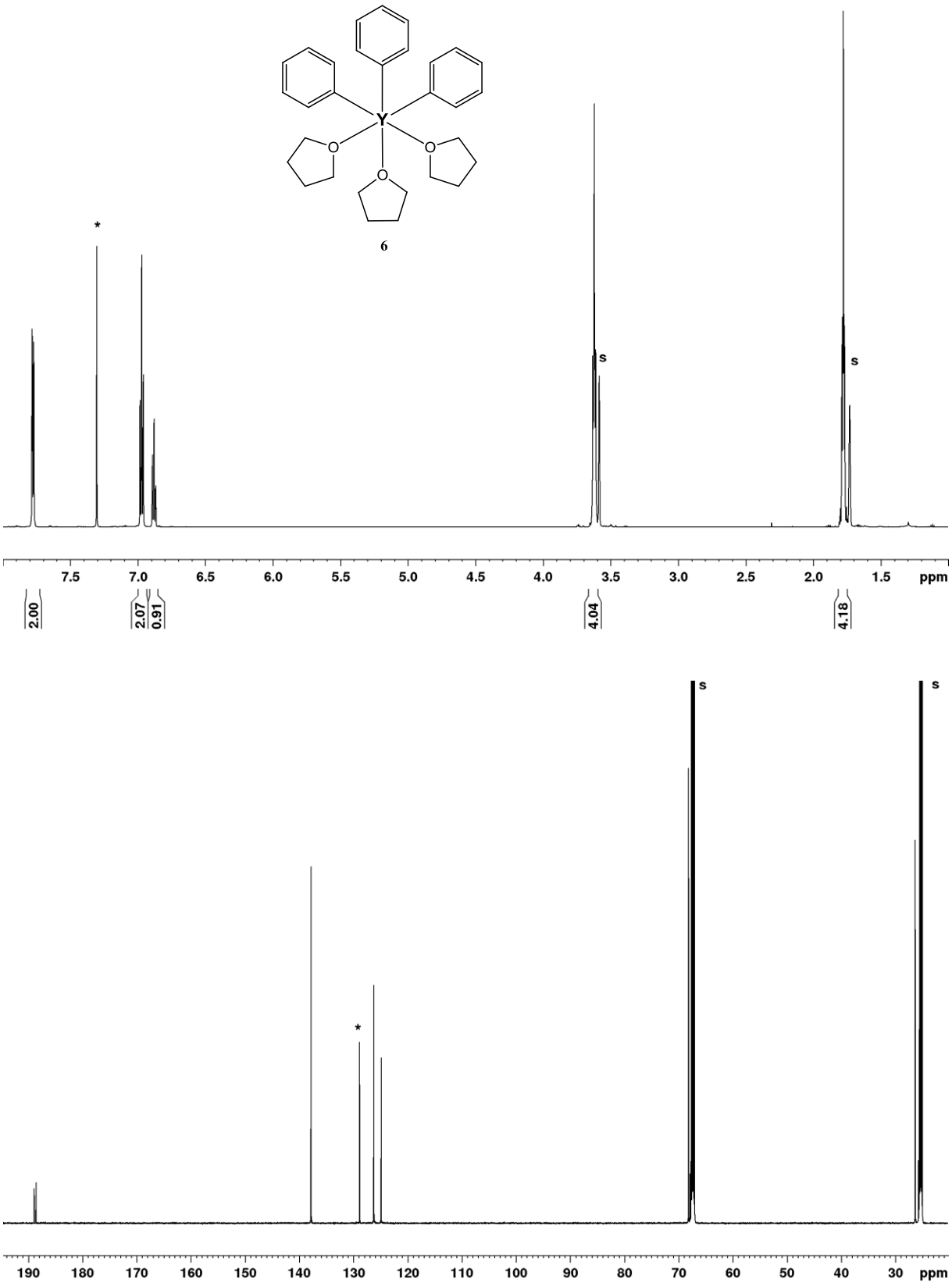

Figure S8. ^{1}H NMR (top) and ^{13}C{^{1}H} spectrum (bottom) of $[Ph_3Y(thf)_3]_n$ (**6**), measured at 600 MHz, and at 150.9 MHz, respectively, in THF-d_8 at 25 °C (* = benzene; s = (residual) signal of THF-d_8).

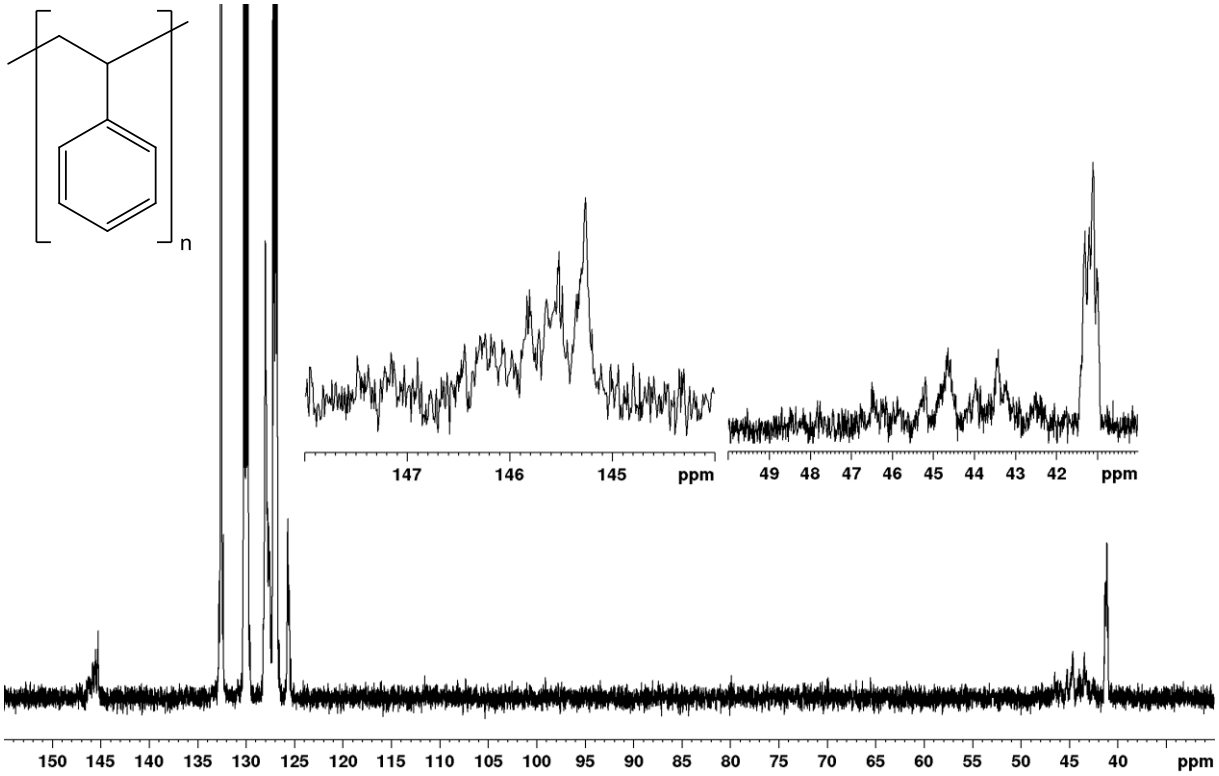

Figure S9. $^{13}C\{^{1}H\}$ spectrum of polystyrene **P1**, measured at 150.9 MHz in *o*-dichlorobenzene-d_4 at 110 °C.

Styrene polymerization

Table S1: Summary of selected polymerization results initiated by lithium compounds.

Entry	Initiator	Time (min)	M/I	c(styrene) (mol/L)	M_n (g/mol)	M_w (g/mol)	PDI
1	*n*-butyllithium	15	100	0.4	29,200	51,800	1.77
2		60	100	0.4	26,400	50,000	1.87
3		120	100	0.4	29,200	51,600	1.76
4	1,4-dilithio-butane	15	100	0.4	113,000	184,000	1.64
5		60	100	0.4	125,000	197,000	1.57
6		120	100	0.4	126,000	196,000	1.56

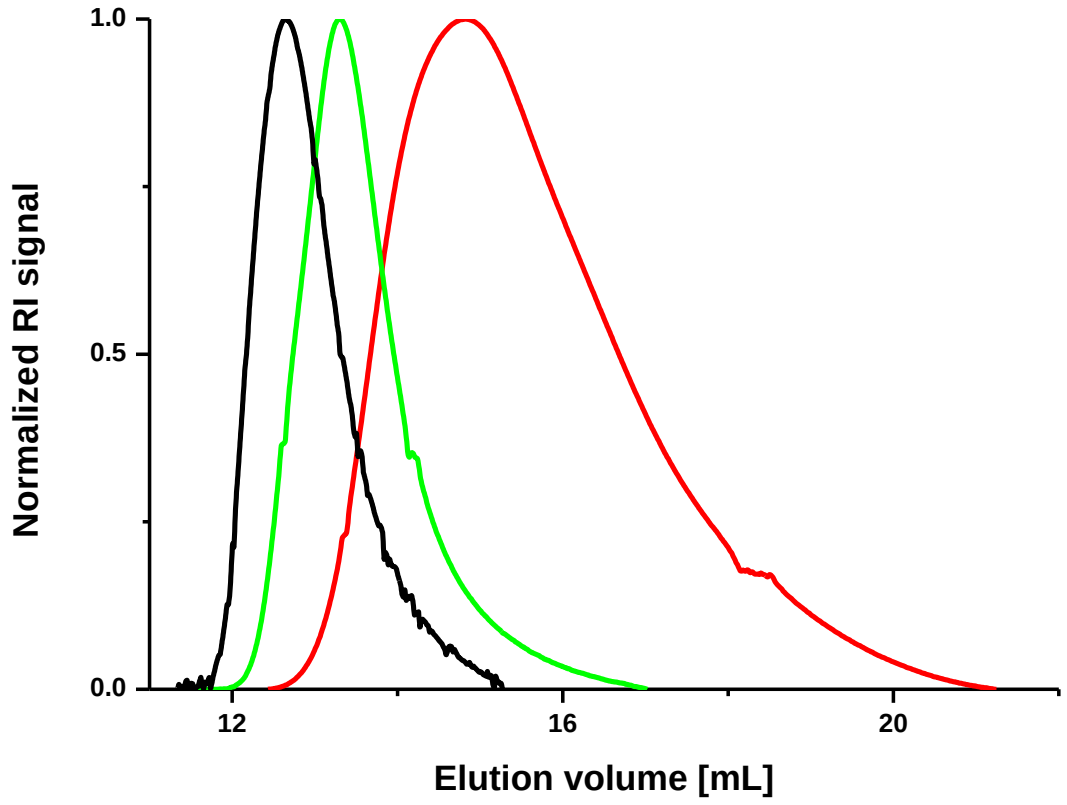

Figure S10. SEC curves of the polymers: **P1** (black line), **P2** (red line) and **P3** (green line); size exclusion chromatography measurements were performed on Agilent 1200 series setup.

Analytical data of prepared polymers

Polystyrene **P1:** Yield: 241 mg (96.0 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.19; H, 7.73. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 – 1.64 (2H, CH_2), 1.76 – 2.24 (1H, C*H*), 6.34 – 6.82 (2H, CH_{Ar}), 6.89 – 7.20 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 269,000 g/mol; M_w = 395,000 g/mol; PDI = 1.47.

Polystyrene **P4:** Yield: 92 mg (90.2 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.26; H, 7.74. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 – 1.61 (2H, CH_2), 1.73 – 2.24 (1H, C*H*), 6.31 – 6.81 (2H, CH_{Ar}), 6.91 – 7.20 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 79,200 g/mol; M_w = 103,000 g/mol; PDI = 1.44.

Polystyrene **P5:** Yield: 93 mg (91.2 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.26; H, 7.74. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.28 – 1.65 (2H, CH_2), 1.73 – 2.23 (1H, C*H*), 6.32 – 6.82 (2H, CH_{Ar}), 6.90 – 7.23 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 51,300 g/mol; M_w = 63,300 g/mol; PDI = 1.23.

Polystyrene **P6:** Yield: 244 mg (96.4 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.04; H, 7.76. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.25 – 1.63 (2H, CH_2), 1.70 – 2.23 (1H, C*H*), 6.36 – 6.83 (2H, CH_{Ar}), 6.89 – 7.21 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 354,000 g/mol; M_w = 567,000 g/mol; PDI = 1.60.

Polystyrene **P7:** Yield: 239 mg (96.0 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.21; H, 7.78. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.24 – 1.68 (2H, CH_2), 1.75 – 2.26 (1H, C*H*), 6.34 – 6.83 (2H, CH_{Ar}), 6.90 – 7.20 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 232,000 g/mol; M_w = 335,000 g/mol; PDI = 1.44.

Styrene polymerization initiated by n-butyllithium:

Polystyrene **P2:** Yield: 920 mg (92.0 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.63; H, 7.78. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.18 – 2.15 (3H, C*H* and CH_2), 6.39 – 6.50 (2H, CH_{Ar}), 6.80 – 7.18 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 22,600 g/mol; M_w = 47,300 g/mol; PDI = 2.09.

Styrene polymerization initiated by 1,4-dilithiobutane:

Polystyrene **P3:** Yield: 920 mg (92.0 %). Elemental analysis (based on the repeating unit: C_8H_8, 104.15): calcd.: C, 92.26; H, 7.74; found: C, 92.56; H, 7.88. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 – 2.16 (3H, C*H* and CH_2), 6.25 – 6.51 (2H, CH_{Ar}), 6.88 – 7.17 (3H, CH_{Ar}). SEC (DMAc, PS-standard): M_n = 114,000 g/mol; M_w = 184,000 g/mol; PDI = 1.61.