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Supplementary Information for

Triamidoamine-Supported Zirconium: Hydrogen Activation, Lewis Acidity, and *rac*-Lactide Polymerization

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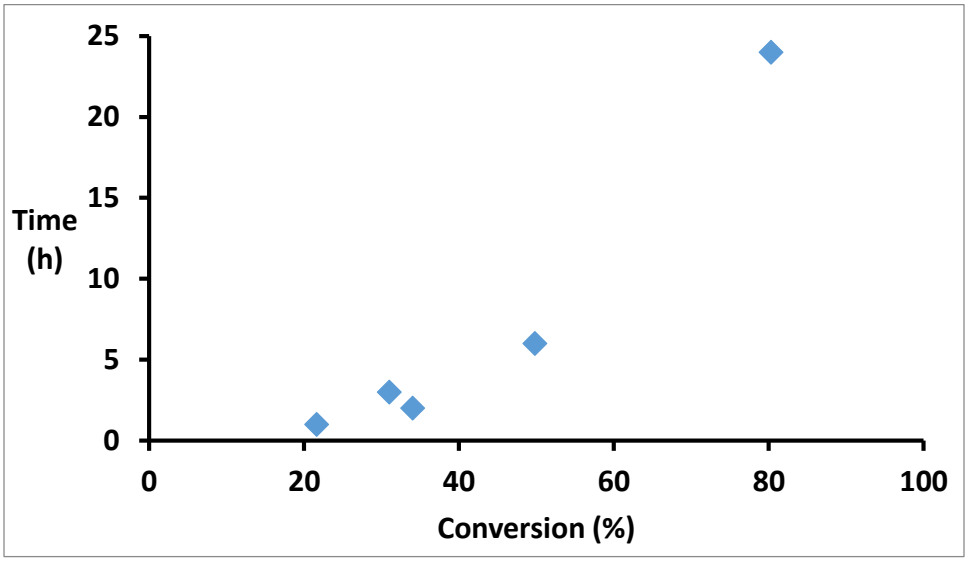

Figure S1. Plot of time vs. conversion for polymerization of 100 equiv *rac*-LA using **1** as initiator. $[LA]_0$ = 0.5 M, toluene, T = 70 ºC.

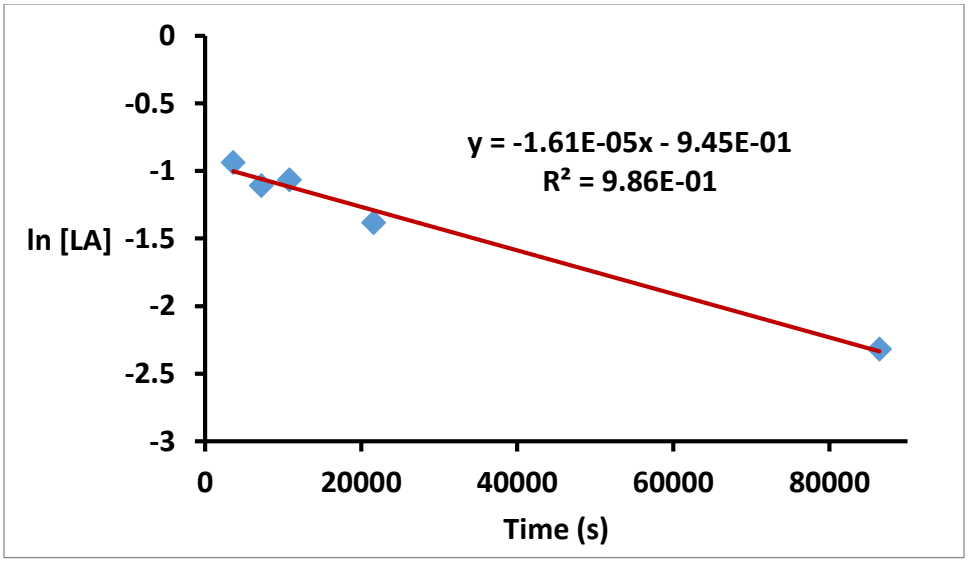

Figure S2. Plot of ln[LA] versus time for polymerization of 100 equiv *rac*-LA using **1** as initiator. $[LA]_0$ = 0.5 M, toluene, T = 70 ºC.

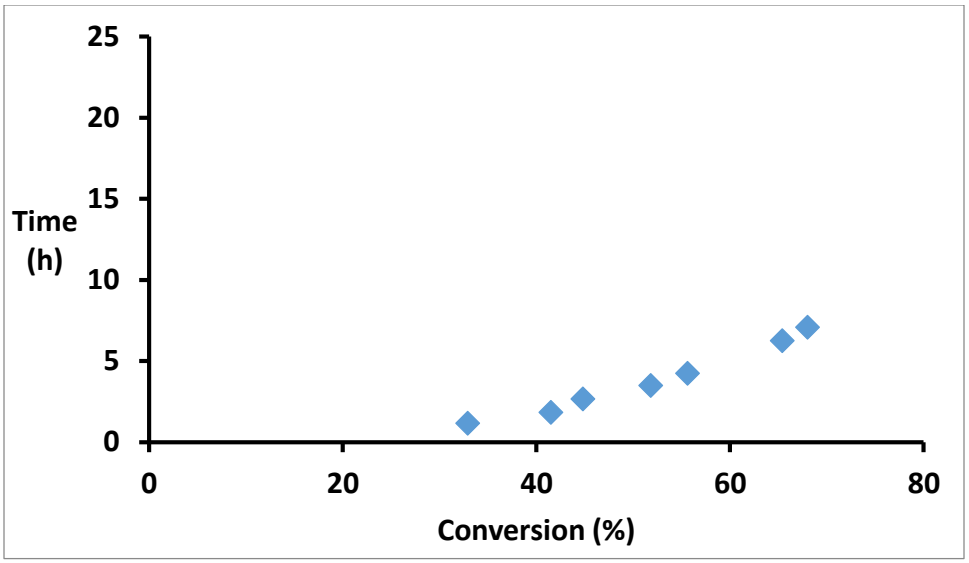

Figure S3. Plot of time vs. conversion for polymerization of 25 equiv *rac*-LA using **1** as initiator. $[LA]_0$ = 0.5 M, toluene, T = 70 ºC.

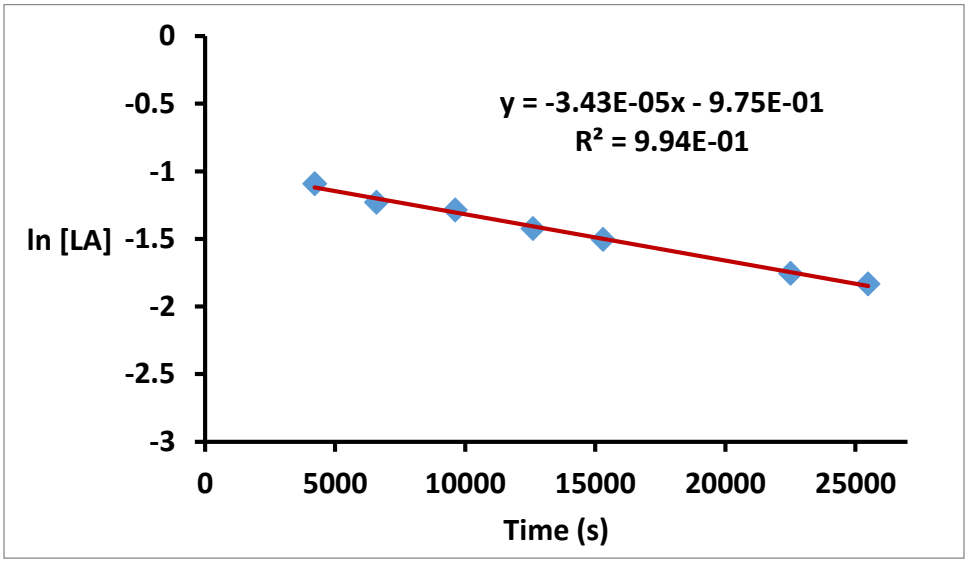

Figure S4. Plot of ln[LA] versus time for polymerization of 25 equiv *rac*-LA using **1** as initiator. $[LA]_0$ = 0.5 M, toluene, T = 70 ºC.

Table S1. Conversion data for PLA samples prepared using different concentrations of **1** as initiator.[a]

$[LA]_0$/[**Cat**]	[Cat]	Time (h)	Conv. (%)
25	0.020	1.17	32.9
25	0.020	1.83	41.5
25	0.020	2.67	44.8
25	0.020	3.5	51.8
25	0.020	4.25	55.6
25	0.020	6.25	65.4
25	0.020	7.08	68
100	0.005	1	21.6
100	0.005	2	34
100	0.005	3	31
100	0.005	6	49.8
100	0.005	24	80.3

[a] $[LA]_0$ = 0.5 M, toluene, 70 °C

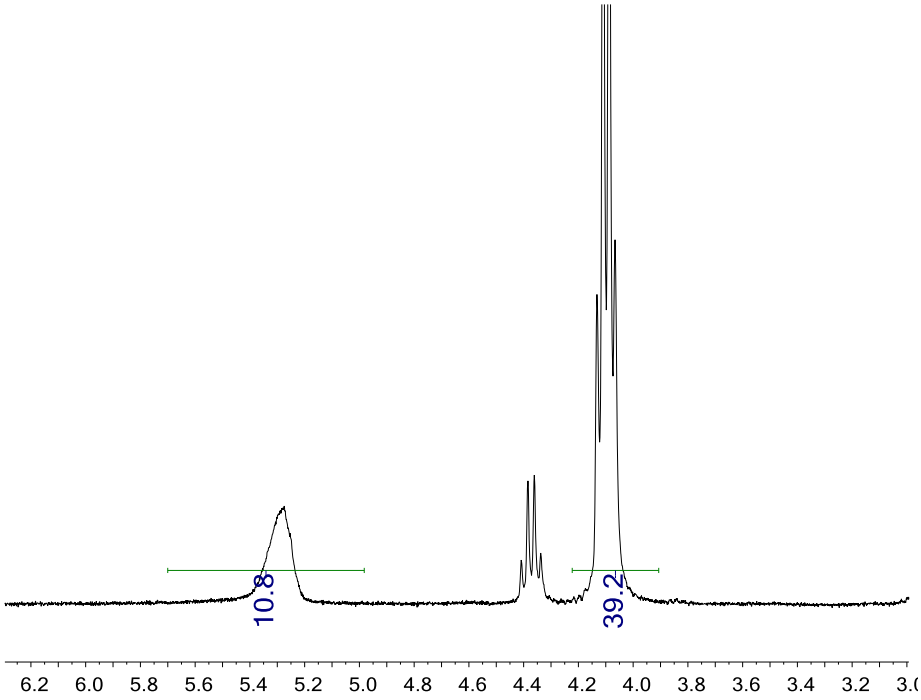

Figure S5. ^{1}H NMR spectrum of the lactide/PLA methine region during lactide polymerization using **1** as initiator ($[LA]_0$/[**1**] = 100, T = 70 ºC, t = 1h, conversion = 21.6%).

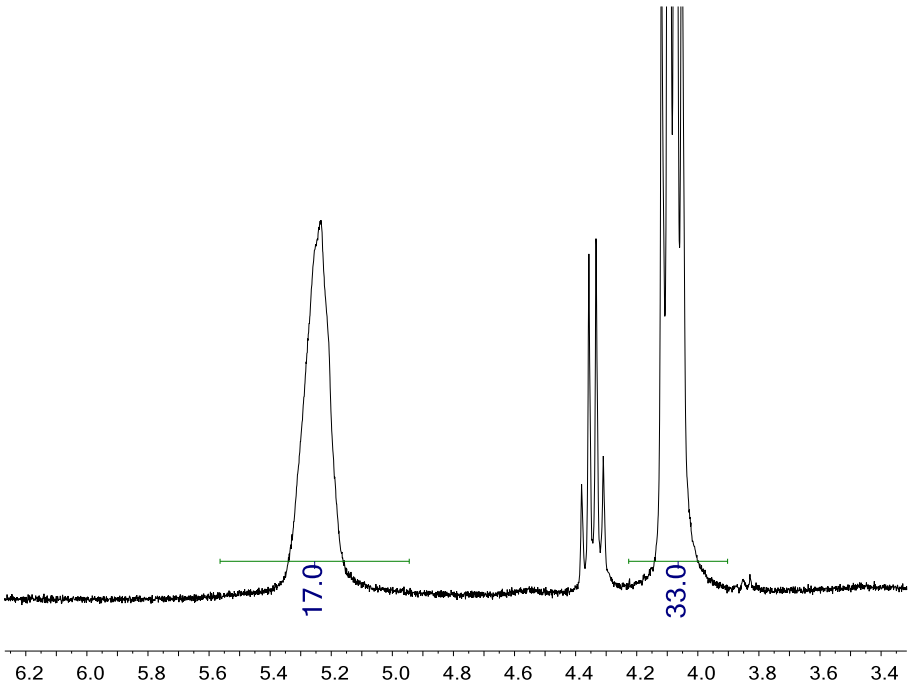

Figure S6. ^{1}H NMR spectrum of the lactide/PLA methine region during lactide polymerization using **1** as initiator ($[LA]_0/[\mathbf{1}] = 100$, T = 70 ºC, t = 2h, conversion = 34%).

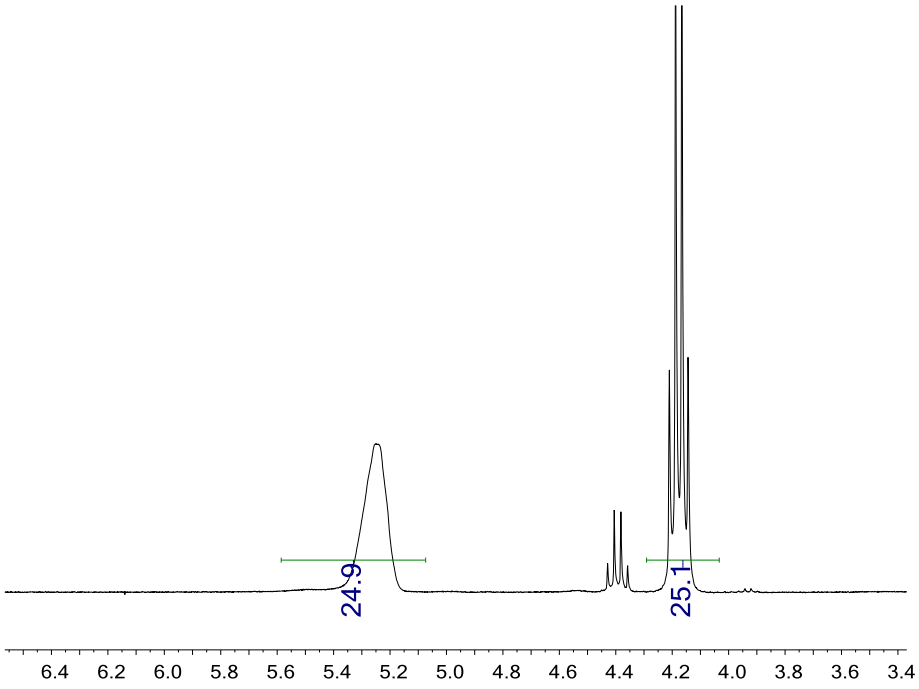

Figure S7. ^{1}H NMR spectrum of the lactide/PLA methine region during lactide polymerization using **1** as initiator ($[LA]_0/[\mathbf{1}] = 100$, T = 70 ºC, t = 6h, conversion = 49.8%).

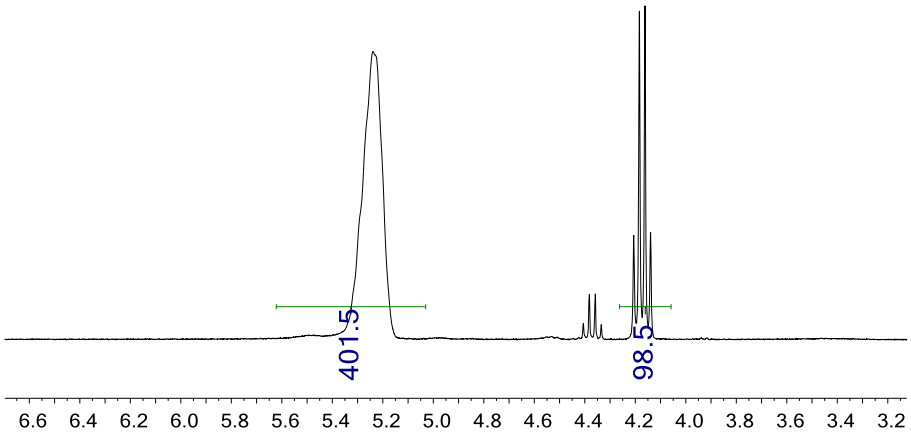

Figure S8. ^{1}H NMR spectrum of the lactide/PLA methine region during lactide polymerization using **1** as initiator ($[LA]_0/[\mathbf{1}] = 100$, T = 70 ºC, t = 24h, conversion = 80.3%).

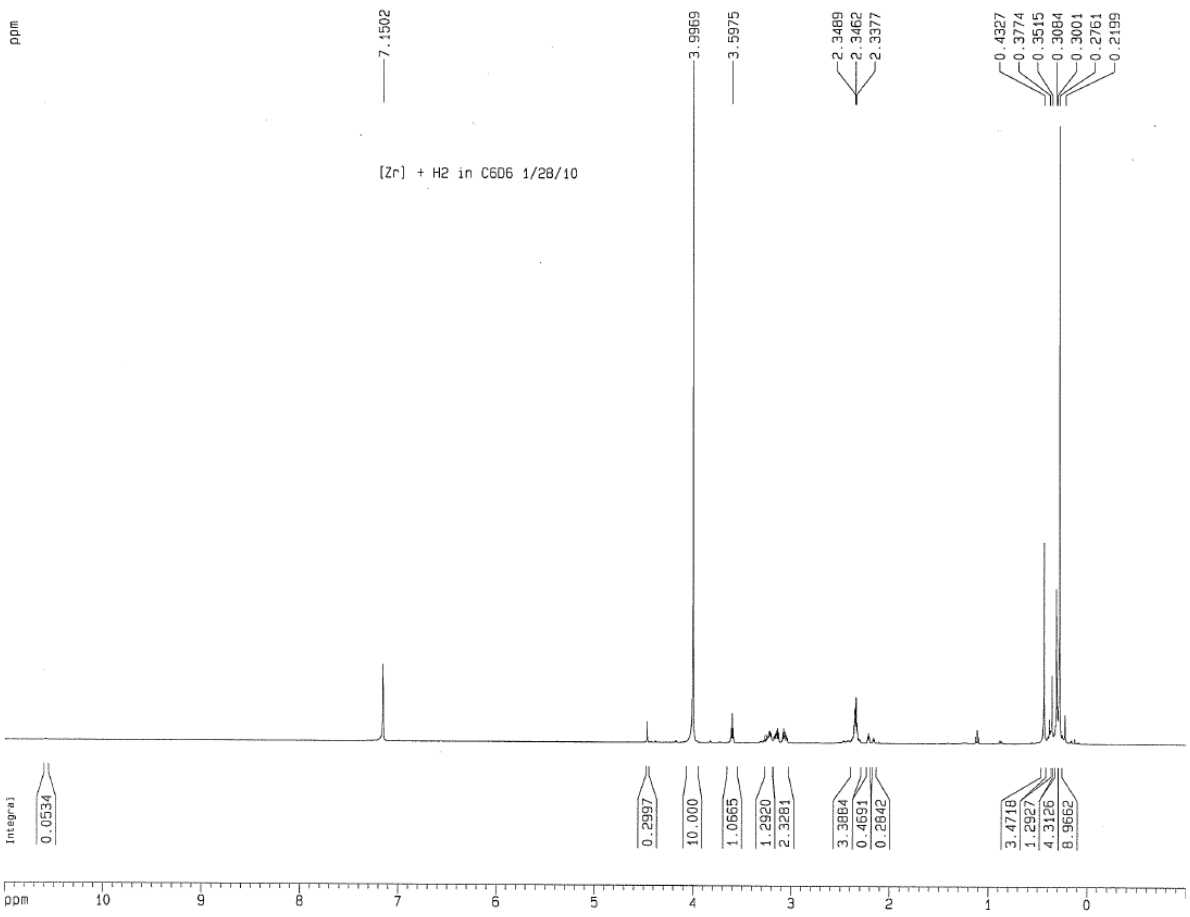

Figure S9. Example ^{1}H NMR spectrum of a benzene-d_6 solution of **1** under H_2 in the presence of ferrocene.

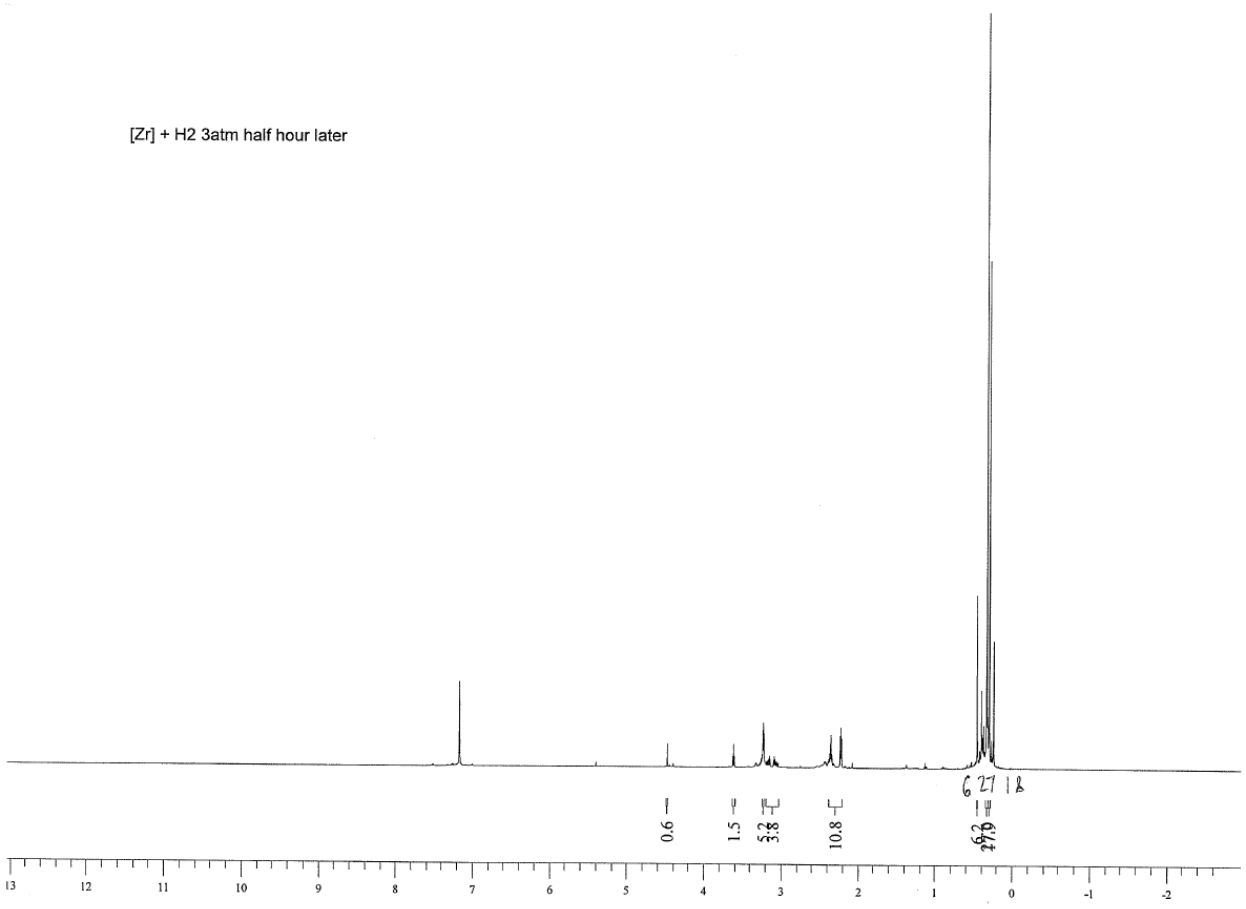

Figure S10. Example ^{1}H NMR spectrum of a benzene-d_6 solution of **1** under H_2 without ferrocene.

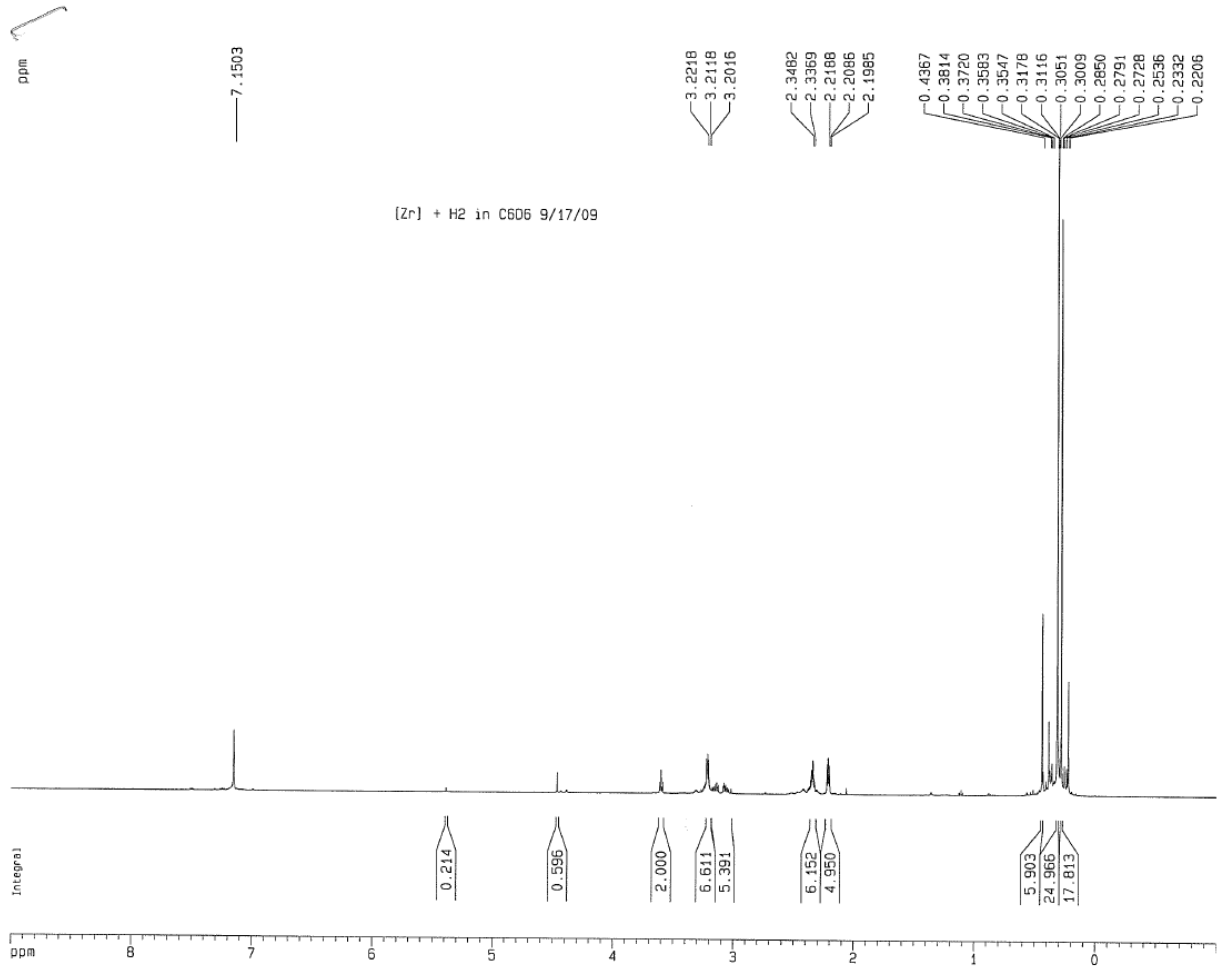

Figure S11. Expanded aromatic and aliphatic region of a ^{1}H NMR spectrum (different from Figure S10) of a benzene-d_6 solution of **1** under H_2 without ferrocene.

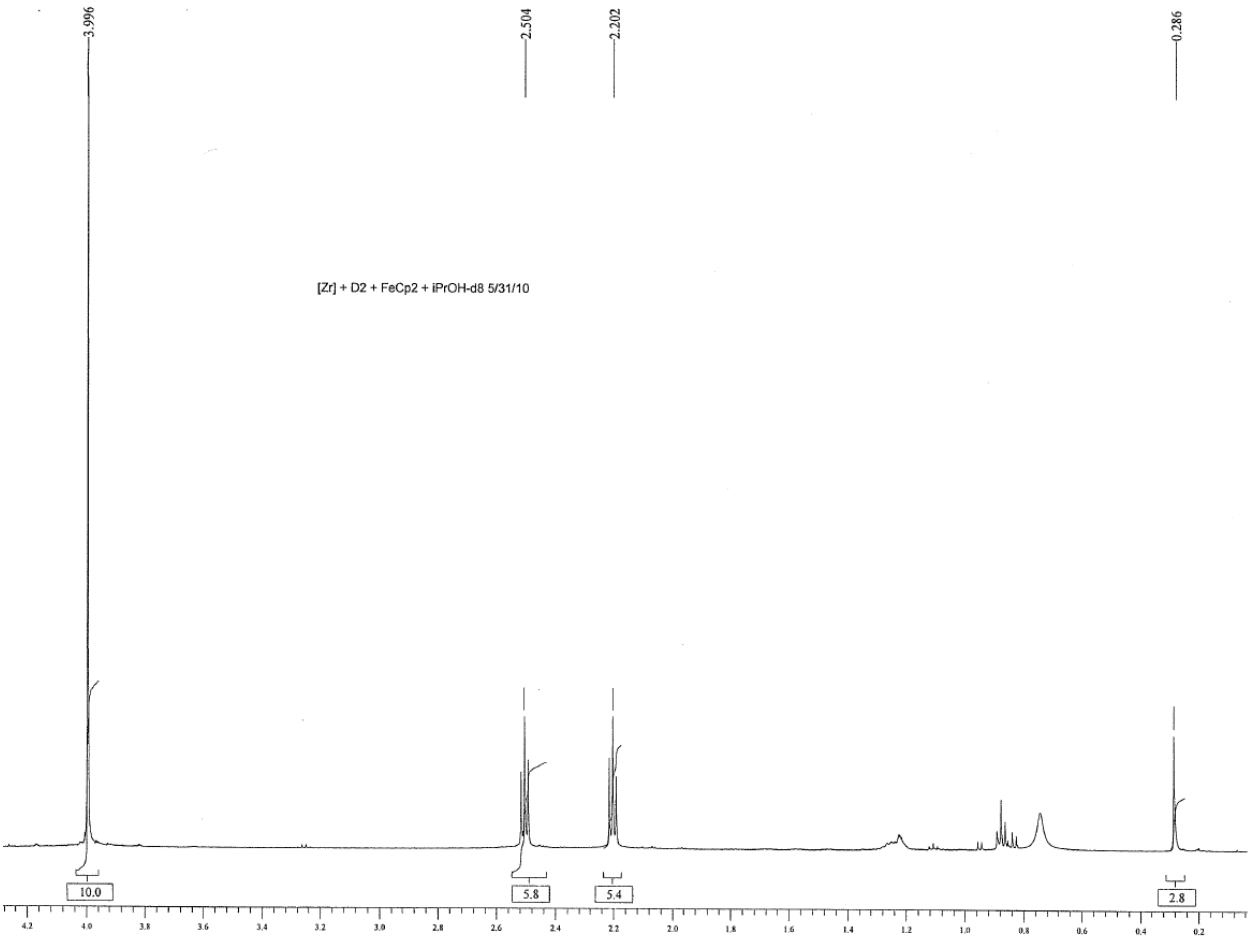

Figure S12. Compound **2** can be a source of $N(CH_2CH_2NHSiMe_3)$-d_n by reaction of **2** with isopropanol. The ^1H NMR spectrum of a benzene-d_6 solution of $N(CH_2CH_2NHSiMe_3)$-d_n includes an internal ferrocene integration standard. This reaction is not reported in the main article text because the purification of product is sufficiently tedious to make isolated yields highly variable.