ESI for:

Unique Reactivity of ε-ketiminopyridine Ligand with Metal-Alkyls. Synthesis and ROP of ε-Caprolactone

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Table S1. Crystallographic data for **1**·(THF)$_2$

Crystal data	
Chemical formula	$C_{28}H_{41}LiN_2O_3$
M_r	460.57
Crystal system, space group	Triclinic, *P*-1
Temperature (K)	150
a, *b*, *c* (Å)	9.217 (1), 10.170 (4), 14.562 (2)
α, β, γ (°)	100.29 (3), 90.202 (13), 91.119 (18)
V (Å^3)	1342.8 (6)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.07
Crystal size (mm)	0.56 × 0.44 × 0.40
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.591, 0.745
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17199, 5186, 4026
R_{int}	0.094
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.067, 0.153, 1.13
No. of reflections	5186
No. of parameters	411
No. of restraints	378
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.24

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Table S2. Crystallographic data for **2**

Crystal data	
Chemical formula	$C_{24}H_{36}N_2OZn$
M_r	433.92
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	150
a, *b*, *c* (Å)	9.3724 (4), 18.9533 (8), 13.5059 (7)
β (°)	96.630 (2)
V (Å^3)	2383.11 (19)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.05
Crystal size (mm)	0.35 × 0.23 × 0.21
Data collection	
Diffractometer	Bruker D8 - Venture
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.392, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40188, 5510, 5003
R_{int}	0.035
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.651
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.035, 0.101, 1.12
No. of reflections	5510
No. of parameters	261
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.41, −0.83

Computer programs: Bruker Instrument Service vV6.2.3, *APEX3* v2016.9-0 (Bruker AXS), *SAINT* V8.37A (Bruker AXS Inc., 2015), XT, VERSION 2014/5, *SHELXL2017*/1 (Sheldrick, 2017), Bruker *SHELXTL*.

Table S3. Crystallographic data for **3**

Crystal data	
Chemical formula	$C_{22}H_{30}N_2OZn$
M_r	403.87
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	11.7931 (13), 11.9320 (6), 16.3490 (14)
β (°)	116.701 (8)
V (Å^3)	2055.2 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.21
Crystal size (mm)	0.43 × 0.19 × 0.16
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.628, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14463, 4650, 3319
R_{int}	0.042
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.097, 1.07
No. of reflections	4650
No. of parameters	241
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.50

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Table S4. Crystallographic data for **4**

Experimental details for **4**

Crystal data	
Chemical formula	$C_{23}H_{35}AlN_2O$
M_r	382.51
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	8.8040 (4), 15.768 (1), 16.0520 (11)
β (°)	93.774 (6)
V (Å^3)	2223.5 (2)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.11
Crystal size (mm)	0.45 × 0.28 × 0.10
Data collection	
Diffractometer	Bruker Nonius KappaCCD area detector
Absorption correction	Multi-scan *SADABS2016*/2 - Bruker AXS area detector scaling and absorption correction
T_{min}, T_{max}	0.695, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26668, 5071, 3694
R_{int}	0.034
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.103, 1.10
No. of reflections	5071
No. of parameters	253
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.23

Computer programs: *COLLECT* (Hooft, 1998) and *DENZO* (Otwinowski & Minor, 1997), *COLLECT* and *DENZO*, *SIR92* (Altomare *et al.*, 1994), *SHELXL2017*/1 (Sheldrick, 2017), *PLATON* (Spek, 2003), *SHELXL97* (Sheldrick, 2008).

Figure S1. ^{1}H NMR spectrum of **1**·(THF)$_2$ in C_6D_6

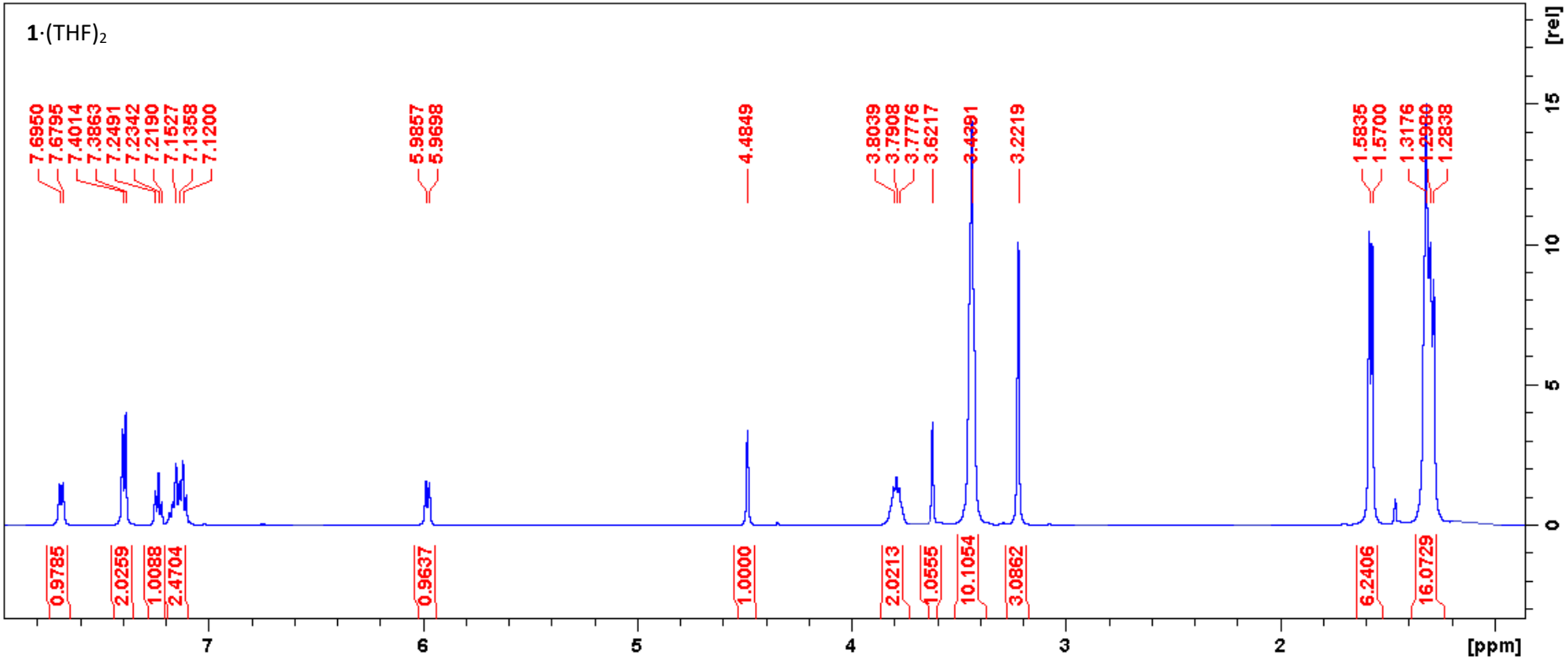


Figure S2. $^{13}C\{^{1}H\}$ APT NMR spectrum of **1**·$(THF)_2$ in C_6D_6

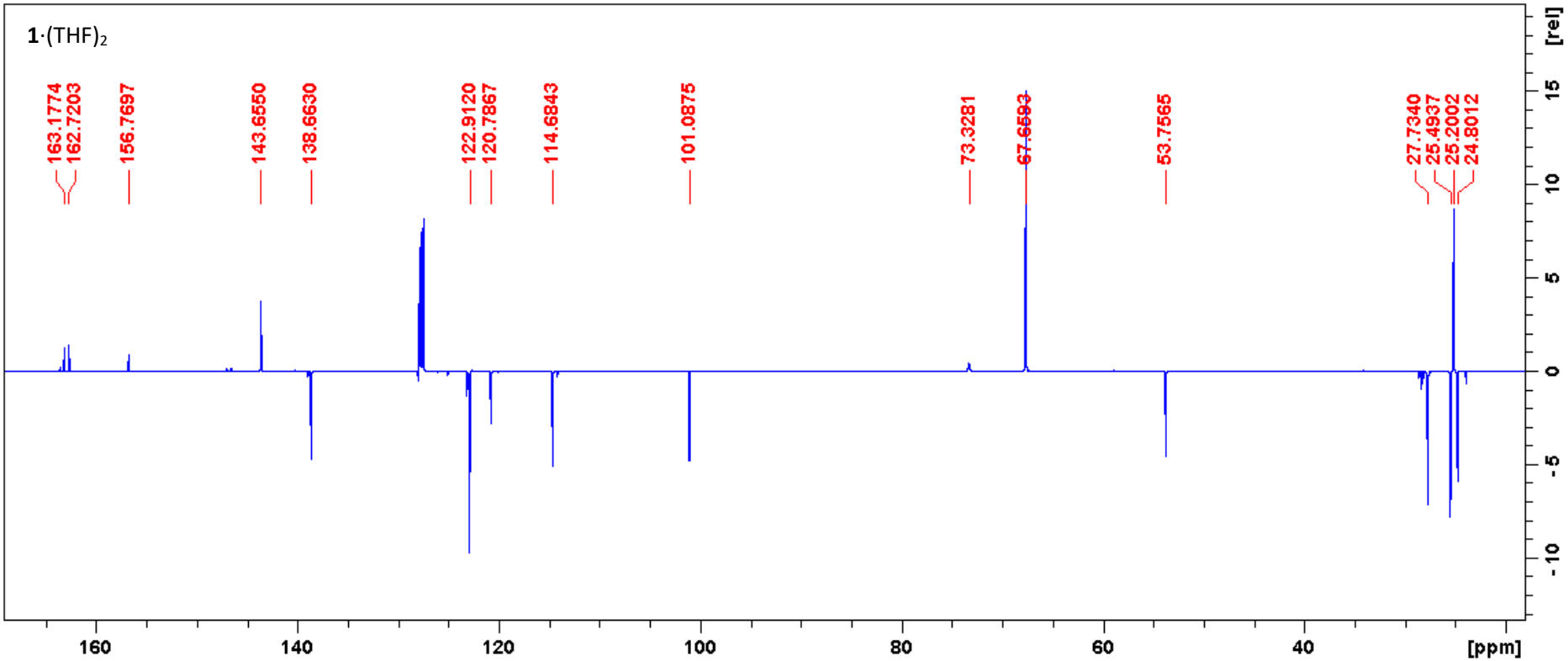


Figure S3. ^{7}Li NMR spectrum of **1**·(THF)$_2$ in C_6D_6

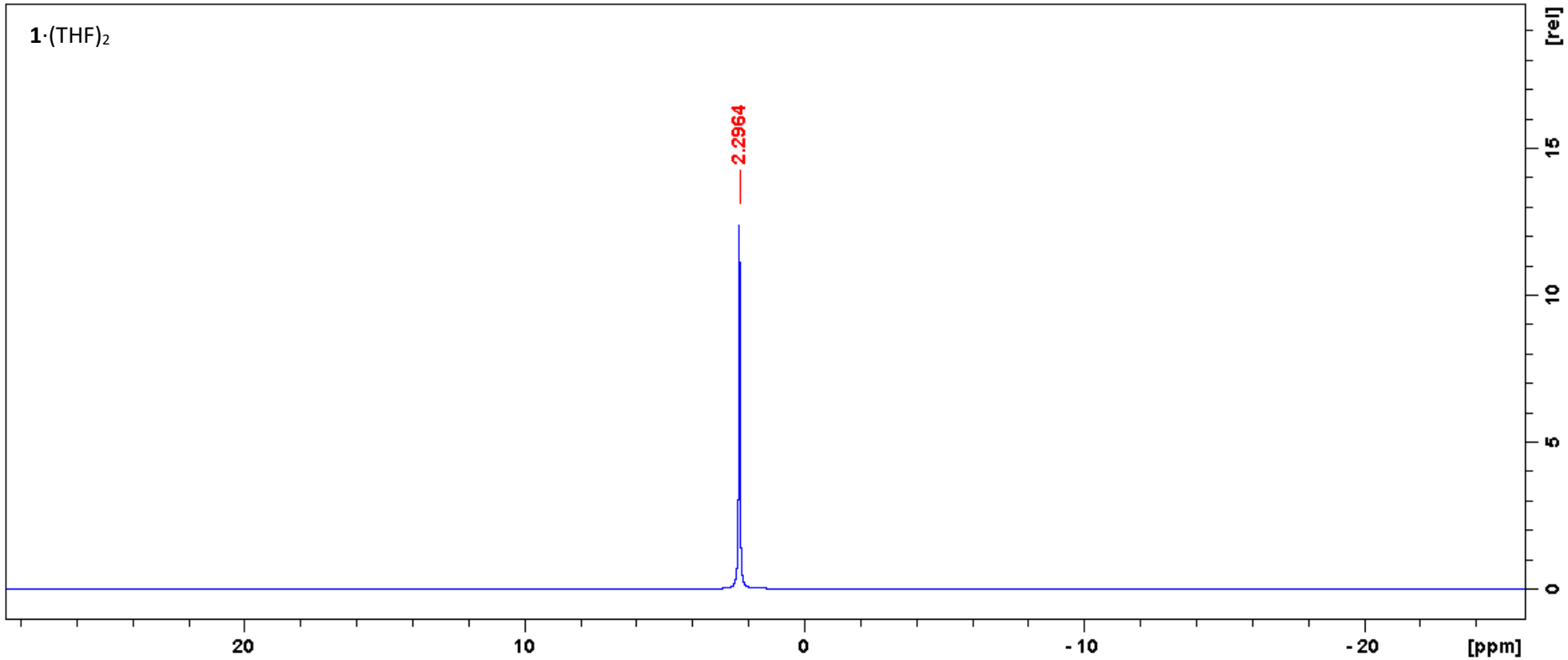
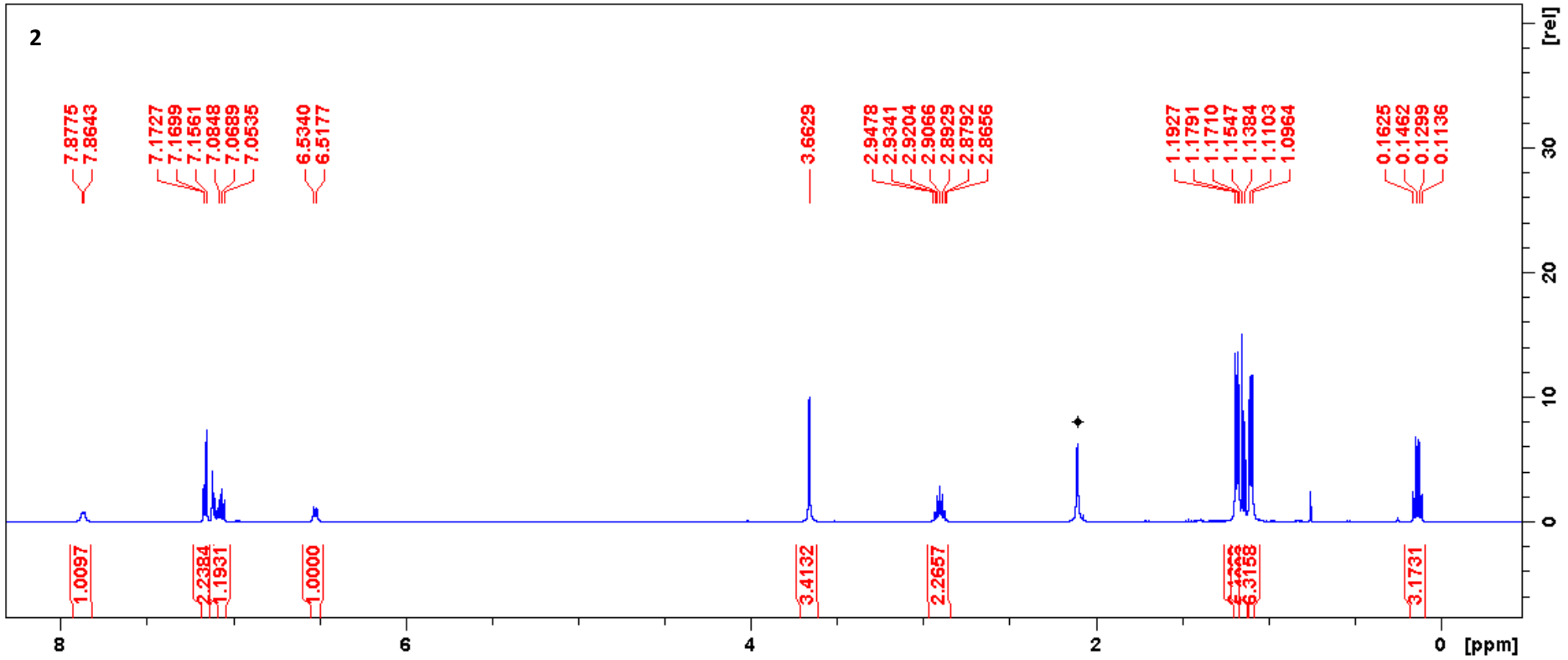


Figure S4. ^{1}H NMR spectrum of **2** in C_6D_6



✦ traces of toluene

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6

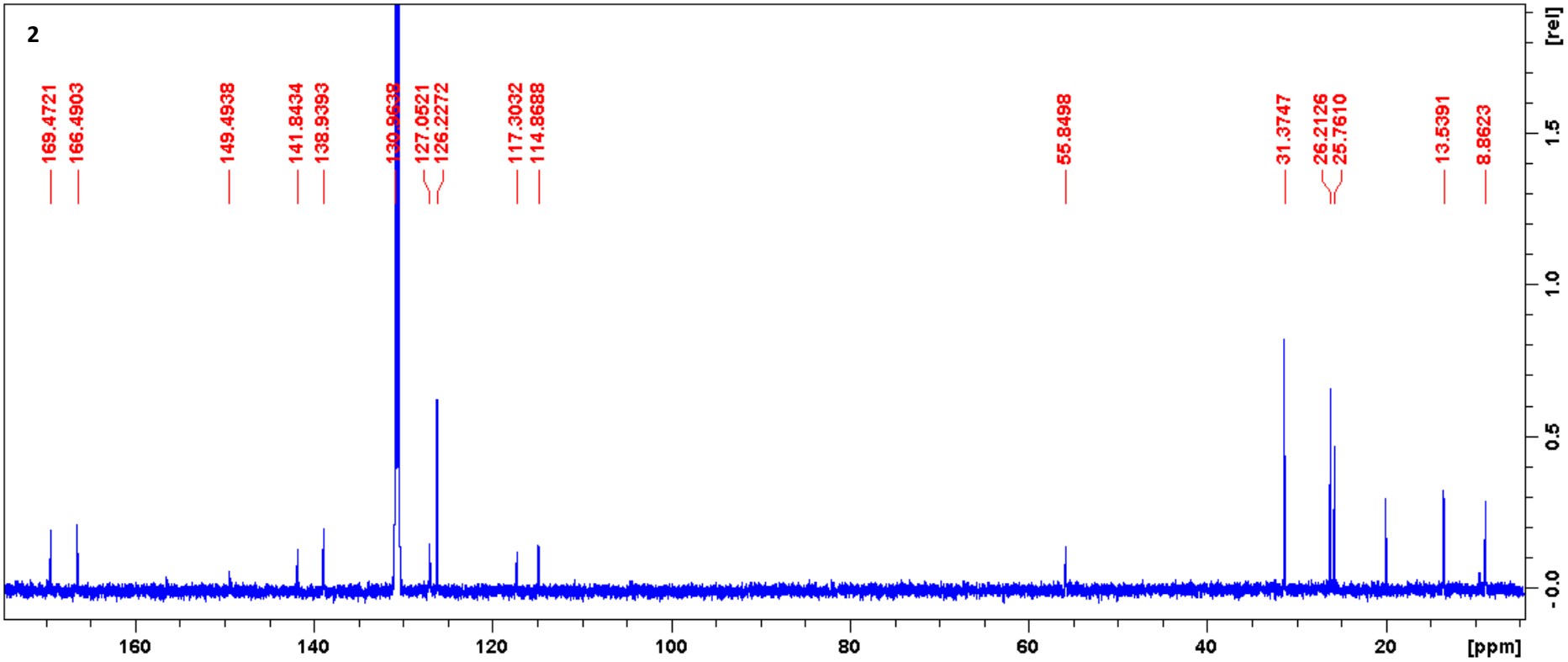


Figure S6. ^{1}H NMR spectrum of **3** in C_6D_6

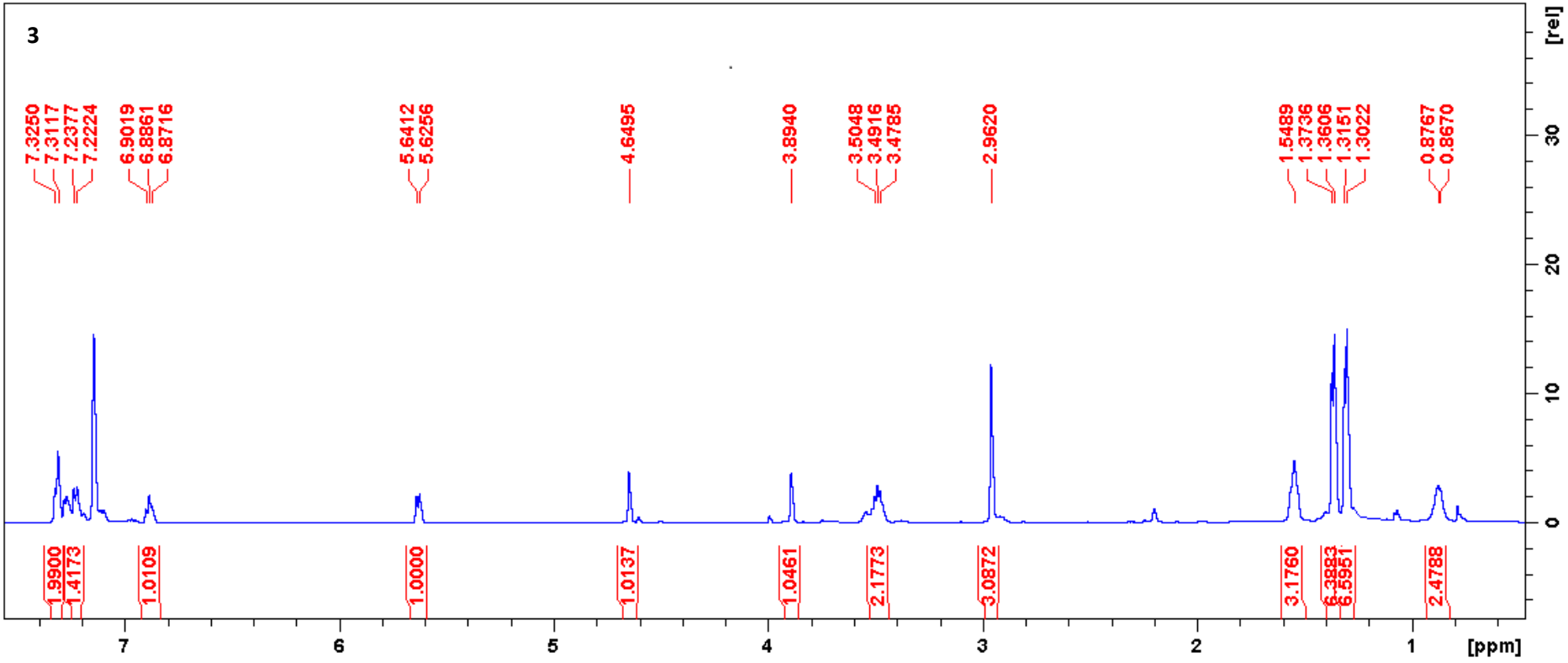


Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6

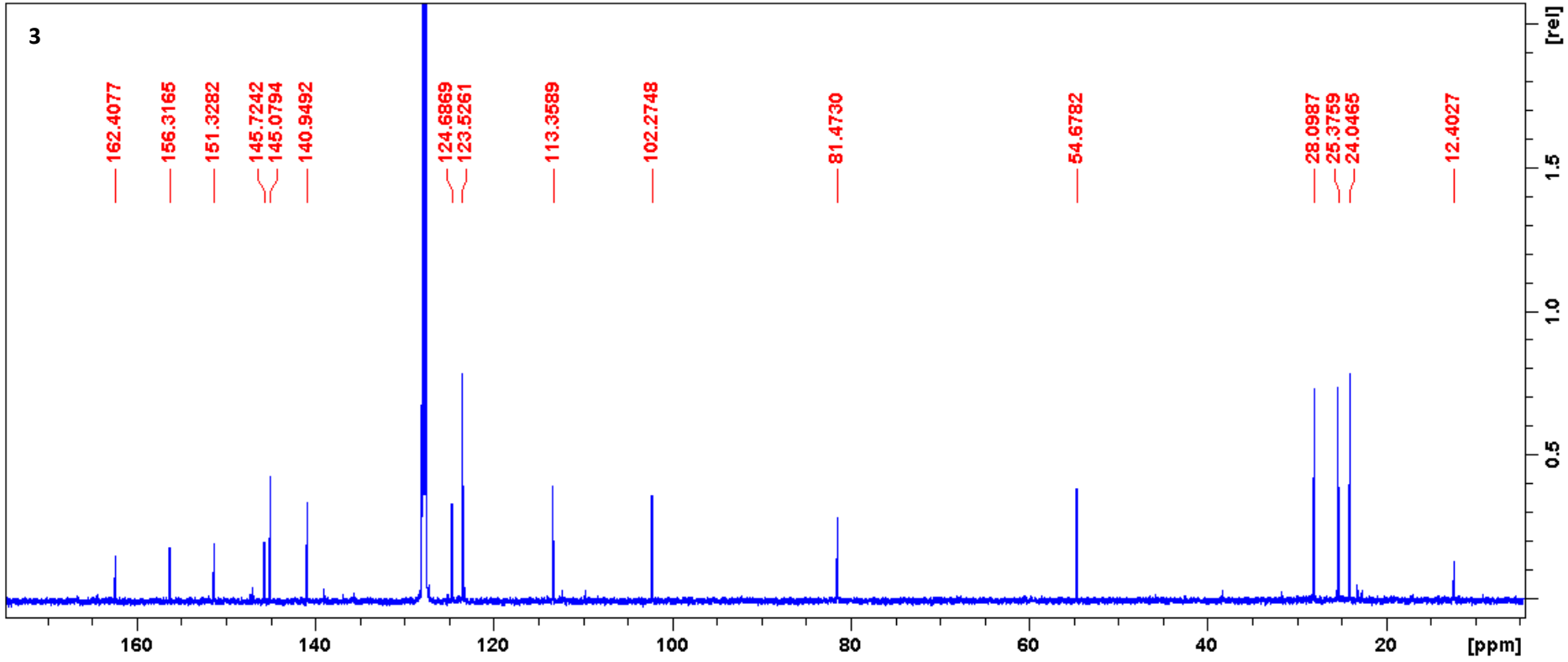


Figure S8. ^{1}H NMR spectrum of **4** in C_6D_6

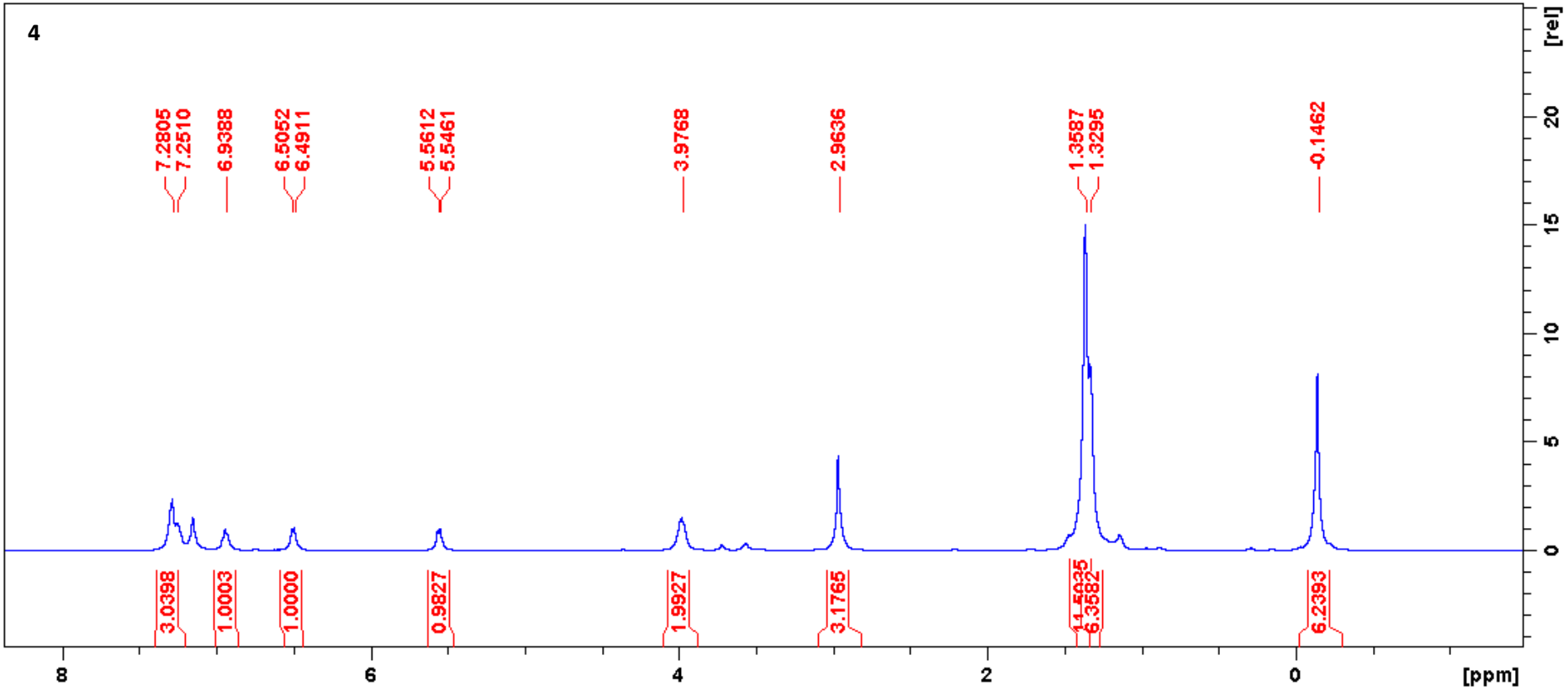


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4** in C_6D_6

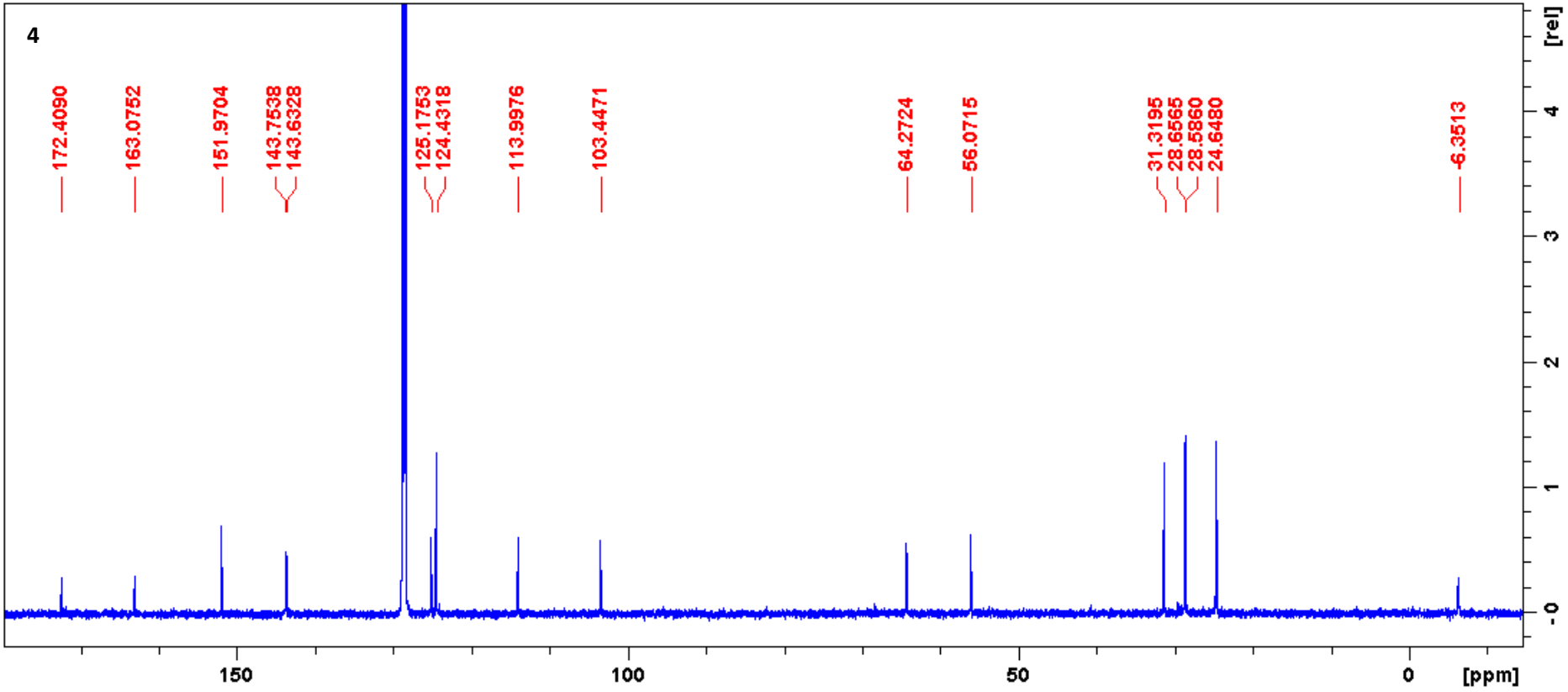


Figure S10. ^{1}H NMR spectrum of **5** in C_6D_6

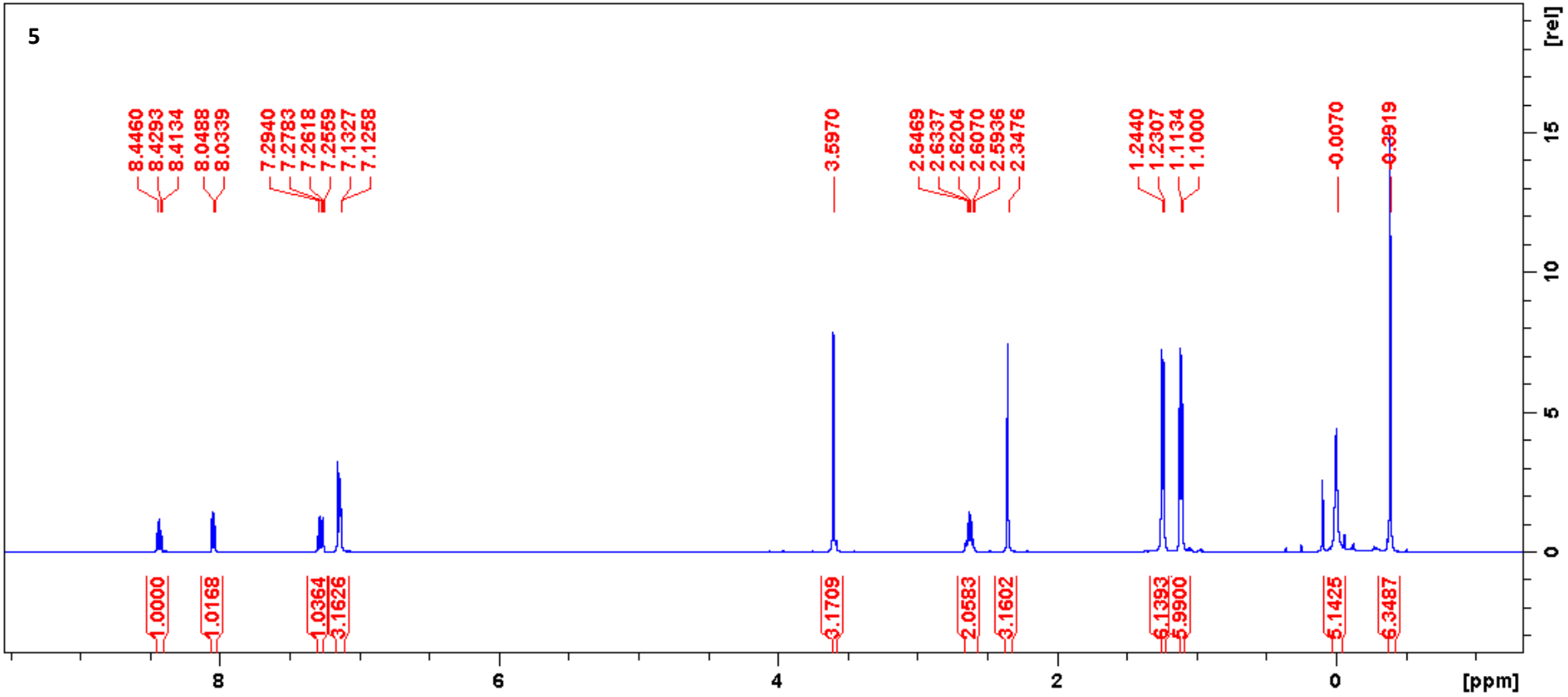


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **5** in C_6D_6

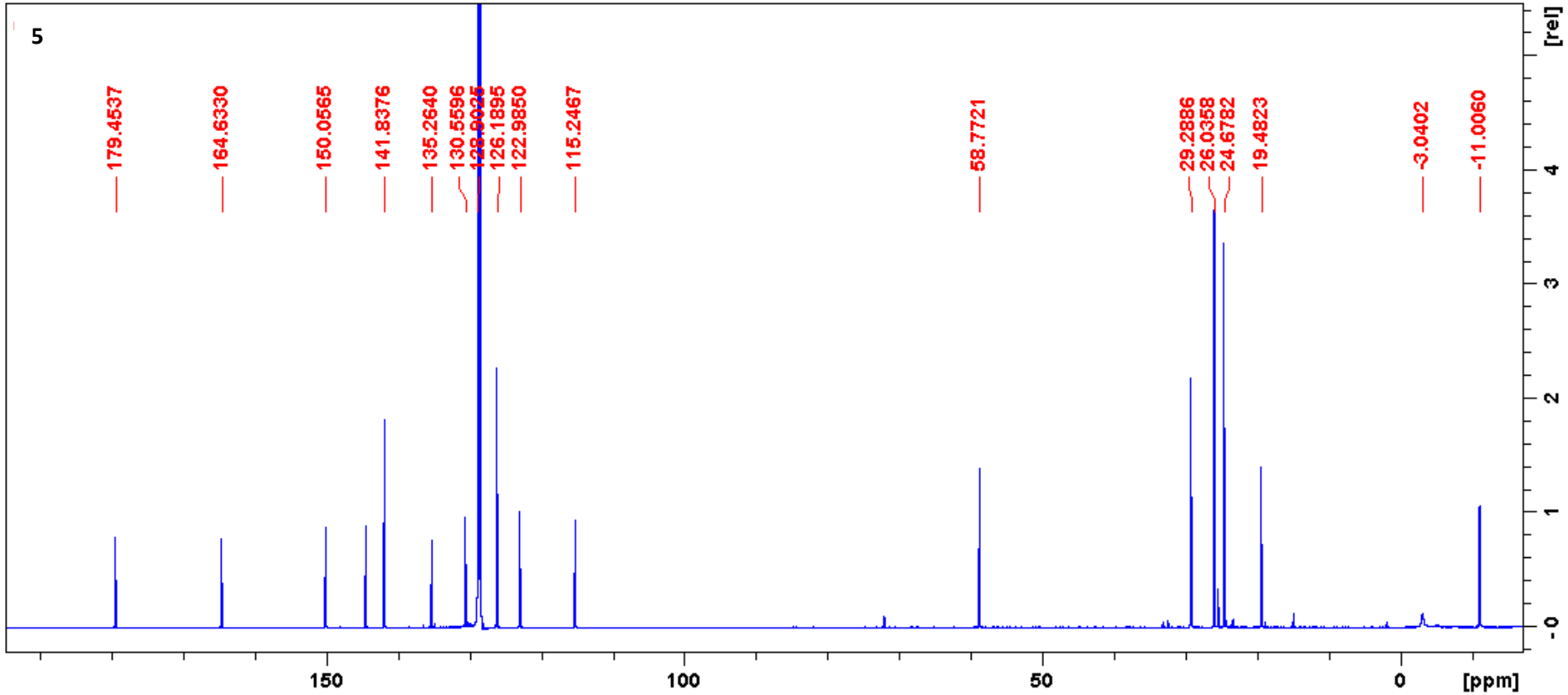
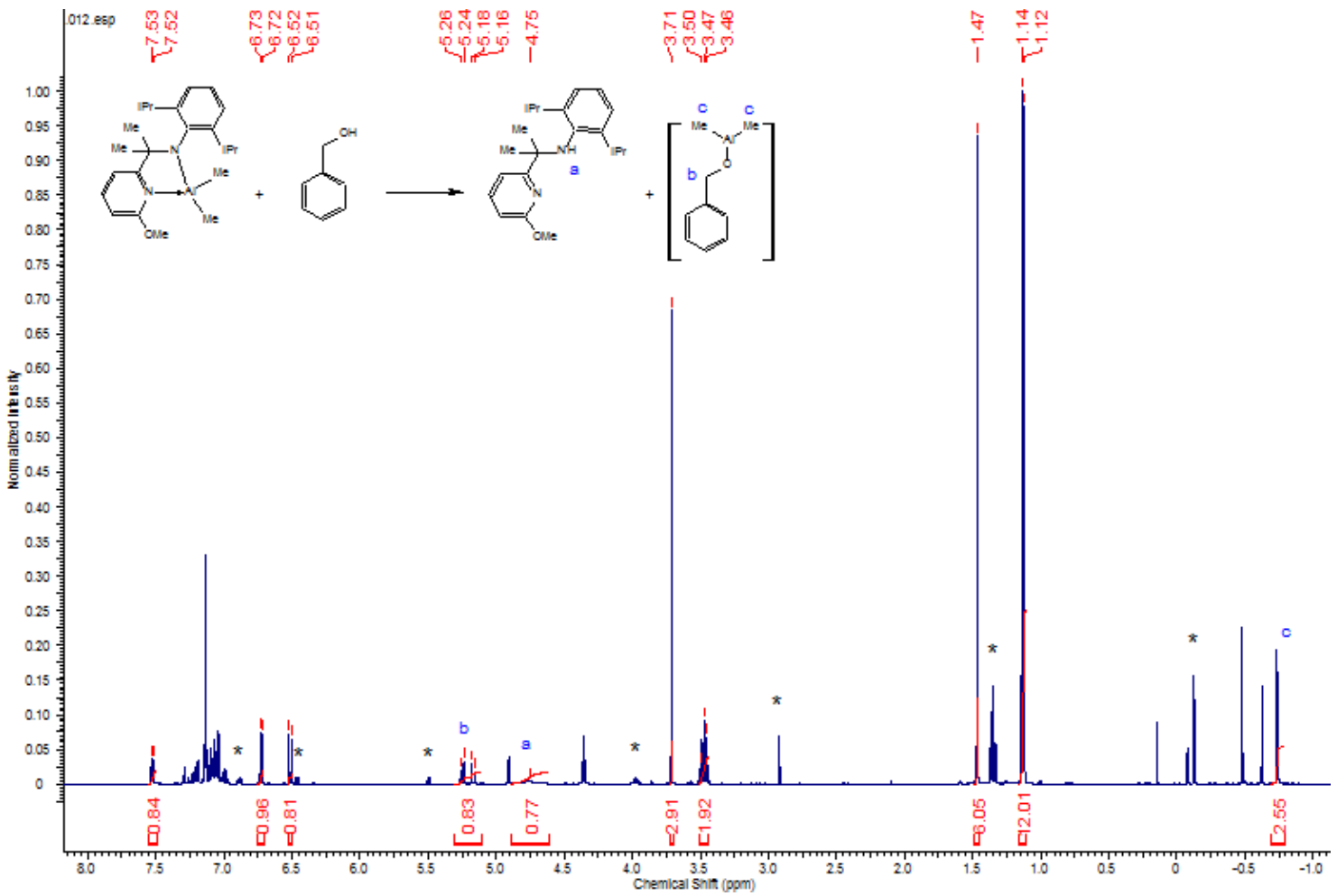
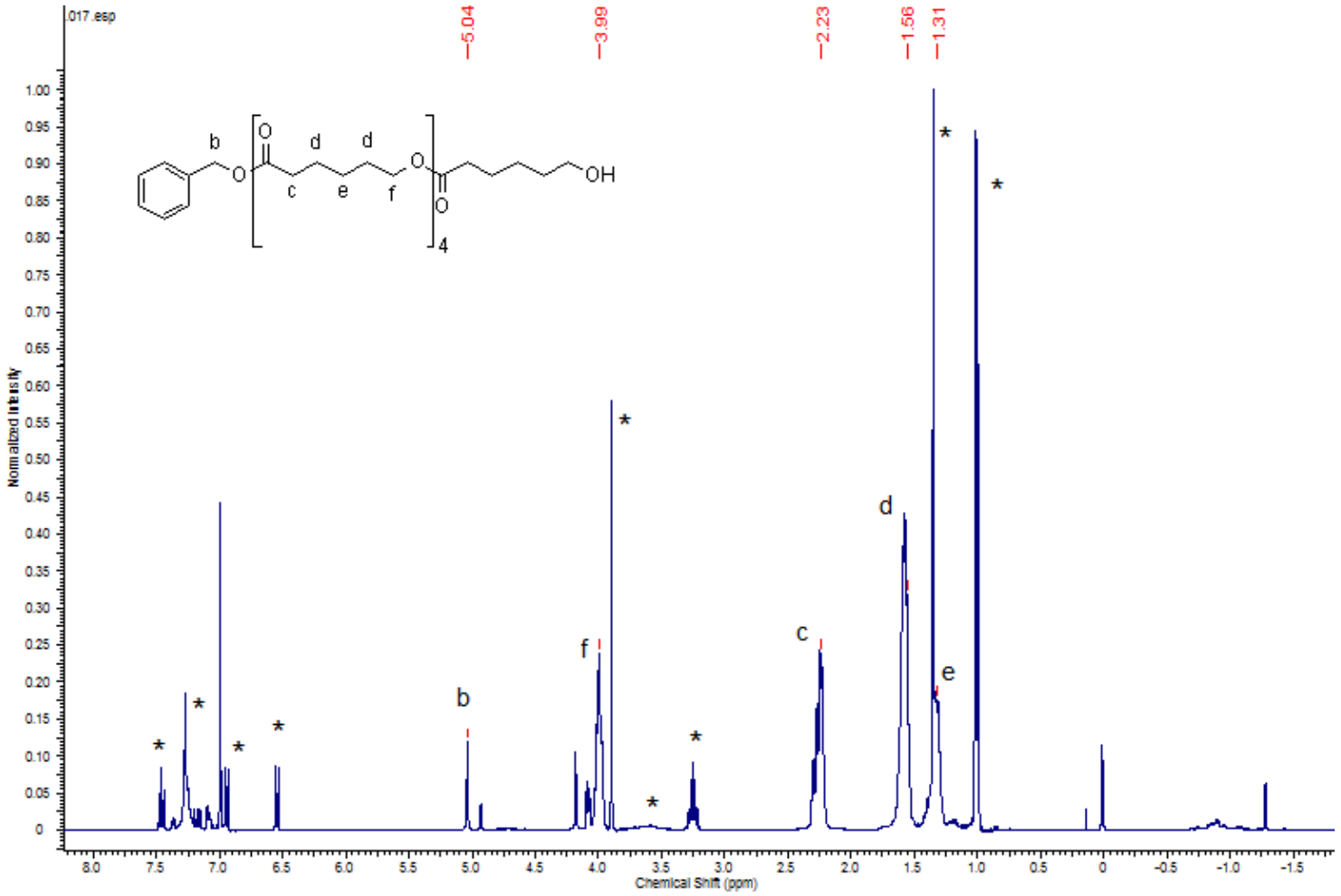


Figure S12. ^{1}H NMR spectrum of reaction mixture **4** + BzOH in C_6D_6



* traces of starting compound **4**

Figure S13. ^{1}H NMR spectrum of reaction mixture **4** + BzOH + ε-CL in C_6D_6



* amino-derivative of L^1

Figure S14. ^{1}H NMR spectrum of PCL in $CDCl_3$