

## Supporting Information for

### Copolymerization of CHO/CO<sub>2</sub> catalyzed by a series of aluminum amino-phenolate complexes and insights into structure-activity relationships

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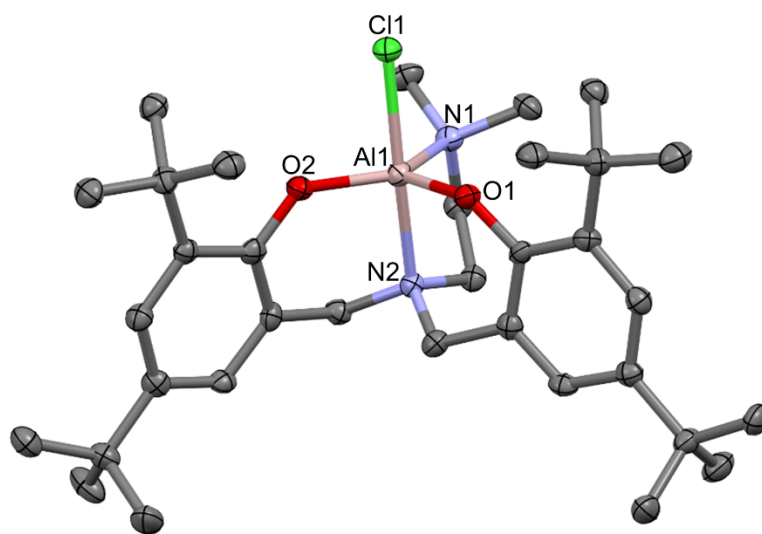
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<b>Figure S1.</b> Molecular structure and partial numbering of <b>2</b> (thermal ellipsoids drawn at 50% probability; H atoms and two co-crystallized toluene molecules excluded for clarity). Selected bond distances (Å) and angles (°): Cl(1)–Al(1), 2.2532(13); Al(1)–O(1), 1.752(3); Al(1)–O(2), 1.745(3); Al(1)–N(1), 2.069(3); Al(1)–N(2), 2.116(3); O(1)–Al(1)–Cl(1), 93.88(9); O(1)–Al(1)–N(1), 113.11(12); O(1)–Al(1)–N(2), 91.21(12); O(2)–Al(1)–Cl(1), 91.05(9); O(2)–Al(1)–O(1), 124.52(13); O(2)–Al(1)–N(1), 122.09(13); O(2)–Al(1)–N(2), 90.72(12); N(1)–Al(1)–Cl(1), 90.40(9); N(1)–Al(1)–N(2), 82.40(12); N(2)–Al(1)–Cl(1), 172.39(10).....	4
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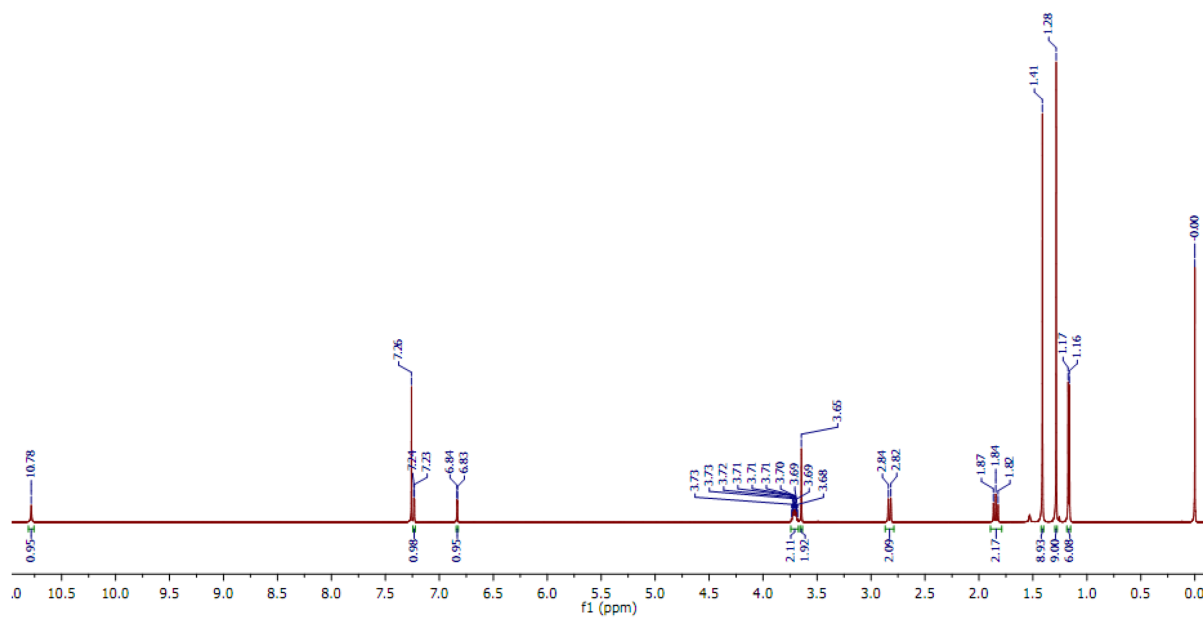
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**Table S1.** Crystallographic and structure refinement data for compounds H[L2], 2, 4, and 5

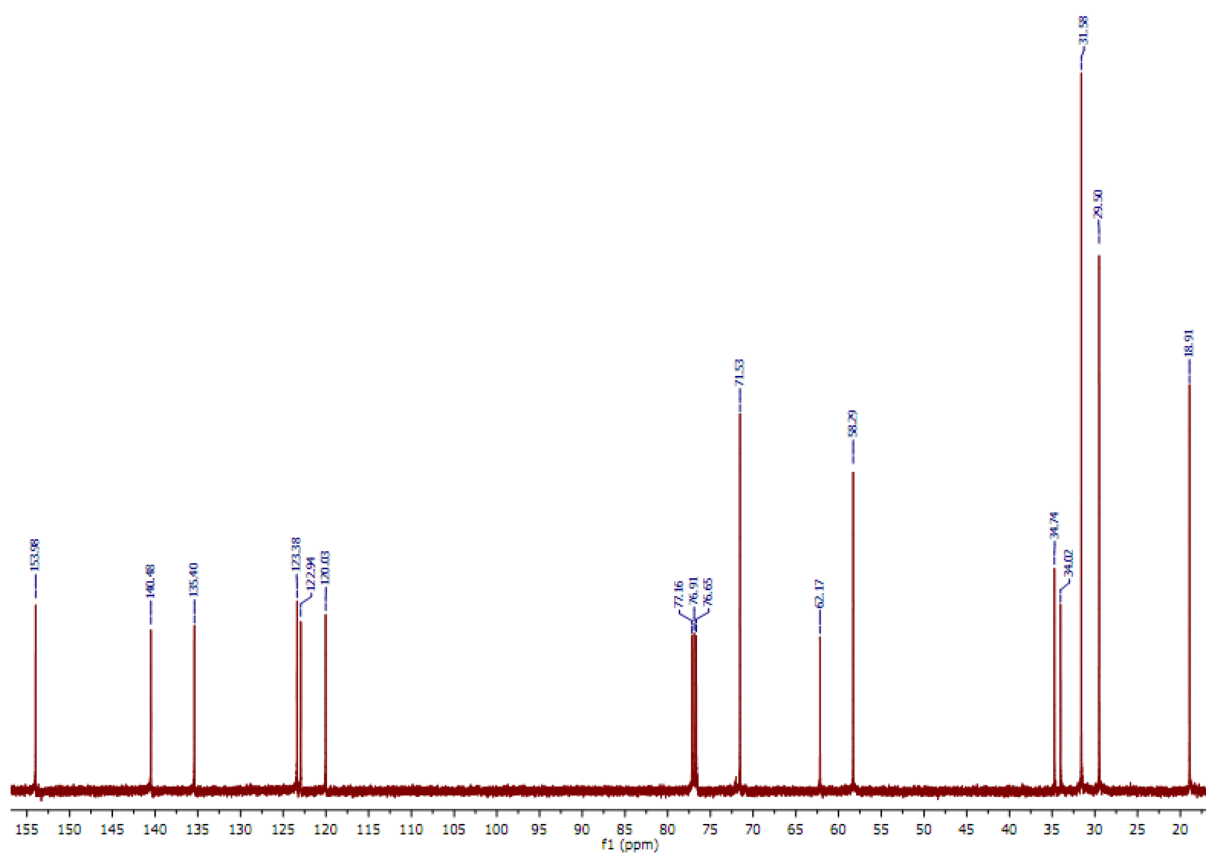
Compounds	H[L2]	2	4	5
Chemical formula	C <sub>21</sub> H <sub>35</sub> NO <sub>2</sub>	C <sub>48</sub> H <sub>70</sub> AlClN <sub>2</sub> O <sub>2</sub>	C <sub>42</sub> H <sub>68</sub> N <sub>2</sub> O <sub>2</sub> AlCl	C <sub>75</sub> H <sub>111</sub> Al <sub>2</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub>
Formula weight	333.51	769.49	695.41	1257.53
Temperature/K	123	100	293(2)	100
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n	P-1	P-1
a/Å	12.013(4)	13.1378(4)	11.4893(3)	7.7750(2)
b/Å	17.863(6)	24.9763(6)	13.7084(4)	11.1513(3)
c/Å	9.836(3)	14.4263(4)	15.1276(3)	21.4322(5)
$\alpha$ /°	90	90	111.101(2)	75.708(2)
$\beta$ /°	101.484(5)	110.413(3)	105.252(2)	89.494(2)
$\gamma$ /°	90	90	93.044(2)	74.480(2)
Volume/Å <sup>3</sup>	2068.5(12)	4436.5(2)	2115.43(10)	1731.77(8)
Z	4	4	2	1
$D_c$ /g cm <sup>-3</sup>	1.071	1.152	1.092	1.206
Radiation type	MoK $\alpha$ ( $\lambda$ = 0.71075)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)	MoK $\alpha$ ( $\lambda$ = 0.71073)
$\mu$ (MoK $\alpha$ )/mm <sup>-1</sup>	0.067	0.145	0.145	0.171
F(000)	736	1672.0	760.0	681.0
Reflections measured	21073	56957	27634	22667
Unique reflections	4291	8121	8009	6588
$R_{int}$	0.0239	0.1011	0.0425	0.0403
$R_I$ (all)	0.0529	0.1157	0.0604	0.0675
$wR(F^2)$ (all)	0.1276	0.1875	0.1249	0.1563
$R_I$ ( $I > 2 \sigma(I)$ ) <sup>a</sup>	0.0497	0.0981	0.0491	0.0598
$wR(F^2)$ ( $I > 2 \sigma(I)$ ) <sup>b</sup>	–	0.1769	0.1161	0.1499
Goodness of fit on $F^2$	1.112	1.181	1.058	1.086
CCDC Ref.	1912327	1936692	1936648	1936691



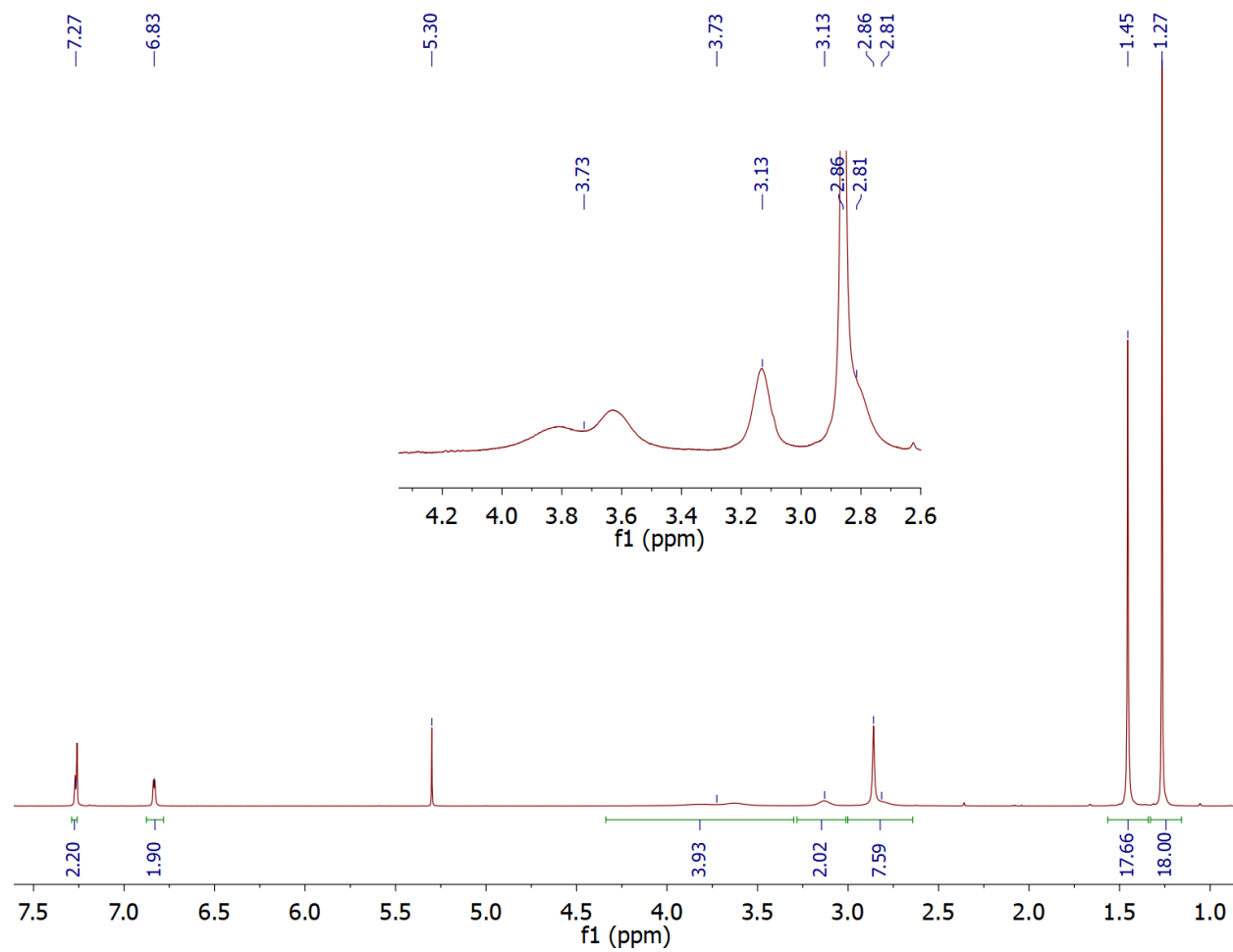
**Figure S1.** Molecular structure and partial numbering of **2** (thermal ellipsoids drawn at 50% probability; H atoms and two co-crystallized toluene molecules excluded for clarity). Selected bond distances (Å) and angles (°): Cl(1)–Al(1), 2.2532(13); Al(1)–O(1), 1.752(3); Al(1)–O(2), 1.745(3); Al(1)–N(1), 2.069(3); Al(1)–N(2), 2.116(3); O(1)–Al(1)–Cl(1), 93.88(9); O(1)–Al(1)–N(1), 113.11(12); O(1)–Al(1)–N(2), 91.21(12); O(2)–Al(1)–Cl(1), 91.05(9); O(2)–Al(1)–O(1), 124.52(13); O(2)–Al(1)–N(1), 122.09(13); O(2)–Al(1)–N(2), 90.72(12); N(1)–Al(1)–Cl(1), 90.40(9); N(1)–Al(1)–N(2), 82.40(12); N(2)–Al(1)–Cl(1), 172.39(10).



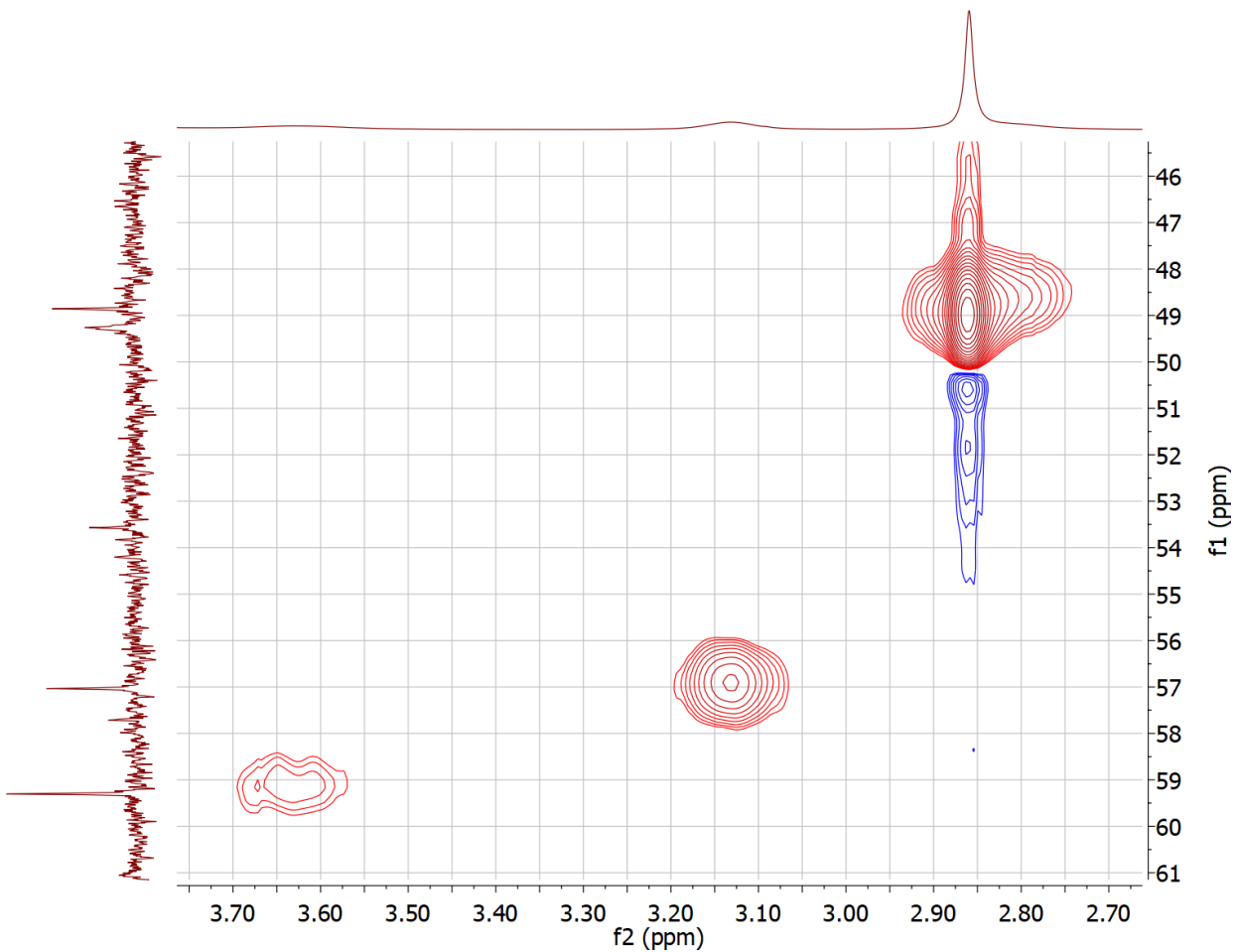
**Figure S2.**  $^1\text{H}$  NMR spectrum of H[L2] in  $\text{CDCl}_3$ , 298 K



**Figure S3.**  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum of H[L2] in  $\text{CDCl}_3$ , 298 K

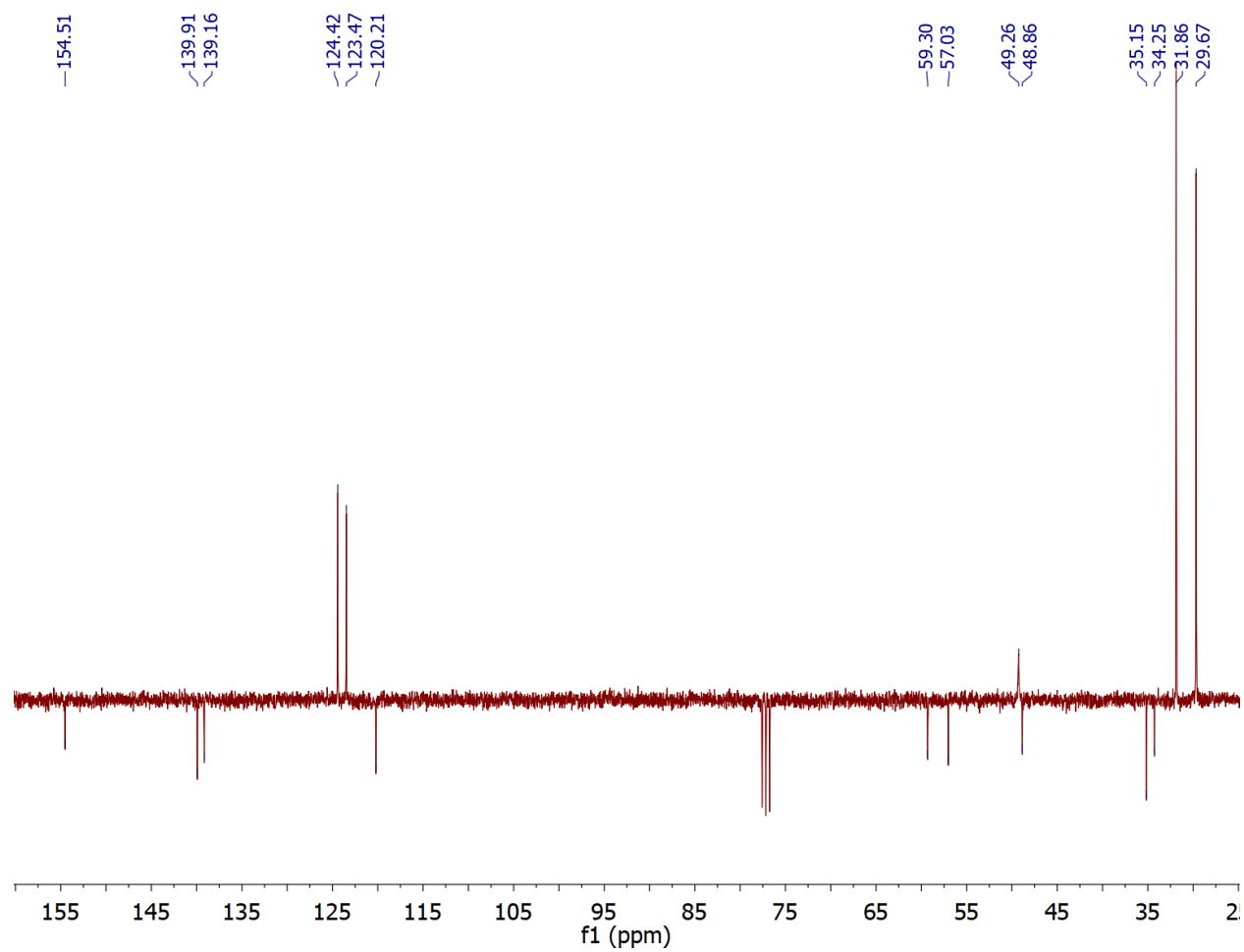


**Figure S4.**  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$ , 298 K

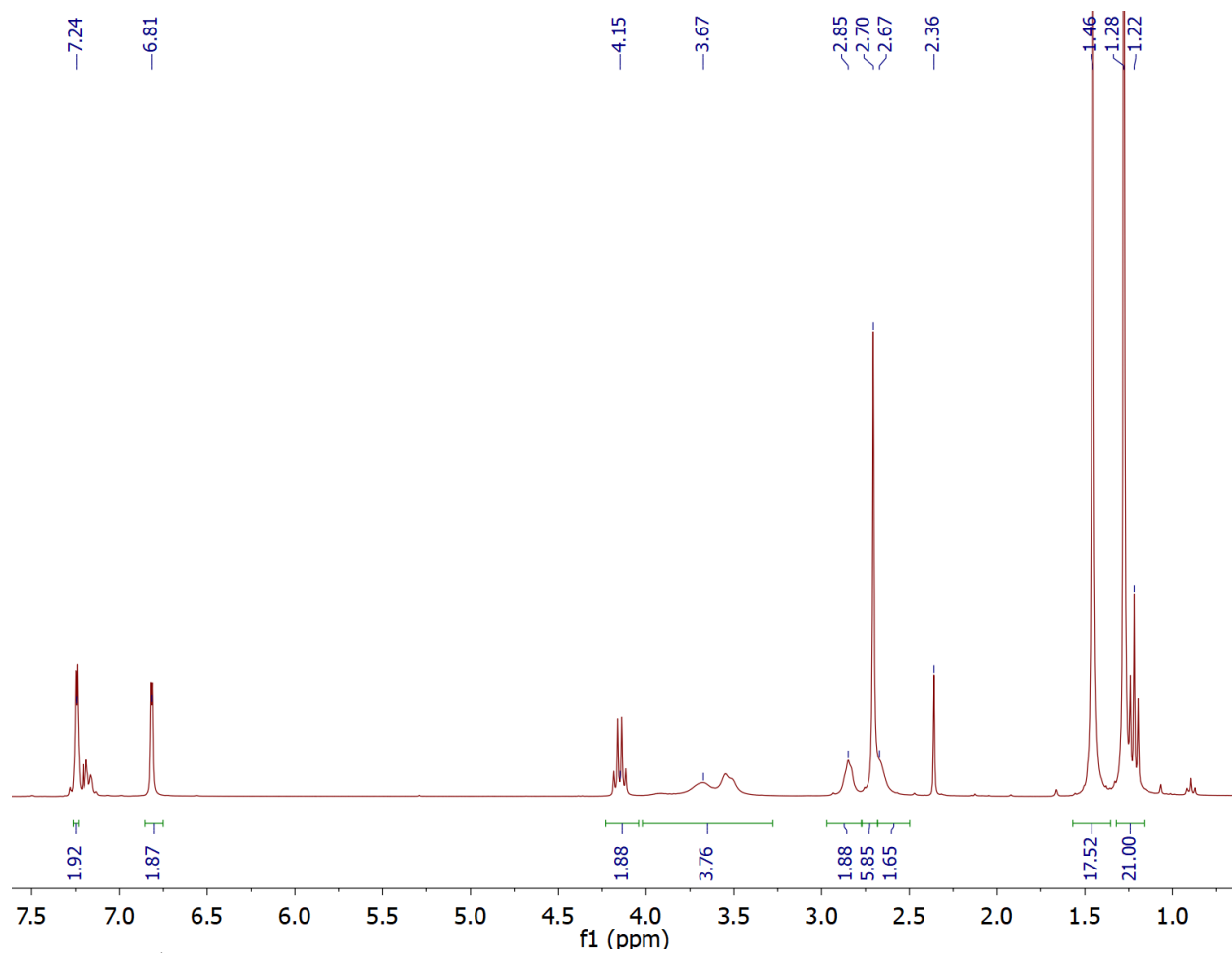


**Figure S5.** HSQC spectrum of **2** in  $\text{CDCl}_3$ , 298 K

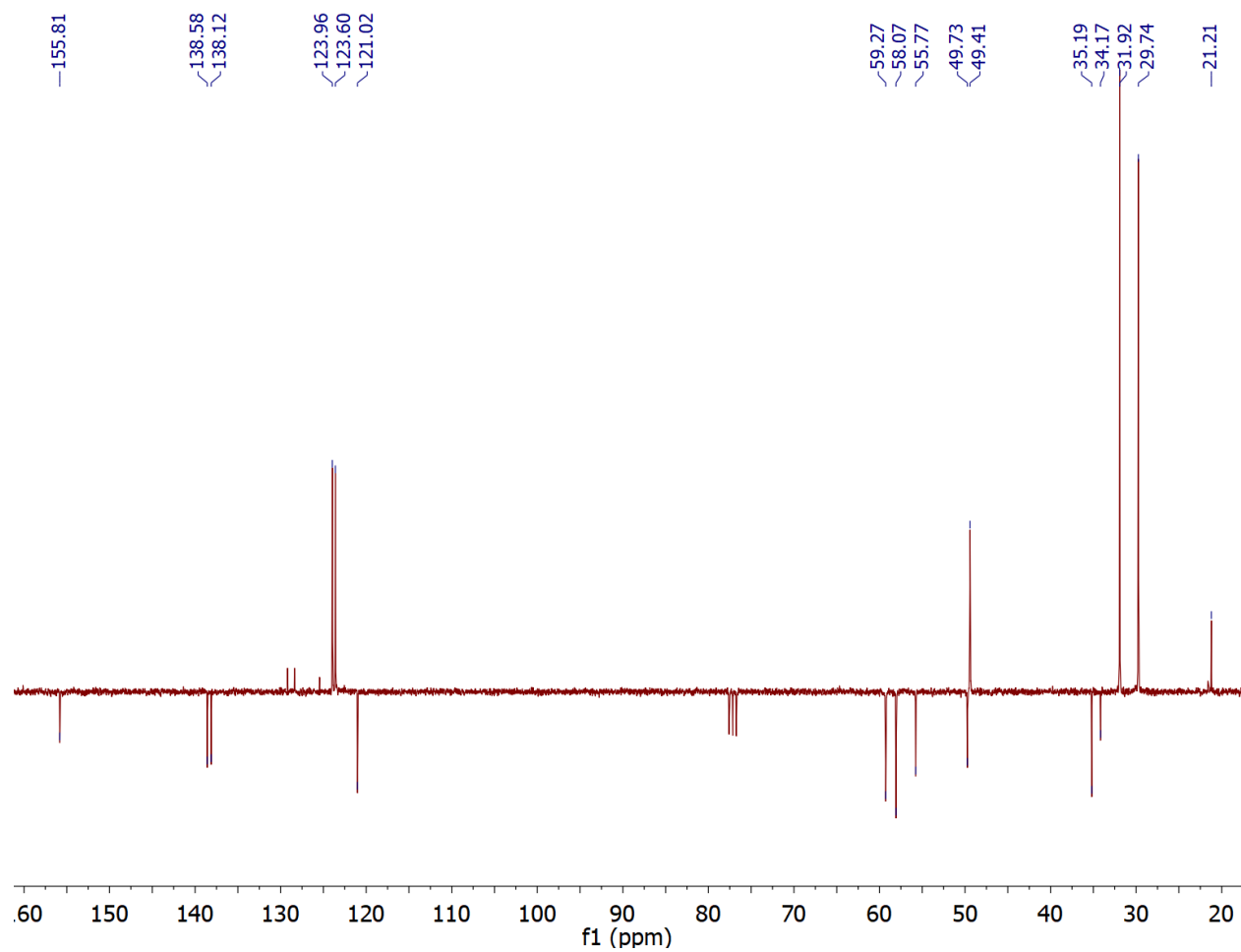




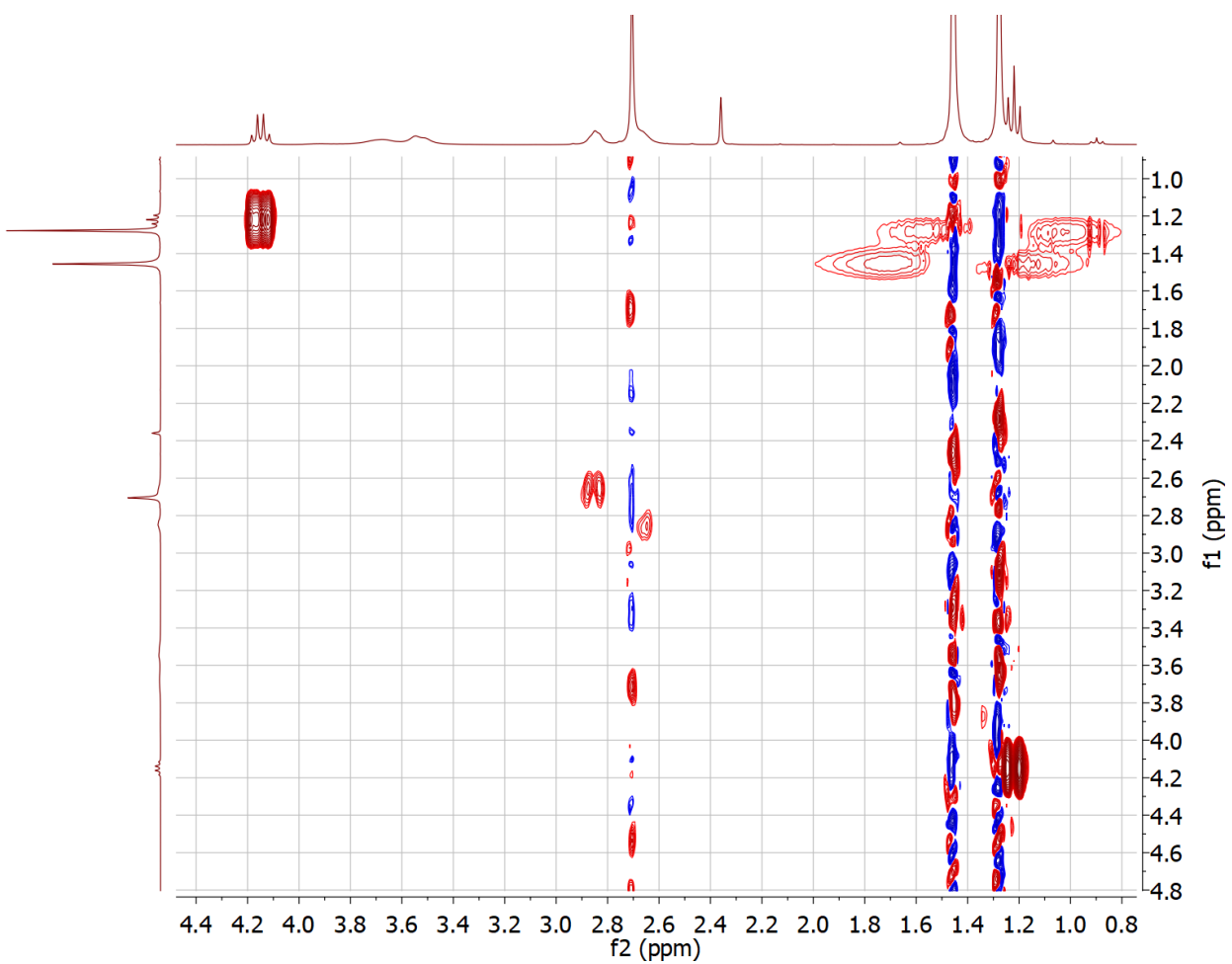
**Figure S6.**  $^{13}\text{C}$ -DEPT NMR spectrum of **2** in  $\text{CDCl}_3$ , 298 K



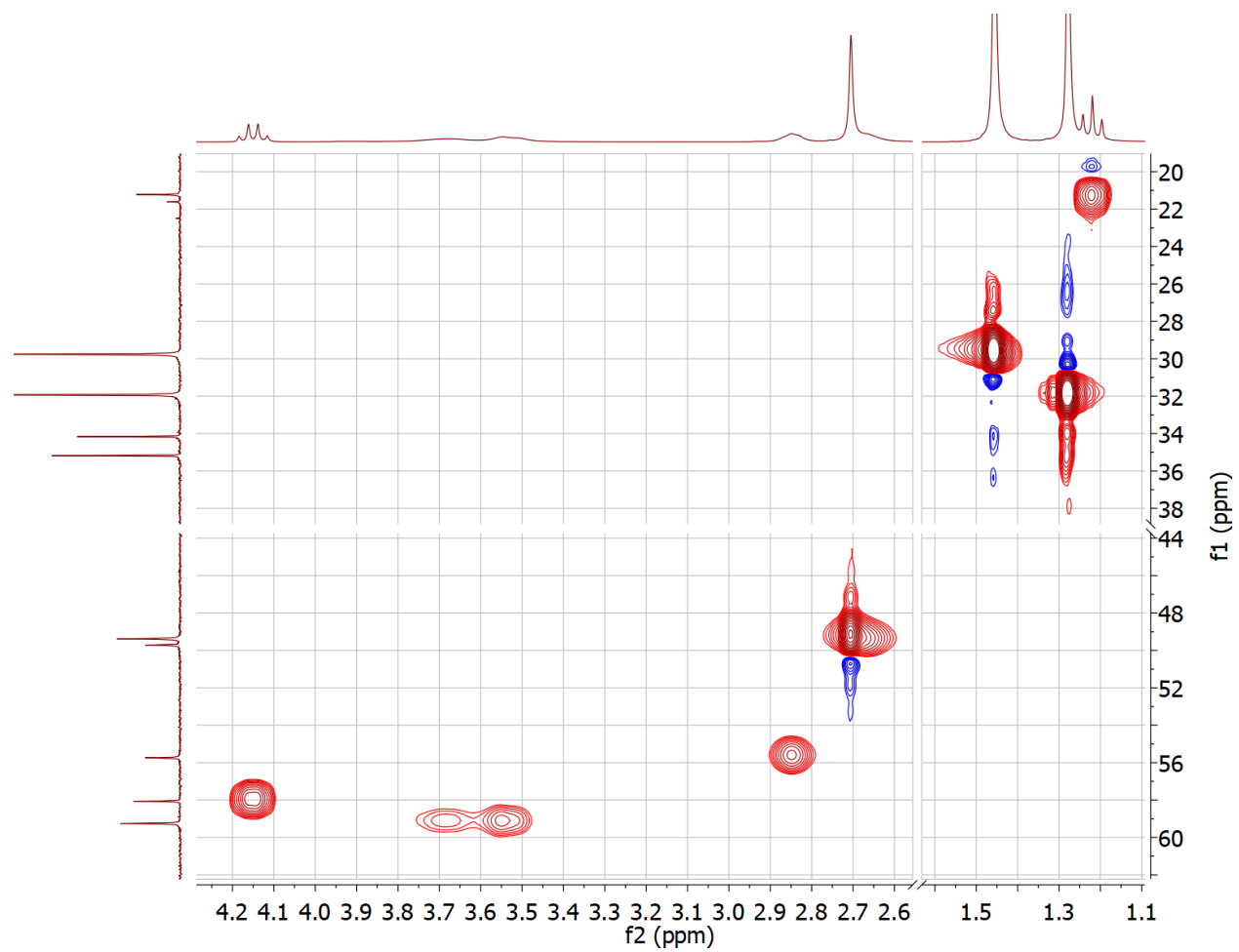
**Figure S7.**  $^1\text{H}$  NMR spectrum of **3** in  $\text{CDCl}_3$ , 298 K (residual toluene resonance at 2.36 ppm)



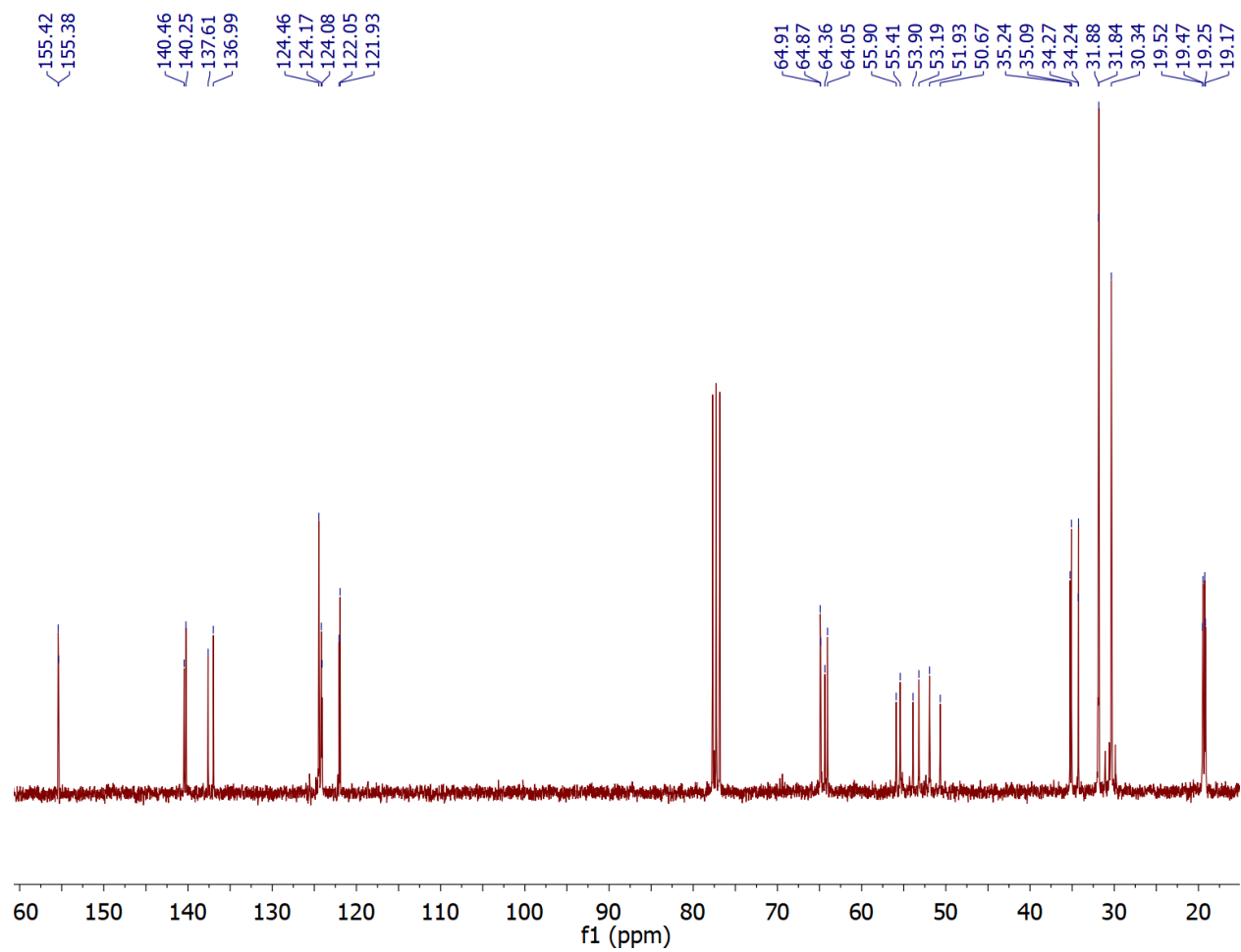
**Figure S8.**  $^{13}\text{C}$ -DEPT NMR spectrum of **3** in  $\text{CDCl}_3$ , 298 K



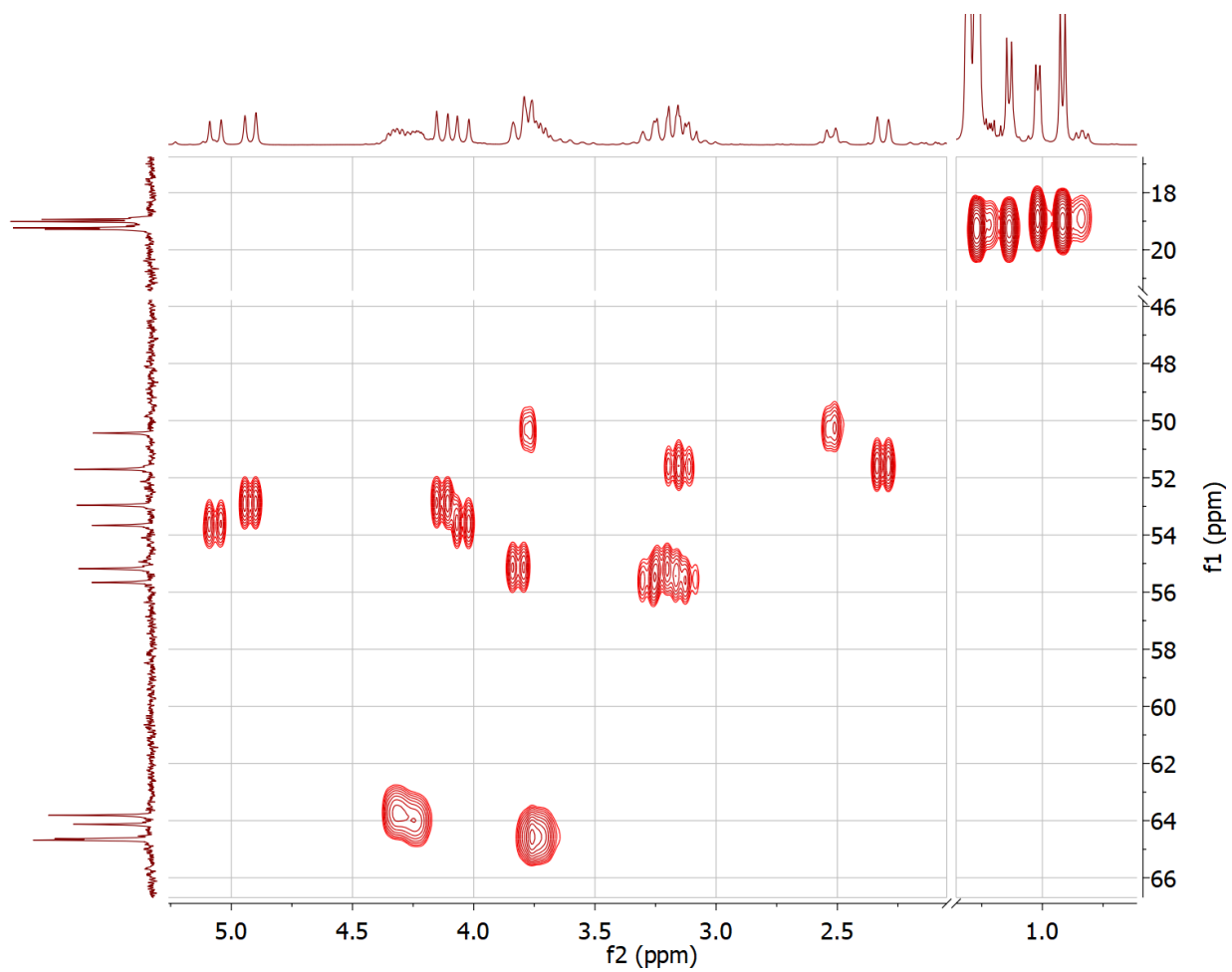
**Figure S9.** COSY spectrum of **3** in  $\text{CDCl}_3$ , 298 K



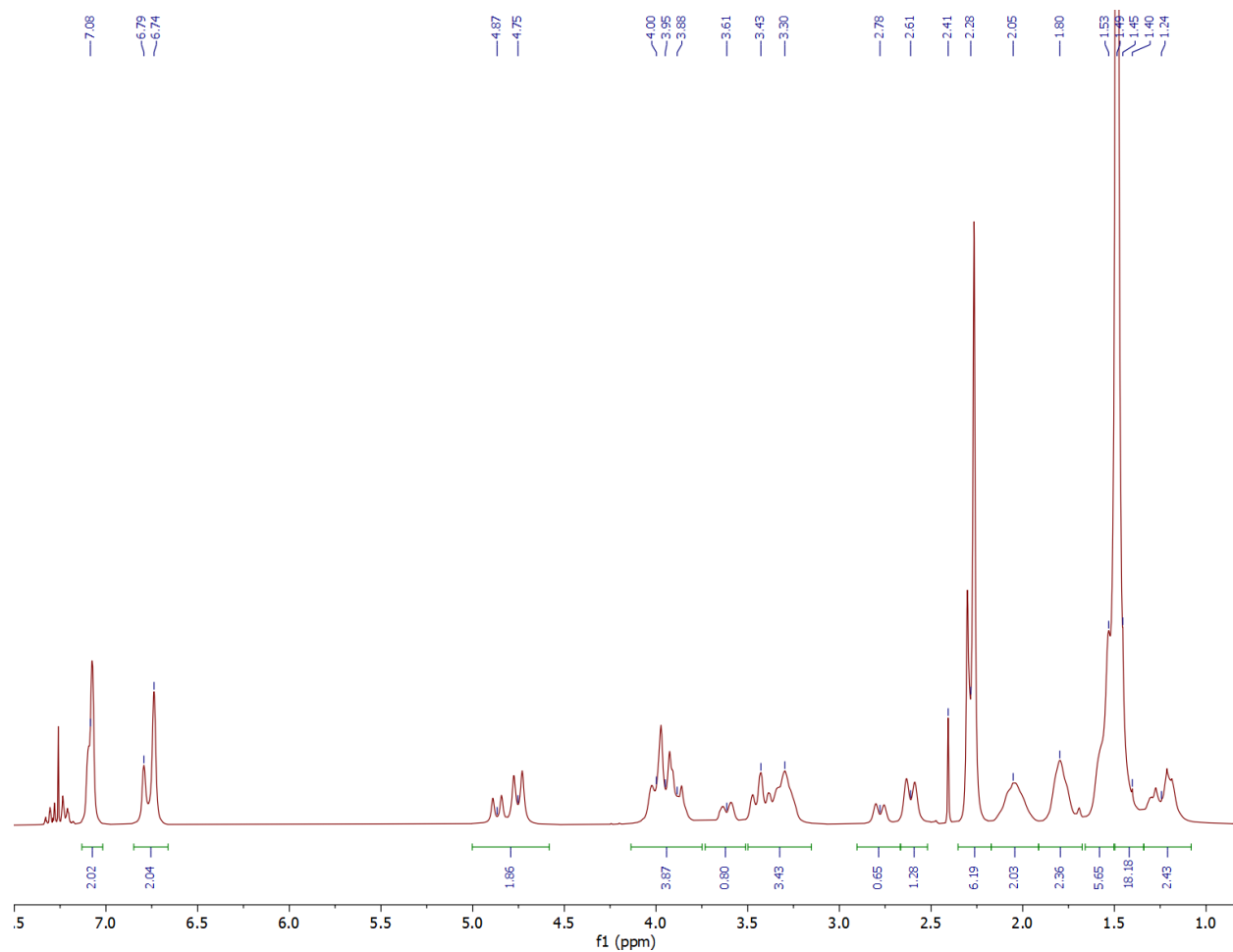
**Figure S10.** HSQC spectrum of **3** in CDCl<sub>3</sub>, 298 K



**Figure S11.** <sup>13</sup>C spectrum of 4 in CDCl<sub>3</sub>, 298 K

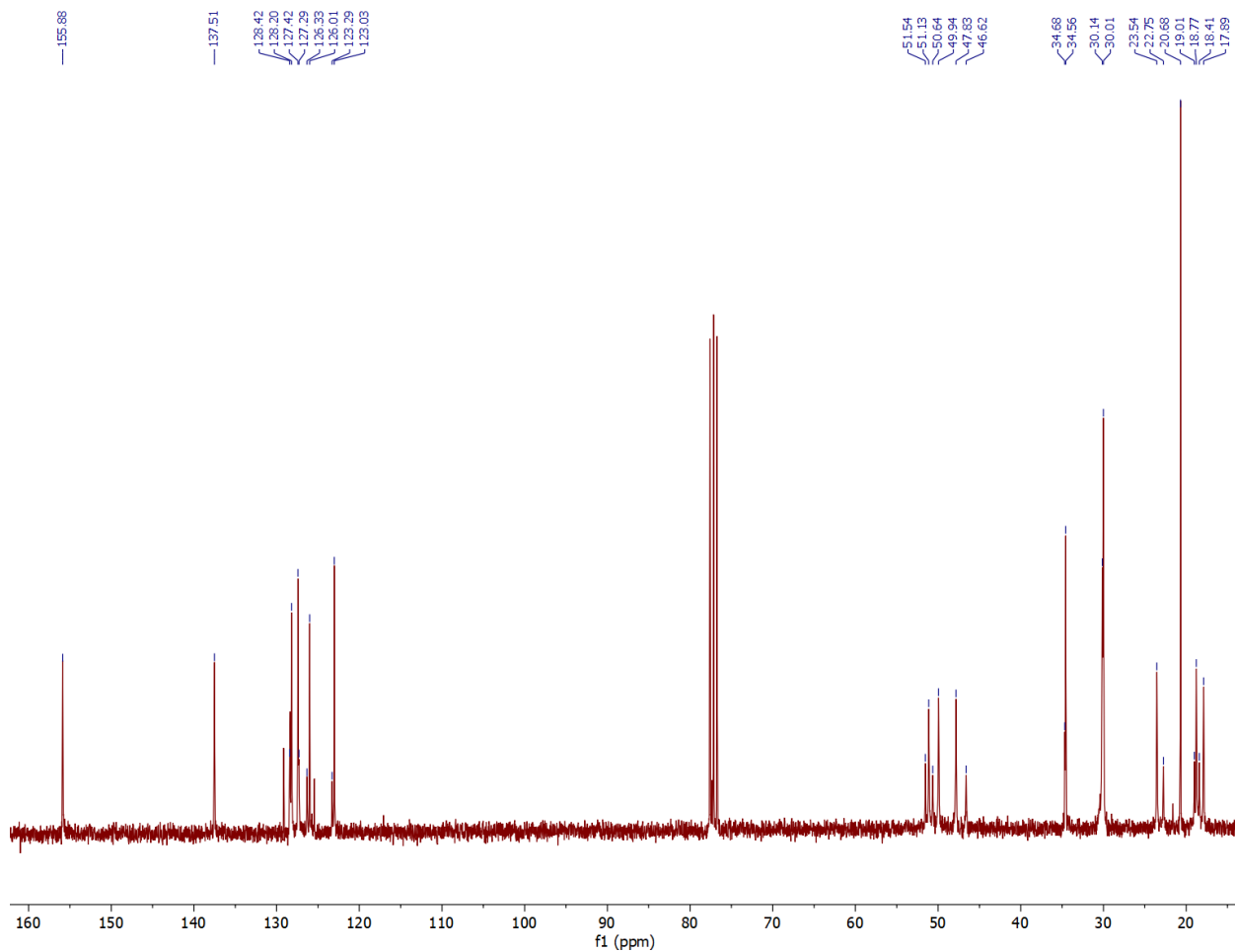


**Figure S12.** HSQC spectrum of **4** in  $\text{CDCl}_3$ , 298 K

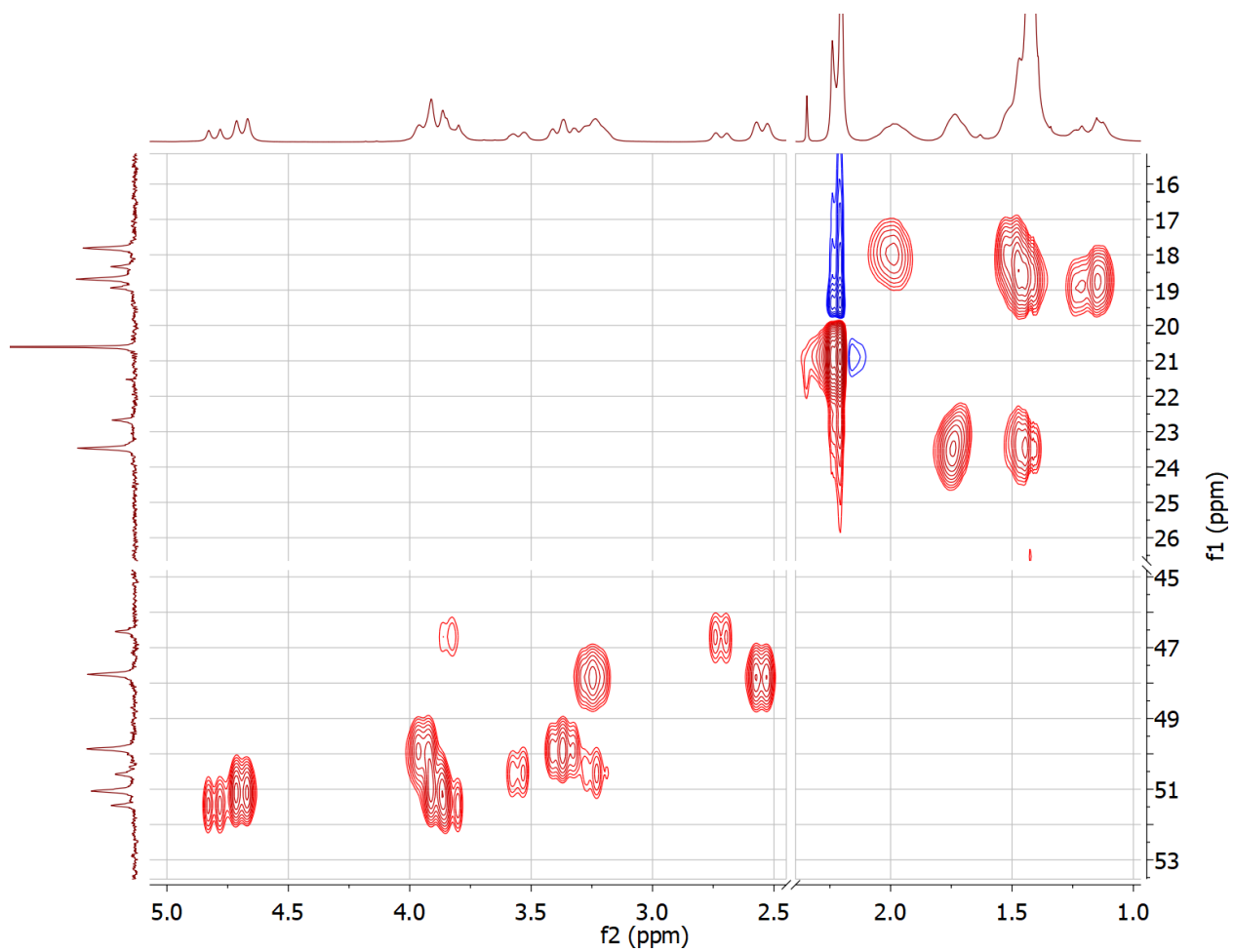


**Figure S13.** <sup>1</sup>H NMR spectrum of **5** in CDCl<sub>3</sub>, 298 K (residual toluene resonance at 2.41 ppm)

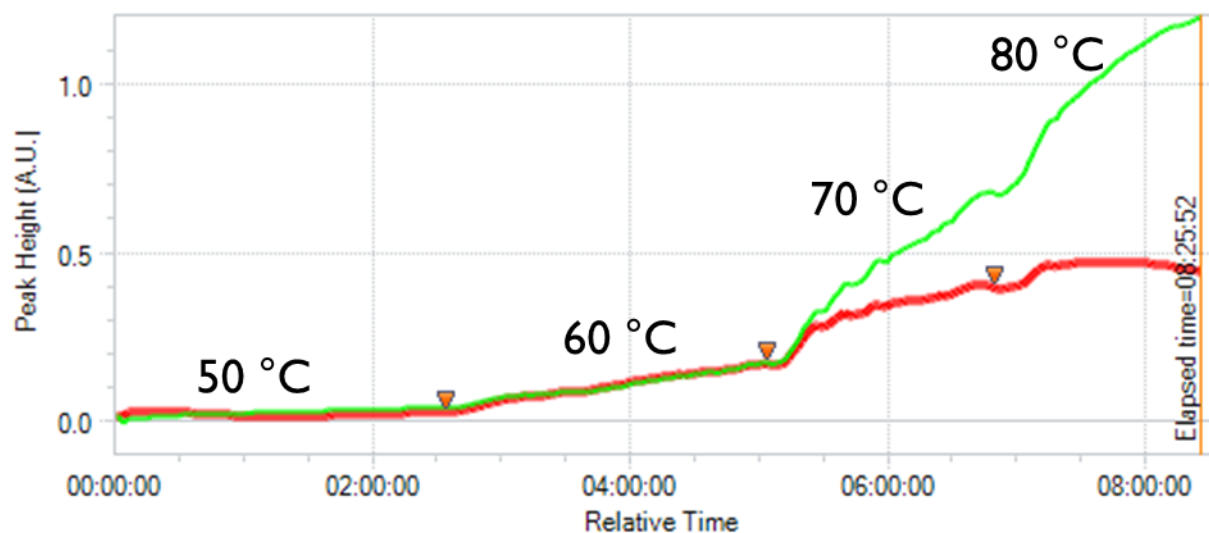




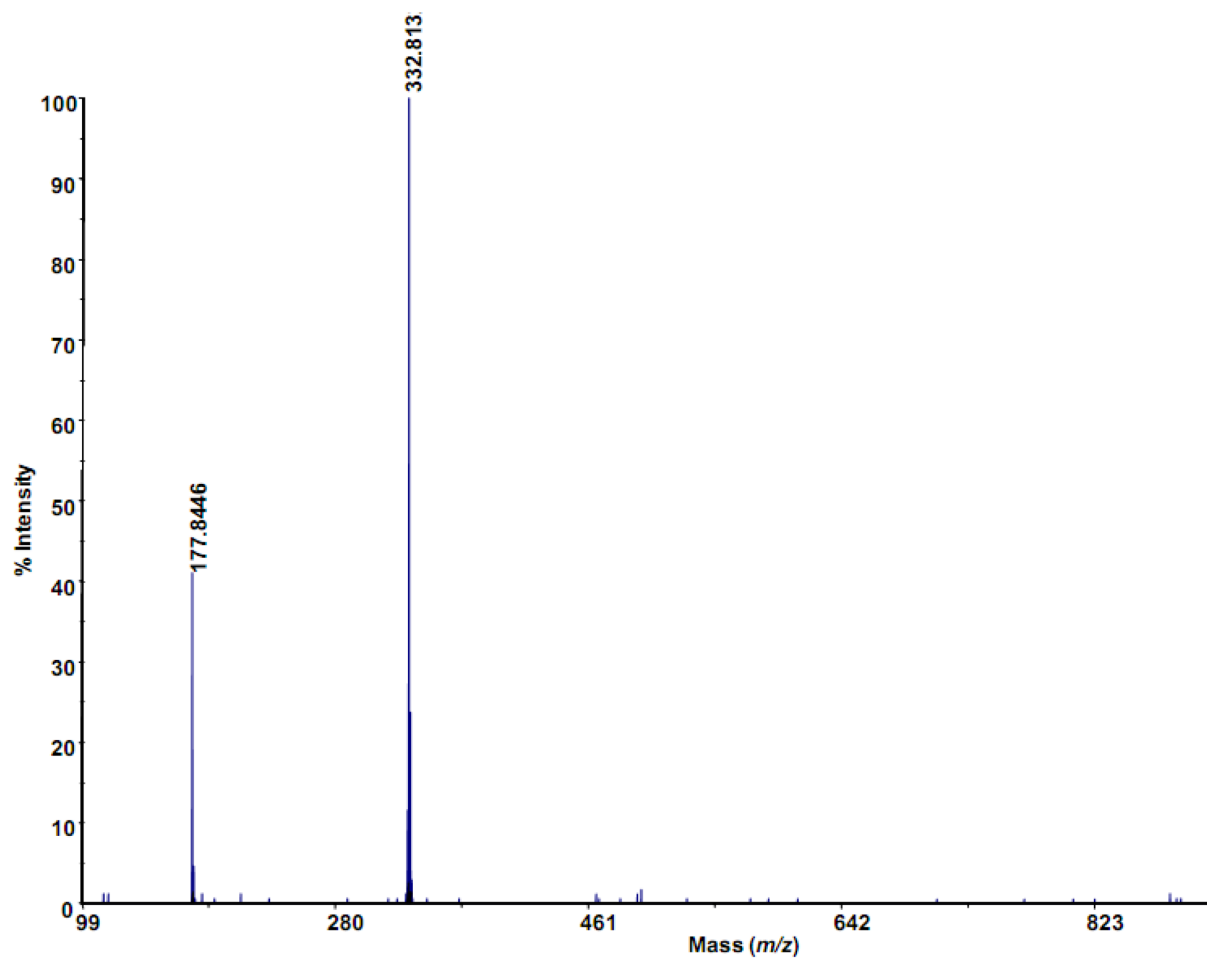
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of **5** in  $\text{CDCl}_3$ , 298 K



**Figure S15.** HSQC spectrum of **5** in  $\text{CDCl}_3$ , 298 K



**Figure S16.** Monitoring of IR absorptions over time at variable temperatures for the reaction of **1**+PPNCl+CHO (1/1/500) at 40 bar CO<sub>2</sub>. Red (1800 cm<sup>-1</sup>, CHC formation) and green (1750 cm<sup>-1</sup>, PCHC formation). Note: Under ideal circumstances, individual and replicant reactions should be performed at each temperature.



**Figure S17.** MALDI-TOF mass spectrum of H[L2]

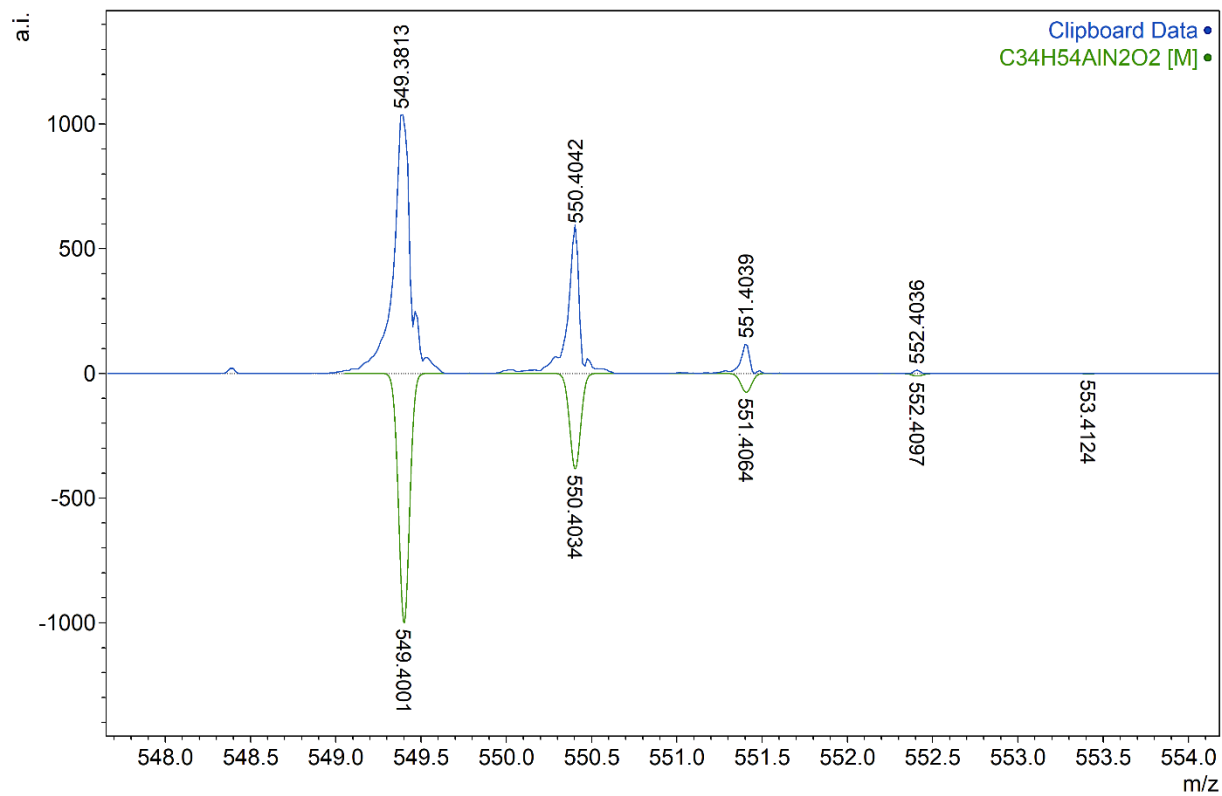
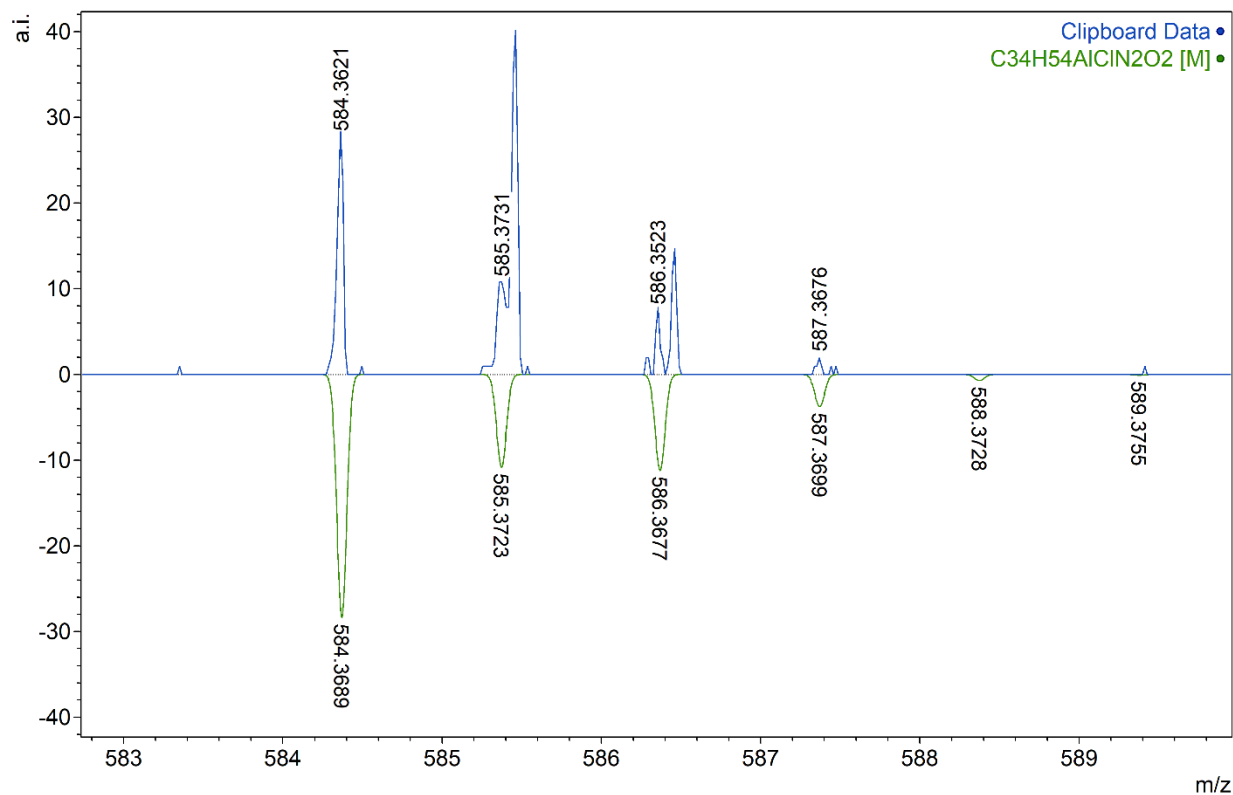
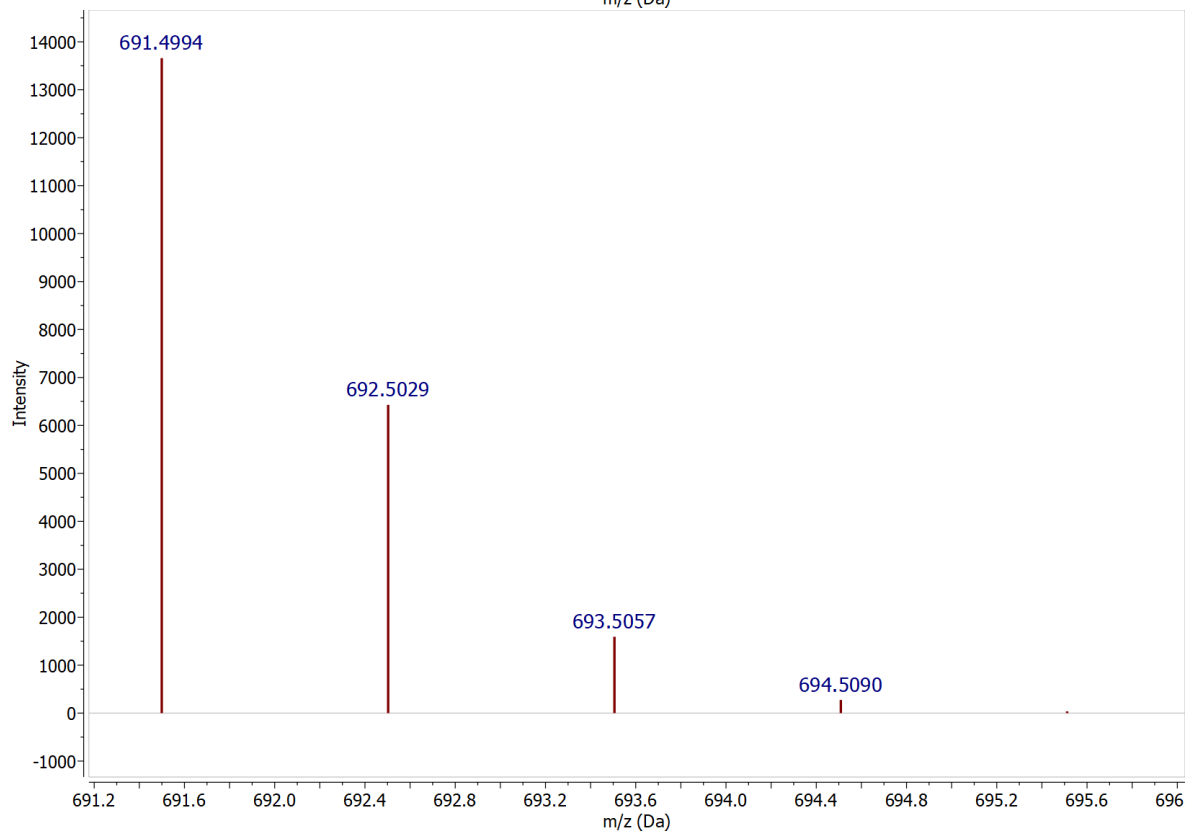
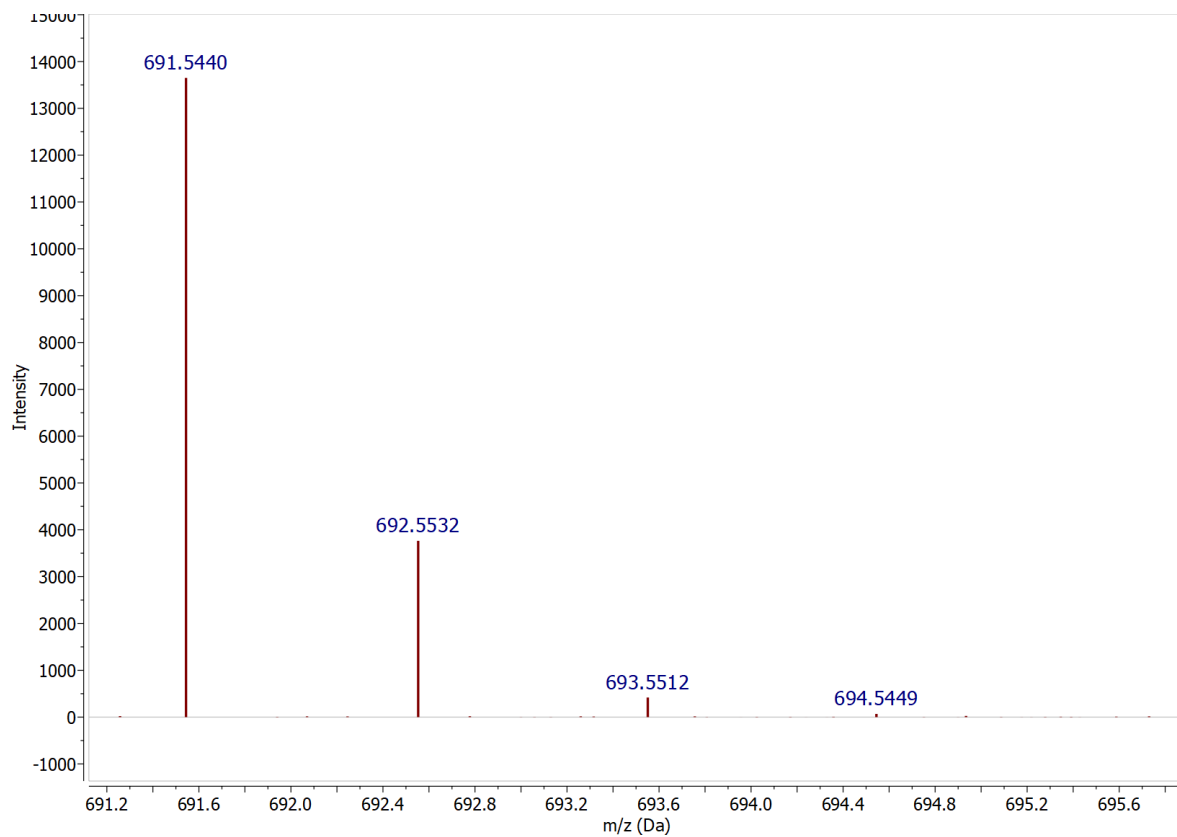
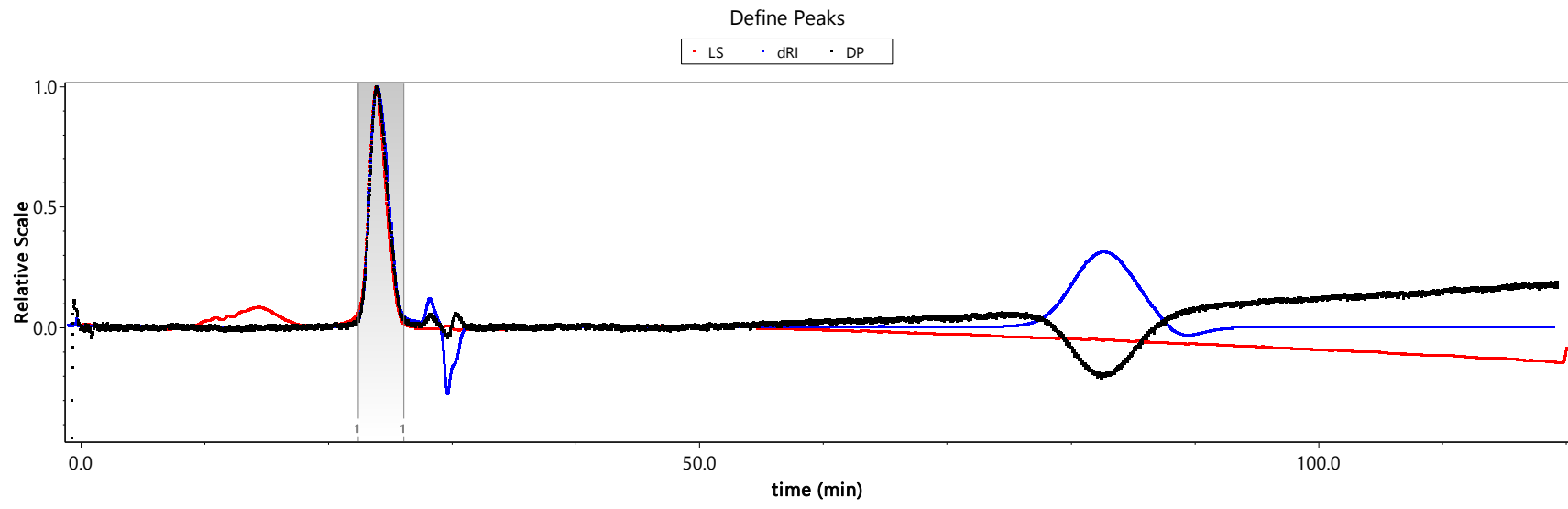


Figure S18. MALDI-TOF MS spectra of 2



**Figure S19.** MALDI-TOF mass spectra of **4.3** (experimental – top, theoretical – bottom)



**Figure S20.** Representative GPC trace of isolated PCHC (Table 1, entry 6; the peaks around 80 min are due to the delay volume)

**Table S2.** Experimental (X-ray) and calculated (M06/6-311+G(d,p)) bond distances of **1**, **2**, **4**, and **5**

Cat.	Al–O(phenolate) (Å)		Al–N(axial) <sup>a</sup> (Å)		Al–N(pendent) (Å)		Al–Cl (Å)	
	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd
<b>1</b>	1.75	1.77	2.10	2.16	2.08	2.07	2.26	2.28
	1.75	1.77						
<b>2</b>	1.75	1.77	2.12	2.19	2.07	2.06	2.25	2.27
	1.75	1.77						
<b>4</b>	1.77	1.77	2.13	2.13	–	–	2.20	2.20
	1.77	1.77						
<b>5</b>	1.77	1.78	2.12	2.15	–	–	2.20	2.20
	1.77	1.78						

<sup>a</sup> In **4** and **5**, the pendent nitrogen donors also assume axial positions.



**Table S3.** Calculated charges of pendent nitrogen in initial pro-ligands and Al-Cl complexes

Complex	Mulliken		MSK		CM5		NBO		DDEC6	
	Initial	Al-Cl	Initial	Al-Cl	Initial	Al-Cl	Initial	Al-Cl	Initial	Al-Cl
<b>1</b>	-0.03	-0.97	-0.49	-0.34	-0.39	-0.32	-0.59	-0.66	-0.22	-0.22
<b>2</b>	-0.10	-1.11	-0.28	-0.20	-0.40	-0.32	-0.59	-0.69	-0.16	-0.15

**Table S4.** Calculated (M06/6-311+G(d,p)) Al charges and relevant bond distances of Al-carbonate derivatives

Cat.	Mulliken	MSK	CM5	NBO	DDEC6	Al-N(pendent) (Å)	Al-carbonate (Å)
<b>1</b>	1.37	1.18	0.48	2.10	1.48	2.08	1.84
<b>2</b>	-0.02	1.12	0.47	2.10	1.48	2.04	1.85
<b>4</b>	-1.69	0.63	0.49	2.18	1.51	2.14, 2.12	1.81
<b>5</b>	-1.69	0.55	0.48	2.18	1.51	2.13, 2.13	1.81

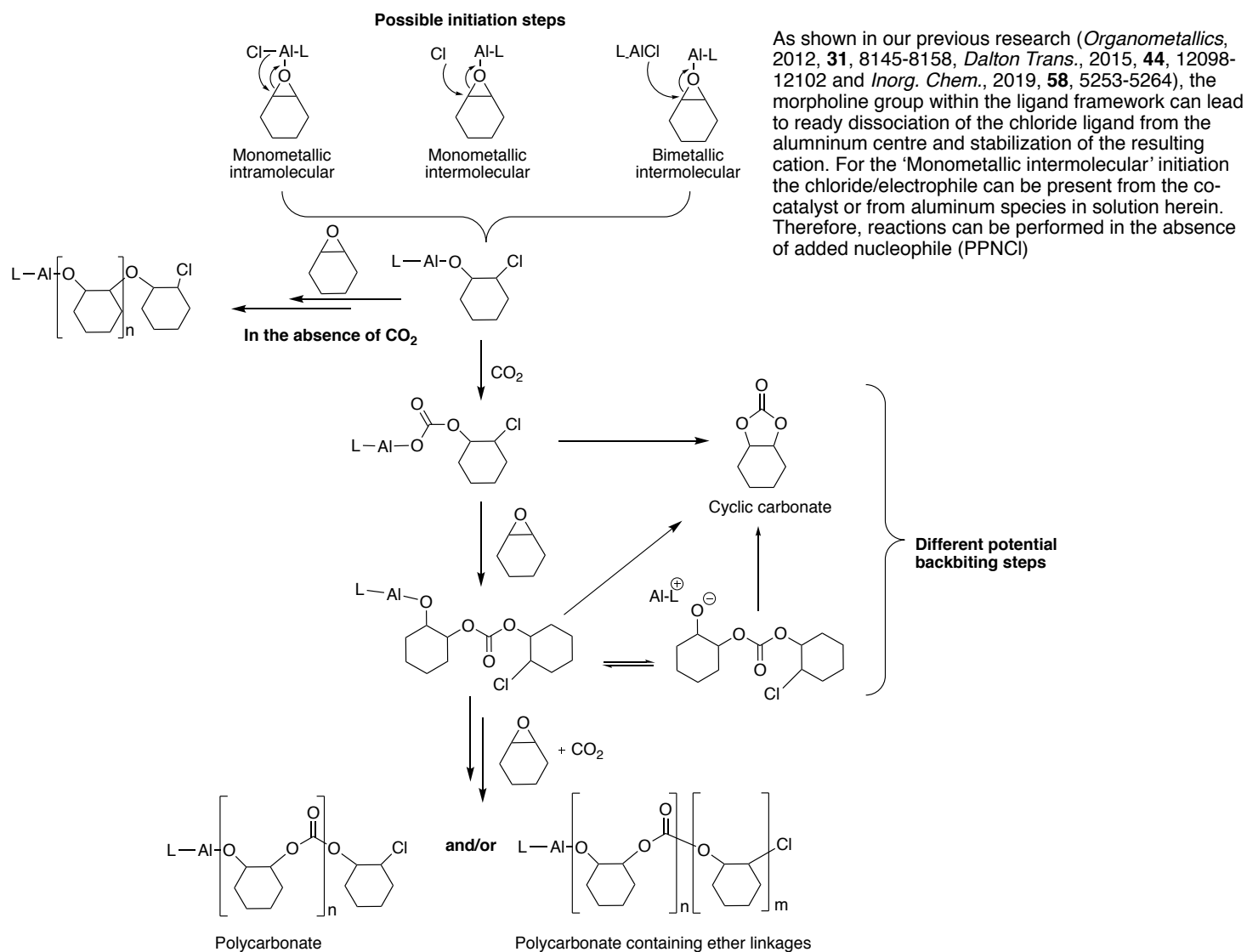
**Table S5.** Highly active catalyst systems for copolymerization of CHO/CO<sub>2</sub>

Entry	Ref	Cat.	Cocat.	T (°C)	P (bar)	% copolymer	TOF (h <sup>-1</sup> )
1 <sup>a</sup>	1	<b>Zn<sub>2</sub></b>	-	100	40	83	85500
2 <sup>b</sup>	2	<b>MgCo</b>	-	140	20	>99	12460
3 <sup>c</sup>	3	<b>Co<sub>2</sub>salen</b>	PPNX	25	20	>99	1409

<sup>a</sup> 0.025 mol% catalyst <sup>b</sup> 0.05 mol% catalyst <sup>c</sup> 0.1 mol% catalyst, 0.2 mol% PPNX (X = 2,4-dinitrophenoxide)

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1. S. Kissling, M. W. Lehenmeier, P. T. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. B. Seemann and B. Rieger, *Chem. Commun.*, 2015, **51**, 4579-4582.
2. A. C. Deacy, A. F. R. Kilpatrick, A. Regoutz and C. K. Williams, *Nat. Chem.*, 2020, **12**, 372-380.
3. Y. Liu, W. M. Ren, J. Liu and X. B. Lu, *Angew. Chem. Int. Ed.*, 2013, **52**, 11594-11598.



**Figure S21.** Possible catalytic mechanisms for ROCOP mediated by Al complexes