

Supporting Information for

Lewis acid catalysed polymerisation of cyclopentenone.

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General Remarks: All manipulations were carried out using standard Schlenk techniques and a dry-box. Toluene and hexane were distilled over sodium while CH_2Cl_2 , 1,2-difluorobenzene, CDCl_3 and CD_2Cl_2 were distilled over CaH_2 . All solvents were stored over 4 Å molecular sieves. The NMR spectra were recorded on a Bruker Avance III 400 (^1H NMR at 400 MHz; ^{13}C NMR at 100 MHz, ^{11}B NMR at 128 MHz, ^{19}F NMR at 376 MHz and ^{27}Al NMR at 104 MHz) instrument. Tetramethylsilane was used as reference for ^1H and ^{13}C NMR, while ^{11}B , ^{19}F and ^{27}Al NMR spectra were recorded with respect to $\text{Et}_2\text{O}\cdot\text{BF}_3$, CCl_3F and $\text{AlCl}_3/\text{D}_2\text{O}$, respectively. The $\text{Dip}^{\text{LAI}}(\text{OTf})_2^{\text{S1}}$, $\text{Ph}^{\text{LH}}^{\text{S2}}$, $\text{Na}[\text{BAr}^{\text{Cl}_4}]^{\text{S3}}$, $\text{Xyl}^{\text{LAI}}\text{Cl}_2^{\text{S4}}$, $[\text{nBu}_4\text{N}]\text{OTf}^{\text{S5}}$ and $(\text{C}_6\text{F}_5)_3\text{B}\cdot\text{OH}_2^{\text{S6}}$ were synthesized according to the literature procedures. All dienophiles and 2,3-dimethylbutadiene were distilled prior to use. All other reagents were used as received. Mass spectrometry was performed by Agilent 6220 TOF MS system with a multimode dual nebuliser ESI/APCI source. FTIR was recorded using Shimadzu *IR Prestige-21* instrument. MALDI-TOF measurements were performed on a Shimadzu-MALDI 7090 instrument using aCHCA and DCTB with AgTFA.

General synthetic procedures and catalytic examinations

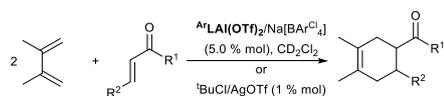
Synthesis of $\text{Xyl}^{\text{LAI}}(\text{OTf})_2$: $\text{Xyl}^{\text{LAI}}\text{Cl}_2$ (0.70 g, 1.74 mmol) and 2.1 equivalent of AgOTf (0.90 g, 3.50 mmol) were mixed in 20 mL 1,2-difluorobenzene. The reaction mixture was left to stir overnight in the absence of light. After filtration, the clear solution obtained was concentrated to 5 mL and transferred to a smaller Schlenk flask, following by layering with 10 mL hexane. Colorless crystals were grown in 2 days. After dryness under vacuum, the product was obtained as white solid. Yield: 0.72 g, 66%. ^1H NMR (400 MHz, CD_2Cl_2 , 25 °C): δ 1.94 (6H, s, CH_3 on backbone), 2.26 (12H, s, ortho- CH_3), 5.60 (1H, s, $\gamma\text{-CH}$), 7.18-7.19 (6H, m, ArH). ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 °C): δ 18.1 (s, CH_3 on backbone), 23.0 (s, CH_3 on Xyl), 99.8 (s, $\gamma\text{-C}$), 128.2 (s, ArC), 129.4 (s, ArC), 133.6 (s, ArC), 137.7 (s, ArC), 175.0 (s, CN). ^{27}Al NMR (104 Hz, CD_2Cl_2 , 25 °C): δ 61.1 (sharp, s). ^{19}F NMR (376 Hz, CD_2Cl_2 , 25 °C): δ -77.3 (sharp, s) HRMS (ESI) calculated for $\text{C}_{23}\text{H}_{26}\text{N}_2\text{O}_6\text{F}_6\text{AlS}_2$ [M + H]: 631.0952; Found: 631.0957.

Synthesis of $\text{Ph}^{\text{LAI}}\text{Cl}_2$: A sample of Ph^{LH} (1.0 g, 3.99 mmol) was added to a 100 mL Schlenk flask under nitrogen gas and dissolved in 40 mL of toluene under stirring. Flask was cooled with an ice bath before 1.30 ml of $n\text{BuLi}$ (2.5M in hexane) was added and the reaction mixture was stirred for 1 hour. This solution was then transferred to a Schlenk flask containing 0.558 g (4.19 mmol) of AlCl_3 suspended in about 20 ml at and the entire solution was left to stir overnight. The solution was then filtered, all volatiles removed under reduced pressure and the resulting residue was washed three times with 5 mL portions of *n*-hexane. After drying under reduced pressure, pale yellow was collected. Yield: 1.11 g, 80 %. ^1H NMR (400 MHz, CDCl_3 , 25 °C): δ 1.84 (s, 6H, CH_3), 5.14 (s, 1H, CH), 7.14 (m, 4H, ortho-Ph) 7.23 (m, 2H, para-Ph), 7.34 (m, 4H, meta-Ph) ppm. ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ 23.4 (CH_3), 126.8 (meta-C-Ph), 127.1 (para-C-Ph), 129.4 (ortho-C-Ph), 142.4 (CN of Ph), 171.0 (CN of ligand) ppm. ^{27}Al NMR (104 Hz, DCM, 25 °C): δ 99.6 (sharp, s). HRMS (ESI) calculated for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{AlCl}_2$ [M + H]: 347.0662; Found: 347.0673.

Synthesis of $\text{Ph}^{\text{LAI}}(\text{OTf})_2$: The same procedure was followed as described for $\text{Xyl}^{\text{LAI}}(\text{OTf})_2$: using 0.28 g (0.81 mmol) of $\text{Ph}^{\text{LAI}}\text{Cl}_2$ while obtaining 0.10 g (23%) of the crystalline product. ^1H NMR (400 MHz, CD_2Cl_2 , 25 °C): δ 1.95 (s, 6H, CH_3), 5.44 (s, 1H, CH), 7.15 (m, 4H, ortho-Ph) 7.32 (m, 2H, para-Ph), 7.41 (m, 4H, meta-Ph) ppm. ^{13}C NMR (100 MHz, CD_2Cl_2 , 25 °C): δ 23.3 (CH_3), 100.1 (CH of ligand), 126.2 (meta-C-Ph), 128.1 (para-C-Ph), 129.9 (ortho-C-Ph), 140.1 (CN of Ph), 174.3 (CN of ligand) ppm. ^{27}Al NMR (104 Hz, CD_2Cl_2 , 25 °C): δ 66.7 (sharp, s). ^{19}F NMR (376 Hz, CD_2Cl_2 , 25 °C): δ -77.8 (sharp, s) HRMS (ESI) calculated for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}_6\text{F}_6\text{AlS}_2$ [M + H]: 575.0326; Found: 575.0353.

General procedure for aluminum-catalyzed Diels-Alder reactions: $\text{NaBAr}^{\text{Cl}_4}$ (10 mg, 0.016 mmol) and 1 equivalent of $\text{Ar}^{\text{LAI}}(\text{OTf})_2$ (Ar = Dip or Xyl) was dissolved in 1 mL CD_2Cl_2 in a J. Young NMR tube. To this solution the diene 2,3-dimethyl-1,3-butadiene (52 mg, 72 μL , 0.64 mmol) and a dienophile (0.5 equiv with respect to the diene) was added. The reaction mixture was left for the time indicated in Tables 1 in the main text. After reaction completion, the corresponding products were purified by flash column chromatography on silica gel using hexane/ethyl acetate mixtures affording analytically pure Diels-Alder products. The trans/cis ratio (if applicable) was determined by ^1H NMR spectroscopy.

Table S1. $\text{DipLAI}(\text{OTf})_2/\text{[BAR}^{\text{Cl}_4}\text{]}$, $\text{XylLAI}(\text{OTf})_2/\text{Na[BAR}^{\text{Cl}_4}\text{]}$ and tBuCl/AgOTf (HBA) catalysed Diels-Alder reactions between 2,3-dimethyl-1,3-butadiene (**3**) and various dienophiles (**4-11**). The results are listed as: time (h), yield (%) and *trans/cis* or *endo:exo* for each run.



#	Enone	Adduct	$\text{DipLAI}(\text{OTf})_2$ / $\text{Na[BAR}^{\text{Cl}_4}\text{]}$	$\text{XylLAI}(\text{OTf})_2$ / $\text{Na[BAR}^{\text{Cl}_4}\text{]}$	HBA
1			1 h	1 h	1 h
			96 %	98 %	90 %
2			1 h	1 h	1 h
			96 %	91 %	89 %
3			12 h	12 h ^b	24 h
			93 %	86 %	58 %
			99:1	99:1	99:1
4			6 h	3 h	24 h
			80 %	97 %	33 % ^[c]
5			2 h ^[a]	-	1 h ^[d]
			92 %	-	-
6			24 h	24 h	1 h ^[d]
			87 %	23 %	-
			99:1	99:1	-

^[a]10% of the catalytic system used. ^[b]15 % of the catalyst used. ^[c]% conversion as estimated by ¹H NMR spectroscopy. ^[d]diene polymerization occurred within the first hour with no evidence for the formation of the product.

General procedure for Aluminum-catalyzed polymerization of cyclopentenone: In a majority of performed polymerization studies 2.5 mol% of the Xyl-based catalytic system was used with respect to cyclopentenone. A typical procedure is as following: $\text{XylLAI}(\text{OTf})_2$ (28 mg, 0.044 mmol) and $\text{NaBAR}^{\text{Cl}_4}$ (28 mg, 0.044 mmol) were dissolved in 2 mL of DCM in a 10 mL round-bottomed flask containing a stir bar in the glove box. To this solution, 2-cyclopenten-1-one (150 μL , 1.78 mmol) was added. The reaction mixture was left to stir for 3h and then quenched with 20 mL of methanol. Addition of methanol also resulted in precipitation of the polymer. This crude material was isolated through filtration, re-dissolved in 0.5 mL of THF, and then precipitated twice into 20 mL of methanol. The obtained polymer was dried under vacuum at 40 °C overnight. Yield: 87 mg, 59%. ¹H NMR (400 MHz, CD_2Cl_2 , 25 °C): δ 1.0 – 3.5 ppm (broad, aliphatic). ¹³C NMR (100 MHz, CD_2Cl_2 , 25 °C): δ 20-25, 38-40, 49-51 (all aliphatic), 119-121 (carbonyl). FTIR (KBr pellets): 1728 cm^{-1} (C=O stretch). GPC: $M_n = 36000$, $M_w = 59900$, $D = 1.66$.

Polymerization of cyclopentenone involving $\text{DipLAI}(\text{OTf})_2$ or $\text{PhLAI}(\text{OTf})_2$ was performed according to the procedure described above except that 5 mol% of these catalytic systems were used. According to the ¹H NMR spectroscopic studies, 75 and 16 % of cyclopentenone was consumed after 5 h and 6 days, respectively, for these two catalytic systems. Please also see Figure S16 for more details.

Polymerization studies involving 2-cyclohexen-1-one and 2-cyclohepten-1-one using the Xyl-based catalytic system were performed the abovementioned procedure resulting in insoluble materials in yields of 50% (6 h) and 23% (24 h), respectively. Due to poor solubilities in most common organic solvents, these materials have been characterized by FTIR only.

2-cyclohexen-1-one: FTIR (KBr pellets): 1707 cm^{-1} (C=O stretch).

2-cyclohepten-1-one: FTIR (KBr pellets): 1681 cm^{-1} (C=O stretch).

Crystallographic methods: A crystal was mounted onto a nylon loop and placed in the cold N_2 stream (T 123 K) of a Rigaku Synergy S diffractometer, fitted with a HyPix6000 hybrid photon counting detector. Data were collected using CuK α ($\lambda = 1.54178 \text{ \AA}$) radiation and processed, including an empirical absorption correction (multi-scan) with the proprietary software CrysAlisPro.^{S7} The structure was solved and refined by conventional methods using the SHELX2018 software.^{S8} Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in calculated positions using a riding model.

Crystallographic data for ^{Xyl}**LAI(OTf)₂**: C₂₃H₂₅AlF₆N₂O₆S₂, M_r 630.55, Triclinic, P-1, a = 9.4060(2) \AA , b = 11.1167(2) \AA , c = 15.5637(3) \AA , $\alpha = 75.810(2)^\circ$, $\beta = 72.977(2)^\circ$, $\gamma = 66.135(2)^\circ$, V = 1408.04(5) \AA^3 , Z = 2, $\rho_c = 1.487 \text{ g cm}^{-3}$, T = 123(2) K, $\lambda = 1.54184 \text{ \AA}$; 28857 reflections collected, 5837 independent reflections ($R_{\text{int}} = 5.75\%$), which were used in all calculations; R1 = 0.0396, wR2 = 0.1015 for $I > 2\sigma(I)$ and R1 = 0.0455, wR2 = 0.1059 for all unique reflections; maximum and minimum residual electron densities 0.379 and -0.421 e\AA^{-3} . CDCC: 2175768.

Crystallographic data for ^{Ph}**LAICl₂**: C₄₁H₄₂Al₂Cl₄N₄, M_r 786.54, Monoclinic, P2₁/n, a = 6.29940(10) \AA , b = 22.3513(4) \AA , c = 14.5043(2) \AA , $\beta = 90.5240(10)^\circ$, V = 2042.12(6) \AA^3 , Z = 2, $\rho_c = 1.279 \text{ g cm}^{-3}$, T = 123(2) K, $\lambda = 1.54178 \text{ \AA}$; 26370 reflections collected, 4275 independent reflections ($R_{\text{int}} = 6.92\%$), which were used in all calculations; R1 = 0.0483, wR2 = 0.1346 for $I > 2\sigma(I)$ and R1 = 0.0517, wR2 = 0.1383 for all unique reflections; maximum and minimum residual electron densities 0.497 and -0.466 e\AA^{-3} . CDCC: 2175769.

Crystallographic data for ^{Ph}**LAI(OTf)₂**: C₁₉H₁₇AlF₆N₂O₆S₂, M_r 574.45, Monoclinic, C2/c, a = 20.7709(3) \AA , b = 10.35930(10) \AA , c = 13.0575(2) \AA , $\beta = 118.364(2)^\circ$, V = 2472.31(7) \AA^3 , Z = 4, $\rho_c = 1.543 \text{ g cm}^{-3}$, T = 123(2) K, $\lambda = 1.54178 \text{ \AA}$; 16389 reflections collected, 2606 independent reflections ($R_{\text{int}} = 6.57\%$), which were used in all calculations; R1 = 0.0416, wR2 = 0.1200 for $I > 2\sigma(I)$ and R1 = 0.0449, wR2 = 0.1235 for all unique reflections; maximum and minimum residual electron densities 0.287 and -0.344 e\AA^{-3} . CDCC: 2175770.

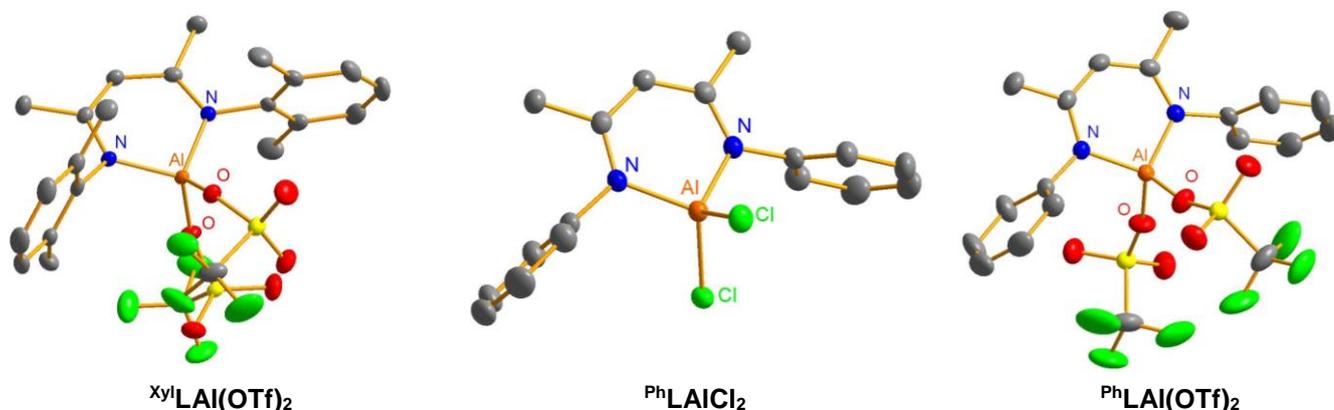


Figure S1. Molecular structures (ellipsoids drawn at 50% probability) for ^{Xyl}**LAI(OTf)₂**, ^{Ph}**LAICl₂** and ^{Ph}**LAI(OTf)₂** as analyzed by single crystal X-ray diffraction. The hydrogen atoms and disordered solvent molecules were omitted for clarity.

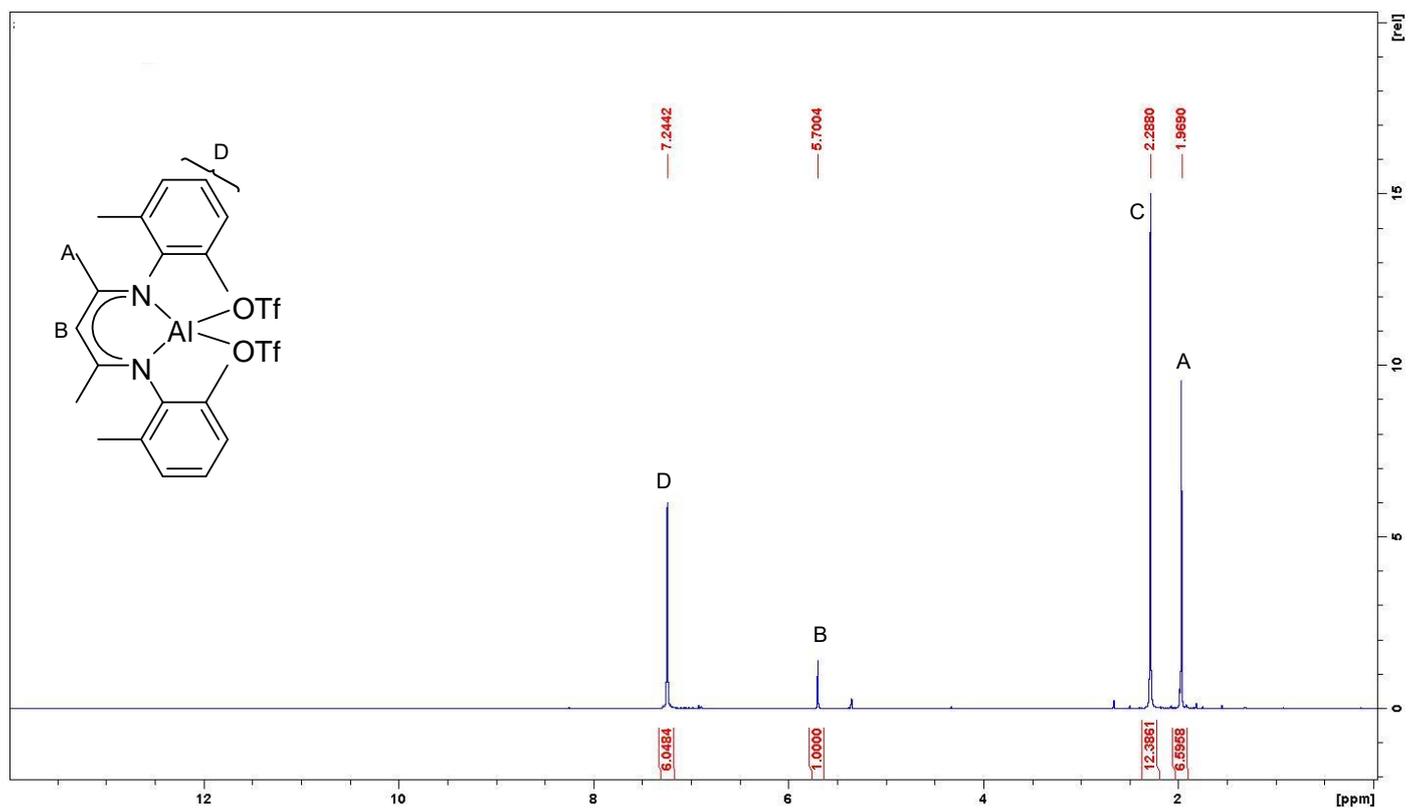


Figure S2. ^1H NMR for $^{xy}\text{LAI}(\text{OTf})_2$ in CD_2Cl_2 .

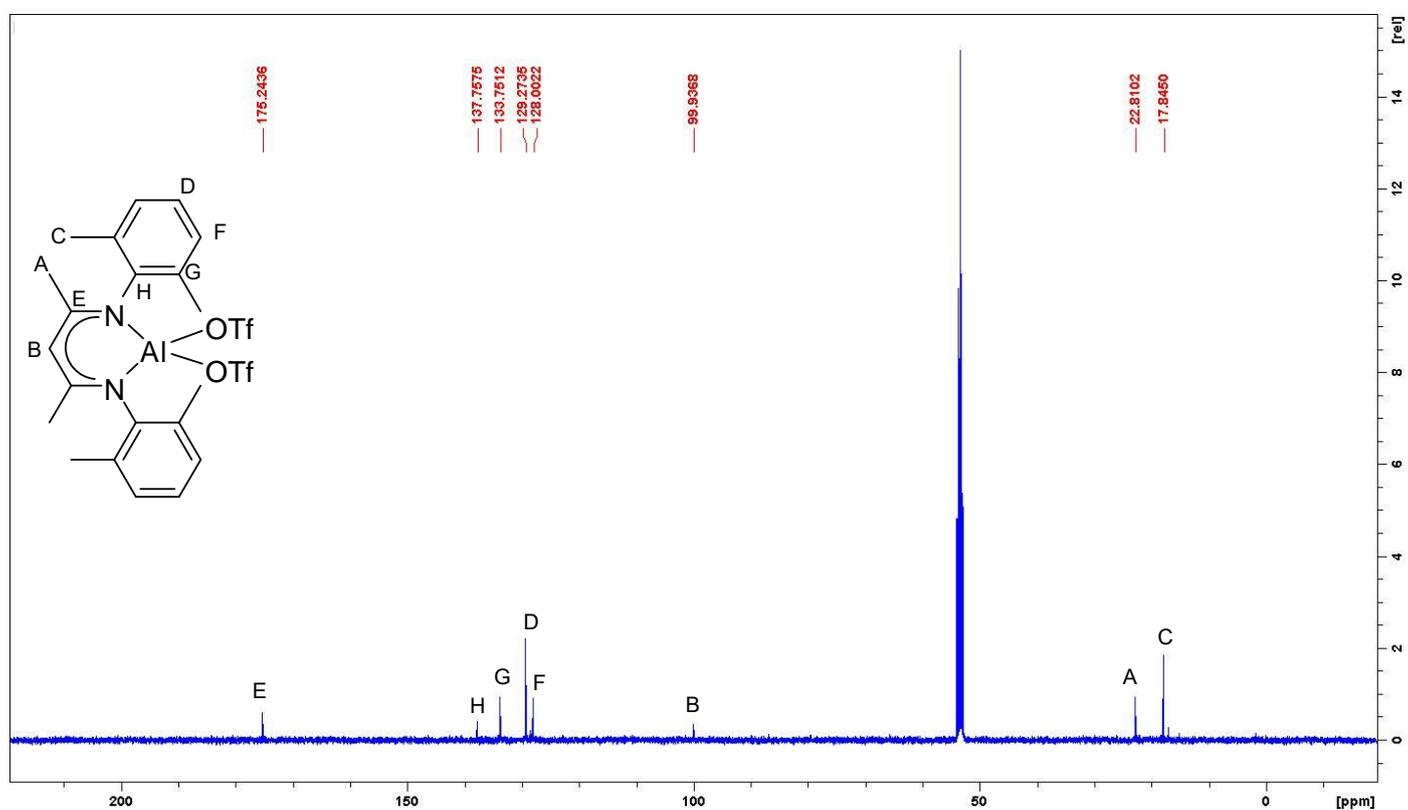


Figure S3. ^{13}C NMR for $^{xy}\text{LAI}(\text{OTf})_2$ in CD_2Cl_2 .

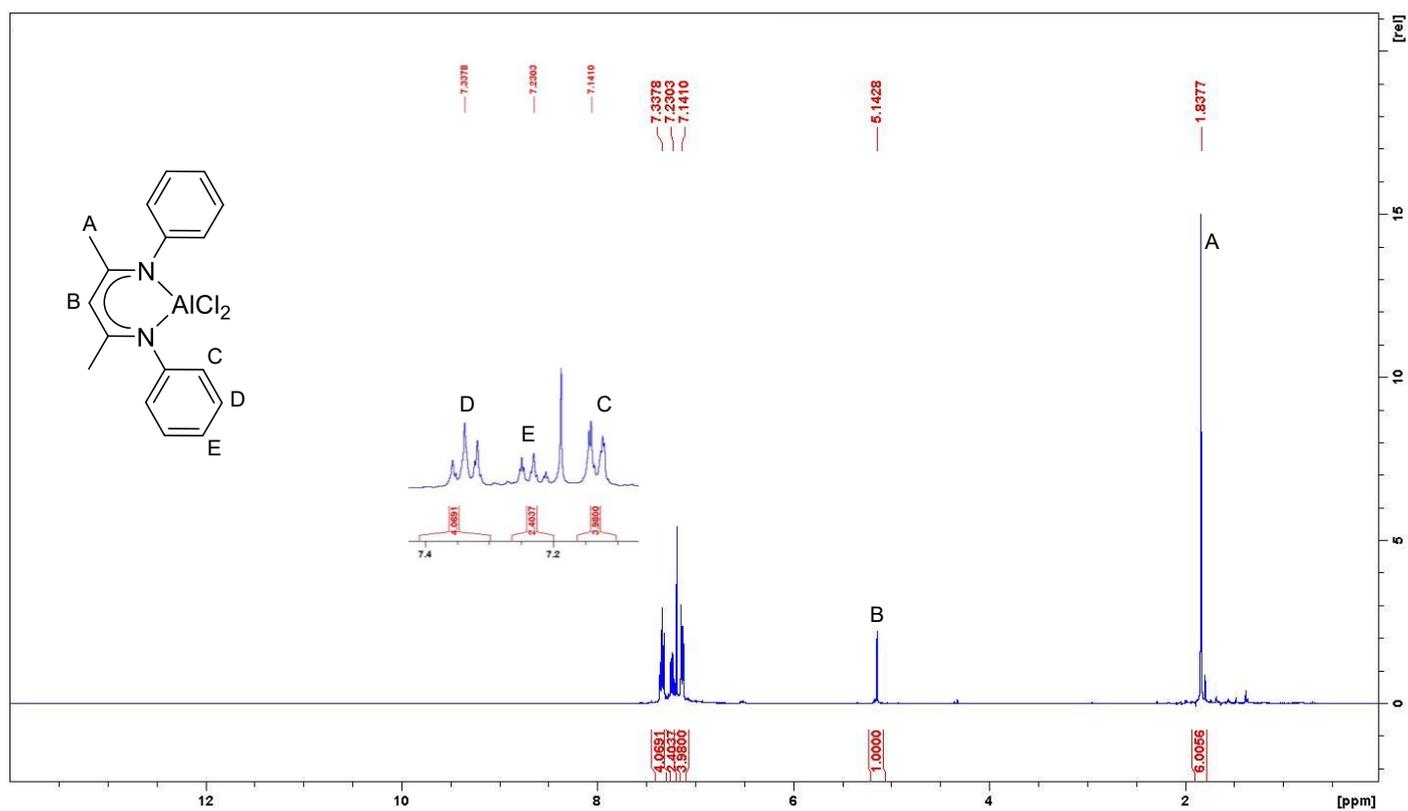


Figure S4. ^1H NMR for PhLAICl_2 in CDCl_3 .

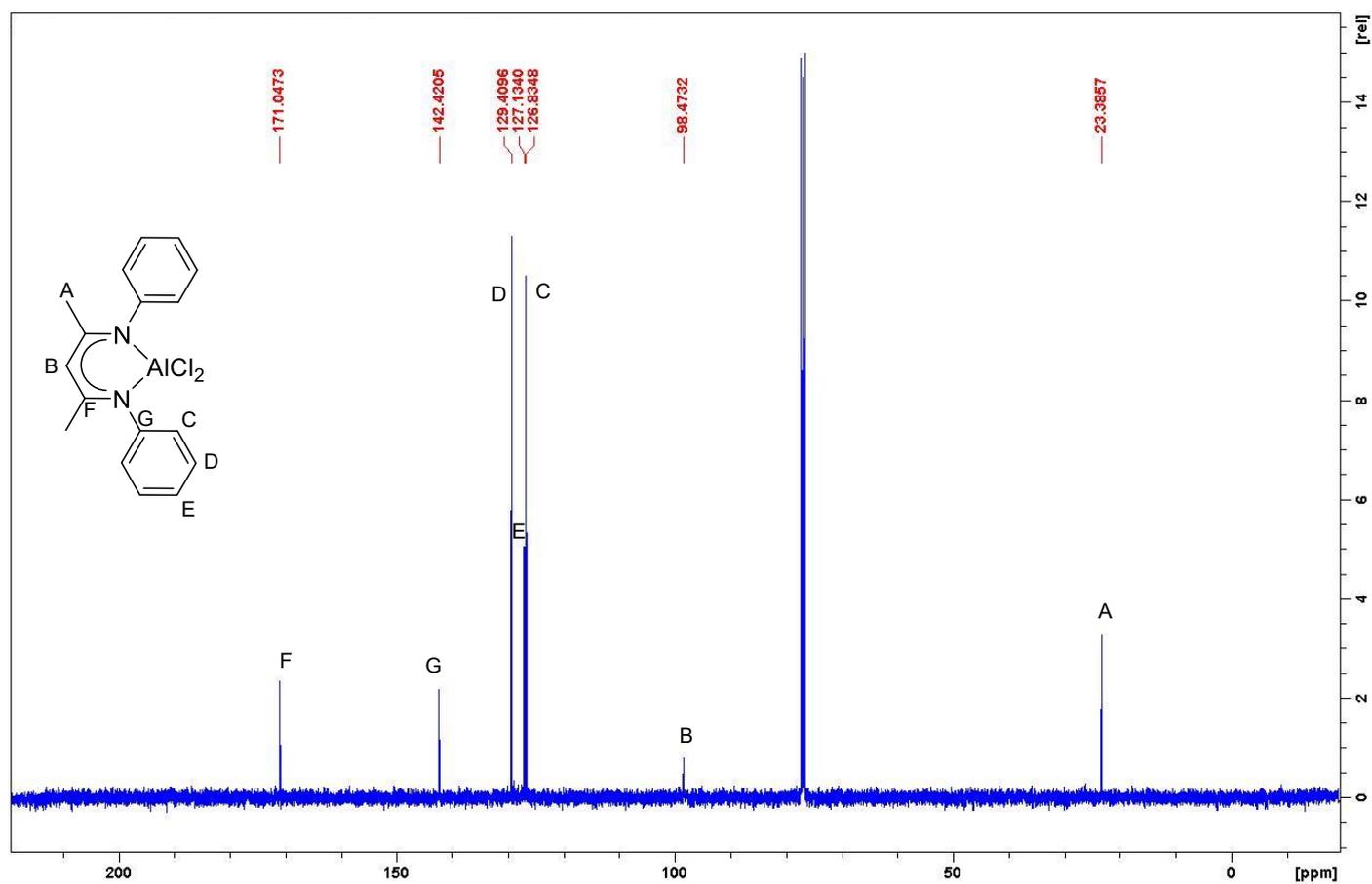


Figure S5. ^{13}C NMR for PhLAICl_2 in CDCl_3 .

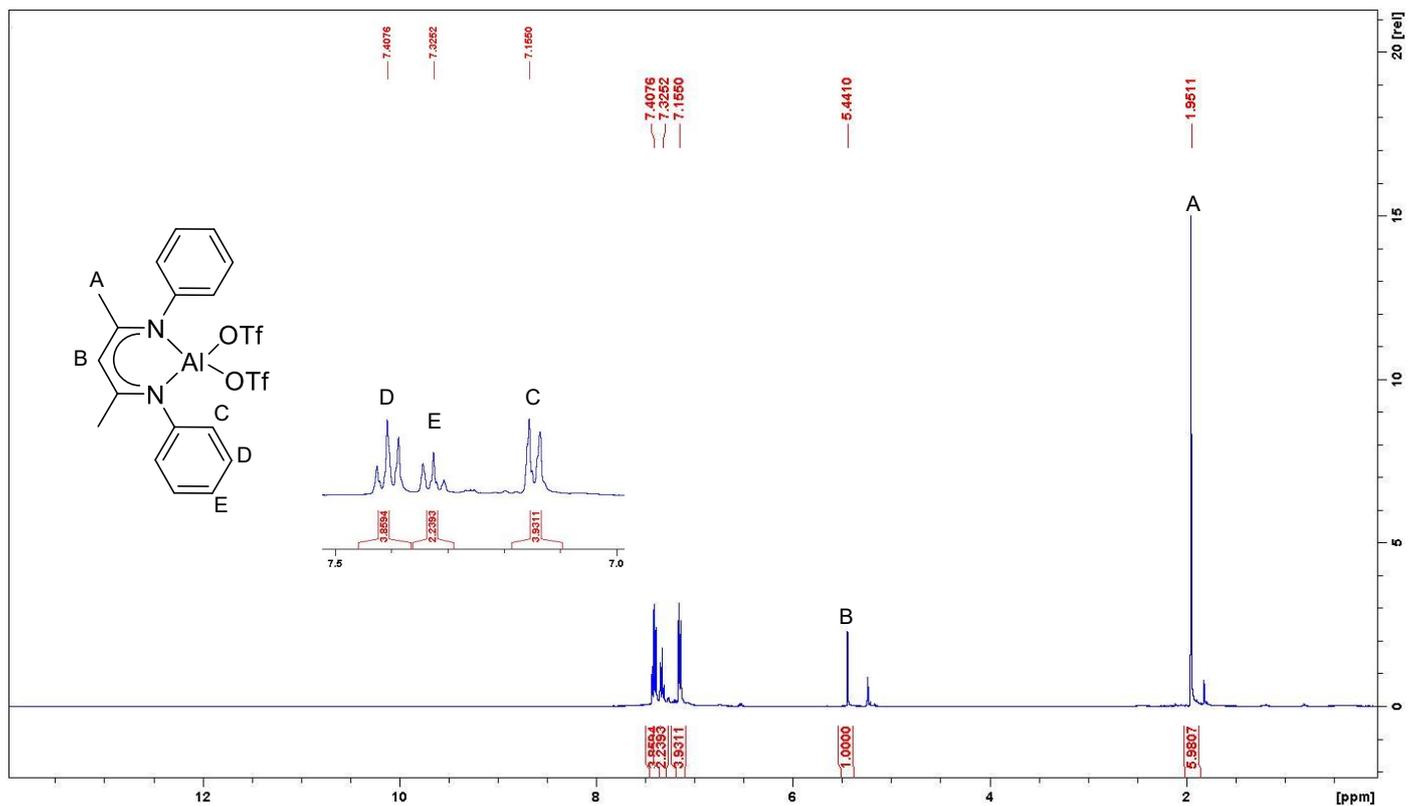


Figure S6. ^1H NMR for $\text{PhLAI}(\text{OTf})_2$ in CD_2Cl_2 .

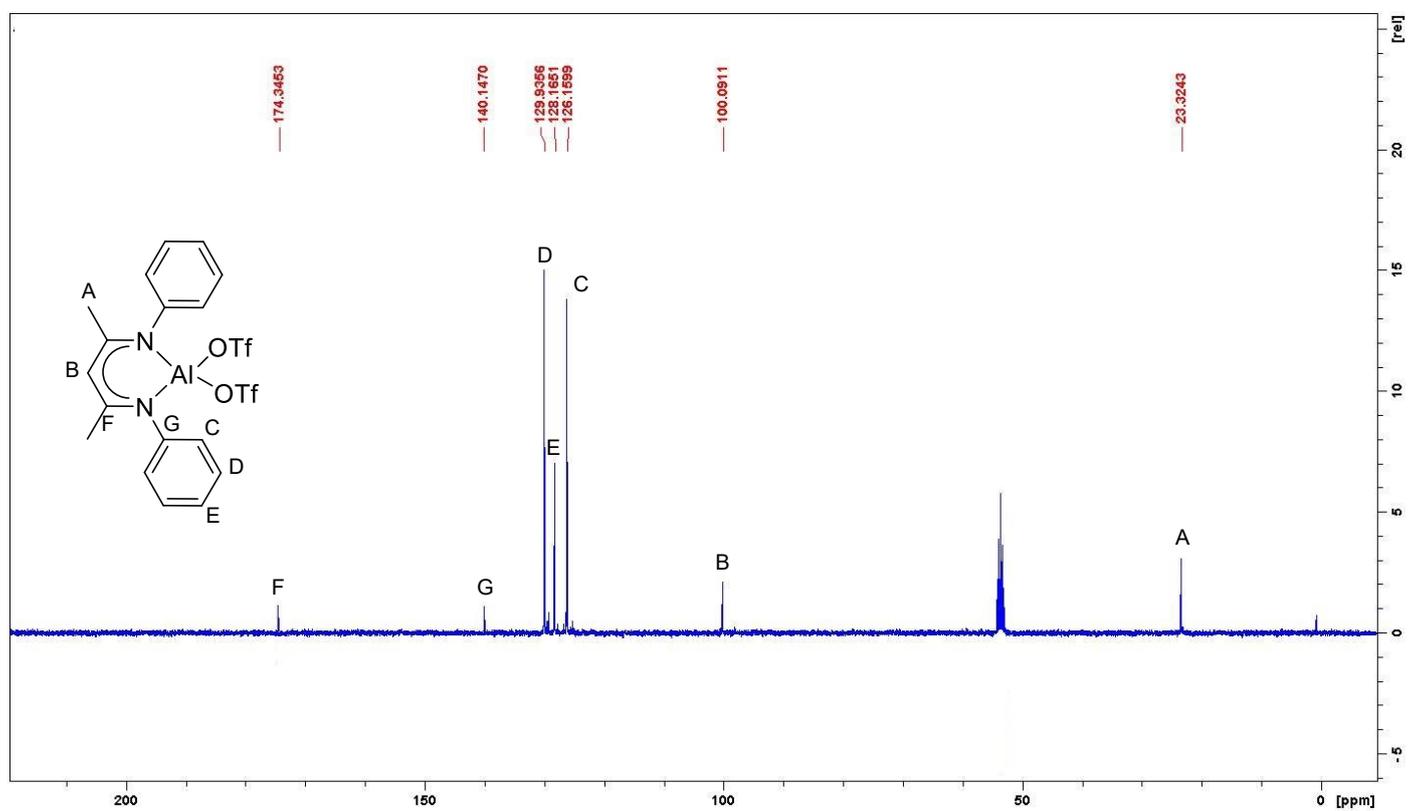


Figure S7. ^{13}C NMR for $\text{PhLAI}(\text{OTf})_2$ in CD_2Cl_2 .

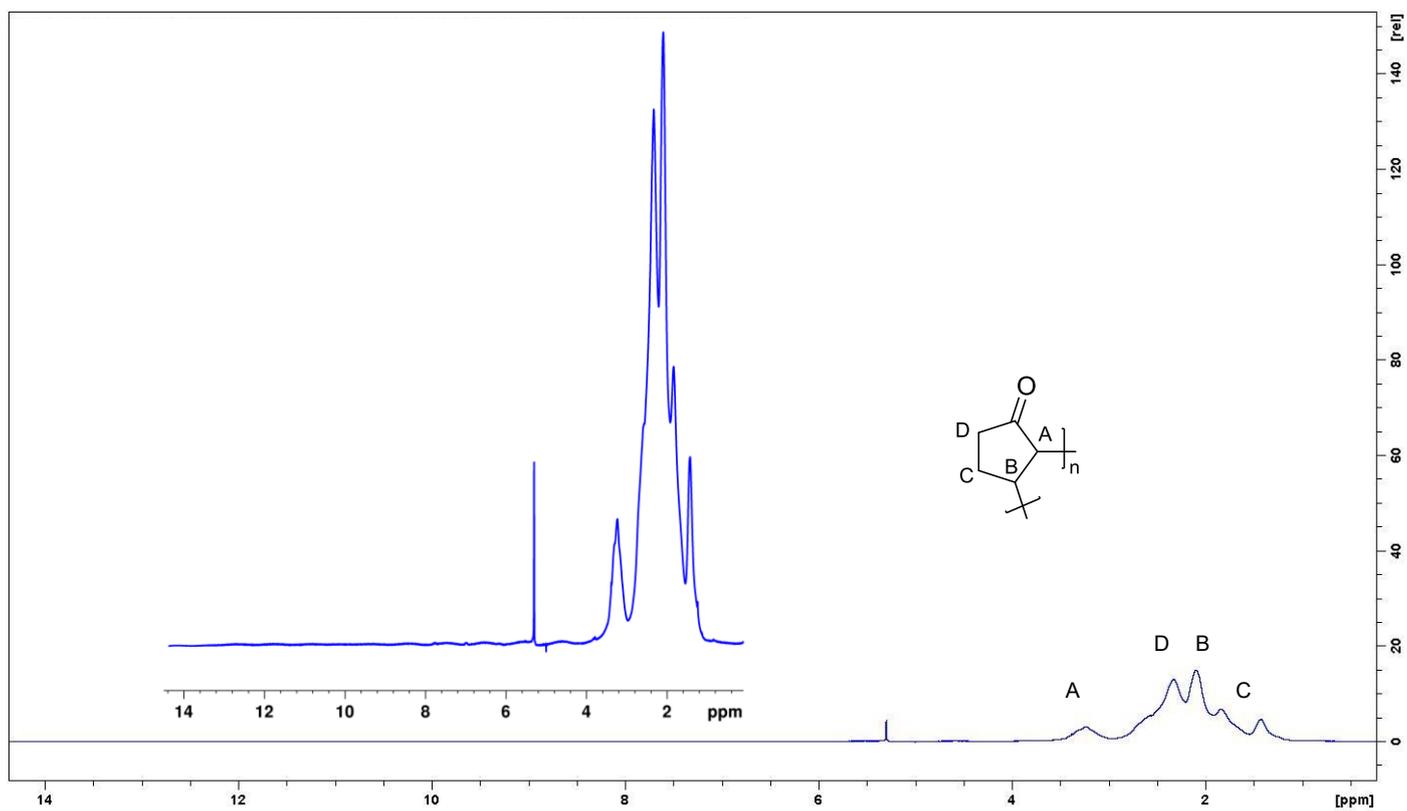


Figure S8. ^1H NMR for the polycyclopentenone in CD_2Cl_2 .

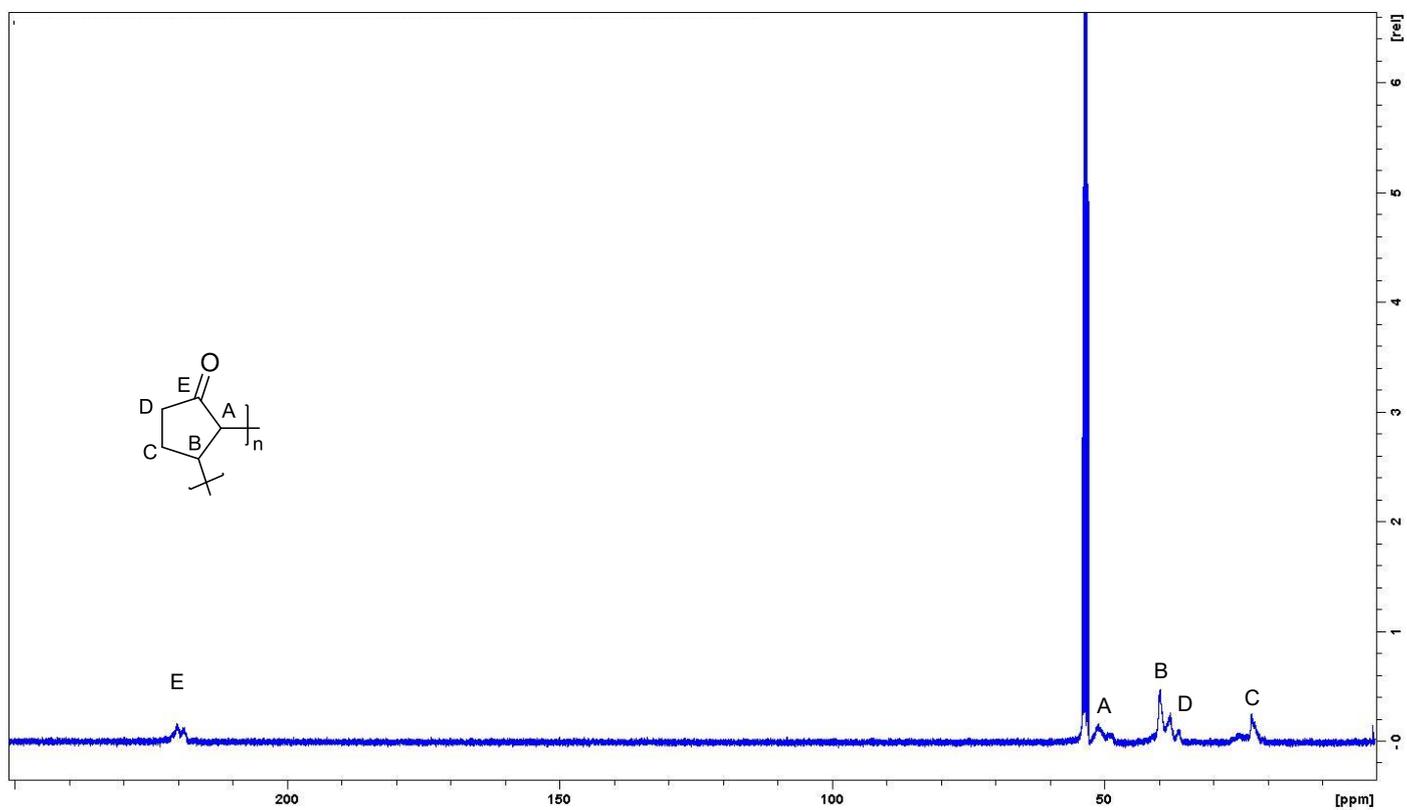


Figure S9. ^{13}C NMR for polycyclopentenone in CD_2Cl_2 .

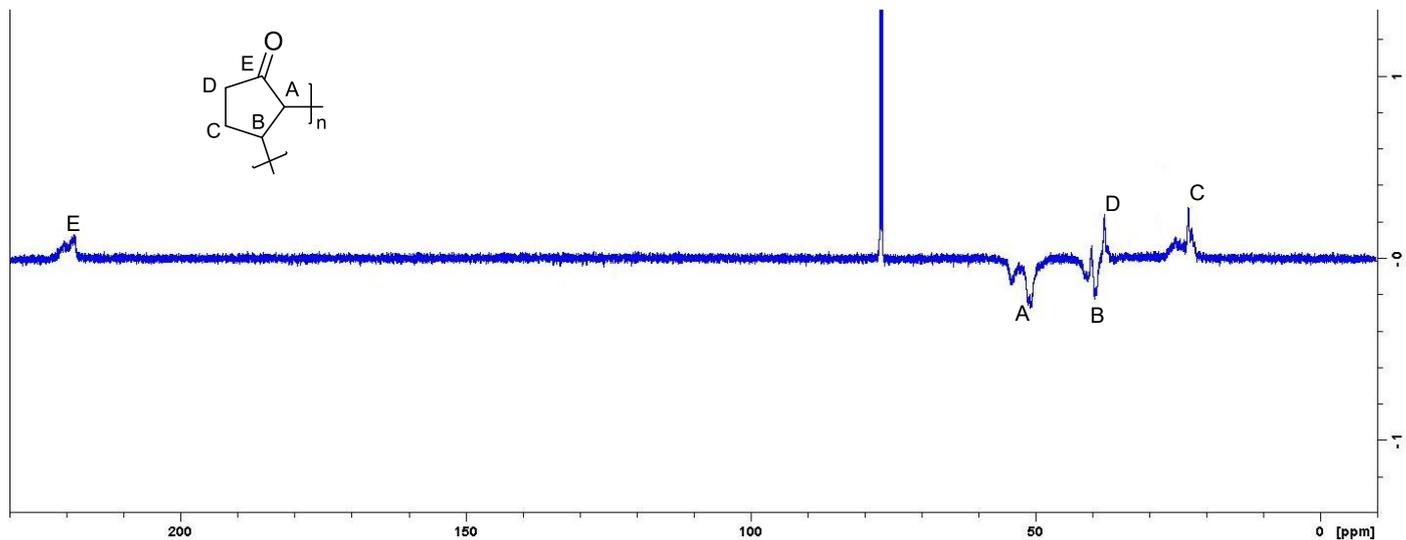


Figure S10. DEPT ^{13}C NMR for the polymer. This spectrum shows that the polymer contains both CH (signals A and B) and CH_2 (signals D and C) fragments.

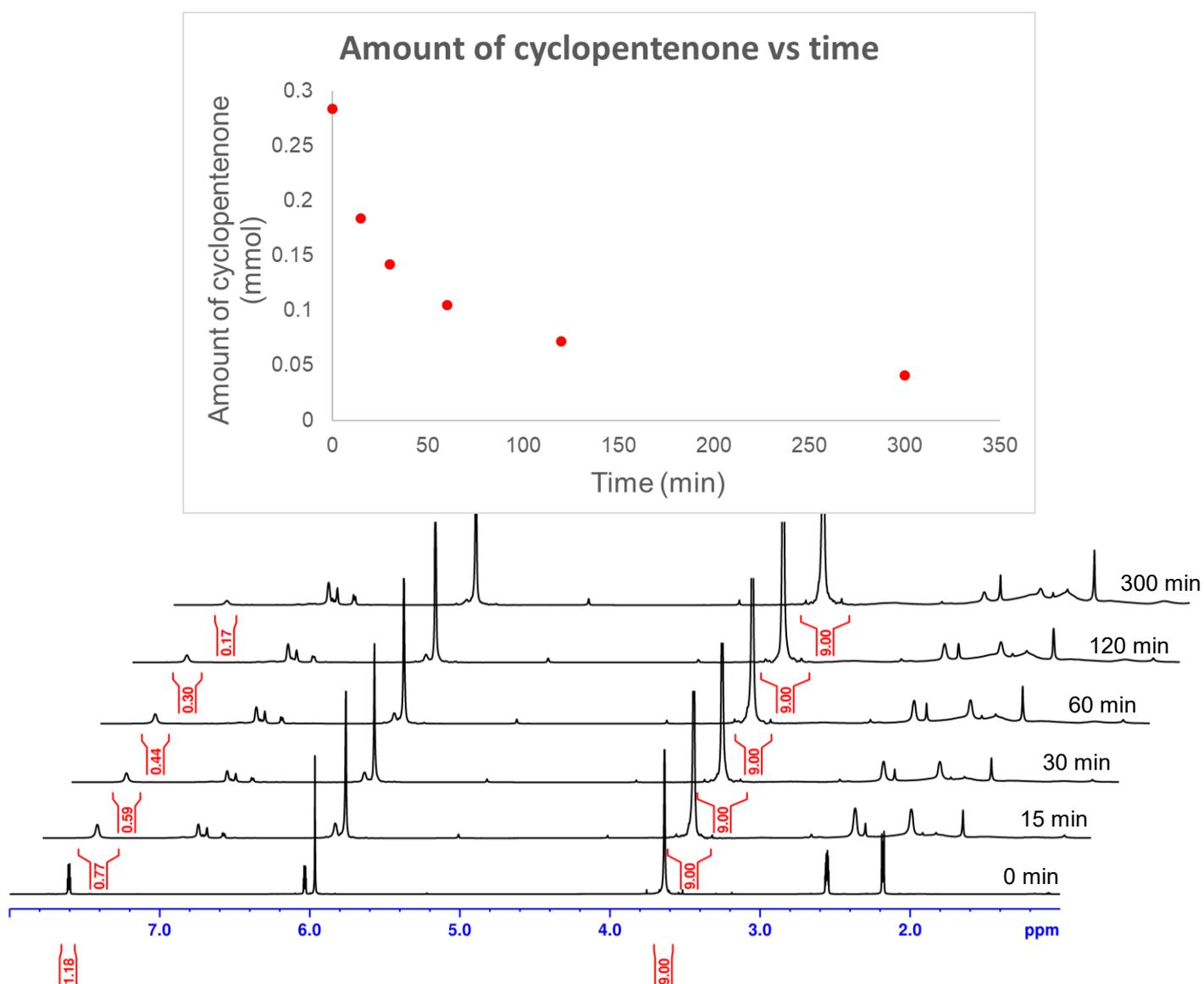


Figure S11. Disappearance of cyclopentenone in the presence of 2.5% of $^x\text{ylLAl}(\text{OTf})_2/\text{NaBAr}^{\text{Cl}_4}$ as observed by the ^1H NMR spectroscopy (bottom; using 1,3,5-trimethoxybenzene as a standard) and a plot of the obtained data (top).

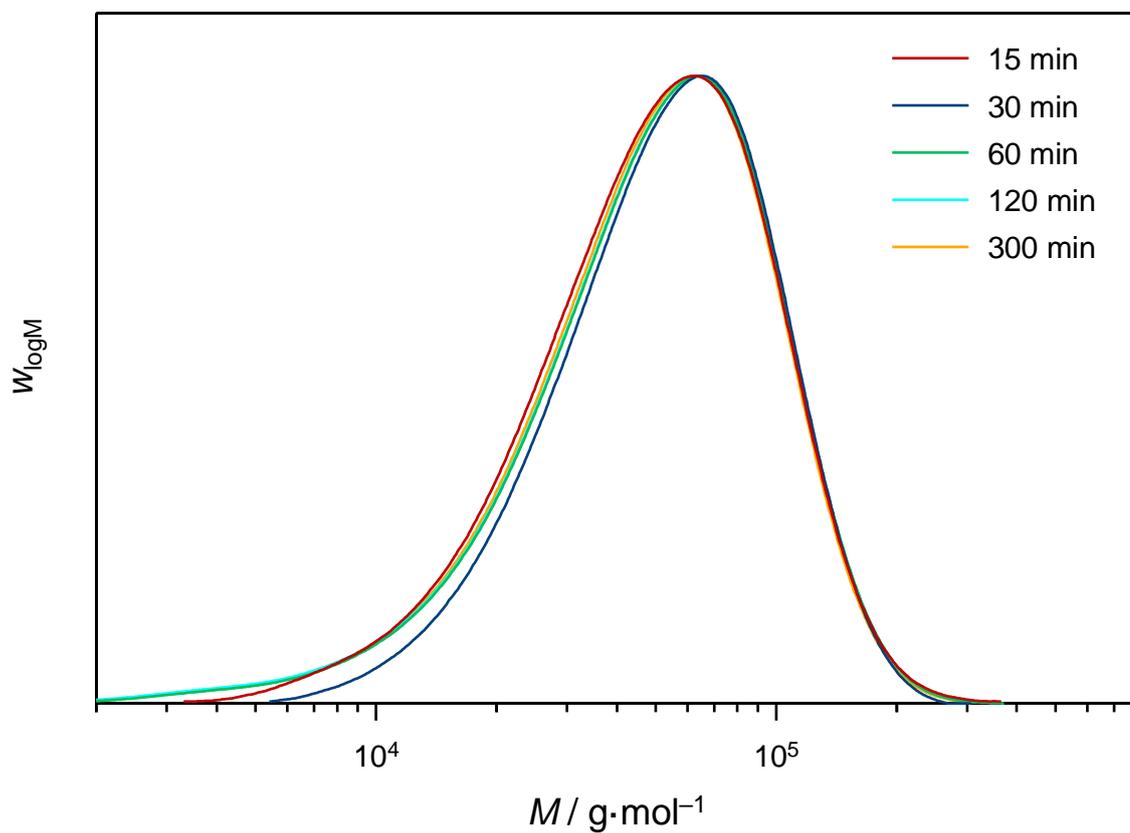


Figure S12. Molar mass distributions obtained from SEC for poly(cyclopentenone) taken at 15 min (brown), 1h (blue), 3h (purple) and 5h (red) after onset of the reaction using 2.5% catalyst loading (relative to polystyrene standards).

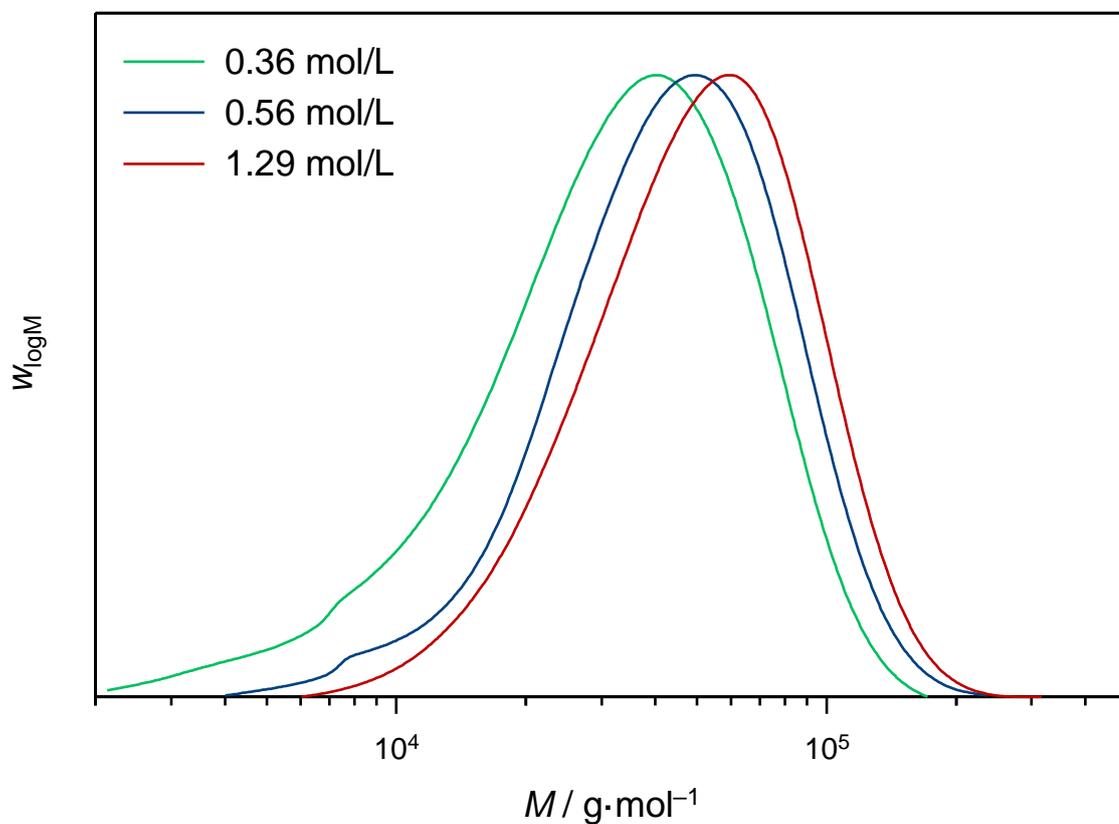


Figure S13. Molar mass distributions obtained from SEC for poly(cyclopentenone) obtained at 1.29 M (red), 0.56 M (green) and 0.36 M (Blue) concentration of the monomer using 2.5% catalyst loading (relative to polystyrene standards).

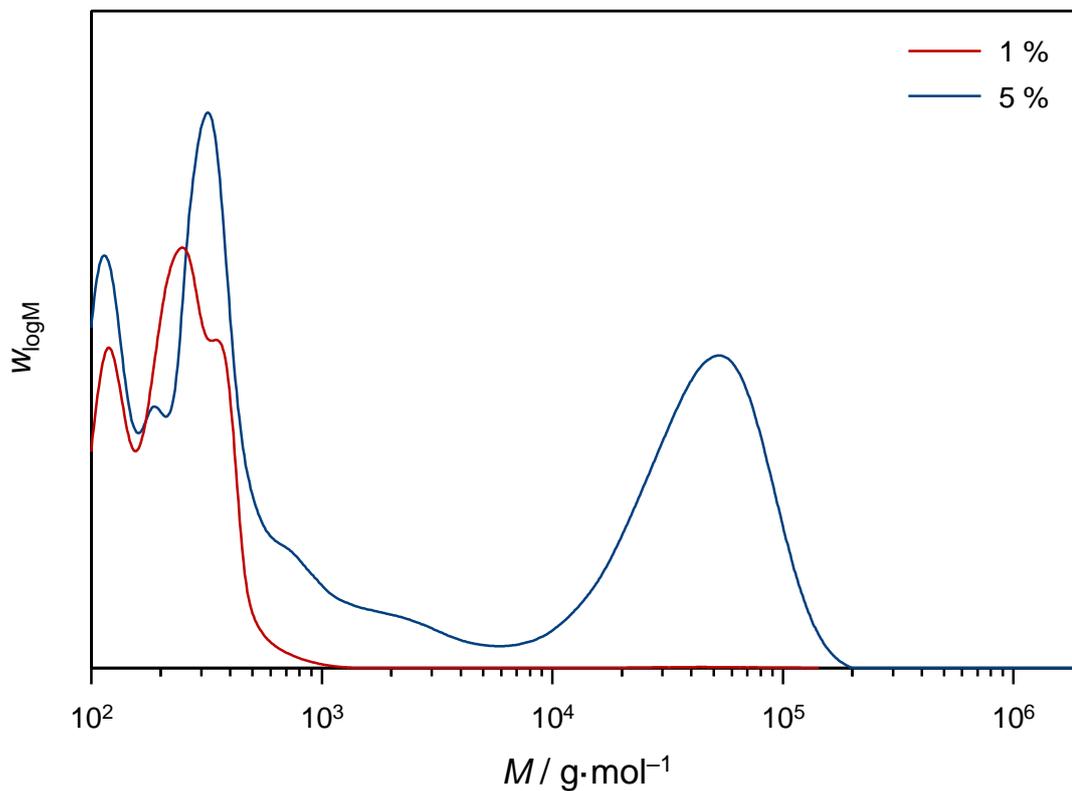


Figure S14. Molar mass distributions obtained from SEC for poly(cyclopentenone) obtained using 1% (red) and 5% (blue) of the catalyst (relative to polystyrene standards).

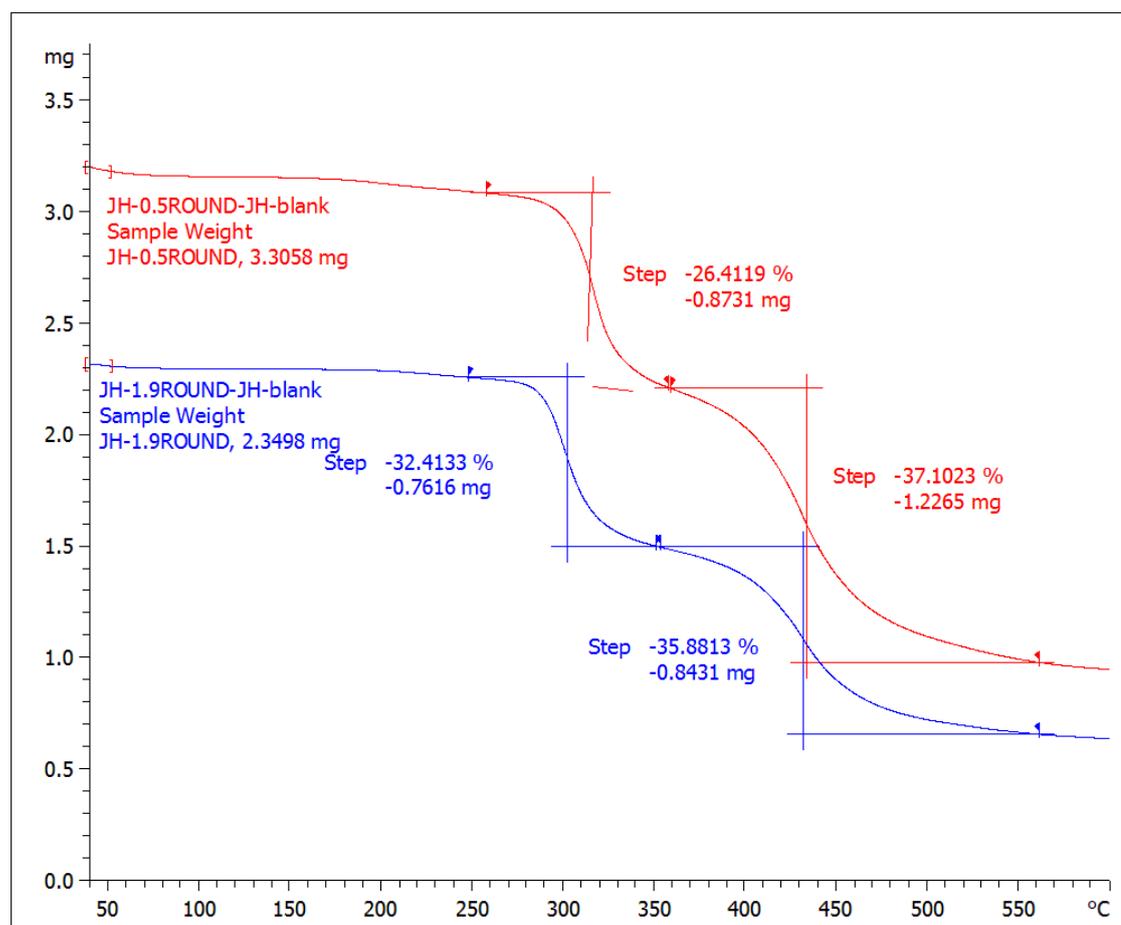


Figure S15. TGA analysis of two independently prepared polymer samples.

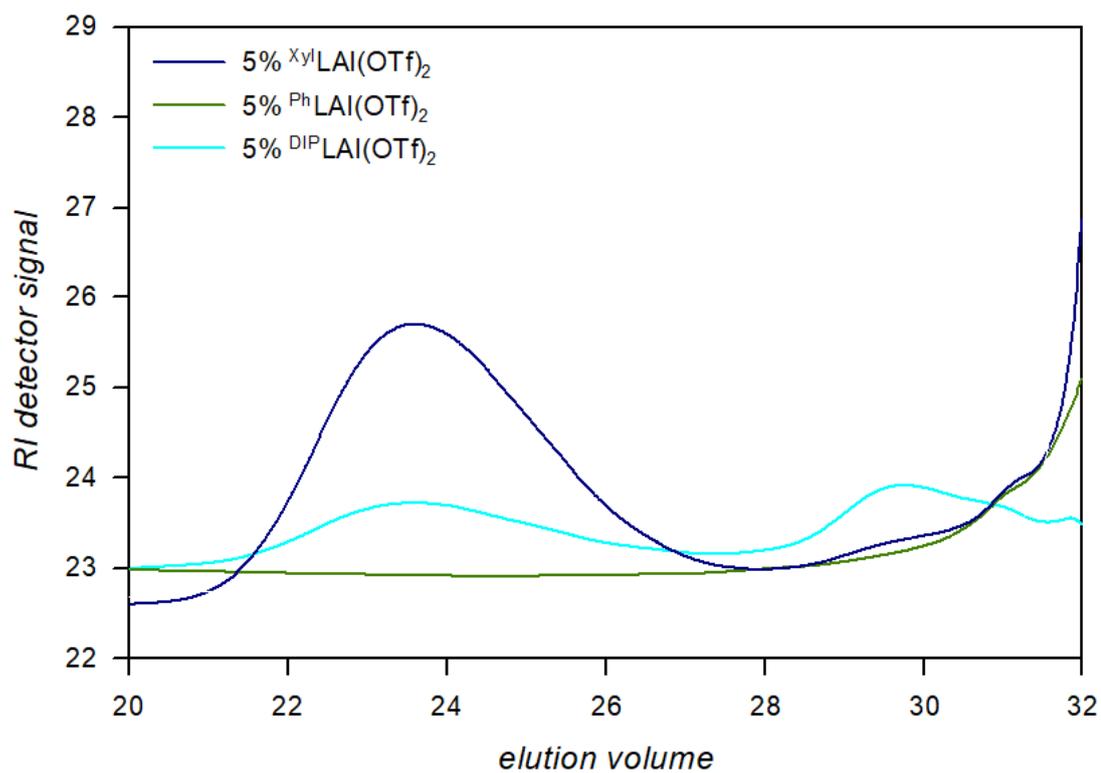


Figure S16. SEC elugrams for polymers obtained when using different aluminium-based Lewis acid complexes in the polymerisation of cyclopentenone.

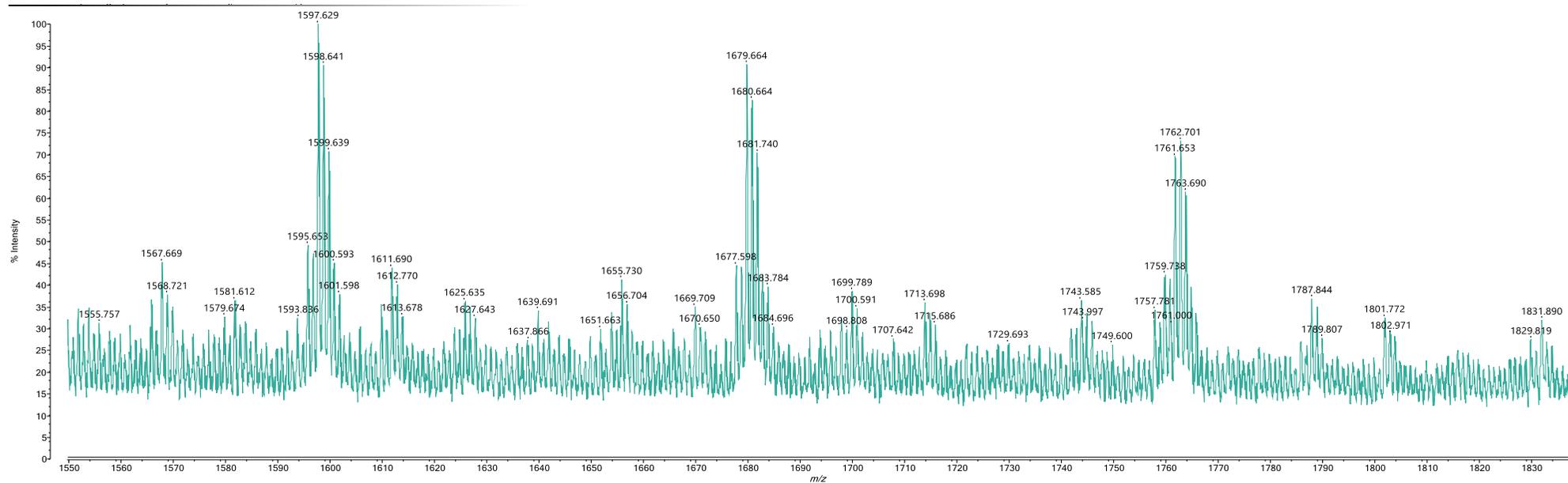
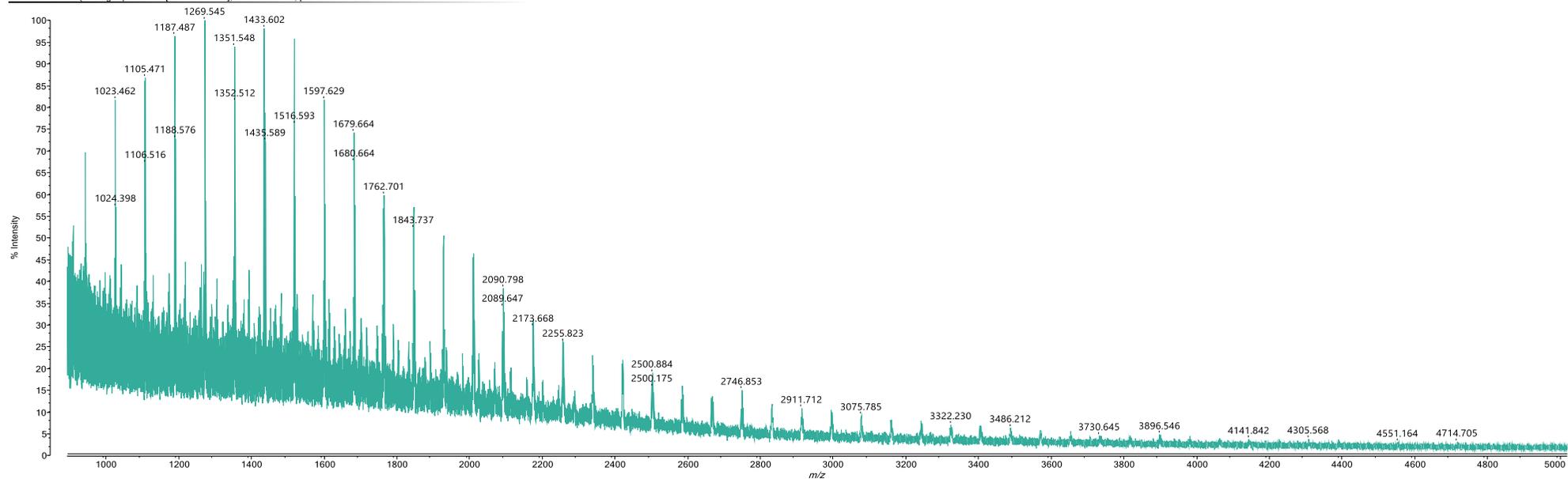


Figure S17. A typical MALDI-ToF mass spectrum of poly(cyclopentanone). The calculated molecular weight (exact mass) of the monomer (C_5H_6O) i.e. the repeating unit is 82.042.

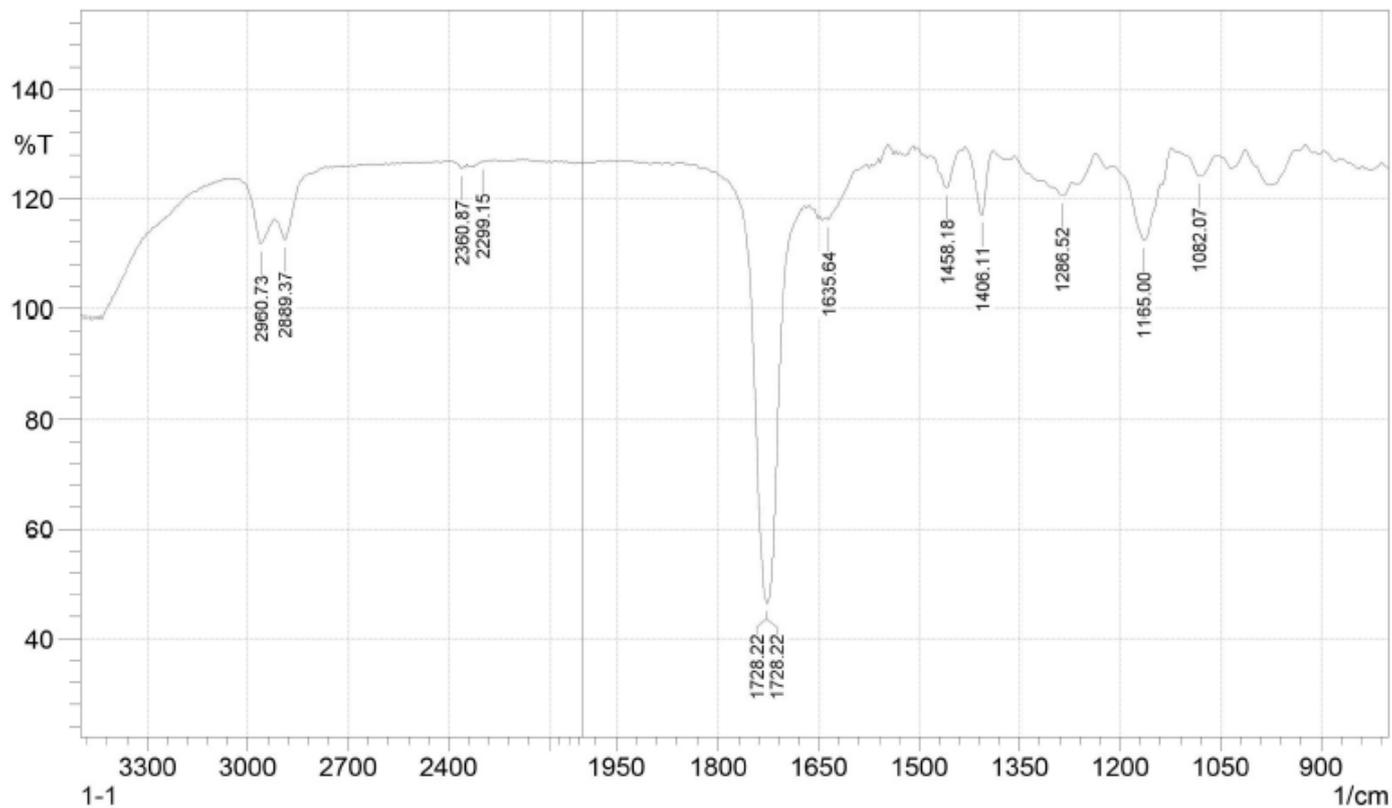


Figure S18. The FTIR spectrum for poly(cyclopentenone).

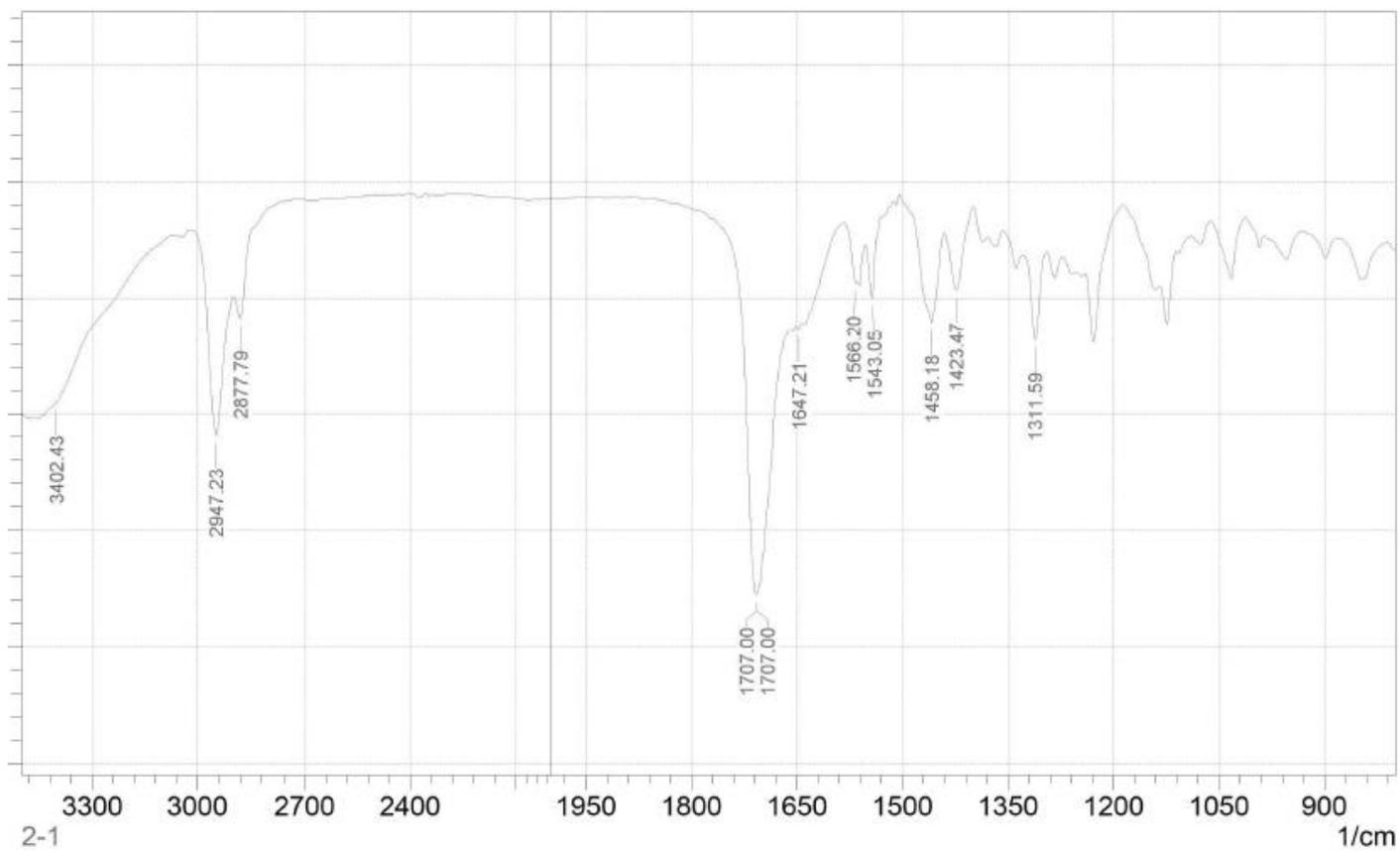


Figure S19. The FTIR spectrum for the polymerization of 2-cyclohexen-1-one.

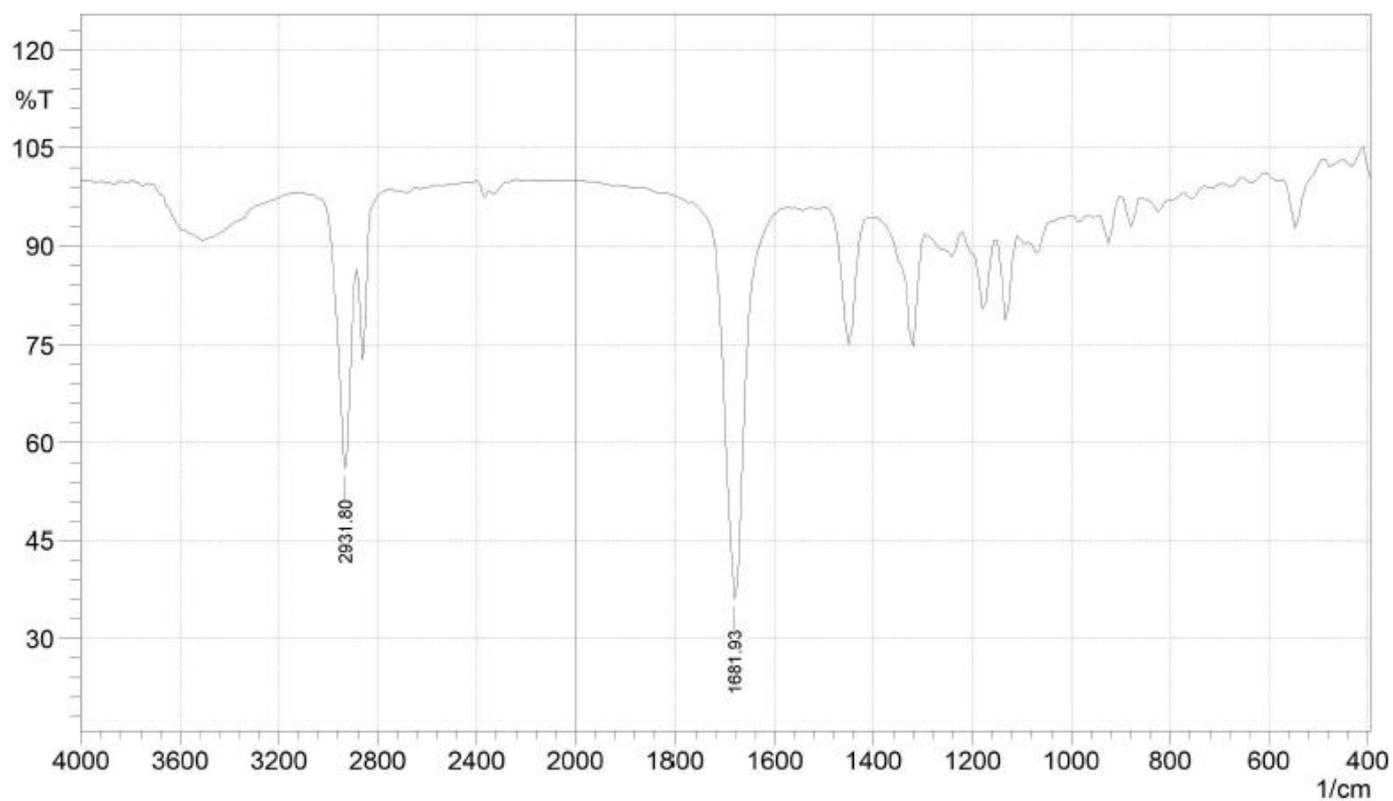


Figure S20. The FTIR spectrum for the polymerization of 2-cyclohepten-1-one.

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