

Supporting Information

Bio-based Synthesis of Cyclopentane-1,3-diamine and its Application in Bifunctional Monomers for Poly-condensation

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Contents:

S1.	Materials and Methods	S2
S1.1	<i>Chemicals</i>	S2
S1.2	<i>Decomposition study of CPDX</i>	S3
S1.3	<i>Overview of attempted hydrogenation reactions to yield CPDA</i>	S3
S2.	Analytical raw data	S6
S2.1	<i>NMR spectroscopy</i>	S6
S2.2	<i>FT-IR spectroscopy.</i>	S30
S2.3	<i>GC-FID chromatograms.</i>	S39
S2.4	<i>High Resolution Mass Spectrometry (HR-MS).</i>	S40
S2.5	<i>Gel Permeation Chromatography (GPC).</i>	S51
S2.6	<i>Thermogravic Analysis (TGA)</i>	S52
S2.7	<i>Differential Scanning Calorimetry (DSC)</i>	S53

S1. Materials and Methods

S1.1 Chemicals:

NOTE: All chemicals were used as received from the supplier without purification, unless stated otherwise (see section S1.2).

Ruthenium on carbon (5wt%, Strem Chemicals), Rhodium on carbon (5wt%, Sigma Aldrich), Palladium on carbon (10wt%, Sigma Aldrich), Platinum on carbon (5wt%, Sigma Aldrich), Ruthenium on alumina (5wt%, Sigma Aldrich), Heterogeneous Palladium Catalysts Kit I (Sigma Aldrich), Iridium on carbon (1wt% Sigma Aldrich), Shvo catalyst (98%, Strem Chemicals), Ru-BINAP-(OAc)₂ (98% Sigma Aldrich), Ru-BINAP-(Cl)-cymene (98% Sigma Aldrich), (Ir-COD-Cl)₂ (97% Sigma Aldrich), triphenylphosphine (99% Sigma Aldrich), 1,3-bis(diphenylphosphanyl)propane (97%, Sigma Aldrich), Josiphos SL-J002-1 (>97%, Sigma Aldrich), Zinc powder (60 – 200 µm mesh, 99+%, Sigma Aldrich), Furfuryl alcohol (97%, Acros), Cyclopentane-1,3-dione (95%, Matrix Chemicals Inc.), benzylamine (99%, Sigma Aldrich), Ammonia in dry methanol (7M, Sigma Aldrich), Hydroxylamine hydrochloride (98%), Hydrazine (50 – 60% in water, Sigma Aldrich), Acetic acid (>99.0%, VWR), *cis*-cyclopentane-1,3-diamine (98.5%, Matrix Chemicals Inc.), *trans*-cyclopentane-1,3-diamine (98.5%, Matrix Chemicals Inc.), γ -butyrolactone (99.5%, Fischer Scientific), γ -valerolactone (99%, Sigma Aldrich), γ -decalactone (98%, Sigma Aldrich), 5-Hydroxymethylfurfural (>98.5%, Matrix Chemicals Inc.), Diethyl adipate (>99%, Sigma Aldrich), Dimethyl isophthalate (99%, Sigma Aldrich), toluene-2,4-diisocyanate (95%, Sigma Aldrich), hexamethylene-1,6-diisocyanate (>99%, Sigma Aldrich), Methanol (HPLC grade, Biosolve) Ethanol (96%, VWR), isopropanol (HPLC grade, Biosolve), *s*-butanol (99%, Acros), *t*-butanol (\geq 99.0%, Sigma Aldrich), Ethyl acetate (HPLC grade, Biosolve), Cyclopentyl methyl ether (99%, Sigma Aldrich), Methyl *tert*-butyl ether (99%, Sigma Aldrich) 1,4-Dioxane (99.8%, Acros), Tetrahydrofuran (HPLC grade, Biosolve), 2-Methyltetrahydrofuran (>99%, dry, Sigma Aldrich), Toluene (HPLC grade, Biosolve), Heptane (99.5%, Sigma Aldrich), (Chloroform (HPLC grade, Biosolve), DMSO (>99%, dry, Sigma Aldrich). Naphthalene (\geq 99%, Alfa Aesar), Acetonitrile (LCMS grade, Biosolve), Celite® R566 (Acros), Silica (60 – 200 µm mesh, Acros), Hexane (HPLC grade, Biosolve), deuterium oxide (99.96%, Cambridge Isotope Laboratories), deuterated chloroform (99.96% Cambridge Isotope Laboratories), deuterated dimethyl sulfoxide (>99.7%, Fisher Scientific).

SI.2 Decomposition study of CPDX:



Figure SI.3.1: Photograph of decomposition studies for CPDX. Left triplet: 20°C; Middle triplet: 40°C; Right triplet: 60°C. Each triplet contains the solvents MeOH, THF, and toluene from left to right.

SI.3 Overview of attempted hydrogenation reactions to yield CPDA:

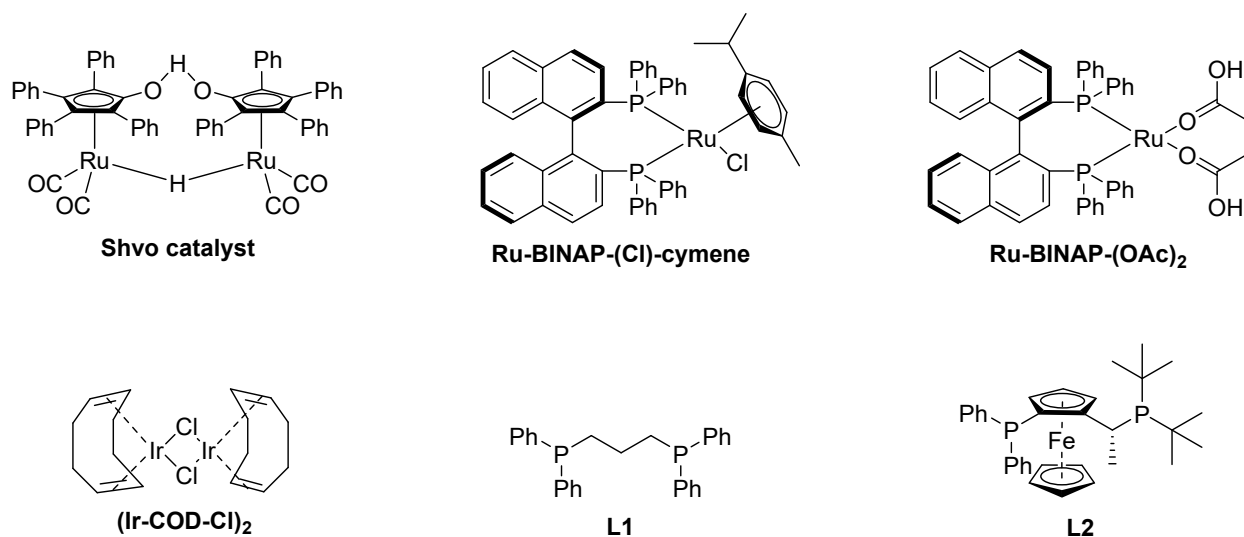


Figure SI.3.1: Tested homogeneous catalysts and ligands for the hydrogenation towards CPDA.

Table SI.3.1: List of attempted hydrogenation reactions of CPDI to afford CPDA:

Catalyst (Cat. / Sub.)	Additive	Solvent	P _{H2} (bar)	T (°C)	t (h)	Stirring (rpm)	Result
Shvo cat. (1%)	-	iPrOH	60	100	20	300	partial hydrog.
Shvo cat. (1%)	-	iPrOH	55	80	20	300	no reaction
Ru/C (10 wt%)	-	MeOH	50	80	20	300	no reaction
Rh/C (10 wt%)	-	MeOH	50	80	20	300	no reaction
Pd/C (10 wt%)	-	MeOH	50	80	20	300	no reaction
Pt/C (10 wt%)	-	MeOH	50	80	20	300	no reaction
Ru/C (10 wt%)	-	iPrOH	50	100	18	300	partial hydrog. + side products
Rh/C (10 wt%)	-	iPrOH	50	100	18	300	side products
Pd/C (10 wt%)	-	iPrOH	50	100	18	300	partial hydrog. + side products
Pt/C (10 wt%)	-	iPrOH	50	100	18	300	side products
Pd/C (10 wt%)	-	water	50	100	18	300	partial hydrog. + side products
Pd/C (10 wt%)	-	EtOAc	50	100	18	300	partial hydrog. + side products
Pd/C (10 wt%)	-	THF	50	100	18	300	partial hydrog. + side products
Pd/C (10 wt%)	-	toluene	50	100	18	300	partial hydrog. + side products
Ru-BINAP-(OAc) ₂	-	THF	50	50	22	300	no reaction
Ru-BINAP-(Cl)-cymene	-	THF	50	50	22	300	no reaction
{Ir(COD)Cl} ₂	-	EtOAc	50	50	3	300	no reaction
{Ir(COD)Cl} ₂	PPh ₃ (4 eq)	EtOAc	50	50	3	300	no reaction
{Ir(COD)Cl} ₂	L1 (2 eq)	EtOAc	50	50	3	300	no reaction
{Ir(COD)Cl} ₂	L2 (2 eq)	EtOAc	50	50	3	300	no reaction
{Ir(COD)Cl} ₂	-	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	PPh ₃ (4 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	L1 (2 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	L2 (2 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	I ₂ (8 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	PPh ₃ (4 eq) + I ₂ (8 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	L1 (2 eq) + I ₂ (8 eq)	MeOH	50	50	20	300	no reaction
{Ir(COD)Cl} ₂	L2 (2 eq) + I ₂ (8 eq)	MeOH	50	50	20	300	no reaction

Table SI.3.2: List of attempted hydrogenation reactions of CPDX to afford CPDA:

Catalyst (Cat. / Sub.)	Additive	Solvent	P _{H2} (bar)	T (°C)	t (h)	Stirring (rpm)	Result
Zn	HCl	water	N/A	20	24	500	no reaction
Zn	AcOH	water	N/A	20	24	500	no reaction
Shvo cat. (5%)	-	MeOH	55	80	20	300	no reaction
Ru/C (10 wt%)	-	MeOH	30	80	20	300	decomposition
Rh/C (10 wt%)	-	MeOH	30	80	20	300	decomposition + trace product
Pd/C (10 wt%)	-	MeOH	30	80	20	300	decomposition
Pt/C (10 wt%)	-	MeOH	30	80	20	300	decomposition
Ru/C (10 wt%)	-	THF	50	20	20	300	no reaction
Rh/C (10 wt%)	-	THF	50	20	20	300	no reaction
Pd/C (10 wt%)	-	THF	50	20	20	300	decomposition
Pt/C (10 wt%)	-	THF	50	20	20	300	decomposition
Ru/C (10 wt%)	-	THF	50	40	20	300	decomposition
Rh/C (10 wt%)	-	THF	50	40	20	300	product
Pd/C (10 wt%)	-	THF	50	40	20	300	decomposition
Pt/C (10 wt%)	-	THF	50	40	20	300	decomposition
Ru/C (10 wt%)	-	THF	50	40	20	300	decomposition
Rh/C (10 wt%)	-	THF	50	40	20	300	product
Pd/C (10 wt%)	-	THF	50	40	20	300	decomposition
Pt/C (10 wt%)	-	THF	50	40	20	300	decomposition
Ru/Al ₂ O ₃ (10 wt%)	-	THF	50	40	20	300	no reaction
Pt/Al ₂ O ₃ (10 wt%)	-	THF	50	40	20	300	decomposition
Pd/Al ₂ O ₃ (10 wt%)	-	THF	50	40	20	300	decomposition
Pd/CaCO ₃ (10 wt%)	-	THF	50	40	20	300	decomposition
Pd/BaSO ₄ (10 wt%)	-	THF	50	40	20	300	decomposition
Pd(OH) ₂ /C (10 wt%)	-	THF	50	40	20	300	decomposition
Ir/C (20 wt%)	-	THF	50	40	20	300	no reaction
Rh/C (10 wt%)	-	2-MeTHF	50	40	20	300	product
Rh/C (10 wt%)	-	MTBE	50	40	20	300	product
Rh/C (10 wt%)	-	CPME	50	40	20	300	product
Rh/C (10 wt%)	-	water	50	40	20	300	product
Rh/C (10 wt%)	-	MeOH	50	40	20	300	product
Rh/C (10 wt%)	-	EtOH	50	40	20	300	product
Rh/C (10 wt%)	-	iPrOH	50	40	20	300	product
Rh/C (10 wt%)	-	tBuOH	50	40	20	300	product
Rh/C (10 wt%)	-	EtOAc	50	40	20	300	product
Rh/C (10 wt%)	-	toluene	50	40	20	300	product
Rh/C (10 wt%)	-	dioxane	50	40	20	300	product
Rh/C (10 wt%)	-	dioxolane	50	40	20	300	decomposition
Rh/C (10 wt%)	-	DMSO	50	40	20	300	decomposition
Rh/C (10 wt%)	-	DMF	50	40	20	300	trace product
Rh/C (10 wt%)	-	CHCl ₃	50	40	20	300	trace product
Rh/C (10 wt%)	7M NH ₃	water	50	40	20	300	no reaction
Rh/C (10 wt%)	3.5M NH ₃	water/MeOH	50	40	20	300	trace product
Rh/C (10 wt%)	-	water/MeOH	50	40	20	300	product

S2. Substrate analysis:

S2.1 NMR spectroscopy:

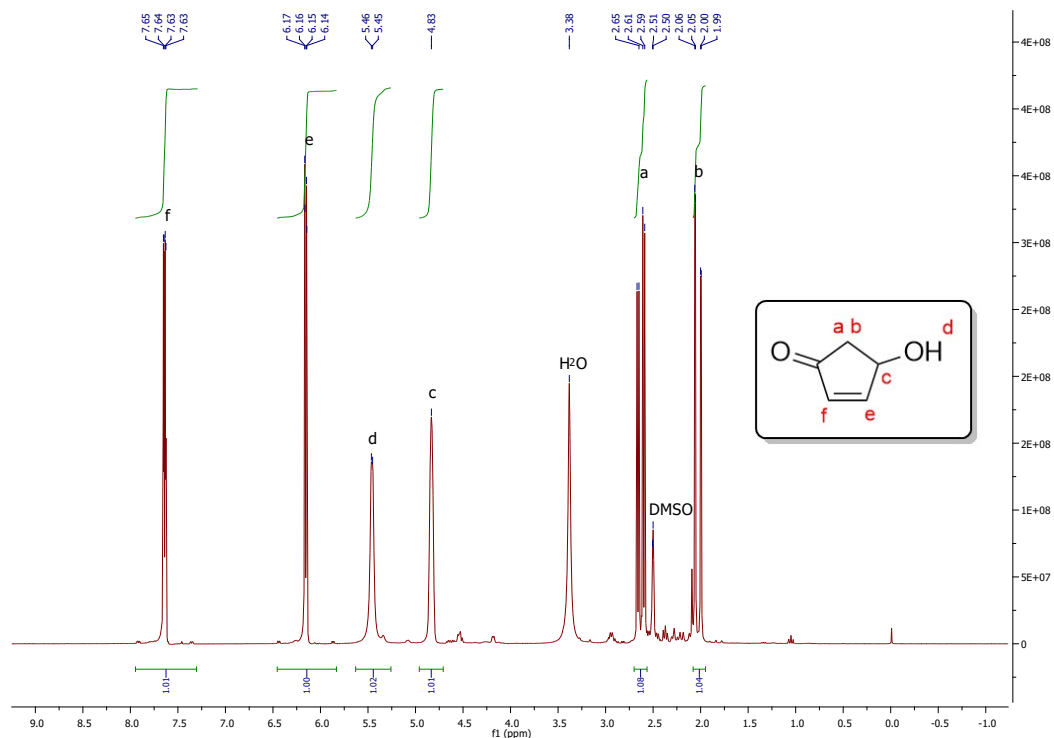


Figure S2.1.1: $^1\text{H-NMR}$ spectrum of 4-HCP in DMSO-d_6 .

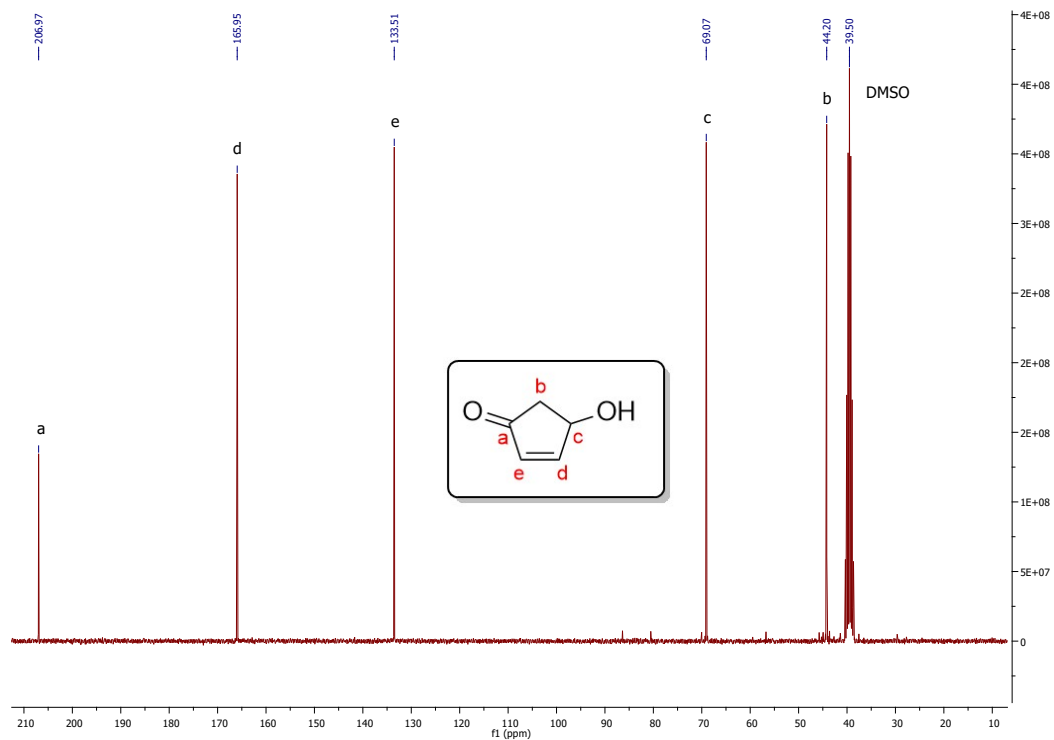


Figure S2.1.2: $^{13}\text{C-NMR}$ spectrum of 4-HCP in DMSO-d_6 .

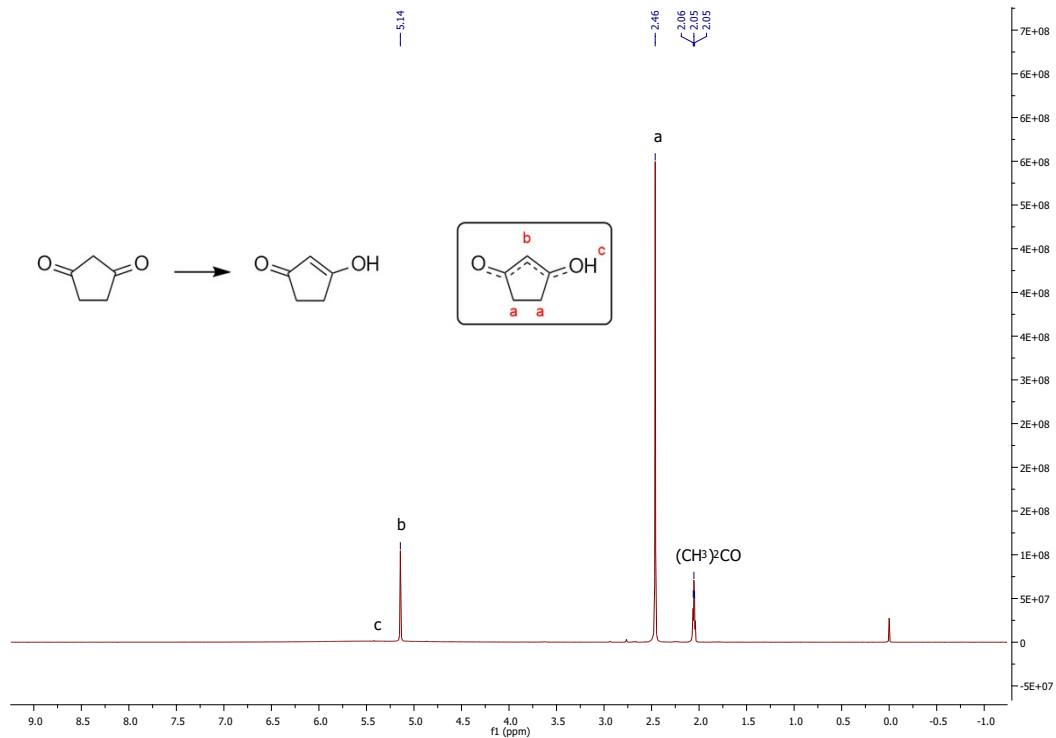


Figure S2.1.3: $^1\text{H-NMR}$ spectrum of CPDO in acetone- d_6 .

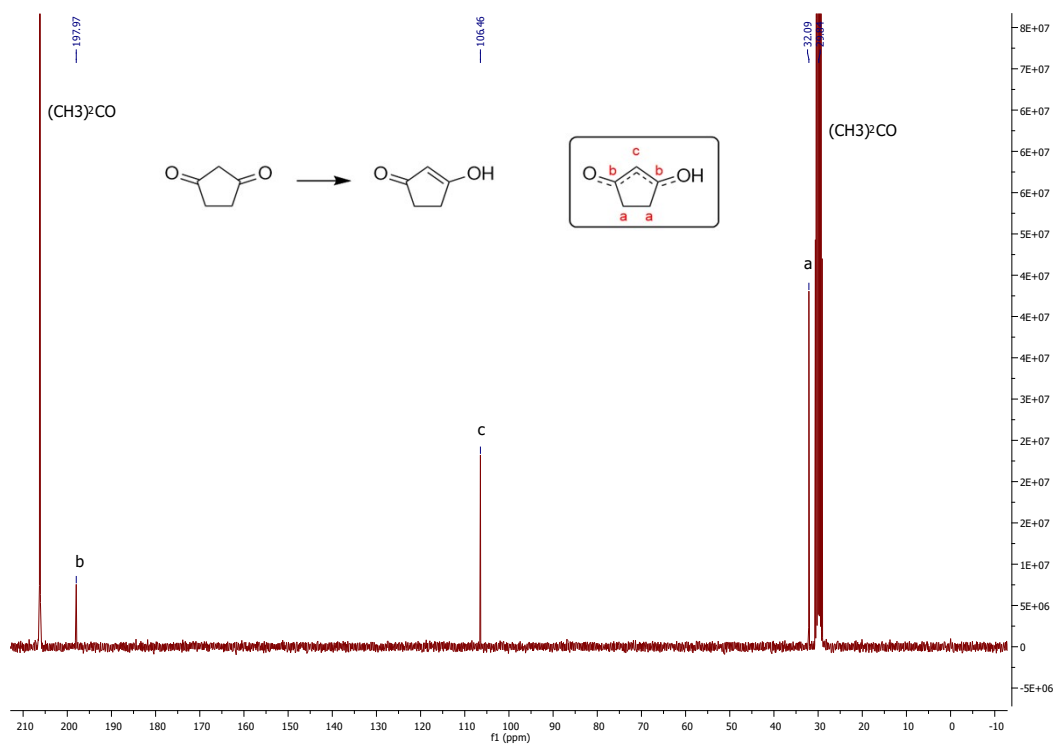


Figure S2.1.4: $^{13}\text{C-NMR}$ spectrum of CPDO in acetone- d_6 .

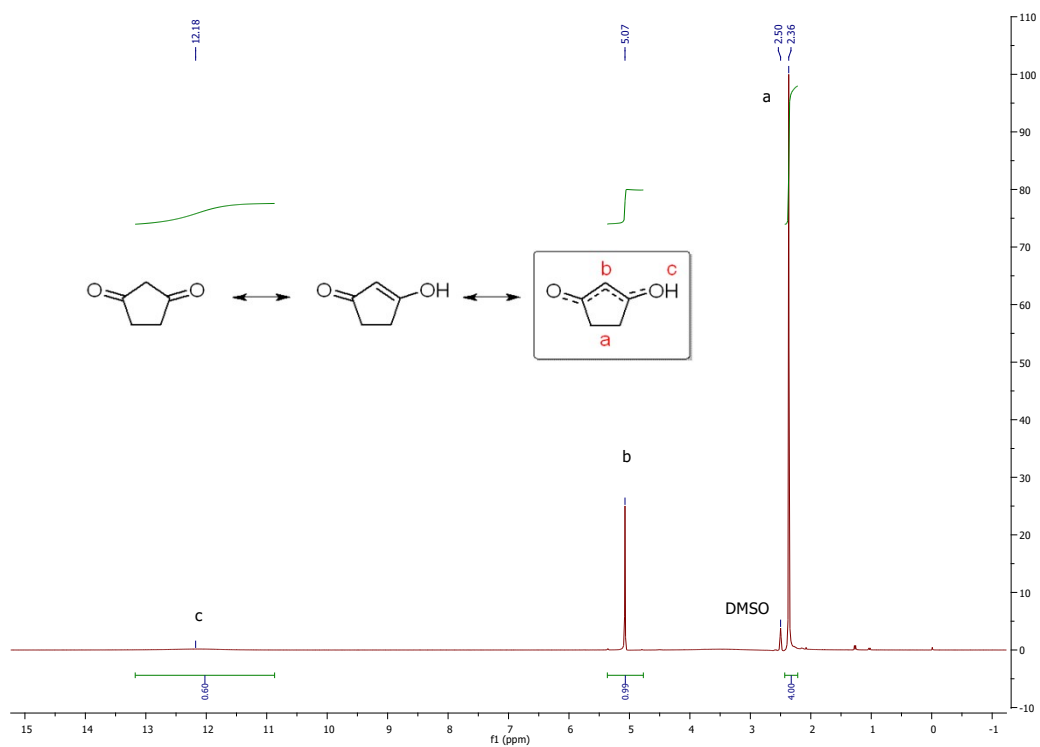


Figure S2.1.5: $^1\text{H-NMR}$ spectrum of CPDO in DMSO-d_6 .

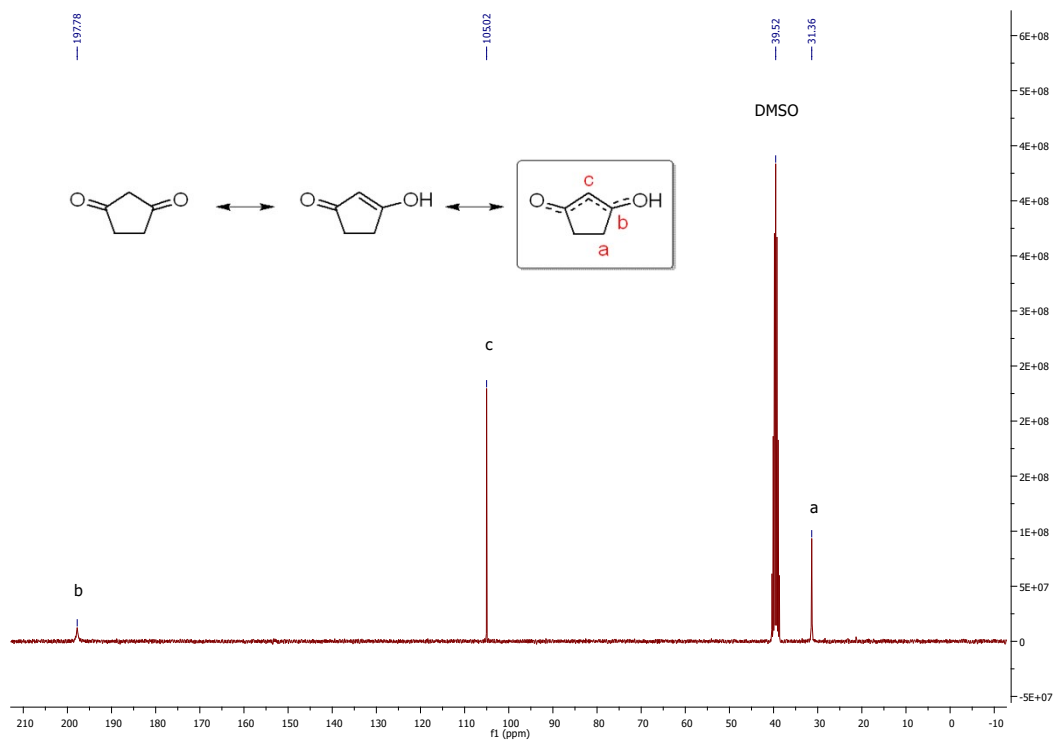


Figure S2.1.6: $^{13}\text{C-NMR}$ spectrum of CPDO in DMSO-d_6 .

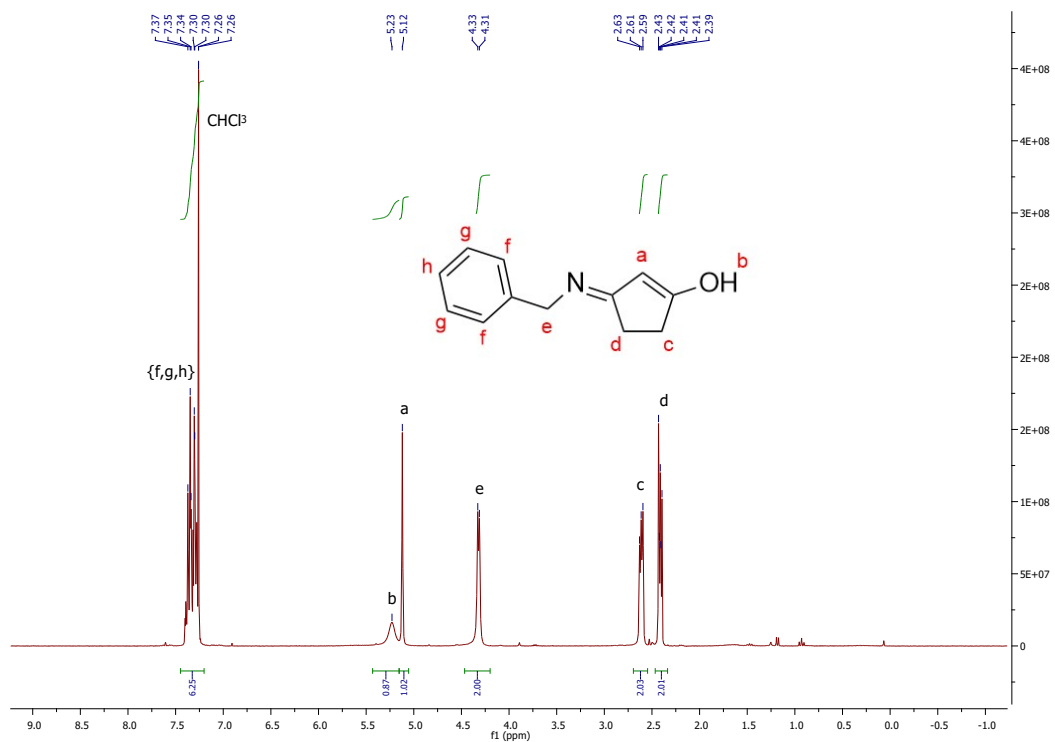


Figure 2.1.7: $^1\text{H-NMR}$ spectrum of compound **1** in CDCl_3 .

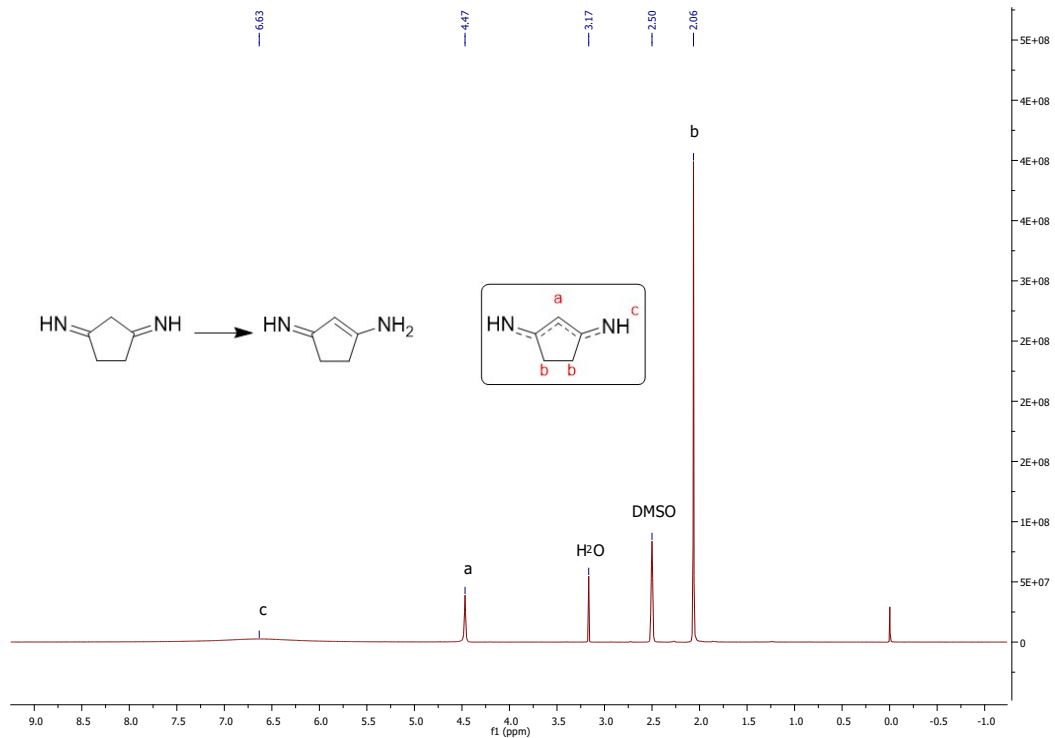


Figure S2.1.8: $^1\text{H-NMR}$ spectrum of CPDI in DMSO-d_6 .

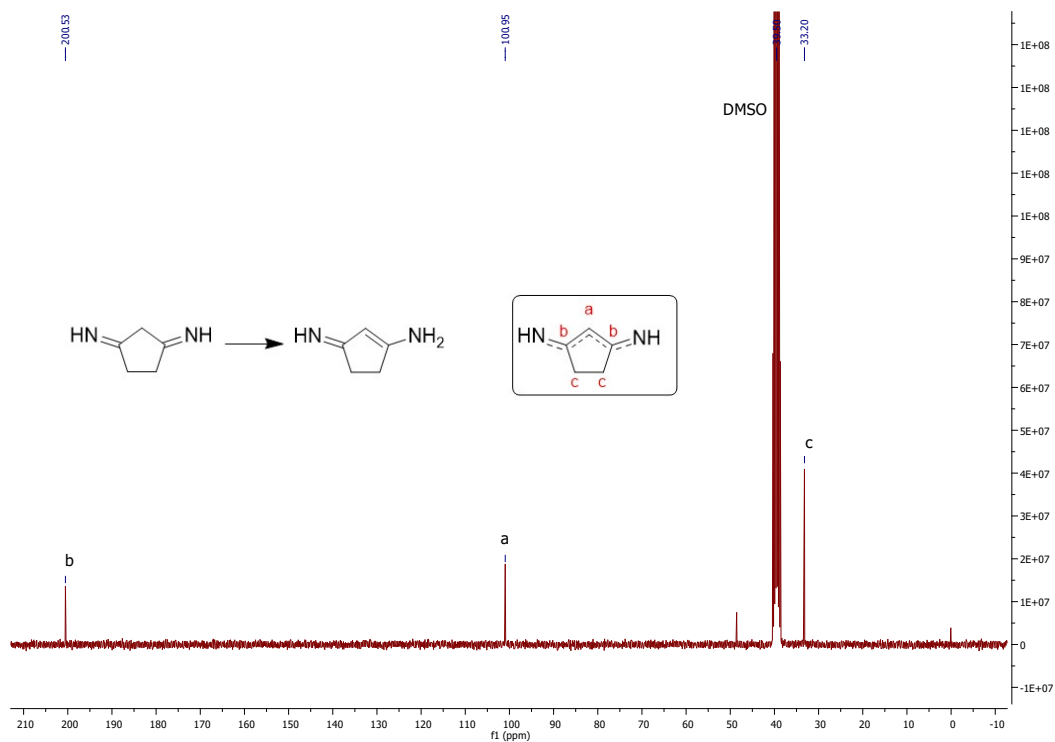


Figure S2.1.9: $^{13}\text{C-NMR}$ spectrum of CPDI in DMSO-d_6 .

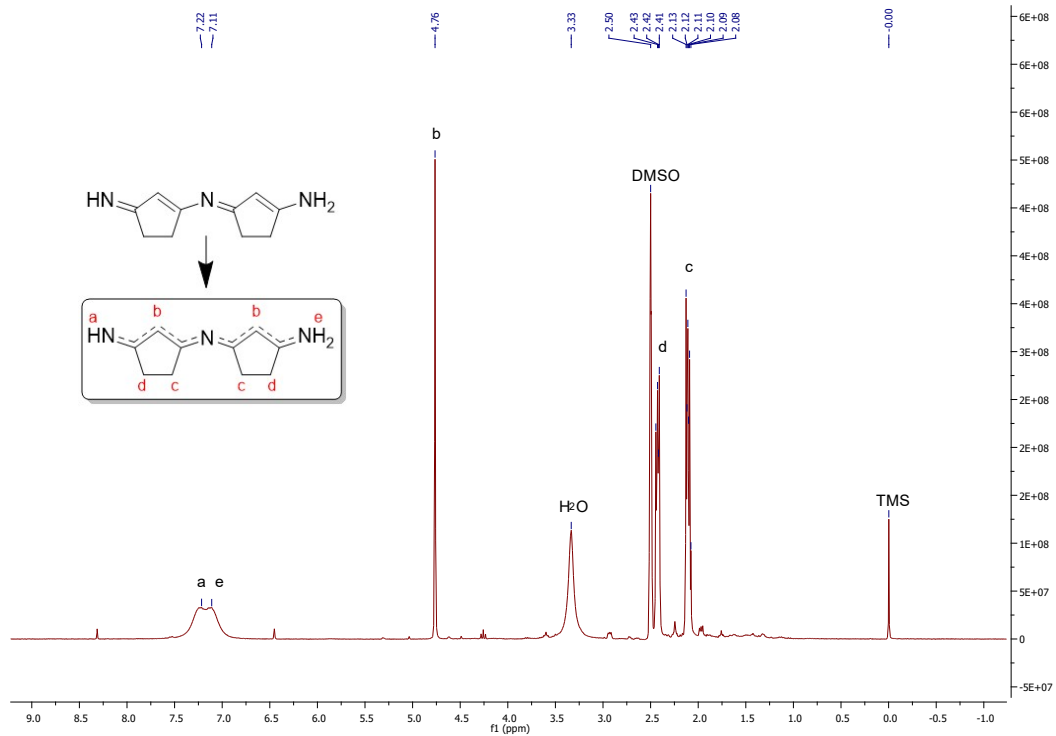


Figure 2.1.10: $^1\text{H-NMR}$ spectrum of compound **2** in $\text{DMSO-}d_6$.

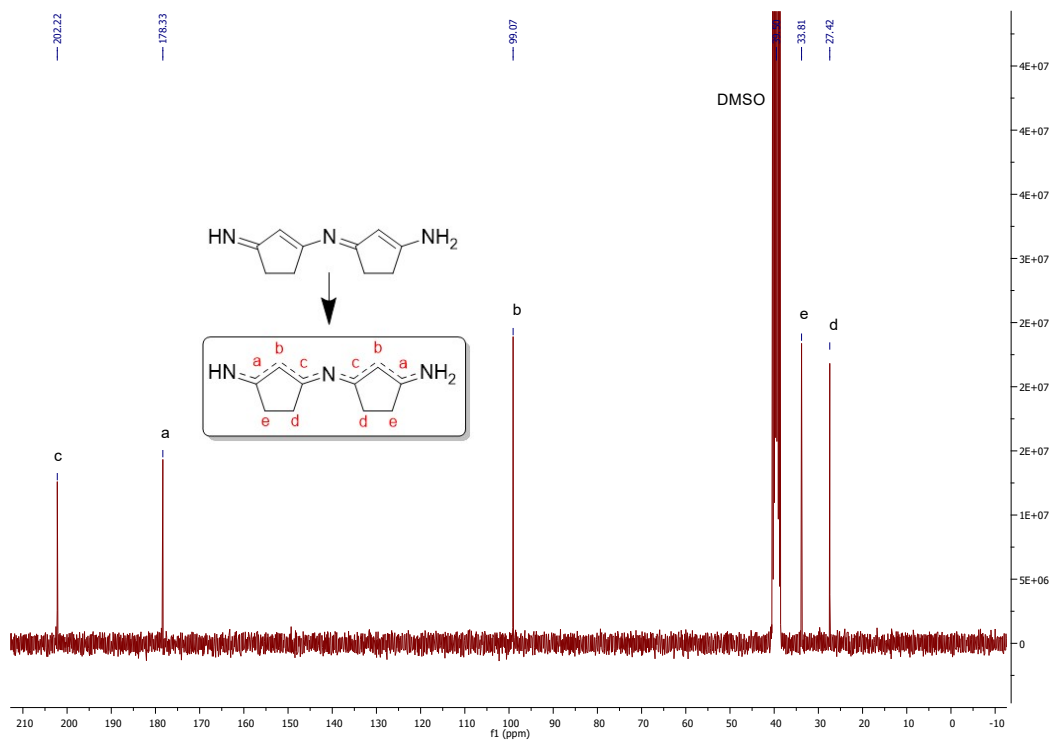


Figure 2.1.11: $^{13}\text{C-NMR}$ spectrum of compound **2** in $\text{DMSO-}d_6$.

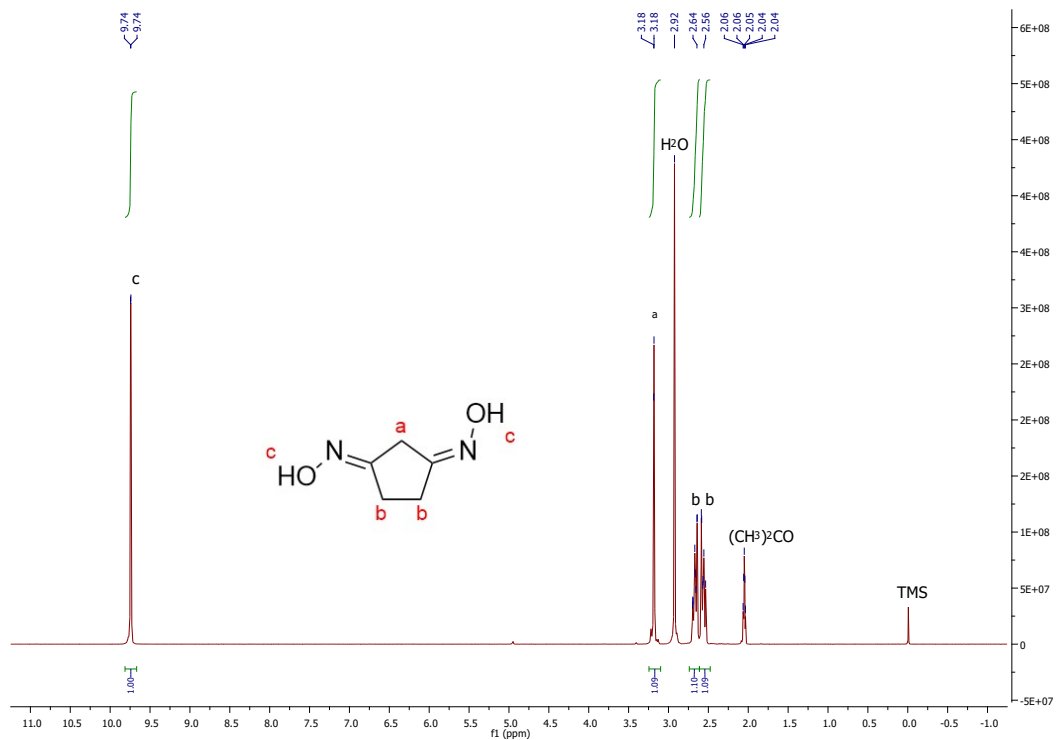


Figure S2.1.12: $^1\text{H-NMR}$ spectrum of CPDX in acetone- d_6 .

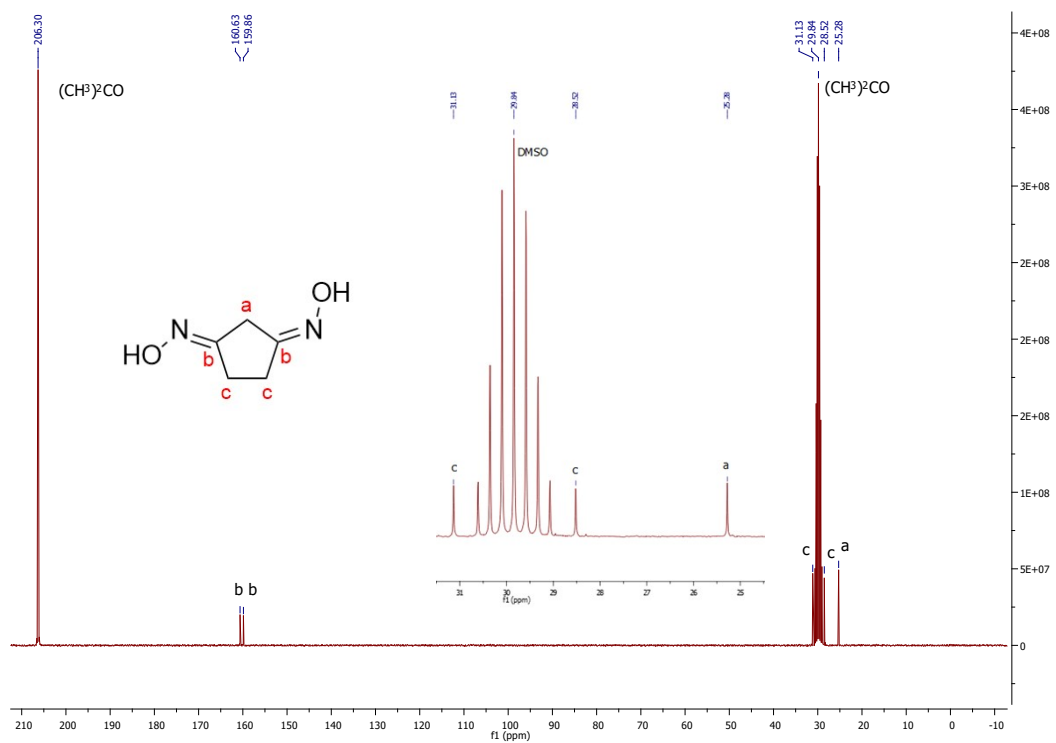


Figure S2.1.13: $^{13}\text{C-NMR}$ spectrum of CPDX in acetone- d_6 .

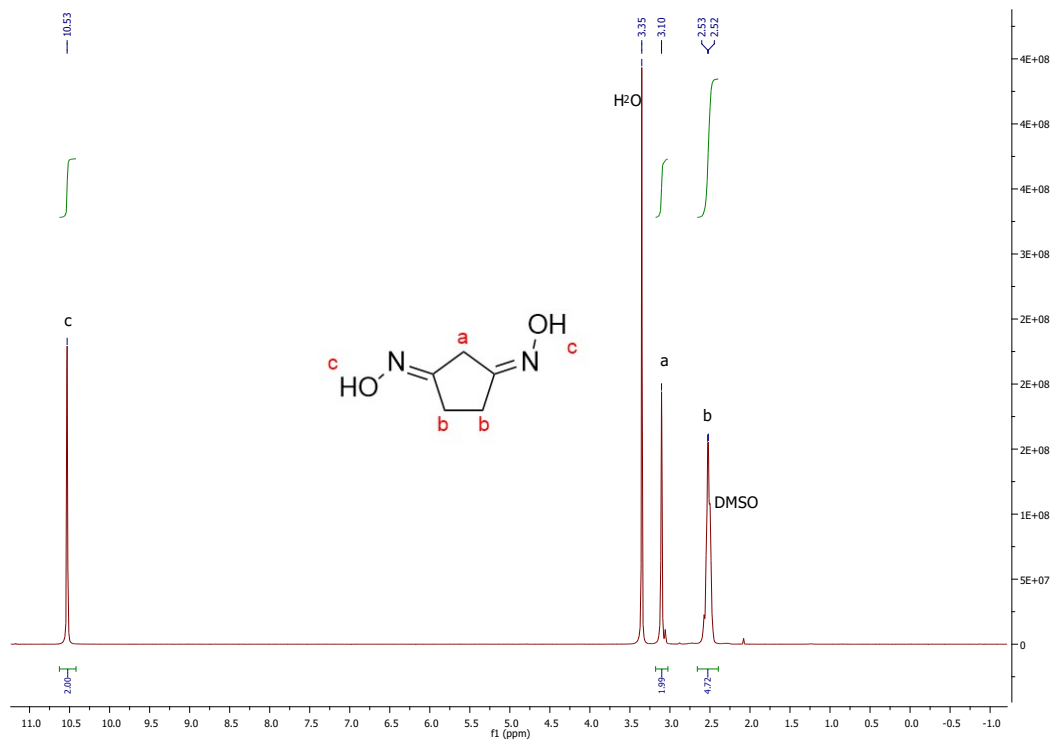


Figure S2.1.14: ¹H-NMR spectrum of CPDX in DMSO-d₆.

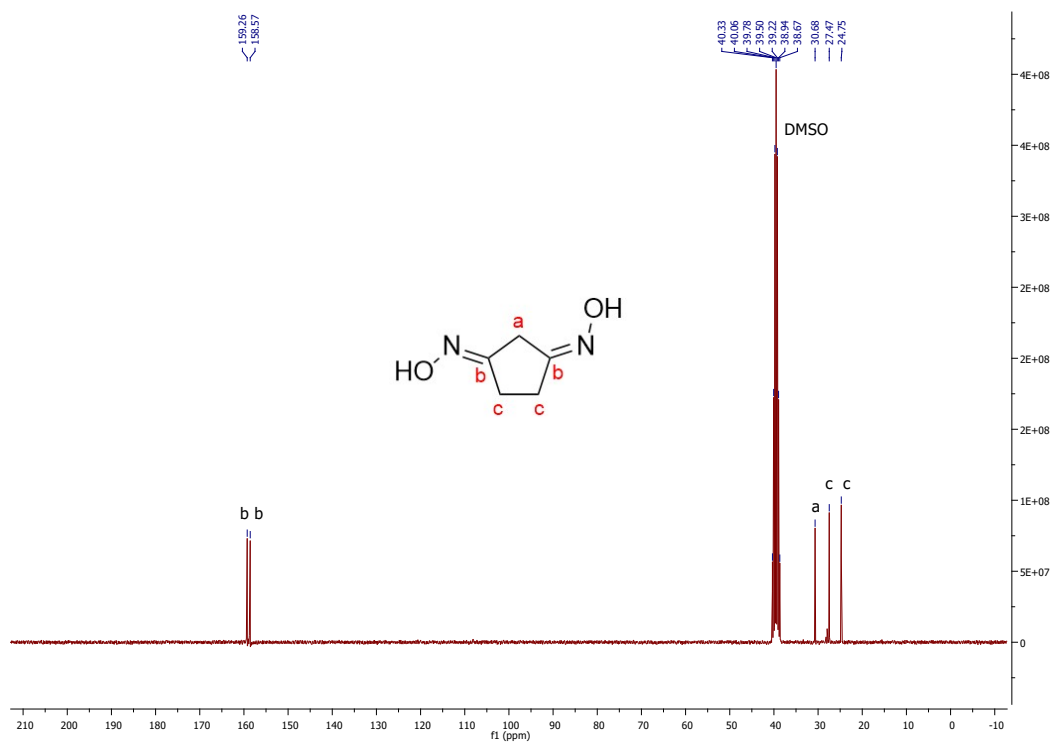


Figure S2.1.15: ¹³C-NMR spectrum of CPDX in DMSO-d₆.

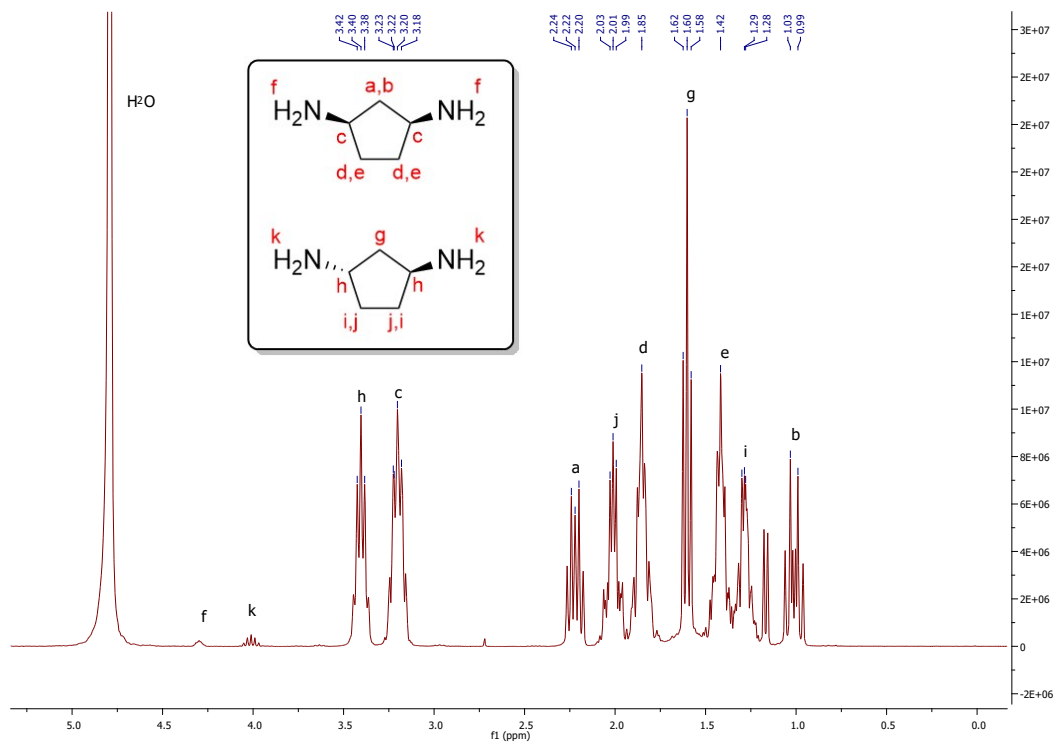


Figure S2.1.16: ^1H -NMR spectrum of CPDA (obtained from preparative hydrogenation) in D_2O .

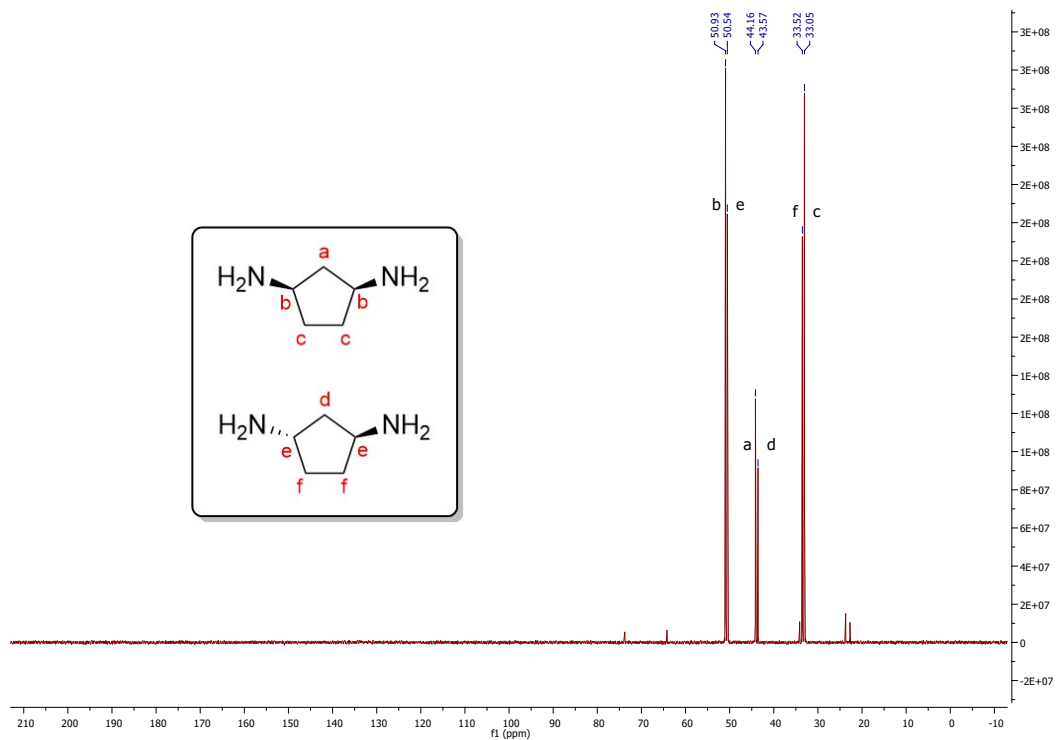


Figure S2.1.17: ^{13}C -NMR spectrum of CPDA (obtained from preparative hydrogenation) in D_2O .

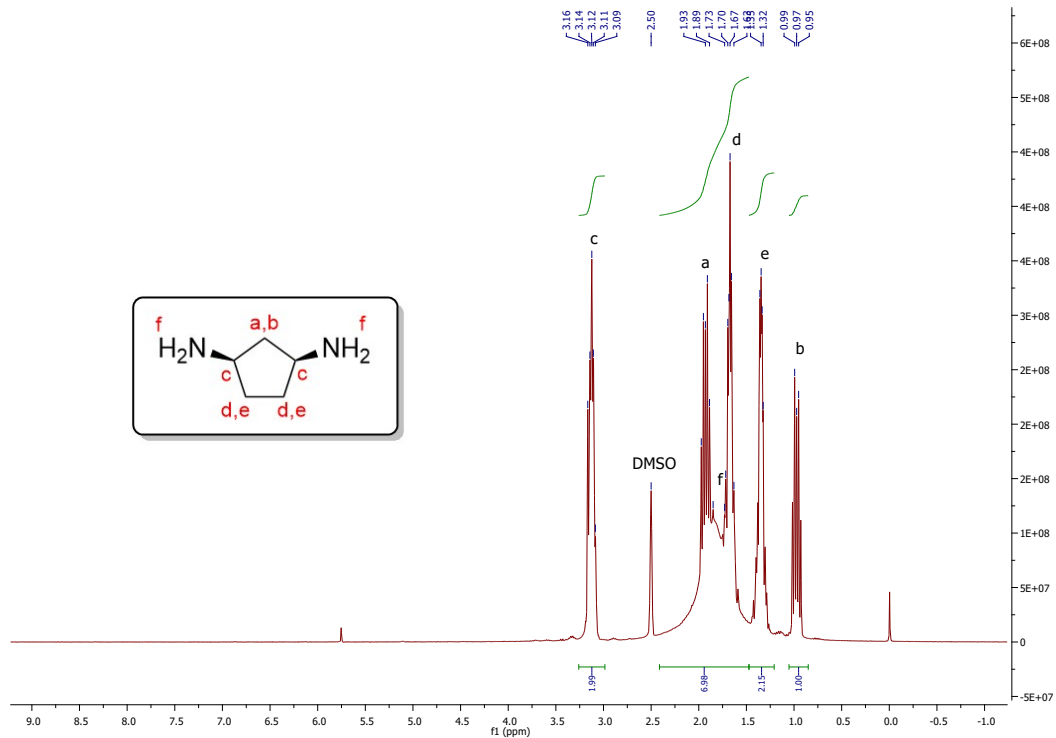


Figure S2.1.18: ¹H-NMR spectrum of cis-CPDA (obtained from Matrix Chemicals) in DMSO-d₆.

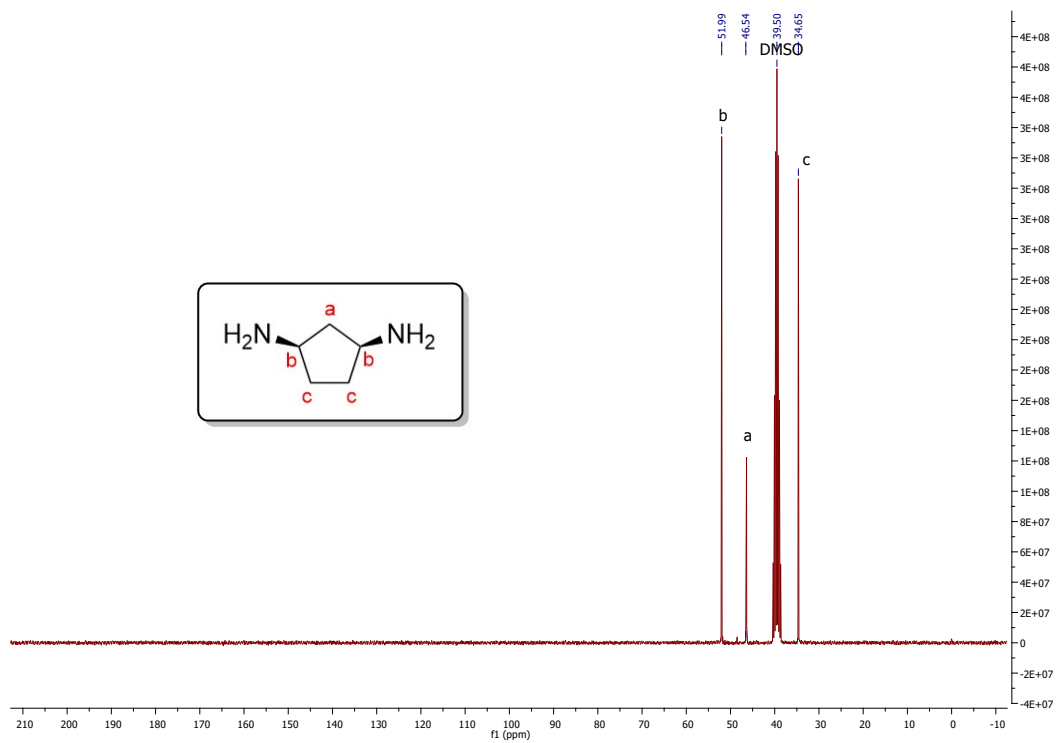


Figure S2.1.19: ¹³C-NMR spectrum of cis-CPDA (obtained from Matrix Chemicals) in DMSO-d₆.

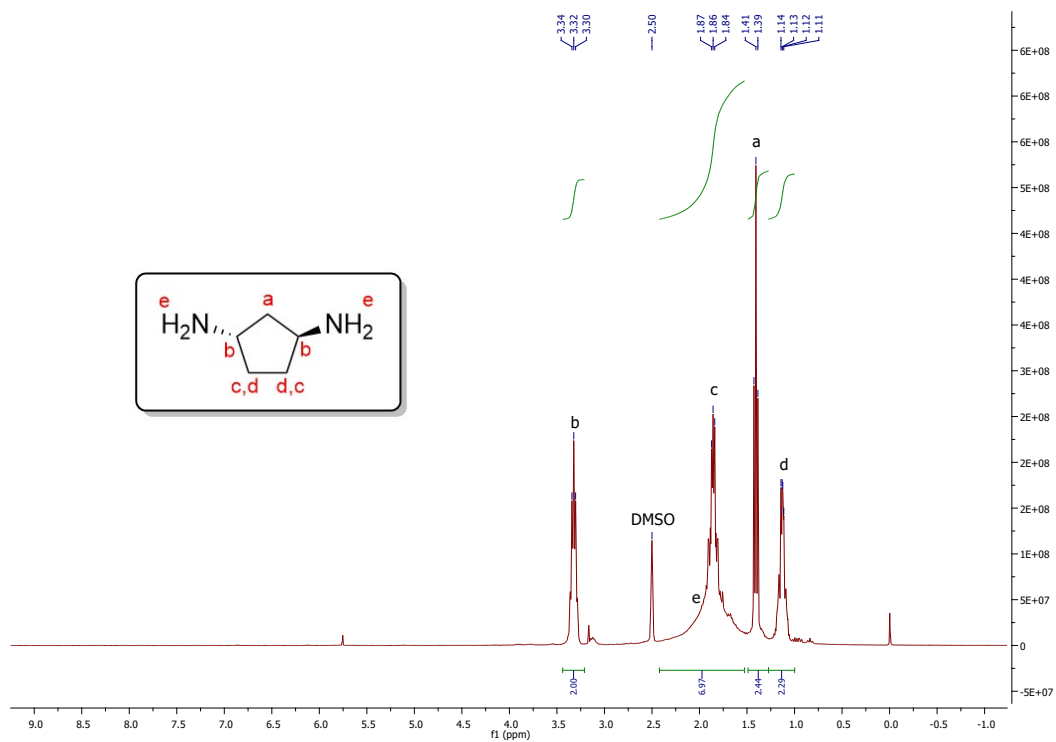


Figure S2.1.20: $^1\text{H-NMR}$ spectrum of *trans*-CPDA (obtained from Matrix Chemicals) in DMSO- d_6 .

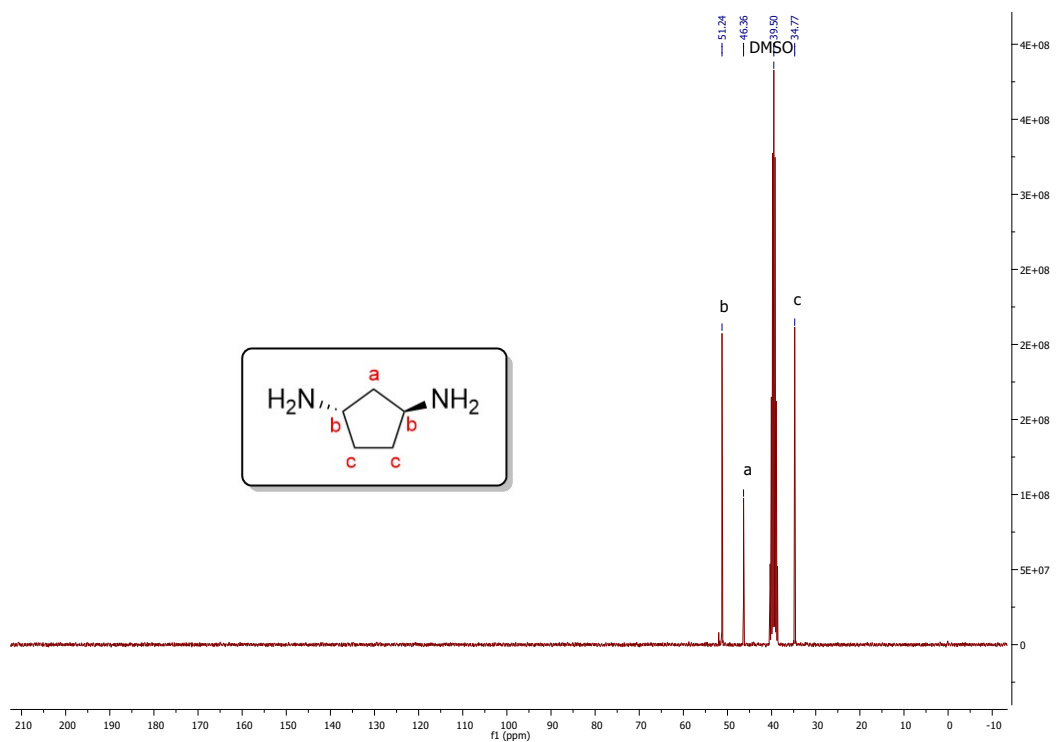


Figure S2.1.21: $^1\text{H-NMR}$ spectrum of *trans*-CPDA (obtained from Matrix Chemicals) in DMSO- d_6 .

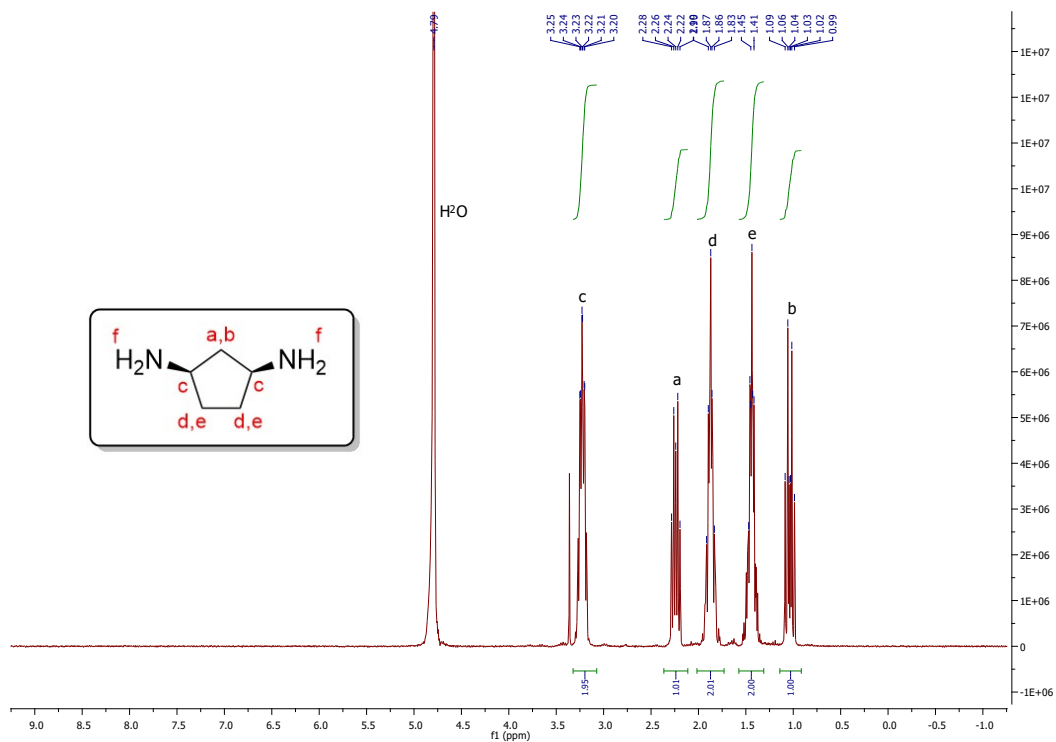


Figure S2.1.22: $^1\text{H-NMR}$ spectrum of *cis-CPDA* (obtained from Matrix Chemicals) in D_2O .

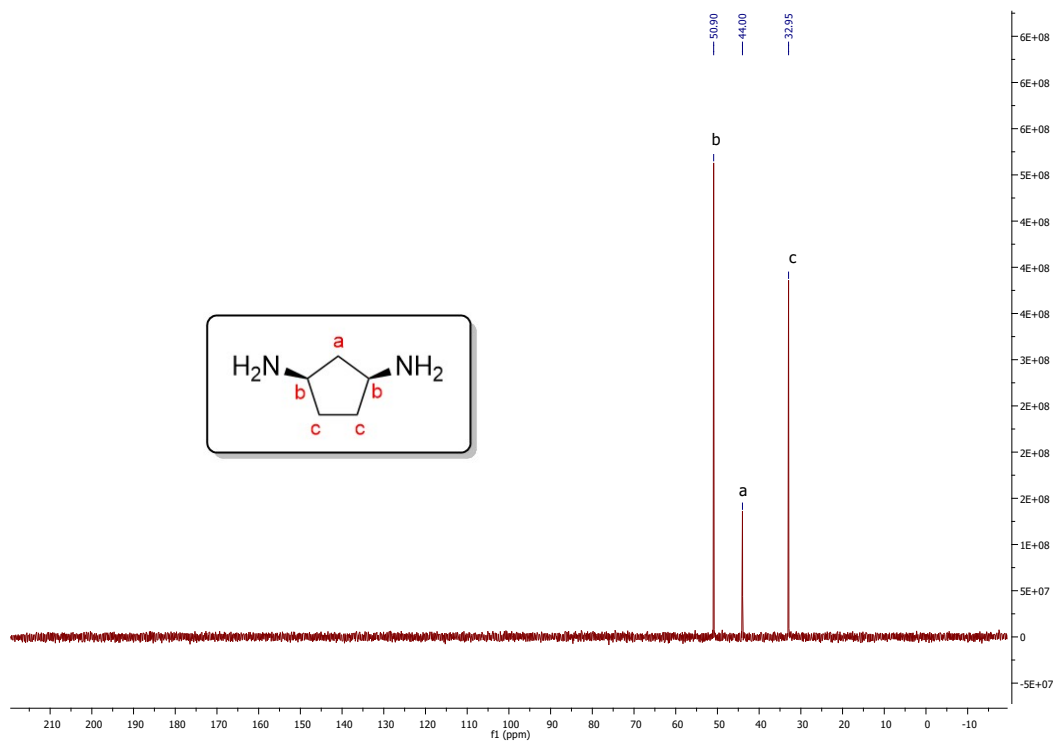


Figure S2.1.23: $^{13}\text{C-NMR}$ spectrum of *cis-CPDA* (obtained from Matrix Chemicals) in D_2O .

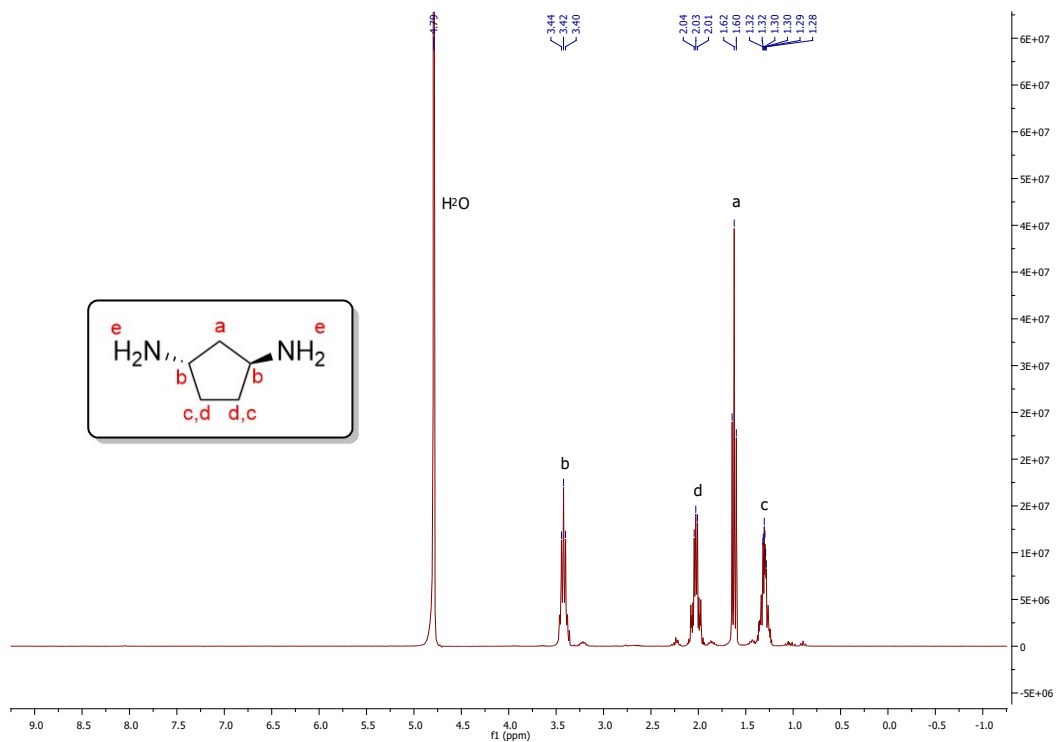


Figure S2.1.24: $^1\text{H-NMR}$ spectrum of *trans*-CPDA (obtained from Matrix Chemicals) in D_2O .

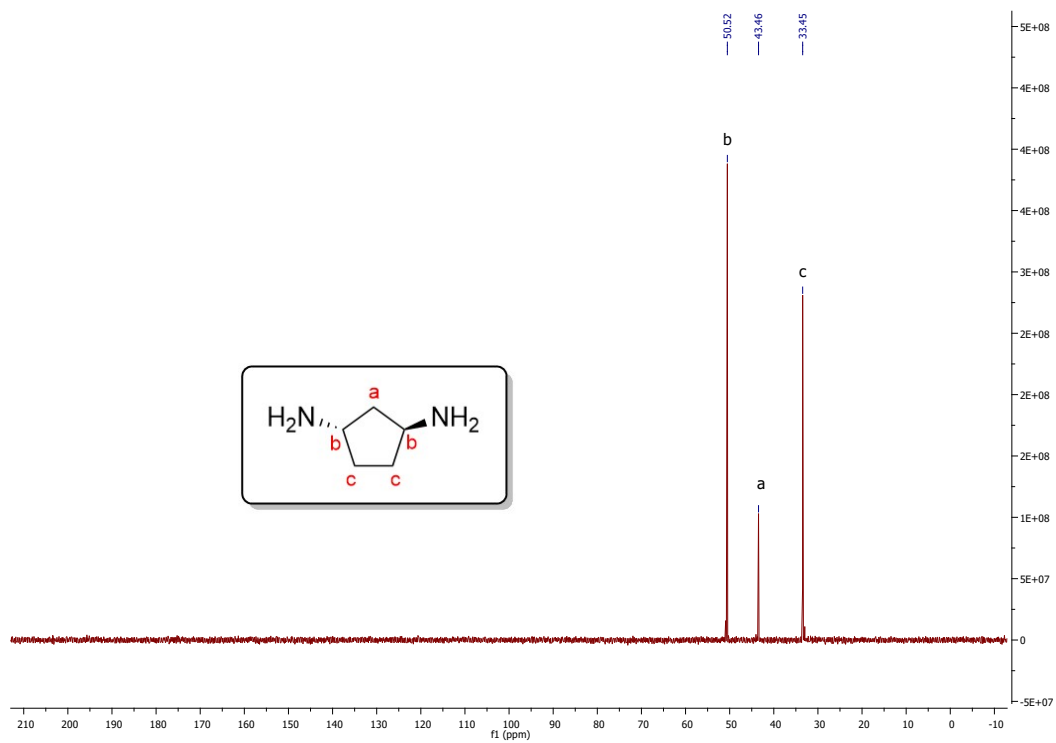


Figure S2.1.25: $^{13}\text{C-NMR}$ spectrum of *trans*-CPDA (obtained from Matrix Chemicals) in D_2O .

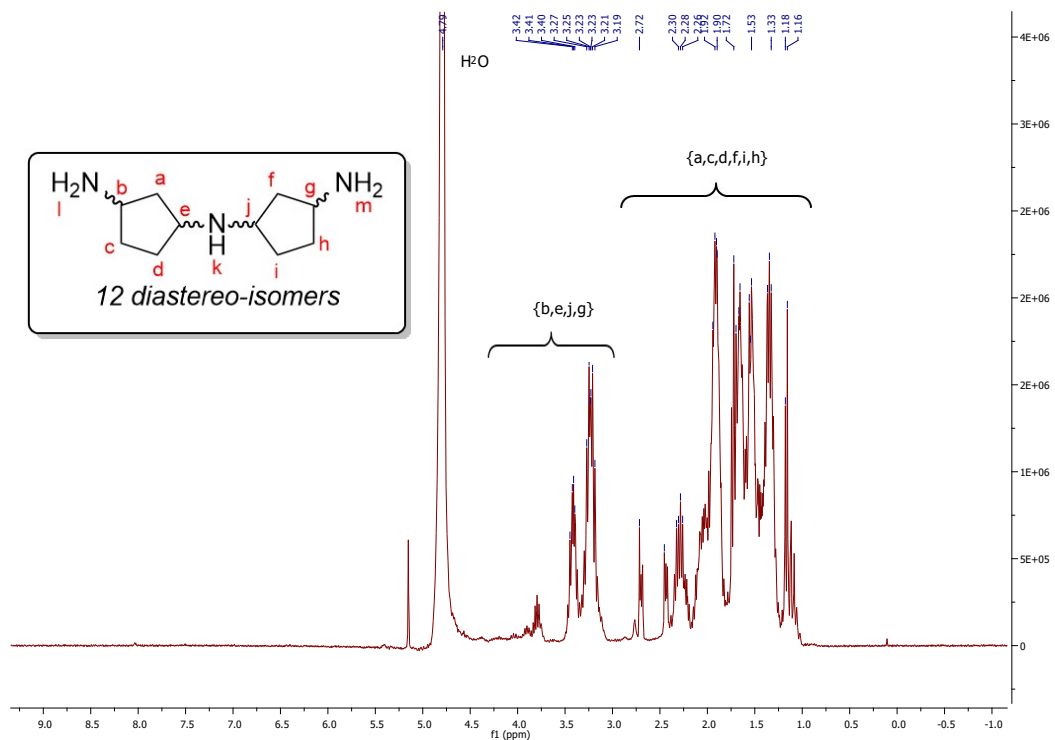


Figure S2.1.26: $^1\text{H-NMR}$ spectrum of CPDA-dimer (obtained from preparative hydrogenation) in D_2O .

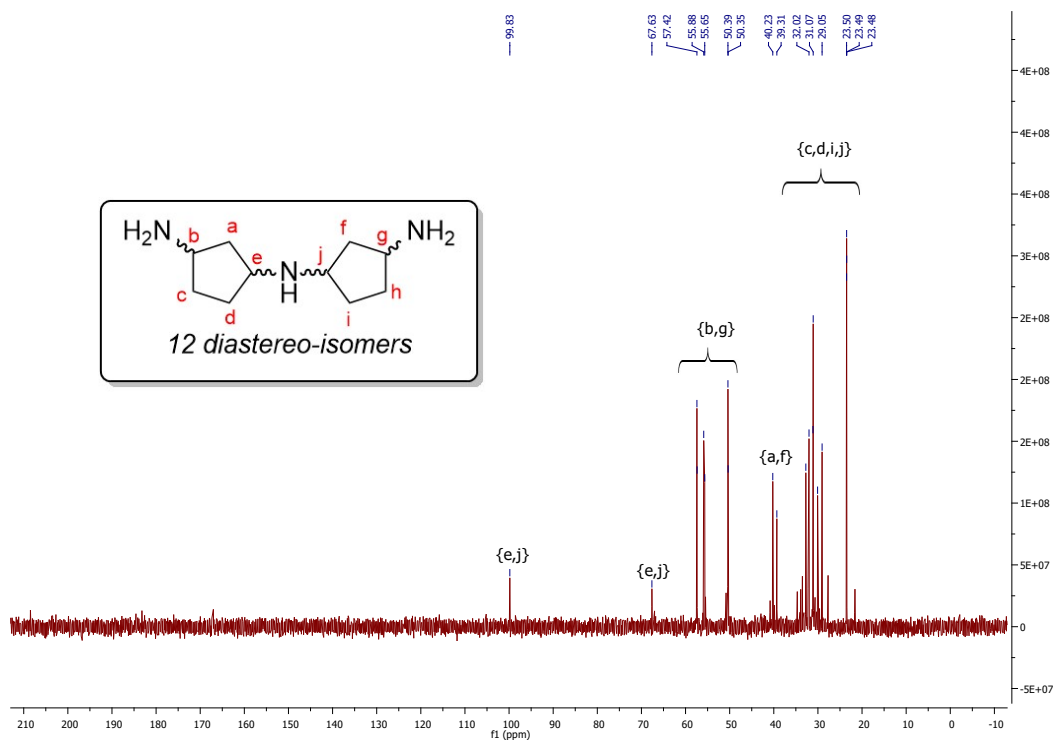


Figure S2.1.27: $^{13}\text{C-NMR}$ spectrum of CPDA-dimer (obtained from preparative hydrogenation) in D_2O .

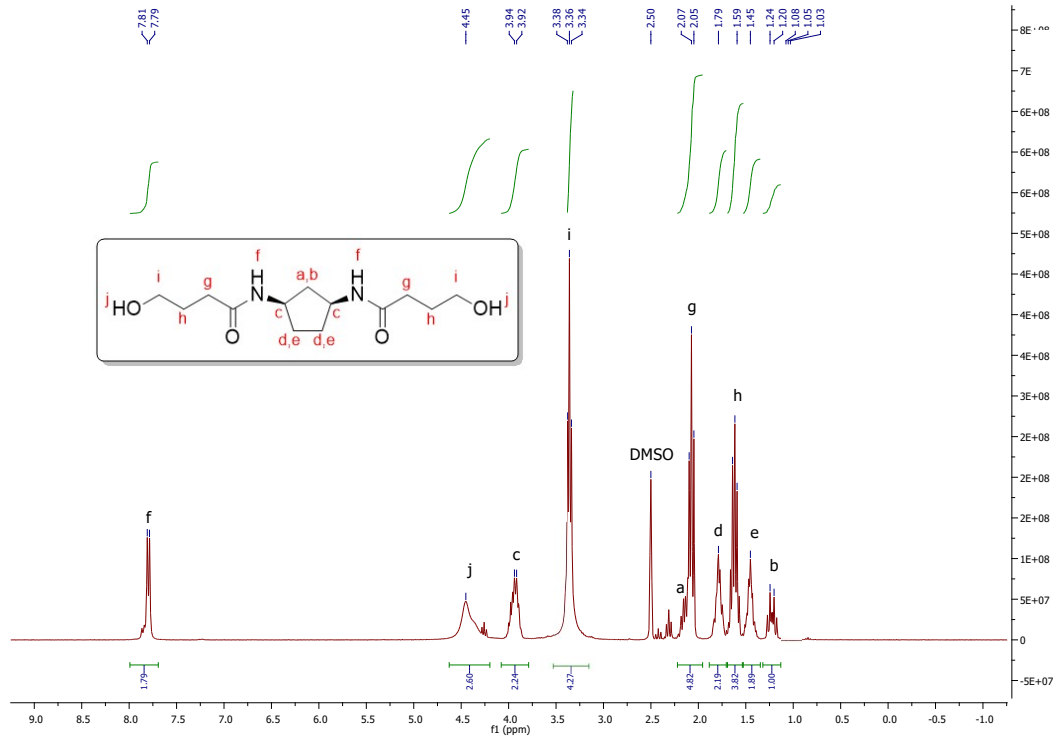


Figure S2.1.28: ¹H-NMR spectrum of **3** in DMSO-d₆.

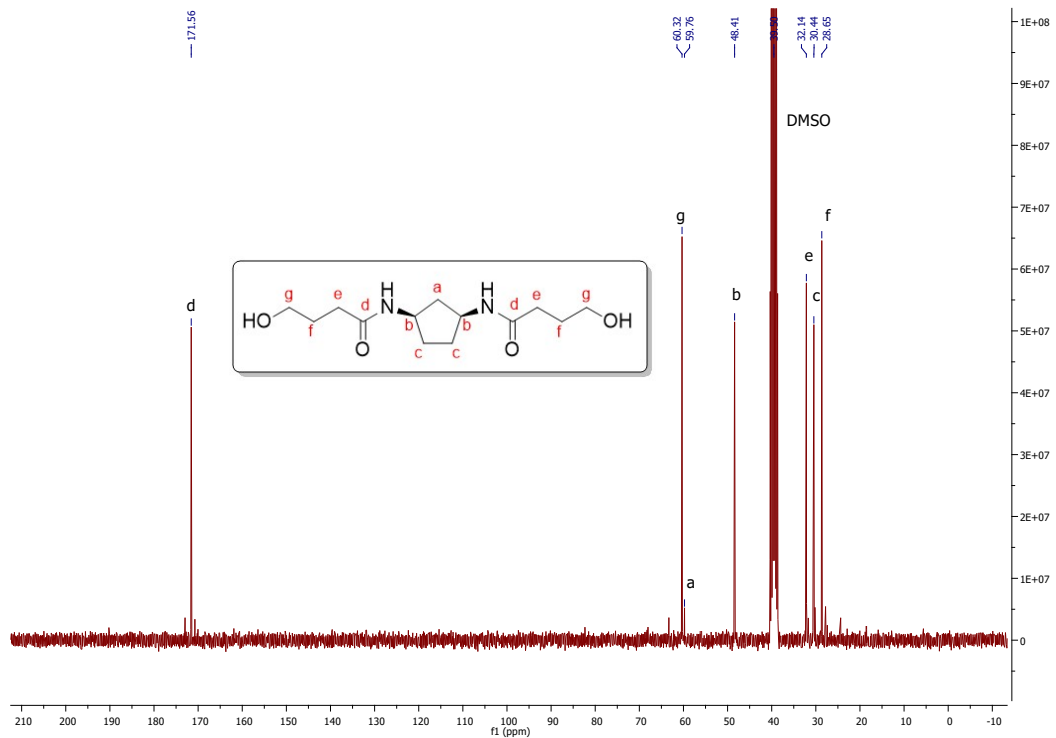


Figure S2.1.29: ¹³C-NMR spectrum of **3** in DMSO-d₆.

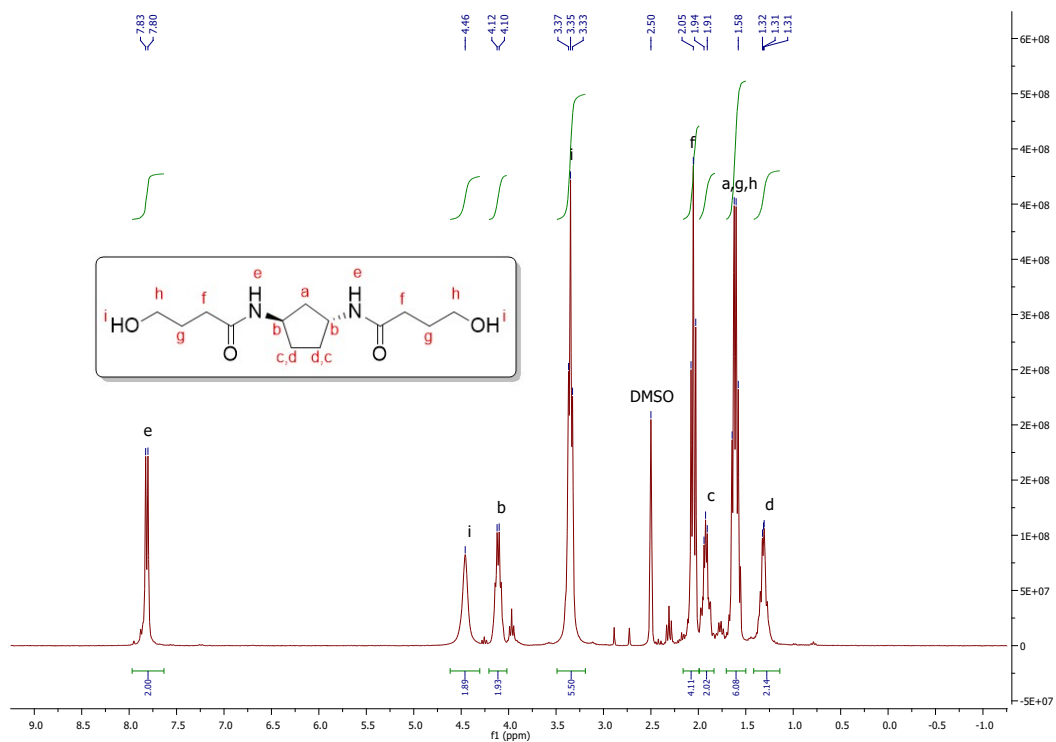


Figure S2.1.30: $^1\text{H-NMR}$ spectrum of 4 in DMSO-d_6 .

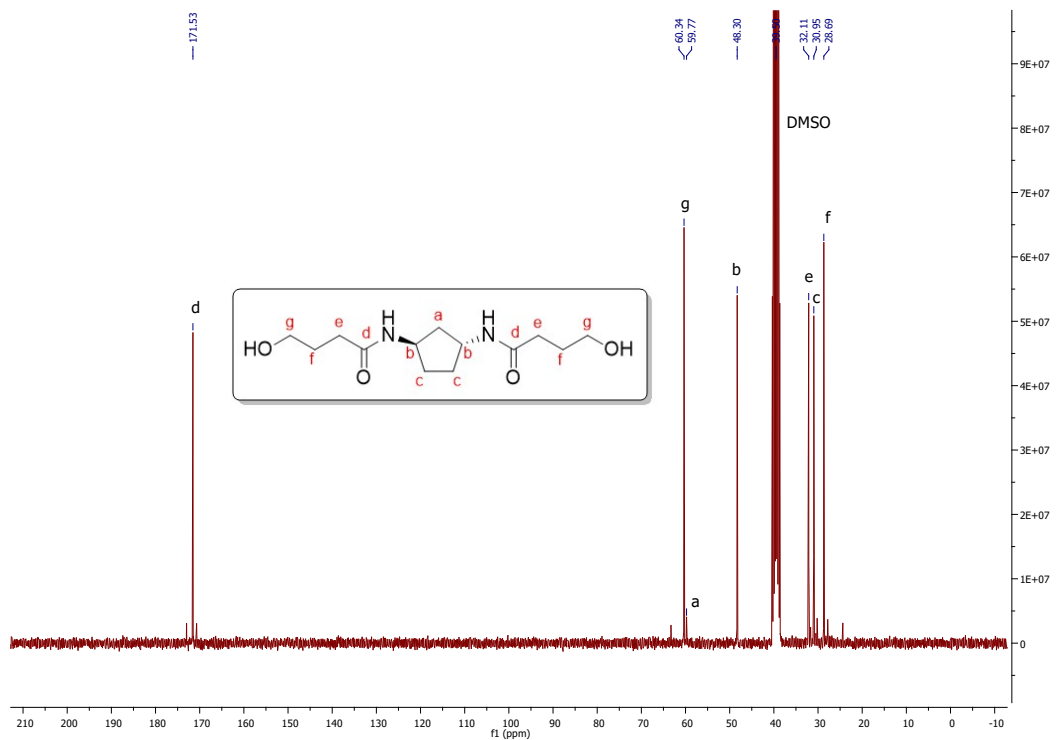


Figure S2.1.31: $^{13}\text{C-NMR}$ spectrum of 4 in DMSO-d_6 .

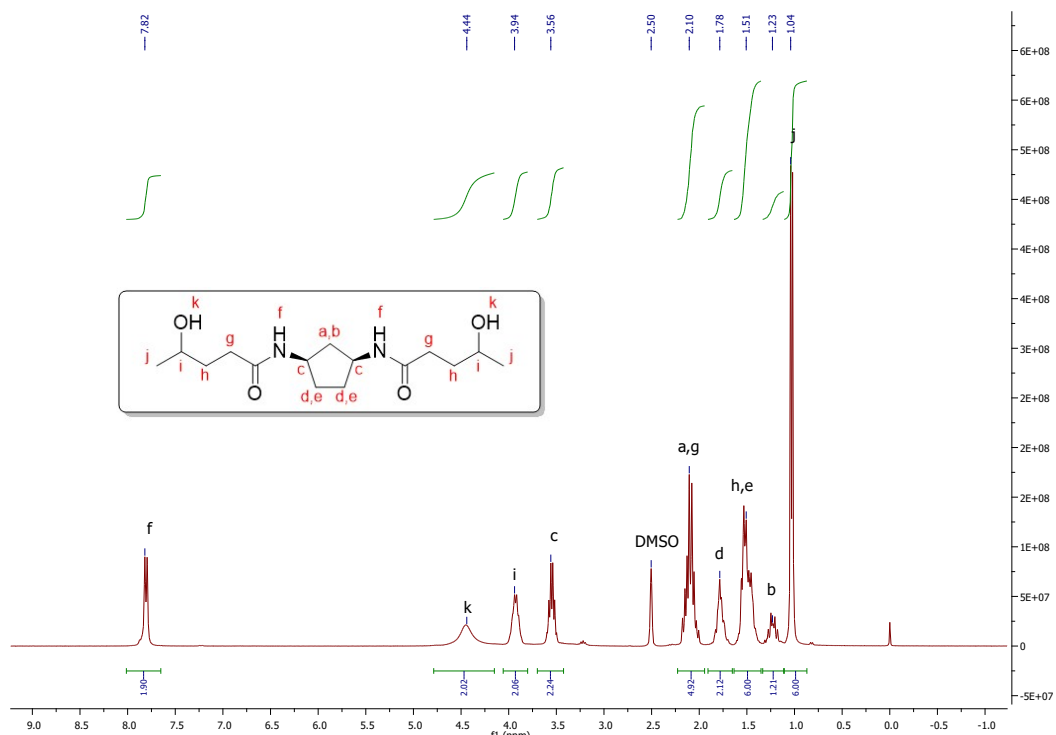


Figure S2.1.32: ^1H -NMR spectrum of 5 in $\text{DMSO}-d_6$.

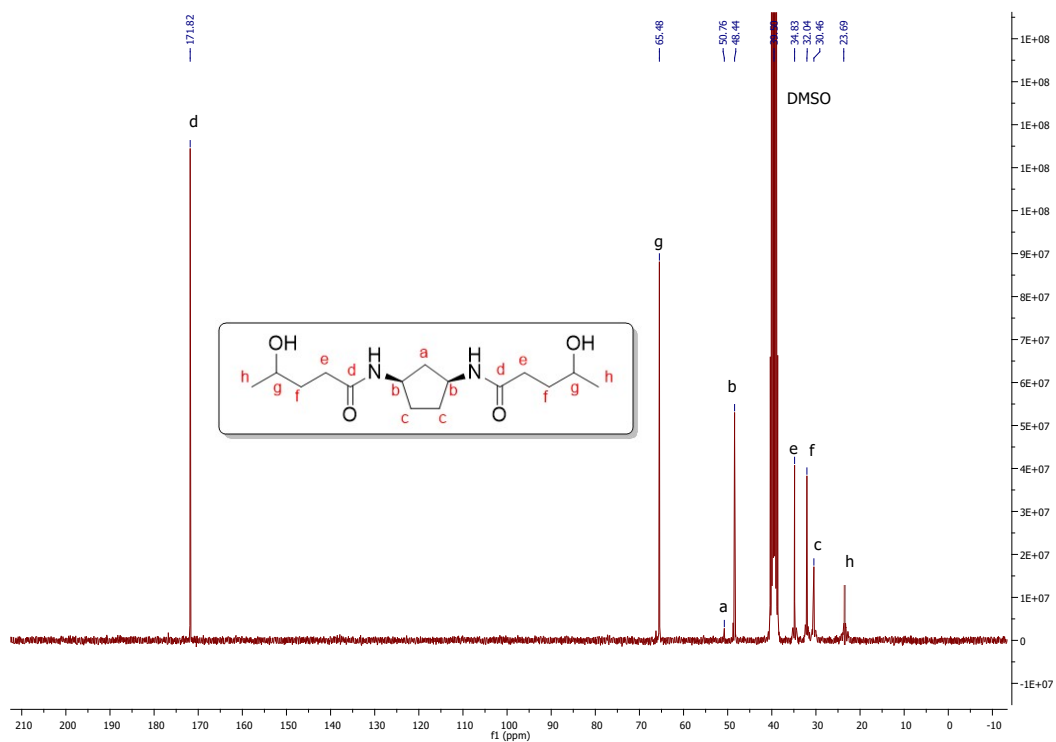


Figure S2.1.33: ^{13}C -NMR spectrum of 5 in $\text{DMSO}-d_6$.

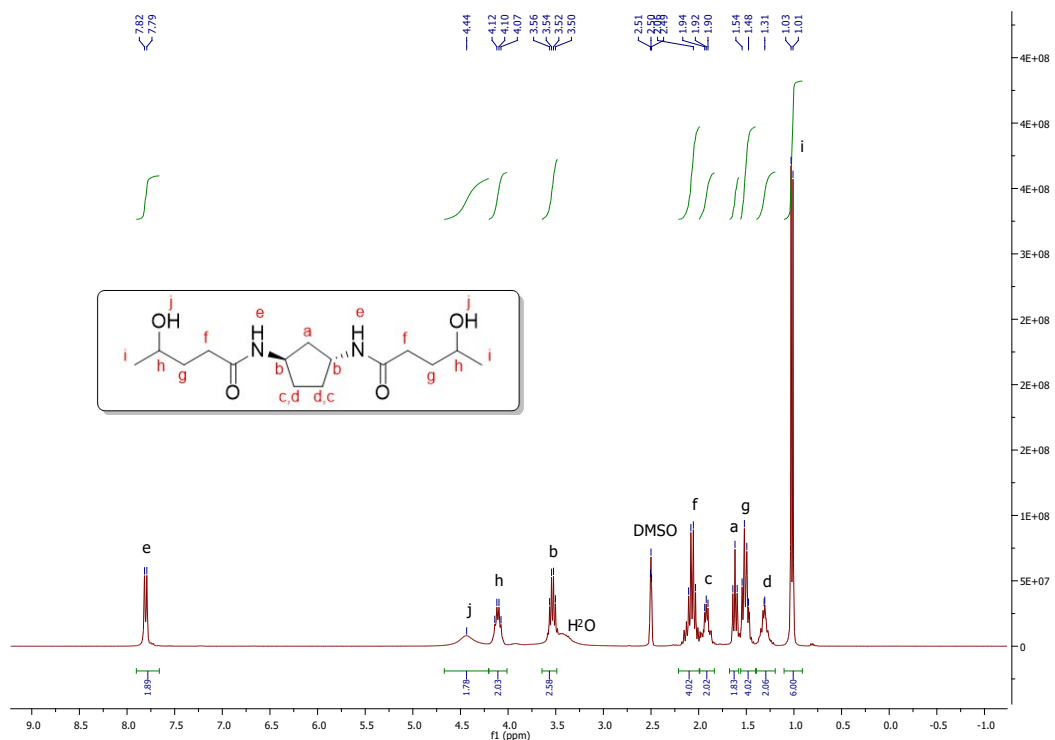


Figure S2.1.34: ^1H -NMR spectrum of **6** in $\text{DMSO-}d_6$.

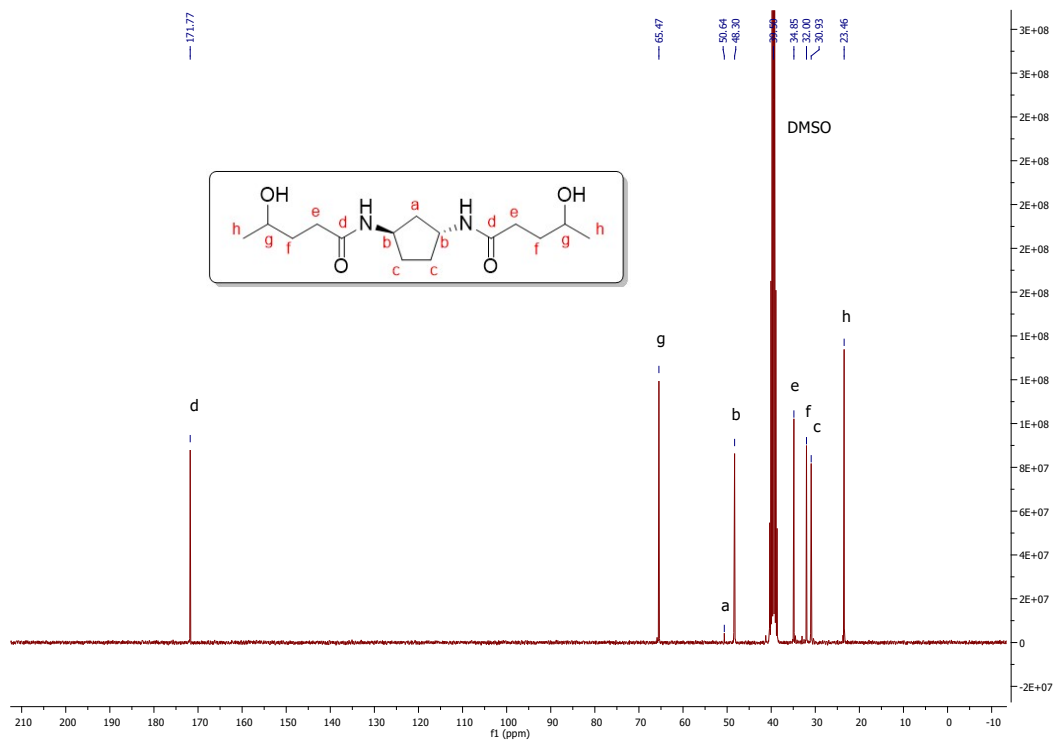


Figure S2.1.35: ^{13}C -NMR spectrum of **6** in $\text{DMSO-}d_6$.

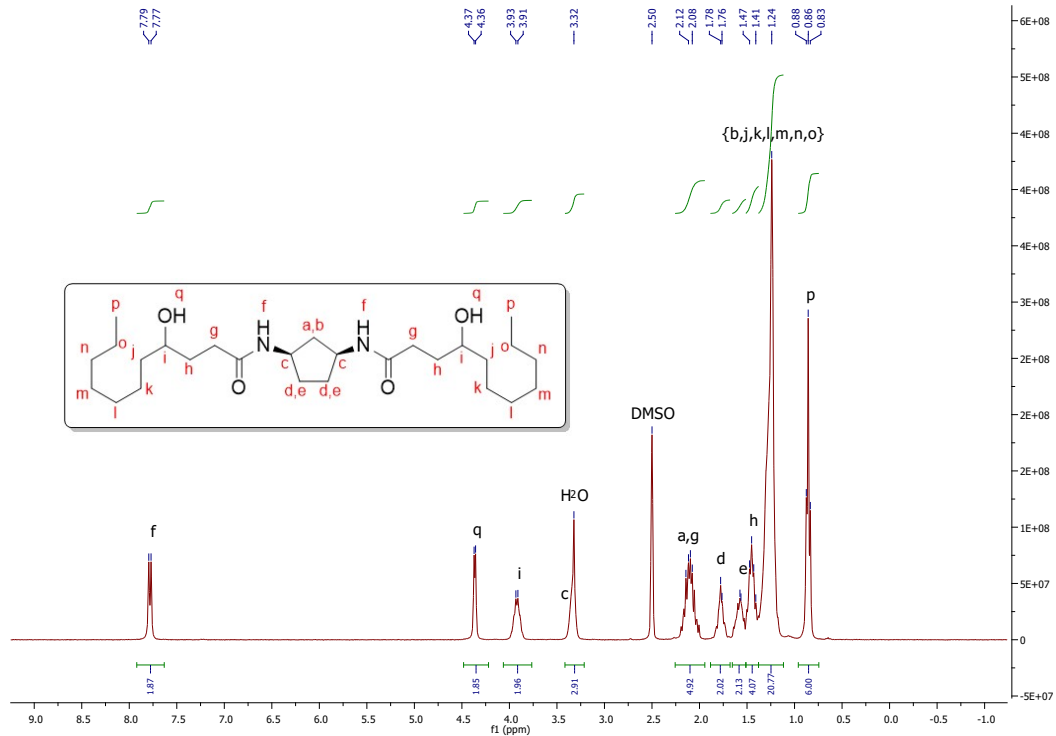


Figure S2.1.36: $^1\text{H-NMR}$ spectrum of 7 in $\text{DMSO-}d_6$.

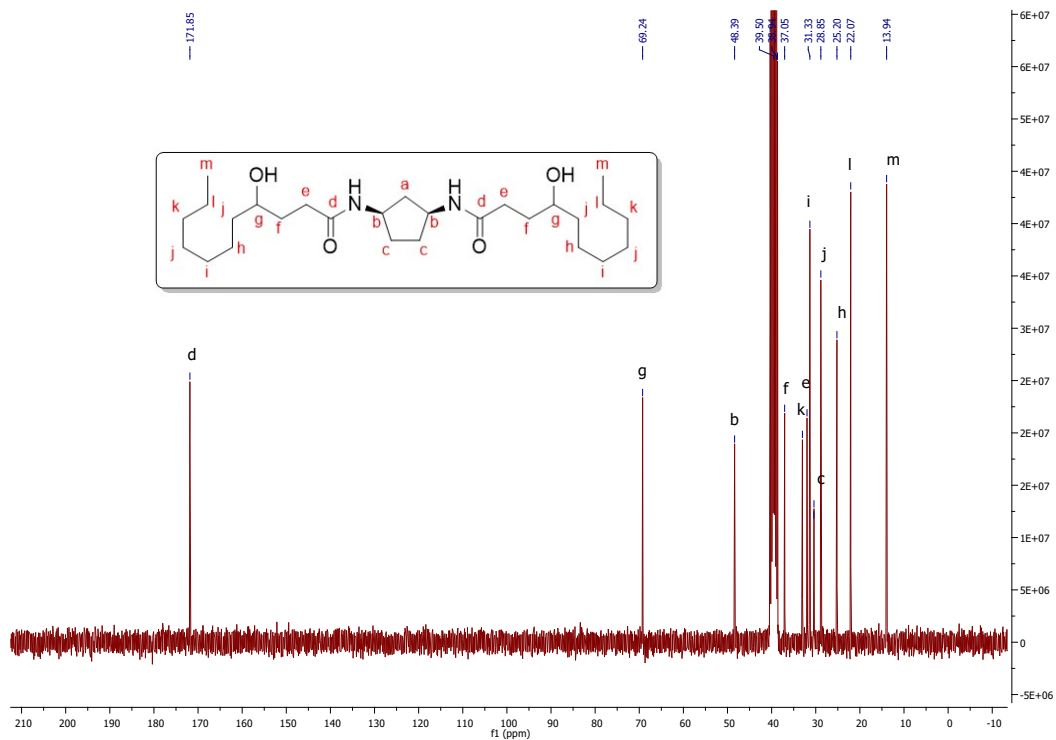


Figure S2.1.37: $^{13}\text{C-NMR}$ spectrum of 7 in $\text{DMSO-}d_6$.

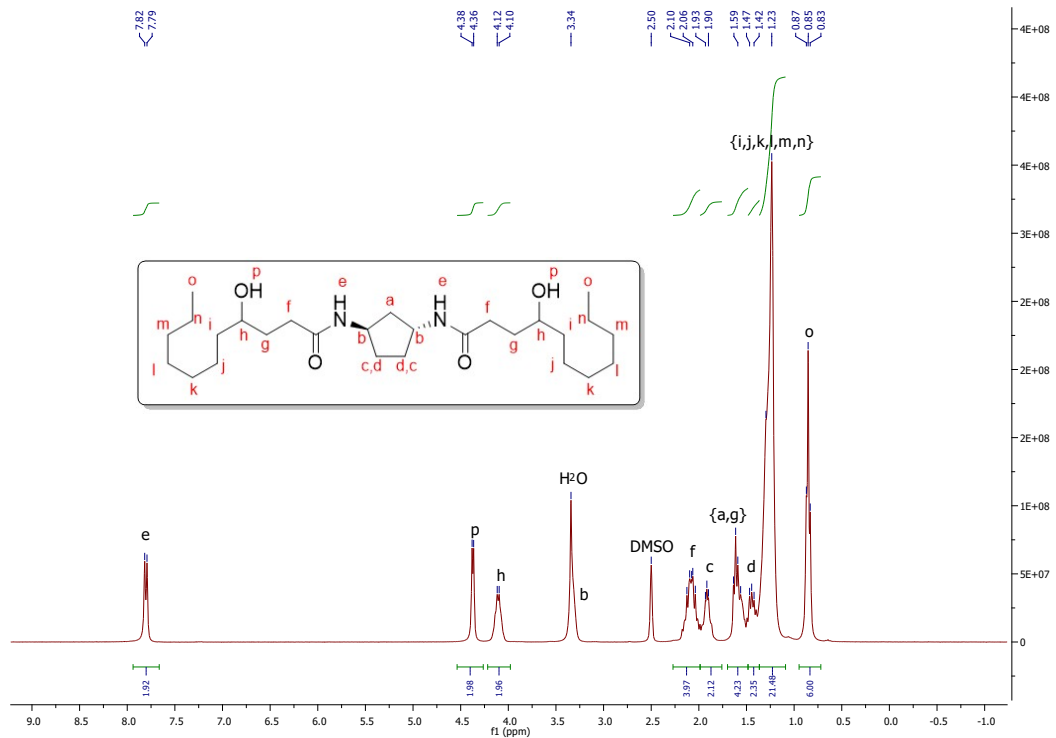


Figure S2.1.38: $^1\text{H-NMR}$ spectrum of **8** in $\text{DMSO-}d_6$.

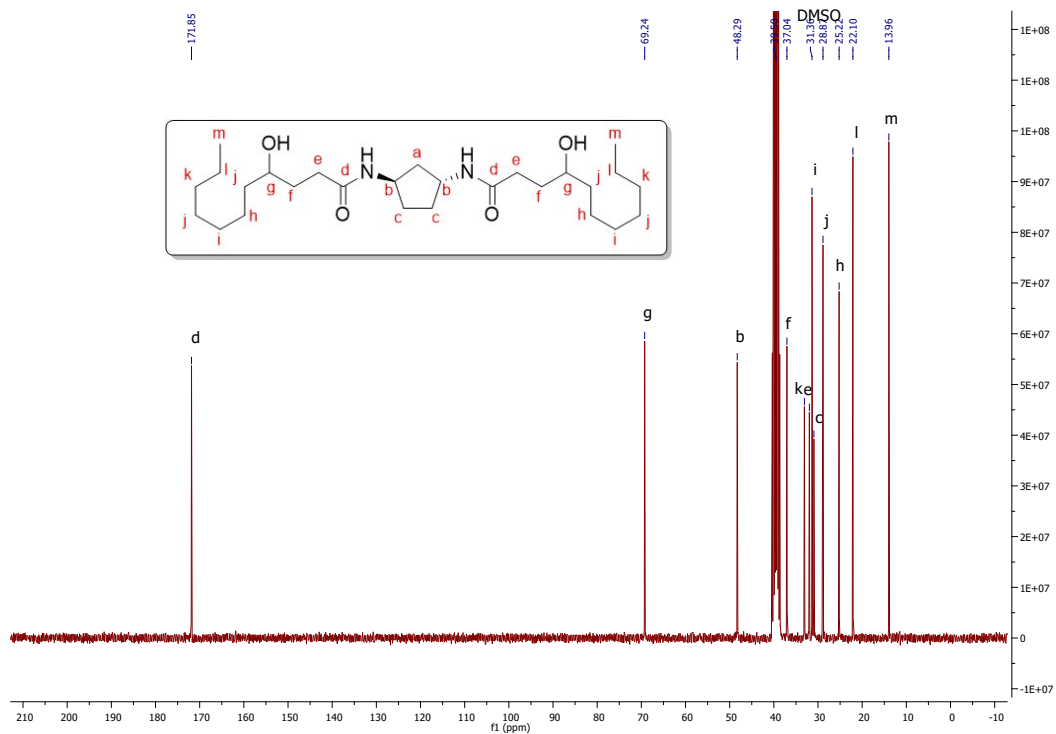


Figure S2.1.39: $^{13}\text{C-NMR}$ spectrum of **8** in $\text{DMSO-}d_6$.

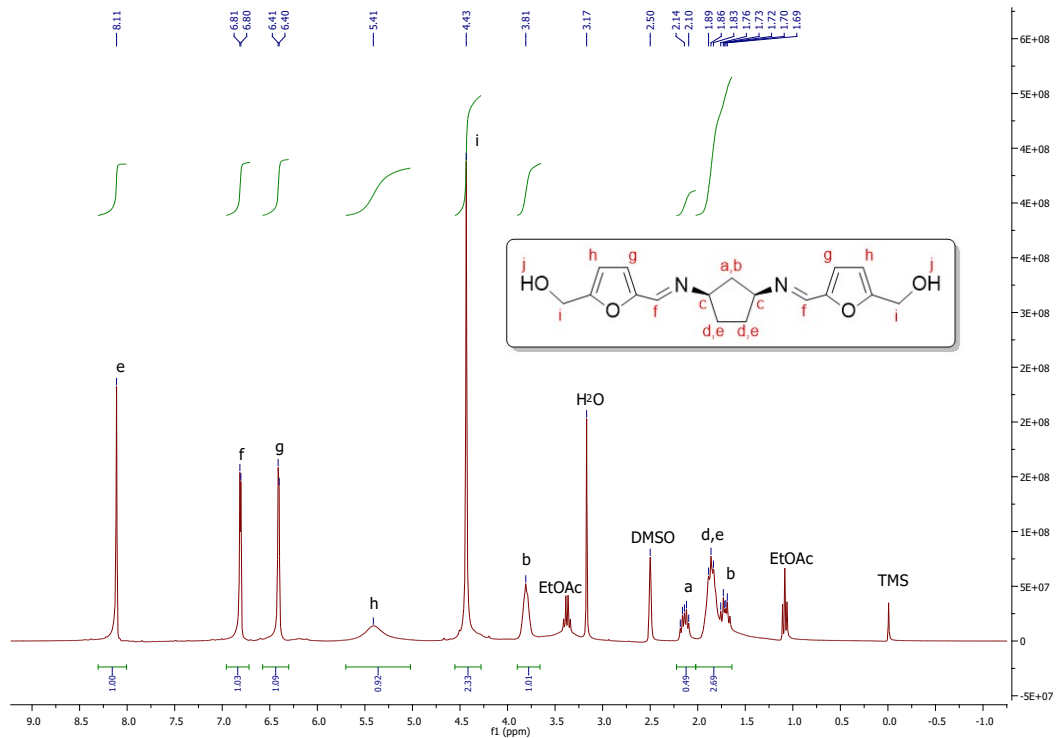


Figure S2.1.40: ¹H-NMR spectrum of **9** in DMSO-*d*₆.

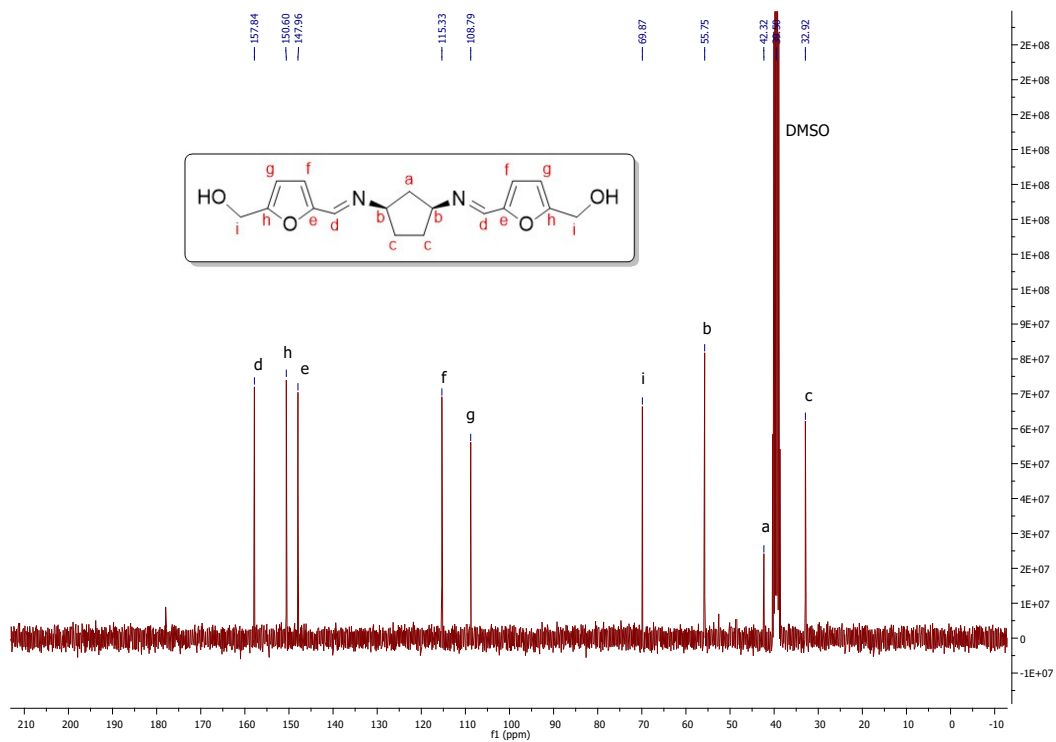


Figure S2.1.41: ¹³C-NMR spectrum of **9** in DMSO-*d*₆.

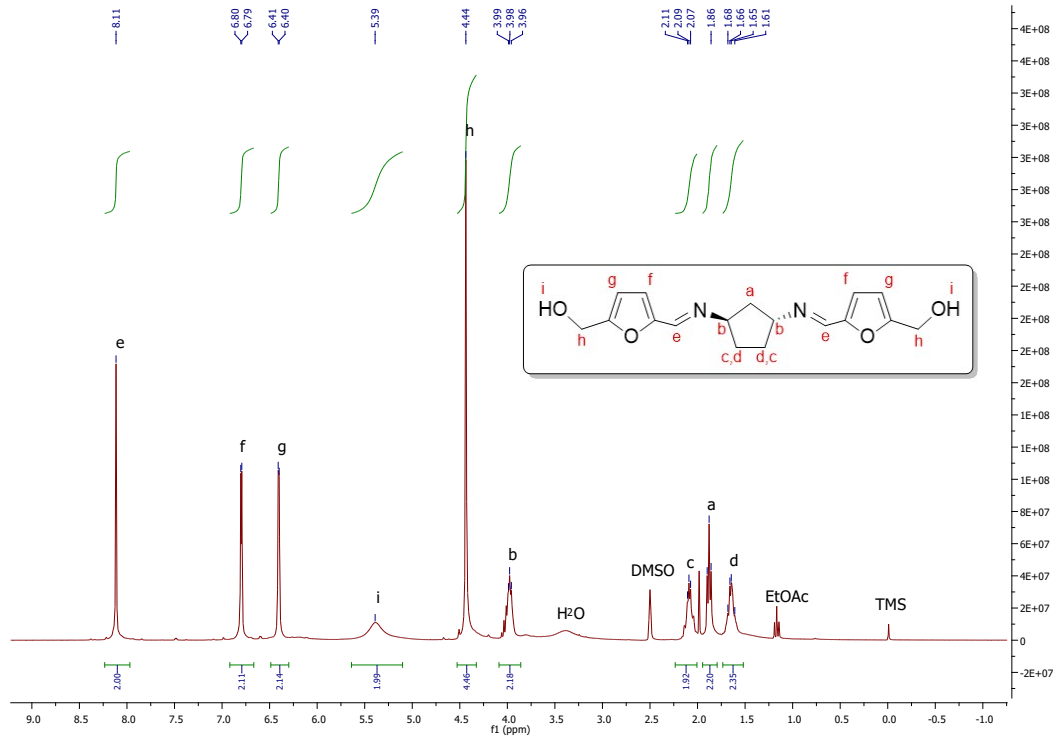


Figure S2.1.42: ^1H -NMR spectrum of **10** in $\text{DMSO-}d_6$.

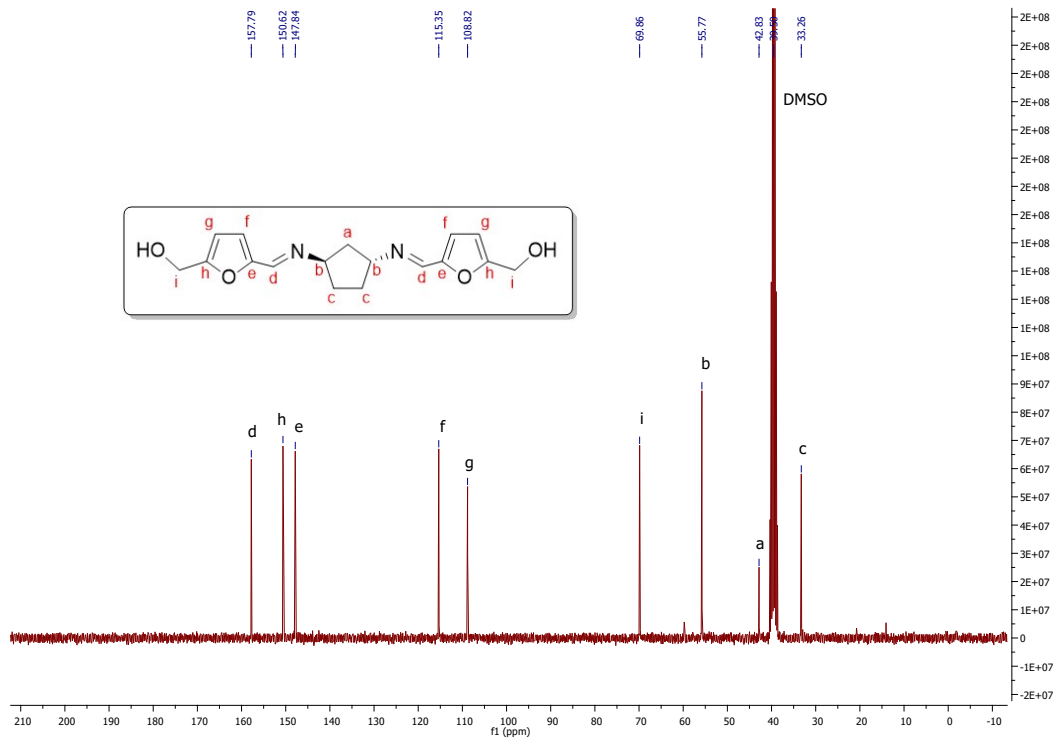


Figure S2.1.43: ^{13}C -NMR spectrum of **10** in $\text{DMSO-}d_6$.

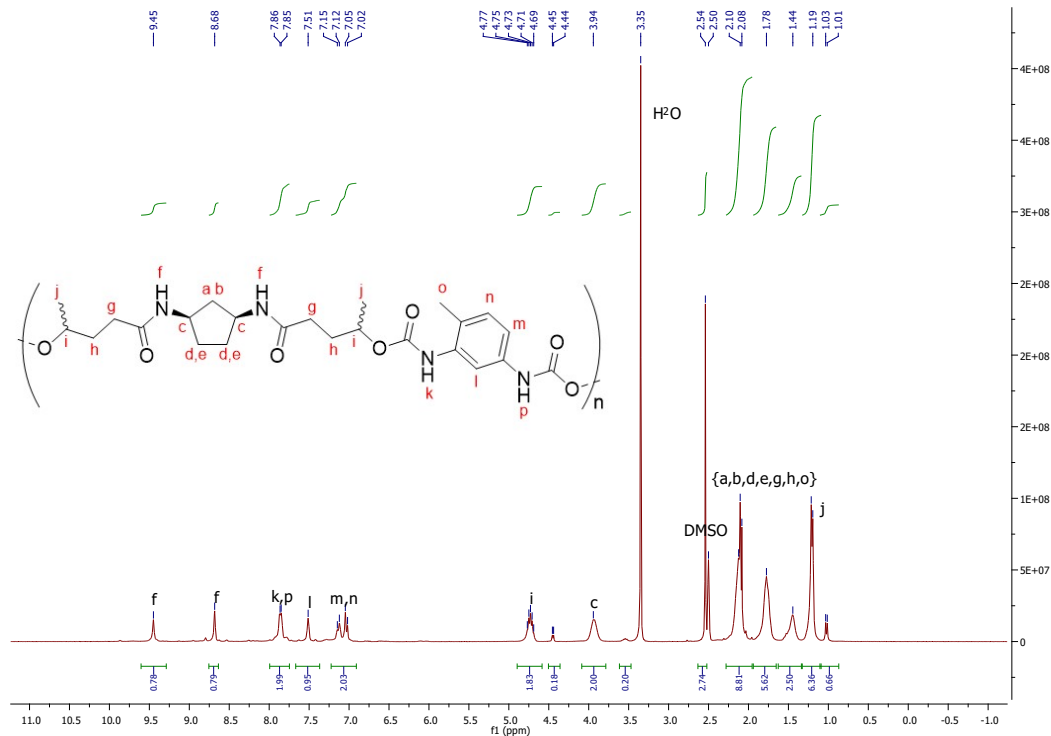


Figure S2.1.44: $^1\text{H-NMR}$ spectrum of polyurethane derived from **TDI** and triblock **5** in DMSO-d_6 .

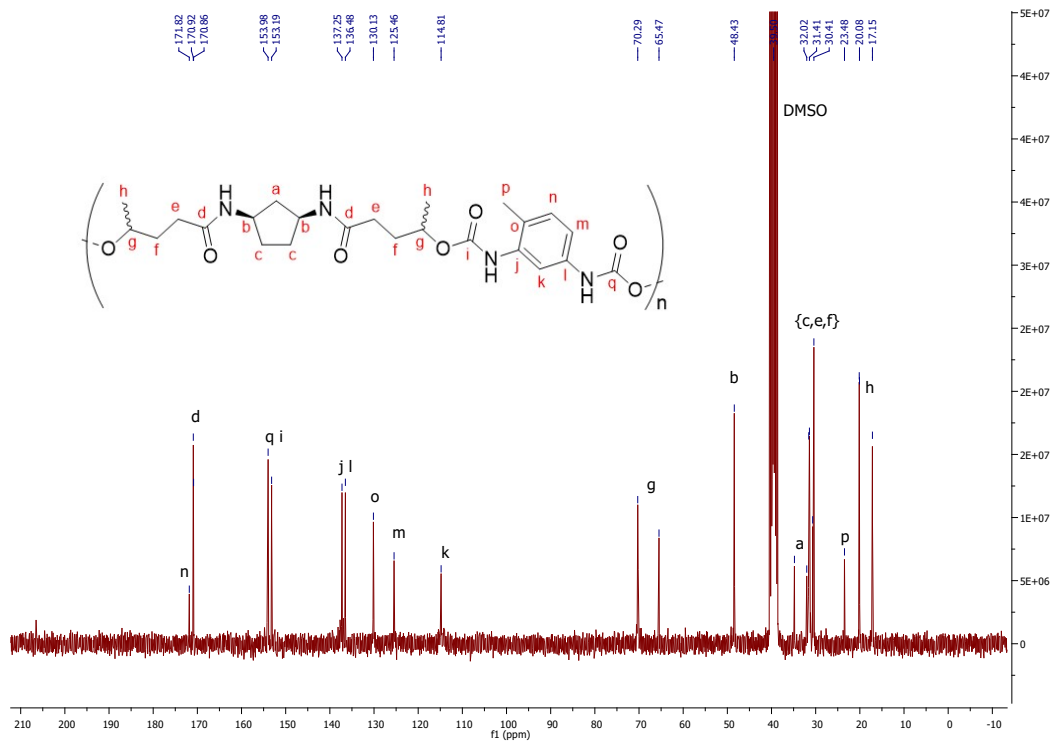


Figure S2.1.45: $^{13}\text{C-NMR}$ spectrum of polyurethane derived from **TDI** and triblock **5** in DMSO-d_6 .

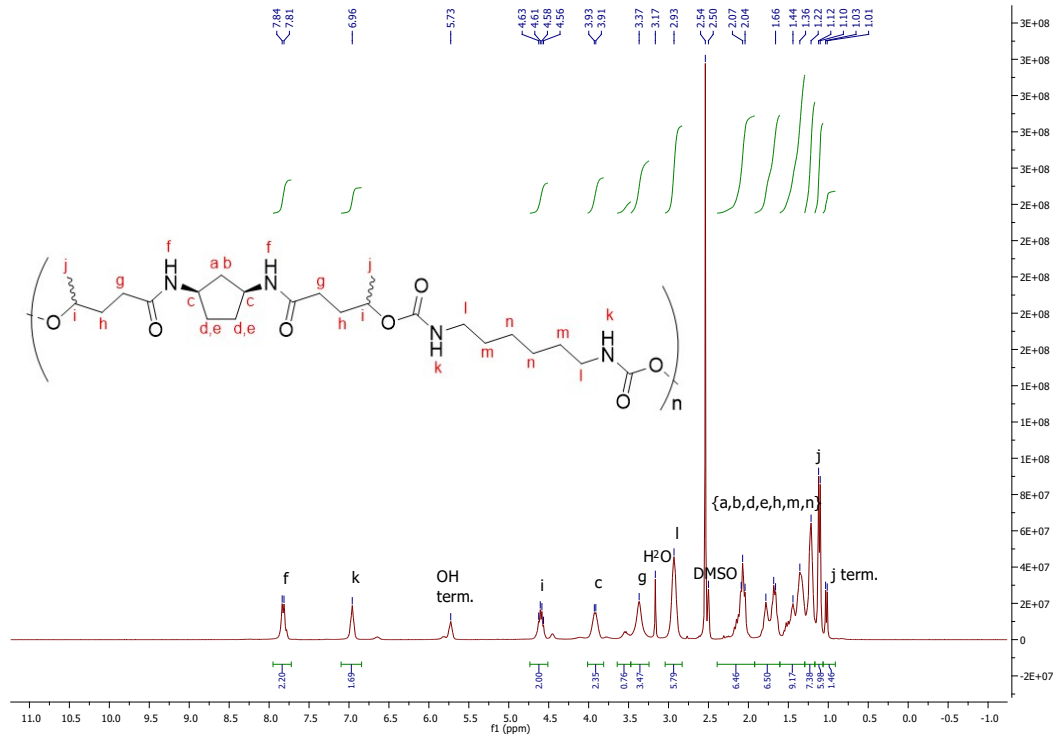


Figure S2.1.46: ^1H -NMR spectrum of polyurethane derived from **HDI** and triblock **5** in $\text{DMSO-}d_6$.

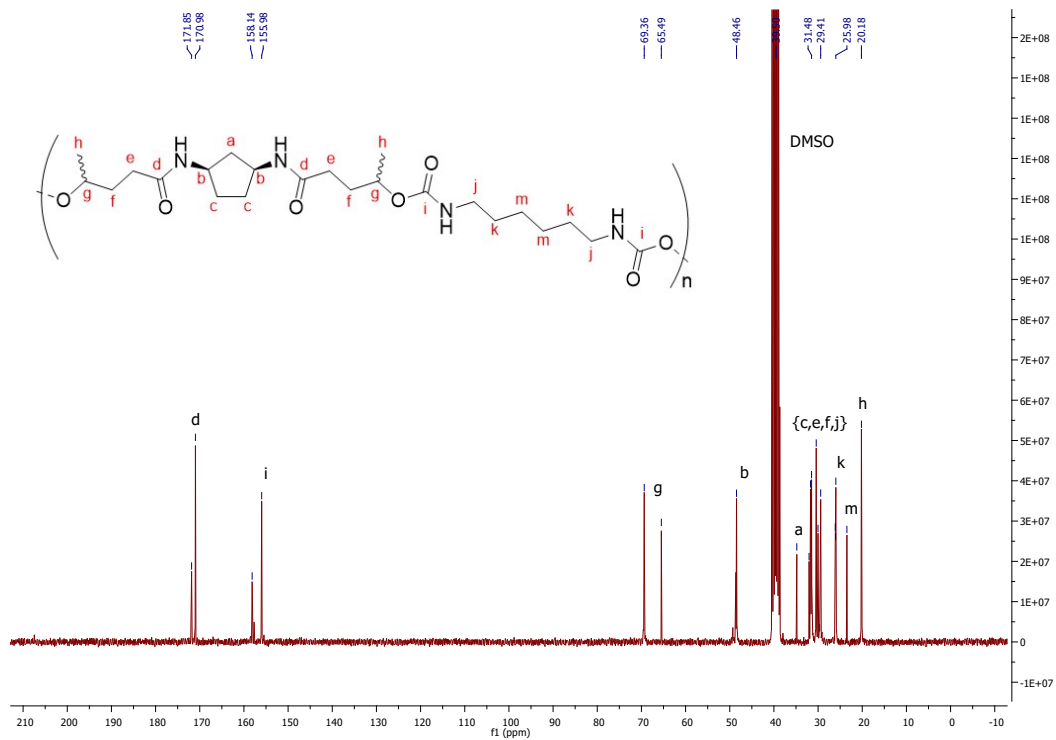


Figure S2.1.47: ^{13}C -NMR spectrum of polyurethane derived from **HDI** and triblock **5** in $\text{DMSO-}d_6$.

S2.2 FT-IR spectroscopy:



Figure S2.2.1: FTIR spectrum of 4-HCP.

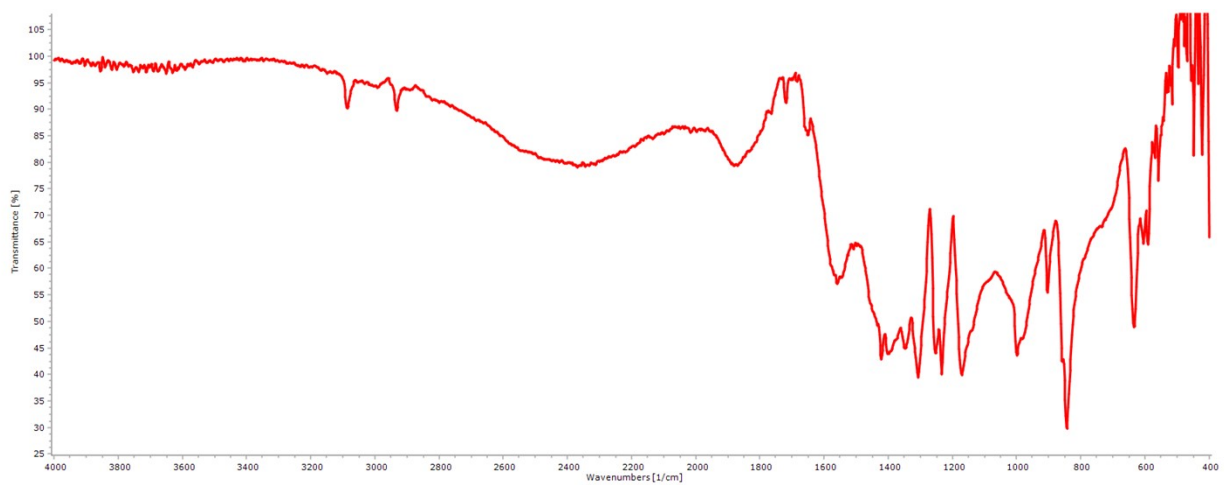


Figure S2.2.2: FTIR spectrum of CPDO.



Figure S2.2.3: FTIR spectrum of compound **1**.

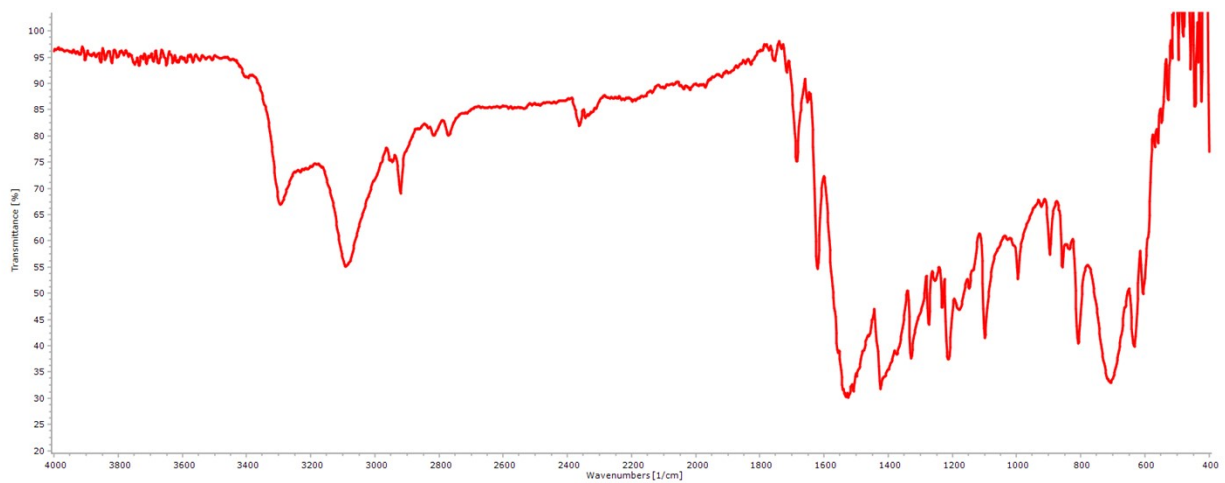


Figure S2.2.4: FTIR spectrum of **CPDI**.

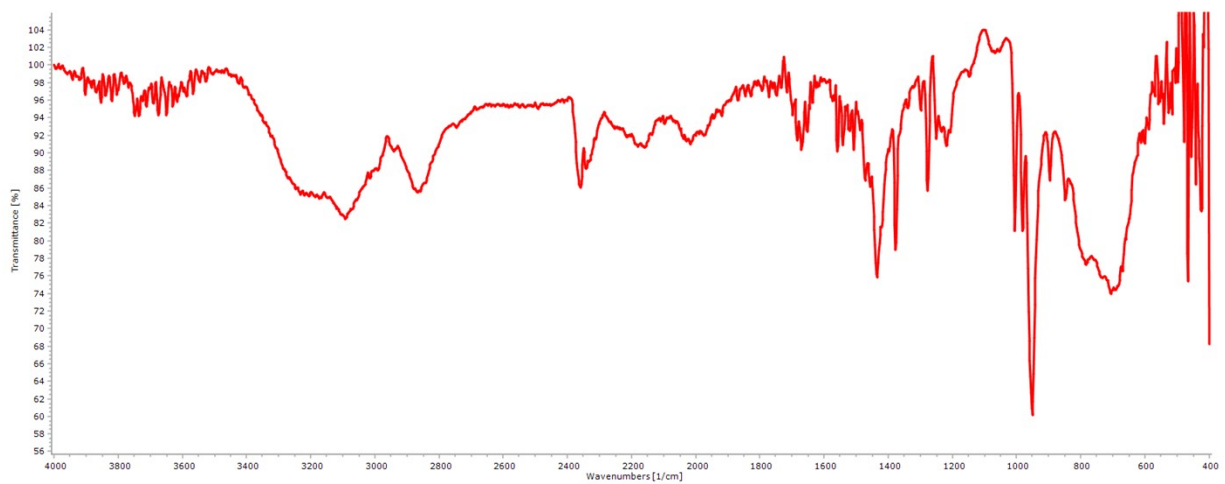


Figure S2.2.5: FTIR spectrum of CPDX.

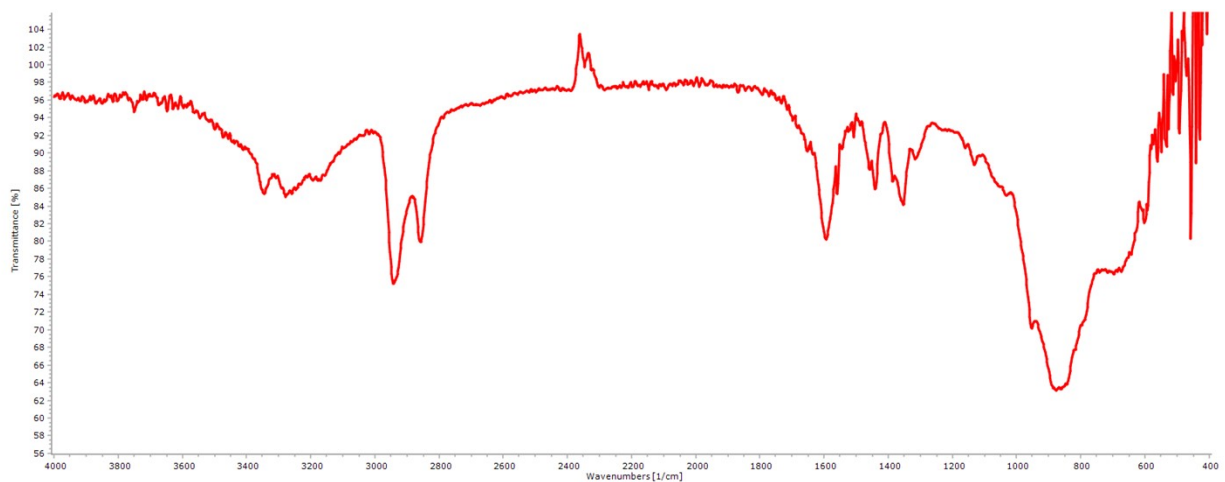


Figure S2.2.6: FTIR spectrum of CPDA (distillate, cis-trans ratio = 1:1).



Figure S2.2.7: FTIR spectrum of CPDA-dimer.

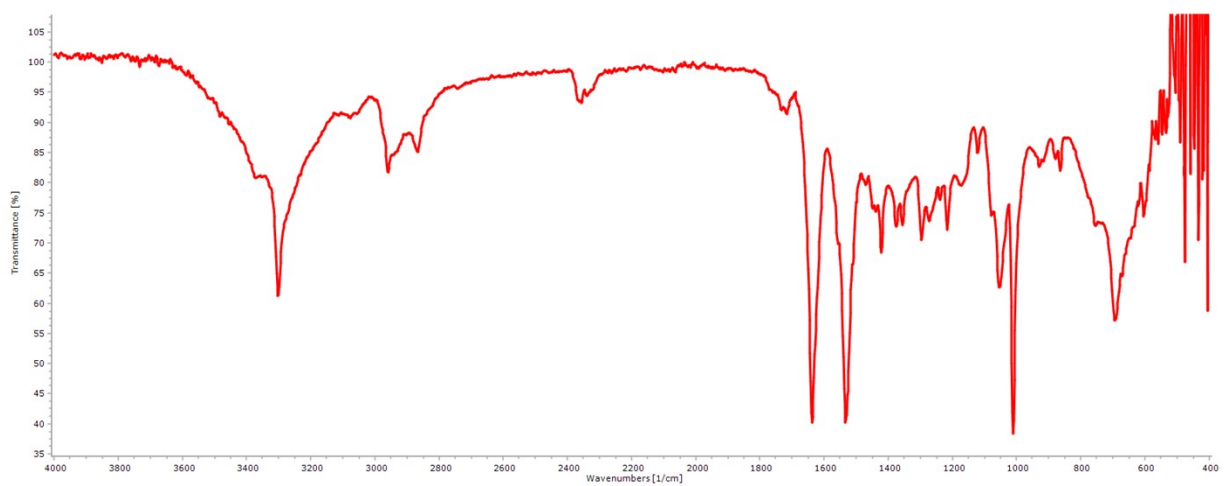


Figure S2.2.8: FTIR spectrum of compound 3.

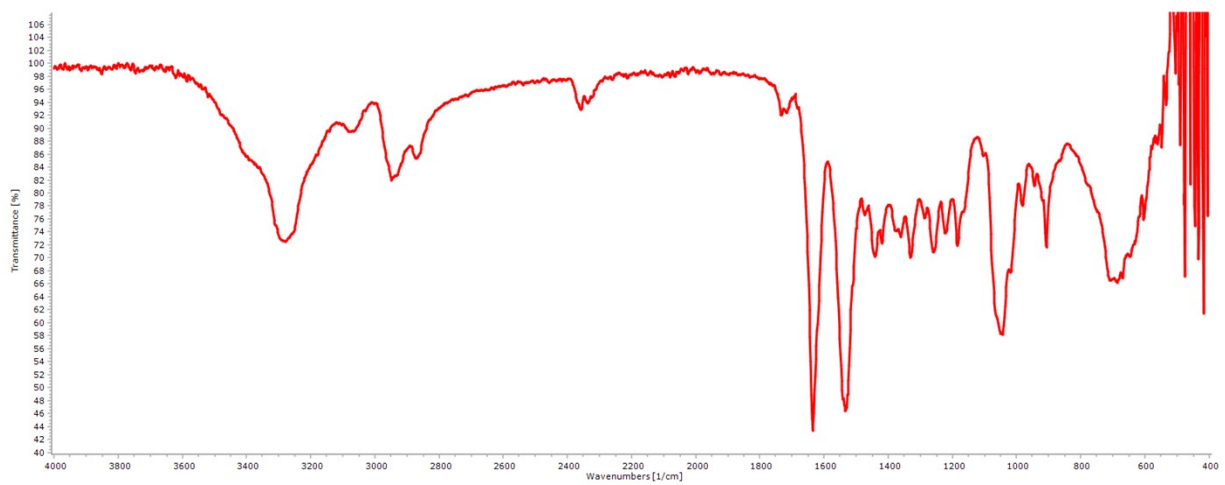


Figure S2.2.9: FTIR spectrum of compound 4.

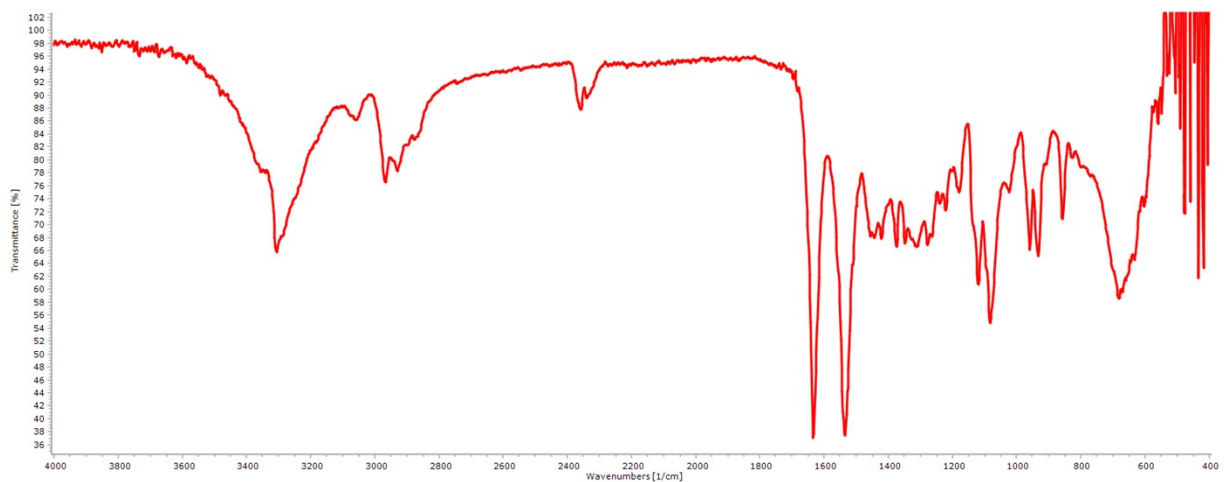


Figure S2.2.10: FTIR spectrum of compound 5.

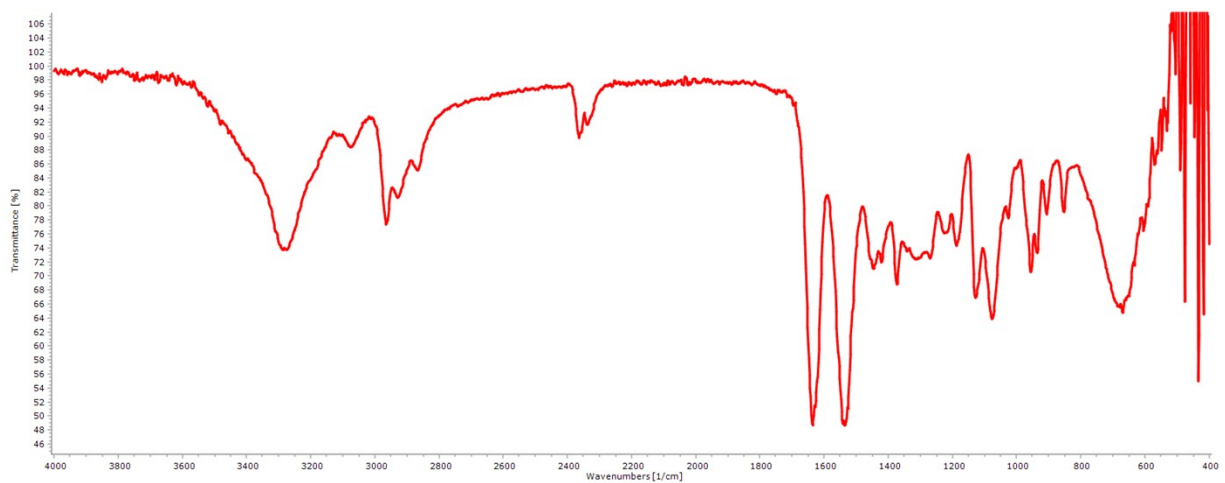


Figure S2.2.11: FTIR spectrum of compound 6.

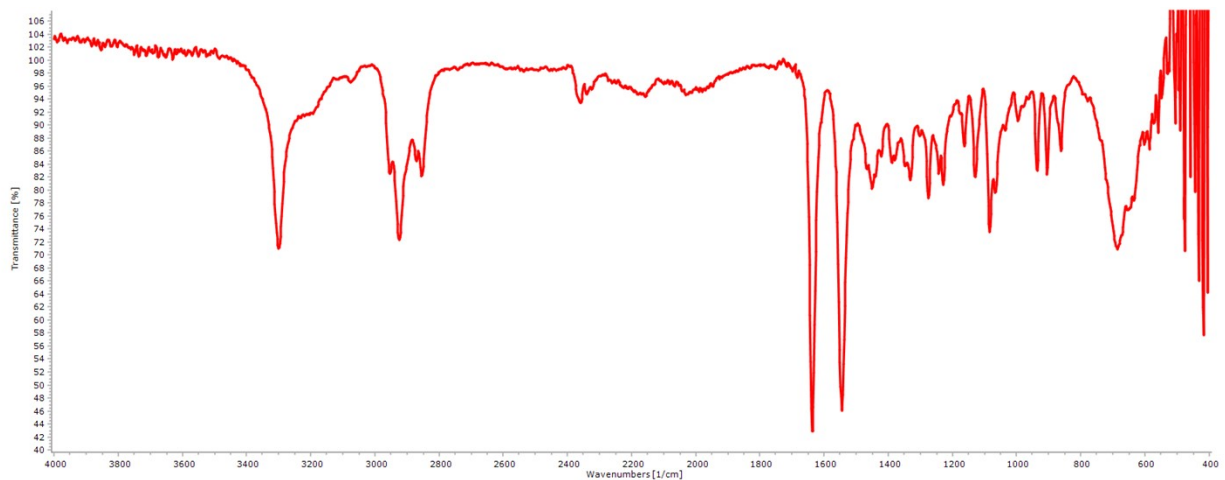


Figure S2.2.12: FTIR spectrum of compound 7.

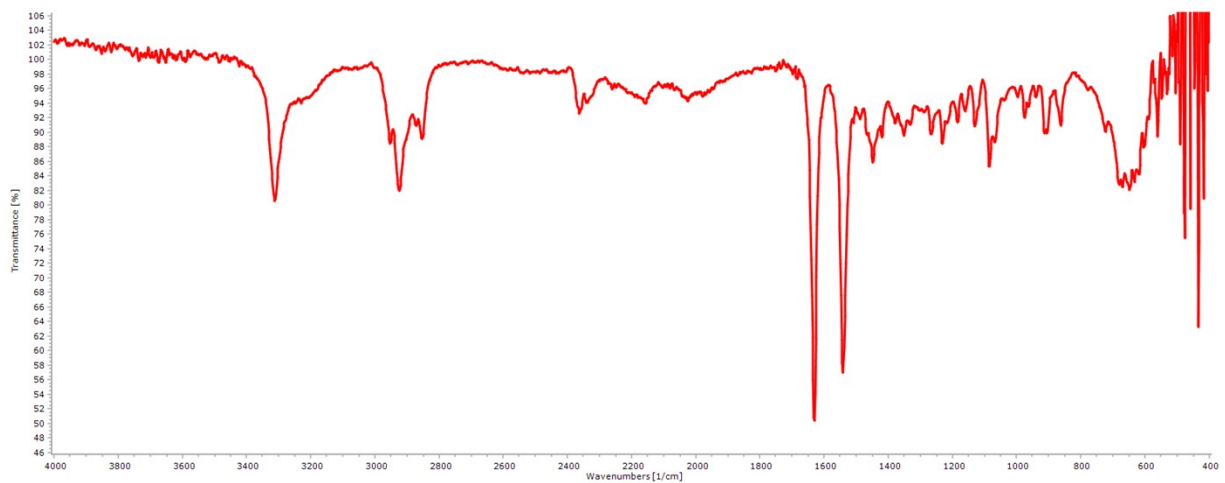


Figure S2.2.13: FTIR spectrum of compound 8.

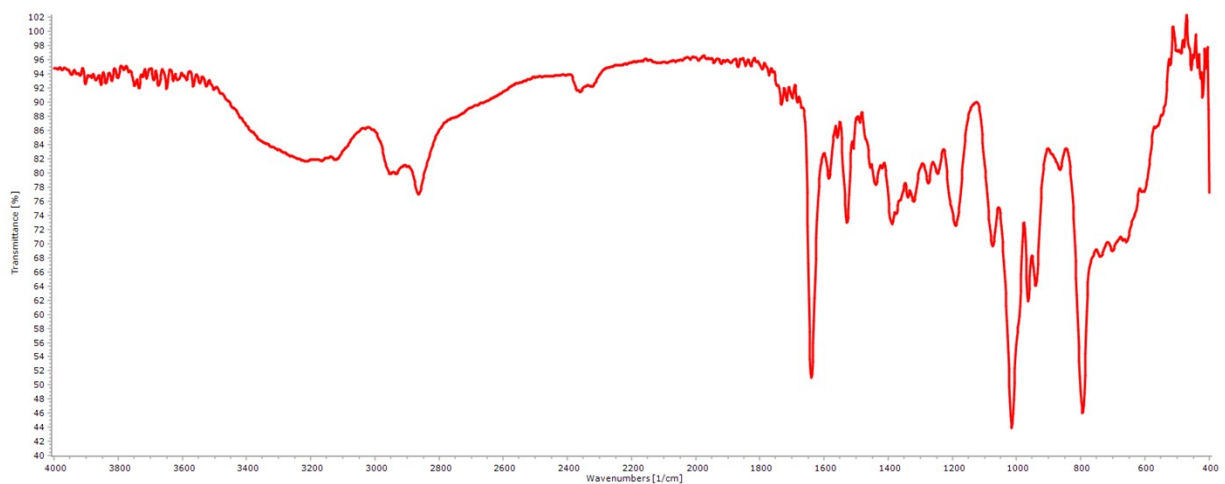


Figure S2.2.14: FTIR spectrum of compound **9**.



Figure S2.2.15: FTIR spectrum of compound **10**.

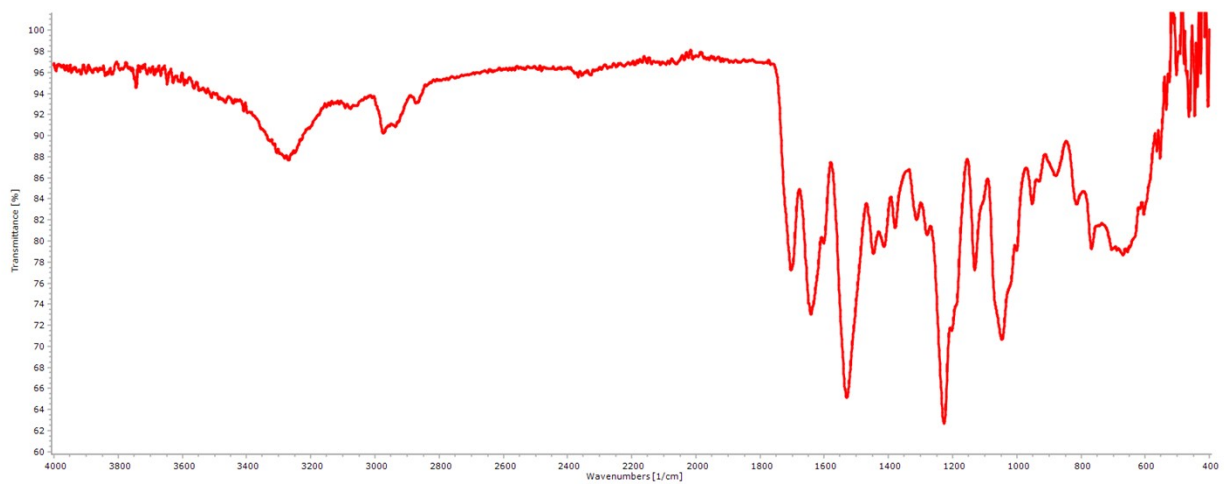


Figure S2.2.16: FTIR spectrum of the polyurethane derived from **TDI** and triblock 5.

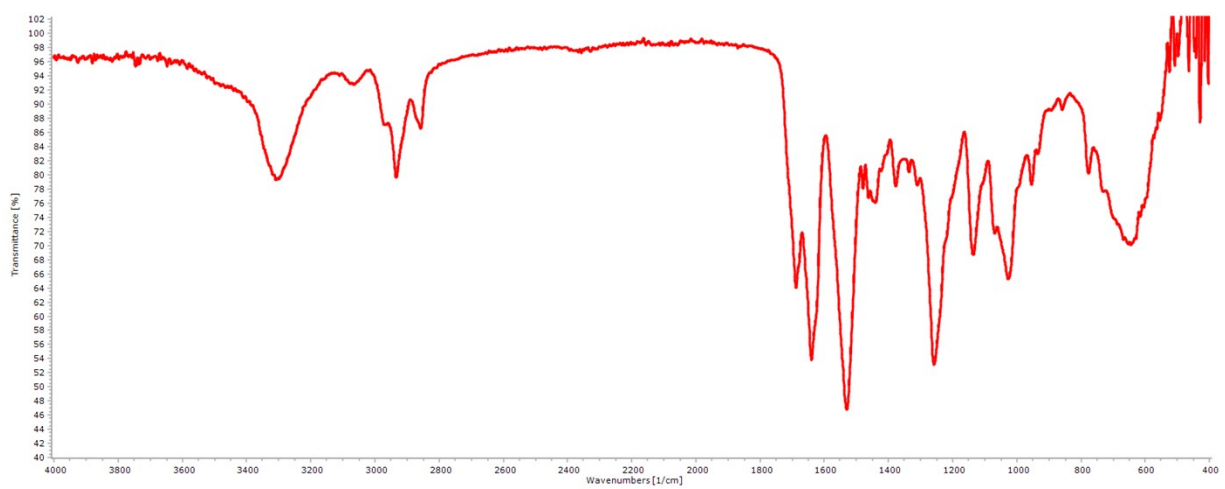


Figure S2.2.17: FTIR spectrum of the polyurethane derived from **HDI** and triblock 5.

S2.3 GC-FID chromatograms:

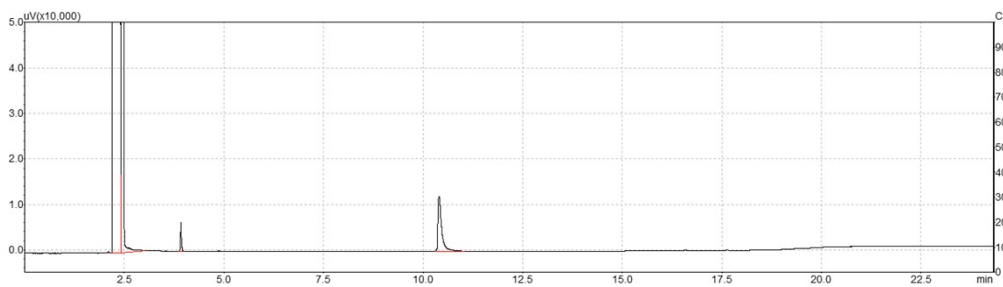


Figure S2.3.1: Gas chromatogram of 4-HCP.

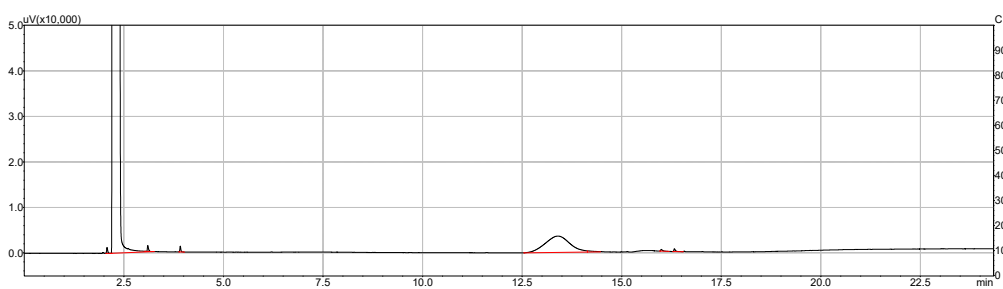


Figure S2.3.2: Gas chromatogram of CPDO.

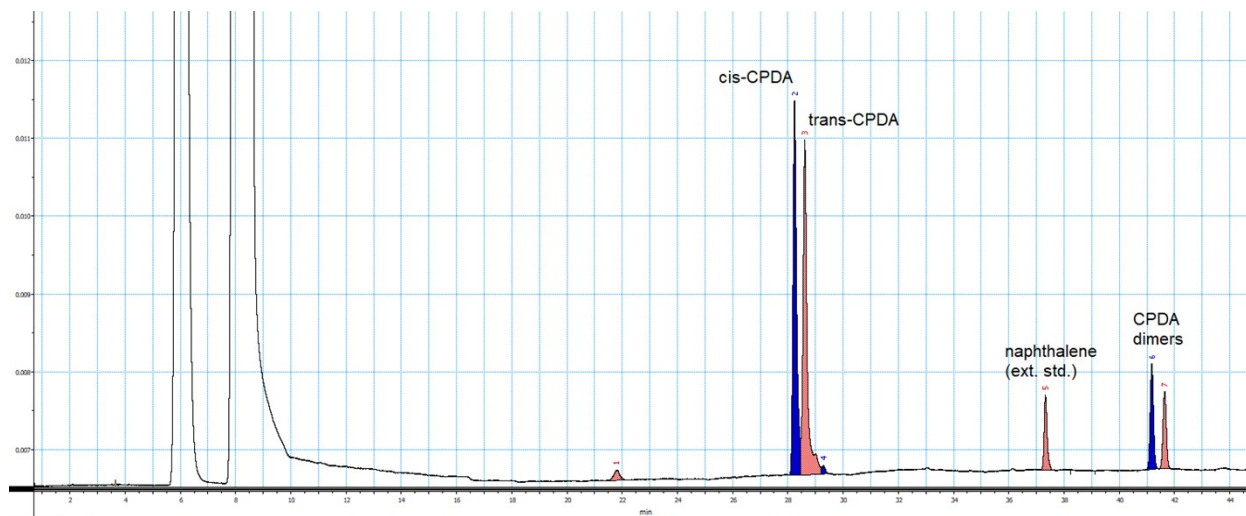


Figure S2.3.3: Representative gas chromatogram of a crude reaction mixture from CPDX to CPDA hydrogenation.

S2.4 High-resolution mass-spectrometry (HR-MS):

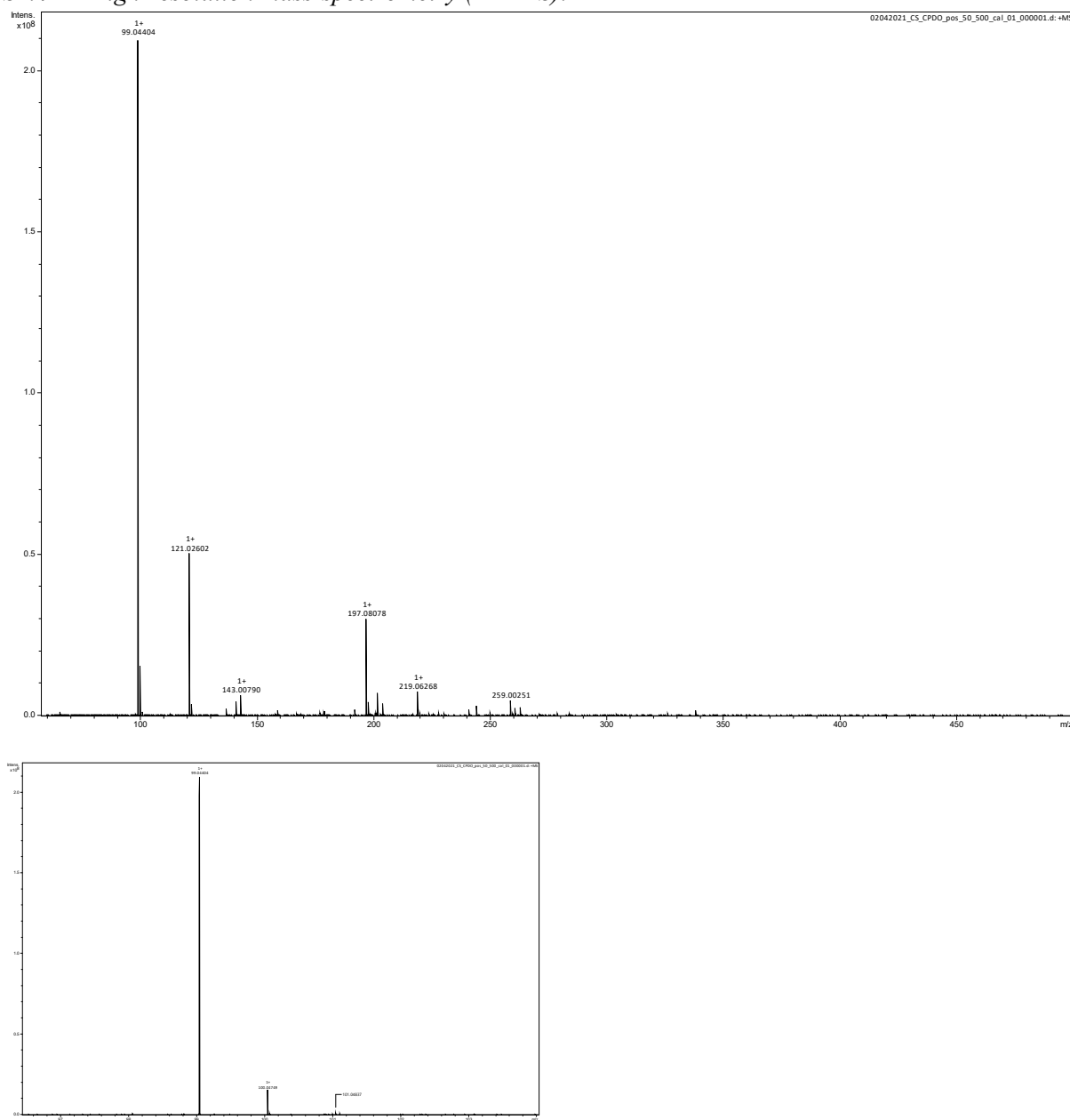


Figure S2.4.1: HR-MS analysis in ESI+ mode of CPDO; full spectrum (top), and zoom of $[\text{CPDO} + \text{H}]^+$ (bottom).

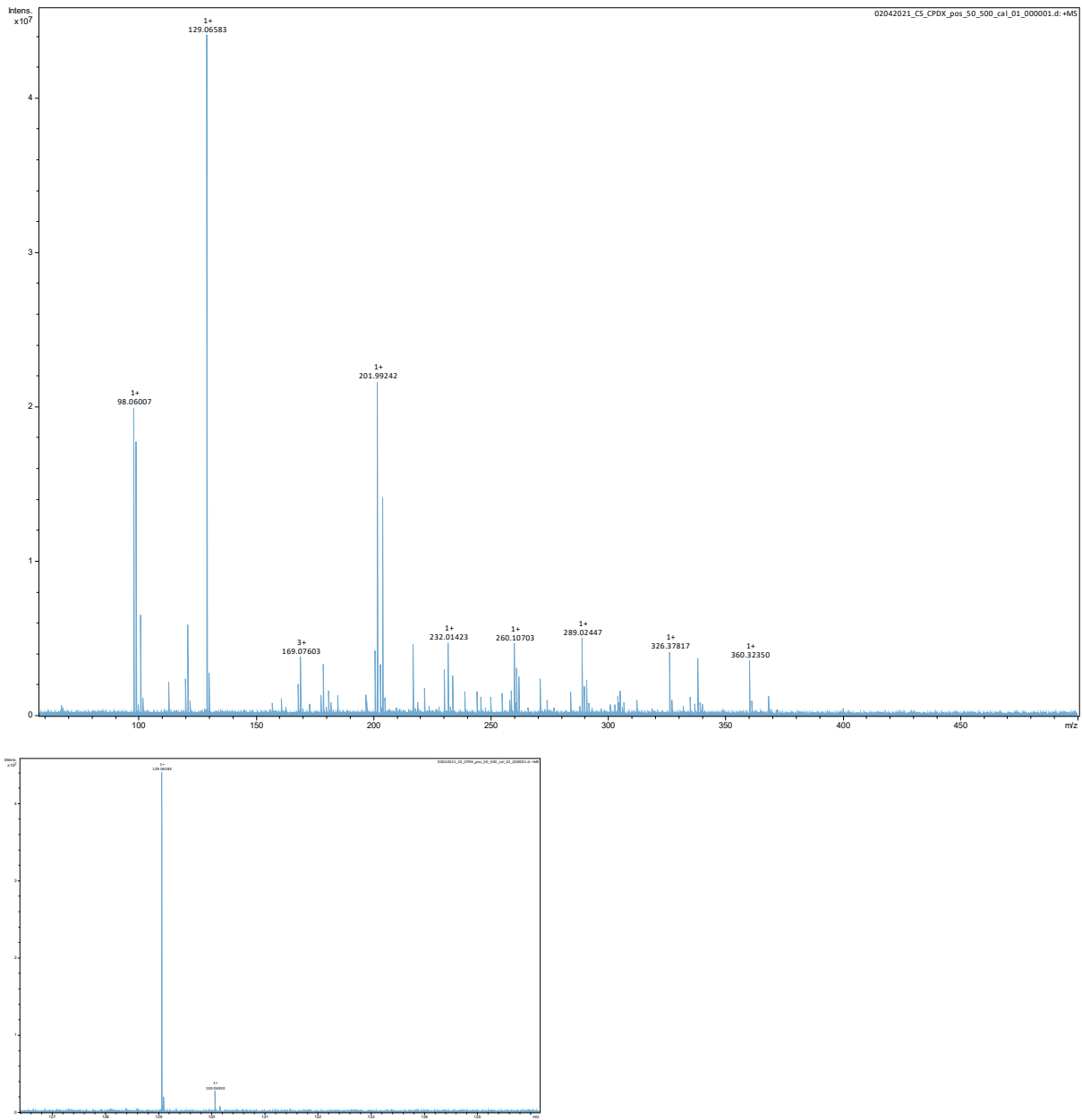


Figure S2.4.2: HR-MS analysis in ESI+ mode of CPDX; full spectrum (top), and zoom of [CPDX + H]⁺ (bottom).

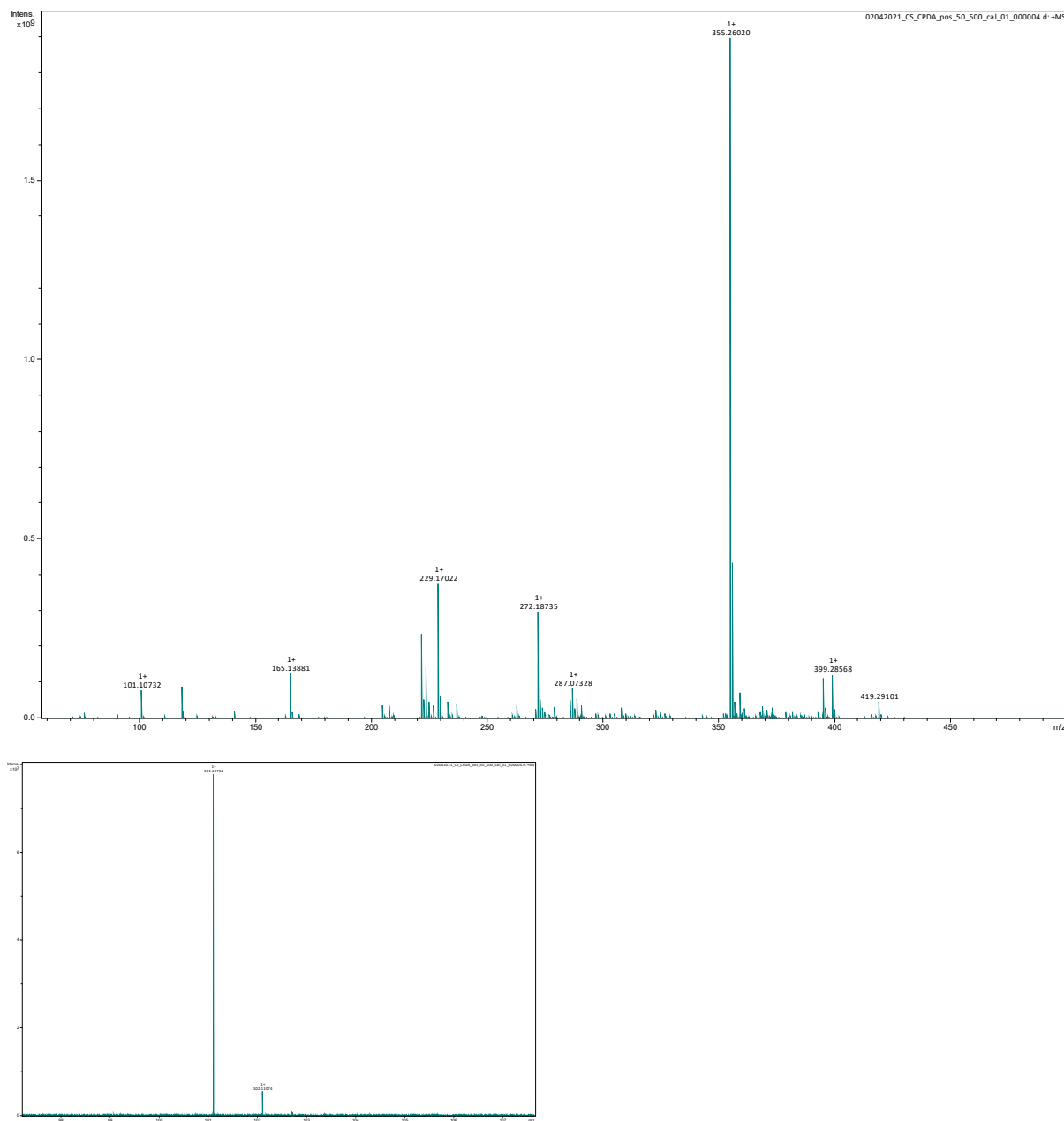


Figure S2.4.3: HR-MS analysis in ESI+ mode of CPDA; full spectrum (top), and zoom of [CPDA + H]⁺ (bottom).

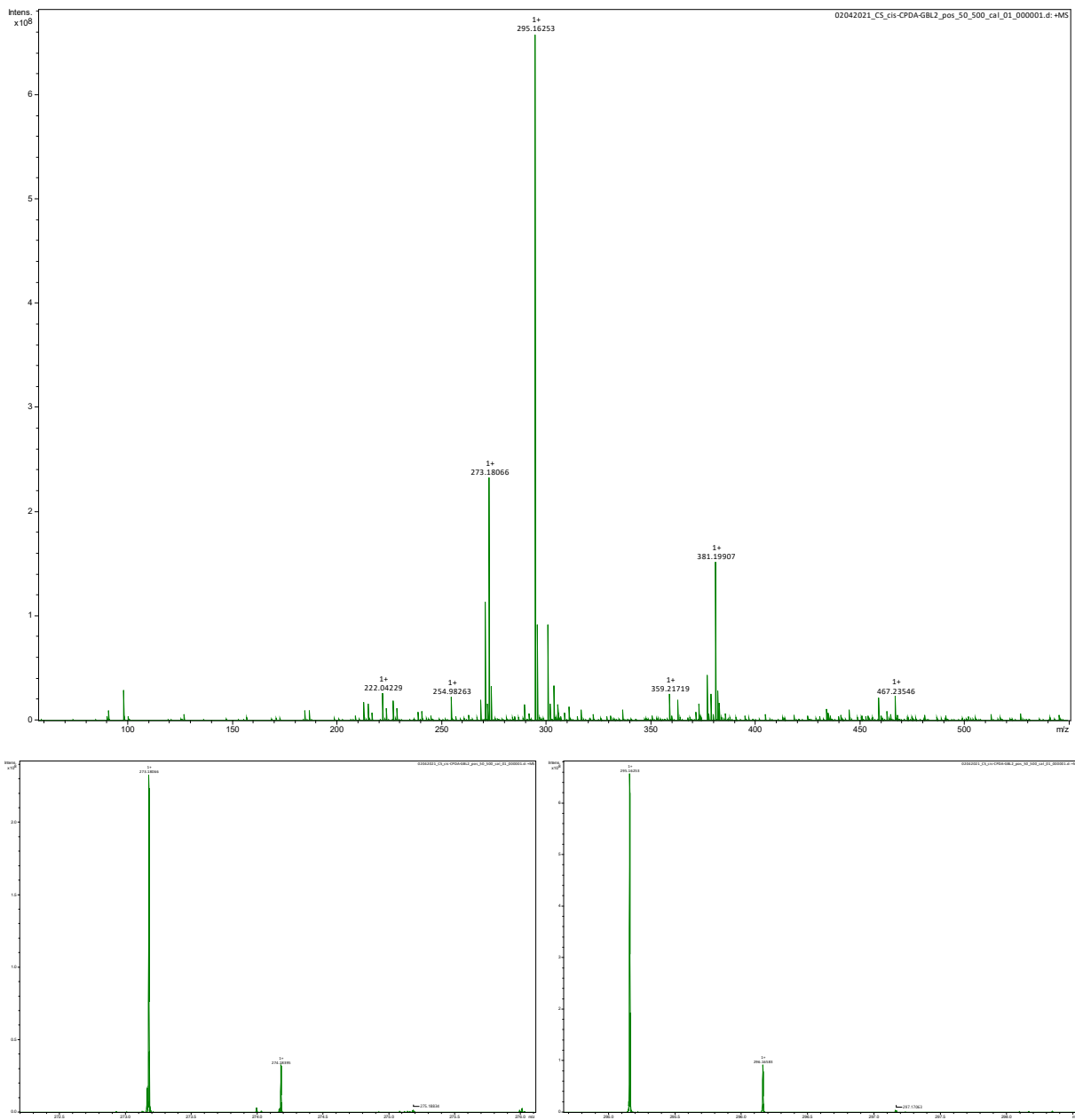


Figure S2.4.4: HR-MS analysis in ESI+ mode of **3**; full spectrum (top); zoom of $[3 + H]^+$ (bottom-left), and zoom of $[3 + Na]^+$ (bottom-right).

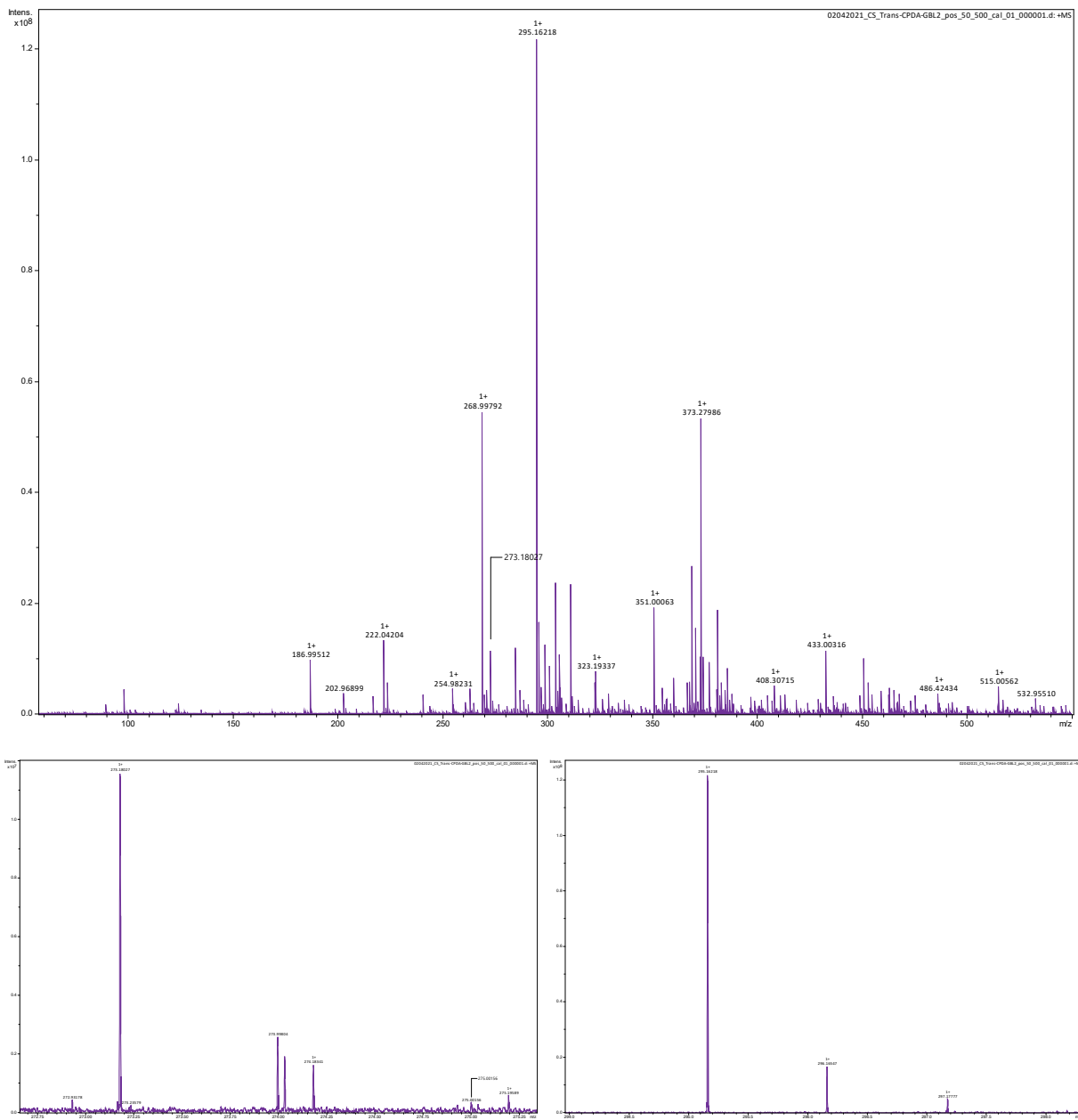


Figure S2.4.4: HR-MS analysis in ESI⁺ mode of 4; full spectrum (top); zoom of $[4 + H]^+$ (bottom-left), and zoom of $[4 + Na]^+$ (bottom-right).

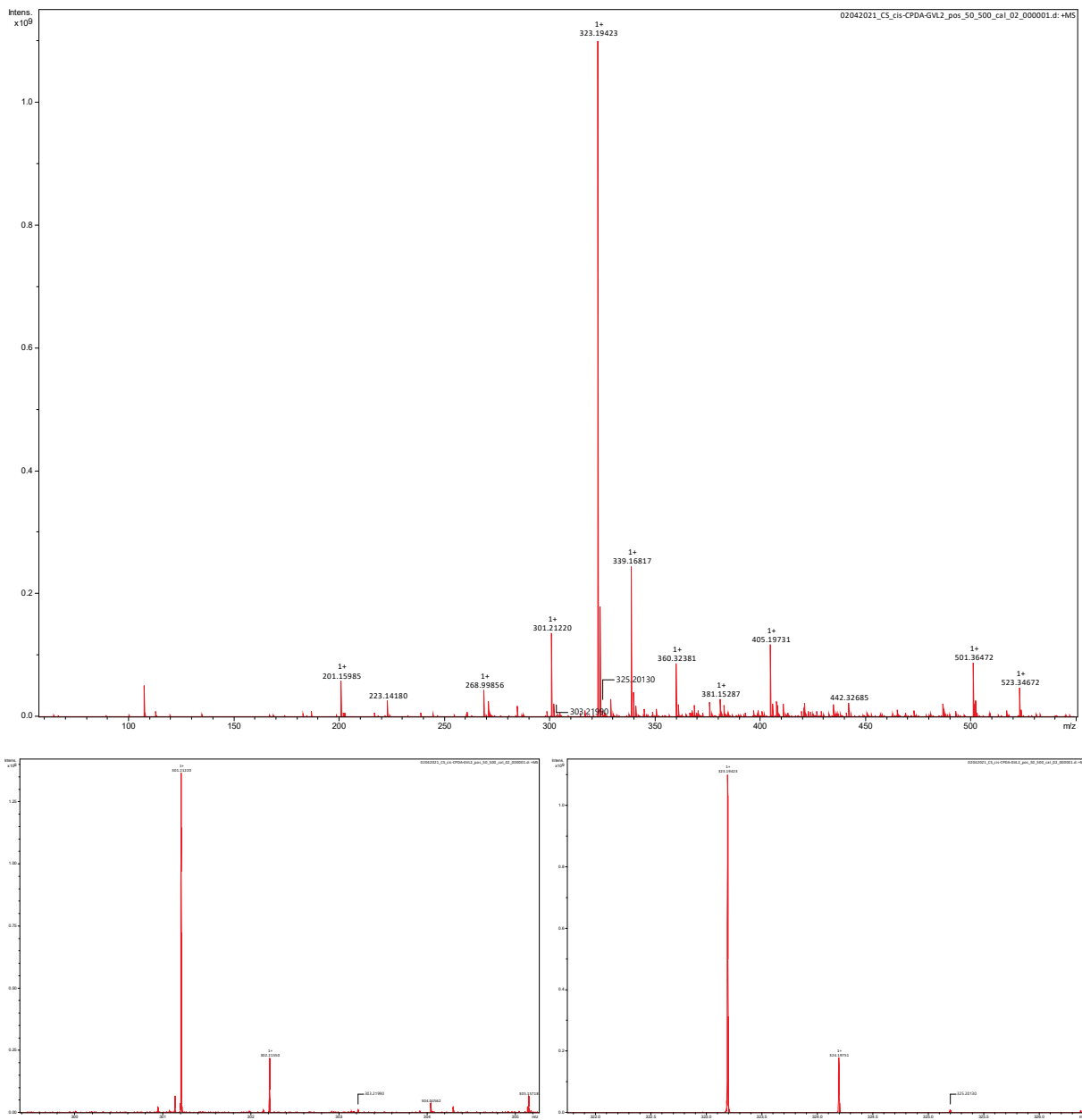


Figure S2.4.5: HR-MS analysis in ESI⁺ mode of **5**; full spectrum (top); zoom of [5 + H]⁺ (bottom-left), and zoom of [5 + Na]⁺ (bottom-right).

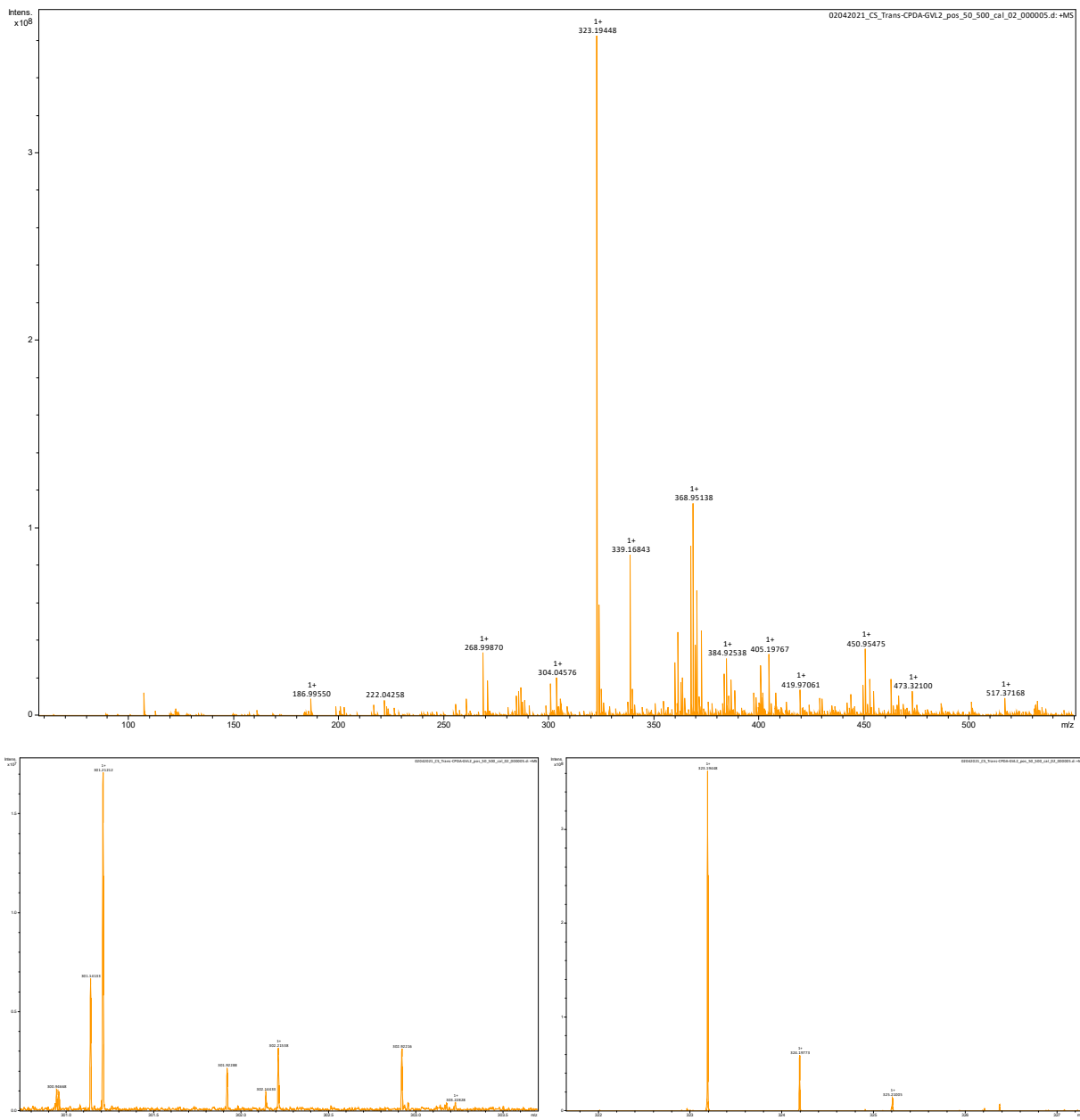


Figure S2.4.6: HR-MS analysis in ESI⁺ mode of **6**; full spectrum (top); zoom of [6 + H]⁺ (bottom-left), and zoom of [6 + Na]⁺ (bottom-right).

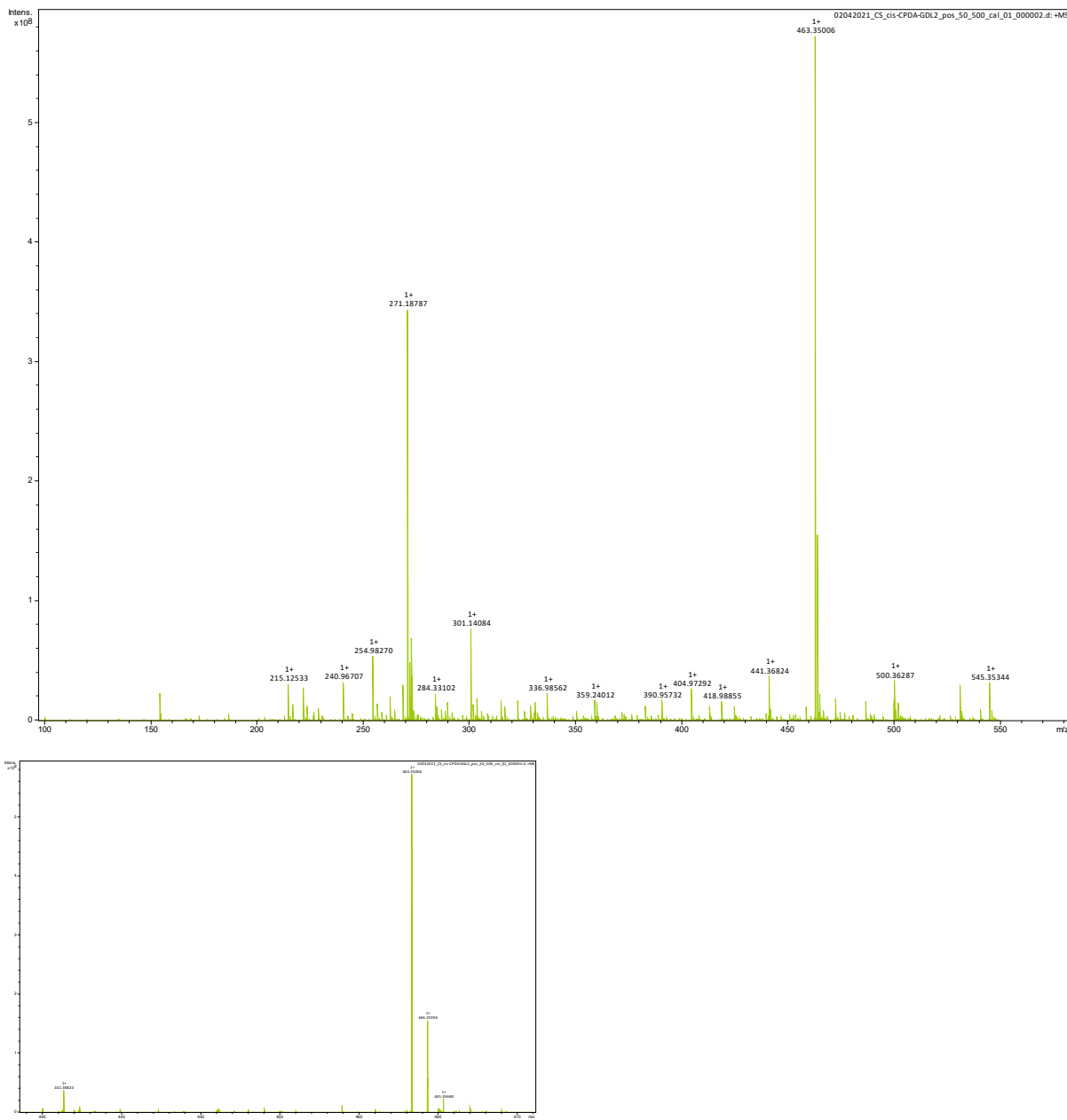


Figure S2.4.7: HR-MS analysis in ESI+ mode of 7; full spectrum (top); zoom of $[7 + H]^+$ and $[7 + Na]^+$ (bottom).

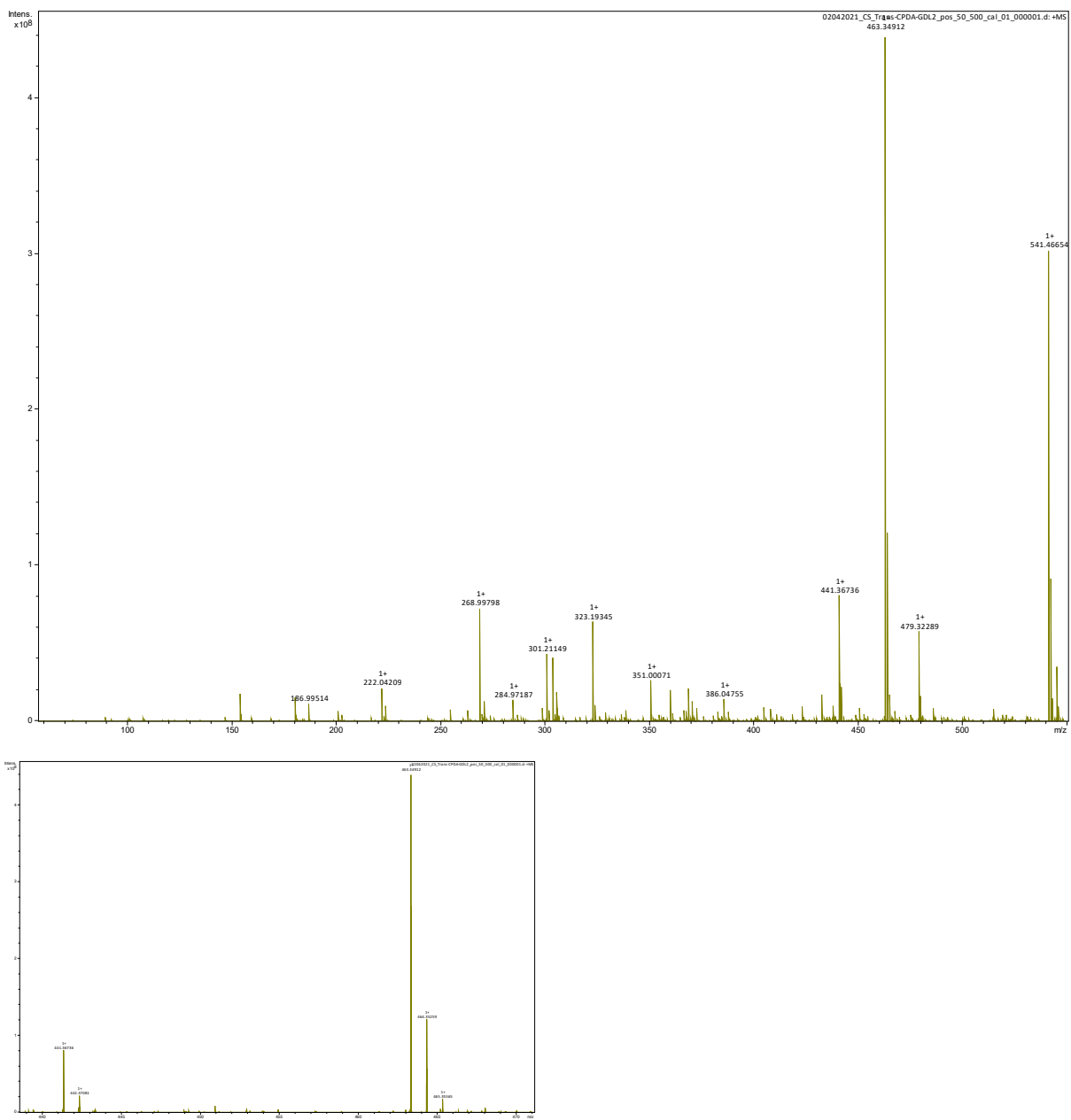


Figure S2.4.8: HR-MS analysis in ESI+ mode of **8**; full spectrum (top); zoom of $[8 + H]^+$ and $[8 + Na]^+$ (bottom).

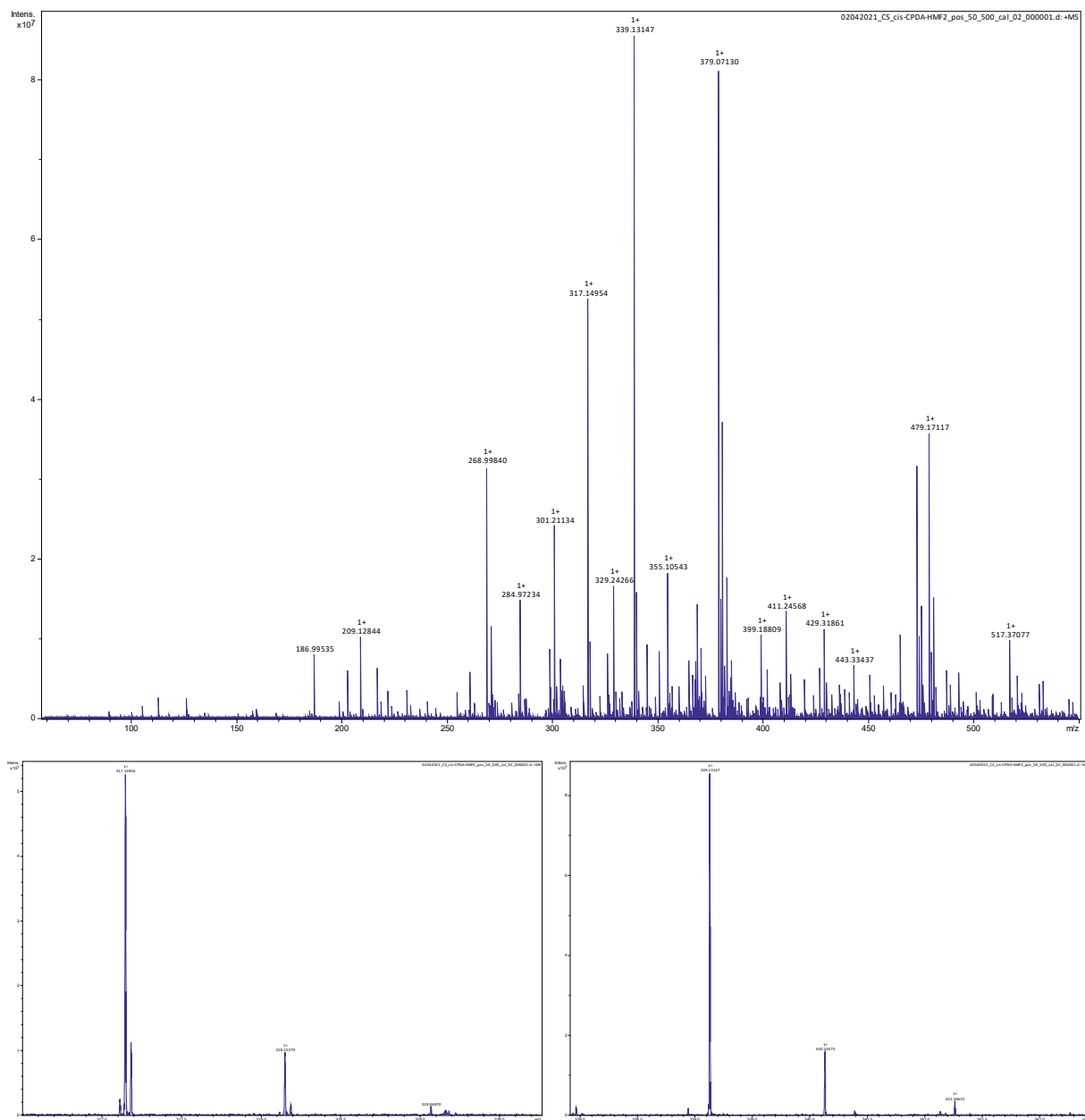


Figure S2.4.9: HR-MS analysis in ESI+ mode of **9**; full spectrum (top); zoom of $[9 + H]^+$ (bottom-left), and zoom of $[9 + Na]^+$ (bottom-right).

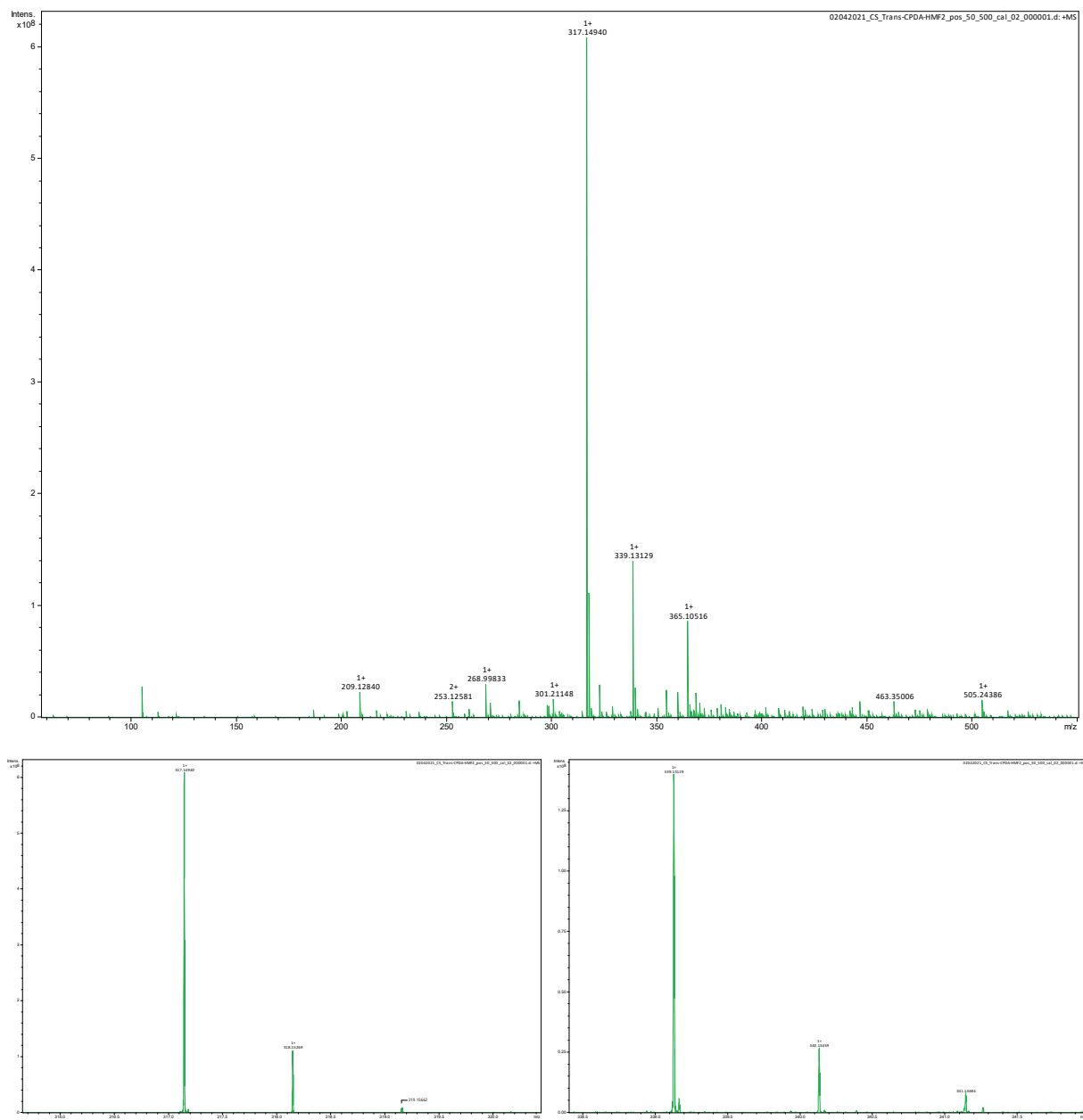


Figure S2.4.10: HR-MS analysis in ESI⁺ mode of **10**; full spectrum (top); zoom of [10 + H]⁺ (bottom-left), and zoom of [10 + Na]⁺ (bottom-right).

S2.5 Gel permeation chromatography (GPC):

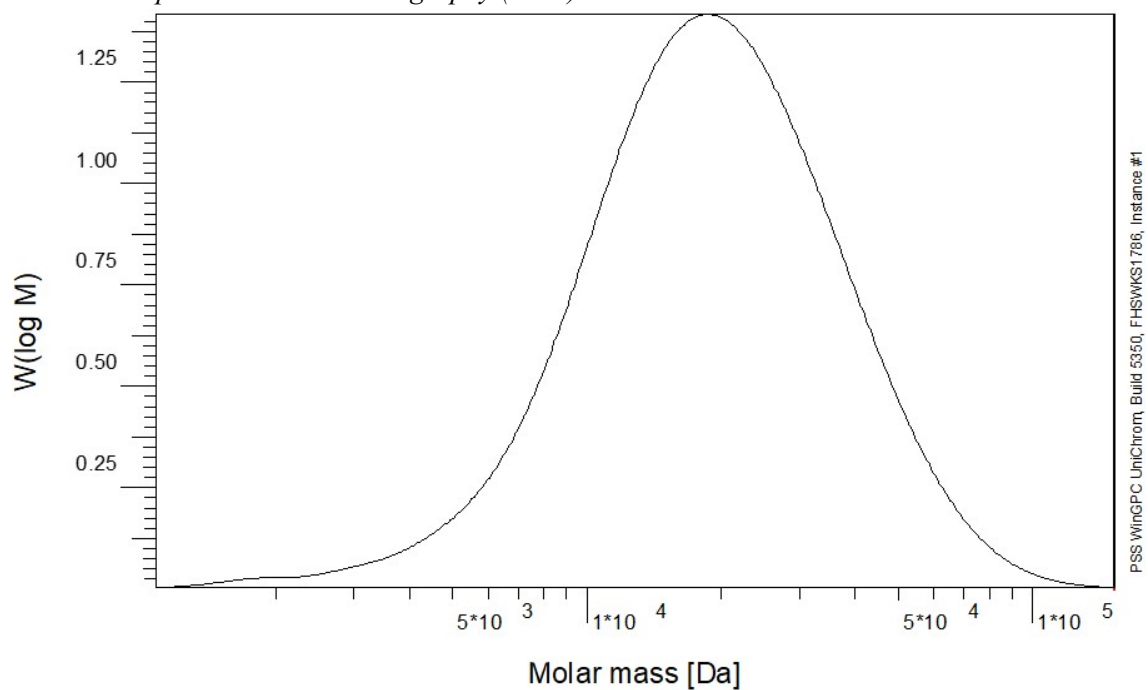


Figure S2.5.1: GPC chromatogram complementary to Table 3, entry 4.

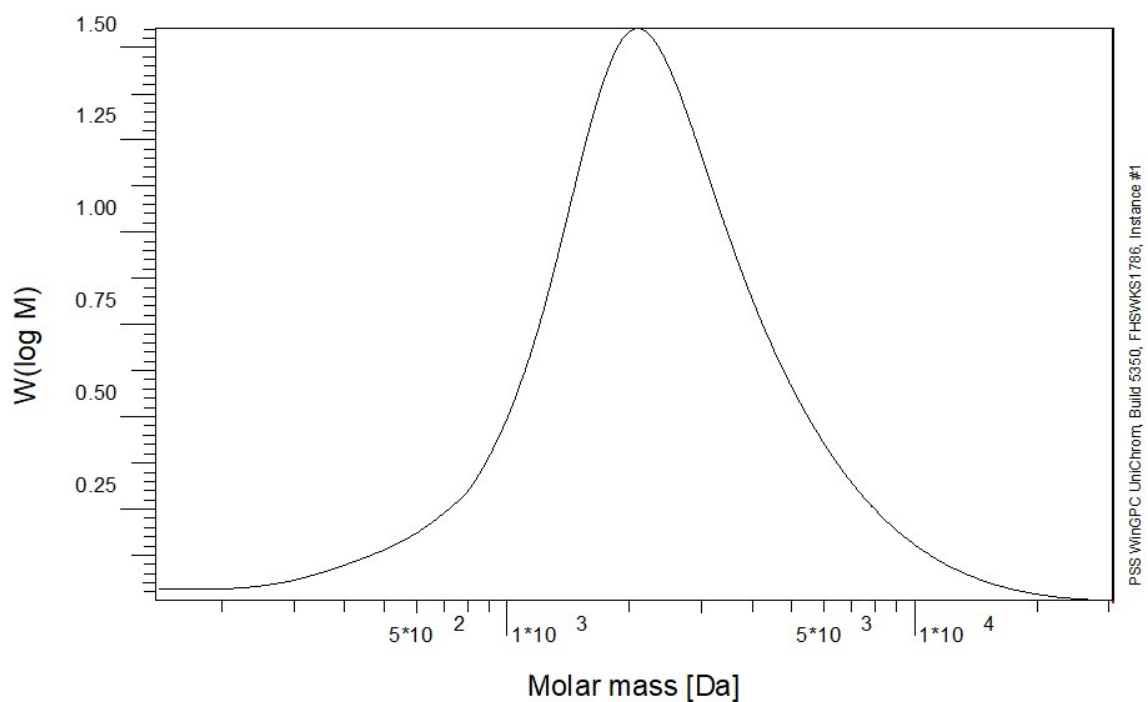


Figure S2.5.1: GPC chromatogram complementary to Table 3, entry 5.

S2.6 Thermogravimetric analysis (TGA):

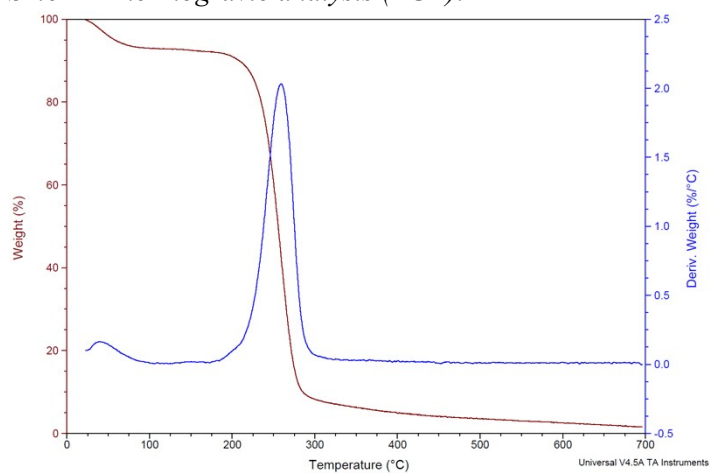


Figure S2.6.1: TGA plot complementary to Table 3, entry 3.

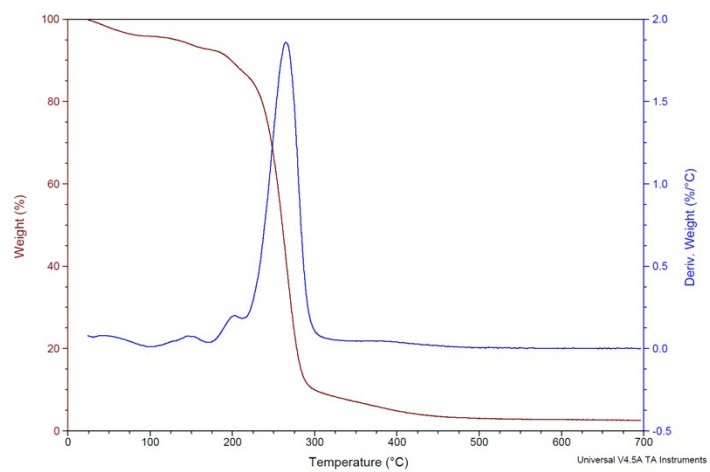


Figure S2.6.2: TGA plot complementary to Table 3, entry 4.

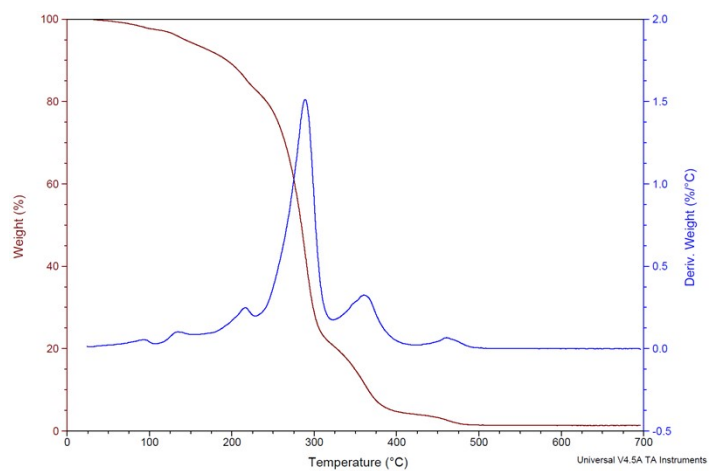


Figure S2.6.3: TGA plot complementary to Table 3, entry 5.

S2.7 Differential Scanning Calorimetry (DSC):

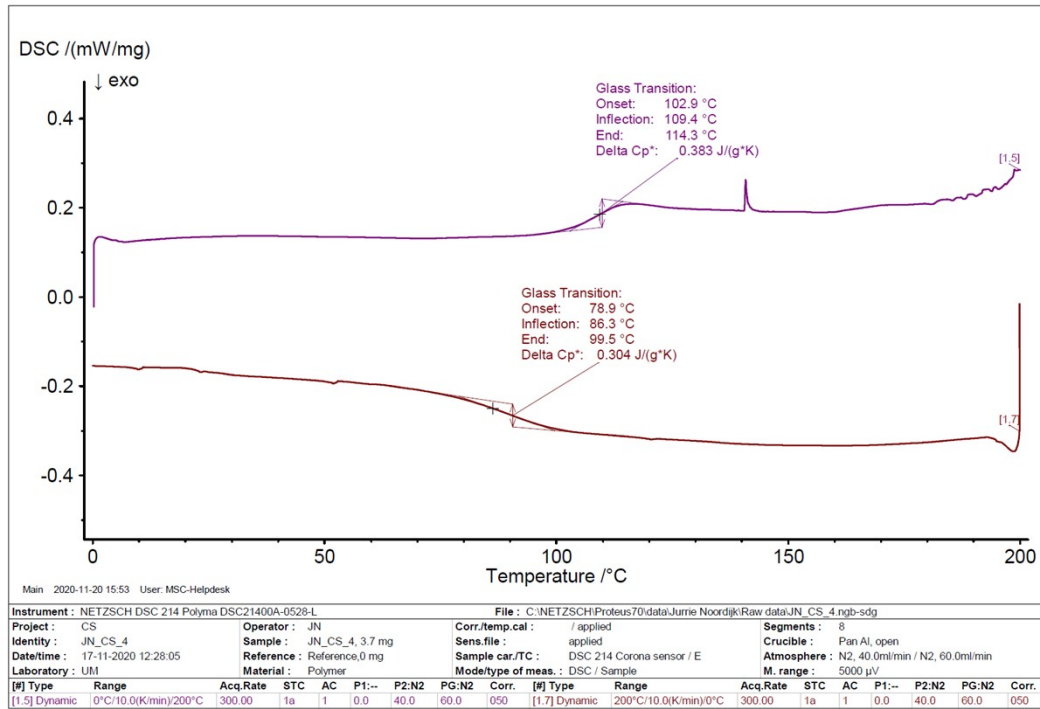


Figure S2.7.1: DSC plot complementary to Table 3, entry 3.

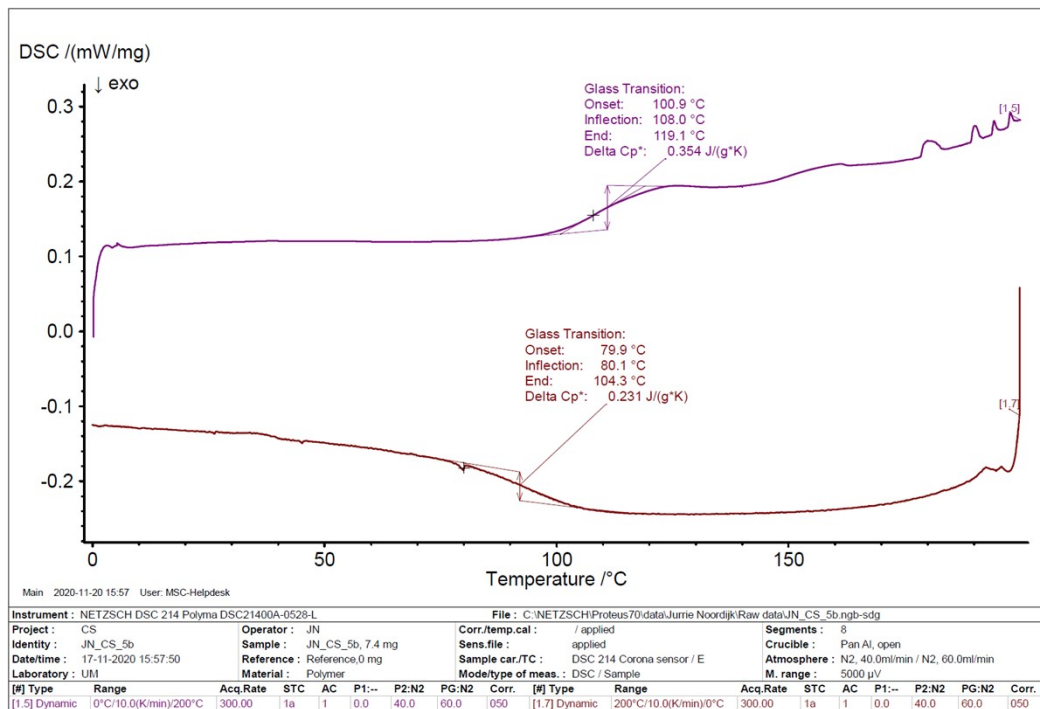


Figure S2.7.2: DSC plot complementary to Table 3, entry 4.

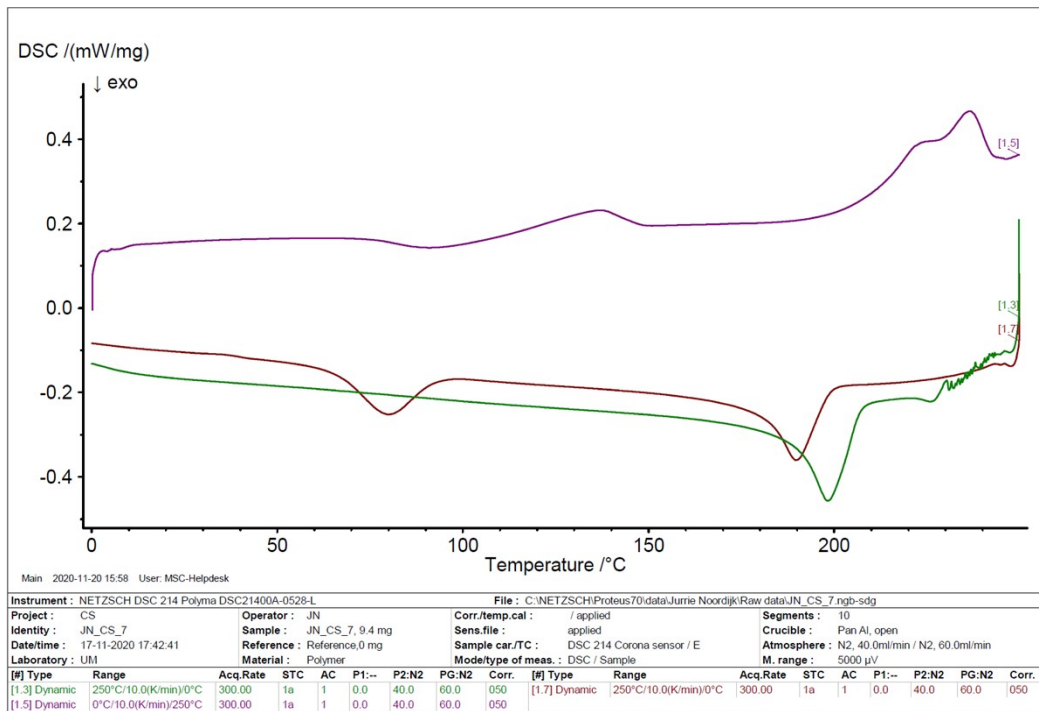


Figure S2.7.3: DSC plot complementary to Table 3, entry 5.