Electronic Supplementary Information (ESI) for

Towards a selective synthetic route of cobalt amino acids complexes and their application in ring opening polymerization of *rac*-lactide

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Contents

*Table S1. Summary of crystal data and structural refinement parameters for **1, 2** and **1a**.*

Parameter	**1**	**2**	**1a**
Empirical formula	$C_{28}H_{56}N_8O_{20}Co_3Cl_4$	$C_{46}H_{67}Cl_2Co_2N_9O_8$	$C_{14}H_{18}CoN_4O_5Cl$
Colour	Orange block	Red plate	Red needle
Formula weight ($gmol^{-1}$)	1143.39	1062.84	416.70
Crystal size (mm)	0.25 x 0.18 x 0.14	0.21 × 0.16 × 0.09	0.35 x 0.22 x 0.08
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	*C*2	*P* $2_1/n$
a (Å)	8.2215(6)	21.1914(10)	7.8928 (7)
b (Å)	10.3798(8)	24.4687(11)	19.9184 (17)
c (Å)	14.8086(11)	11.0348(5)	10.8042 (9)
α (°)	72.939		
β (°)	75.786	93.193(2)	106.081
γ (°)	89.555		
Volume ($Å^3$)	1168.305	5712.9(5)	1632.1(2)
Z	1	8	4
$\rho_{calc.}(g/cm^3)$	1.6251	1.236	1.696
F(000)	589	2232	856
μ K_α (mm^{-1})	μ MoK_α 1.361	μ CuK_α 5.843	μ MoK_α 1.250
Temperature (K)	150(2)	150(2)	150(2)
Reflections collected/unique/ observed [$I > 2\sigma(I)$]	47209/6847/6482	44343/12007/9007	38925/4102/3308
Data/restraints/parameters	6847/0/332	12007/1/616	4102/0/234
Goodness of fit on F^2	1.029	1.005	1.005
Final R indices [I>2σ(I)]	R_1 = 0.0205, wR_2 = 0.0565	R_1 = 0.0617, wR_2 = 0.1593	R_1 = 0.0386, wR_2 = 0.933
R indices (all data)	R_1 = 0.0220, wR_2 = 0.0575	R_1 = 0.0857, wR_2 = 0.1755	R_1 = 0.0557, wR_2 = 0.1017

*Table S2. Summary of crystal data and structural refinement parameters for 7, and **9a**.*

Parameter	**7**	**9a**
Empirical formula	$C_{14}H_{16}N_5O_7Co$	$C_{44}H_{58}Cl_2Co_2N_8O_8$
Colour, habit	Orange block	Red plate
Formula weight ($gmol^{-1}$)	425.25	1015.74
Crystal size (mm)	0.25 × 0.23 × 0.18	0.30 × 0.20 × 0.18
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	P-1

a (Å)	10.4922(7)	14.3084(13)
b (Å)	10.5900(7)	15.7813(15)
c (Å)	15.1072(10)	19.9421(18)
α (°)		71.816(3)
β (°)		77.578(3)
γ (°)		64.570(3)
Volume ($Å^3$)	1678.6(19)	3846.3(6)
Z	4	4
$\rho_{calc.}$(g/cm^3)	1.683	0.882
F(000)	872	1072
μ K_α (mm^{-1})	μ MoK_α1.074	μ MoK_α 0.538
Temperature (K)	295(2)	130(2)
Reflections collected/unique/ observed [$I > 2\sigma(I)$]	59151/7083/6212	131302/ 13517/ 11982
Data/restraints/parameters	7083/0/245	13517/0/623
Goodness of fit on F^2	1.039	1.242
Final R indices [I>2σ(I)]	R_1 = 0.0308, wR_2 = 0.0738	R_1 = 0.1066, wR_2 = 0.3296
R indices (all data)	R_1 = 0.0400, wR_2 = 0.0776	R_1 = 0.1152, wR_2 = 0.3402

*Table S3. Summary of crystal data and structural refinement parameters for **4a** and **Co(bipy)$_2$Cl$_2$** side product.*

Parameter	**4a**	**Co(bipy)$_2$Cl$_2$**
Empirical formula	$C_{14}H_{16}CoF_6N_4O_4P$	$C_{20}H_{16}Cl_2CoN_4$
Colour, habit	Red rod	Red Needle
Formula weight ($gmol^{-1}$)	508.21	442.20
Crystal size (mm)	0.28 x 0.15 x 0.09	0.45 x 0.11 x 0.07
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	$P2_1/c$
a (Å)	21.0340 (16)	8.3937(9)
b (Å)	8.2876 (6)	14.4906(16)
c (Å)	25.1217 (19)	15.5726(18)
α (°)		
β (°)		97.479(4)
γ (°)		
Volume ($Å^3$)	4379.2(6)	1878.0(4)
Z	8	4
$\rho_{calc.}$(g/cm^3)	1.542	1.564
F(000)	2048	900
μ K_α (mm^{-1})	μ MoK_α 0.933	μ MoK_α 1.211

Temperature (K)	172(2)	293(2)
Reflections collected/unique/ observed [$I > 2\sigma(I)$]	209480/4862/4010	37377 /3982 /3144
Data/restraints/parameters	4862/0/271	3982 /0/244
Goodness of fit on F^2	1.039	1.017
Final R indices [I>2σ(I)]	R_1 = 0.0319, wR_2 = 0.0935	R_1 = 0.0300, wR_2 = 0.0747
R indices (all data)	R_1 = 0.0411, wR_2 = 0.0976	R_1 = 0.0525, wR_2 = 0.0790

Table S4. Selected bond angles (°) and bond lengths *(*Å*) for **1**.*

Angles	Deg (°)
N(3)-Co(1)-N(4)	83.28(4)
N(2)-Co(1)-O(3)	86.18(3)
N(1)-Co(1)-O(1)	85.56(3)
O(1)-Co(1)-O(3)	90.04(3)
O(1)-Co(1)-N(4)	175.04(3)
N(1)-Co(1)-N(2)	172.80(3)
N(3)-Co(1)-O(3)	175.77(3)
O(6)-Co(2)-O(5)	92.18(3)
O(2)-Co(2)-O(5)	83.60(3)
O(2)-Co(2)-O(6)	88.27(3)
O(3)-C(8)-O(4)	122.94(9)
O(1)-C(6)-O(2)	124.06(9)

Bonds	Distance, Å
Co(1)-N(1)	1.9349(8)
Co(1)-N(2)	1.9418(8)
Co(1)-N(3)	1.9207(8)
Co(1)-N(4)	1.9147(8)
Co(1)-O(1)	1.9061(7)
Co(1)-O(3)	1.8878(7)
C(6)-O(1)	1.2774(11)
C(6)-O(2)	1.2475(11)
C(8)-O(3)	1.2886(11)
C(8)-O(4)	1.2363(12)
Co(2)-O(2)	2.1382(7)
Co(2)-O(5)	2.0850(7)
Co(2)-O(6)	2.0580(8)

Table S5. Selected bond angles (°) and bond lengths *(*Å*) for* ***2****.*

Angles	Deg (°)
O(3)-C(7)-O(4)	123.0(7)
O(1)-C(1)-O(2)	123.2(8)
N(1)-Co(1)-N(2)	171.1(3)
N(1)-Co(1)-N(3)	90.5(3)
N(2)-Co(1)-N(4)	91.5(3)
N(2)-Co(1)-N(4)	91.34(18)
N(2)-Co(1)-O(3)	86.0(3)
N(3)-Co(1)-O(1)	173.1(3)
N(4)-Co(1)-O(1)	92.2(3)
O(3)-Co(1)-O(1)	91.5(3)

Bonds	Distance, Å
Co(1)-O(1)	1.913(6)
Co(1)-O(3)	1.890(5)
Co(1)-N(1)	1.955(7)
Co(1)-N(2)	1.973(8)
Co(1)-N(3)	1.932(7)
Co(1)-N(4)	1.927(7)
C(1)-O(1)	1.269(11)
C(1)-O(2)	1.237(10)
C(7)-O(3)	1.313(9)
C(7)-O(4)	1.217(9)

Table S6. Selected bond angles (°) and bond lengths *(Å) for* ***1a.***

Angles	Deg (°)
O(3)-C(3)-O(4)	124.4(2)
O(1)-C(1)-O(2)	123.3(2)
N(1)-Co(1)-N(2)	172.42(8)
N(1)-Co(1)-N(4)	92.76(8)
N(2)-Co(1)-O(3)	84.94(8)
N(3)-Co(1)-O(1)	176.15(8)
N(4)-Co(1)-O(3)	176.56(8)
N(4)-Co(1)-O(1)	93.35(8)
N(1)-Co(1)-O(1)	85.58(8)
N(3)-Co(1)-O(3)	93.73(8)
N(4)-Co(1)-N(3)	82.98(8)
O(3)-Co(1)-O(1)	89.96(7)

Bonds	Distance, Å
Co(1)-O(1)	1.9071(17)
Co(1)-O(3)	1.8954(17)
Co(1)-N(1)	1.9572(2)
Co(1)-N(2)	1.9495(2)
Co(1)-N(3)	1.929(2)
Co(1)-N(4)	1.931(2)
C(1)-O(1)	1.299(3)
C(1)-O(2)	1.231(3)
C(3)-O(3)	1.300(3)
C(3)-O(4)	1.224(3)

Table S7. Selected bond angles (°) and bond lengths *(*Å*) for 7.*

Angles	Deg (°)
O(3)-C(3)-O(4)	116.09(19)
O(1)-C(2)-O(2)	123.25(19)
N(3)-Co(1)-N(4)	83.43(10)
N(2)-Co(1)-O(3)	86.40(8)
N(1)-Co(1)-O(1)	84.77(6)
N(3)-Co(1)-O(1)	176.65(8)
N(4)-Co(1)-O(1)	94.60(7)
N(2)-Co(1)-N(1)	171.84(7)
O(3)-Co(1)-O(1)	89.89(7)

Bonds	Distance, Å
Co(1)-O(1)	1.8930(13)
Co(1)-O(3)	1.8886(15)
Co(1)-N(1)	1.9465(15)
Co(1)-N(2)	1.9391(16)
Co(1)-N(3)	1.9271(17)
Co(1)-N(4)	1.9066(18)
C(2)-O(1)	1.293(2)
C(2)-O(2)	1.225(2)
C(3)-O(3)	1.298(3)
C(3)-O(4)	1.220(3)

Table S8. Selected bond angles (°) and bond lengths *(Å) for **9a**.*

Angles	Deg (°)
O(1)-C(1)-O(2)	123.5(5)
O(3)-C(7)-O(4)	122.8(5)
N(1)-Co(1)-N(2)	173.27(18)
N(3)-Co(1)-N(4)	83.31(18)
N()-Co(1)-O(3)	86.55(15)
N(4)-Co(1)-O(1)	93.88(17)
N(4)-Co(1)-O(3)	175.87(16)
N(3)-Co(1)-O(1)	175.85(16)
N(1)-Co(1)-O(3)	88.77(15)
O(3)-Co(1)-O(1)	89.48(15)
O(5)-C(23)-O(7)	123.5(5)
O(7)-C(29)-O(8)	122.8(5)
N(5)-Co(2)-N(6)	173.5(3)
N(7)-Co(2)-N(8)	83.5(3)
N(8)-Co(2)-O(5)	93.4(3)
N(8)-Co(2)-O(7)	175.3(3)
N(7)-Co(2)-O(5)	175.9(2)
N(6)-Co(2)-O(7)	86.6(2)
N(5)-Co(2)-O(5)	86.8(2)
O(7)-Co(2)-O(6)	90.40(15)
N(7)-Co(1)-O(7)	93.20(18)

Bonds	Distance, Å
Co(1)-O(1)	1.878(3)
Co(1)-O(3)	1.881(3)
Co(1)-N(1)	1.937(4)
Co(1)-N(2)	1.945(4)
Co(1)-N(3)	1.921(4)
Co(1)-N(4)	1.919(4)
C(1)-O(1)	1.289(6)
C(1)-O(2)	1.213(6)
C(7)-O(3)	1.272(6)
C(7)-O(4)	1.240(6)
Co(2)-O(5)	1.868(5)
Co(2)-O(7)	1.879(4)
Co(2)-N(5)	1.946(6)
Co(2)-N(6)	1.931(5)
Co(2)-N(7)	1.927(7)
Co(2)-N(8)	1.928(6)
C(29)-O(7)	1.282(7)
C(29)-O(8)	1.243(7)
C(23)-O(5)	1.295(9)
C(23)-O(6)	1.230(11)

Table S9. Selected bond angles (°) and bond lengths *(Å) for* ***4a.***

Angles	Deg (°)
O(3)-C(3)-O(4)	123.75(18)
O(1)-C(1)-O(2)	123.28(2)
N(1)-Co(1)-N(2)	172.25(7)
N(1)-Co(1)-N(4)	92.35(7)
N(2)-Co(1)-O(3)	86.15(7)
N(4)-Co(1)-O(1)	175.36(7)
N(1)-Co(1)-O(1)	85.90(7)
N(3)-Co(1)-O(3)	175.14(7)
N(4)-Co(1)-N(3)	83.19(7)
O(3)-Co(1)-O(1)	91.57(6)

Bonds	Distance, Å
Co(1)-O(1)	1.8825(14)
Co(1)-O(3)	1.8887(14)
Co(1)-N(1)	1.9485(17)
Co(1)-N(2)	1.9339(17)
Co(1)-N(3)	1.9194(17)
Co(1)-N(4)	1.9218(17)
C(1)-O(1)	1.290(3)
C(1)-O(2)	1.229(3)
C(3)-O(3)	1.291(2)
C(3)-O(4)	1.228(2)

Table S10. Selected bond angles (°) and bond lengths *(Å) for* ***Co(bipy)$_2$Cl$_2$***

Angles	Deg (°)
N(1)-Co(1)-N(4)	161.61(6)
N(2)-Co(1)-Cl(2)	170.89(5)
N(3)-Co(1)-Cl(1)	172.34(4)
Cl(1)-Co(1)-Cl(2)	96.60(2)
N(1)-Co(1)-N(3)	92.31(6)
N(2)-Co(1)-N(4)	92.23(6)
N(1)-Co(1)-N(2)	74.64(6)
N(3)-Co(1)-N(4)	74.75(6)

Bonds	Distance, Å
Co(1)-Cl(1)	2.4205(7)
Co(1)-Cl(2)	2.3968(7)
Co(1)-N(1)	2.1461(16)
Co(1)-N(2)	2.1982(16)
Co(1)-N(3)	2.1841(16)
Co(1)-N(4)	2.1390(15)

.

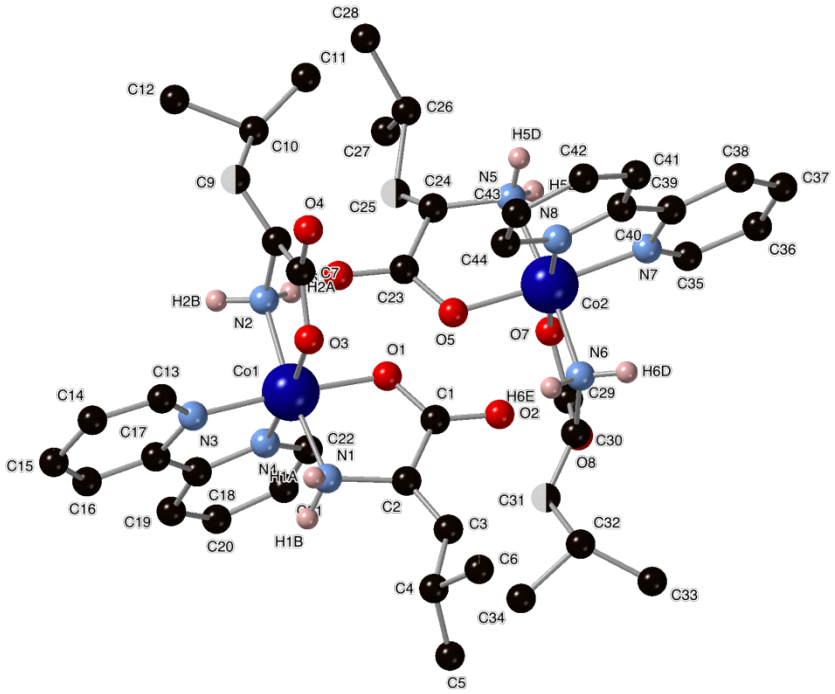

Figure S1. Ellipsoidal plot at 50% probability of the cation of ***9a*** *showing both molecules with the asymmetric unit. Counter anion is* Cl^- *(not shown). Hydrogen atoms bound to amine N atom shown only.*

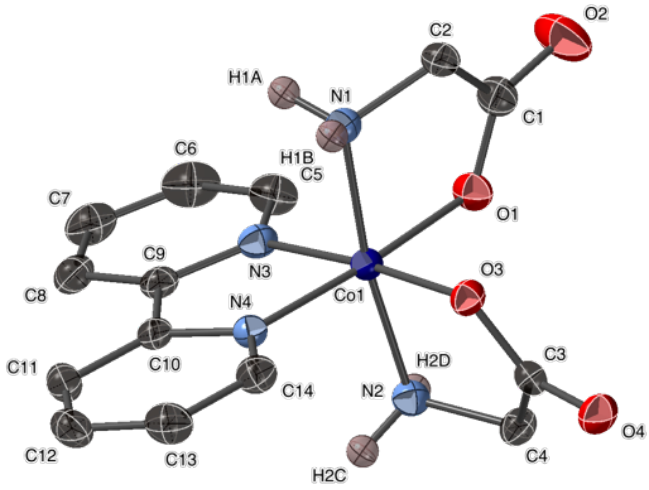

Figure S2. Ellipsoidal plot at 50% probability of the cation of ***4a****. The counter anion is* PF_6^- *(not shown).*

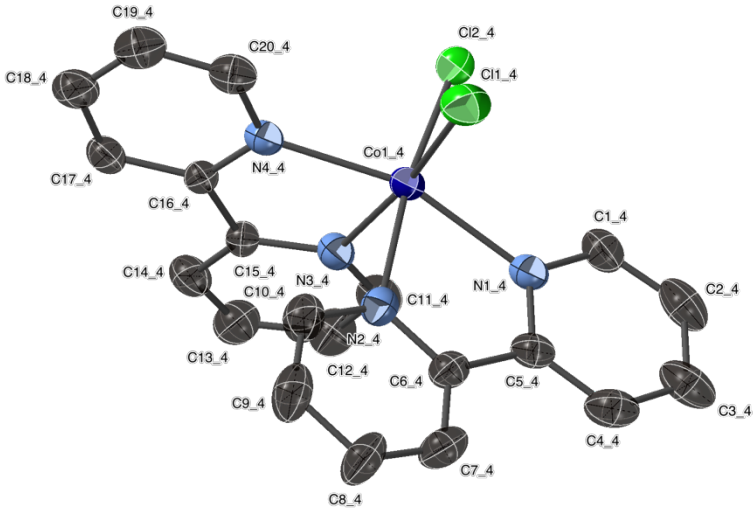

Figure S3. Ellipsoidal plot at 50% probability of Co-bis(bipy)Cl_2.

NMR Spectroscopy.

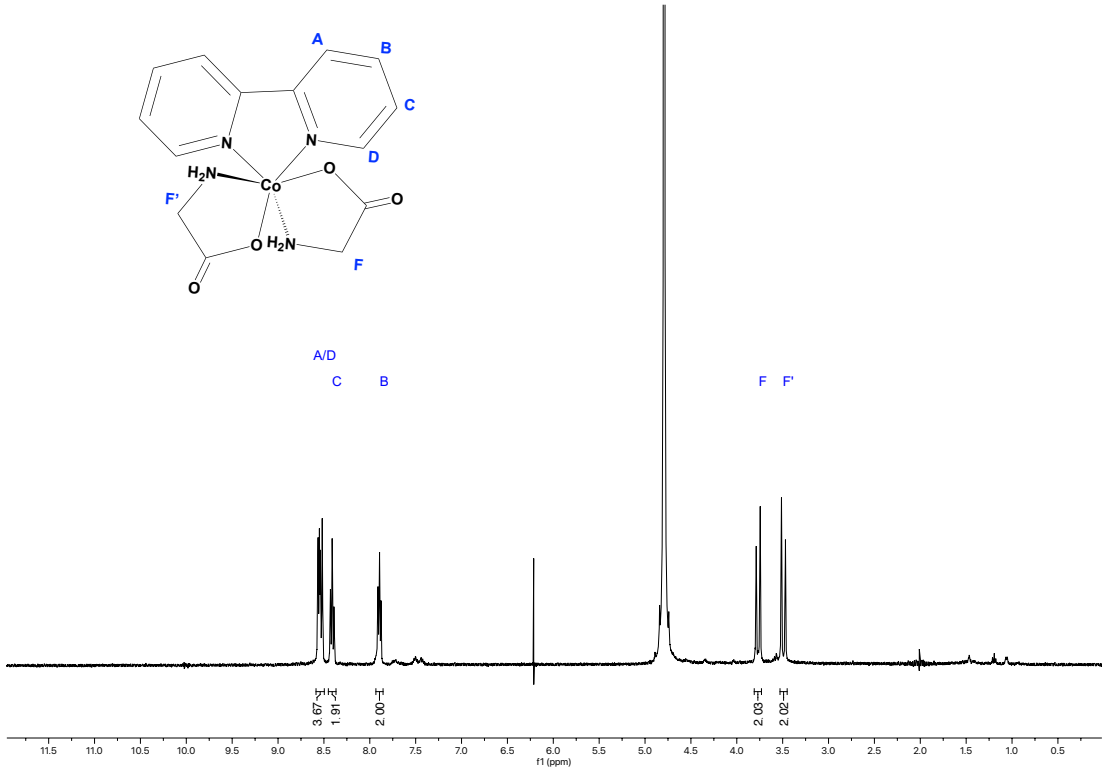

*Figure S4. ^{1}H NMR of **1a** in (D_2O, 298 K)*

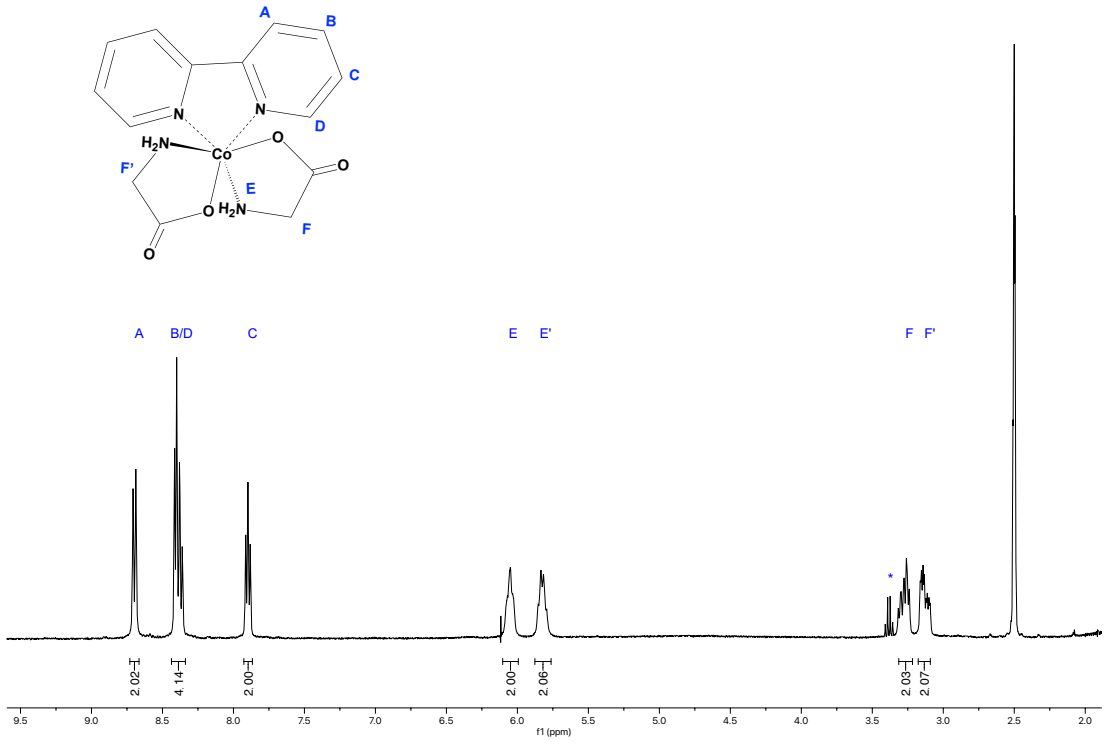

*Figure S5. ^{1}H NMR of **1a** in (DMSO-d_6, 298 K)(*EtOH)*

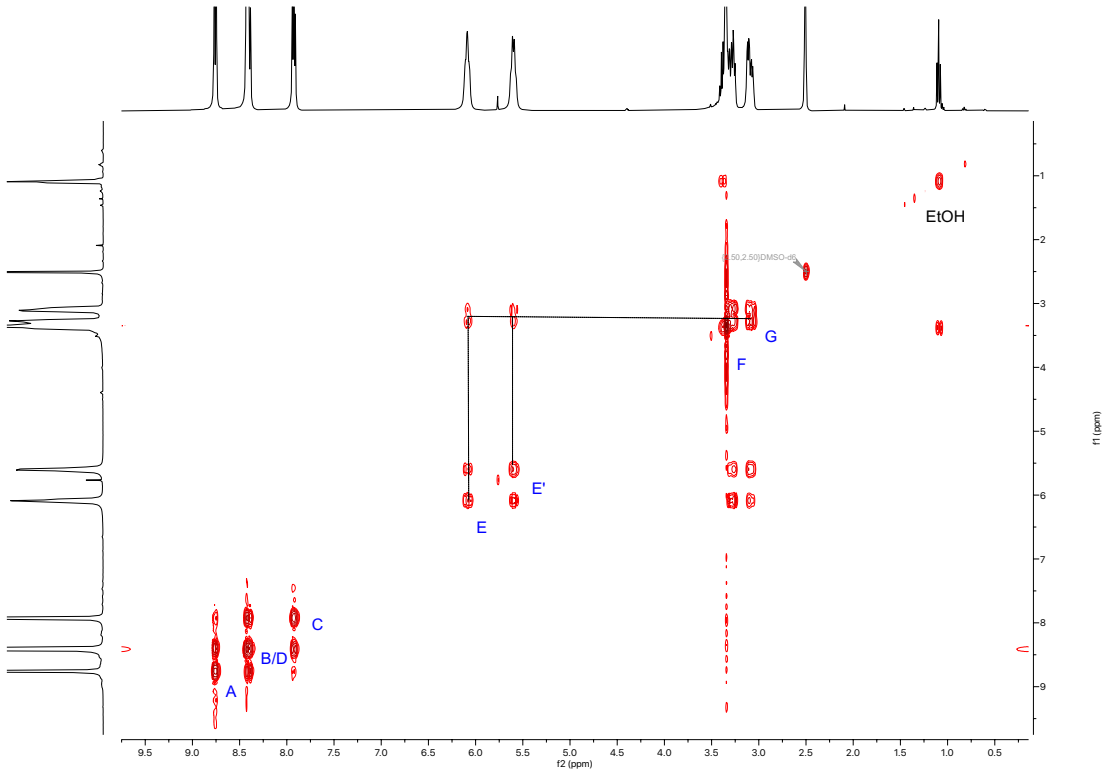

*Figure S6. 2D COSY NMR of **1a** (DMSO-d$_6$, 298 K)*

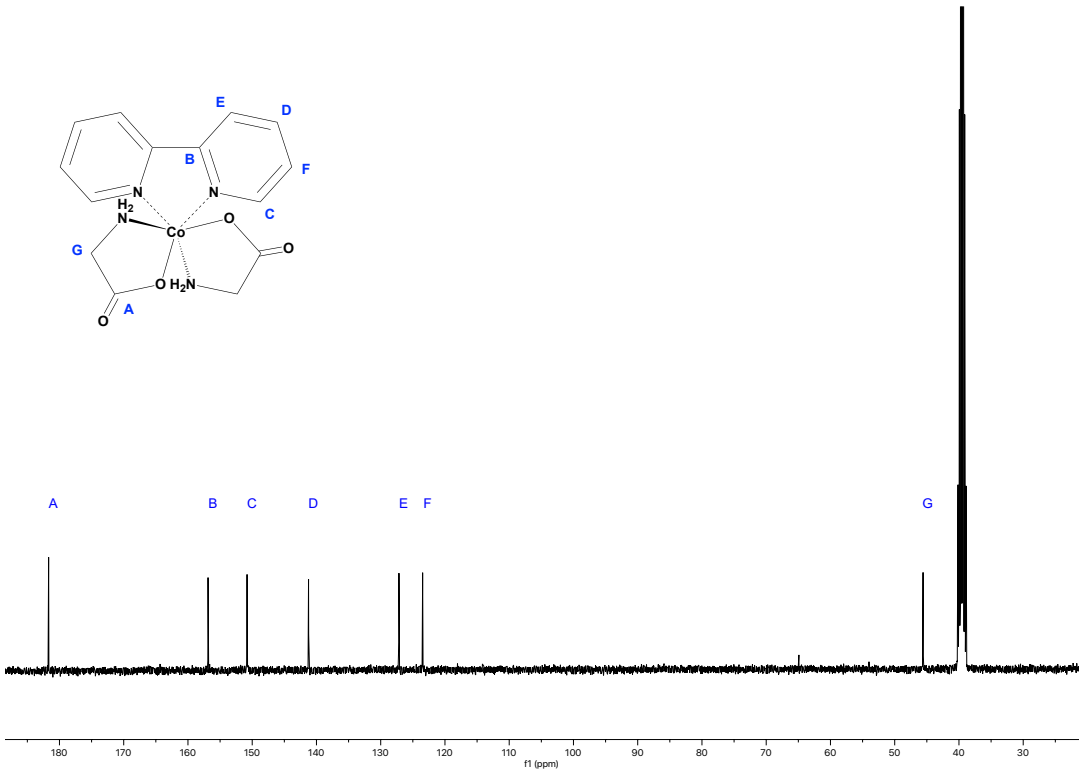

*Figure S7. ^{13}C NMR of **1a** (DMSO-d$_6$, 298 K)*

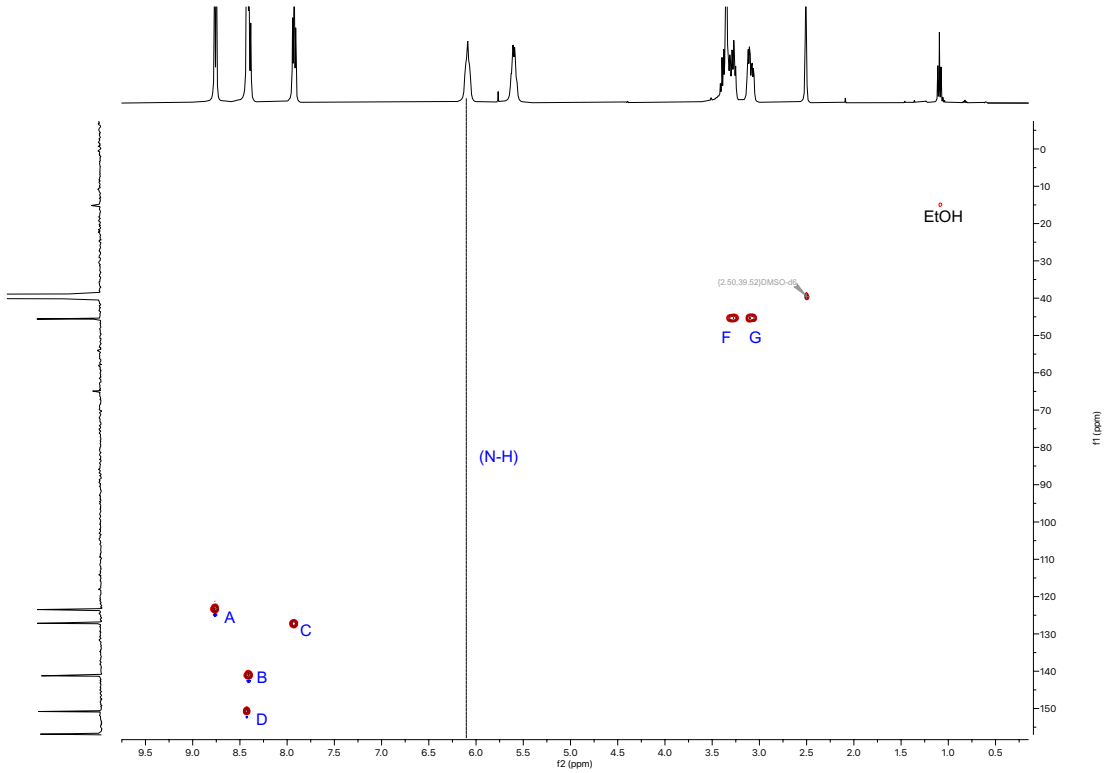

*Figure S8. 2D HSQC NMR of **1a** (DMSO-d_6, 298 K)*

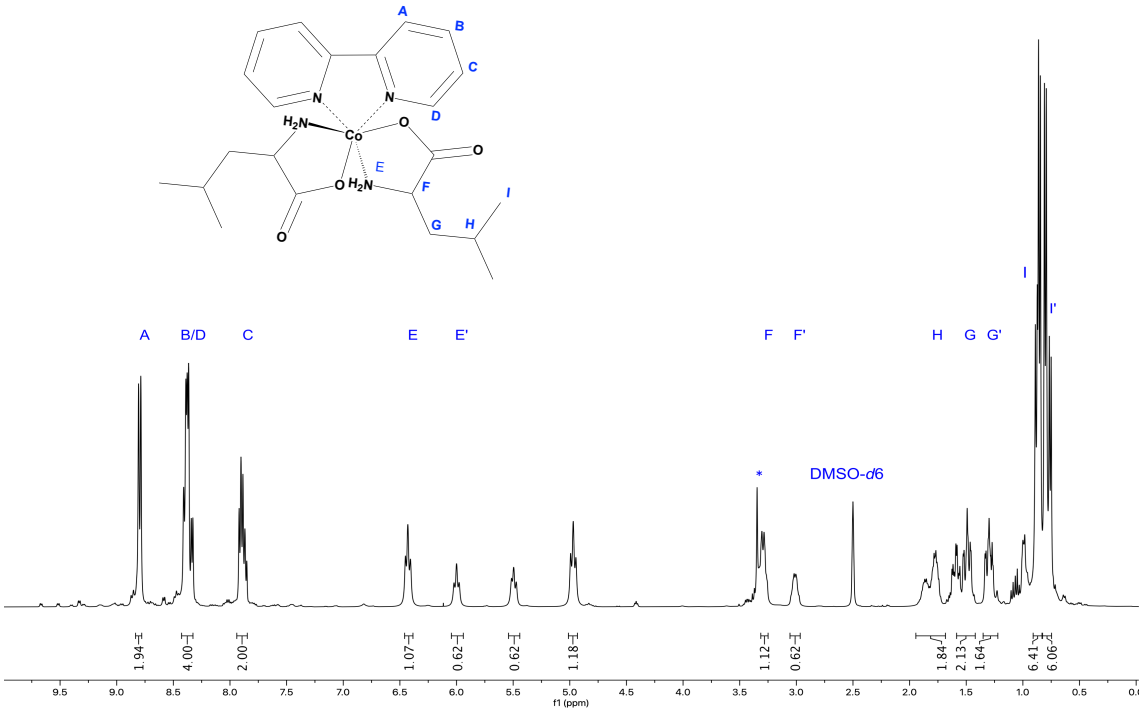

*Figure S9. ^{1}H NMR of **2** (DMSO-d_6, 298 K) (*H_2O)*

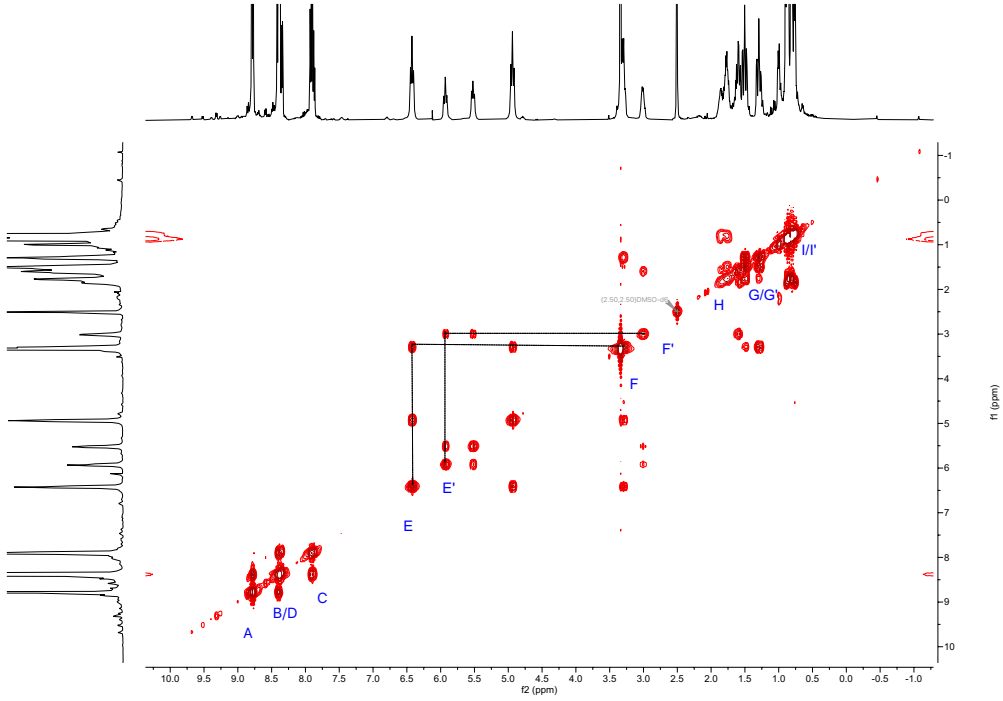

*Figure S10. 2D COSY NMR of **2** (DMSO-d_6, 298 K)*

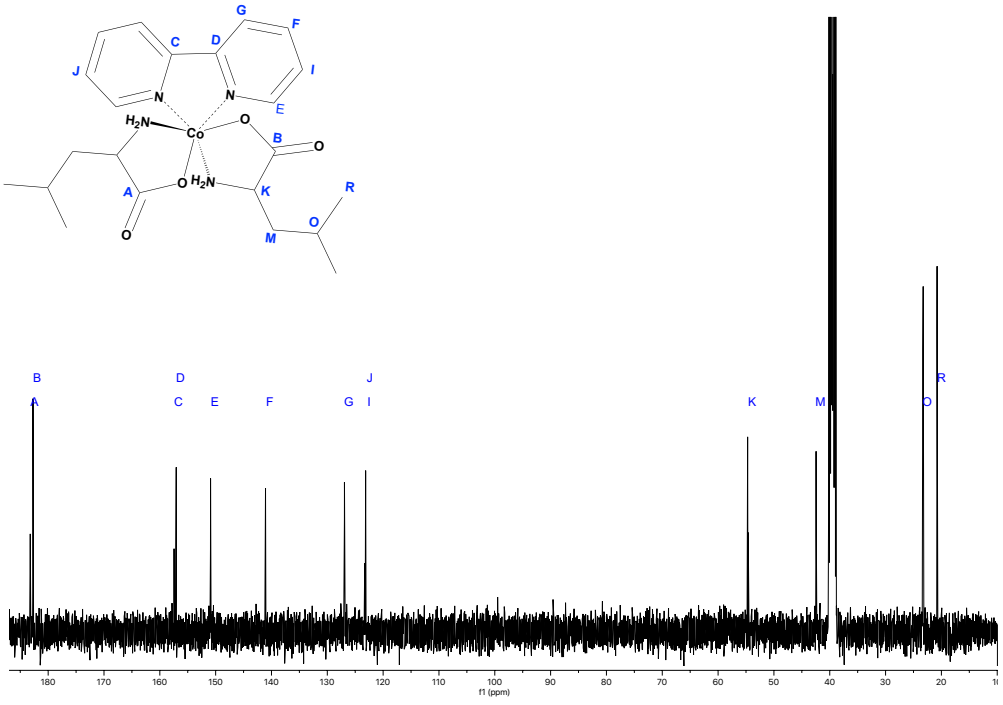

*Figure S11. ^{13}C NMR of **2** (DMSO-d_6, 298 K)*

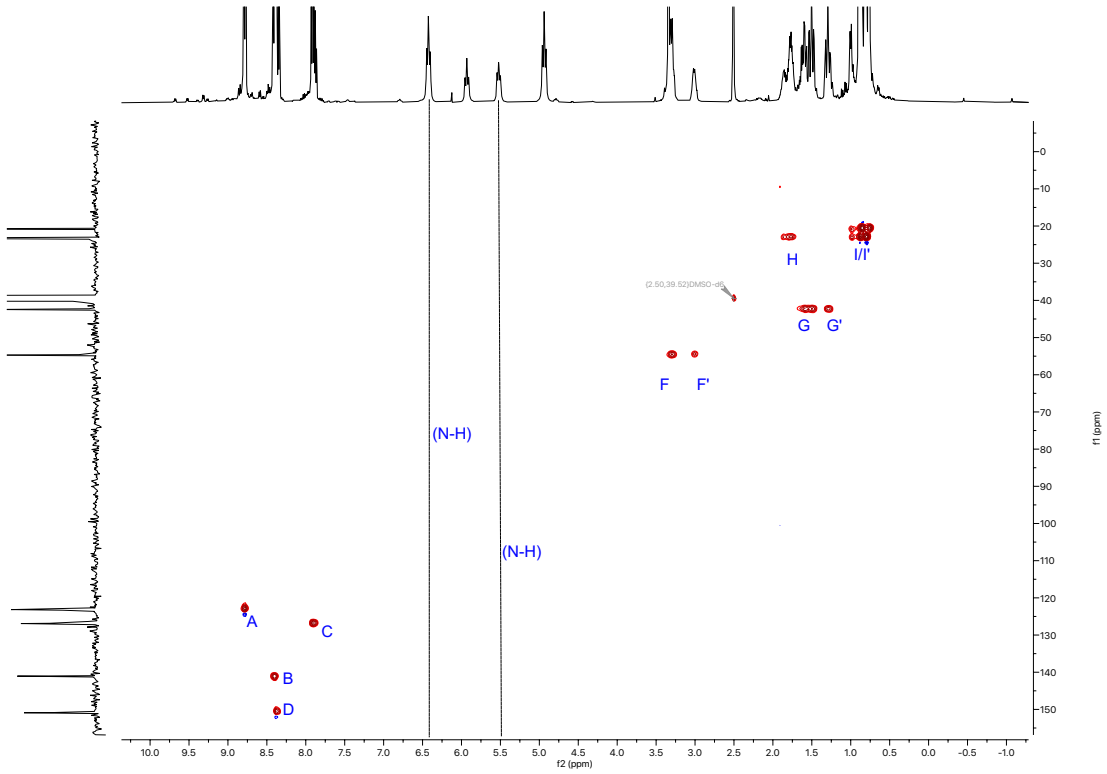

*Figure S12. 2D HSQC NMR of **2** (DMSO-d_6, 298 K)*

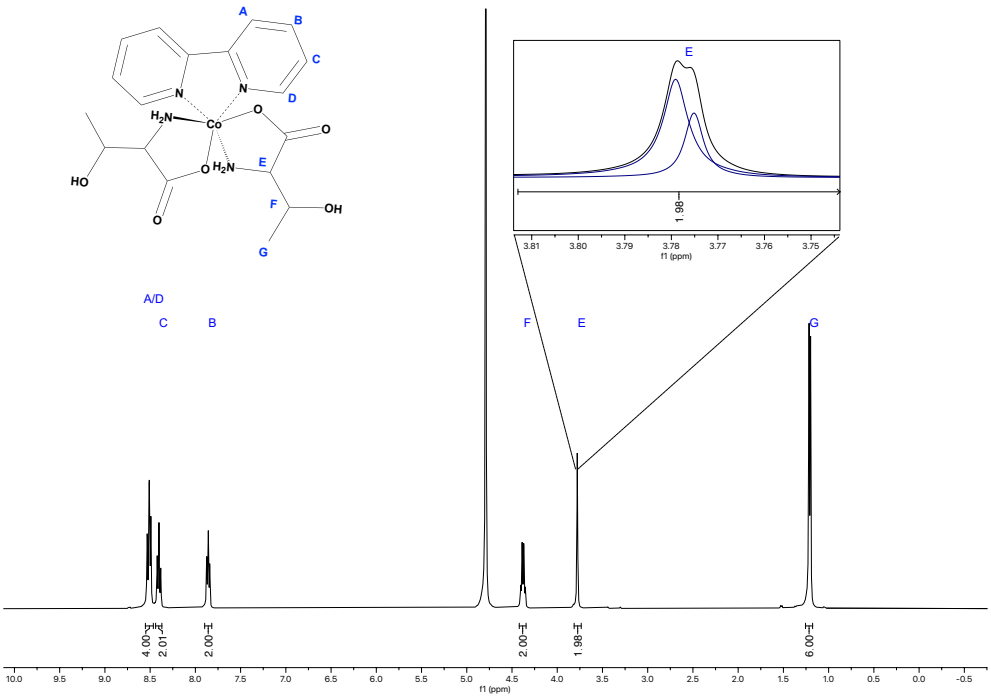

*Figure S13. ^{1}H NMR of **3** in (D_2O, 298 K)*

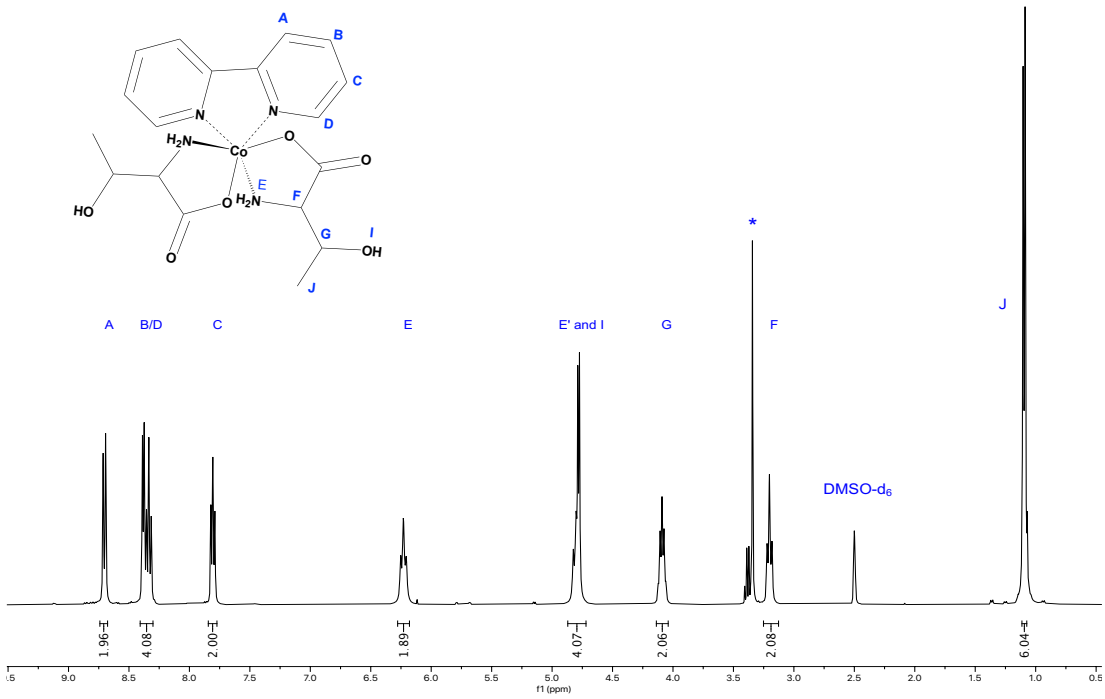

*Figure S14. ^{1}H NMR of **3** in (DMSO-d_6, 298 K)(*EtOH/H_2O)*

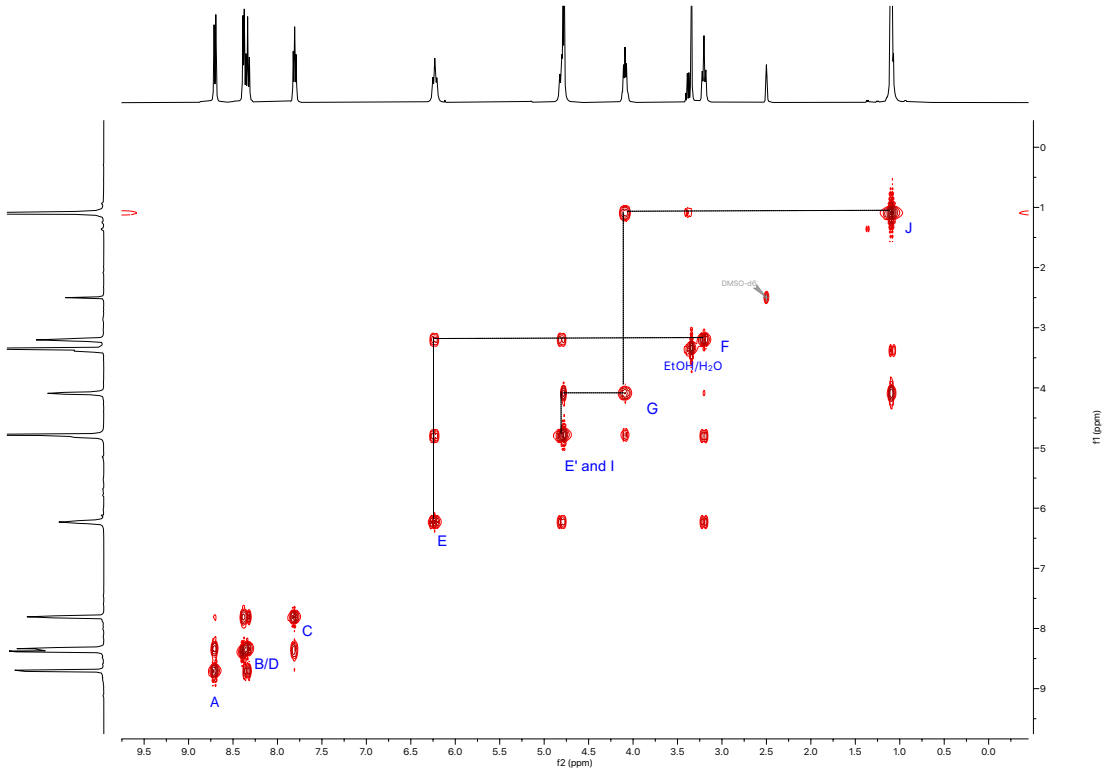

*Figure S15. 2D COSY NMR of **3** (DMSO-d_6, 298 K)*

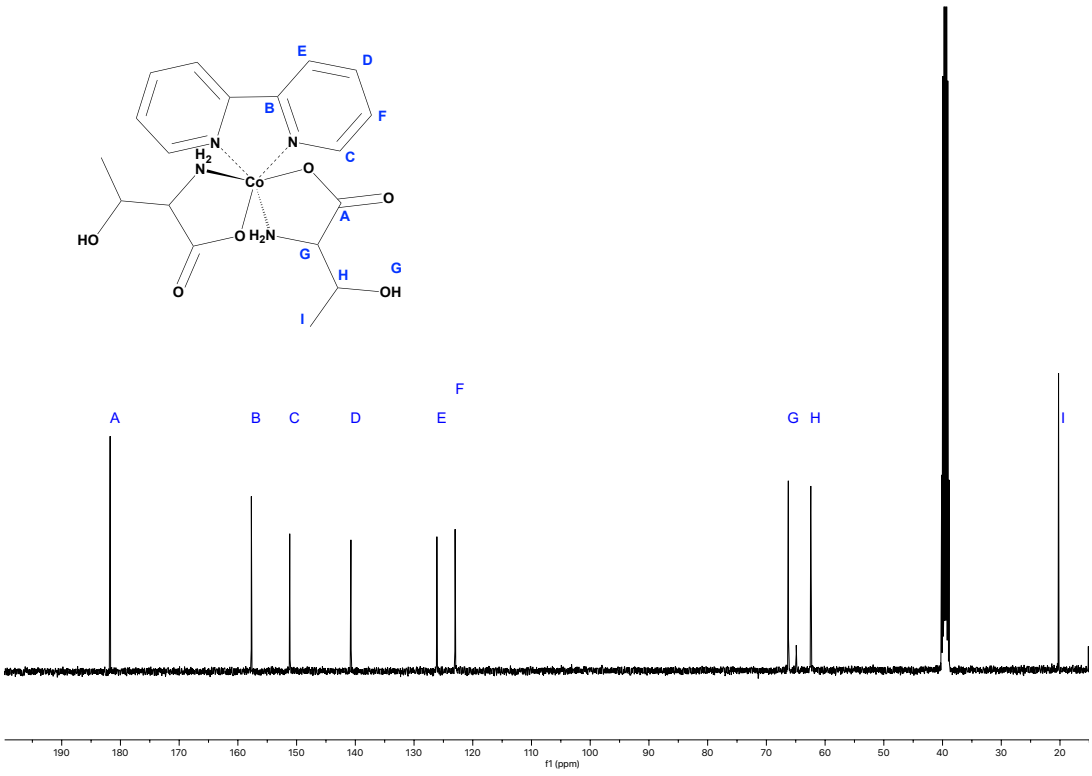

Figure S16. ^{13}C NMR of 3 (DMSO-d6, 298 K)

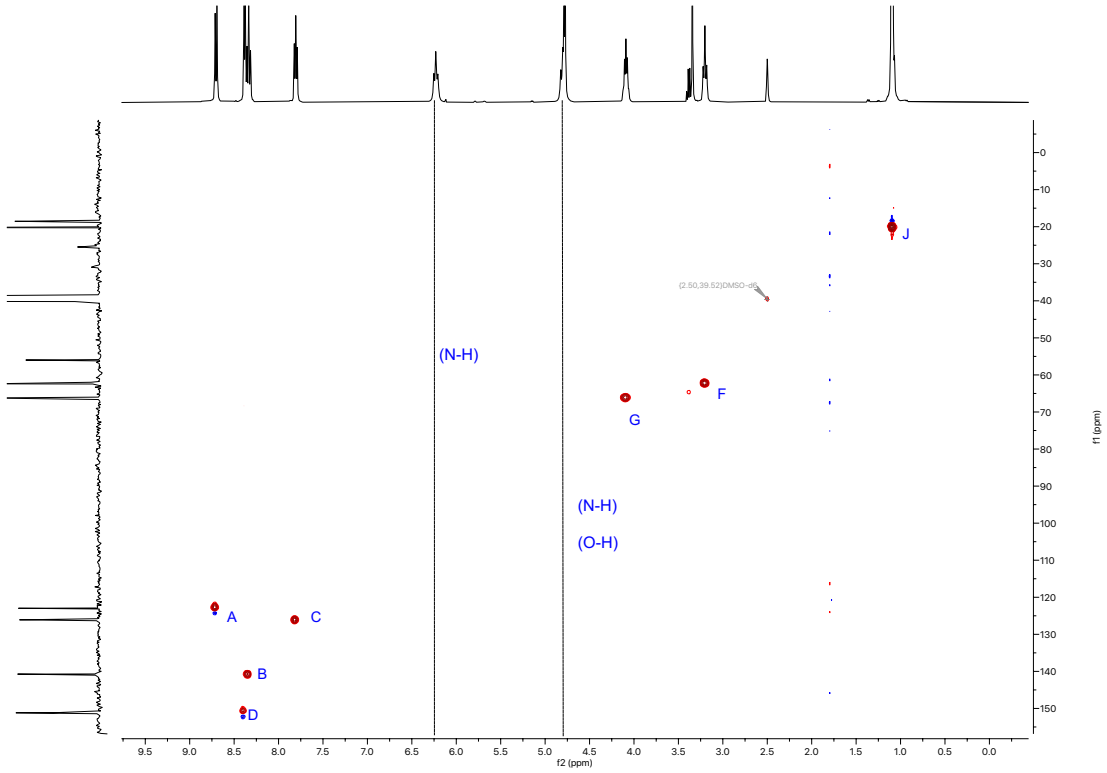

*Figure S17. 2D HSQC NMR of **3** (DMSO-d_6, 298 K)*

IR spectroscopy

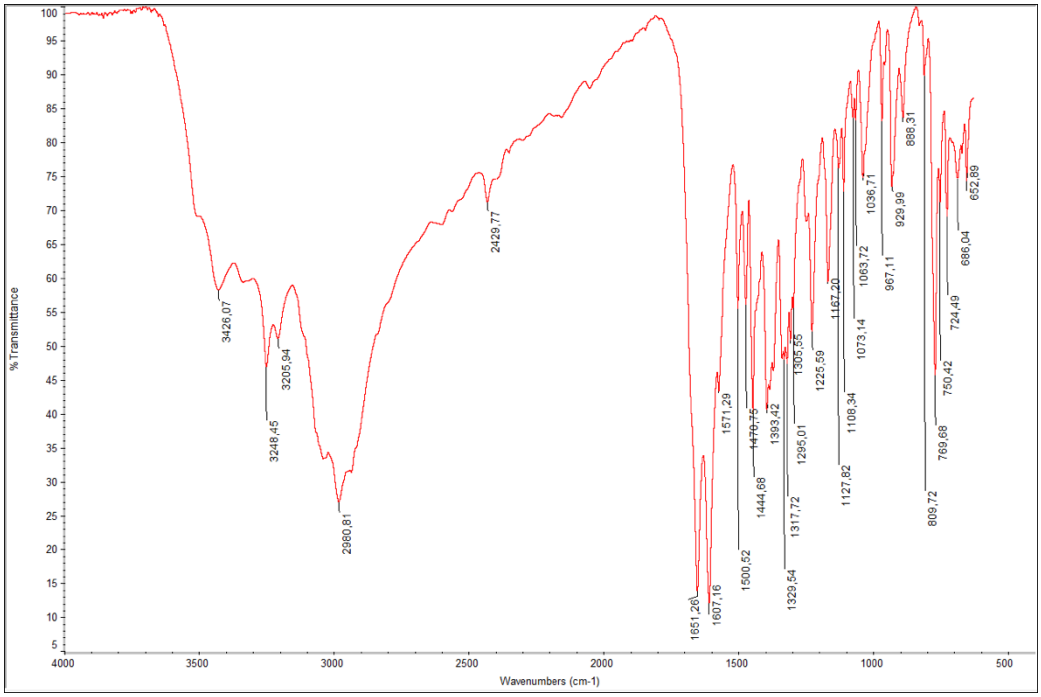

Figure S18. FT-IR spectra of ***1***

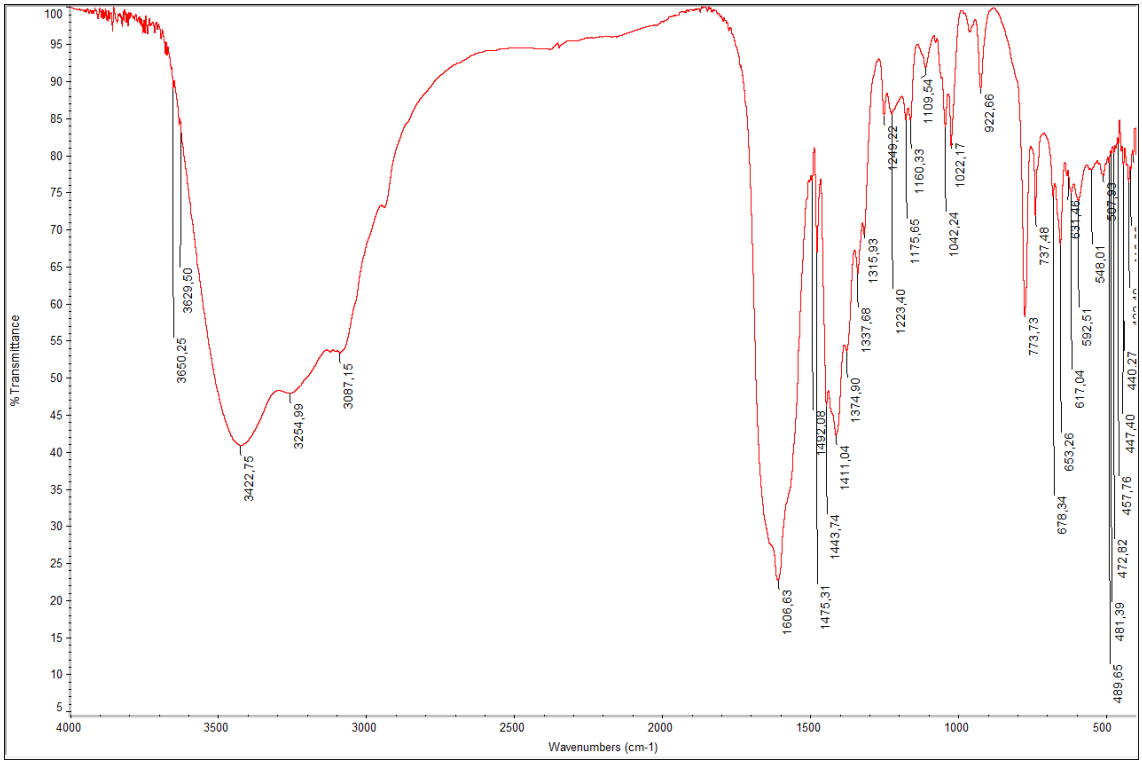

Figure S19. FT-IR of **4**

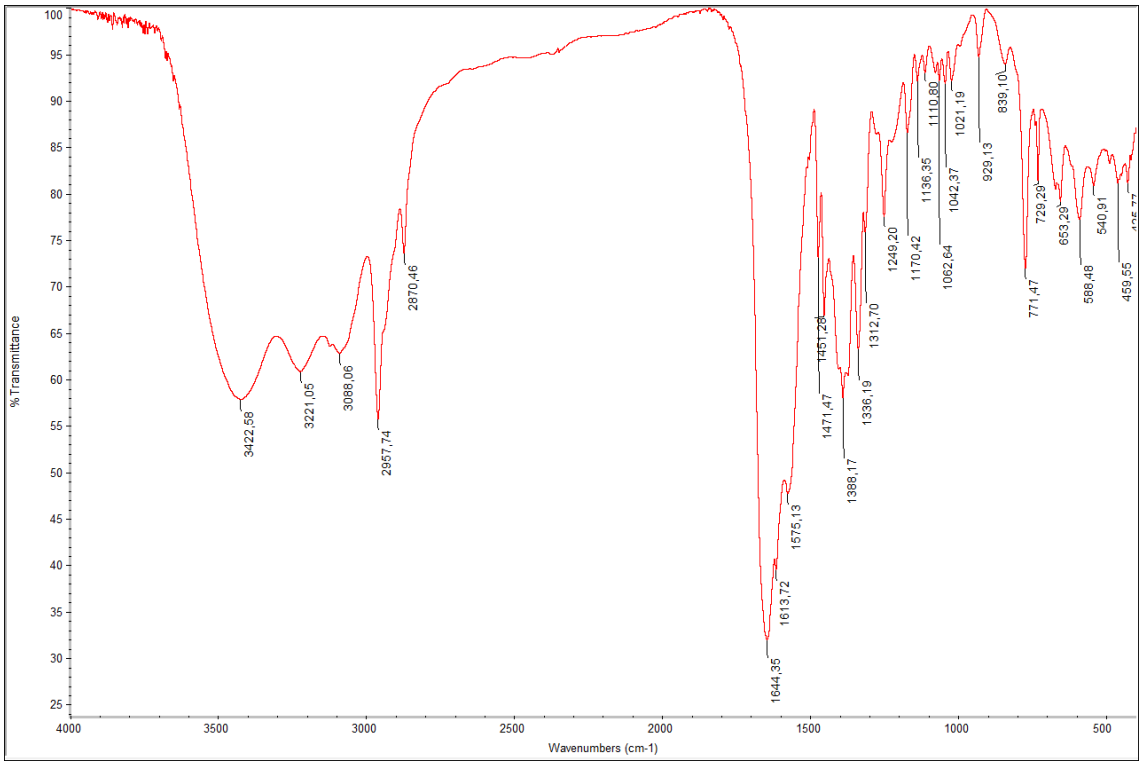

Figure S20. FT-IR of ***5***

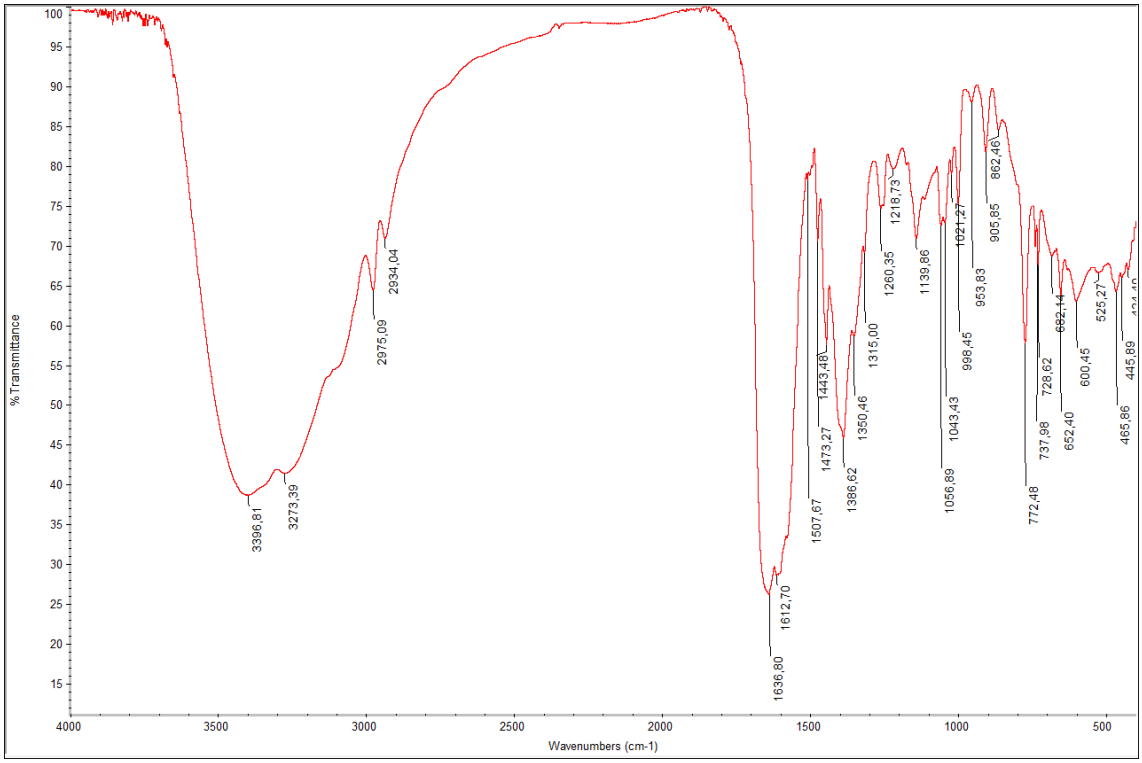

Figure S21. FT-IR of ***6***

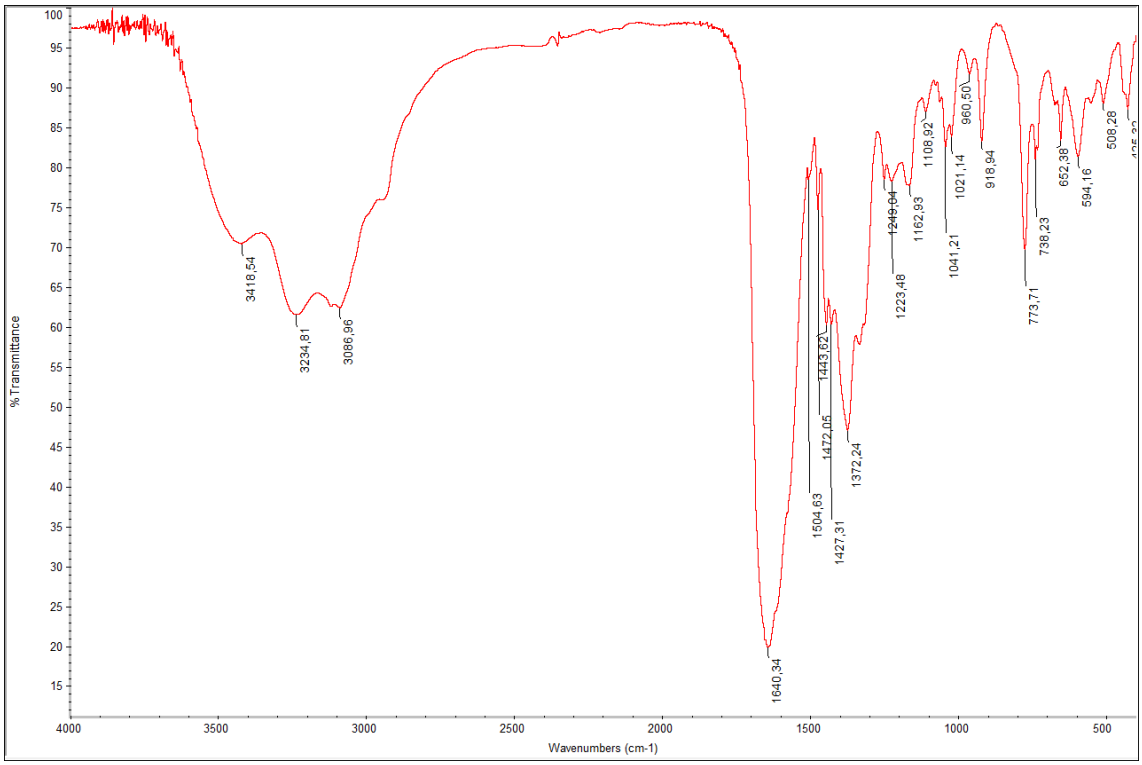

*Figure S22. FT-IR spectra of **8***

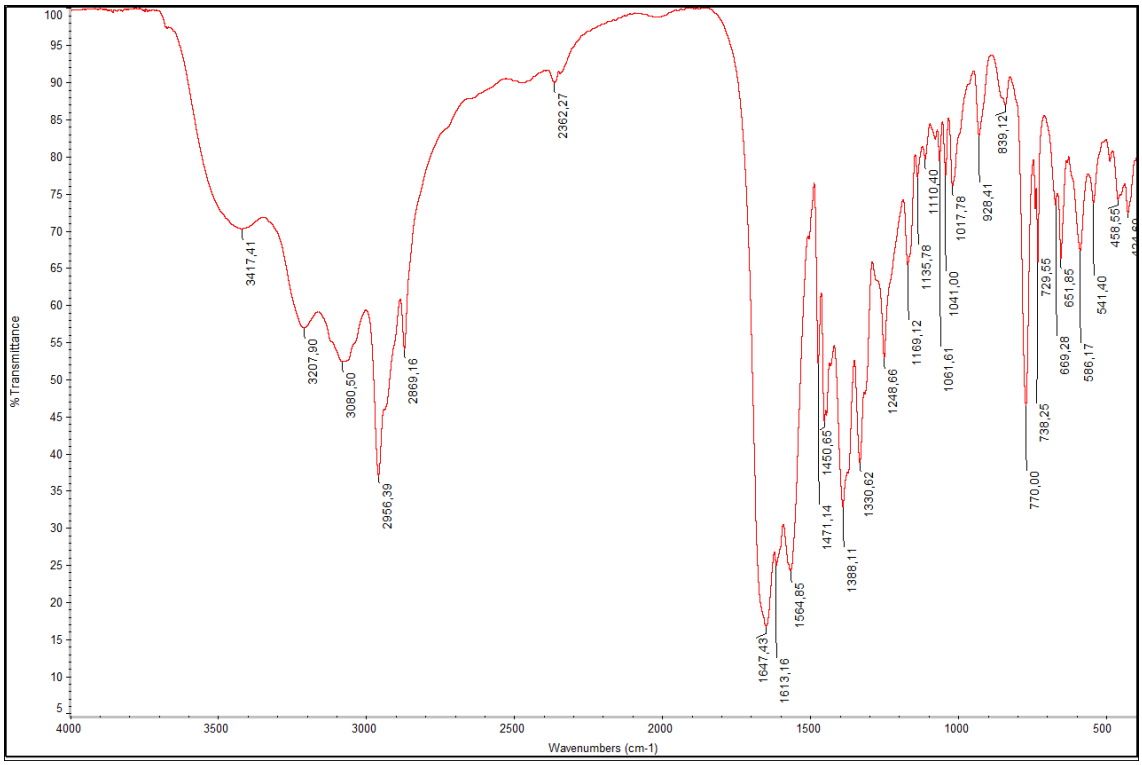

*Figure S23. FT-IR spectra of **9***

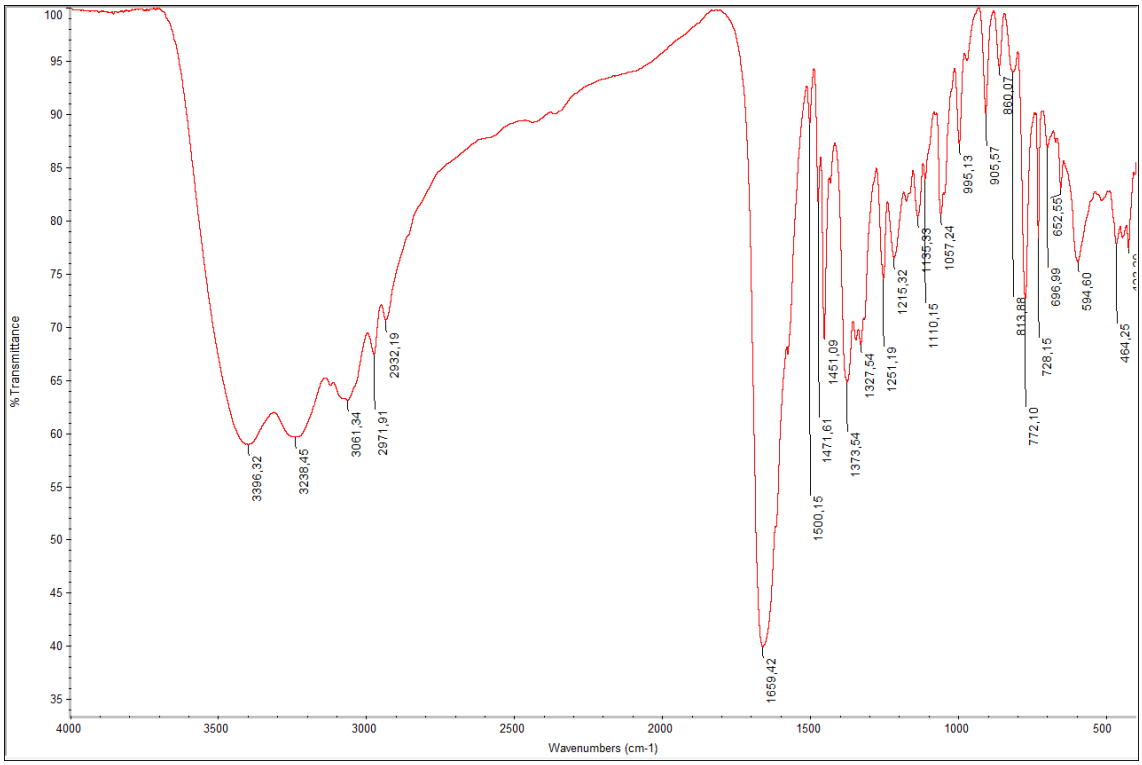

*Figure S24. FT-IR spectra of **10**.*

High-resolution mass spectrometry (HRMS)

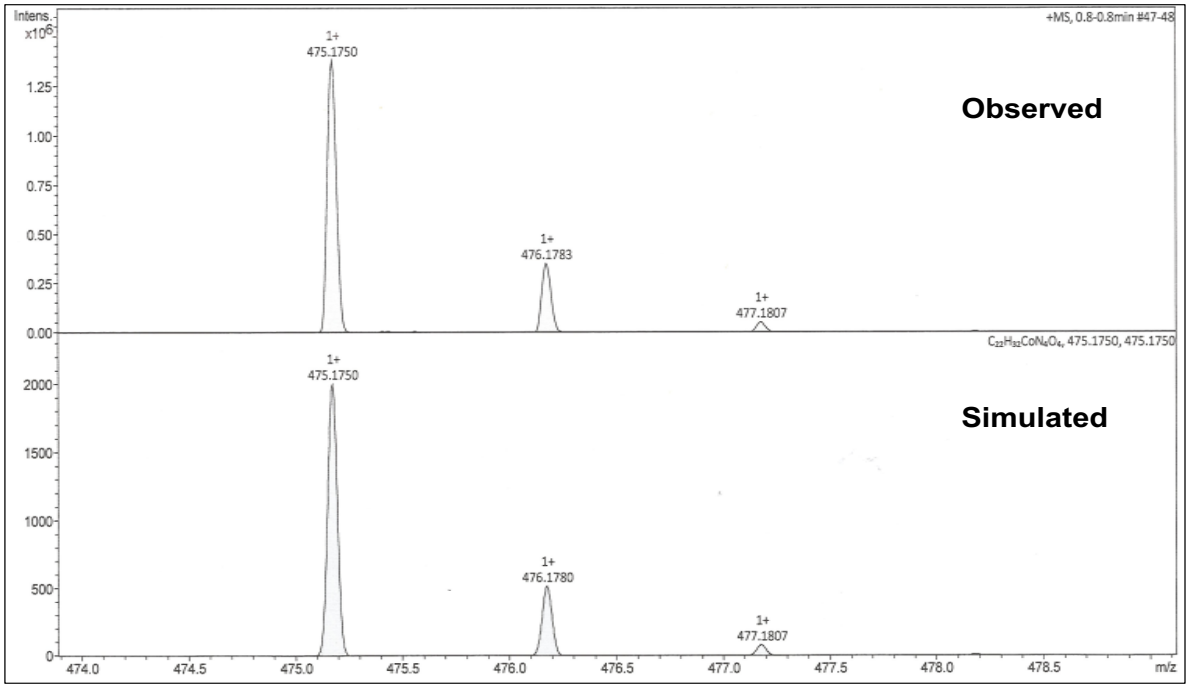

*Figure S25. HRMS-ESI of **2***

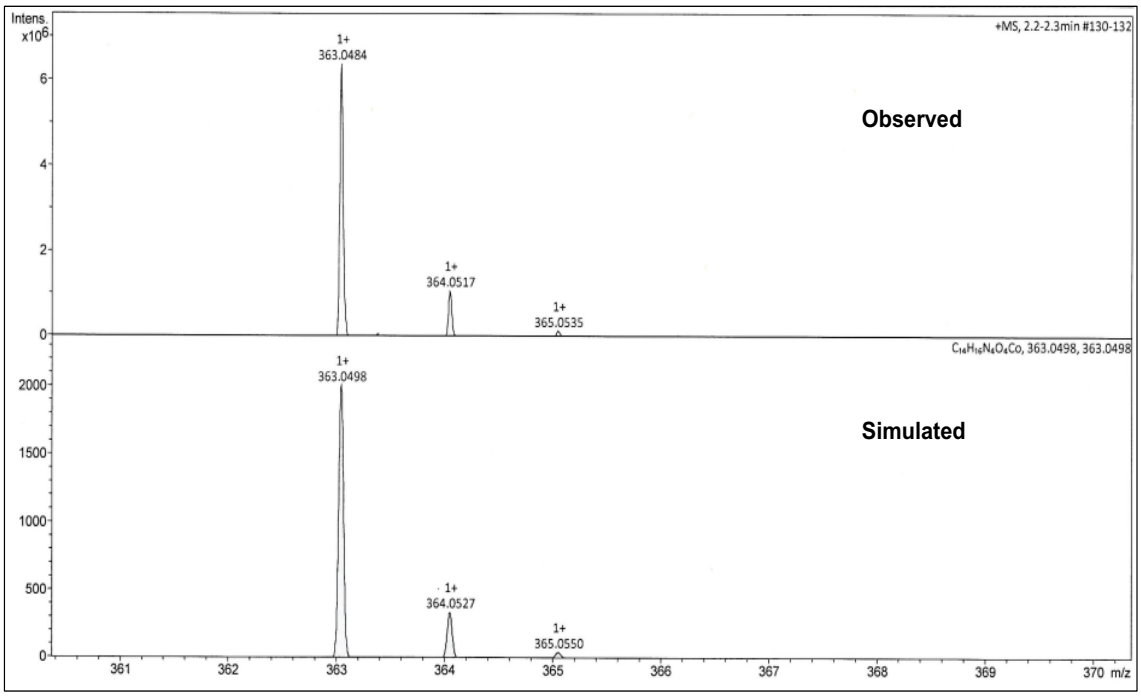

Figure S26. HRMS-ESI of ***4a***

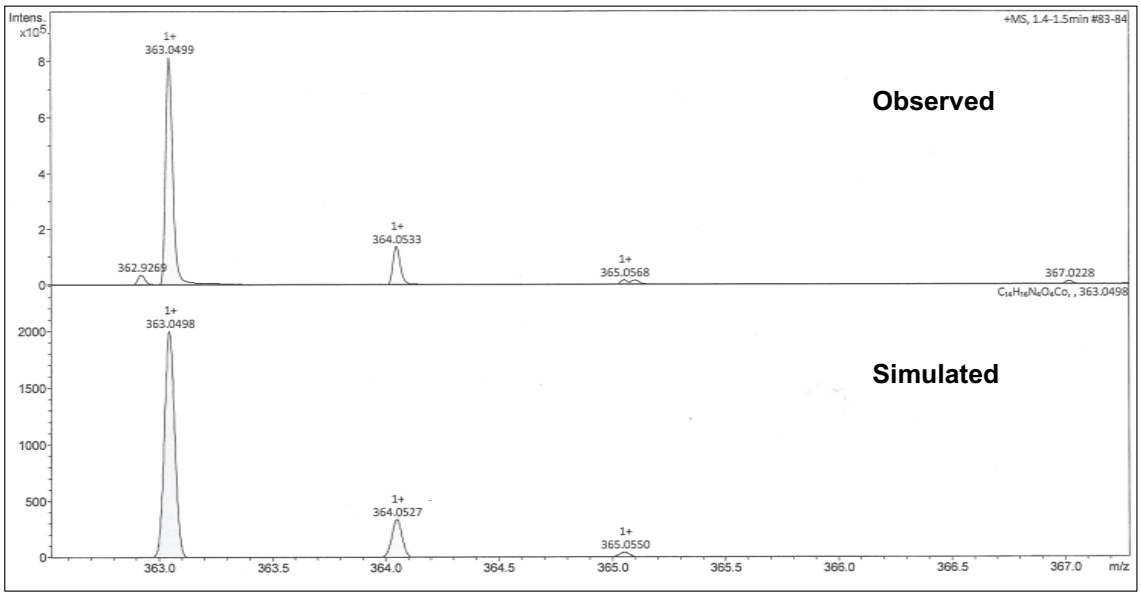

Figure S27. HRMS-ESI of ***8***

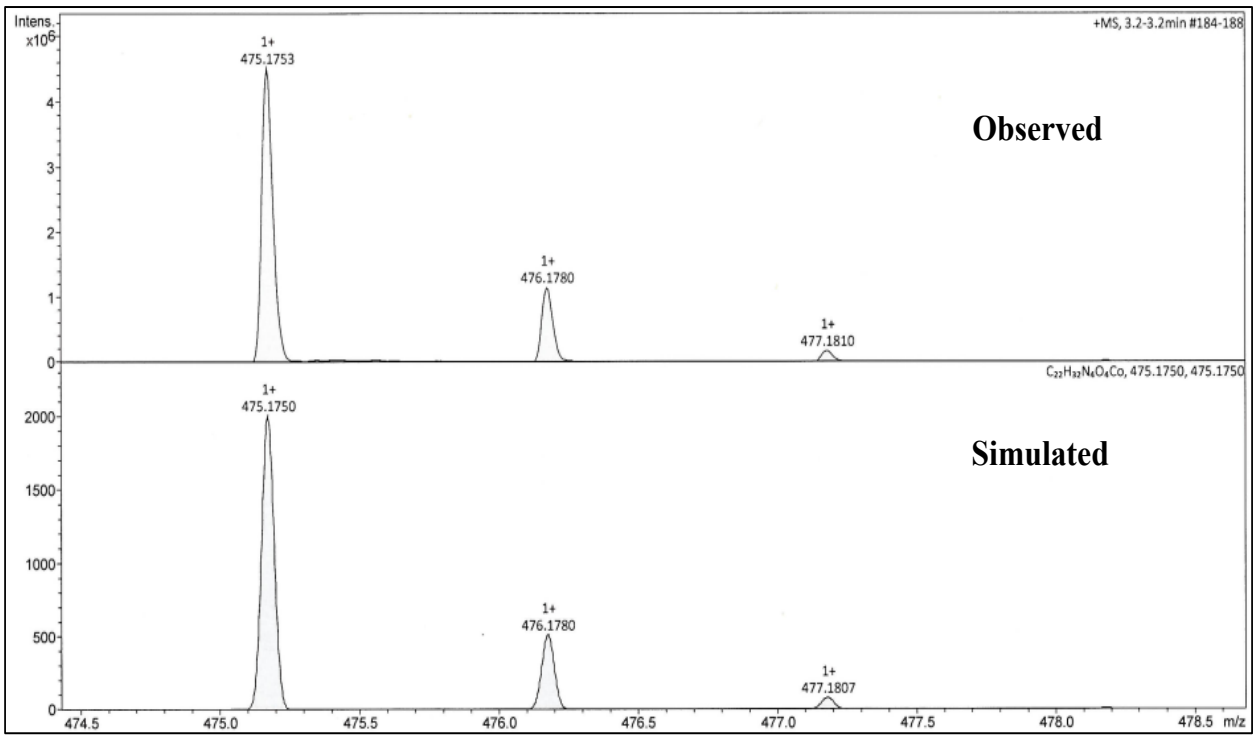

*Figure S28. HRMS-ESI of **9***

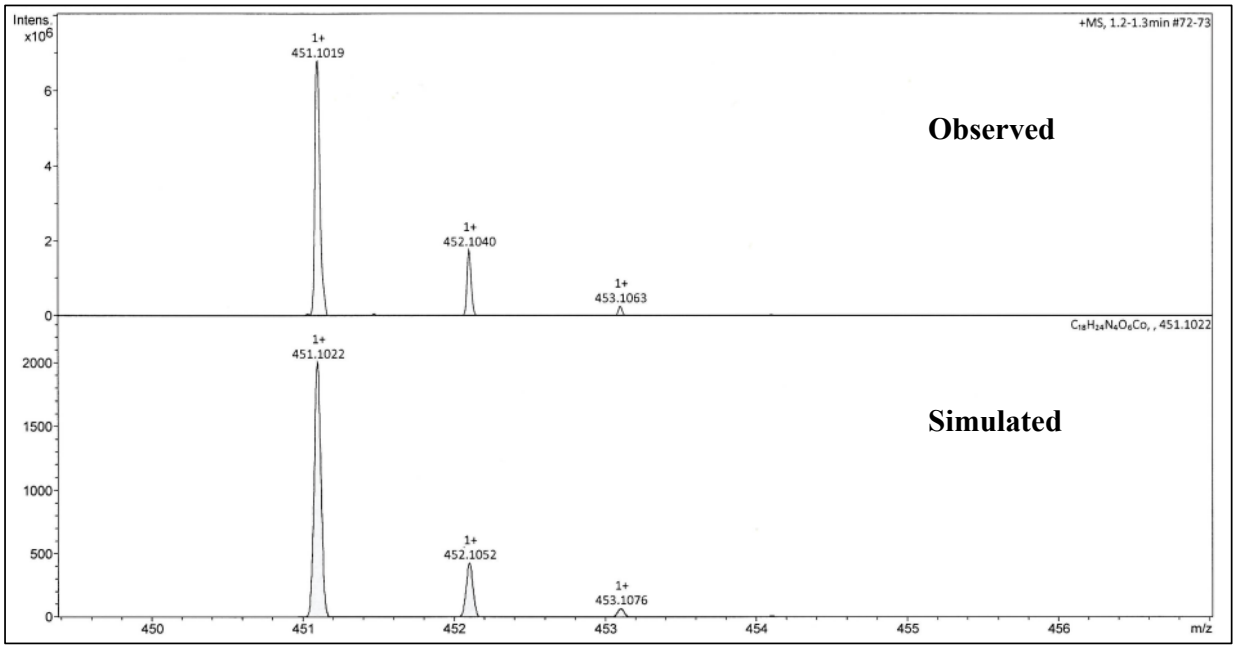

*Figure S29. HRMS-ESI of **10***

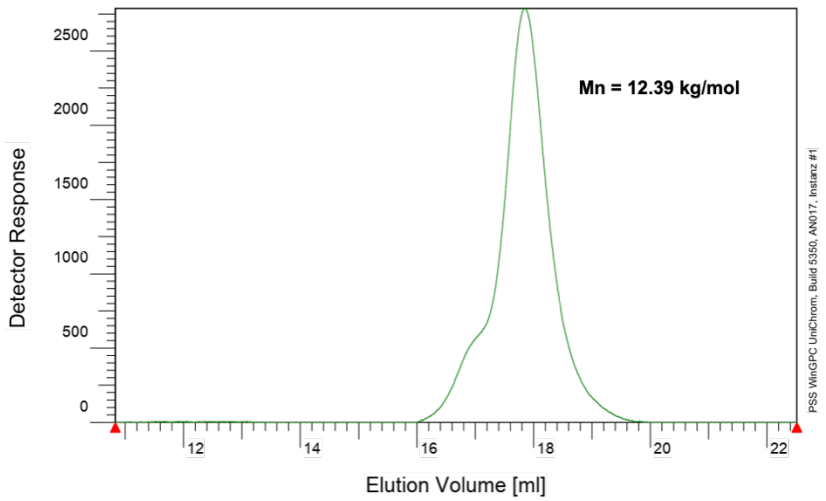

Figure S30. GPC chromatogram of PLA obtained by reaction of rac-lactide and ***8*** *(entry 1) Table 2.*

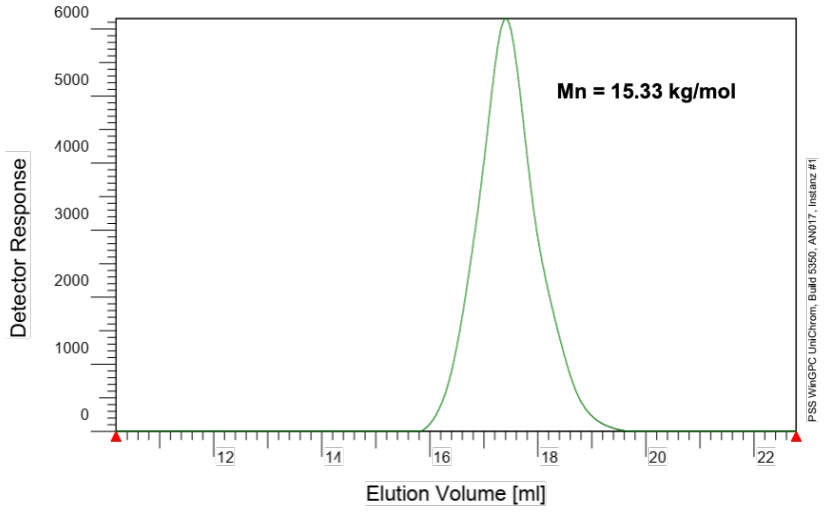

Figure S31. GPC chromatogram of PLA obtained by reaction of rac-lactide and ***9*** *(entry 4) Table 2.*

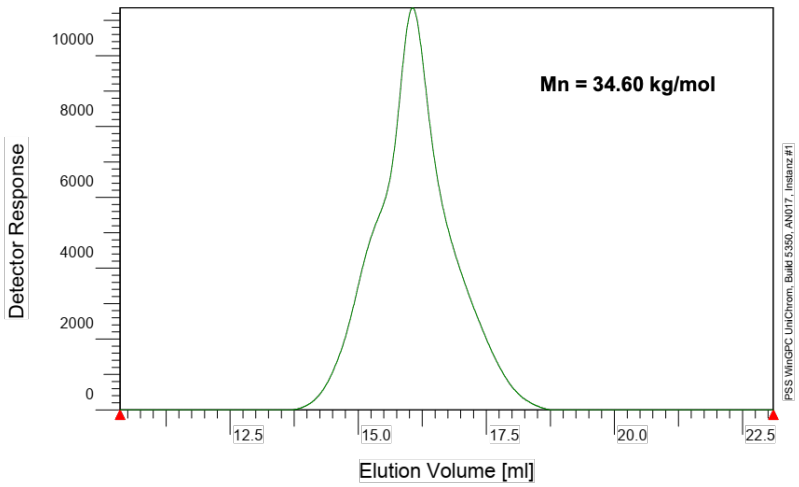

Figure S32. GPC chromatogram of PLA obtained by reaction of rac-lactide and ***9*** *(entry 5) Table 2.*

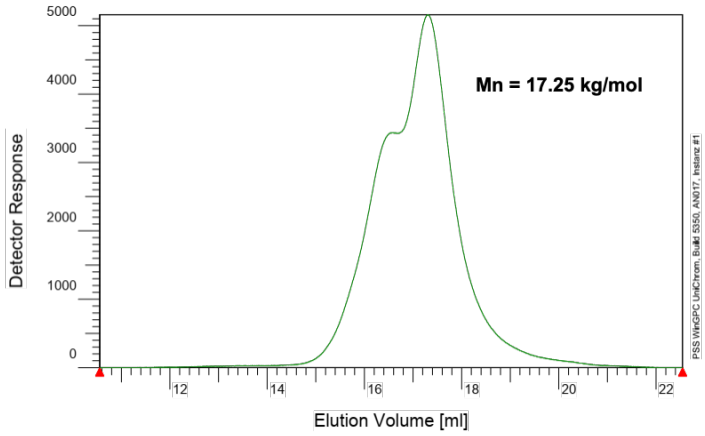

Figure S33. GPC chromatogram of PLA obtained by reaction of rac-lactide and ***10*** *(entry 7) Table 2.*

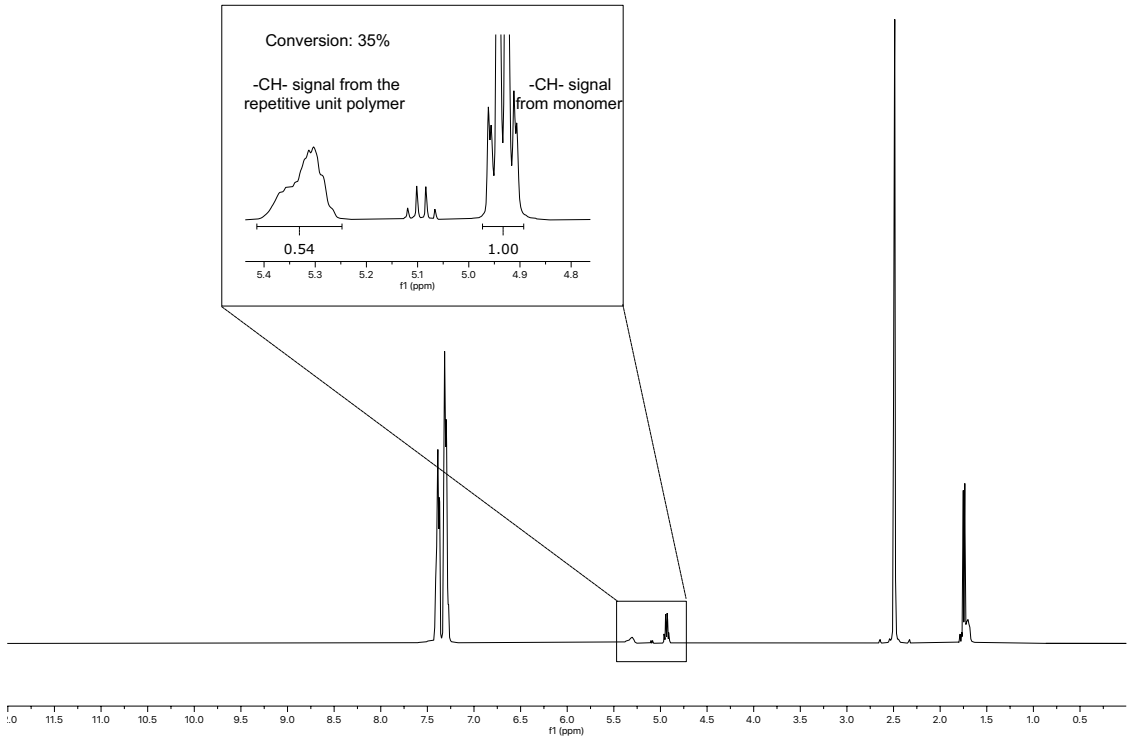

*Figure S34. Representative ^{1}H NMR spectrum of PLA in ($CDCl_3$) prepared by complex **8**. [LA]:[**8**] = 100:1, [LA]= 1 M, Toluene, 403 K.*

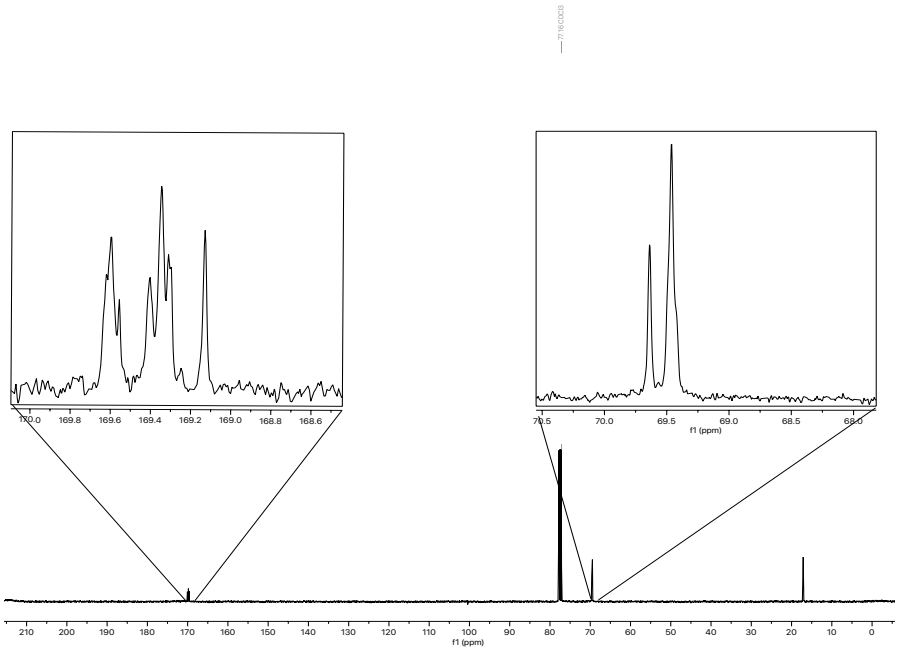

Figure S35. Carbonyl region (170-168 ppm) and methine region (70-67 ppm) of the ^{13}C NMR spectra of PLA.

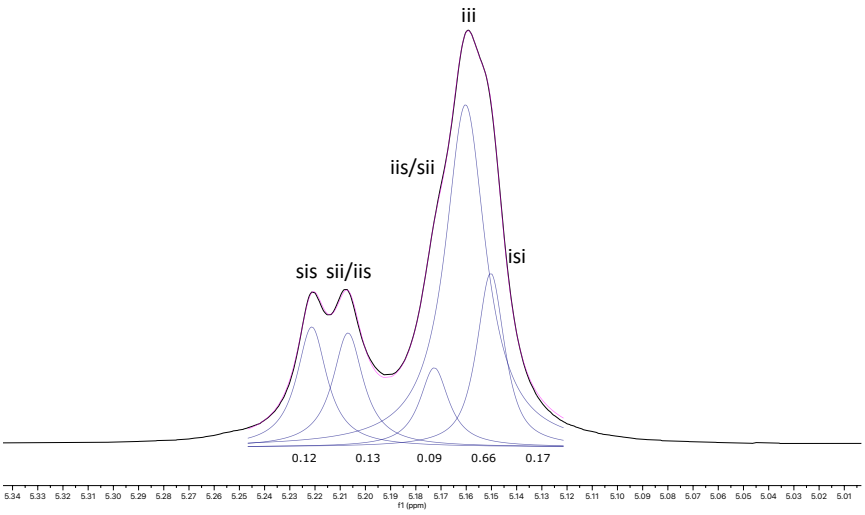

*Figure S36. Representative homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum of PLA in ($CDCl_3$) prepared by complex **8**. [LA]:[8] = 100:1, [LA]= 1 M, Toluene, 403 K.*

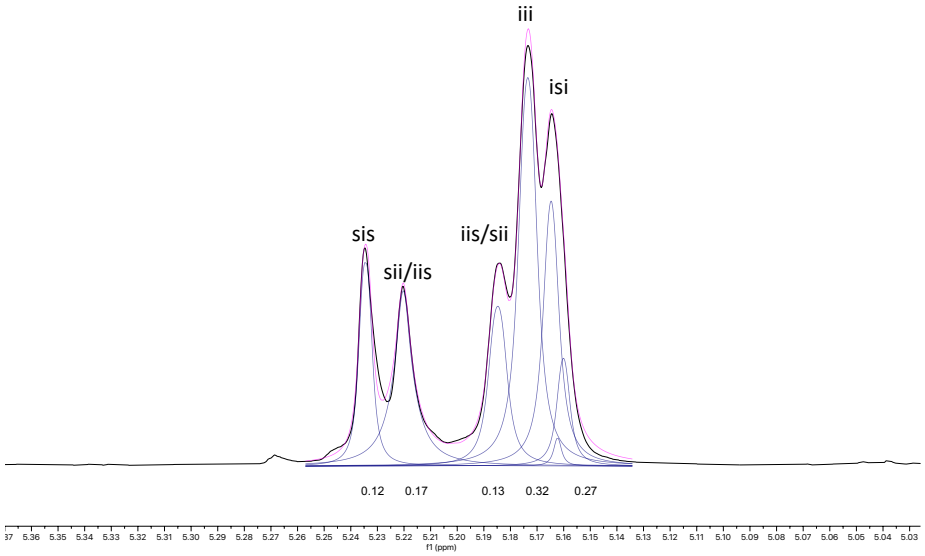

*Figure S37. Representative homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum of PLA in ($CDCl_3$) prepared by complex **9**. [LA]:[9] = 100:1, [LA]= 1 M, Toluene, 403 K.*

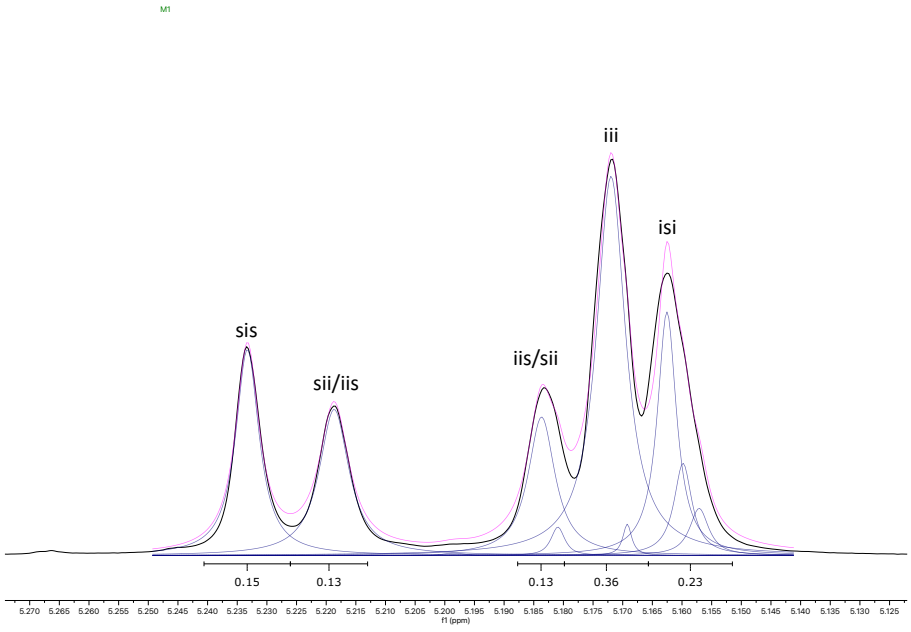

*Figure S38. Representative homonuclear decoupled $^{1}H\{^{1}H\}$ NMR spectrum of PLA in ($CDCl_3$) prepared by complex **10**. [LA]:[10] = 100:1, [LA]= 1 M, Toluene, 403 K.*

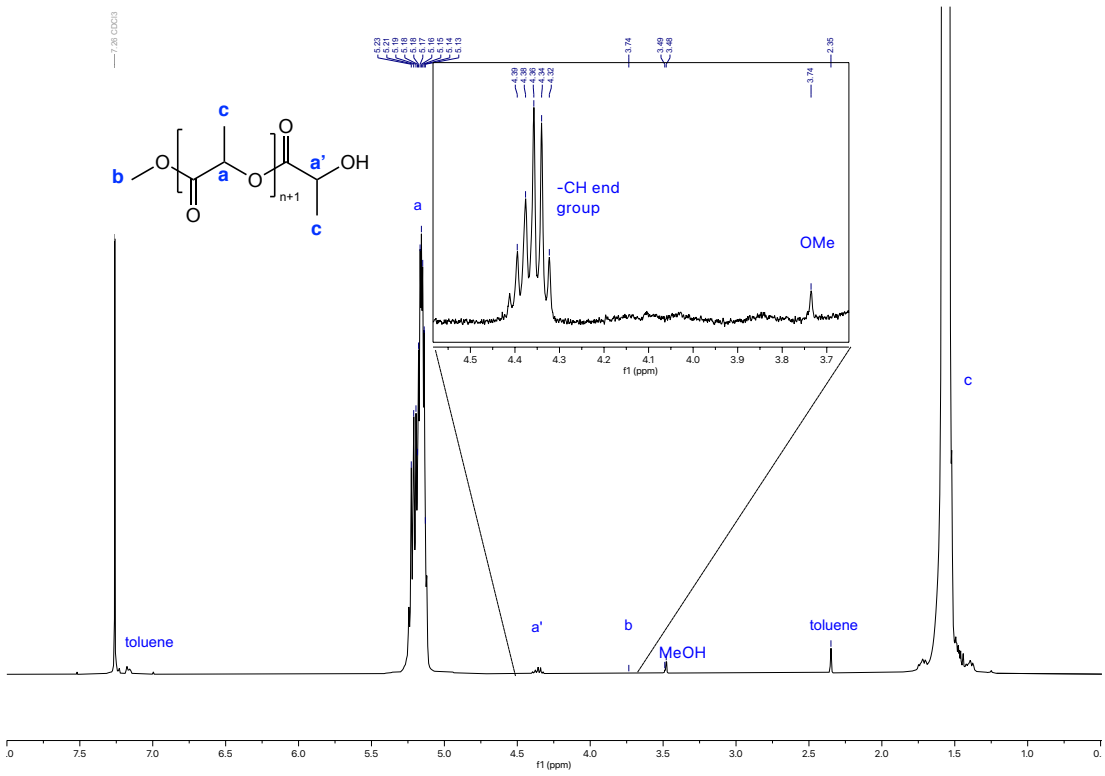

*Figure S39. Representative ^{1}H NMR spectrum of low molecular weight PLA (after precipitation with MeOH) in ($CDCl_3$) prepared by complex **8**. [LA]:[**8**] = 20:1, [LA]= 1 M, Toluene, 403 K.*