

Electronic Supplementary Information

TRANSITION METAL AND GROUP 13 TRIAZAMACROCYCLIC COMPLEXES: COORDINATION CHEMISTRY AND APPLICATIONS IN ^{18}F PET IMAGING

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Chapter 2

Figure S2.1 Ts₃-DET

S2.1.a ¹H NMR spectrum (CDCl₃)

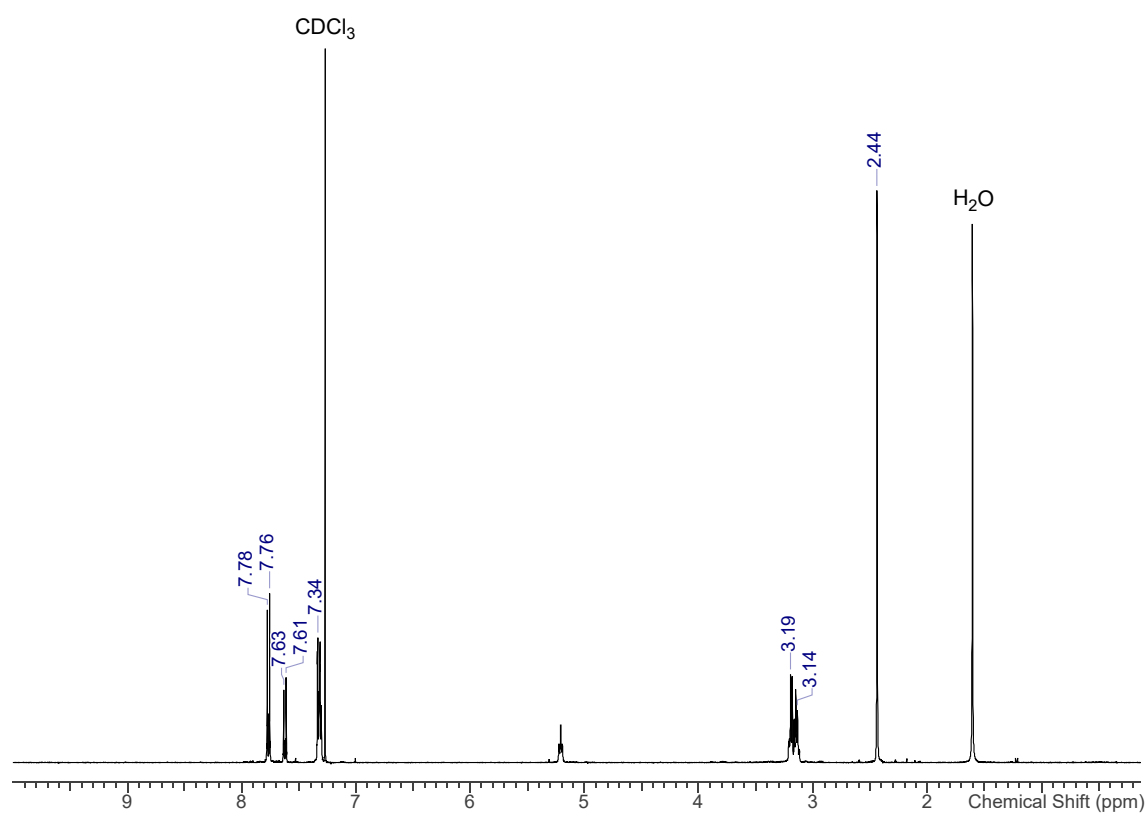


Figure S2.2 EGT

S2.2.a ^1H NMR spectrum (CDCl_3)

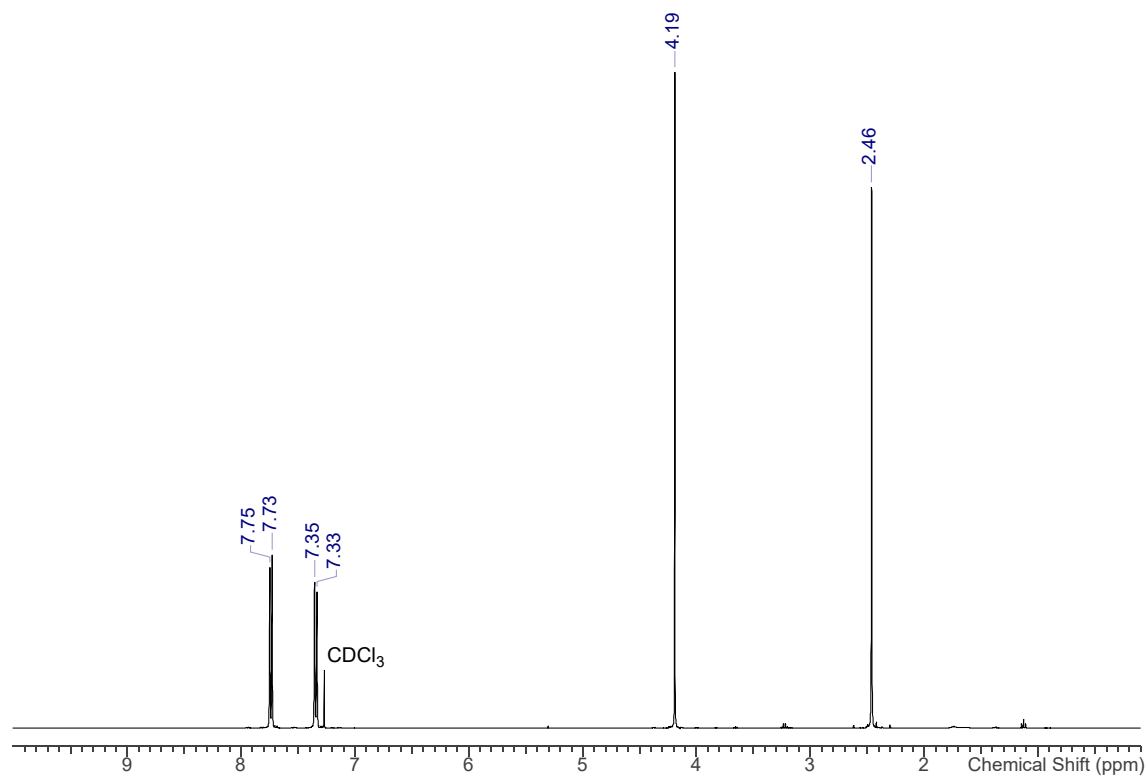
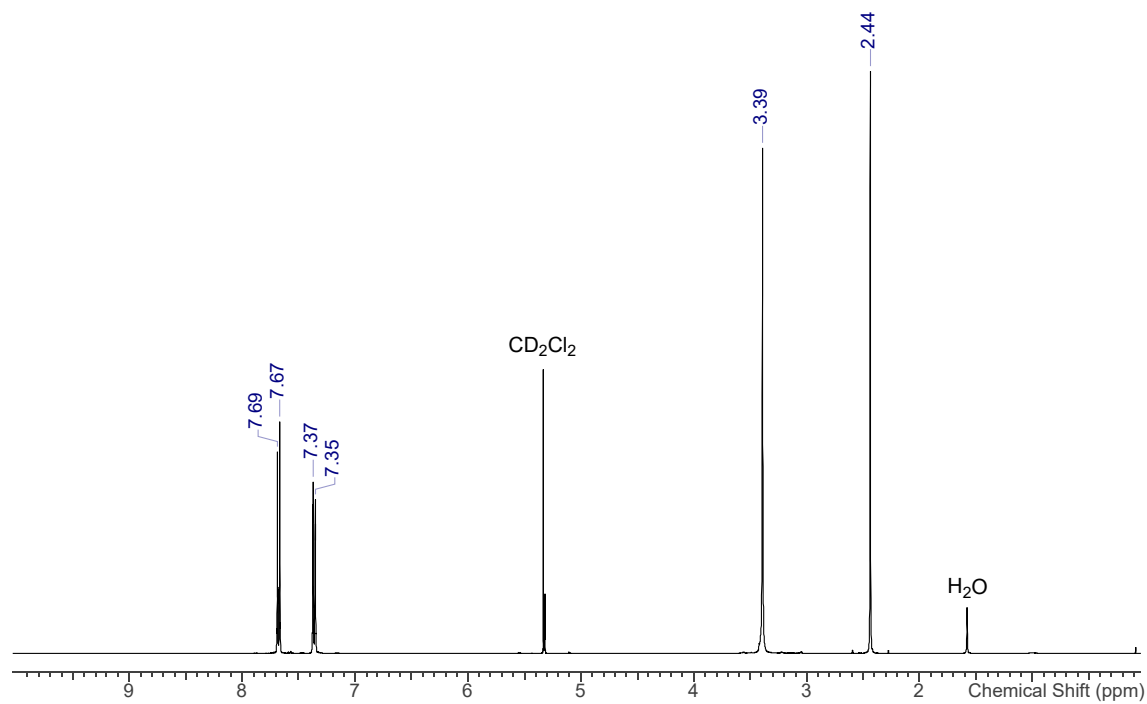


Figure S2.3 $\text{Ts}_3\text{-tacn}$

S2.3.a ^1H NMR spectrum (CD_2Cl_2)



S2.3.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_2Cl_2)

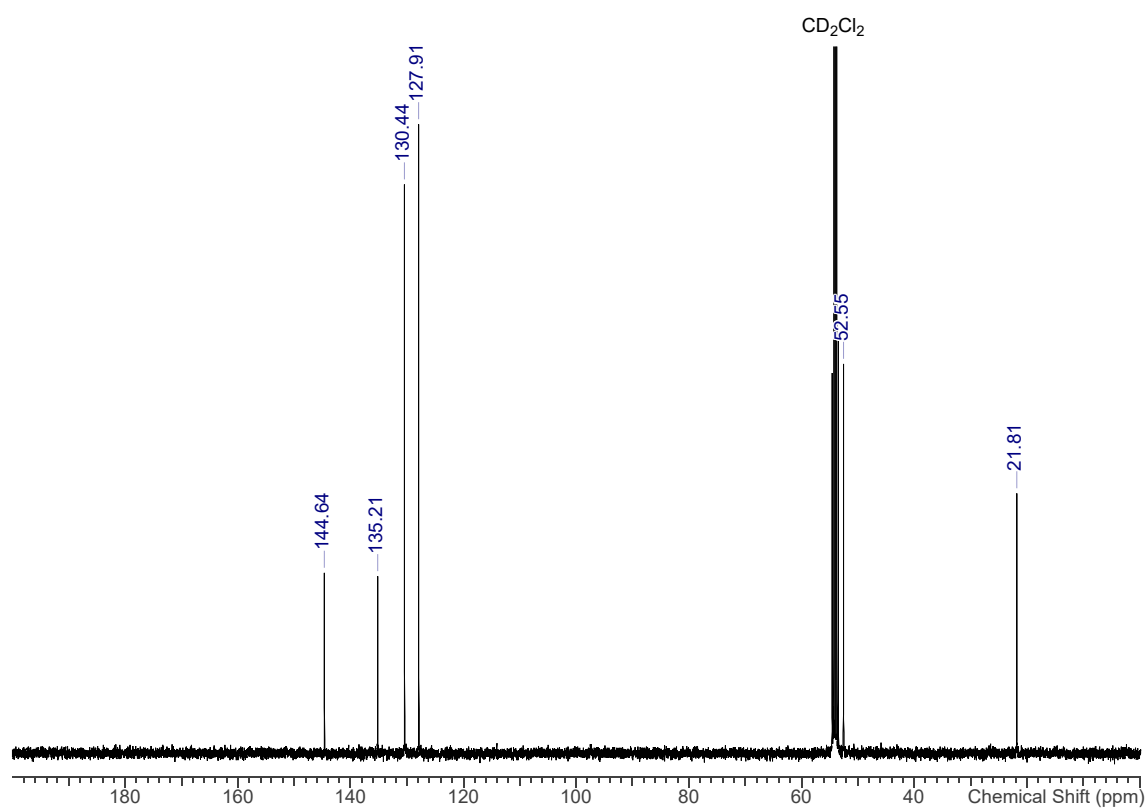


Figure S2.4 Tacn.3HBr

S2.4.a ^1H NMR spectrum (D_2O)

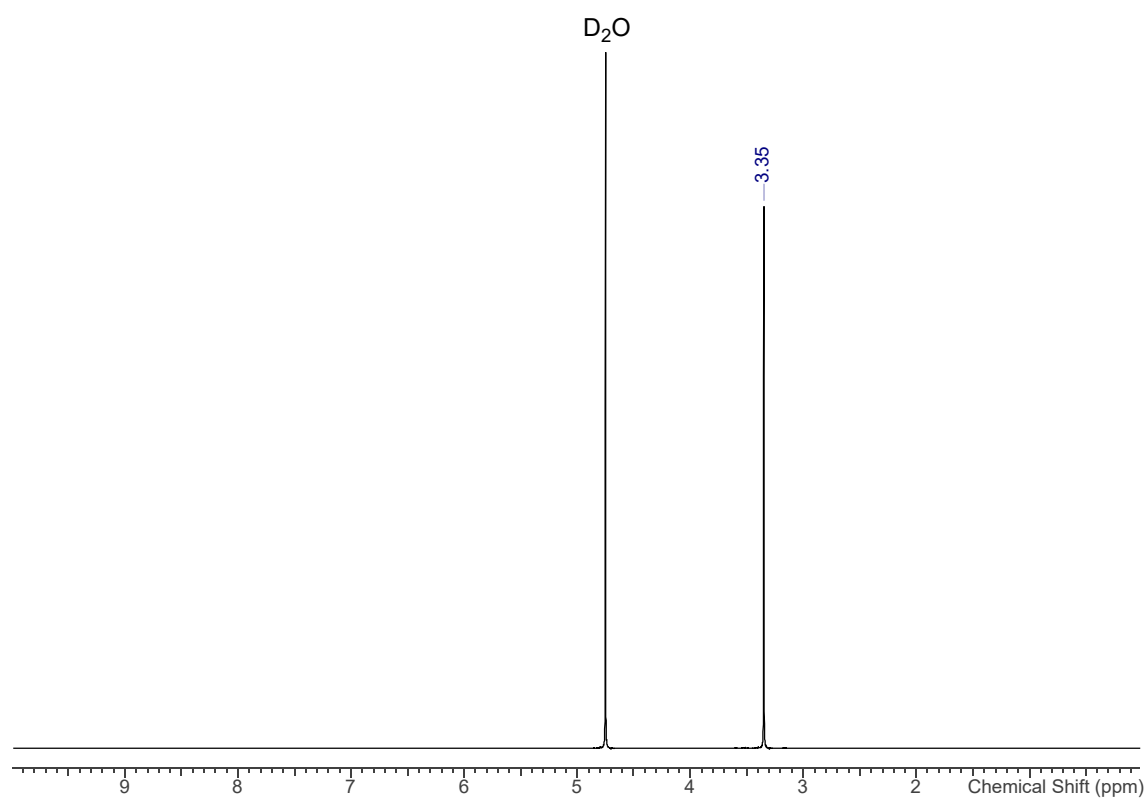


Figure S2.5 Tacn

S2.5.a ^1H NMR spectrum (CDCl_3)

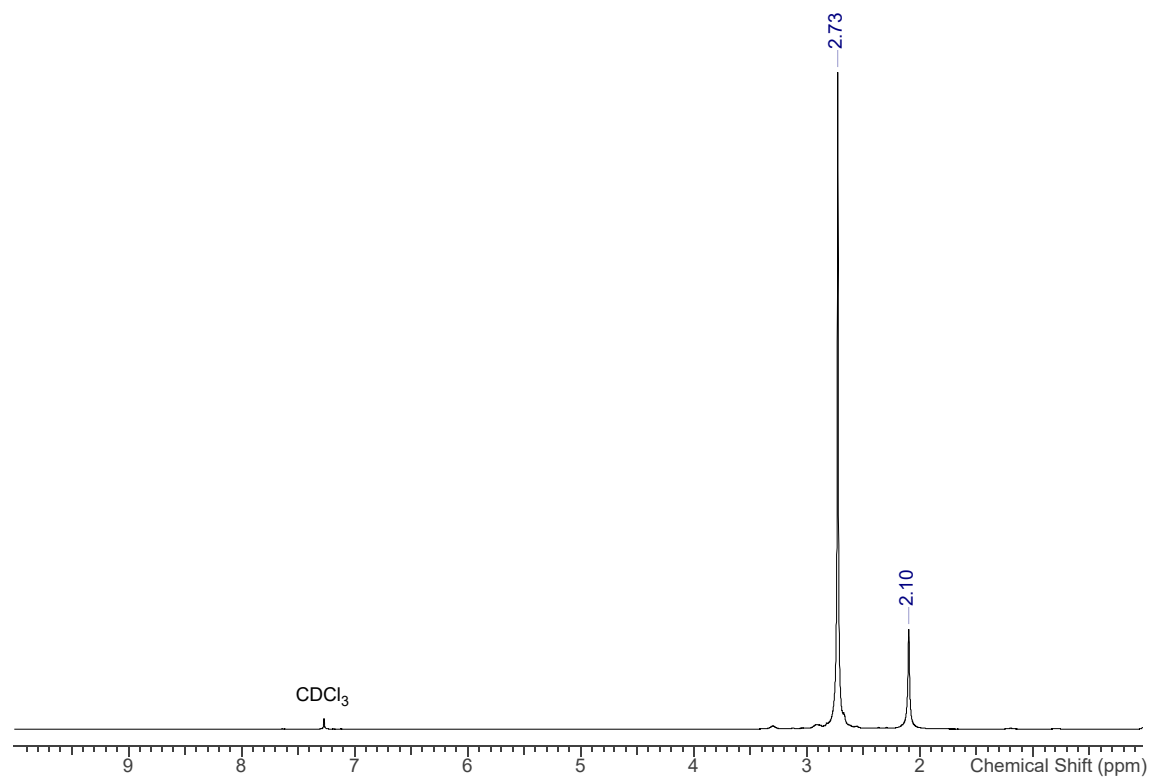
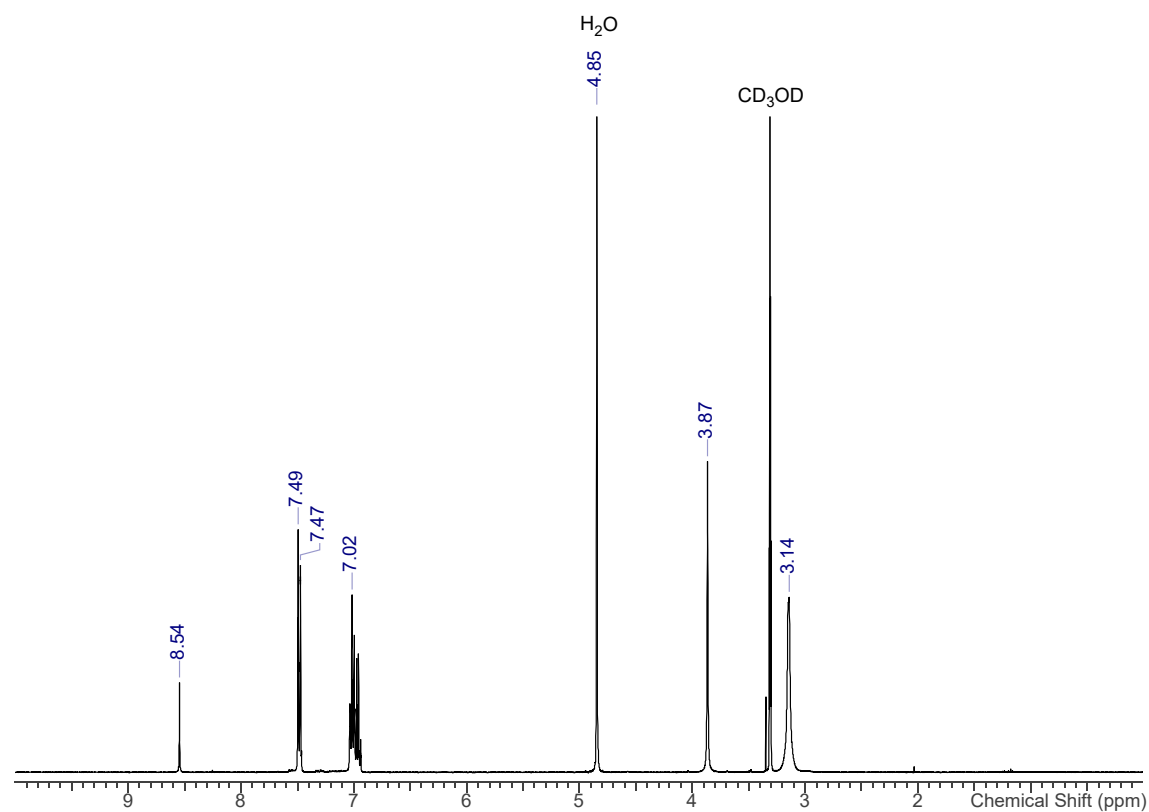
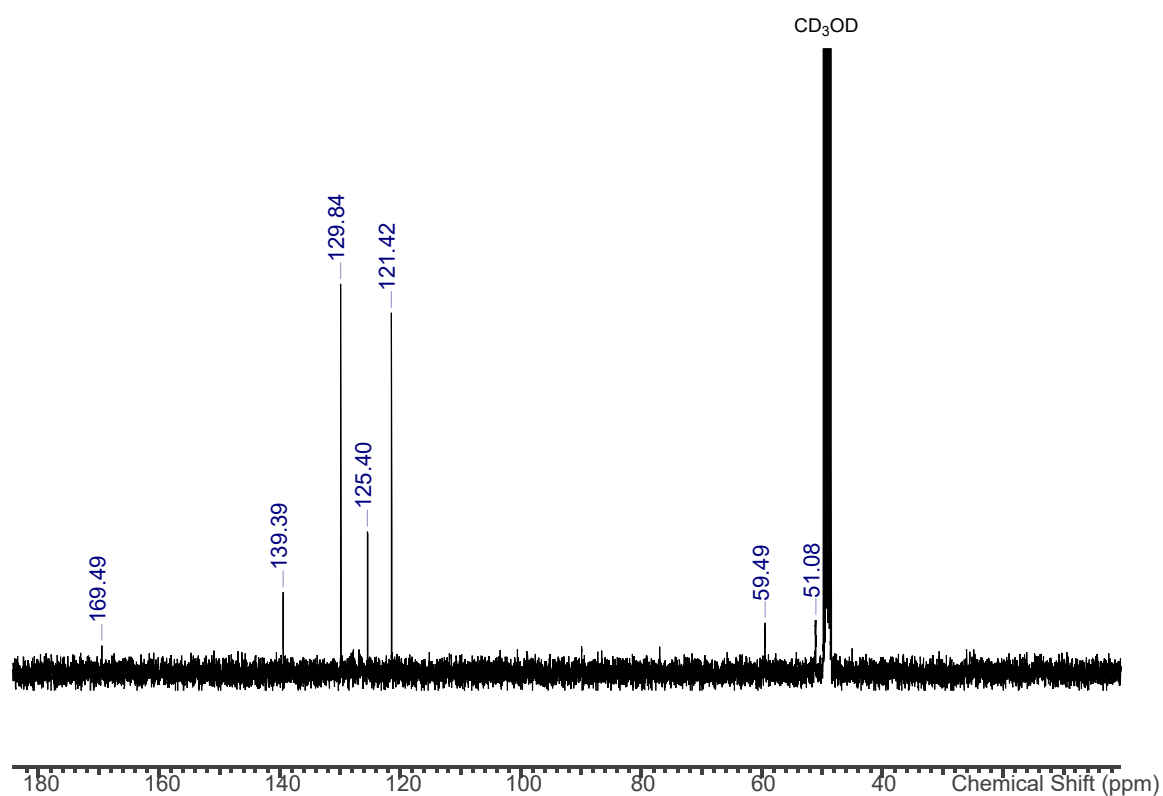


Figure S2.6 Ligand 1

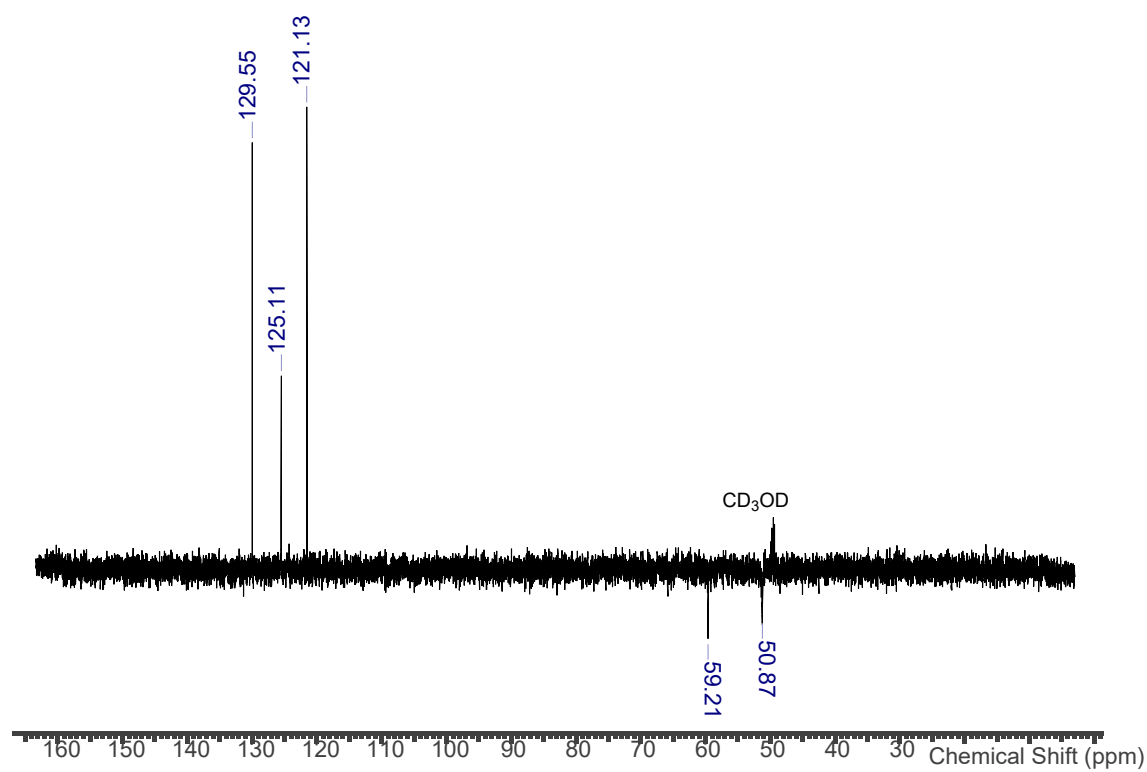
S2.6.a ^1H NMR spectrum (CD_3OD)



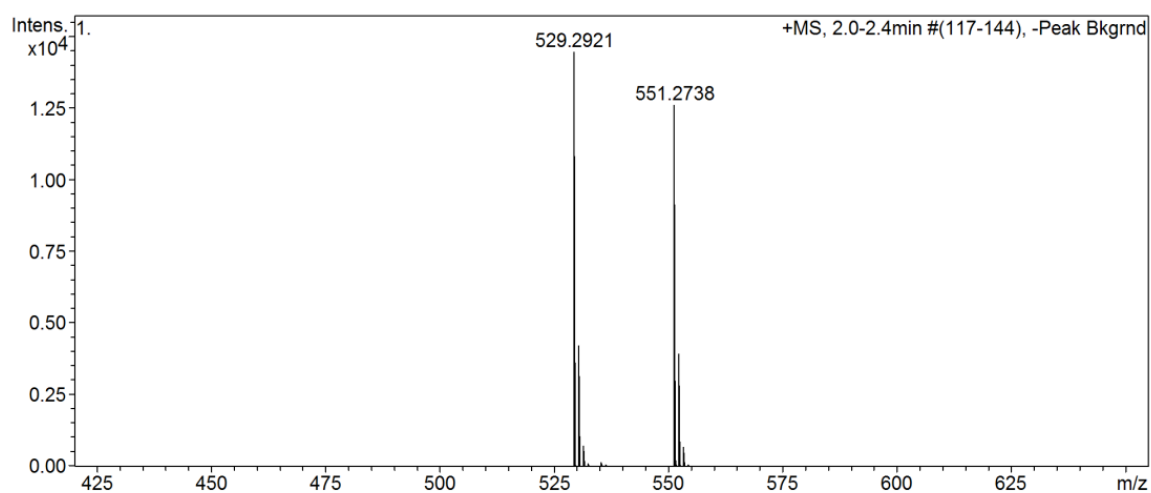
S2.6.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S2.6.c ^{13}C 135-DEPT NMR spectrum (CD_3OD)



S2.6.d HR ESI⁺ MS (MeOH)



S2.6.e IR spectrum (Nujol)

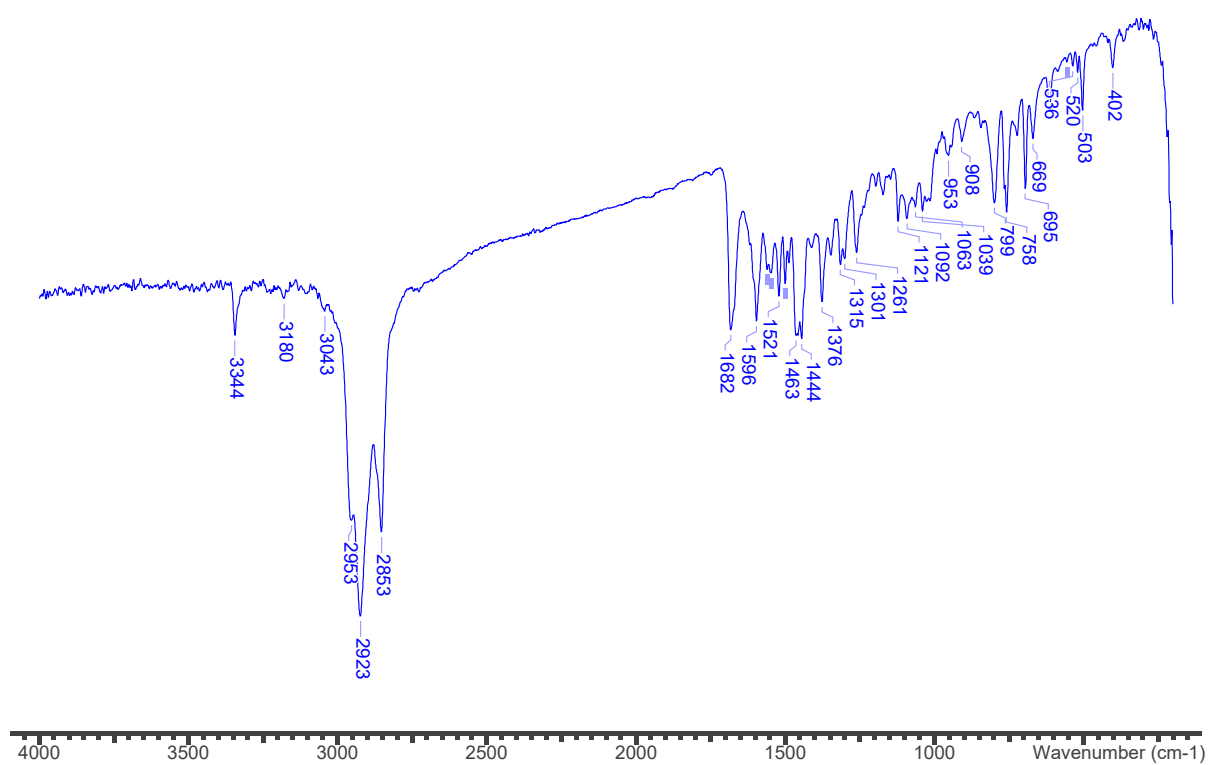
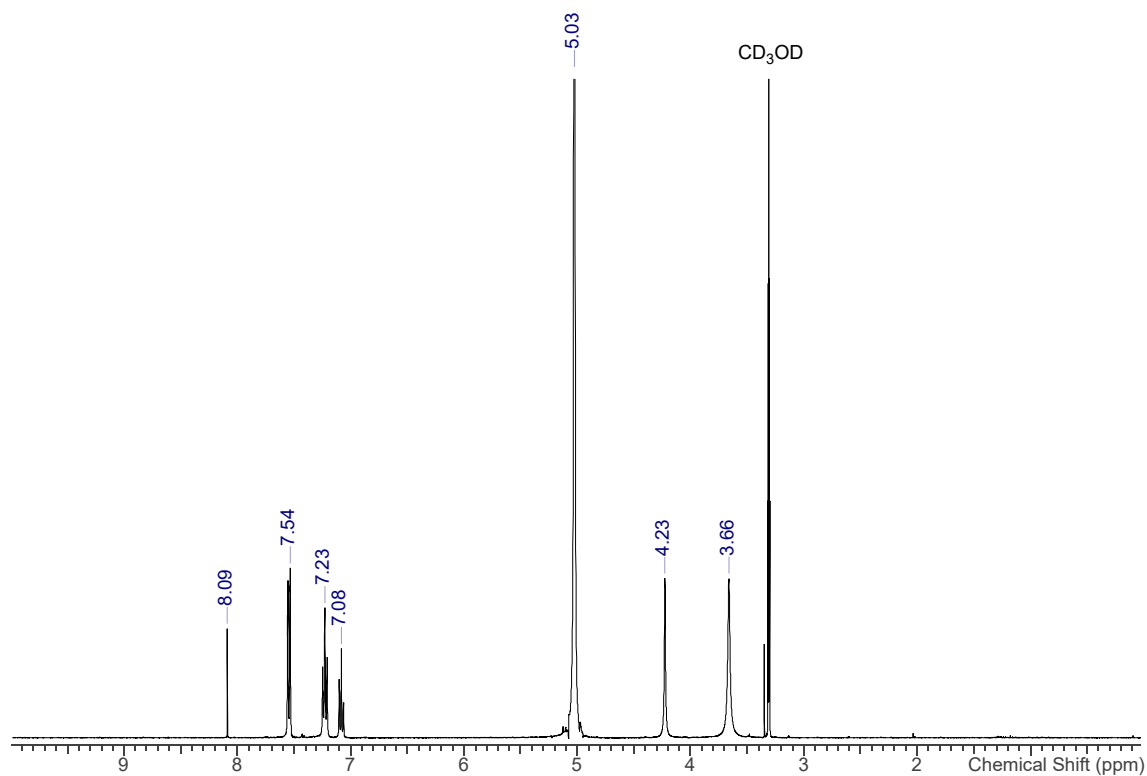


Figure S2.7 Ligand 1.HCl

S2.7.a ^1H NMR spectrum (CD_3OD)



S2.7.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)

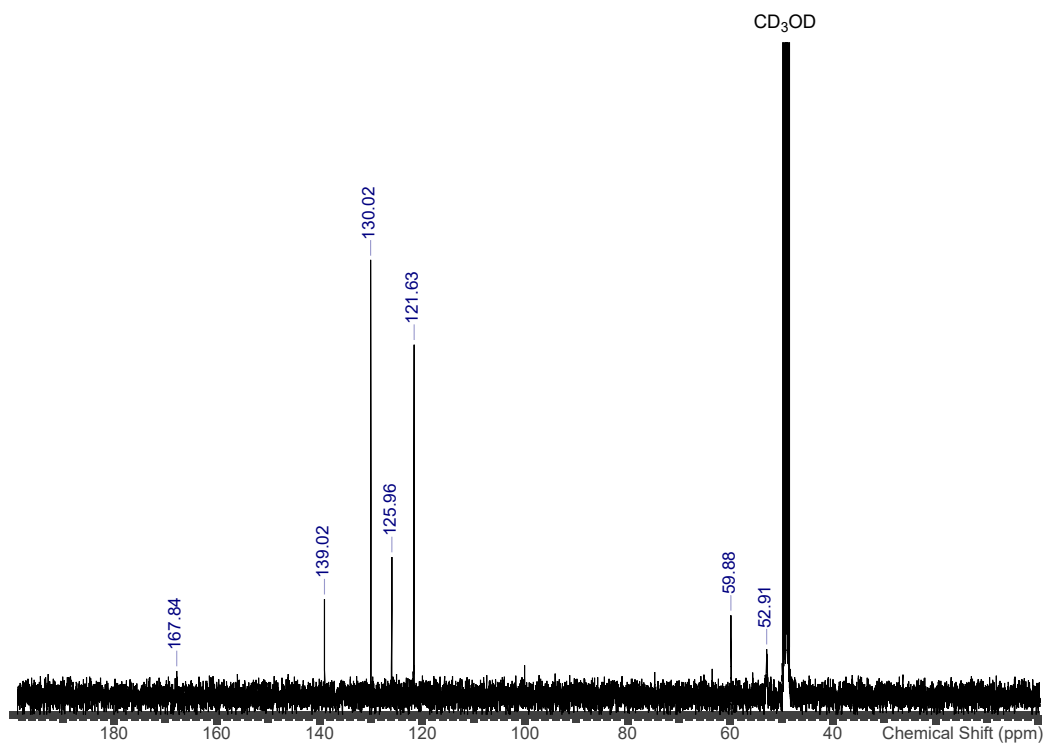
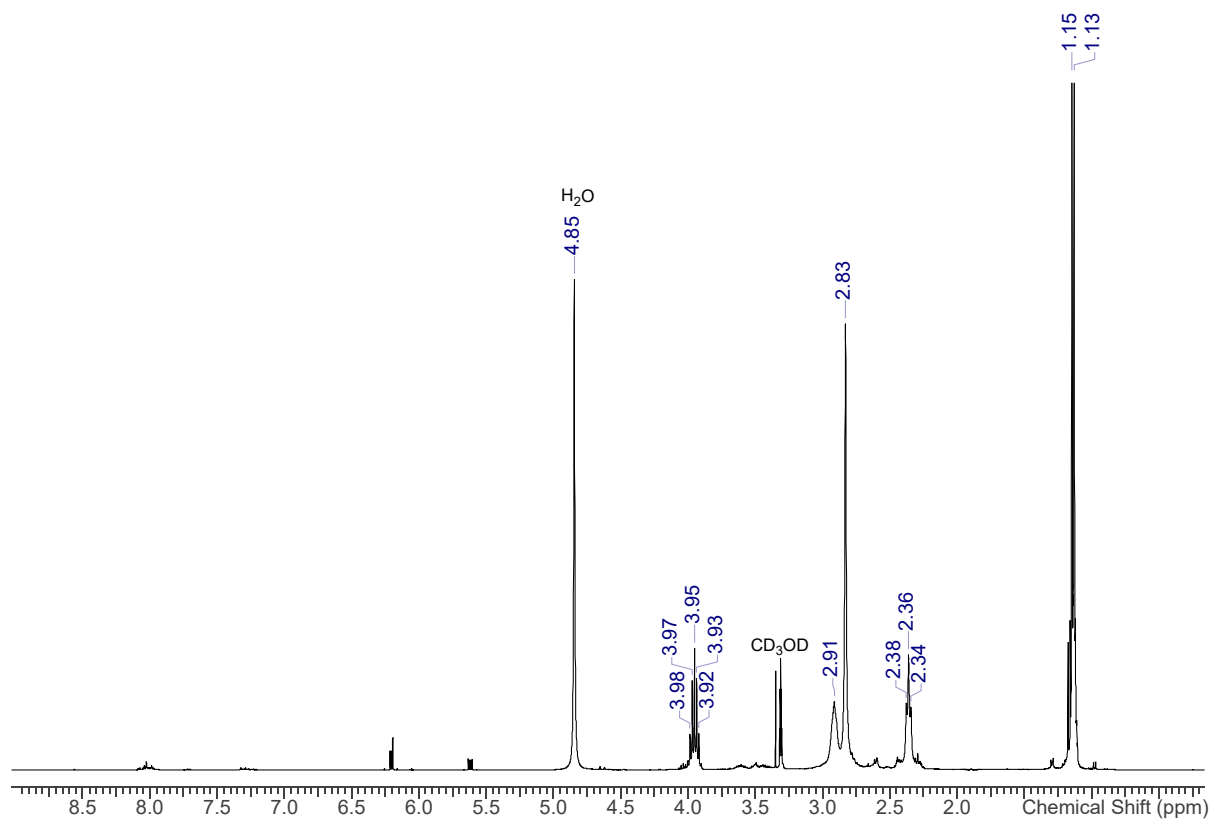
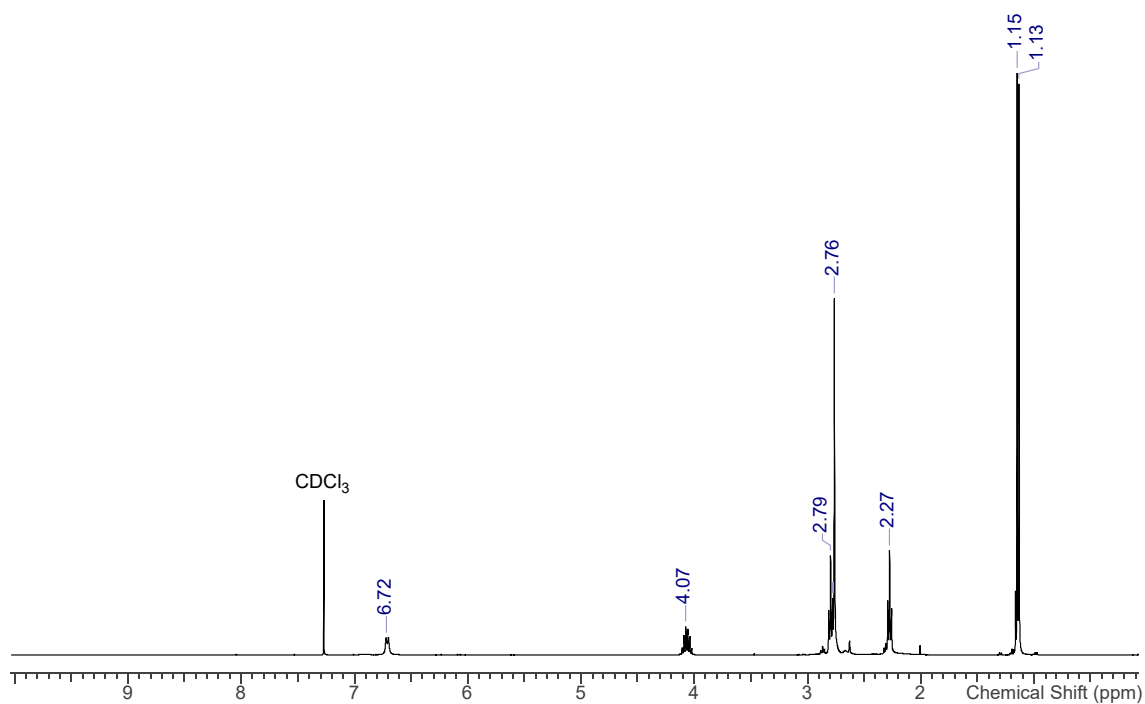


Figure S2.8 Ligand 2

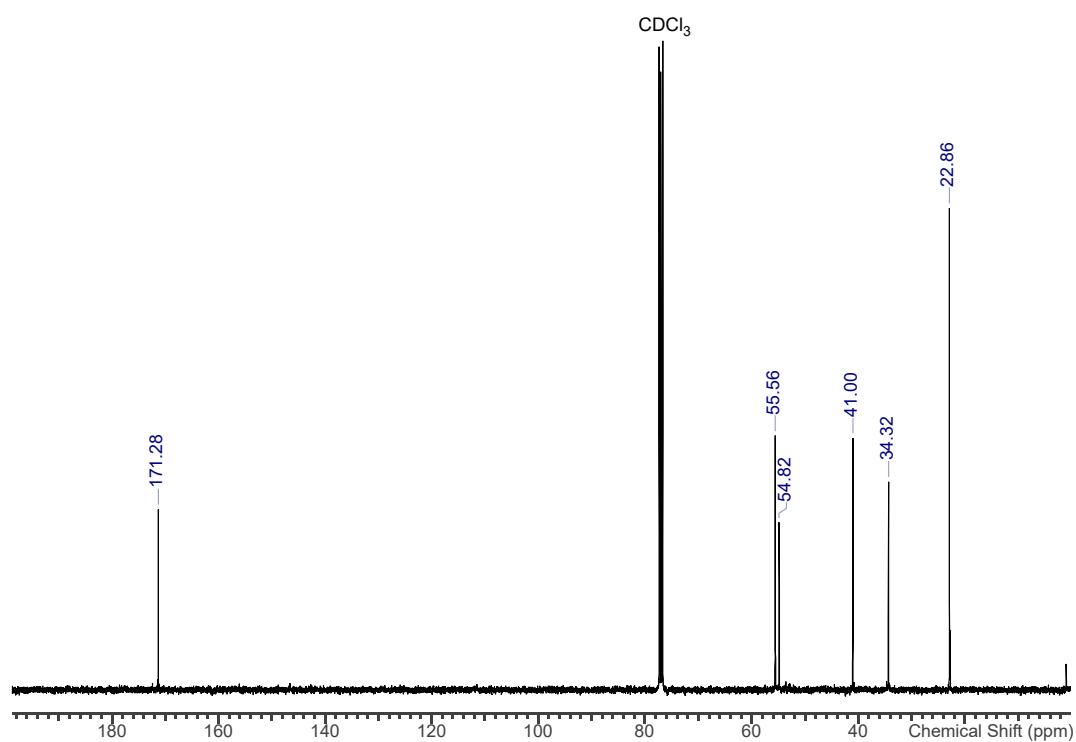
S2.8.a ^1H NMR spectrum (CD_3OD)



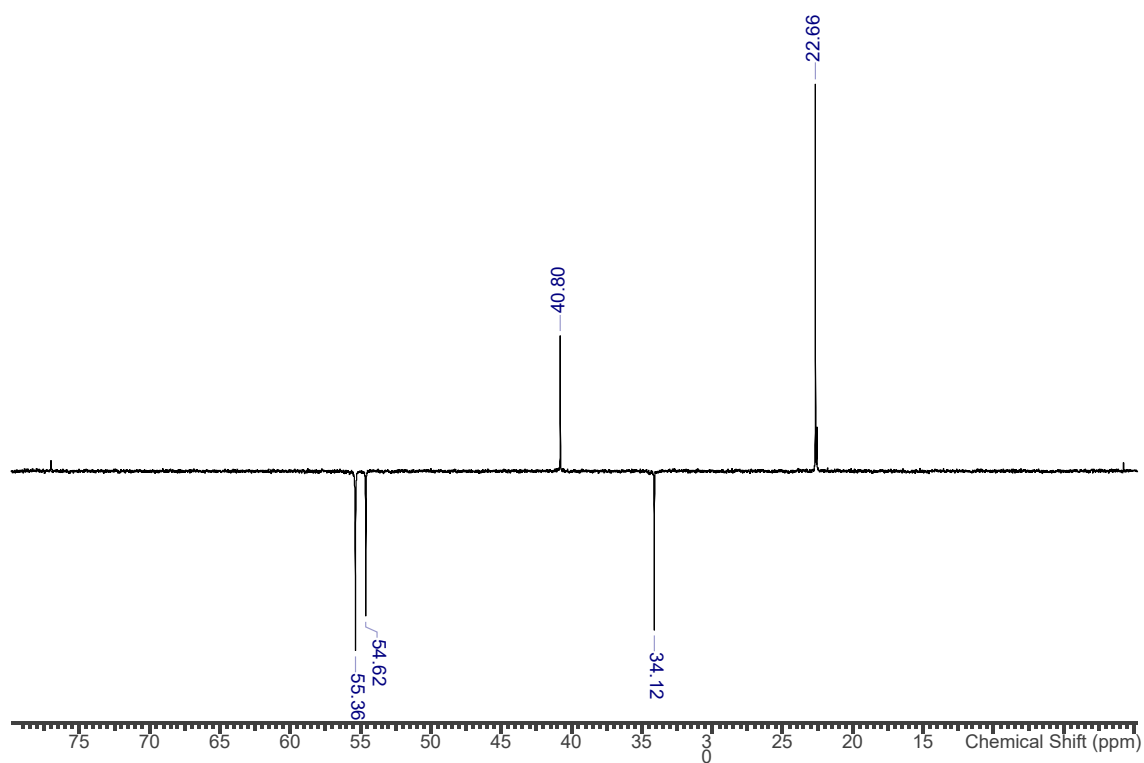
S2.8.b ^1H NMR spectrum (CDCl_3)



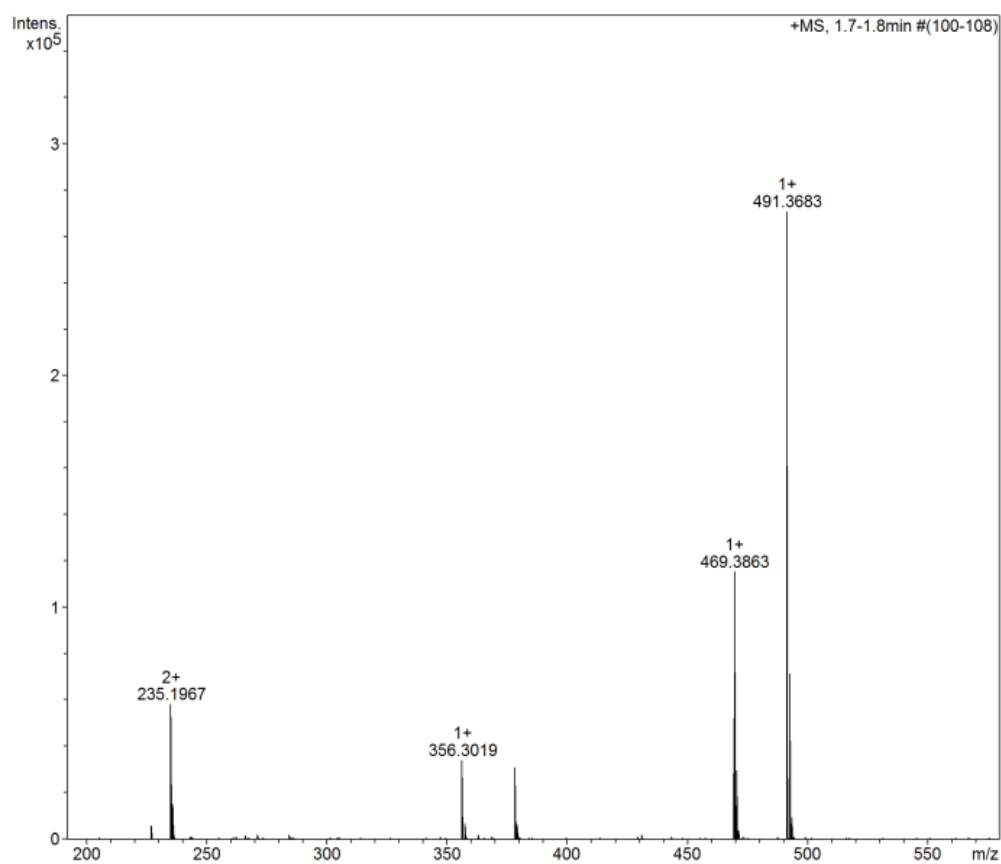
S2.8.c $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)



S2.8.d ^{13}C 135-DEPT NMR spectrum (CDCl_3)



S2.8.e HR ESI⁺ MS spectrum (MeOH)



S2.8.f IR spectrum spectrum (neat film)

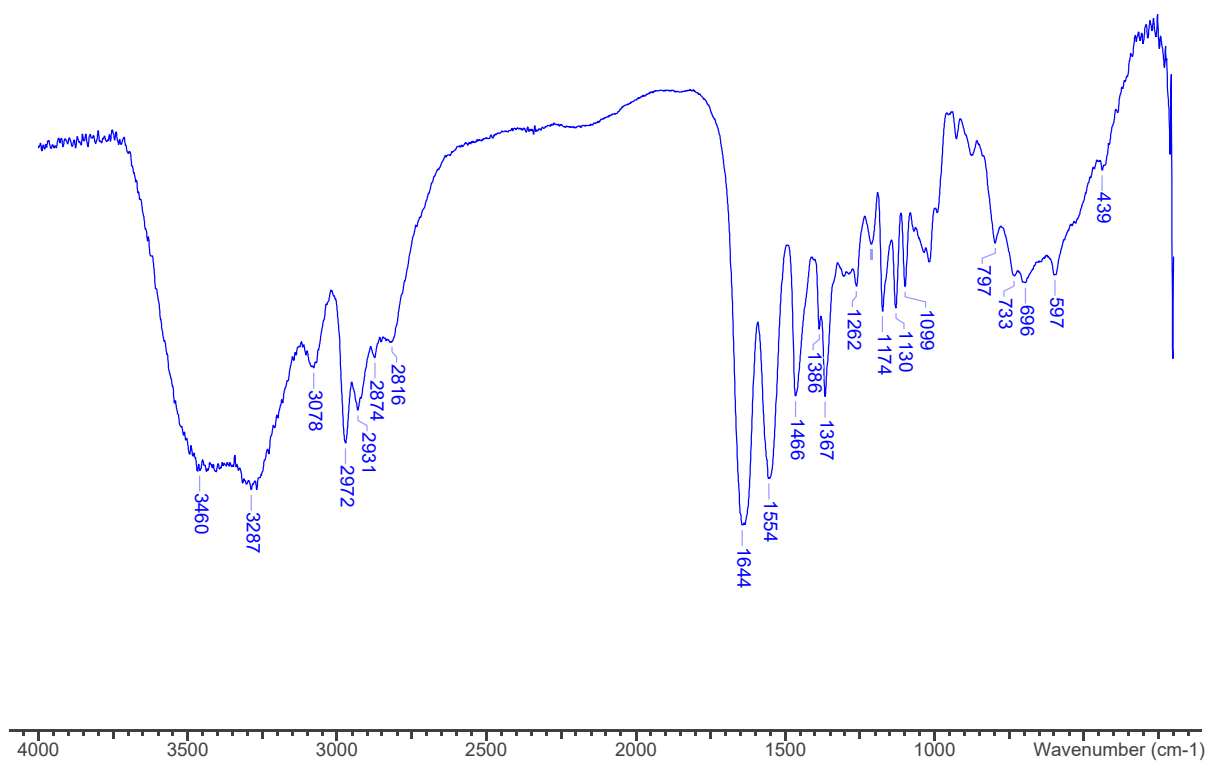
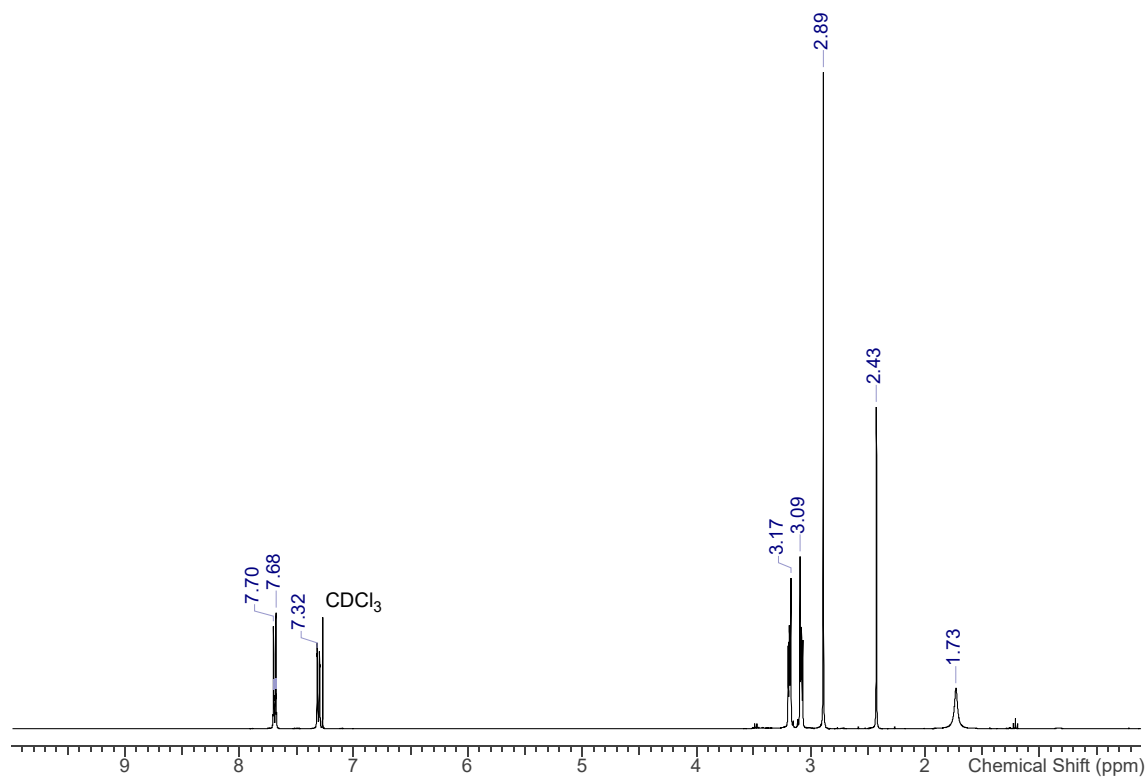


Figure S2.9 Ts-tacn

S2.9.a ^1H NMR spectrum (CDCl_3)



S2.9.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

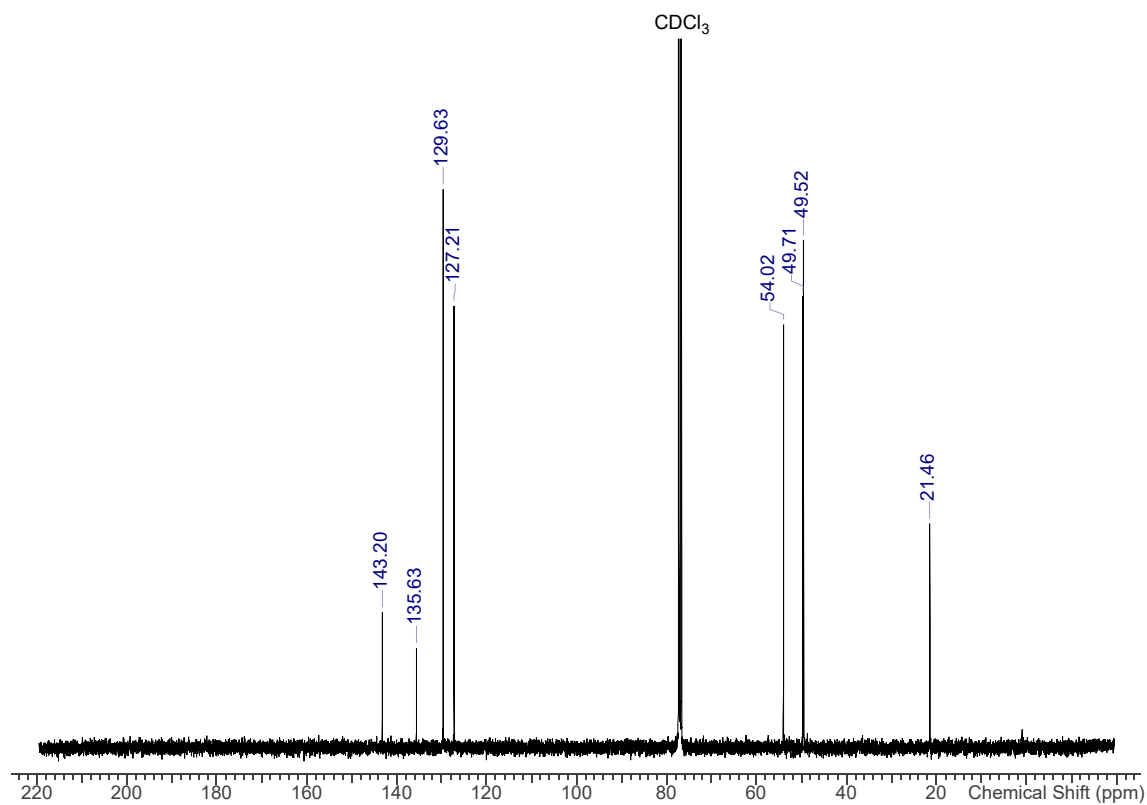
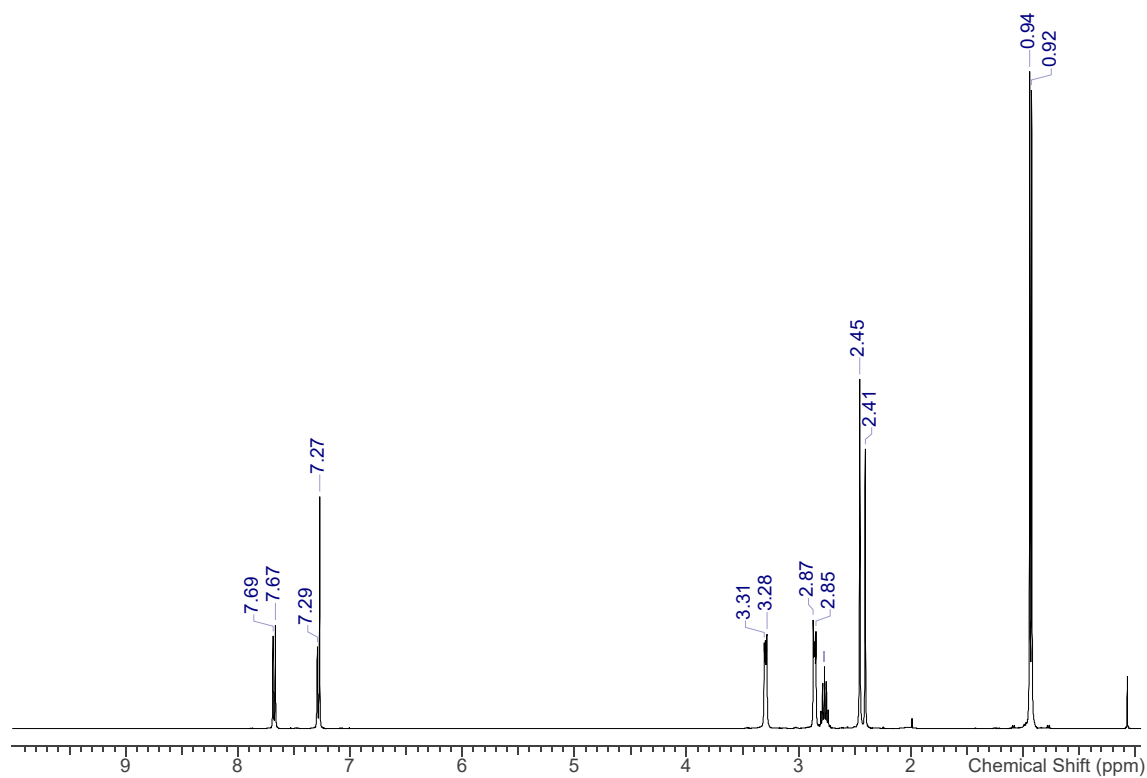


Figure S2.10 ⁱPr₂-Ts-tacn

S2.10.a ¹H NMR spectrum (CDCl₃)



S2.10.b ¹³C{¹H} NMR spectrum (CDCl₃)

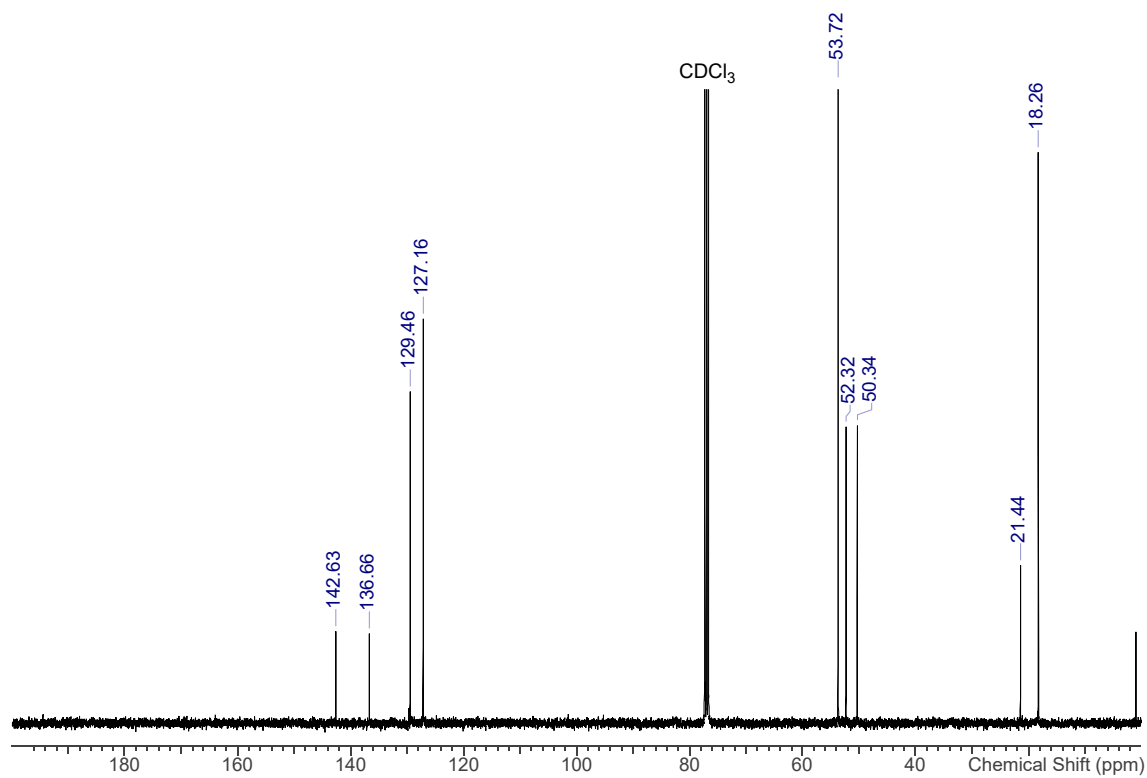
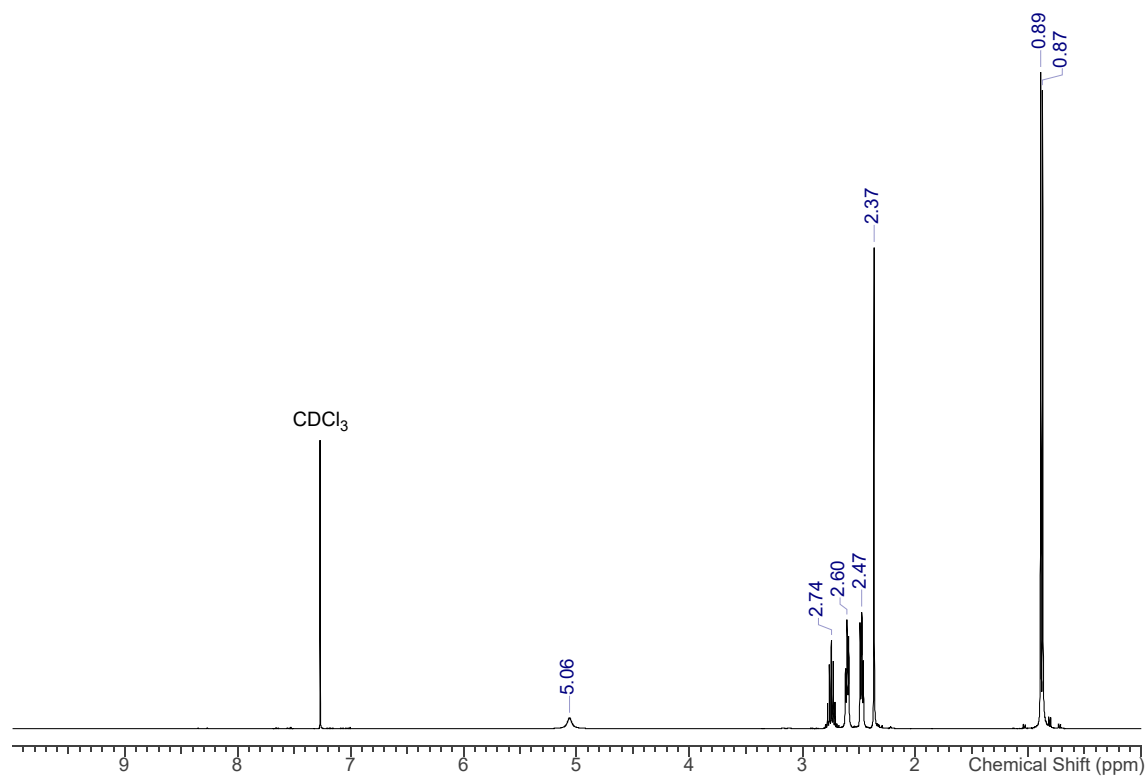


Figure S2.11 $i\text{Pr}_2\text{-tacn}$

S2.11.a ^1H NMR spectrum (CDCl_3)



S2.11.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

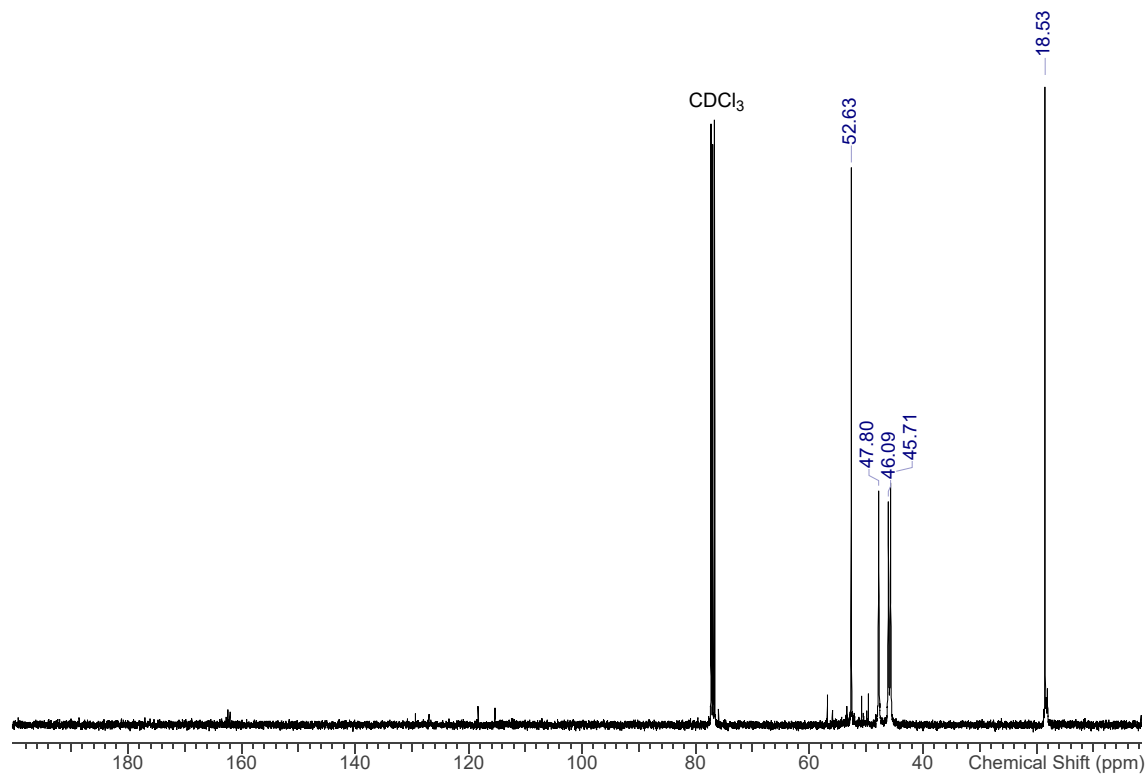
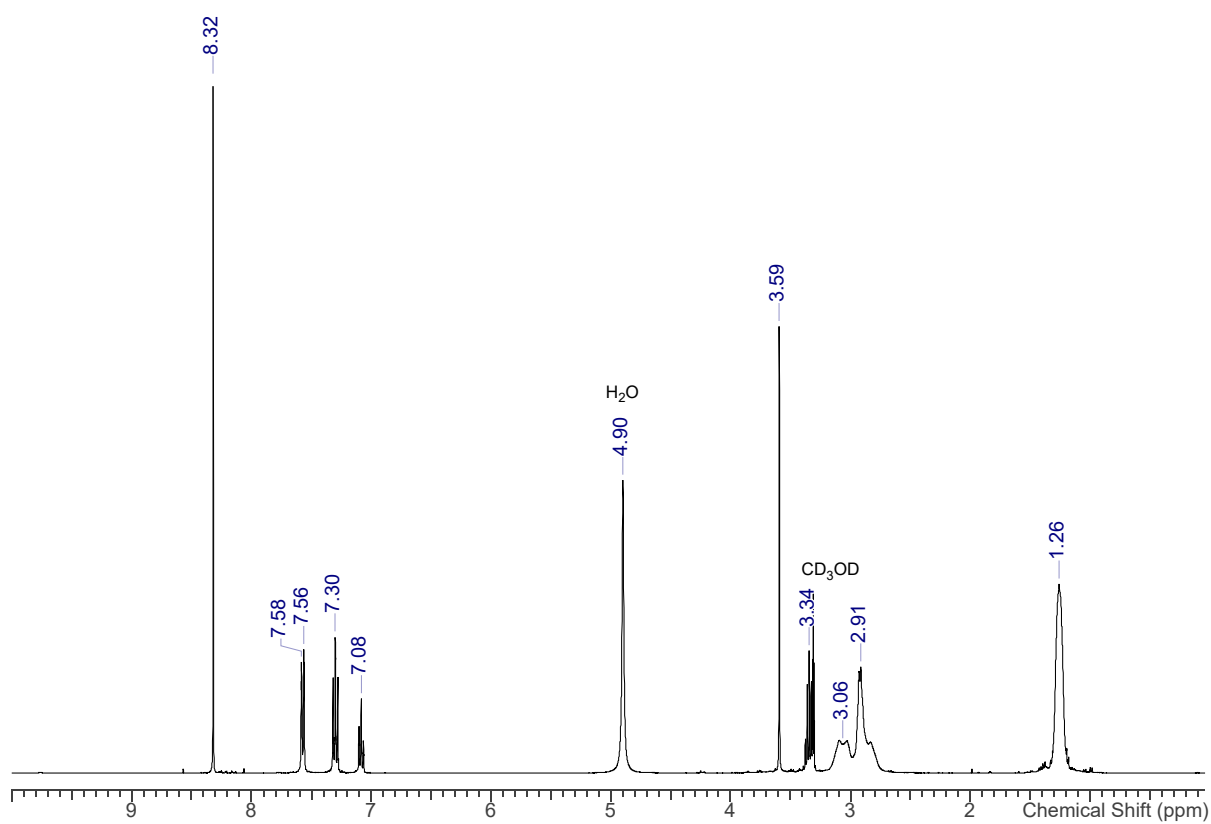
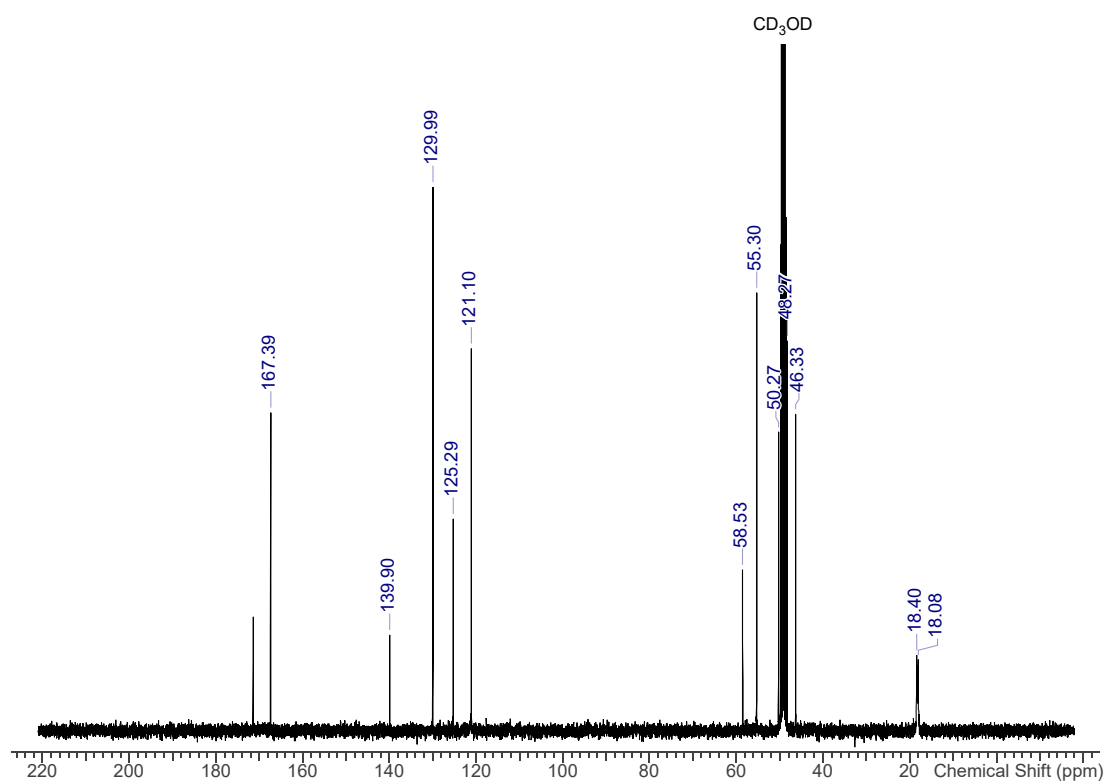


Figure S2.12 [Ligand 3][H]

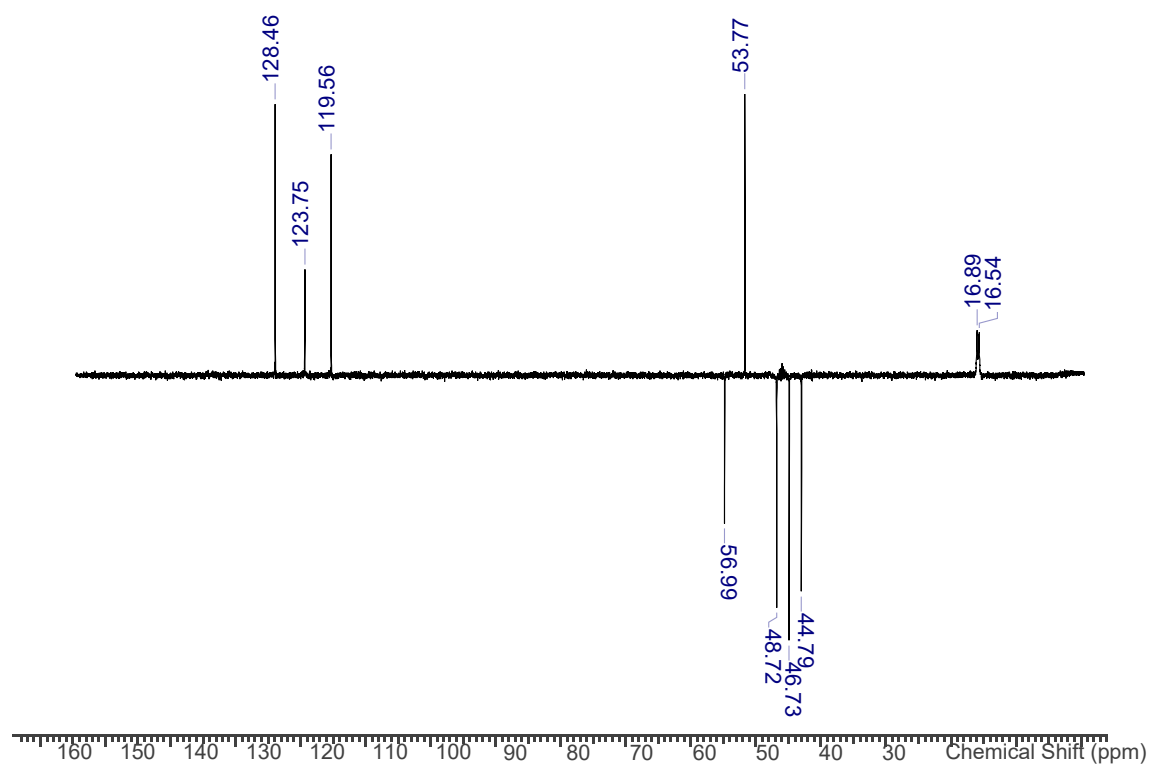
S2.12.a ^1H NMR spectrum (CD_3OD)



S2.12.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S2.12.c ^{13}C 135-DEPT NMR spectrum (CD_3OD)



S2.12.d HR ESI⁺ MS (MeOH)

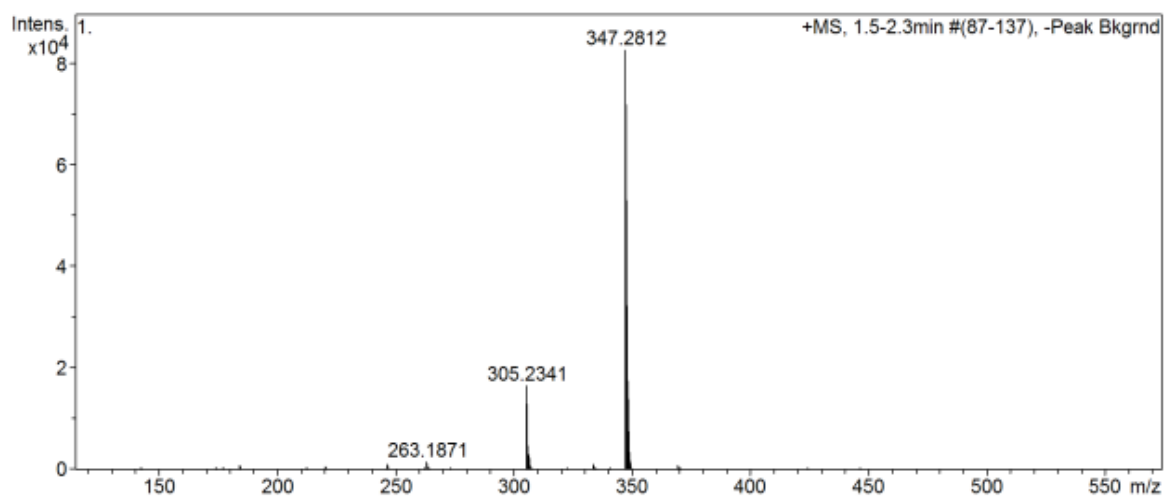
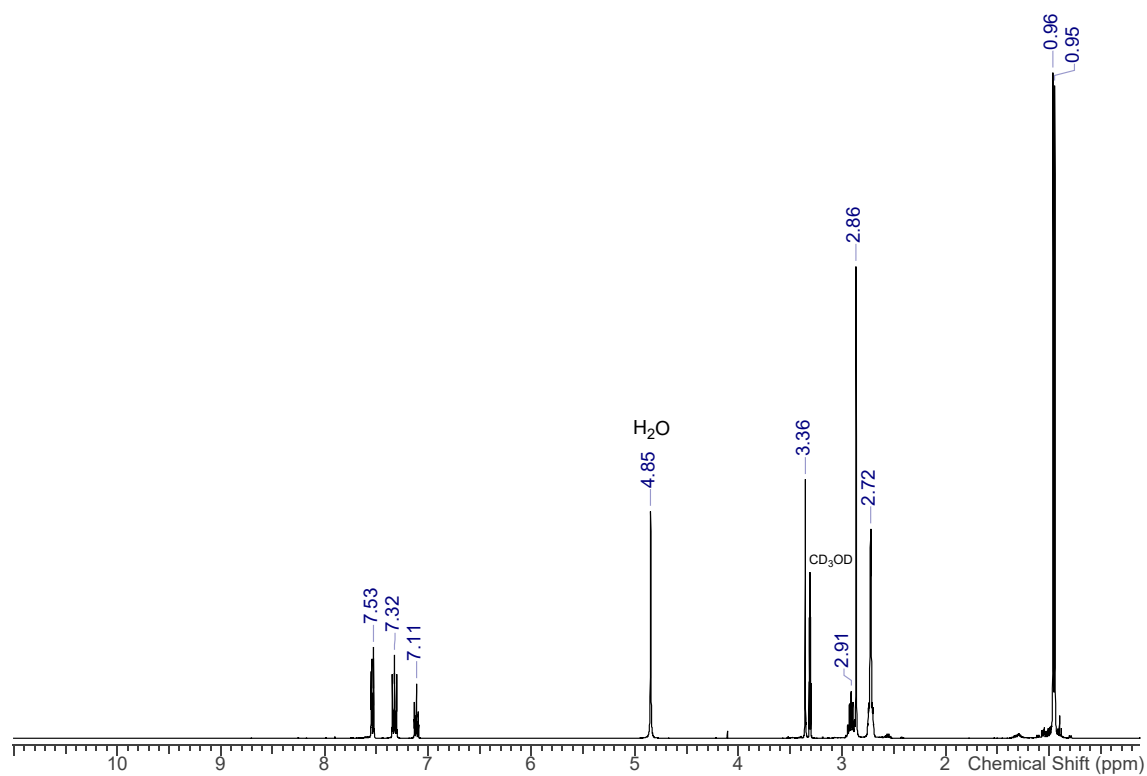
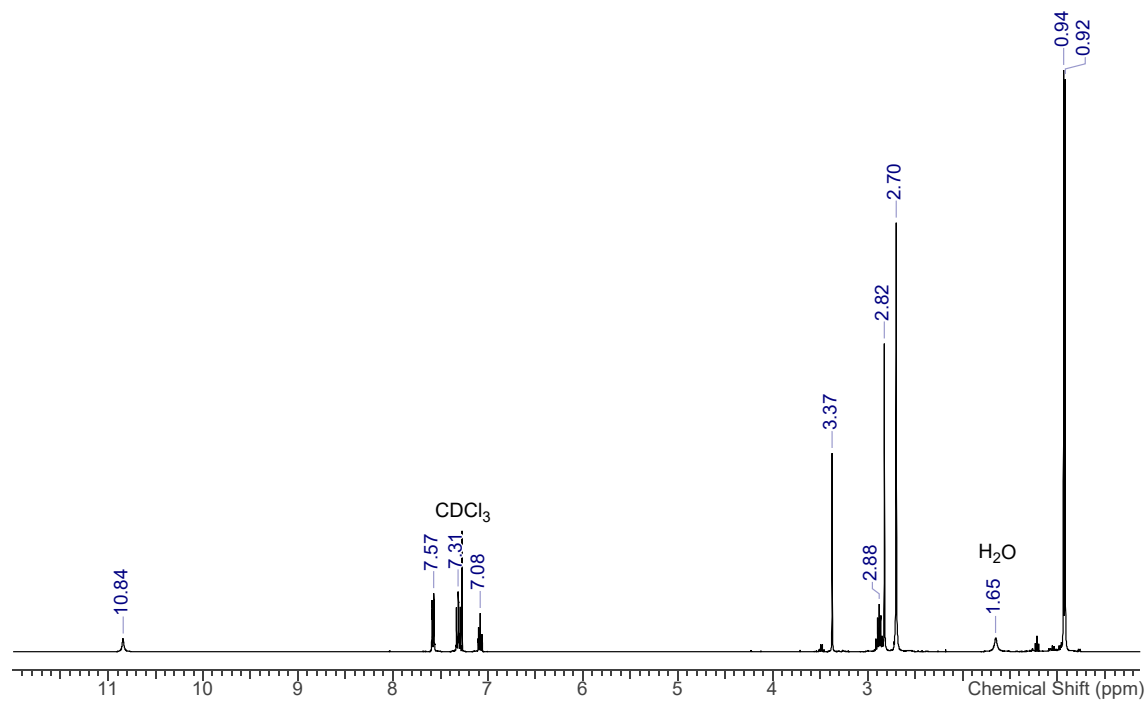


Figure S2.13 Ligand 3

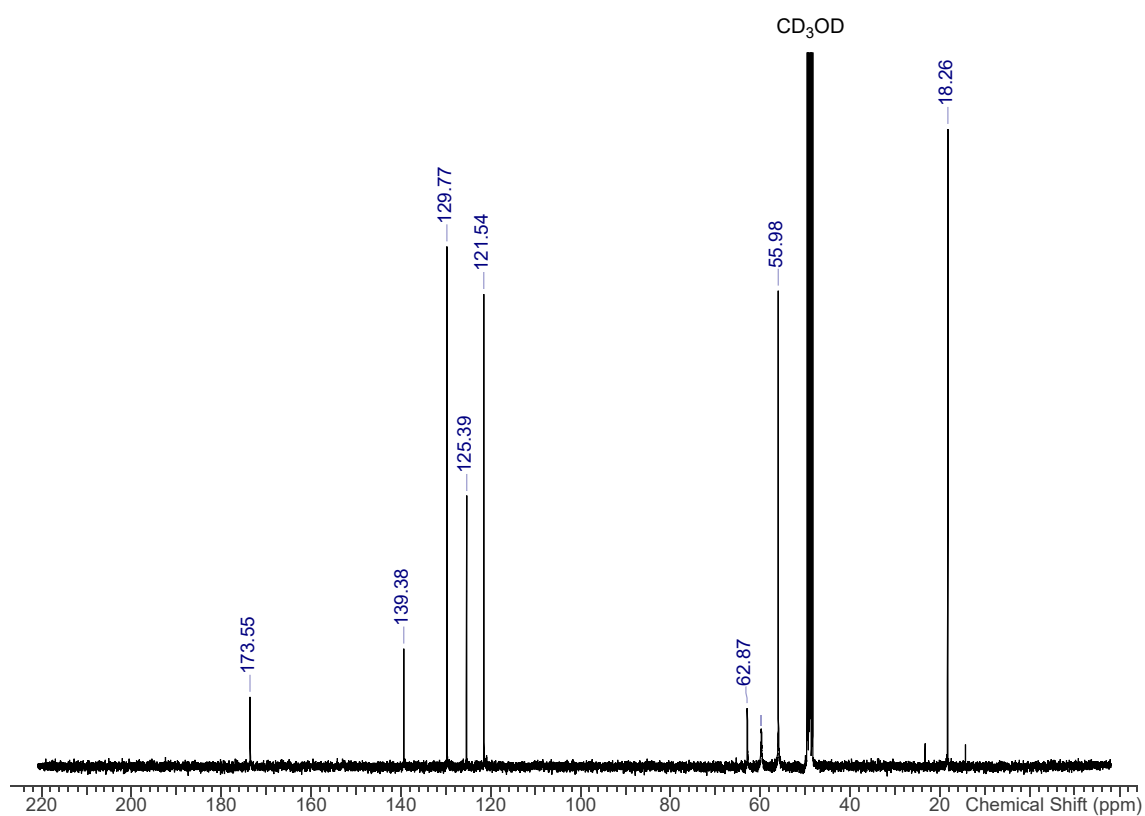
S2.13.a ^1H NMR spectrum (CD_3OD)



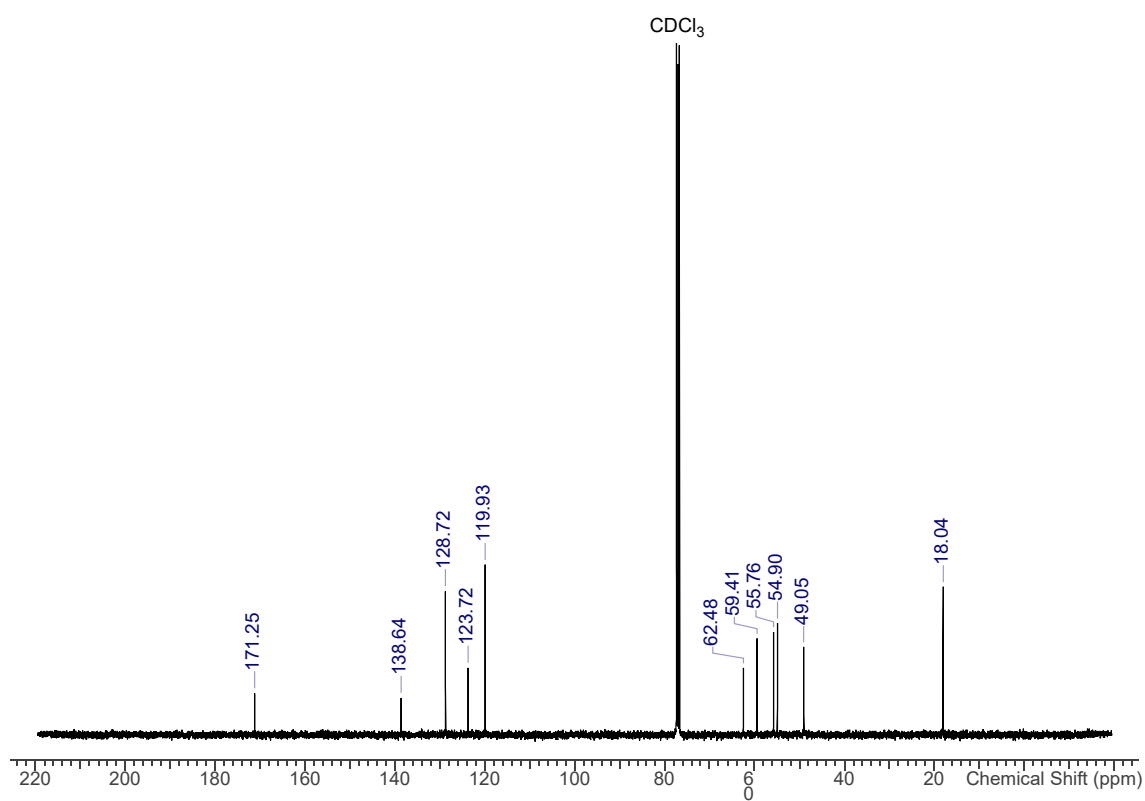
S2.13.b ^1H NMR spectrum (CDCl_3)



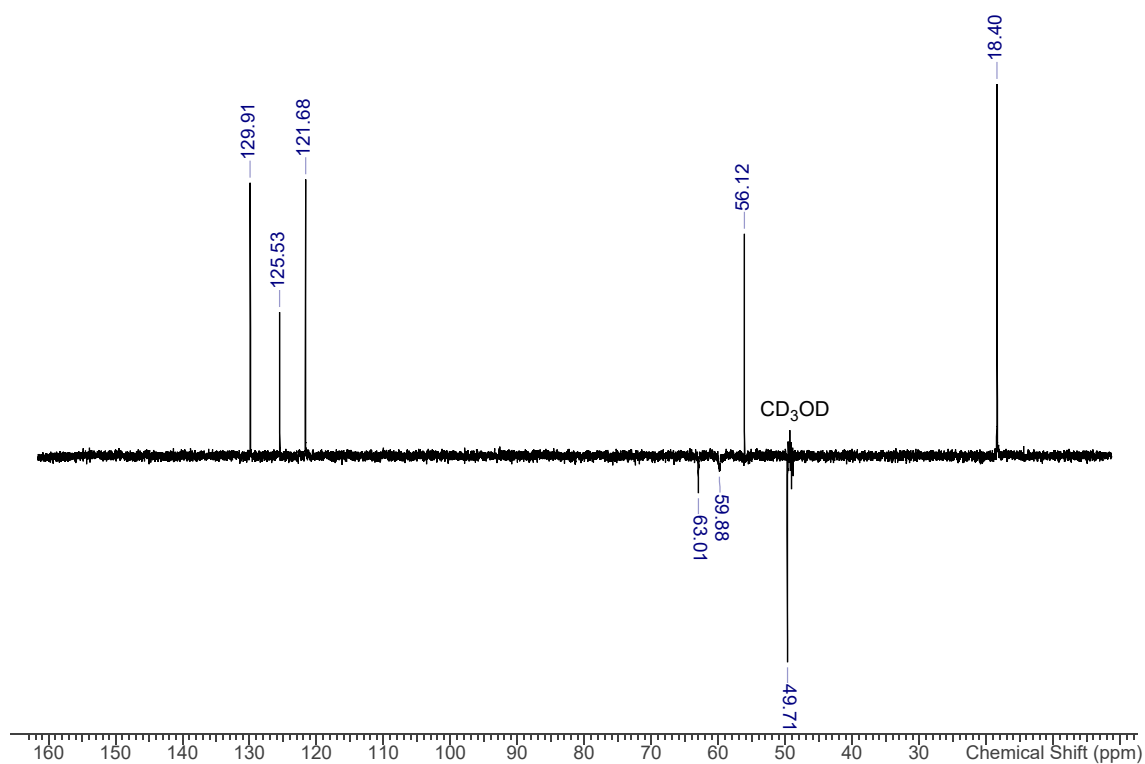
S2.13.c $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



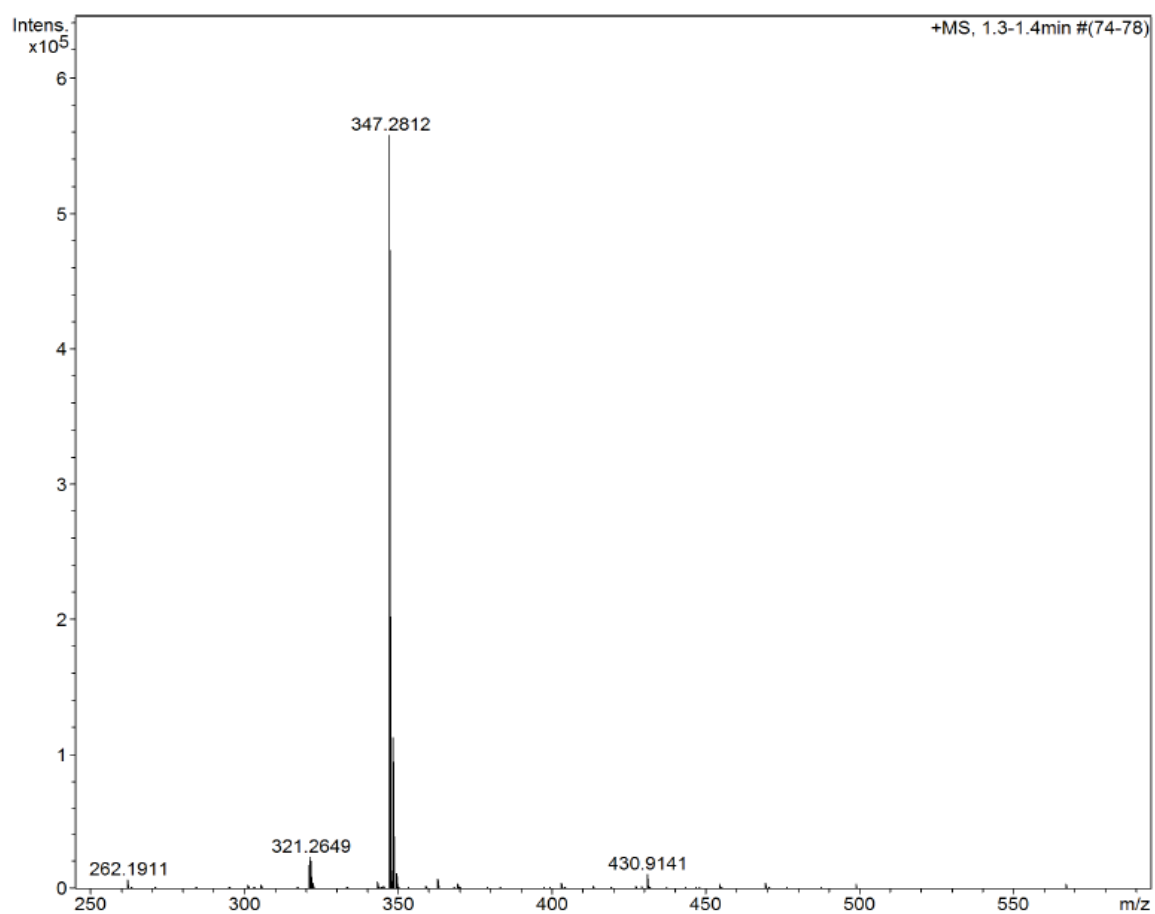
S2.13.d $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)



S2.13.e ^{13}C 135-DEPT NMR spectrum (CD_3OD)



S2.13.f HR ESI⁺ MS (MeOH)



S2.13.g IR spectrum (neat film)

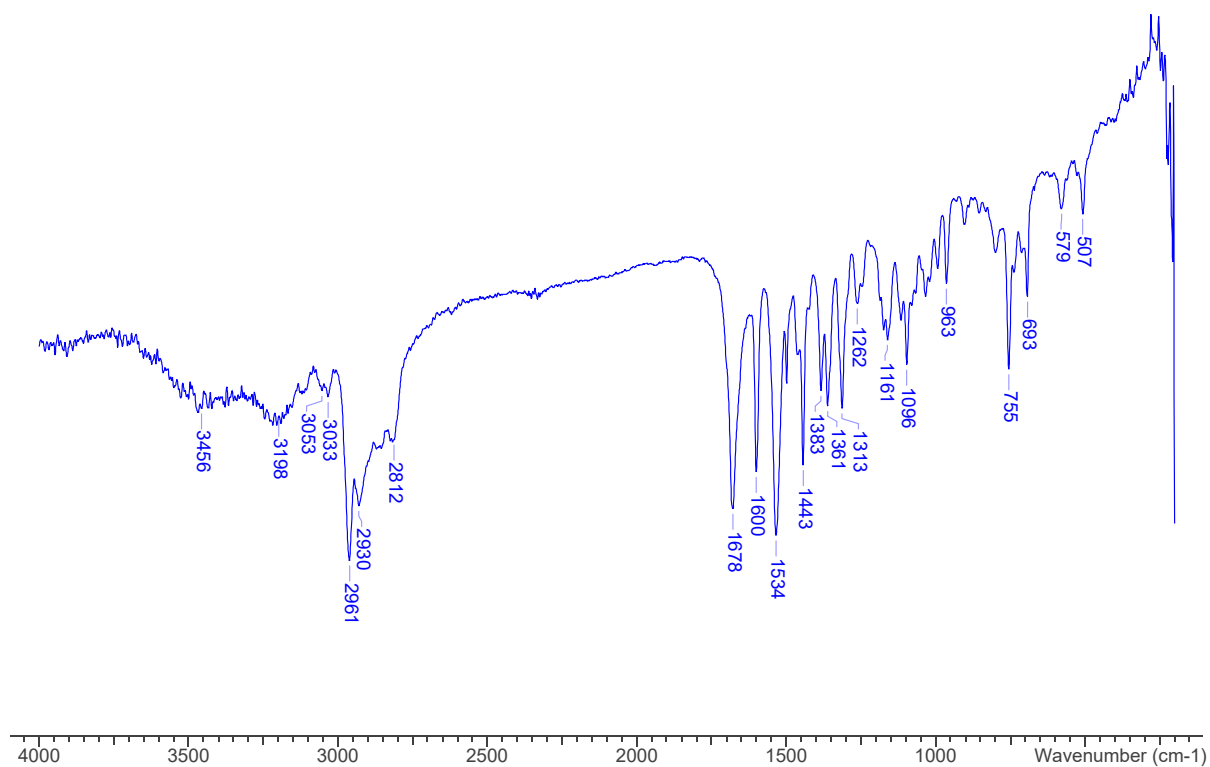
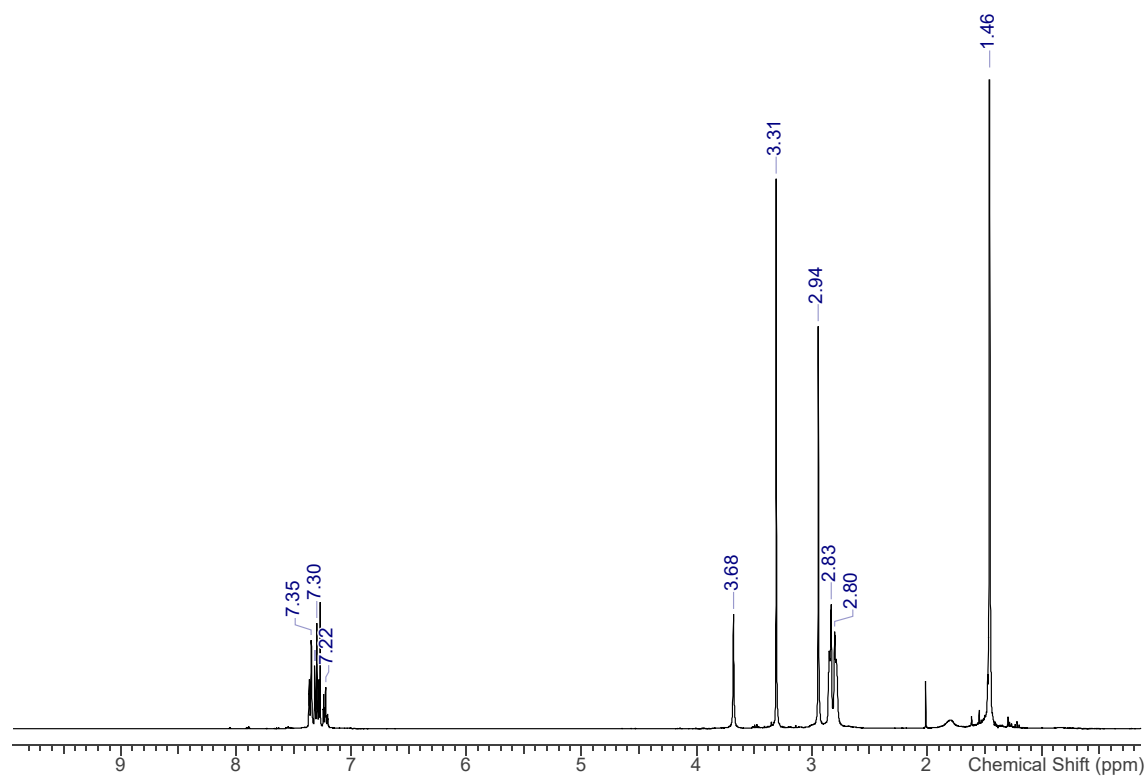


Figure S2.14 Bn-NO₂AtBu

S2.14.a ¹H NMR spectrum (CDCl₃)



S2.14.b ESI⁺ MS (MeOH)

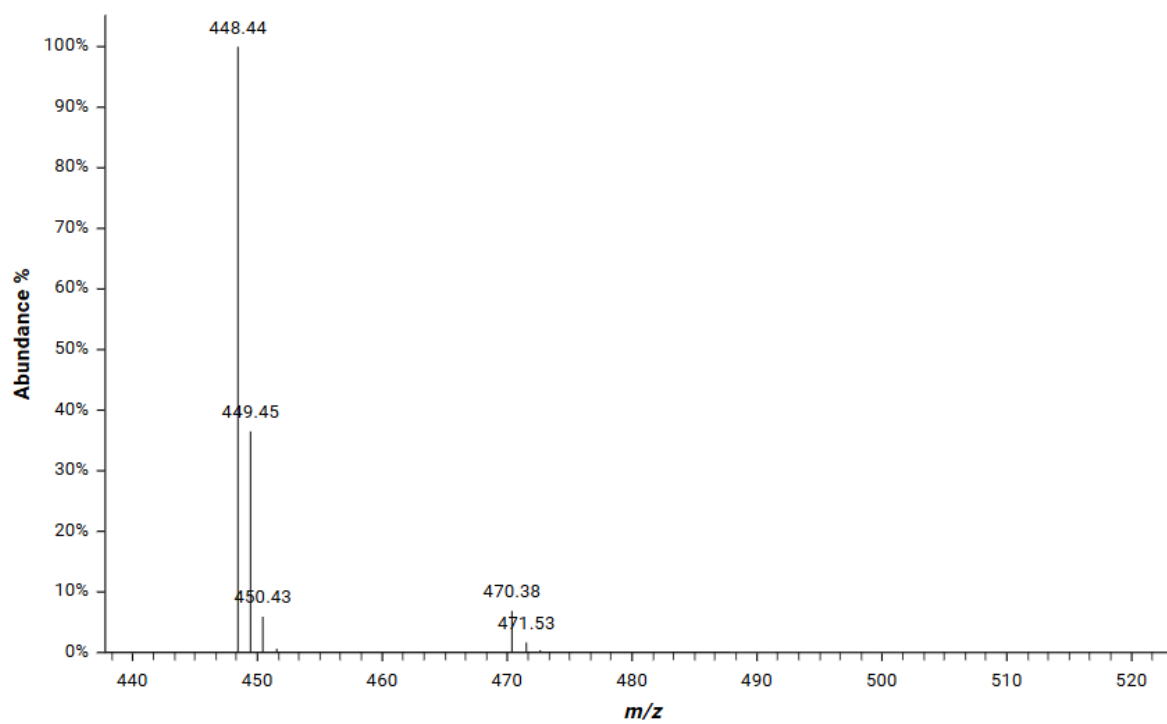
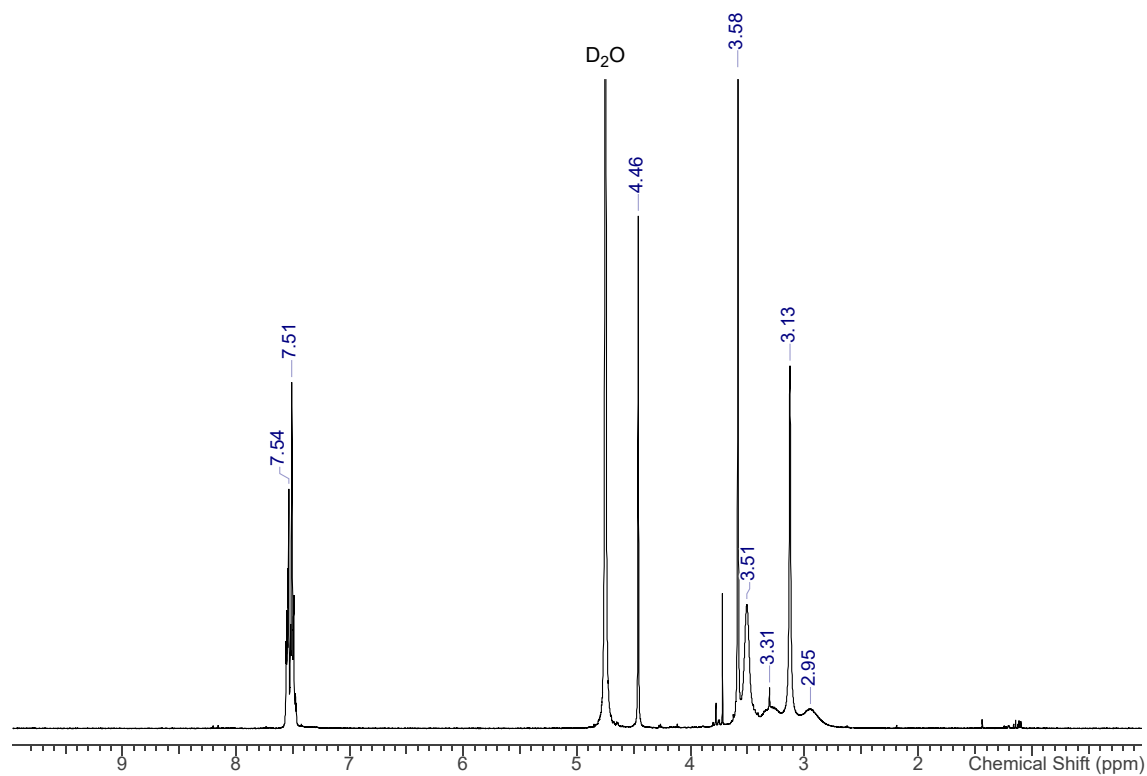
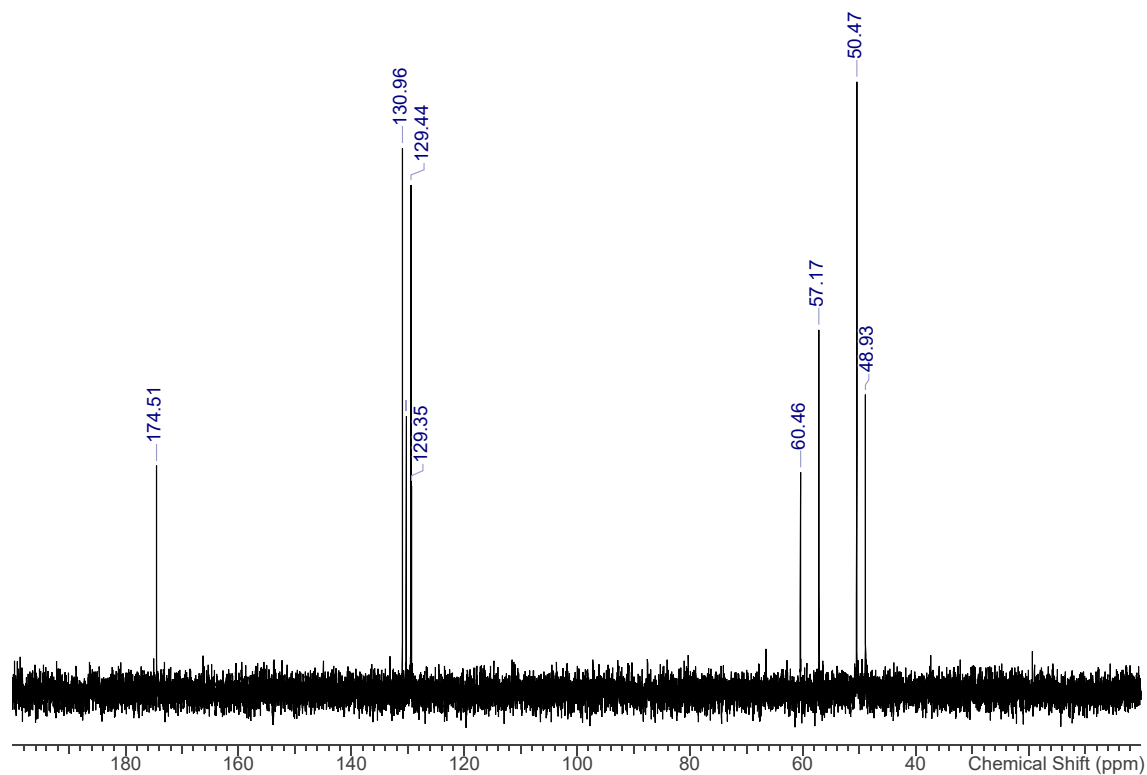


Figure S2.15 H₂-Bn-NODA

S2.15.a ¹H NMR spectrum (D₂O)



S2.15.b ¹³C{¹H} NMR spectrum (D₂O)



S2.15.c ESI⁺ MS (H₂O)

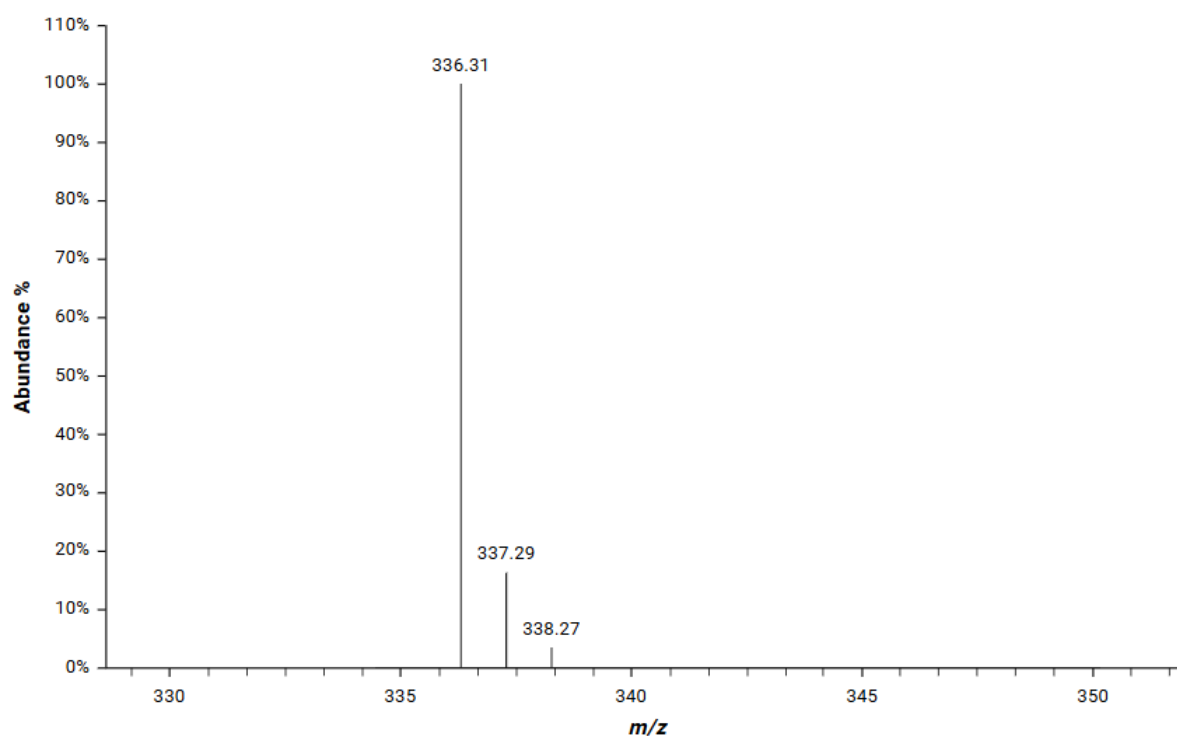
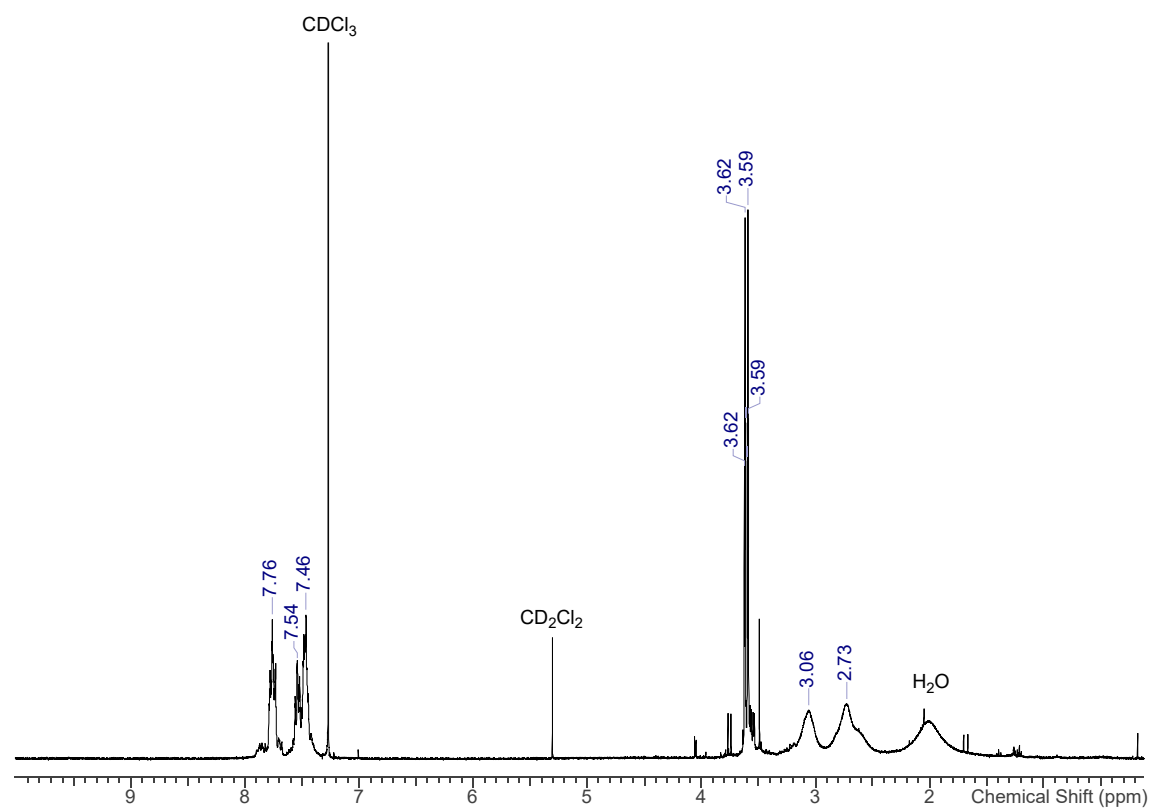
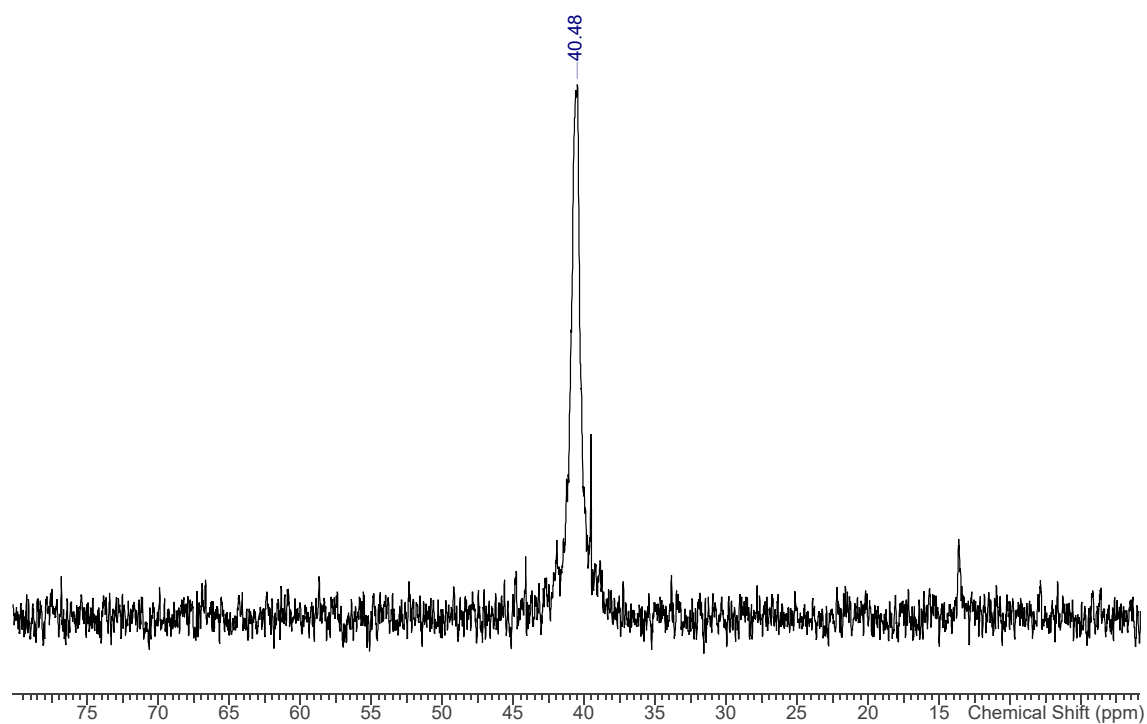


Figure S2.16 NOTP-OMe

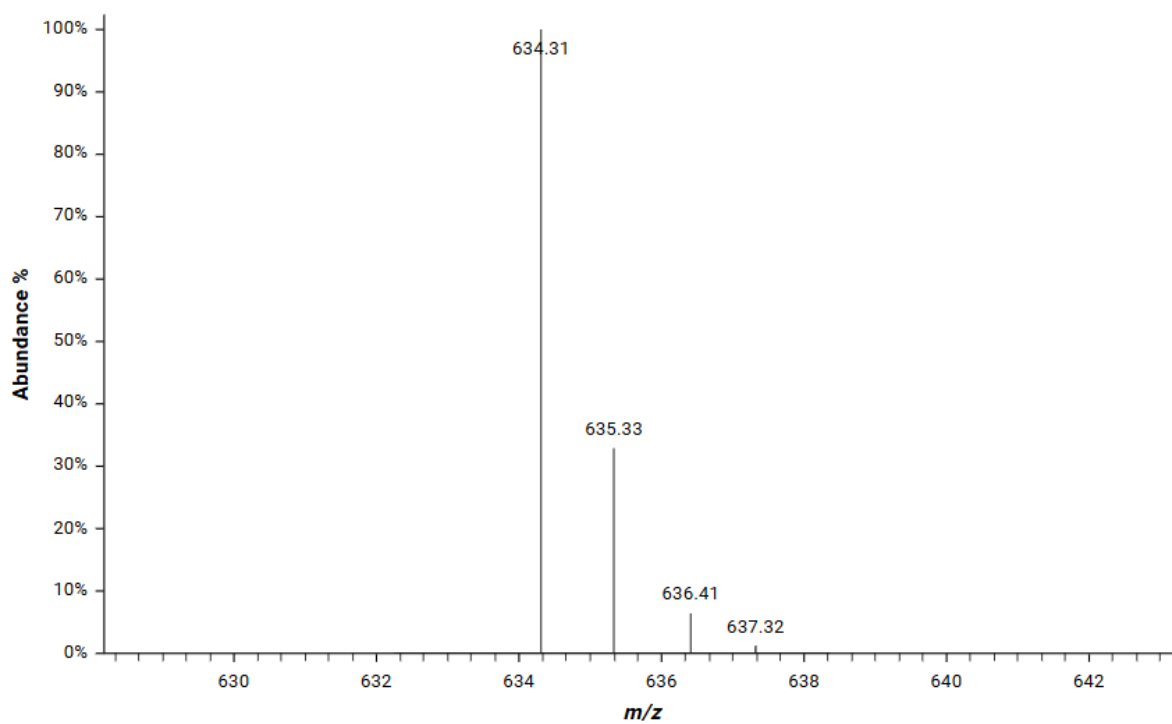
S2.16.a ¹H NMR spectrum (CDCl₃)



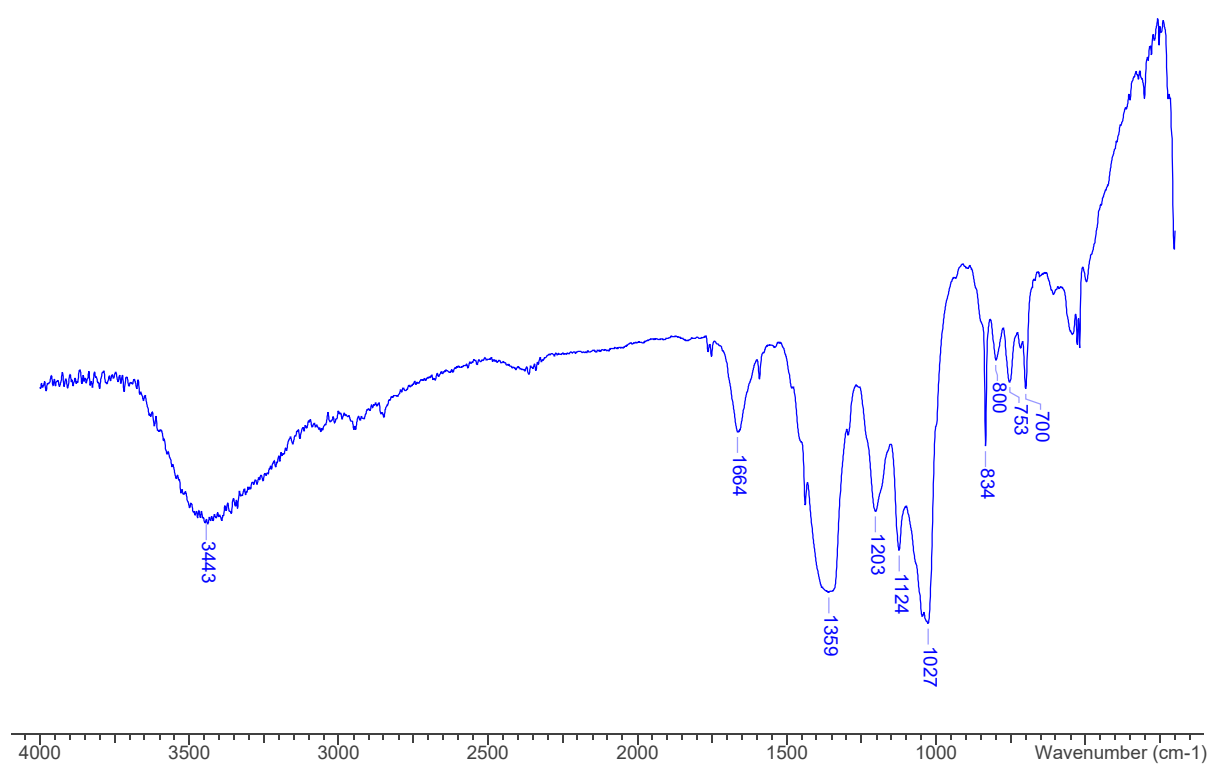
S2.16.b $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3)



S2.16.c ESI⁺ MS (MeOH)



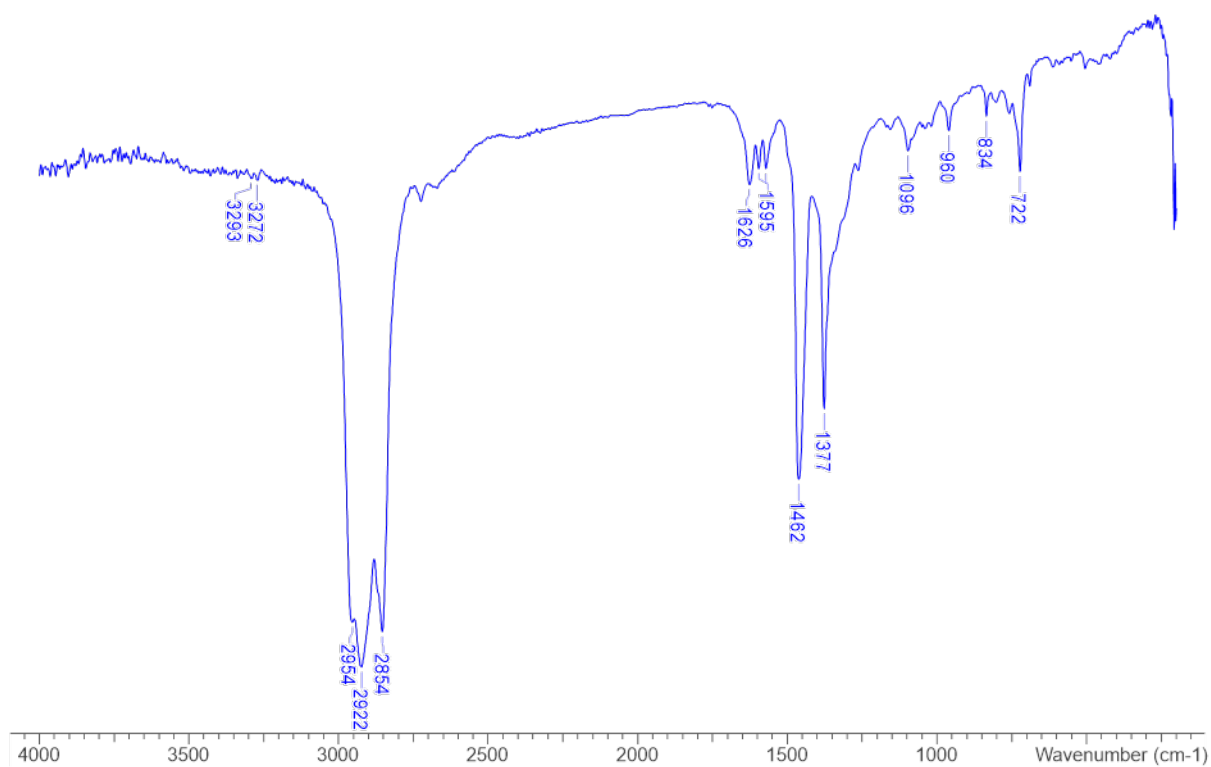
S2.16.d IR spectrum (neat film)



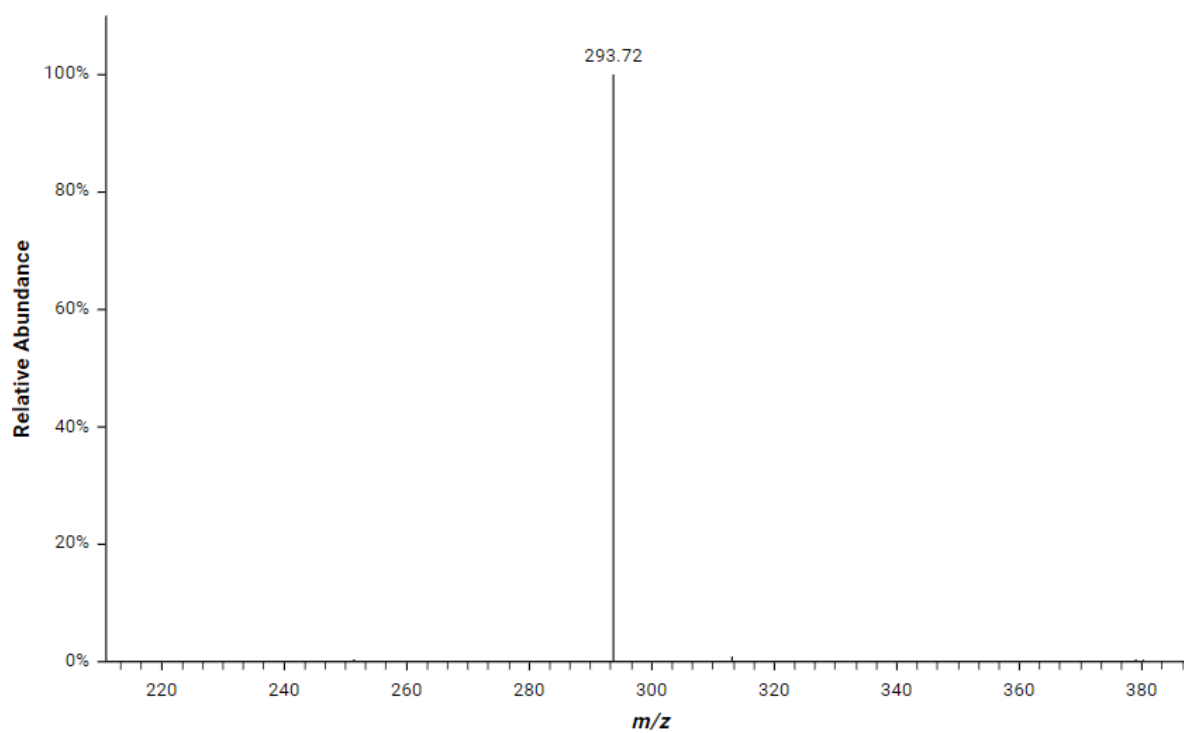
Chapter 3

Figure S3.1 [Co(L¹)]([NO₃])_n

S3.1.a IR spectrum (Nujol)



S3.1.b ESI⁺ MS (MeOH)



S3.1.c UV-Vis spectrum (MeOH)

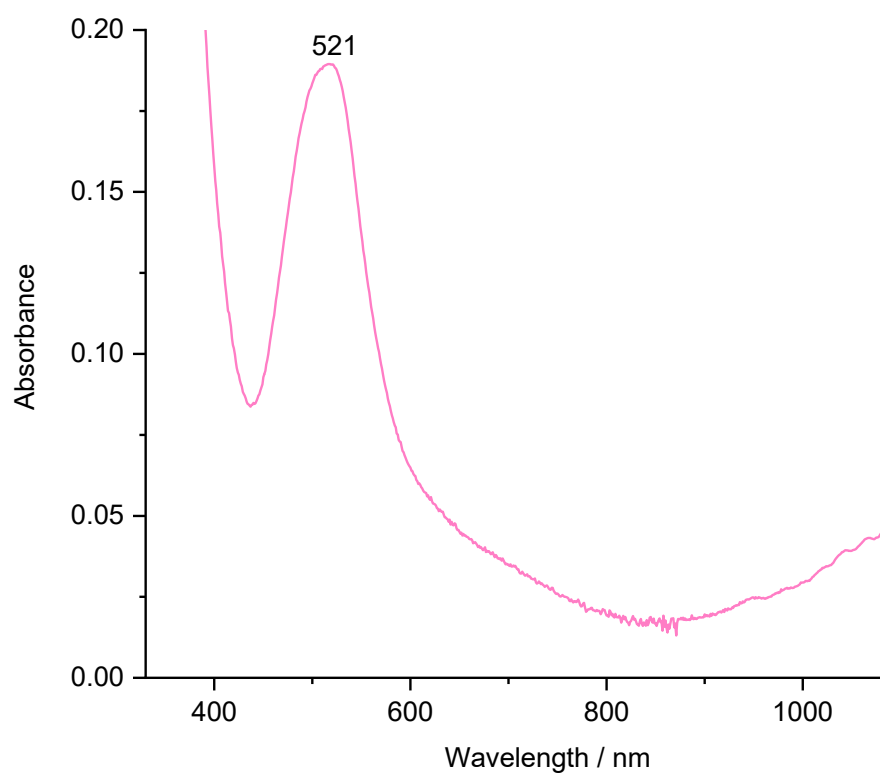
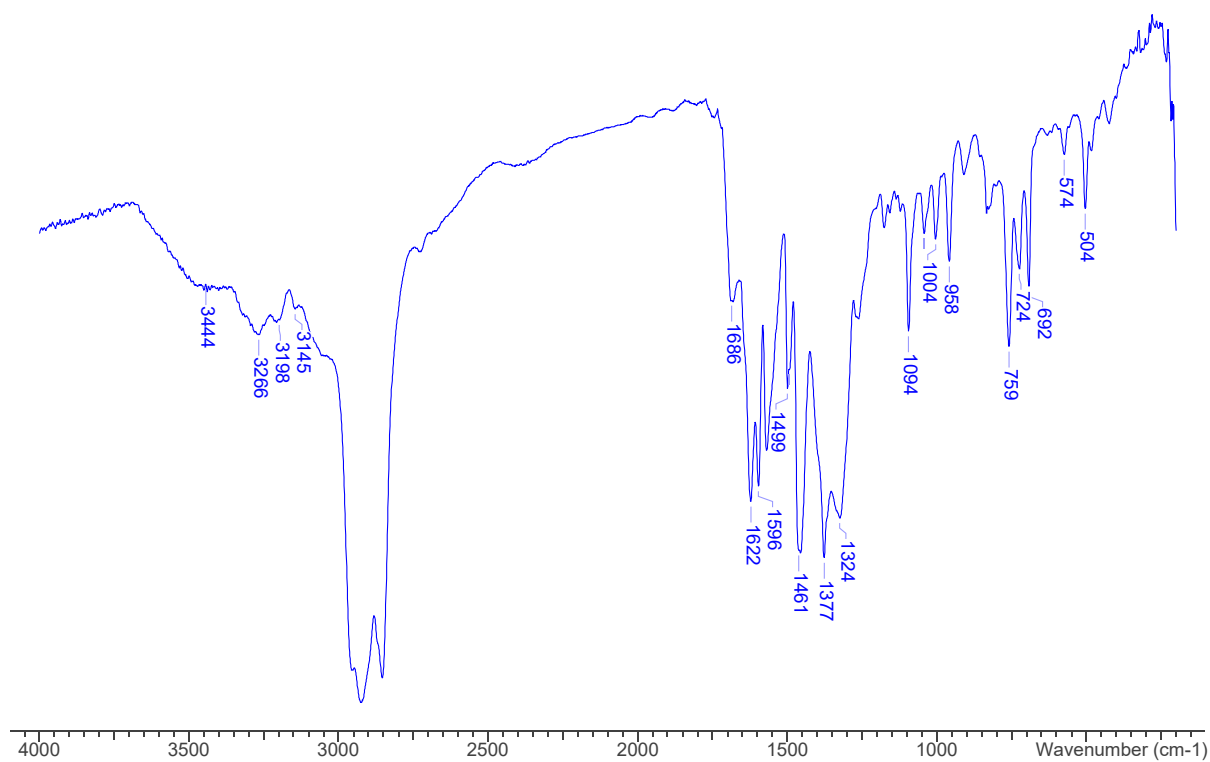
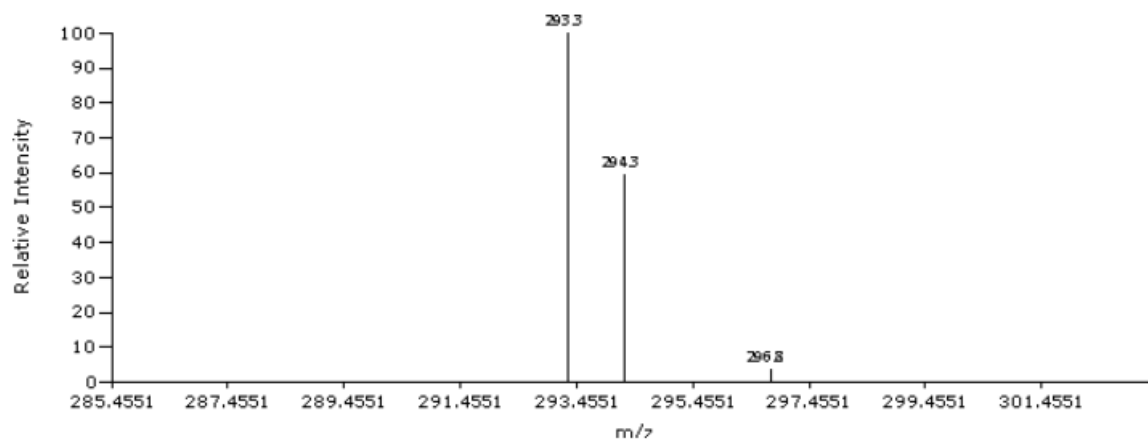


Figure S3.2 [Ni(L¹)](NO₃)₂

S3.2.a IR spectrum (Nujol)



S3.2.b ESI⁺ MS (MeOH)



S3.2.c UV-Vis spectrum (MeOH)

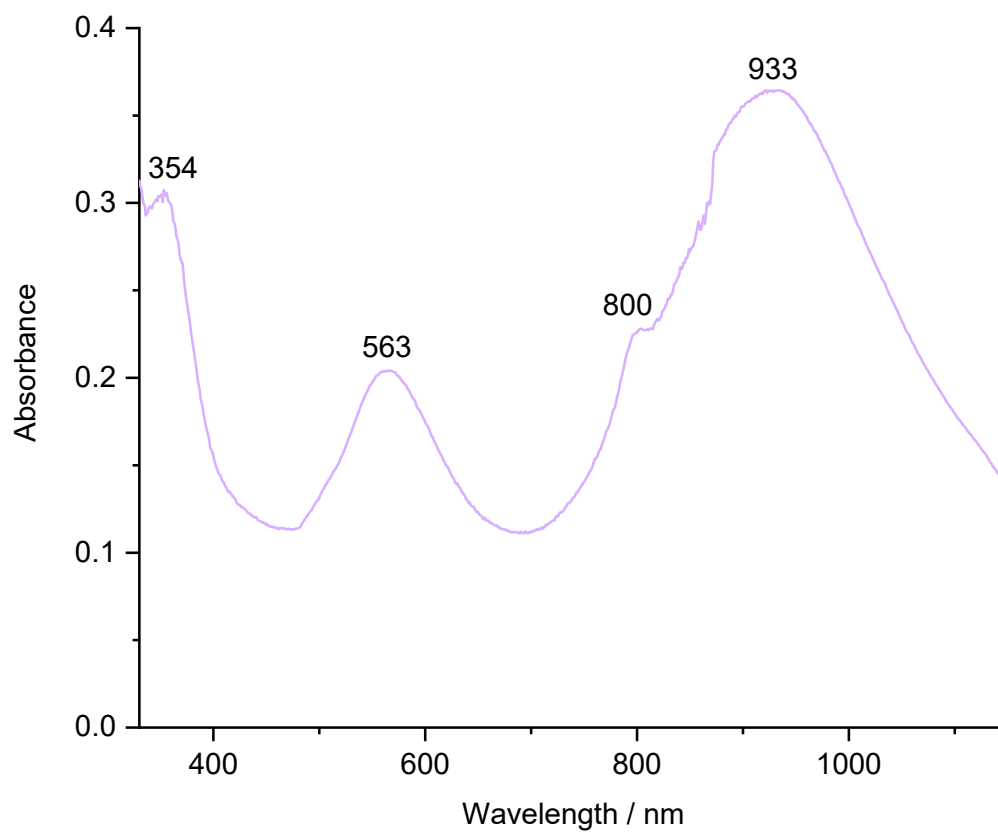
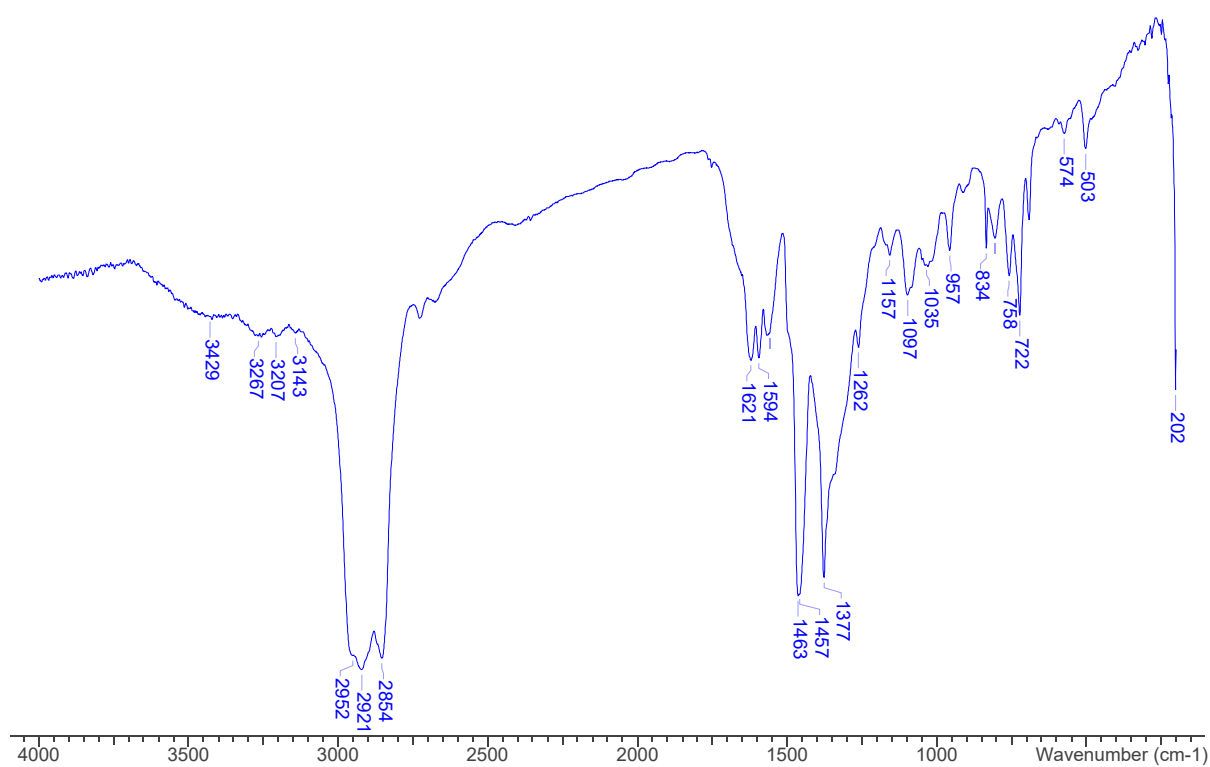
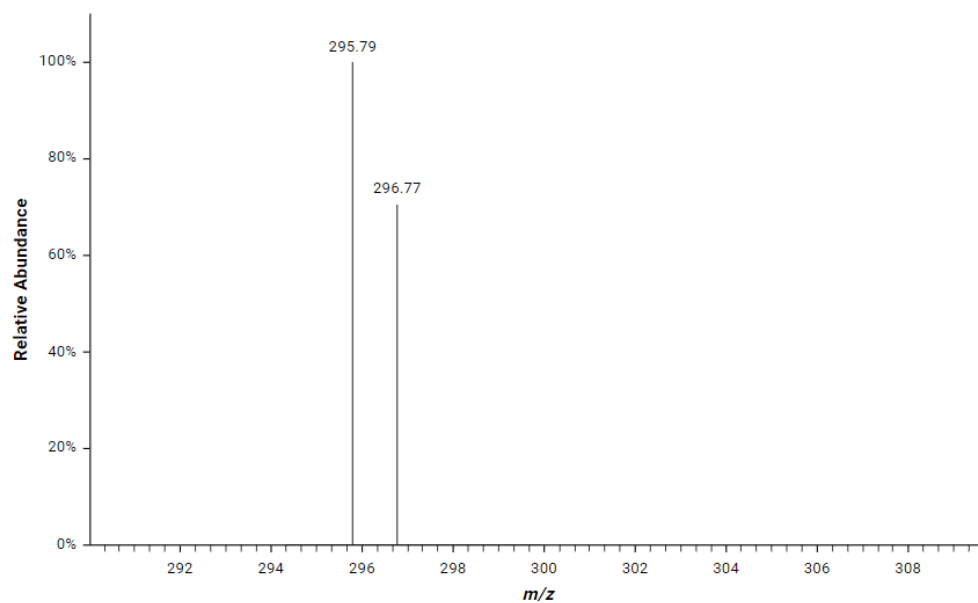


Figure S3.3 $[\text{Cu}(\text{L}^1)](\text{NO}_3)_2$

S3.3.a IR spectrum (Nujol)



S3.3.b ESI⁺ MS (MeOH)



S3.3.c UV-Vis spectrum (MeOH)

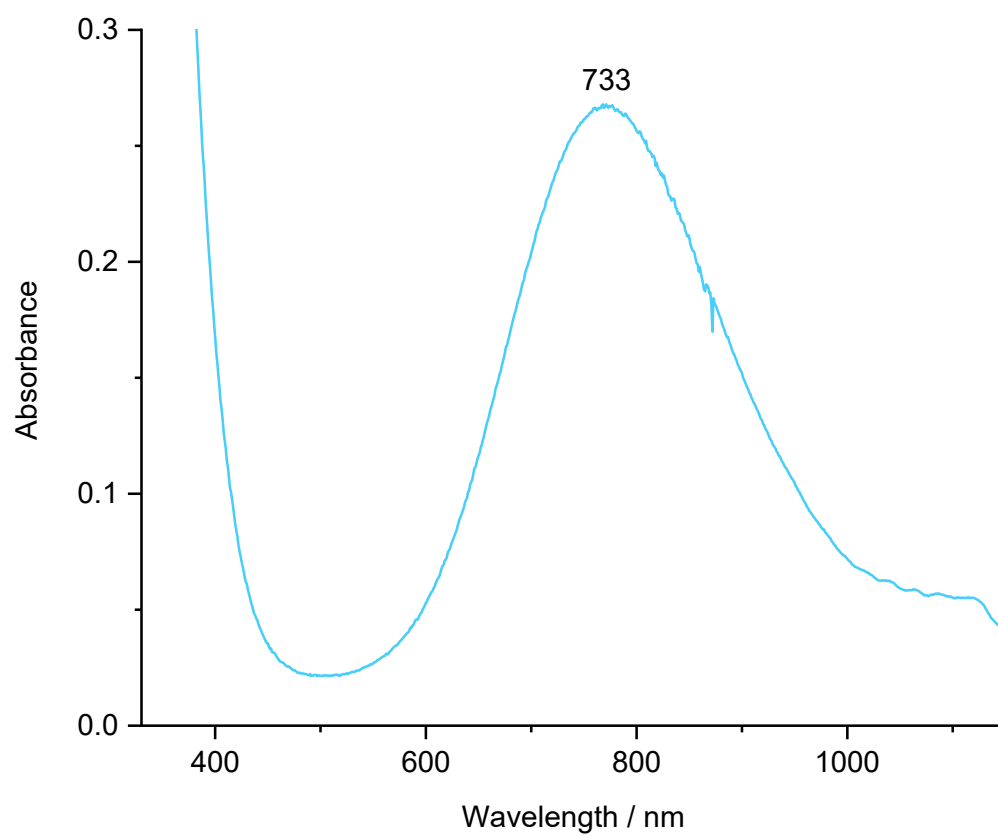
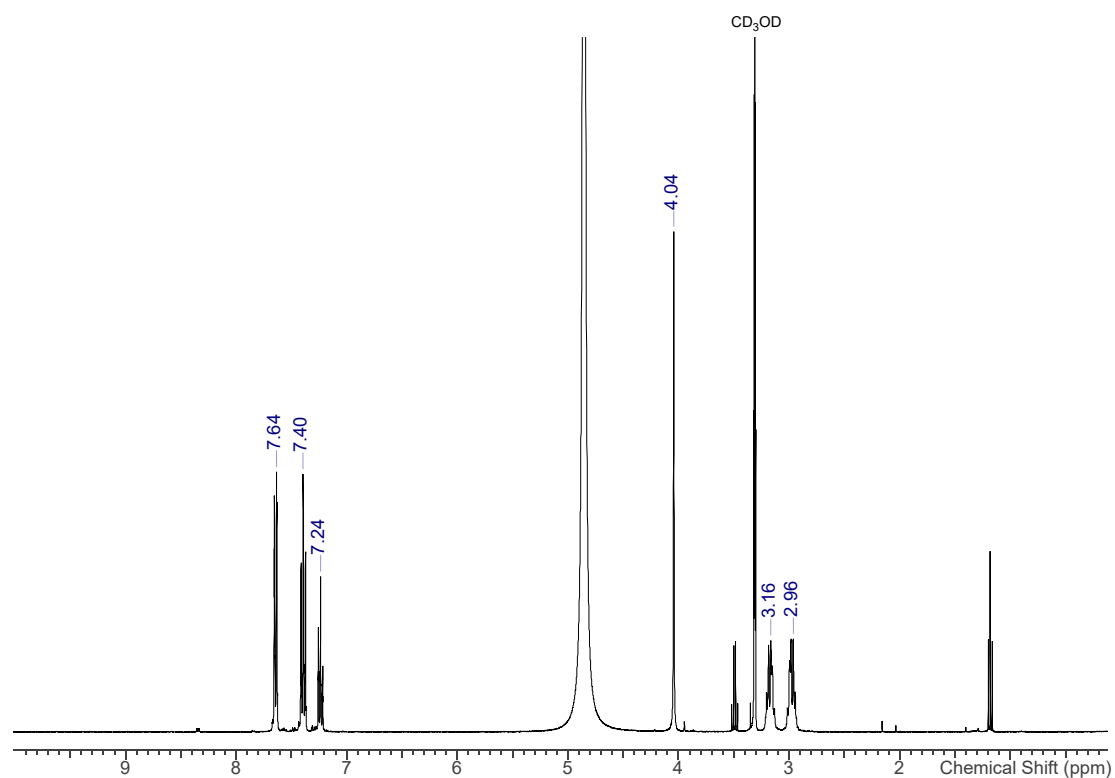
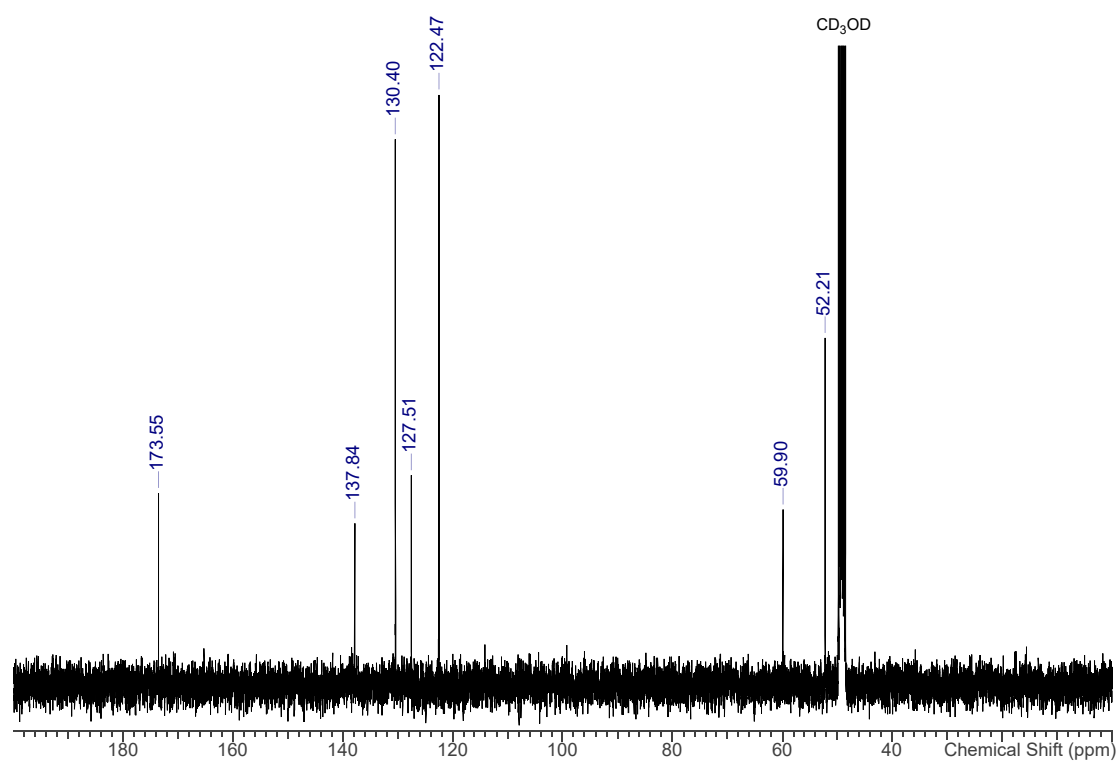


Figure S3.4 [Zn(L¹)] [NO₃]₂

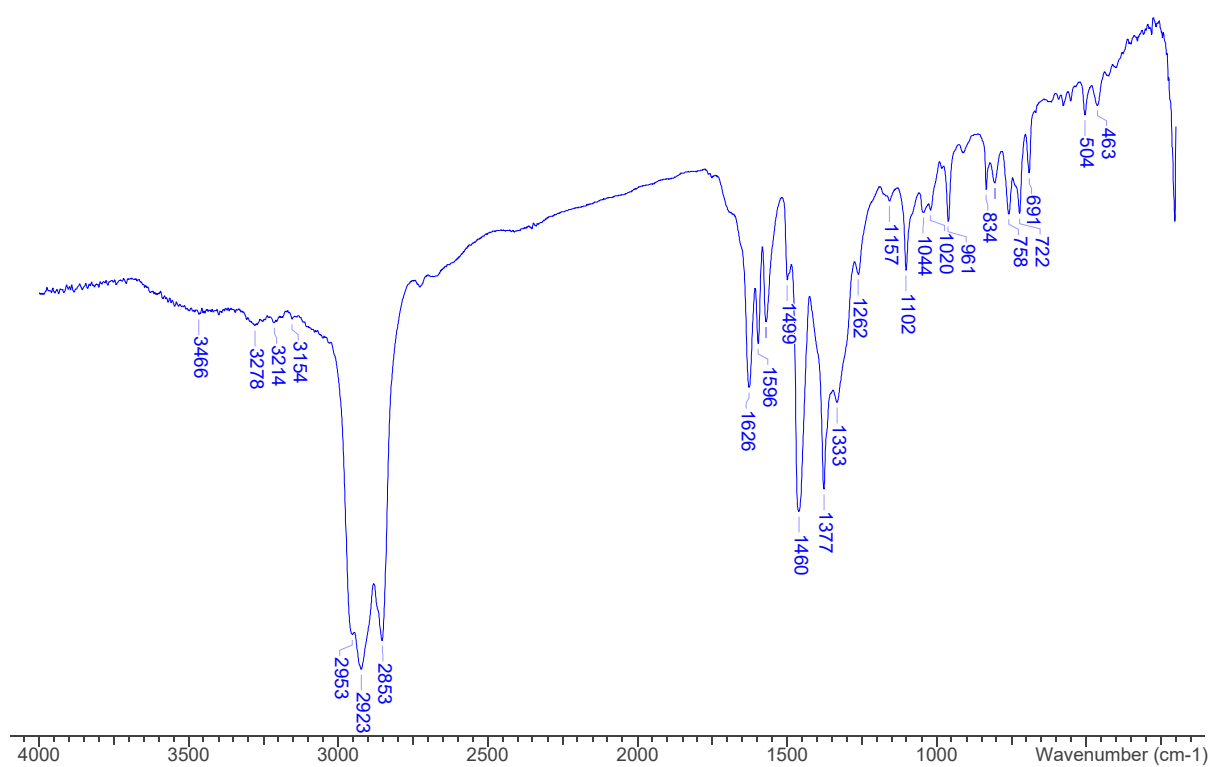
S3.4.a ¹H NMR spectrum (CD₃OD)



S3.4.b ¹³C{¹H} NMR spectrum (CD₃OD)



S3.4.c IR spectrum (Nujol)



S3.4.d ESI⁺ MS (MeOH)

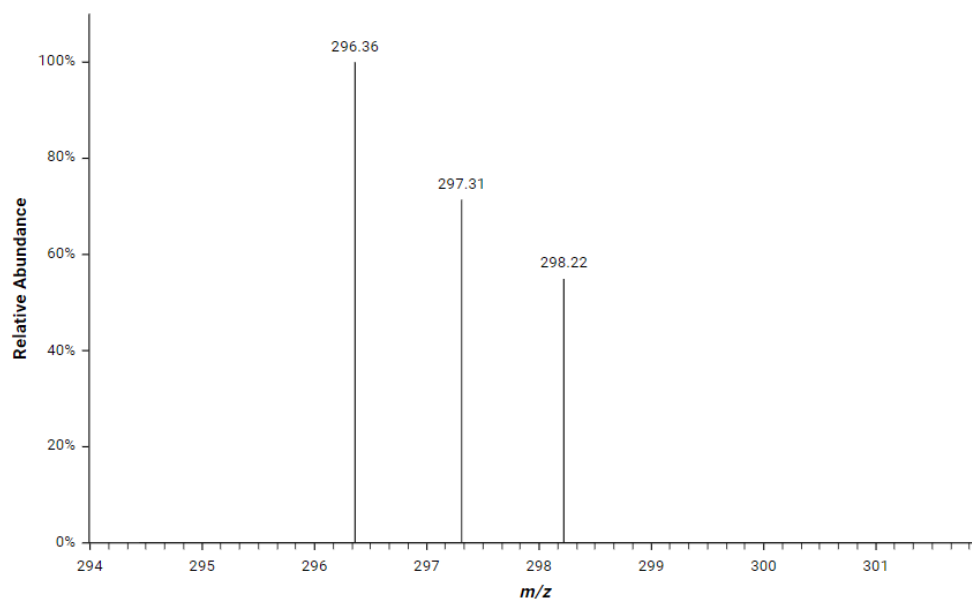
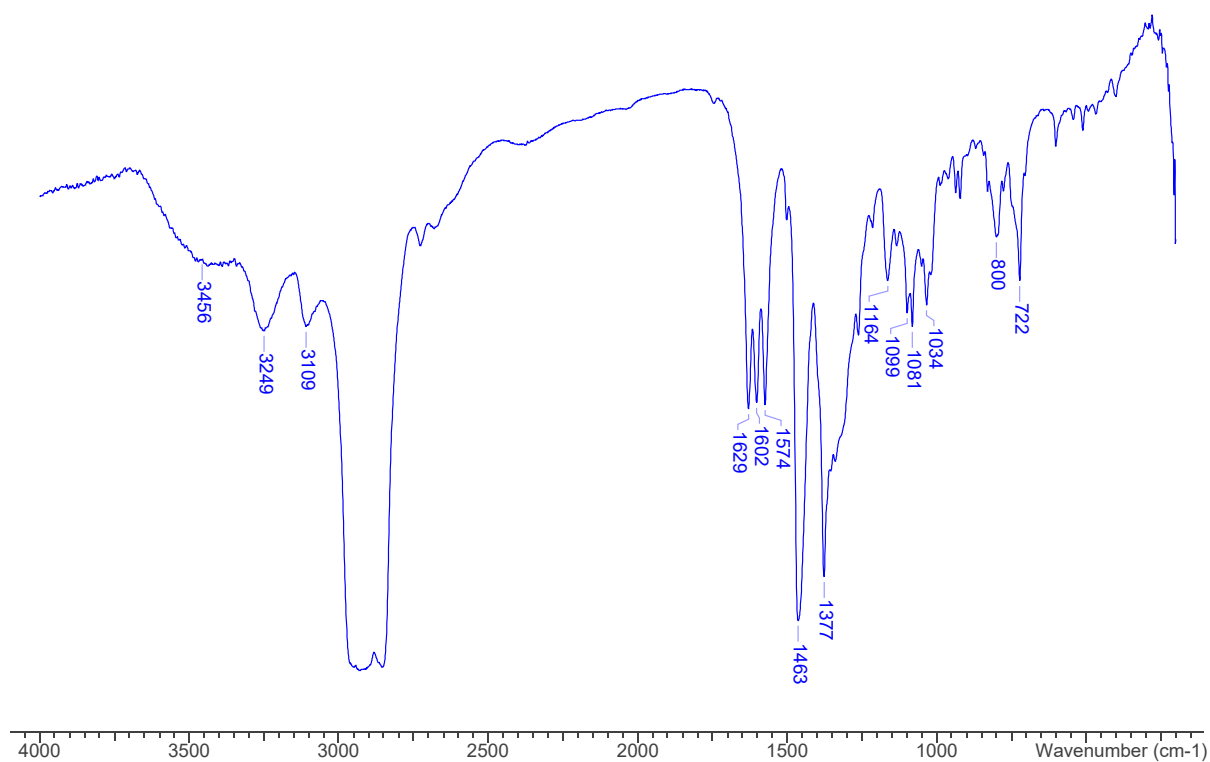
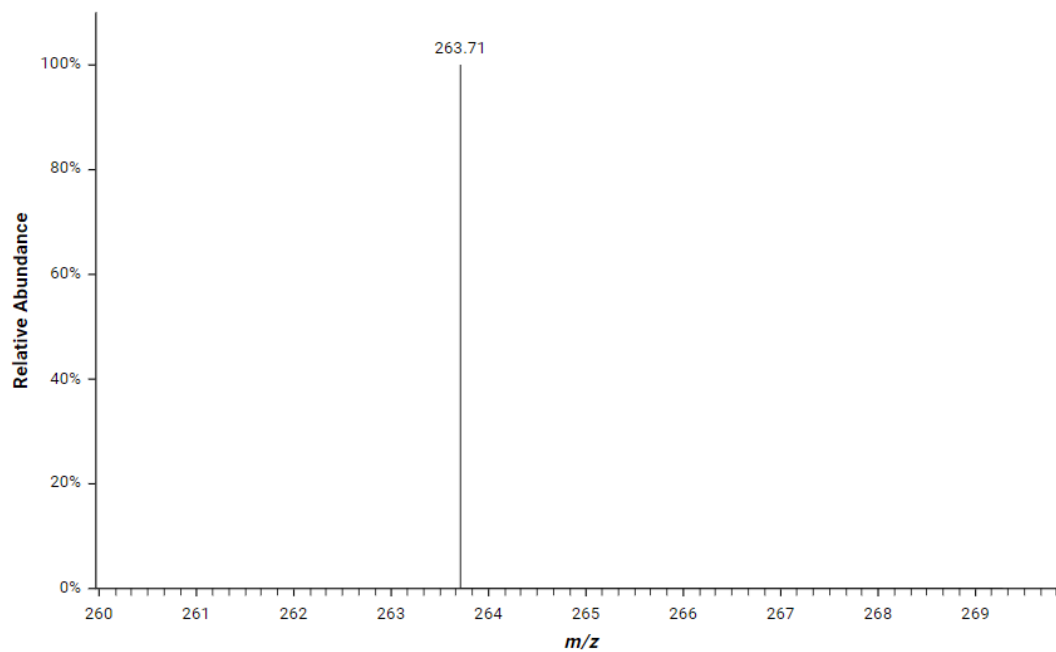


Figure S3.5 [Co(L²)]([NO₃)_n

S3.5.a IR spectrum (Nujol)



S3.5.b ESI⁺ MS (MeOH)



S3.5.c UV-Vis spectrum (MeOH)

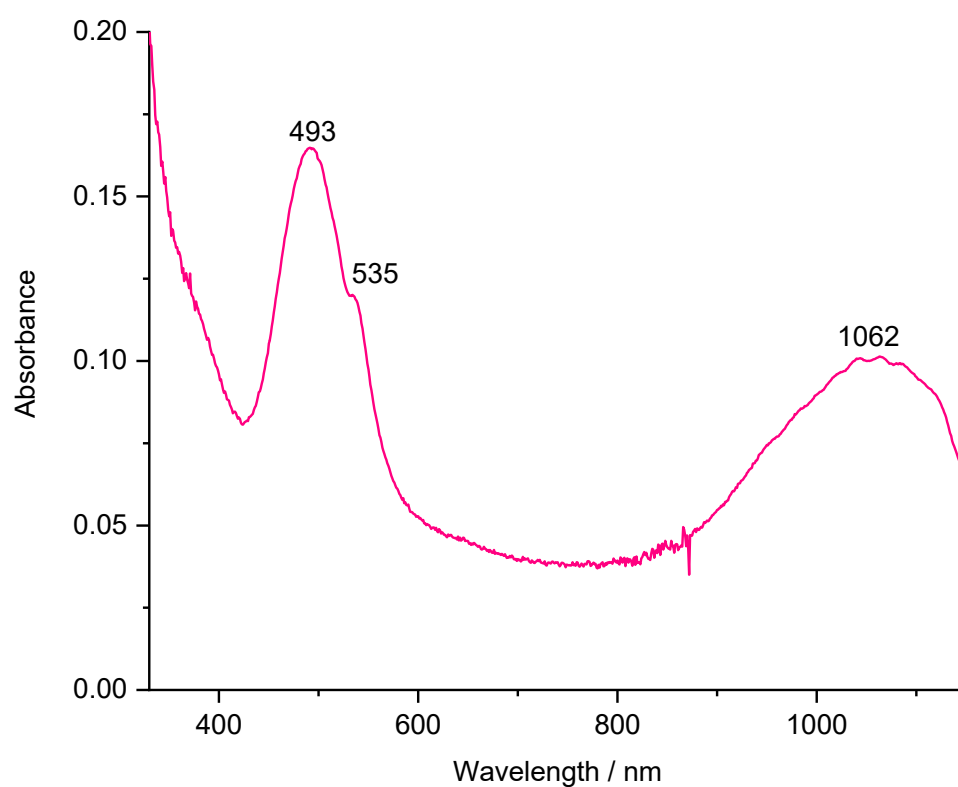
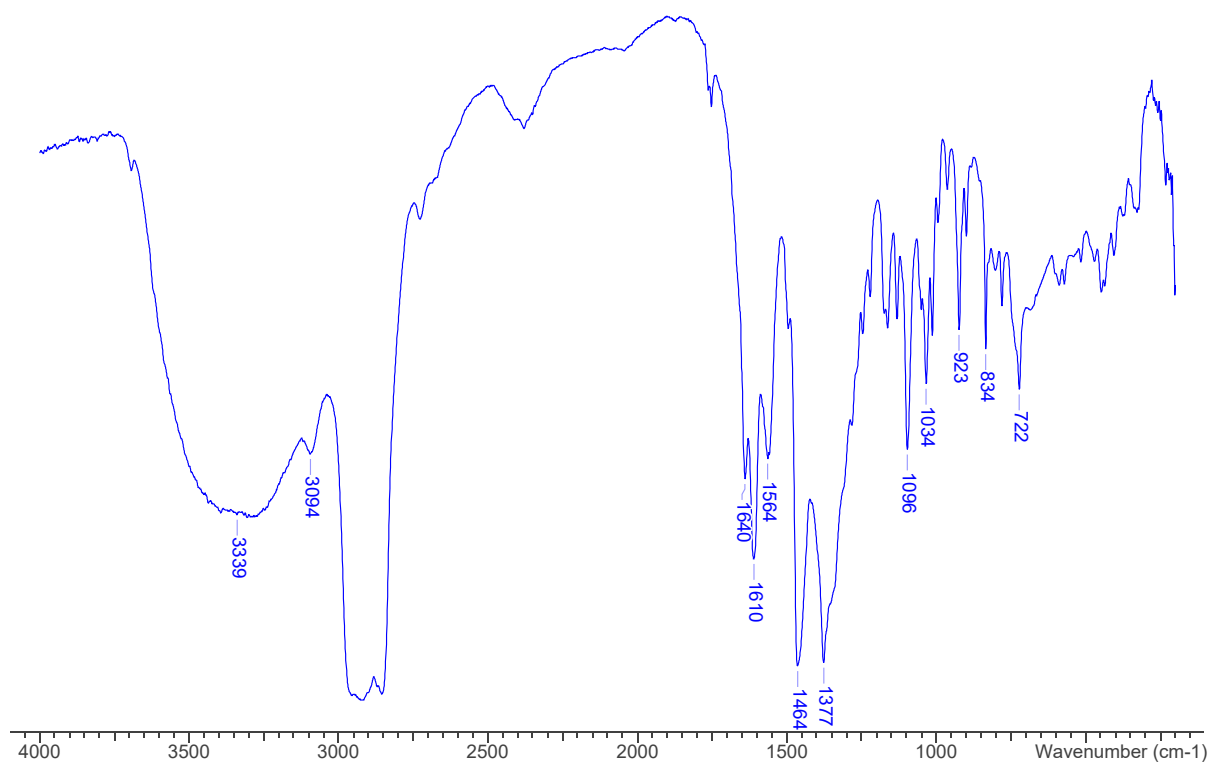
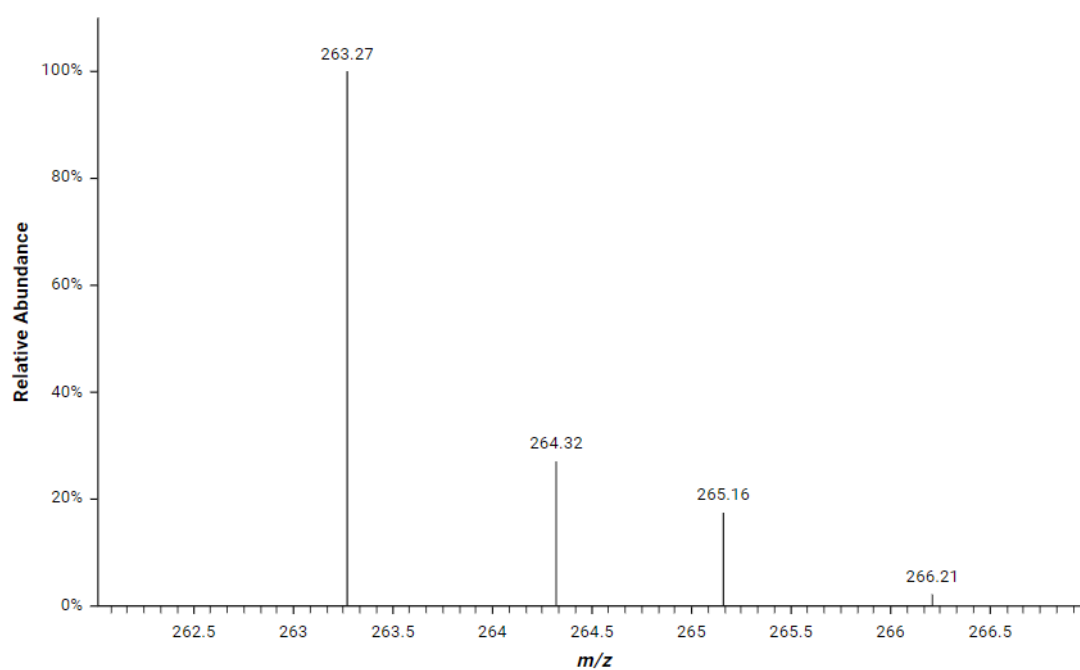


Figure S3.6 $[\text{Ni}(\text{L}^2)][\text{NO}_3]_2$

S3.6.a IR spectrum (Nujol)



S3.6.b ESI⁺ MS (MeOH)



S3.6.c UV-Vis spectrum (MeOH)

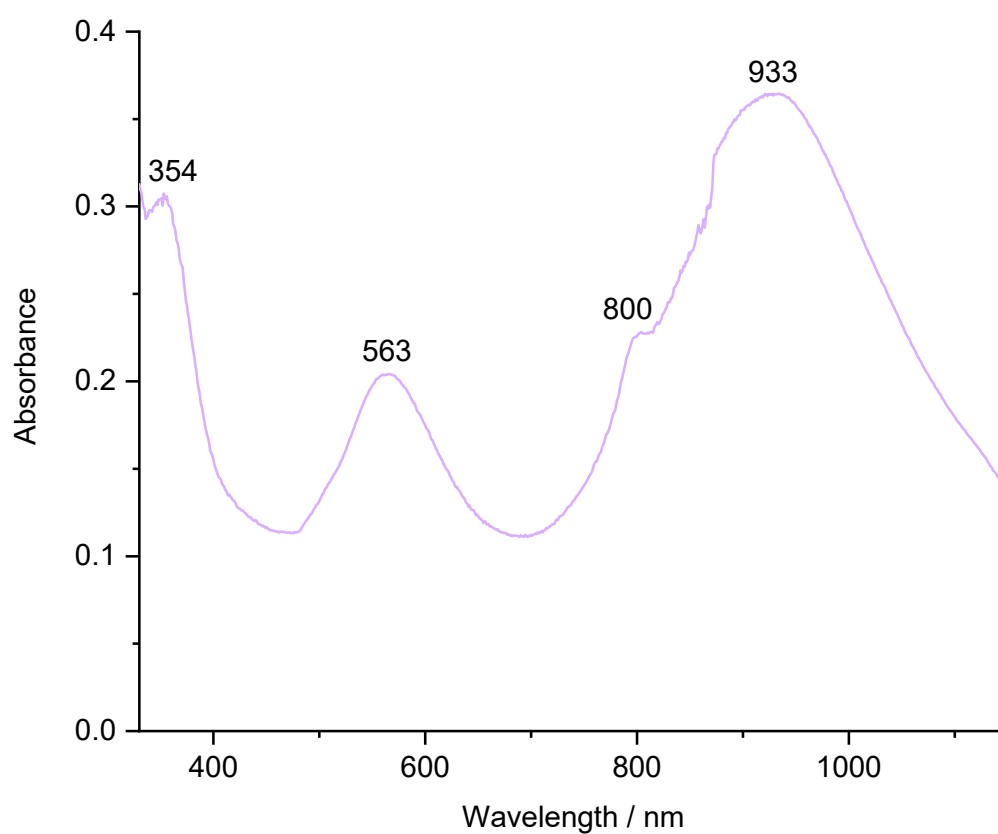
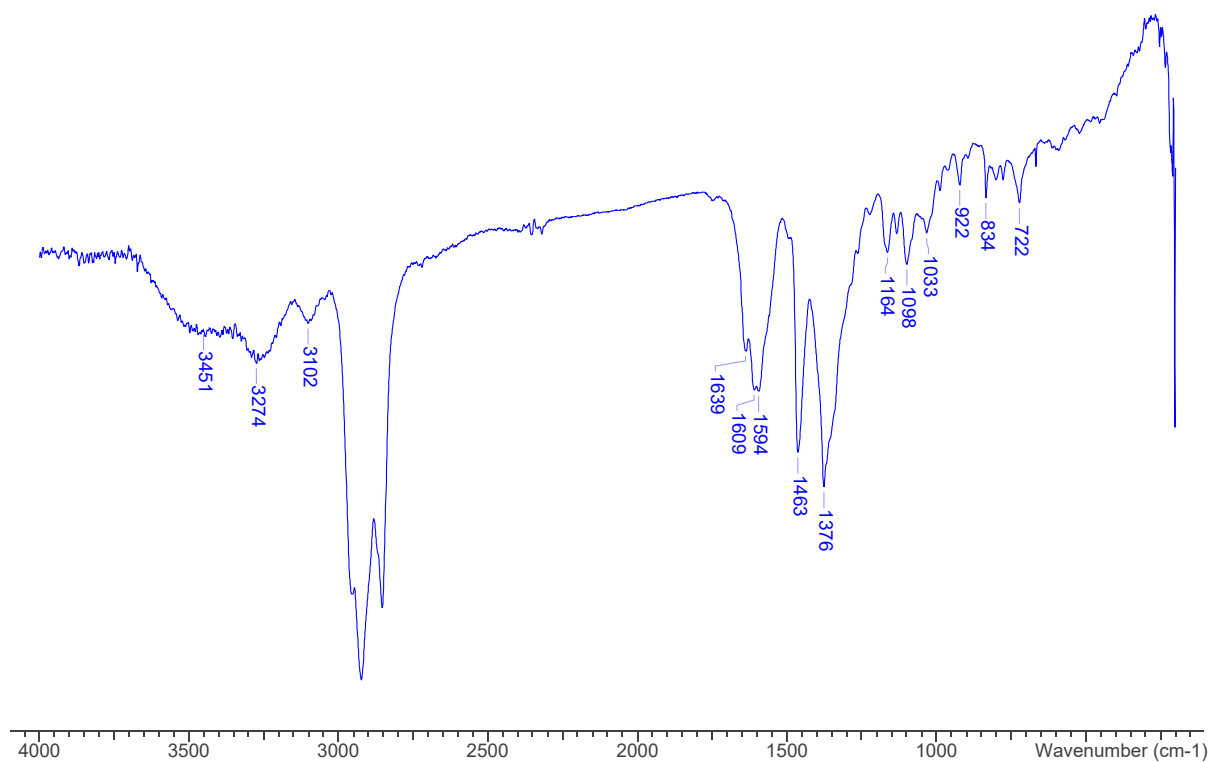
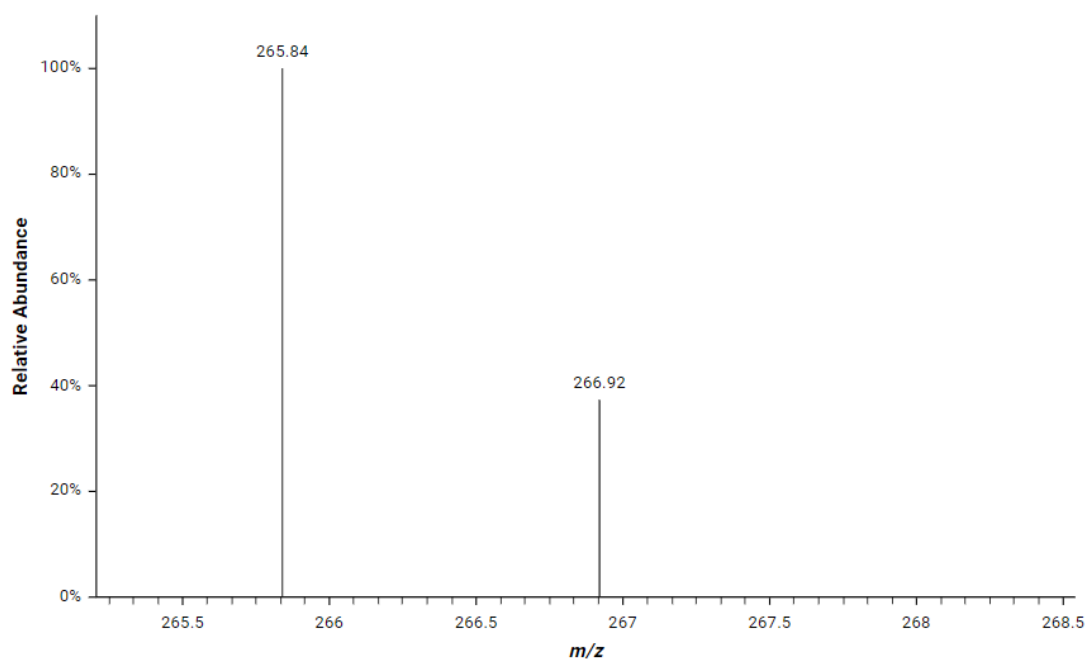


Figure S3.7 $[\text{Cu}(\text{L}^2)]([\text{NO}_3])_2$

S3.7.a IR spectrum (Nujol)



S3.7.b ESI^+ MS (MeOH)



S3.7.c UV-Vis spectrum (MeOH)

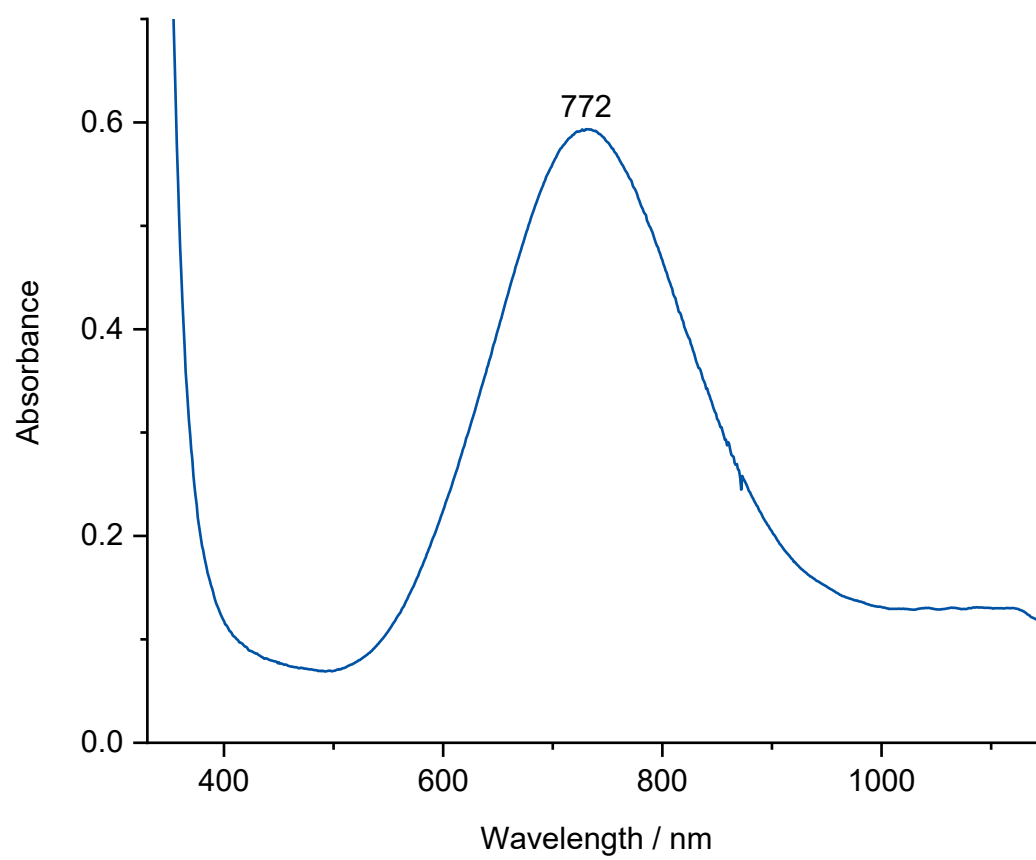
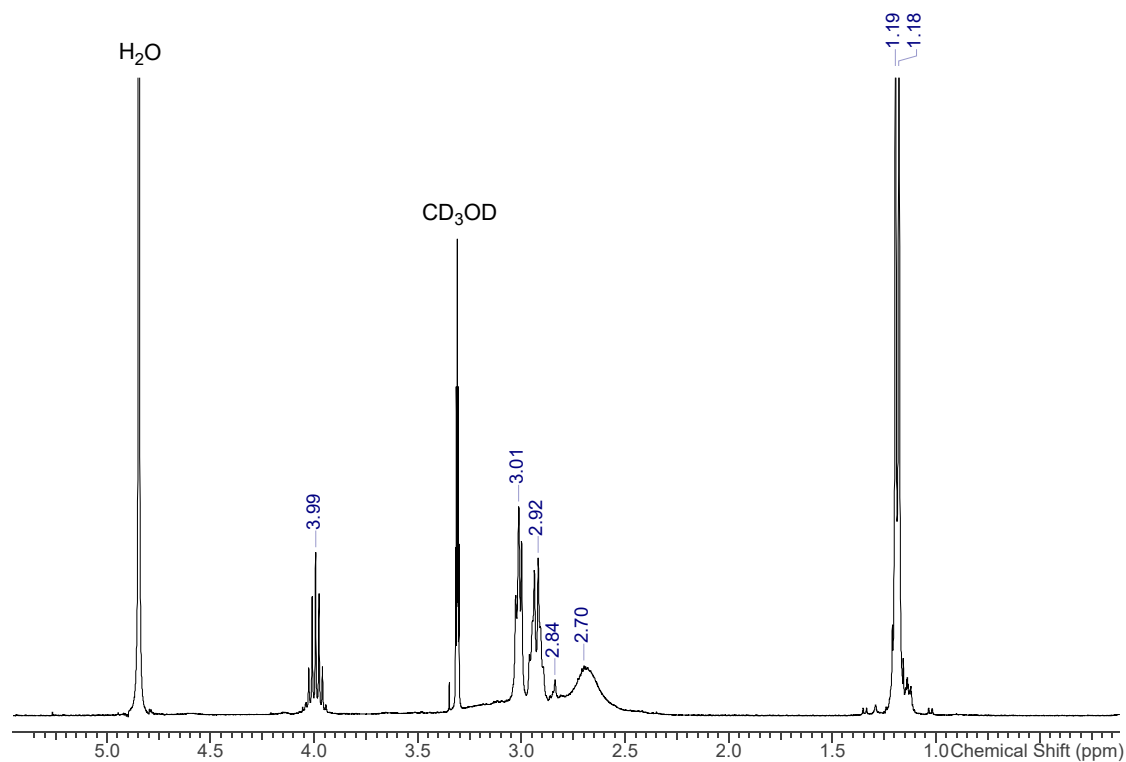
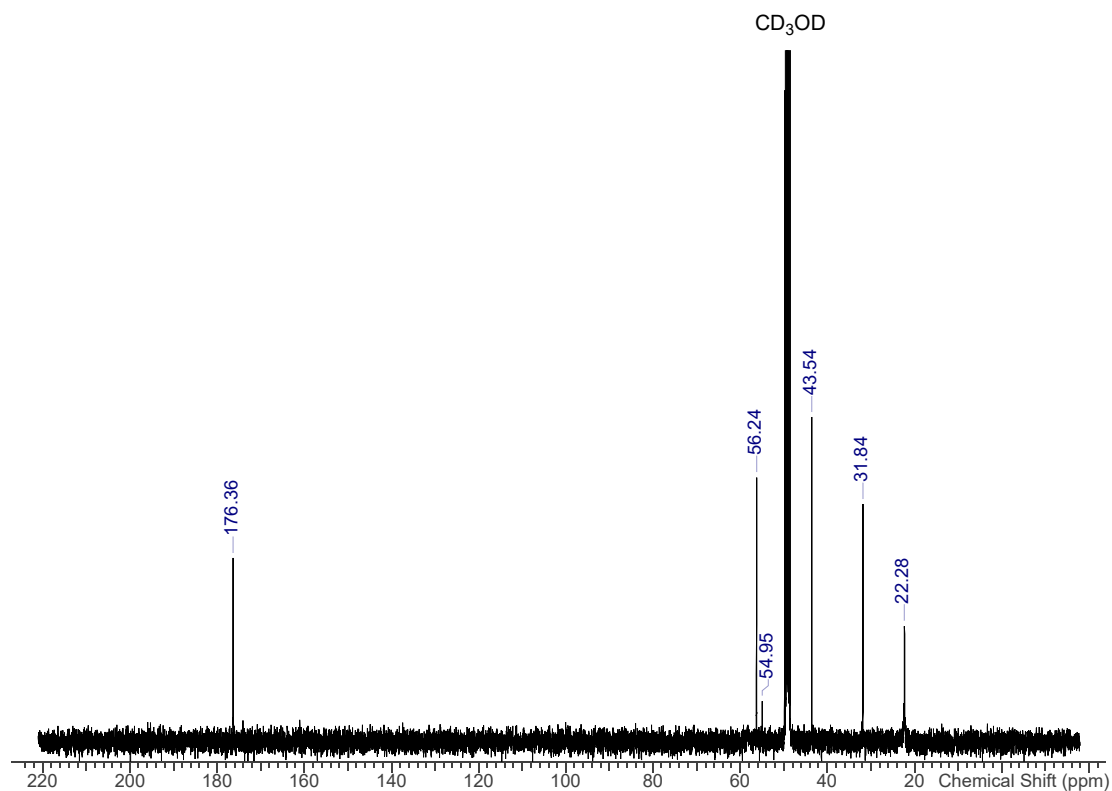


Figure S3.8 [Zn(L²)] [NO₃]₂

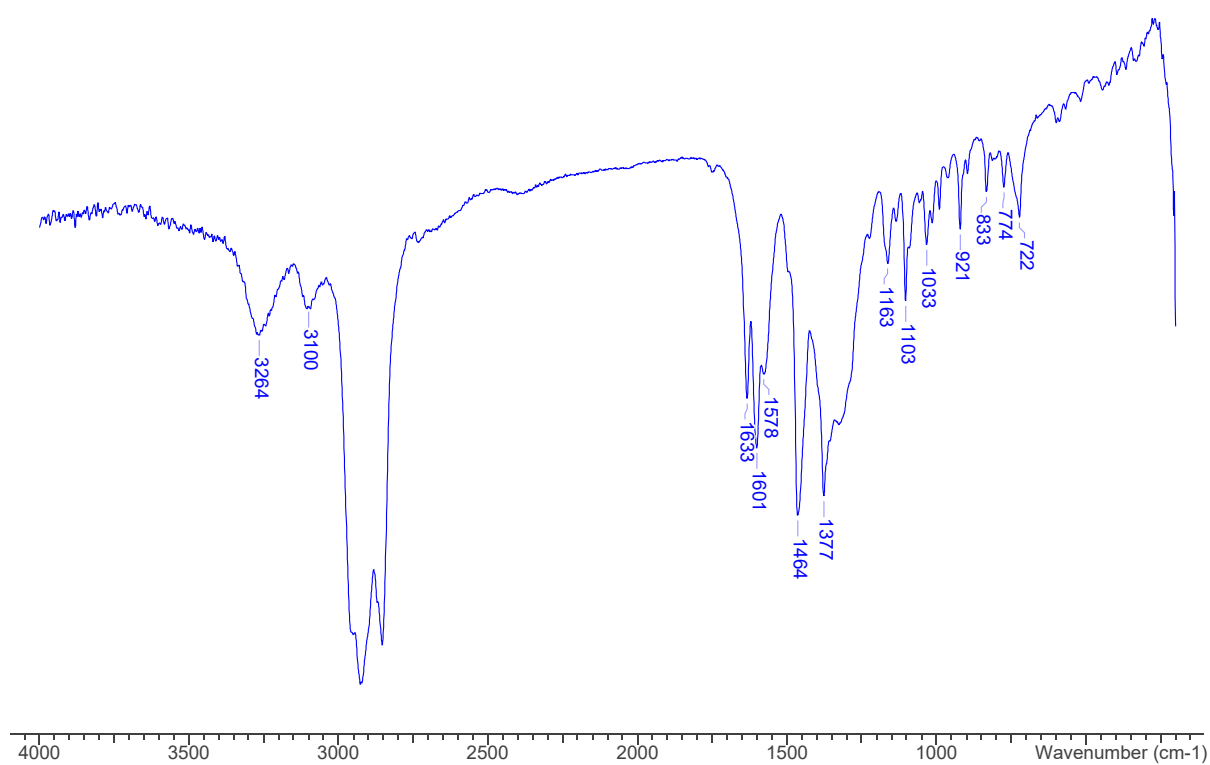
S3.8.a ¹H NMR spectrum (CD₃OD)



S3.8.b ¹³C{¹H} NMR spectrum (CD₃OD)



S3.8.c IR spectrum (Nujol)



S3.8.d ESI⁺ MS (MeOH)

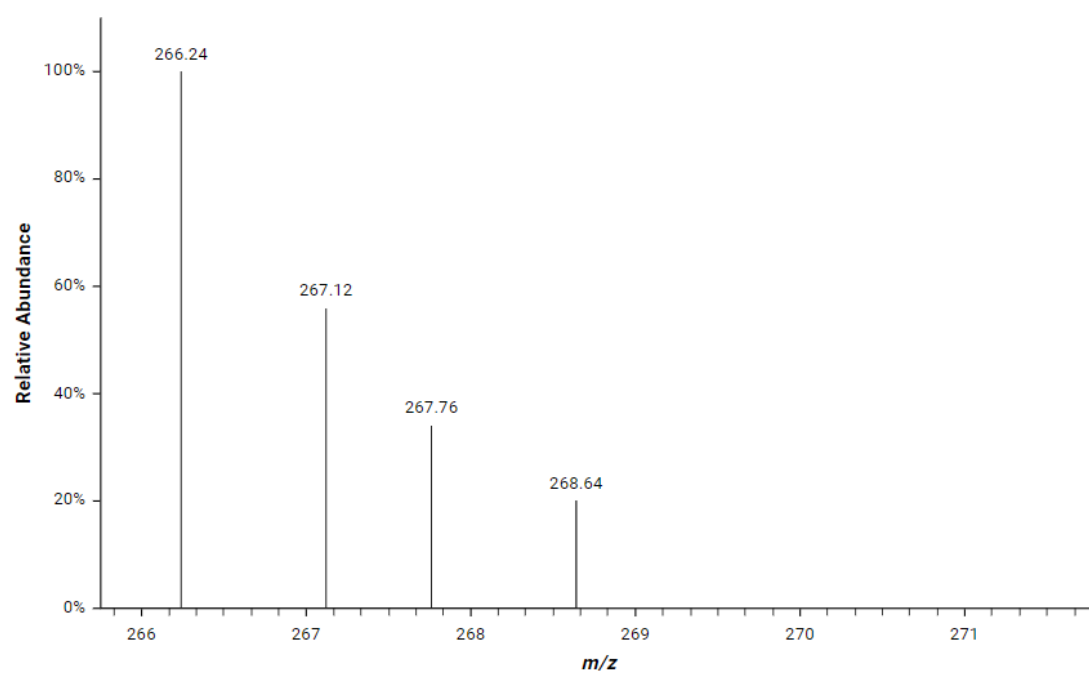
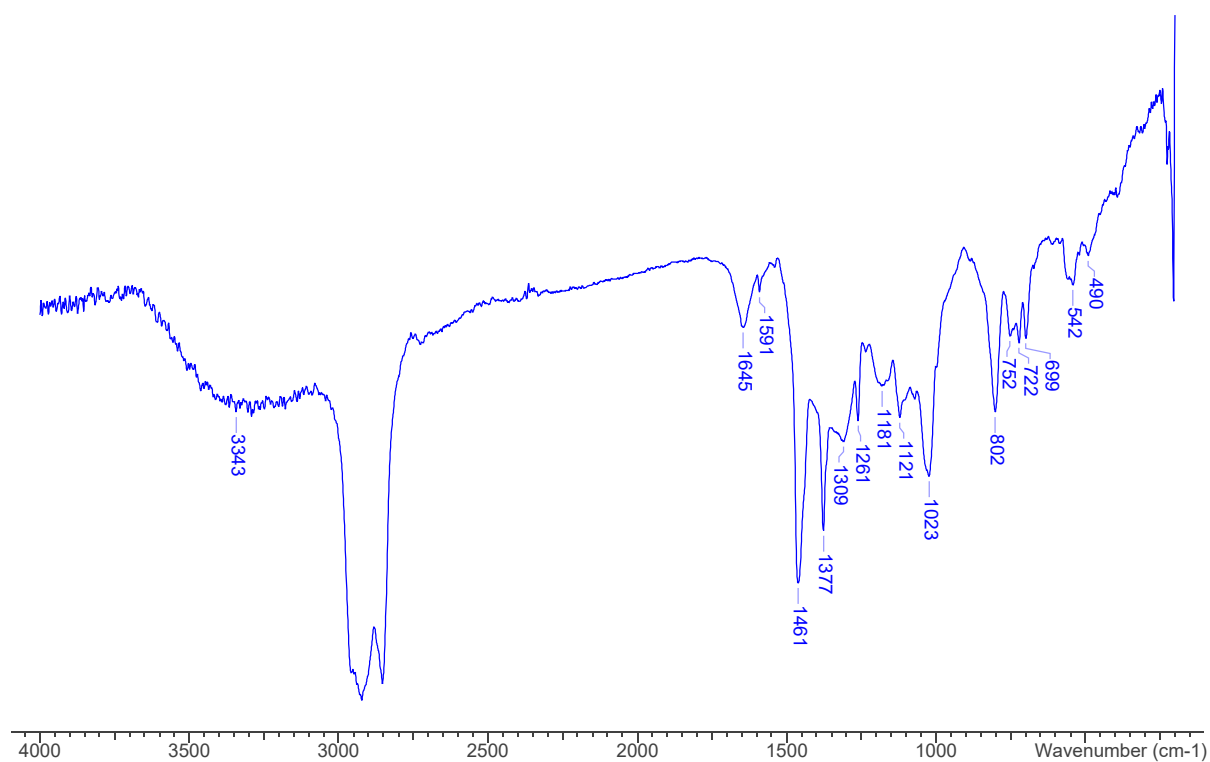
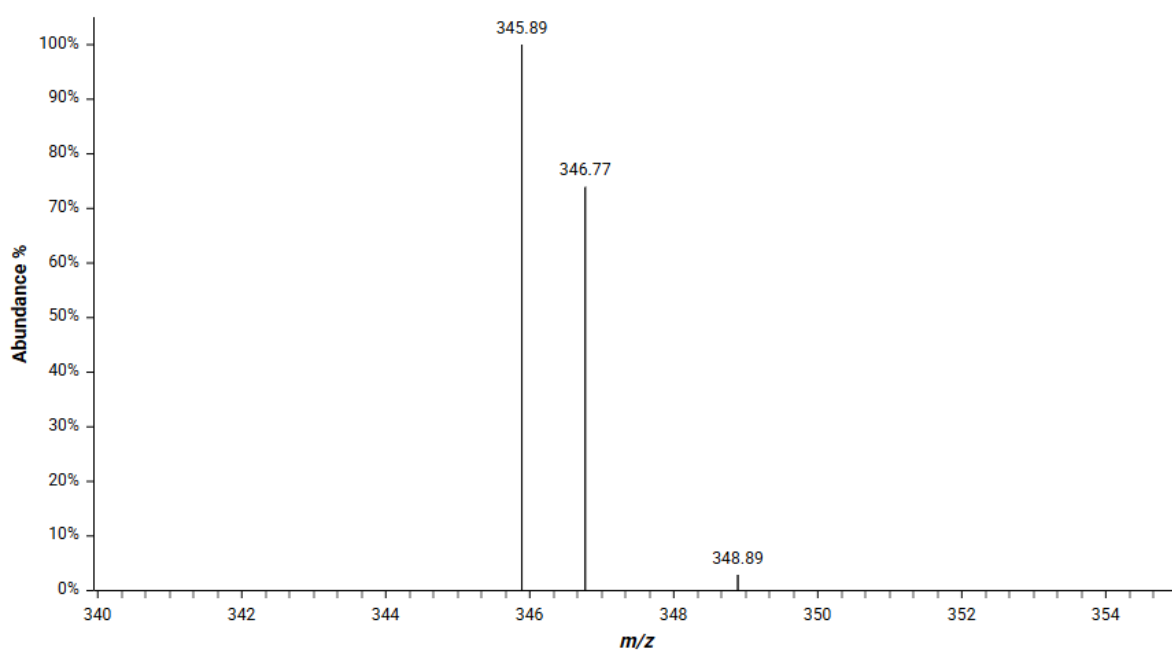


Figure S3.9 [Ni(NOTP-OMe)][NO₃]₂

S3.9.a IR spectrum (Nujol)



S3.9.b ESI⁺ MS (H₂O)



S3.9.c UV-Vis spectrum (MeOH)

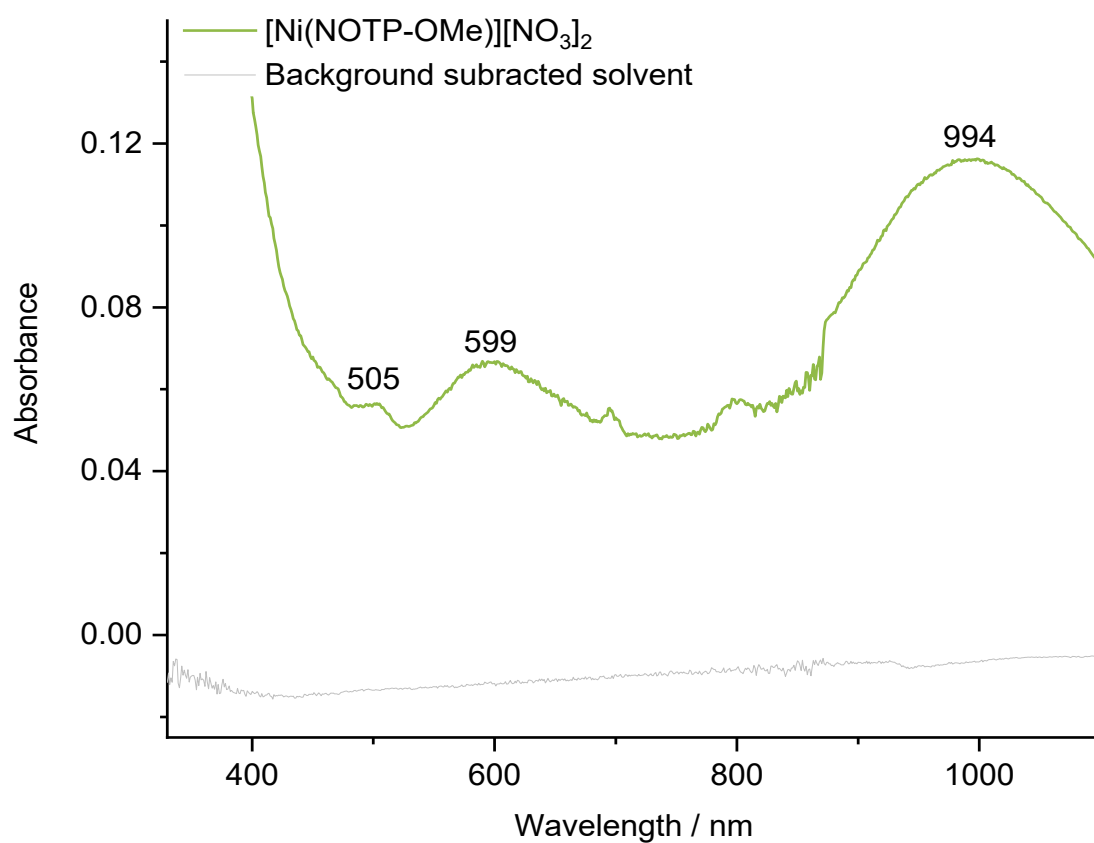
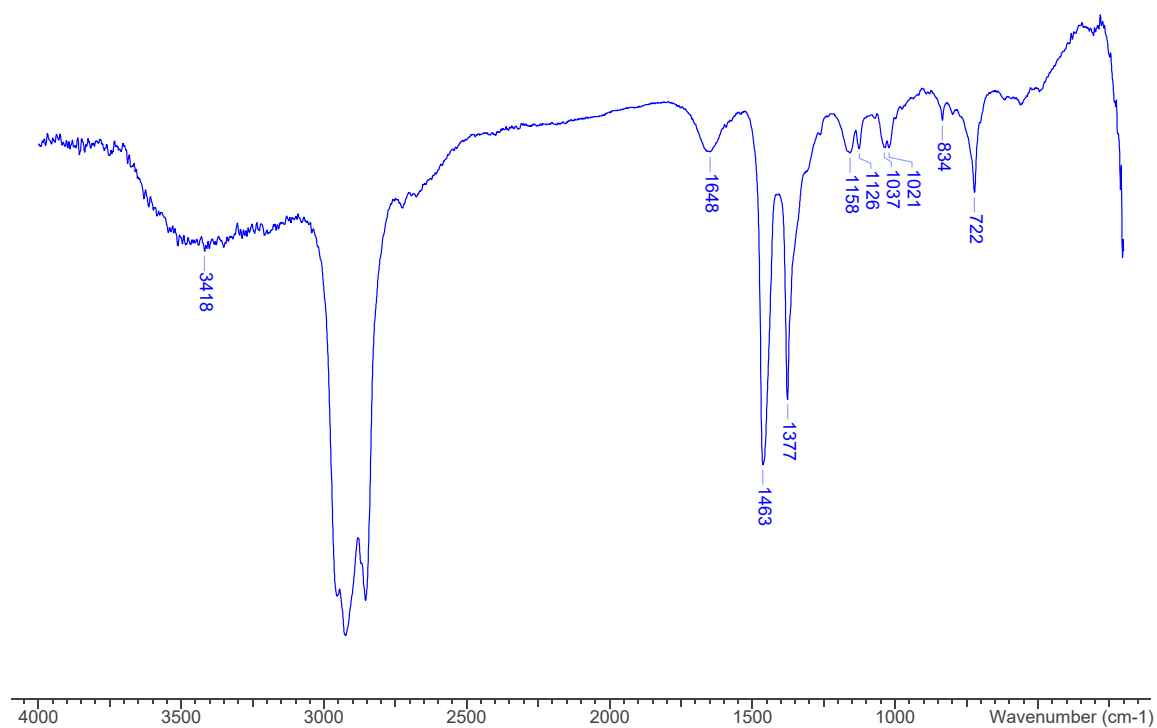
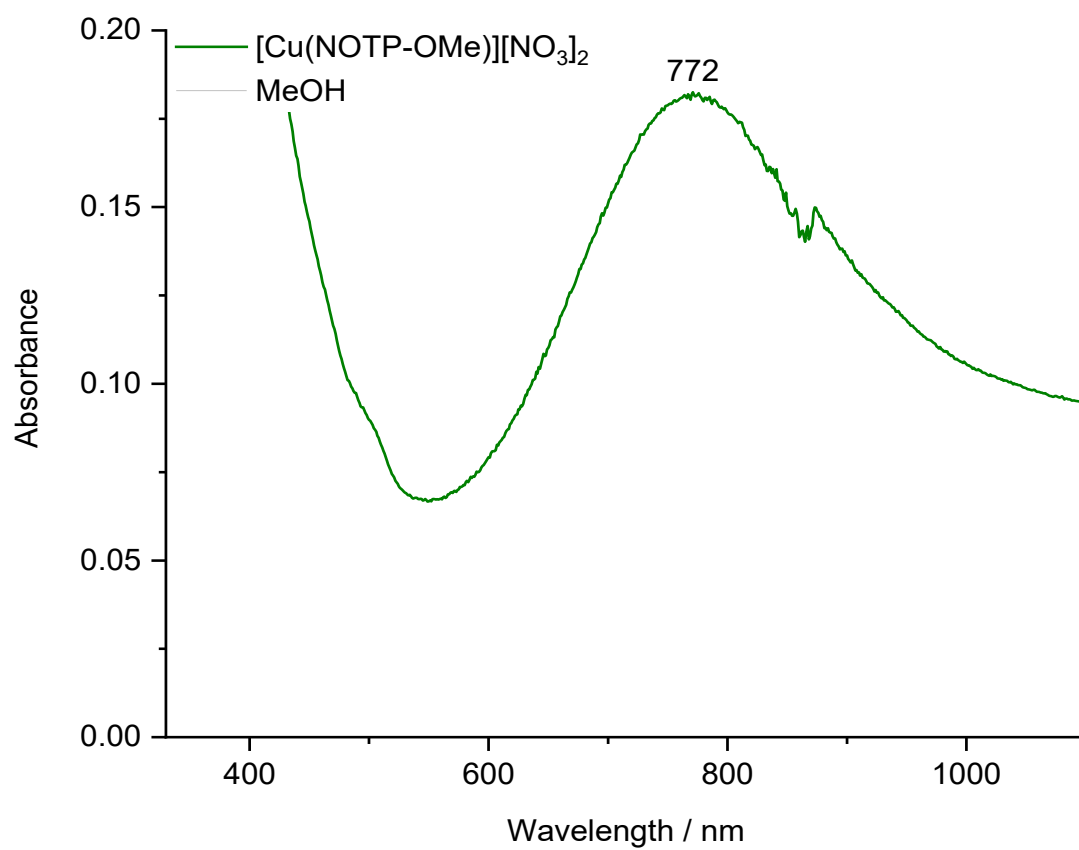


Figure S3.10 [Cu(NOTP-OMe)][NO₃]₂

S3.10.a IR spectrum (Nujol)



S3.10.b UV-Vis spectrum (MeOH)



S3.10.c ESI⁺ MS (H₂O)

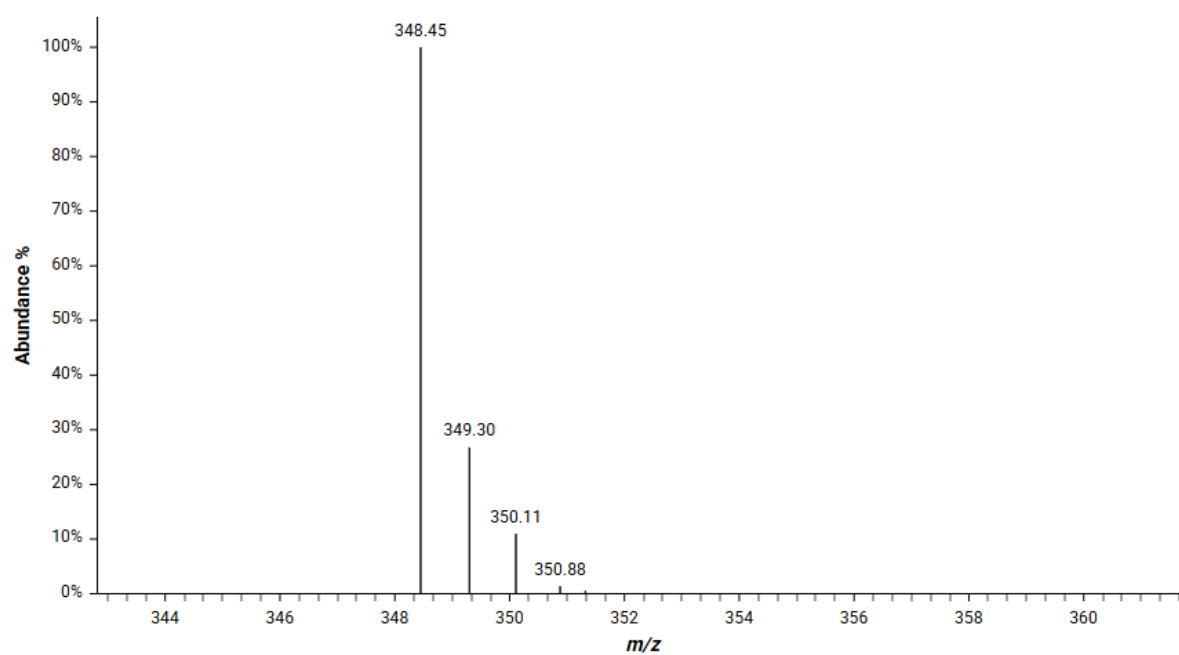
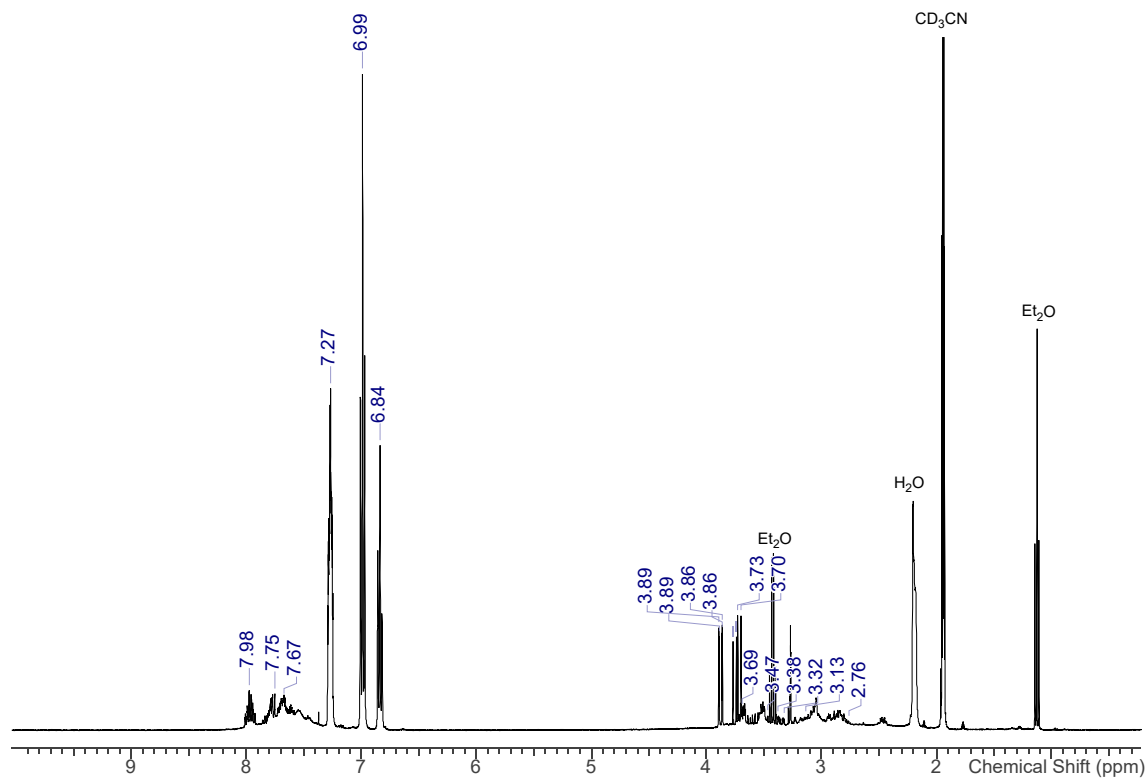
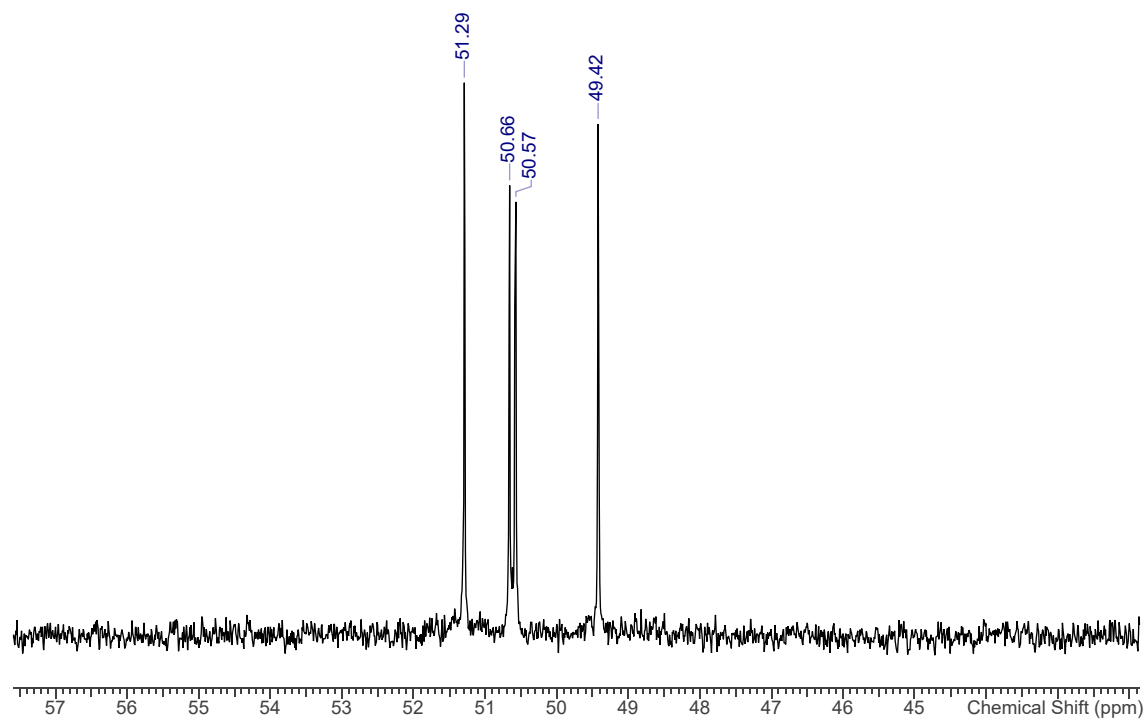


Figure S3.11 $[\text{Zn}(\text{NOTP-OMe})][\text{BPh}_4]_2$

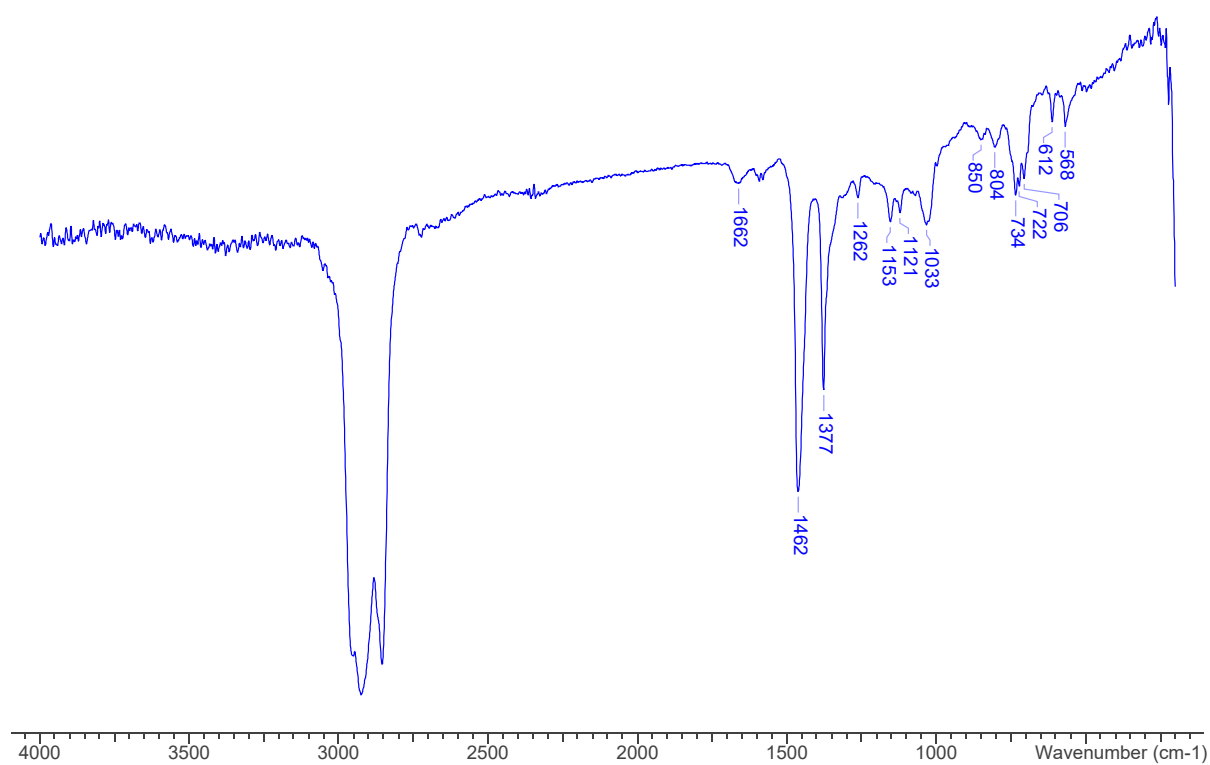
S3.11.a ^1H NMR spectrum (CD_3CN)



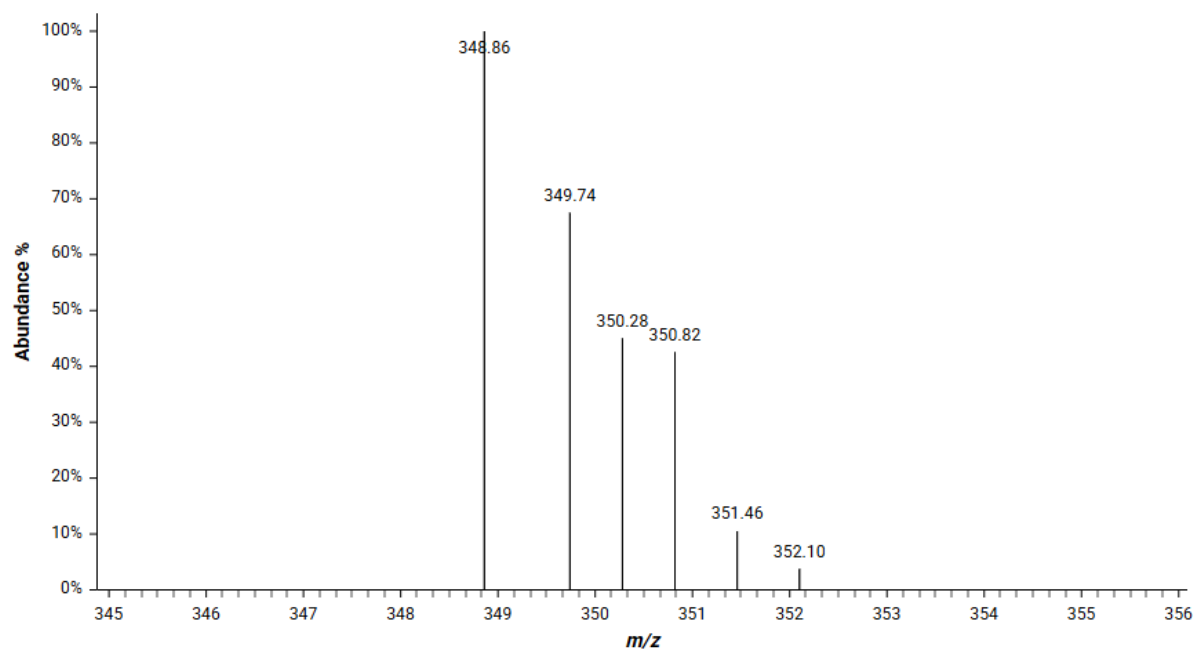
S3.11.b $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CD_3CN)



S3.11.c IR spectrum (Nujol)



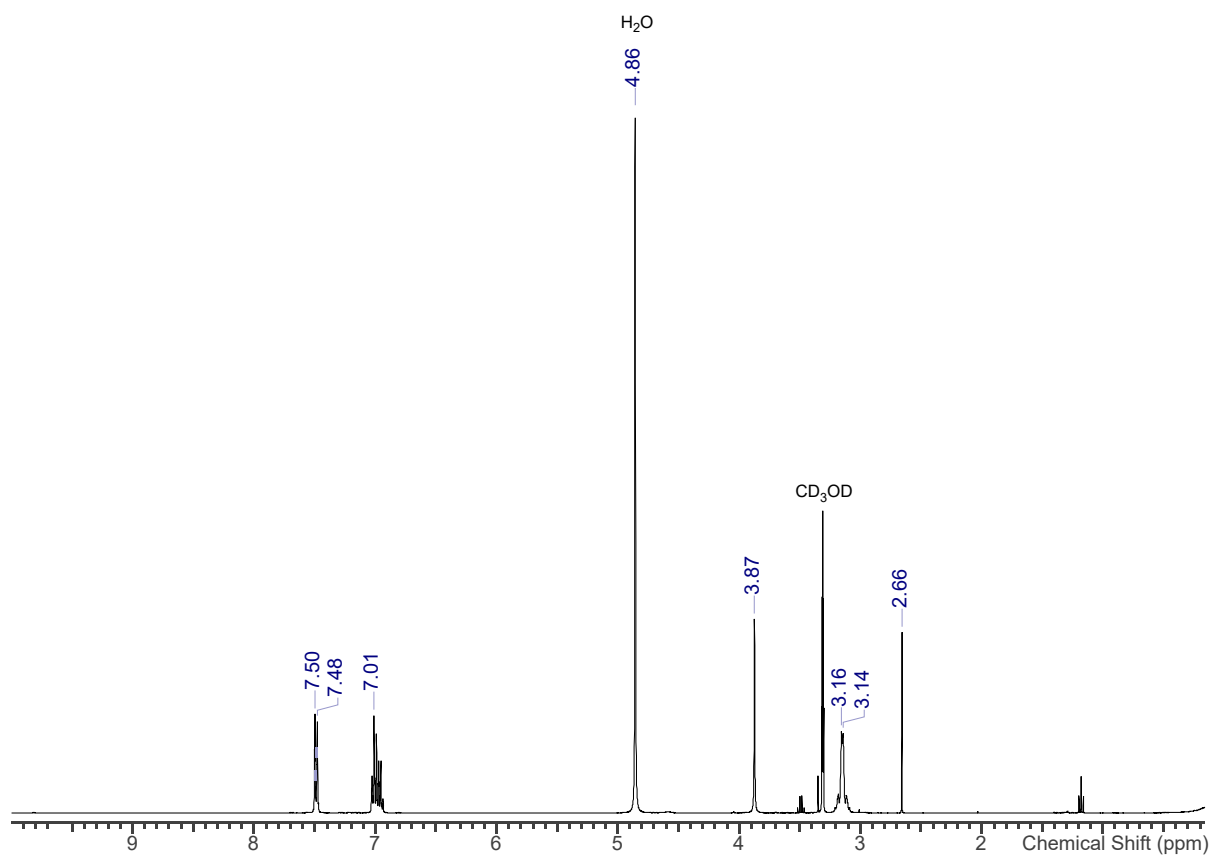
S3.11.d ESI⁺ MS (MeOH)



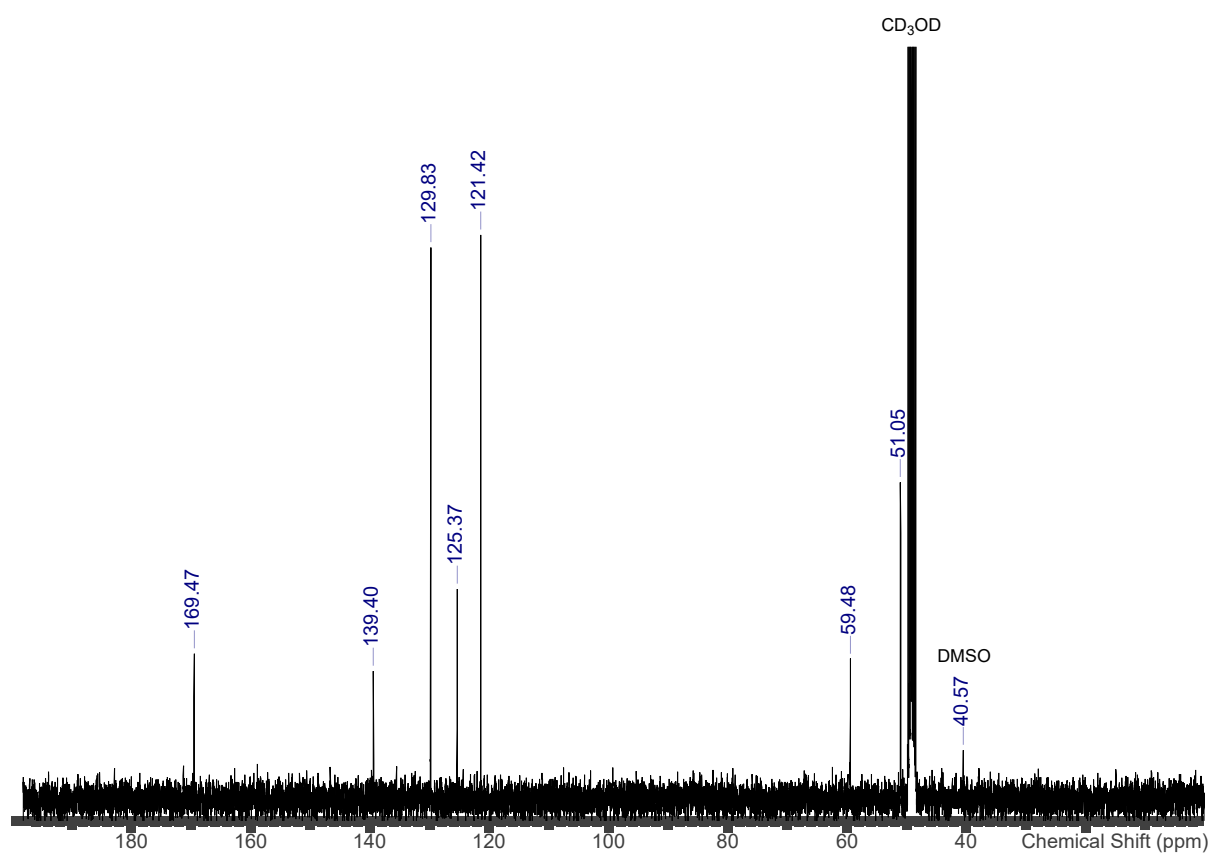
Chapter 4

Figure S4.1 [AlF₃(L¹)]

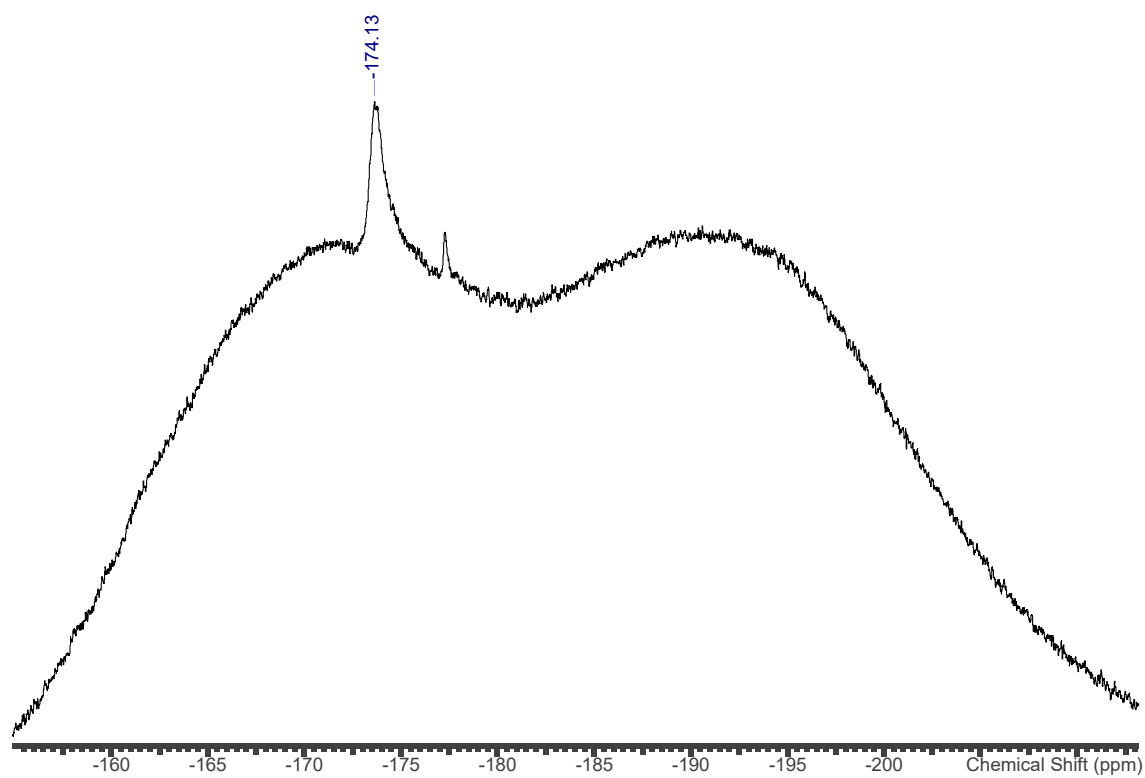
S4.1.a ¹H NMR spectrum (CD₃OD)



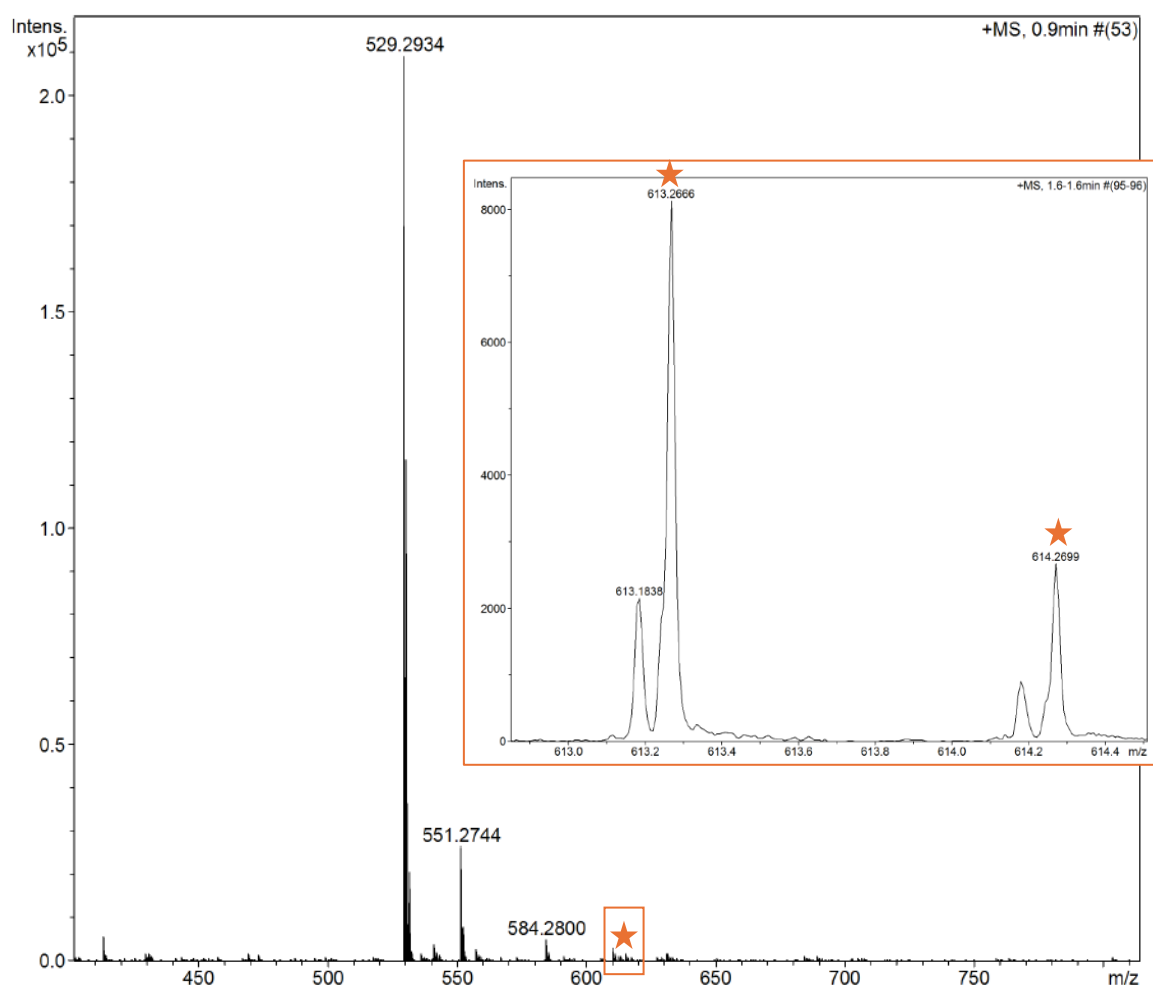
S4.1.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.1.c $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.1.d ESI⁺ MS (direct injection, MeOH)



S4.1.e IR spectrum (Nujol)

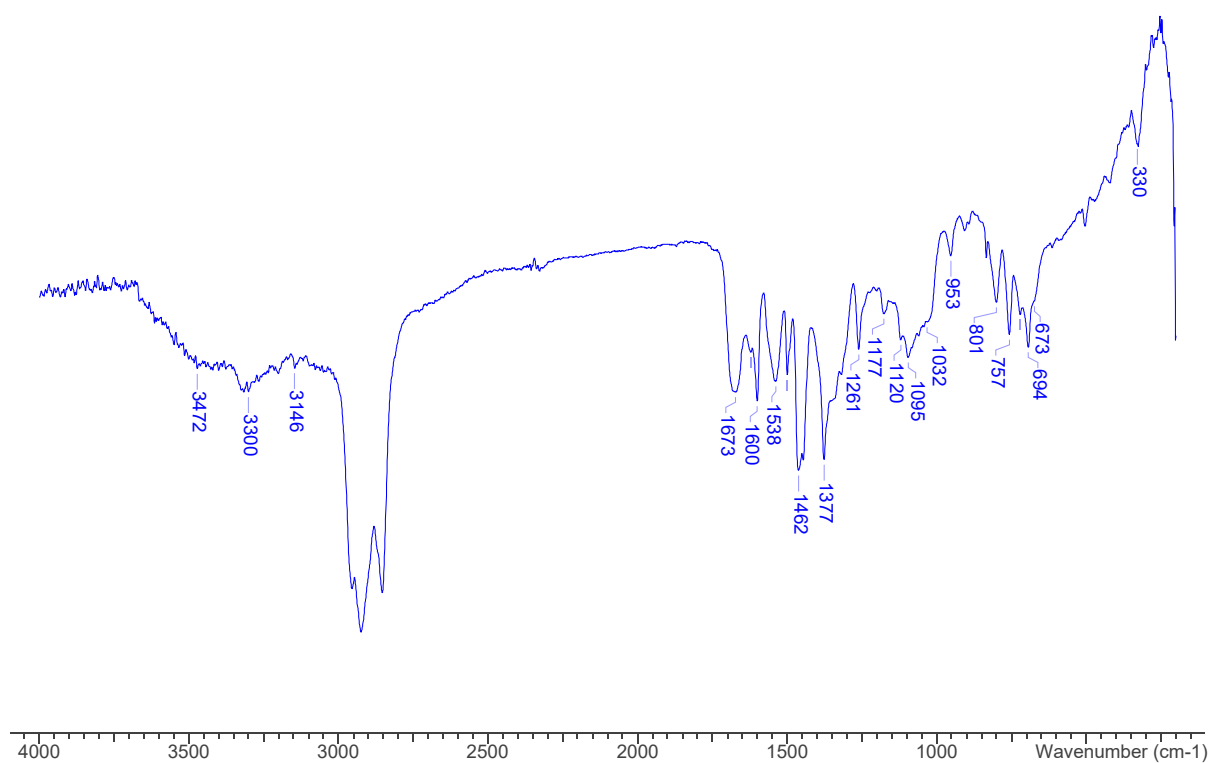
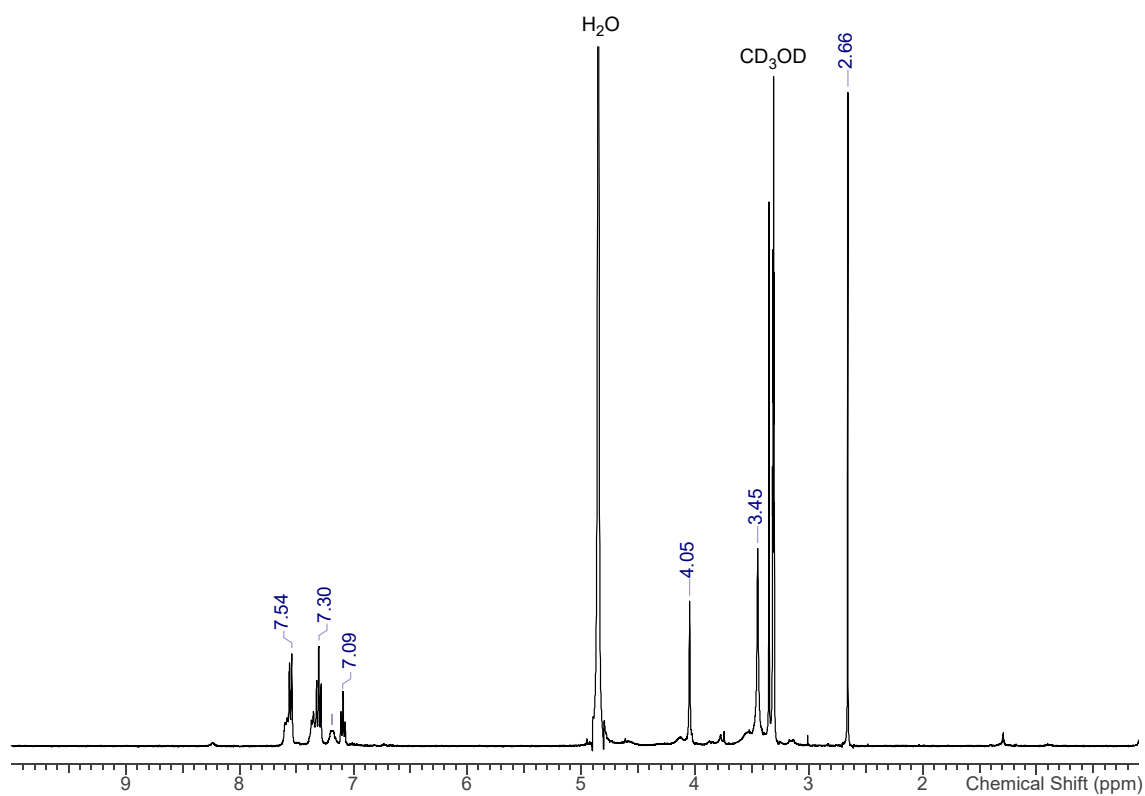
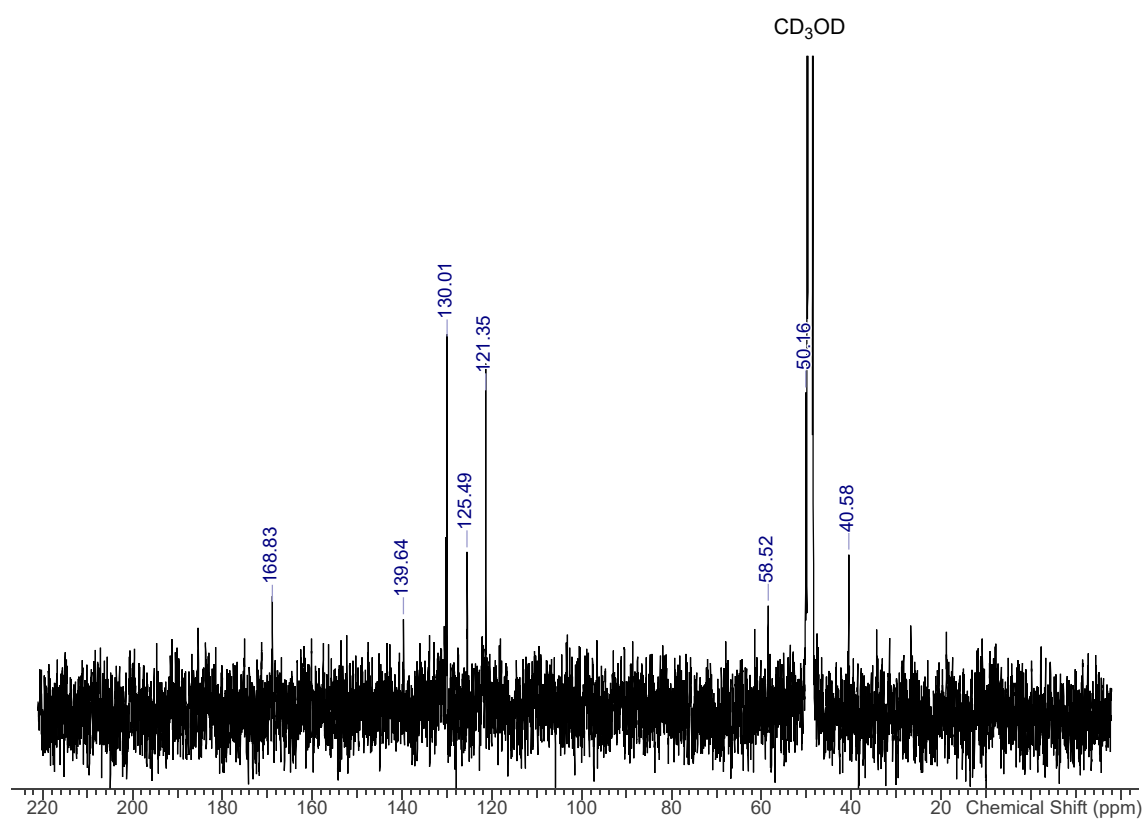


Figure S4.2 [GaF₃(L¹)]

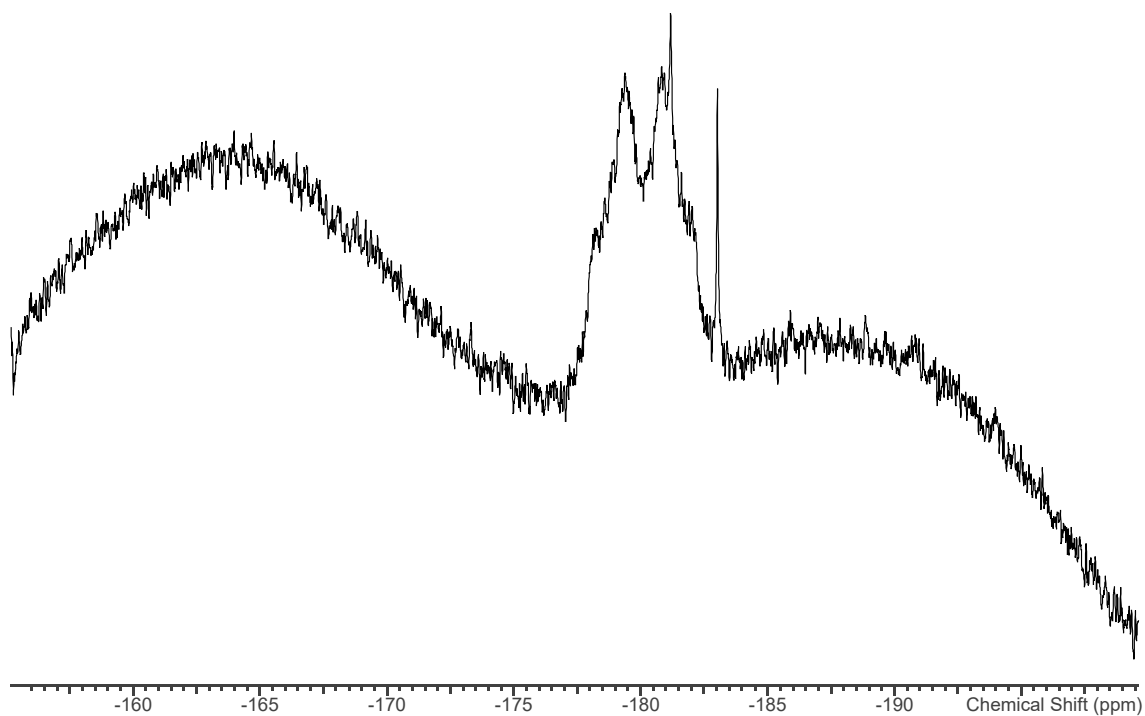
S4.2.a ¹H NMR spectrum (CD₃OD)



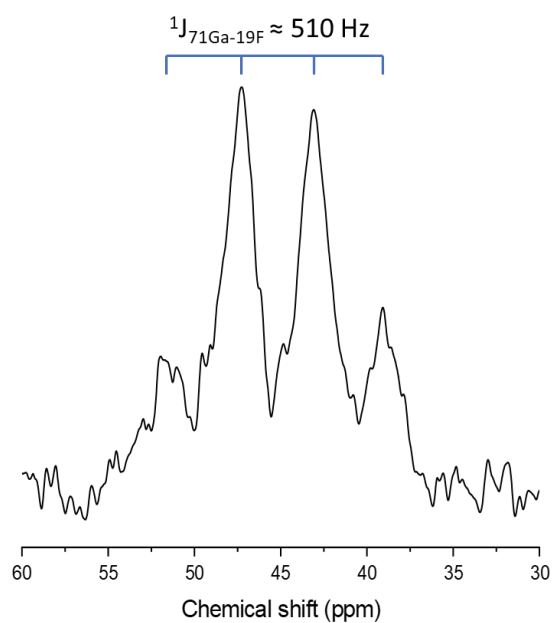
S4.2.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.2.c $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)

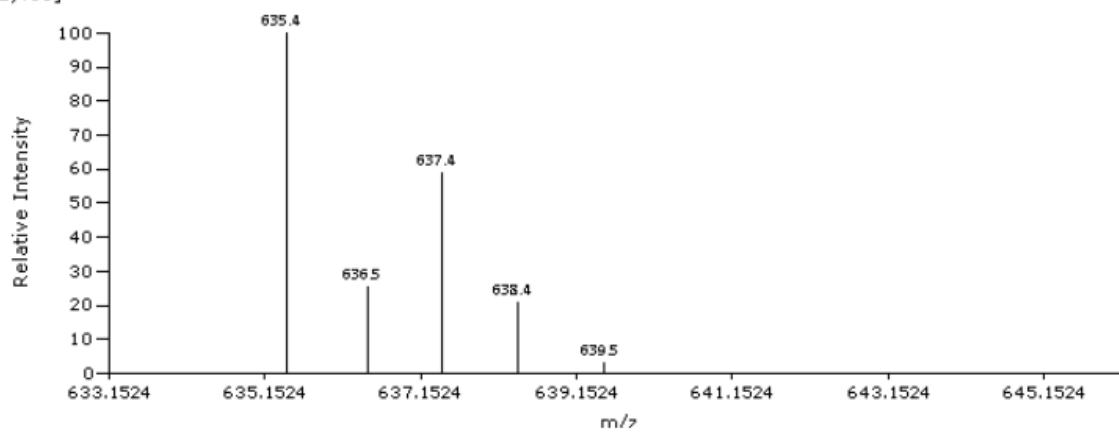


S4.2.d ^{71}Ga NMR spectrum (CD_3OD)



S4.2.e ESI⁺ MS (MeOH)

CBG 9133 83 57, BLUE ESIPOS C18 5 min, RT 1.7785 mins, Scan# 507, NL 4.483E6, 15/09/2021 14:09, m/z [152-1,480]



S4.2.f IR spectrum (Nujol)

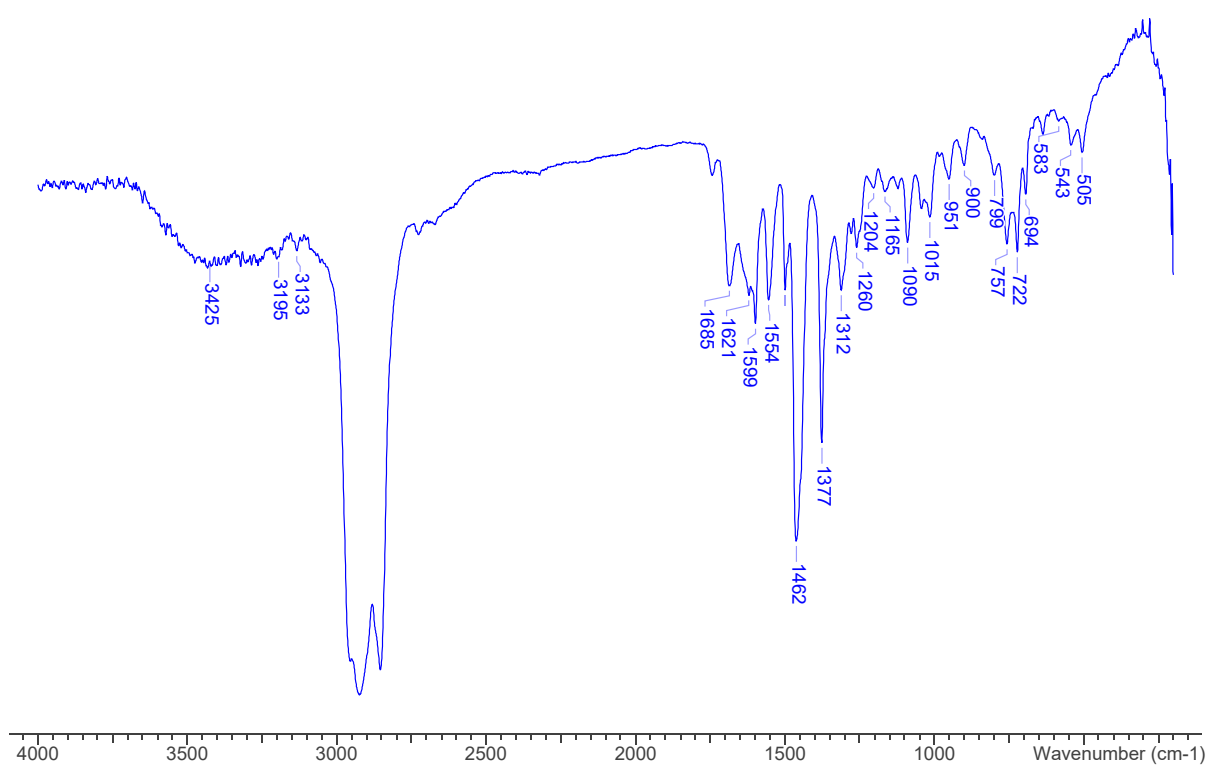


Figure S4.3 [FeF₃(L¹)]

S4.3.a IR spectrum (Nujol)

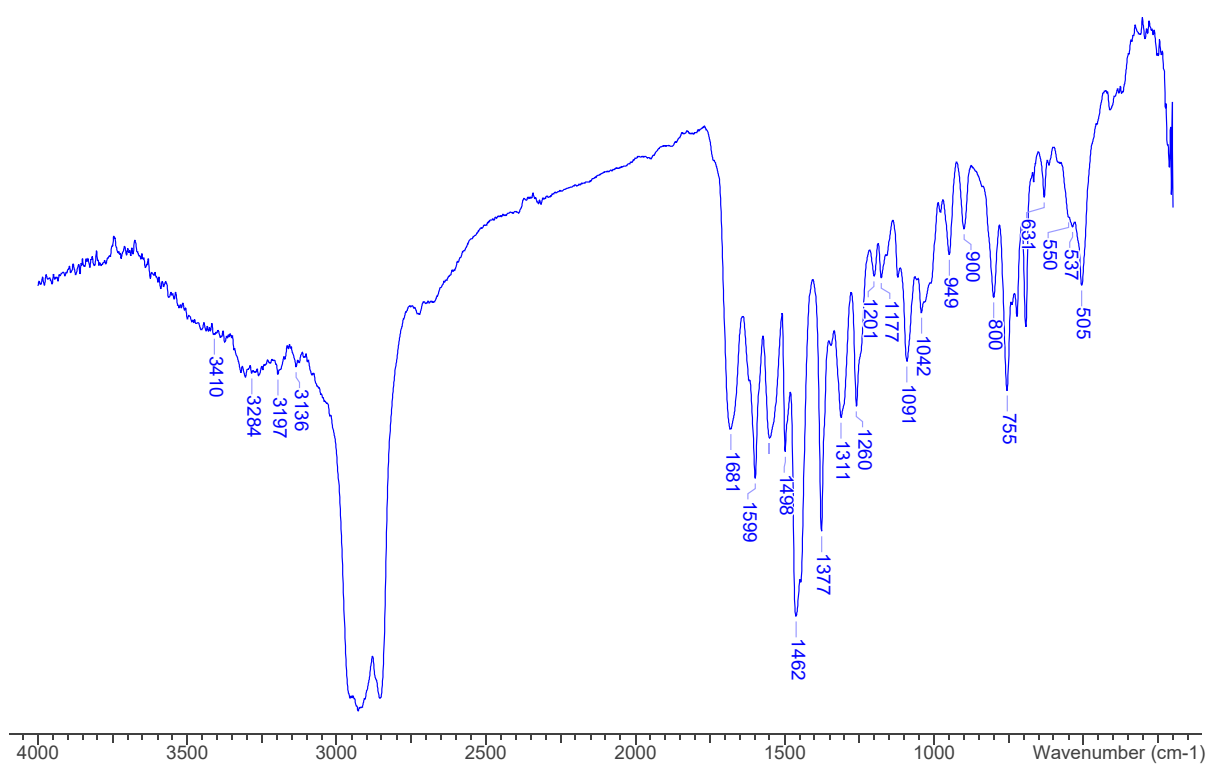
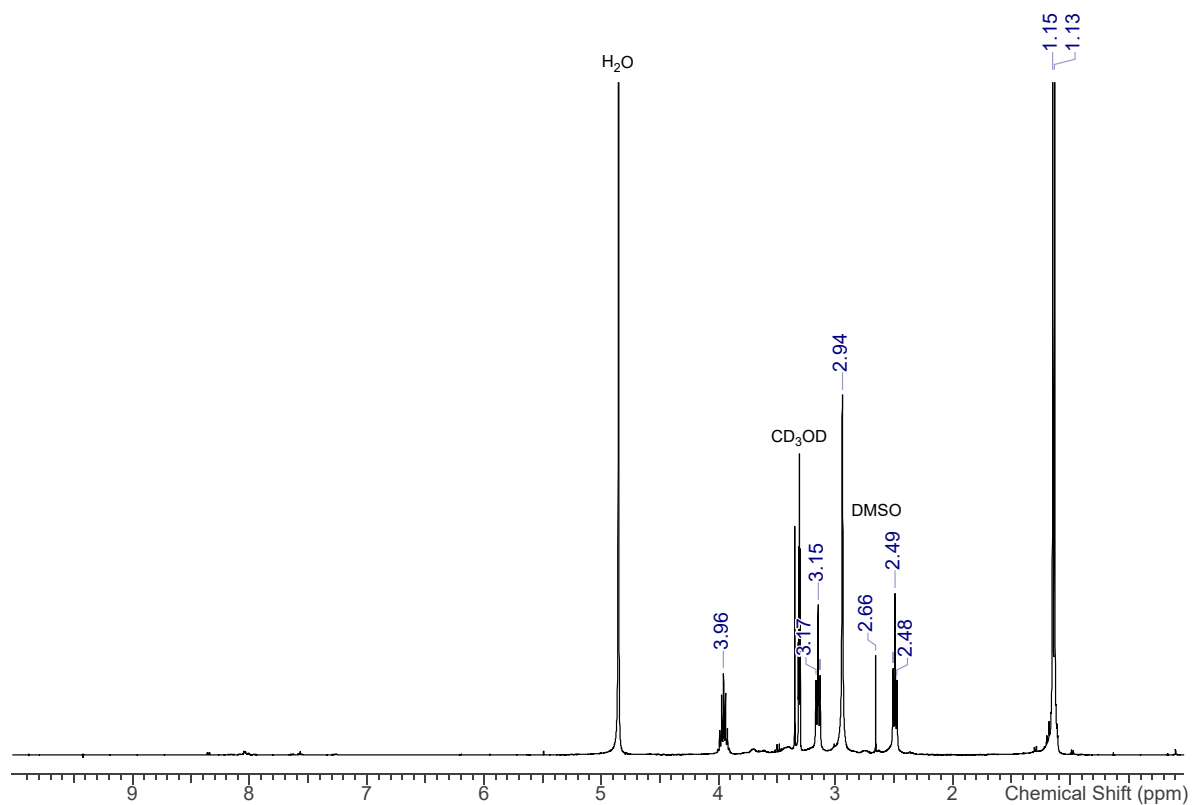
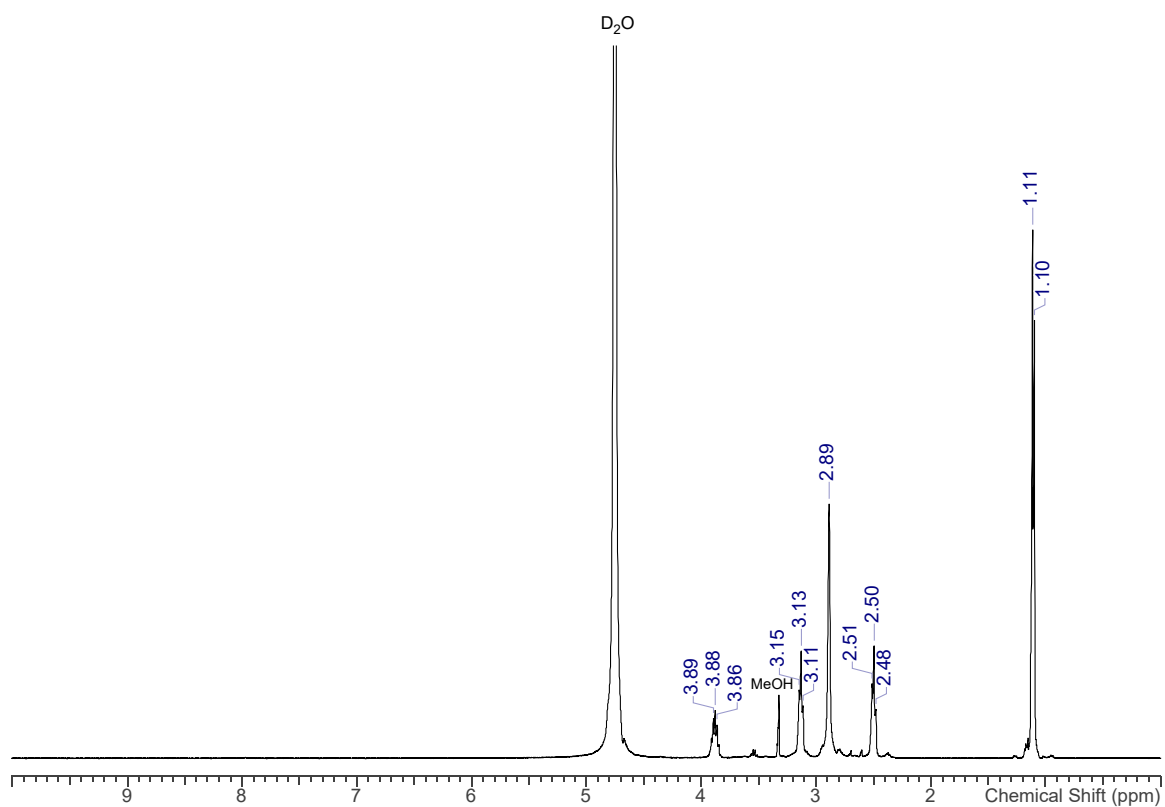


Figure S4.4 [AlF₃(L²)]

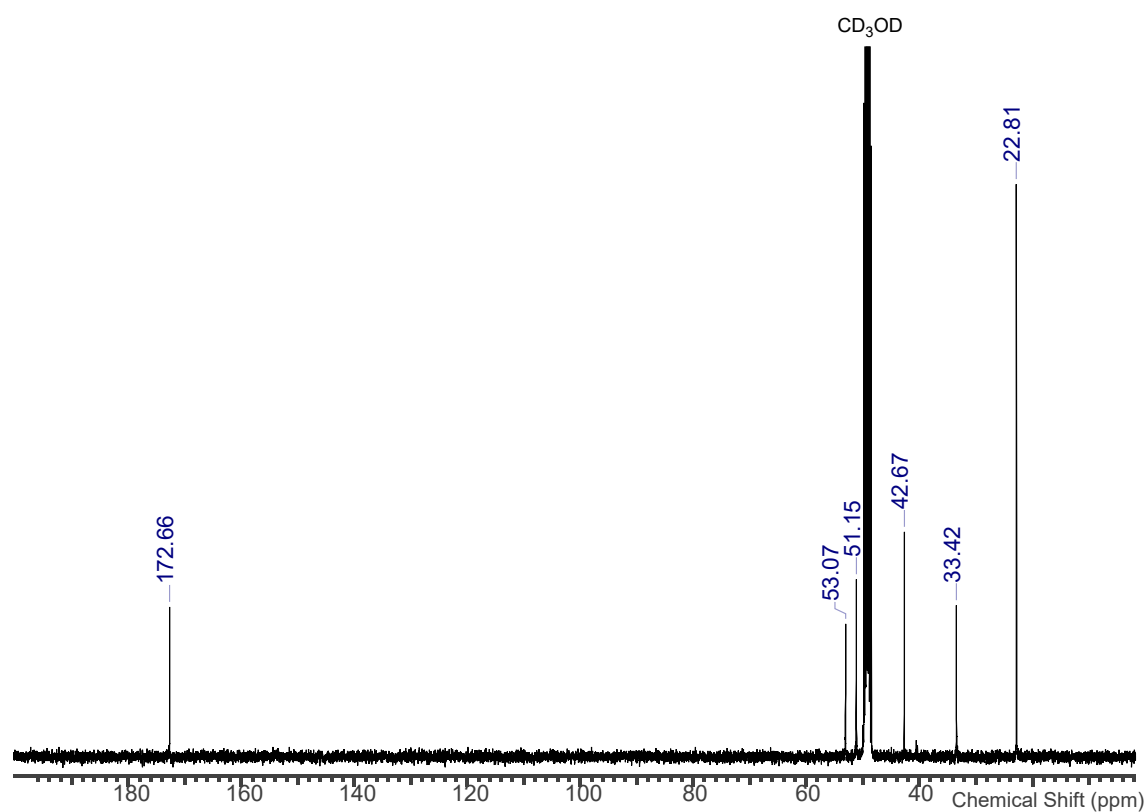
S4.4.a ¹H NMR spectrum (CD₃OD)



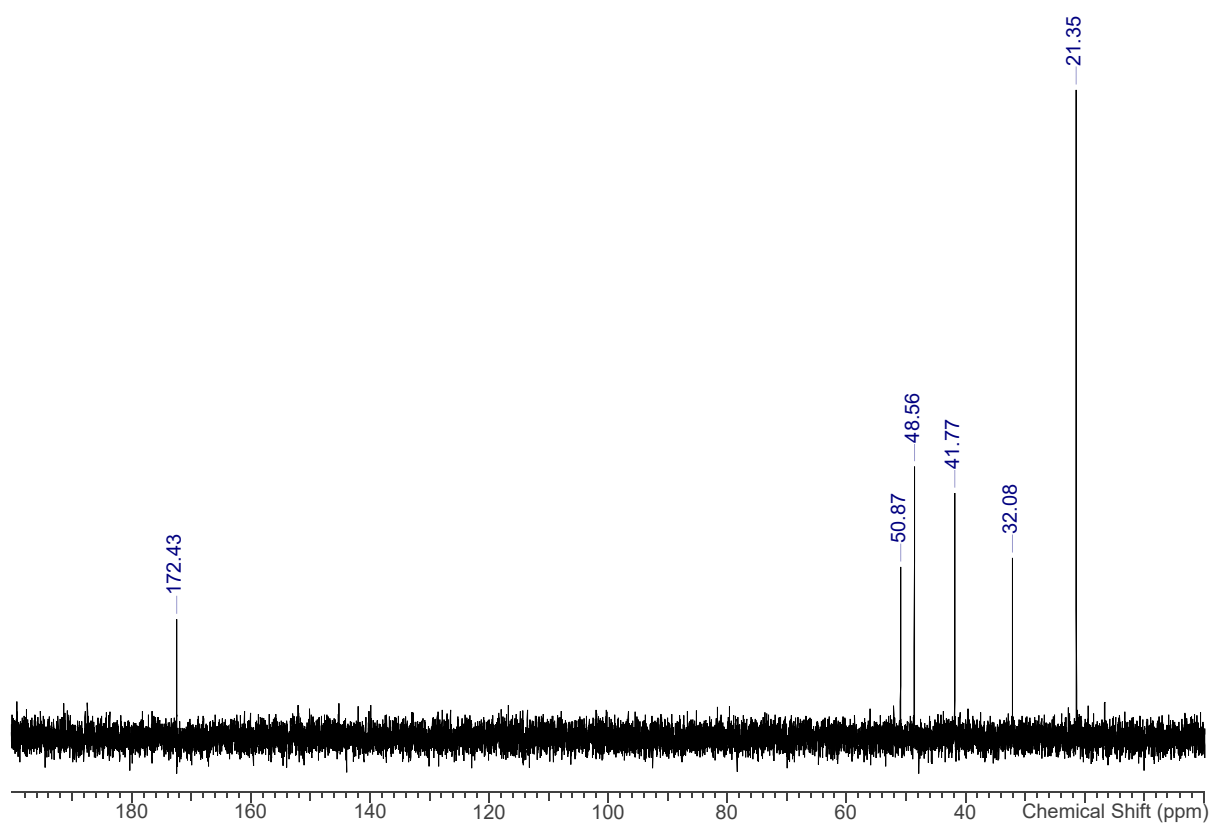
S4.4.b ¹H NMR spectrum (D₂O)



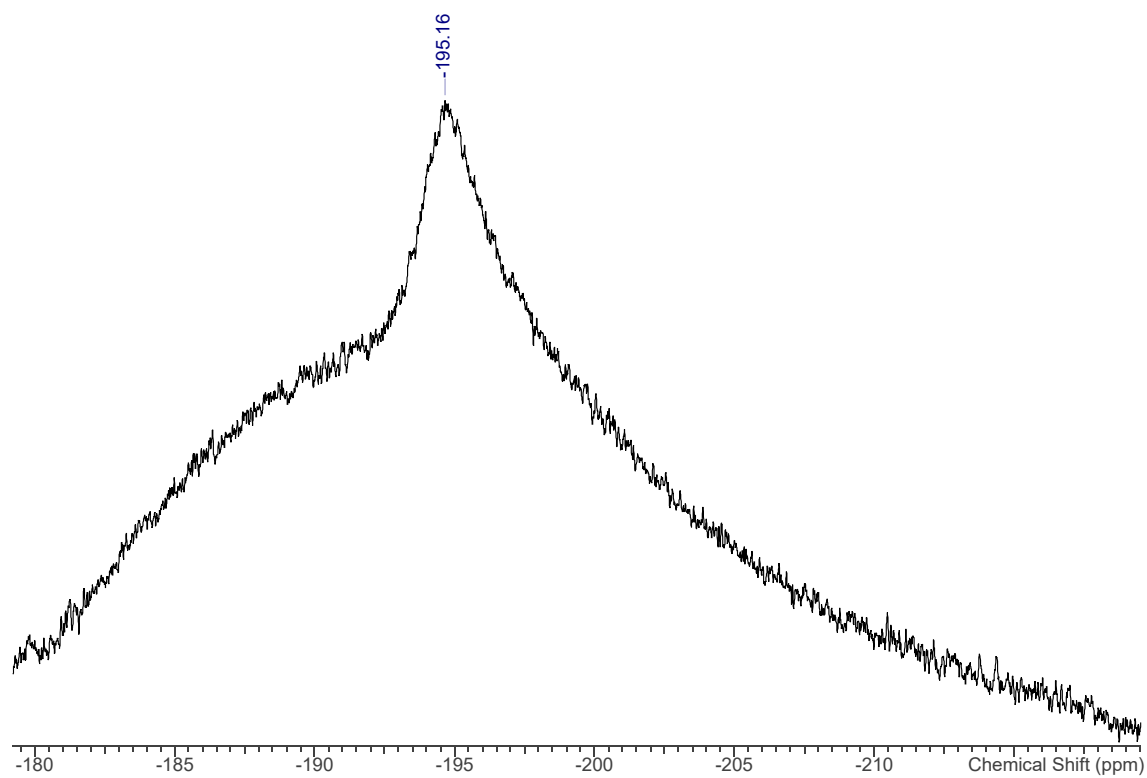
S4.4.c $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



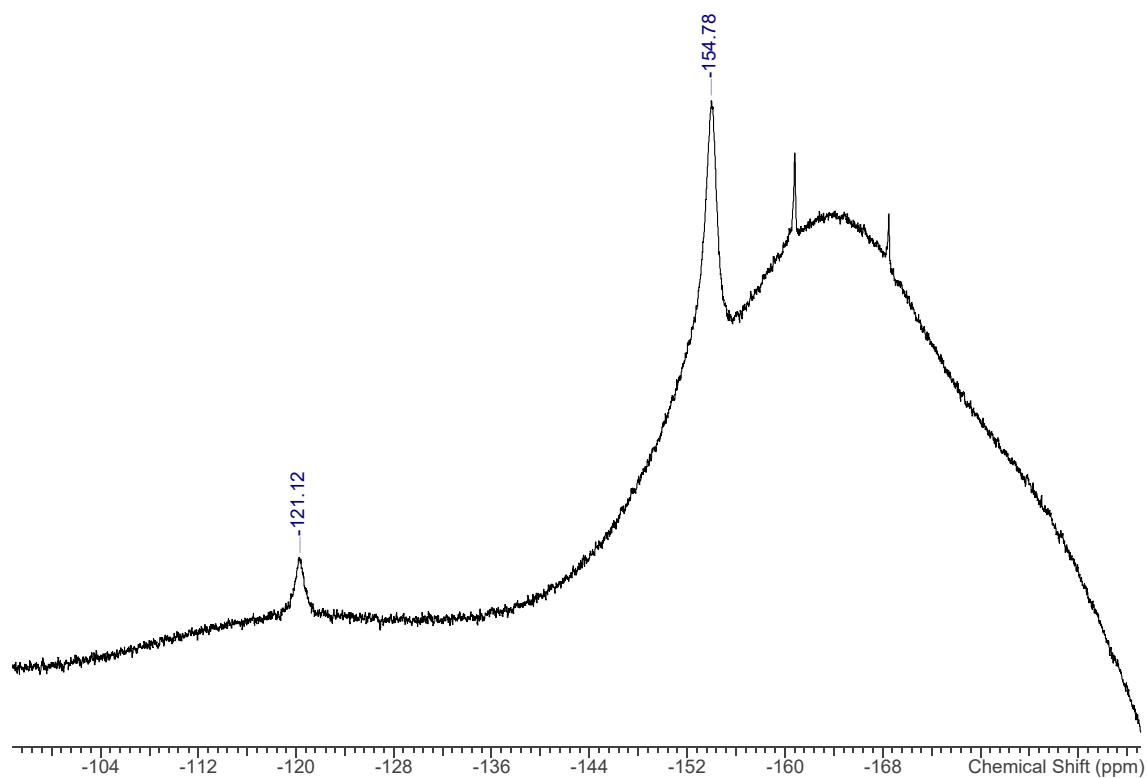
S4.4.d $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (D_2O)



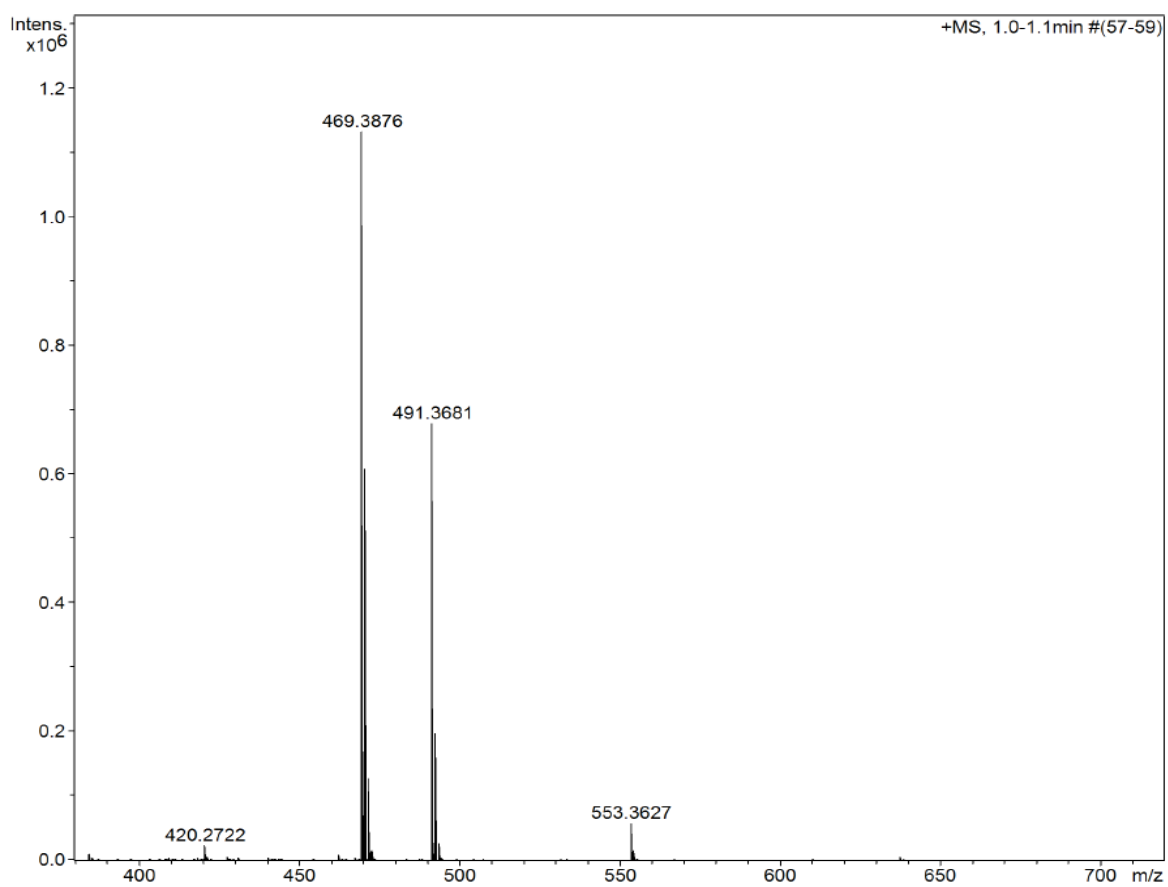
S4.4.e $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.4.f $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O)



S4.4.g ESI⁺ MS (direct injection, MeOH)



S4.4.h IR spectrum (Nujol)

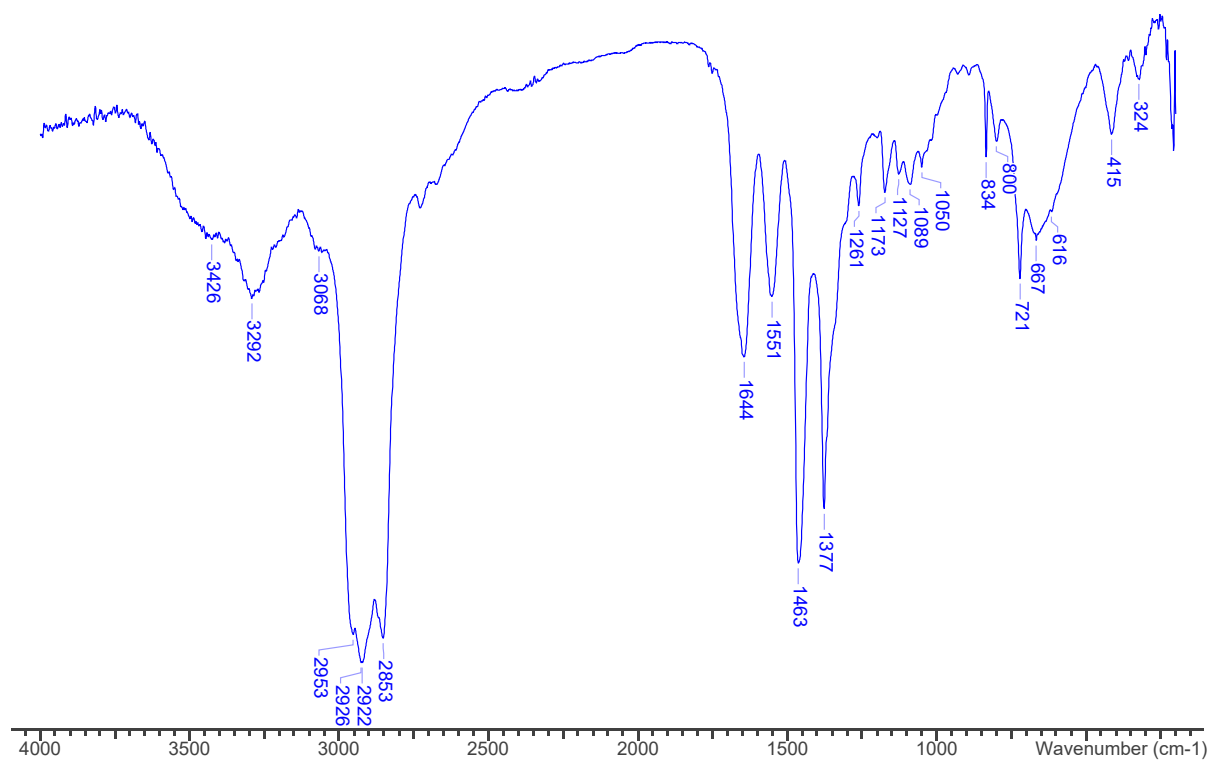
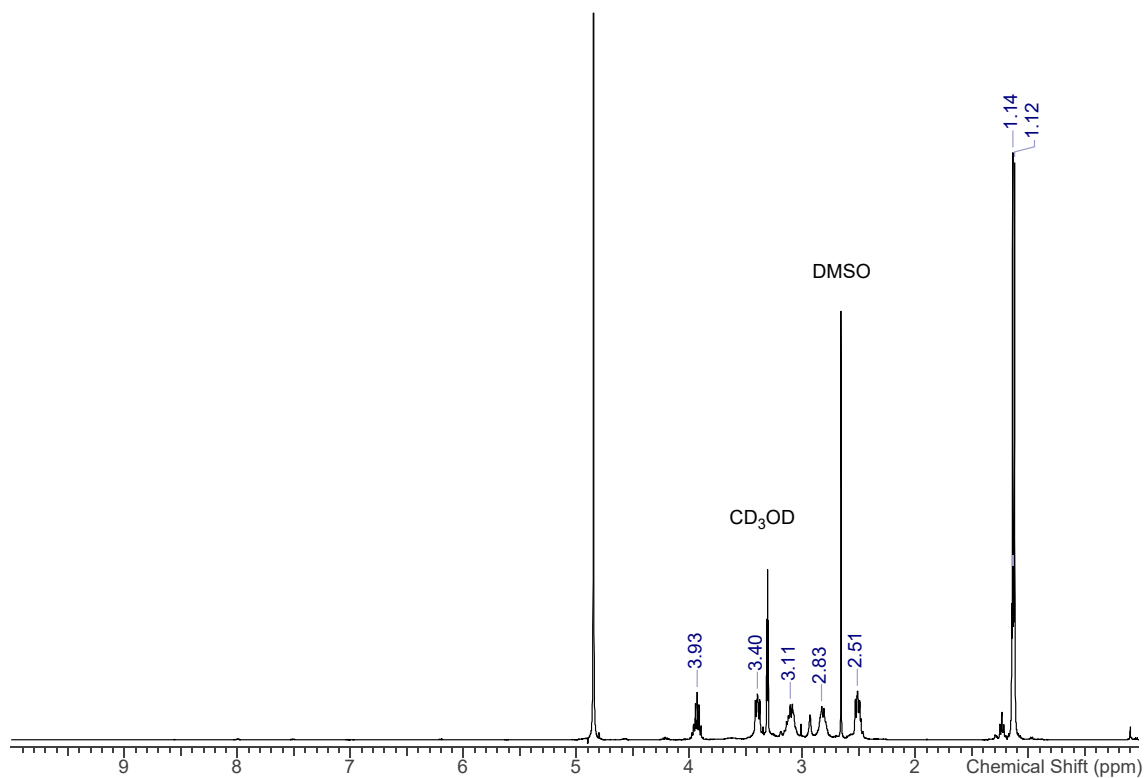
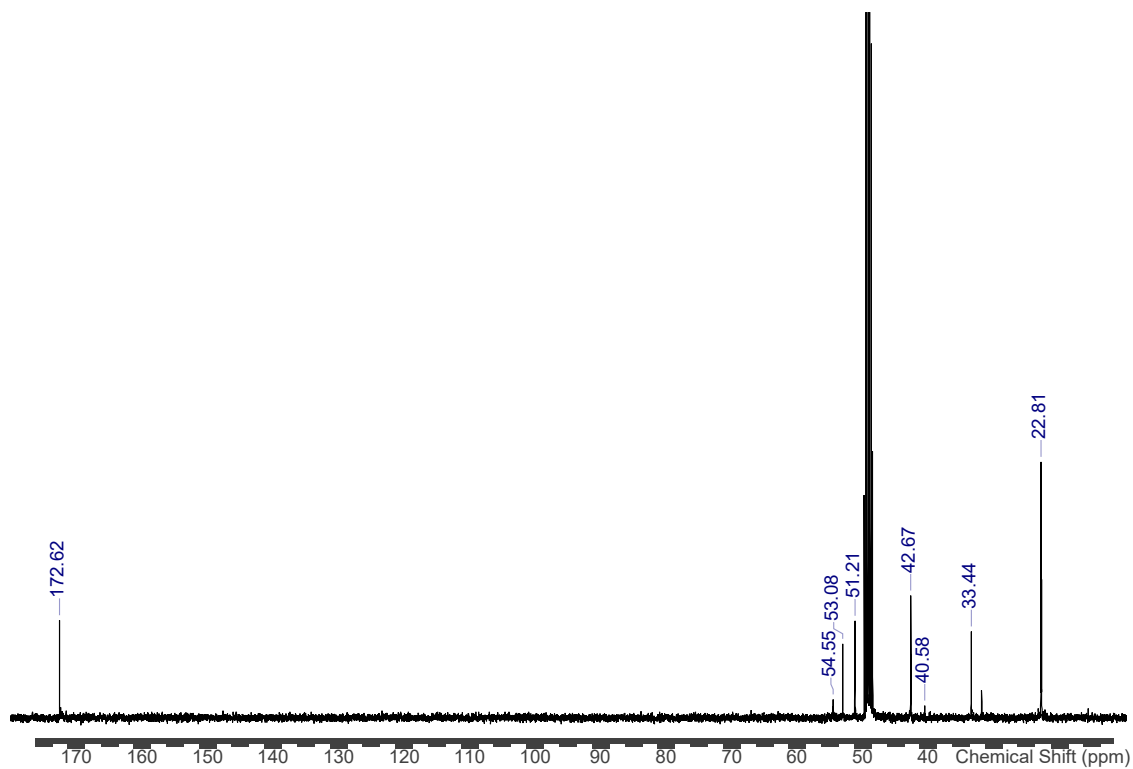


Figure S4.5 [GaF₃(L²)]

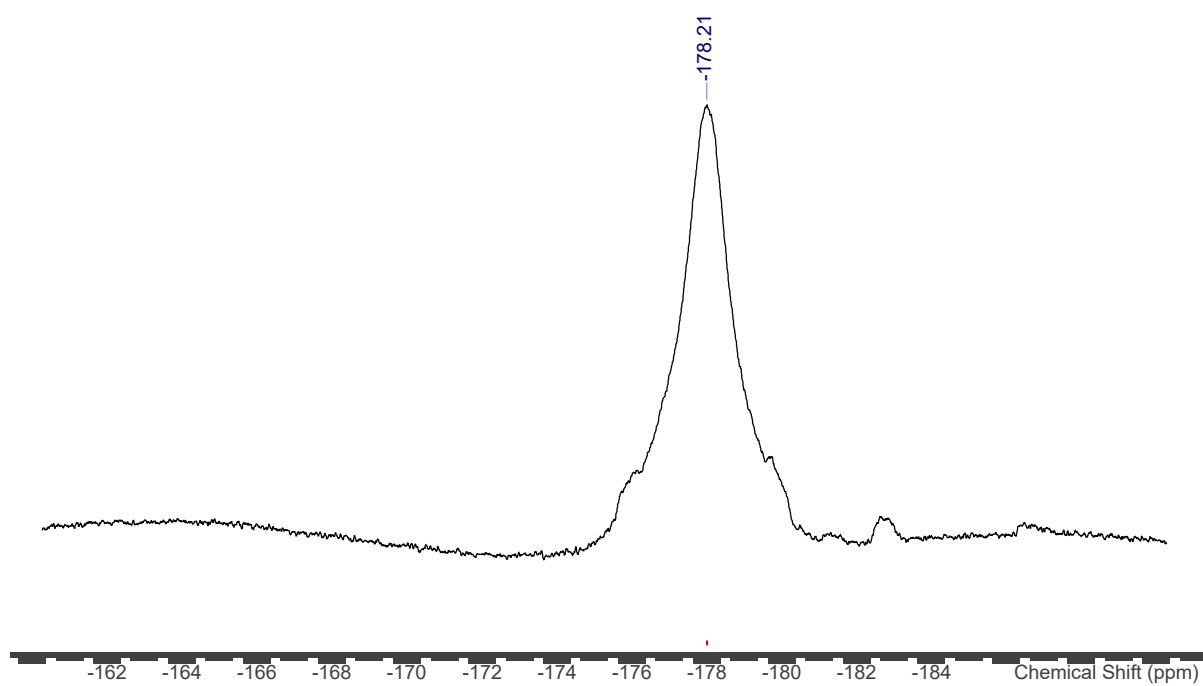
S4.5.a ¹H NMR spectrum (CD₃OD)



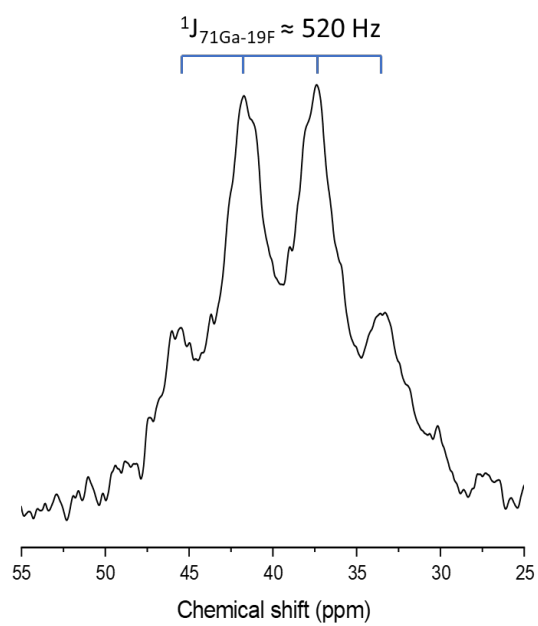
S4.5.b ¹³C{¹H} NMR spectrum (CD₃OD)



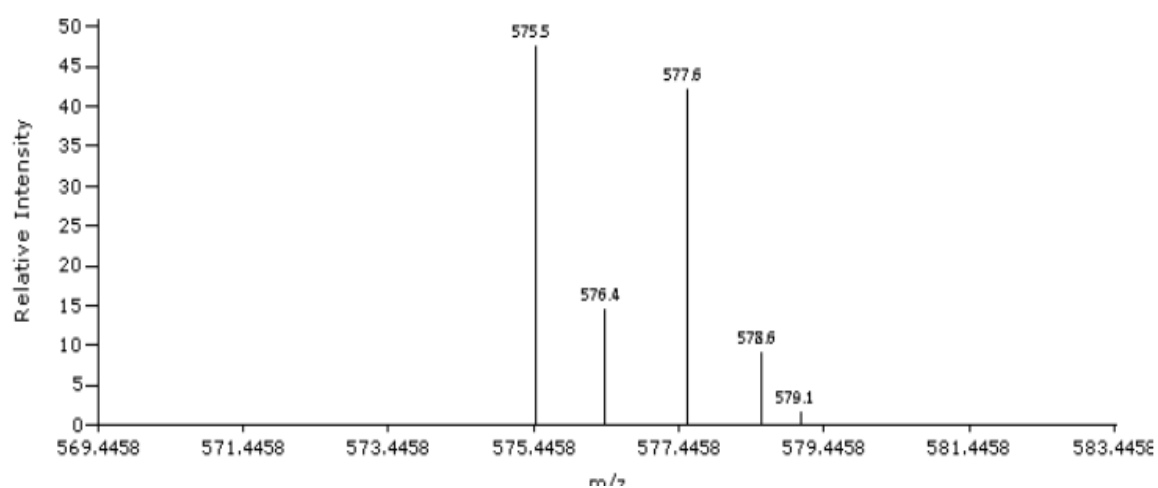
S4.5.c $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.5.d ^{71}Ga NMR spectrum (CD_3OD)



S4.5.e ESI⁺ MS (MeOH)



S4.5.f IR spectrum (Nujol)

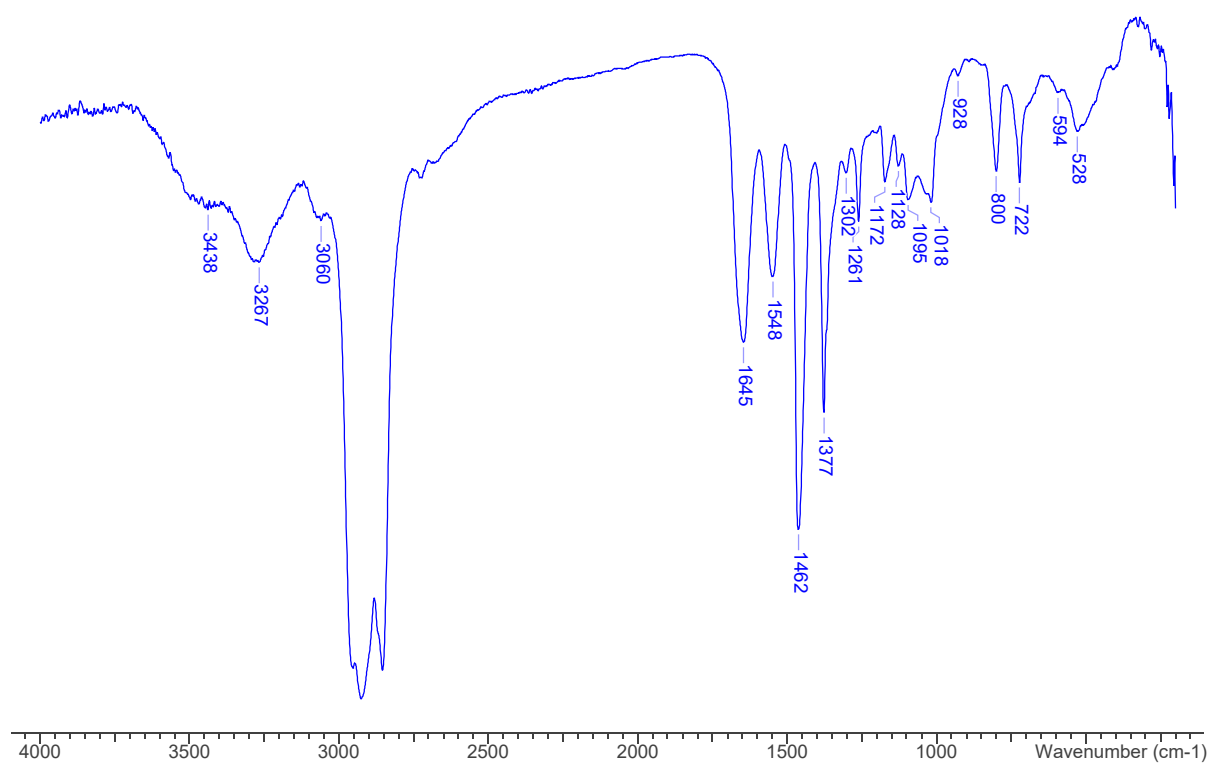
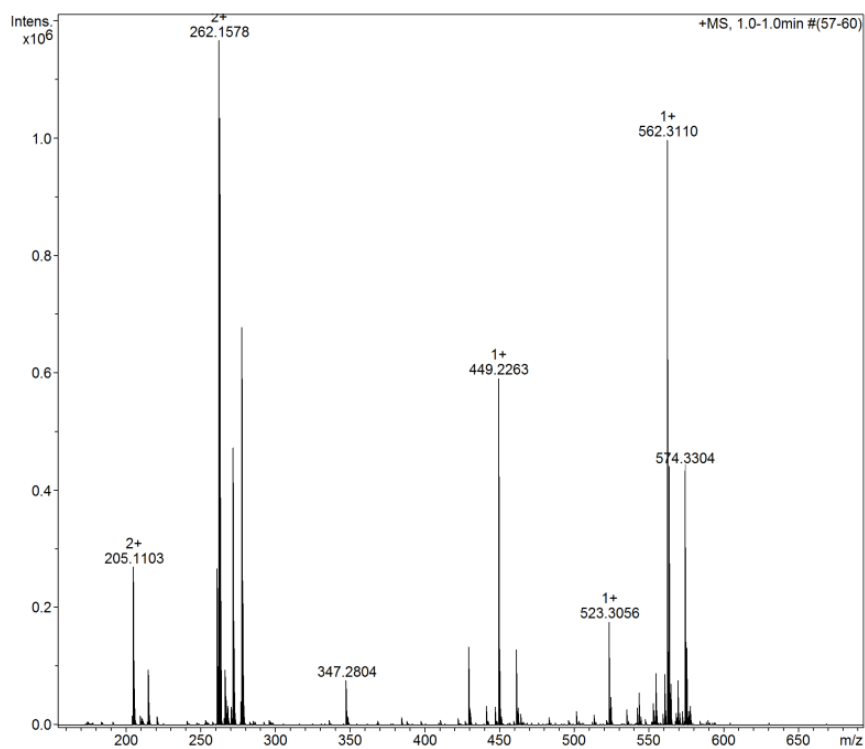


Figure S4.6 [FeF₃(L²)]

S4.6.a ESI⁺ MS (direct injection, MeOH)



S4.6.b IR spectrum (Nujol)

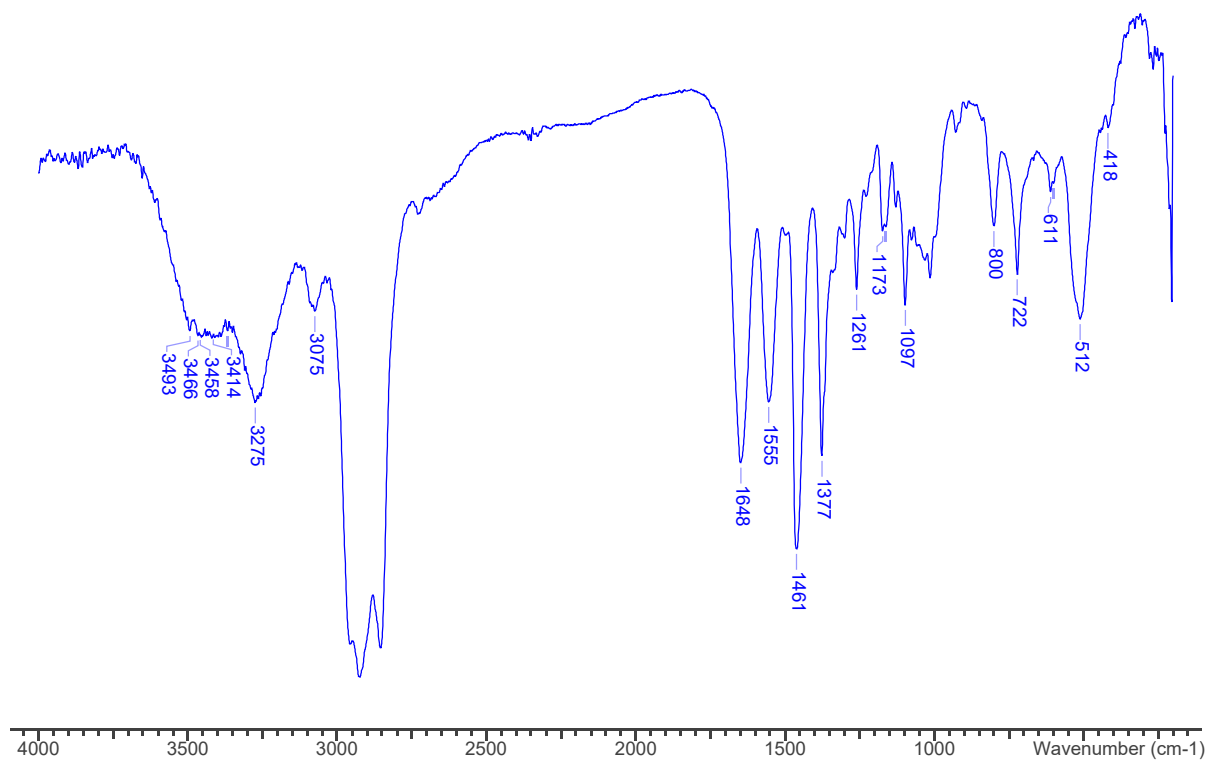
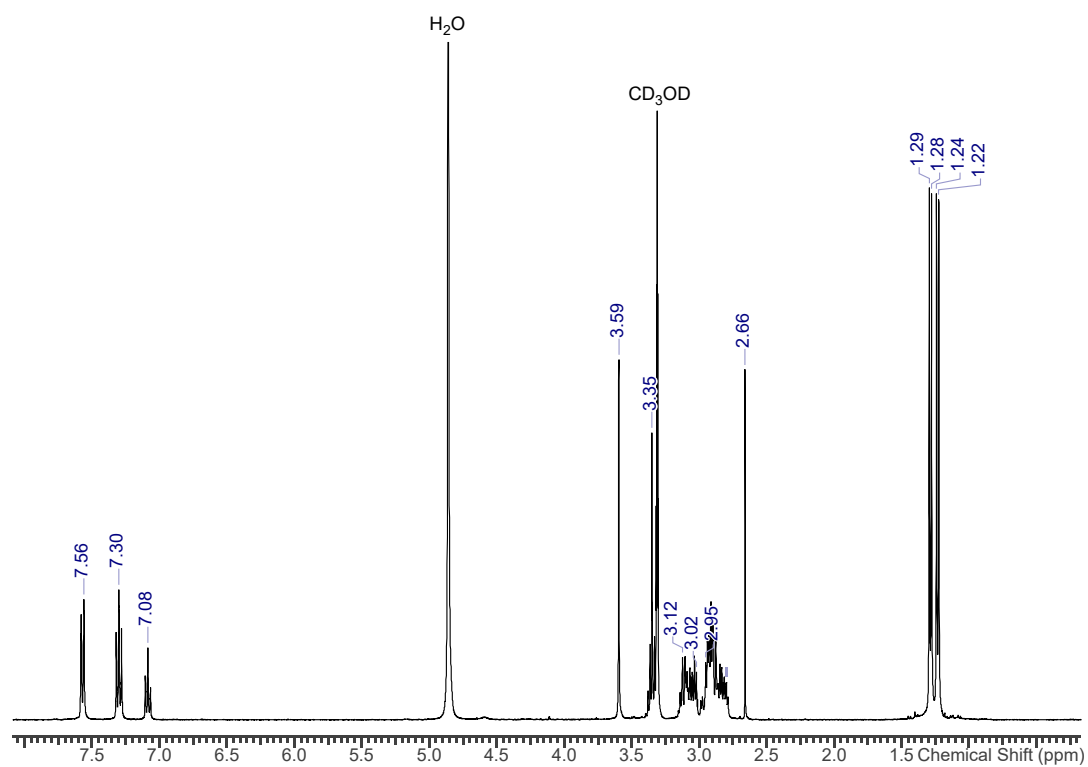
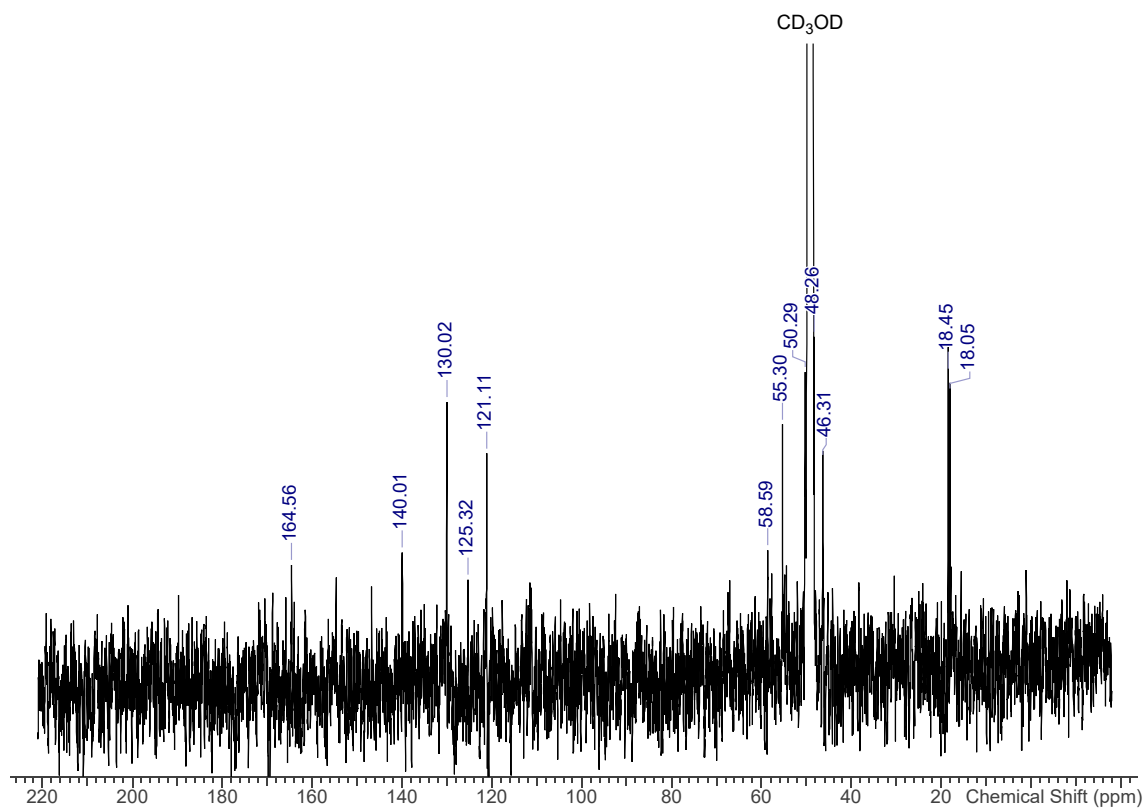


Figure S4.7 [AlF₃(L³)]

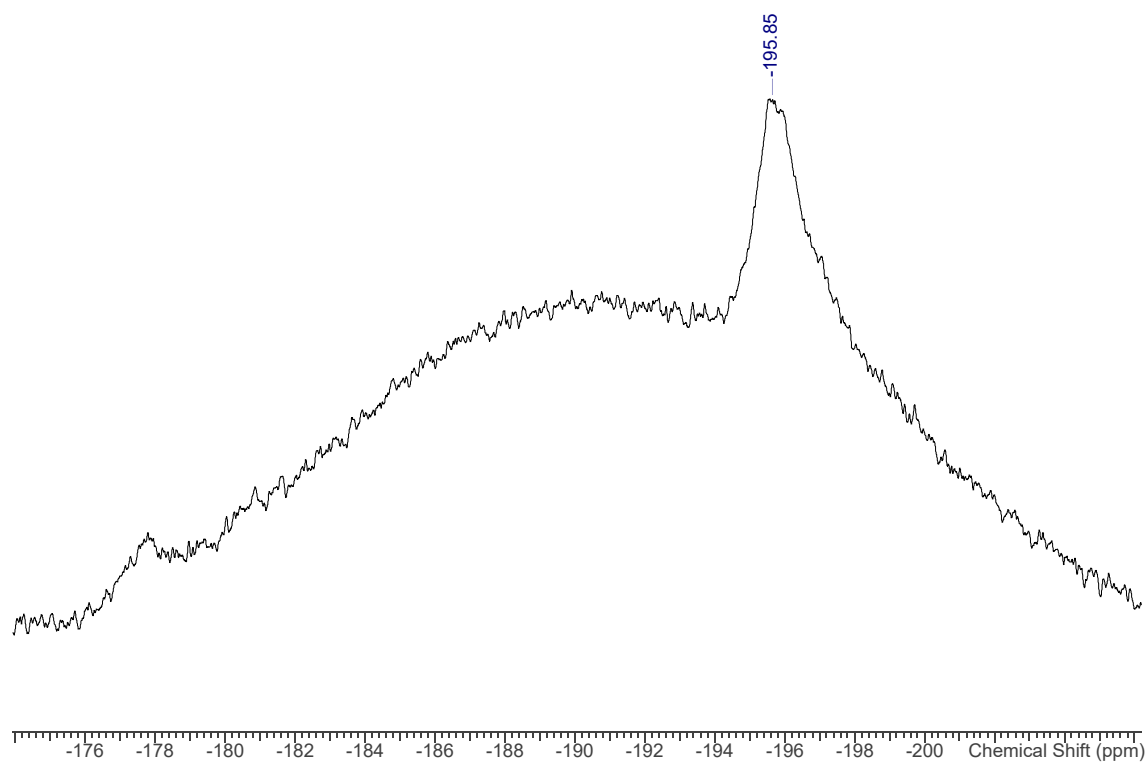
S4.7.a ¹H NMR spectrum (CD₃OD)



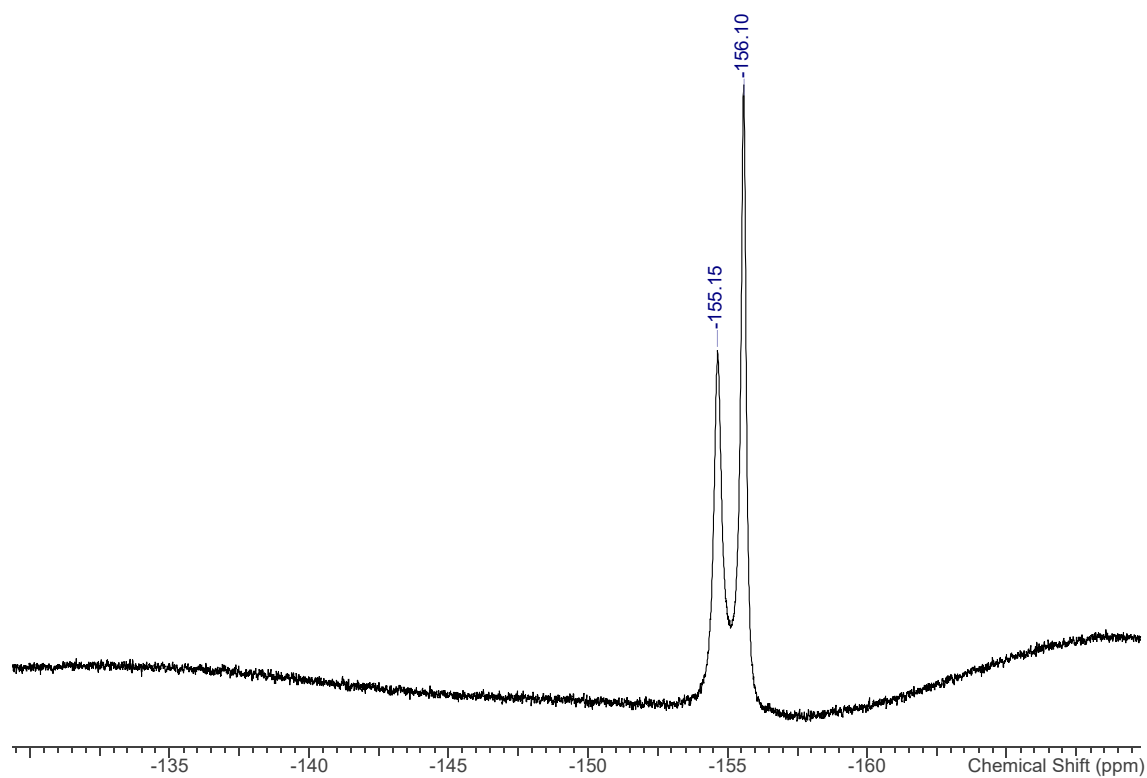
S4.7.b ¹³C{¹H} NMR spectrum (CD₃OD)



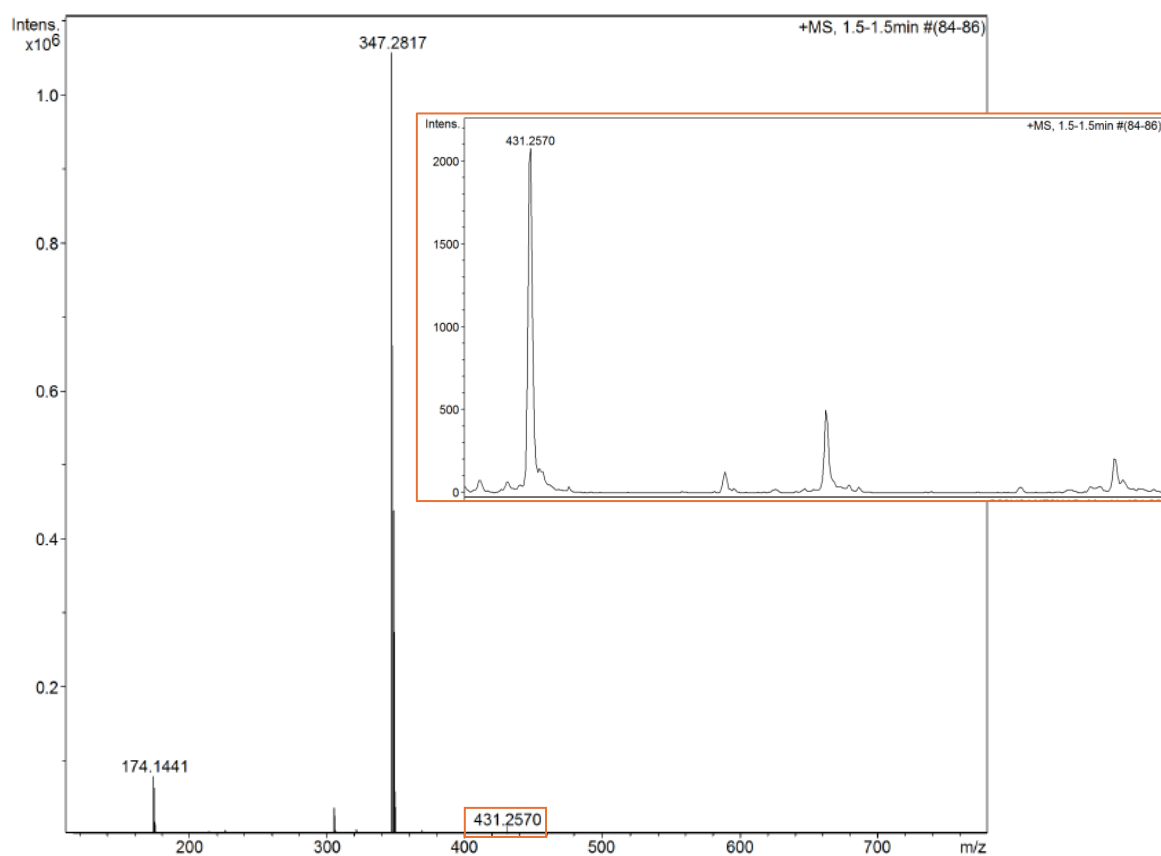
S4.7.c $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



S4.7.d $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O)



S4.7.e ESI⁺ MS (direct injection, MeOH)



S4.7.f IR spectrum (Nujol)

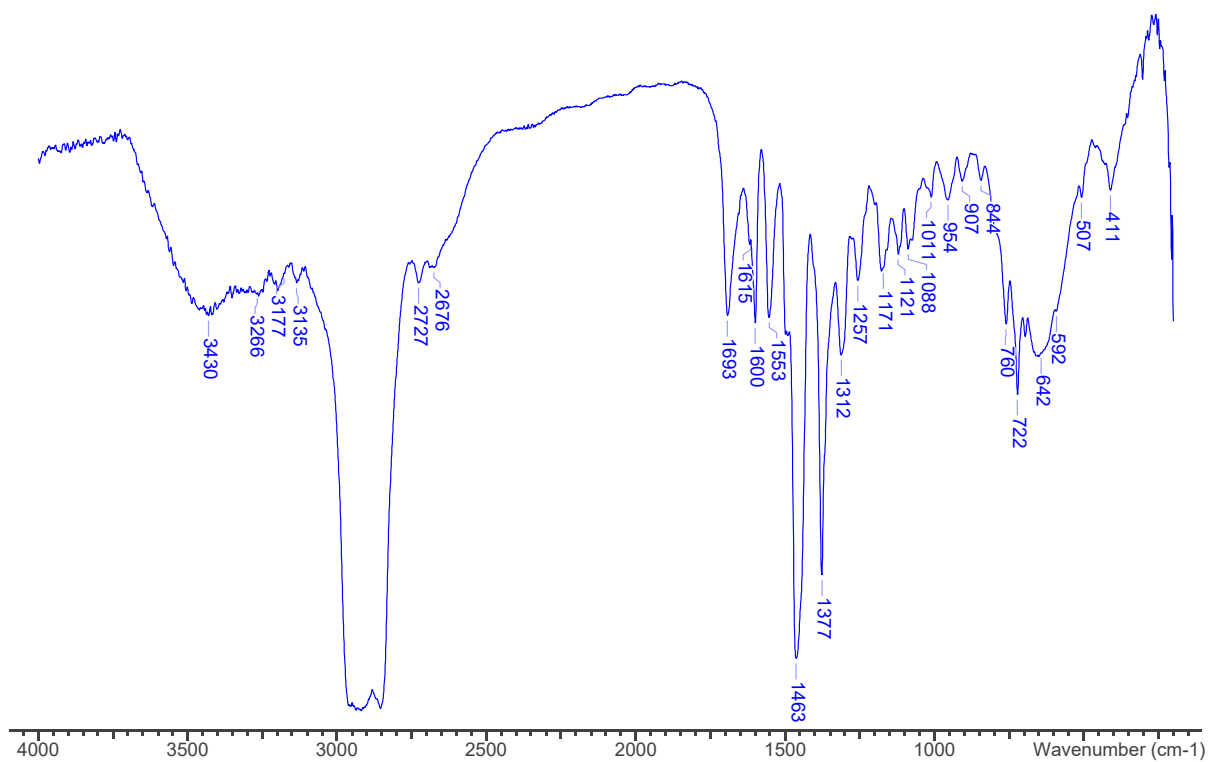
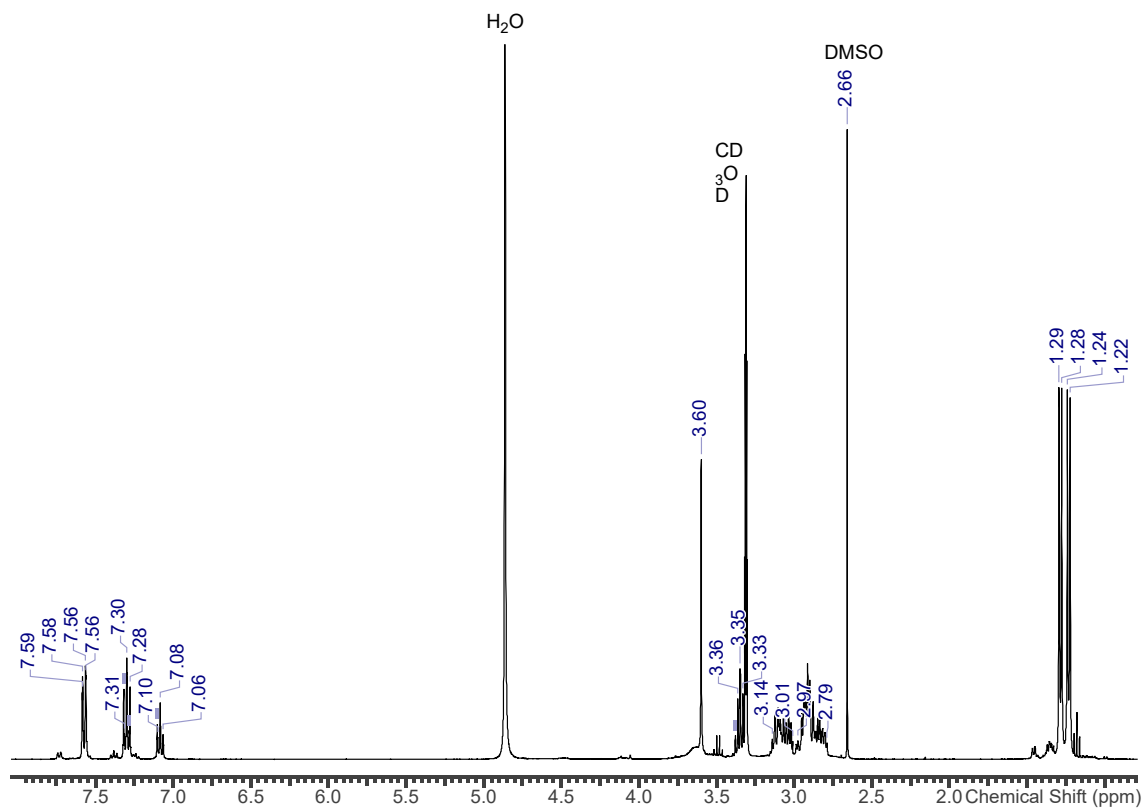
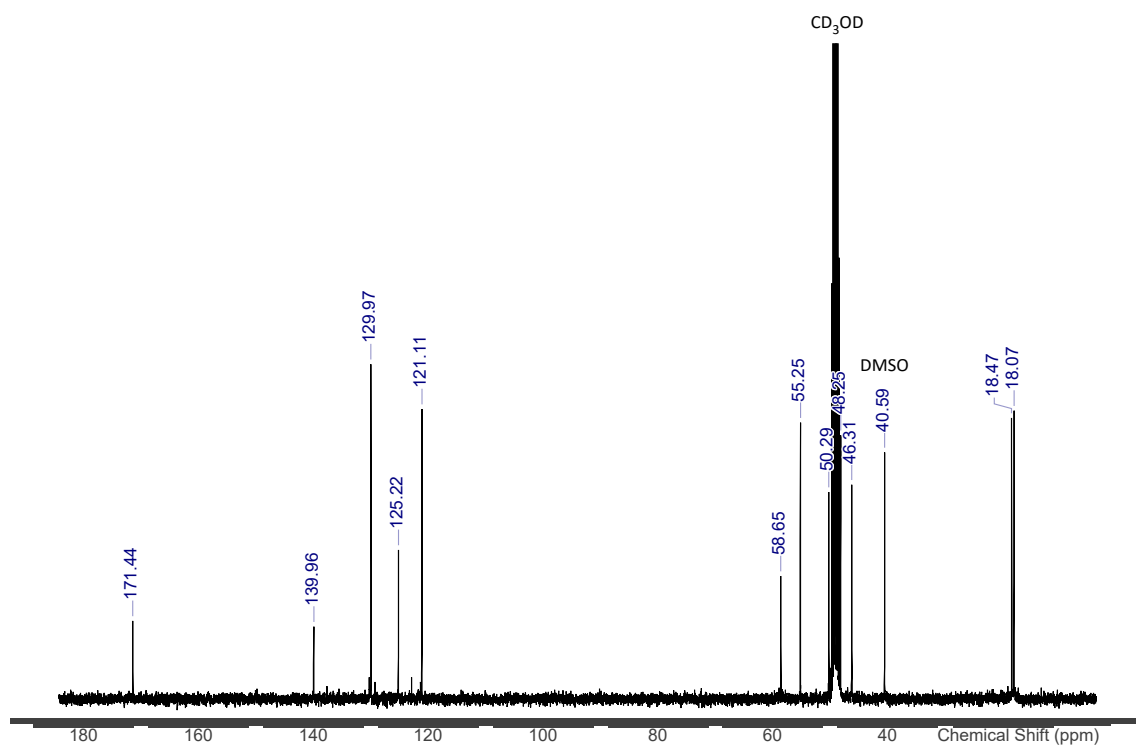


Figure S4.8 [GaF₃(L³)]

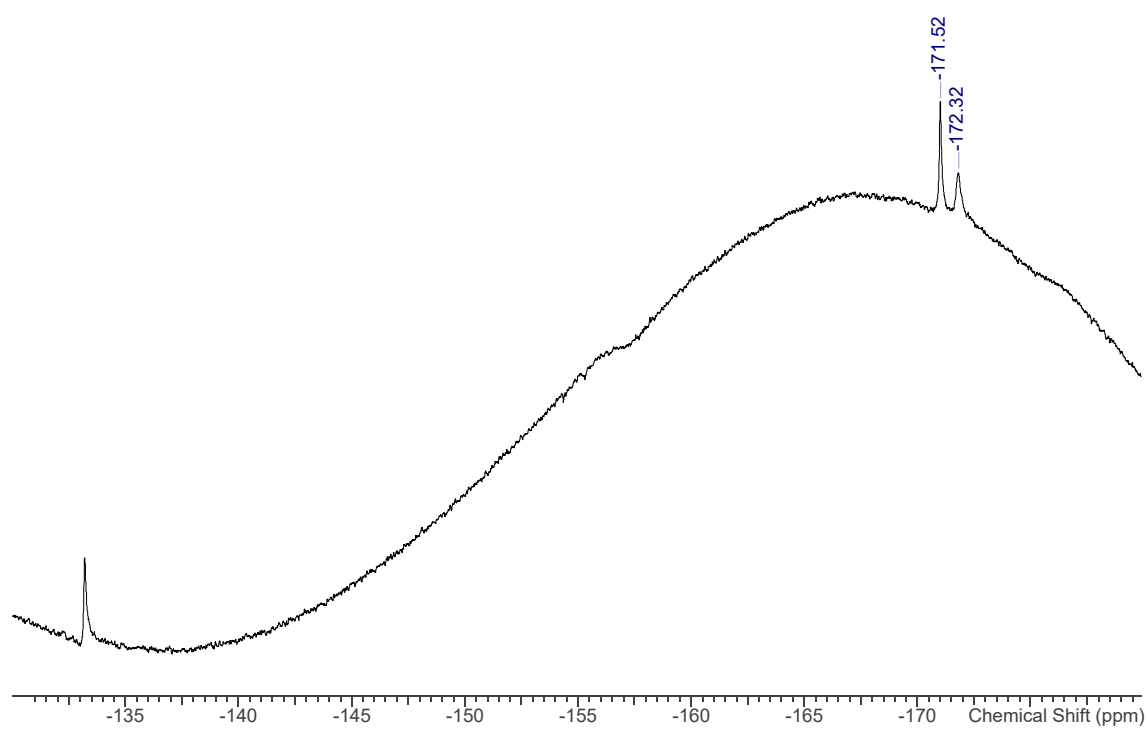
S4.8.a ¹H NMR spectrum (CD₃OD)



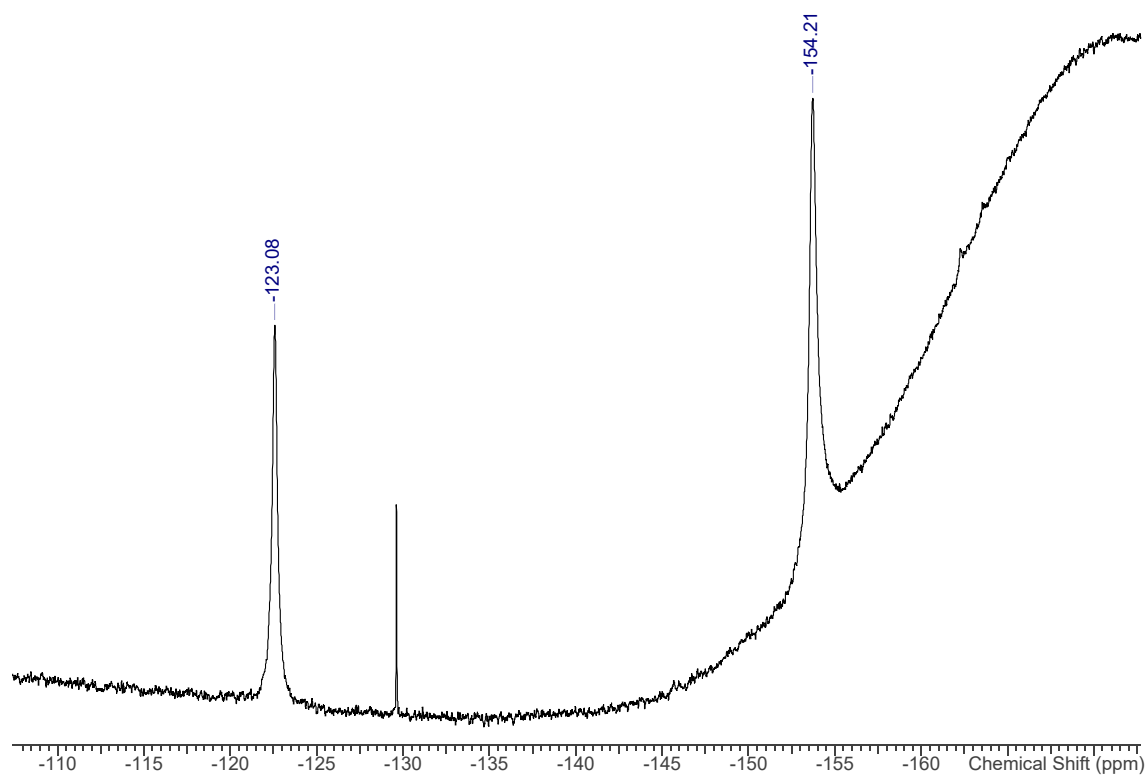
S4.8.b ¹³C{¹H} NMR spectrum (CD₃OD)



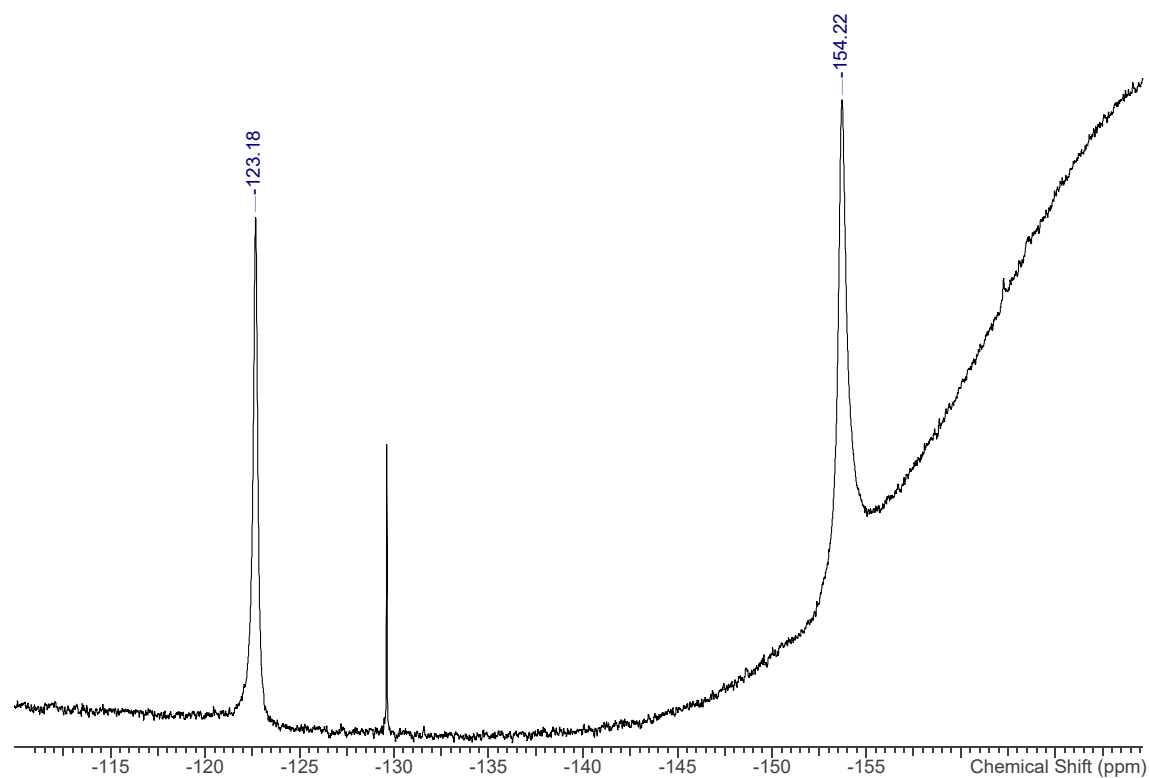
S4.8.c $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)



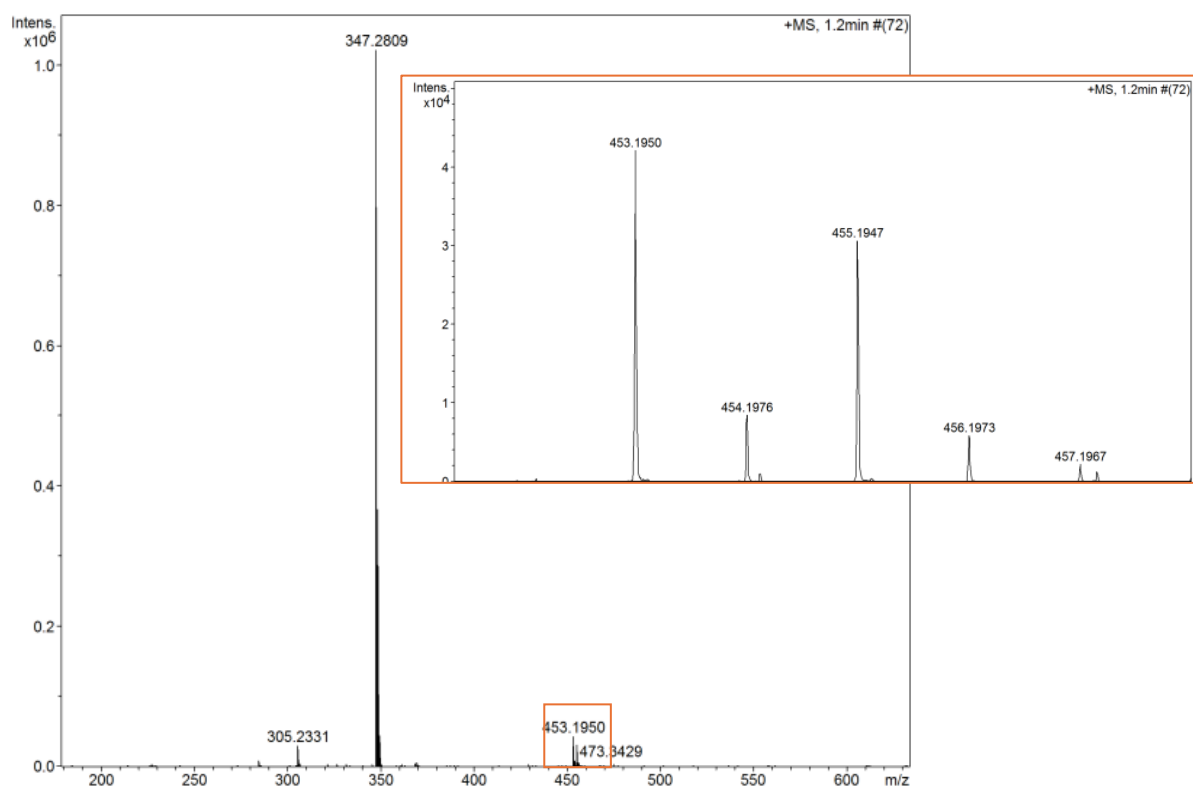
S4.8.d $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O); stability studies, $t = 0$ h



S4.8.e $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O); stability studies, $t = 4\text{ h}$



S4.8.f ESI⁺ MS (direct injection, MeOH)



S4.8.g IR spectrum (Nujol)

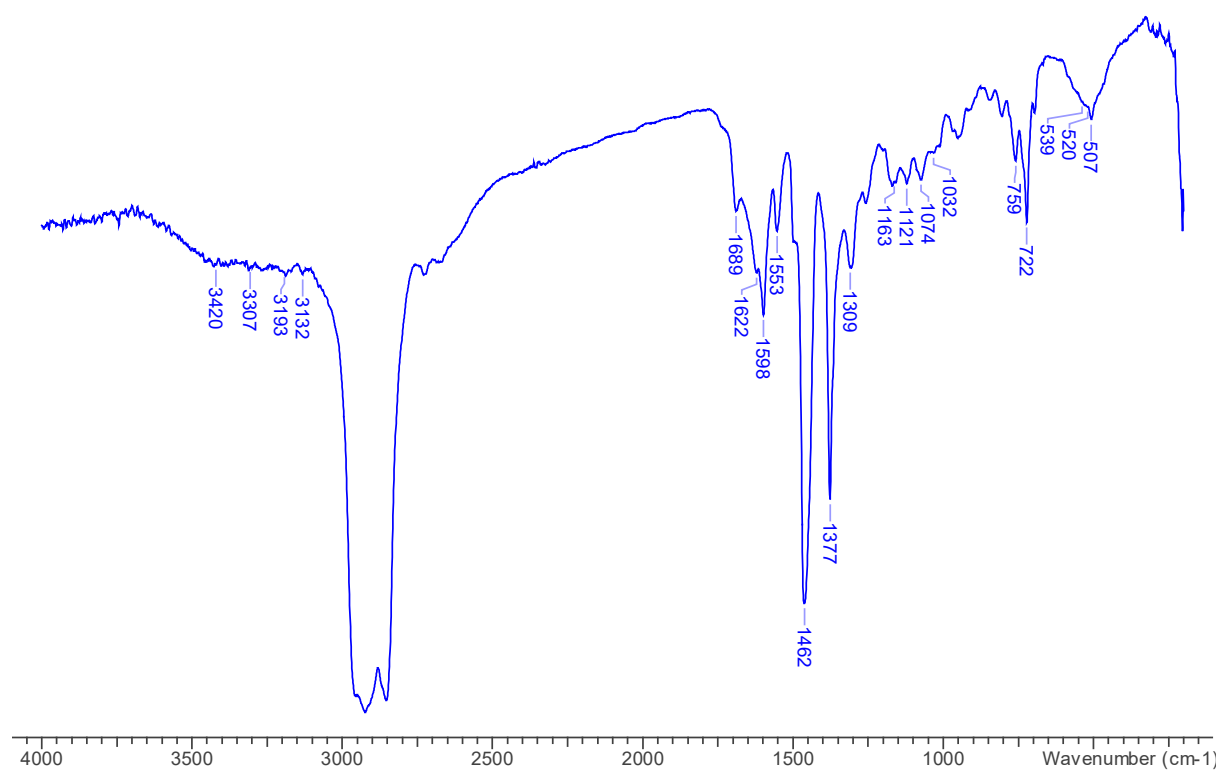
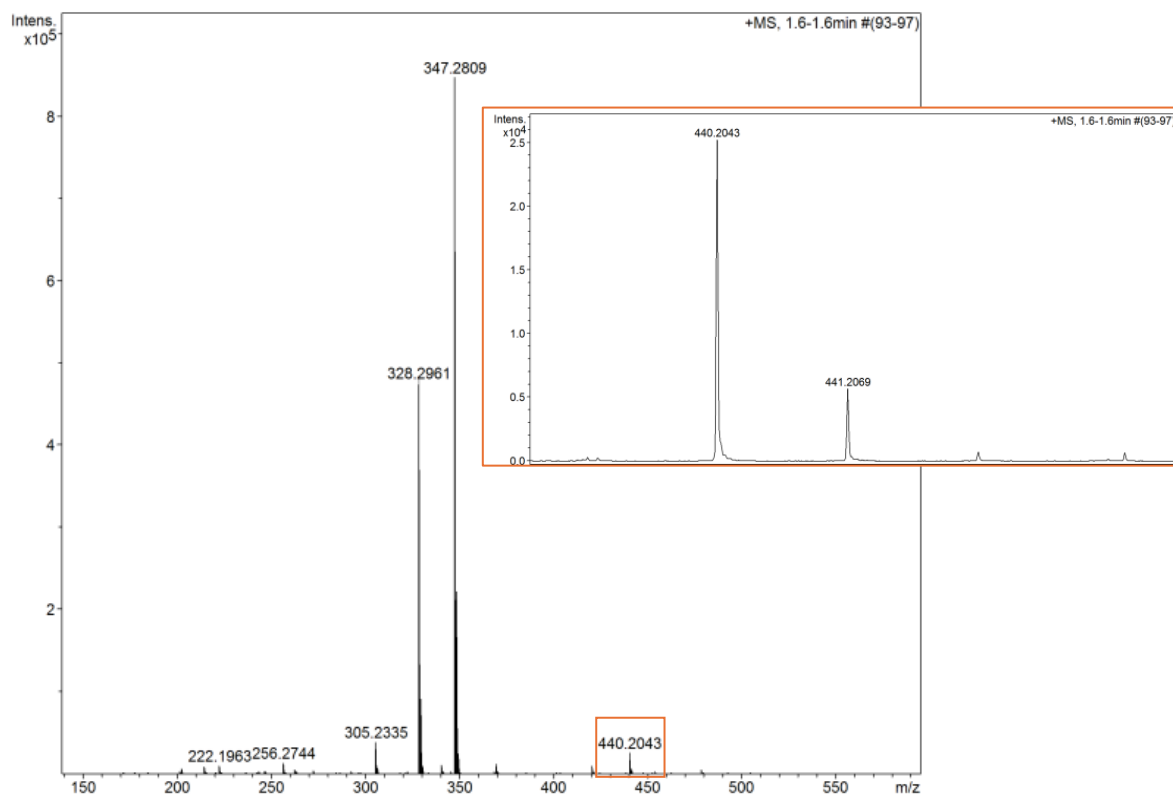
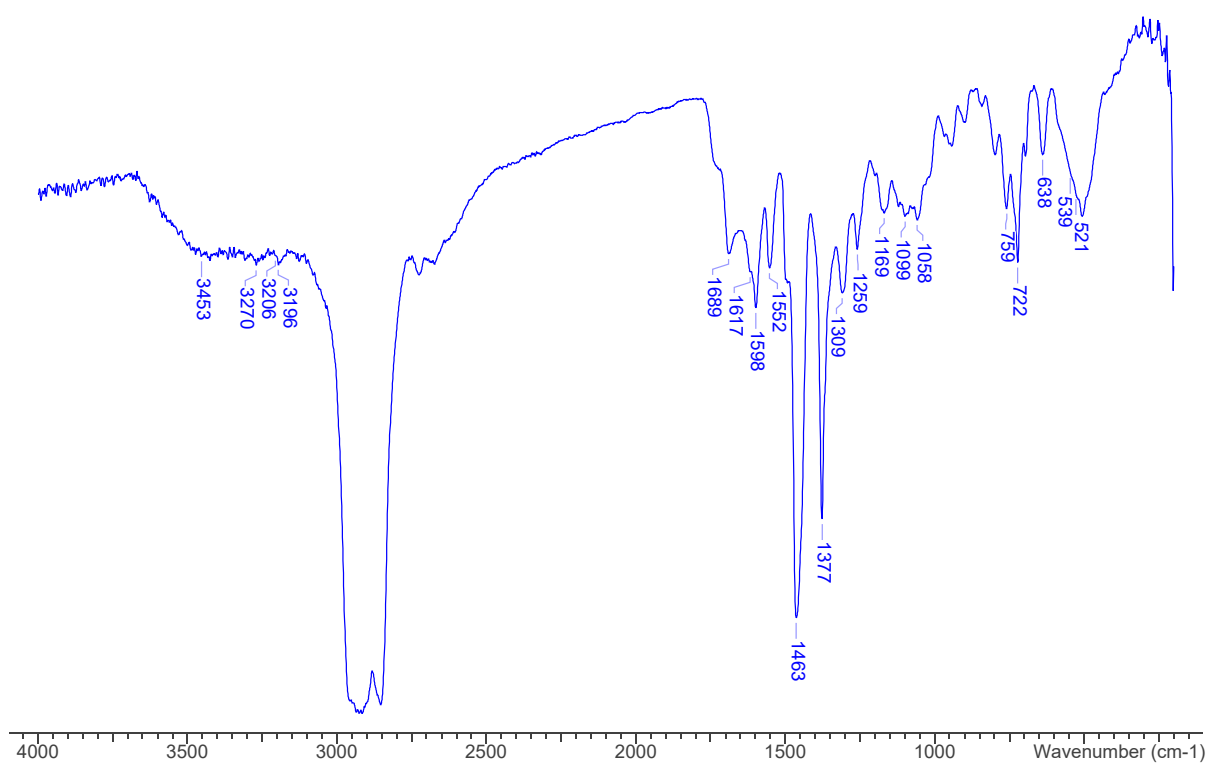


Figure S4.9 [FeF₃(L³)]

S4.9.a ESI⁺ MS (direct injection, MeOH)



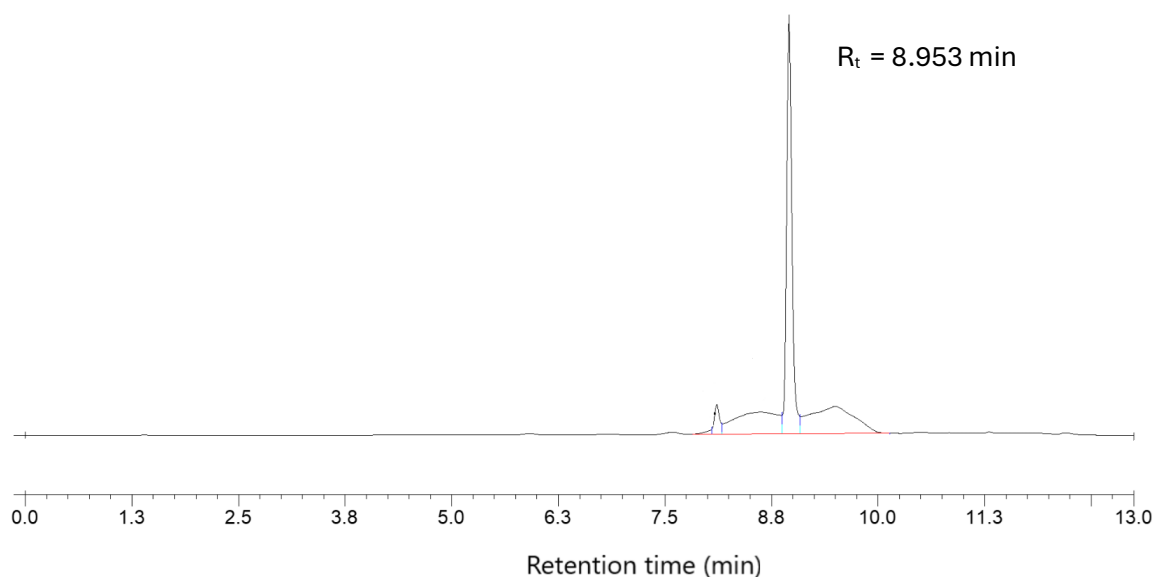
S4.9.b IR spectrum (Nujol)



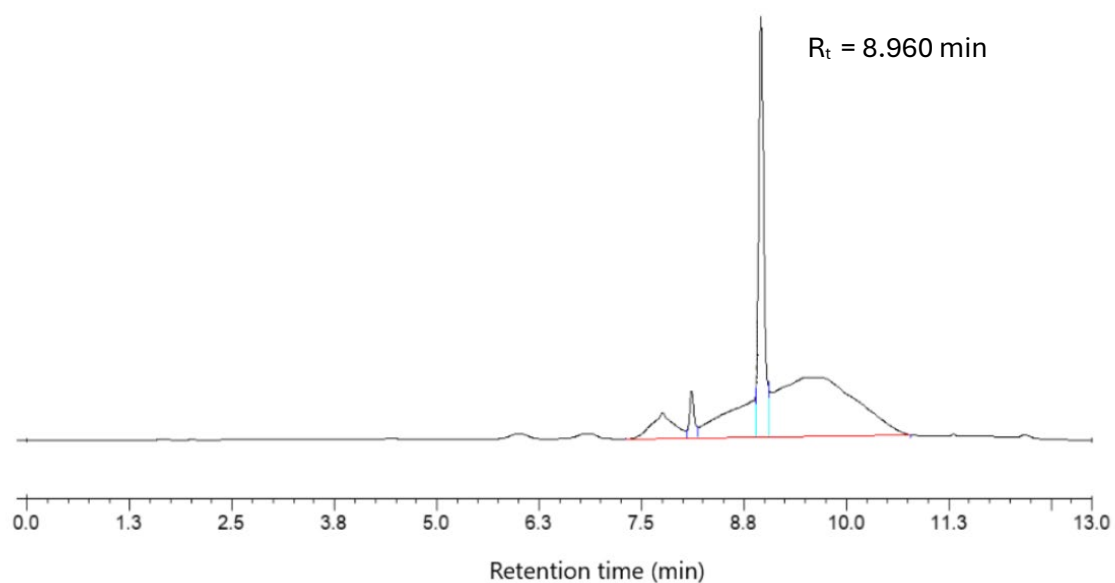
Chapter 5

Figure S5.1 Analytical HPLC traces from stability tests of $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$

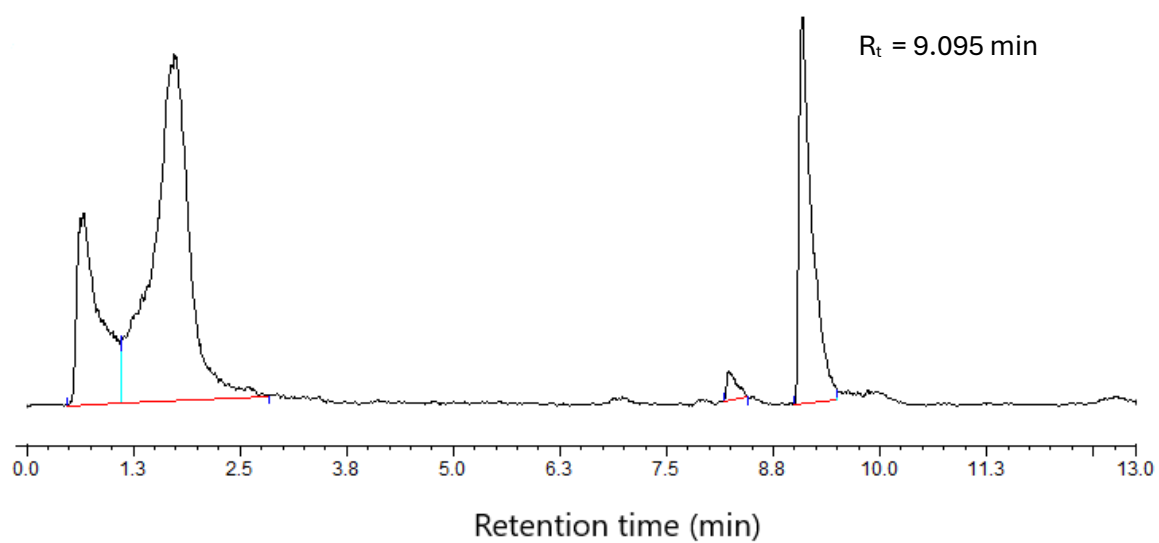
S5.1.a Analytical UV-HPLC trace of $[\text{GaF}_3(\text{L}^1)]$ reference standard analysed on Agilent 1290 HPLC system



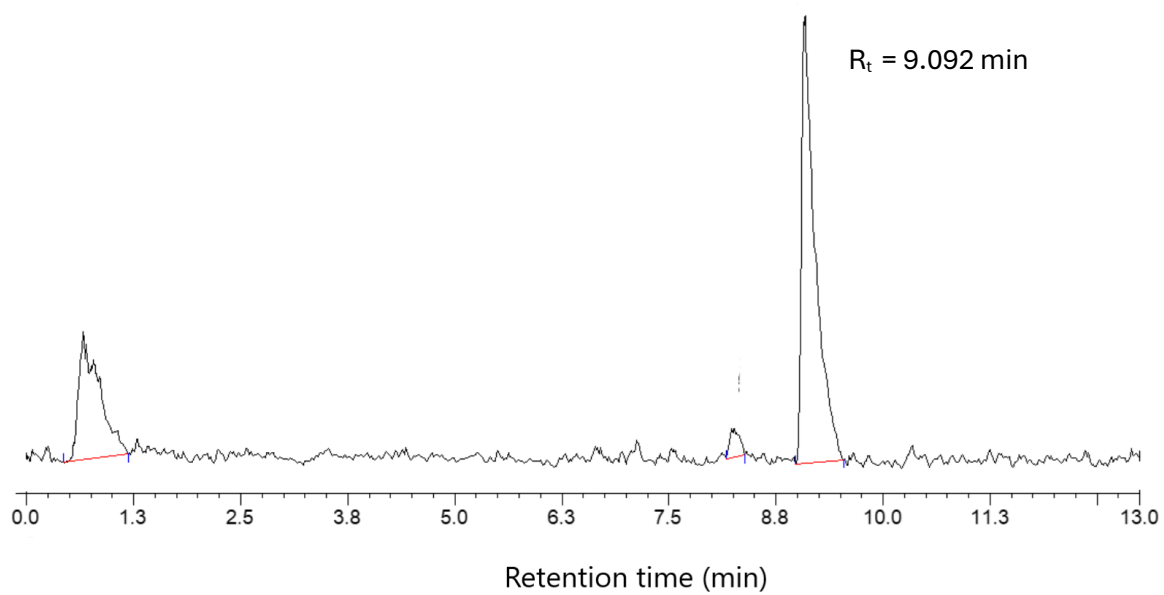
S5.1.b Analytical UV- (top) and radio- (bottom) HPLC traces of crude $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$ prior to SPE purification



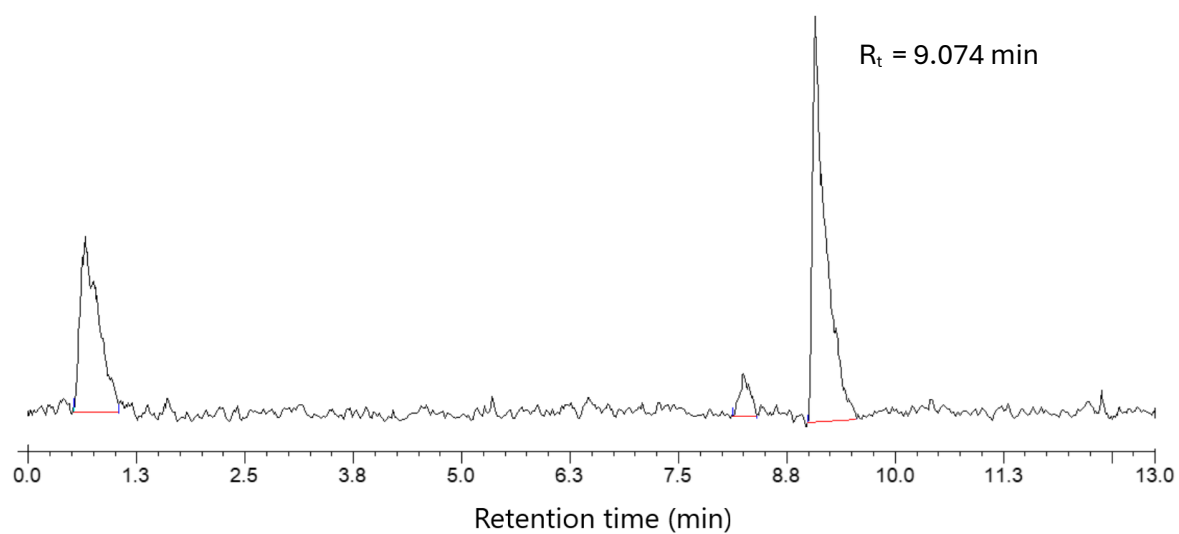
S5.1.c Analytical radio-HPLC trace of $[Ga^{18}FF_2(L^1)]$ at $t = 0$ min. in 10:90 EtOH:H₂O



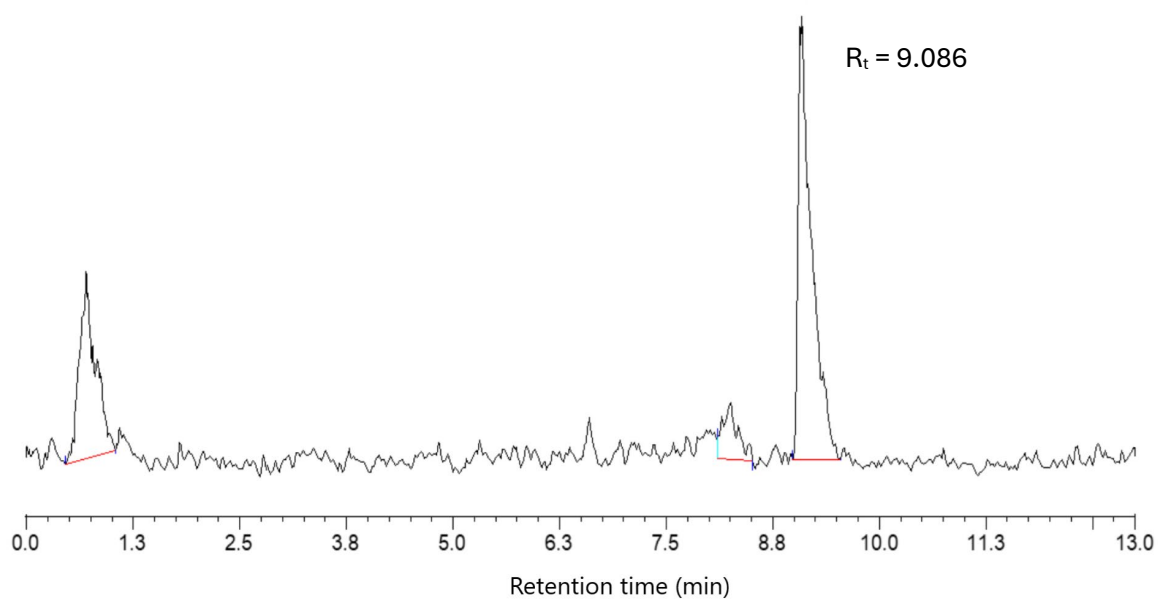
S5.1.d Analytical radio-HPLC trace of $[Ga^{18}FF_2(L^1)]$ at $t = 30$ min. in 10:90 EtOH:H₂O



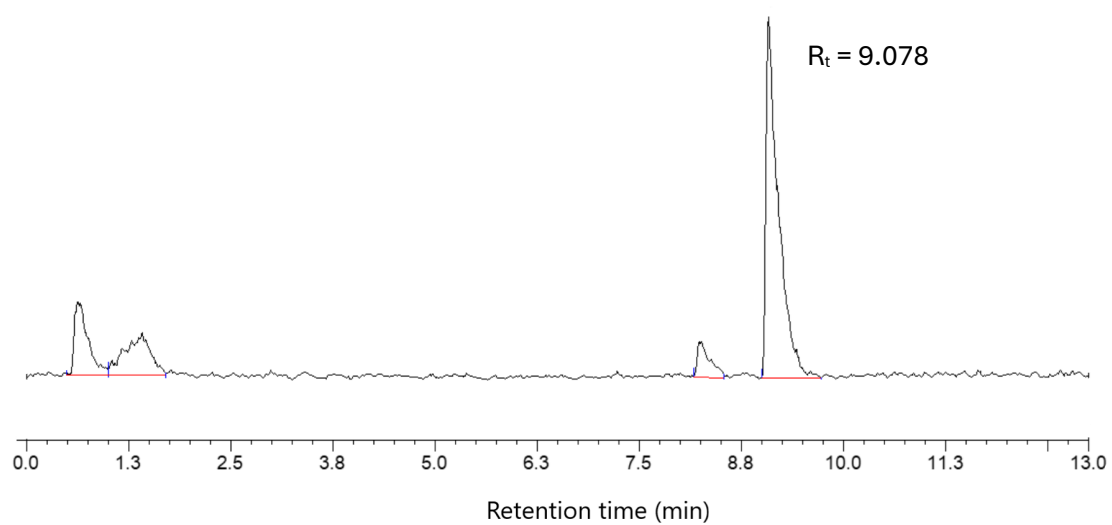
S5.1.e Analytical radio-HPLC trace of $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$ at $t = 80$ min. in 10:90 EtOH:H₂O



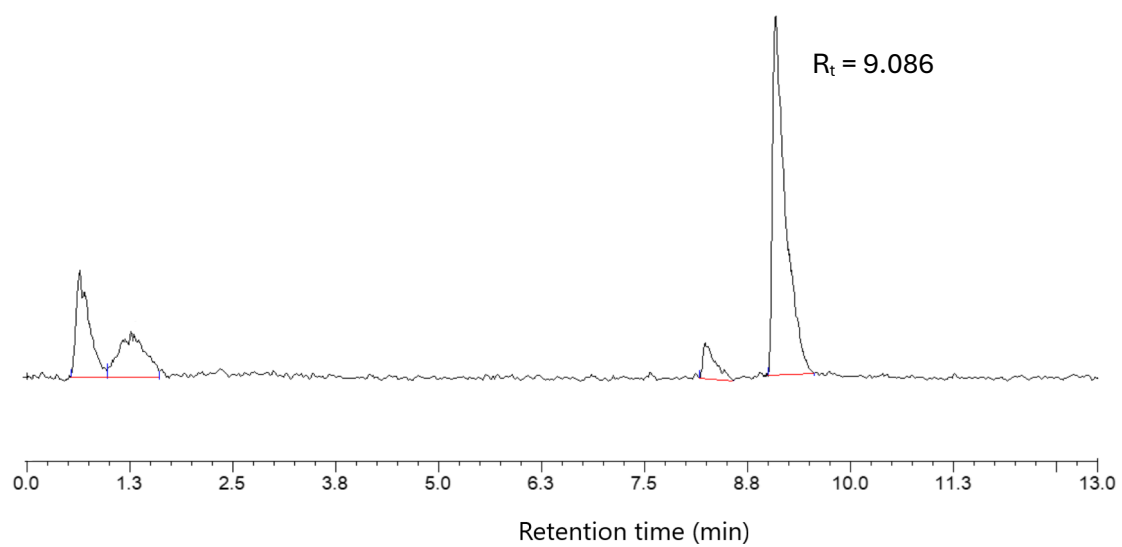
S5.1.f Analytical radio-HPLC trace of $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$ at $t = 120$ min. in 10:90 EtOH:H₂O



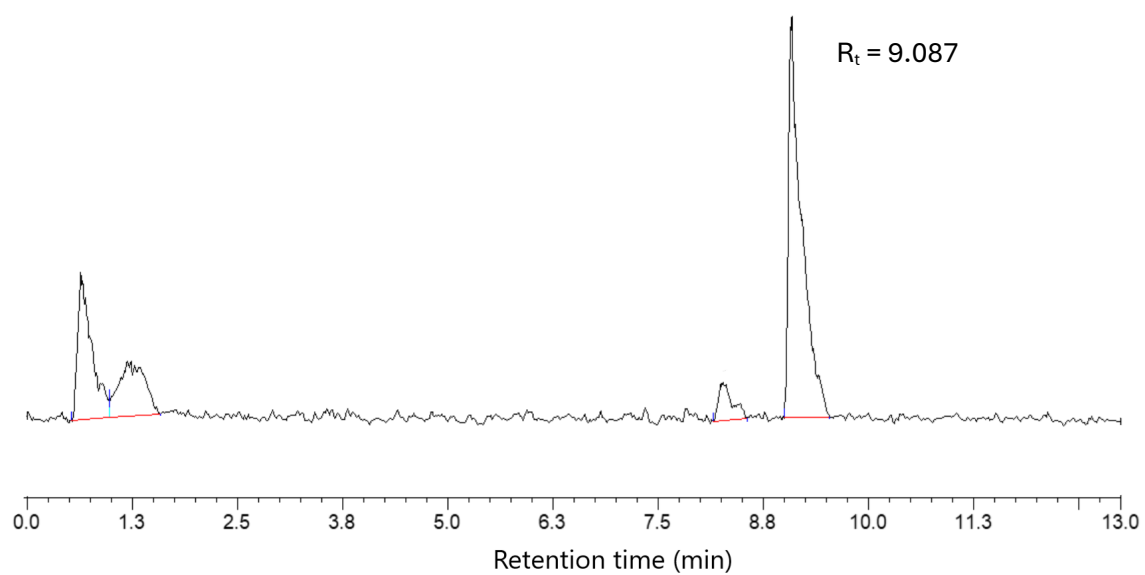
S5.1.g Analytical radio-HPLC trace of $[Ga^{18}FF_2(L^1)]$ at $t = 0$ min. in 10:90 EtOH:PBS



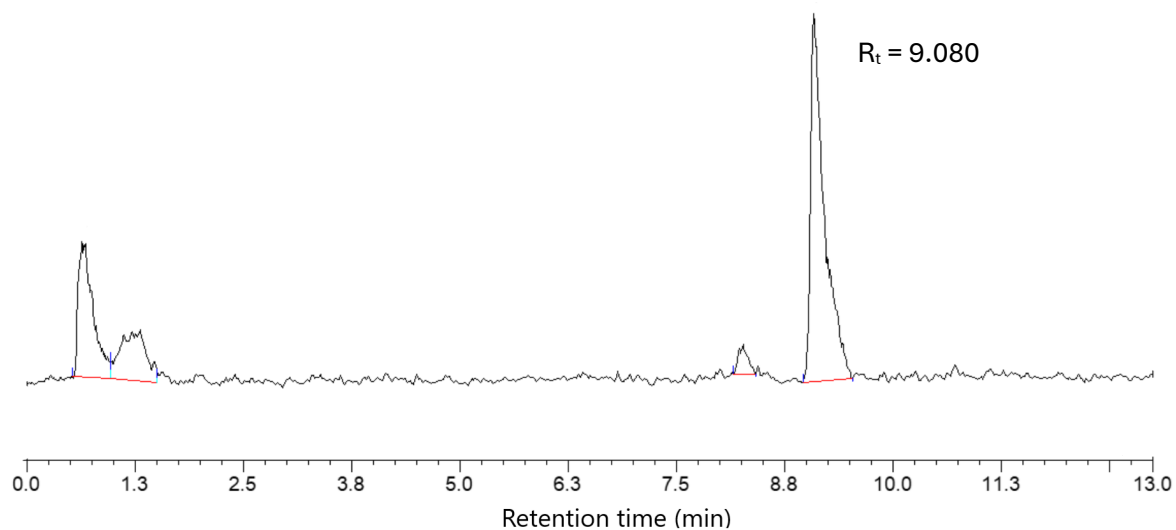
S5.1.h Analytical radio-HPLC trace of $[Ga^{18}FF_2(L^1)]$ at $t = 30$ min. in 10:90 EtOH:PBS



S5.1.i Analytical radio-HPLC trace of $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$ at $t = 80$ min. in 10:90 EtOH:PBS



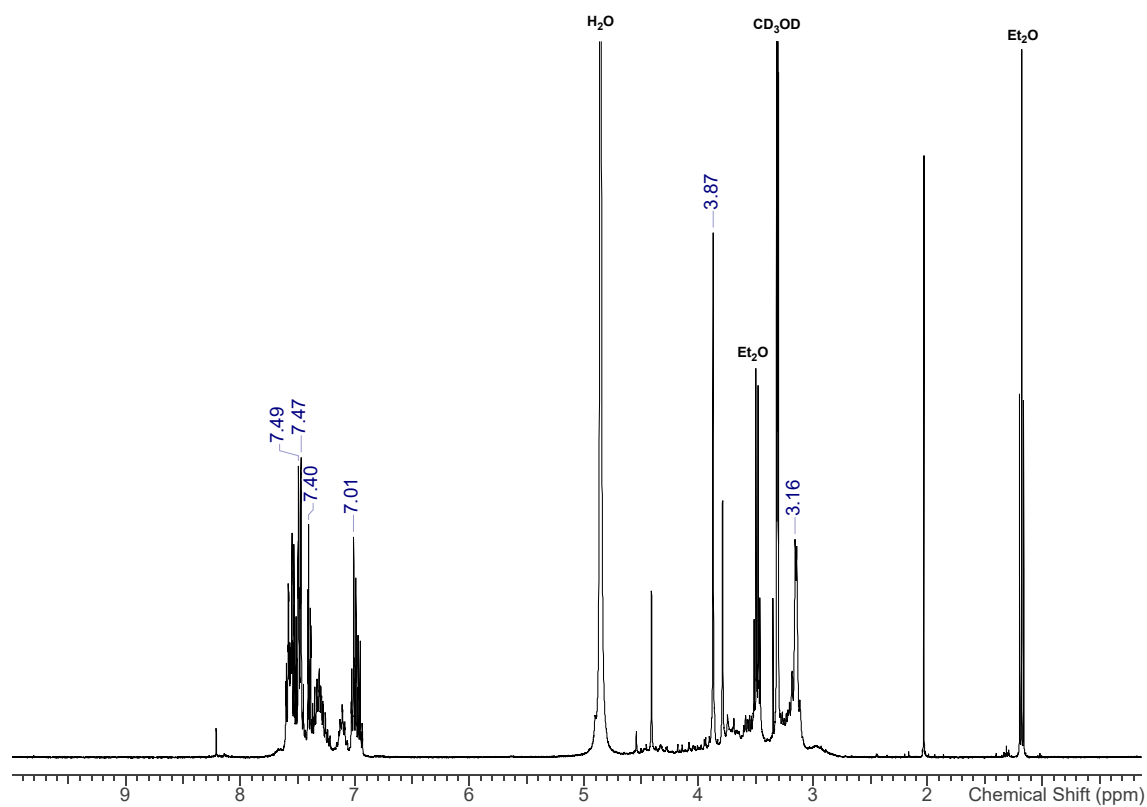
S5.1.j Analytical radio-HPLC trace of $[\text{Ga}^{18}\text{FF}_2(\text{L}^1)]$ at $t = 120$ min. in 10:90 EtOH:PBS



Chapter 6

Figure S6.1 $[\text{Ga}(\text{L}^1)][\text{NO}_3]_3$

S6.1.a ^1H NMR spectrum (CD_3OD)



S6.1.b IR spectrum (Nujol)

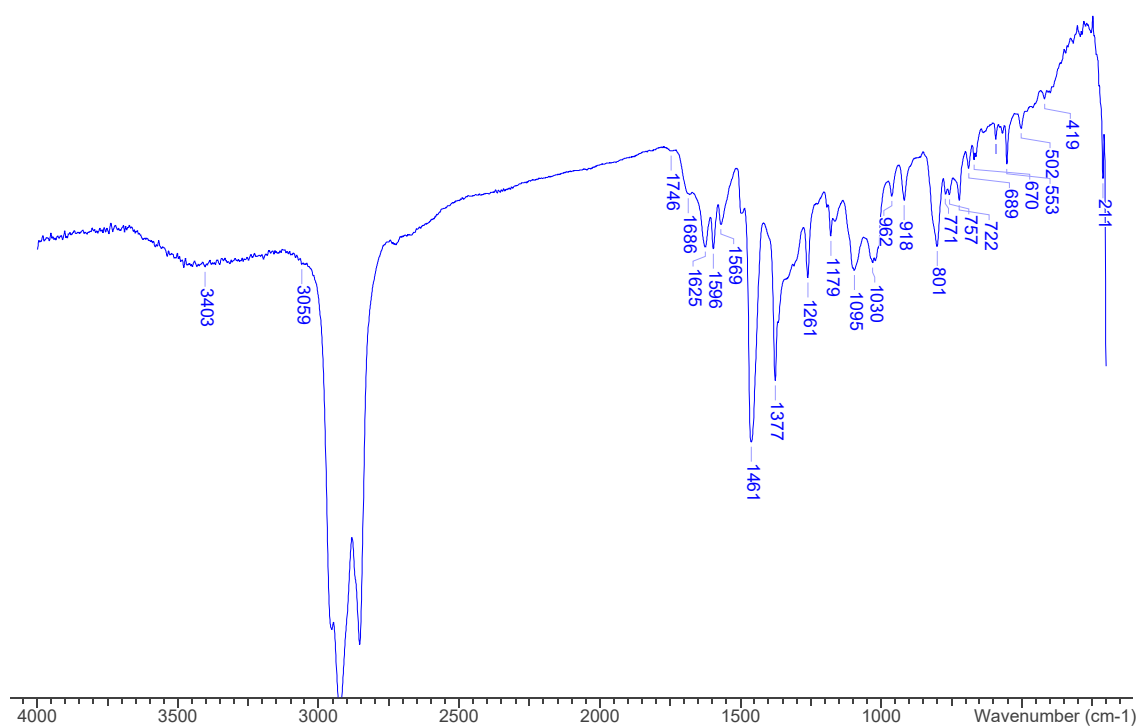
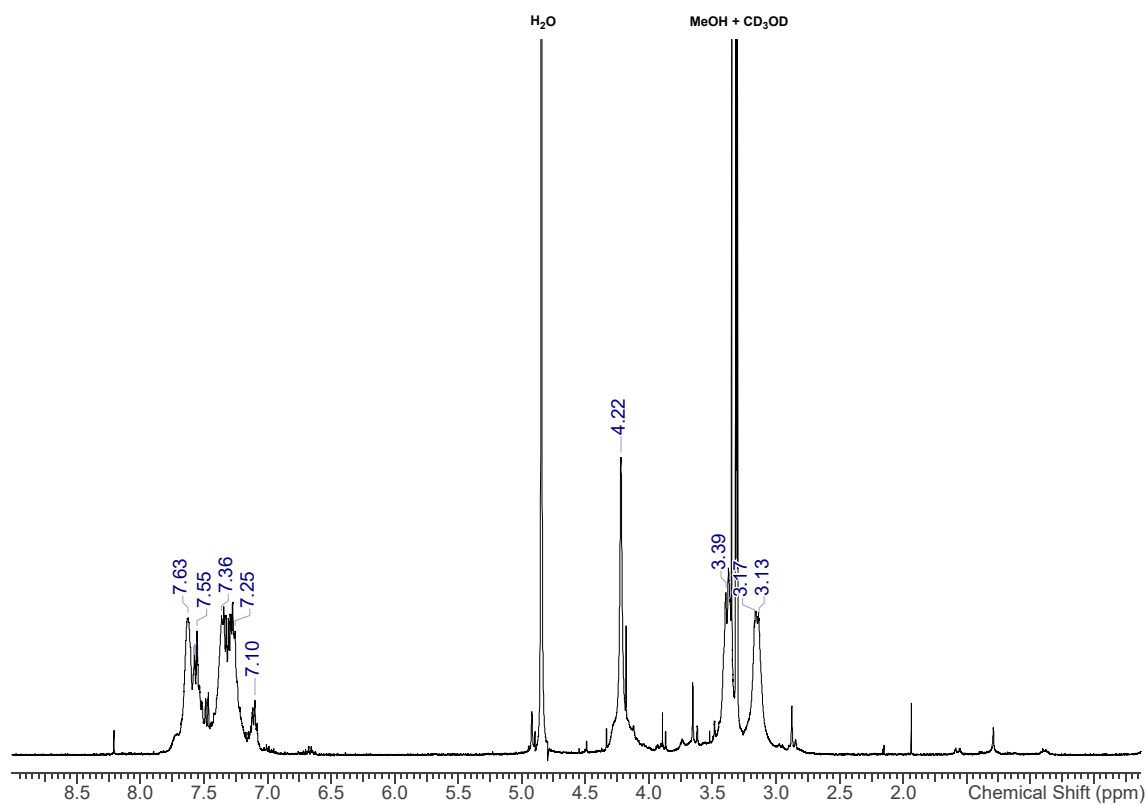


Figure S6.2 [In(L¹)]([NO₃)₃]

S6.2.a ¹H NMR spectrum (CD₃OD)



S6.2.b IR spectrum (Nujol)

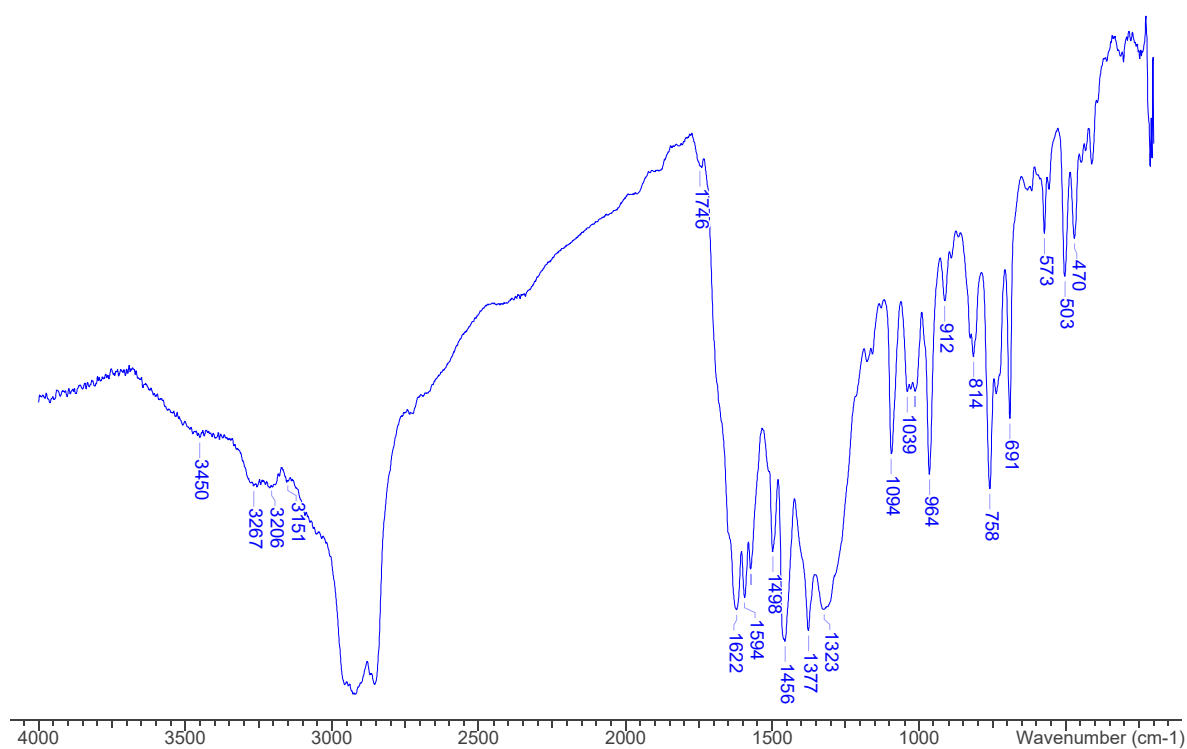
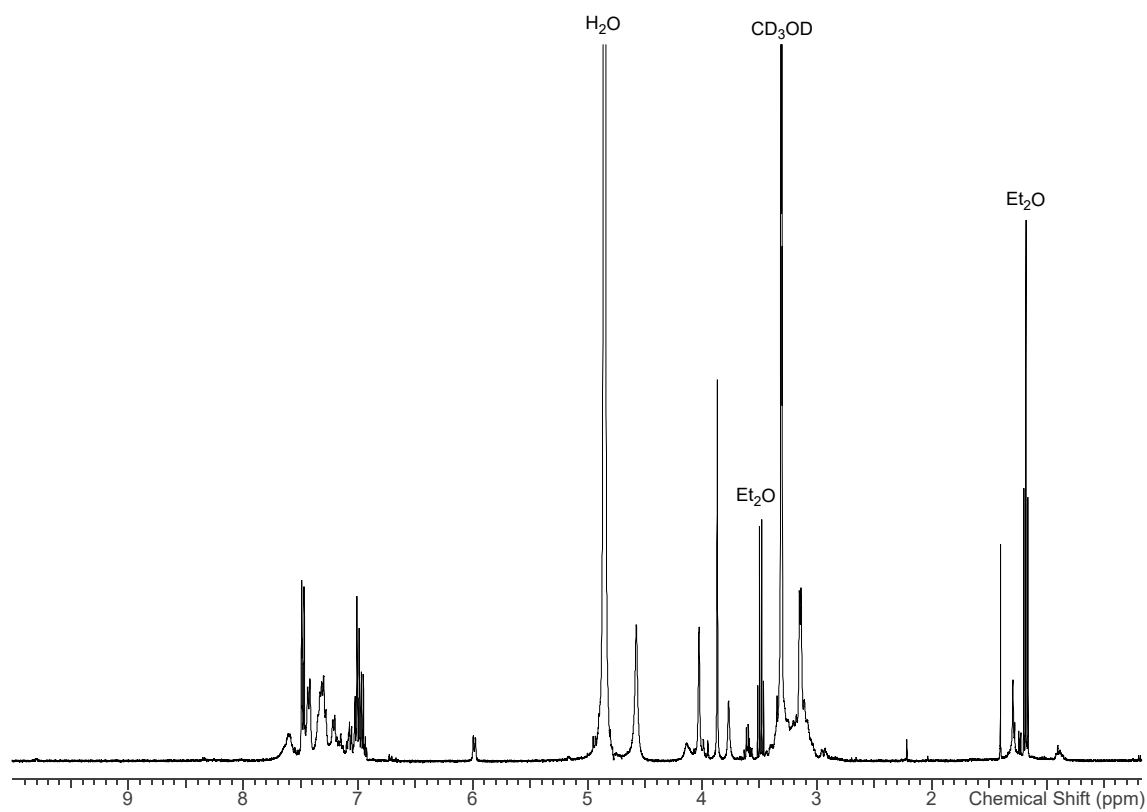


Figure S6.3 Attempted Fluorination of [In(L¹)](NO₃)₃

S6.3.a ¹H NMR spectrum (CD₃OD)



S6.3.b $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3OD)

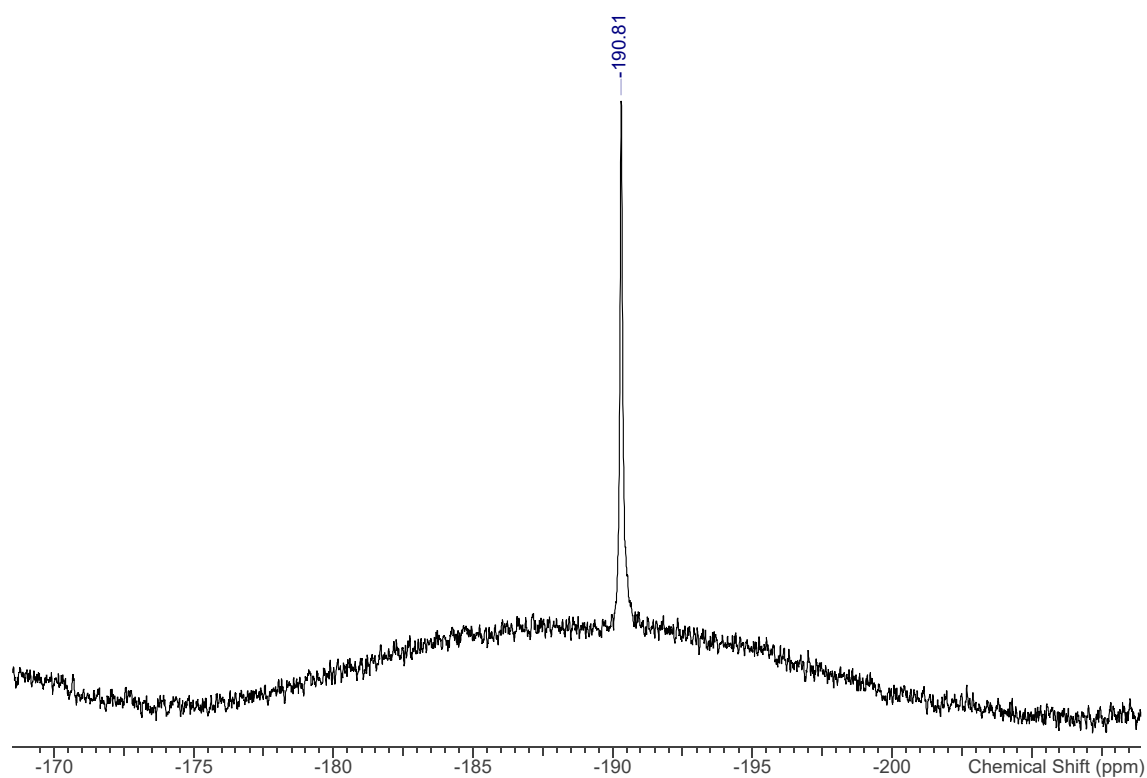


Figure S6.4 Attempted Formation of $[\text{InF}_3(\text{L}^3)]$ via $\text{In}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

S6.4.a ^1H NMR spectrum (CD_3OD)

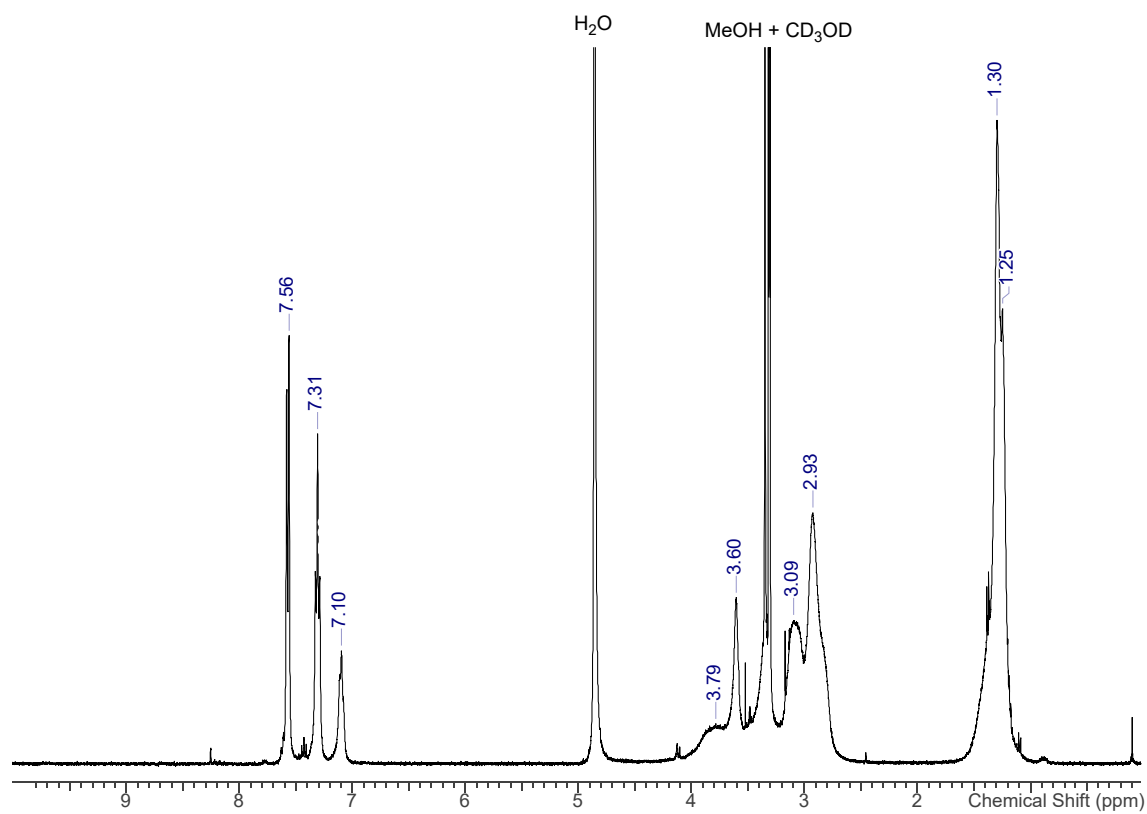
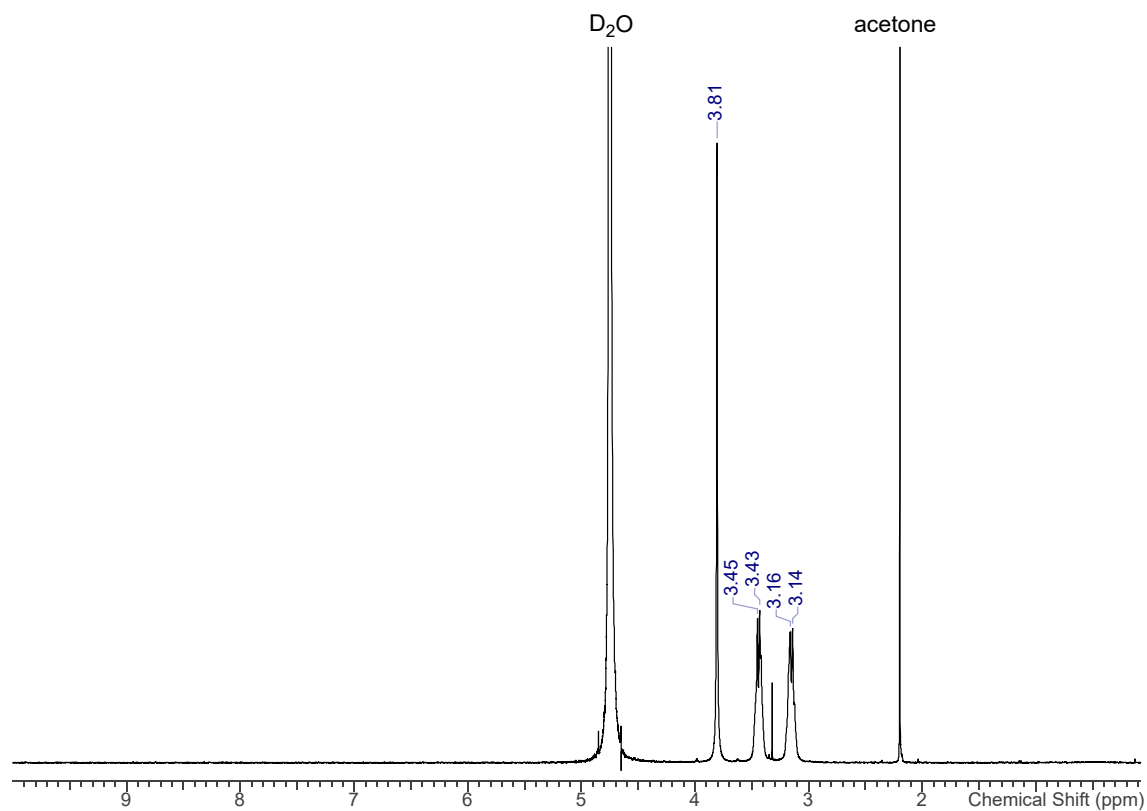
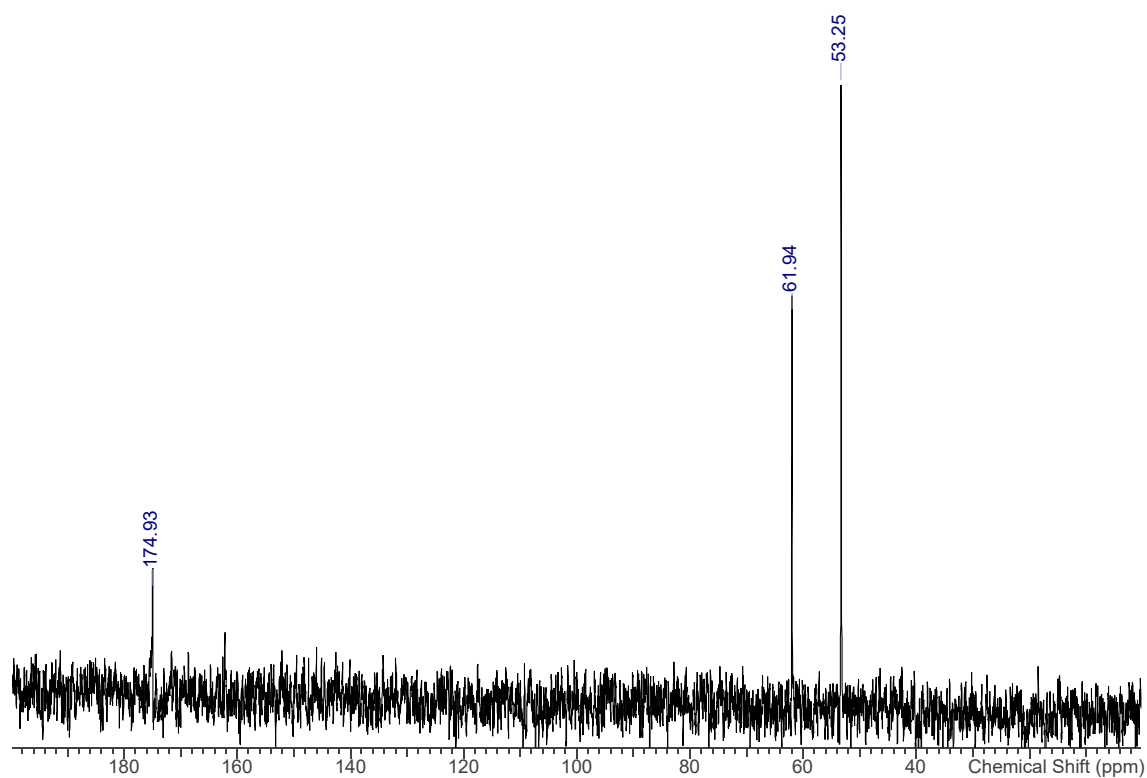


Figure S6.5 [Ga(NOTA)]

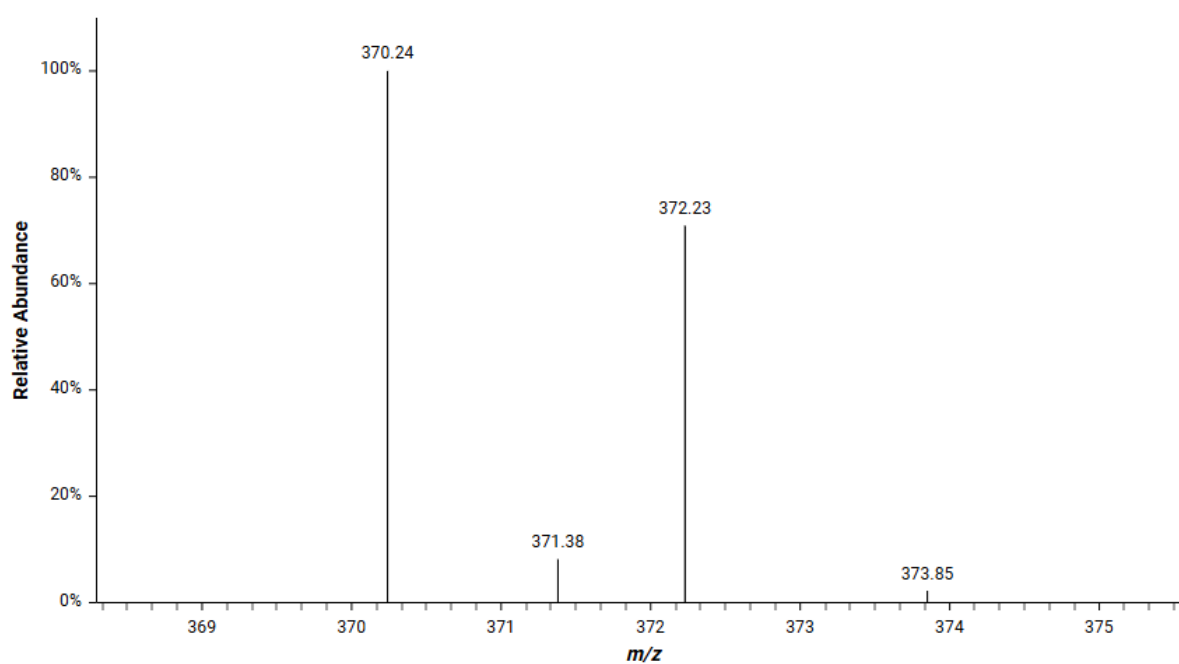
S6.5.a ^1H NMR spectrum (D_2O)



S6.5.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (D_2O)



S6.5.c ESI⁺ MS (H₂O)



S6.5.d IR spectrum (Nujol)

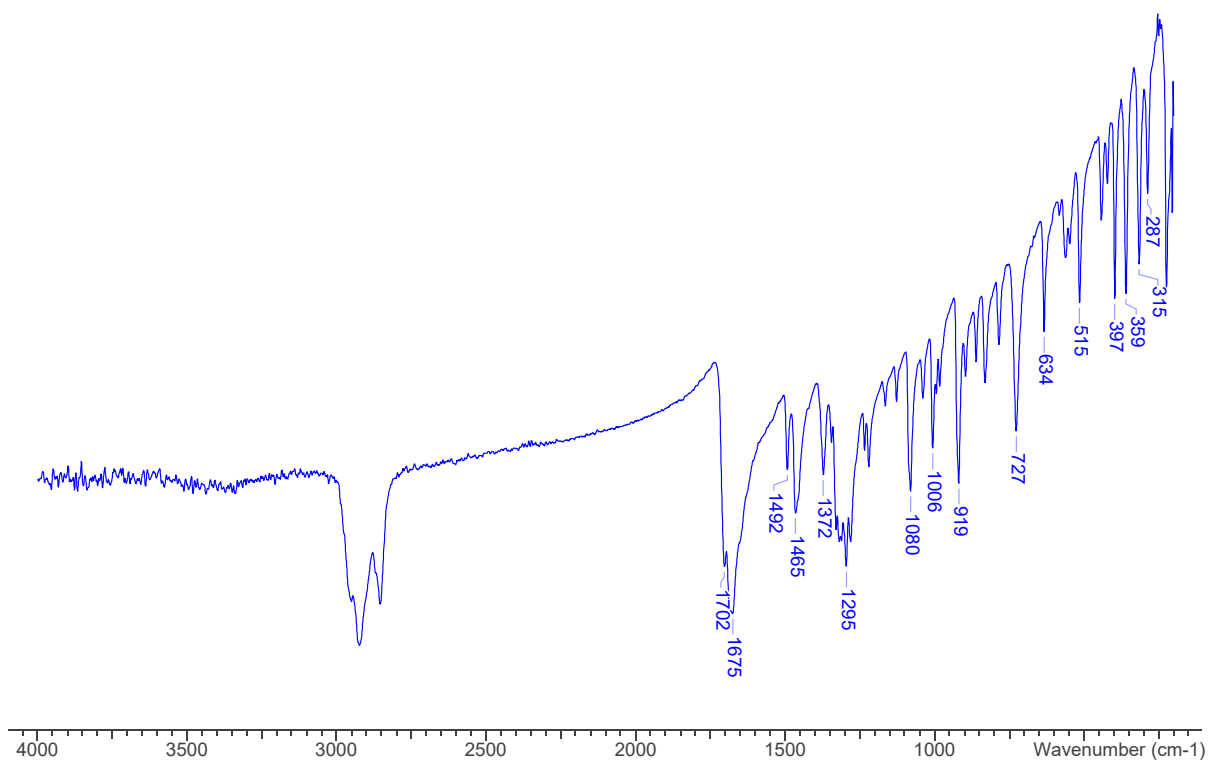
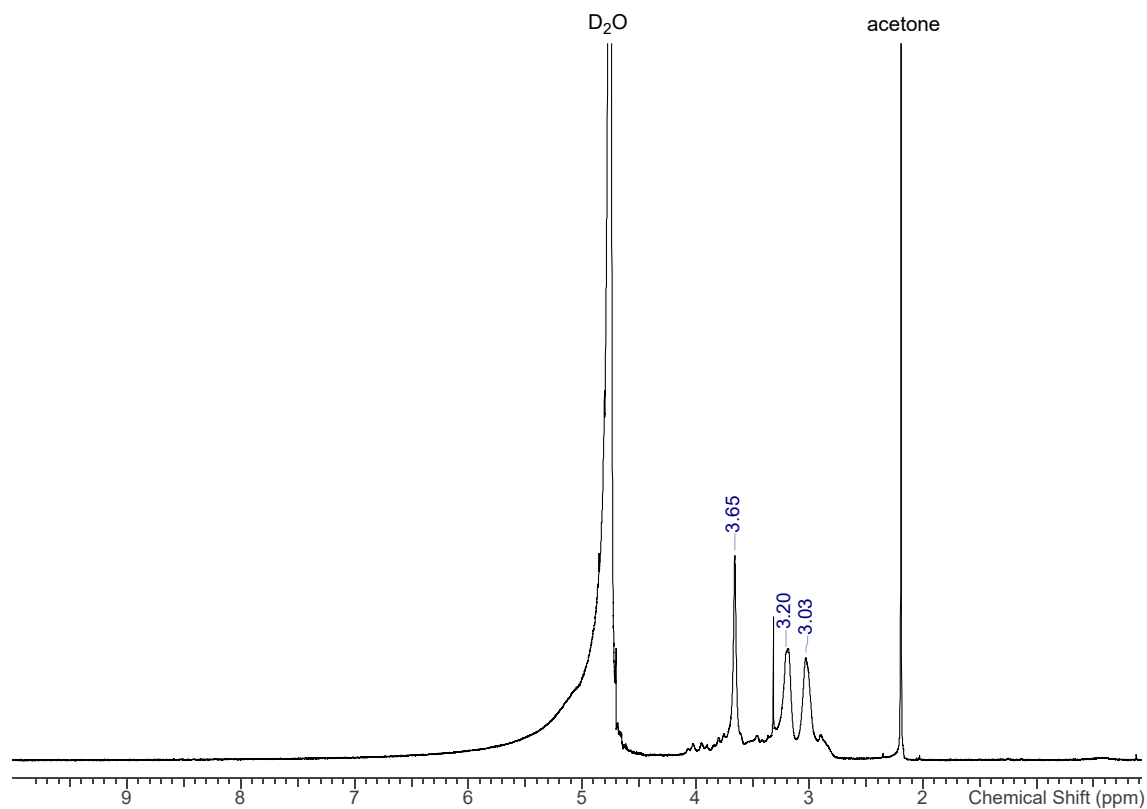
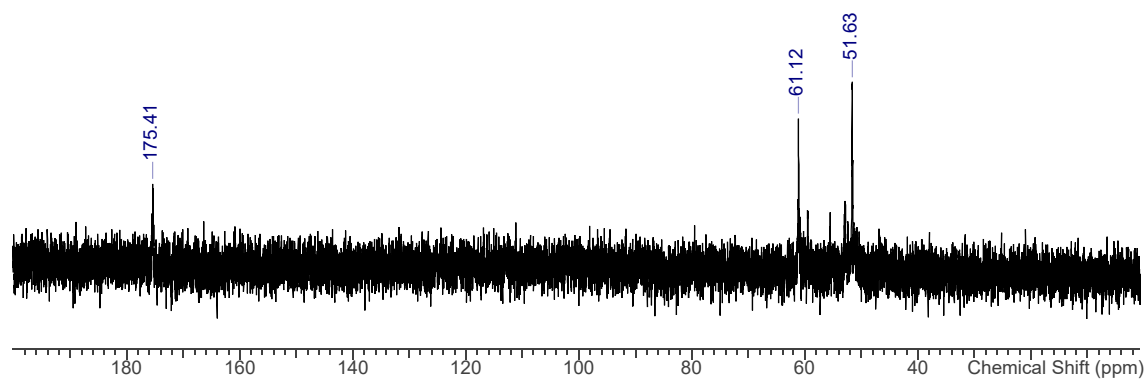


Figure S6.6 [In(NOTA)]

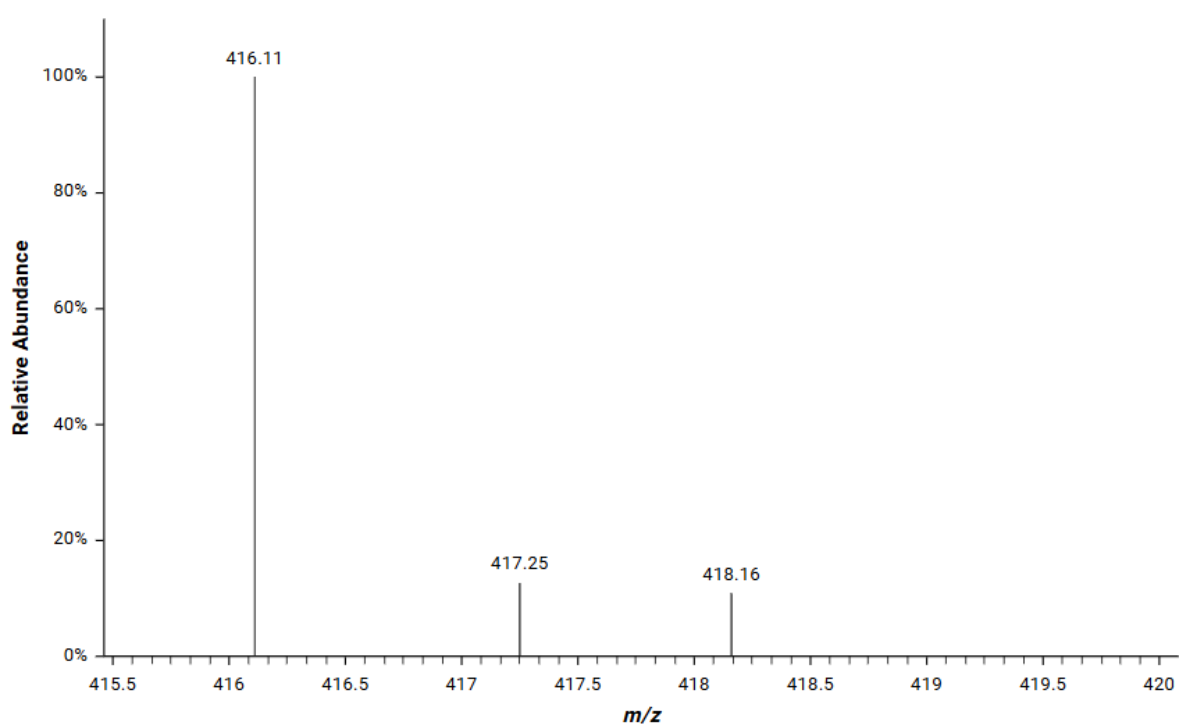
S6.6.a ^1H NMR spectrum (D_2O)



S6.6.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (D_2O)



S6.6.c ESI⁺ MS (H₂O)



S6.6.d IR spectrum (Nujol)

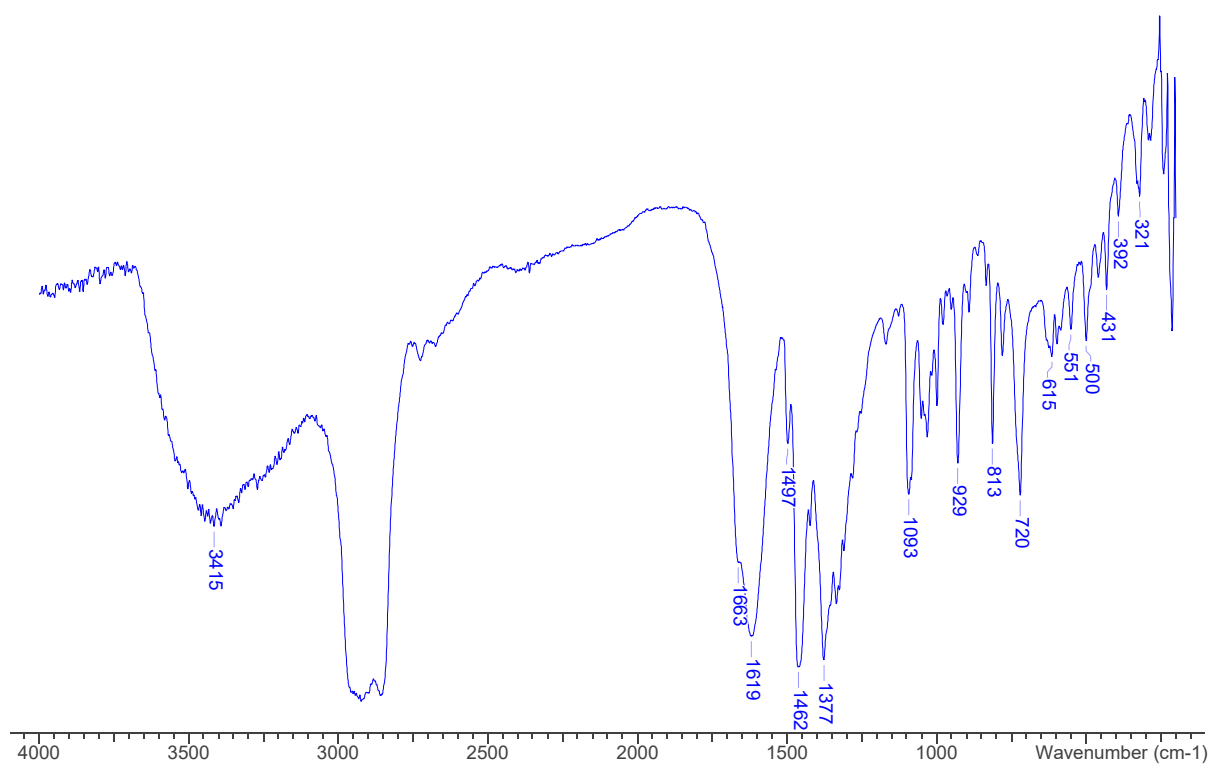
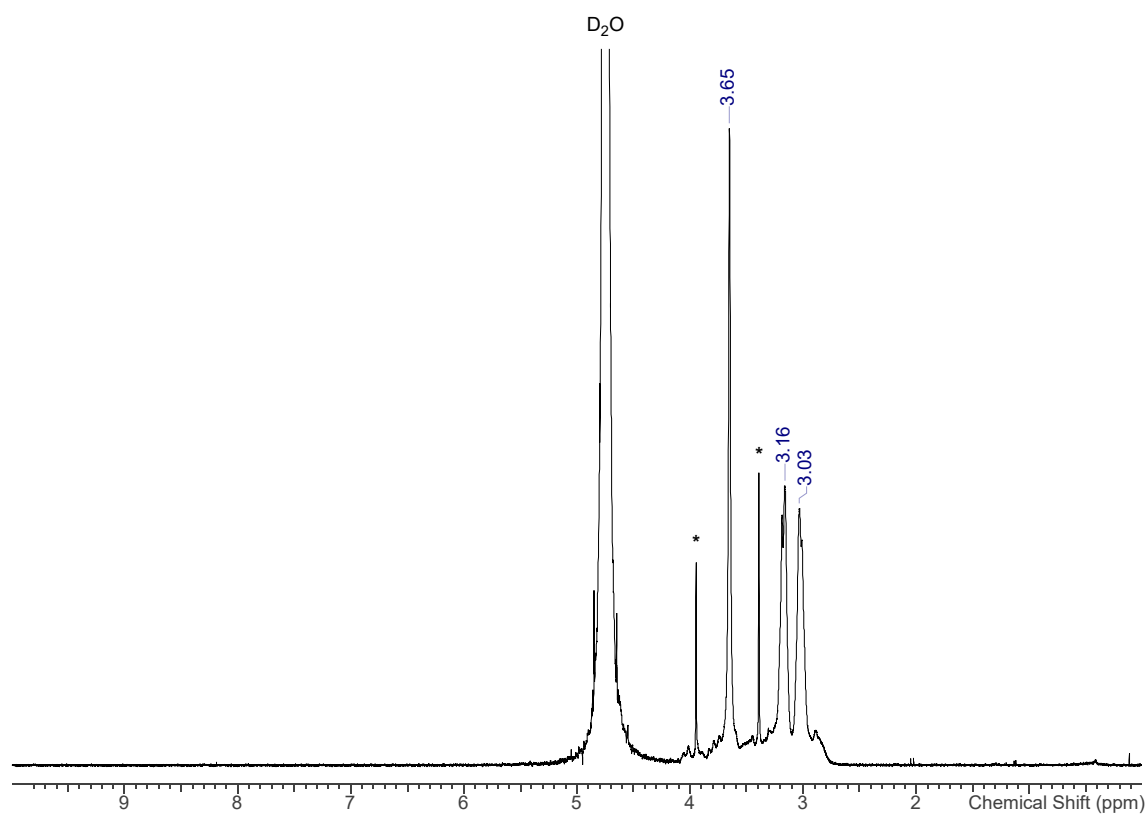
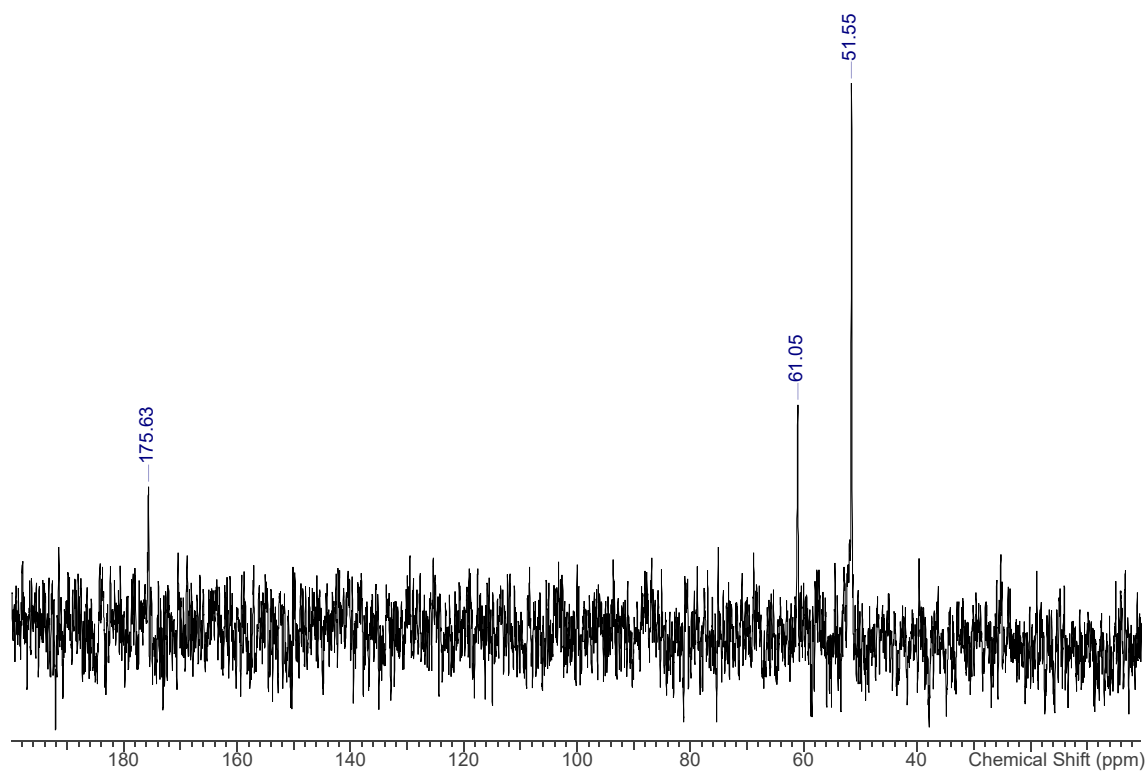


Figure S6.7 [InCl(OTA)][H]

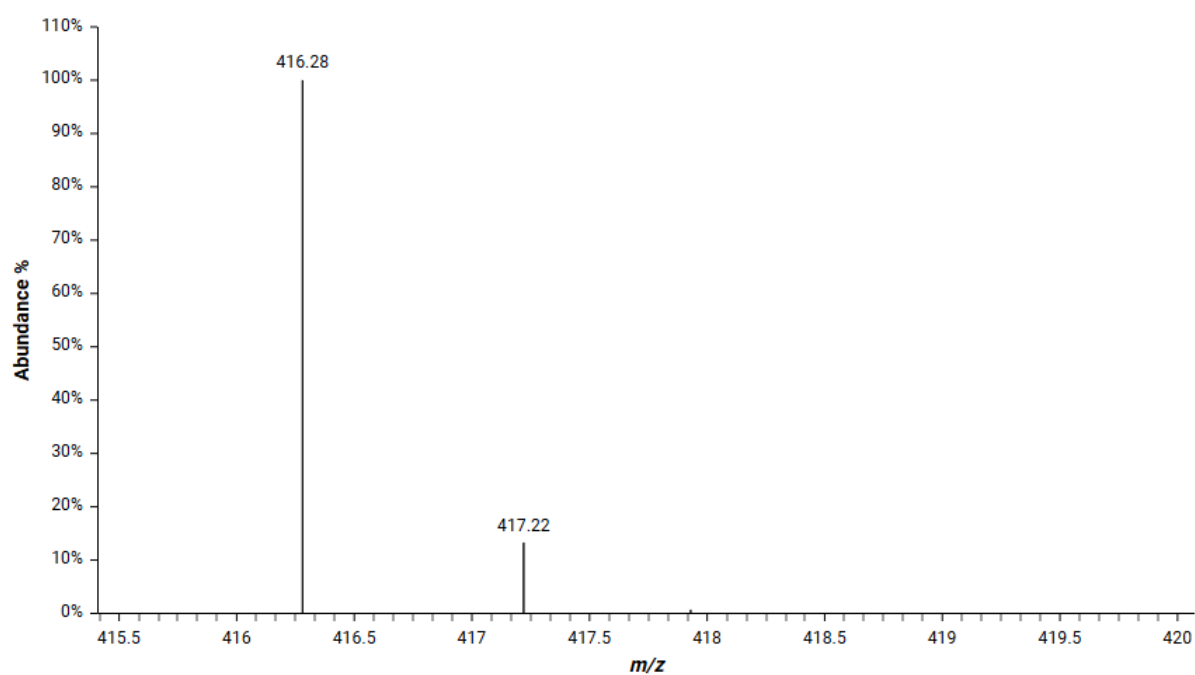
S6.7.a ^1H NMR spectrum (D_2O)



S6.7.b $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (D_2O)



S6.7.c ESI⁺ MS (H₂O)



S6.7.d IR spectrum (Nujol)

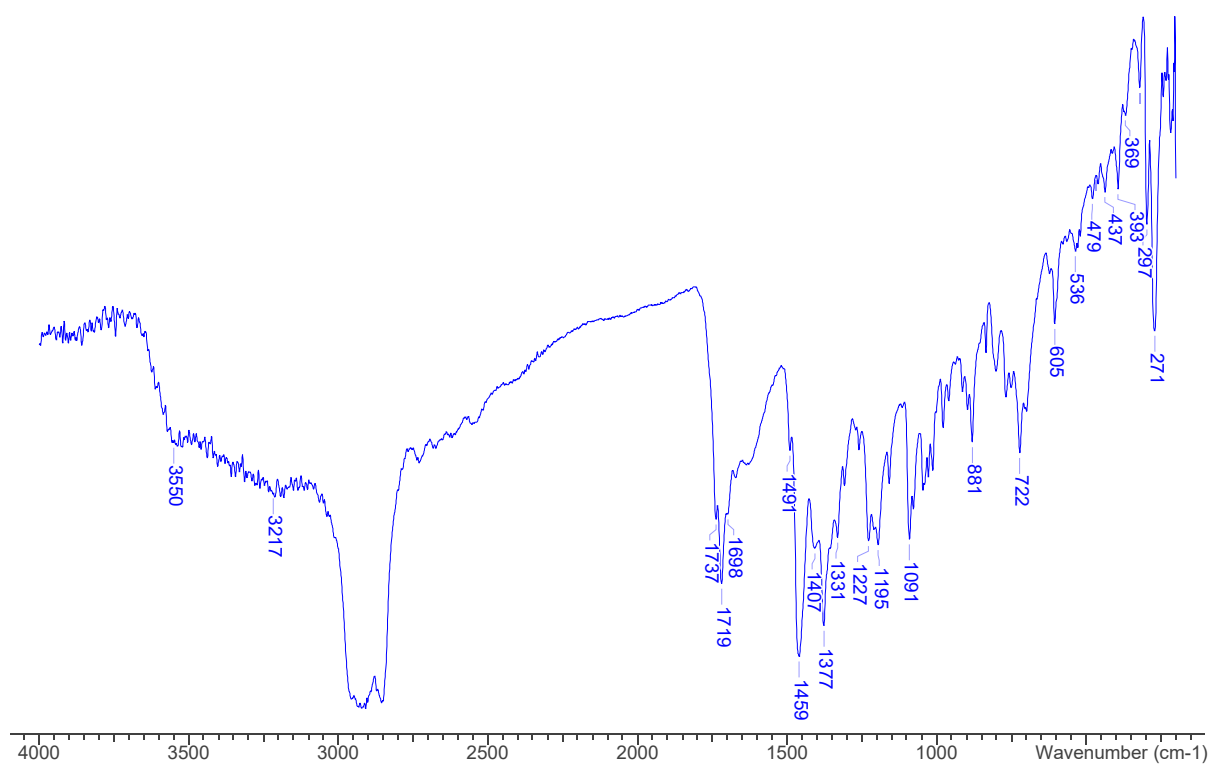


Figure S6.8 Attempted Fluorination of [In(NOTA)]

S6.8.a $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CD_3CN)

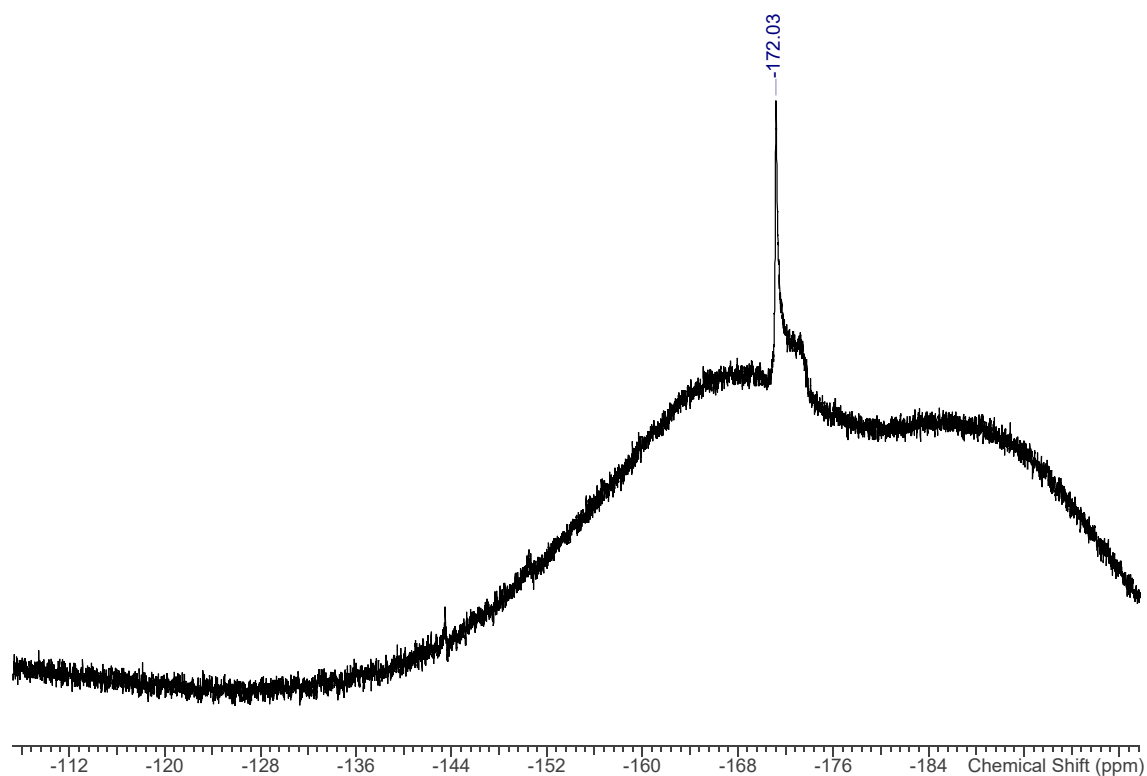
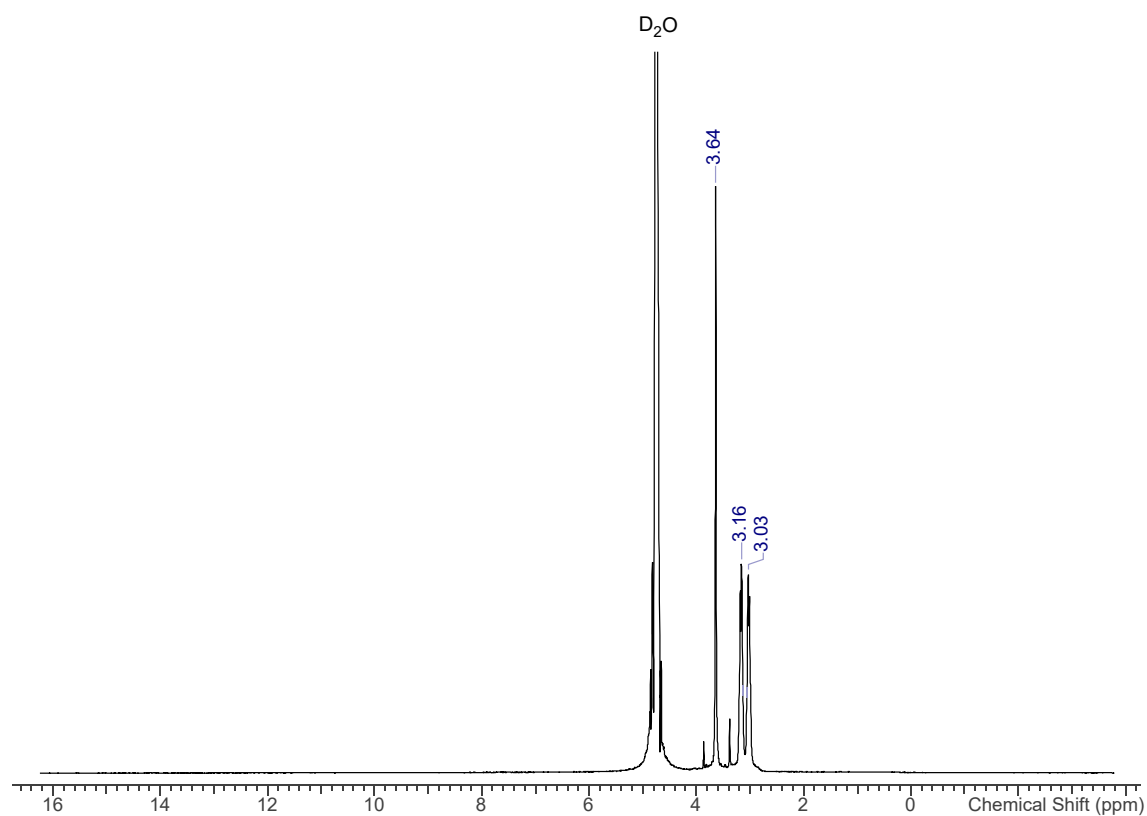


Figure S6.9 Attempted Fluorination of $[\text{InCl}(\text{NOTA})][\text{H}]$

S6.9.a ^1H NMR spectrum (D_2O) ($t = 0$ h)



S6.9.b $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O) ($t = 0$ h)

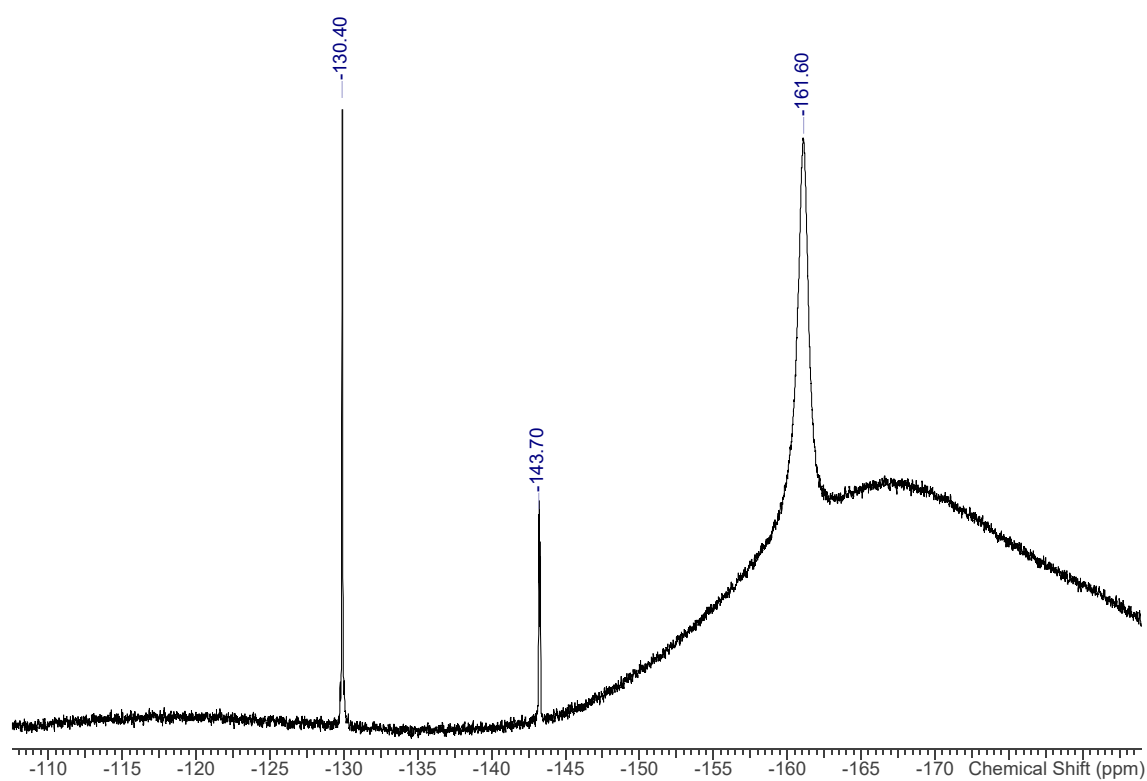
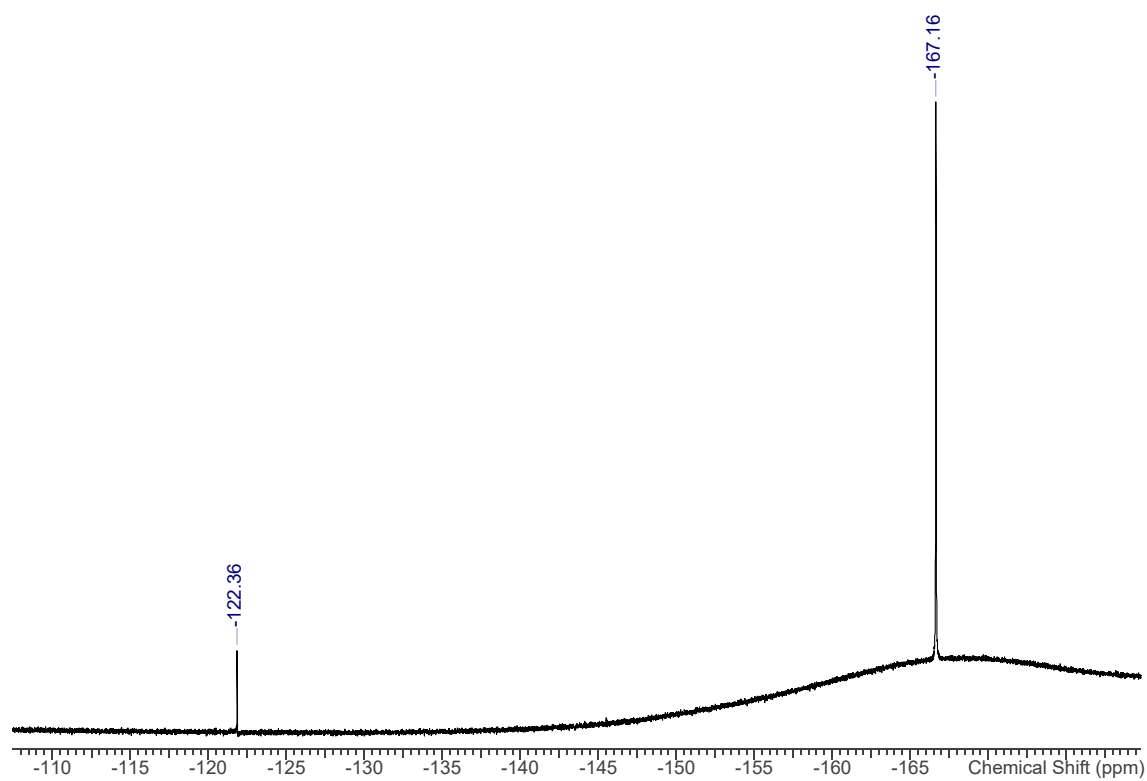


Figure S6.10 Attempted Formation of $[\text{AlF}(\text{Bn-NODA})]$

S6.10.a $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (D_2O)



S6.10.b ESI⁺ MS (H₂O)

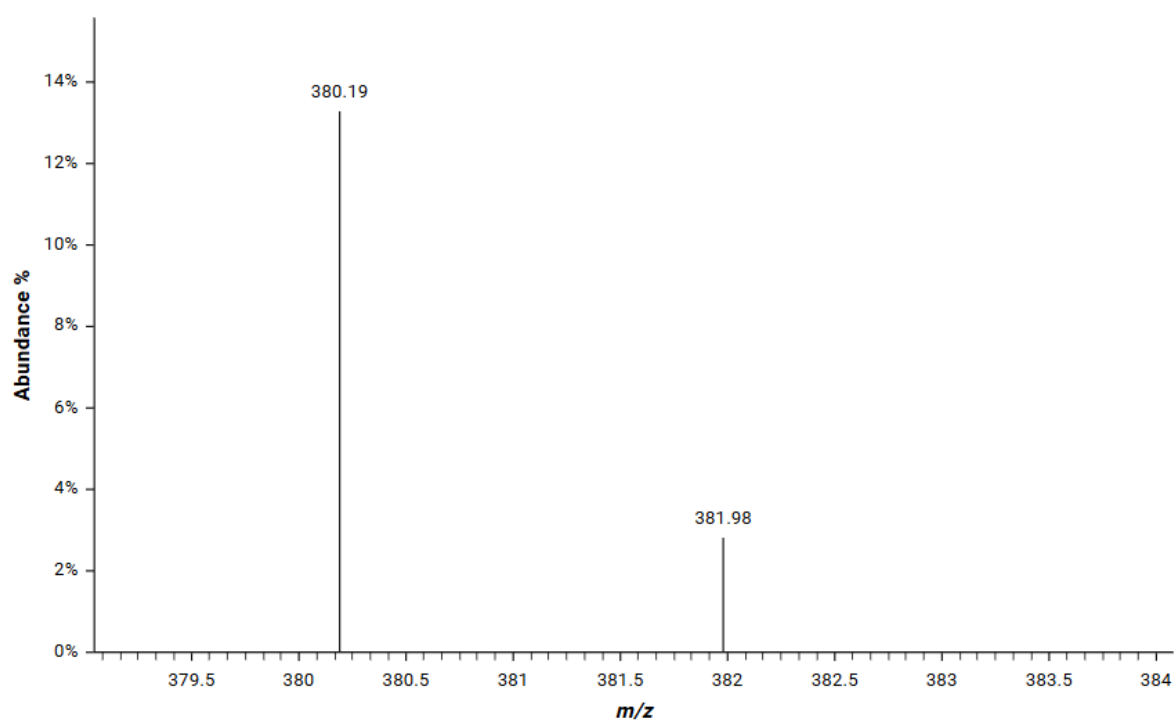
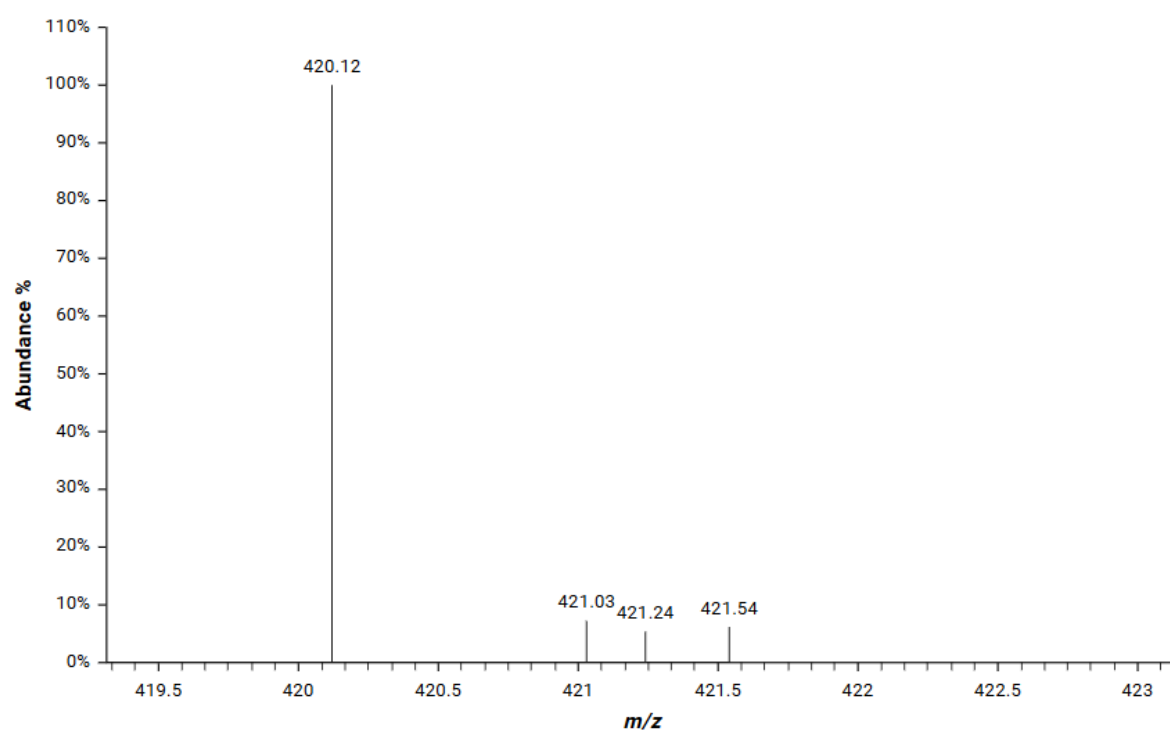
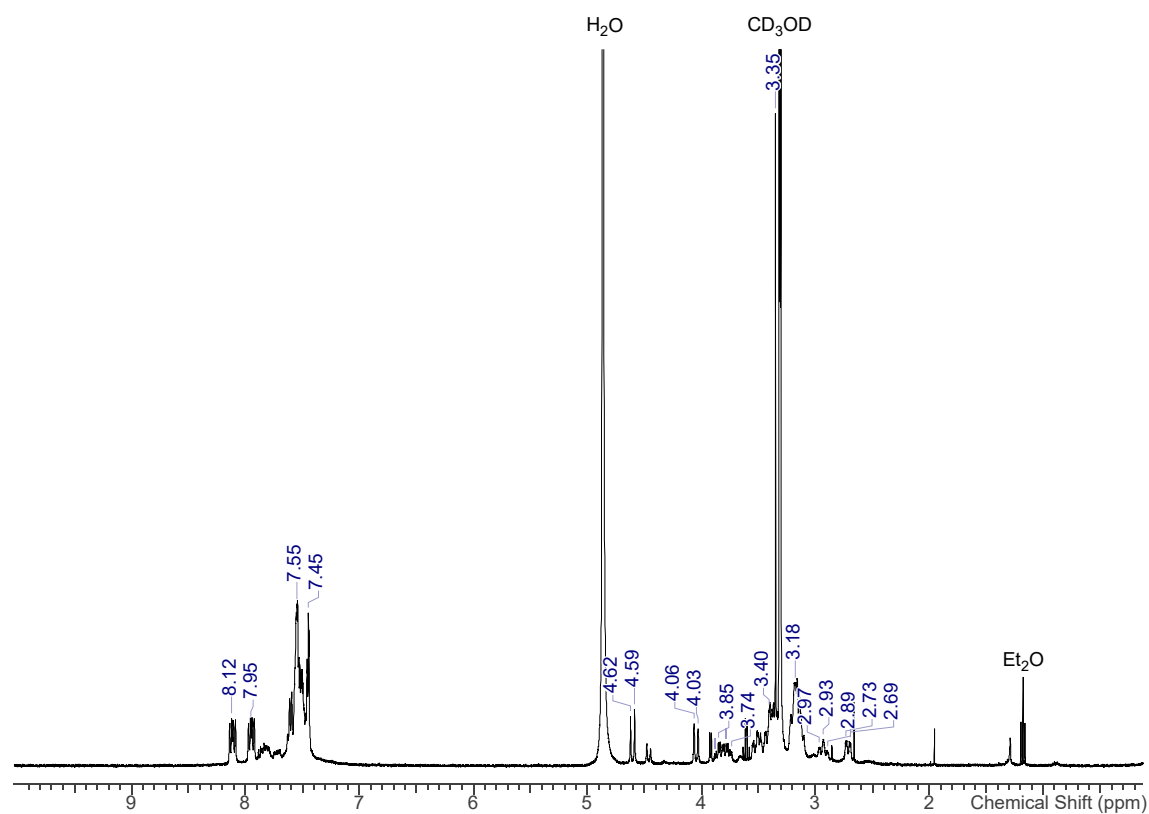
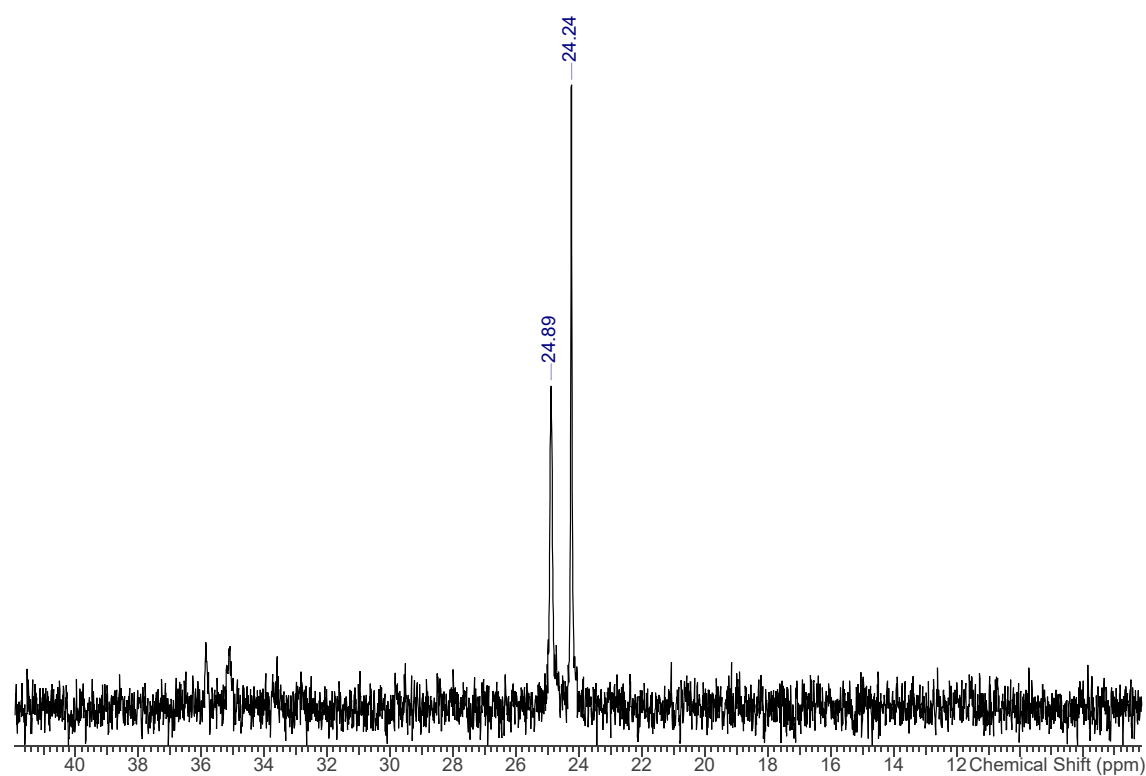


Figure S6.11 [In(NO₃)(Bn-NODP)]

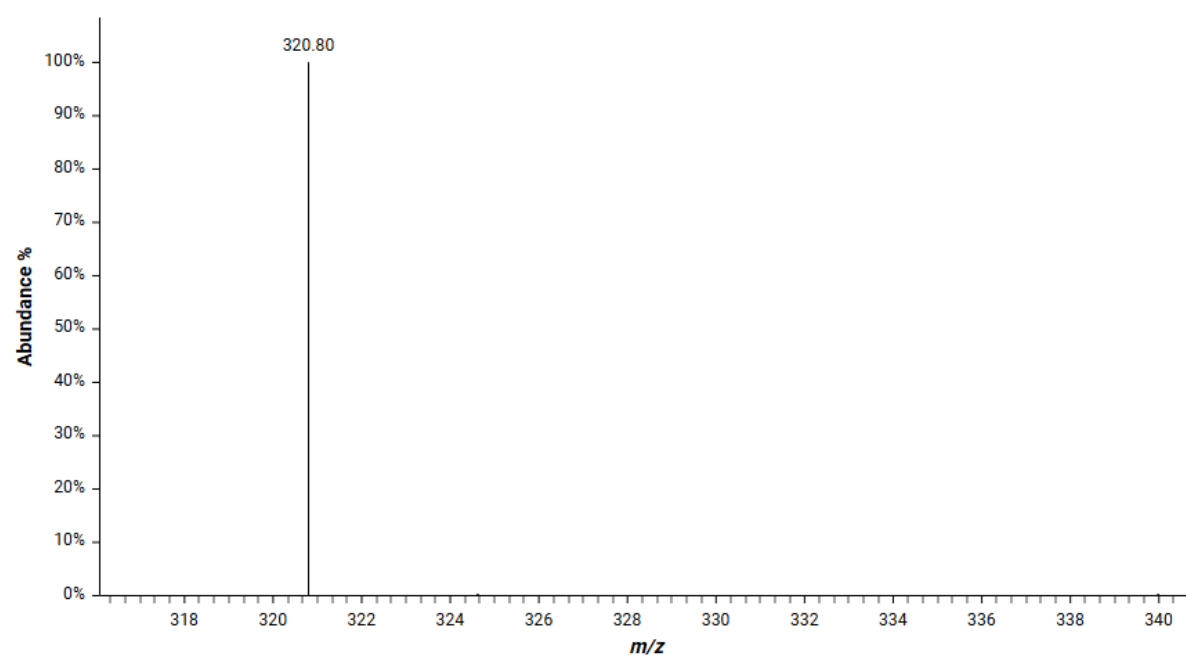
S6.11.a ¹H NMR spectrum (CD₃OD)



S6.11.b ³¹P{¹H} NMR spectrum (CD₃OD)



S6.11.c ESI⁺ MS (MeOH)



S6.11.d IR spectrum (Nujol)

