

**Exploring structure relationships and mitochondrial activity of *fac*-
{M^I(CO)₃}⁺ bis(diarylphosphino)alkyl-/arylamine complexes
(M=⁹⁹Tc, Re)**

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Table of Contents

Figure S1 ^1H NMR spectrum for <i>fac</i> -[Re(Cy- <i>p</i> TolPNP)(CO) ₃ Br] (1A).....	2
Figure S2 ^{31}P NMR spectrum for <i>fac</i> -[Re(Cy- <i>p</i> TolPNP)(CO) ₃ Br] (1A)	3
Figure S3 IR spectrum for <i>fac</i> -[Re(Cy- <i>p</i> TolPNP)(CO) ₃ Br] (1A) ATR.....	4
Figure S4 IR spectrum for <i>fac</i> -[Re(Cy- <i>p</i> TolPNP)(CO) ₃ Br] (1A) DCM.....	5
Figure S5 Disordered <i>fac</i> -[Re(Cy- <i>p</i> TolPNP)(CO) ₃ Br] (1A).....	6
Figure S6 ^1H NMR spectrum for <i>fac</i> -[^{99}Tc (Cy- <i>p</i> TolPNP)(CO) ₃ Cl] (1B).....	7
Figure S7 ^{99}Tc NMR spectrum for <i>fac</i> -[^{99}Tc (Cy- <i>p</i> TolPNP)(CO) ₃ Cl] (1B)	8
Figure S8 ^{31}P NMR spectrum for <i>fac</i> -[^{99}Tc (Cy- <i>p</i> TolPNP)(CO) ₃ Cl] (1B)	9
Figure S9 IR spectrum for <i>fac</i> -[^{99}Tc (Cy- <i>p</i> TolPNP)(CO) ₃ Cl] (1B)	10
Figure S10 ^1H NMR spectrum for <i>fac</i> -[Re(Cb- <i>p</i> TolPNP)(CO) ₃ Br] (2A).....	11
Figure S11 ^{31}P NMR spectrum for <i>fac</i> -[Re(Cb- <i>p</i> TolPNP)(CO) ₃ Br] (2A)	12
Figure S12 IR spectrum for <i>fac</i> -[Re(Cb- <i>p</i> TolPNP)(CO) ₃ Br] (2A) ATR.....	13
Figure S13 IR spectrum for <i>fac</i> -[Re(Cb- <i>p</i> TolPNP)(CO) ₃ Br] (2A) DCM.....	14
Figure S14 ^1H NMR spectrum for <i>fac</i> -[^{99}Tc (Cb- <i>p</i> TolPNP)(CO) ₃ Cl] (2B).....	15
Figure S15 ^{99}Tc NMR spectrum for <i>fac</i> -[^{99}Tc (Cb- <i>p</i> TolPNP)(CO) ₃ Cl] (2B)	16
Figure S16 ^{31}P NMR spectrum for <i>fac</i> -[^{99}Tc (Cb- <i>p</i> TolPNP)(CO) ₃ Cl] (2B)	17
Figure S17 IR spectrum for <i>fac</i> -[^{99}Tc (Cb- <i>p</i> TolPNP)(CO) ₃ Cl] (2B) KBr	18
Figure S18 ^1H NMR spectrum for Chzyl-4- <i>p</i> tol-PNP (1)	19
Figure S19 ^{31}P NMR spectrum for Chzyl-4- <i>p</i> tol-PNP (1).....	20
Figure S20 ^1H NMR spectrum for Cyclobutyl-4- <i>p</i> tol-PNP (2).....	21
Figure S21 ^{31}P NMR spectrum for Cyclobutyl-4- <i>p</i> tol-PNP (2)	22
Figure S22 Illustration of disorder in Ligand 1.....	23

Figure S1 ^1H NMR spectrum for *fac*-[Re(Cy-pTolPNP)(CO)₃Br] (**1A**)

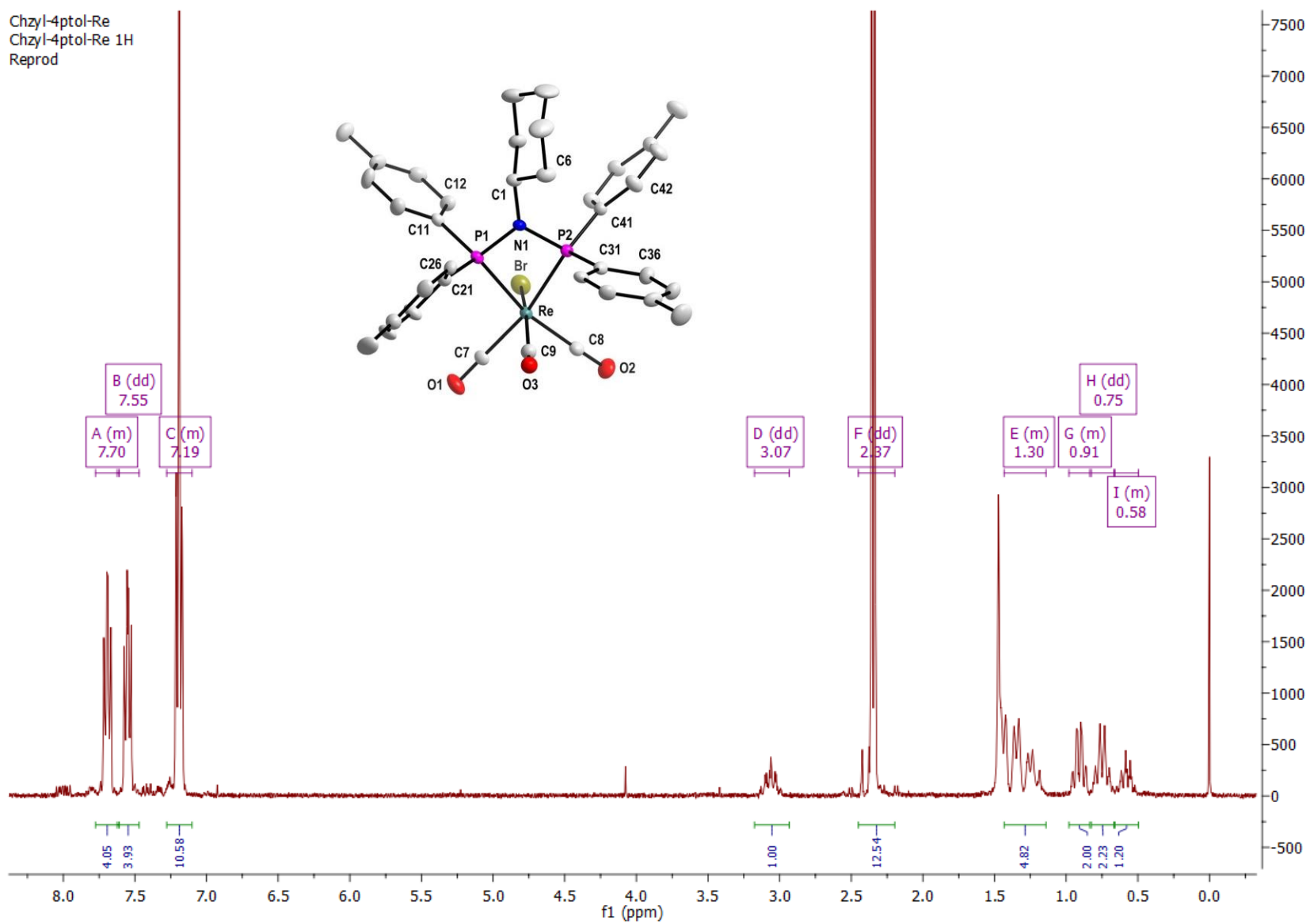


Figure S2 ^{31}P NMR spectrum for *fac*-[Re(Cy-pTolPNP)(CO)₃Br] (**1A**)

Chzyl-4ptol-Re
Chzyl-4ptol-Re 31P
Reprod

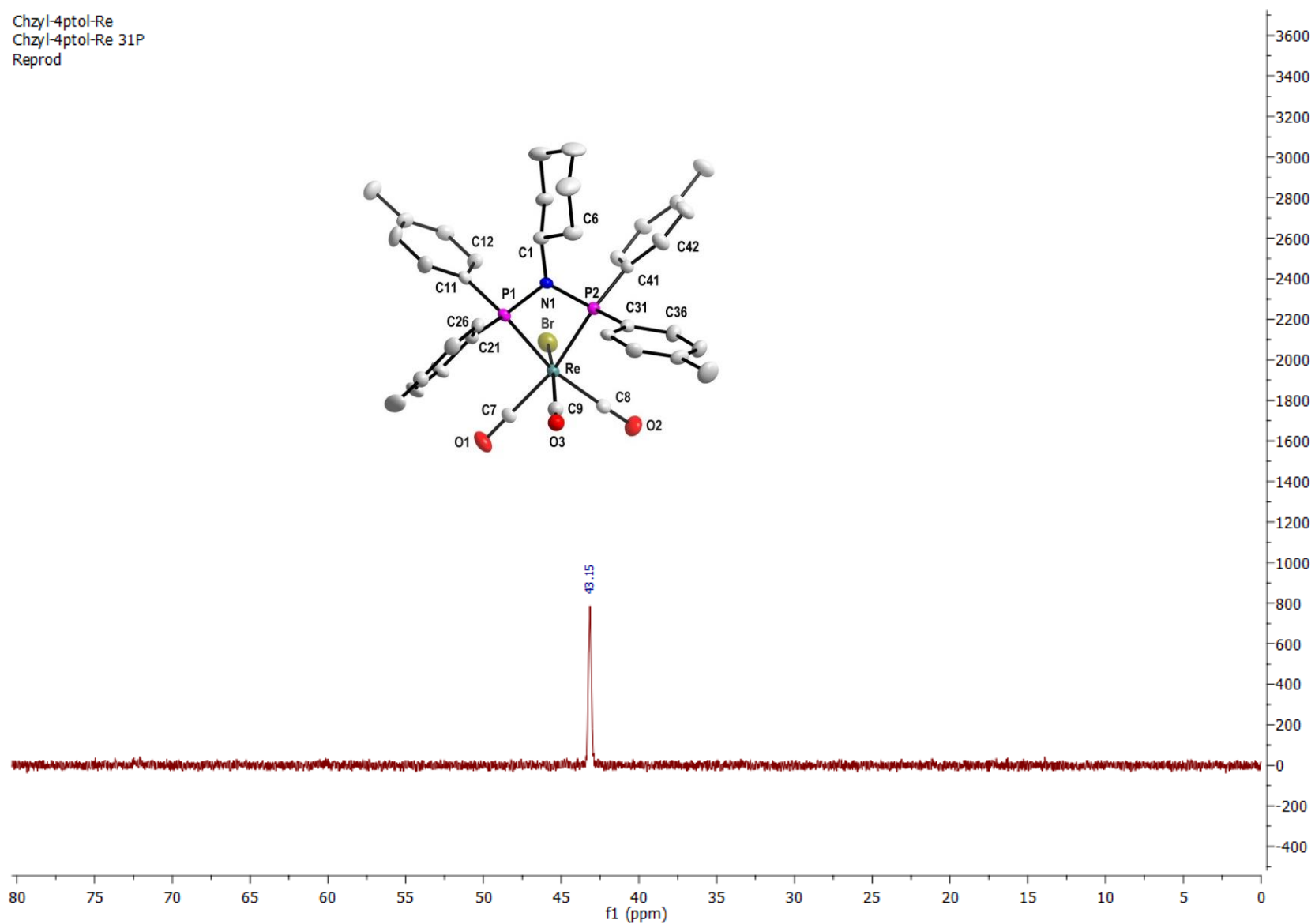


Figure S3 IR spectrum for *fac*-[Re(Cy-pTolPNP)(CO)₃Br] (**1A**) ATR

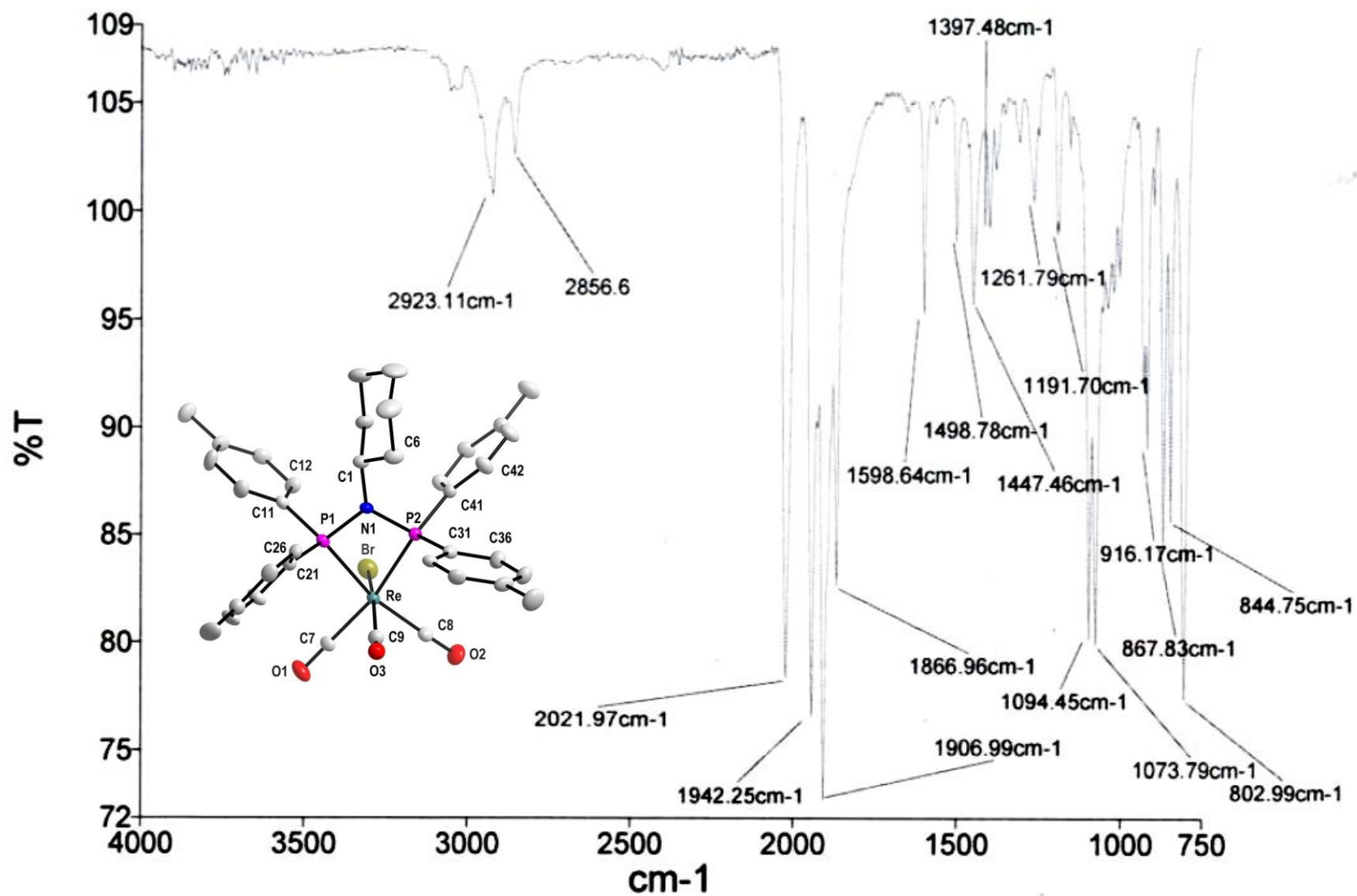


Figure S4 IR spectrum for *fac*-[Re(Cy-pTolPNP)(CO)₃Br] (**1A**) DCM

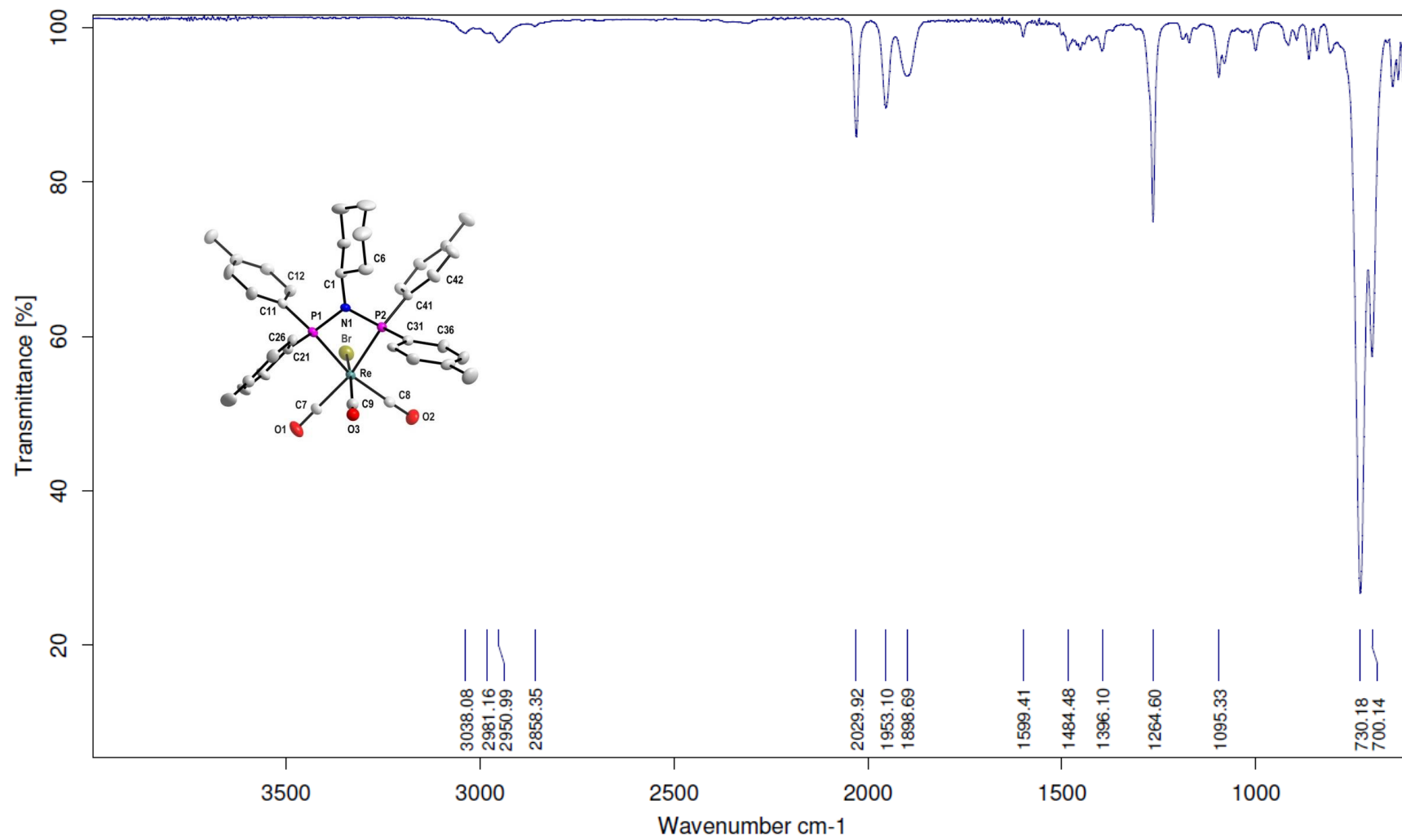


Figure S5 Disordered *fac*-[Re(Cy-pTolPNP)(CO)₃Br] (**1A**); Illustrated by Br1B.

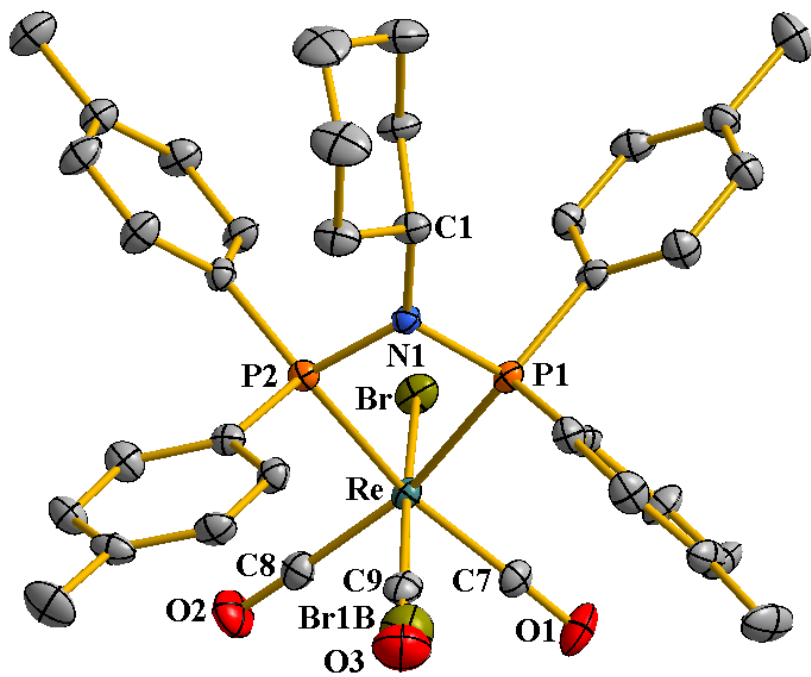


Figure S6 ^1H NMR spectrum for *fac*- $[\text{}^{99}\text{Tc}(\text{Cy-}p\text{TolPNP})(\text{CO})_3\text{Cl}]$ (**1B**)

CyhzyI-Tc-1H
CyhzyI-Tc(1H)

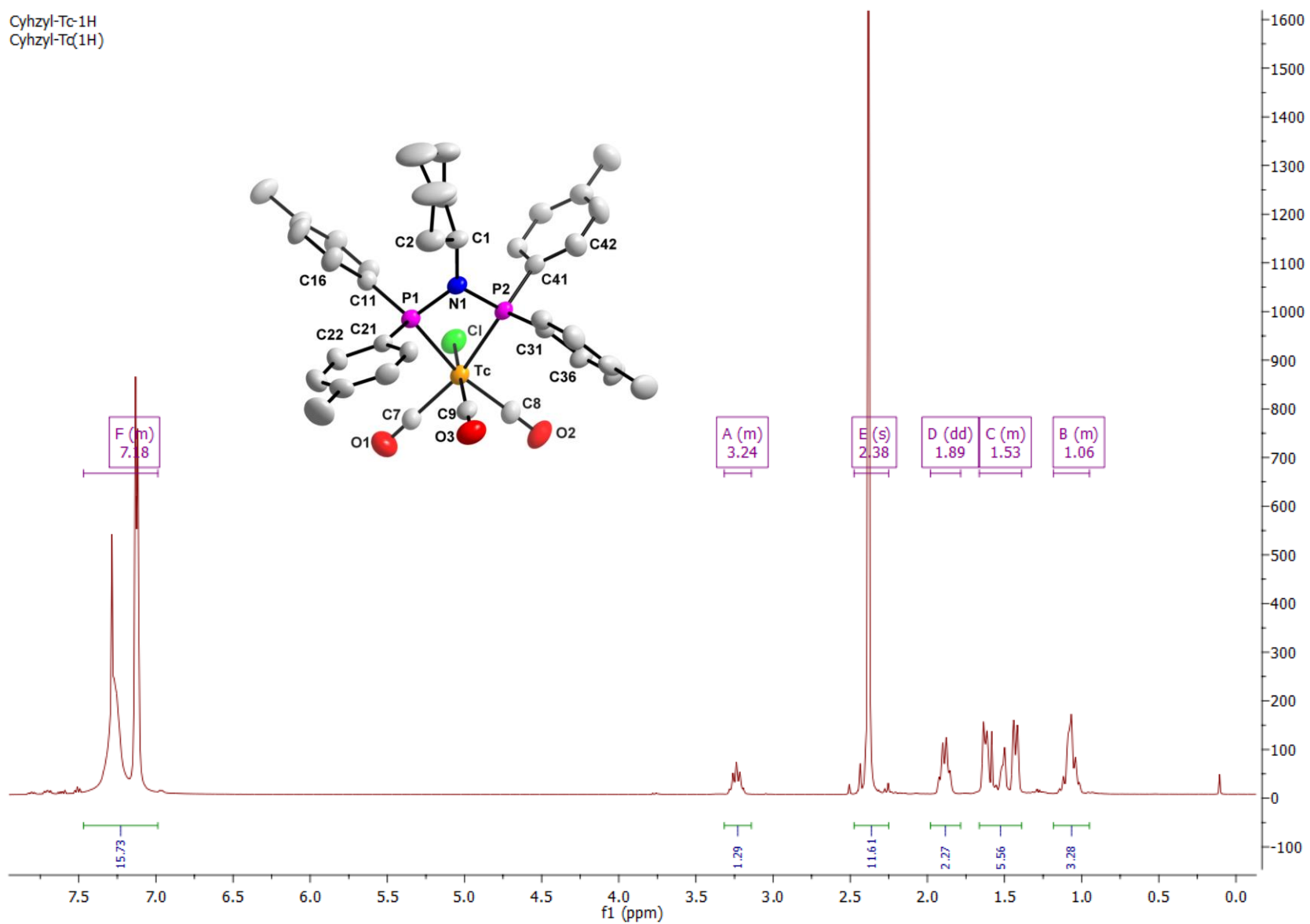


Figure S7 ^{99}Tc NMR spectrum for *fac*-[$^{99}\text{Tc}(\text{Cy-}p\text{TolPNP})(\text{CO})_3\text{Cl}$] (**1B**)

AFX_Tom_Cyclohexyl
99Tc-NMR

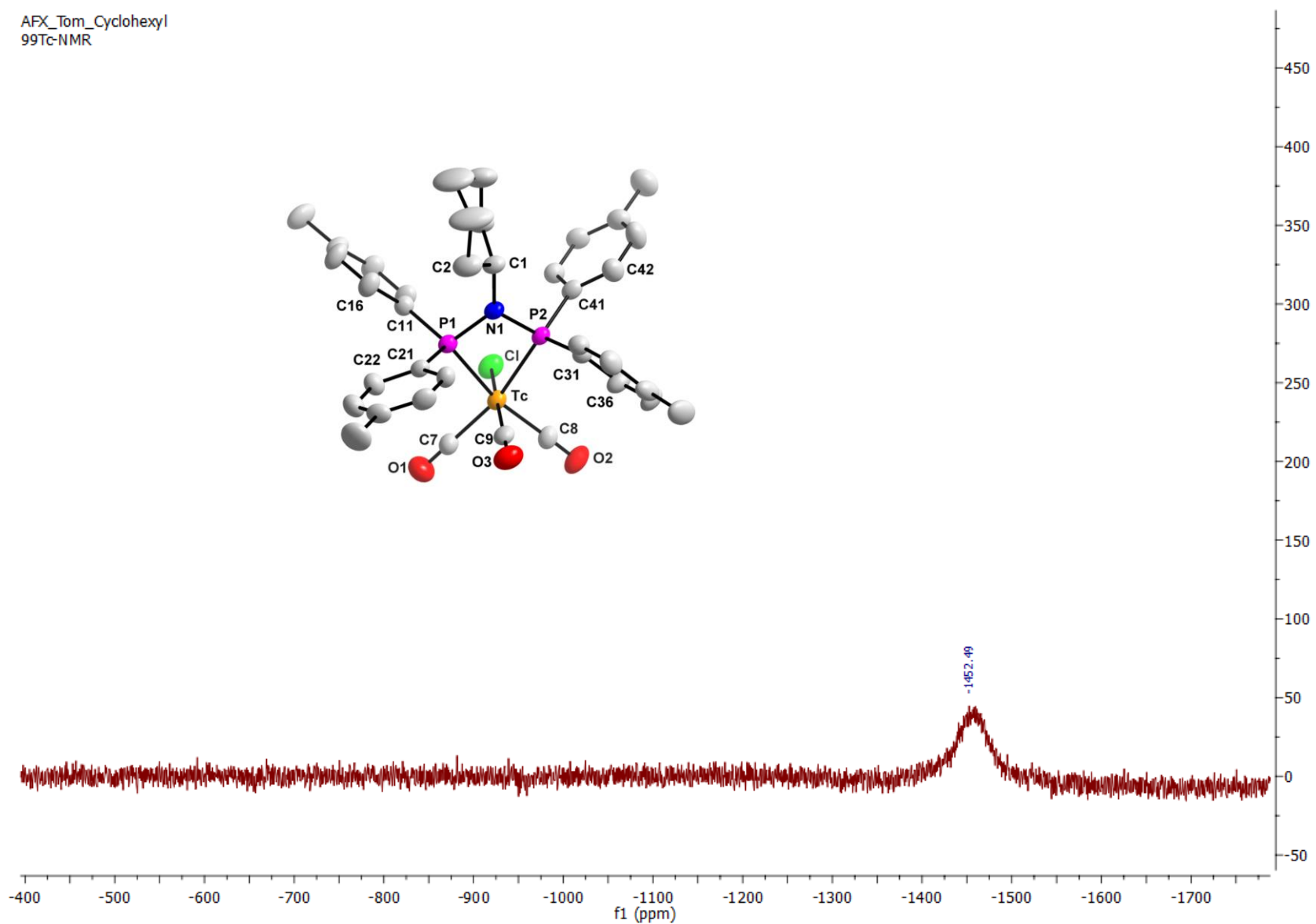


Figure S8 ^{31}P NMR spectrum for *fac*-[$^{99}\text{Tc}(\text{Cy-}p\text{TolPNP})(\text{CO})_3\text{Cl}$] (**1B**)

Cyhz-Tc-31P
Cyhz-Tc 31P

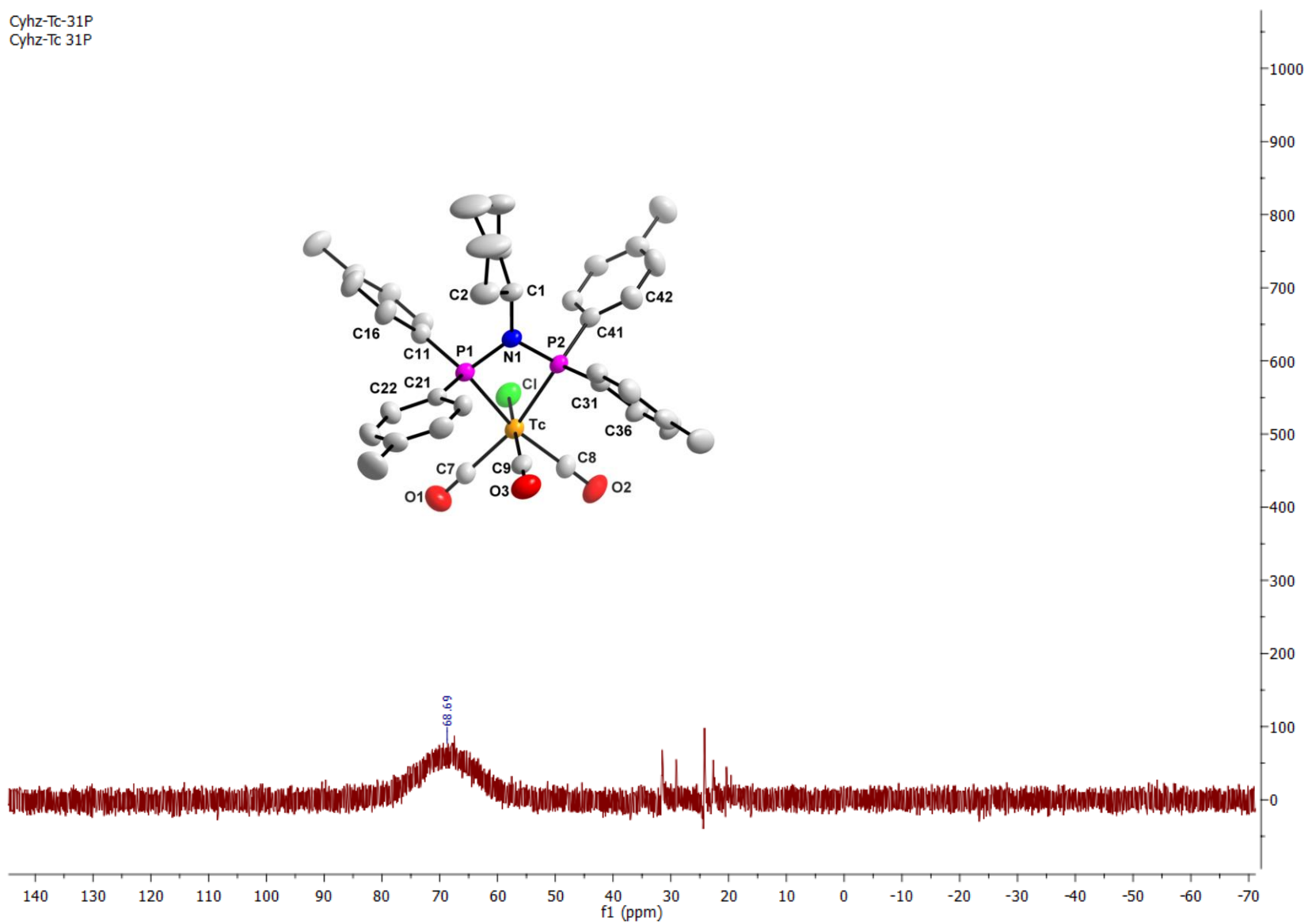


Figure S9 IR spectrum for *fac*-[⁹⁹Tc(Cy-*p*TolPNP)(CO)₃Cl] (**1B**) ATR

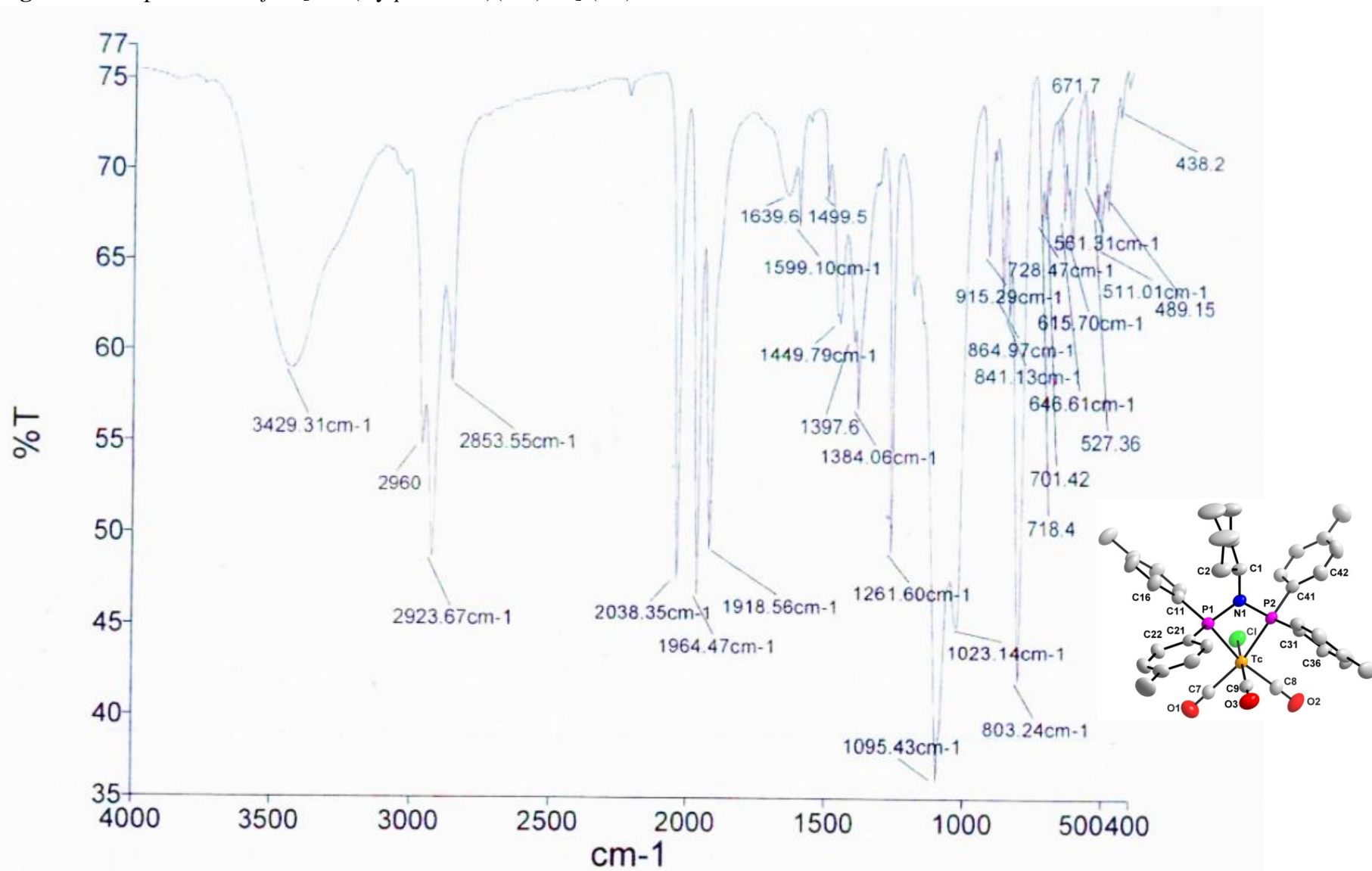


Figure S10 ^1H NMR spectrum for *fac*-[Re(Cb-*p*TolPNP)(CO)₃Br] (**2A**)

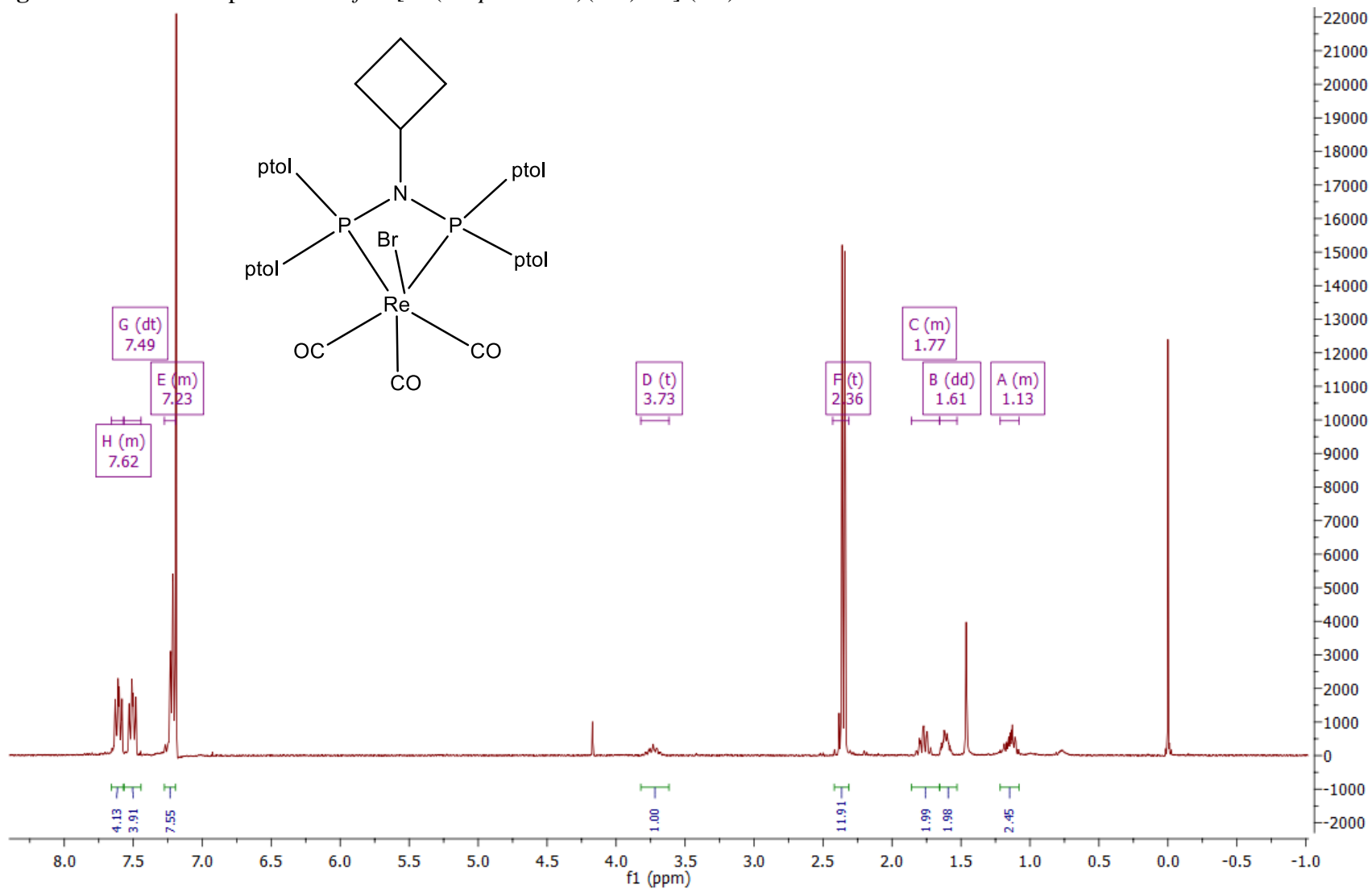


Figure S11 ^{31}P NMR spectrum for *fac*-[Re(Cb-*p*TolPNP)(CO) $_3$ Br] (**2A**)

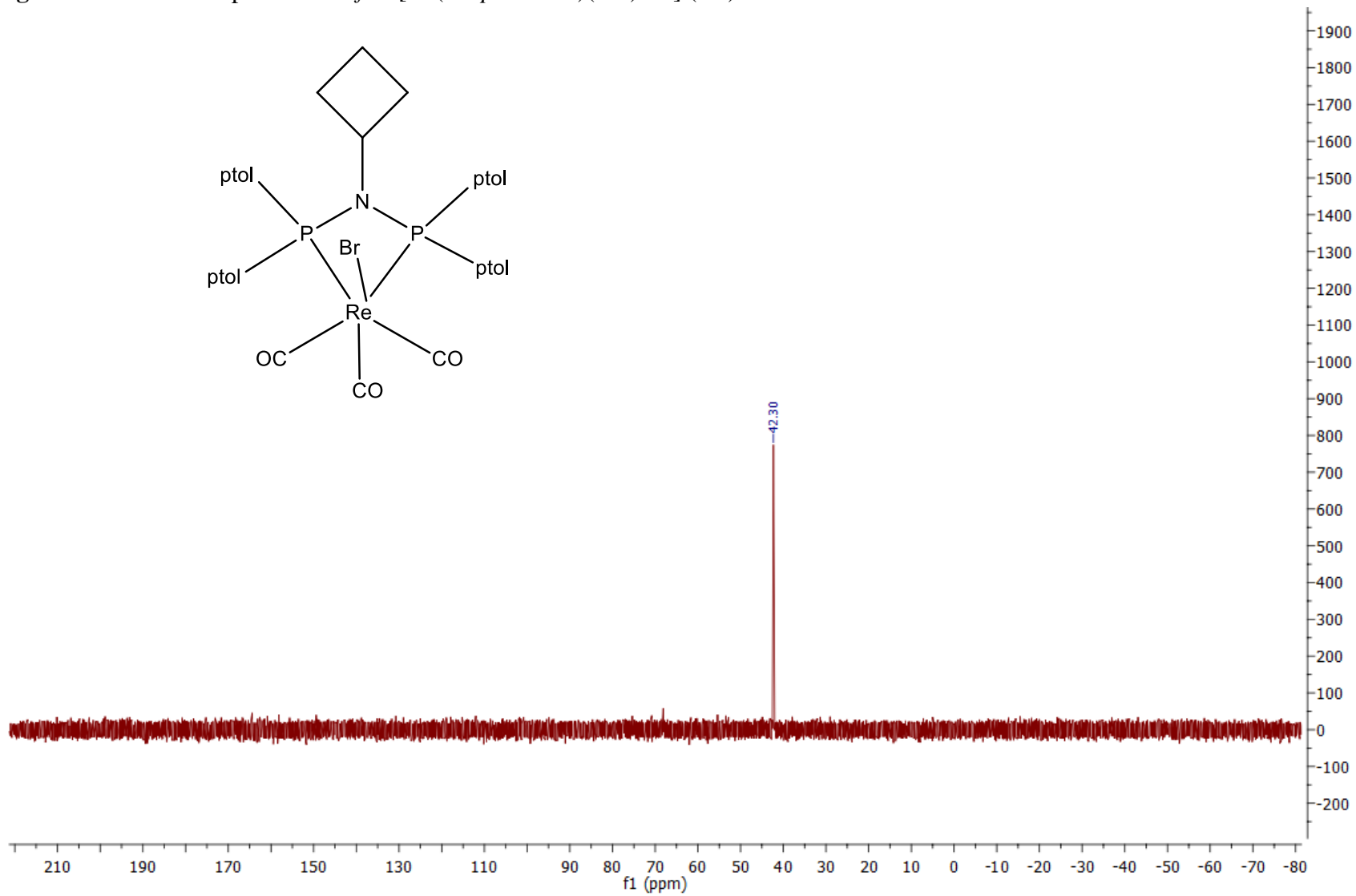


Figure S12 IR spectrum for *fac*-[Re(Cb-*p*TolPNP)(CO)₃Br] (**2A**) ATR

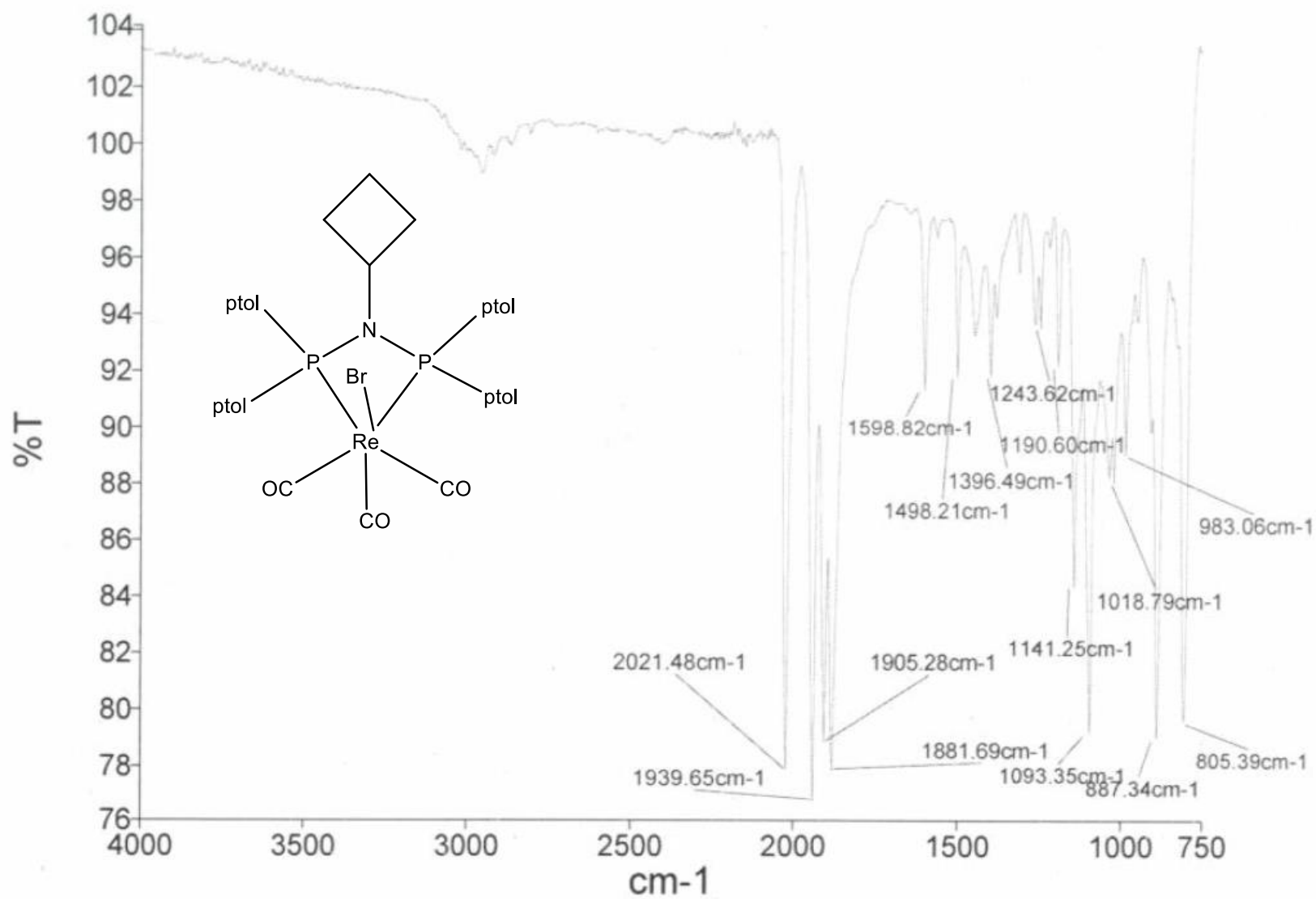


Figure S13 IR spectrum for *fac*-[Re(Cb-*p*TolPNP)(CO)₃Br] (**2A**) in DCM

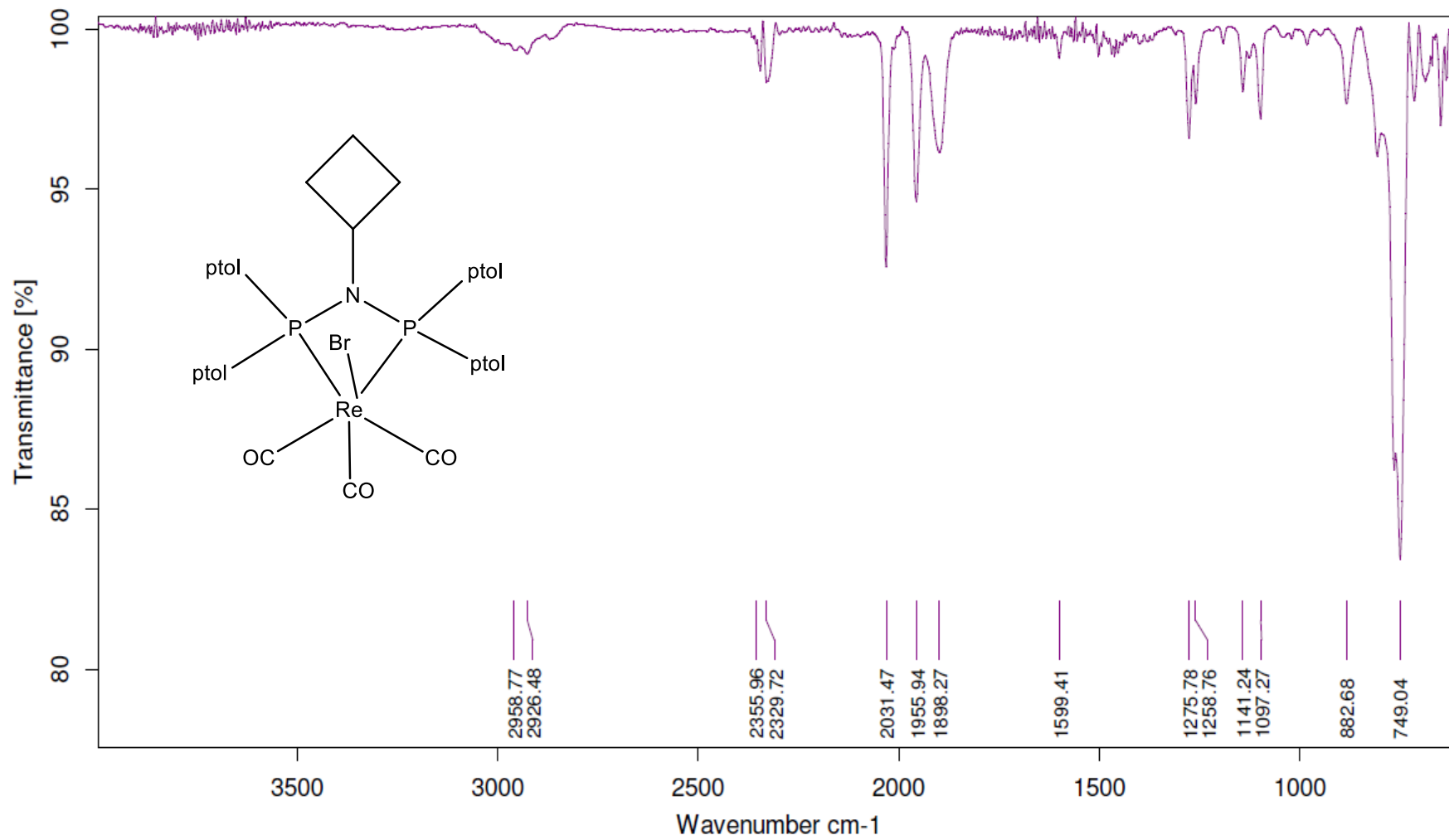


Figure S14 ^1H NMR spectrum for *fac*- $[\text{}^{99}\text{Tc}(\text{Cb-}p\text{TolPNP})(\text{CO})_3\text{Cl}]$ (**2B**)

AFX_Tom_sthsth
1HNMR

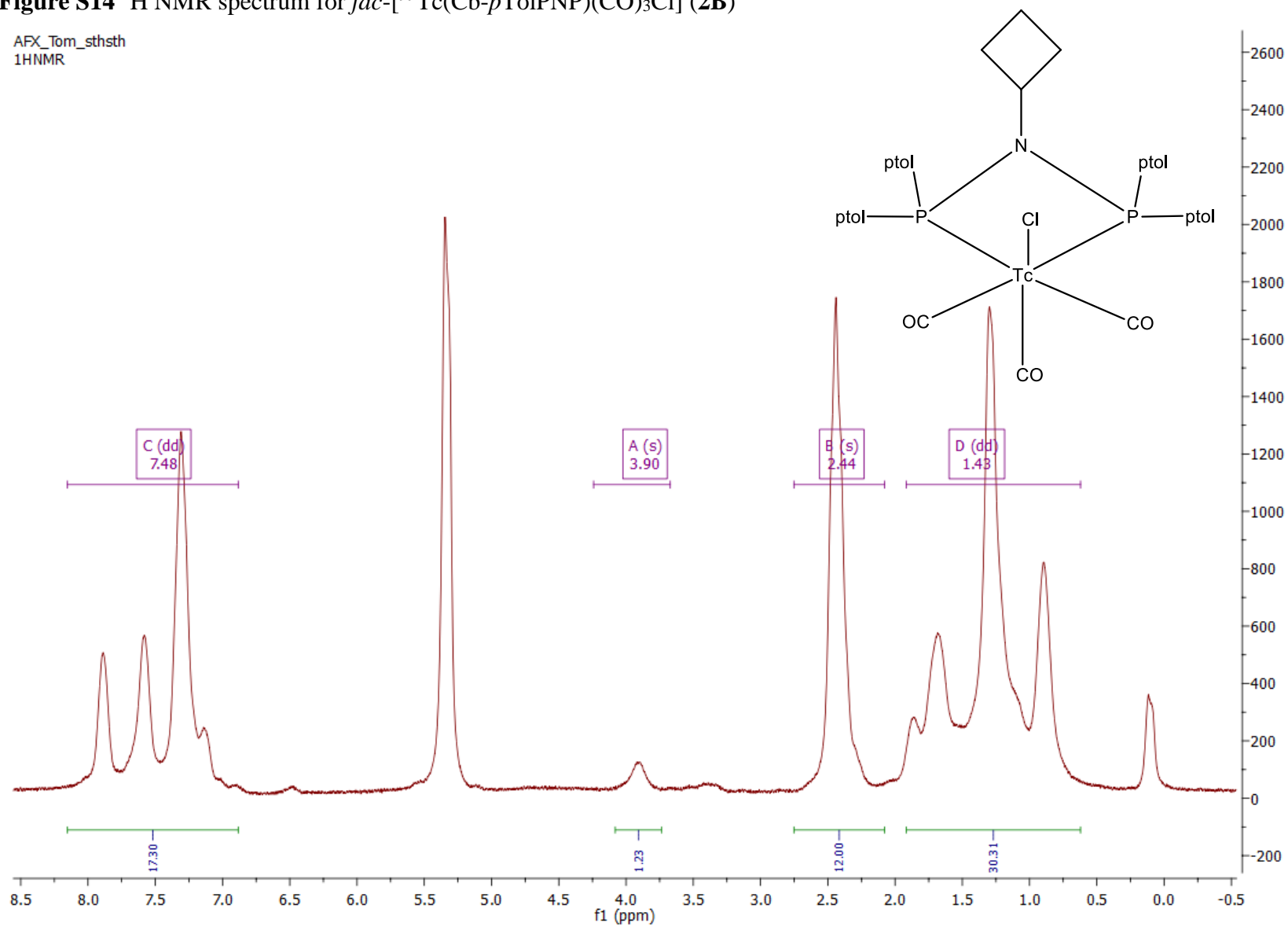


Figure S15 ^{99}Tc NMR spectrum for *fac*-[$^{99}\text{Tc}(\text{Cb-}p\text{TolPNP})(\text{CO})_3\text{Cl}$] (**2B**)

AFX_Tom_sthsth
99Tc-NMR

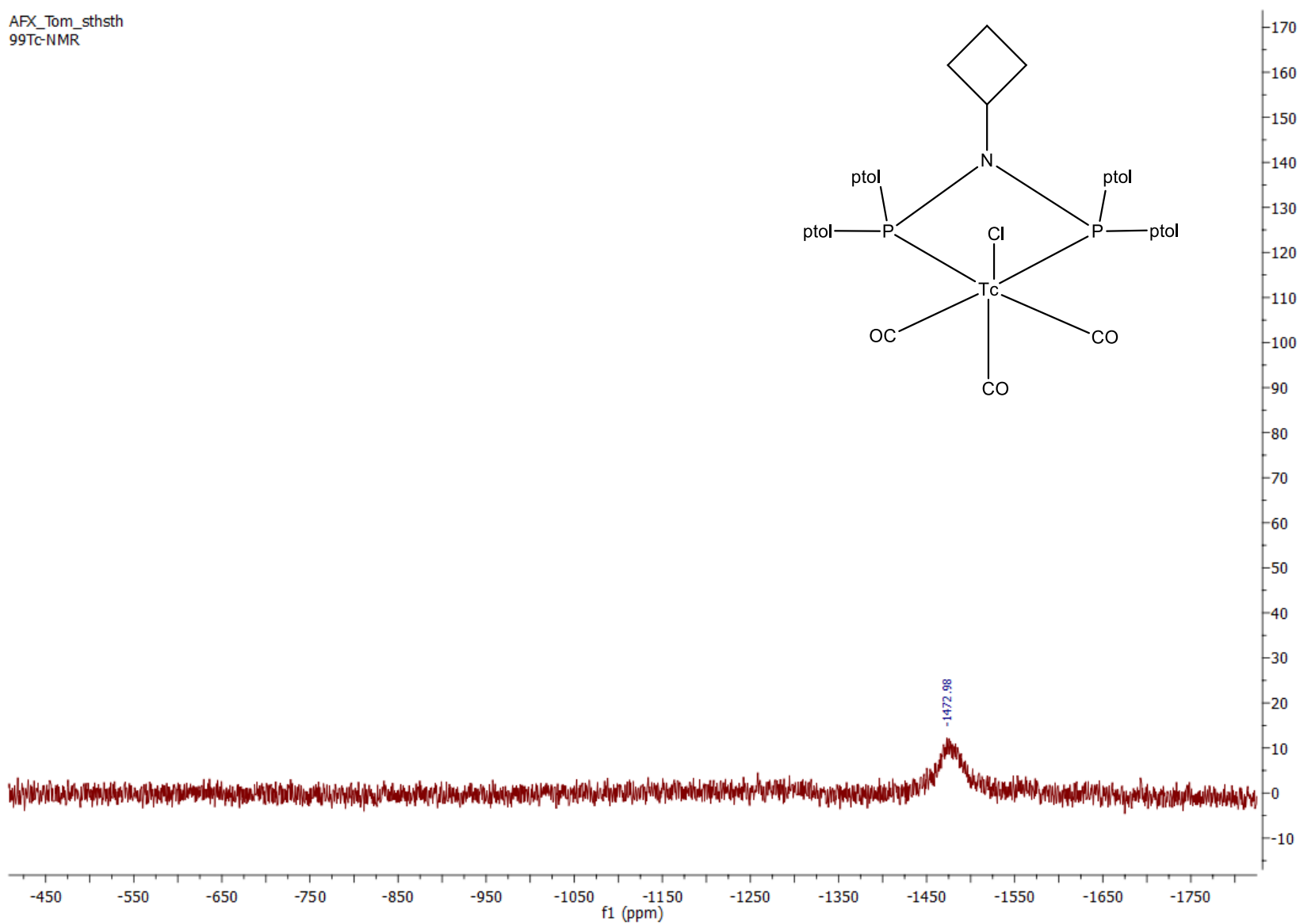


Figure S16 ^{31}P NMR spectrum for *fac*- $[\text{}^{99}\text{Tc}(\text{Cb-}p\text{TolPNP})(\text{CO})_3\text{Cl}]$ (**2B**)

Cybutyl-Tc(complex)-31P
Cybutyl-Tc(complex)-31P

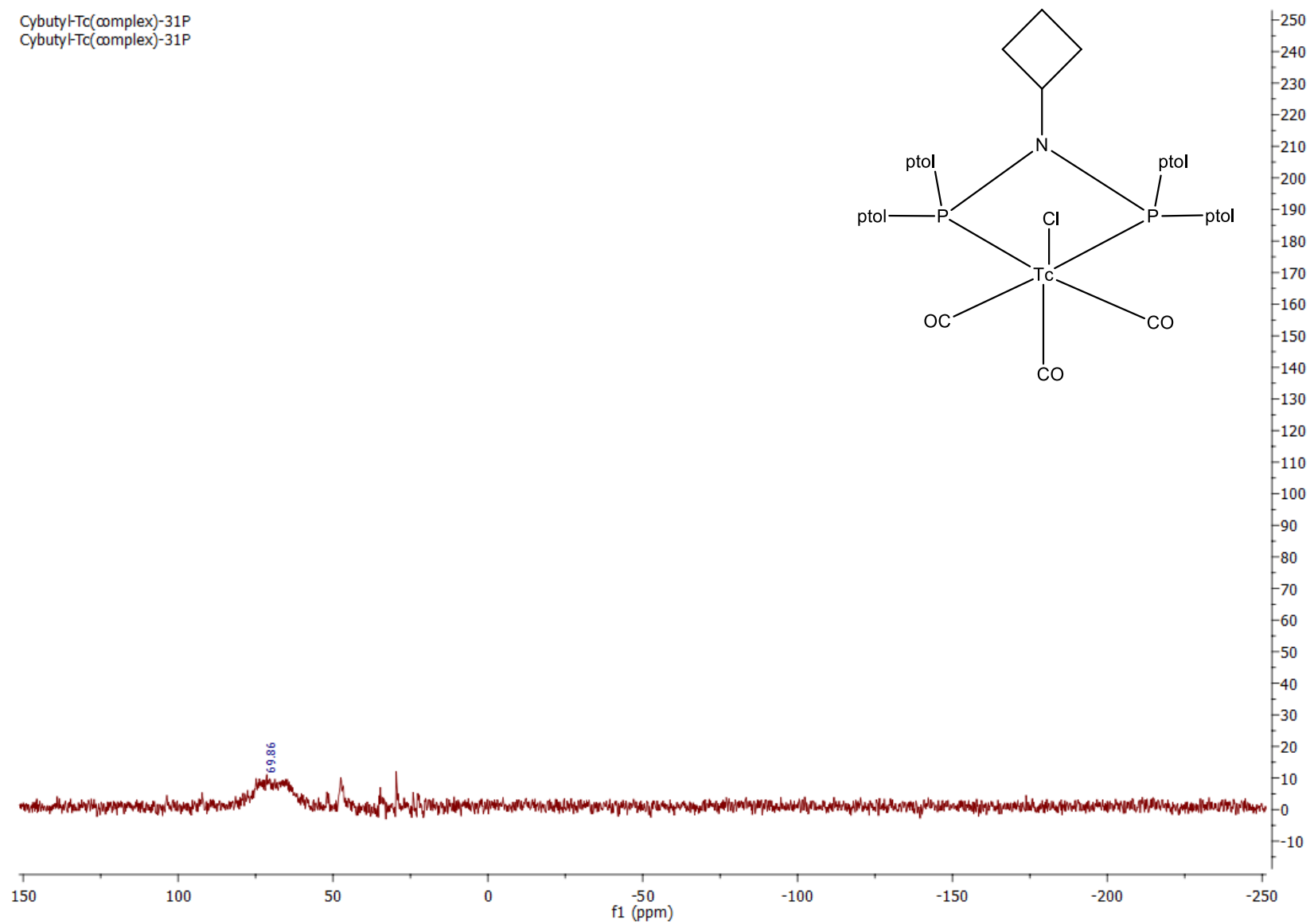


Figure S17 IR spectrum for *fac*-[⁹⁹Tc(Cb-*p*TolPNP)(CO)₃Cl] (**2B**)

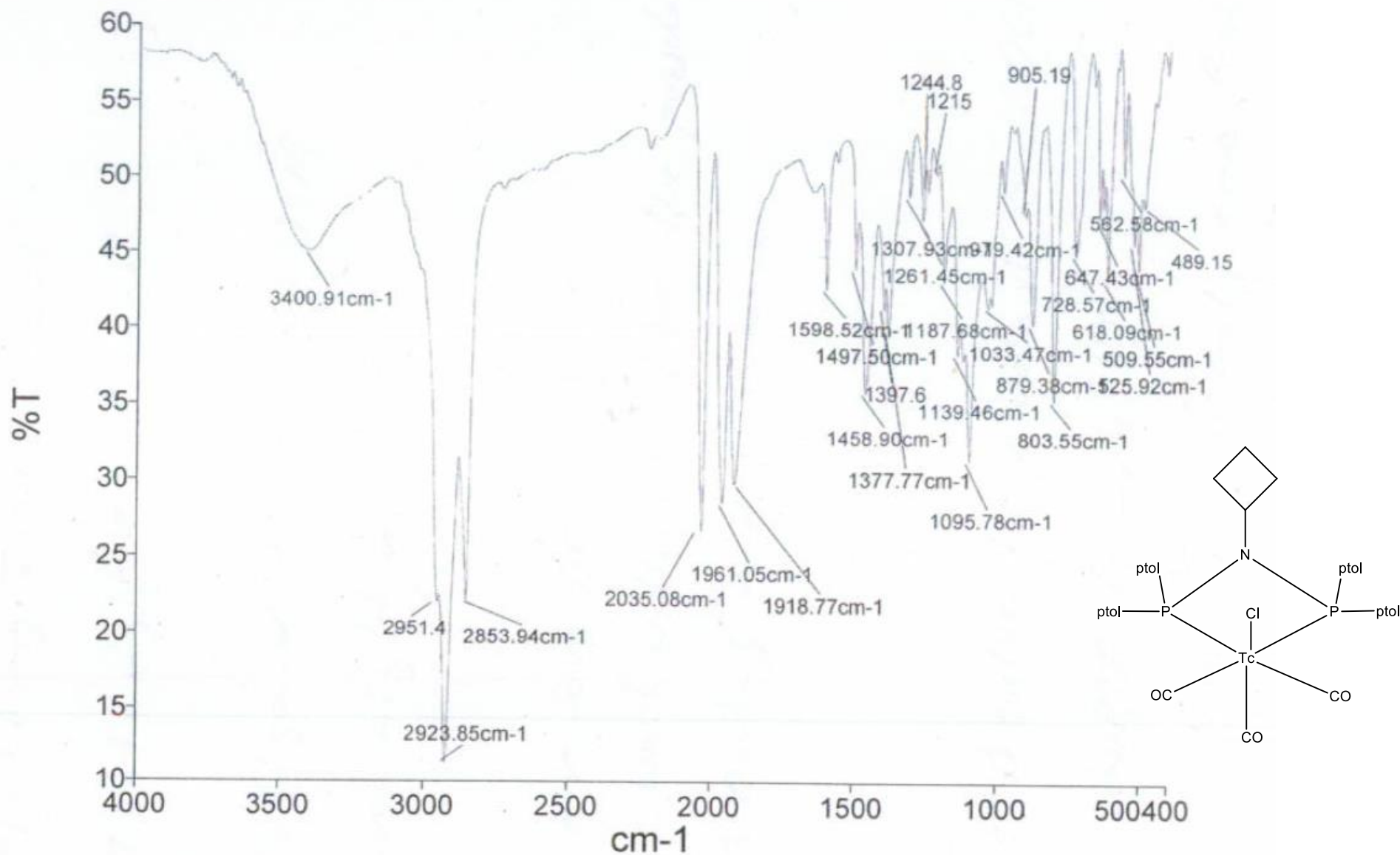


Figure S18 ^1H NMR spectrum for Chzyl-4-*ptol*-PNP (**1**)

Chyl+Cbtyl
cyhex-4ptol-pnp-p1-27-10-14
1H DCM

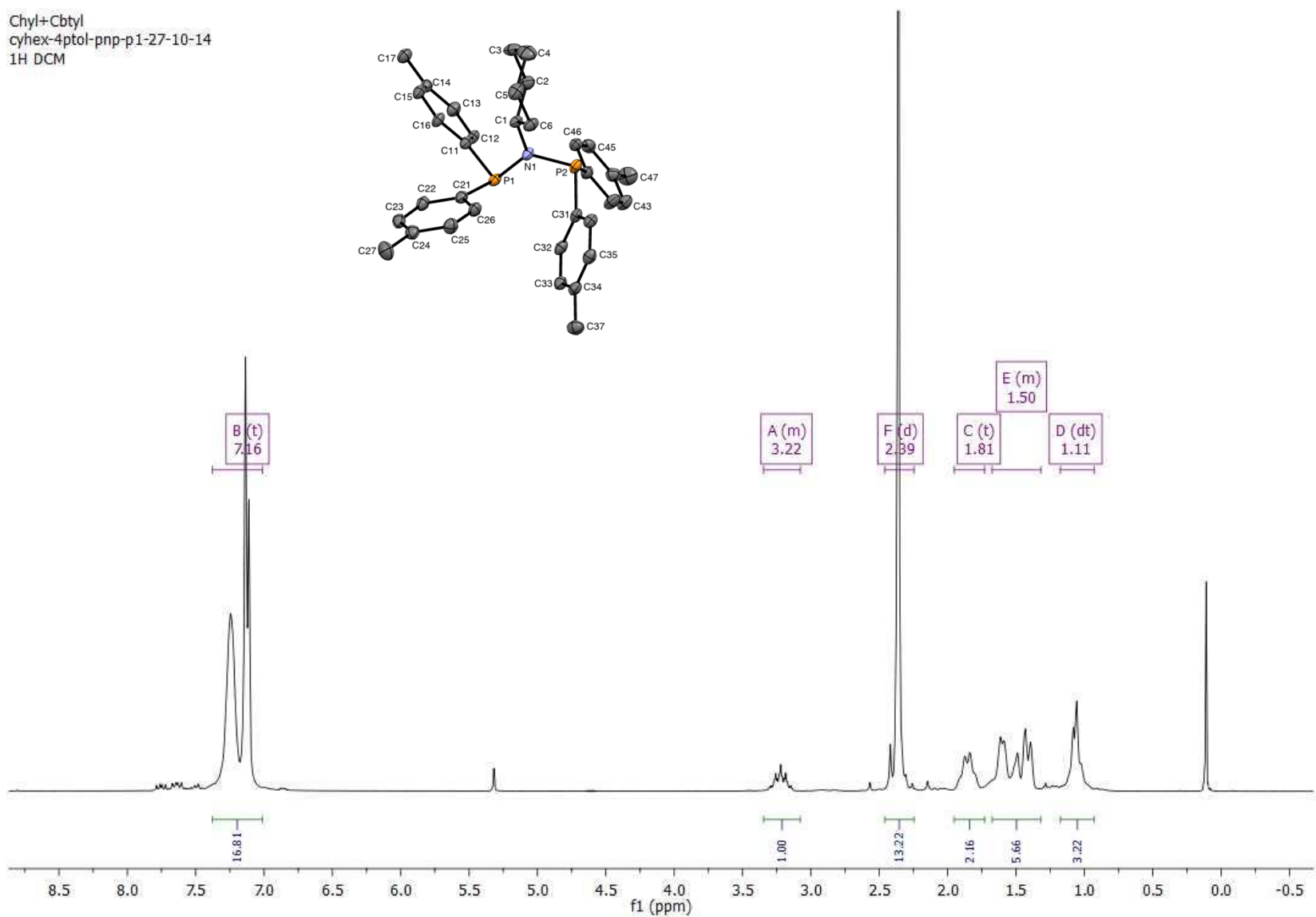


Figure S19 ^{31}P NMR spectrum for Chzyl-4ptol-PNP (**1**)

Chyl+Cbtyl
cyhxy1-4ptol-pnp-P1-27-10-14
 ^{31}P DCM

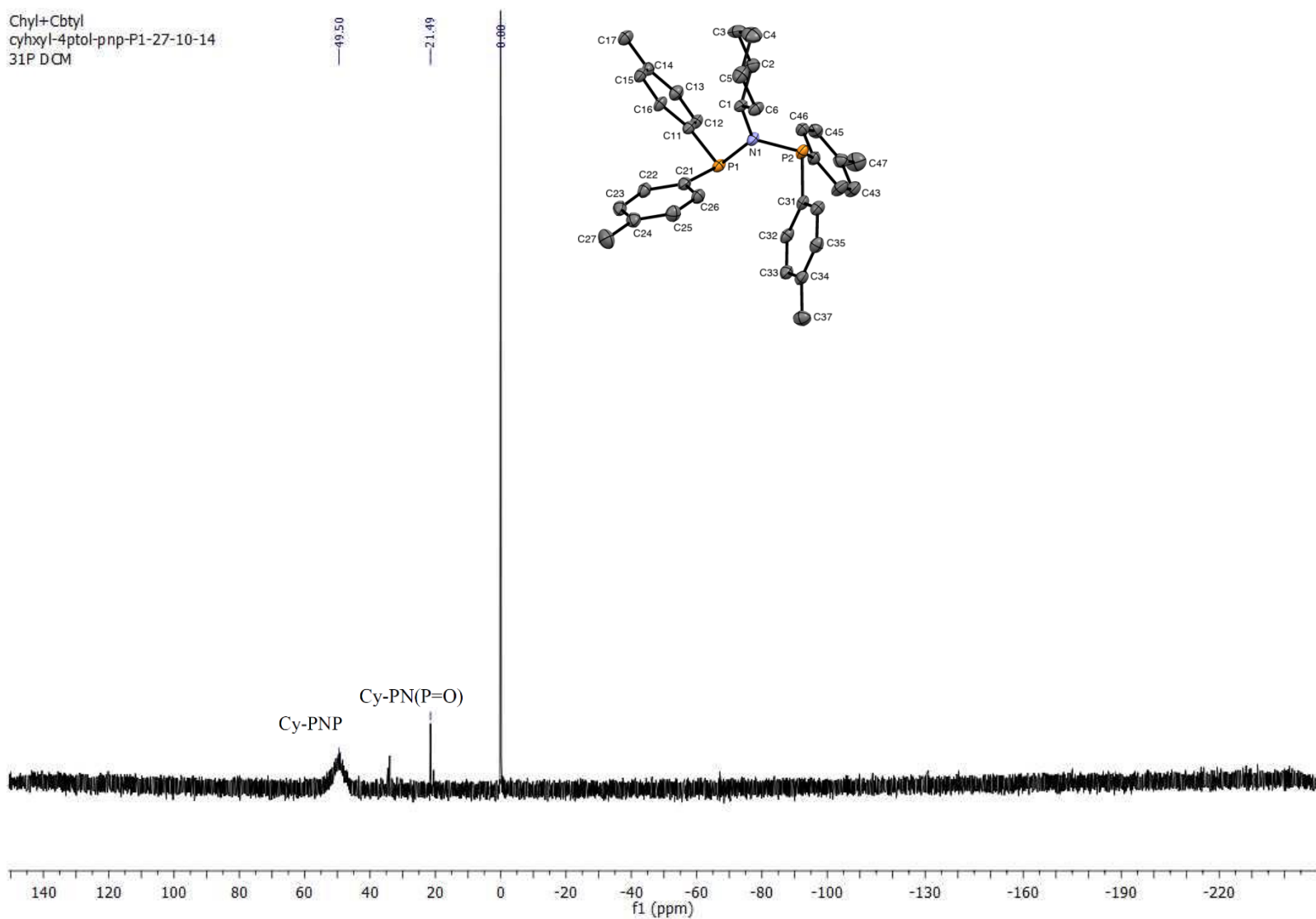


Figure S20 ^1H NMR spectrum for Cyclobutyl-4ptol-PNP (**2**)

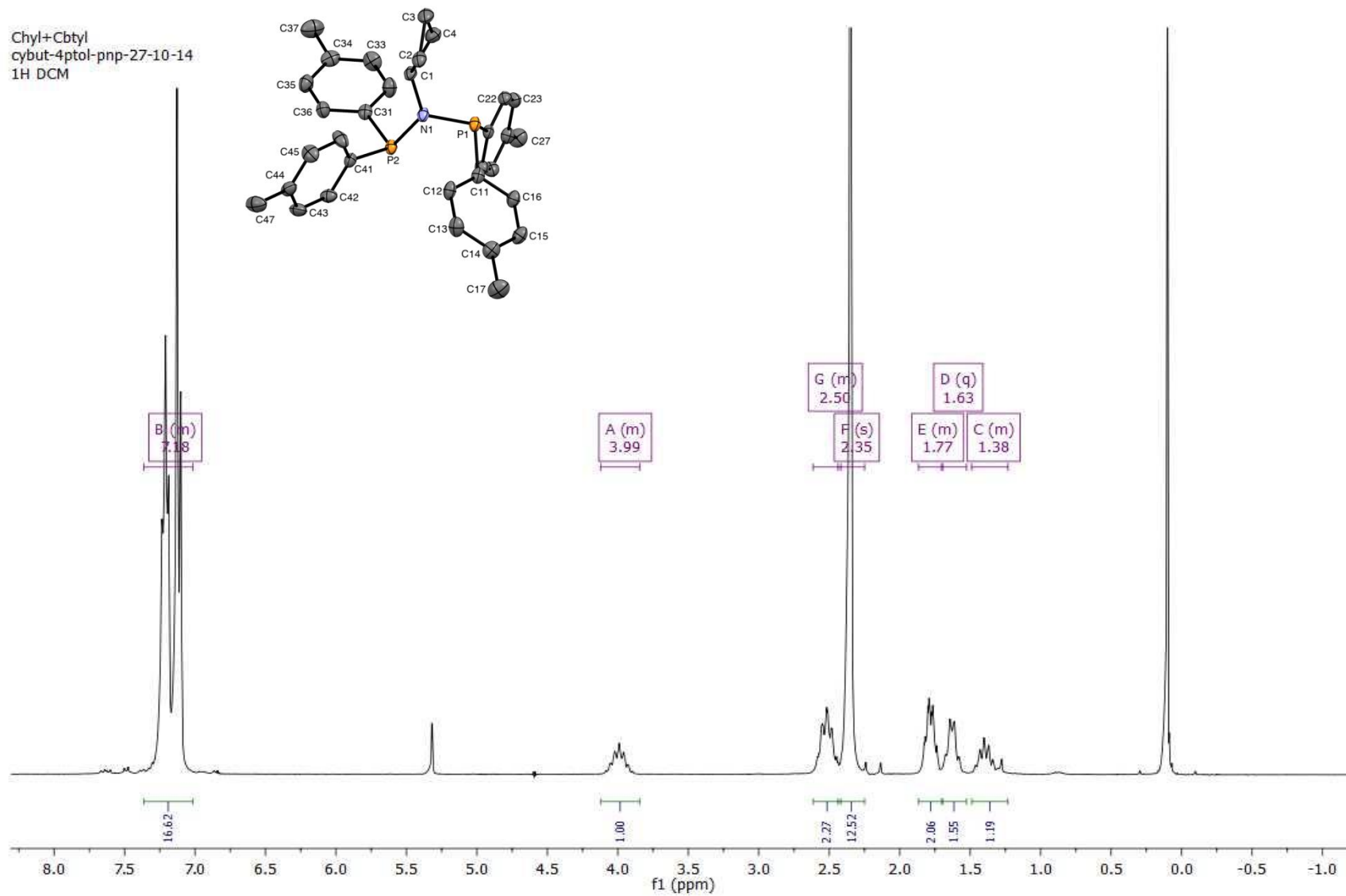


Figure S21 ^{31}P NMR spectrum for Cyclobutyl-4*ptol*-PNP (**2**)

Chyl+Cbtyl
cybut-4ptol-pnp-27-10-14
31P DCM

—48.37

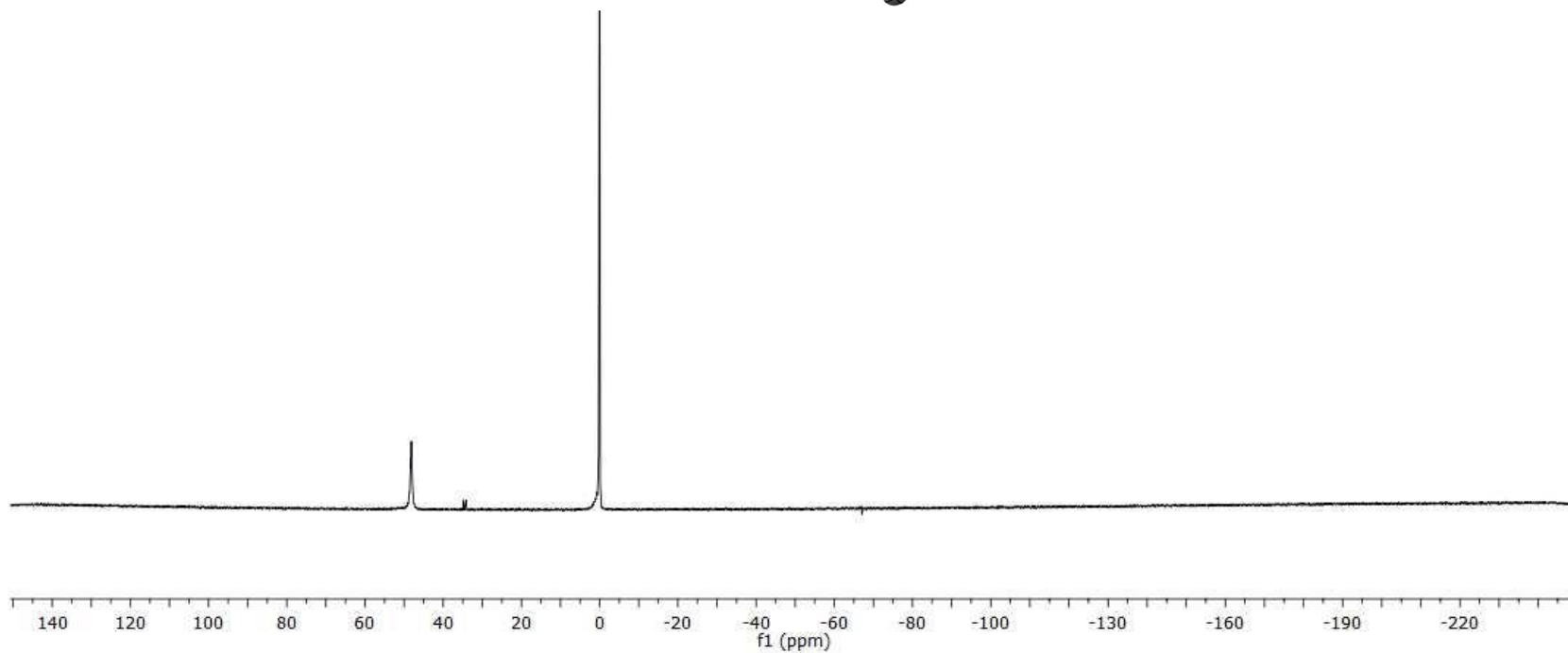
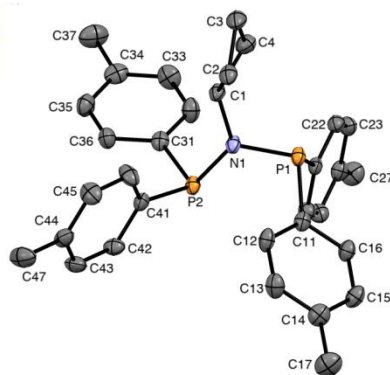


Figure S22 Illustration of (a) disorder in **1**, yielding (b) ca. 80% of the unoxidized Cy-PNP ligand, and (c) ca. 20% of the mono-oxidized product, Cy-PN(P=O)

