Supporting Information for

Synthesis and Coordination Chemistry of $(PNEt_2)_2$-Bridged [2]Ferrocenophane

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Table S1. Optimized coordinates for $(PNMe_2)_2$-bridged [2]ferrocenophane.

39
transNMe2PPFc

Fe	−1.807900	0.014100	−0.010700
P	1.148100	0.797600	0.719100
P	1.096900	−0.940100	−0.712800
N	2.406000	1.733500	0.046100
N	2.206800	−2.081800	−0.126500
C	−0.471900	1.501900	0.213900
C	−1.530100	1.649500	1.175600
C	−2.764800	1.783400	0.485700
C	−2.492900	1.743700	−0.911100
C	−1.091200	1.572800	−1.084800
C	−0.548400	−1.541300	−0.206300
C	−1.191100	−1.566400	1.083300
C	−2.596200	−1.671100	0.886500
C	−2.846900	−1.709000	−0.513900
C	−1.596800	−1.641800	−1.184800
C	2.344400	2.235500	−1.312600
H	1.264700	−2.600900	1.668600
C	3.057000	2.660800	0.955700
H	3.896400	−3.142400	−0.764800
C	3.493900	−2.122400	−0.796500
H	1.698700	3.123600	−1.404100
C	2.270200	−2.489400	1.262400
H	3.101000	2.226700	1.957300
H	−1.401300	1.589000	2.247900
H	−3.741900	1.870600	0.940200
H	−3.227500	1.796900	−1.702900
H	−0.586200	1.453300	−2.033200
H	−0.700100	−1.454700	2.040000
H	−3.345000	−1.679200	1.666500
H	−3.819200	−1.749900	−0.984400
H	−1.447000	−1.597500	−2.254800
H	1.968500	1.459600	−1.983200
H	3.350300	2.513500	−1.649400
H	2.535000	3.629300	1.022600
H	4.082100	2.854600	0.617100
H	3.373100	−1.833800	−1.843400
H	4.234500	−1.450200	−0.336600
H	2.823600	−1.774600	1.890600
H	2.768900	−3.463300	1.333700

Table S2. Optimized coordinates for {$(PNMe_2)_2$-bridged [2]ferrocenophane}$_,$-$Cr(CO)_5$.

50
trans-NMe2PPFcCrCO5

Fe	−2.755400	−0.654700	−0.246900
C	−1.050300	−1.362300	0.556700
C	−1.354900	−2.078300	−0.647500
C	−2.623100	−2.700700	−0.490300
C	−3.113500	−2.388700	0.808800
C	−2.152900	−1.565700	1.459000
C	−2.348800	1.300100	−0.240400
C	−2.390400	0.804500	−1.591100
C	−3.689500	0.278200	−1.833800
C	−4.467400	0.440100	−0.653800
C	−3.656200	1.079000	0.320900
P	0.284200	−0.145300	0.799400
P	−0.999400	1.774600	0.886700
N	0.468800	−0.312200	2.504900
C	0.880400	−1.628400	2.974700
C	1.202200	0.755100	3.163300
N	−0.191300	3.045000	0.153800
C	0.160500	4.199900	0.960400
C	−0.045600	3.259600	−1.272100
H	−0.753700	−2.097000	−1.544100
H	−3.135500	−3.284000	−1.242300
H	−4.065600	−2.694500	1.219400
H	−2.235400	−1.130200	2.444400
H	−1.568800	0.768000	−2.290300
H	−4.012600	−0.201700	−2.747100
H	−5.485500	0.105700	−0.512200
H	−3.937200	1.303600	1.340600
H	0.289700	−2.407200	2.488700
H	1.945100	−1.839400	2.802600
H	0.695200	−1.687300	4.052800
H	0.796900	1.727500	2.871800
H	2.280700	0.744700	2.947200
H	1.072100	0.655300	4.245800
H	−0.421200	5.083800	0.662700
H	−0.048600	3.999000	2.013400
H	1.225900	4.436600	0.852500
H	−0.858700	3.879800	−1.674300
H	−0.037300	2.312200	−1.807700
H	0.904800	3.764300	−1.474900
Cr	2.258900	−0.394300	−0.561800
C	1.933100	−2.240500	−0.550200
O	1.773300	−3.380500	−0.527500
C	3.419200	−0.655400	0.891600
O	4.207600	−0.819700	1.715700
C	2.649100	1.437100	−0.413600
O	2.990400	2.533700	−0.316200
C	1.229400	−0.142300	−2.097300
O	0.646700	0.006800	−3.083800
C	3.709800	−0.628300	−1.669300
O	4.608800	−0.778200	−2.376000

Table S3. Optimized coordinates for {$(PNMe_2)_2$-bridged [2]ferrocenophane}, $Cr(CO)_4$.

48
cis-NMe2PPFc-CrCO4

Fe	−2.589200	−0.377500	−0.000000
Cr	1.862800	−0.843700	−0.000000
P	0.318700	0.525500	−1.089400
P	0.318700	0.525400	1.089400
N	0.780800	1.898200	−1.918400
N	0.780800	1.898100	1.918400
C	−1.380800	0.054900	−1.551800
C	−1.816800	−1.310200	−1.652300
H	−1.175200	−2.177600	1.620200
C	−3.235100	−1.326000	−1.724600
H	−3.855600	−2.210300	1.760500
C	−3.695700	0.019300	−1.694100
H	−4.728100	0.340000	1.706300
C	−2.562500	0.873500	−1.589500
H	−2.599600	1.949100	1.504000
C	−1.380800	0.054800	1.551800
C	−1.816800	−1.310300	1.652300
H	−1.175200	−2.177500	−1.620300
C	−3.235100	−1.326000	1.724600
H	−3.855500	−2.210200	−1.760500
C	−3.695700	0.019300	1.694100
H	−4.728100	0.340000	−1.706300
C	−2.562500	0.873500	1.589500
H	−2.599600	1.949100	−1.504000
C	−0.030000	3.093600	−2.009500
H	2.492500	2.654800	−2.867700
H	2.385500	0.886000	−2.807900
H	1.373200	1.791200	−3.951500
H	0.620900	3.975300	−2.040900
H	−0.672600	3.184600	−1.132000
H	−0.662200	3.104700	−2.909200
C	1.809000	1.801400	−2.942500
H	2.492400	2.654800	2.867900
H	2.385500	0.886000	2.807900
H	1.373100	1.790900	3.951600
H	−0.672600	3.184600	1.132100
H	0.620900	3.975300	2.041100
H	−0.662200	3.104600	2.909200
C	−0.030100	3.093500	2.009500
C	1.808900	1.801300	2.942600
C	0.908100	−2.443600	−0.000000
C	2.830000	−1.548200	1.390800
C	3.061500	0.588100	0.000000
C	2.830000	−1.548200	−1.390900
O	0.408700	−3.487300	−0.000000
O	3.426600	−1.972800	2.286700
O	3.854200	1.428700	0.000000
O	3.426600	−1.972800	−2.286700

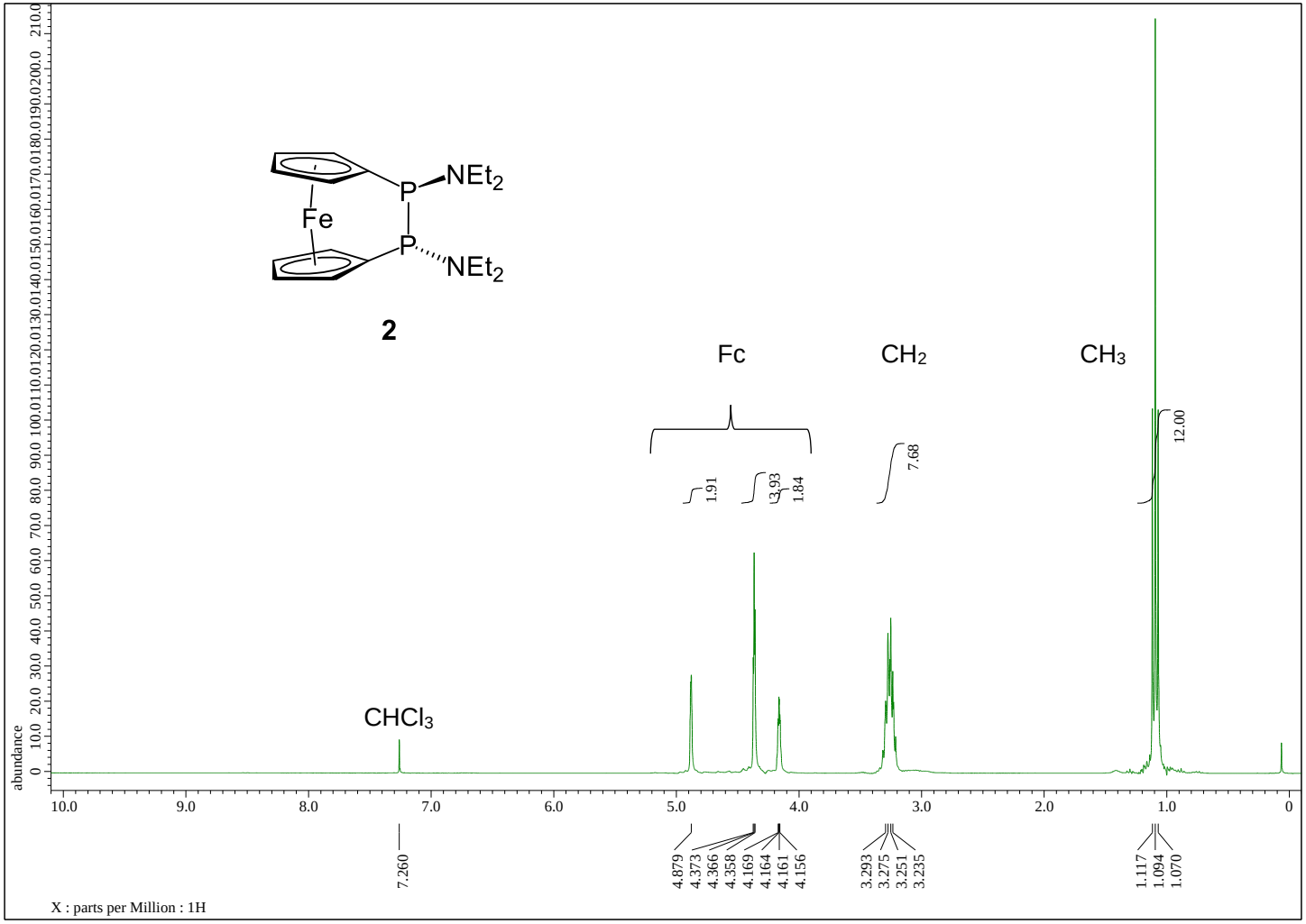

Figure S1. ^{1}H NMR spectrum of $(PNEt_2)_2$-bridged [2]ferrocenophane, **2**.

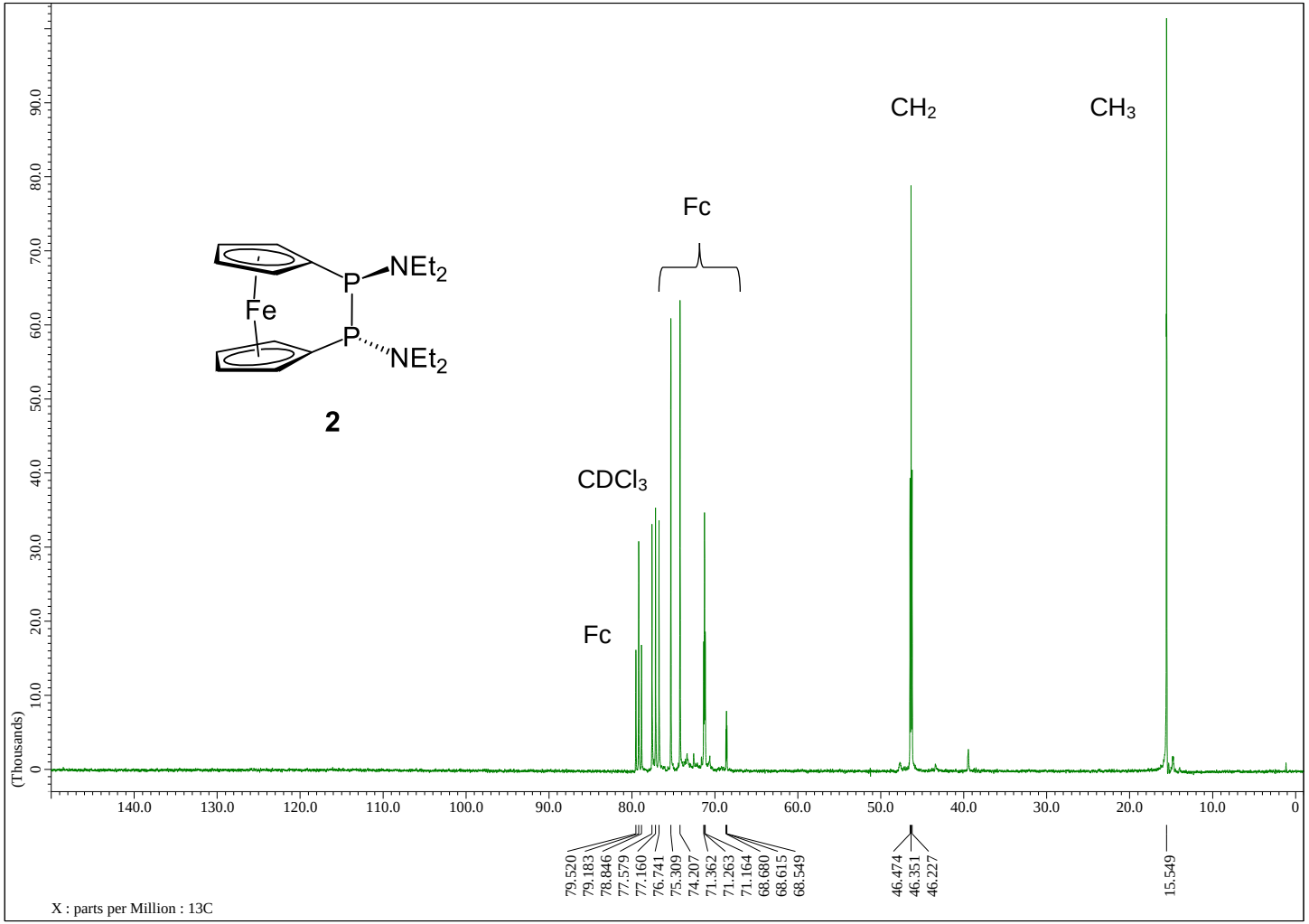

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of $(PNEt_2)_2$-bridged [2]ferrocenophane, **2**.

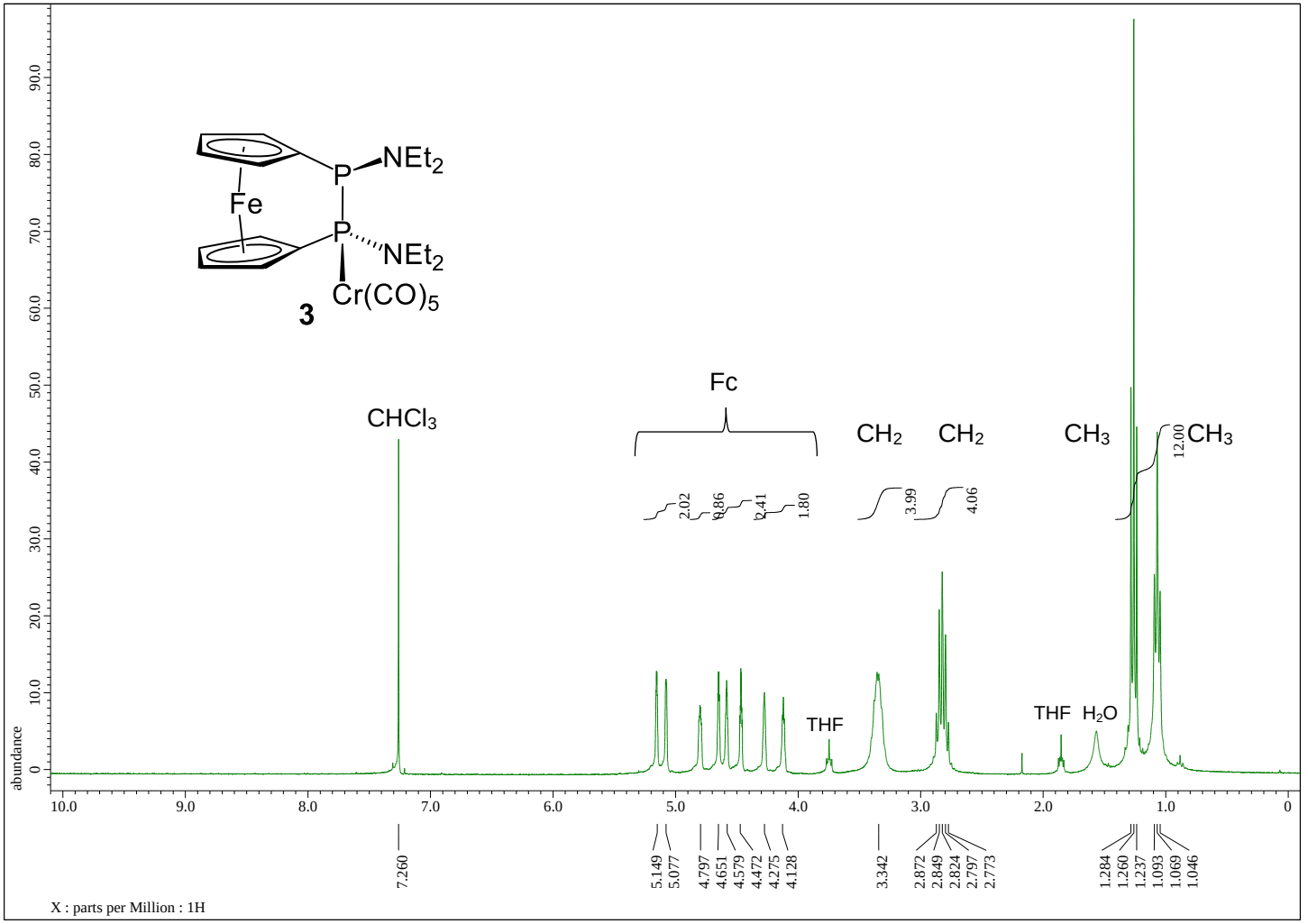

Figure S3. ^{1}H NMR spectrum of [Cr(**2**)(CO)$_5$], **3**.

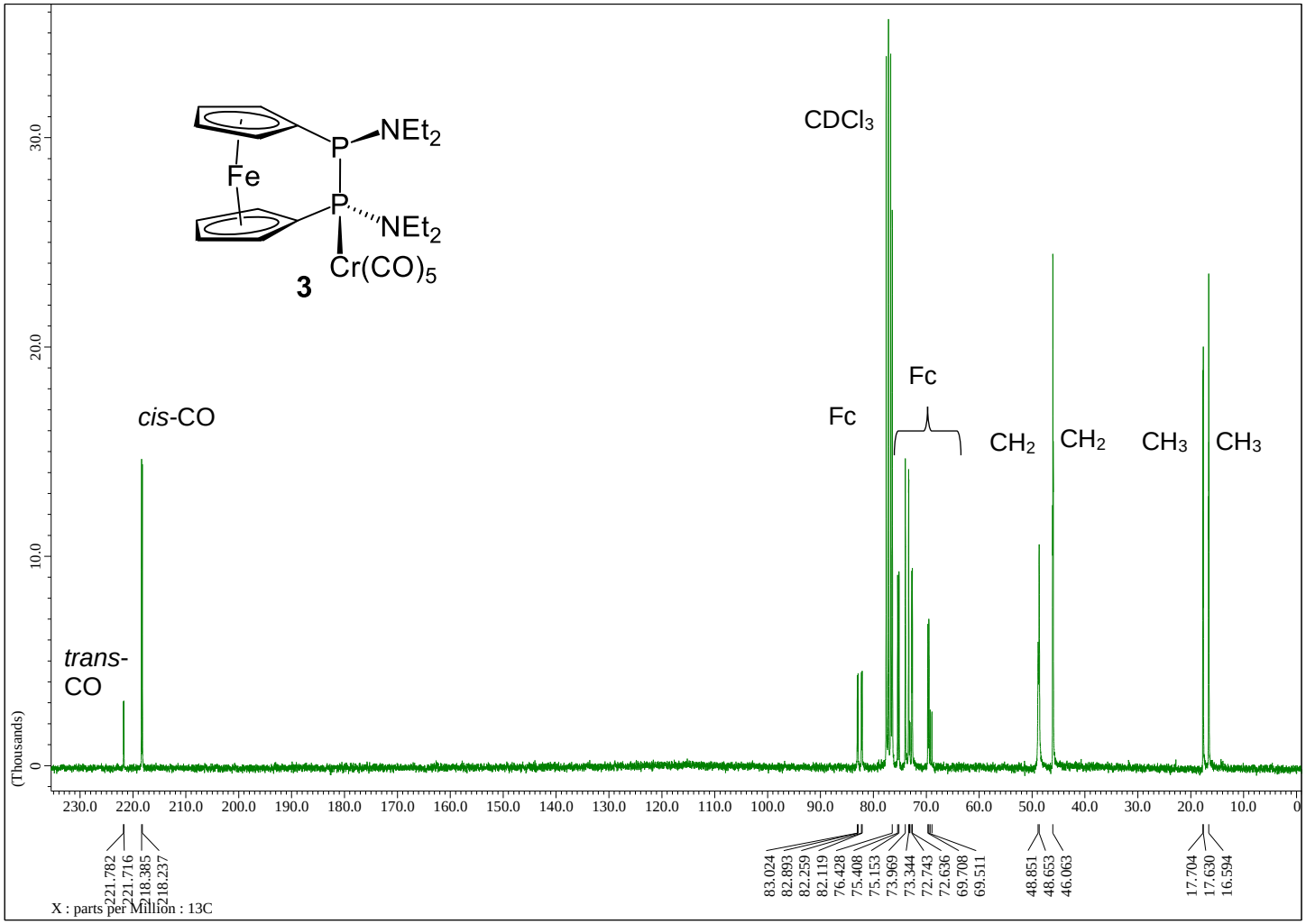

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of [Cr(**2**)$(CO)_5$], **3**.

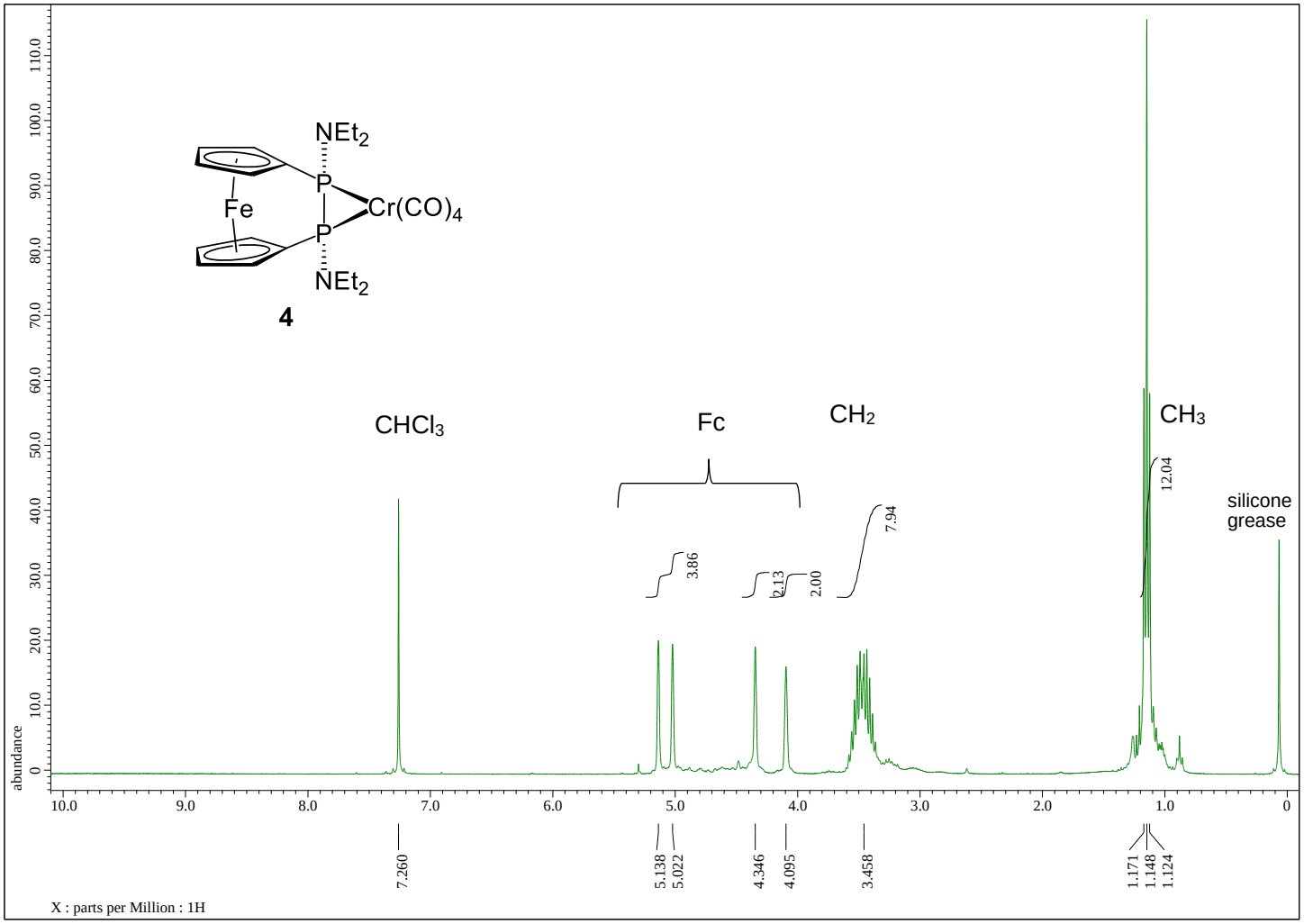

Figure S5. ^{1}H NMR spectrum of $[Cr(\kappa^2\text{-}\mathbf{2})(CO)_4]$, **4**.

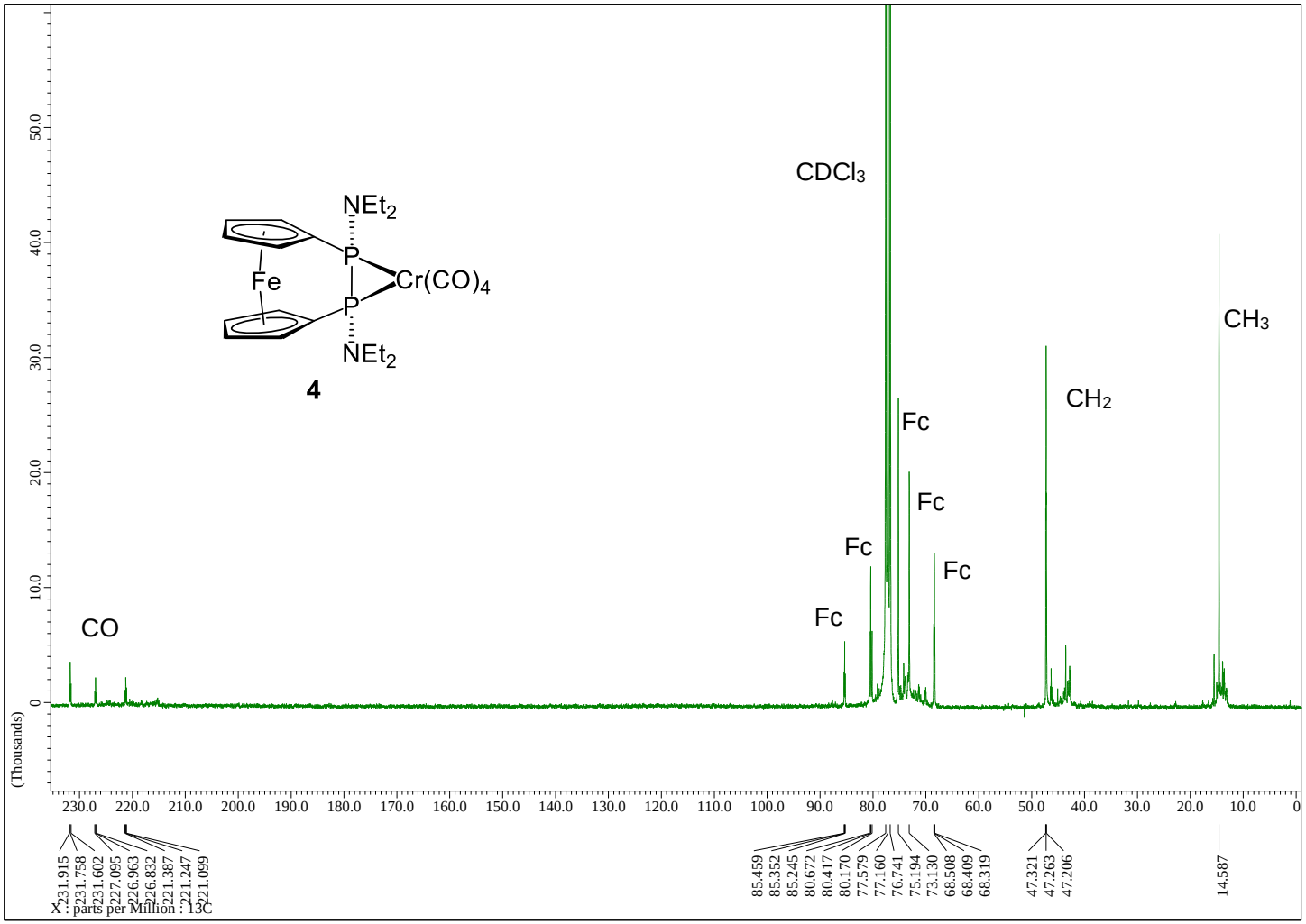

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of $[Cr(\kappa^2\text{-}\mathbf{2})(CO)_4]$, **4**.

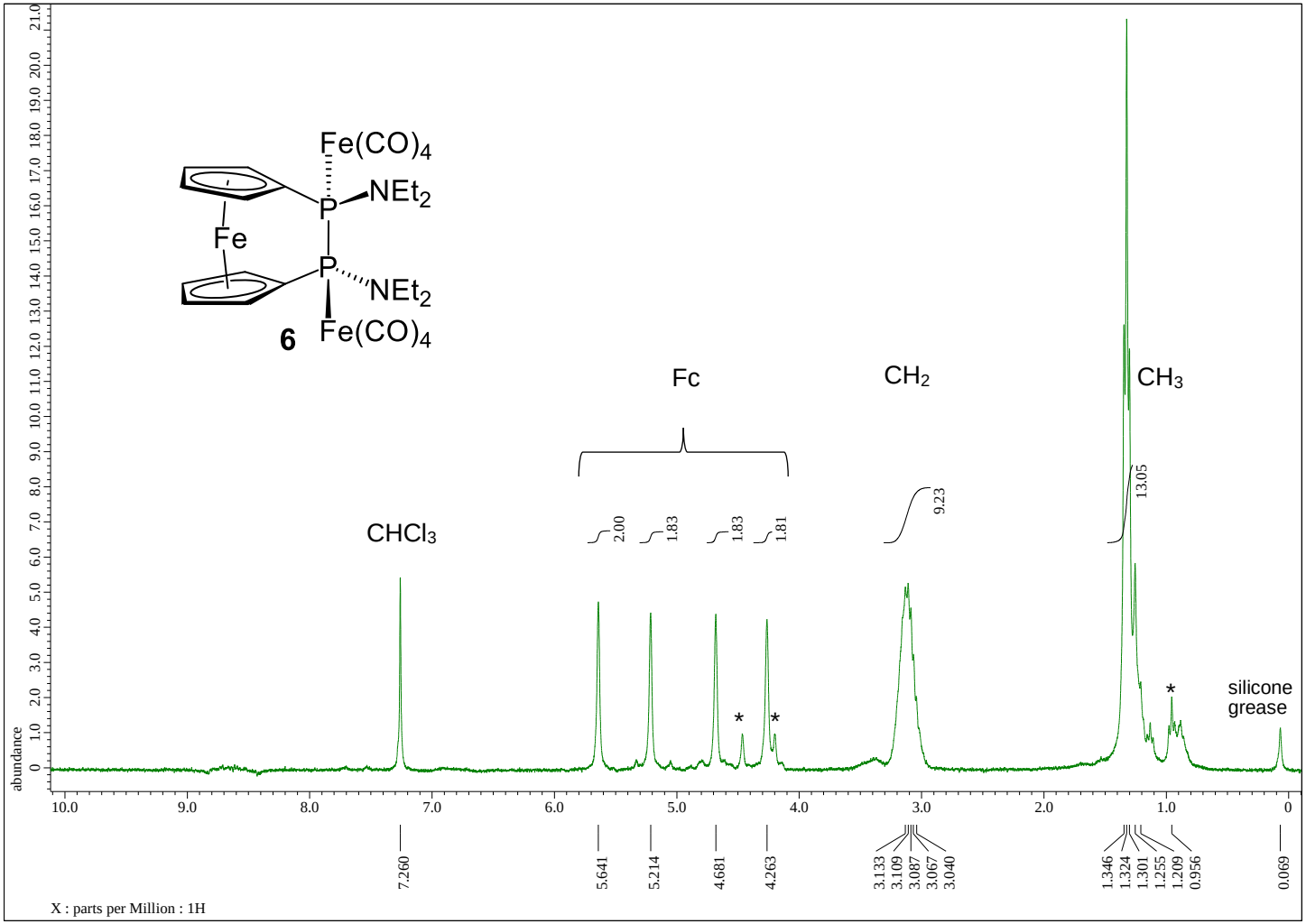

Figure S7. ^{1}H NMR spectrum of (μ-**2**)-[Fe(CO)$_4$]$_2$, **6**. Signals with * is due to **8** which could not be removed.

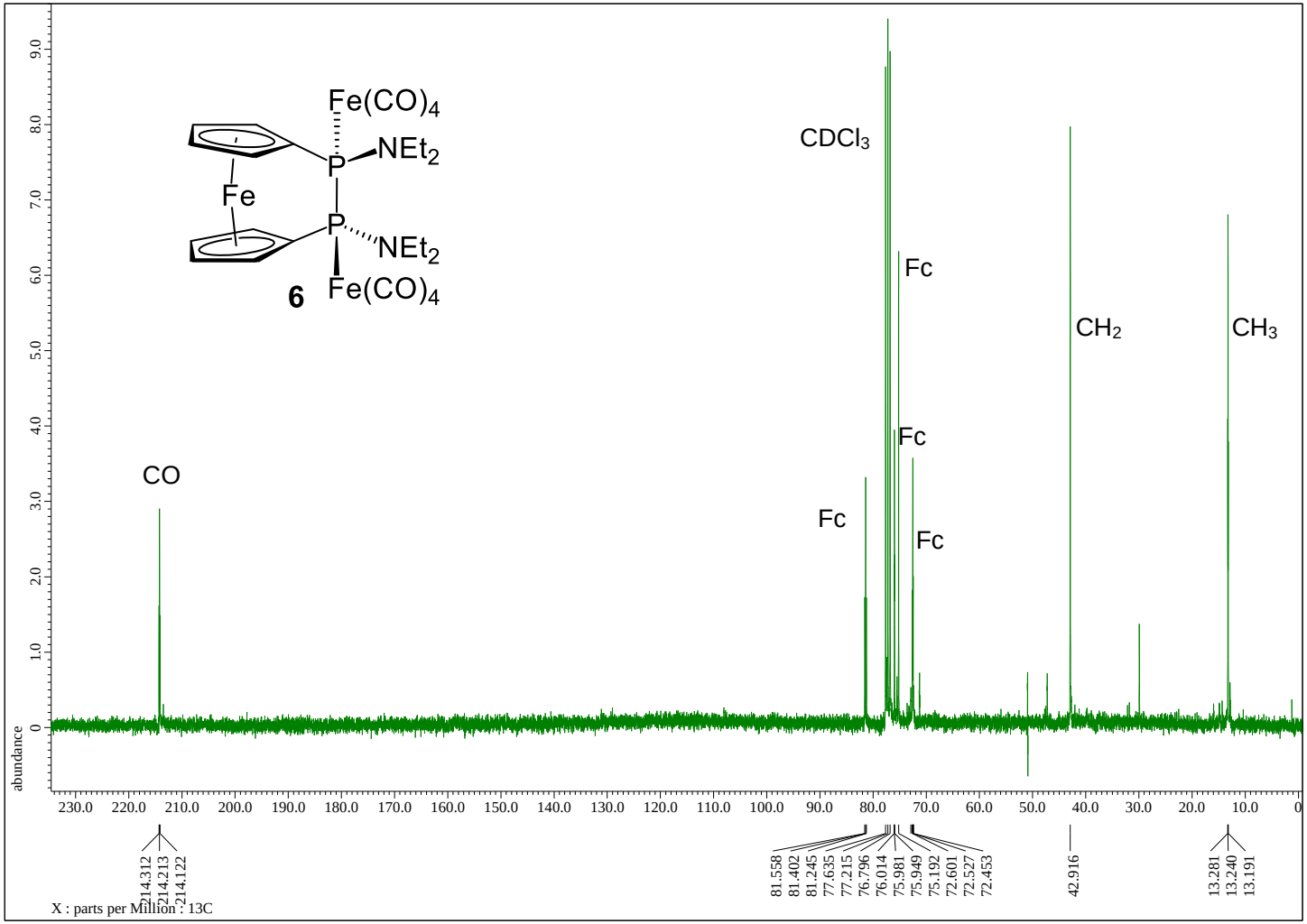

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of (μ-**2**)-$[Fe(CO)_4]_2$, **6**.

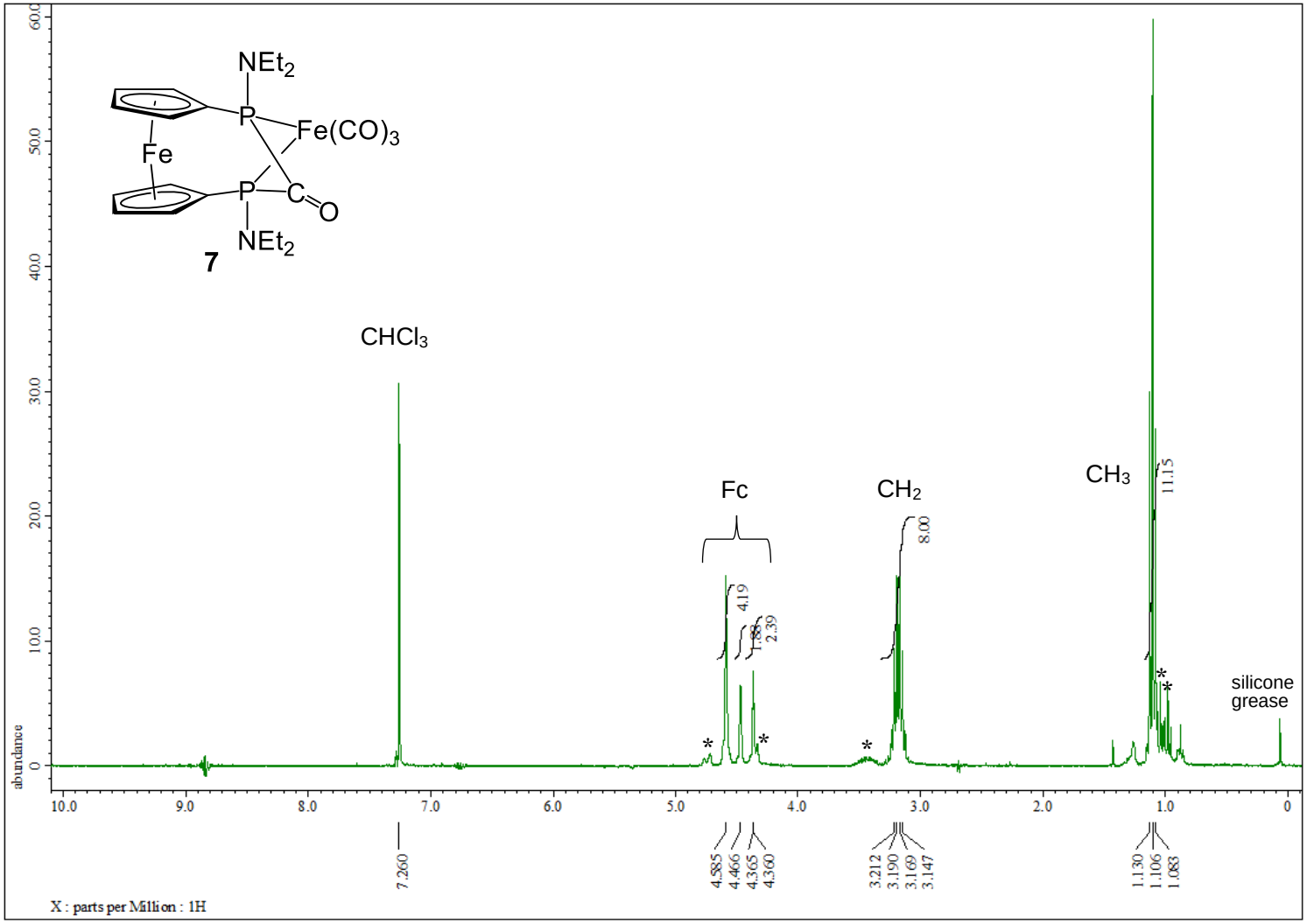

Figure S9. ^{1}H NMR spectrum of the complex **7**. Signals with * is due to impurity which formed during the chromatography, and could not be removed.

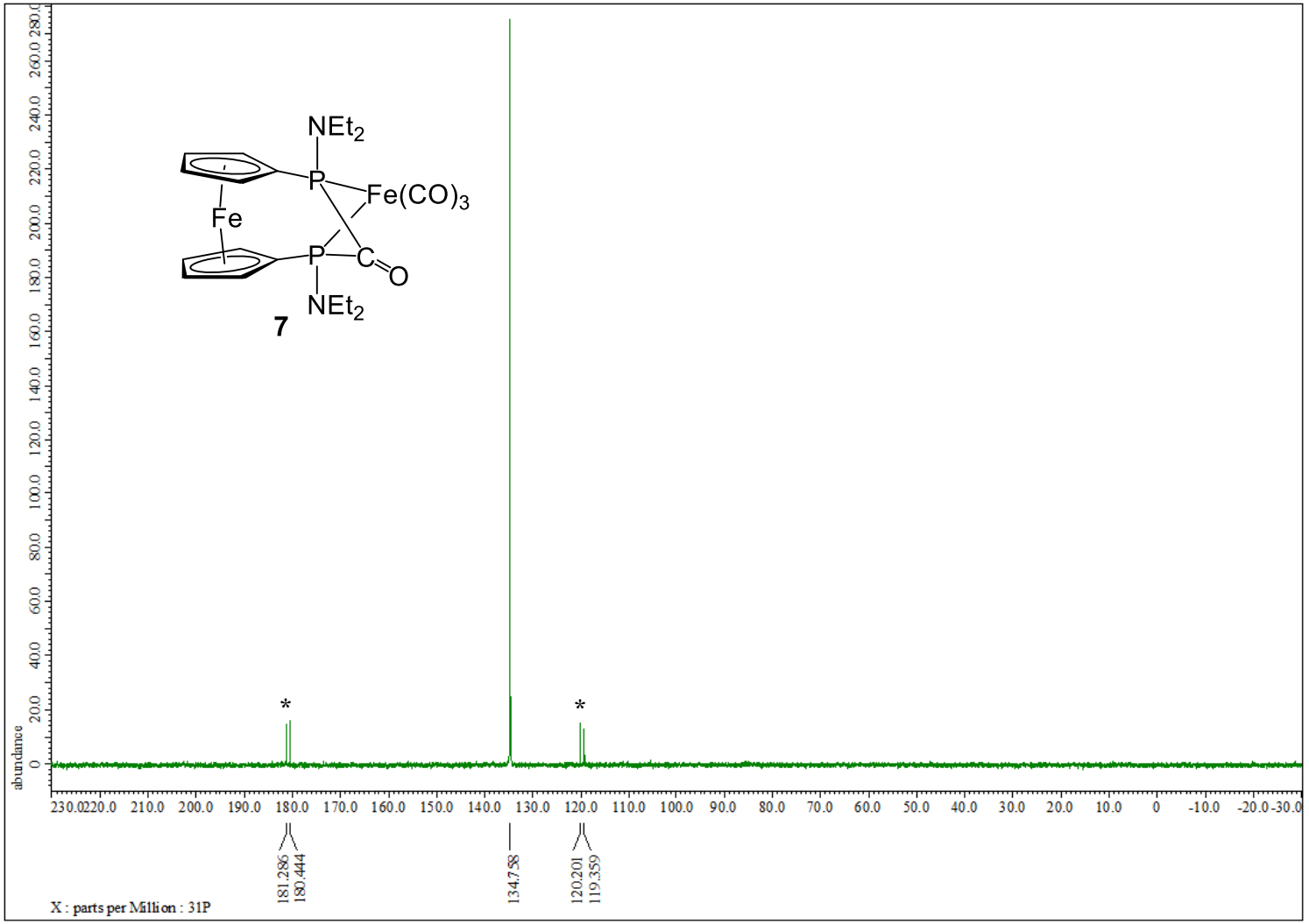

Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of the complex **7**. Signals with * is due to impurity which formed during the chromatography, and could not be removed.

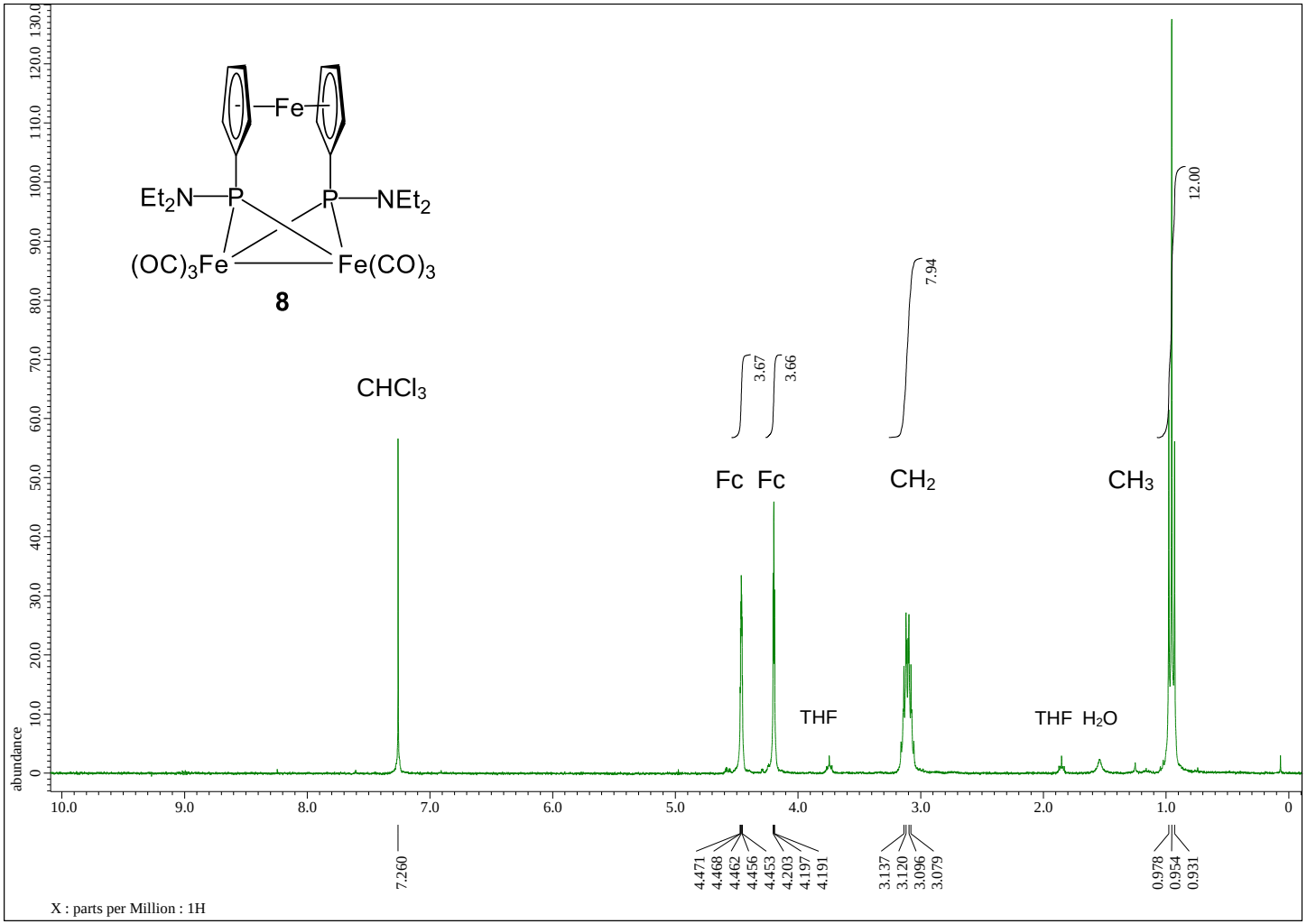

Figure S11. ^{1}H NMR spectrum of μ-{Fe($C_5H_4PNEt_2$)$_2$}[Fe(CO)$_3$]$_2$, **8**.

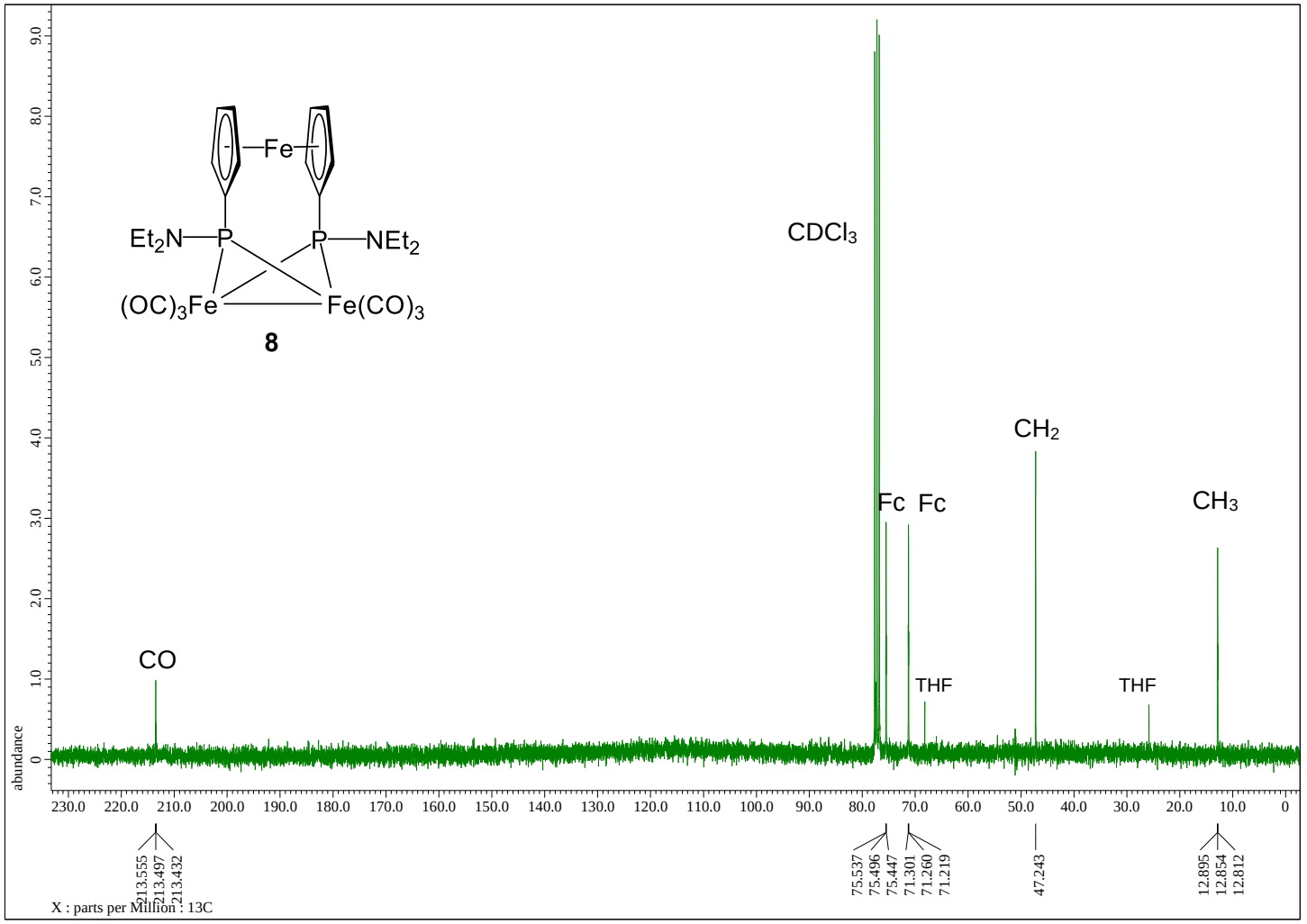

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of μ-$\{Fe(C_5H_4PNEt_2)_2\}[Fe(CO)_3]_2$, **8**.

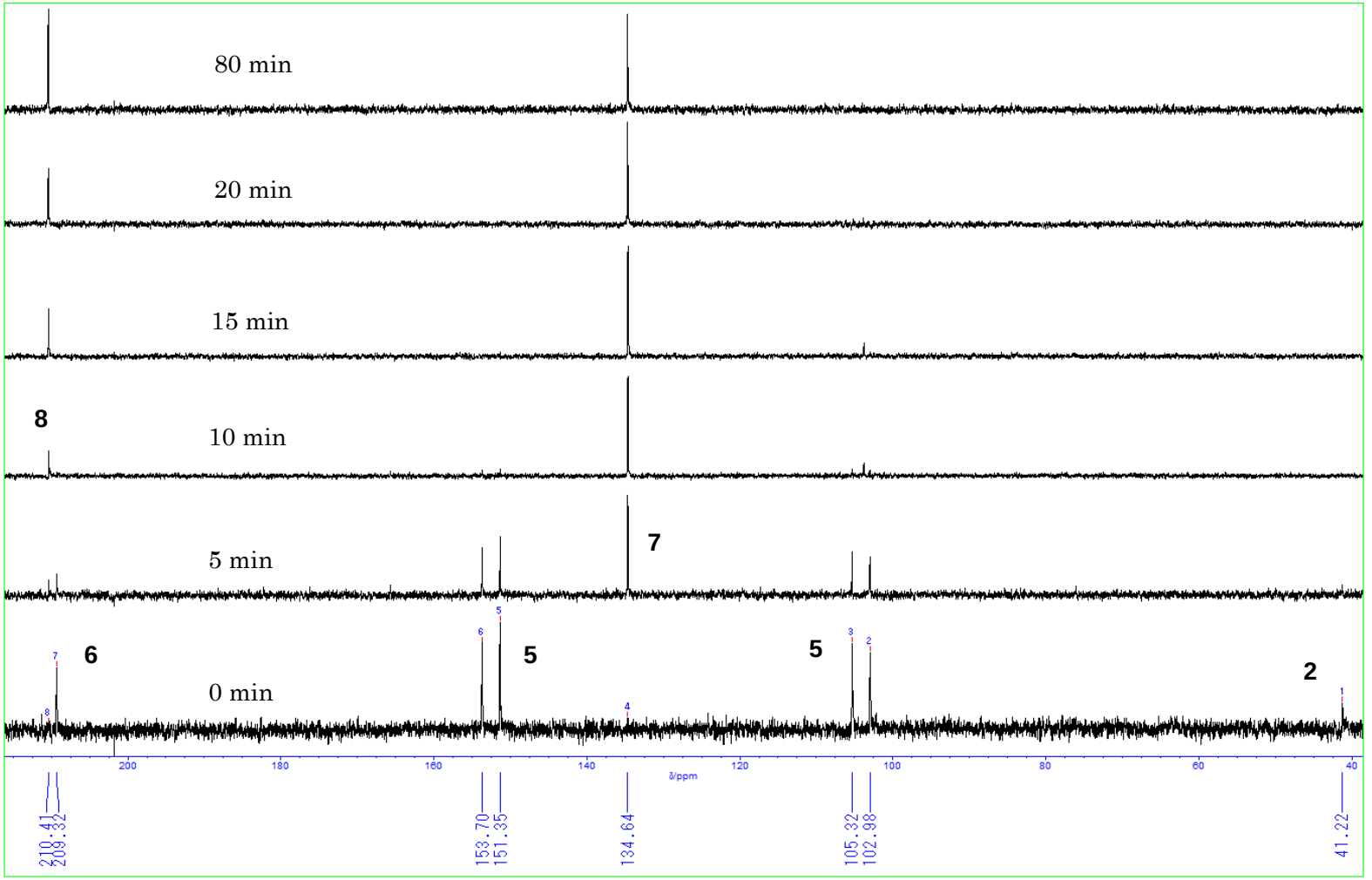

Figure S13. Time course of $^{31}P\{^{1}H\}$ NMR spectra for photochemical reaction of a 1:1 mixture of **2** with $Fe_2(CO)_9$ sealed in an NMR tube. Since the sample in an NMR tube (ϕ 5 mm) can be irradiated much more effectively than that in the Schlenk tube, the reaction proceeds much faster.

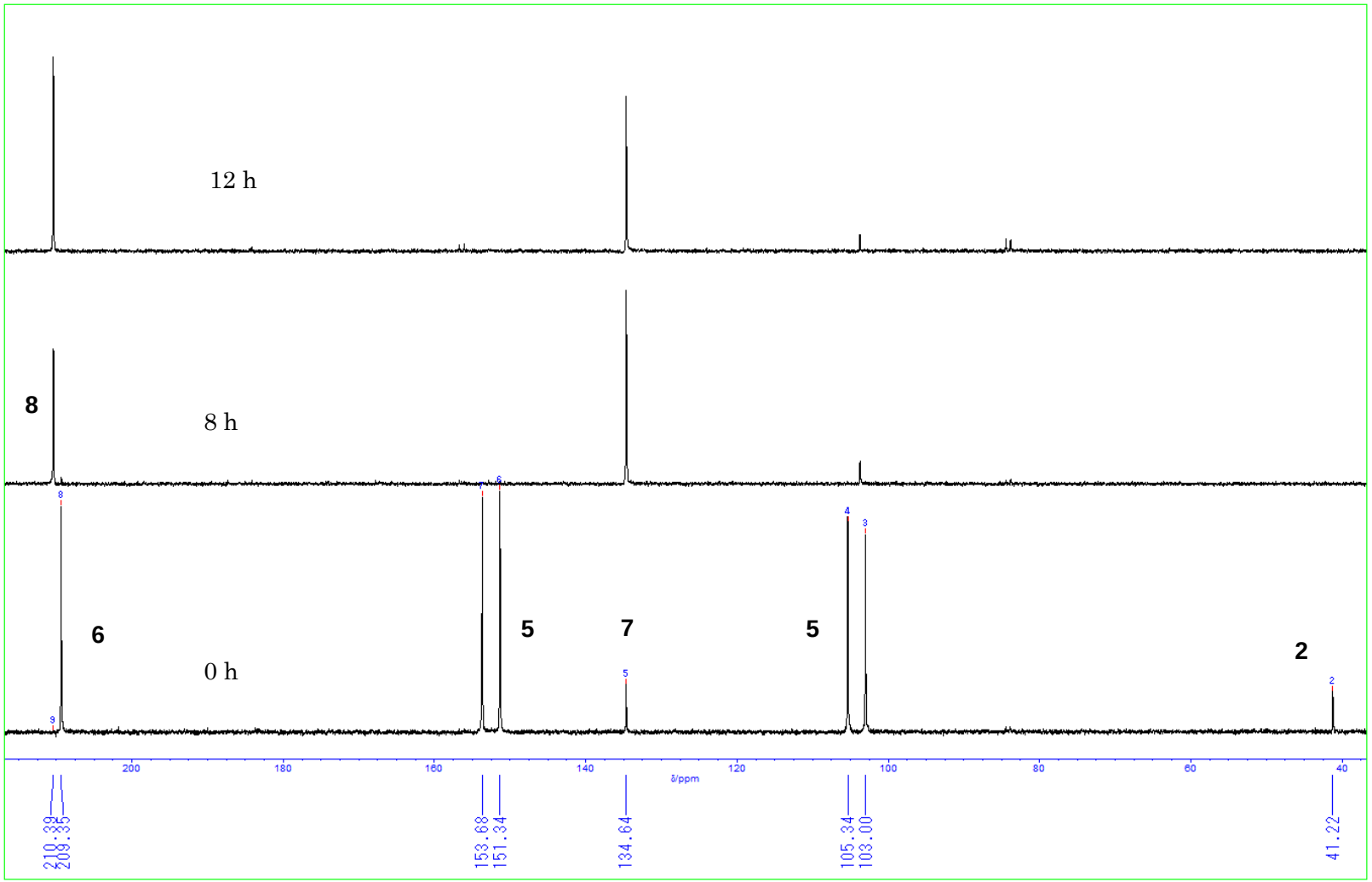

Figure S14. Time course of $^{31}P\{^{1}H\}$ NMR spectra for photochemical reaction of a 1:1 mixture of **2** with $Fe_2(CO)_9$ in a Schlenk tube.

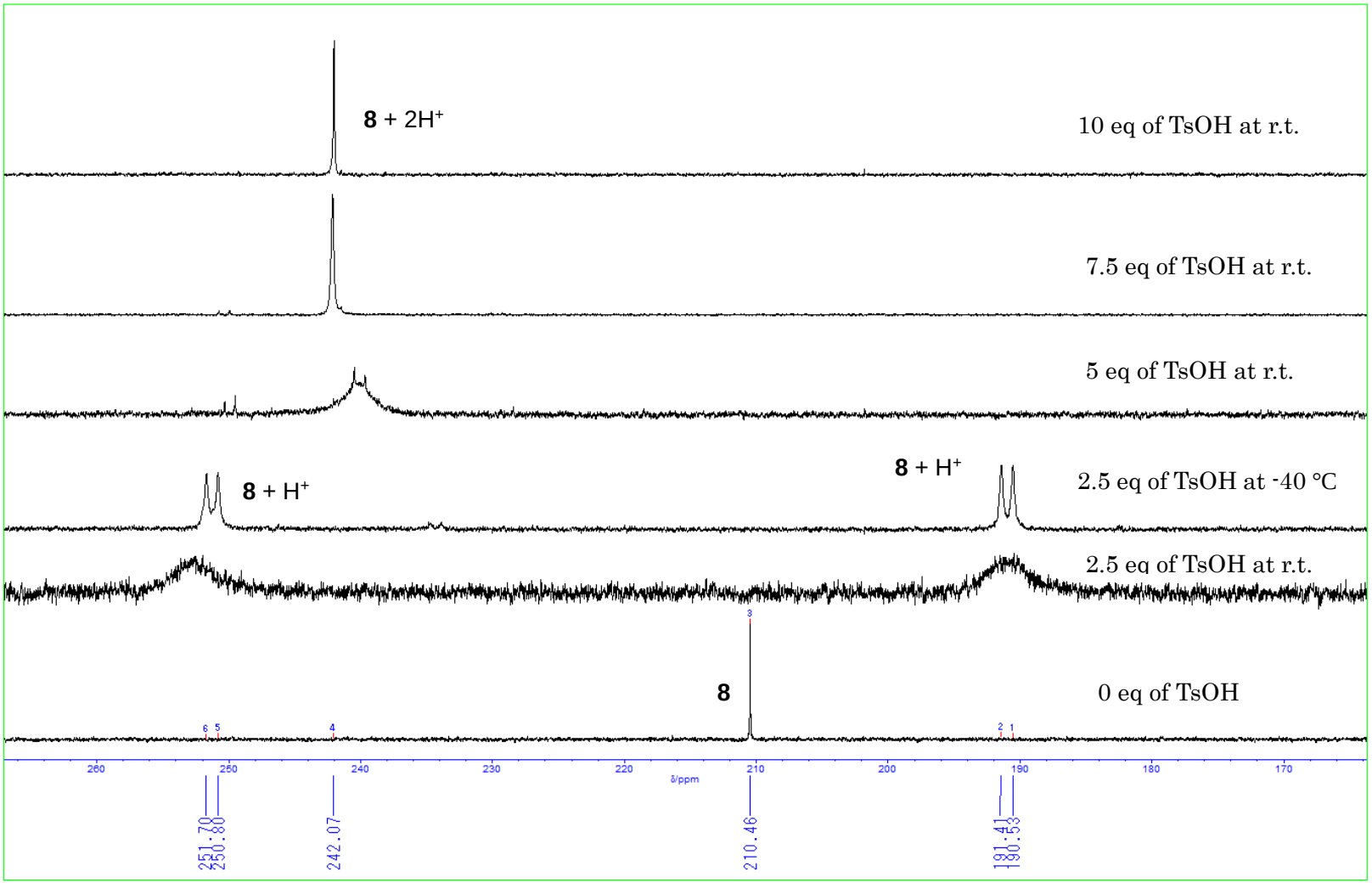

Figure S15. Change in $^{31}P\{^{1}H\}$ NMR spectra of **8** upon addition of TsOH.