Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Cyclopentadienyl Molybdenum Alkylester Complexes as Catalyst Precursors for Olefin Epoxidation

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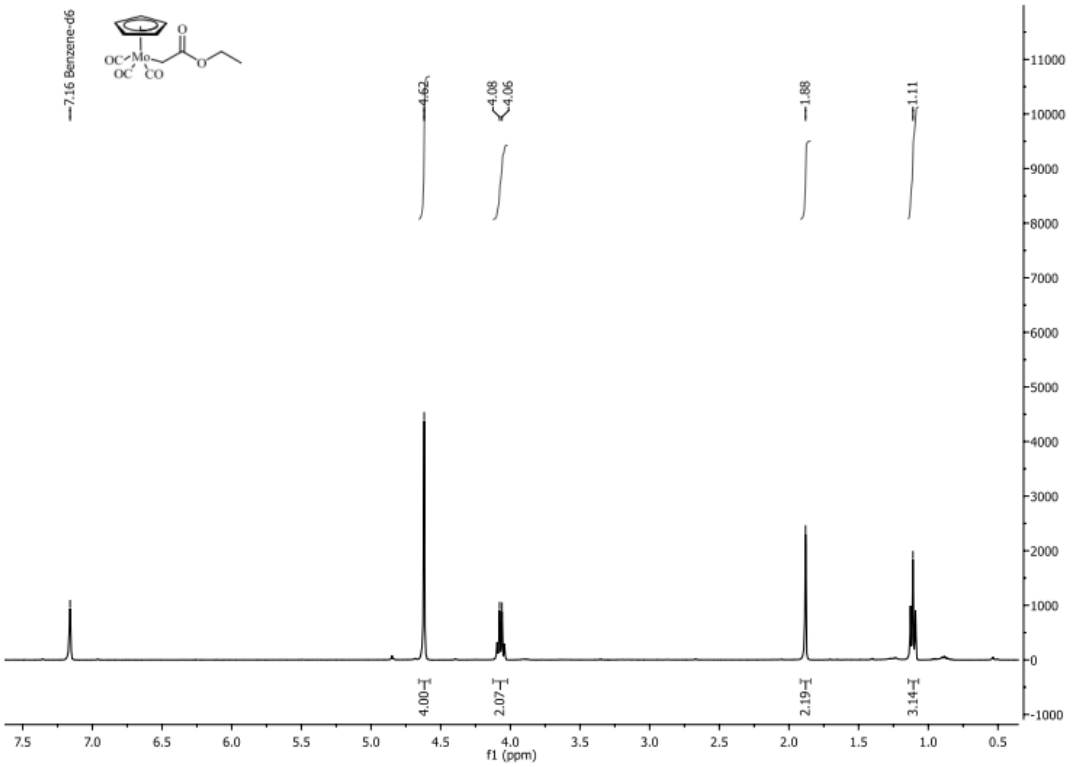
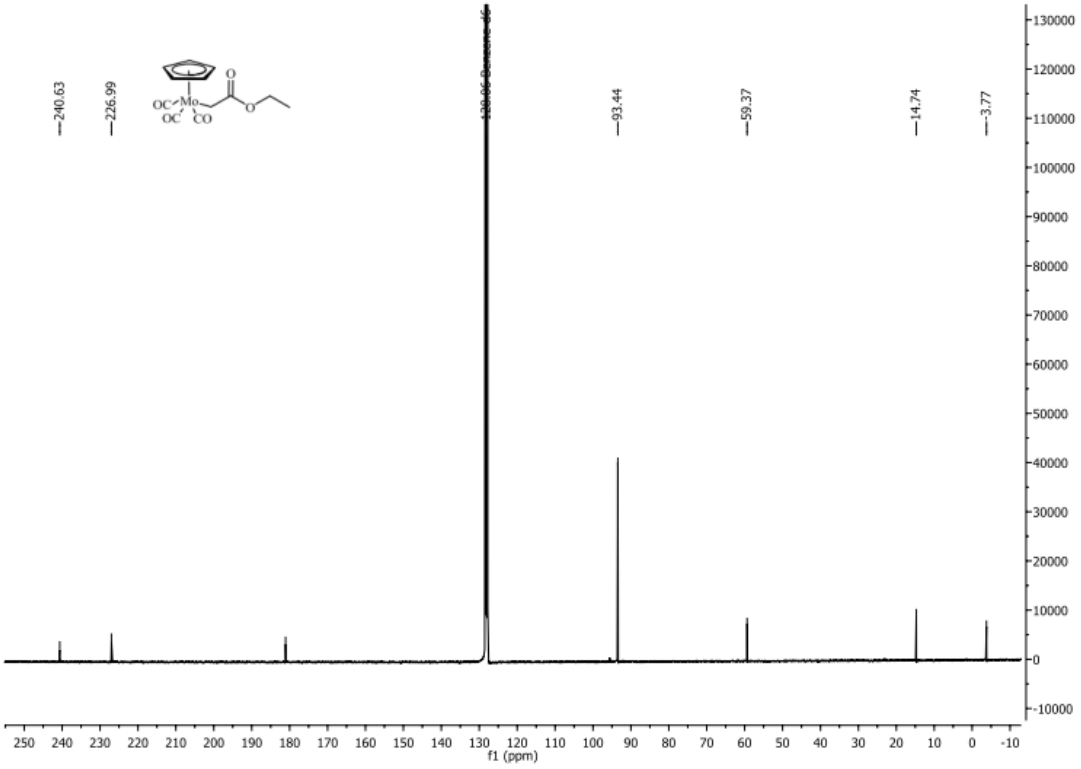
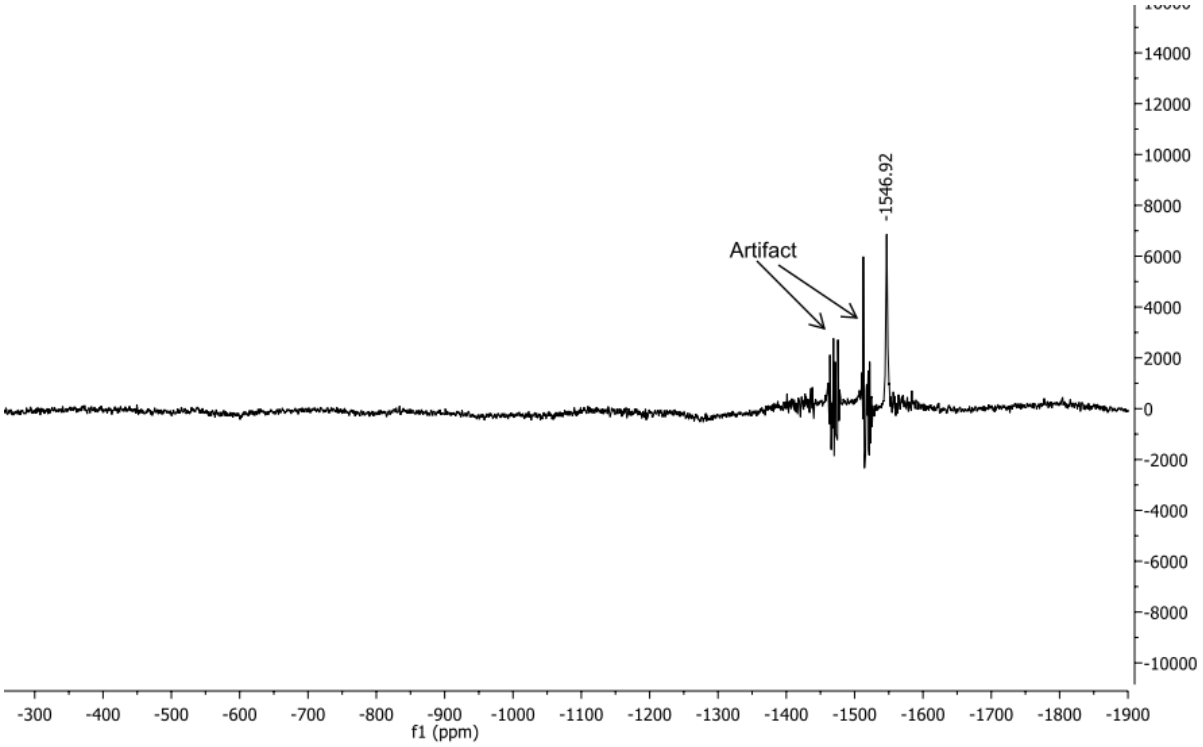
1. Analytical data for **1**







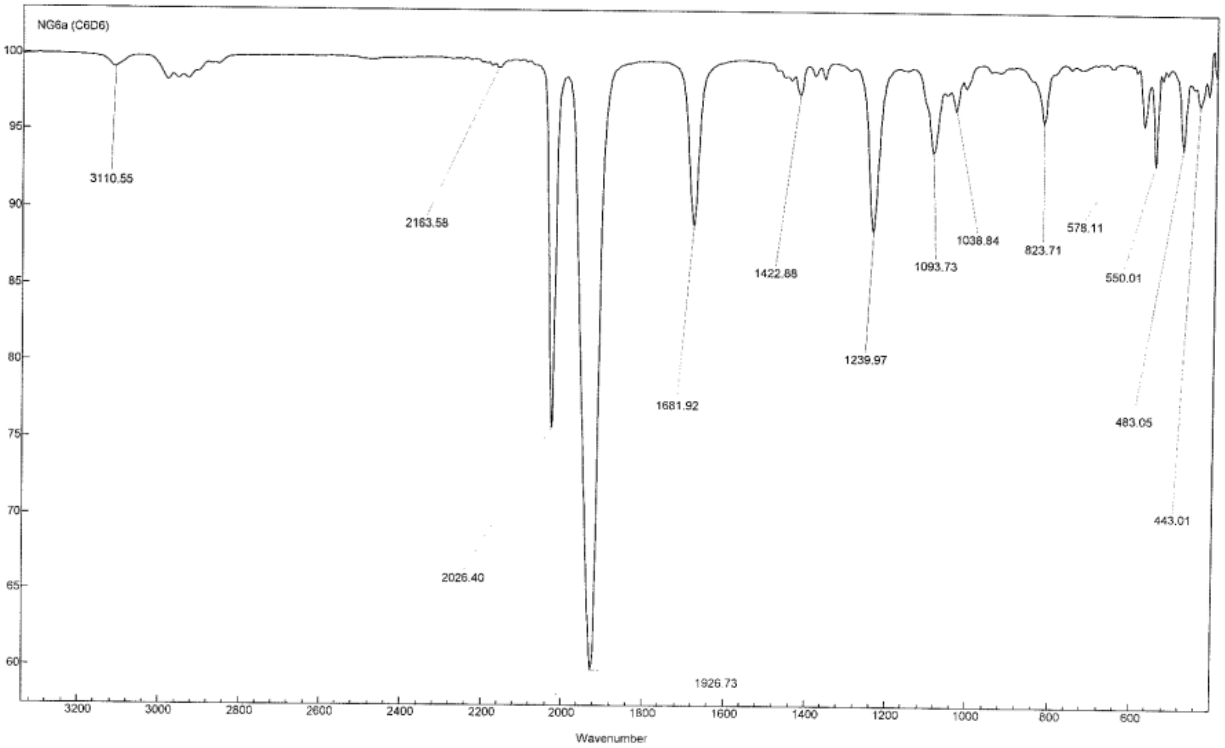
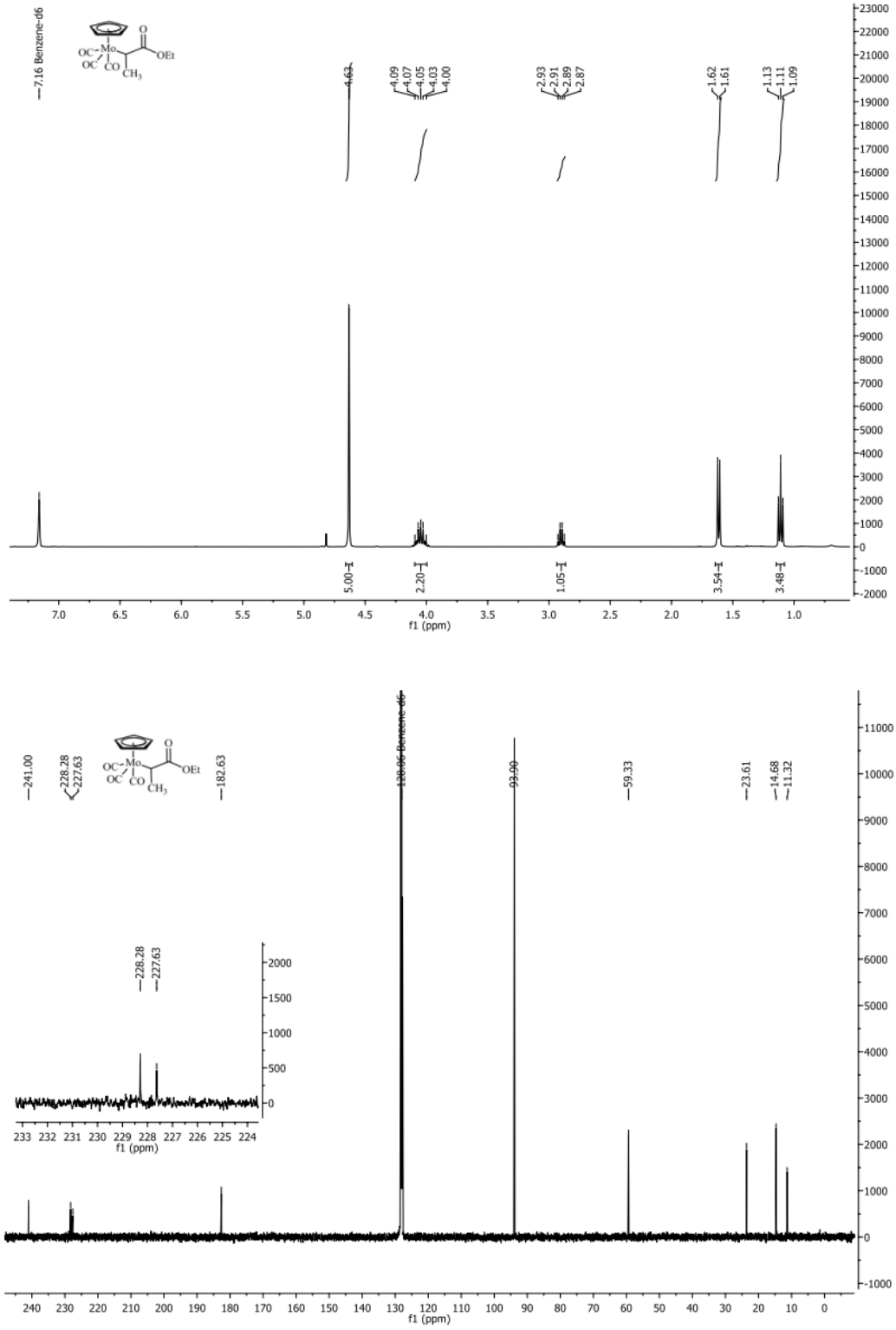
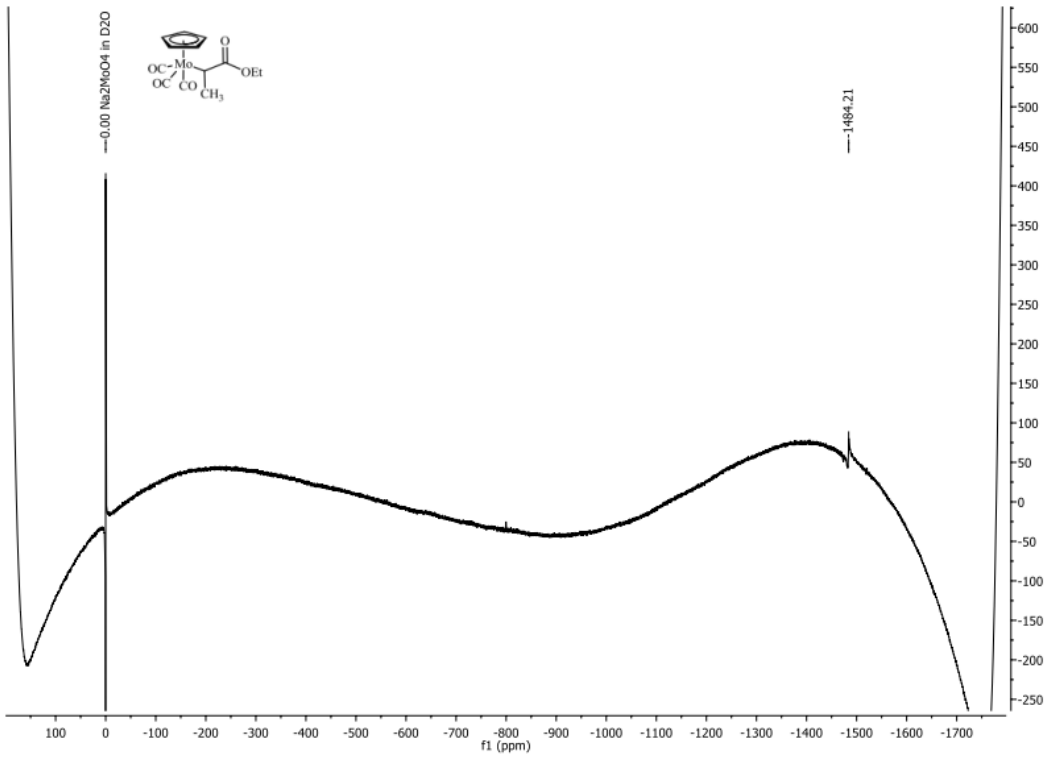


Figure S1. (a) ^{1}H, (b) ^{13}C, (c) ^{95}Mo (d) IR spectra for complex **1**

2. Analytical data for **2**

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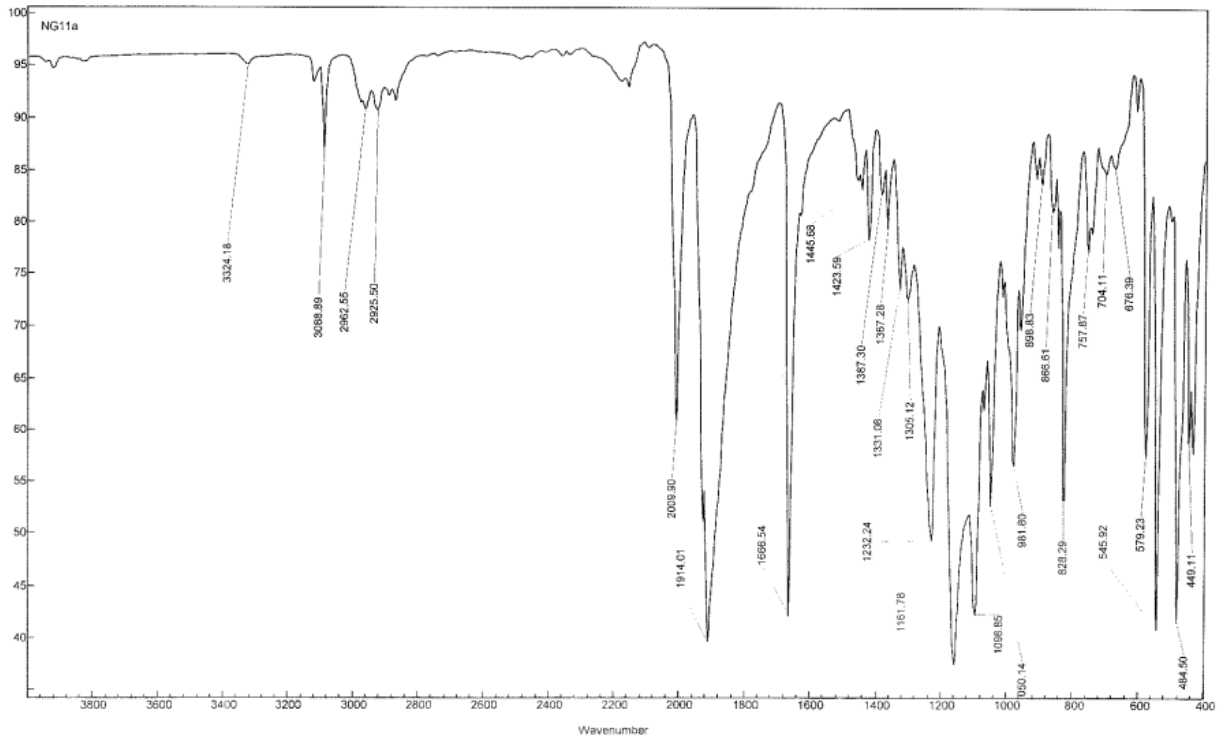
f1 (ppm)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1357.28
1331.08
1305.12
1232.24
1161.78
1098.85
1050.14
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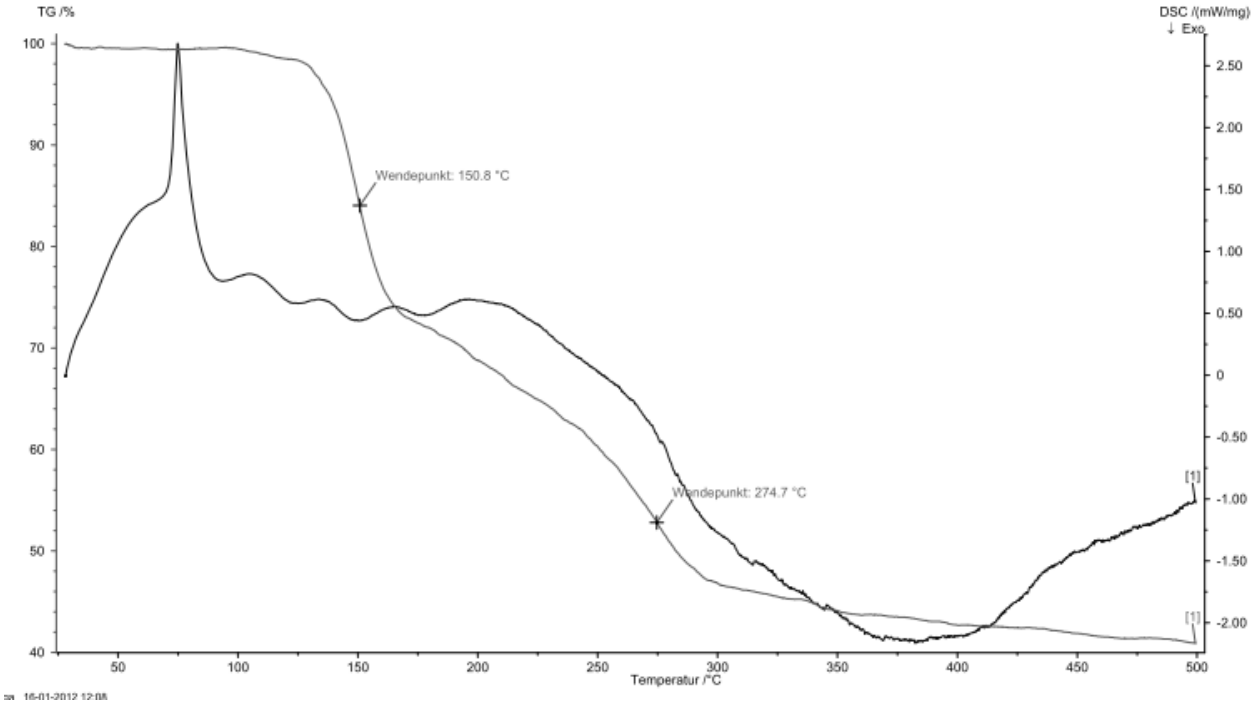
579.23
545.92
484.50
449.11
Wavenumber

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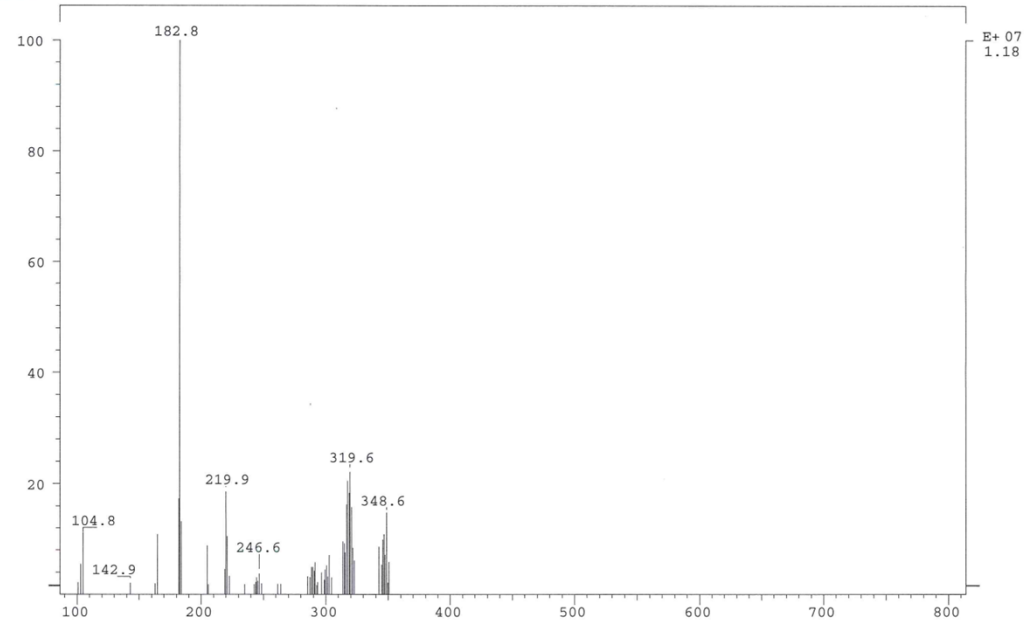


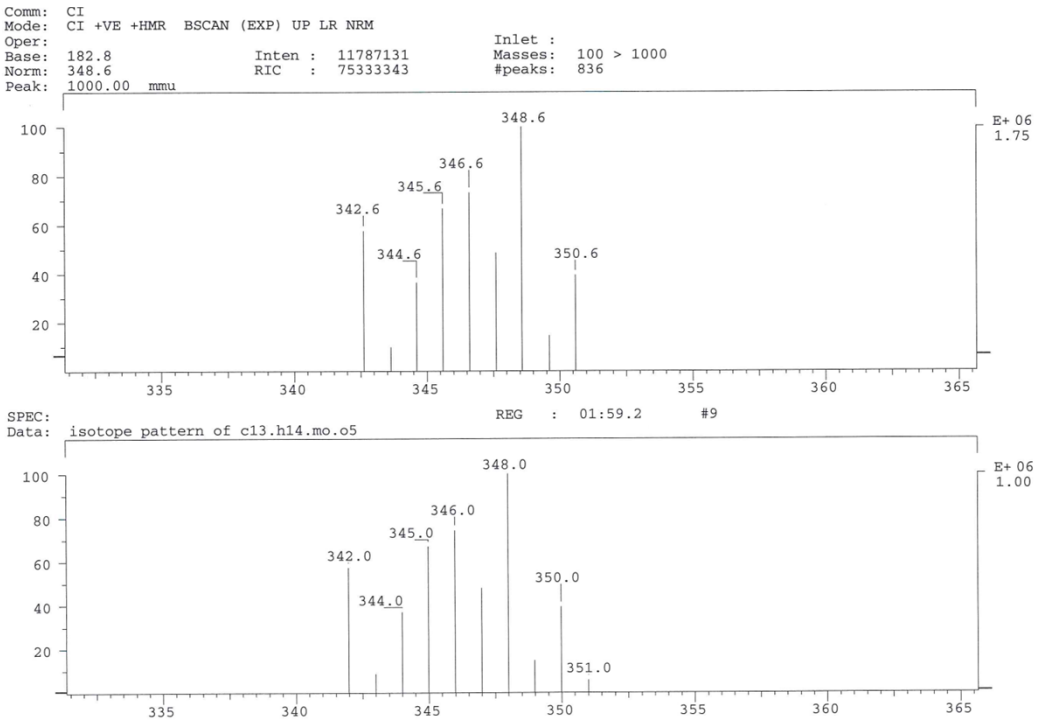
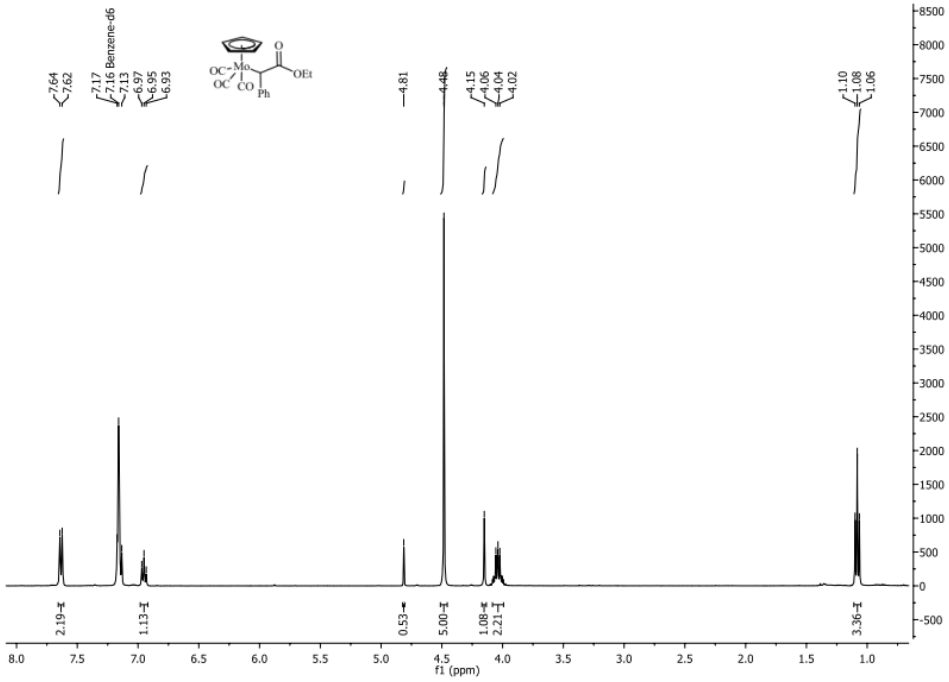
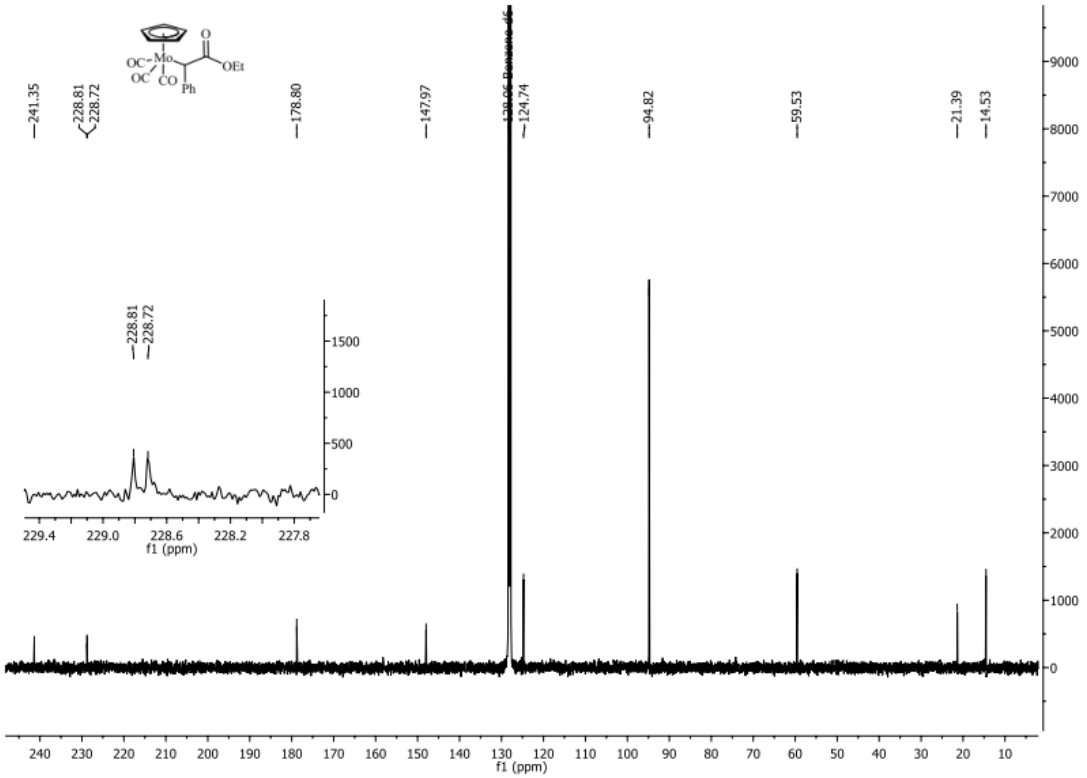


Figure S2. (a) ^{1}H, (b) ^{13}C, (c) ^{95}Mo, (d) IR, (e) TGA-MS, (f) Mass spectra for complex **2**

3. Analytical data for **3**

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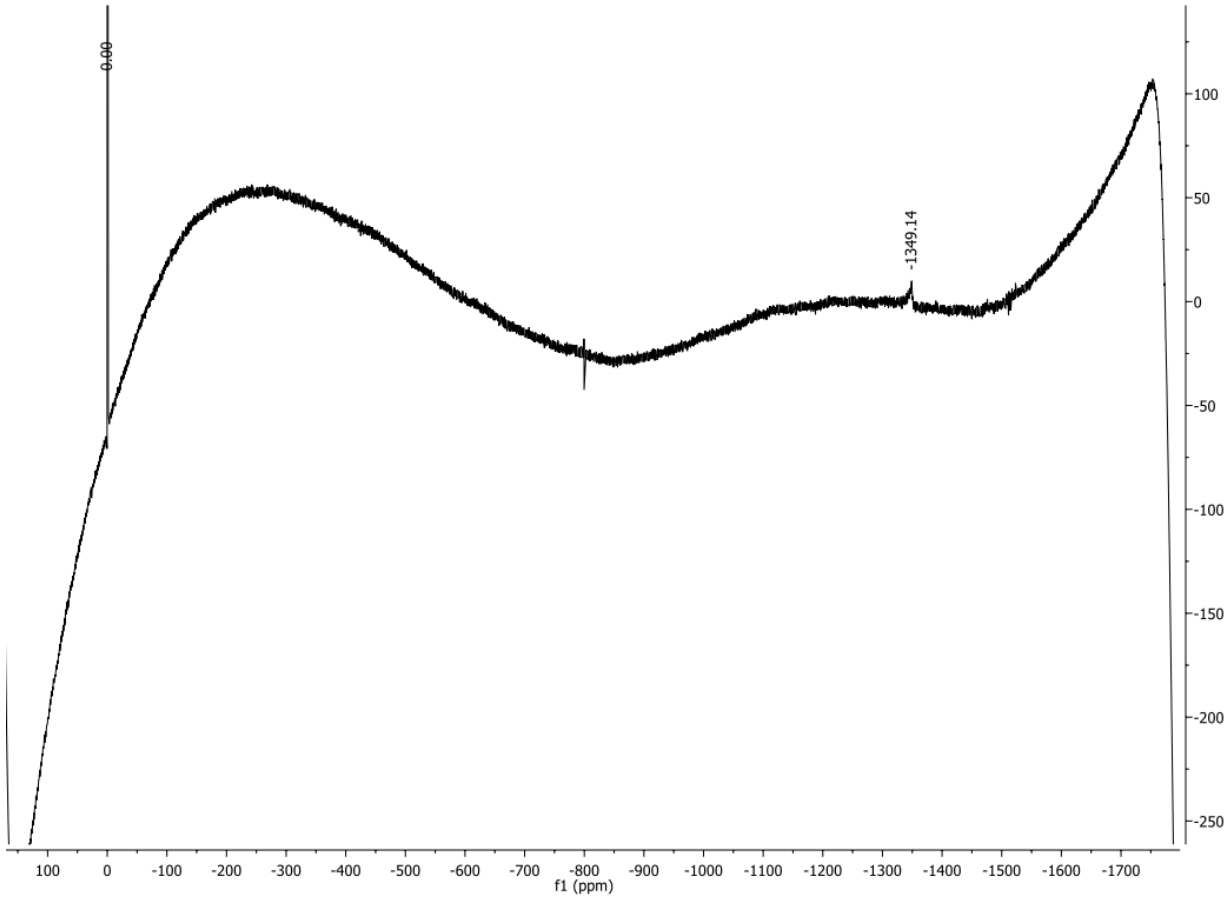
147.97
124.74
94.82
59.53
21.39
14.53
f1 (ppm)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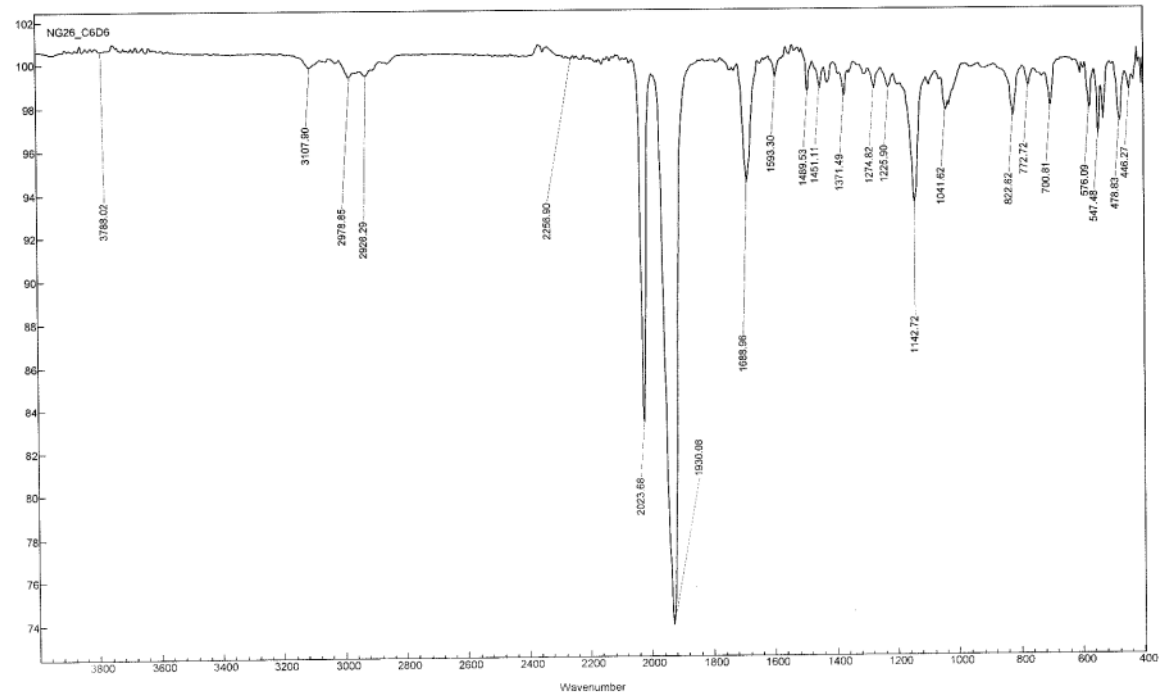
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2928.29
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1930.08
1688.96
1593.30
1489.53
1451.11
1371.49
1274.82
1225.90
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1041.62
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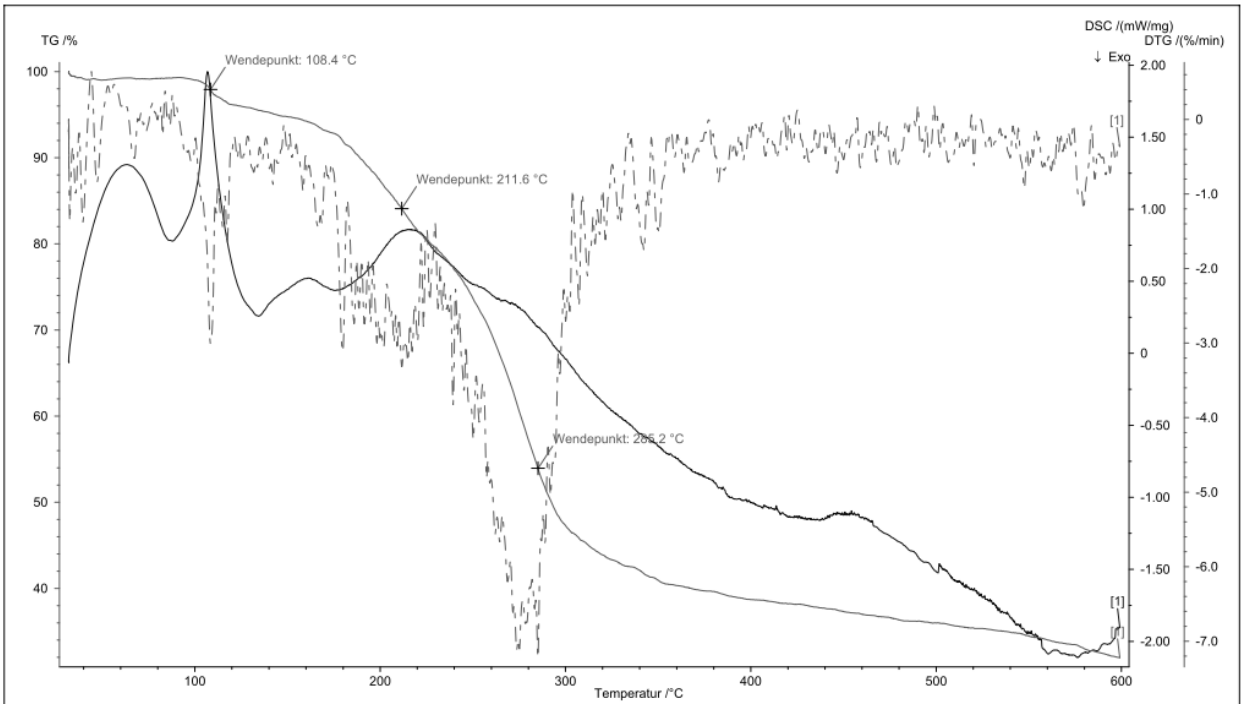
772.72
700.81
576.09
547.48
478.83
446.27
Wavenumber


TG /%
DSC /(mW/mg)
DTG /(%/min)
↓ Exo
Wendepunkt: 108.4 °C
Wendepunkt: 211.6 °C
Wendepunkt: 285.2 °C
[1]
Temperatur /°C

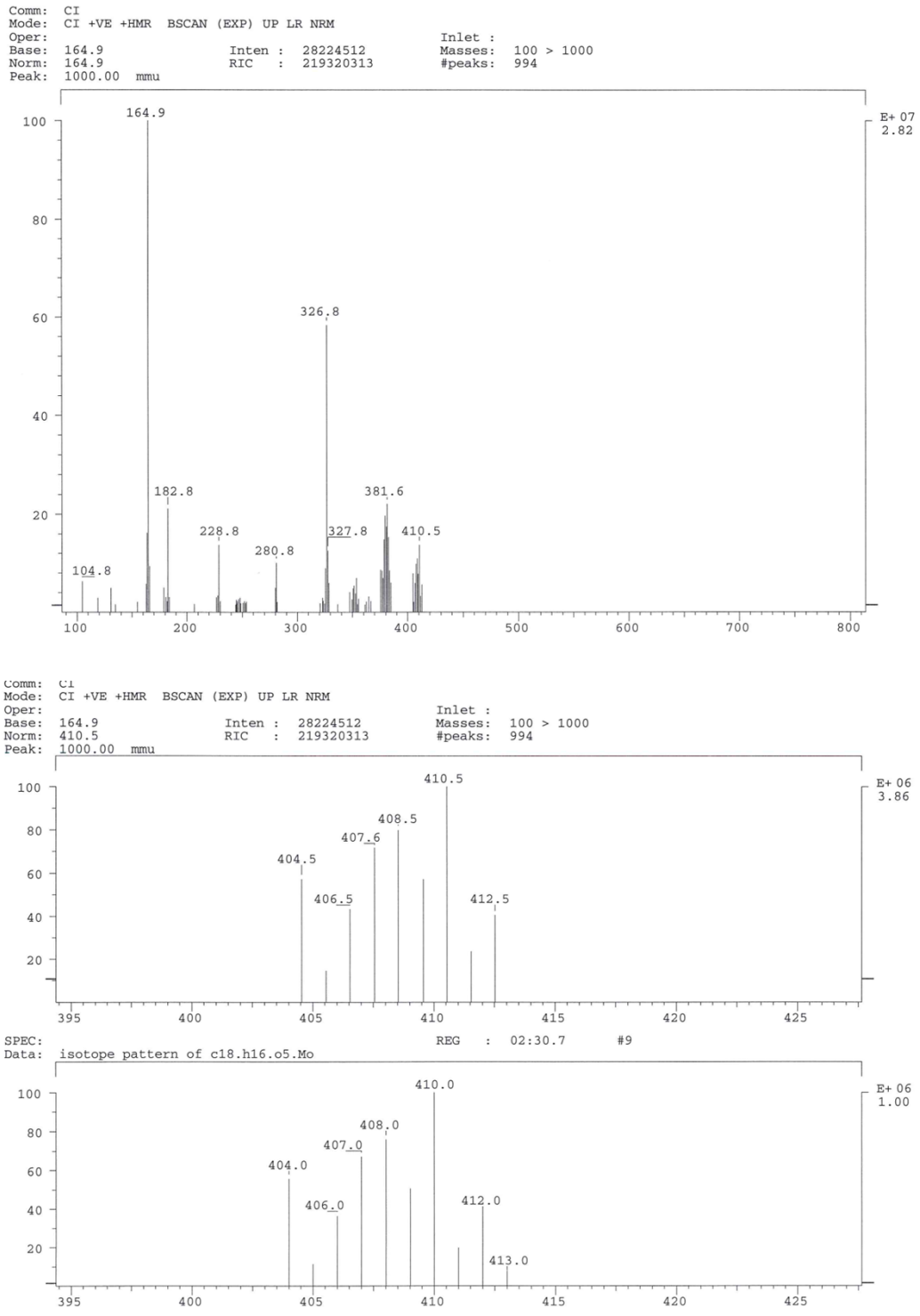
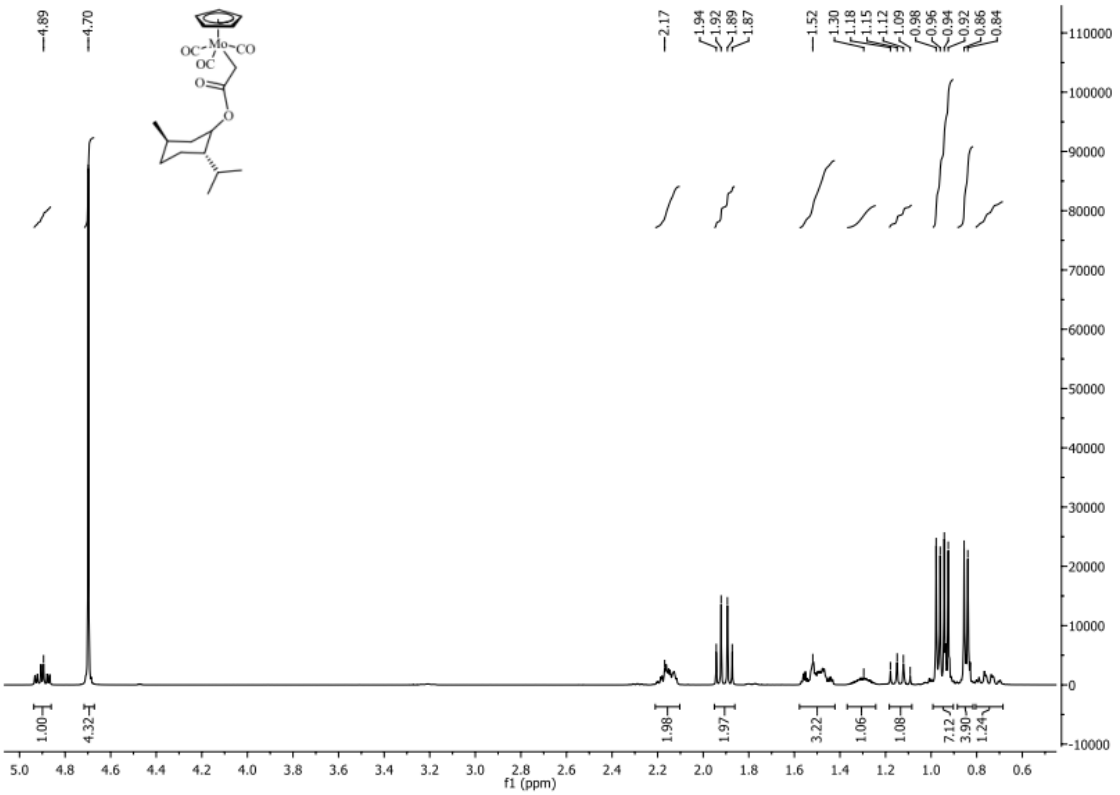
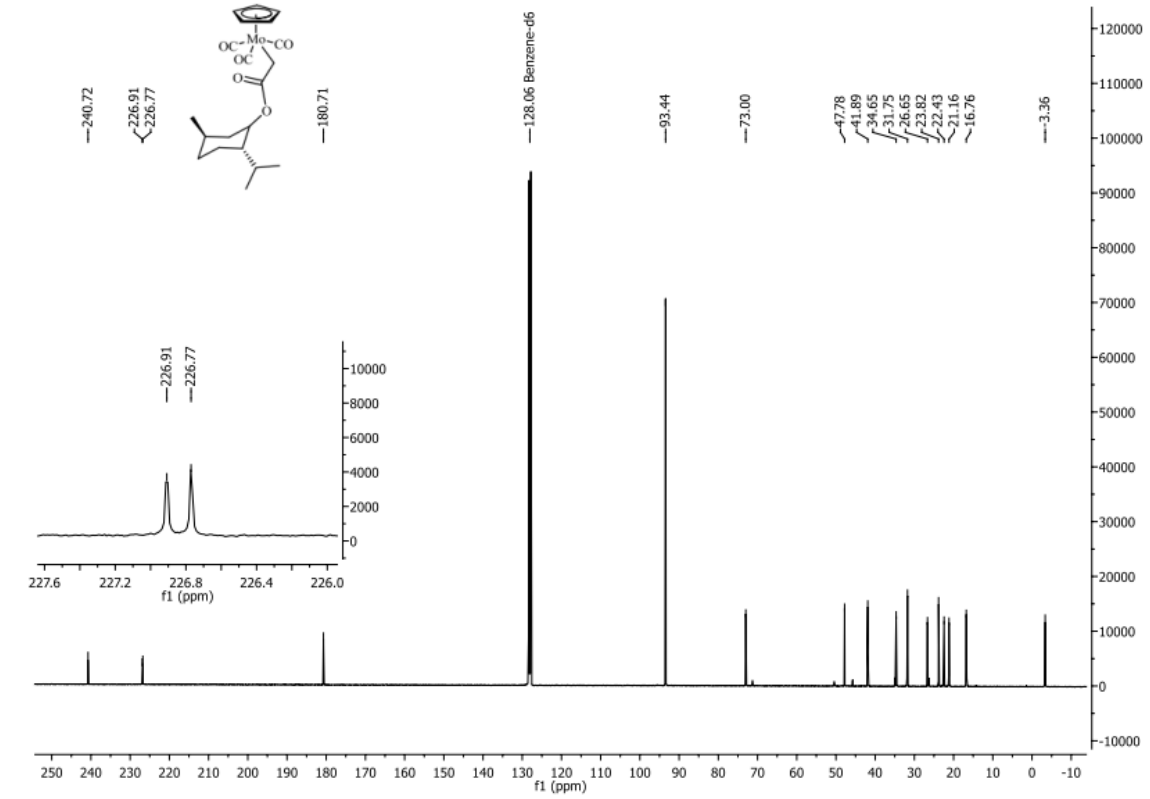
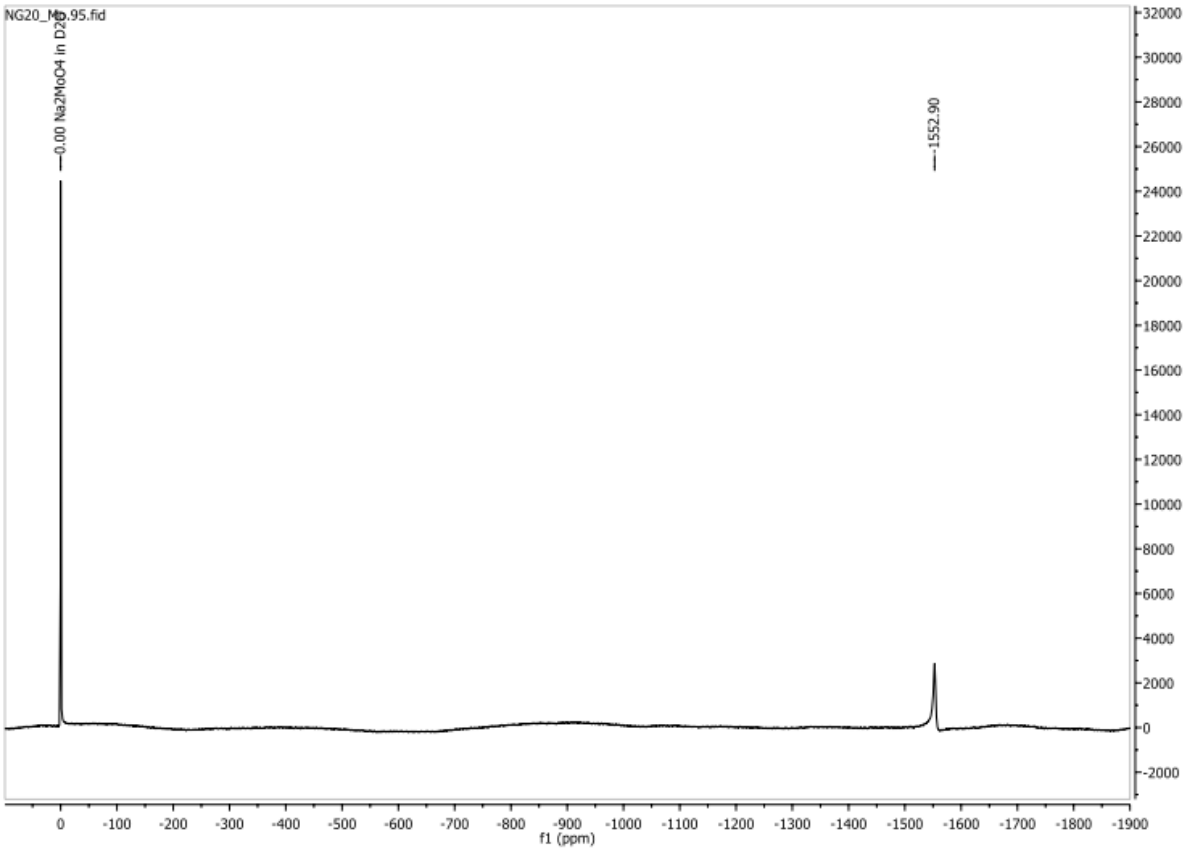


Figure S3. (a) ^{1}H, (b) ^{13}C, (c) ^{95}Mo, (d) IR, (e) TGA-MS, (f) Mass spectra for complex **3**

4. Analytical data for **4**



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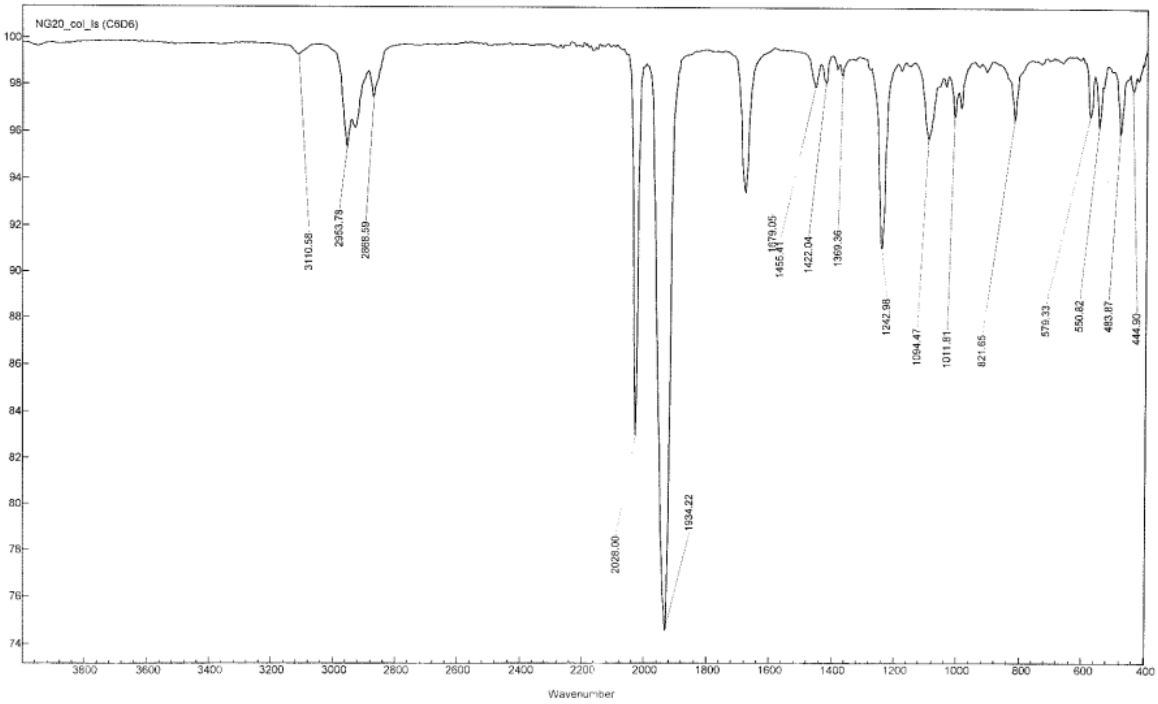
f1 (ppm)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2868.59
2028.00
1934.22
1479.05
1455.41
1422.04
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1094.47
1011.81
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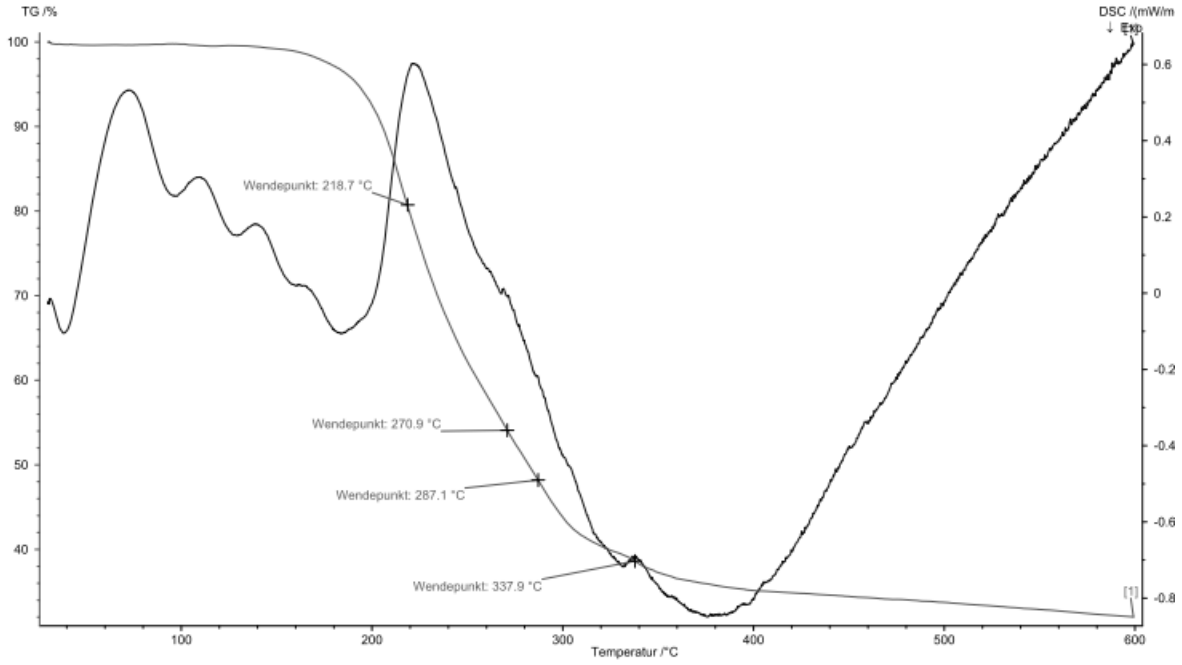
579.33
550.62
483.67
444.90
Wavenumber



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Inlet :
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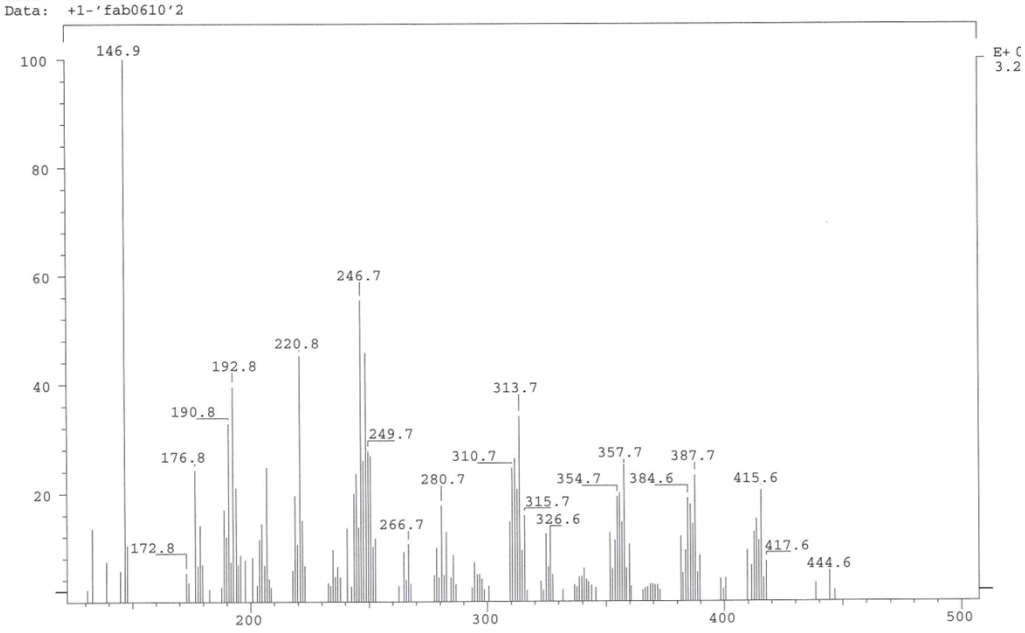
#peaks: 877



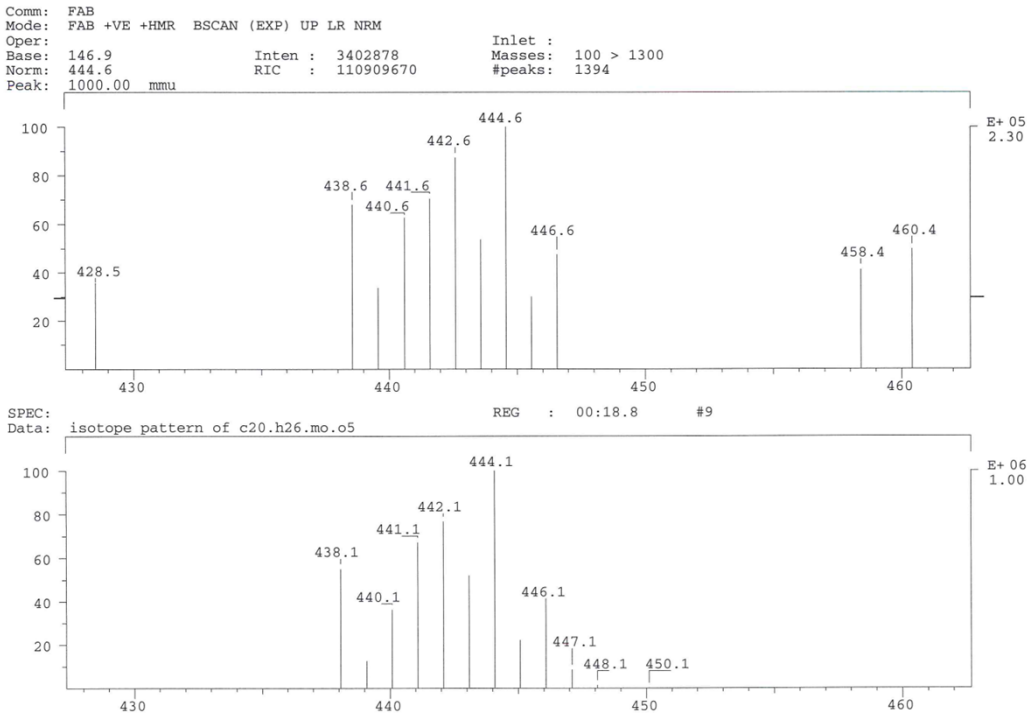
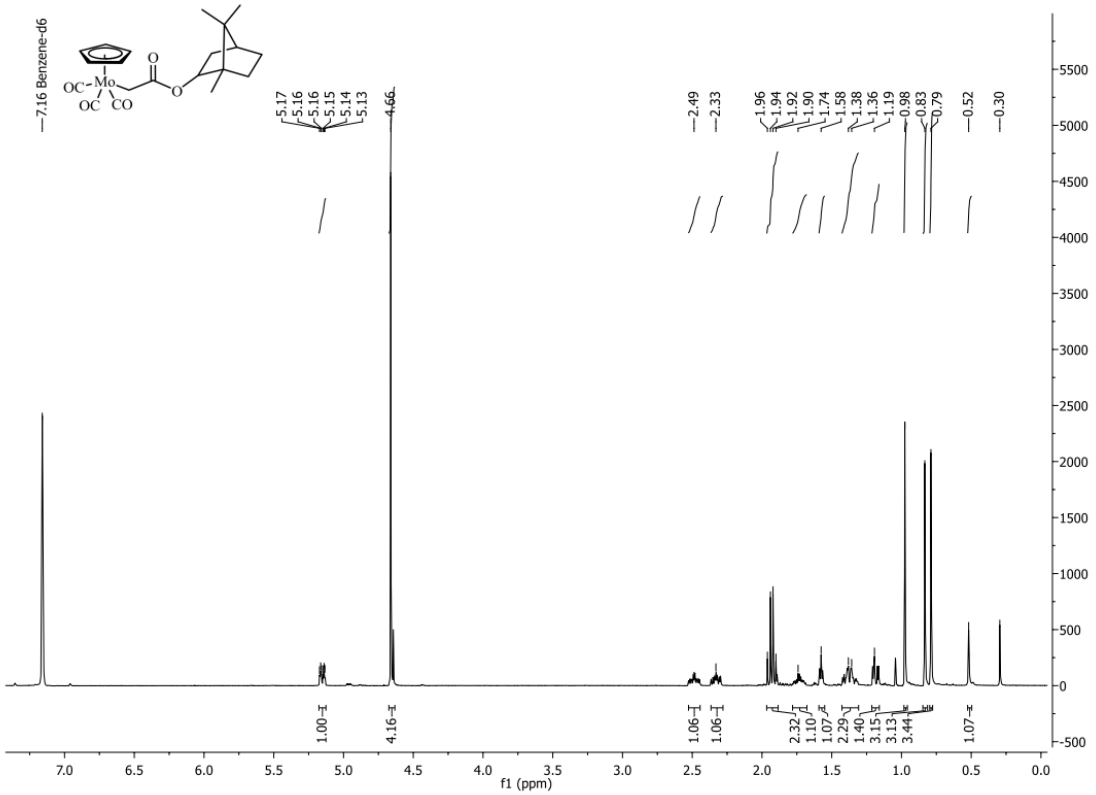
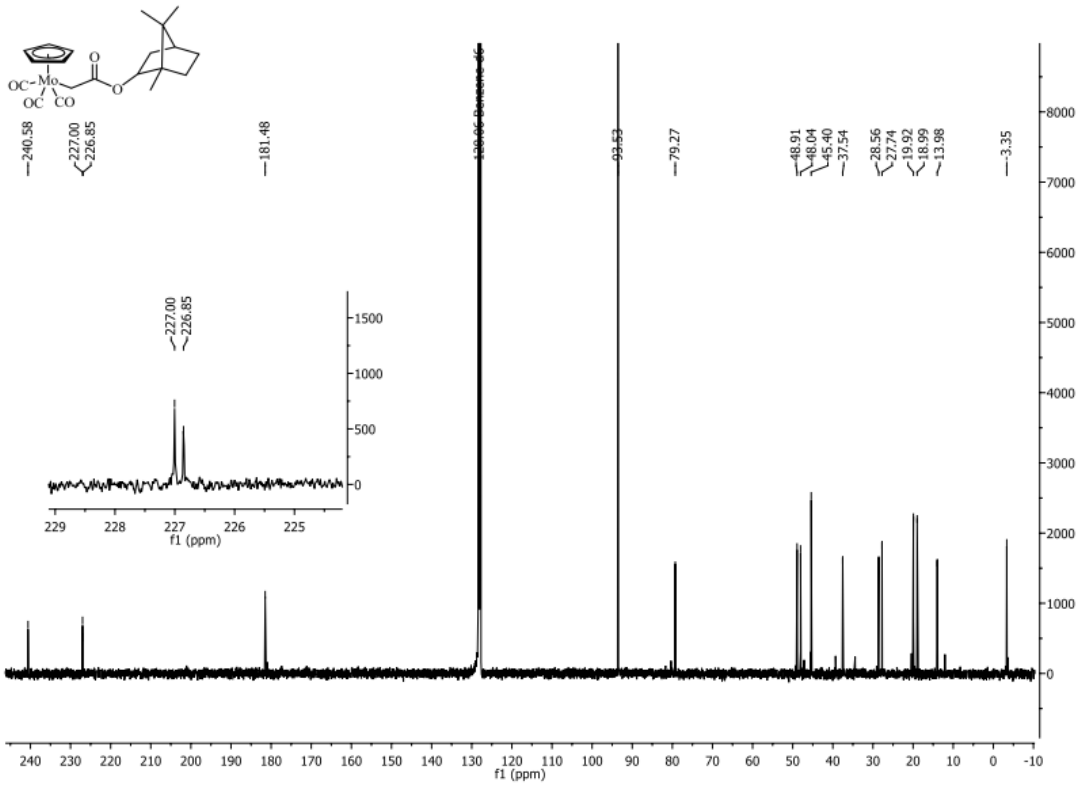


Figure S4. (a) ^{1}H, (b) ^{13}C, (c) ^{95}Mo, (d) IR, (e) TGA-MS, (f) Mass spectra for complex **4**.

5. Analytical data for **5**

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227.00
226.85
181.48
138.06 Benzene-d6
93.53
79.27
68.91
48.04
45.40
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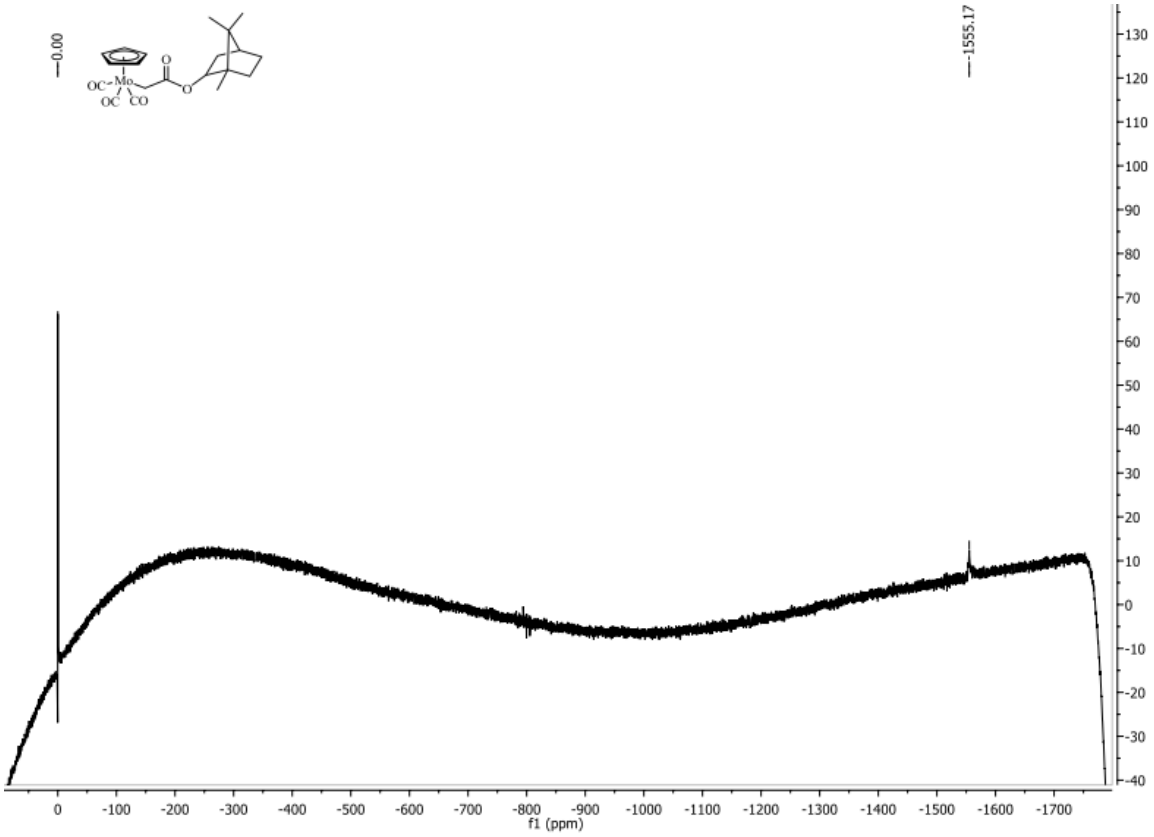
19.92
18.99
13.98
3.35
f1 (ppm)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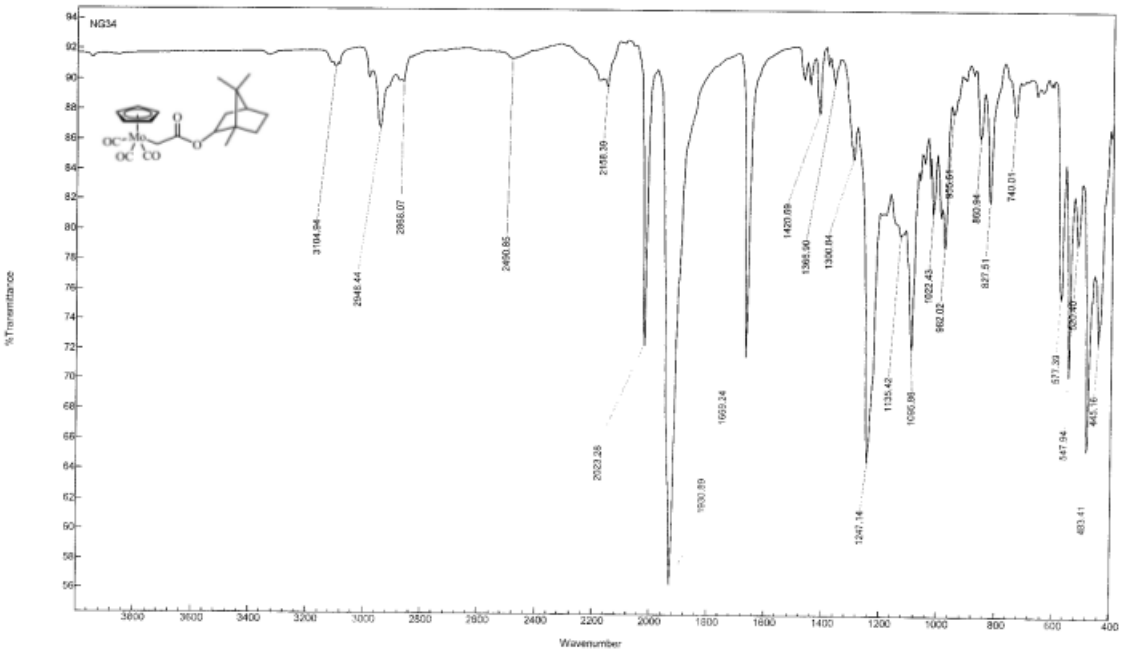
1555.17
f1 (ppm)


NG34
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Wavenumber
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2948.44
2866.07
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2156.39
2023.28
1930.89
1693.24
1420.69
1368.90
1300.84
1247.14
1135.42
1096.98
1022.43
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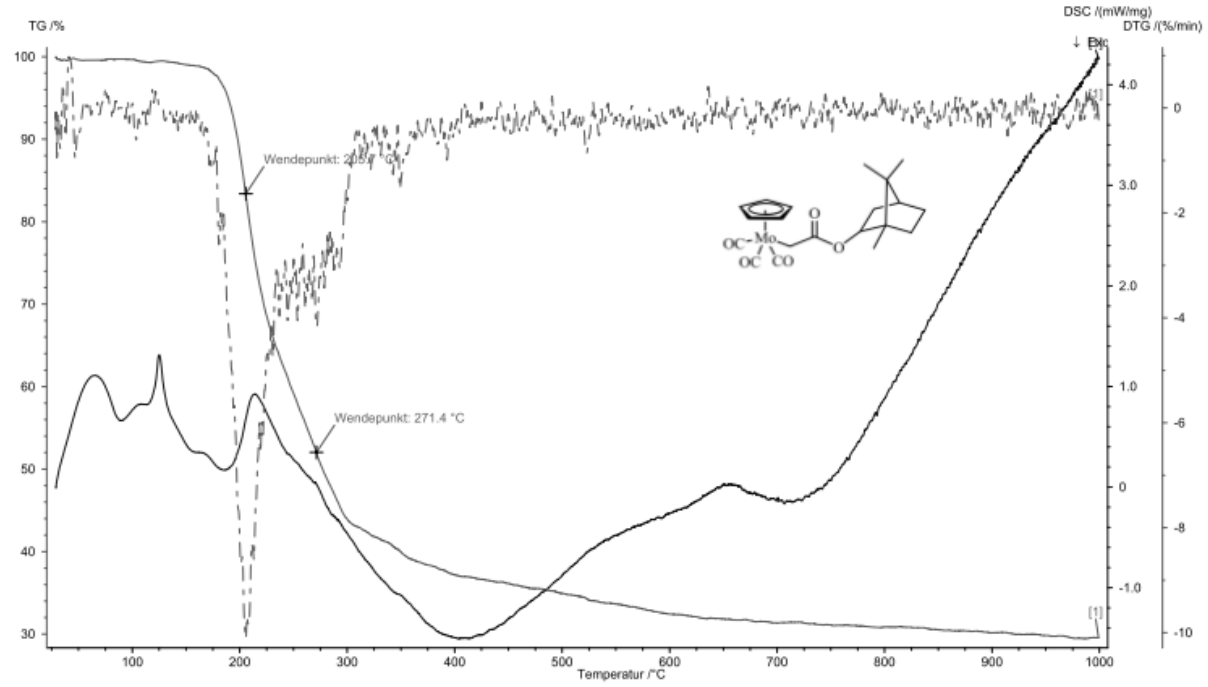

TG /%
DSC /(mW/mg)
DTG /(%/min)
Exo
Wendepunkt: 271.4 °C
Temperatur /°C

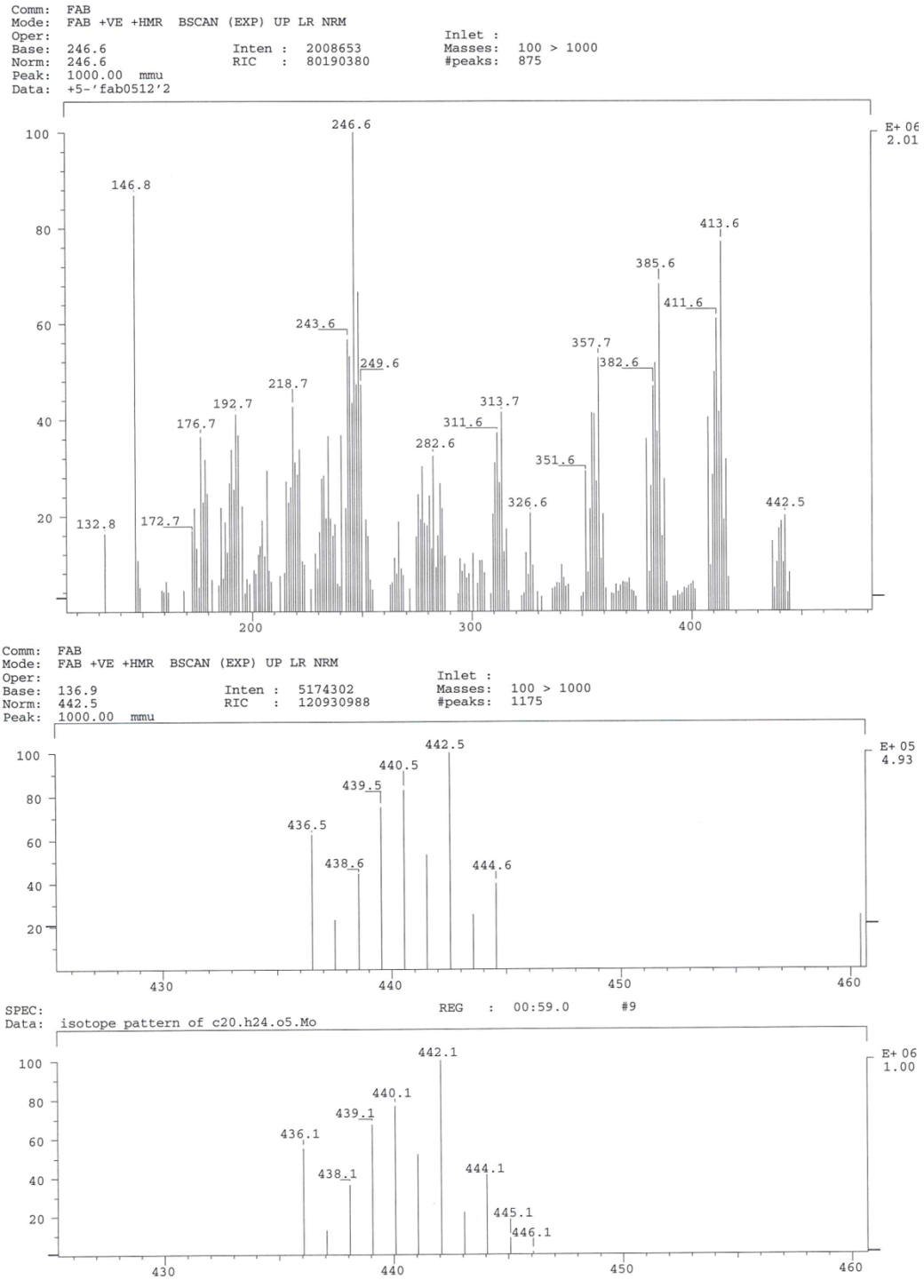


Figure S5. (a) ^{1}H, (b) ^{13}C, (c) ^{95}Mo, (d) IR, (e) TGA-MS, (f) Mass spectra for complex **5**

6.

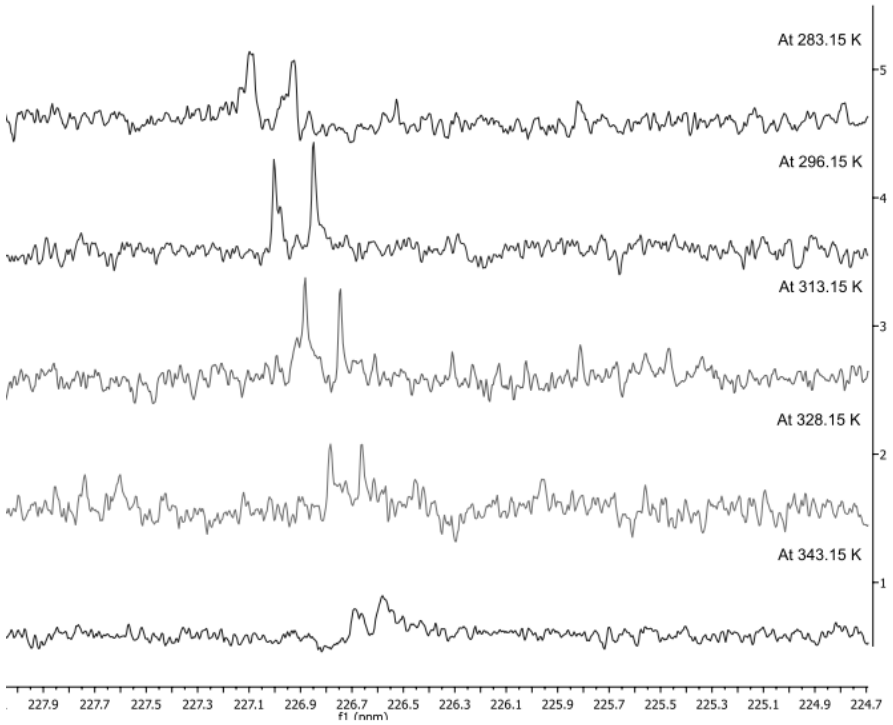
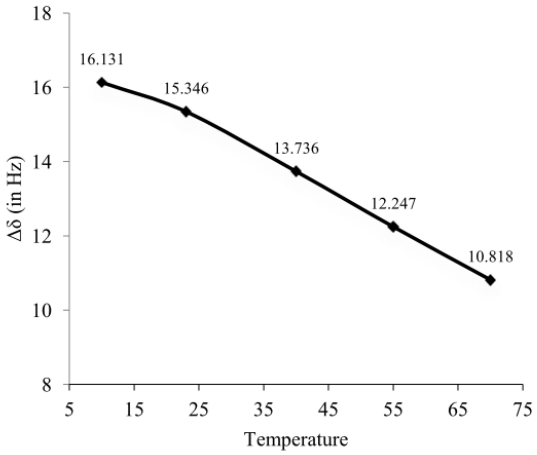
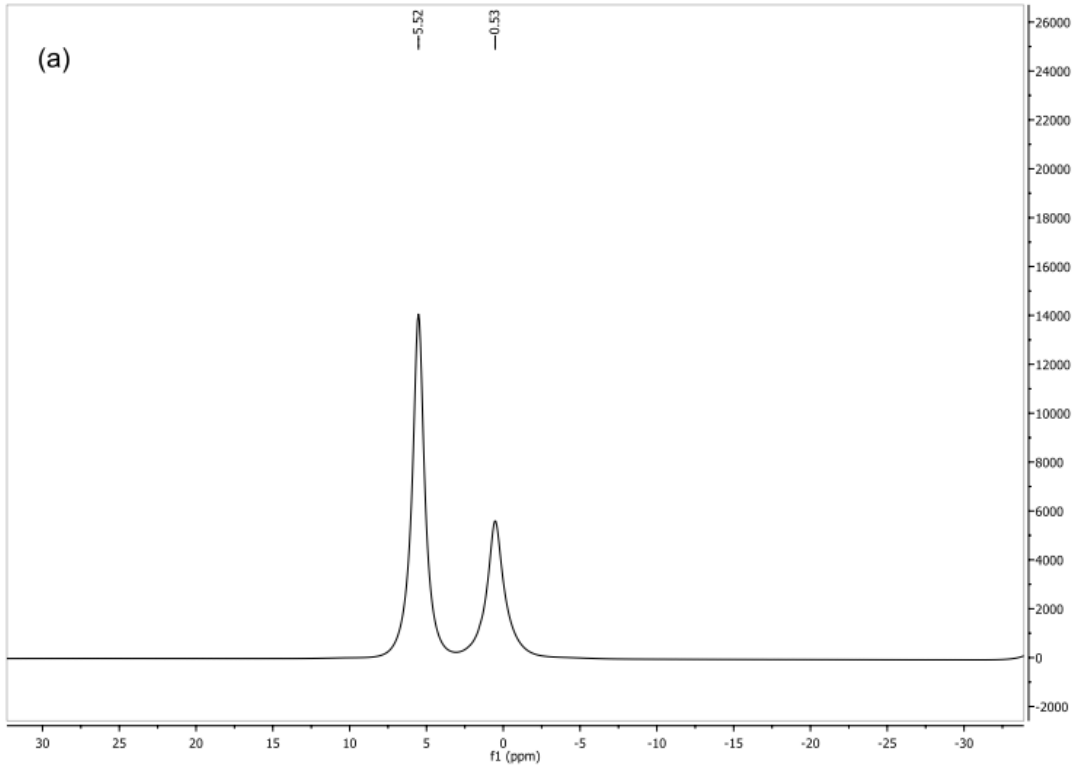


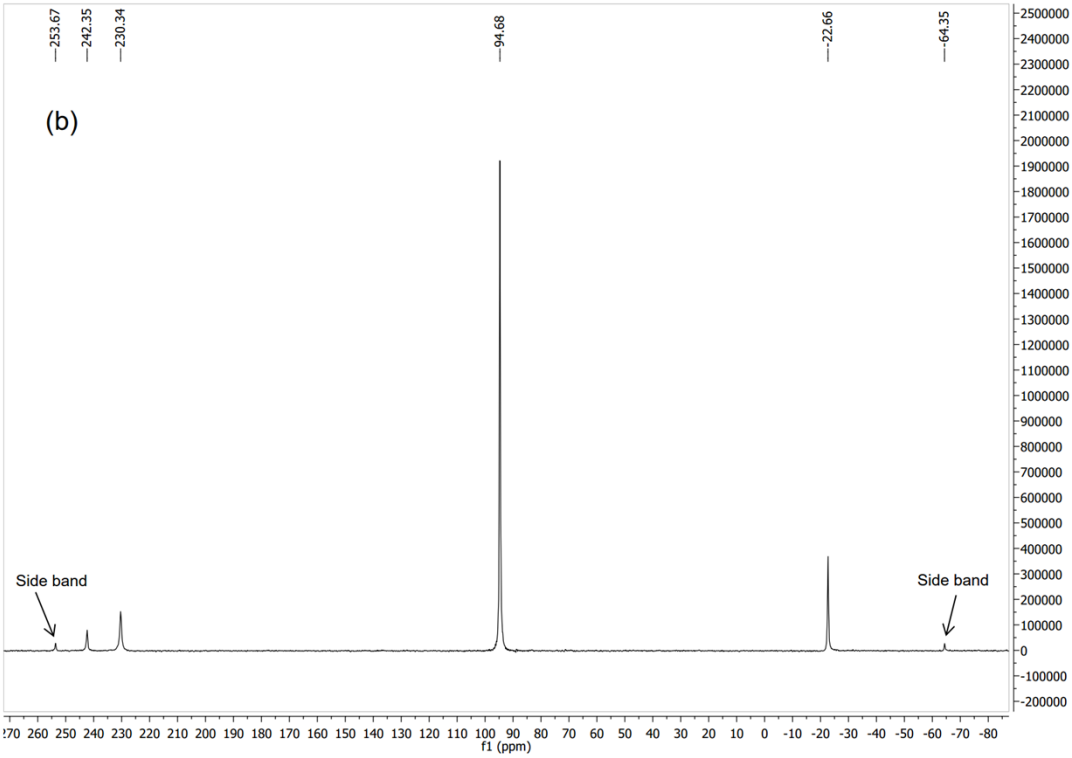
Figure S6. Variable temperature ^{13}C NMR (C_6D_6) of **5** in the *cis*-CO region, showing electronic inequivalence or asymmetry of the carbonyl ligands even at 70°C.



Temperature	δ_1	δ_2	$\Delta\delta = \delta_1-\delta_2$	(in Hz)
10	227.0861	226.9258	0.1603	16.1310
23	227.0022	226.8497	0.1525	15.3461
40	226.8821	226.7456	0.1365	13.7360
55	226.7838	226.6621	0.1217	12.2467
70	226.6888	226.5813	0.1075	10.8177

7. Solid state NMR comparison study of $CpMo(CO)_3CH_3$ and **5**.





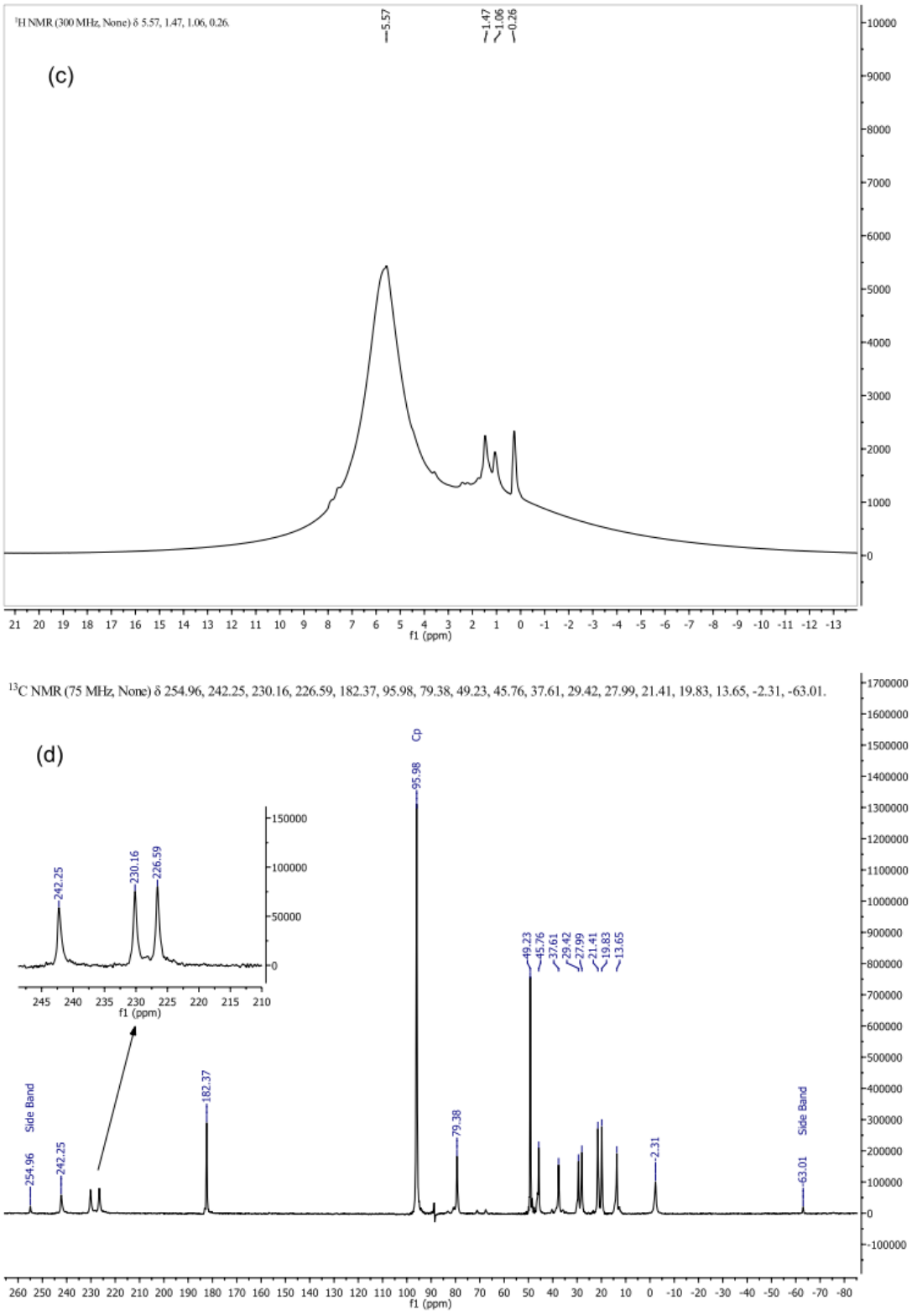


Figure S7. (a) ^{1}H-MAS and (b) ^{13}C-CPMAS spectra for complex $CpMo(CO)_3(CH_3)$; (c) ^{1}H-MAS and (d) ^{13}C-CPMAS for complex **5**.

There are two signals in the ^{1}H-MAS spectrum for $CpMo(CO)_3CH_3$ at δ 5.52 (for C_5H_5) and δ 0.53 (for -CH_3) and for **5**, Cp ligand appears at 5.57 as a broad signal. In ^{13}C-CPMAS spectrum of the methyl complex, side bands of the Cp signal at δ 94.68 appear at δ 253.67 and δ -64.37 (12 kHz). The -CH_3 group appears at δ -22.6 and the molybdenum bound carbonyl ligands at δ 242.35 and δ 230.34. However, ^{13}C-CPMAS for complex **5** shows three distinct peaks for the three Mo-CO groups at δ 242.25, δ 230.16 and δ 226.59. The first rotational side bands of the Cp ligand of **5** appear at δ 254.96 and δ -63.01.

8. X-ray Crystallographic Data for **1, 2** and **5**

Compound 1 (CCDC 934898)

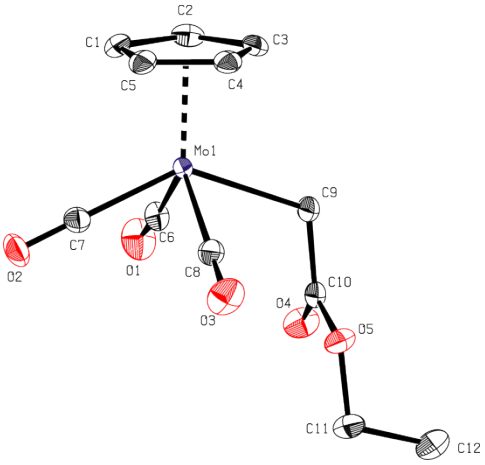


Figure S8. Ortep drawing with 50% ellipsoids for complex **1**.

A clear light yellow fragment-like specimen of $C_{12}H_{12}MoO_5$, approximate dimensions 0.258 mm x 0.358 mm x 0.480 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo fine-focus tube (λ = 0.71073 Å).

Crystal Data

Formula			C12 H12 Mo O5
Formula Weight			332.16
Crystal System			Orthorhombic
Space group		P212121	(No. 19)
a, b, c [Angstrom]	8.5556(1)	10.4982(2)	14.8086(2)
V [Ang**3]			1330.09(3)
Z			4
D(calc) [g/cm**3]			1.659
Mu(MoKa) [/mm]			0.995
F(000)			664
Crystal Size [mm]		0.26 x	0.36 x 0.48

Data Collection

Temperature (K)			123
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			2.4, 25.5
Dataset		-10: 10 ; -12: 12 ; -17: 17	
Tot., Uniq. Data, R(int)		37426,	2464, 0.027
Observed data [I > 2.0 sigma(I)]			2449

Refinement

Nref, Npar			2464, 164
R, wR2, S		0.0208,	0.0544, 1.11
w = 1/[\s^2^(Fo^2^)+(0.0366P)^2^+0.7711P] where P=(Fo^2^+2Fc^2^)/3			

Max. and Av. Shift/Error	0.00, 0.00
Flack x	0.50(4)
Min. and Max. Resd. Dens. [e/Ang^3]	-0.29, 1.82

Compound 2 (CCDC 934899)

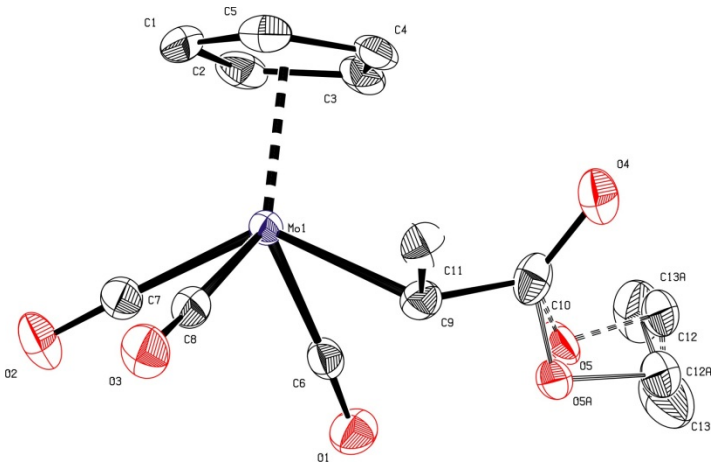


Figure S9. Ortep drawing with 50% ellipsoids for complex **2**.

A clear intense yellow fragment-like specimen of $C_{13}H_{14}MoO_5$, approximate dimensions 0.150 mm x 0.359 mm x 0.554 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a Montel mirror monochromator and a Mo FR591 rotating anode (λ = 0.71073 Å).

Crystal Data

Formula			C13 H14 Mo O5
Formula Weight			346.18
Crystal System			Orthorhombic
Space group		Pbca	(No. 61)
a, b, c [Angstrom]	10.3022(8)	11.1065(9)	23.6758(19)
V [Ang**3]			2709.0(4)
Z			8
D(calc) [g/cm**3]			1.698
Mu(MoKa) [/mm]			0.981
F(000)			1392
Crystal Size [mm]		0.15 x 0.36 x 0.55	

Data Collection

Temperature (K)			123
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			1.7, 25.4
Dataset		-12: 12 ; -13: 13 ; -28: 28	
Tot., Uniq. Data, R(int)		55418, 2486, 0.032	
Observed data [I > 2.0 sigma(I)]			2067

Refinement

Nref, Npar			2486, 203
R, wR2, S		0.0231, 0.0524, 1.13	
w = 1/[\s^2^(Fo^2^)+(0.0135P)^2^+4.3243P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error			0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]			-0.37, 0.67

Compound 5 (CCDC 934900)

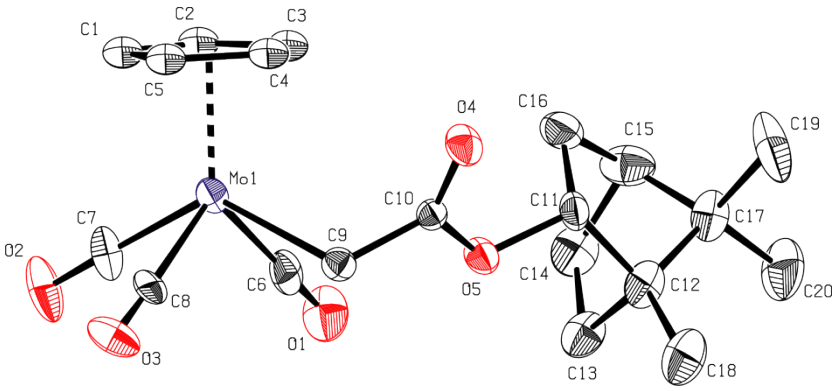


Figure S10. Ortep drawing with 50% ellipsoids for complex **5**.

A clear light yellow plate-like specimen of $C_{20}H_{24}MoO_5$, approximate dimensions 0.030 mm x 0.230 mm x 0.330 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Kappa APEX II CCD system equipped with a graphite monochromator and a Mo fine-focus tube (λ = 0.71073 Å).

Crystal Data

Formula			C20 H24 Mo O5
Formula Weight			440.33
Crystal System			Orthorhombic
Space group		P212121	(No. 19)
a, b, c [Angstrom]	7.4170(2)	7.6621(2)	34.3794(9)
V [Ang**3]			1953.77(9)
Z			4
D(calc) [g/cm**3]			1.497
Mu(MoKa) [/mm]			0.698
F(000)			904
Crystal Size [mm]		0.03 x	0.23 x 0.33

Data Collection

Temperature (K)			123
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			2.4, 25.4
Dataset	-8: 8 ; -9: 9 ; -41: 41		
Tot., Uniq. Data, R(int)		37467,	3579, 0.089
Observed data [I > 2.0 sigma(I)]			3025

Refinement

Nref, Npar	3579, 238
R, wR2, S	0.0550, 0.0943, 1.15
w = 1/[\s^2^(Fo^2^)+(0.0133P)^2^+6.0706P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Flack x	0.02(7)
Min. and Max. Resd. Dens. [e/Ang^3]	-1.29, 0.65

9. Yields and Turnover frequencies (TOFs) for catalysis reactions with **1-5** and different substrates.

Table S1.

TOFs[a] for complexes **1-5** (in mol mol_{Mo}^{-1} h^{-1}) utilized for olefin epoxidation in DCM at 22 °C using TBHP with catalyst:substrate:oxidant = 1:100:200 unless stated otherwise.

Experiment	Substrate	**1**	**2**	**3**	**4**	**5**
(a)	*cis*-cyclooctene, 1 mol% catalyst	120	124	188	118	189
(b)	*cis*-cyclooctene, 0.1 mol% catalyst	236	302	262	263	362
(c)	*cis*-cyclooctene, no co-solvent	220	290	500	188	210
(d)	cis-cyclooctene, 55 °C, $CHCl_3$	775	1024	1187	784	781
(e)	*cis*-stilbene	25	40	33	26	24
(f)	*trans*-stilbene	26	50	91	40	60
(g)	1-octene	38	27	31	37	12
(h)	*trans*-β-methylstyrene	-	85	97	70	48

[a] All values were determined from the steepest part of the conversion vs. time slope.

Table S2.

Yield(%)[a] of respective epoxides using complexes **1-5** for olefin epoxidation in DCM at 22 °C at 4h and 24h[b] using TBHP with catalyst:substrate:oxidant = 1:100:200 unless stated otherwise.

Experiment	Substrate	**1**	**2**	**3**	**4**	**5**
(a)	*cis*-cyclooctene, 1 mol% catalyst	99 (99)	99 (99)	99 (99)	97 (99)	99 (99)
(b)	*cis*-cyclooctene, 0.1 mol% catalyst	22 (99)	29 (99)	43 (99)	21 (99)	20 (99)
(c)	*cis*-cyclooctene, no co-solvent	99 (99)	99 (99)	99 (99)	96 (99)	99 (99)
(d)	cis-cyclooctene, 55 °C, $CHCl_3$	99 (99)	99 (99)	99 (99)	99 (99)	99 (99)
(e)	*cis*-stilbene[c]	45 (59)	52 (65)	56 (66)	42 (63)	49 (65)
(f)	*trans*-stilbene[c]	39 (57)	45 (58)	47 (62)	38 (54)	42 (60)
(g)	1-octene	27 (34)	25 (33)	25 (35)	27 (38)	26 (36)
(h)	*trans*-β-methylstyrene	-	58 (70)	64 (75)	55 (77)	58 (73)

[a] GC-MS yield of corresponding epoxides.
[b] Indicated in parenthesis.
[c] Only their respective epoxides were formed.

10. Results from NMR study of catalytic epoxidation

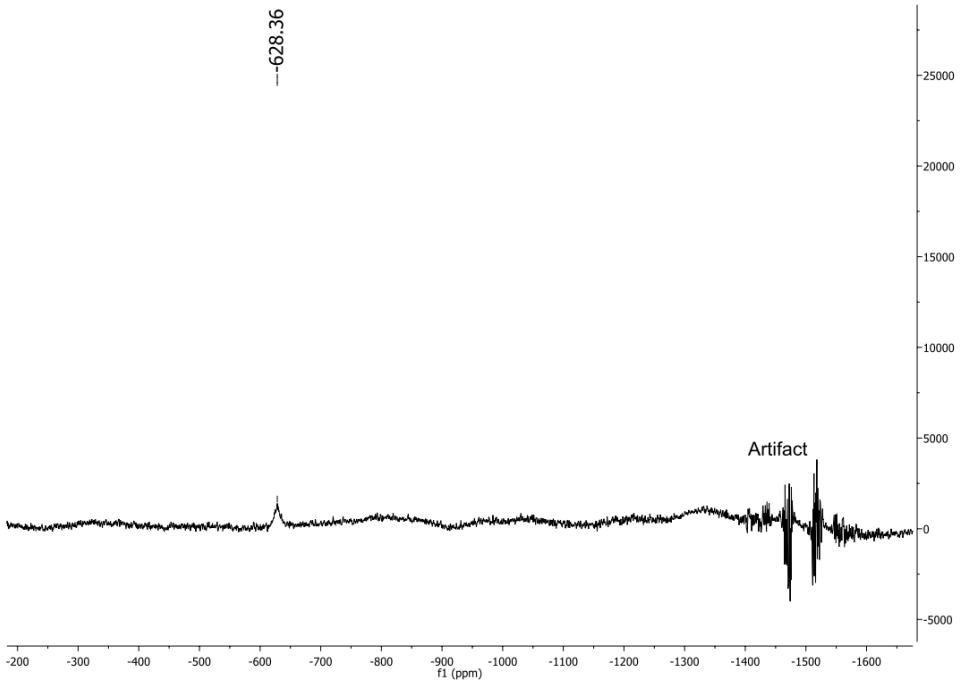


Figure S11. ^{95}Mo NMR measured after 24 h of oxidation of precatalyst 5 with 10 equiv. of TBHP (n-decane) in $CDCl_3$.

Pre-catalyst **5** (0.2335 M in $CDCl_3$) was first oxidized with 50 equiv. TBHP (0.85 mL of 5.5 M in n-decane) at room temperature. After 48 h, 10 equiv. of *cis*-cyclooctene (0.12 mL) was added to the NMR tube and the reaction was monitored for 4 h. The rate of epoxidation of *cis*-cyclooctene is slower and there is an incomplete conversion of cyclooctene even after 4 h and presence of initial excess of TBHP (50 equiv.). (**Figure S12**)

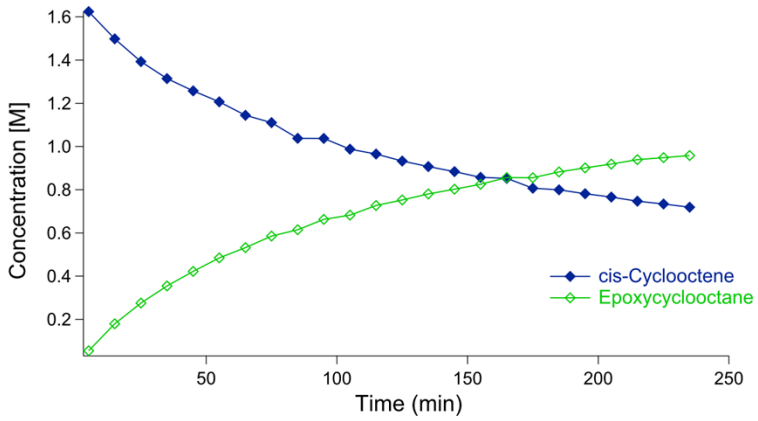


Figure S12. Kinetic plot of epoxidation of *cis*-cyclooctene with TBHP and oxo-peroxo complex obtained after oxidation of **5**.

11. Table S3 - Crystal Data and Details of Structure Determination

Formula 2 Mo O5.36, C17 H22 Mo O5.23, C17 H22 Mo O5, C16 H20 Mo O5			
Formula Weight			1604.45
Crystal System			Monoclinic
Space group		P21	(No. 4)
a, b, c [Angstrom]	22.4707(5)	7.0620(2)	23.4265(5)
alpha, beta, gamma [deg]	90	112.704(1)	90
V [Ang**3]			3429.44(15)
Z			2
D(calc) [g/cm**3]			1.554
Mu(MoKa) [/mm]			0.787
F(000)			1642
Crystal Size [mm]		0.12 x 0.16 x	0.20

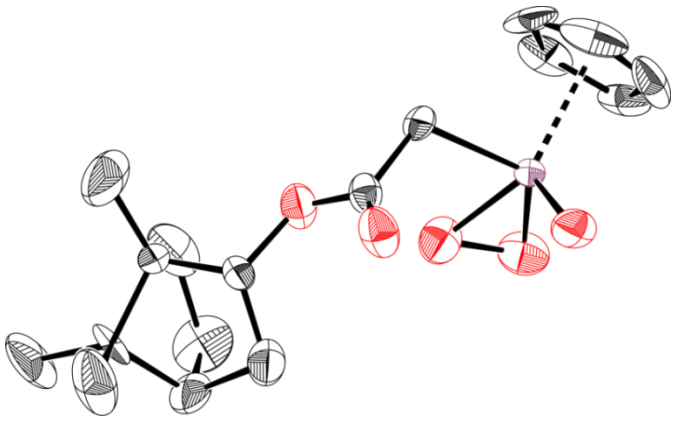
Data Collection

Temperature (K)			296
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]			0.9, 25.5
Dataset	-27: 27 ;	-8: 8 ;	-28: 28
Tot., Uniq. Data, R(int)		76028, 12626,	0.055
Observed data [I > 2.0 sigma(I)]			10042

Refinement

Nref, Npar			12626, 851
R, wR2, S		0.0512, 0.1445,	1.04
w = 1/[\s^2^(Fo^2^)+(0.0723P)^2^+9.7594P] where P=(Fo^2^+2Fc^2^)/3			
Max. and Av. Shift/Error			0.45, 0.01
Flack x			0.00(5)
Min. and Max. Resd. Dens. [e/Ang^3]			-0.84, 1.31

Due to disordered peroxo moieties at two of the four independent molecules in the asymmetric unit, the refinement could not proceed to a satisfying model. The structural proof of the oxo-peroxo species is valid.



A solution of 0.1 mmol of **5** was stirred with 20 equiv. of TBHP in 4 mL $CHCl_3$ at r.t. for 4 h. Excess hydroperoxide was destroyed with activated MnO_2 and the light yellow supernatant was separated by cannular filtration, followed by washing several times with 2 mL of $CHCl_3$. The collected supernatant and washings were concentrated under vacuum and gave a deep yellow oily residue. The residue was re-dissolved in $CDCl_3$ and an attempt to obtain crystals by slow vapour diffusion using pentane, $CDCl_3$ solvent mixture gave very small crystals. Their structure could not be refined completely but proves formation of oxo-peroxo complex **II**.