

Supporting information for:

Efficient alkane hydroxylation catalysis of Nickel(II) complexes with oxazoline donor containing tripodal tetradentate ligands

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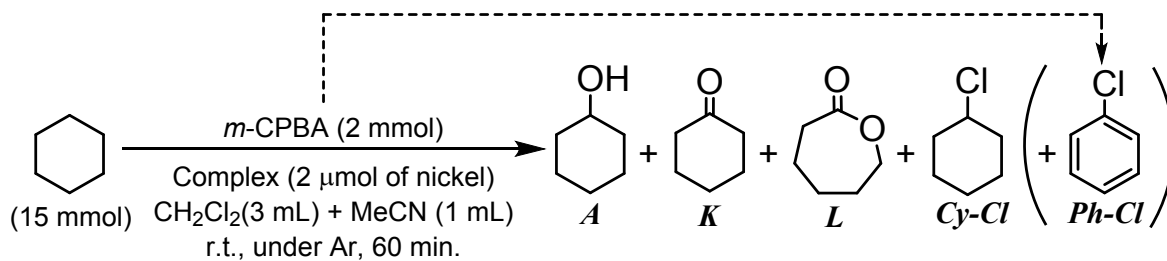
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Table S1 Cyclohexane-*d*₁₂ oxidation mediated by **1** and **7**

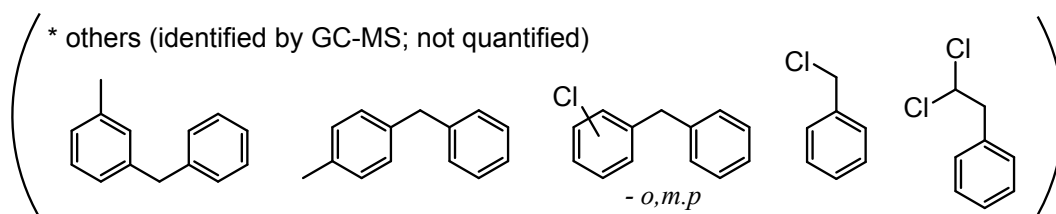
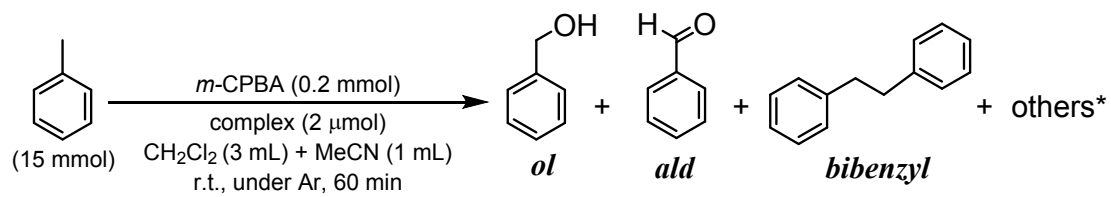


Complex	Substrate	Products / μmol					TON ¹	<i>A</i> /(<i>K</i> + <i>L</i>)	KIE ²
		<i>A</i>	<i>K</i>	<i>L</i>	<i>Cy-Cl</i>	<i>Ph-Cl</i>			
1	C ₆ H ₁₂	1526.7	218.6	12.8	111.7	1056.7	995	6.6	2.67
1	C ₆ D ₁₂	571.5	69.2	36.0	63.2	430.8	423	5.4	
7	C ₆ H ₁₂	1197.8	110.5	59.5	119.3	771.1	829	7.0	3.74
7	C ₆ D ₁₂	320.3	93.9	16.7	199.3	280.1	370	2.9	

¹ TON = (*A* + 2×*K* + 2×*L* + *Cy-Cl*) / Ni

² KIE = *A* from C₆H₁₂ / *A* from C₆D₁₂

Table S2 Toluene oxidation mediated by **1** and **7**



Complex	Products / μmol		
	<i>ol</i>	<i>ald</i>	<i>bibenzyl</i>
1	9.4	14.9	36.7
7	7.6	6.6	3.1

Table S3. Crystallographic data for **1 - 5**.

complex	1	2·2CH₂Cl₂	3
Formula	C ₄₄ H ₅₃ BN ₄ NiO ₅	C ₄₄ H ₅₄ BCl ₄ N ₅ NiO ₆	C ₄₉ H ₅₆ BClN ₄ NiO ₆
Formula Weight	787.42	960.24	901.93
Space Group	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>F</i> dd2 (No. 43)
Crystal System	triclinic	monoclinic	orthorhombic
<i>a</i> / Å	11.790(6)	14.544(5)	63.3792(17)
<i>b</i> / Å	13.799(6)	11.405(4)	58.8576(15)
<i>c</i> / Å	15.362(7)	28.205(10)	9.7929(2)
<i>α</i> / °	64.129(15)	90	90
<i>β</i> / °	83.65(2)	102.024(4)	90
<i>γ</i> / °	81.82(2)	90	90
<i>V</i> / Å ³	2222.6(18)	4576(3)	36530.9(15)
<i>Z</i>	2	4	32
<i>F</i> (000)	836	2008	15232
<i>D</i> (calcd) / g·cm ⁻³	1.177	1.394	1.312
Temp./K	293(2)	113(2)	113(2)
<i>μ</i> (MoK _α) / cm ⁻¹	4.82	7.10	5.37
2 <i>θ</i> _{max} / °	54.898	54.968	54.962
Measured reflections	9293	10430	20846
Observed reflections (<i>I</i> > 2σ(<i>I</i>))	6613	7617	19997
Parameters	496	565	1145
R (<i>I</i> > 2σ(<i>I</i>) / all ^(a))	0.0437 / 0.0618	0.0661 / 0.0807	0.0370 / 0.0394
wR	0.1589	0.1974	0.0770
Goodness of fit <i>S</i> ^(b)	0.725	1.040	1.152

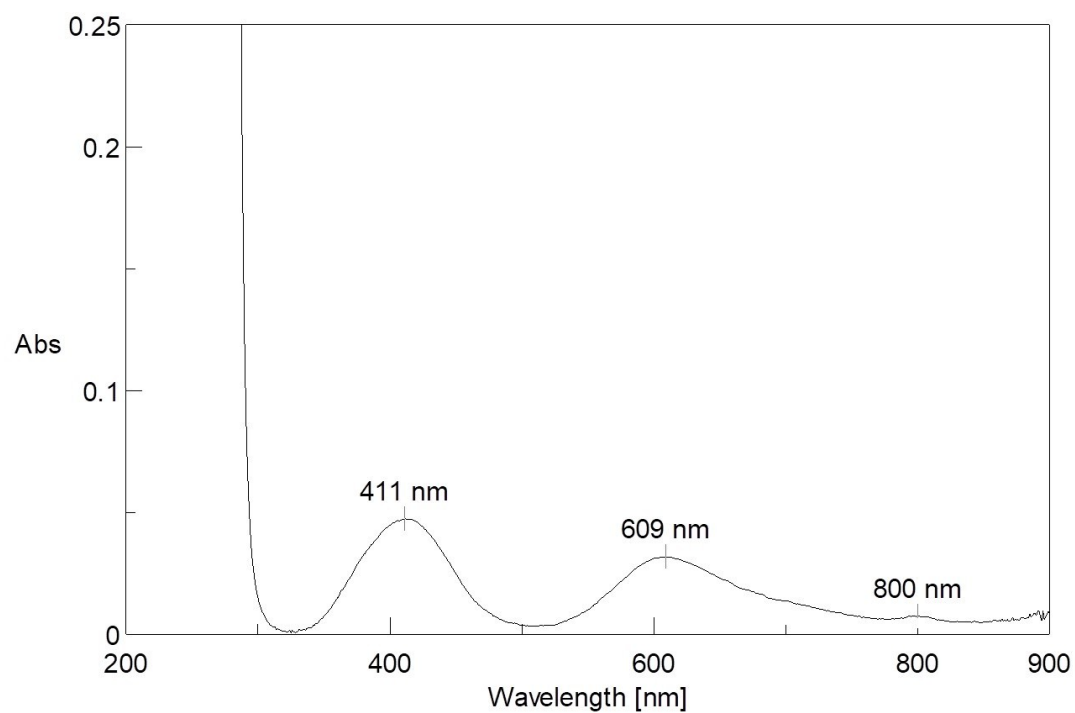
(a) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $R_w = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$. (b) $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

Table S3. (continued)

complex	4	5
Formula	C ₄₂ H ₅₀ B ₁ ClN ₄ NiO ₃	C ₄₈ H ₆₂ BClN ₄ NiO ₃
Formula Weight	763.83	847.98
Space Group	<i>P2₁/c</i> (No. 14)	<i>P2₁</i> (No. 4)
Crystal System	monoclinic	monoclinic
<i>a</i> / Å	14.905(7)	12.0793(6)
<i>b</i> / Å	24.920(12)	13.4525(5)
<i>c</i> / Å	10.988(5)	15.1350(6)
<i>α</i> / °	90	90
<i>β</i> / °	102.752(4)	111.020(2)
<i>γ</i> / °	90	90
<i>V</i> / Å ³	3981(3)	2295.73(17)
<i>Z</i>	4	2
<i>F</i> (000)	1616	904
<i>D</i> (calcd) / g·cm ⁻³	1.275	1.227
Temp./K	113(2)	133(2)
<i>μ</i> (MoK _α) / cm ⁻¹	5.97	5.25
2 <i>θ</i> _{max} / °	54.606	54.962
Measured reflections	8761	9223
Observed reflections (<i>I</i> > 2σ(<i>I</i>))	6909	7510
Parameters	476	532
R (<i>I</i> > 2σ(<i>I</i>) / all ^(a))	0.0667 / 0.0788	0.0214 / 0.0246
wR	0.1957	0.0438
Goodness of fit <i>S</i> ^(b)	1.077	0.892

(a) $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. $R_w = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$. (b) $S = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{(n - p)} \right\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

(a) Complex 1



(b) Complex 2

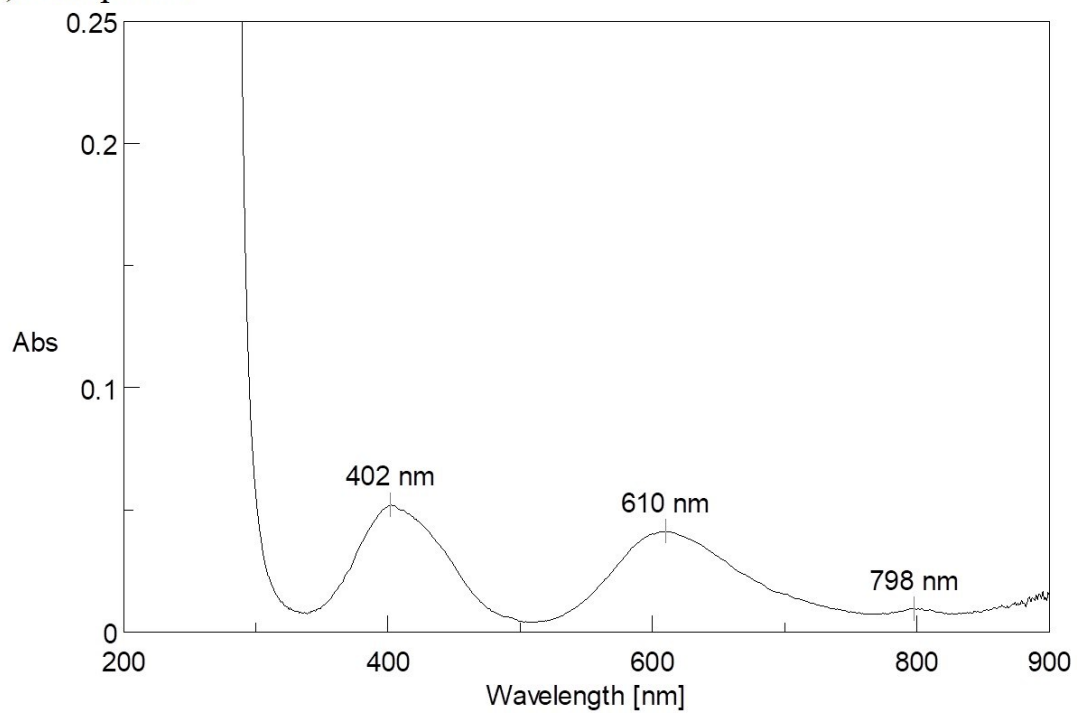
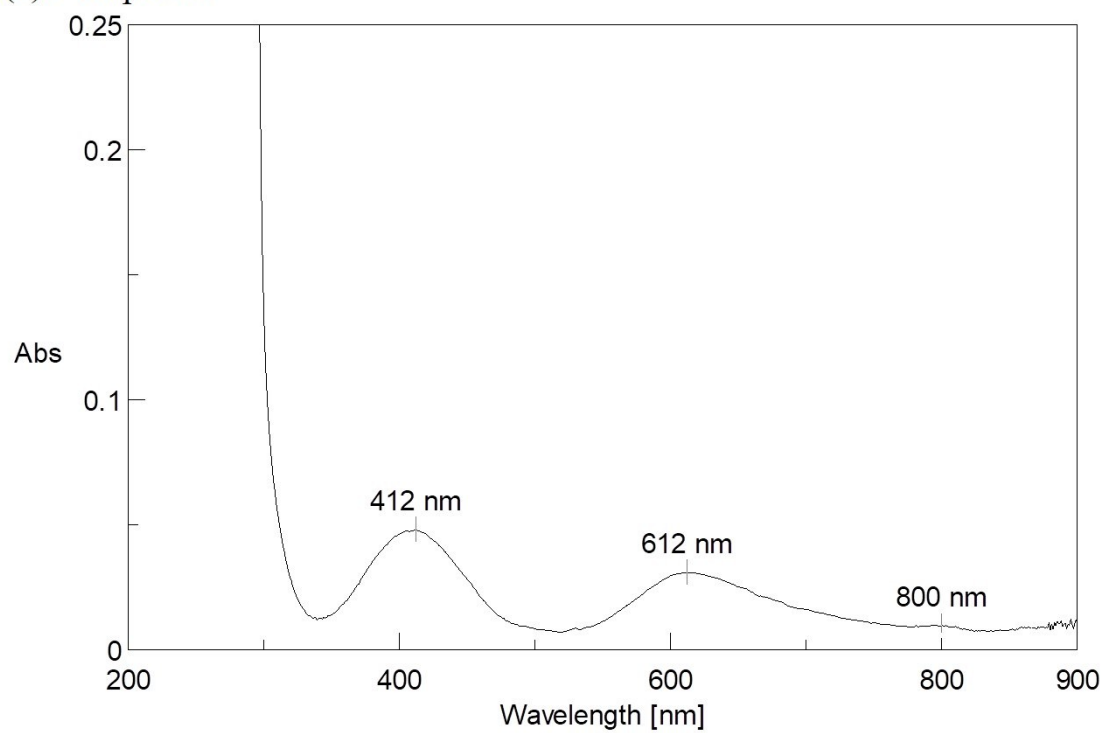


Fig. S1 UV-vis spectra of CH_2Cl_2 solutions of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

(c) Complex 3



(d) Complex 4

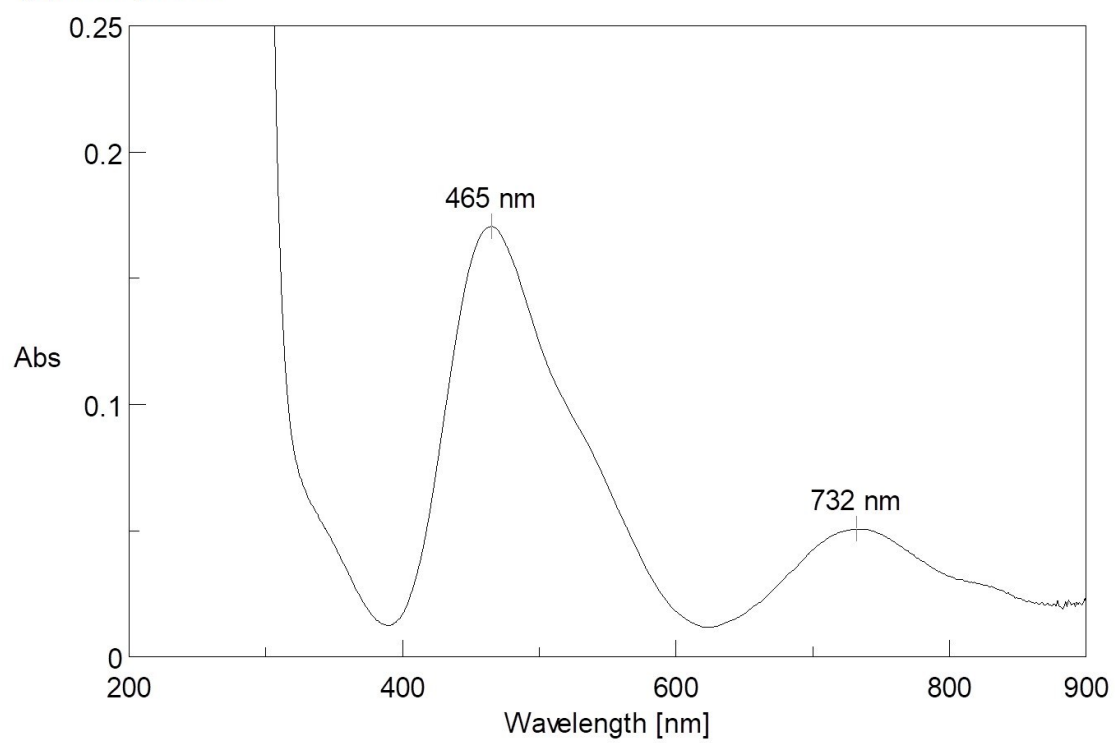
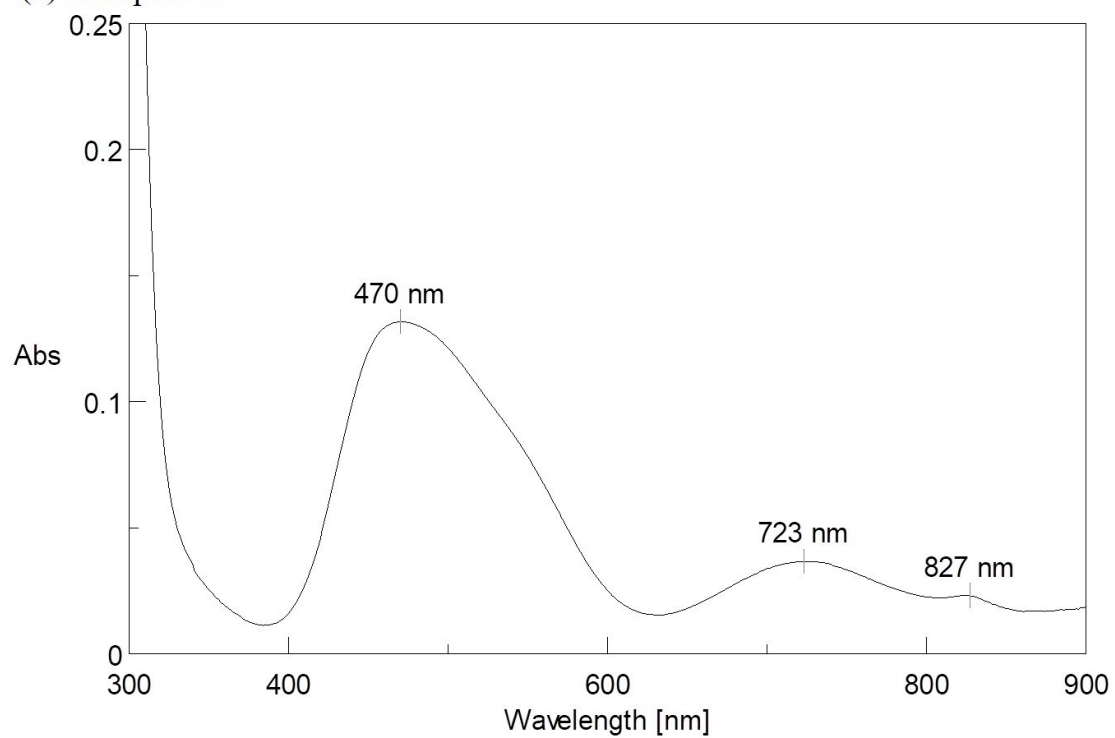


Fig. S1 (continued)

(e) Complex **5**



(f) Complex **6**

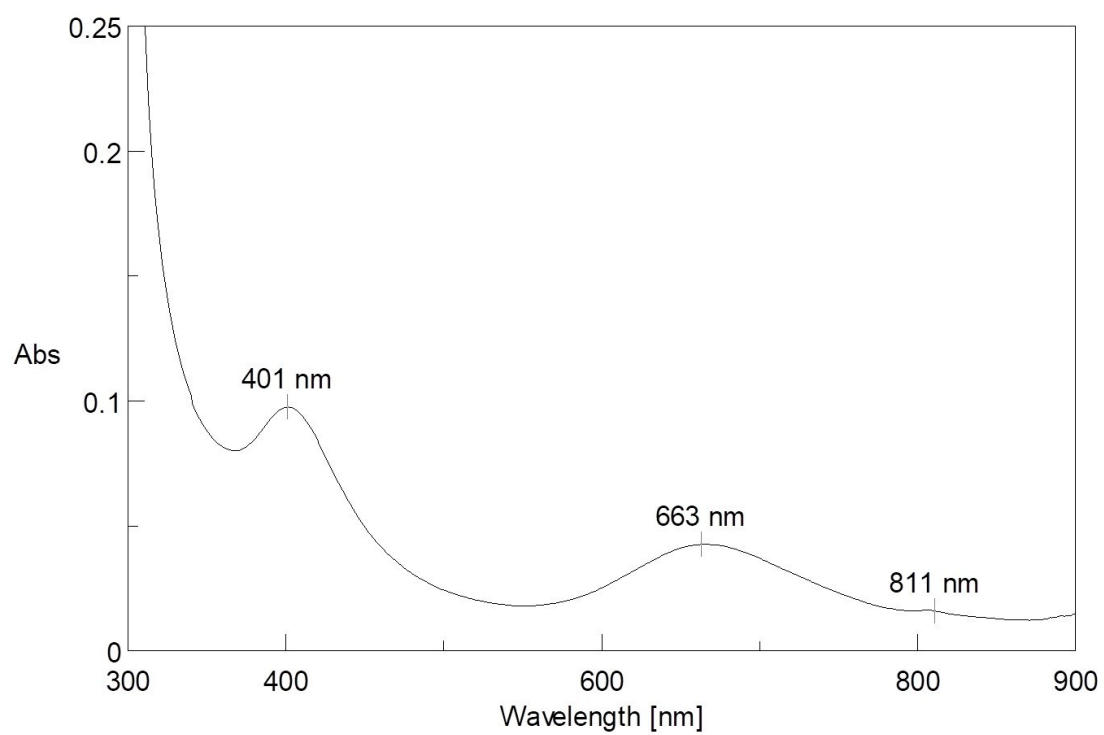
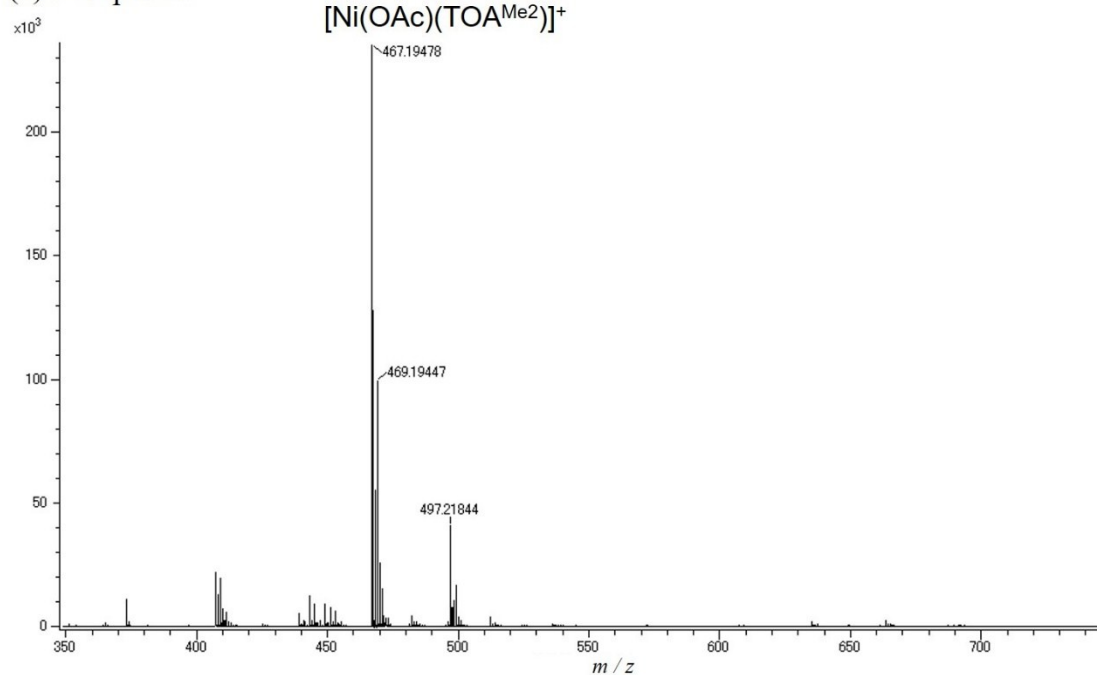


Fig. S1 (continued)

(a) Complex 1



(b) Complex 2

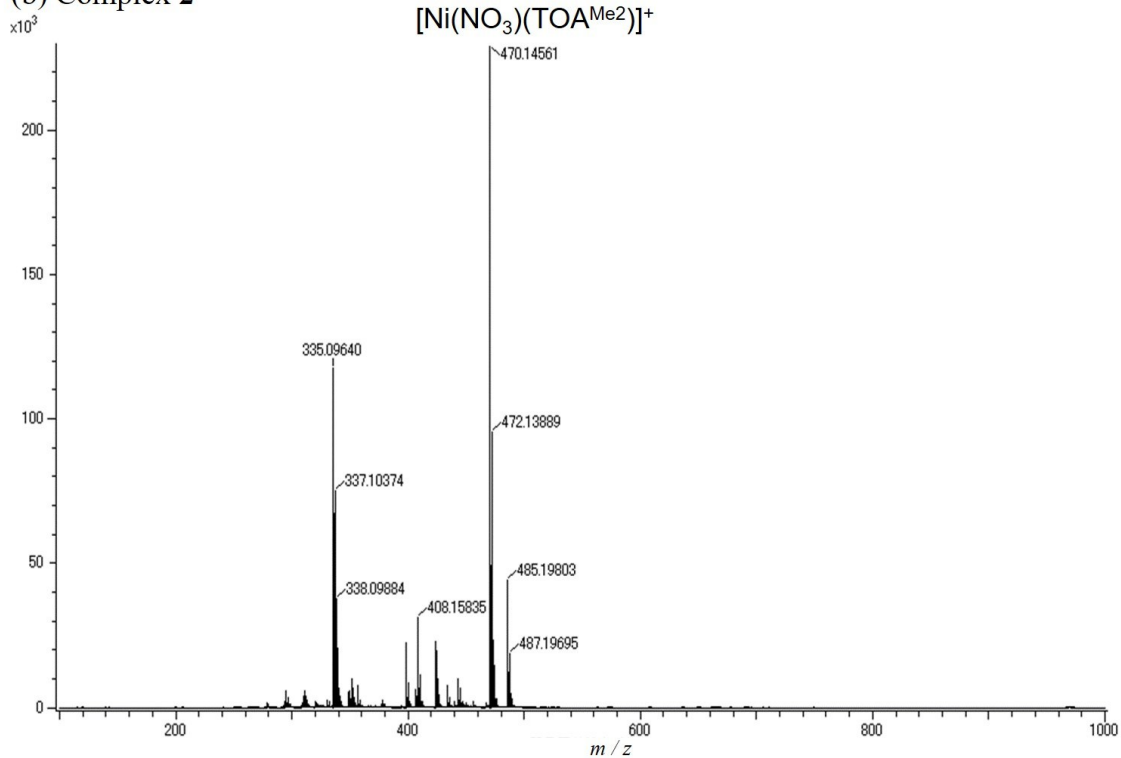
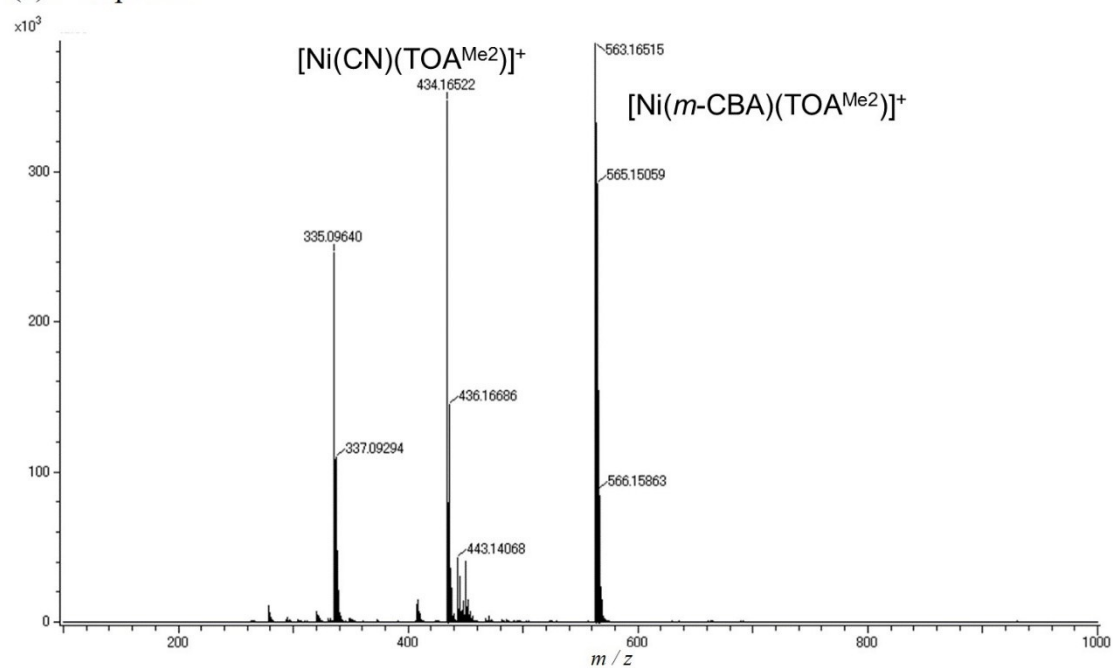


Fig. S2 ESI-MS spectra of MeCN solutions of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f).

(c) Complex 3



(d) Complex 4

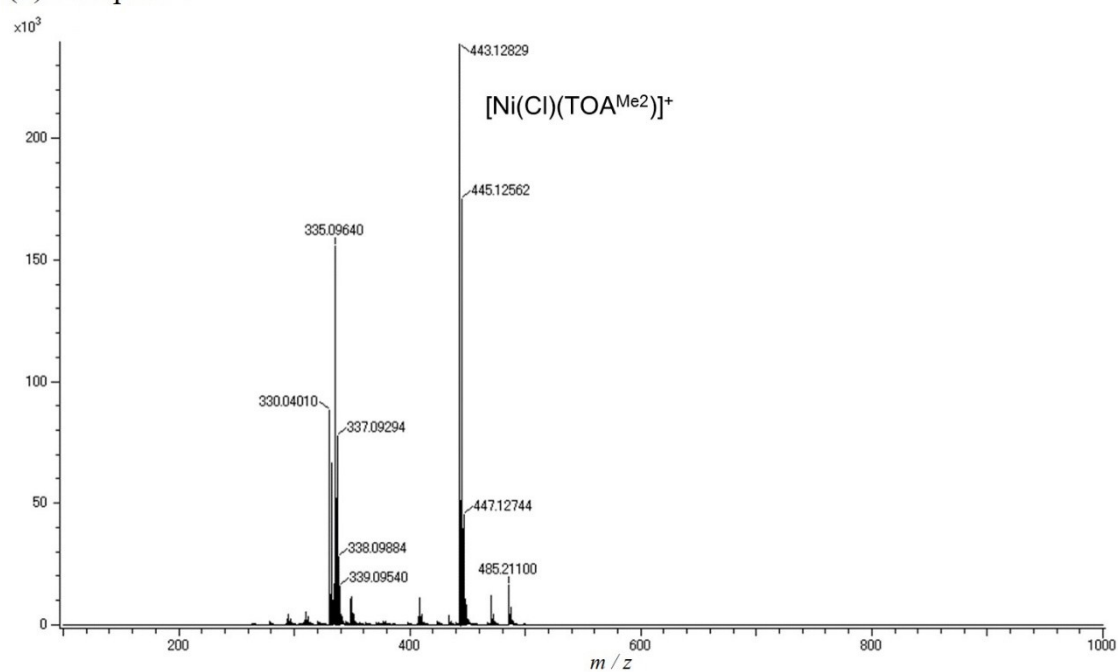
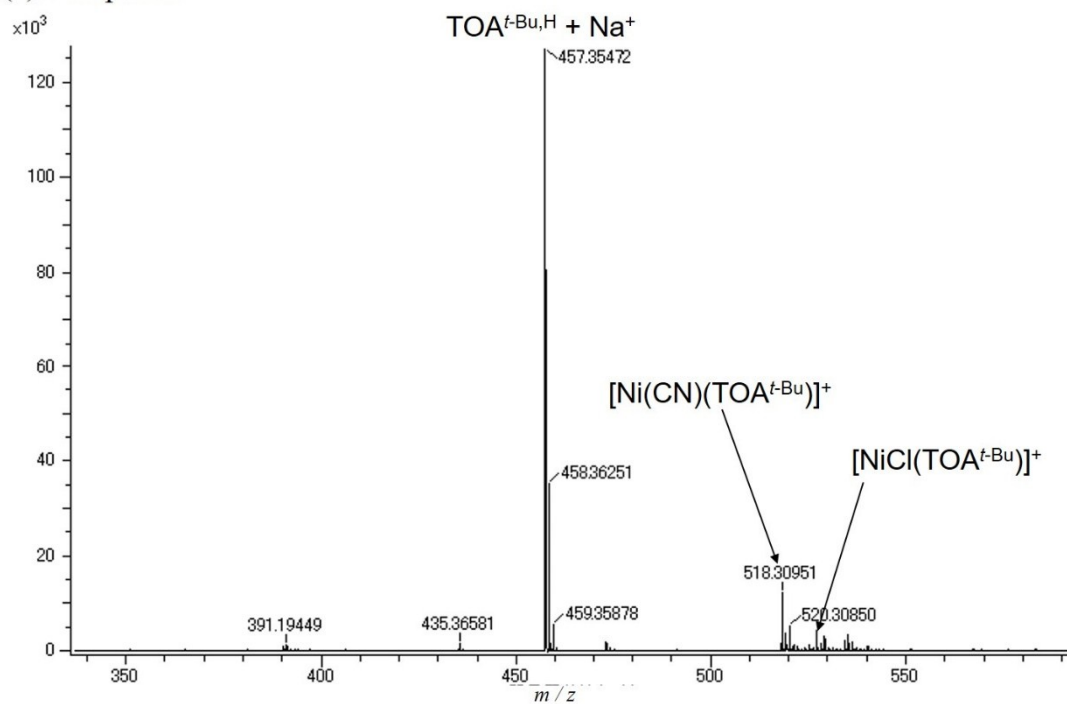


Fig. S2 (continued)

(e) Complex 5



(f) Complex 6

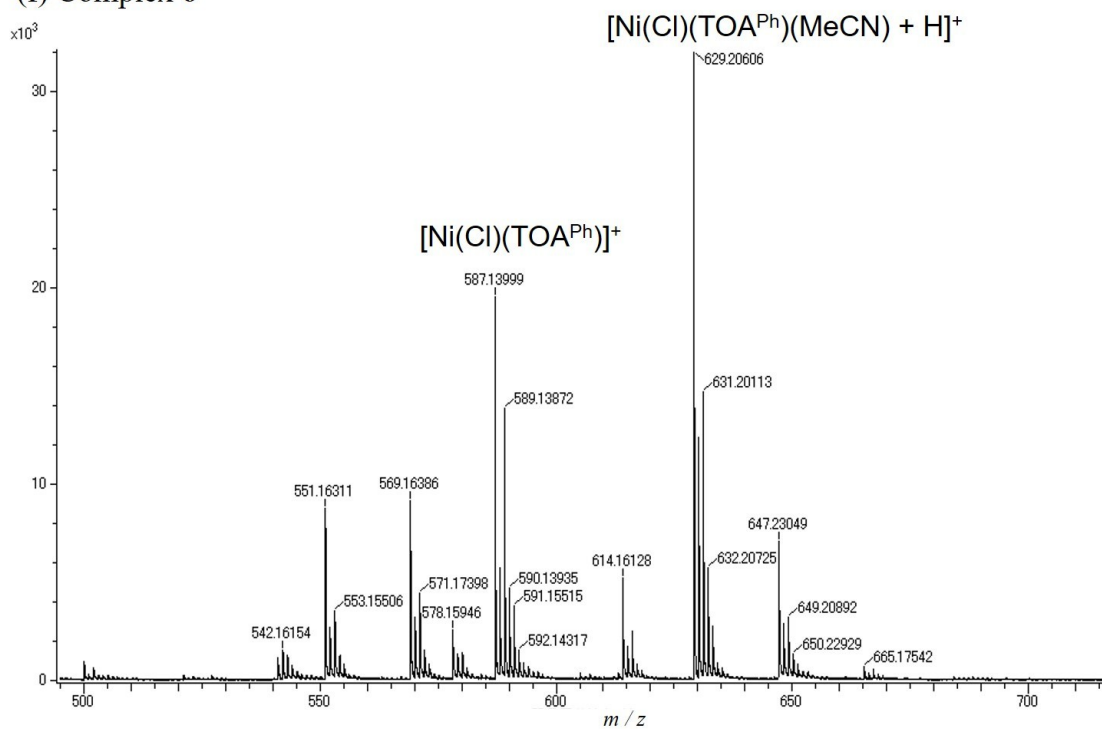
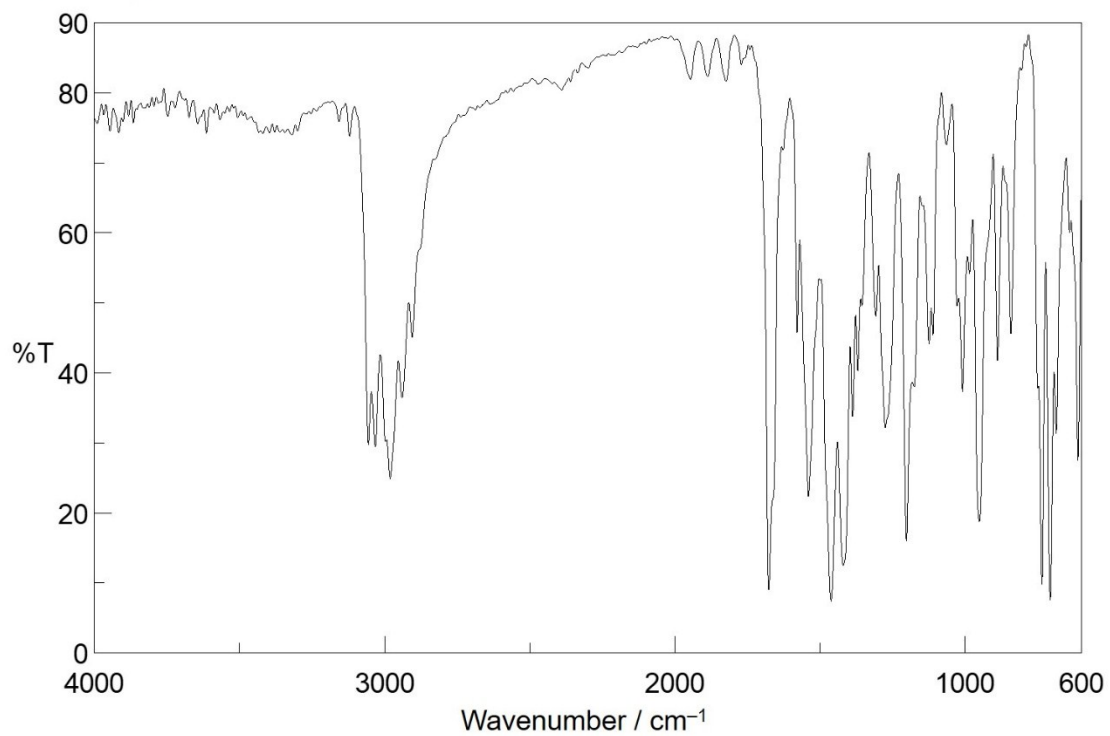


Fig. S2 (continued)

(a) Complex 1



(b) Complex 2

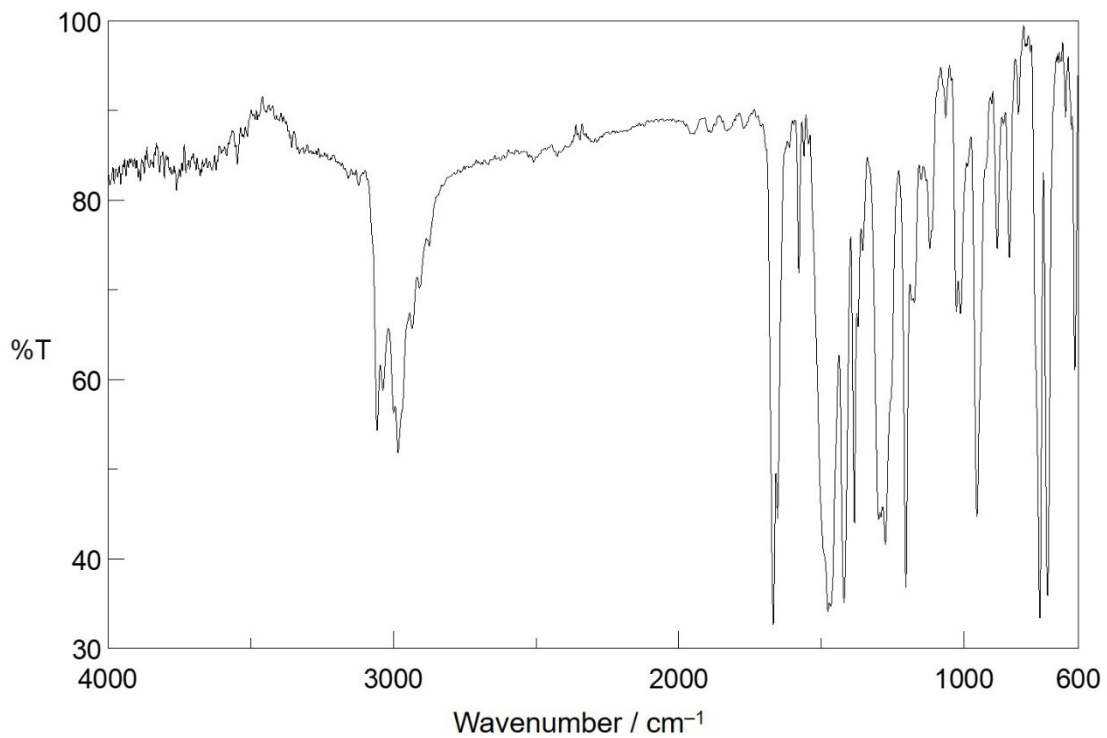
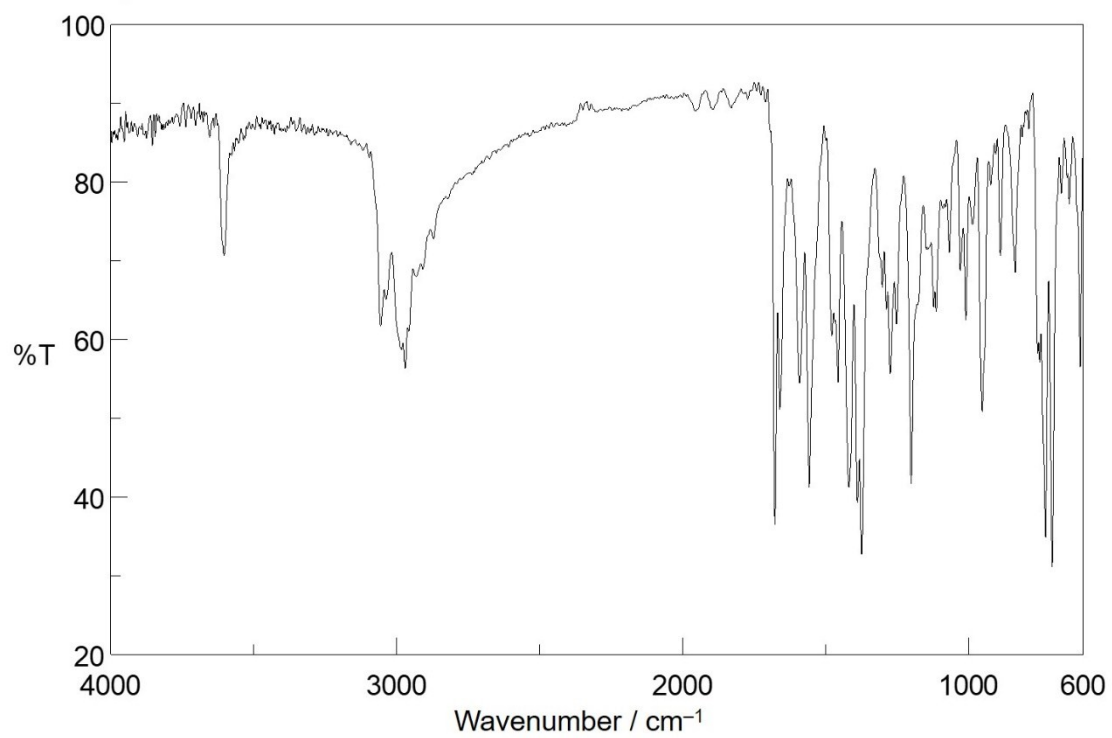


Fig. S3 IR spectra of KBr pellet of **1** (a), **2** (b), **3** (c), **4** (d), **5** (e) and **6** (f)

(c) Complex 3



(d) Complex 4

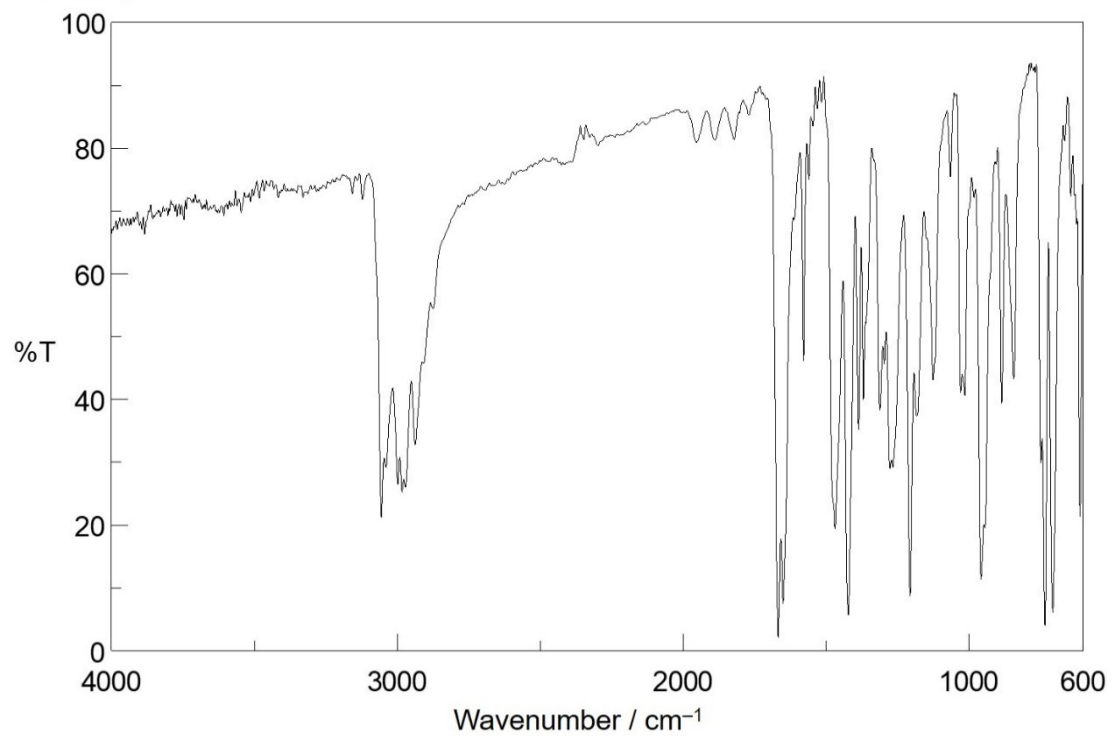
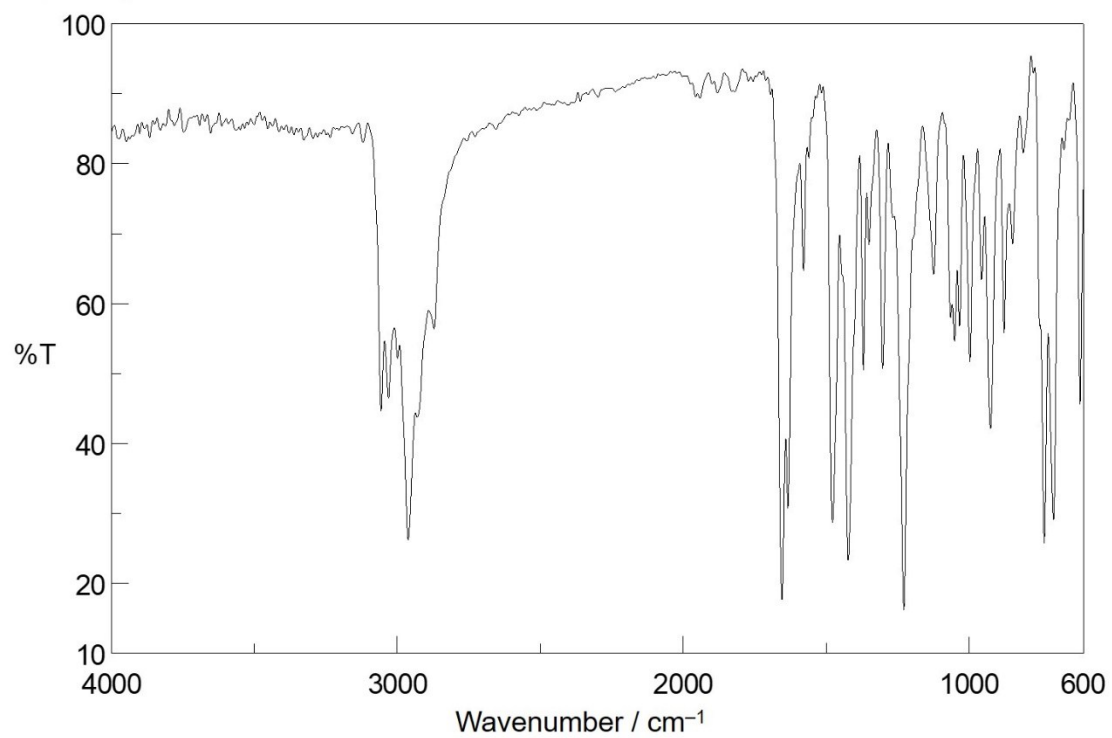


Fig. S3 (continued)

(e) Complex 5



(f) Complex 6

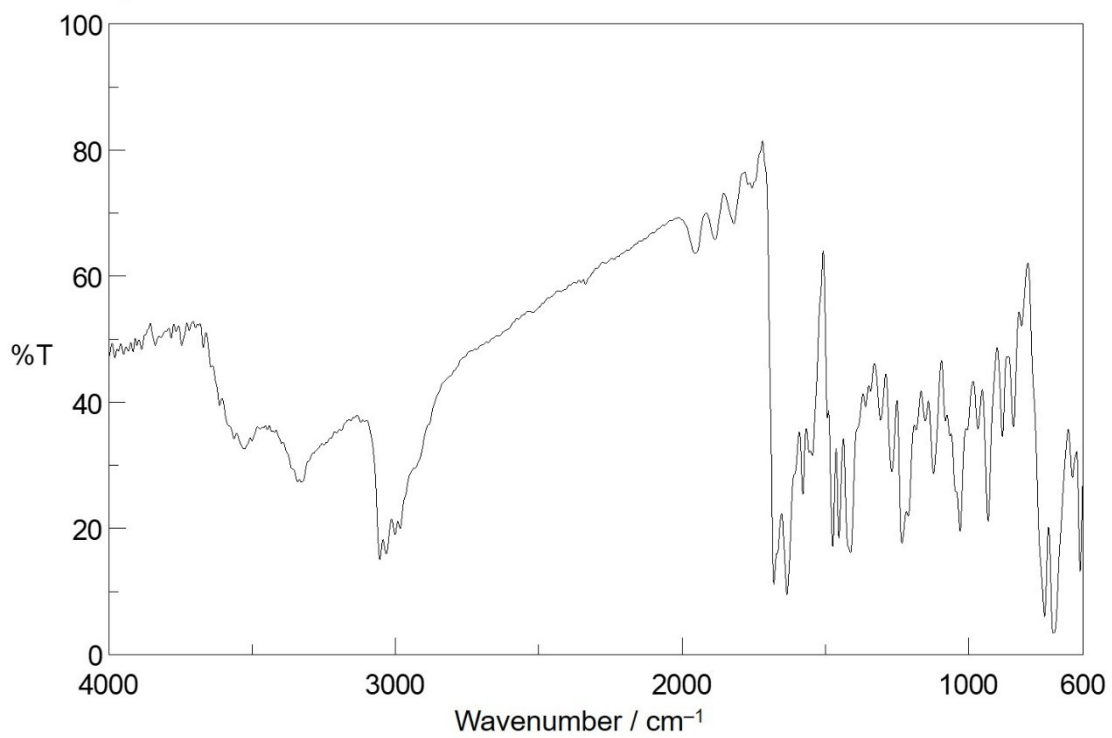


Fig. S3 (continued)

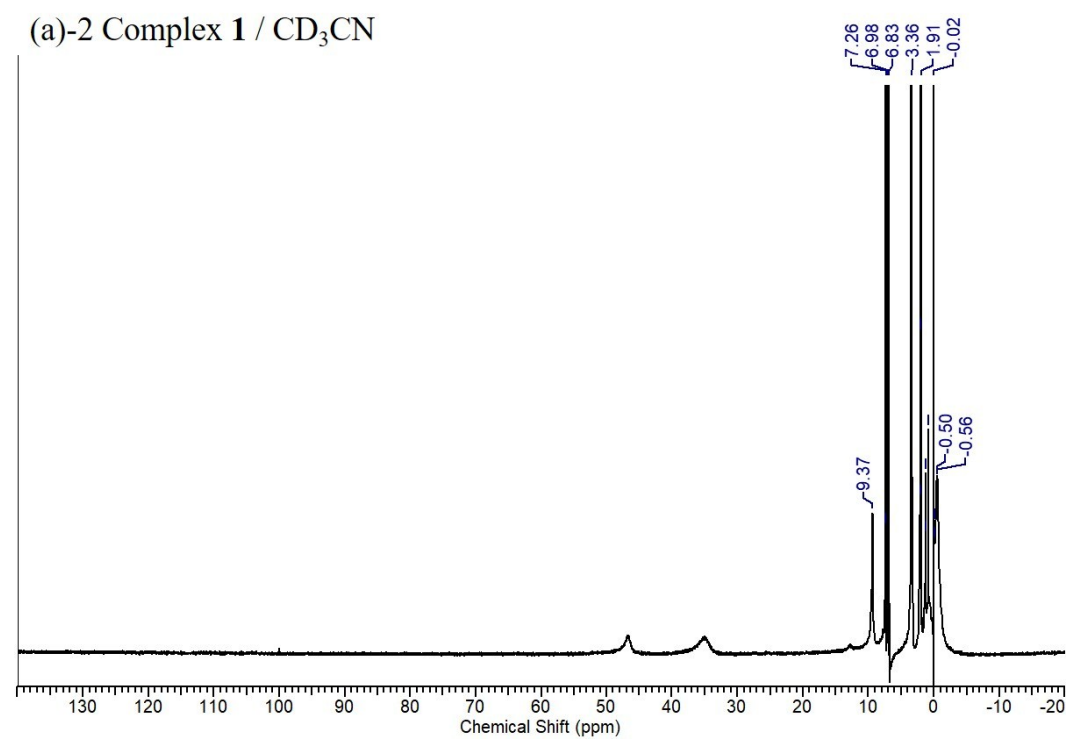
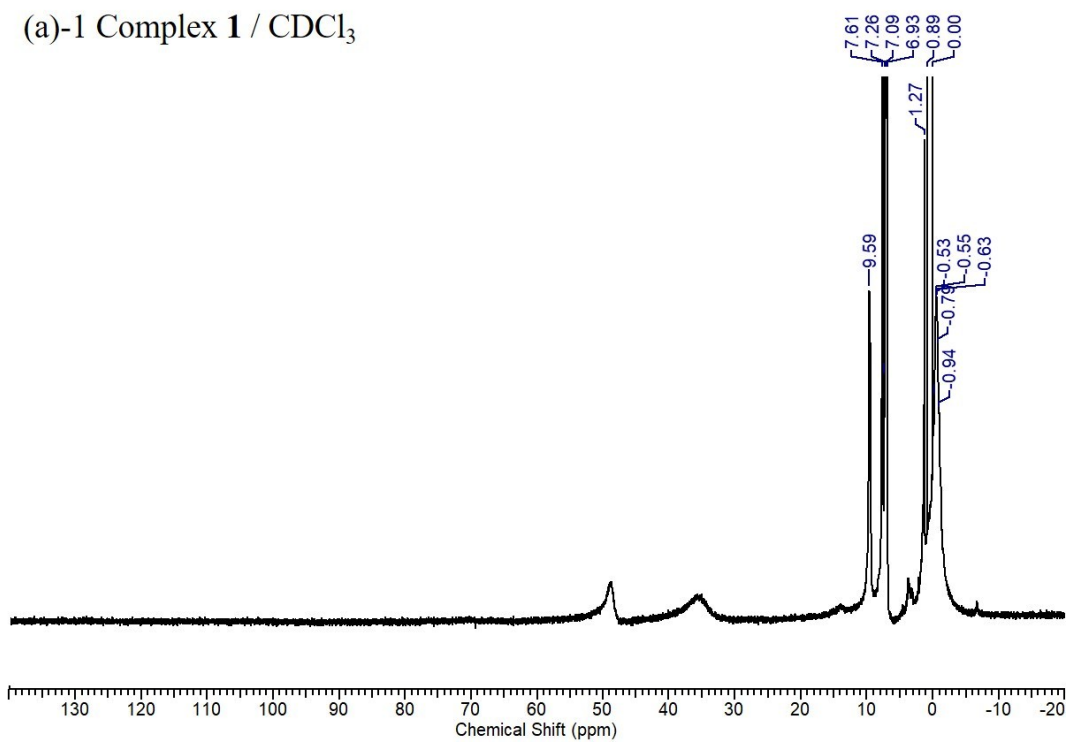
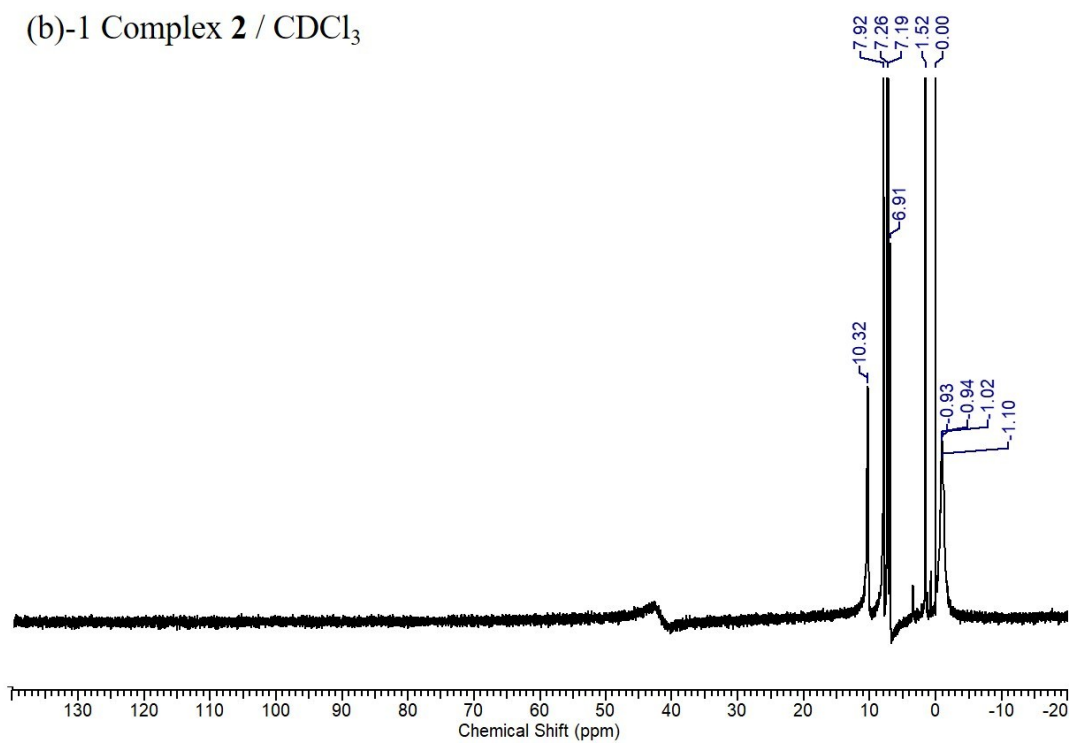


Fig. S4 ¹H NMR spectra of KBr pellet of **1** (a), **2** (b), **4** (c), **5** (d) and **6** (e)

(b)-1 Complex **2** / CDCl₃



(b)-2 Complex **2** / CD₃CN

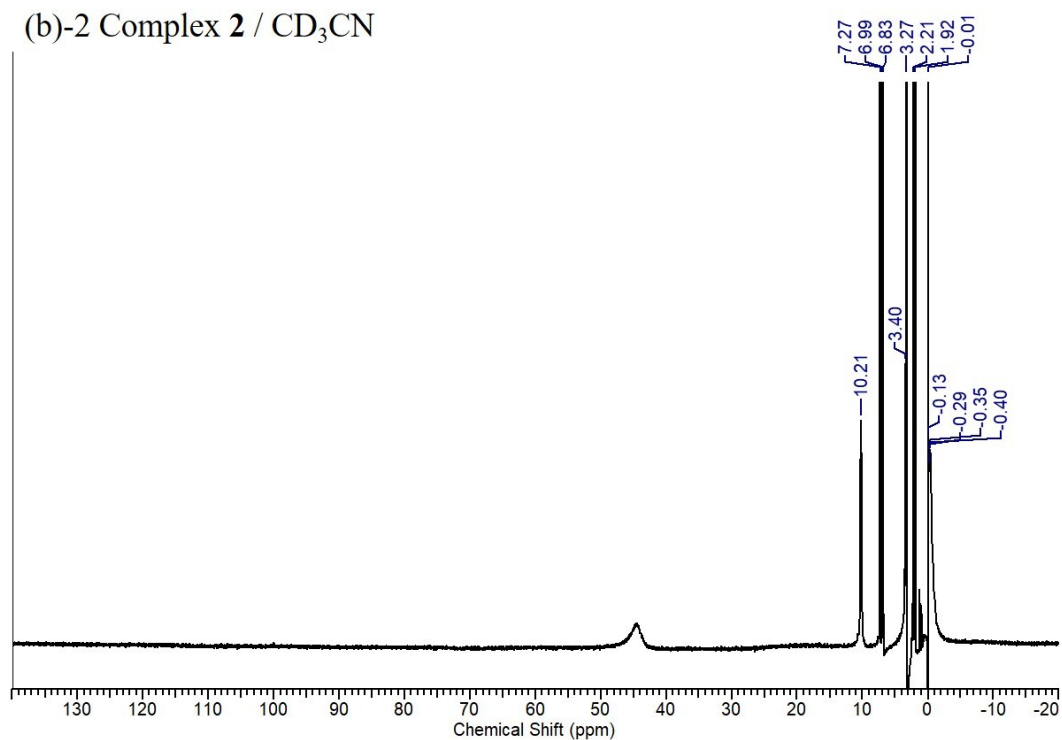


Fig. S4 (continued)

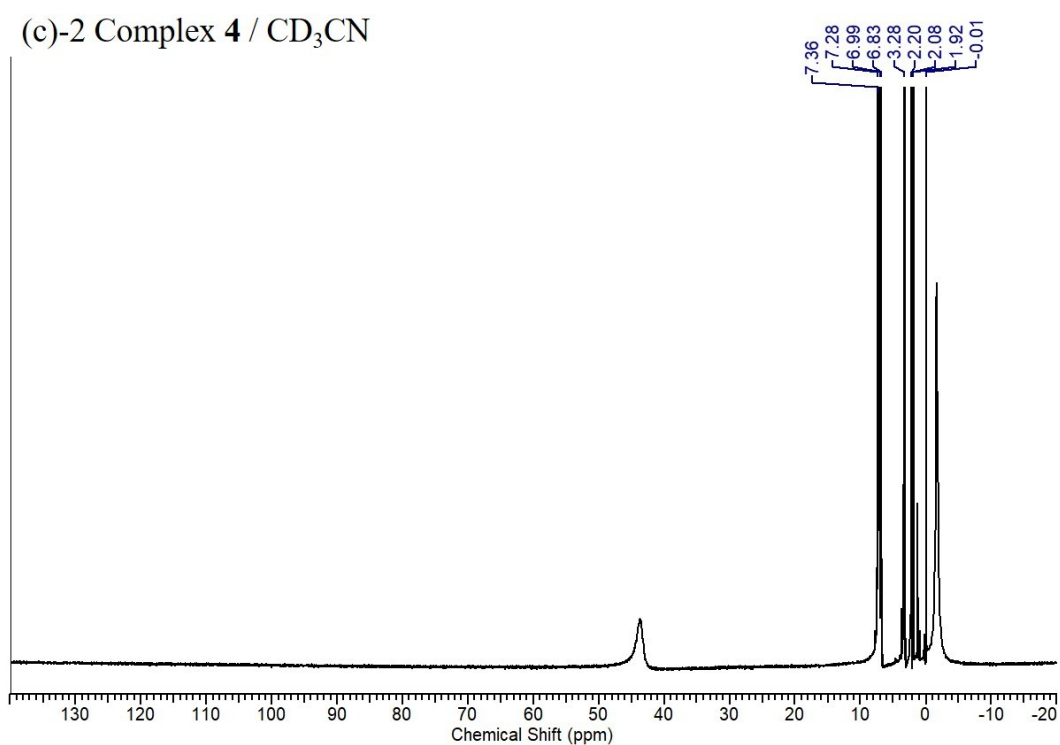
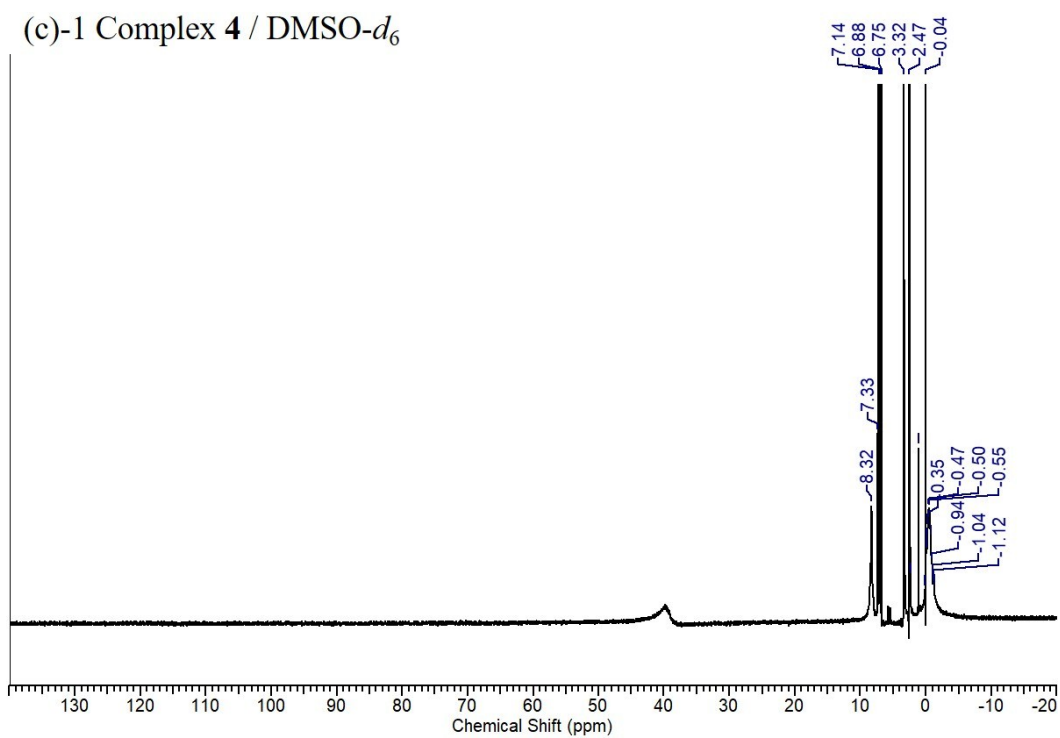


Fig. S4 (continued)

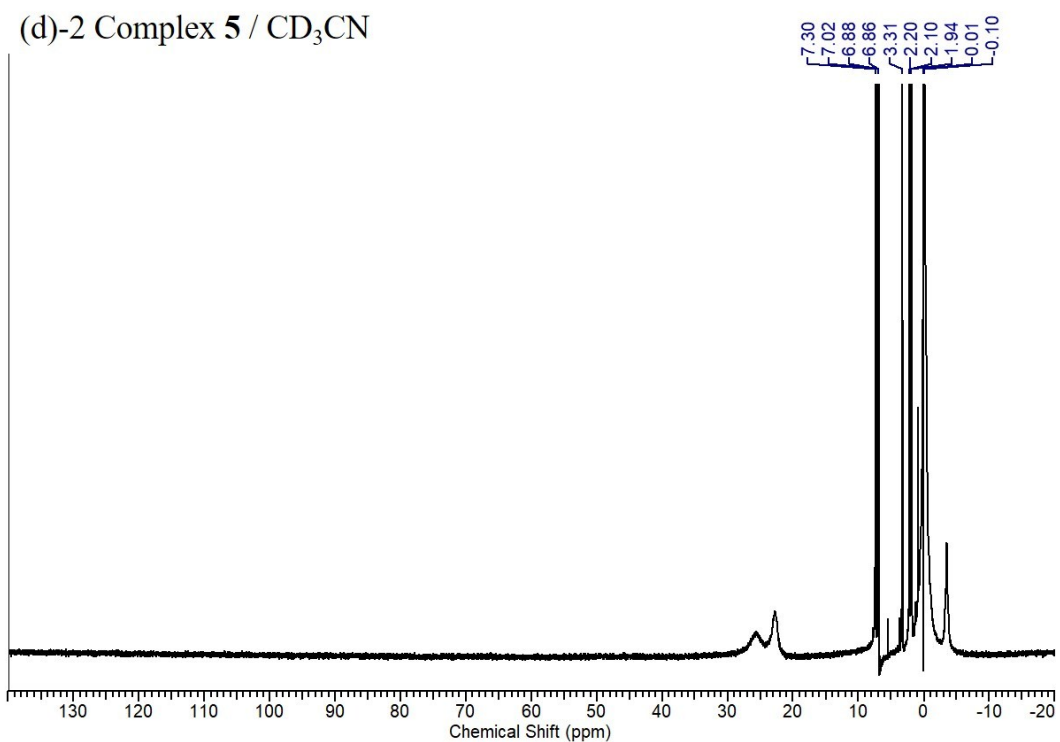
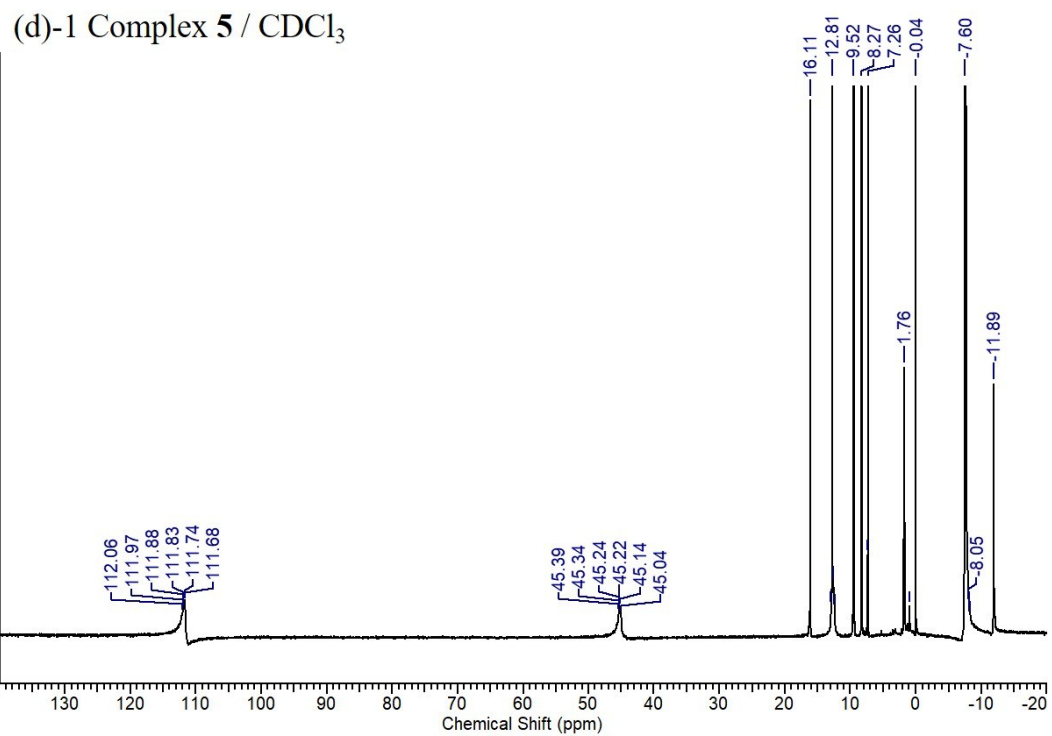


Fig. S4 (continued)

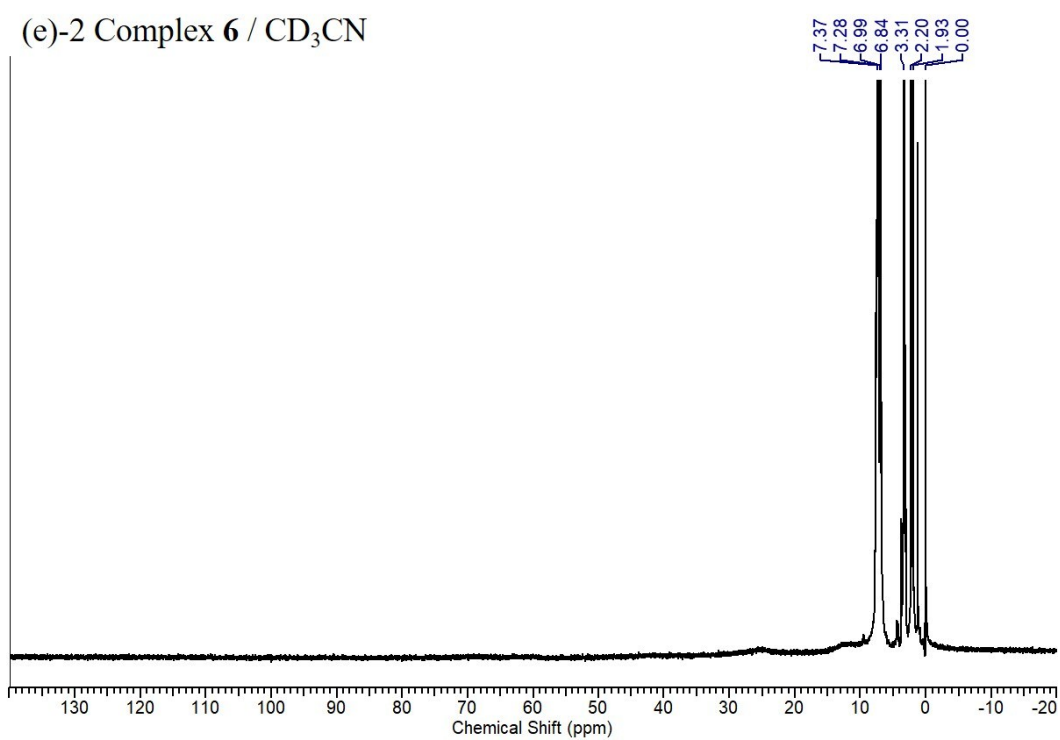
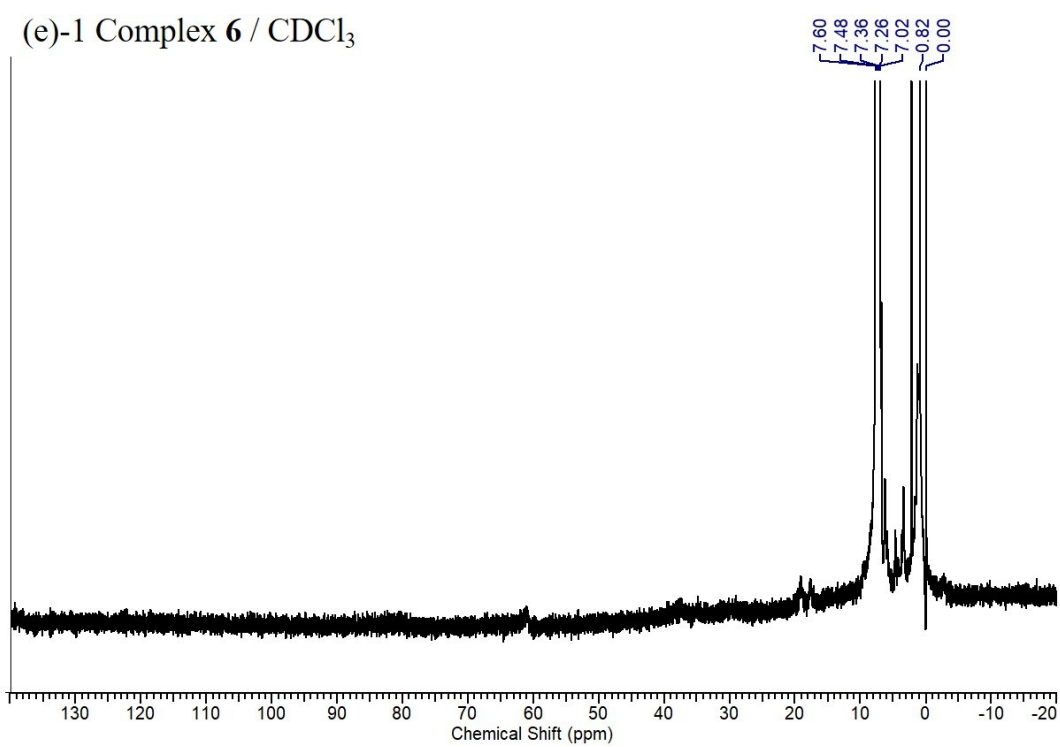


Fig. S4 (continued)

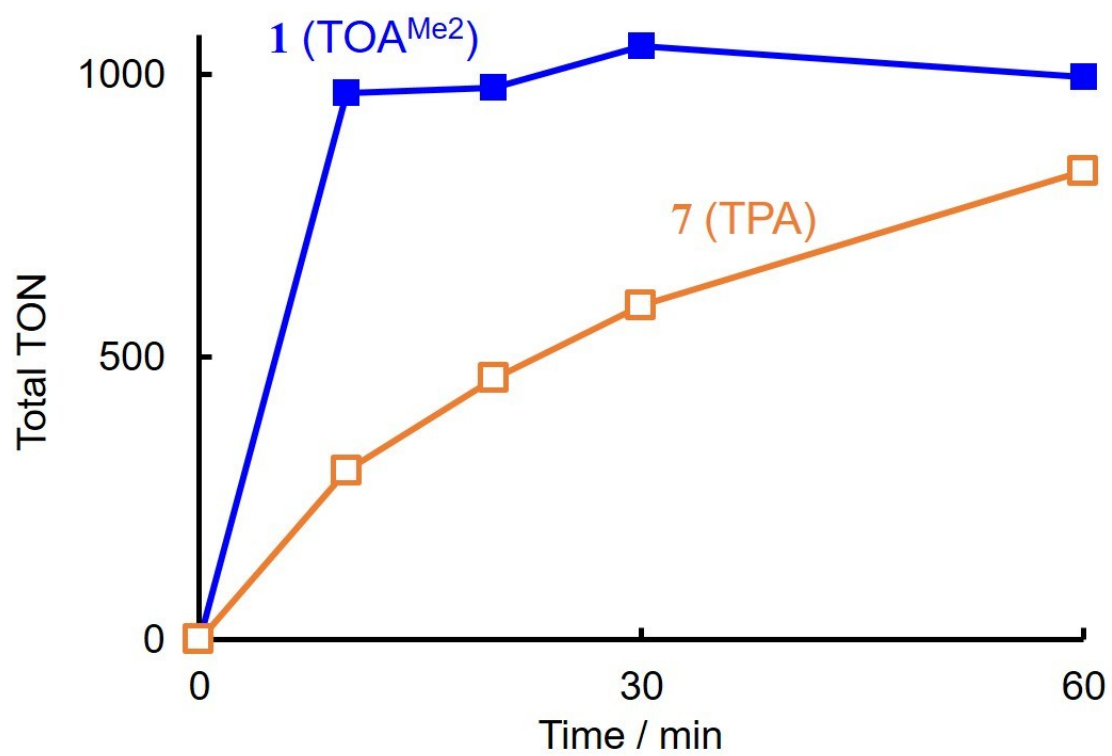


Fig. S5 Time course of total TON of the acetate complexes **1** and **7** on cyclohexane oxidation

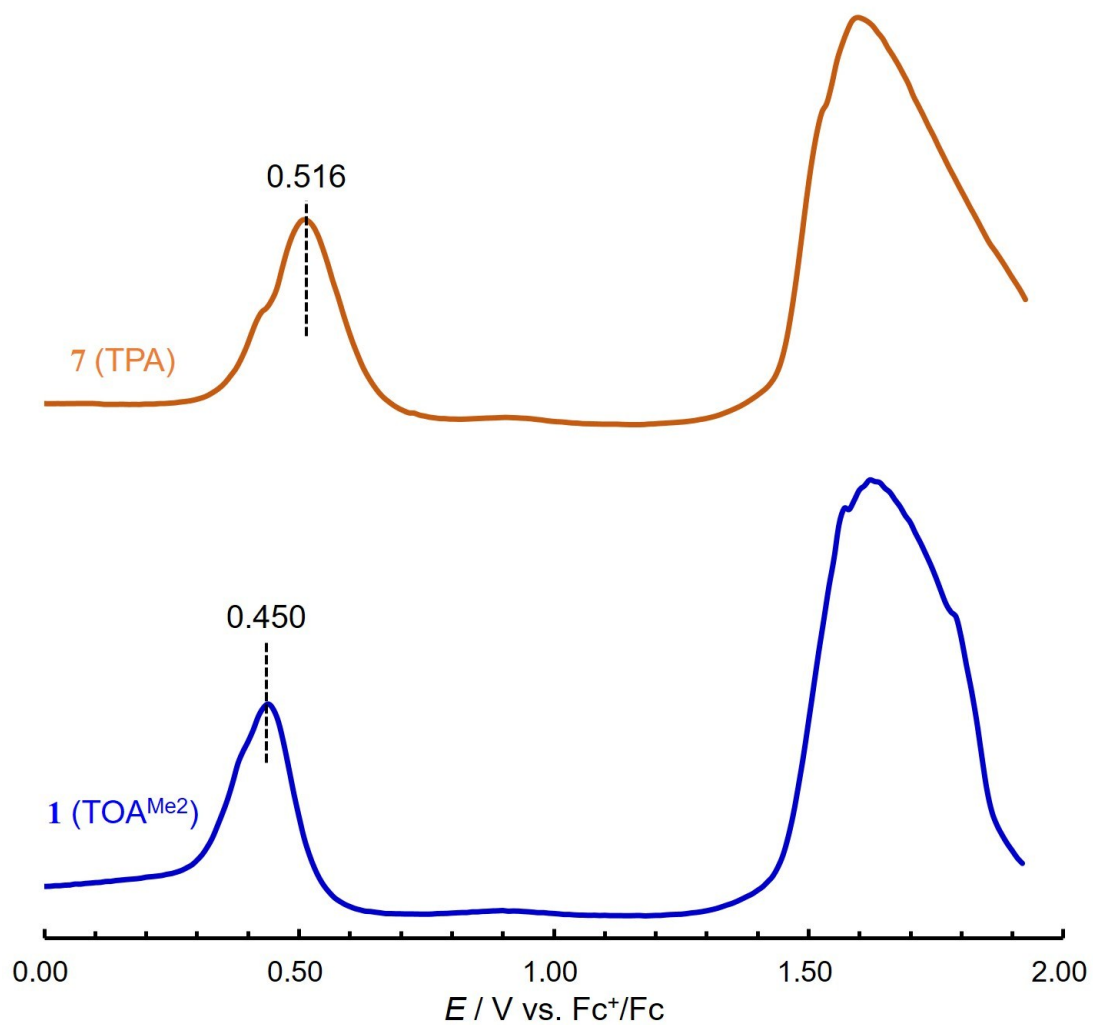


Fig. S6 Differential pulse voltammograms of the acetate complexes **1** and **7** in MeCN with 0.1 M $n\text{Bu}_4\text{NPF}_6$

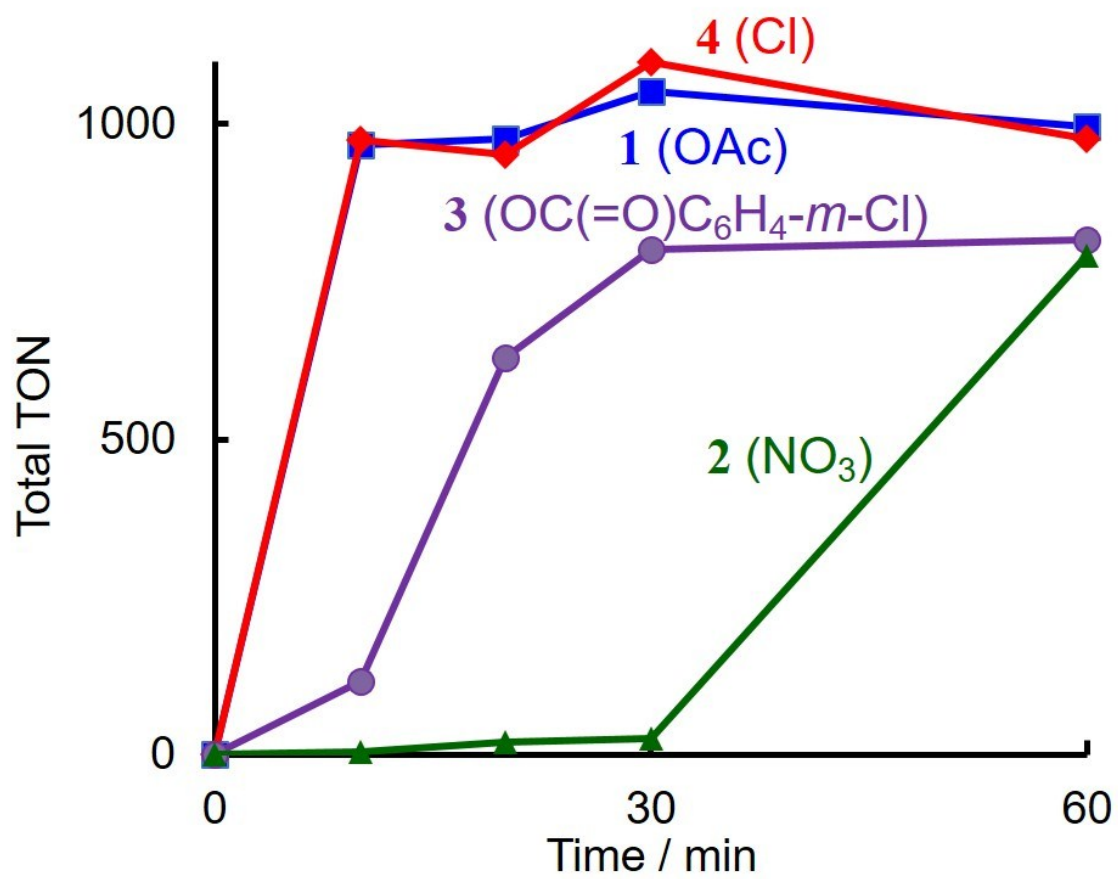


Fig. S7 Time course of total TON of the TOA^{Me2} complexes 1 – 4 on cyclohexane oxidation

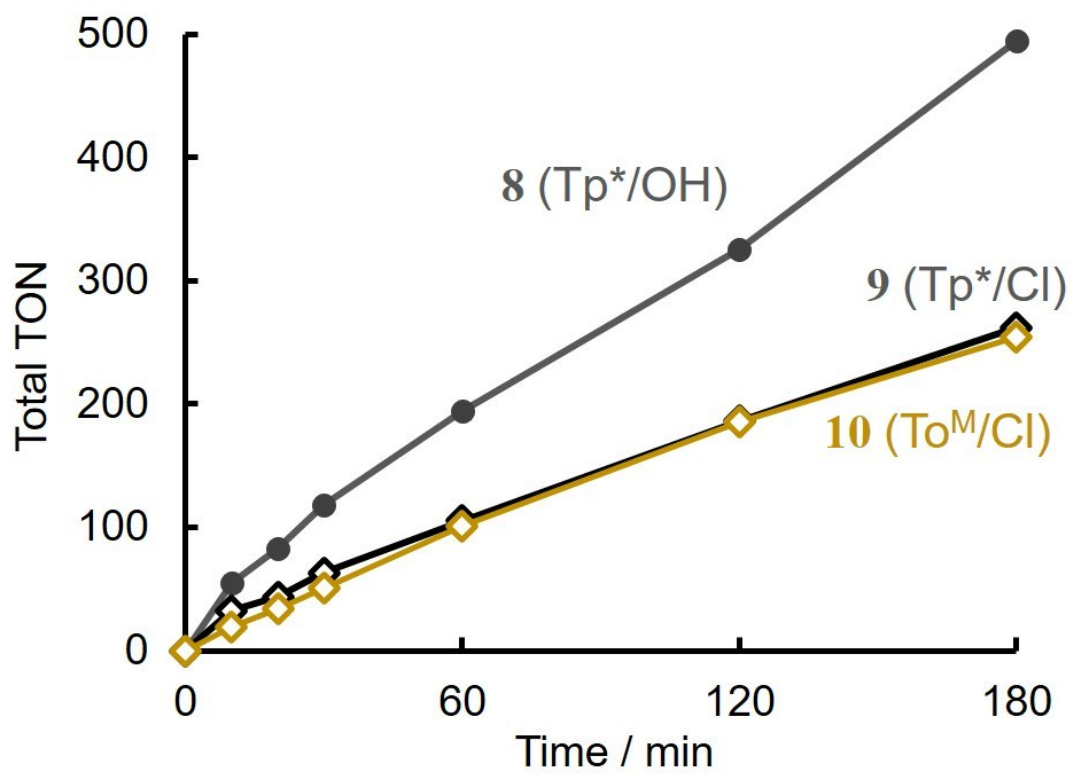


Fig. S8 Time course of total TON of the Tp* and To^M complexes **8** – **10** on cyclohexane oxidation

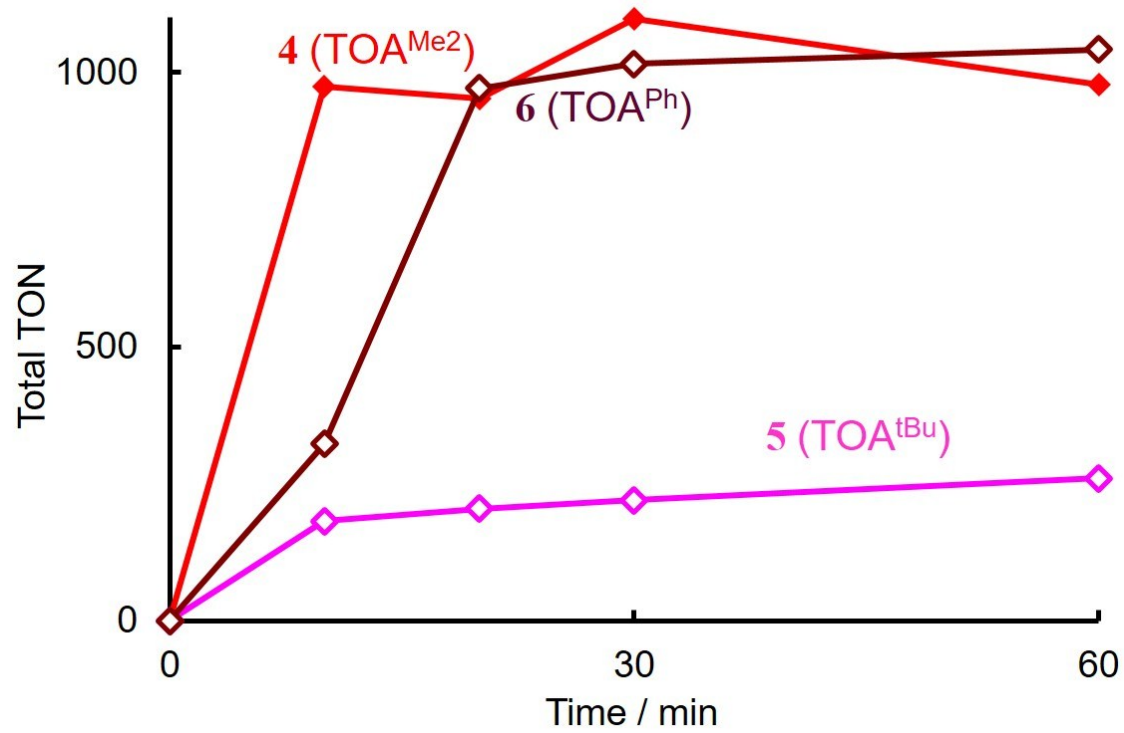


Fig. S9 Time course of total TON of the chlorido complexes 4 – 6 on cyclohexane oxidation

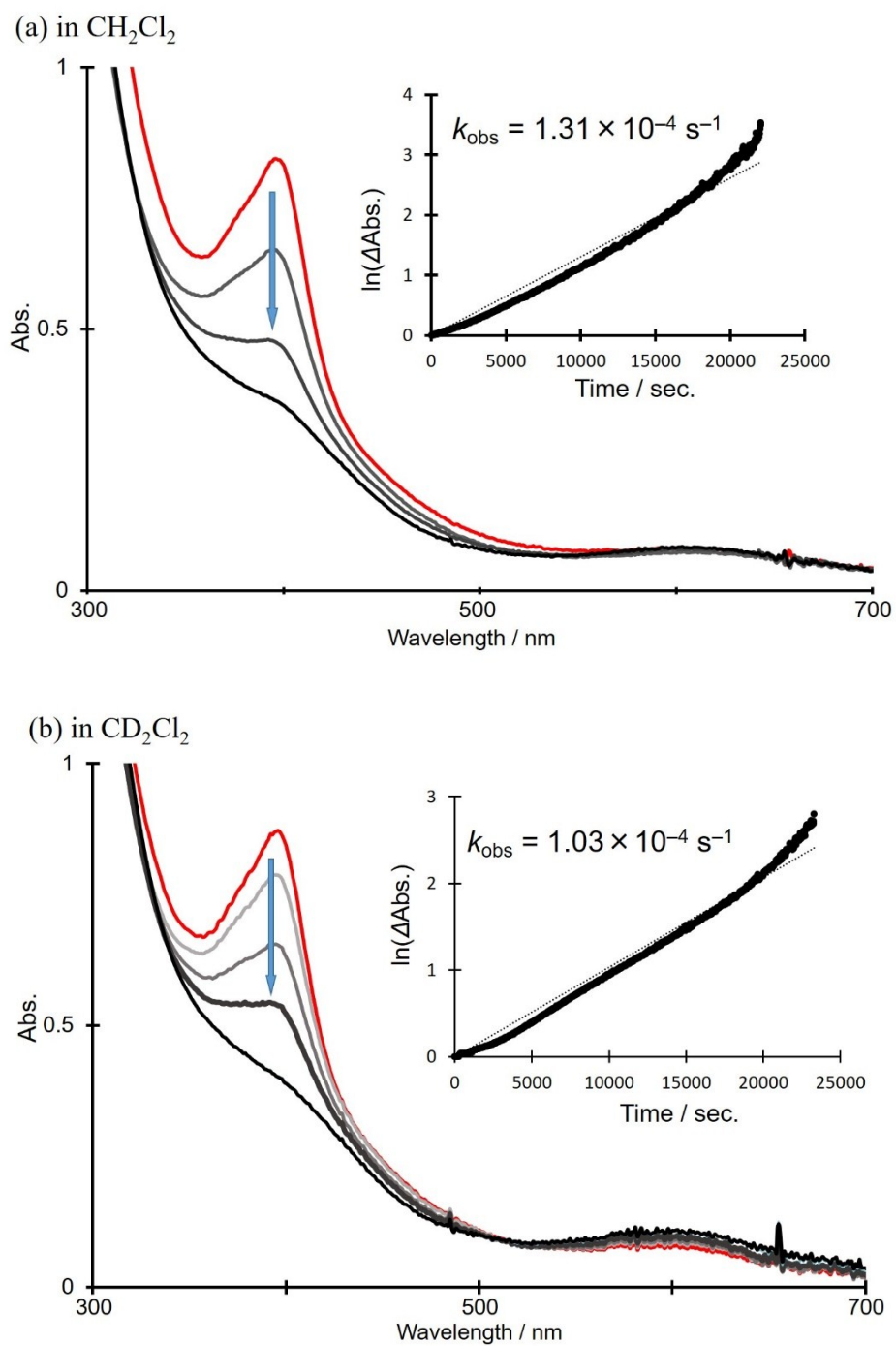


Fig. S10 Decay of the acylperoxido species in CH_2Cl_2 (a) or CD_2Cl_2 (b) at 25°C .