Electronic Supplementary Information

for

Electrochemistry and Catalytic Properties of Amphiphilic Vitamin B_{12} Derivatives in Nonaqueous Media

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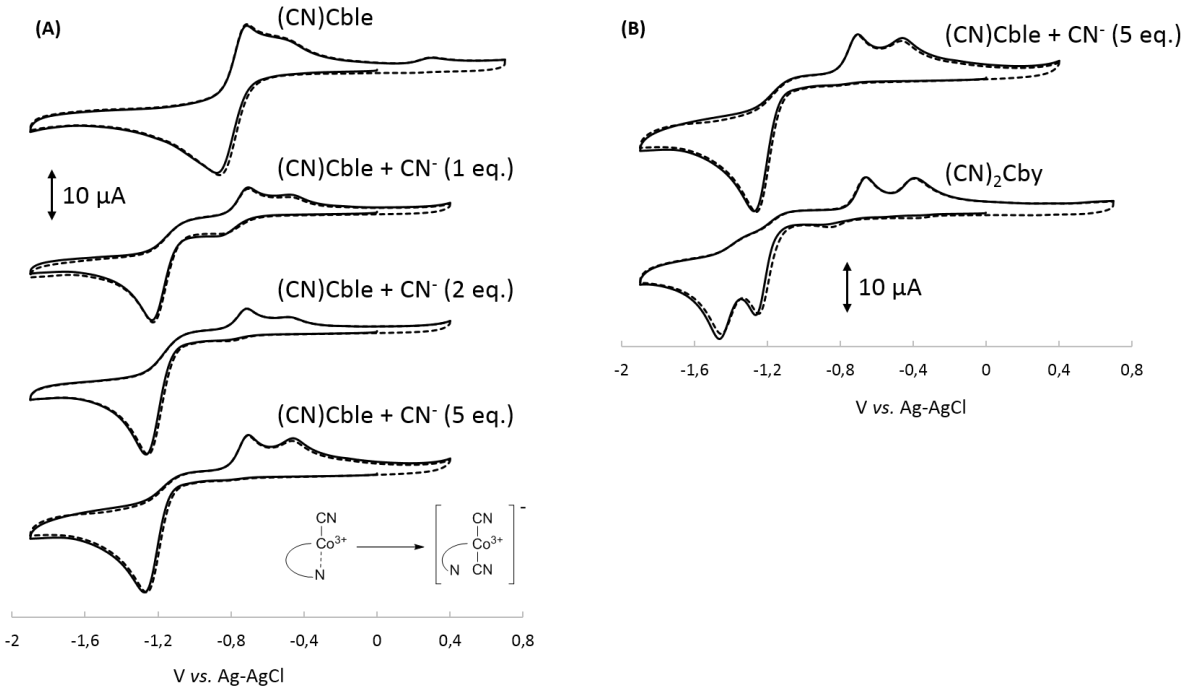
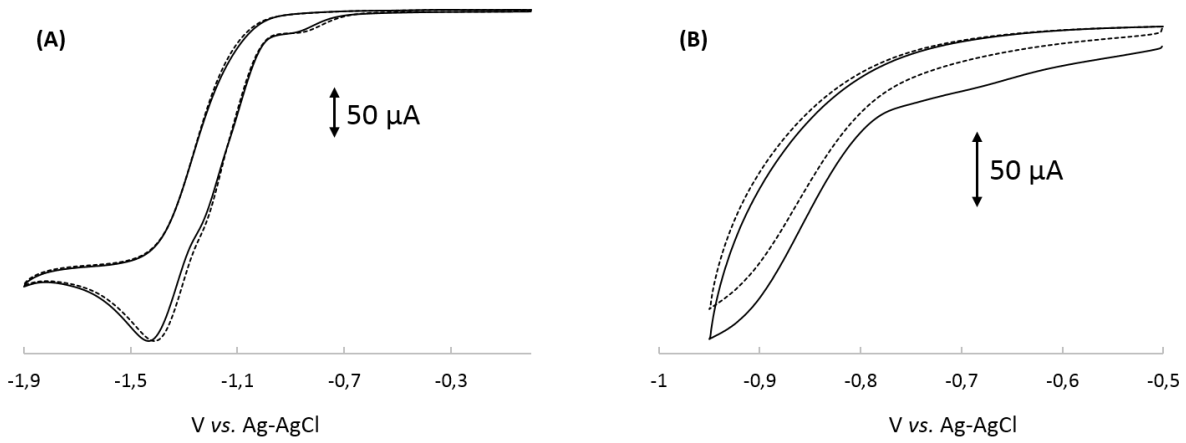
Cyclic voltammetry of (CN)Cble (2) upon addition of cyanide



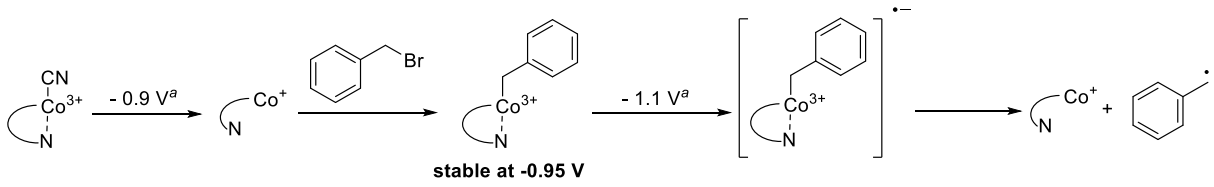
Cyclic voltamperometry spectra of (CN)Cble (**2**) upon addition of external cyanide ($Bu_4N^+CN^-$) (A) and comparison between $[(CN)_2Cble]^-$ and $(CN)_2Cby$ (B).

Conditions: 1.0 mM MeCN solutions of: cyanocobalester (**2**) and $(CN)_2Cby$ (**4**); All solutions contained 0.1 M $Bu_4N^+ClO_4^-$ and measurements were carried out at room temperature under a nitrogen atmosphere using GC working electrode and Pt counter electrode; sweep rate: 0.1 V/s.

Cyclic v voltammetry of (CN)Cble (2) upon addition of benzyl bromide



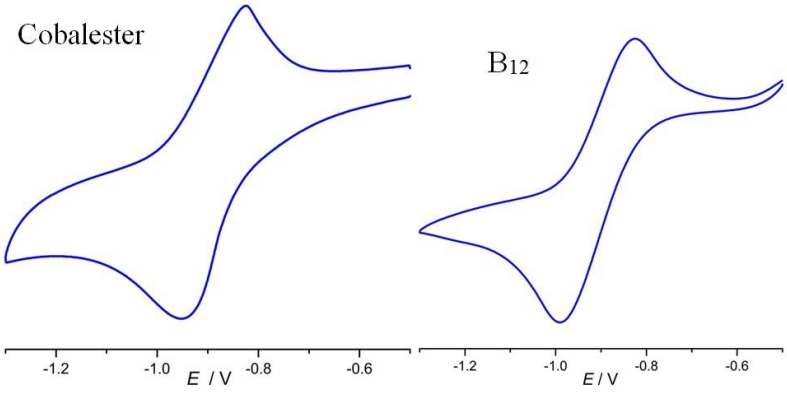
Cyclic voltamperometry spectra of (CN)Cble (**2**) upon addition of benzyl bromide (10 eq.) When the scan was reversed at -0.95 V *vs.* Ag-AgCl (B), no reversible wave was observed. This implies that once Co(I) species is generated, it rapidly reacts with the electrophile forming cobalt-carbon bond:



Cyclic voltammetry measurements of (CN)Cble (2) and cyanocobalamin (1) in aqueous solution[1]

Results presented belowe were published in supplementary information of reference 1:

Cyclic voltammograms of vitamin B_{12} (**1**) and cobalester (**2**) were recorded in deoxygenated 0.2 M solutions of tris buffer in deionized water (C_{B12} = 1.7 mM, $C_{cobalester}$ = 0.7 mM). A three-electrode setup was used in both experiments, including glassy carbon working electrode, Ag/AgCl reference electrode and auxiliary platinum foil (scan rate v = 10 mVs^{-1}, Ar, 20 °C).



Cyclic voltammogram of cobalester (**2**) and cobalamin (**1**).

[1] M. Giedyk S. N. Fedosov and D. Gryko, *Chem. Commun.*, 2014, **50**, 4674.

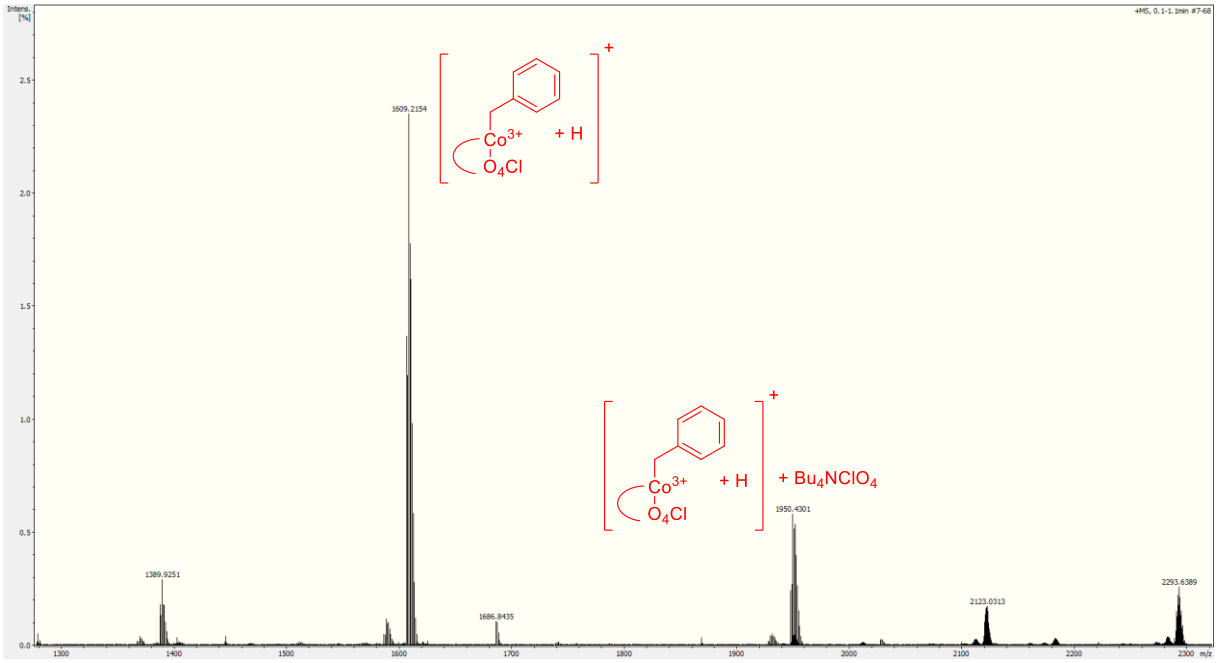
Comparison of redox potentials

for (CN)Cble (2), cobyrinate 3 and 4 and cyanocobalamin (1)

	E [V *vs.* Ag-AgCl]							
	3 in MeCN	**4** in MeCN	**10** in MeCN	**12** in MeCN	**2** in MeCN	**2** in THF	**2** in H_2O	**1** in H_2O
$(CN)Co^{3+}/(CN)Co^{2+}$	-0.4	-	-	-0.9	-0.9	-0.9	-1.0	-1.0
$(solvent)Co^{2+}/Co^{+}$	-0.6	-	-0.6	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*n.d.*
$(CN)Co^{2+}/Co^{+}$	-1.4	-1.4	-	-1.4	-	-1.4	-	-
$[(CN)_2Co^{3+}]/(CN)Co^{2+}$	-1.2	-1.2	-	-	- / -1.2[a]	-	*n.d.*	*n.d.*
$Co^{+}/(solvent)Co^{2+}$	-0.6	-0.7	-0.6	-0.6	-0.7	-0.5	-0.8	-0.8
$(CN)Co^{2+}/(CN)Co^{3+}$	-0.3	-0.4	-	-0.3	-0.5	-0.3	*n.d.*	*n.d.*
$(solvent)Co^{2+}/(solvent)Co^{3+}$	0.6	-	0.6	0.4	0.3	0.5	*n.d.*	*n.d.*

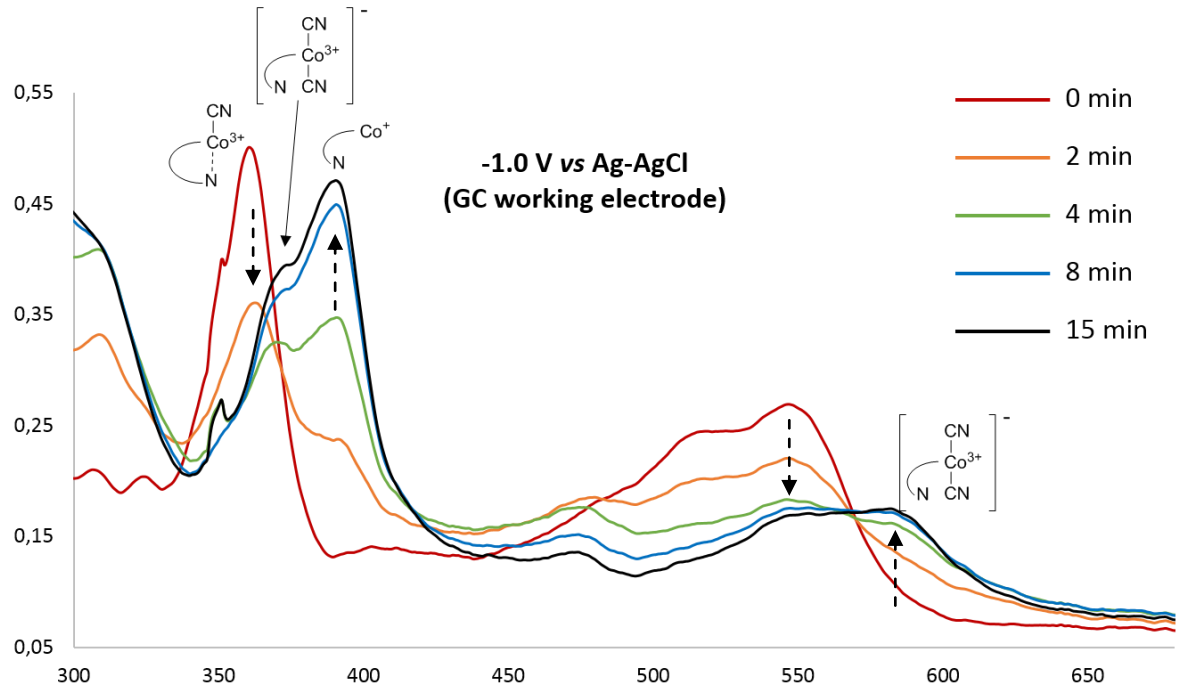
[a] a reduction at this potential was observed when 5 eq. of cyanide was added

ESI MS analysis of benzyl bromide dimerization reaction mixture

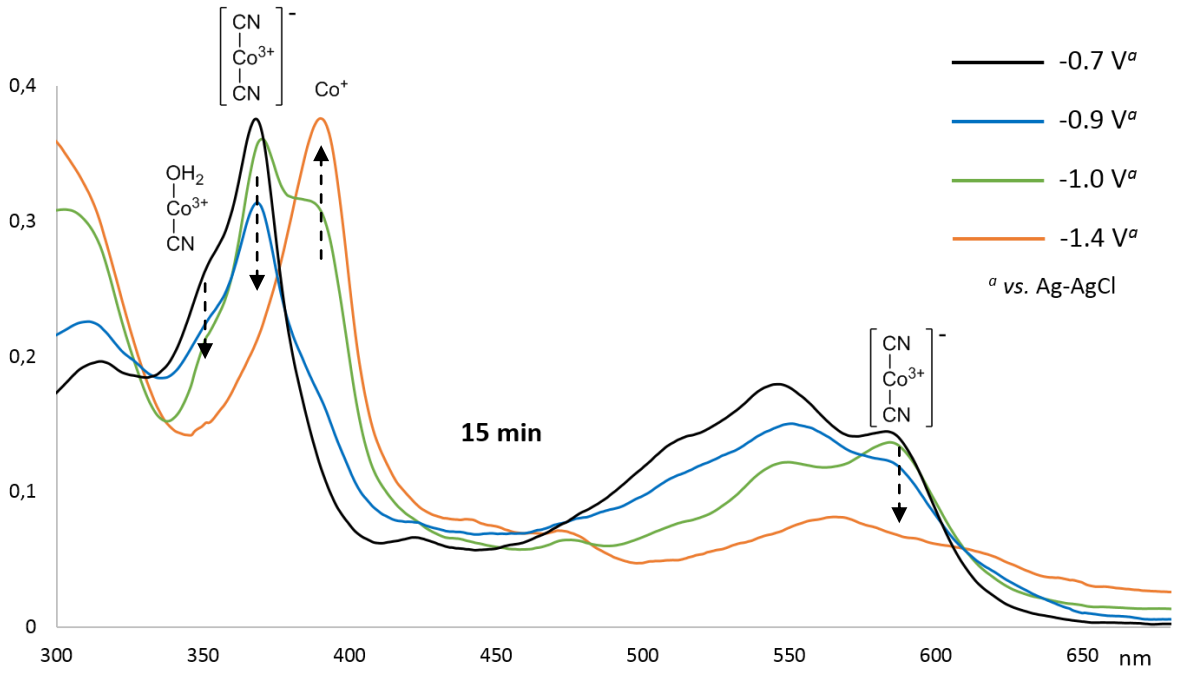


Reaction mixture was analyzed (after 15 min) using ESI MS in the dark. It indicated facile formation of cobalt-benzyl intermediate with m/z = 1609.2.

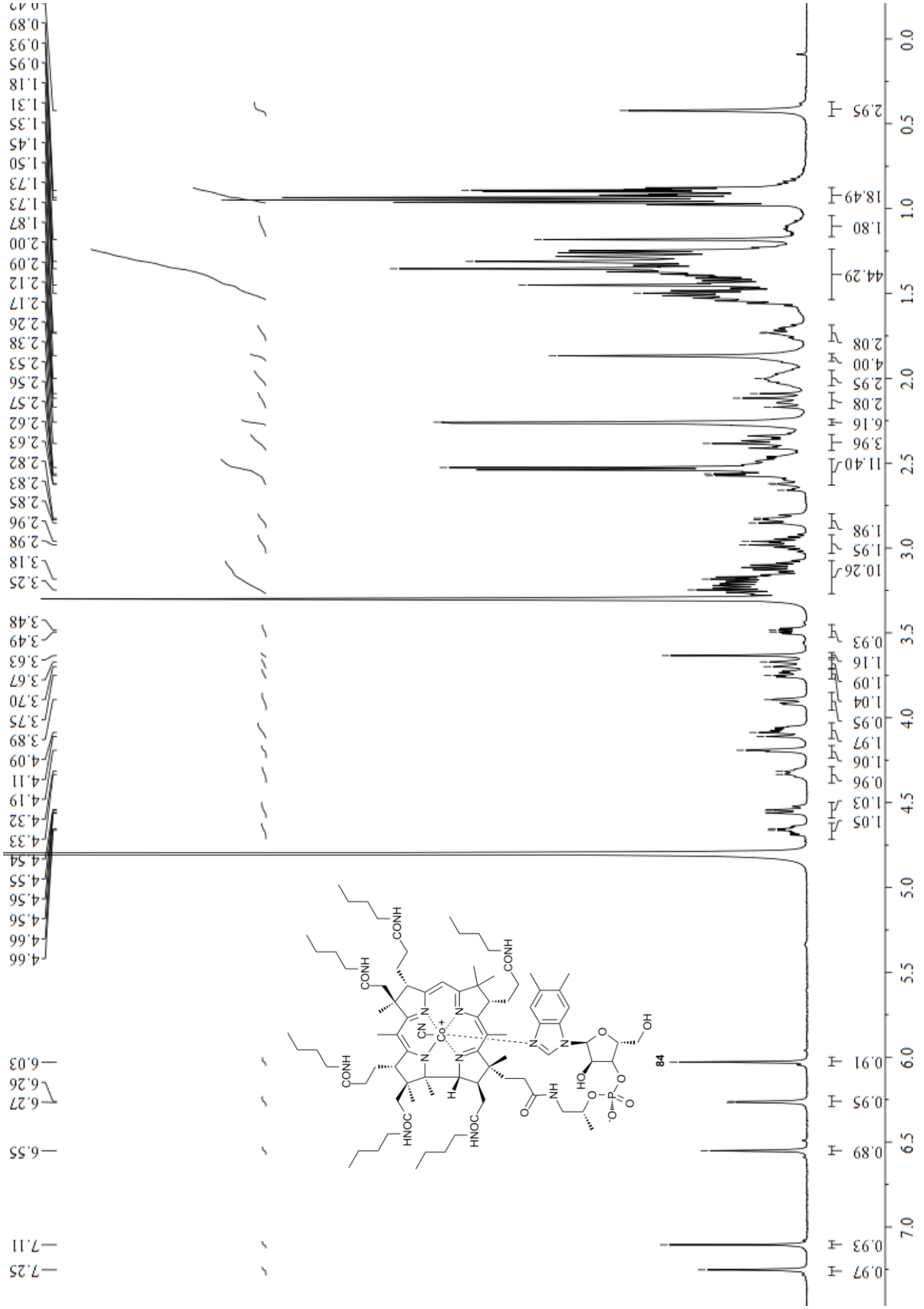
UV-Vis controlled electrolysis of (CN)Cble (2) in MeCN



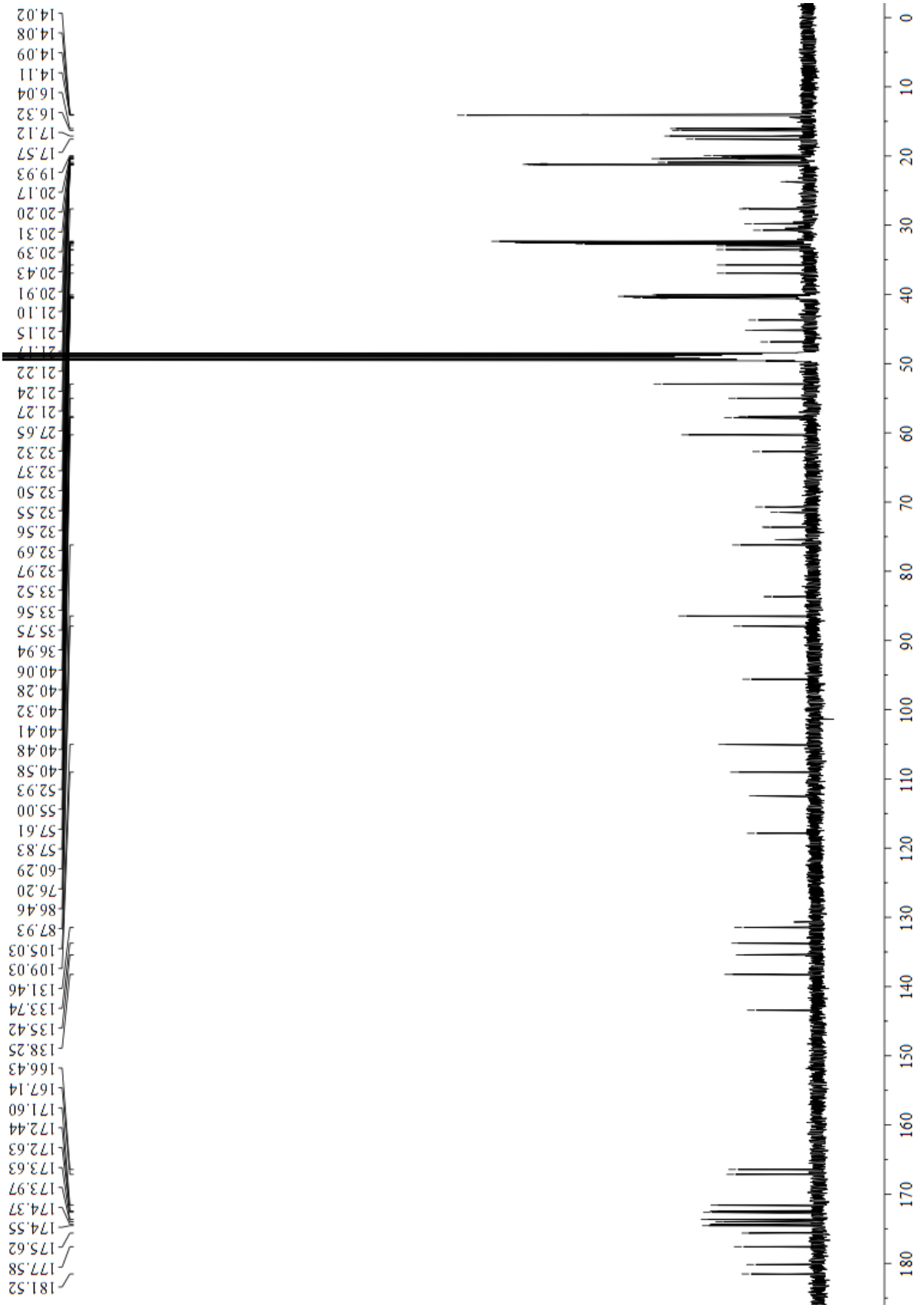
UV-Vis controlled electrolysis of monocyano cobyrinate 3 in MeCN



^{1}H NMR spectra of hexa(*n*-butyl)cobalamin (12) in CD_3OD



^{13}C NMR spectra of hexa(*n*-butyl)cobalamin (12) in CD_3OD



^{1}H NMR spectra of hexa(*n*-butyl)cobalamin (12) in d_6-DMSO