Electronic Supporting Information for:

Hydroquinone/quinone electro- and photochemical interconversion in isolable polypyridylruthenium(II) complexes

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Table S1. Crystallographic data for **HQ_AN** and **Q_AN**.

	HQ_AN	**Q_AN**
Chemical formula	$C_{33.25}H_{28}F_{12}N_6O_3P_2Ru$	$C_{35}H_{27}F_{12}N_7O_2P_2Ru$
Formula weight	950.62	968.64
Temperature (K)	293	93
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*-1
a (Å)	12.4452(2)	8.9275(11)
b (Å)	12.9054(2)	9.3122(12)
c (Å)	49.4032(7)	22.021(3)
α (°)	90	86.863(2)
β (°)	92.6880(10)	87.394(3)
γ (°)	90	87.946(2)
V (Å^3)	7925.9(2)	1825.0(4)
Z	8	2
Calcd density (g/cm^3)	1.593	1.763
μ (Mo $K\alpha$) (mm^{-1})	0.575	0.625
No. unique reflns	11354	8276
No. obsd reflns	9368	6652
Refinement method	*Full-matrix least-squares on* F^2	
Parameters	640	534
R [$I > 2\sigma(I)$] [1]	0.0876	0.0902
wR (all data) [2]	0.2020	0.2449
S	1.276	1.110

[1] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [2] $wR = \{\Sigma_w(F_o^2 - F_c^2)^2/\Sigma_w(F_o^2)^2\}^{1/2}$.

Table S2. Hydrogen-bond geometry (Å, °) for **HQ_AN**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
O1–H1···O2^{i}	0.82	1.96	2.765(8)	169
O2–H2···O5	0.82	1.94	2.730(15)	161
O2–H2···O5^{ii}	0.82	1.96	2.779(15)	179
O5–H5A···O2^{ii}	0.85	2.23	2.779(15)	123
C2–H2A···F1A^{iii}	0.93	2.46	3.258(17)	144
C2–H2A···F3^{iii}	0.93	2.54	3.218(17)	130
C5–H5···F10A	0.93	2.38	3.19(2)	146
C12–H12···O1	0.93	2.46	2.819(7)	103
C24–H24···F3A^{iv}	0.93	2.54	3.38(2)	151
C29–H29···F10^{i}	0.93	2.44	3.20(3)	139
C33–H33C···F7^{v}	0.96	2.54	3.44(2)	157

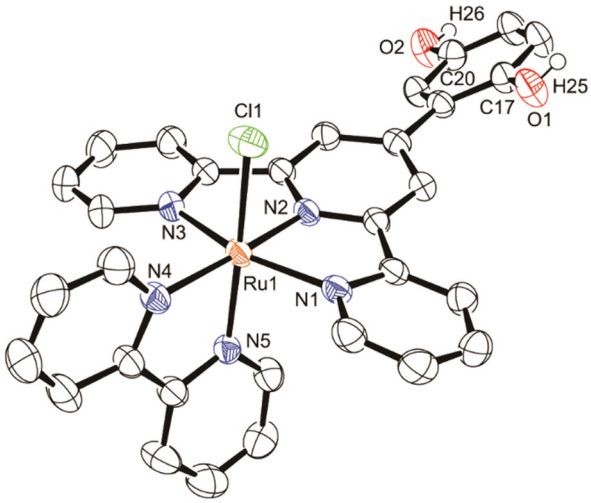
Symmetry codes: (i) 3/2–*x*, 1/2+*y*, 3/2–*z*. (ii) 1–*x*, *y*, 3/2–*z*. (iii) 1/2+*x*, –1/2+*y*, *z*. (iv) –*x*, 1–*y*, 1–*z*. (v) –1/2+*x*, 1/2+*y*, *z*.

Table S3. Hydrogen-bond geometry (Å, °) for **Q_AN**.

D–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
C1–H4···F4^{i}	0.95	2.53	3.181(16)	126
C2–H5···F2^{i}	0.95	2.43	3.310(13)	154
C3–H6···O1^{ii}	0.95	2.43	3.379(9)	175
C9–H9···O2	0.95	2.34	2.828(8)	112
C12–H10···F8^{iii}	0.95	2.46	3.400(13)	169
C17–H14···N7^{ii}	0.95	2.46	3.391(12)	168
C20–H16···F10^{iv}	0.95	2.40	3.110(11)	132
C31–H17···F2^{v}	0.95	2.52	3.181(16)	127
C31–H17···N6	0.95	2.60	3.154(13)	118
C25–H21···F3^{vi}	0.95	2.44	3.34(2)	156
C35–H25···F10	0.98	2.46	3.352(15)	151
C35–H26···F9^{vii}	0.98	2.31	3.271(17)	167

Symmetry codes: (i) *x*, –1+*y*, *z*. (ii) 1–*x*, 1–*y*, 1–*z*. (iii) –1+*x*, –1+*y*, *z*. (iv) –*x*, 2–*y*, 1–*z*. (v) –1+*x*, *y*, *z*. (vi) 1–*x*, 2–*y*, –*z*. (vii) 1–*x*, 2–*y*, 1–*z*.

(**a**)



(**b**)

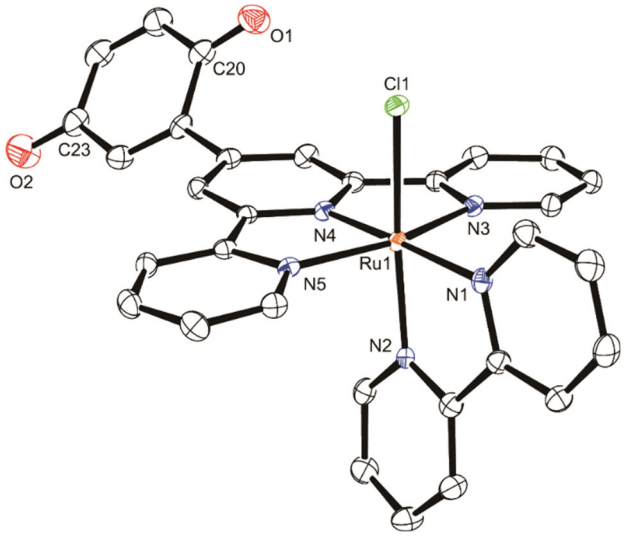


Figure S1. ORTEP views of (**a**) **HQ_Cl** and (**b**) **Q_Cl**. Ellipsoids are shown at the 50% probability level. Counteranions, solvent molecules and hydrogen atoms, with the exception of the OH hydrogens, are removed for clarity (D. Oyama, M. Kido, R. Abe and T. Takase, *ChemistrySelect*, 2017, **2**, 2583–2587.)

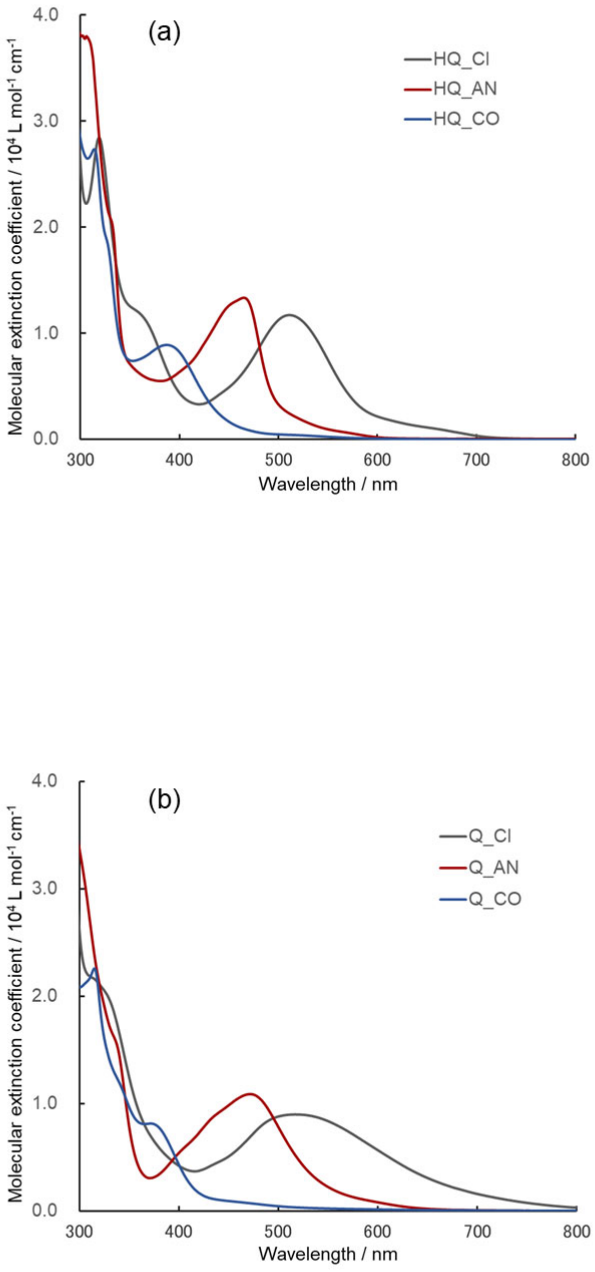


Figure S2. Electronic absorption spectra of (a) **HQ**-complexes and (b) **Q**-complexes in acetonitrile ($c = 1.0\times10^{-4}$ M).

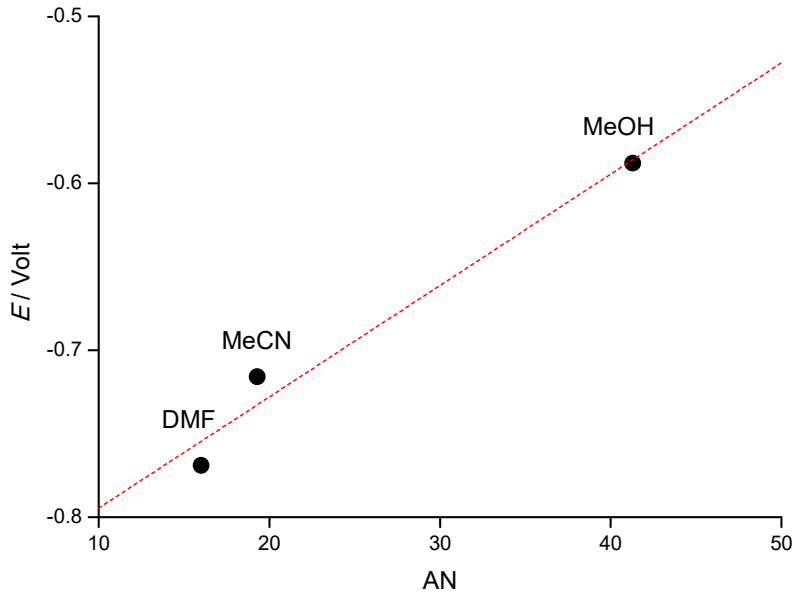
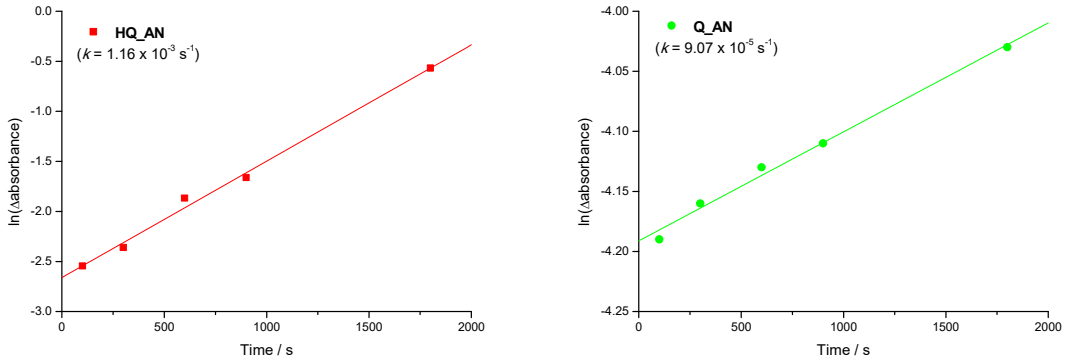


Figure S3. Correlations of the reduction potentials (E_{pc1}) of **Q_Cl** with solvent acceptor numbers (AN).

(a)



(b)

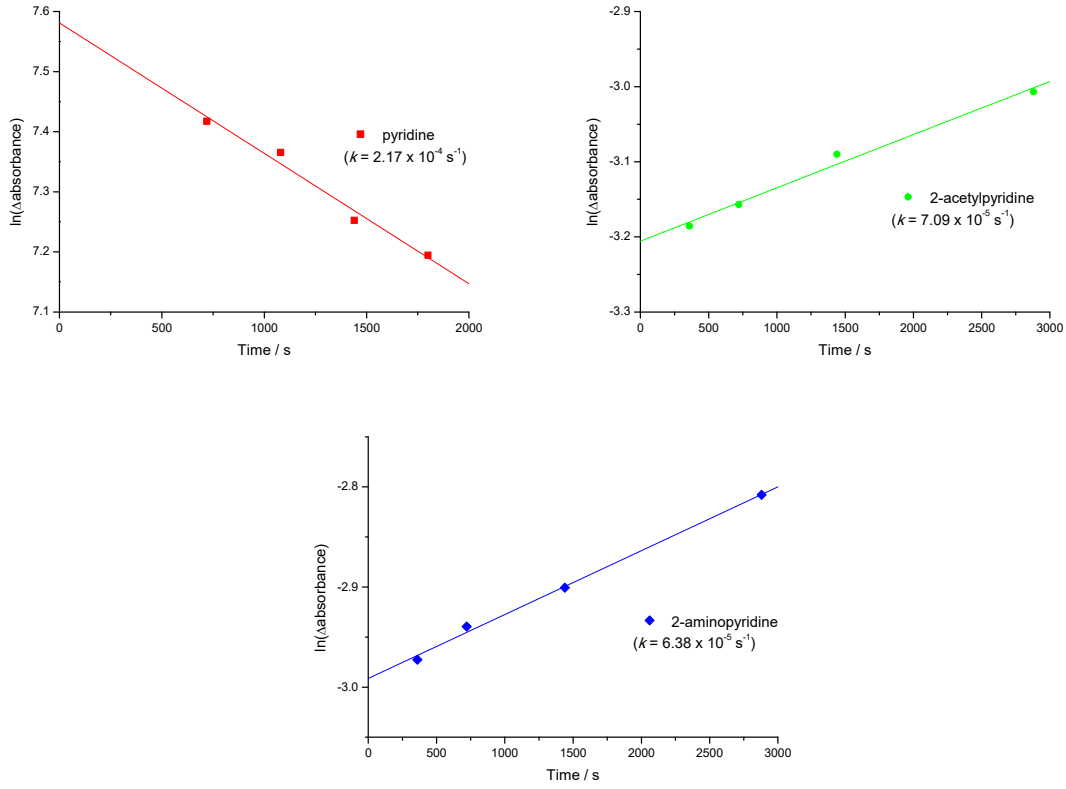


Figure S4. First-order plots of the photoinduced substitution reactions of (a) **HQ_AN** or **Q_AN** (c = 1.0 × 10^{-4} M) with acetone, (b) **HQ_AN** (c = 1.0 × 10^{-4} M) with pyridine derivatives in CH_3CN at 298 K.

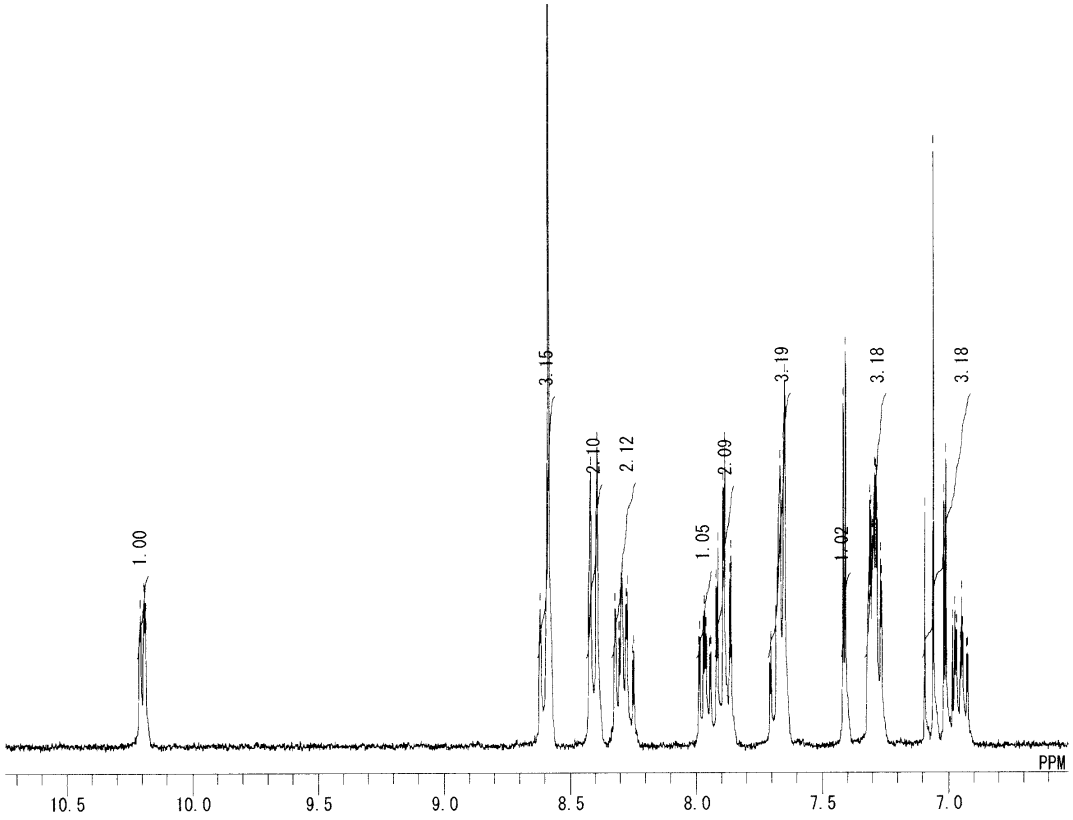


Figure S5. ^{1}H NMR spectrum of **Q_Cl** in CD_3CN.

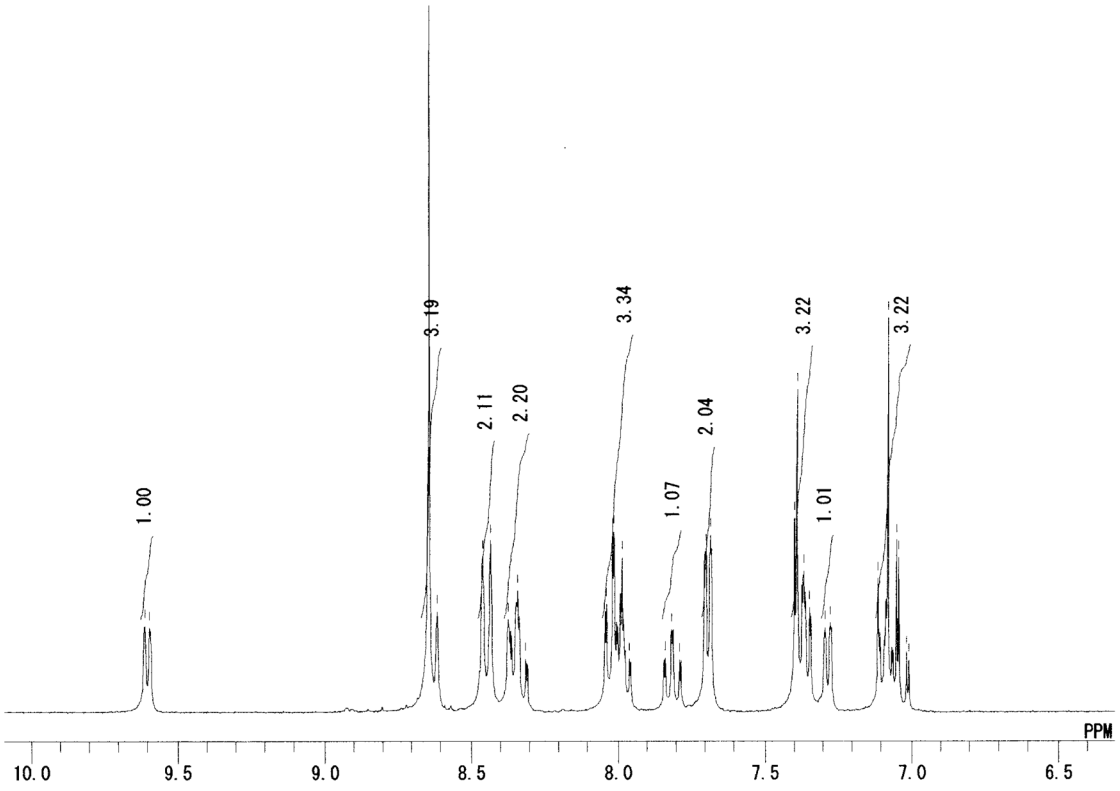


Figure S6. ^{1}H NMR spectrum of **Q_AN** in CD_3CN.

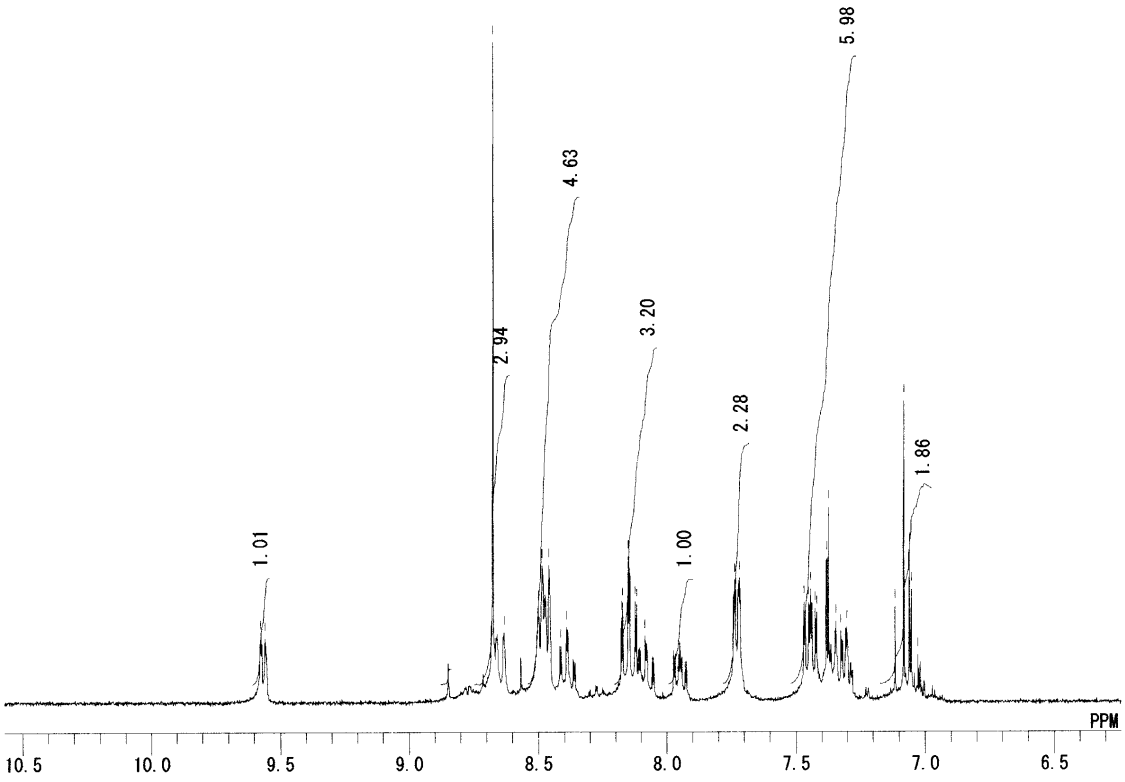


Figure S7. ^{1}H NMR spectrum of **Q_CO** in CD_3CN.

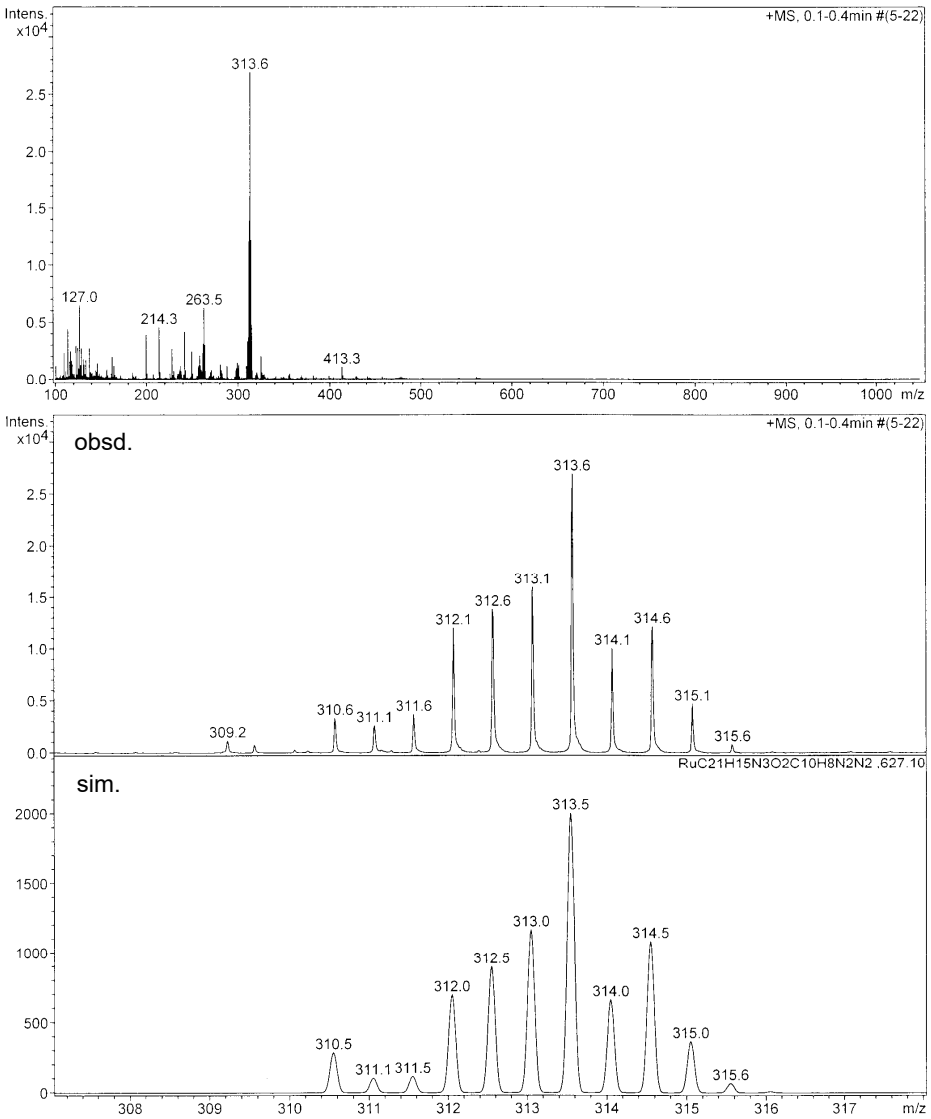


Figure S8. ESI mass spectrum of **HQ_AN** (positive mode, CH_3CN).

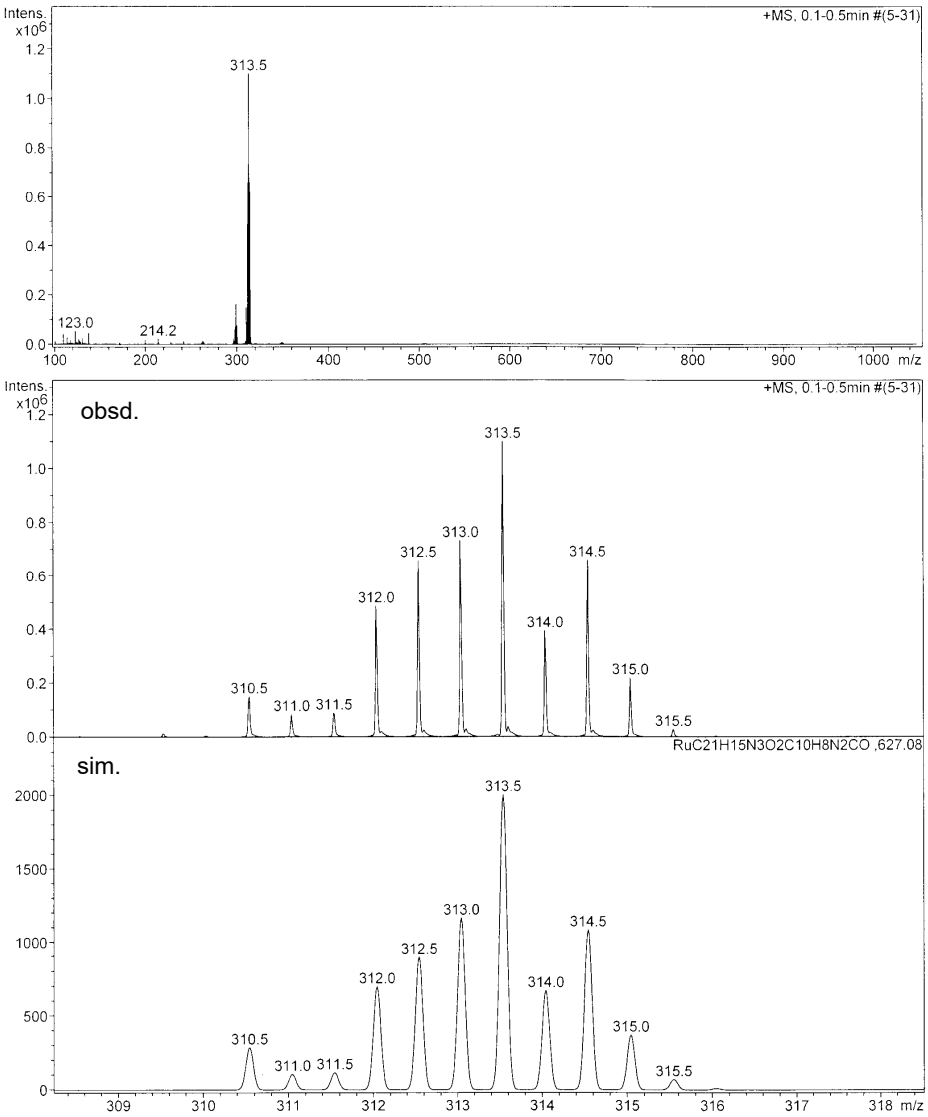


Figure S9. ESI mass spectrum of **HQ_CO** (positive mode, CH_3CN).

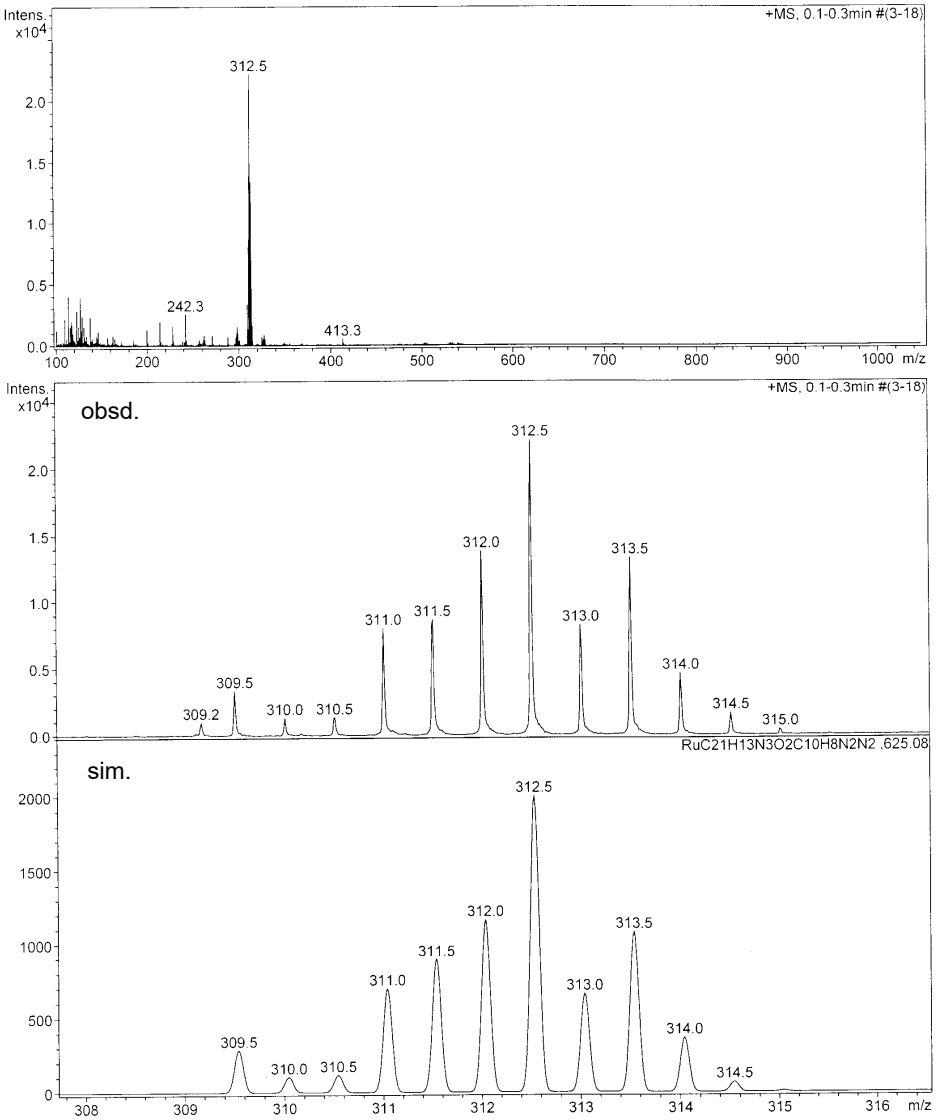


Figure S10. ESI mass spectrum of **Q_AN** (positive mode, CH_3CN).

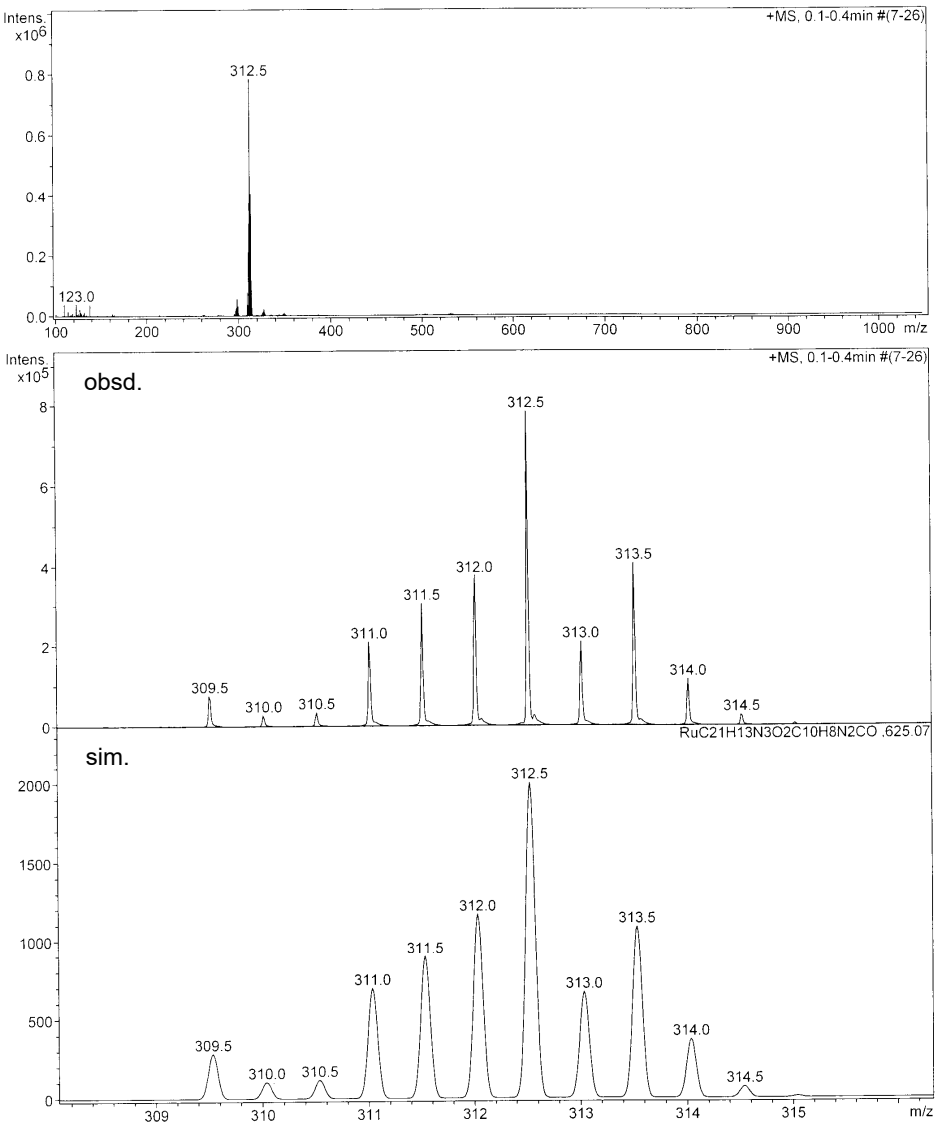


Figure S11. ESI mass spectrum of **Q_CO** (positive mode, CH_3CN).