Supplementary Information

Rapid Atmospheric Carbon Dioxide Fixation by Nickel(II) Complexes: Meridionally Coordinated Diazepane-based 3N Ligands Facilitate Fixation

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Computed Structures of 1 and 2. We have performed computational analysis by using Density Functional Theory (DFT). And the optimized geometry of complexes **1** and **2** are shown in **Fig S1**. The computed structural parameters of the complexes are provided in Table S2.
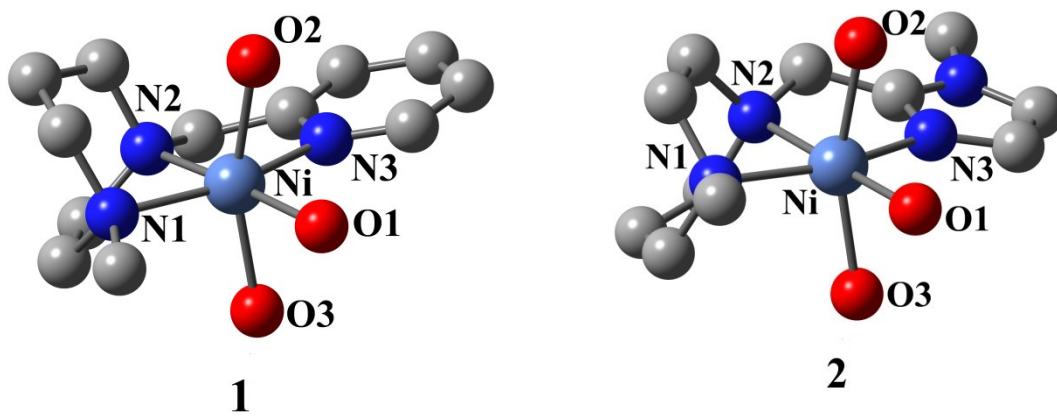

Fig. S1. The computed structures of cations of a) $[Ni(L1)(H_2O)_2](ClO_4)_2$ **1** and $[Ni(L2)(H_2O)_2](ClO_4)_2 \cdot 2H_2O$ **2**

Fig. S2. The packing diagram of $[Ni_2(L1)_2(\mu\text{-}CO_3)(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ **3**

Table S1. Structure refinement details for $[Ni_2(L1)_2(\mu\text{-}CO_3)(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ **3**

	3
Sum formula	$C_{25} H_{42} Cl_2 N_6 Ni_2 O_{17}$
Formula weight	886.96
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
a(Å)	22.909(10)
b(Å)	14.148(6)
c(Å)	12.037(5)
$\alpha(^o)$	90
$\beta(^o)$	101.433(6)
$\gamma(^o)$	90
Volume ($Å^3$)	3824(3)
Z	4
D_c (g.cm^{-3})	1.541
Reflections collected	25799
Goodness-of-fit on F^2	1.022
Final R indices [I>2σ (I)]	0.0629, $wR_2 = 0.1710$
R indices (all data)	0.1049, $wR_2 = 0.2037$

Determination of magnetic moment of complex 1 and the intermediate derived from it

Evans' method was used of ^{1}H-NMR performed to determine the magnetic moment of complex **1** and the intermediate **1a** derived from it.[S1-S2] A coaxial insert (with a sealed capillary) tube containing CD_3OD solvent (with 0.03% TMS) was inserted into the normal NMR tube containing the complex **1** (0.0053 M, with 0.03% TMS). We have calculated the chemical shift value of the TMS peak in the presence of the complex **1** in the outer NMR tube with respect to that of the TMS peak in the coaxial insert. The magnetic moment was calculated using the equation,

$$\mu_{eff} = 0.0618 \, (\Delta v T / 2fM)^{1/2}$$
$$\mu_{eff} = 0.0618 \times (32 \times 298 / 2 \times 400 \times 0.0053)^{1/2}$$
$$\mu_{eff} = 2.93 \text{ BM}$$

Where f = oscillator frequency (400 MHz) of the superconducting spectrometer, T = absolute temperature, M = molar concentration of the complex **1**, and v = difference in frequency (Hz) between the two TMS signals (**Fig. S3**). The magnetic moment of complex **1** was calculated as 2.91 BM in CD_3OD at RT, suggesting the presence of 2 unpaired electrons in complex **1**. When Et_3N (0.0053 M, 50 μL) was added to this solution to generate a red coloured solution no shift was observed illustrating the formation of an intermediate species (low-spin) with no unpaired electron.
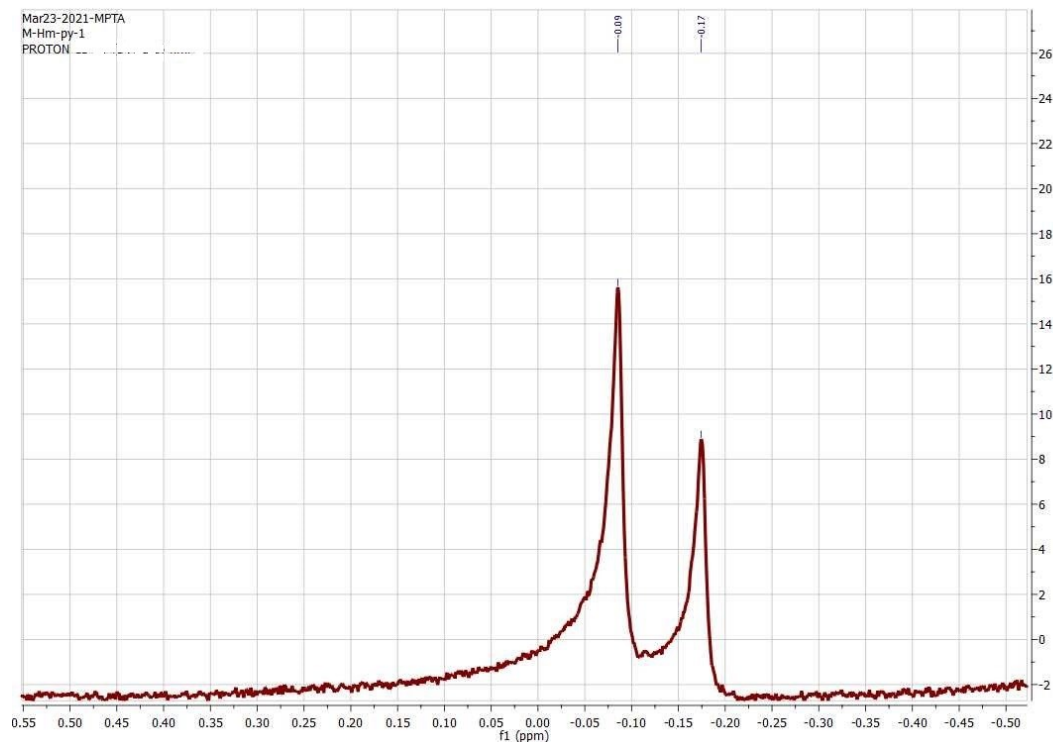

Fig. S3. Evan's method: ^{1}H NMR of spectra $[Ni(L1)(H_2O)_2](ClO_4)_2$ **1**

Table S2. Computed bond angles [°] of complexes **1**, **2** and the intermediates **1a** and **2a**

	1	2	1a	2a
N1–Ni–N2	77.9233	77.6300	83.15489	83.0770
N1–Ni–N3	160.9597	160.4098	168.9002	168.2117
N1–Ni–O1	102.1390	100.0281	100.2062	100.5885
N1–Ni–O2	96.9739	98.6302	-	-
N1–Ni–O3	95.5328	94.97454	-	-
N2–Ni–N3	83.1128	82.78310	86.2089	85.2117
N2–Ni–O1	176.4011	176.7345	176.4794	176.2916
N2–Ni–O2	100.9030	100.96143	-	-
N2–Ni–O3	94.2153	93.7329	-	-
N3–Ni–O1	96.8947	99.5575	90.3757	91.1363
N3–Ni–O2	84.8690	84.6499	-	-
N3–Ni–O3	87.4837	86.5886	-	-
O1–Ni–O2	82.6746	84.1666	-	-
O1–Ni–O3	82.1922	81.5814	-	-
O2–Ni–O3	162.0853	161.7781		-

Fig. S4. Electronic absorption spectra of $[Ni(L1)(H_2O)_3](ClO_4)_2$ **1** and $[Ni(L2)(H_2O)_3](ClO_4)_2 \cdot 2H_2O$ **2** in methanol solution at 25 °C. Conc: **1**, 4.5×10^{-3}; **2**, 3.3×10^{-3} M)
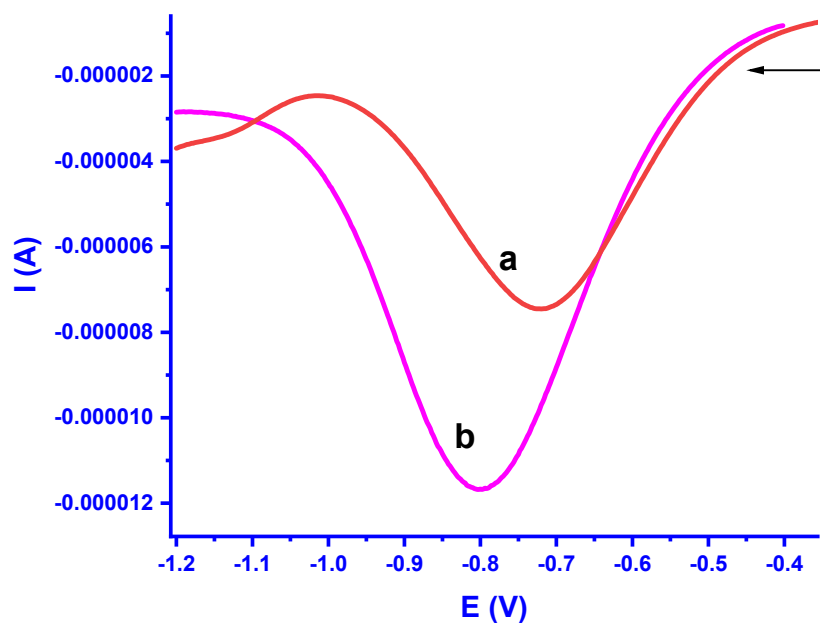

Fig. S5. Differential Pulse Voltammetry (DPV) of complexes **1** (1.9×10^{-3} M) and **3** (1.8×10^{-3} M) in methanol solution at 25 °C. Conditions: supporting electrolyte, 0.1 M TBAP; Scan rate, 50 mVs^{-1}; reference electrode, Calomel; working electrode, Glassy carbon; Counter electrode, platinum plate
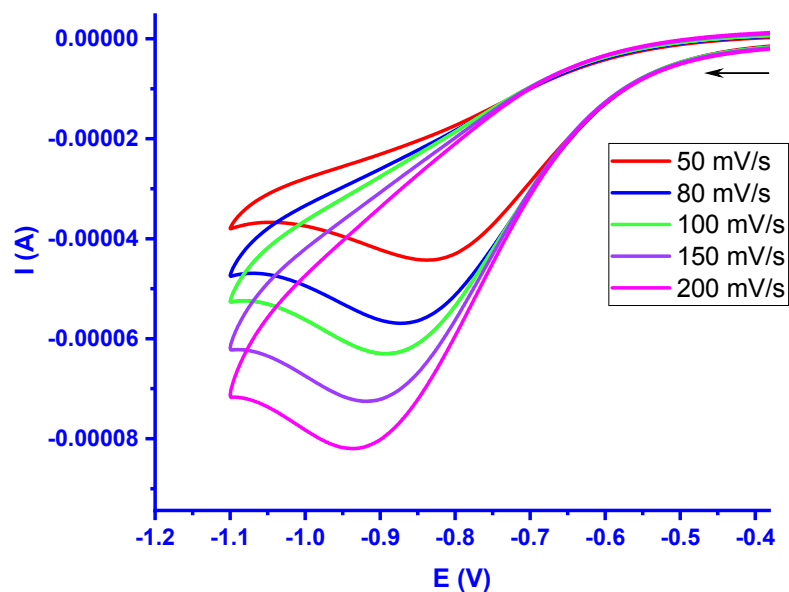
Fig. S6. Cyclic voltammogram (a) and DPV (b) of complex **2** (5.2×10^{-3}) in methanol solution at 25 °C. Conditions: supporting electrolyte, 0.1 M TBAP; Scan rate, 50 mVs^{-1}; reference electrode, Calomel; working electrode, Glassy carbon; Counter electrode, platinum plate.

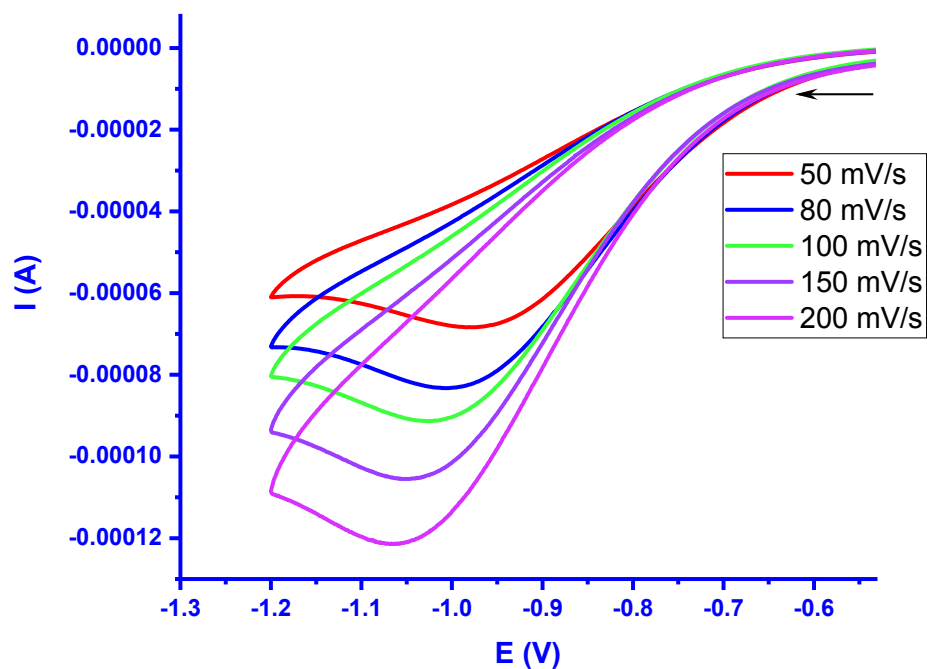**Fig. S7.** Cyclic voltammograms of complex **1** (1.9×10^{-3} M) in methanol solution at 25 °C at different scan rates.

Fig. S8. Cyclic voltammograms of complex **2** (5.2×10^{-3}) in methanol solution at 25 °C at different scan rates.
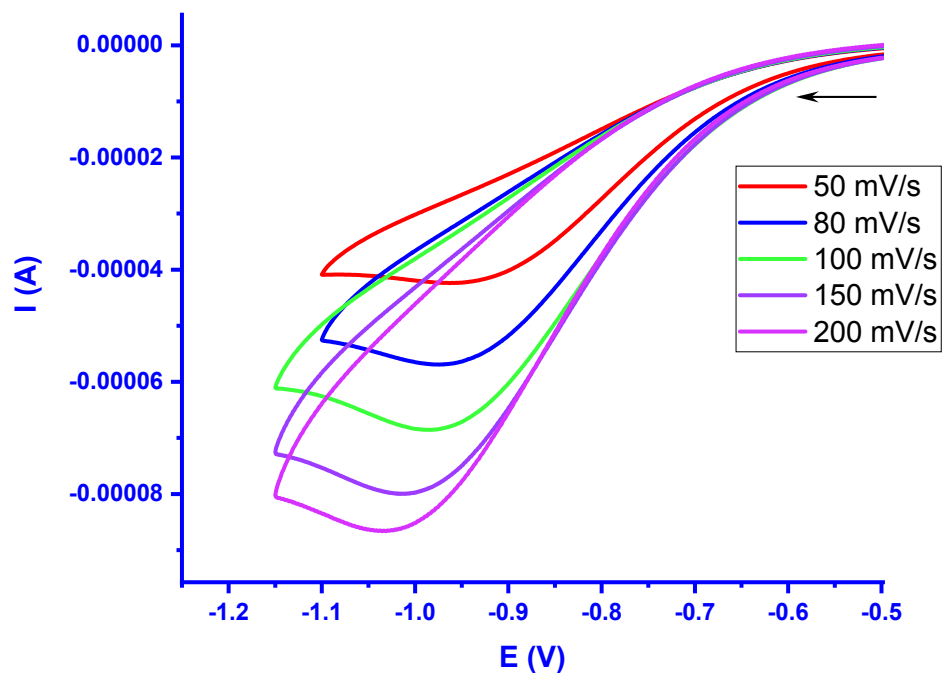
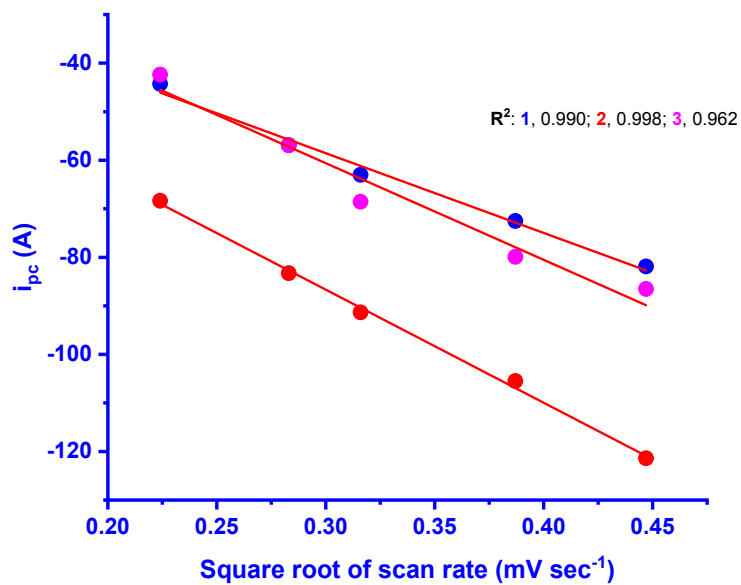**Fig. S9.** Cyclic voltammograms of complex **3** (1.8×10^{-3} M) in methanol solution at 25 °C at different scan rates.

Fig. S10. Plots of i_{pc} (A) vs square root of scan rate (mV sec^{-1})
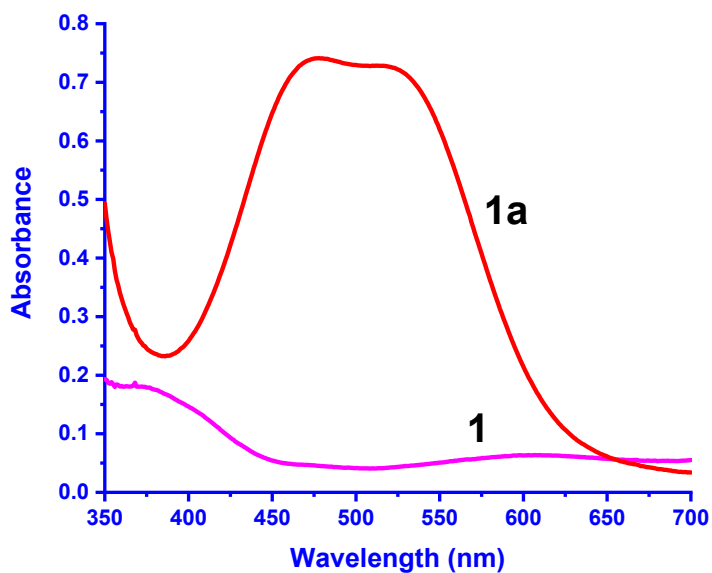
Fig. S11. Electronic absorption spectra of complexes **1** and the intermediate **1a** formed from **1** in methanol solution upon addition of Et$_3$N (2×10^{-4} M) to **1** (1×10^{-4} M) at 25 °C.

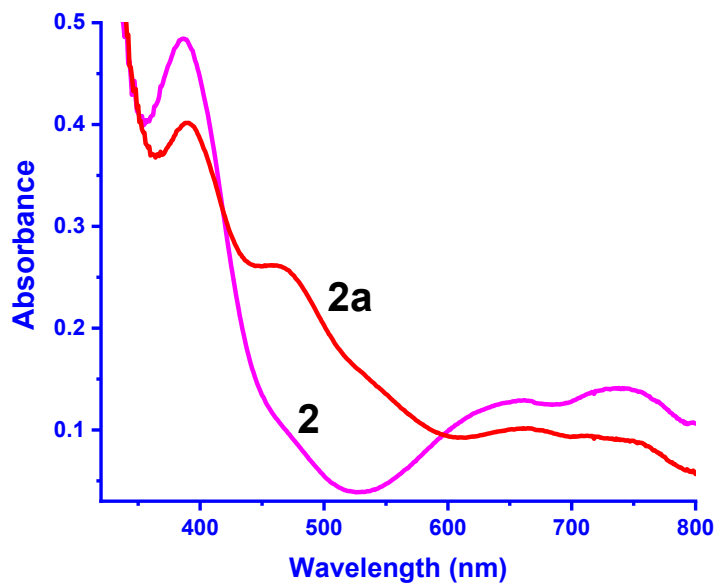**Fig. S12.** Electronic absorption spectra of **2** and the intermediate **2a** formed from **2** in methanol solution upon addition of Et$_3$N (2×10^{-4} M) to **2** (1×10^{-4} M) at 25 °C.
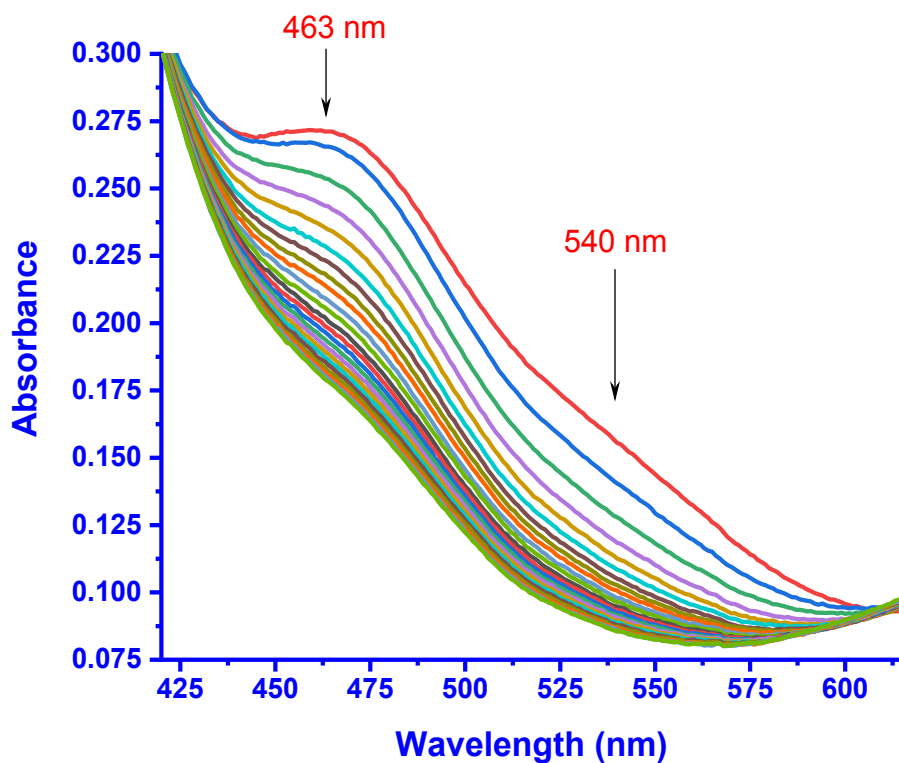
Fig. S13. Decrease in absorption of **2a**, generated in situ by adding Et_3N (4×10^{-4} M) to **2** (2×10^{-4} M), upon exposure to atmospheric CO_2, followed at 1 min interval at 25 °C.

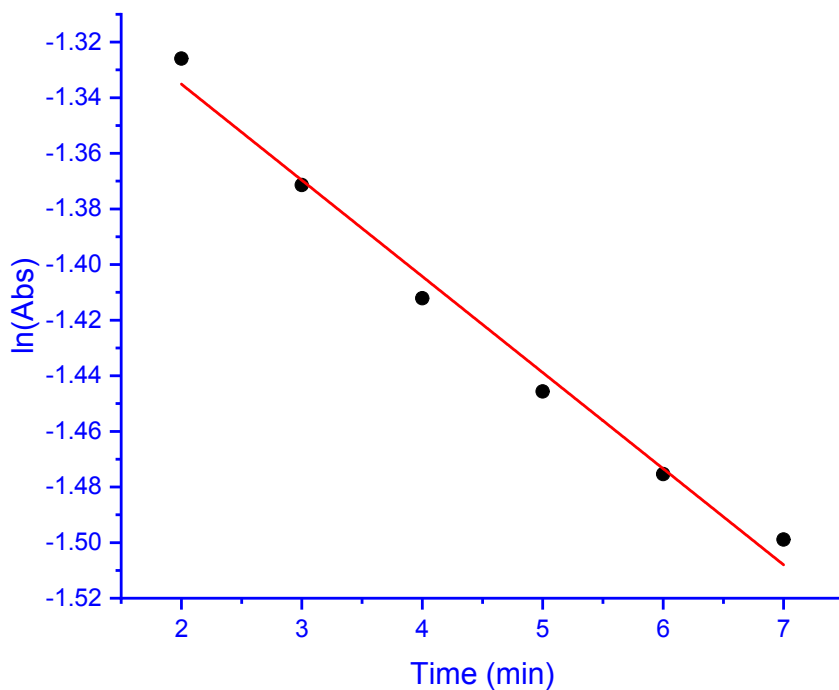**Fig. S14.** Plot of ln(Abs) vs time observed at 463 nm, k_{obs}, $5.8 \pm 0.3 \times 10^{-4}$ s^{-1}; $t_{1/2} = 0.33$ hrs.

Table S3. Computed structural parameters of the HOMO and LUMO energy values for the intermediate complex species **1a** and **2a**

	1a	**2a**
HOMO-2 (eV)	-7.2507	-6.9416
HOMO-1 (eV)	-6.6023	-6.5294
HOMO (eV)	-6.3604	-6.2700
LUMO (eV)	-1.8444	-1.6393
LUMO+1 (eV)	-1.6501	-0.4705
LUMO+2 (eV)	-1.2139	-0.1295

Table S4. Computed energy gap values for complexes **1a** and the intermediate **2a**

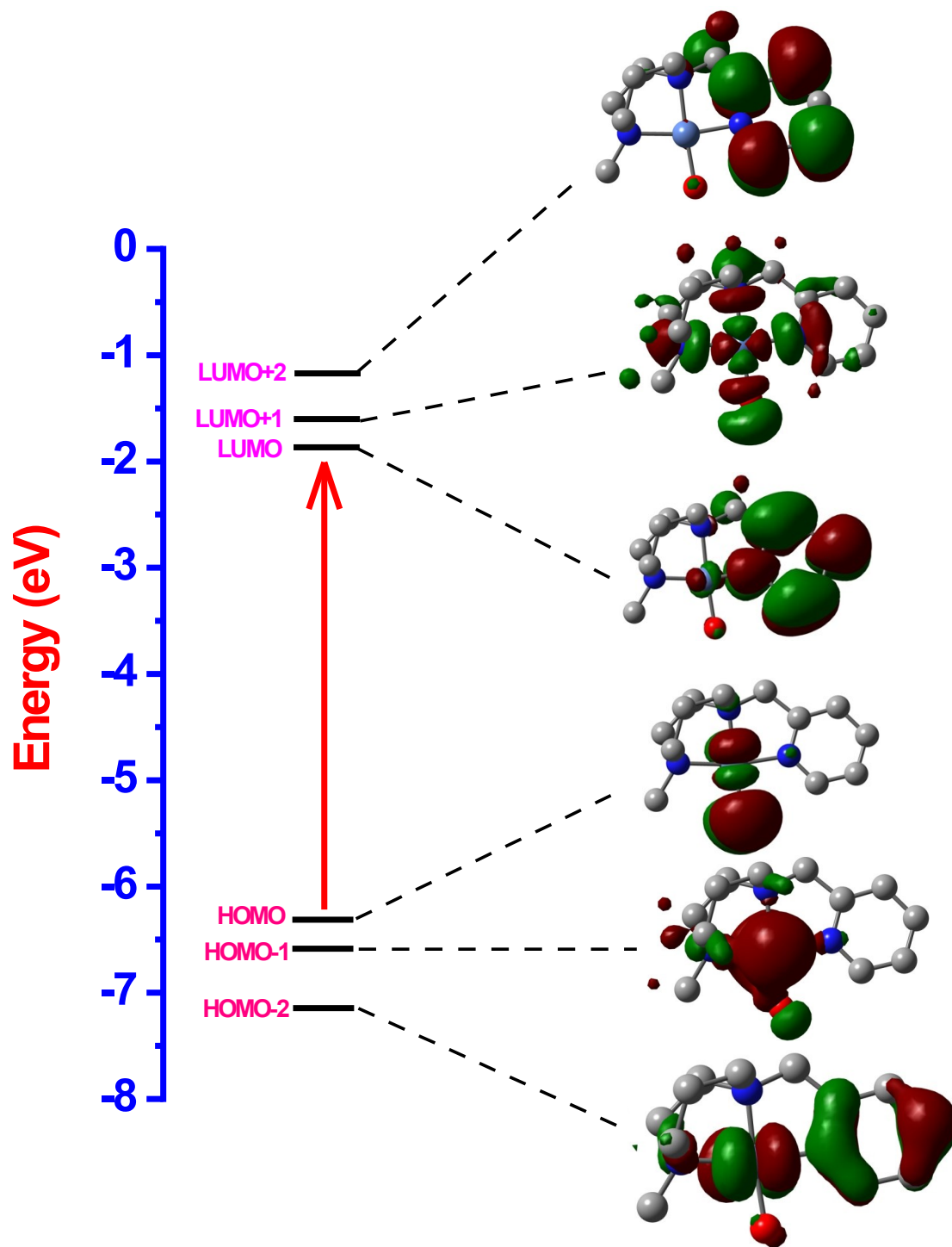| **Band gap (eV)**	**1a**	**2a**
HOMO – LUMO (eV)	4.5160	4.6307
LUMO – LUMO+1 (eV)	0.1943	1.1688

Fig. S15. Schematic MO diagram for the intermediate complex **1a**
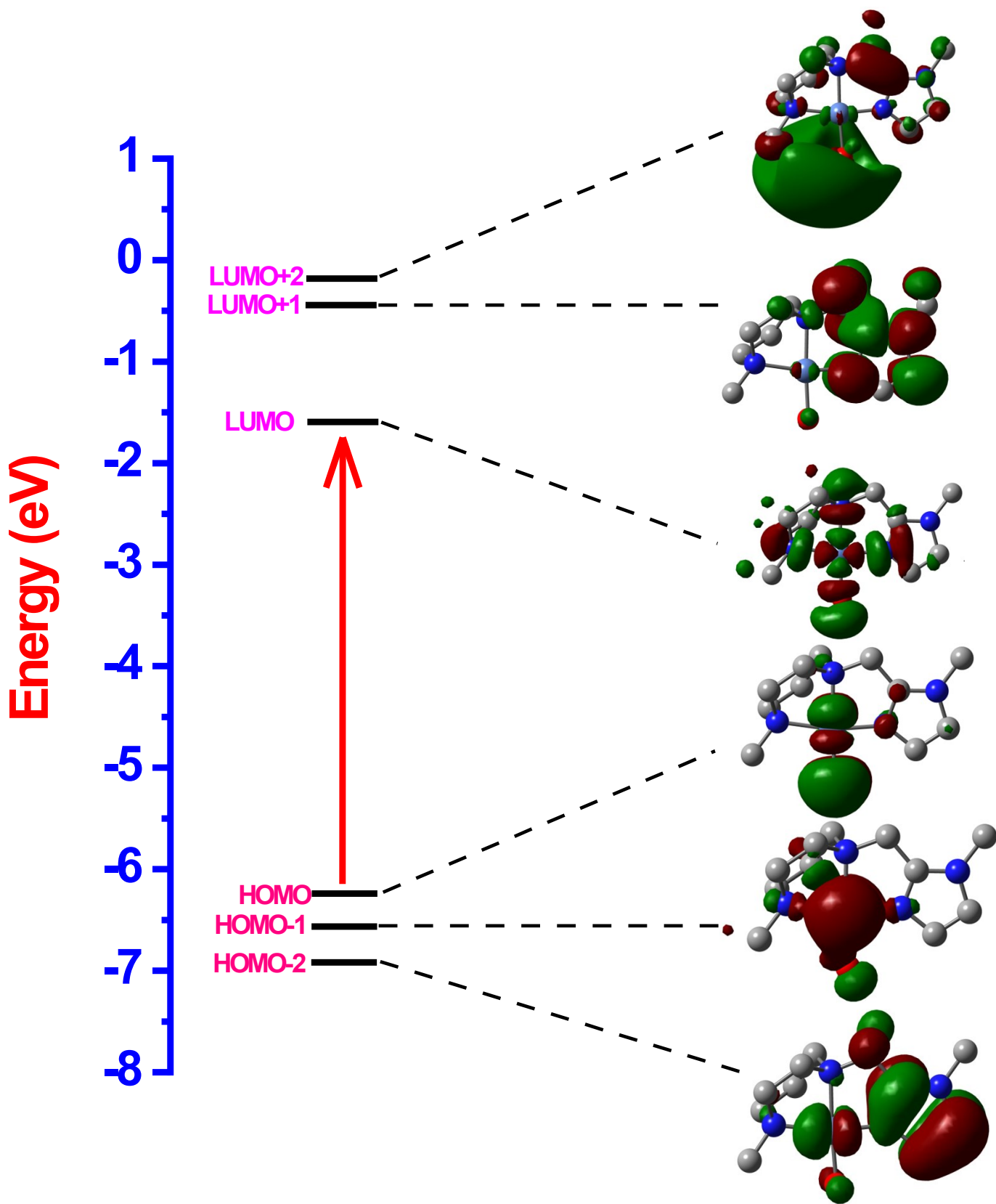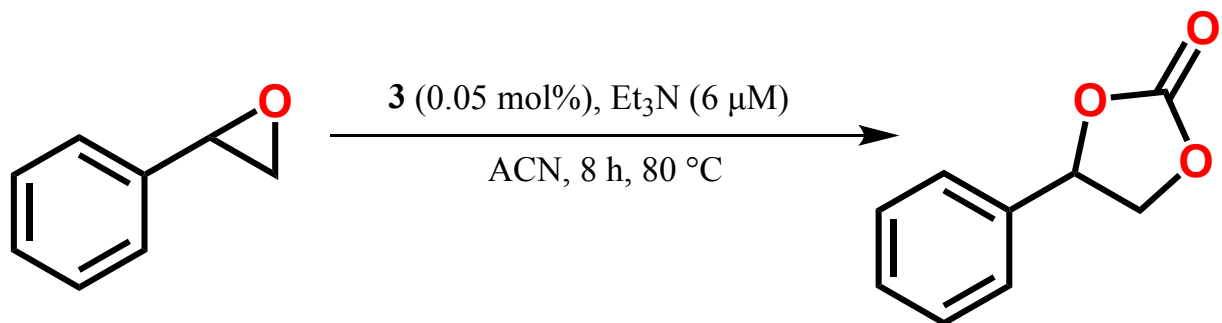
Fig. S16. Schematic MO diagram for the intermediate complex species **2a**

Scheme S1. Conversion of epoxide into cyclic carbonates.

Table S5. Reaction of Styrene epoxide (10 mmol) with 1 atm pure CO_2 using catalyst **3** (0.05 mol%) and Et_3N as a base (6 µM) for a period of 8 hrs.

Entry	Temperature (°C)	Yield (%)	TON	TOF (h⁻¹)	Selectivity (%)
1	30	9	180	23	>99
2	40	25	500	63	>99
3	50	39	780	98	>99
4	60	55	1100	138	>99
5	80	72	1440	180	>99

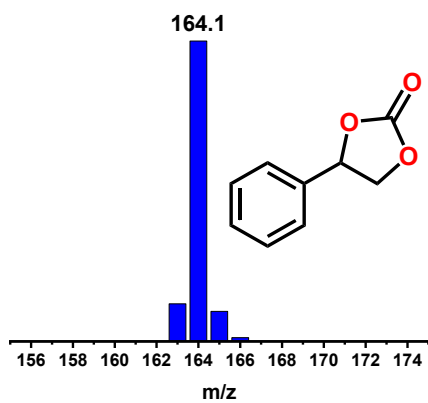Reaction conditions above stated as: **3** (0.05 mol%), Et_3N (6 µM), ACN, 8 h, 80 °C

Fig. S17. GC-MS spectra of 4-phenyl-1,3-dioxolan-2-one.

42 #32   RT: 0.31   AV: 1   NL: 6.27E9
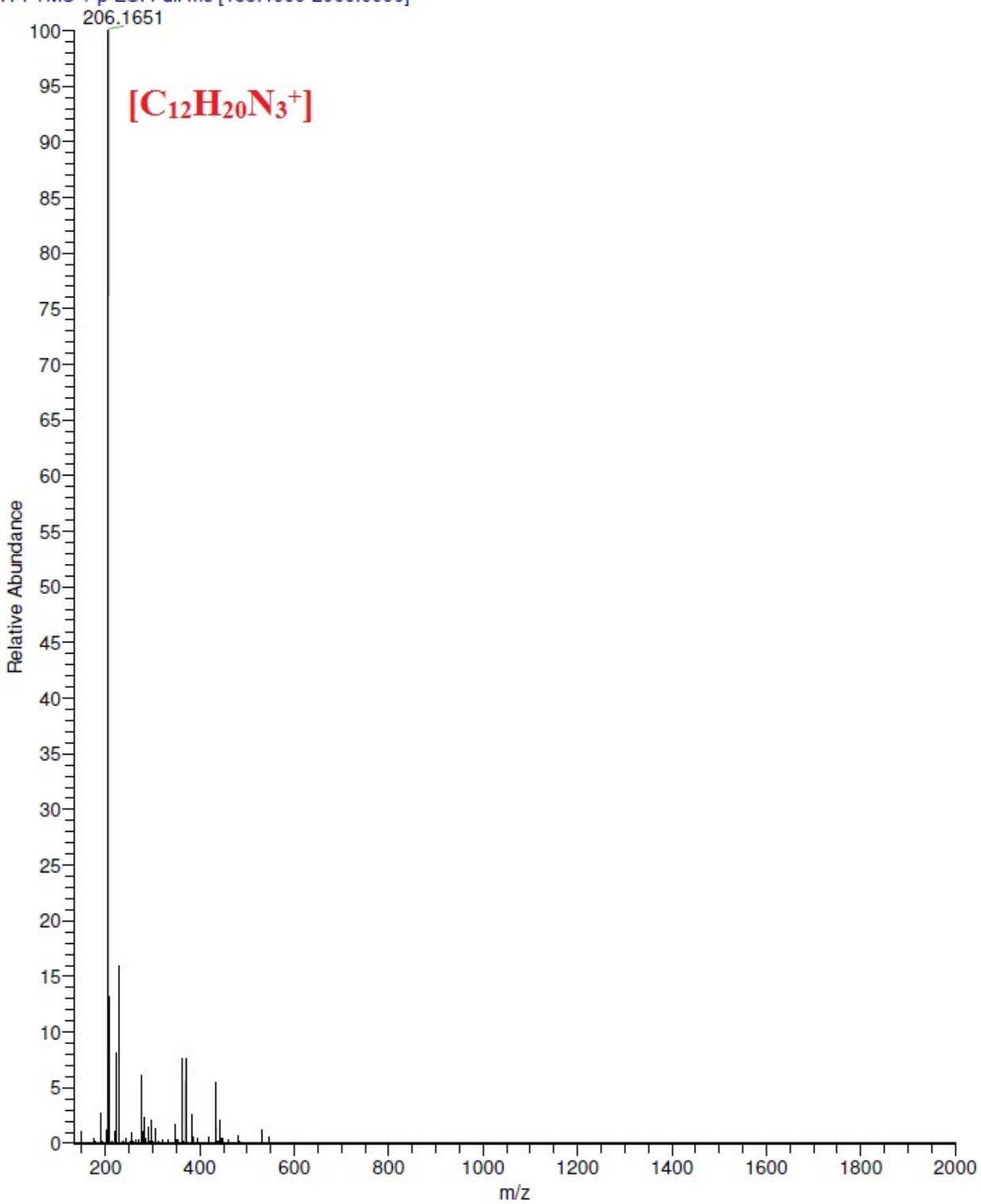T: FTMS + p ESI Full ms [133.4000-2000.0000]

206.1651

$[C_{12}H_{20}N_3^+]$

Fig. S18. High Resolution Mass Spectra of **L1** in methanol solution (1×10^{-3} M) at 25 °C.

Hm-Im-3N #47 RT: 0.46 AV: 1 NL: 9.35E9
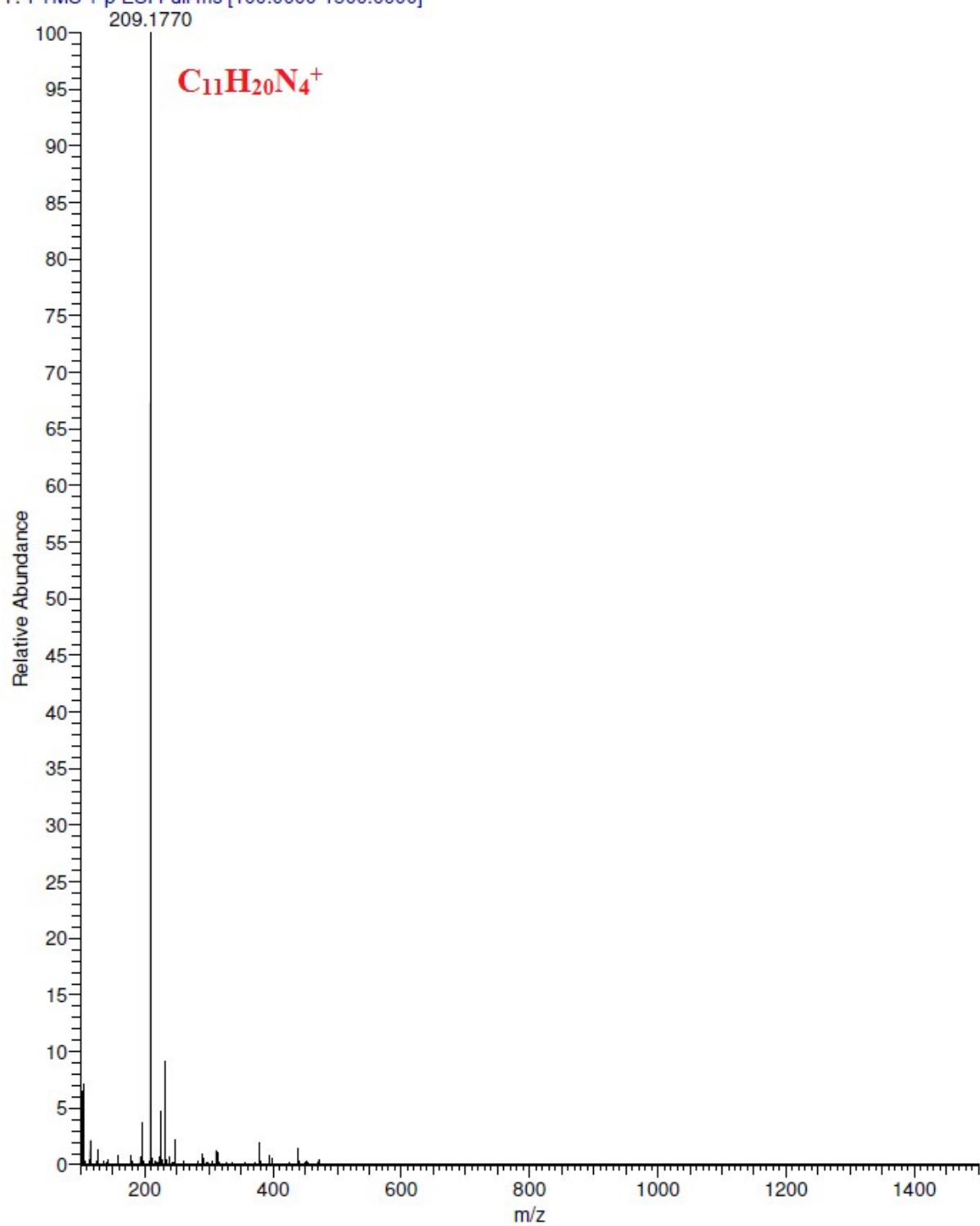T: FTMS + p ESI Full ms [100.0000-1500.0000]

Fig. S19. High Resolution Mass Spectra of **L2** in methanol solution (1×10^{-3} M) at 25 °C.

Ni-Hm-Py-3N #35 RT: 0.35 AV: 1 NL: 3.46E9
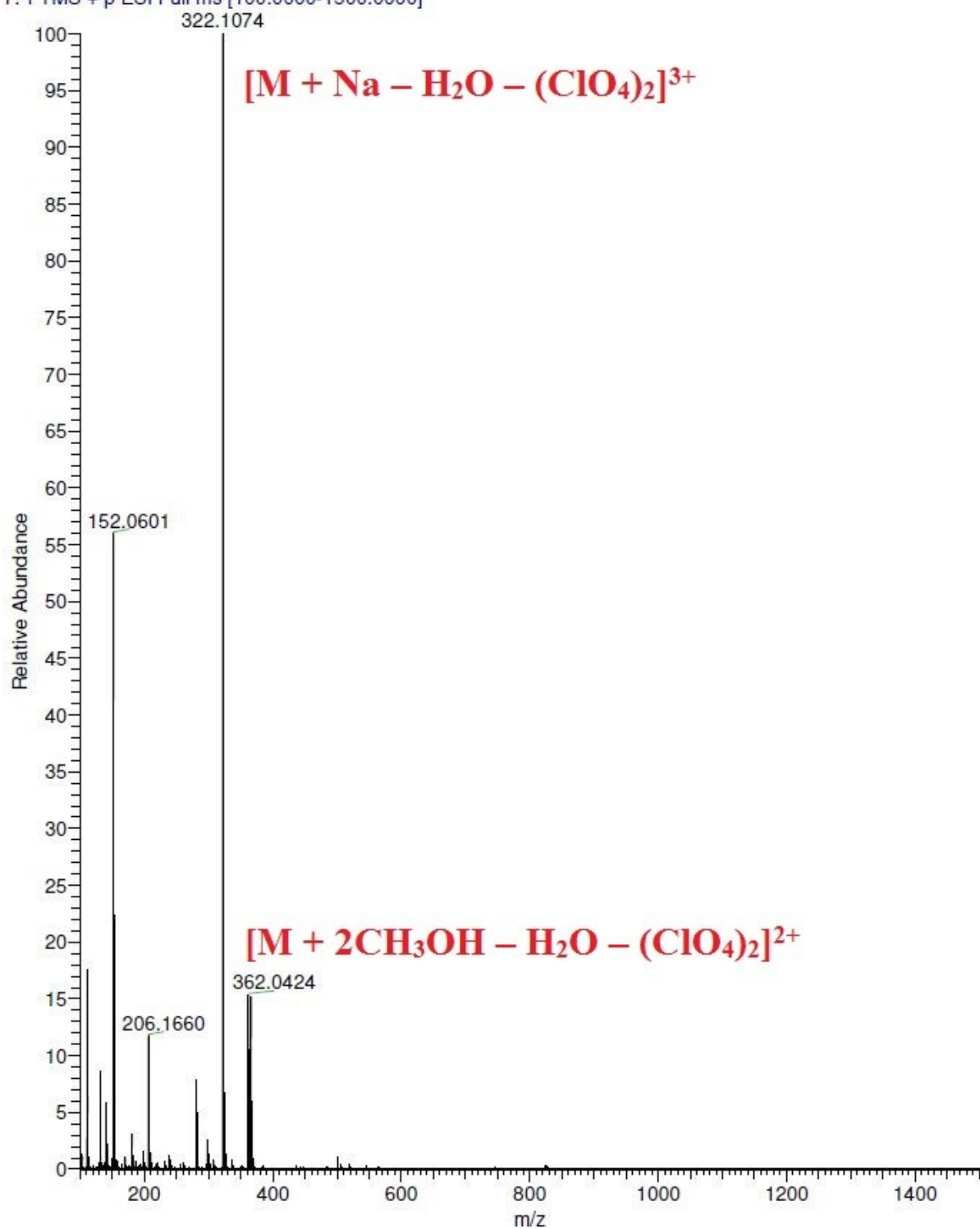T: FTMS + p ESI Full ms [100.0000-1500.0000]

Fig S20. High Resolution Mass Spectra of $[Ni(L1)(H_2O)_3](ClO_4)_2$ **1** in methanol solution (1×10^{-3} M) at 25 °C.

Ni-HM-In-3N #33 RT: 0.33 AV: 1 NL: 1.02E9
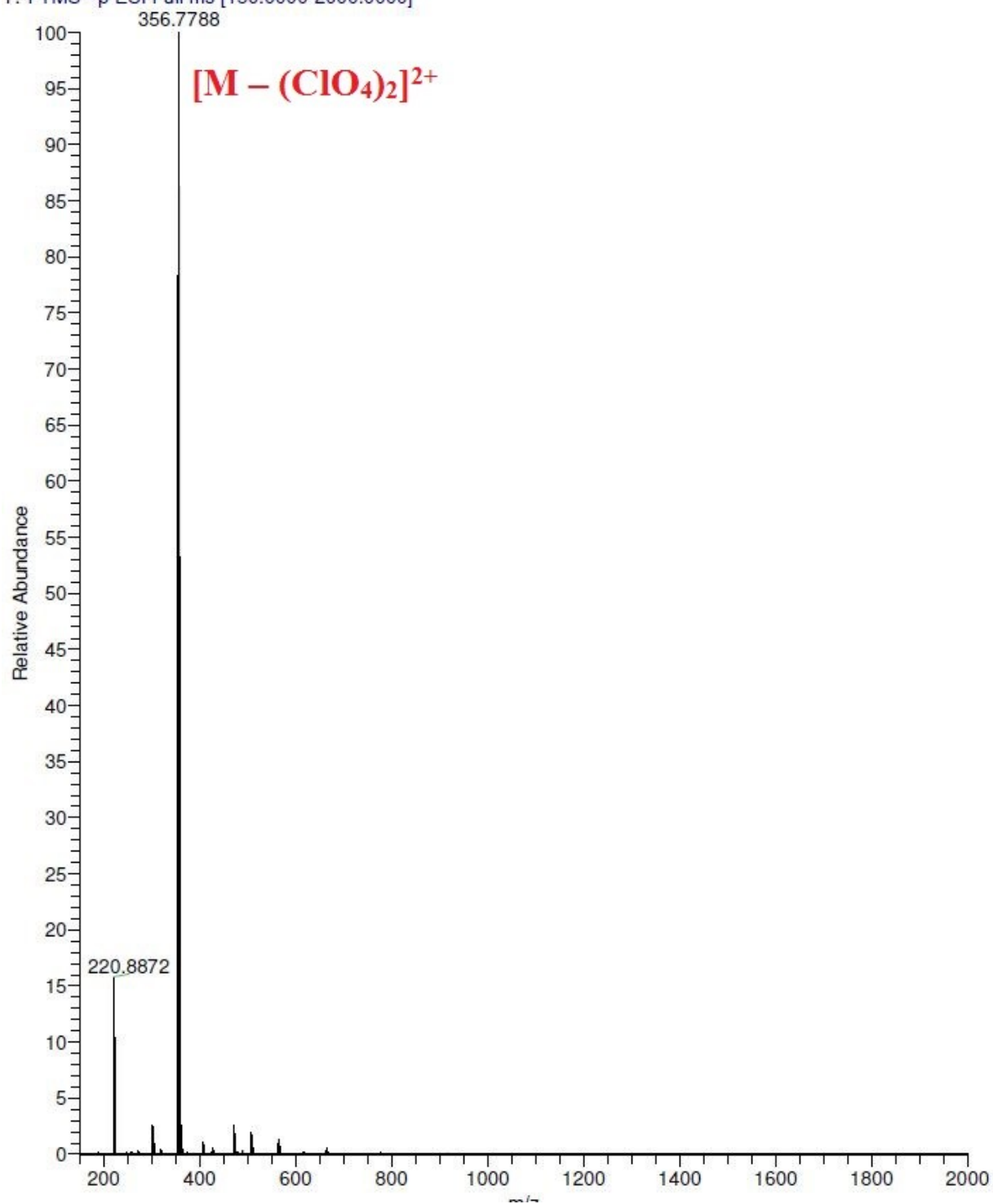T: FTMS - p ESI Full ms [150.0000-2000.0000]

Fig. S21. High Resolution Mass Spectra $[Ni(L2)(H_2O)_3](ClO_4)_2 \cdot 2H_2O$ **2** in methanol solution (1 $\times 10^{-3}$ M) at 25 °C.

Di-Ni-MeOH #37 RT: 0.37 AV: 1 NL: 2.26E9
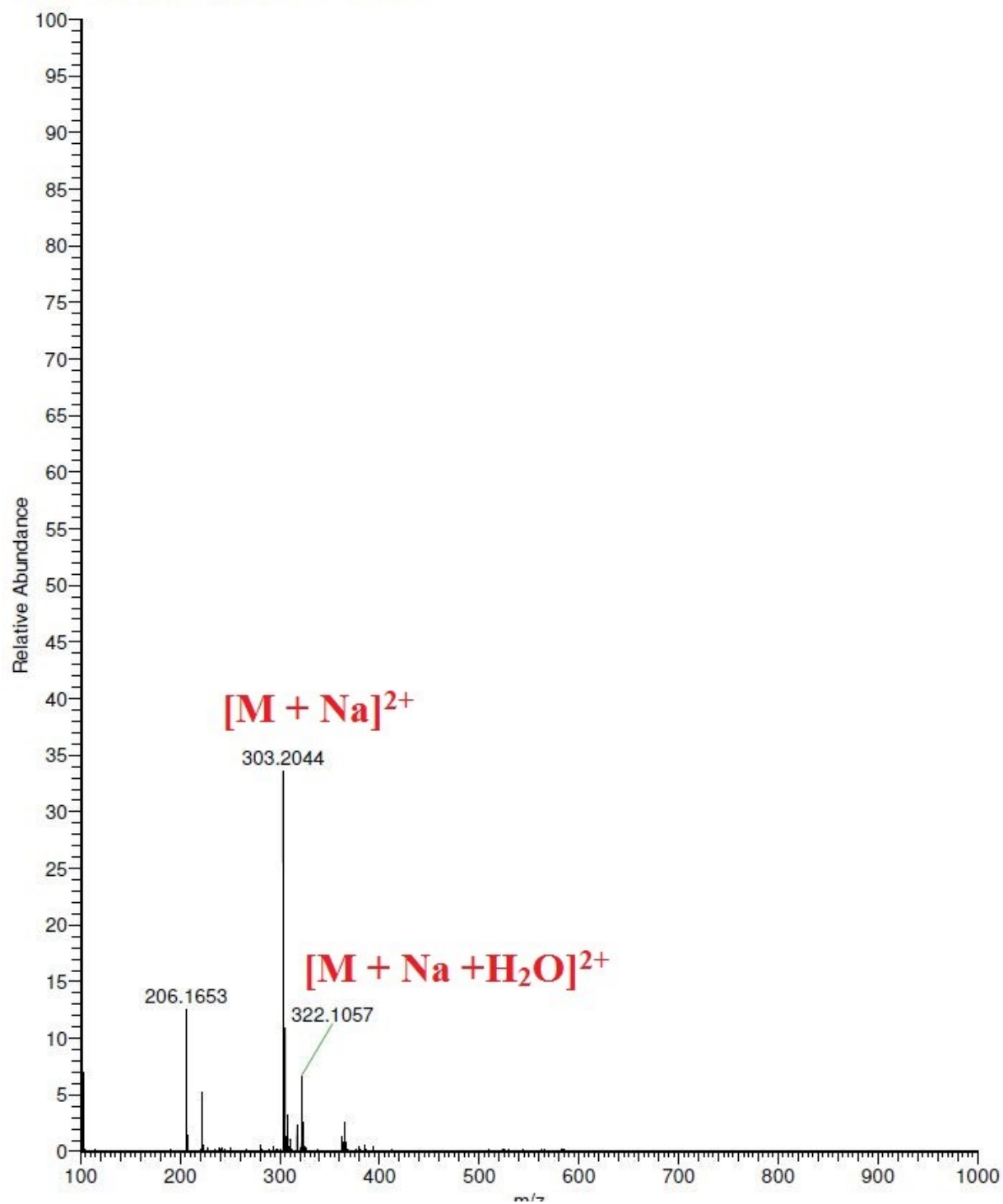T: FTMS + p ESI Full ms [100.0000-1000.0000]

Fig. S22. High Resolution Mass Spectra of intermediate **1a** methanol solution (1 × 10^{-3} M) at 25 °C.

Di-Ni-EtOH #37 RT: 0.36 AV: 1 NL: 1.80E9
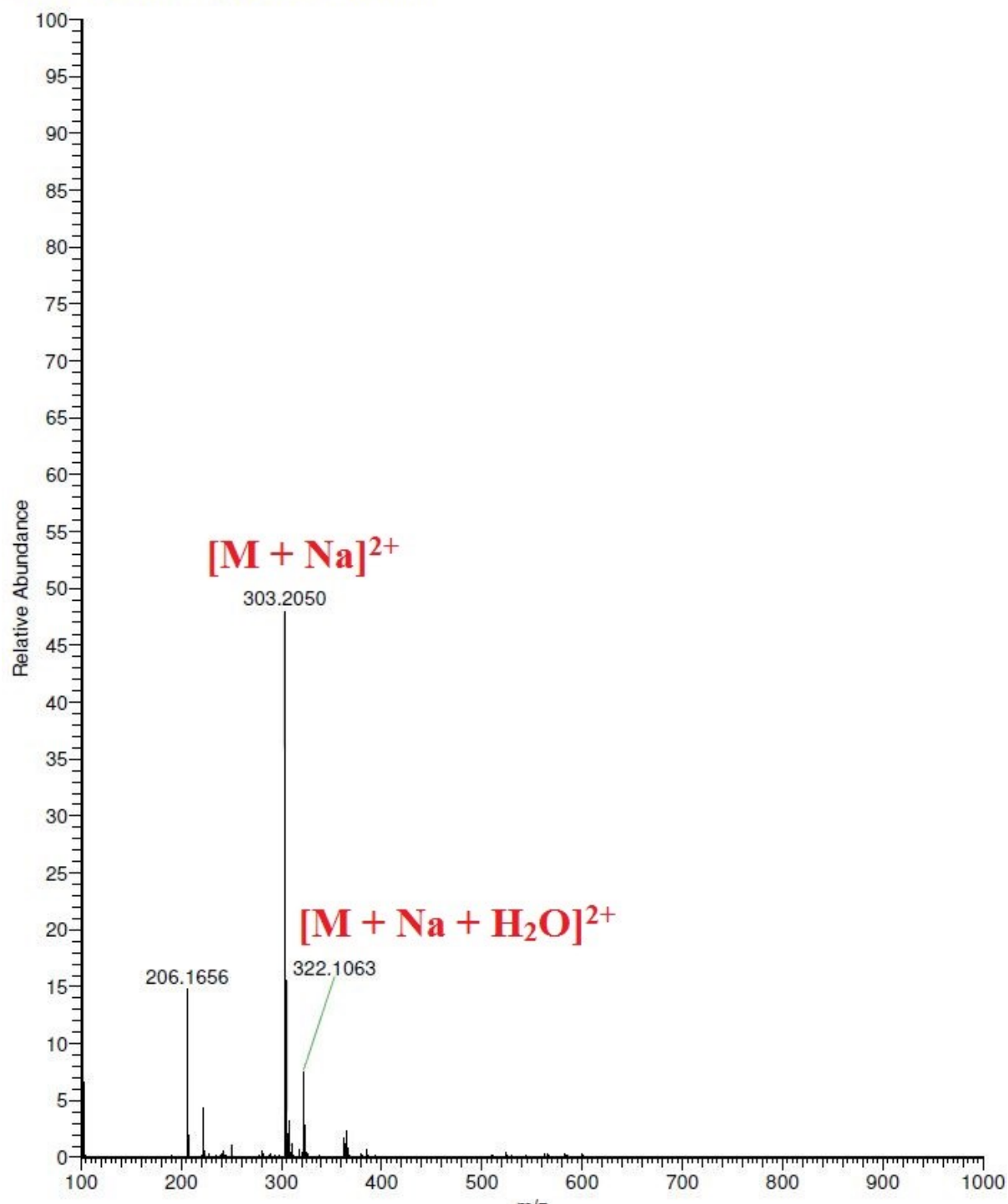T: FTMS + p ESI Full ms [100.0000-1000.0000]

Fig. S23. High Resolution Mass Spectra of the intermediate **1a** in ethanol solution (1×10^{-3} M) at 25 °C.

Ni-Py #37 RT: 0.36 AV: 1 NL: 2.32E9
T: FTMS + p ESI Full ms [100.0000-1000.0000]
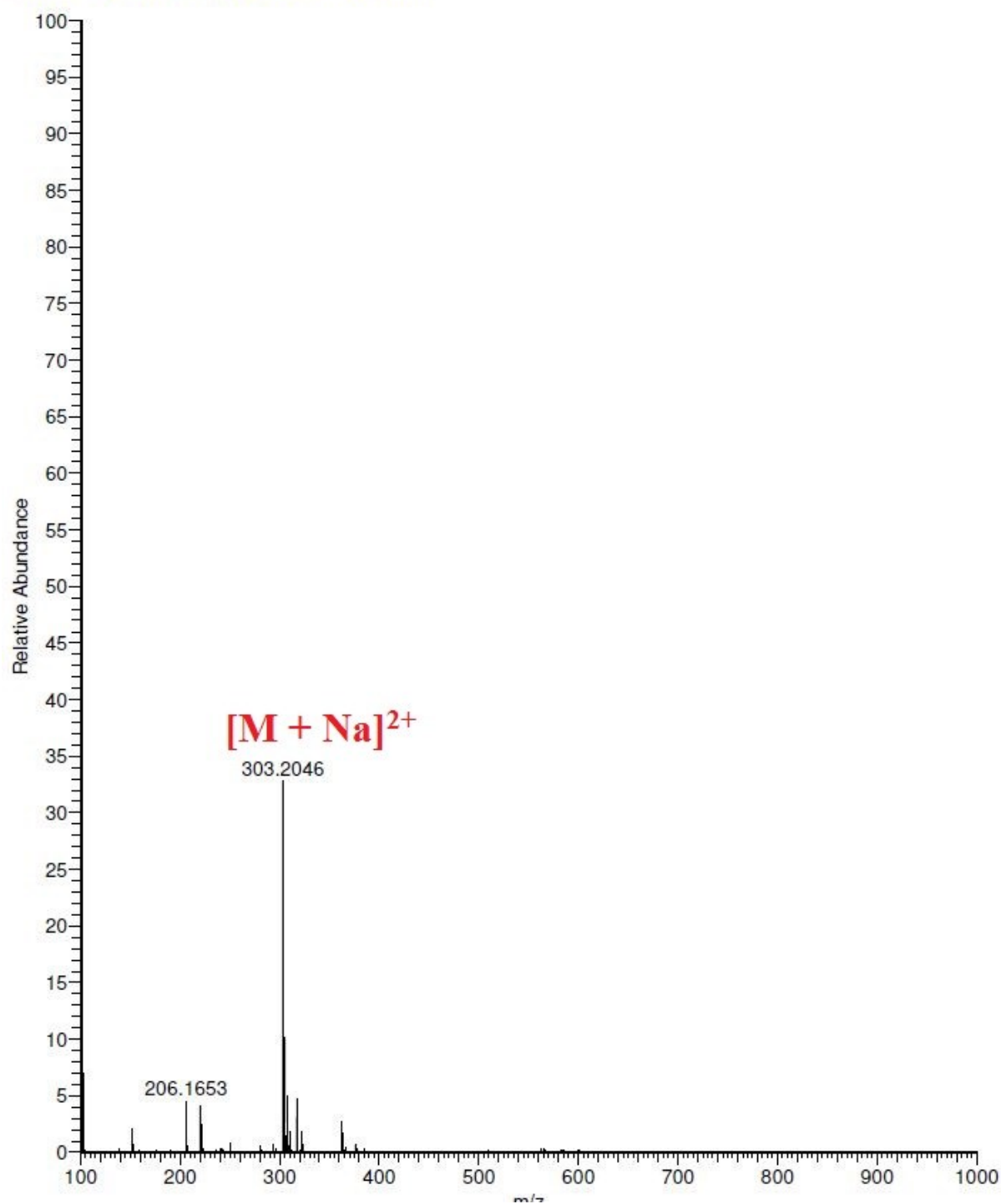
$[M + Na]^{2+}$

303.2046

206.1653

Fig. S24. High Resolution Mass Spectra of the intermediate **1a** in isopropanol solution (1×10^{-3} M) at 25 °C.

dini-Hmpy #44 RT: 0.43 AV: 1 NL: 2.02E9
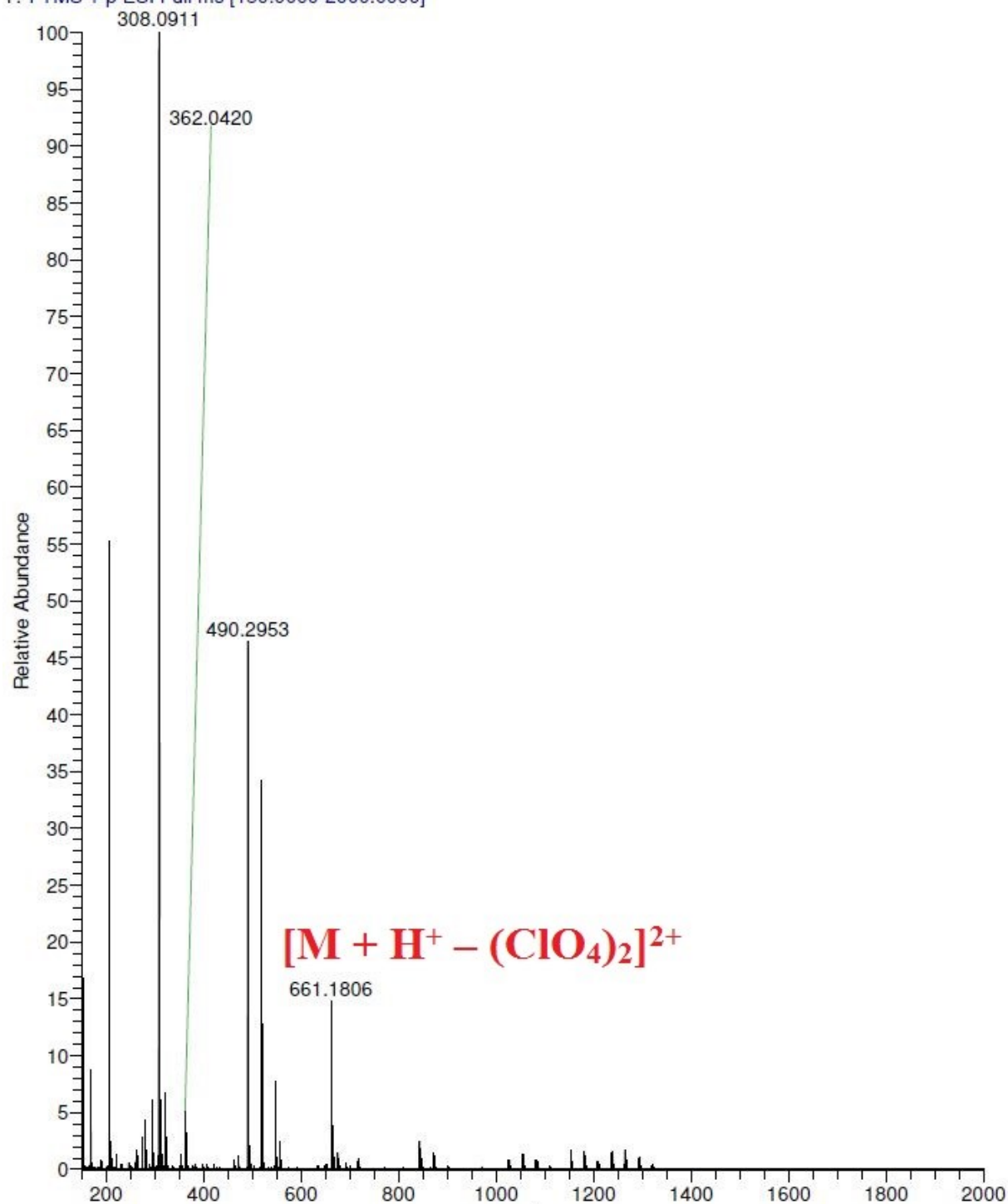T: FTMS + p ESI Full ms [150.0000-2000.0000]

308.0911

362.0420

490.2953

$[M + H^+ - (ClO_4)_2]^{2+}$

661.1806

Relative Abundance

Fig. S25. High Resolution Mass Spectra of $[Ni_2(L1)_2(\mu-CO_3)(H_2O)_2](ClO_4)\cdot 2H_2O$ **3** in methanol solution (1×10^{-3} M) and at 25 °C.

References

S1. D. F. Evans, *J. Chem. Soc*. 1959, 2003-2005.

S2. J. Lölinger, R. Scheffold, *J. Chem. Edu*., 1972, 646-647.