Supplementary Information

C-H Bond Chlorination and Bromination Using Water Soluble Nickel (II) guanidine Complexes

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Physical methods and materials

All commercially available reagents (Sigma Aldrich Co., Finar, TCI, Rankem, etc.) were used without further purification. HPLC-grade solvents such as chloroform, methanol, and dimethylformamide were used for reactions and crystallization. Milli-Q water was used in all experiments. UV-Vis studies were carried out using a Cary 8454 spectrophotometer (Agilent Technologies). The ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz Bruker NMR spectrometer, with chemical shifts given in ppm relative to tetramethylsilane (TMS) as an internal standard. High-resolution mass spectrometry (HRMS) was conducted using a 6540 UHD Accurate-Mass Q-TOF LC/MS system (Agilent, USA) equipped with a 1290 UPLC (Agilent) system. Products from the reaction mixture were identified using an Agilent 5977B GC/MSD equipped with an HP-5 MS capillary column (30 m × 0.32 mm × 0.25 μm) and quantified using an Agilent 7890B GC system with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). Calibration curves for each compound were obtained using authentic standards. The crystal structures of the Ni(II) complexes were determined using a D8 Venture Bruker AXS single-crystal X-ray diffractometer. X-band EPR spectra were recorded using a Bruker EMX1444 EPR spectrometer operating at 9.455 GHz and fitted with a quartz Dewar for measurements at 120 K. The EPR spectra were calibrated with diphenylpicrylhydrazyl (DPPH) (g = 2.0037) and processed using Bruker WinEPR software. A Fourier Transform Infrared (FTIR) spectroscopy study was carried out in Nicolet iS20 (Thermo Fisher). Elemental analysis was done with a PerkinElmer CHN analyzer (2400 series).

Structure determination by X-ray crystallography

The crystal structures of the nickel complexes (ML1) were determined using X-ray diffraction data collected on a D8 Venture Bruker AXS single-crystal X-ray (SC-XRD) diffractometer equipped with a CMOS PHOTON 100 detector and monochromatic microfocus sources (Mo−Kα = 0.71073 Å). The crystal data was collected at room temperature (RT). The structures were solved using the SHELX program implemented in APEX3.[1-4]. Non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model with appropriate HFIX commands. Data collection and structure refinement parameters are summarized in the table below, along with geometrical parameters including bond lengths and bond angles.

Electrochemical measurements

Cyclic voltammetry (CV) experiments were conducted in SP-300 potentiostate, using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode in MeOH medium ([Ni(II)L1/2] = 1 mM, scan rate: 0.1 Vs^{-1} at room temperature (RT). The supporting electrolyte was 0.1 M n-Bu_4NPF_6 (n-Bu = n-butyl). The potential was referenced to the Ag/AgCl couple by adding an Fc as standard to the solution.

Catalytic chlorination with NaOCl

A mixture of nickel complexes (0.05 μmol), substrates (0.25 mmol) and NaOCl (0.30 mmol, 600 μL from $[NaOCl]_{stock}$ = [0.5 M]) were added in 1 mL of H_2O: $CHCl_3$ mixture (7:3 v/v) and stirred vigorously at RT for 30 min under N_2. Then, the water was removed by the workup of the reaction mixture with $CHCl_3$ and dried using $MgSO_4$. A fraction of the resulting mixture was analyzed by GC(FID), and the products were identified by GC-MS. The products were quantified from the calibration curve of authentic compounds. The TON values are reported in Tables 1 and 2 of the manuscript. Chromatographic methods.

Chromatographic methods

Chromatographic separation of the various products shown in this work was performed using the following chromatographic methods: Column: Agilent 7890B GC system equipped with an HP-5 capillary column (30 m × 0.32 mm × 0.25 μm); Agilent 5977B GC/MSD equipped with an HP-5 MS capillary column (30 m × 0.32 mm × 0.25 μm).

For chlorination of cyclohexane, toluene, ethyl benzene

Detector: Flame ionization detector (FID)

Zero air (carrier gas) 300 mL/min

H_2 (fuel gas) 30 mL/min

N_2 (make up) 25 mL/min

Initial column temperature: 60 ℃

Final column temperature: 200 ℃

Temperature ramp: 10 ℃/min

Injector temperature: 250 ℃

Septum purge flow: 3 mL/min

Total flow: 54 mL/min

Split ratio: 50:1

Detector temperature 280 ℃

For Chlorination of 4-methyl biphenyl

Detector: Flame ionization detector (FID)

Zero air (carrier gas) 300 mL/min

H_2 (fuel gas) 30 mL/min

N_2 (make up) 25 mL/min

Initial column temperature: 60 ℃

Final column temperature: 280 ℃

Temperature ramp: 10 ℃/min

Injector temperature: 250 ℃

Septum purge flow: 3 mL/min

Total flow: 34 mL/min

Split ratio: 50:1

Detector temperature 280 ℃

For chlorination of adamantane

Detector: Flame ionization detector (FID)

Zero air (carrier gas) 300 mL/min

H_2 (fuel gas) 30 mL/min

N_2 (make up) 25 mL/min.

Initial column temperature: 60 ℃

Final column temperature: 250 ℃

Temperature ramp 1: 10 ℃/min to 120 ℃/min

Temperature ramp 2: 10 ℃/min to 250 ℃/min

Injector temperature: 225 ℃

Septum purge flow: 3 mL/min

Total flow: 54 mL/min

Split ratio: 50:1

Detector temperature 280 ℃

Catalytic bromination with equi. Molar mixture of NaOCl and NaBr

A mixture of nickel complexes (0.05 μmol), substrates (0.25 mmol) and NaOCl (0.30 mmol, 600 μL) and NaBr (0.30 mmol, 30 mg) were added in 1 mL of H_2O: $CHCl_3$ mixture (7:3 v/v) and stirred vigorously at RT for 30 min under N_2. Then, the water was removed by the workup of the reaction mixture with $CHCl_3$. The bromine generated in the reaction mixture was quenched by sodium thiosulphate. A fraction of the resulting mixture was analyzed by GC(FID), and the products were identified by GC-MS. The products were quantified from the calibration curve of authentic compounds. The TON value of *n*-hexane is quantified by using a known concentration of toluene as an internal standard. The TON values are reported in Table 2 of the manuscript.

Synthesis of biguanide chloride (L2) and ethylenebisbiguanide chloride (L1)

To prepare the biguanide chloride (L2), 0.3 moles of dicyandiamide (25 g) and 0.75 moles of NH_4Cl (41 g) were separately ground to a fine powder and mixed in a 250 mL beaker. The mixture was gently heated in an oil bath with constant stirring until a liquid melt was obtained. This melt was maintained at 160°C–165°C for 10 minutes with constant stirring. After cooling, the solidified melt was crushed into small lumps and dissolved in 150 mL of hot water (90°C–100°C). The resulting mixture was filtered, and the precipitate was washed twice with 25 mL of hot water. The filtrate was treated with a slight excess of ammoniacal copper (II) chloride solution. The precipitated rose-red copper biguanide chloride was filtered, washed with water, and dissolved in 35 mL of hot 10% HCl (not exceeding 90°C). The solution was then cooled in an ice bath. The crude crystals formed were dissolved in 25 mL of boiling water and the solution was cooled on ice. The resulting colourless crystals of biguanide chloride were filtered and washed first with 10 mL of cold water and then with 10 mL of absolute ethanol.[5]

Similarly, ethylenebisbiguanide chloride (L1) was prepared by reacting 0.15 moles of ethylenediamine dihydrochloride (20 g) with 0.3 moles of dicyandiamide (25 g) at 140°C–150°C. The aqueous solution of the cooled and solidified melt was treated with an ammoniacal solution of Cu(II) chloride, precipitating copper(II) ethylenebisbiguanide chloride. The addition of dilute hydrochloric acid removed the copper chloride, yielding crystals of ethylenebisbiguanide chloride in water.[6]

The formation of L1 and L2 was confirmed by measuring their respective melting points, HRMS, FTIR, and elemental analysis (CHN analysis). For both L1 and L2, yield% was approximately 30% .

Characterization of L1, L2

HR-MS

HR-MS m/z: calcd: 229.1633; found: 229.1603 $(M+H)^+$ for L1; HR-MS m/z: calcd: 102.0775; found: 102.0622 $(M+H)^+$ for L2.

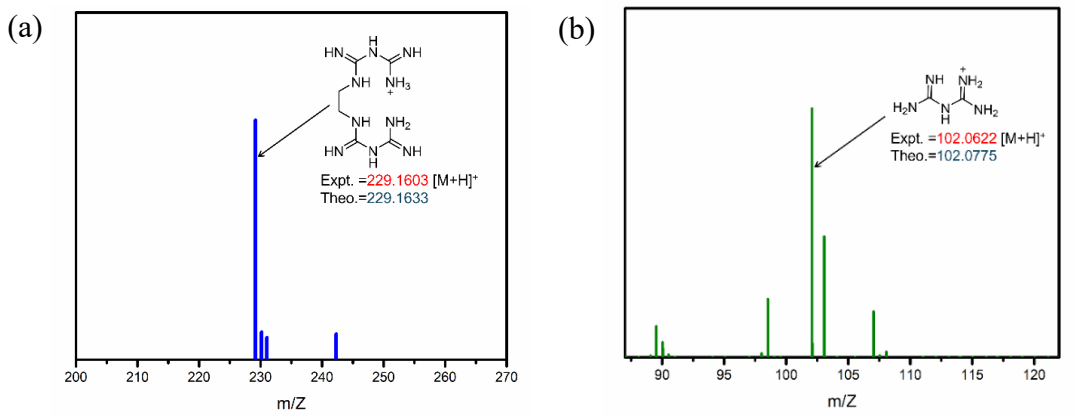


Fig. S1 HR-MS spectrum of (a) L1(Blue) and (b) L2(Green).

FTIR

3345 cm^{-1}, 3129 cm^{-1}, 2191 cm^{-1}, 2152 cm^{-1}, 1650 cm^{-1}, 1562 cm^{-1}, 1490 cm^{-1}, 1293 cm^{-1} for L1; 3330 cm^{-1}, 3053 cm^{-1}, 1704 cm^{-1}, 1640 cm^{-1}, 1534 cm^{-1}, 1439 cm^{-1}, 1269 cm^{-1}, 1184 cm^{-1}, 1109 cm^{-1}, 1056 cm^{-1} for L2.

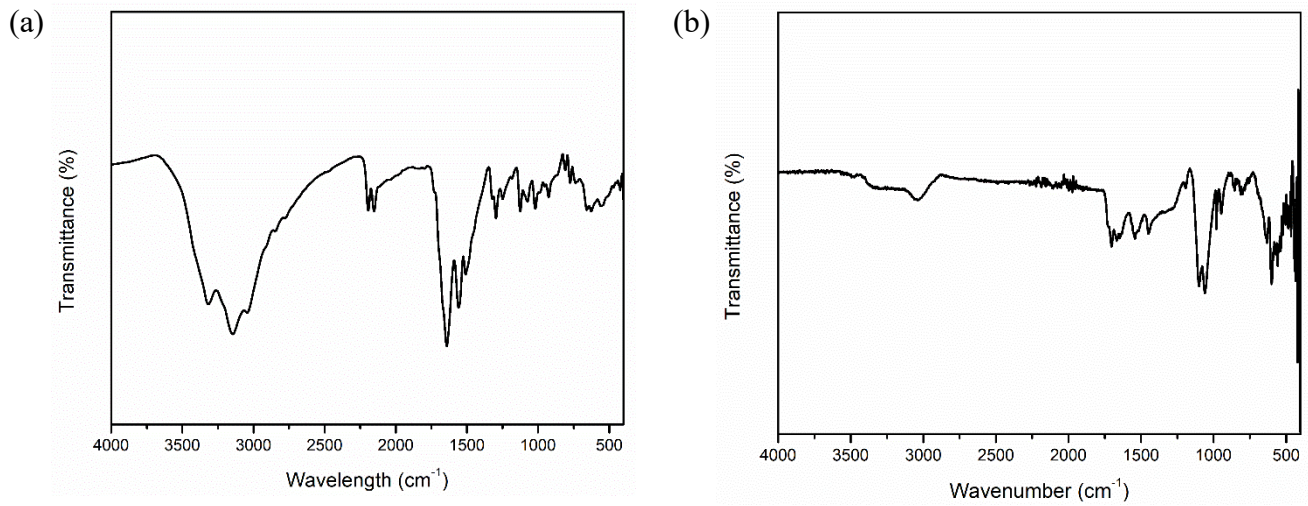


Fig. S2 FT-IR spectrum of (a) L1 and (b) L2.

Elemental Analysis

Anal. calcd for $C_6H_{17}N_{10}Cl$ (L1) (fw = 264.72 gm/mol): C, 27.19; H, 6.42; N, 52.88; found: C, 26.90; H, 6.48; N, 52.13.

Anal. calcd for $C_2H_8N_5Cl$ (L2) (fw = 137.57 gm/mol): C, 17.46; H, 5.862; N, 50.91; found: C, 17.50; H, 5.865; N, 50.95.

Melting Point[7]

L1: 235 °C; L2: 225 °C

Synthesis of Ni (II) complexes (ML1 and ML2)

The synthesis of ML1 (Nickel(II) ethylenebisbiguanide chloride) and ML2 (Nickel(II) biguanide chloride) was carried out using aqueous ammoniacal nickel chloride hexahydrate. First, 1 gm of the L1/L2 ligand was dissolved in a minimum volume of distilled water. Then, a solution of the nickel salt (1.2 equivalents) was added dropwise to the ligand solution. The clear ligand solution turned orange, indicating complexation. The solution was then filtered and left to crystallize for 20-30 days, resulting in the formation of orange, needle-shaped crystals of ML1/ML2. Both complexes are characterized by various analytical techniques such as HRMS, UV-Vis, FTIR, NMR, CHN analysis, and cyclic voltammogram (CV) etc. Single crystals of ML1 were obtained by slow evaporation of water and characterized by SC-XRD.

Characterization of Ni (II) complexes

Distortion parameters

Table S1. Distortion parameter from Selected bond lengths (Å) and bond angles (°) of ML1 complex.

Bond Length [Å]
ML1
1.859 [Ni(1)-N(3)]
1.870 [Ni(1)-N(6)]
1.870 [Ni(1)-N(1)]
1.861 [Ni(1)-N(8)]

Bond Angle [°]
ML1
178.36 [N(3)-Ni(1)-N(6)]
91.98 [N(3)-Ni(1)-N(1)]
89.51 [N(3)-Ni(1)-N(8)]
86.38 [N(6)-Ni(1)-N(1)]
92.13 [N(6)-Ni(1)-N(8)]
τ_4=0.022
τ_δ=0.0219

Equation for the calculation of τ_4 and τ_δ [8-9]

$$\tau_4 = \frac{360^\circ - (\alpha + \beta)}{141^\circ}$$

α = largest L-Ni-L angles

β = second largest L-Ni-L angles

$$\tau_\delta = \frac{360^\circ - (\alpha + \beta)}{141^\circ}\delta$$

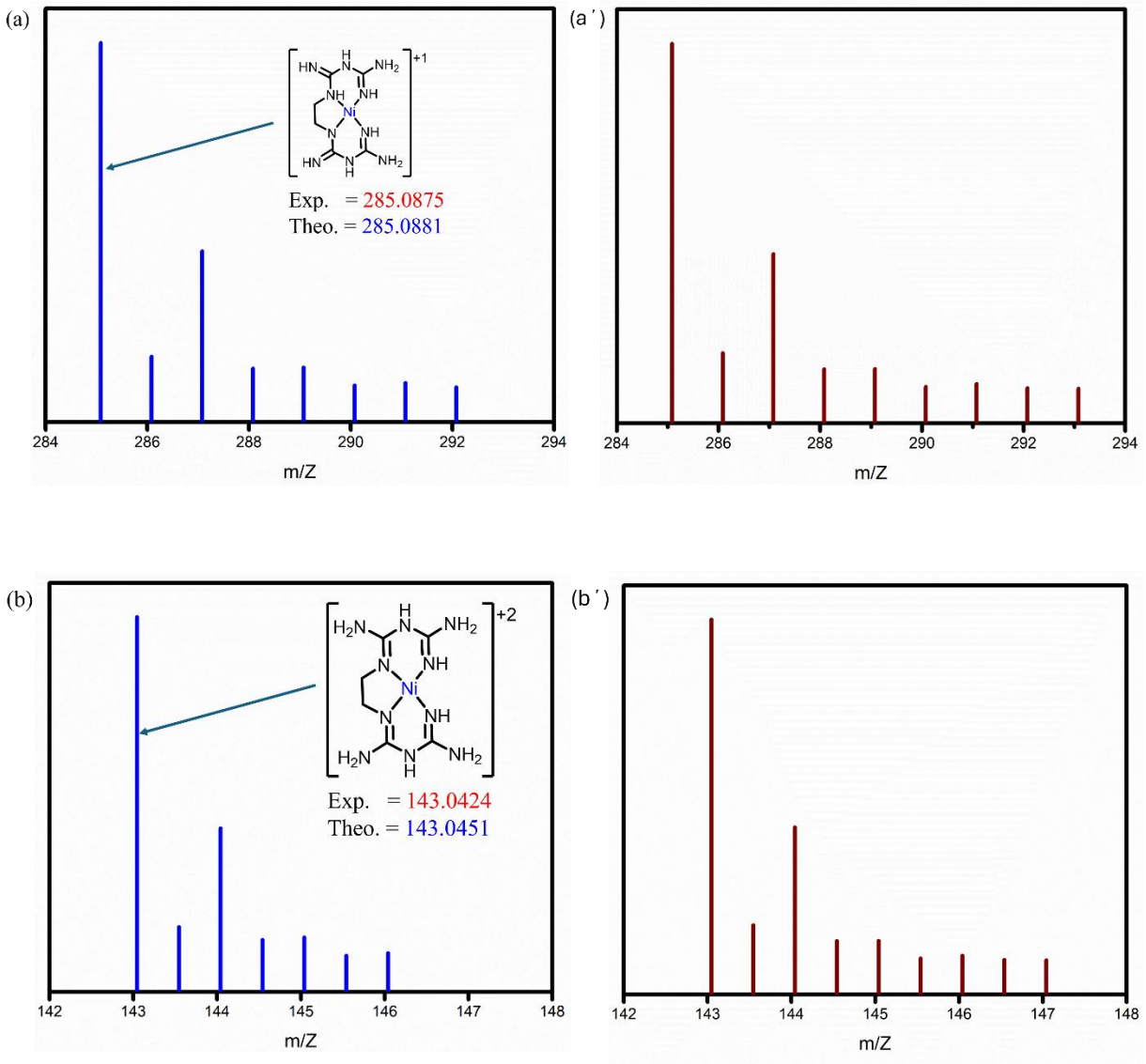
$$\delta = \frac{\alpha}{\beta}$$

HR-MS, UV-Vis, FTIR, NMR, CHN analysis and Cyclic Voltammogram (CV) of ML1 and ML2

HRMS

HR-MS *m/z*: calculated for ML1 ($[NiC_6N_{10}H_{15}]^+$): 285.0875; experimental: 285.0881, calculated for ML1 ($[NiC_6N_{10}H_{16}]^{2+}$): 143.0451; experimental: 143.0424.

HR-MS *m/z*: calculated for ML2 ($[NiC_4N_{10}H_{13}]^+$): 259.0673; experimental: 259.0684, calculated for ML2 ($[NiC_4N_{10}H_{14}]^{2+}$): 130.0373; experimental: 130.0302.



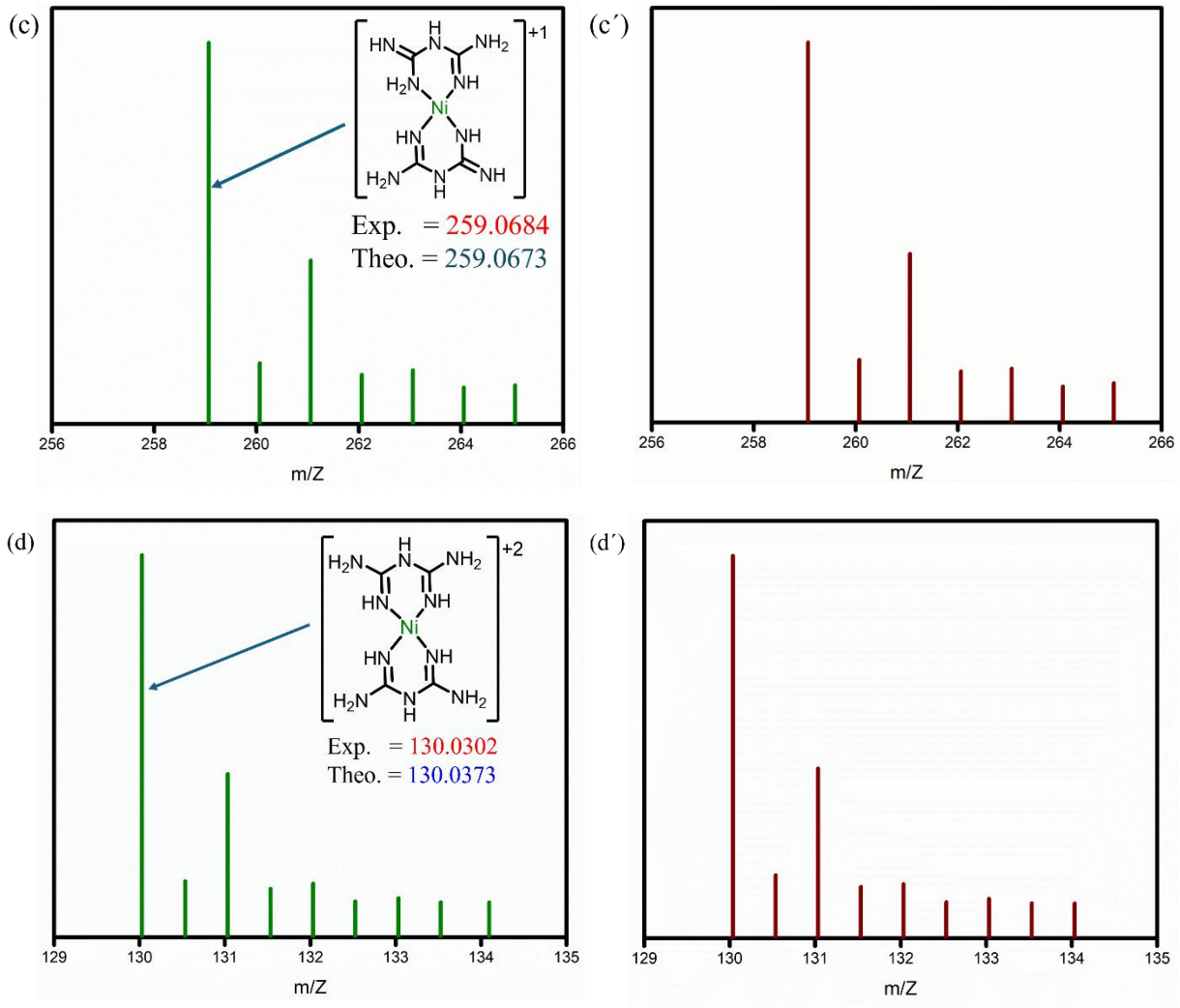


Fig. S3 HR-MS spectrum of experimental ML1 (Blue, a and b), experimental ML2 (Green, c and d) complex and theoretical calculated by Isotope Distribution Calculator (Red, a', b', c', d'). Theoretical *m/z* values were calculated (a', b', c') using Isotope Distribution Calculator under MassHunter software.

NMR

ML1: δ ^{1}H (400 MHz, DMSO-d_6) 2.94 (2 H, s), 4.61 (1 H, s), 6.61 (2 H, s), 6.98 (2 H, s), 9.86 (1 H, s).

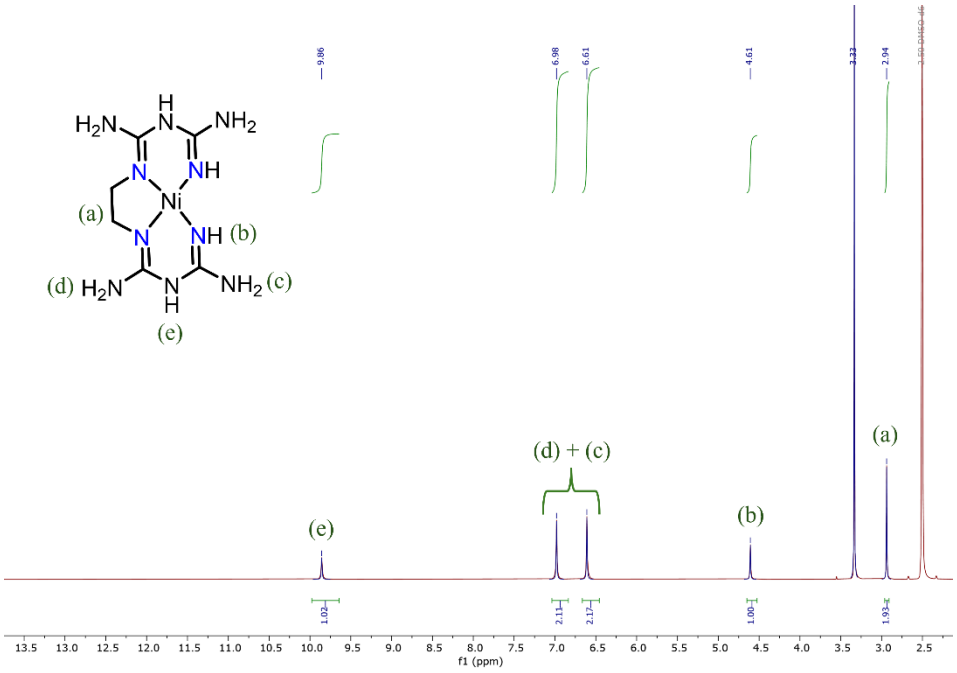
ML2: δ ^{1}H (400 MHz, DMSO-d_6) 4.52 (4 H, s), 6.59 (10 H, s).

ML1: δ ^{13}C (101 MHz, DMSO-d_6) 49.24, 150.12,153.21.

ML2: δ ^{13}C (101 MHz, DMSO-d_6) 152.95.

^{1}H NMR

(a)



(b)

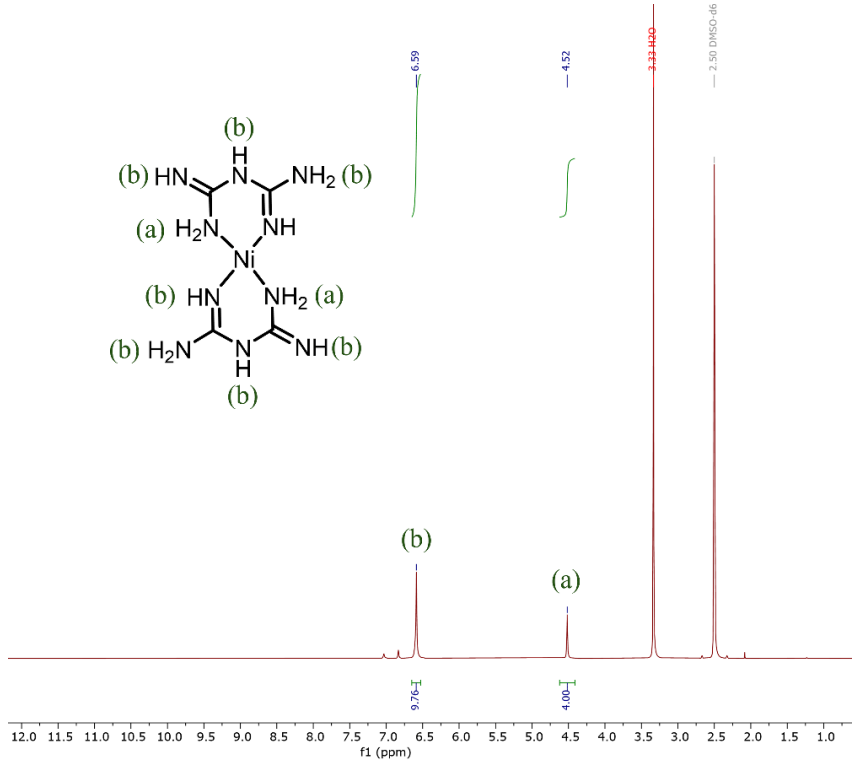
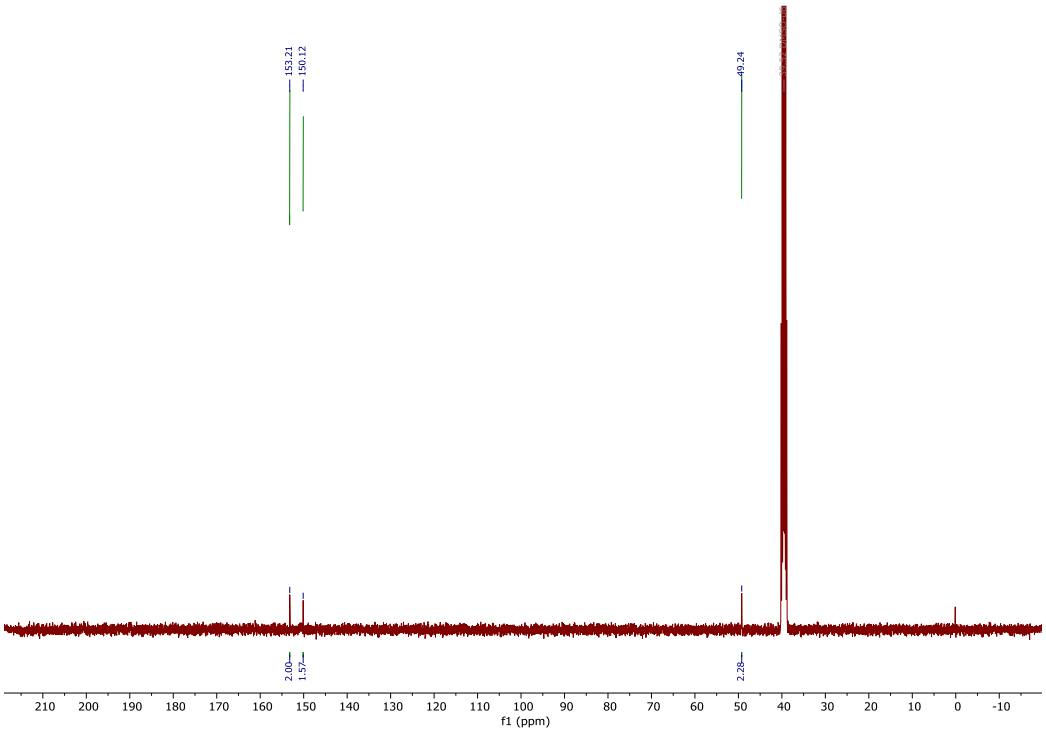


Fig. S4 ^{1}H NMR of ML1(a) and ML2(b) complex.

^{13}C NMR

(a)



(b)

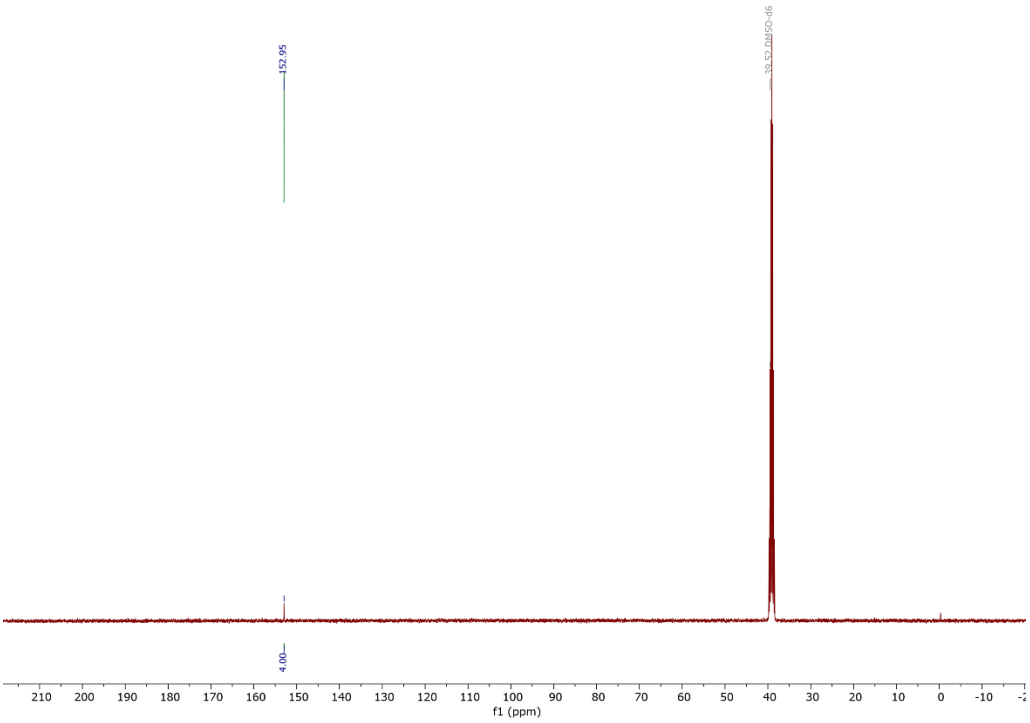


Fig. S5 ^{13}C NMR of ML1(a) and ML2(b) complex. ML1:^{13}C NMR (101 MHz, DMSO-d6) δ 49.23 - 49.26, 150.08 - 150.15, 153.17 - 153.26.

Electrochemical measurements Cyclic voltammetry (CV) experiments were conducted in SP-300 potentiostate, using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl (3 M KCl) reference electrode in MeOH medium ([Ni(II)L1/2] = 1 mM, scanrate: 0.1 Vs^{-1}. The supporting electrolyte was 0.1 M *n*-Bu_4NPF_6 (*n*-Bu = *n*-butyl). The potential was referenced to the Ag/AgCl couple by adding an Fc as standard to the solution. The respective plots are shown in Fig. S6.

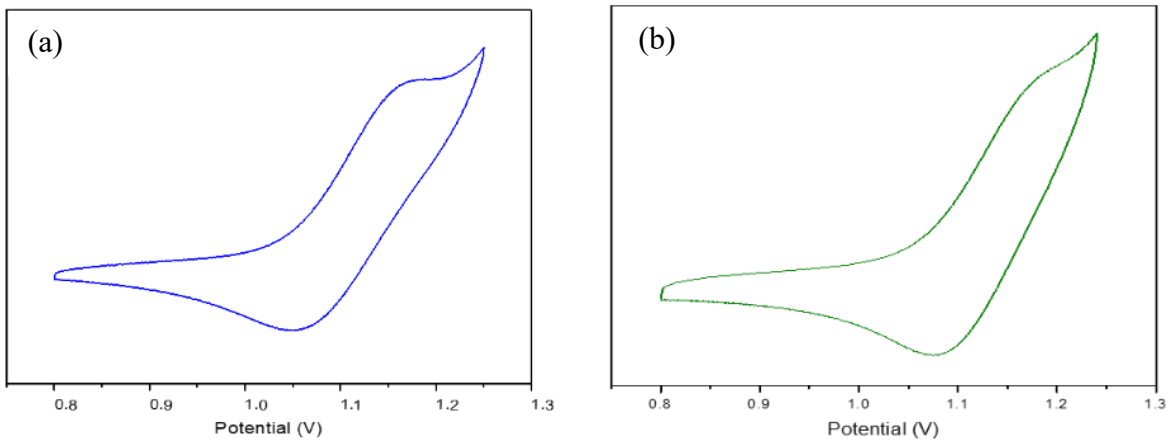


Fig. S6 (a) Cyclic voltammogram of ML1 (1 mM), (b) Cyclic Voltammogram of ML2(1 mM) in MeOH at 25 ℃ Supporting electrolyte: NBu_4PF_6 (0.05 M); Reference electrode: Ag/Ag+; working electrode: Pt-sphere; Counter electrode: Pt wire; Scan rate: 100 mV s^{-1}.

UV-Vis

UV-Vis (ML1): 480 nm; ε = 47.31 $M^{-1}cm^{-1}$ in H_2O.

UV-Vis (ML2): 445 nm; ε = 27.92 $M^{-1}cm^{-1}$ in H_2O.

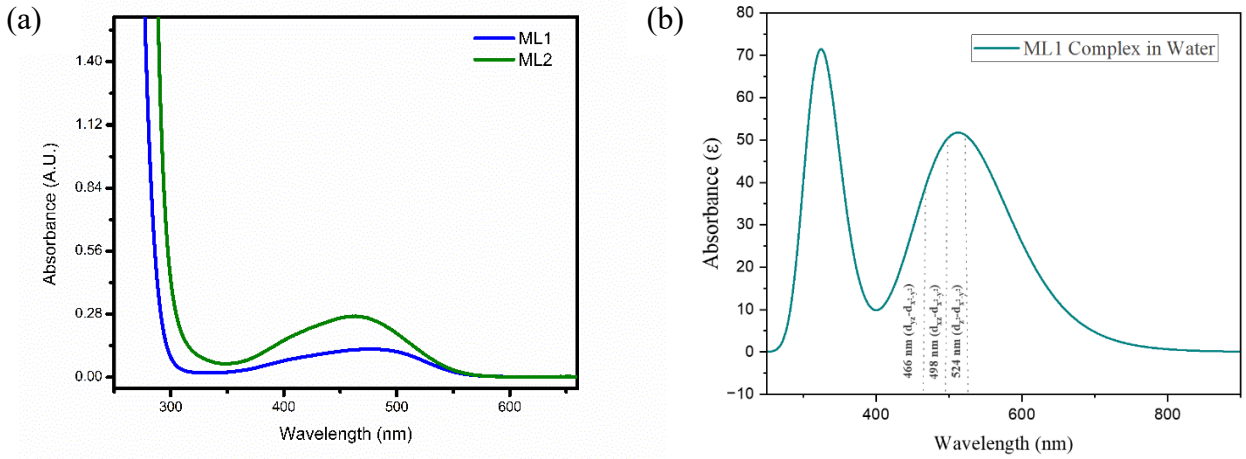


Fig. S7 (a) UV-Vis spectra ML1(blue) and ML2(green). (b) UV-Vis spectra from TD-DFT calculation. The simulated UV-Vis absorption spectra (in Fig S7 (b)) showed that the broad peaks between 300-400 nm correspond to the ligand-to-metal charge transfer (LMCT) transitions. On

the other hand, the broad transition peak at 450-550 nm corresponds to *d-d* transitions from HOMO-2 to LUMO (d_{yz}-$d_{x^2-y^2}$), HOMO-1 to LUMO (d_{xz}-$d_{x^2-y^2}$), and HOMO to LUMO (d_{z^2}-$d_{x^2-y^2}$).

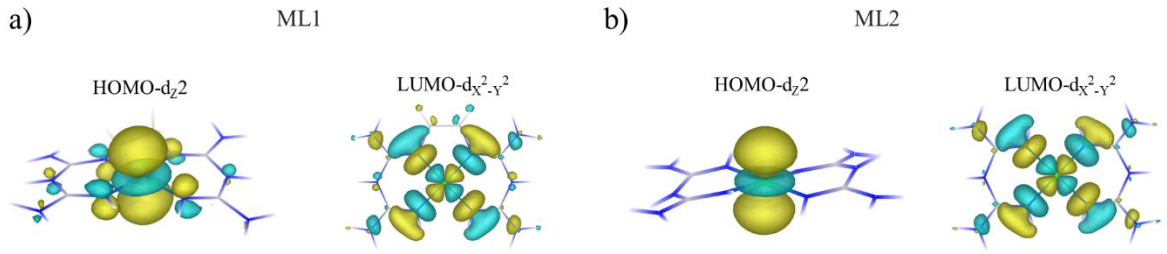


Fig. S8 HOMO-LUMO of frontier molecular orbitals of metal complexes (a) ML1 and (b) ML2

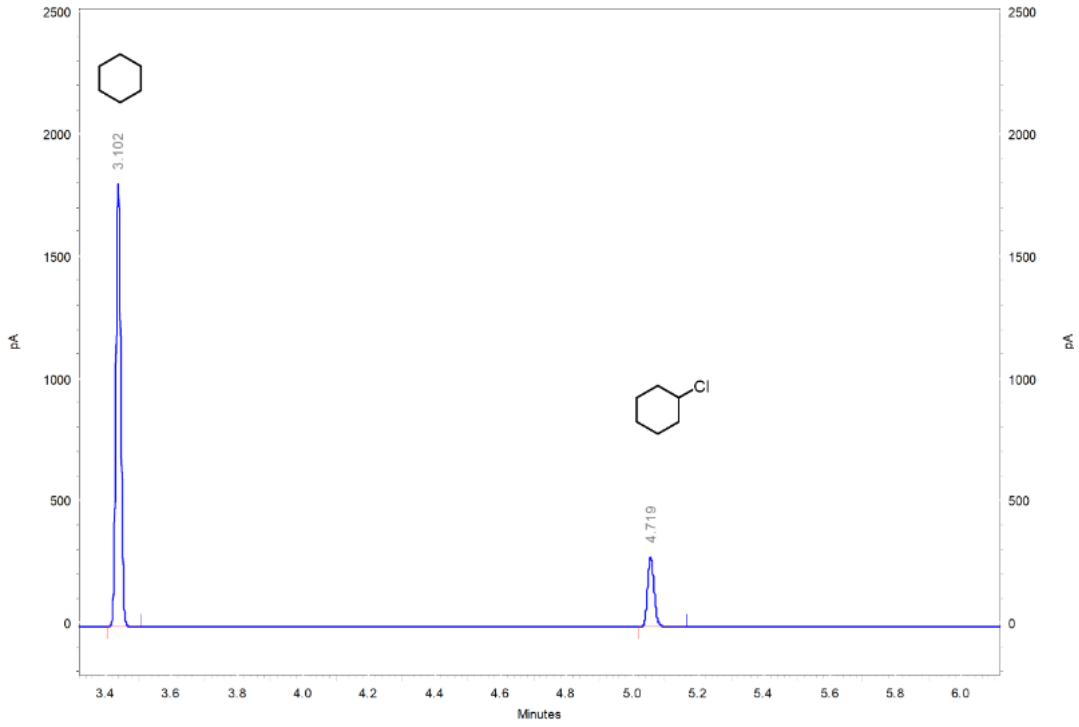
CHN analysis

Anal. calcd for $C_6H_{16}N_{10}NiCl_2.H_2O$ (ML1) (fw = 375.872 gm/mol): C, 19.17; H, 4.83; N, 37.27; found: C, 19.23; H, 4.75; N, 37.35.

Anal. calcd for $C_4H_{14}N_{10}NiCl_2$ (ML2) (fw = 331.819 gm/mol): C, 14.46; H, 4.21; N, 42.19; found: C, 14.23; H, 4.41; N, 40.87.

Gas Chromatography (GC) and GC-MS Analysis

(a)



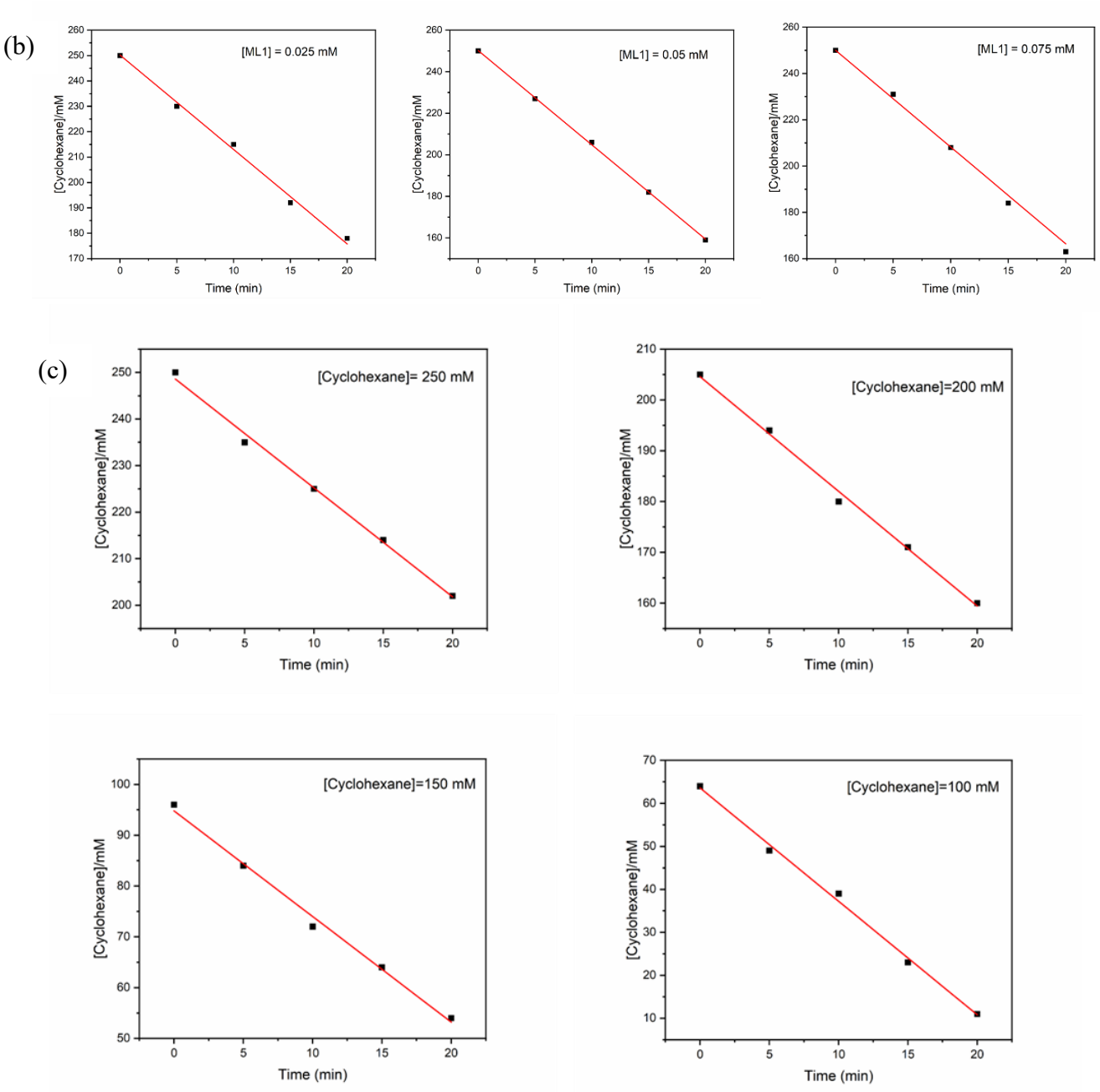


Fig. S9 (a) GC trace for oxidation of cyclohexane using ML1(0.05 µmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance); (b) Initial rate measurement for variation in [ML1] (0.025 µmol – 0.075 µmol). [Cyclohexane] = 250 mM, [NaOCl] = 0.03 mmol, RT, H_2O: $CHCl_3$ (7:3 v/v) 1 mL. After 0.05 µmol, a very insignificant change in the initial rate was observed. During GC analysis, the reaction mixture was diluted 2.6 times. Each data point was the average of three reaction sets measured in GC; (c) Initial rate measurement for [cyclohexane] variation (100 mM - 250 mM). [ML1] = 0.05 µmol, [NaOCl] = 0.30 mmol, RT, H_2O: $CHCl_3$ (7:3 v/v) 1 mL. During GC analysis, the reaction mixture was diluted 2.6 times. Each data point was the average of three reaction sets measured in Gas Chromatography.

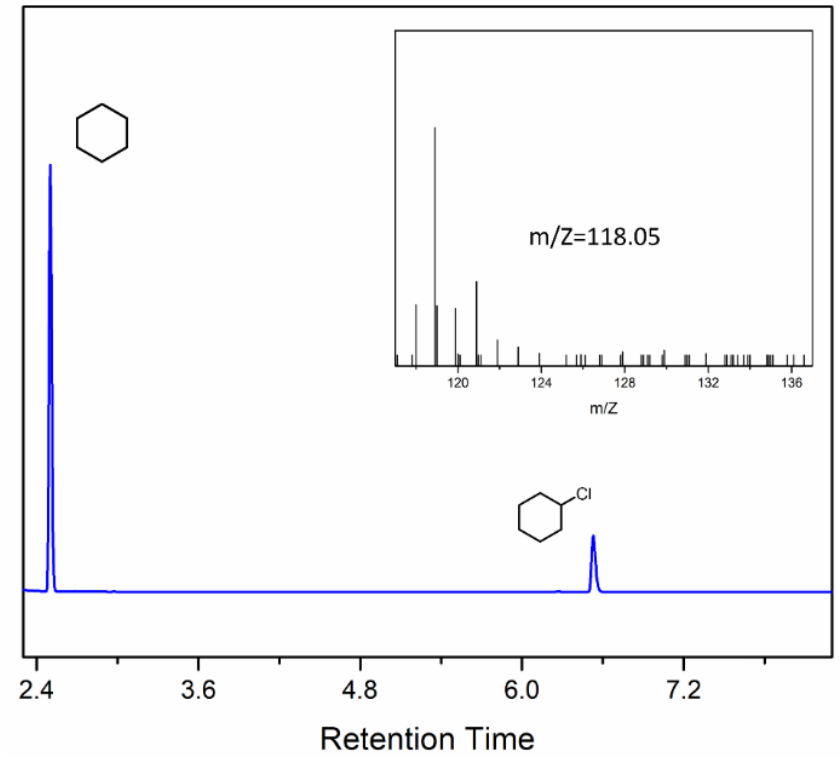


Fig. S10 GC-MS trace for oxidation of cyclohexane using ML1(0.05 µmol) in the presence of AcOH in complete H_2O. The inset shows the GC-MS spectra for 1-chlorocyclohexane.

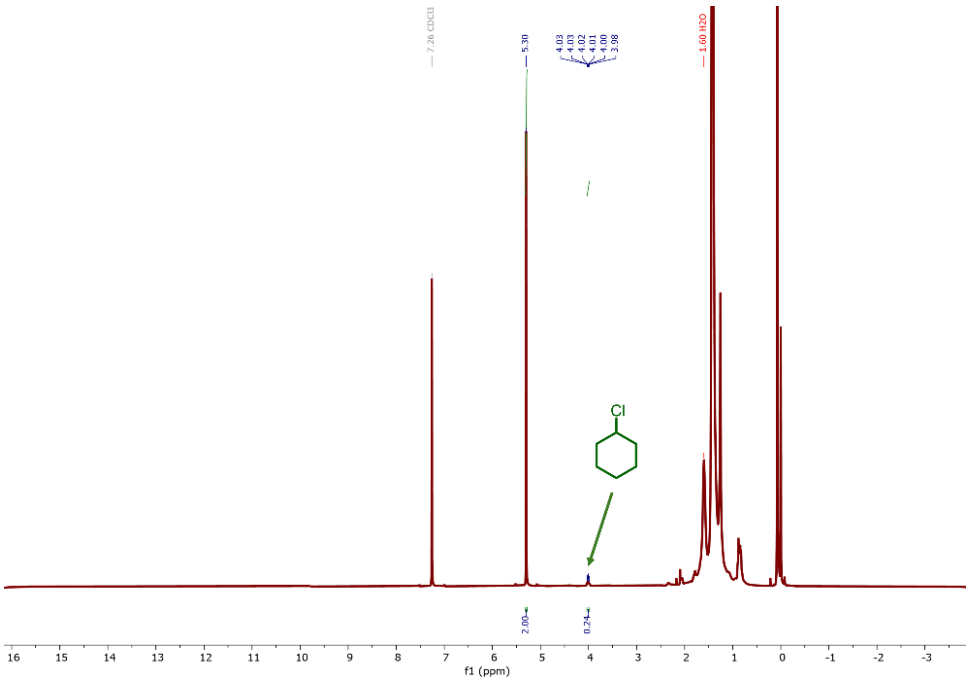


Fig. S11 ^{1}H-NMR spectrum of chlorination of cyclohexane in $CDCl_3$ using DCM as internal standard.

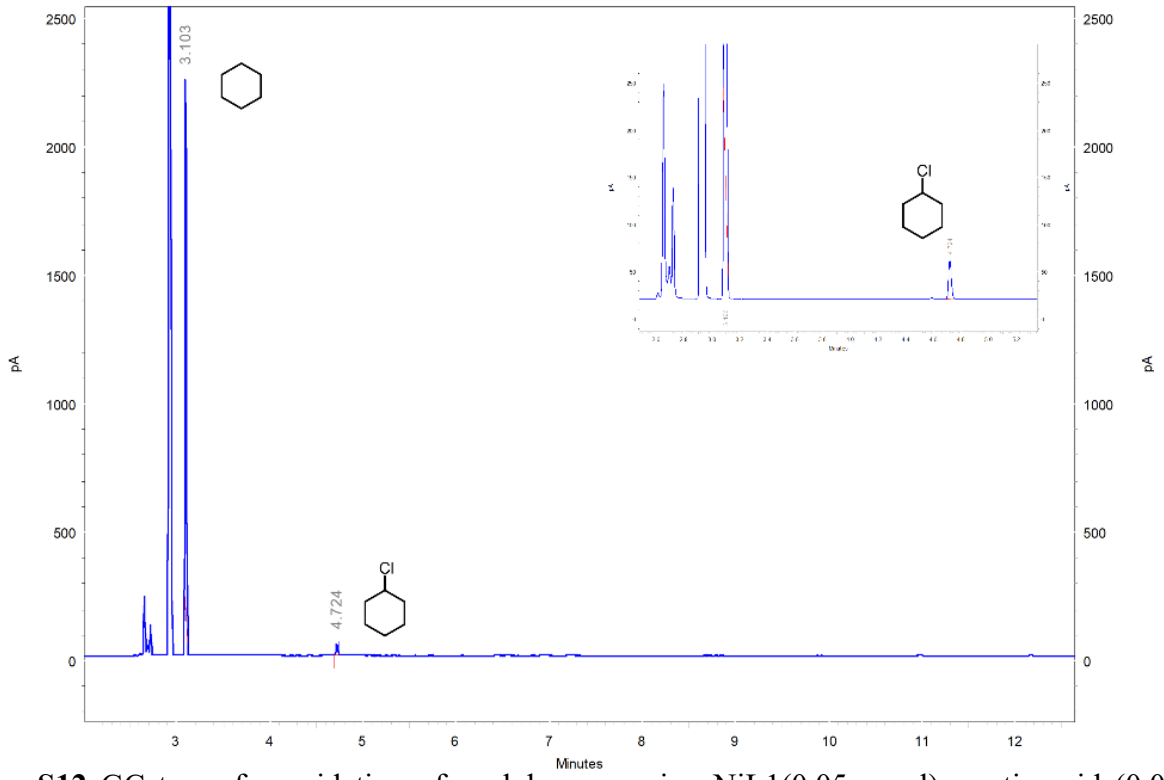


Fig. S12 GC trace for oxidation of cyclohexane using NiL1(0.05 µmol), acetic acid (0.075 mmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

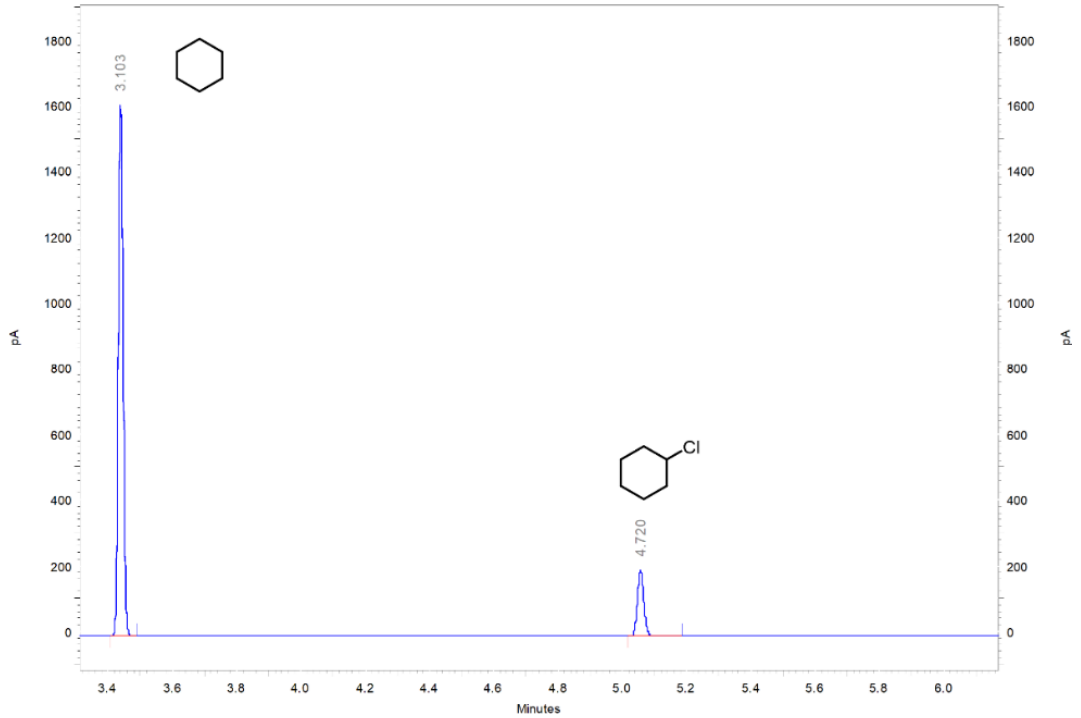


Fig. S13 GC trace for oxidation of cyclohexane using ML2(0.05 µmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

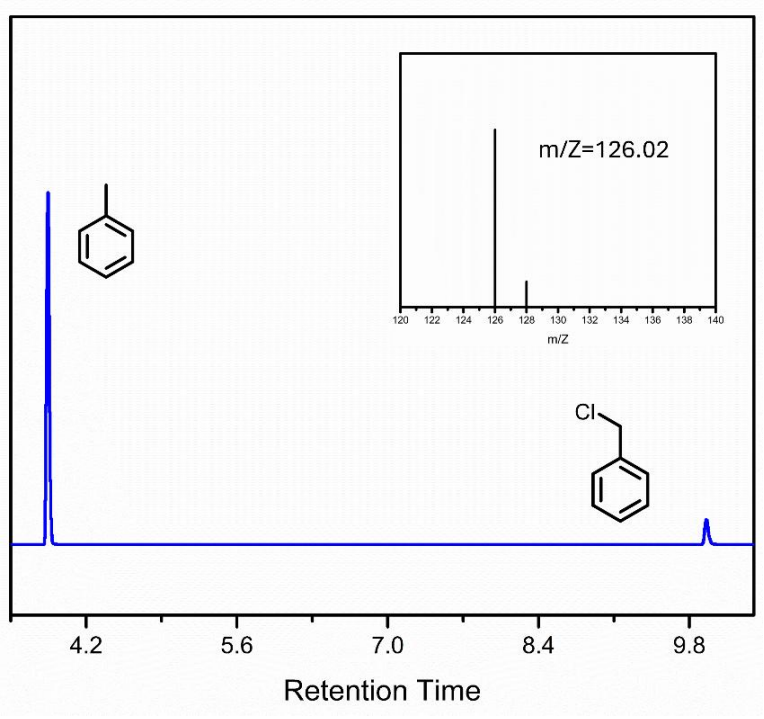


Fig. S14 GC-MS trace for oxidation of toluene using ML1(0.05 µmol) in the presence of AcOH. Inset shows the GC-MS spectra for benzylchloride.

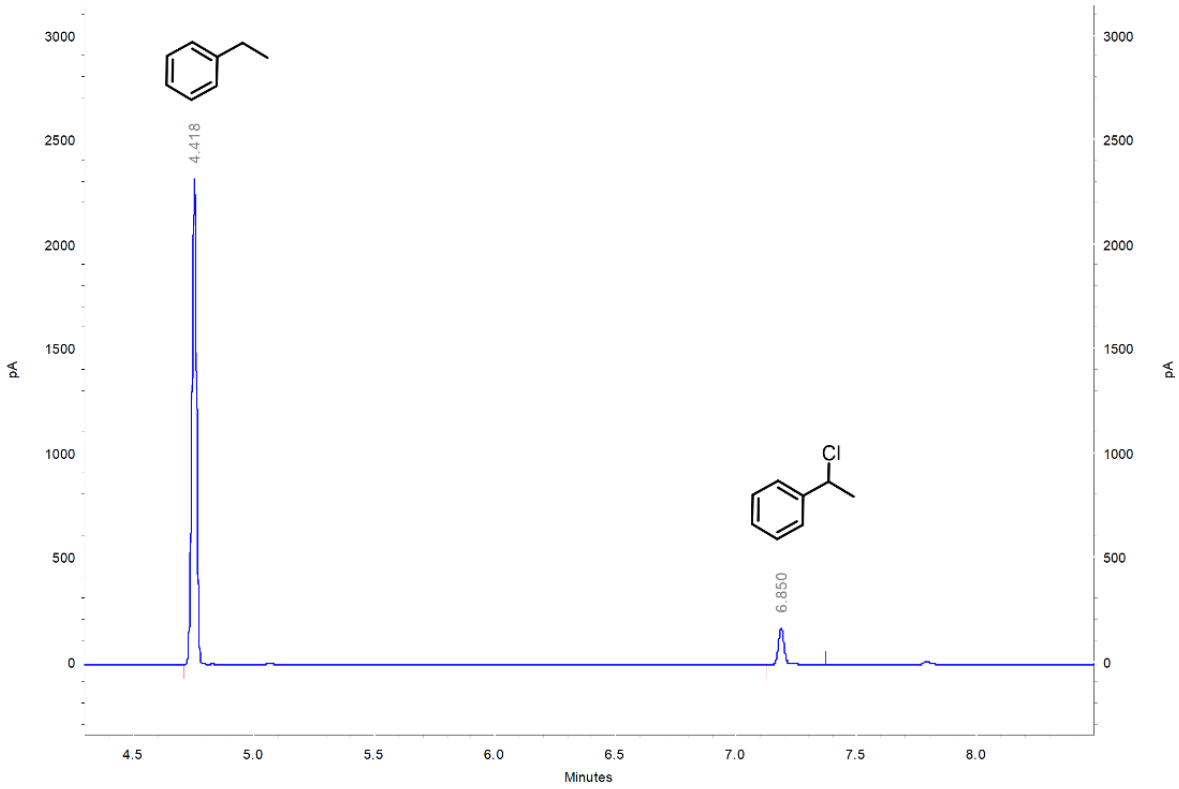


Fig. S15 GC trace for oxidation of ethylbenzene using ML1(0.05 µmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

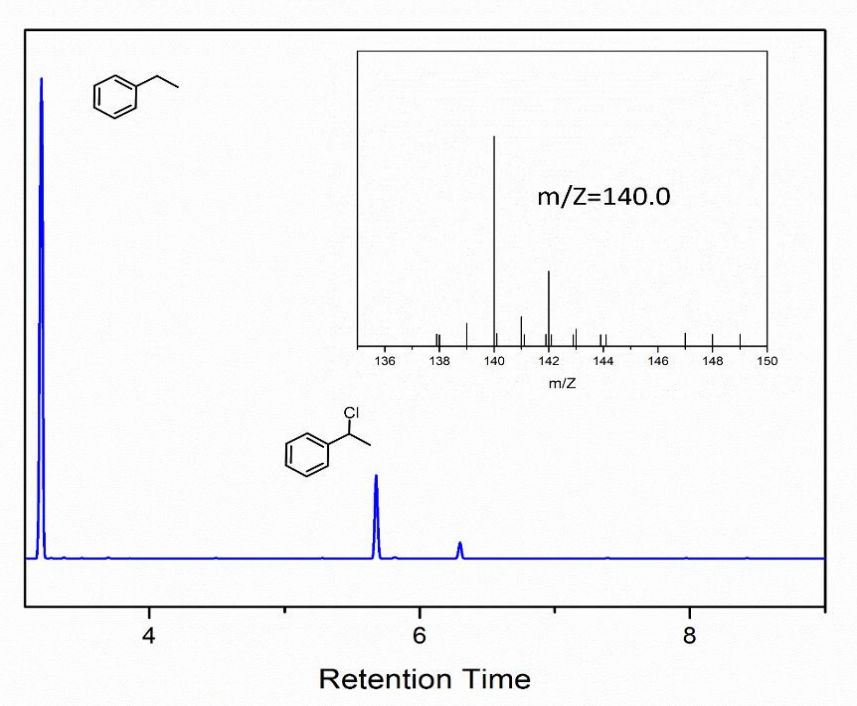


Fig. S16 GC-MS trace for oxidation of ethylbenzene using ML1 in presence of AcOH. Inset shows the GC-MS spectra for (1-chloroethyl)benzene and (2-chloroethyl)benzene).

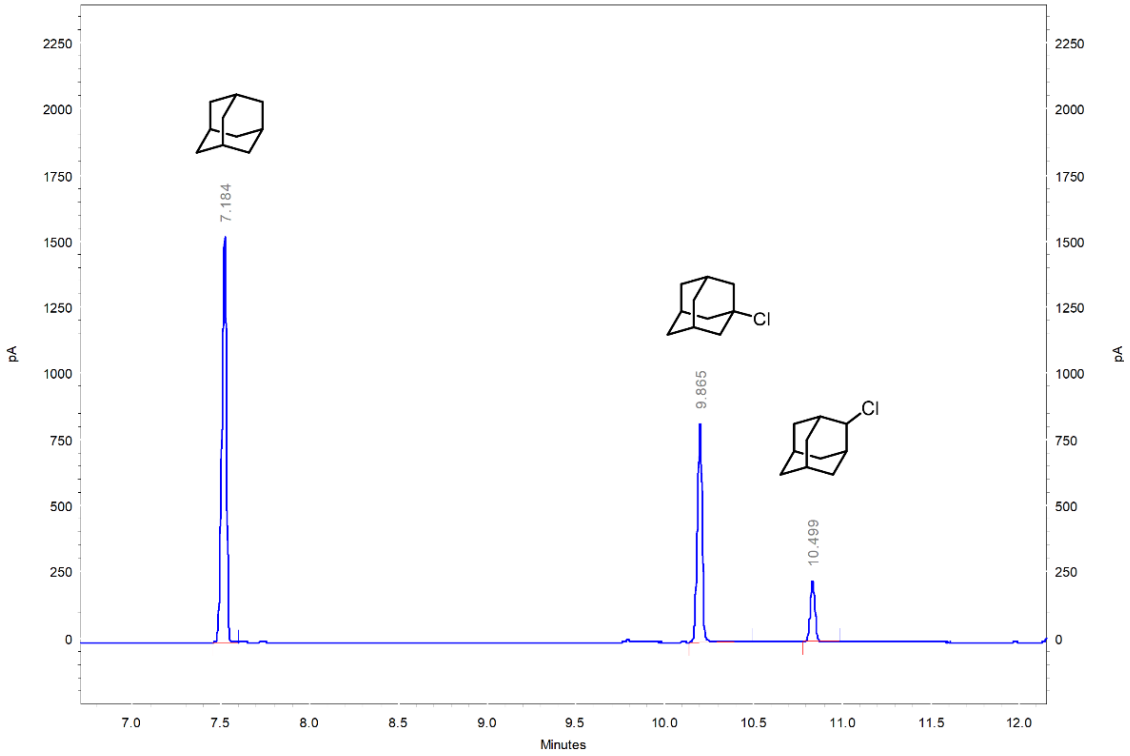


Fig. S17 GC trace for oxidation of Adamantane using ML1(0.05 μmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

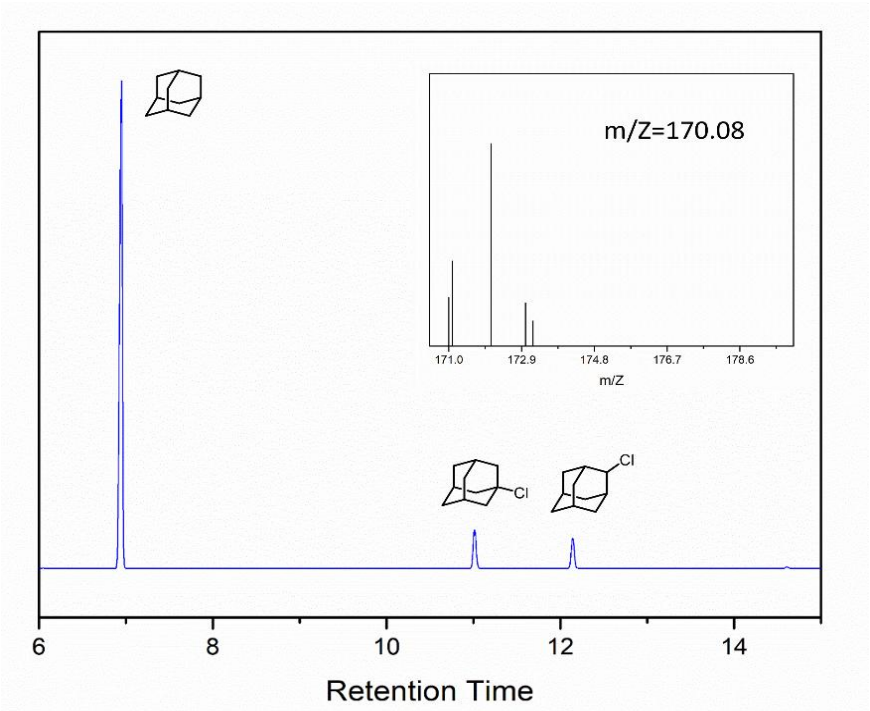


Fig. S18 GC-MS trace for oxidation of adamantane using ML1 in the presence of AcOH. Inset shows the GC-MS spectra for 1-chloroadamantane and 2-chloroadamantane.

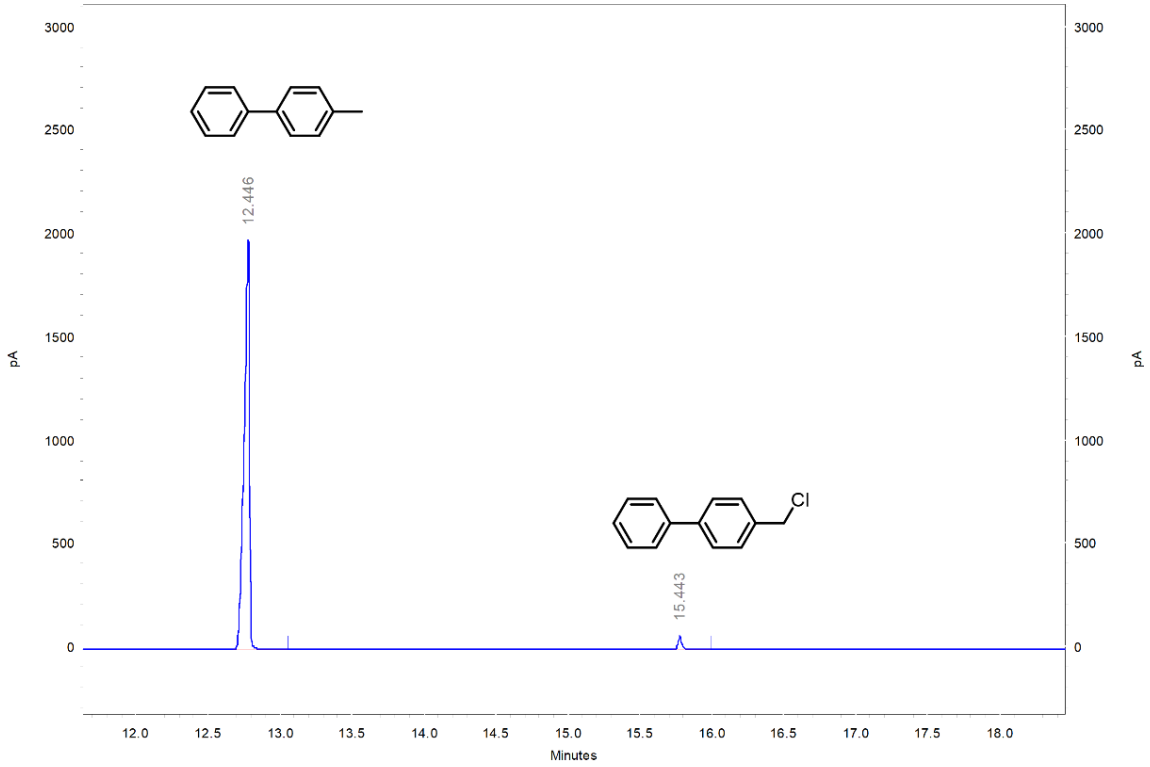


Fig. S19 GC trace for oxidation of 4-methylbiphenyl using ML1(0.05 μmol), solvent H_2O: $CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

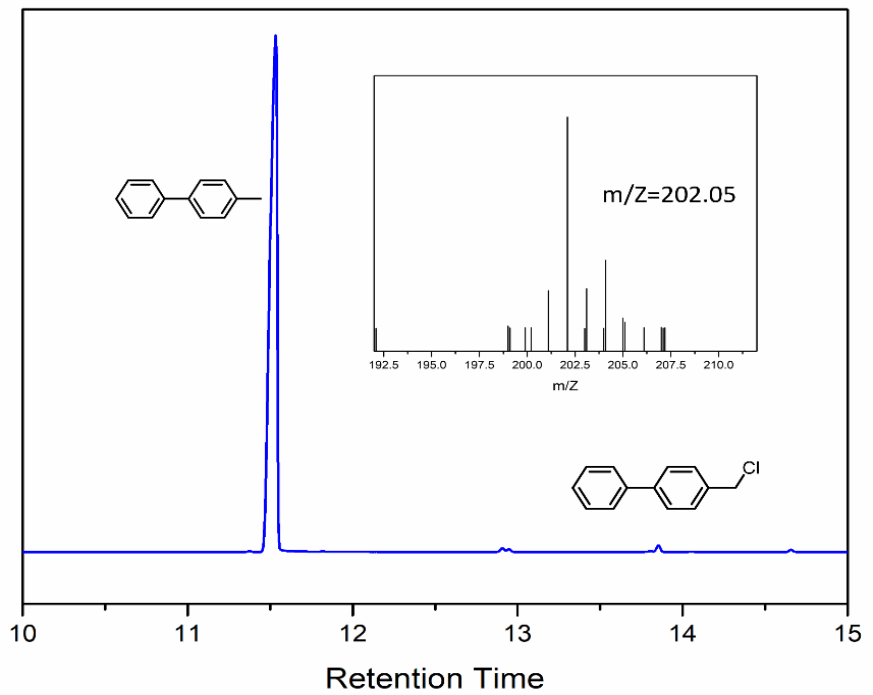


Fig. S20 GC-MS traces for oxidation of 4-methyl biphenyl using ML1(0.05 μmol) in the presence of AcOH. The inset shows the GC-MS spectra for 4-chloromethylbiphenyl. Peaks around 12.9 are unidentified.

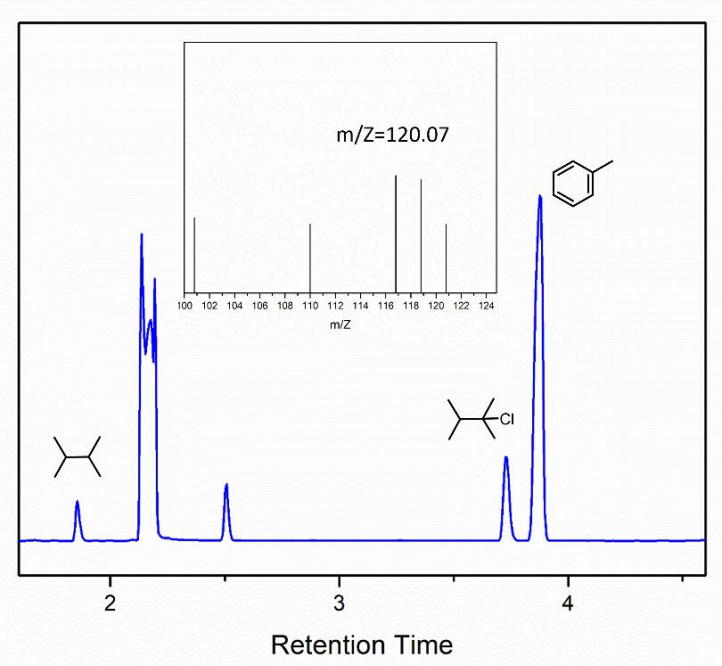


Fig. S21 GC-MS trace for oxidation of 2,3-dimethylbutane using ML1 in the presence of AcOH. Inset shows the GC-MS spectra for 2-chloro-2,3-dimethylbutane and toluene. The product is quantified by taking toluene as an internal standard as we do not have the authentic product. A known amount of toluene was added to the sample.

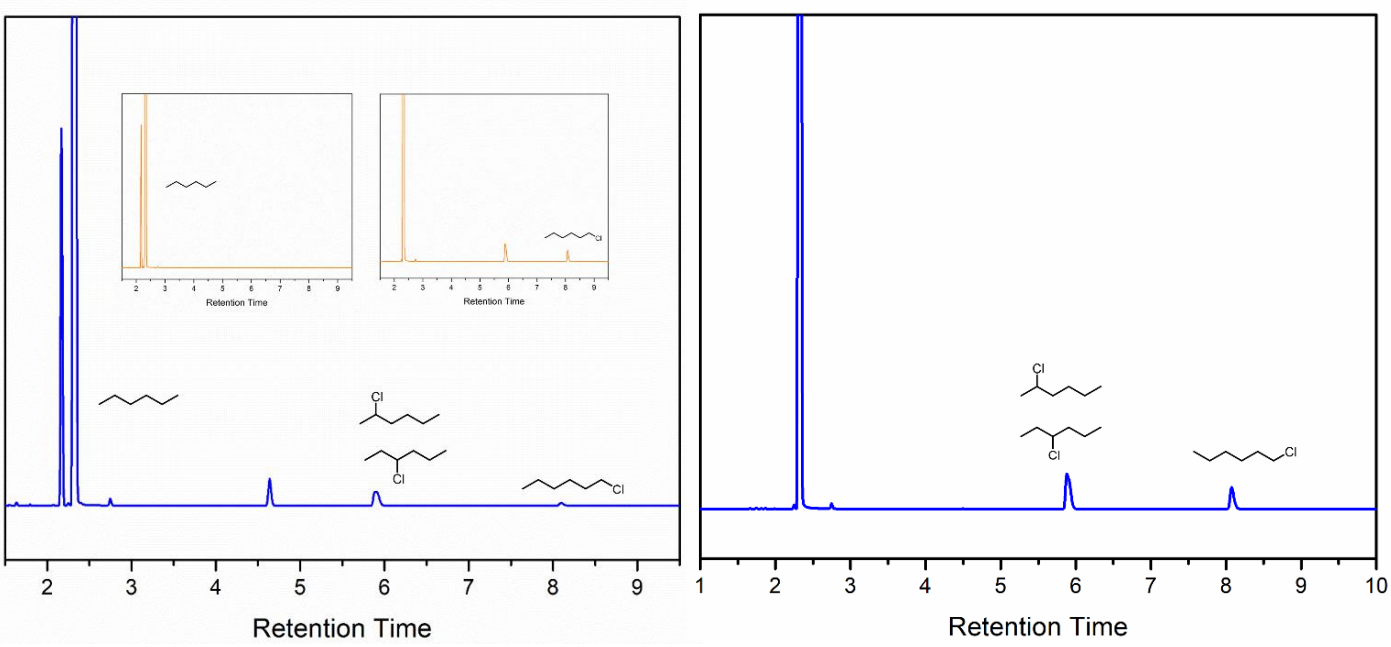


Fig. S22 GC-MS trace for oxidation of n-hexane using ML1(0.05 µmol) in the presence of AcOH in $CHCl_3$: H_2O (7:3). The inset shows the GC-MS spectra for 2° chlorohexane and 1° chlorohexane.

Explanation: GC-MS trace for oxidation of *n*-hexane using ML1(0.05 µmol) in the presence of AcOH(0.15 mmol) in H_2O: $CHCl_3$ (7:3). The inset shows the GC-MS spectra for 2-chlorohexane, 3-chlorohexane and 1-chlorohexane. The standard spectrum for known concentrations of n-hexane, 1-chlorohexane, 2-chlorohexane, and 3-chlorohexane is used for the quantification. The standard sample is prepared by adding 14 mM 2°chlorohexane (7 mM 2-chlorohexane and 7 mM 3-chlorohexane) and 2 mM 1-chlorohexane in $CHCl_3$: H_2O (7:3).

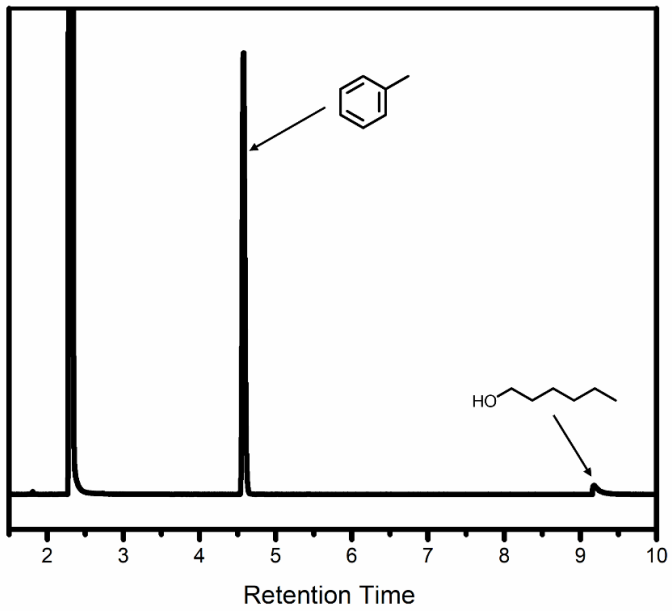


Fig. S23 GC-MS trace of 1-hexanol (2 µmol) using DCM as an internal standard. The inset shows the GC-MS spectra for 1-hexanol in H_2O: $CHCl_3$ (7:3).

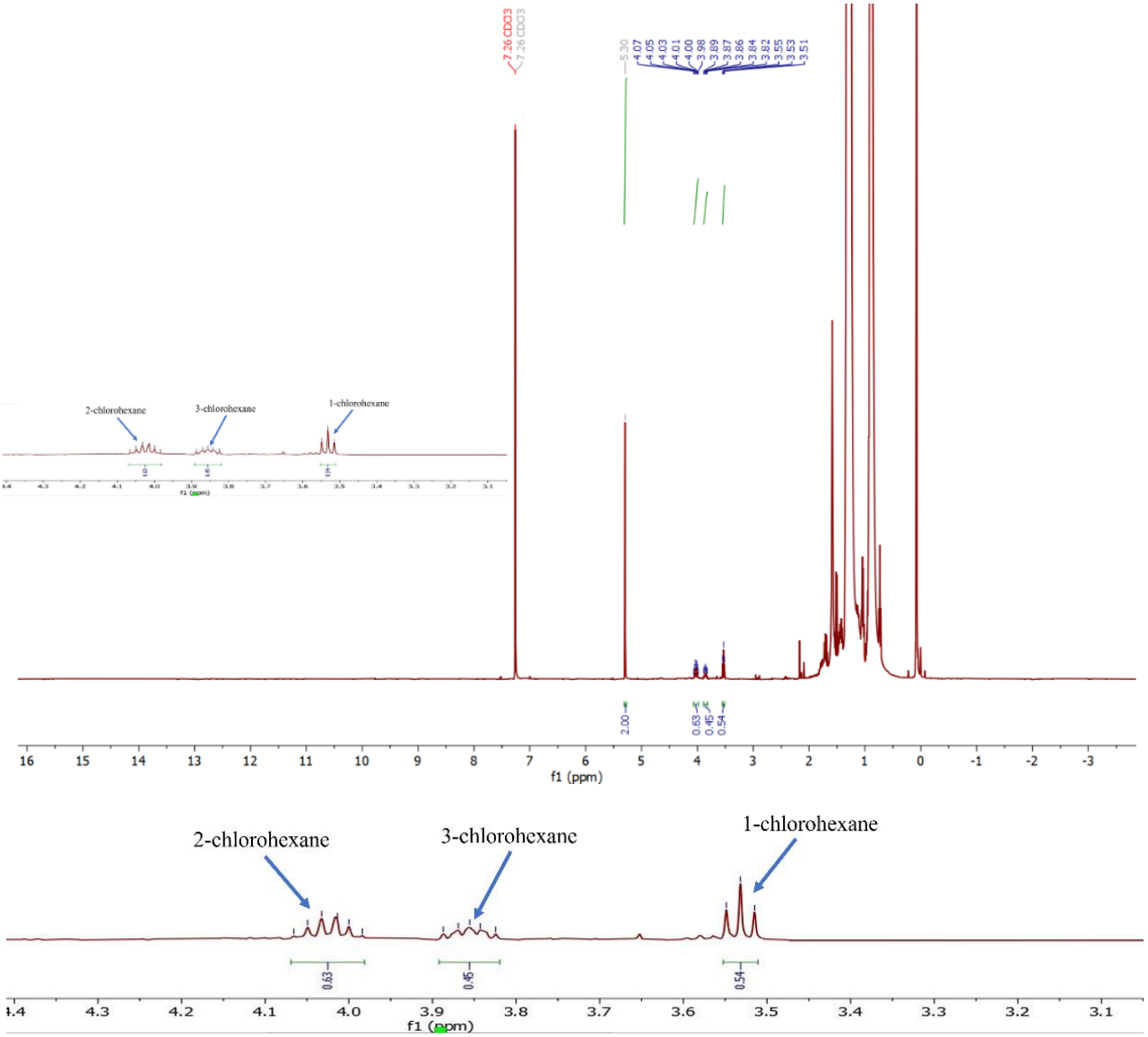


Fig. S24 ^{1}H-NMR spectrum of n-hexane in $CDCl_3$ using DCM as internal standard.

Explanation: The ratio of 1-,2-, and 3-substituted products of this substrate is determined by the integration of chloro products in the ^{1}H-NMR spectroscopy. The TON of 2° chlorohexane is 108 and 1° chlorohexane is 27 determined by the integration of ^{1}H NMR spectroscopy. For quantification 5 mM dichloromethane is used as an internal standard.

Calculation:

$$\frac{n_p}{n_{is}} = \frac{\frac{I_P}{N_p}}{\frac{I_{is}}{N_{is}}}$$

n_p = Number of moles of product
n_{is} = Number of moles of internal standard (0.05×10^{-3} mmoles of DCM)
I_P = Integration of product
N_p = Number of protons
I_{is} = Integration of internal standard (2 for DCM)
N_{is} = Number of protons in DCM (2 for DCM)

For 1-chlorohexane:

$$\Rightarrow \frac{n_p}{0.05\times10^{-3}mmoles} = \frac{\frac{0.54}{2}}{\frac{2}{2}} = 1.35\times10^{-3}mmoles$$

For 2-chlorohexane:

$$\Rightarrow \frac{n_p}{0.05\times10^{-3}mmoles} = \frac{\frac{0.63}{1}}{\frac{2}{2}} = 3.15\times10^{-3}mmoles$$

For 3-chlorohexane:

$$\Rightarrow \frac{n_p}{0.05\times10^{-3}mmoles} = \frac{\frac{0.45}{1}}{\frac{2}{2}} = 2.25\times10^{-3}mmoles$$

Ratio:

1-chlorohexane: 2-chlorohexane: 3-chlorohexane
1: 2.3: 1.6

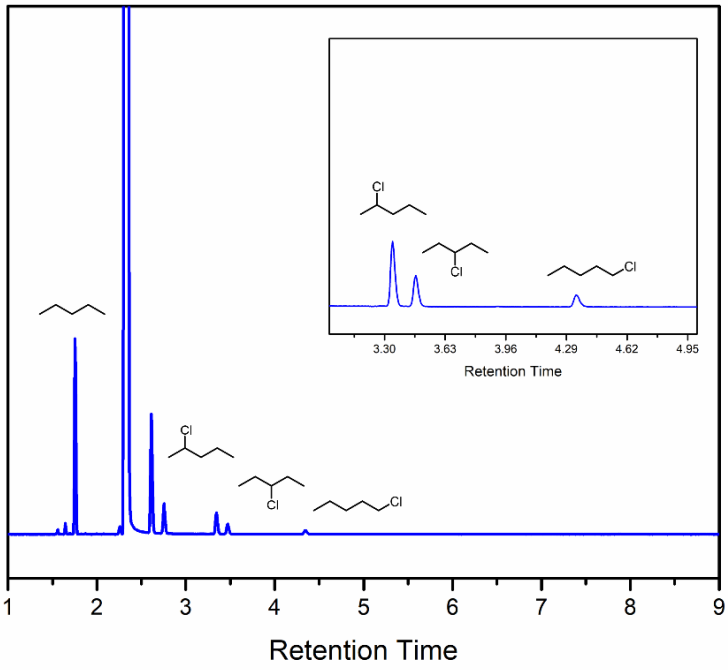


Fig. S25 GC-MS trace for oxidation of n-pentane using ML1(0.05 µmol) in the presence of NaOCl(0.30 mmol), AcOH(0.15 mmol) in H_2O: $CHCl_3$ (7:3). The inset shows the GC-MS spectra for 2-chloropentane, 3-chloropentane and 1-chloropentane.

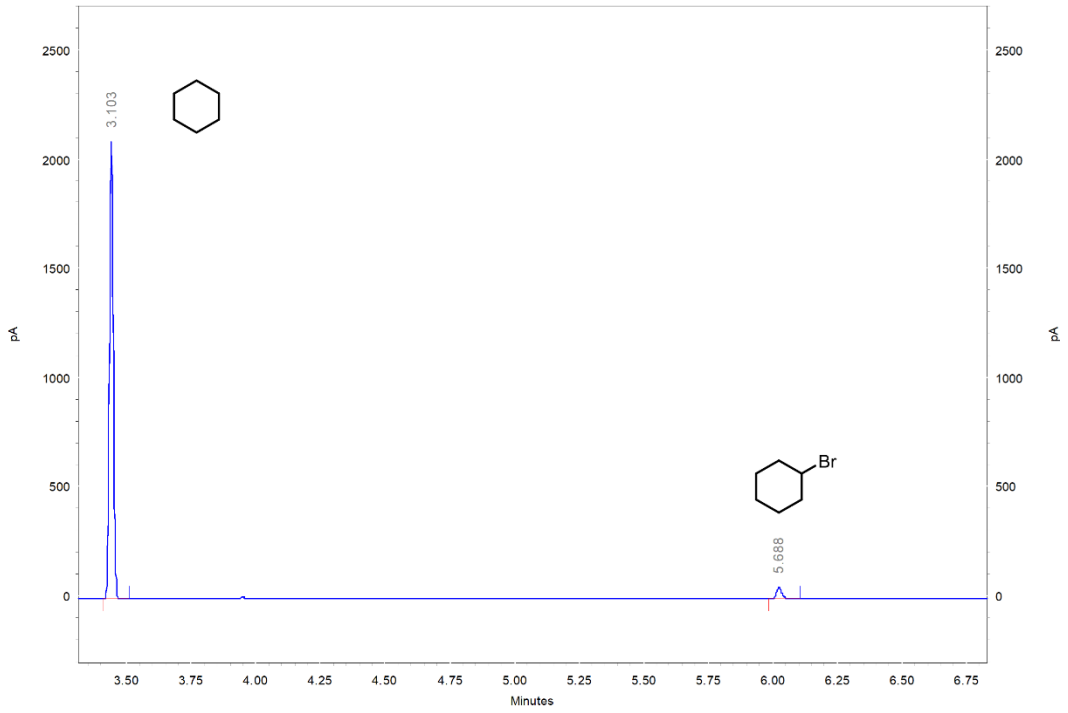


Fig. S26 GC trace for oxidation of cyclohexane using ML1(0.05 µmol), NaBr(0.03 mmol), NaOCl(0.03mmol), acetic acid(0.15 mmol), solvent H_2O:$CHCl_3$ 7:3 (X axis: in minute; Y axis: % abundance).

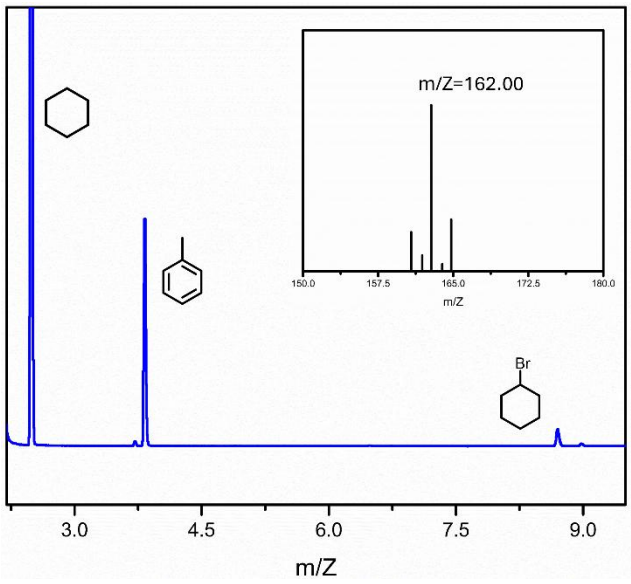


Fig. S27 GC-MS traces for oxidation of cyclohexane using ML1(0.05 µmol) in the presence of AcOH, NaBr(0.03 mmol), NaOCl(0.03mmol), acetic acid(0.15 mmol), solvent H_2O:$CHCl_3$ 7:3. The inset shows the GC-MS spectra for chlorocyclohexane.

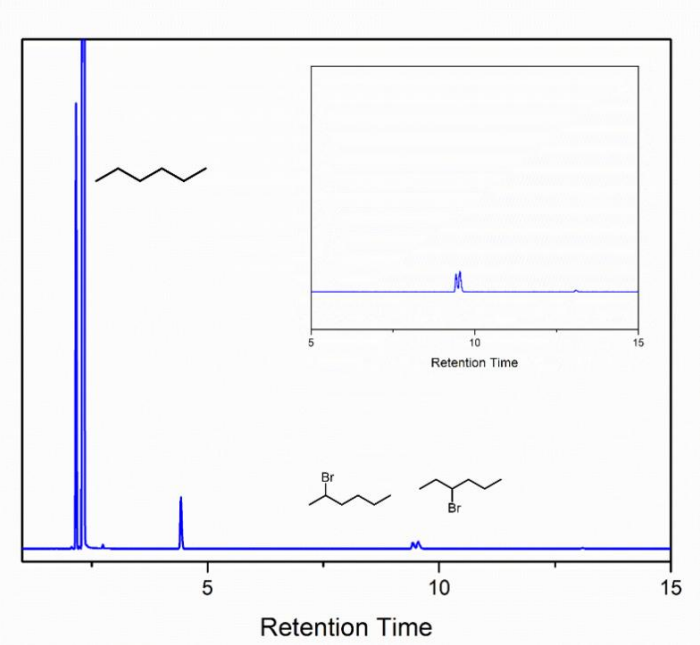


Fig. S28 GC-MS trace for oxidation of n-hexane using ML1(0.05 μmol) in the presence of AcOH (0.15 mmol), NaOCl (0.30 mmol), NaBr (0.30 mmol) in H_2O: $CHCl_3$ (7:3). The inset shows the GC-MS spectra for 2-bromohexane, 3-bromohexane and 1-bromohexane.

Table S2 Conversion for substrates.

Substrate	TON	Conversion (%)
Cyclohexane	680 ± 60	22
Toluene	200 ± 20	6.4
Ethylbenzene	370 ± 30	12
Adamantane	1600 ± 200 (3°); 320 ± 30 (2°)	62; 12.4
Methylbiphenyl	260 ± 25	8.4

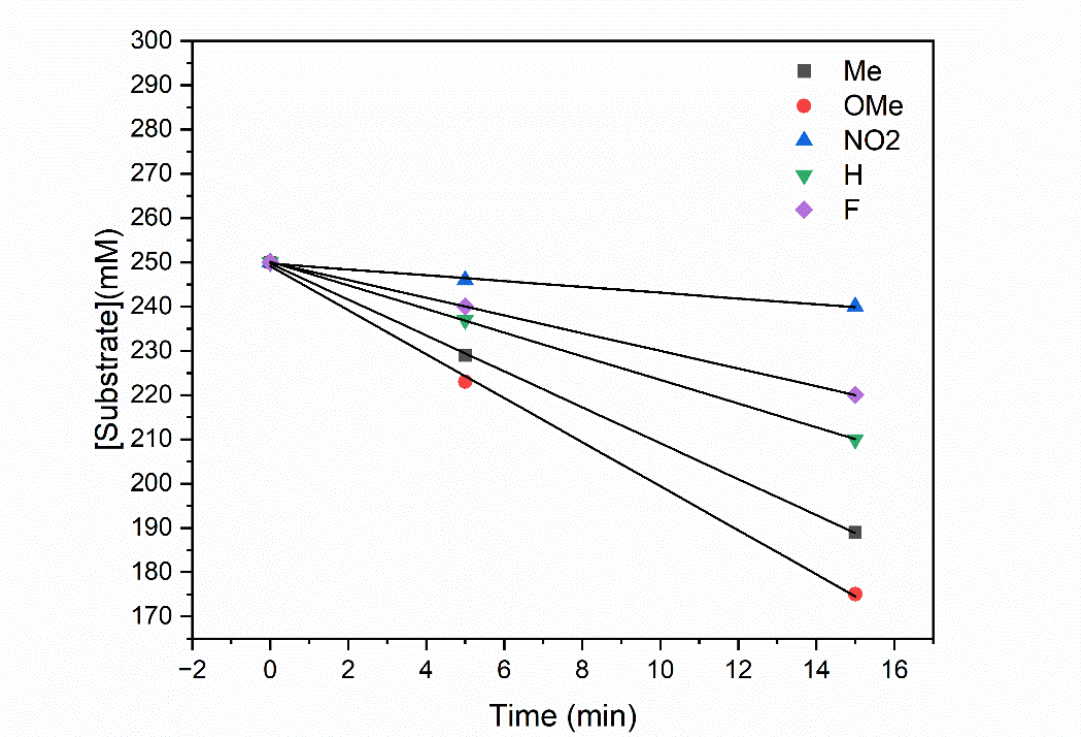


Fig. S29 Initial rate measurement for [ML1] (0.05 mM). [Substrate](4-methylethylbenzene, 4-methoxyethylbenzene, ethylbenzene, fluoroethylbenzene, nitroethylbenzene) = 250-50 mM, [NaOCl] = 300 mM, [AcOH] = 150 mM, Temperature ~25 °C, H_2O:$CHCl_3$ (7:3 v/v) 1mL. During GC MS analysis, the workup of the reaction mixture is done by 500 µl $CHCl_3$. Each data point was the average of three reaction sets measured in GC.

Spectroscopic characterization of the Ni (III) intermediates

Ni(III) intermediates were characterized by UV-Vis, HR-MS and EPR. UV-Vis spectral of complex ML1(0.05 mM) changes on the addition of AcOH and NaOCl.

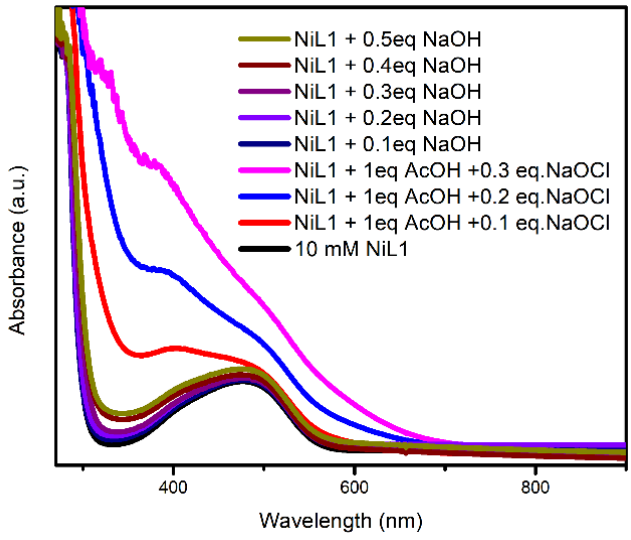


Fig. S30 Ni(III) intermediates were characterized by UV-Vis.

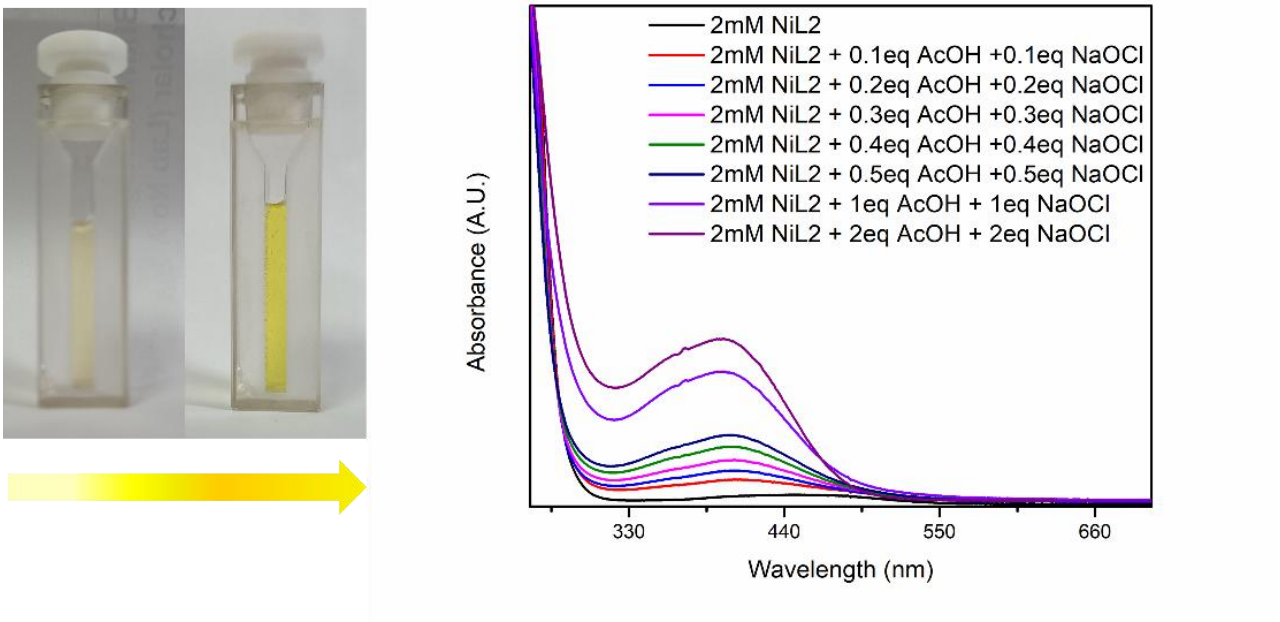
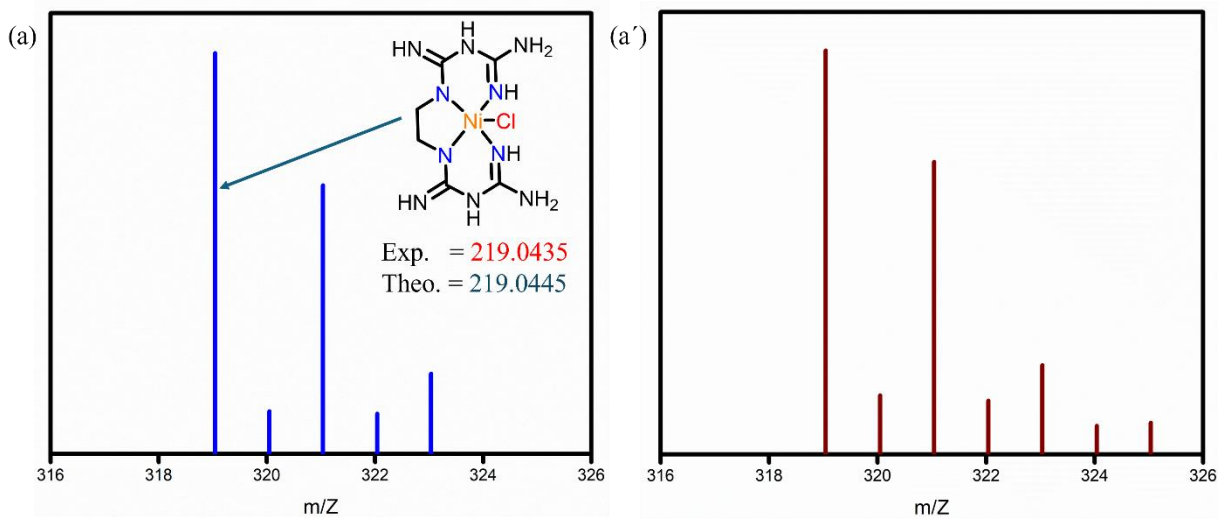


Fig. S31 Color change after addition of AcOH (2 eq.) and NaOCl (2 eq.) to ML2 complex (2 mM).



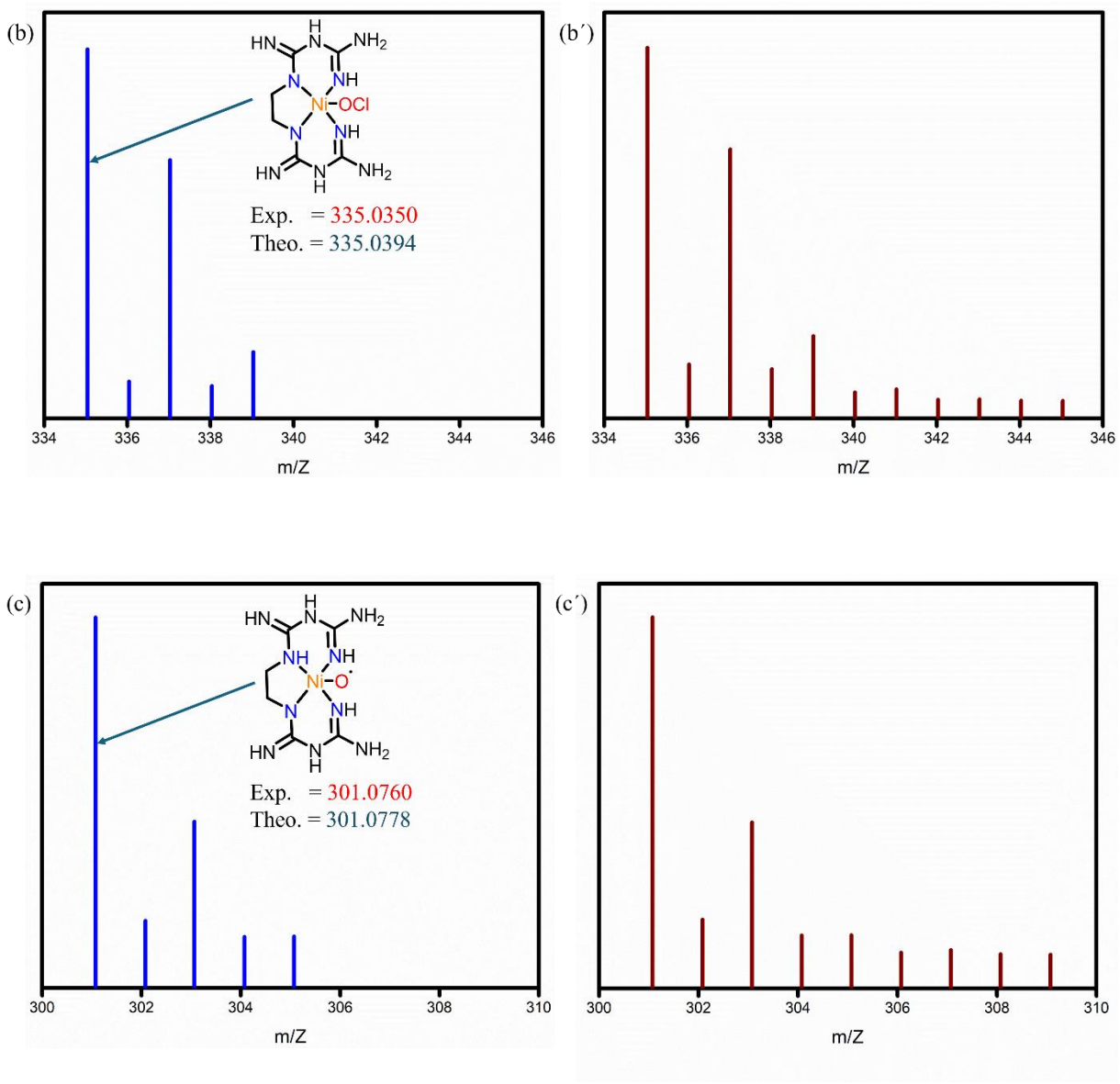


Fig. S32 HR-MS spectrum of high-valent Ni(III) intermediates on the addition of 2 eq. AcOH and 2 eq. NaOCl to 5mM ML1; (a) *m/z* for [Ni(III)L1-Cl], formula: $C_6H_{14}N_{10}ClNi$, ; (b) *m/z* for [Ni(III)L1-OCl], formula: $C_6H_{14}N_{10}ClONi$; (c) *m/z* for [Ni(III)L1-OH], formula: $C_6H_{14}N_{10}ClNi$; The same peak could be attributed to $[Ni(III)L1\text{-}O^{\cdot}]^{+}$ when considering monoanionic form of the ligand L1. Theoretical *m/z* values were calculated (a', b', c') using Isotope Distribution Calculator under MassHunter software.

EPR study

X-band EPR spectra were recorded using a Bruker EMX 1444 EPR spectrometer (fitted with a quartz Dewar for measurement at 120 K) operating at 9.32 GHz. The EPR spectra were calibrated with diphenylpicrylhydrazyl, DPPH (g = 2.0037). Spectra were treated using Bruker WinEPR software and simulated using Bruker SimFonia software.

EPR of ML1

X-band EPR spectrum (ν = 9.32 GHz, power = 2.01 mW, receiver gain = 1 × 10^2, modulation frequency = 100 KHz, modulation amplitude = 10.00 G) recorded for 5 mM solution of ML1 in DMF at 85 K (lower trace). A simulated spectrum (upper trace) with parameters: g_x= 2.271, g_y= 2.23, and g_z= 2.010 was given in the main manuscript (Fig. 3).

EPR of ML2

Multiple trials have been carried out for the ML2 complex. Due to the poor quality of data, its simulation isn't possible. But, from the magnetic field value the g values (g_x, g_y, g_z) are assigned (black arrows). Noteworthy, the g values (g_x, g_y, g_z) for ML2 are completely distinct from ML1.

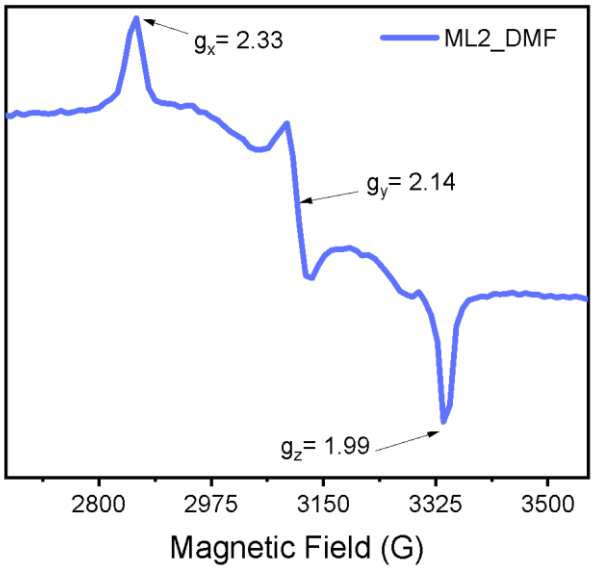
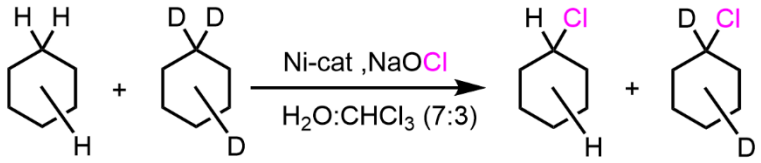


Fig. S33 EPR spectrum of ML2 in DMF at 100K.

Determination of the Kinetic Isotope Effect (KIE)



Scheme S1 Cyclohexane and deuterated cyclohexane chlorination.

A mixture of cyclohexane (0.25 mmol) and cyclohexane-d_{12} (0.25 mmol) were added to a solution of the NiL1 (0.05 µmol) in $H_2O/CHCl_3$ (7:3 v/v) 1mL. Then, acetic acid (0.15 mmol) and NaOCl (0.30 mmol) were added slowly using a gastight syringe to the reaction mixture and it was stirred at RT for 30 minutes. The workup is done using 500 µl $CHCl_3$. The product distribution was calculated by GC-MS. The kinetic isotope effect (KIE) value for chlorocyclohexane production was calculated by (moles of chlorocyclohexane)/(moles of chlorocyclohexane-d_{11}) (Ratio K_H/K_D=12.18).

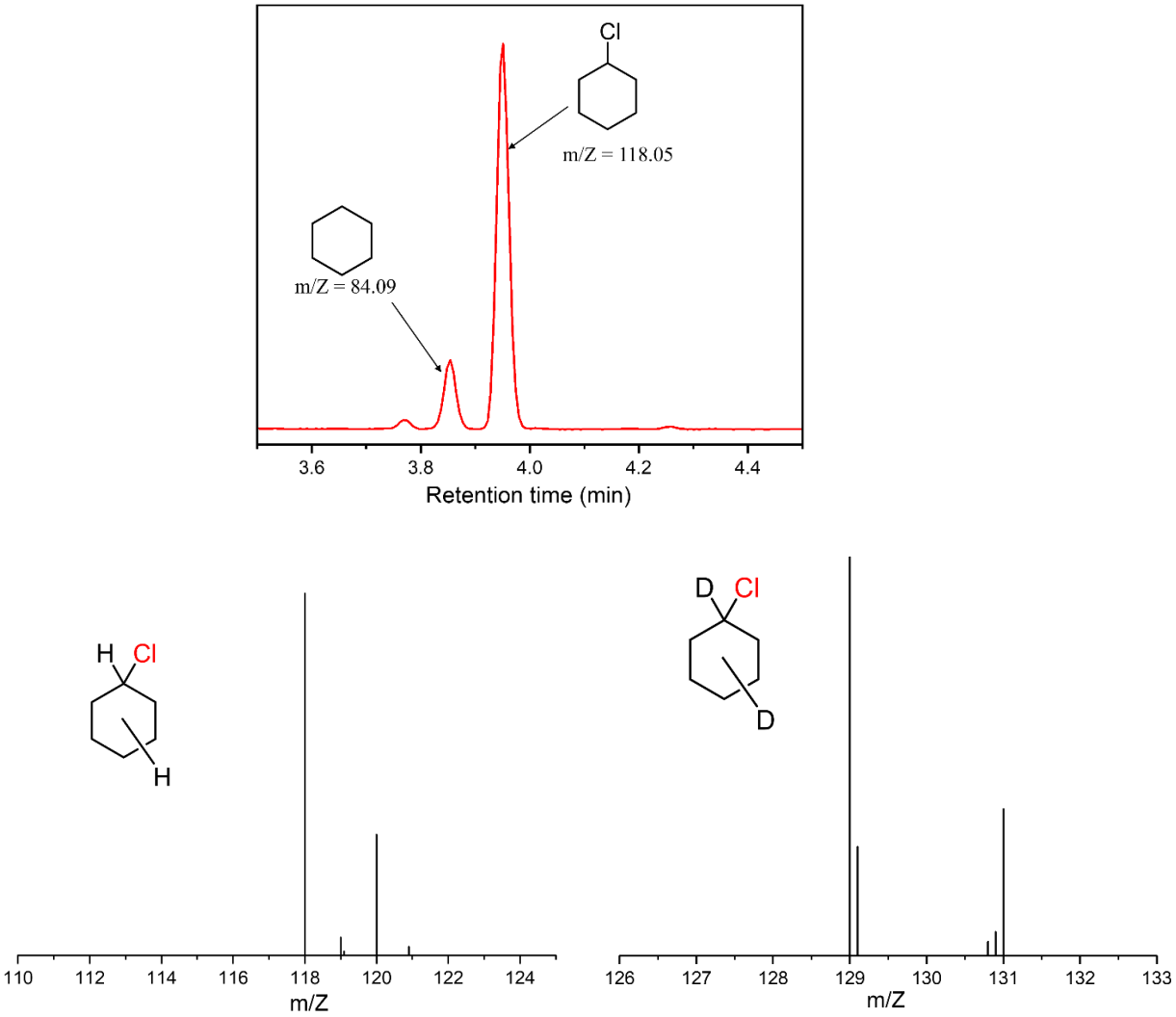


Fig. S34 Isotope patterns of chlorocyclohexane and d_{11}-chlorocyclohexane on the GC-MS spectra obtained after 30 minutes in the reaction of cyclohexane (0.25 mmol) and cyclohexane-d_{12} (0.25 mmol) with NaOCl (0.30 mmol), acetic acid (0.15 mmol) catalyzed by ML1 (0.05 μmol).

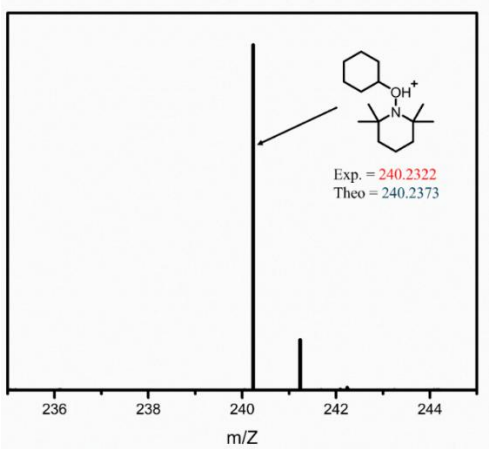
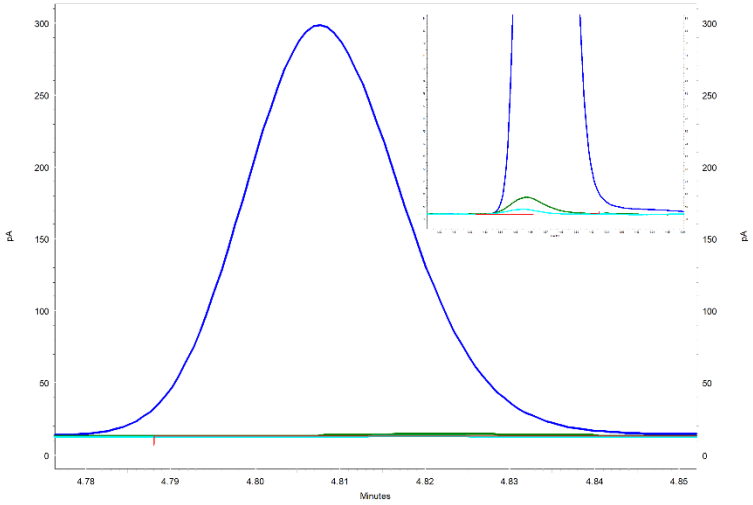


Fig. S35 HR-MS spectrum of TEMPO and cyclohexane adduct on the addition of TEMPO and NaOCl in the presence of ML1(0.05 μmol).

A mixture of cyclohexane (0.25 mmol) and TEMPO (0.50 mmol) were added to a solution of the NiL1 (0.05 µmol) in $H_2O/CHCl_3$ (7:3 v/v) 1mL. Then, acetic acid (0.15 mmol) and NaOCl (0.30 mmol) were added slowly using a gastight syringe to the reaction mixture and it was stirred at RT for 30 minutes. The workup is done using 500 µl $CHCl_3$.The product was identified by HR-MS.



[TEMPO]	Area
-	21,20,683
2 eq.	36,570
3 eq.	10,258

Fig. S36 Effect of TEMPO. GC trace for chlorination cyclohexane using ML1 (0.05 µmol), solvent H_2O: $CHCl_3$ 7:3 (a) Absence of TEMPO (blue) (b) In presence of 2 eq. TEMPO wrt NaOCl(green) (c) In presence of 3 eq. TEMPO wrt NaOCl (cyan). (X axis: in minutes; Y axis: % abundance).

DFT Calculation

The theoretical calculations (DFT) were performed using the Gaussian 09 program.[10] Unrestricted (spin-polarized) calculations were conducted in both the gas phase and implicit water solvent. Geometries were optimized using the B3LYP hybrid functional with the 6-311+G(d,p) basis set.[11-16] Subsequently, a correction of the total energy was performed using the hybrid M06L functional with the 6-311+G(d,p) basis set.[17-18] The polarized continuum model (PCM) was utilized to incorporate the role of solvent.[19] To identify the transition states, Hessian calculations and intrinsic reaction coordinate (IRC) searches were performed. Potential energy scanning was conducted to locate the highest energy point along the potential energy surface. The geometries of these high-energy points were optimized using Berny's optimization approach to obtain the transition states. Frequency analysis was performed to verify the transition states and to identify the imaginary frequency corresponding to the expected reaction coordinate. All the free energies of intermediates were reported with respect to the [Ni(III)-L-O•] intermediate. Zero-point, enthalpy, and entropic corrections were made at room temperature using the harmonic approximation. TD-DFT (Time Dependent-Density Functional Theory) calculations were performed to model the UV-Vis spectra of the Ni complexes and to understand the involved electronic transitions in metal complexes.[20] To understand the characteristic nature of nickel oxyl intermediate and their reactivity, we performed natural bonding orbital analysis (NBO) using Gaussian 09.[21-23]

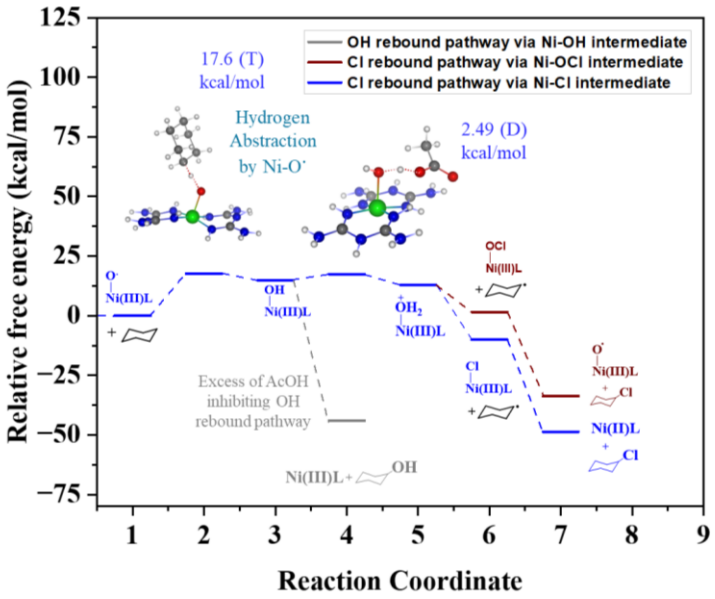


Fig. S37 Free energy diagram of ML2 complex.

NBO Analysis

To quantify the radical nature of Ni oxyl complexes (ML1 and ML2), we analysed the spin densities using Natural Bonding Orbital (NBO) calculations. For both the MLx complexes, we have observed high spin densities (~1.55) on the oxygen centre. The spin densities and the calculated partial charges on Ni and O atoms for the MLx complexes are given in Table S5. The observed Ni-O bond length for the MLx complexes varies in the range of 1.73-1.75 Å, denoting a single bond between Ni and O. The spin density and bond length values indicate the presence of an unpaired electron on the oxygen center (radical behaviour). The late transition metal complexes in C_{4V} symmetry (tetragonal and square pyramidal complexes) have less possibility to form metal oxo species with M-O double bond (M^{n+}=O) due to the occupancy of the antibonding molecular orbitals. This phenomenon is denoted as the "Oxo Wall" concept.[24] The oxyl [Ni (III)-L-O$^{\bullet}$] intermediate observed in our study shows a radical behaviour on account of the Oxo wall.[25, 26] The presence of the unpaired electron on the O atom eventually enhances the reactivity of Ni-oxyl intermediates and allows better activity for the oxidative C-H bond activation.

Table S3 Comparison of ML1 complexes experimental and theoretical bond lengths.

Atom. No.	ML1	ML1 (DFT)
Ni(1)-N(3)	1.859	1.892
Ni(1)-N(6)	1.870	1.902

Ni(1)-N(1)	1.870	1.893
Ni(1)-N(8)	1.861	1.904

Table S4 The computed NBO spin density and NBO charge values, bond distance (Å) of the nickel oxyl intermediate spices.

Properties	**Complex**	**NiL1**	**NiL2**
Spin	$O^{\cdot}$	1.550	1.556
	Ni	1.658	1.670
Charge	$O^{\cdot}$	-0.240	-0.239
	Ni	0.882	0.875
Bond distance	Ni-$O^{\cdot}$	1.72658	1.74961

Cartesian Coordinates (Å) for DFT

ML1-S							
Ni	-0.00102	-0.30190	0.09440	H	-1.11544	-2.51516	0.63702
N	-1.36590	-1.60161	0.27498	H	0.64865	2.36167	1.66065
N	1.30743	1.08029	0.12981	H	1.27620	3.22746	0.24670
N	-1.28671	1.09597	-0.01203	H	-1.28033	3.16077	0.52416
N	1.34008	-1.63618	0.08454	H	3.19574	2.92149	0.29691
N	3.18355	-0.25643	-0.29686	H	4.47555	1.79325	0.21872
N	-3.20187	-0.24855	-0.22122	H	-0.61346	2.78242	-1.08410
N	-3.38104	2.01739	-0.53756	H	-4.38524	1.92805	-0.51248
N	3.44928	-2.53769	-0.39458	H	-4.13046	-0.27766	-0.61875
C	2.60791	-1.50472	-0.18567	H	-3.02110	2.94648	-0.67976
N	-3.54331	-2.47103	0.24993	H	4.45139	-2.43138	-0.34657
N	3.48894	1.97571	0.11884	H	4.10174	-0.21779	-0.71738
C	-2.65225	-1.46605	0.12501	H	3.10291	-3.48453	-0.41850
C	0.70617	2.35261	0.56786	H	1.07364	-2.60519	0.21595
C	2.59711	0.96823	0.00655	H	-4.52442	-2.29506	0.40691
C	-2.56307	0.98460	-0.24362	H	-3.23017	-3.41711	0.40568
C	-0.68418	2.44041	-0.04498				

ML1Oradical-Q							
N	1.29669	-1.58803	-0.55552	H	-0.39471	2.46982	-1.60031
N	-1.24989	1.16289	-0.18476	H	-1.09076	3.29396	-0.18666
N	1.41139	1.09566	0.09823	H	1.44386	3.19390	-0.27403
N	-1.56398	-1.64248	0.03809	H	-2.91241	3.04055	-0.96083
N	-3.27348	-0.05056	-0.09526	H	-4.26093	1.99492	-1.07933
N	3.23388	-0.36005	-0.06231	H	0.68243	2.69147	1.25048
N	3.61934	1.87496	0.32451	H	4.59054	1.74510	0.08489
N	-3.81950	-2.26367	0.18732	H	4.19049	-0.48354	0.24023
C	-2.83278	-1.35607	0.04457	H	3.35409	2.79335	0.64193
N	3.43212	-2.47325	-0.93789	H	-4.78469	-2.05822	-0.02221
N	-3.30396	2.12905	-0.79049	H	-4.25597	0.10254	0.08453
C	2.59877	-1.49362	-0.53805	H	-3.60101	-3.22835	0.38459
C	-0.53637	2.40945	-0.51566	H	-1.38794	-2.63854	0.11710
C	-2.53905	1.10231	-0.36545	H	4.39906	-2.29536	-1.16592
C	2.69305	0.91411	0.12120	H	3.07695	-3.38990	-1.16473
C	0.81922	2.42744	0.19579	Ni	-0.01678	-0.35557	0.30956
H	0.96360	-2.42416	-1.02399	O	0.09525	-0.50811	2.02484

ML1OH-D							
N	-1.34863	-1.60924	-0.43191	H	1.24966	3.18082	-0.78957
N	1.26902	1.13140	-0.21590	H	-1.32156	3.20232	-0.75094
N	-1.31857	1.07629	-0.39952	H	2.86060	2.98580	0.71412
N	1.40820	-1.56815	-0.49001	H	4.25614	1.99248	0.70566
N	3.14002	-0.20224	0.27081	H	-0.58905	2.20234	-2.00378
N	-3.08059	-0.25383	0.35215	H	-4.41073	1.84485	0.18657
N	-3.41581	2.00515	0.14485	H	-3.85298	-0.24384	1.00484
N	3.59090	-2.38962	-0.26683	H	-3.12256	2.96294	0.04712

C	2.66727	-1.41275	-0.19037	H	4.57823	-2.18489	-0.31264
N	-3.41086	-2.52236	0.19407	H	3.99422	-0.23334	0.81039
N	3.25681	2.06825	0.59091	H	3.32017	-3.33962	-0.47193
C	-2.56878	-1.48762	0.01638	H	1.20947	-2.45703	-0.93557
C	0.63451	2.46231	-0.23848	H	-4.41056	-2.39125	0.24194
C	2.49841	1.02679	0.20232	H	-3.08516	-3.47332	0.10946
C	-2.54716	0.98374	0.00597	Ni	0.00471	-0.29783	-0.22421
C	-0.71645	2.31066	-0.92281	O	-0.08212	-0.28276	1.76195
H	-1.12907	-2.54017	-0.76714	H	0.04394	-1.16981	2.12551
H	0.49422	2.81465	0.78998				

ML1OCl-D							
N	-1.35895	-1.25471	-1.00116	H	1.24142	3.48331	-0.29502
N	1.26214	1.35804	-0.15099	H	-1.33224	3.48821	-0.15316
N	-1.32258	1.33897	-0.30384	H	2.91275	3.00275	1.04043
N	1.38984	-1.21023	-1.01970	H	4.29808	2.03401	0.76621
N	3.15106	-0.03362	-0.03972	H	-0.63923	2.80987	-1.62615
N	-3.09413	-0.12939	0.07941	H	-4.43623	1.94805	0.35954
N	-3.44219	2.11809	0.37513	H	-3.88365	-0.27004	0.69540
N	3.55967	-2.08870	-0.98287	H	-3.15628	3.07518	0.49861
C	2.65298	-1.13089	-0.71224	H	4.55056	-1.89795	-0.99255
N	-3.42024	-2.29600	-0.61861	H	4.02279	-0.17124	0.45307
N	3.29426	2.12544	0.72637	H	3.27063	-2.98109	-1.35389
C	-2.57946	-1.24868	-0.54116	H	1.17134	-2.01425	-1.59699
C	0.63771	2.66744	0.11511	H	-4.41929	-2.18692	-0.52690
C	2.51194	1.18063	0.17027	H	-3.08988	-3.20243	-0.91302
C	-2.56303	1.15504	0.03314	Ni	-0.00361	-0.02318	-0.50708
C	-0.73399	2.66461	-0.54604	O	-0.12559	-0.47286	1.53412
H	-1.13848	-2.07943	-1.54748	Cl	0.08901	-2.03747	2.07984
H	0.53129	2.80649	1.19735				

ML1OACR-D							
N	-0.78998	2.04252	0.15204	H	0.46722	5.02787	0.21346
N	-0.38503	-1.54580	-1.00320	H	-1.04207	4.55068	0.86168
N	0.96135	0.73084	-1.43890	H	1.29199	0.06824	-2.13014
N	-2.20117	-0.12691	0.45114	H	0.55083	-1.88342	-1.20471
N	-2.56246	-2.23121	-0.52169	Ni	-0.49861	0.22120	-0.34470
N	1.33256	2.81343	-0.47129	O	0.66066	-0.18904	1.24804
N	2.90820	1.93280	-1.89649	H	0.11273	-0.62742	1.91094
N	-4.14852	-1.36278	0.88129	C	3.69664	-1.18792	2.29273
C	-2.94939	-1.18756	0.30211	H	3.51155	-0.12381	2.13216
N	-0.15643	4.27855	0.47000	H	4.70205	-1.33460	2.68183
N	-1.12051	-3.68266	-1.56785	H	2.96917	-1.53791	3.03015
C	0.06774	3.01906	0.05574	C	3.52568	-1.95830	1.00107
C	-1.30658	-2.46648	-1.02932	O	2.37617	-1.79344	0.36013
C	1.72012	1.78155	-1.29090	H	1.70759	-1.12570	0.80749
H	-0.23786	-3.91154	-1.99832	O	4.38340	-2.70490	0.55778
H	-1.74177	-4.45076	-1.36450	C	-2.60610	0.97996	1.33299

H	3.35466	2.83435	-1.97075	H	-3.68685	1.03108	1.47117
H	2.00881	3.54773	-0.31493	H	-2.13695	0.85398	2.31198
H	3.27886	1.19126	-2.47017	C	-2.14574	2.27123	0.67746
H	-4.62515	-2.25010	0.83796	H	-2.16914	3.06455	1.42664
H	-3.27030	-2.91987	-0.73659	H	-2.81210	2.54423	-0.14565
H	-4.51427	-0.69422	1.53757				

ML1OACP-D							
N	-1.30821	1.79298	0.13068	H	-1.10708	4.99930	-0.33213
N	0.19114	-1.64544	-0.46056	H	-2.49456	4.10599	0.13281
N	1.09658	0.86906	-0.75185	H	1.93354	0.26066	-0.80619
N	-2.17554	-0.64694	0.35658	H	1.17740	-1.78654	-0.22892
N	-1.87600	-2.68041	-0.75923	Ni	-0.47394	0.08730	-0.08799
N	0.51203	3.12793	-0.52293	O	0.43649	-0.03659	1.80972
N	2.69288	2.51859	-0.99455	H	-0.02409	-0.62646	2.42168
N	-3.95535	-2.14388	0.04131	C	5.01773	-1.46433	0.98977
C	-2.67518	-1.77087	-0.08995	H	5.14301	-1.16958	2.03458
N	-1.51709	4.10683	-0.10487	H	5.84649	-1.07870	0.39753
N	0.05885	-3.87117	-1.13019	H	5.02677	-2.55715	0.95914
C	-0.80841	2.96948	-0.15800	C	3.68112	-0.95849	0.47463
C	-0.49756	-2.70607	-0.76166	O	2.63961	-1.32134	1.11432
C	1.43310	2.13061	-0.74154	H	1.31932	-0.47754	1.61635
H	1.06179	-3.93899	-1.21406	O	3.65478	-0.23222	-0.55492
H	-0.45492	-4.73690	-1.06688	C	-2.93511	0.32579	1.15485
H	2.98436	3.47749	-0.88683	H	-3.99940	0.10145	1.21545
H	0.83631	4.07805	-0.63836	H	-2.54136	0.32074	2.17390
H	3.40621	1.79523	-0.98673	C	-2.73161	1.68814	0.51320
H	-4.26797	-3.06332	-0.22920	H	-3.00038	2.46294	1.23595
H	-2.34496	-3.44546	-1.22479	H	-3.36098	1.79157	-0.37583
H	-4.65565	-1.51437	0.39467				

ML1Cl-D							
N	1.39944	-1.48878	-0.72623	H	-0.62834	2.33992	-1.99431
N	-1.32249	1.12493	-0.43378	H	-1.32591	3.26612	-0.66400
N	1.26761	1.17156	-0.28282	H	1.24507	3.23884	-0.78382
N	-1.34235	-1.55085	-0.61587	H	-3.18199	2.97007	-0.04893
N	-3.09792	-0.25080	0.20365	H	-4.45401	1.82708	0.03400
N	3.13695	-0.19071	0.13034	H	0.52210	2.82014	0.79821
N	3.27751	2.06801	0.51234	H	4.27780	1.97960	0.61148
N	-3.35849	-2.53019	0.04822	H	3.97094	-0.25685	0.69839
C	-2.55631	-1.47046	-0.13863	H	2.88901	2.98113	0.68516
N	3.54953	-2.37310	-0.45925	H	-4.35690	-2.43580	0.16233
N	-3.46123	2.00502	0.01414	H	-3.88899	-0.26438	0.83379
C	2.65059	-1.37762	-0.37725	H	-2.99744	-3.47021	-0.01417
C	-0.72775	2.38619	-0.90593	H	-1.08299	-2.48766	-0.90214
C	-2.57248	1.00048	-0.09719	H	4.54365	-2.19823	-0.45106
C	2.50755	1.04378	0.10814	H	3.25938	-3.31522	-0.67437
C	0.63797	2.50475	-0.24497	Ni	0.00333	-0.24751	-0.34742
H	1.18443	-2.36454	-1.18929	Cl	-0.00273	-0.47753	1.98977

ML2S							
Ni	-0.00002	-0.00013	0.00018	H	1.05608	2.25006	-0.51467
N	1.33875	1.33257	-0.18739	H	-3.13869	-3.21929	0.06297
N	-1.33899	-1.33267	0.18702	H	-4.47254	-2.14648	0.16164
N	1.33893	-1.33274	-0.18653	H	4.47251	-2.14642	-0.16273
N	-1.33879	1.33253	0.18763	H	4.12909	0.00050	0.64944
N	-3.21002	0.00019	-0.22814	H	3.13874	-3.21929	-0.06283
N	3.21006	0.00019	0.22794	H	-4.47229	2.14651	0.16467
N	3.48154	-2.27156	-0.01871	H	-4.12904	0.00043	-0.64964
N	-3.48131	2.27174	0.02071	H	-3.13844	3.21938	0.06589
C	-2.62565	1.23160	0.01274	H	-1.05620	2.25005	0.51489
N	3.48140	2.27170	-0.02093	H	4.47225	2.14633	-0.16587
N	-3.48149	-2.27161	0.01819	H	3.13853	3.21933	-0.06644
C	2.62563	1.23160	-0.01286	H	1.05655	-2.25068	-0.51280
C	-2.62578	-1.23150	0.01168	H	-1.05658	-2.25074	0.51286
C	2.62581	-1.23149	-0.01173				

ML2OradicalQ							
N	-1.55970	-1.35478	0.24564	H	3.58722	2.89101	0.83165
N	1.55968	1.35492	0.24498	H	4.77558	1.81503	0.22613
N	-1.25550	1.28487	-0.54104	H	-4.27196	2.13566	-1.37396
N	1.25530	-1.28461	-0.54178	H	-4.26933	0.35188	0.02116
N	3.29031	-0.17338	-0.15538	H	-2.87888	3.13615	-1.36951
N	-3.29047	0.17313	-0.15580	H	4.27178	-2.13552	-1.37423
N	-3.30481	2.25839	-1.11233	H	4.26909	-0.35239	0.02189
N	3.30468	-2.25834	-1.11256	H	2.87872	-3.13601	-1.37001
C	2.55960	-1.25309	-0.61740	H	0.85125	-2.10159	-0.98792
N	-3.81157	-1.97305	0.47875	H	-4.77527	-1.81590	0.22441
N	3.81152	1.97300	0.47849	H	-3.58713	-2.89125	0.83130
C	-2.83065	-1.09306	0.19556	H	-0.85150	2.10209	-0.98675
C	2.83064	1.09298	0.19548	H	1.36881	2.31971	0.49649
C	-2.55979	1.25312	-0.61717	Ni	0.00002	0.00008	0.29538
H	-1.36872	-2.31942	0.49766	O	0.00062	-0.00031	2.03743

ML2OH-D							
N	1.30268	1.33969	-0.45813	H	-4.47070	-2.13945	0.15110
N	-1.34038	-1.32404	0.11807	H	4.40183	-2.14032	-0.27836
N	1.29578	-1.29113	-0.56039	H	3.93876	-0.03173	0.70589
N	-1.36939	1.34218	0.10971	H	3.05640	-3.20729	-0.32771
N	-3.20749	-0.01476	-0.37093	H	-4.50841	2.12451	-0.05455
N	3.11604	-0.00662	0.11817	H	-4.11570	-0.03395	-0.81566
N	3.40119	-2.26421	-0.23139	H	-3.17877	3.20873	-0.09006
N	-3.51113	2.25705	-0.13747	H	-1.09007	2.24913	0.46748
C	-2.64903	1.22615	-0.11373	H	4.41537	2.14170	-0.12174
N	3.41563	2.26796	-0.06255	H	3.07686	3.21791	-0.08070
N	-3.47924	-2.27139	0.01453	H	1.00628	-2.17400	-0.96547
C	2.56450	1.23154	-0.14786	H	-1.02726	-2.17843	0.56687

C	-2.62665	-1.23443	-0.05736	Ni	-0.00867	0.01648	-0.07154
C	2.55621	-1.21922	-0.24178	O	0.56762	-0.11662	1.83546
H	1.02904	2.24977	-0.81047	H	-0.13456	0.13276	2.45133
H	-3.13340	-3.21496	0.10856				

ML2OClD							
N	-1.29808	-1.07076	-0.98708	H	4.48102	2.17896	0.37934
N	1.35219	1.39869	0.14483	H	-4.41381	2.31293	-0.15648
N	-1.29153	1.52623	-0.45517	H	-4.02276	0.03385	0.26948
N	1.38299	-1.17967	-0.53136	H	-3.07199	3.34663	0.12298
N	3.21705	0.25871	-0.66661	H	4.52082	-1.88969	-0.88762
N	-3.14637	0.13348	-0.22508	H	4.12144	0.39106	-1.09946
N	-3.41811	2.41032	-0.02302	H	3.19416	-2.93198	-1.19903
N	3.52487	-1.99742	-1.01108	H	1.11834	-2.15072	-0.40652
C	2.66030	-1.00761	-0.72480	H	-4.42780	-1.88025	-1.03818
N	-3.43374	-2.03126	-0.94974	H	-3.09469	-2.95257	-1.18203
N	3.49108	2.34518	0.27298	H	-0.99291	2.48198	-0.61402
C	-2.57743	-1.01510	-0.74168	H	1.05056	2.11651	0.79538
C	2.63730	1.35820	-0.05307	Ni	0.02274	0.14557	-0.36856
C	-2.56880	1.39114	-0.24387	O	-0.57417	-0.09018	1.67122
H	-1.01770	-1.88027	-1.52931	Cl	-0.01204	-1.33398	2.61690
H	3.14571	3.23236	0.60780				

ML2OACR							
N	0.08420	2.37320	-0.20586	H	4.34706	-1.02741	0.74541
N	1.14055	-1.14011	0.72674	H	4.51701	1.40660	-1.69484
N	-0.94401	0.46773	1.32021	H	-2.24183	4.59540	-0.43543
N	2.18101	0.78243	-0.79178	H	-0.69446	4.62836	-1.18335
N	3.42322	-0.77076	0.42616	H	-0.93202	-0.25006	2.03533
N	-2.16400	2.22029	0.38717	H	0.42501	-1.85128	0.85320
N	-3.16527	0.84540	1.93579	Ni	0.54095	0.56491	0.14115
N	4.49585	0.63152	-1.04986	O	-0.52312	-0.19809	-1.38689
C	3.33488	0.24253	-0.50417	H	0.08177	-0.32047	-2.12921
N	-1.40630	4.09823	-0.70465	C	-3.31771	-2.07154	-1.76212
N	2.71023	-2.72871	1.40343	H	-3.37587	-1.02734	-1.44882
C	-1.10872	2.89933	-0.18064	H	-4.31812	-2.49158	-1.84302
C	2.36852	-1.55616	0.84796	H	-2.83697	-2.09132	-2.74395
C	-2.05655	1.14205	1.23958	C	-2.49782	-2.87784	-0.77880
H	1.99949	-3.32508	1.79842	O	-1.28709	-2.41322	-0.49543
H	3.61729	-3.14035	1.24310	H	-1.03331	-1.50257	-0.94591
H	-3.89821	1.52664	2.06635	O	-2.90111	-3.91054	-0.26960
H	-3.09030	2.59212	0.22954	H	2.20119	1.42682	-1.57366
H	-3.17428	0.04579	2.55046	H	0.80889	2.99066	-0.55252
H	5.31753	0.04748	-1.01010				

ML2OACP							
N	-0.50147	2.38569	0.14953	H	-3.86553	-1.79301	-1.11529
N	-0.77713	-1.35515	-0.36765	H	-4.95540	0.84713	0.82697

N	1.12044	0.48842	-0.77905	H	1.19004	5.13444	-0.10553
N	-2.40307	0.51875	0.57760	H	-0.42675	4.94514	0.45279
N	-3.09234	-1.34733	-0.64018	H	1.53613	-0.44399	-0.94144
N	1.76094	2.70391	-0.33100	H	0.05040	-1.92094	-0.14921
N	3.33017	1.12761	-0.96407	Ni	-0.58581	0.49693	0.00799
N	-4.66859	0.00873	0.34537	O	0.30226	-0.00593	1.84503
C	-3.37125	-0.23672	0.12566	H	-0.34591	-0.26915	2.51219
N	0.43587	4.51734	0.15393	C	3.71763	-3.27696	0.86626
N	-1.89890	-3.26854	-1.08182	H	3.99582	-2.99798	1.88549
C	0.51823	3.19107	-0.00757	H	4.60243	-3.28073	0.23108
C	-1.86862	-1.98923	-0.67789	H	3.29890	-4.28602	0.91025
C	2.05133	1.40517	-0.68742	C	2.66114	-2.31799	0.34490
H	-1.03393	-3.77364	-1.20165	O	1.60252	-2.18540	1.04295
H	-2.74499	-3.81476	-1.01734	H	0.84854	-0.82004	1.63893
H	4.05579	1.82617	-0.92747	O	2.86149	-1.71690	-0.74496
H	2.53185	3.35663	-0.29483	H	-2.69447	1.22944	1.23940
H	3.58757	0.14749	-1.05232	H	-1.38102	2.86185	0.31046
H	-5.36904	-0.70426	0.20731				

ML2ClD							
N	1.27577	1.31665	-0.59360	H	-3.18473	-3.20674	-0.07761
N	-1.37534	-1.33915	-0.05481	H	-4.51359	-2.12180	-0.02541
N	1.27574	-1.31673	-0.59337	H	4.39575	-2.15788	-0.43706
N	-1.37535	1.33914	-0.05502	H	4.00563	-0.00007	0.41881
N	-3.23312	-0.00005	-0.50972	H	3.04679	-3.21931	-0.36424
N	3.13385	-0.00001	-0.09449	H	-4.51362	2.12188	-0.02630
N	3.39671	-2.27297	-0.34764	H	-4.15262	-0.00012	-0.93150
N	-3.52257	2.25917	-0.16201	H	-3.18471	3.20676	-0.07859
C	-2.66403	1.22863	-0.22055	H	-1.08630	2.19975	0.39815
N	3.39653	2.27307	-0.34675	H	4.39562	2.15816	-0.43584
N	-3.52259	-2.25917	-0.16136	H	3.04648	3.21936	-0.36317
C	2.55639	1.22717	-0.35831	H	0.96863	-2.22474	-0.92328
C	-2.66402	-1.22867	-0.22023	H	-1.08624	-2.19960	0.39863
C	2.55642	-1.22717	-0.35858	Ni	-0.03354	0.00000	-0.19121
H	0.96867	2.22477	-0.92319	Cl	0.41044	0.00001	2.12365

Small Molecules

HOCl							
O	0.03628	1.12372	0.00000	Cl	0.03628	-0.60784	0.00000
H	-0.90687	1.34353	0.00000				

HCl							
Cl	0.00000	0.00000	0.07148	H	0.00000	0.00000	-1.21514

H_2O							
O	0.00000	0.00000	0.11703	H	0.00000	-0.76350	-0.46813

H	0.00000	0.76350	-0.46813				

Cyclohexanol							
C	1.87211	0.01518	-0.27728	H	2.91372	0.02599	0.05974
C	1.14611	1.27834	0.20767	H	-1.01840	-0.01152	1.42193
C	-0.33990	1.25463	-0.18459	H	-0.82157	-2.15256	0.23027
C	-1.03406	-0.01442	0.32028	H	-0.42302	-1.31260	-1.26378
C	-0.31865	-1.26891	-0.17298	H	1.26114	-1.32266	1.30642
C	1.16787	-1.25771	0.21453	H	1.66224	-2.14631	-0.18990
H	-0.85120	2.14123	0.21071	H	-0.44077	1.28744	-1.27620
H	1.23399	1.34934	1.29958	O	-2.39230	-0.09739	-0.12920
H	1.62480	2.17444	-0.19939	H	-2.86181	0.69078	0.16289
H	1.89839	0.01288	-1.37449				

cyclohexaneradical							
C	1.26851	-0.71188	-0.24086	H	2.16208	-1.21261	0.14601
C	1.28753	0.77871	0.15901	H	-1.47152	0.83581	1.24876
C	-0.00000	1.46365	-0.16706	H	-2.13189	1.29174	-0.31176
C	-1.28753	0.77871	0.15901	H	-2.16208	-1.21261	0.14601
C	-1.26851	-0.71188	-0.24086	H	-1.30945	-0.78875	-1.33409
C	0.00000	-1.41280	0.26497	H	0.00000	-1.41663	1.36342
H	1.47152	0.83581	1.24876	H	0.00000	-2.46188	-0.04902
H	2.13189	1.29174	-0.31176	H	-0.00000	2.51911	-0.41751
H	1.30945	-0.78875	-1.33409				

cyclohexane							
C	-0.43442	1.40084	-0.22824	H	-0.73837	2.38283	0.14971
C	-1.43054	0.32446	0.22836	H	0.45559	-1.46934	1.32406
C	-0.99640	-1.07651	-0.22817	H	0.73840	-2.38279	-0.14968
C	0.43439	-1.40084	0.22825	H	2.43299	-0.55204	0.14956
C	1.43054	-0.32449	-0.22834	H	1.50005	-0.34036	-1.32413
C	0.99643	1.07653	0.22816	H	1.04514	1.12866	1.32399
H	-1.50000	0.34026	1.32414	H	1.69480	1.83098	-0.14946
H	-2.43295	0.55207	-0.14954	H	-1.04514	-1.12867	-1.32397
H	-0.45570	1.46939	-1.32404	H	-1.69484	-1.83101	0.14926

Clcyclohexane							
C	-1.55887	1.26661	0.19776	H	-2.02900	2.16120	-0.22189
C	-0.05911	1.26737	-0.15072	H	0.06935	-1.30955	-1.23803
C	0.60785	0.00000	0.37439	H	0.43367	-2.14941	0.26588
C	-0.05911	-1.26737	-0.15071	H	-2.02899	-2.16120	-0.22191
C	-1.55888	-1.26662	0.19776	H	-1.68007	-1.33442	1.28641
C	-2.25853	0.00000	-0.31398	H	-2.25053	0.00000	-1.41134
H	0.06934	1.30955	-1.23804	H	-3.30986	0.00000	-0.00959
H	0.43367	2.14942	0.26587	H	0.61130	0.00001	1.46626
H	-1.68006	1.33440	1.28642	Cl	2.39300	-0.00000	-0.06806

Transition state step-2

ML1TS-T							
N	-0.08920	1.30589	1.55046	C	2.62769	-0.29036	-0.25787
H	0.35025	0.97685	2.40199	C	3.32719	0.98899	-0.68734
N	-1.97597	1.51293	-0.38670	H	5.11361	-2.50827	-1.21106
N	-0.48241	3.20349	0.25505	H	5.36175	-0.25272	-2.20329
H	-0.12882	4.12059	0.02169	H	6.50879	-0.43936	-0.88430
N	-2.00797	3.61951	-1.40534	H	5.03396	0.83677	0.64070
H	-1.78775	4.60126	-1.33883	H	5.34407	1.79083	-0.80450
H	-2.74866	3.36833	-2.03851	H	3.01089	-1.48368	-2.00545
C	0.11698	2.57016	1.31889	H	2.68747	-2.43363	-0.55728
C	-1.52607	2.72960	-0.51830	H	1.42243	-0.20513	-0.59967
N	-2.41245	-1.04722	-0.29552	H	2.58283	-0.39053	0.83150
N	-0.43589	-1.38740	1.50045	H	3.15460	1.15828	-1.75778
H	0.15896	-1.21817	2.30288	H	2.91866	1.85376	-0.15628
N	-1.29539	-3.05241	0.11269	H	4.89236	-1.81380	0.39016
H	-1.16240	-3.99483	-0.22646	N	-3.23285	-3.09501	-1.11368
N	0.27870	-3.60431	1.69385	H	-4.00946	-2.67974	-1.59945
H	0.02248	-4.57649	1.61135	H	-3.26346	-4.09470	-0.98924
H	0.92051	-3.37065	2.43561	N	0.94364	3.34194	2.04998
C	-2.34919	-2.33734	-0.43563	H	1.43561	2.94219	2.83401
C	-0.47483	-2.63857	1.13558	H	0.87226	4.34794	2.02888
Ni	-1.07350	0.07726	0.48939	C	-3.06694	1.05542	-1.26187
O	0.21478	-0.14266	-1.03550	H	-3.88503	1.78115	-1.28735
C	4.84840	0.88506	-0.43964	H	-2.68688	0.91263	-2.27911
C	5.44086	-0.36024	-1.11371	C	-3.58307	-0.26077	-0.70658
C	4.71276	-1.63957	-0.67822	H	-4.19137	-0.75342	-1.46557
C	3.19157	-1.53475	-0.92419	H	-4.21164	-0.08518	0.17112

ML2TS-T							
N	0.92099	1.75817	-1.09982	C	-4.51564	-1.88427	0.80972
H	0.80383	1.43129	-2.05344	C	-5.27832	-1.70304	-0.50818
N	0.27882	1.35451	1.45943	C	-4.86375	-0.41419	-1.22804
H	-0.15512	0.83559	2.21487	C	-3.33425	-0.36267	-1.45737
N	0.33934	3.43756	0.40877	C	-2.59992	-0.55541	-0.13966
H	0.40850	4.43340	0.56995	C	-2.98568	-1.83583	0.58481
N	-0.50880	3.27777	2.54461	H	-5.37452	-0.32832	-2.19128
H	-0.93012	4.19019	2.45434	H	-5.08746	-2.56327	-1.16116
H	-0.64197	2.80481	3.42555	H	-6.35516	-1.69319	-0.31689
C	0.55307	2.98480	-0.88505	H	-4.80399	-1.09287	1.51258
C	0.03038	2.63207	1.49298	H	-4.78079	-2.83425	1.28251
N	1.74945	-0.95513	1.41052	H	-3.05100	-1.16067	-2.15315
H	1.61650	-0.78226	2.40028	H	-3.05578	0.58582	-1.92737
N	2.66132	-0.34812	-1.00919	H	-1.42033	-0.61495	-0.38980

H	3.12705	0.25447	-1.67846	H	-2.69615	0.32495	0.50978
N	2.55847	-2.50458	-0.13661	H	-2.68793	-2.69985	-0.02023
H	2.49405	-3.47673	-0.40674	H	-2.46286	-1.91956	1.54363
N	3.69091	-2.14776	-2.10878	H	-5.17009	0.45415	-0.63173
H	4.17558	-3.02620	-1.99992	N	2.10977	-3.18920	2.01267
H	3.92835	-1.60024	-2.92187	H	1.66847	-3.08375	2.91330
C	2.12008	-2.17194	1.13008	H	2.68586	-4.00788	1.88466
C	2.97570	-1.60444	-1.10443	N	0.38249	3.91138	-1.84777
Ni	1.28871	0.38131	0.14487	H	0.63891	3.70780	-2.80226
O	-0.08303	-0.77773	-0.75265	H	-0.18261	4.73406	-1.69824

Transition states-Step4

ML1OACTS4-D							
N	0.03137	1.99177	-0.03350	H	2.16113	4.34283	-0.62982
N	-0.95818	-1.64108	-0.48240	H	0.55104	4.52036	-0.10710
N	1.28872	-0.21625	-0.99468	H	1.47973	-1.17582	-1.26843
N	-2.14418	0.63765	0.33877	H	-0.24756	-2.35965	-0.35238
N	-3.24316	-1.20770	-0.57305	Ni	-0.38716	0.13610	-0.18609
N	2.27497	1.87488	-0.70905	O	0.24177	-0.34799	1.70701
N	3.54886	0.09307	-1.43388	H	-0.53998	-0.56783	2.22711
N	-4.48741	0.52144	0.25370	C	3.36669	-1.19807	1.78274
C	-3.25866	0.02519	0.04547	H	2.80967	-0.26143	1.87398
N	1.34312	3.91184	-0.22909	H	4.39128	-0.99244	1.47920
N	-2.48263	-3.32965	-0.99964	H	3.37011	-1.65124	2.77696
C	1.15528	2.58530	-0.32939	C	2.68415	-2.11912	0.80925
C	-2.17379	-2.06679	-0.66227	O	1.41343	-2.36112	1.03207
C	2.34970	0.54550	-1.03293	H	0.88781	-1.47782	1.48433
H	-1.73800	-4.00595	-1.06471	O	3.26814	-2.60665	-0.15668
H	-3.39488	-3.70107	-0.78075	C	-2.08486	1.88608	1.09622
H	4.36597	0.67790	-1.34703	H	-3.05501	2.37369	1.19979
H	3.12930	2.40665	-0.79366	H	-1.71841	1.66338	2.10307
H	3.71380	-0.90578	-1.35187	C	-1.12056	2.80210	0.37900
H	-5.28566	-0.09383	0.26088	H	-0.81380	3.60229	1.05947
H	-4.12367	-1.53929	-0.94091	H	-1.59076	3.25225	-0.50302
H	-4.60653	1.39523	0.73738				

ML2OACTS4-D							
N	0.23916	2.23549	-0.05768	H	-4.45025	-0.71995	-0.76737
N	-1.29862	-1.20161	-0.43563	H	-4.42197	2.21666	1.02680
N	1.07610	-0.08788	-1.02875	H	2.81302	4.14972	-0.23496
N	-2.15762	1.11055	0.54499	H	1.25670	4.55587	0.33790
N	-3.52049	-0.50524	-0.43568	H	1.05441	-1.00483	-1.46446
N	2.47173	1.68110	-0.44092	H	-0.67341	-2.00119	-0.33054
N	3.36504	-0.21246	-1.41170	Ni	-0.49228	0.48369	-0.11867
N	-4.47904	1.34777	0.51943	O	0.24370	-0.12515	1.69005
C	-3.35183	0.67857	0.24108	H	-0.48955	-0.12748	2.31567
N	1.92864	3.83336	0.13270	C	3.10844	-1.65537	1.62379
N	-3.02000	-2.68732	-0.94794	H	2.73115	-0.65746	1.86092

C	1.49059	2.59277	-0.12902	H	4.12250	-1.59120	1.23394
C	-2.56011	-1.48001	-0.58598	H	3.12560	-2.21070	2.56513
C	2.27577	0.42566	-0.96104	C	2.19406	-2.35581	0.65633
H	-2.36177	-3.44121	-1.06827	O	0.91412	-2.33498	0.95244
H	-3.96687	-2.95633	-0.72827	H	0.60968	-1.37311	1.43896
H	4.27593	0.21341	-1.33837	O	2.60825	-2.91435	-0.35638
H	3.42735	1.98679	-0.32648	H	-0.39527	3.00736	0.11305
H	3.34073	-1.22699	-1.44336	H	-2.15576	1.93798	1.13101
H	-5.36244	0.86395	0.56996				

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