Selective Synthesis of Cyclic Alcohols from Cycloalkanes using Nickel(II) Complexes of Tetradentate Amidate Ligands

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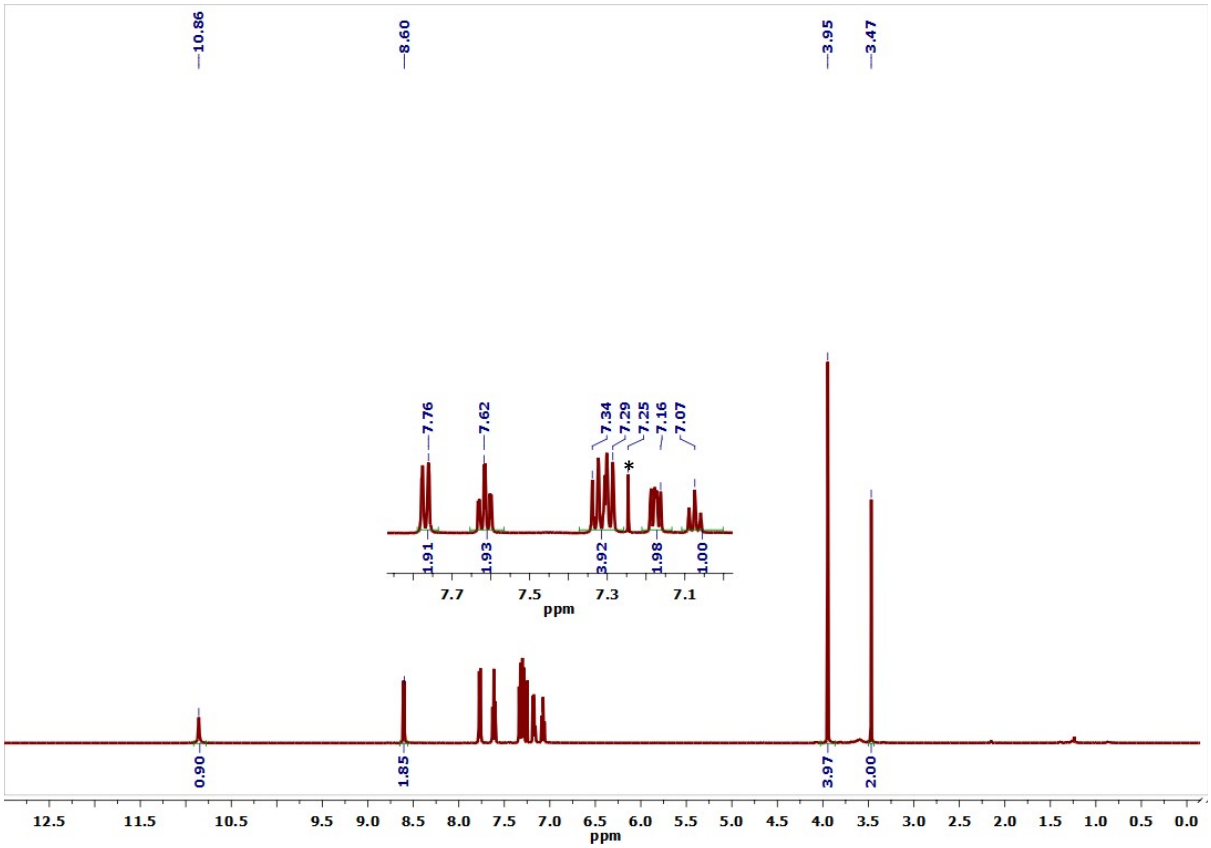


Figure S1. ^{1}H NMR spectrum of ligand L1 (500 MHz, $CDCl_3$). The peak marked with * is the solvent residual peak of $CHCl_3$ in $CDCl_3$.

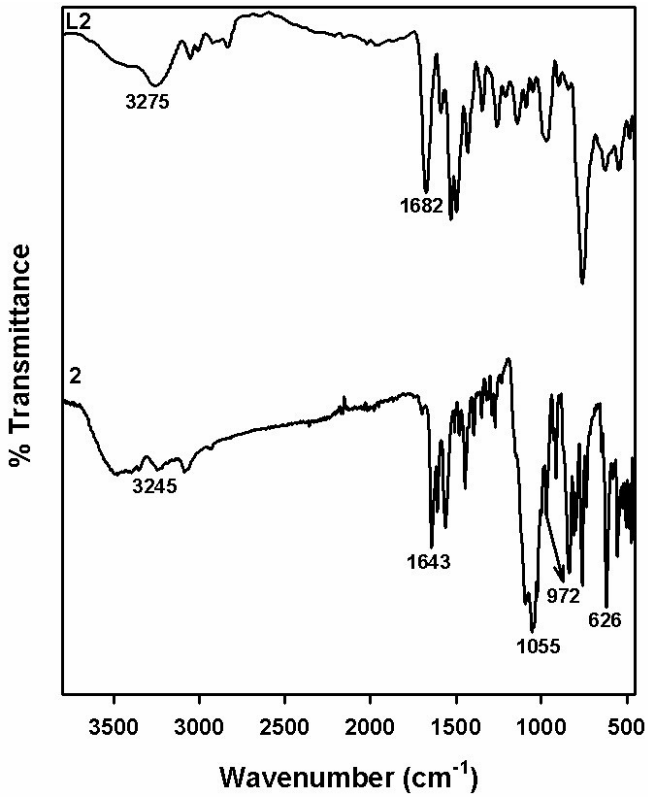


Figure S2. ATR-IR spectrum of ligand L2(top) and complex **2** (bottom).

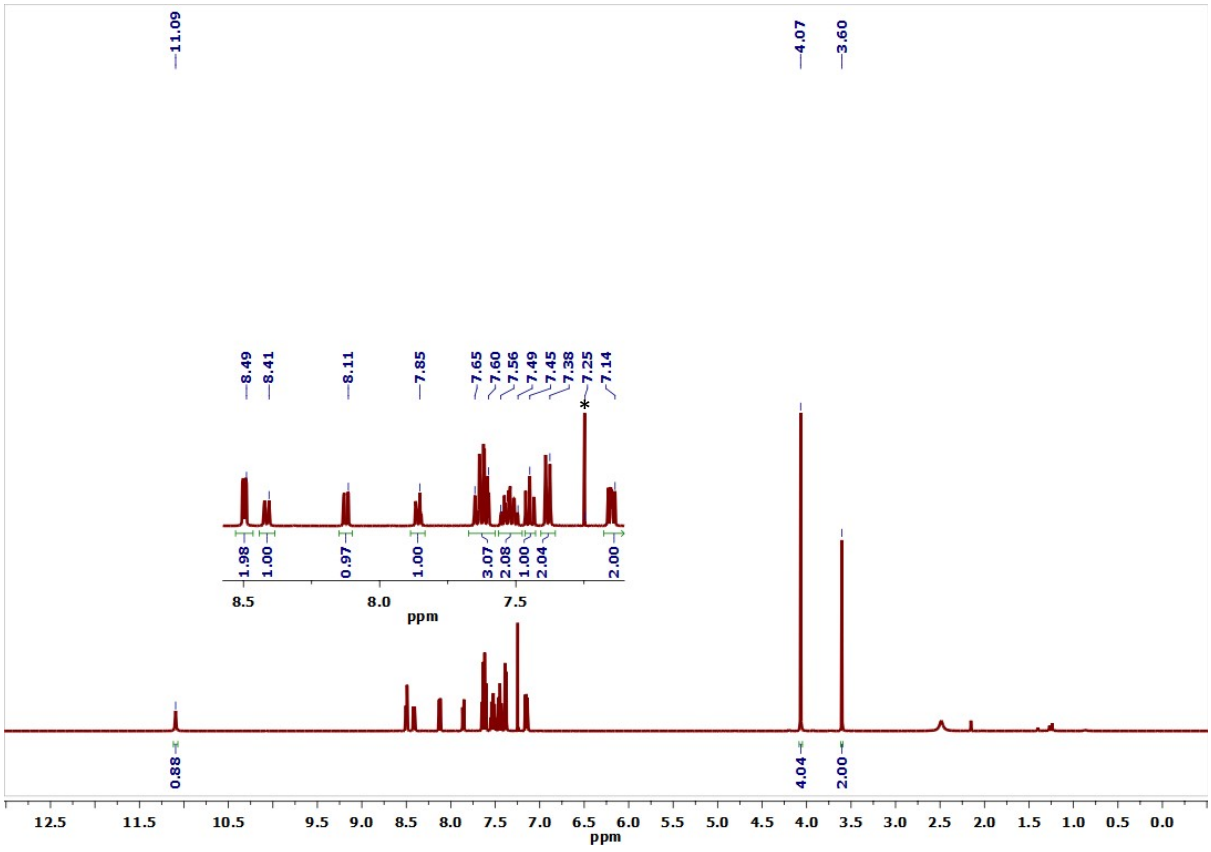


Figure S3. ^{1}H NMR spectrum of ligand L2 (500 MHz, $CDCl_3$). The peak marked with * is the solvent residual peak of $CHCl_3$ in $CDCl_3$.

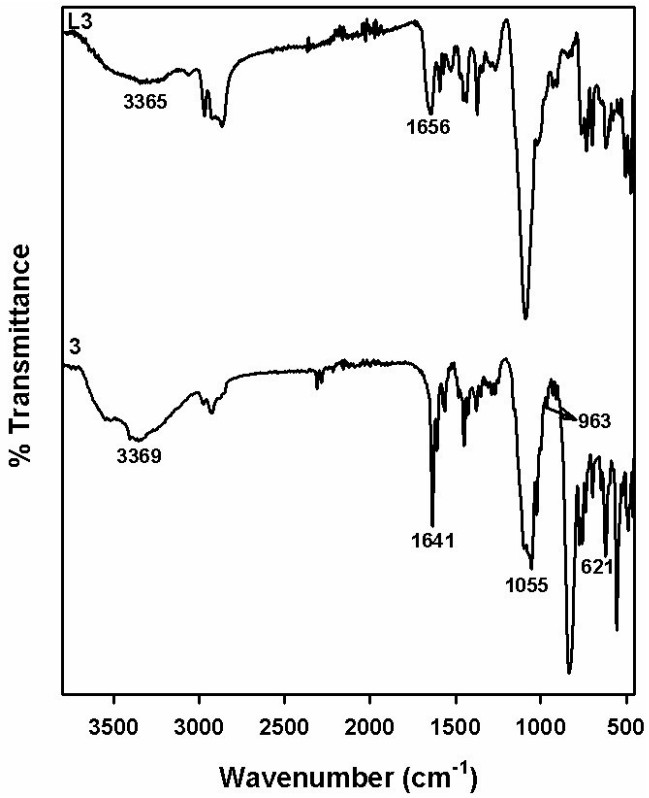


Figure S4. ATR-IR spectrum of ligand L3(top) and complex **3** (bottom).

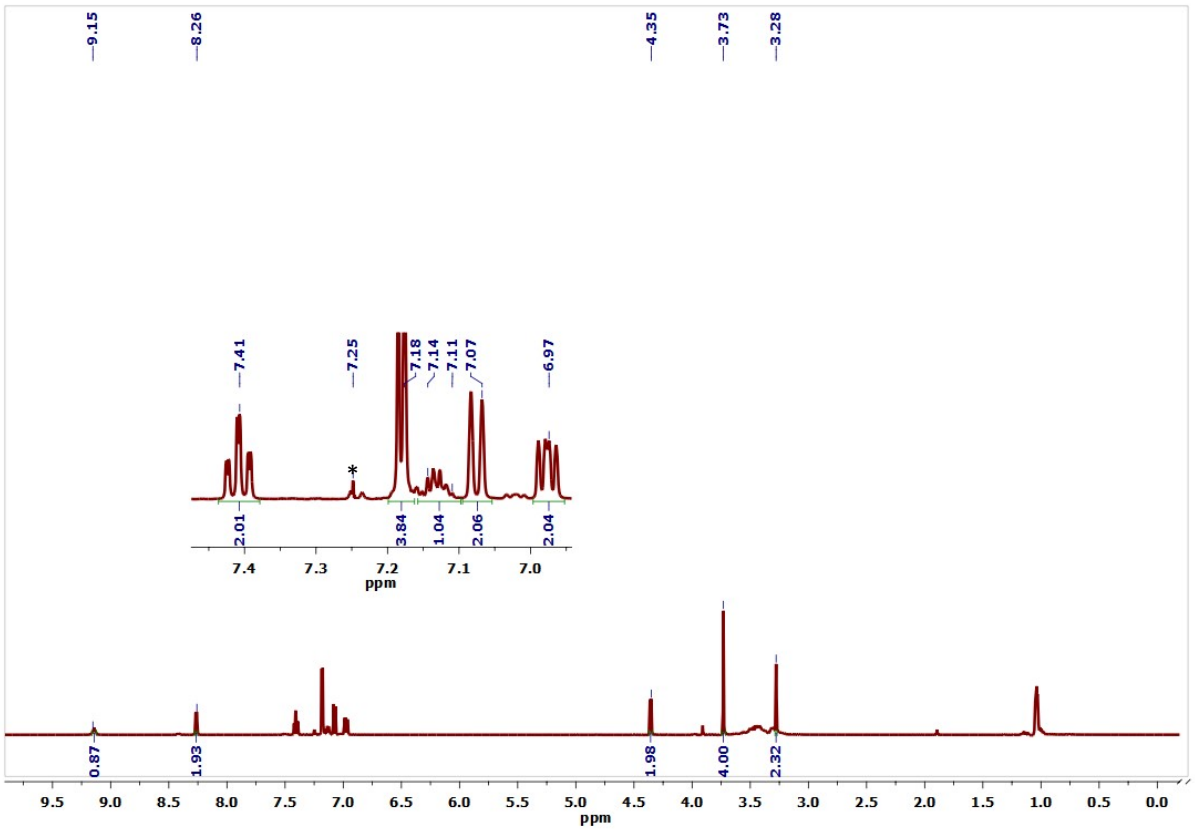


Figure S5. ^{1}H NMR spectrum of ligand L3 (500 MHz, $CDCl_3$). The peak marked with * is the solvent residual peak of $CHCl_3$ in $CDCl_3$.

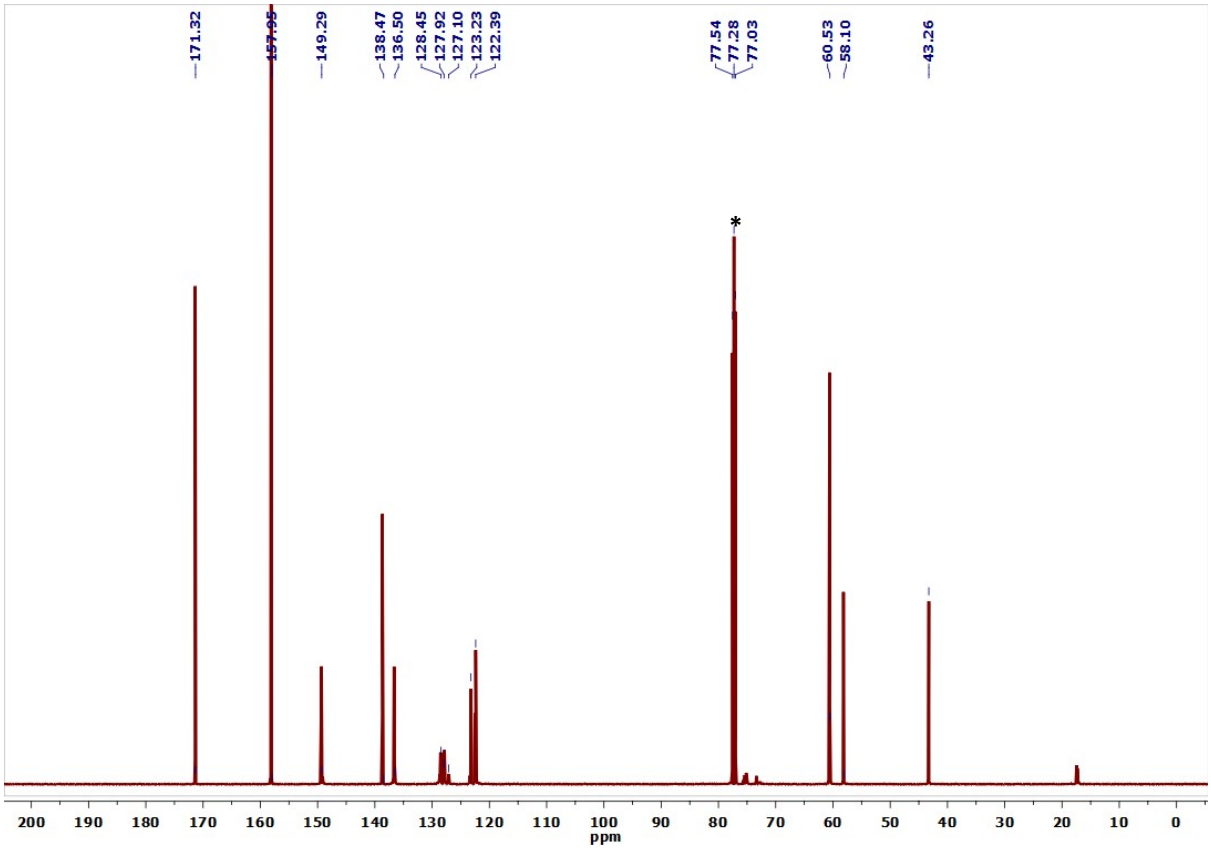


Figure S6. ^{13}C NMR spectrum of ligand L3 (125 MHz, $CDCl_3$). The peak marked with * at 77 ppm is coming from the residual $CDCl_3$.

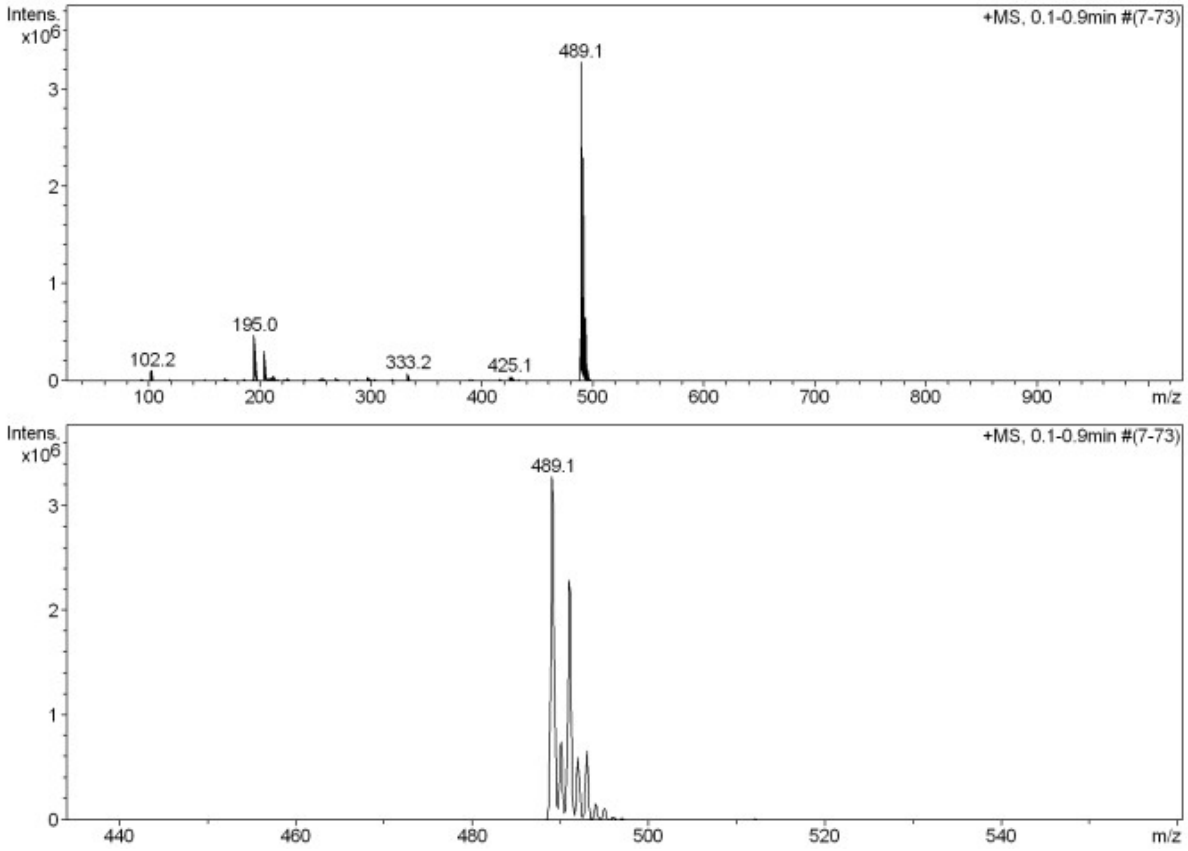


Figure S7. ESI-MS spectrum of complex **1** in acetonitrile (positive ion mode).

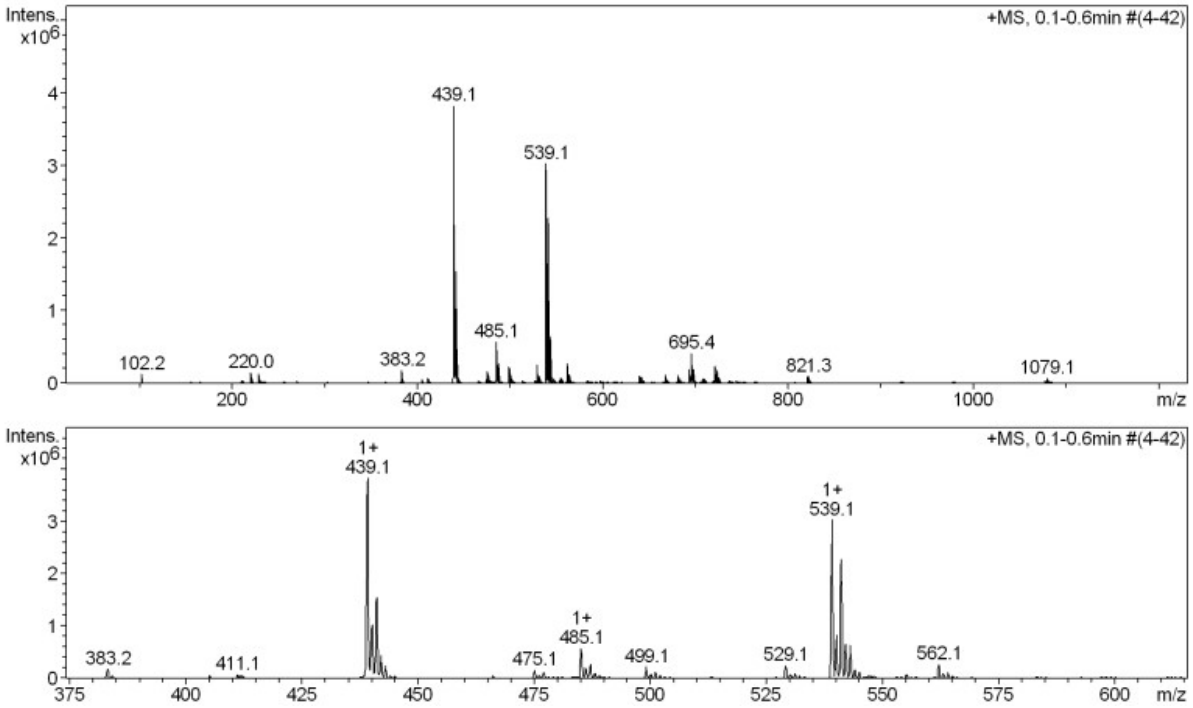


Figure S8. ESI-MS spectrum of complex **2** in acetonitrile (positive ion mode).

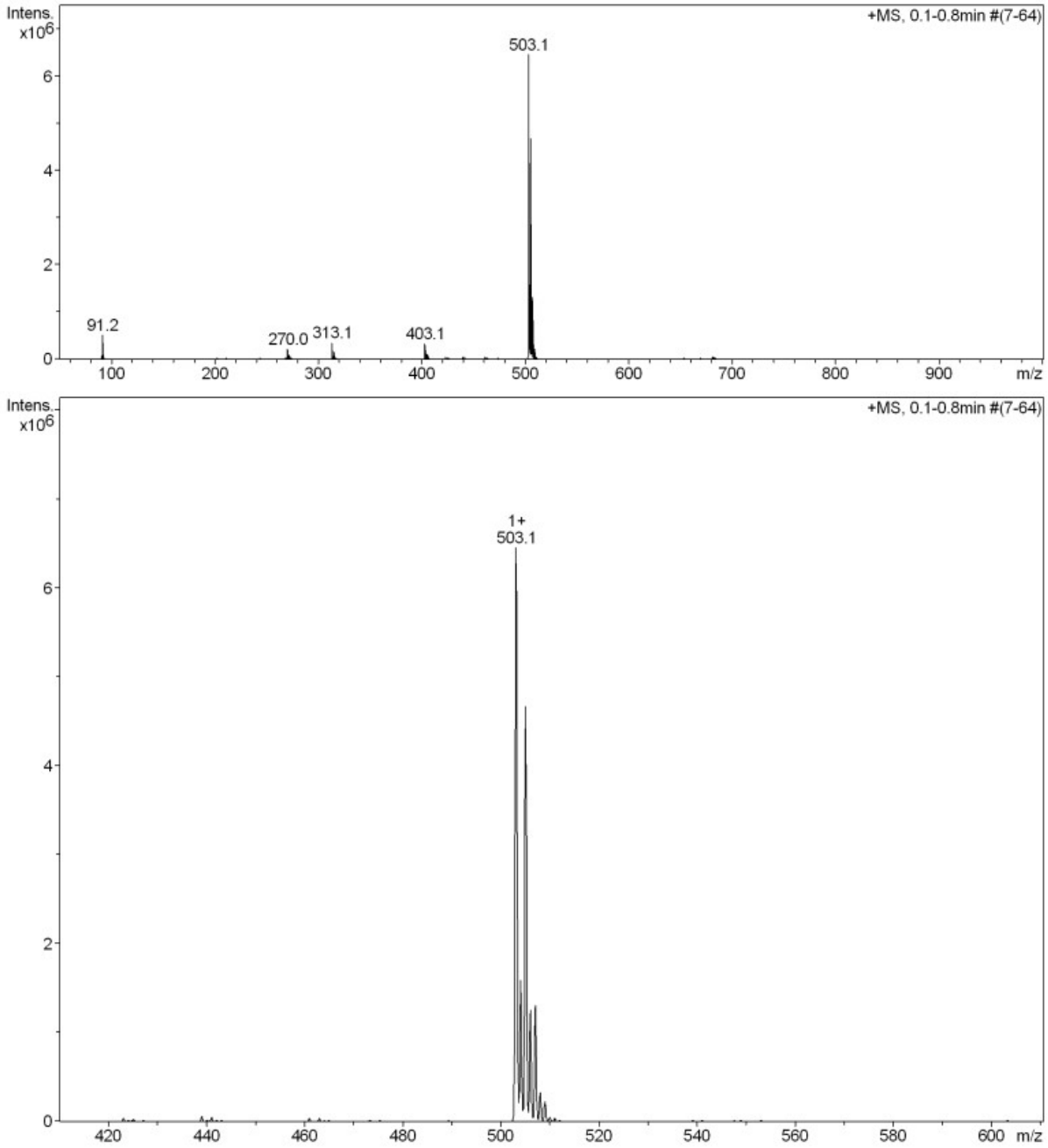


Figure S9. ESI-MS spectrum of complex **3** in acetonitrile (positive ion mode).

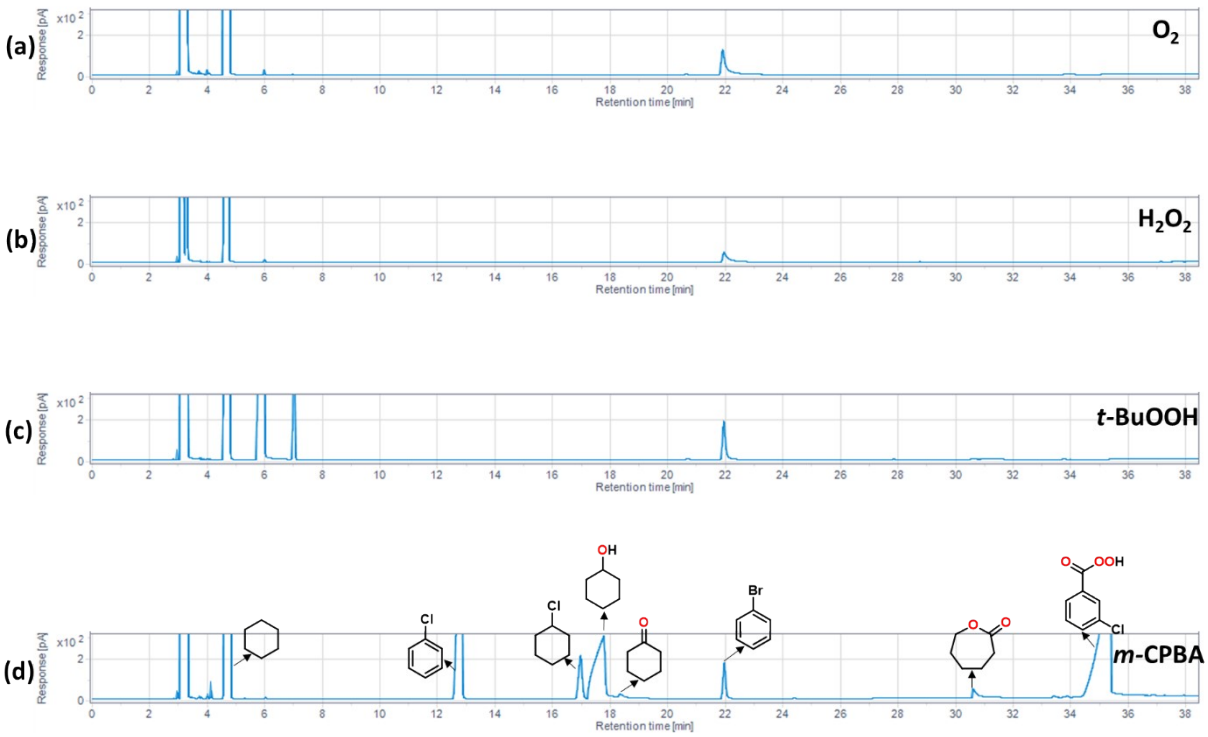


Figure S10. Gas chromatographs for the post-reaction mixture of cyclohexane oxidation catalysed by **1** using oxidants (a) molecular oxygen, (b) hydrogen peroxide, (c) *t*-butyl hydroperoxide, and (d) *m*-CPBA

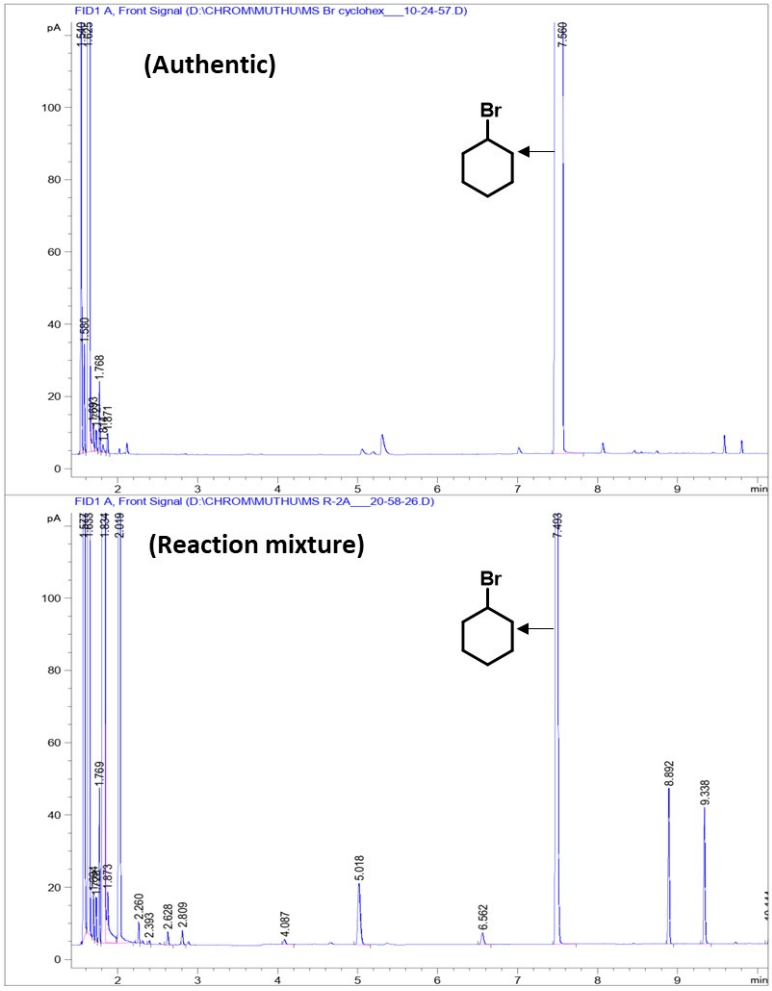


Figure S11. Gas chromatographs of authentic bromocyclohexane sample (top) and post-reaction mixture of cyclohexane oxidation in the presence of carbon tetrabromide.

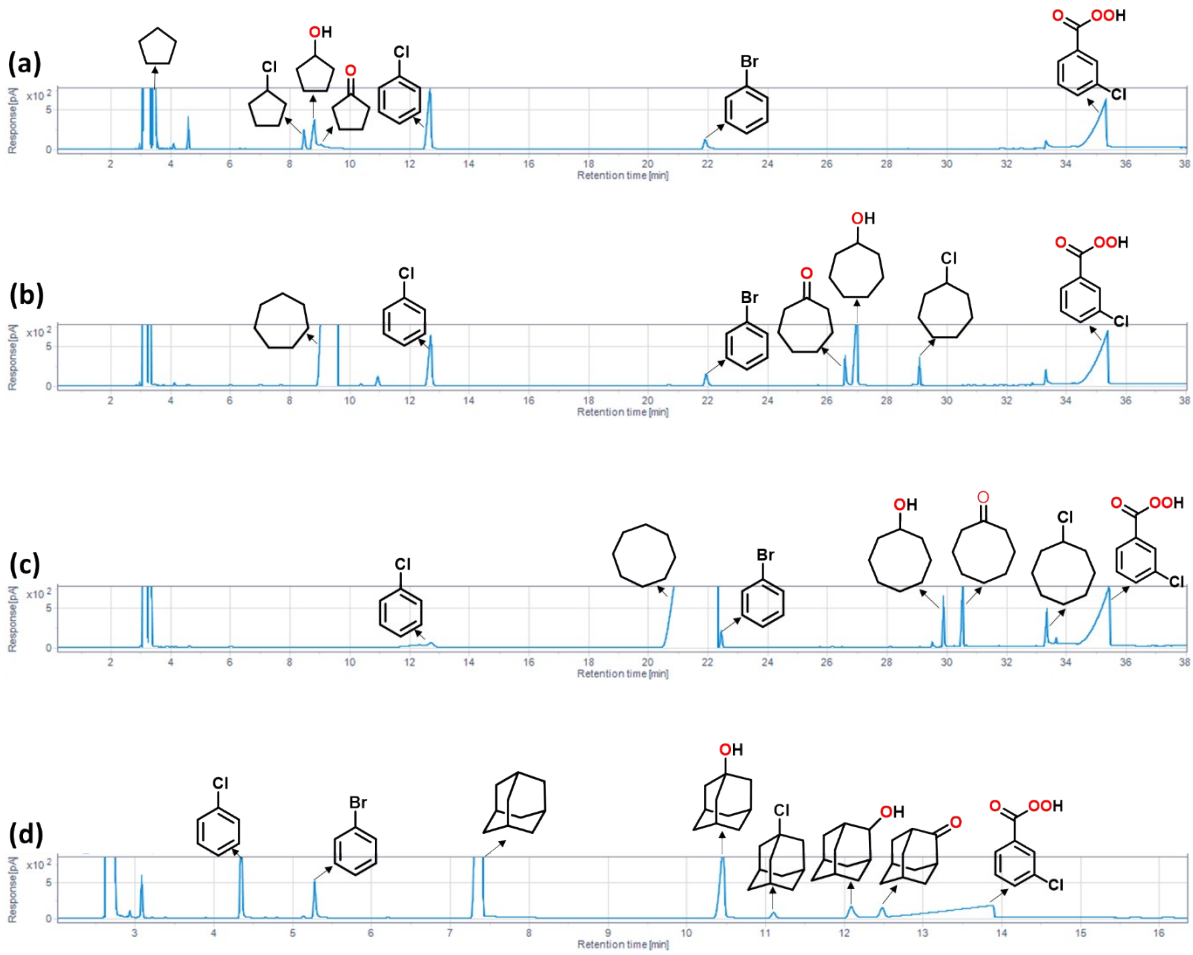


Figure S12. Gas chromatographs for the post-reaction mixture of (a) cyclopentane, (b) cycloheptane, (c) cylooctane and (d) adamantane oxidation using the catalyst **1**.

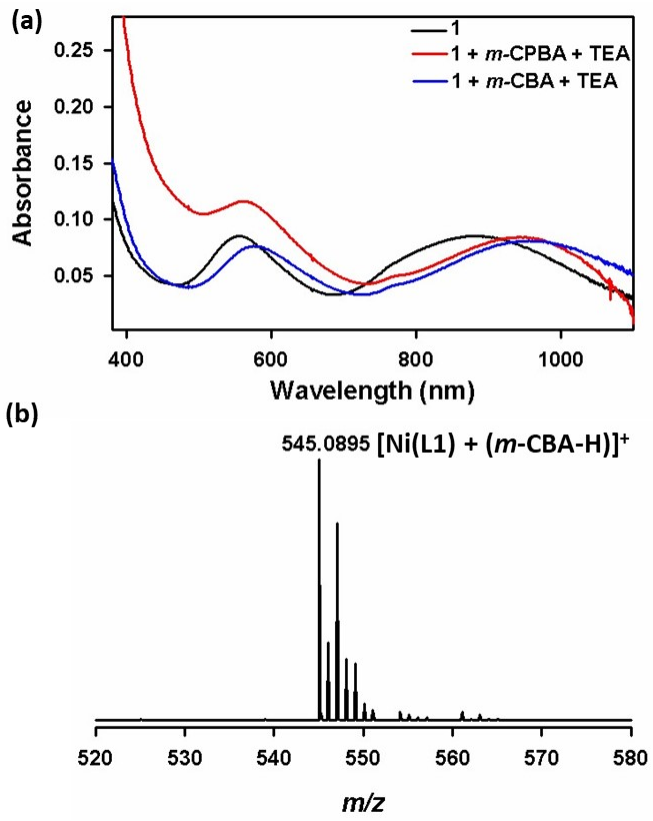
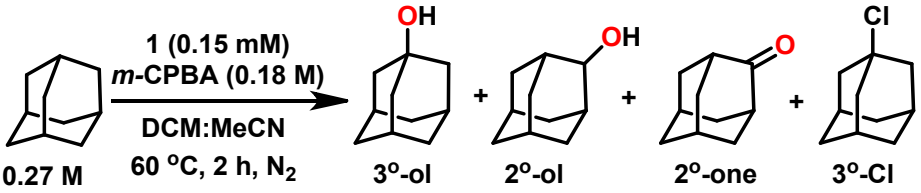


Figure S13. (a) UV-vis spectra of complex **1** (5 mM, black line), the reaction mixture containing **1** (5 mM), TEA (1 equiv.) and *m*-CPBA (1 equiv.) (red line) and the reaction mixture containing **1** (5 mM), TEA (1 equiv.) and *m*-CBA (1 equiv.) (blue line) in acetonitrile at room temperature. (b) HRMS spectrum of the reaction mixture containing **1** (5mM), TEA (1 equiv.) and *m*-CPBA (1 equiv.) in acetonitrile at room temperature.

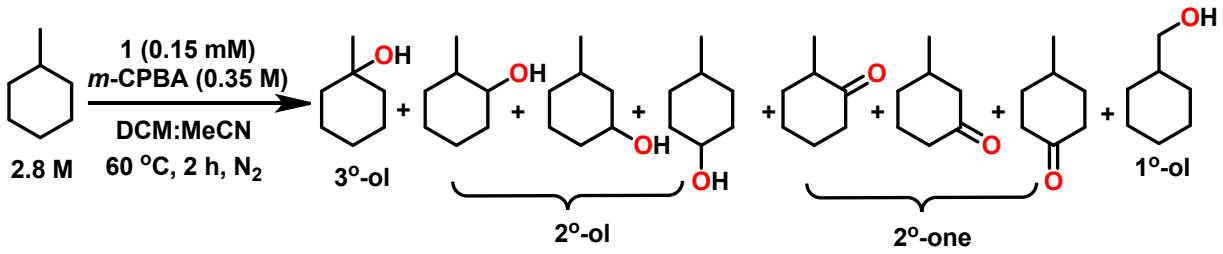
Table S1. Oxidation of adamantane using **1**.



Substrate[a]	3°-ol TON	2°-ol TON	2°-one TON	3°-Cl TON	Total TON[b]	3°/2°[c]
Adamantane	237	83	4	13	337	8.6

3°-ol = 1-adamantanol, 2°-ol = 2-adamantanol, 2°-one = 2-adamantanone, 3°-Cl = 1-chloroadamantane, 2°-Cl = 2-chloroadamantane. [a] Reaction Conditions: Adamantane (0.27 M), Oxidant (0.18 M), Catalyst (0.15 mM) in DCM:MeCN solvent mixture (v/v = 3:1), 2h under N_2. [b] TON = number of mmol of product/number of mmol of catalyst. The TON is the average of three determinations. [c] 3°/2° = 3(TON of 3°-ol + TON of 3°-Cl)/(TON of 2°-ol+ TON of 2°-one + TON of 2°-Cl).

Table S2. Oxidation of methylcyclohexane using **1**.



Catalyst[a]	3°-ol TON	*o*-2°-ol TON	*m*-2°-ol TON	*p*-2°-ol TON	2°-ones TON	1°-ol TON	Total TON[b]	3°-ol :2°-ols
1	390	114	475	27	67	9	1082	36:64
none	94	10	11	5	11	2	133[c]	82:18

3°-ol = 1-methylcyclohexanol, *o*-2°-ol = 2-methylcyclohexanol, *m*-2°-ol = 3-methylcyclohexanol, *p*-2°-ol = 4-methylcyclohexanol, 2°-ones = methylcyclohexanone (2 and 3), 1°-ol = cyclohexylmethanol. [a] Reaction Conditions: Methylcyclohexane (2.8 M), Oxidant (0.35 M), Catalyst (0.15 mM) in DCM:MeCN solvent mixture (v/v = 3:1), 60 °C, 2h under N_2. [b] TON = number of mmol of product/number of mmol of catalyst. The TON is the average of three determinations. [c] values based on 0.15 mM virtual nickel catalyst.