Electronic Supplementary Material (ESI) for Chemical Communications.

Mechanistic Elucidation of C-H Oxidation by Electron Rich Non-heme Iron (IV)-oxo at Room Temperature

Sujoy Rana, Aniruddha Dey and Debabrata Maiti*

Department of Chemistry, Indian Institute of Technology Bombay,

Powai,

Mumbai 400076

RECEIVED DATE (automatically inserted by publisher); E–mail:

dmaiti@chem.iitb.ac.in

Table of Contents

1. General Information:

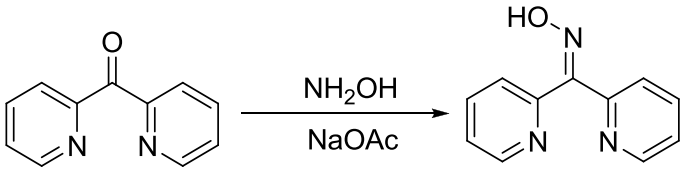
NMR spectra were recorded either on a Bruker 400/500 MHz. All ^{1}H NMR spectra were reported in units of parts per million (ppm) and measured relative to the signals for residual chloroform (7.26 ppm) in $CDCl_3$/ and for residual CH_3CN in CD_3CN at 1.96 ppm, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to $CDCl_3$ (77.23 ppm), unless otherwise stated and were obtained with ^{1}H decoupling. ESI-MS spectra were recorded in Bruker QTOF ESI-MS instrument. EPR spectra were recorded on JES - FA200 ESR Spectrometer with X and Q band (Standard Frequency (X band) - 8.75-9.65 GHz) at 77 K. UV-vis kinetics studies were performed in Agilent 8453 diode array based UV-vis Spectrophotometer. Synthesis of complex **1** and iron(IV)-oxo complexes (**2**) were done inside the glove box. Acetonitrile, cyclobutanol, CD_3CN, $Fe^{II}(OTf)_2$, cumene were bought from Sigma Aldrich. Ethyl benzene was bought from SDFCL. 2-phenyl-2-propanol was bought from Alfa Aesar whereas 1-phenyl ethanol was bought from Sigma Aldrich. $H_2{}^{18}O$ was bought from ICON isotope. 2-(chloromethyl)-4-methoxy-3, 5-dimethylpyridine hydrochloride and di(2-pyridyl) ketone were bought from alfa aeser. Single crystal of complex **1** was diffracted in Rigaku X-ray single crystal diffractometer. All GCMS analysis were carried out by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector). The electrochemical experiment was done out under a dinitrogen atmosphere at 298 K. The half-wave potential E_0 was set equal to 0.5 ($E_{p,a}$ + E_{pc}), where $E_{p,a}$ and $E_{p,c}$ are anodic and cathodic cyclic voltammetry peak potentials, respectively. The supporting electrolyte was Et_4NClO_4, and the complex concentration was in order of $\sim 10^{-3}$ M. All the kinetics data are carried out both under N_2 and air. Air has no effect on the kinetics of the reaction. Kinetics isotope effect was studied in air. Second order rate constant remain same for substrates both in air and N_2 atmosphere. First order rate constant (k_1) were calculated based on non-linear exponential fit in OriginPro8 software.

Computational Details:

Full geometry optimization was performed by using the density functional theory method at (U)B3LYP levels for **2**.[1] Except iron all other elements were assigned the 6-31G* basis set. The LANL2DZ basis set with effective core potential was employed for the iron atom.[2] The vibrational frequency calculation was done to ensure that the optimized geometries represent the local minima and there are only positive eigen values. All calculations were performed with Gaussian 09 program package.[3] Optimized structure was visualized with *ChemCraft*.[4]

2. Synthesis of ligand:

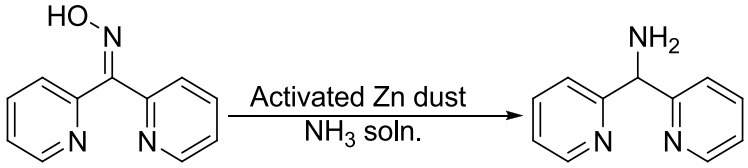
2.1 Preparation of Oxime:



Scheme1. Synthesis of oxime

Hydroxylamine hydrochloride (750.5 mg, 10.8mmol) and sodium acetate (NaOAc) (886mg, 10.8 mmol) were heated at 60 °C in H_2O (10 mL) for 1 hour. To the above, Di(2-pyridyl)ketone (1g, 5.43 mmol) in 2 mL MeOH was then added. The resulting mixture was stirred at 60 °C overnight. The oxime solidified upon cooling the reaction mixture to room temperature. The product oxime was washed with MeOH and the solvent was dried under vacuum. The crude oxime, a pink solid, was used in the next step without further purification.[5]

2.2 Reduction of oxime to amine:



Scheme 2. Reduction of oxime to amine

The above prepared oxime (1 g, 5mmol), NH_4OAc (655 mg, 8.5mmol), NH_3 (25% aqueous, 15 ml), EtOH (20 mL) and H_2O (10 ml) were mixed and heated at 80 °C. Activated Zn dust (1.47 g, 22.5mmol) was then added to the reaction mixture in small amounts for over 30 mins. The resulting mixture was refluxed for 3 hour and then stirred at 25 ^oC overnight. The mixture was filtered and the residue was washed with MeOH and water. The filtrate was concentrated and the resulting aqueous solution was made strongly alkaline with 10 (M) NaOH solution. The amine was then extracted with ethyl acetate and the organic phase was then washed with brine, dried over Na_2SO_4 and concentrated under vacuum to afford brown oil.[5] **^{1}H NMR (400 MHz, $CDCl_3$, δ):** 8.48 (m, 2H, Py), 7.55 (m, 2H, Py), 7.31 (d, 2H), 7.04(m, 2H), 5.25 (s, 1H, CH), 2.43 (s, 2H, NH_2).

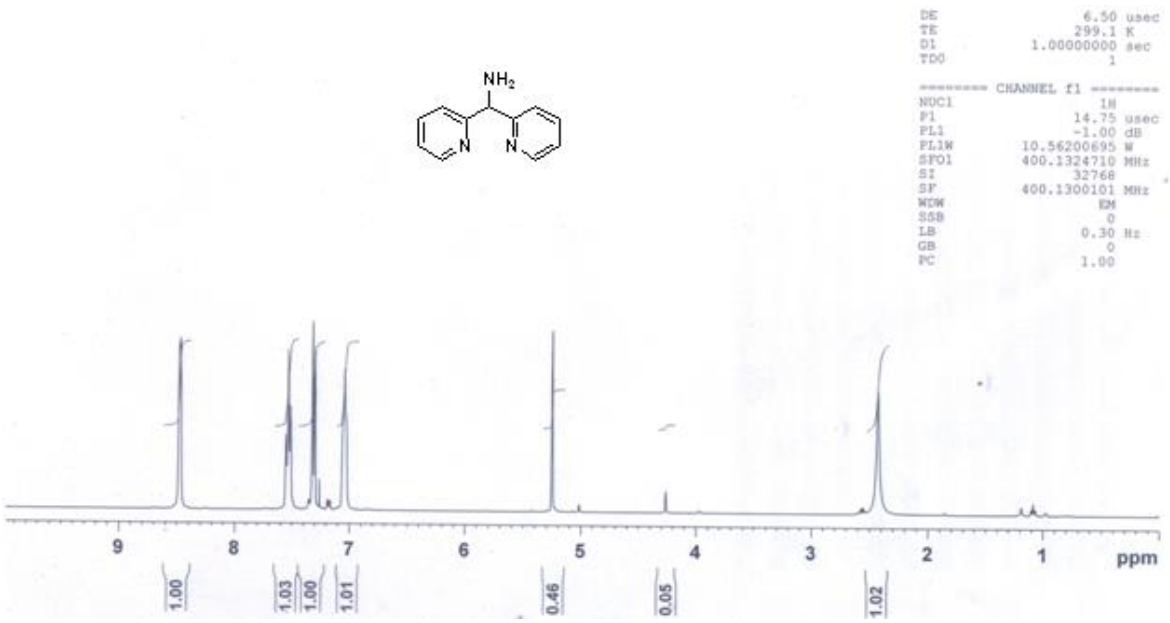
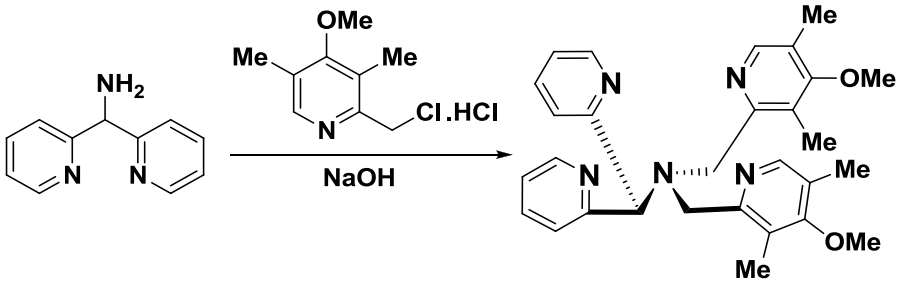


Figure S1. ^{1}H NMR of dipyridin-2-ylmethanamine

2.3 Synthesis of electron rich ligand **N4Py$^{OMe, Me}$**:

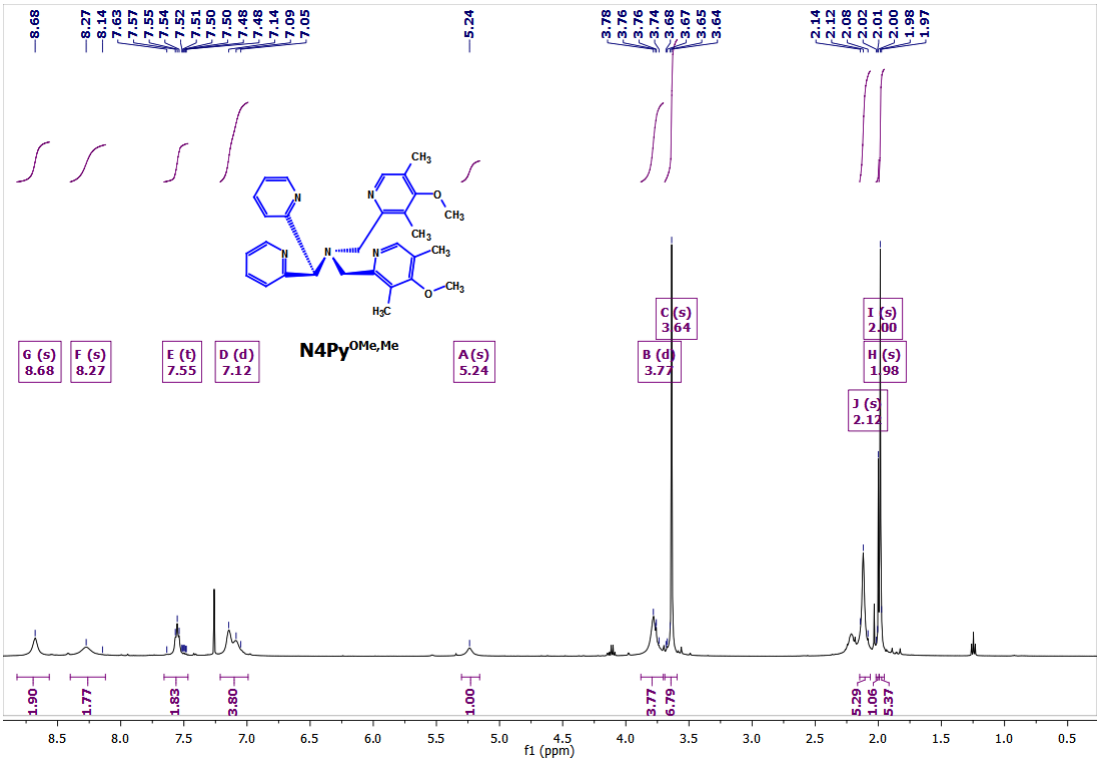


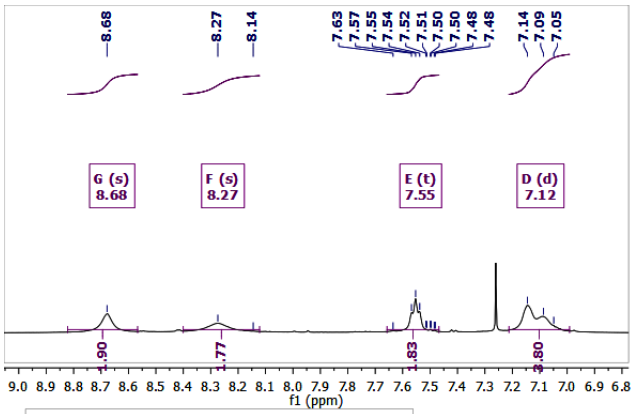
Scheme 3. Synthesis of electron-rich **(N4Py)$^{OMe, Me}$** ligand

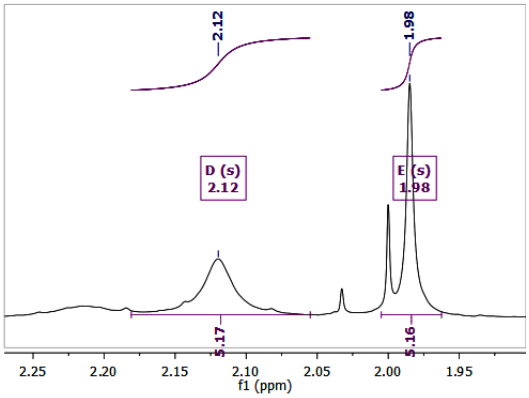
2-(chloromethyl)-4-methoxy-3, 5-dimethylpyridine hydrochloride (9.866 mmol) was added to an aqueous solution of NaOH (2 mL, 5 M) at 0 °C. After stirring for 10 minutes, the solution was added to bis(2-pyrimidyl) methylamine (0.969 g; 5.23 mmol) and another portion of aqueous solution of NaOH (5 M, 2 mL). The solution was allowed to stir for 48 hrs at 25 ˚C and then concentrated $HClO_4$ was added to precipitate a yellow solid, which was recrystallized from hot water. Treatment of this perchlorate salt with 2.5 (M) NaOH solution and extraction with dichloromethane yielded brownish solid N4Py^{OMe,Me} in 35% yield.[6] Subsequently, the ligand was characterized by NMR analysis and HRMS. **^{1}H NMR (500 MHz, $CDCl_3$, δ):** 8.20-8.69 (m, 4H, Py), 7.04-7.65 (m, 6H, Py), 5.24 (s, 1H, CH), 3.78 (s, 4H, CH_2), 3.64 (s, 6H, OCH_3), 2.12 (s, 6H, CH_3), 1.98 (s, 6H, CH_3). **13C NMR (000 MHz, $CDCl_3$)**: 10.72, 13.31, 54.21, 60.02, 72.75, 123.02, 124.58, 124.76, 125.08, 136.82, 149.97, 150.26, 155.84, 158.47, 164.12.

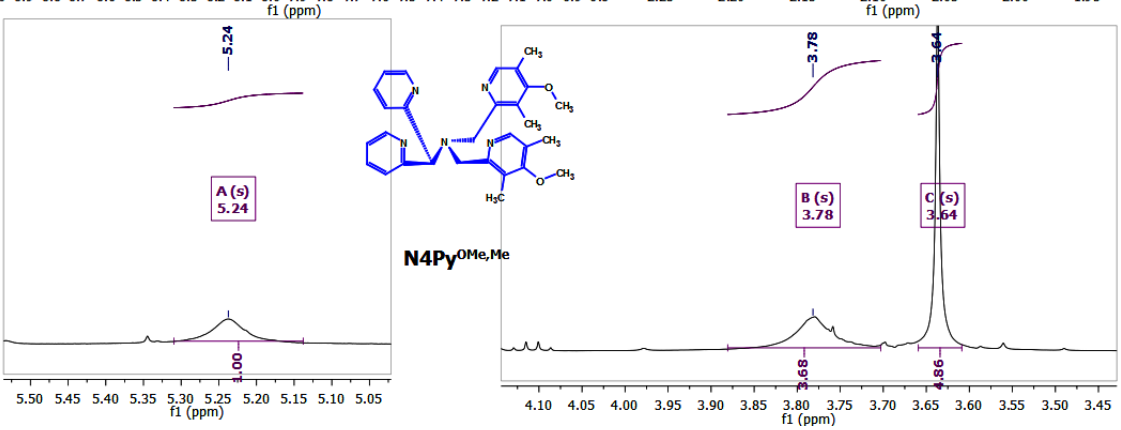
2.4 Characterization spectra of $N4Py^{OMe,Me}$:

^{1}H NMR spectra of $N4Py^{OMe,Me}$









13C NMR of the N4Py^{OMe,Me}

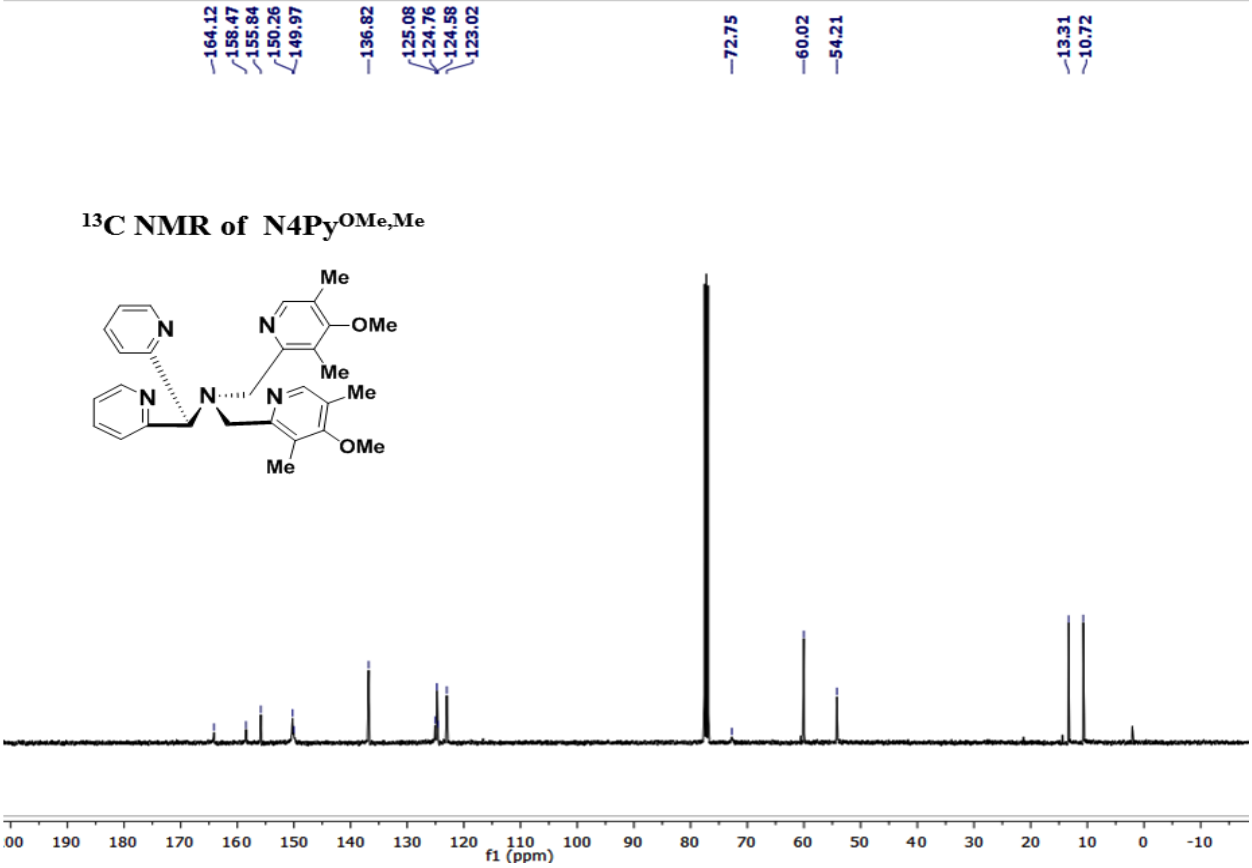


Figure S2. ^{1}H and ^{13}C NMR of ligand N4Py^{OMe,Me}

HRMS data:

Adduct: M+H, Charge: 1, Chemical Formula: C29H34N5O2, Average Mass: 484.612

Monoisotopic Mass: **484.2707** (Calculated); **484.270** (Experimental)

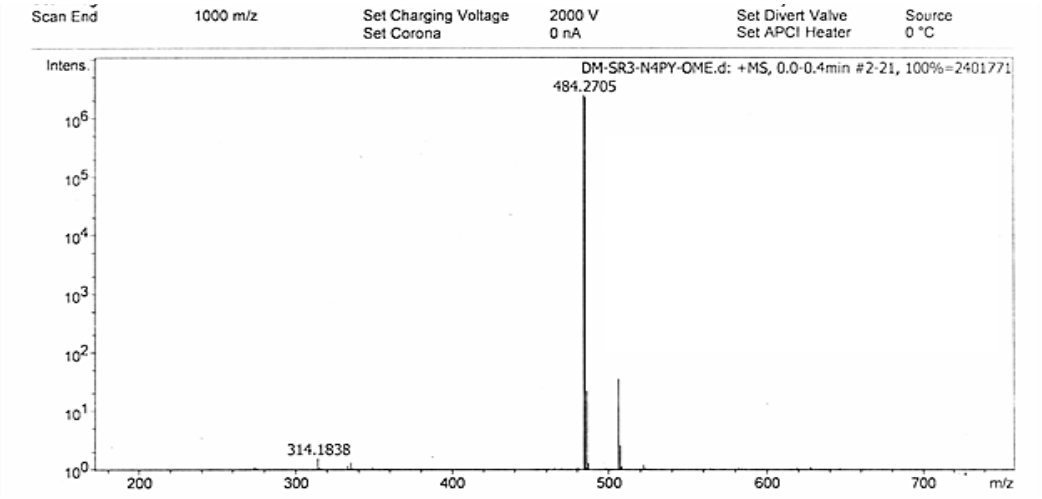


Figure S3. ESI-MS spectra of (N4Py)^{OMe,Me} ligand

3. Synthesis and characterization of $[Fe^{II}(N4Py^{OMe,\ OMe})(CH_3CN)](OTf)_2(CH_3CN)_2$ (1):

The solution of $N4Py^{OMe,Me}$ (0.57 mmol) in 3 mL of CH_3CN, was slowly added to a solution of $Fe^{II}(OTf)_2.2CH_3CN$ (0.57 mmol, 248 mg) [$Fe^{II}(OTf)_2$ was also used] in acetonitrile and the resulting solution was stirred overnight. Reddish-orange powder was obtained after addition of a large volume of Et_2O (5-6 times of the complex was dissolved in acetonitrile and then diethyl ether was added to get a precipitate of the complex) to the resulting solution. Yield was ~65%. Deep red crystals were obtained by slow diffusion with acetonitrile/diethyl ether conducted inside the glove box.[7] The complex was characterized by X-ray crystal study and UV-Vis study (λ_{max}=459 nm, ϵ ~ 6000 $mol^{-1}cm^{-1}L$).[6] It was further characterized by ESI-MS and ^1H NMR in CD_3CN. **^1H NMR (500 MHz, CD_3CN, δ):** 8.85 (d, 2H, Py), 8.68 (s, 2H, Py), 7.95 (m, 2H, Py), 7.91 (m, 2H, Py), 7.33 (m, 2H, Py), 6.32 (s, 1H, CH), 4.35 (q, 4H, CH_2), 3.71 (s, 6H, OCH_3), 2.31 (s, 6H, CH_3), 1.98 (s, 3H, CH_3 of CH_3CN), 1.93 (s, 6H, CH_3). **^{13}C NMR** (101 MHz, CD_3CN) δ 11.6, 13.5, 60.9, 65.5, 77.5, 118.3, 124.4, 125.3, 125.3, 129.0, 139.2, 154.4, 158.3, 163.0, 163.1, 165.6.

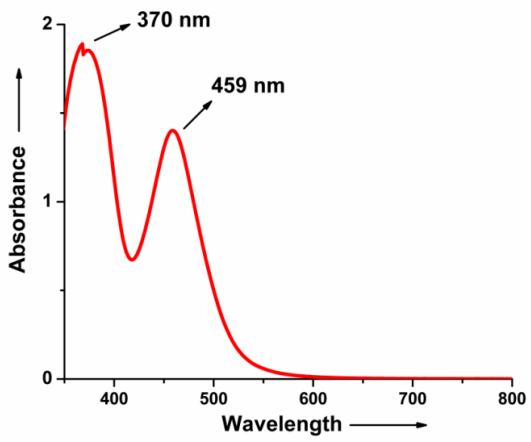


Figure S4. UV-vis spectra of complex $[Fe^{II}(N4Py)^{OMe,Me}(CH_3CN)](CH_3CN)_2(OTf)_2$ (**1**)

3.1 ESI-MS spectra of complex 1

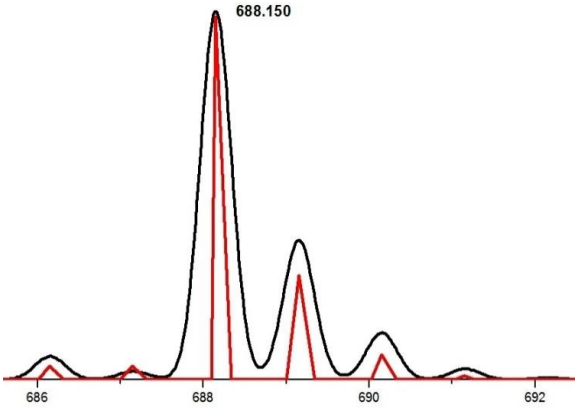


Figure S5. ESI-MS data for complex **1**, [(N4Py) $^{OMe,Me}Fe^{II}(OTf)]^{+}$ (Calculated *m/z*=**688.150**)

3.2 NMR data and spectrum of complex 1:

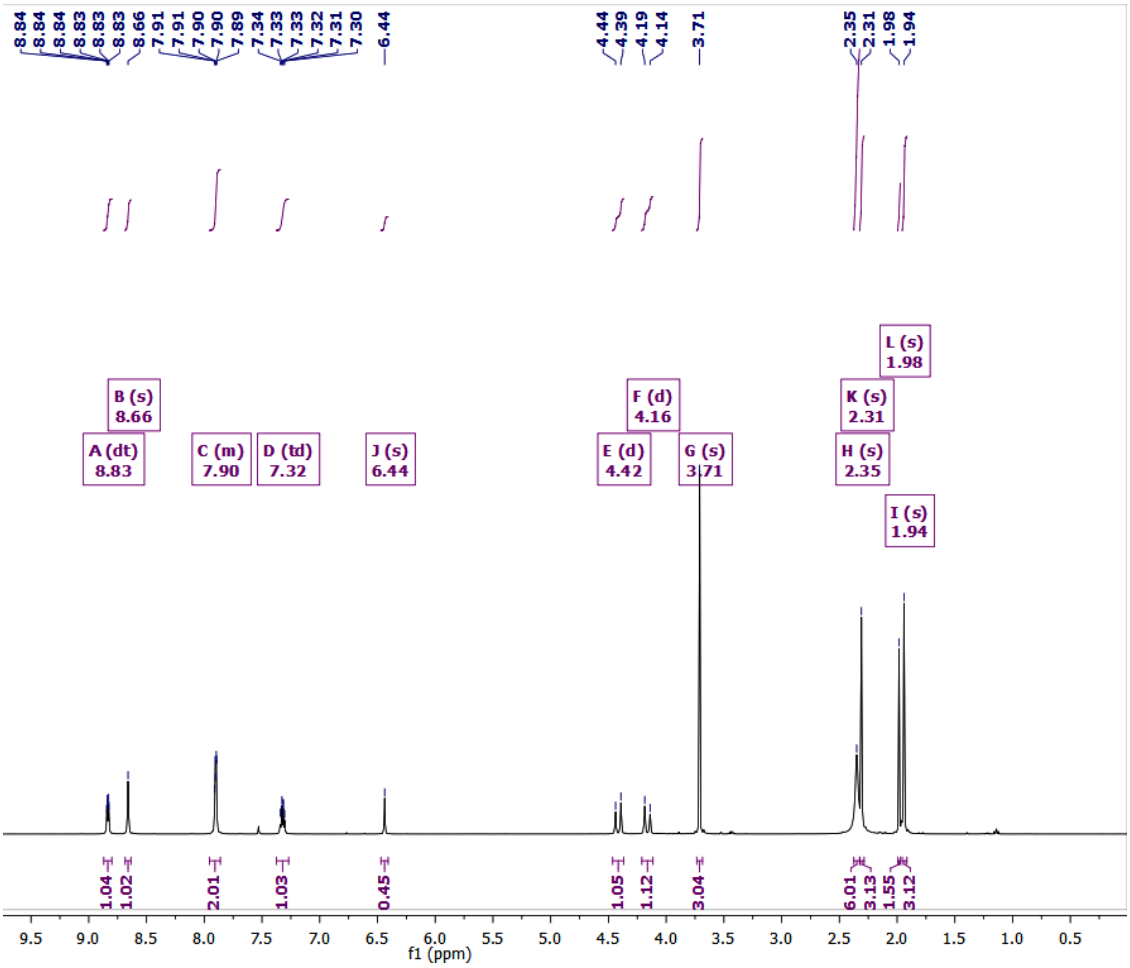


Figure S6. ^{1}H NMR spectrum for complex **1** in CD_3CN

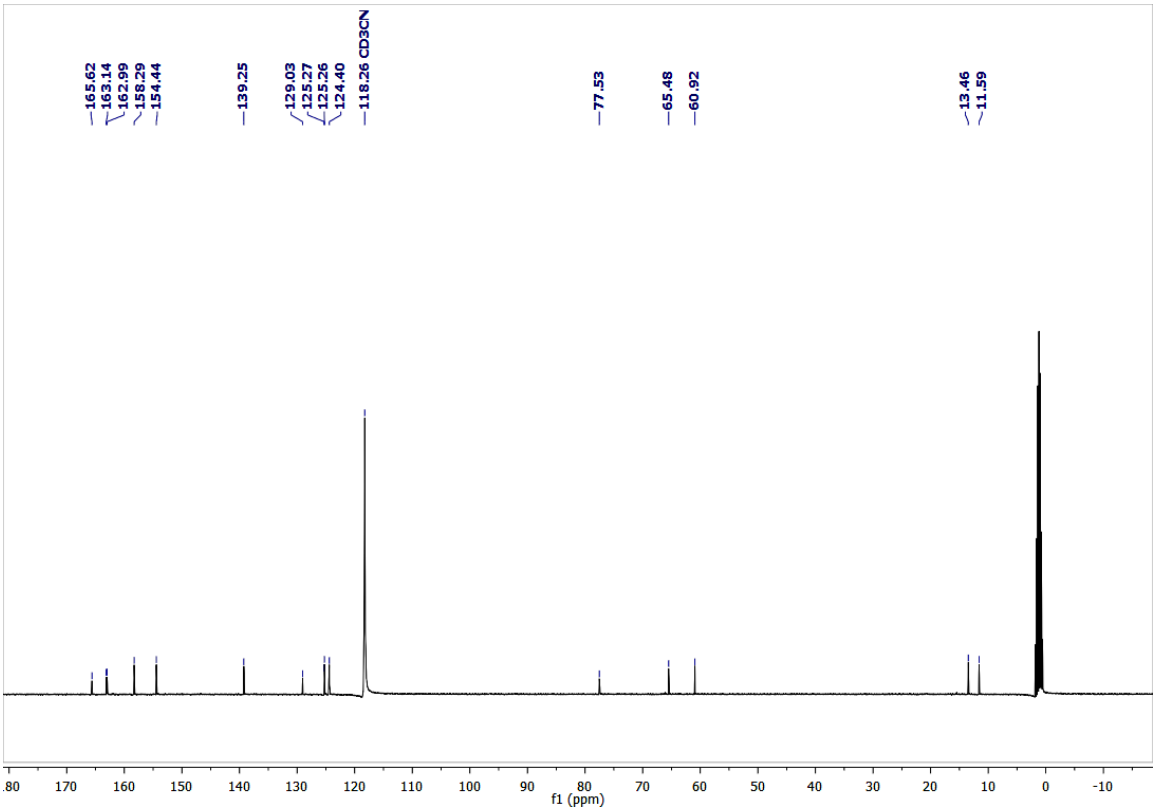
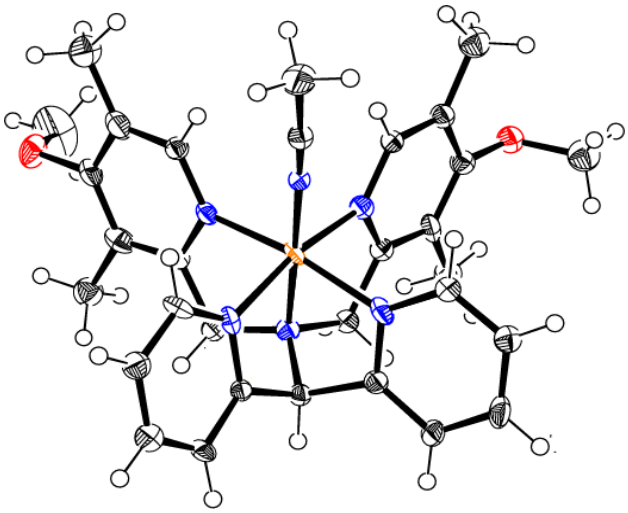


Figure S7. ^{13}C NMR spectrum for complex **1** in CD_3CN

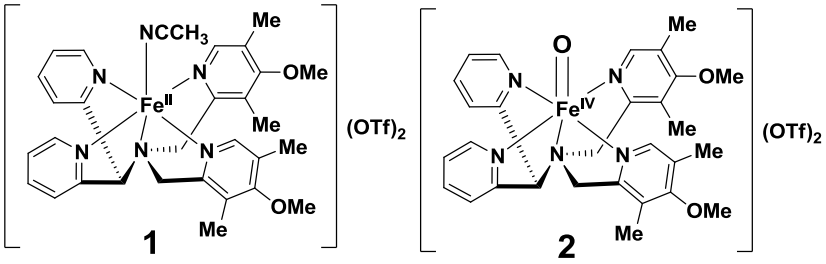
3.3 X-ray Crystallography data of Complex 1

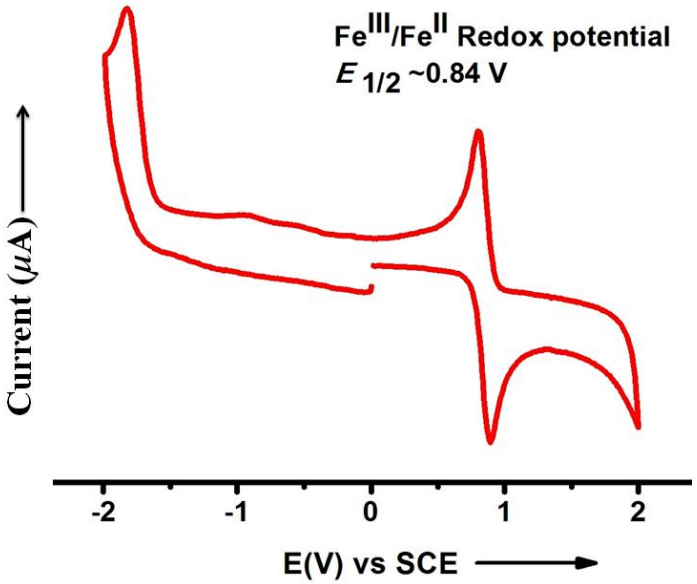


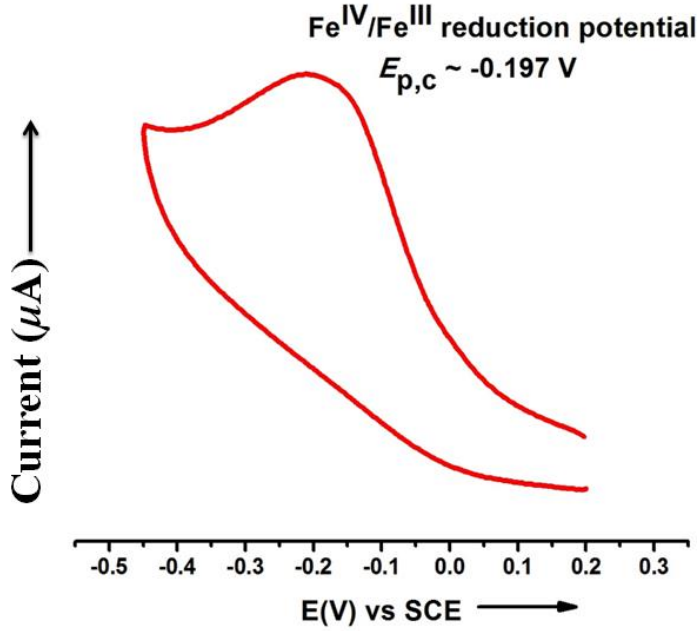
Ortep diagram of Fe-complex with 50% probability (after removal of solvents and anions for clarity)

Figure S8: ORTEP diagram of $[Fe^{II}(N4Py)^{OMe,Me})(CH_3CN)](OTf)_2$ (**1**)

3.4 Electrochemical study of complex 1 and 2 in acetonitrile







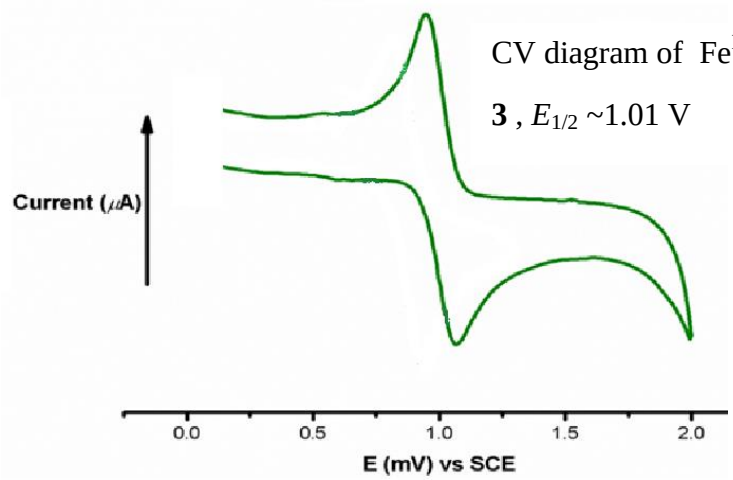


Figure S9. Cyclic voltammetry diagrams of complex **1** and **2** and **3**

4. Synthesis of complex $[Fe^{IV}(N4Py)^{OMe,Me})(O)](OTf)_2$ (**2**)

Initially, 25 mg of the red-solid complex was dissolved in 5-8 mL of acetonitrile in a 20 mL glass vial. 3 equiv. of solid PhIO [8] was added to it and stirred (5-10 min) until the green color appeared.[7,9] The resulting solution was kept overnight in deep freeze at -40 °C in order to get a clear/transparent solution (excess PhIO gets precipitated at the bottom of the vial). After that, measured volume of the transparent solution of iron(IV)-oxo was taken and 50-100 equiv. of substrates were added. The resulting samples were then subjected to ^{1}H-NMR and ESI-MS and for EPR study.

4.1. ESI-MS spectra for species detected during reaction between 2 and ethyl benzene (S10) and cumene (S11)

After synthesizing complex **2** as described in section 4 250-500 equiv. of $H_2{}^{18}O$ was added to the solution of **2** and stirred for 5-10 minutes (under nitrogen atmosphere). The resulting solution was kept at -40 ˚C inside the glove box for 1 hour and then it was kept at room temperature. Then ESI-MS was recorded and found that complex **2** got 18-O labeled. Subsequently 100 equiv. of substrates were added to the labeled **2** and ESI-MS were recorded after 5-10 minutes stirring of the reaction. The Figure d and g (Figure S10) were obtained from the reaction between 18-O labeled **2** and ethyl benzene

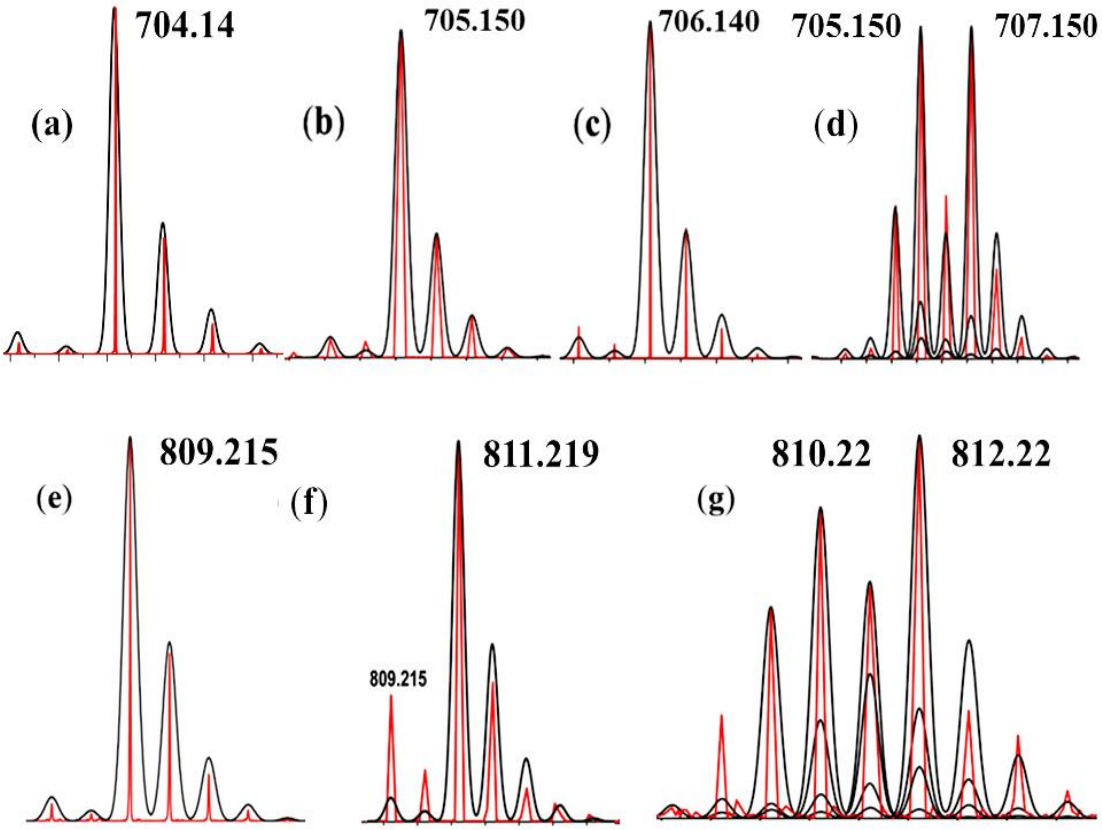


Figure S10. ESI-MS of the intermediates during reaction of **2** and ethylbenzene (red line, experimental and black line, simulated, spectra were recorded after 5 min of addition). ESI-MS of **2** (10a), **3** (10b), 18-O-**2** (10c), 18-O-**3** (10d), **5** (10e), 18-O-**5** (10f), **4** and 18-O-**4** (10g). Fig 10d/10g obtained from reaction mixture 2 and ethyl benzene under labeling condition (with $H_2{}^{18}O$).

Figure S11. ESI-MS of the intermediates, **5a** (11a) and 18-O labeled **5a** (11b) during reaction of **2** and cumene (red line, experimental and black line, simulated)

4.2 UV-vis spectrum and ESI-MS spectrum of Complex 2:

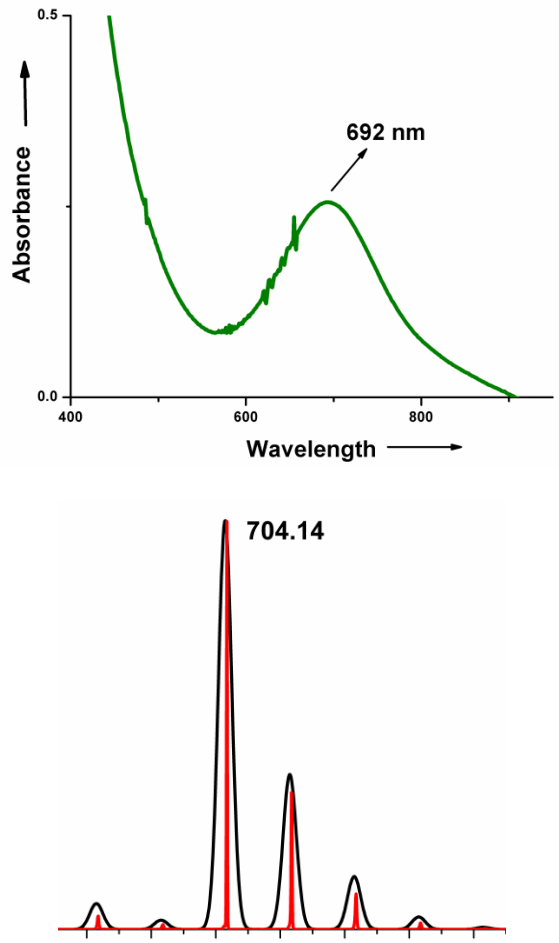
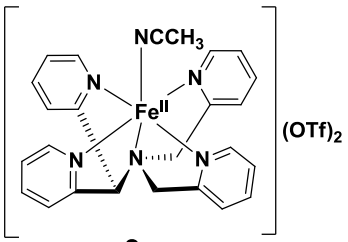


Figure S12. UV-vis and ESI-MS spectra of complex **2 (**red line is experimentally obtained, black line is simulated)

4.3 DFT optimization of complex 2 and 4 using B3LYP level of theory and LANL2DZ basis set



3

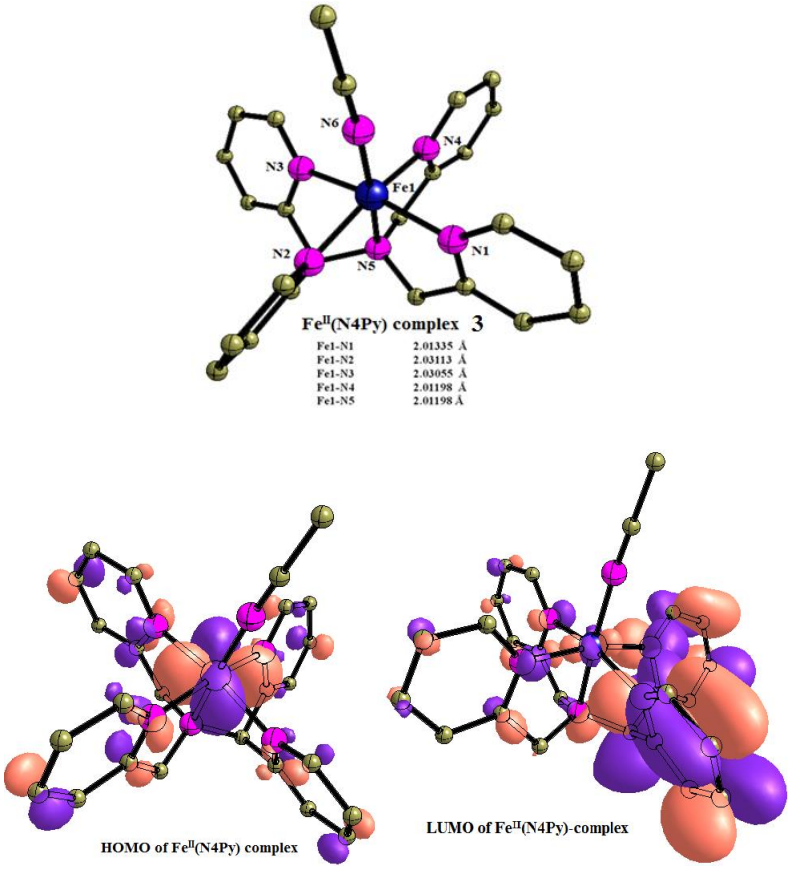
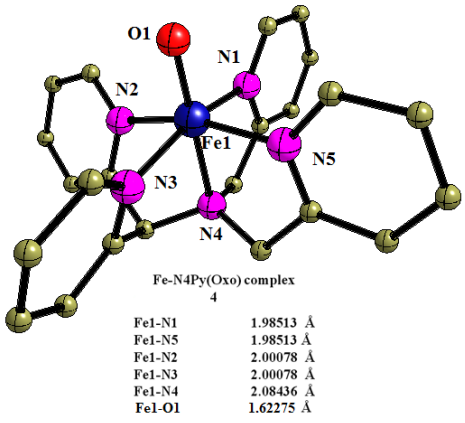
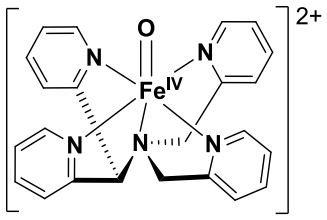


Figure S13. DFT optimized structure and HOMO diagram of Fe^{II}(N4Py) complex **3**





4

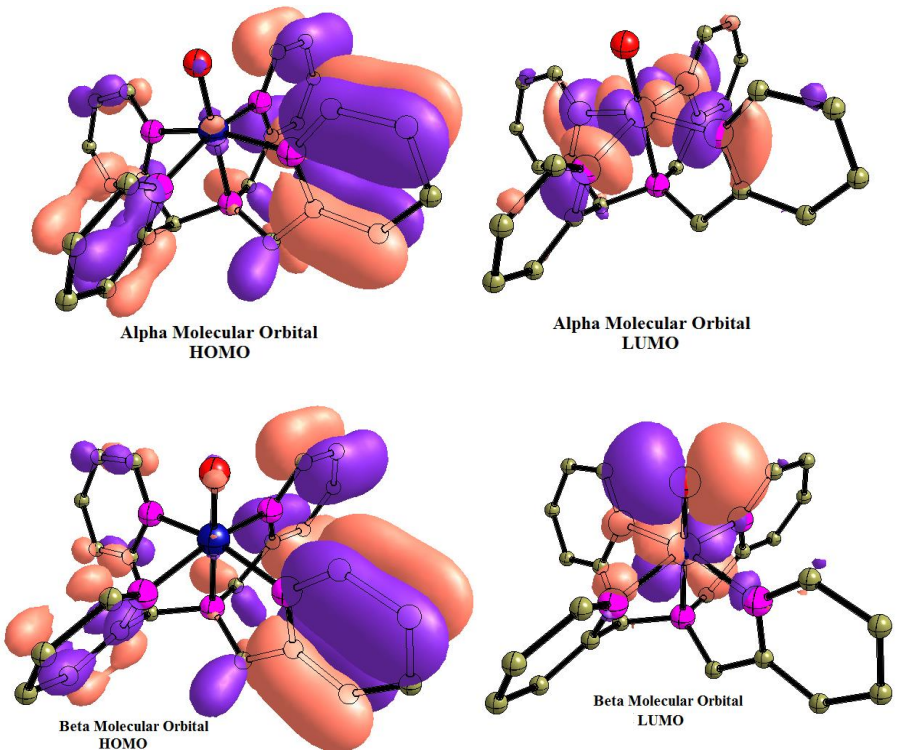
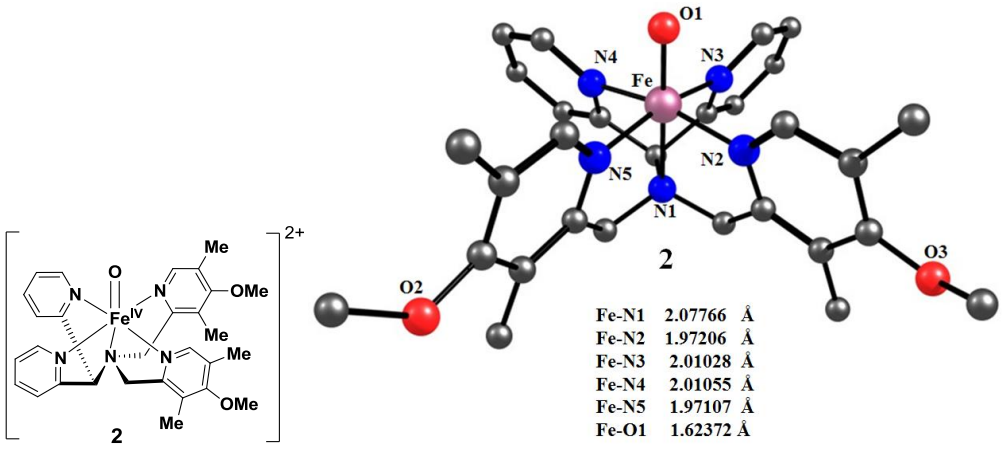


Figure S14. DFT optimized structure and HOMO, LUMO diagram of Fe^{IV}(N4Py)(Oxo) complex



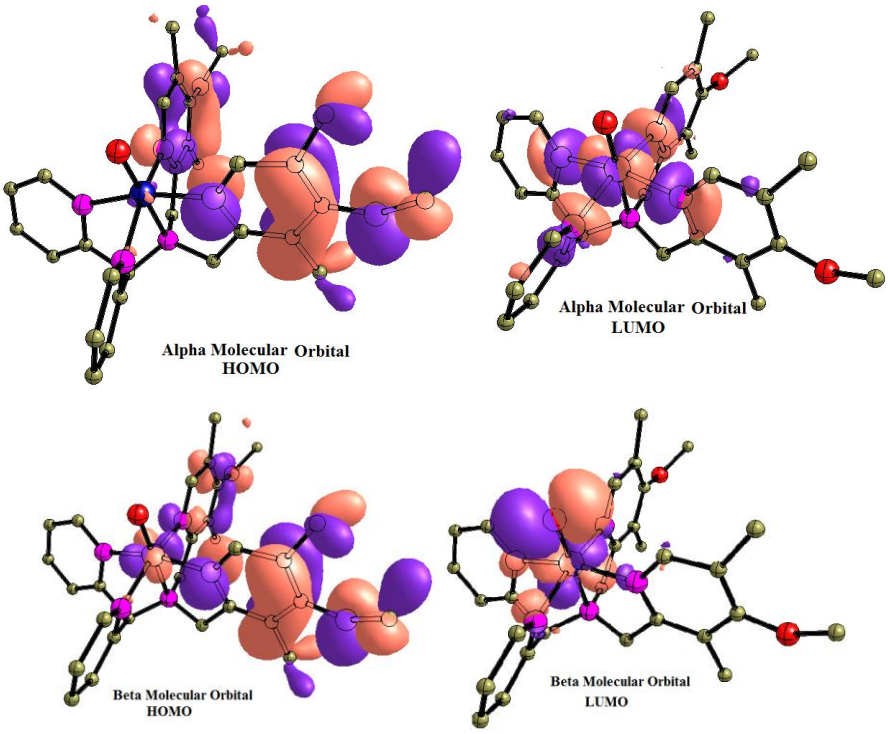


Figure S15. DFT optimized structure and HOMO, LUMO diagram **2**

4.4. Half-life study of complex 2 in acetonitrile

Half life of complex **2** was determined from 0.46 mM solution of complex 2 prepared by using PhIO. The UV-vis was recorded after different time to check the absorbance. It was found that after ~50 hours the absorbance of the parent solution decayed to half in air at ambient temperature (30 °C).

4.5. NMR Data and Spectrum of Complex 2:

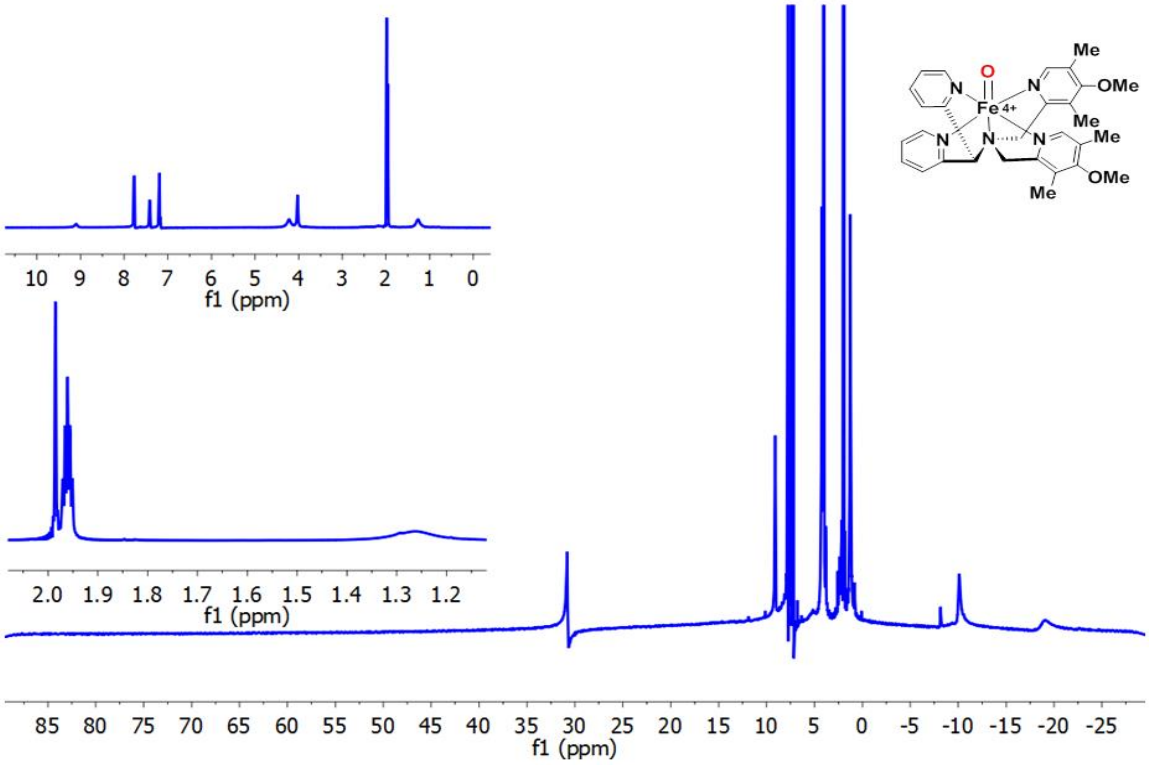


Figure S16. ^{1}H NMR spectrum for complex **2** in CD_3CN prepared by adding PhIO

4.6. EPR data from the reaction mixture of 2 and benzyl alcohol:

All spectra were recorded at liquid nitrogen temperature (77 K). Samples were prepared as described in section **4**. Different substrates (100 equiv.) were added to the clear and transparent solution of **2** at room temperature and subsequently EPR spectra were recorded after 5 minutes.

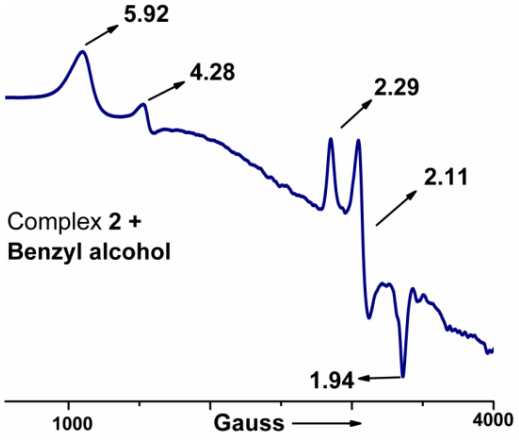


Figure S17

Figure S18. EPR spectra (acetonitrile, 77 K) obtained from reaction between **2** and (a) ethyl benzene (b) cumene

5. Kinetics study with benzylic substrates: Ethyl benzene and Cumene

Initially, 15 mg of the red-solid complex was dissolved in 10 mL of acetonitrile in a 20 mL glass vial. 5 equiv. of solid PhIO [8] was added to it and stirred (5-10 min) until the green color appeared and then another 30 mL of acetonitrile was added to it.[7,9] The resulting solution was kept overnight in deep freeze at -40 °C in order to get a clear/transparent solution (excess PhIO gets

precipitated at the bottom of the vial). After that, 0.5 mL (0.52 mM) of clear solution of 2 was taken in 1 mL UV cuvette and subsequently different conc. of the substrates were added and kinetics was followed by UV-vis study.

5.1 Kinetics study with ethyl benzene as substrate:

Conc. of ethyl benzene (mM)	Rate constant (k_1)(s^{-1})
81.56	0.002
163.134	0.00345
244.7	0.0052
326.26	0.007

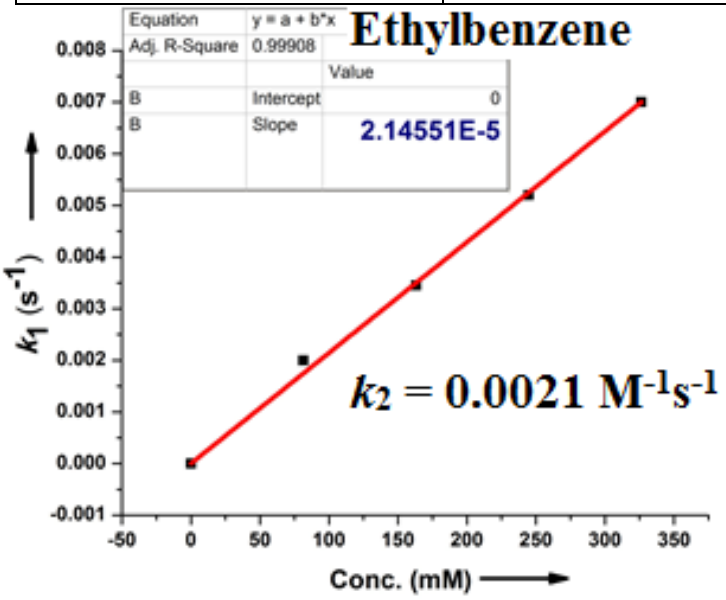


Figure S19. Second order plot for ethyl benzene

5.2 Kinetics study with cumene as substrate:

Conc. of substrate (mM)	Rate constant (k_1) (s^{-1})
71.88	0.00849
143.77	0.016
215.65	0.0236
287.54	0.03

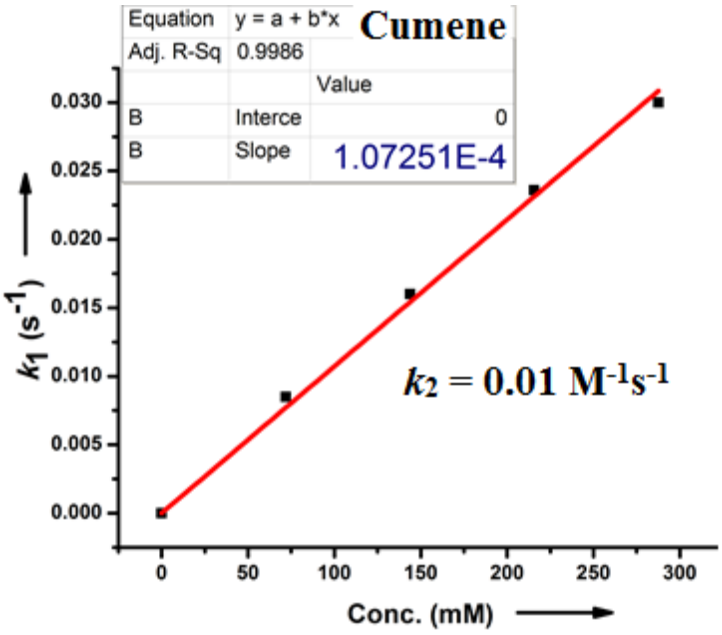


Figure S20. Second order plot for cumene

5.3 Second order plot of ethylbenzene and cumene based on pseudo-first order reaction monitored by UV-vis (λ_{max}= 692 nm)

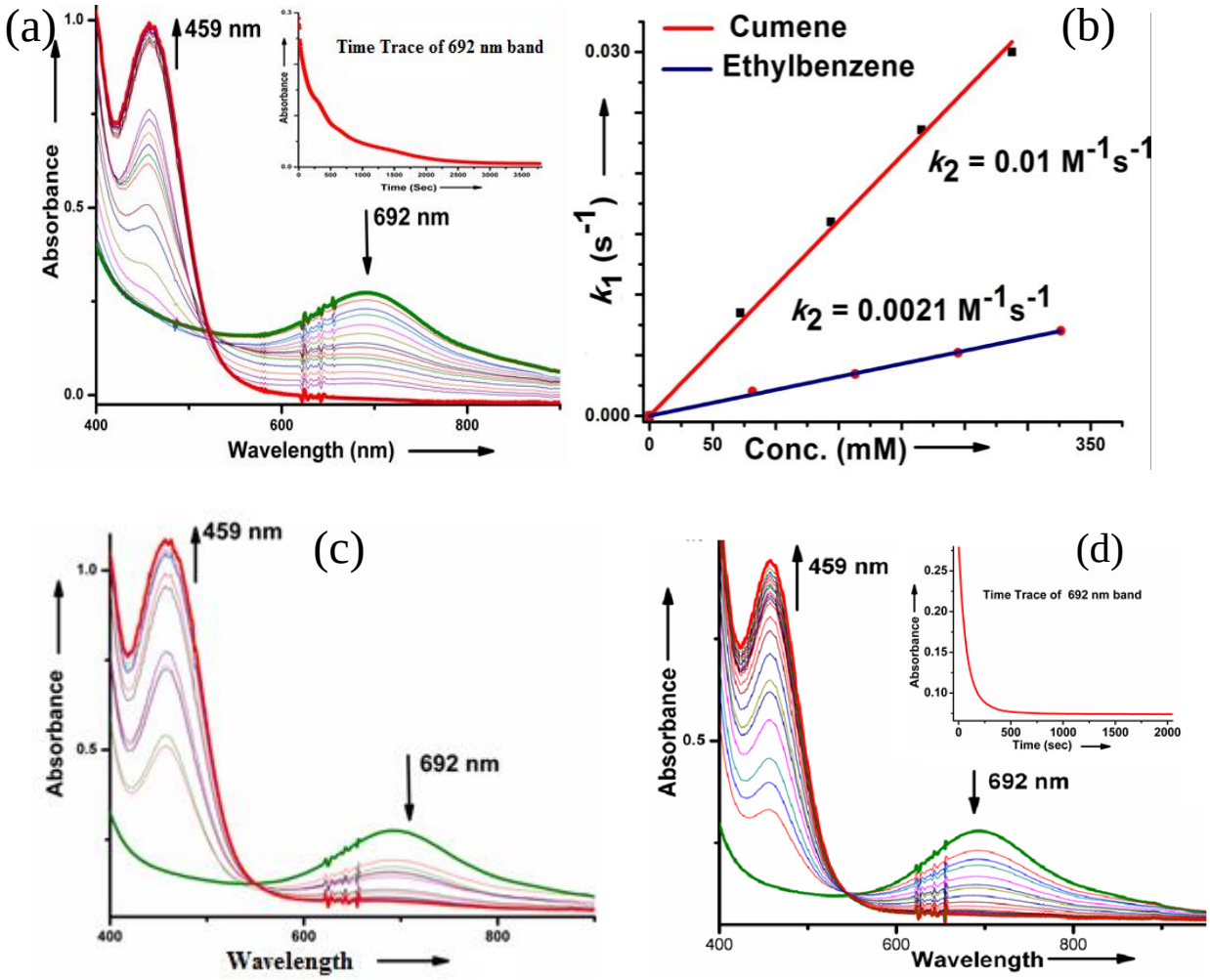
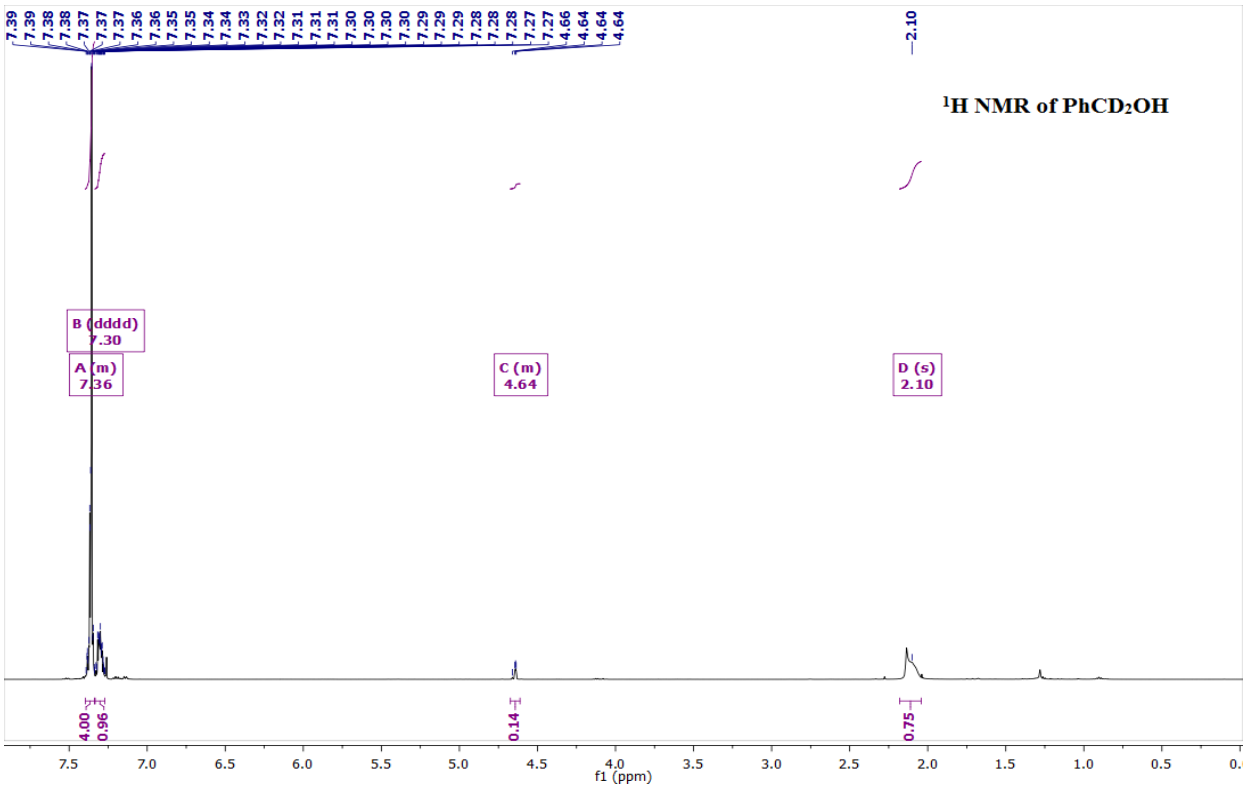


Figure S21. UV-vis change at 692 nm for **2**, in presence of cumene, (b) second order rate kinetics plot for ethyl benzene and cumene (c) spectral change during reaction between **2** and ethyl benzene (d) spectral change during reaction between **2** and benzyl alcohol.

5.4 Kinetic Isotope effect study for benzyl alcohol oxidation:

$PhCD_2OH$ was prepared following the literature report from $PhCH_2OH$ in D_2O under microwave condition.[10] The resulting reaction mixture was extracted with DCM (2x10 mL) and subsequently it was purified by column chromatography. Approximately (~95%) deuterium rich $PhCD_2OH$ was obtained as evident from the NMR study. The resulting product was also characterized by GC-MS. After that kinetic studies were performed with this $PhCD_2OH$. Initially

1.2 (mM) iron(IV)-oxo (**2**) solution was prepared and then second order plot were constructed by varying different conc. of $PhCH_2OH$ and $PhCD_2OH$.



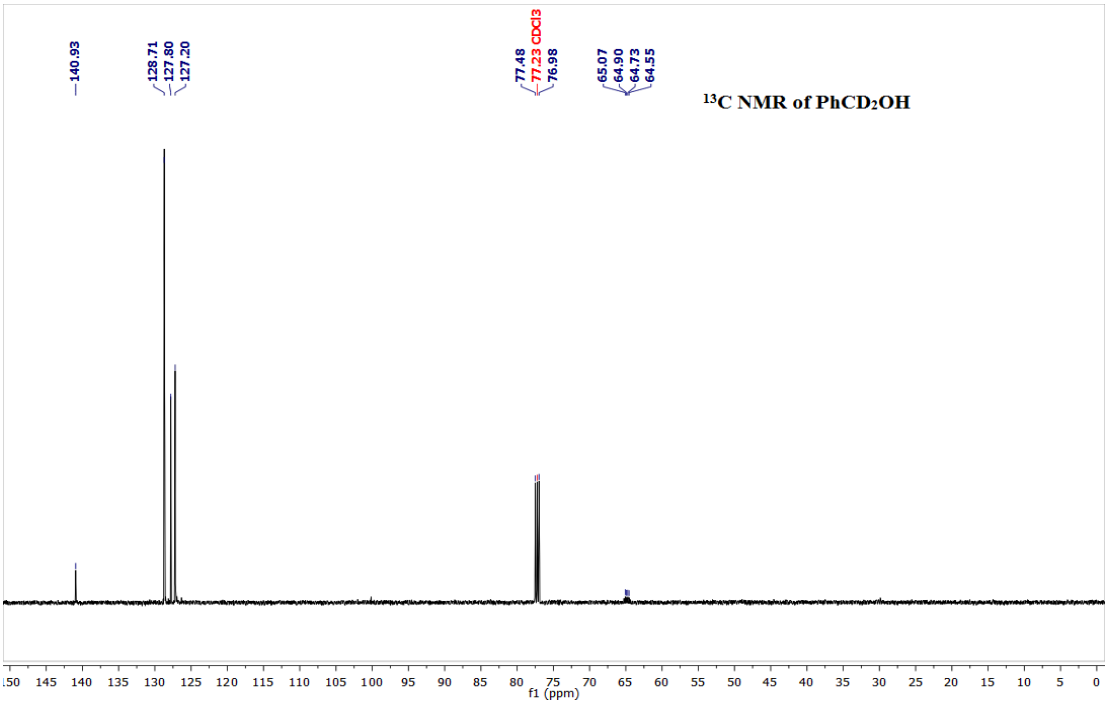
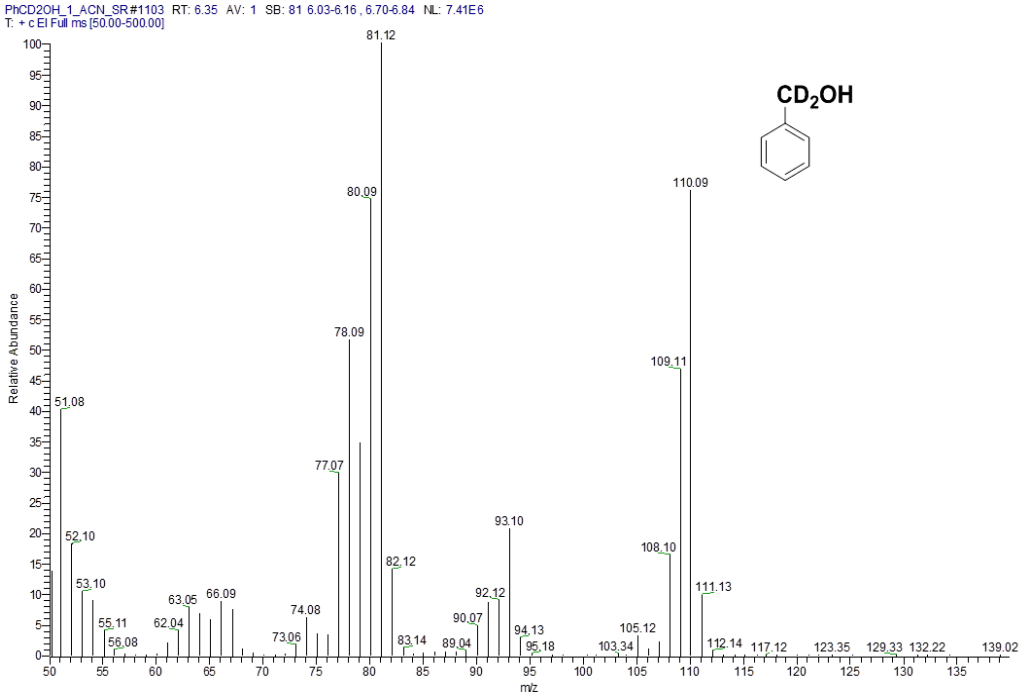


Figure S22. ^{1}H and ^{13}C NMR of PhCD2OH



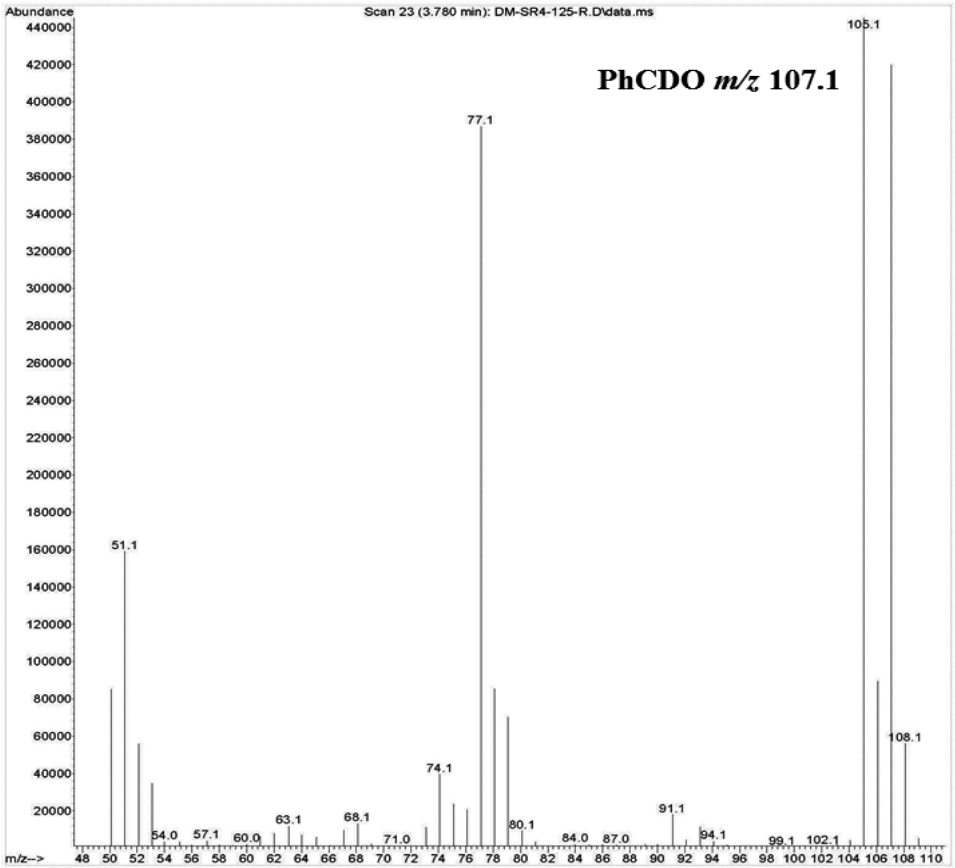


Figure S23. GC-MS spectra of $PhCD_2OH$ and PhCDO

5.4.1 Kinetics study with $PhCH_2OH$

Conc. of $PhCH_2OH$ (mM)	Rate constant (k_1)(s^{-1})
96.17	0.0049
192.34	0.0082
288.51	0.01366
384.68	0.017

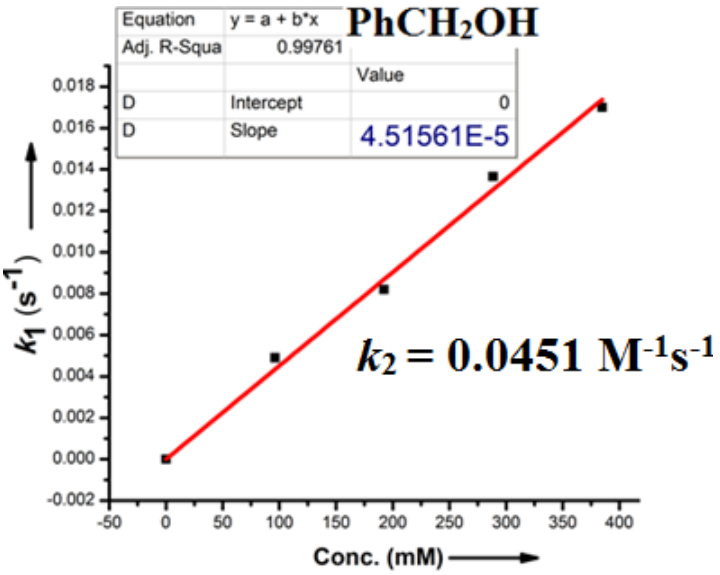


Figure 24

5.4.2 Kinetics study with $PhCD_2OH$

Conc. of $PhCD_2OH$ (mM)	Rate constant (k_1)(s^{-1})
96.68	0.00037
193.37	0.0008
290.04	0.00123
386.72	0.0016

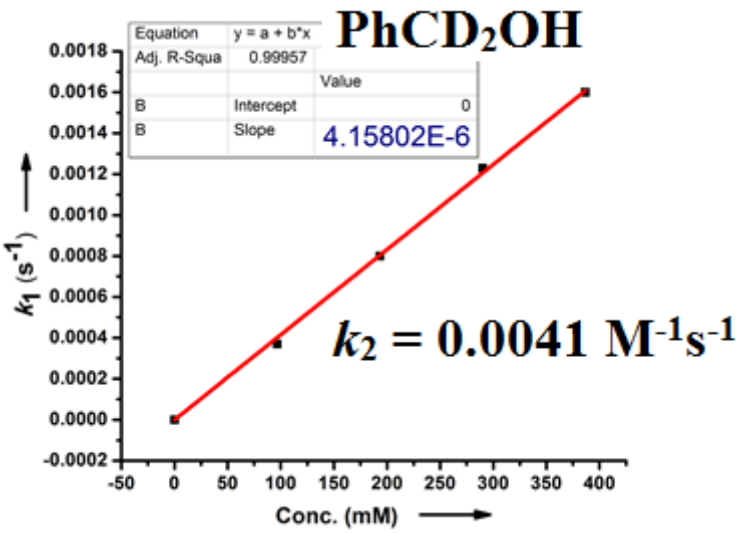
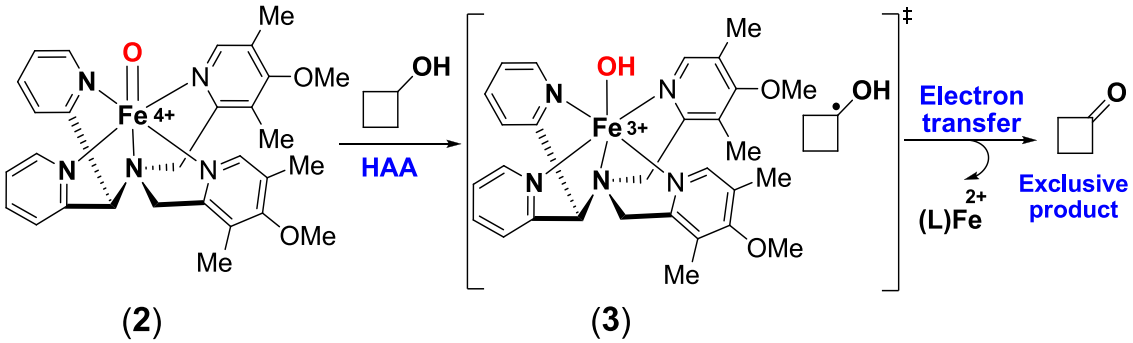


Figure 25

KIE for benzyl alcohol oxidation $\mathbf{k_H/k_D}$ **= 0.0451/0.00415= 11**

6. Cyclobutanol oxidation to cyclobutanone by iron (IV)-oxo (complex 2):



Scheme 4. Cyclobutanol Oxidation by complex **2**

The reaction of cyclobutanol was carried out in CD_3CN. Initially, 50 mg of the complex was dissolved in 5 mL of CD_3CN; PhIO was added to it and then stirred for 5-10 minutes for complete formation of **2**. It was then kept in -40 °C deep freeze for overnight. The resulting transparent green solution was taken and excess 200 equiv. of cyclobutanol was added to it. The reaction was stirred for 24 hour. Subsequently, the, cyclobutanone product was confirmed by ^1H NMR analysis.

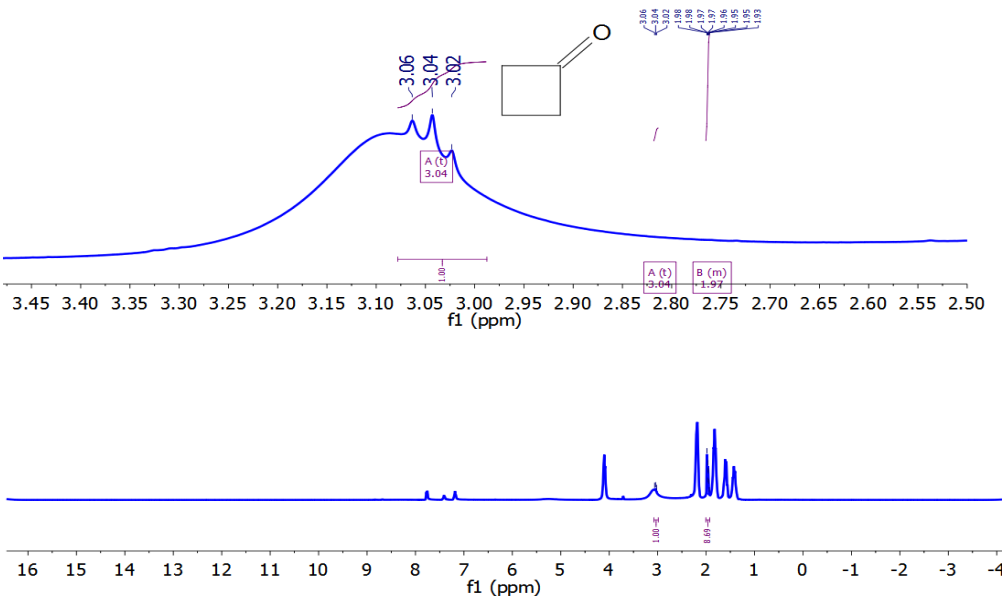
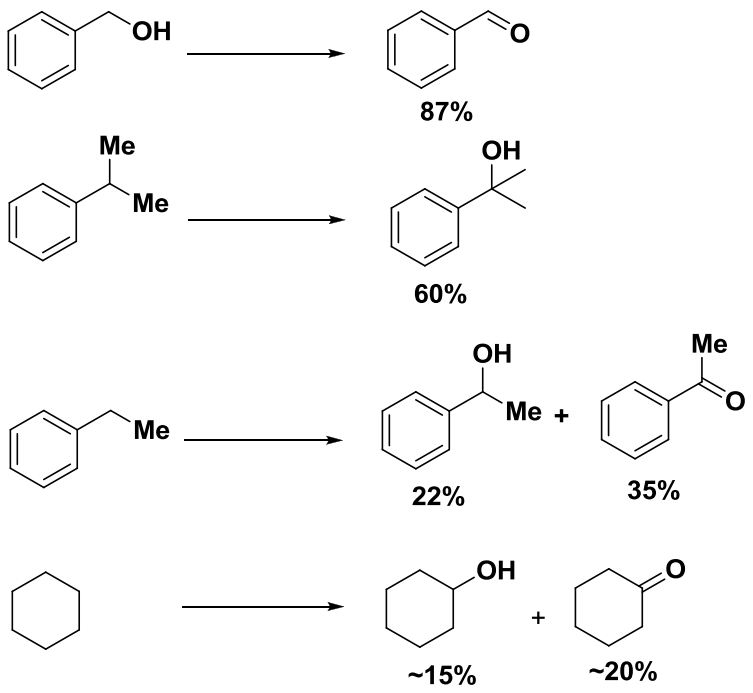


Figure S26. ^{1}H NMR of the reaction mixture of **2** and cyclobutanol in CD_3CN

7. C-H oxidation by iron (IV)-oxo (2):

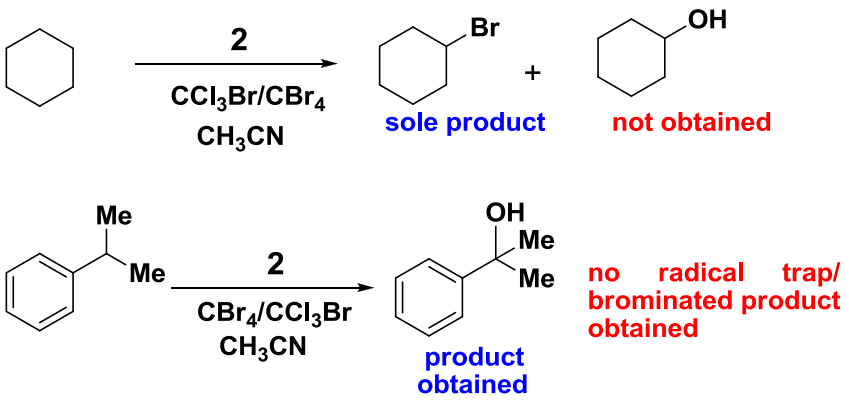
20 mg of the complex **1** was dissolved in 5 mL of acetonitrile in a 20 ml vial. Subsequently, 5 equiv. of PhIO was added and stirred for 5 minutes to ensure complete formation of iron(IV)-oxo (**2**). It was kept in deep freeze (-40 °C) for overnight to get a clear green colored solution of **2**. Then, 50 equiv. of substrates were added and the reaction mixture was stirred for 24 h. Notably, in case of cyclohexane, 500 equivalents of starting material were used. Yields of the hydroxylated products were measured by using standard product as standard. Similarly, after preparation of 2, 250 equiv. of $H_2{}^{18}O$ was added to it and stirred for 5 minutes. It was kept at -40 °C in deep freeze for 2 hour and subsequently 50-100 equivalent of substrates were added. The reactions were carried out inside the glove box for 24 hour stirring.



Scheme 5. C-H oxidations by complex **2**

7.1 Radical Trap experiment for cyclohexane oxidation by 2 using CCl_3Br:

Complex **2** was prepared by using 20 mg of complex **1** and solid PhIO. After that, solution of **2** was kept at -40 °C in deep freeze for overnight. The resulting clear green solution (4 mL) was taken in reaction tube and subsequently 500 equiv. of cyclohexane and 500 equiv. of CCl_3Br were added and the reaction was stirred for 24 hour. Only bromocyclohexane was obtained as sole product. Similar experiment was carried out with cumene using CBr_4 as radical trap.



Scheme 6. Radical trap experiment of cyclohexane and cumene with complex **2**

8. GC-MS Spectra for O-18 labeling study:

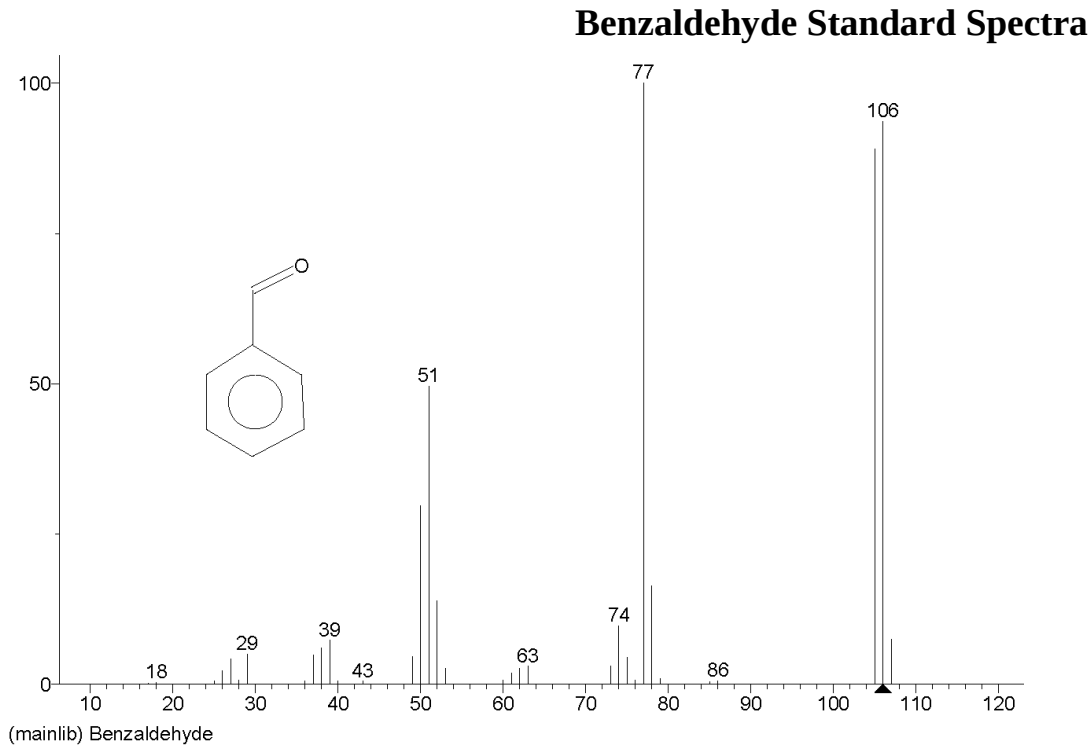


Figure S27

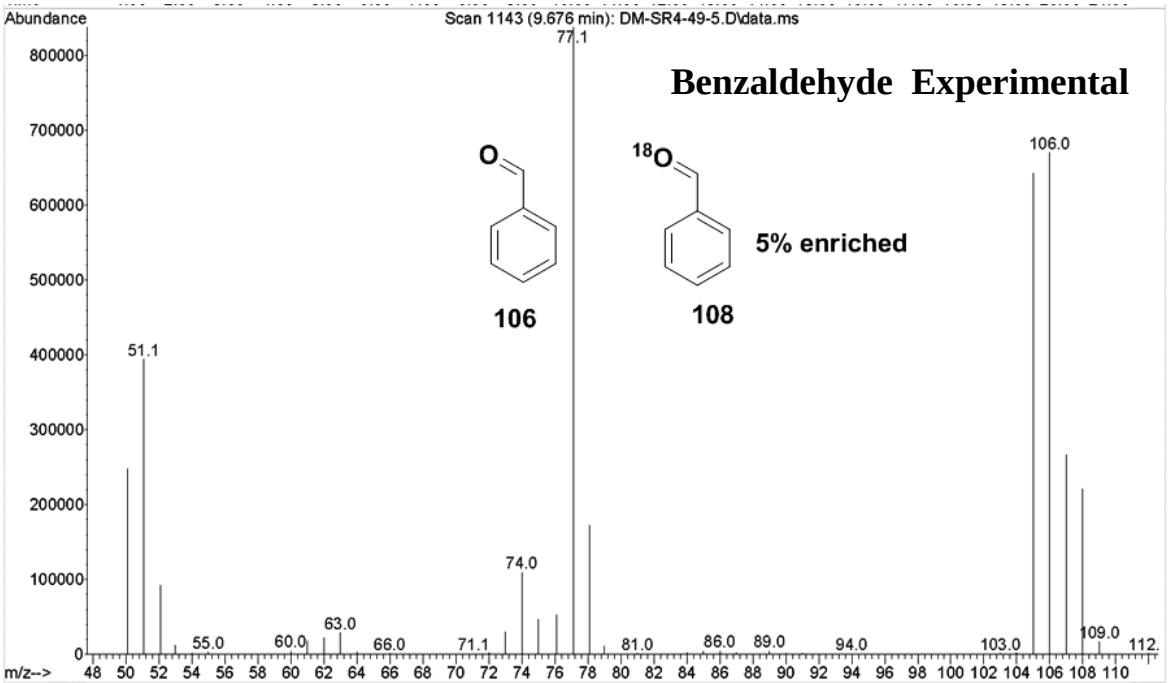


Figure S28

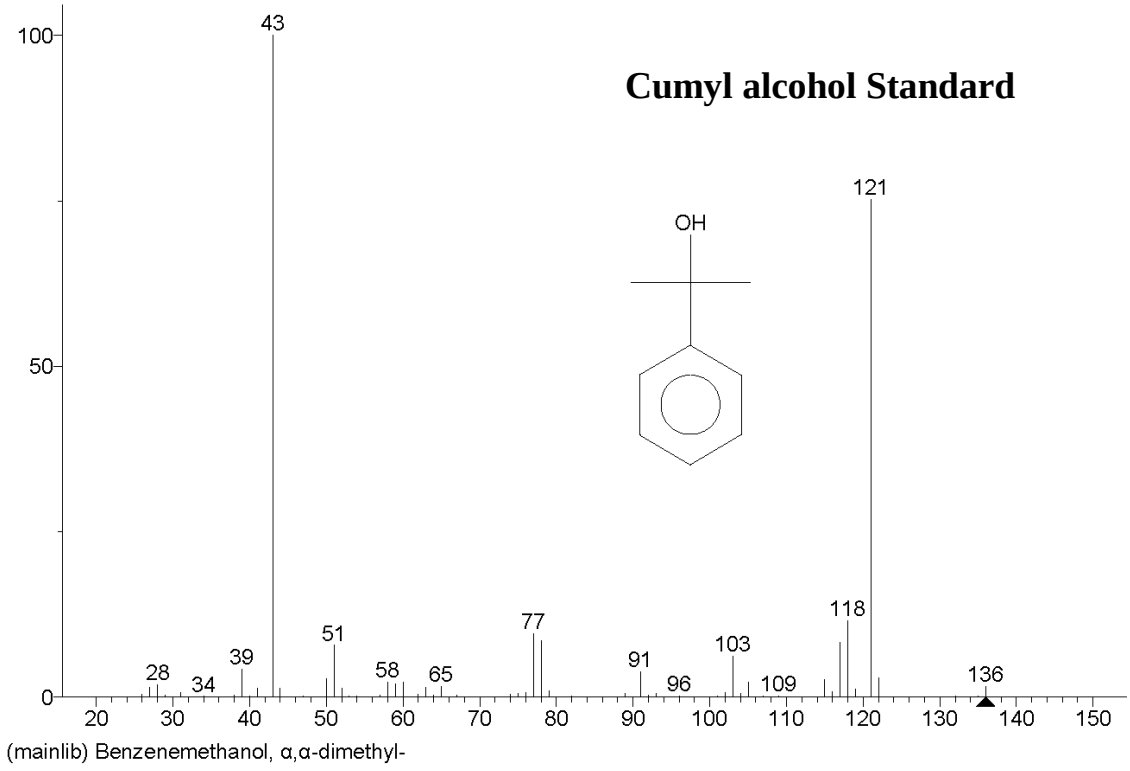


Figure S29

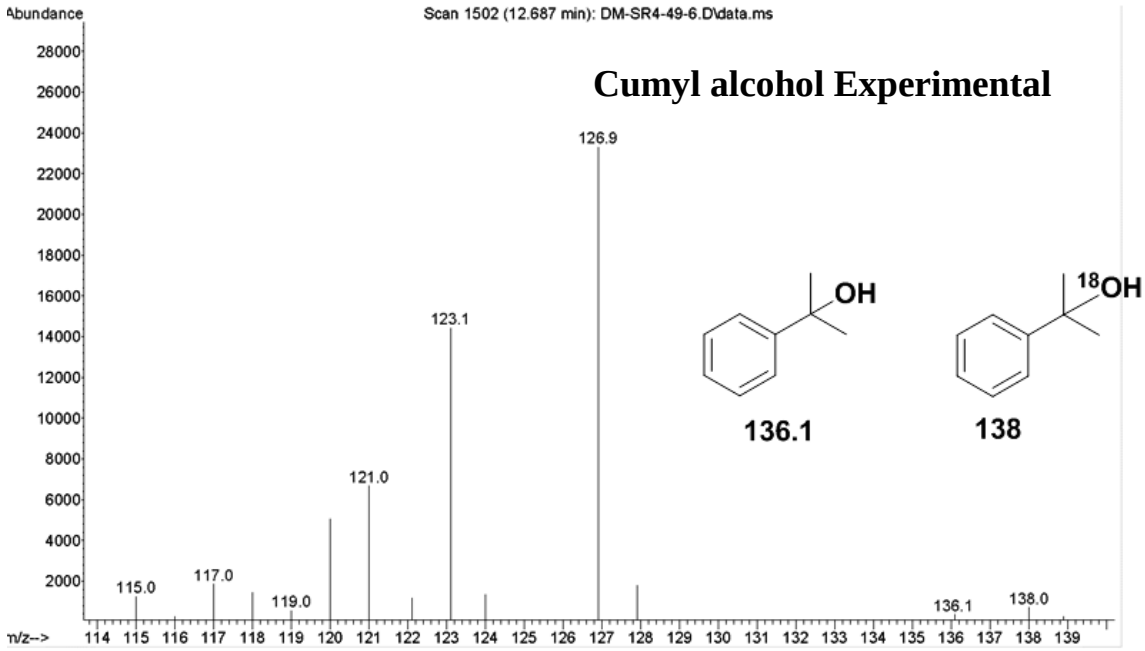


Figure S30

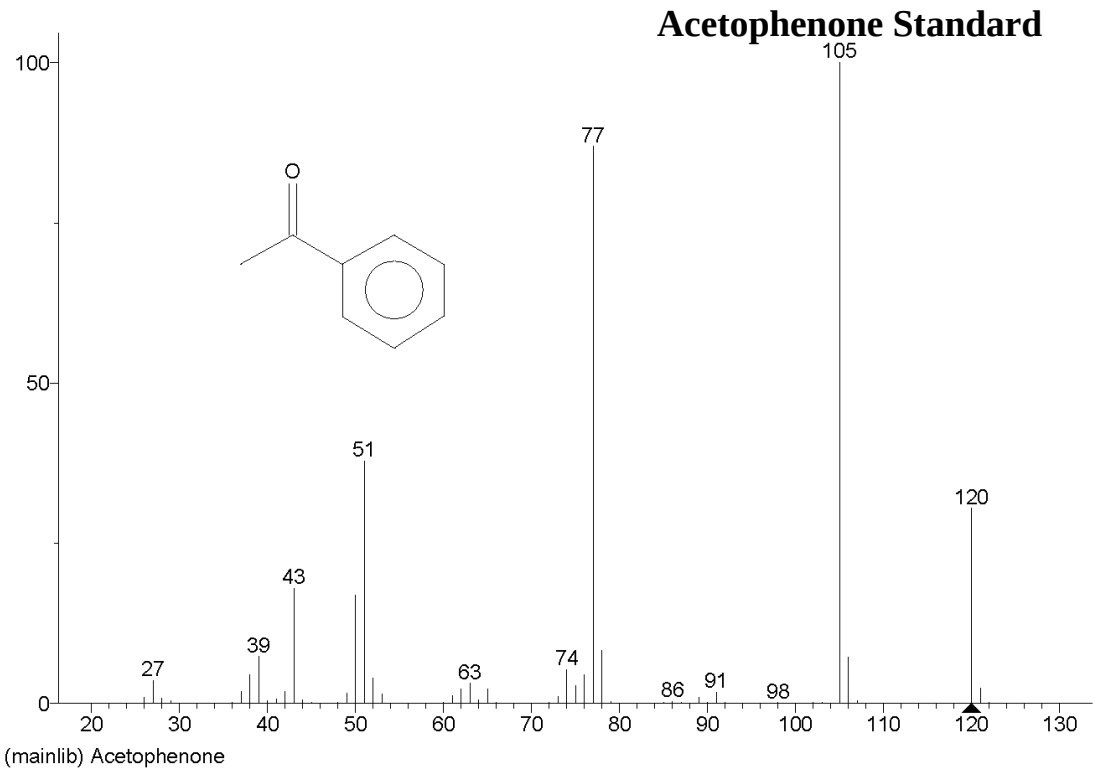


Figure S31

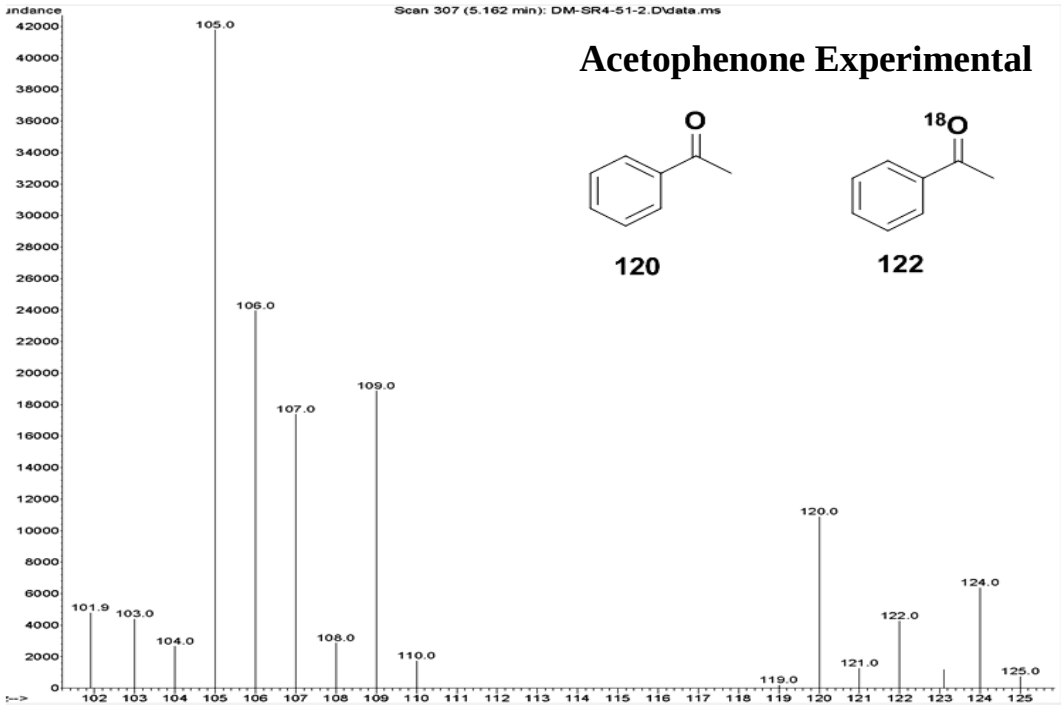


Figure S32

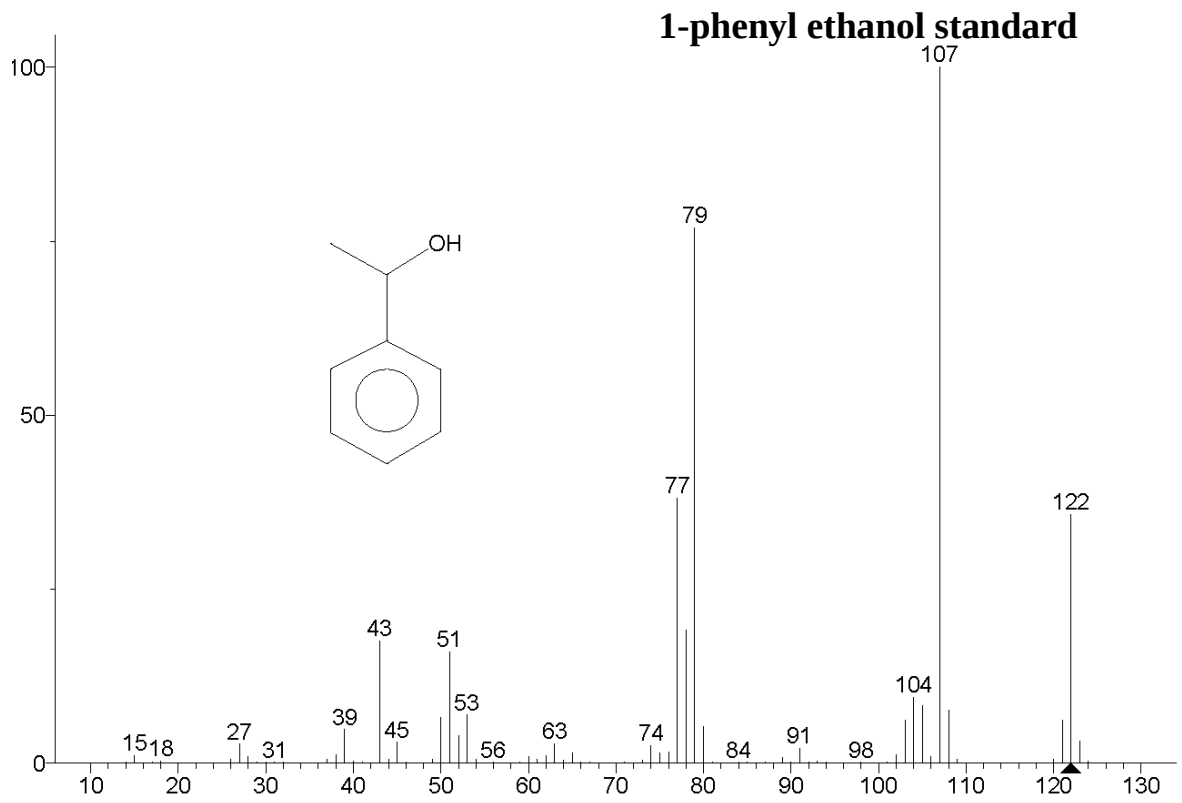


Figure S33

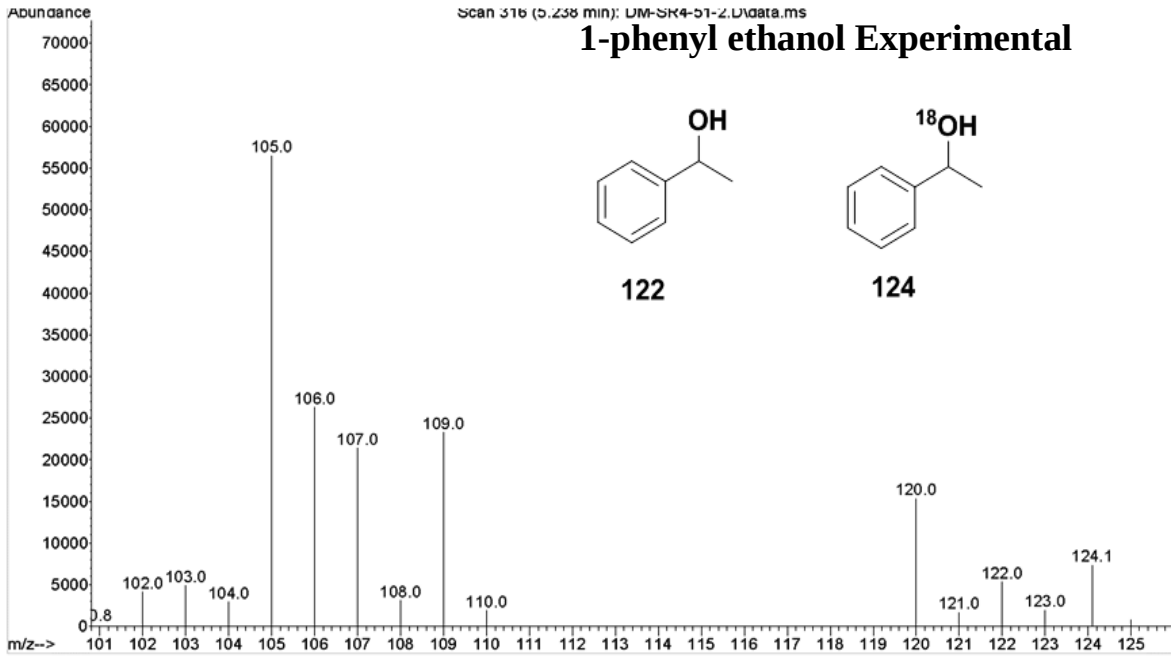


Figure S34

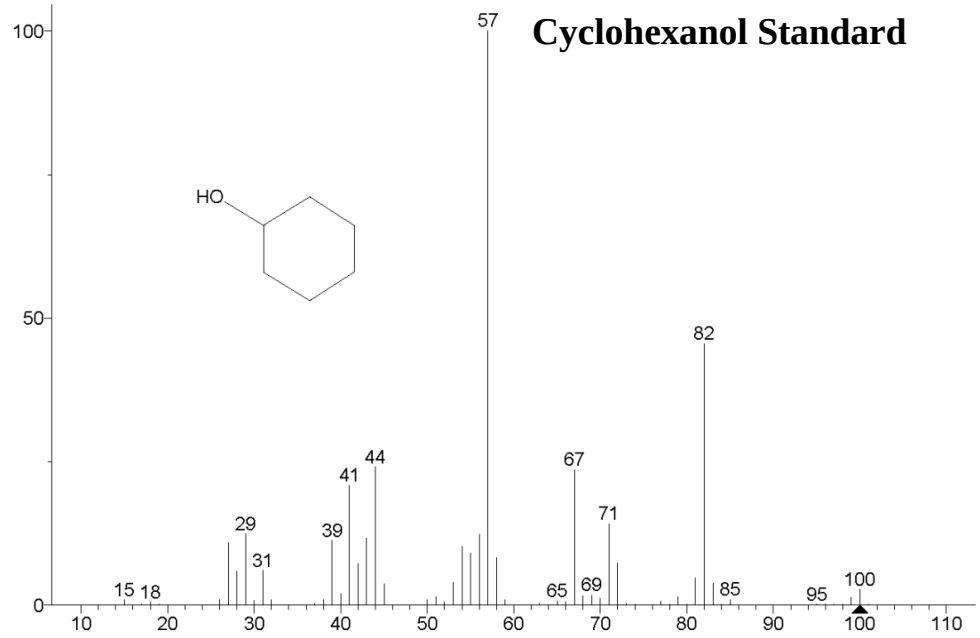
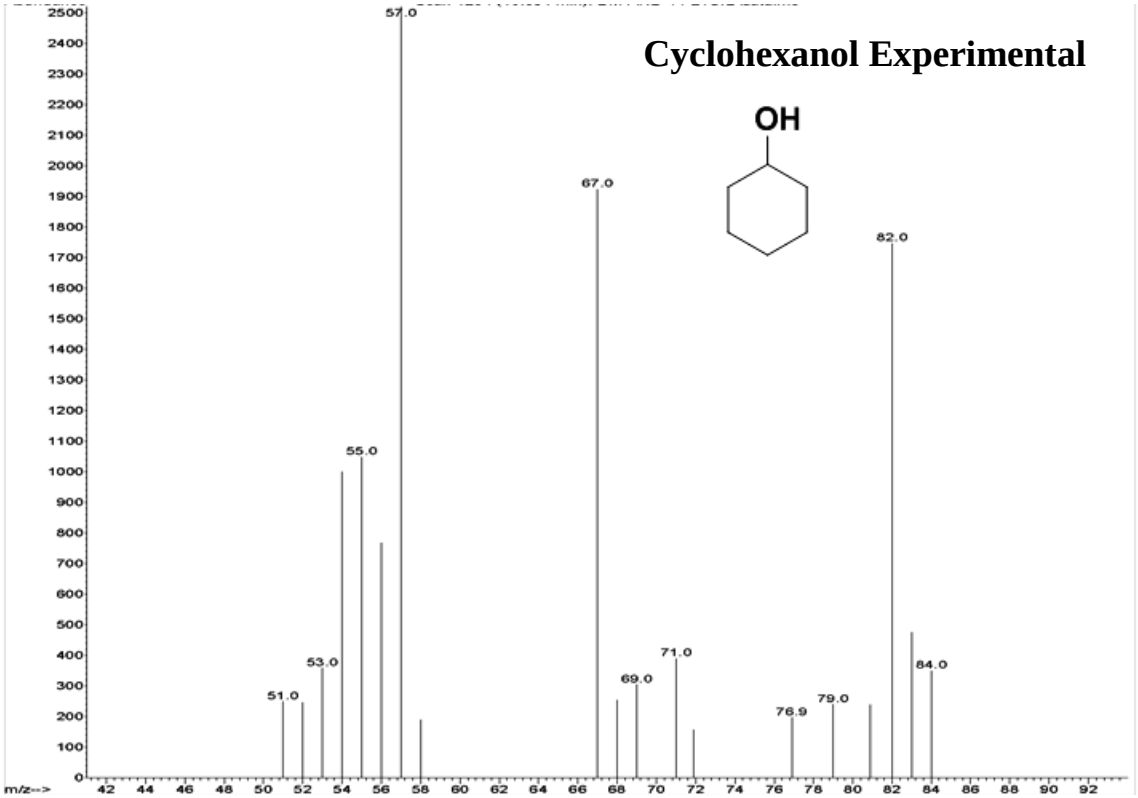

Cyclohexanol Standard
HO
100
50
0
57
82
67
44
41
71
29
39
31
15
18
65
69
85
95
100
10
20
30
40
50
60
70
80
90
100
110

Figure S35


Cyclohexanol Experimental
OH
57.0
67.0
82.0
55.0
53.0
71.0
69.0
84.0
51.0
79.0
76.9
m/z-->

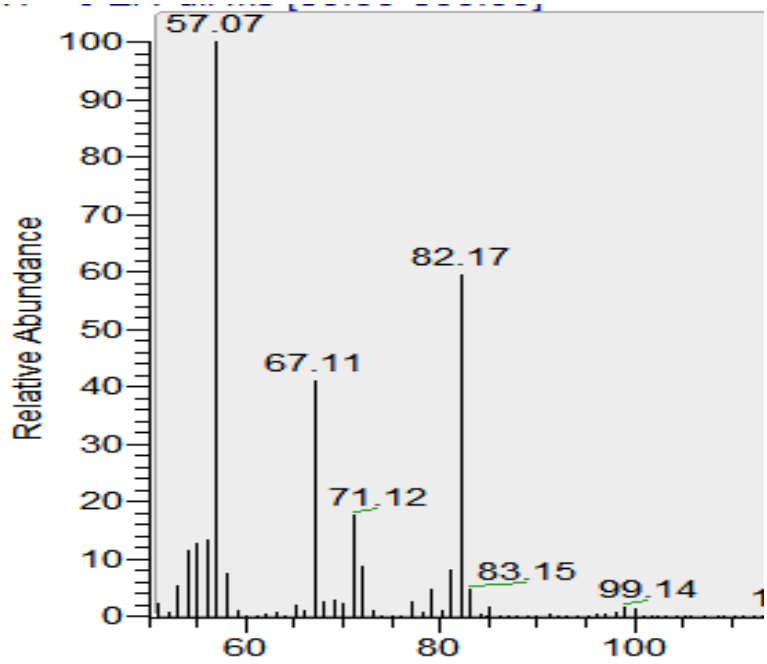


Figure S36

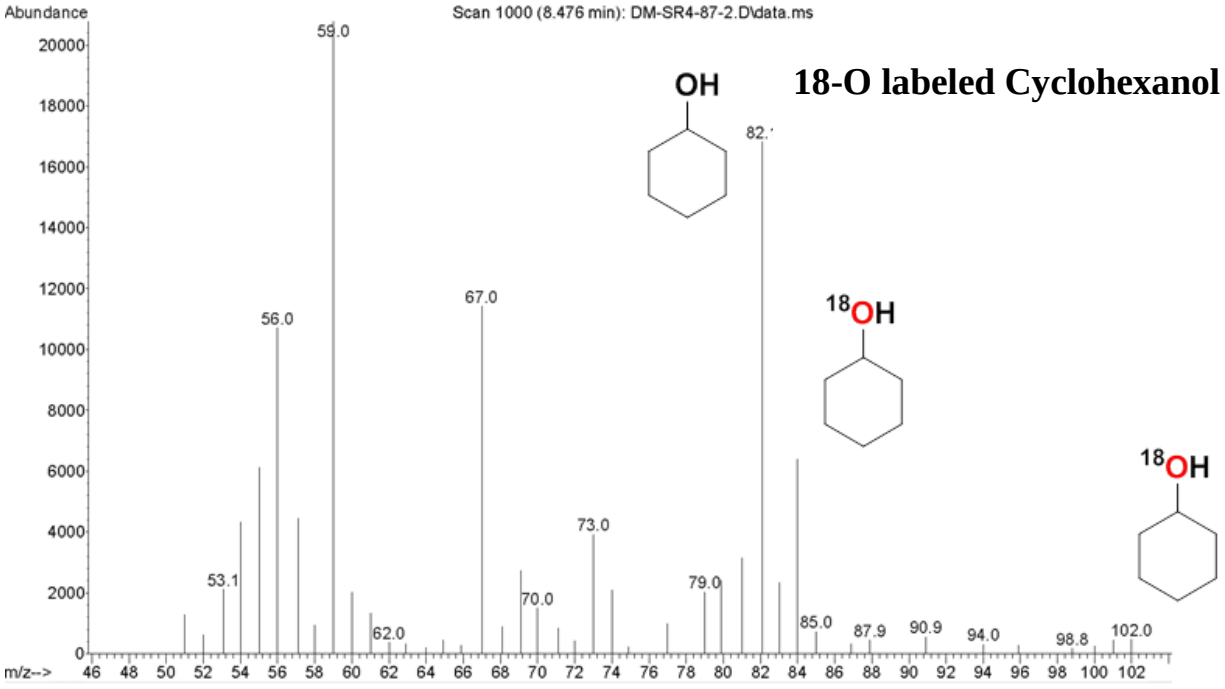


Figure S37

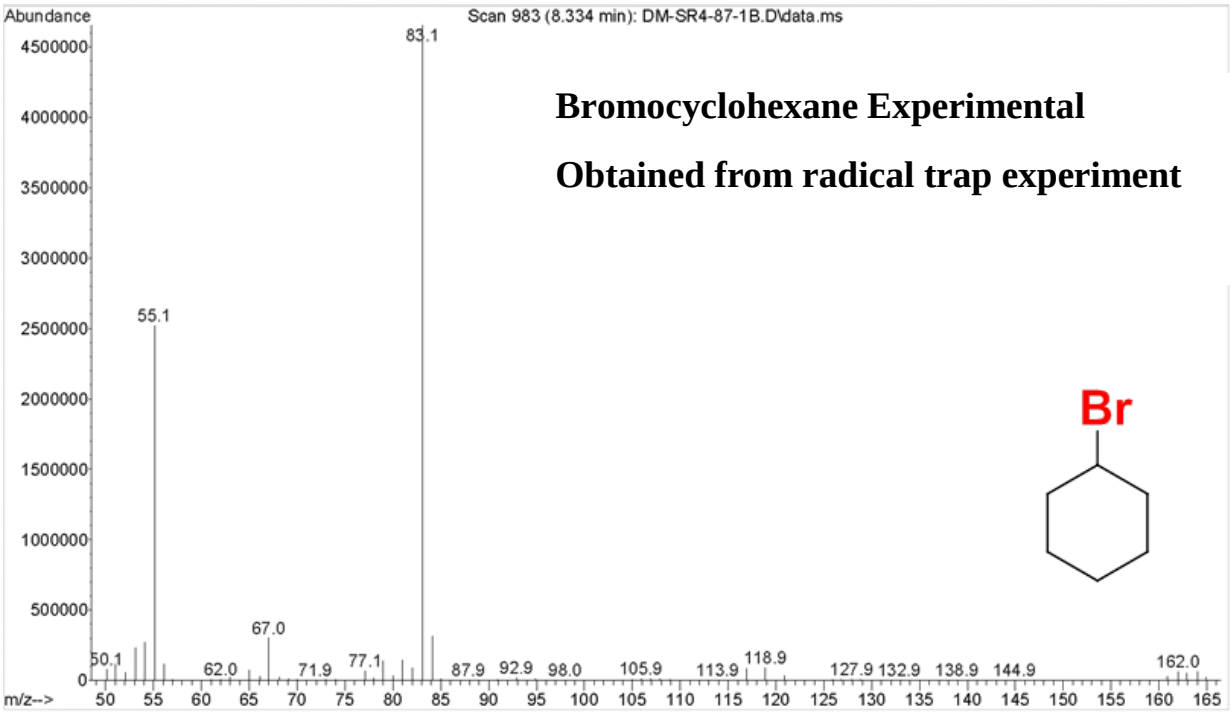

Abundance
Scan 983 (8.334 min): DM-SR4-87-1B.D\data.ms
Bromocyclohexane Experimental
Obtained from radical trap experiment
Br
m/z-->

Figure S38

9. ESI-MS spectra obtained from reaction between 2 and ethyl benzene and cumene both labeling and without labeling condition

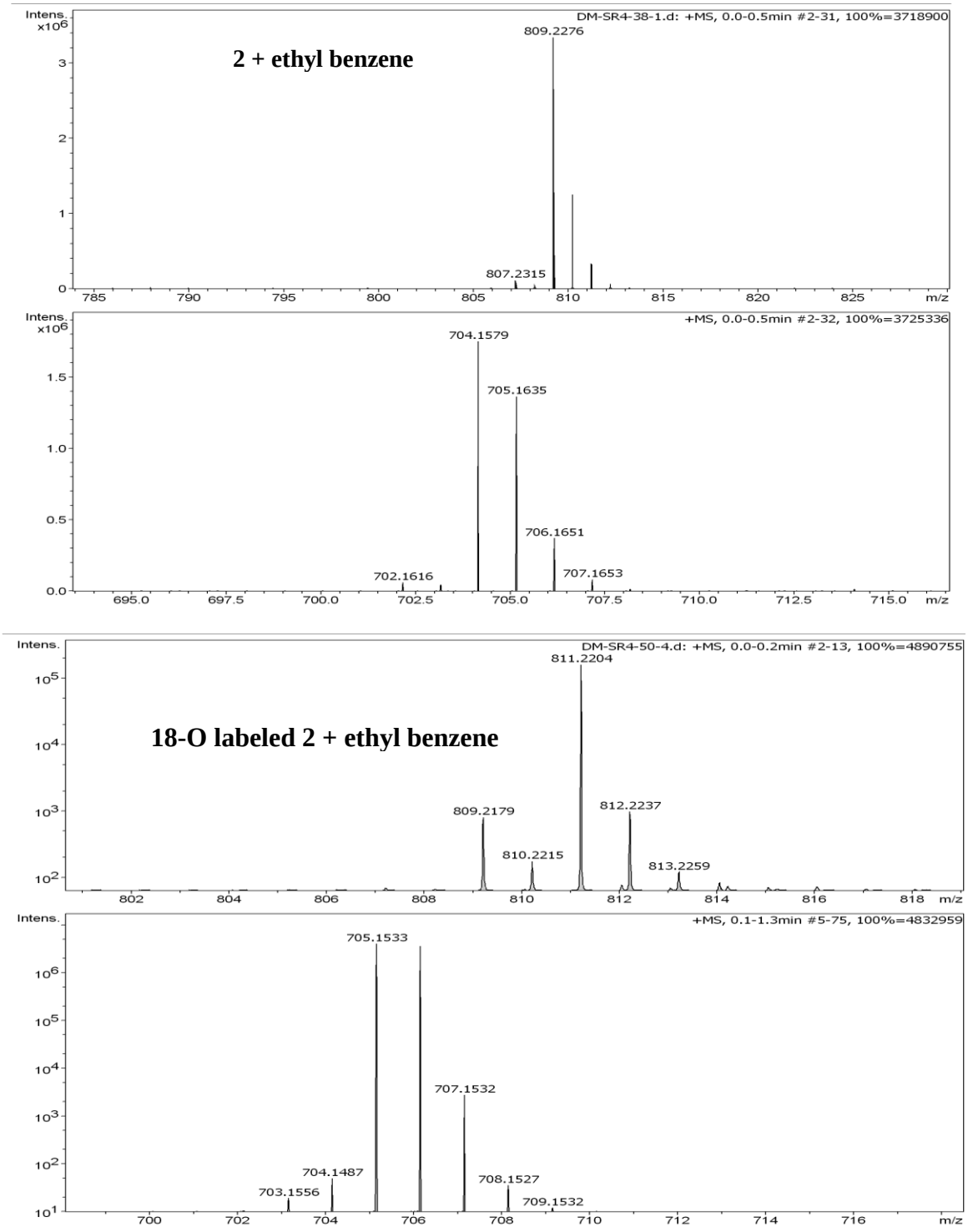


Figure S39

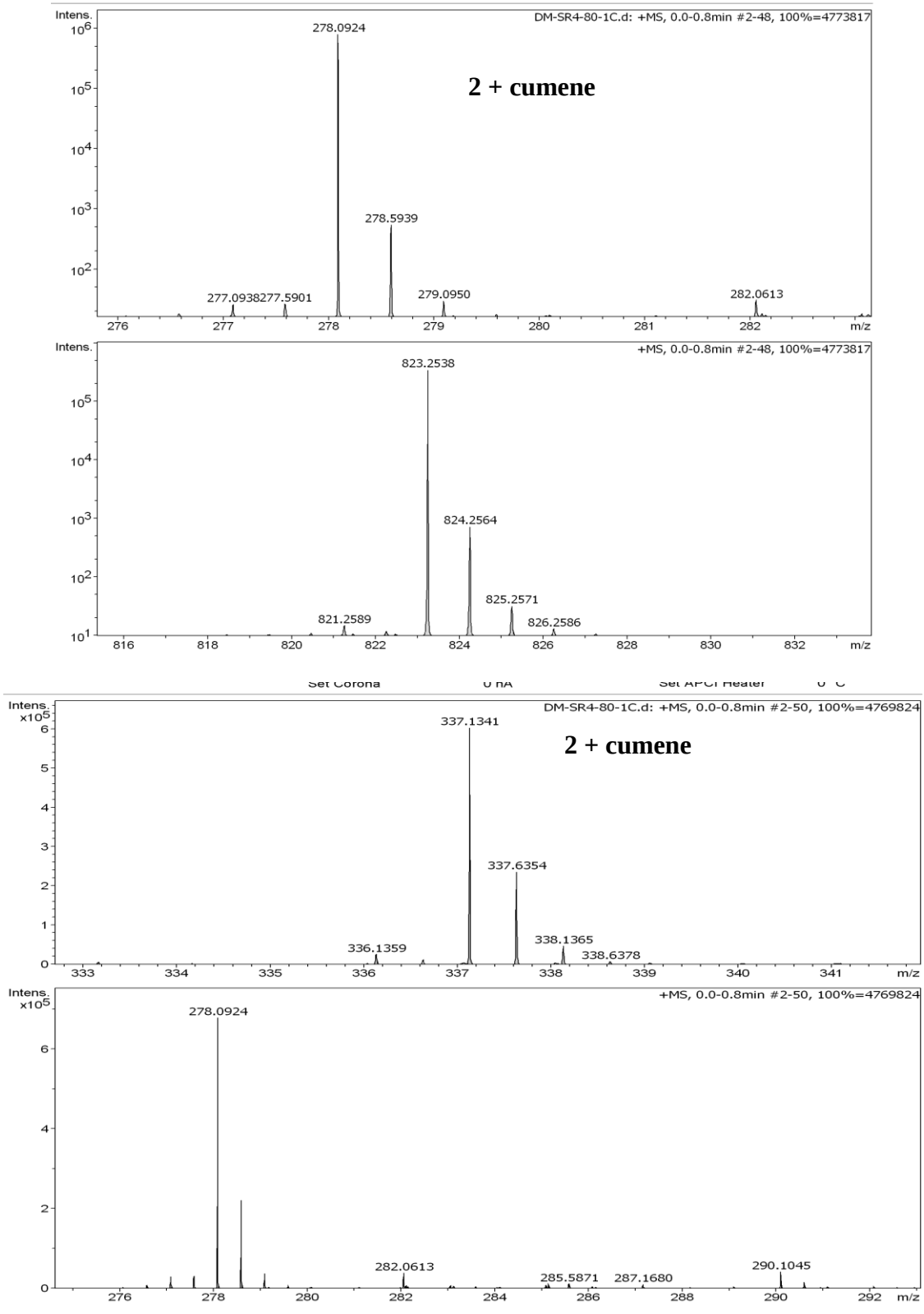

DM-SR4-80-1C.d: +MS, 0.0-0.8min #2-48, 100%=4773817
2 + cumene
278.0924
278.5939
277.0938277.5901
279.0950
282.0613
+MS, 0.0-0.8min #2-48, 100%=4773817
823.2538
824.2564
825.2571
821.2589
826.2586
DM-SR4-80-1C.d: +MS, 0.0-0.8min #2-50, 100%=4769824
2 + cumene
337.1341
337.6354
336.1359
338.1365
338.6378
+MS, 0.0-0.8min #2-50, 100%=4769824
278.0924
282.0613
285.5871
287.1680
290.1045

Figure S40

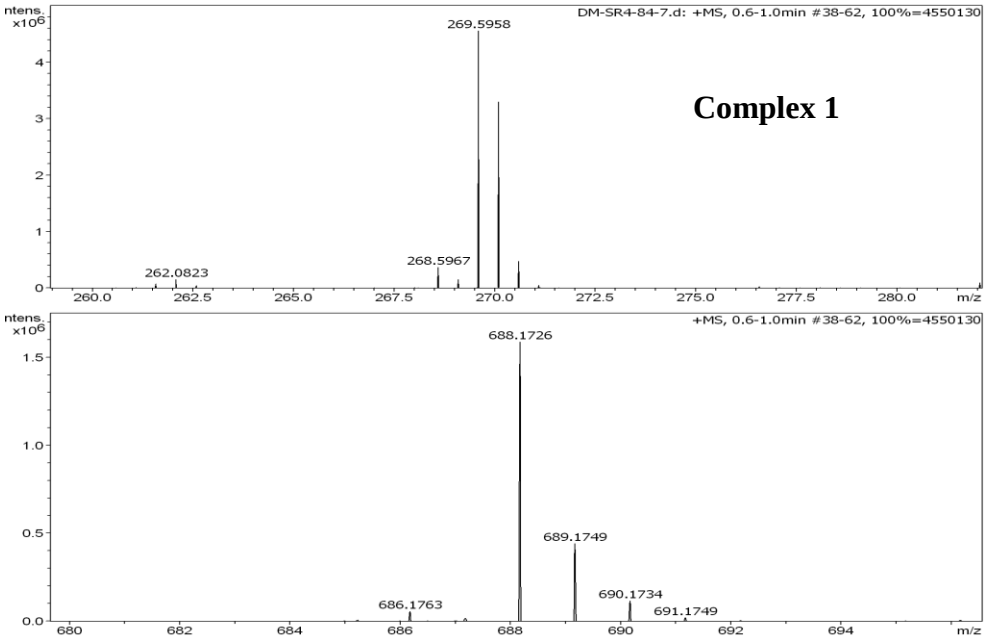


Figure S41

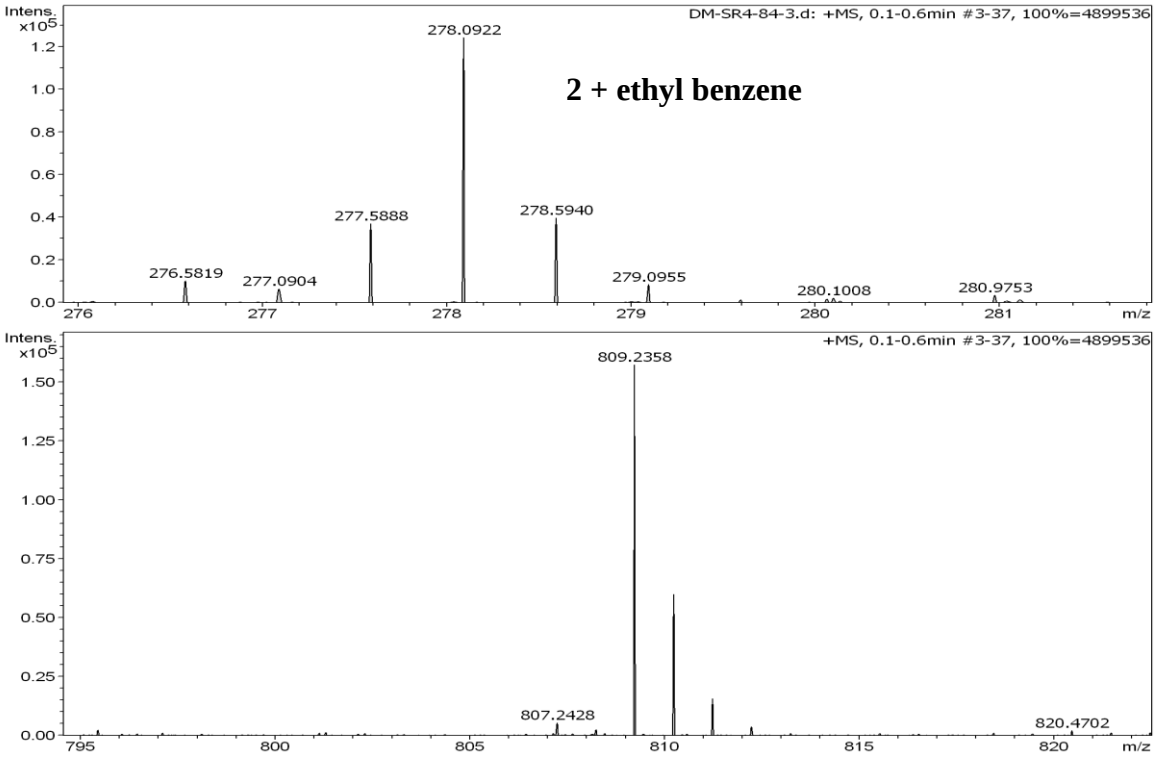


Figure S42

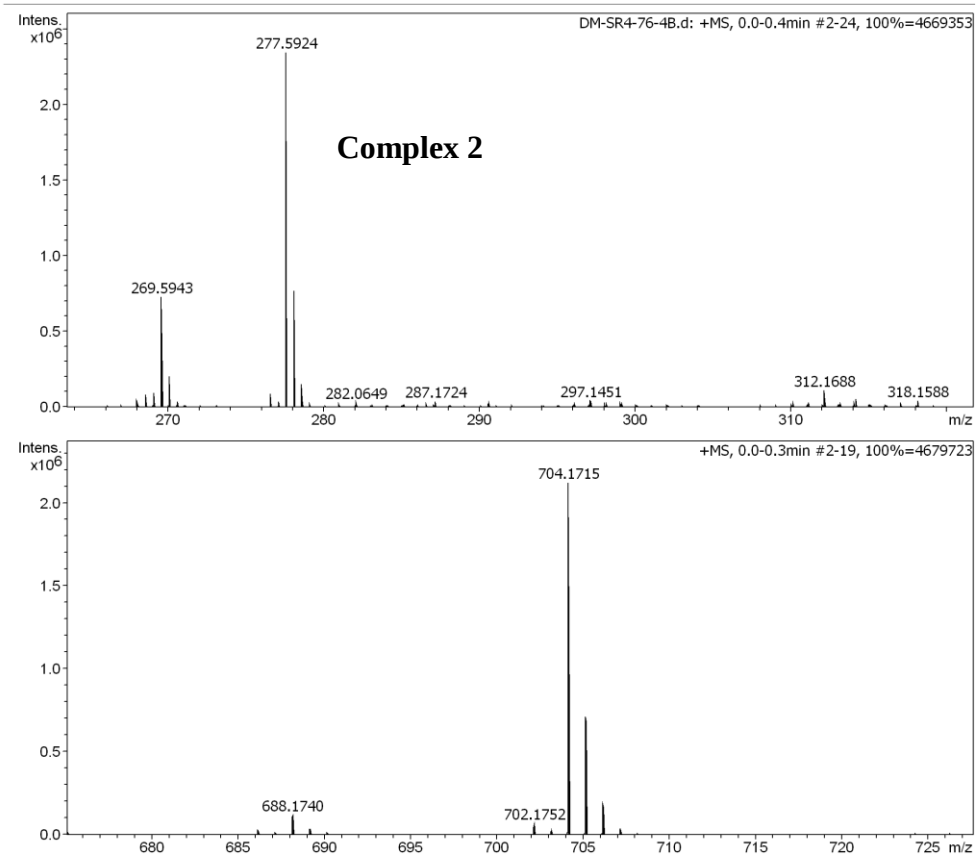

Intens.
x10^6
DM-SR4-76-4B.d: +MS, 0.0-0.4min #2-24, 100%=4669353
277.5924
Complex 2
269.5943
282.0649
287.1724
297.1451
312.1688
318.1588
m/z
Intens.
x10^6
+MS, 0.0-0.3min #2-19, 100%=4679723
704.1715
688.1740
702.1752
m/z

Figure S43

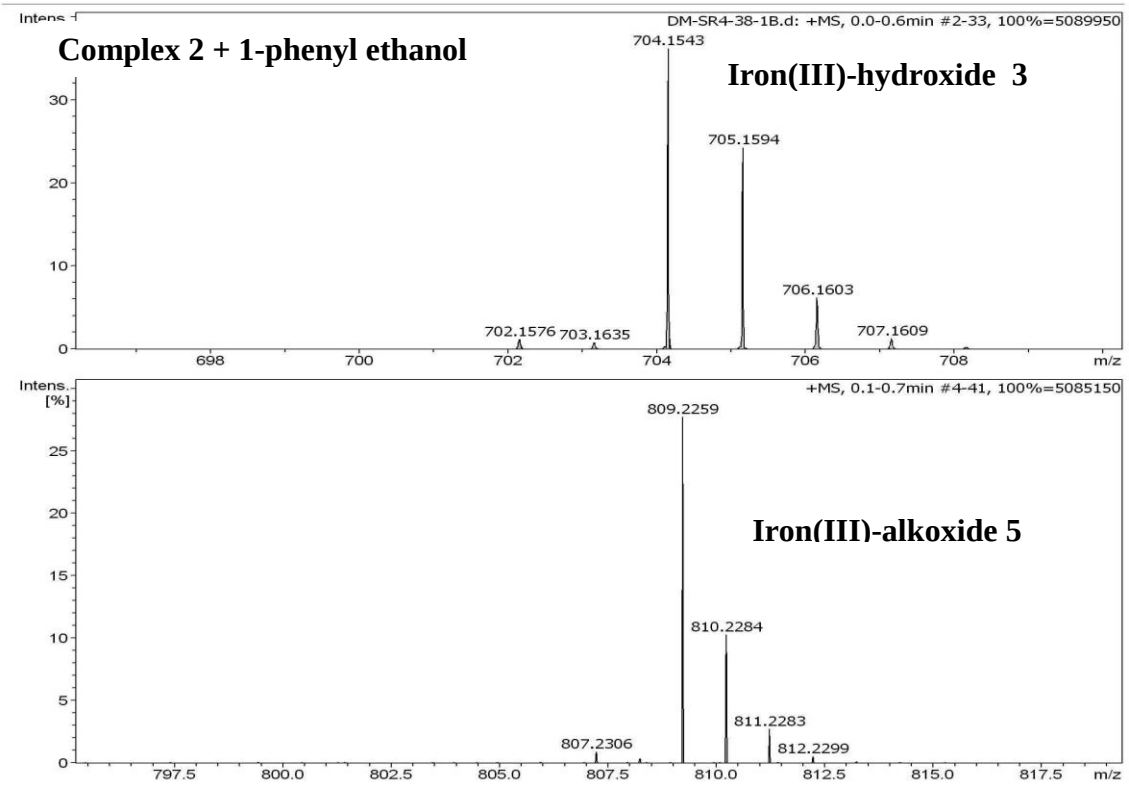


Figure S44

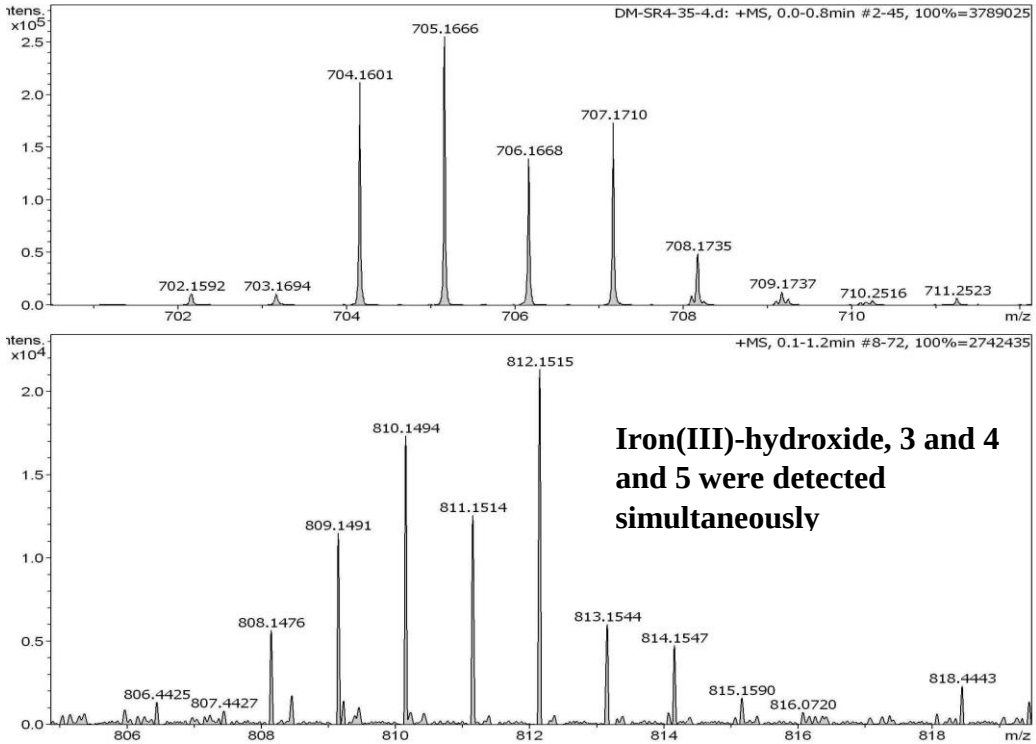


Figure S45

Complex 2 + 2-phenyl-2-propanol + 1

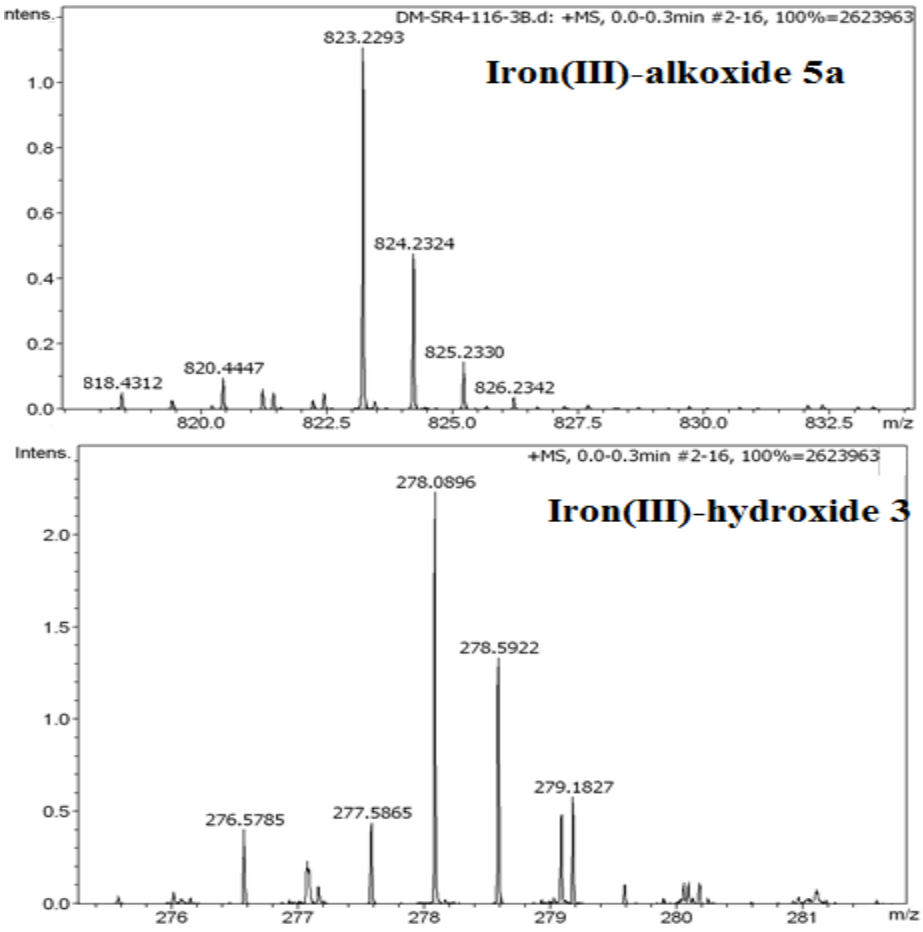


Figure S46

Complex 2 + 2-phenyl-2-propanol

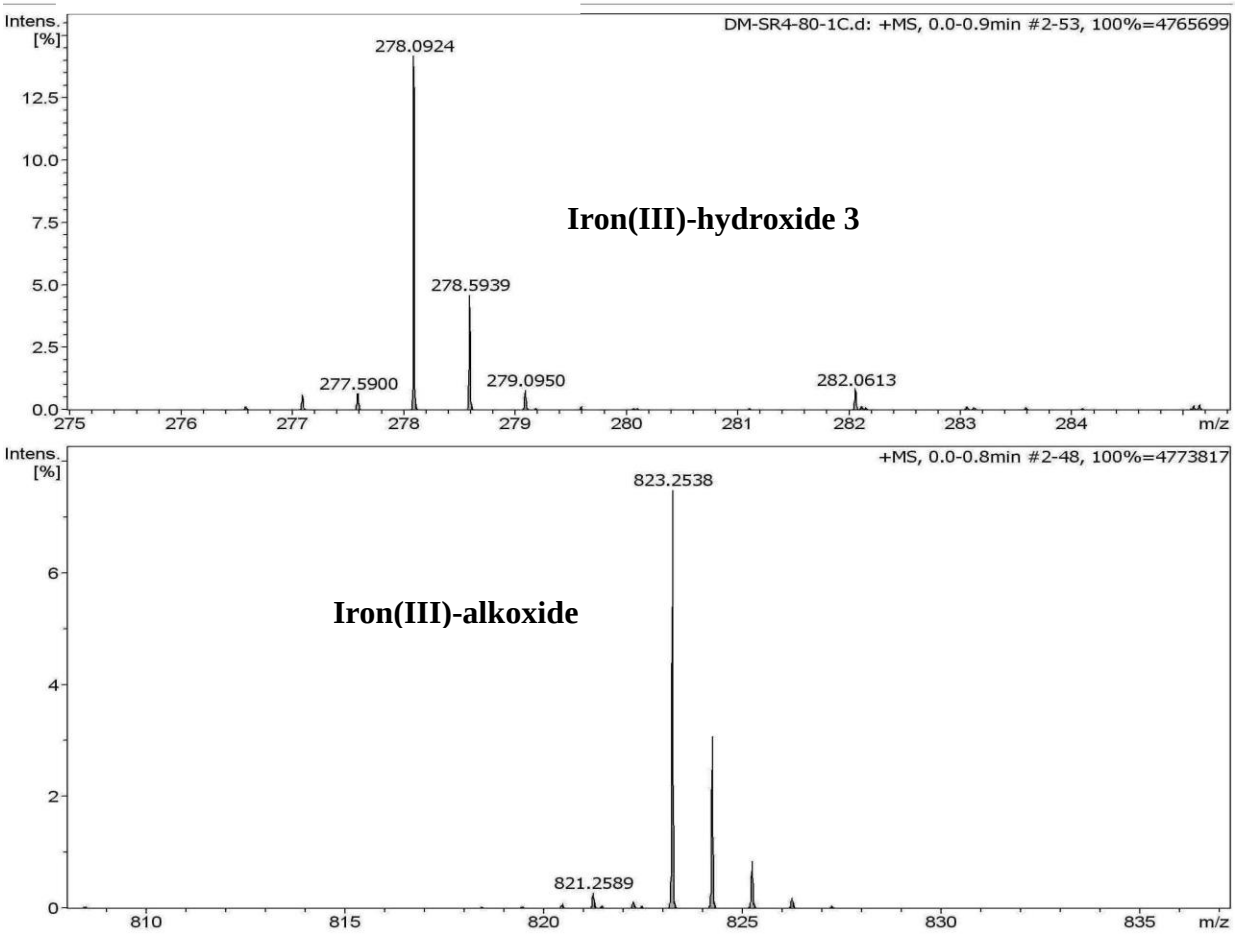


Figure S47

10. References:

1. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* 1988, **37**, 785-789.

2. a) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* 1990, **77**, 123-141; b) Fuentealba, P.; Preuss, H.; Stoll, H.; Szentpaly, L. V. *Chem. Phys. Lett.* 1989, **89**, 418-422.

3. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.;

Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09* (Revision A.02): Gaussian, Inc.: Wallingford CT 2009.

4. D. A. Zhurko, G. A. Zhurko, *ChemCraft 1.5*; Plimus: San Diego, CA. Available at http://www.chemcraftprog.com

5. C. Nájera, J. Gil-Moltó, S. Karlström, *Adv. Syn. Cat.* 2004, **346**, 1798.

6. M. Lubben, A. Meetsma, E. C. Wilkinson, B. Feringa, L. Jr. Que, *Angew. Chem. Ed. Int*. 1995, **34**, 1512.

7. K.-B. Cho, X. Wu, Y.-M. Lee, Y. H. Kwon, S. Shaik, W. Nam, *J. Am. Chem. Soc*. 2012, **134**, 20222.

8. Organic Syntheses, Eds. H. Saltzman and J. G. Sharefkin; Wiley, New York, 1973, Collect. Vol. V, pp. 658.

9. J. Kaizer, E. J. Klinker, N. Y. Oh, J.-U. Rohde, W. J. Song, A. Stubna, J. Kim, E. Münck, W. Nam, L. Jr. Que, *J. Am. Chem. Soc*. 2004, **126**, 472.

10. M. Takahashi, K. Oshima, S. Matsubara, *Chem. Lett.* 2005, **34**, 2.