Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Ni and Zn N-Confused Porphyrin Complexes as Recyclable Catalysts For High Efficiency Solvent-Free CO_2 Fixation into Cyclic Carbonates

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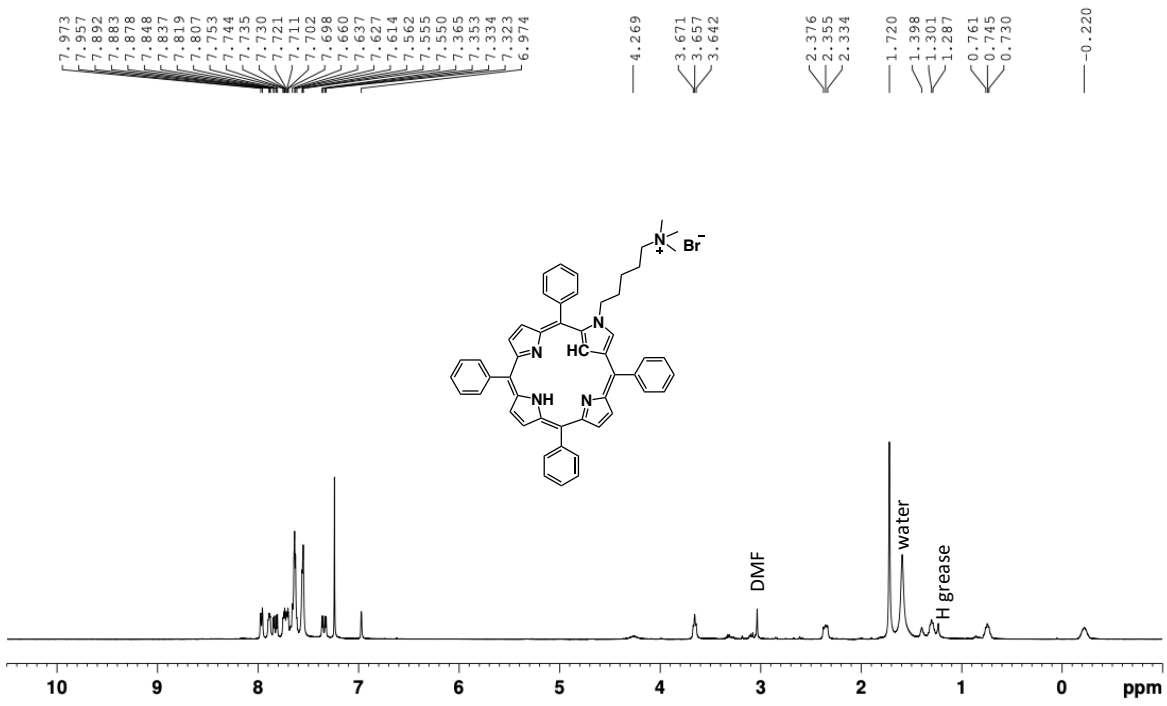
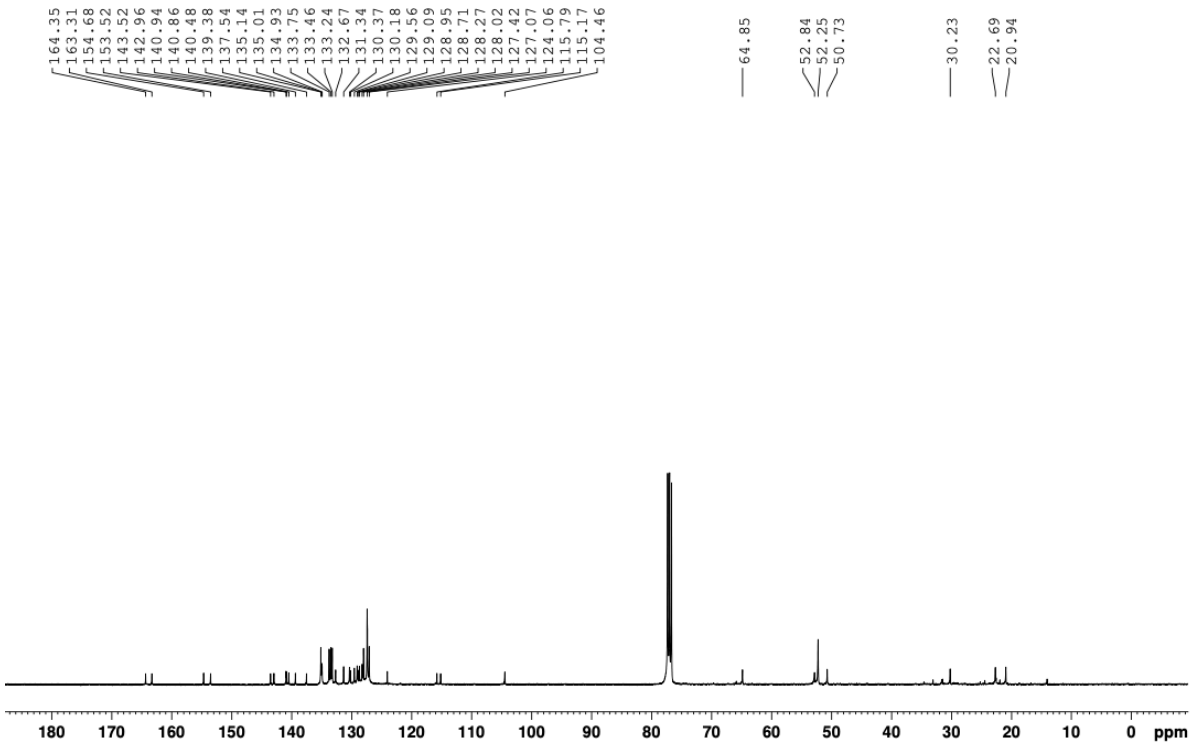
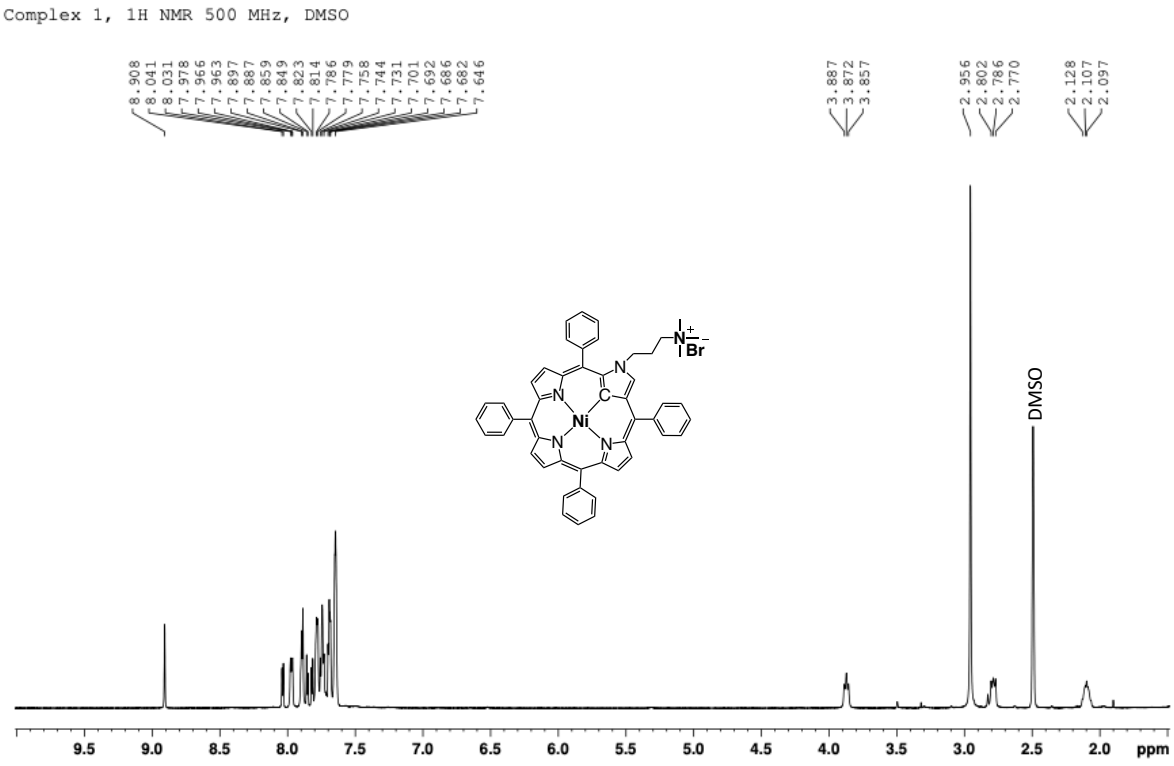
[1] NMR spectra of R^2-NCTPP and complexes **1**, **2**, and **3**.



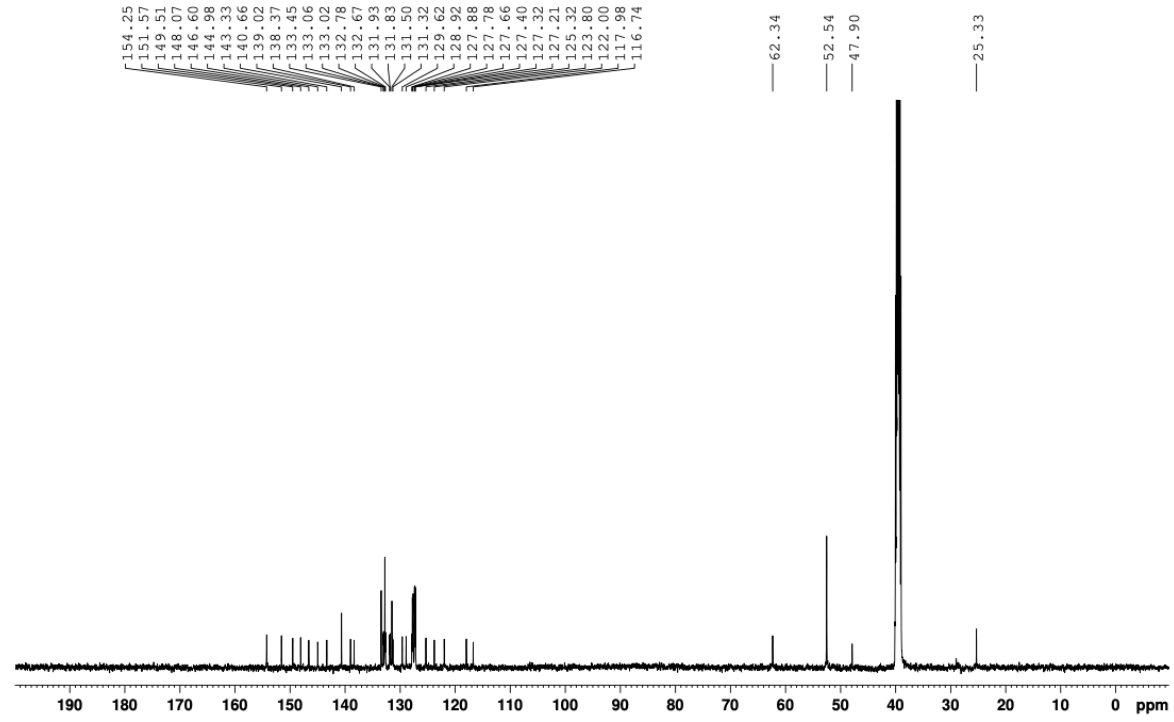
^{1}H NMR of R^2-NCTPP in $CDCl_3$.



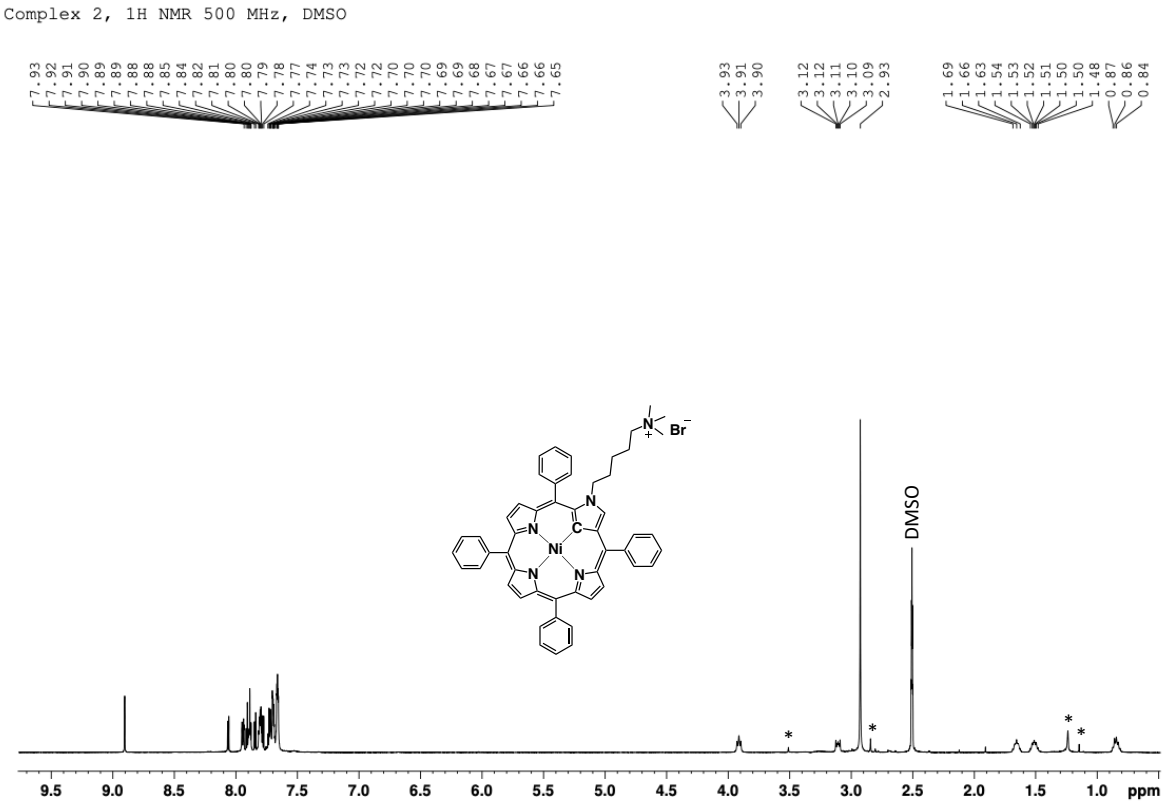
^{13}C NMR of R^2-NCTPP in $CDCl_3$.



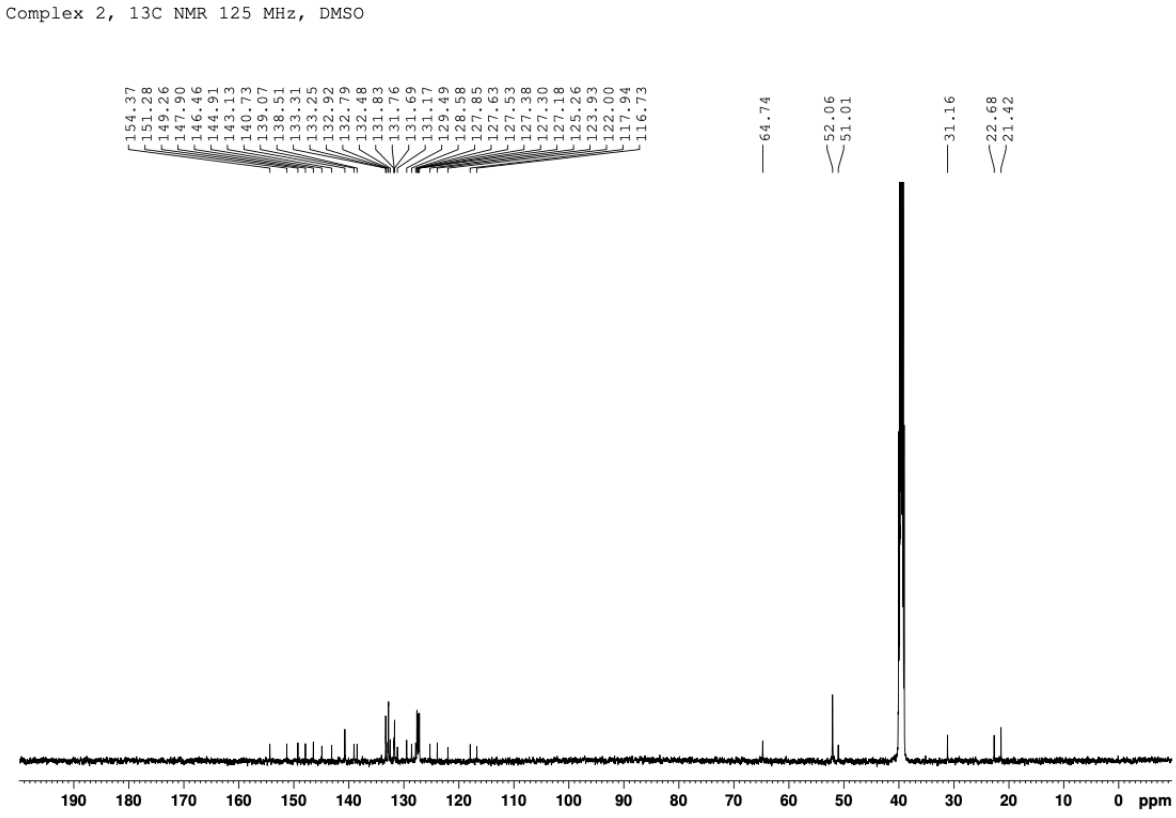
^{1}H NMR of **1** in DMSO-d$_6$



^{13}C NMR of **1** in DMSO-d$_6$

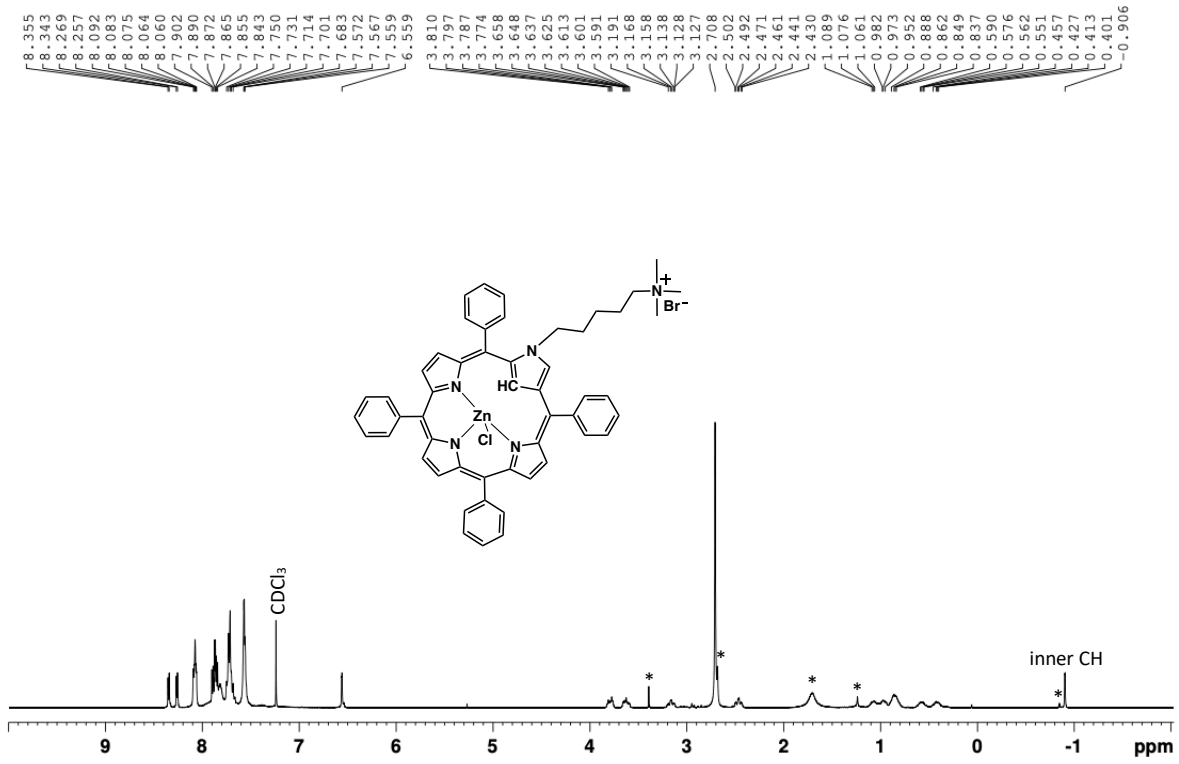


^{1}H NMR of **2** in DMSO-d$_6$



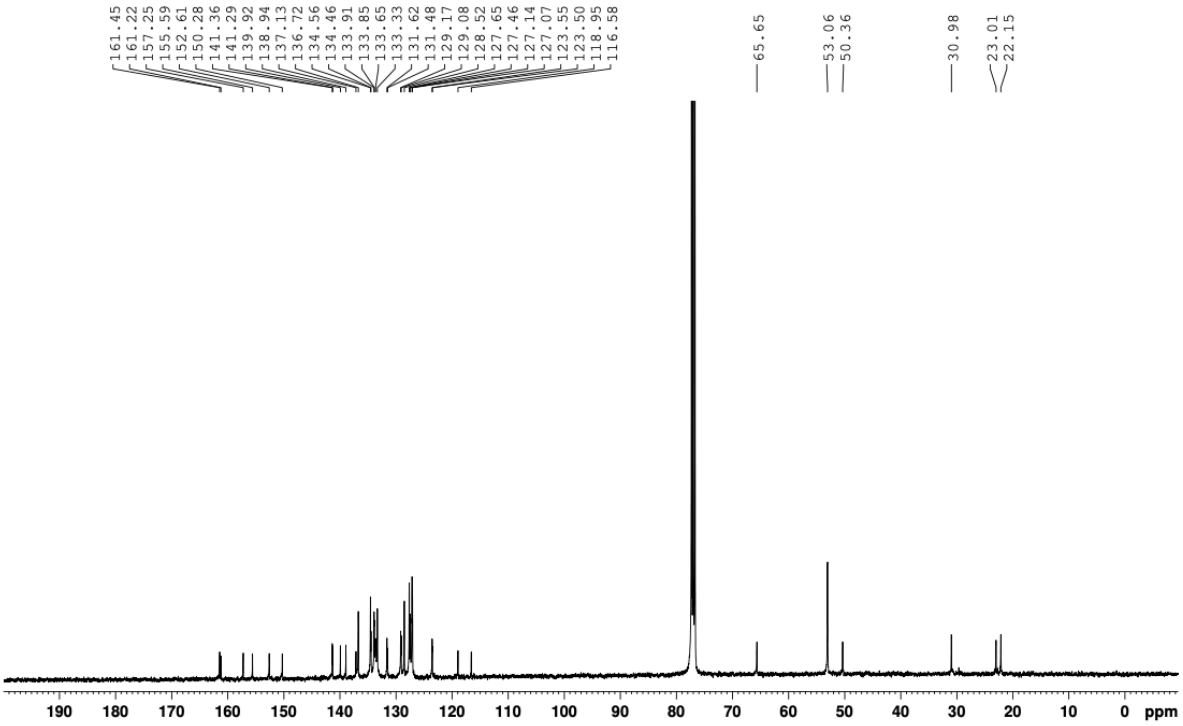
^{13}C NMR of **2** in DMSO-d$_6$

Complex 3, 1H HNMR 400 MHz, CDCl3



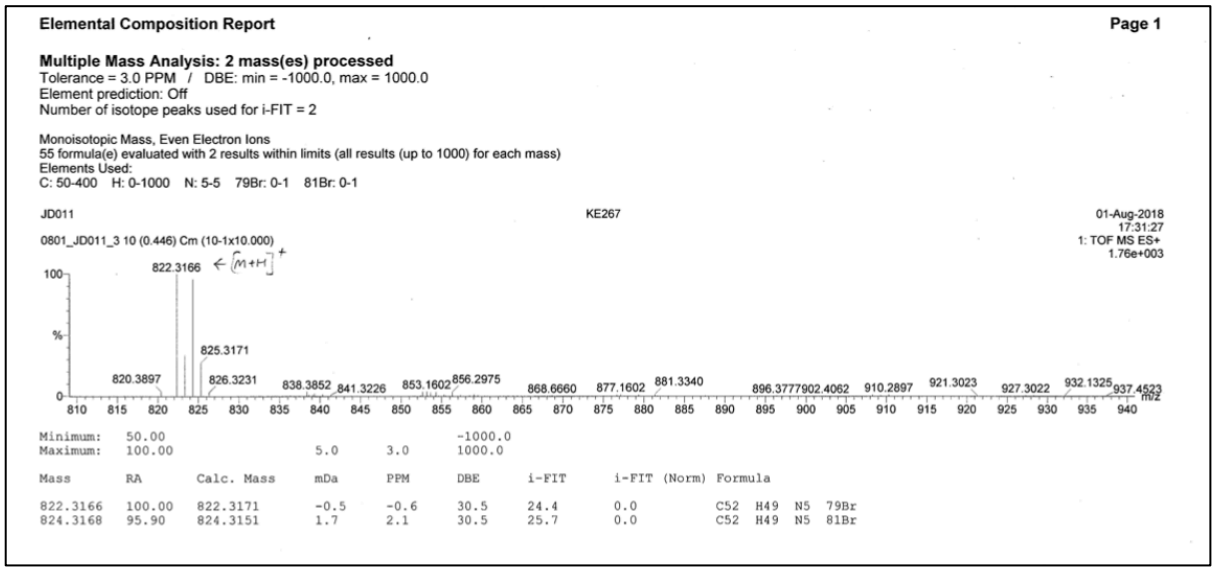
^{1}H NMR of **3** in $CDCl_3$

Complex 3, 13C NMR 100 MHz, CDCl3



^{13}C NMR of **3** in $CDCl_3$

[2] Mass spectra of R^2-NCTPP and complexes **1**, **2**, and **3**.



Elemental Composition Report Page 1

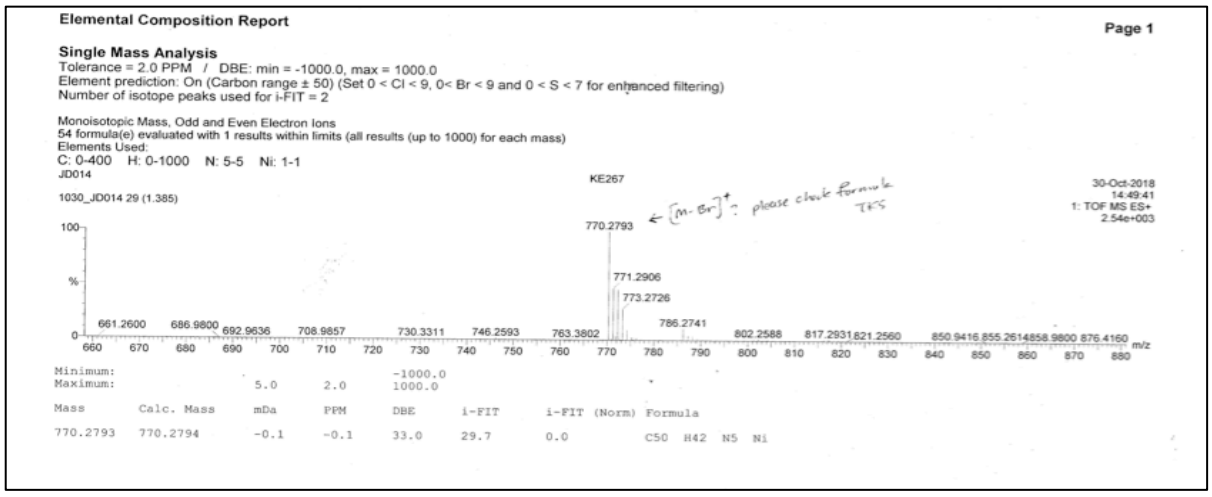
Multiple Mass Analysis: 2 mass(es) processed
Tolerance = 3.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
55 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 50-400 H: 0-1000 N: 5-5 79Br: 0-1 81Br: 0-1

JD011 KE267 01-Aug-2018 17:31:27
0801_JD011_3 10 (0.446) Cm (10-1x10.000) 1: TOF MS ES+ 1.76e+003

Minimum:	50.00				-1000.0			
Maximum:	100.00		5.0	3.0	1000.0			
Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
822.3166	100.00	822.3171	-0.5	-0.6	30.5	24.4	0.0	C52 H49 N5 79Br
824.3168	95.90	824.3151	1.7	2.1	30.5	25.7	0.0	C52 H49 N5 81Br

HRMS(ESI) of R^2-NCTPP



Elemental Composition Report Page 1

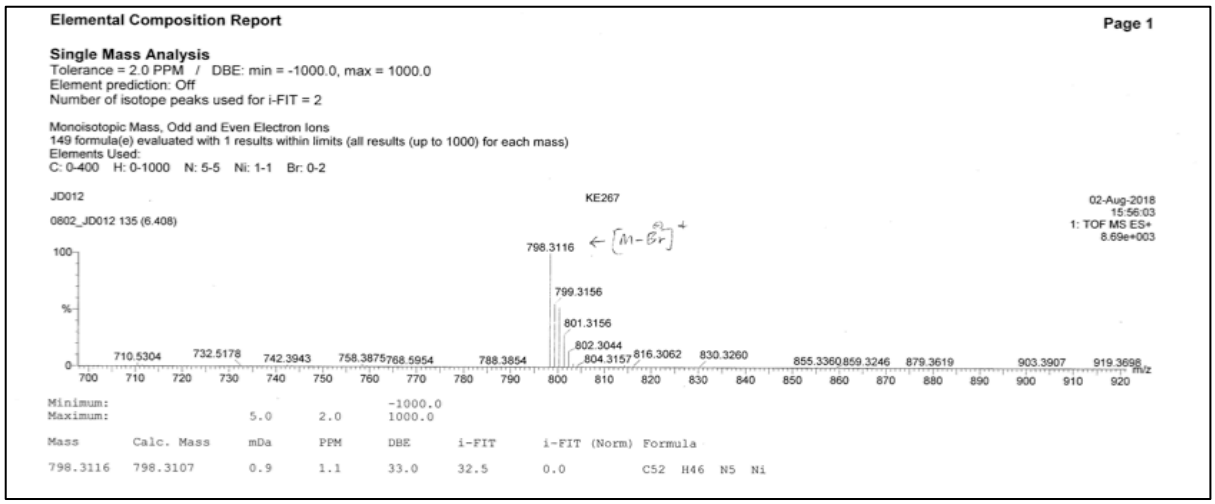
Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: On (Carbon range ± 50) (Set 0 < Cl < 9, 0< Br < 9 and 0 < S < 7 for enhanced filtering)
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
54 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 N: 5-5 Ni: 1-1

JD014 KE267 30-Oct-2018 14:49:41
1030_JD014 29 (1.385) 1: TOF MS ES+ 2.54e+003

Minimum:				-1000.0			
Maximum:		5.0	2.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
770.2793	770.2794	-0.1	-0.1	33.0	29.7	0.0	C50 H42 N5 Ni

HRMS(ESI) of **1**



Elemental Composition Report Page 1

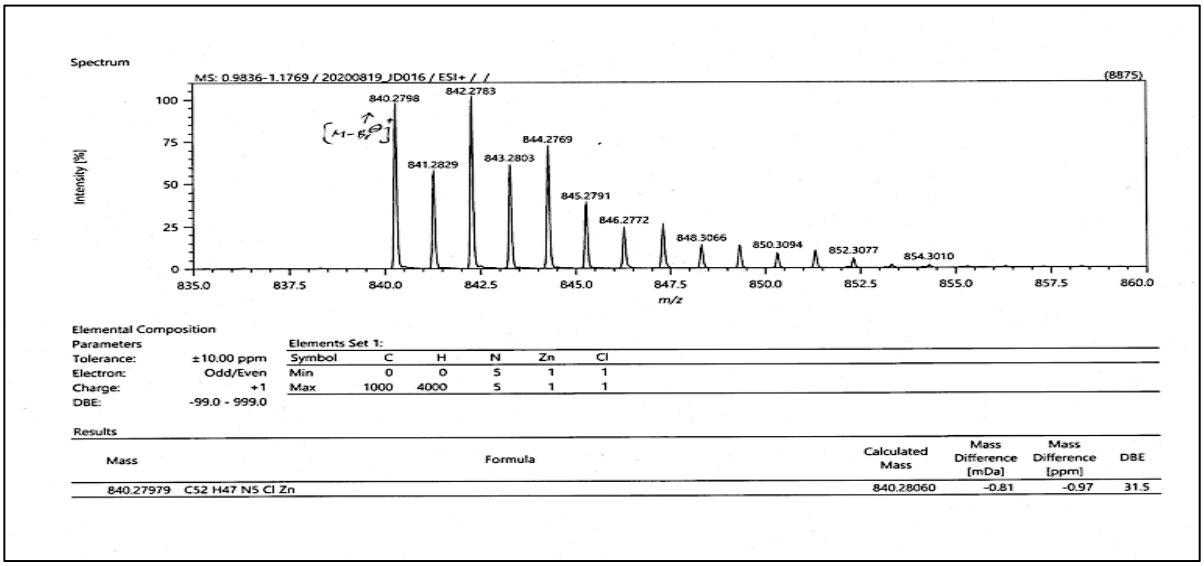
Single Mass Analysis
Tolerance = 2.0 PPM / DBE: min = -1000.0, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Odd and Even Electron Ions
149 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-400 H: 0-1000 N: 5-5 Ni: 1-1 Br: 0-2

JD012 KE267 02-Aug-2018 15:56:03
0802_JD012 135 (6.408) 1: TOF MS ES+ 8.69e+003

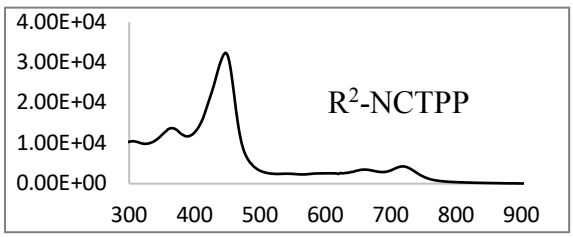
Minimum:				-1000.0			
Maximum:		5.0	2.0	1000.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
798.3116	798.3107	0.9	1.1	33.0	32.5	0.0	C52 H46 N5 Ni

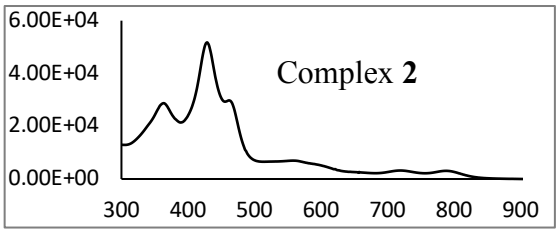
HRMS(ESI) of **2**

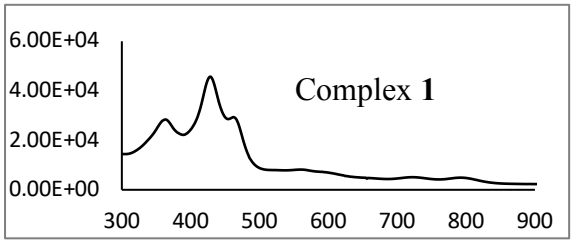

Spectrum
MS: 0.9836-1.1769 / 20200819_JD016 / ESI+ / /
(8875)
Intensity [%]
m/z
840.2798
842.2763
841.2829
843.2803
844.2769
845.2791
846.2772
848.3066
850.3094
852.3077
854.3010
Elemental Composition
Parameters
Tolerance: ±10.00 ppm
Electron: Odd/Even
Charge: +1
DBE: -99.0 - 999.0
Elements Set 1:
Symbol C H N Zn Cl
Min 0 0 5 1 1
Max 1000 4000 5 1 1
Results
Mass
Formula
Calculated Mass
Mass Difference [mDa]
Mass Difference [ppm]
DBE
840.27979 C52 H47 N5 Cl Zn
840.28060 -0.81 -0.97 31.5

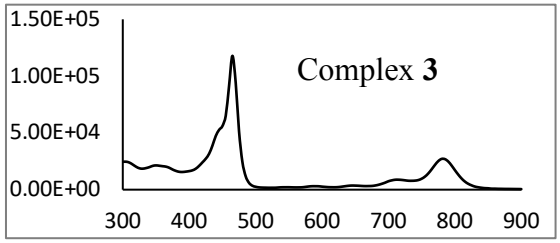
HRMS(ESI) of **3**

[3] UV-Vis absorption spectra of R^2-NCTPP, complexes **1**, **2**, and **3** in DCM [ε ($cm^{-1}M^{-1}$)] vs λ (nm).









[4] Sample % yield calculation from ^{1}H NMR data.

Total crude catalytic product is weighed, from which a portion (e.g.,30 mg) is taken for ^{1}H NMR analysis. A known amount of dimethyl sulfone is added to the ^{1}H NMR sample as internal standard. The number of moles of catalytic product in the ^{1}H NMR sample is directly related to the ratio of the integration of the known catalytic product peak per number of proton in proportion to the standard's integration per proton:

$$\frac{n_{(p,NMR)}}{\left(\frac{I}{H}\right)_p} = \frac{n_{(s,NMR)}}{\left(\frac{I}{H}\right)_s}$$

where $n_{(p,NMR)}$ = number of moles of the product contained in the NMR tube
$n_{(s,NMR)}$ = number of moles of the standard contained in the NMR tube
$(I/H)_p$ = integration per number of protons on a selected product ^{1}H NMR peak
$(I/H)_s$ = integration per number of protons of the internal standard ^{1}H NMR peak

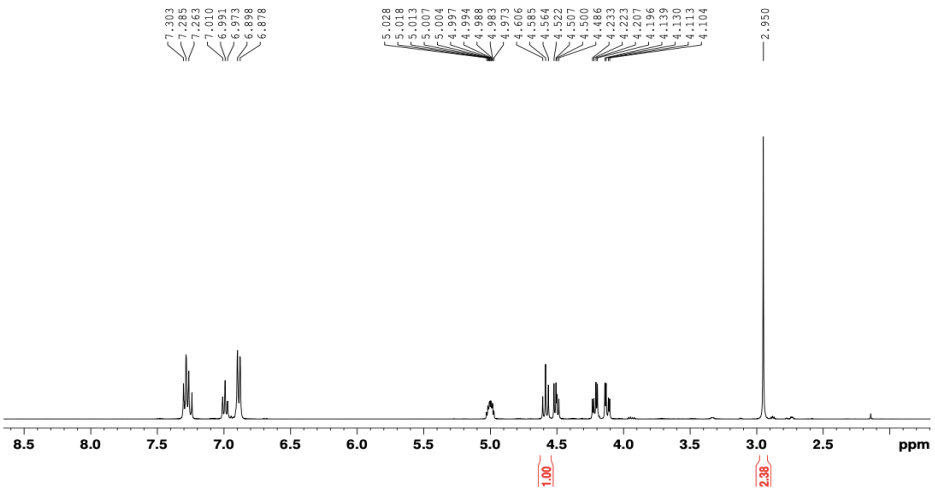
The total number of moles of product in the crude reaction mixture is calculated by multiplying $n_{(p,NMR)}$ by the ratio of the mass of the crude product to the mass of the crude NMR sample:

$$n_p = n_{(p,NMR)}\left(\frac{m_{crude}}{m_{NMR}}\right)$$

where n_p = total number of moles of the catalytic product
m_{crude} = mass of the total crude product
m_{NMR} = mass of the NMR sample

Percent yield, is taken as the ratio of n_p to the theoretical yield (in moles) multiplied by 100.

Sample (actual) data for the conversion of 1,2-epoxy-3-phenoxypropane (molar mass: 150.17, density: 1.109 g/mL, purity: 99.0%) to 4-(phenoxymethyl)-1,3-dioxolan-2-one (molar mass: 194.1) using dimethyl sulfone (molar mass: 94.13, purity: 98.0%) as standard:



initial volume of substrate:	0.99 mL
mass, crude product:	1418.6 mg
mass, NMR sample:	26.69 mg
mass, standard:	4.97 mg
Integration for the standard:	2.38 (δ 2.95, s)
Corresponding # of standard protons:	6
Integration for the product:	1 (δ 4.59, t)
Corresponding # of standard protons:	1

$$\frac{n_{(p,NMR)}}{\left(\frac{I}{H}\right)_p} = \frac{n_{(s,NMR)}}{\left(\frac{I}{H}\right)_s} \Rightarrow \frac{n_{(p,NMR)}}{\frac{1}{1}} = \frac{0.0517\ mmol}{\frac{2.38}{6}}$$

$$n_{(p,NMR)} = 0.130\ mmol$$

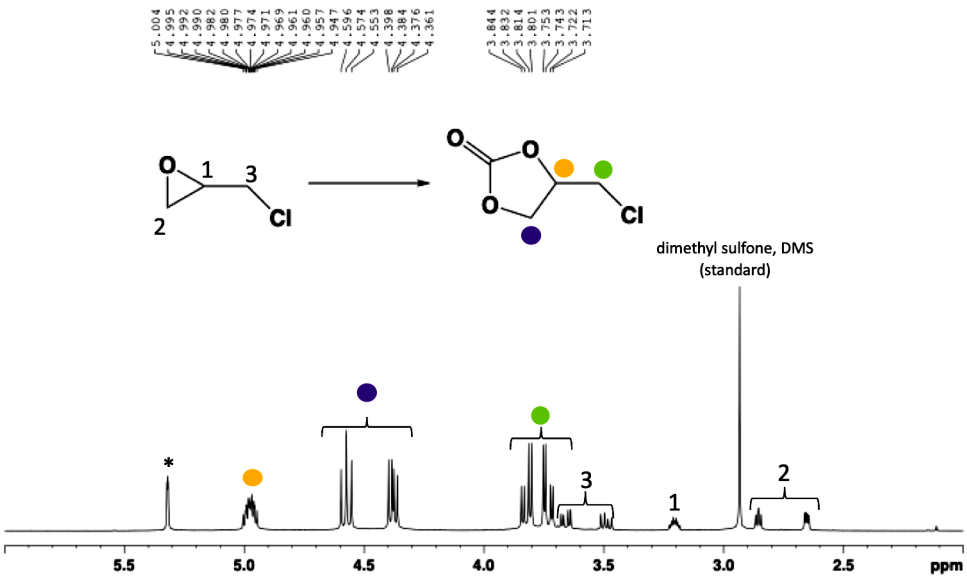
$$n_p = n_{(p,NMR)}\ x \left(\frac{m_{crude}}{m_{NMR}}\right) = 0.130\ mmol\ x \left(\frac{1418.6\ mg}{26.69\ mg}\right) = 6.93\ mmol$$

$$= 0.99\ mL\ x\ \left(1109 \frac{mg}{mL}\right)\ x\ 0.99\ x\ \left(\frac{mmol\ substrtate}{150.17\ mg}\right) x \left(\frac{1\ mmol\ product}{1\ mmol\ substrate}\right) \quad Theoretical\ yield$$

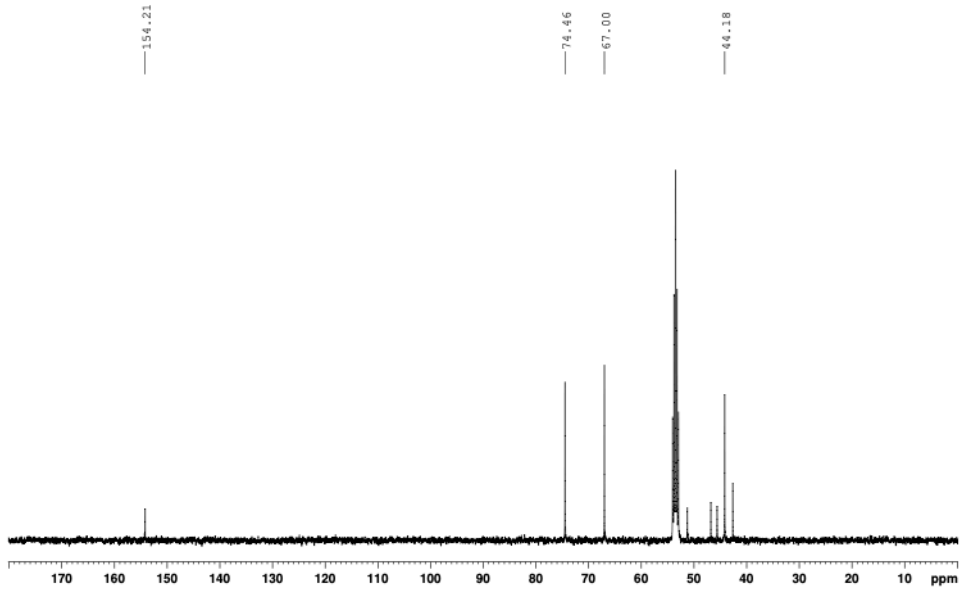
$$= 7.24\ mmol$$

$$\%\ yield = \frac{6.93\ mmol}{7.24\ mmol} x100 = \mathbf{96\%}$$

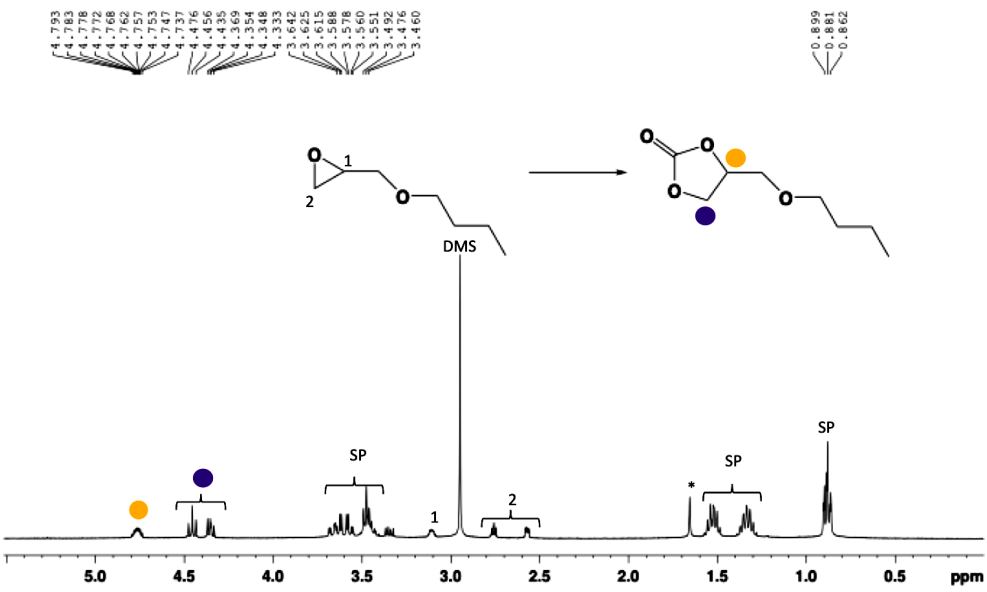
[5] NMR spectra of substrates and cyclic carbonate products.



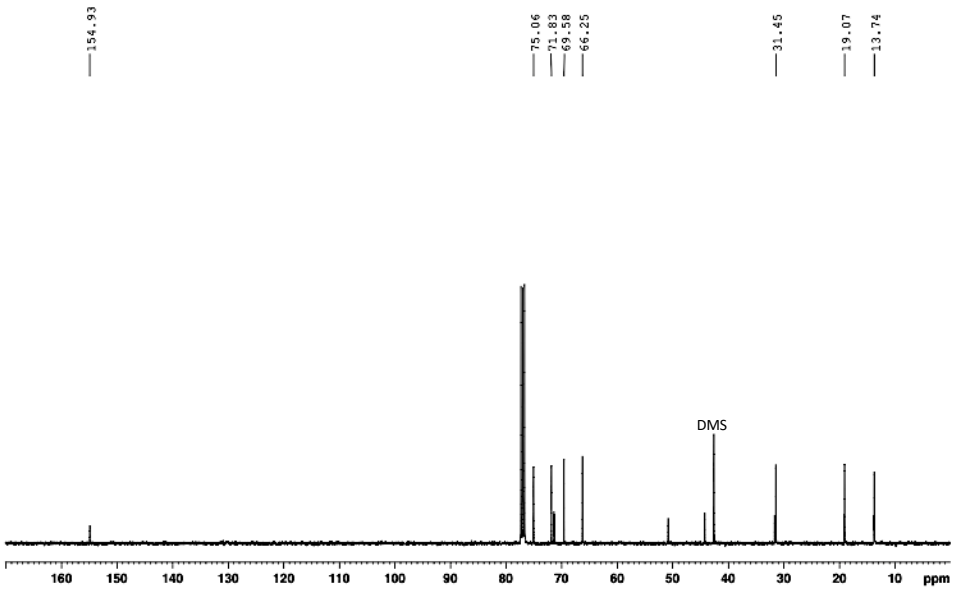
400 ^{1}H NMR of ECH/product mixture in CD_2Cl_2



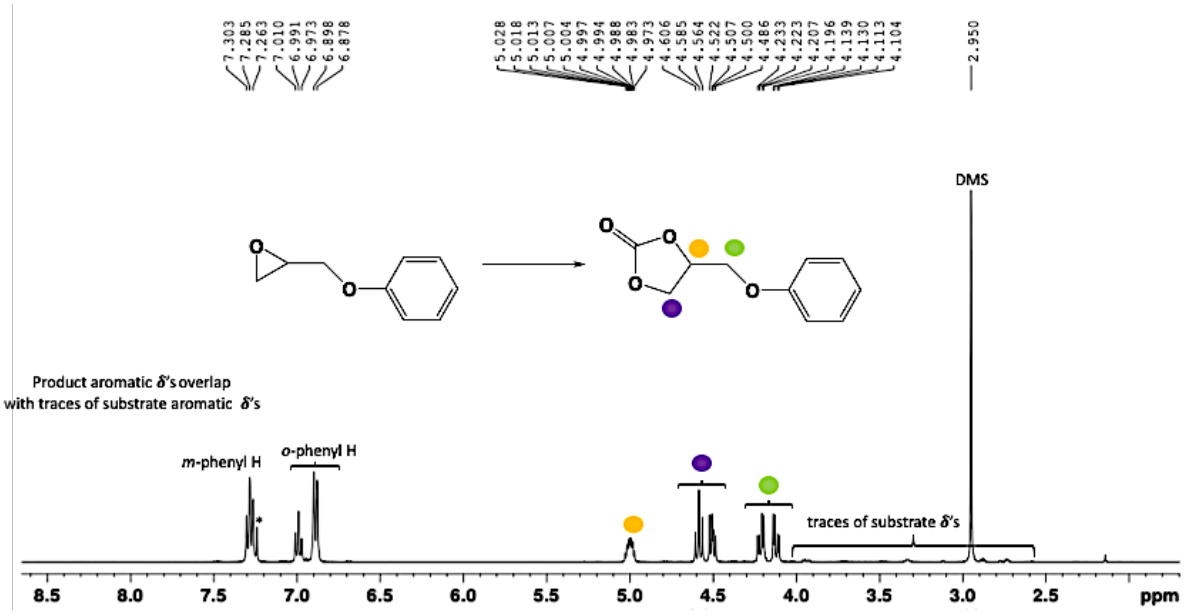
100 ^{13}C NMR of ECH/product mixture in CD_2Cl_2



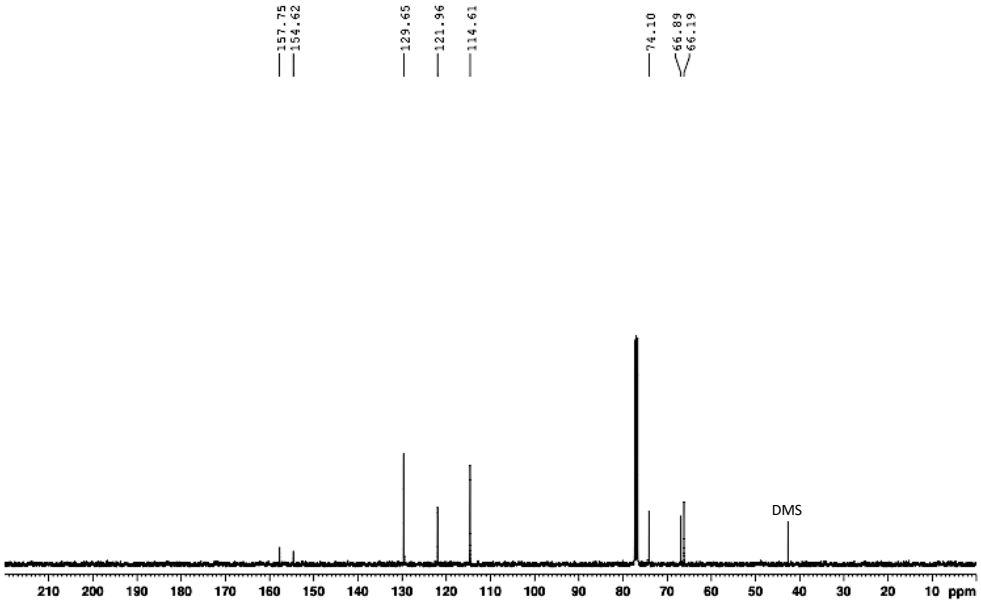
400 ^{1}H NMR of BGE/product mixture in $CDCl_3$
(SP = overlap of substrate and product chemical shifts)



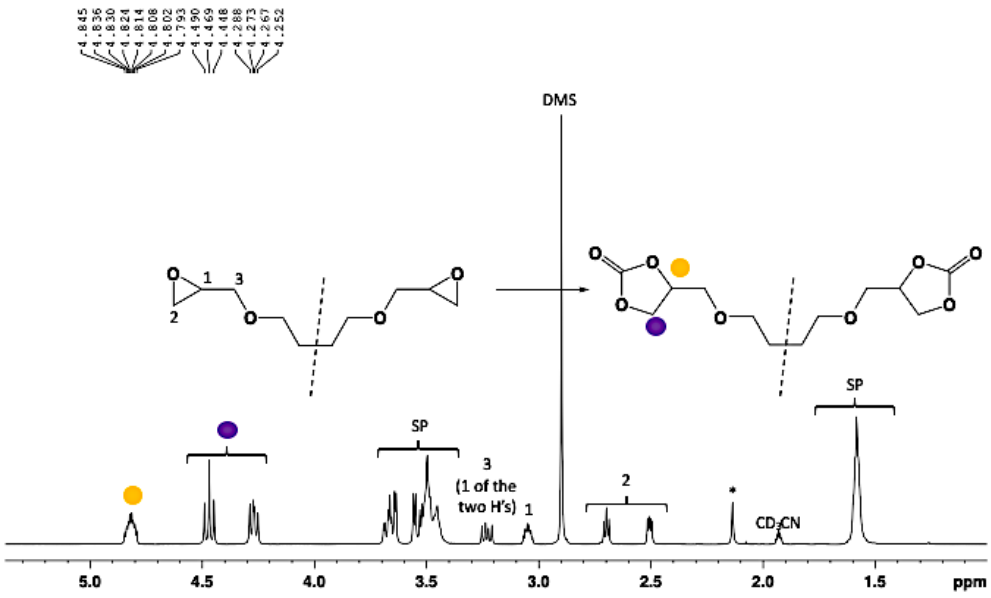
100 ^{13}C NMR of BGE/product mixture in $CDCl_3$



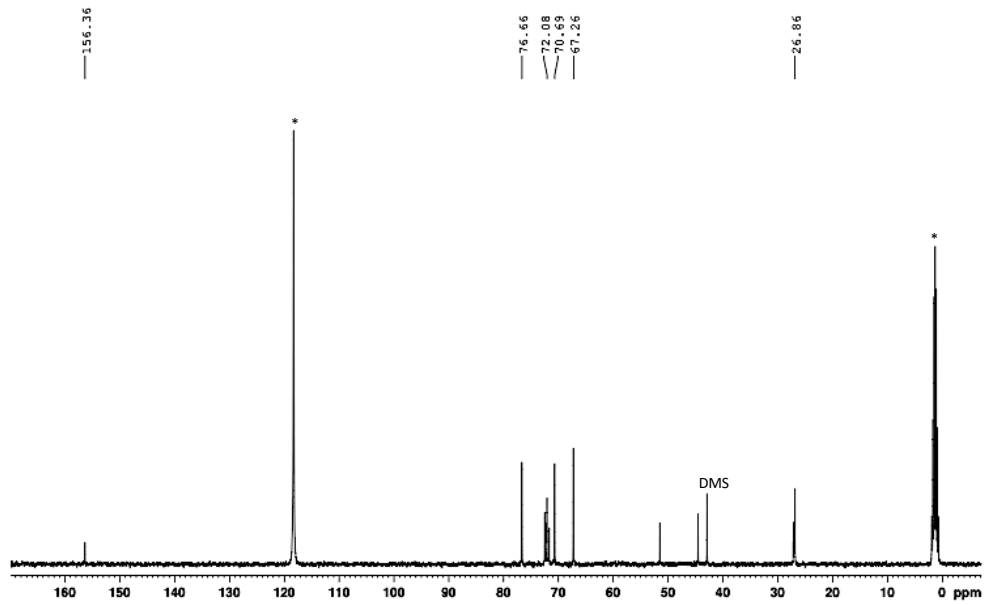
400 ^{1}H NMR of EPP/product mixture in $CDCl_3$



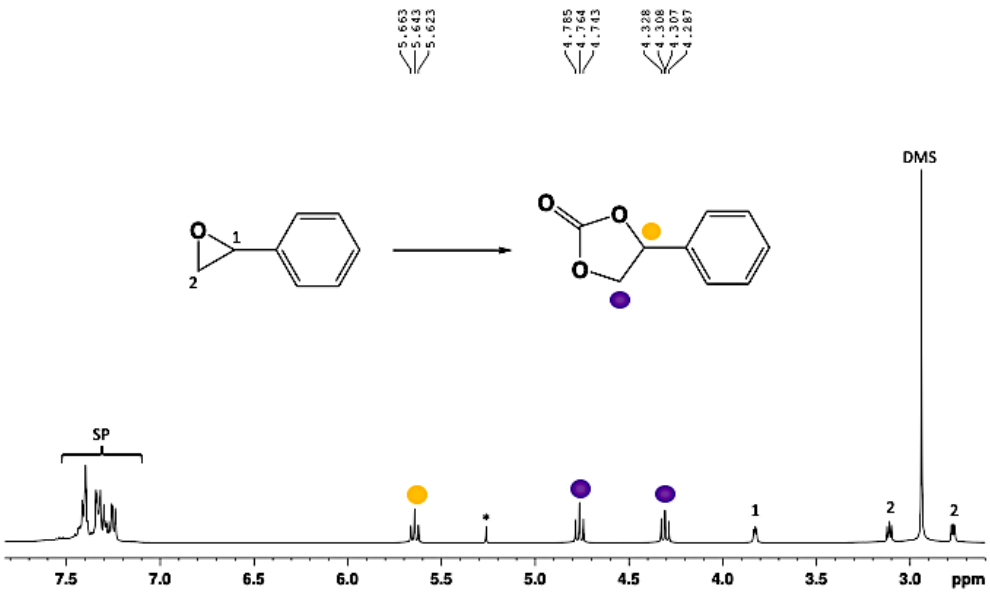
100 ^{13}C NMR of EPP/product mixture in $CDCl_3$



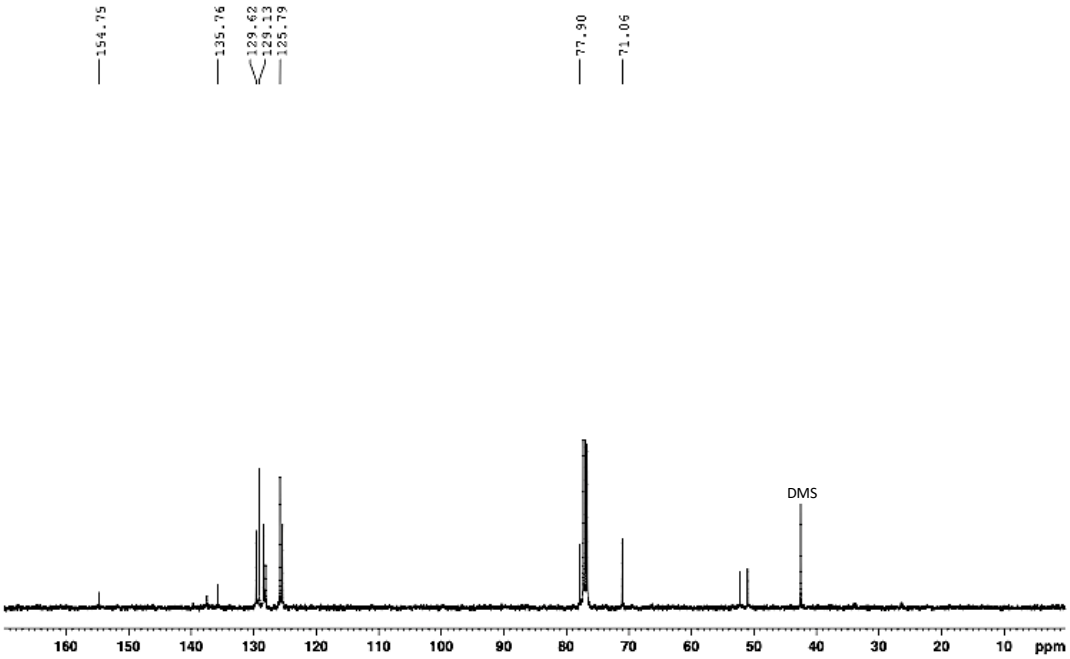
400 ^{1}H NMR of BDDGE/product mixture in CD_3CN
(SP = overlap of substrate and product chemical shifts)



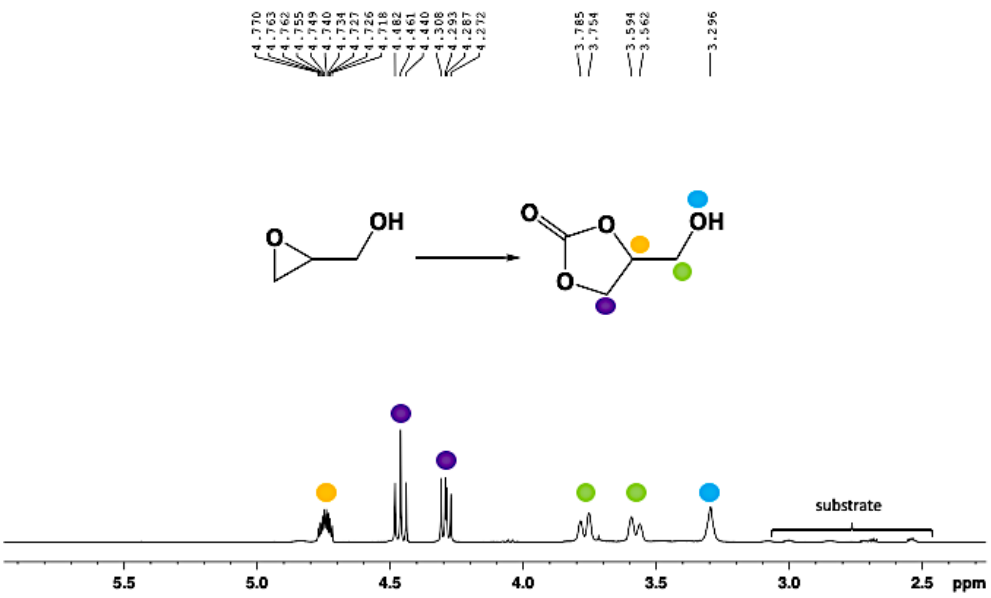
100 ^{13}C NMR of BDDGE/product mixture in CD_3CN



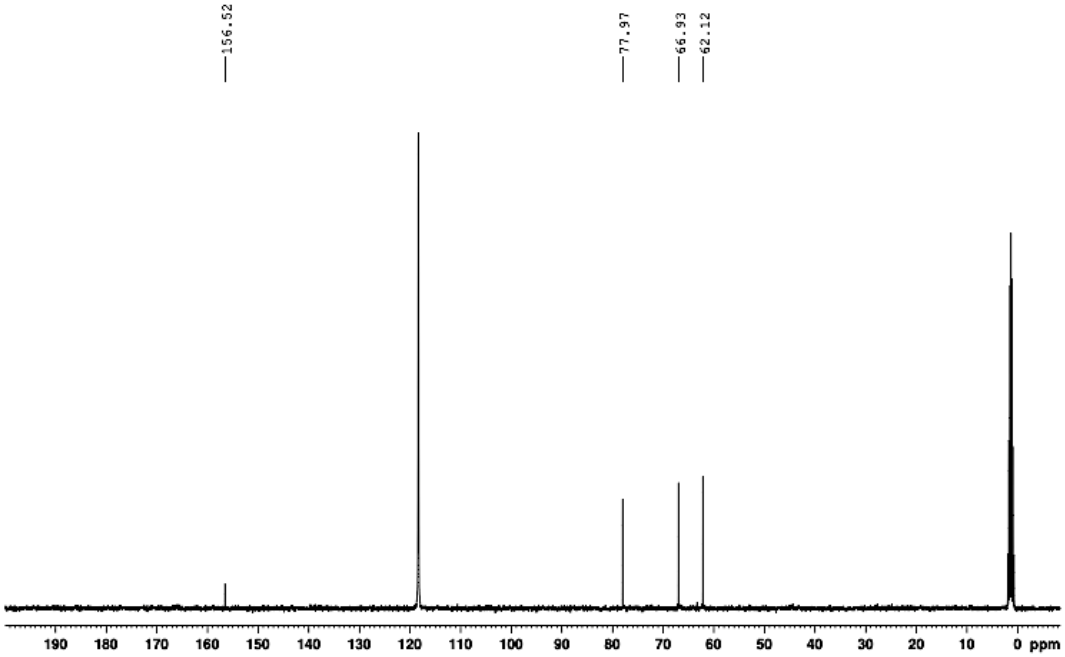
400 ^{1}H NMR of SO/product mixture in $CDCl_3$
(SP = overlap of substrate and product chemical shifts)



100 ^{13}C NMR of SO/product mixture in $CDCl_3$

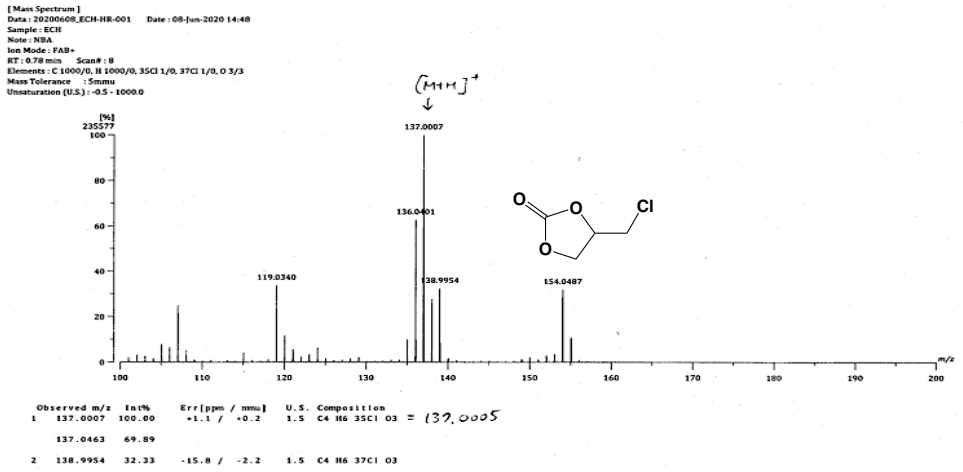


400 ^{1}H NMR of Gly/product mixture in CD_3CN

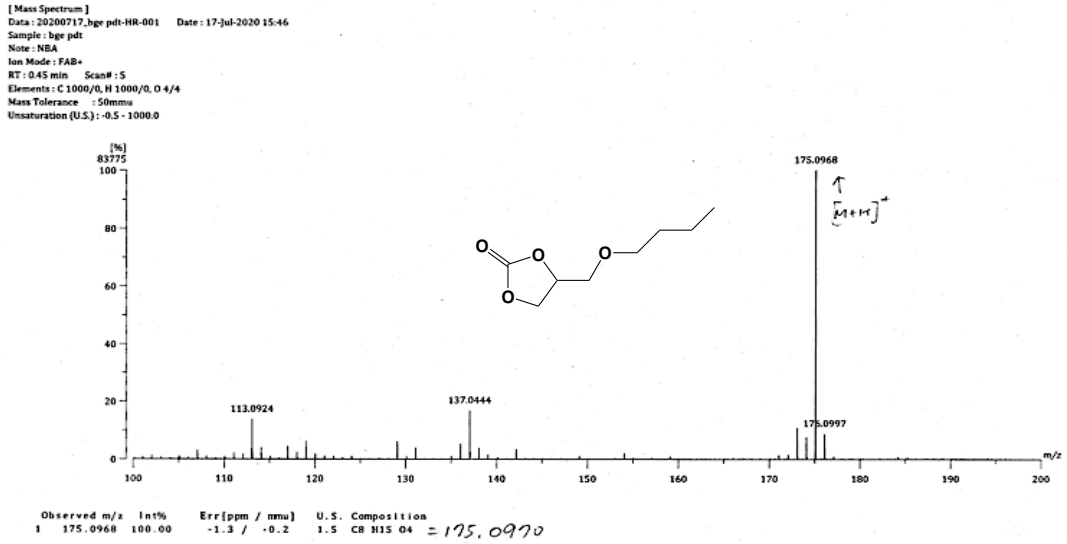


100 ^{13}C NMR of Gly/product mixture in CD_3CN

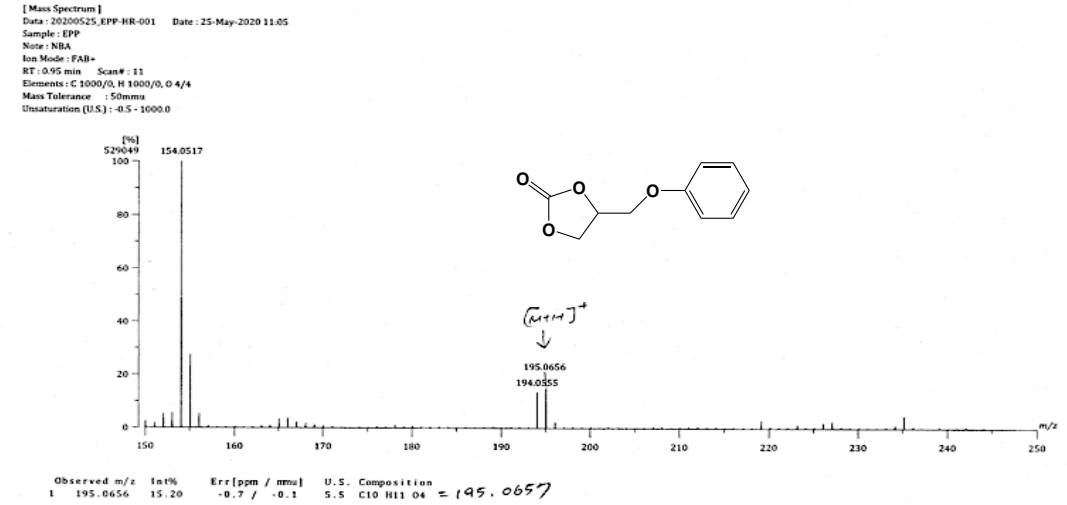
[6] Mass spectra of cyclic carbonate products



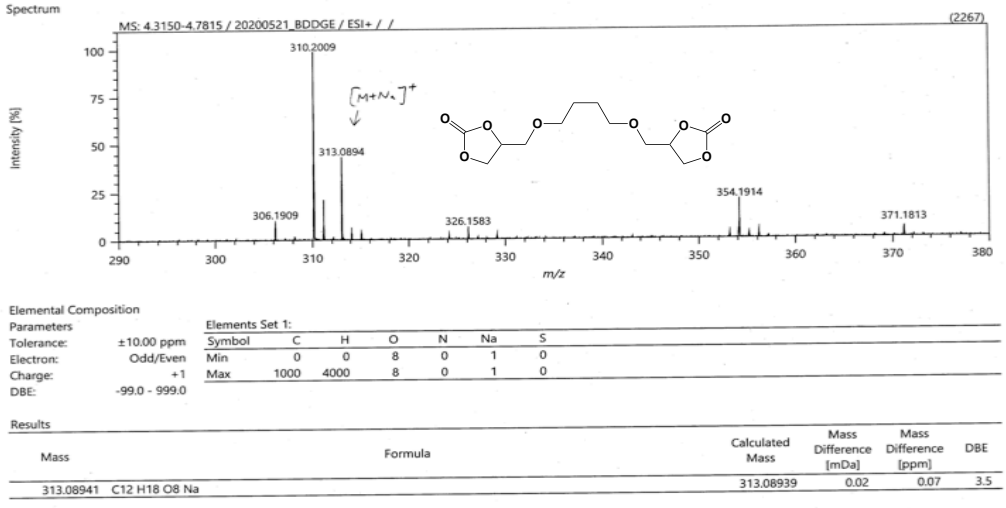
HRMS(FAB) spectrum of 4-(chloromethyl)-1,3-dioxolan-2-one (*m/z* 137.0007 $[M+H]^+$)



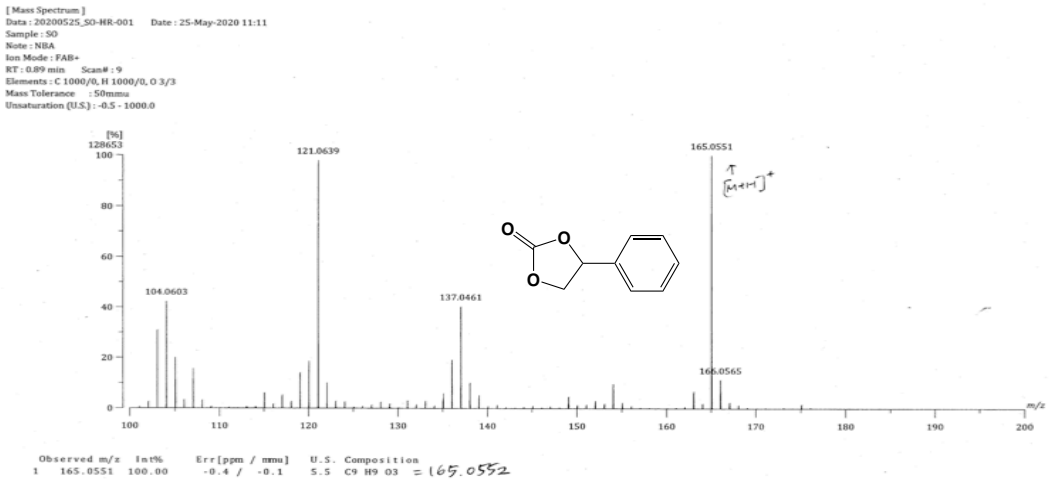
HRMS(FAB) spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one (*m/z* 175.0968 $[M+H]^+$)



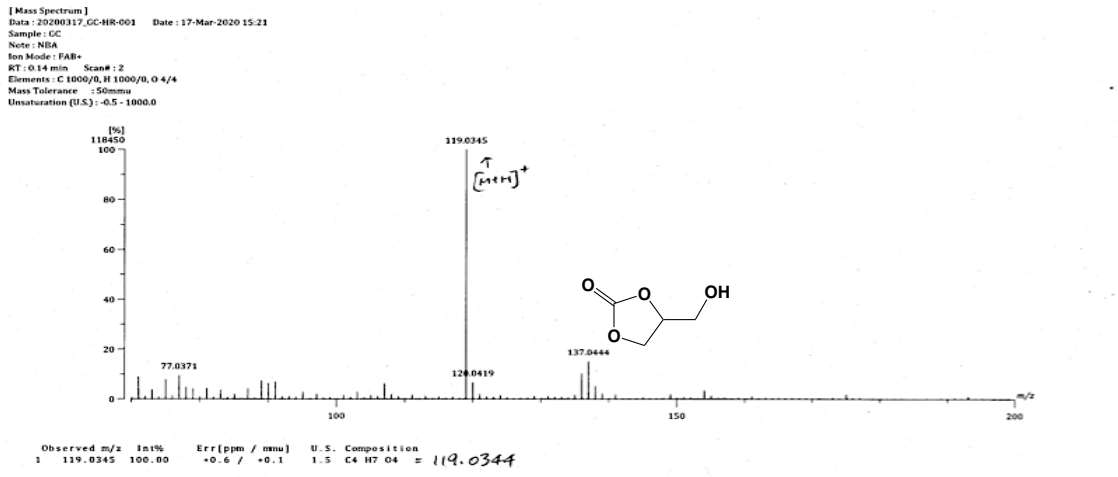
HRMS(FAB) spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one (*m/z* 195.0656 $[M+H]^+$)



HRMS(ESI) spectrum of 4,4'-((butane-1,4-diylbis(oxy))bis(methylene))bis(1,3-dioxolan-2-one) (*m/z* 313.0894 $[M+Na]^+$)

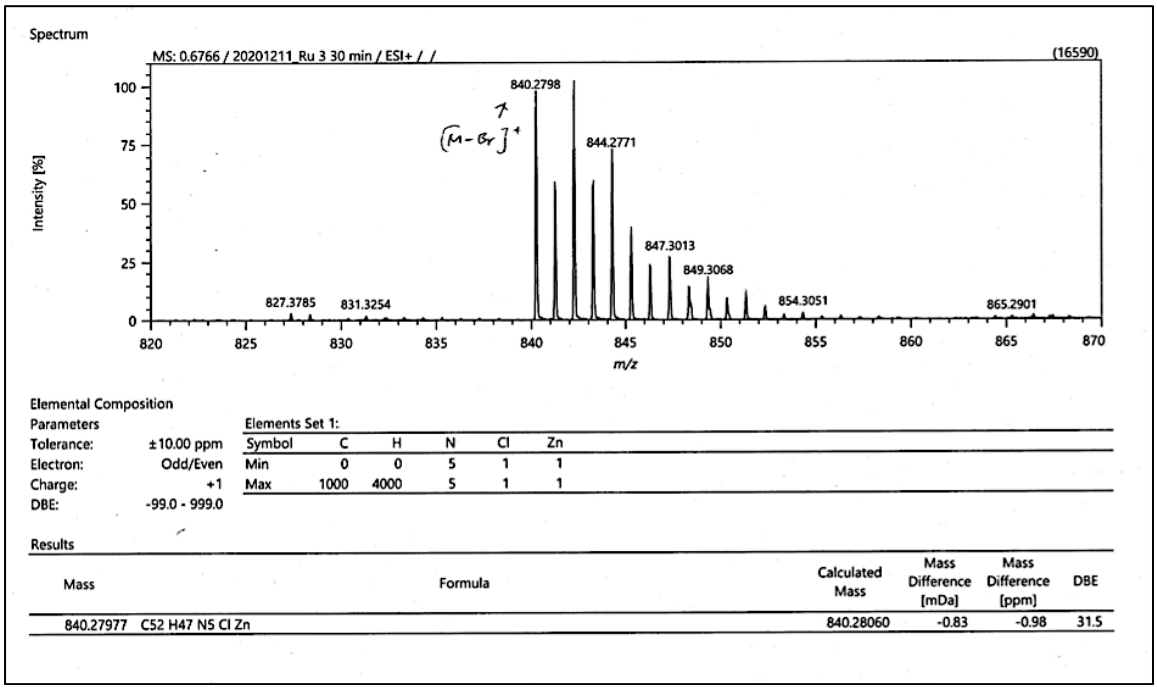


HRMS(FAB) spectrum of 4-phenyl-1,3-dioxolan-2-one (*m/z* 165.0551 $[M+H]^+$)



HRMS(FAB) spectrum of 4-(hydroxymethyl)-1,3-dioxolan-2-one (*m/z* 119.0345 $[M+H]^+$)

[7] HRMS(ESI) spectrum of **3** after 90 minutes of reaction at Run 3



Elemental Composition

Parameters		Elements Set 1:					
Tolerance:	±10.00 ppm	Symbol	C	H	N	Cl	Zn
Electron:	Odd/Even	Min	0	0	5	1	1
Charge:	+1	Max	1000	4000	5	1	1
DBE:	-99.0 - 999.0						

Results

Mass	Formula	Calculated Mass	Mass Difference [mDa]	Mass Difference [ppm]	DBE
840.27977	C52 H47 N5 Cl Zn	840.28060	-0.83	-0.98	31.5

[8] **Global Electrophilicity Index (GEI).** The global electrophilicity index (GEI) was first derived by oar and co-workers[1] as a measure of a molecule's ability to take up electrons, and is denoted as ω.

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta} \qquad \text{Eq. S1}$$

In the above equation, μ and η are chemical potential and chemical hardness, respectively. Hardness is resistance to deformation or change,[2] and is the reciprocal of softness ($1/\eta$). Moreover, μ is the negative of electronegativity, χ.[3] Chemical potential and chemical hardness are both related to the energies of the frontier molecular orbitals by the following equations:

$$\mu = \frac{1}{2}(E_{HOMO} + E_{LUMO}) \qquad \text{Eq. S2}$$

$$\eta = (E_{LUMO} - E_{HOMO}) \qquad \text{Eq. S3}$$

Table S1 Components of GEI calculation for complexes 1-3 in eV (FMO energies are from DFT calculations performed at the indicated levels of theory

Level of theory	Catalyst	E_{HOMO}	E_{LUMO}	$\chi = (-\mu)$	η	GEI, ω
M06/ 6-31g(d)	**1**	-4.746	-2.186	3.466	2.560	2.347
	2	-4.556	-2.029	3.293	2.527	2.146
	3	-4.695	-2.417	3.556	2.278	2.776
B3LYP/ 6-31g(d)	**1**	-4.309	-2.080	3.195	2.229	2.289
	2	-4.351	-2.125	3.238	2.227	2.354
	3	-4.735	-2.840	3.787	1.894	3.786

Fukui Function. A tool that can be used to illustrate and compare local reactivities are the Fukui Indices and Dual Descriptors. Fukui[4] Function was first introduced as a Density Functional approach to describe chemical reactivity. It is defined as the response of the chemical potential at a fixed number of electrons to changing external potential.[5] As a reactivity predictor, it takes the following forms:

$$f^+(\vec{r}) = \rho_{N+1}(\vec{r}) - \rho_N(\vec{r}) \qquad \text{Eq. S4}$$

$$f^-(\vec{r}) = \rho_N(\vec{r}) - \rho_{N-1}(\vec{r}) \qquad \text{Eq. S5}$$

where $\rho(\vec{r})$ is electron density and N, $N+1$, and $N-1$ denote the states where the system has N electrons, one electron added to it (anionic form), and one electron removed from it (cationic form), respectively. The areas of a system that have high $f^+(\vec{r})$ and $f^-(\vec{r})$ distributions are the sites favorable to receive electrons (high electrophilicity) and donate electrons (high nucleophilicity), respectively. Moreover, these functions are related to Frontier Molecular Orbital Theory by the following expressions obtained from frozen orbital approximation.[6-7]

$$f^+(\vec{r}) = |\emptyset_{LUMO}(\vec{r})|^2 \qquad \text{Eq. S6}$$

$$f^-(\vec{r}) = |\emptyset_{HOMO}(\vec{r})|^2 \qquad \text{Eq. S7}$$

[9] Cartesian Coordinates of the Optimized Structure of **1**, **2**, and **3** [M06/6-31g(d) level of theory]

Complex **1**

C	1.020242	-4.11256	-0.92587
C	2.354691	-3.94207	-0.77826
C	2.559825	-2.55899	-0.45689
N	1.374095	-1.86601	-0.45585
C	0.412797	-2.83638	-0.69864
C	-2.96155	0.28193	-0.83971
N	-2.84438	-1.02438	-0.59558
C	-1.44993	-1.33039	-0.57204
C	-0.69529	-0.14758	-0.6684
C	-1.68073	0.855868	-0.90443
C	5.214661	-0.1587	0.709987
C	5.0187	1.16732	0.853052
C	3.682556	1.43884	0.379373
N	3.042387	0.275999	0.015947
C	3.989358	-0.70316	0.177088
C	0.159579	4.099843	-1.10179
C	1.419625	4.243132	-0.6352
C	1.884904	2.928617	-0.29393
N	0.94117	1.975427	-0.55728
C	-0.15559	2.703505	-1.02743
C	-0.95711	-2.63339	-0.71371
C	-1.43172	2.214307	-1.2012
C	3.813751	-2.04298	-0.11764
C	3.166139	2.708424	0.232864
C	-1.83753	-3.77893	-1.05598
C	-2.51504	3.095883	-1.69326
C	4.98041	-2.95759	-0.02948
C	-2.03442	-4.848	-0.17838
C	-2.88698	-5.89526	-0.51392
C	-3.54158	-5.89515	-1.74134
C	-3.32805	-4.85074	-2.6375
C	-2.48237	-3.80202	-2.29762
C	-3.67721	3.299443	-0.94395
C	-4.71065	4.086345	-1.43715
C	-4.59039	4.700484	-2.67912
C	-3.43291	4.514844	-3.43028
C	-2.40542	3.715122	-2.94485
C	5.021923	-3.98001	0.924217
C	6.122612	-4.82348	1.017209
C	7.203332	-4.65881	0.15601
C	7.175097	-3.64622	-0.79744
C	6.073161	-2.8032	-0.88847

C	4.009255	3.884296	0.572154
C	3.673278	4.721087	1.640714
C	4.459818	5.823644	1.95437
C	5.594033	6.109872	1.200515
C	5.936137	5.287904	0.131655
C	5.149277	4.18459	-0.17938
Ni	1.161836	0.057192	-0.43328
C	-3.96586	-1.83469	-0.11921
C	-3.76879	-2.42793	1.286342
H	0.484799	-5.02091	-1.17609
H	3.141441	-4.67973	-0.87943
H	-3.94301	0.752634	-0.83083
H	6.094423	-0.74115	0.957053
H	5.705187	1.912072	1.23802
H	-0.52626	4.871216	-1.43048
H	1.998441	5.152222	-0.52604
H	-1.51283	-4.84841	0.77982
H	-3.03704	-6.71626	0.185496
H	-4.2088	-6.71382	-2.00479
H	-3.82327	-4.85365	-3.60692
H	-2.31767	-2.97885	-2.99254
H	-3.80622	2.828633	0.030574
H	-5.61359	4.197009	-0.83857
H	-5.3995	5.317703	-3.06652
H	-3.33302	4.985084	-4.40754
H	-1.50871	3.548476	-3.5415
H	4.176745	-4.10222	1.601395
H	6.139645	-5.60994	1.770249
H	8.066067	-5.31907	0.22728
H	8.013847	-3.51362	-1.479
H	6.045766	-2.01178	-1.63718
H	2.782619	4.495025	2.227196
H	4.186424	6.461225	2.793743
H	6.208767	6.974516	1.445288
H	6.817742	5.510175	-0.4676
H	5.409997	3.542469	-1.02046
H	-4.15011	-2.65278	-0.82275
H	-4.84319	-1.17173	-0.12144
H	-4.29202	-3.39387	1.292626
C	-4.35119	-1.63033	2.44822
H	-2.71275	-2.6897	1.442242
Br	-5.74805	1.219495	1.117299
H	-4.7777	-2.30425	3.202967
H	-5.13621	-0.94103	2.095861
N	-3.39037	-0.75431	3.247797
C	-4.22858	0.079065	4.169496

H	-4.82905	-0.58775	4.796639
H	-3.56194	0.683829	4.792182
H	-4.87341	0.715361	3.543203
C	-2.601	0.177694	2.375966
H	-1.94283	-0.40023	1.718581
H	-3.32638	0.777999	1.809264
H	-1.9947	0.812433	3.030168
C	-2.45834	-1.59554	4.041066
H	-1.80776	-0.94265	4.631224
H	-3.03941	-2.24245	4.706385
H	-1.84633	-2.20076	3.366272

Complex **2**

C	-1.42812	4.160457	-0.92453
C	-2.45015	4.070118	-0.04109
C	-2.61625	2.675668	0.254809
N	-1.69263	1.914136	-0.40818
C	-0.91985	2.833249	-1.1056
C	2.217513	-0.42144	-1.95156
N	2.087079	0.895083	-2.14546
C	0.771313	1.249664	-1.71577
C	0.093763	0.115028	-1.24764
C	1.030243	-0.9404	-1.4275
C	-5.24545	0.345745	1.618441
C	-5.35928	-0.93569	1.215602
C	-4.18757	-1.22381	0.421617
N	-3.38257	-0.11735	0.314913
C	-4.04306	0.865771	1.009436
C	-0.87688	-4.13248	-1.02372
C	-2.20707	-4.16017	-0.78987
C	-2.60874	-2.80291	-0.53471
N	-1.56707	-1.93338	-0.69155
C	-0.47944	-2.75569	-0.9999
C	0.26097	2.554765	-1.77353
C	0.79175	-2.32591	-1.29582
C	-3.68054	2.19936	1.033435
C	-3.8877	-2.48384	-0.05482
C	0.90608	3.628708	-2.56776
C	1.899158	-3.27651	-1.54272
C	-4.48677	3.18267	1.799433
C	1.518289	4.734813	-1.9717
C	2.155778	5.695781	-2.74977
C	2.178836	5.571021	-4.13527
C	1.551322	4.485381	-4.74097
C	0.921008	3.521966	-3.96282
C	3.021904	-3.25944	-0.70762

C	4.086489	-4.12391	-0.93497
C	4.04892	-5.00875	-2.00779
C	2.940852	-5.02835	-2.85063
C	1.872387	-4.16911	-2.62079
C	-3.90211	3.899744	2.848799
C	-4.63388	4.838798	3.565792
C	-5.96617	5.079692	3.244217
C	-6.5585	4.378763	2.198631
C	-5.82381	3.441465	1.480728
C	-4.9222	-3.54592	0.056833
C	-4.8067	-4.58261	0.988166
C	-5.79825	-5.55058	1.099555
C	-6.92408	-5.4953	0.283138
C	-7.05341	-4.46539	-0.64267
C	-6.06044	-3.49793	-0.75275
Ni	-1.63347	-0.00635	-0.51562
C	3.255756	1.750327	-2.33495
C	3.80773	2.267712	-1.00952
H	-1.03243	5.050187	-1.39997
H	-3.07559	4.864834	0.347865
H	3.144987	-0.93515	-2.18989
H	-5.91017	0.911407	2.260349
H	-6.13272	-1.65477	1.4593
H	-0.20619	-4.96154	-1.21582
H	-2.86656	-5.01849	-0.75414
H	1.500726	4.827239	-0.88552
H	2.63733	6.546879	-2.27041
H	2.678865	6.322931	-4.74328
H	1.554008	4.388332	-5.82532
H	0.440196	2.661572	-4.42812
H	3.072779	-2.5921	0.155583
H	4.929445	-4.08883	-0.24489
H	4.881903	-5.68696	-2.18795
H	2.90839	-5.71338	-3.69697
H	1.010242	-4.17261	-3.28798
H	-2.85864	3.706695	3.097848
H	-4.16183	5.382528	4.382876
H	-6.54078	5.814802	3.805431
H	-7.59748	4.568911	1.93355
H	-6.28245	2.905515	0.650012
H	-3.92897	-4.61665	1.633528
H	-5.69374	-6.34807	1.833671
H	-7.7009	-6.25312	0.371808
H	-7.93189	-4.41496	-1.28421
H	-6.15835	-2.68719	-1.47461
H	3.007239	2.577208	-3.0036

H	4.011663	1.137662	-2.84715
H	4.427553	3.156139	-1.21032
C	4.623333	1.232647	-0.25139
H	2.966393	2.612986	-0.38802
Br	5.111665	-2.54299	2.149159
H	5.539732	1.002827	-0.82162
C	4.990679	1.697124	1.15491
H	4.071895	1.708159	1.759665
H	5.367078	2.733029	1.124142
H	4.075588	0.279442	-0.16384
C	6.018805	0.743483	1.724113
H	7.011974	0.937765	1.294474
H	5.740854	-0.30824	1.520941
N	6.214929	0.802884	3.231883
C	7.277202	-0.19793	3.583788
C	6.645495	2.156812	3.658343
C	4.955255	0.416795	3.954363
H	5.851676	2.877906	3.444906
H	8.198248	0.08065	3.061683
H	7.433509	-0.16659	4.66687
H	6.917288	-1.18972	3.258858
H	6.847777	2.141421	4.73414
H	7.554805	2.429651	3.112331
H	4.635972	-0.5663	3.566569
H	5.188996	0.359608	5.022361
H	4.195781	1.184061	3.786283

Complex **3**

N	1.976634	-0.55162	0.867294
N	-1.7839	2.050166	-0.34041
N	-3.84975	0.060252	-0.0467
N	-1.78268	-1.94233	-0.20419
C	0.425679	-0.01105	-0.6695
C	1.969157	0.787627	0.741174
C	1.028729	1.178105	-0.20884
C	0.633346	2.543141	-0.37659
C	-0.69657	2.899287	-0.49336
C	-1.15355	4.254675	-0.69159
C	-2.49961	4.231185	-0.59081
C	-2.87931	2.853718	-0.36128
C	-4.22727	2.472786	-0.15765
C	-4.65827	1.154803	-0.03866
C	-6.04807	0.740121	-0.02367
C	-6.05235	-0.60993	-0.06468
C	-4.66536	-1.0325	-0.11143
C	-4.23437	-2.3432	-0.27096

C	-2.87357	-2.72772	-0.38409
C	-2.4815	-4.08129	-0.70096
C	-1.13078	-4.11801	-0.64943
C	-0.68878	-2.78765	-0.30776
C	0.64032	-2.45422	-0.06783
C	1.011235	-1.07867	0.002059
C	1.638348	-3.51825	0.129046
C	1.353349	-4.62039	0.954245
C	2.294992	-5.62029	1.150454
C	3.541013	-5.53645	0.532926
C	3.844103	-4.44224	-0.27015
C	2.903282	-3.43819	-0.46844
C	1.688517	3.568269	-0.26814
C	2.860624	3.454034	-1.03016
C	3.860735	4.416539	-0.94429
C	3.731707	5.489994	-0.06663
C	2.590461	5.594883	0.722783
C	1.579605	4.646813	0.621574
C	-5.26536	3.538724	-0.10757
C	-5.62467	4.25951	-1.25057
C	-6.60518	5.243502	-1.19139
C	-7.24895	5.516709	0.011916
C	-6.90667	4.800201	1.15406
C	-5.92177	3.820194	1.094274
C	-5.26221	-3.41481	-0.36681
C	-6.13547	-3.478	-1.45711
C	-7.09532	-4.48048	-1.54274
C	-7.19481	-5.43892	-0.53948
C	-6.32914	-5.38913	0.549151
C	-5.371	-4.38576	0.633823
H	2.530087	1.417558	1.422355
H	-0.51593	5.10728	-0.89513
H	-3.18792	5.064708	-0.66095
H	-6.8998	1.410303	-0.01681
H	-6.90996	-1.27186	-0.08048
H	-3.16182	-4.88977	-0.94101
H	-0.47882	-4.95523	-0.86723
H	0.3938	-4.66368	1.467539
H	2.059795	-6.46141	1.800878
H	4.282302	-6.31831	0.691724
H	4.822779	-4.32354	-0.73455
H	3.186075	-2.58202	-1.08501
H	2.958445	2.616455	-1.72212
H	4.73947	4.341483	-1.58648
H	4.514543	6.244229	-0.00056
H	2.48677	6.418045	1.427603

H	0.696589	4.716974	1.254657
H	-5.12652	4.035393	-2.19417
H	-6.8737	5.794491	-2.09155
H	-8.01823	6.285748	0.058858
H	-7.4057	5.007107	2.09955
H	-5.64579	3.259027	1.987089
H	-6.04827	-2.73027	-2.24542
H	-7.76429	-4.51568	-2.40121
H	-7.94533	-6.22477	-0.60682
H	-6.4039	-6.13362	1.340254
H	-4.69482	-4.34065	1.487461
C	2.658684	-1.20736	1.99094
H	2.222375	-2.20257	2.111476
H	2.396395	-0.63363	2.891884
C	4.168603	-1.30388	1.812528
H	4.568568	-1.83652	2.689712
H	4.410895	-1.91023	0.927544
C	4.866124	0.037588	1.65374
H	4.465256	0.523167	0.753731
H	4.633806	0.706087	2.503635
C	6.375713	-0.11	1.509863
H	6.795915	-0.50659	2.446202
H	6.581246	-0.86177	0.729004
C	7.084999	1.203183	1.229588
H	6.531254	2.047033	1.667667
N	7.291262	1.584344	-0.23353
C	6.007537	1.578356	-1.01412
H	5.27675	2.19739	-0.48254
H	6.221394	2.016405	-1.99596
H	5.668742	0.536172	-1.15327
C	8.269792	0.65451	-0.89206
H	9.17472	0.61361	-0.27724
H	7.801394	-0.33637	-1.02409
H	8.504733	1.065113	-1.87938
C	7.847135	2.96588	-0.25031
H	7.108837	3.654139	0.17541
H	8.770247	2.991783	0.337984
H	8.061017	3.249061	-1.28525
Br	5.925809	-1.86509	-1.52294
H	-0.24183	-0.10775	-1.52002
Zn	-1.89539	0.067769	0.397122
Cl	-1.16979	0.144449	2.525064
H	8.098794	1.215546	1.650498

[10] Cartesian Coordinates of the Optimized Structure of **1**, **2**, and **3** [B3LYP/6-31g(d) level of theory]

Complex **1**

C	0.585609	4.065106	1.129592
C	1.758199	4.18692	0.45496
C	2.145856	2.862226	0.047521
N	1.217371	1.929244	0.456684
C	0.214601	2.676311	1.076036
C	-2.56569	-1.01512	1.08135
N	-2.66349	0.297348	1.304399
C	-1.3477	0.853159	1.185302
C	-0.43214	-0.16302	0.83361
C	-1.22404	-1.35355	0.821755
C	5.186114	0.992376	-1.21342
C	5.408003	-0.31352	-0.93914
C	4.204883	-0.81848	-0.30978
N	3.25883	0.178786	-0.19062
C	3.86957	1.310353	-0.69744
C	1.192423	-4.23799	0.684661
C	2.53172	-4.0706	0.574408
C	2.763958	-2.65746	0.395875
N	1.587182	-1.94643	0.475177
C	0.597042	-2.92746	0.647377
C	-1.03881	2.198351	1.452408
C	-0.76097	-2.69123	0.761388
C	3.358751	2.597372	-0.61117
C	4.025981	-2.14574	0.049754
C	-1.95905	3.122905	2.184804
C	-1.73135	-3.81545	0.890119
C	4.143619	3.751538	-1.14921
C	-2.55946	4.227716	1.560539
C	-3.39919	5.083379	2.277581
C	-3.64836	4.850713	3.631566
C	-3.04861	3.75984	4.266576
C	-2.21094	2.904252	3.55027
C	-2.79035	-3.9388	-0.0248
C	-3.72692	-4.96521	0.1018
C	-3.62109	-5.8912	1.141125
C	-2.57794	-5.77429	2.06379
C	-1.64509	-4.74367	1.943606
C	3.643754	4.505086	-2.22405
C	4.362091	5.586781	-2.7356
C	5.593443	5.938402	-2.17773
C	6.099432	5.201803	-1.10456
C	5.380402	4.119281	-0.59453

C	5.20442	-3.06861	-0.01572
C	5.328261	-4.02736	-1.03414
C	6.439889	-4.86979	-1.09004
C	7.448243	-4.76705	-0.12865
C	7.338957	-3.81498	0.886818
C	6.226804	-2.97244	0.941167
Ni	1.400288	-0.00234	0.40816
C	-3.96325	0.975399	1.343214
C	-4.33591	1.668214	0.002277
H	0.007505	4.847563	1.598028
H	2.333181	5.082563	0.271265
H	-3.4413	-1.64808	1.096253
H	5.84661	1.693985	-1.70136
H	6.282974	-0.90628	-1.16304
H	0.645154	-5.16337	0.783069
H	3.300038	-4.82909	0.569077
H	-2.36553	4.414121	0.50803
H	-3.85541	5.933487	1.777295
H	-4.29979	5.517296	4.189823
H	-3.22771	3.577536	5.322678
H	-1.74191	2.060022	4.048017
H	-2.90976	-3.22787	-0.83759
H	-4.53875	-5.01401	-0.61833
H	-4.34932	-6.69213	1.239192
H	-2.49474	-6.47964	2.886712
H	-0.85256	-4.64419	2.679791
H	2.688331	4.231523	-2.6634
H	3.960949	6.152329	-3.57258
H	6.153365	6.780709	-2.57509
H	7.053036	5.47217	-0.6587
H	5.773069	3.556632	0.247741
H	4.549737	-4.10562	-1.78802
H	6.519732	-5.60314	-1.8882
H	8.313413	-5.4232	-0.17229
H	8.11835	-3.72763	1.639271
H	6.14327	-2.23386	1.733813
H	-3.9664	1.699292	2.153442
H	-4.69778	0.206531	1.599376
H	-4.65075	2.691856	0.22137
C	-5.45186	0.899042	-0.70644
H	-3.43799	1.731318	-0.61874
Br	-5.16839	-2.38659	-2.40695
H	-6.36461	0.926682	-0.10395
H	-5.18785	-0.14911	-0.89132
N	-5.85541	1.449905	-2.07791
C	-7.08702	0.697718	-2.52859

H	-7.89134	0.894223	-1.81815
H	-7.36497	1.060359	-3.51941
H	-6.83797	-0.36752	-2.56113
C	-4.75679	1.206799	-3.0861
H	-3.86147	1.744726	-2.77647
H	-4.57615	0.12825	-3.12837
H	-5.09526	1.581841	-4.05315
C	-6.17592	2.915095	-2.01187
H	-6.5844	3.222539	-2.97523
H	-6.91395	3.082645	-1.22545
H	-5.26841	3.479957	-1.80339

Complex **2**

C	-1.47554	4.204514	-0.81637
C	-2.50114	4.09913	0.068081
C	-2.67799	2.696589	0.337982
N	-1.75203	1.943298	-0.35106
C	-0.96966	2.875252	-1.03322
C	2.161644	-0.39038	-1.95401
N	2.043078	0.928702	-2.1169
C	0.726926	1.296434	-1.67801
C	0.038459	0.148084	-1.22552
C	0.965686	-0.91708	-1.43051
C	-5.31686	0.336693	1.67732
C	-5.43708	-0.94156	1.250052
C	-4.26787	-1.22425	0.442408
N	-3.45538	-0.11275	0.35468
C	-4.11036	0.867794	1.074853
C	-0.96569	-4.12415	-1.10428
C	-2.29915	-4.15115	-0.86524
C	-2.69988	-2.79542	-0.56957
N	-1.64265	-1.925	-0.70845
C	-0.55444	-2.74616	-1.04123
C	0.219495	2.607125	-1.71038
C	0.723468	-2.30673	-1.32733
C	-3.7413	2.205053	1.115802
C	-3.97539	-2.47994	-0.07063
C	0.854402	3.7267	-2.47455
C	1.833099	-3.27117	-1.5866
C	-4.54301	3.179017	1.919997
C	1.495445	4.796928	-1.83171
C	2.061496	5.83701	-2.57222
C	1.989041	5.826852	-3.96659
C	1.34297	4.772366	-4.61712
C	0.779579	3.731649	-3.8776
C	2.921064	-3.34125	-0.70049

C	3.974868	-4.22622	-0.93469
C	3.963103	-5.04931	-2.06255
C	2.890411	-4.98278	-2.95579
C	1.834186	-4.10095	-2.72068
C	-3.96266	3.826917	3.022844
C	-4.69317	4.743305	3.780744
C	-6.01841	5.031966	3.44696
C	-6.60617	4.399555	2.34925
C	-5.87437	3.48292	1.592094
C	-5.02368	-3.54733	0.010538
C	-4.93453	-4.59166	0.944992
C	-5.92763	-5.56968	1.019756
C	-7.02887	-5.51955	0.16167
C	-7.13141	-4.48396	-0.76926
C	-6.13756	-3.50574	-0.84248
Ni	-1.69477	0.014743	-0.491
C	3.213618	1.767588	-2.42042
C	3.939308	2.27292	-1.16056
H	-1.07601	5.103537	-1.26137
H	-3.11337	4.889153	0.477427
H	3.074669	-0.90583	-2.21708
H	-5.98248	0.889696	2.323678
H	-6.21495	-1.65482	1.481307
H	-0.31023	-4.95385	-1.32505
H	-2.95581	-5.00805	-0.84697
H	1.549856	4.810818	-0.74691
H	2.556885	6.656103	-2.05771
H	2.428041	6.636884	-4.54246
H	1.27248	4.761673	-5.70142
H	0.274943	2.914438	-4.38565
H	2.952855	-2.72387	0.193365
H	4.789816	-4.25479	-0.21649
H	4.783165	-5.73881	-2.2462
H	2.875328	-5.61492	-3.84007
H	1.007595	-4.04482	-3.42377
H	-2.93309	3.601858	3.287468
H	-4.2274	5.229077	4.634228
H	-6.58801	5.745338	4.036534
H	-7.63437	4.622999	2.076914
H	-6.3324	3.00251	0.73206
H	-4.08393	-4.6301	1.619915
H	-5.84256	-6.36822	1.752117
H	-7.80197	-6.2811	0.219669
H	-7.98452	-4.43634	-1.44102
H	-6.21896	-2.70154	-1.56877
H	2.901349	2.601647	-3.04182

H	3.888277	1.148489	-3.02103
H	4.609301	3.085779	-1.47015
C	4.747783	1.187743	-0.43992
H	3.203891	2.716181	-0.47857
Br	5.100745	-2.74347	2.407273
H	5.554533	0.843733	-1.1028
C	5.343411	1.669103	0.894357
H	4.520393	1.870037	1.589102
H	5.878974	2.614143	0.741515
H	4.11625	0.314445	-0.23908
C	6.28109	0.593213	1.439907
H	7.198203	0.553579	0.84503
H	5.81136	-0.39741	1.423189
N	6.744277	0.778511	2.888084
C	7.749887	-0.30903	3.184573
C	7.388374	2.11787	3.0879
C	5.583347	0.616982	3.840093
H	6.647165	2.902493	2.939965
H	8.602374	-0.18279	2.515486
H	8.069788	-0.2085	4.222807
H	7.258338	-1.27282	3.019722
H	7.779965	2.167579	4.104868
H	8.202459	2.228865	2.369633
H	5.141353	-0.36843	3.662672
H	5.967535	0.693968	4.858474
H	4.859196	1.41044	3.660253

Complex **3**

N	-1.90436	0.757992	-0.10047
N	2.858186	0.750832	0.605376
N	3.590997	-1.6665	-0.85754
N	0.765187	-2.38516	-0.81055
C	-0.03852	-0.04432	0.877939
C	-1.19374	1.812233	0.349051
C	-0.01905	1.369444	0.974135
C	1.034599	2.231647	1.422076
C	2.3716	1.857025	1.306559
C	3.480078	2.612303	1.848694
C	4.618151	1.997831	1.440251
C	4.22158	0.845367	0.653879
C	5.171804	-0.00358	0.017826
C	4.855781	-1.17009	-0.68066
C	5.821152	-2.10141	-1.24705
C	5.118139	-3.15431	-1.73351
C	3.712704	-2.89195	-1.45418
C	2.656633	-3.78278	-1.67364

C	1.312183	-3.55004	-1.27138
C	0.316552	-4.60665	-1.27323
C	-0.84135	-4.06306	-0.82796
C	-0.58361	-2.65892	-0.56985
C	-1.57315	-1.74939	-0.19055
C	-1.19991	-0.42319	0.210374
C	-2.99856	-2.16351	-0.1521
C	-3.61744	-2.8203	-1.23389
C	-4.95535	-3.20607	-1.15976
C	-5.70407	-2.93661	-0.01079
C	-5.10997	-2.27569	1.067527
C	-3.77024	-1.89423	0.994319
C	0.650458	3.564761	1.944633
C	-0.39016	3.674114	2.888539
C	-0.77649	4.917715	3.386058
C	-0.14627	6.081051	2.937032
C	0.872625	5.99095	1.98531
C	1.268172	4.74767	1.493774
C	6.62316	0.364044	0.123089
C	7.336621	0.167036	1.316061
C	8.689607	0.500349	1.40149
C	9.352691	1.033184	0.293466
C	8.654501	1.230837	-0.89953
C	7.300436	0.899681	-0.98326
C	2.964675	-5.10002	-2.31842
C	3.747678	-6.06615	-1.66594
C	4.02908	-7.28967	-2.27685
C	3.530579	-7.56928	-3.55105
C	2.747862	-6.61821	-4.2097
C	2.46682	-5.39553	-3.59811
H	-1.49428	2.823127	0.118099
H	3.391396	3.48553	2.478444
H	5.636852	2.289365	1.648351
H	6.892923	-1.96437	-1.2478
H	5.504319	-4.04065	-2.21525
H	0.498415	-5.6324	-1.55804
H	-1.78182	-4.56512	-0.65747
H	-3.04963	-3.00411	-2.14092
H	-5.41676	-3.70534	-2.0076
H	-6.74954	-3.22832	0.039427
H	-5.69018	-2.01194	1.948453
H	-3.31228	-1.387	1.83911
H	-0.87322	2.771725	3.25118
H	-1.56495	4.976878	4.131723
H	-0.44886	7.050878	3.32252
H	1.355556	6.891706	1.616587

H	2.040347	4.687526	0.733577
H	6.826347	-0.25474	2.177954
H	9.226427	0.338064	2.332463
H	10.40621	1.291263	0.359457
H	9.161671	1.64573	-1.76657
H	6.757962	1.059054	-1.91114
H	4.128582	-5.85752	-0.66992
H	4.633669	-8.02584	-1.75368
H	3.749376	-8.52158	-4.02654
H	2.357954	-6.82543	-5.20274
H	1.862919	-4.65554	-4.11607
C	-3.07494	0.921759	-0.98535
H	-3.18326	-0.00067	-1.55366
H	-2.82651	1.71489	-1.6977
C	-4.38698	1.240026	-0.25402
H	-5.1828	1.183041	-1.00851
H	-4.59538	0.450065	0.472696
C	-4.45591	2.605374	0.442565
H	-3.61105	2.722911	1.133141
H	-4.37261	3.411298	-0.30143
C	-5.75986	2.735681	1.24736
H	-6.61446	2.526432	0.593273
H	-5.77395	1.964928	2.027597
C	-5.90013	4.138407	1.83335
H	-4.94874	4.500696	2.232829
N	-6.89632	4.27747	2.991252
C	-6.3049	3.734598	4.271187
H	-5.36163	4.248607	4.461198
H	-7.00921	3.940018	5.078937
H	-6.16729	2.652412	4.1799
C	-8.18456	3.545346	2.700763
H	-8.54304	3.84494	1.714915
H	-7.99914	2.469087	2.753223
H	-8.91149	3.829239	3.463091
C	-7.18679	5.742208	3.173604
H	-6.24539	6.274583	3.317639
H	-7.69546	6.116686	2.284522
H	-7.82397	5.869322	4.049217
Br	-6.74879	0.134545	3.727439
H	0.600944	-0.72769	1.418602
Zn	1.898023	-0.60198	-0.7187
Cl	1.338104	0.639694	-2.61453
H	-6.2341	4.845193	1.068711

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