Supporting Information

1-Methyl-1,4-cyclohexadiene as a traceless reducing agent for the synthesis of catechols and hydroquinones

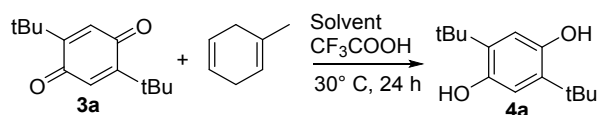*Andrea Baschieri,*, [a] Riccardo Amorati,*, [a] Luca Valgimigli [a] and Letizia Sambri [b]*

[a] Dipartimento di Chimica "Giacomo Ciamician", Università di Bologna, Via S. Giacomo 11, 40126 Bologna, Italy. E-mail: andrea.baschieri2@unibo.it (A.B.); riccardo.amorati@unibo.it (R.A.)

[b] Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy.

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Table S1: Representative results of the screening of solvents.[a]

Entry	Solvent	4a Conv.[b] [%]
1	Tetrahydrofuran	0
2	Acetonitrile	5
3	Dichloromethane	98
4	Methanol	1
5	Dimethyl sulfoxide	0
6	Hexane	92
7	Cyclohexane	94
8	Toluene	>99

[a]Reaction conditions: **1a** (0.09 mmol), 1-methyl-1,4-cyclohexadiene (3.6 mmol), trifluoroacetic acid (3.6 mmol), solvent (1.0 mL), 30 °C, 24 h. [b]Conversion was determined by ^{1}H NMR spectroscopy.

Table S2: Representative results of the screening of MeCHD equivalents on product conversion.[a]
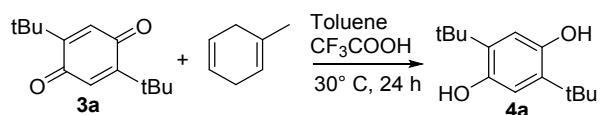
Entry	MeCHD (equiv)	4a Conv.[b] [%]
1	0	0
2	2	20
3	5	40
4	10	52
5	20	85
6	30	>99
7	40	>99

[a]Reaction conditions: **1a** (0.09 mmol), trifluoroacetic acid (3.6 mmol), solvent (1.0 mL), 30 °C, 24 h. [b]Conversion was determined by ^{1}H NMR spectroscopy.

Table S3: MeCHD conversion to toluene in absence or presence of quinone **1a**.[a]

Entry	Time (h)	**1a**	**2a** Conv.[b] [%]	Toluene:MeCHD[c] [%]
1	0	no	/	2.47
2	1	no	/	2.29
3	2.5	no	/	2.50
4	5.5	no	/	2.64
5	7	no	/	2.81
6	24	no	/	3.03
7	0	yes	0	2.83
8	1	yes	42	4.33
9	2.5	yes	78	5.42
10	5.5	yes	100	6.03
11	7	yes	100	5.65
12	24	yes	100	6.53

[a]Reaction conditions: Experiment performed in a NMR tube: **1a** (0.045 mmol), CD$_2$Cl$_2$ (0.75 mL), MeCHD (1.35 mmol), 30 °C. [b]Conversion was determined by ^{1}H NMR spectroscopy, [c] ^{1}H NMR signal: 2.38 ppm for Toluene, 1.70 ppm for MeCHD.

Table S4: Conversion of the *para*-quinone **3a** to the hydroquinone **4a** in the presence of the *ortho*-quinone **1a**.[a]

Entry	MeCHD (equiv)	**1a:3a**	**2a** Conv.[b] [%]	**4a** Conv.[b] [%]
1	30	0:100	/	< 0.5
2	30	10:90	>99	< 1
3	30	50:50	>99	4.5
4	0	50:50	< 0.5	< 0.5
5[c]	0	50:50	>99	< 0.5

[a]Reaction conditions: **1a**+**3a** (0.18 mmol), Toluene (2.0 mL), 30 °C, 24 h. [b]Conversion was determined by ^{1}H NMR spectroscopy, [c] **2a** was used instead of **1a**.

Table S5: Oxygen effect on the reduction reaction of **1a** and **3a**.[a]
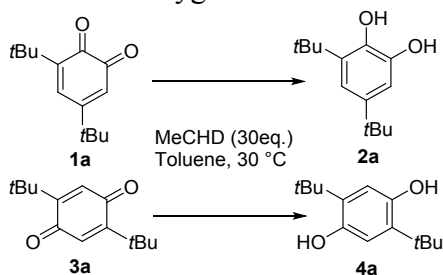
Entry	Comp.	Prod.	t [h]	TFA [equiv]	Conv.[b] [%]
1	**1a**	**2a**	1	/	55
2	**1a**	**2a**	1	/	71[c]
3	**3a**	**4a**	5	40	45
4	**3a**	**4a**	5	40	62[c]

[a]Reaction conditions: **1a** or **3a** (0.18 mmol), 1-methyl-1,4-cyclohexadiene (5.4 mmol), toluene (2.0 mL), 30 °C. [b]Conversion was determined by ^{1}H NMR spectroscopy, [c]Experiment performed under nitrogen atmosphere.
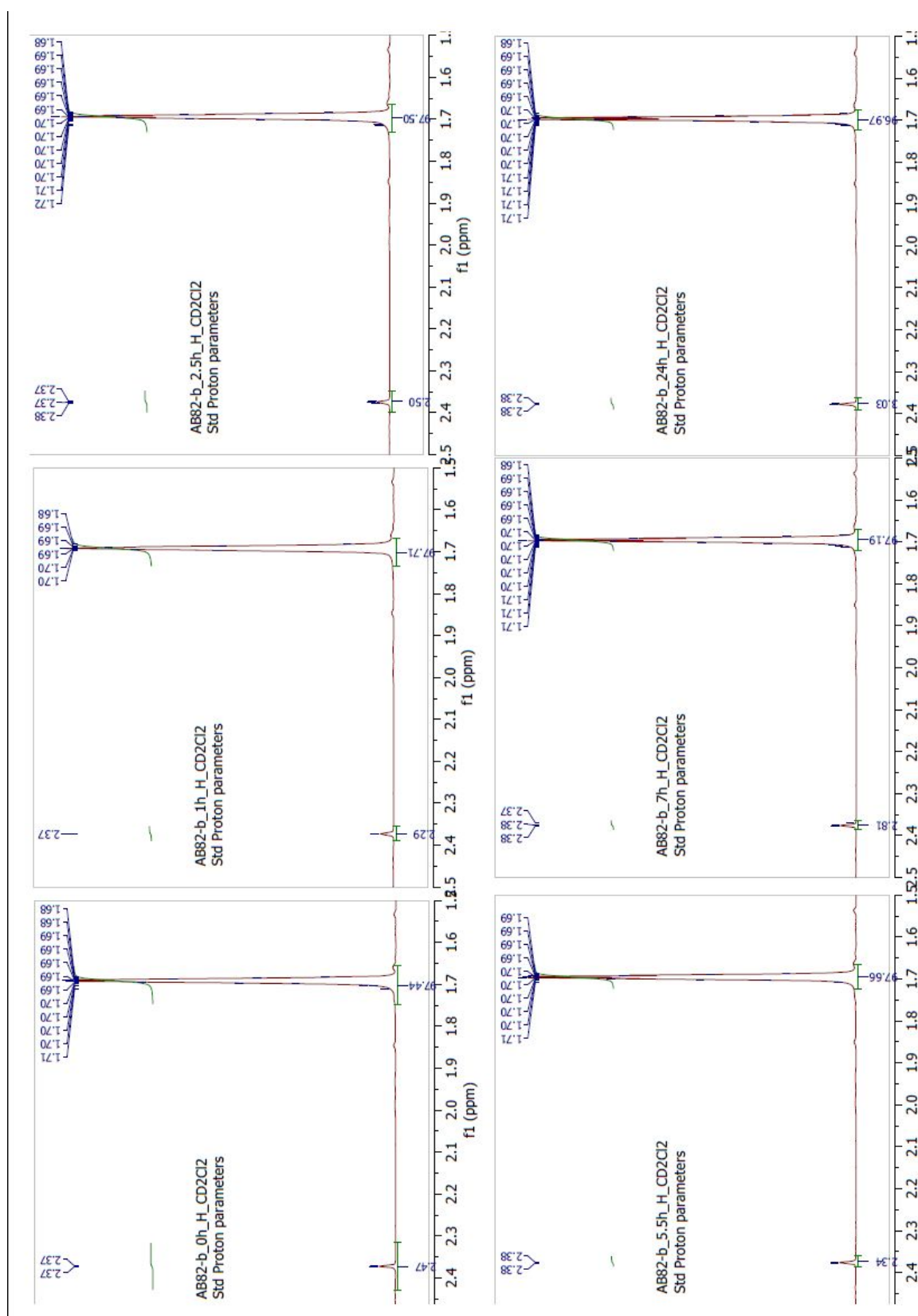
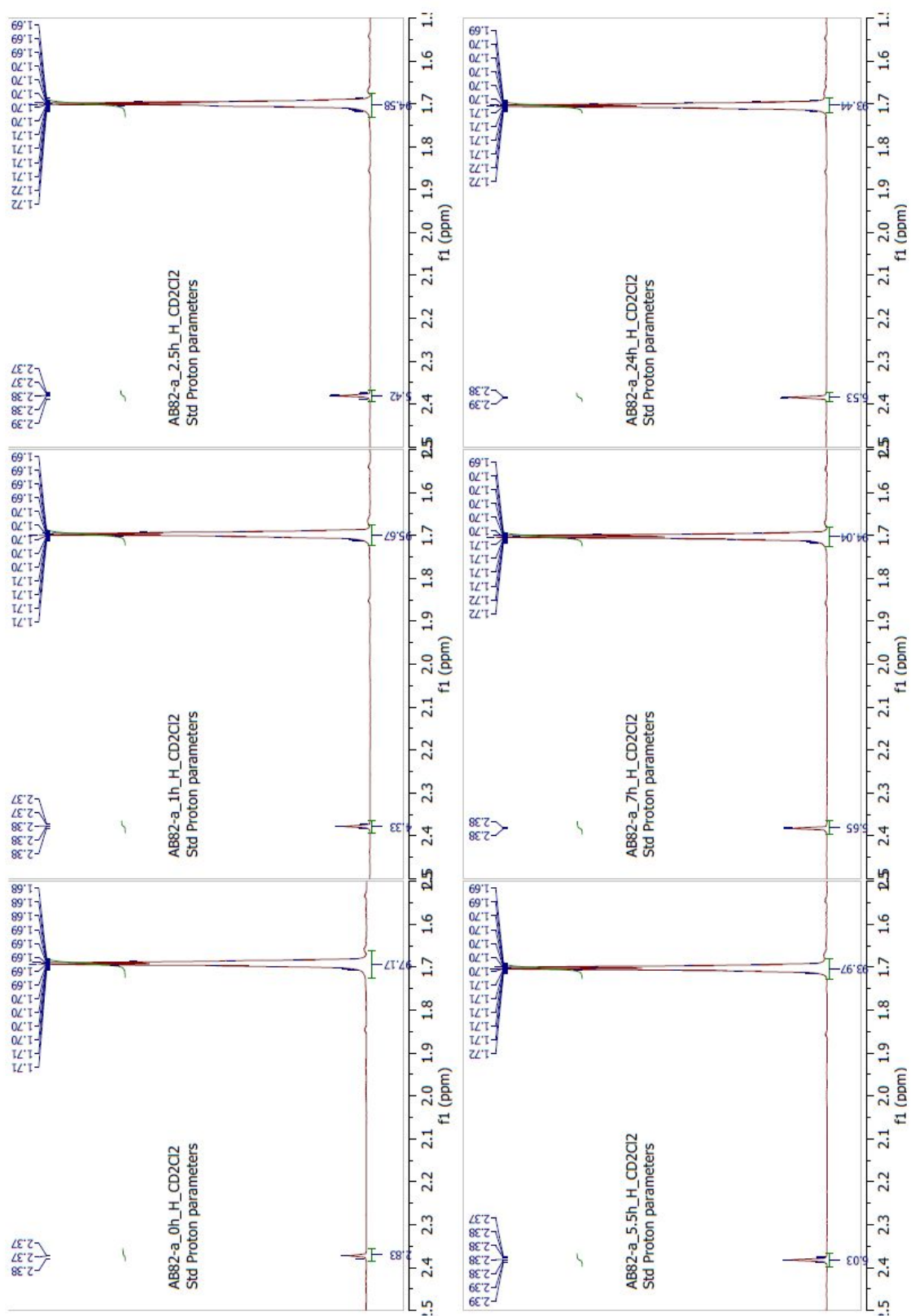Figure S1. MeCHD conversion to toluene in absence of quinone **1a**.

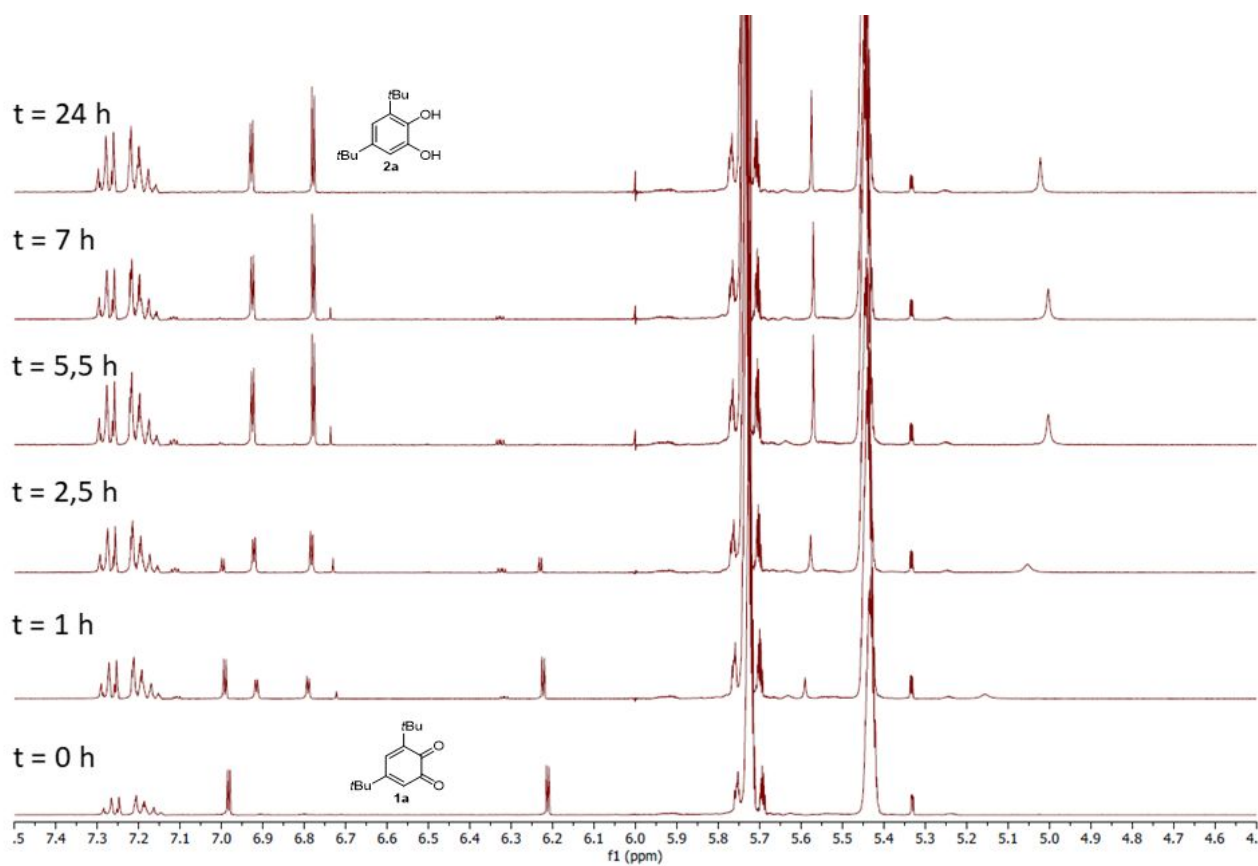Figure S2. MeCHD conversion to toluene in presence of quinone **1a**.

Figure S3. Conversion of compound **1a** to catechol **2a** in a NMR tube after 24 h. Experiment performed in CD₂Cl₂ as solvent.
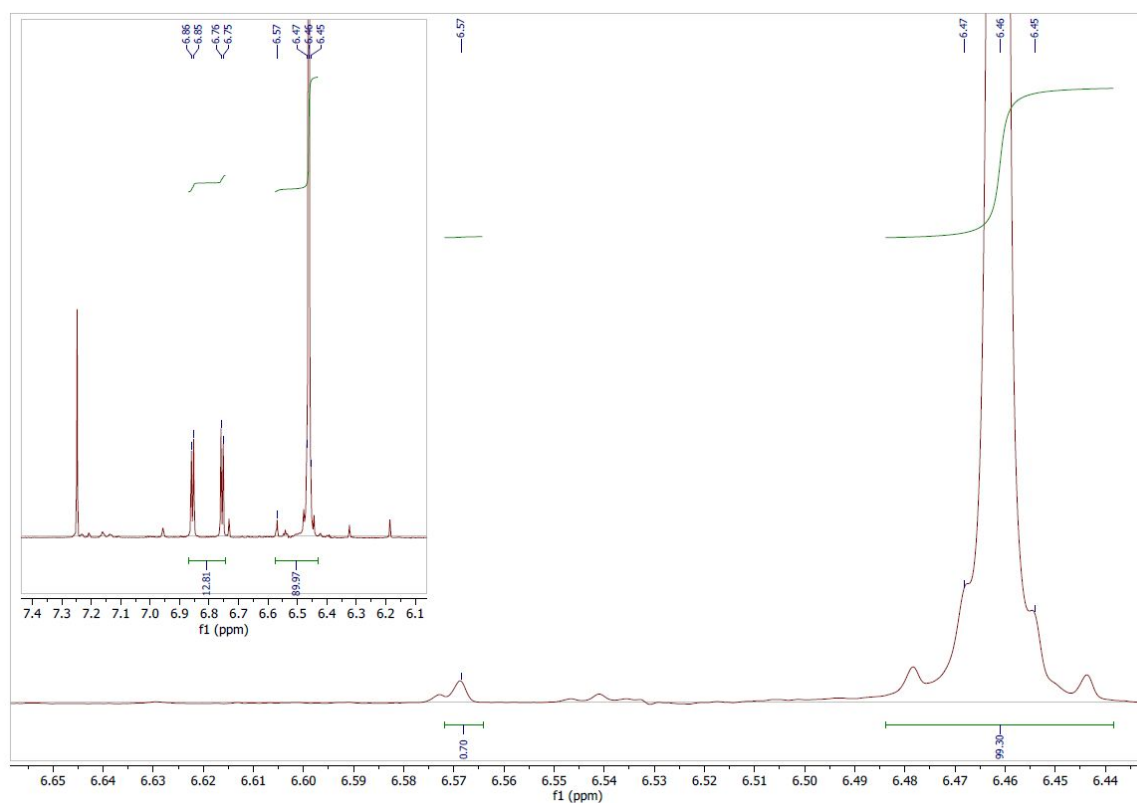
Figure S4. Conversion of compound **3a** (6.46 ppm) to hydroquinone **4a** (6.57 ppm) in the presence of 10% of **1a** (6.86 – 6.75ppm).
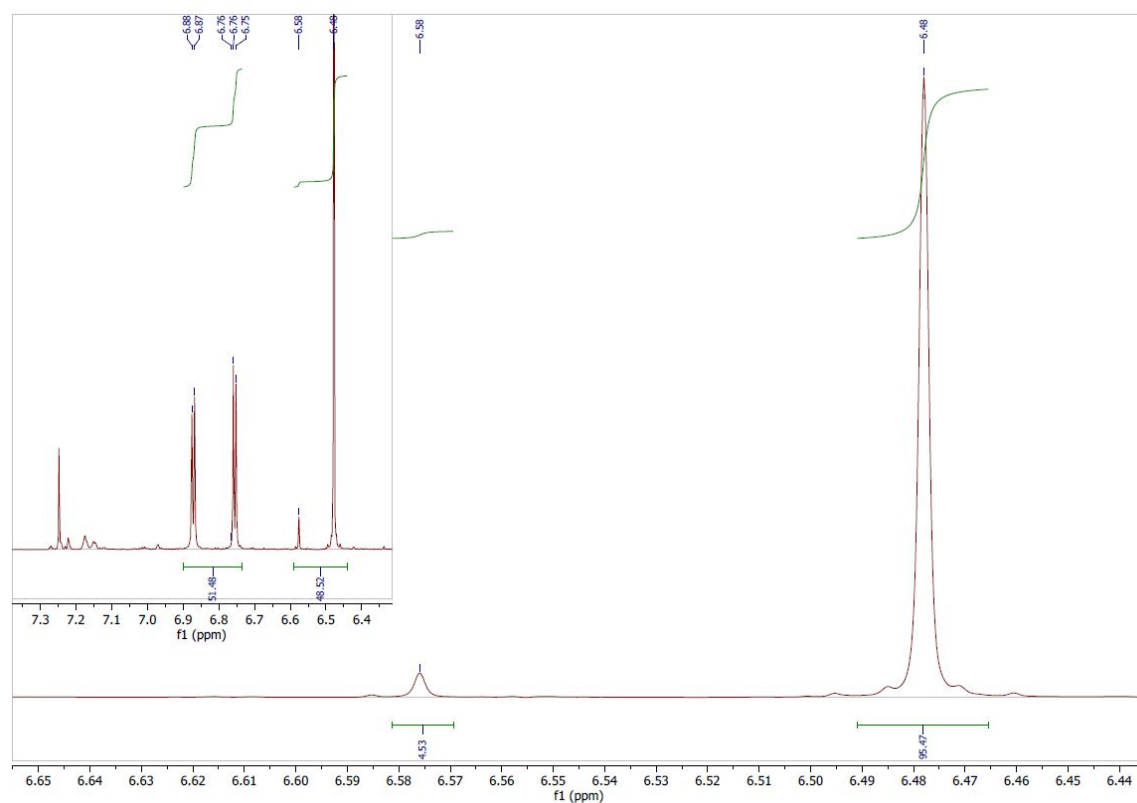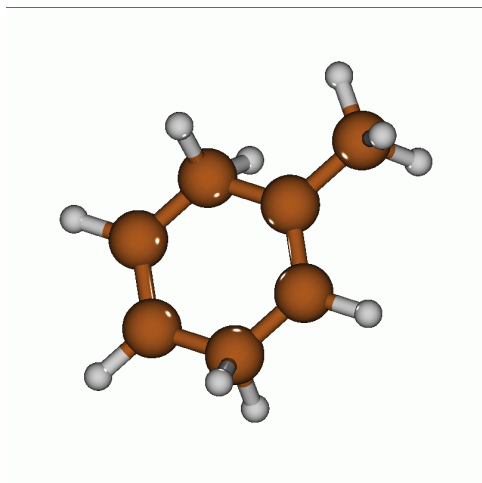

Figure S5. Conversion of compound **3a** (6.48 ppm) to hydroquinone **4a** (6.58 ppm) in the presence of 50% of **1a** (6.88 – 6.75ppm).

Calculation results

MeCHD

CBS-QB3 Enthalpy= -272.164977 CBS-QB3 Free Energy= -272.203348

No imaginary frequencies

C,0,-0.0787811878,-0.1034861486,-0.0869357301\C,0,-0.0063476486,-0.0996329964,1.4156458034\C,0,1.1244187133,-0.008416848,2.1180414246\C,0,2.4722387743,0.1023808941,1.4430178477\C,0,2.4060505779,0.0991201444,-0.059412642\C,0,1.2687917812,0.0073509239,-0.7431904888\H,0,-0.9527207987,-0.177520367,1.946139765\C,0,1.1429134471,-0.0089634765,3.6229323731\H,0,2.9799877723,1.0153349738,1.7910398294\H,0,3.3503316389,0.1768935316,-0.5916762037\H,0,1.2905815645,0.0106882465,-1.8295570985\H,0,-0.5860846852,-1.0166256926,-0.4335352926\H,0,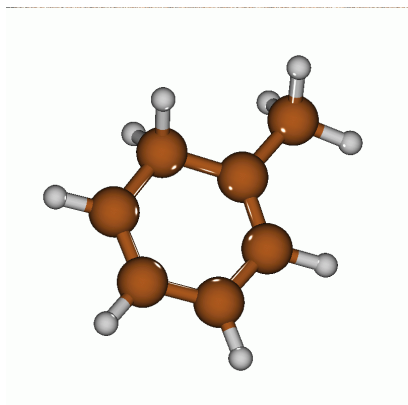-0.7274677817,0.7162783117,-0.4311740461\H,0,3.1211872618,-0.7172893946,1.7885891941\H,0,1.7417079374,-0.842553157,4.0093427103\H,0,1.5986789371,0.9096557946,4.0117265248\H,0,0.1367698011,-0.0916527348,4.0387737128

MeCHD alkyl radical

(most stable isomer)

CBS-QB3 Enthalpy= -271.549665 CBS-QB3 Free Energy= -271.588237

(More stable of 1.23 kcal/mol than the isomer on C6)

No imaginary frequencies

C,0,-0.0046266383,0.0000025732,0.0515359345

\C,0,0.0860672715,0.0000754893,1.4647901112\C,0,1.3575553274,-0.000024

7762,2.0890826192\C,0,2.5227396356,-0.0001434669,1.3753942072\C,0,2.49

23356129,-0.0002157599,-0.1322979838\C,0,1.1141062368,-0.0001235438,-0

.726106327\C,0,3.8739575416,-0.0001879839,2.024533029\H,0,1.4064208173

,0.0000273718,3.1746221411\H,0,3.066663178,0.8657233046,-0.5103970728\

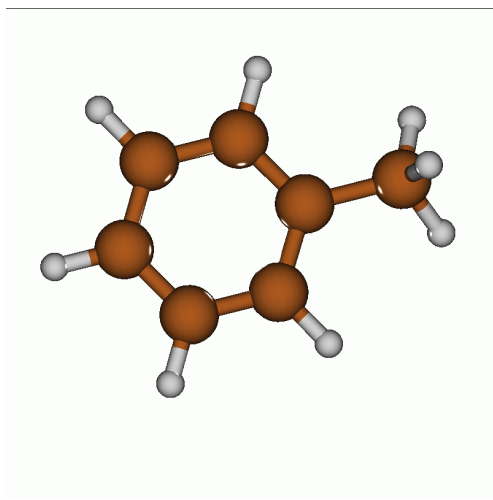H,0,1.0320187869,-0.0001688812,-1.8079254068\H,0,-0.9838283557,0.00004

35382,-0.4168421167\H,0,-0.8121460019,0.0001563297,2.0694542785\H,0,3.

0665045464,-0.8663056125,-0.5102938156\H,0,4.4591154673,-0.8787481071,

1.7231470544\H,0,4.4591323923,0.8783900949,1.7232250611\H,0,3.79931563

14,-0.0002311139,3.1138140185

Toluene

CBS-QB3 Enthalpy= -271.013230

CBS-QB3 Free Energy= -271.051271

No imaginary frequencies

C,0,0.0116868395,0.0151036436,0.0067474\C,0,
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042070711\C,0,2.448674194,-0.0098325615,1.4137427051\C,0,2.4416489389,
-0.0024410963,0.0206458743\C,0,1.2340099208,0.0109529665,-0.6733178602
\H,0,-0.9036463588,0.0204962946,1.9526532351\H,0,1.232142791,-0.002952
7708,3.1887678658\H,0,3.3875853037,-0.0169410219,1.955823287\H,0,3.377
6253741,-0.0029527708,-0.5273169748\H,0,1.239224127,0.0204962946,-1.75
89073203\C,0,-1.2958460554,-0.0024272324,-0.7481570689\H,0,-1.20437467
44,0.4957132395,-1.7162711785\H,0,-1.6265280909,-1.0294400949,-0.93907
64312\H,0,-2.0885217776,0.4957132395,-0.1848834744

3,5-di-methylcatechol
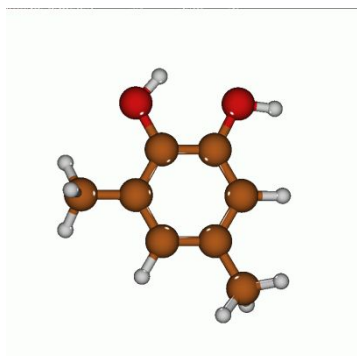
CBS-QB3 Enthalpy=   -460.541498

CBS-QB3 Free Energy=   -460.589309

No imaginary frequencies

C,0,0.0357424462,-0.0007135469,0.0294106757\C,0,0.0000848981,-0.0240101374,1.4229008737\C,0,1.2166429977,-0.0249595392,2.1168751133\C,0,2.4165577942,-0.0031618179,1.4219443149\C,0,2.4347425336,0.0200850512,0.0217558578\C,0,1.2365255672,0.0215105585,-0.690510451\O,0,3.6605279045,-0.0022473292,2.0177256861\O,0,3.6233290097,0.0414690829,-0.654110749\C,0,1.2696605153,0.046622788,-2.1961593274\H,0,-0.8979304371,0.0003720112,-0.5240226318\C,0,-1.3089384995,-0.0477278072,2.1762035349\H,0,1.2273464979,-0.0427976935,3.2039837626\H,0,3.5638962958,-0.0189942545,2.9743536454\H,0,4.3312899358,0.0368218257,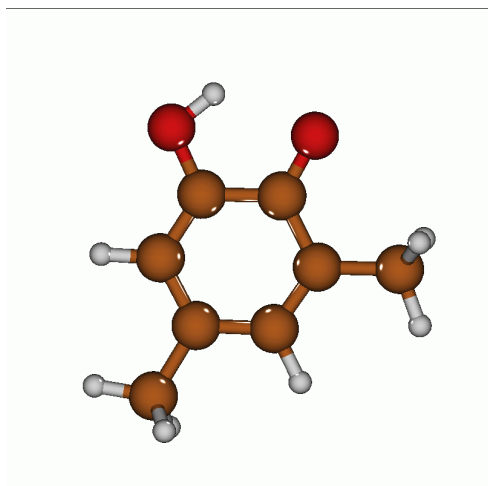0.0024980877\H,0,0.2592652377,0.0449689714,-2.6085913725\H,0,1.7927266818,0.9341789182,-2.5645293457\H,0,1.8073866102,-0.8194387459,-2.59345892\H,0,-2.1574977544,-0.0434720409,1.489411885\H,0,-1.394786354,-0.9405089869,2.8041627735\H,0,-1.4097607291,0.8220026927,2.8335926034

Phenoxyl radical from 3,5-di-methylcatechol (most stable isomer)

CBS-QB3 Enthalpy=   -459.923251   CBS-QB3 Free Energy=   -459.969991

No imaginary frequencies

C,0,0.0538210097,-0.052448066,0.020694

4563\C,0,0.0394835135,-0.0118546049,1.4454996965\C,0,1.2397188459,0.06

070454,2.1533254866\C,0,2.4353138713,0.0923562347,1.4543160451\C,0,2.4

760968851,0.051828271,-0.0073688345\C,0,1.2129373983,-0.0234209015,-0.

7143542369\O,0,3.6212534048,0.1613617298,2.0604752924\O,0,3.6018082898

,0.084715193,-0.5589484708\C,0,1.2468786871,-0.0652839647,-2.212895231

4\H,0,-0.899013324,-0.1087833317,-0.4976807677\C,0,-1.2799536632,-0.04

82871869,2.1665149996\H,0,1.2524811487,0.0926048151,3.2364046091\H,0,4

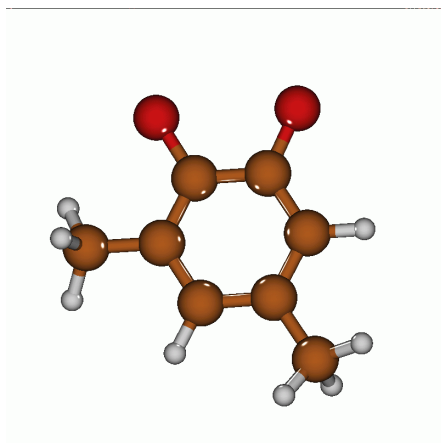.26827428,0.1681373074,1.3236119087\H,0,0.2408552873,-0.1210685192,-2.

6318785395\H,0,1.7479245906,0.8207513756,-2.6137361051\H,0,1.823776382

3,-0.9262340712,-2.5632199959\H,0,-1.9107459942,0.7963526075,1.8696492

312\H,0,-1.834233088,-0.9603604504,1.9208570286\H,0,-1.1496107779,-0.0

110709776,3.2487847848

3,5-di-methyl orthoquinone

CBS-QB3 Enthalpy=   -459.313646

CBS-QB3 Free Energy=   -459.359148

No imaginary frequencies

C,0,0.0837404273,-0.0506020499,0.01827677

92\C,0,0.0689041716,-0.0031520019,1.4876064743\C,0,1.2190932724,0.0826

436149,2.1901863369\C,0,2.5184294117,0.131131807,1.5184591101\C,0,2.51

63979144,0.0789443271,-0.04305997\C,0,1.2024445623,-0.0146183386,-0.73

32595615\O,0,3.5758472081,0.2084469521,2.1075775543\O,0,3.564333646,0.

1150076883,-0.6487101389\C,0,1.2151286095,-0.062946311,-2.2309791128\H

,0,-0.8824681598,-0.1191292393,-0.474948336\C,0,-1.2766356302,-0.05460

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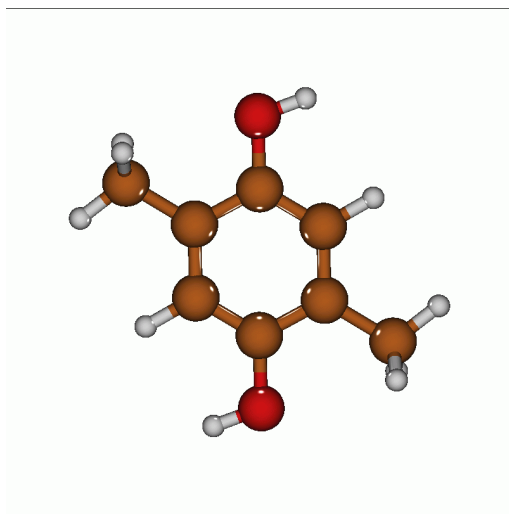
72733,-0.1310352507,-2.6352321197\H,0,1.7026423009,0.8262761448,-2.640

7073859\H,0,1.797418664,-0.9189835732,-2.5836314608\H,0,-1.902858352,0

.7809591358,1.8224526881\H,0,-1.8066112978,-0.9738248697,1.8811897574\

H,0,-1.1910734764,-0.0135850964,3.2397391219

2,5MeQH2

CBS-QB3 Enthalpy=   -460.539744

CBS-QB3 Free Energy=   -460.586115

No imaginary frequencies

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63\C,0,-0.0224297309,0.0000138424,1.4136457703\C,0,1.2118909102,-0.000
0057473,2.0642486853\C,0,2.4149377868,-0.0000218601,1.3603284457\C,0,2
.4204562911,-0.000010177,-0.0387918967\C,0,1.1859246506,0.0000146992,-
0.6895646918\C,0,-1.3258054415,0.0000203451,2.1678447156\O,0,3.6375765
238,-0.0000329792,1.990468449\O,0,-1.2397208551,0.0000389311,-0.615653
5187\H,0,1.2315150557,-0.0000031829,3.1514793297\C,0,3.7233426568,-0.0
000225882,-0.793173988\H,0,1.1668226538,0.0000227693,-1.7768292829\H,0
,-1.1008488141,0.0000738325,-1.5676658302\H,0,3.4985389648,-0.00018693
64,2.9424345386\H,0,-1.928895973,0.8766978808,1.9136096736\H,0,-1.9287
928441,-0.8767886455,1.913809474\H,0,-1.1552739069,0.0001486424,3.2460
964559\H,0,3.5524978853,-0.0000258559,-1.8715010245\H,0,4.3265271036,0
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Radical from 2,5-dimethyl-hydroquinone
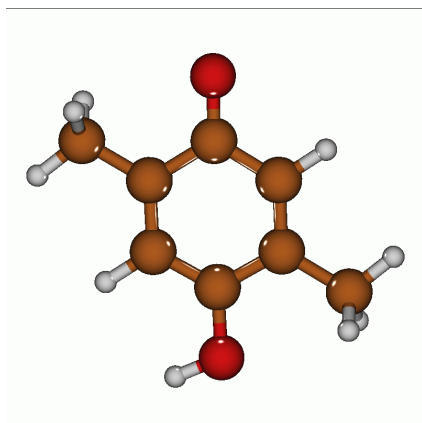
CBS-QB3 Enthalpy=   -459.913793

CBS-QB3 Free Energy=   -459.960006

No imaginary frequencies

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0000166954,2.0839574341\C,0,2.4002059716,-0.0000307986,1.3541919876\C,
0,2.415371561,-0.0000165795,-0.0678720668\C,0,1.2042488972,0.000012989
3,-0.7102106184\C,0,-1.3263112439,0.0000159136,2.1951365166\O,0,3.6075
243592,-0.0000582623,1.9725161048\O,0,-1.1542833704,0.0000581839,-0.62
5824652\H,0,1.2468784996,-0.0000282866,3.1710142417\C,0,3.7323777667,-
0.0000330673,-0.7980520646\H,0,1.1494165843,0.0000253718,-1.7932073638
\H,0,3.4830362819,-0.0000732097,2.928412326\H,0,-1.9249538338,0.872920
2058,1.9196506553\H,0,-1.9248727812,-0.872994841,1.9198032107\H,0,-1.1
736057746,0.0001098366,3.2760155213\H,0,3.572801059,-0.0000286224,-1.8
768050302\H,0,4.329389412,0.8775668728,-0.5343052085\H,0,4.3293655753,
-0.8776499609,-0.5343082356

2,5-dimethyl-para benzoquinone
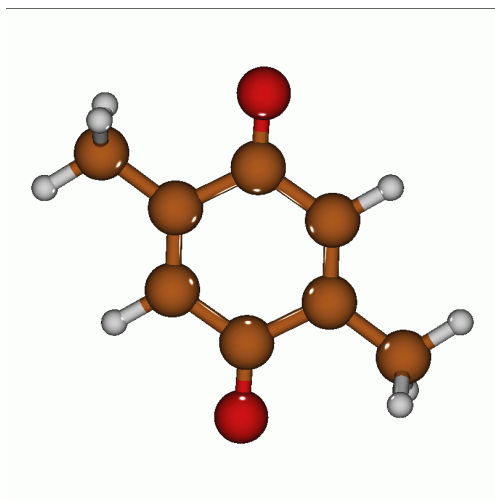
CBS-QB3 Enthalpy=   -459.328177

CBS-QB3 Free Energy=   -459.373569

No imaginary frequencies

C,0,-0.0594448586,0.0000059266,-0.00564302
54\C,0,-0.0239823974,0.0000208585,1.4943871112\C,0,1.1683244096,0.0000
178304,2.1127202737\C,0,2.4537125254,-0.0000061674,1.381924252\C,0,2.4
182192156,-0.0000079059,-0.1180232195\C,0,1.2259210918,-0.0000039976,-
0.7364474763\C,0,-1.3426754495,0.0000256135,2.2028462748\O,0,3.5169351
589,0.0000052115,1.9804793927\O,0,-1.1225923423,0.0000132214,-0.604130
1024\H,0,1.2576904895,0.0000296544,3.1942755578\C,0,3.736896581,-0.000
0167052,-0.8265364789\H,0,1.1365703918,-0.0000100879,-1.8179958997\H,0
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74182,-0.0000230691,-1.9088403367\H,0,4.3267903971,0.8740345188,-0.537
195107\H,0,4.3267845068,-0.8740680616,-0.537183786

O-protonated 2,5-dimethyl-para benzoquinone

cbs-qb3 geom=check scrf=(solvent=toluene)
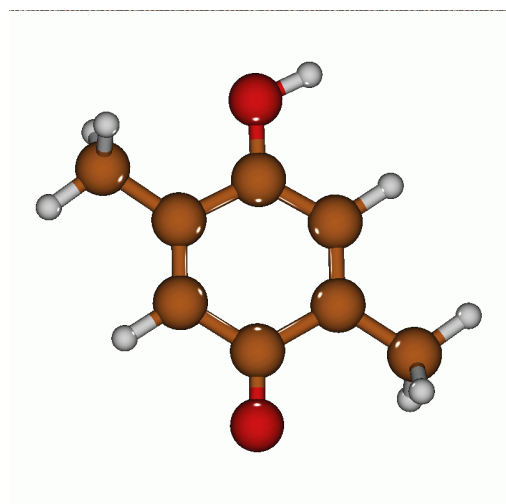
CBS-QB3 Enthalpy= -459.686027

CBS-QB3 Free Energy= -459.732043

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0,-0.03455444,0.0000159205,1.5047341727\C,0,1.1756051843,-0.0000044993
,2.1166718542\C,0,2.3784644145,-0.0000215846,1.3481747801\C,0,2.420253
8016,-0.0000163338,-0.1129730139\C,0,1.2281847264,0.0000077291,-0.7428
925661\C,0,-1.3314610124,0.000012467,2.2184788841\O,0,3.5371150142,-0.
0000486382,1.92963604\O,0,-1.1182847191,0.0000501673,-0.6021245158\H,0
,1.2613910705,-0.0000111026,3.1978200386\C,0,3.749151736,-0.0000384578
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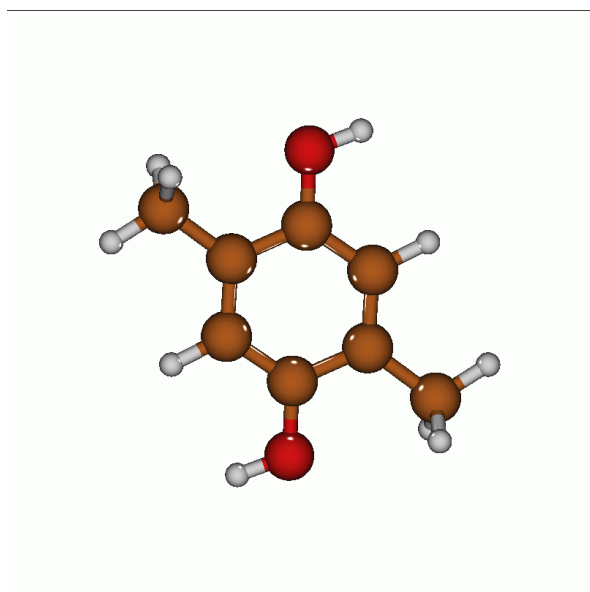
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2,5MeQH2 (in toluene)

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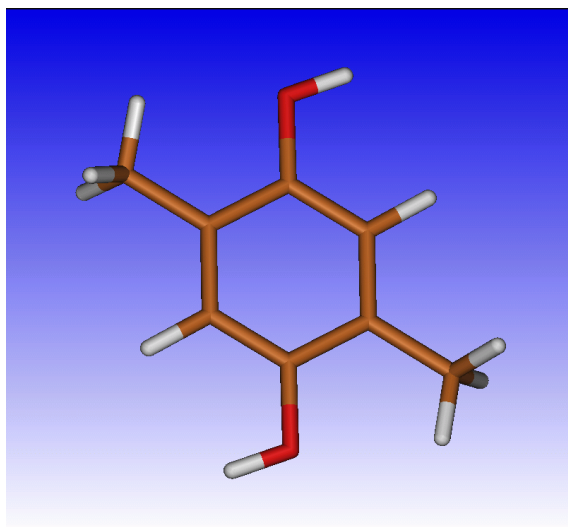
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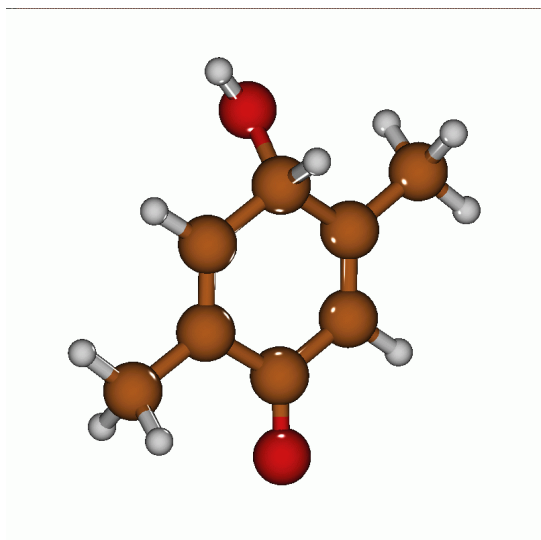
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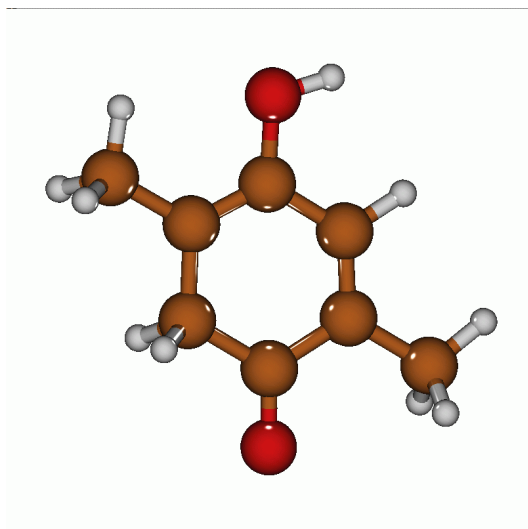
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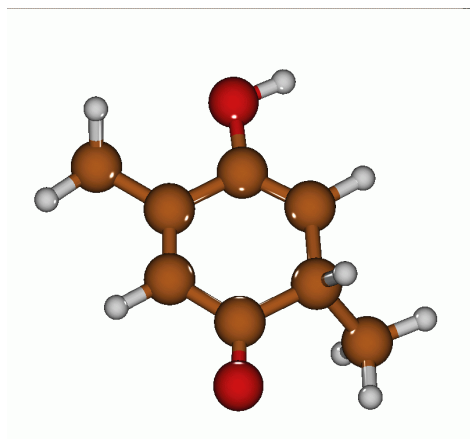
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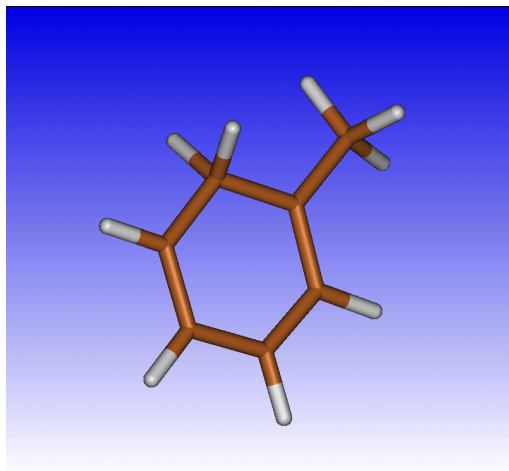
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MeCHD

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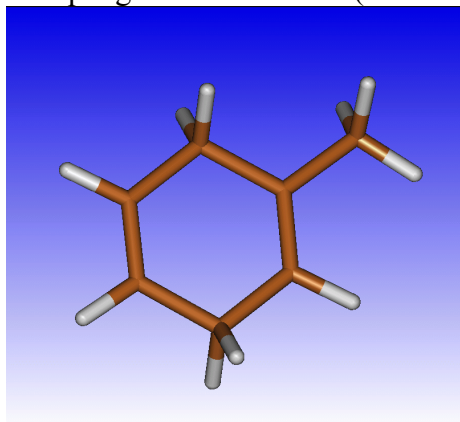
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H
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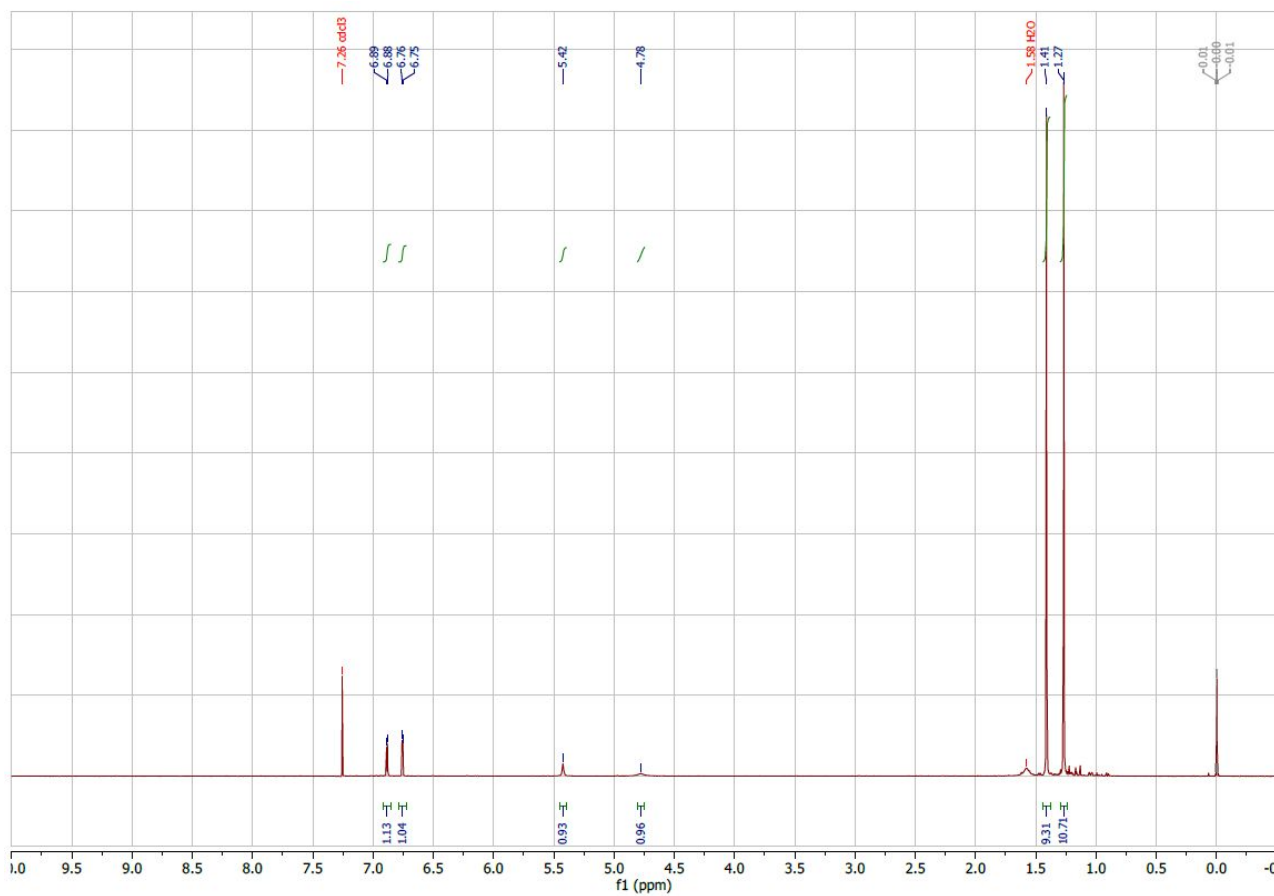
Figure S6. ^{1}H NMR spectrum of compound **2a**.
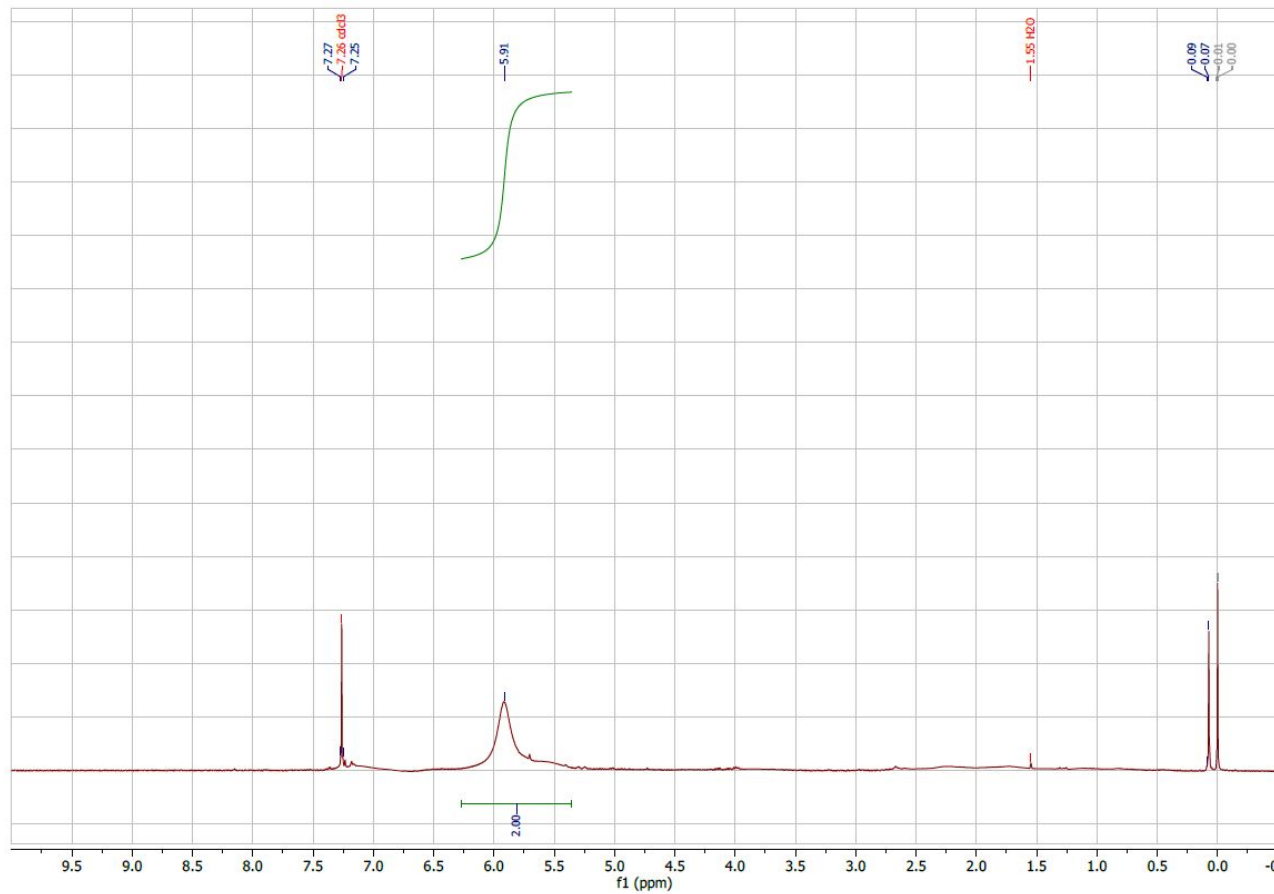
Figure S7. ^{1}H NMR spectrum of compound **2b**
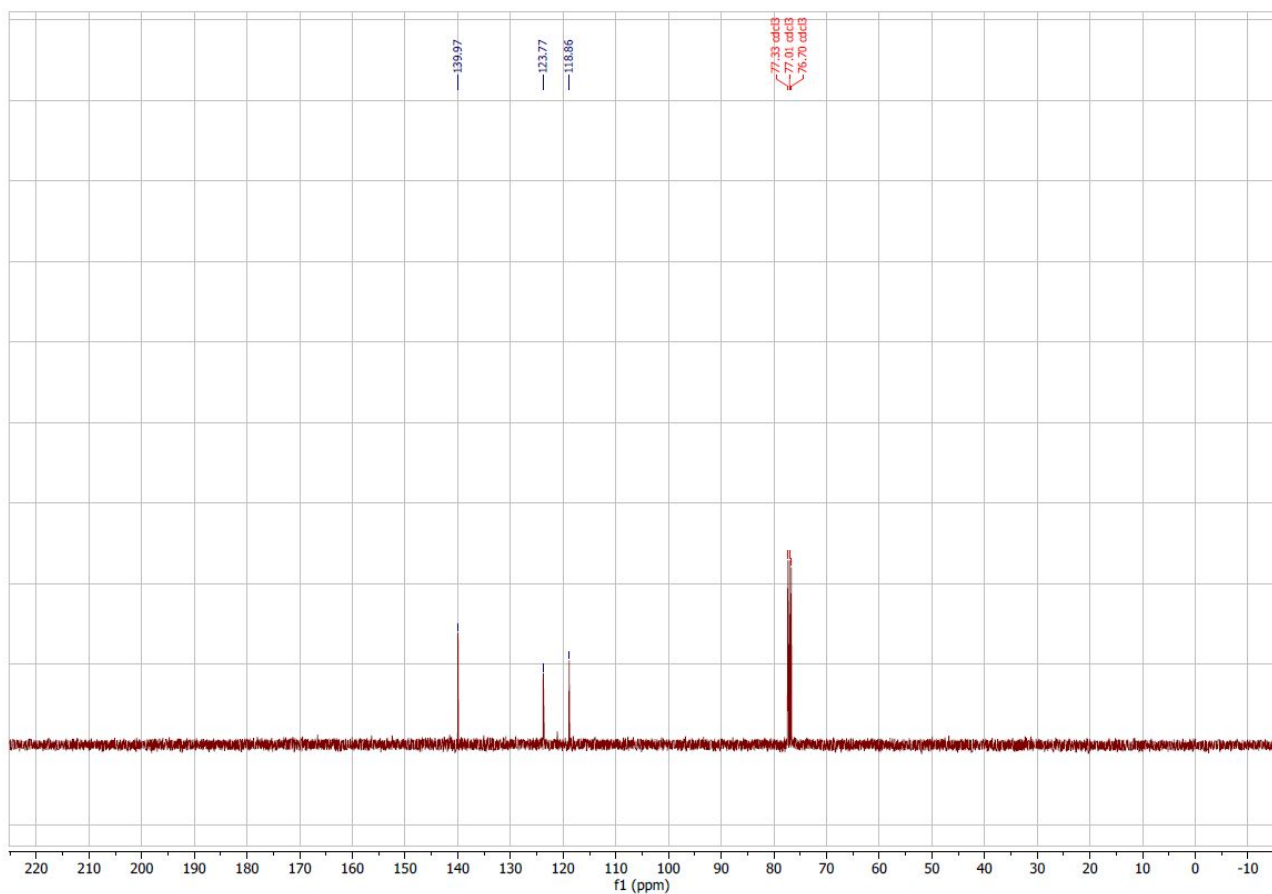
Figure S8. $^{13}C\{^1H\}$ NMR spectrum of compound **2b**.
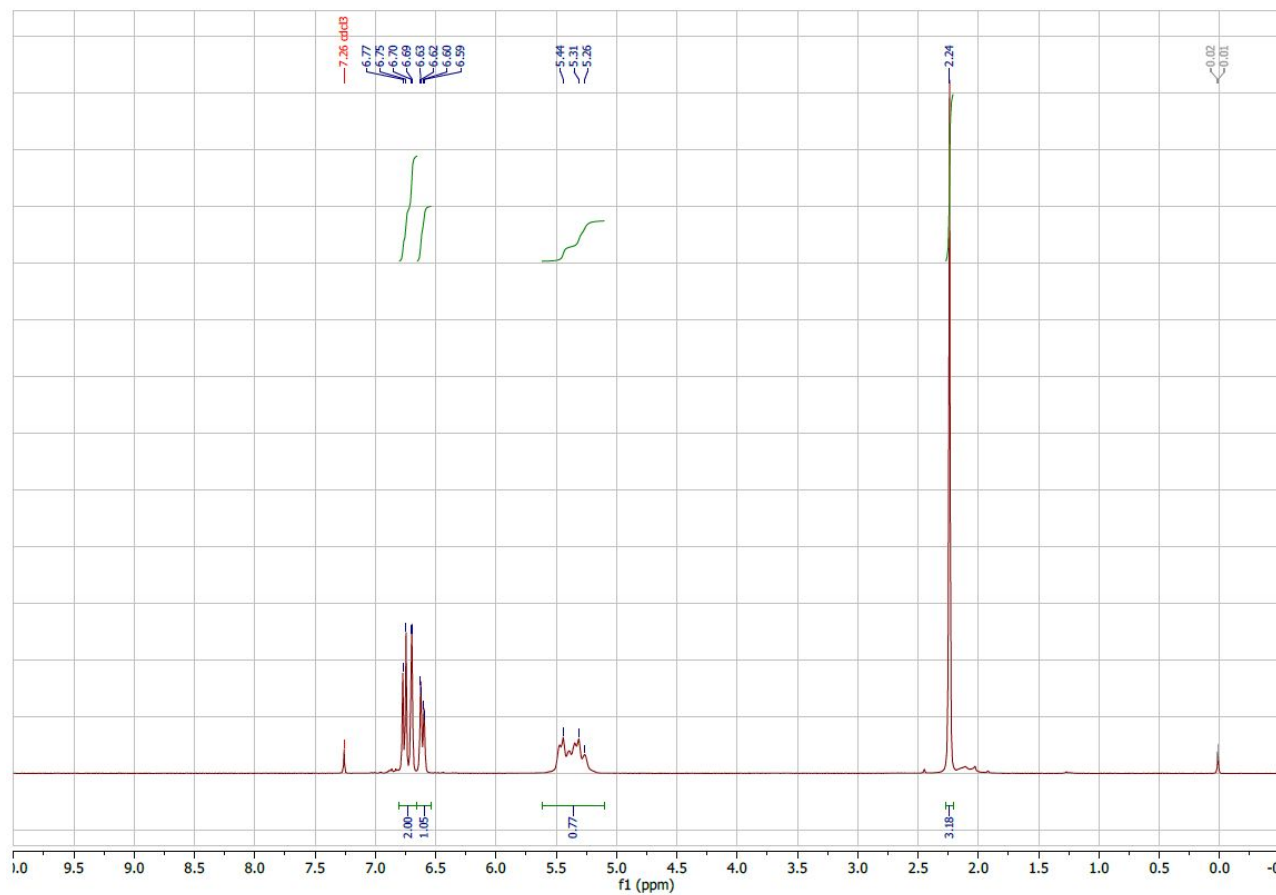
Figure S9. ^1H NMR spectrum of compound **2c**.

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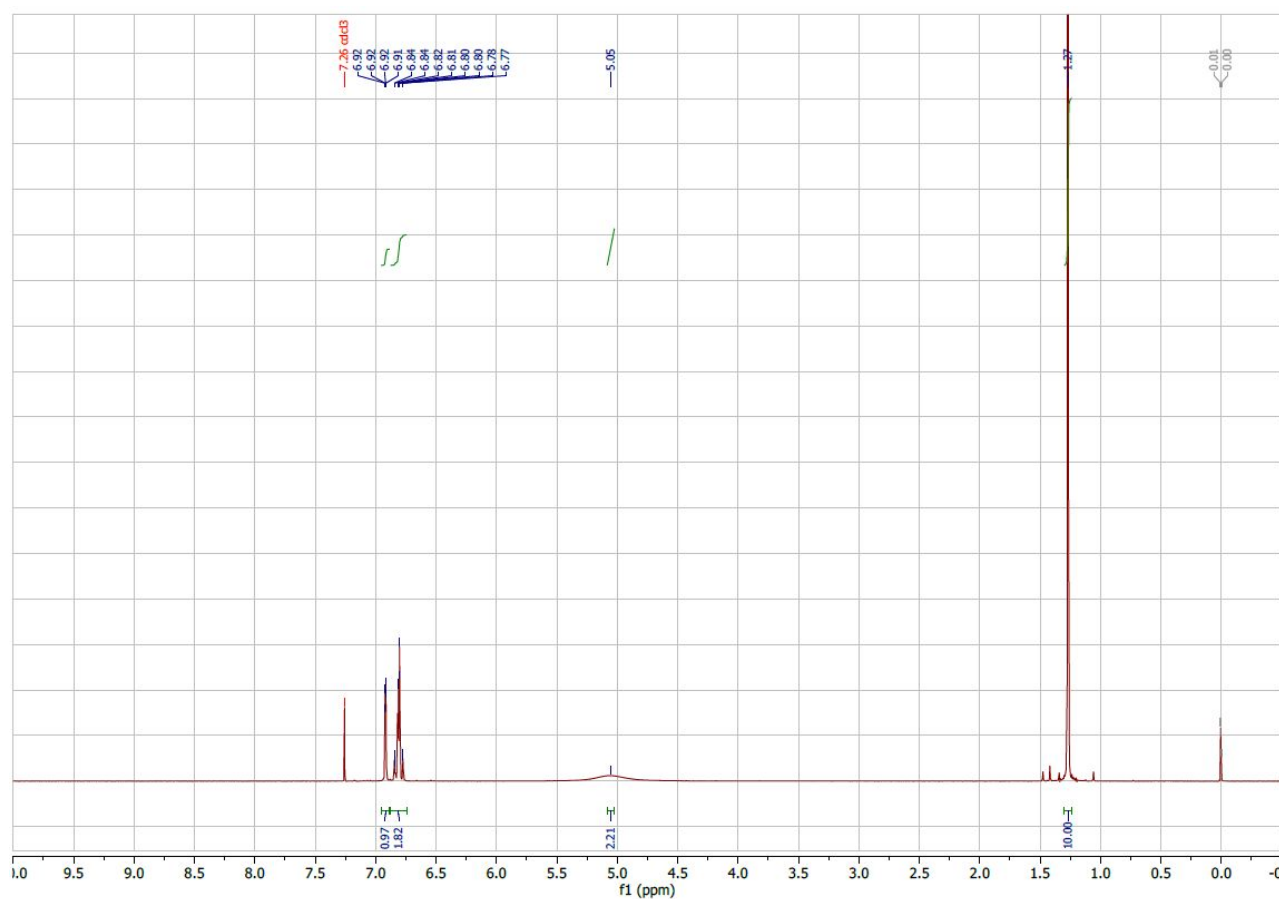
Figure S10. ^{1}H NMR spectrum of compound **2d**.
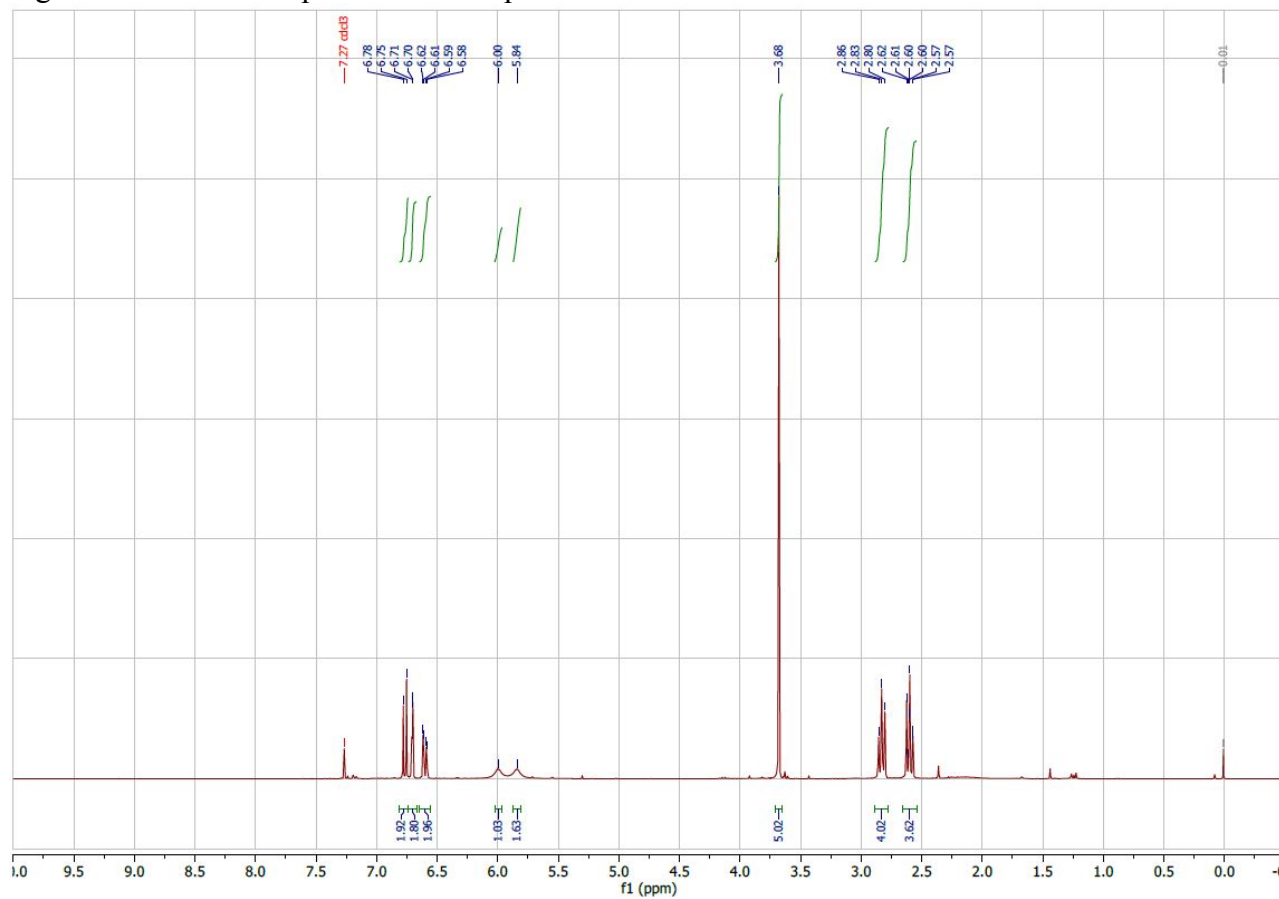
Figure S11. ^{1}H NMR spectrum of compound **2e**.
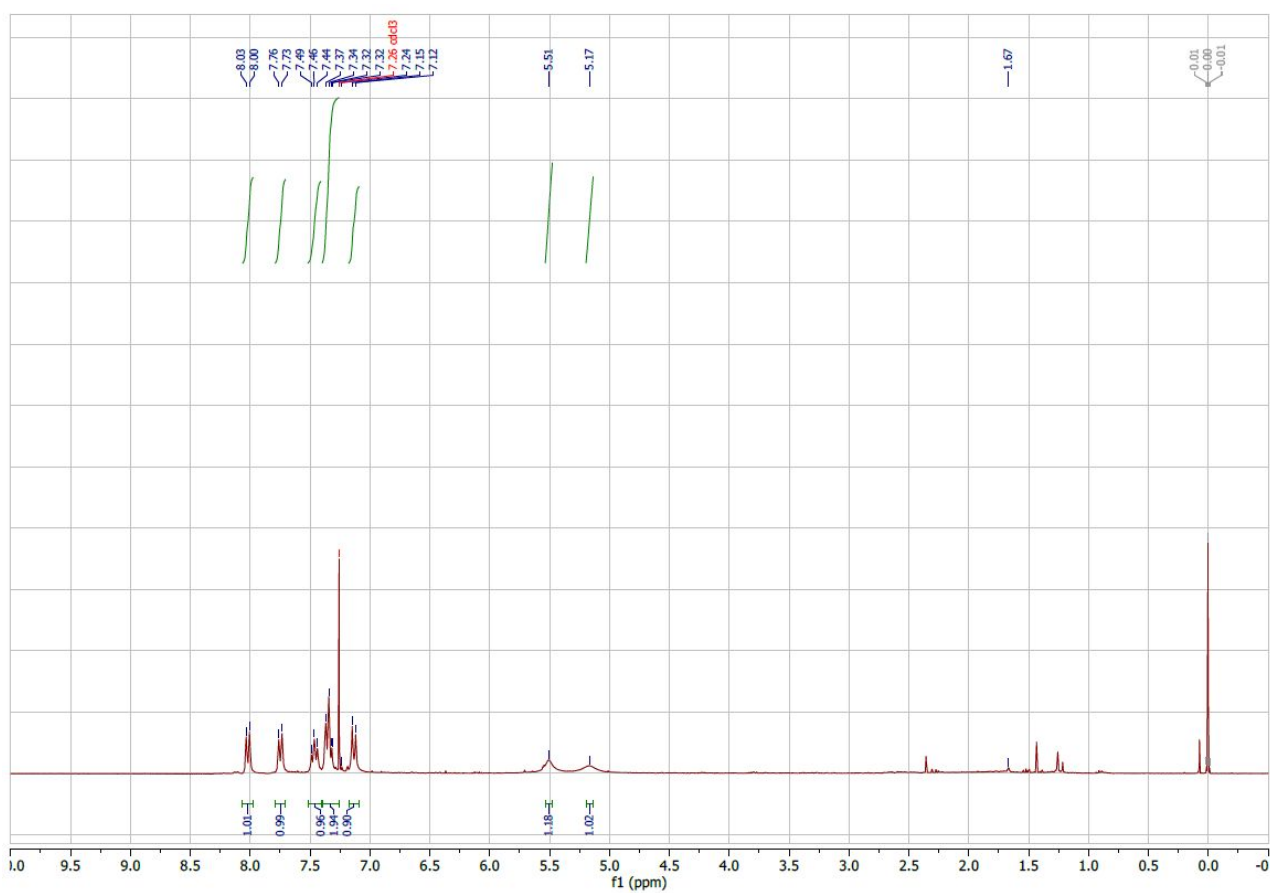
Figure S12. ^{1}H NMR spectrum of compound **2f**.
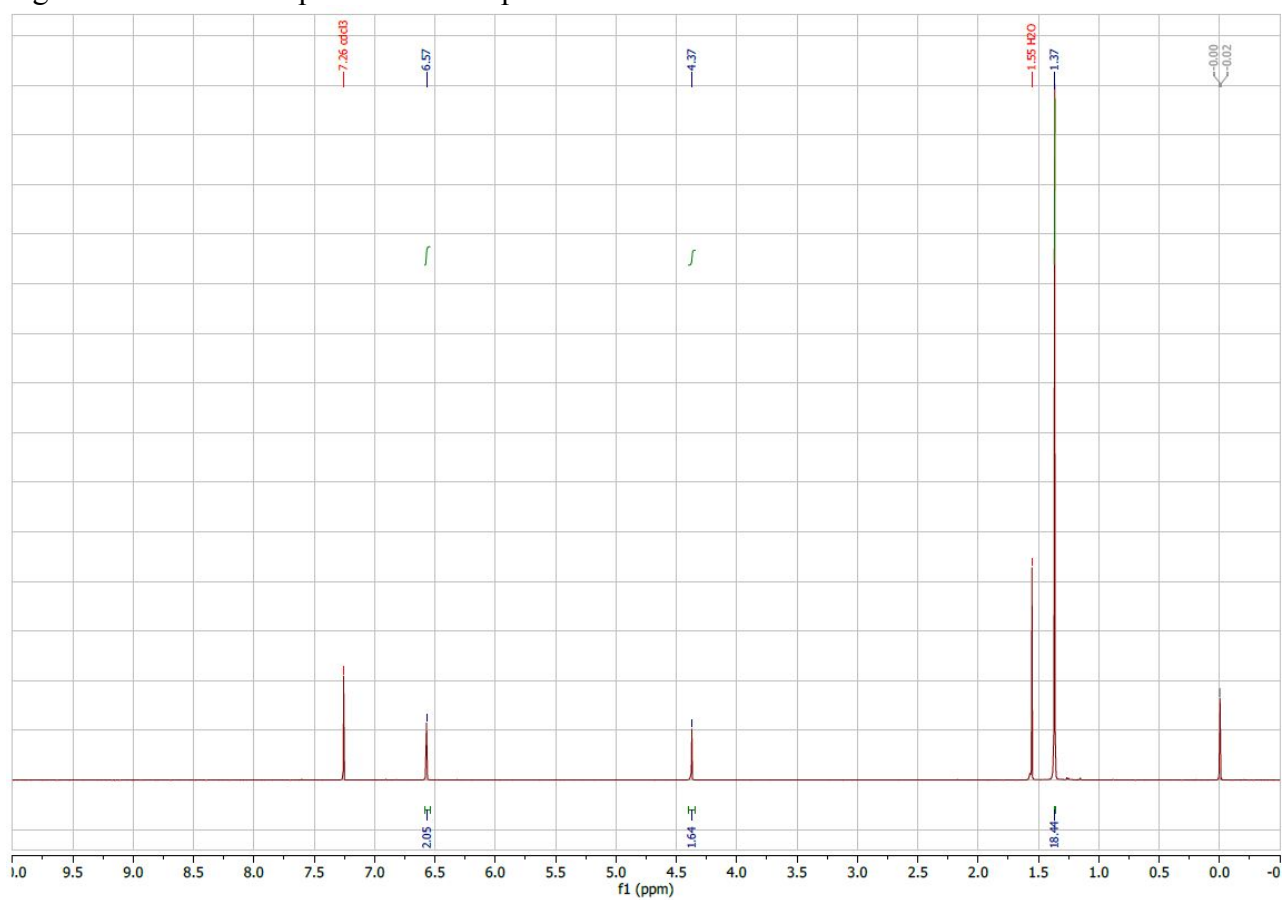
Figure S13. ^{1}H NMR spectrum of compound **4a**.
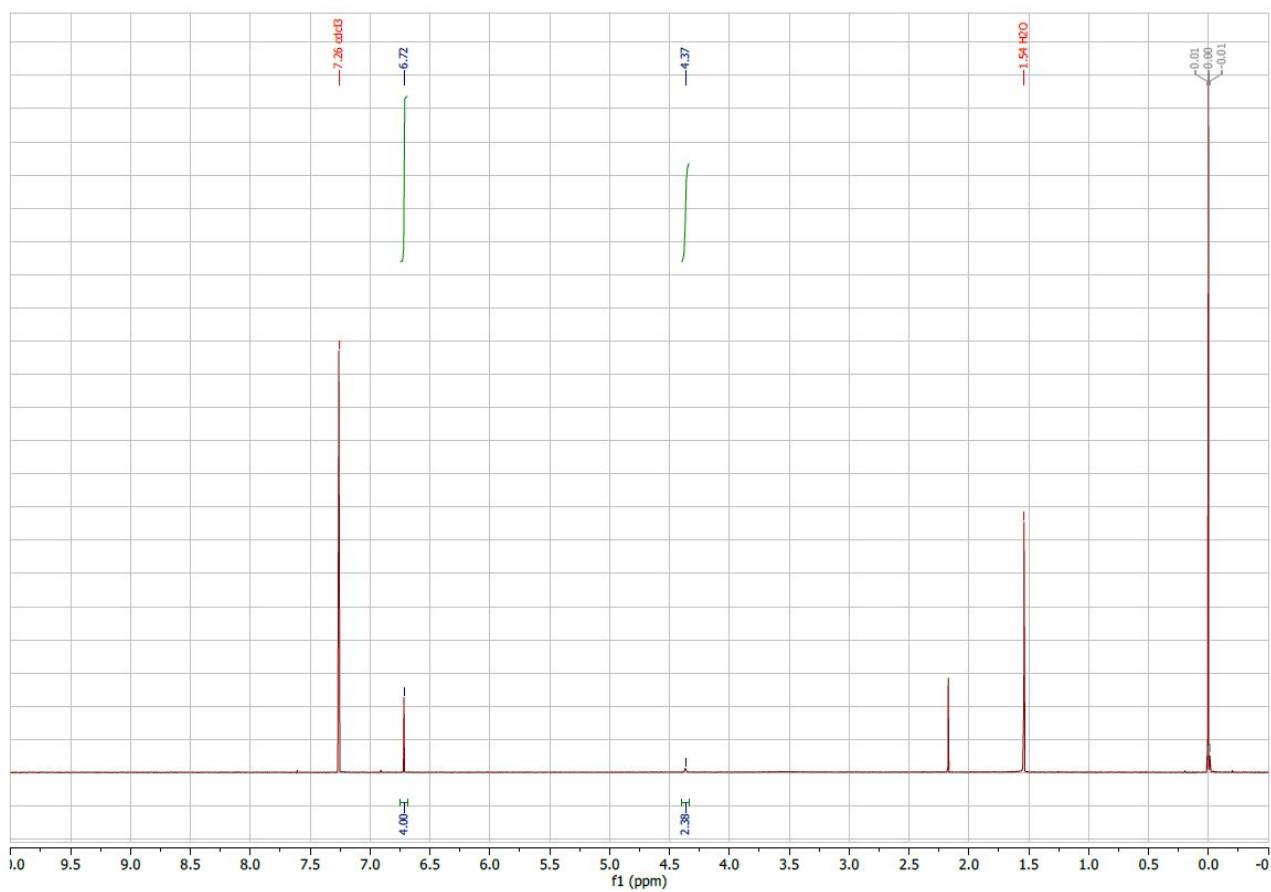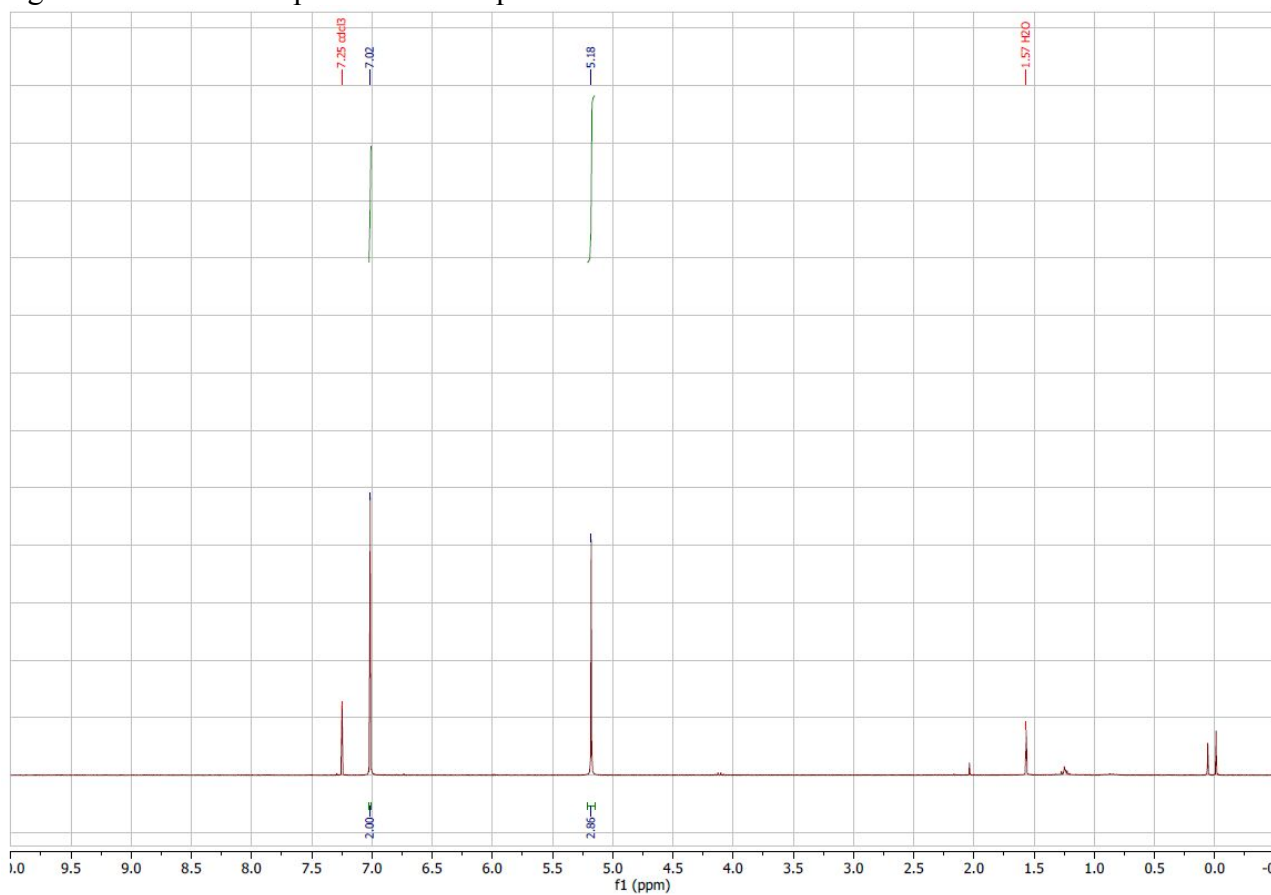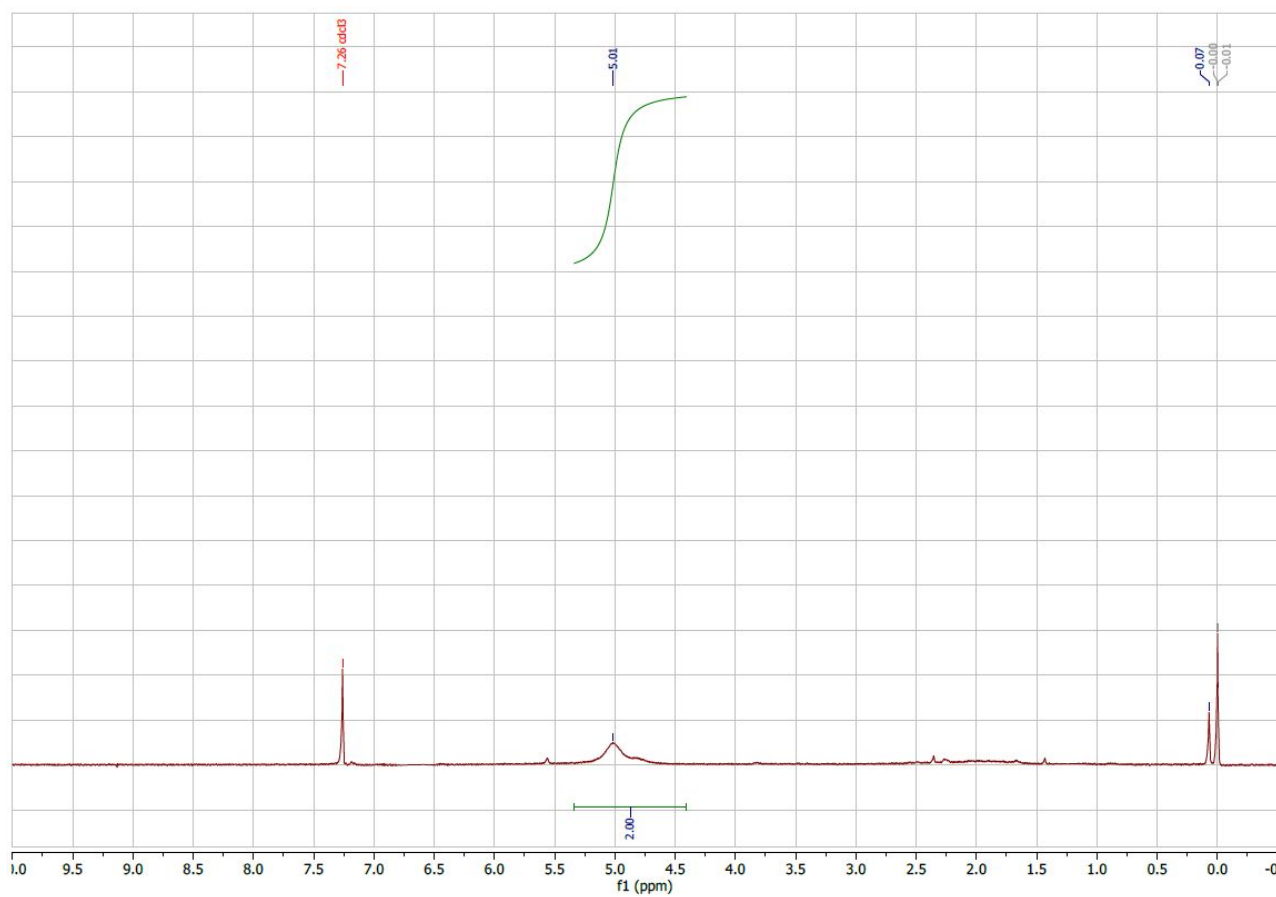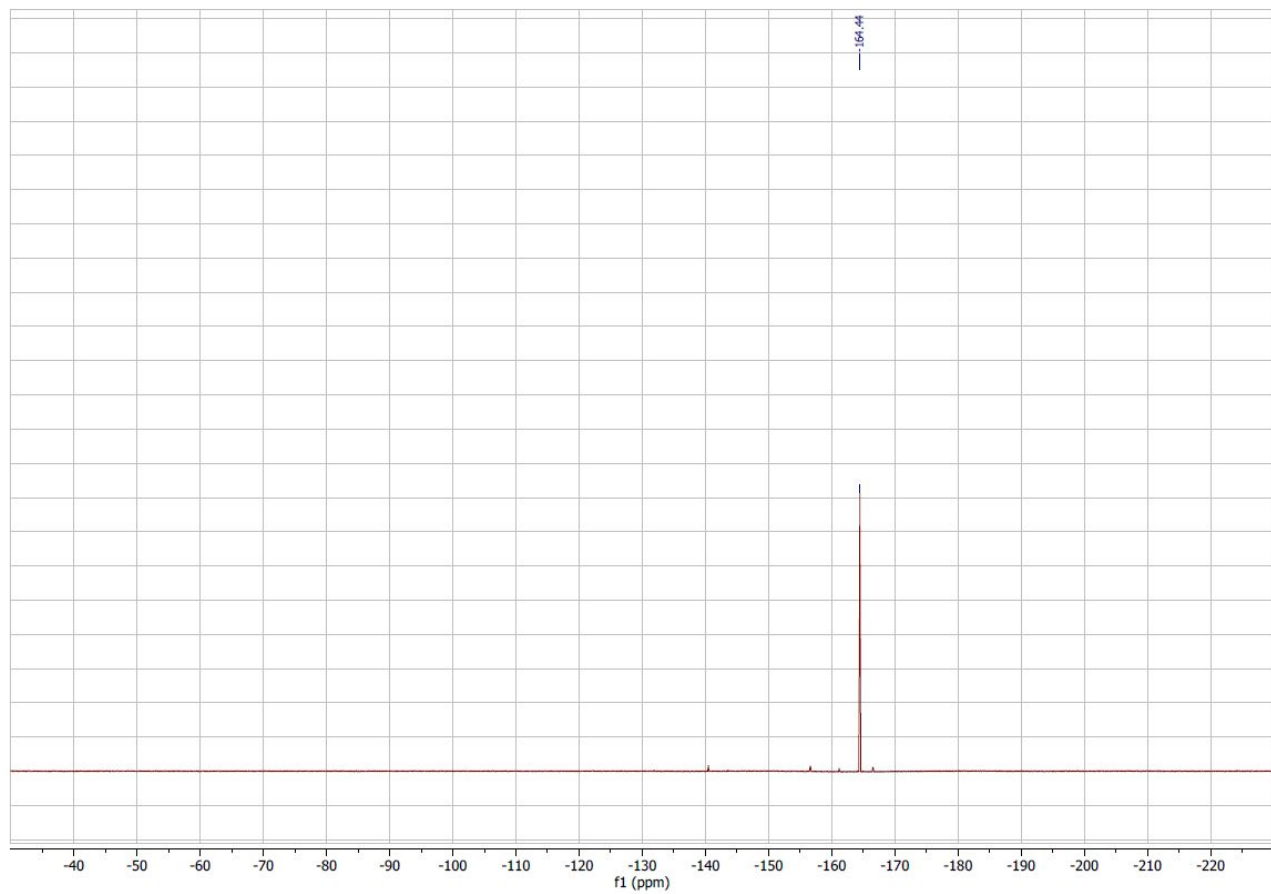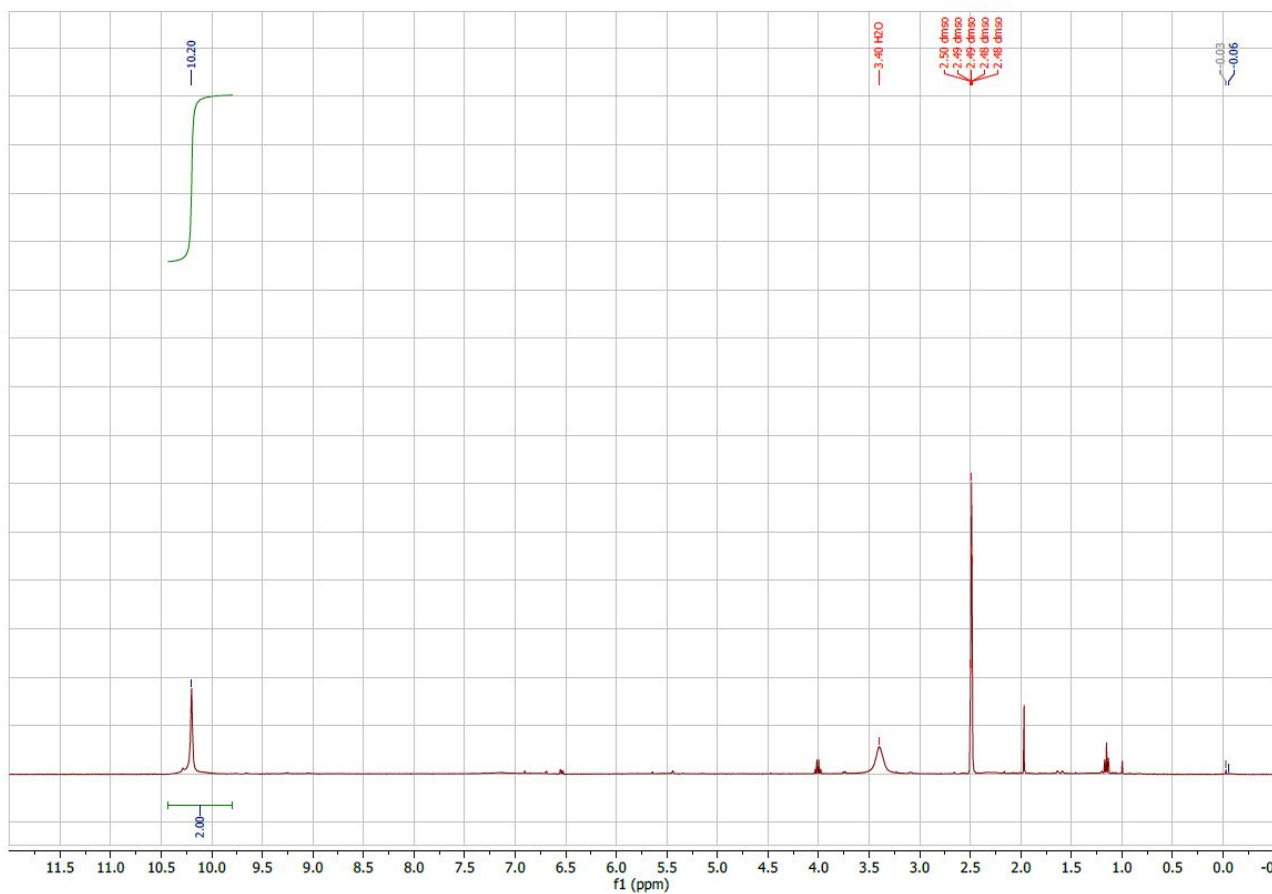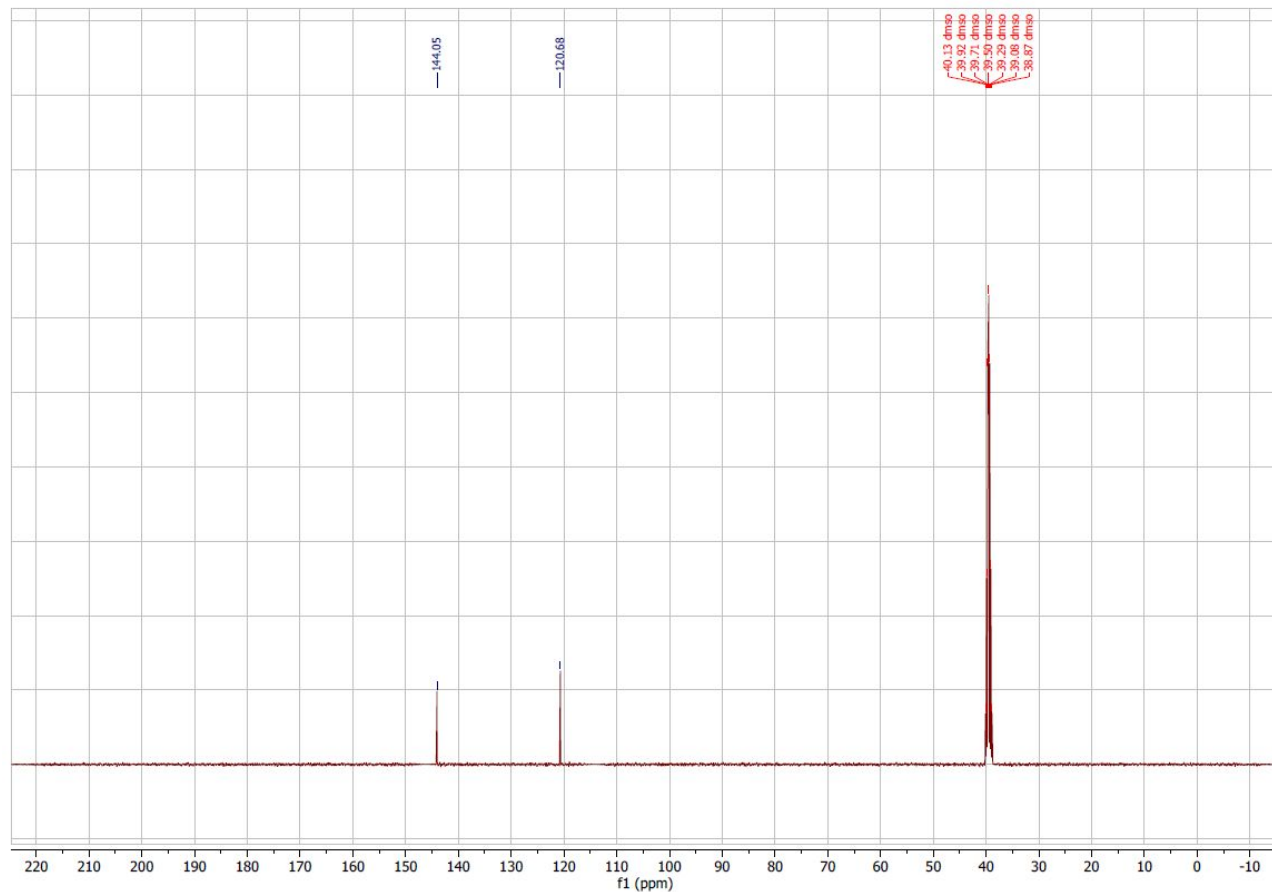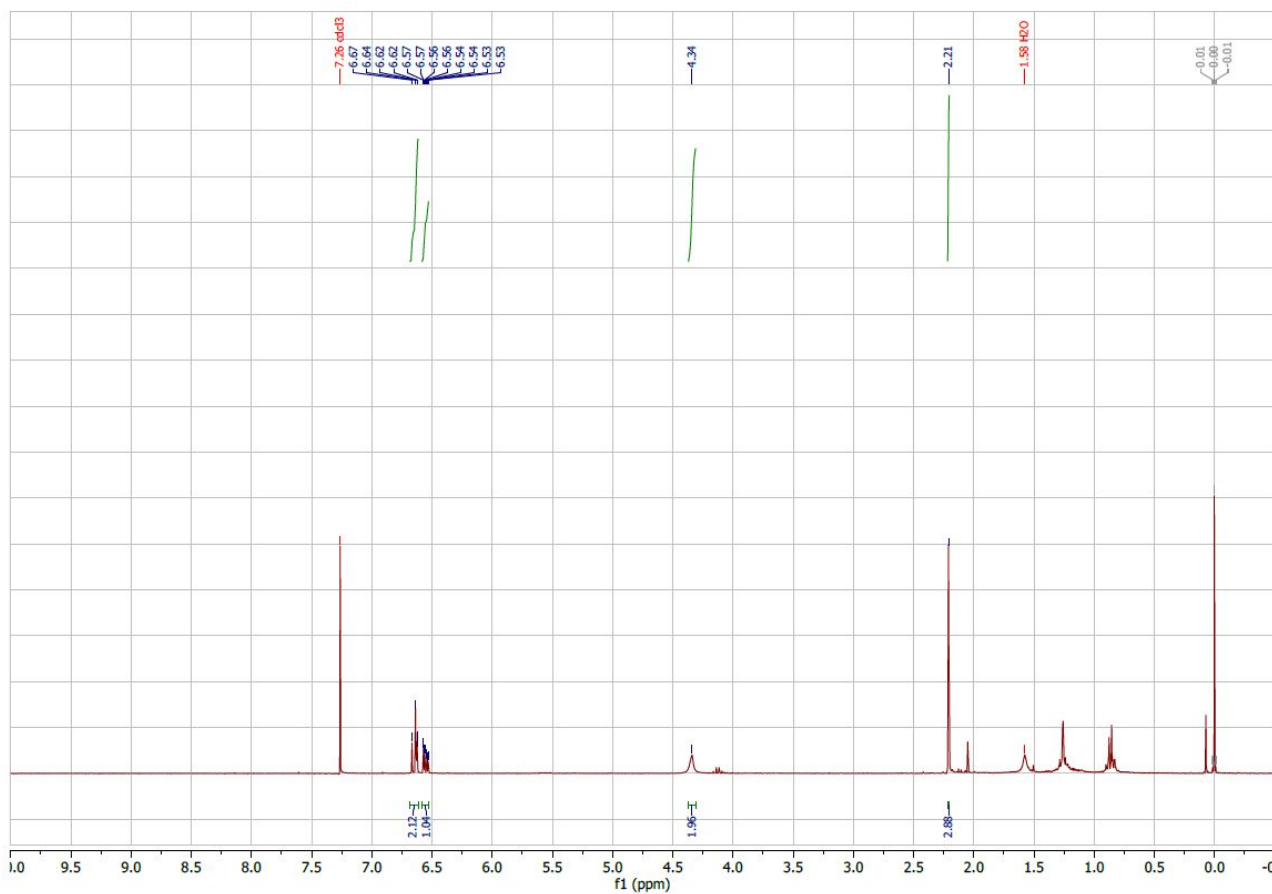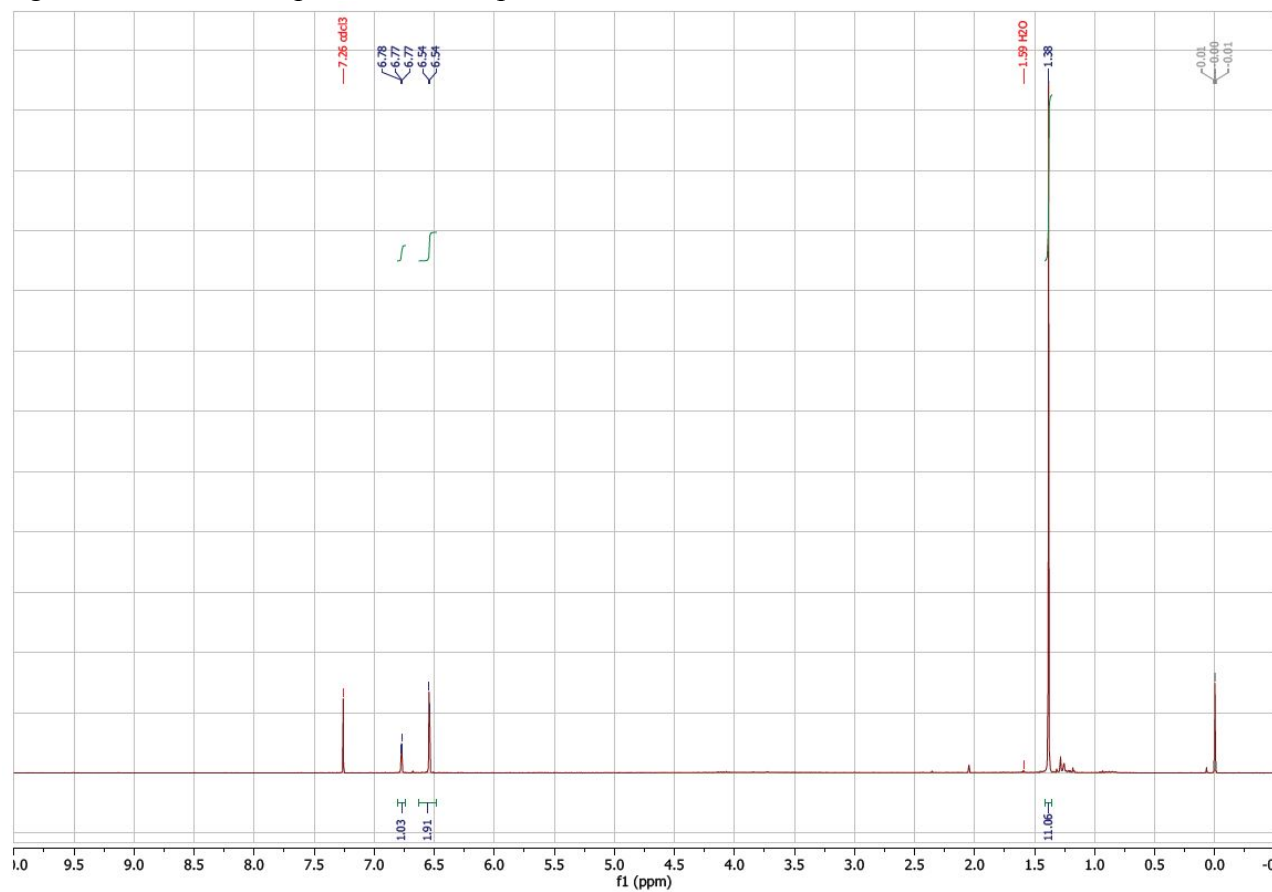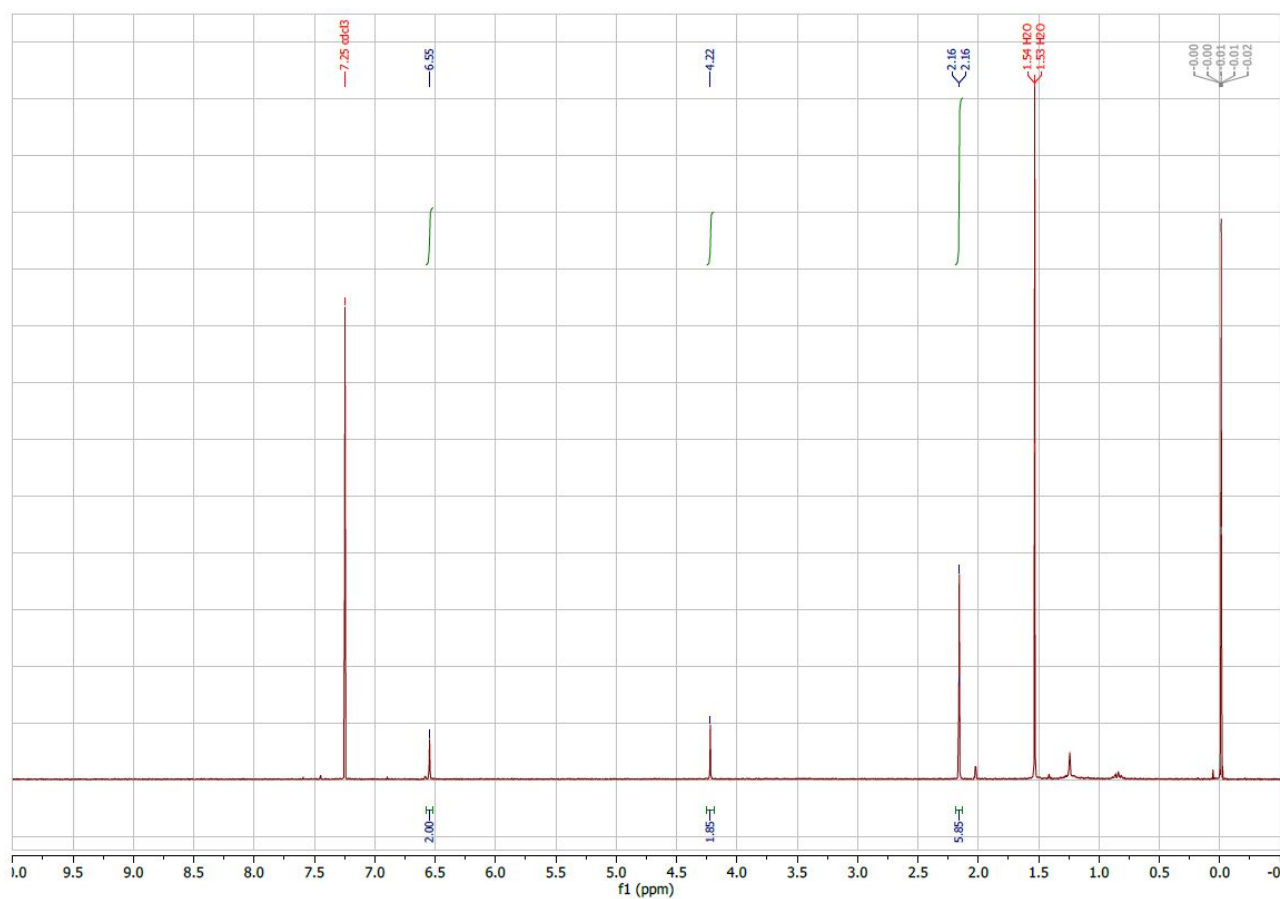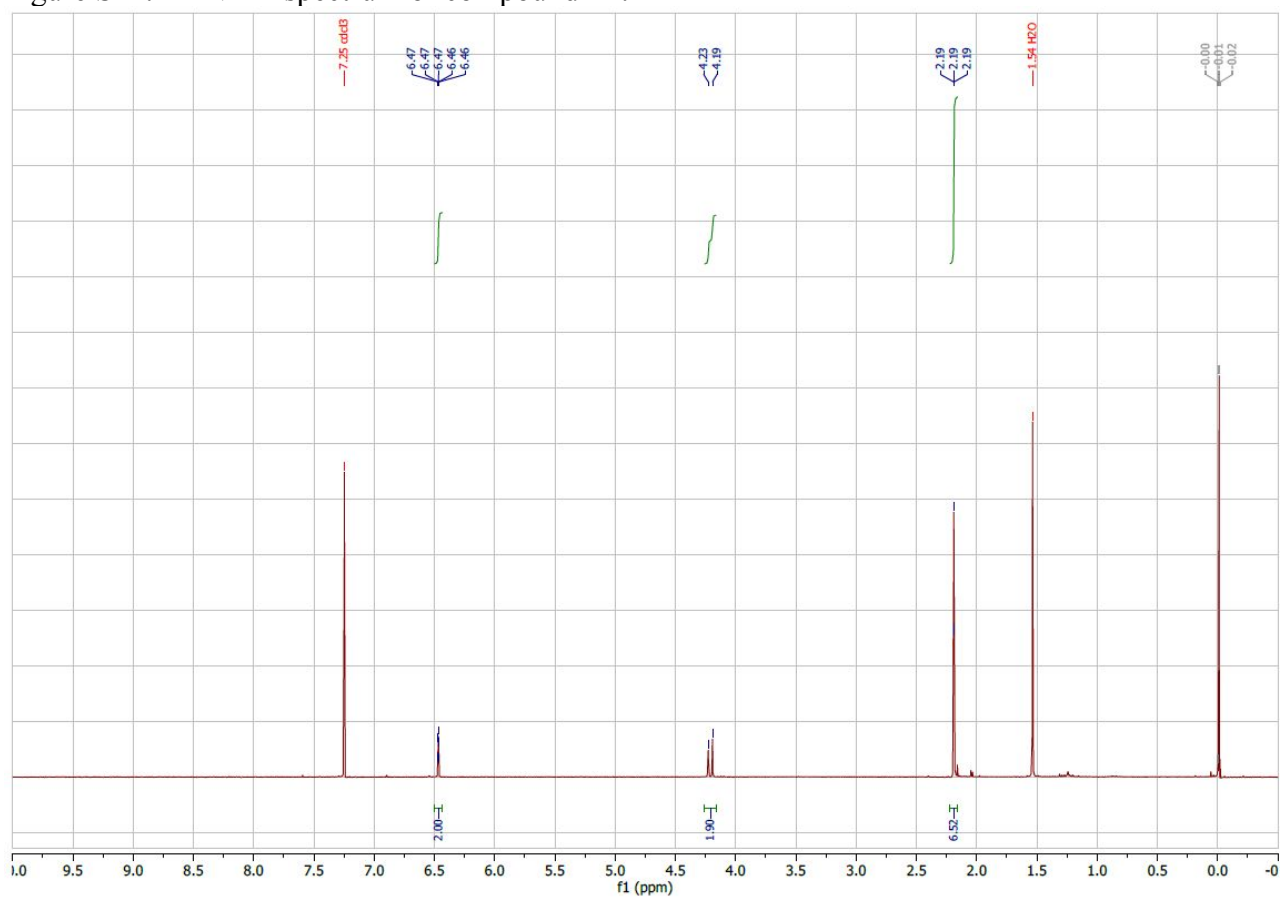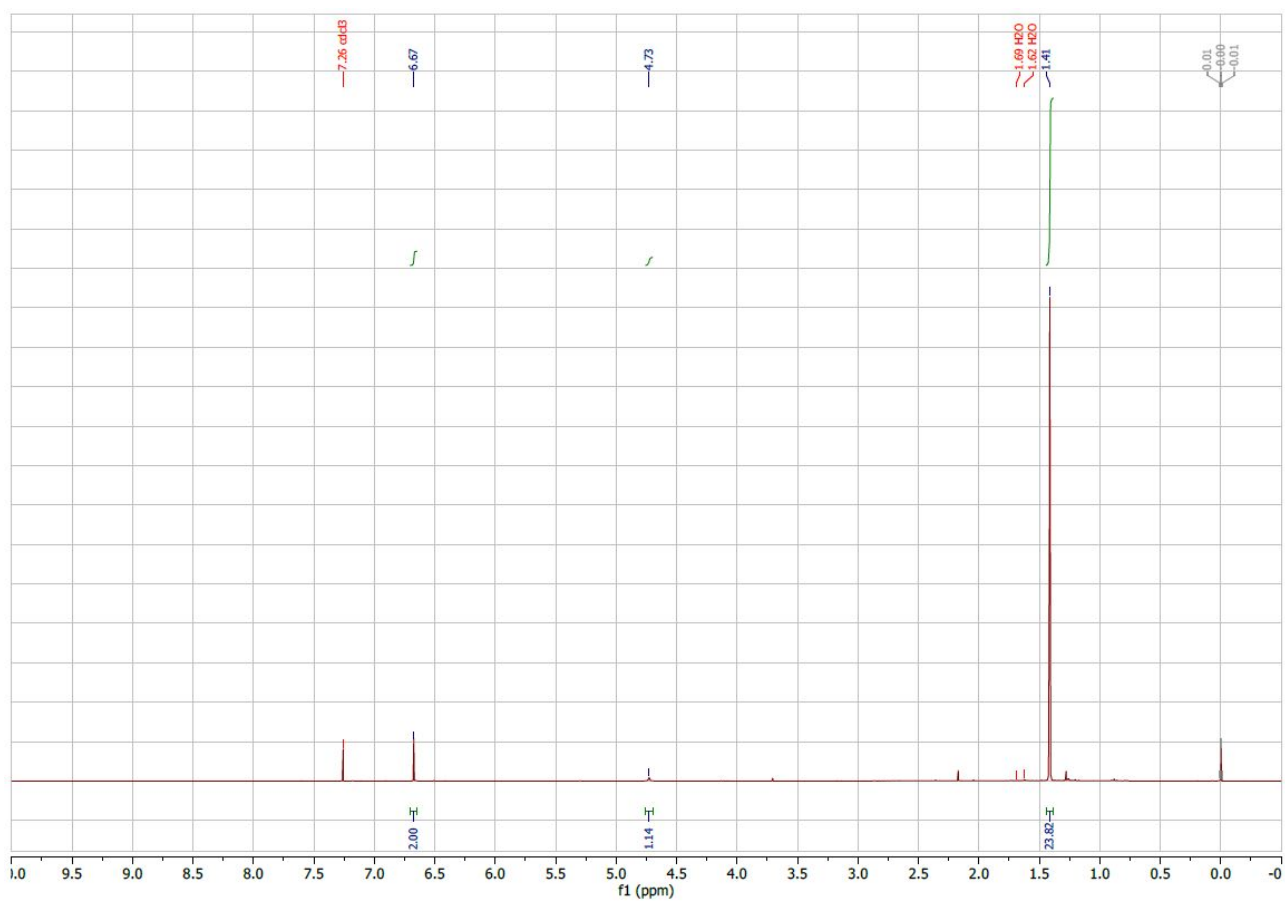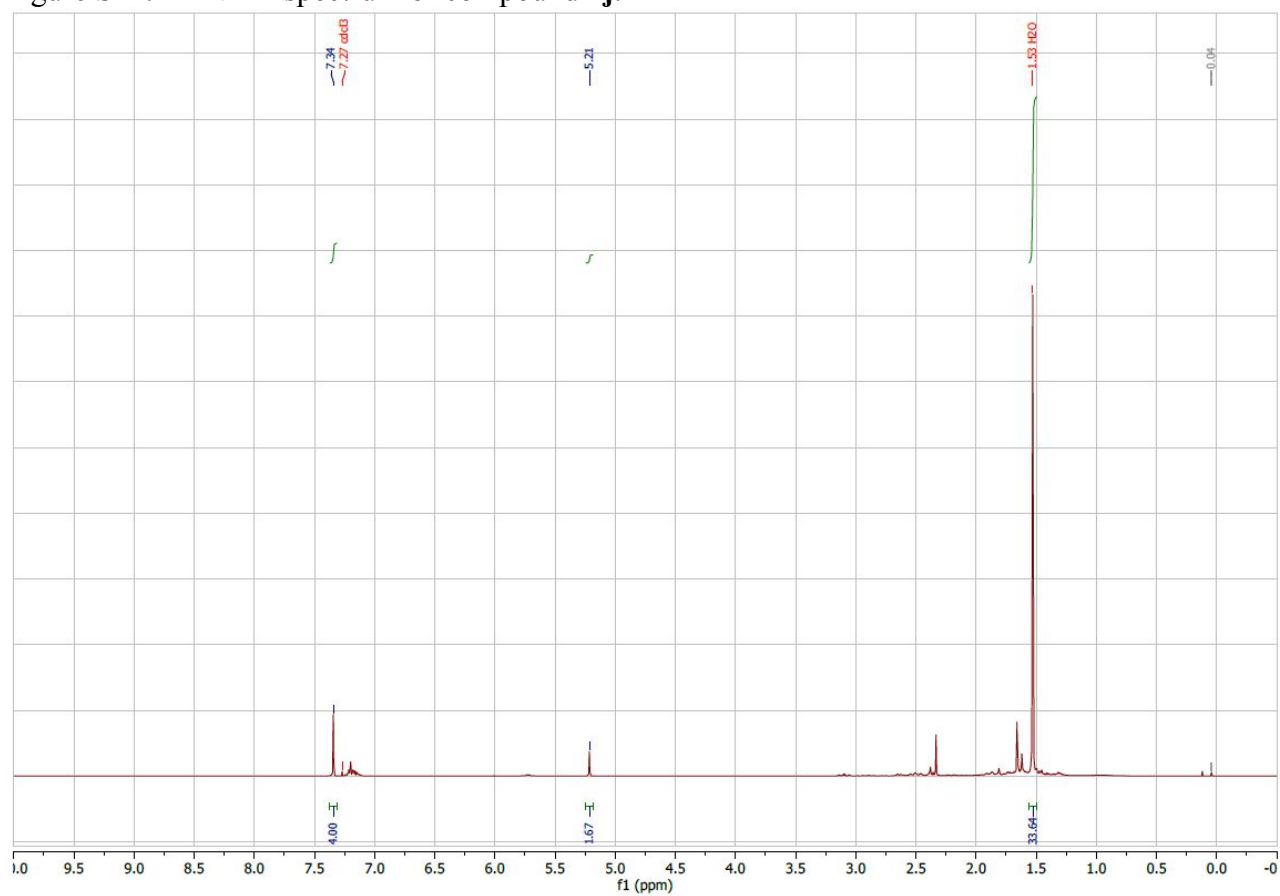
Figure S14. ¹H NMR spectrum of compound **4b**.

Figure S15. ¹H NMR spectrum of compound **4c**.

Figure S16. ^{1}H NMR spectrum of compound **4d**.

Figure S17. ^{19}F NMR spectrum of compound **4d**.

Figure S18. ^{1}H NMR spectrum of compound **4e**.

Figure S19. ^{13}C{^{1}H} NMR spectrum of compound **4e**.

Figure S20. ^{1}H NMR spectrum of compound **4f**.

Figure S21. ^{1}H NMR spectrum of compound **4g**.

Figure S22. ^{1}H NMR spectrum of compound **4h**.

Figure S23. ^{1}H NMR spectrum of compound **4i**.

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Figure S24. ^{1}H NMR spectrum of compound **4j**.

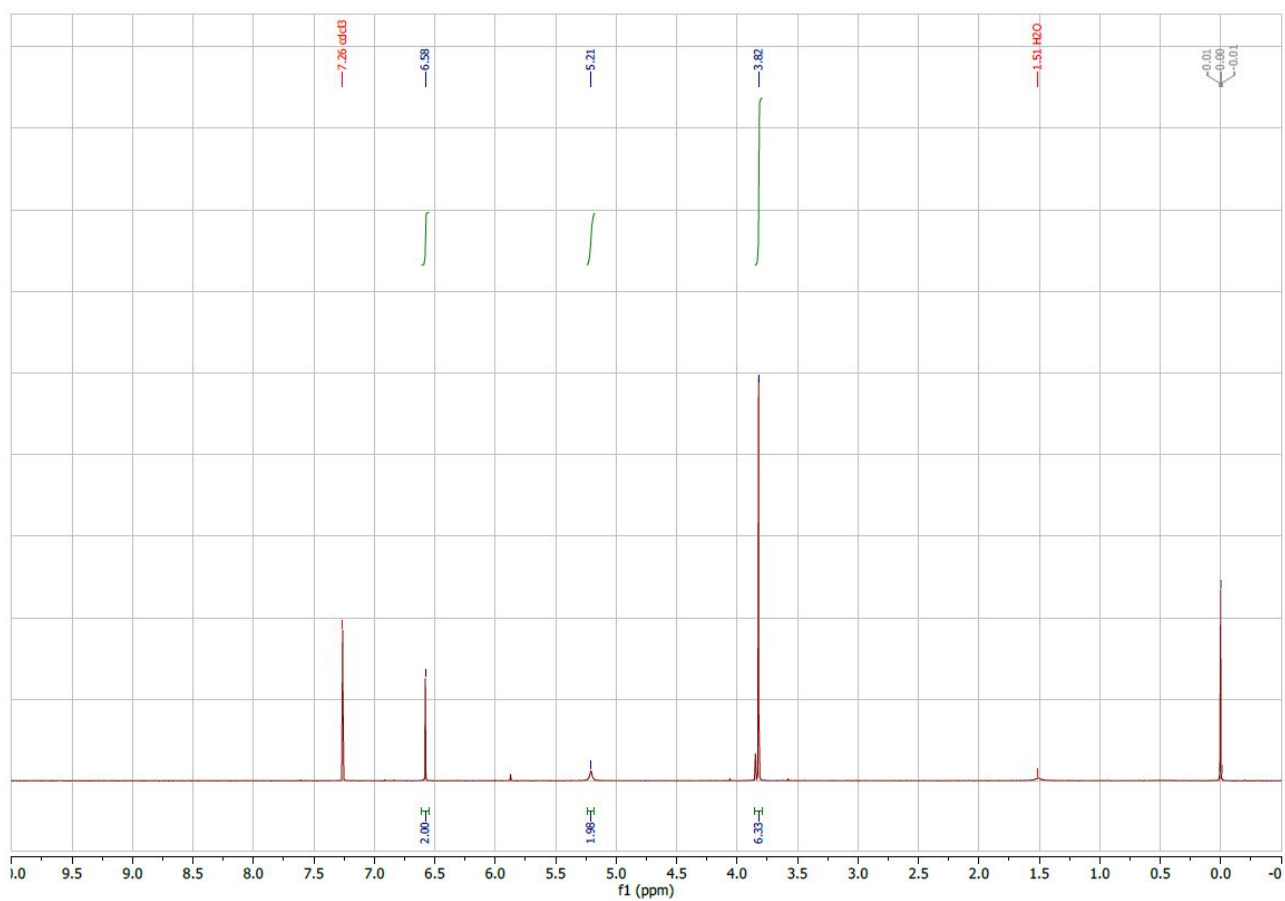Figure S25. ^{1}H NMR spectrum of compound **4jj**.

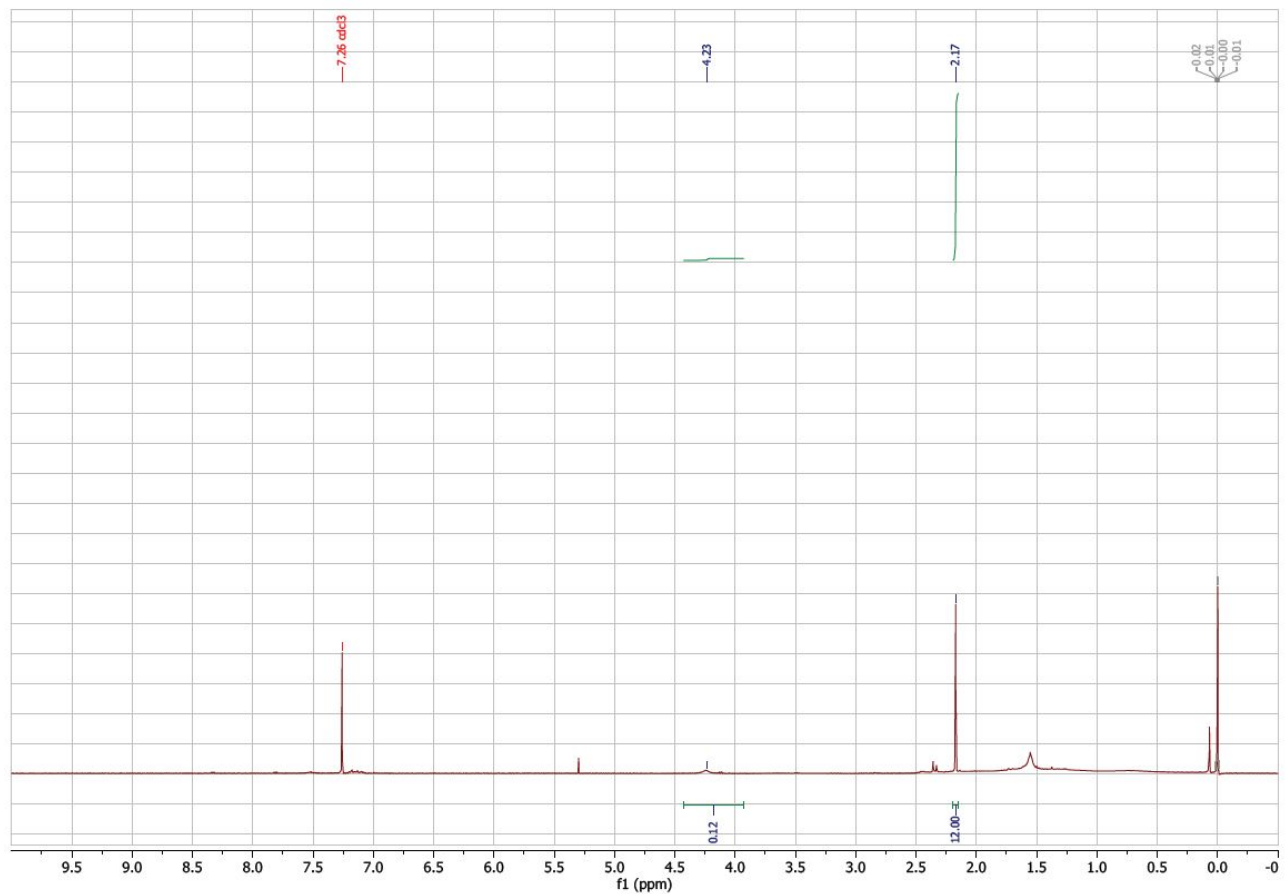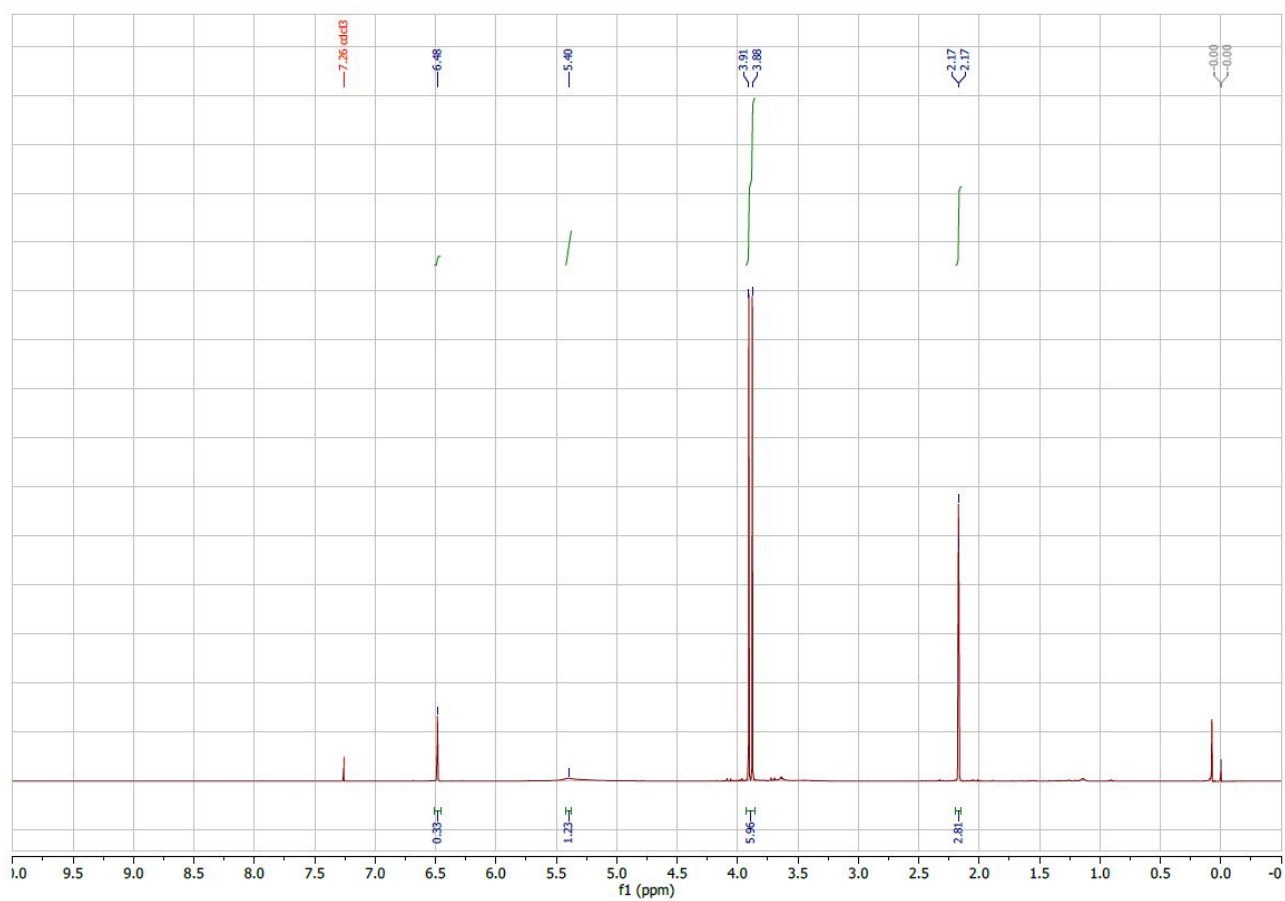Figure S26. ^{1}H NMR spectrum of compound **4k**.

Figure S27. ^{1}H NMR spectrum of compound **4l**.

Figure S28. ^{1}H NMR spectrum of compound **4CoQ$_0$**.