SUPPORTING INFORMATION:

Thermodynamic Targeting of Electrocatalytic CO_2 Reduction: Advantages, Limitations, and Insights for Catalyst Design

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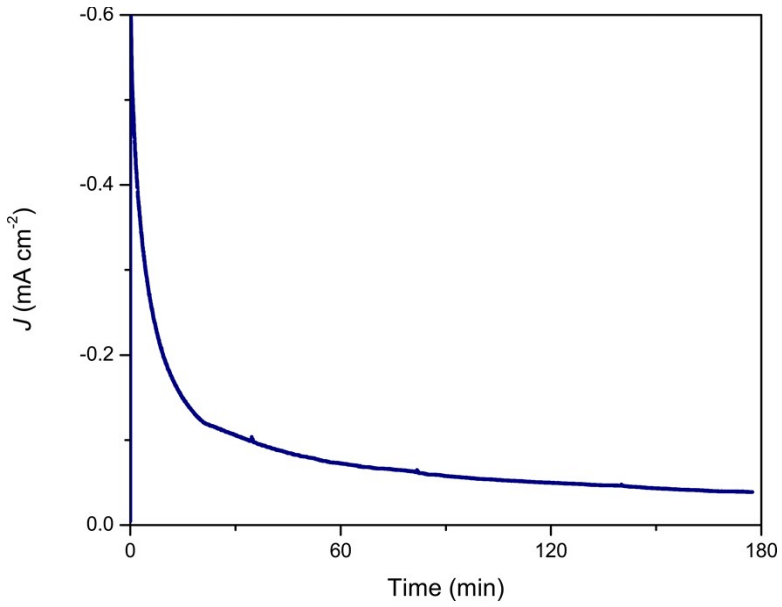

Figure S1. Controlled potential electrolysis at -1.75 V vs. Ag/AgCl in the presence of **1** under CO_2. Conditions: 0.1 M $TBAPF_6$ in acetonitrile with 0.1 M phenol, glassy carbon working electrode, graphite rod counter electrode, Ag/AgCl reference electrode. 3.87 C total charge passed corresponding to a total TON of 1.34.

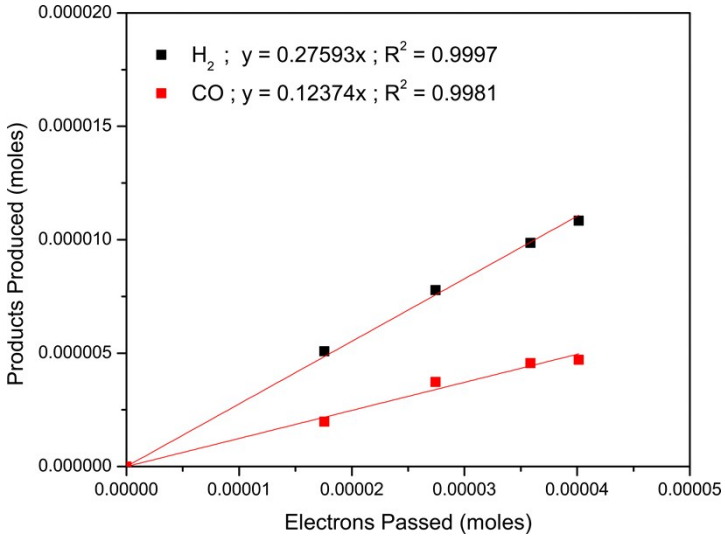

Figure S2. Plot of charge passed vs. gas products produced during controlled potential electrolysis shown in Figure S1. Slopes of 0.27593 and 0.12374 for the 2-electron products of H_2 and CO correspond to Faradaic Efficiencies of 55% ± 5% and 25% ± 5%, respectively.

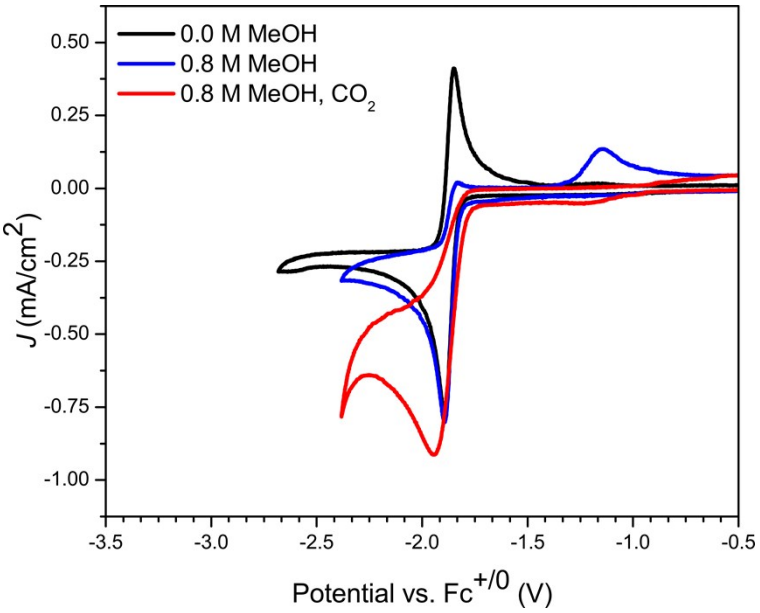

Figure S3. Cyclic voltammograms of **1** (1 mM) under nitrogen with no added proton source (black), with 0.8 M methanol under nitrogen (blue), and 0.8 M methanol under CO_2 (red). Conditions: 0.1 M Bu_4NPF_6 in acetonitrile at 100 mV s^{-1}; glassy carbon working electrode; platinum counter electrode; Ag/AgCl reference electrode.

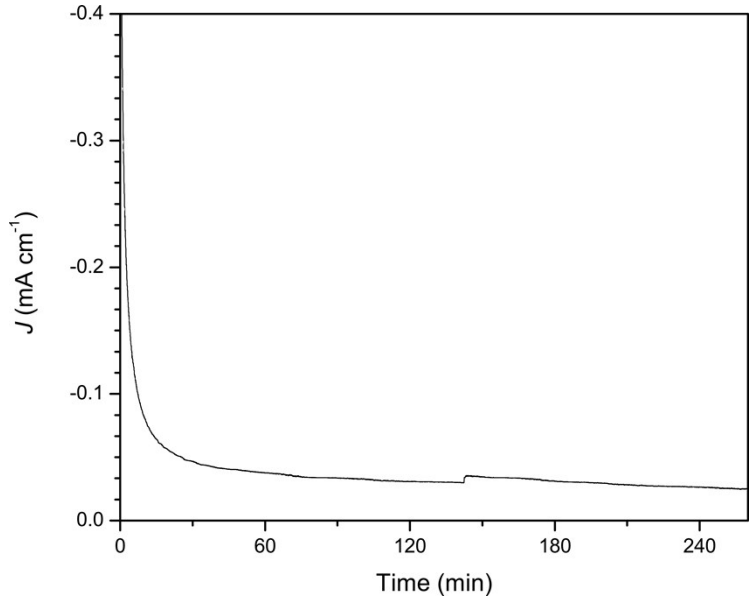

Figure S4. Controlled potential electrolysis at -1.75 V vs. Ag/AgCl in the presence of **1** under CO_2. Conditions: 0.1 M $TBAPF_6$ in acetonitrile with 0.4 M methanol, glassy carbon working electrode, graphite rod counter electrode, Ag/AgCl reference electrode. 2.52 C total charge passed corresponding to a total TON of 0.82.

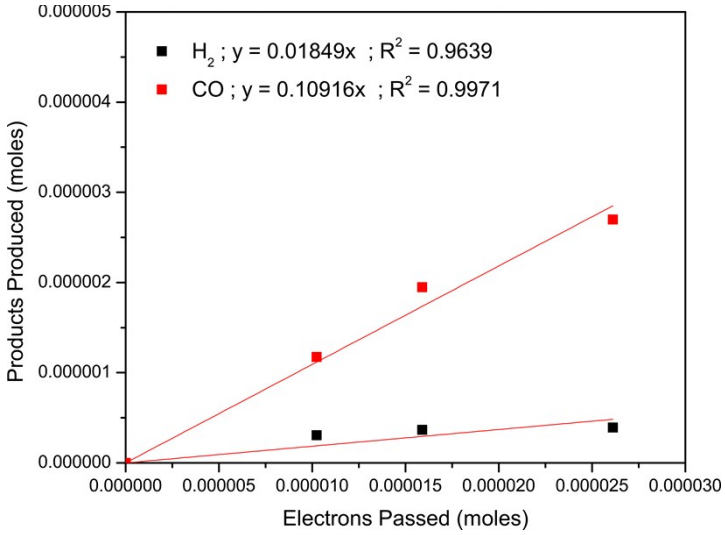

Figure S5. Plot of charge passed vs. gas products produced during controlled potential electrolysis shown in Figure S4. Slopes of 0.01849 and 0.10916 for the 2-electron products of H_2 and CO correspond to Faradaic Efficiencies of 4% ± 5% and 22% ± 5%, respectively.

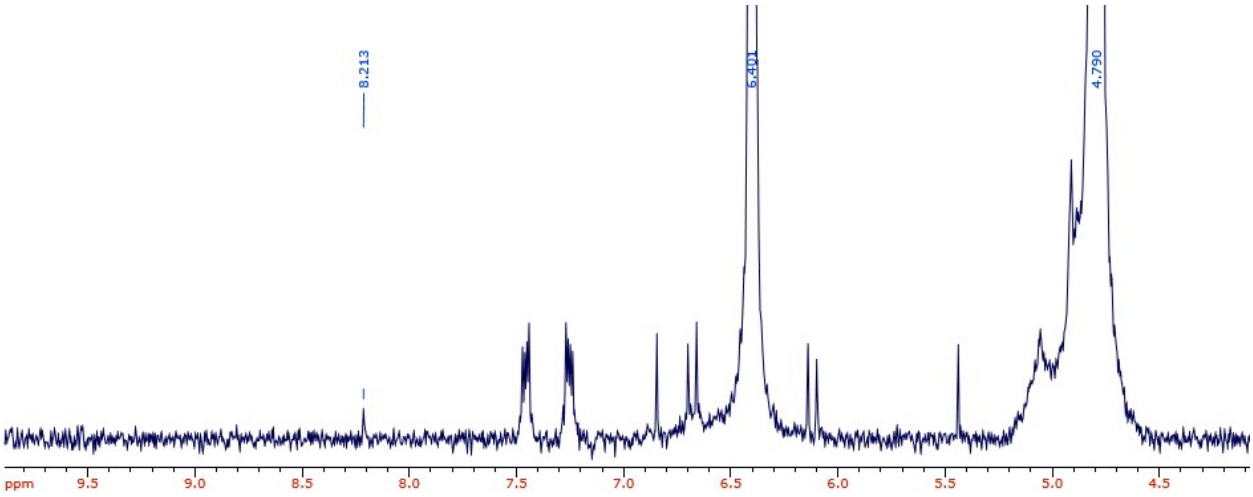

Figure S6. ^{1}H NMR of bulk work-up of CPE from Figure S4 in D_2O, showing formate resonance at 8.21 ppm and maleic acid internal standard at 6.40 ppm. Identical workup of control CPE under the same conditions save for the absence of **1** was void of a formate resonance.

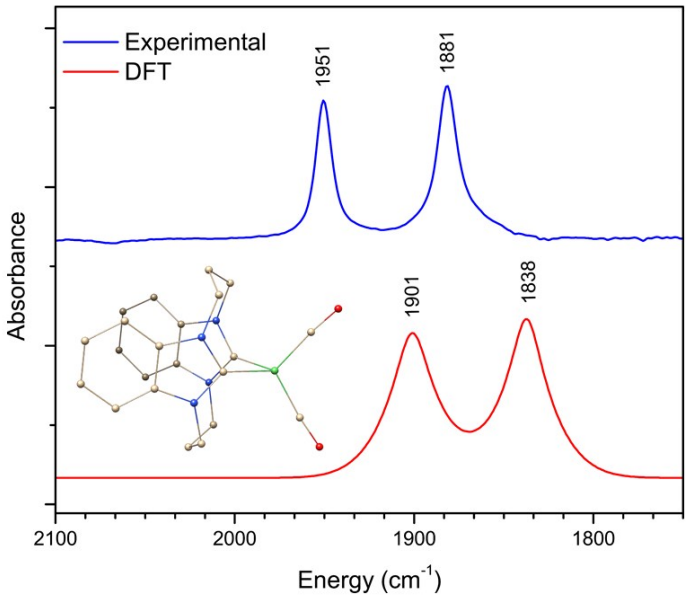

Figure S7. Experimental (blue) and DFT-calculated (red) FTIR spectra of the carbonyl stretches of the proposed degradation species $[Ni(bis\text{-}NHC)(CO)_2]^0$, and its optimized structure used for frequency calculations. For details on optimized structure used for calculations and input files, see Computational Methods section below.

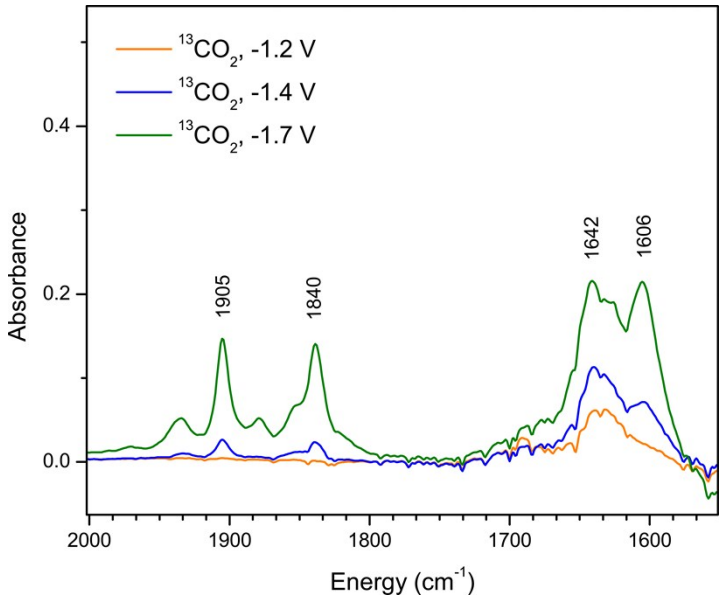

Figure S8. IR-SEC of **1** (3 mM) in $^{13}CO_2$-saturated acetonitrile in the absence of an added proton source, sweeping from -1.2 to -1.7 V vs. Ag pseudoreference electrode. Conditions: glassy carbon working electrode; platinum counter electrode; silver pseudoreference electrode; 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte.

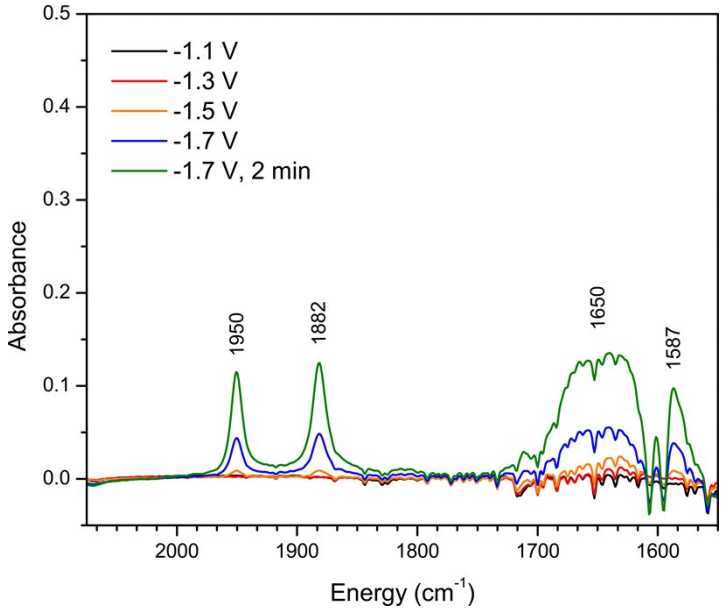

Figure S9. IR-SEC of **1** (3 mM) in CO_2-saturated acetonitrile in the presence of phenol (0.1 M), sweeping from -1.1 to -1.8 V vs. Ag pseudoreference electrode. Conditions: glassy carbon working electrode; platinum counter electrode; silver pseudoreference electrode; 0.1 M tetrabutylammonium hexafluorophosphate supporting electrolyte.

Computational Details.

Density Functional Theory Analysis. Calculations were performed in the ORCA software suite (version 3.0.3) at the B3LYP level of theory with the RIJCOSX approximation.[1-5] Nickel and phosphorous atoms were treated with the DEF2-TZVP basis sets while DEF2-SVP was used for all other atoms.[6-14] Dispersion corrections were applied using the atom-pairwise dispersion correction with a Becke-Johnson damping scheme (D3BJ), while solvation was accounted for using the COSMO solvation model in acetonitrile.[15-17] Analytical frequency calculations were performed at the same level of theory to ensure all optimized structures were minima. Molecular graphics were constructed with the UCSF Chimera package.[18]

Representative input file:

```
%pal nprocs 8 end
! UKS B3LYP/G RIJCOSX D3BJ def2-SVP def2-SVP/J
! COSMO(Acetonitrile) SlowConv GRIDX5 FinalGrid6 VeryTightSCF opt
%basis
newgto Ni "def2-TZVP" end
newgto P "def2-TZVP" end
end
%SCF
        MaxIter 2000
end
* xyz “Charge” “Multiplicity”
        “XYZ Coordinates”
*
```

Table S1. Optimized geometry coordinates for complex **1**.

Atom	X	Y	Z
Ni	4.97707778	8.40393549	21.1819899
P	5.11146001	8.24230151	23.3727802
P	4.72682809	10.5719634	21.4589486
N	3.78649624	8.15910268	18.5226092
N	5.95504704	8.38351775	18.4328389
N	4.14397913	5.67407972	20.5751104
C	4.63057078	4.48842091	20.0169429
N	6.31233968	5.89671774	20.4782489
C	5.16668374	6.52348727	20.8400985
C	6.02914044	4.63207297	19.9533793
C	4.14734712	7.90446513	17.1960975
C	3.61431425	7.52351375	24.1029398
H	2.72826234	8.08634822	23.7782275
H	3.6819742	7.55209834	25.2005726
H	3.51503741	6.47986302	23.7744312
C	3.3983534	7.56564175	16.0674815
H	2.31475844	7.44708599	16.1086992
C	6.48668504	7.28868343	24.0619961
H	6.41748076	6.24734443	23.718364
H	6.44969969	7.31186786	25.1613009
H	7.44088408	7.7149659	23.7228788
C	5.54597852	8.0510361	17.13789
C	4.80831397	2.32078403	19.0536834
H	4.34934172	1.39931432	18.6896665
C	7.34996808	8.50959993	18.8556068
H	7.37088324	9.16867522	19.7341824
H	7.89209692	9.02521016	18.0511206
C	2.07871234	6.55147213	19.4316854
H	0.98944351	6.52469009	19.5887468
H	2.28717256	5.87913539	18.5836735
C	2.72558306	6.00522652	20.7089924
H	2.63127499	6.73386026	21.5254513
H	2.20370868	5.09293174	21.0276646
C	5.50522235	7.52565369	14.8187415
H	6.01882089	7.36604231	13.8684285
C	7.63834518	6.51290983	20.4917451
H	8.36280677	5.72837138	20.7480543

H	7.65172194	7.24641486	21.3104224
C	8.03931146	7.17910159	19.1720387
H	9.11877943	7.38577777	19.2355161
H	7.90695993	6.47334244	18.3357395
C	2.43731483	7.99417387	19.0616385
H	1.73304121	8.36993608	18.3071096
H	2.35115154	8.64933114	19.9393635
C	6.84650666	3.62392451	19.4386365
H	7.930708	3.73157962	19.3835491
C	6.2529592	7.86866043	15.9479193
H	7.33661576	7.98288811	15.8971644
C	4.88608576	8.43514064	19.2645612
C	6.24766081	11.4851131	21.0772453
H	7.0898825	11.0755512	21.6510718
H	6.12066341	12.5488967	21.3271196
H	6.46763048	11.3900238	20.0049462
C	3.41784259	11.4038758	20.5269719
H	3.60222391	11.2835	19.4500607
H	3.39904098	12.4751828	20.7760892
H	2.44452357	10.9591096	20.7762902
C	4.10525909	7.37613362	14.8776231
H	3.55959791	7.10310157	13.972294
C	5.24603449	9.93429628	24.0723948
H	4.95232777	9.93389463	25.1324475
H	6.30849537	10.22012	24.0256954
C	3.99200654	3.32920902	19.5716329
H	2.90823208	3.21281209	19.6183572
C	6.20867449	2.46560451	18.9879593
H	6.80979211	1.65356904	18.5737611
C	4.3863018	10.8840831	23.2347119
H	4.57217283	11.9401604	23.4800896
H	3.31394905	10.6914811	23.3969502

Table S2. Optimized XYZ coordinates for complex $\mathbf{1^0}$.

Atom	X	Y	Z
Ni	4.95745898	8.39721725	21.251133
P	3.35589443	9.4195295	22.3559524
P	6.4370423	9.35396602	22.5742975
N	3.81529631	8.07376176	18.5118471
N	5.98164367	8.29774121	18.4468967
N	4.12389949	5.63382117	20.4840434
C	4.59999967	4.55725395	19.7466026
N	6.29039018	5.85855655	20.4217565
C	5.14306624	6.4778652	20.8979814
C	6.00290208	4.7028629	19.7062487
C	4.20788259	7.64949679	17.2483944
C	2.64352089	10.943032	21.5817948
H	3.47267785	11.5735323	21.2300682
H	2.01309619	11.5205638	22.2789535
H	2.0408304	10.6643266	20.7042942
C	3.4963338	7.16371997	16.1500455
H	2.41227816	7.04056183	16.180045
C	1.80602981	8.74161605	23.1091354
H	1.12986312	8.40013067	22.310711
H	1.27167611	9.48556923	23.7245268
H	2.06186547	7.87362511	23.7353614
C	5.61044126	7.79596599	17.2055622
C	4.77340239	2.55347811	18.4532243
H	4.3058028	1.70125558	17.9539469
C	7.3637685	8.46036932	18.8656578
H	7.3461101	9.12596889	19.7371363
H	7.9131825	8.96338317	18.0535049
C	2.04496212	6.52013142	19.3907046
H	0.95716618	6.53100862	19.5720255
H	2.20727564	5.84448837	18.5345215
C	2.71126089	5.93406184	20.6432234
H	2.63733036	6.63894836	21.4805671
H	2.19067714	5.00428517	20.9237853
C	5.62505263	6.98017712	14.9579361
H	6.16631269	6.70855479	14.0482966
C	7.62066583	6.44073198	20.4941558
H	8.33415307	5.63777711	20.7381917

H	7.60446236	7.15274281	21.3276792
C	8.07768059	7.14693562	19.2108576
H	9.14968712	7.37708208	19.3302006
H	8.00711679	6.45093749	18.3578758
C	2.45355813	7.94803911	19.0060237
H	1.77001414	8.32003178	18.2260553
H	2.37460554	8.60940197	19.8757991
C	6.80835841	3.77878306	19.0390362
H	7.89345475	3.89006437	18.9992727
C	6.33991776	7.46677633	16.0621964
H	7.4250538	7.57753829	16.0250482
C	4.89562328	8.46008291	19.2923689
C	7.12369019	8.33674461	23.9605726
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H	7.69526001	8.93813197	24.6877718
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C	7.96520639	10.311206	22.1524096
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H	8.41545541	10.7968383	23.0343488
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H	3.49048476	10.9821451	24.2841537
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H	6.77184313	1.95842167	17.8795265
C	5.53710719	10.6565968	23.5563328
H	6.09951561	10.9288072	24.4656576
H	5.49749178	11.5519894	22.9139774

Table S3. Optimized XYZ coordinates for complex $\mathbf{1^H}$.

Atom	X	Y	Z
Ni	4.90001326	8.20598014	21.2126126
P	3.75563287	9.94589505	21.8323588
P	6.87846636	9.37175224	22.2800915
N	3.71506885	7.96684746	18.5635187
N	5.86245689	8.27490475	18.3864369
N	4.23855841	5.47930557	20.5399182
C	4.73189685	4.34198548	19.901465
N	6.38393315	5.79224697	20.330019
C	5.23824791	6.37273927	20.7901114
C	6.11800926	4.5434154	19.765836
C	4.03199267	7.70644361	17.2303674
C	3.50031766	11.2422543	20.5718314
H	4.47667999	11.5444664	20.1684056
H	2.99000222	12.1217365	20.99252
H	2.90224429	10.8384081	19.7427302
C	3.25679534	7.31759426	16.1355594
H	2.18155162	7.15465078	16.2206666
C	2.09255327	9.72822975	22.5491183
H	1.41141194	9.29286077	21.804132
H	1.67972925	10.6921726	22.8830702
H	2.15999285	9.04001035	23.4033679
C	5.41937267	7.9071772	17.1154043
C	4.93326689	2.22657732	18.8226375
H	4.48632569	1.30592124	18.4415009
C	7.26987191	8.45492563	18.723101
H	7.30698702	9.10943269	19.5990474
H	7.74615448	8.98659069	17.8872254
C	2.09747932	6.28305182	19.5060412
H	1.01563758	6.21476469	19.7029382
H	2.29572134	5.62578018	18.6434046
C	2.81899761	5.7448225	20.7480082
H	2.74473046	6.45608157	21.5813216
H	2.34789913	4.80279953	21.0625758
C	5.31074224	7.34137955	14.8036363
H	5.79489349	7.18751554	13.8367806
C	7.6974374	6.42559457	20.3019013
H	8.44582936	5.64250115	20.4855165

H	7.73612278	7.12252118	21.1467184
C	8.02595143	7.14867417	18.9905118
H	9.09900325	7.39691168	19.0215961
H	7.8949184	6.45839743	18.1407816
C	2.38802457	7.73951073	19.126921
H	1.65250049	8.0755715	18.3826517
H	2.2897115	8.38708669	20.004093
C	6.93799761	3.59157259	19.1567627
H	8.0122463	3.74474688	19.0436462
C	6.08500417	7.73236886	15.9004107
H	7.16053397	7.88806038	15.8054187
C	4.83116737	8.30031463	19.2789475
C	7.25535459	8.54972448	23.8770674
H	6.31430393	8.29850605	24.3851509
H	7.87126972	9.18661857	24.5312474
H	7.79229035	7.60900701	23.683221
C	8.55994232	9.95894057	21.8032595
H	9.1883047	9.10372897	21.5140348
H	9.0527941	10.4914859	22.6322163
H	8.48374932	10.6367358	20.9397632
C	3.92248554	7.13664972	14.9194575
H	3.35254655	6.82722238	14.0409549
C	4.65273992	10.8267653	23.1727778
H	4.18113829	11.8051504	23.3550182
H	4.51992513	10.2203589	24.0820544
C	4.1136123	3.18036266	19.4341109
H	3.03908463	3.02047251	19.5346367
C	6.32006782	2.42873173	18.68604
H	6.92720773	1.66131867	18.2008018
C	6.13716107	10.9745301	22.8337462
H	6.70160051	11.3822925	23.6876176
H	6.2665529	11.6795472	21.9963811
H	4.58919521	7.8416483	22.6215854

References

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