Electronic Supplementary Material

Effects of ancillary ligands in acceptorless benzyl alcohol dehydrogenation mediated by phosphine-free cobalt complexes

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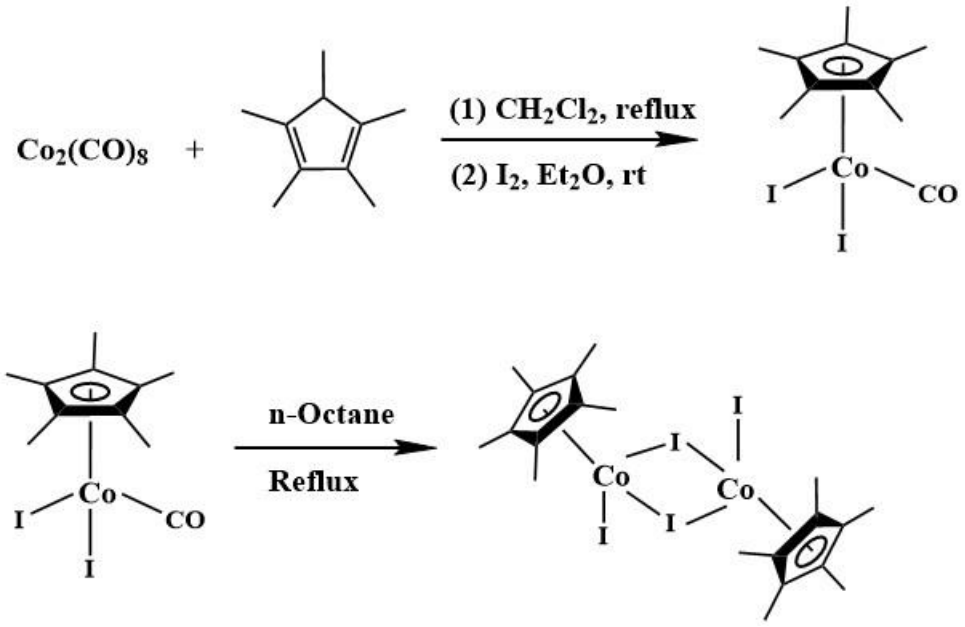
Scheme S1. Synthesis of $Cp^*Co(CO)I_2$ (A) and $[Cp^*CoI_2]_2$ (B).

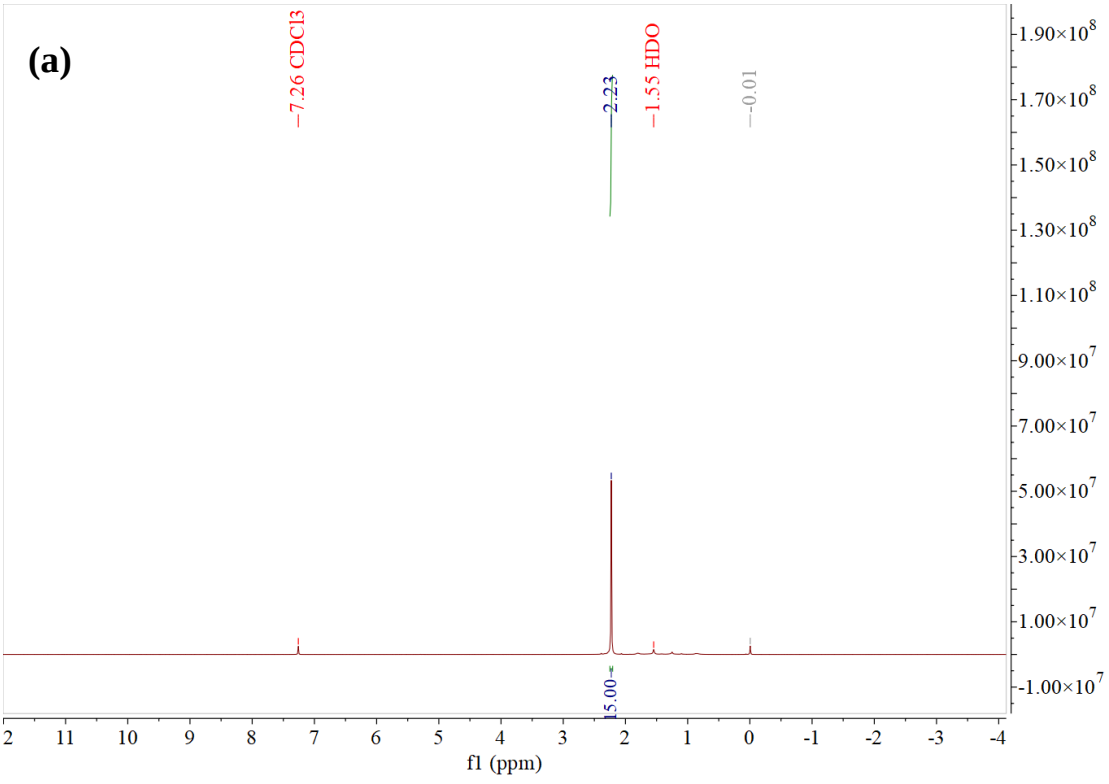


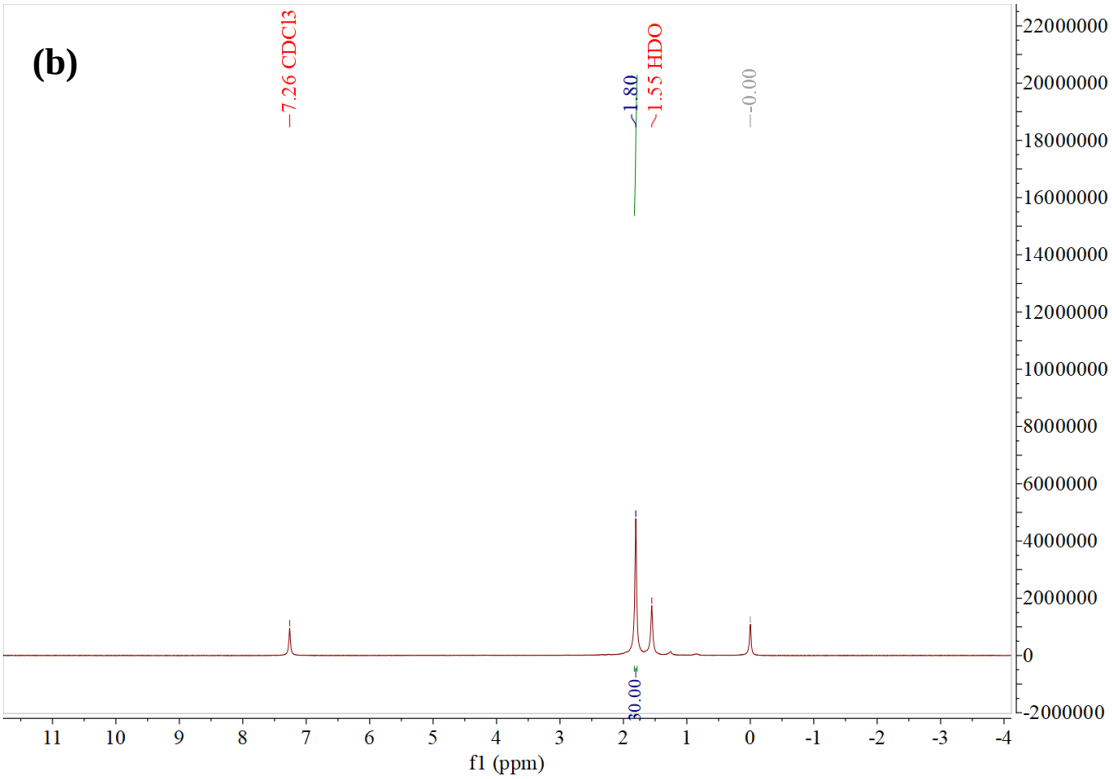
Preparation of A: [1]

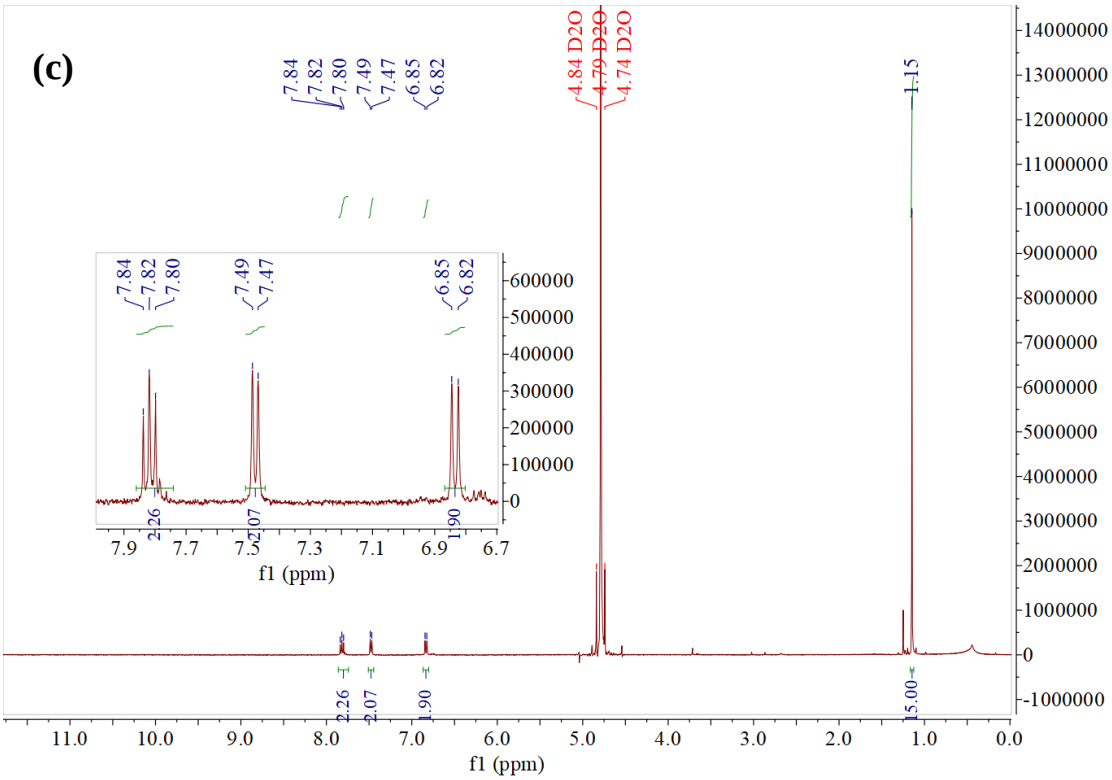
To a well-dried 2-necked 500-mL flask were successively added $Co_2(CO)_8$ (5.0 g, 14.6 mmol), degassed CH_2Cl_2 (100 mL) and pentamethylcyclopentadiene (5.55 mL, 35.4 mmol). The mixture was refluxed under argon stream for 6 h and then cooled to room temperature. The solvent was removed under a vacuum. The residue was dissolved in degassed Et_2O (50 mL) and then iodine (9.0 g, 35.5 mmol) in degassed Et_2O (50 mL) was added dropwisely at room temperature with stirring. [Caution: During the addition, the mixture was refluxed due to the exothermic reaction and CO gas evolution was observed.] After the mixture was stirred at room temperature for 1 h, the solvent was evaporated. Resulting residue was purified by silica gel column chromatography (hexane then CH_2Cl_2/hexane=4/1) to afford deep purple crystalline solid (12.0 g, 86% yield based on Co);

Preparation of B: [2]

To a round-bottomed flask was charged with n-octane (50 mL) and A (4.0 g). The mixture was heated to reflux under argon for 12 h. After cooling to room temperature, the solid precipitate was collected in a sintered-glass filtration funnel, washed with pentane, and dried under high vacuum to afford B (3.2 g, 84%) as a black powder.




(b)
7.26 CDCl3
1.80
1.55 HDO
0.00
30.00
f1 (ppm)


(c)
7.84
7.82
7.80
7.49
7.47
6.85
6.82
4.84 D2O
4.79 D2O
4.74 D2O
1.15
2.26
2.07
1.90
15.00
f1 (ppm)

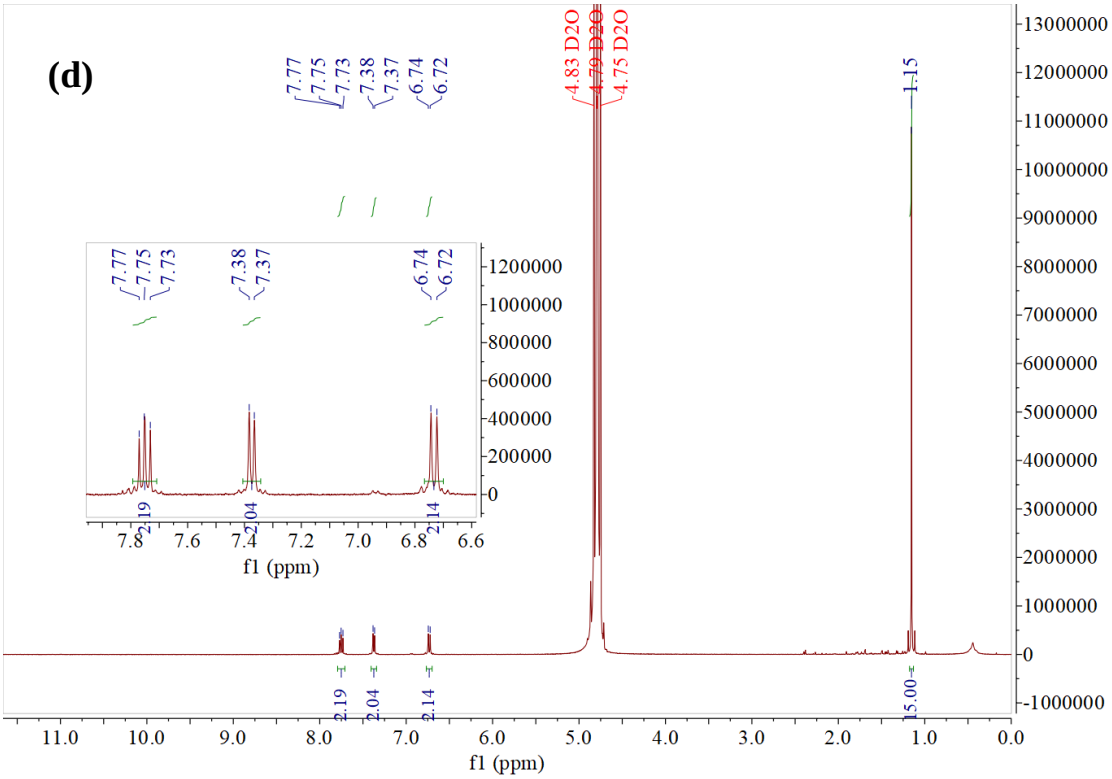
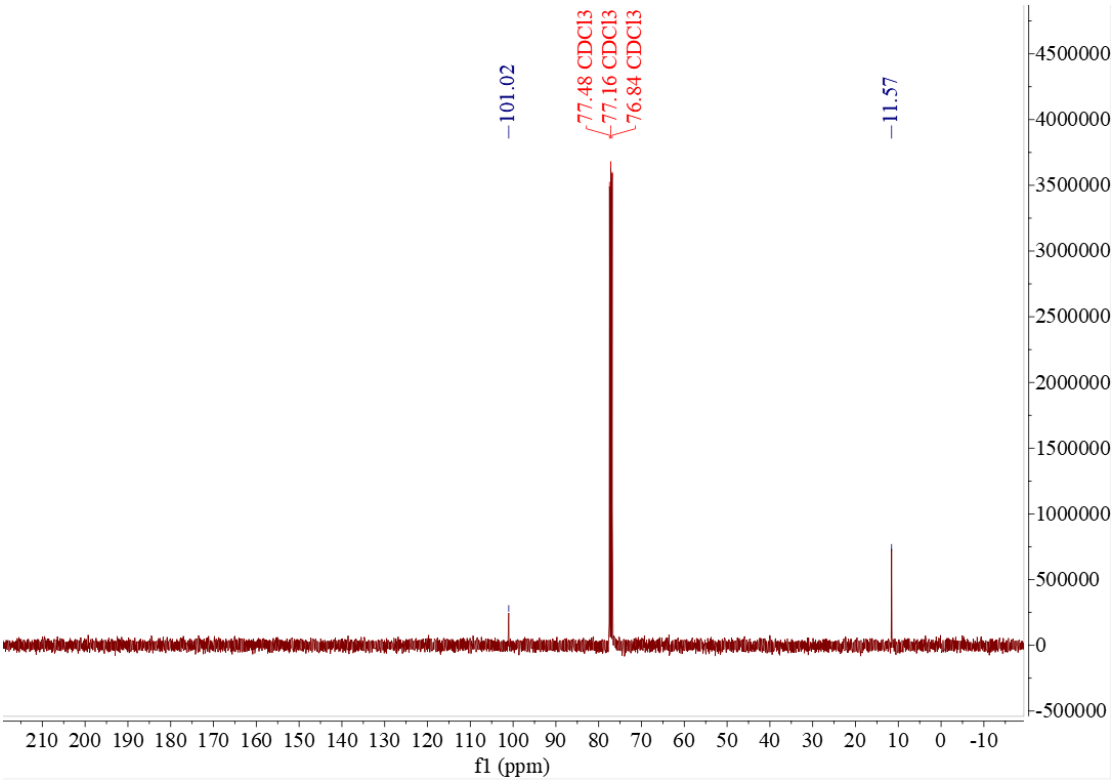
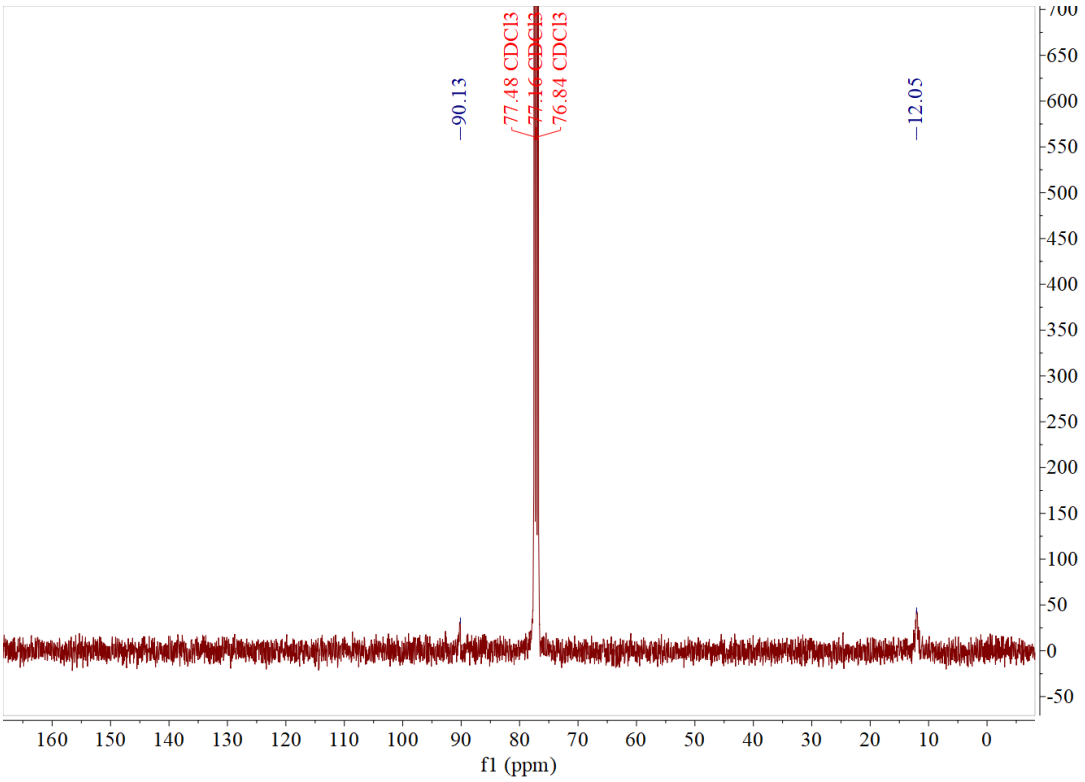
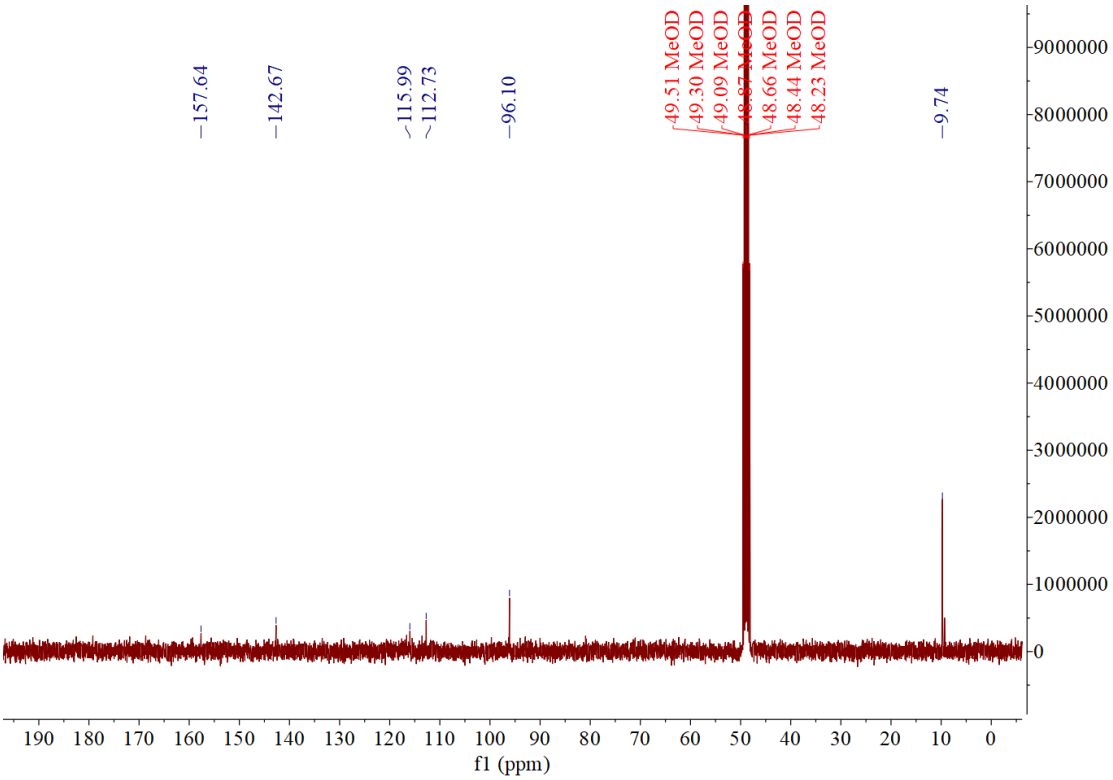


Fig. S1 ^{1}H NMR of complexes A, B, C and D; (inlet of c and d) Enlarged spectrum of 6DHBP




90.13
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
12.05
f1 (ppm)


157.64
142.67
115.99
112.73
96.10
49.51 MeOD
49.30 MeOD
49.09 MeOD
48.87 MeOD
48.66 MeOD
48.44 MeOD
48.23 MeOD
9.74
f1 (ppm)

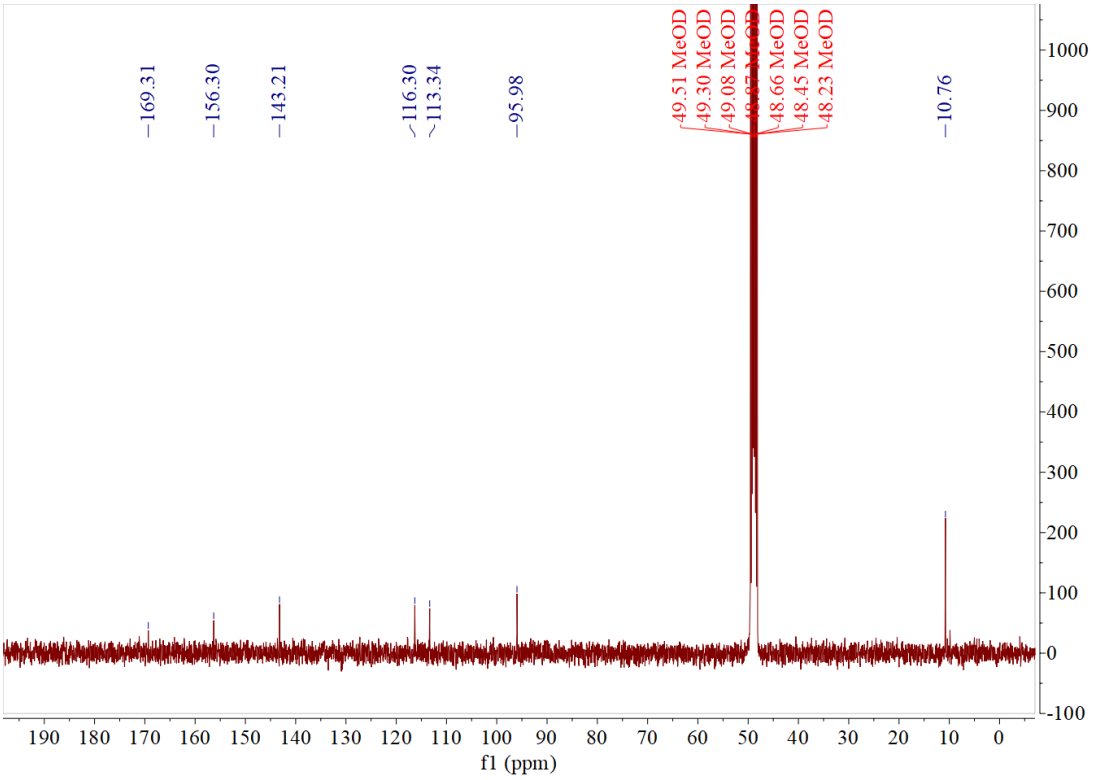


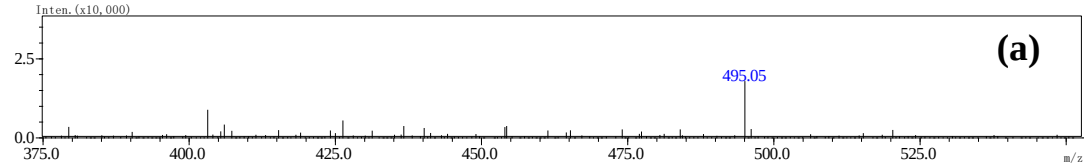
Fig. S2 ^{13}C NMR of complexes A, B, C and D;

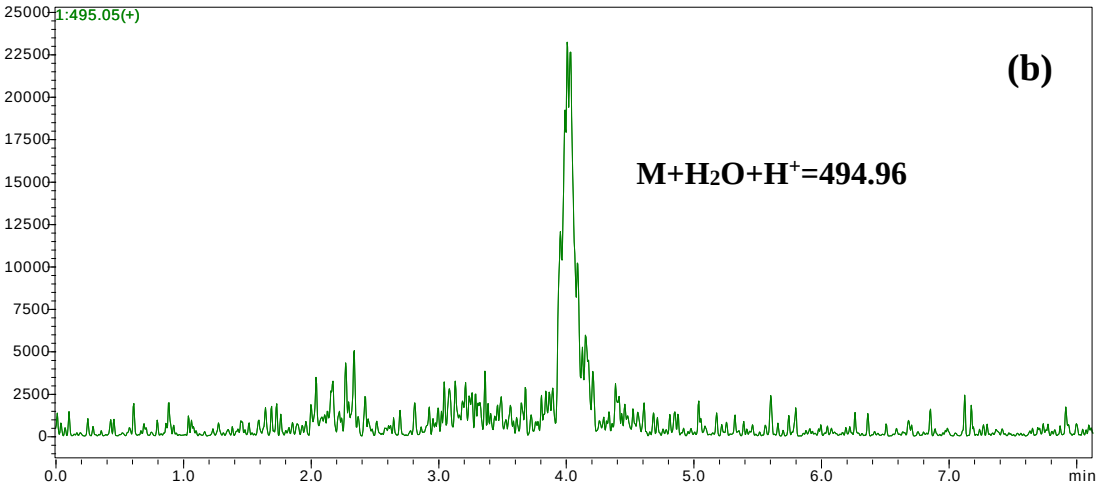
Complex A: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 15H, Cp*), ^{13}C NMR(400 MHz, $CDCl_3$): δ =11.57, 101.02 ;

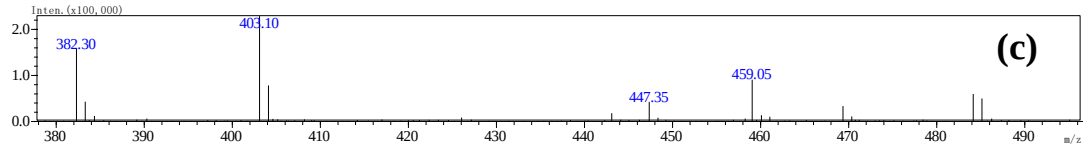
Complex B: ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 1.80 (s, 30H, Cp*), ^{13}C NMR(400 MHz, $CDCl_3$): δ =12.05, 90.13;

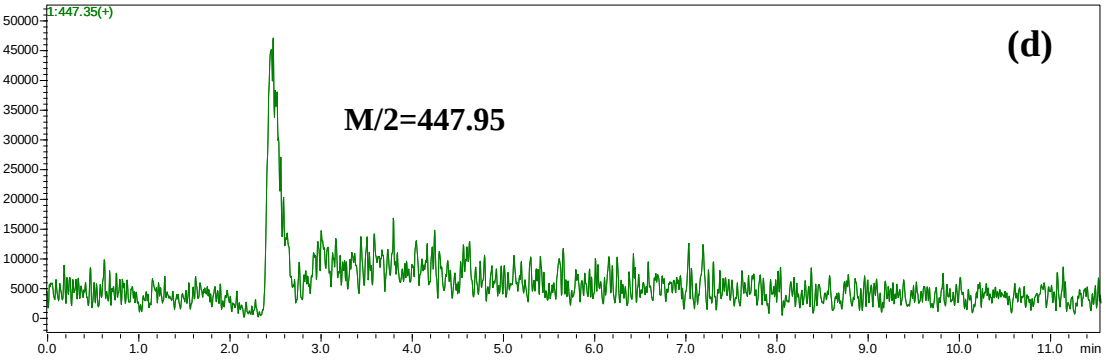
Complex C: ^{1}H NMR (400 MHz, D_2O) : δ 7.82 (t, J = 8 Hz, 2H (DHBP)), 7.47 (d, J = 8 Hz, 2H (DHBP)), 6.82 (d, J = 12 Hz, 2H (DHBP)), 1.15 (s, 15H, Cp*), ^{13}C NMR(400 MHz, MeOH): δ =9.74, 96.10, 112.73, 115.99, 142.67, 157.64;

Complex D: ^{1}H NMR (400 MHz, D_2O) : δ 7.75 (t, J = 4 Hz, 2H (DHBP)), 7.37 (d, J = 8 Hz, 2H (DHBP)), 6.72 (d, J = 8 Hz, 2H (DHBP)), 1.15 (s, 15H, Cp*), ^{13}C NMR(400 MHz, MeOH): δ = 10.76, 95.98, 113.34, 116.30, 143.21, 156.30, 169.31.


Inten. (x10, 000)
2.5
0.0
495.05
(a)
375.0
400.0
425.0
450.0
475.0
500.0
525.0
m/z


1:495.05(+)
(b)
M+H2O+H+=494.96
min


Inten. (x100, 000)
2.0
1.0
0.0
382.30
403.10
447.35
459.05
(c)
m/z


1:447.35(+)
(d)
M/2=447.95
min

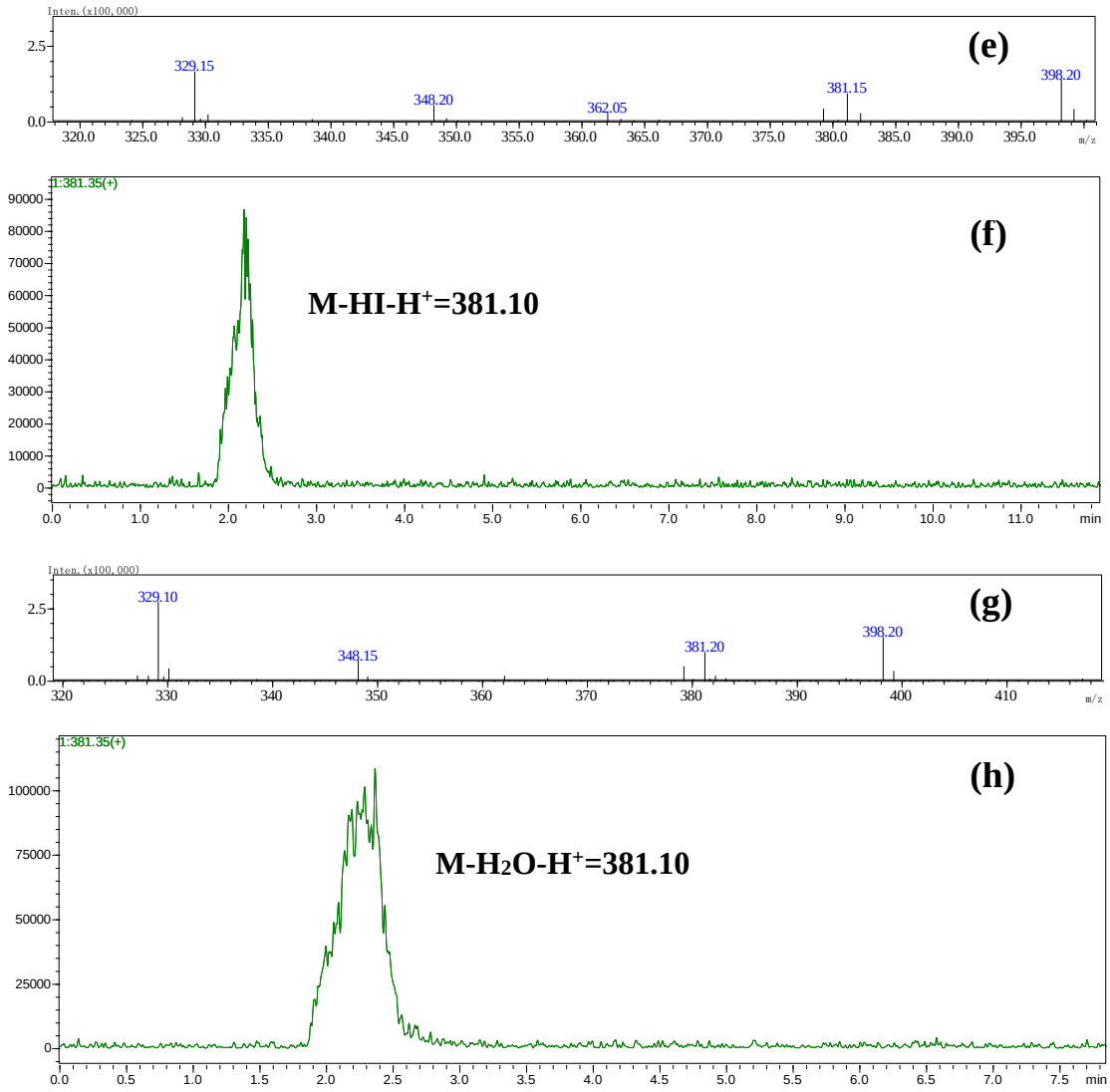


Fig. S3 (a) (c) (e) (g) Mass spectrum of A, B, C and D; (b) (d) (f) (h) Mass chromatogram of A, B, C and D.

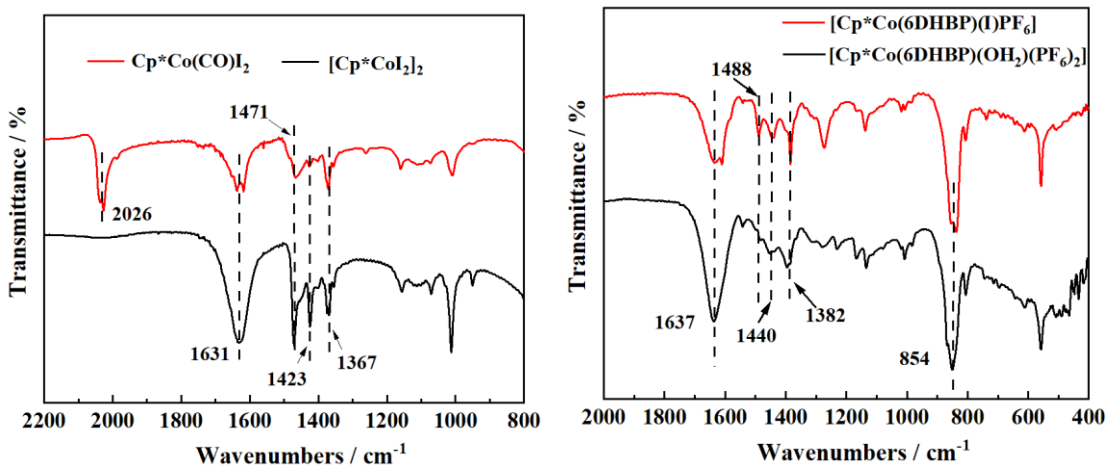


Fig. S4 FTIR of complexes A-D.

Table S1. Performance comparison of catalysts reported for AAD reaction

Cat.	Temp./ºC	Loading/mol%	Time/h	Yield/%	Reference
Cp*Ir-2	150	5	24	77	[3]
Ru-PNN	130	0.025	48	41	[4]
Ru-PNP	100	5	48	35	[5]
Ni-NNN	150	0.5	24	28	[6]
Cp*Co	130	1	14	44	This work

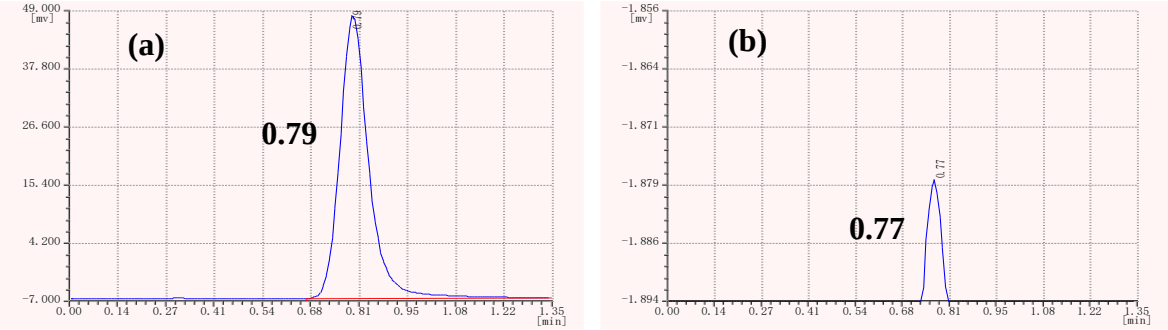


Fig. S5 GC analyses of the hydrogen gas. (a) The chromatogram of the standard gas of pure hydrogen. (b) The chromatogram of the evolved gas by the acceptorless alcohol dehydrogenate reaction.

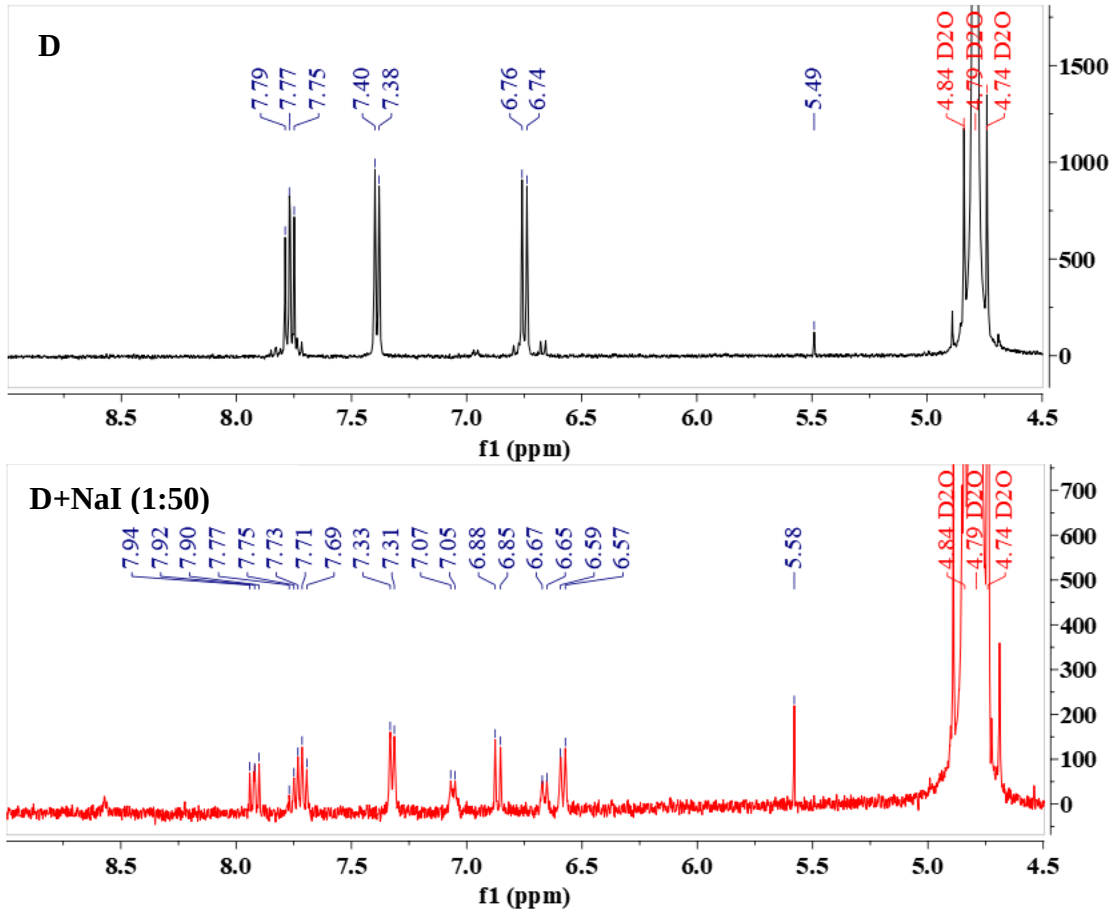


Fig. S6 ^{1}H NMR of complex D before and after adding NaI

Complex A:

I	12.65940000	7.41980000	10.83760000
C	10.71040000	11.25640000	11.65520000
C	11.86940000	10.91580000	10.88360000
C	11.41780000	10.46580000	9.58000000
C	10.00000000	10.46520000	9.58060000
C	9.55120000	10.91460000	10.88480000
C	10.71100000	11.87280000	13.02260000
H	9.82680000	11.59020000	13.59800000
H	10.71120000	12.96640000	12.93560000
H	11.59560000	11.58980000	13.59740000
C	13.29600000	11.15720000	11.26880000
H	13.94520000	10.36060000	10.89960000
H	13.41880000	11.20900000	12.35300000
H	13.64600000	12.10840000	10.84760000
C	12.29780000	10.15300000	8.41060000

H	11.85000000	9.39620000	7.76340000
H	13.27260000	9.78200000	8.72880000
H	12.45220000	11.06120000	7.81300000
C	9.12140000	10.15120000	8.41220000
H	8.14560000	9.78340000	8.73120000
H	9.56740000	9.39160000	7.76720000
H	8.96900000	11.05800000	7.81200000
C	8.12460000	11.15400000	11.27140000
H	7.47660000	10.35500000	10.90480000
H	7.77200000	12.10340000	10.84840000
H	8.00320000	11.20800000	12.35560000
Co	10.71160000	9.16660000	11.18180000
I	8.76640000	7.41720000	10.83760000
C	10.71180000	8.62940000	12.89220000
O	10.71200000	8.34520000	14.00060000

Complex B:

C	12.91040000	10.97180000	11.65520000
C	13.57720000	10.45260000	10.49860000
C	12.91280000	10.96900000	9.33920000
C	11.94320000	11.95000000	9.78600000
C	11.94140000	11.95140000	11.20400000
C	13.28440000	10.68260000	13.07700000
H	12.44920000	10.86920000	13.75540000
H	14.12200000	11.31720000	13.39420000
H	13.58560000	9.63940000	13.19900000
C	14.80480000	9.59940000	10.50080000
H	14.85840000	8.95860000	9.62020000
H	14.85620000	8.95960000	11.38240000
H	15.68520000	10.25760000	10.50140000
C	13.28960000	10.67600000	7.91900000
H	12.45760000	10.86500000	7.23780000
H	13.58680000	9.63120000	7.79980000
H	14.13100000	11.30620000	7.60320000
C	11.14000000	12.87540000	8.92580000
H	10.11660000	12.98160000	9.29440000
H	11.08740000	12.52940000	7.89300000
H	11.60800000	13.86880000	8.92620000
C	11.13600000	12.87820000	12.06060000
H	10.11320000	12.98300000	11.68980000
H	11.60360000	13.87200000	12.05920000
H	11.08140000	12.53440000	13.09420000
I	9.57660000	9.64900000	12.36640000

I	9.57700000	9.64880000	8.62640000
Co	11.47220000	9.94880000	10.49640000
I	12.10960000	7.37560000	10.49600000
C	7.20920000	7.34980000	9.78680000
C	7.21040000	7.34900000	11.20460000
C	6.24200000	8.32980000	11.65480000
C	5.57640000	8.84920000	10.49780000
C	6.24080000	8.33160000	9.33900000
C	8.01220000	6.42340000	8.92720000
H	8.06340000	6.76760000	7.89360000
H	7.54500000	5.42960000	8.93000000
H	9.03600000	6.31860000	9.29500000
C	8.01460000	6.42160000	12.06180000
H	8.06900000	6.76580000	13.09520000
H	9.03720000	6.31580000	11.69120000
H	7.54600000	5.42840000	12.06040000
C	5.86800000	8.62020000	13.07640000
H	5.56780000	9.66360000	13.19780000
H	6.70260000	8.43300000	13.75520000
H	5.02960000	7.98680000	13.39400000
C	4.34960000	9.70400000	10.49920000
H	4.29720000	10.34460000	9.61840000
H	4.29900000	10.34400000	11.38060000
H	3.46860000	9.04680000	10.49980000
C	5.86480000	8.62360000	7.91840000
H	5.56240000	9.66660000	7.79900000
H	5.02740000	7.98880000	7.60060000
H	6.69920000	8.43940000	7.23840000
Co	7.68140000	9.35080000	10.49660000
I	7.04720000	11.92520000	10.49560000

Complex C:

C	11.63580000	7.65380000	9.70780000
C	12.76420000	6.81880000	9.68740000
H	12.64940000	5.75900000	9.48440000
C	14.00920000	7.37660000	9.92460000
H	14.89640000	6.75220000	9.92260000
C	14.11600000	8.75280000	10.13340000
H	15.08720000	9.21040000	10.26640000
C	12.95740000	9.52320000	10.12700000
C	12.95660000	10.99700000	10.12680000
C	14.11440000	11.76860000	10.13340000
H	15.08600000	11.31200000	10.26660000

C	14.00640000	13.14480000	9.92440000
H	14.89300000	13.77000000	9.92240000
C	12.76100000	13.70120000	9.68660000
H	12.64500000	14.76100000	9.48360000
C	11.63340000	12.86500000	9.70700000
C	9.15600000	9.09820000	11.69120000
C	9.79560000	10.25900000	12.25140000
C	9.15540000	11.41940000	11.69120000
C	8.26220000	10.98700000	10.67300000
C	8.26240000	9.53020000	10.67300000
C	9.35040000	7.70440000	12.20100000
H	8.91960000	6.95840000	11.53580000
H	8.85160000	7.61760000	13.17440000
H	10.40480000	7.46280000	12.36260000
C	10.76800000	10.25920000	13.39240000
H	11.41000000	11.14380000	13.37720000
H	11.41040000	9.37500000	13.37720000
H	10.23860000	10.25900000	14.35360000
C	9.34940000	12.81340000	12.20080000
H	8.91800000	13.55900000	11.53540000
H	10.40360000	13.05540000	12.36220000
H	8.85060000	12.90020000	13.17420000
C	7.33560000	11.84920000	9.87500000
H	7.14700000	11.42320000	8.88860000
H	7.74540000	12.84960000	9.73080000
H	6.37500000	11.94520000	10.39720000
C	7.33620000	8.66760000	9.87500000
H	7.14900000	9.09260000	8.88780000
H	6.37500000	8.57260000	10.39620000
H	7.74580000	7.66680000	9.73240000
N	11.72420000	8.96580000	9.97480000
N	11.72280000	11.55320000	9.97440000
O	10.39680000	13.32020000	9.46740000
O	10.39960000	7.19760000	9.46840000
I	9.85320000	10.25840000	7.55280000
Co	10.23320000	10.25900000	10.17220000
H	10.43400000	6.28120000	9.16000000
H	10.43040000	14.23640000	9.15840000

Complex D:

C	10.57700000	8.84680000	8.58080000
C	11.65920000	7.98660000	8.81860000

H	11.58760000	6.93160000	8.57400000
C	12.81840000	8.52480000	9.35700000
H	13.67020000	7.88420000	9.56060000
C	12.90240000	9.90260000	9.59480000
H	13.82600000	10.33760000	9.95500000
C	11.79400000	10.69460000	9.32420000
C	11.79460000	12.17120000	9.32340000
C	12.90320000	12.96240000	9.59420000
H	13.82620000	12.52680000	9.95520000
C	12.82040000	14.34000000	9.35540000
H	13.67260000	14.98020000	9.55900000
C	11.66180000	14.87880000	8.81660000
H	11.59100000	15.93380000	8.57180000
C	10.57880000	14.01940000	8.57880000
C	7.94080000	10.26740000	10.39020000
C	8.56420000	11.43580000	10.97500000
C	7.94160000	12.60340000	10.38840000
C	7.11300000	12.16520000	9.32340000
C	7.11220000	10.70460000	9.32480000
C	8.12480000	8.86740000	10.87620000
H	7.84500000	8.12780000	10.12720000
H	7.47380000	8.71820000	11.74740000
H	9.14700000	8.67360000	11.20940000
C	9.46360000	11.43620000	12.17220000
H	10.10200000	12.32200000	12.20400000
H	10.10200000	10.55080000	12.20500000
H	8.86300000	11.43660000	13.09060000
C	8.12620000	14.00400000	10.87260000
H	7.84620000	14.74280000	10.12280000
H	9.14840000	14.19820000	11.20500000
H	7.47540000	14.15420000	11.74380000
C	6.27880000	13.01040000	8.41660000
H	6.27000000	12.61560000	7.39800000
H	6.62560000	14.04360000	8.38540000
H	5.24040000	13.01660000	8.77120000
C	6.27680000	9.85880000	8.41980000
H	6.26900000	10.25120000	7.40000000
H	5.23820000	9.85580000	8.77380000
H	6.62120000	8.82480000	8.39140000
N	10.62060000	10.14980000	8.88700000
N	10.62160000	12.71640000	8.88500000
O	9.42480000	14.41560000	8.00760000
O	9.42240000	8.45200000	8.00940000
O	8.78900000	11.42740000	6.93740000

H	9.13460000	12.20220000	6.47080000
H	9.11720000	10.63800000	6.48220000
Co	9.09180000	11.43360000	8.96080000
H	9.44900000	7.50660000	7.79540000
H	9.45260000	15.36060000	7.79320000

Reference

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