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Electronic Supplementary Information

Noninnocent ligands: heteroleptic nickel complexes with α-diimine and 1,2-diketone derivatives

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Table S1. Crystal Data and refinement details for compounds **2**–**6**.

Compound	**2**	**3**	**4**
formula	$C_{42}H_{50}N_2NiO_2$	$C_{37}H_{48}N_2NiO_2$	$C_{42}H_{60}N_2NiO_2$
Mw	673.55	611.48	683.63
crystal system	Orthorhombic	Monoclinic	Monoclinic
space group	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
a (Å)	10.5244(19)	14.730(3)	13.551(2)
b (Å)	18.501(3)	15.912(3)	16.226(3)
c (Å)	19.839(4)	15.083(3)	22.289(4)
α (°)	90	90	90
β (°)	90	92.038(2)	106.116(2)
γ (°)	90	90	90
V (Å^3)	3862.9(12)	3533.0(12)	4708.4(13)
Z	4	4	4
μ (mm^{-1})	0.537	0.581	0.441
F(000)	1440	1312	1480
ϴ range	1.505–24.707	1.383–25.136	1.564–25.090
total reflns	6554	6256	8320
R_{int}	0.0433	0.0518	0.0492
unique reflns	5341	4741	6441
R_1, wR_2 (all data)	0.0530, 0.0981	0.0704, 0.1618	0.0609, 0.1420
GOF (F^2)	0.973	1.087	0.968

Compound	**5**	**6**
formula	$C_{60}H_{86}N_4Ni_2O_2$	$C_{46}H_{60}N_2NiO_3$
Mw	1012.74	770.66
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$
a (Å)	13.990(2)	11.400(2)
b (Å)	22.730(4)	28.893(5)
c (Å)	19.155(3)	13.698(2)
α (°)	90	90
β (°)	109.140(2)	92.651(3)
γ (°)	90	90
V (Å^3)	5754.5(16)	4507.1(14)
Z	4	4
μ (mm^{-1})	0.697	0.478
F(000)	2184	1652
ϴ range	1.582–24.97	1.410–25.053
total reflns	10062	7944

unique reflns	7388	5283
R_{int}	0.0431	0.0493
R_1, wR_2 (all data)	0.0739, 0.1608	0.0910, 0.1686
GOF (F^2)	1.091	1.012

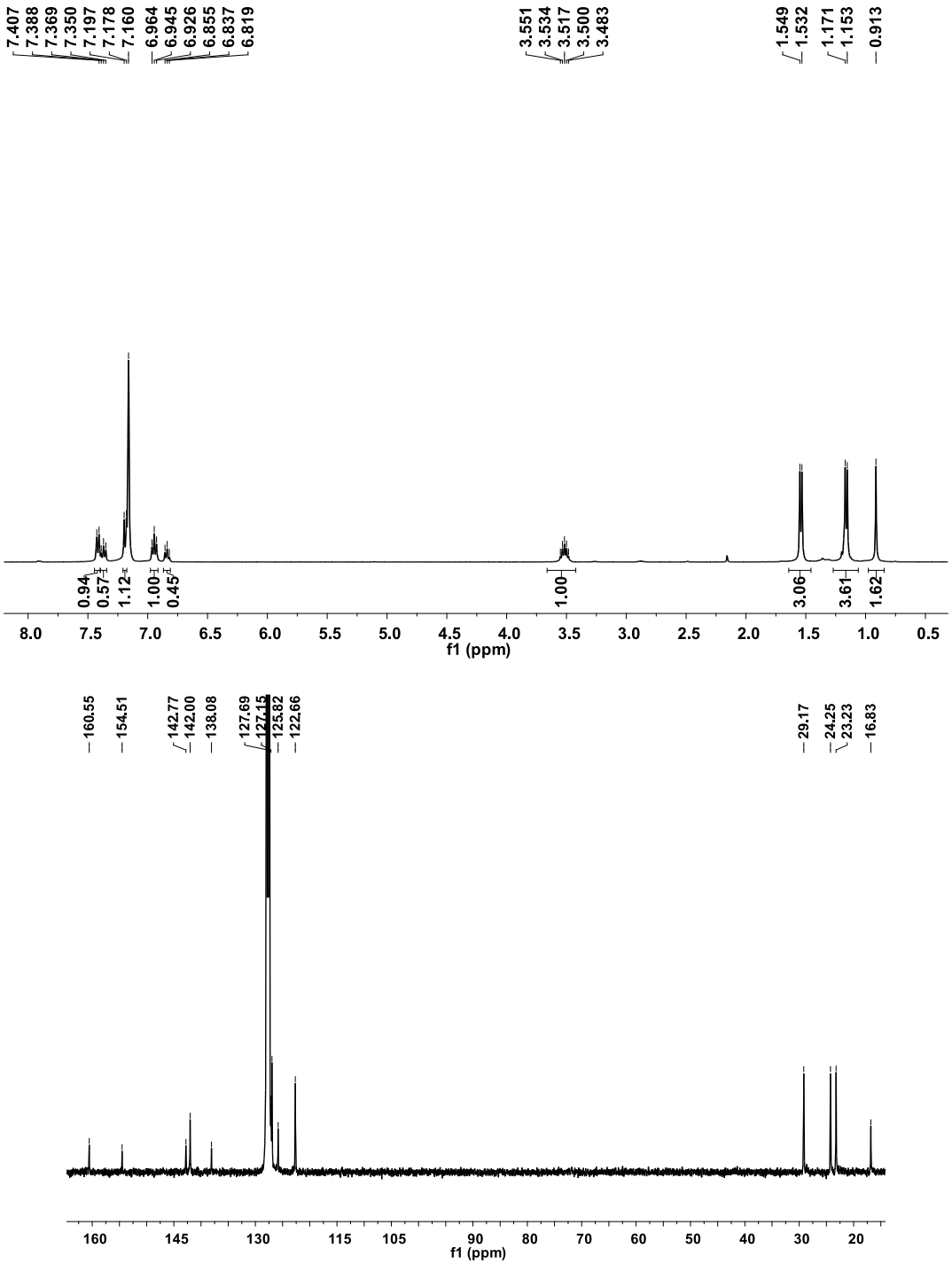

Fig. S1. ^{1}H and ^{13}C NMR of compound [$L^{0}Ni^{II}(PhC(O)–C(O)Ph)^{2–}$] (**2**).

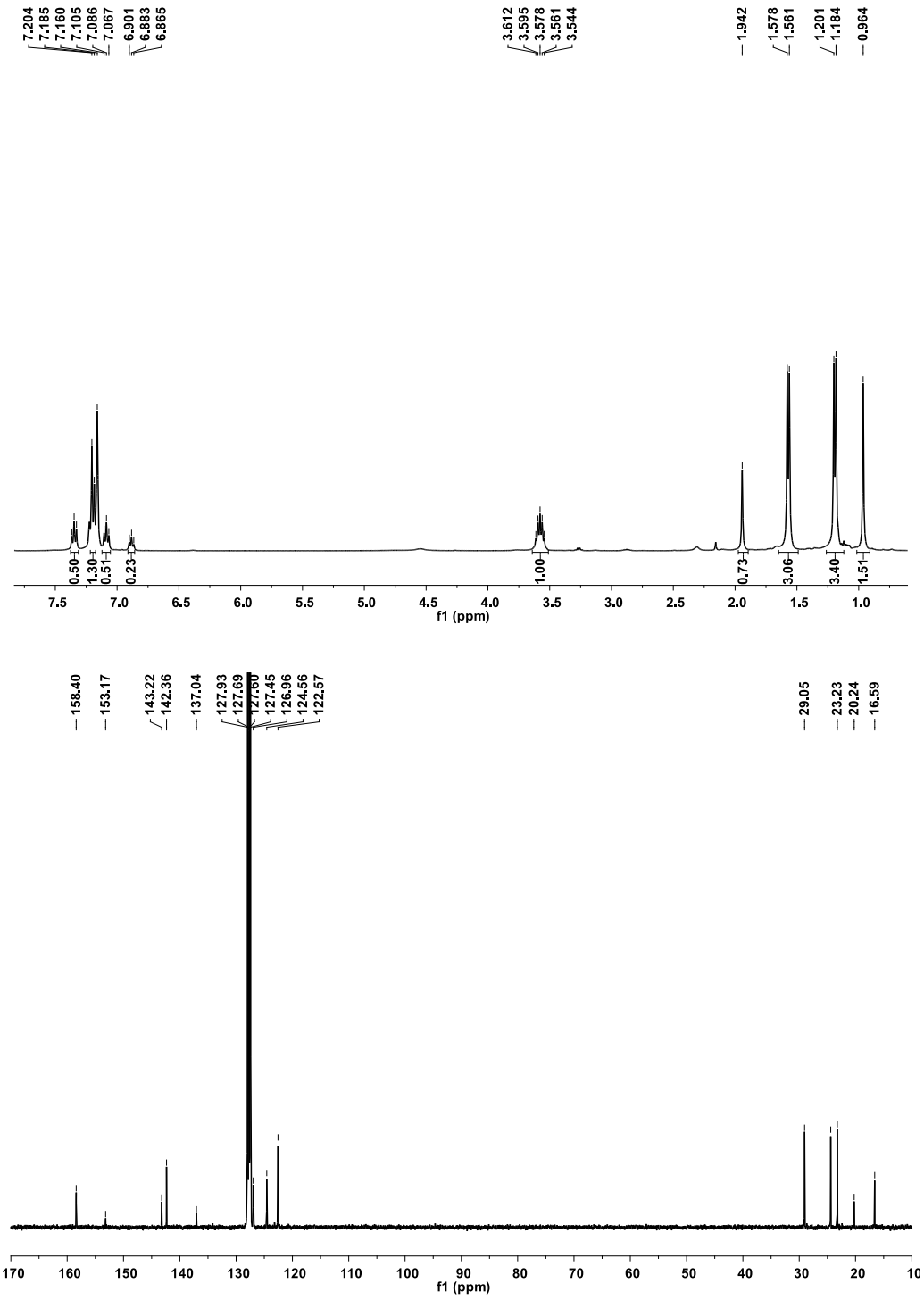

Fig. S2. ^{1}H and ^{13}C NMR of compound [$L^{0}Ni^{II}(PhC(O)–C(O)Me)^{2–}$] (**3**).

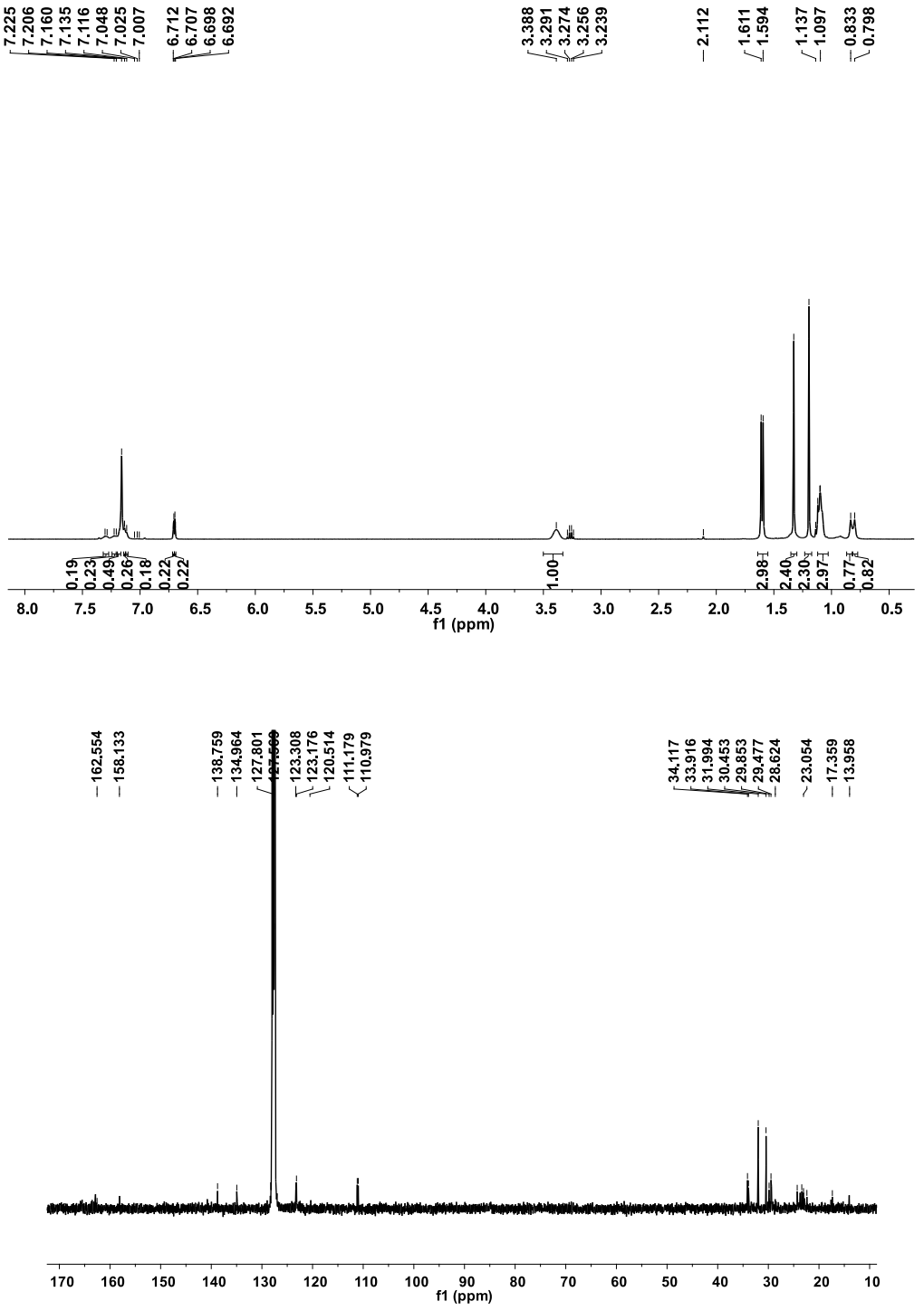

Fig. S3. ^{1}H and ^{13}C NMR of compound [LNi(3,5-*t*$Bu_2C_6H_2O_2$)] (**4**).

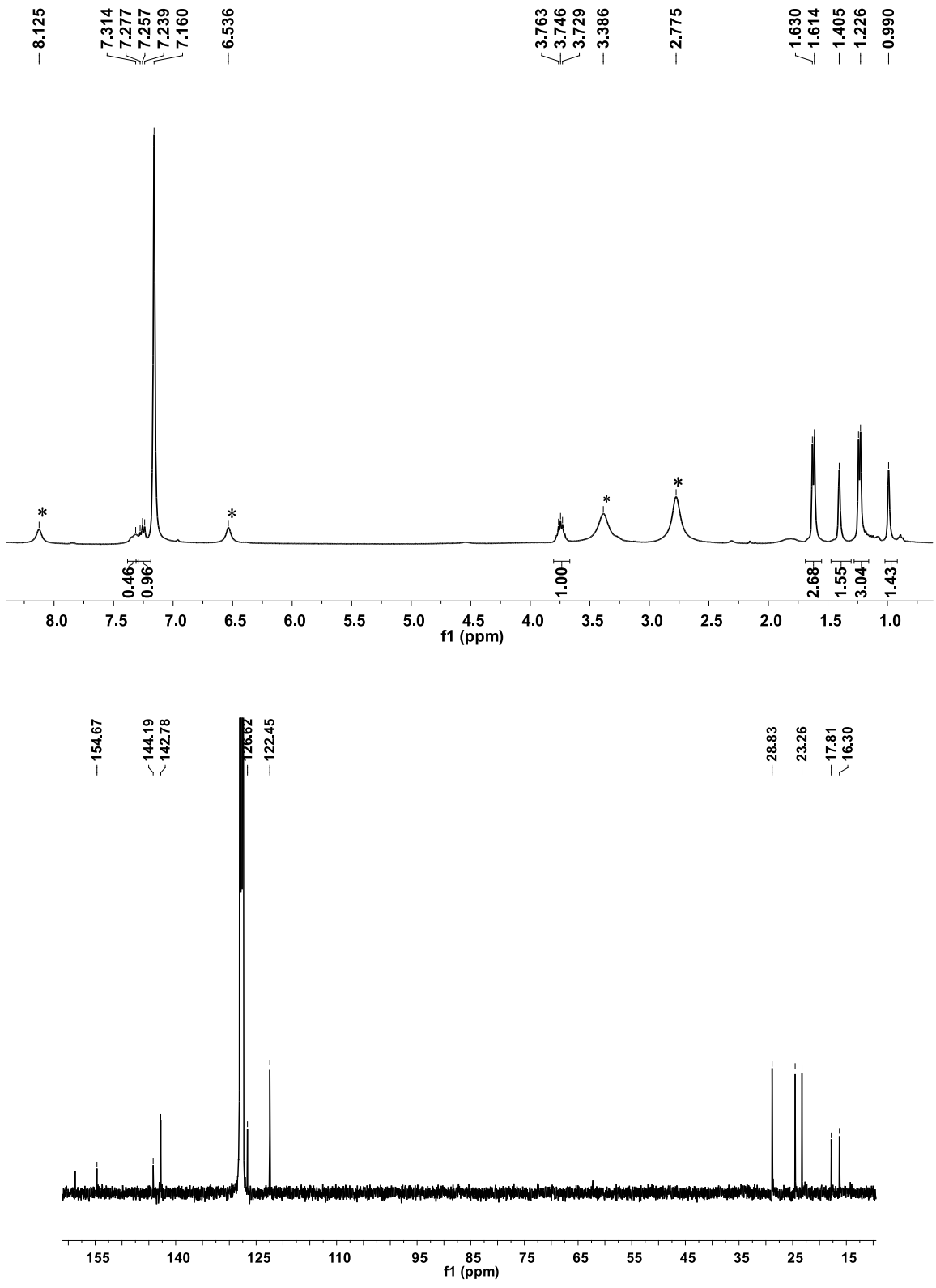

Fig. S4. ^{1}H and ^{13}C NMR of compound **5** (signals marked with * are from [{LNi}$_2$]).

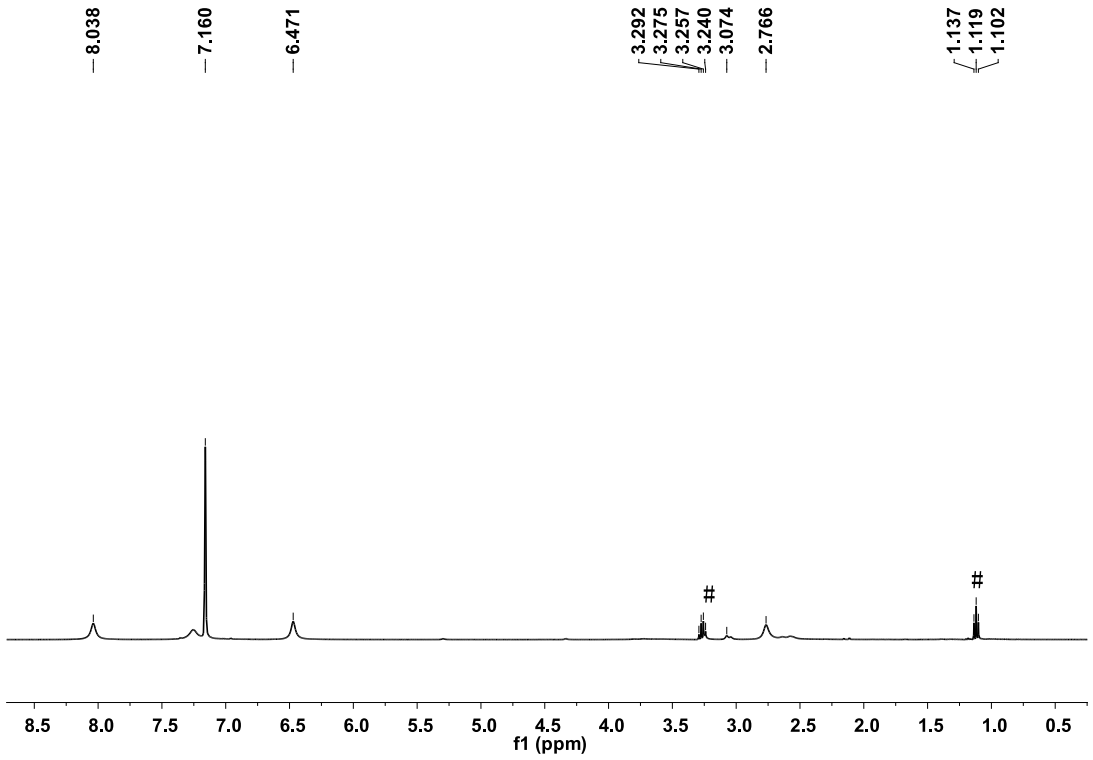

Fig. S5. ^{1}H NMR of paramagnetic compound [{LNi}$_2$] (# denotes signals corresponding to Et_2O).

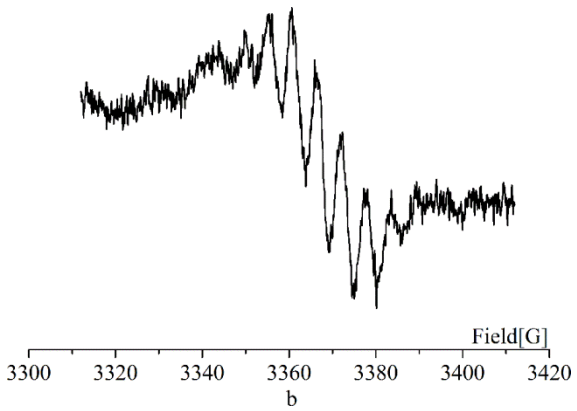

Fig. S6. EPR spectrum of **5** in C_6D_6 in relatively high concentration at room temperature.

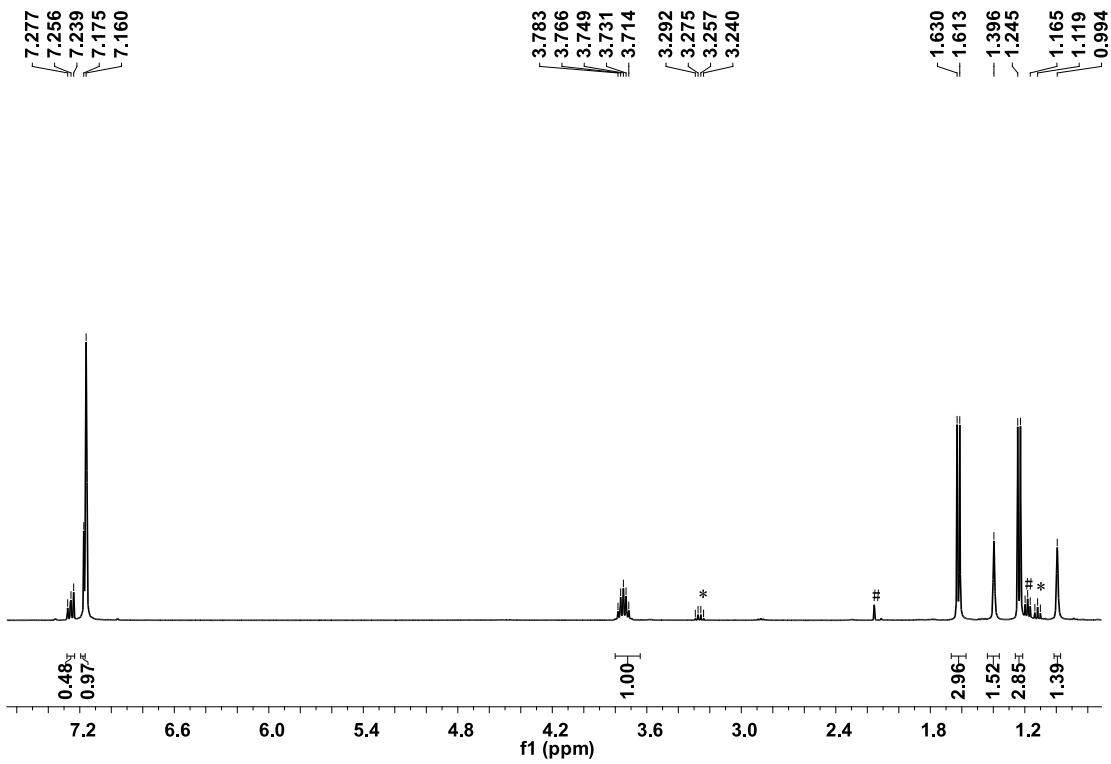

Fig. S7. ^{1}H NMR of compound [LNi(OC[Me]C[Me]O)] (* denotes signals of Et_2O, # denotes the signals corresponding to trace side products).

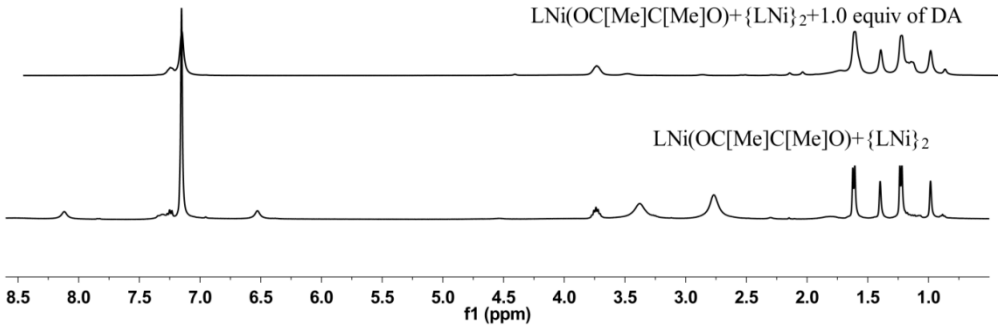

Fig. S8. ^{1}H NMR spectra of compound **5** with addition of 1.0 equiv of DA.

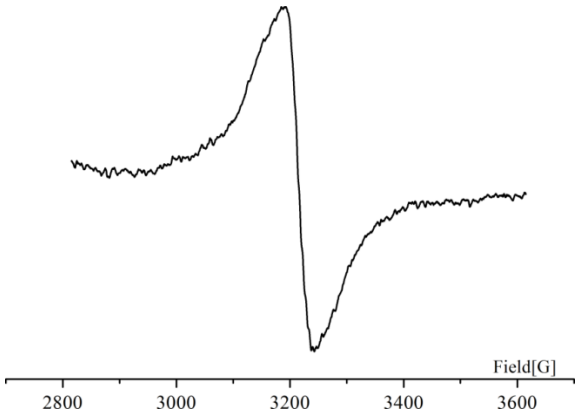

Fig. S9. EPR spectrum of **6** recorded in THF at room temperature.

S2. DFT computations

The model compounds [L'Ni(PhC(O)−C(O)Ph)] (**2'**), [L'Ni(PhC(O)−C(O)Me)] (**3'**), [(L'Ni){μ-η^2,η^2-(MeC(O)−C(O)Me)}(NiL')] (**5'**), and [Na(H_2O)][L'Ni{PhC(O)−C(O)Ph}] (**6'**) (L' = [(PhNC(Me))$_2$], in which the 2,6-*i*$Pr_2C_6H_3$ groups were replaced by Ph, and the solvent Et_2O molecule on Na atom in **6** was replaced by H_2O in **6'**) were performed using the Gaussian 09 software package[1] with the BP86 functional and 6-311G* basis set.[2] Geometry optimizations gave bond distances that were in good agreement with the X-ray structures.

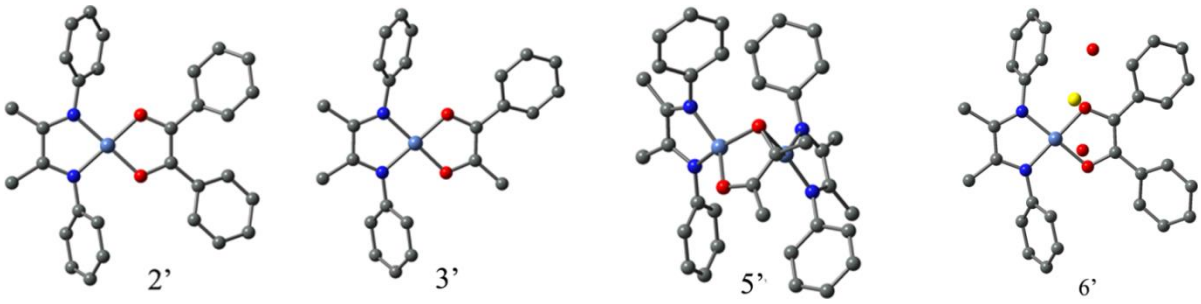

Fig. S10. Optimized structures of **2'**–**6'**.

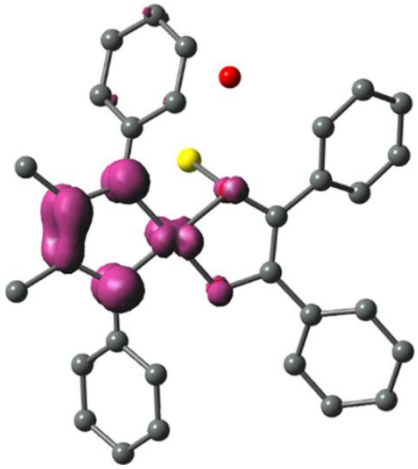

Fig. S11. Spin density of the model compound **6'**.

Table S2. Cartesian coordinates of the optimized geometry for **2'** (singlet state).

Ni	-0.91263300	-0.00015000	-0.00017600	C	-3.52938100	0.70885800	-0.07022500
O	0.42323500	-1.23537100	-0.02231300	C	-4.79141900	-1.50848500	0.25383700
O	0.42293100	1.23536900	0.02191800	H	-5.24339700	-1.81453300	-0.70723600
N	-2.28625100	-1.24256500	0.06320900	H	-5.54912500	-0.92260400	0.79601100
N	-2.28653000	1.24191900	-0.06377800	H	-4.59699000	-2.42929800	0.82200600
C	-3.52924200	-0.70982900	0.06895000	C	-4.79166600	1.50721600	-0.25570500

H	-5.24461500	1.81242300	0.70518000
H	-5.54868400	0.92145100	-0.79897700
H	-4.59703300	2.42848600	-0.82304700
C	-2.08017800	-2.64037100	0.21583900
C	-1.31618900	-3.11299400	1.30014500
C	-1.10082400	-4.48557900	1.46008200
H	-0.51543800	-4.84268500	2.31320600
C	-1.62675000	-5.39963700	0.53597300
H	-1.45206000	-6.47237000	0.66181000
C	-2.37038200	-4.92983400	-0.55588000
H	-2.77004700	-5.63410000	-1.29224900
C	-2.59636600	-3.55914100	-0.71896400
C	-2.08080200	2.63986700	-0.21568100
C	-2.59748500	3.55795100	0.71952000
C	-2.37182600	4.92880300	0.55730900
H	-2.77187400	5.63252800	1.29398800
C	-1.62802000	5.39944000	-0.53406300
H	-1.45356500	6.47229000	-0.65922400
C	-1.10162700	4.48606200	-1.45858100
H	-0.51611700	4.84382900	-2.31134100
C	-1.31668300	3.11332300	-1.29952700
C	1.64771600	-0.69931300	-0.09013000
C	1.64755500	0.69963500	0.08985200
C	2.75125300	-1.63097700	-0.36332100
C	2.58317800	-3.00134900	-0.05384800
H	1.64381100	-3.32358000	0.40163700
C	3.59035800	-3.92678800	-0.33986700
H	3.44334100	-4.98161300	-0.08570300
C	4.78179900	-3.51250500	-0.95232400
H	5.56950200	-4.23854400	-1.17694300
C	4.94868800	-2.16103400	-1.29125200
H	5.86283900	-1.83084600	-1.79512000
C	3.94503600	-1.23113800	-1.00871700
H	4.07645100	-0.18768600	-1.30534900
C	2.75081800	1.63157300	0.36312800
C	3.94512900	1.23194400	1.00769200
H	4.07721600	0.18840600	1.30370100
C	4.94846100	2.16216900	1.29027000
H	5.86303000	1.83211700	1.79346800
C	4.78075400	3.51377000	0.95224600
H	5.56822600	4.24005400	1.17688900
C	3.58879200	3.92783000	0.34065500
H	3.44110300	4.98273900	0.08722800
C	2.58194000	3.00206500	0.05456600
H	1.64216800	3.32409700	-0.40022200
H	-0.90509100	2.39081100	-2.00724600
H	-3.15093200	3.18573600	1.58647400
H	-0.90496900	-2.38995800	2.00755000
H	-3.14968900	-3.18759800	-1.58628400

Table S3. Cartesian coordinates of the optimized geometry for **3'** (singlet state).

Ni	-0.53287400	0.04112500	-0.01859700
O	1.26086800	-0.22790200	-0.00267800
O	-0.67074500	-1.77323500	-0.00508600
N	-0.41597900	1.88938900	-0.08536300
N	-2.36022900	0.33720900	0.00659500
C	-1.61045300	2.52811500	-0.10599900
C	-2.72193000	1.64166000	-0.04404600
C	-1.77093500	4.01893100	-0.24519700
H	-0.88187200	4.47357000	-0.70385100
H	-1.92718600	4.52377100	0.72544600
H	-2.64144900	4.25748200	-0.87590200
C	-4.14475200	2.12913500	0.02356800
H	-4.79245100	1.39821100	0.52797400
H	-4.58032800	2.30915600	-0.97623100
H	-4.20414300	3.07898200	0.57683800
C	0.80804300	2.60914100	-0.05060400
C	1.79300700	2.35785400	-1.02547400
C	3.00305700	3.05853900	-0.99648500
H	3.75836800	2.85706900	-1.76216800
C	3.25382100	4.00409500	0.00764900
H	4.20360100	4.54710000	0.02819400
C	2.28505500	4.24059700	0.99368600
H	2.47925800	4.96188200	1.79383300
C	1.07040100	3.54825600	0.96826400
C	-3.33056000	-0.70024700	0.04002700
C	-4.29531200	-0.83803200	-0.97793800
C	-5.23424400	-1.87356000	-0.92294300
H	-5.97465000	-1.97398900	-1.72284500

C	-5.22071000	-2.78477200	0.14267700	H	6.90483500	-2.53422000	0.08409600
H	-5.95637100	-3.59370800	0.18376600	C	4.94517400	-3.31580900	-0.42683900
C	-4.25238300	-2.65917400	1.14856400	H	5.33247200	-4.27405000	-0.78854800
H	-4.22990300	-3.37035200	1.98017000	C	3.56911900	-3.07071100	-0.46838800
C	-3.30647400	-1.63107700	1.09653600	H	2.90753400	-3.82836700	-0.89470900
C	1.60643400	-1.52917300	-0.02825800	C	0.46477600	-3.89228700	0.07669700
C	0.50784400	-2.39459000	-0.00209100	H	-0.46602500	-4.19258400	0.58197000
C	3.03807700	-1.83947200	-0.01382400	H	1.32006200	-4.30227200	0.63486400
C	3.94512300	-0.85311200	0.44651300	H	0.45536100	-4.36236600	-0.92398400
H	3.54411800	0.10814800	0.77600300	H	1.59181100	1.61003900	-1.79377600
C	5.31808500	-1.10371800	0.48227400	H	0.32619400	3.70765400	1.75398100
H	5.99853000	-0.32859000	0.85014300	H	-2.54247400	-1.52671000	1.86915200
C	5.82836800	-2.33884500	0.05393900	H	-4.28411000	-0.14491300	-1.82406800

Table S4. Cartesian coordinates of the optimized geometry for **5'** (singlet state).

Ni	0.62780700	1.03877600	0.47532100	C	3.35071100	-3.37838600	-2.37257400
Ni	-0.69164100	-1.03643800	0.54415400	H	4.32688100	-3.72416400	-2.73019300
N	2.33264200	1.36913000	-0.10571100	C	2.64033800	-2.39928500	-3.08851800
N	-0.43686500	-2.03491300	-0.99119600	H	3.06367000	-1.97432600	-4.00611100
N	-2.50634900	-1.30506100	0.18216800	C	-4.78524300	0.92923900	2.14198600
N	0.11863600	2.13933900	-0.97563900	H	-4.93309300	2.00037800	2.32240700
C	-1.57570400	-2.49655100	-1.57257600	C	-5.40980300	-1.38061100	2.53311300
C	0.82992900	-2.49354100	-1.45395700	H	-6.04023600	-2.12845000	3.02853400
C	-2.76154900	-2.01313500	-0.94913300	O	-0.76006300	0.52377300	1.60921400
C	-3.56611300	-0.85591700	1.01499500	O	0.66566400	-1.67471000	1.72290600
C	1.39168200	-1.95333000	-2.63241300	C	0.42083700	0.56620800	2.36376100
C	-4.14972400	-2.24244000	-1.49801600	C	1.06402900	-0.71919700	2.49219900
H	-4.83006400	-1.43799000	-1.17375400	C	3.98358700	-0.38437500	0.38224000
H	-4.59534400	-3.19559300	-1.15065500	C	5.12724600	-0.82231600	1.06737700
H	-4.14473700	-2.26676700	-2.60118700	H	5.49177500	-1.84275400	0.90369500
C	-3.76849800	0.51874400	1.26866100	C	4.18269700	1.78833600	1.47030000
C	-1.56205000	-3.43748400	-2.75042700	C	3.50595200	0.92855000	0.57788900
H	-0.87083000	-4.28000300	-2.56971900	C	5.32377000	1.33977900	2.15462900
H	-1.21794100	-2.94420800	-3.68014500	H	5.84256700	2.01662200	2.84352500
H	-2.56425100	-3.85319100	-2.93855600	C	5.80197300	0.03380900	1.95433400
C	1.54859500	-3.47052100	-0.73093600	H	6.69344800	-0.31443500	2.48764300
C	-4.39607900	-1.80244200	1.66311600	C	0.50062200	1.64263500	3.41853800
C	-5.61246400	-0.01172300	2.77755500	H	0.05737900	2.57752600	3.03886700
H	-6.40463100	0.31723300	3.45930300	H	1.54834800	1.84732700	3.69917000
C	2.80003600	-3.90584900	-1.19138700	H	-0.05065900	1.35355100	4.33566900
H	3.34572200	-4.66962900	-0.62494200	C	2.18487200	-0.97500600	3.46153000

H	2.55875700	-2.00175200	3.33130600	H	3.87803800	3.59040400	-1.95119500
H	1.83861600	-0.84325100	4.50458000	H	3.80468800	2.09558400	-2.91078300
H	3.01945600	-0.26856000	3.29935000	H	4.59663800	2.08647500	-1.31626200
C	-1.19967700	2.51744300	-1.34937700	C	1.00648300	3.28835300	-3.03859700
C	-2.11307800	1.56399900	-1.84946200	H	0.14832700	2.90488200	-3.61794400
C	-1.62492400	3.85597300	-1.18394600	H	1.91161500	3.20547600	-3.66205100
C	-2.93254000	4.23157100	-1.52042800	H	0.81673100	4.36683600	-2.87287100
H	-3.24900300	5.27174800	-1.37980100	H	1.11671100	-3.86958600	0.19141000
C	-3.41919700	1.95036400	-2.18684400	H	0.84154200	-1.17412500	-3.17065000
H	-4.11694000	1.20037000	-2.57650000	H	-3.12934700	1.25061500	0.77030400
C	-3.83667500	3.28152700	-2.02571500	H	-4.21730900	-2.86998200	1.49253100
H	-4.85975300	3.57523900	-2.28492000	H	-1.78691900	0.52572700	-1.96570500
C	2.43356500	2.13086700	-1.22684100	H	-0.92125100	4.58746000	-0.77095000
C	1.16593800	2.52845800	-1.74605300	H	3.45284800	-1.04735100	-0.30869100
C	3.74393300	2.49440400	-1.87984300	H	3.80375600	2.80632000	1.61460900

Table S5. Cartesian coordinates of the optimized geometry for **6'** (doublet state).

C	-0.04038500	-3.63164700	-0.47049400	H	-6.78480800	-0.50837500	0.58158200
C	-1.42413800	-3.41229200	-0.36796700	C	-5.13113700	-1.73132700	1.27509100
C	0.58796600	-4.99025000	-0.64185600	H	-5.66768500	-2.10458000	2.15371600
H	1.53209000	-4.92107100	-1.20329700	C	-3.81610300	-2.14735000	1.04061800
H	-0.07931800	-5.66816500	-1.19607200	C	0.71604400	1.58178900	-0.36428400
H	0.82105900	-5.49169700	0.31565200	C	-0.65117900	1.75909800	-0.23023500
C	-2.44475300	-4.52192000	-0.40016800	C	1.82858700	2.53344000	-0.24780500
H	-2.63936400	-4.96055200	0.59476400	C	3.09224900	2.18547500	-0.79567300
H	-2.10891400	-5.34576900	-1.04908300	H	3.17217400	1.25685500	-1.36572500
H	-3.40910400	-4.16209000	-0.78682300	C	4.20680600	3.02121800	-0.63808100
C	2.09932700	-2.49260400	-0.40995900	H	5.16347300	2.73655600	-1.08983200
C	2.74834700	-3.16992500	0.65844600	C	4.09949400	4.22358900	0.07536800
C	4.14182100	-3.14126400	0.78917700	H	4.96883300	4.87637400	0.19807200
H	4.61706800	-3.67732900	1.61730500	C	2.85971700	4.57486400	0.63435300
C	4.92912100	-2.42890500	-0.13211300	H	2.76346600	5.50091500	1.21057200
H	6.01970400	-2.42617700	-0.04393300	C	1.74681200	3.74360300	0.48590700
C	4.29492500	-1.75204300	-1.19230100	H	0.79943900	4.02454100	0.95242600
H	4.89794500	-1.21264800	-1.93028300	C	-1.46452700	2.98368900	-0.25235300
C	2.90524500	-1.77645800	-1.33008100	C	-1.08162800	4.14292300	-0.96749800
C	-3.10486800	-1.68045900	-0.08696000	H	-0.14544600	4.14075400	-1.53222900
C	-3.73259200	-0.75672600	-0.94860000	C	-1.89652300	5.27787000	-0.98244900
C	-5.04694100	-0.34598000	-0.71036900	H	-1.58026200	6.16061500	-1.54797800
H	-5.52020600	0.36503200	-1.39485900	C	-3.12453500	5.28219300	-0.30245400
C	-5.75589100	-0.83306800	0.39807300	H	-3.76348400	6.17071100	-0.32133700

C	-3.53339800	4.12852500	0.38080300
H	-4.49865800	4.11095800	0.89778700
C	-2.71937000	2.99164100	0.40209300
H	-3.05371100	2.08229100	0.90733900
N	0.69959600	-2.46986300	-0.52540700
N	-1.77451200	-2.08693400	-0.34699100
Na	1.68085200	-0.38446000	1.62976500
Ni	-0.33427500	-0.90764700	-0.41167500
O	1.09860400	0.26809200	-0.50361800
O	-1.34954800	0.59643400	-0.06131500

O	3.89381700	0.21132000	1.67143100
O	-0.35180900	0.11307300	2.55839400
H	4.38164100	-0.48160000	1.17949100
H	3.95004500	1.01797800	1.11658200
H	-0.64636500	0.78677500	3.19239100
H	-0.91554900	0.21971800	1.74582500
H	-3.31777800	-2.82371900	1.74116100
H	-3.17222000	-0.37548000	-1.80423300
H	2.41005700	-1.25102500	-2.14835000
H	2.14113700	-3.71658100	1.38713300

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