Electronic Supplementary Information

Synthetic Analogs for Evaluating the Influence of N-H---S Hydrogen Bonding on the Formation of Thioester in Acetyl Coenzyme A Synthase

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Figures

Figure S-1 through **Figure S-4**. $^{31}P\{^{1}H\}$ NMR spectra of addition of thioesters to *in situ* generated (dRpe)Ni(COD).

Figure S-5. $^{31}P\{^{1}H\}$ NMR spectra (C_6D_6) of the thiolate exchange reaction showing the equilibrium mixture reached by mixing **2** and **8** (upper spectrum) or **3** and **7** (lower spectrum).

Figure S-6 through **Figure S-12**. $^{31}P\{^{1}H\}$ NMR spectral titrations of **2-4, 7-10** with CO.

Figure S-13. Thermal ellipsoid plot **1**.

Figure S-14. Thermal ellipsoid plot of $(dppe)Ni(CO)_2$.

Figure S-15 through **Figure S-17**. $^{31}P\{^{1}H\}$, ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra of **6** in C_6D_6.

Figure S-18. Chemical Ionization mass spectrum of **6**.

Table S1. Percent yields of (dRpe)Ni(C(O)Me)(SAr) in low temperature NMR scale reactions.

Table S2 through **Table S12.** DFT optimized atomic coordinates for molecules contained in Figure 5.

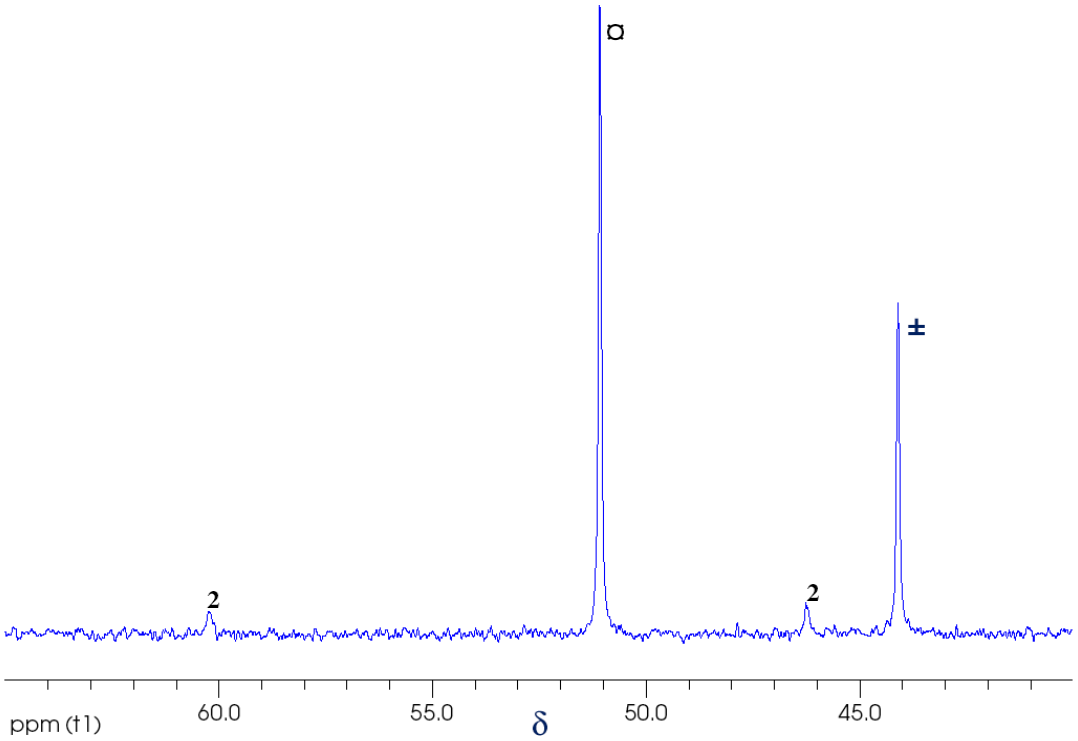

Figure S-1. $^{31}P\{^{1}H\}$ NMR spectrum (THF) of the products of the oxidative addition of $CH_3C(O)SPh$ to (dppe)Ni(COD). ¤ = (dppe)Ni(COD), ± = $Ni(dppe)_2$

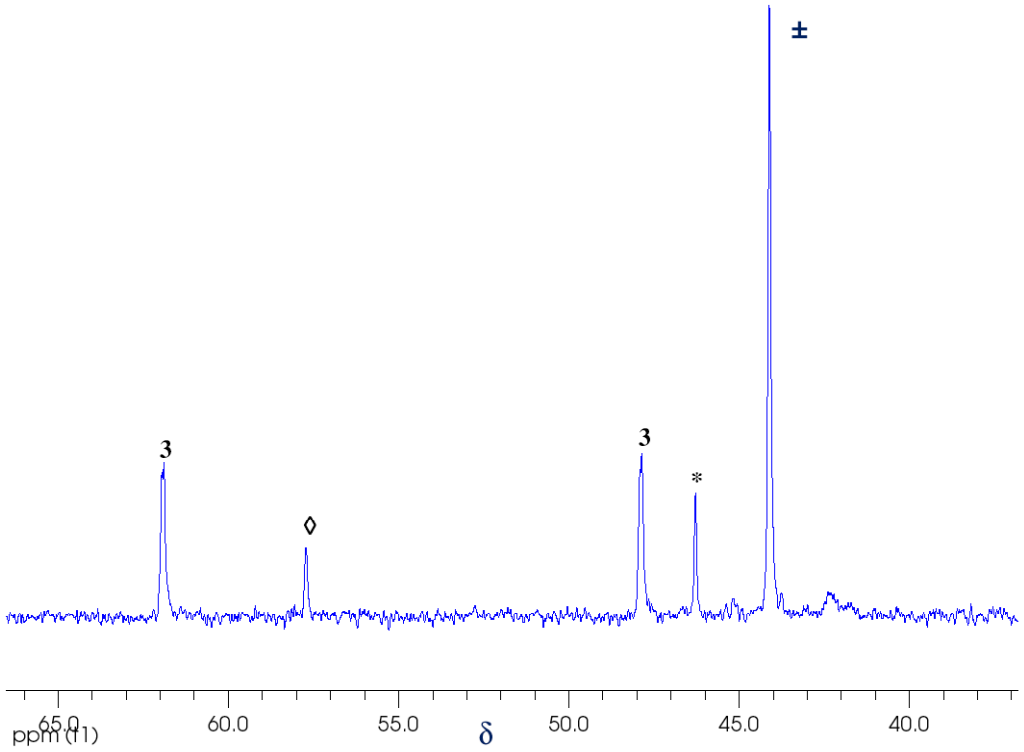

Figure S-2. $^{31}P\{^{1}H\}$ NMR spectrum (THF) of the products of the oxidative addition of $CH_3C(O)SC_6F_5$ to (dppe)Ni(COD). ◊ = $(dppe)Ni(SC_6F_5)_2$, * = $(dppe)Ni(CO)_2$, ± = $Ni(dppe)_2$

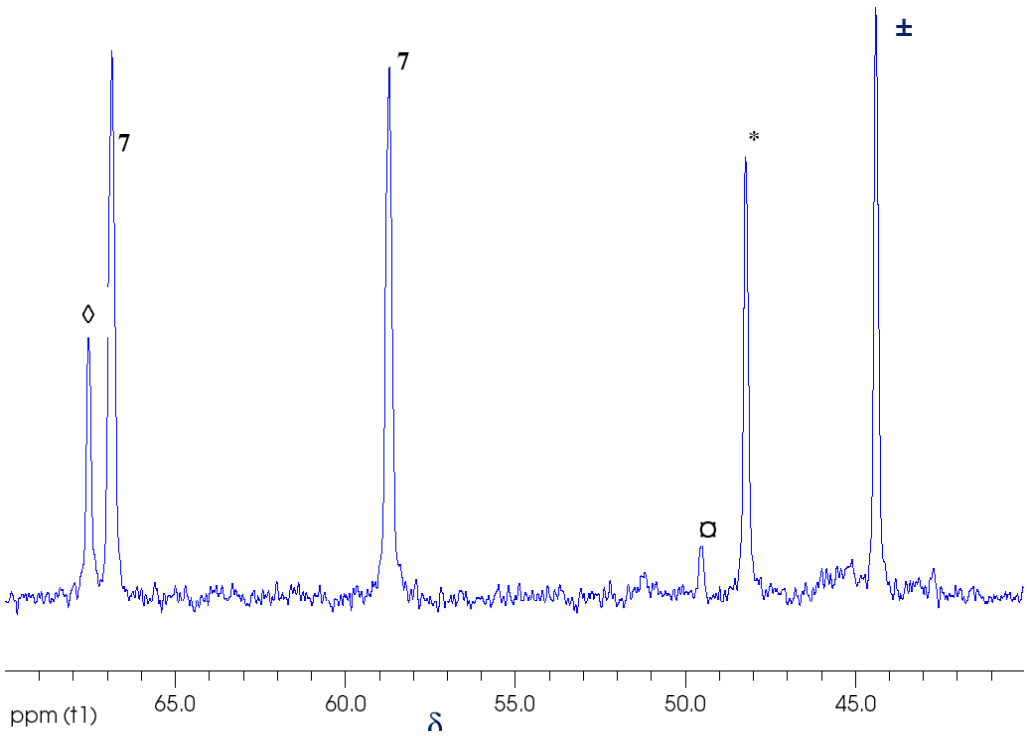

Figure S-3. $^{31}P\{^{1}H\}$ NMR spectrum (THF) of the products of the oxidative addition of $CH_3C(O)SPh$ to (depe)Ni(COD). ◊ = (depe)Ni$(SPh)_2$, * = (depe)Ni$(CO)_2$, ¤ = (depe)Ni(COD), ± = Ni(depe)$_2$

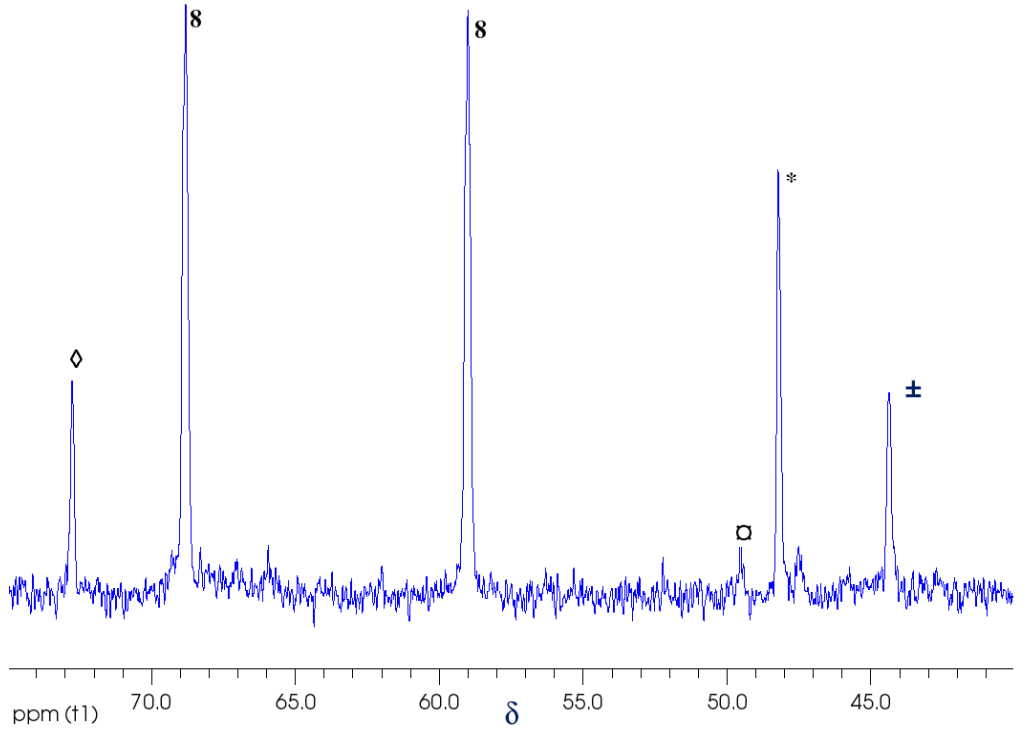

Figure S-4. $^{31}P\{^{1}H\}$ NMR spectrum (THF) of the products of the oxidative addition of $CH_3C(O)SC_6F_5$ to (depe)Ni(COD). ◊ = (depe)Ni$(SC_6F_5)_2$, * = (depe)Ni$(CO)_2$, ¤ = (depe)Ni(COD), ± = Ni(depe)$_2$

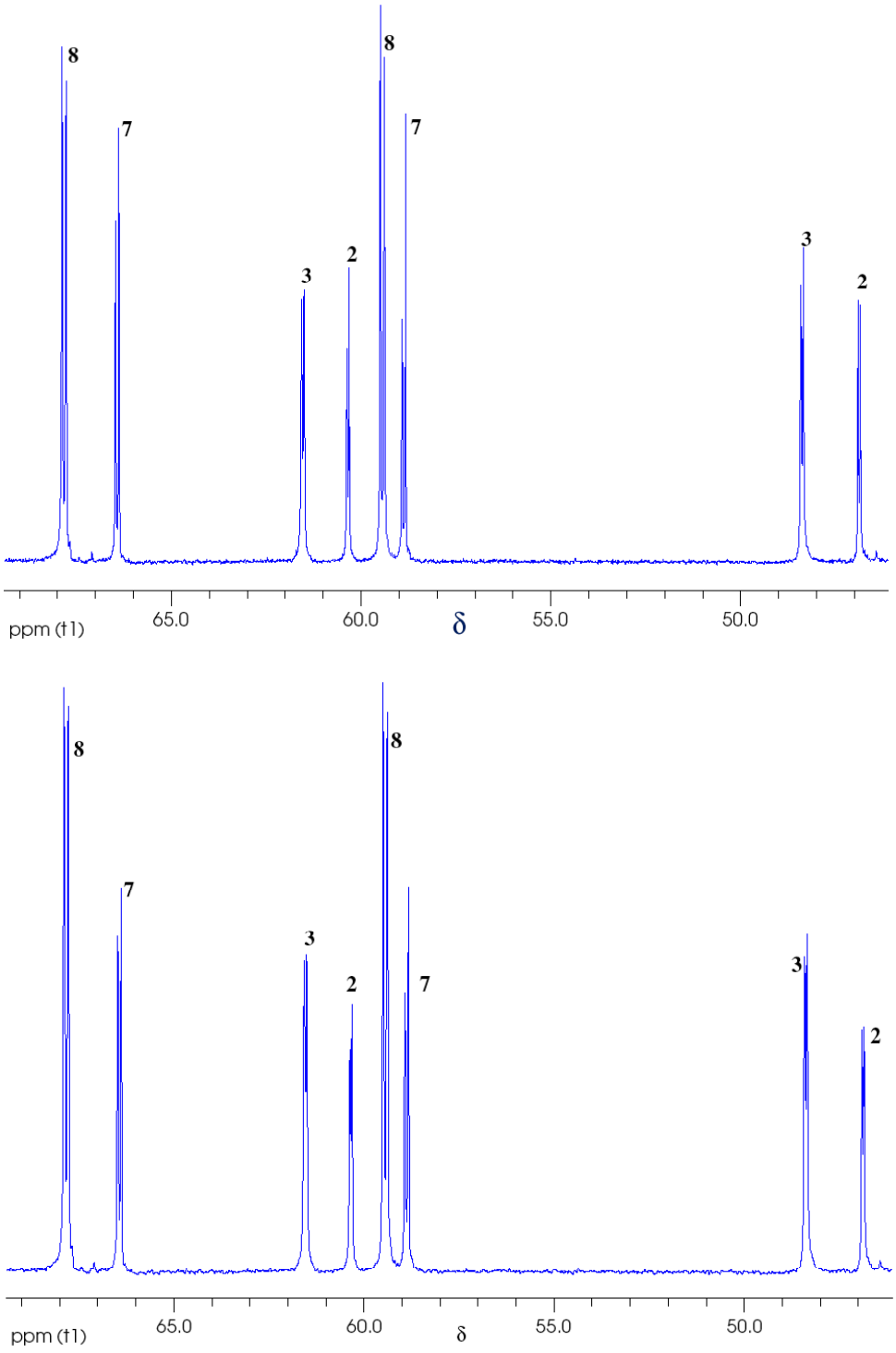

Figure S-5. $^{31}P\{^{1}H\}$ NMR spectra (C_6D_6) of the thiolate exchange reaction showing the equilibrium mixture reached by mixing **2** and **8** (upper spectrum) or **3** and **7** (lower spectrum).

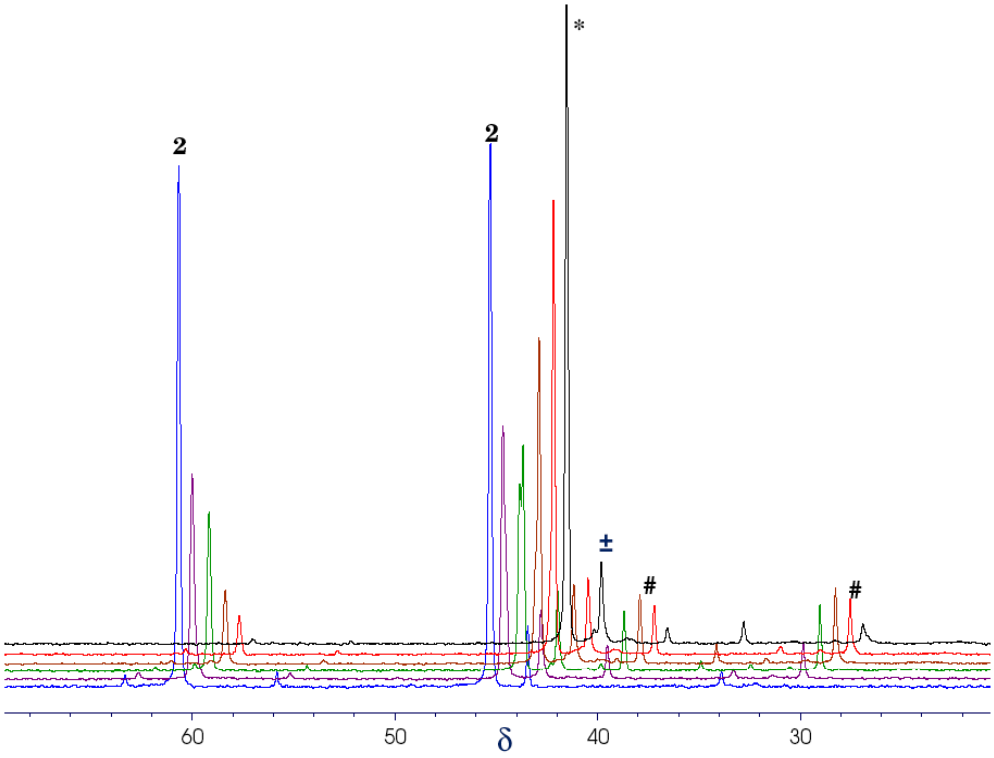

Figure S-6. $^{31}P\{^{1}H\}$ NMR spectral titration of **2** with 0.5 equivalents of CO in THF at -78 ºC * = $(dppe)Ni(CO)_2$, # = (dppe)Ni(C(O)Me)(SPh), **±** = $Ni(dppe)_2$

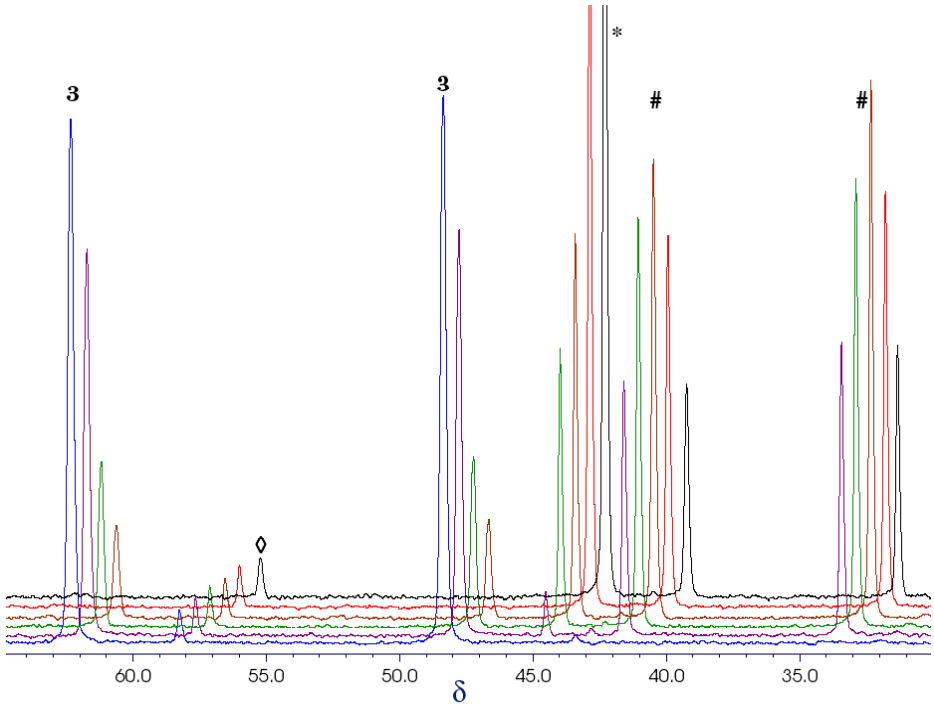

Figure S-7. $^{31}P\{^{1}H\}$ NMR spectral titration of **3** with 0.5 equivalents of CO in THF at -78 ºC * = $(dppe)Ni(CO)_2$, # = (dppe)Ni(C(O)Me)(SPh), ◊ = $(dppe)Ni(SC_6F_5)_2$

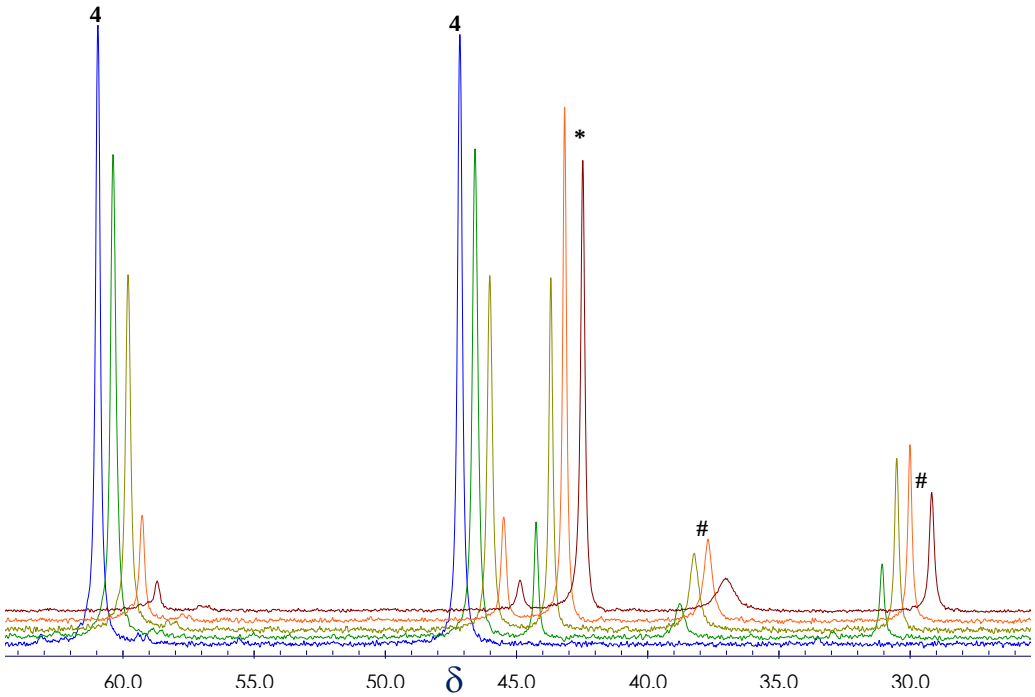

Figure S-8. $^{31}P\{^{1}H\}$ NMR spectral titration of **4** with 0.5 equivalents of CO in THF at -78 ºC, * = $(dppe)Ni(CO)_2$, # = (dppe)Ni(C(O)Me)(o-pabt).

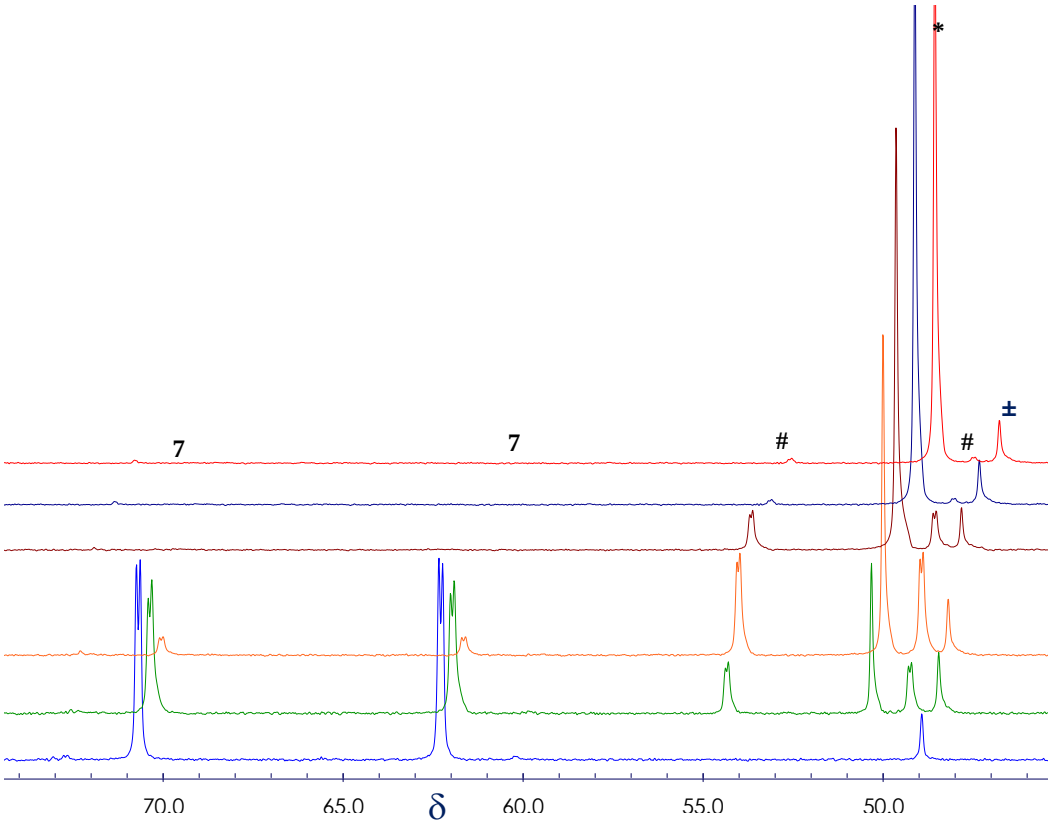

Figure S-9. $^{31}P\{^{1}H\}$ NMR spectral titration of **7** with 0.5 equivalents of CO in THF at -78 ºC, * = $(depe)Ni(CO)_2$, # = (depe)Ni(C(O)Me)(SPh) ± = $Ni(depe)_2$.

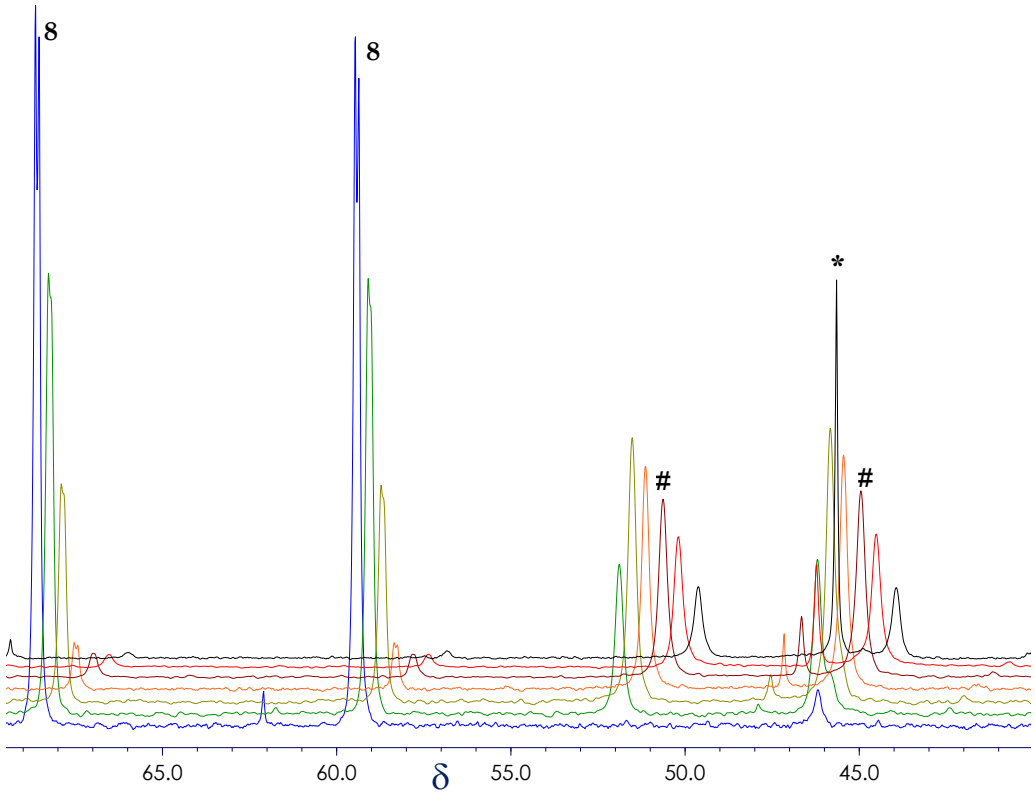

Figure S-10. $^{31}P\{^{1}H\}$ NMR spectral titration of **8** with 0.5 equivalents of CO in THF at -78 ºC, * = $(depe)Ni(CO)_2$, # = $(depe)Ni(C(O)Me)(SC_6F_5)$.

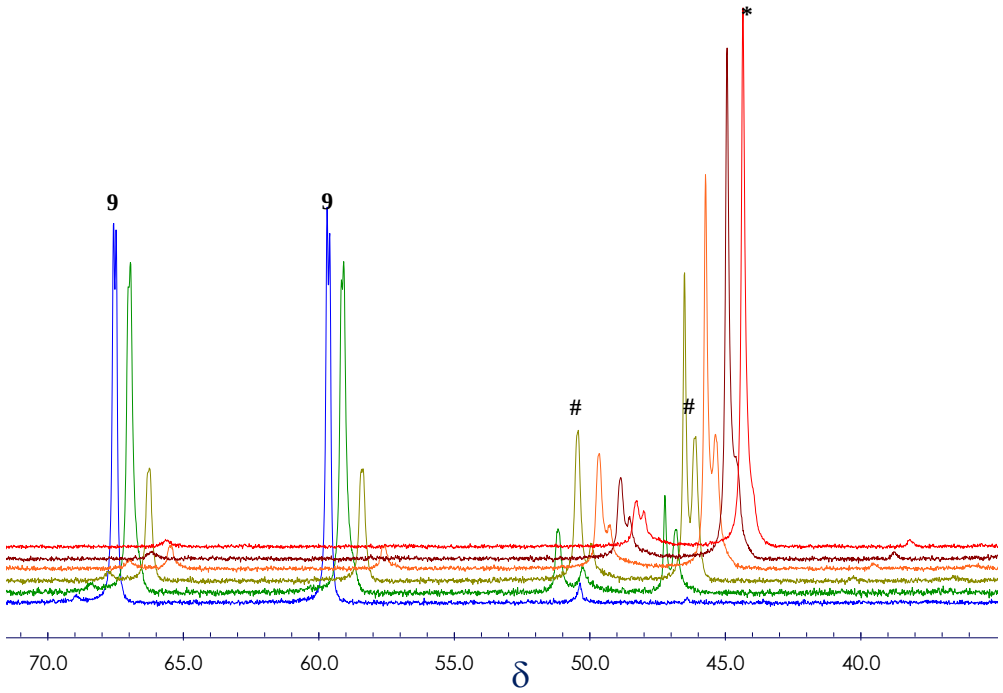

Figure S-11. $^{31}P\{^{1}H\}$ NMR spectral titration of **9** with 0.5 equivalents of CO in THF at -78 ºC, * = $(depe)Ni(CO)_2$, # = (depe)Ni(C(O)Me)(*o*-pabt).

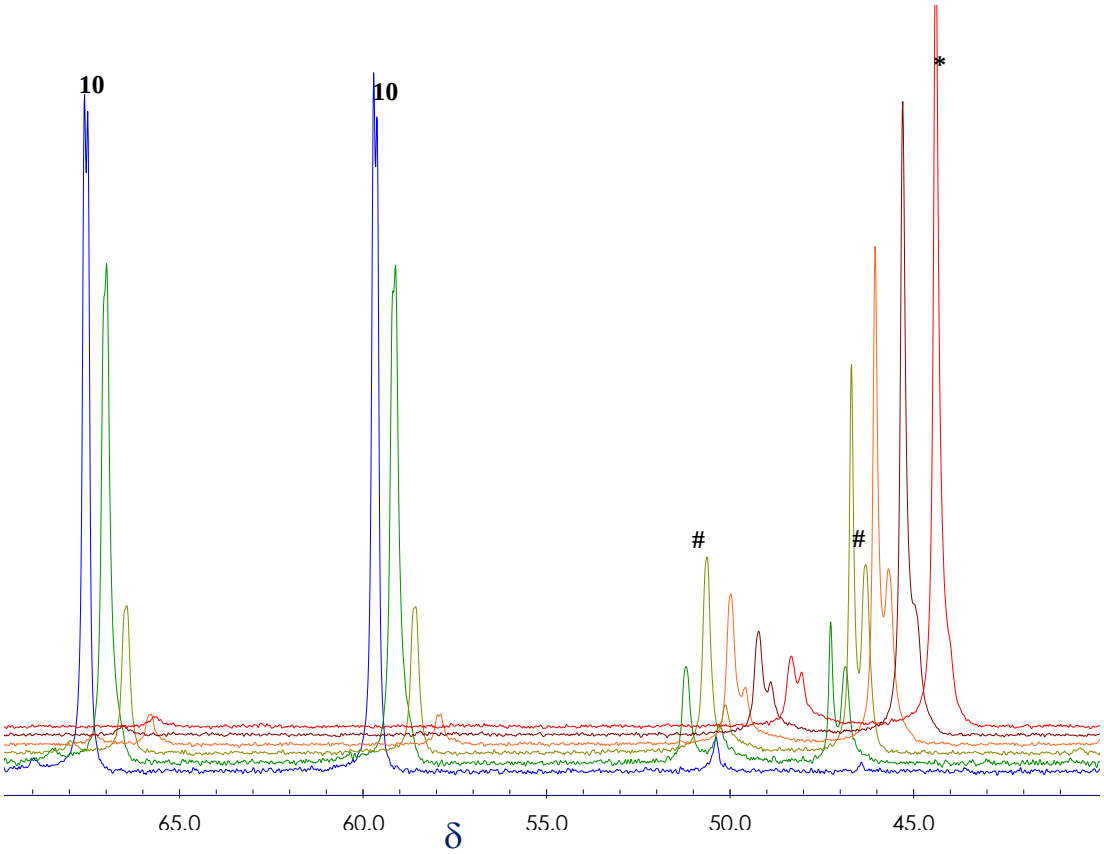

Figure S-12. $^{31}P\{^{1}H\}$ NMR spectral titration of **10** with 0.5 equivalents of CO in THF at -78 ºC , * = $(depe)Ni(CO)_2$, # = (depe)Ni(C(O)Me)(*p*-pabt).

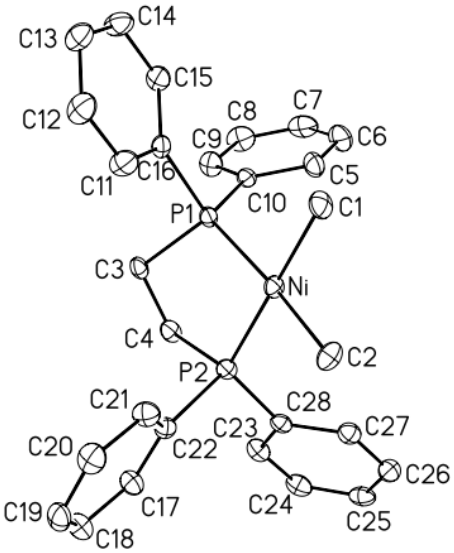

Figure S-13. Thermal ellipsoid plot **1**.

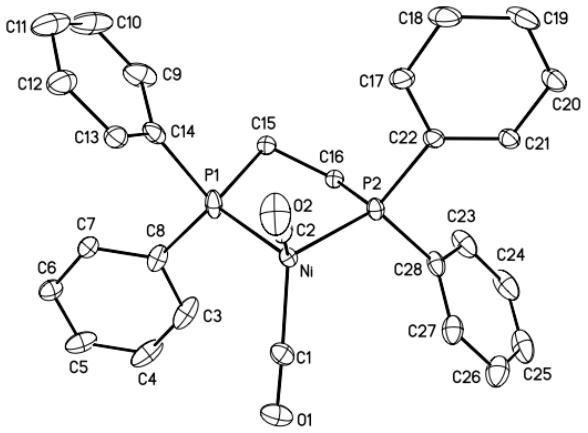

Figure S-14. Thermal ellipsoid plot of (dppe)Ni(CO)$_2$.

Table S-1: Percent spectroscopic yields of (dRpe)Ni(C(O)Me)(SAr) in low temperature NMR scale carbonylation reactions.

Compound	Percent yield of (dRpe)Ni(C(O)Me)(SAr) formed
2	11
3	56
4	26
7	53
8	74
9	55
10	39

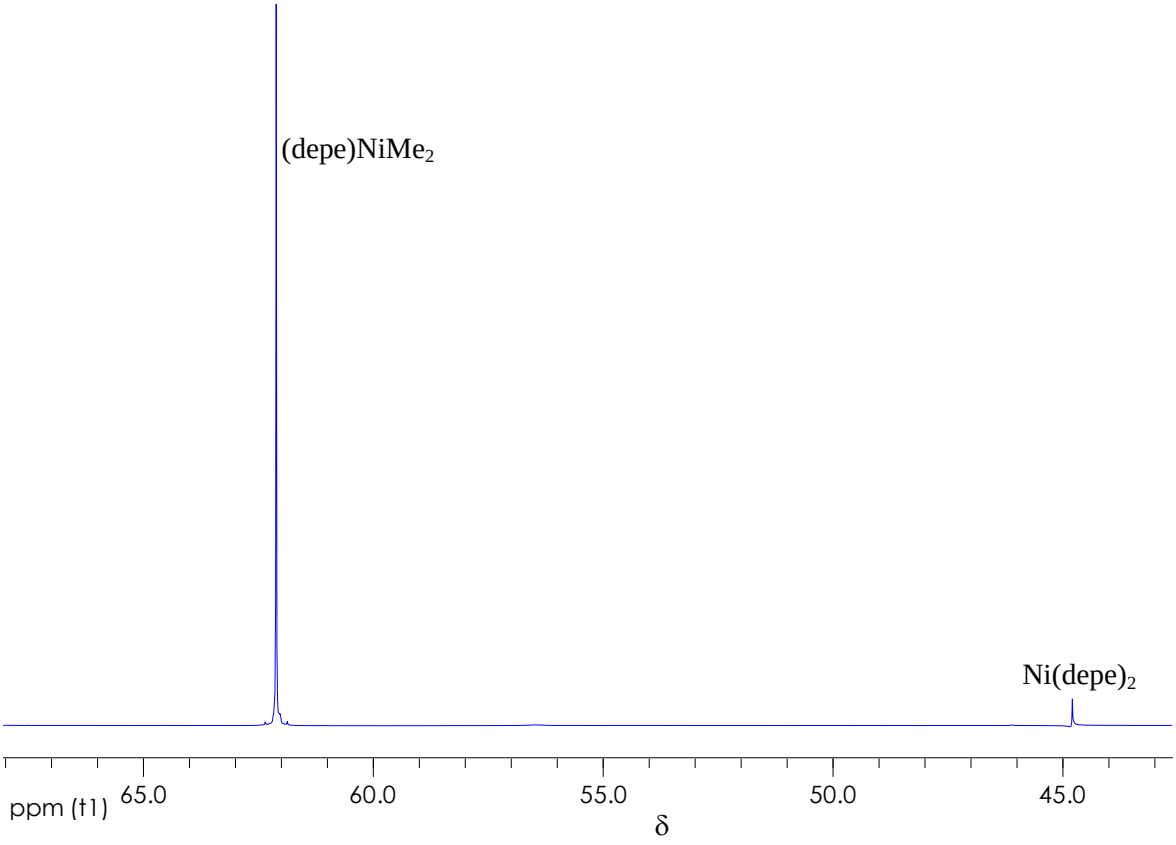

Figure S-15. $^{31}P\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

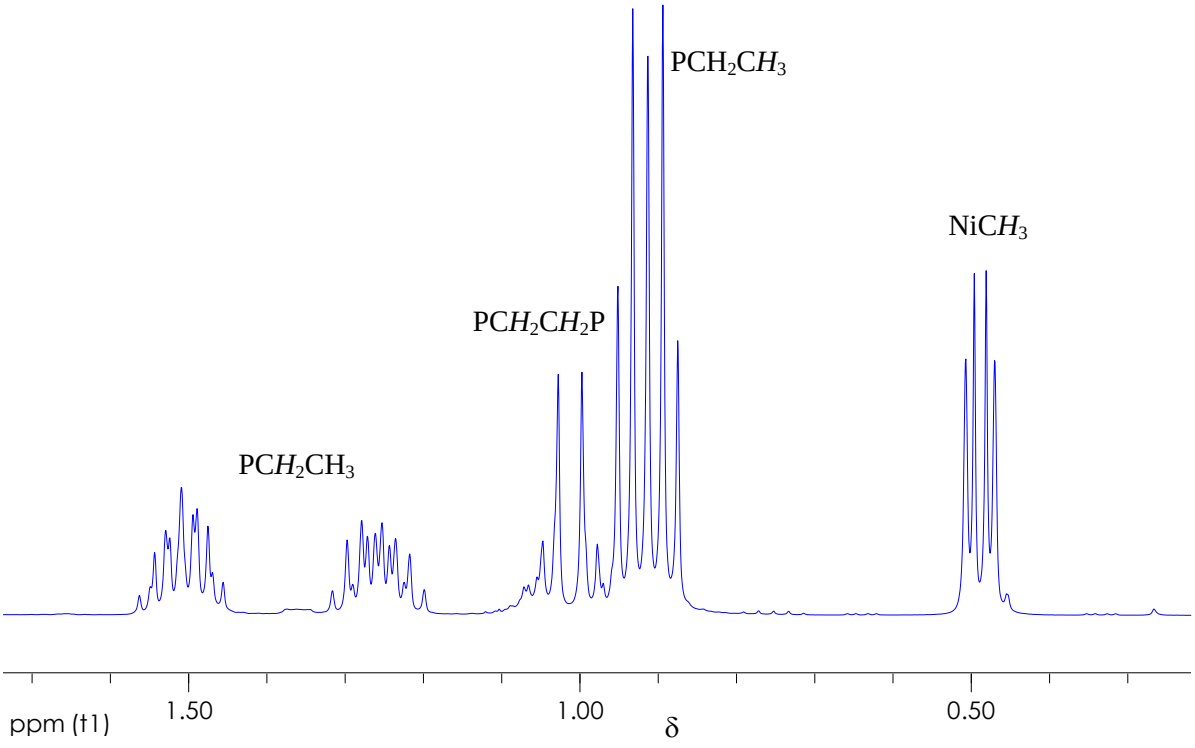

Figure S-16. ^{1}H NMR spectrum of **6** in C_6D_6.

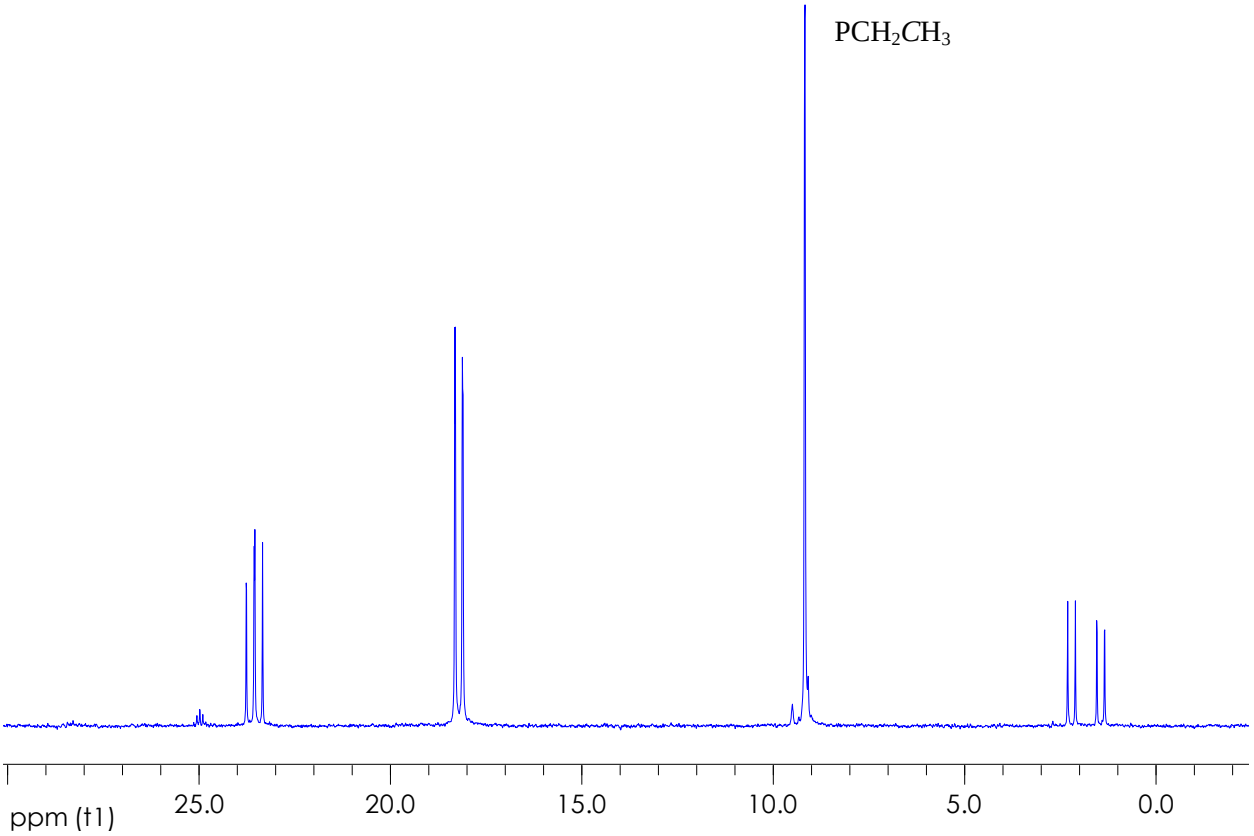

Figure S-17. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

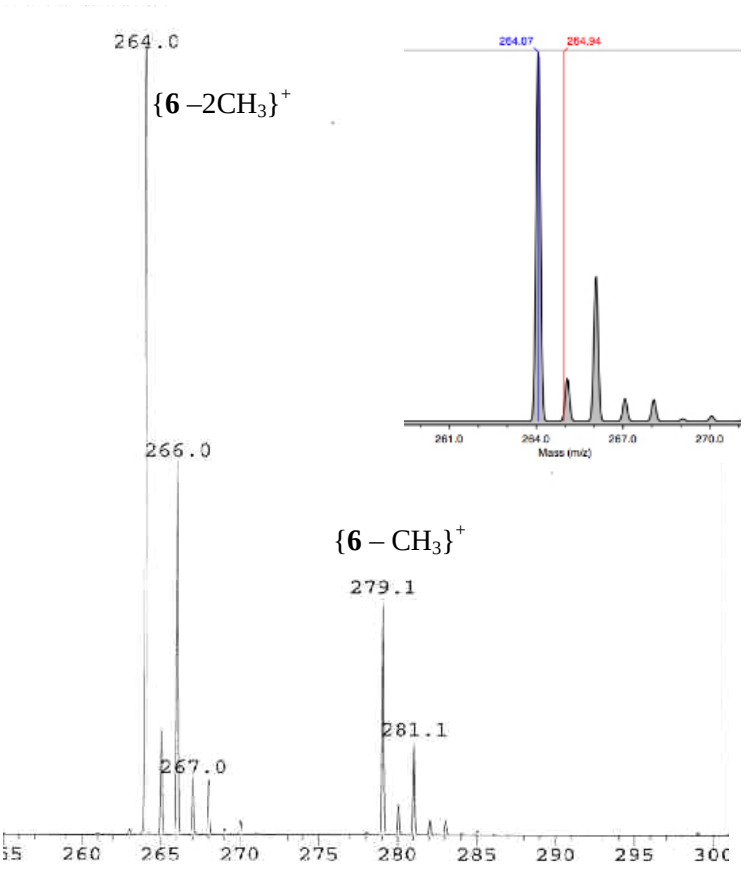

Figure S-18. Chemical Ionization mass spectrum of **6**. Inset shows the calculated isotope pattern for {**6**-2CH_3}$^+$.

Table S-2. DFT optimized coordinates of (depe)Ni(Me)(*o*-pabt).

Ni	-1.02354844	0.36009129	-0.14487086
S	0.58705720	1.22503000	1.13853153
P	-2.19786974	-0.05282817	1.68834153
P	-2.55292242	-0.59251430	-1.31222657
O	5.18424788	-0.57517488	-0.79546034
N	3.13223404	0.01626616	0.07683586
C	-0.10726774	0.80694478	-1.83105168
C	3.04916151	1.39080431	-0.21321863
C	4.07051235	2.10265124	-0.88575131
C	3.92156478	3.47427124	-1.14036431
C	2.76199714	4.15704135	-0.73349727
C	1.74630023	3.45486194	-0.06471865
C	1.86491463	2.07590959	0.20800084
C	4.14559068	-0.87535101	-0.20054184
C	3.93048022	-2.34317554	0.28587819
C	5.10027045	-2.66398257	1.24750716
C	2.58686897	-2.58914885	0.99848860
C	4.03214760	-3.24405100	-0.96823291
C	-2.53394029	1.35103812	2.87187715
C	-3.02108692	2.64166057	2.20503424
C	-1.59180849	-1.36092895	2.87886292
C	-1.43120334	-2.76146954	2.27748526
C	-3.91382083	-0.62005662	1.16675191
C	-3.84783658	-1.36822051	-0.17418955
C	-2.00771677	-2.03677050	-2.36682497
C	-3.08515539	-2.81334398	-3.13530529
C	-3.53974350	0.46427000	-2.49732331

C	-4.17472894	1.70285599	-1.85402357
H	2.29631209	-0.31114837	0.58832870
H	-0.59071203	0.54668156	-2.79816330
H	0.88929536	0.31908168	-1.80379692
H	0.04278938	1.90633659	-1.80502991
H	4.96733387	1.55102704	-1.19480594
H	4.72727510	4.01316420	-1.66457581
H	2.64712612	5.23461536	-0.93232501
H	0.83396744	3.97435164	0.26807963
H	5.04466246	-2.04731562	2.16951561
H	6.06914588	-2.45411079	0.75279719
H	5.07601166	-3.73328710	1.54733163
H	2.48368136	-1.97782681	1.92017389
H	2.50903511	-3.65451825	1.30217822
H	1.71959391	-2.36915270	0.33980813
H	4.00911154	-4.31671290	-0.68054480
H	4.97744283	-3.03952647	-1.50855662
H	3.18982786	-3.05742918	-1.66789763
H	-3.24776895	0.99205940	3.64656886
H	-1.56124001	1.53051432	3.37868488
H	-3.16627227	3.44043113	2.96173757
H	-3.99056196	2.50629845	1.68057977
H	-2.27784711	3.00213164	1.46507695
H	-0.61009434	-0.97783908	3.23333113
H	-2.27240292	-1.37684894	3.75894011
H	-0.98380481	-3.45750012	3.01703272
H	-0.76569169	-2.74339815	1.38960475
H	-2.40470080	-3.19731489	1.96863849
H	-4.38973996	-1.23230664	1.96305617
H	-4.52021365	0.30504886	1.06518167
H	-4.83961404	-1.41615729	-0.67261089
H	-3.51559299	-2.41628545	-0.01413520
H	-1.23838359	-1.62948363	-3.05621016
H	-1.45874491	-2.70439020	-1.66813518
H	-2.63044949	-3.66778796	-3.67912669
H	-3.59627270	-2.18275285	-3.89115134
H	-3.86295944	-3.23088282	-2.46252759
H	-2.82324865	0.76657555	-3.29080209
H	-4.31022454	-0.17344031	-2.98182650
H	-4.68756121	2.32273247	-2.61849543
H	-3.40886691	2.33531334	-1.36007786
H	-4.93393942	1.43082987	-1.09092234

Table S-3. DFT optimized coordinates of (depe)Ni(CO)(Me)(*o*-pabt).

Ni	-0.95042692	0.38318101	-0.31608764
S	0.83342578	1.23198631	1.10605814
P	-2.13625228	0.28656048	1.76579514
P	-2.76796685	-0.99680492	-1.10706820
O	5.35384265	-0.81621160	-0.75893928
O	-1.16681778	2.86482907	-1.88965959
N	3.34795081	-0.10640970	0.13094691
C	-1.18639306	1.91551984	-1.21790180
C	0.28964589	-0.32006251	-1.80069772
C	3.31521710	1.25818027	-0.20663772
C	4.35905972	1.90518878	-0.90783916
C	4.26780563	3.27377012	-1.20374139
C	3.14427440	4.01973502	-0.80324386
C	2.10737883	3.38719424	-0.10210871
C	2.16149308	2.00770436	0.20350606
C	4.30901452	-1.05430130	-0.14768924
C	4.00428352	-2.50788162	0.33376717
C	5.25893460	-3.00563515	1.08784747
C	2.76737280	-2.63075878	1.24506869
C	3.79965821	-3.35420189	-0.94741221
C	-2.45265486	1.89265793	2.66763388
C	-3.02568209	3.02683300	1.81228000
C	-1.50984782	-0.75353337	3.19112022
C	-1.26931999	-2.23250596	2.86847562
C	-3.86815362	-0.35781721	1.42959879
C	-3.87742307	-1.45303650	0.34584015
C	-2.23658777	-2.66450361	-1.76552167

C	-3.31800833	-3.70104668	-2.09658593
C	-3.95158395	-0.39486549	-2.42920572
C	-4.71859478	0.88188550	-2.06341409
H	2.49720503	-0.39365880	0.63880760
H	-0.19184005	-0.43793260	-2.79400917
H	0.58886606	-1.32022089	-1.41553229
H	1.18497860	0.32236905	-1.90360776
H	5.22815094	1.30562926	-1.20663111
H	5.09012133	3.76050790	-1.75228342
H	3.07479543	5.09490593	-1.03326770
H	1.22598164	3.96045530	0.22420538
H	5.40978510	-2.44347356	2.03368908
H	6.16036355	-2.86471910	0.46010661
H	5.15986156	-4.08264521	1.34001071
H	2.86852572	-2.02230679	2.16851594
H	2.63196026	-3.68752017	1.55838385
H	1.83251414	-2.32370372	0.72830804
H	3.66587120	-4.42646391	-0.68897169
H	4.67921450	-3.25828420	-1.61481753
H	2.90315589	-3.01948731	-1.51142866
H	-3.10891623	1.67380796	3.53967464
H	-1.45849627	2.18353376	3.06981410
H	-3.15201790	3.94473030	2.42308416
H	-4.02154660	2.77700869	1.38910786
H	-2.35075320	3.27438739	0.96895486
H	-0.55455913	-0.26651246	3.48538094
H	-2.21052023	-0.63803739	4.04817275
H	-0.79431695	-2.74834559	3.72853401
H	-0.59318020	-2.35046135	1.99606564
H	-2.21370881	-2.77275148	2.64752667
H	-4.34147617	-0.71298221	2.37093900
H	-4.45457014	0.52195088	1.08800250
H	-4.91136166	-1.67323747	0.00304438
H	-3.46934017	-2.40111495	0.75627037
H	-1.60904365	-2.44297955	-2.65529959
H	-1.53058200	-3.05972322	-1.00307370
H	-2.85335713	-4.64512991	-2.45141865
H	-3.99987806	-3.35419101	-2.89992265
H	-3.94026648	-3.95469916	-1.21328597
H	-3.31823845	-0.22118253	-3.32677586
H	-4.65698106	-1.21421502	-2.68874260
H	-5.33891816	1.22332755	-2.91791919
H	-4.03191980	1.71090695	-1.79676009
H	-5.40632264	0.72009044	-1.20690239

Table S-4. DFT optimized coordinates of (depe)Ni(COMe)(*o*-pabt).

Ni	-0.96893776	0.32221017	-0.11857575
S	0.53448826	1.54271468	0.97459746
P	-2.39889296	0.66140753	1.59904189
P	-2.43184190	-1.01510949	-1.02430304
O	5.13098554	-0.91159659	-0.17299966
O	0.83660959	-0.98542689	-1.75213515
N	3.05948709	-0.05112939	0.36360431
C	0.16776719	0.03372043	-1.62450695
C	0.21840203	1.14400095	-2.67075797
C	3.14937827	1.27812982	-0.07630662
C	4.31319564	1.81275001	-0.68048190
C	4.33935146	3.14853968	-1.10823720
C	3.21710192	3.97807318	-0.93913597
C	2.06083060	3.45590578	-0.33640028
C	1.99986670	2.11396452	0.09725534
C	3.98831729	-1.06637340	0.26564193
C	3.51384020	-2.48058259	0.71984752
C	4.55232425	-3.00451769	1.73794208
C	2.10244732	-2.50615624	1.33905819
C	3.53486959	-3.36252825	-0.55412987
C	-2.80201332	2.41260460	2.10188461
C	-3.13539912	3.34691024	0.93367181
C	-2.00855560	-0.09465315	3.26239986
C	-1.77448101	-1.60953946	3.24476892
C	-4.06131132	-0.05759950	1.09849604

C	-3.87212262	-1.26890906	0.17091268
C	-1.81792329	-2.75169219	-1.31988087
C	-2.79949702	-3.77509419	-1.90428770
C	-3.24960271	-0.55114422	-2.64190653
C	-3.95399421	0.81101251	-2.62445653
H	2.12888346	-0.27289757	0.74537625
H	5.18042686	1.15060630	-0.79751088
H	5.25503062	3.54319798	-1.57739812
H	3.23996336	5.02900452	-1.26894540
H	1.17472405	4.09228542	-0.18430619
H	4.53120014	-2.41253711	2.67770551
H	5.57273825	-2.93421199	1.31233468
H	4.34382904	-4.06466283	1.99548415
H	2.03516627	-1.87320557	2.24984586
H	1.84320208	-3.54335284	1.64052151
H	1.33436957	-2.16852469	0.61075270
H	3.28240654	-4.41448453	-0.30037891
H	4.54118647	-3.34171030	-1.01787820
H	2.79940260	-2.99385874	-1.29866805
H	-3.62138207	2.38563058	2.85449538
H	-1.88809776	2.76977120	2.62361116
H	-3.32323003	4.37761480	1.29977339
H	-4.04359694	3.02531454	0.38127361
H	-2.29279706	3.38814517	0.21363176
H	-1.08603769	0.43135204	3.59213188
H	-2.81519100	0.18271268	3.97692647
H	-1.45873827	-1.96874508	4.24613643
H	-0.97642212	-1.88275607	2.52364069
H	-2.69252754	-2.17168075	2.97249967
H	-4.67107631	-0.31301573	1.99206092
H	-4.59569682	0.75767383	0.56576905
H	-4.80267982	-1.51238507	-0.38519605
H	-3.60713175	-2.17010561	0.76380140
H	-0.90991088	-2.63993750	-1.94865441
H	-1.43993418	-3.08255294	-0.32831300
H	-2.31776550	-4.77308310	-1.97048097
H	-3.12470969	-3.50535967	-2.92987759
H	-3.71082826	-3.89281922	-1.28097278
H	-2.43584562	-0.56095349	-3.39922135
H	-3.95941661	-1.35812150	-2.92466267
H	-4.35011168	1.06277014	-3.63003902
H	-3.26282985	1.62348359	-2.31821358
H	-4.81438838	0.82145695	-1.92291557
H	-0.79673295	1.52793806	-2.89779140
H	0.79967819	1.99208382	-2.25031301
H	0.72041491	0.78329282	-3.59305153

Table S-5. DFT optimized coordinates of (depe)Ni(CO)(COMe)(*o*-pabt).

Ni	-1.10011371	-0.04618711	-0.20224751
S	0.97543528	0.78509865	1.29752591
P	-2.27165743	0.44076890	1.74657280
P	-3.04794199	-1.11408740	-0.94266575
O	5.68785600	-0.20272753	-0.87984932
O	0.90771434	-1.99795912	-1.16635553
O	-1.64162181	2.35663261	-1.40873182
N	3.65407226	0.05462222	0.17434169
C	-0.90678891	1.38902149	-1.54524176
C	0.10040368	1.32084727	-2.68337373
C	0.13115725	-1.24000174	-0.73812433
C	3.29371352	1.37091013	-0.15459173
C	4.11785006	2.23182245	-0.91670363
C	3.70645845	3.54624109	-1.18852142
C	2.47413467	4.02573517	-0.70651812
C	1.64780860	3.17825151	0.04533976
C	2.02522695	1.84390232	0.33590035
C	4.78523697	-0.65631523	-0.17159087
C	4.86394327	-2.12272277	0.35604454
C	6.29248943	-2.32810812	0.90928348
C	3.82944893	-2.46005461	1.44857940
C	4.64542462	-3.03911901	-0.87477167
C	-2.40340374	2.15922373	2.46496958

C	-3.06846069	3.20878655	1.56757837
C	-1.69341351	-0.49531479	3.25960063
C	-1.54631059	-2.01063524	3.08667640
C	-4.05985881	-0.09228559	1.51251246
C	-4.18130257	-1.28981484	0.55082745
C	-2.82204254	-2.88018759	-1.51980208
C	-4.06727810	-3.74649086	-1.74890887
C	-4.14178328	-0.38942492	-2.28094061
C	-4.75737483	0.97778177	-1.95467909
H	1.11808971	1.34434844	-2.23864670
H	0.00412307	0.35669332	-3.22139601
H	-0.02225444	2.17671773	-3.37868325
H	2.93169310	-0.40078432	0.75654813
H	5.07674936	1.83929678	-1.27830202
H	4.36305839	4.20213440	-1.78251748
H	2.15545741	5.05954716	-0.91504099
H	0.68060392	3.53937903	0.42623751
H	6.46352189	-1.71605661	1.82010323
H	7.04259220	-2.02781619	0.15207404
H	6.45481661	-3.39369681	1.17614996
H	3.92509154	-1.79413652	2.33193441
H	3.98188140	-3.50210846	1.80086743
H	2.78510550	-2.39885256	1.07593803
H	4.77668126	-4.10534606	-0.59120207
H	5.37622733	-2.79519235	-1.67194930
H	3.62304055	-2.91608711	-1.28876251
H	-2.91843409	2.08044897	3.44852272
H	-1.34654124	2.43514127	2.67134095
H	-3.00059778	4.21183722	2.03789418
H	-4.14756094	3.00009990	1.40794659
H	-2.58096807	3.25787492	0.57373329
H	-0.70917712	-0.03977612	3.50471065
H	-2.38229357	-0.24879752	4.09783917
H	-1.09379488	-2.46508144	3.99229668
H	-0.88998000	-2.25216119	2.22490215
H	-2.52414912	-2.51124813	2.92476974
H	-4.53658722	-0.31317928	2.49233380
H	-4.58509357	0.79085118	1.09141754
H	-5.23398346	-1.44573446	0.22960428
H	-3.85805240	-2.22423420	1.05764886
H	-2.21119204	-2.80905462	-2.44658992
H	-2.15216889	-3.34400013	-0.76393654
H	-3.77375087	-4.76566405	-2.07754850
H	-4.73141884	-3.33124355	-2.53457858
H	-4.67010378	-3.86175357	-0.82455161
H	-3.48896797	-0.31557770	-3.17841441
H	-4.93565274	-1.12900673	-2.52504692
H	-5.32267343	1.36307512	-2.82870770
H	-3.98019758	1.72442554	-1.69730344
H	-5.47469562	0.91394428	-1.10989093

Table S-6. DFT optimized coordinates of Me(CO)(*o*-pabt).

S	1.73353400	-1.26272800	-1.09935600
O	-2.22266300	1.84376200	0.61286000
O	1.95689700	-3.51606700	0.24795100
N	-0.65985000	0.34485800	-0.17980300
C	2.13282900	-1.61532900	1.74398600
C	0.53230900	1.08402000	-0.12542100
C	0.58362400	2.43540400	0.29622000
C	1.80620500	3.12194500	0.31666100
C	2.99994200	2.49416800	-0.08141300
C	2.96240300	1.15510000	-0.49870200
C	1.74875600	0.43778600	-0.51313800
C	1.95791300	-2.31803400	0.41655800
C	-1.94853100	0.73395600	0.15810200
C	-3.06720300	-0.32483500	-0.07519900
C	-4.05584200	0.30147200	-1.08994800
C	-2.56275800	-1.68128700	-0.60720800
C	-3.77872700	-0.52529400	1.28484200
H	1.24531900	-0.99170600	1.97509600
H	3.00461400	-0.93136600	1.71592400

H	2.27237800	-2.38246200	2.52890700
H	-0.35448400	2.91658100	0.60003600
H	3.95435900	3.04281000	-0.07222200
H	3.88184300	0.64379100	-0.82408900
H	-4.40418000	1.28918100	-0.72881700
H	-3.57968000	0.44530900	-2.08282200
H	-4.93784500	-0.35893400	-1.22577900
H	-1.85765900	-2.17588100	0.09472500
H	-3.41867500	-2.37483100	-0.74054400
H	-2.06946200	-1.59069900	-1.59880900
H	-4.66558900	-1.18168900	1.16286100
H	-3.10349400	-0.99798900	2.02921600
H	-4.11072800	0.44977900	1.69223000
H	-0.53409800	-0.60122400	-0.56276600
H	1.82038900	4.17297900	0.64663800

Table S-7. DFT optimized coordinates of (depe)Ni(Me)(*p*-pabt).

Ni	1.95223400	0.09606200	-0.10207300
S	0.54301600	-1.59263100	0.22352900
P	3.37475600	1.68188600	-0.33643900
P	3.60731000	-1.28468000	0.39907200
O	-6.01043300	0.54281600	1.63586400
N	-5.32835200	-0.26018600	-0.41285600
C	0.53772600	1.37067600	-0.61700500
C	3.13804200	3.27535700	0.61449800
C	2.75508900	3.08322700	2.08568700
C	3.66450600	2.36065100	-2.05633400
C	4.09058300	1.31915700	-3.09662300
C	5.08060800	1.11115600	0.24040600
C	5.24001900	-0.40761800	0.06530900
C	3.72854900	-1.90454100	2.15790400
C	3.81071300	-0.81155300	3.22849800
C	3.76702800	-2.89715000	-0.52998100
C	3.66172300	-2.76908800	-2.05313900
C	-1.92260500	-0.62202500	1.12641700
C	-3.28907800	-0.32319900	1.01670500
C	-3.95508100	-0.53002800	-0.21436700
C	-3.21836200	-1.03468400	-1.31234700
C	-1.85408900	-1.32701400	-1.18872200
C	-1.17606100	-1.13051500	0.03755400
C	-6.26781700	0.23966700	0.47137500
C	-7.70562700	0.37392400	-0.12599700
C	-7.68473400	1.24493800	-1.40571700
C	-8.25620400	-1.03708200	-0.45217800
C	-8.59727600	1.04298300	0.93674400
H	-5.66607500	-0.46484900	-1.35574700
H	0.82348800	2.40320900	-0.91665300
H	-0.16656000	1.44106900	0.23813400
H	-0.00019200	0.90281800	-1.46783600
H	4.06908800	3.87569700	0.50856700
H	2.33906600	3.83076100	0.07894900
H	2.59677100	4.06316300	2.58225400
H	3.54304800	2.54857200	2.65634800
H	1.81902700	2.49563000	2.17669800
H	2.69836500	2.82439000	-2.34990100
H	4.40846100	3.18467600	-1.98076600
H	4.16593600	1.77756200	-4.10468600
H	3.35710800	0.48882800	-3.15474700
H	5.08318500	0.88001900	-2.86295800
H	5.88144200	1.68083300	-0.27932700
H	5.13778700	1.38324500	1.31593200
H	6.04932700	-0.81961000	0.70611100
H	5.50478400	-0.65075900	-0.98569800
H	2.80335600	-2.50562600	2.29537500
H	4.59102500	-2.60443800	2.22606600
H	3.79764600	-1.25687300	4.24509500
H	2.94964900	-0.11611100	3.15386900
H	4.74363400	-0.21446400	3.14638200
H	4.71723800	-3.38769000	-0.22152600
H	2.93424500	-3.52435800	-0.14454600
H	3.72838800	-3.76713600	-2.53431700

H	4.47346800	-2.14365100	-2.48148300
H	2.69074500	-2.31538300	-2.33863400
H	-1.41279300	-0.46493400	2.09021000
H	-3.85845200	0.06782000	1.86905100
H	-3.72517200	-1.20153500	-2.27909300
H	-1.29754100	-1.72370600	-2.05225100
H	-8.71898500	1.39462300	-1.78245100
H	-7.10640400	0.78269800	-2.23455500
H	-7.24783000	2.24549800	-1.20691700
H	-9.29992200	-0.96550700	-0.82613200
H	-8.26162700	-1.68266000	0.45032200
H	-7.66039300	-1.55559900	-1.23310500
H	-9.63708300	1.13559500	0.55930300
H	-8.22370200	2.05426800	1.19358600
H	-8.60932800	0.45351400	1.87412900

Table S-8. DFT optimized coordinates of (depe)Ni(CO)(Me)(*p*-pabt).

Ni	-1.79754100	0.17360100	0.39956400
S	-0.34496700	-1.27503600	-0.64978400
P	-3.50215600	1.71884000	0.00596000
P	-3.52357600	-1.47667000	-0.48640100
O	6.12313500	1.47013500	-0.93195400
O	-1.53342400	-0.14329000	3.31653000
N	5.59285200	-0.49119300	0.15389800
C	-0.45236400	1.72956900	0.78926900
C	-3.07707900	3.14389200	-1.12673700
C	-2.44936500	2.73350800	-2.46356500
C	-4.22052700	2.66614500	1.45161200
C	-4.94551800	1.81485200	2.50003000
C	-4.99963800	0.93820800	-0.82555600
C	-5.15759300	-0.54340600	-0.43217600
C	-3.48125900	-2.21232400	-2.21247400
C	-3.28605900	-1.20863300	-3.35436900
C	-3.93080300	-3.03536800	0.47279500
C	-4.11764200	-2.86152300	1.98387700
C	2.05795400	0.14461300	-0.93546100
C	3.43719200	0.33699200	-0.77820300
C	4.20289500	-0.61193100	-0.05890600
C	3.55012500	-1.74857000	0.47916500
C	2.17553700	-1.93650200	0.30566500
C	1.39418600	-0.98830000	-0.40268600
C	6.46958700	0.49583100	-0.26565900
C	7.94889700	0.27393200	0.18360000
C	8.03152200	0.27940800	1.73043200
C	8.47717200	-1.07156600	-0.37246500
C	8.79235200	1.43177300	-0.38198900
C	-1.78235300	-0.10830300	2.17706800
H	0.49405500	1.32466900	1.19793500
H	-0.24796700	2.19182000	-0.19958400
H	-0.84147400	2.50664800	1.48205700
H	6.00426200	-1.25180500	0.69931800
H	-3.99085700	3.76060700	-1.28025700
H	-2.36478300	3.76677900	-0.54380500
H	-2.14589900	3.62864300	-3.04508500
H	-3.15438300	2.15560300	-3.09669700
H	-1.54843900	2.10511100	-2.30845400
H	-3.35508600	3.19052600	1.91189700
H	-4.89378100	3.45491700	1.04718600
H	-5.27621500	2.44398300	3.35247900
H	-4.28699300	1.02088900	2.90696100
H	-5.85237600	1.32779200	2.08405700
H	-5.91922700	1.52120800	-0.59860500
H	-4.82656000	1.02879200	-1.91872600
H	-5.91644100	-1.05246200	-1.06625500
H	-5.51347600	-0.62108800	0.61754700
H	-2.62551500	-2.92156300	-2.18653100
H	-4.40309300	-2.81938300	-2.36203600
H	-3.16744900	-1.73806400	-4.32277200
H	-2.37625800	-0.59444200	-3.19495200
H	-4.15370900	-0.52434500	-3.46333500
H	-4.83057900	-3.50210400	0.01125700

H	-3.07885600	-3.71956500	0.26895100
H	-4.32768600	-3.84018800	2.46398000
H	-4.96820600	-2.19079800	2.22831700
H	-3.21121500	-2.43984200	2.46127300
H	1.47584900	0.88917100	-1.49890700
H	3.94185300	1.21410500	-1.20184300
H	4.13446600	-2.49893300	1.03984800
H	1.68779900	-2.83025800	0.72507100
H	9.08873800	0.18333100	2.05765800
H	7.46931600	-0.55996300	2.19253900
H	7.63008700	1.22462400	2.15082700
H	9.54830200	-1.20035000	-0.10781000
H	8.39341700	-1.11113900	-1.47828600
H	7.93452100	-1.94989300	0.03823500
H	9.85359900	1.31395700	-0.07872100
H	8.42460200	2.40987800	-0.01450100
H	8.74129500	1.46014600	-1.48836600

Table S-9. DFT optimized coordinates of (depe)Ni(COMe)(*p*-pabt).

Ni	1.96534497	0.01925983	-0.11664237
S	0.49678486	-1.61300260	0.14593828
P	3.44149400	1.60975849	-0.19149735
P	3.60114281	-1.42551470	0.47176134
O	-5.88853663	1.17174786	1.25640741
O	0.20518712	2.18493080	-0.03128044
N	-5.44685863	-0.51973386	-0.24419706
C	0.66438624	1.28060523	-0.71661905
C	0.20977698	1.08984666	-2.16539108
C	3.09546993	3.14859642	0.81057132
C	2.61567005	2.87526053	2.23753373
C	3.92300951	2.37234188	-1.83278287
C	4.47298144	1.38630858	-2.86948059
C	5.06918180	0.97999295	0.52394337
C	5.24579475	-0.53007153	0.29035806
C	3.59734019	-2.10967157	2.20986484
C	3.57661191	-1.05520317	3.32172960
C	3.83483346	-2.99938258	-0.50678666
C	3.82382666	-2.80980196	-2.02756398
C	-1.85630258	-0.19999162	0.81536035
C	-3.23464383	0.05148188	0.75093961
C	-4.05092172	-0.70550628	-0.12272913
C	-3.44795438	-1.70550485	-0.92227644
C	-2.06890041	-1.94150882	-0.85737802
C	-1.24263683	-1.19249420	0.01537046
C	-6.28162939	0.36725327	0.41268306
C	-7.78281703	0.26947561	-0.01083665
C	-7.92455938	0.61052485	-1.51508336
C	-8.32183401	-1.15600639	0.26412022
C	-8.57621951	1.29020753	0.82609858
H	-5.89771055	-1.14124252	-0.91906643
H	4.00768302	3.77722161	0.79422094
H	2.31006089	3.68715511	0.25059585
H	2.41877255	3.83110457	2.76599040
H	3.36551299	2.31579633	2.83468429
H	1.67305400	2.29392021	2.21875667
H	2.99749349	2.85808891	-2.21042718
H	4.65116932	3.18911946	-1.63109208
H	4.65704963	1.89395435	-3.83911551
H	3.76324981	0.55324641	-3.05263389
H	5.43740768	0.94137256	-2.54642304
H	5.92067319	1.56823016	0.11797078
H	5.01746124	1.19777535	1.61182788
H	6.01367170	-0.96590674	0.96564940
H	5.58401158	-0.72341719	-0.74995836
H	2.67291791	-2.72604132	2.25333605
H	4.46187748	-2.80150988	2.32169708
H	3.48706302	-1.53824764	4.31689359
H	2.71434060	-0.36766242	3.20225057
H	4.50466410	-0.44545019	3.33821974
H	4.76783192	-3.49809059	-0.16109211
H	2.98599530	-3.64762056	-0.19903170

H	3.92699585	-3.78653357	-2.54459017
H	4.65716987	-2.16448577	-2.37764575
H	2.87127745	-2.34725694	-2.35773334
H	-1.23557446	0.39365030	1.50225980
H	-3.69931989	0.82597514	1.37361192
H	-4.07014044	-2.30524355	-1.60958400
H	-1.61705016	-2.72218184	-1.48964440
H	-8.99537679	0.60279243	-1.81100436
H	-7.39931809	-0.11698820	-2.17010933
H	-7.51751338	1.61847654	-1.73817168
H	-9.40543137	-1.20818244	0.02490753
H	-8.19559841	-1.43552216	1.33060090
H	-7.81718434	-1.93276535	-0.34956952
H	-9.65083282	1.25752918	0.54962944
H	-8.19851428	2.31873442	0.66351797
H	-8.48248238	1.07752978	1.90936562
H	-0.29840372	2.00630149	-2.53346639
H	1.05611833	0.81262656	-2.82576429
H	-0.50881762	0.24305094	-2.18435726

Table S-10. DFT optimized coordinates of (depe)Ni(CO)(COMe)(*p*-pabt).

Ni	-1.85110195	0.16343994	0.12963725
S	-0.16410152	-1.66433925	-0.21728940
P	-3.80762447	1.46704291	0.56847624
P	-3.36788099	-1.55189818	-0.43444945
O	6.45466706	0.14282903	-1.70029347
O	-0.17171620	1.17515138	2.35480502
O	-1.75958686	1.10236006	-2.49548637
N	5.65868135	-0.16844695	0.43880685
C	0.12560999	1.99489622	-1.32835276
C	-4.09609893	3.19986462	-0.09967792
C	-4.20135561	3.34365515	-1.62319748
C	-4.20660121	1.80278968	2.37130437
C	-4.22411759	0.58099563	3.29635073
C	-5.29003234	0.51298032	-0.07803891
C	-5.10101206	-1.00856623	0.05638504
C	-3.54006020	-2.14249353	-2.20172093
C	-4.12432056	-1.12719190	-3.19021451
C	-3.19832908	-3.19863214	0.43606721
C	-2.98618413	-3.11735819	1.95039419
C	2.35100979	-0.93267787	-1.16495542
C	3.70785081	-0.59881142	-1.04972655
C	4.30175940	-0.50050858	0.23162229
C	3.50113792	-0.74986475	1.37321563
C	2.14972574	-1.08792387	1.24730618
C	1.53720146	-1.18817539	-0.02940216
C	6.64661960	0.12736061	-0.48491909
C	8.03974406	0.44852622	0.14459606
C	7.93167512	1.70855047	1.03884260
C	8.53503190	-0.75687021	0.98159799
C	9.02705863	0.71674691	-1.00651849
C	-1.15063157	1.17042142	-1.43678799
C	-0.85541697	0.76343059	1.50566342
H	0.95325106	1.33934579	-0.98645852
H	-0.00657746	2.77559355	-0.55110579
H	0.38336357	2.46144353	-2.30232153
H	5.94287001	-0.14659025	1.42061379
H	-5.00641414	3.60612399	0.39668989
H	-3.24053354	3.79663308	0.28654030
H	-4.27919145	4.41587061	-1.89994178
H	-5.10603064	2.84133364	-2.02425637
H	-3.32291049	2.91740443	-2.14543059
H	-3.42160560	2.51875062	2.70197685
H	-5.17404160	2.35153469	2.41832656
H	-4.34570927	0.89352053	4.35434955
H	-3.28213496	0.00015406	3.22148281
H	-5.06466109	-0.10421908	3.06049740
H	-6.22423884	0.85767975	0.41780559
H	-5.37039479	0.78970609	-1.15050403
H	-5.85998291	-1.56342353	-0.53711352
H	-5.22904240	-1.32330960	1.11347928

H	-2.50662915	-2.42445518	-2.49853514
H	-4.14105848	-3.07933261	-2.18342690
H	-4.11847153	-1.54610651	-4.21819821
H	-3.52525367	-0.19506040	-3.19828126
H	-5.17954617	-0.87503086	-2.95121519
H	-4.09234000	-3.81027265	0.17914283
H	-2.32114596	-3.68376104	-0.04362537
H	-2.86656318	-4.13369821	2.38014798
H	-3.84218893	-2.63939570	2.47197485
H	-2.06960002	-2.53854279	2.18443820
H	1.90143785	-1.01230639	-2.16740644
H	4.32558086	-0.41059485	-1.93671171
H	3.95028541	-0.68095988	2.37951050
H	1.55266496	-1.28856597	2.14961073
H	8.93037171	1.97765392	1.44420034
H	7.25588576	1.56049786	1.90812404
H	7.55311537	2.57837627	0.46302987
H	9.55498231	-0.55706846	1.37378973
H	8.58192595	-1.68060364	0.36847359
H	7.88630124	-0.96740761	1.85871655
H	10.03098307	0.95859860	-0.59934813
H	8.68595479	1.56211228	-1.63579719
H	9.11708692	-0.16614722	-1.66970867

Table S-11. DFT optimized coordinates of Me(CO)(*p*-pabt).

S	4.05135306	0.33025812	-0.93040958
O	-2.68354025	-1.55253518	-0.61602761
O	6.05103135	-0.46249027	0.57713843
N	-1.90473827	0.50342417	0.07301355
C	3.94646571	-0.76878211	1.73781464
C	1.47600192	-0.76080925	-0.93893459
C	0.08989191	-0.74491438	-0.72705079
C	-0.52131541	0.40438000	-0.16842876
C	0.28646142	1.52080528	0.16238854
C	1.66929251	1.49356393	-0.05145625
C	2.28525421	0.34477539	-0.59669374
C	-2.90108177	-0.43592579	-0.14924377
C	-4.35002988	-0.00133184	0.22642360
C	-4.86802048	-1.03521402	1.25567245
C	-4.45952176	1.42042584	0.81493546
C	-5.18770612	-0.09602327	-1.07239678
C	4.84297679	-0.36480610	0.58565142
H	3.22339608	-1.54676043	1.41975604
H	3.35037973	0.09508874	2.09498325
H	4.58451882	-1.15486281	2.55517161
H	-2.21130135	1.39511228	0.46729728
H	1.94232245	-1.65323602	-1.38526354
H	-0.53887799	-1.60460233	-0.98974567
H	-0.17925038	2.42546680	0.58881276
H	2.28159143	2.37291554	0.20192586
H	-5.93903548	-0.85124818	1.48244403
H	-4.30071583	-0.97774664	2.20869666
H	-4.76095887	-2.06194324	0.85416203
H	-5.51845504	1.64862904	1.05581328
H	-4.12350077	2.20115115	0.09806099
H	-3.88850966	1.53005345	1.76265111
H	-6.25937055	0.09623845	-0.85558665
H	-5.09109794	-1.10551266	-1.51799811
H	-4.85155871	0.64649932	-1.82669765

Table S-12. DFT optimized coordinates of (depe)Ni$(CO)_2$.

Ni	-0.26148124	0.07149670	1.09402892
P	-1.52502196	-0.40470233	-0.67540475
P	1.55423089	0.17506243	-0.19045558
O	-0.05721852	-2.13780654	3.03617055
O	-0.96974837	2.60949317	2.41739779
C	-0.13954717	-1.27828648	2.24947357
C	-0.69016328	1.61553503	1.87001861
C	-3.06148511	0.57061198	-1.13056615
C	-2.91442186	2.09331463	-1.05153745

C	-2.21297095	-2.13442566	-0.91302676
C	-1.19119566	-3.26996188	-0.79512688
C	-0.43608025	-0.14650323	-2.19886604
C	1.04501608	-0.44375856	-1.90488545
C	3.00486814	-0.93298364	0.23267203
C	4.16538406	-1.05254073	-0.76361915
C	2.41041747	1.80792002	-0.53120752
C	1.47860425	2.93390754	-0.99279761
H	-3.38901380	0.25115612	-2.14577806
H	-3.84645010	0.22406928	-0.42325994
H	-3.87343828	2.59336432	-1.30178024
H	-2.15148273	2.47641104	-1.76156235
H	-2.61659359	2.41883043	-0.03483433
H	-2.99498959	-2.24229038	-0.12950856
H	-2.73764541	-2.17085158	-1.89427724
H	-1.69182627	-4.25875388	-0.85827166
H	-0.65096812	-3.22708532	0.17258524
H	-0.43632804	-3.23436030	-1.60856305
H	-0.81172577	-0.74683361	-3.05658949
H	-0.56327095	0.92243197	-2.47446895
H	1.70691156	-0.02749932	-2.69487829
H	1.21813160	-1.54143846	-1.88542773
H	3.36487819	-0.57155517	1.22089285
H	2.54889643	-1.92643959	0.43353753
H	4.93106215	-1.76371109	-0.38735972
H	4.67802443	-0.08270731	-0.92977317
H	3.82900047	-1.42815415	-1.75245544
H	2.89744335	2.08335311	0.43025261
H	3.22602168	1.64495375	-1.26920557
H	2.03328398	3.89054356	-1.09001060
H	0.65096061	3.09282004	-0.27202545
H	1.02763986	2.71597041	-1.98387738