Electronic Supplementary Material (ESI) for Dalton Transactions.

Nickel Promoted Functionalization of CO_2 to Anhydrides and Ketoacids

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-Electronic Supplementary Information -

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Computational Details

All geometry optimizations were performed using Gaussian 09 Revision A.02,[1] using the M06l functional. The LANL2DZ basis set was used for Ni and the 6-31G++(d,p) basis set was used for all other atoms. The LANL2DZ pseudo-potential was used for Ni. Frequency calculations were performed on all optimized structures to ensure that they were true minima.

The coordinates for optimized structures are given below:

Complex **3a**

Atomic#			
6	3.084495	-2.228680	0.112031
6	1.882711	-3.152368	0.018585
6	0.662283	-2.438805	0.566093
6	2.527309	1.852514	-0.021043
6	2.830137	3.203378	-0.121642
6	1.823622	4.095246	-0.480781
6	0.551198	3.599020	-0.743854
6	0.313530	2.230911	-0.631385
6	-1.016988	1.617580	-0.948309
6	-2.038185	0.431901	1.547689
6	-1.192305	1.549700	2.170773
6	-3.476584	0.920439	1.398135
6	-1.981598	-0.781993	2.478785
6	-2.341120	-0.974480	-1.229238
6	-3.430833	-0.110574	-1.869441
6	-3.000147	-2.143959	-0.495574
6	-1.429313	-1.527061	-2.331127
7	1.290906	1.372474	-0.257611
28	0.891292	-0.573323	0.091438
8	2.730135	-0.959692	0.150076
8	4.247428	-2.607350	0.124355
15	-1.194278	-0.011778	-0.079911
1	2.024914	5.159964	-0.559124
1	-0.259075	4.260375	-1.038316
1	3.839345	3.543374	0.085477
1	3.260408	1.094867	0.246370
1	-1.843203	2.312221	-0.751073
1	-1.050855	1.397887	-2.023744
1	-3.020917	0.680816	-2.503866
1	-4.095849	0.352500	-1.136377
1	-4.050581	-0.744242	-2.515481
1	-2.030036	-2.086606	-3.058292
1	-0.911126	-0.730246	-2.877384

1	-3.518026	-2.776586	-1.226370
1	-3.748926	-1.811256	0.229936
1	-4.154120	0.131300	1.059119
1	-3.846002	1.266927	2.371313
1	-3.560356	1.763920	0.703109
1	-1.558288	1.754192	3.183780
1	-1.255254	2.486833	1.606722
1	-0.136003	1.266721	2.245826
1	-2.386421	-0.505263	3.459726
1	-2.566738	-1.628725	2.110473
1	-0.951578	-1.122869	2.622672
1	-2.272685	-2.772542	0.026105
1	-0.664627	-2.194239	-1.922215
1	-0.281717	-2.906564	0.264324
1	0.685321	-2.393692	1.664355
1	1.746044	-3.385370	-1.046844
1	2.098228	-4.111573	0.507831

Complex **3b**

Atomic#

6	3.631042	0.028941	-0.006873
6	3.179638	-1.415287	-0.194615
6	1.781567	-1.543458	0.387917
6	4.185843	-2.418865	0.345079
6	0.842316	3.069055	-0.023696
6	0.313927	4.351526	-0.073907
6	-1.033797	4.513915	-0.381033
6	-1.801679	3.384361	-0.641765
6	-1.209993	2.124837	-0.579811
6	-1.966796	0.869797	-0.890972
6	-2.011157	-0.722476	1.589545
6	-1.899424	0.668684	2.226423
6	-3.482839	-1.122193	1.519775
6	-1.231103	-1.707303	2.464514
6	-1.621696	-2.011190	-1.230624
6	-3.044796	-1.898699	-1.783693
6	-1.465636	-3.357470	-0.521192
6	-0.626950	-1.938550	-2.394960
7	0.096488	1.971977	-0.260491
28	0.888913	0.134219	0.012366
8	2.620328	0.868505	0.051002
8	4.804240	0.374038	0.055338
15	-1.152559	-0.588766	-0.083715
1	-1.480781	5.503293	-0.421288
1	-2.855047	3.468833	-0.894533
1	0.953206	5.203232	0.132731

1	1.885739	2.863917	0.203511
1	-3.032304	0.967986	-0.648345
1	-1.914298	0.689737	-1.973149
1	-3.188328	-0.998846	-2.389531
1	-3.807653	-1.906144	-1.001104
1	-3.240572	-2.756736	-2.438240
1	-0.860295	-2.722196	-3.125946
1	-0.675113	-0.976582	-2.918762
1	-1.580672	-4.163936	-1.255055
1	-2.227670	-3.510209	0.249149
1	-3.623310	-2.151447	1.176080
1	-3.924416	-1.055382	2.521961
1	-4.066065	-0.461982	0.867291
1	-2.265241	0.621773	3.258746
1	-2.499985	1.419393	1.700856
1	-0.861221	1.019747	2.252512
1	-1.649208	-1.700949	3.478311
1	-1.279217	-2.735621	2.096840
1	-0.176200	-1.423985	2.531569
1	-0.481996	-3.473254	-0.056702
1	0.403742	-2.075970	-2.054465
1	1.270924	-2.456424	0.056655
1	1.819938	-1.559551	1.488694
1	3.111117	-1.546944	-1.287164
1	3.902269	-3.447478	0.097276
1	4.257939	-2.343070	1.435618
1	5.180771	-2.215782	-0.061984

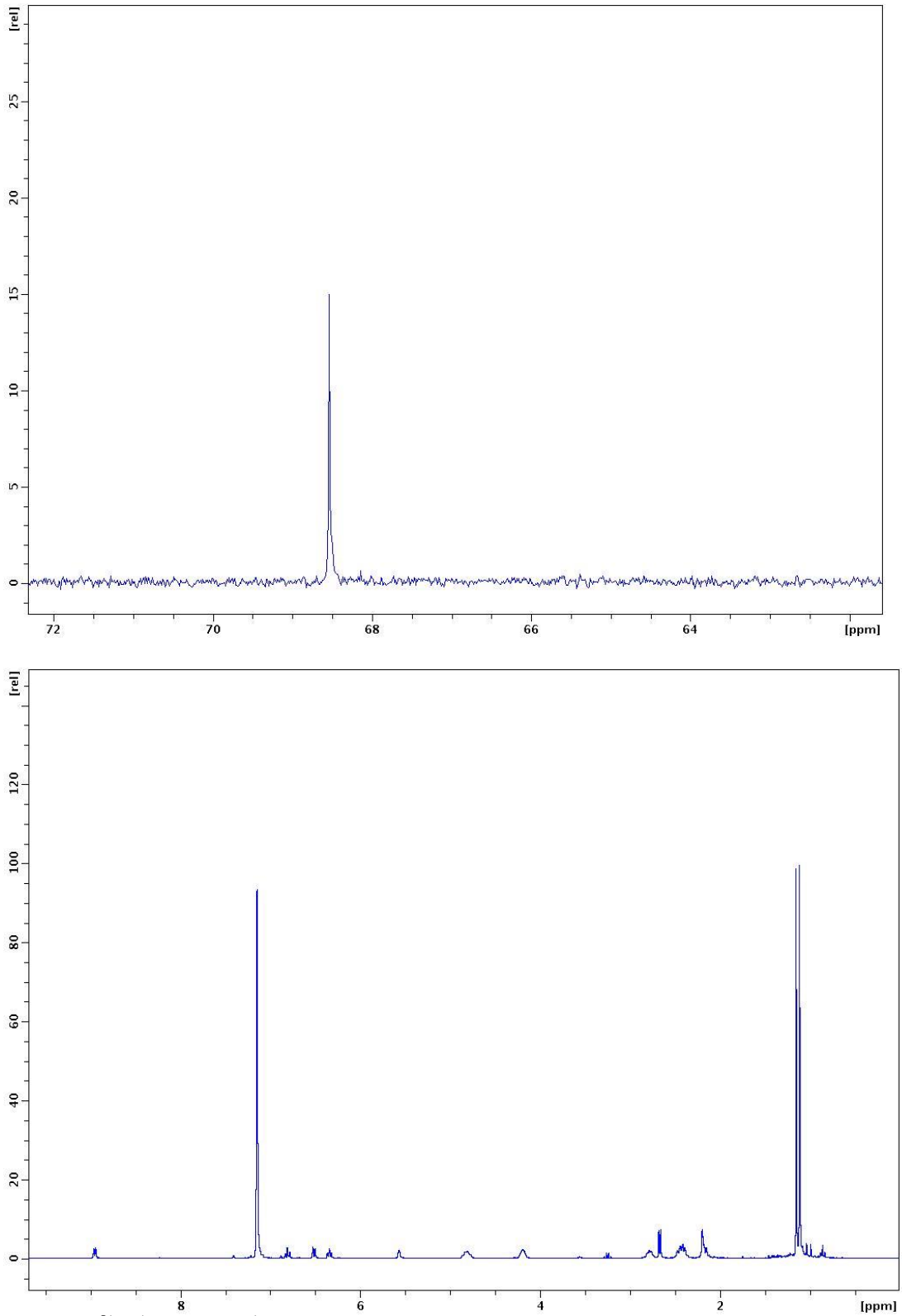


Figure S1. ^{31}P $\{^{1}H\}$ (top) and ^{1}H NMR (bottom) spectra of **1** in C_6D_6 at ambient temperature. A trace quantity of COD is present in the spectrum.

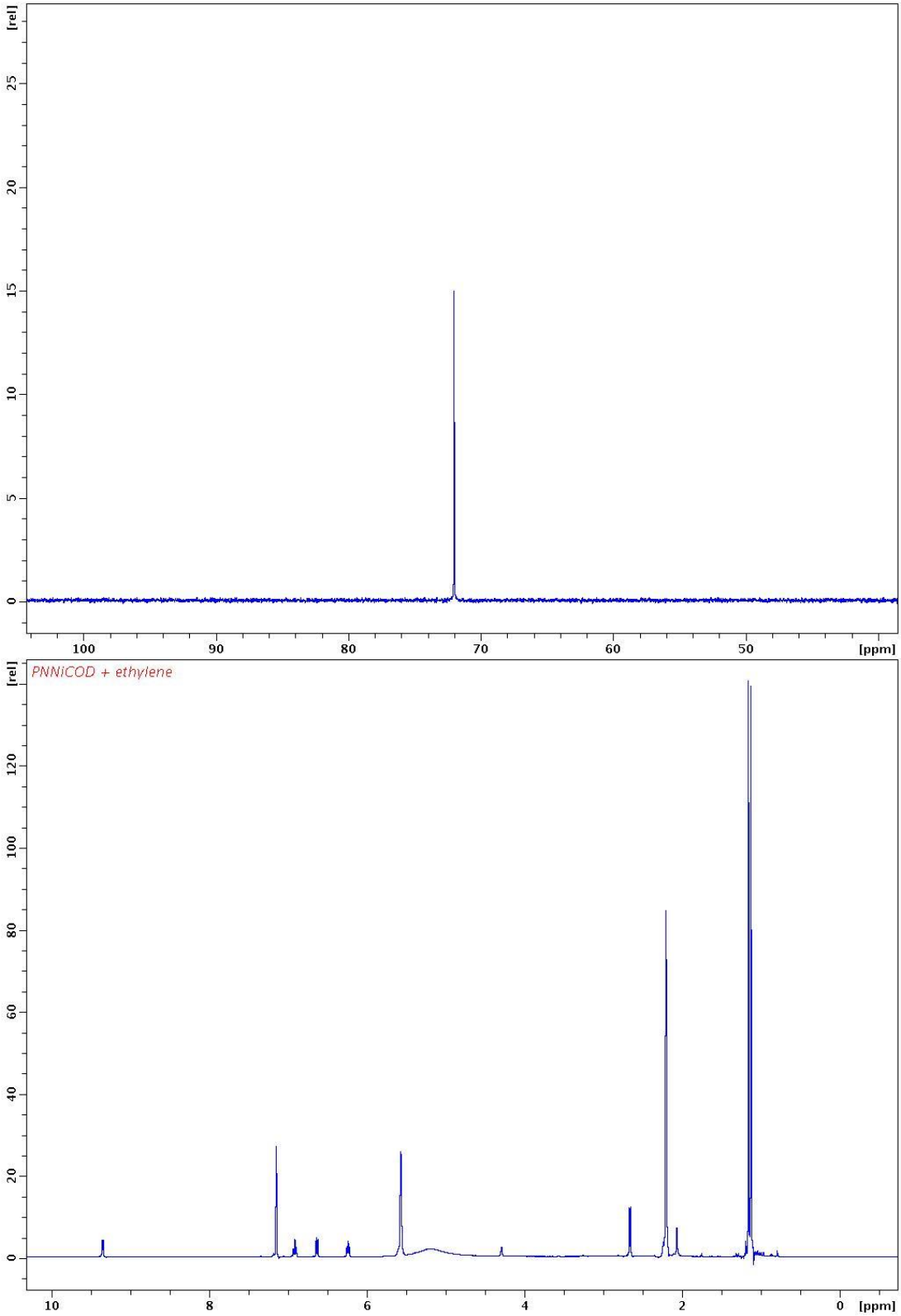


Figure S2. ^{31}P {^{1}H} (top) and ^{1}H NMR (bottom) spectra of **2a** in C_6D_6 at ambient temperature. Free COD and ethylene are present in the spectrum.

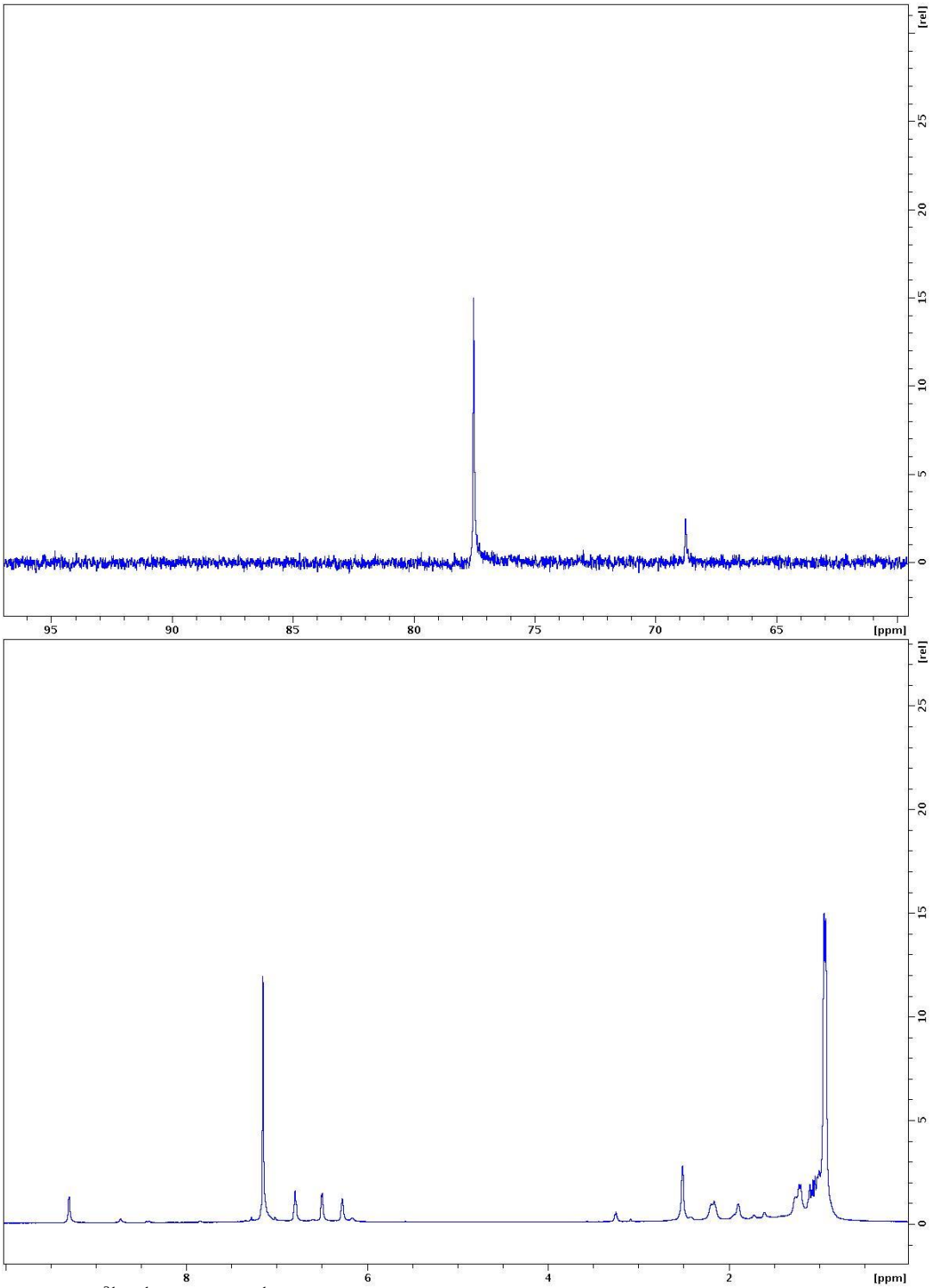
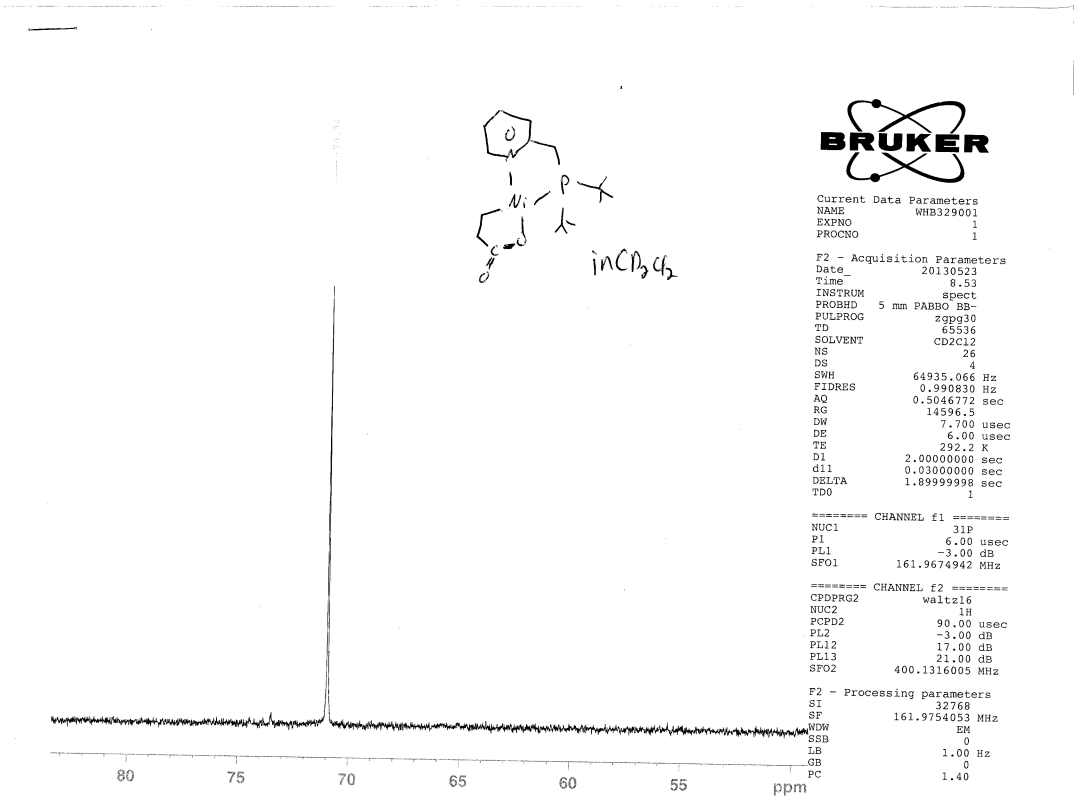


Figure S3. $^{31}P\{^{1}H\}$ (top) and ^{1}H NMR (bottom) spectra of **2c** in C_6D_6 at ambient temperature. A small contaimination from the starting material **1** is present in the top spectrum. .



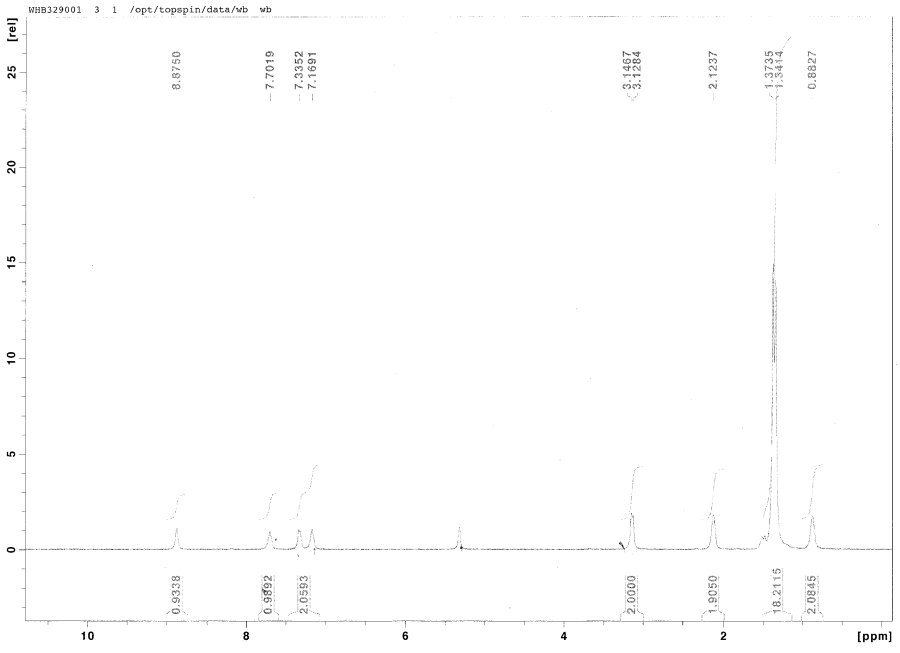


Figure S4. ^{31}P $\{^{1}H\}$ (top) and ^{1}H NMR (bottom) spectra of **3a** in CD_2Cl_2 at ambient temperature.

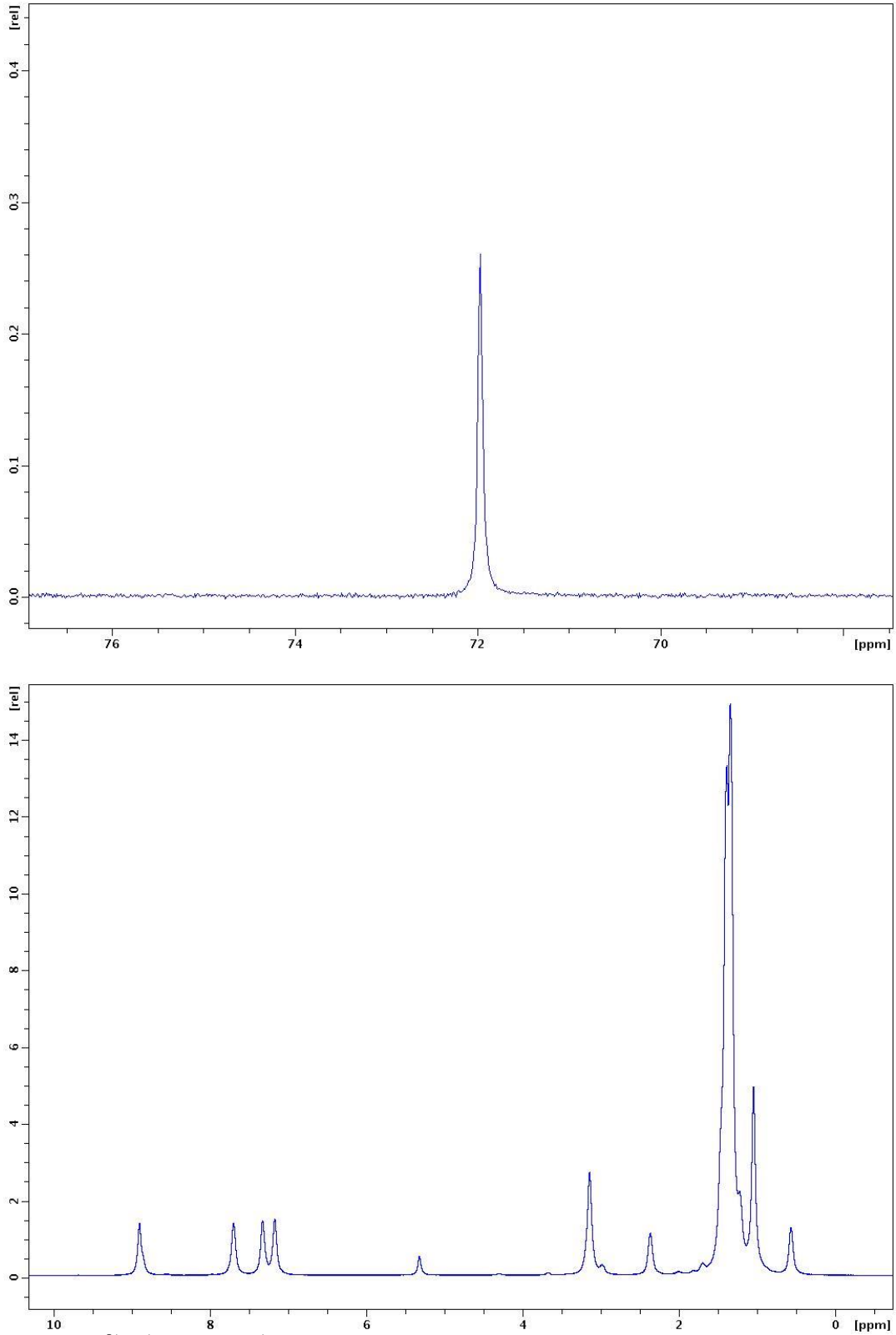


Figure S5. ^{31}P {^{1}H} (top) and ^{1}H NMR (bottom) spectra of **3b** in CD_2Cl_2 at ambient temperature.

References

[1] Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.