

Supplementary Information

Effect of Photolysis on Zirconium Amino Phenoxides for the Hydrophosphination of Alkenes: Improving Catalysis

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Computational Details

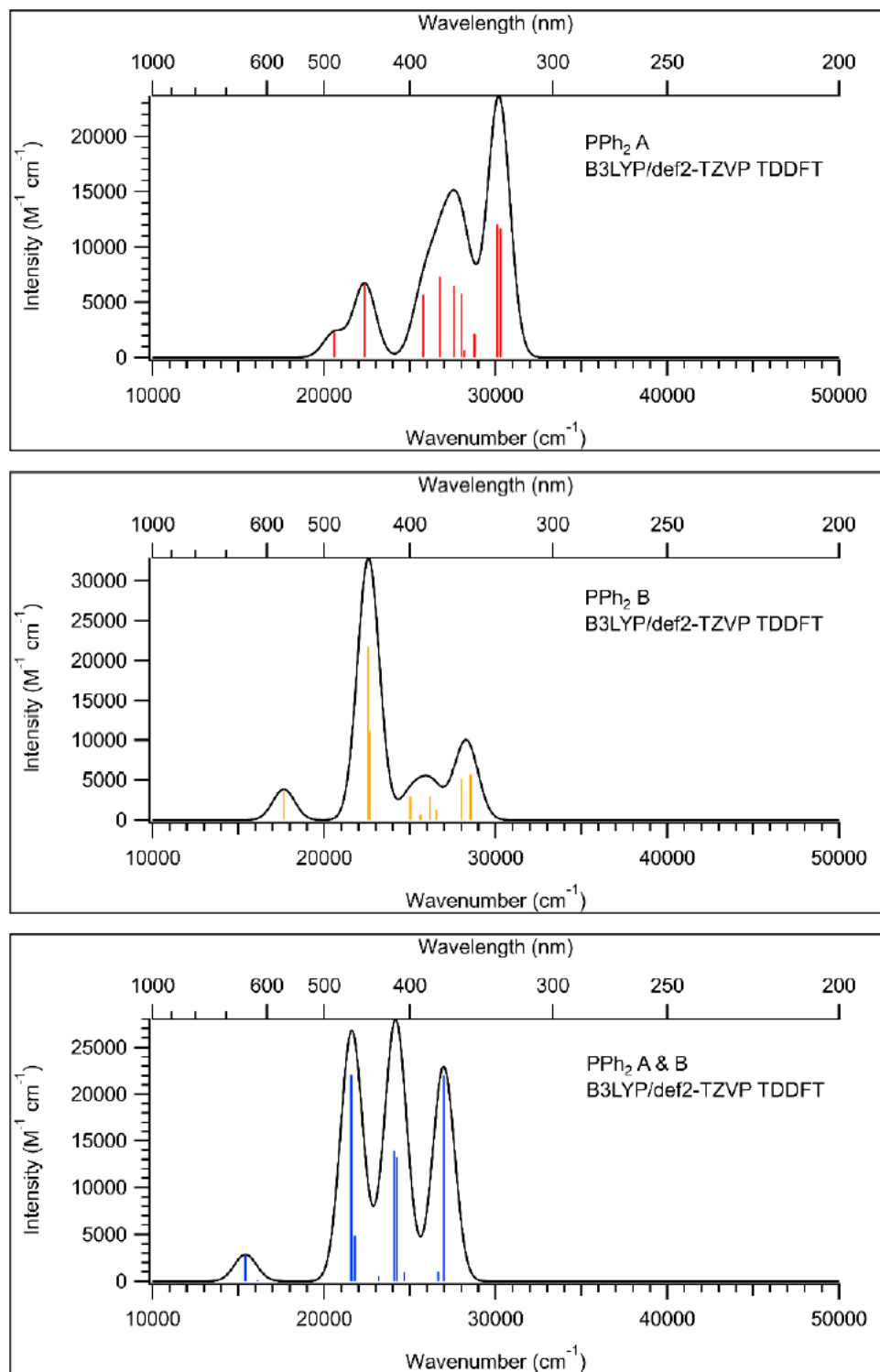


Figure S1. Electronic transitions for compounds **A** (red), **B** (yellow), and **AB** (blue) calculated using TD-DFT at the B3LYP/def2-TZVP level of theory.

Compound A:

Excited State	Transition (MO#-->MO#)	Contribution (rounded)
1	173→174	90%
	173→175	1%
	173→176	5%
2	173→175	91%
	172→174	1%
	173→176	3%
3	173→176	62%
	172→175	10%
	172→174	9%
	173→177	8%
	173→180	1%
4	172→174	36%
	172→175	30%
	173→176	16%

Figure S2. Molecular orbital transitions for compound A.

Compound A MO 173 → 174

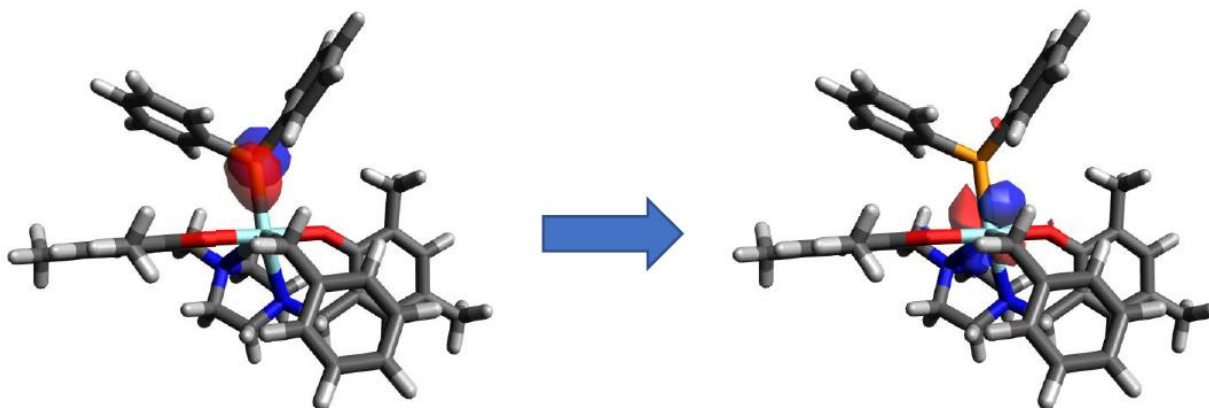


Figure S3. Electronic transitions from MO 173 → 174 in compound A. This is a visual example of a P 3*p* → Zr 4*d* transition.

Compound B:

Excited State	Transition (MO#-->MO#)	Contribution
1	173→174	86%
	173→175	11%
2	173→175	62%
	172→176	22%
	173→174	6%
	172→174	5%
3	173→176	74%
	173→175	16%
	173→174	4%
	172→174	2%
4	173→177	84%
	172→174	10%
	171→174	1%

Figure S4. Molecular orbital transitions for compound **B**.**Compound AB:**

Excited State	Transition (MO#-->MO#)	Contribution
1	197→198	86%
	197→200	6%
	196→198	3%
	197→199	3%
2	197→199	95%
	197→198	3%
3	196→199	83%
	197→200	12%
4	197→200	77%
	196→199	13%
	197→198	5%
	196→200	1%
5	196→198	33%
	197→201	31%
	196→200	26%
	196→201	2%
	197→198	2%

Figure S5. Molecular orbital transitions for compound **AB**.

Cartesian Coordinates

B3LYP/def2-TZVP geometry optimized Cartesian coordinates for compound **2**.

Zr	1.712500	22.381900	9.017200
N	-0.337600	21.307500	9.606300
O	1.850300	20.444200	8.375200
C	-1.177700	21.191200	8.382400
H	-2.114200	21.119500	8.625200
H	-0.930200	20.397300	7.882200
C	-0.944200	22.438600	7.540800
H	-0.349000	22.241600	6.801400
H	-1.784300	22.763900	7.181300
C	1.421300	19.170800	8.535100
C	1.970800	18.126300	7.787200
C	1.491100	16.846100	8.032500
H	1.859200	16.141800	7.548000
C	0.492400	16.550700	8.963100
C	-0.044400	17.622000	9.643600
H	-0.734800	17.466800	10.248300
C	0.404800	18.923100	9.462000
C	-0.215700	19.994500	10.298800
H	-1.099000	19.702000	10.574100
H	0.318500	20.113800	11.100700
C	3.024100	18.391900	6.688300
C	2.398500	19.275300	5.615900
H	1.626900	18.839600	5.248000
H	3.038100	19.436400	4.917400
H	2.134500	20.113800	6.005400
C	4.278000	19.045500	7.285900

H	4.907400	19.230500	6.586100
H	4.675200	18.448600	7.925500
H	4.033000	19.866200	7.722300
C	3.483500	17.102700	5.998200
H	2.731000	16.679000	5.581000
H	3.865500	16.511900	6.649900
H	4.140900	17.314600	5.332200
C	0.048200	15.103300	9.198700
C	1.224600	14.315400	9.786600
H	1.949300	14.303500	9.155400
H	0.948000	13.414200	9.971800
H	1.516500	14.736200	10.599400
C	-0.392100	14.461700	7.907500
H	-1.148500	14.939200	7.556400
H	-0.635800	13.548500	8.069800
H	0.328700	14.494500	7.272700
C	-1.102800	15.031700	10.202600
H	-0.828700	15.428600	11.032200
H	-1.340100	14.112500	10.351700
H	-1.860400	15.506200	9.855200
C	3.047000	21.886500	10.789400
H	3.913800	21.644800	10.427500
H	3.172600	22.713100	11.282300
C	2.691700	20.845000	11.783600
C	2.982300	19.484200	11.586500
H	3.448000	19.218600	10.826600
C	2.580000	18.529200	12.514600
H	2.771600	17.628000	12.377600

C	1.899800	18.929100	13.625600
H	1.644700	18.284500	14.247100
C	1.571100	20.251100	13.868400
H	1.087600	20.504800	14.622300
C	2.000000	21.185200	12.925800
H	1.810900	22.083400	13.076100
N	-0.337600	23.456200	8.428100
O	1.850300	24.319500	9.659200
C	-1.177700	23.572600	9.652000
H	-2.114200	23.644200	9.409100
H	-0.930200	24.366400	10.152100
C	-0.944200	22.325200	10.493600
H	-0.349000	22.522100	11.233000
H	-1.784300	21.999900	10.853100
C	1.421300	25.592900	9.499300
C	1.970800	26.637400	10.247100
C	1.491100	27.917700	10.001900
H	1.859200	28.621900	10.486400
C	0.492400	28.213100	9.071300
C	-0.044400	27.141800	8.390800
H	-0.734800	27.296900	7.786000
C	0.404800	25.840600	8.572300
C	-0.215700	24.769300	7.735500
H	-1.099000	25.061700	7.460200
H	0.318500	24.649900	6.933600
C	3.024100	26.371800	11.346000
C	2.398500	25.488500	12.418500
H	1.626900	25.924200	12.786400

H	3.038100	25.327300	13.117000
H	2.134500	24.649900	12.028900
C	4.278000	25.718300	10.748500
H	4.907400	25.533200	11.448200
H	4.675200	26.315100	10.108900
H	4.033000	24.897600	10.312000
C	3.483500	27.661000	12.036100
H	2.731000	28.084800	12.453300
H	3.865500	28.251900	11.384500
H	4.140900	27.449100	12.702200
C	0.048200	29.660500	8.835600
C	1.224600	30.448300	8.247700
H	1.949300	30.460200	8.878900
H	0.948000	31.349500	8.062600
H	1.516500	30.027500	7.435000
C	-0.392100	30.302100	10.126900
H	-1.148500	29.824600	10.478000
H	-0.635800	31.215300	9.964600
H	0.328700	30.269200	10.761700
C	-1.102800	29.732100	7.831700
H	-0.828700	29.335200	7.002100
H	-1.340100	30.651200	7.682600
H	-1.860400	29.257600	8.179200
C	3.047000	22.877300	7.245000
H	3.913800	23.119000	7.606900
H	3.172600	22.050600	6.752100
C	2.691700	23.918800	6.250700
C	2.982300	25.279600	6.447900

H	3.448000	25.545200	7.207700
C	2.580000	26.234500	5.519700
H	2.771600	27.135800	5.656800
C	1.899800	25.834700	4.408800
H	1.644700	26.479300	3.787200
C	1.571100	24.512600	4.165900
H	1.087600	24.259000	3.412100
C	2.000000	23.578600	5.108500
H	1.810900	22.680300	4.958200

B3LYP/def2-TZVP geometry optimized Cartesian coordinates for compound **A**.

Zr	1.839158	22.448103	8.852881
N	-0.265872	21.327092	9.606617
O	1.899026	20.494111	8.207482
C	-1.186538	21.204953	8.456988
H	-2.211377	20.999796	8.820855
H	-0.875367	20.348570	7.846898
C	-1.122157	22.517729	7.651929
H	-0.589437	22.387993	6.697760
H	-2.136710	22.891415	7.415911
C	1.472597	19.227612	8.359317
C	1.944539	18.160540	7.535183
C	1.455533	16.877307	7.797685
H	1.820370	16.057194	7.181032
C	0.519448	16.573886	8.799951
C	0.047328	17.643388	9.559157
H	-0.692308	17.479241	10.345624
C	0.509723	18.948436	9.357885
C	-0.005566	20.031201	10.269502

H	-0.935685	19.674084	10.754422
H	0.717283	20.233768	11.078118
C	2.947101	18.396887	6.391077
C	2.327089	19.367201	5.362392
H	1.429860	18.923086	4.904797
H	3.049314	19.581905	4.559605
H	2.043746	20.314773	5.833703
C	4.264088	18.982005	6.946506
H	4.969025	19.175934	6.123051
H	4.737144	18.272554	7.642192
H	4.088323	19.921022	7.482480
C	3.304075	17.103337	5.638635
H	2.421466	16.631348	5.182179
H	3.795419	16.365364	6.290151
H	4.005850	17.346563	4.827316
C	0.070406	15.122263	9.020587
C	1.294651	14.264576	9.410961
H	2.062432	14.270385	8.623718
H	0.994022	13.219008	9.580169
H	1.756665	14.646422	10.333000
C	-0.548649	14.560838	7.722083
H	-1.435067	15.141089	7.425951
H	-0.855290	13.513374	7.865910
H	0.165807	14.588643	6.886823
C	-0.972402	15.001732	10.142306
H	-0.570472	15.339319	11.109204
H	-1.272653	13.950123	10.257926
H	-1.880441	15.583353	9.923401

P	3.160375	21.910229	11.136140
N	-0.385828	23.508930	8.458259
O	2.001121	24.422041	9.369205
C	-1.049393	23.628880	9.776044
H	-2.127700	23.830020	9.630133
H	-0.618912	24.487492	10.304308
C	-0.815673	22.316649	10.551927
H	-0.082124	22.453621	11.361633
H	-1.756099	21.944489	11.002416
C	1.529951	25.682746	9.291070
C	2.154643	26.786324	9.947256
C	1.561631	28.045437	9.796615
H	2.038291	28.890594	10.292014
C	0.392844	28.293661	9.059025
C	-0.196727	27.193539	8.438952
H	-1.105606	27.312377	7.846463
C	0.356373	25.912236	8.534066
C	-0.294937	24.806542	7.747230
H	-1.313794	25.127353	7.457187
H	0.261972	24.616237	6.813655
C	3.426414	26.624133	10.795626
C	3.129754	25.696727	11.993115
H	2.344923	26.135613	12.629133
H	4.035525	25.574395	12.607060
H	2.802793	24.698838	11.677860
C	4.570412	26.054335	9.929563
H	5.476047	25.919612	10.540006
H	4.811163	26.749881	9.110787

H	4.309902	25.083814	9.497016
C	3.925021	27.961176	11.373724
H	3.190515	28.422201	12.051766
H	4.180016	28.686896	10.586944
H	4.837484	27.773032	11.958587
C	-0.180241	29.715880	8.971351
C	0.882889	30.667660	8.381787
H	1.788137	30.700138	9.003731
H	0.484218	31.691450	8.312872
H	1.179883	30.346793	7.372699
C	-0.568995	30.203533	10.384414
H	-1.330168	29.545888	10.829364
H	-0.980391	31.224108	10.339344
H	0.298851	30.220424	11.058537
C	-1.429954	29.784868	8.079303
H	-1.212863	29.471725	7.047275
H	-1.800281	30.820057	8.042349
H	-2.245529	29.156600	8.467264
C	3.047004	22.942461	6.950814
H	3.923012	23.398213	7.449378
H	3.333907	21.965219	6.539382
C	2.493828	23.839333	5.916259
C	2.714182	25.234057	5.942667
H	3.345914	25.653983	6.728494
C	2.139203	26.081262	4.995928
H	2.332307	27.155014	5.050058
C	1.323999	25.568086	3.981930
H	0.875070	26.231432	3.241077

C	1.106379	24.187953	3.924295
H	0.488735	23.765323	3.128105
C	1.681959	23.339940	4.871146
H	1.512473	22.262040	4.798067
C	4.933875	22.419871	10.971917
C	5.589044	22.911905	12.115681
H	5.029894	22.993289	13.050131
C	6.931190	23.292893	12.070936
H	7.417521	23.668965	12.973471
C	7.648773	23.199179	10.875343
H	8.696394	23.502729	10.837341
C	7.015957	22.713061	9.729829
H	7.567746	22.630529	8.790858
C	5.674086	22.325058	9.780482
H	5.202365	21.933926	8.876706
C	3.364488	20.118793	11.549898
C	4.233624	19.247104	10.870596
H	4.822647	19.620135	10.031891
C	4.358056	17.912092	11.255072
H	5.039657	17.255131	10.710359
C	3.610607	17.411149	12.325192
H	3.709227	16.365817	12.623467
C	2.748034	18.263174	13.016655
H	2.175477	17.890410	13.868765
C	2.635344	19.603787	12.638359
H	1.992053	20.276351	13.211587

B3LYP/def2-TZVP geometry optimized Cartesian coordinates for compound **B**.

Zr	1.763930	22.189712	9.084369
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N	-0.421960	21.150019	9.800429
O	1.791954	20.206385	8.577105
C	-1.267090	20.945521	8.600798
H	-2.315522	20.777807	8.913339
H	-0.929889	20.040802	8.083191
C	-1.136607	22.187300	7.698527
H	-0.531240	21.979679	6.802750
H	-2.129240	22.535187	7.352247
C	1.292198	18.962267	8.738486
C	1.714755	17.853355	7.944459
C	1.127548	16.609871	8.204559
H	1.451751	15.763227	7.601382
C	0.151278	16.381098	9.187524
C	-0.258031	17.489335	9.927664
H	-1.025035	17.389607	10.698491
C	0.291237	18.758668	9.718286
C	-0.210348	19.899496	10.563975
H	-1.162800	19.595420	11.041374
H	0.498707	20.134807	11.374548
C	2.790279	17.992798	6.855575
C	2.369812	19.067461	5.830954
H	1.403420	18.804893	5.371132
H	3.120445	19.139285	5.029155
H	2.283554	20.051622	6.305497
C	4.128175	18.379279	7.519769
H	4.899498	18.563950	6.757783
H	4.476460	17.567377	8.176619
H	4.025198	19.290921	8.117323

C	3.018405	16.686222	6.076224
H	2.107036	16.342712	5.563464
H	3.381389	15.872739	6.722570
H	3.785721	16.861783	5.308302
C	-0.434942	14.975584	9.384343
C	0.701633	13.963442	9.641051
H	1.405027	13.916297	8.797918
H	0.287337	12.954193	9.786986
H	1.274072	14.232947	10.541206
C	-1.203818	14.562268	8.109664
H	-2.035373	15.255377	7.915738
H	-1.619600	13.548557	8.220032
H	-0.550993	14.564872	7.224904
C	-1.406196	14.913613	10.573140
H	-0.918422	15.207210	11.514490
H	-1.775169	13.884972	10.695559
H	-2.282339	15.561762	10.422055
C	3.094717	21.763469	10.885543
H	3.915194	21.381589	10.239516
H	3.371702	22.767099	11.238267
C	2.815243	20.839298	12.002645
C	3.091631	19.458128	11.919257
H	3.556116	19.063719	11.012894
C	2.779236	18.590545	12.965820
H	3.008211	17.527309	12.867270
C	2.180924	19.070989	14.134924
H	1.938716	18.391275	14.953440
C	1.909052	20.438093	14.243391

H	1.456017	20.834800	15.154802
C	2.222748	21.306392	13.197356
H	2.016661	22.375091	13.305229
N	-0.460998	23.233992	8.480454
O	1.742233	24.168310	9.642359
C	-1.222142	23.444959	9.733186
H	-2.287663	23.622565	9.492277
H	-0.839876	24.344977	10.226407
C	-1.042912	22.199014	10.623831
H	-0.384688	22.400274	11.482102
H	-2.015462	21.853823	11.025610
C	1.311034	25.421280	9.431580
C	1.843308	26.539432	10.141790
C	1.336679	27.803360	9.824246
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B3LYP/def2-TZVP geometry optimized Cartesian coordinates for compound **AB**.

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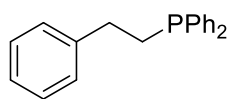
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C	4.546260	21.352320	7.018260
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C	5.257260	21.440420	5.825800
H	4.850430	22.014550	4.987260

Spectra of Hydrophosphination Reactions



Phenethyl(diphenyl)phosphine

Spectra are consistent with literature [1]. After 2 hours under irradiation from an LED lamp the reaction goes to 83% consumption of styrene with **1** measured by ^1H NMR spectroscopy.

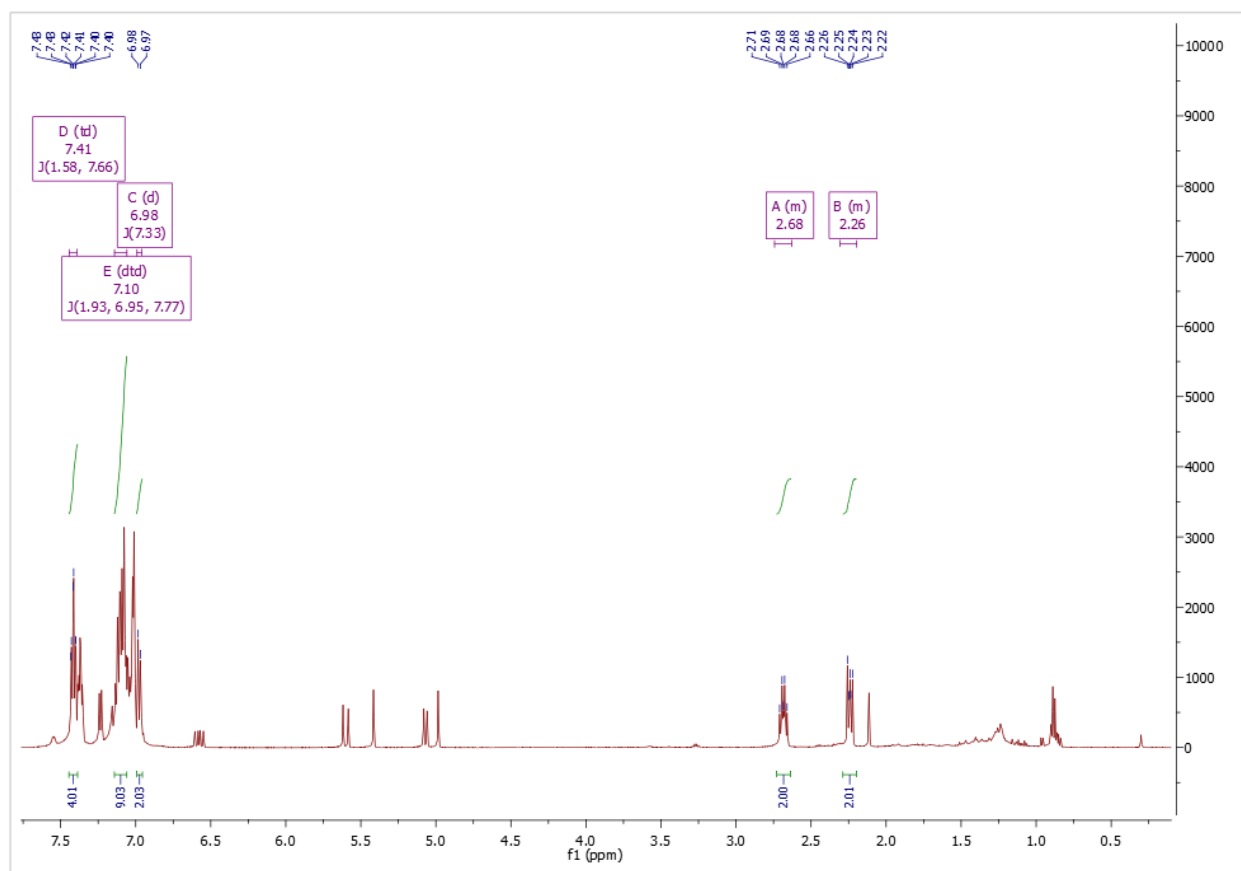
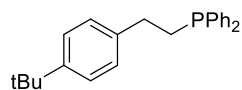


Figure S6. ^1H NMR spectrum of the hydrophosphination of styrene with Ph_2PH and **1** in C_6D_6 after 2 hours under LED irradiation.



(p-(*tert*-butyl)phenethyl)(diphenyl)phosphine

Spectra are consistent with literature [2]. After 2 hours under irradiation from an LED lamp the reaction goes to 70% consumption of 4-*tert*-butylstyrene with **1** measured by ^1H NMR spectroscopy.

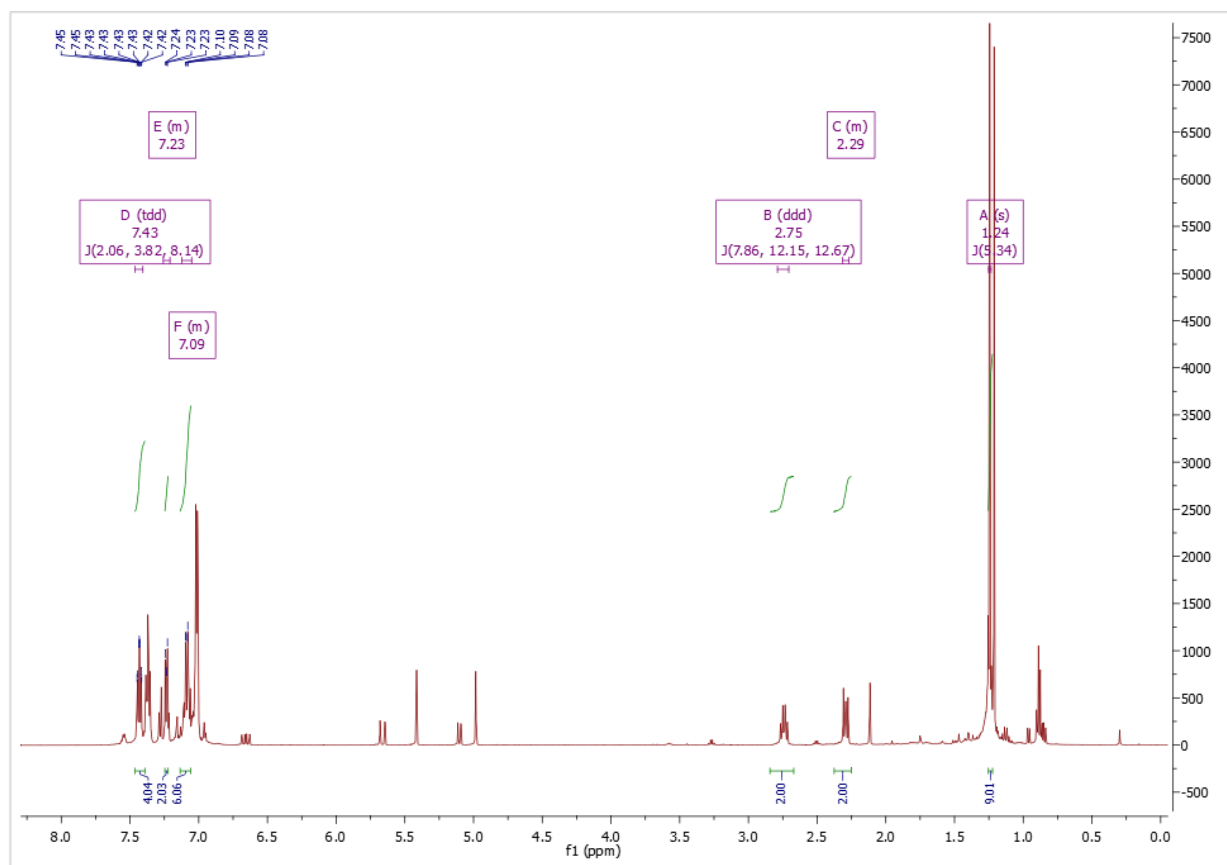


Figure S7. ^1H NMR spectrum of the hydrophosphination of 4-*tert*-butylstyrene with Ph_2PH and **1** in C_6D_6 after 2 hours under LED irradiation. Shifts corresponding to 2 missing protons on the product are obscured by starting material.



Spectra are consistent with literature [2]. After 2 hours under irradiation from an LED lamp the reaction goes to 91% consumption of 4-bromostyrene with **1** measured by ^1H NMR spectroscopy.

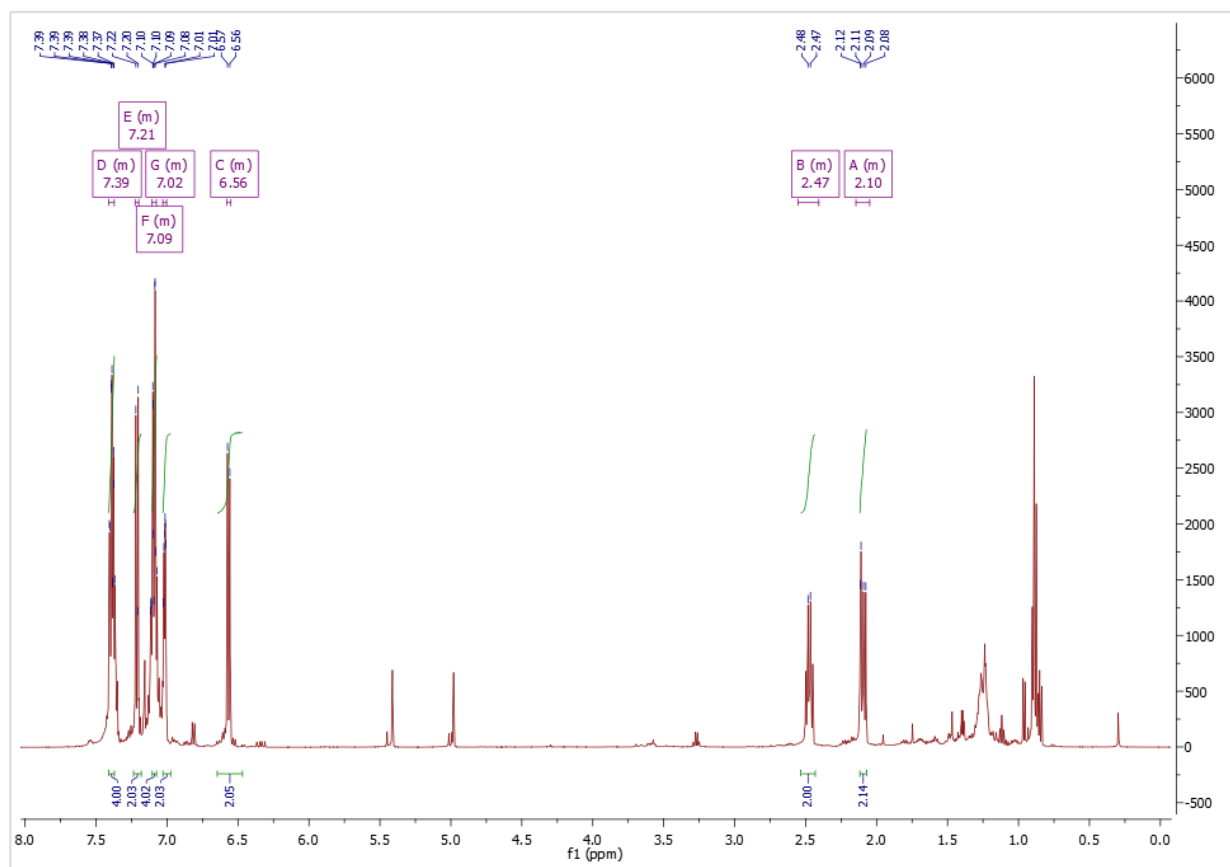
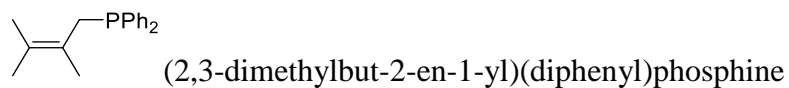


Figure S8. ^1H NMR spectrum of the hydrophosphination of 4-bromostyrene with Ph_2PH and **1** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [3]. After 2 hours under irradiation from an LED lamp the reaction goes to 65% consumption of 2,3-dimethylbutadiene with **1** measured by ^1H NMR spectroscopy.

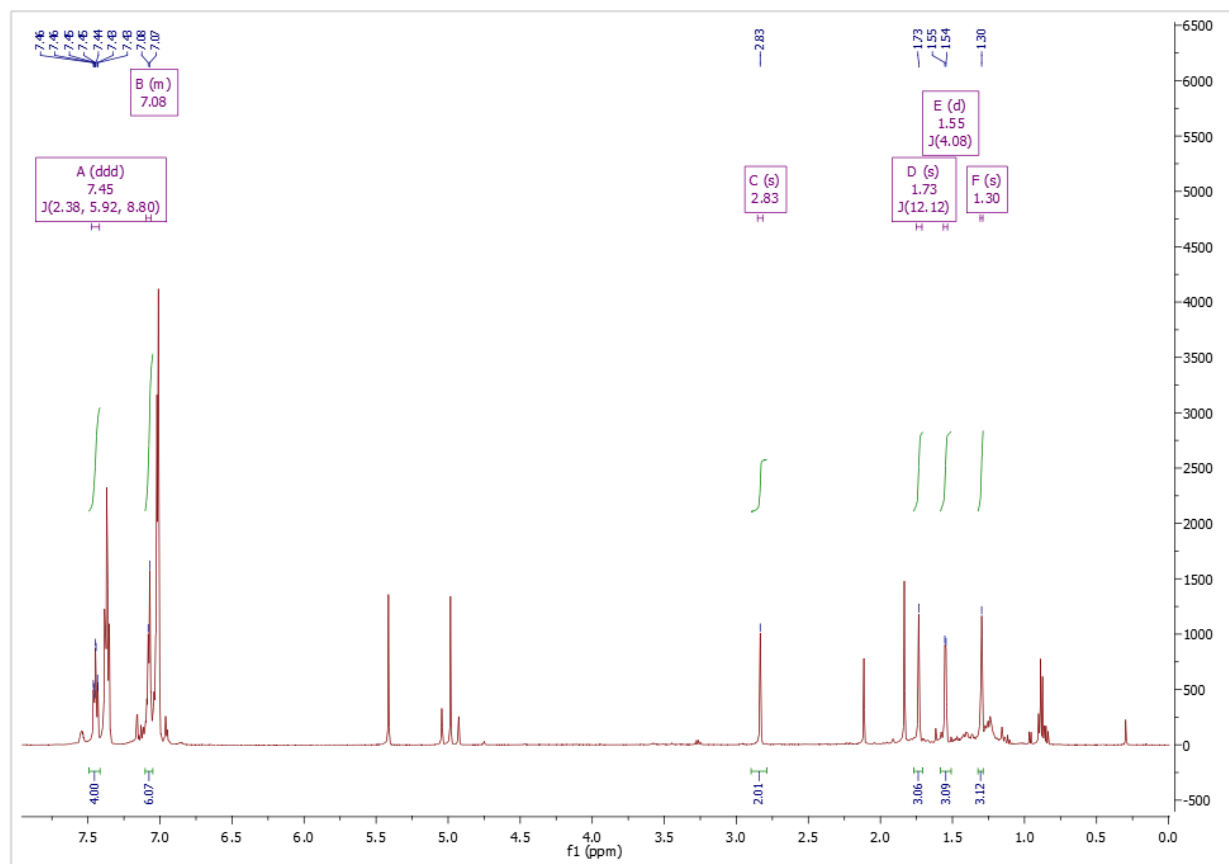
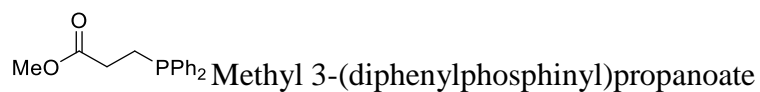


Figure S9. ^1H NMR spectrum of the hydrophosphination of 2,3-dimethylbutadiene with Ph_2PH and **1** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [1]. After 2 hours under irradiation from an LED lamp the reaction goes to 90% consumption of methyl acrylate with **1** measured by ^1H NMR spectroscopy.

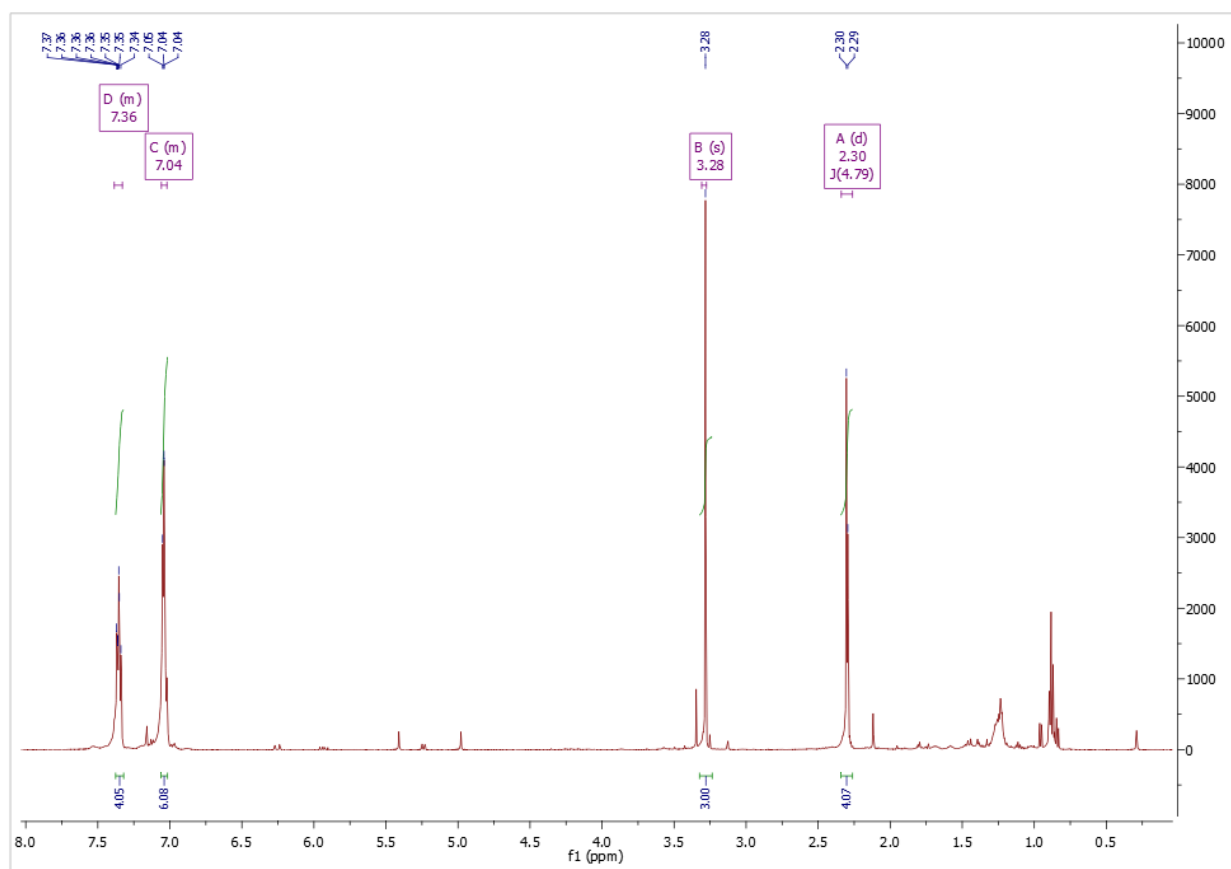


Figure S10. ^1H NMR spectrum of the hydrophosphination of methyl acrylate with Ph_2PH and **1** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [4]. After 24 hours under irradiation from an LED lamp the reaction goes to 68% consumption of *trans*-chalcone with **1** measured by ^1H NMR spectroscopy.

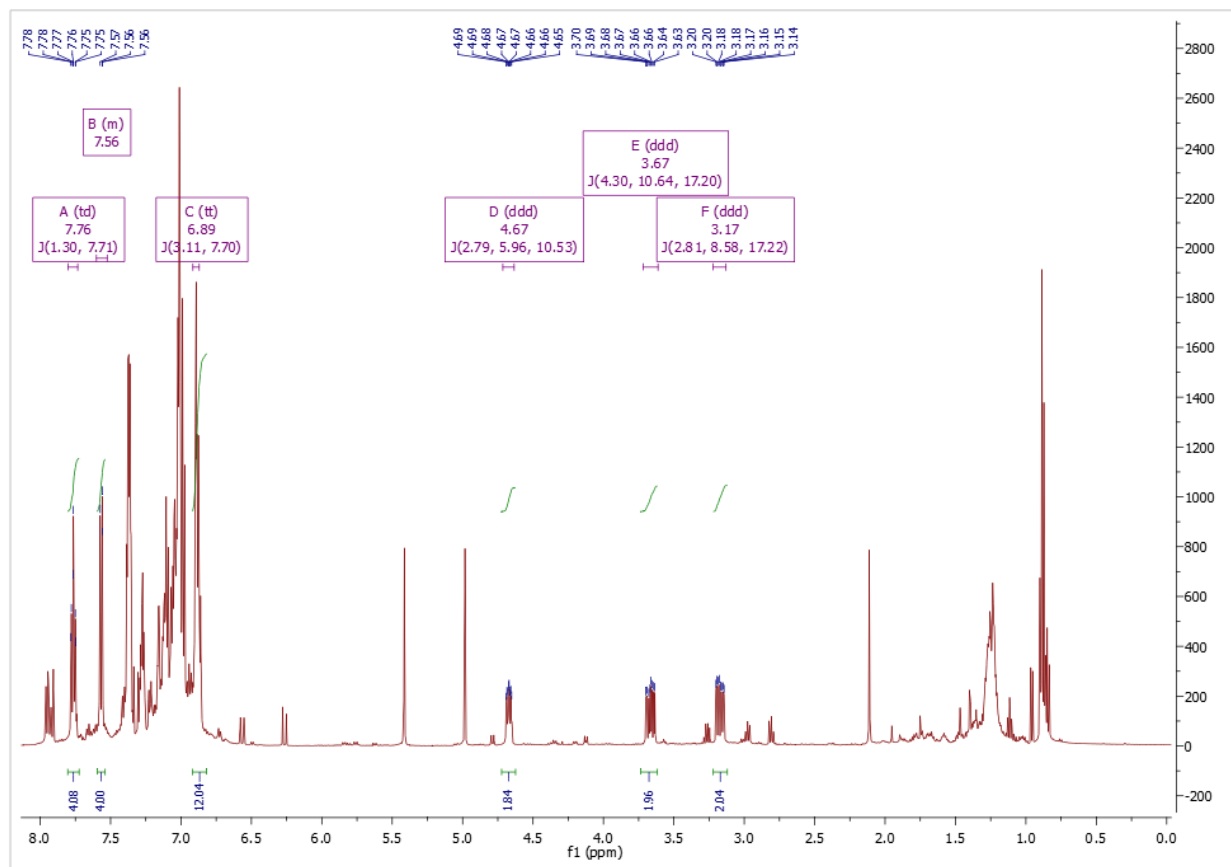
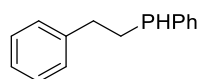


Figure S11. ^1H NMR spectrum of the hydrophosphination of *trans*-chalcone with Ph_2PH and **1** in C_6D_6 after 24 hours under LED irradiation.



Phenethyl(phenyl)phosphine

Spectra are consistent with literature [5]. After 2 hours under irradiation from an LED lamp the reaction goes to quantitative consumption of styrene with **1** measured by ^1H NMR spectroscopy.

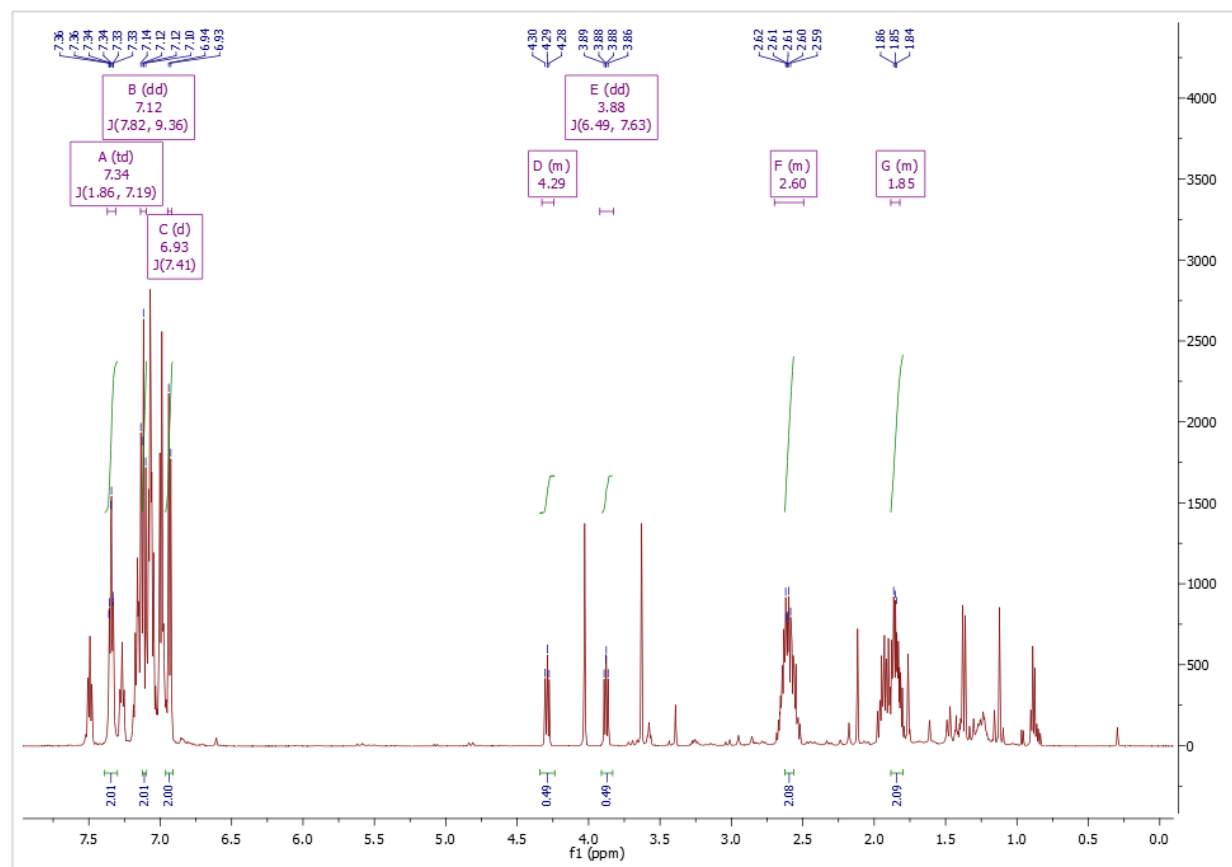
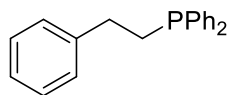


Figure S12. ^1H NMR spectrum of the hydrophosphination of styrene with PhPH_2 and **1** in C_6D_6 after 2 hours under LED irradiation.



Phenethyl(diphenyl)phosphine

Spectra are consistent with literature [1]. After 2 hours under irradiation from an LED lamp the reaction goes to 91% consumption of styrene with **2** measured by ^1H NMR spectroscopy.

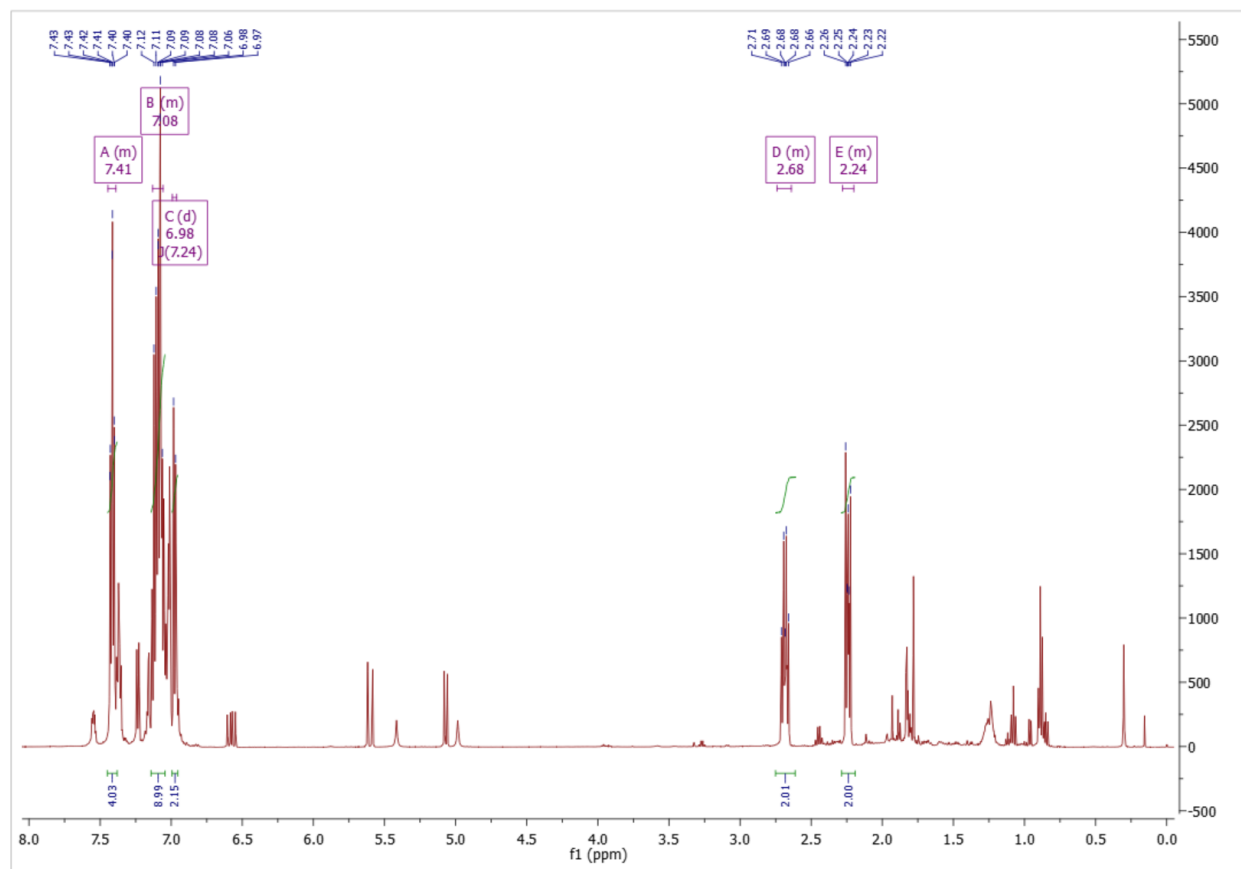


Figure S13. ^1H NMR spectrum of the hydrophosphination of styrene with Ph_2PH and **2** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [2]. After 2 hours under irradiation from an LED lamp the reaction goes to 88% consumption of 4-*tert*-butylstyrene with **2** measured by ^1H NMR spectroscopy.

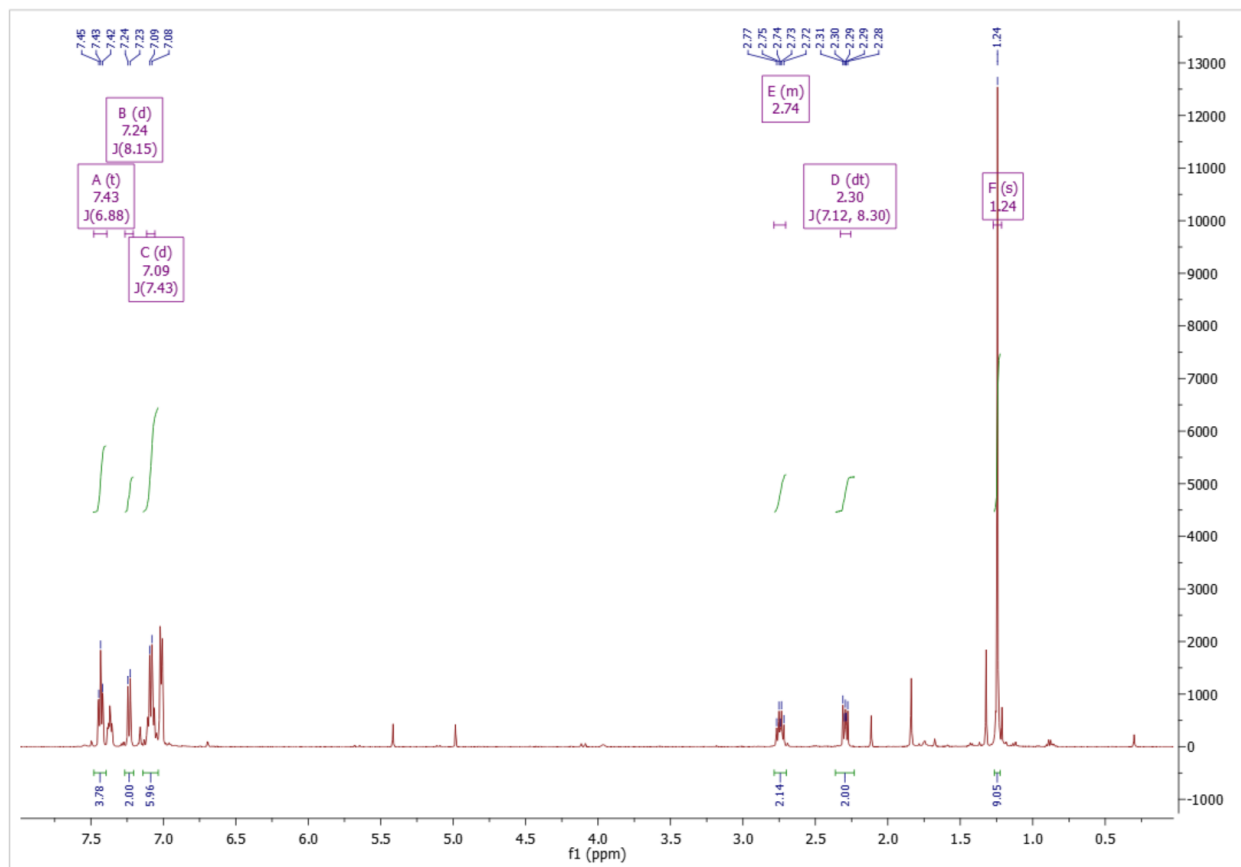
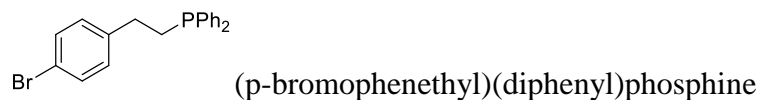


Figure S14. ^1H NMR spectrum of the hydrophosphination of 4-*tert*-butylstyrene with Ph_2PH and **2** in C_6D_6 after 2 hours under LED irradiation. Shifts corresponding to 2 missing protons on the product are obscured by starting material.



Spectra are consistent with literature [2]. After 2 hours under irradiation from an LED lamp the reaction goes to >99% consumption of 4-bromostyrene with **2** measured by ^1H NMR spectroscopy.

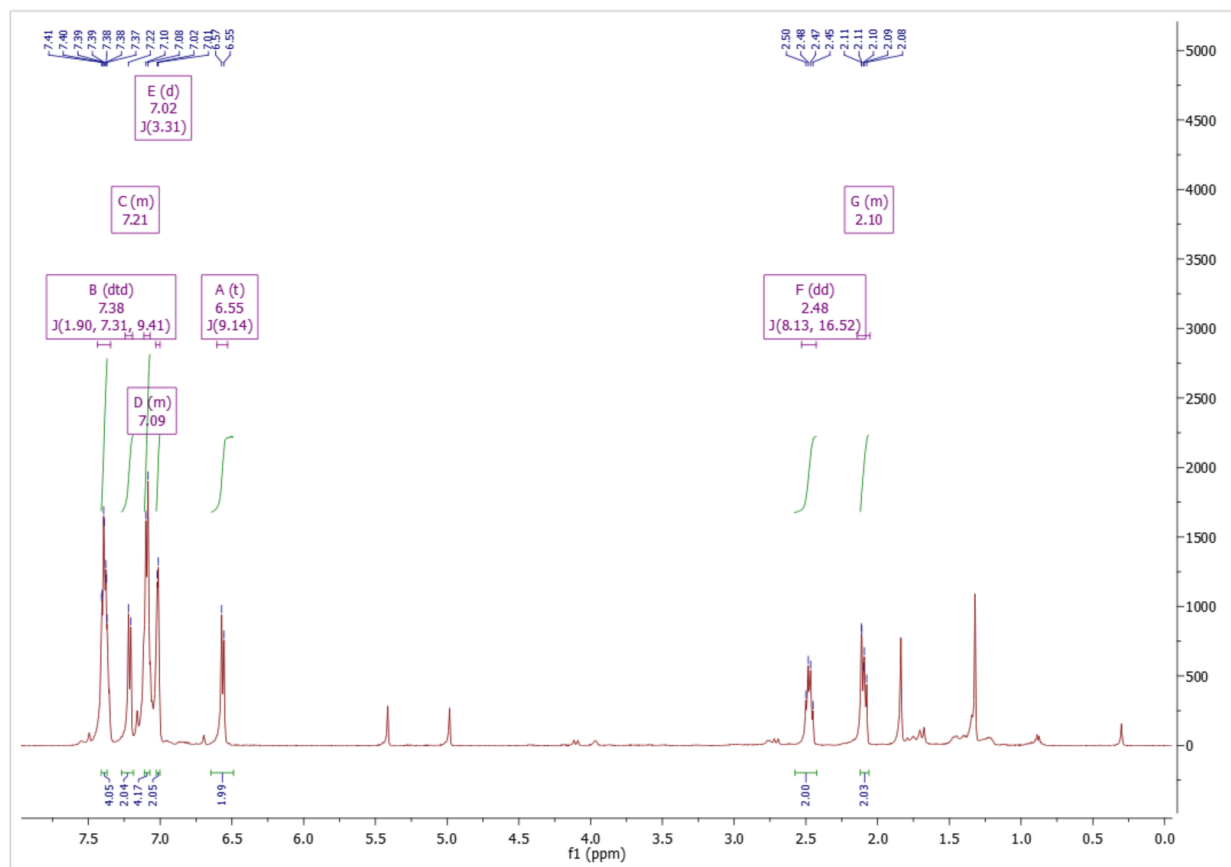
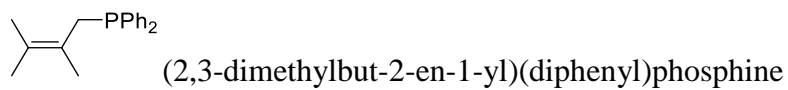


Figure S15. ^1H NMR spectrum of the hydrophosphination of 4-bromostyrene with Ph_2PH and **2** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [3]. After 2 hours under irradiation from an LED lamp the reaction goes to 66% consumption of 2,3-dimethylbutadiene with **2** measured by ^1H NMR spectroscopy.

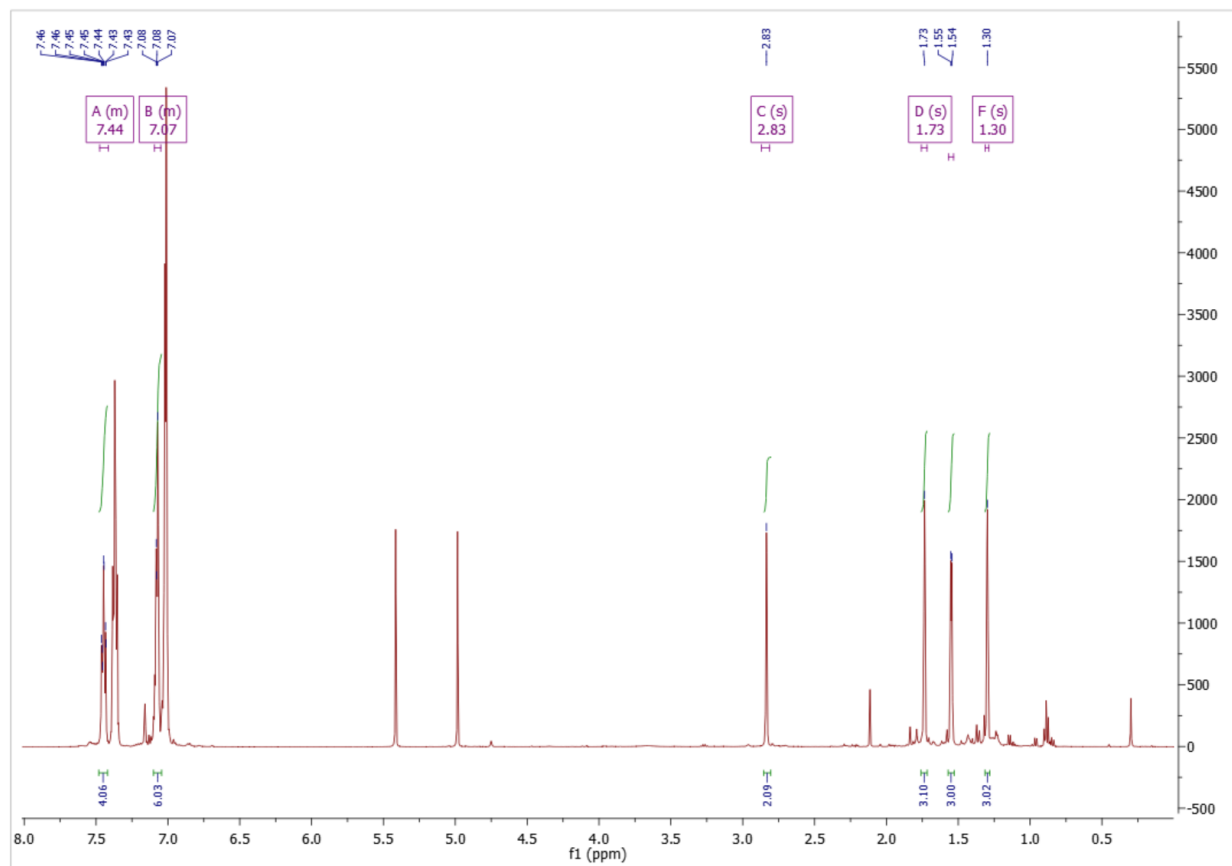
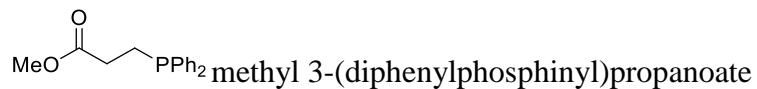


Figure S16. ^1H NMR spectrum of the hydrophosphination of 2,3-dimethylbutadiene with Ph_2PH and **2** in C_6D_6 after 2 hours under LED irradiation.



Spectra are consistent with literature [1]. After 2 hours under irradiation from an LED lamp the reaction goes to quantitative consumption of methyl acrylate with **2** measured by ^1H NMR spectroscopy.

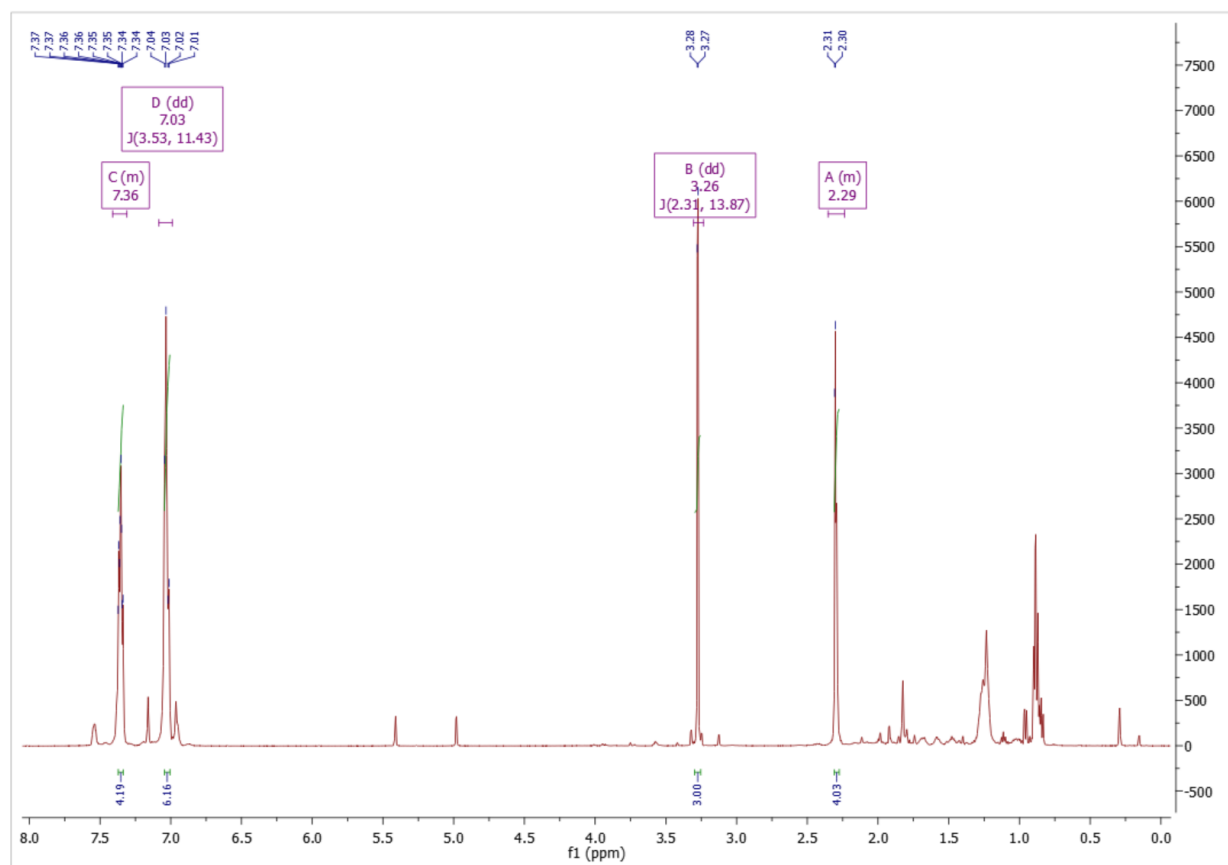
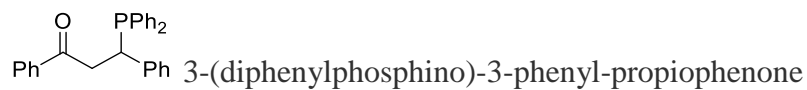


Figure S17. ^1H NMR spectrum of the hydrophosphination of methyl acrylate with Ph₂PH and **2** in C₆D₆ after 2 hours under LED irradiation.



Spectra are consistent with literature [4]. After 24 hours under irradiation from an LED lamp the reaction goes to 68.1% consumption of *trans*-chalcone with **2** measured by ^1H NMR spectroscopy.

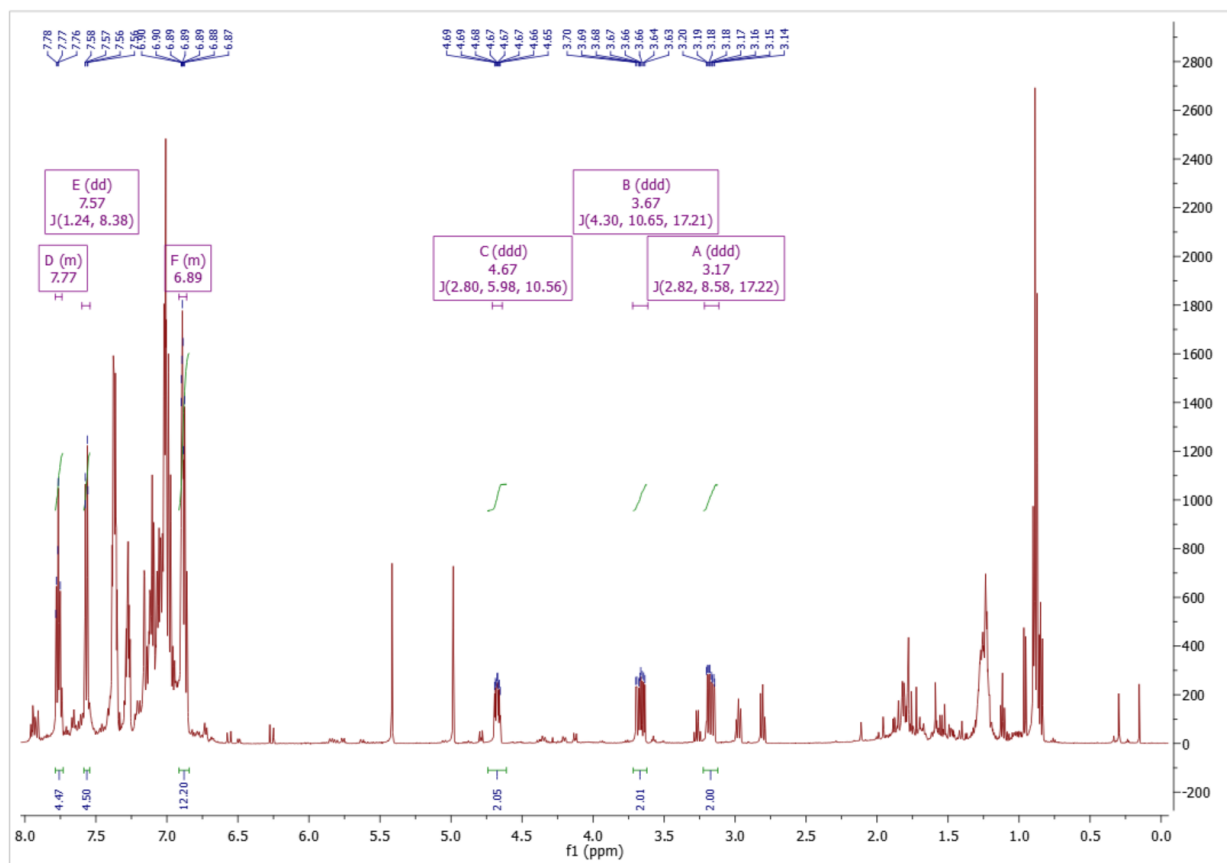
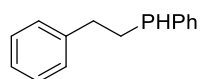


Figure S18. ^1H NMR spectrum of the hydrophosphination of *trans*-chalcone with Ph₂PH and **2** in C₆D₆ after 24 hours under LED irradiation.



Phenethyl(phenyl)phosphine

Spectra are consistent with literature [5]. After 2 hours under irradiation from an LED lamp the reaction goes to quantitative consumption of styrene with **2** measured by ^1H NMR spectroscopy.

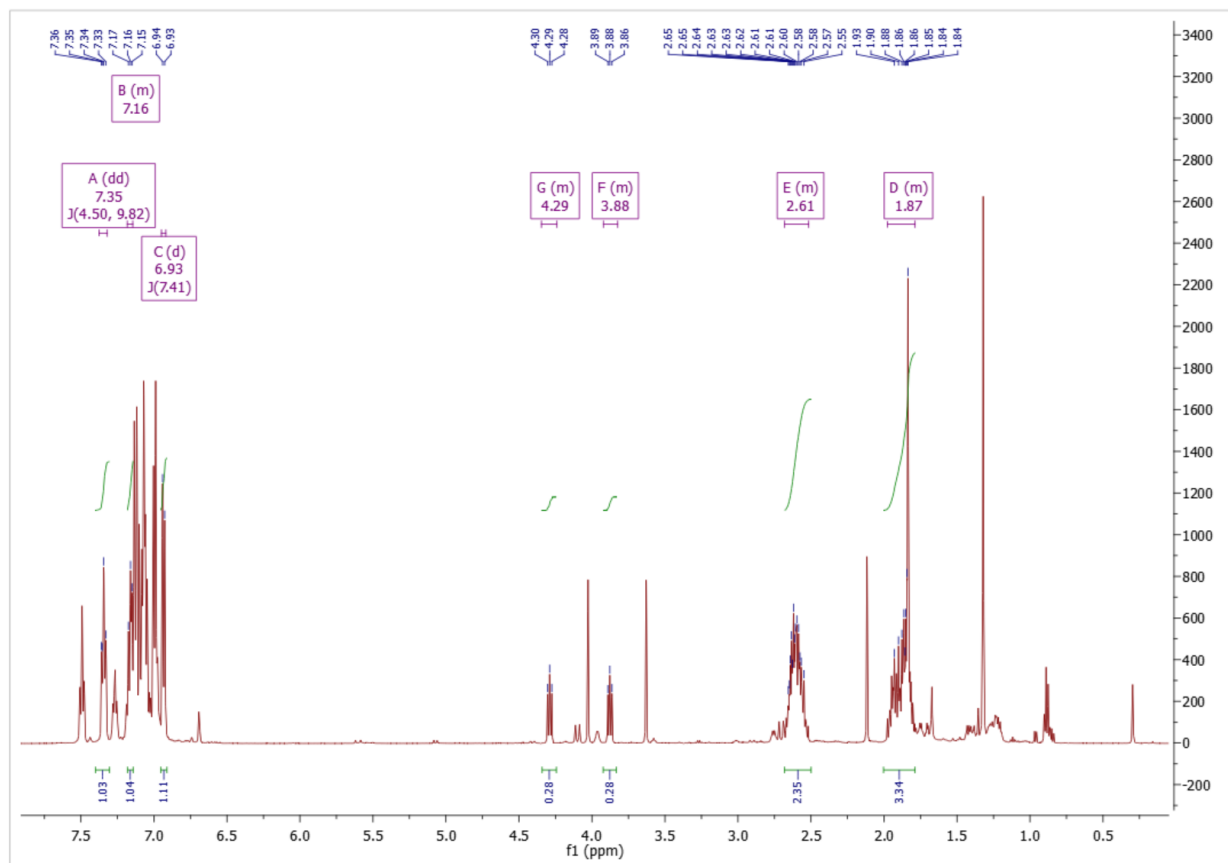


Figure S19. ^1H NMR spectrum of the hydrophosphination of styrene with PhPH_2 and **2** in C_6D_6 after 2 hours under LED irradiation.

References

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