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Phosphine-catalyzed [3 + 2] annulation of 2-aminoacrylates with allenoates and mechanistic studies

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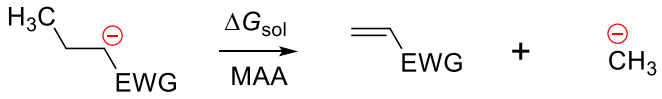
1. Computational details

Methyl anion affinities:

Methyl anion affinities (MAA) have been calculated using the same methodology employed successfully in earlier studies[1] as the free energy at 298.15 K (ΔG_{sol}) for reaction shown in equation S1. [MAA = (ΔG_{sol} of eq. S1)].



(S1)

Geometry optimizations have been performed with a combination of the B3LYP[2]/6-31G(d,p)[3] level of theory. Thermochemical corrections to Gibbs energies (corr. ΔG) and enthalpy (corr. ΔH) at 298.15 K have been calculated using the rigid rotor/harmonic oscillator model without any scaling. Thermal corrections to Gibbs energies (corr. ΔG) are further treated with the quasi-harmonic approximation with a cutoff value of 100 cm^{-1} using *Goodvibes*.[4]

Single point total electronic energies (ΔE_{tot}) have subsequently been calculated using a combination of the B3LYP hybrid functional and the larger 6-311++G(3df,2pd) basis set.[3, 5] Solvent effects on MAA values have been estimated by adding single point solvation corrections (ΔG_{Solv}). ΔG_{Solv} was calculated for gas phase optimized geometries using the SMD[6] continuum solvation model.

ΔG_{sol} [B3LYP/6-311++G(3df,2pd)] = ΔE_{tot} [B3LYP/6-311++G(3df,2pd)] + corr. qh-ΔG [B3LYP/6-31G(d,p)] + ΔG_{Solv} [SMD(DCM)/B3LYP/6-31G(d,p)]

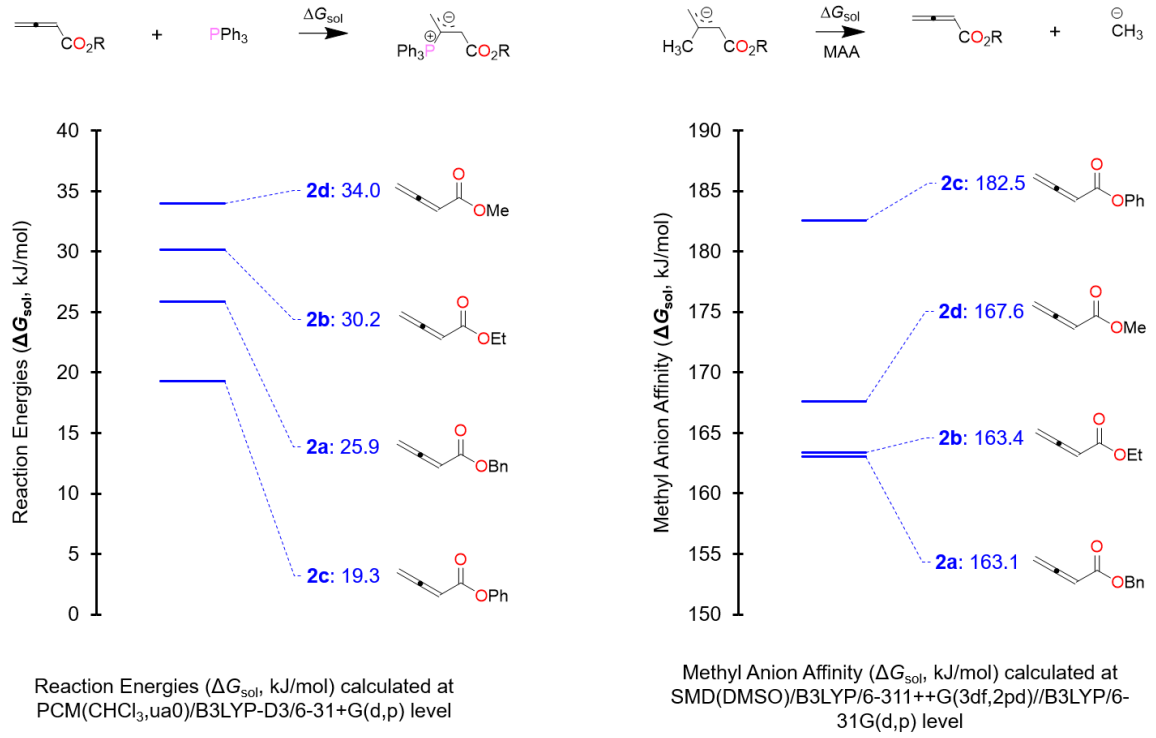
ΔH_{sol} [B3LYP/6-311++G(3df,2pd)] = ΔE_{tot} [B3LYP/6-311++G(3df,2pd)] + corr. ΔH [B3LYP/6-31G(d,p)] + ΔG_{Solv} [SMD(DCM)/B3LYP/6-31G(d,p)]

For reaction energy profile:

Geometry optimizations have been performed with a combination of the B3LYP hybrid functional[2] complemented by the D3 dispersion correction[7] and the 6-31+G(d,p)[3] basis set under implicit solvation that is implemented using polarizable continuum model[8] (solvent=chloroform, radii=ua0). [these settings referred in text as the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory]. Thermochemical corrections to Gibbs energies (corr. ΔG) and enthalpy (corr. ΔH) at 298.15 K have been calculated using the rigid rotor/harmonic oscillator model without any scaling. Thermal corrections to Gibbs energies (corr. ΔG) are further treated with the quasi-harmonic approximation with a cutoff value of 100 cm^{-1} using *Goodvibes*.[4]

Free energies in solution have been corrected to a reference state of 1 mol/l at 298.15 K through addition of RTln(24.46) = +7.925 kJ/mol (= 0.0030185 Hartree) to the gas phase (1 atm) free energies. The value for R = 8.31451 J K^{-1} mol^{-1}. All calculations have been performed with *Gaussian 09*, Rev. D.[9]

2. Summary



Reaction Energies (ΔG_{sol}, kJ/mol) calculated at PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level

Methyl Anion Affinity (ΔG_{sol}, kJ/mol) calculated at SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level

Figure S1. Comparison of methyl anion affinities and PPh_3 additional reaction energies (ΔG_{sol}, in kJ/mol) calculated at the SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) and PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) levels of theory respectively for selected allenoates (**2a-d**).

3. Methyl anion affinities (MAA)

Table S1. Methyl anion affinities (in kJ/mol) calculated at the SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) levels of theory for selected allenoates (**2a-d**).

Label	Filename	Based on Best Conformer				Based on Boltzmann Avg.		
		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}
2a	b5	+235.1	+215.5	+162.8		+235.3	+215.7	**+163.1**
2b	b9	+234.8	+215.0	+163.9		+233.9	+214.2	**+163.4**
2c	b3	+254.9	+234.6	+182.4		+254.7	+234.5	**+182.5**
2d	b2	+237.9	+218.1	+168.3		+237.0	+217.4	**+167.6**

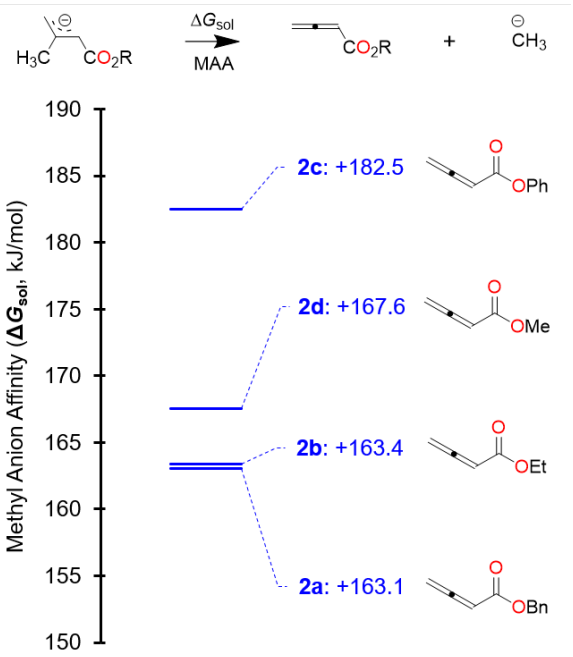


Figure S2. Methyl anion affinities (ΔG_{sol}, in kJ/mol) calculated at the SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) levels of theory for selected allenoates (**2a-d**).

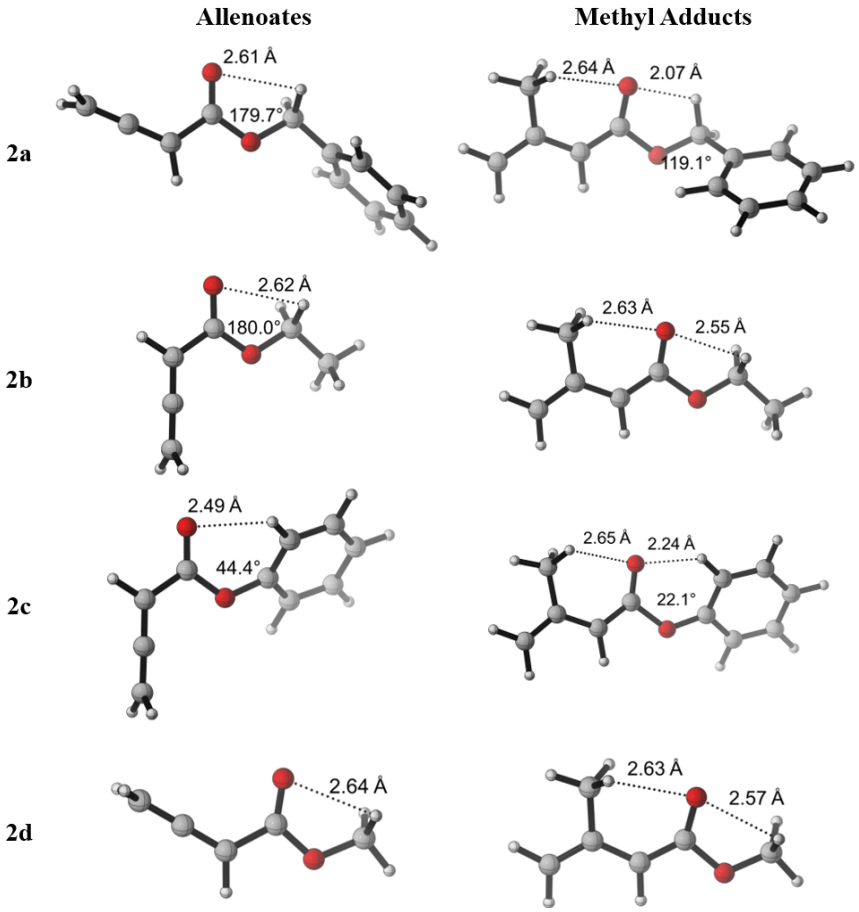


Figure S3. Structure of gas phase lowest free energy (ΔG_{sol}) conformers of allenoates (**2a-d**) and corresponding methyl adducts obtained at the SMD(DMSO)/B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) levels of theory.

Table S2. QM properties for gas phase optimized conformers of selected allenoates (**2a-d**) and their corresponding methyl anion adducts (ma).

Marker	File Name (for internal reference)	B3LYP\6-31G(d,p)										ΔE_{tot} (hartree) [B3LYP/6-311++G(3df,2pd) //B3LYP/6-31G(d)]
		Low Frequency			$HOMO_E$ (hartree)	$LUMO_E$ (hartree)	corr. ZPE (hartree)	corr. ΔH (hartree)	corr. qh-ΔG^a (hartree)	ΔG_{Solv} (kcal/mol)	ΔE_{tot} (hartree)	
CH_3^{-1}	ch3anion	-29	0	0	0.13514	0.37353	0.027840	0.031650	0.008651	-78.9	-39.7960280	-39.8566374
2a	b5_4	-5	0	0	-0.24727	-0.03919	0.181227	0.193953	0.141116	-7.02	-575.6037632	-575.7921996
	b5_1	-4	0	0	-0.24701	-0.03854	0.181201	0.193941	0.141147	-7.13	-575.6035430	-575.7919823
	b5_5	-6	0	0	-0.24577	-0.04012	0.180694	0.193671	0.138773	-7.62	-575.6028220	-575.7918664
	b5_2	-10	-4	0	-0.24860	-0.03739	0.180669	0.193673	0.138840	-8.02	-575.6025513	-575.7920488
	b5_3	-9	-6	-2	-0.24944	-0.03704	0.180668	0.193687	0.137059	-8.11	-575.6025457	-575.7921399
	b5_6	-7	0	0	-0.25240	-0.04233	0.180759	0.193545	0.140618	-9.68	-575.5899441	-575.7788268
	b5_7	-5	-4	0	-0.24709	-0.04689	0.180359	0.193420	0.138954	-10.42	-575.5886826	-575.7783665
2a+CH_3^{-1}	ma_b5_8	-4	-2	0	0.01177	0.10767	0.218810	0.233115	0.177360	-50.02	-615.5820983	-615.7962934
	ma_b5_10	-4	0	0	0.01134	0.10428	0.218343	0.232780	0.175863	-50.12	-615.5820501	-615.7970296
	ma_b5_5	-12	-4	0	0.01334	0.10755	0.219050	0.233230	0.177707	-50.42	-615.5780057	-615.7924501
	ma_b5_1	-4	0	0	0.01349	0.10423	0.218647	0.232947	0.176380	-50.69	-615.5771846	-615.7925760
2b	b9_3	-11	-8	0	-0.26273	-0.03757	0.127844	0.137752	0.094110	-4.78	-383.8659710	-383.9992046
	b9_4	-9	0	0	-0.26358	-0.03816	0.128117	0.137886	0.094594	-4.51	-383.8657690	-383.9985832
	b9_1	-6	0	0	-0.26502	-0.03649	0.127816	0.137737	0.094346	-4.95	-383.8656605	-383.9989643
	b9_2	0	0	0	-0.26617	-0.03722	0.128127	0.137895	0.094797	-4.66	-383.8655085	-383.9983477
	b9_5	-7	-6	0	-0.26221	-0.04301	0.127553	0.137534	0.093872	-7.69	-383.8522707	-383.9861814
	b9_6	0	0	0	-0.26215	-0.04213	0.127832	0.137635	0.094436	-7.81	-383.8509049	-383.9845082
	b9_7	-9	-3	0	-0.26186	-0.03990	0.127589	0.137538	0.093823	-6.71	-383.8508840	-383.9844083
2b+CH_3^{-1}	ma_b9_5	0	0	0	0.02324	0.20347	0.165761	0.177116	0.130641	-49.99	-423.8378318	-423.9976439
	ma_b9_4	-9	-7	0	0.02535	0.20546	0.165292	0.176929	0.129827	-50.78	-423.8366995	-423.9976867
	ma_b9_2	-11	-2	0	0.02475	0.20153	0.165979	0.177211	0.131136	-50.33	-423.8338096	-423.9938747
	ma_b9_3	-11	-2	0	0.02475	0.20153	0.165979	0.177211	0.131136	-50.33	-423.8338096	-423.9938747
	ma_b9_8	-11	-2	0	0.02475	0.20153	0.165979	0.177211	0.131136	-50.33	-423.8338096	-423.9938747
	ma_b9_1	-9	-3	0	0.02685	0.20334	0.165542	0.177043	0.130322	-51.18	-423.8326363	-423.9938176
	ma_b9_6	-9	-3	0	0.02685	0.20334	0.165542	0.177043	0.130322	-51.18	-423.8326363	-423.9938176
	ma_b9_12	-1	0	0	0.02570	0.20378	0.165970	0.177255	0.130907	-51.71	-423.8324293	-423.9935107
	ma_b9_10	-10	-4	-1	0.02758	0.20556	0.165503	0.177047	0.130016	-52.47	-423.8314089	-423.9935981
	ma_b9_11	-10	-4	-1	0.02758	0.20556	0.165503	0.177047	0.130016	-52.47	-423.8314089	-423.9935980
	ma_b9_7	-9	-3	0	0.02079	0.20281	0.165466	0.176945	0.130143	-51.66	-423.8295742	-423.9919704

	ma_b9_9	0	0	0	0.01990	0.20267	0.165738	0.177011	0.130660	-51.24	-423.8281844	-423.9895380
2c	b3_2	-7	-5	-3	-0.23821	-0.04796	0.151706	0.163245	0.113531	-6.51	-536.2852306	-536.4625979
	b3_1	-4	0	0	-0.23821	-0.04769	0.151697	0.163246	0.113691	-6.60	-536.2850363	-536.4623199
	b3_3	-4	0	0	-0.24699	-0.04823	0.151426	0.163026	0.112892	-8.43	-536.2774258	-536.4553970
	b3_4	-5	0	0	-0.23990	-0.04880	0.151322	0.162888	0.113686	-8.29	-536.2746318	-536.4527299
2c+CH_3^{-1}	ma_b3_3	-10	-2	0	0.00062	0.12682	0.189411	0.202626	0.149500	-48.10	-576.2722893	-576.4757030
	ma_b3_1	0	0	0	0.00318	0.12594	0.189773	0.202793	0.150231	-48.63	-576.2669971	-576.4708625
	ma_b3_6	-5	0	0	0.00453	0.12814	0.189621	0.202750	0.149888	-49.86	-576.2653644	-576.4696981
2d	b2_2	-7	-6	0	-0.26480	-0.03898	0.099484	0.108095	0.067212	-4.29	-344.5441270	-344.6671856
	b2_1	-10	-4	-3	-0.26749	-0.03802	0.099406	0.108053	0.067112	-4.50	-344.5438333	-344.6669600
	b2_3	-9	0	0	-0.26444	-0.04472	0.099201	0.107814	0.066623	-7.45	-344.5299781	-344.6537030
2d+CH_3^{-1}	ma_b2_2	-4	-3	0	0.02715	0.20713	0.136814	0.147217	0.101911	-50.82	-384.5146697	-384.6660460
	ma_b2_1	-9	0	0	0.02849	0.20501	0.137156	0.147382	0.102660	-51.18	-384.5107363	-384.6624460
	ma_b2_5	-9	0	0	0.02934	0.20724	0.137115	0.147391	0.102557	-52.47	-384.5094172	-384.6620716
	ma_b2_4	-15	-4	0	0.02222	0.20420	0.137117	0.147217	0.102685	-51.66	-384.5073991	-384.6600719

[a]Truhlar Quasi-harmonic treatment is used for thermal corrections

4. Reaction Energies

4.1. Phosphine addition to allenoates

Table S3. Reaction energies (kJ/mol) of tertiary phosphine (**PPh_3**) addition to selected allenoates (**2a-d**) calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory.

Label	For Internal Reference	Based on Best Conformer				Based on Boltzmann Avg.		
		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}		ΔE_{tot}	ΔH_{sol}	ΔG_{sol}
2a	b5	-52.6	-44.3	+26.1		-52.5	**-43.8**	**+25.9**
2b	b9	-44.4	-36.0	+31.1		-44.6	**-36.3**	**+30.2**
2c	b3	-59.7	-50.9	+18.2		-58.5	**-49.7**	**+19.3**
2d	b2	-37.9	-29.8	+34.2		-38.0	**-29.8**	**+34.0**

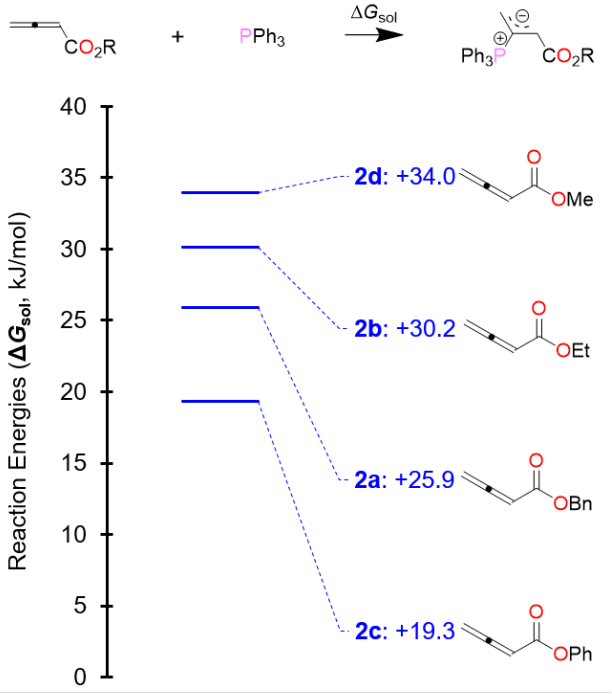


Figure S4. Reaction energies (**ΔG_{sol}**, in kJ/mol) of tertiary phosphine (**PPh_3**) addition to selected allenoates (**2a-d**) calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory.

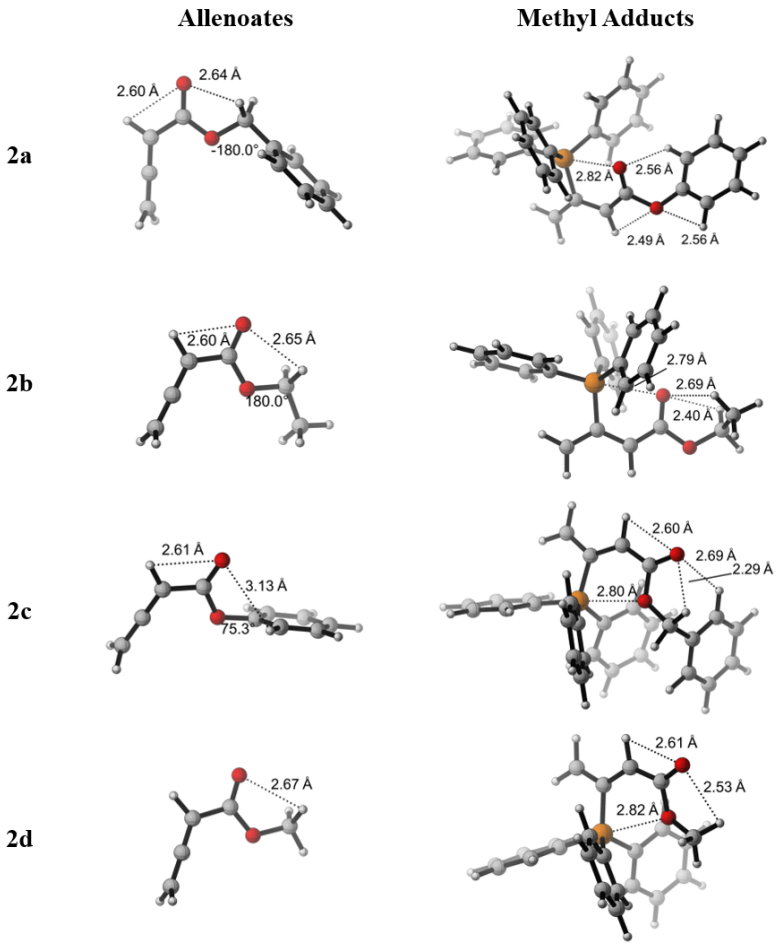


Figure S5. Structure of gas phase lowest free energy (ΔG_{sol}) conformers of allenoates (**2a-d**) and corresponding methyl adducts obtained at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) levels of theory.

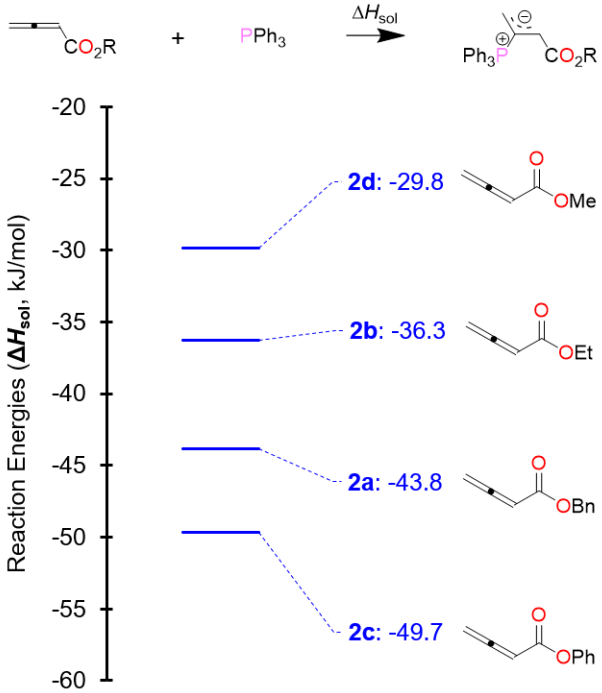


Figure S6. Reaction energies (ΔH_{sol}, in kJ/mol) of tertiary phosphine (**PPh_3**) addition to selected allenoates (**2a-d**) calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory.

Table S4. QM properties for gas phase optimized conformers of selected allenoates (**2a-d**) and their corresponding phosphine (**PPh_3**) adducts (pa) calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory..

Marker	File Name (for internal reference)	Low Frequency			$HOMO_E$ (hartree)	$LUMO_E$ (hartree)	corr. ZPE (hartree)	corr. ΔH (hartree)	corr. qh-ΔG^a (hartree)	ΔE_{tot} (hartree)
PPh_3	pPh3_3	-2	0	0	-0.22360	-0.03397	0.273033	0.289876	0.231712	-1036.3855710
	pPh3_1	-1	0	0	-0.22359	-0.03396	0.273060	0.289903	0.231744	-1036.3855781
2a	b5_5	-12	-5	0	-0.26098	-0.05587	0.180006	0.192967	0.142494	-575.6504163
	b5_2	0	0	0	-0.26130	-0.05630	0.180025	0.192950	0.142607	-575.6502496
	b5_4	-8	0	0	-0.25978	-0.05586	0.180373	0.193139	0.143027	-575.6505818
	b5_1	-9	0	0	-0.25976	-0.05611	0.180330	0.193110	0.143047	-575.6503912
	b5_6	-25	-4	0	-0.26050	-0.06335	0.179903	0.192759	0.142768	-575.6407300
	b5_7	-16	-9	-6	-0.26314	-0.06372	0.179781	0.192818	0.142286	-575.6395839
2a+PPh_3	pa_b5_2	-13	-5	-2	-0.16507	-0.05491	0.457157	0.486182	0.404373	-1612.0531770
	pa_b5_1	0	0	0	-0.16404	-0.05853	0.457429	0.486377	0.404341	-1612.0530653
	pa_b5_4	0	0	0	-0.16564	-0.05488	0.457131	0.486110	0.404226	-1612.0524028
	pa_b5_6	-9	-7	-4	-0.17008	-0.05761	0.456439	0.485584	0.403482	-1612.0469502
2b	b9_3	-28	-14	0	-0.28115	-0.05512	0.127171	0.137092	0.093394	-383.8975114
	b9_1	0	0	0	-0.28591	-0.05542	0.127238	0.137106	0.093792	-383.8974101
	b9_4	-15	0	0	-0.28131	-0.05541	0.127385	0.137181	0.093816	-383.8970117
	b9_2	0	0	0	-0.28593	-0.05555	0.127428	0.137202	0.094080	-383.8968967
	b9_5	-20	-14	-8	-0.28638	-0.06273	0.127012	0.136976	0.093411	-383.8873482
	b9_7	-12	-7	0	-0.28179	-0.05757	0.127076	0.136993	0.093347	-383.8859527
	b9_6	-31	-5	0	-0.28680	-0.06177	0.127182	0.137020	0.093850	-383.8863984
2b+PPh_3	pa_b9_13	-14	-11	0	-0.16475	-0.05047	0.404168	0.430198	0.353848	-1420.2969775
	pa_b9_14	-12	-9	-7	-0.16475	-0.05037	0.404180	0.430176	0.353853	-1420.2969735
	pa_b9_4	0	0	0	-0.16437	-0.05084	0.404032	0.430147	0.353412	-1420.2965152
	pa_b9_5	-18	-11	0	-0.16475	-0.05037	0.404186	0.430207	0.353903	-1420.2969737
	pa_b9_12	-9	0	0	-0.16487	-0.05061	0.404325	0.430241	0.354074	-1420.2965698
	pa_b9_8	-7	0	0	-0.17101	-0.05021	0.404178	0.430229	0.353593	-1420.2923243
	pa_b9_2	0	0	0	-0.17042	-0.05016	0.404420	0.430317	0.354076	-1420.2911201

	pa_b9_3	-10	-6	0	-0.17037	-0.05015	0.404416	0.430327	0.354036	-1420.2909051
2c	b3_2	-10	0	0	-0.25788	-0.06146	0.150779	0.162389	0.114755	-536.3273056
	b3_1	-17	0	0	-0.25776	-0.06239	0.150739	0.162364	0.114807	-536.3269929
	b3_3	-14	-3	0	-0.26039	-0.06689	0.150626	0.162242	0.114644	-536.3222235
	b3_4	-11	0	0	-0.25501	-0.06357	0.150579	0.162143	0.114783	-536.3207979
2c+PPh$_3$	pa_b3_8	-12	-6	0	-0.17412	-0.05382	0.427861	0.455643	0.376142	-1572.7326064
	pa_b3_6	-7	-3	0	-0.17227	-0.05314	0.427684	0.455572	0.375934	-1572.7314141
	pa_b3_7	-12	-3	0	-0.17226	-0.05313	0.427693	0.455577	0.375942	-1572.7314140
	pa_b3_13	-10	0	0	-0.17325	-0.06218	0.427817	0.455809	0.376155	-1572.7299516
	pa_b3_12	-3	0	0	-0.17112	-0.06228	0.427712	0.455711	0.375647	-1572.7292037
	pa_b3_4	-6	0	0	-0.17399	-0.05386	0.427809	0.455622	0.375949	-1572.7294707
	pa_b3_10	-11	-8	0	-0.17516	-0.05830	0.427305	0.455243	0.375361	-1572.7212905
2d	b2_2	-9	0	0	-0.28294	-0.05659	0.098946	0.107542	0.067020	-344.5723041
	b2_1	-12	-9	0	-0.28782	-0.05670	0.098903	0.107511	0.067151	-344.5722484
	b2_3	-19	0	0	-0.28857	-0.06462	0.098817	0.107402	0.067188	-344.5617654
2c+PPh$_3$	pa_b2_1	-2	0	0	-0.16481	-0.05557	0.375676	0.400505	0.326206	-1380.9692956
	pa_b2_3	-6	0	0	-0.16869	-0.05846	0.375239	0.400001	0.326027	-1380.9623911

[a]Truhlar Quasi-harmonic treatment is used for thermal corrections

5. Reaction Energy Profile

Bond dissociation energy curve

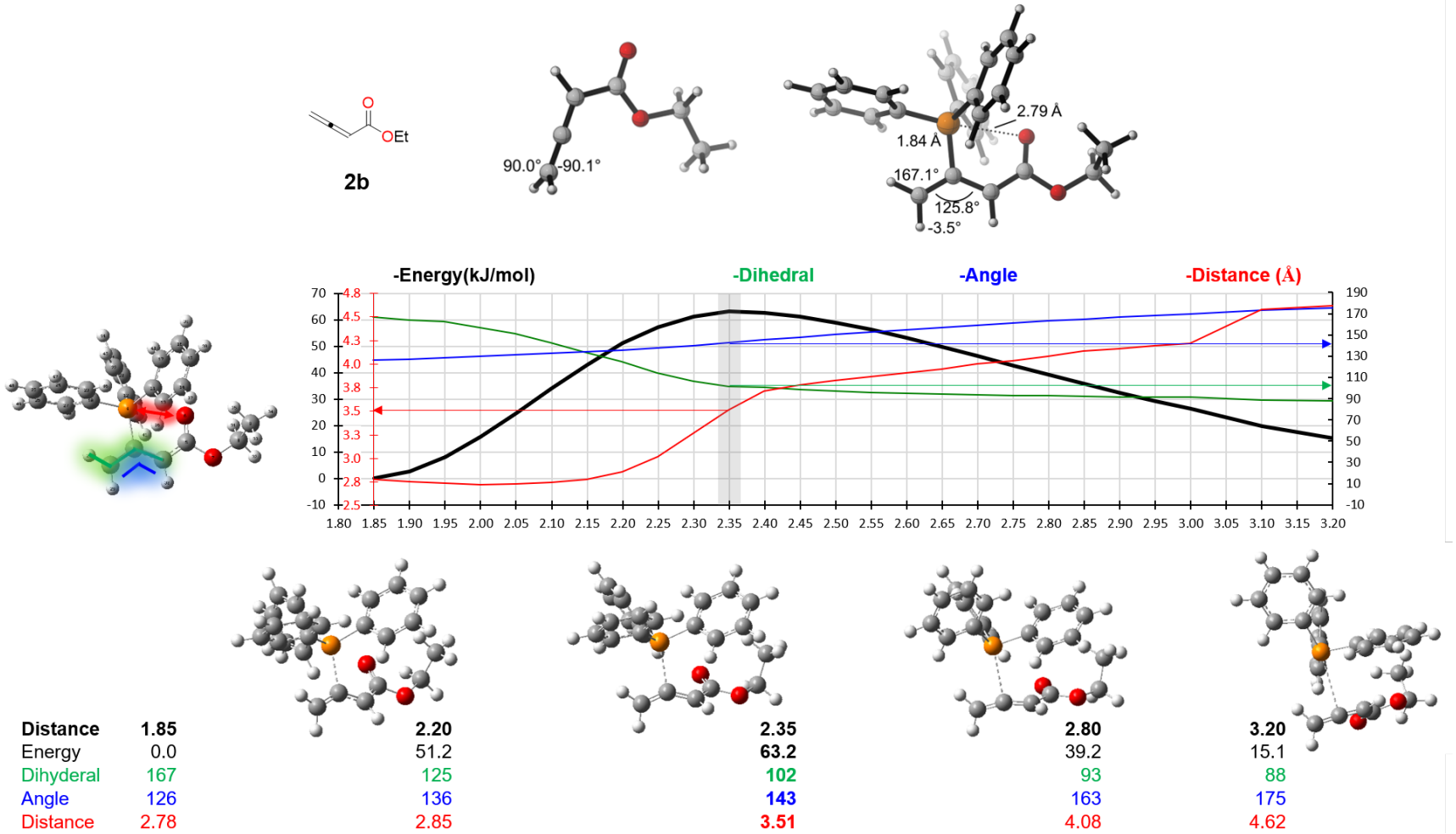


Figure S7. The P-C bond (between **PPh_3** and **2b**) dissociation energy curve (black curve, ΔE_{tot}, in kJ/mol) for the phosphine adduct of allenoate **2b** calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory. The change in various other structural properties along the dissociation curve is also depicted.

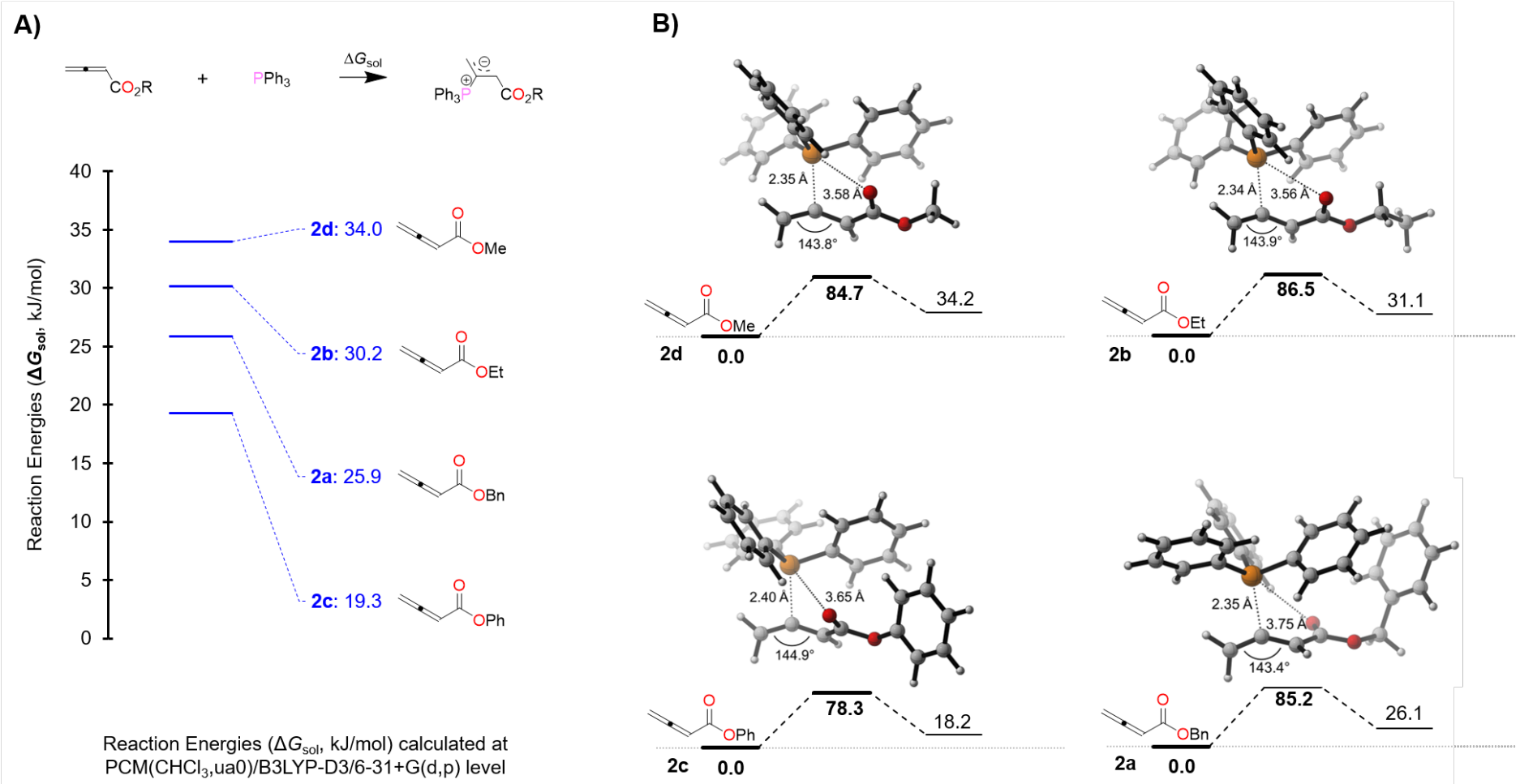


Figure S8. (A) Reaction energies (**Δ*G*sol**, in kJ/mol, Boltzmann averaged); and **(B)** reaction barriers (**Δ*G*sol**, in kJ/mol, based on best conformer) of tertiary phosphine (**PPh3**) addition to selected allenoates (**2a-d**) calculated at the PCM($CHCl_3$,ua0)/B3LYP-D3/6-31+G(d,p) level of theory.

6. References

[1] (a) H. Mayr, J. Ammer, M. Baidya, B. Maji, T. A. Nigst, A. R. Ofial, T. Singer, *J. Am. Chem. Soc.* **2015**, *137*, 2580-2599; (b) D. S. Allgäuer, H. Jangra, H. Asahara, Z. Li, Q. Chen, H. Zipse, A. R. Ofial, H. Mayr, *J. Am. Chem. Soc.* **2017**, *139*, 13318-13329; (c) Z. Li, H. Jangra, Q. Chen, P. Mayer, A. R. Ofial, H. Zipse, H. Mayr, *J. Am. Chem. Soc.* **2018**, *140*, 5500-5515.

[2] (a) A. D. Becke, *J. Chem. Phys* **1993**, *98*, 5648-5652. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785-789.

[3] (a) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724-728; (b) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650-654.

[4] R. Paton, I. Funes-Ardoiz, *GoodVibes*, **2016**.

[5] T. Clark, J. Chandrasekhar, G. W. Spitznagel, P. V. R. Schleyer, *J. Comput. Chem.* **1983**, *4*, 294-301.

[6] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[7] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104. (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[8] (a) E. Cances, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032-3041. (b) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3094.

[9] M. J. T. Frisch, 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.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; 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, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.;, Gaussian 09 Revision D. 01, Gaussian, Inc., Wallingford CT, **2013**.