Supplemental Material for

Chem. Eur. J. **2013**, *19*, 6429 – 6434.

The *aza*-Morita-Baylis-Hillman Reaction: a Mechanistic and Kinetic Study

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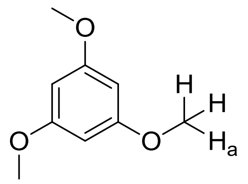
General information

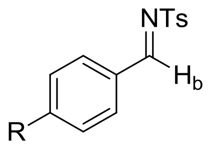
All air and water sensitive manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All commercial chemicals were of reagent grade and were used as received unless otherwise noted. $CDCl_3$ was refluxed for at least one hour over CaH_2 and subsequently distilled before use, and methyl vinyl ketone was distilled freshly before use. Tosylimine was prepared according to the literature.[1] ^{1}H NMR kinetic data were measured on a Varian Mercury 200 at 23 °C. All ^{1}H chemical shifts are reported in ppm (δ) relative to $CHCl_3$ (7.26).

General procedure for the kinetic measurements

Two stock solutions were prepared in dry calibrated 5 mL flasks; stock solution A: 0.15 M in tosylimine, 0.18 M in methyl vinyl ketone and 0.1 M in 1,3,5-trimethoxy benzene (internal standard) in $CDCl_3$, stock solution B: 0.0375 M in catalyst in $CDCl_3$. Under a nitrogen atmosphere, 0.5 mL of stock solution A and 0.1 mL of stock solution B were injected into a NMR tube, which was sealed by melting its opening with a flame. The sample was periodically submitted to NMR analysis in order to collect the kinetic information.



TMB



tosylimine

$I_{H(a)}$ is the overall intensity of the methyl groups of the internal standard 1,3,5-trimethoxy benzene (**TMB**), $I_{H(b)}$ is the intensity of the imine proton of the substrate, $I_{H(a0)}$ is the overall intensity of the methyl groups of **TMB** at the reaction start, $I_{H(b0)}$ is the intensity of the imine proton of the substrate at the reaction start.

$$\text{conversion} \cdot 100\,\% \quad = \quad (1 - I_{H(b0)} \cdot I_{H(a0)} / I_{H(a)} \cdot I_{H(b0)})$$

Fitting:

The kinetic data collected for the MBH reaction was found to fit the following first-order kinetic rate law:

$$\text{conversion} \cdot 100\,\% \quad = \quad \text{conv}_{max}\,(1 - \exp(-k(t\text{-}t0))$$

Half-life time: $t_{1/2} = \ln 2 / k$

Kinetic measurements data

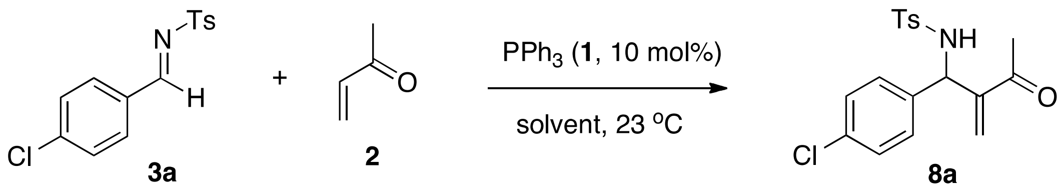


Table S1. Turnover curves for the azaMBH reaction of tosylimine **3a** with methylvinyl ketone (**2**) using PPh_3 (**1**, 10 mol%) as the catalyst in selected solvents.

in $CDCl_3$		**in CD_2Cl_2**		**in DMSO-d6**		**in DMF-d7**		**in THF-d8**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
5.2	7.0	2.5	4.0	2.4	3.0	1.8	3.6	2.0	8.0
8.5	9.1	3.3	6.1	4.1	5.1	2.7	5.6	1.7	10.1
12.0	11.1	5.0	8.1	5.5	7.1	4.0	7.7	2.8	12.1
15.4	13.2	6.5	10.2	6.1	9.2	5.2	9.8	2.6	14.2
18.4	15.3	7.9	12.3	7.7	11.3	6.1	11.8	2.0	16.3
21.3	17.3	9.6	14.3	8.7	13.3	7.0	13.9	3.1	18.3
27.1	21.7	12.3	18.7	10.5	17.7	8.4	18.3	2.7	22.7
32.9	26.0	15.0	23.0	12.5	22.0	9.7	22.6	3.9	27.0
37.9	30.4	18.1	27.4	14.8	26.4	11.6	26.9	4.2	31.4
42.6	34.7	20.8	31.7	16.5	30.7	13.1	31.3	4.8	35.7
46.8	39.1	23.5	36.1	18.6	35.1	14.1	35.6	5.3	40.1
52.6	45.2	26.9	42.2	21.5	41.2	16.6	41.7	5.6	46.2
57.5	51.2	30.5	48.2	24.2	47.2	18.3	47.8	5.0	52.2
62.3	57.3	33.8	54.3	26.8	53.3	20.1	53.8	6.2	58.3
66.0	63.4	36.8	60.4	29.0	59.4	22.1	59.9	6.8	64.4
69.5	69.4	40.0	66.4	31.5	65.4	23.8	66.0	7.3	70.4
75.1	80.5	45.3	77.5	35.4	76.5	27.1	77.0	8.8	81.5
79.4	91.6	50.6	88.6	39.0	87.6	29.3	88.1	9.9	92.6
83.3	102.6	55.1	99.6	43.2	98.6	32.1	99.2	9.9	103.6
86.3	113.7	59.5	110.7	46.4	109.7	34.6	110.2	11.6	114.7
88.6	124.8	63.4	121.8	49.1	120.8	36.7	121.3	12.7	125.8
90.7	135.8	67.2	132.8	51.9	131.8	38.9	132.4	13.7	136.8
93.6	156.9	73.4	153.9	57.5	152.9	41.9	153.4	15.1	157.9
95.3	178.0	78.5	175.0	62.1	174.0	46.9	174.5	15.9	179.0
96.9	199.0	82.9	196.0	66.3	195.0	48.6	195.6	17.9	200.0

97.7	220.1	86.5	217.1	70.5	216.1	53.5	216.6	18.8	221.1
98.2	241.2	89.5	238.2	73.4	237.2	56.4	237.7	21.9	242.2
98.9	262.2	91.9	259.2	76.5	258.2	59.1	258.8	23.0	263.2
99.5	293.6	94.4	290.6	80.4	289.6	61.6	279.9	24.9	294.6
99.9	325.0	96.3	322.0	83.8	321.0	63.8	300.9	28.2	326.0
99.5	356.4	97.9	353.4	86.5	352.4	65.8	322.0	29.8	357.4
99.6	387.8	98.9	384.8	89.2	383.8	68.0	343.1	32.2	388.8
99.9	419.1	99.4	416.1	91.2	415.1	69.8	364.1	34.5	420.1
100.0	450.5	99.8	447.5	92.6	446.5	72.0	385.2	36.6	451.5
100.3	481.9	100.0	478.9	94.0	477.9	73.3	406.3	39.0	482.9
100.0	513.3	100.0	510.3	95.1	509.3	75.2	427.3	41.3	514.3
100.0	574.3	100.0	571.3	97.2	570.3	76.4	448.4	44.1	575.3
100.0	635.3	100.0	632.3	98.2	631.3	77.8	469.5	48.9	636.3
						79.2	490.5		
						80.7	511.6		
						81.2	532.7		
						82.5	553.7		
						83.3	574.8		
						84.4	595.9		
						85.4	616.9		
						86.0	638.0		
						86.8	659.1		
						92.9	912.8		
						95.1	1032.0		

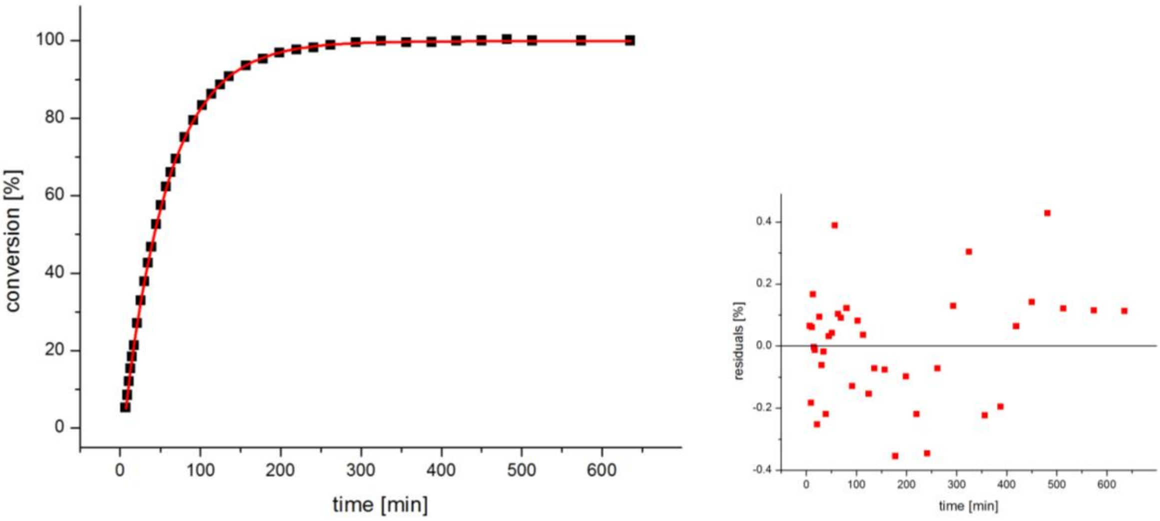


Figure S1. Measurement in $CDCl_3$ (cf. Table S1).

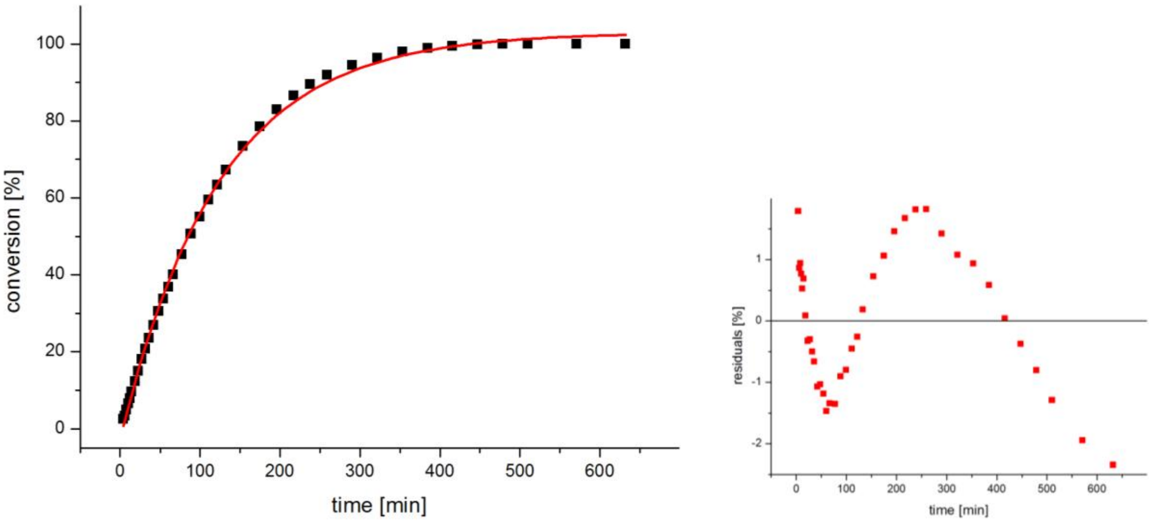


Figure S2. Measurement in CD_2Cl_2 (cf. Table S1).

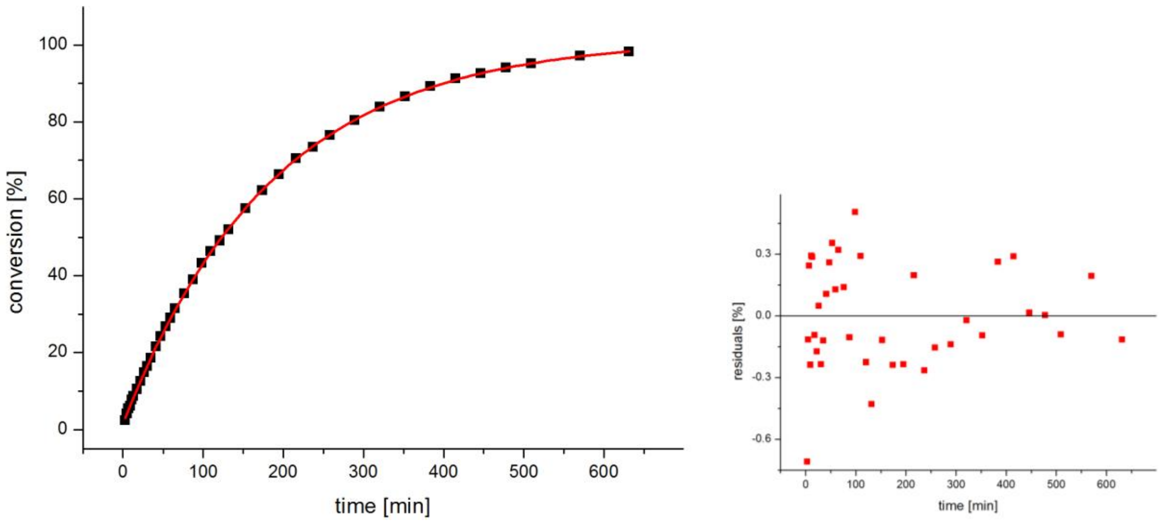


Figure S3. Measurement in DMSO-d_6 (cf. Table S1).

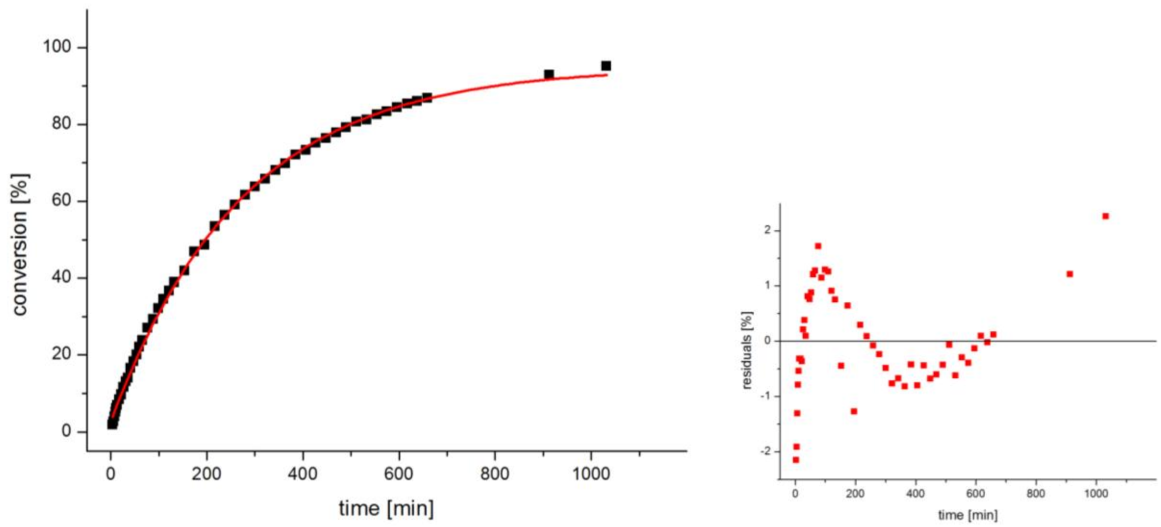


Figure S4. Measurement in DMF-d_7 (cf. Table S1).

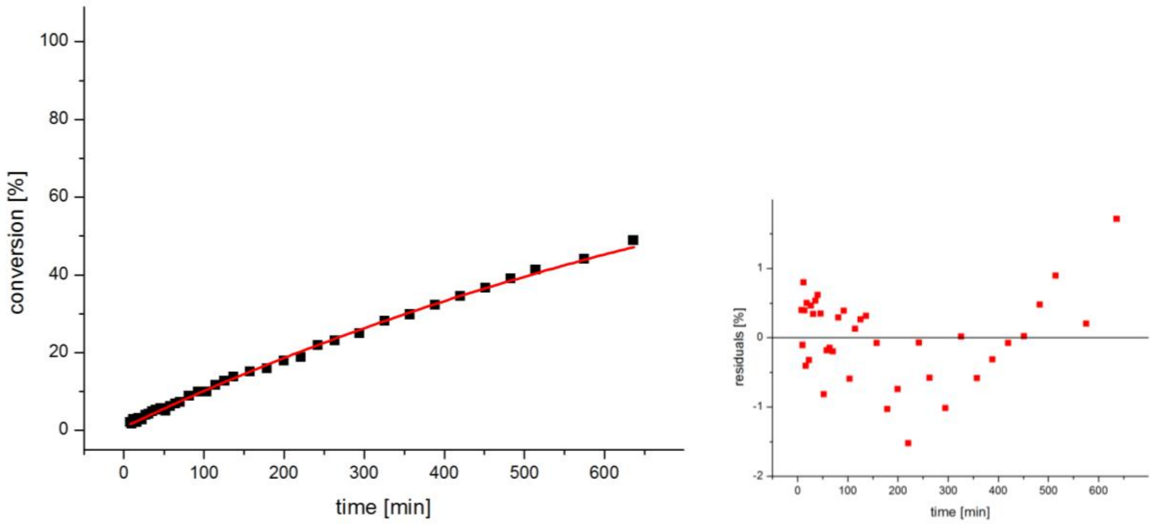


Figure S5. Measurement in THF-d_8 (cf. Table S1). In this case the reaction is assumed to reach a maximum conversion of $conv_{max}$ = 100% eventually.

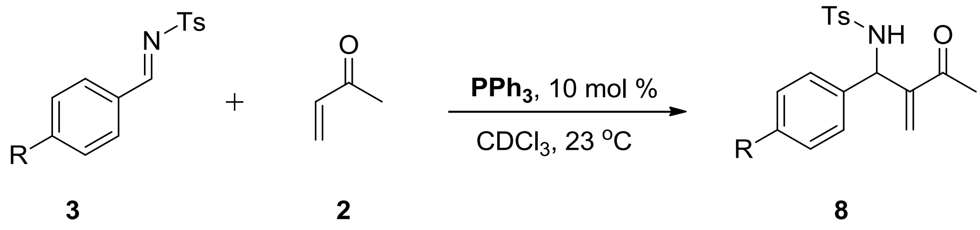


Table S2. azaMBH reaction of tosylimines with methylvinyl ketone (**2**) using PPh_3 (**1**, 10 mol%) as the catalyst in $CDCl_3$.

R = Br		**R = H**		**R = OMe**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
6.17	3.10	3.91	3.23	1.35	6.33
9.13	5.17	8.69	5.30	6.40	13.47
11.91	7.23	9.98	7.37	9.88	20.60
15.84	9.30	12.26	9.43	12.33	27.73
19.24	11.37	13.52	11.50	15.92	34.88
21.80	13.27	17.23	13.57	18.38	41.55
27.67	17.77	21.08	17.92	20.93	49.13
33.65	22.12	25.28	22.27	23.85	56.27
38.81	26.47	28.52	26.60	27.56	68.40
43.56	30.80	32.73	30.95	30.45	80.53
48.23	35.15	35.57	35.30	34.37	92.67
54.10	41.22	40.21	41.37	37.15	104.80
58.95	47.28	43.64	47.43	40.09	116.93
62.91	53.35	47.87	53.50	43.11	129.07
67.47	59.42	50.65	59.57	45.95	141.20
70.95	65.48	53.76	65.63	47.68	153.33
76.48	76.55	57.89	76.70	49.75	165.48
80.09	87.62	62.94	87.77	49.70	177.62
84.89	98.68	65.12	98.83	52.50	189.75
87.34	109.75	68.08	109.90	55.19	201.88
89.24	120.83	70.30	120.97	56.42	214.02
91.20	131.90	74.87	132.03	59.10	226.15
94.12	152.97	77.86	153.10	60.10	238.28
95.23	174.03	81.04	174.17	59.49	250.42
96.31	195.10	82.11	195.23	60.86	262.55

97.74	216.17	86.18	216.30	63.26	274.68
97.75	237.23	87.88	237.37	64.20	286.82
98.04	258.30	87.46	258.45	64.44	298.95
98.25	279.37	89.88	279.52	65.46	311.08
98.97	300.43	91.10	300.58	67.33	323.22
98.78	321.50	92.10	321.65	67.30	335.35
98.78	342.57	90.95	342.72	69.68	347.48
98.80	363.63	94.01	363.78	69.40	369.62
99.10	384.70	94.21	384.85	71.68	391.75
99.01	405.77	92.42	405.92	72.68	413.88
99.34	426.83	94.31	426.98	73.27	436.02
99.01	447.90	93.98	448.05	74.91	458.15
99.28	468.98	93.30	469.12	75.87	480.30
98.22	490.05	95.68	490.18	76.48	502.43
99.23	511.12	95.93	511.25	77.27	524.57
98.47	532.18	96.58	532.32	77.53	546.70
99.23	553.25	94.59	553.38	78.10	568.83
98.28	574.32	96.93	574.45	79.34	590.97
99.14	595.38	95.31	595.50	78.66	613.10
99.39	616.45	96.26	616.57	79.97	635.23
99.01	637.52	97.53	637.63	80.80	657.37
98.76	658.58	98.04	658.70	81.35	679.50
99.21	679.65	97.50	679.77	80.70	721.78
98.88	700.72	97.18	700.83	82.91	764.05
99.20	721.78	97.05	721.90	83.20	806.33
99.17	742.85	97.54	742.97	83.97	848.60
99.38	763.92	97.63	764.03	84.34	890.88
		96.27	785.10	85.18	933.15
				85.09	975.43
				85.25	1017.7
				86.02	1059.98
				86.42	1122.12
				86.79	1184.25
				87.01	1246.38
				87.30	1308.52

R = Me		**R = NO_2**		**R = NMe_2**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
2.01	3.30	18.36	8.27	0.00	0.00
2.80	5.37	23.85	10.33	4.44	166.00
5.96	7.43	38.08	14.68	10.73	928.00
8.14	9.50	48.64	19.03	15.68	1386.00
8.54	11.57	59.46	23.38	23.54	2391.00
10.49	13.63	70.77	27.72	25.50	2819.00
14.30	17.98	81.49	32.07	29.99	3823.00
18.05	22.32	87.81	38.13	31.93	4399.00
22.86	26.67	90.98	44.20	32.56	5268.00
24.84	31.02	93.49	50.27	33.85	5847.00
27.64	35.35	95.73	56.33	34.43	6669.00
31.51	41.42	96.41	62.40	35.14	7286.00
37.17	47.48	97.42	73.47	36.54	8335.00
38.60	53.55	97.91	84.53	37.05	9936.00
41.59	59.63	98.79	95.60	37.52	11019.00
45.17	65.70	98.88	106.67	38.97	12457.00
49.74	76.77	99.27	117.73	39.43	13944.00
53.68	87.83	98.79	128.80	39.21	15345.00
57.44	98.90	99.67	149.87	39.31	19913.00
61.44	109.97	99.58	170.95	39.80	22944.00
63.73	121.03	99.45	192.00	39.60	31169.00
65.69	132.10	99.43	213.08	40.01	44153.00
70.43	153.17	98.83	234.15		
74.45	174.23	99.39	255.22		
77.71	195.30	99.14	276.28		
78.64	216.37	99.47	297.35		
80.77	237.43	98.87	318.42		
82.82	258.50	99.16	339.48		
84.38	279.57	99.15	360.55		
86.26	300.63	100.50	381.62		
87.88	321.72	99.49	402.68		
87.96	342.77	97.58	423.75		
88.91	363.85	99.26	454.82		
89.98	384.92	99.36	465.88		

90.91	405.98	99.18	486.95		
91.18	427.05	99.67	508.00		
91.83	448.12	99.91	529.07		
92.12	469.18	99.10	550.13		
93.05	490.25	99.58	571.20		
92.91	511.32	99.84	592.27		
93.37	532.38	99.48	613.33		
93.88	553.45	100.17	634.40		
93.84	574.52	99.74	655.47		
94.14	595.58	100.16	676.53		
93.95	616.65				
94.80	637.72				
94.69	658.78				
95.01	679.85				
94.79	700.92				
94.95	722.00				
95.41	743.07				
95.40	764.13				
95.37	785.20				
95.56	806.27				

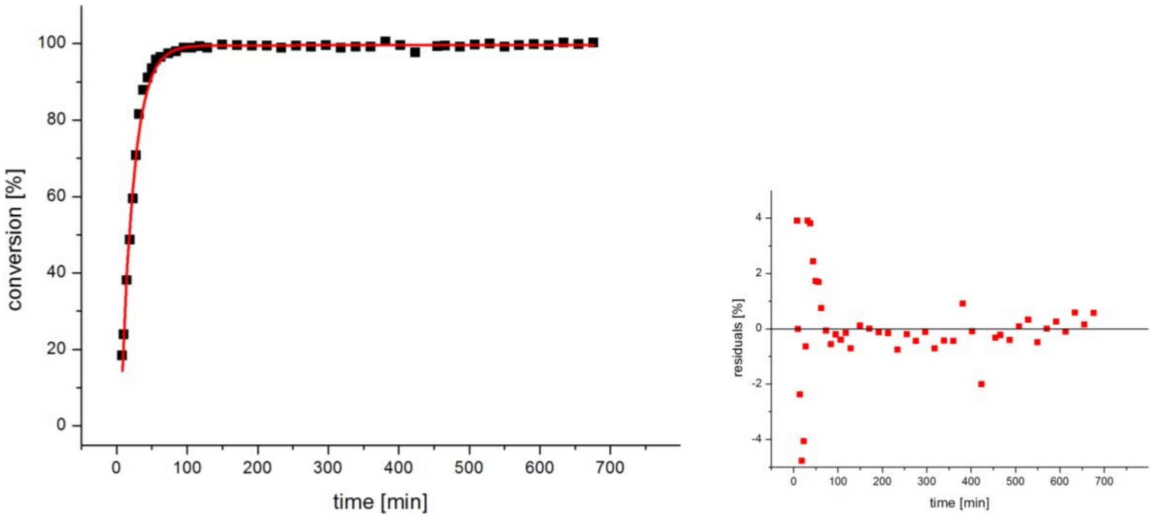


Figure S6. Measurement with NO_2-substituted imine in $CDCl_3$ (cf. Table S2).

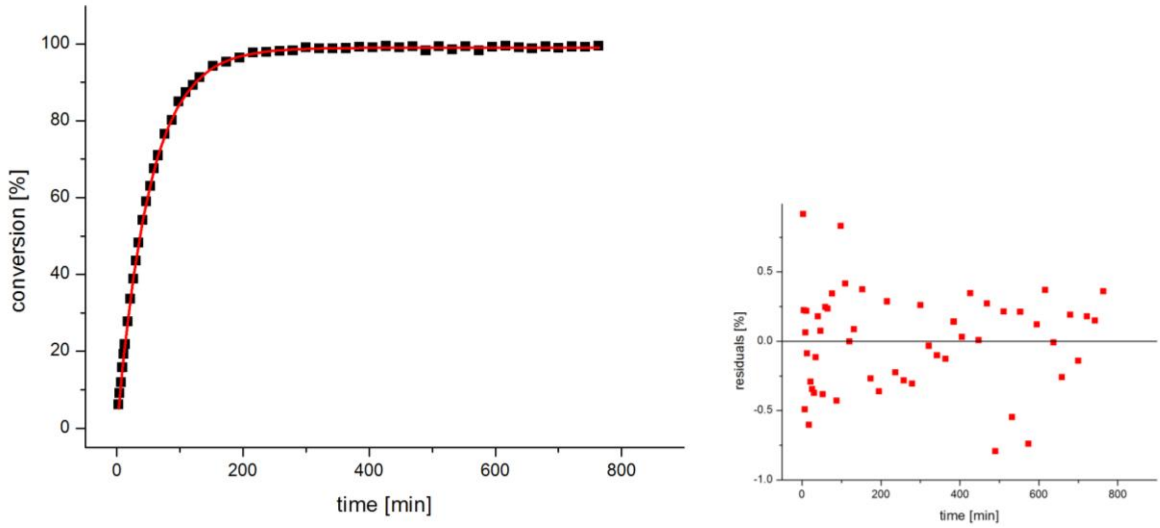


Figure S7. Measurement with Br-substituted imine in $CDCl_3$ (cf. Table S2).

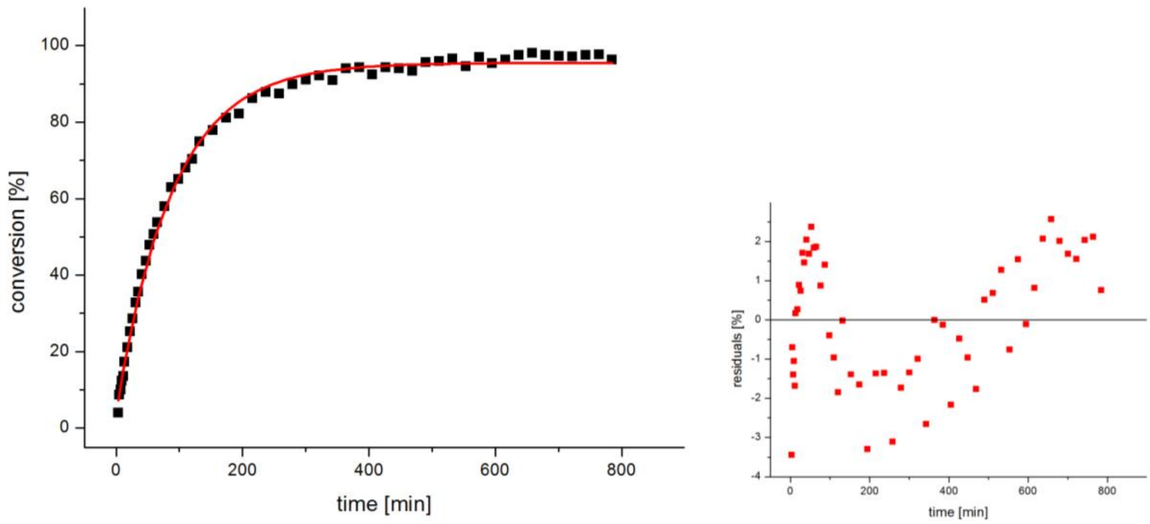


Figure S8. Measurement with unsubstituted imine in $CDCl_3$ (cf. Table S2).

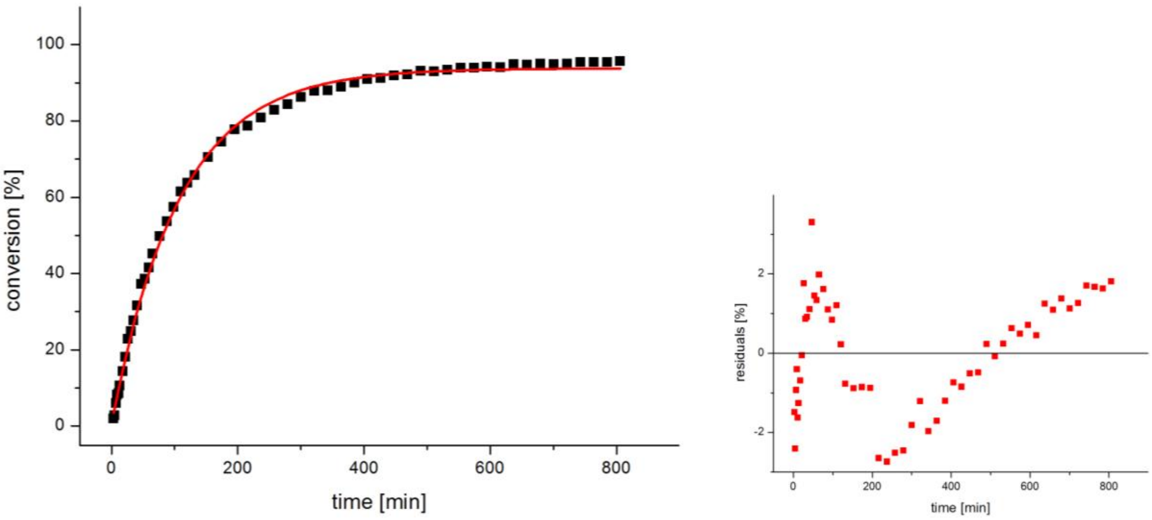


Figure S9. Measurement with Me-substituted imine in $CDCl_3$ (cf. Table S2).

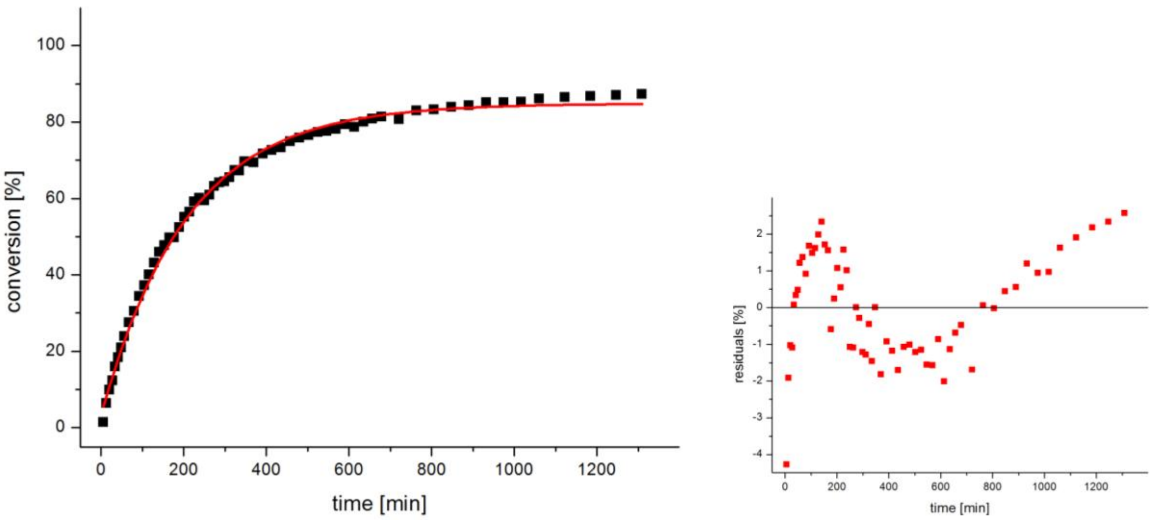


Figure S10. Measurement with OMe-substituted imine in $CDCl_3$ (cf. Table S2).

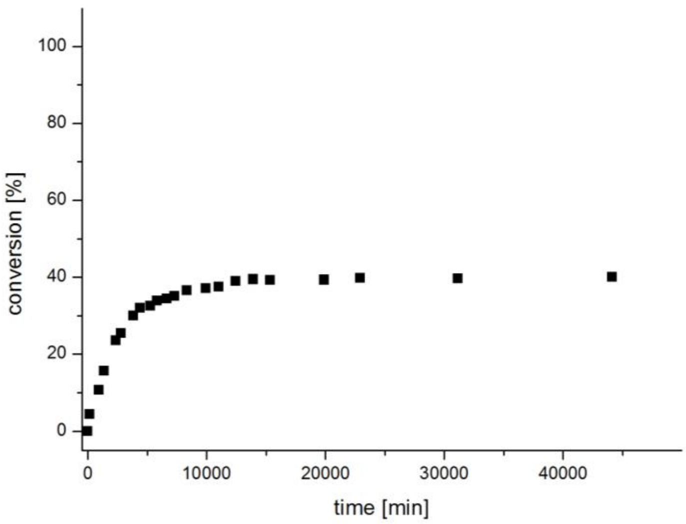


Figure S11. Measurement with NMe_2-substituted imine in $CDCl_3$ (cf. Table S2).

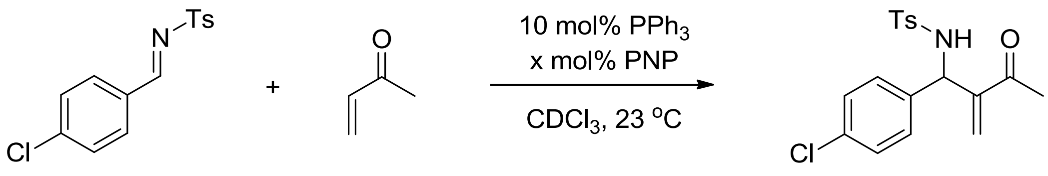


Table S3. Co-catalyst effect in the PPh_3 catalyzed aMBH reaction of *p*-chlorotosylimines, MVK and PNP (x mol %) in $CDCl_3$

1 % PNP		2.5% PNP		5% PNP		10% PNP	
conv. [%]	time [min]	conv. [%]	time [min]	conv. [%]	time [min]	conv. [%]	time [min]
0.4	3.0	6.9	5.0	3.0	5.0	5.1	4.0
4.7	5.1	11.8	7.1	8.3	7.1	8.4	6.1
9.1	7.1	15.9	9.1	13.4	9.1	13.2	8.1
13.2	9.2	19.8	11.2	17.7	11.2	16.3	10.2
16.9	11.3	23.9	13.3	21.9	13.3	20.3	12.3
20.4	13.3	27.8	15.3	25.8	15.3	24.3	14.3
27.6	17.7	34.9	19.7	32.7	19.7	29.9	18.7
34.4	22.0	42.0	24.0	39.7	24.0	35.7	23.0
40.3	26.4	47.9	28.4	45.9	28.4	40.9	27.4
46.6	30.7	53.4	32.7	51.5	32.7	46.5	31.7
51.2	35.1	58.6	37.1	56.7	37.1	51.3	36.1
57.5	41.2	64.9	43.2	62.8	43.2	56.3	42.2
63.2	47.2	70.6	49.2	68.6	49.2	61.6	48.2
68.4	53.3	75.4	55.3	73.4	55.3	66.6	54.3
72.3	59.4	79.3	61.4	77.4	61.4	69.9	60.4
76.6	65.4	82.7	67.4	81.3	67.4	73.9	66.4
81.4	76.5	87.9	78.5	86.6	78.5	77.9	77.5
86.3	87.6	91.8	89.6	90.4	89.6	83.2	88.6
88.9	98.6	94.5	100.6	93.2	100.6	86.5	99.6
92.2	109.7	96.7	111.7	95.2	111.7	88.9	110.7
93.5	120.8	97.9	122.8	96.3	122.8	90.7	121.8
95.3	131.8	99.1	133.8	97.5	133.8	93.0	132.8
96.7	152.9			98.7	154.9	93.3	153.9
97.9	174.0			99.5	176.0	95.8	175.0
98.7	195.0			99.3	197.0	95.0	196.0
99.1	216.1			99.7	218.1	96.7	217.1

99.1	237.2			99.7	239.2	95.5	238.2
98.6	258.2			100.1	260.2	97.2	259.2
98.6	289.6			100.3	291.6	97.6	290.6
99.3	321.0			99.7	323.0	96.0	322.0
99.1	352.4			100.0	354.4	98.0	353.4
98.4	383.8			100.2	385.8	97.7	384.8
98.9	415.1			100.1	417.1	97.4	416.1
99.0	446.5			100.3	448.5		
99.1	477.9			100.0	479.9		
99.7	509.3			99.7	511.3		
99.0	570.3			99.9	572.3		
99.3	631.3			99.7	633.3		

20% PNP		**30 % PNP**		**40% PNP**		**100 % PNP**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
0.1	6.0	0.1	5.0	0.1	8.0	0.1	5.0
2.6	8.1	2.4	7.1	0.9	10.1	0.2	7.1
5.0	10.1	4.2	9.1	2.2	12.1	0.2	9.1
7.8	12.2	6.1	11.2	3.5	14.2	0.9	11.2
9.7	14.3	7.6	13.3	4.7	16.3	2.0	13.3
12.7	16.3	9.5	15.3	5.4	18.3	1.7	15.3
15.3	20.7	12.3	19.7	7.8	22.7	2.7	19.7
20.0	25.0	15.2	24.0	9.3	27.0	3.0	24.0
22.1	29.4	18.3	28.4	11.2	31.4	3.7	28.4
26.4	33.7	20.6	32.7	13.1	35.7	4.2	32.7
29.4	38.1	23.0	37.1	14.6	40.1	5.0	37.1
33.7	44.2	25.8	43.2	16.7	46.2	5.7	43.2
36.1	50.2	29.1	49.2	19.1	52.2	6.2	49.2
40.6	56.3	32.2	55.3	20.6	58.3	7.0	55.3
43.6	62.4	34.8	61.4	22.8	64.4	7.2	61.4
46.5	68.4	37.6	67.4	24.4	70.4	7.5	67.4
52.6	79.5	41.6	78.5	27.5	81.5	8.8	78.5
56.6	90.6	45.9	89.6	30.8	92.6	9.0	89.6
61.8	101.6	49.6	100.6	33.4	103.6	10.1	100.6
66.5	112.7	52.8	111.7	36.3	114.7	10.4	111.7
68.8	123.8	55.5	122.8	38.9	125.8	11.4	122.8

72.5	134.8	58.3	133.8	41.1	136.8	11.8	133.8
76.5	155.9	62.6	154.9	45.0	157.9	13.0	154.9
81.3	177.0	66.5	176.0	48.4	179.0	13.5	176.0
84.4	198.0	69.6	197.0	50.9	200.0	13.7	197.0
89.3	219.1	72.5	218.1	53.2	221.1	15.2	218.1
88.2	240.2	74.9	239.2	54.6	242.2	15.9	239.2
89.0	261.2	76.1	260.2	55.3	263.2	16.6	260.2
92.4	292.6	78.7	291.6	57.2	294.6	16.4	291.6
93.5	324.0	80.3	323.0	58.0	326.0	17.3	323.0
94.9	355.4	81.3	354.4	58.7	357.4	18.6	354.4
94.7	386.8	82.5	385.8	59.4	388.8	19.0	385.8
94.5	418.1	83.3	417.1	59.9	420.1	19.5	417.1
92.6	449.5	83.7	448.5	60.7	451.5	21.1	448.5
96.0	480.9	84.1	479.9	61.3	482.9	21.6	479.9
94.1	512.3	84.4	511.3	61.8	514.3	22.3	511.3
93.8	573.3	84.8	572.3			23.6	572.3
94.4	634.3	85.3	633.3			24.3	633.3

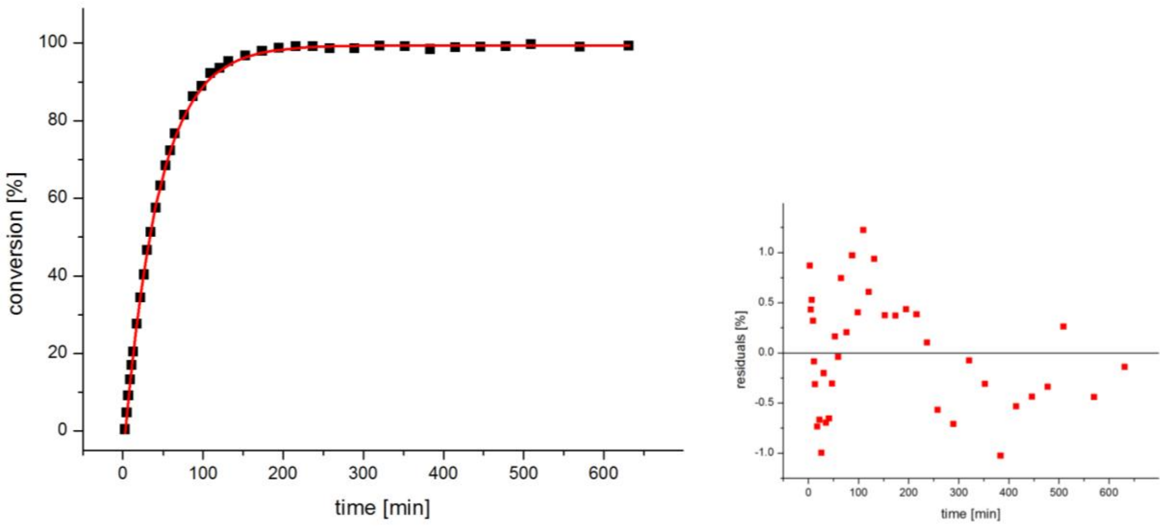


Figure S12. Measurement with 1 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

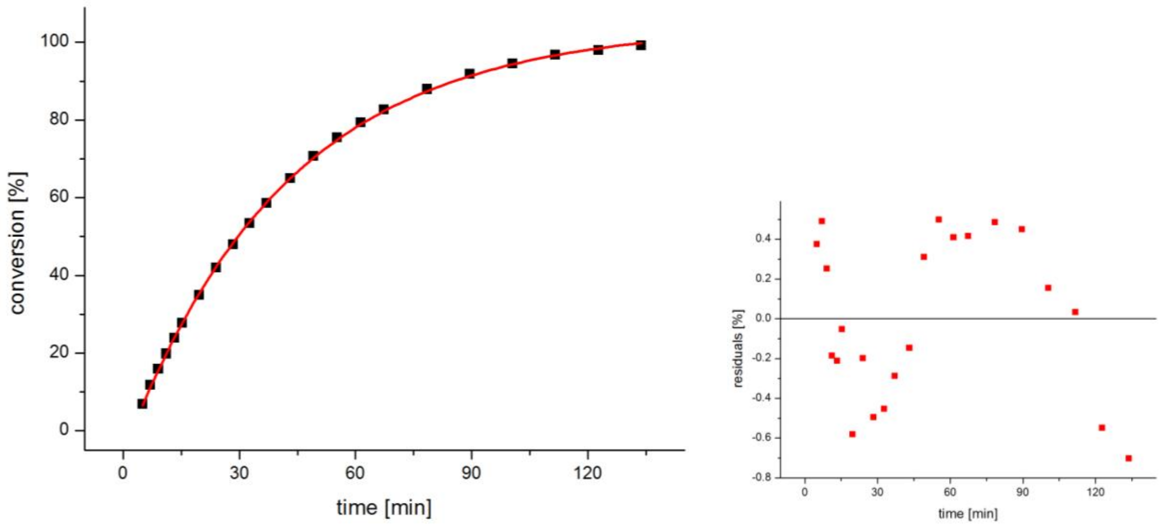


Figure S13. Measurement with 2.5 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

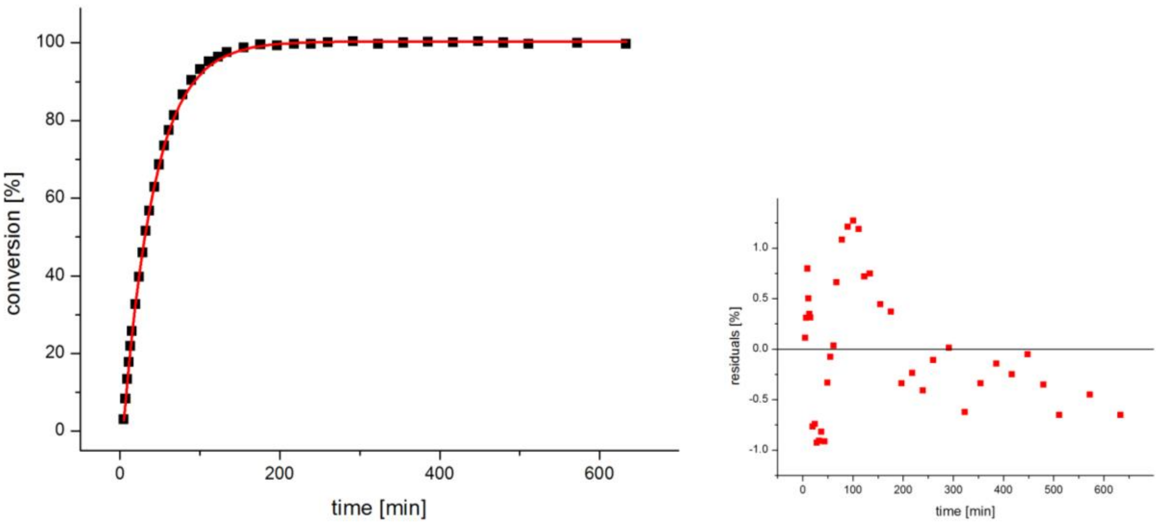


Figure S14. Measurement with 5 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

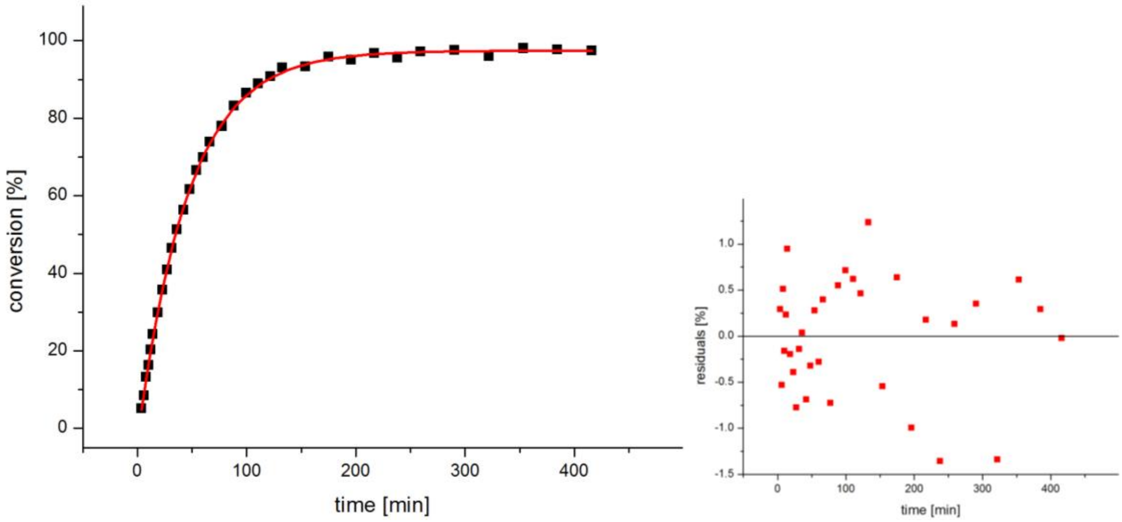


Figure S15. Measurement with 10 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

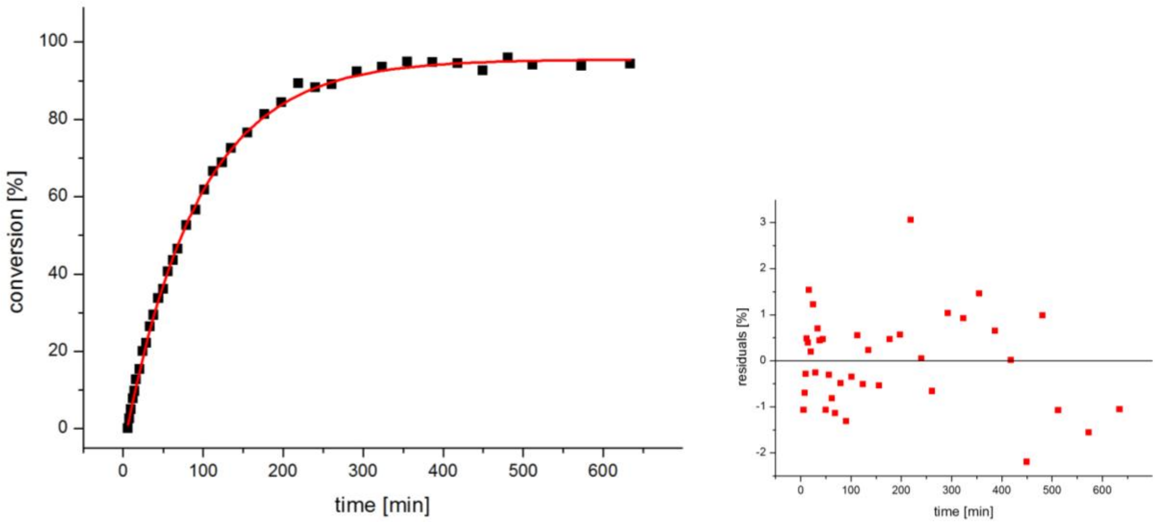


Figure S16. Measurement with 20 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

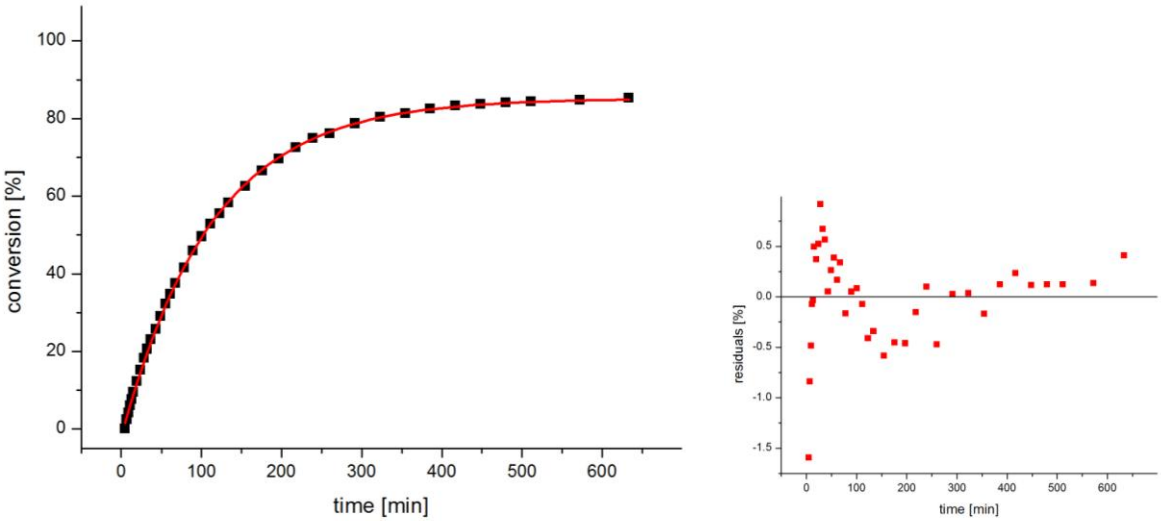


Figure S17. Measurement with 30 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

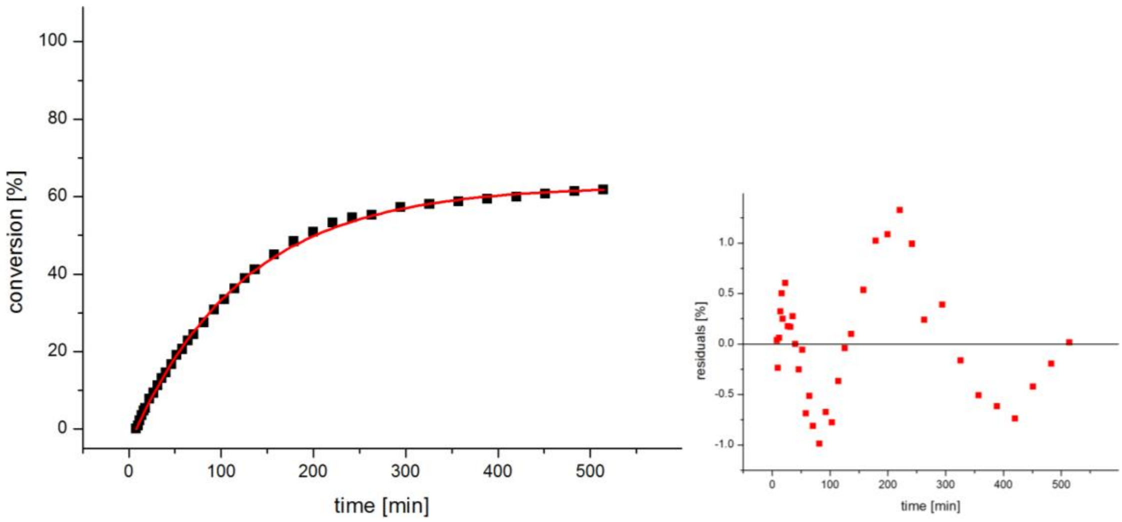


Figure S18. Measurement with 40 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

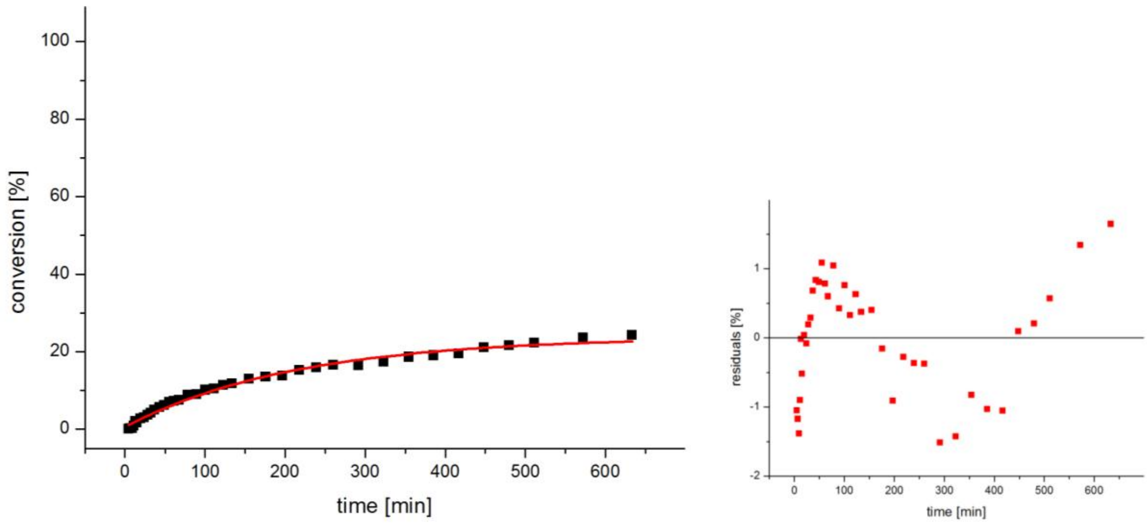


Figure S19. Measurement with 100 mol% PNP (**9**) in $CDCl_3$ (cf. Table S3).

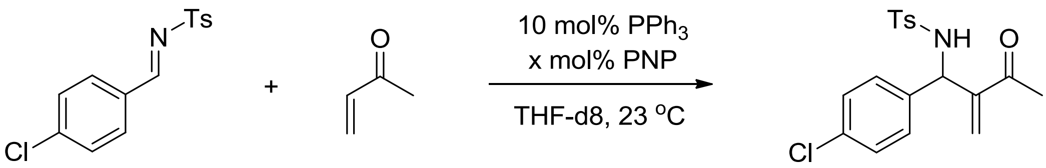


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Table S4. Co-catalyst effect in the PPh_3 catalyzed aMBH reaction of *p*-chlorotosylimines, MVK and PNP (x mol %) in THF-d8.

10 % PNP		**20% PNP**		**50% PNP**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
0.9	4.0	3.7	7.0	2.0	7.0
1.4	6.1	4.5	9.1	2.7	9.1
2.2	8.1	5.1	11.1	3.3	11.1
2.4	10.2	5.8	13.2	4.9	13.2
3.4	12.3	6.7	15.3	5.3	15.3
3.6	14.3	7.6	17.3	8.1	17.3
4.8	18.7	9.6	21.7	11.2	21.7
6.2	23.0	11.2	26.0	14.0	26.0
6.8	27.4	12.5	30.4	15.8	30.4
7.7	31.7	14.3	34.7	18.3	34.7
9.5	36.1	16.3	39.1	21.0	39.1
10.9	42.2	18.5	45.2	24.3	45.2
12.3	48.2	20.8	51.2	26.7	51.2
13.5	54.3	23.2	57.3	30.5	57.3
15.0	60.4	25.5	63.4	33.4	63.4
15.8	66.4	27.4	69.4	35.8	69.4
18.5	77.5	31.4	80.5	40.9	80.5
20.4	88.6	34.8	91.6	46.0	91.6
23.5	99.6	38.3	102.6	49.9	102.6
25.3	110.7	41.7	113.7	53.6	113.7
28.0	121.8	45.5	124.8	57.5	124.8
30.8	132.8	48.6	135.8	61.2	135.8
34.3	153.9	52.5	156.9	66.9	156.9
38.2	175.0	57.9	178.0	72.0	178.0
42.1	196.0	62.7	199.0	76.8	199.0
45.5	217.1	66.5	220.1	80.8	220.1

48.6	238.2	69.2	241.2	84.0	241.2
51.3	259.2	74.0	262.2	88.9	262.2
55.9	290.6	78.0	293.6	90.5	293.6
59.8	322.0	82.7	325.0	93.5	325.0
64.2	353.4	85.5	356.4	96.0	356.4
68.0	384.8	88.7	387.8	98.0	387.8
71.0	416.1	93.0	419.1	97.2	419.1
73.9	447.5	93.0	450.5	100.0	450.5
77.1	478.9	99.2	660.0	100.0	481.9
79.3	510.3	100.0	670.0	100.0	513.3
84.6	571.3	100.0	680.0	100.0	574.3
87.6	632.3			100.0	635.3

70% PNP		**100% PNP**		**120 % PNP**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
13.6	22.0	5.8	6.0	3.6	12.0
14.1	24.1	9.4	8.1	3.8	14.1
15.9	26.1	9.3	10.1	4.7	16.1
17.1	28.2	10.9	12.2	5.6	18.2
18.1	30.3	10.5	14.3	6.2	20.3
19.3	32.3	13.2	16.3	6.4	22.3
22.1	36.7	13.7	20.7	8.0	26.7
23.1	41.0	16.8	25.0	9.3	31.0
25.1	45.4	20.3	29.4	10.4	35.4
26.8	49.7	23.0	33.7	12.5	39.7
28.7	54.1	24.1	38.1	14.3	44.1
31.2	60.2	26.5	44.2	15.6	50.2
34.1	66.2	29.5	50.2	17.8	56.2
36.4	72.3	32.2	56.3	19.1	62.3
38.6	78.4	36.3	62.4	21.0	68.4
40.7	84.4	37.4	68.4	22.7	74.4
44.5	95.5	41.1	79.5	25.6	85.5
47.5	106.6	47.7	90.6	27.8	96.6
51.5	117.6	49.7	101.6	30.8	107.6
55.1	128.7	52.5	112.7	34.2	118.7
58.5	139.8	56.1	123.8	36.7	129.8

60.5	150.8	58.8	134.8	39.2	140.8
65.9	171.9	66.8	155.9	44.2	161.9
70.6	193.0	70.8	177.0	50.5	183.0
75.0	214.0	74.2	198.0	53.9	204.0
78.0	235.1	77.4	219.1	57.3	225.1
80.4	256.2	80.7	240.2	60.5	246.2
83.5	277.2	85.1	261.2	64.2	267.2
86.7	308.6	86.9	292.6	66.3	298.6
89.5	340.0	89.9	324.0	70.9	330.0
91.4	371.4	92.8	355.4	74.3	361.4
93.8	402.8	94.2	386.8	78.0	392.8
94.8	434.1	95.8	418.1	81.0	424.1
96.0	465.5	98.2	449.5	83.5	455.5
97.4	496.9	98.9	480.9	84.6	486.9
97.0	528.3	99.7	512.3	86.9	518.3
98.6	589.3	100.0	573.3	91.0	579.3
		100.0	634.3	92.4	640.3

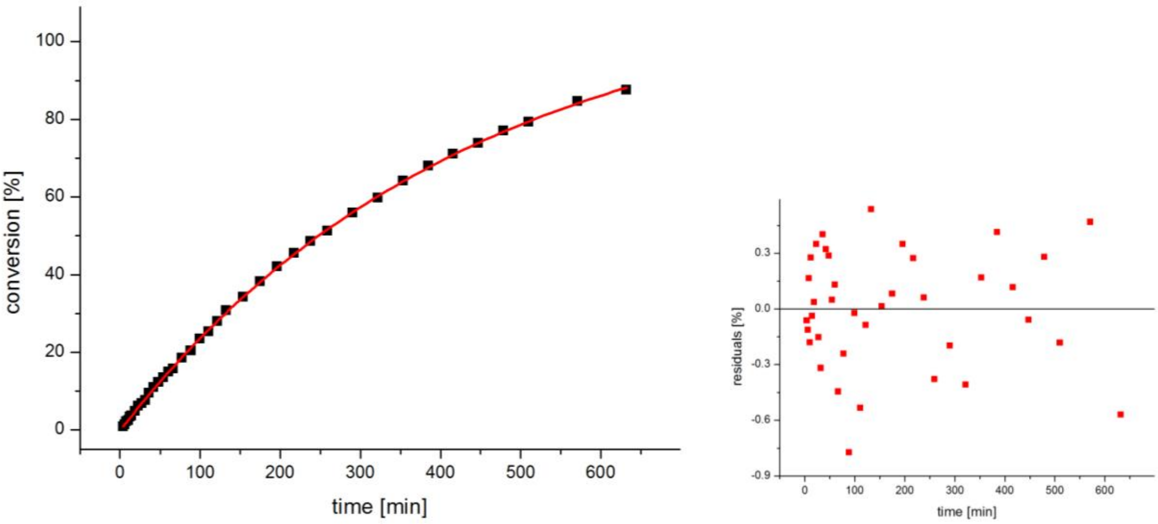


Figure S20. Measurement with 10 mol% PNP (**9**) in THF-d_8 (cf. Table S4).

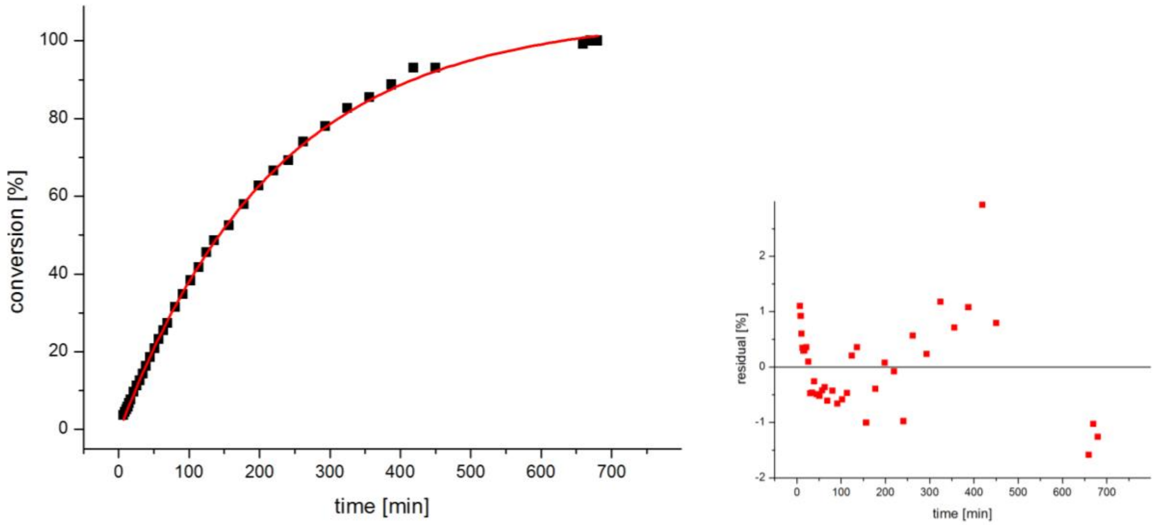


Figure S21. Measurement with 20 mol% PNP (**9**) in THF-d_8 (cf. Table S4).

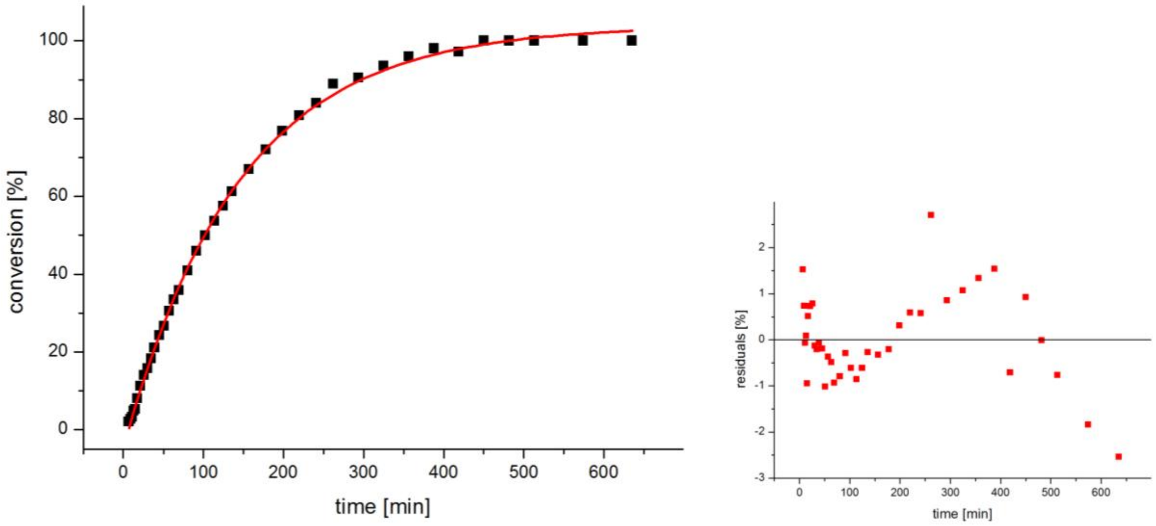


Figure S22. Measurement with 50 mol% PNP (**9**) in THF-d_8 (cf. Table S4).

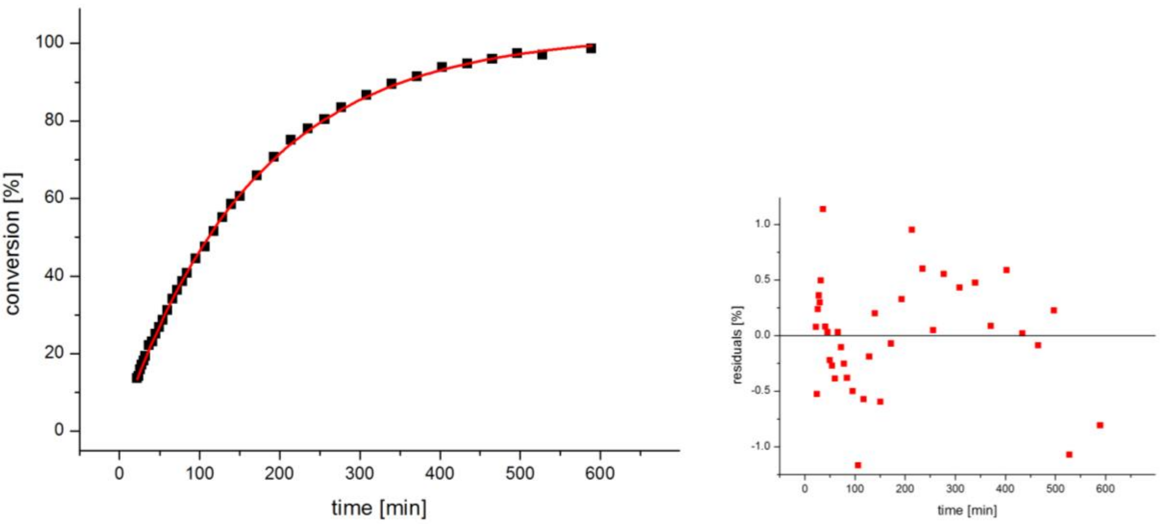


Figure S23. Measurement with 70 mol% PNP (**9**) in THF-d_8 (cf. Table S4).

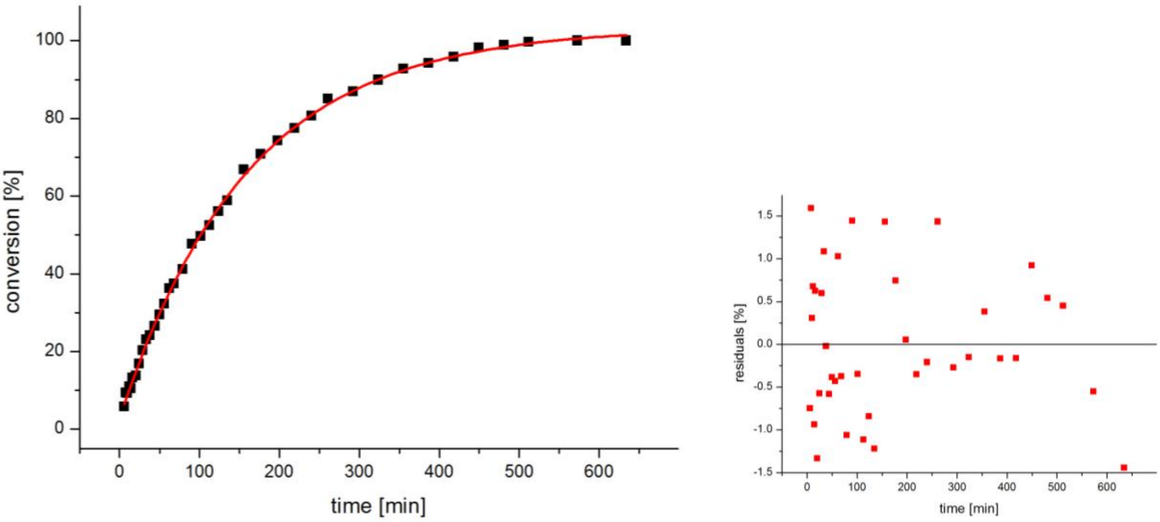


Figure S24. Measurement with 100 mol% PNP (**9**) in THF-d_8 (cf. Table S4).

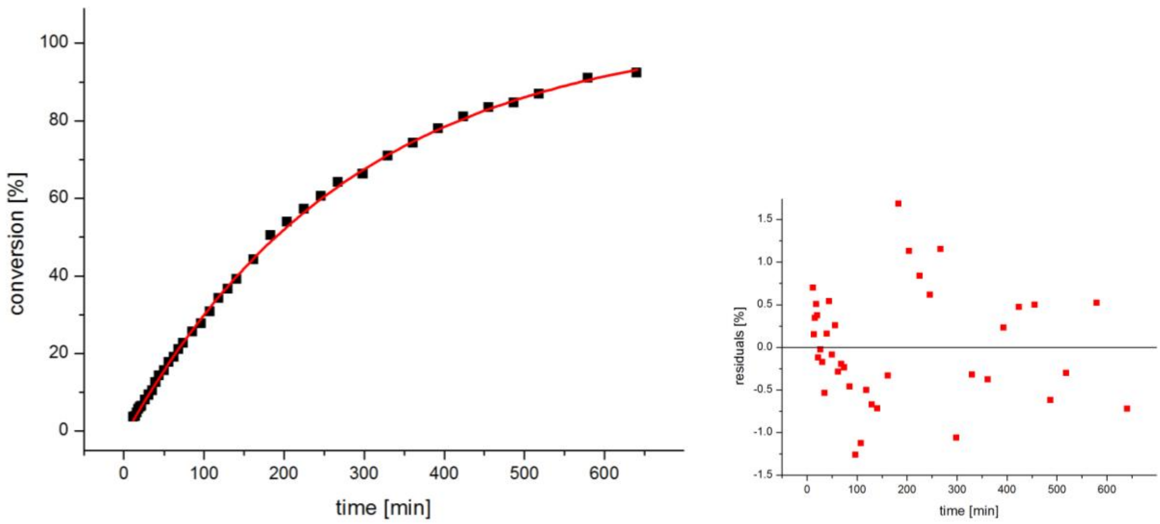
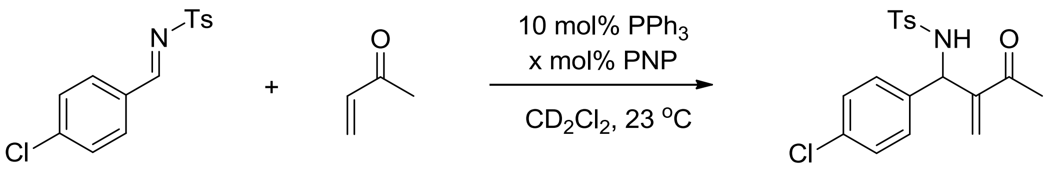


Figure S25. Measurement with 120 mol% PNP (**9**) in THF-d_8 (cf. Table S4).



3a **2** **8a**

Table S5. Co-catalyst effect in the PPh_3 catalyzed aMBH reaction of *p*-chlorotosylimines, MVK and PNP (x mol %) in CD_2Cl_2.

2.5 % PNP		**5.0% PNP**		**10% PNP**		**20% PNP**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
7.2	10.0	2.3	4.0	6.7	12.0	4.6	3.0
9.1	12.1	5.0	6.1	9.4	14.1	7.9	5.1
11.4	14.1	7.4	8.1	11.5	16.1	7.6	7.1
13.1	16.2	9.2	10.2	13.8	18.2	9.0	9.2
15.4	18.3	11.5	12.3	15.5	20.3	10.6	11.3
17.2	20.3	13.0	14.3	17.5	22.3	11.7	13.3
20.4	24.7	17.4	18.7	21.8	26.7	15.3	17.7
24.5	29.0	21.1	23.0	25.5	31.0	16.9	22.0
28.2	33.4	24.7	27.4	29.3	35.4	19.5	26.4
31.2	37.7	28.6	31.7	32.0	39.7	21.4	30.7
34.2	42.1	31.7	36.1	35.5	44.1	22.8	35.1
38.5	48.2	36.2	42.2	39.7	50.2	26.6	41.2
43.2	54.2	40.7	48.2	44.2	56.2	28.2	47.2
47.0	60.3	44.6	54.3	47.9	62.3	30.2	53.3
50.4	66.4	48.4	60.4	51.5	68.4	33.5	59.4
53.5	72.4	52.4	66.4	54.5	74.4	36.9	65.4
59.6	83.5	58.6	77.5	59.6	85.5	40.8	76.5
65.0	94.6	63.9	88.6	66.8	96.6	44.5	87.6
69.9	105.6	68.9	99.6	71.6	107.6	48.5	98.6
74.3	116.7	73.2	110.7	75.2	118.7	52.1	109.7
77.3	127.8	77.3	121.8	78.2	129.8	55.8	120.8
80.9	138.8	80.5	132.8	81.2	140.8	59.5	131.8
86.3	159.9	85.9	153.9	86.4	161.9	64.1	152.9
90.1	181.0	89.7	175.0	90.6	183.0	69.8	174.0
93.0	202.0	92.9	196.0	93.1	204.0	75.5	195.0

95.2	223.1	95.3	217.1	95.5	225.1	79.0	216.1
97.7	244.2	96.8	238.2	96.8	246.2	81.5	237.2
98.1	265.2	98.3	259.2	97.4	267.2	84.8	258.2
98.3	296.6	99.1	290.6	98.4	298.6	88.0	289.6
100.0	328.0	99.5	322.0	99.3	330.0	91.3	321.0
100.0	359.4	100.0	353.4	100.0	361.4	93.2	352.4
100.0	390.8	100.0	384.8	100.0	392.8	97.1	383.8
100.0	422.1	100.0	416.1	100.0	424.1	95.9	415.1
100.0	453.5	100.0	447.5	100.0	455.5	97.1	446.5
100.0	484.9	100.0	478.9	100.0	486.9	98.4	477.9
100.0	516.3	100.0	510.3	100.0	518.3	97.5	509.3
100.0	577.3	100.0	571.3	100.0	579.3	100.0	570.3
100.0	638.3	100.0	632.3	100.0	640.3		

30% PNP		**50 % PNP**		**100% PNP**	
conv. [%]	**time** [min]	**conv.** [%]	**time** [min]	**conv.** [%]	**time** [min]
0.1	3.0	1.0	4.0	1.6	14.0
0.6	5.1	1.5	6.1	1.9	16.1
1.7	7.1	1.1	8.1	1.6	18.1
2.3	9.2	1.4	10.2	1.9	20.2
2.7	11.3	1.5	12.3	1.2	22.3
3.5	13.3	1.9	14.3	2.3	24.3
5.1	17.7	2.0	18.7	1.5	28.7
6.2	22.0	2.2	23.0	2.1	33.0
7.7	26.4	1.8	27.4	2.3	37.4
8.9	30.7	2.3	31.7	2.1	41.7
9.3	35.1	2.5	36.1	2.0	46.1
11.2	41.2	2.5	42.2	2.0	52.2
12.5	47.2	2.9	48.2	2.0	58.2
14.0	53.3	3.5	54.3	2.3	64.3
15.3	59.4	3.5	60.4	2.5	70.4
16.5	65.4	3.3	66.4	2.7	76.4
17.9	76.5	4.0	77.5	1.9	87.5
20.2	87.6	4.2	88.6	5.6	98.6
22.6	98.6	4.9	99.6	2.4	109.6
24.3	109.7	4.7	110.7	5.5	120.7

25.4	120.8	5.0	121.8	4.9	131.8
27.3	131.8	5.3	132.8	5.3	142.8
30.9	152.9	5.9	153.9	6.5	163.9
33.8	174.0	6.3	175.0	7.0	185.0
35.9	195.0	6.2	196.0	7.0	206.0
39.2	216.1	7.3	217.1	6.9	227.1
42.2	237.2	7.8	238.2	7.1	248.2
44.7	258.2	7.5	259.2	7.0	269.2
49.1	289.6	8.1	290.6	7.3	300.6
51.8	321.0	8.5	322.0	5.8	332.0
55.2	352.4	9.2	353.4	6.0	363.4
58.5	383.8	9.2	384.8	6.9	394.8
61.5	415.1	9.5	416.1	5.4	426.1
63.8	446.5	9.8	447.5	4.8	457.5
66.6	477.9	10.3	478.9	7.0	488.9
69.0	509.3	10.3	510.3	6.4	520.3
73.0	570.3	11.1	571.3	7.5	581.3
77.1	631.3				

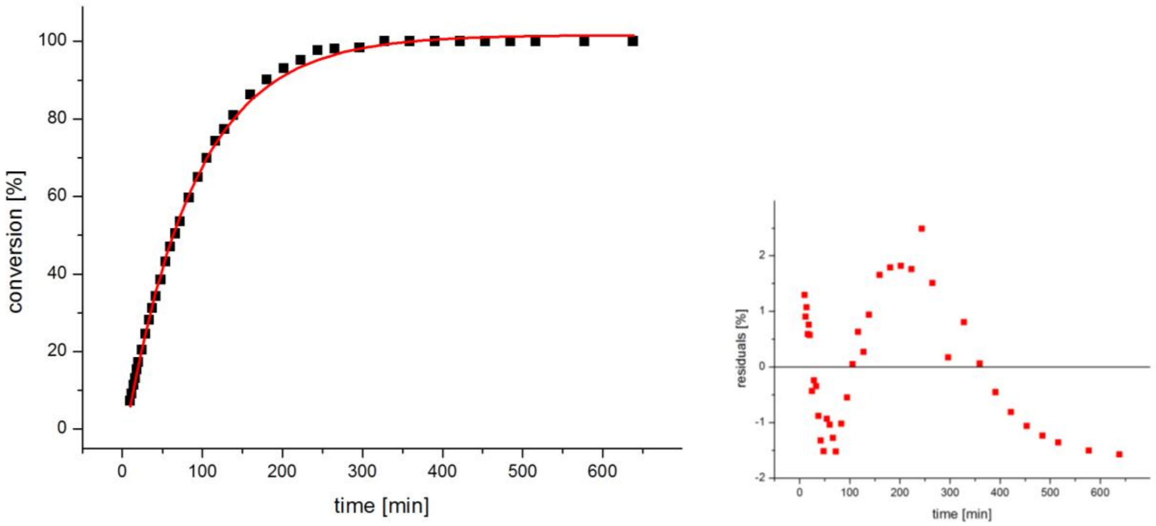


Figure S26. Measurement with 2.5 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

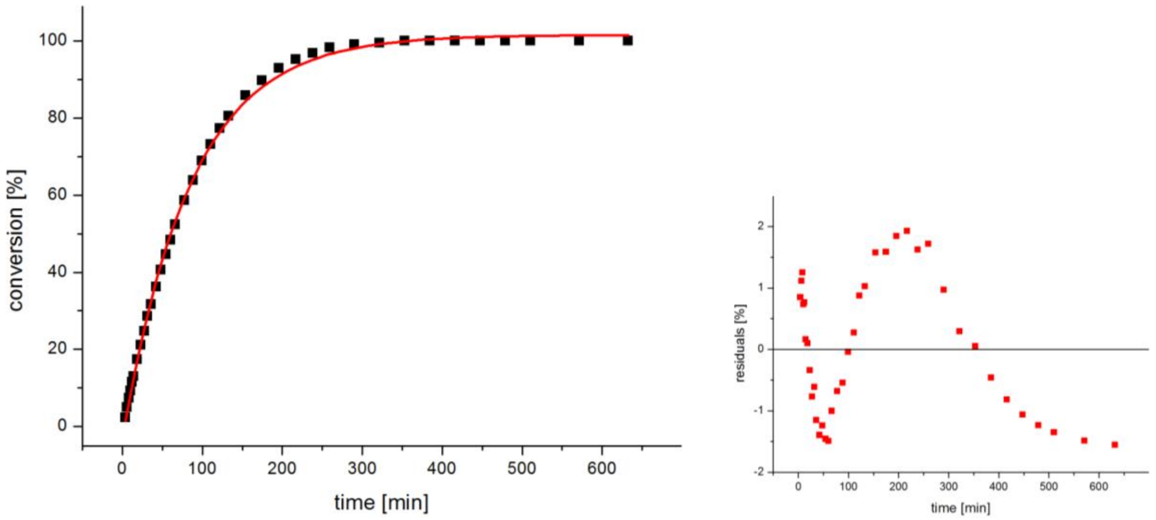


Figure S27. Measurement with 5 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

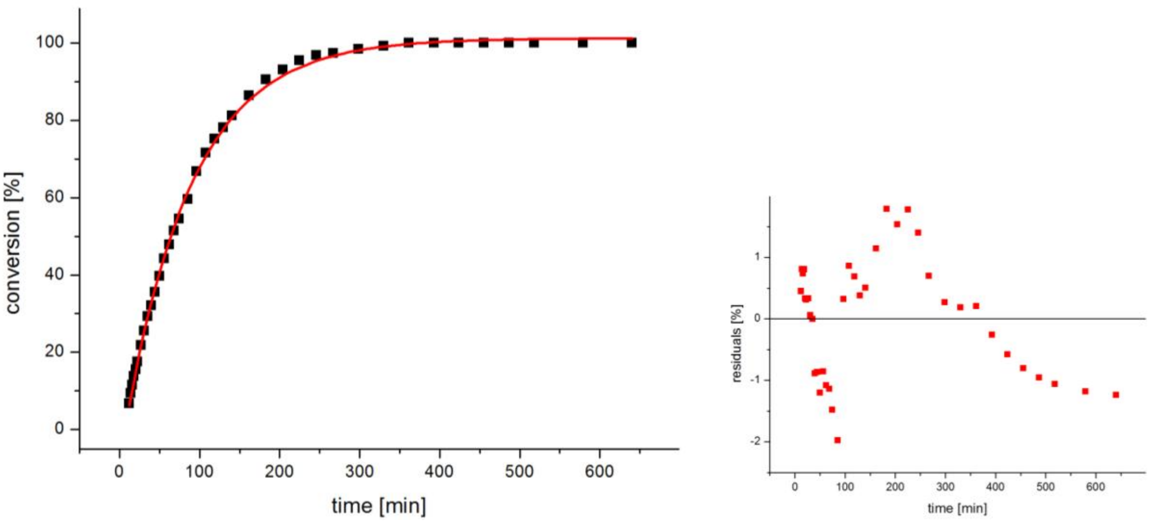


Figure S28. Measurement with 10 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

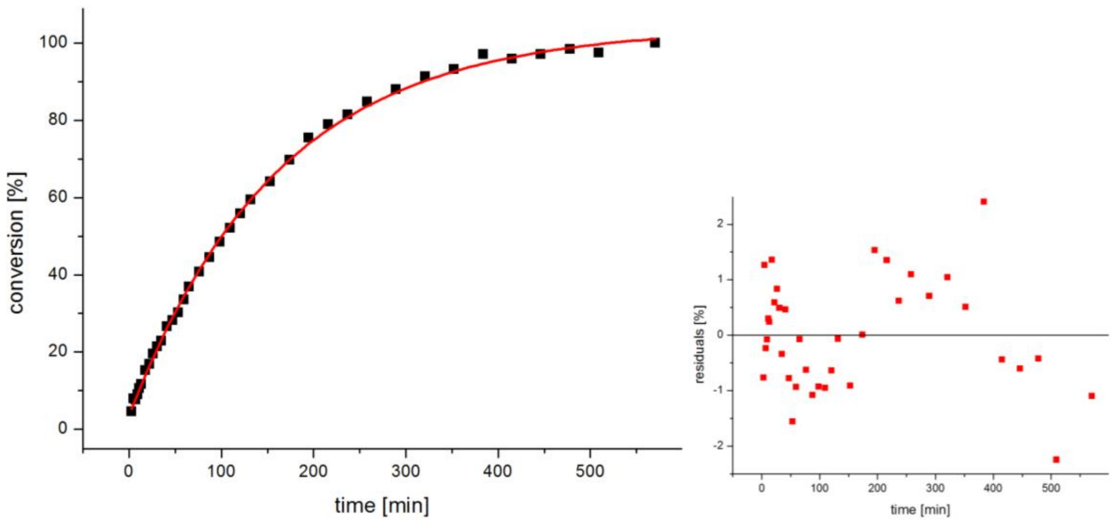


Figure S29. Measurement with 20 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

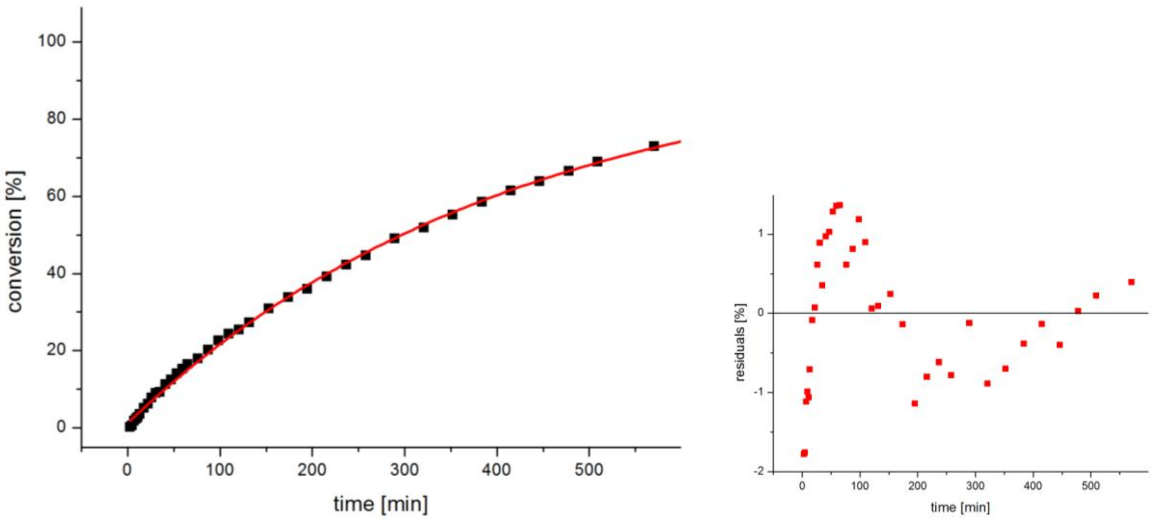


Figure S30. Measurement with 30 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

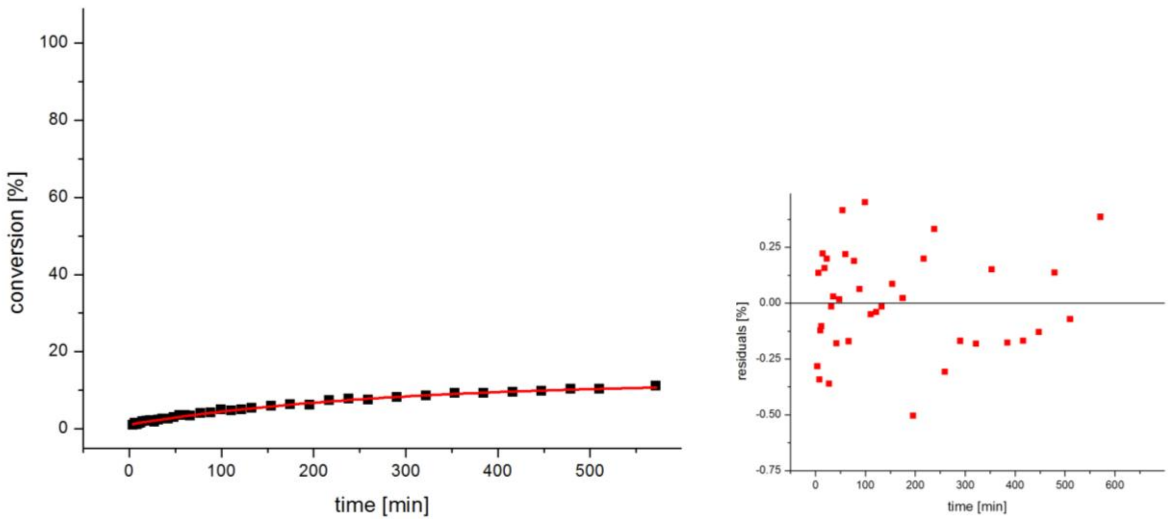


Figure S31. Measurement with 50 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

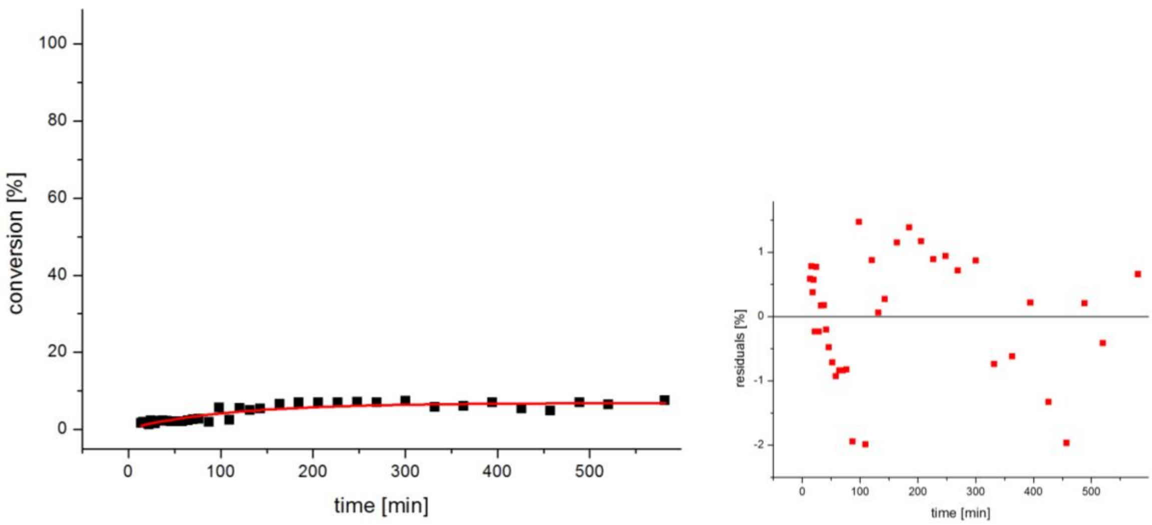
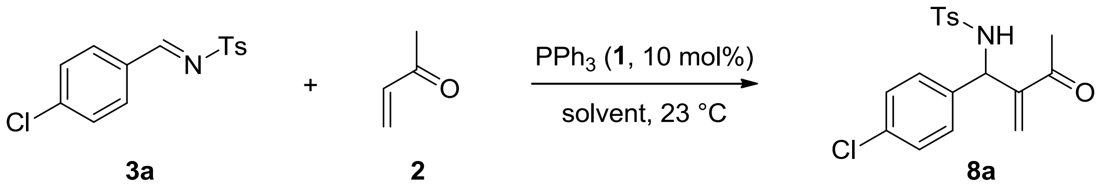


Figure S32. Measurement with 100 mol% PNP (**9**) in CD_2Cl_2 (cf. Table S5).

Descriptors of solvent properties

In the main part of the manuscript (cf. Figure 2) we already discussed the linear correlation of the halflife-times vs. the Gutmann Acceptor Numbers (AN) for the following reaction:



Beside the AN we checked for correlations between the rate constants and the dielectric constants or the $E_T(30)$-values of the solvents. The following parameters have been used (dielectric const. / $E_T(30)$): $CDCl_3$ 4.8/39.1, CD_2Cl_2 8.9/40.7, DMSO-d6 46.7/45.1, DMF-d7 36.7/43.2, THF-d8 7.6/37.4.

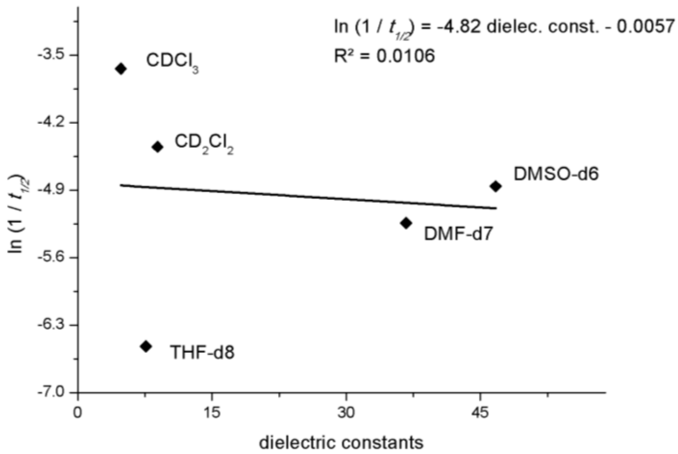


Figure S33. Correlation of the dielectric constants with the rate data.

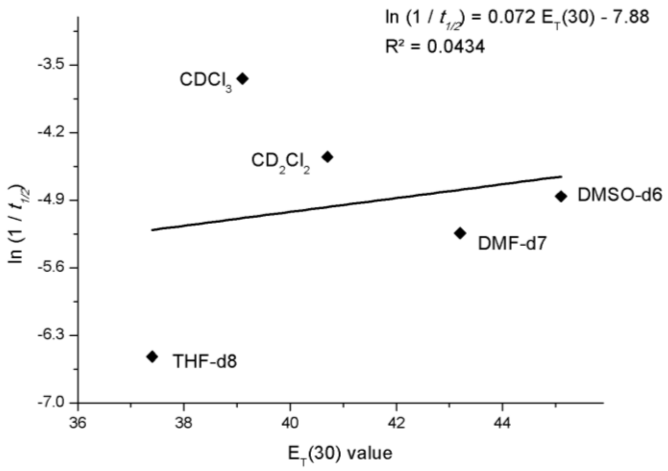
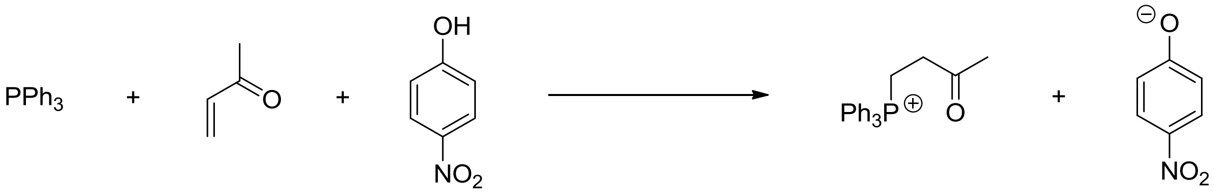


Figure S34. Correlation of the $E_T(30)$-values with the rate data.

As can be seen from Figure S33 and S34 there is no significant correlation between rate data and solvent dielectric or $E_T(30)$ parameters.

Equilibrium measurements

A set of ^{31}P measurements for the reaction of triphenylphosphane (**1**), MVK (**2**) and PNP (**9**) lacking imine (**3**) was first performed in order to detect zwitterion **4** or protonated intermediate **5** and thus gain a deeper insight into the mechanism of the reaction. The concentrations used in the kinetic studies are, unfortunately, too low for acceptable ^{31}P NMR spectra and significantly higher concentrations were therefore chosen in these measurements (see Table S6). Under these conditions intermediate **5** appears to be the only phosphane-derived species aside from catalyst **1** as described in Scheme S1. The ratio between these two species depends on the concentration of PNP (**9**) as documented in Table S6 and can be expressed with individual equilibrium constants *K* for each concentration.



1 **2** **9** **5**

Scheme S1. The reaction of triphenylphosphane (**1**), MVK (**2**) and PNP (**9**) lacking imine **3**.

Table S6. Results for the reaction with 0.32 M triphenylphosphane (**1**), 3.20 M MVK (**2**) and different concentrations of PNP (**9**) in $CDCl_3$.

Entry	**PNP (9)** [mol/L]	[**5**] / [**5**] + [**1**] [%]	**Int. [5]** [mol/L]	***K*** [M^{-1}]
1	0.11	34	0.109	13.1
2	0.16	44	0.141	1.9
3	0.32	78	0.250	4.1
4	0.48	88	0.282	3.5
5	0.64	99	0.317	36.2

Measurements at the lowest and highest concentrations of PNP in Table S6 are considered to be the least accurate due to several technical factors. However, measurements at intermediate concentrations (entries 2 - 5) yield approx. the same equilibrium constant of *K* = 3±1.

The effects of added imine were tested using the concentrations of entry 2 in Table S6. After addition of 0.16 M imine **3a** to this solution the only detectable phosphane-derived species continue to be **1** and **5**.

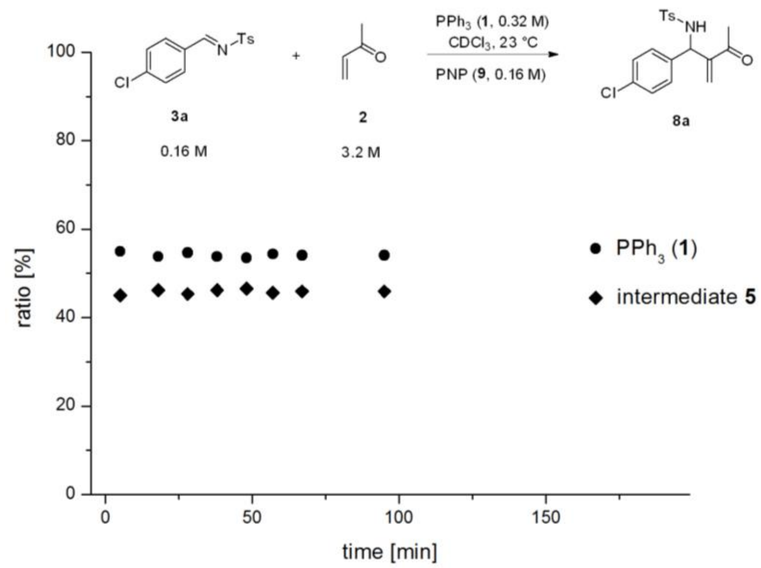


Figure S35. Reaction of **3a** (0.16 M) with MVK (**2**, 3.2 M), PNP (**9**, 0.16 M) and PPh_3 (**1**, 0.32 M) in $CDCl_3$.

It is clearly visible that the ratio of protonated intermediate **5** and PPh_3 (**1**) is not changing during the whole reaction, which, on average, includes 46 % of intermediate **5** and 54 % of PPh_3 (**1**). When all of the imine is consumed at the end of the reaction the ratio of **1** to **5** is still the same. In the reaction without imine 44 % of the intermediate **5** were detected (cf. entry 2, Table S1), the deviation of 2 % being well within the expected accuracy of these measurements.

How the amount of intermediate **5** depends on the choice of solvent and the amount of of PNP (**9**) added to the reaction mixture is depicted in Figure S34. The ratio of **5** to catalyst **1** clearly responds to the choice of solvent only in a rather moderate way, but depends quite strongly on the amount of added PNP.

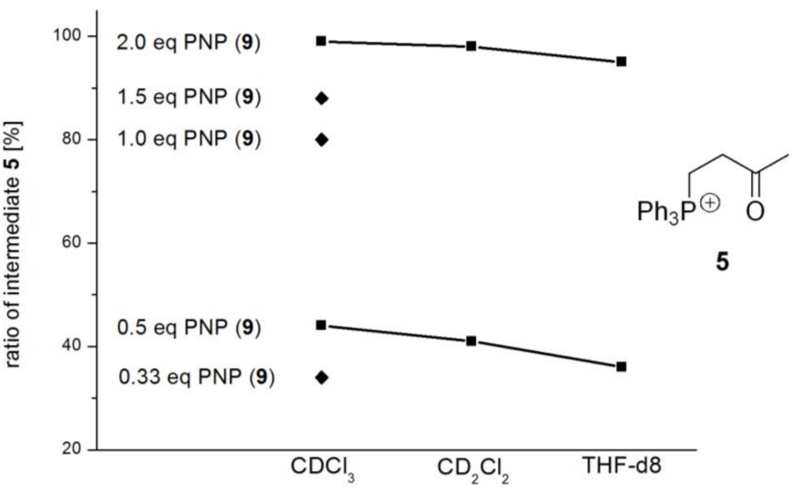
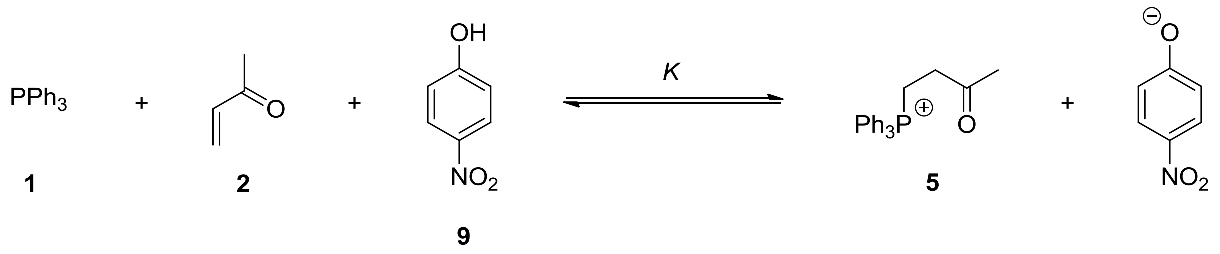


Figure S36. Ratio of protonated intermediate **5** in different solvents and amounts of PNP (**9**).

The distribution of **5** and **1** at different phenol concentrations can be described using the simple forward/backward equilibration reaction. Simulating this process (Scheme 2) with different equlibrium constants for all concentrations in CDCl3 showed that best results are obtained with $K = 4.0\ M^{-1}$ (Table S7).



Scheme S2. The used scheme for the simulation of the equilibrium reaction.

Table S7. Simulated results for the reaction with 0.32 M triphenylphosphane (**1**), 3.20 M MVK (**2**) and different concentrations of PNP (**9**) in $CDCl_3$.

	0.11 M PNP (9)	**0.16 M PNP (9)**	**0.32 M PNP (9)**	**0.48 M PNP (9)**	**0.64 M PNP (9)**	Ødev.
Int. 5 [%] exp.	**34**	**44**	**78**	**88**	**99**	**0 %**
Int. 5 [%] ***K* = 3.0**	33	46	75	87	92	2.8 %
Int. 5 [%] ***K* = 3.5**	33	46	76	88	92	2.4 %
Int. 5 [%] ***K* = 3.8**	33	47	77	89	93	2.4 %
Int. 5 [%] ***K* = 3.9**	33	47	77	89	93	2.4 %
Int. 5 [%] ***K* = 4.0**	33	47	78	89	93	2.2 %
Int. 5 [%] ***K* = 4.1**	33	47	78	89	93	2.2 %
Int. 5 [%] ***K* = 4.2**	33	47	78	90	93	2.4 %
Int. 5 [%] ***K* = 4.5**	33	47	79	90	94	2.4 %
Int. 5 [%] ***K* = 5.0**	33	48	80	91	94	3.0 %

Control experiment: imine (3a) and PNP (9)

In order to check the influence of the acidic co-catalyst (PNP, **9**) on the imine (**3a**) we performed a set of experiment in which 10 mol%, 40 mol%, 70 mol% and 100 mol% of PNP (**9**) was added to a solution of imine (**3a**, 0.125 M, $CDCl_3$). The experiments were followed by ^{1}H-NMR-spectroscopy, however no change of the imine signals could be detected. The spectra of the experiment with 100 mol% PNP (**9**) are displayed below, in which spectrum 1 is before the addition of PNP (**9**).

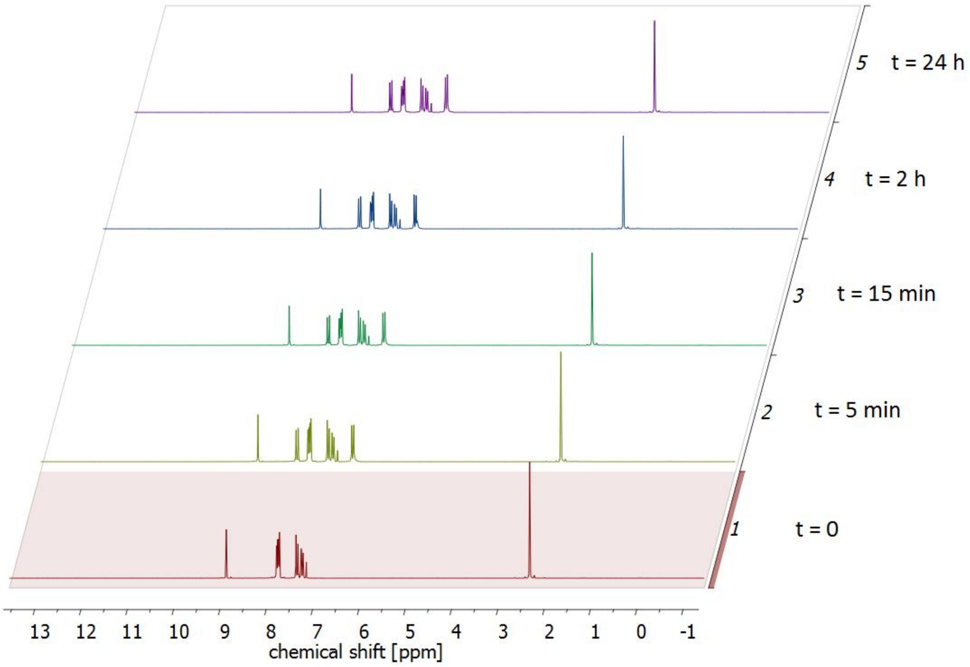


Figure S37. Spectra of the mixture between imine (**3a**) and PNP (**9**) in $CDCl_3$.

It can be maintained that addition of one equivalent of PNP (**9**) to the imine (**3a**) does not lead to a change of the signals. Therefore a activation of the imine through H-bonding seems to be unlikely.

Quantum chemical calculations for ^{31}P NMR shifts

The geometries of all systems (complexes between solute and one molecule of solvent) have been optimized at the MPW1K/6-31G(d) level of theory. The conformational space of the systems has first been searched using the MM3 force field and the systematic search routine in the TINKER program, and, in some cases, also with MM3* and OPLS force fields and the systematic routine implemented in MACROMODEL 9.7. All stationary points located at force field level have then been reoptimized at MPW1K/6-31G(d) level. The thermal corrections to Gibbs free energy to 298.15 K have been calculated for all minima from unscaled vibrational frequencies obtained at the same level. For conformationally flexible systems thermal corrections to Gibbs free energy have been combined with single point energies calculated at the MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d) level to yield Gibbs free energies G_{298} at 298.15 K. NMR chemical shift on the GIAO-MPW1K/ 6-311++G(2d,2p)//MPW1K/6-31G(d) level combined with polarizable continuum model (IEFPCM) for all found minima have been calculated. As the reference system the complex between triphenylphosphane and one molecule of solvent has been used.[18] Chemical shifts have been calculated as Boltzmann-averaged values over all available conformers relying on the Gibbs free energies. All quantum mechanical calculations have been performed with Gaussian 03.

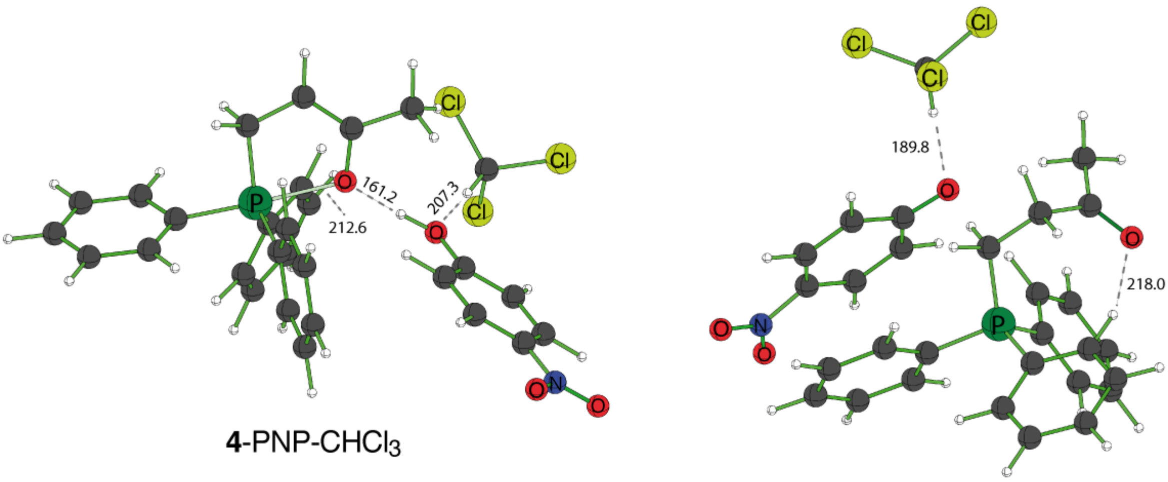
Table S8. ^{31}P NMR chemical shifts, total energies, free energies in gas and in solution.

	MPW1K/6-311++G (2d,2p) + PCM/UAHF/MPW1K/ 6-311++G(2d,2p)	MP2(FC)/6-31+G(2d,p)//MPW1K/6-31G(d) + PCM/UAHF/MPW1K/6-311++G(2d,2p)		
species	δ, ppm	E_{tot}	„G“$_{298}$, gas	G“$_{298}$,CHCl3
5*ArO*CHCl$_3$_1	31.3915	-3192.678599	-3192.239505	-3192.224589
5*ArO*CHCl$_3$_2	22.7087	-3192.670886	-3192.236324	-3192.223942
5*ArO*CHCl$_3$_3	18.423	-3192.67204	-3192.234901	-3192.223172
5*ArO*CHCl$_3$_4	22.4782	-3192.670493	-3192.235328	-3192.223089
5*ArO*CHCl$_3$_5	21.0232	-3192.665688	-3192.233148	-3192.221356
5*ArO*CHCl$_3$_6	26.9253	-3192.670591	-3192.236568	-3192.220982
5*ArO*CHCl$_3$_7	33.9335	-3192.662721	-3192.232324	-3192.220356
5*ArO*CHCl$_3$_8	30.253	-3192.668728	-3192.231606	-3192.21881
5*ArO*CHCl$_3$_9	-35.0522	-3192.672189	-3192.234253	-3192.217871
5*ArO*CHCl$_3$_10	22.3094	-3192.663438	-3192.230808	-3192.217788
5*ArO*CHCl$_3$_11	29.9289	-3192.663664	-3192.22963	-3192.217598
5*ArO*CHCl$_3$_12	26.2319	-3192.669796	-3192.232716	-3192.21737
5*ArO*CHCl$_3$_13	26.4131	-3192.660097	-3192.226807	-3192.214457
5*ArO*CHCl$_3$_14	-68.8475	-3192.66627	-3192.231177	-3192.214397

5*ArO*$CHCl_3$_15	21.0137	-3192.655187	-3192.223636	-3192.214186
5*ArO*$CHCl_3$_16	-63.3754	-3192.665937	-3192.230089	-3192.213595
5*ArO*$CHCl_3$_17	-49.3724	-3192.663535	-3192.226437	-3192.212524
5*ArO*$CHCl_3$_18	27.1949	-3192.658977	-3192.223906	-3192.211556
5*ArO*$CHCl_3$_19	-38.8093	-3192.656937	-3192.223565	-3192.21139
5*ArO*$CHCl_3$_20	-41.3591	-3192.656076	-3192.223992	-3192.211067
5*ArO*$CHCl_3$_21	-65.3327	-3192.661775	-3192.226016	-3192.211036
5*ArO*$CHCl_3$_22	-40.5328	-3192.660825	-3192.224896	-3192.211
5*ArO*$CHCl_3$_23	32.7952	-3192.647088	-3192.218017	-3192.209969
5*ArO*$CHCl_3$_24	32.0927	-3192.645574	-3192.215242	-3192.209298
4*ArOH*$CHCl_3$_1	-13.5311	-3192.674249	-3192.239322	-3192.218701
4* ArOH*$CHCl_3$_2	10.058	-3192.669981	-3192.235725	-3192.216139
4* ArOH*$CHCl_3$_3	18.0117	-3192.661357	-3192.229095	-3192.212299
4* ArOH*$CHCl_3$_4	26.838	-3192.65833	-3192.225378	-3192.210797
4* ArOH*$CHCl_3$_5	24.848	-3192.658376	-3192.224501	-3192.210589
4* ArOH*$CHCl_3$_6	24.0445	-3192.656156	-3192.224677	-3192.209649
4* ArOH*$CHCl_3$_7	24.2368	-3192.652908	-3192.220668	-3192.208429

Table S9. Boltzmann-averaged chemical shifts.

Species	<δ>, ppm
5*ArO*$CHCl_3$	+26.6
4* ArOH*$CHCl_3$	-12.0
Ph_3PO*$CHCl_3$	+29.6



4-PNP-$CHCl_3$

5-PNP-$CHCl_3$

Fig. S38. Structures of the most stable conformations of the complex of zwitterion **4** with *para*-nitrophenol and chloroform (left), and of the complex of cation **5** with *para*-nitrophenolate and chloroform (right) optimized at the MPW1K/6-31G(d) level of theory.

Archive entries for the best conformations

5*ArO*$CHCl_3$_1

1\1\GINC-CALYPSO\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\04-Dec-
2010\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid geom=check gues
s=read\\cati10_2_003_sol2\\0,1\P,0,1.9558330473,-0.0715572651,-0.26882
9354\C,0,3.5715661312,-0.4170088042,-0.9936755184\C,0,4.2058071195,0.5
20922279,-1.8046085339\C,0,4.1979706039,-1.6340590092,-0.7129860812\C,
0,5.4476139646,0.2370238595,-2.3479923885\H,0,3.7395245927,1.472791576
6,-2.005786059\C,0,5.4384386473,-1.9055493746,-1.2628782832\H,0,3.7249
458677,-2.3585315759,-0.0624923832\C,0,6.0611620337,-0.9755788639,-2.0
817095135\H,0,5.9353441841,0.9678804723,-2.9752320051\H,0,5.9202438617
,-2.8469376903,-1.0455154527\H,0,7.0296625018,-1.1943205015,-2.5066428
129\C,0,1.4233034284,1.5715142605,-0.7666115374\C,0,1.1731744564,1.841
7865903,-2.1134349533\C,0,1.2304416618,2.5651323408,0.1872200203\C,0,0
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931278018\O,0,2.1959583606,-3.471208369,1.021989217\H,0,0.1403036048,-
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70899914,-1.9163928633\C,0,-2.3468428841,1.1785729121,-0.566888692\C,0
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,1.8182658867\C,0,-2.2208415171,2.8051969529,1.6834494183\C,0,-2.42826
34892,3.3542377316,0.4196632736\C,0,-2.5146025751,2.5303238745,-0.7011
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1.0140211505,2.7938758771\H,0,-2.182156562,3.4628070476,2.537296139\H,
0,-2.697195998,2.9790165338,-1.6640957716\O,0,-1.8081779514,-0.6687943
71,0.8052974555\N,0,-2.4733345395,4.7640111501,0.2607621337\O,0,-2.348
5874483,5.4653469854,1.2497683426\O,0,-2.6026569585,5.2186648732,-0.86
41491016\H,0,-3.0789227291,-1.8037094507,-0.0301102999\C,0,-3.72672689
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720261\Cl,0,-2.8496202762,-3.0207860195,-2.0174019587\Cl,0,-5.21684924
,-1.6852815245,-1.0040749339\\Version=AM64L-G03RevD.01\State=1-A\HF=-3
186.9509902\MP2=-3192.6785988\RMSD=6.413e-09\Thermal=0.\PG=C01 [X(C29H
27Cl3N1O4P1)]\\@

5*ArO*CHCl$_3$_2

1\1\GINC-IBLIS\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\09-Dec-20
10\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid geom=check guess=
read\\compl9_newconf_02_6_sol2\\0,1\P,1.828769,0.107767,-0.002438\C,1.
132769,-0.12449,1.63799\C,1.256406,-1.343125,2.298917\C,0.542768,0.957
948,2.283219\C,0.78759,-1.476355,3.596099\H,1.691562,-2.198889,1.80546
9\C,0.093217,0.82123,3.583547\H,0.409743,1.893642,1.763722\C,0.21232,-
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75558\H,-0.15299,-0.500525,5.251126\C,1.604924,1.755365,-0.693107\C,2.
336605,2.820044,-0.167381\C,0.785935,1.955949,-1.800429\C,2.245777,4.0
73834,-0.744709\H,2.971751,2.687409,0.695447\C,0.715422,3.2103,-2.3808
02\H,0.178471,1.143385,-2.160922\C,1.441794,4.266796,-1.856334\H,2.805
684,4.896706,-0.326781\H,0.073804,3.364052,-3.234731\H,1.374053,5.2450
22,-2.308581\C,1.523454,-1.20251,-1.193787\C,2.19817,-1.1251,-2.413314
\C,0.731571,-2.307911,-0.908742\C,2.073794,-2.146318,-3.336799\H,2.805
742,-0.263871,-2.652963\C,0.621941,-3.33171,-1.836178\H,0.173771,-2.36
1584,0.012059\C,1.290693,-3.253861,-3.045226\H,2.58733,-2.076256,-4.28

3917\H,-0.010059,-4.178037,-1.615163\H,1.194504,-4.050961,-3.767346\C,
3.64599,0.031368,0.240706\C,4.207508,-1.314605,0.651161\C,5.720874,-1.
330446,0.56935\C,6.400884,-2.564474,1.089714\H,7.45958,-2.526496,0.855
647\H,6.276014,-2.625864,2.171298\H,5.95864,-3.464792,0.664859\O,6.334
143,-0.401647,0.113437\H,3.914822,-1.57956,1.667667\H,4.110708,0.34804
6,-0.691716\H,3.919165,0.780697,0.981186\H,3.833838,-2.115776,0.008638
\O,-0.894292,0.28086,-0.318837\C,-1.750057,-0.671655,-0.253422\C,-2.17
8594,-1.220159,0.987328\C,-2.310935,-1.250797,-1.424593\C,-3.063116,-2
.267582,1.047199\H,-1.793139,-0.782661,1.896218\C,-3.198562,-2.294336,
-1.364868\H,-2.012884,-0.841963,-2.379036\C,-3.570077,-2.814111,-0.128
026\H,-3.381191,-2.679631,1.991562\H,-3.616695,-2.72795,-2.259231\N,-4
.472744,-3.91672,-0.064505\O,-4.893334,-4.378201,-1.108808\O,-4.775456
,-4.351897,1.030769\H,-1.86599,1.926952,-0.066589\C,-2.455091,2.834807
,0.08122\Cl,-1.406048,4.048224,0.832012\Cl,-3.01475,3.393788,-1.493523
\Cl,-3.811975,2.458111,1.132645\\Version=AM64L-G03RevD.01\State=1-A\HF
=-3186.9404154\MP2=-3192.670886\RMSD=8.550e-09\Thermal=0.\PG=C01 [X(C2
9H27Cl3N1O4P1)]\\@

5*ArO*CHCl$_3$_3

1\1\GINC-CALYPSO\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\09-Dec-
2010\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid\\cati10_spmp2-5
_2_003_trib_sol2\\0,1\P,0,1.453579,-1.060727,0.592572\C,0,0.538253,-2.
18863,-0.462332\C,0,-0.655763,-2.7527,-0.024097\C,0,1.07932,-2.564938,
-1.692363\C,0,-1.300262,-3.694018,-0.80836\H,0,-1.108005,-2.435332,0.9
01828\C,0,0.417498,-3.498343,-2.471818\H,0,2.014077,-2.147575,-2.03957
9\C,0,-0.766892,-4.066967,-2.029913\H,0,-2.235414,-4.113542,-0.470509\
H,0,0.834117,-3.780854,-3.427089\H,0,-1.279247,-4.793268,-2.643144\C,0
,0.676594,-0.613722,2.156142\C,0,0.292824,-1.605222,3.055357\C,0,0.533
161,0.72644,2.500777\C,0,-0.248465,-1.256943,4.281857\H,0,0.390479,-2.
651615,2.804193\C,0,0.016429,1.066295,3.737804\H,0,0.799661,1.496239,1
.795813\C,0,-0.381238,0.077938,4.62554\H,0,-0.564207,-2.030121,4.96592
\H,0,-0.094511,2.108097,3.997867\H,0,-0.799204,0.348723,5.583716\C,0,2
.251766,0.32221,-0.23426\C,0,3.301164,0.968745,0.416132\C,0,1.885879,0
.711887,-1.517441\C,0,3.983337,1.992277,-0.217676\H,0,3.576242,0.70114
7,1.426298\C,0,2.587388,1.721377,-2.151919\H,0,1.035157,0.251547,-1.98
8967\C,0,3.633998,2.359664,-1.506794\H,0,4.783174,2.502982,0.297311\H,
0,2.300541,2.021975,-3.147702\H,0,4.168837,3.155173,-2.003799\C,0,2.85
7997,-2.085211,1.226809\C,0,3.738525,-2.845466,0.234748\C,0,4.606496,-
1.984647,-0.660117\C,0,5.872701,-1.437387,-0.06457\H,0,6.625905,-2.227
183,-0.061856\H,0,6.236198,-0.610482,-0.665201\H,0,5.737089,-1.120325,
0.967726\O,0,4.315658,-1.792735,-1.812979\H,0,4.391489,-3.492844,0.823
269\H,0,3.455919,-1.443085,1.873339\H,0,3.127241,-3.483503,-0.397766\H
,0,2.396618,-2.817078,1.888423\O,0,-0.573662,0.431215,-0.201426\C,0,-1

.799193,0.046211,-0.263251\C,0,-2.403657,-0.297561,-1.500693\C,0,-2.61
6164,-0.070746,0.893255\C,0,-3.69652,-0.748047,-1.575902\H,0,-1.806551
,-0.204598,-2.396058\C,0,-3.90922,-0.525722,0.820369\H,0,-2.194864,0.2
13035,1.846061\C,0,-4.450485,-0.874155,-0.412706\H,0,-4.144617,-1.0146
92,-2.519597\H,0,-4.522265,-0.617583,1.702684\N,0,-5.787585,-1.368968,
-0.484302\O,0,-6.233767,-1.667816,-1.575663\O,0,-6.41805,-1.47724,0.55
0597\H,0,-0.580063,2.350935,-0.411716\C,0,-0.656554,3.43853,-0.469195\
Cl,0,-2.177198,3.93088,0.259981\Cl,0,-0.586594,3.912982,-2.164933\Cl,0
,0.711478,4.123974,0.422809\\Version=AM64L-G03RevD.01\State=1-A\HF=-31
86.9310262\MP2=-3192.6720401\RMSD=9.554e-09\Thermal=0.\PG=C01 [X(C29H2
7Cl3N1O4P1)]\\@

5*ArO*CHCl$_3$_4

1\1\GINC-NODE7\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\ZIP04\09-Dec-20
10\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid\\compl9_newconf_s
pmp2-5_01_2_sol2\\0,1\P,0,-1.892148,-0.124083,0.455979\C,0,-1.773043,1
.587574,1.000245\C,0,-2.683025,2.520035,0.50209\C,0,-0.853196,1.965016
,1.973569\C,0,-2.670172,3.819261,0.977033\H,0,-3.392708,2.25008,-0.265
932\C,0,-0.86154,3.262578,2.455181\H,0,-0.113186,1.255954,2.303582\C,0
,-1.766367,4.187644,1.960391\H,0,-3.366821,4.541078,0.578258\H,0,-0.14
2234,3.554851,3.20469\H,0,-1.759262,5.20119,2.332873\C,0,-1.221079,-1.
30259,1.636296\C,0,-1.669508,-1.221224,2.955681\C,0,-0.358461,-2.32562
8,1.262096\C,0,-1.253445,-2.15455,3.886255\H,0,-2.325797,-0.420436,3.2
65881\C,0,0.042981,-3.264895,2.198847\H,0,0.031687,-2.375736,0.258388\
C,0,-0.402973,-3.182718,3.505948\H,0,-1.592361,-2.078495,4.908587\H,0,
0.727447,-4.045047,1.903288\H,0,-0.079582,-3.911997,4.233674\C,0,-1.44
5527,-0.396607,-1.261522\C,0,-1.524666,-1.663852,-1.831095\C,0,-1.0890
18,0.694781,-2.046667\C,0,-1.246204,-1.835755,-3.176891\H,0,-1.776652,
-2.526023,-1.231954\C,0,-0.829807,0.517832,-3.392941\H,0,-0.986101,1.6
72328,-1.603773\C,0,-0.905832,-0.745503,-3.959334\H,0,-1.289853,-2.823
641,-3.610157\H,0,-0.54777,1.36811,-3.995082\H,0,-0.690205,-0.881141,-
5.008583\C,0,-3.700936,-0.419744,0.571205\C,0,-4.189543,-1.818998,0.23
2339\C,0,-4.75371,-1.923952,-1.17228\C,0,-5.015982,-3.312098,-1.679949
\H,0,-5.612845,-3.267056,-2.584748\H,0,-4.068252,-3.80231,-1.905397\H,
0,-5.519629,-3.919449,-0.928973\O,0,-5.006401,-0.944293,-1.822249\H,0,
-3.440596,-2.593314,0.402246\H,0,-3.971962,-0.147555,1.589598\H,0,-5.0
12658,-2.084169,0.900957\H,0,-4.201879,0.278887,-0.096202\O,0,0.809266
,0.419232,0.327316\C,0,1.757288,-0.431286,0.185107\C,0,2.048053,-1.038
75,-1.068558\C,0,2.566568,-0.835392,1.28234\C,0,3.030866,-1.986913,-1.
201395\H,0,1.472944,-0.728773,-1.928378\C,0,3.552347,-1.779003,1.14868
4\H,0,2.378025,-0.375167,2.24132\C,0,3.780438,-2.367983,-0.092105\H,0,
3.241526,-2.44637,-2.153952\H,0,4.157415,-2.082144,1.988177\N,0,4.7843
06,-3.371733,-0.226456\O,0,5.418637,-3.689152,0.762395\O,0,4.956053,-3

.872855,-1.322085\H,0,1.506574,2.139827,-0.180925\C,0,1.953971,3.09262
5,-0.473494\Cl,0,3.222379,2.779673,-1.64865\Cl,0,2.610209,3.862566,0.9
69964\Cl,0,0.681266,4.096996,-1.185869\\Version=AM64L-G03RevD.01\State
=1-A\HF=-3186.9360538\MP2=-3192.6704926\RMSD=8.262e-09\Thermal=0.\PG=C
01 [X(C29H27Cl3N1O4P1)]\\@

4*ArOH*CHCl$_3$_1

1\1\GINC-GOLEM\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\18-Apr-20
11\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid geom=check guess=
read\\zwphcl_many_01\\0,1\C,2.919882,-0.635119,2.175616\H,3.736585,0.0
17981,2.492478\H,3.380798,-1.618616,2.035643\C,1.754398,-0.630284,3.09
3541\C,0.561784,-0.391933,2.532279\O,0.514175,-0.19518,1.227487\C,-0.7
29055,-0.32411,3.275726\H,-1.192811,0.653213,3.142341\H,-0.583038,-0.4
99546,4.338201\H,-1.429329,-1.066265,2.89375\H,1.886591,-0.799764,4.14
9339\O,-1.80178,-0.335305,0.037912\H,-0.910697,-0.245631,0.475832\C,4.
268315,0.030625,-0.107426\C,4.981948,-1.155185,-0.293856\C,4.944105,1.
235878,-0.272793\C,6.322827,-1.136953,-0.632775\H,4.481532,-2.10847,-0
.190423\C,6.288194,1.256577,-0.618231\H,4.424671,2.172094,-0.136977\C,
6.980669,0.072767,-0.79776\H,6.853194,-2.067275,-0.774524\H,6.790712,2
.204051,-0.747514\H,8.026553,0.089706,-1.067127\C,2.02359,1.665099,0.2
96456\C,1.657342,2.182191,-0.939645\C,2.063246,2.49832,1.410522\C,1.33
2503,3.523638,-1.060659\H,1.605406,1.542682,-1.807712\C,1.743129,3.839
621,1.281006\H,2.317562,2.097058,2.380466\C,1.380121,4.35544,0.046087\
H,1.036144,3.916205,-2.0218\H,1.77357,4.481505,2.149045\H,1.128965,5.4
01168,-0.051688\C,1.90495,-1.271416,-0.746093\C,2.290727,-1.133929,-2.
0776\C,1.128945,-2.36377,-0.369298\C,1.867719,-2.050195,-3.02539\H,2.9
35485,-0.321314,-2.37765\C,0.744956,-3.300507,-1.313384\H,0.82333,-2.4
77726,0.657672\C,1.099271,-3.137132,-2.643094\H,2.153252,-1.921086,-4.
058696\H,0.153281,-4.150636,-1.009212\H,0.779967,-3.859724,-3.379454\P
,2.499821,-0.071039,0.479397\C,-2.398681,0.841799,-0.128554\C,-3.65276
5,0.864279,-0.743476\C,-1.81131,2.038909,0.288824\C,-4.307694,2.058081
,-0.940227\H,-4.097175,-0.066099,-1.061296\C,-2.466755,3.233728,0.0896
99\H,-0.839322,2.017755,0.756805\C,-3.70887,3.237208,-0.522854\H,-5.27
5115,2.094751,-1.413023\H,-2.027484,4.166715,0.401142\N,-4.387901,4.48
9879,-0.734343\O,-5.47598,4.462448,-1.266484\O,-3.83261,5.50432,-0.370
19\H,-2.662582,-2.221159,0.037437\C,-3.156583,-3.17913,0.14957\Cl,-2.1
87564,-4.156941,1.253499\Cl,-4.758892,-2.88674,0.811994\Cl,-3.256129,-
3.934695,-1.437884\\Version=AM64L-G03RevD.01\State=1-A\HF=-3186.938561
8\MP2=-3192.674249\RMSD=9.023e-09\Thermal=0.\PG=C01 [X(C29H27Cl3N1O4P1
)]\\@

4*ArOH*CHCl$_3$_2

1\1\GINC-AZAZEL\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\17-Apr-2

011\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid geom=check guess
=read\\zwphcl_many_02\\0,1\C,-2.292676,-2.164869,-1.728302\H,-3.311078
,-2.439436,-1.996229\H,-1.84436,-3.048135,-1.258292\C,-1.512044,-1.628
524,-2.874408\C,-0.494123,-0.813655,-2.546946\O,-0.292254,-0.58056,-1.
272983\C,0.37852,-0.113526,-3.536176\H,1.426498,-0.370734,-3.381493\H,
0.290424,0.964765,-3.404386\H,0.109343,-0.367128,-4.558376\H,-1.798198
,-1.860446,-3.886477\O,1.888443,0.444458,-0.407606\H,1.030295,0.066731
,-0.782925\C,-4.108096,-1.335354,0.267515\C,-4.343405,-2.635811,0.7174
67\C,-5.150011,-0.415944,0.307764\C,-5.590552,-3.008703,1.182448\H,-3.
543002,-3.36344,0.717213\C,-6.400848,-0.789964,0.779194\H,-4.991501,0.
597387,-0.027875\C,-6.624568,-2.083959,1.213191\H,-5.755401,-4.019253,
1.525965\H,-7.199417,-0.0632,0.805452\H,-7.598841,-2.373208,1.578668\C
,-2.58469,0.774312,-0.891755\C,-2.027586,1.811844,-0.153562\C,-3.30208
3,1.05066,-2.051402\C,-2.198869,3.120501,-0.569076\H,-1.448795,1.60053
5,0.732848\C,-3.458061,2.363236,-2.468057\H,-3.734307,0.249269,-2.6312
78\C,-2.91077,3.396869,-1.726693\H,-1.76216,3.922736,0.005939\H,-4.007
638,2.574516,-3.373293\H,-3.034979,4.419247,-2.051801\C,-1.472042,-1.1
87152,1.159143\C,-1.993121,-0.680839,2.349016\C,-0.281867,-1.905282,1.
183515\C,-1.311934,-0.862763,3.539723\H,-2.932376,-0.147389,2.349873\C
,0.378781,-2.111481,2.382321\H,0.13356,-2.280309,0.264834\C,-0.12829,-
1.5831,3.558091\H,-1.713273,-0.451035,4.453601\H,1.301699,-2.671569,2.
389765\H,0.398063,-1.733263,4.489121\P,-2.423083,-0.936516,-0.361493\C
,2.869816,-0.447146,-0.397264\C,4.090201,-0.084927,0.182099\C,2.728546
,-1.726754,-0.948249\C,5.137535,-0.975482,0.217884\H,4.197863,0.904584
,0.59841\C,3.778079,-2.61849,-0.912365\H,1.792903,-2.003671,-1.407785\
C,4.974925,-2.240436,-0.327365\H,6.082533,-0.709539,0.662025\H,3.68617
3,-3.605715,-1.334606\N,6.068495,-3.176288,-0.285971\O,7.104567,-2.814
758,0.228066\O,5.89244,-4.275615,-0.765646\H,1.935283,2.404242,0.28826
3\C,1.963016,3.424426,0.655075\Cl,0.809289,3.552085,1.984207\Cl,1.5194
25,4.493062,-0.67033\Cl,3.596534,3.762553,1.217031\\Version=AM64L-G03R
evD.01\State=1-A\HF=-3186.9385877\MP2=-3192.6699808\RMSD=5.039e-09\The
rmal=0.\PG=C01 [X(C29H27Cl3N1O4P1)]\\@

4*ArOH*CHCl$_3$_3

1\1\GINC-YIN\SP\RMP2-FC\6-31+G(2d,p)\C29H27Cl3N1O4P1\BORIS\17-Apr-2011
\0\\#p MP2(FC)/6-31+g(2d,p) scf=tight int=finegrid geom=check guess=re
ad\\zwphcl_many_09\\0,1\C,2.491458,-1.061555,-1.831584\H,1.924806,-1.9
26046,-1.479722\H,3.448529,-1.408057,-2.217246\C,1.728673,-0.283383,-2
.83018\C,0.430757,-0.003643,-2.542997\O,-0.072493,-0.324751,-1.398255\
C,-0.453129,0.703685,-3.527589\H,-0.80207,1.648496,-3.109982\H,-1.3373
74,0.100743,-3.732135\H,0.056922,0.903151,-4.466842\H,2.193542,-0.0020
15,-3.760587\O,-2.544831,-0.36256,-1.069485\H,-1.525467,-0.31978,-1.23
3101\C,-3.012339,0.7624,-0.556291\C,-4.388578,0.87945,-0.328981\C,-2.1

70967,1.83554,-0.234786\C,-4.911528,2.034364,0.204043\H,-5.029639,0.04
9403,-0.583508\C,-2.696172,2.991128,0.294953\H,-1.11035,1.73433,-0.404
384\C,-4.061743,3.086898,0.513554\H,-5.968618,2.139109,0.384818\H,-2.0
63514,3.826341,0.545662\N,-4.60276,4.295614,1.072387\O,-5.800368,4.355
4,1.250528\O,-3.831447,5.19447,1.338446\C,2.350736,-1.110835,1.174138\
C,1.05475,-1.628012,1.166976\C,3.190095,-1.328018,2.265009\C,0.610958,
-2.363394,2.253163\H,0.412806,-1.435215,0.317053\C,2.732697,-2.061996,
3.345384\H,4.193619,-0.929886,2.271365\C,1.446607,-2.580161,3.33766\H,
-0.390726,-2.766072,2.247712\H,3.381709,-2.230667,4.19169\H,1.094374,-
3.155361,4.181326\C,4.699365,-0.031107,-0.141654\C,5.467888,-1.178957,
-0.339125\C,5.330544,1.17372,0.148851\C,6.846294,-1.117204,-0.250797\H
,4.991762,-2.126042,-0.551215\C,6.712953,1.230753,0.232082\H,4.745628,
2.066966,0.306299\C,7.470099,0.089275,0.031802\H,7.433794,-2.009923,-0
.404135\H,7.195834,2.170543,0.454112\H,8.546975,0.136963,0.096561\C,2.
242764,1.504475,-0.165502\C,1.588841,1.943422,0.981505\C,2.433942,2.37
4488,-1.237995\C,1.128559,3.24694,1.055989\H,1.430637,1.268544,1.80872
2\C,1.962967,3.673947,-1.157498\H,2.934184,2.036335,-2.131287\C,1.3118
39,4.109628,-0.01365\H,0.619785,3.584717,1.946207\H,2.103196,4.345893,
-1.99077\H,0.946433,5.124323,0.04476\P,2.897904,-0.161999,-0.253628\H,
-3.111965,-2.239637,-0.604292\C,-3.372453,-3.243875,-0.286388\Cl,-4.94
0885,-3.647405,-0.972563\Cl,-3.43942,-3.24691,1.47736\Cl,-2.12359,-4.3
41849,-0.867138\\Version=AM64L-G03RevD.01\State=1-A\HF=-3186.9444404\M
P2=-3192.6613571\RMSD=3.830e-09\Thermal=0.\PG=C01 [X(C29H27Cl3N1O4P1)]
\\@

Spectroscopic elucidation of intermediate 5

The assignment of intermediate **5** was achieved by different NMR techniques.

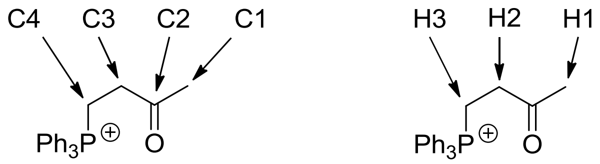

Figure S39. Notation on protonated intermediate **5**.

The first signals were assigned by two characteristic protons in ^{1}H NMR spectrum corresponding to H2 and H3. C1 and H1 were also characterized with HMBC and HSQC, C2 with 3*J*C-P and HMBC, C3 and H3 with HSQC and 2*J*C-P, C4 and H4 with HSQC and 1*J*C-P.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.95 (3H, s, H1), 2.77–2.84 (2H, m, H2), 3.31–3.38 (2H, m, H3), 7.46–7.57 (15H, m, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.76 (d, C4, $^{1}J_{C\text{-}P}$ = 55 Hz), 29.4 (C1), 35.21 (d, C3, $^{2}J_{C\text{-}P}$ = 3 Hz)), 117.0, 117.05, 117.07, 117.86, 130.61, 130.71, 133.21, 133.31, 203.02 (d, C2, $^{3}J_{C\text{-}P}$ = 12 Hz). MS(ESI) (M+) m/z: 333.2. ^{31}P NMR (108 MHz, $CDCl_3$): 25.7.

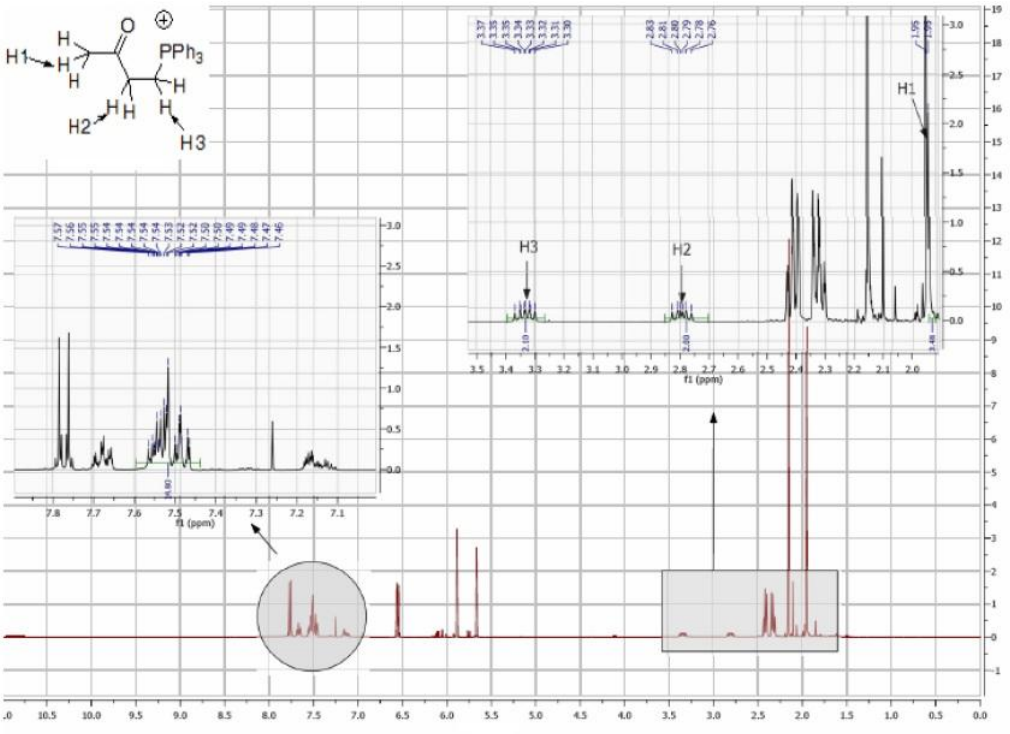

Figure S40. ^{1}H NMR (400 MHz) of **5** in the reaction of PPh_3 (**1**), PNP (**9**) and MVK (2) in $CDCl_3$.

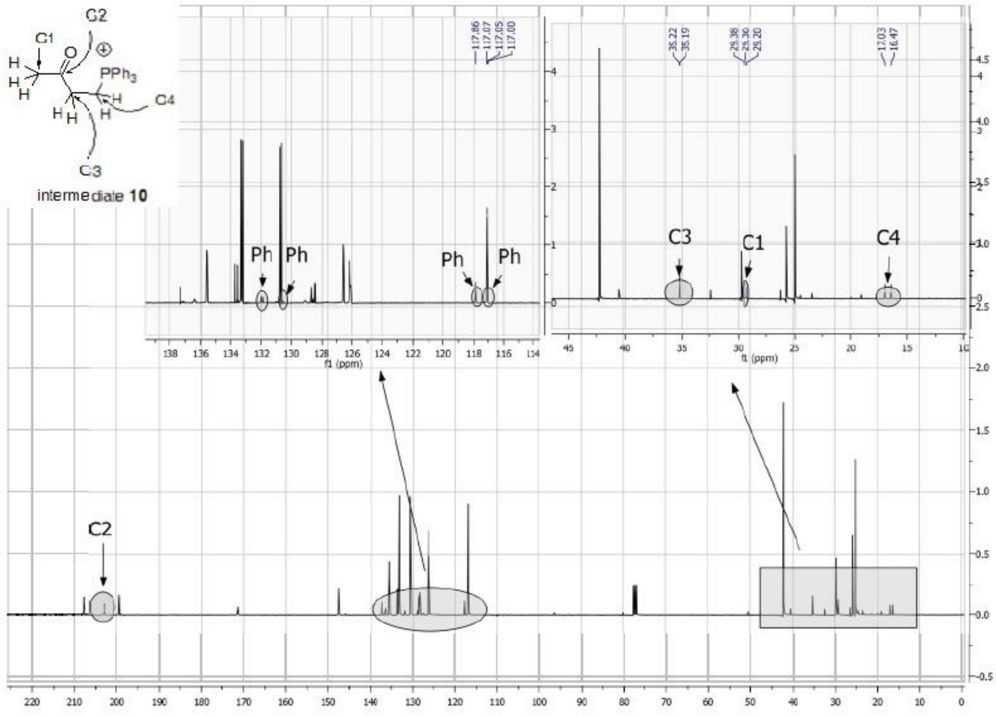

Figure S41. ^{13}C NMR (100 MHz) of **5** in the reaction of PPh_3 (**1**), PNP (**9**) and MVK (2) in $CDCl_3$.

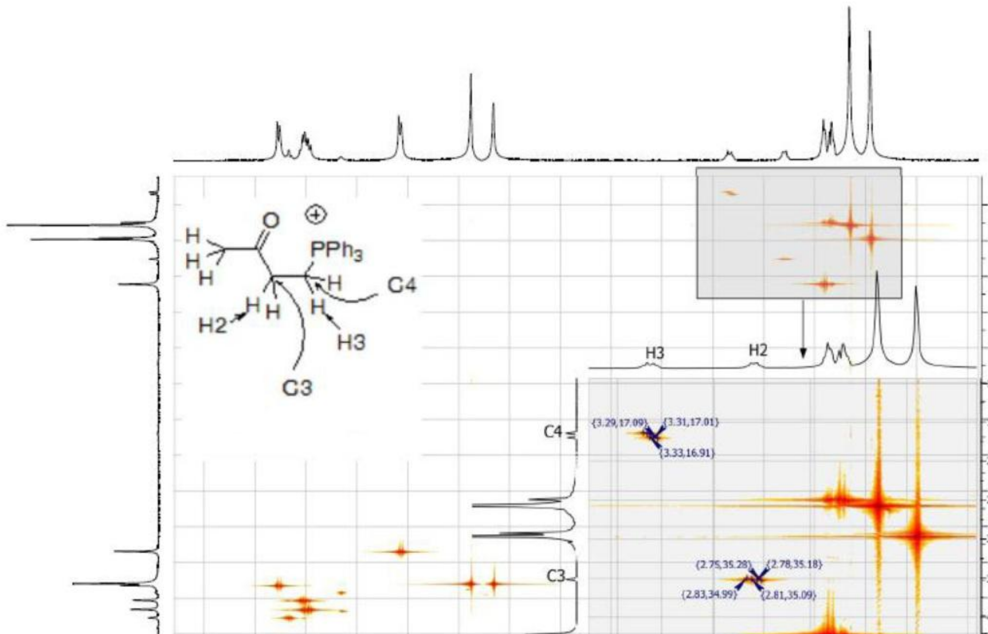

Figure S42. HSQC: C3 and H2 of **5** were characterized with HSQC and $^2J_{C\text{-}P}$; C4 and H3 were characterized with HSQC and $^1J_{C\text{-}P}$.

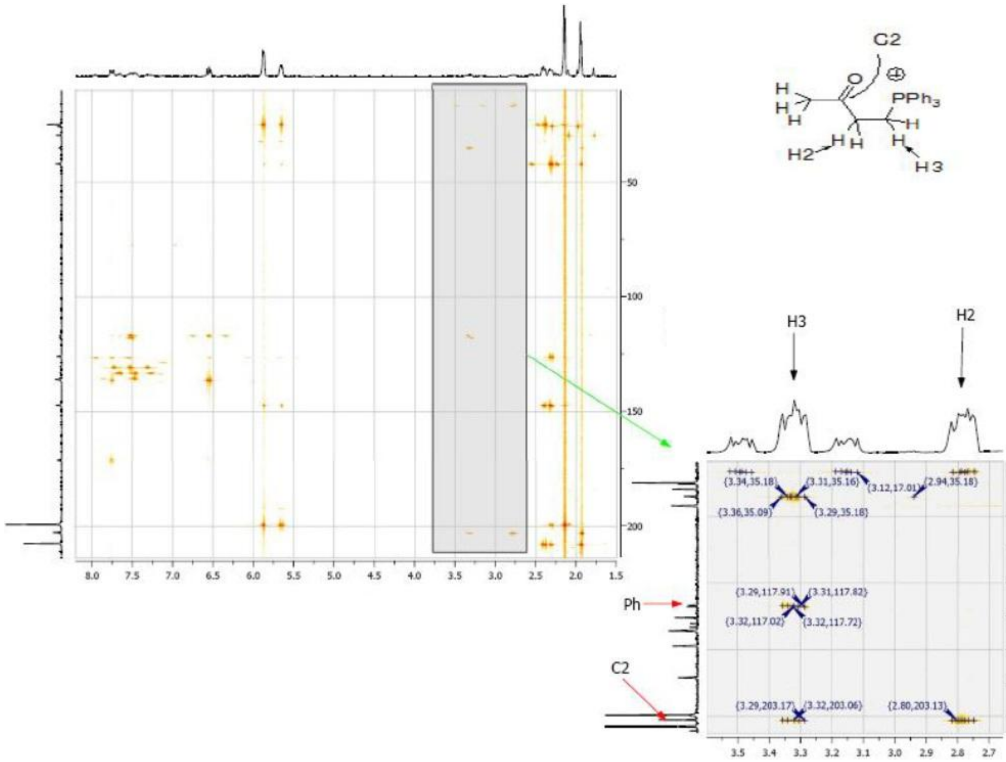

Figure S43. HMBC: C2 and Ph group of **5** were characterized with HMBC and $^{3}J_{C\text{-}P}$.

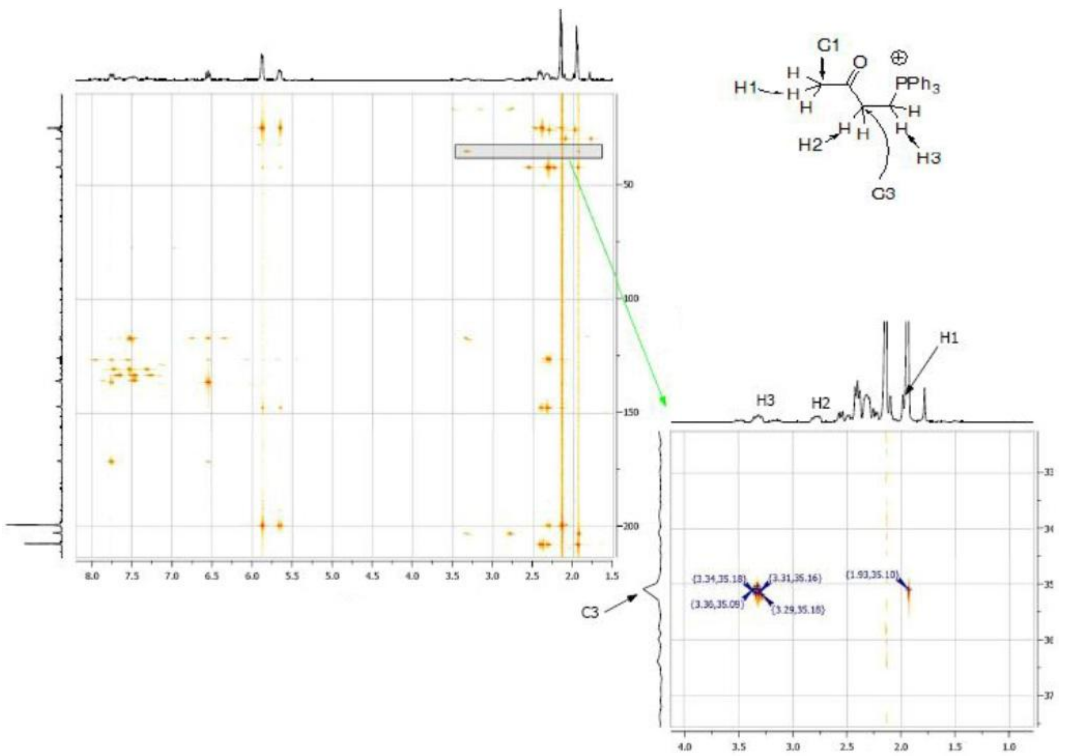

Figure S44. HMBC: H1 of **5** was characterized with HMBC.

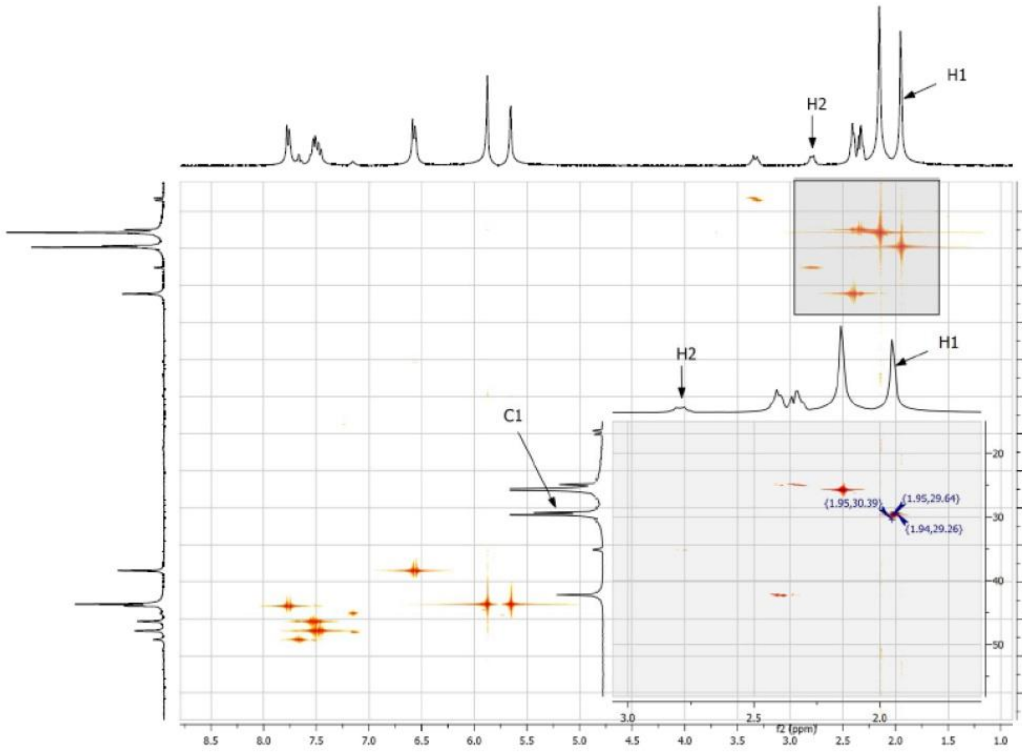

Figure S45. HSQC: c1 of **5** was characterized with HSQC.