Supporting Information

Bi-functional and mono-component organocatalysts for the ring-opening alternating *co*-polymerisation of anhydride and epoxide

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1 General Remarks

Materials and Methods

Moisture and air-sensitive materials were manipulated in flame-dried glassware under nitrogen atmosphere by using either Schlenk technique or an MBraun glovebox. Chemicals were purchased from commercial sources and used without further purification if not stated otherwise. Anhydrous tetrahydrofuran (THF), dichloromethane (CH_2Cl_2) and toluene were purchased from Acros Organics (AcroSeal™ packaging). Phthalic anhydride (PA) was purchased from Fisher Scientific, stirred over calcium hydride for 7 d (suspended in ethyl acetate) and sublimed under reduced pressure at 90 °C. (±)-Propylene oxide (PO) was purchased from Acros Organics (AcroSeal™ packaging). (±)-Butylene oxide (BO) and benzylic alcohol (BA) were purchased from Sigma Aldrich and dried over molecular sieves. Cyclohexene oxide (CHO) was purchased from TCI Chemicals, stirred over calcium hydride for 1 d and distilled under reduced pressure at 60 °C. All monomers and catalysts were stored in the glovebox.

Nuclear magnetic resonance spectroscopy (NMR)

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD (400 MHz proton frequency, equipped with a 5 mm BBFO probe with z-gradient) spectrometer using Bruker TopSpin v2.1 software. The frequency, temperature, and solvent are given individually for each NMR string. MestReNova v.14.2.0 software was used for data processing. The spectra were referenced to the (residual) solvent signal of:

- CD_2Cl_2: $\delta_{^1H}$ = 5.32 ppm $\delta_{^{13}C}$ = 54.0 ppm
- $CDCl_3$: $\delta_{^1H}$ = 7.26 ppm $\delta_{^{13}C}$ = 77.2 ppm
- DMSO-d_6: $\delta_{^1H}$ = 2.50 ppm $\delta_{^{13}C}$ = 39.5 ppm
- toluene-d_8: $\delta_{^1H}$ = 2.09 ppm $\delta_{^{13}C}$ = 20.4 ppm

Signals were assigned by their chemical shifts, scalar couplings and by acquisition of additional 2D NMR spectra [^{1}H-^{1}H correlation spectroscopy (COSY), ^{1}H-^{13}C heteronuclear single quantum coherence (HSQC) and ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC)] and labelled according to their fine structure with s (singlet), d (doublet), t (triplet), a combination of these (e.g. dt for doublet of triplets), and m (unresolved multiplet).

^{1}H NMR diffusion-ordered spectroscopy (DOSY) was performed using Bruker's pulse program *ledbpgp2s*. The spectra were measured with a spectral width of 10 ppm (16384 points, 5.00 ppm offset) in the direct dimension, 16 points in the indirect dimension and were accumulated over 16 scans per increment with a recovery delay D1 of 3 s and 32 dummy scans. A diffusion delay D20 of 0.06 s (Δ), a gradient pulse length P30 of 1500 μs (P30 = δ/2) and a linear gradient between 5 % and 95 % were used. The raw data was Fourier transformed in the direct dimension, phase- and baseline-corrected and referenced to the solvent signal prior to their DOSY transform *via* Peak Fit and Bayesian method, respectively. The obtained diffusion coefficients are only used to qualitatively separate signals of different species (e.g., monomer *vs.* dimer) because a quantitative interpretation is hampered by the different nature of species (ionic, neutral, ability to form hydrogen bonds, different solvation and flexibility) affecting the absolute diffusion behaviour.[1,2]

Thin-layer chromatography (TLC)

Thin-layer chromatography (TLC) analysis was done on silica TLC plates with green fluorescing indicator from Merck. The spots were visualized either by ultraviolet light (UV, 254 nm) or by one of the following TLC stains: potassium permanganate ($KMnO_4$), ninhydrine and *p*-anisaldehyde and are reported as the retention factor (R_f), together with the developing solvent and the visualization technique.

Size-exclusion chromatography (SEC)

Size-exclusion chromatography (SEC) was performed on a GPCMAX system at 35 °C equipped with a Viscotek VE3580 refractive index (RI) detector and three columns: one guard column (PLgel 5 μm Guard) and two linear columns (PLgel 5 μm Mixed-D. $CHCl_3$ was used as the eluent (at a flow rate of 0.5 mL/min) and as solvent to dissolve the polymer samples [4 mg/mL, with 1.4 %(V/V) toluene]. Polystyrene standards (1.2-940 kg/mol) were used as calibrants to convert the elution volume into molar masses without applying correction factors. The obtained molar masses must, thus, not be interpreted

as absolute values. The data was processed by OmniSEC v.5.1 software. Bimodal SEC traces were deconvoluted under the assumption that they are a superposition of 2 Gaussian functions.

Mass spectrometry (MS)

The catalysts were analysed by high-resolution mass spectrometry (HRMS) on a Waters Synapt G2-S Quadrupole-Time-of-Flight mass spectrometer coupled to a travelling wave Ion Mobility spectrometer with matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI), respectively. MALDI samples were prepared by mixing 10 μL of the catalyst solution (1 $^{mg}/_{mL}$ in methanol) with 50 μL of 2,5-dihydroxybenzoic acid solution (DHB, 20 $^{mg}/_{mL}$ in methanol) and depositing 0.5 μL thereof on a MALDI target plate. ESI samples were prepared by ten-fold dilution of the catalyst solution (1 $^{mg}/_{mL}$ in acetonitrile) with methanol and measured by direct infusion.

The polymers were analysed by MS on a Bruker UltrafleXtreme MALDI TOF/TOF mass spectrometer equipped with a SmartbeamII laser (355 nm, UV) in positive mode. MALDI samples were prepared by mixing 40 μL of the polymer solution (1 $^{mg}/_{mL}$ in THF) with 10 μL of either sodium trifluoroacetate (NaTFA) or potassium trifluoroacetate (KTFA) (each 5 $^{mg}/_{mL}$ in THF) and 40 μL of *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile solution (DCTB, 40 $^{mg}/_{mL}$ in THF) and depositing 0.5 μL thereof on a MALDI target plate. Additionally, each measured polymer sample was measured together with SpheriCal™ calibrants (ion peaks between 3600 $^{m}/_{z}$ and 7300 $^{m}/_{z}$) to enable an internal calibration. The raw data were processed by mMass v.5.5.0, smoothed by a Gaussian (0.1 $^{m}/_{z}$ window size, 5 repetitions) and calibrated using a quadratic function.

Infrared spectroscopy (IR)

Fourier-transform infrared spectroscopy (FTIR) was performed on a Perkin Elmer Spectrum 100 FT-IR spectrometer equipped with an ATR probe from Graseby Specac LTD. The samples were measured as solids (neat). Signals were labelled according to their intensity s (strong), m (medium) and w (weak). If the signal assignment was possible, the type of vibration ν (valence) or δ (deformation) is additionally listed.

2 Syntheses

2.1 General procedures

Catalyst synthesis

Similar to a literature-known procedure,[3] (thio)urea-azide (1.0 eq.) is dissolved in anhydrous THF or anhydrous diethyl ether in a Schlenk tube with rubber septum under inert atmosphere. Trivalent phosphorous (1.0 eq.) is added in one portion and the mixture is stirred at room temperature (rt.) overnight. Conversion of the azide is followed by TLC, conversion of the trivalent phosphorous is followed by ^{31}P NMR of the reaction mixture dissolved in $CDCl_3$. After full conversion of the azide is affirmed, the target compound is isolated according to one of the subsequent purification procedures.

Catalyst purification A

After full conversion of the azide (as affirmed by TLC), the mixture is concentrated, first under a stream of nitrogen gas, and, second *in vacuo* overnight. The catalyst is isolated from the crude material in its protonated state by reverse column chromatography using a gradient of 0.1 M hydrochloric acid:acetonitrile (from 3:1 to 1:1). Thereafter, the protonated catalyst is dissolved in ethyl acetate and deprotonated with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The organic phase is washed with saturated potassium hydroxide solution (5x), dried over magnesium sulphate, concentrated under reduced pressure at 40 °C and dried *in vacuo* at rt.

Catalyst purification B

After full conversion of the azide (as affirmed by TLC), the mixture is concentrated, first under a stream of nitrogen gas, and, second *in vacuo* overnight. The solid remains are suspended in a 1:1 solvent mixture of anhydrous diethyl ether and *n*-pentane (or *n*-heptane). After ultrasonication for 30–60 min, the solid remains are isolated by decanting the supernatant liquid, washing with a small amount of the same solvent mixture and drying *in vacuo* at rt. overnight. The purification procedure (by ultrasonication) is repeated once, after which the target compound is obtained.

Polymerisation

Inside a glovebox, catalyst (1.0 eq.), optionally a co-catalyst (1.0 eq.) and PA (1.0 eq.) were filled into a 8 mL crimp-neck vial equipped with a magnetic stirring bar. BA solution in toluene (1.0 eq. in 0.33 mL) were added and the mixture was stirred until the solids were fully dissolved (1–10 min). The remaining PA (0.103 g, 0.69 mmol, 99.0 eq.) and epoxide (500.0 eq.) were added subsequently, the vial was closed and transferred out of the glovebox into a pre-heated oil bath. After the specified time (c.f. table SI–1, SI–2 and SI–3), the vial was removed from the oil bath and an aliquot was taken immediately via syringe. This aliquot was injected into $CDCl_3$ and measured by ^{1}H NMR to determine the consumption of PA monomer and the ester-to-ether bond ratio (chemo-selectvity). At rt., the vial was opened and the volatiles removed under a stream of nitrogen overnight. On the following day, the remains were dissolved in 1 %(n/n) acetic acid in CH_2Cl_2 and precipitated in methanol. The precipitate was collected and dried, first under a stream of nitrogen, and, second *in vacuo*. The polymerisation results are listed in table SI–1.

2.2 Polymerisations conducted and results

Table SI–1: Influence of the catalyst: The polymerisations were conducted at 90 °C for 24 h with a ratio of 1 / 1 / 100 / 500 (catalyst / BA / PA / epoxide) in toluene (0.33 mL).

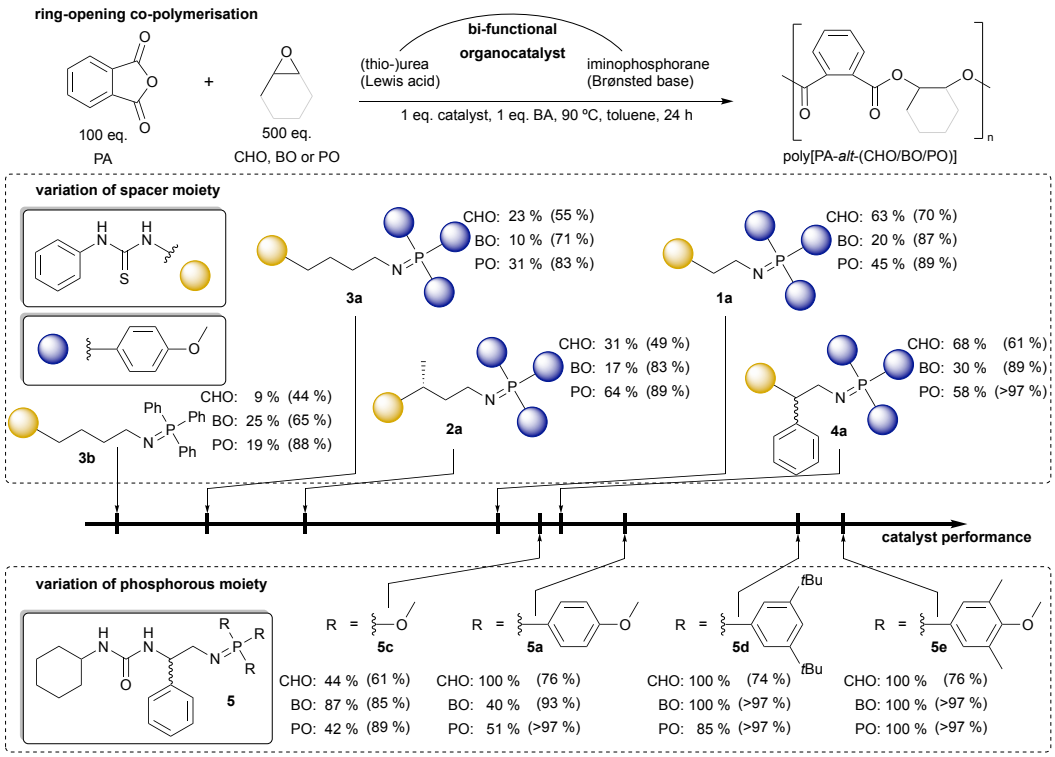
entry	catalyst			conv.[a]	ester[b]	$\overline{M_n}$[c]	deconvoluted SEC[d]	
	#: (thio)urea	spacer	phoshpine	[%(n/n)]	[%(n/n)]	[kg/mol]	[kg/mol]	[kg/mol]
epoxide = CHO								
01	**1a**: Ph-C(S)	C_2(H)	$P(C_6H_7O)_3$	63	70	3.6 (1.4)	3.5 (1.1)	6.8(1.1)
02	**2a**: Ph-C(S)	C_3(Me)	$P(C_6H_7O)_3$	31	49	2.3 (1.3)	2.7 (1.1)	4.3(1.1)
03	**3a**: Ph-C(S)	C_4(H)	$P(C_6H_7O)_3$	23	55	1.1 (1.2)	—	—
04	**3b**: Ph-C(S)	C_4(H)	$P(C_6H_5)_3$	9	44	0.6 (1.7)	—	—
05	**4a**: Ph-C(S)	C_2(Ph)	$P(C_6H_7O)_3$	68	61	3.3 (1.2)	3.4 (1.1)	6.2(1.1)
06	**5a**: Cy-C(O)	C_2(Ph)	$P(C_6H_7O)_3$	100	76	5.3 (1.3)	3.9 (1.1)	7.8(1.1)
07	**5c**: Cy-C(O)	C_2(Ph)	$P(CH_3O)_3$	44	61	2.6 (1.3)	2.1 (1.1)	4.2(1.2)
08	**5d**: Cy-C(O)	C_2(Ph)	$P(C_{14}H_{21})_3$	100	74	4.3 (1.3)	3.3 (1.1)	6.9(1.0)
09	**5e**: Cy-C(O)	C_2(Ph)	$P(C_9H_{11}O)_3$	100	76	4.0 (1.3)	3.0 (1.1)	6.2(1.1)
epoxide = BO								
10	**1a**: Ph-C(S)	C_2(H)	$P(C_6H_7O)_3$	20	87	0.9 (1.2)	—	—
11	**2a**: Ph-C(S)	C_3(Me)	$P(C_6H_7O)_3$	17	83	0.6 (1.9)	—	—
12	**3a**: Ph-C(S)	C_4(H)	$P(C_6H_7O)_3$	10	71	0.6 (1.8)	—	—
13	**3b**: Ph-C(S)	C_4(H)	$P(C_6H_5)_3$	25	65	0.4 (1.5)	—	—
14	**4a**: Ph-C(S)	C_2(Ph)	$P(C_6H_7O)_3$	30	89	1.3 (1.6)	1.4 (1.2)	4.0(1.1)
15	**5a**: Cy-C(O)	C_2(Ph)	$P(C_6H_7O)_3$	40	93	2.2 (1.2)	2.2 (1.2)	5.0(1.0)
16	**5c**: Cy-C(O)	C_2(Ph)	$P(CH_3O)_3$	87	85	2.0 (1.7)	3.5 (1.2)	6.9(1.0)
17	**5d**: Cy-C(O)	C_2(Ph)	$P(C_{14}H_{21})_3$	100	>97	4.7 (1.2)	3.6 (1.1)	7.6(1.0)
18	**5e**: Cy-C(O)	C_2(Ph)	$P(C_9H_{11}O)_3$	100	>97	5.6 (1.2)	4.5 (1.1)	9.3(1.0)
epoxide = PO								
19	**1a**: Ph-C(S)	C_2(H)	$P(C_6H_7O)_3$	45	89	1.1 (1.8)	—	—
20	**2a**: Ph-C(S)	C_3(Me)	$P(C_6H_7O)_3$	64	89	3.1 (1.1)	—	—
21	**3a**: Ph-C(S)	C_4(H)	$P(C_6H_7O)_3$	31	83	—	—	—
22	**3b**: Ph-C(S)	C_4(H)	$P(C_6H_5)_3$	19	88	0.9 (1.3)	—	—
23	**4a**: Ph-C(S)	C_2(Ph)	$P(C_6H_7O)_3$	58	>97	2.6 (1.1)	—	—
24	**5a**: Cy-C(O)	C_2(Ph)	$P(C_6H_7O)_3$	51	>97	2.7 (1.2)	—	—
25	**5c**: Cy-C(O)	C_2(Ph)	$P(CH_3O)_3$	42	89	0.9 (1.3)	—	—
26	**5d**: Cy-C(O)	C_2(Ph)	$P(C_{14}H_{21})_3$	85	>97	1.5 (1.9)	1.0 (1.1)	2.5(1.6)
27	**5e**: Cy-C(O)	C_2(Ph)	$P(C_9H_{11}O)_3$	100	>97	4.7 (1.3)	3.4 (1.1)	7.2(1.0)

[a] Conversion of monomeric PA into PA units:
PA monomer (2H @ 8.1 ppm) *vs.* ester [CHO unit (2H @ 5.2 ppm), BO unit (1H @ 5.5 ppm), PO unit (1H @ 5.4 ppm)].

[b] Ester/ether-ratio of the polymer: ester [CHO unit (2H @ 5.2 ppm), BO unit (1H @ 5.5 ppm), PO unit (1H @ 5.4 ppm)] *vs.* ether [CHO unit (2H @ 3.6 ppm), BO unit (1H @ 3.6 ppm), PO unit (1H @ 3.7 ppm)].

[c] Measured by SEC, dispersity $Đ$ in brackets.

[d] deconvolution results (using 2 Gaussians) of the originally bimodal SEC trace (dispersity $Đ$ in brackets).



Scheme SI–1: Summary of the screening results presented in table SI–1: The catalysts are rated based on their catalytic activity [conversion of PA in %(n/n)] and chemo-selectivity [ratio of ester linkages in %(n/n); values in brackets] in the ROAC of PA/CHO, PA/BO and PA/PO after 24 h at 90 °C. Their performances are illustratively depicted on an axis. A shorter spacer length (**1a**>**2a**>**3a**), higher solubility (**4a**>**1a**), lower Lewis acidity (**5a**>**4a**), higher Brønsted basicity (**3a**>**3b**) and greater steric demand of the iminophosphorane moiety (**5e**>**5d**>**5a**>**5c**) increase the catalyst performance.

Table SI–2: Influence of polymerisation conditions: The polymerisations of PA and CHO were conducted at different temperatures, with different monomer ratios or with different catalysts at 90 °C in toluene (0.33 mL). Additional aliquots were taken throughout the polymerisation to follow the conversion of PA and the ester/ether-ratio of the polymer.

entry	polymerisation conditions	t[a] [h]	conv.[b] [%(n/n)]	ester[c] [%(n/n)]	$\overline{M_n}$[d] [kg/mol]	deconvoluted SEC[e] [kg/mol]	
reference polymerisation [feed ratio of 1 / 1 / 100 / 500 (cat. **5e** / BA / PA / CHO); T = 90 °C]							
01-1		6	17	92	—	—	—
01-2		21	100	75	4.4 (1.2)	3.4 (1.1)	6.5(1.1)
variation of the polymerisation temperature [feed ratio of 1 / 1 / 100 / 500 (cat. **5e** / BA / PA / CHO)]							
02-1	60 °C	24	10	87	—	—	—
02-2		48	38	82	—	—	—
02-3		72	79	76	—	—	—
02-4		91	100	77	5.0 (1.3)	4.3 (1.1)	8.8(1.1)
03-1	75 °C	24	33	75	—	—	—
03-2		48	100	74	5.5 (1.3)	4.5 (1.1)	9.2(1.1)
04-1	120 °C	2	10	60	—	—	—
04-2		3.45	36	75	—	—	—
04-3		6.25	78	79	—	—	—
04-4		8	93	83	5.2 (1.3)	4.3 (1.1)	9.2(1.1)
04-5		32	100	83	5.8 (1.3)	4.5 (1.1)	9.8(1.1)
04-6		56	100	78	5.6 (1.4)	4.5 (1.1)	9.8(1.1)
05-1	150 °C	2	67	78	—	—	—
05-2		3.45	100	81	6.8 (1.3)	5.1 (1.1)	11.2(1.1)
variation of the PA/CHO-ratio in the feed [feed ratio of 1 / 1 / 100 (cat. **5e** / BA / PA); T = 90 °C]							
06-1	100 / 250 (PA / CHO)	6	10	76	—	—	—
06-2		21	61	83	—	—	—
06-3		45	100	79	4.1 (1.3)	3.1 (1.1)	6.4(1.1)
07-1	100 / 125 (PA / CHO)	6	7	66	—	—	—
07-2		21	38	85	—	—	—
07-3		45	81	85	—	—	—
07-4		66	100	81	3.0 (1.3)	2.6 (1.1)	5.0(1.1)
variation of the catalyst [feed ratio of 100 / 500 (PA / CHO); T = 90 °C]							
08-1	1.0 eq. urea **6**	6	6	44	—	—	—
08-2		21	23	60	—	—	—
08-3		48	69	78	1.9 (1.5)	—	—
09-1	1.0 eq. base **7**	6	5	46	—	—	—
09-2		21	12	53	—	—	—
09-3		48	47	53	1.6 (1.3)	—	—
10-1	1.0 eq. base **7** | 1.0 eq. urea **6**	6	17	70	—	—	—
10-2		21	71	79	—	—	—
10-3		26	92	81	3.2 (1.3)	2.9 (1.0)	5.0(1.1)
11-1	1.0 eq. cat. **5e** | 1.5 eq. urea **6**	6	26	76	—	—	—
11-2		21	100	78	4.0 (1.2)	3.0 (1.1)	5.8(1.1)
12-1	1.0 eq. cat. **5e** | 1.0 eq. base **7**	6	26	76	—	—	—
12-2		21	100	74	3.8 (1.3)	3.0 (1.1)	5.7(1.1)
13	1.0 eq. cat. **29a** | 1.0 eq. HCl	112	0	—	—	—	—
14	1.0 eq. cat. **5e** | 1.0 eq. PPNCl	2	100	>97	6.5 (1.6)	—	—

[a] Polymerisation time.

[b] Conversion of monomeric PA into PA units: PA monomer (2H @ 8.1 ppm) *vs.* ester [CHO unit (2H @ 5.2 ppm)].

[c] Ester/ether-ratio of the polymer: ester [CHO unit (2H @ 5.2 ppm)] *vs.* ether [CHO unit (2H @ 3.6 ppm)].

[d] Measured by SEC, dispersity $Đ$ in brackets.

[e] deconvolution results (using 2 Gaussians) of the originally bimodal SEC trace (dispersity $Đ$ in brackets).

Table SI–3: Influence of the feed ratio: The polymerisations of PA and CHO were conducted with different ratios of monomers, catalyst **5e** and initiator (BA at 150 °C in toluene (0.33 mL). Additional aliquots were taken throughout the polymerisation to follow the conversion of PA and the ester/ether-ratio of the polymer.

entry	feed ratio cat. **5e** / BA / PA / CHO	t[a] [h]	conv.[b] [%(n/n)]	ester[c] [%(n/n)]	$TOF_{avg.}$[d] [1/h]	$TOF_{inc.}$[e] [1/h]	$\overline{M_n}$[f] [kg/mol]
01-1	1 / 1 / 100 / 500	0.25	4	—	14.5	—	—
01-2		0.5	4	—	7.7	7.7	—
01-3		1	9	62	7.5	7.2	—
01-4		2	31	64	13.3	19.2	1.4 (1.2)
01-5		4	93	68	20.2	27.0	2.4 (1.3)
01-6		6	100	64	14.5	3.1	2.5 (1.3)
02-1	0.5 / 1 / 100 / 500	0.25	1	—	5.9	—	—
02-2		0.5	2	—	5.9	6.0	—
02-3		1	4	63	5.8	5.7	—
02-4		2	10	68	8.1	10.4	1.1 (1.2)
02-5		4	42	52	16.9	25.7	1.4 (1.2)
02-6		6	95	57	25.9	43.9	2.1 (1.3)
03-1	0.25 / 1 / 100 / 500	0.25	6	—	5.9	—	—
03-2		0.5	7	—	9.9	10.4	—
03-3		1	8	59	6.9	3.9	—
03-4		2	12	45	8.9	10.4	1.0 (1.2)
03-5		4	26	37	13.5	25.7	1.1 (1.2)
03-6		6	53	35	21.1	36.3	1.4 (1.2)
04-1	1 / 0 / 100 / 500	0.25	3	—	9.0	—	—
04-2		0.5	4	—	6.4	3.8	—
04-3		1	8	66	6.6	6.9	—
04-4		2	25	68	11.0	15.3	1.3 (1.2)
04-5		4	90	67	19.9	28.7	2.3 (1.3)
04-6		6	100	66	14.8	4.5	2.6 (1.3)

Table SI–3 continues on the following page.

[a] Polymerisation time.

[b] Conversion of monomeric PA into PA units: PA monomer (2H @ 8.1 ppm) *vs.* ester [CHO unit (2H @ 5.2 ppm)].

[c] Ester/ether-ratio of the polymer: ester [CHO unit (2H @ 5.2 ppm)] *vs.* ether [CHO unit (2H @ 3.6 ppm)].

[d] Average turnover frequency (TOF) derived from the conversion of PA with respect to t = 0 h.

[e] Incremental TOF derived from the conversion of PA with respect to the previous time point.

[f] Measured by SEC, dispersity *Đ* in brackets.

Table SI–3: Continuation of table SI–3—Influence of the feed ratio: The polymerisations of PA and CHO were conducted with different ratios of monomers, catalyst **5e** and initiator (BA at 150 °C in toluene (0.33 mL). Additional aliquots were taken throughout the polymerisation to follow the conversion of PA and the ester/ether-ratio of the polymer.

entry	feed ratio cat. **5e** / BA / PA / CHO	t[a] [h]	conv.[b] [%(n/n)]	ester[c] [%(n/n)]	$TOF_{avg.}$[d] [1/h]	$TOF_{inc.}$[e] [1/h]	$\overline{M_n}$[f] [kg/mol]
05-1	1 / 1 / 100 / 250	0.25	2	—	6.2	—	—
05-2		0.5	3	—	5.5	4.9	—
05-3		1	7	48	5.8	6.1	—
05-4		2	15	65	6.8	7.9	1.0 (1.2)
05-5		4	51	69	11.3	15.7	1.1 (1.3)
05-6		6	93	71	13.8	18.8	1.4 (1.2)
06-1	1 / 1 / 100 / 125	0.25	1	—	2.3	—	—
06-2		0.5	2	—	2.9	3.5	—
06-3		1	4	58	5.8	4.8	—
06-4		amount of aliquot too little for analysis					
06-5		4	24	62	5.4	6.0	1.1 (1.2)
06-6		6	44	59	6.5	8.7	1.0 (1.2)
07-1	1 / 1 / 50 / 500	0.25	4	—	6.6	—	—
07-2		0.5	7	—	6.1	5.6	—
07-3		1	14	71	6.1	6.1	—
07-4		2	34	67	7.2	8.3	1.1 (1.2)
07-5		4	74	59	7.8	8.5	1.3 (1.2)
07-6		6	96	55	6.8	4.7	1.3 (1.3)
08-1	1 / 1 / 200 / 500	amount of aliquot too little for analysis					
08-2		0.5	3	—	10.3	—	—
08-3		1	6	68	10.4	10.4	—
08-4		2	15	63	14.0	17.7	1.4 (1.2)
08-5		4	79	68	36.3	58.6	3.3 (1.4)
08-6		6	100	71	30.8	19.8	4.4 (1.3)

[a] Polymerisation time.

[b] Conversion of monomeric PA into PA units: PA monomer (2H @ 8.1 ppm) *vs.* ester [CHO unit (2H @ 5.2 ppm)].

[c] Ester/ether-ratio of the polymer: ester [CHO unit (2H @ 5.2 ppm)] *vs.* ether [CHO unit (2H @ 3.6 ppm)].

[d] Average TOF derived from the conversion of PA with respect to t = 0 h.

[e] Incremental TOF derived from the conversion of PA with respect to the previous time point.

[f] Measured by SEC, dispersity $Đ$ in brackets.

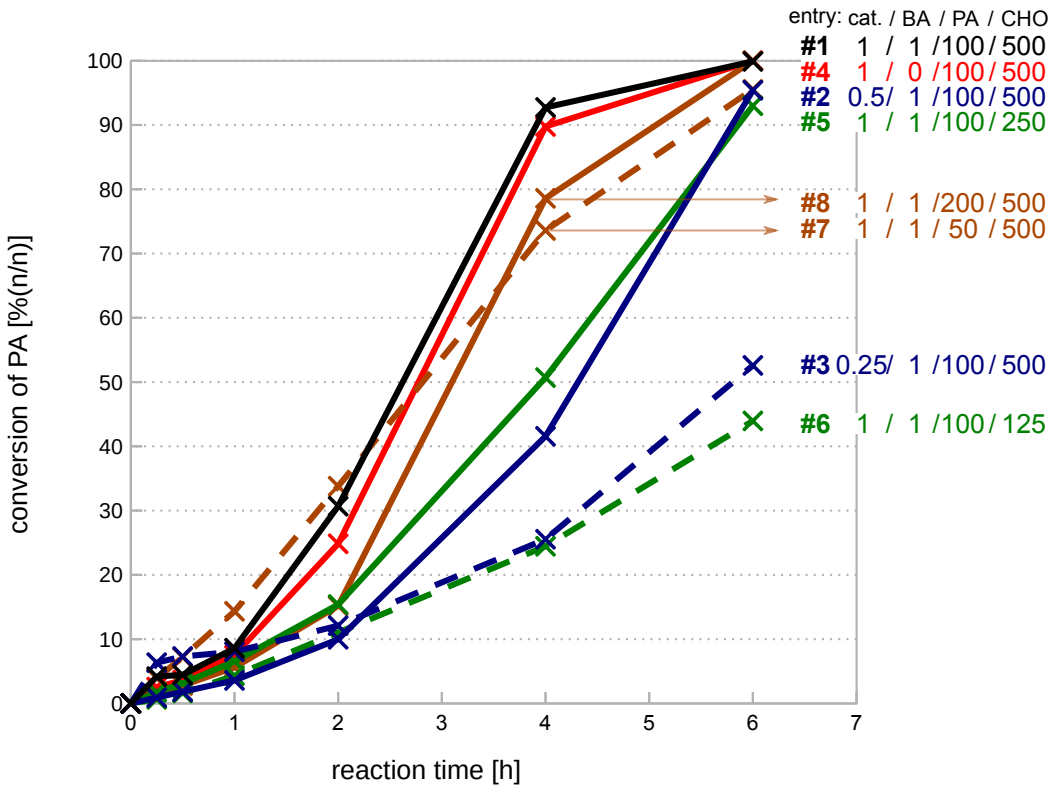


Figure SI–1: Relative conversion of PA over time (graphical representation of the data in table SI–3): Compared to the polymerisation rate of PA [#1: 1 / 1 / 100 / 500 (cat. / BA / PA / CHO), black line] a reduction in polymerisation rate is obtained for lower feed ratios of catalyst **5a** (#2 and #3, blue lines) and CHO (#5 and #6, green lines). The absence of BA has a negligible effect on the polymerisation rate (#4, red line). BA acts as initiator in the polymerisation, however, as water and impurities of the monomers are also able to initiate the polymerisation, the extra 1 eq. of initiator (that is BA) is negligible. For the sake of completeness, the conversion of PA in dependence of the PA feed ratio is shown (#7 and #8, brown lines), although a direct comparison to the other entries is hampered (change in reference; different ratios of PA). The influence of different PA ratios is better visualized by the time-course of incremental TOF of PA (c.f. figure 2.2). Lines are drawn between consecutive data points to guide the reader's eye.

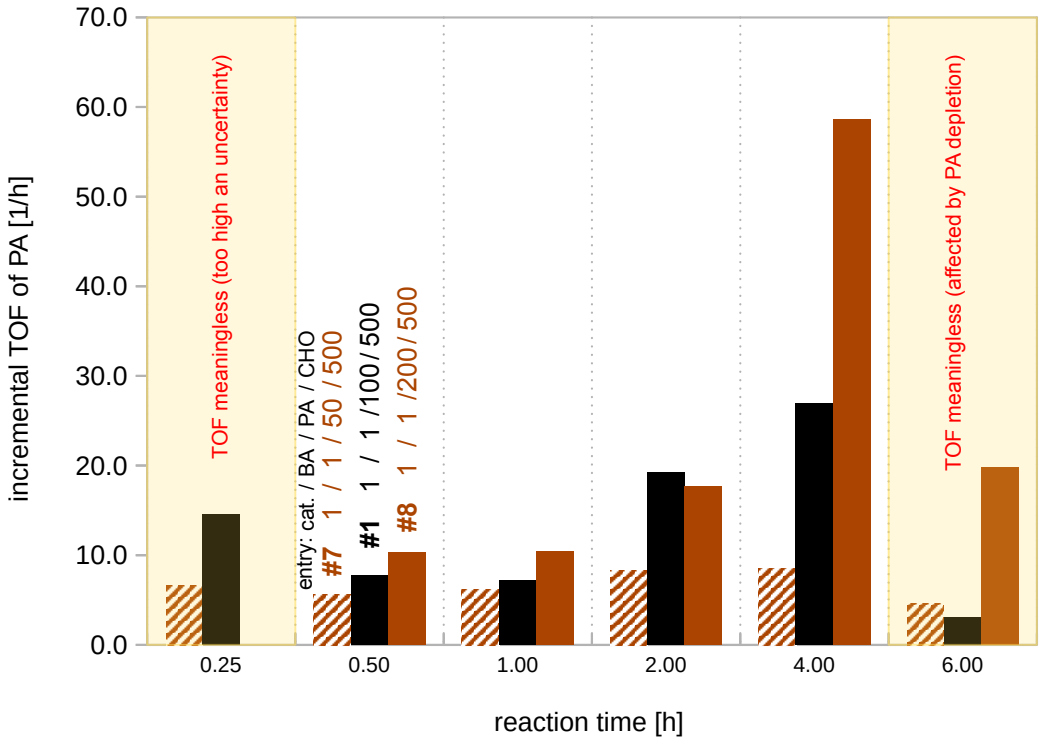
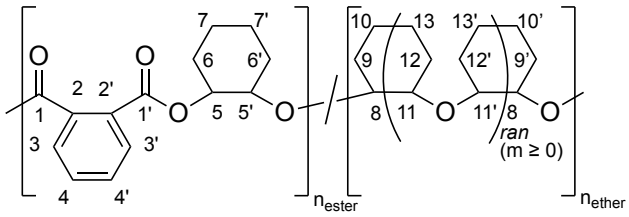


Figure SI–2: Time-course of incremental TOF of PA: The lowest feed ratio of PA (brown striped, #7, 50 eq.) shows a near-steady TOF over time. Higher PA ratios of 100 eq (black, #1) and 200 eq. (brown, #8) lead to an increase in TOF over time. This increase over time is ascribed to an increasing viscosity that accelerates the ROAC.

2.2.1 Poly[(PA-*alt*-CHO)-*ran*-CHO] (table SI–1, entry #9)



Poly[(PA-*alt*-CHO)-*ran*-CHO] (table SI–1, entry #9, 96 mg) was obtained as a white powder after synthesis according to the general procedure (c.f. p. SI–4) from PA (104 mg, 0.70 mmol, 100 eq.) and CHO (0.35 mL, 3.5 mmol, 500 eq.) using catalyst (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**5e**, 4.9 mg, 7.0 mmol, 1.0 eq.) and BA (1.0 eq. in 0.33 mL anhydrous toluene).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.32–1.48 (m, $\underline{2n_{ester}}H^7$)
1.32–1.85 (m, $\underline{2n_{ether}}H^9 + \underline{2n_{ether}}H^{10} + \underline{4m}H^{12} + \underline{4m}H^{13}$)
1.53 (*br.*, $\underline{2n_{ester}}H^6$)
1.77 (*br.*, $\underline{2n_{ester}}H^7$)
1.88 (*br.*, $\underline{2n_{ether}}H^{10}$)
2.09 (*br.*, $\underline{2n_{ether}}H^9$)
2.23 (*br.*, $\underline{2n_{ester}}H^6$)
3.22–3.67 (m, $\underline{2m}H^{11}$)
4.84–5.04 (m, $\underline{2n_{ether}}H^8$)
5.14 (*br.*, $\underline{2n_{ester}}H^5$)
7.41 (*br.*, $\underline{2n_{ester}}H^4$)
7.59 (*br.*, $\underline{2n_{ester}}H^3$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 23.5 (*br.*, $\underline{2n_{ester}}C^7$)
30.1 (*br.*, $\underline{2n_{ester}}C^6$)
74.8 (*br.*, $\underline{2n_{ester}}C^5$)
129.0 (*br.*, $\underline{2n_{ester}}C^3$)
131.2 (*br.*, $\underline{2n_{ester}}C^4$)
132.2 (*br.*, $\underline{2n_{ester}}C^2$)
166.8 (*br.*, $\underline{2n_{ester}}C^1$) ppm.

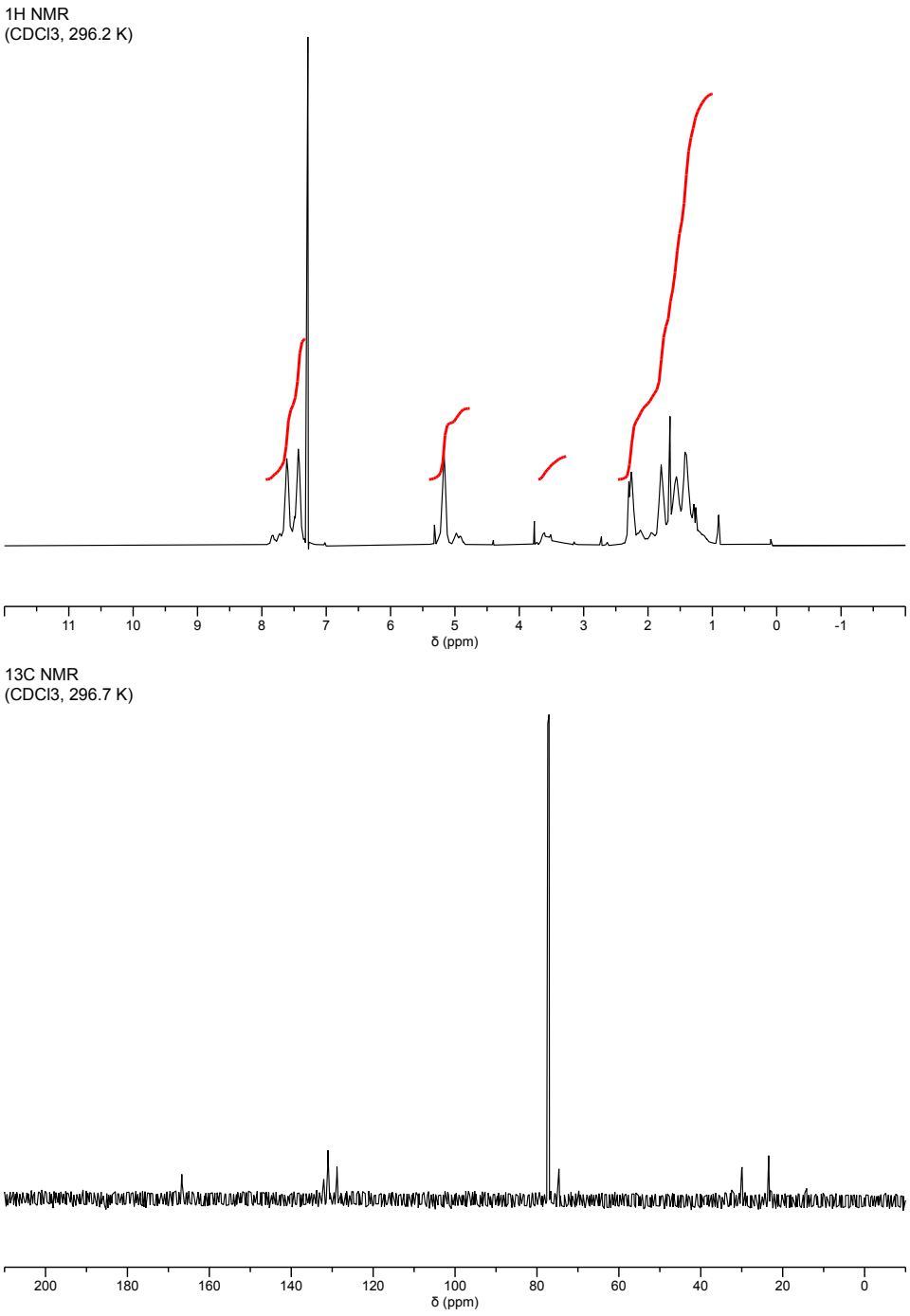


Figure SI–3: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of poly[(PA-*alt*-CHO)--*ran*-CHO] (table SI–1, entry #9).

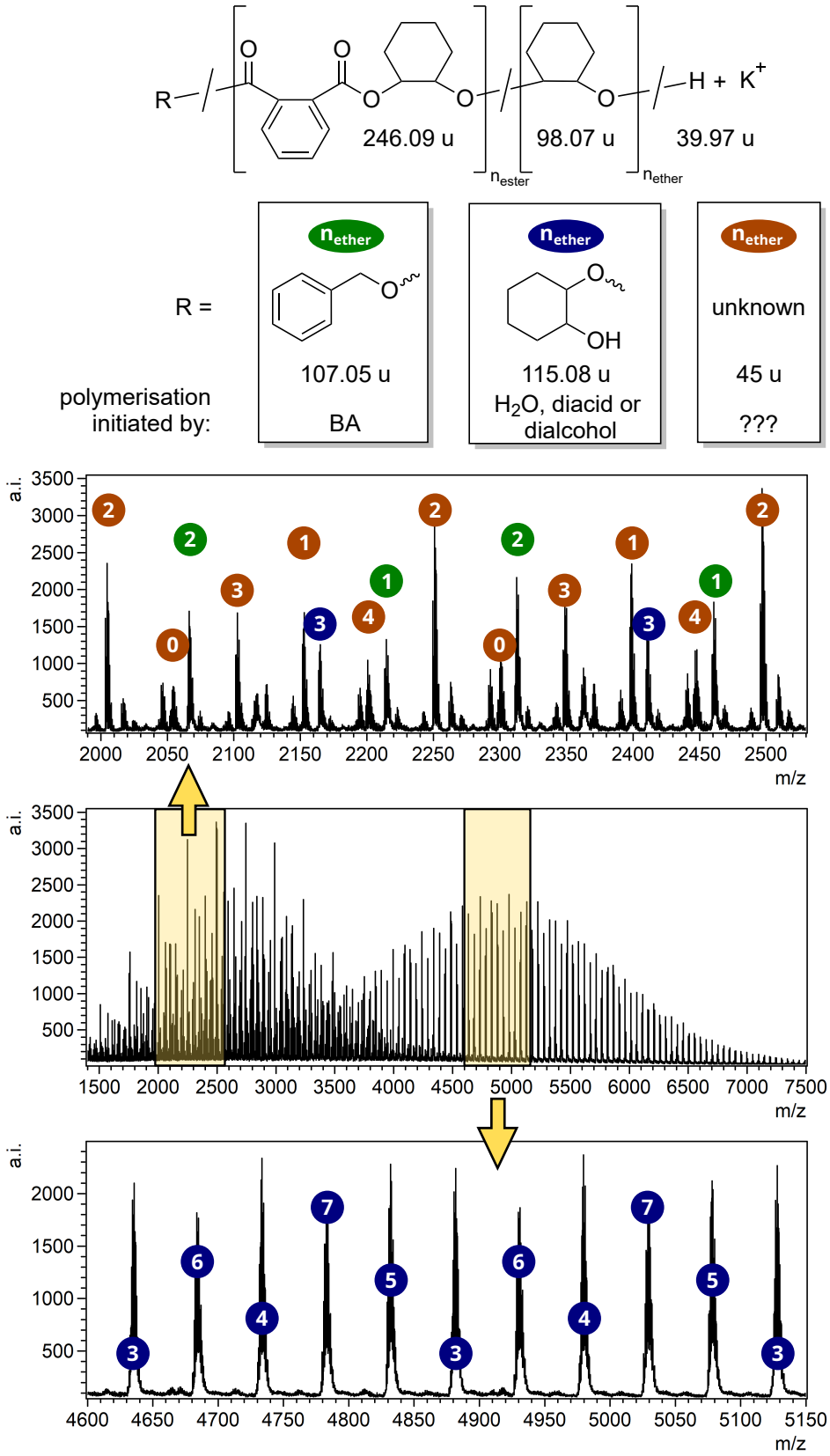


Figure SI–4: MALDI MS data of poly[(PA-*alt*-CHO)-*ran*-CHO]: Three species were observed that originate from different initiating species [BA, water (or diacid / dialcohol either obtained by ring-opening of the monomers with water or present as impurities of the monomers) and an unknown species (45 u). Furthermore, each species gives rise to multiple series as a consequence of ether-bond formation [the number of ether bonds (n_{ether}) is indicated by the number inside the coloured circles].

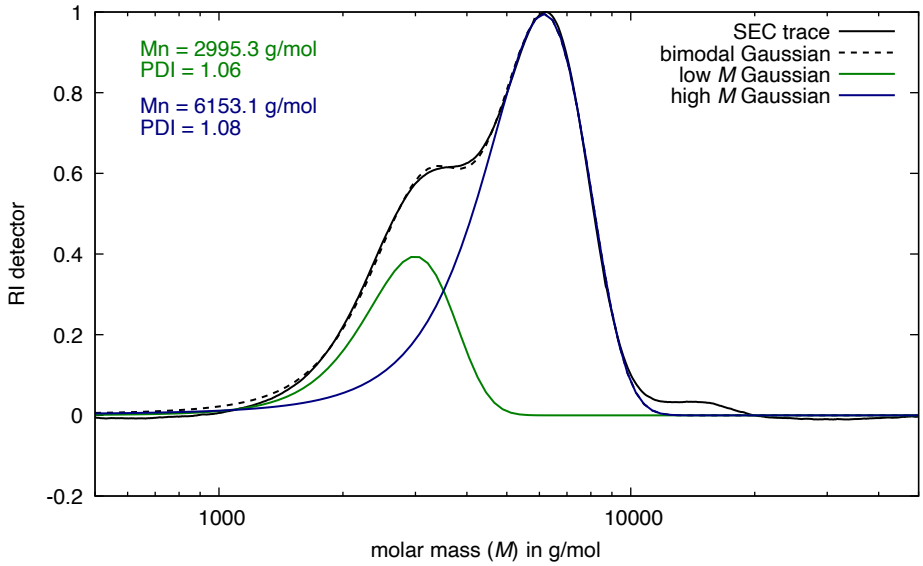
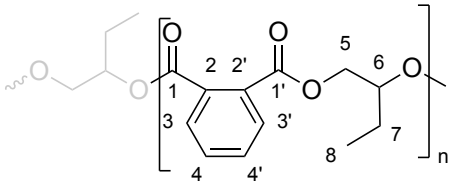
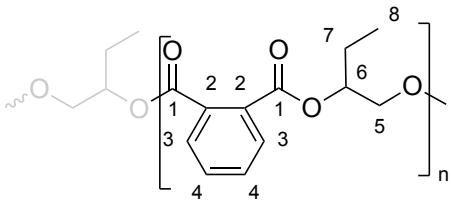


Figure SI–5: SEC data of poly[(PA-*alt*-CHO)-*ran*-CHO]: A bimodal distribution is measured (black solid line) and is deconvoluted using a superposition of 2 Gaussian functions (black dashed line). The individual Gaussian represent the polyester initiated by BA (green line) and water/monomer impurities (blue line).

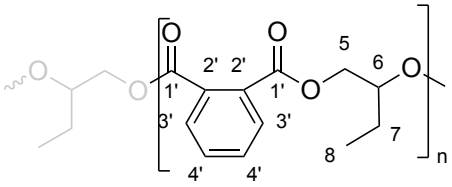
2.2.2 Poly(PA-*alt*-BO) (table SI–1, entry #18)



head-tail (HT)



head-head (HH)



tail-tail (TT)

Poly(PA-*alt*-BO) (table SI–1, entry #18, 79 mg) was obtained as a white foam after synthesis according to the general procedure (c.f. p. SI–4) from PA (104 mg, 0.70 mmol, 100 eq.) and BO (0.30 mL, 3.5 mmol, 500 eq.) using catalyst (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**5e**, 4.9 mg, 7.0 mmol, 1.0 eq.) and BA (1.0 eq. in 0.33 mL anhydrous toluene).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 0.97 (t, $^3J_{HH} = 7.2$ Hz, $\underline{3n}H^8$)
1.75 (*pseudo*-p, $^3J_{HH} = 7.1$ Hz, $\underline{2n}H^7$)
4.35–4.56 (m, $\underline{2n}H^5$)
5.31 (*br.*, $\underline{1n}H^6$)
7.47 (*br.*, $\underline{2n}H^4$)
7.69 (*br.*, $\underline{2n}H^3$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 9.6 (s, $\underline{1n}C^8$)
24.0 (s, $\underline{1n}C^7$)
65.7 (s, $\underline{1n}C^5$)
74.2 (s, $\underline{1n}C^6$)
128.9–129.5 (m, $\underline{2n}C^3$)
131.0–131.5 (m, $\underline{2n}C^4$)
131.6–132.4 (m, $\underline{2n}C^2$)
167.1 (s, $\underline{2n}C^1$) ppm.

the regio-isomer signals seem to overlap and only a singlet was observed for C^2.

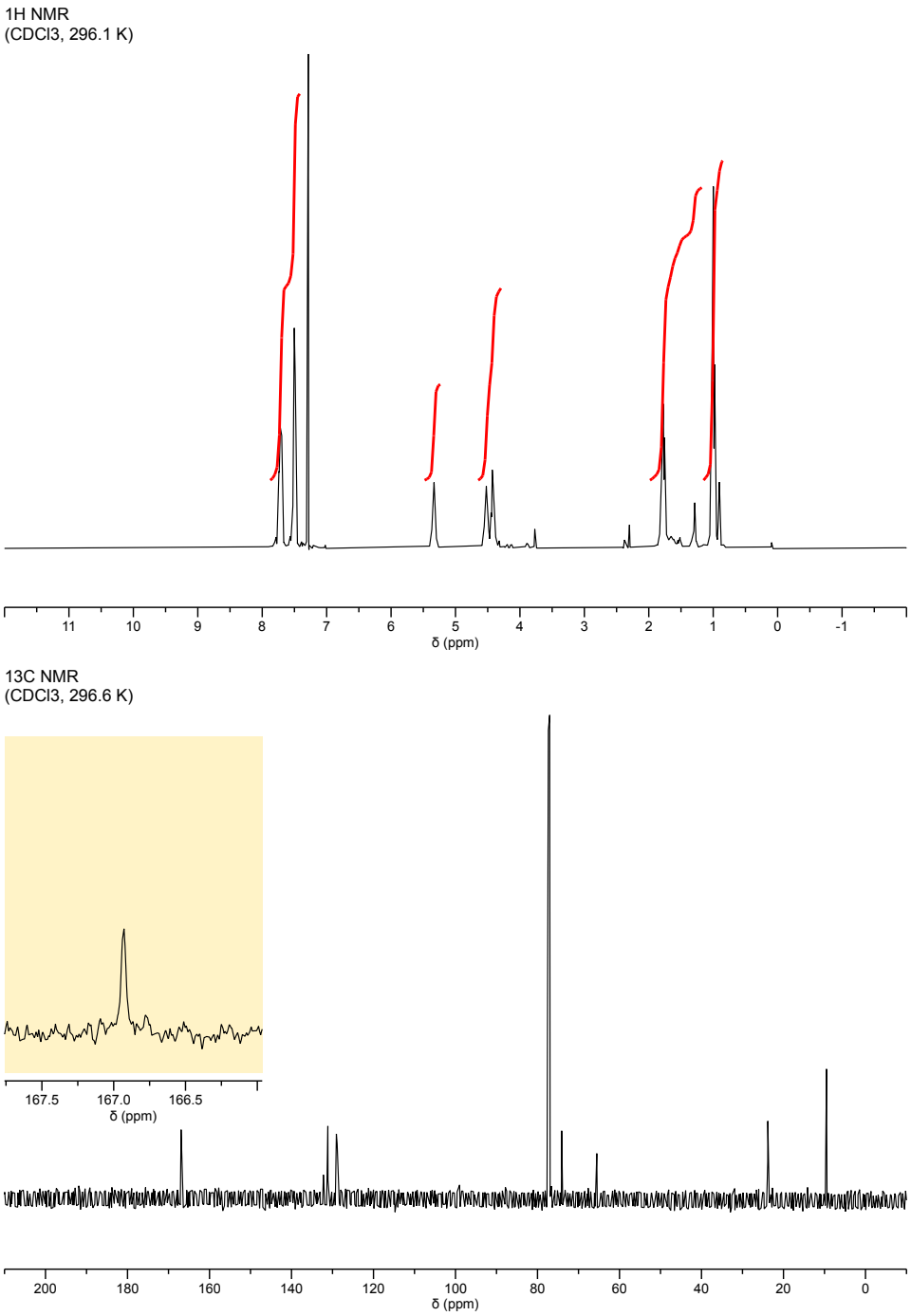


Figure SI–6: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of poly(PA-*alt*-BO) (table SI–1, entry #18).

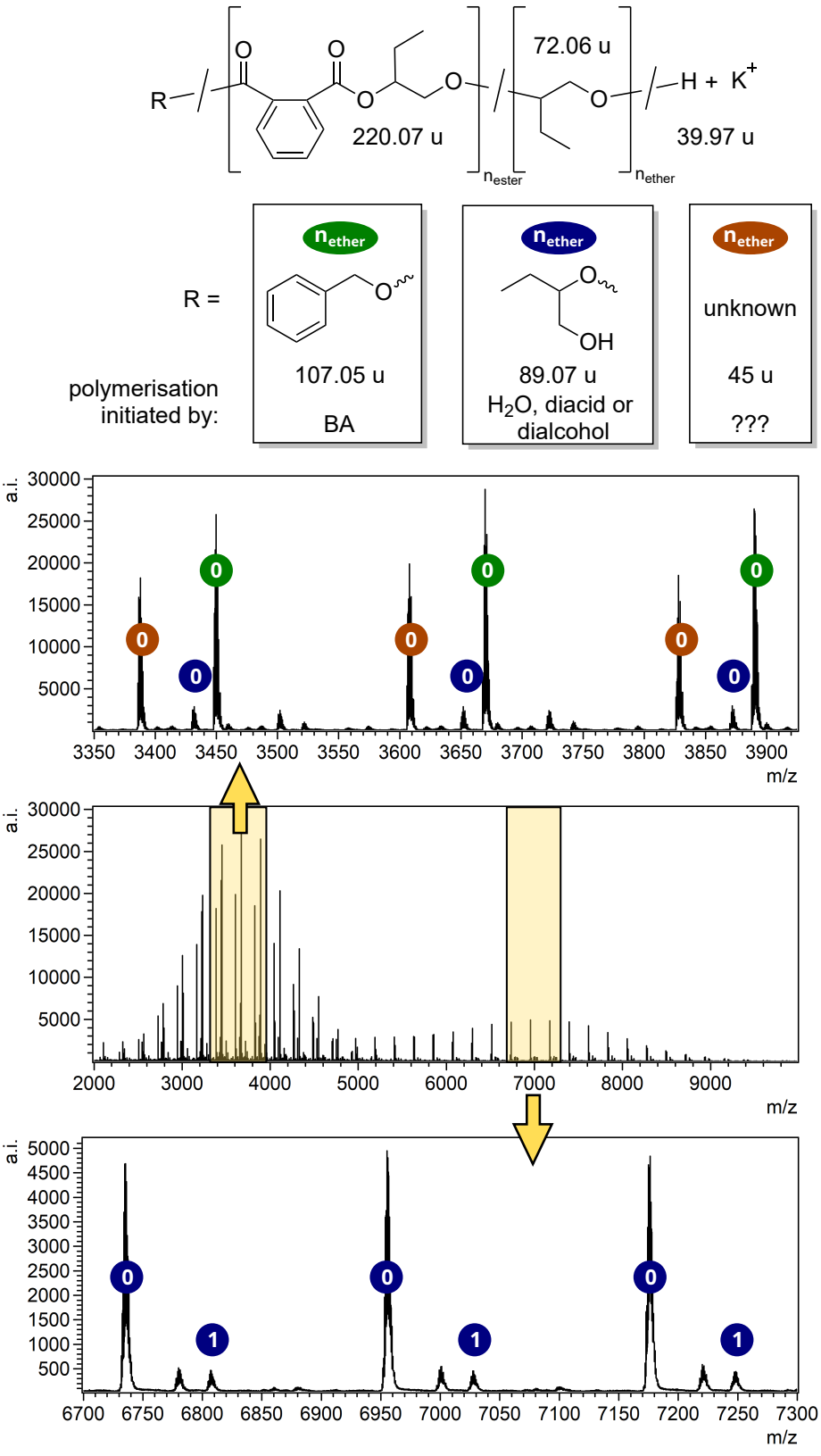


Figure SI–7: MALDI MS data of poly(PA-*alt*-BO): Three species were observed that originate from different initiating species [BA, water (or diacid / dialcohol either obtained by ring-opening of the monomers with water or present as impurities of the monomers) and an unknown species (45 u). The most intense signals belong to the three species without any ether bond (n_{ether} = 0, perfectly alternating polymerisation), however, series with 1 ether bond are also found [the number of ether bonds (n_{ether}) is indicated by the number inside the coloured circles].

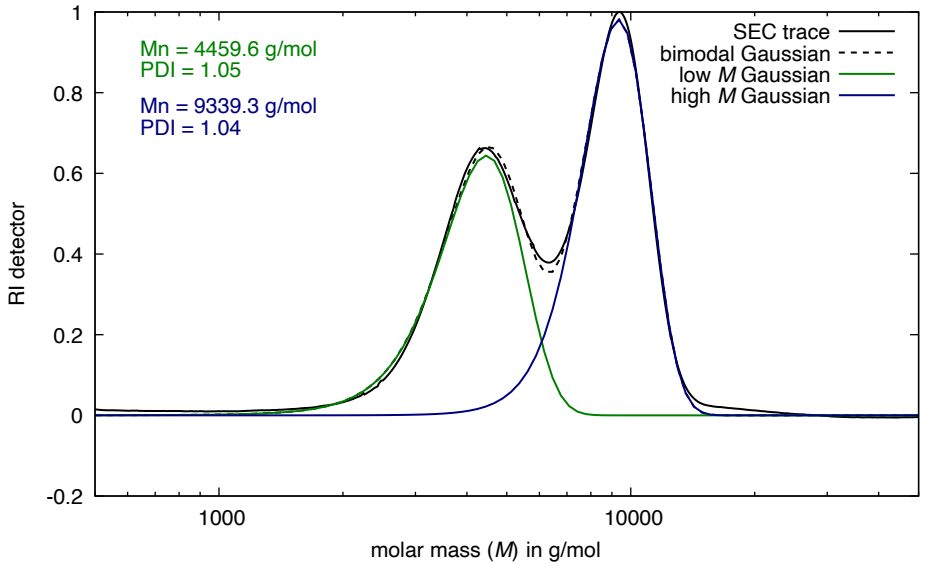
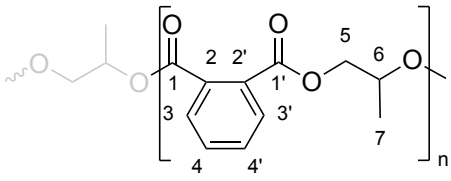
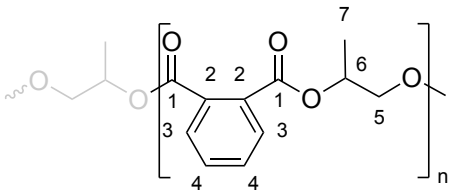


Figure SI–8: SEC data of poly(PA-*alt*-BO): A bimodal distribution is measured (black solid line) and is deconvoluted using a superposition of 2 Gaussian functions (black dashed line). The individual Gaussian represent the polyester initiated by BA (green line) and water/monomer impurities (blue line).

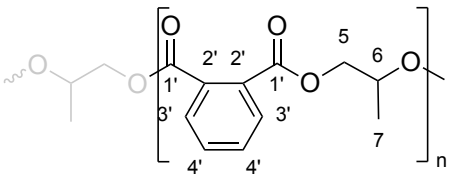
2.2.3 Poly(PA-*alt*-PO) (table SI–1, entry #27)



head-tail (HT)



head-head (HH)



tail-tail (TT)

Poly(PA-*alt*-PO) (table SI–1, entry #27, 78 mg) was obtained as an off-white foam after synthesis according to the general procedure (c.f. p. SI–4) from PA (104 mg, 0.70 mmol, 100 eq.) and PO (0.24 mL, 3.5 mmol, 500 eq.) using catalyst (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**5e**, 4.9 mg, 7.0 mmol, 1.0 eq.) and BA (1.0 eq. in 0.33 mL anhydrous toluene).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.31–1.43 (m, $\underline{3}$nH^7)
4.28–4.49 (m, $\underline{2}$nH^5)
5.41 (*br.*, $\underline{1}$nH^6)
7.48 (*br.*, $\underline{2}$nH^4)
7.69 (*br.*, $\underline{2}$nH^3) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 16.5 (s, $\underline{1}$nC^7)
67.1 (s, $\underline{1}$nC^5)
69.8 (s, $\underline{1}$nC^6)
128.8–129.3 (m, $\underline{2}$nC^3)
131.0–131.5 (m, $\underline{2}$nC^4)
131.5–132.4 (m, $\underline{2}$nC^2)
166.8 (s, 2C^1) $\mapsto$ HH regio-isomer
166.9 (s, 1C^1) $\mapsto$ HT regio-isomer
167.0 (s, 1C^1) $\mapsto$ HT regio-isomer
167.2 (s, 2C^1) ppm. $\mapsto$ TT regio-isomer

assignment of regio-isomer signals of C^1 according to literature data.[4]

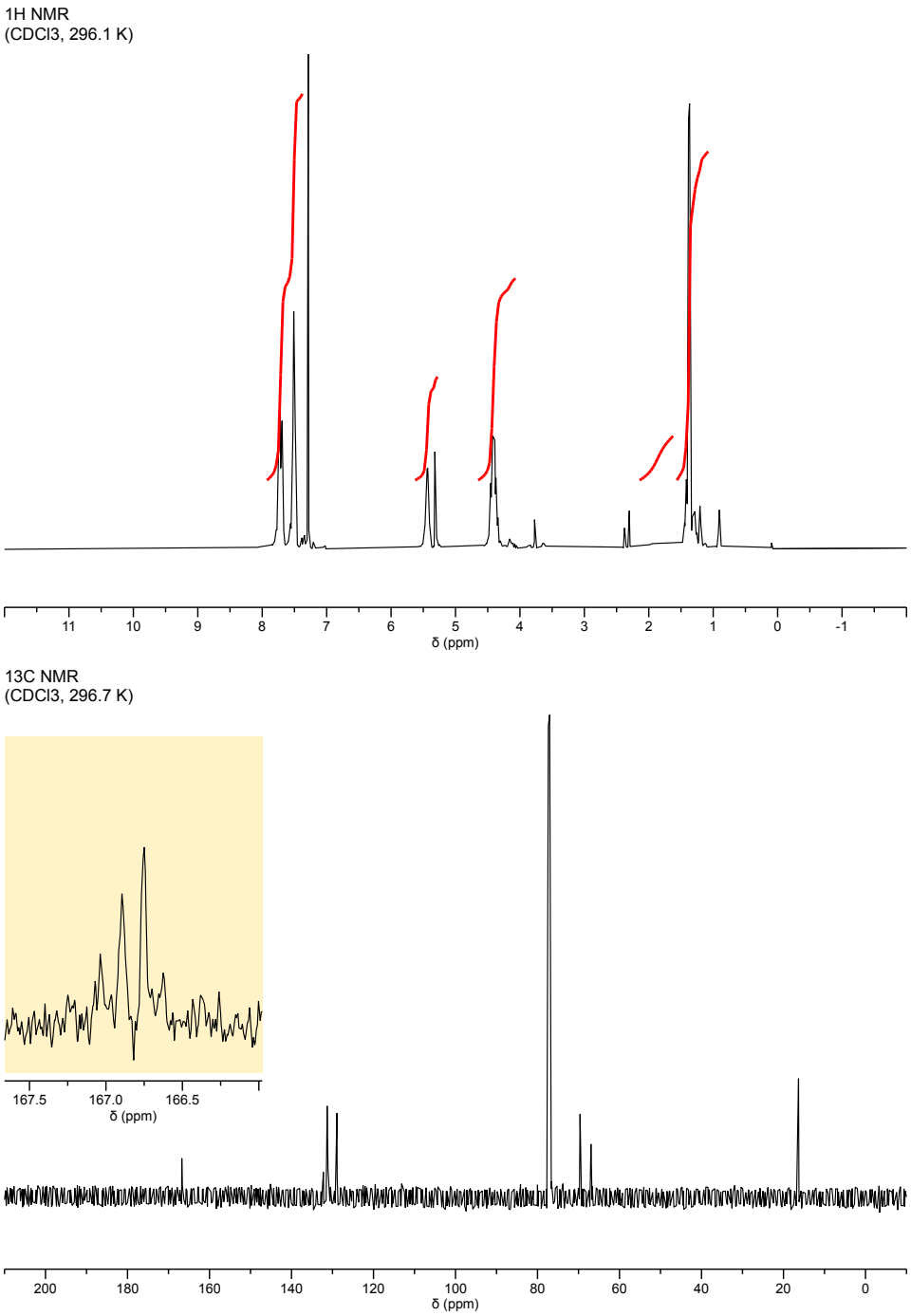


Figure SI–9: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of poly(PA-*alt*-PO) (table SI–1, entry #27).

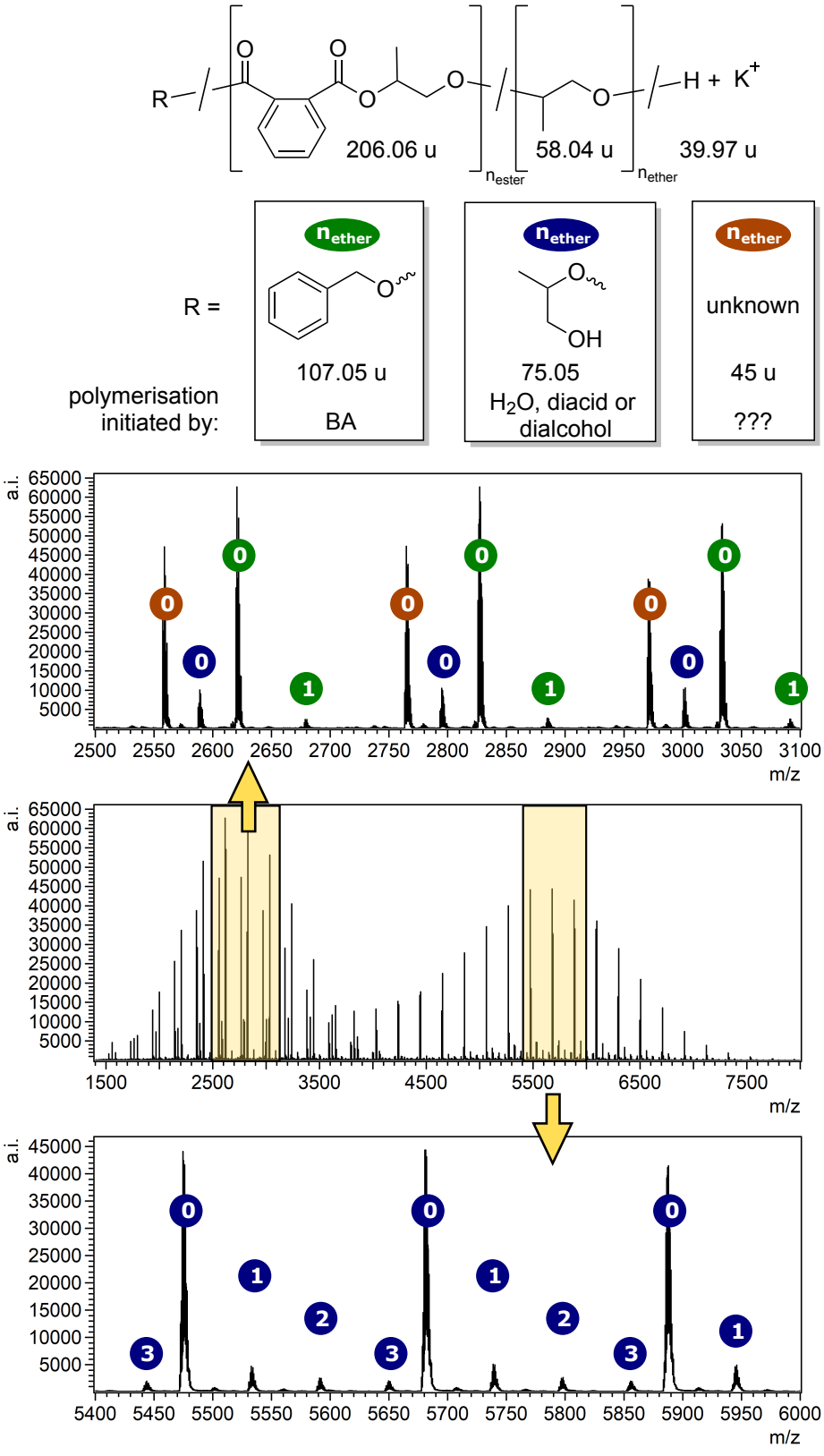


Figure SI–10: MALDI MS data of poly(PA-*alt*-PO): Three species were observed that originate from different initiating species [BA, water (or diacid / dialcohol either obtained by ring-opening of the monomers with water or present as impurities of the monomers) and an unknown species (45 u). The most intense signals belong to the three species without any ether bond (n_{ether} = 0, perfectly alternating polymerisation), however, series with 1 ether bond are also found [the number of ether bonds (n_{ether}) is indicated by the number inside the coloured circles].

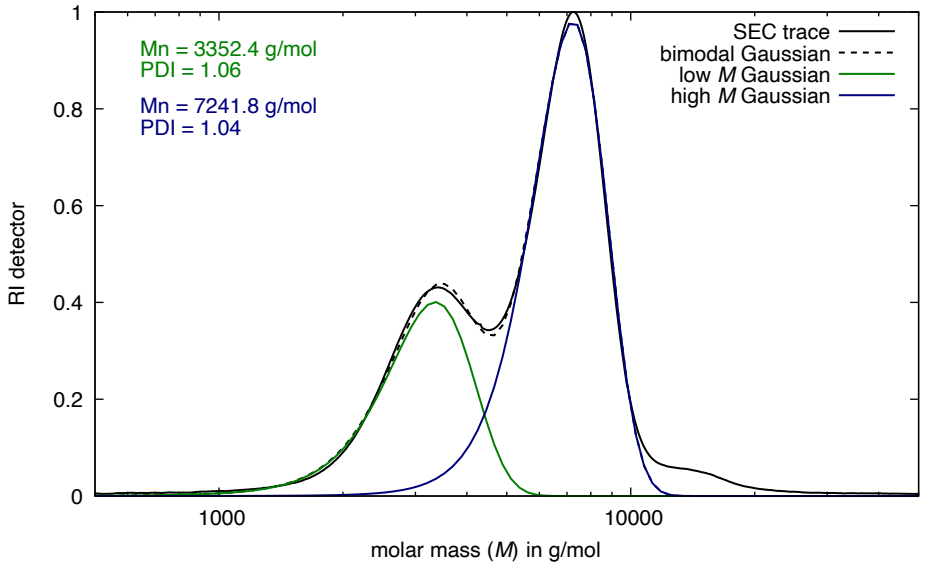
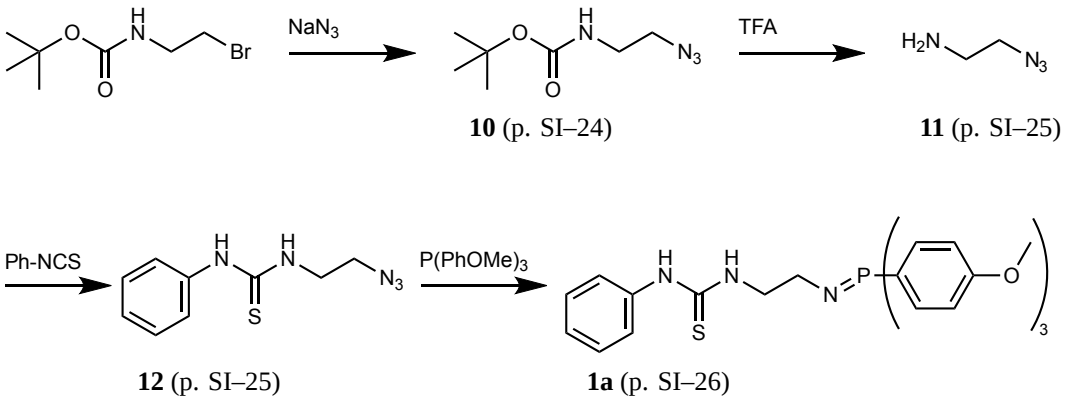


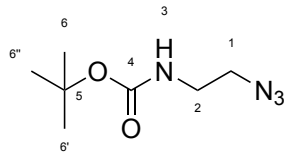
Figure SI–11: SEC data of poly(PA-*alt*-PO): A bimodal distribution is measured (black solid line) and is deconvoluted using a superposition of 2 Gaussian functions (black dashed line). The individual Gaussian represent the polyester initiated by BA (green line) and water/monomer impurities (blue line).

2.3 Bi-functional catalyst with ethyl-spacer (cat. 1a)



Scheme SI–2: 4-step synthesis of bi-functional catalyst **1a**.

2.3.1 Boc-2-aminoethan-1-azide (10)



In a 250 mL Schlenk flask under inert atmosphere at rt., *tert*-butyl (2-bromoethyl)carbamate (8.20 g, ∼60 % purity, 21.5 mmol, 1.0 eq.) was dissolved in dimethylsulfoxide (40 mL). Sodium azide (2.56 g, 39.5 mmol, 1.8 eq.) was added in one portion and the solution was stirred for 20 h. After full conversion of the starting material (as judged by TLC), the organic phase was diluted with diethyl ether (80 mL) and water (80 mL). The organic phase was separated and the aqueous phase was extracted twice using diethyl ether. The combined organic phase was washed with water (2x) and brine (1x), dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. Boc-2-aminoethan-1-azide (**10**, 4.59 g, 22.0 mmol, 61 %) was obtained with 89 %(w/w) purity (impurity is diethyl ether) as colourless liquid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.47 (visible by *p*-anisaldehyde stain and $KMnO_4$ stain).

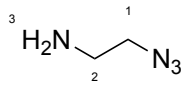
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.44 (s, 9H^6)
3.29 (*pseudo*-q, $^3J_{HH} = 5.7$ Hz, 2H^2)
3.41 (*pseudo*-t, $^3J_{HH} = 5.4$ Hz, 2H^1)
4.83 (*br.*, 1H^3) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 28.4 (s, 3C^6)
40.2 (s, 1C^2)
51.4 (s, 1C^1)
79.9 (s, 1C^5)
155.9 (s, 1C^4) ppm.

2.3.2 2-Aminoethan-1-azide (11)

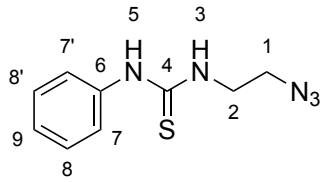


Similar to a literature-known procedure,[5] boc-2-aminoethan-1-azide (**10**, 1.05 g, 5.0 mmol, 1.0 eq.) was dissolved in anhydrous CH_2Cl_2 (3.6 mL) under inert atmosphere in a 25 mL Schlenk tube equipped with a dropping funnel. The solution was cooled down to –78 °C in a dry ice bath before trifluroacetic acid (TFA, 3.8 mL, 50.0 mmol, 10.0 eq.) was slowly added through the dropping funnel. The dry ice bath was removed and the obtained colourless solution was stirred for 2 h at rt., after which full conversion of the starting material (as judged by TLC) was affirmed. Once again, the mixture was cooled down to –78 °C and triethylamine (7.4 mL, 52.5 mmol, 10.5 eq.) was slowly added through the dropping funnel. The solution was allowed to reach rt. within 60 min and used without isolation of the target compound as starting material for the subsequent reaction (c.f. p. SI–25).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by ninhydrine stain).

2.3.3 2-(Ph-thiourea)ethan-1-azide (12)



Similar to a literature-known procedure,[5] phenyl isothiocyanate (0.74 g, 5.5 mmol, 1.1 eq.) dissolved in anhydrous CH_2Cl_2 (3.6 mL) was added to 2-aminoethan-1-azide (**11**, 0.43 g, 5.0 mmol, 1.0 eq.) as obtained from the previous reaction (in solution, c.f. p. SI–25) at rt. under inert atmosphere. After full conversion was affirmed by TLC, the reaction was quenched with water and the target compoundextracted with CH_2Cl_2 (3x). The combined organic phase was washed with brine, dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. The crude product was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (from 9:1, via 7:3 to 5:5). 2-(Ph-thiourea)ethan-1-azide (**12**, 0.85 g, 3.7 mmol, 74 %) was obtained with 96 %(w/w) purity (impurity is ethyl acetate) as light yellow oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.30 (visible by UV light and $KMnO_4$ stain).

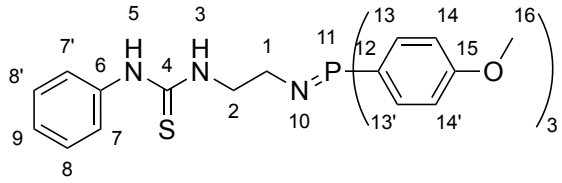
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 3.57–3.65 (m, 2H^1)
3.81 (*pseudo*-q, $^3J_{HH} = 5.6$ Hz, 2H^2)
6.27 (*br.*, 1H^3)
7.23 (d, $^3J_{HH} = 7.4$ Hz, 2H^7)
7.34 (t, $^3J_{HH} = 7.5$ Hz, 1H^9)
7.46 (*pseudo*-t, $^3J_{HH} = 7.8$ Hz, 2H^8)
7.94 (*br.*, 1H^5) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 44.6 (s, 1C^2)
50.6 (s, 1C^1)
125.6 (s, 2C^7)
127.9 (s, 1C^9)
130.5 (s, 2C^8)
135.8 (s, 1C^6)
181.2 (s, 1C^4) ppm.

2.3.4 2-(Ph-thiourea)ethan-1-N=P(*p*-OMe-phenyl)$_3$ (1a)



2-(Ph-thiourea)ethan-1-N=P(*p*-OMe-phenyl)$_3$ (**1a**, 1.41 g, 2.6 mmol, 70 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from 2-(Ph-thiourea)ethan-1-azide (**15**, 0.45 g, 1.5 mmol, 1.0 eq.) and P(*p*-OMe-phenyl)$_3$ (1.30 g, 3.7 mmol, 1.0 eq.) in anhydrous THF (6 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

Two species are observed in the NMR spectra (one of which is labelled with an apostrophe). In case the signals of both species overlap, the overlapped signal is labelled with an asterisks.

signals of H^3 and H^5 were not observed.

$\delta =$ 3.19 (*br.*, $2H^1 + 2H^{1'}$)
3.56 (*br.*, $2H^{2'}$)
3.74 (*br.*, $2H^2$)
3.82 (s, $9H^{16} + 9H^{16'}$)
6.89 (d, $^3J_{HH} = 7.4$ Hz, $6H^{14} + 6H^{14'}$)
6.95–7.24 (m, $2H^7 + 2H^{7'} + 2H^8 + 2H^{8'} + 1H^9 + 1H^{9'}$)
7.30–7.37 (m, $6H^{13}$)
7.38–7.51 (m, $6H^{13'}$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, $CDCl_3$)

signals of C^4, C^6 and $3C^{12}$ were not observed.

$\delta =$ 43.2 (s, $1C^{1'}$)
48.1 (s, $1C^1$)
49.0 (s, $1C^2$)
50.6 (s, $1C^2$)
55.5 (s, $3C^{16*}$)
114.3 (*br.*, $6C^{14*}$)
125.0 (s, $2C^{7*}$ or $2C^{8*}$ or $1C^{9*}$)
128.1 (s, $2C^{7*}$ or $2C^{8*}$ or $1C^{9*}$)
129.9 (s, $2C^{7*}$ or $2C^{8*}$ or $1C^{9*}$)
134.4 (*br.*, $6C^{13*}$)
162.4 (s, $3C^{15*}$) ppm.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, $CDCl_3$)

$\delta =$ 14.2 (*br.*, $1P^{11}$)
16.9 (*br.*, $1P^{11'}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{30}H_{33}N_3O_3PS$): 546.1975 u
found: 546.1969 m/z $[M+H]^+$ (target compound **1a**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3190 (w, N–H, ν)
2959, 2810 (w, C–H, ν)
1592 (s, C=$C_{arom.}$, ν)
1496 (s, C=$C_{arom.}$, ν)
1247 (s, C–N, ν)
1168 (s, C–O_{ether}, ν)
1028, 800, 605 (s, fingerprint, δ) $^1/_{cm}$.

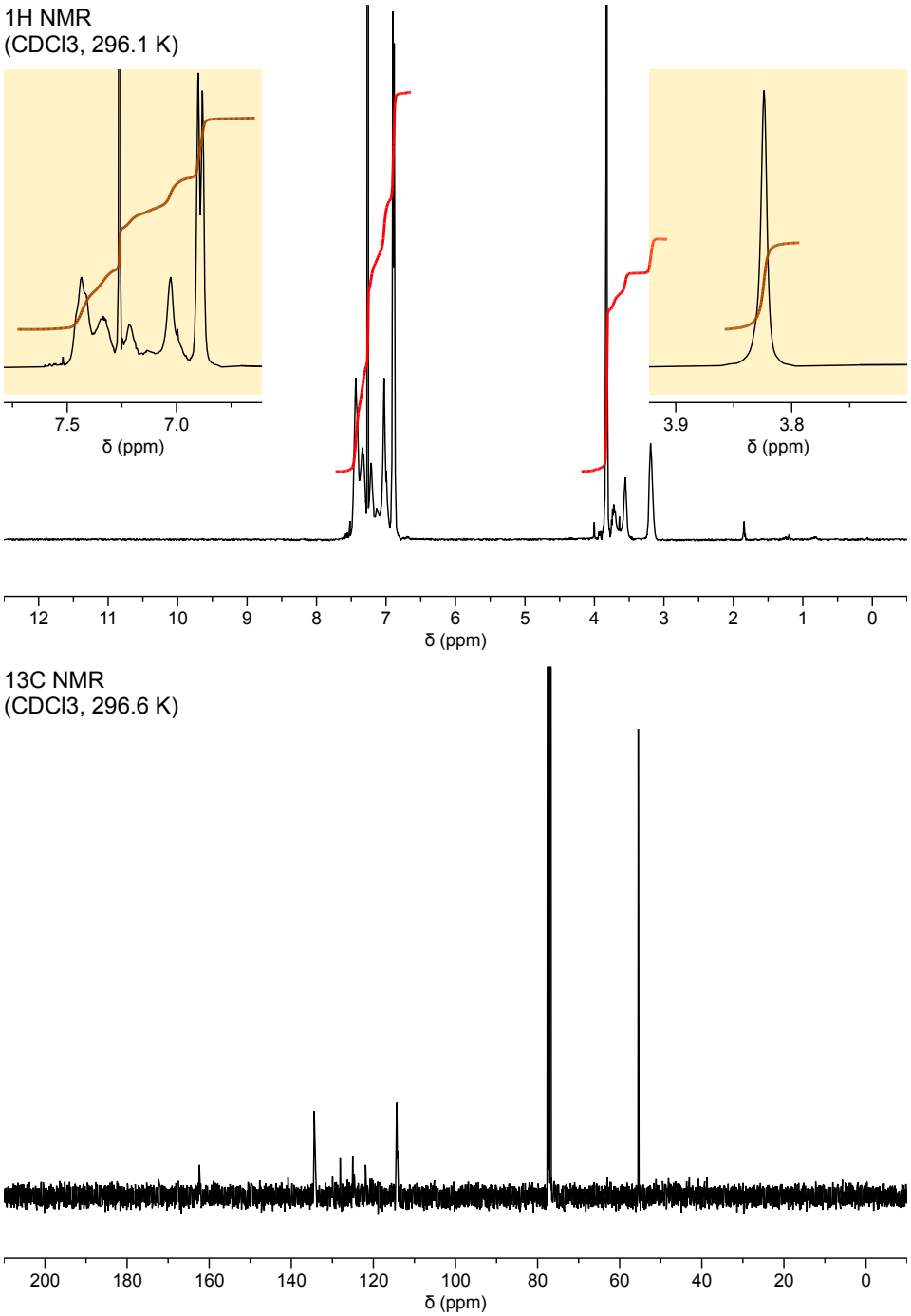
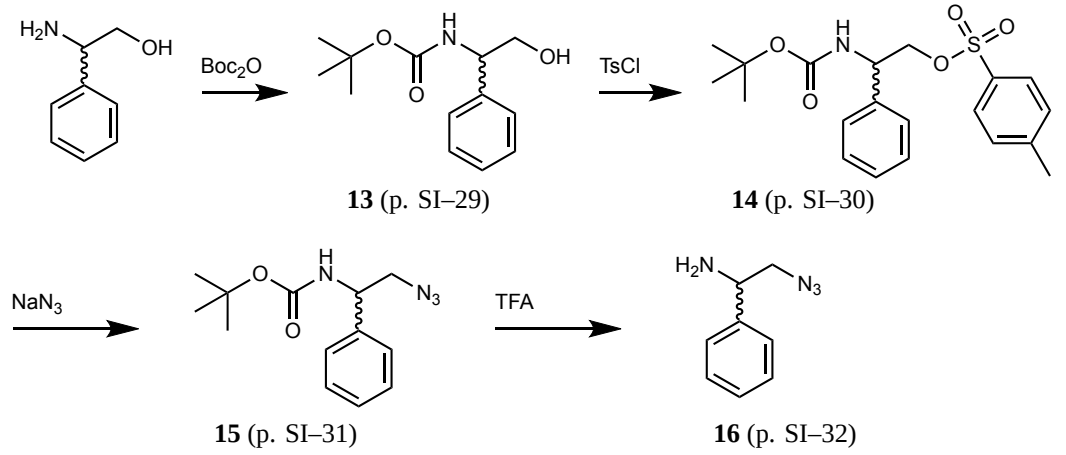
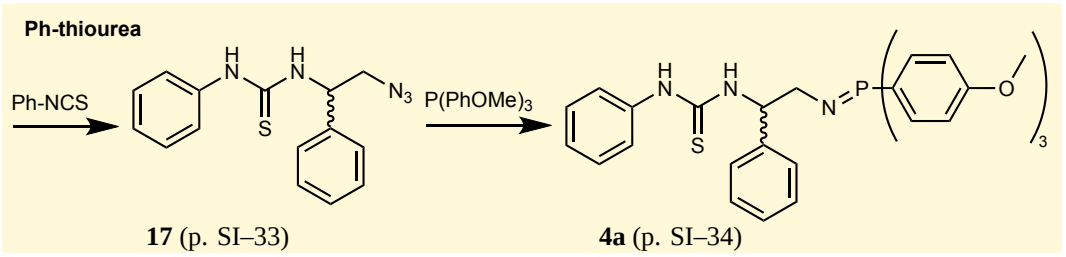
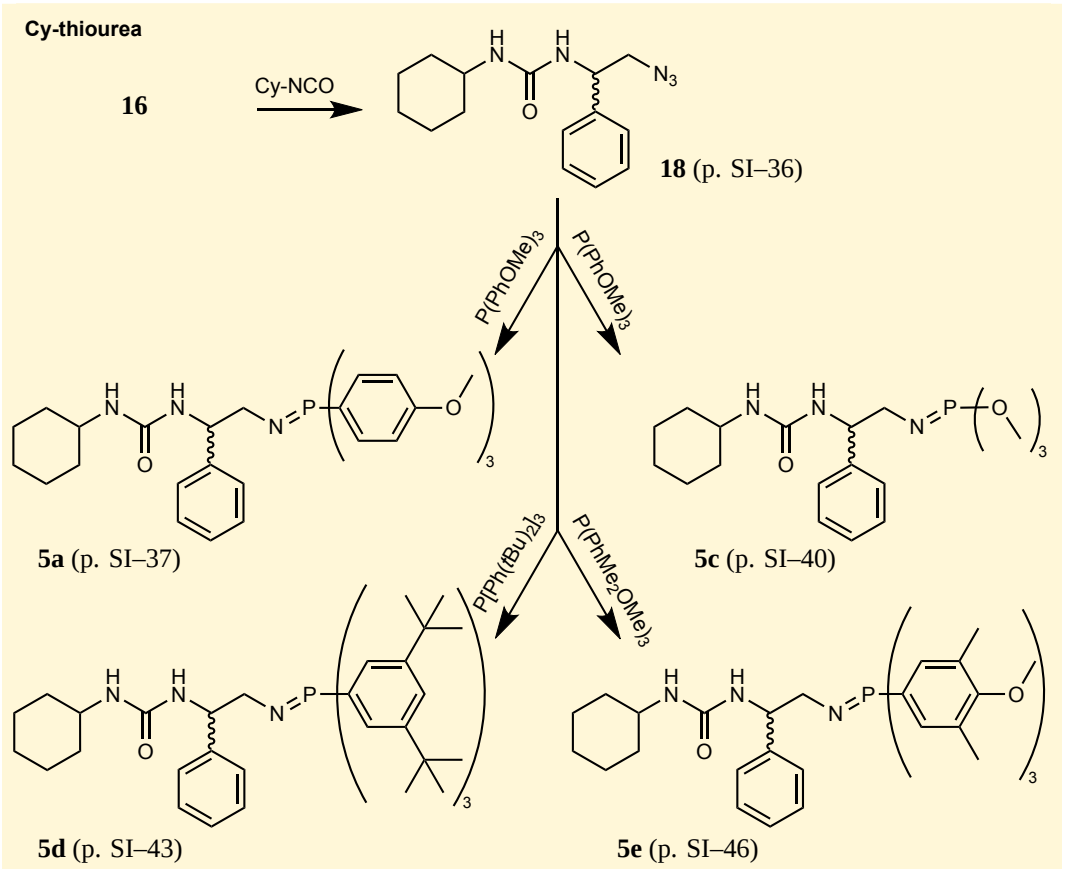


Figure SI–12: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of 2-(Ph-thiourea)ethan-1-N=P(*p*-OMe-phenyl)$_3$ (**1a**).

2.4 Bi-functional catalysts with (±)-2-phenylethyl-spacer (cat. 4a, 5a, 5c, 5d & 5e)

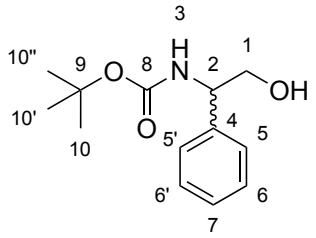






Scheme SI–3: 6-step syntheses of bi-functional catalysts **4a**, **5a**, **5c**, **5d** & **5e**.

2.4.1 (±)-Boc-2-amino-2-phenylethan-1-ol (13)



According to a literature-known procedure,[6] (±)-phenylglycinol (8.23 g, 60.0 mmol, 1.0 eq.) was suspended in CH_2Cl_2 (120 mL) in a 250 mL 3-neck flask with dropping funnel at rt.. Di-*tert*-butyl dicarbonate (14.40 g, 66.0 mmol, 1.1 eq.) was added in one portion. Over the course of 10 min, triethylamine (9.5 mL, 67.6 mmol, 1.1 eq.) was added from a dropping funnel. The initially white, heterogeneous mixture was stirred at rt. for 20 h and turned into a yellow, clear solution within the first 1 h of stirring. After full conversion (as judged by TLC), the organic phase was washed twice with water, the organic phase was separated and the combined aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with brine, dried over magnesium sulphate, concentrated under reduced pressure at 40 °C and dried *in vacuo* at rt. (±)-Boc-2-amino-2-phenylethan-1-ol (**13**, 13.64 g, 57.5 mmol, 96 %) was obtained as an off-white solid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.10 (visible by UV light).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

NMR signals are in accordance with literature data;[7] their assignment is based on chemical shift predictions (by ChemDraw 20.1).

$\delta =$ 1.43 (s, 9H^{10})
2.48 (s, 1H^{OH})
3.83 (s, 2H^{1})
4.77 (s, 1H^{2})
5.29 (s, 1H^{3})
7.27–7.39 (m, 5H^{5,6,7}) ppm.

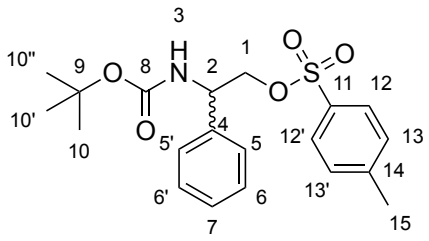
^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 28.5 (s, 3C^{10})
57.0 (s, 1C^{1})
67.1 (s, 1C^{1})
80.1 (s, 1C^{9})
126.7 (s, 2C^{5})
127.9 (s, 1C^{7})
128.9 (s, 2C^{6})
139.6 (s, 1C^{4})
156.2 (s, 1C^{8}) ppm.

ATR-IR: (neat)

$\tilde{\nu} =$ 3250 (w, O–H and N–H, ν)
$\sim$3050 (w, C–H$_{arom.}$, ν)
2973, 2933, 2871 (w, C–H$_{aliph.}$, ν)
1745 (m, C=O$_{free}$, ν)
1673 (s, C=O$_{associated}$, ν)
1553 (m, N–H, δ)
1157 (s, C–O$_{urethane}$, ν)
1052 (s, C–O$_{alcohol}$, ν)
760, 700 (m, C–H$_{arom.}$, δ) $^1/_{cm}$.

2.4.2 (±)-Boc-2-amino-2-phenylethan-1-tosylate (14)



According to a literature-known procedure,[8] (±)-boc-2-amino-2-phenylethan-1-ol (**13**, 5.00 g, 21.1 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (30 mL) and triethylamine (3.3 mL, 23.2 mmol, 1.1 eq.) in a 250 mL 3-neck flask at 0 °C. 4-Toluenesulfonyl chloride (4.02 g, 21.1 mmol, 1.0 eq.) was added in one portion. The reaction mixture turned yellow within 10 min and was stirred for 24 h at rt. After full conversion of the starting material (as judged by TLC), the organic phase was washed with water, the organic phase was separated and the aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with 20 %(w/w) citric acid (100 mL) dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. Thus obtained yellow oil was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (from 5:1 to 2:1) and dried *in vacuo* at rt. (±)-Boc-2-amino-2-phenylethan-1-tosylate (**14**, 3.58 g, 9.5 mmol, 43 %) was obtained as a white solid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]
$R_f =$ 0.37 (visible by UV light and *p*-anisaldehyde stain).

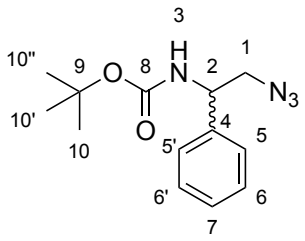
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)
$\delta =$ 1.41 (s, 9H^{10})
2.43 (s, 3H^{15})
4.10–4.36 (m, 2H^{1})
4.91 (s, 1H^{2})
5.11 (s, 1H^{3})
7.17–7.22 (m, 2H^{13})
7.27–7.35 (m, 5H^{5,6,7})
7.66 (d, $^3J_{HH} = 8.2$ Hz, 2H^{12}) ppm.

NMR signals are in accordance with literature data;[9,10] their assignment is based on chemical shift predictions (by ChemDraw 20.1).

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)
$\delta =$ 21.8 (s, 3C^{15})
28.4 (s, 1C^{10})
53.5 (s, 1C^{2})
71.6 (s, 1C^{1})
80.2 (s, 1C^{9})
126.7 (s, 2C^{5})
128.0 (s, 2C^{12})
128.1 (s, 1C^{7})
128.8 (s, 2C^{6})
130.0 (s, 2C^{13})
132.5 (s, 1C^{4})
137.9 (s, 1C^{11})
145.1 (s, 1C^{14})
155.0 (s, 1C^{8}) ppm.

ATR-IR: (neat)
$\tilde{\nu} =$ ∼3050 (w, C–H$_{arom.}$, ν)
2922 (w, C–H$_{aliph.}$, ν)
1733 (m, C=O, ν)
1362, 1177 (m, S=O, ν)
1123 (s, C–O$_{urethane}$, ν)
1033 (s, C–O$_{alcohol}$, ν)
816, 766, 700 (s, C–H$_{arom.}$, δ) 1/cm.

2.4.3 (±)-Boc-2-amino-2-phenylethan-1-azide (15)



According to a literature-known procedure,[3] (±)-boc-2-amino-2-phenylethan-1-tosylate (**14**, 3.58 g, 9.2 mmol, 1.0 eq.) was dissolved in N,N-dimethylformamide (DMF, 30 mL) in a 25 mL three-neck flask at rt. Sodium azide (0.65 g, 10.1 mmol, 1.1 eq.) was added in one portion. The solution was stirred for 20 h at 45 °C. After full conversion of the starting material (as judged by TLC), the organic phase was diluted with diethyl ether (30 mL) and water (65 mL). The organic phase was separated and the aqueous phase was extracted twice using diethyl ether. The combined organic phase was washed with water (2x) and brine (1x) and dried over magnesium sulphate. The crude product was purified by column chromatography using a *n*-heptane:ethyl acetate (9:1) eluent mixture and dried *in vacuo* at rt. (±)-Boc-2-amino-2-phenylethan-1-azide (**15**, 1.16 g, 4.4 mmol, 48 %) was obtained as a white solid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.47 (visible by UV light and *p*-anisaldehyde stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

NMR signals are in accordance with literature data;[3,11] their assignment is based on chemical shift predictions (by ChemDraw 20.1).

$\delta =$ 1.44 (s, 9H^{10})
3.46–3.77 (m, 2H^{1})
4.88 (s, 1H^{2})
5.07 (s, 1H^{3})
7.27–7.41 (m, 5H^{5,6,7}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

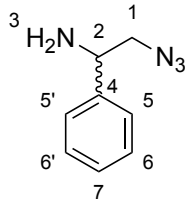
$\delta =$ 28.5 (s, 1C^{10})
54.2 (s, 1C^{2})
55.8 (s, 1C^{1})
80.3 (s, 1C^{9})
126.7 (s, 2C^{5})
128.2 (s, 1C^{7})
129.0 (s, 2C^{6})
139.4 (s, 1C^{4})
155.2 (s, 1C^{8}) ppm.

assignment of C^5 and C^6 according to the predicted chemical shifts (ChemDraw 20.1).

ATR-IR: (neat)

$\tilde{\nu} =$ 3386 (w, N–H, ν)
3034 (w, C–H$_{arom.}$, ν)
2984, 2933 (w, C–H$_{aliph.}$, ν)
2097 (s, –N$_3$, ν)
1677 (s, C=O, ν)
1513 (s, N–H, δ)
1157 (s, C–O, ν)
755, 698 (s, C–H$_{arom.}$, δ) 1/cm.

2.4.4 (±)-2-Amino-2-phenylethan-1-azide (16)



According to a literature-known procedure,[3] (±)-boc-2-amino-2-phenylethan-1-azide (**15**, 1.16 g, 4.4 mmol, 1.0 eq.) was cooled down to 0 °C in a 100 mL Schlenk flask equipped with a dropping funnel under inert atmosphere. TFA (5 mL) was slowly added through the dropping funnel. The obtained colourless solution was stirred for 3 h at rt., after which full conversion of the starting material (as judged by TLC) was affirmed. TFA was evaporated under a stream of nitrogen gas behind a blast shield. Water (20 mL) and diethyl ether (15 mL) were added to the residue. At 0 °C, 10 %(w/w) (sodium hydroxide solution mL) was slowly added through the dropping funnel. The organic phase was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phase was washed with brine, dried over magnesium sulphate and concentrated behind a blast shield under a stream of nitrogen gas. Thus obtained 2-amino-2-phenylethan-1-azide (**16**) was used without purification as starting material for the subsequent reaction (c.f. p. SI–33 and p. SI–36).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.02 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

no NMR data reported in the literature.[3,12]

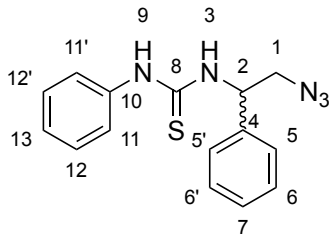
$\delta =$ 3.70–3.85 (m, 2H^1)
4.27 (dd, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 5.6$ Hz, 1H^2)
7.30–7.49 (m, 5H^{5,6,7})
8.19 (s, 2H^3) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 55.7 (s, 1C^2)
59.3 (s, 1C^1)
126.6 (s, 2C^5)
128.0 (s, 1C^7)
128.9 (s, 2C^6)
142.4 (s, 1C^4) ppm.

assignment of C^5 and C^6 is based on chemical shift predictions (by ChemDraw 20.1)

2.4.5 (±)-2-(Ph-thiourea)-2-phenylethan-1-azide (17)



Similar to a literature-known procedure,[3] 2-amino-2-phenylethan-1-azide (**16**, 0.47 g, 2.9 mmol, 1.0 eq.) was dissolved in anhydrous diethyl ether (15 mL) in a 50 mL Schlenk tube under inert atmosphere. phenyl isothiocyanate (0.43 g, 3.2 mmol, 1.1 eq.) was added and the resulting colourless solution was stirred overnight. After full conversion was affirmed by TLC, the product was concentrated, first under a stream of nitrogen gas, and, second *in vacuo* overnight. The crude material was purified by column chromatography using a gradient of *n*-heptane:ethyl acetate (from 1:0 to 1:1) and dried *in vacuo* at rt. (±)-2-(Ph-thiourea)-2-phenylethan-1-azide (**17**, 0.46 g, 1.5 mmol, 53 %) was obtained as an off-white solid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.49 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 3.77 (dd, $^2J_{HH} = 12.5$ Hz, $^3J_{HH} = 4.5$ Hz, 1H^1)
3.89 (dd, $^2J_{HH} = 12.5$ Hz, $^3J_{HH} = 5.0$ Hz, 1H^1)
5.82–5.91 (m, 1H^2)
6.57 (d, $^3J_{HH} = 7.9$ Hz, 1H^3)
7.25–7.27 (m, 2H^6)
7.27–7.29 (m, 2H^{12})
7.32–7.41 (m, 4H^{5,7,13})
7.43–7.53 (m, 2H^{11})
8.15 (*br.*, 1H^9) ppm.

differentiation between signals H^5/H^6 and H^{11}/H^{12} is based on chemical shift predictions (by ChemDraw 20.1).

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

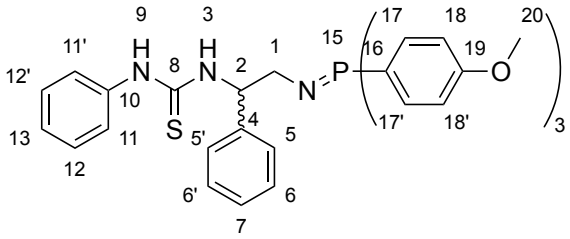
$\delta =$ 55.1 (s, 1C^1)
57.8 (s, 1C^2)
125.3 (s, 2C^{11})
126.7 (s, 1C^5)
127.8 (s, 1C^7)
128.4 (s, 2C^{13})
129.1 (s, 1C^6)
130.5 (s, 2C^{12})
135.9 (s, 1C^{10})
138.1 (s, 1C^4)
180.4 (s, 1C^8) ppm.

differentiation between signals C^5/C^6, C^7/C^{13} and C^{11}/C^{12} is based on chemical shift predictions (by ChemDraw 20.1).

HRMS: (MALDI positive)

calc. (for $C_{15}H_{16}N_5S$): 298.11209 u
found: 298.11067 m/z $[M+H]^+$ (target compound **17**).

2.4.6 (±)-2-(Ph-thiourea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (4a)



(±)-2-(Ph-thiourea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (**4a**, 0.33 g, 0.5 mmol, 35 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (±)-2-(Ph-thiourea)-2-phenylethan-1-azide (**17**, 0.45 g, 1.5 mmol, 1.0 eq.) and P(*p*-OMe-phenyl)$_3$ (0.53 g, 1.5 mmol, 1.0 eq.) in anhydrous THF (4 mL) and isolation according to the purification method A (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 295 K, CD_2Cl_2)

A second species is observed in the NMR spectra with too low an intensity to assign its signals.

signals of H^3 and H^9 were not observed.

$\delta =$ 3.26 (dd, $^2J_{HH} = 9.1$ Hz, $^3J_{HH} = 2.3$ Hz, $1H^1$)
3.83 (s, $9H^{20}$)
3.96 (*pseudo*-t, $^2J_{HH} = 9.2$ Hz, $^3J_{HH} = 9.2$ Hz, $1H^1$)
6.06 (dd, $^3J_{HH} = 9.2$ Hz, $^3J_{HH} = 2.2$ Hz, $1H^2$)
6.96 (dd, $^3J_{HH} = 8.9$ Hz, $^4J_{PH} = 2.2$ Hz, $6H^{18}$)
7.14–7.43 (m, $2H^5 + 2H^6 + 1H^7 + 2H^{11} + 2H^{12} + 1H^{13}$)
7.52 (dd, $^3J_{PH} = 11.4$ Hz, $^3J_{HH} = 8.8$ Hz, $6H^{17}$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, CD_2Cl_2)

$\delta =$ 45.4 (s, $1C^1$)
55.8 (s, $3C^{20}$)
59.8 (s, $1C^2$)
114.3 (d, $^3J_{PC} = 13.0$ Hz, $6C^{18}$)
125.2 (d, $^1J_{PC} = 100(\pm5)$ Hz, $3C^{16}$)
125.7 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
126.0 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
126.4 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
128.2 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
128.9 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
129.2 (s, $2C^5$ or $2C^6$ or $1C^7$ or $2C^{11}$ or $2C^{12}$ or $1C^{13}$)
135.0 (s, $1C^{10}$)
134.1 (d, $^2J_{PC} = 11.1$ Hz, $6C^{17}$)
142.4 (s, $1C^4$)
162.8 (s, $3C^{19}$) ppm.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, CD_2Cl_2)

$\delta =$ 25.7 (s, $1P^{15}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{36}H_{37}N_3O_3PS$): 622.2288 u
found: 622.2289 m/z $[M+H]^+$ (target compound **4a**).

ATR-IR: (neat)
$\tilde{\nu}$ = 2929 (w, C–H, ν)
1593 (s, C=$C_{arom.}$, ν)
1498 (s, C=$C_{arom.}$, ν)
1251 (s, C–N, ν)
1115, 802, 697, 663 (s, fingerprint, δ) $^1/_{cm}$.

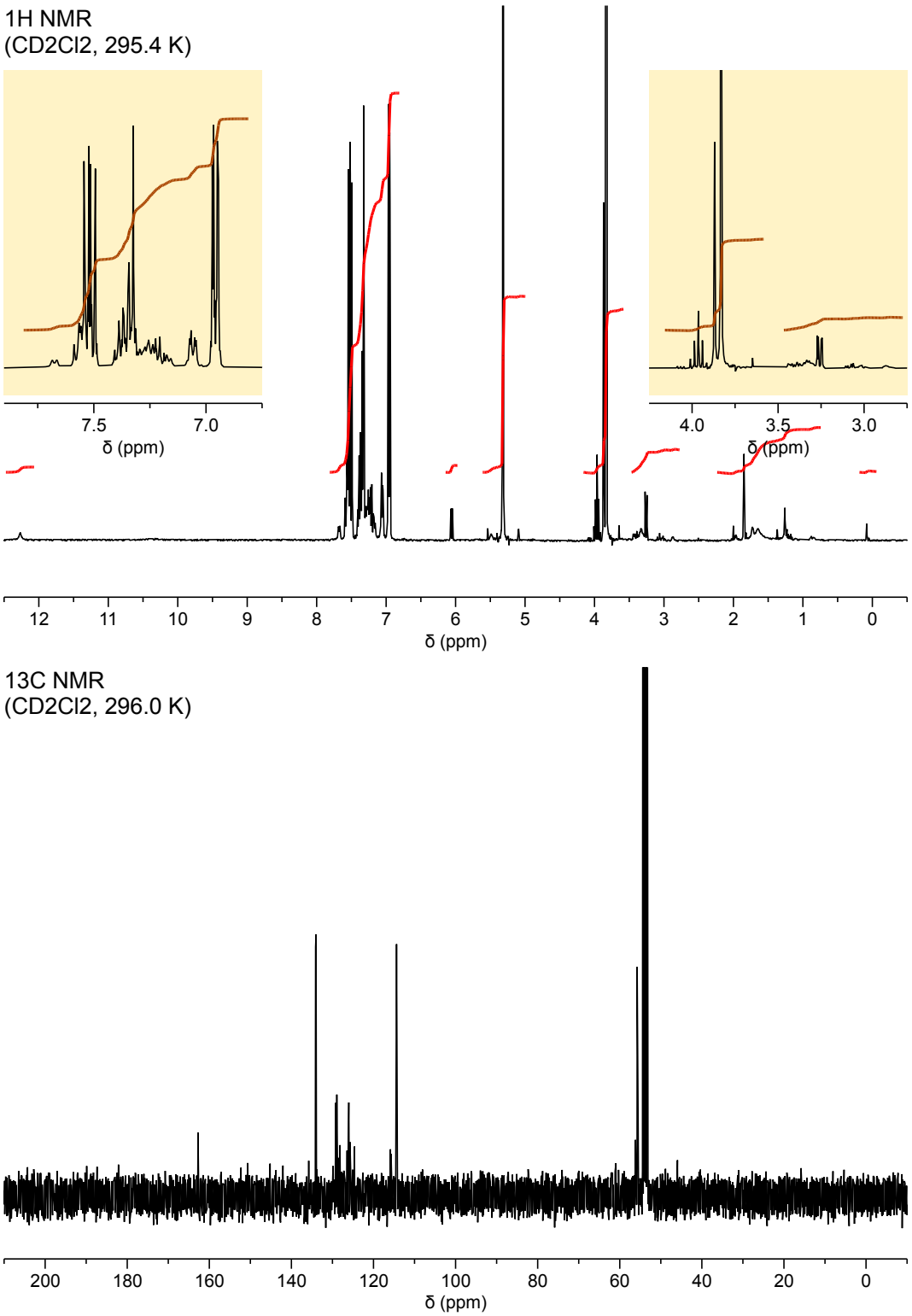
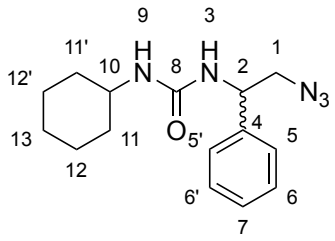


Figure SI–13: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (±)-2-(Ph-thiourea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (**4a**).

2.4.7 (±)-2-(Cy-urea)-2-phenylethan-1-azide (18)



Similar to a literature-known procedure,[3] 2-amino-2-phenylethan-1-azide (**16**, 0.72 g, 4.4 mmol, 1.0 eq.) was dissolved in anhydrous THF (15 mL) in a 100 mL Schlenk flask under inert atmosphere. Cyclohexyl isocyanate (0.61 g, 4.9 mmol, 1.1 eq.) was added and the resulting colourless solution was stirred overnight. After full conversion was affirmed by TLC, the product was concentrated, first under a stream of nitrogen gas, and, second *in vacuo* overnight. The crude material was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (from 5:1 to 2:1) and dried *in vacuo* at rt. (±)-2-(Cy-urea)-2-phenylethan-1-azide (**18**, 0.41 g, 1.4 mmol, 32 %) was obtained as a white solid.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.24 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 0.99–1.11 (m, 2H^{11})
1.09–1.21 (m, 1H^{13})
1.24–1.41 (m, 2H^{12})
1.53–1.62 (m, 1H^{13})
1.61–1.70 (m, 2H^{12})
1.84–1.96 (m, 2H^{11})
3.45–3.59 (m, 1H^{10})
3.59–3.73 (m, 2H^{1})
4.22 (d, $^3J_{HH} = 7.9$ Hz, 1H^3 or 1H^9)
4.73 (d, $^3J_{HH} = 7.1$ Hz, 1H^3 or 1H^9)
4.98 (*pseudo*-q, $J_{HH} = 5.4$ Hz, 1H^2)
7.29-7.40 (m, 2H^5 + 2H^6 + 1H^7) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

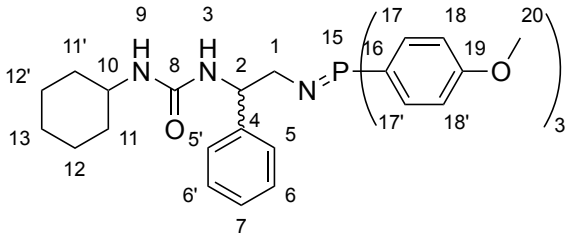
$\delta =$ 24.9 (s, 2C^{12})
25.7 (s, 1C^{13})
33.9 (s, 2C^{11})
53.9 (s, 1C^{2})
56.1 (s, 1C^{1})
126.8 (s, 2C^{5})
128.2 (s, 1C^{7})
129.1 (s, 2C^{6})
139.7 (s, 1C^{4})
156.6 (s, 1C^{8}) ppm.

differentiation between signals C^5/C^6 is based on chemical shift predictions (by ChemDraw 20.1).

HRMS: (MALDI positive)

calc. (for $C_{15}H_{22}N_5O$): 288.18189 u
found: 288.18052 m/z $[M+H]^+$ (target compound **18**).

2.4.8 (±)-2-(Cy-urea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (5a)



(±)-2-(Cy-urea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (**5a**, 0.74 g, 1.2 mmol, 89 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (±)-2-(Cy-urea)-2-phenylethan-1-azide (**18**, 0.37 g, 1.3 mmol, 1.0 eq.) and P(*p*-OMe-phenyl)$_3$ (0.46 g, 1.3 mmol, 1.0 eq.) in anhydrous diethyl ether (12 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, CD_2Cl_2)

A second species is observed in the NMR spectra with too low an intensity to assign its signals.

$\delta =$ 0.92–1.11 (m, 2H^{11} + 1H^{13})
1.20–1.37 (m, 2H^{12})
1.46–1.64 (m, 2H^{12} + 1H^{13})
1.74–1.89 (m, 2H^{11})
3.15 (ddd, $^3J_{PH} = 16.4$ Hz, $^2J_{HH} = 12.1$ Hz, $^3J_{HH} = 7.2$ Hz, 1H^1)
3.32 (ddd, $^3J_{PH} = 12.0$ Hz, $^2J_{HH} = 12.0$ Hz, $^3J_{HH} = 3.9$ Hz, 1H^1)
3.37–3.51 (m, 1H^{10})
3.83 (s, 9H^{20})
4.43–4.54 (m, 1H^2)
5.34 (s, 1H^9) , 5.77 (s, 1H^3)
6.94 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{PH} = 2.0$ Hz, 6H^{18})
7.15–7.24 (m, 1H^7)
7.19–7.29 (m, 4H^{5,6})
7.46 (dd, $^3J_{PH} = 11.0$ Hz, $^3J_{HH} = 8.7$ Hz, 6H^{17}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, CD_2Cl_2)

$\delta =$ 25.4 (s, 2C^{12})
26.0 (s, 1C^{13})
34.1 (s, 2C^{11})
49.3 (s, 1C^{10})
52.7–53.0 (m, 1C^1)
55.7 (s, 3C^{20})
59.1 (d, $^3J_{PC} = 17.5$ Hz, 1C^2)
114.3 (d, $^3J_{PC} = 12.5$ Hz, 6C^{18})
123.0 (d, $^1J_{PC} = 104.2$ Hz, 3C^{16})
127.0 (s, 1C^7)
127.1 (s, 2C^5)
128.5 (s, 2C^6)
134.5 (d, $^2J_{PC} = 10.4$ Hz, 6C^{17})
144.2 (s, 1C^4)
158.7 (s, 1C^8)
162.5 (d, $^4J_{PC} = 2.7$ Hz, 3C^{19}) ppm.

$^{31}P\{^{1}H\}$ NMR: (162 MHz, 296 K, CD_2Cl_2)

$\delta =$ 12.7 (*br.*, $1P^{15}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{36}H_{43}N_3O_4P$):	612.2986 u
found:	612.2948 m/z $[M+H]^+$ (target compound **5a**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3300 (w, N–H, ν)
2928, 2851 (w, C–H, ν)
1657 (m, C=O, ν)
1594 (s, $C{=}C_{arom.}$, ν)
1500 (s, $C{=}C_{arom.}$, ν)
1249 (s, C–N, ν)
1175 (s, $C{-}O_{ether}$, ν)
1117, 802, 700, 602 (s, fingerprint, δ) 1/cm.

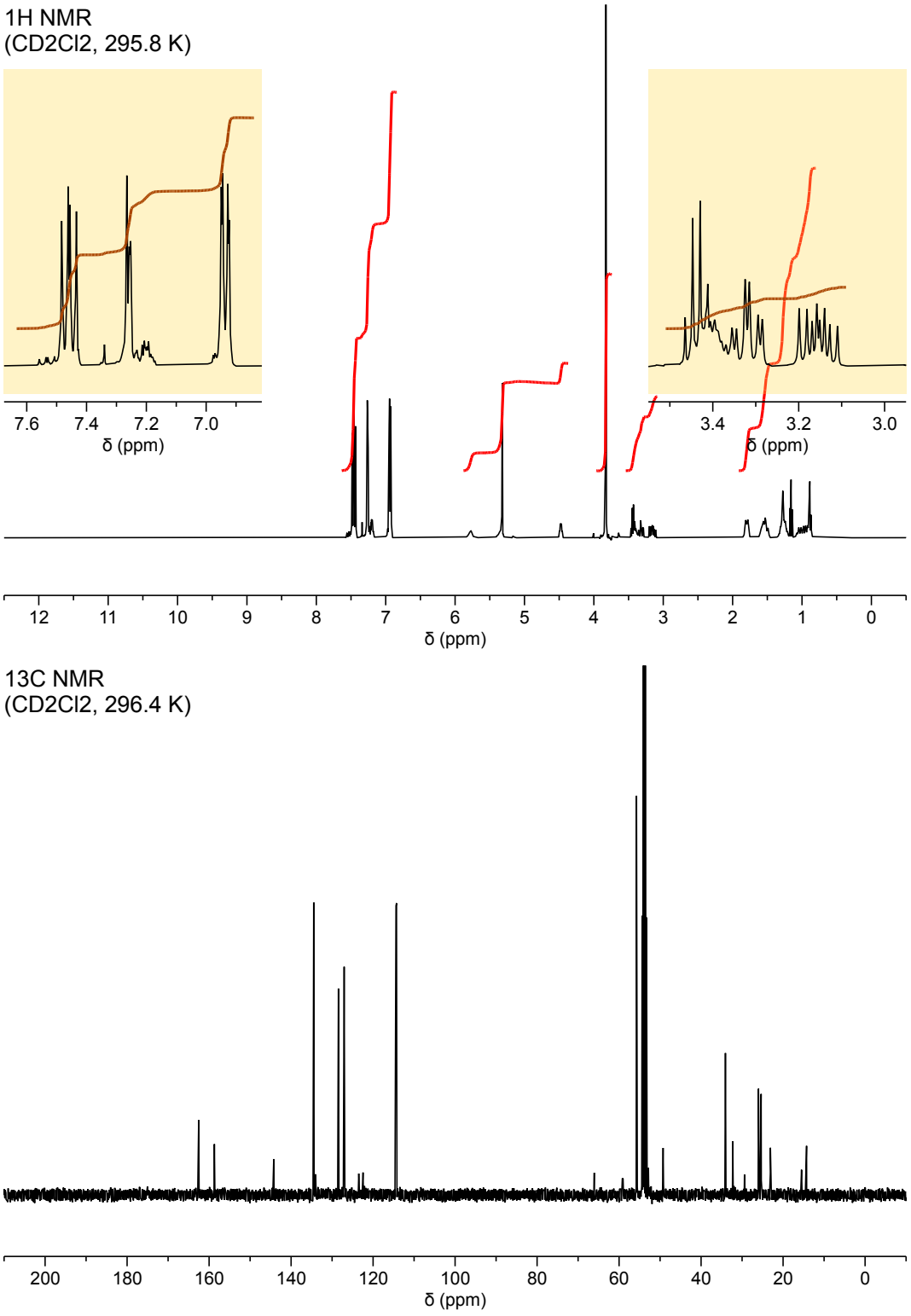
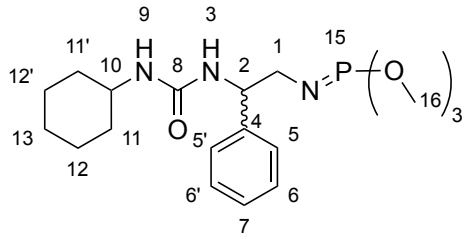


Figure SI–14: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (±)-2-(Cy-urea)-2-phenylethan-1-N=P(*p*-OMe-phenyl)$_3$ (**5a**).

2.4.9 (±)-2-(Cy-urea)-2-phenylethan-1-N=P(OMe)$_3$ (5c)



(±)-2-(Cy-urea)-2-phenylethan-1-N=P(OMe)$_3$ (**5c**, 0.33 g, 0.9 mmol, 39 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (±)-2-(Cy-urea)-2-phenylethan-1-azide (**18**, 0.37 g, 1.3 mmol, 1.0 eq.) and P(OMe)$_3$ (0.27 g, 2.2 mmol, 1.0 eq.) in anhydrous THF (4 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and $KMnO_4$ stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

Two species are observed in the NMR spectra (one of which is labelled with an apostrophe). In case the signals of both species overlap, the overlapped signal is labelled with an asterisks.

$\delta =$ 0.95–1.08 (m, 2H^{11*} + 1H^{13*})
1.14–1.29 (m, 2H^{12*})
1.42-1.64 (m, 2H^{12*} + 1H^{13*})
1.68–1.86 (m, 2H^{11*})
2.94–3.21 (m, 2H^{1} + 1H$^{1'}$)
3.35–3.64 (m, 1H$^{1'}$ + 1H^{10*} + 9H^{16*})
4.76–4.83 (m, 1H^{2})
5.01–5.09 (m, 1H$^{2'}$)
5.39 (d, $^3J_{HH} = 7.8$ Hz, 1H$^{9'}$)
6.23 (d, $^3J_{HH} = 8.2$ Hz, 1H$^{3'}$)
6.44 (d, $^3J_{HH} = 7.3$ Hz, 1H^{3})
7.11–7.25 (m, 2H^{5*} + 2H^{6*} + 2H^{6*}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 24.5–25.1 (m, 2C^{12*})
25.5–25.7 (m, 1C^{13*})
33.4–34.1 (m, 2C^{11*})
47.3 (s, 1C^{1})
48.5 (s, 1C^{10*})
51.6 (s, 1C$^{2'}$)
52.7–54.0 (m, 3C^{16*})
55.0 (d, $^2J_{PH} = 4.6$ Hz, 1C$^{1'}$)
55.2 (*br.*, 1C^{2})
126.4–126.8 (m, 2C^{5*} or 2C^{6*})
126.9–127.3 (m, 1C^{7*})
128.2–128.6 (m, 2C^{5*} or 2C^{6*})
140.4–142.9 (m, 1C^{4*})
157.5–158.3 (m, 1C^{8*}) ppm.

^{31}P{^{1}H} NMR: (162 MHz, 297 K, $CDCl_3$)

$\delta =$ 11.8 (s, 1P^{15})
13.8 (s, 1P$^{15'}$) ppm.

HRMS: (ESI positive)

calc. (for $C_{18}H_{31}N_3O_4P$):	384.2047 u
found:	384.2036 m/z $[M+H]^+$ (target compound **5c**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3354 (w, N–H, ν)
2927, 2851 (w, C–H, ν)
1676 (m, C=O, ν)
1550 (s, CH_3, δ)
1222 (s, C–N, ν)
1028 (s, P–O, ν)
830, 700 (s, fingerprint, δ) 1/cm.

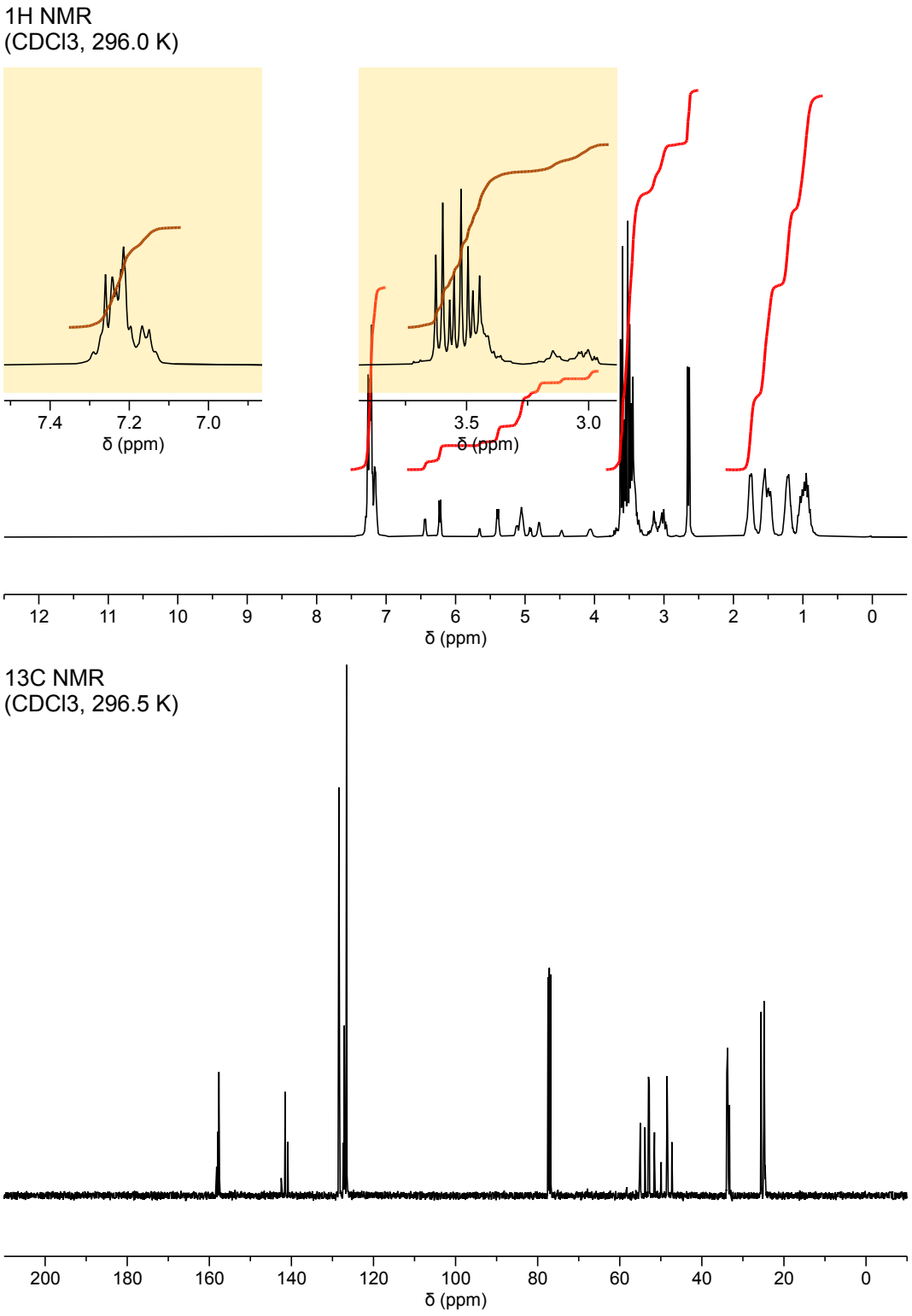
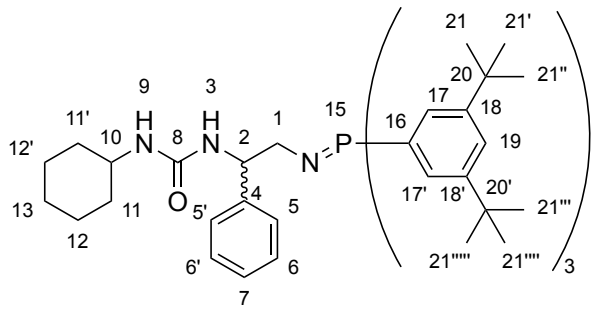


Figure SI–15: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (±)-2-(Cy-urea)-2-phenylethan-1-N=P(OMe)$_3$ (**5c**).

2.4.10 (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-*t*Bu)$_2$-phenyl]$_3$ (5d)



(±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-*t*Bu)$_2$-phenyl]$_3$ (**5d**, 0.12 g, 0.14 mmol, 41 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (±)-2-(Cy-urea)-2-phenylethan-1-azide (**18**, 0.10 g, 0.35 mmol, 1.0 eq.) and P[(*m*-*t*Bu)$_2$-phenyl]$_3$ (0.22 g, 0.35 mmol, 1.0 eq.) in anhydrous THF (0.6 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and $KMnO_4$ stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

Two species are observed in the NMR spectra (one of which is labelled with an apostrophe). In case the signals of both species overlap, the overlapped signal is labelled with an asterisks.

$\delta =$ 0.88–1.06 (m, 2H^{11*} + 1H^{13*})
1.16–1.24 (m, 2H^{12*})
1.23 (s, 18H^{21})
1.25 (s, 18H$^{21'}$)
1.42–1.62 (m, 2H^{12*} + 1H^{13*})
1.66–1.87 (m, 2H^{11*})
2.69–2.83 (m, 2H$^{1'}$)
3.25–3.37 (m, 2H^{1})
3.38–3.52 (m, 1H^{10*})
4.50 (*br.*, 1H^{2})
4.71 (*pseudo*-t, $^3J_{HH} = 5.9$ Hz, 1H$^{2'}$)
7.04–7.23 (m, 2H^{5*} + 2H^{6*} + 1H^{7*})
7.39 (d, $^3J_{HH} = 14.6$ Hz, 6H^{17})
7.43 (dd, $^3J_{HH} = 12.8$ Hz, $^3J_{PH} = 1.8$ Hz, 6H$^{17'}$)
7.55 (d, $^5J_{PH} = 1.2$ Hz, 3H$^{19'}$)
7.60 (*br.*, 3H^{19}) ppm.

signals of H^3 and H^9 were not observed.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 25.0 (*br.*, 2C^{12*})
25.4–25.8 (m, 1C^{13*})
31.3 (s, 18C^{21*})
33.3–34.0 (m, 2C^{11*})
35.0–35.2 (m, 6C^{20*})
48.3 (s, 1C$^{1'}$)
48.3–48.6 (m, 1C^{10*})
56.4 (s, 3C$^{2'}$)
125.7 (d, $^4J_{PC} = 2.6$ Hz, 3C^{19*})
126.4 (d, $^2J_{PC} = 10.6$ Hz, 6C$^{17'}$)
126.6–126.8 (m, 2C^{5*})

signals of C^1, C^2 and C^{16} were not observed.

126.9–127.2 (m, $2C^{7*} + 6C^{17}$)
128.3 (s, $2C^{6*}$)
132.0 (d, $^{1}J_{PC} = 103.2$ Hz, $6C^{16'}$)
142.0 (s, $1C^{4*}$)
150.8 (d, $^{3}J_{PC} = 11.7$ Hz, $6C^{18*}$)
158.2 (s, $1C^{8'}$)
159.2 (s, $1C^{8}$) ppm.

$^{31}P\{^{1}H\}$ NMR: (162 MHz, 296 K, $CDCl_3$)

$\delta =$ 19.7 (*br.*, $1P^{15}$)
33.4 (s, $1P^{15'}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{57}H_{85}N_3OP$): 858.6425 u
found: 858.6378 m/z $[M+H]^+$ (target compound **5d**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3317 (w, N–H, ν)
2959, 2867 (s, C–H, ν)
1638 (m, C=O, ν)
1546 (m, $C=C_{arom.}$, ν)
1477 (m, $C=C_{arom.}$, ν)
1362 (s, $C(CH_3)_3$, δ)
1248 (s, C–N, ν)
1146, 708, 609 (s, fingerprint, δ) 1/cm.

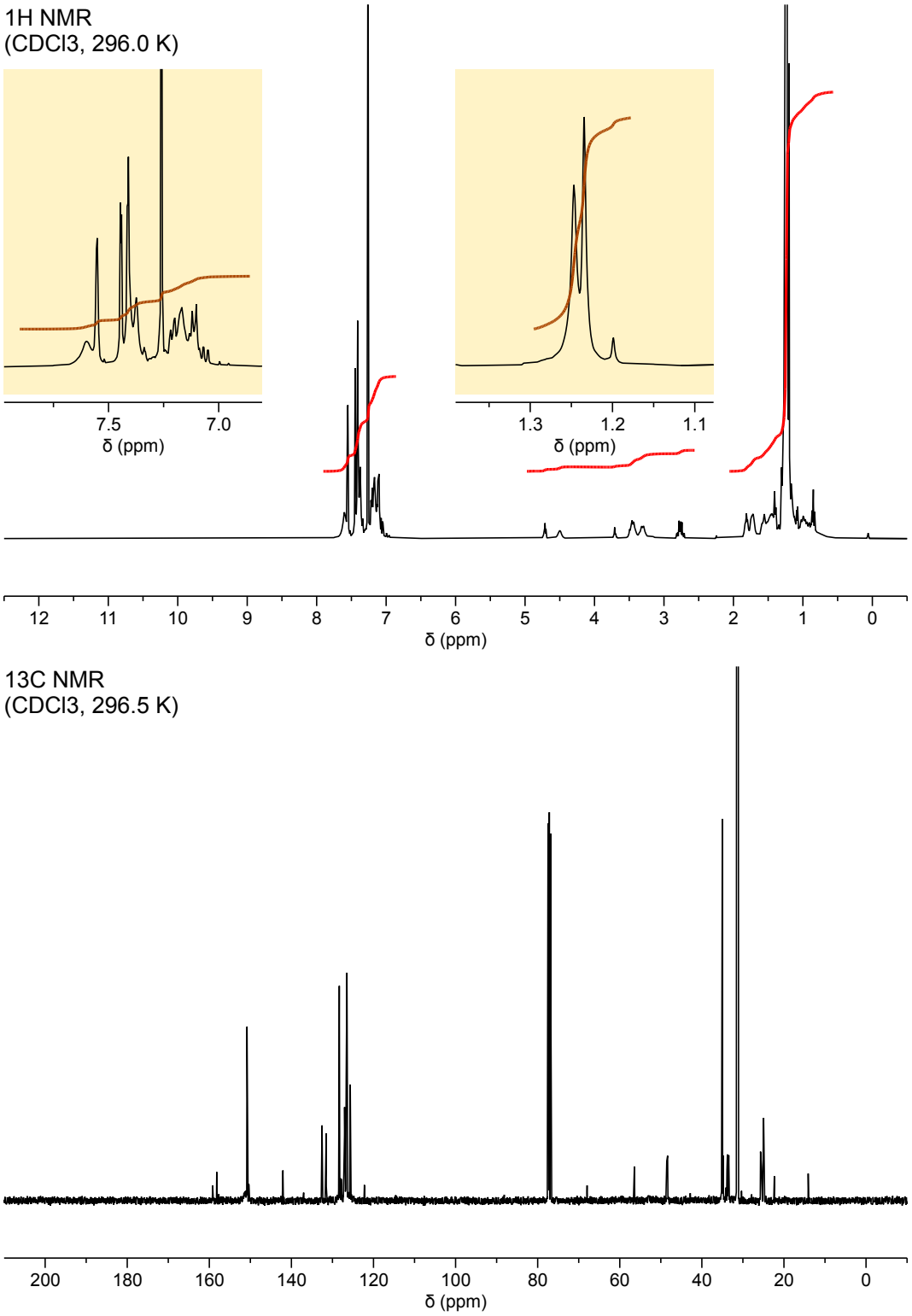
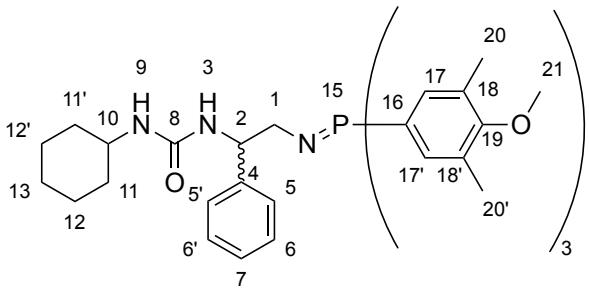


Figure SI–16: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-*t*Bu)$_2$-phenyl]$_3$ (**5d**).

2.4.11 (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (5e)



(±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**5e**, 0.19 g, 0.28 mmol, 28 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (±)-2-(Cy-urea)-2-phenylethan-1-azide (**18**, 0.29 g, 1.00 mmol, 1.0 eq.) and P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (0.45 g, 1.00 mmol, 1.0 eq.) in anhydrous THF (1.7 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and $KMnO_4$ stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

Two species are observed in the NMR spectra (one of which is labelled with an apostrophe). In case the signals of both species overlap, the overlapped signal is labelled with an asterisks.

$\delta =$ 0.89–1.03 (m, 2H^{11*} + 1H^{13*})
1.11–1.29 (m, 2H^{12*})
1.38–1.60 (m, 2H^{12*} + 1H^{13*})
1.68–1.82 (m, 2H^{11*})
2.22 (s, 18H$^{20'}$)
2.24 (s, 18H^{20})
2.66–2.81 (m, 1H$^{1'}$)
3.10–3.22 (m, 1H^{1})
3.38–3.49 (m, 1H^{10*})
3.69 (s, 9H$^{21'}$)
3.72 (s, 9H^{21})
4.49 (*br.*, 1H^{2})
4.65–4.74 (m, 1H$^{2'}$)
7.08–7.18 (m, 2H^{5*} + 2H^{6*} + 1H^{7*})
7.20 (d, $^3J_{PH} = 12.0$ Hz, 6H^{17})
7.25 (d, $^3J_{PH} = 11.6$ Hz, 6H$^{17'}$) ppm.

signals of H^3 and H^9 were not observed.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 16.2 (s, 6C$^{20'}$)
16.3 (s, 2C^{20})
24.5–25.3 (m, 2C^{12*})
25.5 (s, 1C^{13*})
33.3–33.9 (m, 2C^{11*})
48.1 (s, 1C$^{1'}$)
48.2–48.8 (m, 1C^{10*})
51.6 (*br.*, 1C^{1})
56.4 (s, 1C$^{2'}$)
58.5 (*br.*, 1C^{2})
59.5 (s, 3C$^{21'}$)

59.6 (s, $3C^{21}$)
126.4–126.7 (m, $2C^{5*}$)
126.9 (s, $1C^{7*}$)
127.5 (d, $^{1}J_{PC} = 106.0$ Hz, $3C^{16'}$)
128.2 (s, $2C^{6*}$)
131.3 (d, $^{3}J_{PC} = 13.4$ Hz, $6C^{18'}$)
131.9 (d, $^{3}J_{PC} = 13.5$ Hz, $6C^{18}$)
132.6 (d, $^{2}J_{PC} = 10.6$ Hz, $6C^{17'}$)
133.4 (d, $^{2}J_{PC} = 10.4$ Hz, $6C^{17}$)
144.1 (s, $1C^{4*}$)
158.1 (s, $1C^{8'}$)
158.8 (s, $1C^{8}$)
160.0 (d, $^{4}J_{PC} = 3.2$ Hz, $3C^{19'}$)
160.6 (s, $3C^{19}$) ppm.

signal of C^{16} was not observed.

$^{31}P\{^{1}H\}$ NMR: (162 MHz, 297 K, $CDCl_3$)

$\delta =$ 17.9 (*br.*, $1P^{15}$)
28.8 (*br.*, $1P^{15'}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{42}H_{55}N_3O_4P$): 696.3925 u
found: 696.3890 m/z $[M+H]^+$ (target compound **5e**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3313 (w, N–H, ν)
2926, 2851 (m, C–H, ν)
1629 (m, C=O, ν)
1545 (m, $C{=}C_{arom.}$, ν)
1475 (m, $C{=}C_{arom.}$, ν)
1220 (s, C–N, ν)
1007, 700, 622 (s, fingerprint, δ) 1/cm.

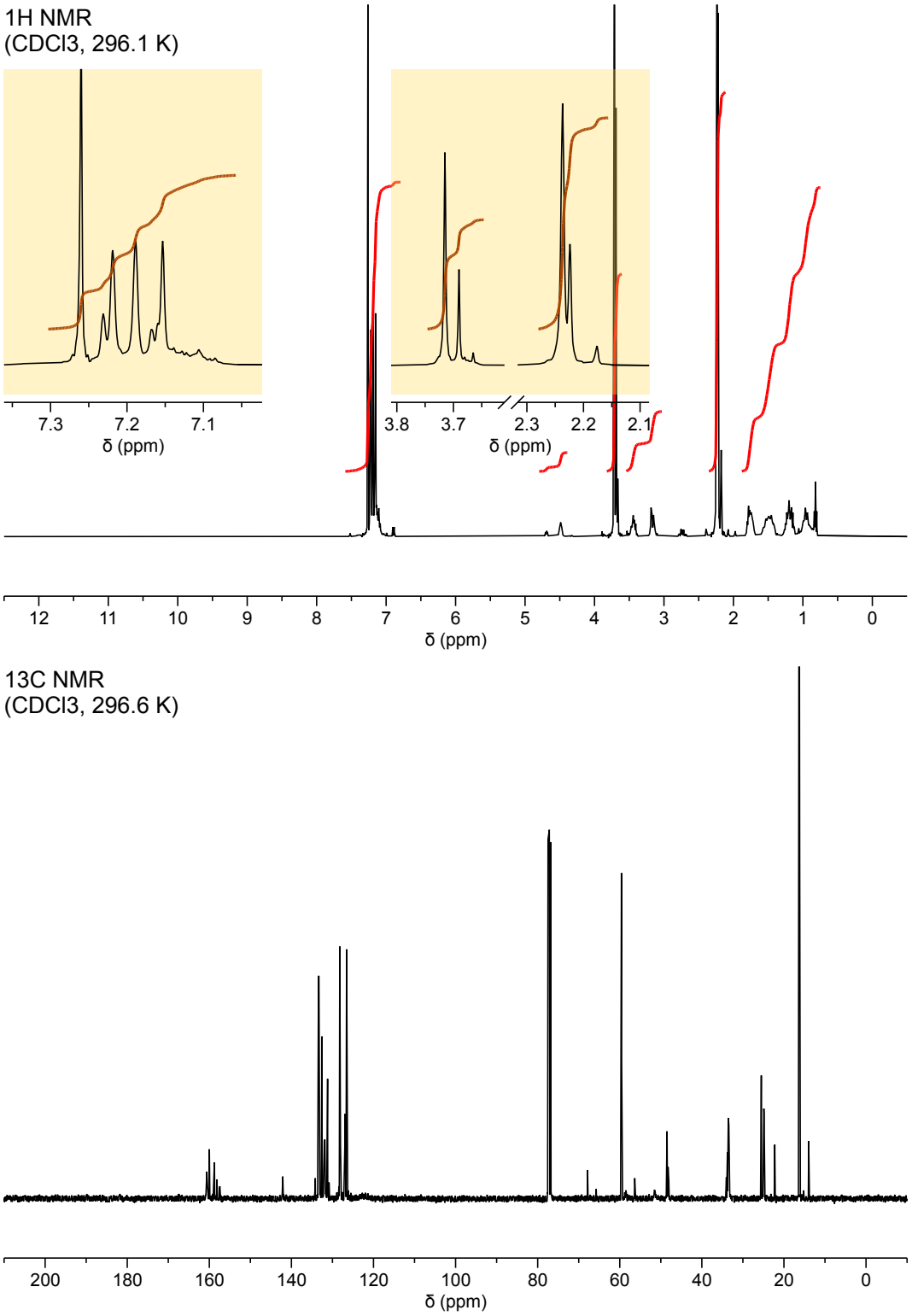
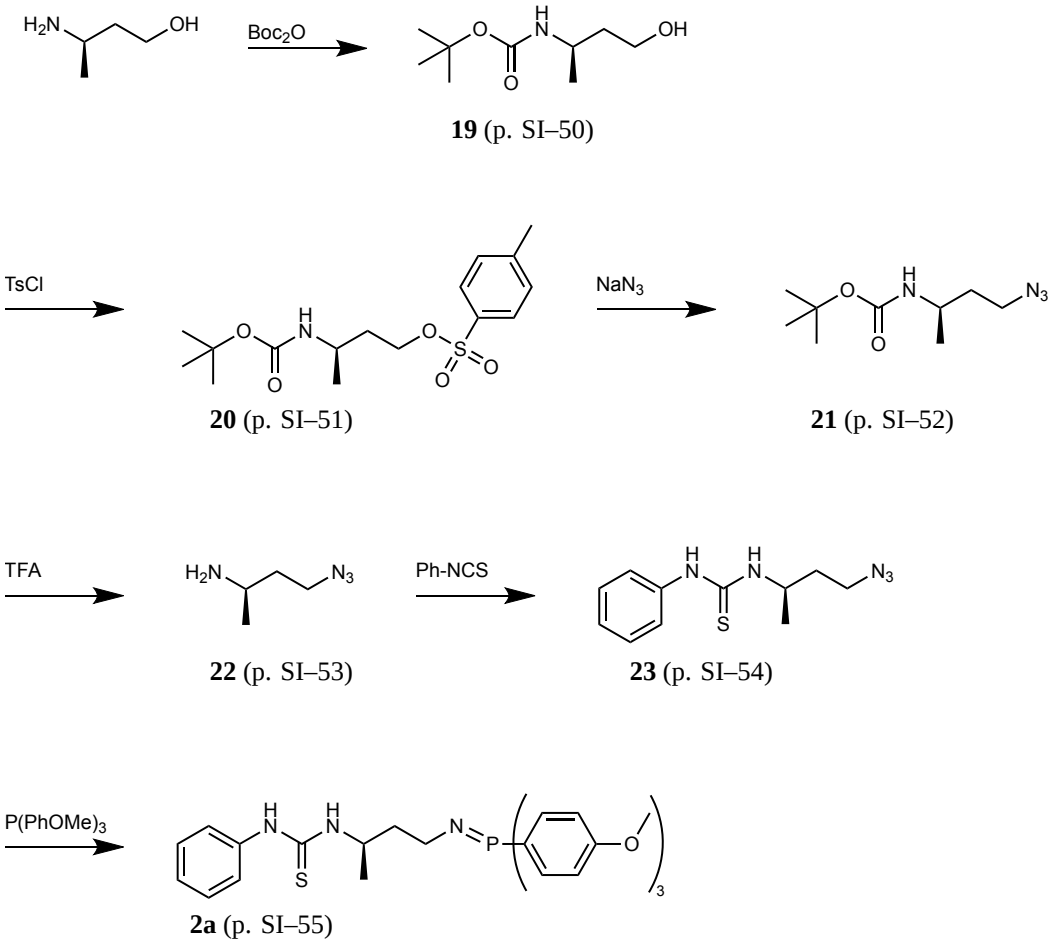


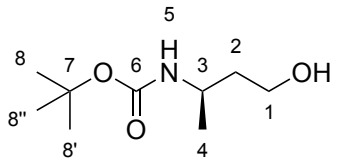
Figure SI–17: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (±)-2-(Cy-urea)-2-phenylethan-1-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**5e**).

2.5 Bi-functional catalyst with (*R*)-3-methylpropyl-spacer (cat. 2a)



Scheme SI–4: 6-step synthesis of bi-functional catalyst **2a**.

2.5.1 (*R*)-Boc-3-aminobutan-1-ol (19)



Similar to a literature-known procedure,[6] (*R*)-3-aminobutan-1-ol (4.55 g, 50.0 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (100 mL) in a 250 mL 3-neck flask with dropping funnel at rt. Di-*tert*-butyl dicarbonate (12.00 g, 55.0 mmol, 1.1 eq.) was added in one portion. Over the course of 10 min, triethylamine (7.7 mL, 55.0 mmol, 1.1 eq.) was added from the dropping funnel and the mixture was stirred at rt. for 20 h. After full conversion (as affirmed by TLC), the organic phase was washed with water, the organic phase was separated and the aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with brine, dried over magnesium sulphate, concentrated under reduced pressure at 40 °C and dried *in vacuo*. (*R*)-Boc-3-aminobutan-1-ol (**19**, 10.40 g, 47.5 mmol, 95 %) was obtained with 87 %(w/w) purity as a colourless oil.

TLC: [ethly acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.16 (visible by ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.17 (d, $^3J_{HH} = 6.7$ Hz, 3H^4)
1.27–1.36 (m, 1H^2)
1.43 (s, 9H^8)
1.72–1.87 (m, 1H^2)
3.46–3.56 (m, 1H^{OH})
3.57–3.69 (m, 2H^1)
3.82–3.93 (m, 1H^3)
4.41–4.55 (m, 1H^5) ppm.

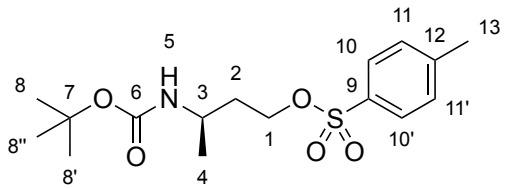
^{1}H NMR signals are in accordance with literature data.[13]

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 21.6 (s, 1C^4)
28.5 (s, 3C^8)
40.9 (s, 1C^3)
43.1 (s, 1C^2)
59.0 (s, 1C^1)
79.9 (s, 1C^7)
156.9 (s, 1C^6) ppm.

no ^{13}C NMR data reported in the literature.[13]

2.5.2 (*R*)-Boc-3-aminobutan-1-tosylate (20)



Similar to a literature-known procedure,[8] (*R*)-boc-3-aminobutan-1-ol (**19**, 10.39 g, 47.5 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (70 mL) and in a 250 mL 3-neck flask. Triethylamine (7.3 mL, 52.3 mmol, 1.1 eq.) and 4-toluenesulfonyl chloride (9.06 g, 47.5 mmol, 1.0 eq.) were added subsequently. The reaction mixture turned brown within 20 min and was stirred for 20 h. After full conversion of the starting material (as affirmed by TLC), the organic phase was washed with water, the organic phase was separated and the combined aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with 20 %(w/w) citric acid (100 mL) and brine, dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. Thus obtained crude material was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (9:1 and 7:3) and concentrated under reduced pressure at 40 °C. (*R*)-Boc-3-aminobutan-1-tosylate (**20**, 1.23 g, 3.6 mmol, 8 %) was obtained as a yellow oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.30 (visible by UV light and *p*-anisaldehyde stain).

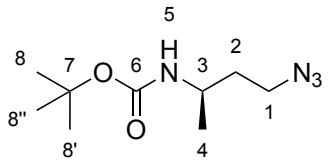
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.11 (d, $^3J_{HH} = 6.6$ Hz, 3H^4)
1.40 (s, 9H^8)
1.71–1.89 (m, 2H^2)
2.44 (s, 3H^{13})
3.61–3.77 (m, 1H^3)
4.08 (t, $^3J_{HH} = 6.6$ Hz, 2H^1)
4.34 (*br.*, 1H^5)
7.34 (d, $^3J_{HH} = 8.0$ Hz, 2H^{11}) ppm.
7.78 (d, $^3J_{HH} = 8.0$ Hz, 2H^{10}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 21.3 (s, 1C^4)
21.8 (s, 1C^{13})
28.5 (s, 3C^8)
36.2 (s, 1C^2)
43.9 (s, 1C^3)
70.0 (s, 1C^1)
79.5 (s, 1C^7)
128.1 (s, 2C^{10})
130.0 (s, 2C^{11})
133.1 (s, 1C^9)
144.9 (s, 1C^{12})
155.3 (s, 1C^6) ppm.

2.5.3 (*R*)-Boc-3-aminobutan-1-azide (21)



Similar to a literature-known procedure,[3] (*R*)-boc-3-aminobutan-1-tosylate (**20**, 1.23 g, 3.6 mmol, 1.0 eq.) was dissolved in DMF (12 mL) in a 100 mL flask at rt. Sodium azide (0.26 g, 3.9 mmol, 1.1 eq.) was added in one portion. The solution was stirred for 20 h at 45 °C. After full conversion of the starting material (as affirmed by TLC), the organic phase was diluted with diethyl ether (10 mL) and water (25 mL). The organic phase was separated and the aqueous phase was extracted twice using diethyl ether. The combined organic phase was washed with water (2x) and brine (1x), dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. (*R*)-Boc-3-aminobutan-1-azide (**21**, 0.67 g, 3.1 mmol, 87 %) was obtained as a yellow oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.45 (visible by UV light, *p*-anisaldehyde stain and ninhydrine stain).

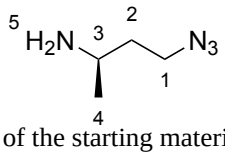
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.16 (d, $^3J_{HH} = 6.7$ Hz, 3H^4)
1.44 (s, 9H^8)
1.63–1.78 (m, 2H^2)
3.35 (t, $^3J_{HH} = 7.1$ Hz, 2H^1)
3.68–3.83 (m, 1H^3)
4.38 (*br.*, 1H^5) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 21.4 (s, 1C^4)
28.5 (s, 3C^8)
36.4 (s, 1C^2)
44.6 (s, 1C^3)
48.7 (s, 1C^1)
78.9 (s, 1C^7)
155.3 (s, 1C^6) ppm.

2.5.4 (*R*)-3-Aminobutan-1-azide (22)



Similar to a literature-known procedure,[3] (*R*)-boc-3-aminobutan-1-azide (**21**, 0.67 g, 3.1 mmol, 1.0 eq.) was cooled down to 0 °C in a 100 mL Schlenk flask equipped with a dropping funnel under inert atmosphere. TFA (3 mL) was slowly added through the dropping funnel. The obtained colourless solution was stirred for 3 h at rt., after which full conversion of the starting material (as affirmed by TLC) was reached. TFA was evaporated under a stream of nitrogen gas behind a blast shield. Water (15 mL) and diethyl ether (20 mL) were added to the residue. At 0 °C, 15 (10 %(w/w) sodium hydroxide solution mL) was slowly added through the dropping funnel. The organic phase was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phase was washed with brine, dried over magnesium sulphate and concentrated behind a blast shield under a stream of nitrogen gas. Thus obtained target compound **22** was used without purification as starting material for the subsequent reaction (c.f. p. SI–54).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

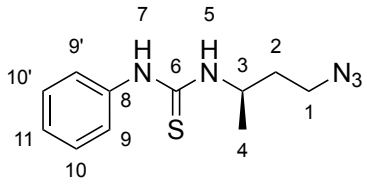
$\delta =$ 1.11 (d, $^3J_{HH} = 6.3$ Hz, 3H^4)
1.50–1.78 (m, 2H^2)
2.97–3.10 (m, 1H^3)
3.38 (t, $^3J_{HH} = 6.9$ Hz, 2H^1) ppm.

signal of H^5 is not observed.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 24.5 (s, 1C^4)
38.6 (s, 1C^2)
44.7 (s, 1C^3)
49.1 (s, 1C^1) ppm.

2.5.5 (*R*)-3-(Ph-thiourea)butan-1-azide (23)



Similar to a literature-known procedure,[3] (*R*)-3-aminobutan-1-azide (**29a**, 3.1 g, 1.0 mmol, w eq.)as dissolved in anhydrous THF (11 mL) in a 100 mL Schlenk flask under inert atmosphere. Phenyl isothiocyanate (0.47 g, 3.4 mmol, 1.1 eq.) was added and the resulting colourless solution was stirred overnight. After full conversion was affirmed by TLC, the product was concentrated, first under a stream of nitrogen gas, and, second *in vacuo* overnight. Thus obtained yellow oil was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (from 9:1, via 7:3 to 5:5) and dried *in vacuo* at rt. (*R*)-3-(Ph-thiourea)butan-1-azide (**23**, 0.25 g, 1.0 mmol, 32 %) was obtained as a colorless oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.29 (visible by ninhydrine stain).

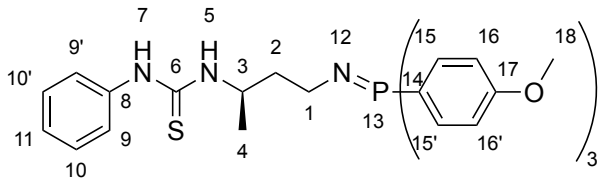
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.22 (d, $^3J_{HH} = 6.7$ Hz, 3H^4)
1.68–1.88 (m, 2H^2)
3.35–3.52 (m, 2H^1)
4.66–4.74 (m, 1H^3)
6.09 (d, $^3J_{HH} = 8.1$ Hz, 1H^5)
7.20 (d, $^3J_{HH} = 7.5$ Hz, 2H^9)
7.33 (t, $^3J_{HH} = 7.4$ Hz, 1H^{11})
7.45 (*pseudo*-t, $^3J_{HH} = 7.7$ Hz, 2H^{10})
7.63–7.69 (m, 1H^7) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 20.0 (s, 1C^4)
35.1 (s, 1C^2)
48.4 (s, 1C^1)
49.8 (s, 1C^3)
125.7 (s, 2C^9)
127.7 (s, 1C^{11})
130.4 (s, 2C^{10})
135.9 (s, 1C^8)
180.1 (s, 1C^6) ppm.

2.5.6 (*R*)-3-(Ph-thiourea)butan-1-N=P(*p*-OMe-phenyl)$_3$ (2a)



(*R*)-3-(Ph-thiourea)butan-1-N=P(*p*-OMe-phenyl)$_3$ (**2a**, 0.42 g, 0.7 mmol, 73 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from (*R*)-3-(Ph-thiourea)-butan-1-azide (**23**, 0.25 g, 1.0 mmol, 1.0 eq.) and P(*p*-OMe-phenyl)$_3$ (0.35 g, 1.0 mmol, 1.0 eq.) in anhydrous THF (2 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

A second species is observed in the NMR spectra with too low an intensity to assign its signals.

$\delta =$ 1.26 (d, $^3J_{HH} = 6.5$ Hz, 3H^4)
1.55 (*br.*, 2H^2)
3.04–3.19 (m, 1H^1)
3.27 (*br.*, 1H^1)
3.82 (s, 9H^{18})
4.48 (*br.*, 1H^3)
6.86 (d, $^3J_{HH} = 7.3$ Hz, 6H^{16})

signals of H^5 and H^7 were not observed.

6.91–6.98 (m, 1H^{11})
7.04 (*pseudo*-t, $^3J_{HH} = 7.4$ Hz, 2H^{10})
7.12 (d, $^3J_{HH} = 7.7$ Hz, 2H^9)
7.37 (*pseudo*-t, $^3J_{PH} = 9.3$ Hz, $^3J_{HH} = 9.3$ Hz, 6H^{15}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, $CDCl_3$)

$\delta =$ 22.5 (s, 1C^4)
40.9 (s, 1C^1)
42.5 (s, 1C^2)
47.1 (s, 1C^3)
55.5 (s, 3C^{18})
114.2 (d, $^3J_{PC} = 12.1$ Hz, 6C^{16})
124.7 (s, 1C^{11})
126.3 (s, 2C^9)
128.3 (s, 2C^{10})
134.3 (d, $^2J_{PC} = 10.3$ Hz, 6C^{15})
141.3 (s, 1C^8)
162.3 (s, 3C^{17}) ppm.

signals of C^6 and 3C^{14} were not observed.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, $CDCl_3$)

$\delta =$ 16.5 (*br.*, 1P^{13}) ppm.

HRMS: (MALDI positive)

calc. (for $C_{32}H_{37}N_3O_3PS$): 574.2288 u
found: 574.2253 m/z $[M+H]^+$ (target compound **2a**).

ATR-IR: (neat)

$\tilde{\nu}$ = 2965, 2837 (w, C–H, ν)
1592 (s, C=$C_{arom.}$, ν)
1497 (s, C=$C_{arom.}$, ν)
1252 (s, C–N, ν)
1176 (s, C–O_{ether}, ν)
1104, 1021, 801 (s, fingerprint, δ) $^1/_{cm}$.

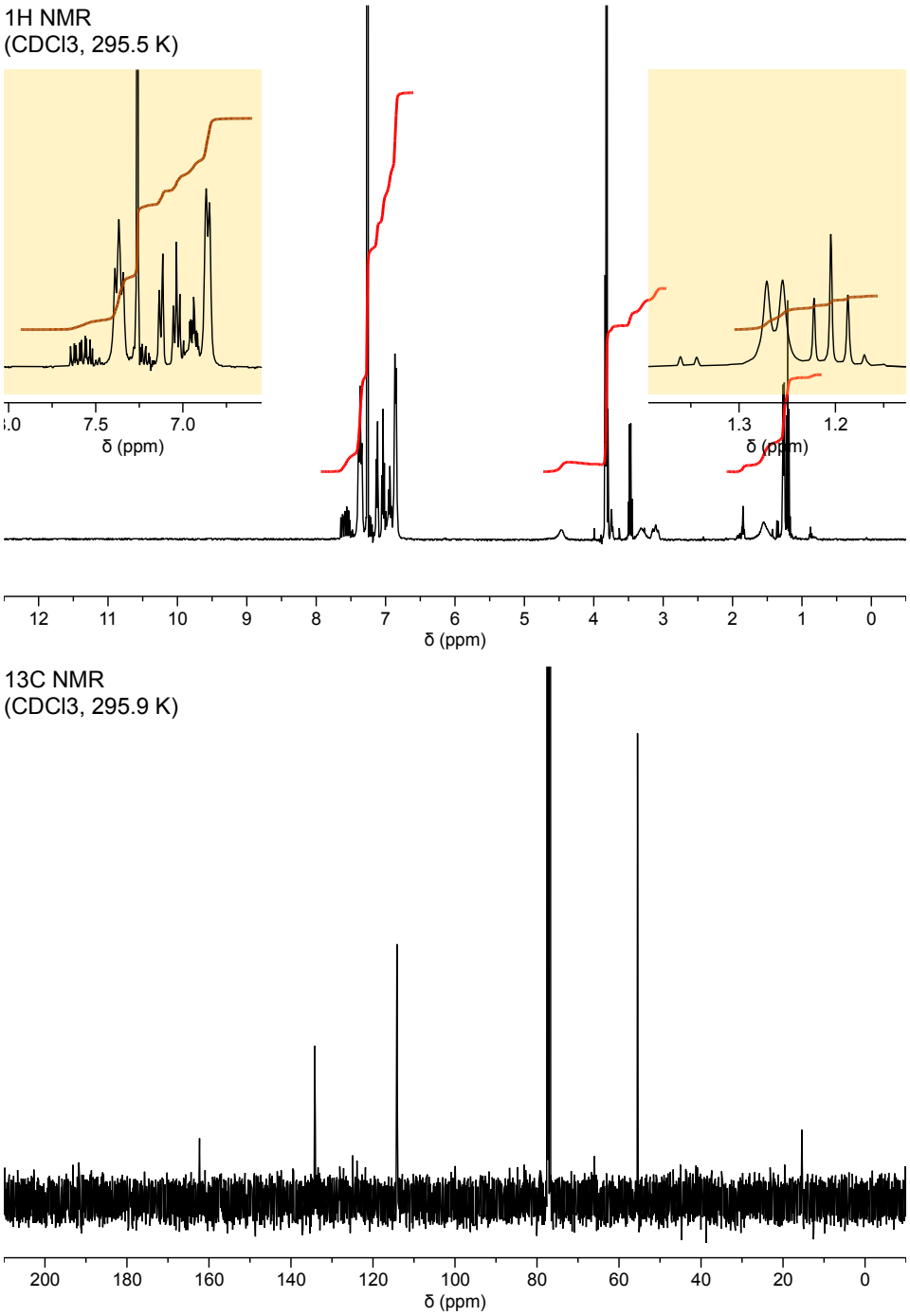
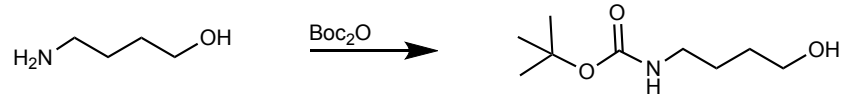
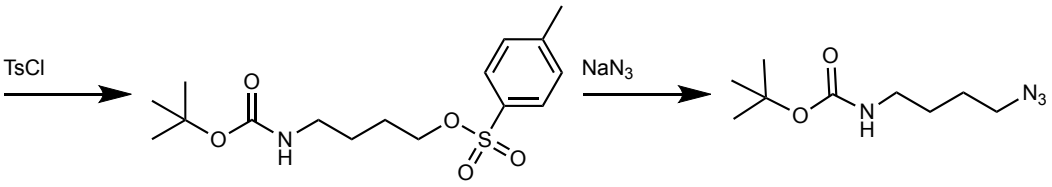


Figure SI–18: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of (*R*)-3-(Ph-thiourea)butan-1-N=P(*p*-OMe-phenyl)$_3$ (**2a**).

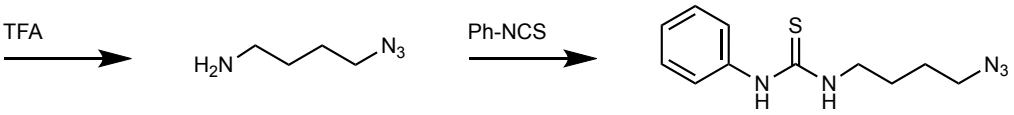
2.6 Bi-functional catalysts with butyl-spacer (cat. 3a & 3b)



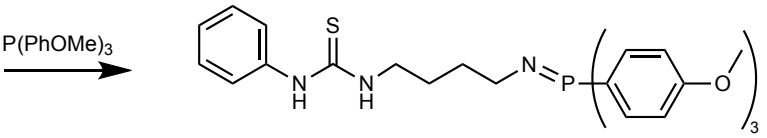
24 (p. SI–58)



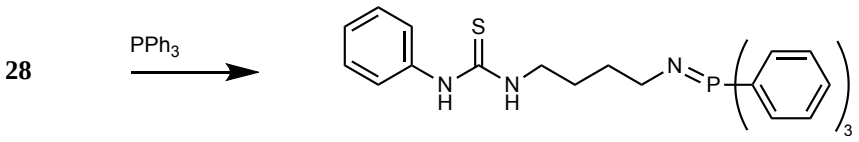
25 (p. SI–59) **26** (p. SI–60)



27 (p. SI–61) **28** (p. SI–62)



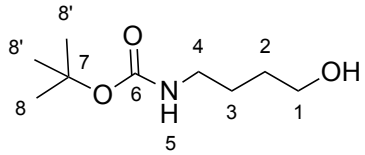
3a (p. SI–63)



3b (p. SI–65)

Scheme SI–5: 6-step syntheses of bi-functional catalysts **3a** & **3b**.

2.6.1 Boc-4-aminobutan-1-ol (24)



According to a literature-known procedure,[14] 4-aminobutan-1-ol (4.55 g, 50.0 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (100 mL) in a 250 mL 3-neck flask with dropping funnel at rt. Di-*tert*-butyl dicarbonate (12.00 g, 55.0 mmol, 1.1 eq.) was added in one portion. Over the course of 10 min, triethylamine (7.7 mL, 55.0 mmol, 1.1 eq.) was added from the dropping funnel and the mixture was stirred at rt. for 20 h. After full conversion (as affirmed by TLC), the organic phase was washed with water, the organic phase was separated and the aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with brine, dried over magnesium sulphate, concentrated under reduced pressure at 40 °C and dried *in vacuo*. Boc-4-aminobutan-1-ol (**24**, 9.78 g, 45.9 mmol, 92 %) was obtained with 89 %(w/w) purity as a colourless oil.

TLC: [ethly acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.20 (visible by *p*-anisaldehyde stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

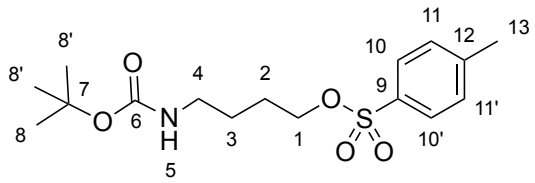
NMR signals are in accordance with literature data.[14]

$\delta =$ 1.43 (s, 9H^8)
1.54–1.65 (m, 4H^{2,3})
1.71 (*br.*, 1H^{OH})
3.06–3.22 (m, 2H^4)
3.62–3.69 (m, 1H^1)
4.63 (*br.*, 1H^5) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 26.8 (s, 1C^2)
28.6 (s, 3C^8)
29.8 (s, 1C^3)
40.4 (s, 1C^4)
62.6 (s, 1C^1)
79.3 (s, 1C^7)
156.3 (s, 1C^6) ppm.

2.6.2 Boc-4-aminobutan-1-tosylate (25)



Similar to a literature-known procedure,[8] boc-4-aminobutan-1-ol (**24**, 9.79 g, 46.0 mmol, 1.0 eq.) was dissolved in CH_2Cl_2 (65 mL) and triethylamine (7.1 mL, 50.6 mmol, 1.1 eq.) in a 250 mL 3-neck flask. 4-Toluenesulfonyl chloride (8.77 g, 46.0 mmol, 1.0 eq.) and 4-dimethylaminopyridine (0.28 g, 2.3 mmol, 0.05 eq.) were added subsequently. The reaction mixture was stirred for 20 h and turned brown. After full conversion of the starting material (as affirmed by TLC), the organic phase was washed with water, the organic phase was separated and the combined aqueous phase was extracted twice using CH_2Cl_2. The combined organic phase was washed with 20 %(w/w) citric acid (100 mL) and brine, dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. Thus obtained crude material was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (9:1 and 7:3) and concentrated under reduced pressure at 40 °C. Boc-4-aminobutan-1-tosylate (**25**, 7.41 g, 20.8 mmol, 45 %) was obtained with 96 %(w/w) purity as a colourless oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.20 (visible by UV light and *p*-anisaldehyde stain).

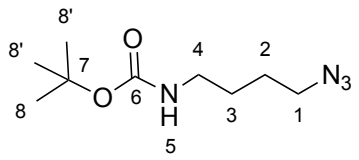
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.42 (s, 9H^8)
1.48–1.57 (m, 2H^3)
1.63–1.73 (m, 2H^2)
2.45 (s, 3H^{13})
3.08 (*pseudo*-q, $^3J_{HH} = 6.7$ Hz, 2H^4)
4.03 (t, $^3J_{HH} = 6.6$ Hz, 2H^1)
4.50 (*br.*, 1H^5)
7.34 (d, $^3J_{HH} = 8.2$ Hz, 2H^{11}) ppm.
7.78 (d, $^3J_{HH} = 8.3$ Hz, 2H^{10}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 21.8 (s, 1C^{13})
26.3 (s, 2C^2 + 1C^3)
28.5 (s, 3C^8)
39.9 (s, 1C^4)
70.3 (s, 1C^1)
79.4 (s, 1C^7)
128.0 (s, 2C^{10})
130.0 (s, 2C^{11})
133.2 (s, 1C^9)
144.9 (s, 1C^{12})
155.1 (s, 1C^6) ppm.

2.6.3 Boc-4-aminobutan-1-azide (26)



Similar to a literature-known procedure,[3] Boc-4-aminobutan-1-tosylate (**25**, 7.38 g, 20.7 mmol, 1.0 eq.) was dissolved in DMF (70 mL) in a 500 mL flask at rt. Sodium azide (1.48 g, 22.8 mmol, 1.1 eq.) was added in one portion. The solution was stirred for 20 h at 45 °C. After full conversion of the starting material (as affirmed by TLC), the organic phase was diluted with diethyl ether (50 mL) and water (150 mL). The organic phase was separated and the aqueous phase was extracted twice using diethyl ether. The combined organic phase was washed with water (2x) and brine (1x), dried over magnesium sulphate and concentrated under reduced pressure at 40 °C. Boc-4-aminobutan-1-azide (**26**, 4.20 g, 19.6 mmol, 95 %) was obtained as a yellow oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.41 (visible by UV light, *p*-anisaldehyde stain and ninhydrine stain).

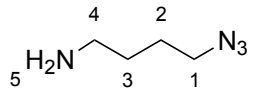
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.44 (s, 9H^8)
1.51–1.65 (m, 4H^{2,3})
3.10–3.19 (m, 2H^4)
3.30 (t, $^3J_{HH} = 6.5$ Hz, 2H^1)
4.56 (*br.*, 1H^5) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 26.3 (s, 1C^3)
27.5 (s, 1C^2)
28.5 (s, 3C^8)
40.1 (s, 1C^4)
51.2 (s, 1C^1)
79.4 (s, 1C^7)
156.1 (s, 1C^6) ppm.

2.6.4 4-Aminobutan-1-azide (27)



Similar to a literature-known procedure,[3] Boc-4-aminobutan-1-tosylate (**26**, 2.14 g, 10.0 mmol, 1.0 eq.) was cooled down to 0 °C in a 100 mL Schlenk flask equipped with a dropping funnel under inert atmosphere. trifluoroacetic acid (10 mL) was slowly added through the dropping funnel. The obtained colourless solution was stirred for 3 h at rt., after which full conversion of the starting material (as affirmed by TLC) was reached. TFA was evaporated under a stream of nitrogen gas behind a blast shield. Water (40 mL) and diethyl ether (40 mL) were added to the residue. At 0 °C, 40 (10 %(w/w) sodium hydroxide solution mL) was slowly added through the dropping funnel. The organic phase was separated and the aqueous phase was extracted twice with diethyl ether. The combined organic phase was washed with brine, dried over magnesium sulphate and concentrated behind a blast shield under a stream of nitrogen gas. Thus obtained product was used without purification as starting material for the subsequent reaction (c.f. p. SI–62).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

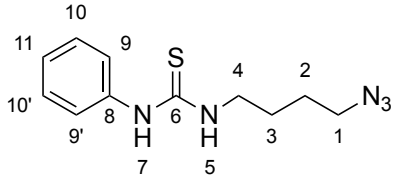
$\delta =$ 1.46–1.57 (m, 2H^3)
1.59–1.72 (m, 2H^2)
2.72 (t, $^3J_{HH} = 6.9$ Hz, 2H^4)
3.29 (t, $^3J_{HH} = 6.8$ Hz, 2H^1) ppm.

signal of H^5 is not observed.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 26.4 (s, 1C^2)
31.0 (s, 1C^3)
41.9 (s, 1C^4)
51.5 (s, 1C^1) ppm.

2.6.5 4-(Ph-thiourea)butan-1-azide (28)



Similar to a literature-known procedure,[3] 4-aminobutan-1-azide (**27**, 1.14 g, 10.0 mmol, 1.0 eq.) was dissolved in anhydrous THF (35 mL) in a 100 mL Schlenk flask under inert atmosphere. Phenyl isothiocyanate (1.49 g, 11.0 mmol, 1.1 eq.) was added and the resulting colourless solution was stirred overnight. After full conversion was affirmed by TLC, the product was concentrated, first under a stream of nitrogen gas, and, second *in vacuo*. Thus obtained yellow oil was purified by column chromatography using a step gradient of *n*-heptane:ethyl acetate (from 9:1 via 7:3 to 1:1) and dried *in vacuo* at rt. 4-(Ph-thiourea)butan-1-azide (**28**, 0.16 g, 0.6 mmol, 6 %) was obtained as a yellow oil.

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.24 (visible by UV light and ninhydrine stain).

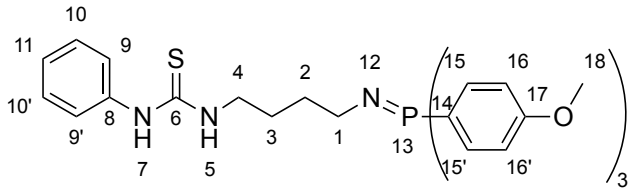
^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 1.59–1.72 (m, 4H^{2,3})
3.31 (t, $^3J_{HH} = 6.3$ Hz, 2H^1)
3.67 (t, $^3J_{HH} = 6.6$ Hz, 2H^4)
6.05 (*br.*, 1H^5)
7.20 (d, $^3J_{HH} = 7.5$ Hz, 2H^9)
7.32 (t, $^3J_{HH} = 7.4$ Hz, 1H^{11})
7.45 (*pseudo*-t, $^3J_{HH} = 7.7$ Hz, 2H^{10})
7.62–7.93 (m, 1H^7) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 26.3 (s, 1C^2)
26.5 (s, 1C^3)
45.0 (s, 1C^4)
51.2 (s, 1C^1)
125.6 (s, 1C^9)
127.7 (s, 2C^{11})
130.5 (s, 2C^{10})
136.0 (s, 1C^8)
181.0 (s, 1C^6) ppm.

2.6.6 4-(Ph-thiourea)-butan-1-N=P(*p*-OMe-phenyl)$_3$ (3a)



4-(Ph-thiourea)-butan-1-N=P(*p*-OMe-phenyl)$_3$ (**3a**, 0.340 g, 0.59 mmol, 93 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from 4-(Ph-thiourea)-butan-1-azide (**28**, 0.160 g, 0.64 mmol, 1.0 eq.) and P(*p*-OMe-phenyl)$_3$ (0.225 g, 0.64 mmol, 1.0 eq.) in anhydrous THF (1 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

A second species is observed in the NMR spectra with too low an intensity to assign its signals.

$\delta =$ 1.59–1.67 (m, 2H^2)
1.67–1.76 (m, 2H^3)
2.98–3.12 (m, 2H^1)
3.62 (*br.*, 2H^4)
3.80 (s, 9H^{18})
6.91 (d, $^3J_{HH} = 7.2$ Hz, 6H^{16})
7.03–7.11 (m, 2H^9 + 1H^{11})
7.40–7.49 (m, 6H^{15}) ppm.

signals of H^5 and H^7 were not observed.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, $CDCl_3$)

$\delta =$ 26.6 (s, 1C^3)
30.2 (s, 1C^2)
44.2 (s, 1C^1)
44.8 (s, 1C^4)
55.5 (s, 3C^{18})
114.4 (d, $^3J_{PC} = 12.6$ Hz, 6C^{16})
124.1 (s, 2C^9)
124.7 (s, 1C^{11})
128.9 (s, 2C^{10})
134.5 (d, $^2J_{PC} = 10.5$ Hz, 6C^{15})
138.3 (s, 1C^8)
162.5 (s, 3C^{17}) ppm.

signals of C^6 and 3C^{14} were not observed.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, $CDCl_3$)

$\delta =$ 15.9 (*br.*, 1P^{13}) ppm.

HRMS: (MALDI positive)

calc. (for $C_{32}H_{37}N_3O_3PS$): 574.2288 u
found: 574.2253 m/z $[M+H]^+$ (target compound **3a**).

ATR-IR: (neat)

$\tilde{\nu} =$ 2929, 2837 (w, C–H, ν)
1593 (s, C=$C_{arom.}$, ν)
1497 (s, C=$C_{arom.}$, ν)
1251 (s, C–N, ν)
1177 (m, C–O_{ether}, ν)
1115, 1021, 802 (s, fingerprint, δ) $^1/_{cm}$.

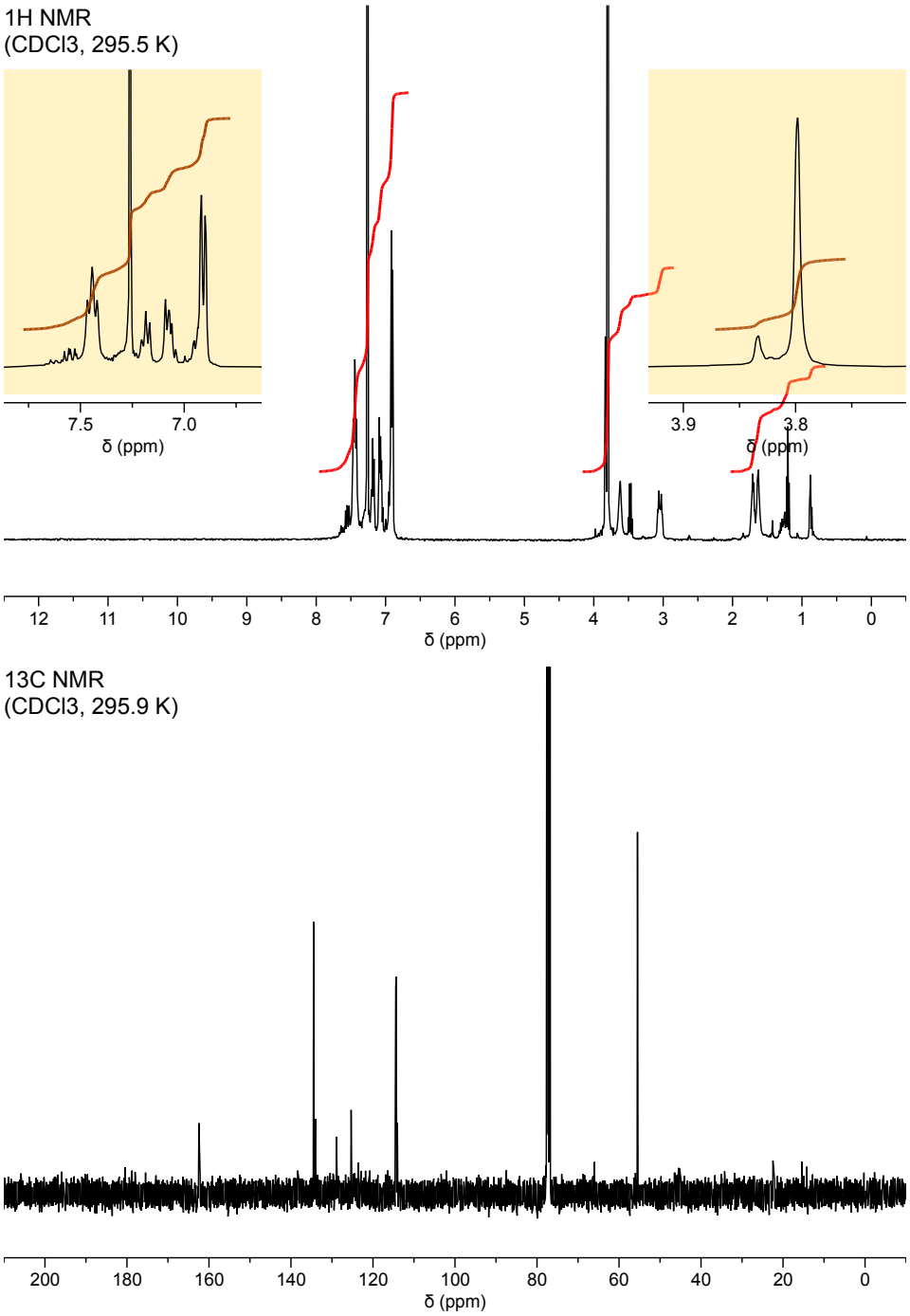
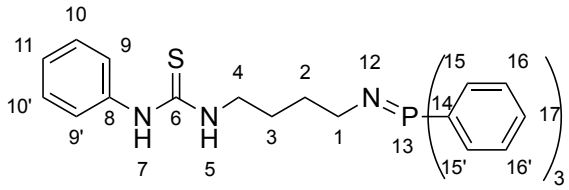


Figure SI–19: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of 4-(Ph-thiourea)-butan-1-N=P(*p*-OMe-phenyl)$_3$ (**3a**).

2.6.7 4-(Ph-thiourea)-butan-1-N=PPh$_3$ (3b)



4-(Ph-thiourea)-butan-1-N=PPh$_3$ (**3b**, 0.148 g, 0.31 mmol, 73 %) was obtained as a white solid after synthesis according to the general procedure (c.f. p. SI–4) from 4-(Ph-thiourea)-butan-1-azide (**28**, 0.109 g, 0.42 mmol, 1.0 eq.) and PPh$_3$ (0.110 g, 0.42 mmol, 1.0 eq.) in anhydrous THF (0.7 mL) and isolation according to the purification method B (c.f. p. SI–4).

TLC: [ethyl acetate:*n*-heptane (1:2 per volume)]

$R_f =$ 0.00 (visible by UV light and ninhydrine stain).

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

Two species are observed in the NMR spectra (one of which is labelled with an apostrophe). In case the signals of both species overlap, the overlapped signal is labelled with an asterisks.

$\delta =$ 1.42 (*pseudo*-p, $^3J_{HH} = 6.6$ Hz, 2H$^{2'}$)
1.59 (*pseudo*-p, $^3J_{HH} = 6.6$ Hz, 2H$^{3'}$)
2.63–1.69 (m, 2H^2)
1.69–1.74 (m, 2H^3)
2.60 (t, $^3J_{HH} = 6.5$ Hz, 2H$^{1'}$)
3.07 (*br.*, 2H^1)
3.57 (t, $^3J_{HH} = 6.8$ Hz, 2H$^{4'}$)
3.60–3.64 (m, 2H^4)
7.01–7.41 (m, 2H^9 + 2H^{10} + 1H^{11} + 2H$^{9'}$ + 2H$^{10'}$ + 1H$^{11'}$)
7.43–7.69 (m, 2H^{15} + 2H^{16} + 1H^{17} + 2H$^{15'}$ + 2H$^{16'}$ + 1H$^{17'}$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 296 K, $CDCl_3$)

$\delta =$ 26.0 (s, 1C^3 + 1C$^{3'}$)
30.2 (s, 1C$^{2'}$)
31.1 (s, 1C^2)
41.8 (s, 1C$^{1'}$)
44.1 (s, 1C^1)
44.7 (s, 1C^4 + 1C$^{4'}$)
181.3 (s, 1C^6 + 1C$^{6'}$) ppm.

^{13}C aromatic region has too low an intensity to be assigned.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, $CDCl_3$)

$\delta =$ 18.4 (*br.*, 1P^{13})
27.9 (s, 1P$^{13'}$) ppm.

HRMS: (MALDI positive)

calc. (for $C_{29}H_{31}N_3PS$): 484.1971 u
found: 484.2001 m/z $[M+H]^+$ (target compound **3b**).

ATR-IR: (neat)

$\tilde{\nu} =$ 3390 (w, N–H, ν)
3160, 3018, 2928 (w, C–H, ν)
1587 (m, C=C$_{arom.}$, ν)
1528 (s, C=C$_{arom.}$, ν)
1196 (s, C–N, ν)
1108, 692 (s, fingerprint, δ) 1/cm.

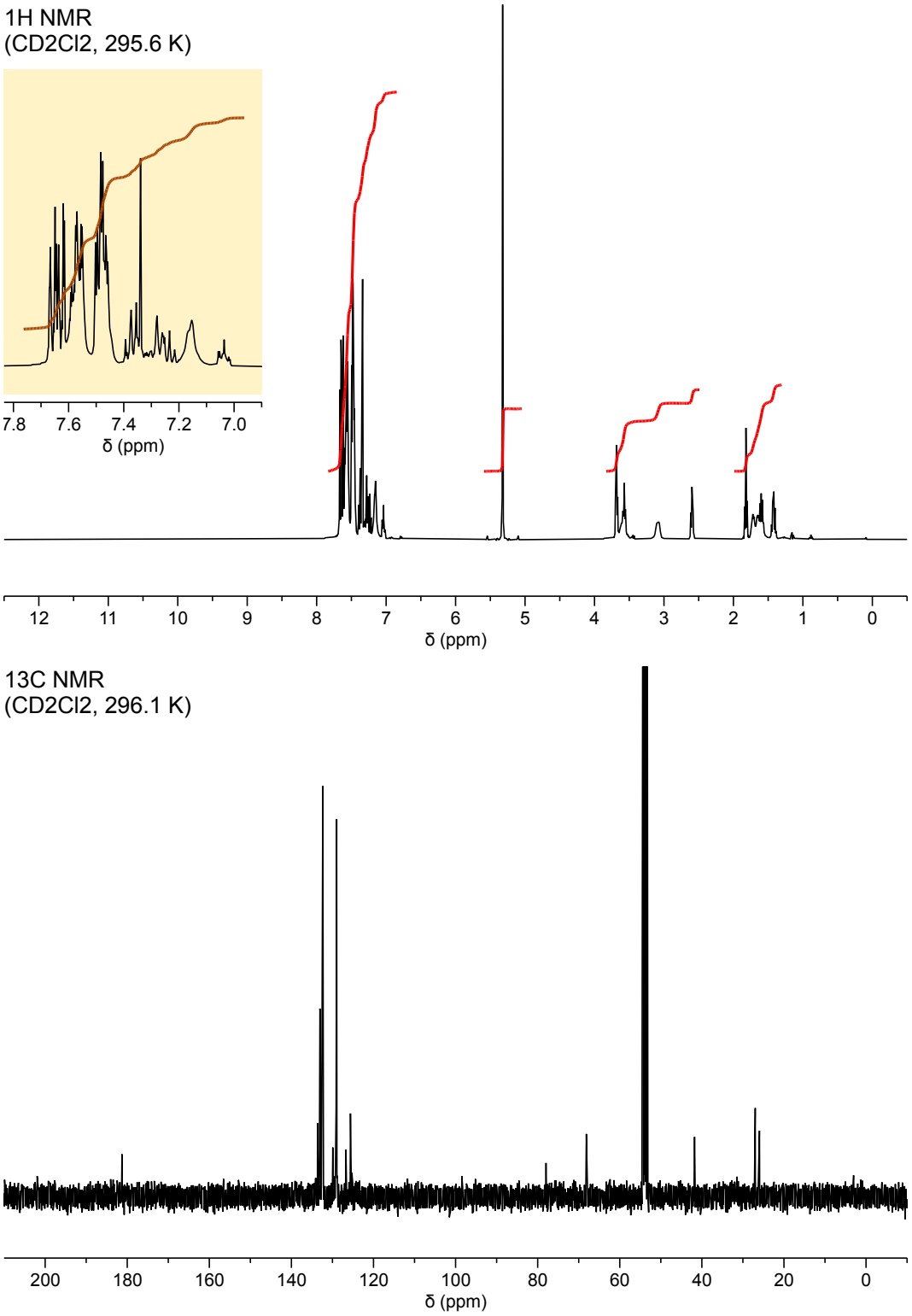
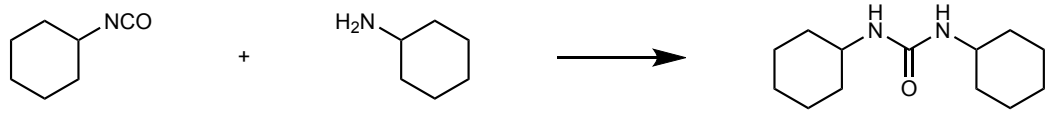
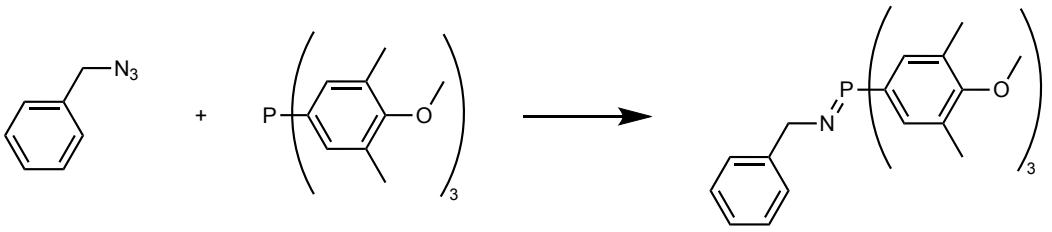


Figure SI–20: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of 4-(Ph-thiourea)-butan-1-N=PPh_3 (**3b**).

2.7 Mono-functional catalysts (urea 6 & base 7)



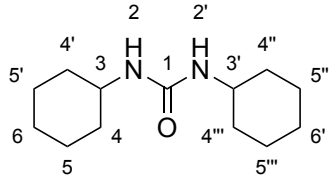
6 (p. SI–68)



7 (p. SI–70)

Scheme SI–6: 1-step syntheses of mono-functional catalysts (urea **6** and base **7**).

2.7.1 Dicyclohexylurea (6)



According to a literature-known procedure,[15] cyclohexyl isocynate (1.00 g, 8.0 mmol, 1.0 eq.) was dissolved in anhydrous CH_2Cl_2 (5 mL) in a 25 mL Schlenk tube under inert atmosphere. Cyclohexylamine (1.1 mL, 9.6 mmol, 1.2 eq.) and triethylamine (2.3 mL, 16.0 mmol, 2.0 eq.) were added drop-wise via syringe and the resulting white suspension was stirred overnight. The precipitate was collected, washed with CH_2Cl_2 (2x) and dried *in vacuo* at rt. Dicyclohexylurea (**6**, 1.562 g, 7.0 mmol, 87 %) was obtained as a white solid.

^{1}H NMR: (400 MHz, 296 K, DMSO-d_6)

$\delta =$ 0.98–1.09 (m, 4H^4)
1.09–1.18 (m, 2H^6)
1.18–1.31 (m, 4H^5)
1.45–1.55 (m, 2H^6)
1.56–1.67 (m, 4H^5)
1.67–1.77 (m, 4H^4)
3.25–3.39 (m, 2H^3)
5.57 (d, $^3J_{HH} = 8.0$ Hz, 2H^2) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, DMSO-d_6)

$\delta =$ 24.5 (s, 4C^5)
25.3 (s, 2C^6)
33.4 (s, 4C^4)
47.5 (s, 2C^3)
156.6 (s, 1C^1) ppm.

^{13}C NMR assignment according to SDBS (2022-12-19).

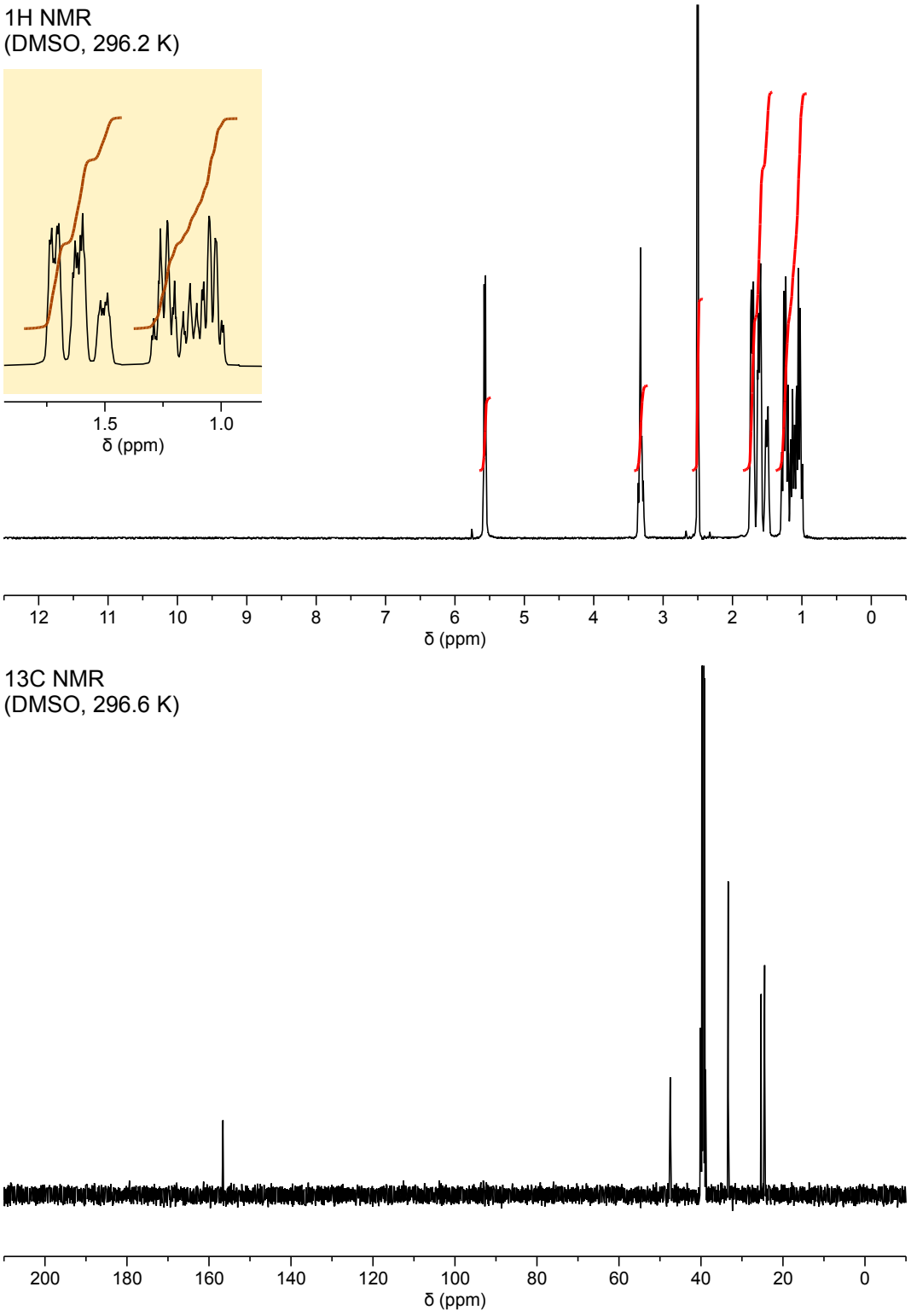
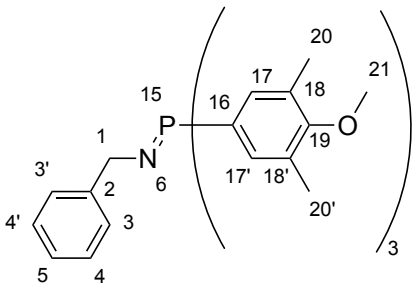


Figure SI–21: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of dicyclohexylurea (**6**).

2.7.2 Benzyl-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (7)



In a 10 mL Schlenk tube, P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (0.11 g, 0.25 mmol, 1.0 eq.) was evacuated and flushed with nitrogen gas (3x). 0.5 M benzyl azide solution in CH_2Cl_2 (0.5 mL, 0.25 mmol, 1.0 eq.) were added drop-wise via syringe and the resulting solution was stirred overnight. Full conversion of the starting material was affirmed by ^{31}P and ^{1}H NMR (therefore, 2/5 of the solution were removed from the reaction mixture and used as aliquot). The remaining 3/5 of the solution were first dried under a stream of nitrogen gas, and, second *in vacuo*. Benzyl-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**7**, 0.08 g, 0.14 mmol, 93 %) was obtained as a white foam.

^{1}H NMR: (400 MHz, 296 K, $CDCl_3$)

$\delta =$ 2.27 (d, $^{5}J_{PH} = 4.6$ Hz, 18H^{20})
3.75 (d, $^{7}J_{PH} = 5.6$ Hz, 9H^{21})
4.25 (d, $^{3}J_{PH} = 17.8$ Hz, 2H^{1})
7.08–7.21 (m, 2H^{3} or 2H^{4})
7.27–7.37 (m, 2H^{3} or 2H^{4} + 1H^{5} + 6H^{17}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, $CDCl_3$)

$\delta =$ 16.4 (s, 6C^{20})
50.3 (s, 1C^{1})
59.8 (d, $^{6}J_{PC} = 5.4$ Hz, 3C^{21})
127.7 (s, 1C^{5})
127.9 (s, 2C^{3} or 3C^{4})
131.4 (d, $^{3}J_{PC} = 13.6$ Hz, 6C^{18})
132.9 (d, $^{2}J_{PC} = 10.6$ Hz, 6C^{17})
133.8 (s, 2C^{3} or 3C^{4})
160.1 (s, 3C^{19}) ppm.

signals of C^{2} and C^{16} were not observed.

^{31}P{^{1}H} NMR: (162 MHz, 297 K, $CDCl_3$)

$\delta =$ 28.5 (s, 1P^{15}) ppm.

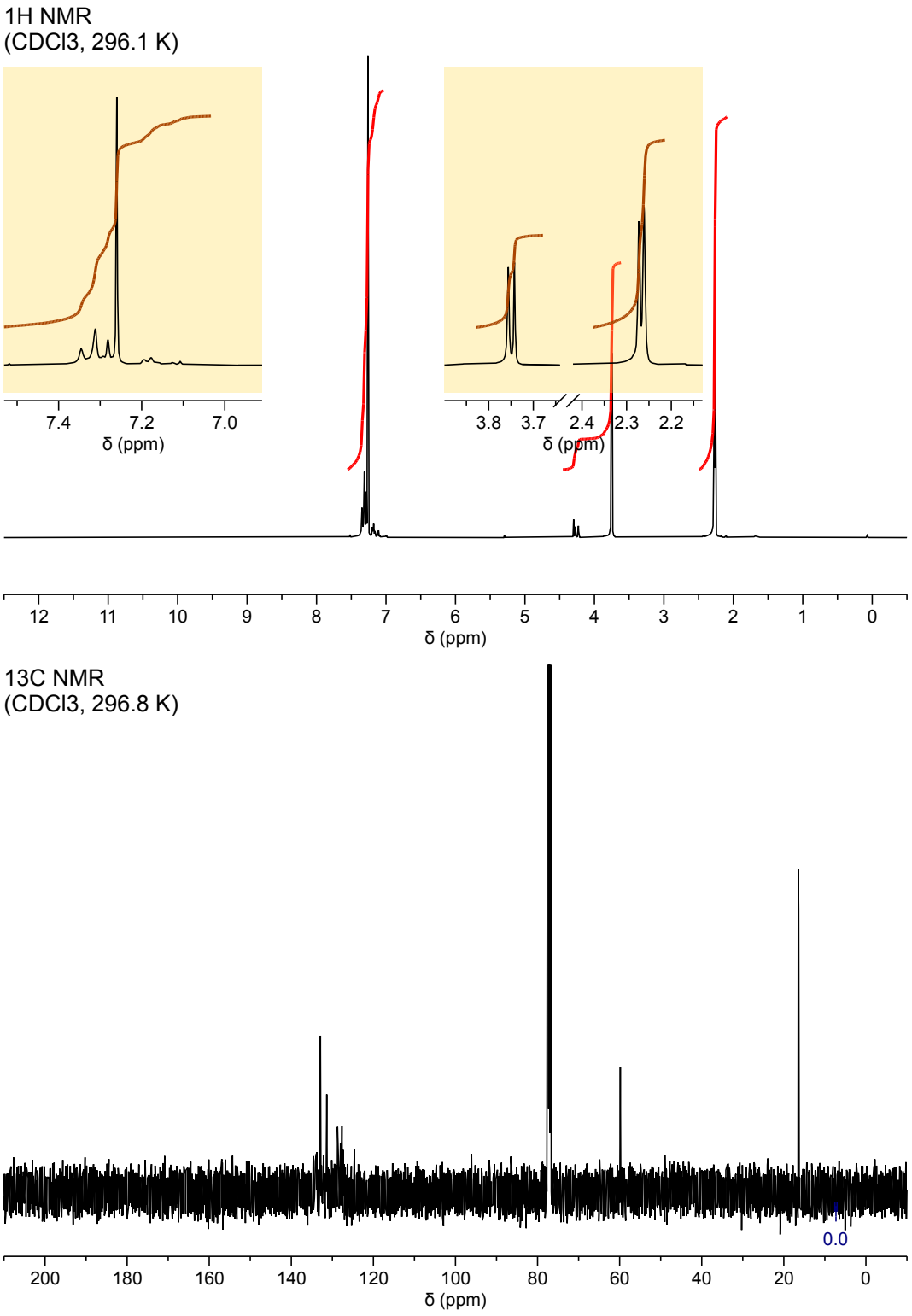


Figure SI–22: ^{1}H NMR spectrum (top) and ^{13}C NMR spectrum (bottom) of benzyl-N=P[(*m*-Me)$_2$-(*p*-OMe)-phenyl]$_3$ (**7**).

3 NMR studies of catalyst 5a in toluene-d_8

Table SI–4: Composition of NMR samples: Given quantities of catalyst **5a**, BA, PA and CHO as well as toluene-d_8 (0.5 mL) were filled into an NMR tube that was flame-sealed afterwards.

sample composition	catalyst **5a**		BA		PA		CHO	
	m [mg]	n [µmol]	m [mg]	n [µmol]	m [mg]	n [µmol]	m [mg]	n [µmol]
1: —/—/——/[**5a**]	5.1	8.6	—		—		—	
2: —/—/——/[**5a**]HCl[a]	2.1	3.5	—		—		—	
3: BA/—/——/[**5a**]	4.9	8.3	1.4	13.0	—		—	
4: BA/—/CHO/[**5a**]	6.4	10.8	1.1	10.8	—		6.0	61.1
5: BA/PA/——/[**5a**]	5.2	8.8	1.1	10.2	1.6	10.8	—	
6: BA/PA/CHO/[**5a**]	5.8	9.8	1.4	13.0	2.1	14.2	0.8	8.2
7: —/PA/——/[**5a**]	4.7	7.9	—		1.6	10.8	—	

[a] The protonated catalyst **5a** was obtained by washing the catalyst (dissolved in ethyl acetate) with hydrochloric acid followed by isolation of the protonated catalyst from the organic phase.

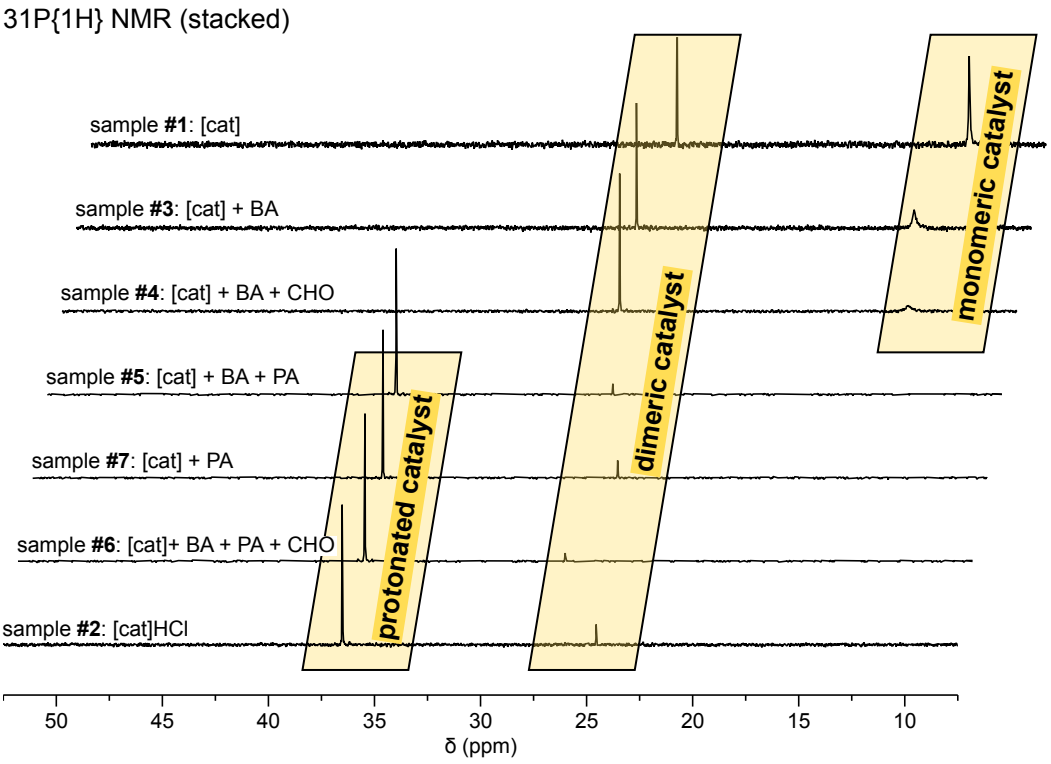
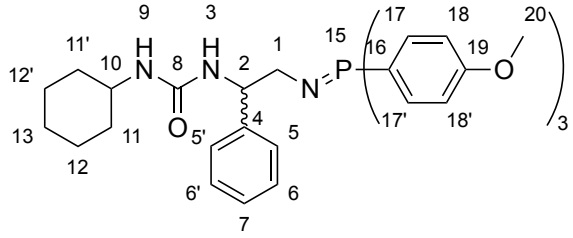


Figure SI–23: Stacked ^{31}P NMR spectra of samples #1 to #7 (table SI–4): Three species of the catalyst **5a** are observed, which correspond to a monomeric species ($\delta_{^{31}P} \sim 12$ ppm), a dimeric species ($\delta_{^{31}P} \sim 25$ ppm) and a protonated species ($\delta_{^{31}P} \sim 37$ ppm).

NMR assignment of monomeric catalyst 5a in toluene-d_8



^{1}H NMR: (400 MHz, 296 K, toluene-d_8)

NMR data of sample 1 in table SI–4.

$\delta =$ 0.82–1.06 (m, 2H^{11} + 1H^{13})
1.13–1.31 (m, 2H^{12})
1.35–1.43 (m, 1H^{13})
1.42–1.55 (m, 2H^{12})
1.89–1.99 (m, 2H^{11})
3.26 (s, 9H^{20})
3.49 (ddd, $^3J_{PH} = 16.8$ Hz, $^2J_{HH} = 11.5$ Hz, $^3J_{HH} = 7.1$ Hz, 1H^1)
3.64 (ddd, $^2J_{HH} = 11.9$ Hz, $^3J_{PH} = 11.8$ Hz, $^3J_{HH} = 3.9$ Hz, 1H^1)
3.76–3.89 (m, 1H^{10})
4.92 (ddd, $^3J_{HH} = 7.9$ Hz, $^4J_{PH} = 4.4$ Hz, $^3J_{HH} = 4.3$ Hz, 1H^2)
5.67 (d, $^3J_{HH} = 7.4$ Hz, 1H^9)
6.28 (d, $^3J_{HH} = 4.6$ Hz, 1H^3)
6.69 (dd, $^3J_{HH} = 8.8$ Hz, $^4J_{PH} = 2.0$ Hz, 6H^{18})
7.04–7.14 (m, 2H^6 + 1H^7)
7.38 (d, $^3J_{HH} = 7.2$ Hz, 2H^5)
7.56 (dd, $^3J_{PH} = 10.9$ Hz, $^3J_{HH} = 8.7$ Hz, 6H^{17}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, toluene-d_8)

^{13}C chemical shifts were extracted from HSQC and HMBC NMR spectra.

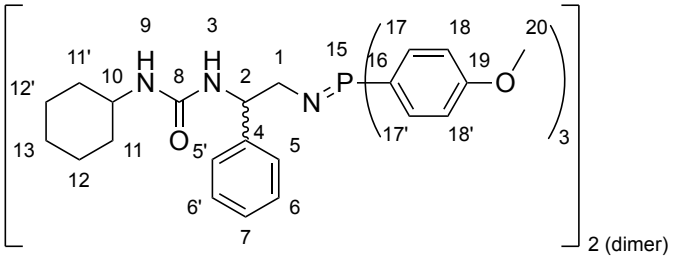
$\delta =$ 25.4 (s, 2C^{12})
26.1 (s, 1C^{13})
34.1 (s, 2C^{11})
48.8 (s, 1C^{10})
53.6 (s, 1C^1)
54.7 (s, 3C^{20})
59.9 (s, 1C^2)
114.3 (d, $^3J_{PC} = 12.5$ Hz, 6C^{18})
123.1 (d, $^1J_{PC} = 100 \pm 5$ Hz, 3C^{16})
134.7 (d, $^2J_{PC} = 10.3$ Hz, 6C^{17})
144.5 (s, 1C^4)
162.4 (d, $^4J_{PC} = 3.0$ Hz, 3C^{19}) ppm.

signals of 2C^5, 2C^6, C^7 and C^8 were not observed.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, toluene-d_8)

$\delta =$ 11.1 (*br.*, 1P^{15}) ppm.

NMR assignment of dimeric catalyst 5a in toluene-d_8



^{1}H NMR: (400 MHz, 296 K, toluene-d_8)

NMR data of sample 1 in table SI–4.

$\delta =$ 0.82–1.06 (m, $2H^{11} + 1H^{13}$)
1.13–1.31 (m, $2H^{12}$)
1.35–1.43 (m, $1H^{13}$)
1.42–1.55 (m, $2H^{12}$)
1.89–1.99 (m, $2H^{11}$)
2.48 (dd, $^{2}J_{HH} = 9.2$ Hz, $^{3}J_{HH} = 3.2$ Hz, $1H^{1}$)
2.91 (dd, $^{3}J_{HH} = 9.4$ Hz, $^{2}J_{HH} = 9.3$ Hz, $1H^{1}$)
3.23 (s, $9H^{20}$)
3.76–3.89 (m, $1H^{10}$)
5.05 (dd, $^{3}J_{HH} = 9.6$ Hz, $^{3}J_{HH} = 3.1$ Hz, $1H^{2}$)
5.33 (d, $^{3}J_{HH} = 8.1$ Hz, $1H^{9}$)
6.38 (d, $^{3}J_{HH} = 7.9$ Hz, $1H^{3}$)
6.66 (dd, $^{3}J_{HH} = 8.9$ Hz, $^{4}J_{PH} = 2.1$ Hz, $6H^{18}$)
7.04–7.31 (m, $2H^{5} + 2H^{6} + 1H^{7}$)
7.68 (dd, $^{3}J_{PH} = 11.3$ Hz, $^{3}J_{HH} = 8.8$ Hz, $6H^{17}$) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, toluene-d_8)

^{13}C chemical shifts were extracted from HSQC and HMBC NMR spectra.

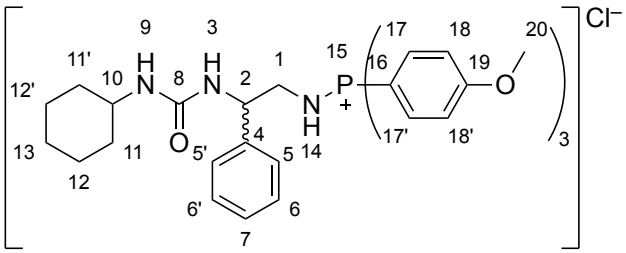
$\delta =$ 25.4 (s, $2C^{12}$)
26.1 (s, $1C^{13}$)
34.1 (s, $2C^{11}$)
48.7 (s, $1C^{1}$)
48.8 (s, $1C^{10}$)
54.7 (s, $3C^{20}$)
56.5 (s, $1C^{2}$)
114.2 (d, $^{3}J_{PC} = 12.8$ Hz, $6C^{18}$)
125.7 (d, $^{1}J_{PC} = 105 \pm 5$ Hz, $3C^{16}$)
134.2 (d, $^{2}J_{PC} = 11.0$ Hz, $6C^{17}$)
143.5 (s, $1C^{4}$)
162.6 (d, $^{4}J_{PC} = 3.0$ Hz, $3C^{19}$) ppm.

signals of $2C^{5}$, $2C^{6}$, C^{7} and C^{8} were not observed.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, toluene-d_8)

$\delta =$ 24.9 (s, $1P^{15}$) ppm.

NMR assignment of protonated catalyst 5a in toluene-d_8



^{1}H NMR: (400 MHz, 296 K, toluene-d_8)

NMR data of sample 2 in table SI–4.

$\delta =$ 1.03–1.56 (m, 2H^{11} + 2H^{12} + 2H^{13})
1.62–1.74 (m, 2H^{12})
1.88–2.06 (m, 2H^{11})
3.12–3.21 (m, 1H^{1})
3.33 (s, 9H^{20})
3.39–3.53 (m, 1H^{1})
3.83 (*br.*, 1H^{10})
5.19–5.27 (mz, 1H^{2})
6.95 (*br.*, 1H^{9}) $\mapsto$ observed in ^{1}H-^{1}H COSY, but hidden in ^{1}H NMR (by solvent signals)
6.81 (dd, $^{3}J_{\mathrm{HH}} = 8.9$ Hz, $^{4}J_{\mathrm{PH}} = 2.6$ Hz, 6H^{18})
7.03–7.08 (m, 2H^{6} + 1H^{7})
7.43 (d, $^{3}J_{\mathrm{HH}} = 7.3$ Hz, 2H^{5})
7.61 (dd, $^{3}J_{\mathrm{PH}} = 12.3$ Hz, $^{3}J_{\mathrm{HH}} = 8.8$ Hz, 6H^{17})
8.58 (d, $^{3}J_{\mathrm{HH}} = 8.6$ Hz, 1H^{3})
8.77 (*pseudo*-q, $^{3}J_{\mathrm{HH}} = 7.3$ Hz, $^{2}J_{\mathrm{PH}} = 7.3$ Hz, 1H^{14}) ppm.

^{13}C{^{1}H} NMR: (101 MHz, 297 K, toluene-d_8)

^{13}C chemical shifts were extracted from HSQC and HMBC NMR spectra.

$\delta =$ 25.3 (s, 2C^{12})
26.2 (s, 1C^{13})
34.1 (*br.*, 2C^{11})
48.9 (s, 1C^{1})
49.0 (s, 1C^{10})
55.3 (s, 3C^{20})
55.9 (s, 1C^{2})
115.6 (d, $^{3}J_{\mathrm{PC}} = 14.5$ Hz, 6C^{18})
113.7 (d, $^{1}J_{\mathrm{PC}} = 118\pm5$ Hz, 3C^{16})
126.8 (s, 1C^{7})
127.6 (s, 2C^{5})
128.4 (s, 2C^{6})
135.9 (d, $^{2}J_{\mathrm{PC}} = 12.5$ Hz, 6C^{17})
142.5 (s, 1C^{4})
164.5 (d, $^{4}J_{\mathrm{PC}} = 2.9$ Hz, 3C^{19}) ppm.

signal of C^{8} was not observed.

^{31}P{^{1}H} NMR: (162 MHz, 296 K, toluene-d_8)

$\delta =$ 36.5 (s, 1P^{15}) ppm.

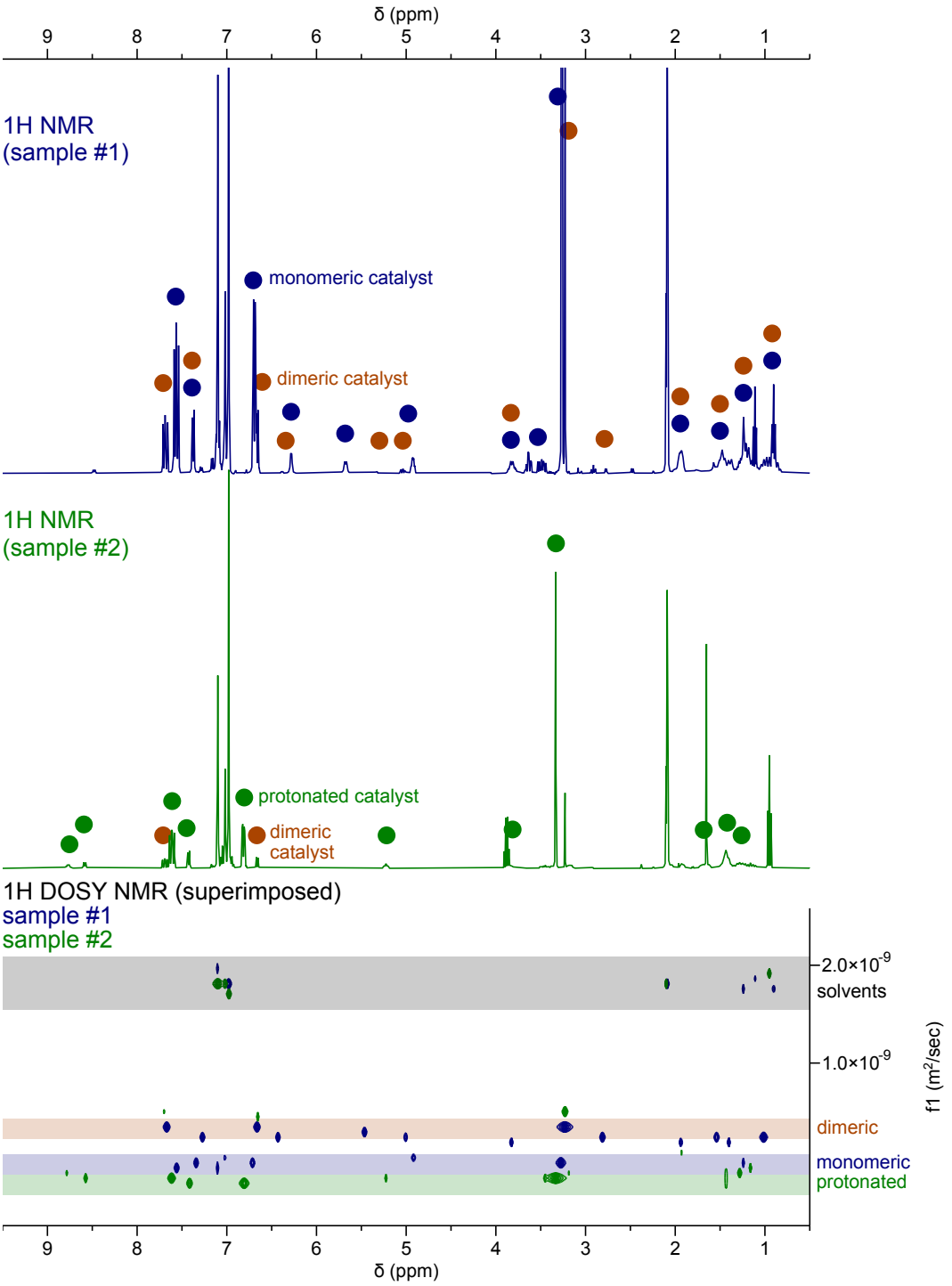


Figure SI–24: ^{1}H NMR spectra (top) and ^{1}H DOSY NMR spectra (bottom) of sample #1 (blue signals, [cat. **5a**]) and sample #2 (green signals, [cat. **5a**]HCl) in toluene-d_8 (c.f. table SI–4): Three species of the catalyst are observed, which correspond to a monomeric species (blue circles, only in sample #1), a dimeric species (brown circles, in samples #1 and #2) and a protonated species (green circles, only in sample #2).

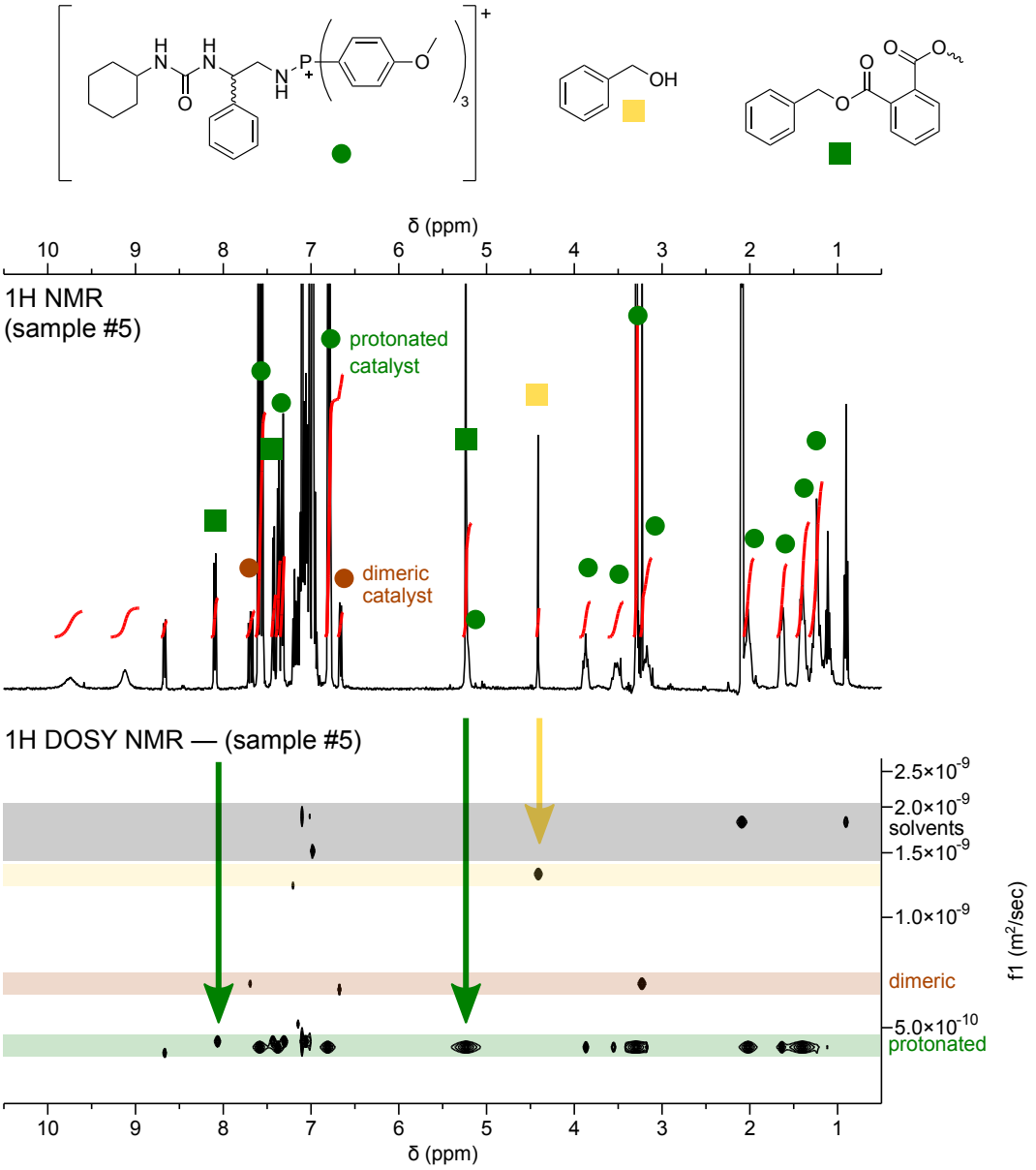


Figure SI–25: ^{1}H NMR spectrum (top) and ^{1}H DOSY NMR spectrum (bottom) of sample #5 ([cat. **5a**], BA and PA in toluene-d_8 c.f. table SI–4): The catalyst is predominantly protonated (green circles) and only a smaller fraction of the catalyst is in the dimeric form (brown circles). BA is found in a free form (yellow rectangle). A series of new signals is further found that could belong to a species formed by ring-opening of PA by BA (green rectangles), which is the initiation step of the polymerization and that has the same diffusion behaviour as the catalyst. The same diffusion behaviour is ascribed to a strong interaction between the catalyst and the ring-opened PA that lead to a tight association of both species.

4 DFT studies

Computational details

All the density functional theory (DFT) calculations were performed using the Gaussian09[16] program packages with empirical dispersion (D3BJ) corrected PBE0 functional.[17] Geometry optimizations were carried out in the gas phase with the 6-31G (d) basis set[18] and vibrational analysis were conducted at 273 K. All geometries were characterised as minimum or transition state through frequency calculations. Normal modes of all the intermediates (INT) were verified by calculations of the vibrational frequencies and exhibited no imaginary frequencies. Only one imaginary frequency connecting to bond formation or bond breaking was attained for the transition states (TS). The reported free energies were built through single point energy calculations on the 6-31G (d) geometries using the triple-ζ TZVP basis set.[19] Solvent effects were included with the PCM model using toluene as the solvent.[20] To this PBE0/TZVP electronic energy in solvent, thermal corrections were added from the gas-phase frequency calculations at the PBE0/6-31G(d) level.

Steric maps

Steric maps were built by using the software free of charge available at: SambVca - Home Page (unisa.it). To build the steric map, the optimised geometry of the TS1 of catalysts **5a**, **5c** and **5e** has been placed with the N atom of the BB moiety at the origin, with the N-H bond of the BB moiety aligned along the z-axis at positive z values, and with the P atom in the xz plane. After alignment of the structure, the epoxide and the chain were removed so as to evaluate only the bulk generated by the system skeleton. Parameters used for calculations: Sphere radius of 5.0 Å, mesh spacing of 0.1, bonding radii scaled by 1.17, H atoms not included.

^{31}P NMR chemical shift predictions

The NMR DFT calculations were performed with the ADF package.[21–23] Single point calculations on the Gaussian optimized geometries have been performed with the PBE0 functional and triple-ξ basis set with two polarization functions on all atoms (TZ2P). Electrons of the core shell have been treated within the frozen core approximation.[24] The data generated by these single point calculations were used to calculate the chemical shifts reported in the main text.

Table SI–5: Effect of the basicity of the iminophosphorane moiety on the ROAC of PA/PO. The catalysts are ordered with increasing basicity (from top to bottom).

catalyst	conv.[a]	$\Delta G^{\ddagger}$	ΔE[b]	N–H bond length[c]	
#: (thio)urea | spacer | phoshpine	[%]	[kcal/mol]	[kcal/mol]	TS1 [Å]	INT3 [Å]
5c: Cy-C(O) | C_2(Ph) | P($CH_3O)_3$	42	29.1	0.0	1.47	1.88
5e: Cy-C(O) | C_2(Ph) | P($C_9H_{11}O)_3$	100	25.4	−7.1	1.07	1.78
5a: Cy-C(O) | C_2(Ph) | P($C_6H_7O)_3$	51	28.7	−8.6	1.07	1.73

[a] Conversion of monomeric PA into PA units: PA monomer (2H @ 8.1 ppm) *vs.* ester [CHO unit (2H @ 5.2 ppm)].

[b] energy difference between the protonated and non-protonated form of the catalyst using catalyst **5c** as reference.

[c] of the iminophosphorane moiety.

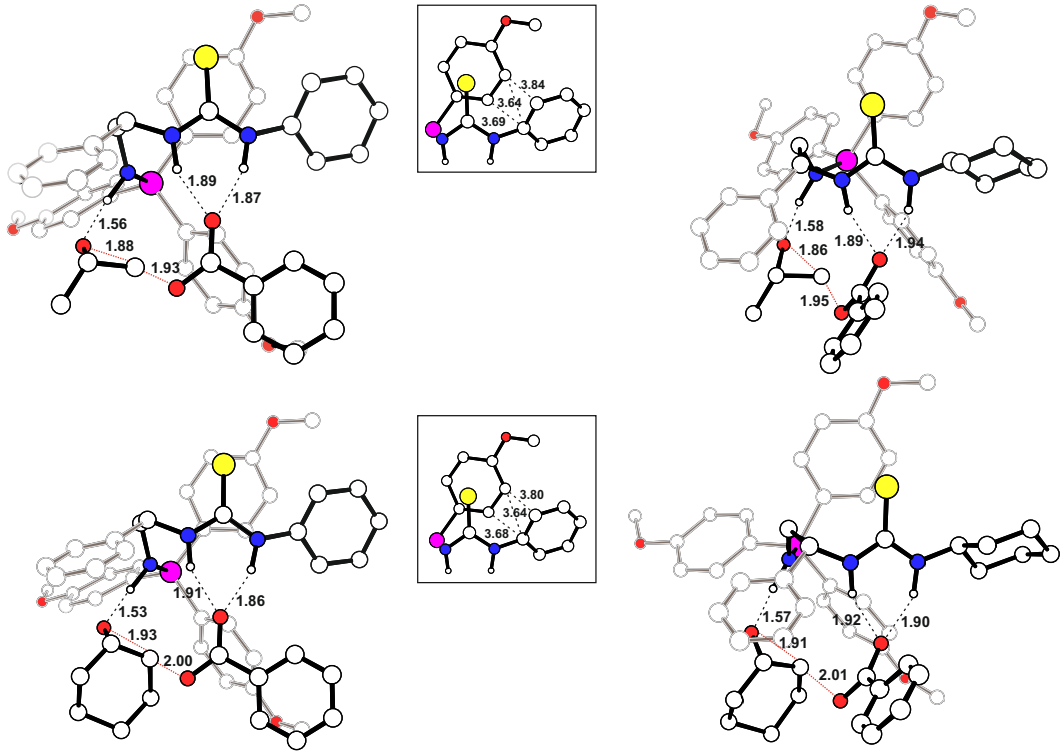


Figure SI–26: DFT optimised geometries of TS1 for catalysts **4a** (left) and **4a-Cy** (right) for the ROAC of PA/PO (top) and PA/CHO (bottom). Bond distances (dashed lines) are reported in Å.

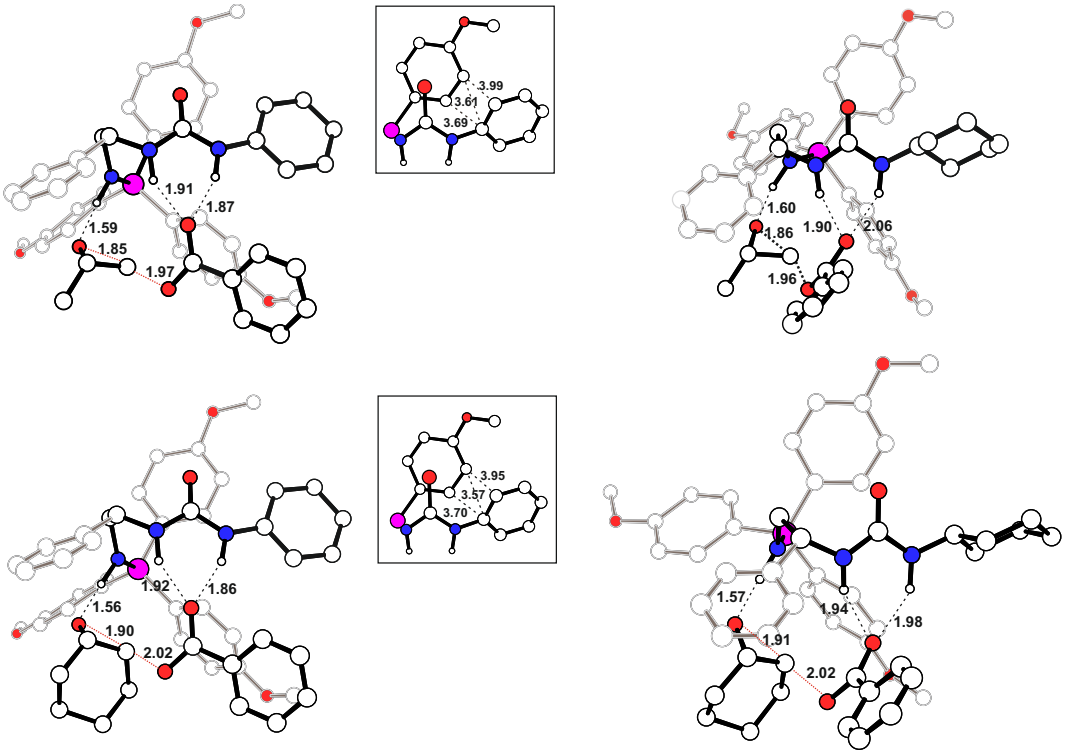


Figure SI–27: DFT optimised geometries of TS1 for catalysts **5a-Ph** (left) and **5a** (right) for the ROAC of PA/PO (top) and PA/CHO (bottom). Bond distances (dashed lines) are reported in Å.

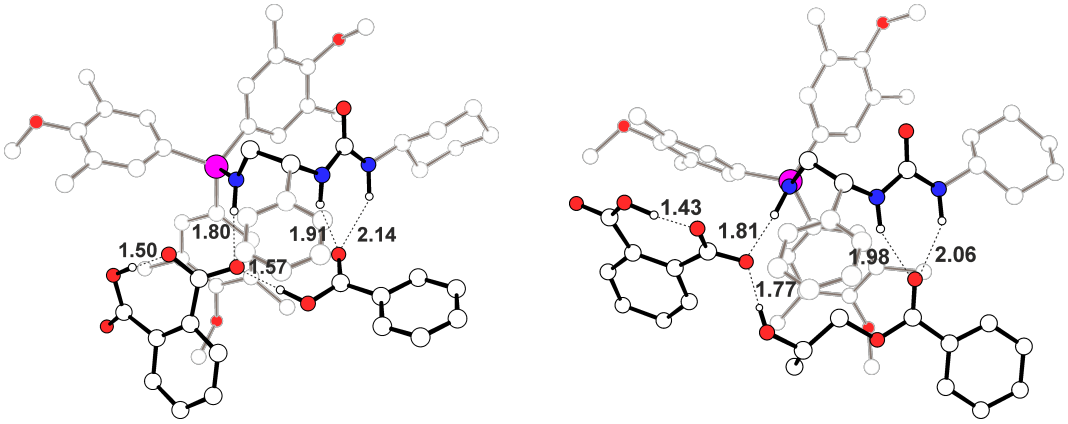


Figure SI–28: DFT optimised geometries of $INT1_{diacid}$ (left) and $INT3_{diacid}$ (right) for the the ROAC of PA/PO and catalyst **5e**. Bond distances (dashed lines) are reported in Å.

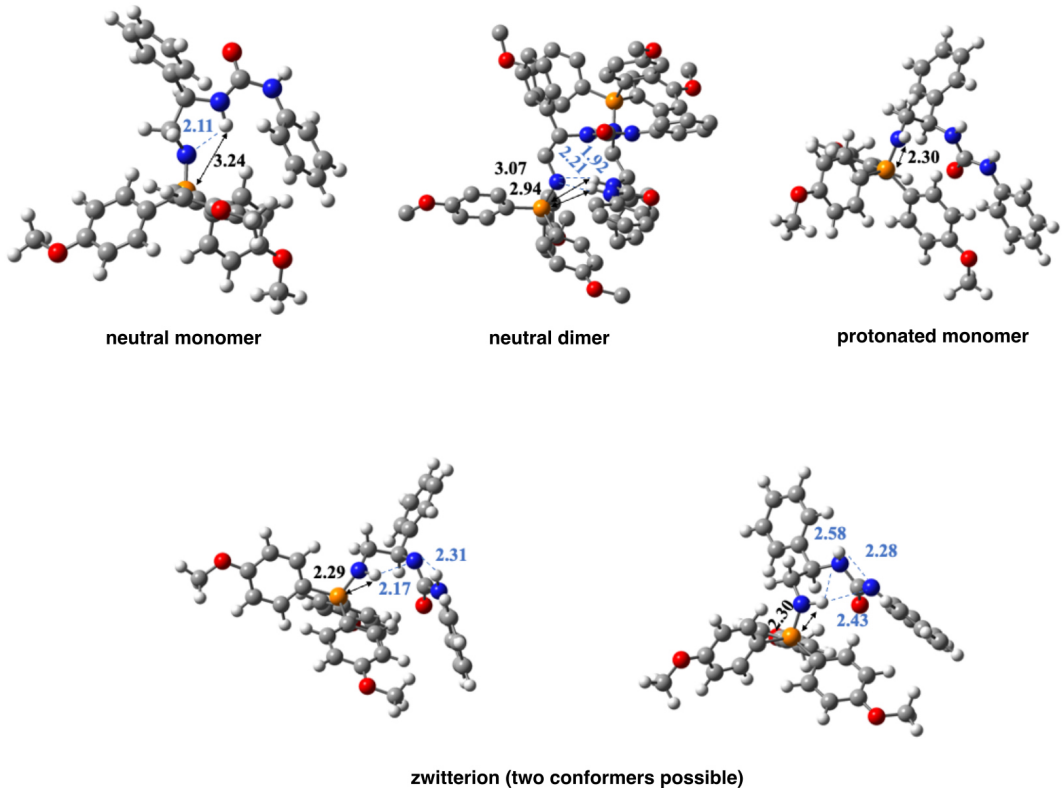


Figure SI–29: DFT optimised geometries of catalyst **5a-Ph** as neutral monomer (top left), neutral dimer (top middle), protonated monomer (top right) and zwitterion (bottom) that were used to calculate the ^{31}P NMR chemical shifts.

5 Appendix

A References

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B List of Acronyms

ATR	attenuated total reflection
BA	benzylic alcohol
BO	(±)-butylene oxide
CH_2Cl_2	dichloromethane
CHO	cyclohexene oxide
COSY	correlation spectroscopy
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCTB	*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile
DFT	density functional theory
DHB	2,5-dihydroxybenzoic acid
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
DOSY	diffusion-ordered spectroscopy
ESI	electrospray ionization
FTIR	Fourier-transform infrared spectroscopy
HH	head-head (regio-isomer descriptor)
HMBC	heteronuclear multiple bond correlation
HRMS	high-resolution mass spectrometry
HSQC	heteronuclear single quantum coherence
HT	head-tail (regio-isomer descriptor)
IR	infrared
KTFA	potassium trifluoroacetate
MALDI	matrix-assisted laser desorption/ionization
MS	mass spectrometry
NaTFA	sodium trifluoroacetate
NMR	nuclear magnetic resonance (spectroscopy)
PA	phthalic anhydride
PO	(±)-propylene oxide
RI	refractive index
rt.	room temperature
SDBS	Spectral Database for Organic Compounds (https://sdbs.db.aist.go.jp)
SEC	size-exclusion chromatography
TFA	trifluroacetic acid
THF	tetrahydrofuran
TLC	thin-layer chromatography
TOF	turnover frequency
TT	tail-tail (regio-isomer descriptor)
UV	ultraviolet

C List of Symbols

Symbol	Unit	Description
δ	ppm	chemical shift
$Đ$	—	dispersity
$[M]^+$	$^{m}/_{z}$	molecular ion peak
$\overline{M_n}$	$^{kg}/_{mol}$	number-average molar mass
M_p	$^{kg}/_{mol}$	molar mass of the highest intensity
$\overline{M_w}$	$^{kg}/_{mol}$	mass-average molar mass
$\tilde{\nu}$	$^{1}/_{cm}$	wavenumber
R_f	—	retention factor