Supporting Information

1 Materials and Methods

1.1 Materials and General Procedure

N,*N*’-diphenylethylenediamine **6** (DPEDA) (1), (+)-(*S*)-1-(2-pyrrolidinomethyl) pyrrolidine **7** ((+)-PMP) (2, 3), trityl methacrylate **8** (TrMA) (4) and [Rh(COD)$_2$]OTf (5) were prepared according to published procedures. All other reagents and solvents were purchased from commercial sources and used as received unless otherwise noted.

Diethyl ether (Et_2O), tetrahydrofuran (THF), toluene and benzene were distilled from sodium/benzophenone and dichloromethane (CH_2Cl_2) was distilled from calcium hydride (all under argon) just before use. If necessary, they were degassed either by pump-thaw and freeze or by bubbling argon through the solvent for half an hour.

Argon (4.8) was led over a Cu-catalyst to remove oxygen and then led through 4Å molecular sieve, blue gel, sulfuric acid (conc.), phosphorus pentoxide on silica (SicaPent) and finally over potassium hydroxide to remove water.

Preparations of air-sensitive materials were carried out by using either standard Schlenk and vacuum line techniques or a glove box.

1.2 Physical Methods

NMR-spectra were recorded on a Bruker DRX 500 or an ARX 300. Chemical shifts (ppm) of ^{1}H-NMR- and ^{13}C-NMR-spectra were referred to TMS or residual solvent peaks as internal standard. ^{15}N-NMR shifts (determined by (^{1}H,^{15}N)-HMBC-spectroscopy) were referred to nitromethane (CH_3NO_2) and ^{31}P-NMR spectra to 85% H_3PO_4 in D_2O as external standards, respectively. The fine structure of the proton signals were specified with "s" (singlet), "d" (doublet), "t" (triplet), "q" (quartet), "m" (multiplet), "dd" (double-doublet) and "br." (broad).

Thin Layer chromatography (TLC): Recorded on SilG/UV$_{254}$ by Macherey Nagel & Co., Dueren (thickness of layer 0.25 mm).

Flash-chromatography was carried out on silica gel 60 (15-40 µm) by Merck at a pressure of 2-2.5 bar.

Gel-permeation chromatography (GPC) was carried out at 30°C with JASCO HPLC-pumps, two columns with exclusion sizes of 70,000 and 4,000,000; commonly with 1 mg polymer dissolved in 0.2 mL THF (with 1 drop toluene per 10 mL THF as an internal standard). Flow 0.6 mL/min (pressure: 10 bar), JASCO UV-detector: 254 nm for polymers and 217 nm for measurement of the PMMA-standards, JASCO OR-detector OR-990.

Specific optical roations were determined on a Perkin Elmer Polarimeter 241 with Haake D8 thermostat in 1 dm cuvettes.

CD-spectra were recorded on a JASCO spectropolarimeter J-810 in 1 cm cuvettes.

IR-spectra were recorded on a Perkin-Elmer spectrometer Paragon 1000 PC.

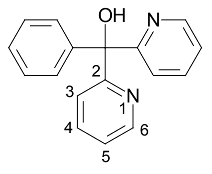
Elemental analyses were performed by the service of the institute of Organic chemistry of the Technical University of Darmstadt on a Perkin-Elmer 240B (till 11.2002) and a Vario EL by Elementar (since 12.2002), respectively.

Melting points (mp.) were determined on a Gallenkamp apparatus and are uncorrected.

1.3 Preparation

1.3.1 Phenyl[*bis*(2-pyridyl)]methyl methacrylate 5 (PB2PyMA)

Phenyl[*bis*(2-pyridyl)]methanol (PB2PyMeOH)

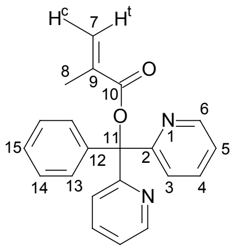


PB2PyMeOH

In modification of the published procedure (6) a solution of 10.076 g (50 mmol, 1.0 eq) 2-bromopyridine in 25 mL dry Et_2O was added to a solution of 15.424 g (T=3.404 mmol/g, 52.5 mmol, 1.05 eq) *n*BuLi in 50 mL dry Et_2O cooled at –78°C under Ar. After stirring for one hour 7.900 g (55 mmol, 1.1 eq) 2-benzoylpyridine in 33 mL dry THF were added. The reaction mixture was allowed to warm to room temperature overnight and then poured into an ice-cooled solution of 10% HCl. The acid extract was washed two times with Et_2O, neutralized with $NaHCO_3$ and then made alkaline with NaOH (pH 9-10). The aqueous layer was extracted three times with Et_2O, the combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. After recrystallization of the orange residue once from pentane and once from *tert*-butyl methyl ether 7.521g (58 %) of the product (ref. (6): 50%) was obtained as slightly yellow crystals.

$\mathbf{R_F}$ = 0.29 (ethyl acetate/light petroleum = 1:2).
mp. = 97°C (ref. (6): 97-98°C).
$\mathbf{^1H}$**-NMR** (300 MHz, $CDCl_3$, 300 K): $\delta = 6.905$ (br. s, -O*H*), 7.190 (ddd, 5-H_2), 7.24-7.30 (m, Ph-H_5), 7.685 (ddd, 4-H_2), 7.805 (ddd, 3-H_2), 8.540 (ddd, 6-H_2) ppm.
$J_{3,4}$ = 8.0 Hz, $J_{4,5}$ = 7.4 Hz, $J_{5,6}$ = 4.9, Hz, $J_{3,5}$ = 1.2 Hz, $J_{3,6}$ = 1.0 Hz, $J_{4,6}$ = 1.8 Hz.

Phenyl[*bis*(2-pyridyl)]methyl methacrylate 5 (PB2PyMA)



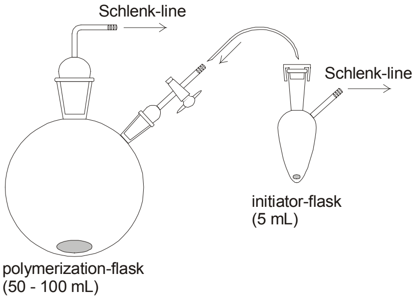
PB2PyMA **5**

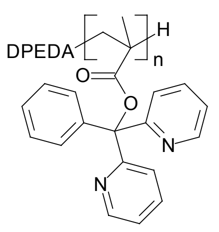
In modification of the published procedure (6) a solution of 4.872 g (18.6 mmol, 1.0 eq) PB2PyMeOH in 44 mL dry THF was added to 1.490 g (37.1 mmol, 2.0 eq) KH in 16 mL dry THF at room temperature under Ar. After H_2-evolution had stopped (1-1.5 h) 2.330 g (22.3 mmol, 1.2 eq) of freshly distilled methacryloyl chloride in 5 mL dry THF was added slowly. After complete acylation (checked by TLC, ca. 5-10 min.), the reaction mixture was poured into an ice-cooled mixture of 200 mL H_2O and 100 mL Et_2O and the separated aqueous layer was extracted with Et_2O twice. The combined organic extracts were washed with saturated aqueous $NaHCO_3$ and then with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. After recrystallization of the resulting crude product (5.938 g) from toluene/pentane twice, 3.975 g (64.8%) PB2PyMA **5** (ref. (6): 37%) were obtained as colorless crystals.

$\mathbf{R_F}$ = 0.13 (ethyl acetate/light petroleum = 1:2).
mp. = 118°C (ref. (6): 120.0°C).

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ = 2.045 (dd, 8-H_3), 5.675 (dq, 7-H^t), 6.337 (dq, 7-H^c), 7.138 (ddd, 5-H_2), 7.19-7.35 (m, 14-H_2, 15-H), 7.41-7.53 (m, 13-H_2), 7.668 (ddd, 4-H_2), 7.767 (ddd, 3-H_2), 8.551 (ddd, 6-H_2) ppm.
$J_{3,4}$ = 8.1 Hz, $J_{4,5}$ = 7.4 Hz, $J_{5,6}$ = 4.8 Hz, $J_{3,5}$ = 1.1 Hz, $J_{3,6}$ = 1.0 Hz, $J_{4,6}$ = 1.8 Hz, $J_{c\text{-}7,t\text{-}7}$ = 1.6 Hz, $J_{c\text{-}7,8}$ = 1.0 Hz, $J_{t\text{-}7,8}$ = 1.5 Hz.
^{15}N-NMR (50 MHz, $CDCl_3$, 300 K): δ = - 66.8 ppm.

1.3.2 Polymerization of phenyl-[*bis*(2-pyridyl)]methyl methacrylate 5 to *poly*-(PB2PyMA) p5





poly-(PB2PyMA) **p5**

In modification of the published procedure (6) 1.322 g (4 mmol, 20.0 eq) PB2PyMA **5** were put in an absolutely dry polymerization flask, lyophilized from benzene. The flask was evacuated and refilled with Ar three times. Then the monomer was dissolved in 20 mL dry toluene and cooled to –78°C. 42.5 mg (0.2 mmol, 1.0 eq) *N*,*N'*-diphenylethylenediamine **6** (DPEDA) were put in an absolutely dry initiator flask, lyophilized from benzene and the flask was flushed with dry argon. After the evacuation and subsequent flushing with Ar had been repeated twice, the amine was dissolved in 1 mL dry toluene and cooled to 0°C. Then, 83 mg (c = 2.418 mmol/g, 0.2 mmol, 1.0 eq) *n*BuLi were added slowly and the resulting mixture was warmed to room temperature (ca. 5 minutes), followed by cooling again to 0°C and dropwise addition of 37.02 mg (39.1 µl, 0.24 mmol, 1.2 eq) (+)-(*S*)-1-(2-pyrrolidinomethyl)pyrrolidine (+)-**7** ((+)-PMP, freshly distilled from CaH_2). The resulting green initiator solution was stirred for one minute at 0°C and for another ten minutes at room temperature, cooled to –78°C and added to the polymerization-flask via cannula. After stirring for 24 hours at –78°C the polymerization was quenched by adding 1.5 mL methanol. The polymer was precipitated in 400 mL ice-cooled methanol, separated by centrifugation and dried in vacuum. The obtained 0.496 g (37%) polymer-oligomer mixture was dissolved in toluene/CH_2Cl_2, reprecipitated in 300 mL benzene/hexane (1:1 by volume), separated by centrifugation and the residue dried in vacuum. This way, 0.412 g (30%) of a polymeric fraction **p5** insoluble in methanol and benzene-hexane was isolated.

80 mg of this polymer were transformed into the corresponding poly methyl methacrylate (PMMA) by acidic hydrolization (in refluxing methanol containing sulfuric acid) and subsequent methylation of the resulting poly acrylic acid with diazomethane. The obtained PMMA was used to analyze the tacticity (by ^{1}H-NMR

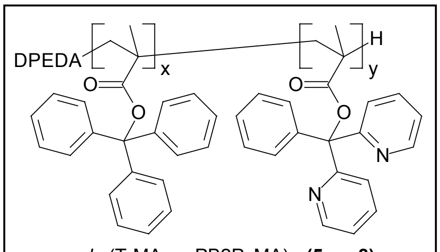
spectroscopy) as well as the degree of polymerization (DP) and molecular weight distribution (by GPC (PMMA standard)).

Tacticity: 73% mm.
GPC: DP = 40, M_w/M_n = 1.42.
Specific optical rotation (c = 1 in $CHCl_3/CF_3CH_2OH$ = 9:1 by volume):

$[\alpha]_D^{25}$	$[\alpha]_{578}^{25}$	$[\alpha]_{546}^{25}$	$[\alpha]_{436}^{25}$	$[\alpha]_{365}^{25}$
+141	+148	+172	+320	+573

^{1}H-NMR (CD_2Cl_2, 500 MHz, 300 K): δ = 0.14-1.02 (br. m, CH_3), 1.12-1.39, 1.41-1.98 (br. m, CH_2), 2.37-2.95 (br. m, CH_3), 5.80-7.99, 8.00-8.70 (br. m, Ar-H_{13}) ppm.

1.3.3 Copolymerization of trityl methacrylate 8 and phenyl[*bis*(2-pyridyl)]methyl methacrylate 5 to *poly*-(TrMA-*co*-PB2PyMA) p(5-*co*-8)



poly-(TrMA-*co*-PB2PyMA) **p(5-co-8)**

In modification of the published procedure (7), the polymerization was carried out analogous to the synthesis of *poly*-(PB2PyMA) **p5** (see above) by adding a chiral base mixture of 42.5 mg (0.2 mmol, 1.0 eq) DPEDA **6** in 1 mL dry toluene, 78.8 mg (c = 2.520 mmol/g, 0.2 mmol, 1.0 eq) *n*BuLi and 37.02 mg (39.1 µl, 0.24 mmol, 1.2 eq) (+)-PMP [(+)-**7**] to a solution of 0.657 g (2 mmol, 10.0 eq) <u>tr</u>ityl <u>m</u>eth<u>a</u>crylate **8** (TrMA) and 0.661 g (2 mmol, 10.0 eq) PB2PyMA **5** in 25 mL dry toluene. The resulting orange reaction mixture was stirred 16 hours at -78°C, diluted with 10 mL dry toluene and stirred for another eight hours. After quenching the reaction by adding 1.5 mL methanol, precipitation of the copolymer in 300 mL ice-cooled methanol and subsequent centrifugation, 1.218 g (90%) of a fraction insoluble in methanol was obtained. This polymer-oligomer mixture was dissolved in toluene/THF poured into 300 mL benzene/hexane (1:1 by volume) and the precipitated polymer was separated by centrifugation. After drying the residue in vacuum, 1.053 g (77%) of a polymeric fraction **p(5-*co*-8)** insoluble in methanol and benzene/hexane were isolated.

60 mg of this polymer were transformed into the corresponding poly methyl methacrylate (PMMA) by acidic hydrolization (in refluxing methanol containing hydrochloric acid) and subsequent methylation of the resulting poly acrylic acid with diazomethane. The obtained PMMA was used to analyze tacticity (by ^{1}H-NMR spectroscopy) as well as degree of polymerization (DP) and molecular weight distribution (by GPC (PMMA standard)). The molar ratios of the incorporated monomers were determined by ^{1}H-NMR spectroscopic analysis of the relative amounts of alcohol derivatives, which were separated after the acidic hydrolyzation.

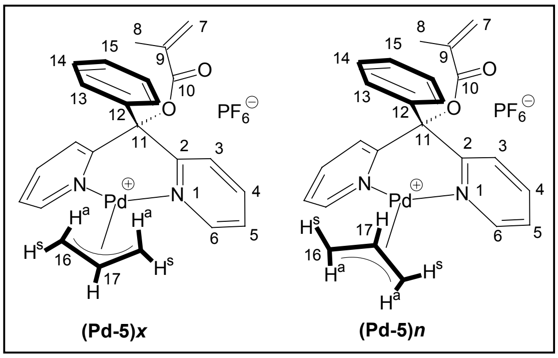
Tacticity: 99% mm.
GPC: DP = 65, M_w/M_n = 1.26.
[TrMA]:[PB2PyMA] calcd.: 50.0 : 50.0
found: 50.4 : 49.6.

Specific optical rotation (c = 1 in $CHCl_3/CF_3CH_2OH$ = 9:1):

$[\alpha]_D^{25}$	$[\alpha]_{578}^{25}$	$[\alpha]_{546}^{25}$	$[\alpha]_{436}^{25}$	$[\alpha]_{365}^{25}$
+377	+395	+456	+844	+1494

^{1}H-NMR (CD_2Cl_2, 300 MHz, 300 K): δ = 0.00-0.78 (br. s, CH_3), 0.80-0.96, 1.19-1.36, 1.37-1.95 (br. m, CH_2), 2.26-2.89 (br. m, CH_3), 5.92-8.02, 8.05-8.72 (br. m, Ar-H_{14}) ppm.

1.3.4 Complexation of PB2PyMA 5 with palladium to Pd-5 (Pd-PB2PyMA)



The part of the complex not used for the X-ray structural analysis was washed with Et_2O, and dried in high vacuum. This way 98 mg (78.7%) of a 2.74:1 mixture (derived from ^{1}H-NMR spectroscopic analysis) of *exo*-complex **(Pd-5)*x*** and *endo*-complex **(Pd-5)*n*** (assignments were confirmed by NOESY-spectroscopy, not shown) were isolated.

Spectroscopic data of **(Pd-5)*x***:

^{1}H-NMR (CD_2Cl_2, 500 MHz, 223 K): δ = 1.958 (d, 16-H^a_2), 2.032 (s, 8-H_3), 3.869, d, 16-H^s_2), 5.78-5.89 (m, 17-H), 5.845, 6.362 (br. s, 7-H_2), 7.133 (d, 13-H_2), 7.311 (ddd, 14-H_2), 7.364 (br. t, 15-H), 7.445 (ddd, 5-H_2), 8.02-8.14 (3-H_2, 4-H_2), 8.505 (br. d, 6-H_2) ppm.

$J_{4,5}$ = 6.6 Hz, $J_{5,6}$ = 5.3, $J_{13,14}$ = 7.8, $J_{14,15}$ = 7.2, $J_{a\text{-}16,17}$ = 12.4, $J_{s\text{-}16,17}$ = 6.9 Hz.

^{13}C-NMR (CD_2Cl_2, 75 MHz, 223 K): δ = 19.34 (8-C), 63.88 (16-C), 89.29 (11-C), 117.79 (17-C), 125.13 (5-C), 125.69 (3-C), 128.56 (14-C), 129.36 (7-C), 130.85 (15-C), 133.06 (13-C), 136.70 (12-C), 139.01 (9-C), 141.10 (4-C), 154.32 (6-C), 158.37 (2-C), 165.18 (10-C) ppm.

Spectroscopic data of **(Pd-5)*n***:

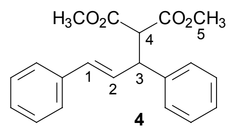
^{1}H-NMR (CD_2Cl_2, 500 MHz, 223 K): δ = 2.004 (s, 8-H_3), 3.144 (d, 16-H^a_2), 3.798, d, 16-H^s_2), 4.401 (tt, 17-H), 5.815, 6.320 (br. s, 7-H_2), 6.911 (d, 13-H_2), 7.256 (ddd, 14-H_2), 7.366 (br. t, 15-H), 7.510 (ddd, 5-H_2), 8.02-8.14 (3-H_2, 4-H_2), 8.743 (br. d, 6-H_2) ppm.

$J_{4,5}$ = 7.2 Hz, $J_{5,6}$ = 5.3, $J_{13,14}$ = 7.4, $J_{14,15}$ = 7.2, $J_{a\text{-}16,17}$ = 12.4, $J_{s\text{-}16,17}$ = 6.8 Hz.

^{13}C-NMR (CD_2Cl_2, 75 MHz, 223 K): δ = 19.34 (8-C), 62.44 (16-C), 88.94 (11-C), 120.78 (17-C), 125.25 (5-C), 125.93 (3-C), 128.51 (14-C), 129.27 (7-C), 130.40 (15-C), 132.23 (13-C), 136.70 (12-C), 139.31 (9-C), 141.27 (4-C), 154.26 (6-C), 157.89 (2-C), 165.06 (10-C) ppm.

1.3.5 Allylic substitution reaction

Spectroscopic data of 1,3-diphenylprop-2-enyl malonate 4



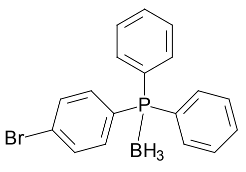
4

Enantiomeric excess of the obtained malonate **4** was determined by ^{1}H-NMR-spectroscopic analysis in the presence of 20 mol% of the chiral shift reagent [Eu(hfc)$_3$] (hfc=3-(heptafluoropropyl-hydroxomethylene)-D-camphorate).
The configuration of the substitution product was determined by comparison with an optically pure sample of (*S*)-**4** prepared according to ref. (8).

R$_F$ = 0.34 (ethyl acetate/light petroleum = 1:5)
^{1}H-NMR ($CDCl_3$, 200 MHz, 300 K): δ = 3.504 (s, 5-H_3), 3.690 (s, 5-H_3), 3.972 (d, 4-H), 4.249 (dd, 3-H), 6.353 (dd, 2-H), 6.468 (d, 1-H), 7.12-7.38 (m, Ph-H_{10}) ppm.
$J_{1,2}$ = 15.9 Hz, $J_{2,3}$ = 8.1 Hz, $J_{3,4}$ = 10.9 Hz.

1.3.6 Diphenyl-4-[(diphenyl-phosphanyl-borane)phenyl]methyl methacrylate 12 (D4[DPB]MA)

Diphenyl-4-[bromophenyl]phosphanyl-borane 10 (D4[BrP]PB)



D4[BrP]PB **10**

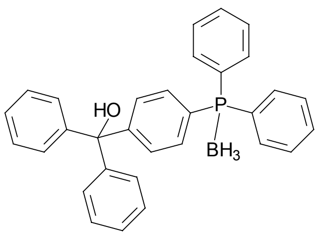
According to the published synthesis of the unprotected phosphane derivative (9, 10), a solution of 11.80 g (50.0 mmol, 1 eq) 1,4-dibromobenzene **9** in 50 mL dry THF was added dropwise to a solution of 21.41 g *n*BuLi (50.0 mmol, 1 eq) in 20 mL dry THF cooled a –78°C under Ar. Then, 11.03 g (50.0 mmol, 1 eq) of freshly distilled chlorodiphenyl phosphane in 35 mL dry THF were added slowly. The red reaction mixture was allowed to warm to room temperature overnight.
After complete conversion (checked by TLC analysis, ethyl acetate/light petroleum = 1:10, R$_F$ = 0.59), the solution was cooled to 0°C and 75.0 mL BH_3-THF-complex (1 M in THF, 75.00 mmol, 1.5 eq) were added. The colorless solution was stirred at 0°C until complete conversion (checked by TLC analysis, ca. 10 hours). Then, the reaction mixture was diluted by adding 200 mL Et_2O and poured into 300 mL water and the separated aqueous fraction was extracted two times with Et_2O. The combined organic extracts were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. After recrystallization from ethyl acetate/light petroleum, 15.98 g (90%) of the desired phosphane-borane complex **10** were isolated.

R$_F$ = 0.35 (ethyl acetate/light petroleum = 1:10).
mp. = 145.2°C.
IR (KBr): ν = 1059.7 (Br-C_{Aryl}), 1436.5 (P-C_{Aryl}), 2386.5 (P-BH_3), 3059.2, 3075.6 (arom. C-H) cm^{-1}.
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 1.249 (vbr. q, BH_3), 7.402 – 7.590 (m, Ar-H_{14}) ppm.

^{13}C-NMR (50 MHz, $CDCl_3$, 300 K, TMS): δ = 126.48 (d, 2.8 Hz), 127.96 (d, 1.2 Hz), 128.89 (d, 10.1 Hz), 129.13 (d, 1.6 Hz), 131.47 (d, 2.4 Hz), 132.03 (d, 10.5 Hz), 133.09 (d, 10.1 Hz), 134.64 (d, 10.5 Hz) ppm.
^{31}P-NMR (202 MHz, $CDCl_3$, 300 K): δ = 19.30 (vbr. q) ppm.

$C_{18}H_{17}BBrP$ (355.02)	calcd.:	C 60.90	H 4.83
	found:	C 60.84	H 4.85

Diphenyl-4-[(diphenyl-phosphanyl-borane)phenyl]methanol 11 (D4[DPBP]MeOH)



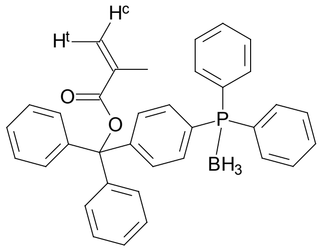
D4[DPBP]MeOH **11**

Under Ar, 14.52 g (40.90 mmol, 1.0 eq) (D4[BrP]PB) **10** in 75 mL dry THF were added slowly to a solution of 18.55 g (42.95 mmol, 1.05 eq) *n*BuLi in 60 mL dry THF at –78°C. After 20 minutes 7.83 g (42.95 mmol, 1.05 eq) benzophenone in 50 mL dry THF were added dropwise to the green reaction mixture. After complete conversion (checked by TLC analysis, ca. 2 hours), the slightly yellow solution was poured into 600 mL of an ice-cooled, saturated solution of NH_4Cl and Et_2O. The separated aqueous layer was extracted two times with Et_2O, the combined organic extracts were washed with brine, dried over Na_2SO_4 and the solvent was removed under reduced pressure. Recrystallization from ethyl acetate/light petroleum yielded 18.74 g (99%) **11** as a colorless, crystalline solid.

R_F = 0.22 (ethyl acetate/light petroleum = 1:5).
mp. = 180.3°C.
IR (KBr): ν = 1437.5 ($P\text{-}C_{Aryl}$), 2380.3 ($P\text{-}BH_3$), 3060.4 (arom. C-H) cm^{-1}.
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 1.258 (vbr. q, BH_3), 2.788 (br. s, OH), 7.551 – 7.609 (m, Ar-H_4), 7.463 – 7.537 (m, Ar-H_4), 7.365 – 7.447 (m, Ar-H_6), 7.225 – 7.336 (m, Ar-H_{10}) ppm.
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K, TMS): δ = 60.33 (s, R_3*C*-OH), further: 127.54 (s), 127.83 (s), 128.08 (s), 128.27 (d, 10 Hz), 128.27 (s), 128.74 (d, 10 Hz), 128.97 (s, quart. C), 129.43 (s, quart. C), 131.21 (d, 3Hz), 132.74 (d, 9.6 Hz)133.21 (d, 10 Hz) 146.12 (s), 150.07 (d, 2.5 Hz) ppm.
^{31}P-NMR (202 MHz, $CDCl_3$, 300 K): δ = 18.61 (vbr.q, P-BH_3), [27.22 (s, P=O)] ppm.

$C_{31}H_{28}BOP$ (458.34)	calcd.:	C 81.24	H 6.16
	found:	C 80.95	H 6.26

Diphenyl-4-[(diphenyl-phosphanyl-borane)phenyl]methyl methacrylate 12 (D4[DPBP]MA)



D4[DPBP]MA **12**

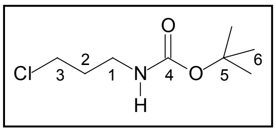
Under Ar, a suspension of 3.53 g (88.14 mmol, 3 eq) KH in 20 mL dry THF was cooled to 0°C and a solution of 13.47 g (29.38 mmol, 1 eq) D4[DPBP]MeOH **11** in 400 mL dry THF was added slowly. After stirring at 0°C overnight, 4.61 g (44.07 mmol, 1.5 eq) of freshly distilled methacryloyl chloride were dropped into the red reaction mixture. The now colorless solution was stirred at 0°C for another 12 hours. After that, the mixture was poured into 400 mL of an ice-cooled solution of saturated $NaHCO_3$, followed by addition of 200 mL water and 200 mL ethyl acetate. The two layers were separated and the aqueous fraction was extracted twice with ethyl acetate (300 mL each time) and once with CH_2Cl_2 (100 mL). The combined organic extracts were washed with brine (150 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. After recrystallization from ethyl acetate (temperature of the solution below 60°C), 11.14 g (72%) of the desired monomer **12** were isolated as a colorless, crystalline solid.

R_F = 0.35 (ethyl acetate/light petroleum = 1:5).
mp. = 148.7°C.
IR (KBr): ν = 1435.7 (P-C_{Aryl}), 1722.2, (C=O), 2379.4 (P-BH_3), 3059.6 (arom. C-H) cm^{-1}.
^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 1.253 (vbr. q, BH_3), 1.975 (d, CH_3), 5.622 (dq, H^c), 6.225 (m, H^t) , 7.236 – 7.322 (m, Ar-H_6), 7.340 – 7.373 (m, Ar-H_4), 7.396 – 7.521 (m, Ar-H_{10}), 7.543 – 7.598 (m, Ar-H_4) ppm.
$J_{\mathrm{H}c,\mathrm{H}t}$ = 1.5 Hz, $J_{\mathrm{H}c,\mathrm{CH}_3}$ = 1.0 Hz.
^{13}C-NMR (126 MHz, $CDCl_3$, 300 K, TMS): δ = 18.50 (s, CH_3), 89.54 (s, OCR_3), 125.88 (s, $H_2\mathit{C}$=C), 137.26 (s, H_2C=C), 165.11 (s, C=O), further: 127.55 (s), 127.88 (s), 128.34 (s), 128.43 (d, 10.8 Hz), 128.75 (d, 9.9 Hz), 128.820 (s), 129.28 (s), 131.23 (d, 1.6 Hz), 132.64 (d, 9.7 Hz), 133.24 (d, 9.7 Hz), 142.77 (s), 146.64 (dd, 2.3 Hz) ppm.
^{31}P-NMR (202 MHz, $CDCl_3$, 300 K): δ = 18.49 (vbr. q, P-BH_3) ppm.

$C_{35}H_{32}BO_2P$ (526.42)	calcd.:	C 79.86	H 6.13
	found:	C 79.76	H 6.19

1.3.7 3-(Diphenylphosphanyl-borane)-propylisocyanate 16 (3DPBPIC)

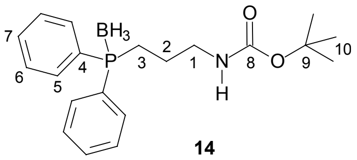
N-Boc-3-Chloropropylamine



(Boc: *tert*-butoxy carbonyl). To a suspension of 9.996 g (76.88 mmol, 1.1 eq) 3-chloropropylamine hydrochloride **13** in 115 mL dioxane at 0°C were added 11.79 g $NaHCO_3$ (140.3 mmol, 2.0 eq) in 110 mL of water and 15.250 g (69.87 mmol, 1.0 eq) of $(Boc)_2O$. After 30 minutes, the mixture was allowed to reach room temperature and stirred until complete conversion (ca. 6 hours). The volume of the mixture was reduced to the half under reduced pressure, then it was extracted three times with Et_2O. The combined organic layers were washed with brine and dried with $MgSO_4$. Removal of the solvent in vacuum gave 12.91 g (95%) of the product as a colorless oil. Spectroscopic data are in accordance with those reported in ref. (11).

^{1}H-NMR (300 MHz, $CDCl_3$, 300 K): δ = 1.44 (s, 6-H_9), 1.97 (quint., 2-H_2), 3.28 (q, 1-H_2), 3.59 (t, 3-H_2), 4.5-5.0 (br. s, N*H*) ppm.
$J_{1,2}$ = 6.4 Hz, $J_{2,3}$ = 6.4 Hz
^{13}C-NMR (75 MHz, $CDCl_3$, 300 K): δ = 28.47 (6-C), 32.67 (2-C), 38.00 (3-C), 42.47 (1-C), 79.44 (5-C), 156.08 (4-C) ppm.

N-Boc-3-(Diphenylphosphanyl-borane)-propylamine 14



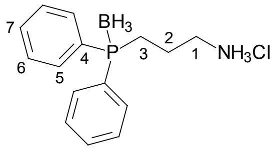
14

A solution of 70.26 mmol (1.01 eq) lithium-diphenylphosphide-borane (freshly prepared according to ref. (12)) was added via cannula to a solution of 13.430 g (69.3 mmol, 1.0 eq) *N*-Boc-3-chloropropylamine in 20 mL dry THF at -10°C under Ar. The mixture was slowly warmed to room temperature by stirring overnight. After removal of the solvent under reduced pressure, the residue was dissolved in ethyl acetate and brine, the aqueous phase being extracted two more times with ethyl acetate. The combined organic layers were dried over $MgSO_4$. After removal of the solvent in vacuum, the crude product was purified by flash chromatography on silica (light petroleum/ethyl acetate 5:1) to yield **14** as a white solid (15.019 g, 61%).

$\mathbf{R_F}$ = 0.20 (light petroleum/ethyl acetate 5:1)
mp. = 112°C
^{1}**H-NMR** (500 MHz, $CDCl_3$, 300 K): δ = 0.5-1.4 (m, BH_3), 1.42 (s, 10-H_9), 1.65-1.74 (m, 2-H_2), 2.19-2.26 (m, 3-H_2), 3.14-3.21 (m, 1-H_2), 4.6 (br.s, NH), 7.41-7.50 (m, Ph-H_6), 7.63-7.68 (m, Ph-H_4) ppm.
^{13}**C-NMR** (125 MHz, $CDCl_3$, 300 K): δ = 23.11 (d, 3-C), 24.06 (2-C), 28.50 (10-C), 41.36 (1-C), 79.54 (9-C), 129.0 (d, 6-C), 129.4 (d, 4-C), 131.4 (d, 7-C), 132.2 (d, 5-C), 156.1 (8-C) ppm.
$J_{3,P}$ = 37.6 Hz, $J_{4,P}$ = 55.2 Hz, $J_{5,P}$ = 9.2 Hz, $J_{6,P}$ = 9.9 Hz, $J_{7,P}$ = 2.8 Hz
^{31}**P-NMR** (202 MHz, $CDCl_3$, 300 K): δ = 16.7 (br. s)
EI-MS: *m/z* (%) = 356 (1) [M^+-H]; 343 (20) [M^+-BH_3]; 286 (77) [M^+-BH_3, -C_4H_9]
IR (KBr): ν = 3332 (NH); 2379, 2341 (BH_3); 1686 (amide I C=O); 1535 (amide II C=O) cm^{-1}

$\mathbf{C_{20}H_{29}BNO_2P}$ (357.23):	calcd.:	C 67.24	H 8.183	N 3.921
	found:	C 67.30	H 8.110	N 3.995

3-(Diphenylphosphanyl-borane)-propylamine hydrochloride 15



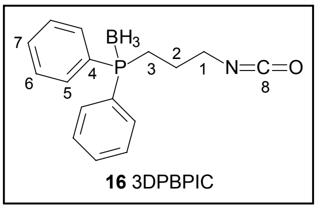
15

A solution of 11.547 g (32.323 mmol, 1.0 eq) *N*-Boc-3-(diphenylphosphanyl-borane)-propylamine **14** in 150 mL methanol was added to a solution of HCl (119.1 mmol, 3.7 eq) in 50 mL methanol (previously prepared by adding acetylchloride to methanol in an ice bath). The flask was connected to a gas bubbler to monitor conversion. After stirring for 26 hours, the solvent was removed in vacuum. The crude product was recrystallized from 105 mL chloroform/ethanol (20:1) to yield 7.351 g (77%) **15** as a white solid.

$\mathbf{R_F}$ = 0.41 (CH_2Cl_2:MeOH:NH_3 = 90:10:1)
mp. = 175°C (dec.)
^{1}**H-NMR** (500 MHz, $CDCl_3$, 300 K): δ = 0.6-1.4 (m, BH_3), 1.90-1.98 (m, 2-H_2), 2.43-2.50 (m, 3-H_2), 3.01 (tq, 1-H_2), 7.40-7.48 (m, Ph-H_6), 7.69-7.74 (m, Ph-H_4), 8.5 (s, NH_3) ppm.
$J_{1,2}$ = 6.0 Hz.

^{13}C-NMR (125 MHz, $CDCl_3$, 300 K): δ = 21.3 (d, 2-C), 22.7 (d, 3-C), 40.4 (d, 1-C), 128.9 (d, 4-C), 128.9 (d, 6-C), 131.3 (d, 7-C), 132.2 (d, 5-C) ppm.
$J_{1,P}$ = 15.5 Hz, $J_{2,P}$ = 1.7 Hz, $J_{3,P}$ = 38.5 Hz, $J_{4,P}$ = 55.6 Hz, $J_{5,P}$ = 9.2 Hz, $J_{6,P}$ = 9.7 Hz, $J_{7,P}$ = 2.3 Hz.
^{31}P-NMR (202 MHz, $CDCl_3$, 300 K): δ = 16.7 (br. s)
IR (KBr): ν = 3000 (NH_3^+), 2382 (B-H), 1598 (NH_3^+), 1437 (P-Ph) cm^{-1}

3-(Diphenylphosphanyl-borane)-propylisocyanate 16 (3DPBPIC)



16 3DPBPIC

A flat-bottom 250 mL flask was charged with 1.171 g (3.989 mmol, 1.0 eq) of 3-(diphenylphosphanyl-borane)-propylamine hydrochloride **15**, 40 mL of $CHCl_3$ and 40 mL of saturated aqueous $NaHCO_3$. This biphasic mixture was stirred for ca. 10 minutes until all of the hydrochloride salt was dissolved. To the rapidly stirred mixture, 4.3 mL (8.127 mmol, 2.0 eq) of a phosgene solution (20% in toluene) were added in a single portion and the flask connected to a gas bubbler. Stirring was continued for approximately 8 minutes until gas evolution had stopped. The layers were separated, the aqueous layer was extracted with two 30 mL portions of $CHCl_3$ and the combined organic layers were dried over $MgSO_4$. Removal of the solvent in vacuum yielded 1.104 g (98%) of **16** as a colorless oil.

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ = 0.6-1.4 (br. m, BH_3), 1.77-1.85 (m, 2-H_2), 2.25-2.31 (m, 3-H_2), 3.38 (t, 1-H_2), 7.42-7.51 (m, 6/7-H_6), 7.65-7.70 (m, 5-H_4) ppm.
$J_{1,2}$ = 6.3 Hz.
^{13}C-NMR (75.5 MHz, $CDCl_3$, 300 K): δ = 23.14 (d, 3-C), 25.01 (d, 2-C), 43.75 (d, 1-C), 122.29 (8-C), 128.99 (d, 4-C), 129.10 (d, 6-C), 131.55 (d, 7-C), 132.19 (d, 5-C) ppm.
$J_{1,P}$ = 14.9 Hz, $J_{2,P}$ = 1.1 Hz, $J_{3,P}$ = 38.1 Hz, $J_{4,P}$ = 55.4 Hz, $J_{5,P}$ = 9.3 Hz, $J_{6,P}$ = 10.0 Hz, $J_{7,P}$ = 2.3 Hz.
^{31}P-NMR (202 MHz, $CDCl_3$, 300 K): δ = 16.5 (br. s)
EI-MS: *m/z* (%) = 282 (10) [M^+ -H], 269 (37) [M^+ -BH_3], 241 (100) [M^+ -BH_3 -CO]
IR (KBr): ν = 2382 (BH_3), 2276 (NCO), 1437 (P-Ph) cm^{-1}

$C_{16}H_{19}BNOP$ (283.11):	calcd:	C 67.88	H 6.77	N 4.95
	found:	C 67.62	H 6.86	N 4.97

2 Supporting Figures

2.1 Plot of optical rotation of *poly*-(TrMA), *poly*-(PB2PyMA) p5 and *poly*-(TrMA-*co*-PB2PyMA) p(8-*co*-5) against time.

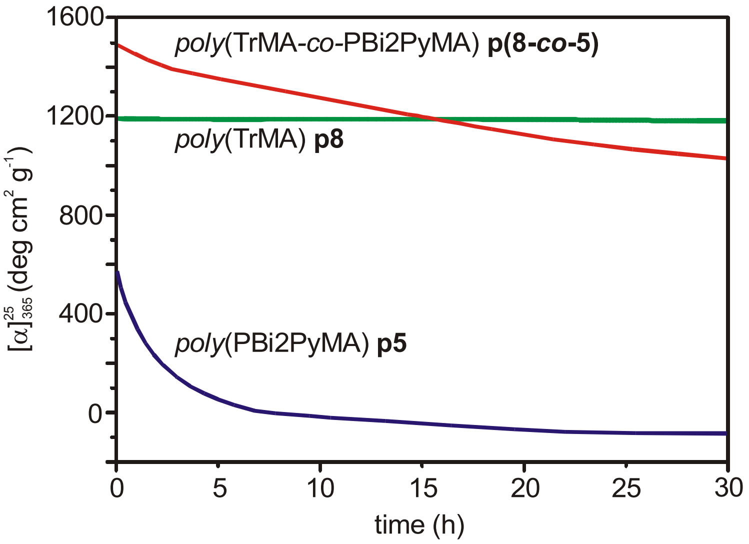
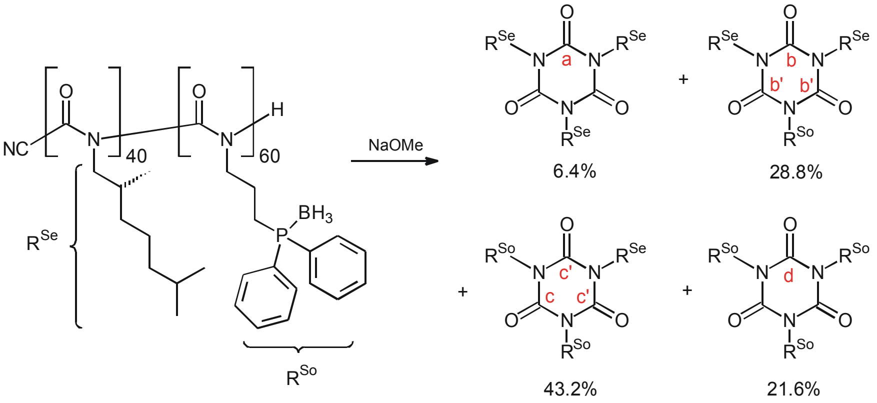


Figure 3: Specific optical rotations were measured at 25°C in THF (*poly*-(TrMA) **p8**) or CH_3Cl/F_3CCH_2OH (9:1 by volume, *poly*-(PB2PyMA) **p5** and *poly*-(TrMA-*co*-PB2PyMA)) **p(8-*co*-5)**.

Stability of helical conformation in solution: **p5** << **p(8-*co*-5)** < **p8**

2.2 Analysis of monomer distribution in *poly*-(DPBPIC-*co*-DMHIC) p(16-*co*-17)

Monomer distribution was determined by base induced degradation of an aliquot of the copolymer **p(16-*co*-17)** ([**16**]:[**17**]=60:40) with $NaOCH_3$ and ^{13}C-NMR-spectroscopy of the resulting mixture of *N*-substituted isocyanurates (trimers), analogous to a method described in the literature (13). The carbonyl region showed six signals, which were assigned to the four possible trimers as shown below (Scheme 8 and Figure 4).



Scheme 8: base induced degradation to trimers and assignment of different carbonyl groups. Percentages show theoretical amounts of trimers according to statistical distribution of monomers in the copolymer.

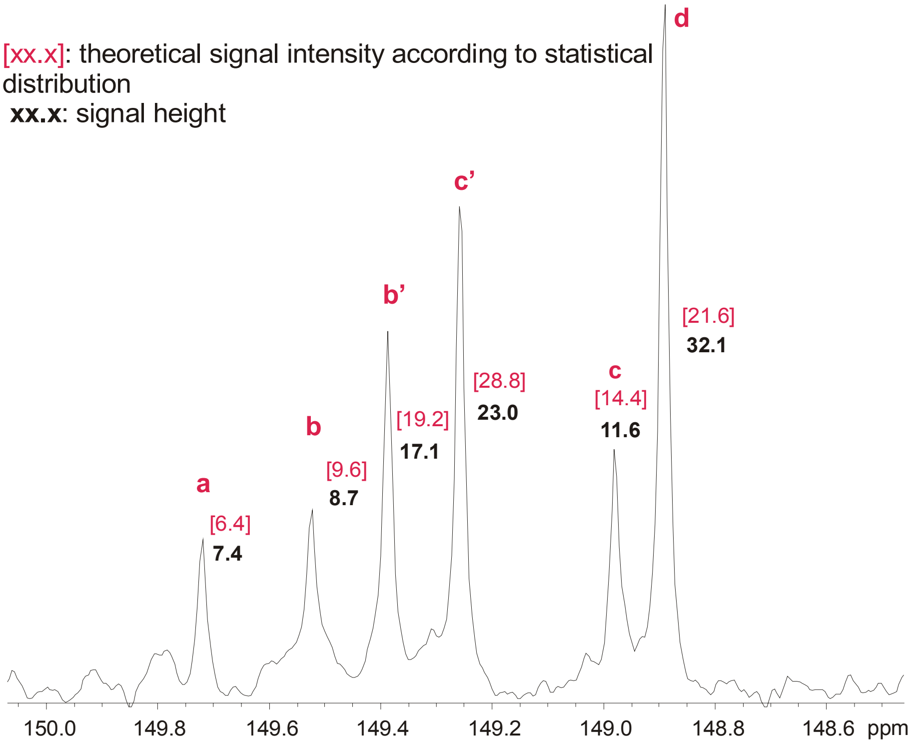


Figure 4: ^{13}C-NMR carbonyl region of the mixture of trimers obtained from **p(16-*co*-17)** ([**16**]:[**17**]=60:40). Assignment of peaks according to Scheme 8.

Calculated and found values of the relative amounts of the four cyclic trimers are similar, indicating a statistical distribution of the comonomers along the polymer chain of **p(16-*co*-17)**.

2.3 Monte-Carlo simulation (MM3*) of *oligo*-(3OHPIC) 21_{16}

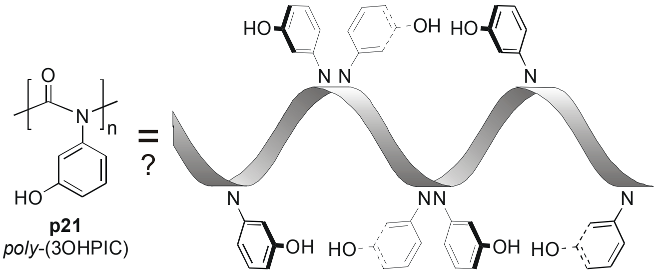


Figure 5: Schematic representation of the proposed multiple site BINOL analogue *poly*-(3OHPIC) **p21** (BINOL: 2,2’-dihydroxy-1,1’-binaphthyl).

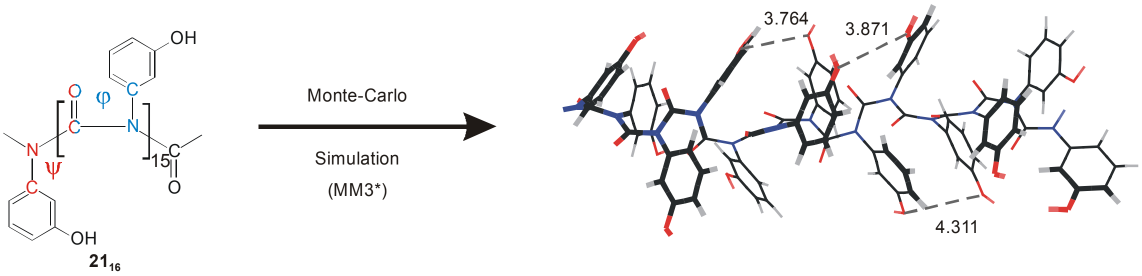
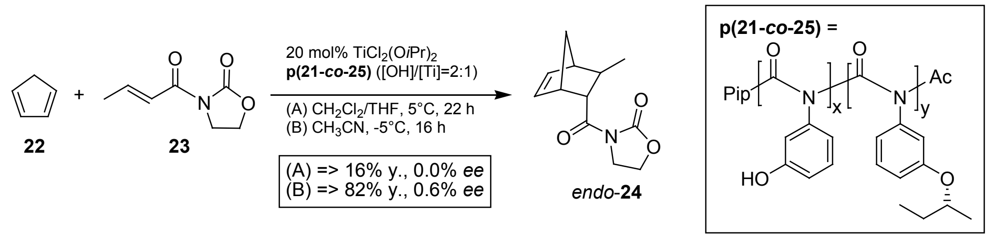


Figure 6: Monte-Carlo simulation (MM3*)(ref. 14) of $\mathbf{21_{16}}$ (φ=+174° and ψ=-56° ref. (15); all C-N- and C-O-bonds rotatable; 20000 calculation steps each with 500 energy minimization steps).

It is known that polyisocyanates are not stable towards bases including amines. Therefore we decided to chose oxygen and phosphorus as the ligating atoms. Alcohols and phenols are of particular interest because many examples of very successful catalysts with hydroxyl containing ligands like BINOL are known (16-18). In analogy to BINOL we thus chose poly(3-hydroxyphenyl isocyanate) **p21** (*poly*-(3OHPIC)) as the starting point of our examinations (Figure 5). In order to get some structural insight prior to the synthetic work, we carried out Monte Carlo simulations (MM3*) (14) on the hexadecamer $\mathbf{21_{16}}$ (Figure 6). The calculations indicate that the minimal distances between two phenolic oxygen atoms in consecutive turns are about 3.8 Å, which is very close to the O-O-distances in BINOL (19).

From these calculations we drew the conclusion that *poly*(3-hydroxyphenyl isocyanate) **p21** (*poly*-(3OHPIC)) might function as a multiple site analogon of the very prosperous ligand BINOL, which prompted us to explore the potential of this polymer as a ligand (Scheme 9).



Scheme 9: Titanium catalyzed asymmetric Diels-Alder reaction of **22** and **23**.

A helically chiral copolymer of **21** with 3-[(*R*)-1-*sec*-butoxy]phenyl isocyanate **25** ((*R*)-3BOPIC) was an active catalyst for the titanium catalyzed asymmetric Diels-Alder reaction of cyclopentadiene **22** and *N*-crotonyl-oxazolidin-2-one **23**. Unfortunately, the system performed very poor in the model reaction with respect to both reactivity and enantioselectivity (*rac*-*endo*-**24,** 16% yield). Since the analogous reaction with (*S*)-BINOL as a ligand gave a similar result (22% yield, 3.2% *ee*) we suspected a detrimental effect of the coordinating solvent THF. In accordance to that, the complexation and catalysis in CH_3CN at -5°C, the *endo*-product again was almost racemic (0.6% *ee*), although this time the catalyst was much more active (82% yield). Regrettably, the insolubility of the polymeric complex in non-coordinating solvents like CH_2Cl_2 prevented a further analysis of the solvent effect on catalyst performance.
Details of this investigation will be published elsewhere.

3 Supporting Data Set 1. X-ray Structural Data of Pd-PB2PyMA Pd-5

Empirical formula	$C_{24}H_{23}F_6N_2O_2PPd$	
Formula weight	622.81 gmol^{-1}	
Crystal size	0.80 x 0.28 x 0.04 mm^3, colorless needles	
Crystal system, space group	orthorhombic, P212121	
Unit cell dimensions	a = 9.969(2) Å	α = 90 deg
	b = 12.936(2) Å	β = 90 deg
	c = 19.391(2) Å	γ = 90 deg
Temperature	303(2) K	
Calculated density	1.654 gcm^{-3}	

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Refinement of F^2^ against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2^, conventional R-factors R are based on F, with F set to zero for negative F^2^. The threshold expression of F^2^ > 2sigma(F^2^) is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2^ are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

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3.1.1 Table 4. Atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$U_{eq} = (1/3)\cdot\Sigma\Sigma U_{ij} a_i \cdot a_j \cdot a_{ij}$

Atom	x (10^4)	y (10^4)	z (10^4)	U_{eq} (10^3)
C(1)	-3680(5)	-8894(5)	-878(3)	62(2)
C(2)	-4375(5)	-8868(7)	-1469(4)	92(2)
C(3)	-4258(6)	-8120(6)	-1973(3)	73(2)
C(4)	-421(6)	-10175(4)	-1005(2)	53(1)
C(5)	804(7)	-10617(4)	-864(3)	67(2)
C(6)	1955(6)	-10118(4)	-1039(3)	67(2)
C(7)	1860(5)	-9165(4)	-1331(2)	52(1)
C(8)	611(5)	-8736(4)	-1448(2)	39(1)
C(9)	437(4)	-7689(3)	-1809(2)	38(1)
C(10)	24(5)	-7948(4)	-2554(2)	37(1)
C(11)	869(5)	-7818(4)	-3100(2)	48(1)
C(12)	403(5)	-8107(4)	-3744(3)	51(2)
C(13)	-865(6)	-8458(4)	-3813(2)	51(2)
C(14)	-1658(4)	-8571(3)	-3242(2)	51(1)
C(15)	-570(4)	-6948(3)	-1475(2)	39(1)
C(16)	-1106(4)	-6152(3)	-1882(2)	53(1)
C(17)	-1946(5)	-5422(4)	-1602(3)	64(2)
C(18)	-2287(6)	-5475(4)	-920(3)	72(2)
C(19)	-1790(5)	-6265(5)	-521(3)	69(2)
C(20)	-958(5)	-6980(4)	-795(3)	51(1)
C(21)	2282(5)	-6787(3)	-1274(2)	45(1)
C(22)	3378(5)	-6042(4)	-1421(3)	49(1)
C(23)	3989(6)	-5581(5)	-809(3)	89(2)
C(24)	3757(5)	-5804(4)	-2062(3)	68(2)
N(1)	-523(4)	-9241(3)	-1307(2)	43(1)
N(2)	-1218(4)	-8339(3)	-2605(2)	44(1)
O(1)	1693(3)	-7148(2)	-1868(1)	44(1)
O(2)	1956(3)	-7056(3)	-715(2)	63(1)
Pd(1)	-2340(1)	-8667(1)	-1702(1)	45(1)

P(1)	4630(1)	-7244(1)	-4052(1)	55(1)
F(1)	5612(4)	-6807(3)	-3503(2)	128(2)
F(2)	4215(4)	-8131(3)	-3539(2)	114(1)
F(3)	3479(3)	-6556(3)	-3743(2)	118(1)
F(4)	3620(4)	-7677(3)	-4590(2)	126(2)
F(5)	5047(3)	-6329(3)	-4549(1)	100(1)
F(6)	5752(4)	-7911(4)	-4361(3)	160(2)

3.1.2 Table 5. Bond lengths [Å] and angles [deg]

C(1)-C(2)	1.339(8)	C(19)-H(19)	0.9300
C(1)-Pd(1)	2.103(5)	C(20)-H(20)	0.9300
C(1)-H(1A)	0.954(19)	C(21)-O(2)	1.184(5)
C(1)-H(1B)	0.955(19)	C(21)-O(1)	1.375(5)
C(2)-C(3)	1.381(9)	C(21)-C(22)	1.485(6)
C(2)-Pd(1)	2.095(5)	C(22)-C(24)	1.335(5)
C(2)-H(2)	0.955(19)	C(22)-C(23)	1.460(6)
C(2)-H(3B)	1.62(5)	C(23)-H(23A)	0.9600
C(3)-Pd(1)	2.106(6)	C(23)-H(23B)	0.9600
C(3)-H(3A)	0.969(19)	C(23)-H(23C)	0.9600
C(3)-H(3B)	0.972(19)	C(24)-H(24A)	0.9300
C(4)-N(1)	1.347(5)	C(24)-H(24B)	0.9300
C(4)-C(5)	1.376(7)	N(1)-Pd(1)	2.102(4)
C(4)-H(4)	0.9300	N(2)-Pd(1)	2.121(4)
C(5)-C(6)	1.360(7)	P(1)-F(6)	1.535(4)
C(5)-H(5)	0.9300	P(1)-F(1)	1.553(3)
C(6)-C(7)	1.360(6)	P(1)-F(4)	1.554(3)
C(6)-H(6)	0.9300	P(1)-F(3)	1.571(3)
C(7)-C(8)	1.382(5)	P(1)-F(2)	1.574(3)
C(7)-H(7)	0.9300	P(1)-F(5)	1.581(3)
C(8)-N(1)	1.333(5)		
C(8)-C(9)	1.535(6)	C(2)-C(1)-Pd(1)	71.1(3)
C(9)-O(1)	1.438(4)	C(2)-C(1)-H(1A)	111(3)
C(9)-C(15)	1.531(6)	Pd(1)-C(1)-H(1A)	109(3)
C(9)-C(10)	1.539(6)	C(2)-C(1)-H(1B)	95(3)
C(10)-N(2)	1.341(5)	Pd(1)-C(1)-H(1B)	91(3)
C(10)-C(11)	1.364(5)	H(1A)-C(1)-H(1B)	150(4)
C(11)-C(12)	1.384(6)	C(1)-C(2)-C(3)	125.4(7)
C(11)-H(11)	0.9300	C(1)-C(2)-Pd(1)	71.7(3)
C(12)-C(13)	1.350(6)	C(3)-C(2)-Pd(1)	71.3(4)
C(12)-H(12)	0.9300	C(1)-C(2)-H(2)	124(4)
C(13)-C(14)	1.368(5)	C(3)-C(2)-H(2)	106(4)
C(13)-H(13)	0.9300	Pd(1)-C(2)-H(2)	112(4)
C(14)-N(2)	1.345(5)	C(1)-C(2)-H(3B)	95.4(16)
C(14)-H(14)	0.9300	C(3)-C(2)-H(3B)	36.7(12)
C(15)-C(20)	1.376(6)	Pd(1)-C(2)-H(3B)	75.2(19)
C(15)-C(16)	1.402(5)	H(2)-C(2)-H(3B)	140(5)
C(16)-C(17)	1.374(6)	C(2)-C(3)-Pd(1)	70.4(3)
C(16)-H(16)	0.9300	C(2)-C(3)-H(3A)	125(4)
C(17)-C(18)	1.368(7)	Pd(1)-C(3)-H(3A)	115(3)
C(17)-H(17)	0.9300	C(2)-C(3)-H(3B)	85(3)
C(18)-C(19)	1.374(6)	Pd(1)-C(3)-H(3B)	89(3)
C(18)-H(18)	0.9300	H(3A)-C(3)-H(3B)	146(5)
C(19)-C(20)	1.350(6)	N(1)-C(4)-C(5)	121.7(5)

N(1)-C(4)-H(4)	119.1
C(5)-C(4)-H(4)	119.1
C(6)-C(5)-C(4)	120.2(5)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(7)-C(6)-C(5)	118.3(5)
C(7)-C(6)-H(6)	120.8
C(5)-C(6)-H(6)	120.8
C(6)-C(7)-C(8)	119.7(5)
C(6)-C(7)-H(7)	120.2
C(8)-C(7)-H(7)	120.2
N(1)-C(8)-C(7)	122.3(4)
N(1)-C(8)-C(9)	115.4(4)
C(7)-C(8)-C(9)	122.1(4)
O(1)-C(9)-C(15)	107.4(3)
O(1)-C(9)-C(8)	111.5(3)
C(15)-C(9)-C(8)	115.7(4)
O(1)-C(9)-C(10)	105.3(3)
C(15)-C(9)-C(10)	111.0(3)
C(8)-C(9)-C(10)	105.5(3)
N(2)-C(10)-C(11)	124.0(4)
N(2)-C(10)-C(9)	113.4(4)
C(11)-C(10)-C(9)	122.5(4)
C(10)-C(11)-C(12)	117.5(4)
C(10)-C(11)-H(11)	121.3
C(12)-C(11)-H(11)	121.3
C(13)-C(12)-C(11)	119.6(5)
C(13)-C(12)-H(12)	120.2
C(11)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	119.9(4)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.1
N(2)-C(14)-C(13)	122.0(4)
N(2)-C(14)-H(14)	119.0
C(13)-C(14)-H(14)	119.0
C(20)-C(15)-C(16)	117.0(4)
C(20)-C(15)-C(9)	124.8(4)
C(16)-C(15)-C(9)	118.2(4)
C(17)-C(16)-C(15)	121.0(5)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(18)-C(17)-C(16)	119.9(5)
C(18)-C(17)-H(17)	120.1
C(16)-C(17)-H(17)	120.1
C(17)-C(18)-C(19)	119.5(5)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(20)-C(19)-C(18)	120.7(5)
C(20)-C(19)-H(19)	119.7
C(18)-C(19)-H(19)	119.7
C(19)-C(20)-C(15)	121.9(5)
C(19)-C(20)-H(20)	119.0
C(15)-C(20)-H(20)	119.0
O(2)-C(21)-O(1)	123.3(4)
O(2)-C(21)-C(22)	124.7(5)
O(1)-C(21)-C(22)	112.0(4)
C(24)-C(22)-C(23)	123.0(5)
C(24)-C(22)-C(21)	122.4(5)
C(23)-C(22)-C(21)	114.6(5)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	120.0
C(22)-C(24)-H(24B)	120.0
H(24A)-C(24)-H(24B)	120.0
C(8)-N(1)-C(4)	117.7(4)
C(8)-N(1)-Pd(1)	118.9(3)
C(4)-N(1)-Pd(1)	122.7(4)
C(10)-N(2)-C(14)	117.0(4)
C(10)-N(2)-Pd(1)	120.1(3)
C(14)-N(2)-Pd(1)	122.8(3)
C(21)-O(1)-C(9)	118.1(3)
C(2)-Pd(1)-N(1)	135.4(3)
C(2)-Pd(1)-C(1)	37.2(2)
N(1)-Pd(1)-C(1)	102.8(2)
C(2)-Pd(1)-C(3)	38.4(2)
N(1)-Pd(1)-C(3)	172.9(2)
C(1)-Pd(1)-C(3)	70.1(2)
C(2)-Pd(1)-N(2)	135.5(3)
N(1)-Pd(1)-N(2)	85.21(15)
C(1)-Pd(1)-N(2)	171.9(2)
C(3)-Pd(1)-N(2)	101.8(2)
F(6)-P(1)-F(1)	90.7(3)
F(6)-P(1)-F(4)	90.4(2)
F(1)-P(1)-F(4)	178.7(2)
F(6)-P(1)-F(3)	179.4(3)
F(1)-P(1)-F(3)	89.6(2)
F(4)-P(1)-F(3)	89.3(2)
F(6)-P(1)-F(2)	91.6(3)
F(1)-P(1)-F(2)	89.85(19)
F(4)-P(1)-F(2)	89.5(2)
F(3)-P(1)-F(2)	88.9(2)
F(6)-P(1)-F(5)	89.5(2)
F(1)-P(1)-F(5)	88.87(17)
F(4)-P(1)-F(5)	91.77(19)
F(3)-P(1)-F(5)	90.0(2)
F(2)-P(1)-F(5)	178.3(2)

3.1.3 Table 6. Anisotropic displacement parameters (Å^2)

	U_{11} (10^3)	U_{22} (10^3)	U_{33} (10^3)	U_{23} (10^3)	U_{13} (10^3)	U_{12} (10^3)
C(1)	39(3)	72(5)	74(4)	-1(4)	20(3)	-9(3)
C(2)	34(4)	155(9)	87(6)	-9(6)	12(4)	3(4)
C(3)	49(4)	99(6)	70(4)	8(4)	-2(4)	14(4)
C(4)	80(4)	40(3)	38(3)	-3(3)	0(3)	3(3)
C(5)	100(5)	39(3)	61(4)	2(3)	-27(4)	11(4)
C(6)	69(5)	51(4)	81(4)	-17(3)	-31(4)	20(3)
C(7)	51(3)	41(3)	63(3)	-7(3)	-12(3)	9(2)
C(8)	61(3)	34(3)	21(2)	-2(2)	-8(2)	4(3)
C(9)	43(3)	38(3)	34(3)	-4(2)	1(2)	-3(2)
C(10)	40(3)	39(3)	30(3)	1(2)	-2(2)	4(2)
C(11)	49(3)	55(3)	40(3)	-3(3)	6(3)	-6(3)
C(12)	61(4)	51(4)	42(3)	-1(3)	6(3)	-1(3)
C(13)	72(4)	64(4)	18(2)	-2(3)	0(3)	0(3)
C(14)	63(3)	49(3)	41(3)	-2(3)	-12(3)	-11(3)
C(15)	40(3)	34(3)	42(3)	-6(2)	8(2)	-3(2)
C(16)	63(3)	38(3)	58(3)	-7(3)	3(3)	-1(3)
C(17)	69(4)	40(3)	84(4)	-2(3)	1(4)	9(2)
C(18)	70(4)	47(3)	101(5)	-24(3)	15(4)	-5(3)
C(19)	90(4)	61(4)	56(3)	-22(4)	32(3)	2(4)
C(20)	68(4)	42(3)	43(3)	0(3)	0(3)	0(3)
C(21)	45(3)	49(3)	41(3)	-5(2)	-5(3)	5(3)
C(22)	49(3)	52(4)	47(3)	-6(3)	-4(3)	-7(3)
C(23)	84(5)	102(5)	81(4)	9(4)	-21(4)	-31(4)
C(24)	73(4)	65(4)	68(4)	-1(3)	17(3)	-16(3)
N(1)	61(3)	35(3)	32(2)	2(2)	-3(2)	-6(2)
N(2)	51(3)	42(3)	39(2)	-3(2)	2(2)	-5(2)
O(1)	41(2)	58(2)	32(2)	-3(2)	0(1)	-7(2)
O(2)	82(3)	77(2)	31(2)	1(2)	-3(2)	-18(2)
Pd(1)	51(1)	47(1)	38(1)	2(1)	2(1)	-3(1)
P(1)	58(1)	67(1)	40(1)	-2(1)	-1(1)	-3(1)
F(1)	139(3)	166(4)	79(2)	25(2)	-46(2)	-77(3)
F(2)	142(3)	101(3)	100(3)	38(2)	-13(2)	-36(2)
F(3)	119(3)	108(3)	127(3)	-16(2)	49(2)	22(2)
F(4)	134(3)	178(4)	67(2)	-19(2)	-32(2)	-56(3)
F(5)	137(3)	107(3)	57(2)	24(2)	5(2)	-31(3)
F(6)	123(3)	139(4)	218(5)	-10(4)	68(3)	44(3)

3.1.4 Table 7. Hydrogen coordinates and equivalent isotropic displacement parameters (Å^2)

$U_{eq} = (1/3)\cdot\Sigma\Sigma U_{ij}a_i\cdot a_j\cdot a_{ij}$

Atom	x (10^4)	y (10^4)	z (10^4)	U_{eq} (10^3)
H(1A)	-3590(50)	-9580(20)	-710(20)	74
H(1B)	-3730(40)	-8168(17)	-790(20)	74
H(2)	-4740(50)	-9460(30)	-1690(30)	110
H(3A)	-4500(50)	-8210(40)	-2453(13)	87
H(3B)	-4210(50)	-7640(30)	-1590(20)	87
H(4)	-1200	-10531	-889	63

H(5)	844	-11258	-648	80
H(6)	2787	-10422	-961	80
H(7)	2632	-8804	-1452	62
H(11)	1725	-7546	-3042	57
H(12)	960	-8059	-4128	61
H(13)	-1198	-8624	-4247	62
H(14)	-2529	-8815	-3296	61
H(16)	-890	-6119	-2348	63
H(17)	-2282	-4892	-1876	77
H(18)	-2851	-4981	-727	87
H(19)	-2028	-6308	-58	83
H(20)	-638	-7509	-515	61
H(23A)	4354	-6117	-523	107
H(23B)	3321	-5205	-556	107
H(23C)	4693	-5119	-947	107
H(24A)	4439	-5325	-2134	82
H(24B)	3339	-6117	-2436	82

3.1.5 Table 8. Torsion angles [deg]

Pd(1)-C(1)-C(2)-C(3)	-49.5(6)
C(1)-C(2)-C(3)-Pd(1)	49.6(6)
N(1)-C(4)-C(5)-C(6)	-1.0(8)
C(4)-C(5)-C(6)-C(7)	2.4(8)
C(5)-C(6)-C(7)-C(8)	-0.6(7)
C(6)-C(7)-C(8)-N(1)	-2.6(7)
C(6)-C(7)-C(8)-C(9)	-176.8(4)
N(1)-C(8)-C(9)-O(1)	173.3(3)
C(7)-C(8)-C(9)-O(1)	-12.1(5)
N(1)-C(8)-C(9)-C(15)	50.2(5)
C(7)-C(8)-C(9)-C(15)	-135.3(4)
N(1)-C(8)-C(9)-C(10)	-72.9(4)
C(7)-C(8)-C(9)-C(10)	101.7(4)
O(1)-C(9)-C(10)-N(2)	-171.8(3)
C(15)-C(9)-C(10)-N(2)	-55.9(5)
C(8)-C(9)-C(10)-N(2)	70.1(4)
O(1)-C(9)-C(10)-C(11)	10.1(5)
C(15)-C(9)-C(10)-C(11)	126.1(4)
C(8)-C(9)-C(10)-C(11)	-107.9(5)
N(2)-C(10)-C(11)-C(12)	0.2(7)
C(9)-C(10)-C(11)-C(12)	178.1(4)
C(10)-C(11)-C(12)-C(13)	2.7(8)
C(11)-C(12)-C(13)-C(14)	-2.9(8)
C(12)-C(13)-C(14)-N(2)	0.1(7)
O(1)-C(9)-C(15)-C(20)	-102.1(5)
C(8)-C(9)-C(15)-C(20)	23.2(6)
C(10)-C(9)-C(15)-C(20)	143.3(4)
O(1)-C(9)-C(15)-C(16)	75.5(5)
C(8)-C(9)-C(15)-C(16)	-159.2(4)
C(10)-C(9)-C(15)-C(16)	-39.2(5)
C(20)-C(15)-C(16)-C(17)	2.0(6)
C(9)-C(15)-C(16)-C(17)	-175.7(4)
C(15)-C(16)-C(17)-C(18)	-1.1(7)
C(16)-C(17)-C(18)-C(19)	-0.4(8)
C(17)-C(18)-C(19)-C(20)	0.8(8)
C(18)-C(19)-C(20)-C(15)	0.3(8)
C(16)-C(15)-C(20)-C(19)	-1.7(7)
C(9)-C(15)-C(20)-C(19)	175.9(4)
O(2)-C(21)-C(22)-C(24)	176.4(6)
O(1)-C(21)-C(22)-C(24)	-2.8(6)
O(2)-C(21)-C(22)-C(23)	-4.5(7)
O(1)-C(21)-C(22)-C(23)	176.3(4)
C(7)-C(8)-N(1)-C(4)	3.9(6)
C(9)-C(8)-N(1)-C(4)	178.4(4)
C(7)-C(8)-N(1)-Pd(1)	-166.6(3)
C(9)-C(8)-N(1)-Pd(1)	8.0(5)
C(5)-C(4)-N(1)-C(8)	-2.1(7)
C(5)-C(4)-N(1)-Pd(1)	168.0(4)
C(11)-C(10)-N(2)-C(14)	-2.9(6)
C(9)-C(10)-N(2)-C(14)	179.0(4)
C(11)-C(10)-N(2)-Pd(1)	172.7(4)
C(9)-C(10)-N(2)-Pd(1)	-5.4(5)
C(13)-C(14)-N(2)-C(10)	2.7(6)
C(13)-C(14)-N(2)-Pd(1)	-172.7(4)
O(2)-C(21)-O(1)-C(9)	14.5(6)
C(22)-C(21)-O(1)-C(9)	-166.4(3)
C(15)-C(9)-O(1)-C(21)	59.5(5)
C(8)-C(9)-O(1)-C(21)	-68.2(5)
C(10)-C(9)-O(1)-C(21)	177.9(3)
C(1)-C(2)-Pd(1)-N(1)	35.5(6)
C(3)-C(2)-Pd(1)-N(1)	174.7(3)
C(3)-C(2)-Pd(1)-C(1)	139.2(7)
C(1)-C(2)-Pd(1)-C(3)	-139.2(7)
C(1)-C(2)-Pd(1)-N(2)	-174.7(3)
C(3)-C(2)-Pd(1)-N(2)	-35.5(6)
C(8)-N(1)-Pd(1)-C(2)	-161.2(4)
C(4)-N(1)-Pd(1)-C(2)	28.8(5)
C(8)-N(1)-Pd(1)-C(1)	-140.1(3)

C(4)-N(1)-Pd(1)-C(1)	49.9(4)	C(2)-C(3)-Pd(1)-N(2)	155.4(4)
C(8)-N(1)-Pd(1)-C(3)	-133.4(18)	C(10)-N(2)-Pd(1)-C(2)	159.4(4)
C(4)-N(1)-Pd(1)-C(3)	56.6(19)	C(14)-N(2)-Pd(1)-C(2)	-25.3(5)
C(8)-N(1)-Pd(1)-N(2)	39.5(3)	C(10)-N(2)-Pd(1)-N(1)	-41.3(3)
C(4)-N(1)-Pd(1)-N(2)	-130.5(3)	C(14)-N(2)-Pd(1)-N(1)	134.0(3)
C(2)-C(1)-Pd(1)-N(1)	-155.3(5)	C(10)-N(2)-Pd(1)-C(1)	135.9(14)
C(2)-C(1)-Pd(1)-C(3)	25.6(5)	C(14)-N(2)-Pd(1)-C(1)	-48.8(16)
C(2)-C(1)-Pd(1)-N(2)	27.6(17)	C(10)-N(2)-Pd(1)-C(3)	137.8(4)
C(2)-C(3)-Pd(1)-N(1)	-32(2)	C(14)-N(2)-Pd(1)-C(3)	-46.9(4)
C(2)-C(3)-Pd(1)-C(1)	-24.9(4)		

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