Supporting Information

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Mass Spectrometric Screening of Chiral Catalysts by Monitoring the Back Reaction of Quasienantiomeric Products: Pd-Catalyzed Allylic Substitution

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General

All reactions were performed in flame-dried glassware under argon using Schlenk techniques or under purified N₂ in a glovebox (Mbraun Labmaster 130).

Air- or moisture-sensitive reagents were transferred using oven-dried gas-tight syringes or canulas and were introduced into the apparatus through septa. Solvents were distilled from calcium hydride (dichloromethane, triethylamine) or sodium (diethyl ether, tetrahydrofuran) and stored under nitrogen. Solvents were degassed by using the “freeze-pump-thaw” technique (three cycles). Reagents were purchased from Acros, Aldrich, Fluka, Strem or Lancaster and used without further purification. Column chromatography: Merck silica gel 60 (Darmstadt, 40-63 nm). For TLC analyses precoated Macherey-Nagel Polygram SIL G/UV₂₅₄ plates were used and the compounds visualized with the help of UV light. All NMR experiments were performed on Bruker Avance 400 or 500 spectrometers. ¹H and ¹³C spectra are referenced relative to tetramethylsilane using the solvent residual peaks and the solvent signals, respectively, as internal standards.¹ MS spectra: VG70-250 or Finnigan MAT 95Q (EI). Elemental analyses were performed by the Micro Analytical Laboratory of the University of Basel. IR spectra: Perkin Elmer 1600 FTIR spectrometer. Melting points were determined on a Büchi 535 apparatus and are uncorrected. Optical rotations were measured on a Perkin Elmer polarimeter 341 equipped with a Na lamp.

ESI-MS spectra were recorded on a Varian 1200L Quadrupol MS/MS spectrometer using mild desolvation conditions (39 psi nebulizing gas, 4.9 kV spray voltage, 19 psi drying gas at 200 °C, 75 V capillary voltage, 1500 V detector voltage). Every spectrum consisted of at least 50 averaged scans. Samples were diluted immediately prior to their analysis and measured using direct injection.
4-Methylcinnamaldehyde (14) was prepared according to a published procedure.[2]

To a stirred solution of 4-iodotoluene (4.81 g, 22.3 mmol) in abs. DMF (85 mL) were added acrolein diethyl acetal (8.05 g, 61.8 mmol), [(nBu)4N]OAc (13.4 g, 44.5 mmol), K2CO3 (4.27 g, 30.9 mmol), KCl (1.64 g, 22.0 mmol) and Pd(OAc)2 (111 mg, 0.500 mmol). The mixture was stirred for 3 h at 90 °C. After cooling the reaction to r.t. 2 M HCl (100 mL) was slowly added and the resulting mixture stirred for 10 min. It was then diluted with Et2O and washed with water. The organic layer was dried over MgSO4 and concentrated under reduced pressure. The residue was purified by column chromatography (5 cm × 20 cm, silica gel, hexanes/EtOAc 10:1) to give aldehyde 14 (2.57 g, 79%) as slightly yellow solid.

**m.p.** 40-42 °C.

**Rf** = 0.44 (hexanes/EtOAc 4:1).

1H NMR (400 MHz, CDCl3): \(\delta = 2.39\) (s, 3 H, CH3), 6.65 (ddd, \(\delta J = 16.0, 7.7\) Hz, \(\delta J = 0.7\) Hz, 1 H, ArCHCH), 7.22 (d, \(\delta J = 8.3\) Hz, 2 H, Ar-m-H), 7.43 (d, \(\delta J = 16.0\) Hz, 1 H, ArCHCH), 7.45 (d, \(\delta J = 7.9\) Hz, 2 H, Ar-o-H), 9.67 (d, \(\delta J = 7.7\) Hz, \(\delta J = 0.9\) Hz, 1 H, CHO) ppm.

13C{1H} NMR (101 MHz, CDCl3): \(\delta = 21.7\) (CH3), 128.7 (Ar-o-CH), 127.8 (ArCHCH), 129.9 (Ar-m-CH), 131.4 (Ar-i-C), 142.1 (Ar-p-C), 153.1 (ArCHCH), 194.0 (CHO) ppm.

IR (KBr): \(\tilde{\nu} = 3028, 2967, 2923, 2841, 2756, 1932, 1678, 1608, 1512, 1417, 1298, 1251, 1181, 1127, 1010, 979, 805\) cm\(^{-1}\).

MS (EI, 70 eV): \(m/z\) (%) = 146 (21, M\(^+\)), 131 (100, [M–CH3]\(^+\)), 117 (29, [M–CHO]\(^+\)), 115 (34), 103 (21), 91 (30).

**Elemental analysis** calcd. (%) for C10H10O (146.19): C 82.16, H 6.89; found: C 82.03, H 6.97.
At –78 °C 4-bromotoluene (3.05 g, 17.8 mmol) in abs. THF (36 mL) was treated with nBuLi in hexane (2.5 M, 9.70 mL, 24.3 mmol) under argon resulting in the precipitation of a colorless solid. The mixture was warmed to –25 °C, until all the precipitate dissolved, recooled to –78 °C and treated with a solution of aldehyde 14 (1.81 g, 12.4 mmol) in abs. THF (6 mL). The mixture was allowed to warm to r.t. overnight and then quenched with saturated aqueous NH₄Cl solution (75 mL). The THF was removed in vacuo, the residue extracted with Et₂O and the combined extracts were washed with saturated aqueous solutions of NH₄Cl and NaCl. After drying over MgSO₄ the solvent was evaporated. The residue was purified by flash column chromatography (5 cm × 20 cm, silica gel, hexanes/EtOAc 5:1) and 15 was obtained as a colorless solid (2.78 g, 94%).

m.p. 64 °C.

R_f = 0.30 (hexanes/EtOAc 5:1).

^1H NMR (400 MHz, CDCl₃): δ = 2.10 (br s, 1 H, OH), 2.35 (s, 3 H, CH₃), 2.37 (s, 3 H, CH₃), 5.34 (d, ^3J = 6.5 Hz, 1 H, CHOH), 6.31 (dd, ^3J = 15.7, 6.5 Hz, 1 H, ArCHCH), 6.67 (d, ^3J = 15.7 Hz, 1 H, ArCHCH), 7.10-7.25 (m, 4 H, Ar-H), 7.27-7.40 (m, 4 H, Ar-H) ppm.

^13C{¹H} NMR (101 MHz, CDCl₃): δ = 21.3 (CH₃), 21.3 (CH₃), 75.2 (CHOH), 126.4 (CH), 126.6 (CH), 129.4 (CH), 129.4 (CH), 130.4 (CH), 130.8 (CH), 133.9 (3-Ar-i-C), 137.6 (Ar-p-C), 137.8 (Ar-p-C), 140.1 (1-Ar-i-C) ppm.

IR (KBr): ʋ = 3262, 3022, 2915, 1905, 1801, 1716, 1509, 1417, 1207, 1087, 1021, 966, 805, 743, 713, 656, 512 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 238 (21, M⁺), 223 (16, [M–CH₃]⁺), 119 (100), 105 (20), 91 (21, C₇H₇⁺).

Elemental analysis calcd. (%) for C₁₇H₁₈O (238.32): C 85.67, H 7.61, O 6.71; found: C 85.68, H 7.69, O 6.66.
1,3-Di-(4'-tolyl)-prop-2-enyl benzoate (16)

A solution of alcohol 15 (1.90 g, 7.90 mmol), abs. NEt$_3$ (1.75 g, 17.3 mmol) and 4-(dimethylamino)-pyridine (25.0 mg, 205 µmol) in abs. CH$_2$Cl$_2$ (32 mL) was treated dropwise with benzoyl chloride (1.46 g, 10.4 mmol) at –78 °C. The mixture was allowed to warm to r.t. overnight. After quenching the reaction with saturated aqueous NH$_4$Cl solution (20 mL), the aqueous phase was extracted with CH$_2$Cl$_2$ and the combined extracts were dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (5 cm × 20 cm, silica gel, hexanes/EtOAc/NEt$_3$ 18:1:1) to yield benzoate 16 as a colorless solid (2.48 g, 91%).

m.p. 58-59 °C.

R$_f$ = 0.56 (hexanes/EtOAc 4:1).

$^1$H NMR (400 MHz, CDCl$_3$): δ = 2.33 (s, 3 H, CH$_3$), 2.36 (s, 3 H, CH$_3$), 6.40 (dd, $^3$$J$ = 16.0, 6.9 Hz, 1 H, ArCHCH$_2$), 6.66 (d, $^3$$J$ = 6.9 Hz, 1 H, CHOBz), 6.68 (d, $^3$$J$ = 16.0 Hz, 1 H, ArCHCH$_2$), 7.11 (d, $^3$$J$ = 7.8 Hz, 2 H, Ar-H), 7.21 (d, $^3$$J$ = 8.1 Hz, 2 H, Ar-H), 7.29 (d, $^3$$J$ = 8.1 Hz, 2 H, Ar-H), 7.39-7.49 (m, 4 H, Ar-H), 7.55 (m, 1 H, Bz-p-H), 8.12 (d, $^3$$J$ = 7.8 Hz, 2 H, Bz-o-H) ppm.

$^{13}$C{1H} NMR (101 MHz, CDCl$_3$): δ = 21.3 (CH$_3$), 21.4 (CH$_3$), 76.8 (CHOBz), 126.8 (CH), 126.8 (CH), 127.2 (CH), 128.4 (CH), 129.4 (CH), 129.5 (CH), 129.9 (CH), 130.3 (Bz-i-C), 132.7 (CH), 133.1 (CH), 133.6 (3-pTol-i-C), 136.6 (pTol-p-C), 138.0 (pTol-p-C), 138.1 (1-pTol-i-C), 166.8 (PhCO$_2$) ppm.

IR (KBr): $\tilde{\nu}$ = 3026, 2920, 1907, 1716, 1602, 1512, 1450, 1312, 1264, 1176, 1103, 1066, 1025, 968, 805, 709, 578 cm$^{-1}$.

MS (EI, 70 eV): m/z (%) = 342 (12, M$^+$), 237 (42, [M–C$_2$H$_2$O]$^+$), 221 (61, [M–OBz]$^+$), 220 (100), 205 (44), 129 (15), 105 (75), 77 (21, C$_6$H$_5$)$^+$.  

Elemental analysis calcd. (%) for C$_{24}$H$_{22}$O$_2$ (342.43): C 84.18, H 6.48; found: C 84.40, H 6.60.
**4-Ethylcinnamaldehyde (17)**

![Image of 4-Ethylcinnamaldehyde (17)]

To a stirred solution of 1-ethyl-4-iodobenzene (4.81 g, 20.7 mmol) in abs. DMF (85 mL) were added acrolein diethyl acetal (8.06 g, 61.9 mmol), [(nBu)₄]NOAc (12.4 g, 41.3 mmol), K₂CO₃ (4.28 g, 31.0 mmol), KCl (1.54 g, 20.7 mmol) and Pd(OAc)₂ (139 mg, 0.600 mmol). The mixture was stirred for 15 h at 90 °C. After cooling the reaction to r.t. 2 M HCl was slowly added and the mixture stirred for 10 min. It was then diluted with Et₂O and washed with water. The organic layer was dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography (5 cm × 20 cm, silica gel, hexanes/EtOAc 10:1) to give 4-ethylcinnamaldehyde (17, 2.04 g, 88%) as yellow solid.

**m.p.** 25 °C.

**Rf** = 0.30 (hexanes/EtOAc 4:1).

**¹H NMR** (400 MHz, CDCl₃): δ = 1.24 (t, ³J = 7.7 Hz, 3 H, CH₃), 2.65 (q, ³J = 7.7 Hz, 2 H, CH₂), 6.65 (dd, ³J = 16.2, 7.9 Hz, 1 H, ArCHC₃H), 7.25 (d, ³J = 8.1 Hz, 2 H, Ar-m-H), 7.43 (d, ³J = 16.2 Hz, 1 H, ArCHCH), 7.47 (d, ³J = 8.2 Hz, 2 H, Ar-o-H), 9.67 (d, ³J = 7.9 Hz, 1 H, CHO) ppm.

**¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 15.3 (CH₃), 28.9 (CH₂), 127.8 (ArCHCH), 128.7 (Ar-o-CH), 128.8 (Ar-m-CH), 131.6 (Ar-i-C), 148.3 (Ar-p-C), 153.1 (ArCHCH), 193.9 (CHO) ppm.

**IR** (KBr): ʋ = 3028, 2967, 2932, 2873, 2818, 2736, 1913, 1678, 1621, 1566, 1511, 1456, 1423, 1389, 1297, 1249, 1181, 1056, 1010, 907, 858, 752 cm⁻¹.

**MS** (EI, 70 eV): m/z (%) = 160 (12, M⁺), 131 (100, [M–C₂H₅]⁺), 115 (15), 103 (16), 91 (10).

**Elemental analysis** calcd. (%) for C₁₁H₁₂O (160.21): C 82.46, H 7.55; found: C 82.35, H 7.53.
At −78 °C 1-ethyl-4-iodobenzene (2.70 g, 11.6 mmol) in abs. THF (30 mL) was treated with nBuLi in hexane (2.5 M, 6.40 mL, 16.0 mmol) under argon. The orange suspension was allowed to warm to −25 °C, re-cooled to −78 °C and treated with a solution of 17 (1.29 g, 8.10 mmol) in abs. THF (4 mL). The mixture was warmed to r.t. overnight and then quenched with saturated aqueous NH₄Cl solution (30 mL). The THF was removed in vacuo, the residue was extracted with Et₂O and the combined extracts were washed with saturated aqueous solutions of NH₄Cl and NaCl. After drying over MgSO₄ the solvent was evaporated. The residue was purified by flash column chromatography (5 cm × 20 cm, silica gel, pentane/Et₂O 5:1) and alcohol 18 was obtained as a colorless solid (1.09 g, 51%).

m.p. 61-63 °C.

$R_f = 0.31$ (hexanes/EtOAc 4:1).

$^1$H NMR (400 MHz, CDCl₃): δ = 1.23 (m, 6 H, CH₃), 2.08 (d, $^3$J = 3.7 Hz, 1 H, OH), 2.68 (m, 4 H, CH₂), 5.36 (d, $^3$J = 6.6 Hz, 1 H, CHOH), 6.32 (dd, $^3$J = 15.8, 6.6 Hz, 1 H, ArCHCH), 6.65 (d, $^3$J = 15.8 Hz, 1 H, ArCHCH), 7.13-7.17 (m, 2 H, Ar-H), 7.19-7.23 (m, 2 H, Ar-H), 7.30-7.36 (m, 4 H, Ar-H) ppm.

$^{13}$C{$^1$H} NMR (101 MHz, CDCl₃): δ = 15.7 (CH₃), 15.7 (CH₃), 28.7 (CH₂), 28.7 (CH₂), 75.2 (CHOH), 126.5 (Ar-CH), 126.7 (Ar-CH), 128.2 (Ar-CH), 128.2 (Ar-CH), 130.4 (ArCHCH), 130.8 (ArCHCH), 134.2 (3-Ar-i-C), 140.3 (Ar-p-C), 144.0 (Ar-p-C), 144.1 (1-Ar-i-C) ppm.

IR (KBr): $\nu$ = 3392, 3021, 2963, 2929, 2871, 1512, 1457, 1419, 1179, 1090, 967, 832 cm$^{-1}$.

MS (El, 70 eV): m/z (%) = 266 (16, M$^+$), 237 (47, [M–C₂H₅]$^+$), 133 (100), 119 (18, C₈H₇O$^+$), 91 (7, C₇H₇$^+$).

Elemental analysis calcd. (%) for C₁₉H₂₂O (266.38): C 85.67, H 8.32; found: C 85.48, H 8.38.
1,3-Di-(4’-ethylphenyl)-prop-2-enyl benzoate (19)

At –78 °C a solution of alcohol 18 (492 mg, 1.84 mmol), abs. NEt₃ (379 mg, 3.80 mmol) and 4-(dimethylamino)-pyridine (6.00 mg, 49.0 µmol) in abs. CH₂Cl₂ (8 mL) was treated dropwise with benzoyl chloride (379 mg, 2.40 mmol). The mixture was allowed to warm to r.t. overnight. The reaction was quenched with saturated aqueous NH₄Cl solution (5 mL). The aqueous phase was extracted with CH₂Cl₂ and the combined extracts were dried over MgSO₄. The solvent was removed under reduced pressure and the residue was re-crystallized from hexanes/CH₂Cl₂ to yield benzoate 19 as a colorless solid (512 mg, 75%).

m.p. 79 °C.

Rᶠ = 0.53 (hexanes/EtOAc 4:1).

¹H NMR (400 MHz, CDCl₃): δ = 1.21 (t, 3J = 7.5 Hz, 3 H, CH₃), 1.24 (t, 3J = 7.6 Hz, 3 H, CH₃), 2.62 (q, 3J = 7.6 Hz, 2 H, CH₂), 2.66 (q, 3J = 7.5 Hz, 2 H, CH₂), 6.42 (dd, 3J = 15.9, 6.7 Hz, 1 H, ArCHCH), 6.66 (d, 3J = 6.7 Hz, 1 H, CHOBz), 6.71 (d, 3J = 15.9 Hz, 1 H, ArCHCH), 7.12 (d, 3J = 8.2 Hz, 2 H, Ar-H), 7.21 (d, 3J = 8.2 Hz, 2 H, Ar-H), 7.31 (d, 3J = 8.0 Hz, 2 H, Ar-H), 7.40-7.48 (m, 4 H, Ar-H), 7.54 (m, 1 H, Bz-p-H), 8.11 (d, 3J = 8.1 Hz, 2 H, Bz-o-H) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 15.6 (CH₃), 15.7 (CH₃), 28.7 (CH₂), 28.7 (CH₂), 76.8 (CHOBz), 126.9 (CH), 127.2 (CH), 128.2 (CH), 128.3 (CH), 128.5 (CH), 129.9 (CH), 130.6 (Bz-i-C), 132.7 (CH), 133.1 (CH), 133.9 (3-Ar-i-C), 136.8 (1-Ar-i-C), 144.4 (Ar-p-C), 144.5 (Ar-p-C), 165.8 (PhCO₂) ppm.

IR (KBr): ν = 3027, 2961, 2868, 1915, 1710, 1601, 1452, 1312, 1266, 1174, 1103, 1065, 975, 824, 706, 580 cm⁻¹.

MS (EI, 70 eV): m/z (%) = 370 (16, M⁺), 265 (56, [M–C₆H₅O⁺]), 249 (62, [M–OBz⁺]), 248 (100), 219 (52), 205 (21), 113 (29), 105 (96, C₆H₅⁻), 77 (25, C₆H₃⁺).

Elemental analysis calcd. (%) for C₂₆H₂₆O₂ (370.48): C 84.29, H 7.07; found: C 84.27, H 7.30.
General procedure for Pd-catalyzed allylic alkylations

In a Young tube a solution of [Pd(C3H5)Cl]2 (8.00 mg, 2.50 mol%) and chiral ligand 10 (19.3 mg, 5.90 mol%) in CH2Cl2 (2 mL) was degassed three times by freeze-pump-thaw cycles. The ampoule was sealed at 0.01 mbar and the solution stirred at 50 °C for 2 h. A solution of the substrate (875 μmol, 1.00 equiv.) in CH2Cl2 (3.5 mL) in a Young tube was subsequently treated with acetyl acetone (263 mg, 2.63 mmol, 3.00 equiv.), followed by BSA (535 mg, 2.63 mmol, 3.00 equiv.) and catalytic amounts of dried KOAc (ca. 5.00 mg). After three freeze-pump-thaw cycles the catalyst solution was added via syringe and the resulting mixture stirred at 0 °C. After 40 h the reaction was diluted with Et2O and ice-cold saturated aqueous NH4Cl solution was added. The aqueous phase was extracted twice with Et2O and the combined extracts were dried over MgSO4. After evaporation of the solvent column chromatography (3 cm × 20 cm, silica gel, hexanes/EtOAc/NEt3 18:1:1) afforded the product. The enantiomeric excess was determined on a chiral HPLC column.

(R)-3-(1’,3’-Di-(4”-tolyl)-prop-2’-enyl)-pentane-2,4-dione ((R)-6a)

![Chemical structure of (R)-6a](image)

Compound (R)-6a was obtained as colorless solid in 90% yield with > 99.5% ee using Phox ligand (R)-10.

m.p. 95 °C.

$R_f = 0.47$ (hexanes/EtOAc 4:1).

$^1$H NMR (400 MHz, CDCl3): $\delta = 1.93$ (s, 3 H, COCH3), 2.24 (s, 3 H, COCH3), 2.30 (s, 6 H, CH3), 4.24-4.35 (m, 2 H, CHCH(COCH3)2 and CHCH(COCH3)2), 6.09 (dd, $^3J = 15.8$, 7.0 Hz, 1 H, ArCHCCH3), 6.36 (d, $^3J = 15.8$ Hz, 1 H, ArCHCH3), 7.02-7.21 (m, 8 H, Ar-H) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CDCl3): $\delta = 21.2$ (CH3), 21.3 (CH3), 29.9 (COCH3), 30.1 (COCH3), 49.0 (CHCH(COCH3)2), 74.8 (CHCH(COCH3)2), 126.4 (CH), 127.9 (CH), 128.5 (CH), 129.3 (CH), 129.8 (CH), 131.4 (CH), 134.0 (3-Ar-i-C), 137.0 (C), 137.3 (C), 137.6 (C), 203.1 (COCH3), 203.2 (COCH3) ppm.
**IR** (KBr): $\tilde{\nu} = 3026, 2929, 2863, 1914, 1727, 1512, 1416, 1359, 1276, 1139, 1065, 1038, 973, 927, 820, 721, 581, 527 \text{ cm}^{-1}$.

**MS** (FAB, NBA+KCl): $m/z$ (%) = 359 (24, [M+K]$^+$), 302 (29, [M–C$_7$H$_5$O]$^+$), 277 (100, C$_{17}$H$_{17}^+$), 129 (19), 105 (22, C$_8$H$_9^+$), 43 (36, CH$_3$CO$^+$).

$[\alpha]^20_D = -11.0 \ (c = 1.00, \text{CHCl}_3)$.

**HPLC** (Daicel Chiracel AD-H, heptane/iPrOH 97:3, 0.9 mL*min$^{-1}$, 20°C, 254 nm): $t_R = 16.3 \ (R), 17.8 \ (S)$ min ($> 99.5\%$ ee).

**Elemental analysis** calcd. (%) for C$_{22}$H$_{24}$O$_2$ (320.42): C 82.46, H 7.55; found: C 82.14, H 7.60.

**(S)-3-((1',3'-Di-(4''-tolyl)-prop-2'-enyl)-pentane-2,4-dione ((S)-6a)**

![Chemical structure of (S)-6a](image)

Compound (S)-6a was obtained as colorless solid in 94% yield with $> 99.5\%$ ee using Phox ligand (S)-10.

$[\alpha]^20_D = +11.4 \ (c = 1.00, \text{CHCl}_3)$.

**(R)-3-((1',3'-Di-(4''-ethylphenyl)-prop-2'-enyl)-pentane-2,4-dione ((R)-6b)**

![Chemical structure of (R)-6b](image)

Compound (R)-6b was obtained as colorless solid in quantitative yield with $> 99\%$ ee using Phox ligand (R)-10.
m.p. 65 °C.

\( R_f = 0.48 \) (hexanes/EtOAc 4:1).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 1.19 \) (t, \( ^3J = 7.7 \) Hz, 3 H, CH\(_2\)CH\(_3\)), 1.20 (t, \( ^3J = 7.7 \) Hz, 3 H, CH\(_2\)CH\(_3\)), 1.93 (s, 3 H, COCH\(_3\)), 2.24 (s, 3 H, COCH\(_3\)), 2.58 (q, \( ^3J = 7.7 \) Hz, 2 H, CH\(_2\)), 2.59 (q, \( ^3J = 7.7 \) Hz, 2 H, CH\(_2\)), 4.25-4.35 (m, 2 H, CHCH(COCH\(_3\))\(_2\) and CHCH(COCH\(_3\))\(_2\)), 6.10 (ddd, \( ^3J = 15.8, 7.0 \) Hz, \( ^4J = 1.0 \) Hz, 1 H, ArCH\(_3\)), 6.37 (d, \( ^3J = 15.8 \) Hz, 1 H, ArCH\(_3\)), 7.04-7.24 (m, 8 H, Ar-H) ppm.

\(^{13}\)C\{\(^1\)H\} NMR (101 MHz, CDCl\(_3\)): \( \delta = 15.5 \) (CH\(_2\)CH\(_3\)), 15.7 (CH\(_2\)CH\(_3\)), 28.5 (CH\(_2\)), 28.7 (CH\(_2\)), 29.9 (COCH\(_3\)), 30.2 (COCH\(_3\)), 49.0 (CHCH(COCH\(_3\))\(_2\)), 74.8 (CHCH(COCH\(_3\))\(_2\)), 126.5 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 128.7 (CH), 131.4 (CH), 134.4 (3-Ar-i-C), 137.5 (C), 143.3 (C), 144.0 (C), 203.1 (COCH\(_3\)), 203.2 (COCH\(_3\)) ppm.

IR (KBr): \( \tilde{\nu} = 3008, 2962, 2871, 1914, 1730, 1510, 1456, 1417, 1357, 1277, 1239, 1167, 1140, 1052, 1016, 969, 821, 620, 532, 491 \) cm\(^{-1}\).

MS (FAB, NBA+KCl): \( m/z \) (%): 387 (25, [M+K]+), 330 (26), 305 (22), 249 (100, C\(_{19}\)H\(_{21}\)+), 119 (22), 57 (17), 43 (36, CH\(_3\)CO+).

\( [\alpha]_{D}^{20} = -9.8 \) (c = 1.00, CHCl\(_3\)).

HPLC (Daicel Chiracel AD-H, heptane/iPrOH 99:1, 0.9 mL*min\(^{-1}\), 30°C, 254 nm): \( t_R = 24.4 \) (R), 25.9 (S) min (> 99% ee).

Elemental analysis calcd. (%) for C\(_{24}\)H\(_{28}\)O\(_2\) (348.48): C 82.72, H 8.10, O 9.18; found: C 82.40, H 8.05, O 9.35.

\((S)-3-(1',3'-Di-(4''-ethylphenyl)-prop-2'-enyl)-pentane-2,4-dione ((S)-6b)\)

![Compound](S)-6b

Compound \((S)-6b\) was obtained in quantitative yield with > 99% ee using Phox ligand \((S)-10\).

\( [\alpha]_{D}^{20} = +10.1 \) (c = 1.00, CHCl\(_3\)).
General procedure for Pd-catalyzed allylic aminations

In a Young tube a solution of [Pd(C₅H₅)Cl]₂ (8.00 mg, 2.50 mol%) and chiral ligand 10 (19.3 mg, 5.90 mol%) in CH₂Cl₂ (2 mL) was degassed by three freeze-pump-thaw cycles. The ampoule was sealed at 0.01 mbar and the solution stirred at 50 °C for 2 h. After cooling to r.t. the mixture was added to a degassed solution of the substrate (875 µmol, 1.00 equiv.) and potassium phthalimide (194 mg, 1.05 mmol, 1.20 equiv.) in CH₂Cl₂ (4 mL) and the resulting solution was stirred at r.t in a Young tube under argon. After 3 d the reaction was diluted with Et₂O and ice-cold saturated aqueous NH₄Cl solution was added. The organic phase was extracted twice with Et₂O and the combined extracts were dried over MgSO₄. After evaporation of the solvent column chromatography (3 cm × 20 cm, silica gel, hexanes/EtOAc/NEt₃ 18:1:1) afforded the product. The enantiomeric excess was determined on a chiral HPLC column.

*N-(R)-(1,3-Di-(4’-tolyl)-prop-2-enyl)-phthalimide ((R)-13a)*

![Chemical structure](image)

Compound (R)-13a was obtained as colorless oil in quantitative yield with 97% ee using Phox ligand (S)-10.

\[ R_f = 0.27 \text{ (hexanes/EtOAc 4:1).} \]

\[ \text{^1H NMR (400 MHz, CDCl}_3\text{): } \delta = 2.32 \text{ (s, 3 H, CH}_3\text{), 2.33 \text{ (s, 3 H, CH}_3\text{), 6.07 (d, } ^3J = 8.7 \text{ Hz, 1 H, CHN), 6.65 (d, } ^3J = 15.8 \text{ Hz, 1 H, ArCHCH), 6.97 (dd, } ^3J = 15.8, 8.7 \text{ Hz, 1 H, ArCHCH), 7.17 (m, 4 H, Ar-H), 7.39 (m, 4 H, Ar-H), 7.68-7.73 (m, 2 H, Ar-H), 7.81-7.85 (m, 2 H, Ar-H) ppm.} \]

\[ \text{^{13}C\{^1H\} NMR (101 MHz, CDCl}_3\text{): } \delta = 21.2 \text{ (CH}_3\text{), 21.4 \text{ (CH}_3\text{), 56.5 \text{ (CHN), 123.5 (CH), 124.5 (CH), 126.8 (CH), 127.5 (CH), 129.4 (CH), 132.2 (C), 133.7 (C), 134.1 (CH), 134.2 (CH), 136.2 (C), 137.6 (C), 138.0 (C), 168.0 (NCO) ppm.} \]


IR (KBr): $\tilde{\nu} = 3024, 2923, 1773, 1712, 1612, 1513, 1467, 1381, 1328, 1232, 1180, 1107, 1080, 971, 802, 718, 630 \text{ cm}^{-1}$.

MS (EI, 70 eV): $m/z$ (%) = 367 (10, M$^+$), 352 (6, [M–CH$_3$]$^+$), 349 (5), 221 (21, [M–C$_8$H$_4$NO$_2$]$^+$), 220 (100), 205 (22), 129 (7).

$[\delta]_{D}^{20} = -11.2 \ (c = 0.500, \text{CHCl}_3$).

HPLC (Daicel Chiracel $OD-H$, heptane/iPrOH 99:1, 0.5 mL min$^{-1}$, 20°C, 254 nm): $t_R = 16.9 \ (R)$, 18.5 $S$ min (97% ee).

HRMS (EI) m/z calcd. (%) for C$_{25}$H$_{21}$NO$_2$ (367.44): 367.15600; found: 367.15723.

$N$-($S$)-($1,3$-Di-($4'$-ethylphenyl)-$prop-2$-enyl)-$phthalimide \ ((S)$-13b$)

(S)-13b was obtained as colorless oil in quantitative yield with 97% ee using Phox ligand ($R$)-10.

$R_f = 0.30$ (hexanes/EtOAc 4:1).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 1.19 (t, $^3J = 7.6$ Hz, 3 H, CH$_3$), 1.20 (t, $^3J = 7.6$ Hz, 3 H, CH$_3$), 2.61 (q, $^3J = 7.6$ Hz, 2 H, CH$_2$), 2.62 (q, $^3J = 7.6$ Hz, 2 H, CH$_2$), 6.08 (d, $^3J = 8.5$ Hz, 1 H, CHN), 6.66 (d, $^3J = 15.9$ Hz, 1 H, ArCHCH), 6.99 (dd, $^3J = 15.9$, 8.5 Hz, 1 H, ArCHCH), 7.12 (m, 4 H, Ar-H), 7.42 (m, 4 H, Ar-H), 7.68-7.72 (m, 2 H, Ar-H), 7.82-7.86 (m, 2 H, Ar-H) ppm.

$^{13}$C{$^1$H} NMR (101 MHz, CDCl$_3$): $\delta$ = 15.6 (CH$_3$), 15.7 (CH$_3$), 28.6 (CH$_2$), 28.8 (CH$_2$), 56.5 (CHN), 123.5 (CH), 124.7 (CH), 126.9 (CH), 127.6 (CH), 128.2 (CH), 128.2 (CH), 132.2 (C), 133.9 (C), 134.1 (CH), 134.2 (CH), 136.4 (C), 143.9 (C), 144.5 (C), 168.0 (NCO) ppm.

IR (KBr): $\tilde{\nu} = 2965, 1772, 1713, 1611, 1512, 1466, 1383, 1326, 1226, 1181, 1121, 973 \text{ cm}^{-1}$. 

**MS** (EI, 70 eV): \(m/z\) (%) = 395 (10, M⁺), 366 (53, [M−C₂H₅]⁺), 249 (23, [M−C₈H₄NO₂]⁺), 248 (100), 219 (43), 104 (9).

\[\Delta^{20}D = +10.8 (c = 0.500, \text{CHCl}_3).\]

**HPLC** (Daicel Chiracel OD-H, heptane/iPrOH 99:1, 0.5 mL*min⁻¹, 25°C, 254 nm):
\(t_R = 16.8\) (S), 18.3 (R) min (97% ee).

**HRMS** (EI) \(m/z\) calcd. (%) for C₂₇H₂₅NO₂ (395.49): 395.18966; found: 395.18853.

**General procedure for ESI-MS screening**

In a typical reaction a precatalyst solution (50.0 µL, 2.50 mM in toluene) prepared from equimolar amounts of ligand and [Pd(C₃H₅)(MeCN)₂]OTf was mixed with a solution of equimolar amounts of quasienantiomers (50.0 µL, 125 mM in toluene, 2 × 25.0 equiv. substrate per equiv. of Pd). The reaction was started by addition of 4 equiv. of a nucleophile solution (50.0 µL, 10.0 mM in toluene, freshly prepared from NaH, diethyl ethylmalonate and [15]crown-5 in THF with subsequent evaporation to dryness). The screening of single catalysts was performed at r.t., whereas mixtures of complexes were tested at −20 °C. After the reaction mixture had been stirred for 30 s, an aliquot was taken, diluted to 10⁻⁵ M (1 mL CH₂Cl₂) and analyzed by ESI-MS. Reactions in Tables 1 and 2 were repeated several times with consistent results. The selectivities derived from the mass spectra were calculated from the ratios of the peak heights of the two signal clusters. The mass spectra were acquired in the centroid mode.

**General procedure for preparative allylic substitutions using rac-1,3-diphenyl-2-propenyl benzoate**

In a Young tube a solution of [Pd(C₃H₅)(MeCN)₂]OTf (2.00 mg, 2.00 mol%) and chiral ligand (5.28 mmol, 2.00 mol%) in toluene (2 mL) was degassed by three freeze-pump-thaw cycles. The mixture was stirred for 1 h at r.t. In a second Young tube a solution of the substrate (83.0 mg, 264 μmol, 1.00 equiv.) in toluene (1.3 mL) was subsequently treated with acetyl acetone (79.3 mg, 792 μmol, 3.00 equiv.) followed by BSA (161 mg, 792 μmol, 3.00 equiv.) and catalytic amounts of dried KOAc (ca. 2.00 mg). After three freeze-pump-thaw cycles the catalyst solution was added and the resulting mixture stirred at r.t, until all
starting material was consumed according to TLC analysis. The reaction was diluted with Et₂O and ice-cold saturated aqueous NH₄Cl solution was added. The aqueous phase was extracted twice with Et₂O and the combined extracts were dried over MgSO₄. After evaporation of the solvent column chromatography (3 cm × 20 cm, silica gel, hexanes/EtOAc/NEt₃ 18:1:1) afforded the product as colorless solid. The enantiomeric excess was determined by HPLC analysis (Daicel Chiracel AD-H, heptane/iPrOH 97:3, 0.9 mL·min⁻¹, 20°C, 254 nm): \( t_R = 16.3 \) (R), 17.9 (S) min. The spectroscopic properties of the product were in agreement with published data.[³]

**General procedure for preparative allylic aminations using rac-1,3-diphenyl-2-propenyl benzoate**

In a Young tube a solution of \([\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2\) (2.00 mg, 2.00 mol%) and chiral ligand (10.9 µmol, 4.00 mol%) in CH₂Cl₂ (0.6 mL) was degassed by three freeze-pump-thaw cycles. The ampoule was sealed at 0.01 mbar and the solution stirred at 50 °C for 2 h. After cooling to r.t. the catalyst solution was added to a degassed solution of the substrate (85.9 mg, 273 µmol, 1.00 equiv.) and potassium phthalimide (60.7 mg, 328 µmol, 1.20 equiv.) in CH₂Cl₂ (1 mL) in a Young tube and the resulting mixture was stirred at r.t. under argon, until all starting material was consumed according to TLC analysis. The reaction was diluted with Et₂O and ice-cold saturated aqueous NH₄Cl solution was added. The aqueous phase was extracted twice with Et₂O and the combined extracts were dried over MgSO₄. After evaporation of the solvent column chromatography (3 cm × 20 cm, silica gel, hexanes/EtOAc/NEt₃ 18:1:1) afforded the product as colorless solid. The enantiomeric excess was determined by HPLC analysis (Daicel Chiracel OD-H, heptane/iPrOH 99:1, 0.5 mL·min⁻¹, 20°C, 254 nm): \( t_R = 37.6 \) (S), 51.8 (R) min. The spectroscopic properties of the product were in agreement with published data.[⁴]

**Literature**

