

Asymmetric Michael addition reactions of 2-silyloxyfurans catalyzed by binaphthyldiimine-Ni(II) complexes

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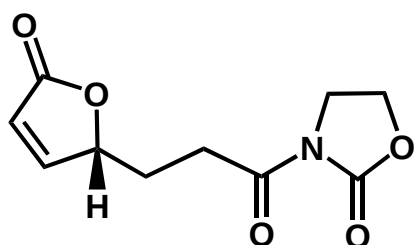
Electronic Supplementary Information

General. All reactions were carried out under an argon atmosphere in dried glassware. Air- and moisture-sensitive compounds were introduced by the use of a cannula through a rubber septum. ¹H NMR spectra were recorded in CDCl₃ on a 60 MHz or 400 MHz instrument. The chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. Enantiomeric ratios were determined using a chiral column via HPLC analysis. Analytical thin-layer chromatography was performed using silica gel 60F₂₅₄ aluminium sheets. For preparative column chromatography, Wakogel C-300HG and Silica gel 60 (size 0.040 – 0.063 mm) were employed.

Materials. Chiral 1,1'-binaphthyl-2,2'-diamine and 2-quinolinecarbaldehyde were purchased from Aldrich Co. 3-Alkenoyl-2-oxazolidinones were prepared according to reported procedures.¹ 4-Methyl- and 4-phenyl-2-quinolinecarbaldehyde were prepared from the corresponding 4-Methyl- and 4-phenylquinaldine according to reported procedure.² Dichloromethane, ethyl acetate, and hexane were purified by distillation, first from CaCl₂ and then CaH₂ under argon. Benzene, and THF were freshly distilled from a sodium benzophenone ketyl still under argon. BINIM-DC, BINIM-OH, BINIM-DCOH, and BINIM-2NAP were prepared according to the procedures reported previously.³

A General Procedure for Michael Addition Reactions Catalyzed by BINIM-2QN-Ni(II) Complex was Exemplified by the Reaction of 2-(Trimethylsilyloxy)furan (**1**) with 3-Acryloyl-2-oxazolidinone (**2a**). A mixture of Ni(ClO₄)₂•6H₂O (9.1 mg, 0.025 mmol), (*R*)-BINIM-4Me-2QN (15 mg, 0.025 mmol), and 4Å molecular sieves (MS 4A, 30 mg) in CHCl₃ (0.5 mL) was stirred at room temperature for 6 h under argon atmosphere. After cooling the mixture to –25 °C, 3-acryloyl-2-oxazolidinone (**2a**) (35 mg, 0.25 mmol) in CHCl₃ (0.5 mL), PFP (46 mg, 0.25 mmol) in CHCl₃ (0.5 mL), and silyloxyfuran **1** (50 µL, 0.03 mmol) were added successively to the catalyst suspension, and then the mixture was stirred for 1 h. The mixture was quenched with H₂O (3.0 mL), extracted with CH₂Cl₂, and then dried over MgSO₄. After removal of solvent, the mixture was purified by chromatography to give **3a** (50.4 mg, 90%). The enantiomeric excess of **3a** was determined by HPLC (Daicel Chiralpak AD).

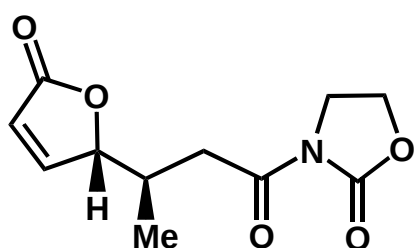
(*R*)-3-[3-(2',5'-Dihydro-5'-oxo-2'-furyl)]propanoyl-1,3-oxazolidin-2-one (**3a**):



Colorless plates; $[\alpha]_D^{24}$ –33.9° (*c* 0.83, CHCl₃, 91% ee); mp 88–89 °C (CH₂Cl₂-hexane); IR (KBr) 3104, 2986, 2924, 1779, 1684, 1474, 1387, 1362, 1302, 1223, 1206, 1177, 1115, 1038, 961, 905, 826, 762, 689 cm^{–1}; ¹H NMR (400 MHz, CDCl₃) δ 1.90–1.99

(1H, m), 2.26 (1H, ddt, *J* = 4.4, 14.6, and 7.3 Hz), 3.05–3.18 (2H, m), 4.04 (2H, t, *J* = 8.1 Hz), 4.45 (2H, t, *J* = 8.1 Hz), 5.17–5.20 (1H, m), 6.14 (1H, dd, *J* = 2.0 and 5.9 Hz), 7.52 (1H, dd, *J* = 1.5 and 5.9 Hz); ¹³C NMR (100 MHz, CDCl₃) 27.6, 30.6, 42.5, 62.2, 81.9, 121.6, 153.2, 155.6, 171.7, 172.4; HPLC (Chiralpak AD, 1:1 *i*-PrOH/hexane, UV 254 nm, flow 0.5 mL/min, 35 °C) *t*_R 23.6 min (minor), 29.6 min (major).

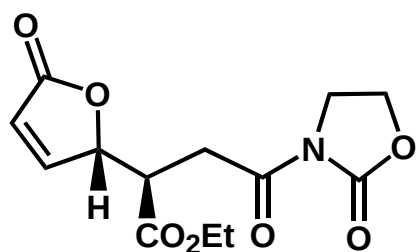
(*R,R*)-3-[3-(2',5'-Dihydro-5'-oxo-2'-furyl)]butanoyl-1,3-oxazolidin-2-one (**3b**):⁴



Colorless crystals; $[\alpha]_D^{24}$ –61.4° (*c* 0.95, CHCl₃, 89% ee); IR (KBr) 3110, 2978, 2926, 1790, 1732, 1682, 1601, 1472, 1433, 1395, 1373, 1343, 1325,

1300, 1282, 1213, 1165, 1096, 1015, 899, 824, 760, 721 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.10 (3H, d, $J = 6.8$ Hz), 2.47–2.57 (1H, m), 2.86 (1H, dd, $J = 7.3$ and 16.8 Hz), 3.16 (1H, dd, $J = 5.9$ and 16.8 Hz), 4.02–4.06 (2H, m), 4.40–4.49 (2H, m), 5.02 (1H, ddd, $J = 1.5, 2.0$, and 6.8 Hz), 6.61 (1H, dd, $J = 2.0$ and 5.9 Hz), 7.54 (1H, dd, $J = 1.5$ and 5.9 Hz); ^{13}C NMR (100 MHz, CDCl_3) 16.0, 33.2, 37.4, 42.5, 62.1, 86.0, 122.1, 153.3, 154.4, 171.1, 172.2; HPLC (Chiralpak AD, 1:4 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_R 81.7 min (major), 94.3 min (minor).

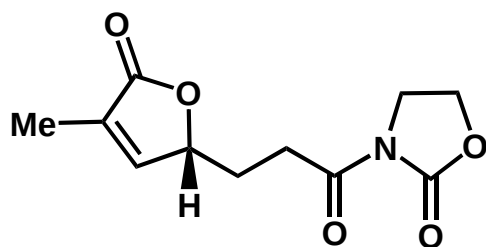
(*R,R*)-3-[3-(2',5'-Dihydro-5'-oxo-2'-furyl)-3-(ethoxycarbonyl)propanoyl]-1,3-oxazolidin-2-one (**3c**):



Colorless needles; $[\alpha]_D^{24} -60.2^\circ$ (*c* 1.04, CHCl_3 , 93% ee); mp 116–119 °C (CH_2Cl_2 -hexane); IR (KBr) 3113, 2994, 2932, 1771, 1717, 1682, 1476, 1393, 1339, 1289, 1227, 1184, 1127, 1090, 1049, 965, 924, 872, 833, 808, 795, 762, 704 cm^{-1} ; ^1H

NMR (400 MHz, CDCl_3) δ 1.29 (3H, t, $J = 7.1$ Hz), 3.18 (1H, ddd, $J = 4.6, 7.3$ and 7.8 Hz), 3.27 (1H, dd, $J = 4.6$ and 18.3 Hz), 3.55 (1H, dd, $J = 7.8$ and 18.3 Hz), 3.97–4.07 (2H, m), 4.17–4.28 (2H, m), 4.45 (2H, t, $J = 8.1$ Hz), 5.40 (1H, ddd, $J = 1.5, 2.0$ and 7.3 Hz), 6.18 (1H, dd, $J = 2.0$ and 5.9 Hz), 7.64 (1H, dd, $J = 1.5$ and 5.9 Hz), ^{13}C NMR (100 MHz, CDCl_3) 14.2, 33.1, 42.4, 43.9, 61.7, 62.3, 81.4, 122.1, 153.1, 154.6, 170.0, 170.4, 171.5; HPLC (Chiralpak AD, 1:3 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_R 45.0 min (minor), 50.4 min (major).

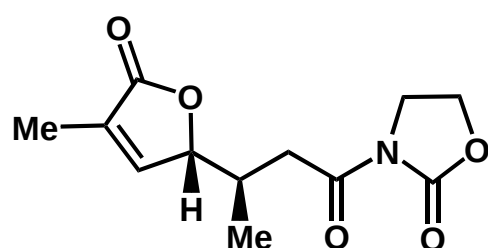
(*R*)-3-[3-(4'-Methyl-2',5'-Dihydro-5'-oxo-2'-furyl)propanoyl]-1,3-oxazolidin-2-one (**7a**):



Colorless prisms; $[\alpha]_D^{23} -20.3^\circ$ (*c* 0.94, CHCl_3 , 97% ee); mp 73–75 °C (CH_2Cl_2 -hexane); IR (KBr) 2982, 2938, 2922, 1790, 1748, 1698, 1655, 1472, 1387, 1273, 1219, 1202, 1105, 1046, 1020, 1003, 959, 934, 914, 853, 756,

739, 681 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.93 (3H, dd, $J = 1.7$ and 2.0 Hz), 1.85–1.96 (1H, m), 2.22 (1H, ddt, $J = 4.6$, 14.4 , and 7.6 Hz), 3.04–3.18 (2H, m), 3.99–4.09 (2H, m), 4.40–4.50 (2H, m), 4.99–5.04 (1H, m), 7.08–7.09 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) 10.7, 28.1, 30.7, 42.5, 62.2, 79.7, 130.1, 147.9, 153.2, 171.8, 173.5; HPLC (Chiralpak AD, 1:3 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 $^\circ\text{C}$) t_R 63.5 min (minor), 66.7 min (major).

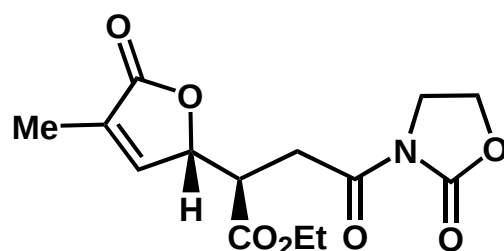
(*R,R*)-3-[3-(4'-Methyl-2',5'-Dihydro-5'-oxo-2'-furyl)butanoyl]-1,3-oxazolidin-2-one (7b):



Colorless prisms; $[\alpha]_D^{25} -40.1^\circ$ (c 0.89, CHCl_3 , 93% ee); mp 111–113 $^\circ\text{C}$ (CH_2Cl_2 -hexane); IR (KBr) 3011, 2986, 2971, 2922, 2884, 1790, 1748, 1696, 1472, 1393, 1319, 1277, 1225, 1101, 1028, 988, 924, 847 cm^{-1} ; ^1H NMR (400

MHz, CDCl_3) δ 1.07 (3H, d, $J = 6.8$ Hz), 1.93 (3H, dd, $J = 1.7$ and 2.0 Hz), 2.39–2.49 (1H, m), 2.85 (1H, dd, $J = 7.6$ and 16.8 Hz), 3.15 (1H, dd, $J = 5.6$ and 16.8 Hz), 4.04 (2H, t, $J = 8.1$ Hz), 4.42–4.47 (2H, m), 4.83–4.86 (1H, m), 7.11–7.12 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) 10.8, 15.9, 33.6, 37.7, 42.6, 62.1, 83.8, 130.7, 146.6, 153.3, 171.3, 173.4; HPLC (Chiralpak AD, 1:3 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 $^\circ\text{C}$) t_R 39.5 min (major), 51.2 min (minor).

(*R,R*)-3-[3-(2',5'-Dihydro-5'-oxo-2'-furyl)-3-ethoxycarbonylpropanoyl]-1,3-oxazolidin-2-one (7c):

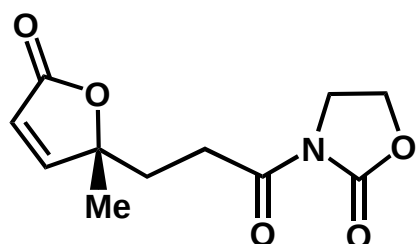


Colorless plates; $[\alpha]_D^{24} -49.4^\circ$ (c 1.05, CHCl_3 , 97% ee); mp 112–113 $^\circ\text{C}$ (CH_2Cl_2 -hexane); IR (KBr) 2990, 2932, 1773, 1725, 1688, 1480, 1453, 1397, 1341, 1300, 1273, 1236, 1182, 1130, 1105, 1067,

1034, 1003, 959, 874, 855, 826 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.28 (3H, t, $J = 7.1$ Hz), 1.94 (3H, dd, $J = 1.7$ and 2.0 Hz), 3.14 (1H, ddd, $J = 4.2$, 7.3 , and 8.1 Hz),

3.23 (1H, dd, $J = 4.2$ and 18.3 Hz), 3.52 (1H, dd, $J = 8.1$ and 18.3 Hz), 3.97–4.07 (2H, m), 4.16–4.27 (2H, m), 4.45 (2H, t, $J = 8.1$ Hz), 5.21–5.24 (1H, m), 7.18–7.20 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) 10.8, 14.2, 33.3, 42.4, 44.3, 61.5, 62.3, 79.3, 130.8, 146.7, 153.1, 170.2, 170.5, 172.7; HPLC (Chiralpak AD, 1:5 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_{R} 63.6 min (minor), 73.5 min (major).

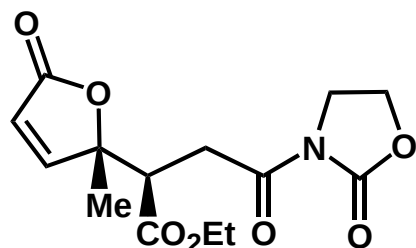
(*R,R*)-3-(2'-Methyl-2',5'-Dihydro-5'-oxo-2'-furyl)propanoyl-1,3-oxazolidin-2-one
(**9a**):



Colorless plates; $[\alpha]_{\text{D}}^{23} -45.3^\circ$ (c 1.05, CHCl_3 , 88% ee); mp 92–94 °C (CH_2Cl_2 -hexane); IR (KBr) 3110, 3090, 2986, 2940, 2911, 1790, 1746, 1699, 1389, 1360, 1311, 1246, 1225, 1196, 1113, 1036, 1009, 953, 831, 766, 712, 689 cm^{-1} ; ^1H NMR (400 MHz,

CDCl_3) δ 1.52 (3H, s), 2.13 (1H, ddd, $J = 6.3, 8.5$, and 14.4 Hz), 2.27 (1H, ddd, $J = 6.3, 8.5$, and 14.4 Hz), 2.88 (1H, ddd, $J = 6.3, 8.5$, and 17.3 Hz), 2.95 (1H, ddd, $J = 6.3, 8.5$, and 17.3 Hz), 3.96–4.06 (2H, m), 4.43 (2H, t, $J = 8.1$ Hz), 6.04 (1H, d, $J = 5.6$ Hz), 7.39 (1H, d, $J = 5.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) 24.1, 29.5, 32.2, 42.5, 62.1, 87.7, 120.5, 153.1, 159.6, 171.7, 171.8; HPLC (Chiralpak AD, 1:2 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_{R} 23.9 min (minor), 46.6 min (major).

(*R,R*)-3-(2'-Methyl-2',5'-Dihydro-5'-oxo-2'-furyl)propanoyl-3-ethoxycarbonyl-1,3-oxazolidin-2-one (**9c**):



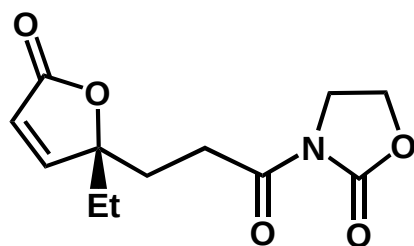
Colorless prisms; $[\alpha]_{\text{D}}^{24} -27.1^\circ$ (c 1.05, CHCl_3 , 78% ee); mp 135–137 °C (CH_2Cl_2 -hexane); IR (KBr) 3108, 2988, 2938, 1790, 1732, 1698, 1481, 1454, 1367, 1304, 1221, 1141, 1101, 1040, 1015, 961, 856, 818, 762, 698 cm^{-1} ; ^1H NMR (400 MHz,

CDCl_3) δ 1.30 (3H, t, $J = 7.1$ Hz), 1.50 (3H, s), 3.23 (1H, dd, $J = 3.4$ and 10.7 Hz), 3.35 (1H, dd, $J = 3.4$ and 18.3 Hz), 3.60 (1H, dd, $J = 10.7$ and 18.3 Hz), 3.99–4.03

(2H, m), 4.16–4.28 (2H, m), 4.40–4.49 (2H, m), 6.08 (1H, d, $J = 5.9$ Hz), 7.64 (1H, d, $J = 5.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) 14.2, 20.0, 33.5, 42.4, 48.8, 61.5, 62.3, 86.8, 120.1, 153.2, 159.5, 170.0, 170.6, 170.8; HPLC (Chiralpak AD, 1:19 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_R 224.5 min (*syn*), 252.6 min (*anti*-minor), 273.2 (*anti*-major), 287.3 (*syn*).

syn isomer ^1H NMR (400 MHz, CDCl_3) δ 1.30 (3H, t, $J = 7.1$ Hz), 1.57 (3H, s), 3.11 (1H, dd, $J = 4.6$ and 18.1 Hz), 3.20 (1H, dd, $J = 9.5$ and 18.1 Hz), 3.46 (1H, dd, $J = 4.6$ and 9.5 Hz), 3.97–4.03 (2H, m), 4.16–4.28 (2H, m), 4.38–4.49 (2H, m), 6.13 (1H, d, $J = 5.9$ Hz), 7.55 (1H, d, $J = 5.9$ Hz)

(*R,R*)-3-(2'-Ethyl-2',5'-Dihydro-5'-oxo-2'-furyl)propanoyl-1,3-oxazolidin-2-one
(**9b**):



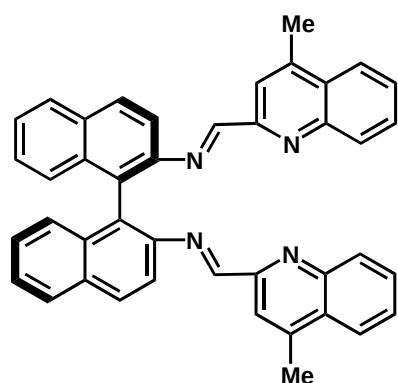
Colorless prisms; $[\alpha]_D^{24} -32.6^\circ$ (c 0.95, CHCl_3 , 86% ee); mp 61–63 °C (CH_2Cl_2 -hexane); IR (KBr) 3096, 2976, 2940, 1746, 1705, 1478, 1456, 1395, 1362, 1316, 1229, 1204, 1121, 1080, 1038, 963, 914, 845, 831, 762, 708, 691 cm^{-1} ; ^1H NMR (400

MHz, CDCl_3) δ 0.87 (3H, t, $J = 7.6$ Hz), 1.78–1.97 (2H, m), 2.14 (1H, ddd, $J = 6.3$, 8.5, and 14.4 Hz), 2.29 (1H, ddd, $J = 6.3$, 8.5, and 14.4 Hz), 2.84 (1H, ddd, $J = 6.3$, 8.5, and 17.3 Hz), 2.91 (1H, ddd, $J = 6.3$, 8.5, and 17.3 Hz), 3.96–4.06 (2H, m), 4.43 (2H, t, $J = 8.1$ Hz), 6.09 (1H, d, $J = 5.6$ Hz), 7.34 (1H, d, $J = 5.6$ Hz); ^{13}C NMR (100 MHz, CDCl_3) 7.8, 29.2, 30.1, 30.8, 42.5, 62.1, 90.6, 121.6, 153.1, 158.3, 171.9, 172.1; HPLC (Chiralpak AD, 1:2 *i*-PrOH/hexane, UV 225 nm, flow 0.5 mL/min, 35 °C) t_R 23.1 min (minor), 46.1 min (major).

Preparations of BINIM-2QN, BINIM-4Me-2QN, and BINIM-4Ph-2QN were exemplified by the reaction of (*R*)-1,1'-binaphthyl-2,2'-diamine with 2-Quinolinecarbaldehyde. A suspension of MS 4A (3.2 mm pellets, 6.0 g), (*R*)-1,1'-binaphthyl-2,2'-diamine (0.286 g, 1.0 mmol), and 2-quinolinecarbaldehyde

(0.315 g, 2.0 mmol) was heated under reflux in benzene (9.0 mL) for 4 h. After the MS 4A was removed by filtration, the filtrate was concentrated in vacuo. The resulting solids were recrystallized from diethyl ether to give (*R*)-BINIM-2QN (0.278 g, 49%): Yellow plates; mp 125.5–129 °C (diethyl ether); $[\alpha]_D^{25} = +34.50^\circ$ ($c = 1.00$, CH₂Cl₂); IR (KBr) 1614 (C=N), 1591, 1558, 1502, 1425, 1203, 1111, 968, 895 cm⁻¹; ¹H NMR (60 MHz, CDCl₃) $\delta = 7.26$ – 8.13 (24H, m), 8.65 (2H, s); HRMS (EI) m/z 562.2134. Calcd for C₄₀H₂₆N₄: M, 562.2156. Anal. Calcd for C₄₀H₂₆N₄: C, 85.38; H, 4.66; N, 9.96%. Found: C, 85.22; H, 4.90; N, 9.76%.

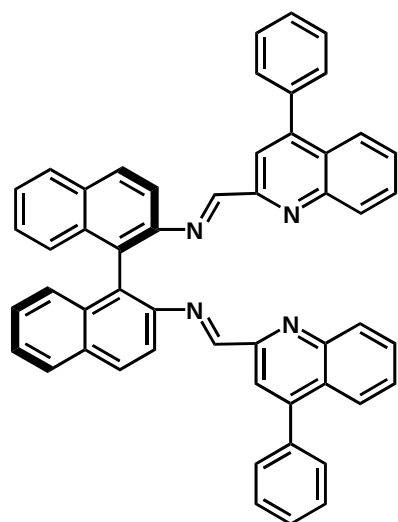
(*R*)-BINIM-4Me-2QN



Yellow prisms; $[\alpha]_D^{25} +7.67$ (C 1.00, CH₂Cl₂); mp 114–119 °C (diethyl ether-hexane); IR (KBr) 3056, 2953, 2922, 2868, 1595, 1557, 1505, 1447, 1427, 1412, 1379, 1346, 1281, 1217, 1157, 1128, 1026, 961, 866, 823, 799, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.52 (6H, s), 7.28–7.32 (2H, m), 7.39–7.45 (6H, m), 7.49–7.55 (4H, m), 7.61–7.65 (2H, m),

7.89–7.96 (6H, m), 8.03–8.05 (2H, m), 8.58 (2H, s); ¹³C NMR (100 MHz, CDCl₃) 18.9, 118.1, 118.8, 123.6, 125.1, 126.4, 126.96, 127.0, 127.8, 127.9, 128.7, 129.1, 129.2, 129.9, 132.0, 133.4, 144.3, 147.2, 147.3, 154.2, 160.8.

(*R*)-BINIM-4Ph-2QN



Yellow prisms; $[\alpha]_D^{23} -111.1^\circ$ (c 1.01, CH₂Cl₂); mp 126–128 °C (diethyl ether-hexane); IR (KBr) 3055, 2953, 2926, 1633, 1614, 1589, 1552, 1504, 1408, 1221, 1026, 968, 920, 821, 798, 769, 747, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.23–8.00 (32H, m), 8.66 (2H, s); ¹³C NMR (100 MHz) 117.7, 118.6, 125.1, 125.6, 126.3, 126.99, 127.01, 127.2, 127.7, 128.1, 128.2, 128.6, 129.16, 129.19, 129.4, 129.8,

132.0, 133.5, 137.6, 146.4, 148.1, 148.2, 154.3, 159.9.

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