Supporting Information for

The Suzuki-Miyaura reaction as a tool for modification of phenoxylnitroxyl radicals of the 4H-imidazole N-oxide series

Yury A. Ten, a Oleg G. Salnikov, b Svetlana A. Amitina, a Dmitri V. Stass, b,c Tatyana V. Rybalova, a,b Maxim S. Kazantsev, a,b Artem S. Bogomyakov, d Evgeny A. Mostovich a,b and Dmitrii G. Mazhukin a,b

a NN Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS, 9 Acad. Lavrentyeva Ave., Novosibirsk, 630090, Russia;
b Novosibirsk State University, 2 Pirogova Str., Novosibirsk, 630090, Russia
c Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 3 Institutskaya Str., Novosibirsk, 630090, Russia
d International Tomography Center SB RAS, 3A Institutskaya Str., Novosibirsk, 630090, Russia

*Corresponding author: Dmitrii G. Mazhukin
E-mail: d-mazhukin@yandex.ru
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Synthesis and Characterization of Starting Compound

1-(4-Iodophenyl)-2-methylpropan-1-one (2). Freshly sublimed and powdered AlCl₃ (66 g, 0.495 mol) was added in portions of ~22 g with stirring in a 1 hour interval into solution of 128 mL (1.44 mol) of iodobenzene in a 51 mL (0.50 mol) of freshly distilled iso-butyryl chloride. The temperature of reaction mixture was maintained at 50 °C and each subsequent addition of the catalyst was done when the temperature was fall down to 30 °C. The dark reaction solution was held at rt for 15 h, heated in a water bath to 45 °C and stirred for 1 h until the hydrogen chloride evolution ceased completely. The reaction mixture was poured into ice water, the bottom layer was separated, the aqueous layer was extracted with CH₂Cl₂ (3×30 mL). The combined organic extracts were washed with aqueous Na₂SO₃, the solvent was removed in vacuo by a rotary evaporator. The residue was distilled with a steam to remove unreacted iodobenzene. The bottoms were separated from the aqueous layer, the latter was further extracted with CH₂Cl₂ (3×30 mL). Combined organic extracts were dried with anhydrous Na₂SO₄, filtered through a short column filled with 20 g of Al₂O₃, the solvent was evaporated, and the oily residue was distilled in vacuo. Slightly yellowish viscous liquid, isolated yield 37%, bp 135-140 °C (6 Torr) (lit.,¹ 130-138 °C (5 Torr));¹ H NMR (400 MHz, CDCl₃): δH 1.19 (d, J = 7 Hz, 6H, CH(C₆H₃)₂), 3.45−3.50 (m, 1H, CH(CH₃)₂), 7.65 (d, J = 9 Hz, 2H, CHAr), 7.81 (d, J = 9 Hz, 2H, CHAr). Found, %: C 43.97; H 4.09; I 46.20. C₁₀H₁₁IO. Calculated, %: C 43.79; H 4.01; I 46.31.

2-Bromo-1-(4-iodophenyl)-2-methylpropan-1-one (3). To a solution of 50.5 g (184 mmol) of 1-(4-iodophenyl)-2-methylpropan-1-one 2 in a mixture of 90 mL of diethyl ether and 7 mL of dioxane, 1.00 mL (19 mmol) of bromine was added and the mixture was stirred for 15-20 min until clear decolorization. The remaining amount of bromine (8.00 mL, 155 mmol) was dropped from the separatory funnel with stirring for 2 h at 25 °C, controlling the conversion of the ketone to the bromo derivative by TLC (hexane - diethyl ether, 2:1). Ice water (40 mL), followed by 16.00 g (190 mmol) of sodium bicarbonate were added to the reaction mixture with stirring. The precipitate of product formed on the boundary between the two layers was filtered, washed with water and dried in air to a constant weight (17.4 g). The aqueous filtrate was extracted with Et₂O (2×20 mL), extract was combined with an organic layer, dried over anhydrous Na₂SO₄, filtered, evaporated, residue of bromoketone (44.0 g) was solidified on cooling to 0 °C and used in the next step without further purification. Light pale crystals, isolated yield 61.4 g (~100%), mp 84-85 °C (hexane – diethyl ether) (Caution: lacrimator!). Found, %: C 33.95; H 2.78. C₁₀H₁₀BrIO. Calculated, %: C 34.03; H 2.86.
(E)-2-(Hydroxyamino)-1-(4-iodophenyl)-2-methylpropan-1-one oxime (4). A suspension of 69.50 g (1.00 mol) of hydroxylamine hydrochloride in 80 mL of water was diluted with 600 mL of methanol and then a solution of 33.60 g (0.84 mol) of NaOH in 40 mL of water was added slowly with stirring and cooling to 10-15 °C. The precipitate of NaCl was filtered off and filtrate was mixed with a solution of 70.60 g (0.20 mol) of 2-bromo-1-(4-iodophenyl)-2-methylpropan-1-one 3 in 240 ml of MeOH followed by heating and refluxing of the mixture for 7 h. The methanol was removed under vacuum, the oily residue was mixed with 200 mL of chloroform, the organic layer was separated and extracted with a cooled 3% aq solution of hydrochloric acid (500 mL). The aqueous extract was washed with CHCl₃ (3×50 ml), cooled to 0 °C and neutralized by carefully adding a concentrated aqueous ammonia solution (until pH≤8). The precipitate of 2-hydroxylamino oxime 4 was filtered, washed with water and dried in air to constant weight. Colorless fine-needle crystals, isolated yield 45.10 g (70%), mp 167-169 °C (MeOH).

1H NMR (500 MHz, DMSO-d₆): δH 1.12 (s, 6H, 2CH₃), 5.18 (brs, 1H, NHOH), 6.99 (AB, JAB = 8.5 Hz, 2H, Hₐ Ar), 7.32 (s, 1H, NHOH), 7.73 (AB, JAB = 8.5 Hz, 2H, H₂ Ar), 10.59 (s, 1H, C=NOH). 13C NMR (125 MHz, DMSO-d₆): δC 23.4 (C(CH₃)₂), 60.7 (C(CH₃)₂), 94.0 (C-I), 130.6 (CHAr), 133.4 (Ar-C=N), 136.5 (CHAr), 160.3 (C=N). Found, %: C 37.82; H 4.31; I 40.05; N 8.84. C₁₀H₁₃IN₂O₂. Calculated, %: C 37.52; H 4.09; I 39.64; N 8.75.

2-(Hydroxyamino)-1-(4-iodophenyl)-2-methylpropan-1-one hydrobromide (5). A mixture of crystallized 2-hydroxylamino oxime 4 (3.20 g, 10 mmol) and 37 mL of 48% aq hydrobromic acid (323 mmol) was heated until complete dissolution and gently refluxed for 2 h. The solution was cooled in an ice bath; the precipitate formed was filtered off, washed with acetonitrile (3×2 mL), dried and crystallized from 48% HBr using hot filtration. The solution was refrigerated at 0 °C for 12 h, the precipitate was filtered, washed with MeCN and dried at 60 °C to constant weight. An analytical sample was obtained by crystallization of substance from water. Colorless shiny plates, isolated yield 3.40 g (93%), mp 182-183 °C (dec., H₂O). 1H NMR (300 MHz, DMSO-d₆): δH 1.67 (s, 6H, 2CH₃), 7.72 (AB, JAB = 8.5 Hz, 2H, Hₐ Ar), 7.94 (AB, JAB = 8.5 Hz, 2H, H₂ Ar), 10.80 (s, 1H, N⁺HOH), 10.90-12.00 (brs, 2H, N⁺HOH). 13C NMR (75 MHz, DMSO-d₆): δC 20.3 (C(CH₃)₂), 69.0 (C(CH₃)₂), 102.7 (C-I), 130.5 (CHAr), 132.8 (Ar-C=O), 137.8 (CHAr), 198.4 (C=O). Found, %: C 31.16; H 3.55; Br 20.70; I 33.58. C₁₀H₁₃BrINO₂. Calculated, %: C 31.12; H 3.39; Br 20.70; I 32.87; N 3.63.

Free base of 5 was obtained by careful addition of an aqueous solution of potassium carbonate to the suspension of the hydrobromide, followed by stirring, precipitation and filtration of 2-hydroxyamino ketone. 1H NMR (500 MHz, CDCl₃): δH 1.41 (s, 6H, 2CH₃), 4.85 (brs, 2H, NHOH), 7.65 (AB, JAB = 8.5 Hz, 2H, Hₐ Ar), 7.75 (AB, JAB = 8.5 Hz, 2H, H₂ Ar). 13C NMR (125 MHz, CDCl₃): δC 23.2 (C(CH₃)₂), 67.3 (C(CH₃)₂), 99.3 (C-I), 130.0 (CHAr), 135.9 (Ar-C=O), 137.4 (CHAr), 204.5 (C=O).

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2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-(4-iodophenyl)-1-hydroxy-5,5-dimethyl-2,5-dihydro-1H-imidazole (7). Ammonium acetate 7.70 g (100 mmol) was added to a solution of 3.86 g (10 mmol) of 2-hydroxylamino ketone hydrobromide 5 in 20 ml MeOH, mixture was stirred until a complete dissolution, followed by addition of 2.56 g (10.5 mmol) of 3,5-di-tert-butyl-4-hydroxybenzaldehyde 6. Mixture was diluted with 20 ml MeOH and stirred at rt for 6 h. The precipitate formed was cooled at + 4 °C for 12 h, filtrated, washed thoroughly with water and dried in air to constant weight. Colorless crystals, isolated yield 3.80 g (73%), mp 192-194 °C (methanol). IR (solid, KBr, ν max, cm⁻¹): 3607 (OH), 3420, 3252, 2959 (CH), 1610 (C=N), 1585. UV (in EtOH, λ max, nm, (lg ε)): 264 (3.77).

1H NMR (400 MHz, CDCl₃): δH 1.09 (s, 3H, C(CH₃)₂), 1.31 (s, 3H, C(CH₃)₂), 1.43 (s, 18H, t-Bu), 5.22 (s, 1H, N-CH-N), 5.41 (s, 1H, Ar-OH), 6.05 (s, 1H, N-OH), 7.18 (s, 2H, C₃H₄Ar-OH), 7.50 (AB, JAB = 8 Hz, 2H, HₐAr-I), 7.73 (AB, JAB = 8 Hz, 2H, HₐAr-I). 13C NMR (100 MHz, CDCl₃): δC 16.8 (5-Me), 24.6 (5-Me), 30.1 (C(CH₃)₃), 34.2 (C(CH₃)₃), 71.3 (C-5), 90.9 (C-2), 97.2 (C-I), 125.0 (2,6-CH ArOH), 129.1 (CHₐAr), 129.8 (CHₐCₐ), 132.4 (CₐCₐ), 135.6 (Cₐt-Bu), 137.5 (CHₐAr), 154.0 (C-OH), 175.6 (C-4). Found, %: C 57.97, H 6.49, N 5.24, I 24.30. C₂₅H₃₃IN₂O₂. Calculated, %: C 57.70, H 6.39, N 5.38, I 24.38.

2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-(4-iodophenyl)-4,4-dimethyl-4H-imidazole 3-oxide (1). Manganese dioxide (1.27 g, 14.6 mmol) was added to a suspension of 3.80 g (7.3 mmol) of 2,5-dihydroimidazole 7 in 100 mL of CHCl₃ and the mixture was stirred for 4 h, after which additional amount of oxidant (0.25 g, 2.9 mmol) was added and stirring continued for 2.5 h. Upon reaching a complete conversion of imidazoline 7 (TLC control), the mixture was filtered through the finely porous glass filter, the precipitate was washed thoroughly with chloroform (3×10 mL) and the filtrate was evaporated. The residue was triturated with 5 ml of hexane, the precipitate was filtered and washed with hexane (2×5 mL).

Dark yellow needles, isolated yield 3.59 g (95%), mp 244.4 °C (dec., EtOH), Rf 0.15 (CHCl₃/MeOH, 20:1). IR (solid, KBr, ν max, cm⁻¹): 3620 (OH), 2957 (CH), 1582 (C=N), 1530, 1421. UV (in EtOH, λ max, nm, (lg ε)): 309 (4.19), 398 (3.43). 1H NMR (300 MHz, CDCl₃): δH 1.50 (s, 18H, t-Bu), 1.71 (s, 6H, C(CH₃)₃), 5.64 (s, 1H, Ar-OH), 7.77 (AB, JAB = 8.5 Hz, 2H, HₐAr-I), 7.84 (AB, JAB = 8.5 Hz, 2H, HₐAr-I). 13C NMR (75 MHz, CDCl₃): δC 24.1 (4-Me), 30.1 (C(CH₃)₃), 34.4 (C(CH₃)₃), 80.4 (C-4), 98.5 (C-I), 118.9 (CₐC-2), 125.4 (2,6-CH ArOH), 128.4 (CHₐAr), 130.0 (CₐAr-C=N), 135.8 (Cₐt-Bu), 138.2 (CHₐAr), 146.5 (C-2), 156.1 (C-OH), 174.7 (C-5). Found, %: C 57.79, H 6.49, N 5.38, I 24.25. C₂₅H₃₁IN₂O₂. Calculated, %: C 57.92, H 6.03, N 5.40, I 24.48.
2,6-Di-tert-butyl-4-[4-(4-iodophenyl)-5,5-dimethyl-1-oxido-1H-imidazol-2(5H)-ylidene]cyclohexa-2,5-dienone (8). Lead dioxide (722 mg, 3 mmol) was added portionwise for 2 h to a solution of 259 mg (0.5 mmol) of 4H-imidazole 1 in 10 mL of chloroform with continuous stirring until complete conversion of the starting material (TLC control). The dark brown solution was carefully decanted from the oxidant, solvent was evaporated, the oily residue was triturated with 3 mL of hexane and the solvent was removed by passing the air current to obtain a dark brown crystalline radical 8.

Shiny almost black crystals, isolated yield 241 mg (93%), mp 199-202 °C (dec., MeCN). \( R_f \) 0.8 (CHCl\(_3\)). IR (solid, KBr, \( \nu_{\text{max}} \), cm\(^{-1}\)): 2953 (CH), 1584, 1557 (C=N). UV (in EtOH, \( \lambda_{\text{max}} \), nm, (lg \( \varepsilon \))): 231 (3.85), 314 (4.22), 354 (4.35), 367 (4.39), 480 (3.96), 851 (2.99), 948 (2.97). ESR (PhMe): m (21 lines), \( A_N \) = 0.536 mT, \( A_{N'} \) = 0.061 mT, \( A_{H'} \) = 0.163 mT, \( A_{H''} \) = 0.150 mT, \( g_{\text{iso}} \) = 2.0059. HRMS (ESI): calculated for \( C_{25}H_{30}IN_2O_2 \), 517.14, observed 518.20 ([M + 1]).
Suzuki-Miyaura Couplings, Oxidation to Hybrid Radicals and Characterization Data

5-(Biphenyl-4-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-4H-imidazole 3-oxides (10a-d) (general procedure). A solution of 5-(4-iodophenyl)-4H-imidazole 1 (259 mg, 0.5 mmol) and 0.5 mmol of arylboronic acid 9a-d in 15 mL of PhMe was purged with argon for 20 min, then 0.035 mmol of freshly prepared Pd[P(C6H5)3]4 was added. The mixture was diluted with 5 mL of a degassed 2M aqueous solution of K2CO3 and 2 mL of ethanol and refluxed under an argon stream with stirring for 24 h at 110 °C. After cooling to ambient temperature, toluene (10 mL) and water (5 mL) were added to the reaction flask, the organic layer was separated and filtered, solvent was removed under vacuum. The solid residue was triturated with 7 mL of hexane, precipitate was filtered, washed with hexane (2×3 mL) and crystallized from hexane/ethyl acetate, 4:1.

5-(Biphenyl-4-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (10a). Bright yellow crystals, isolated yield 169 mg (72%), mp 190.6 °C (hexane-EtOAc), Rf 0.3 (CHCl3/MeOH, 50:1). IR (solid, KBr, νmax cm⁻¹): 3626 (OH), 2956 (CH), 1601 (C=N), 1531, 1421, 1375, 1238. UV (in EtOH, λmax nm, (lg ε)): 313 (4.54), 397 (3.86). 1H NMR (400 MHz, CDCl3): δH 1.52 (s, 18H, t-Bu), 1.78 (s, 6H, C(CH3)2), 5.64 (s, 1H, Ar-OH), 7.43 (m, 1H, PhH), 7.46 – 7.51 (m, 2H, PhH), 7.63 – 7.67 (m, 2H, PhH), 7.73 (AB, JAB = 9.0 Hz, 2H, H5-Ar), 8.16 (AB, JAB = 9.0 Hz, 2H, H5-Ar), 8.77 (s, 2H, CH Ar-OH). 13C NMR (100 MHz, CDCl3): δC 24.3 (4-Me), 30.2 (C(CH3)3), 34.4 (C(CH3)3), 80.5 (C=4), 125.5, 127.0, 127.5, 127.7, 128.1, 129.0 (CHph + CHar), 129.5 (C(Ar)-C-5), 135.7 (C-t-Bu), 139.8 (C(Ph)-C(Ar)), 144.1 (C(Ph)-C(Ar)), 146.6 (C-2), 156.1 (C-OH), 175.5 (C-5). Found, %: C 79.24, H 7.57, N 5.71. C31H35N2O2. Calculated, %: C 79.45, H 7.74, N 5.98.
2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-(3',5'-dimethyl-[1,1'-(N-N-O)]biphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (10b). Dark yellow crystals, isolated yield 170 mg (66%), mp 116.6 °C (dec., hexane-EtOAc), Rf 0.45 (CHCl3/MeOH, 50:1). IR (solid, KBr, νmax cm⁻¹): 3624 (OH), 2956 (CH), 1599 (C=N), 1529, 1421, 1373, 1236. UV (in EtOH, λmax nm, (lg ε)): 255 (4.07), 313 (4.43), 388 (3.87).

1H NMR (400 MHz, CDCl3): δ 1.38 (t, J = 7.2 Hz, 3H, OCH2C6H3), 1.52 (s, 18H, t-Bu), 1.79 (s, 6H, C(CH3)2), 4.07 (q, J = 7.2 Hz, 2H, OCH2C6H3), 5.63 (s, 1H, Ar-OH), 6.98 – 7.06 (m, 1H, 2H, 3',5'-HAr), 7.31 – 7.37 (m, 2H, 4',6'-HAr), 7.71 (AB, JAB = 8 Hz, 2H, H5-Ar), 8.11 (AB, JAB = 8 Hz, 2H, H5-Ar), 8.77 (s, 2H, CH Ar-OH). 13C NMR (100 MHz, CDCl3): δc 14.7 (OCH2C6H3), 24.3 (4-Me), 30.2 (C(CH3)3), 34.5 (C(CH3)3), 64.0 (OCH2C6H3), 80.5 (C-4), 112.6 (CAr-3'), 119.3 (GA(Ar)-C-2), 120.9 (CAr-5'), 125.6, 126.8, 129.3, 130.0, 130.6 (CHA), 129.0 (CAr-1'), 129.4 (GA(Ar)-C-5), 135.8 (C-t-Bu), 142.2 (s, CAr-1), 146.6 (C-2), 155.8 (C-OEt), 156.0 (C-OH), 175.8 (C-5). Found, %: C 77.05, H 7.58, N 5.39. C33H40N2O3. Calculated, %: C 77.31, H 7.86, N 5.46.

2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-(3',5'-dimethyl-[1,1'-(N-N-O)]biphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (10c). Dark yellow crystals, isolated yield 186 mg (75%), mp 135.6 °C (dec., hexane-EtOAc), Rf 0.4 (CHCl3/MeOH, 50:1). IR (solid, KBr, νmax cm⁻¹): 3627 (OH), 2956 (CH), 1600 (C=N), 1530, 1421, 1375, 1247. UV (in EtOH, λmax nm, (lg ε)): 316 (4.45), 399 (3.71). 1H NMR (500 MHz, CDCl3): δ 1.51 (s, 18H, t-Bu), 1.78 (s, 6H, C(CH3)2), 2.39 (s, 6H, CH2ArCH2), 5.64 (s, 1H, OH), 7.04 (s, 1H, 4'-HAr), 7.25 (s, 2H, 2',6'-HAr), 7.71 (AB, JAB = 8 Hz, H5-Ar, 2H, 2,6-HAr), 8.13 (AB, JAB = 8 Hz, H5-Ar, 2H, 3,5-HAr), 8.76 (s, 2H, 2-ArH); 13C NMR (125 MHz, CDCl3): δ 21.3 (2CH3-Ar'), 24.2 (C(CH3)2), 30.1 (C(CH3)3), 34.4 (C(CH3)3), 80.4 (s, C-4), 119.1 (GA(Ar)-C-2), 124.9, 125.5, 127.4, 127.5, 129.7 (CHA+Ar'), 129.3 (GA(Ar)-C-5), 135.7 (C-t-Bu), 138.4 (GA(Ar)-C3), 139.7 (CAr-1'), 144.4 (CAr-1), 146.6 (C-2), 156.0 (CAr-OH), 175.6 (C-5). Found, %: C 79.55; H 7.16; N 5.39. C33H39N2O2. Calculated, %: C 79.80; H 8.12; N 5.64.
2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-(4'-(trifluoromethyl)biphenyl-4-yl)-4H-imidazole 3-oxide (10d). Dark yellow crystals, isolated yield 228 mg (85%), mp 260 °C (dec., hexane-EtOAc), $R_f$ 0.25 (CHCl$_3$/MeOH, 50:1). IR (solid, KBr, $v_{\text{max}}$, cm$^{-1}$): 3630 (OH), 2957 (CH), 1616, 1599 (C=N), 1533, 1421, 1375, 1325. UV (in EtOH, $\lambda_{\text{max}}$, nm, (lg $\varepsilon$)): 314 (4.60), 401 (3.80). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.52 (s, 18H, t-Bu), 1.78 (s, 6H, C(CH$_3$)$_2$), 5.64 (s, 1H, OH), 7.72 – 7.78 (brs, 6H, ArH), 8.18 (d, $J_{AB} = 7$ Hz, 2H, H$_5$-Ar), 8.76 (s, 2H, 2-ArH); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 24.1 (4-Me), 30.1 (C(CH$_3$)$_3$), 34.4 (C(CH$_3$)$_3$), 80.5 (C-4), 119.0 (C(Ar)-C-2), 123.9 (q, $^2J_{CF} = 270$ Hz, CF$_3$), 125.4, 125.8, 127.2, 127.6, 127.7 (CH$_3$), 130.0 (q, $^3J_{CF} = 33$ Hz, C$_i$-CF$_3$), 130.3 (C(Ar)-C-5), 135.8 (C-t-Bu), 142.4 (C$_{Ar}$-1), 143.2 (C$_{Ar}$-1'), 146.5 (C-2), 156.0 (C-OH), 174.9 (C-5). Found, %: C 71.45; H 6.78; F 10.53; N 5.21. C$_{32}$H$_{35}$F$_3$N$_2$O$_2$. Calculated, %: C 71.62; H 6.57; F 10.62; N 5.22.

Cross-coupling of hybrid radical 8 with arylboronic acid. Catalyst, Pd(PPh$_3$)$_4$ (7 mg, 0.006 mmol) was added to a mixture of 62 mg (0.12 mmol) of the iodo-substituted phenoxyl-nitroxide 8 and 4-(trifluoromethyl)phenylboronic acid 9d (23 mg, 0.12 mmol) in 3.5 mL of toluene, solution was purged with argon for 20 min and diluted with 1.2 mL of a 2M aqueous solution of potassium carbonate and 0.4 mL of EtOH. Brown mixture was flushed with argon and refluxed with the stirring for 24 h at 110 °C under an inert atmosphere. After cooling, the orange organic layer was separated, residue was extracted with toluene (2×3 mL), combined organic extracts was filtered and the solvent was distilled off. Solid residue was treated with hexane (5 mL) and precipitate of 5-biphenyl-4H-imidazole 10d was filtered off and dried to afford 55 mg (85%) of diamagnetic product, whose $R_f$, mp and IR spectrum completely correspond to those for cross-coupling product, 4H-imidazole N-oxide 10d.

Oxidation of 5-biphenyl-4H-imidazoles 10a-d to hybrid radicals 11a-d (general procedure). To a solution of 0.2 mmol of 4H-imidazole N-oxide 10a-d in 7 mL of chloroform, 574 mg (2.4 mmol) of lead dioxide was added and reaction mixture was stirred at rt for 3–5 h until the substrate disappears completely (TLC-control). The dark brown solution was filtered through a double paper filter, the solvent was rotary evaporated and residue was flash chromatographed with a chloroform
on a column with a silica. The bright colored fraction was collected, condensed under vacuum and the residue was mixed with 3 mL of hexane and cooled at -10 °C for 1 h. Formed precipitate was rapidly filtered and dried on air to give analytically pure radical 11a-d.

2,6-Di-tert-butyl-4-[1-oxido-5,5-dimethyl-1H-imidazol-2(5H)-yliden]cyclohexa-2,5-dienone (11a). Dark brown crystals, isolated yield 89 mg (95%), mp 180.9 °C (dec., MeCN). Rf 0.6 (CHCl3). IR (solid, KBr, \( \nu_{\text{max}} \), cm\(^{-1}\)): 2955 (CH), 1604, 1584, 1557 (C=C, C=N), 1450, 1381, 1272. UV (in EtOH, \( \lambda_{\text{max}} \), nm, (lg \( \varepsilon \))): 313 (4.54), 397 (3.86). ESR (PhMe): m (21 lines), \( A_N = 0.541 \) mT, \( A_N' = 0.061 \) mT, \( A_H' = 0.161 \) mT, \( A_H'' = 0.149 \) mT, \( g_{\text{iso}} = 2.0059 \). Found, %: C 79.46; H 7.45; N 5.98. C\(_{31}\)H\(_{35}\)N\(_2\)O\(_2\). Calculated, %: C 79.62; H 7.54; N 5.99.

2,6-Di-tert-butyl-4-[1-oxido-5,5-dimethyl-4-(2'-ethoxybiphenyl-4-yl)-1H-imidazol-2(5H)-yliden]cyclohexa-2,5-dienone (11b). Dark brown fine crystals, isolated yield 94 mg (92%), mp 115.8 °C (dec., MeCN). Rf 0.75 (CHCl3). IR (solid, KBr, \( \nu_{\text{max}} \), cm\(^{-1}\)): 2956 (CH), 1605, 1581, 1558 (C=C, C=N), 1485, 1448, 1257, 1234, 752. UV (in EtOH, \( \lambda_{\text{max}} \), nm, (lg \( \varepsilon \))): 256 (4.05), 351 (4.35), 364 (4.35), 469 (3.84). ESR (PhMe): m (21 lines), \( A_N = 0.542 \) mT, \( A_N' = 0.060 \) mT, \( A_H' = 0.160 \) mT, \( A_H'' = 0.148 \) mT, \( g_{\text{iso}} = 2.0059 \). Found, %: C 77.36; H 7.69; N 5.20. C\(_{33}\)H\(_{39}\)N\(_2\)O\(_3\). Calculated, %: C 77.46; H 7.68; N 5.47.

2,6-Di-tert-butyl-4-[1-oxido-5,5-dimethyl-4-(3',5'-dimethylbiphenyl-4-yl)-1H-imidazol-2(5H)-yliden]cyclohexa-2,5-dienone (11c). Dark brown fine crystals, isolated yield 89 mg (90%), mp 186.8 – 187.8 °C (dec., MeCN). Rf 0.6 (CHCl3). IR (solid, KBr, \( \nu_{\text{max}} \), cm\(^{-1}\)): 2958 (CH), 1604, 1583, 1556 (C=C, C=N), 1514, 1440,
UV (in EtOH, $\lambda_{\text{max}}$, nm, (lg $\varepsilon$)): 349 (4.49), 365 (4.50), 472 (3.97). ESR (PhMe): m (21 lines), $A_N = 0.542$ mT, $A_N' = 0.060$ mT, $A_H' = 0.161$ mT, $A_H'' = 0.149$ mT, $g_{\text{iso}} = 2.0059$. Found, %: C 79.79; H 7.68; N 5.42. C$_{33}$H$_{39}$N$_2$O$_2$. Calculated, %: C 79.96; H 7.93; N 5.65.

5,5'-(1-oxido-5,5-dimethyl-4-(4'-(trifluoromethyl)biphenyl-4-yl)-1H-imidazol-2(5H)-yliden]cyclohexa-2,5-dienone (11d). Dark brown fine crystals, isolated yield 102 mg (95%), mp 163.5 °C (dec., MeCN). $R_f$ 0.55 (CHCl$_3$). IR (solid, KBr, $\nu_{\text{max}}$, cm$^{-1}$): 2956 (CH), 1618, 1608, 1582, 1556 (C=C, C=N), 1444, 1327, 1162, 1124, 1070, 831. UV (in EtOH, $\lambda_{\text{max}}$, nm, (lg $\varepsilon$)): 253 (3.98), 271 (4.09), 341 (4.50), 366 (4.50), 469 (4.02). ESR (PhMe): m (21 lines), $A_N = 0.538$ mT, $A_N' = 0.061$ mT, $A_H' = 0.163$ mT, $A_H'' = 0.151$ mT, $g_{\text{iso}} = 2.0059$. Found, %: C 71.80; H 6.19; F 10.51; N 5.23. C$_{32}$H$_{34}$F$_3$N$_2$O$_2$. Calculated, %: C 71.76; H 6.40; F 10.64; N 5.23.

5,5'-(1,1'-Biphenyl)-4,4'-diyl)bis(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4,4-dimethyl-4H-imidazole 3-oxide) (13). To a solution of 155 mg (0.3 mmol) of 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-(4-iodophenyl)-4,4-dimethyl-4H-imidazole 3-oxide 1 in 5 mL of DMF, 40 mg (0.156 mmol) of bis(pinacolato)diboron was added, followed by 88 mg (0.9 mmol) of potassium acetate. Argon was passed through the dark brown solution during 3 min, after that 11 mg (0.015 mmol) of [Pd(PPh$_3$)$_2$]Cl$_2$ was introduced and the mixture was stirred for 9 h at 110 °C under Ar atmosphere. The resulting suspension was cooled overnight at 0 °C, the precipitate was filtered and washed with diethyl ether (5×1 mL). Soxhlet extractions of dark yellow powder with 100 ml of chloroform removed catalytic residues and inorganic impurities. The solvent was evaporated, residue was triturated with Et$_2$O (5 mL) and the precipitate was filtrated. Dark orange powder, isolated yield 97 mg (83%), dec $> 260$ °C (CHCl$_3$), $R_f$ 0.05 (CHCl$_3$/MeOH, 20:1). IR (solid, KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3601 (OH), 2956 (CH), 1605, 1526, 1419, 1375, 1319, 1238. UV (in EtOH, $\lambda_{\text{max}}$, nm, (lg $\varepsilon$)): 333 (n/d*), 412 (n/d). $^1$H NMR (400 MHz, CF$_3$COOH): $\delta$ 1.57 (s, 36H, t-Bu), 2.06 (s, 12H, 2C(CH$_3$)$_2$), 8.05 ($AB, J_{AB} = 8.0$ Hz, 4H, H$_4$, 5,5'-Ar), 8.51 ($AB, J_{AB} = 8.0$ Hz, 4H, H$_8$, 5,5'-Ar), 8.82 (s, 4H, 2,2'-ArH); $^{13}$C NMR (100 MHz, CF$_3$COOH): $\delta$ 24.9 (4,4'-Me), 31.3 (C(CH$_3$)$_3$), 36.8 (C(CH$_3$)$_3$), 82.6 (C-
4, C-4'), 116.4 (C(Ar)-C-2(2')), 130.9, 133.1, 134.7 (3 CH, Ar), 131.0, 141.0, 149.0 (3 C(Ar), 166.0, 166.3 (C-OH and C-2(2'), 194.3 (C-5(5')). Found, %: C 72.40; H 7.52; N 6.65. C$_{50}$H$_{62}$N$_{4}$O$_{4}$ $\times \frac{1}{2}$ CHCl$_{3}$. Calculated, %: C 72.00; H 7.43; N 6.65.

(* n/d – not determined due to extremely low solubility in EtOH)

To a mixture of 518 mg (1 mmol) 4H-imidazole 3-oxide 1 and bis(pinacolato)diboron (301 mg, 1.2 mmol) in 7 mL of DMF potassium acetate (295 mg, 3 mmol) was added. Argon was flushed through the suspension during 7 min, after that catalyst, [Pd(PPh$_{3}$)$_{2}$]Cl$_{2}$ (35 mg, 0.05 mmol) was introduced in the reaction flask and the mixture was stirred for 3 h at 95 $^\circ$C under Ar atmosphere. The resulting suspension was cooled overnight at 0 $^\circ$C, the precipitate was filtered and washed with water (3×3 mL) and air-dried to afford biphenyl-bis(imidazole) 13 (111 mg, 28%). Organic filtrate was evaporated, residue was triturated with chloroform (15 mL), precipitate was filtrated and discarded, CHCl$_{3}$ solution was washed with water (2×3 mL), dried with MgSO$_{4}$ and solvent was removed. Oily residue was chromatographed on a column with a silica (eluent chloroform), dark yellow fraction was collected, condensed under vacuum, triturated with 3 mL of hexane and cooled at -10 $^\circ$C overnight. Formed precipitate was rapidly filtered and dried on air to give dioxaborolane 14. Yellow-greenish crystals, isolated yield 206 mg (40%), mp 167-169 $^\circ$C (hexane), R$_{f}$ 0.25 (CHCl$_{3}$). IR (solid, KBr, $\nu_{\text{max}}$, cm$^{-1}$): 3630 (OH), 2955 (CH), 2872, 1608, 1535, 1460, 1423, 1362, 1325, 1238, 1144, 1092. UV (in EtOH, $\lambda_{\text{max}}$, nm, (lg $\varepsilon$)): 237 (3.99), 305 (4.43), 397 (3.65). $^1$H NMR (300 MHz, CDCl$_{3}$): $\delta$ 1.35 (s, 12H, [OCMe$_{2}$]$_{2}$), 1.50 (s, 18H, t-Bu), 1.74 (s, 12H, N-C(CH$_{3}$)$_{2}$), 5.63 (s, 1H, OH), 7.91 (AB, $J_{\text{AB}}$ = 8.3 Hz, 2H, H$_{A}$ 5-Ar), 8.04 (AB, $J_{\text{AB}}$ = 8.3 Hz, 2H, H$_{B}$ 5-Ar), 8.73 (s, 2H, 2-ArH); $^{13}$C NMR (75 MHz, CDCl$_{3}$): $\delta$ 24.1 (4-Me), 24.7 (OC(CH$_{3}$)$_{2}$), 30.1 (C(CH$_{3}$)$_{3}$), 34.4 (C(CH$_{3}$)$_{3}$), 80.6 (C-4), 84.0 (OC(CH$_{3}$)$_{2}$), 119.0 (C(Ar)-C-2), 125.5, 126.2 (CH$_{Ar+Ar'}$), 132.7 (C-C=N), 135.1 (CH-C-B), 135.7 (C-B), 146.6 (C-2), 156.1 (C-OH), 175.8 (C-5); $^{11}$B NMR (192.6 MHz, CDCl$_{3}$): $\delta$ +30.7. Found, %: C 71.63; H 8.39; B 2.00; N 5.27. C$_{31}$H$_{43}$BN$_{2}$O$_{4}$. Calculated, %: C 71.81; H 8.36; B 2.09; N 5.40.
Synthesis of Hybrid Diradical 15. Lead dioxide (935 mg, 3.9 mmol) was added into suspension of bis(imidazole) 13 (102 mg, 0.13 mmol) in 20 mL of chloroform and reaction mixture was vigorously stirred at 20 °C during 20 min. Excess of oxidant was removed by filtration through double paper filter, filtrate was gentle evaporated, residue was triturated with hexane (3 mL), precipitate was filtrated and washed with ether (2 mL). Flash chromatography of crude material (eluent CHCl₃) gave analytically pure sample of diradical 15.

Dark brown powder, isolated yield 87 mg (75%), dec > 200 °C (CHCl₃-hexane), Rf 0.85 (CHCl₃). IR (solid, KBr, ν<sub>max</sub>, cm⁻¹): 2957 (CH), 1606, 1581, 1558 (C=C, C=N), 1441, 1378, 1255. Raman spectrum (solid, ν<sub>max</sub>, cm⁻¹ (intensity)): 1604 (vs), 1557 (w), 1504 (m), 1419 (w), 1328 (w), 1287 (w), 1199 (m), 1152 (w), 407 (w). UV (in EtOH, λ<sub>max</sub>, nm, (lg ε)): 306 (n/d*), 372 (n/d), 471 (shoulder, n/d). Found, %: C 67.92; H 6.98; N 6.10. C₅₀H₆₂N₄O₄ × CHCl₃. Calculated, %: C 68.03; H 6.83; N 6.22. HRMS (EI): Observed 782.4756; C₅₀H₆₀N₄O₄ ([M+2]^+); calculated 782.4766.

(* n/d – not determined due to low solubility in EtOH)
*Residual signals at $\delta_H$ 1.24 and 10.76 ppm (in $^1$H NMR spectrum) and $\delta_C$ 24.1, 79.9 and 158.9 (in $^{13}$C NMR spectrum) corresponds to small impurity of 2-hydroxyoxime, 2-hydroxy-1-(4-iodophenyl)-2-methylpropan-1-one oxime.
Fig. S1. ESR spectrum of iodo-substituted phenoxy-nitroxide 8, recorded at 20 °C in a degassed toluene; the black line is the experimental spectrum, the red line is its mathematical reconstruction.

$g_{iso} = 2.0059$, $A_N = 0.536$ mT, $A_N = 0.061$ mT, $A_H = 0.163$ mT, $A_H = 0.150$ mT

Fig. S2. ESR spectrum of hybrid radical 11b, recorded at 20 °C in a degassed toluene;

$g_{iso} = 2.0059$, $A_N = 0.542$ mT, $A_N = 0.060$ mT, $A_H = 0.160$ mT, $A_H = 0.148$ mT
Fig. S3. ESR spectrum of hybrid radical 11c, recorded at 20 °C in a degassed toluene; $g_{\text{iso}} = 2.0059$, $A_N = 0.542$ mT, $A_{\|} = 0.060$ mT, $A_H = 0.161$ mT, $A_H = 0.149$ mT

Fig. S4. ESR spectrum of hybrid radical 11d, recorded at 20 °C in a degassed toluene; $g_{\text{iso}} = 2.0059$, $A_N = 0.538$ mT, $A_{\|} = 0.061$ mT, $A_H = 0.163$ mT, $A_H = 0.151$ mT
Fig. S5. High resolution mass-spectrum of diradical 15

\[ T_{\text{source}} = 115^\circ C \]
\[ T_{\text{probe}} = 320^\circ C \]

| m/z | Intensity | Relative, % | m/z | Intensity | Relative, % |
|-----|-----------|-------------|-----|-----------|-------------|
| 17.9| 17006592.0| 31.55       | 709.7| 3589695.0| 6.66        |
| 40.9| 16285696.0| 30.22       | 748.7| 3304957.0| 6.13        |
| 43.0| 10874880.0| 20.18       | 749.8| 2444696.0| 4.54        |
| 43.9| 7640791.0 | 14.18       | 750.8| 9628672.0| 17.86       |
| 55.0| 10024704.0| 18.60       | 751.8| 5287260.0| 9.81        |
| 56.0| 6618133.0 | 12.28       | 752.8| 2217491.0| 4.11        |
| 57.0| 17448192.0| 32.37       | 754.8| 1948813.0| 3.62        |
| 69.0| 6873538.0 | 12.75       | 755.8| 1208484.0| 2.24        |
| 71.0| 8475136.0 | 15.72       | 756.8| 6710196.0| 12.45       |
| 273.2| 53899008.0| 100.00      | 757.8| 3654739.0| 6.78        |
| 274.2| 10070784.0| 18.68       | 758.8| 2196376.0| 4.07        |
| 751.8| 3219035.0 | 5.97        | 759.8| 1253594.0| 2.33        |

Calculated, [M]^+ : m/z = 780.4609 \( \text{C}_{50}\text{H}_{60}\text{N}_{4}\text{O}_{4} \)^+  
Calculated, [M+2]^+ : m/z = 782.4766 \( \text{C}_{50}\text{H}_{62}\text{N}_{4}\text{O}_{4} \)^+  
Found,            : m/z = 782.4756 \([\text{M+2}]^+\)
Cyclic voltammetry

**Scheme S1.** Plausible paths of electrochemical oxidation and reduction reactions of 4H-imidazoles 10a-d.

**Table S1.** Oxidation and reduction potentials of 4H-imidazole N-oxides 10a-d. Potentials calibrated vs Fc/Fc⁺.

| Entry | $E_{Ox}^1$ | $E_{Ox}^2$ | $E_{Ox}^3$ | $E_{Red}$ |
|-------|-----------|-----------|-----------|----------|
| 10a   | 0.57      | 0.78      | 1.25      | -1.87    |
| 10b   | 0.51      | 0.78      | 1.22      | -1.91    |
| 10c   | 0.47      | 0.77      | 1.21      | -1.90    |
| 10d   | 0.54      | 0.78      | 1.28      | -1.80    |

**Scheme S2.** Proposed oxidation reaction of the diradical 15.
X-Ray of 11a (Additional data)

**Table S2.** Intermolecular interactions parameters of radical 11a

| π-π-Interactions | Cg… Cg*, (Å) | D_{pln}*, (Å) | α*, (°) |
|------------------|-------------|---------------|--------|
| π (C6÷C11) … π (C6÷C11) | 4.012(2) | 3.467(1), 3.593(2) | 4.0(2) |
| π (C12÷C17) … π (C12÷C17) | 4.279(2) | 3.531(1) | 0 |
| H…O, (Å) | C…O, (Å) | C-H…O, (°) |
| C17-H … O2 | 2.55 | 3.401(5) | 153 |

* Cg… Cg- center to center distance of aromatic rings, D_{pln} distance from the center of ring to the plane of ring interacted with, α - angle between planes of interacting moieties.

**References:**

1. L. Legrand and N. Lozac'h, *Bull. Soc. Chim. France.*, 1959, 1686.
2. X. Wang, M. Liu, L. Xu, Q. Wang, J. Chen, J. Ding and H. Wu, *J. Org. Chem.*, 2013, **78**, 5273.
3. S. Rinker, P. R. James, M. Neumann, O. Erpeldinger and F. Kraushaar, US Pat., 20100267992A1, 2010.