Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information
for

The Suzuki-Miyaura reaction as a tool for modification of phenoxyl-nitroxyl radicals of the 4*H*-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

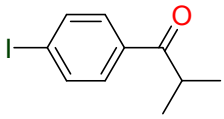
[c] Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 3 Institutskaya Str., Novosibirsk, 630090, Russia

[d] International Tomography Center SB RAS, 3A Institutskaya Str., Novosibirsk, 630090, Russia

*Corresponding author: Dmitrii G. Mazhukin
E-mail: d-mazhukin@yandex.ru

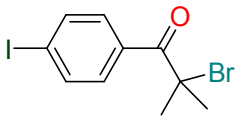
List of Contents

Synthesis and Characterization of Starting Compound



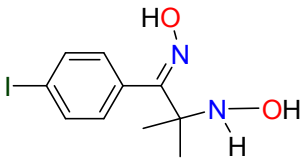
1-(4-Iodophenyl)-2-methylpropan-1-one (2). Freshly sublimed and powdered $AlCl_3$ (66 g, 0.495 mol) was added in portions of ~22 g with stirring in a 1 hour interval into solution of 128 mL (1.44 mol) of iodobenzene in a 51 mL (0.50 mol) of freshly distilled *iso*-butyryl chloride. The temperature of 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 CH_2Cl_2 (3×30 mL). The combined organic extracts were washed with aqueous Na_2SO_3, 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 CH_2Cl_2 (3×30 mL). Combined organic extracts were dried with anhydrous Na_2SO_4, filtered through a short column filled with 20 g of Al_2O_3, 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, $CDCl_3$)[2]: δ_H 1.19 (d, J = 7 Hz, 6H, CH(C$\underline{H}_3$)$_2$), 3.45−3.50 (m, 1H, C$\underline{H}$(CH$_3$)$_2$), 7.65 (d, J = 9 Hz, 2H, CH_{Ar}), 7.81 (d, J = 9 Hz, 2H, CH_{Ar}). Found, %: C 43.97; H 4.09; I 46.20. $C_{10}H_{11}IO$. Calculated, %: C 43.79; H 4.01; I 46.31.



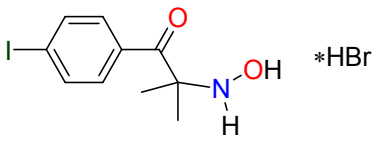
2-Bromo-1-(4-iodophenyl)-2-methylpropan-1-one (3). To a solution of 50.5 g (184 mmol) of 1-(4-iodophenyl)-2-methylpropan-1-one **2** in a mixture of 90 mL of diethyl ether and 7 mL of dioxane, 1.00 mL (19 mmol) of bromine was added and the mixture was stirred for 15-20 min until clear decolorization. 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 Et_2O (2×20 mL), extract was combined with an organic layer, dried over anhydrous Na_2SO_4, 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. $C_{10}H_{10}BrIO$. 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 $CHCl_3$ (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.

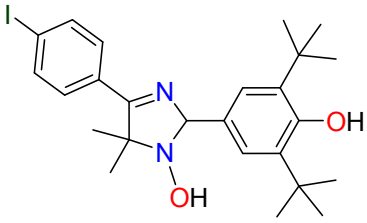
Colorless fine-needle crystals, isolated yield 45.10 g (70%), mp 167-169 °C (MeOH). ^{1}H NMR (500 MHz, DMSO-d_6): δ_H 1.12 (s, 6H, $2CH_3$), 5.18 (brs, 1H, N*H*OH), 6.99 (*AB*, J_{AB} = 8.5 Hz, 2H, H_A Ar), 7.32 (s, 1H, NHO*H*), 7.73 (*AB*, J_{AB} = 8.5 Hz, 2H, H_B Ar), 10.59 (s, 1H, C=NO*H*). ^{13}C NMR (125 MHz, DMSO-d_6): δ_C 23.4 (C(*C*H_3)$_2$), 60.7 (*C*(CH$_3$)$_2$), 94.0 (C-I), 130.6 (CH_{Ar}), 133.4 (*C*$_{Ar}$-C=N), 136.5 (CH_{Ar}), 160.3 (C=N). Found, %: C 37.82; H 4.31; I 40.05; N 8.84. $C_{10}H_{13}IN_2O_2$. 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.

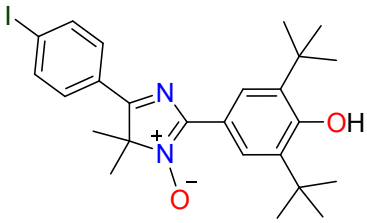
Colorless shiny plates, isolated yield 3.40 g (93%), mp 182-183 °C (dec., H_2O). ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 1.67 (s, 6H, $2CH_3$), 7.72 (*AB*, J_{AB} = 8.5 Hz, 2H, H_A Ar), 7.94 (*AB*, J_{AB} = 8.5 Hz, 2H, H_B Ar), 10.80 (s, 1H, N^+H_2OH), 10.90-12.00 (brs, 2H, N^+H_2OH). ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 20.3 (C(*C*H_3)$_2$), 69.0 (*C*(CH$_3$)$_2$), 102.7 (C-I), 130.5 (CH_{Ar}), 132.8 (*C*$_{Ar}$-C=O), 137.8 (CH_{Ar}), 198.4 (C=O). Found, %: C 31.16; H 3.55; Br 20.70; I 33.04; N 3.58. $C_{10}H_{13}BrINO_2$. Calculated, %: C 31.11; 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. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 1.41 (s, 6H, $2CH_3$), 4.85 (brs, 2H, NHOH), 7.65 (*AB*, J_{AB} = 8.5 Hz, 2H, H_A Ar), 7.75 (*AB*, J_{AB} = 8.5 Hz, 2H, H_B Ar). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 23.2 (C(*C*H_3)$_2$), 67.3 (*C*(CH$_3$)$_2$), 99.3 (C-I), 130.0 (CH_{Ar}), 135.9 (*C*$_{Ar}$-C=O), 137.4 (CH_{Ar}), 204.5 (C=O).



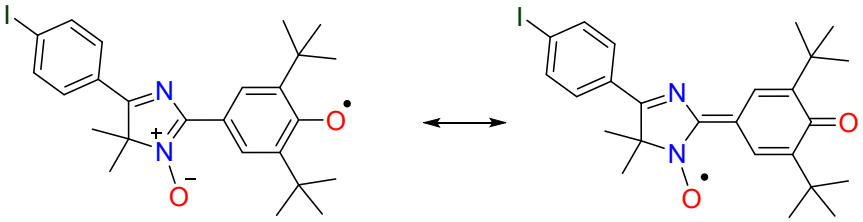
2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-(4-iodophenyl)-1-hydroxy-5,5-dimethyl-2,5-dihydro-1*H*-imidazole (7). Ammonium acetate 7.70 g (100 mmol) was added to a solution of 3.86 g (10 mmol) of 2-hydroxylamino ketone hydrobromide **5** in 20 ml MeOH, mixture was stirred until a complete dissolution, followed by addition of 2.56 g (10.5 mmol) of 3,5-di-*t*-butyl -4-hydroxybenzaldehyde **6**.[3] 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). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.09 (s, 3H, $C(CH_3)_2$), 1.31 (s, 3H, $C(CH_3)_2$), 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, C*H* Ar-OH), 7.50 (*AB*, J_{AB} = 8 Hz, 2H, H_A Ar-I), 7.73 (*AB*, J_{AB} = 8 Hz, 2H, H_B Ar-I). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 16.8 (5-Me), 24.6 (5-Me), 30.1 ($C(\underline{C}H_3)_3$), 34.2 ($\underline{C}(CH_3)_3$), 71.3 (C-5), 90.9 (C-2), 97.2 (C-I), 125.0 (2,6-CH ArOH), 129.1 (CH_{Ar}), 129.8 (C_{Ar}), 132.4 (C_{Ar}), 135.6 (*C*-*t*-Bu), 137.5 (CH_{Ar}), 154.0 (C-OH), 175.6 (C-4). Found, %: C 57.97, H 6.49, N 5.24, I 24.30. $C_{25}H_{33}IN_2O_2$. 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-4*H*-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 $CHCl_3$ 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).

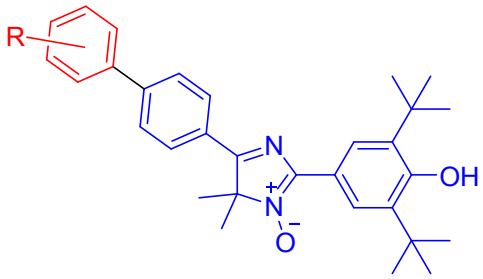
Dark yellow needles, isolated yield 3.59 g (95%), mp 244.4 °C (dec., EtOH), R_f 0.15 ($CHCl_3$/MeOH, 20:1). IR (solid, KBr, ν_{max}, cm^{-1}): 3620 (OH), 2957 (CH), 1582 (C=N), 1530, 1421. UV (in EtOH, λ_{max}, nm, (lg ε)): 309 (4.19), 398 (3.43). ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.50 (s, 18H, *t*-Bu), 1.71 (s, 6H, $C(CH_3)_2$), 5.64 (s, 1H, Ar-OH), 7.77 (*AB*, J_{AB} = 8.5 Hz, 2H, H_A Ar-I), 7.84 (*AB*, J_{AB} = 8.5 Hz, 2H, H_B Ar-I), 8.71 (s, 2H, C*H* Ar-OH). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 24.1 (4-Me), 30.1 ($C(\underline{C}H_3)_3$), 34.4 ($\underline{C}(CH_3)_3$), 80.4 (C-4), 98.5 (C-I), 118.9 ($\underline{C}_i$-C-2), 125.4 (2,6-CH ArOH), 128.4 (CH_{Ar}), 130.0 ($\underline{C}_{Ar}$-C=N), 135.8 (*C*-*t*-Bu), 138.2 (CH_{Ar}), 146.5 (C-2), 156.1 (C-OH), 174.7 (C-5). Found, %: C 57.79, H 5.95, N 5.38, I 24.25. $C_{25}H_{31}IN_2O_2$. Calculated, %: C 57.92, H 6.03, N 5.40, I 24.48.



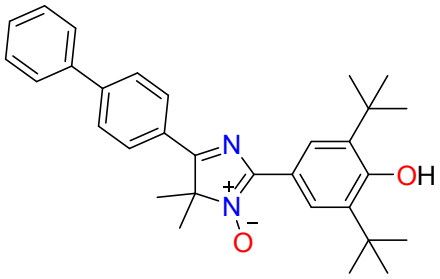
2,6-Di-*tert*-butyl-4-[4-(4-iodophenyl)-5,5-dimethyl-1-oxido-1*H*-imidazol-2(5*H*)-ylidene]cyclohexa-2,5-dienone (8). Lead dioxide (722 mg, 3 mmol) was added portionwise for 2 h to a solution of 259 mg (0.5 mmol) of 4*H*-imidazole **1** in 10 mL of chloroform with continuous stirring until complete conversion 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, ν_{max}, cm^{-1}): 2953 (CH), 1584, 1557 (C=N). UV (in EtOH, λ_{max}, nm, (lg ε)): 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_{iso} = 2.0059. HRMS (ESI): calculated for $C_{25}H_{30}IN_2O_2$, 517.14, observed 518.20 ([M + 1]).

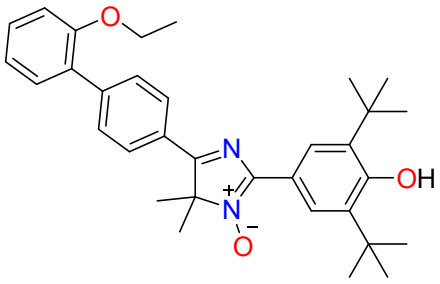
Suzuki-Miyaura Couplings, Oxidation to Hybrid Radicals and Characterization Data



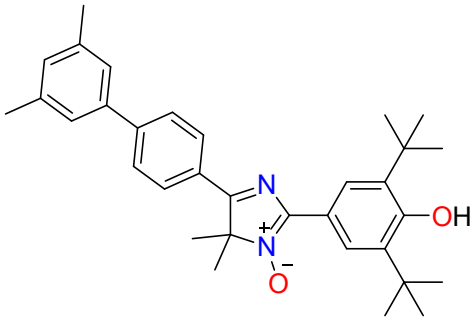
5-(Biphenyl-4-yl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxides (10a-d) (*general procedure*). A solution of 5-(4-iodophenyl)-4*H*-imidazole **1** (259 mg, 0.5 mmol) and 0.5 mmol of arylboronic acid **9a-d** in 15 mL of PhMe was purged with argon for 20 min, then 0.035 mmol of freshly prepared $Pd[P(C_6H_5)_3]_4$ was added. The mixture was diluted with 5 mL of a degassed 2M aqueous solution of K_2CO_3 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.



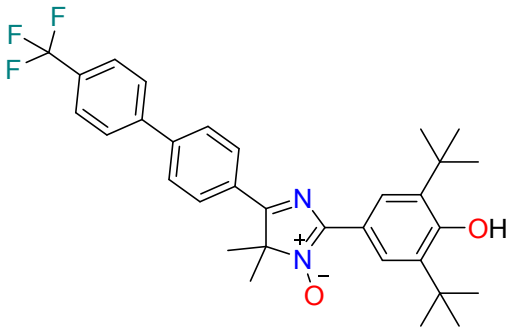
5-(Biphenyl-4-yl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide (10a). Bright yellow crystals, isolated yield 169 mg (72%), mp 190.6 °C (hexane-EtOAc), R_f 0.3 ($CHCl_3$/MeOH, 50:1). IR (solid, KBr, ν_{max}, cm^{-1}): 3626 (OH), 2956 (CH), 1601 (C=N), 1531, 1421, 1375, 1238. UV (in EtOH, λ_{max}, nm, (lg ε)): 313 (4.54), 397 (3.86). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.52 (s, 18H, *t*-Bu), 1.78 (s, 6H, $C(CH_3)_2$), 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*, J_{AB} = 9.0 Hz, 2H, H_A 5-Ar), 8.16 (*AB*, J_{AB} = 9.0 Hz, 2H, H_B 5-Ar), 8.77 (s, 2H, C*H* Ar-OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 24.3 (4-Me), 30.2 ($C(\underline{C}H_3)_3$), 34.4 ($\underline{C}(CH_3)_3$), 80.5 (C-4), 125.5, 127.0, 127.5, 127.7, 128.1, 129.0 (CH_{Ph} + CH_{Ar}), 129.5 (C_i(Ar)-C-5), 135.7 (*C*-*t*-Bu), 139.8 (C_i(Ph)-C_i(Ar)), 144.1 (C_i(Ph)-C_i(Ar)), 146.6 (C-2), 156.1 (C-OH), 175.5 (C-5). Found, %: C 79.24, H 7.57, N 5.71. $C_{31}H_{35}N_2O_2$. Calculated, %: C 79.45, H 7.74, N 5.98.



2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(2'-ethoxybiphenyl-4-yl)-4,4-dimethyl-4*H*-imidazole 3-oxide (10b). Dark yellow crystals, isolated yield 170 mg (66%), mp 116.6 °C (dec., hexane-EtOAc), R_f 0.45 ($CHCl_3$/MeOH, 50:1). IR (solid, KBr, ν_{max}, cm^{-1}): 3624 (OH), 2956 (CH), 1599 (C=N), 1529, 1421, 1373, 1236. UV (in EtOH, λ_{max}, nm, (lg ε)): 255 (4.07), 313 (4.43), 388 (3.87). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 1.38 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3), 1.52 (s, 18H, *t*-Bu), 1.79 (s, 6H, $C(CH_3)_2$), 4.07 (q, *J* = 7.2 Hz, 2H, OCH_2CH_3), 5.63 (s, 1H, Ar-OH), 6.98 – 7.06 (m, 1H, 2H, 3',5'-H_{Ar}), 7.31 – 7.37 (m, 2H, 4',6'-H_{Ar}), 7.71 (*AB*, J_{AB} = 8.0 Hz, 2H, H_A 5-Ar), 8.11 (*AB*, J_{AB} = 8.0 Hz, 2H, H_B 5-Ar), 8.77 (s, 2H, C*H* Ar-OH). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 14.7 ($OCH_2\underline{C}H_3$),24.3 (4-Me), 30.2 ($C(\underline{C}H_3)_3$), 34.5 ($\underline{C}(CH_3)_3$), 64.0 (OCH_2), 80.5 (C-4), 112.6 (C_{Ar}-3'), 119.3 ($\underline{C_i}$(Ar)-C-2), 120.9 (C_{Ar}-5'), 125.6, 126.8, 129.3, 130.0, 130.6 (CH_{Ar}), 129.0 (C_{Ar}-1'), 129.4 ($\underline{C_i}$(Ar)-C-5), 135.8 (*C*-*t*-Bu), 142.2 (s, C_{Ar}-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. $C_{33}H_{40}N_2O_3$. Calculated, %: C 77.31, H 7.86, N 5.46.

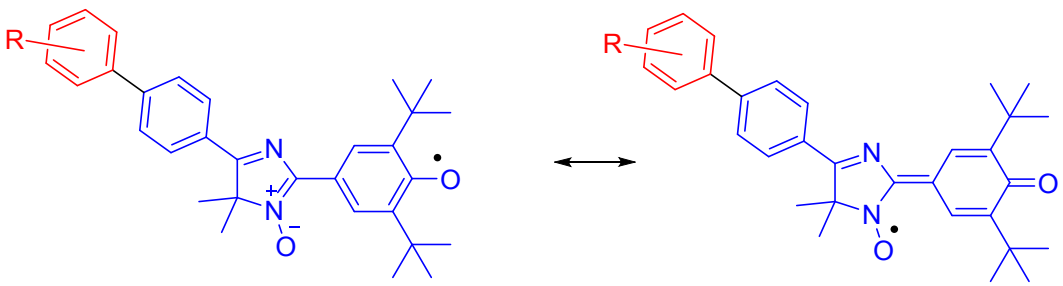


2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(3',5'-dimethyl-[1,1'-biphenyl]-4-yl)-4,4-dimethyl-4*H*-imidazole 3-oxide (10c). Dark yellow crystals, isolated yield 186 mg g (75%), mp 135.6 °C (dec., hexane-EtOAc), R_f 0.4 ($CHCl_3$/MeOH, 50:1). IR (solid, KBr, ν_{max}, cm^{-1}): 3627 (OH), 2956 (CH), 1600 (C=N), 1530, 1421, 1375, 1247. UV (in EtOH, λ_{max}, nm, (lg ε)): 316 (4.45), 399 (3.71). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.51 (s, 18H, *t*-Bu), 1.78 (s, 6H, $C(CH_3)_2$), 2.39 (s, 6H, $C\underline{H_3}ArC\underline{H_3}$), 5.64 (s, 1H, OH), 7.04 (s, 1H, 4'-H_{Ar}), 7.25 (s, 2H, 2',6'-H_{Ar}), 7.71 (*AB*, J_{AB} = 8 Hz, H_A, 2H, 2,6-H_{Ar}), 8.13 (*AB*, J_{AB} = 8 Hz, H_B, 2H, 3,5-H_{Ar}), 8.76 (s, 2H, 2-ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3 ($2\underline{C}H_3$-Ar'), 24.2 ($C(\underline{C}H_3)_2$), 30.1 ($C(\underline{C}H_3)_3$), 34.4 ($\underline{C}(CH_3)_3$), 80.4 (s, C-4), 119.1 ($\underline{C_i}$(Ar)-C-2), 124.9, 125.5, 127.4, 127.5, 129.7 ($CH_{Ar+Ar'}$), 129.3 ($\underline{C_i}$(Ar)-C-5), 135.7 ($\underline{C}$-*t*-Bu), 138.4 ($\underline{C_{Ar}}$-CH_3), 139.7 (C_{Ar}-1'), 144.4 (C_{Ar}-1), 146.6 (C-2), 156.0 (C_{Ar}-OH), 175.6 (C-5). Found, %: C 79.55; H 8.16; N 5.39. $C_{33}H_{40}N_2O_2$. Calculated, %: C 79.80; H 8.12; N 5.64.



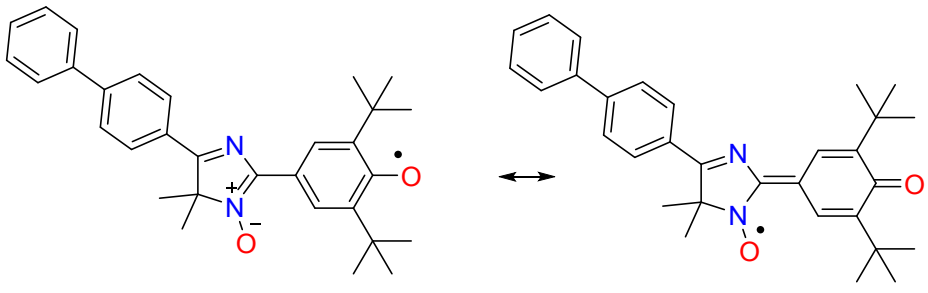
2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-(4'-(trifluoromethyl)biphenyl-4-yl)-4*H*-imidazole 3-oxide (10d). Dark yellow crystals, isolated yield 228 mg (85%), mp 260 °C (dec., hexane-EtOAc), R_f 0.25 ($CHCl_3$/MeOH, 50:1). IR (solid, KBr, ν_{max}, cm^{-1}): 3630 (OH), 2957 (CH), 1616, 1599 (C=N), 1533, 1421, 1375, 1325. UV (in EtOH, λ_{max}, nm, (lg ε)): 314 (4.60), 401 (3.80). ^{1}H NMR (400 MHz, $CDCl_3$): δ 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_B 5-Ar), 8.76 (s, 2H, 2-ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.1 (4-Me), 30.1 ($C(\underline{C}H_3)_3$), 34.4 ($\underline{C}(CH_3)_3$), 80.5 (C-4), 119.0 ($\underline{C_i}$(Ar)-C-2), 123.9 (q, $^2J_{CF}$ = 270 Hz, CF_3), 125.4, 125.8, 127.2, 127.6, 127.7 (CH_{Ar}), 130.0 (q, $^3J_{CF}$ = 33 Hz, $\underline{C_i}$-CF_3), 130.3 ($\underline{C_i}$(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. $C_{32}H_{35}F_3N_2O_2$. 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-4*H*-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, 4*H*-imidazole *N*-oxide **10d**.

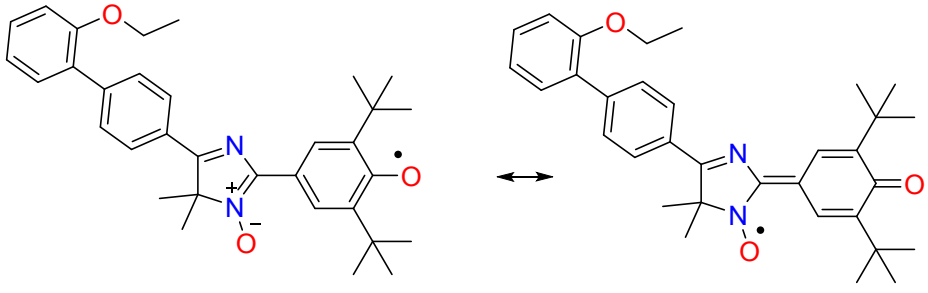


Oxidation of 5-biphenyl-4*H*-imidazoles 10a-d to hybrid radicals 11a-d (*general procedure*). To a solution of 0.2 mmol of 4*H*-imidazole *N*-oxide **10a-d** in 7 mL of chloroform, 574 mg (2.4 mmol) of lead dioxide was added and reaction mixture was stirred at rt for 3÷-5 h until the substrate disappears 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

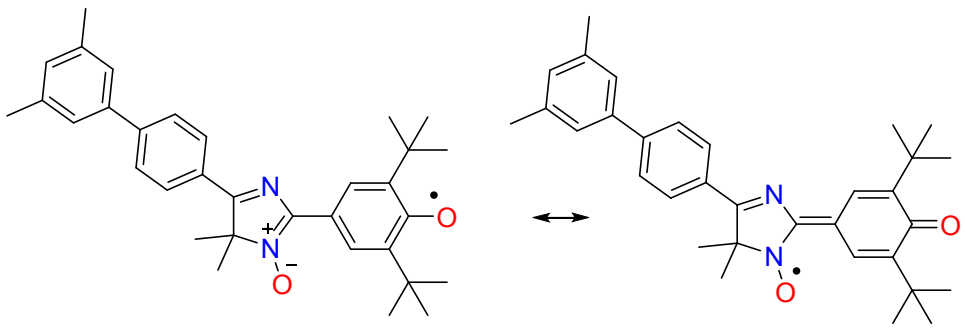
on a column with a silica. The bright colored fraction was collected, condensed under vacuum and the residue was mixed with 3 mL of hexane and cooled at -10 °C for 1 h. Formed precipitate was rapidly filtered and dried on air to give analytically pure radical **11a-d**.



2,6-Di-*tert*-butyl-4-[1-oxido-4-(biphenyl-4-yl)-5,5-dimethyl-1*H*-imidazol-2(5*H*)-yliden]cyclohexa-2,5-dienone (11a). Dark brown crystals, isolated yield 89 mg (95%), mp 180.9 °C (dec., MeCN). R_f 0.6 ($CHCl_3$). IR (solid, KBr, ν_{max}, cm^{-1}): 2955 (CH), 1604, 1584, 1557 (C=C, C=N), 1450, 1381, 1272. UV (in EtOH, λ_{max}, nm, (lg ε)): 313 (4.54), 397 (3.86). UV (in EtOH, λ_{max}, nm, (lg ε)): 256 (3.91), 339 (4.47), 352 (4.50), 465 (3.96). 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_{iso} = 2.0059. Found, %: C 79.46; H 7.45; N 5.98. $C_{31}H_{35}N_2O_2$. Calculated, %: C 79.62; H 7.54; N 5.99.

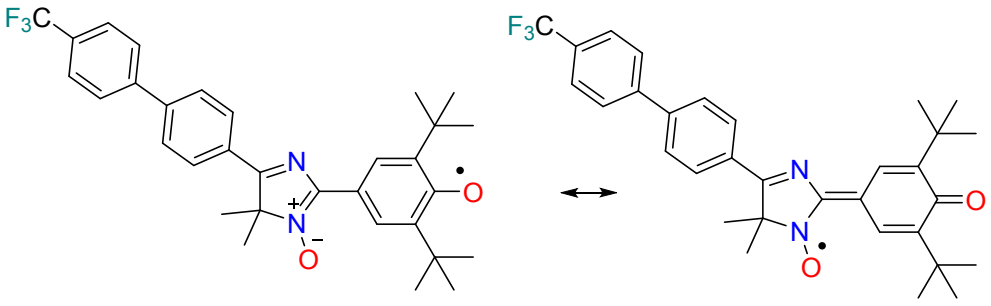


2,6-Di-*tert*-butyl-4-[1-oxido-5,5-dimethyl-4-(2'-ethoxybiphenyl-4-yl)-1*H*-imidazol-2(5*H*)-yliden]cyclohexa-2,5-dienone (11b). Dark brown fine crystals, isolated yield 94 mg (92%), mp 115.8 °C (dec., MeCN). R_f 0.75 ($CHCl_3$). IR (solid, KBr, ν_{max}, cm^{-1}): 2956 (CH), 1605, 1581, 1558 (C=C, C=N), 1485, 1448, 1257, 1234, 752. UV (in EtOH, λ_{max}, nm, (lg ε)): 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_{iso} = 2.0059. Found, %: C 77.36; H 7.69; N 5.20. $C_{33}H_{39}N_2O_3$. Calculated, %: C 77.46; H 7.68; N 5.47.

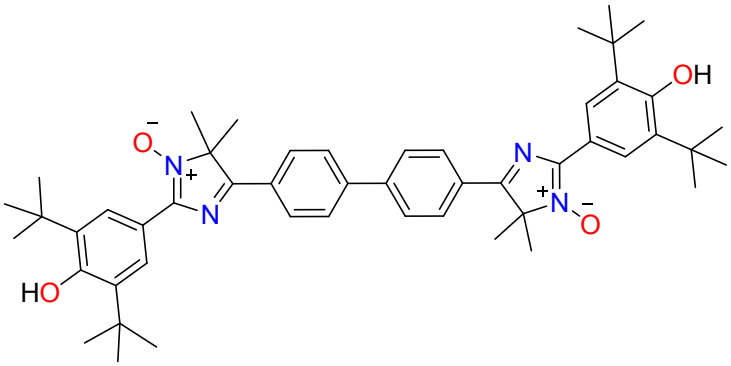


2,6-Di-*tert*-butyl-4-[1-oxido-5,5-dimethyl-4-(3',5'-dimethylbiphenyl-4-yl)-1*H*-imidazol-2(5*H*)-yliden]cyclohexa-2,5-dienone (11c). Dark brown fine crystals, isolated yield 89 mg (90%), mp 186.8 – 187.8 °C (dec., MeCN). R_f 0.6 ($CHCl_3$). IR (solid, KBr, ν_{max}, cm^{-1}): 2958 (CH), 1604, 1583, 1556 (C=C, C=N), 1514, 1440,

1383, 837. UV (in EtOH, λ_{max}, nm, (lg ε)): 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_{iso} = 2.0059. Found, %: C 79.79; H 7.68; N 5.42. $C_{33}H_{39}N_2O_2$. Calculated, %: C 79.96; H 7.93; N 5.65.



2,6-Di-*tert*-butyl-4-[1-oxido-5,5-dimethyl-4-(4'-(trifluoromethyl)biphenyl-4-yl)-1*H*-imidazol-2(5*H*)-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, ν_{max}, cm^{-1}): 2956 (CH), 1618, 1608, 1582, 1556 (C=C, C=N), 1444, 1327, 1162, 1124, 1070, 831. UV (in EtOH, λ_{max}, nm, (lg ε)): 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_{iso} = 2.0059. Found, %: C 71.80; H 6.19; F 10.51; N 5.23. $C_{32}H_{34}F_3N_2O_2$. Calculated, %: C 71.76; H 6.40; F 10.64; N 5.23.

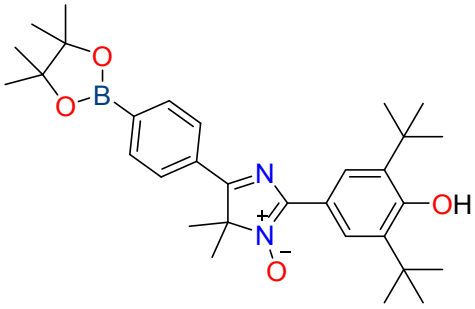


5,5'-([1,1'-Biphenyl]-4,4'-diyl)bis(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide) (13). To a solution of 155 mg (0.3 mmol) of 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5-(4-iodophenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide **1** in 5 mL of DMF, 40 mg (0.156 mmol) of bis(pinacolato)diboron 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 $[Pd(PPh_3)]Cl_2$ 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_2O (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, ν_{max}, cm^{-1}): 3601 (OH), 2956 (CH), 1605, 1526, 1419, 1375, 1319, 1238. UV (in EtOH, λ_{max}, nm, (lg ε)): 333 (n/d*), 412 (n/d). ^{1}H NMR (400 MHz, CF_3COOH): δ 1.57 (s, 36H, *t*-Bu), 2.06 (s, 12H, 2C(CH_3)$_2$), 8.05 (*AB*, J_{AB} = 8.0 Hz, 4H, H_A 5,5'-Ar), 8.51 (*AB*, J_{AB} = 8.0 Hz, 4H, H_B 5,5'-Ar), 8.82 (s, 4H, 2,2'-ArH); ^{13}C NMR (100 MHz, CF_3COOH): δ 24.9 (4,4'-Me), 31.3 (C($\underline{C}H_3$)$_3$), 36.8 ($\underline{C}$(CH_3)$_3$), 82.6 (C-

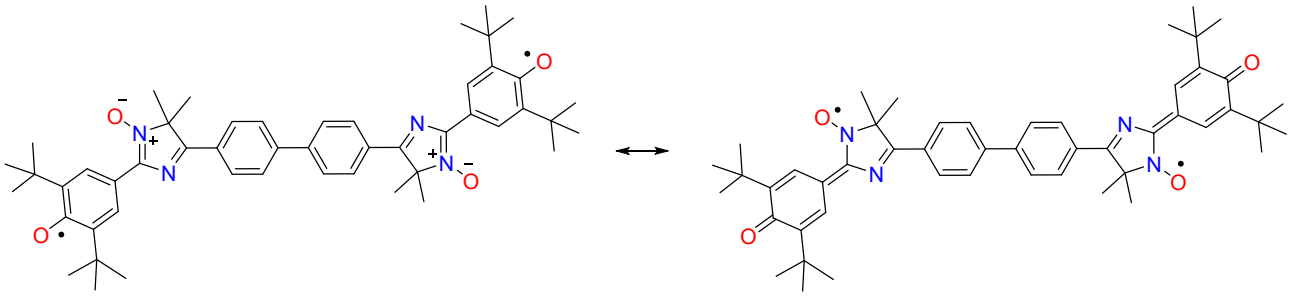
4, C-4'), 116.4 (<u>*C*</u>$_i$(Ar)-C-2(2')), 130.9, 133.1, 134.7 (3 CH_{Ar}), 131.0, 141.0, 149.0 (3 C_{Ar}), 166.0, 166.3 (C-OH and C-2(2'), 194.3 (C-5(5')). Found, %: C 72.40; H 7.52; N 6.65. $C_{50}H_{62}N_4O_4$ × ½ $CHCl_3$. Calculated, %: C 72.00; H 7.43; N 6.65.

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



2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-4*H*-imidazole 3-oxide (14). To a mixture of 518 mg (1 mmol) 4*H*-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, $[Pd(PPh_3)]Cl_2$ (35 mg, 0.05 mmol) was introduced in the reaction flask and the mixture was stirred for 3 h at 95 °C under Ar atmosphere. The resulting suspension was cooled overnight at 0 °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 °C overnight. Formed precipitate was rapidly filtered and dried on air to give dioxaborolane **14**.

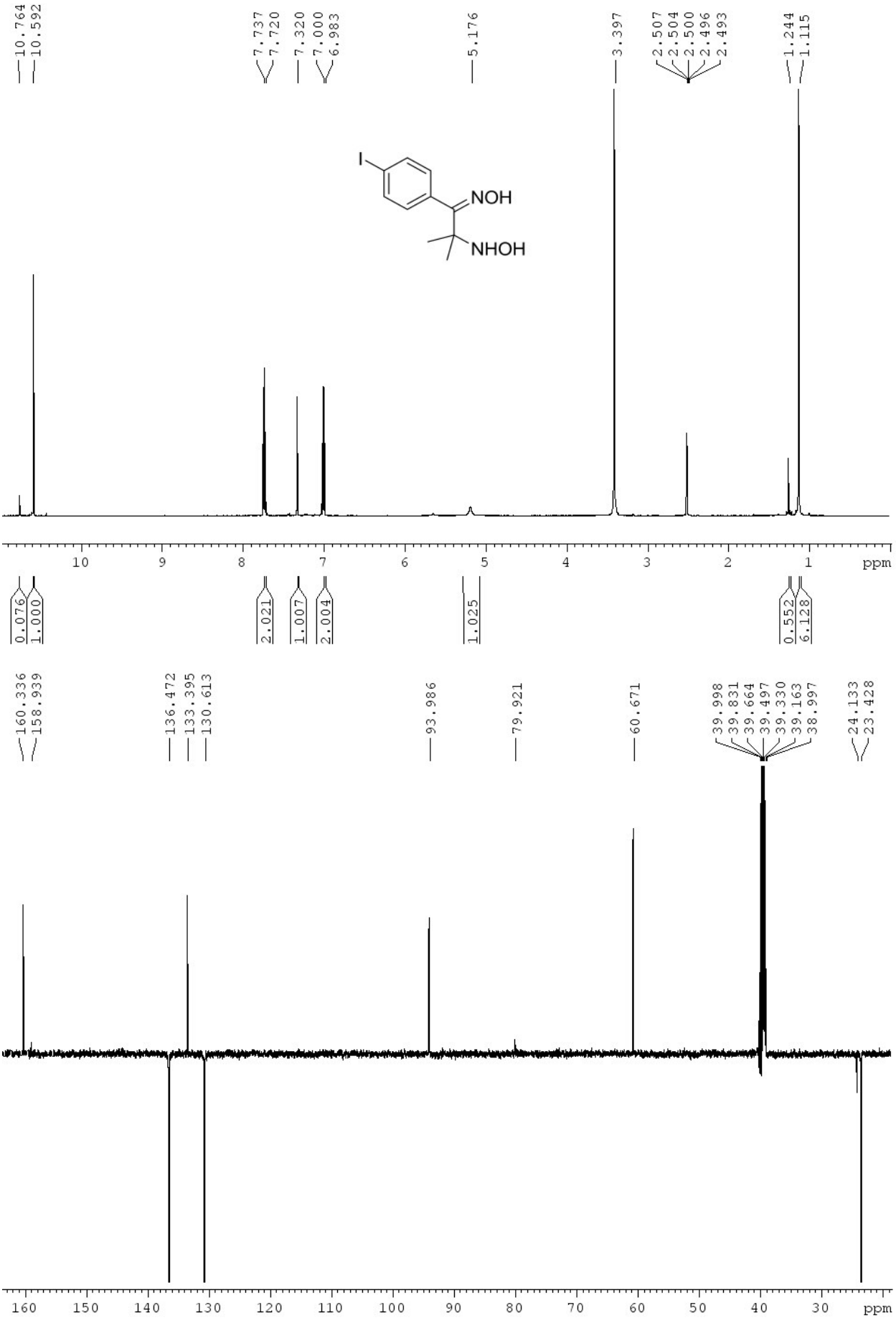
Yellow-greenish crystals, isolated yield 206 mg (40%), mp 167-169 °C (hexane), R_f 0.25 ($CHCl_3$). IR (solid, KBr, ν_{max}, cm^{-1}): 3630 (OH), 2955 (CH), 2872, 1608, 1535, 1460, 1423, 1362, 1325, 1238, 1144, 1092. UV (in EtOH, λ_{max}, nm, (lg ε)): 237 (3.99), 305 (4.43), 397 (3.65). ^{1}H NMR (300 MHz, $CDCl_3$): δ 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_{AB} = 8.3 Hz, 2H, H_A 5-Ar), 8.04 (*AB*, J_{AB} = 8.3 Hz, 2H, H_B 5-Ar), 8.73 (s, 2H, 2-ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.1 (4-Me), 24.7 (OC(<u>*C*</u>$H_3)_2$), 30.1 (C(<u>*C*</u>$H_3)_3$), 34.4 (<u>*C*</u>$(CH_3)_3$), 80.6 (C-4), 84.0 (O<u>*C*</u>$(CH_3)_2$), 119.0 (<u>*C*</u>$_i$(Ar)-C-2), 125.5, 126.2 ($CH_{Ar+Ar'}$), 132.7 (<u>*C*</u>$_i$-C=N), 135.1 (<u>*C*</u>H-C-B), 135.7 (C-B), 146.6 (C-2), 156.1 (C-OH), 175.8 (C-5); ^{11}B NMR (192.6 MHz, $CDCl_3$): δ +30.7. Found, %: C 71.63; H 8.39; B 2.00; N 5.27. $C_{31}H_{43}BN_2O_4$. Calculated, %: C 71.81; H 8.36; B 2.09; N 5.40.



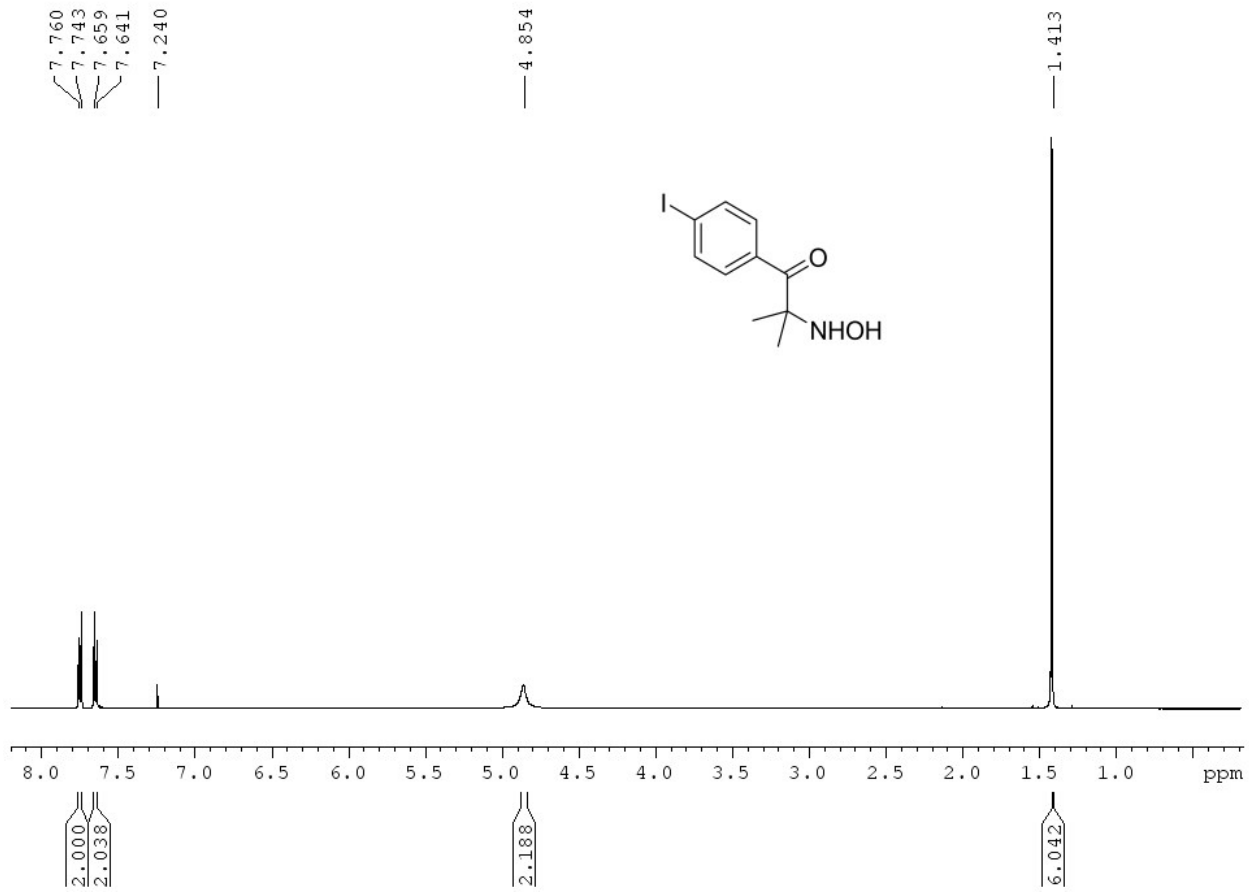
Synthesis of Hybrid Diradical 15. Lead dioxide (935 mg, 3.9 mmol) was added into suspension of bis(imidazole) **13** (102 mg, 0.13 mmol) in 20 mL of chloroform and reaction mixture was vigorously stirred at 20 °C during 20 min. Excess of oxidant was removed by filtration through double paper filter, 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 $CHCl_3$) gave analytically pure sample of diradical **15**.

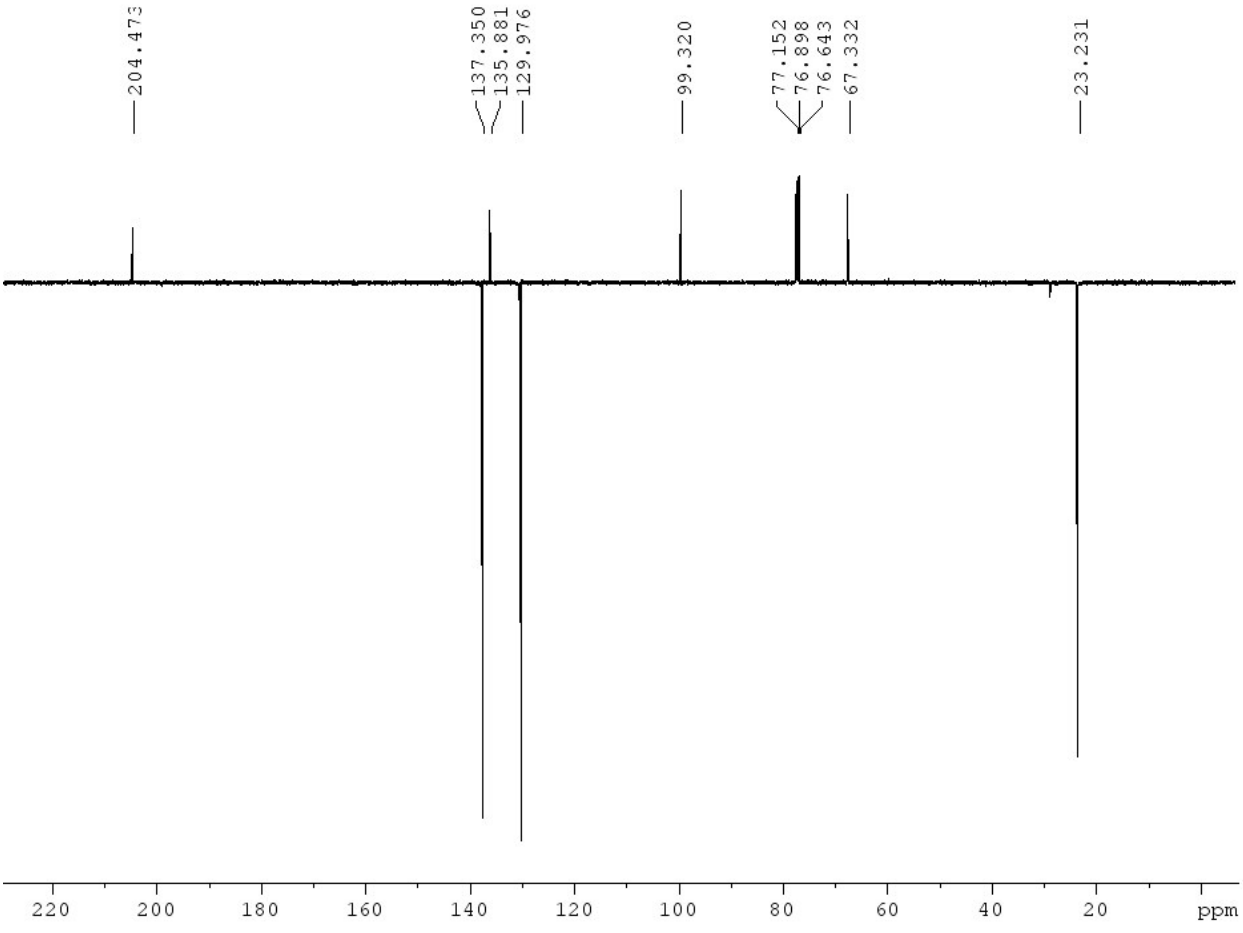
Dark brown powder, isolated yield 87 mg (75%), dec > 200 °C ($CHCl_3$-hexane), R_f 0.85 ($CHCl_3$). IR (solid, KBr, ν_{max}, cm^{-1}): 2957 (CH), 1606, 1581, 1558 (C=C, C=N), 1441, 1378, 1255. Raman spectrum (solid, ν_{max}, cm^{-1} (intensity)): 1604 (vs), 1557 (w), 1504 (m), 1419 (w), 1328 (w), 1287 (w), 1199 (m), 1152 (w), 407 (w). UV (in EtOH, λ_{max}, nm, (lg ε)): 306 (n/d*), 372 (n/d), 471 (shoulder, n/d). Found, %: C 67.92; H 6.98; N 6.10. $C_{50}H_{60}N_4O_4 \times CHCl_3$. Calculated, %: C 68.03; H 6.83; N 6.22. HRMS (EI): Observed 782.4756; $C_{50}H_{62}N_4O_4$ ($[M+2]^{+\cdot}$); calculated 782.4766.

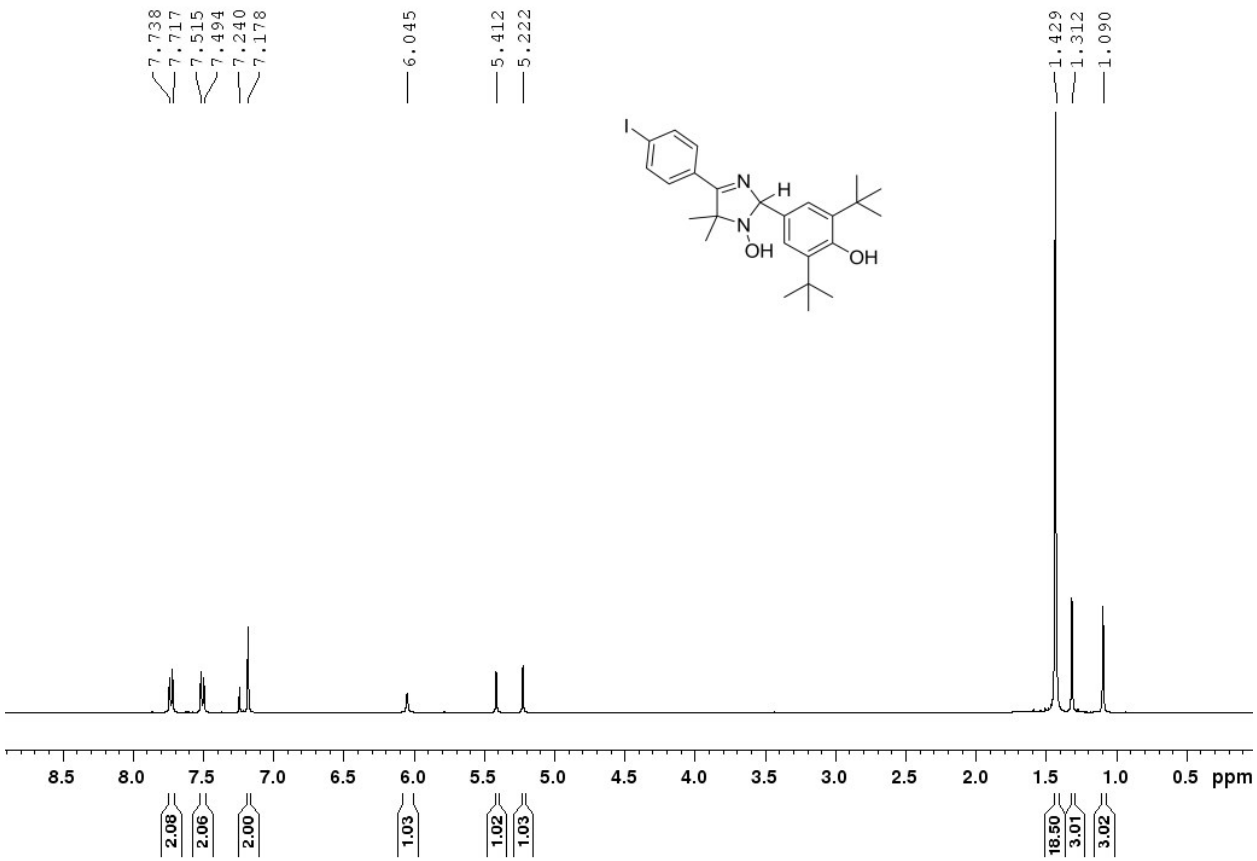
(n/d – not determined due to low solubility in EtOH)*

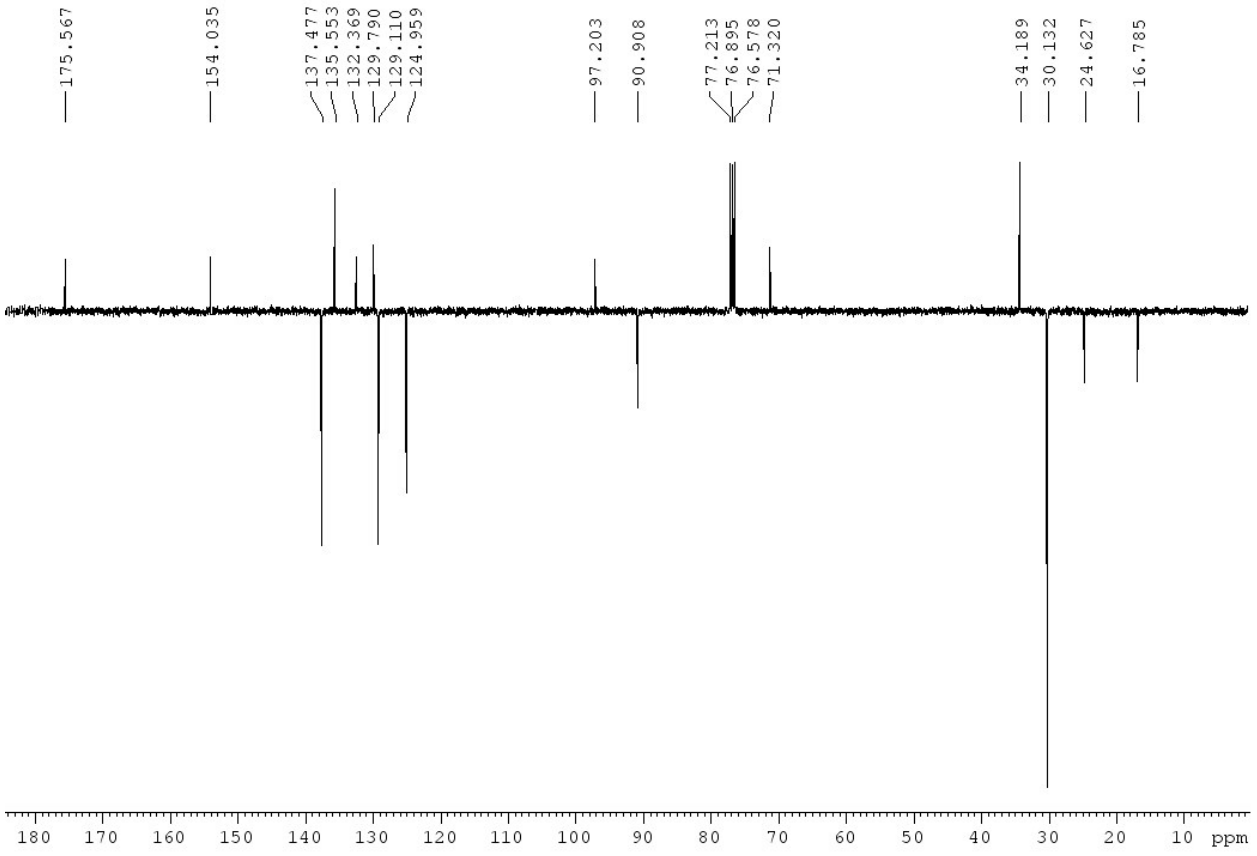


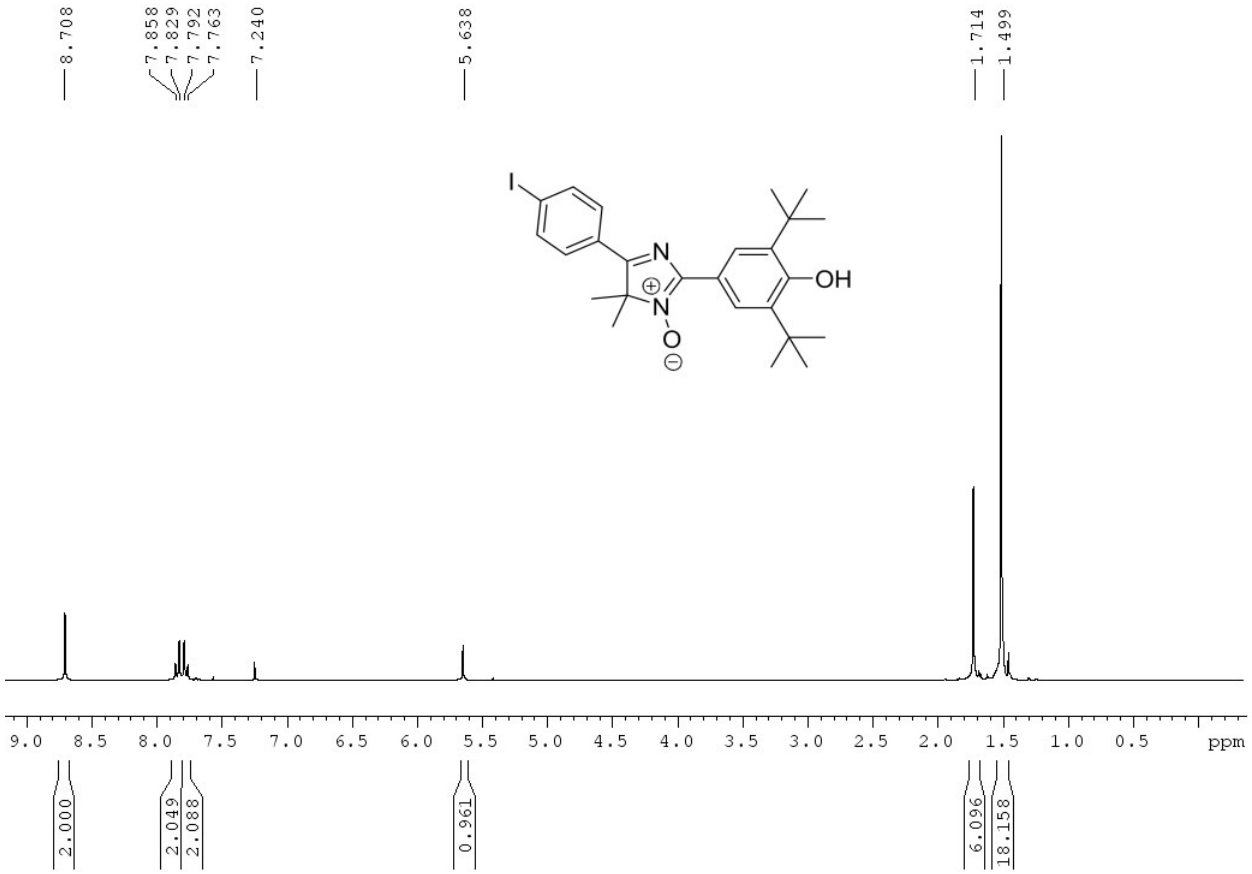
*Residual signals at δ_H 1.24 and 10.76 ppm (in ^{1}H NMR spectrum) and δ_C 24.1, 79.9 and 158.9 (in ^{13}C NMR spectrum) corresponds to small impurity of 2-hydroxyoxime, 2-hydroxy-1-(4-iodophenyl)-2-methylpropan-1-one oxime.

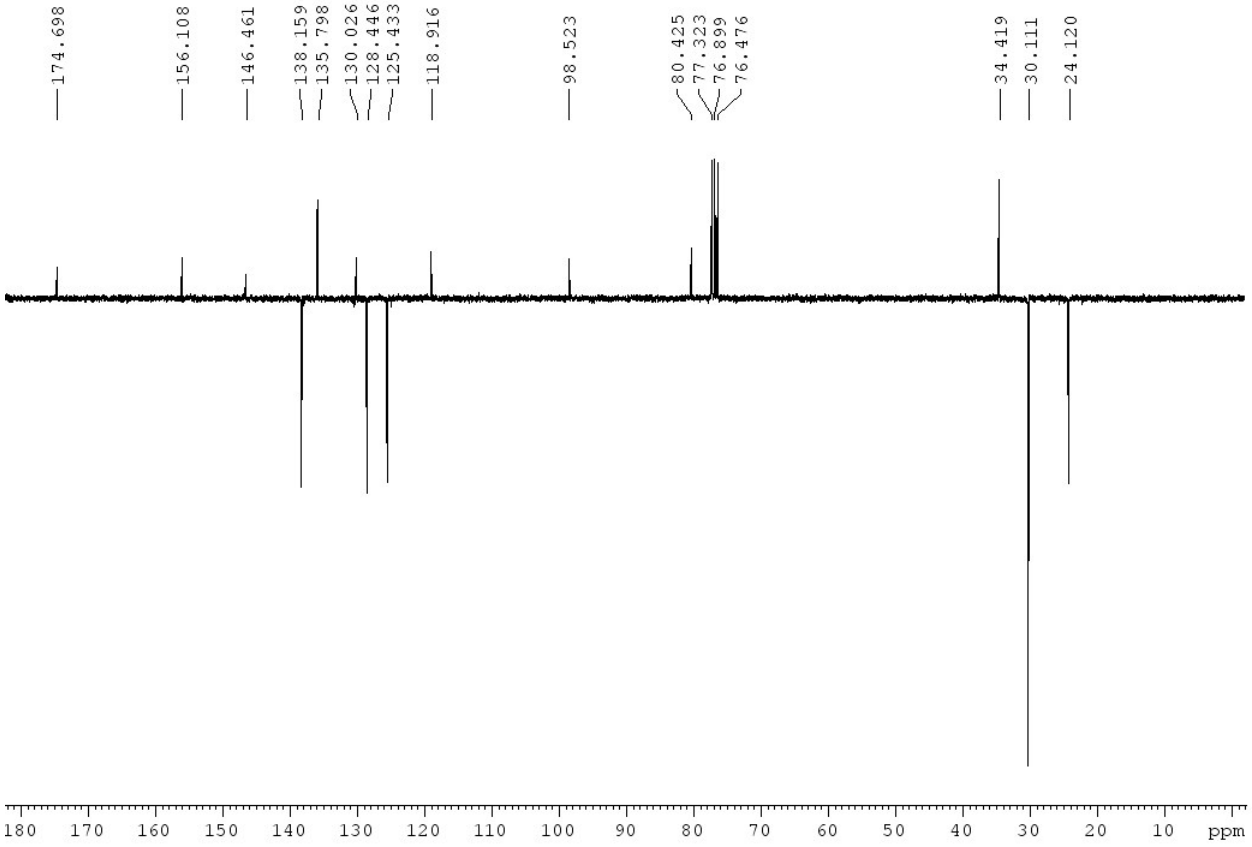

7.760
7.743
7.659
7.641
7.240
4.854
1.413
I
O
NHOH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.000
2.038
2.188
6.042

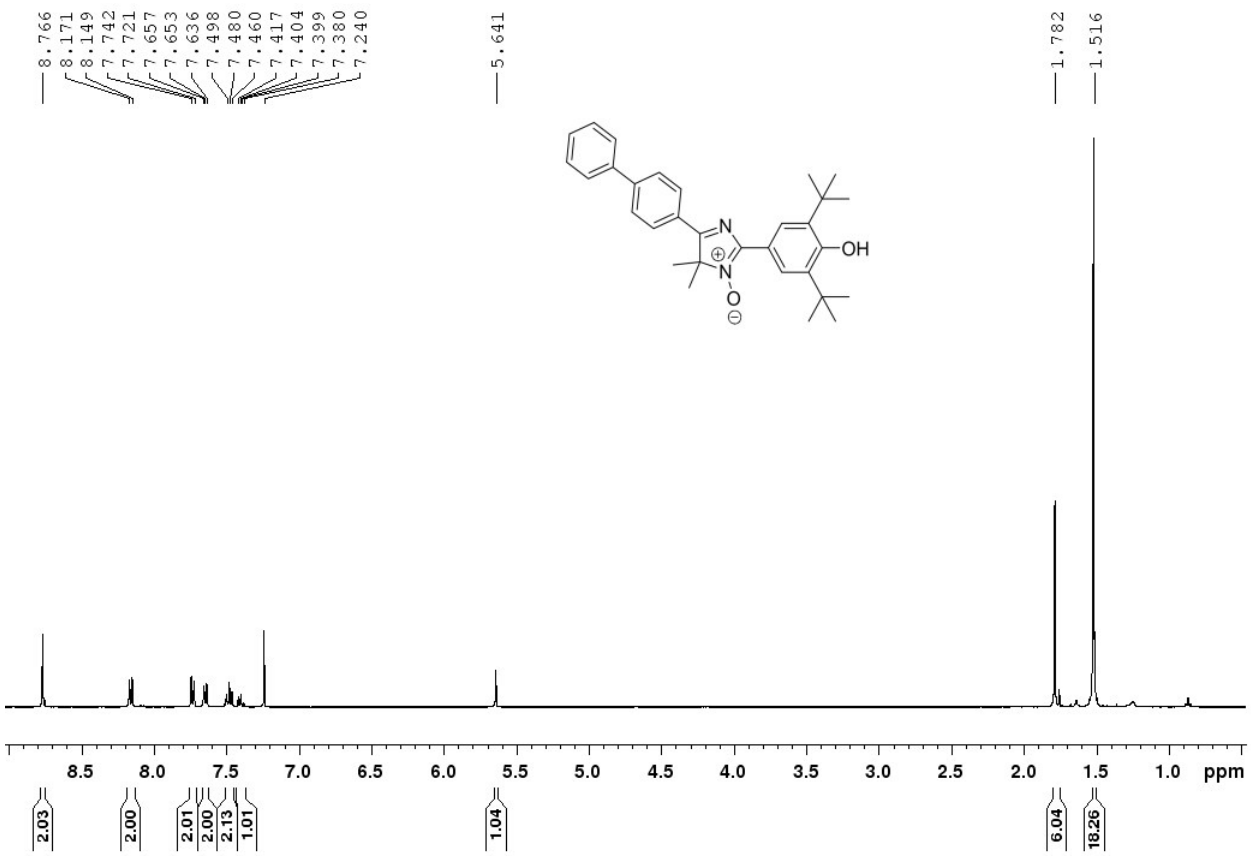

204.473
137.350
135.881
129.976
99.320
77.152
76.898
76.643
67.332
23.231
220
200
180
160
140
120
100
80
60
40
20
ppm

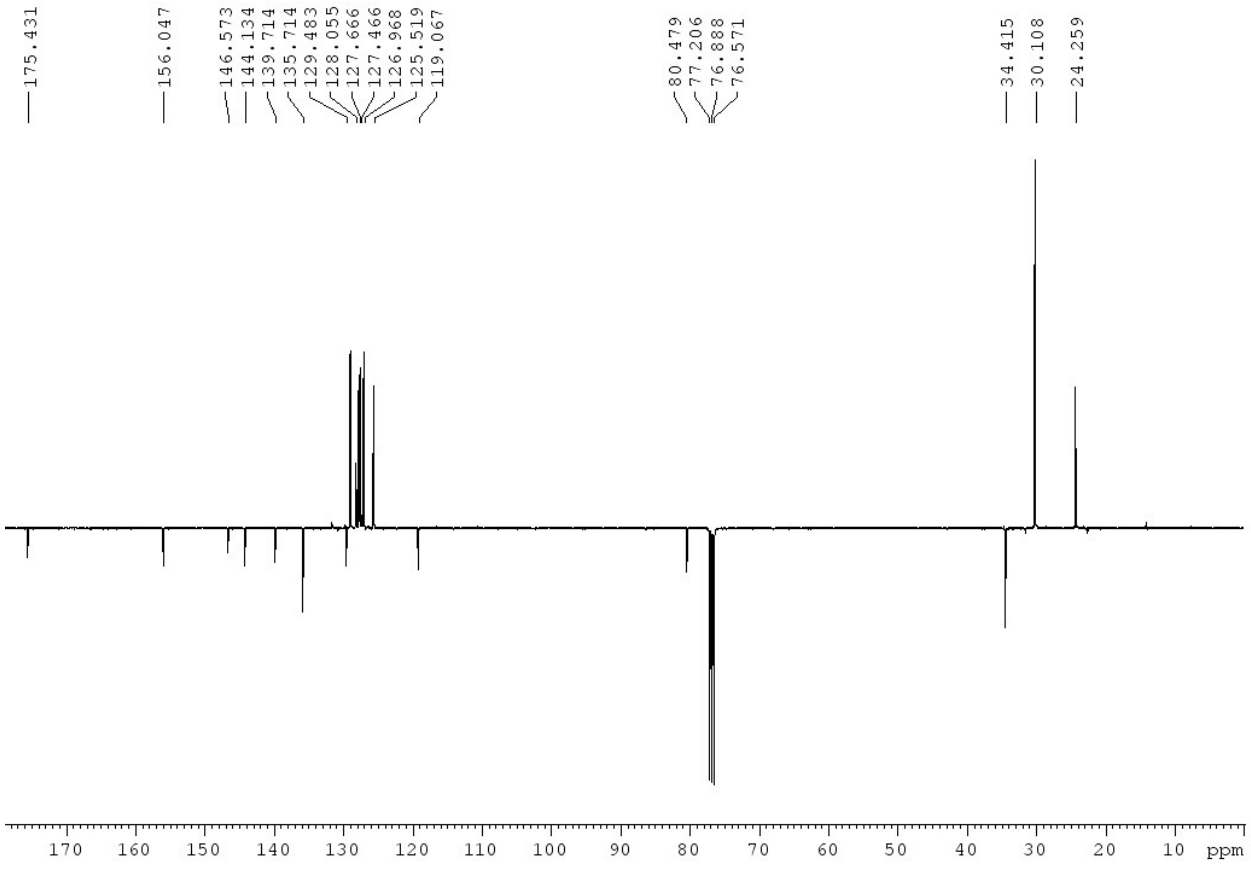

7.738
7.717
7.515
7.494
7.240
7.178
6.045
5.412
5.222
1.429
1.312
1.090
I
N
H
N
OH
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.08
2.06
2.00
1.03
1.02
1.03
18.50
3.01
3.02

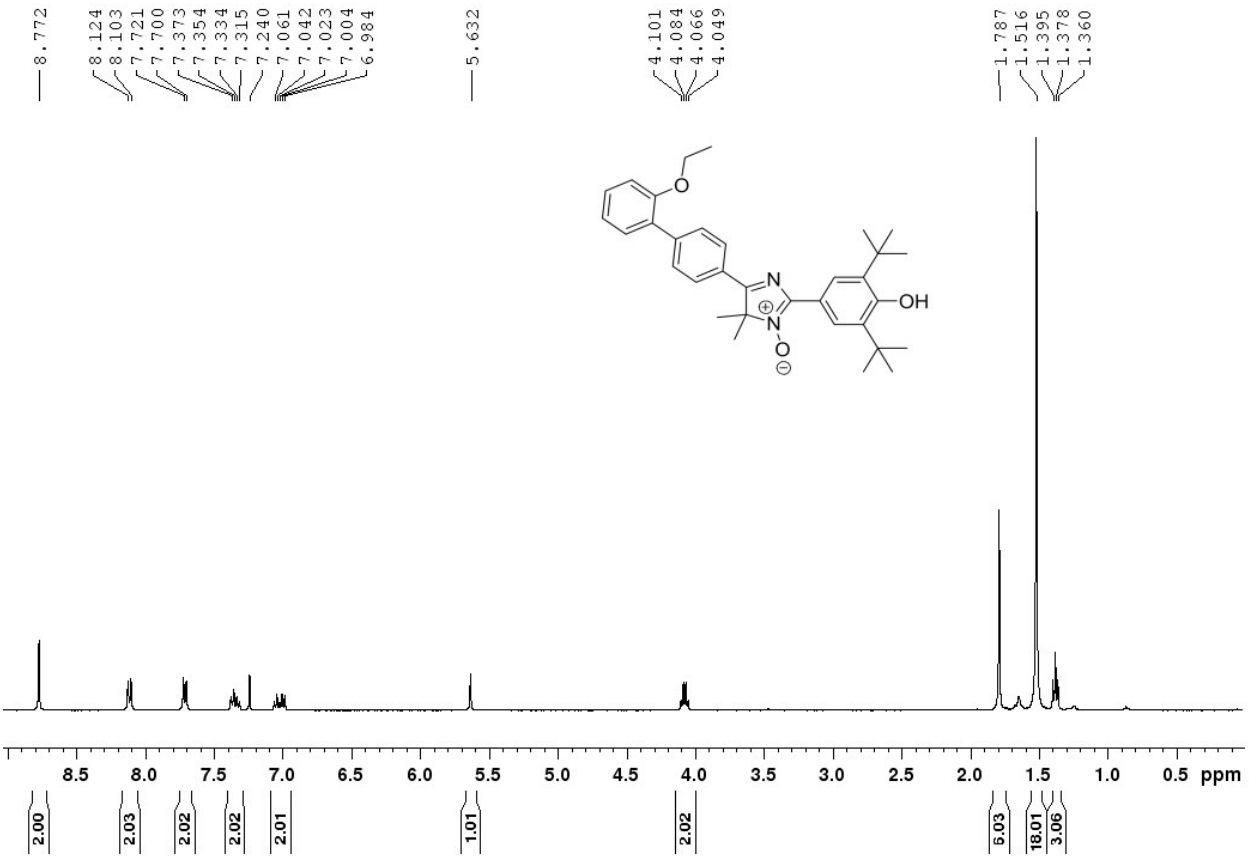

175.567
154.035
137.477
135.553
132.369
129.790
129.110
124.959
97.203
90.908
77.213
76.895
76.578
71.320
34.189
30.132
24.627
16.785
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

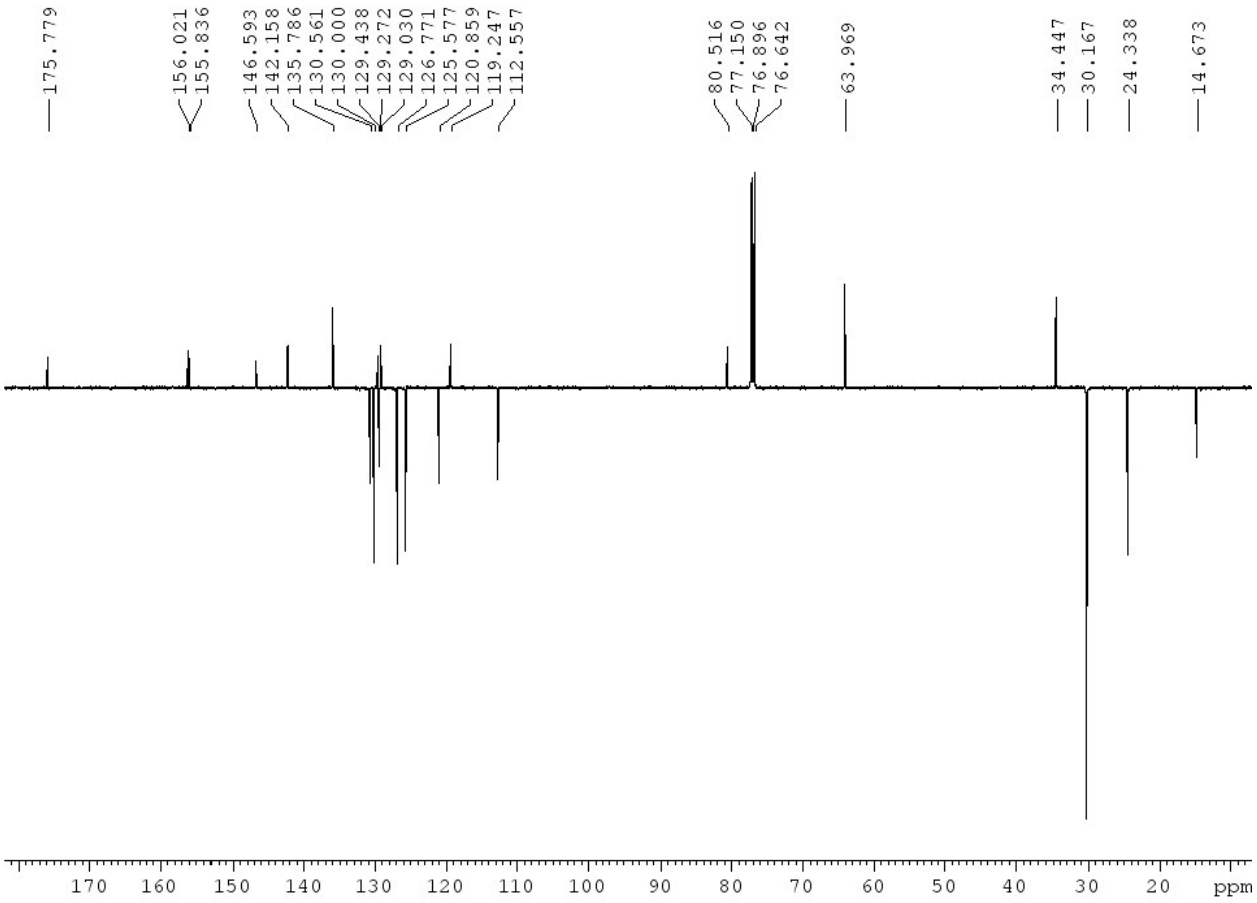

8.708
7.858
7.829
7.792
7.763
7.240
5.638
1.714
1.499
I
N
N
O
OH
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.000
2.049
2.088
0.961
6.096
18.158

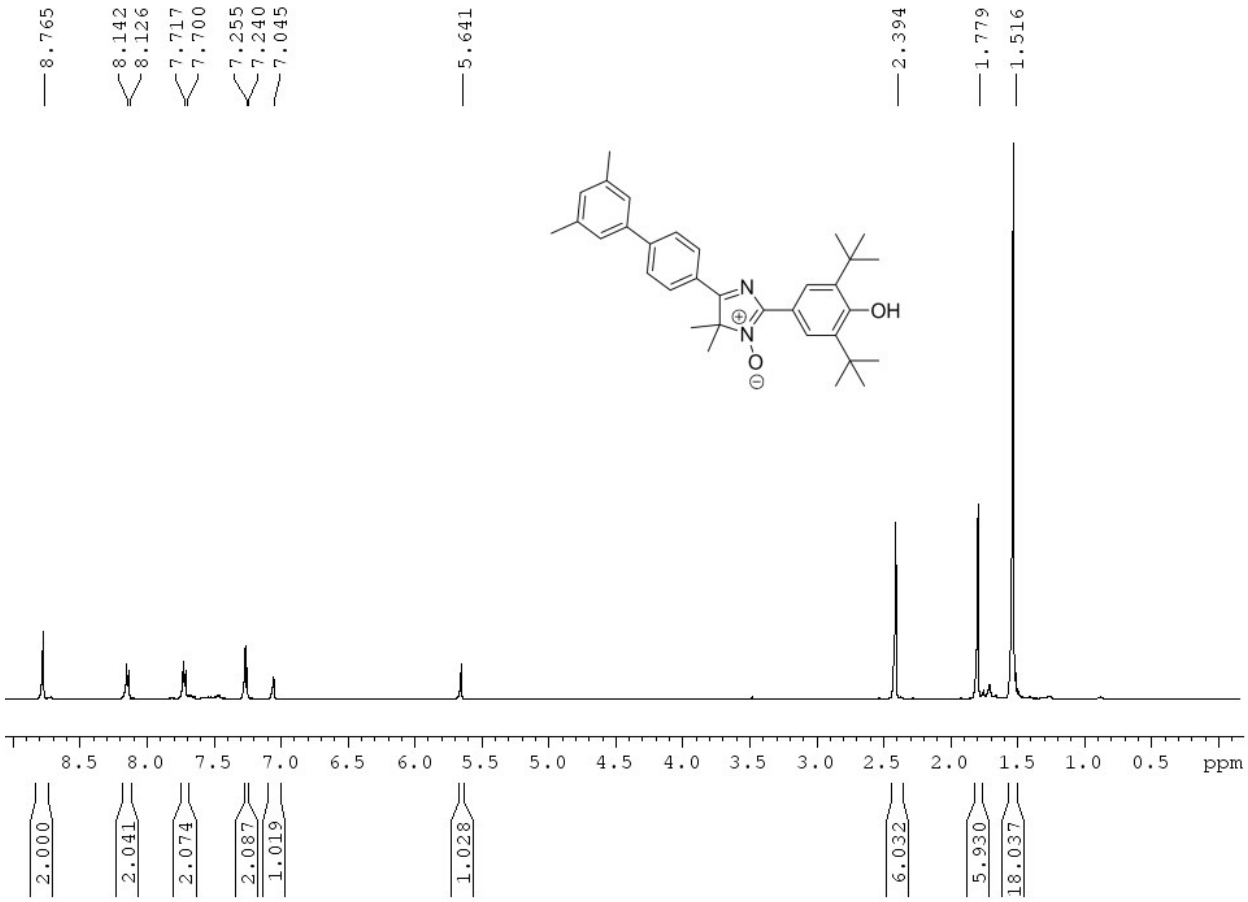

174.698
156.108
146.461
138.159
135.798
130.026
128.446
125.433
118.916
98.523
80.425
77.323
76.899
76.476
34.419
30.111
24.120
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

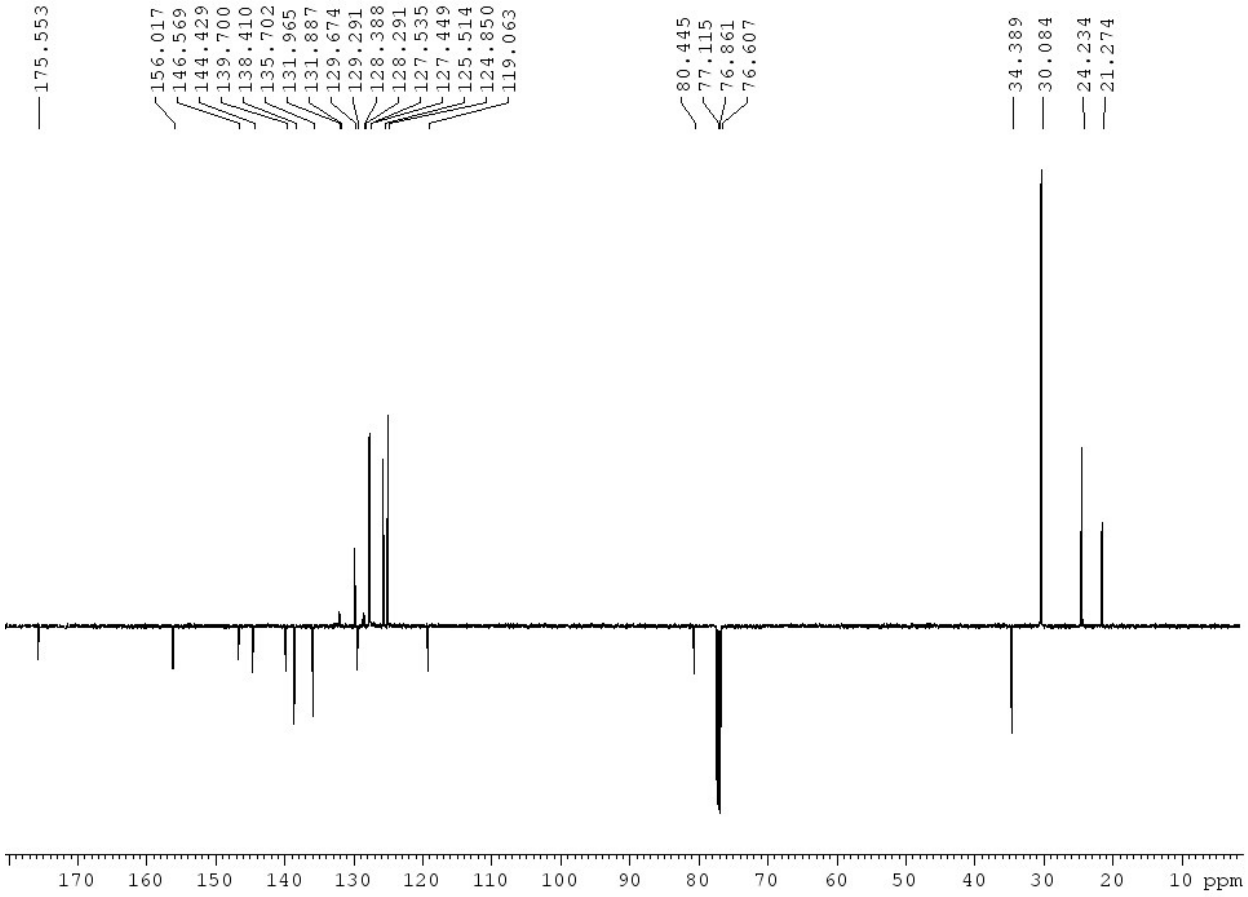

8.766
8.171
8.149
7.742
7.721
7.657
7.653
7.636
7.498
7.480
7.460
7.417
7.404
7.399
7.380
7.240
5.641
1.782
1.516
OH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.03
2.00
2.01
2.00
2.13
1.01
1.04
6.04
18.26

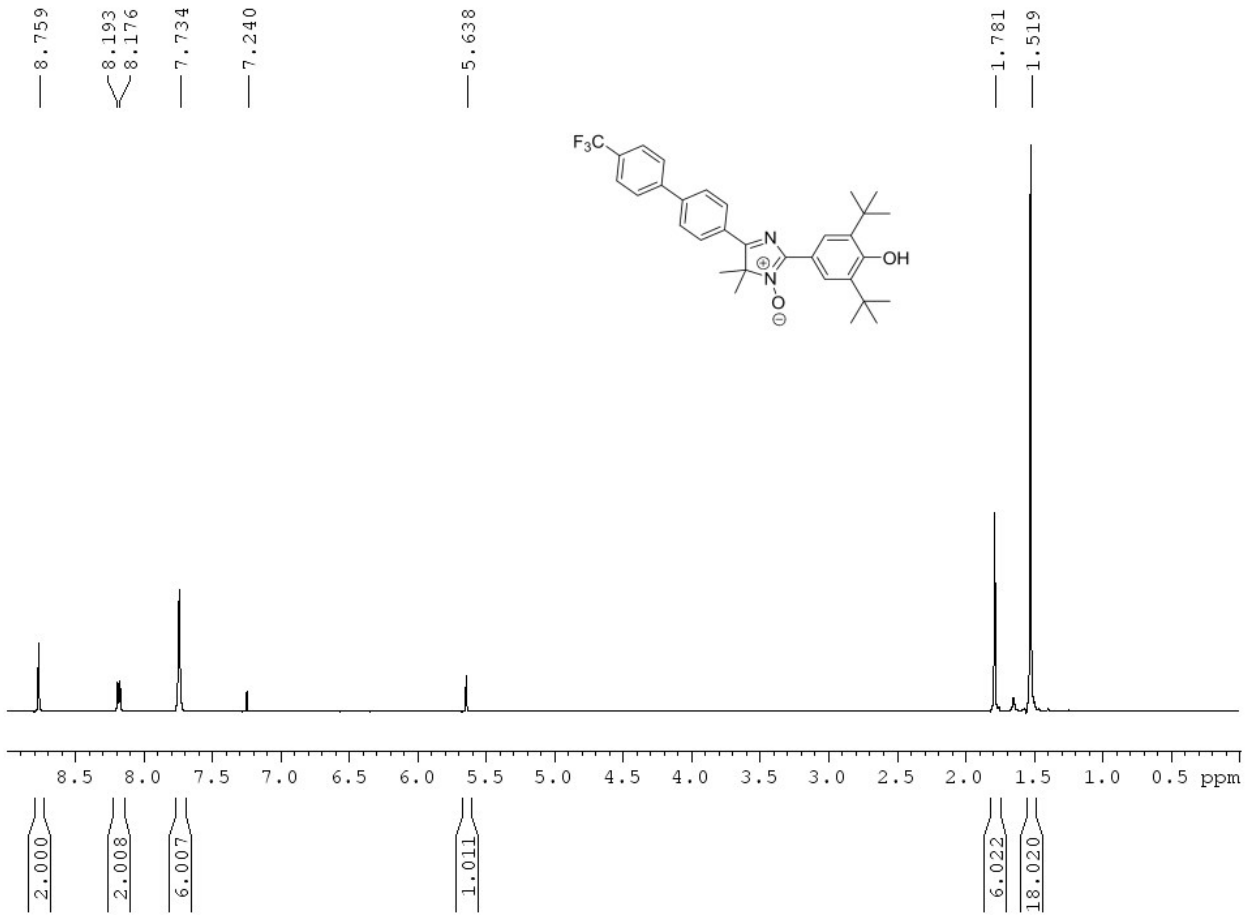

175.431
156.047
146.573
144.134
139.714
135.714
129.483
128.055
127.666
127.466
126.968
125.519
119.067
80.479
77.206
76.888
76.571
34.415
30.108
24.259
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

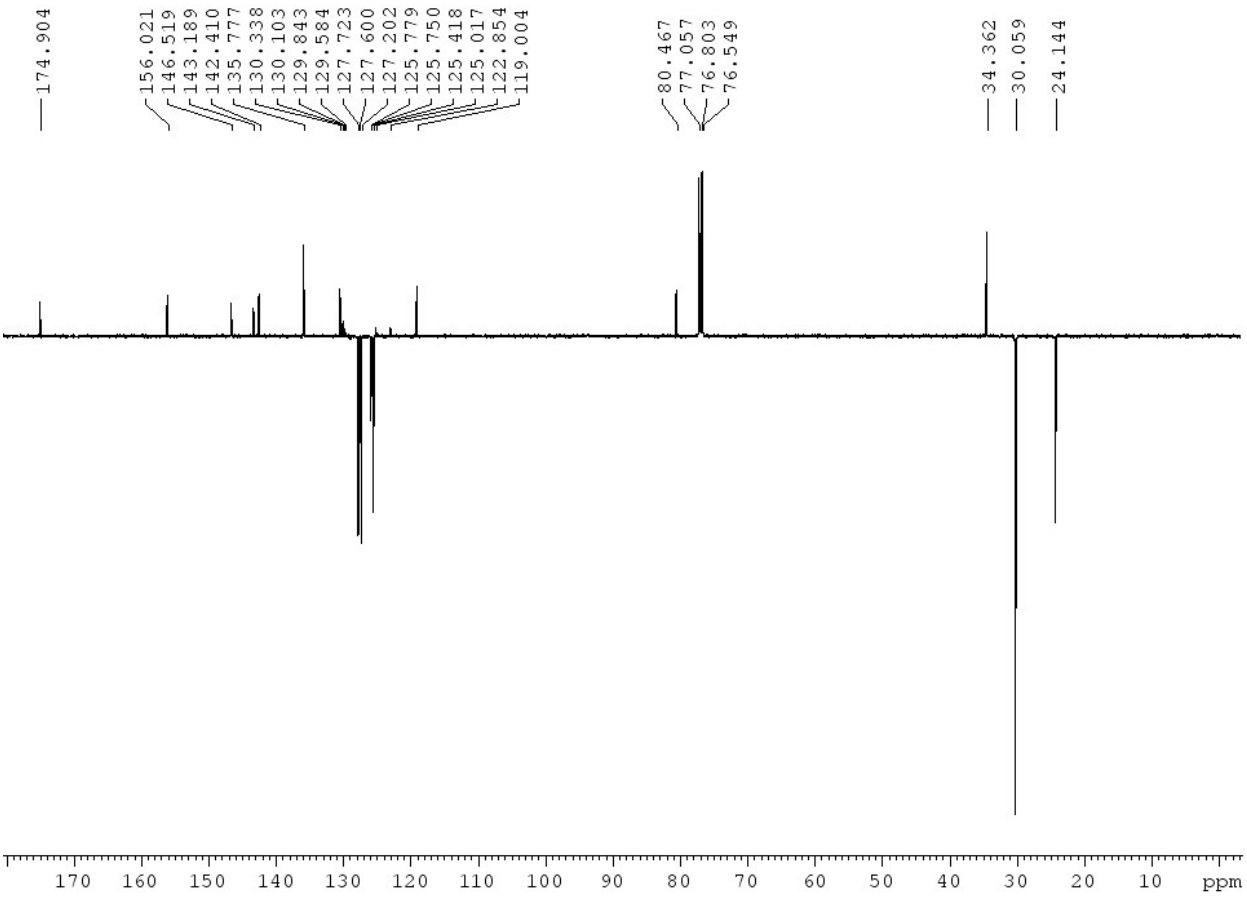

8.772
8.124
8.103
7.721
7.700
7.373
7.354
7.334
7.315
7.240
7.061
7.042
7.023
7.004
6.984
5.632
4.101
4.084
4.066
4.049
1.787
1.516
1.395
1.378
1.360
OH
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.03
2.02
2.02
2.01
1.01
2.02
6.03
18.01
3.06

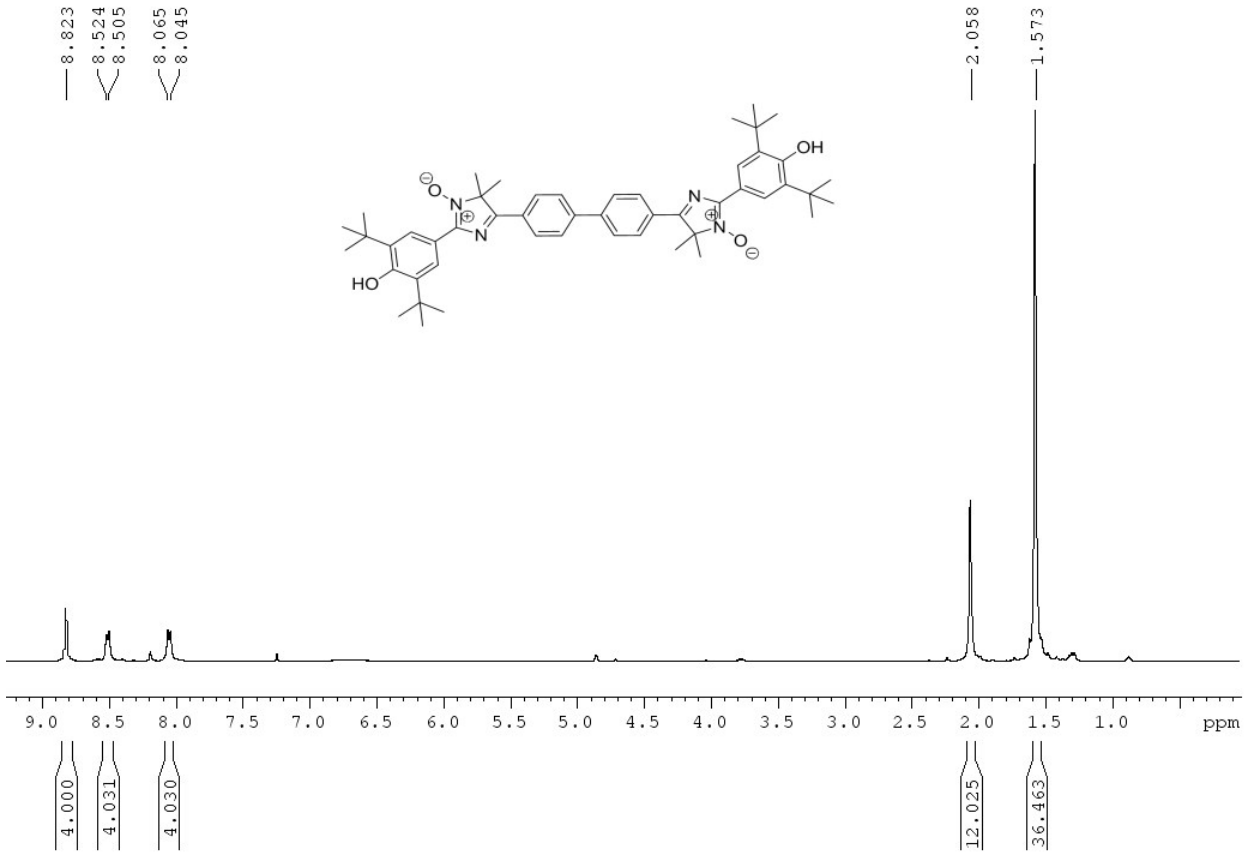

175.779
156.021
155.836
146.593
142.158
135.786
130.561
130.000
129.438
129.272
129.030
126.771
125.577
120.859
119.247
112.557
80.516
77.150
76.896
76.642
63.969
34.447
30.167
24.338
14.673
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

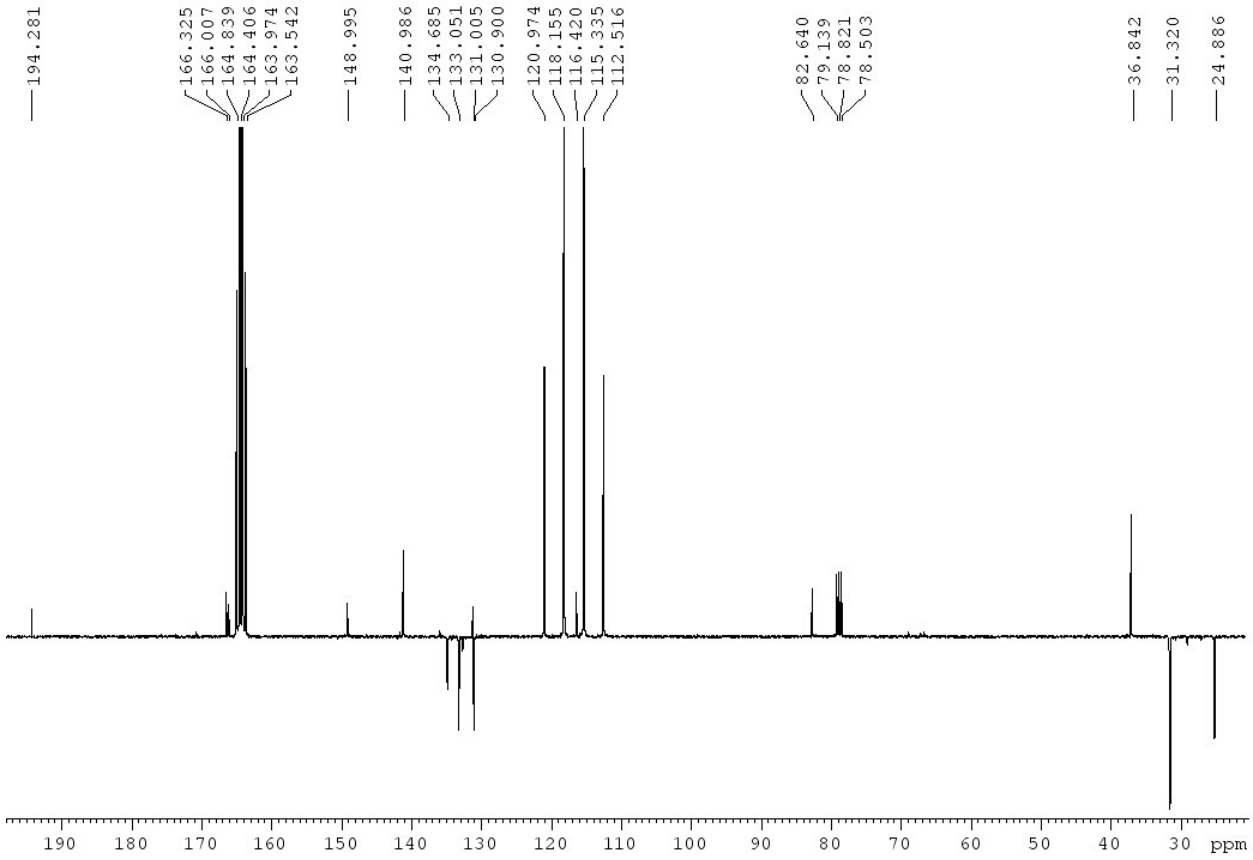

8.765
8.142
8.126
7.717
7.700
7.255
7.240
7.045
5.641
2.394
1.779
1.516
OH
N
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.000
2.041
2.074
2.087
1.019
1.028
6.032
5.930
18.037

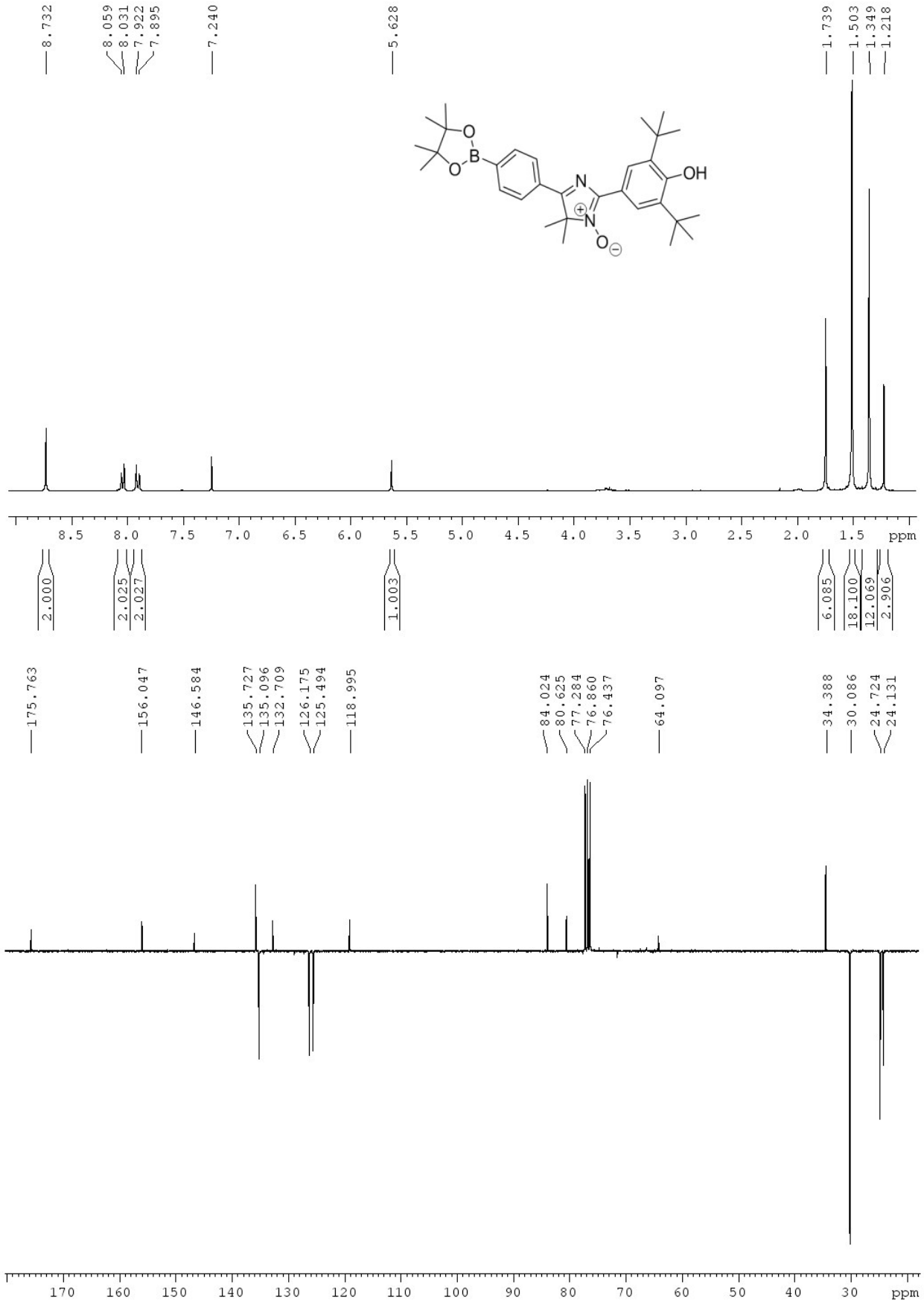

175.553
156.017
146.569
144.429
139.700
138.410
135.702
131.965
131.887
129.674
129.291
128.388
128.291
127.535
127.449
125.514
124.850
119.063
80.445
77.115
76.861
76.607
34.389
30.084
24.234
21.274
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

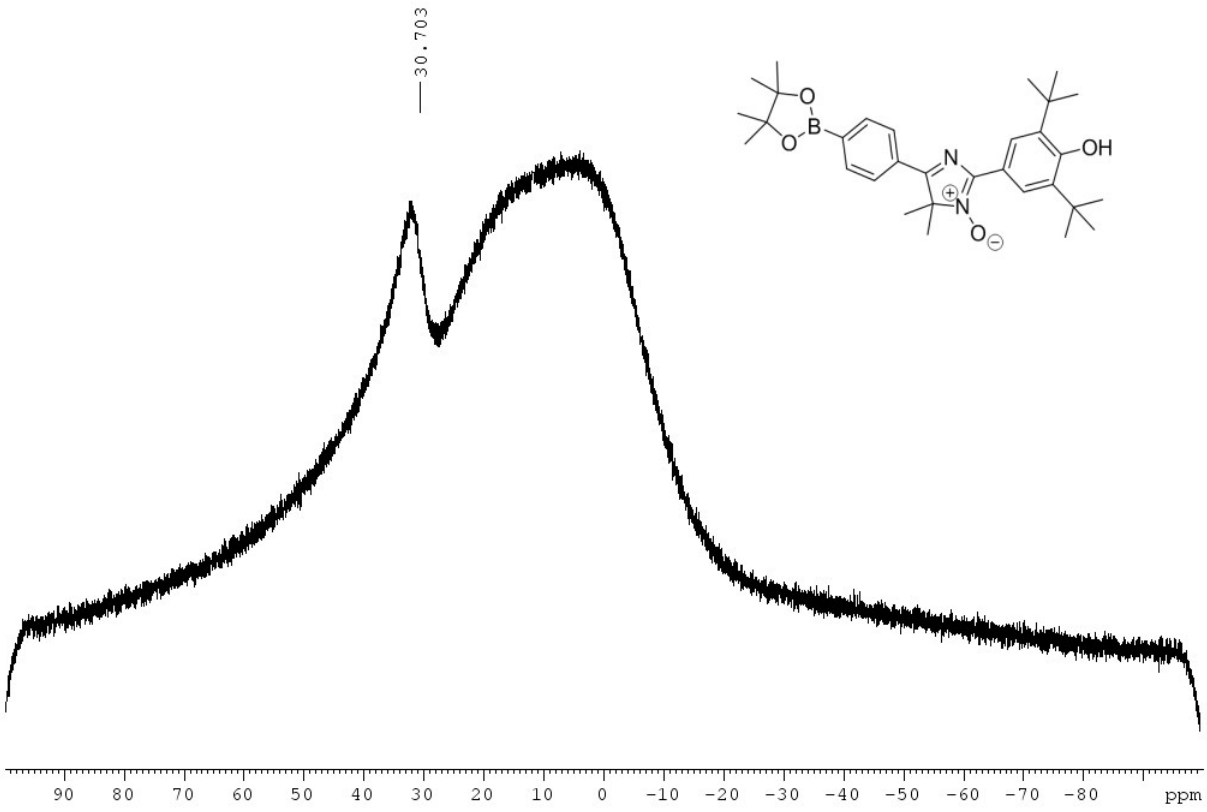

8.759
8.193
8.176
7.734
7.240
5.638
1.781
1.519
F3C
N
N
O
OH
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.000
2.008
6.007
1.011
6.022
18.020


174.904
156.021
146.519
143.189
142.410
135.777
130.338
130.103
129.843
129.584
127.723
127.600
127.202
125.779
125.750
125.418
125.017
122.854
119.004
80.467
77.057
76.803
76.549
34.362
30.059
24.144
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.823
8.524
8.505
8.065
8.045
2.058
1.573
OH
HO
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.000
4.031
4.030
12.025
36.463


194.281
166.325
166.007
164.839
164.406
163.974
163.542
148.995
140.986
134.685
133.051
131.005
130.900
120.974
118.155
116.420
115.335
112.516
82.640
79.139
78.821
78.503
36.842
31.320
24.886
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm


8.732
8.059
8.031
7.922
7.895
7.240
5.628
1.739
1.503
1.349
1.218
OH
ppm
2.000
2.025
2.027
1.003
6.085
18.100
12.069
2.906
175.763
156.047
146.584
135.727
135.096
132.709
126.175
125.494
118.995
84.024
80.625
77.284
76.860
76.437
64.097
34.388
30.086
24.724
24.131
ppm


30.703
O
B
O
N
N
O
OH
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm

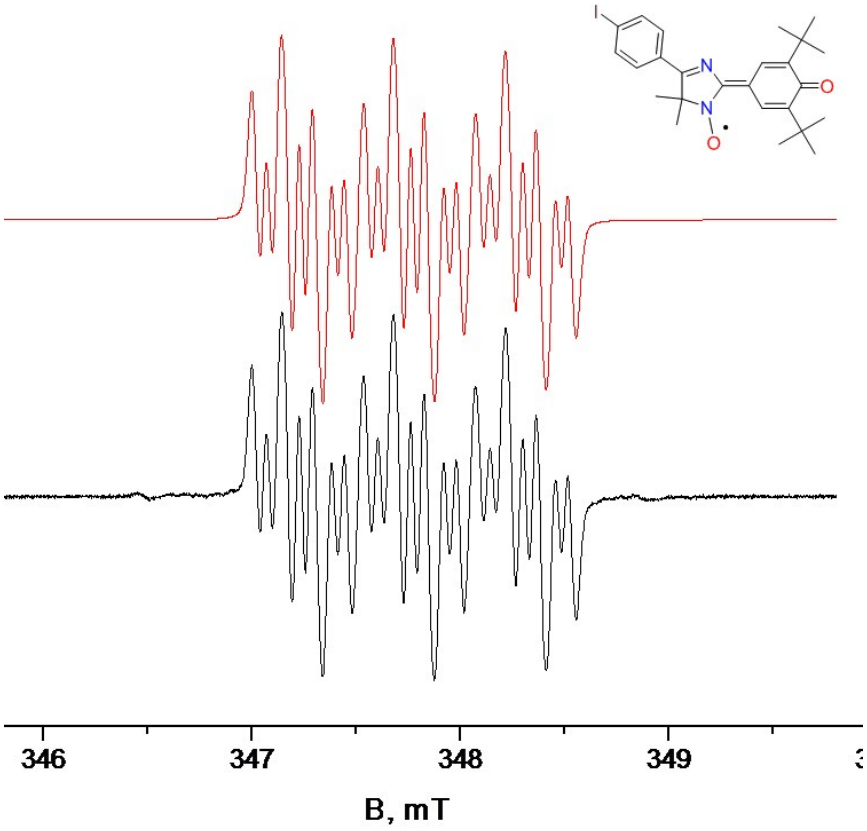


Fig. S1. ESR spectrum of iodo-substituted phenoxyl-nitroxide **8**, recorded at 20 °C in a degassed toluene; the black line is the experimental spectrum, the red line is its mathematical reconstruction.
g_{iso} = 2.0059, A_N = 0.536 mT, A_N = 0.061 mT, A_H = 0.163 mT, A_H = 0.150 mT

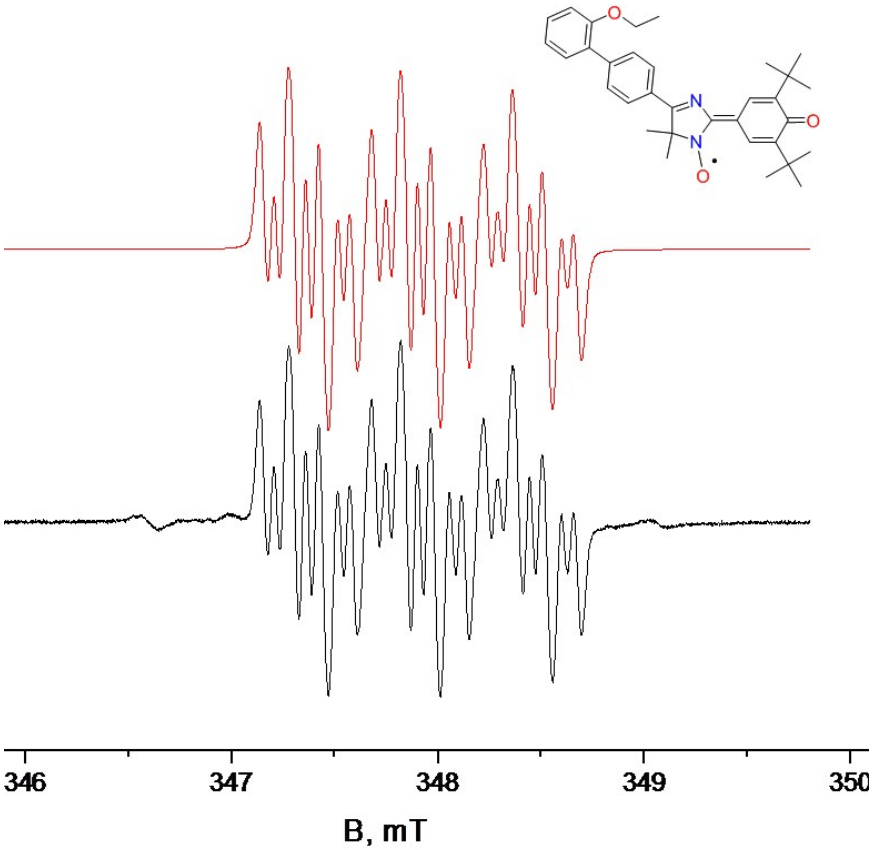


Fig. S2. ESR spectrum of hybrid radical **11b**, recorded at 20 °C in a degassed toluene;
g_{iso} = 2.0059, A_N = 0.542 mT, A_N = 0.060 mT, A_H = 0.160 mT, A_H = 0.148 mT

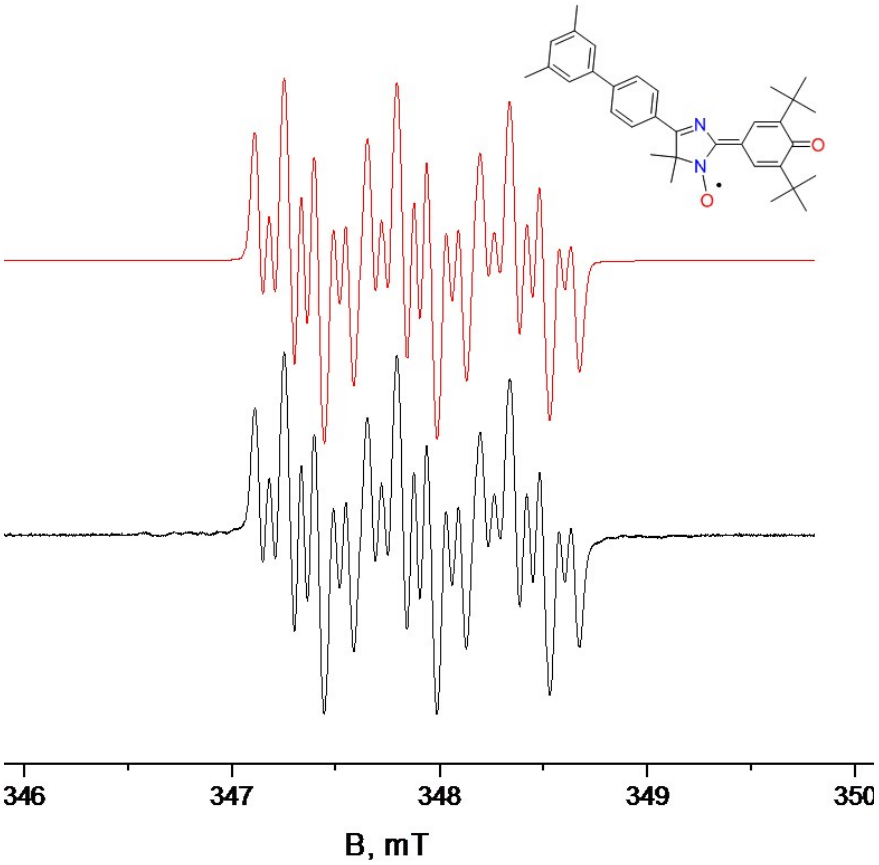


Fig. S3. ESR spectrum of hybrid radical **11c**, recorded at 20 °C in a degassed toluene; g_{iso} = 2.0059, A_N = 0.542 mT, A_N = 0.060 mT, A_H = 0.161 mT, A_H = 0.149 mT

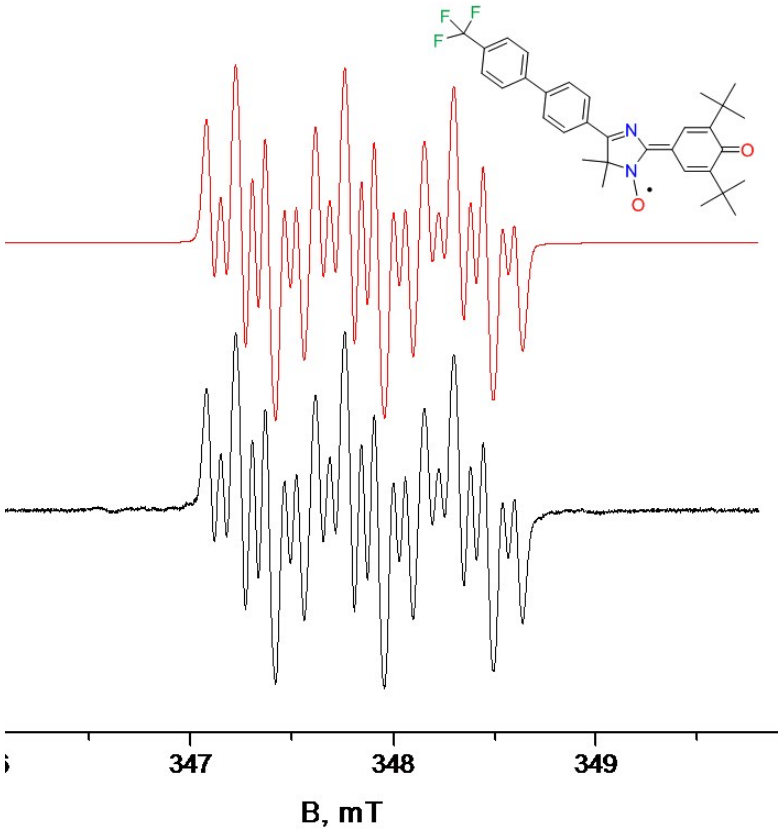
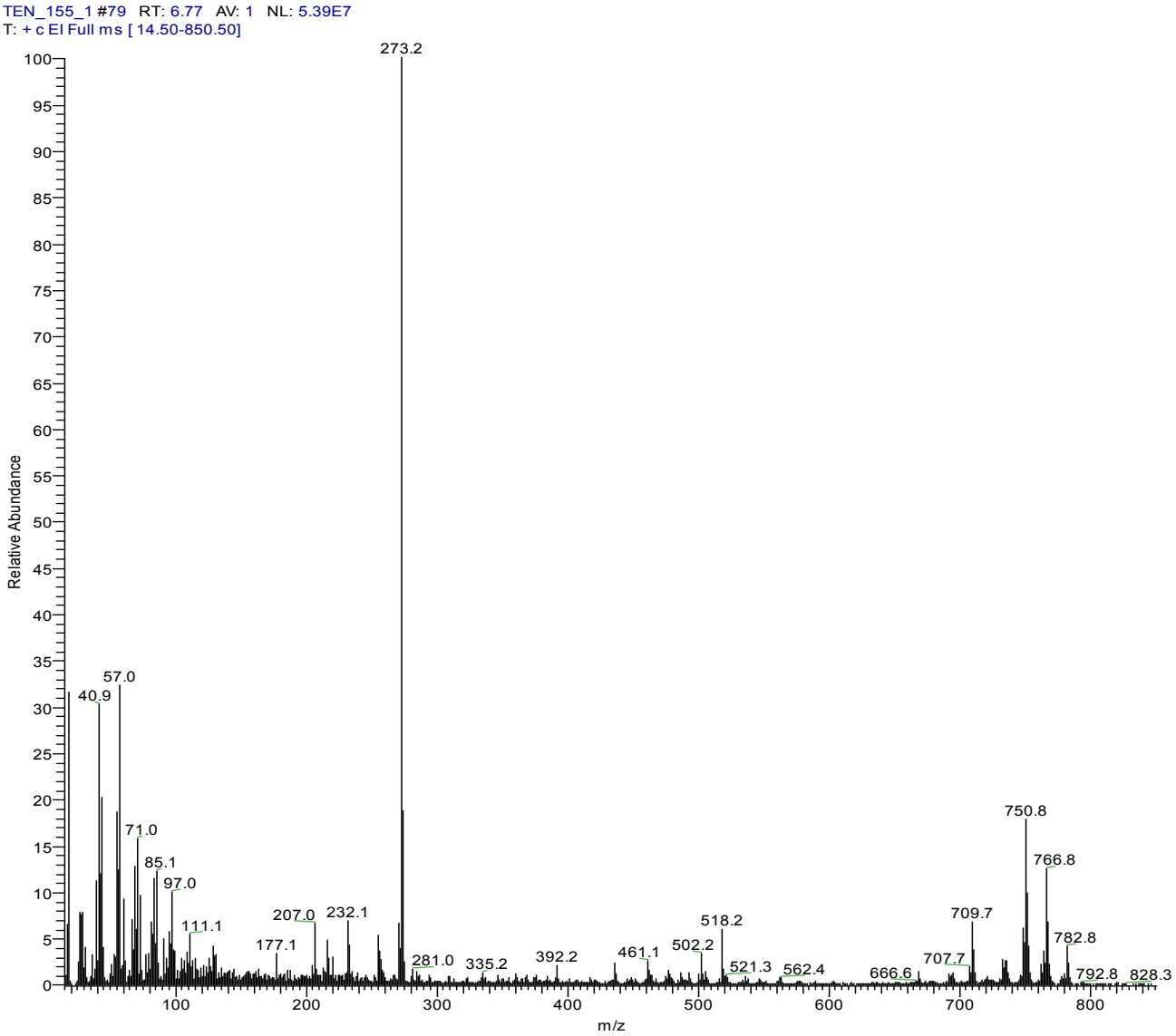


Fig. S4. ESR spectrum of hybrid radical **11d**, recorded at 20 °C in a degassed toluene; g_{iso} = 2.0059, A_N = 0.538 mT, A_N = 0.061 mT, A_H = 0.163 mT, A_H = 0.151 mT

Fig. S5. High resolution mass-spectrum of diradical **15**

T_{source} = 115˚C

T_{probe} = 320˚C



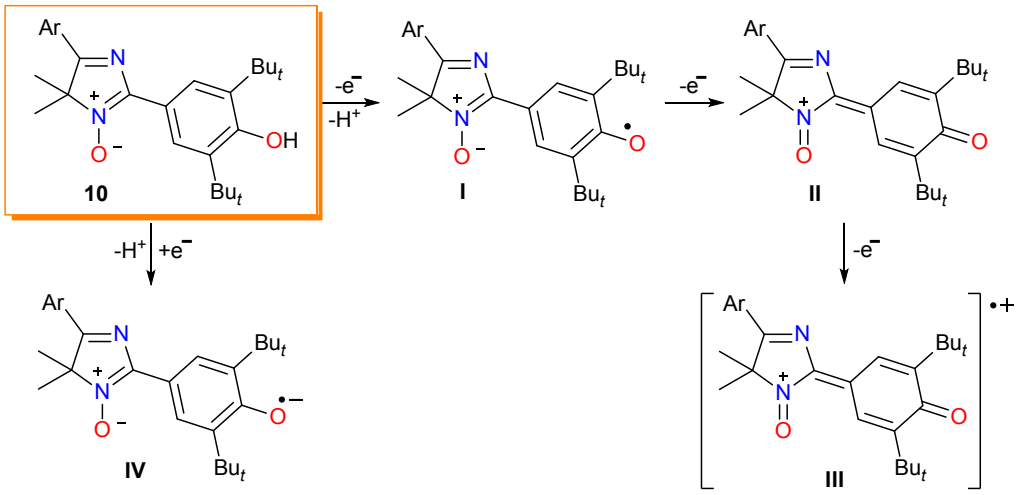
m/z	Intensity	Relative, %	m/z	Intensity	Relative, %
17.9	17006592.0	31.55	709.7	3589695.0	6.66
40.9	16285696.0	30.22	748.7	3304957.0	6.13
43.0	10874880.0	20.18	749.8	2444696.0	4.54
43.9	7640791.0	14.18	750.8	9628672.0	17.86
55.0	10024704.0	18.60	751.8	5287260.0	9.81
56.0	6618133.0	12.28	752.8	2217491.0	4.11
57.0	17448192.0	32.37	764.8	1948813.0	3.62
69.0	6873538.0	12.75	765.8	1208484.0	2.24
71.0	8475136.0	15.72	766.8	6710196.0	12.45
273.2	53899008.0	100.00	767.8	3654739.0	6.78
274.2	10070784.0	18.68	**782.8**	**2196376.0**	**4.07**
518.2	3219035.0	5.97	783.8	1253594.0	2.33

Calculated, $[M]^{+\cdot}$: m/z = 780.4609 $(C_{50}H_{60}N_4O_4)^{+\cdot}$

Calculated, $[M+2]^{+\cdot}$: m/z = 782.4766 $(C_{50}H_{62}N_4O_4)^{+\cdot}$

Found, : m/z = 782.4756 **$[M+2]^{+\cdot}$**

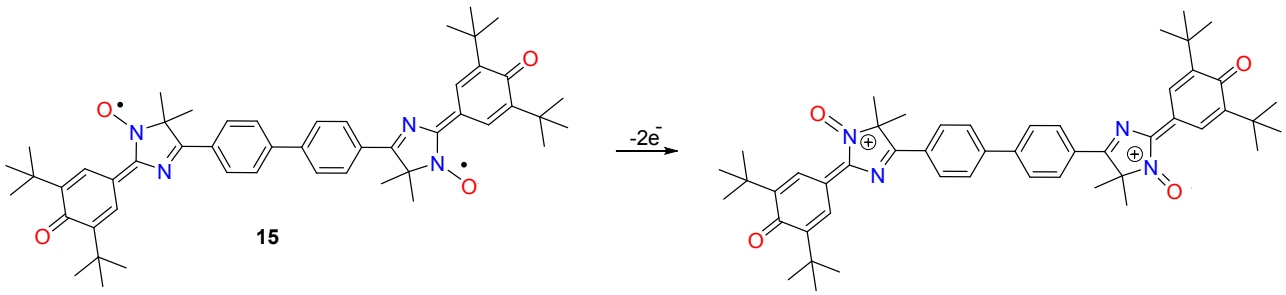
Cyclic voltammetry



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

Table S1. Oxidation and reduction potentials of 4*H*-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.