

Supplementary Materials

for the paper

“5-Aryl-2-(3,5-dialkyl-4-hydroxyphenyl)-4,4-dimethyl-4H-imidazole 3-Oxides and Their Redox Species: How Antioxidant Activity of 1-Hydroxy-2,5-dihydro-1H-imidazoles Correlates with the Stability of Hybrid Phenoxyl-Nitroxides”

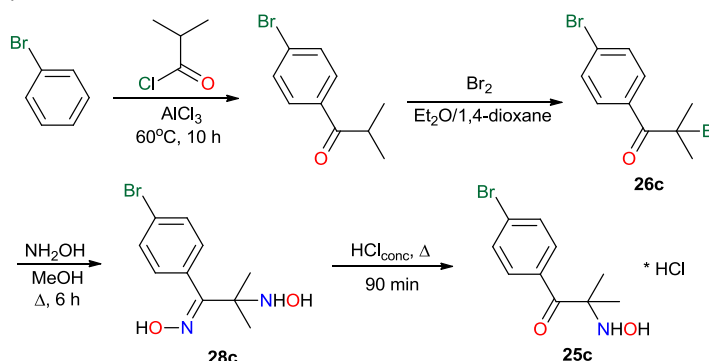
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Synthesis

Synthesis of 1-(4-bromophenyl)-2-(hydroxylamino)-2-methylpropan-1-one hydrochloride (**25c**×HCl) was carried out in four steps: 1) *Friedel-Crafts* acylation of bromobenzene by isobutyryl chloride [1]; 2) bromination of the obtained *para*-bromo-*isobutyrophenone*; 3) treatment of bromoketone **26c** with excess of hydroxylamine, followed by 4) acid catalyzed hydrolysis of 2-hydroxylaminooxime **28c**, according to Scheme S1.



Scheme S1. Preparation of 2-hydroxylamino ketone hydrochloride **25c**×HCl.

1-(4-Bromophenyl)-2-methylpropan-1-one. Freshly sublimed AlCl_3 (53.5 g, 0.4 mol) was added to the vigorously stirred warm (+30°C) mixture of bromobenzene (127 mL, 1.2 mol) and *iso*-butyryl chloride (50 mL, 0.475 mol) in five portions during 20 min, so as the temperature of the reaction mixture did not exceed +45°C. The slurry was warmed to 55–60°C and stirring was continued during 11 h. After cooling to ambient temperature, the reaction mass was poured into the mixture of concentrated HCl with ice (1/1, 300 mL). An organic layer was extracted by chloroform (3×50 mL),

washed with water (30 mL) and saturated aq NaHCO₃ (100 mL), dried over anhydrous Na₂SO₄ and evaporated. The residue was distilled in vacuo and three fractions were collected consequently: a) unreacted bromobenzene boiling at 40÷85°C, b) mixture of dibromobenzene and *iso*-butyrophenone boiling at 85÷115°C and c) the purposed product with b.p. 115÷134°C (8 mm). The latter fraction was redistilled in vacuo using short column, the yield 67% of 1-(4-bromophenyl)-2-methylpropan-1-one in terms of the catalyst was achieved.

Slightly yellowish oily liquid, total mass 60.6 g, b. p. 127÷132°C (8 mm). ¹H NMR spectrum of ketone was identical to that published in literature [2,3].

2-Bromo-1-(4-bromophenyl)-2-methylpropan-1-one (26c). Bromine (31.5 mL, 0.6 mol) was added dropwise to a stirred solution of 1-(4-bromophenyl)-2-methylpropan-1-one (136g, 0.6 mol) in a mixture of 300 ml of diethyl ether and 20 ml of 1,4-dioxane in such a rate that the next drop was added to the colorless solution. The mixture was stirred during 90 min and then cooled in an ice bath. Water (100 mL) and sodium bicarbonate (57 g, 0.6 mol) in small portions were added consequently to the solution. The organic layer was separated, the water layer was extracted with Et₂O (2×20 mL), combined ether extract was dried over MgSO₄, filtered through the thin layer of alumina and the solvent was evaporated giving bromoketone **26c**, which was used for the next step without further purification.

Pale-yellow viscous liquid (*caution – lacrimator!*), total mass 196.4 g (contains ~7% 1,4-dioxane as an admixture). ¹H NMR spectrum of a sample was identical to that published in literature [4].

(E)-1-(4-Bromophenyl)-2-(hydroxyamino)-2-methylpropan-1-one oxime (28c). A suspension of 104.18 g (1.50 mol) of hydroxylamine hydrochloride in 900 mL of methanol was heated until dissolution, then rapidly cooled and neutralized thoroughly in a cold bath with a solution of 50.50 g (1.26 mol) of NaOH in 75 mL of water. The precipitate of NaCl was filtered off and filtrate was mixed with a solution of 98.00 g (~0.30 mol) of 2-bromo-1-(4-bromophenyl)-2-methylpropan-1-one **26c** in 200 mL of MeOH followed by heating and refluxing of the mixture for 15 h. The methanol was removed under vacuum, the semi crystalline residue was triturated with 300 mL of water, and the precipitate of 2-hydroxylaminooxime **28c** was filtered, thoroughly washed with cold water and dried in air to constant weight.

Colorless powder, isolated yield 62.15 g (76%), mp 170–172 °C (MeOH). Elemental analysis: found: C, 44.16; H, 4.83; Br, 29.36; N, 10.09; calcd. for C₁₀H₁₃BrN₂O₂: C, 43.97; H, 4.80; Br, 29.26; N, 10.26%. ¹H NMR (500 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.11 (6H, s, (CH₃)₂); 5.17 (1H, br.s, NHOH); 7.13 (2H, AA'BB', *J* = 8.4, H_A: H-3,5 ArBr); 7.37 (1H, s, NHOH); 7.56 (2H, AA'BB', *J* = 8.4, H_B: H-2,6 ArBr); 10.64 (1H, s, C=NOH). ¹³C NMR (125 MHz, DMSO-*d*₆), δ, ppm: 23.6 (C-CH₃); 60.9 (C-CH₃); 121.1 (C-Br); 130.7, 130.9 (CH Ar); 133.2 (C-1 Ar); 160.5 (C=N).

1-(4-Bromophenyl)-2-(hydroxyamino)-2-methylpropan-1-one hydrochloride (25c×HCl). A mixture of 2-hydroxylamino oxime **28c** (13.60 g, 50 mmol) and 40 mL of conc. hydrochloric acid (ρ 1.18 g/mL) was refluxed during 50 min, then it was cooled until rt and kept for 16 h. The formed precipitate was filtered off, washed with 10 mL of hydrochloric acid and transferred into a flask filled with 60 mL of hydrochloric acid. The mixture was heated again until the complete crystals dissolution (10-15 min). After cooling and refrigeration of the mixture at 0 °C for 24 h, the formed precipitate of **25c×HCl** was filtered off, washed with cold acetonitrile (3×6 mL) and dried in air to constant weight.

Colorless crystals, isolated yield 12.80 g (84%), mp 168–172 °C (MeCN / EtOH, 3:1). Elemental analysis: found: C, 40.84; H, 4.41; Br, 27.00; Cl, 11.96; N, 4.94; calcd. for C₁₀H₁₃BrClNO₂: C 40.77; H 4.45; Br 27.13; Cl 12.04; N 4.75 %. ¹H NMR (500 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.64 (6H, s, (CH₃)₂); 7.71 (2H, AA'BB', *J* = 8.7, H_A: H-3,5 ArBr); 7.82 (2H, AA'BB', *J* = 8.7, H_B: H-2,6 ArBr); 10.92 (1H, br.s, N+H₂). ¹³C NMR (125 MHz, DMSO-*d*₆), δ, ppm: 20.5 (C-CH₃); 69.1 (C-CH₃); 127.8 (C-Br); 131.0, 132.2 (CH Ar); 132.9 (C-1 Ar); 198.2 (C=O).

Synthesis of 1-(4-fluorophenyl)-2-(hydroxyamino)-2-methylpropan-1-one hydrochloride (**25b×HCl**) from fluorobenzene was performed in a similar way.

Physicochemical, analytical and spectral data for compounds **23a,c-e**; **20a-s** and **21a-s**

4-Hydroxy-3,5-dimethylbenzaldehyde (23a). Colorless crystals, yield before crystallization 95%, m. p. 114-115°C (water-ethanol) (lit. m. p. 113-115°C [5]).

4-Hydroxy-3,5-diisopropylbenzaldehyde (23c). Colorless crystals, yield before crystallization 85%, m. p. 107-108°C (*i*-PrOH)(lit. m. p. 101-103°C (*i*-PrOH)[6]), ¹H and ¹³C NMR spectra were similar to those presented in literature [7].

3,5-Dicyclohexyl-4-hydroxybenzaldehyde (23d). Colorless crystals, yield after crystallization 94%, m. p. 175-176°C (benzene, decomp.)(lit. m.p. 175-176°C (PhH / petroleum ether) [8]). Elemental analysis: found: C, 79.60; H, 9.24; calcd. for C₁₉H₂₆O₂: C, 79.68; H, 9.15%. UV (EtOH), λ_{max}nm, (lg ε): 231 (4.26), 294 (4.18). ¹H NMR (500 MHz, CDCl₃), δ, ppm (*J*, Hz): 1.19-1.32 (2H, m, 2C₆H₁₁); 1.35-1.49 (8H, m, 2C₆H₁₁); 1.70-1.79 (2H, m, 2C₆H₁₁); 1.80-1.94 (8H, m, 2C₆H₁₁); 2.72-2.82 (2H, m, Ar-CH-(CH₂)₅); 5.86 (1H, br.s, OH); 7.58 (2H, s, H-2,6); 9.82 (1H, s, CHO). ¹³C NMR (125 MHz, CDCl₃), δ, ppm: 26.0, 26.7, 32.9 (3 CH₂); 37.3 (CH-C=C); 126.6 (CH Ar); 129.5 (C Ar); 133.5 (C Ar); 155.9 (C-OH Ar); 191.8 (CHO).

3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde (23e). Colorless crystals, yield after crystallization 80%, m. p. 190°C (PhMe)(lit. m. p. 189 °C (PhMe)), ¹H NMR spectrum was similar to that presented in literature [9].

2-(4-Hydroxy-3,5-dimethylphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydro-1H-imidazol-1-ol (20a). Colorless powder, yield 1.62 g (87%), m.p. 198-202 °C (EtOH, dec.). Elemental analysis: found: C, 73.52; H, 7.24; N, 9.02; calcd. for C₁₉H₂₂N₂O₂: C, 73.52; H, 7.14; N, 9.03%. IR-spectrum, ν, cm⁻¹, (KBr): 3248 (OH), 2979, 2935 (CH), 1602 (C=N), 1488, 1215, 1157. ¹H NMR (300 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.37 (3H, s, 5-CH₃); 1.39 (3H, s, 5-CH₃); 2.19 (6H, s, 3,5-CH₃ Ar); 5.31 (1H, s, H-2); 7.00 (2H, s, H-2,6 Ar); 7.42-7.53 (3H, m, Ph); 7.75 (1H, s, N-OH); 7.81-7.87 (2H, m, Ph); 8.14 (1H, s, Ar-OH). ¹³C NMR (75 MHz, DMSO-*d*₆), δ, ppm: 16.5 (5-CH₃); 16.7 (Ar-CH₃); 25.4 (5-CH₃); 70.4 (C-5); 89.3 (C-2); 123.5 (CH₃-C Ar); 127.4; 127.9; 128.5; 130.4 (CH (Ar + Ph)); 131.3; 133.0 (C(Ar)-Het and C(Ph)-Het); 152.7 (C-OH); 175.4 (C-4).

2-(3-Cyclohexyl-4-hydroxy-5-methylphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydro-1H-imidazol-1-ol (20b). Colorless powder, yield 1.97 g (87%), m.p. 190-192 °C (MeOH, dec.). Elemental analysis: found: C, 75.85; H, 7.97; N, 7.00; calcd. for C₂₄H₃₀N₂O₂: C, 76.16; H, 7.99; N, 7.40%. IR-spectrum, ν, cm⁻¹, (KBr): 3234 (OH), 2928, 2851 (CH), 1595 (C=N), 1446, 1221, 1158. ¹H NMR (300 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.17-1.48 (5H, m, C₆H₁₁); 1.38 (3H, s, 5-CH₃); 1.40 (3H, s, 5-CH₃); 1.66-1.85 (5H, m, C₆H₁₁); 2.21 (3H, s, 5-CH₃ Ar); 2.89-3.01 (1H, m, Ar-CH-(CH₂)₅); 5.35 (1H, s, H-2); 7.01 (1H, s, H-6 Ar); 7.07 (1H, s, H-2 Ar); 7.42-7.54 (3H, m, Ph); 7.79 (1H, s, N-OH); 7.82-7.88 (2H, m, Ph); 8.07 (1H, s, Ar-OH). ¹³C NMR (75 MHz, DMSO-*d*₆), δ, ppm: 16.5 (5-CH₃); 17.0 (Ar-CH₃); 25.4 (5-CH₃); 25.9; 26.7; 33.0 (3 CH₂); 36.5 (CH in C₆H₁₁); 70.5 (C-5); 89.5 (C-2); 123.8 (CH₃-C Ar); 123.9; 127.4; 128.5; 130.4 (CH (Ar + Ph)); 131.5; 133.0; 133.5 (C(Ar)-Het, C(Ar)-C₆H₁₁ and C(Ph)-Het); 151.6 (C-OH); 175.5 (C-4).

2-(4-Hydroxy-3,5-diisopropylphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydro-1H-imidazol-1-ol (20c). Colorless plates, yield 1.65 g (75%), m.p. 209-210 °C (MeOH, dec.). Elemental analysis: found: C, 75.31; H, 8.22; N, 7.63; calcd. for C₂₃H₃₀N₂O₂: C, 75.37; H, 8.25; N, 7.64%. IR-spectrum, ν, cm⁻¹, (KBr): 3282 (OH), 2964, 2871 (CH), 1591 (C=N), 1570, 1461, 1282. ¹H NMR (300 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.18 (12H, d, *J* = 6.9, CH₃-CH-CH₃); 1.40 (6H, s, 5-CH₃); 3.33 (2H, sept., *J* = 6.9, CH₃-CH-CH₃); 5.38 (1H, s, H-2); 7.09 (2H, s, H-2,6 Ar); 7.43-7.53 (3H, m, Ph); 7.81 (1H, s, N-OH); 7.82-7.88 (2H, m, Ph); 8.00 (1H, s, Ar-OH). ¹³C NMR (75 MHz, DMSO-*d*₆), δ, ppm: 16.6 (5-CH₃); 23.1 (Ar-CH-CH₃); 25.4 (5-CH₃); 26.3 (Ar-CH-CH₃); 70.6 (C-5); 89.7 (C-2); 122.7 (CH Ar), 127.4; 128.6; 130.4 (CH Ph); 131.9; 133.1 (C(Ar)-Het and C(Ph)-Het); 134.5 (C(Ar)-CH-CH₃); 150.3 (C-OH); 175.5 (C-4).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydro-1H-imidazol-1-ol (20d). Faint yellow powder, yield 2.45 g (91%), m.p. 223-225 °C (MeCN, dec.). Elemental analysis: found: C, 78.01; H, 8.54; N, 6.34; calcd. for $C_{29}H_{38}N_2O_2$: C, 77.99; H, 8.58; N, 6.27%. IR-spectrum, ν , cm^{-1} (KBr): 3285 (OH), 2930, 2850 (CH), 1592 (C=N), 1566, 1448. 1H NMR (400 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.29-1.53 (10H, m, C_6H_{11}); 1.37 (3H, s, 5- CH_3); 1.39 (3H, s, 5- CH_3); 1.65-1.79 (10H, m, C_6H_{11}); 2.91-2.98 (2H, m, Ar-CH-(CH_2) $_5$); 5.34 (1H, s, H-2); 7.03 (2H, s, H-2,6 Ar); 7.44-7.52 (3H, m, Ph); 7.79 (1H, s, N-OH); 7.83-7.87 (2H, m, Ph); 7.93 (1H, s, Ar-OH).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydro-1H-imidazol-1-ol (20e). Colorless powder, yield 1.85 g (78%), m.p. 200-202 °C (EtOH, dec.). Elemental analysis: found: C, 76.17; H, 8.58; N, 7.14; calcd. for $C_{25}H_{34}N_2O_2$: C, 76.10; H, 8.69; N, 7.10%. IR-spectrum, ν , cm^{-1} (KBr): 3435 (OH), 2964 (CH), 1603 (C=N), 1575, 1435, 1365, 1239. 1H NMR (300 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.39 (3H, s, 5- CH_3); 1.41 (21H, s, 5- CH_3 and 2 *t*-Bu); 5.37 (1H, s, H-2); 6.89 (1H, s, Ar-OH); 7.21 (2H, s, H-2,6 Ar); 7.41-7.54 (3H, m, Ph); 7.79-7.87 (2H, m, Ph); 7.81 (1H, s, N-OH). ^{13}C NMR (75 MHz, DMSO- d_6), δ , ppm: 16.6 (5- CH_3); 25.5 (5- CH_3); 30.4 ($C(CH_3)_3$); 34.5 ($C(CH_3)_3$); 70.5 (C-5); 89.8 (C-2); 124.2 (CH Ar); 127.4; 128.6; 130.5 (CH Ph); 131.8; 133.1 (C(Ar)-Het and C(Ph)-Het); 138.5 (C(Ar)-*t*-Bu); 153.5 (C-OH); 175.7 (C-4).

4-(4-Fluorophenyl)-2-(4-hydroxy-3,5-dimethylphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20f). Colorless powder, yield 1.71 g (87%), m.p. 198-202 °C (80% EtOH, dec.). Elemental analysis: found: C, 69.23; H, 6.77; F, 5.95; N, 8.21; calcd. for $C_{19}H_{21}FN_2O_2$: C, 69.49; H, 6.45; F, 5.79; N, 8.53%. IR-spectrum, ν , cm^{-1} (KBr): 3469, 3241 (OH), 2939 (CH), 1606 (C=N), 1511, 1222, 1155. 1H NMR (400 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.35 (3H, s, 5- CH_3); 1.38 (3H, s, 5- CH_3); 2.18 (6H, s, 3,5- CH_3 Ar); 5.29 (1H, s, H-2); 6.99 (2H, s, H-2,6 ArOH); 7.28 (2H, ddd, $^3J_{HF}$ = 8.0, 3J = 7.5, 4J = 1.5, H-3',5' ArF); 7.76 (1H, s, N-OH); 7.90 (2H, ddd, 3J = 7.5, $^4J_{HF}$ = 5.0, 4J = 1.5, H-2',6' ArF); 8.14 (1H, s, Ar-OH).

2-(3-Cyclohexyl-4-hydroxy-5-methylphenyl)-4-(4-fluorophenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20g). Light yellow microcrystals, yield 2.16 g (91%), m.p. 184-185 °C (MeOH, dec.). Elemental analysis: found: C, 73.02; H, 7.26; F, 4.86; N, 7.19; calcd. for $C_{24}H_{29}FN_2O_2$: C, 72.70; H, 7.37; F, 4.79; N, 7.07. IR-spectrum, ν , cm^{-1} (KBr): 3257 (OH), 2926, 2852 (CH), 1606 (C=N), 1513, 1237, 1156. 1H NMR (300 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.18-1.45 (5H, m, C_6H_{11}); 1.36 (3H, s, 5- CH_3); 1.40 (3H, s, 5- CH_3); 1.67-1.87 (5H, m, C_6H_{11}); 2.20 (3H, s, 5- CH_3 Ar); 2.88-3.02 (1H, m, Ar-CH-(CH_2) $_5$); 5.33 (1H, s, 2-H); 6.99 (1H, d, 4J = 1.5, H-6' ArOH); 7.05 (1H, d, 4J = 1.5, H-2' ArOH); 7.28 (2H, ddd, $^3J_{HF}$ = 8.0, 3J = 7.5, 4J = 1.5, H-3',5' ArF); 7.79 (1H, s, N-OH); 7.91 (2H, ddd, 3J = 7.5, $^4J_{HF}$ = 5.0, 4J = 1.5, H-2',6' ArF); 8.02 (1H, s, Ar-OH). ^{13}C NMR (75 MHz, DMSO- d_6), δ , ppm: 16.2 (5- CH_3); 16.8 (Ar- CH_3); 25.1 (5- CH_3); 25.7; 26.5; 32.8; 32.9 (4 CH_2); 36.4 (CH in C_6H_{11}); 70.2 (C-5); 89.3 (C-2); 115.3 (d, $^2J_{CF}$ = 21.5, C-3',5' ArF); 123.6 (C-6'(2') ArOH); 123.6 (Me-C ArOH); 127.2 (C-2'(6') ArOH); 129.2 (d, $^4J_{CF}$ = 3.0, C-1' ArF); 129.7 (d, $^3J_{CF}$ = 8.6, C-2',6' ArF); 131.3 (C-5'(1') ArOH); 133.3 (C-1'(5') ArOH); 151.4 (C-OH); 163.2 (d $^1J_{CF}$ = 247, C-4' ArF); 174.1 (C-4).

4-(4-Fluorophenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20h). Colorless powder, yield 1.95 g (85%), m.p. 175-177 °C (MeOH, dec.). Elemental analysis: found: C, 72.11; H, 7.55; F, 5.21; N, 7.35; calcd. for $C_{23}H_{29}FN_2O_2$: C, 71.85; H, 7.60; F, 4.94; N, 7.29%. IR-spectrum, ν , cm^{-1} (KBr): 3283 (OH), 2964, 2870 (CH), 1606 (C=N), 1512, 1470, 1236, 1157. 1H NMR (300 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.17 (12H, d, J = 6.8, CH_3 -CH- CH_3); 1.37 (3H, s, 5- CH_3); 1.39 (3H, s, 5- CH_3); 3.32 (2H, septet, J = 6.8, CH_3 -CH- CH_3); 5.35 (1H, s, H-2); 7.06 (2H, s, H-2,6 ArOH); 7.29 (2H, ddd, $^3J_{HF}$ = 8.0, 3J = 7.5, 4J = 1.5, H-3',5' ArF); 7.81 (1H, s, N-OH); 7.91 (2H, ddd, 3J = 7.5, $^4J_{HF}$ = 5.0, 4J = 1.5, H-2',6' ArF); 7.99 (1H, s, Ar-OH).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-4-(4-fluorophenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20i). Faint yellow crystals, yield 2.28 g (82%), m.p. 199-203 °C (MeOH, dec.). Elemental analysis: found: C, 74.60; H, 7.84; F, 4.27; N, 6.10; calcd. for $C_{29}H_{37}FN_2O_2$: C, 74.97; H, 8.03; F, 4.09; N, 6.03%. IR-

spectrum, ν , cm^{-1} , (KBr): 3310 (OH), 2928, 2852 (CH), 1606 (C=N), 1513, 1465, 1237. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ , ppm (J , Hz): 1.15-1.48 (10H, m, C_6H_{11}); 1.36 (3H, s, 5- CH_3); 1.40 (3H, s, 5- CH_3); 1.67-1.85 (10H, m, C_6H_{11}); 2.89-3.02 (2H, m, Ar-CH-(CH_2)₅); 5.34 (1H, s, H-2); 7.03 (2H, s, H-2,6 ArOH); 7.29 (2H, ddd, $^3J_{\text{HF}} = 8.0$, $^3J = 7.5$, $^4J = 1.5$, H-3',5' ArF); 7.81 (1H, s, N-OH); 7.91 (2H, ddd, $^3J = 7.5$, $^4J_{\text{HF}} = 5.0$, $^4J = 1.5$, H-2',6' ArF); 7.91 (1H, s, Ar-OH). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$), δ , ppm: 16.4 (5- CH_3); 25.4 (5- CH_3); 25.9; 26.6; 33.1; 33.2 (4 CH_2); 36.5 (CH in C_6H_{11}); 70.5 (C-5); 89.7 (C-2); 115.6 (d, $^2J_{\text{CF}} = 21.5$, C-3',5' ArF); 123.2 (C-2',6' ArOH); 129.5 (d, $^4J_{\text{CF}} = 2.9$, C-1' ArF); 129.9 (d, $^3J_{\text{CF}} = 8.6$, C-2',6' ArF); 131.7 (C-1' ArOH); 133.8 (C-3',5' ArOH); 150.3 (C-OH); 163.4 (d, $^1J_{\text{CF}} = 247$, C-4' ArF); 174.4 (C-4).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-(4-fluorophenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20j). Colorless crystals, yield 1.88 g (76%), m.p. 185-190 °C (EtOH, dec.). Elemental analysis: found: C, 72.83; H, 7.95; F, 4.63; N, 6.44; calcd. for $\text{C}_{25}\text{H}_{33}\text{FN}_2\text{O}_2$: C, 72.79; H, 8.06; F, 4.61; N, 6.79%. IR-spectrum, ν , cm^{-1} , (KBr): 3620, 3419, 3264, (OH), 2959 (CH), 1608 (C=N), 1512, 1438, 1235. ^1H NMR (300 MHz, $\text{DMSO-}d_6$), δ , ppm (J , Hz): 1.37 (3H, s, 5- CH_3); 1.38 (3H, s, 5- CH_3); 1.41 (18H, s, *t*-Bu); 5.34 (1H, s, H-2); 6.88 (1H, s, Ar-OH); 7.19 (2H, s, H-2,6 ArOH); 7.30 (2H, ddd, $^3J_{\text{HF}} = 8.0$, $^3J = 7.5$, $^4J = 1.5$, H-3',5' ArF); 7.81 (1H, s, N-OH); 7.91 (2H, ddd, $^3J = 7.5$, $^4J_{\text{HF}} = 5.0$, $^4J = 1.5$, H-2',6' ArF). ^{13}C NMR (75 MHz, $\text{DMSO-}d_6$), δ , ppm: 16.4 (5- CH_3); 25.4 (5- CH_3); 30.4 (C(CH_3)₃); 34.5 (C(CH_3)₃); 70.4 (C-5); 89.7 (C-2); 115.6 (d, $^2J_{\text{CF}} = 21.5$, C-3',5' ArF); 124.2 (C-2',6' ArOH); 129.4 (d, $^4J_{\text{CF}} = 3.0$, C-1' ArF); 129.8 (d, $^3J_{\text{CF}} = 8.6$, C-2',6' ArF); 131.7 (C-1' ArOH); 138.5 (C-3',5' ArOH); 153.5 (C-OH); 163.4 (d, $^1J_{\text{CF}} = 247$, C-4' ArF); 174.6 (C-4).

4-(4-Bromophenyl)-2-(4-hydroxy-3,5-dimethylphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20k). Colorless fine crystals, yield 2.28 g (98%), m.p. 204-205 °C (MeOH, dec.). Elemental analysis: found: C, 58.70; H, 5.28; Br, 20.70; N, 7.23; calcd. for $\text{C}_{19}\text{H}_{21}\text{BrN}_2\text{O}_2$: C, 58.62; H, 5.44; Br, 20.53; N, 7.20%. IR-spectrum, ν , cm^{-1} , (KBr): 3248 (OH), 2984, 2935 (CH), 1602 (C=N), 1489, 1210, 1157. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ , ppm (J , Hz): 1.34 (3H, s, 5- CH_3); 1.37 (3H, s, 5- CH_3); 2.18 (6H, s, 3,5- CH_3 Ar); 5.29 (1H, s, H-2); 6.99 (2H, s, H-2,6 ArOH); 7.65 (2H, AA'BB', $J = 8.5$, H_A: H-3',5' ArBr); 7.77 (2H, AA'BB', $J = 8.5$, H_B: H-2',6' ArBr); 7.78 (1H, s, N-OH); 8.18 (1H, s, Ar-OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$), δ , ppm: 16.5 (5- CH_3); 16.8 (Ar- CH_3); 25.2 (5- CH_3); 70.4 (C-5); 89.3 (C-2); 123.5 (CH₃-C Ar); 124.2 (C-Br); 127.9; 129.6; 131.7 (CH ArOH and ArBr); 131.1; 132.0 (C(ArBr)-Het and C(ArOH)-Het); 152.8 (C-OH); 174.7 (C-4).

4-(4-Bromophenyl)-2-(3-cyclohexyl-4-hydroxy-5-methylphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20l). Colorless powder, yield 2.55 g (93%), m.p. 204-205 °C (MeOH, dec.). Elemental analysis: found: C, 63.35; H, 6.34; Br, 17.41; N, 6.30; calcd. for $\text{C}_{24}\text{H}_{29}\text{BrN}_2\text{O}_2$: C, 63.02; H, 6.39; Br, 17.47; N, 6.12%. IR-spectrum, ν , cm^{-1} , (KBr): 3262 (OH), 2974, 2929, 2851 (CH), 1612 (C=N), 1485, 1230, 1158. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ , ppm (J , Hz): 1.17-1.29 (1H, m, C_6H_{11}); 1.30-1.46 (4H, m, C_6H_{11}); 1.35 (3H, s, 5- CH_3); 1.37 (3H, s, 5- CH_3); 1.66-1.84 (5H, m, C_6H_{11}); 2.19 (3H, s, 5- CH_3 ArOH); 2.86-3.00 (1H, m, Ar-CH-(CH_2)₅); 5.32 (1H, s, 2-H); 6.97 (1H, d, $^4J = 1.6$, H-6' ArOH); 7.04 (1H, d, $^4J = 1.6$, H-2' ArOH); 7.65 (2H, AA'BB', $J = 8.4$, H_A: H-3',5' ArBr); 7.78 (2H, AA'BB', $J = 8.4$, H_B: H-2',6' ArBr); 7.80 (1H, s, N-OH); 8.03 (1H, s, Ar-OH). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$), δ , ppm: 16.4 (5- CH_3); 17.0 (Ar- CH_3); 25.2 (5- CH_3); 25.9; 26.6; 32.9; 33.0 (4 CH_2); 36.5 (CH in C_6H_{11}); 70.4 (C-5); 89.6 (C-2); 123.8 (C-2' ArOH); 123.8; 124.2 (C-Br and Me-C ArOH); 127.3 (C-6' ArOH); 129.5 (C-2',6' ArBr); 131.6 (C-3',5' ArBr); 131.3; 132.0 (C(ArBr)-Het and C(ArOH)-Het); 133.4 (C-5' ArOH); 151.6 (C-OH); 174.6 (C-4).

4-(4-Bromophenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20m). Colorless powder, yield 2.08 g (78%), m.p. 195-197 °C (MeOH, dec.). Elemental analysis: found: C, 62.31; H, 6.43; Br, 17.94; N, 6.51; calcd. for $\text{C}_{23}\text{H}_{29}\text{BrN}_2\text{O}_2$: C, 62.02; H, 6.56; Br, 17.94; N, 6.29%. IR-spectrum, ν , cm^{-1} , (KBr): 3428, 3285 (OH), 2965, 2870 (CH), 1601 (C=N), 1467, 1289, 1203. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ , ppm (J , Hz): 1.15 (12H, d, $J = 6.8$, CH_3 -CH- CH_3); 1.35 (3H, s, 5- CH_3); 1.37 (3H, s, 5- CH_3); 3.30 (2H, septet, $J = 6.8$, CH_3 -CH- CH_3); 5.35 (1H, s, H-2); 7.05 (2H, s, H-2,6 ArOH); 7.66

(2H, AA'BB', $J = 8.4$, H_A: H-3',5' ArBr); 7.78 (2H, AA'BB', $J = 8.4$, H_B: H-2',6' ArBr); 7.83 (1H, s, N-OH); 8.01 (1H, s, Ar-OH). ¹³C NMR (100 MHz, DMSO-*d*₆), δ , ppm: 16.5 (5-CH₃); 23.1 (Ar-CH-CH₃); 25.3 (5-CH₃); 26.4 (Ar-CH-CH₃); 70.6 (C-5); 89.8 (C-2); 122.7 (C-2',6' ArOH); 124.2 (C-Br); 129.5 (C-2',6' ArBr); 131.7 (C-3',5' ArBr); 131.7; 132.1 (C(Ar)-Het and C(Ph)-Het); 134.6 (C(Ar)-CH-CH₃); 150.4 (C-OH); 174.8 (C-4).

4-(4-Bromophenyl)-2-(3,5-dicyclohexyl-4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20n). Colorless powder, yield 2.80 g (89%), m.p. 208-210 °C (EtOH, dec.). Elemental analysis: found: C, 66.17; H, 7.26; Br, 15.35; N, 5.23; calcd. for C₂₉H₃₇BrN₂O₂: C, 66.28; H, 7.10; Br, 15.20; N, 5.33%. IR-spectrum, ν , cm⁻¹, (KBr): 3269 (OH), 2926, 2850 (CH), 1591 (C=N), 1466, 1447, 1284, 1239. ¹H NMR (400 MHz, DMSO-*d*₆), δ , ppm (J , Hz): 1.16-1.30 (2H, m, C₆H₁₁); 1.30-1.46 (8H, m, C₆H₁₁); 1.35 (3H, s, 5-CH₃); 1.38 (3H, s, 5-CH₃); 1.67-1.83 (10H, m, C₆H₁₁); 2.88-2.98 (2H, m, Ar-CH-(CH₂)₅); 5.33 (1H, s, 2-H); 7.02 (2H, s, H-2,6 ArOH); 7.66 (2H, AA'BB', $J = 8.8$, H_A: H-3',5' ArBr); 7.79 (2H, AA'BB', $J = 8.8$, H_B: H-2',6' ArBr); 7.82 (1H, s, N-OH); 7.92 (1H, s, Ar-OH). ¹³C NMR (100 MHz, DMSO-*d*₆), δ , ppm: 16.4 (5-CH₃); 25.3 (5-CH₃); 25.9; 26.6; 33.1; 33.2 (4 CH₂); 36.5 (CH in C₆H₁₁); 70.5 (C-5); 89.8 (C-2); 123.2 (C-2',6' ArOH); 124.2 (C-Br); 129.5 (C-2',6' ArBr); 131.6 (C-3',5' ArBr); 131.5; 132.0 (C(ArBr)-Het and C(ArOH)-Het); 133.8 (C-3',5' ArOH); 150.3 (C-OH); 174.6 (C-4).

4-(4-Bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20o). Colorless fine crystals, yield 2.52 g (88%), m.p. 203-204 °C (MeOH, dec.). Elemental analysis: found: C, 63.50; H, 6.91; Br, 17.10; N, 5.68; calcd. for C₂₅H₃₃BrN₂O₂: C, 63.42; H, 7.03; Br, 16.88; N, 5.92%. IR-spectrum, ν , cm⁻¹, (KBr): 3627, 3244, (OH), 2958 (CH), 1612 (C=N), 1436, 1215. ¹H NMR (300 MHz, DMSO-*d*₆), δ , ppm (J , Hz): 1.38 (3H, s, 5-CH₃); 1.40 (21H, s, *t*-Bu and 5-CH₃); 5.36 (1H, s, H-2); 6.89 (1H, s, Ar-OH); 7.19 (2H, s, H-2',6' ArOH); 7.67 (2H, AA'BB', $J = 8.6$, H_A: H-3',5' ArBr); 7.79 (2H, AA'BB', $J = 8.6$, H_B: H-2',6' ArBr); 7.83 (1H, s, N-OH). ¹³C NMR (75 MHz, DMSO-*d*₆), δ , ppm: 16.4 (5-CH₃); 25.3 (5-CH₃); 30.4 (C(CH₃)₃); 34.5 (C(CH₃)₃); 70.4 (C-5); 89.9 (C-2); 124.2 (C-2',6' ArOH); 124.2 (C-Br); 129.4 (C-2',6' ArBr); 131.7 (C-3',5' ArBr); 131.6; 132.1 (C(ArBr)-Het and C(ArOH)-Het); 138.5 (C-3',5' ArOH); 153.5 (C-OH); 174.8 (C-4).

2-(4-Hydroxy-3,5-dimethylphenyl)-4-(4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20p). Colorless fine needles, yield 1.33 g (68%), m.p. 231.3-231.5 °C (EtOH). Elemental analysis: found: C 69.70; H 6.54; N 8.50; calcd. for C₁₉H₂₂N₂O₃: C, 69.92; H, 6.79; N, 8.58%. IR-spectrum, ν , cm⁻¹, (KBr): 3261 (OH), 2984, 2935 (CH), 2627, 2569 (OH), 1610, 1601, 1576 (C=N and C=C), 1518, 1286, 1213, 1155. ¹H NMR (400 MHz, DMSO-*d*₆), δ , ppm (J , Hz): 1.33 (3H, s, 5-CH₃); 1.39 (3H, s, 5-CH₃); 2.18 (6H, s, 3,5-CH₃ Ar); 5.23 (1H, s, H-2); 6.83 (2H, AA'BB', $J = 8.5$, H_A: H-3',5' 4-ArOH); 6.98 (2H, s, H-2,6 2-ArOH); 7.68 (1H, s, N-OH); 7.72 (2H, AA'BB', $J = 8.5$, H_B: H-2',6' 4-ArOH); 8.15 (1H, br.s, 2-Ar-OH); 9.99 (1H, br.s, 4-Ar-OH). ¹³C NMR (100 MHz, DMSO-*d*₆), δ , ppm: 16.6 (5-CH₃); 16.8 (Ar-CH₃); 25.7 (5-CH₃); 70.1 (C-5); 88.9 (C-2); 115.3 (C-3',5' 4-ArOH); 123.5 (CH₃-C Ar); 123.8 (C-1' 4-ArOH); 128.0; 129.3 (C-2',6' 2-ArOH and 4-ArOH); 131.8 (C-1' 2-ArOH); 152.7 (C-OH 2-ArOH); 159.6 (C-OH 4-ArOH); 174.7 (C-4).

2-(4-Hydroxy-3,5-diisopropylphenyl)-4-(4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20q). Faint yellow powder, yield 1.61 g (70%), m.p. 218.7 °C (H₂O/CHCl₃, dec.). Elemental analysis: found: C, 70.64; H, 7.76; N, 7.13; calcd. for C₂₃H₃₀N₂O₃ × ½H₂O: C, 70.56; H, 7.98; N, 7.16%. IR-spectrum, ν , cm⁻¹, (KBr): 3577, 3431, 3286, 3078, (OH), 2964, 2931, 2870 (CH), 1608 (C=N), 1560, 1518, 1464, 1298, 1161. ¹H NMR (400 MHz, DMSO-*d*₆), δ , ppm (J , Hz): 1.15 (12H, d, $J = 5.6$, CH₃-CH-CH₃); 1.33 (3H, s, 5-CH₃); 1.38 (3H, s, 5-CH₃); 3.30 (2H, septet, $J = 5.6$, CH₃-CH-CH₃); 5.28 (1H, s, H-2); 6.83 (2H, AA'BB', $J = 7.1$, H_A: H-3',5' 4-ArOH); 7.05 (2H, s, H-2,6 2-ArOH); 7.70 (2H, AA'BB', $J = 7.1$, H_B: H-2',6' 4-ArOH); 7.72 (1H, s, N-OH); 7.95 (1H, br.s, 2-Ar-OH); 9.97 (1H, br.s, 4-Ar-OH). ¹³C NMR (100 MHz, DMSO-*d*₆), δ , ppm: 16.6 (5-CH₃); 23.2 (Ar-CH-CH₃); 25.7 (5-CH₃); 26.4 (Ar-CH-CH₃); 70.3 (C-5); 89.4 (C-2); 115.4 (C-3',5' 4-ArOH); 122.8 (C-2',6' 2-ArOH); 123.9 (C-1' 4-ArOH); 129.3 (C-2',6' 4-

ArOH); 132.3 (C-1 2-ArOH); 134.6 (C-3,5 2-ArOH); 150.3 (C-OH 2-ArOH); 159.6 (C-OH 4-ArOH); 174.8 (C-4).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-4-(4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol (20r). Colorless powder, yield 2.03 g (73%), m.p. 214.5-215.0 °C (EtOH). Elemental analysis: found: C, 75.13; H, 8.13; N, 5.89; calcd. for $C_{29}H_{38}N_2O_3$: C, 75.29; H, 8.28; N, 6.06%. IR-spectrum, ν , cm^{-1} , (KBr): 3279 (OH), 2924, 2850 (CH), 1603 (C=N), 1448, 1284, 1234. 1H NMR (300 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.10-1.48 (10H, m, C_6H_{11}); 1.33 (3H, s, 5- CH_3); 1.39 (3H, s, 5- CH_3); 1.63-1.86 (10H, m, C_6H_{11}); 2.80-3.05 (2H, m, Ar-CH(CH_2) $_5$); 5.26 (1H, s, 2-H); 6.84 (2H, AA'BB', J = 8.3, H_A : H-3',5' 4-ArOH); 7.01 (2H, s, H-2,6 2-ArOH); 7.71 (1H, s, N-OH); 7.72 (2H, AA'BB', J = 8.3, H_B : H-2',6' 4-ArOH); 7.90 (1H, br.s, 2-Ar-OH); 9.97 (1H, br.s, 4-Ar-OH). ^{13}C NMR (75 MHz, DMSO- d_6), δ , ppm: 16.6 (5- CH_3); 25.7 (5- CH_3); 26.0; 26.7; 33.2; 33.3 (4 CH_2); 36.6 (CH in C_6H_{11}); 70.3 (C-5); 89.4 (C-2); 115.4 (C-3',5' 4-ArOH); 123.3 (C-2',6' 2-ArOH); 123.9 (C-1' 4-ArOH); 129.3 (C-2',6' 4-ArOH); 132.2 (C-1' 2-ArOH); 133.8 (C-3',5' 2-ArOH); 150.2 (C-OH 2-ArOH); 159.6 (C-OH 4-ArOH); 174.7 (C-4).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4-(4-hydroxyphenyl)-5,5-dimethyl-2,5-dihydro-1H-imidazol-1-ol methanolate (20s $\times$ CH $_3$ OH). Colorless plates, yield 2.02 g (76%), m.p. 237.9 °C (MeOH, dec.). Elemental analysis: found: C, 70.83; H, 8.49; N, 6.54; calcd. for $C_{25}H_{34}N_2O_3 \times CH_3OH$: C, 70.56; H, 8.65; N, 6.33%. IR-spectrum, ν , cm^{-1} , (KBr): 3611 (OH), 2957 (CH), 1609, 1590 (C=N), 1536, 1513, 1462, 1422, 1362, 1194. 1H NMR (500 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.35 (3H, s, 5- CH_3); 1.39 (3H, s, 5- CH_3); 1.40 (18H, s, *t*-Bu); 3.18 (3H, s, CH_3OH); 4.07 (1H, br.s, CH_3OH); 5.28 (1H, s, H-2); 6.79 (1H, s, 2-Ar-OH); 6.83 (2H, AA'BB', J_{AB} = 8.6, H-3,5 4-Ar-OH); 7.19 (2H, s, H-2,6 2-ArOH); 7.68 (1H, s, N-OH); 7.71 (2H, AA'BB', J_{AB} = 8.6, H-2,6 4-Ar-OH); 9.89 (1H, br.s, 4-Ar-OH). ^{13}C NMR (125 MHz, DMSO- d_6), δ , ppm: 16.8 (5- CH_3); 26.0 (5- CH_3); 30.7 (C(CH_3) $_3$); 34.7 (C(CH_3) $_3$); 48.9 (CH_3OH); 70.5 (C-5); 89.8 (C-2); 115.5 (C-3',5' 4-ArOH); 124.1 (C-1' 4-ArOH); 124.4 (C-2',6' 2-ArOH); 129.4 (C-2',6' 4-ArOH); 132.4 (C-1' 2-ArOH); 138.6 (C-3',5' 2-ArOH); 153.6 (C-OH 2-ArOH); 159.8 (C-OH 4-ArOH); 175.0 (C-4).

2-(4-Hydroxy-3,5-dimethylphenyl)-4,4-dimethyl-5-phenyl-4H-imidazole 3-oxide (21a). Yellow needles, yield 1.34 g (87%), m.p. 208-210 °C (EtOH, dec.). Elemental analysis: found: C, 74.05; H, 6.53; N, 9.12; calcd. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08%. IR-spectrum, ν , cm^{-1} , (KBr): 3552, 3393 (OH), 2940 (CH), 1603 (C=N), 1550, 1522, 1327, 1179. UV (EtOH), $\lambda_{max}nm$, (lg ϵ): 301 (4.37), 385 (3.63). 1H NMR (300 MHz, $CDCl_3$), δ , ppm (J , Hz): 1.75 (6H, s, 4,4- CH_3); 2.31 (6H, s, 3,5- CH_3 Ar); 5.33 (1H, br.s, Ar-OH); 7.46-7.55 (3H, m, Ph); 8.06-8.12 (2H, m, Ph); 8.47 (2H, s, H-2',6' Ar).

2-(3-Cyclohexyl-4-hydroxy-5-methylphenyl)-4,4-dimethyl-5-phenyl-4H-imidazole 3-oxide (21b). Bright yellow needles, yield 1.53 g (81%), m.p. 211-212 °C (MeCN, dec.). Elemental analysis: found: C, 76.28; H, 7.43; N, 7.34; calcd. for $C_{24}H_{28}N_2O_2$: C, 76.56; H, 7.50; N, 7.44%. IR-spectrum, ν , cm^{-1} , (KBr): 3406 (OH), 3060 (CH), 2931, 2850, 1604 (C=N), 1545, 1472, 1326, 1187. UV (EtOH), $\lambda_{max}nm$, (lg ϵ): 301 (4.33), 386 (3.60). 1H NMR (400 MHz, DMSO- d_6), δ , ppm (J , Hz): 1.20-1.48 (5H, m, CH(CH_2) $_5$); 1.64 (6H, s, 4,4- CH_3); 1.69-1.87 (5H, m, CH(CH_2) $_5$); 2.27 (3H, s, 5- CH_3 Ar); 2.93-3.03 (1H, m, CH(CH_2) $_5$); 7.54-7.62 (3H, m, Ph); 8.14-8.19 (2H, m, Ph); 8.30 (1H, d, 4J = 2.0, H-6' ArOH); 8.50 (1H, d, 4J = 2.0, H-2' ArOH); 8.83 (1H, br.s, OH). ^{13}C NMR (100 MHz, DMSO- d_6), δ , ppm: 17.1 (Ar- CH_3); 23.6 (4- CH_3); 25.8; 26.5; 32.9 (3 CH_2); 36.4 (CH in C_6H_{11}); 80.3 (C-4); 118.9 (C-1' Ar); 123.6 (C-2' Ar); 124.3 (C-3' Ar); 127.2; 129.2; 131.7 (3CH Ph); 127.3 (C-6' Ar); 130.2; 133.9 (C-5' Ar and C-1 Ph); 144.3 (C-2); 154.3 (C-OH); 174.9 (C-5).

2-(4-Hydroxy-3,5-diisopropylphenyl)-4,4-dimethyl-5-phenyl-4H-imidazole 3-oxide (21c). Bright yellow tiny needles, yield 1.55 g (87%), m.p. 212-215 °C (EtOH, dec.). Elemental analysis: found: C, 75.61; H, 7.75; N, 7.77; calcd. for $C_{23}H_{28}N_2O_2$: C, 75.79; H, 7.74; N, 7.69%. IR-spectrum, ν , cm^{-1} , (KBr): 3197 (OH), 2960, 2871 (CH) 1600 (C=N), 1541, 1461, 1430, 1186, 1124. 1H NMR (300 MHz, $CDCl_3$), δ , ppm (J , Hz): 1.30 (12H, d, J = 6.6, (CH_3 -CH- CH_3) $_2$); 1.76 (6H, s, 4,4- CH_3); 3.25 (2H, septet, J = 6.6, (CH_3 -CH- CH_3) $_2$); 6.12 (1H, s, OH); 7.40-7.51 (3H, m, Ph); 8.02-8.10 (2H, m, Ph); 8.59 (2H, s, H-2',6' ArOH).

¹³C NMR (75 MHz, CDCl₃), δ, ppm: 25.0 (Ar-CH-CH₃); 26.5 (4-CH₃); 29.6 (Ar-CH-CH₃); 83.0 (C-4); 122.2 (C-1' Ar), 126.6 (C-2',6' Ar); 129.7; 131.3; 134.0 (3CH Ph); 133.0 (C-1 Ph); 136.3 (C-3',5' Ar); 149.1 (C-2); 155.2 (C-OH); 178.7 (C-5).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-4H-imidazole 3-oxide (21d). Yellow powder, yield 2.07 g (93%), m.p. 249-250 °C (MeOH, dec.). Elemental analysis: found: C, 78.49; H, 8.15; N, 6.31; calcd. for C₂₉H₃₆N₂O₂: C, 78.34; H, 8.16; N, 6.30%. IR-spectrum, ν, cm⁻¹, (KBr): 3156 (OH), 2922, 2850 (CH), 1596 (C=N), 1536, 1449, 1431, 1195. UV (EtOH), λ_{max}nm, (lg ε): 303 (4.46), 387 (3.69). ¹H NMR (300 MHz, CDCl₃), δ, ppm (J, Hz): 1.23-1.67 (14H, m, CH(CH₂)₅); 1.75 (6H, s, 4,4-CH₃); 1.74-1.96 (6H, m, CH(CH₂)₅); 2.72-2.83 (2H, m, CH(CH₂)₅); 5.22 (1H, s, OH); 7.48-7.55 (3H, m, Ph); 8.07-8.13 (2H, m, Ph); 8.57 (2H, s, H-2',6' ArOH).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-5-phenyl-4H-imidazole 3-oxide (21e). Bright yellow needles, yield 1.89 g (97%), m.p. 240-242 °C (EtOH, dec.). Elemental analysis: found: C, 76.59; H, 8.22; N, 7.26; calcd. for C₂₅H₃₂N₂O₂: C, 76.49; H, 8.22; N, 7.14%. IR-spectrum, ν, cm⁻¹, (KBr): 3602 (OH), 2955 (CH), 1598 (C=N), 1531, 1423, 1374, 1241. ¹H NMR (300 MHz, CDCl₃), δ, ppm (J, Hz): 1.51 (18H, s, *t*-Bu); 1.75 (6H, s, 4,4-CH₃); 5.63 (1H, s, OH); 7.45-7.53 (3H, m, Ph); 8.06-8.11 (2H, m, Ph); 8.75 (2H, s, H-2',6' Ar). ¹³C NMR (75 MHz, CDCl₃), δ, ppm: 23.9 (4-CH₃); 29.8 (C(CH₃)₃); 34.1 (C(CH₃)₃); 80.2 (C-4); 118.8 (C-1' Ar); 125.2 (C-2',6' Ar); 126.9; 128.6; (2CH Ph); 130.4 (C-1 Ph); 131.2 (CH Ph); 135.5 (C-3',5' Ar); 146.1 (C-2); 155.7 (C-OH); 175.4 (C-5).

5-(4-Fluorophenyl)-2-(4-hydroxy-3,5-dimethylphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21f). Yellowish green needles, yield 1.40 g (86%), m.p. 205-210 °C (*t*-BuOMe, dec.). Elemental analysis: found: C, 69.89; H, 5.87; F, 5.75; N, 8.74; calcd. for C₁₉H₁₉FN₂O₂: C, 69.92; H, 5.87; F, 5.82; N, 8.58%. IR-spectrum, ν, cm⁻¹, (KBr): 3075 (OH), 2946 (CH), 1603 (C=N), 1550, 1507, 1149. UV (EtOH), λ_{max}nm, (lg ε): 301 (4.48), 383 (3.73). ¹H NMR (400 MHz, DMSO-*d*₆), δ, ppm (J, Hz): 1.62 (6H, s, 4,4-CH₃); 2.25 (6H, s, 3,5-CH₃ 2-ArOH); 7.38 (2H, ddd, ³J_{HF} = 8.5, ³J = 8.2, ⁴J = 1.5, H-3'',5'' ArF); 8.22 (2H, ddd, ³J = 8.2, ⁴J_{HF} = 5.6, ⁴J = 1.5, H-2'',6'' ArF); 8.34 (2H, s, H-2',6' 2-ArOH); 8.95 (1H, br.s, OH).

2-(3-Cyclohexyl-4-hydroxy-5-methylphenyl)-5-(4-fluorophenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21g). Yellowish green needles, yield 1.69 g (86%), m.p. 236-238 °C (MeOH, dec.). Elemental analysis: found: C, 73.03; H, 6.85; F, 4.92; N, 7.27; calcd. for C₂₄H₂₇FN₂O₂: C, 73.03; H, 6.90; F, 4.82; N, 7.10%. IR-spectrum, ν, cm⁻¹, (KBr): 3408 (OH), 2931, 1602 (C=N), 1541, 1504, 1186, 1150. UV (EtOH), λ_{max}nm, (lg ε): 302 (4.48), 388 (3.74). ¹H NMR (400 MHz, CDCl₃), δ, ppm (J, Hz): 1.22-1.60 (5H, m, CH(CH₂)₅); 1.73 (6H, s, 4,4-CH₃), 1.74-1.93 (5H, m, CH(CH₂)₅); 2.32 (3H, s, 5-CH₃ 2-ArOH), 2.76-2.86 (1H, m, CH(CH₂)₅); 5.40 (1H, s, OH); 7.19 (2H, ddd, ³J_{HF} = 8.5, ³J = 8.2, ⁴J = 1.5, H-3'',5'' ArF); 8.10 (2H, ddd, ³J = 8.2, ⁴J_{HF} = 5.6, ⁴J = 1.5, H-2'',6'' ArF); 8.44 (1H, d, ⁴J = 1.6, H-6' ArOH); 8.55 (1H, d, ⁴J = 1.6, H-2' ArOH).

5-(4-Fluorophenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21h). Yellowish green crystals, yield 1.87 g (96%), m.p. 220-231 °C (MeCN, dec.). Elemental analysis: found: C, 72.21; H, 7.10; F, 4.95; N, 7.30; calcd. for C₂₃H₂₇FN₂O₂: C, 72.23; H, 7.12; F, 4.97; N 7.32%. IR-spectrum, ν, cm⁻¹, (KBr): 3227 (OH), 2960 (CH), 1603 (C=N), 1549, 1509, 1463, 1432, 1194, 1144. ¹H NMR (300 MHz, DMSO-*d*₆), δ, ppm (J, Hz): 1.22 (12H, d, J = 6.9, CH₃-CH-CH₃); 1.65 (6H, s, 4-CH₃); 3.37 (2H, septet, J = 6.9, CH₃-CH-CH₃); 7.39 (2H, ddd, ³J_{HF} = 8.0, ³J = 7.5, ⁴J = 1.5, H-3',5' 5-ArF); 8.24 (2H, ddd, ³J = 7.5, ⁴J_{HF} = 5.0, ⁴J = 1.5, H-2',6' ArF); 8.48 (2H, s, 2,6-H 2-ArOH); 8.81 (1H, s, OH). ¹³C NMR (75 MHz, DMSO-*d*₆), δ, ppm: 23.2 (Ar-CH₃); 23.8 (4,4-CH₃); 26.6 (CH₃-CH-CH₃); 80.6 (C-4); 116.6 (d, ²J_{CF} = 22, C-3',5' ArF); 119.5 (C-1 ArOH); 123.1 (C-2,6 ArOH); 127.3 (d, ⁴J_{CF} = 3.2, C-1' ArF); 130.2 (d, ³J_{CF} = 8.8, C-2',6' ArF); 135.2 (C-3,5 ArOH); 144.8 (C-2); 153.4 (C-OH); 164.3 (d, ¹J_{CF} = 250, C-4' ArF); 174.1 (C-5).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-5-(4-fluorophenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21i). Yellowish green crystals, yield 2.22 g (96%), m.p. 255-257 °C (MeOH, dec.). Elemental analysis: found: C, 75.39; H, 7.61; F, 4.32; N, 6.08; calcd. for C₂₉H₃₅FN₂O₂: C, 75.29; H, 7.63; F, 4.11; N, 6.06%. IR-

spectrum, ν , cm^{-1} , (KBr): 3109, 2924 (CH), 1604 (C=N), 1536, 1508, 1431, 1238, 1193. ^1H NMR (300 MHz, $\text{DMSO}-d_6$), δ , ppm (J , Hz): 1.20-1.51 (10H, m, $\text{CH}(\text{CH}_2)_5$); 1.63 (6H, s, 4,4- CH_3); 1.68-1.86 (10H, m, $\text{CH}(\text{CH}_2)_5$); 2.93-3.05 (2H, m, $\text{CH}(\text{CH}_2)_5$); 7.37 (2H, ddd, $^3J_{\text{HF}} = 8.0$, $^3J = 7.3$, $^4J = 1.6$, H-3',5' 5-ArF); 8.22 (2H, ddd, $^3J = 7.5$, $^4J_{\text{HF}} = 5.0$, $^4J = 1.4$, H-2',6' ArF); 8.41 (2H, s, 2,6-H 2-ArOH); 8.68 (1H, s, OH).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(4-fluorophenyl)-4,4-dimethyl-4H-imidazole 3-oxide methanolate (21j) $\times \text{CH}_3\text{OH}$. Yellowish green crystals, yield 1.99 g (90%), m.p. 230-232 °C (MeOH, dec.). Elemental analysis: found: C, 71.01; H, 7.96; N, 6.43; calcd. for $\text{C}_{25}\text{H}_{31}\text{FN}_2\text{O}_2 \times \text{CH}_3\text{OH}$: C, 70.56; H, 7.97; N, 6.33%. IR-spectrum, ν , cm^{-1} , (KBr): 3434 (OH), 2963 (CH), 1603, 1540 (C=N), 1508, 1421, 1369, 1240. ^1H NMR (300 MHz, CDCl_3), δ , ppm (J , Hz): 1.54 (18H, s, $\text{C}(\text{CH}_3)_3$); 1.77 (6H, s, 4,4- CH_3); 3.49 (3H, s, CH_3OH); 5.68 (1H, s, OH); 7.24 (2H, ddd, $^3J_{\text{HF}} = 8.0$, $^3J = 7.5$, $^4J = 1.5$, H-3',5' 5-ArF); 8.12 (2H, ddd, $^3J = 7.5$, $^4J_{\text{HF}} = 5.0$, $^4J = 1.4$, H-2',6' ArF); 8.77 (2H, s, 2,6-H 2-ArOH). ^{13}C NMR (75 MHz, CDCl_3), δ , ppm: 23.8 (4,4- CH_3); 29.8 ($\text{C}(\text{CH}_3)_3$); 33.9 ($\text{C}(\text{CH}_3)_3$); 50.3 (CH_3OH); 80.1 (C-4); 115.8 (d, $^2J_{\text{CF}} = 22$, C-3',5' ArF); 118.7 (C-1 ArOH); 125.2 (C-2,6 ArOH); 126.8 (d, $^4J_{\text{CF}} = 3.4$, C-1' ArF); 129.1 (d, $^3J_{\text{CF}} = 8.6$, C-2',6' ArF); 135.5 (C-3,5 ArOH); 146.1 (C-2); 155.8 (C-OH); 164.3 (d, $^1J_{\text{CF}} = 253$, C-4' ArF); 175.0 (C-5).

5-(4-Bromophenyl)-2-(4-hydroxy-3,5-dimethylphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21k). Bright yellow crystals, yield 1.77 g (91%), m.p. 228-230 °C (AcOH, dec.). Elemental analysis: found: C, 58.99; H, 4.88; Br, 20.31; N, 7.34; calcd. for $\text{C}_{19}\text{H}_{19}\text{BrN}_2\text{O}_2$: C, 58.93; H, 4.95; Br, 20.63; N, 7.23%. IR-spectrum, ν , cm^{-1} , (KBr): 3421 (OH), 2943 (CH), 1589 (C=N), 1539, 1476, 1178. UV (EtOH), $\lambda_{\text{max}}\text{nm}$, (lg ϵ): 306 (4.51), 396 (3.76). ^1H NMR (400 MHz, $\text{DMSO}-d_6$), δ , ppm (J , Hz): 1.61 (6H, s, $\text{C}(\text{CH}_3)_2$); 2.24 (6H, s, 3,5- CH_3 Ar); 7.73 (2H, AA'BB', $J = 8.8$, H_A : H-3',5' 5-ArBr); 8.07 (2H, AB, $J = 8.8$, H_B : H-2',6' 5-ArBr); 8.32 (2H, s, H-2,6 2-Ar); 9.05 (1H, br.s, OH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$), δ , ppm: 16.8 (Ar- CH_3); 23.5 (4,4- CH_3); 80.4 (C-4); 118.5 (C-1 ArOH); 124.2 (Ar-C-Me); 125.5 (C-Br); 127.7, 129.2 (CH Ar); 129.3 (C-1' ArBr); 132.3 (CH Ar); 144.4 (C-2); 155.6 (C-OH); 174.0 (C-5).

5-(4-Bromophenyl)-2-(3-cyclohexyl-4-hydroxy-5-methylphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21l). Dark yellow needles, yield 2.15 g (94%), m.p. 238-239 °C (MeOH, dec.). Elemental analysis: found: C, 63.21; H, 6.05; Br, 17.54; N, 6.12; calcd. for $\text{C}_{24}\text{H}_{27}\text{BrN}_2\text{O}_2$: C, 63.30; H, 5.98; Br, 17.55; N, 6.15%. IR-spectrum, ν , cm^{-1} , (KBr): 3370 (OH), 2930 (CH), 1602 (C=N), 1587, 1543, 1468, 1181. ^1H NMR (300 MHz, CDCl_3), δ , ppm (J , Hz): 1.20-1.65 (5H, m, $\text{CH}(\text{CH}_2)_5$); 1.72 (6H, s, 4,4- CH_3); 1.73-1.95 (5H, m, $\text{CH}(\text{CH}_2)_5$); 2.33 (3H, s, 5- CH_3 2-ArOH); 2.73-2.88 (1H, m, $\text{CH}(\text{CH}_2)_5$); 5.25 (1H, s, OH); 7.63 (2H, AA'BB', $J = 8.7$, H_A : H-3',5' 5-ArBr); 7.95 (2H, AB, $J = 8.7$, H_B : H-2',6' 5-ArBr); 8.43 (1H, d, $^4J = 1.5$, H-6' ArOH); 8.56 (1H, d, $^4J = 1.5$, H-2' ArOH).

5-(4-Bromophenyl)-2-(4-hydroxy-3,5-diisopropylphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21m). Dark yellow needles, yield 2.14 g (97%), m.p. 228-230 °C (70% aq. AcOH, dec.). Elemental analysis: found: C, 61.95; H, 6.16; Br, 18.03; N, 6.12; calcd. for $\text{C}_{23}\text{H}_{27}\text{BrN}_2\text{O}_2$: C, 62.31; H, 6.14; Br, 18.02; N, 6.32%. IR-spectrum, ν , cm^{-1} , (KBr): 3243 (OH), 2958 (CH), 1604, 1588 (C=N), 1546, 1460, 1432, 1194, 1138. ^1H NMR (300 MHz, CDCl_3), δ , ppm (J , Hz): 1.30 (12H, d, $J = 6.9$, $\text{CH}_3\text{-CH-CH}_3$); 1.73 (6H, s, 4- CH_3); 3.22 (2H, septet, $J = 6.9$, $\text{CH}_3\text{-CH-CH}_3$); 5.94 (1H, s, OH); 7.63 (2H, AA'BB', $J = 8.9$, H_A : H-3',5' 5-ArBr); 7.95 (2H, AA'BB', $J = 8.9$, H_B : H-2',6' 5-ArBr); 8.55 (2H, s, H-2,6 2-ArOH). ^{13}C NMR (75 MHz, CDCl_3), δ , ppm: 22.2 (Ar-CH- CH_3); 23.7 (4,4- CH_3); 26.9 (Ar-CH- CH_3); 80.2 (C-4); 119.4 (C-1 ArOH); 123.8 (C-2,6 ArOH); 126.0 (C-Br); 128.3 (C-2',6' ArBr); 129.2 (C-1' ArBr); 131.9 (C-3',5' ArBr); 133.6 (C-3,5 ArOH); 146.3 (C-2); 152.5 (C-OH); 174.7 (C-5).

5-(4-Bromophenyl)-2-(3,5-dicyclohexyl-4-hydroxyphenyl)-4,4-dimethyl-4H-imidazole 3-oxide (21n). Dark yellow crystals, yield 2.62 g (100%), m.p. 248-250 °C (EtOH, dec.). Elemental analysis: found: C, 66.60; H, 6.81; Br, 15.30; N, 5.29; calcd. for $\text{C}_{29}\text{H}_{35}\text{BrN}_2\text{O}_2$: C, 66.53; H, 6.74; Br, 15.26; N, 5.35%. IR-spectrum, ν , cm^{-1} , (KBr): 3236 (OH), 2922 (CH), 1587 (C=N), 1539, 1432, 1195. ^1H NMR (400 MHz, CDCl_3), δ , ppm (J , Hz): 1.20-1.62 (10H, m, $\text{CH}(\text{CH}_2)_5$); 1.71 (6H, s, 4- CH_3); 1.75-1.95 (10H, m, $\text{CH}(\text{CH}_2)_5$); 2.72-2.86 (2H, m, $\text{CH}(\text{CH}_2)_5$); 5.66 (1H, s, OH); 7.63 (2H, AA'BB', $J = 7.2$, H_A : H-3',5' 5-ArBr);

7.95 (2H, *AA'**BB'*, *J* = 7.2, *H_B*: H-2',6' 5-ArBr); 8.53 (2H, s, 2,6-H 2-ArOH). ¹³C NMR (100 MHz, CDCl₃), δ, ppm: 24.0 (4,4-CH₃); 26.0, 26.9, 32.9 (CH₂ in C₆H₁₁); 37.6 (CH in C₆H₁₁); 80.4 (C-4); 119.8 (C-1 Ar-OH); 124.5 (C-2,6 ArOH); 126.2 (C-Br); 128.6 (C-2',6' ArBr); 129.5 (C-1' ArBr); 132.2 (C-3',5' ArBr); 133.0 (C-3,5 ArOH); 146.5 (C-2); 152.5 (C-OH); 174.8 (C-5).

5-(4-Bromophenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide acetate (21o×CH₃COOH). Dark yellow crystals, yield 2.19 g (93%), m.p. 230-232 °C (70% aq AcOH, dec.). Elemental analysis: found: C, 61.00; H, 6.60; N, 5.24; calcd. for C₂₅H₃₁BrN₂O₂×CH₃COOH: C, 61.02; H, 6.64; N, 5.27%. IR-spectrum, ν, cm⁻¹, (KBr): 3619 (OH), 2957 (CH), 1586 (C=N), 1530, 1422, 1237. ¹H NMR (300 MHz, CDCl₃), δ, ppm (*J*, Hz): 1.54 (18H, s, C(CH₃)₃); 1.77 (6H, s, 4-CH₃); 2.08 (3H, s, CH₃COOH); 5.72 (1H, br.s, OH); 7.65 (2H, *AA'**BB'*, *J* = 8.7, *H_A*: H-3',5' 5-ArBr); 7.98 (2H, *AA'**BB'*, *J* = 8.7, *H_B*: H-2',6' 5-ArBr); 8.75 (2H, s, 2,6-H 2-ArOH); 10.75 (1H, br.s, CH₃COOH). ¹³C NMR (75 MHz, CDCl₃), δ, ppm: 20.7 (CH₃COOH); 23.9 (4,4-CH₃); 30.1 (C(CH₃)₃); 34.4(C(CH₃)₃); 80.5 (C-4); 118.7 (C-1 Ar-OH); 125.8 (C-2,6 ArOH); 126.4 (C-Br); 128.6 (C-2',6' ArBr); 129.4 (C-1' ArBr); 132.2 (C-3',5' ArBr); 135.8 (C-3,5 ArOH); 147.2 (C-2); 156.3 (C-OH); 175.5 (C-5); 175.8 (CH₃COOH).

2-(4-Hydroxy-3,5-dimethylphenyl)-5-(4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide (21p). Dark yellow crystals, yield 1.35 g (83%), m.p. 270.4 °C (chromatography, dec.). Elemental analysis: found: C, 70.52; H, 6.35; N, 8.49; calcd. for C₁₉H₂₀N₂O₃: C 70.35; H 6.21; N 8.64%. IR-spectrum, ν, cm⁻¹, (KBr): 3072, 2980, 2920, 2796, 2675, 2586, 2469 (CH, OH), 1605, 1556 (C=N, C=C), 1500, 1327, 1146. UV (EtOH), λ_{max}nm, (lg ε): 248 (3.99), 308 (4.40), 330 (4.33), 384 (3.91). ¹H NMR (500 MHz, CDCl₃+DMSO-*d*₆), δ, ppm (*J*, Hz): 1.62 (6H, s, 4-CH₃); 2.24 (6H, s, 3,5-CH₃ 2-Ar); 3.38 (2H, br.s, 2(5)-Ar-OH); 6.88 (2H, *AA'**BB'*, *J* = 8.6, *H_A*: H-3',5' 5-ArOH); 7.94 (2H, *AA'**BB'*, *J* = 8.6, *H_B*: H-2',6' 5-ArOH); 8.33 (2H, s, H-2,6 2-ArOH). ¹³C NMR (125 MHz, CDCl₃+DMSO-*d*₆), δ, ppm: 16.5 (Ar-CH₃); 23.8 (4,4-CH₃); 79.4 (C-4); 115.7 (C-3',5' 5-ArOH); 118.5 (C-1 2-ArOH); 121.5 (C-1' 5-ArOH); 123.7 (CH₃-C 2-ArOH); 127.9; 129.0 (C-2',6' 2-ArOH and 4-ArOH); 144.8 (C-2); 155.4 (C-OH 2-ArOH); 160.8 (C-OH 4-ArOH); 175.4 (C-5).

2-(4-Hydroxy-3,5-diisopropylphenyl)-5-(4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide (21q). Yellow green powder, yield 343 mg (90%), m.p. 299.7-299.9 °C (CHCl₃). Elemental analysis: found: C, 67.82; H 6.86; N 6.91; calcd. for C₂₃H₂₈N₂O₃×¹/₄ CHCl₃: C 68.06; H 6.94; N 6.83%. IR-spectrum, ν, cm⁻¹, (KBr): 3495, 3063 (OH), 2962, 2871 (CH), 2820, 2767, 2690, 2631, 2515, 1605 (C=N), 1591 (C=C), 1552, 1512, 1468, 1433, 1284, 1188, 1144. UV (EtOH), λ_{max}nm, (lg ε): 249 (3.70), 308 (4.09), 331 (4.04), 386 (3.60). ¹H NMR (500 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.22 (12H, d, *J* = 6.9, CH₃-CH-CH₃); 1.62 (6H, s, 4-CH₃); 3.41 (2H, septet, *J* = 6.9, CH₃-CH-CH₃); 6.95 (2H, br.s, H-3',5' 5-Ar-OH); 8.04 (2H, br.s, H-2',6' 5-Ar-OH); 8.48 (2H, s, H-2,6 2-ArOH); 8.77 (1H, br.s, 2-Ar-OH); 10.34 (1H, br.s, 5-Ar-OH). ¹³C NMR (125 MHz, DMSO-*d*₆), δ, ppm: 22.9 (CH₃-CH-CH₃); 23.9 (4,4-CH₃); 26.3 (CH₃-CH-CH₃); 79.8 (C-4); 116.0 (C-3',5' 5-ArOH); 119.5 (C-1 2-ArOH); 121.7 (C-1' 5-ArOH); 122.9 (C-2,6 2-ArOH); 129.5 (C-2',6' 5-ArOH); 134.9 (C-3,5 2-ArOH); 144.6 (C-2); 153.0 (C-OH 2-ArOH); 160.9 (C-OH 5-ArOH); 175.2 (C-5).

2-(3,5-Dicyclohexyl-4-hydroxyphenyl)-5-(4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide methanolate (21r). Yellow green tiny needles, yield 2.09 g (85%), m.p. 278.8-279.2 °C (MeOH). Elemental analysis: found: C 73.00; H 8.09; N 5.56; calcd. for C₂₉H₃₆N₂O₃×CH₃OH: C, 73.14; H, 8.18; N, 5.69%. IR-spectrum, ν, cm⁻¹, (KBr): 3593, 3070 (OH), 2928, 2852 (CH), 1606 (C=N), 1587 (C=C), 1510, 1444, 1433, 1294, 1190, 1146. UV (EtOH), λ_{max}nm, (lg ε): 250 (3.95), 257 (3.93), 309 (4.38), 332 (4.33), 384 (3.88). ¹H NMR (400 MHz, CDCl₃+DMSO-*d*₆), δ, ppm (*J*, Hz): 1.13-1.51 (10H, m, C₆H₁₁); 1.53-1.95 (10H, m, C₆H₁₁); 1.62 (6H, s, 4-CH₃); 2.86-3.04 (2H, m, Ar-CH-(CH₂)₅); 3.19 (3H, s, CH₃OH); 6.91 (2H, *AA'**BB'*, *J* = 5.6, H-3',5' 5-ArOH); 7.97 (2H, *AA'**BB'*, *J* = 5.6, H-2',6' 5-ArOH); 8.41 (2H, s, H-2,6 2-ArOH); 8.50 (1H, br.s, 2-ArOH); 10.16 (1H, br.s, 5-ArOH). ¹³C NMR (100 MHz, CDCl₃+DMSO-*d*₆), δ, ppm: 24.2 (4,4-CH₃); 26.2; 26.8; 33.3 (CH₂ in C₆H₁₁); 36.7 (CH in C₆H₁₁); 49.1 (CH₃OH); 79.8 (C-4); 116.2 (C-3',5' 5-ArOH); 119.5 (C-1 2-ArOH); 121.9 (C-1' 5-ArOH); 124.0 (C-2,6 2-ArOH); 129.5 (C-2',6' 5-ArOH); 134.2 (C-3,5 2-ArOH); 145.5 (C-2); 153.4 (C-OH 2-ArOH); 161.2 (C-OH 5-ArOH); 175.7 (C-5).

2-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-5-(4-hydroxyphenyl)-4,4-dimethyl-4*H*-imidazole 3-oxide (21s). Yellow orange powder, yield 1.67 g (82%), m.p. 285-290 °C (MeOH, dec.). Elemental analysis: found: C 73.73; H 7.95; N 6.64; calcd. for C₂₅H₃₂N₂O₃: C 73.50; H 7.90; N 6.86%. ¹H NMR (500 MHz, DMSO-*d*₆), δ, ppm (*J*, Hz): 1.44 (18H, s, *t*-Bu); 1.61 (6H, s, 4-CH₃); 6.94 (2H, *AA'**BB'*, *J*_{AB} = 4.6, H-3,5 5-ArOH); 7.49 (1H, br.s, 2-ArOH); 8.01 (2H, *AA'**BB'*, *J*_{AB} = 4.6, H-2,6 5-ArOH); 8.63 (2H, s, H-2,6 2-ArOH); 10.30 (1H, br.s, 5-ArOH). ¹³C NMR (125 MHz, DMSO-*d*₆), δ, ppm: 24.1 (4-CH₃); 30.4 (C(CH₃)₃); 34.9 (C(CH₃)₃); 80.1 (C-4); 116.3 (C-3',5' 5-ArOH); 119.5 (C-1 2-ArOH); 121.9 (C-1' 5-ArOH); 124.6 (C-2,6 2-ArOH); 129.6 (C-2',6' 5-ArOH); 138.7 (C-3,5 2-ArOH); 144.8 (C-2); 156.1 (C-OH 2-ArOH); 161.1 (C-OH 5-ArOH); 175.2 (C-5).

Typical reactions occurring at inhibited and non-inhibited hydrocarbon oxidation [10].

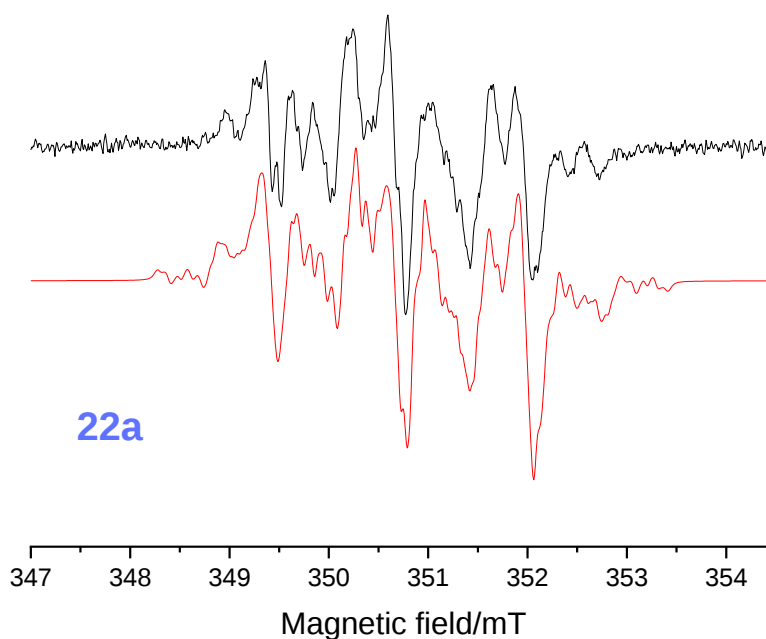
<i>Initiation of oxidation chains:</i>	(0) $\text{RH} \rightarrow \text{R}^\bullet$
<i>Propagation of oxidation chains:</i>	(1) $\text{R}^\bullet + \text{O}_2 \rightarrow \text{RO}_2^\bullet$ (2) $\text{RO}_2^\bullet + \text{RH} \rightarrow \text{ROOH} + \text{R}^\bullet$
<i>Degenerated branching of oxidation chains:</i>	(3) $\text{ROOH} \rightarrow \text{RO}^\bullet + \bullet\text{OH}$ (3') $\text{ROOR} \rightarrow \text{RO}^\bullet + \bullet\text{OR}$
<i>Termination of oxidation chains:</i>	(4) $\text{R}^\bullet + \text{R}^\bullet \rightarrow \text{R-R}$ (5) $\text{RO}_2^\bullet + \text{R}^\bullet \rightarrow \text{ROOR}$ (6) $\text{RO}_2^\bullet + \text{RO}_2^\bullet \rightarrow \text{O}_2 + \text{molecular products}$ (7) $\text{RO}_2^\bullet + \text{ArOH} \rightarrow \text{ROOH} + \text{ArO}^\bullet$ (7') $\text{RO}^\bullet + \text{ArOH} \rightarrow \text{ROH} + \text{ArO}^\bullet$ (7'') $\text{R}^\bullet + \text{ArOH} \rightarrow \text{RH} + \text{ArO}^\bullet$ (8) $\text{RO}_2^\bullet + \text{ArO}^\bullet \rightarrow \text{molecular products}$

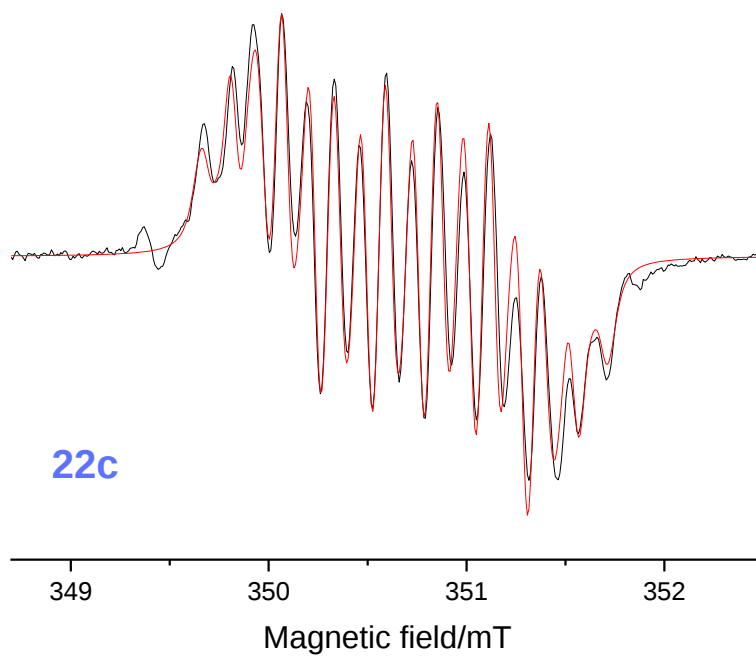
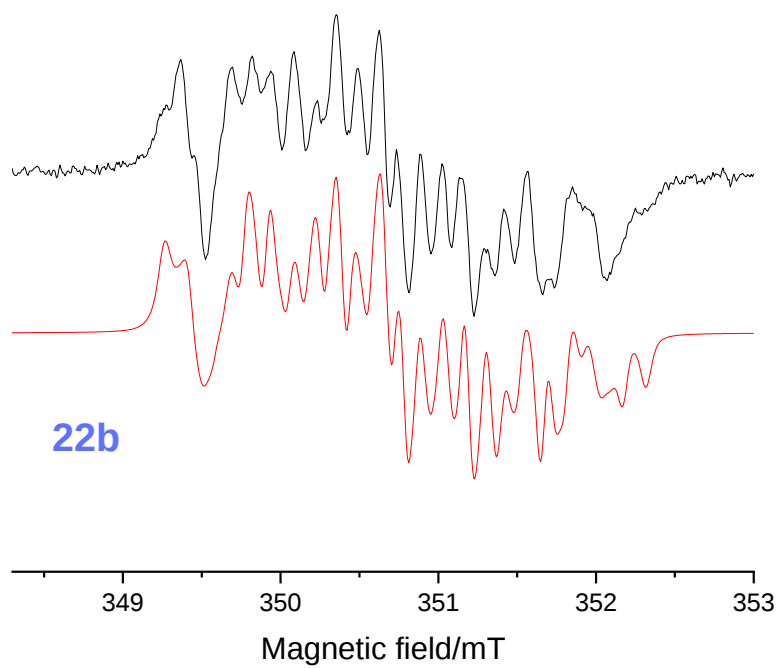
where RH – hydrocarbon (lipid); $\text{R}^\bullet$, $\text{RO}^\bullet$ and $\text{RO}_2^\bullet$ – alkyl, alkoxy and peroxy radicals, correspondingly; ROOH – organic hydroperoxide ; ArOH – radical inhibitor: $\text{ArO}^\bullet$ – inhibitor radical.

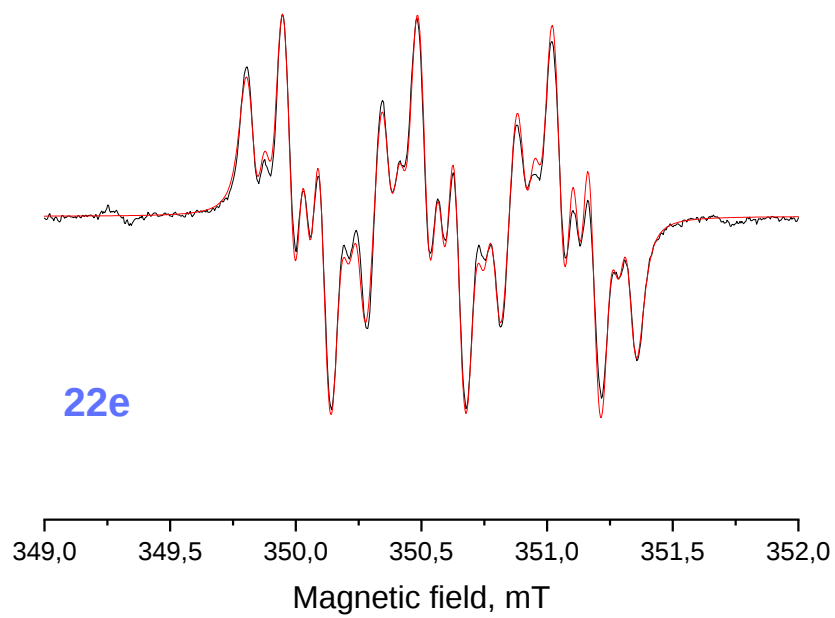
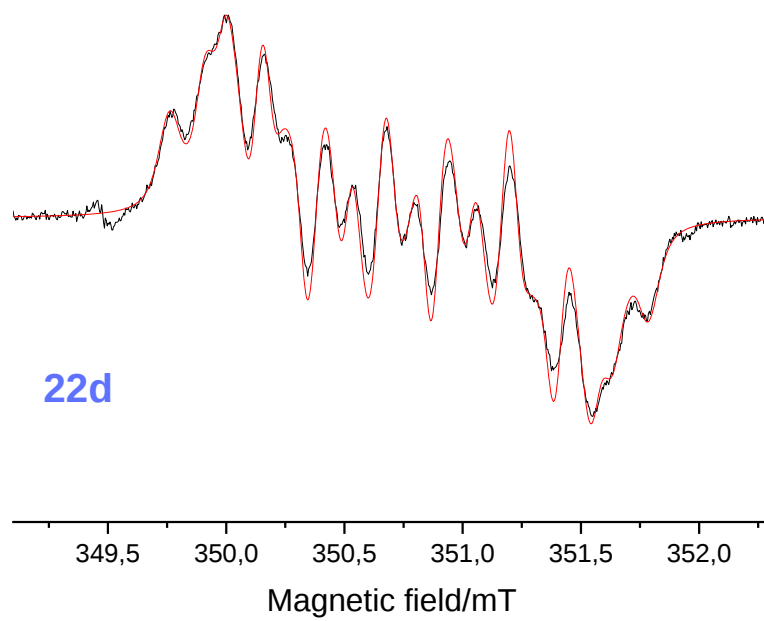
ESR spectra recorded for diluted and oxygen-free toluene solutions of phenoxy-nitroxides

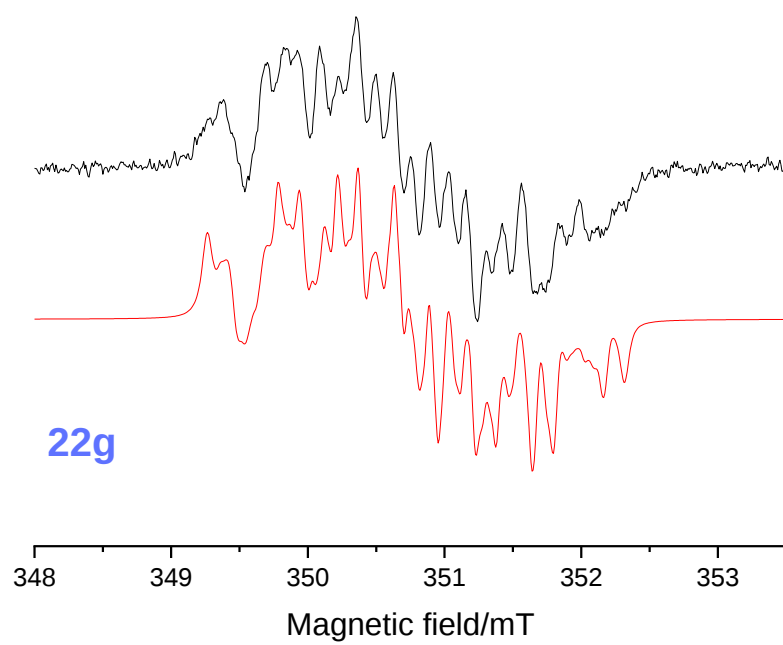
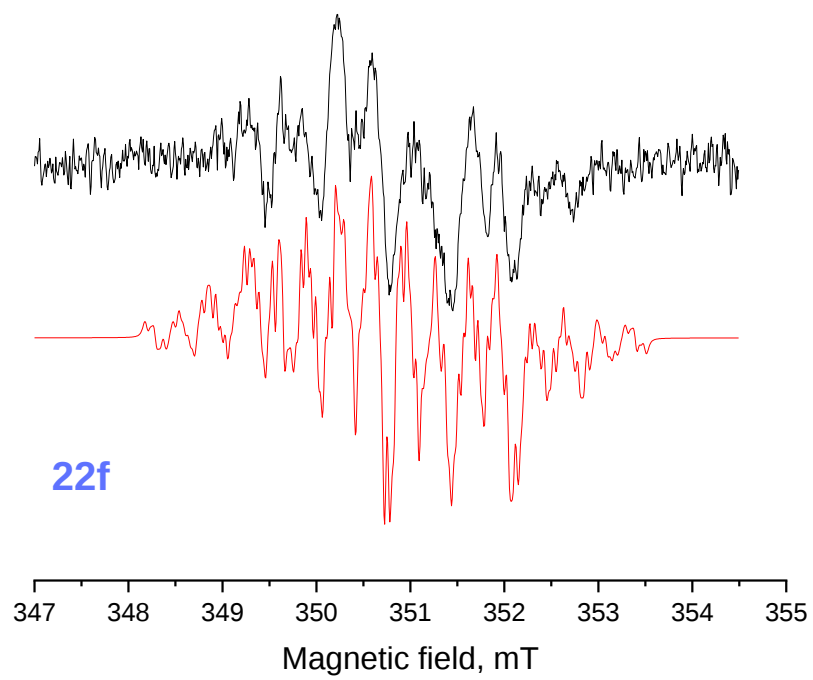
22a-o

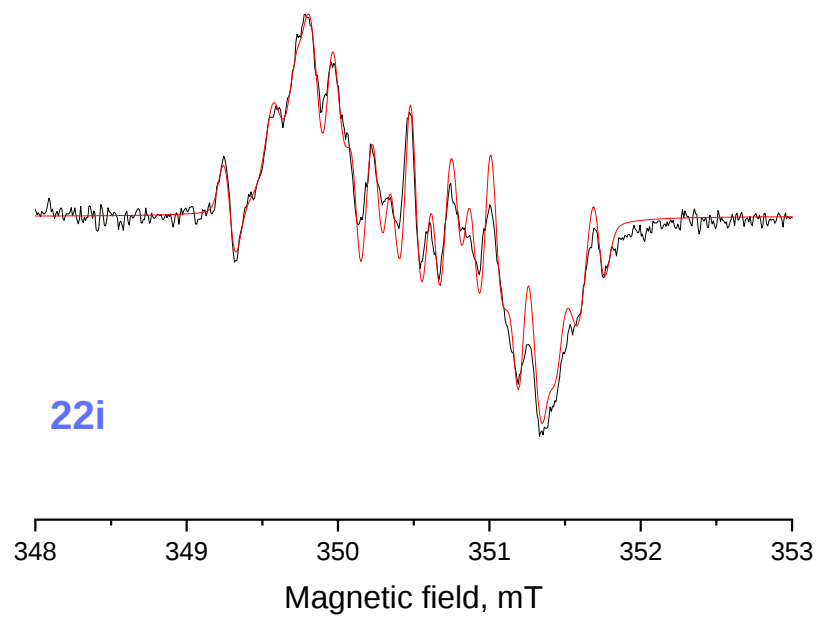
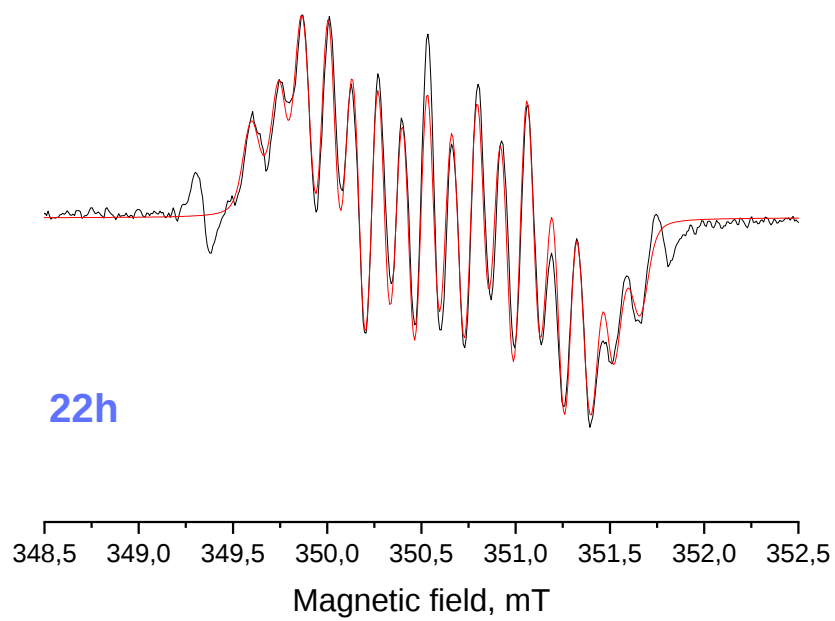
(black line – experimental spectra, red line – simulated spectra). ESR parameters used for the simulations are listed in Table 3 (See part 2.3.). The presented spectra were simulated suggesting that they represent superpositions of two spectra: spectrum of HPNs **22** + spectrum of its decomposition product –nitroxide radical with unknown structure ($g = 2.0059$, $A_N = 1.27$ mT). The impurity content was suggested to be 1-5 molar percent depending on the compound.

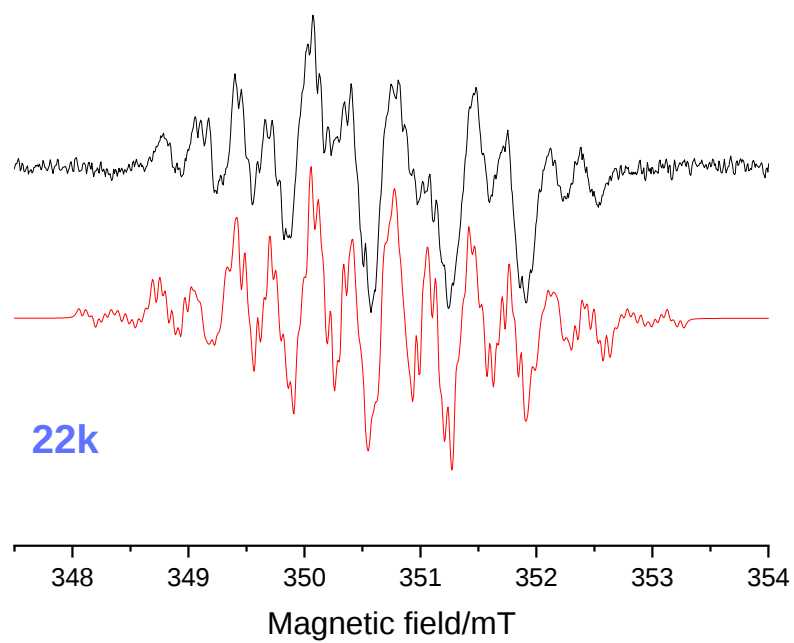
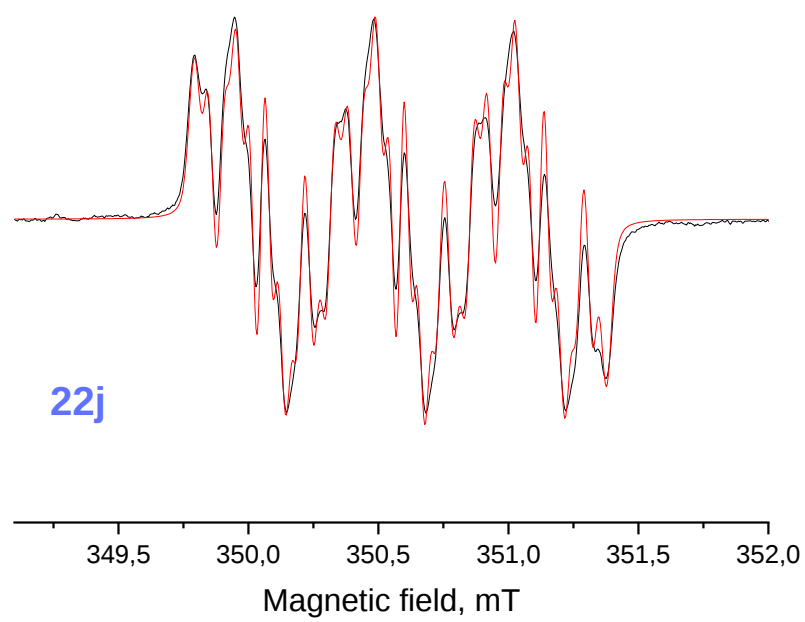


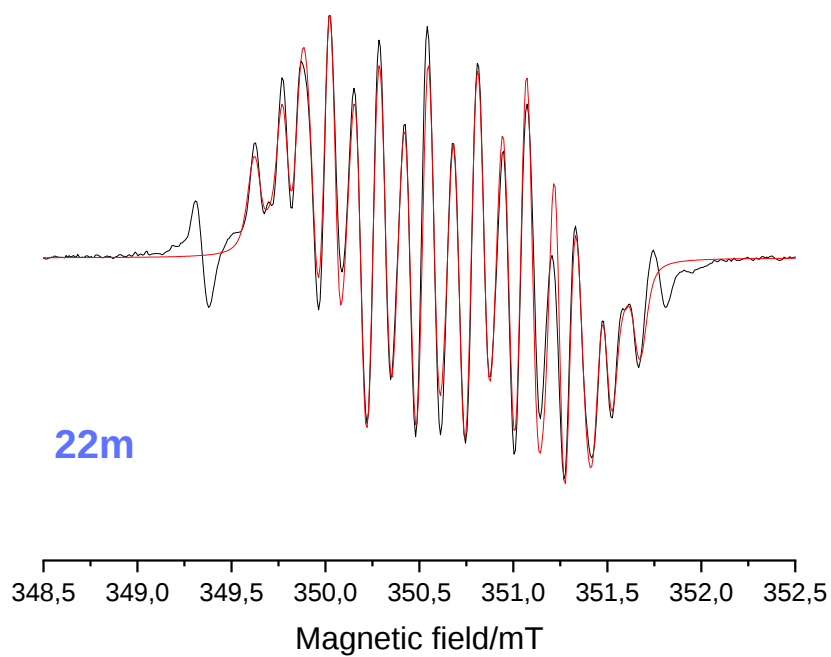
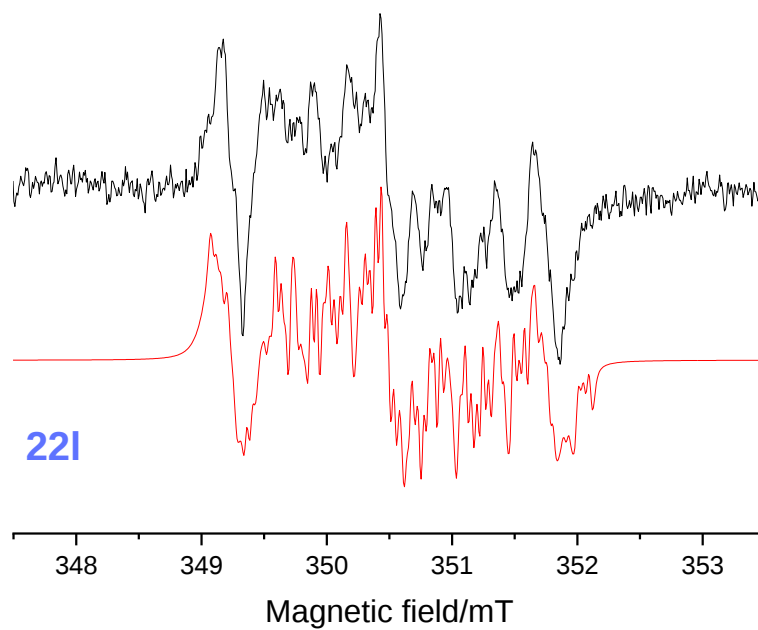


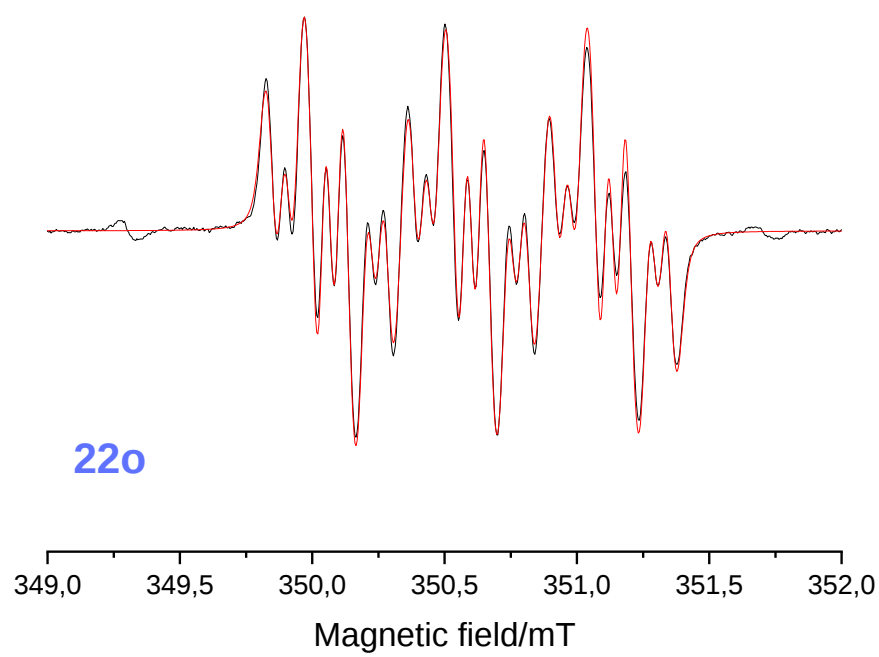
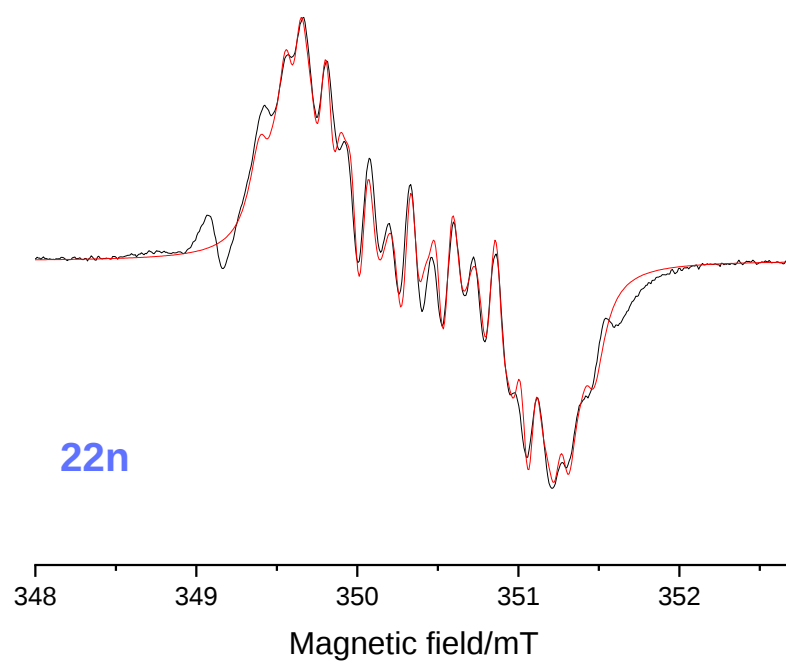












Molecular geometry and *hfs* constants for HPNs 22a-e,j,o calculated at UB3LYP/6-31G(d) level of theory, solvent effect was taken into account using CPCM model (solvent – toluene) (Figures S1-S5).

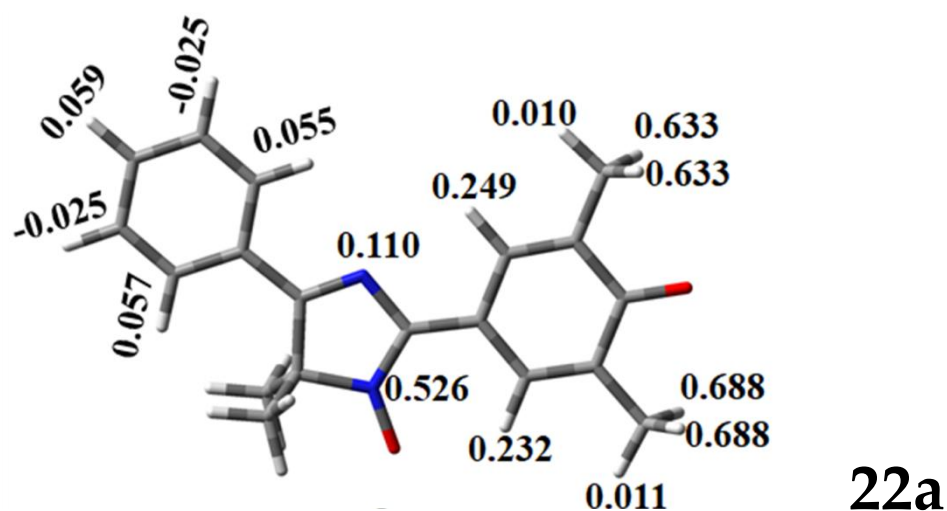


Figure S1.

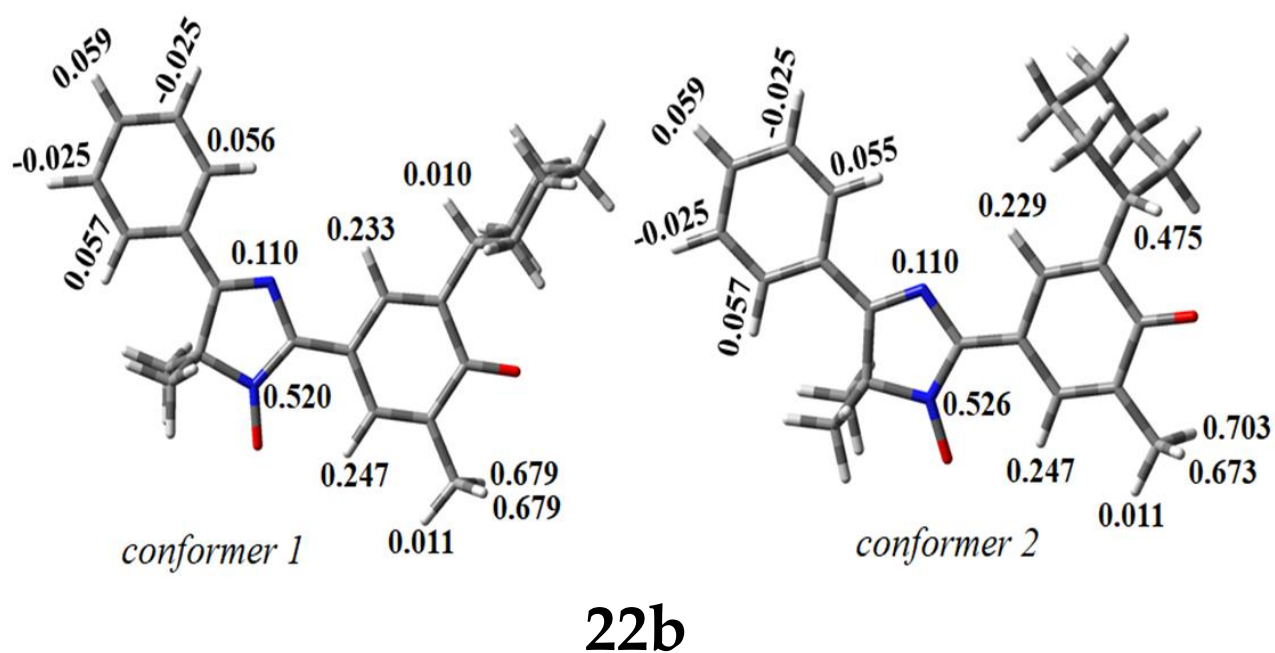
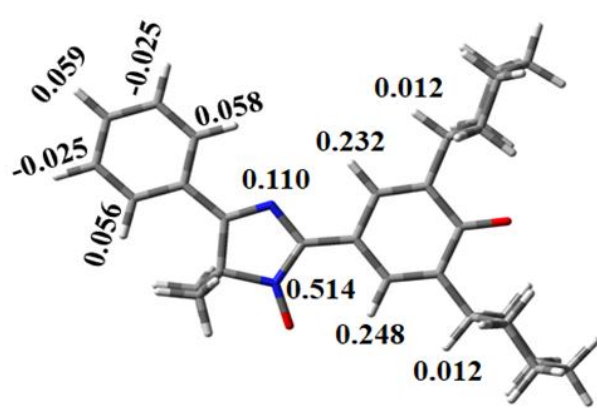
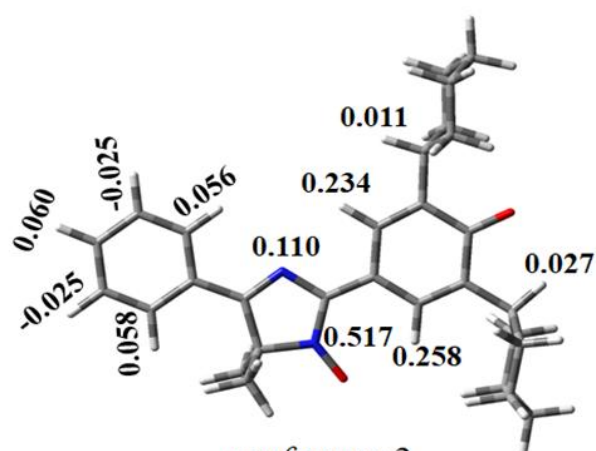


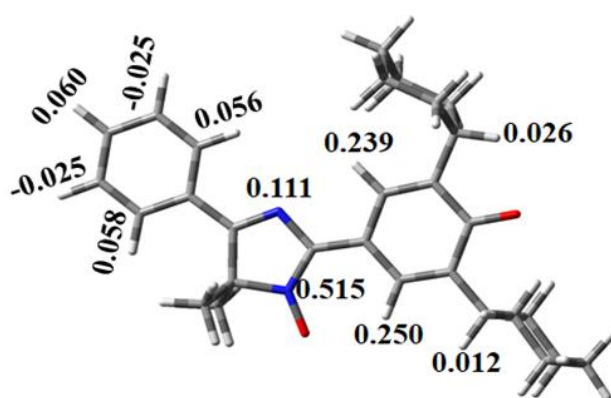
Figure S2



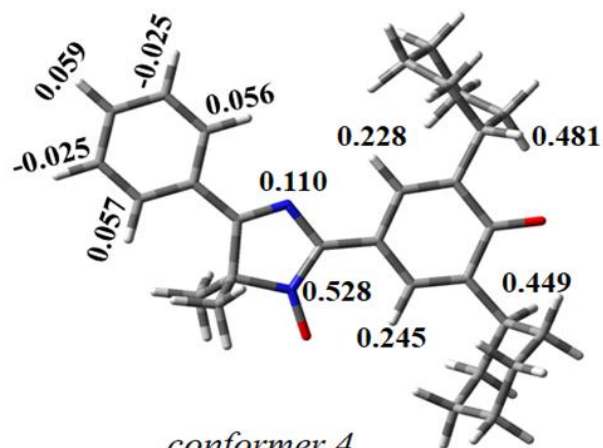
conformer 1



conformer 2



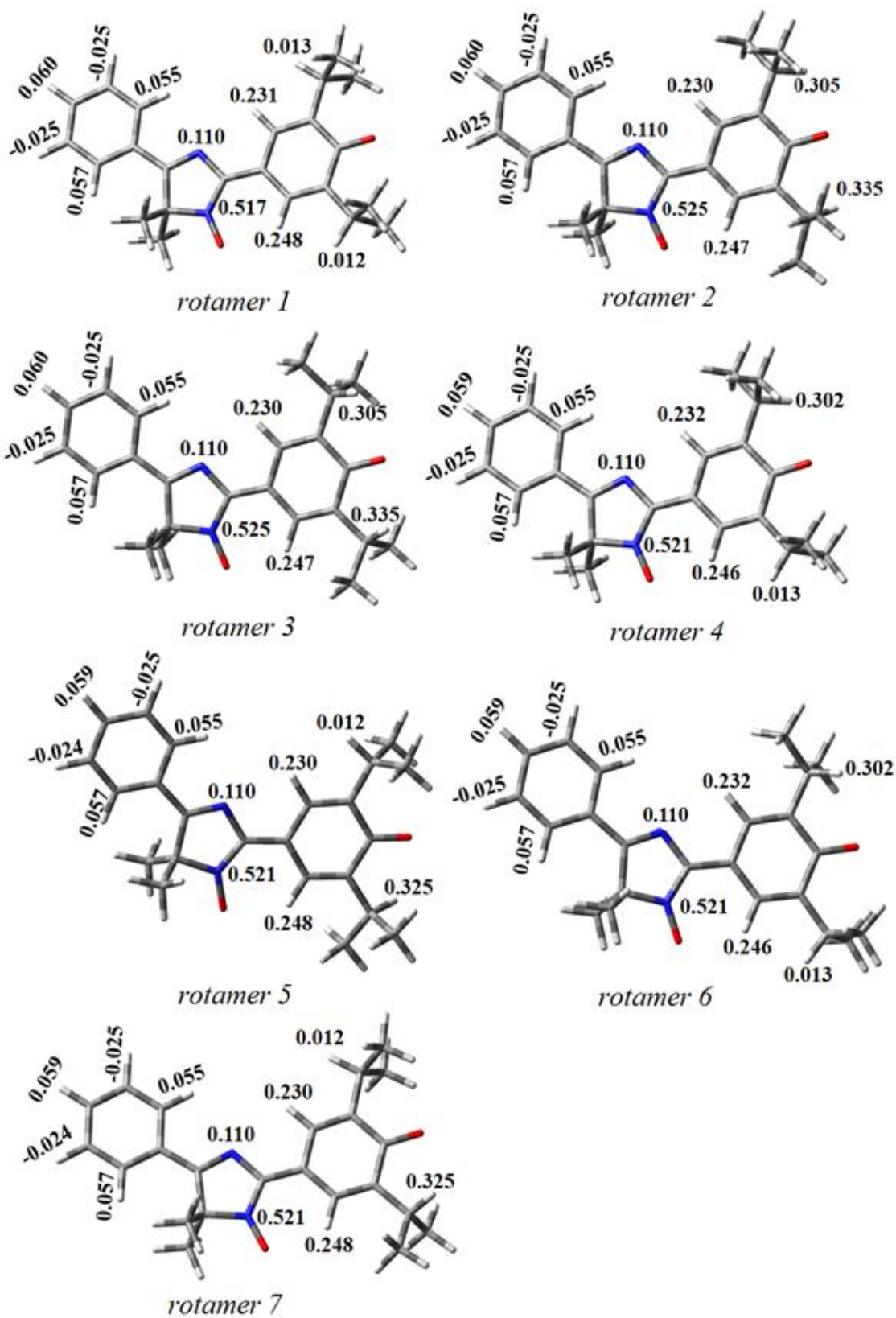
conformer 3



conformer 4

22d

Figure S3



22c

Figure S4

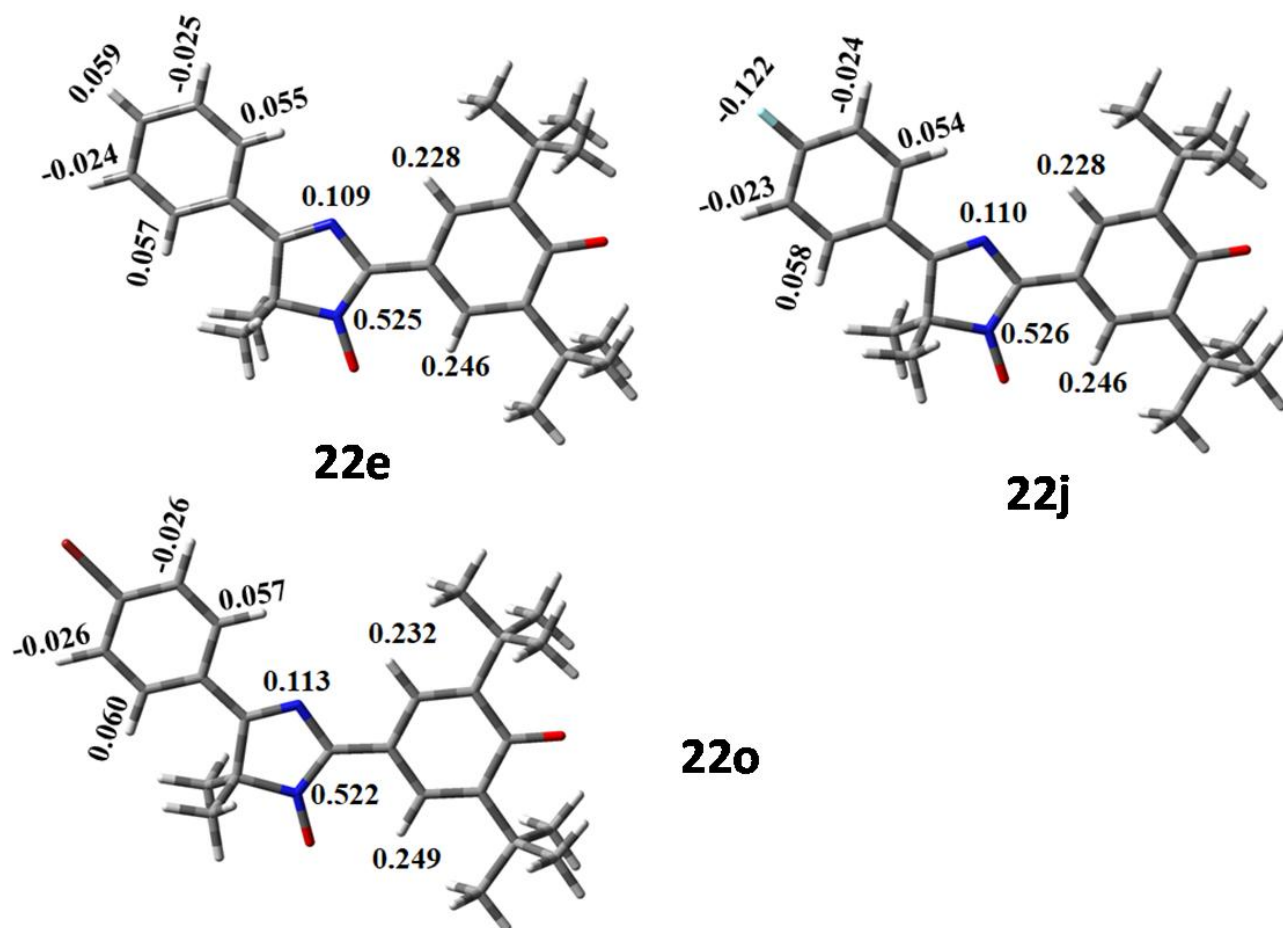


Figure S5

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