**Hydrazo coupling – an efficient transition-metal-free C–H functionalization of 8-hydroxyquinoline and phenol through base catalysis**

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**Materials and methods**

**Procedures for synthesis and products characterization**

**NMR spectra of the synthesized compounds**

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Materials and methods

All the starting materials were of reagent grade and higher purity, purchased from Acros (Belgium) and Sigma-Aldrich (USA) and used without additional purification. Solvents were dried and purified according to standard procedures; acetonitrile was purchased from PanReac and used without further purification. TLC was performed on Merck Kieselgel 60F_{254} (Germany) with UV visualization. Column chromatography was performed on silica gel 40–63 μm from Merck (Germany).

$^1$H and $^{13}$C NMR spectra (δ, ppm; $J$, Hz) were registered on an AMX III-400 spectrometer (Bruker BioSpin GMBH, Karlsruhe, Germany) with the working frequency of 400 MHz for $^1$H NMR (Me$_4$Si as an internal standard for organic solvents), 100.6 MHz for $^{13}$C NMR (with carbon-proton interaction decoupling). $^{15}$N NMR and 2D NMR spectra were registered on an AM-300 spectrometer (Bruker BioSpin GMBH, Karlsruhe, Germany) with the working frequency of 300 MHz for $^1$H NMR (Me$_4$Si as an internal standard for organic solvents), 75.5 MHz for $^{13}$C NMR (with carbon-proton interaction decoupling), 40.5 MHz for $^{15}$N NMR (with nitrogen-proton interaction decoupling) at 27°C. Proton and carbon shifts were additionally determined using HH and CH correlations – COSY, HSQC, HMBC (over ranges of 2 and 3 bonds: $^2$J$_{H-C-C}$, $^3$J$_{H-C-C-C}$).

High-resolution mass spectra (HRMS) were registered on a Bruker Daltonics micrOTOF-Q II hybrid quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI); measurements were done in positive ion mode. The voltage on the capillary was 4500 V; range of scanned masses, m/z 50-3000; external calibration (Electrospray Calibrant Solution; Fluka, Germany); nebulizer pressure: 0.4 bar; flow rate: 3 μl/min; nitrogen as dry gas (6 l/min); interface temperature: 180 °C. The samples were injected into the mass spectrometer chamber using a syringe injection or from the Agilent 1260 HPLC system equipped with an Agilent Poroshell 120 EC-C18 column (3.0×50 mm; 2.7 μm) and an identically packed security guard using an autosampler. The samples were in 50% methanol (LC-MS grade; Panreac, Spain) in water (MilliQ ultrapure water; Merck Millipore KGaA, Germany). The column was eluted with a gradient of acetonitrile (A) concentrations in water (B) with a flow rate of 400 μl/min in the following gradient parameters: 0-15% A for 6 min, 15-85% A for 1.5 min, 85-0% A for 0.1 min, and 0% A for 2.4 min.
Procedures for synthesis and products characterization

General method for gram-scale synthesis of 1a, b

A solution of 2.000 g of 8-hydroxyquinoline (13.8 mmol) and 21 mg of NaH (0.69 mmol, 80% grade) in 40 ml of THF in 100 ml flask was cooled with liq. N2 to approx. -5.0°C. A portion of azodicarboxylate ester was added (14.47 mmol) while stirring at room temperature. After 1.5 min the reaction mass began to heat up to 60°C and changed its color to light orange. The reaction mixture was kept stirring for 1.5 hours until it was complete according to the TLC detection (eluting system of CCl4 : dioxane (9:1) + 1% AcOH). The solvent was evaporated and the reaction mixture was partitioned in CH2Cl2 / saturated aqueous solution of NaHCO3. Organic layer was dried over Na2SO4, solvents were evaporated, the residue was dissolved in toluene and re-evaporated, and dried in vacuo.

Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a)

The product was obtained as a crème-colored solid according to the general procedure starting from 2.925 g of diisopropyl azodicarboxylate to give 4.773 g yield (99.7%).

1H NMR (DMSO-d6, δ, Hz): 9.91 (2×br.s, 1H, NH), 9.47 (2×br.s, 1H, OH), 8.87 (dd, J = 1.6 Hz, J = 4.2 Hz, 1H, CH-2), 8.31 (dd, J = 1.5 Hz, J = 8.3 Hz, 1H, CH-4), 7.56 (dd, J = 4.2 Hz, J = 8.3 Hz, 1H, CH-3), 7.52 (d, J = 8.8 Hz, 1H, CH-6), 7.38 (d, J = 8.8 Hz, 1H, CH-5), 4.85 (sept, 2H, J = 6.2, CH (i-Pr)), 1.21 (d, 12H, Me (i-Pr)).

13C NMR (DMSO-d6, δ, Hz): 156.87 & 154.59 (2×s, CO-NH (2 conformers)), 148.89 (s, C2), 148.68 (s, CO-N), 138.1 (s, C9), 136.38 (s, C4), 128.17 (s, C8), 127.48 (2×s, C5 & C10), 126.03 (s, C7), 122.46 (s, C3), 117.37 (s, C6), 69.98 & 69.00 (2×s, C (i-Pr)), 22.32 & 22.25 (2×s, Me (i-Pr)).

15N NMR (DMSO-d6, δ, Hz): 297.94 (s, N1), 119.18 (s, NH-CO).

HRMS of C17H21N3O5 (m/z): calculated for [M+H]+ 348.1554, found 348.1562.

Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b)

The product was obtained as a crème-colored solid according to the general procedure starting from 3.173 g of di-tert-butyl azodicarboxylate to give 5.170 g yield (99.9%).

1H NMR (DMSO-d6, δ, Hz): 9.73 (2×br.s, 1H, NH), 9.35 (2×br.s, 1H, OH), 8.86 (dd, J = 2.5 Hz, J = 4.2 Hz, 1H, CH-2), 8.50 (d, J = 8.4 Hz, 1H, CH-4), 7.61 (dd, J = 8.6 Hz, J = 4.1 Hz, 1H, CH-3), 7.51 (d, J = 8.2 Hz, 1H, CH-6), 7.08 (d, J = 8.2 Hz, 1H, CH-5), 1.46 & 1.41 & 1.19 (3×br.s, 18H, Me (t-Bu) (conformers)).
$^{13}$C NMR (DMSO-d$_6$, $\delta$, Hz): 155.27 & 154.00 (s, CO-NH (conformers)), 153.16 (s, CO-N), 148.11 (s, C2), 138.14 (s, C9), 132.30 (s, C4), 129.30 (s, C10), 126.96 (s, C8), 126.35 (s, C5), 125.87 (s, C7), 121.82 (s, C3), 110.39 (s, C6), 80.55 & 80.12 & 79.63 (3×s, C (t-Bu) (conformers), 28.02 & 27.74 (2×s, Me (t-Bu) (conformers)).

$^{15}$N NMR (DMSO-d$_6$, $\delta$, Hz): 299.3 (s, N1), 245.5 (s, NH-CO), 111.2 (s, N-CO).

HRMS of C$_{19}$H$_{25}$N$_3$O$_5$ ($m/z$): calculated for [M+H]$^+$ 376.1867, found 376.1867.

7-(1,2-Bis(tert-butoxycarbonyl)hydrazinyl)-8-hydroxyquinoline N-oxide (1c)

**Method 1:**

Starting 8-hydroxyquinoline N-oxide was synthesized according to the following protocol:

To a pre-cooled to ~0°C stirred solution of 0.500 g of 8-hydroxyquinoline (3.45 mmol) in methylene chloride a portion of 1.98 ml of $m$-CPBA (4.5 mmol, 70% solution) was added. The reaction was kept stirring at room temperature for 3 h, and during that period 8-hydroxyquinoline N-oxide formed the beige precipitate. The precipitate was filtered from the reaction mixture and washed three times with 15 ml of CH$_2$Cl$_2$. The resulting crude product mixture had traces of the starting 8-hydroxyquinoline and was applied on a silica gel column heterogeneously in CCl$_4$. The column was eluted in CCl$_4$ : dioxane (9:1) system with an additive of 1% acetic acid. The fraction containing the target product was concentrated giving yellowish crystals in 0.471 g (85%) yield and was stored in the dark at +4°C to prevent its decomposition. The spectral data corresponded with that described in the previous paper [T. Storz, R. Marti, R. Meier, P. Nury, M. Roeder and K. Zhang, *Org. Proc. Res. Dev.*, 2004, 8 (4), 663.].

Full amount of the synthesized 8-hydroxyquinoline N-oxide was subjected to the synthesis of the target product.

Product 1c was obtained as a crème-colored solid according to the general method for gram-scale synthesis of 1a, b starting from 0.705 g of di-tert-butyl azodicarboxylate to give 0.948 g yield (83%).

**Method 2:**

To a pre-cooled to ~0°C stirred solution of 0.500 g of 1b (1.33 mmol) in 5 ml of methylene chloride a portion of 0.300 g of $m$-CPBA (1.73 mmol) solution in 2 ml of methylene chloride was added dropwise. The reaction was stirred at room temperature for 5 h and the completion was monitored by the TLC in CCl$_4$ : dioxane (9:1) + 1% AcOH eluting system (N.B.: chloroform-ethanol eluting systems demonstrated identical R$_f$ for 1b and 1c). The reaction mixture was partitioned in CH$_2$Cl$_2$ / saturated aqueous solution of NaHCO$_3$. The organic layer
was dried over Na₂SO₄, solvents were evaporated, the residue was dissolved in CHCl₃ and applied on a silica gel column. The column was eluted in a gradient of ethanol (0 → 6%), target fractions were evaporated in vacuo to give 0.481 g (92%) of beige-colored solid product.

¹H NMR (DMSO-d₆, δ, Hz): 8.27 (d, J = 5.8 Hz, 1H, CH-2), 8.20 (br.s, 1H, NH), 8.50 (d, J = 5.9 Hz, 1H, CH-4), 7.60 (d, J = 8.3 Hz, 1H, CH-6), 7.29 (dd, J = 8.7 Hz, J = 6.1 Hz, 1H, CH-3), 7.01 (d, J = 8.5 Hz, 1H, CH-5), 1.46 & 1.45 & 1.35 (3×br.s, 18H, Me (t-Bu) (conformers)).

¹³C NMR (DMSO-d₆, δ, Hz): 155.60 (s, CO-NH), 154.53 (s, CO-N), 154.21 (s, C2), 138.1 (s, C9), 134.71 (s, C4), 130.17 (s, C7), 129.69 (s, C10), 128.59 (s, C8), 126.44 (s, C5), 120.88 (s, C3), 114.25 (s, C6), 80.80 & 81.96 (2×s, C (t-Bu)), 28.33 & 28.19 (2×s, Me (t-Bu) (2 conformers)).


**General method for synthesis of 1d-1h**

A solution of 0.100 g of di-tert-butyl azodicarboxylate (0.43 mmol) and 5.9 mg of sodium hydride (0.20 mmol, 90% grade) were mixed with an appropriate amount of a phenolic reagent (0.39 mmol) in 3 ml of THF while stirring at room temperature. The reaction mixture was kept stirring for 6 hours. The solvent was evaporated and the reaction mixture was partitioned in CH₂Cl₂ / saturated aqueous solution of NaHCO₃. Organic layer was dried over Na₂SO₄, solvents were evaporated, the residue was dissolved in toluene and re-evaporated, and dried in vacuo.

**Di-tert-butyl 1-(5-fluoro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1d)**

The product was obtained according to the general procedure starting from 0.064 g of 5-fluoro-8-hydroxyquinoline (0.39 mmol). The resulting crude product was applied on a silica gel column, the column was eluted in CCl₄ : dioxane (9:1) system with an additive of 1% acetic acid. The fraction containing the target product was concentrated in vacuo to give 0.108 g of 1d as a green-colored solid (70% yield).

¹H NMR (DMSO-d₆, δ, Hz): 9.95 (br.s, 2H, NH + OH), 8.86 (d, J = 4.2 Hz, 1H, CH-2), 8.25 (d, J = 8.4 Hz, 1H, CH-4), 7.47 (s, 1H, CH-6), 7.31 (dd, J = 8.4 Hz, J = 4.2 Hz, 1H, CH-3), 1.42 & 1.40 (2×br.s, 18H, Me (t-Bu)).

HRMS of C₁₉H₂₄FN₃O₅ (m/z): calculated for [M+H]^+ 394.1773, found 394.1764.
Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e)

The product was obtained according to the general procedure starting from 0.071 g of 5-chloro-8-hydroxyquinoline (0.39 mmol). The resulting crude orange-colored product was applied on a silica gel column, the column was eluted in CCl₄ : dioxane (9:1) system with an additive of 1% acetic acid. The fraction containing the target product was concentrated in vacuo to give 0.156 g of 1e as a beige-colored solid (97% yield).

$^1$H NMR (DMSO-d₆, δ, Hz): 9.92-9.38 (br.s, 2H, NH + OH), 8.86 (dd, J = 1.0 Hz, J = 4.1 Hz, 1H, CH-2), 8.40 (dd, J = 8.4 Hz, J = 1.5 Hz, 1H, CH-4), 7.64 (dd, J = 8.4 Hz, J = 4.2 Hz, 1H, CH-3), 7.56 (s, 1H, CH-6), 1.42 & 1.39 (2×br.s, 18H, Me (t-Bu)).

$^{13}$C NMR (DMSO-d₆, δ, Hz): 155.74 (s, CO-NH), 153.31 (s, CO-N), 148.65 (s, C2), 140.25 (s, C9), 132.31 (s, C4), 127.03 (br.s, C5+C7), 125.94 (s, C8), 125.06 (s, C6), 122.75 (s, C3), 115 (s, C10), 80.89 & 80.24 (2×s, C (t-Bu)), 28.50 & 28.28 (2×s, Me (t-Bu)).

HRMS of C₁₉H₂₄ClN₃O₅ (m/z): calculated for [M+H]+ 410.1477, found 410.1480; calculated for [M+Na]+ 432.1297, found 432.1302.

Di-tert-butyl 1-(1-hydroxynaphth-2-yl)hydrazinyl-1,2-dicarboxylate (1f)

The product was obtained according to the general procedure starting from 0.057 g of 1-naphthol (0.39 mmol). The resulting crude orange-colored product was applied on a silica gel column, the column was eluted in CHCl₃ : EtOH (97:3) system. The fraction containing the target product was concentrated in vacuo to give 0.124 g of 1f as beige viscous liquid (80% yield).

$^1$H NMR (DMSO-d₆, δ, Hz): 9.90-9.70 (br.s, 2H, NH+OH), 8.29 (dd, J = 0.8 Hz, J = 9.0 Hz, 1H, CH-8), 8.05 (d, J = 8.2 Hz, 1H, CH-5), 7.62-7.52 (m, 3H, CH-6+CH-7+CH-8), 7.43 (d, 1H, J = 7.3 Hz, CH-3), 7.34 (d, 1H, , J = 7.3 Hz, CH-2), 1.47 & 1.26 (2×s, 18H, Me (t-Bu)).

HRMS of C₂₀H₂₆N₂O₅ (m/z): calculated for [M+Na]+ 397.1734, found 397.1740.

Tetra-tert-butyl N,N’-(4-hydroxynaphthalene-1,3-diyl)-bis-(hydrazinyl-1,2-dicarboxylate) (1g)

The product was obtained according to the general procedure starting from 0.029 g of 1-naphthol (0.20 mmol). The resulting crude orange-colored product was applied on a silica gel column, the column was eluted in CHCl₃. The fraction containing the target product was concentrated in vacuo to give 0.099 g of 1g as yellowish viscous liquid (84% yield).

$^1$H NMR (DMSO-d₆, δ, Hz): 9.94-9.29 (m, 3H, 2×NH + OH), 8.22 (d, J = 7.5 Hz, 1H, CH-5), 8.01 (s, 1H, CH-3), 7.54 (m, 3H, CH-6 + CH-7 + CH-8), 1.46 & 1.43 & 1.40 & 1.30 & 1.22 (5×s, 36H, Me (t-Bu) (conformers)).
\(^{13}\)C NMR (DMSO-d\(_6\), \(\delta\), Hz): 158.25 (s, CO-NH), 155.38 (s, CO-NH) 154.14 (s, CO-N), 153.59 (s, CO-N), 148.35 (s, Cl), 130.45 (s, C4), 126.79 (s, C5), 124.91 (s, C6), 123.32 (s, C7), 122.68 (s, C8), 122.08 (s, C10), 121.69 (s, C9), 81.22 & 80.35 & 79.47 & 78.82 (4\(\times\)s, C (t-Bu)), 28.08 & 27.91 & 27.66 (3\(\times\)s, Me (t-Bu)).

HRMS of C\(_{30}\)H\(_{44}\)N\(_4\)O\(_9\) (m/z): calculated for [M+Na]\(^+\) 627.3000, found 627.3003; calculated for [M+K]\(^+\) 643.2740, found 643.2739.

**Di-tert-butyl 1-(4-chloro-1-hydroxynaphth-2-yl)hydrazinyl-1,2-dicarboxylate (1h)**

The product was obtained according to the general procedure starting from 0.070 g of 4-chloro-1-naphthol (0.39 mmol). The resulting crude orange-colored product was washed with CCl\(_4\) and the precipitate was collected and dried in vacuo to give 0.153 g of 1h as an off-white solid (95% yield).

\(^1\)H NMR (DMSO-d\(_6\), \(\delta\), Hz): 9.96 (br.s, 1H, NH), 9.70 (br.s, 1H, OH), 8.29 (dd, \(J = 0.8\) Hz, \(J = 9.0\) Hz, 1H, CH-8), 8.09 (d, \(J = 8.2\) Hz, 1H, CH-5), 7.71 (ddd, \(J = 6.9\) Hz, \(J = 8.2\) Hz, \(J = 1.0\) Hz, 1H, CH-6), 7.63 (dd, 1H, \(J = 6.9\) Hz, \(J = 9.0\) Hz, \(J = 1.0\) Hz, CH-7), 7.43 (s, 1H, CH-3), 1.44 & 1.30 (2\(\times\)s, 18H, Me (t-Bu)).

\(^{13}\)C NMR (DMSO-d\(_6\), \(\delta\), Hz): 157.57 (s, CO-NH), 153.38 (s, CO-N), 148.65 (s, C8), 130.17 (s, C9), 128.34 (s, C6), 128.10 (s, C10), 126.59 (s, C7), 126.43 (s, C5), 125.83 (s, C4), 123.48 (s, C), 123.27 (s, C8), 119.65 (s, C2), 81.53 & 81.46 (2\(\times\)s, C (t-Bu)), 27.87 & 27.69 (2\(\times\)s, Me (t-Bu)).

HRMS of C\(_{20}\)H\(_{25}\)ClN\(_2\)O\(_5\) (m/z): calculated for [M+NH\(_4\)]\(^+\) 426.1790, found 426.1797; calculated for [M+Na]\(^+\) 431.1344, found 431.1350; calculated for [M+K]\(^+\) 447.1084, found 447.1089.

**Di-tert-butyl 1-(8-(tert-butyldiphenylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1i)**

A solution of 1 g of compound 1b (2.66 mmol) in 10 ml of pyridine in 50 ml flask was treated with 0.751 ml of tert-butyldiphenylsilyl chloride (2.93 mmol). The reaction was set at 37\(^\circ\)C overnight. The solvent was evaporated and the reaction mass was quenched with saturated aqueous solution of NaHCO\(_3\), partitioned in CH\(_2\)Cl\(_2\)/H\(_2\)O. Organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was evaporated. The residue was diluted with toluene and concentrated in vacuo, applied on a silica gel column (20 \(\times\) 200 mm) and eluted in CCl\(_4\) : dioxane (9:1) eluting system with an additive of 1% acetic acid. The fraction containing the target product was concentrated to give 1.625 g of 1i as an off-white solid (90% yield).
$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.73-9.30 (2×br.s, 1H, NH), 8.65 (br.s, 1H, CH-2), 8.40 (br.s, 1H, CH-4), 7.73 (d, J = 7.3 Hz, 4H, o-Ph), 7.68 (m, 1H, CH-6), 7.68 (dd, J = 8.3 Hz, J = 3.8 Hz, 1H, CH-3), 7.35 (m, 7H, CH-3 + m-Ph + p-Ph), 6.95 (d, J = 8.2 Hz, 1H, CH-5), 1.44 & 1.39 & 1.14 (3×br.s, 18H, Me (t-Bu) (conformers)), 1.10 (s, 9H, 3×Me (t-Bu in TBDPS)).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 155.25 (s, CO-NH), 150.96 (s, CO-N), 148.62 (s, C2), 140.41 (s, C9), 134.69 & 134.44 (2×s, o-Ph (2 conformers)), 133.21 (s, C4), 131.85 (s, t-Ph), 129.72 (s, m-Ph), 129.12 (s, C5), 127.68 & 127.45 (2×s, m-Ph (2 conformers)), 126.28 (s, C10), 125.89 (s, C7), 121.67 (s, C3), 115.74 (s, C6), 80.71 & 79.73 (2×s, C (t-Bu)), 27.99 & 27.72 (2×s, Me (t-Bu) (2 conformers)), 26.58 (s, 3×Me (t-Bu of TBDPS)), 19.58 (s, C (t-Bu of TBDPS)).

HRMS of C$_{235}$H$_{43}$N$_3$O$_5$Si (m/z): calculated for [M+H]$^+$ 614.3045, found 614.3039.

Di-tert-butyl 1-(8-(tert-butyldimethylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1j)

A solution of 1.000 g of 1b (2.66 mmol) in 20 ml of pyridine was treated with 0.442 g of tert-butyldimethylsilyl chloride (2.93 mmol) at 37°C for 5 h. The reaction was quenched with the saturated aqueous solution of NaHCO$_3$, the solvent was evaporated and the reaction mass was partitioned in CH$_2$Cl$_2$ / saturated aqueous solution of NaHCO$_3$. Organic layer was dried over Na$_2$SO$_4$, evaporated of solvents, dissolved in CCl$_4$ and applied on a silica gel column. The column was eluted in CCl$_4$, target fractions were evaporated and re-evaporated in vacuo to give 1.080 g of the off-white solid product (83% yield).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.76-9.33 (2×br.s, 1H, NH), 8.86 (dd, J = 1.4 Hz, J = 4.1 Hz, 1H, CH-2), 7.54 (m, 2H, CH-4 + CH-5), 7.08 (m, 2H, CH-3 + CH-6), 1.44 & 1.41 & 1.17 (3×br.s, 18H, Me (t-Bu) (conformers)), 1.02 (s, 9H, 3×Me (t-Bu in TBDMS)), 0.22 (s, 9H, 3×Me (Me in TBDMS)).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 155.35 (s, CO-NH), 151.64 (s, CO-N), 148.73 (s, C2), 140.87 (s, C9), 132.11 (s, C4), 128.87 (s, C10), 128.17 (s, C8), 126.36 (s, C5), 125.82 (s, C7), 121.67 (s, C3), 116.72 (s, C6), 80.69 & 79.74 (2×s, C (t-Bu)), 28.03 & 27.76 (2×s, Me (t-Bu) (2 conformers)), 25.75 (s, 3×Me (t-Bu of TBDMS)), 18.50 (s, C (t-Bu in TBDMS)), -3.96 (s, 2×Me (Me of TBDMS)).

HRMS of C$_{25}$H$_{39}$N$_3$O$_5$Si (m/z): calculated for [M+H]$^+$ 490.2732, found 490.2722.

Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k)

A solution of 1 g of compound 1b (2.66 mmol) in 10 ml of pyridine in 50 ml flask was treated with 0.340 ml benzoyl chloride (2.93 mmol). The reaction was set at 37°C overnight. The
solvent was evaporated and the reaction mass was quenched with saturated aqueous solution of NaHCO$_3$, partitioned in CH$_2$Cl$_2$/H$_2$O. Organic layer was dried over Na$_2$SO$_4$ and the solvent was evaporated. The residue was diluted with toluene and concentrated in vacuo, applied on a silica gel column (20 × 200 mm) and eluted in CCl$_4$ : dioxane (9:1) eluting system with an additive of 1% acetic acid. The fraction containing the target product was concentrated as an off-white solid in 1.140 g yield (90%).

$^1$H-NMR (DMSO-d$_6$, δ, Hz): 10.02-9.40 (2×br.s., 1H, NH), 8.90 (dd, $J = 1.33$ Hz, $J = 4.2$ Hz, 1H, CH-2), 8.58 (m, 1H, CH-4), 8.24 (dd, $J = 1.41$ Hz, $J = 8.48$ Hz, 2H, o-Bz), 8.01-7.48 (m, 6H, CH-3, CH-6, CH-5, m-Bz, p-Bz), 1.48 & 1.44 & 1.25 (3×br.s, 18H, Me (t-Bu)).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 164.61 (s, CO (Bz)) 155.35 (CONH), 150.77 (s, CO-N), 146.50 (s, C2), 140.46 (s, C9), 137.00 (s, C4), 134.07 (s, p-Bz), 132.79 (C7), 132.46 (s, C10), 129.97 (s, o-Bz), 129.22 (s, C5), 129.00 (s, m-Bz), 128.82 (s, C8), 128.51 (s, i-Bz), 126.14 (s, C-7), 122.16 (s, C3), 121.35 (s, C6), 81.20 & 80.00 (2×s, C (t-Bu)), 28.00 & 27.70 (2×s, Me (t-Bu) (2 conformers)).

HRMS of C$_{26}$H$_{29}$N$_3$O$_6$ (m/z): calculated for [M+H]$^+$ 480.2129, found 480.2128; calculated for [M+Na]$^+$ 502.1949, found 502.1946; calculated for [M+K]$^+$ 518.1688, found 518.1686.

**General method for gram-scale synthesis of 2a, b**

A solution of 0.500 g of phenol (5.31 mmol) and 8.0 mg of NaH (0.27 mmol, 80% grade) in 10 ml of THF in 50 ml flask was cooled with liq. N$_2$ to approx. -5.0°C. A portion of azodicarboxylate ester was added (5.57 mmol) while stirring at room temperature. The reaction mass changed its color to dark orange and was kept stirring for 1.5 hours more. The solvent was evaporated and the reaction mass was partitioned in CH$_2$Cl$_2$ / saturated aqueous solution of NaHCO$_3$. Organic layer was dried over Na$_2$SO$_4$, evaporated of solvents, re-evaporated with toluene and dried in vacuo. The organic layer was applied on a silica gel column and eluted in chloroform. Products were obtained as colorless solids.

**Diisopropyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2a)**

The product was obtained as a colorless solid according to the general procedure starting from 1.095 ml of diisopropyl azodicarboxylate to give 1.416 g yield (90%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.71 & 9.37 (2×br.s., 1H, NH (2 conformers)), 9.37-9.71 (br.s, 1H, OH), 7.13 (d, $J = 8.7$ Hz, 2H, CH-2 & CH-6), 6.72 (d, $J = 8.8$ Hz, 2H, CH-3 & CH-5), 4.82(2×sept, $J = 6.1$, 2H, CH (i-Pr)), 1.21 & 1.18 (2×d, 12H, Me (i-Pr)).
$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 155.71 (s, C4), 155.55 (2×s, CO-NH), 154.25 (s, CO-N), 133.9 (s, C1), 125.98 (br.s, C2 & C6), 114.9 (s, C3 & C5), 69.36 & 68.34 (2×s, C (i-Pr)), 21.87 & 21.77 (2×s, Me (i-Pr)).

HRMS of C$_{14}$H$_{20}$N$_2$O$_5$ (m/z): calculated for [M+H]$^+$ 297.1445, found 297.1442; calculated for [M+Na]$^+$ 319.1264, found 319.1256; calculated for [M+K]$^+$ 335.1004, found 335.0998.

**Di-tert-butyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2b)**

The product was obtained as a colorless solid according to the general procedure starting from 1.284 g of di-tert-butyl azodicarboxylate to give 1.551 g yield (90%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.47 & 9.37 & 9.06 (3×br.s, 1H, NH+OH (conformers)), 7.09 (d, J = 8.7 Hz, 2H, CH-2 & CH-6), 6.69 (d, J = 8.8 Hz, 2H, CH-3 & CH-5), 1.42 & 1.39 (2×s, 18H, Me (t-Bu)).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 155.60 (s, C4), 155.53 (s, CO-NH), 154.00 (s, CO-N), 134.67 (s, C1), 126.49 (s, C2 & C6), 114.9 (br.s, C3 & C5), 80.75 & 79.96 (2×s, C (t-Bu)), 28.54 & 28.30 (2×s, Me (t-Bu)).

HRMS of C$_{16}$H$_{24}$N$_2$O$_5$ (m/z): calculated for [M+H]$^+$ 325.1758, found 325.1763; calculated for [M+Na]$^+$ 347.1577, found 347.1577; calculated for [M+K]$^+$ 363.1317, found 363.1315.

**Di-tert-butyl 1-(4-hydroxy-2,5-dimethylphenyl)hydrazinyl-1,2-dicarboxylate (2c)**

The product was obtained as a colorless solid according to the general procedure starting from 0.1 g of di-tert-butyl azodicarboxylate to give 0.310 g yield (93%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.46 & 9.39 (2×br.s, 1H, NH (conformers)), 9.20 (s, 1H, OH), 7.00 (s, 1H, CH-5), 6.55 (s, 1H, CH-2), 2.09 & 2.04 (2×br.s, 6H, 2×Me), 1.42 & 1.31 (2×s, 18H, Me (t-Bu)).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 155.07 (s, CO-NH), 154.22 (s, CO-N), 153.64 (s, C4), 133.66 (s, C2), 132.53 (s, C1), 129.27 (s, C6), 128.93 (s, C5), 115.51 (s, C3), 79.85 & 79.24 (2×s, C (t-Bu)), 28.07 & 27.83 (2×s, Me (t-Bu)), 17.13 (a, 2-Me), 15.53 (a, 5-Me).

HRMS of C$_{16}$H$_{24}$N$_2$O$_5$ (m/z): calculated for [M+H]$^+$ 353.2071, found 353.2073; calculated for [M+Na]$^+$ 375.1890, found 375.1891.

**4-Hydroxyphenylhydrazine (3)**
A dozen of 4Å molecular sieves were placed into a flask with 2.5 g of 2b (7.71 mmol) in CH₂Cl₂ (15 ml), and the reaction mixture was treated with 1.142 ml BF₃ · Et₂O (9.25 mmol) at room temperature. Gases were released and after 60 min the reaction mass was diluted with MeOH (10 ml) and transferred into a new flask. Solvents and an excess of the starting reagent were evaporated in vacuo and re-evaporated to yield 0.956 g of colorless solid product 4 (100% yield).

¹H NMR (DMSO-d₆, δ, Hz): 9.69 (br.s, 3H, NH + NH₂ (one of two) + OH), 7.18 (d, J = 8.8 Hz, 2H, CH-3 + CH-5), 7.08 (t (equal intensity), J_H, 15N = 51.1 Hz, 1H, NH₂ – accumulated residual signal of the NH₂-NH- fragment protons coupled to the corresponding ¹⁵N atoms (natural abundance)), 6.90 (d, J = 8.8 Hz, 2H, CH-2 + CH-6).

¹³C NMR (DMSO-d₆, δ, Hz): 157.26 (s, C4), 124.31 (s, C3+C5), 122.10 (s, C1), 116.16 (s, C2+C6).

HRMS of C₆H₈N₂O (m/z): calculated for [M+H]⁺ 125.0709, found 125.0713.

7-Hydrazino-8-hydroxyquinoline (4)

A dozen of 4Å molecular sieves were placed into a flask with 0.5 g of 1b (1.33 mmol) in CH₂Cl₂ (5 ml), and the reaction mixture was treated with 0.165 ml BF₃ · Et₂O (1.33 mmol) at room temperature. The reaction mixture changed its color to maroon and gas was released. After 30 min the reaction mass was diluted with MeOH (2 ml) and transferred into a new flask. Solvents and an excess of the starting reagent were evaporated in vacuo and re-evaporated to yield 190 mg of maroon-colored solid product 4 (98% yield).

¹H NMR (DMSO-d₆, δ, Hz): 10.63 (br.s, 2H, NH + OH), 8.95 (d, J = 4.5 Hz, 1H, CH-2), 8.80 (d, J = 8.4 Hz, 1H, CH-4), 7.76 (dd, J = 4.5 Hz, J = 8.5 Hz, 1H, CH-3), 7.52 (d, J = 8.3 Hz, C5), 7.52 (d, J = 8.3 Hz, C6).

HRMS of C₉H₉N₃O (m/z): calculated for [M+H]⁺ 176.018, found 176.020.

General method of “one-pot” synthesis of hydrazones

A dozen of 4Å molecular sieves were placed into a flask with 0.275 g of 1b (0.73 mmol) in CH₂Cl₂ (5 ml). The flask was flushed with Ar to avoid oxidation of the product. The appropriate amount of the corresponding aldehyde (0.95 mmol) was added and the reaction mixture was treated with 0.181 ml BF₃ · Et₂O (1.46 mmol) at room temperature while stirring. The reaction mixture changed its color to yellow and later to maroon; gases were released. After 30 min the reaction mass was quenched with MeOH (2 ml), transferred into a new flask, solvents and by-products were evaporated, and re-evaporated from toluene to yield deeply colored products. The products are insoluble in chloroalkanes (CH₂Cl₂, CHCl₃, or CCl₄) but readily
soluble in alcohols and acetone. The purification of products from the excess of aldehyde was achieved by flash chromatography using dry loading of the reaction mixture: a portion of the reaction mass residue was adsorbed from ethanolic solution into 5 cm³ of silica gel in the flask, carefully evaporated to dryness and then applied onto a Shott’s filter with three times the amount of silica gel. The separation was performed using the dry column vacuum chromatography (DCVC), first eluted with 50 ml of choroform to allow the aldehydes to pass through the column, and then eluted with ethanol to collect the pure product compound. Targets fractions were evaporated resulting in dark red-colored products.

**7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a)**

The product was synthesized according to the general procedure starting from 0.133 ml of benzaldehyde and isolated as a maroon-colored solid in 0.181 g of 5a (94% yield).

¹H NMR (DMSO-d₆, δ, Hz): 10.91 (br.s. 1H, NH), 9.44 (d, J = 8.6 Hz, 1H, CH-2), 9.03 (d, J = 3.7 Hz 1H, CH-4), 8.24 (s, 1H, CH=N), 8.00 (m, 1H, C5), 7.72 (d, 2H, J = 7.5 Hz, o-Ph), 7.65 (d, C6) 7.45-7.34 (m, 4H, o-Ph + m-Ph + C3).

¹³C NMR: 145.99 (s, C2), 144.06 (s, C9), 143.64 (s, C4), 141.06 (s, C4), 140.18 & 139.69 (s, CH=N (2 conformers)),135.02 (s, C6), 134.18 (s, i-Ph), 129.57 (s, C8), 128.54 (s, m-Ph), 128.13 (s, C7), 125.92 (s, o-Ph ), 122.10 (s, C10), 119.69 (s, C3), 118.30 (s, C5) 118.24 (2×s, p-Ph), 110.30 (s, C7).

¹⁵N NMR (DMSO-d₆, δ, Hz): 323.0 (s, N1), 138.8 (s, NH).

HRMS of C₁₆H₁₃N₃O (m/z): calculated for [M+H]+ 264.1131, found 264.1136.

**7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-hydroxyquinoline (5b)**

**Method 1**

The product was synthesized as a maroon-colored solid according to the general procedure starting from 0.100 ml of o-fluorobenzaldehyde to give 0.111 g of 5b (54% yield).

**Method 2**

To a solution of 0.00 g of 5h (0.58 mmol) in 5 ml of pyridine a portion of 0.107 g of ammonium fluoride (2.89 mmol) was added while stirring at room temperature. The reaction was kept stirring overnight. The separation was performed via flash chromatography using dry loading of the reaction mixture and was purified the same way as described in “General method of “one-pot” synthesis of hydrazones”: first, the Schott filter was eluted with 20 ml of choroform, then the pure product compound was eluted with ethanol and collected. Target fractions were evaporated resulting in 0.80 g of the burgundy-colored solid product (49% yield).
HRMS of C_{16}H_{12}FN_{3}O (m/z): calculated for [M+H]^+ 282.1037, found 282.1034.

7-(2-ortho-Chlorobenzylidenohydrazinyl)-8-hydroxyquinoline (5c)
The product was synthesized as a maroon-colored solid according to the general procedure starting from 0.107 ml of o-chlorobenzaldehyde to give 0.153 g of 5c (70% yield).
HRMS of C_{16}H_{12}ClN_{3}O (m/z): calculated for [M+H]^+ 298.0742, found 298.0745.

7-(2-para-Methoxybenzylidenohydrazinyl)-8-hydroxyquinoline (5d)
The product was synthesized as a maroon-colored solid according to the general procedure starting from 0.116 ml of p-methoxybenzaldehyde to give 0.183 g of 5d (85% yield).
HRMS of C_{17}H_{15}N_{3}O_{2} (m/z): calculated for [M+H]^+ 294.1237, found 294.1237.

7-(2-para-Nitrobenzylidenohydrazinyl)-8-hydroxyquinoline (5e)
The product was synthesized as a maroon-colored solid according to the general procedure starting from 0.144 mg of para-nitrobenzaldehyde to give 0.203 g of 5e (90% yield).
HRMS of C_{16}H_{12}N_{4}O_{3} (m/z): calculated for [M+H]^+ 309.0982, found 309.0982.

7-(2-meta,para-Dibromobenzylidenohydrazinyl)-8-hydroxyquinoline (5f)
The product was synthesized as a maroon-colored solid according to the general procedure starting from 0.252 g of m,p-dibromobenzaldehyde to give 0.268 g of 5f (87% yield).

^1H NMR (DMSO-d$_6$, δ, Hz): 10.87 (br.s, 1H, NH), 9.08 (d, J 8.0 Hz, 1H, CH-2), 9.10 (d, J 3.6 Hz, 1H, CH-4), 8.10 (s, 1H, CH=N), 8.03 (s, 1H, Ar-6), 7.81 (m, 1H, CH-3), 7.75 (d, J 8.2 Hz, 1H, Ar-3), 7.62 (d, J 8.2Hz, 1H, Ar-2), 7.55 (d, J 8.4Hz, 1H CH-5), 7.29 (d, J 8.4Hz, 1H, CH-6), 7.16 (m, 1H, CH-3).

^13C NMR (DMSO-d$_6$, δ, Hz): 145.90 (s, C2), 143.39 (s, C9), 136.98 (s, CH=N), 136.20 (s, C4), 133.95 (s, Ar-3), 133.05 (s, C5), 130.22 (s, Ar-6), 128.88 (s, C8), 126.31 (s, Ar-2), 124.37 (Ar-4), 122.90 (s, Ar-5), 122.06 (s, Ar-1), 120.24 (s, C3), 118.25 (s, C7), 115.23 (s, C10), 110.33 (s, C6).

HRMS of C_{16}H_{11}Br_{2}N_{3}O (m/z): calculated for [M+H]^+ 419.9342, found 419.9344.

7-(Benzyldenedehydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5g)
A dozen of 4Å molecular sieves were placed into a flask with 0.5 g of 1i (0.81 mmol) in CH$_2$Cl$_2$ (5 ml), a portion of 0.108 g of benzaldehyde (1.62 mmol) was added, and the reaction mixture was treated with 0.200 ml BF$_3$ · Et$_2$O (1.46 mmol) at room temperature while stirring. The reaction mixture changed its color to bordeaux red; gases were released. After 30 min the reaction mass was quenched with EtOH (2 ml), transferred into a new flask, solvents and by-
products were evaporated, and re-evaporated from toluene. The products are insoluble in chloroalkanes (CH₂Cl₂, CHCl₃, or CCl₄) but readily soluble in alcohols and acetone. The purification of products from the excess of aldehyde was achieved by flash chromatography using dry loading of the reaction mixture: a portion of the reaction mass residue was adsorbed from ethanolic solution into 5 cm³ of silica gel in the flask, carefully evaporated to dryness and then applied onto a Shott’s filter with three the amount of silica gel. The separation was performed using the dry column vacuum chromatography (DCVC), first eluted with 50 ml of choroform to allow the aldehydes to pass through the column, and then eluted with ethanol to collect the pure product compound. The fraction was concentrated to give 0.347 g of the product 5g as a bordeaux red solid (85% yield).

¹H NMR (DMSO-d₆, δ, Hz): 10.55 (br.s. 1H, NH), 8.97 (d, J = 8.6 Hz, 1H, CH-2), 8.75 (d, J = 3.7 Hz 1H, CH-4), 8.18 (s, 1H, CH=N), 7.73 (dd, 4H, J = 7.5 Hz, J = 1.8 Hz, o-Ph (TBDPs)), 7.66 (m, 2H, m-Ph), 7.50-7.25 (m, 10H, m-Ph (TBDPs) + p-Ph (TBDPs) + m-Ph + C3 + C5 + C6), 6.92 (d, 1H, J 7.6 Hz, p-Ph), 1.11 (s, 9H, 3× Me (TBDPs)).

¹³C NMR: 148.06 (s, C2), 143.23 (s, C9), 139.04 (s, C4), 135.59 (s, CH=N), 134.91 (s, o-Ph (TBDPs)), 133.35 (s, C6), 131.70 (s, C8), 129.75 (s, p-Ph (TBDPs)), 128.90 (s, i-Ph (TBDPs)), 128.67 (s, m-Ph), 128.28 (s, p-Ph), 127.71 (s, m-Ph (TBDPs)), 126.97 (s, i-Ph), 125.88 (s, o-Ph), 122.10 (s, C10), 120.01 (s, C3), 117.93 (s, C5), 107.49 (s, C7), 26.65 (s, 3×Me (t-Bu of TBDPS)), 19.48 (s, C (t-Bu of TBDPS)).

HRMS of C₃₂H₃₁N₃OSi (m/z): calculated for [M+H]^+ 502.2309, found 502.2309.

7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5h).

A dozen of 4Å molecular sieves were placed into a flask with 0.5 g of 1i (0.81 mmol) in CH₂Cl₂ (5 ml), a portion of 0.112 ml of o-fluorobenzaldehyde (1.06 mmol) was added, and the reaction mixture was treated with 0.200 ml BF₃ · Et₂O (1.62 mmol) at room temperature while stirring. The reaction mixture changed its color to bordeaux red; gases were released. After 30 min the reaction mass was quenched with EtOH (2 ml), transferred into a new flask, solvents and by-products were evaporated, and re-evaporated from toluene. The products are insoluble in chloroalkanes (CH₂Cl₂, CHCl₃, or CCl₄) but readily soluble in alcohols and acetone. The purification of products from the excess of aldehyde was achieved by flash chromatography using dry loading of the reaction mixture: a portion of the reaction mass residue was adsorbed from ethanolic solution into 5 cm³ of silica gel in the flask, carefully evaporated to dryness and then applied onto a Shott’s filter with three times the amount of silica gel. The separation was performed using the dry column vacuum chromatography (DCVC), first eluted with 50 ml of
choroform to allow the aldehydes to pass through the column, and then eluted with ethanol to collect the pure product compound. The fraction was concentrated to give 0.311 g of the product 5g as a burgundy red solid (74% yield).

\[ \text{H NMR (DMSO-d}_6, \delta, \text{ Hz): 11.03 (br.s, 1H, NH), 9.30 (dd, } J = 8.7 \text{ Hz, } J = 1.2 \text{ Hz, 1H, CH-2), 9.10 (dd, } J = 5.2 \text{ Hz, } J = 1.3 \text{ Hz, 1H, CH-4), 8.34 (s, 1H, CH=N), 7.98 (m, } 1\text{H, H-6), 7.98 (m, } 1\text{H, C-5), 7.75 (m, 4H, o-Ph), 7.43 (m, 7H, Ar-6 + m-Ph + p-Ph), 7.24-7.13 (m, 3H, Ar-4 + Ar-5 + CH-3), 6.76 (d, } J = 8.6 \text{ Hz, 1H, Ar-3), 1.14 (s, 9H, 3×Me (t-Bu in TBDPS)).} \]

\[ \text{13C NMR (DMSO-d}_6, \delta, \text{ Hz): 159.92 (d, } J_{C-F} = 248.5 \text{ Hz, 2-Ar), 145.92 (s, C2), 139.54 (s, C4), 139.29 (s, C9), 134.98 (s, o-Ph), 132.98 (s, C5), 132.88 (s, CH=N), 132.20 (s, Ar-4), 131.23 (s, i-Ph), 130.35 (s, p-Ph), 128.11 (s, m-Ph), 125.66 (s, Ar-5), 124.63 (Ar-6), 122.54 (d, } J_{C-F} = 10.2 \text{ Hz, 1-Ar), 121.35 (s, C10), 120.30 (s, C3), 118.29 (s, C6), 115.78 (d, } J_{C-F} = 20.8 \text{ Hz, 3-Ar), 108.79 (s, C7), 26.16 (s, 3×Me (t-Bu of TBDPS)).} \]

HRMS of C$_{32}$H$_{30}$FN$_3$OSi (m/z): calculated for [M+H]$^+$ 520.2215, found 520.2218.

7-(2-ortho-Chlorobenzylidenohydrazinyl)-8-(benzoyloxy)quinoline (5i)

A dozen of 4Å molecular sieves were placed into a flask with 0.5 g of 1k (1.04 mmol) in CH$_2$Cl$_2$ (5 ml), a portion of 0.152 ml of o-chlorobenzaldehyde (1.35 mmol) was added, and the reaction mixture was treated with 0.258 ml BF$_3$ · Et$_2$O (2.08 mmol) at room temperature while stirring. The reaction mixture changed its color to bordeaux red; gases were released. After 30 min the reaction mass was quenched with CHCl$_3$ (2 ml), transferred into a new flask, solvents and by-products were evaporated, and re-evaporated from toluene. The residue was dissolved in CHCl$_3$, applied on a silica gel column and eluted in EtOH-CHCl$_3$ (95:5) system. The fraction containing the target product was concentrated giving a burgundy-colored solid in 0.397 g yield (95%).

\[ \text{1H NMR (DMSO-d}_6, \delta, \text{ Hz): 11.30 (br.s, 1H, NH), 9.11 (d, } J = 8.6 \text{ Hz, 1H, CH-2), 8.97 (d, } J = 3.7 \text{ Hz 1H, CH-4), 8.68 (s, 1H, CH=N), 8.23 (d, } J = 7.2 \text{ Hz, 2H, o-Bz), 8.14 (dd, } 1\text{H, } J = 7.5 \text{ Hz, } J = 1.8 \text{ Hz, Ar-6), 7.80 (m, 3H, p-Bz + CH-5), 7.65 (m, 3H, m-Bz + CH-6), 7.50 (dd, } J = 7.5 \text{ Hz, } J = 1.6 \text{ Hz, 1H, Ar-2), 7.49-7.40 (m, 2H, Ar-3 + Ar-4).} \]

\[ \text{13C NMR (DMSO-d}_6, \delta, \text{ Hz): 165.62 (s, CO (Bz)), 149.20 (s, C2), 139.80 (s, C9), 137.67 (s, C10), 137.27 (s, C4), 137.14 (s, C8), 135.14 (s, CH=N), 134.50 (s, p-Bz), 132.80 (s, C6), 132.50 (s, Ar-1), 130.55 (s, o-Bz), 130.33 (s, Ar-3), 129.52 (s, Ar-4), 129.40 (s, m-Bz), 127.99 (s, Ar-2), 126.83 (s, Ar-5), 125.48 (s, i-Bz), 120.80 (s, C3), 117.99 (s, C5), 107.66 (s, C7).} \]

HRMS of C$_{23}$H$_{16}$ClN$_3$O$_2$ (m/z): calculated for [M+H]$^+$ 402.1004, found 402.1000.

7-(Benzylidenohydrazinyl)-8-(benzoyloxy)quinoline (5j)
A dozen of 4Å molecular sieves were placed into a flask with 0.5 g of 1k (1.04 mmol) in CH$_2$Cl$_2$ (5 ml), a portion of 0.138 ml of benzaldehyde (1.35 mmol) was added, and the reaction mixture was treated with 0.258 ml BF$_3$ · Et$_2$O (2.08 mmol) at room temperature while stirring. The reaction mixture changed its color to bordeaux red; gases were released. After 30 min the reaction mass was quenched with CHCl$_3$ (2 ml), transferred into a new flask, solvents and by-products were evaporated, and re-evaporated from toluene. The residue was dissolved in CHCl$_3$, applied on a silica gel column and eluted in CHCl$_3$ : EtOH (95:5) system. The fraction containing the target product was concentrated giving a burgundy-colored solid in 0.340 g yield (89%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 10.93 (br.s, 1H, NH), 9.08 (d, J = 8.6 Hz, 1H, CH-2), 8.84 (br.s, 1H, CH-4), 8.56 (s, 1H, CH=N), 8.25(d, J 7.2 Hz, 2H, o-Ph), 8.15-8.02 (m, 3H, p-Bz + CH-5), 7.72 (m, 3H, m-Bz + C6), 7.59 (m, 3H, m-Ph+C3), 7.38 (m, 1H, p-Ph).

$^{13}$C NMR: 165.11 (s, CO (Bz)), 150.30 (s, CH-2), 140.73 & 140.22 & 139.13 (4×s, C-8 & CH-4 & CH-5 & CH=N), 135.39 (s, i-Ar), 133.84 (s, p-Bz), 130.48 (s, CH-9), 129.87 (s, o-Bz), 129.31 (s, i-Bz), 128.96 (s, m-Ar), 128.79 (s, m-Bz), 128.66 (s, p-Ar), 126.12 (s., o-Ar), 122.43 (s, CH-7), 120.27 (s, CH-3), 117.33 (s, C-10), 105.92 (s, CH-6).

HRMS of C$_{23}$H$_{17}$N$_3$O$_2$ (m/z): calculated for [M+H]$^+$ 368.1394, found 368.1394.

**Diphenyl disulfide (6a)**

The product was obtained as white solid according to the General method for synthesis of 1d-1h starting from 0.093 ml of thiophenol and 0.21 g of di-tert-butyl azodicarboxylate to give 0.090 g yield (90%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 7.53 (m, 4H, o-Ph), 7.39 (m, 4H, m-Ph), 7.30 (m, 2H, p-Ph).

$^{13}$C NMR (DMSO-d$_6$, δ, Hz): 135.76 (s, i-Ph), 129.41 (s, o-Ph), 127.54 (s, p-Ph), 127.18 (s, m-Ph).

**Bis(quinolin-8-yl) disulfide (6b)**

The product was obtained as yellowish solid according to the General method for synthesis of 1d-1h starting from 0.100 g of 8-mercaptoquinoline (sodium salt) and 0.21 g of di-tert-butyl azodicarboxylate to give 0.077 g yield (88%).

$^1$H NMR (DMSO-d$_6$, δ, Hz): 9.03 (dd, , J = 1.6 Hz, J = 4.2 Hz, 2H, CH-2), 8.47 (dd, J = 1.5 Hz, J = 8.3 Hz, 2H, CH-4), 7.85 (d, J = 7.9 Hz 2H, CH-7), 7.77 (d, 2H, J = 7.5 Hz,CH-7), 7.69 (dd, J = 4.2 Hz, J = 8.3 Hz, 2H, CH-3), 7.54 (dd, J = 7.8 Hz, J = 7.5 Hz, 2H, CH-6).
$^{13}$C NMR (DMSO-$d_6$, δ, Hz): 150.44 (s, C2), 137.11 (s, C4), 134.76 (s, C9), 128.59 (s, C8), 127.49 (s, C7), 126.32 (s, C5), 125.83 (s, C10), 124.47 (s, C3), 122.92 (s, C6).
1H NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a) in DMSO-d6.
$^{13}$C NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1 $^a$) in DMSO-d$_6$
COSY NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1) in DMSO-d6
NOESY NMR spectrum of
Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a)
in DMSO-d6
HSQC NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a) in DMSO-d6
Zoom-in plot of HSQC NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a) in DMSO-d6
HMBC NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1\(^ a \)) in DMSO-d6
Zoom-in plot of HMBC NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1a) in DMSO-d$_6$
$^{15}$N HSQC SI NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1 \textsuperscript{a}) in DMSO-d$_6$
$^{15}$N HMBC 6Hz NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1\textsuperscript{a}) in DMSO-d$_6$
15N-HMBC 9Hz NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1\textsuperscript{a}) in DMSO-d6
1H NMR spectrum of 
Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) 
in DMSO-d6
$^{13}$C NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d$_6$
COSY NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
NOESY NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
HSQC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
Zoom-in plot of HSQC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
HMBC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
Zoom-in plot of HMBC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6.
15N HSQC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
15N HMBC NMR spectrum of Di-tert-butyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1b) in DMSO-d6
$^1$H NMR spectrum of 7-(1,2-bis(tert-butoxycarbonyl)hydrazinyl)-8-hydroxyquinoline N-oxide (1c) in CDCl$_3$
$^{13}$C NMR spectrum of 7-(1,2-Bis(tert-butoxycarbonyl)hydrazinyl)-8-hydroxyquinoline 1-oxide (1c) in CDCl$_3$
$^1$H NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d$_6$
$^{13}$C NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d$_6$.
COSY NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d6
NOESY NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d6
HSQC NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d6
HMBC NMR spectrum of Di-tert-butyl 1-(5-chloro-8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1e) in DMSO-d6
$^1$H NMR spectrum of Tetra-tert-butyl N,N'-(4-hydroxynaphthalene-1,3-diyl)-bis(hydrazinyl-1,2-dicarboxylate) (1g) in DMSO-d$_6$
13C NMR spectrum of Tetra-tert-butyl N,N'-(4-hydroxynaphthalene-1,3-diyl)-bis-(hydrazinyl-1,2-dicarboxylate) (1g) in DMSO-d6
1H NMR spectrum of Di-tert-butyl 1-(4-chloro-1-hydroxynaphth-2-yl)hydrazinyl-1,2-dicarboxylate (1h) in DMSO-d6
$^{13}$C NMR spectrum of Di-tert-butyl 1-(4-chloro-1-hydroxynaphth-2-yl)hydrazinyl-1,2-dicarboxylate (1h) in DMSO-d$_6$
$^1$H NMR spectrum of Di-tert-butyl 1-(8-(tert-butyl)diphenylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1i) in DMSO-d$_6$
$^{13}$C NMR spectrum of Di-tert-butyl 1-(8-(tert-butyldiphenylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1i) in DMSO-d$_6$
$^1$H NMR spectrum of Di-tert-butyl 1-(8-(tert-butyldimethylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1j) in DMSO-d$_6$
13C NMR spectrum of Di-tert-butyl 1-(8-(tert-butyldimethylsilyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1j) in DMSO-d6
$^{1}$H NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d$_6$
$^1$H NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d$_6$
COSY NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d6
HSQC NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d6
Zoom-in plot of HSQC NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d$_6$. 

1H (ppm) vs 13C (ppm)
HMBC NMR spectrum of Di-tert-butyl 1-{8-(benzoyloxy)quinolin-7-yl}hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d$_6$
Zoom-in of HMBC NMR spectrum of Di-tert-butyl 1-(8-(benzoyloxy)quinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1k) in DMSO-d6
$^1$H NMR spectrum of Diisopropyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2a) in DMSO-d$_6$
$^{13}$C NMR spectrum of Diisopropyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2a) in DMSO-$d_6$
1H NMR spectrum of Di-tert-butyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2b) in DMSO-d6
$^{13}$C NMR spectrum of Di-tert-butyl 1-(4-hydroxyphenyl)hydrazinyl-1,2-dicarboxylate (2b) in DMSO-d$_6$
1H NMR spectrum of 4-Hydroxyphenylhydrazine (3) in DMSO-d$_6$
13C NMR spectrum of 4-Hydroxyphenylhydrazine (3) in DMSO-d6
13C NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
COSY NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
NOESY NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
HSQC NMR spectrum of 7-(2-Benzylidenehydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
HMBC NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
15N HSQC-SI NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
1H (ppm)

15N HMBC NMR spectrum of 7-(2-Benzylidenohydrazinyl)-8-hydroxyquinoline (5a) in DMSO-d6
1H NMR spectrum of 7-(2-meta,para-Dibromobenzilenedihydrazinyl)-8-hydroxyquinoline (5f) in DMSO-d6
13C NMR spectrum of 7-(2-meta,para-Dibromobenzylidenedihydrazinyl)-8-hydroxyquinoline (5f) in DMSO-d6
HSQC NMR spectrum of 7-(2-meta,para-Dibromobenzyldienohydrazinyl)-8-hydroxyquinoline (5f) in DMSO-d$_6$. 

1H (ppm) vs 13C (ppm). 

The spectrum shows the chemical shifts of the protons (1H) and the carbon nuclei (13C) in the DMSO-d$_6$ solvent. The grid lines help in identifying the peak assignments.
$^{13}$C NMR spectrum of Diisopropyl 1-(8-hydroxyquinolin-7-yl)hydrazinyl-1,2-dicarboxylate (1 \textsuperscript{a}) in DMSO-d$_6$
H NMR spectrum of 7-(Benzyldienohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5g) in DMSO-d6
13C NMR spectrum of 7-(Benzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5g) in DMSO-d$_6$
$^{1}H$ NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5h) in DMSO-d$_6$
13C NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5h) in DMSO-d6.
HSQC NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5h) in DMSO-d6
Zoom-in plot of HSQC NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenylsilyloxy)quinoline (5h) in DMSO-d6.
HMBC NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butylphenylsilyloxy)quinoline (5h) in DMSO-d6
Zoom-in plot of HMBC NMR spectrum of 7-(2-ortho-Fluorobenzylidenohydrazinyl)-8-(tert-butyldiphenyldisilyloxy)quinoline (5h) in DMSO-d6
1H NMR spectrum of 7-(2-ortho-Chlorobenzylidenohydrazinyl)-8-(benzoyloxy)quinoline (5i) in DMSO-d6

Zoom-in plot in Hz
13C NMR spectrum of 7-(2-ortho-Chlorobenzylidenohydrazinyl)-8-(benzoyloxy)quinoline (5i) in DMSO-d6

- 165.52
- 149.20
- 139.80
- 137.67
- 135.14
- 134.50
- 132.80
- 132.50
- 130.33
- 129.52
- 129.40
- 127.99
- 126.83
- 125.48
- 120.80
- 117.99
- 107.66
\textbf{13C NMR spectrum of 7-(Benzylidenohydrazinyl)-8-(benzoyloxy)quinoline (5j) in DMSO-d6}

\begin{tabular}{cccccccccccccc}
 & 105.92 & 117.33 & 120.27 & 122.43 & 126.12 & 128.66 & 128.79 & 128.96 & 130.48 & 133.84 & 135.39 & 139.13 & 139.26 & 140.22 & 140.73 & 150.30 & 165.11 \\
\end{tabular}
$^{1}H$ NMR spectrum of Diphenyl disulfide (6a) in DMSO-d$_6$
13C NMR spectrum of Diphenyl disulfide (6a) in DMSO-d6
1H NMR spectrum of Bis(quinolin-8-yl) disulfide in DMSO-d6 (6b) in DMSO-d6
13C NMR spectrum of Bis(quinolin-8-yl) disulfide in DMSO-d6 (6b) in DMSO-d6.
**Chemical Formula:** C_{17}H_{21}N_{3}O_{5}  
**Exact Mass:** 347,1481

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**Graph 1:**

- **Intens.**
- **m/z:** 262.1192, 550.2575, 348.1562, 717.2972, 919.3998

**Graph 2:**

- **Intens.**
- **m/z:** 348.1562

**Graph 3:**

- **Intens.**
- **m/z:** 348.1554
**Chemical Formula:** C_{19}H_{25}N_{3}O_{5}

**Exact Mass:** 375.1794
Chemical Formula: C_{19}H_{25}N_{3}O_{6}
Exact Mass: 391.1743

Analysis Info
Analysis Name: D:\Data\QD-21.d
Method: la_2.2.m
Sample Name: QD-21
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Operator: BDAL@DE
Instrument: compact

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Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Source
Set APCI Heater: 0 °C

Graphs showing mass spectra with m/z values and ion intensities.
Chemical Formula: C₁₉H₂₄FN₃O₅
Exact Mass: 393.1700

Analysis Info
Analysis Name D:\Data\QD-28.d
Method LA_2.2.m
Sample Name QD-28
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Acquisition Date 4/2/2019 9:01:37 PM
Operator BDAL@DE
Instrument compact 8255754.20088

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![MS spectrum](QD-28.d: +MS, 0.1min #8)

![MS spectrum](QD-28.d: +MS, 0.1min #8)
Chemical Formula: C_{19}H_{24}ClN_{3}O_{5}
Exact Mass: 409.1404
Chemical Formula: C$_{20}$H$_{26}$N$_{2}$O$_{5}$
Exact Mass: 374.1842

Analysis Info
Analysis Name: D:\Data\QD-06.d
Method: la_2.2.m
Sample Name: QD-06
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Operator: BDAL@DE
Instrument: compact 8255754.20088

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Set Corona: 0 nA
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Source
Set APCI Heater: 0 °C
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
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Set APCI Heater: 0 °C
### Chemical Formula

Chemical Formula: $C_{30}H_{44}N_{4}O_{9}$

Exact Mass: 604.3108

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### Graphs

1. Mass spectrum with peaks at m/z 627.3003 (1+), 643.2739 (1+), and 1231.6117 (7+).
2. Mass spectrum with peaks at m/z 627.3000 (1+), 643.2740 (1+), and 622.3447 (1+).
3. Mass spectrum with peaks at m/z 627.3000 (1+), 643.2740 (1+), and 627.3000 (1+).
Chemical Formula: $\text{C}_{20}\text{H}_{25}\text{ClN}_2\text{O}_5$

Exact Mass: 408.1452
Chemical Formula: $C_{35}H_{43}N_3O_5Si$
Exact Mass: 613.2972

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**Graphs**

1. Intensity vs. m/z for QD-20.d: $+M_3, 1.0\text{ min} \#55$
2. Intensity vs. m/z for QD-20.d: $+M_3, 1.0\text{ min} \#55$
3. Intensity vs. m/z for QD-20.d: $C_{35}H_{43}N_3O_5Si, M+nH, 614.3045$
Chemical Formula: C_{25}H_{39}N_{3}O_{5}Si
Exact Mass: 489.2659

Analysis Info
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Sample Name: QD-18
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Acquisition Date: 3/17/2019 5:49:11 PM
Operator: BDAL@DE
Instrument: compact
Instrument Number: 8255754.20088

Acquisition Parameter
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Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Charging Voltage: 2000 V
Set Corona: 0 nA
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Source
Set APCI Heater: 180 °C
Set Dry Heater: 180 °C
Set Divert Valve: Source
Set APCI Heater: 0 °C
**Chemical Formula:** C$_{26}$H$_{29}$N$_3$O$_6$

**Exact Mass:** 479.2056

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**Analysis Info**

- **Analysis Name:** D:\Data\QD-17.d
- **Method:** la_2.2.m
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- **Operator:** BDAL@DE
- **Instrument:** compact 8255754.20088

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**Acquisition Parameter**

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- **Set Charging Voltage:** 2000 V
- **Set Corona:** 0 nA
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- **Set Dry Heater:** 180 °C
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- **Set Divert Valve:** Source
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**Graphs**

1. Intensity vs. m/z
   - QD-17.d: MS, 0.5 min #29
   - +MS, 0.5 min #29
   - QD-17.d: C$_{26}$H$_{29}$N$_3$O$_6$, M+nH, 480.2129
   - QD-17.d: C$_{26}$H$_{29}$N$_3$O$_6$, M+nNa, 502.1949
   - QD-17.d: C$_{26}$H$_{29}$N$_3$O$_6$, M+nK, 518.1688

---

**S104**
**Chemical Formula:** \( \text{C}_{14}\text{H}_{20}\text{N}_{2}\text{O}_{5} \)

**Exact Mass:** 296.1372

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**Analysis Info**

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**Graphs:**

1. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
2. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
3. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
4. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
5. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
6. Mass spectrum for acquisition QD-07.d: +MS, 0.7 min #43
Chemical Formula: $C_{16}H_{24}N_{2}O_{5}$

Exact Mass: 324.1685
**Analysis Info**

**Analysis Name**  D:\Data\QD-08.d  
**Method**  la_2.2.m  
**Sample Name**  QD-08  
**Comment**  
**Acquisition Date**  3/17/2019 5:24:35 PM  
**Operator**  BDAL@DE  
**Instrument**  compact  
**Exact Mass**  263,1059

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**Diagram:**

1. QD-08.d: +MS, 0.1 min #7
2. QD-08.d: +MS, 0.1 min #7
3. QD-08.d: C_{16}H_{13}N_{3}O, M+NH, 264.1131
Chemical Formula: C₁₆H₁₂FΝ₃O
Exact Mass: 281.0964

Analysis Info
Analysis Name: D:\Data\QD-19.d
Method: la_2.2.m
Sample Name: QD-19

Acquisition Date: 3/17/2019 5:51:47 PM
Operator: BDAL@DE
Instrument: compact

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z

Ion Polarity: Positive
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Charging Voltage: 2000 V
Set Corona: 0 nA
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Source
Set APCI Heater: 0 °C

Chemical Structure:

5b
5d
Chemical Formula: \( C_{17}H_{15}N_{3}O_{2} \)
Exact Mass: 293.1164

### Analysis Info

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**Acquisition Date:** 3/17/2019 5:26:18 PM

**Operator:** BDAL@DE

**Instrument:** compact 82554.20088

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![MS chromatograms](image-url)

S109
Chemical Formula: C_{16}H_{12}N_{4}O_{3}
Exact Mass: 308.0909

**Analysis Info**

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<td>Source</td>
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![Mass Spectral Graph](image1)

![Mass Spectral Graph](image2)

![Mass Spectral Graph](image3)
**Analysis Info**

- **Analysis Name**: D:\Data\QD-01.d
- **Method**: la_2.2.m
- **Sample Name**: QD-01
- **Comment**:  
- **Acquisition Date**: 3/17/2019 4:45:36 PM
- **Operator**: BDAL@DE
- **Instrument**: compact
- **Exact Mass**: 418.9269

**Acquisition Parameter**

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![Graph of Acquisition Data]
5i
Chemical Formula: C$_{23}$H$_{16}$ClN$_3$O$_2$
Exact Mass: 401.0931

Analysis Info
Analysis Name: D:\Data\QD-16.d
Method: la_2.2.m
Sample Name: QD-16
Comment: Acquisition Date: 3/17/2019 5:45:42 PM
Operator: BDAL@DE
Instrument: compact

Acquisition Parameter
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Focus: Active
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Scan End: 3000 m/z
Ion Polarity: Positive
Set Capillary: 4500 V
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Set Corona: 0 nA
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 6.0 l/min
Set Divert Valve: Source
Set APCI Heater: 0 °C

Intensities vs. m/z plots showing the mass spectrum with peaks at various m/z ratios.
Chemical Formula: C$_{23}$H$_{17}$N$_{3}$O$_{2}$

Exact Mass: 367.1321

### Analysis Info
- **Analysis Name**: D:\Data\QD-10.d
- **Method**: la_2.2.m
- **Sample Name**: QD-10
- **Comment**

### Acquisition Date
- **3/17/2019 5:29:01 PM**

### Operator
- **BDAL@DE**

### Instrument
- **compact 82554.20088**

### Acquisition Parameter
- **Source Type**: ESI
- **Ion Polarity**: Positive
- **Focus**: Active
- **Set Capillary**: 4500 V
- **Set End Plate Offset**: -500 V
- **Scan Begin**: 50 m/z
- **Scan End**: 3000 m/z
- **Set Charging Voltage**: 2000 V
- **Set Corona**: 0 nA
- **Set Nebulizer**: 0.4 Bar
- **Set Dry Heater**: 180 °C
- **Set Dry Gas**: 6.0 l/min
- **Set Divert Valve**: Source
- **Set APCI Heater**: 0 °C
- **Source Temperature**: 0 °C