

SUPPORTING INFORMATION

Ultrasound assisted synthesis of hybrid quinoline-imidazole derivatives: a green synthetic approach

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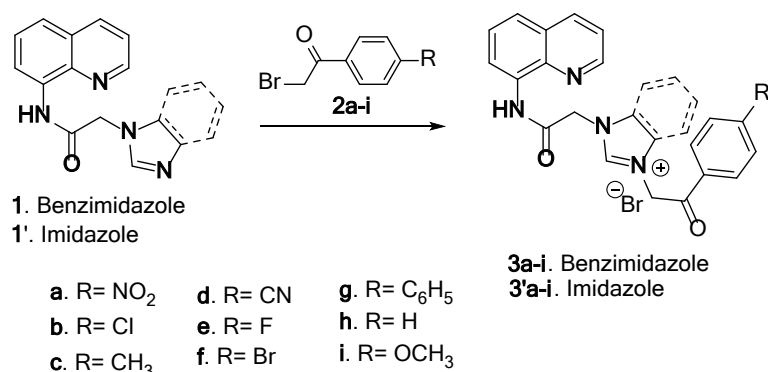
1. General Information

All the reagents and solvents were purchased from commercial sources and used without further purification. Melting points were recorded on a MEL-TEMP II apparatus in open capillary tubes and are uncorrected. Analytical thin-layer chromatography (TLC) was performed with commercial Merck silica gel 60 F₂₅₄ plates and visualized with UV light ($\lambda_{\text{max}} = 254$ or 365 nm).

The NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer operating at 500 MHz for ¹H and 125 MHz for ¹³C{¹H}. The NMR apparatus is equipped with a 5 mm PABBO detection probe, and the program used for acquisition and processing data is *TopSpin 3.2 PL5*. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet. Chemical shifts were reported in δ units (ppm) relative to the residual peaks of solvents (ref: DMSO, ¹H: 2.50 ppm; ¹³C{¹H}: 39.52 ppm or CDCl₃, ¹H: 7.26 ppm; ¹³C: 77.16 ppm). Coupling constants (*J*) were given in Hz. Infrared (IR) data were recorded as films on potassium bromide (KBr) pellets on a FT-IR Shimadzu Prestige 8400s spectrophotometer. The microanalyses were in satisfactory agreement with the calculated values: C, ± 0.15 ; H, ± 0.10 ; N, ± 0.30 . Ultrasound assisted reactions were accomplished using Sonics (Sonics VCX-130, USA), with a nominal power of 130W and a frequency of 20 kHz. For this ultrasonic reactor the titanium standard horn

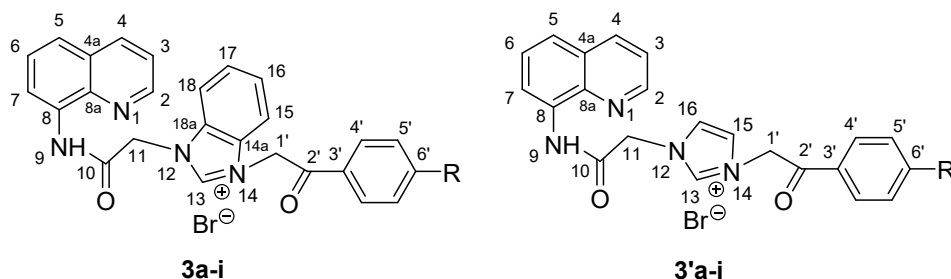
(diameter: 6 mm; length: 116 mm) was fixed firmly to the ultrasonic converter. The titanium horn was directly immersed in the used solvent.

2. General procedure for *N*-alkylation under TH and US irradiation



TH: To a solution of parental hybrid compound **1** or **1'** (1 mmol) in 12 mL acetone, corresponding phenacyl bromide **2a-i** (1.2 mmol) was gradually added. The mixture was stirred at room temperature for 48 h to 96 h (as is presented in Tabel 1). The obtained precipitate was separated by filtration and was washed with 5-7 mL of acetone. No other purification required.

US: The solution that contains parental hybrid compound **1** or **1'** (1 mmol) and corresponding phenacyl bromide **2a-i** (1.2 mmol) was placed in a reaction vessel and was exposed under US irradiation. The best results (see Tabel 1) were obtained applying a pulse irradiation (5 s pulse / 5 s pause, 100% from the full power of the generator). Once the irradiation cycle was completed, the reaction vessel was removed and processed as indicated for TH.



3-(2-(4-nitrophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3a**)

Yellow powder (from acetone); mp 217-219 °C; IR (KBr) ν/cm^{-1} : 3358, 3030, 2970, 1667, 1707, 1537, 1338. ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm} : 6.01 (2H: H₁₁, s), 6.58 (2H: H_{1'}, s), 7.61-7.58 (1H: H₆, *J*= 8.0 Hz, t), 7.76-7.70 (4H: H₃, H₅, H₁₆, H₁₇, m), 8.17-8.14 (2H: H₁₅, H₁₈, m), 8.39-8.37 (2H: 2xH_{4'}, *J*_{4',5'}= 9.0 Hz, d), 8.50-8.46 (3H: 2xH_{5'}, H₄, m), 8.58-8.57 (1H: H₇, *J*_{7,6'}= 7.5 Hz, d), 9.05-9.04 (1H: H₂, *J*_{2,3'}= 5.5 Hz, *J*_{2,4'}= 1.5 Hz, add), 9.83 (1H: H₁₃, s), 11.04 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*6): δ_{ppm} : 49.76 (C₁₁), 53.90 (C_{1'}), 113.77 (C₁₈), 114.16 (C₁₅), 117.44 (C₇), 122.38 (C₃), 122.96 (C₅), 124.09 (2xC_{5'}), 126.83 (C₁₆), 126.91 (C₆), 126.96 (C₁₇), 128.01 (C_{4a}), 129.94 (2xC_{4'}), 131.42 (C_{18a}), 131.62 (C_{14a}), 134.05 (C₈), 136.75 (C₄), 138.37 (C_{8a}), 138.51 (C_{3'}), 144.65 (C₁₃), 149.16 (C₂), 150.60 (C_{6'}), 164.25 (C₁₀), 190.58 (C_{2'}). Anal. calcd. C₂₆H₂₀BrN₅O₄: C, 57.16; H, 3.69; N, 12.82; Found: C, 57.23; H, 3.56; N, 12.68.

3-(2-(4-chlorophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3b**)

White powder (from acetone); mp 208-210 °C; IR (KBr) ν/cm^{-1} : 3331, 3024, 2999, 1685, 1529, 742; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*₆): δ_{ppm} : 6.00 (2H: H₁₁, s), 6.51 (2H: H_{1'}, s), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.78-7.69 (6H: H₃, H₅, H₁₆, H₁₇, 2xH_{5'}, m), 8.17-8.12 (4H: H₁₅, H₁₈, 2xH_{4'}, m), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, $J_{4,2} = 1.5$ Hz, add), 8.58-8.56 (1H: H₇, $J_{7,6} = 8.0$ Hz, d), 9.05-9.04 (1H: H₂, $J_{2,3} = 5.5$ Hz, $J_{2,4} = 1.5$ Hz, add), 9.83 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*₆): δ_{ppm} : 49.72 (C₁₁), 53.43 (C_{1'}), 113.75 (C₁₈), 114.07 (C₁₅), 117.43 (C₇), 122.37 (C₃), 122.95 (C₅), 126.81 (C₆), 126.90 (C₁₆, C₁₇), 128.00 (C_{4a}), 129.21 (2xC_{5'}), 130.36 (2xC_{4'}), 131.41 (C_{18a}), 131.62 (C_{14a}), 132.57 (C₈), 134.04 (C₄), 136.73 (C_{3'}), 138.36 (C_{8a}), 139.44 (C_{6'}), 144.68 (C₁₃), 149.15 (C₂), 164.24 (C₁₀), 190.34 (C_{2'}). Anal. calcd. C₂₆H₂₀BrClN₄O₂: C, 58.28; H, 3.76; N, 10.46; Found: C, 58.37; H, 3.81; N, 10.31.

3-(2-oxo-2-(*p*-tolyl)ethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3c**)

White powder (from acetone); mp 187-190 °C; IR (KBr) ν/cm^{-1} : 3278, 3038, 2970, 1740, 1670, 1541, 1230, 1170; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*₆): δ_{ppm} : 2.45 (3H: *p*-CH₃, s), 5.97 (2H: H₁₁, s), 6.46 (2H: H_{1'}, s), 7.49-7.48 (2H: 2xH_{5'}, $J_{5',4'} = 8.0$ Hz, d), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.76-7.69 (4H: H₃, H₅, H₁₆, H₁₇, m), 8.05-8.03 (2H: 2xH_{4'}, $J_{4',5'} = 8.5$ Hz, d), 8.09-8.08 (1H: H₁₈, $J_{18,17} = 7.5$ Hz, d), 8.13-8.12 (1H: H₁₅, $J_{15,16} = 7.5$ Hz, d), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, $J_{4,2} = 1.0$ Hz, add), 8.58-8.57 (1H: H₇, $J_{7,6} = 7.5$ Hz, d), 9.04-9.03 (1H: H₂, $J_{2,3} = 5.0$ Hz, $J_{2,4} = 1.0$ Hz, add), 9.80 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*₆): δ_{ppm} : 21.41 (*p*-CH₃), 49.72 (C₁₁), 53.23 (C_{1'}), 113.77 (C₁₅), 114.04 (C₁₈), 117.49 (C₇), 122.43 (C₃), 123.02 (C₅), 126.87 (C₆), 126.96 (C₁₆, C₁₇), 128.05 (C_{4a}), 128.59 (2xC_{4'}), 129.65 (2xC_{5'}), 131.35 (C_{18a}), 131.46 (C_{14a}), 131.68 (C_{3'}), 134.07 (C₈), 136.79 (C₄), 138.41 (C_{8a}), 144.77 (C₁₃), 145.38 (C_{6'}), 149.21 (C₂), 164.28 (C₁₀), 190.65 (C_{2'}). Anal. calcd. C₂₇H₂₃BrN₄O₂: C, 62.92; H, 4.50; N, 10.87; Found: C, 62.82; H, 4.55; N, 10.97.

3-(2-(4-cyanophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3d**)

White powder (from acetone); mp 195-197 °C; IR (KBr) ν/cm^{-1} : 3317, 3005, 2901, 2236, 1712, 1537, 1228, 1067; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*₆): δ_{ppm} : 5.98 (2H: H₁₁, s), 6.50 (2H: H_{1'}, s), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.76-7.70 (4H: H₃, H₅, H₁₆, H₁₇, m), 8.14-8.12 (2H: H₁₈, H₁₅, $J_{15,16} = J_{18,17} = 7.5$ Hz, d), 8.18-8.17 (2H: 2xH_{5'}, $J_{5',4'} = 8.0$ Hz, d), 8.30-8.28 (2H: 2xH_{4'}, $J_{4',5'} = 8.0$ Hz, d), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, d), 8.57-8.56 (1H: H₇, $J_{7,6} = 7.5$ Hz, d), 9.046-9.041 (1H: H₂, $J_{2,3} = 2.5$ Hz, ad), 9.78 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*₆): δ_{ppm} : 49.76 (C₁₁), 53.72 (C_{1'}), 113.79 (C₁₈), 114.12 (C₁₅), 116.25 (C_{6'}), 117.49 (C₇), 118.09 (*p*-CN), 122.43 (C₃), 123.01 (C₅), 126.90 (C₁₇), 126.96 (C₆), 127.01 (C₁₆), 128.05 (C_{4a}), 129.09 (2xC_{4'}), 131.45 (C_{18a}), 131.64 (C_{14a}), 133.09 (2xC_{5'}), 134.07 (C₈), 136.79 (C₄), 137.11 (C_{3'}), 138.40 (C_{8a}), 144.69 (C₁₃), 149.21 (C₂), 164.27 (C₁₀), 190.78 (C_{2'}). Anal. calcd. C₂₇H₂₀BrN₅O₂: C, 61.61; H, 3.83; N, 13.30; Found: C, 61.56; H, 3.78; N, 13.40.

3-(2-(4-fluorophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3e**)

White powder (from acetone); mp 208-210 °C; IR (KBr) ν/cm^{-1} : 3329, 3001, 2901, 1703, 1686, 1535, 1233, 1079; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*₆): δ_{ppm} : 5.98 (2H: H₁₁, s), 6.48 (2H: H_{1'}, s), 7.55-7.51 (2H: 2xH_{5'}, $J_{5',4'} = 8.5$ Hz, $J_{5',F} = 9.0$ Hz, t), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.76-7.68 (4H: H₃, H₅, H₁₆, H₁₇, m), 8.14-8.10 (2H: H₁₈, H₁₅, $J_{18,17} = J_{15,16} = 8.5$ Hz, t), 8.25-8.22 (2H: 2xH_{4'}, $J_{4',5'} = 8.5$ Hz, $J_{4',F} = 5.5$ Hz, aq), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, $J_{4,2} = 1.0$ Hz, dd), 8.58-8.56 (1H: H₇, $J_{7,6} = 7.5$ Hz, d), 9.04-9.03 (1H: H₂, $J_{2,3} = 5.0$ Hz, $J_{2,4} = 1.0$ Hz, add), 9.80 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*₆): δ_{ppm} : 49.75 (C₁₁), 53.35 (C_{1'}), 113.78 (C₁₈), 114.07 (C₁₅), 116.28 (2xC_{5'}, $J_{C5'-F} = 21.25$ Hz, d), 117.49 (C₇), 122.43 (C₃), 123.01 (C₅), 126.88 (C₁₇), 126.96 (C₆), 126.97 (C₁₆), 128.05 (C_{4a}), 130.67 (C_{3'}, $J_{C3'-F} = 2.50$ Hz, d), 131.45 (C_{14a}), 131.64 (2xC_{4'}, C_{18a}, $J_{C4'-F} = 7.50$ Hz, d), 134.07 (C₈), 136.79 (C₄), 138.41 (C_{8a}), 144.74 (C₁₃), 149.21 (C₂), 164.28 (C₁₀), 165.82 (C_{6'}, $J_{C6'-F} = 252.50$ Hz, d), 189.89 (C_{2'}). Anal. calcd. C₂₆H₂₀BrFN₄O₂: C, 60.13; H, 3.88; N, 10.79; Found: C, 60.23; H, 3.81; N, 10.82.

3-(2-(4-bromophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3f**)

White powder (from acetone); mp 235-236 °C; IR (KBr) ν/cm^{-1} : 3300, 3020, 2970, 1732, 1700, 1530, 1229, 1170, 670; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*6): δ_{ppm} : 5.99 (2H: H₁₁, s), 6.49 (2H: H_{1'}, s), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.73-7.68 (3H: H₃, H₁₆, H₁₇, m), 7.76-7.74 (1H: H₅, $J_{5,6} = 8.0$ Hz, d), 7.92-7.91 (2H: 2xH_{5'}, $J_{5',4} = 8.5$ Hz, d), 8.09-8.07 (2H: 2xH_{4'}, $J_{4',5} = 8.5$ Hz, d), 8.14-8.11 (2H: H₁₅, H₁₈, $J_{15,16} = J_{18,17} = 7.5$ Hz, t), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.5$ Hz, $J_{4,2} = 2.0$ Hz, dd), 8.58-8.56 (1H: H₇, $J_{7,6} = 7.0$ Hz, d), 9.05-9.04 (1H: H₂, $J_{2,3} = 5.5$ Hz, $J_{2,4} = 1.5$ Hz, dd), 9.82 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*6): δ_{ppm} : 49.73 (C₁₁), 53.40 (C_{1'}), 113.75 (C₁₈), 114.07 (C₁₅), 117.43 (C₇), 122.38 (C₃), 122.95 (C₅), 126.82 (C₆), 126.91 (C₁₇, C₁₆), 128.00 (C_{4a}), 128.72 (C_{6'}), 130.40 (2xC_{4'}), 131.45 (C_{18a}), 131.62 (C_{14a}), 132.17 (2xC_{5'}), 132.88 (C_{3'}), 134.04 (C₈), 136.74 (C₄), 138.36 (C_{8a}), 144.68 (C₁₃), 149.15 (C₂), 164.25 (C₁₀), 190.57 (C_{2'}). Anal. calcd. C₂₆H₂₀Br₂N₄O₂: C, 53.82; H, 3.47; N, 9.66; Found: C, 53.93; H, 3.42; N, 9.56.

3-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3g**)

White powder (from acetone); mp 205-207 °C; IR (KBr) ν/cm^{-1} : 3309, 3001, 2915, 1688, 1529, 1203, 1073; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*6): δ_{ppm} : 6.01 (2H: H₁₁, s), 6.56 (2H: H_{1'}, s), 7.49-7.48 (1H: H_{10'}, $J_{10',9'} = 7.5$ Hz, t), 7.57-7.54 (2H: 2xH_{9'}, $J_{9',10'} = 7.5$ Hz, t), 7.61-7.58 (1H: H₆, $J_{6,7} = 8.0$ Hz, t), 7.74-7.70 (3H: H₃, H₁₆, H₁₇, m), 7.77-7.75 (1H: H₅, $J_{5,6} = 8.0$ Hz, d), 7.84-7.82 (2H: 2xH_{8'}, $J_{8',9} = 8.0$ Hz, d), 8.01-7.99 (2H: 2xH_{5'}, $J_{5',4} = 8.5$ Hz, d), 8.16-8.14 (2H: H₁₈, H₁₅, m), 8.25-8.23 (2H: 2xH_{4'}, $J_{4',5'} = 8.0$ Hz, d), 8.49-8.47 (1H: H₄, $J_{4,3} = 8.0$ Hz, $J_{4,2} = 1.5$ Hz, add), 8.59-8.58 (1H: H₇, $J_{7,6} = 8.0$ Hz, d), 9.05-9.04 (1H: H₂, $J_{2,3} = 5.5$ Hz, $J_{2,4} = 1.5$ Hz, add), 9.87 (1H: H₁₃, s), 11.05 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*6): δ_{ppm} : 49.73 (C₁₁), 53.42 (C_{1'}), 113.75 (C₁₈), 114.07 (C₁₅), 117.44 (C₇), 122.38 (C₅), 122.95 (C₃), 126.82 (C₆), 126.91 (C₁₇, C₁₆), 127.16 (2xC_{5'}, 2xC_{8'}), 128.01 (C_{4a}), 128.76 (C_{10'}), 129.21 (2xC_{9'}, 2xC_{4'}), 131.44 (C_{18a}), 131.66 (C_{14a}), 132.61 (C_{6'}), 134.06 (C₈), 136.74 (C₄), 138.37 (C_{8a}), 138.58 (C₆), 144.74 (C₁₃), 145.81 (C_{5'}), 149.16 (C₂), 164.27 (C₁₀), 190.71 (C_{2'}). Anal. calcd. C₃₂H₂₅BrN₄O₂: C, 66.56; H, 4.36; N, 9.70; Found: C, 66.75; H, 4.41; N, 9.60.

1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3-(2-oxo-2-phenylethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3h**)

White powder (from acetone); mp 203-206 °C; IR (KBr) ν/cm^{-1} : 3290, 3040, 2969, 1698, 1680, 1575, 1220; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*6): δ_{ppm} : 6.02 (2H: H₁₁, s), 6.56 (2H: H_{1'}, s), 7.60-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.76-7.66 (6H: H₃, H₅, H₁₆, H₁₇, 2xH_{5'}, m), 7.81-7.79 (1H: H_{6'}, $J_{6',5'} = 7.5$ Hz, t), 8.16-8.13 (4H: H₁₅, H₁₈, 2xH_{4'}, m), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, d), 8.58-8.56 (1H: H₇, $J_{7,6} = 7.5$ Hz, d), 9.047-9.042 (1H: H₂, $J_{2,3} = 2.5$ Hz, ad), 9.89 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*6): δ_{ppm} : 49.73 (C₁₁), 53.48 (C_{1'}), 113.76 (C₁₈), 114.10 (C₁₅), 117.46 (C₇), 122.38 (C₃), 122.96 (C₅), 126.81 (C₆), 126.91 (C₁₇, C₁₆), 128.01 (C_{4a}), 128.48 (2xC_{5'}), 129.08 (2xC_{4'}), 131.43 (C_{18a}), 131.66 (C_{14a}), 133.82 (C_{6'}), 134.05 (C₈), 134.60 (C_{3'}), 136.74 (C₄), 138.38 (C_{8a}), 144.72 (C₁₃), 149.17 (C₂), 164.27 (C₁₀), 191.21 (C_{2'}). Anal. calcd. C₂₆H₂₁BrN₄O₂: C, 62.28; H, 4.22; N, 11.17; Found: C, 62.38; H, 4.27; N, 11.02.

3-(2-(4-methoxyphenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-benzo[*d*]imidazol-3-ium bromide (**3i**)

White powder (from acetone); mp 224-228 °C; IR (KBr) ν/cm^{-1} : 3412, 3005, 2974, 1680, 1602, 1550, 1246, 1176; $^1\text{H-NMR}$ (500 MHz, DMSO-*d*6): δ_{ppm} : 3.90 (3H: *p*-OCH₃, s), 5.97 (2H: H₁₁, s), 6.44 (2H: H_{1'}, s), 7.21-7.19 (2H: 2xH_{5'}, $J_{5',4} = 8.5$ Hz, d), 7.61-7.57 (1H: H₆, $J = 8.0$ Hz, t), 7.76-7.69 (4H: H₃, H₅, H₁₆, H₁₇, m), 8.09-8.07 (1H: H₁₈, $J_{18,17} = 8.0$ Hz, d), 8.13-8.11 (3H: H₁₅, 2xH_{4'}, $J_{4',5'} = 8.5$ Hz, $J_{15,16} = 8.5$ Hz, d), 8.48-8.46 (1H: H₄, $J_{4,3} = 8.0$ Hz, d), 8.58-8.56 (1H: H₇, $J_{7,6} = 7.5$ Hz, d), 9.046-9.040 (1H: H₂, $J_{2,3} = 3.0$ Hz, ad), 9.81 (1H: H₁₃, s), 11.04 (1H: H₉, s). $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, DMSO-*d*6): δ_{ppm} : 49.72 (C₁₁), 52.99 (C_{1'}), 55.87 (*p*-OCH₃), 113.76 (C₁₈), 114.03 (C₁₅), 114.40 (2xC_{5'}), 117.49 (C₇), 122.43 (C₃), 123.01

(C₅), 126.65 (C_{3'}), 126.85 (C₆), 126.96 (C₁₇, C₁₆), 128.05 (C_{4a}), 130.95 (2xC_{4'}), 131.46 (C_{18a}), 131.70 (C_{14a}), 134.07 (C₈), 136.79 (C₄), 138.41 (C_{8a}), 144.79 (C₁₃), 149.21 (C₂), 164.29 (C_{6'}, C₁₀), 189.39 (C_{2'}). Anal. calcd. C₂₇H₂₃BrN₄O₃: C, 61.03; H, 4.36; N, 10.54; Found: C, 61.13; H, 4.30; N, 10.44.

3-(2-(4-nitrophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'a**)

Yellow powder (from acetone); mp 216-218 °C; IR (KBr) v/cm⁻¹: 3315, 3044, 2989, 1714, 1684, 1524, 1346, 1190; ¹H-NMR (500 MHz, DMSO-*d*₆): δ_{ppm}: 5.63 (2H: H₁₁, s), 6.23 (2H: H_{1'}, s), 7.63-7.59 (1H: H₆, *J* = 8.0 Hz, t), 7.70-7.68 (1H: H₃, *J*_{3,4} = 8.0 Hz, *J*_{3,2} = 4.0 Hz, add), 7.76-7.74 (1H: H₅, *J*_{5,6} = 8.5 Hz, d), 7.79 (1H: H₁₆, s), 7.93 (1H: H₁₅, s), 8.32-8.30 (2H: 2xH₄, *J*_{4,5} = 8.5 Hz, d), 8.47-8.45 (3H: 2xH_{5'}, H₄, *J*_{5',4'} = 8.5 Hz, *J*_{4,3} = 8.5 Hz, d), 8.60-8.58 (1H: H₇, *J*_{7,6} = 8.5 Hz, d) 9.01-9.00 (1H: H₂, *J*_{2,3} = 3.0 Hz, ad), 9.22 (1H: H₁₃, s), 10.91 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): δ_{ppm}: 52.09 (C_{1'}), 55.99 (C₁₁), 117.51 (C₇), 122.33 (C₃), 122.86 (C₅), 123.60 (C₁₆), 123.81 (C₁₅), 124.16 (2xC_{4'}), 126.91 (C₆), 128.00 (C_{4a}), 129.66 (2xC_{5'}), 134.09 (C₈), 136.71 (C₄), 138.39 (C_{3'}), 138.41 (C_{8a}), 138.72 (C₁₃), 149.10 (C₂), 150.56 (C_{6'}), 164.58 (C₁₀), 190.73 (C_{2'}). Anal. calcd. C₂₂H₁₈BrN₅O₄: C, 53.24; H, 3.66; N, 14.11; Found: C, 53.34; H, 3.71; N, 14.01.

3-(2-(4-chlorophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'b**)

White powder (from acetone); mp 226-229 °C; IR (KBr) v/cm⁻¹: 3320, 3010, 2970, 1670, 1530, 740; ¹H-NMR (500 MHz, DMSO-*d*₆): δ_{ppm}: 5.61 (2H: H₁₁, s), 6.14 (2H: H_{1'}, s), 7.62-7.59 (1H: H₆, *J* = 8.0 Hz, t), 7.70-7.67 (1H: H₃, *J*_{3,4} = 8.0 Hz, *J*_{3,2} = 4.0 Hz, dd), 7.77-7.73 (4H: H₁₆, H₅, 2xH_{5'}, m), 7.91 (1H: H₁₅, s), 8.10-8.08 (2H: 2xH₄, *J*_{4,5} = 8.5 Hz, d), 8.47-8.45 (1H: H₄, *J*_{4,3} = 8.0 Hz, *J*_{4,2} = 1.5 Hz, add), 8.59-8.58 (1H: H₇, *J*_{7,6} = 7.5 Hz, d), 9.01-9.00 (1H: H₂, *J*_{2,3} = 4.0 Hz, *J*_{2,4} = 1.5 Hz, add), 9.20 (1H: H₁₃, s), 10.90 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): δ_{ppm}: 52.06 (C₁₁), 55.57 (C_{1'}), 117.52 (C₇), 122.33 (C₃), 122.86 (C₅), 123.62 (C₁₅), 123.73 (C₁₆), 126.91 (C₆), 128.00 (C_{4a}), 129.27 (2xC_{5'}), 130.08 (2xC_{4'}), 132.49 (C_{3'}), 134.08 (C₈), 136.71 (C₄), 138.39 (C_{8a}), 138.72 (C₁₃), 139.38 (C_{6'}), 149.09 (C₂), 164.57 (C₁₀), 190.48 (C_{2'}). Anal. calcd. C₂₂H₁₈BrClN₄O₂: C, 54.40; H, 3.73; N, 11.53; Found: C, 54.47; H, 3.75; N, 11.42.

3-(2-oxo-2-(*p*-tolyl)ethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'c**)

White powder (from acetone); mp 218-219 °C; IR (KBr) v/cm⁻¹: 3288, 3042, 2989, 1745, 1686, 1541, 1238, 1184, 1066; ¹H-NMR (500 MHz, DMSO-*d*₆): δ_{ppm}: 2.42 (3H: *p*-CH₃, s), 5.61 (2H: H₁₁, s), 6.12 (2H: H_{1'}, s), 7.45-7.44 (2H: 2xH₅, *J*_{5,4} = 7.5 Hz, d), 7.62-7.59 (1H: H₆, *J* = 8.0 Hz, t), 7.70-7.67 (1H: H₃, *J*_{3,4} = 8.0 Hz, *J*_{3,2} = 4.0 Hz, aq), 7.75-7.74 (1H: H₅, *J*_{5,6} = 8.5 Hz, d), 7.78 (1H: H₁₆, s), 7.90 (1H: H₁₅, s), 7.98-7.96 (2H: 2xH₄, *J*_{4,5} = 8.0 Hz, d), 8.46-8.45 (1H: H₄, *J*_{4,3} = 8.0 Hz, d), 8.59-8.58 (1H: H₇, *J*_{7,6} = 7.5 Hz, d), 9.007-9.002 (1H: H₂, *J*_{2,3} = 2.5 Hz, ad), 9.21 (1H: H₁₃, s), 10.89 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): δ_{ppm}: 21.37 (*p*-CH₃), 52.06 (C₁₁), 55.46 (C_{1'}), 117.55 (C₇), 122.37 (C₃), 122.91 (C₅), 123.69 (C₁₆, C₁₅), 126.95 (C₆), 128.03 (C_{4a}), 128.31 (2xC_{4'}), 129.67 (2xC_{5'}), 131.27 (C_{3'}), 134.10 (C₈), 136.75 (C₄), 138.42 (C_{8a}), 138.76 (C₁₃), 145.24 (C_{6'}), 149.15 (C₂), 164.60 (C₁₀), 190.81 (C_{2'}). Anal. calcd. C₂₃H₂₁BrN₄O₂: C, 59.36; H, 4.55; N, 12.04; Found: C, 59.24; H, 4.72; N, 12.18.

3-(2-(4-cyanophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'd**)

White powder (from acetone); mp 214-215 °C; IR (KBr) v/cm⁻¹: 3310, 3010, 2920, 2220, 1725, 1530, 1230, 1060; ¹H-NMR (500 MHz, DMSO-*d*₆): δ_{ppm}: 5.62 (2H: H₁₁, s), 6.19 (2H: H_{1'}, s), 7.62-7.59 (1H: H₆, *J*_{6,7} = 7.5 Hz, *J*_{6,5} = 8.0 Hz, t), 7.70-7.67 (1H: H₃, *J*_{3,4} = 8.5 Hz, *J*_{3,2} = 4.5 Hz, dd), 7.75-7.73 (1H: H₅, *J*_{5,6} = 8.0 Hz, d), 7.78 (1H: H₁₆, s), 7.92 (1H: H₁₅, s), 8.14-8.13 (2H: 2xH_{5'}, *J*_{5',4'} = 8.0 Hz, d), 8.23-8.21 (2H: 2xH₄, *J*_{4,5} = 8.5 Hz, d), 8.46-8.44 (1H: H₄, *J*_{4,3} = 8.0 Hz, d) 8.59-8.58 (1H: H₇, *J*_{7,6} = 7.5 Hz, d), 9.00-8.99 (1H: H₂, *J*_{2,3} = 4.0 Hz, ad), 9.21 (1H: H₁₃, s), 10.90 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): δ_{ppm}: 52.11 (C₁₁), 55.92 (C_{1'}), 116.21 (C_{6'}), 117.57 (C₇), 118.05 (*p*-CN), 122.38 (C₃), 122.92 (C₅), 123.63 (C₁₆), 123.83 (C₁₅), 126.95 (C₆), 128.04 (C_{4a}), 128.84 (2xC_{4'}), 133.14 (2xC_{5'}), 134.10 (C₈),

136.75 (C₄), 137.01 (C_{3'}), 138.42 (C_{8a}), 138.75 (C₁₃), 149.15 (C₂), 164.60 (C₁₀), 190.95 (C_{2'}). Anal. calcd. C₂₃H₁₈BrN₅O₂: C, 58.00; H, 3.81; N, 14.70; Found: C, 57.94; H, 3.75; N, 14.55.

3-(2-(4-fluorophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'e**)

White powder (from acetone); mp 226-227 °C; IR (KBr) v/cm⁻¹: 3306, 3052, 2987, 1701, 1692, 1543, 1233, 1160; ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm}: 5.62-5.61 (2H: H₁₁, J_{11,F}= 6.0 Hz, d), 6.16-6.14 (2H: H_{1'}, J_{1',F}= 11.0 Hz, d), 7.51-7.47 (2H: 2xH_{5'}, J_{5',4'}= 8.5 Hz, J_{5',F}= 9.0 Hz, td), 7.63-7.59 (1H: H₆, J_{6,7}= 7.5 Hz, J_{6,5}= 8.0 Hz, td), 7.70-7.67 (1H: H₃, J_{3,4}= 8.0 Hz, J_{3,2}= 4.0 Hz, aq), 7.79-7.73 (2H: H₅, H₁₆, J_{5,6}= 8.5 Hz, J_{16,15}= 9.0 Hz, dd), 7.91-7.90 (1H: H₁₅, J_{15,16}= 5.5 Hz, ad), 8.18-8.16 (2H: 2xH_{4'}, J_{4',5'}= 8.5 Hz, J_{4',F}= 5.5 Hz, at), 8.46-8.44 (1H: H₄, J_{4,3}= 8.0 Hz, J_{4,2}= 1.5 Hz, dd), 8.59-8.58 (1H: H₇, J_{7,6}= 7.5 Hz, d), 9.007-9.004 (1H: H₂, J_{2,3}= 1.5 Hz, ad), 9.22-9.20 (1H: H₁₃, J_{13,F}= 11.5 Hz, d), 10.89 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*6): δ_{ppm}: 52.08 (C₁₁), 55.55 (C_{1'}), 116.31 (2xC_{5'}, J_{C5'-F}= 22.00 Hz, d), 117.55 (C₇), 122.37 (C₃), 122.91 (C₅), 123.67 (C₁₆), 123.74 (C₁₅), 126.94 (C₆), 128.03 (C_{4a}), 130.58 (C_{3'}, J_{C3'-F}= 2.75 Hz, d), 131.36 (2xC_{4'}, J_{C4'-F}= 9.75 Hz, d), 134.10 (C₈), 136.75 (C₄), 138.42 (C_{8a}), 138.76 (C₁₃), 149.15 (C₂), 164.60 (C₁₀), 165.72 (C_{6'}, J_{C6'-F}= 252.12 Hz, d), 190.05 (C_{2'}). Anal. calcd. C₂₂H₁₈BrFN₄O₂: C, 56.30; H, 3.87; N, 11.94; Found: C, 56.40; H, 3.92; N, 11.80.

3-(2-(4-bromophenyl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'f**)

White powder (from acetone); mp 255-256 °C; IR (KBr) v/cm⁻¹: 3303, 3038, 2971, 1742, 1702, 1544, 1231, 1169, 673; ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm}: 5.62 (2H: H₁₁, s), 6.16 (2H: H_{1'}, s), 7.63-7.60 (1H: H₆, J= 8.0 Hz, t), 7.66-7.65 (2H: 2xH_{5'}, J_{5',4'}= 7.5 Hz, d), 7.70-7.68 (1H: H₃, J_{3,4}= 8.5 Hz, J_{3,2}= 4.5 Hz, dd), 7.81-7.74 (2H: H₁₆, H₅, m), 7.91 (1H: H₁₅, s), 8.09-8.07 (2H: 2xH_{4'}, J_{4',5'}= 7.5 Hz, d), 8.47-8.45 (1H: H₄, J_{4,3}= 8.5 Hz, J_{4,2}= 1.5 Hz, add), 8.60-8.59 (1H: H₇, J_{7,6}= 7.5 Hz, d), 9.01-9.00 (1H: H₂, J_{2,3}= 4.0 Hz, J_{2,4}= 1.5 Hz, add), 9.21 (1H: H₁₃, s), 10.91 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*6): δ_{ppm}: 52.05 (C₁₁), 55.58 (C_{1'}), 117.51 (C₇), 122.33 (C₃), 122.86 (C₅), 123.65 (C₁₅), 123.70 (C₁₆), 126.91 (C₆), 128.00 (C_{4a}), 128.17 (2xC_{4'}), 129.12 (2xC_{5'}), 133.73 (C_{3'}), 134.09 (C₈), 134.53 (C_{6'}), 136.71 (C₄), 138.39 (C_{8a}), 138.73 (C₁₃), 149.09 (C₂), 164.59 (C₁₀), 191.33 (C_{2'}). Anal. calcd. C₂₂H₁₈Br₂N₄O₂: C, 49.84; H, 3.42; N, 10.57; Found: C, 49.78; H, 3.38; N, 10.67.

3-(2-([1,1'-biphenyl]-4-yl)-2-oxoethyl)-1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-1*H*-imidazol-3-ium bromide (**3'g**)

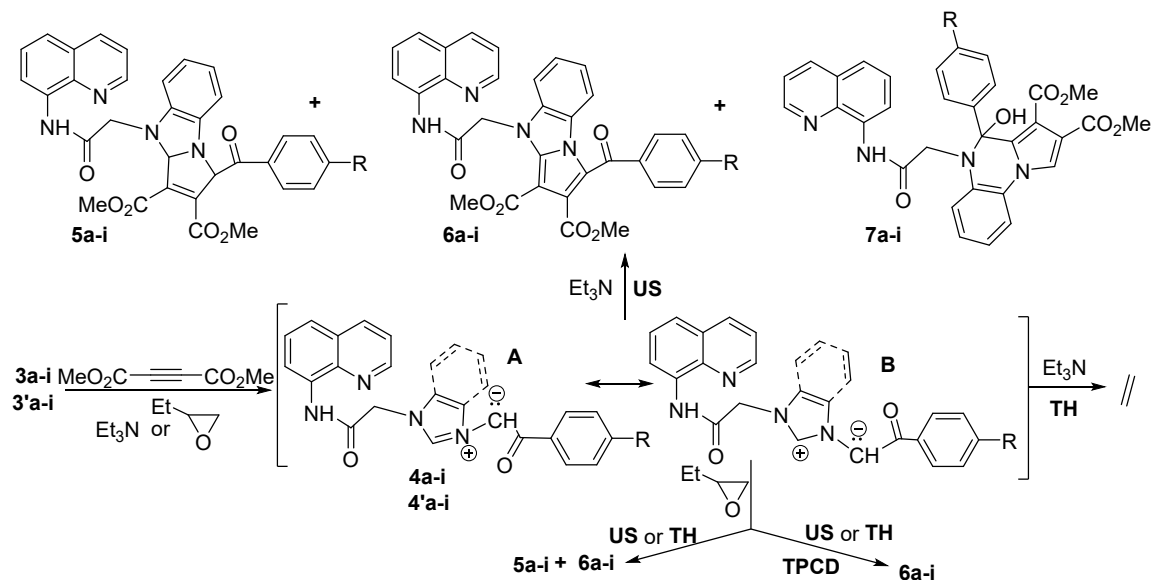
White powder (from acetone); mp 246-248 °C; IR (KBr) v/cm⁻¹: 3320, 3067, 2977, 1686, 1538, 1329, 1183; ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm}: 5.63 (2H: H₁₁, s), 6.21 (2H: H_{1'}, s), 7.48-7.46 (1H: H_{10'}, J_{10',9'}= 7.0 Hz, t), 7.55-7.52 (2H: 2xH_{9'}, J_{9',10'}= 7.5 Hz, t), 7.63-7.60 (1H: H₆, J= 8.0 Hz, t), 7.70-7.68 (1H: H₃, J_{3,4}= 8.0 Hz, J_{3,2}= 4.0 Hz, dd), 7.76-7.74 (1H: H₅, J_{5,6}= 8.0 Hz, d), 7.82-7.80 (3H: 2xH_{8'}, H₁₆, m), 7.93 (1H: H₁₅, s), 7.97-7.96 (2H: 2xH_{5'}, J_{5',4'}= 8.0 Hz, d), 8.17-8.15 (2H: 2xH_{4'}, J_{4',5'}= 8.0 Hz, d), 8.47-8.45 (1H: H₄, J_{4,3}= 8.0 Hz, J_{4,2}= 1.0 Hz add), 8.61-8.59 (1H: H₇, J_{7,6}= 7.5 Hz, d), 9.01-9.00 (1H: H₂, J_{2,3}= 3.0 Hz, J_{2,4}= 1.0 Hz, add), 9.24 (1H: H₁₃, s), 10.92 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*6): δ_{ppm}: 52.06 (C₁₁), 55.58 (C_{1'}), 117.51 (C₇), 122.33 (C₃), 122.86 (C₅), 123.66 (C₁₅), 123.71 (C₁₆), 126.91 (C₆), 127.10 (2xC_{5'}), 127.18 (2xC_{8'}), 128.00 (C_{4a}), 128.74 (C_{10'}), 128.93 (2xC_{9'}), 129.19 (2xC_{4'}), 132.54 (C₇), 134.09 (C₈), 136.71 (C₄), 138.39 (C_{8a}), 138.52 (C_{3'}), 138.75 (C₁₃), 145.69 (C_{6'}), 149.09 (C₂), 164.60 (C₁₀), 190.87 (C_{2'}). Anal. calcd. C₂₈H₂₃BrN₄O₂: C, 63.76; H, 4.40; N, 10.62; Found: C, 63.86; H, 4.45; N, 10.47.

1-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3-(2-oxo-2-phenylethyl)-1*H*-imidazol-3-ium bromide (**3'h**)

White powder (from acetone); mp 246-248 °C; IR (KBr) v/cm⁻¹: 3292, 3045, 2973, 1695, 1684, 1585, 1540, 1231, 1190; ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm}: 5.61 (2H: H₁₁, s), 6.13 (2H: H_{1'}, s), 7.63-7.59 (1H: H₆, J= 8.0 Hz, t), 7.70-7.68 (1H: H₃, J_{3,4}= 8.5 Hz, J_{3,2}= 4.0 Hz, dd), 7.78-7.74 (2H: H₅, H₁₆, m), 7.90-7.87 (4H: H_{6'}, 2xH_{5'}, H₁₅, m), 8.01-8.00 (2H: 2xH_{4'}, J_{4',5'}= 8.0 Hz, d), 8.47-8.45 (1H: H₄, J_{4,3}= 8.0

Hz, d) 8.60-8.58 (1H: H₇, $J_{7,6}$ = 8.0 Hz, d), 9.01-9.00 (1H: H₂, $J_{2,3}$ = 4.0 Hz, ad), 9.18 (1H: H₁₃, s), 10.91 (1H: H₉, s). ¹³C{¹H}-NMR (125 MHz, DMSO-*d*₆): δ_{ppm} : 52.06 (C₁₁), 55.53 (C_{1'}), 117.51 (C₇), 122.33 (C₃), 122.86 (C₅), 123.61 (C₁₆), 123.74 (C₁₅), 126.91 (C₆), 128.00 (C_{4a}), 128.65 (C_{3'}), 130.11 (2xC_{4'}), 132.22 (2xC_{5'}), 132.80 (C_{6'}), 134.09 (C₈), 136.71 (C₄), 138.39 (C_{8a}), 138.72 (C₁₃), 149.09 (C₂), 164.58 (C₁₀), 190.70 (C_{2'}). Anal. calcd. C₂₂H₁₉BrN₄O₂: C, 58.55; H, 4.24; N, 12.41; Found: C, 58.65; H, 4.29; N, 12.25.

3. General procedure for Huisgen 3+2 dipolar cycloaddition under TH and US irradiation



3.1. General procedure for the reaction of hybrid quinoline-imidazolium salts (3a-i) with DMAD in the presence of triethylamine in chloroform under conventional TH and US irradiation

TH: To a suspension of a quinoline-imidazolium salt **3a-i** or **3'a-i** (1 mmol) in 20 mL of chloroform, dimethyl acetylenedicarboxylate (**DMAD**) (2.5 mmol) was added under stirring, then a solution of 2.5 mmol of triethylamine in 4 mL of chloroform was added dropwise on ice bath and the reaction mixture was stirred for 1 h at room temperature. The chloroformic solution was washed with water (3 x 30 mL) and dried on Na₂SO₄ anhydrous. The solvent was removed under vacuum, but only decomposition products are being obtained.

US: A mixture of quinoline imidazolium-salt **3a-i** (1 mmol), dimethyl acetylenedicarboxylate (**DMAD**) (2.5 mmol) and triethylamine (2.5 mmol) in 20 mL of chloroform was placed in the reaction vessel and exposed to US irradiation for 2 to 4 min. The results were obtained using a pulse irradiation (5 s pulse / 5 s pause) and 50% from the full power of the generator. After each minute of irradiation a TLC was performed to see when the reaction is done. The chloroformic solution was washed with water (3 x 30 mL) and dried on Na₂SO₄ anhydrous. The residue was triturated with MeOH giving the mixtures of the adducts dihydro-benzopyrrolo-imidazolo-quinoline, benzopyrrolo-imidazolo-quinoline and benzopyrrolo imidazolo-quinoline. with a mixture of CHCl₃/MeOH giving the three types of cycloadducts: dihydro-benzopyrrolo-imidazolo quinolines (**5d**, **5i**), benzopyrrolo-imidazolo quinolines (**6a-c**, **6e-h**) and dihydro-pyrrolo-quinoxaline quinolines (**7a**, **7b**, **7d-f**)

3.2. General procedure for the reaction of hybrid quinoline-imidazolium salts (3a-i) with DMAD in 1,2-epoxybutane under conventional TH and US irradiation

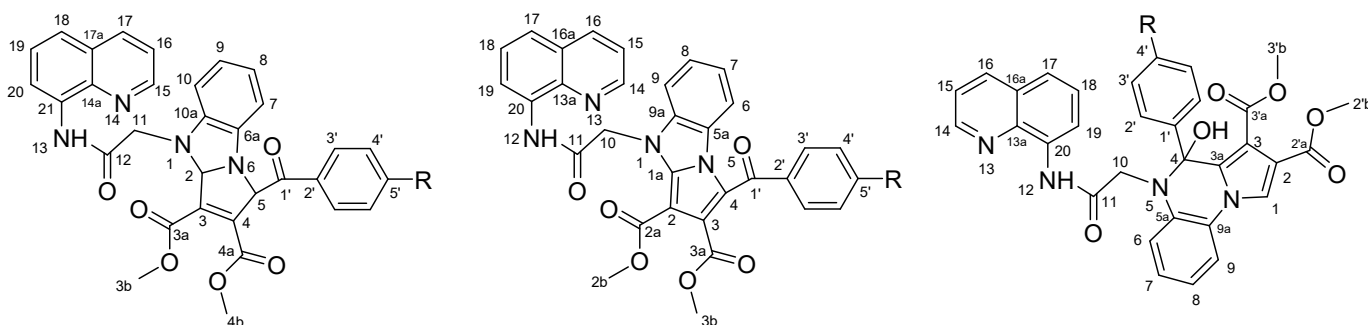
TH: To a suspension of quinoline imidazolium salt **3a-i** (1 mmol) in 20 mL of 1,2-epoxybutane, dimethyl acetylenedicarboxylate (**DMAD**) (2.5 mmol) was added and stirred at room temperature for 12 to 16 h. The solvent was removed in vacuo, then 5-7 mL of MeOH added and left for 3-5 h under stirring. The solid formed was filtered and recrystallized from CHCl₃/MeOH giving the mixture of two adducts dihydro-benzopyrrolo-imidazolo-quinoline and benzopyrrolo-imidazolo-quinoline. two classes of adducts the dihydro-benzopyrrolo-imidazolo quinolines (**5b-i**) and benzopyrrolo-imidazolo quinoline compounds (**6a-i**).

US: A mixture of quinoline-imidazolium salt **3a-i** (1 mmol) and DMAD (2.5 mmol) in 20 mL of 1,2-epoxybutane was placed in the reaction vessel and exposed to US irradiation for 150 to 180 min. The results were obtained using a pulse irradiation (5 s pulse / 5 s pause) and 50% from the full power of the generator. After each 10-20 minute of irradiation a TLC was performed to see the reactant consumption. Once the irradiation cycle was performed the reactions were processed as indicated above for TH.

3.3. General procedure for the reaction of hybrid quinoline-imidazolium salts (3a-i) with DMAD in 1,2-epoxybutane and TPCD under conventional TH and US irradiation

TH: To a suspension of quinoline-imidazolium salt **3a-i** (1 mmol) in 20 mL of 1,2-epoxybutane, dimethyl acetylenedicarboxylate (**DMAD**) (2.5 mmol) and 0.4 g TPCD were added. The reaction mixture was stirred at room temperature for 5 to 8 h. The solid part was filtered through a pad of Celite 545 and washed with 50-70 mL of CHCl₃. The filtrate was evaporated under vacuum, then the crude mixture was triturated with MeOH and the solid part was filtered and recrystallized from CHCl₃/MeOH to obtain benzopyrrolo-imidazolo quinoline compounds (**6a-i**).

US: A mixture of quinoline-imidazolium salt **3a-i** (1 mmol), DMAD (2.5 mmol) and 0.4 g of TPCD in 20 mL of 1,2-epoxybutane, was placed in the reaction vessel and exposed to US irradiation for 16-20 min. The results were obtained using a pulse irradiation (5 s pulse / 5 s pause) and 50% from the full power of the generator. After each 3-5 minute of irradiation a TLC was performed to see when the reaction is done. Once the irradiation cycle was performed the reactions were processed as indicated above for TH.



dimethyl 1-(4-chlorobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5b**)

White powder (precipitated with dichloromethane/diethylether); mp 185-187 °C; IR (KBr) v/cm⁻¹: 3309, 3013, 2984, 1706, 1495, 1292, 752; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.40 (3H: H_{3b}, s), 3.79 (3H: H_{4b}, s), 4.04-4.01 (1H: H_{11b}, J_{11b,11a} = 17.5 Hz, d), 4.17-4.14 (1H: H_{11a}, J_{11a,11b} = 17.5 Hz, d), 4.647-4.642 (1H: H₂, J_{2,5} = 2.5 Hz, ad), 5.64-5.63 (1H: H₅, J_{5,2} = 2.5 Hz, ad), 6.54-6.53 (1H: H₁₀, J_{10,9} = 7.0 Hz, ad), 6.60-6.59 (1H: H₉, J = 8.0 Hz, t), 6.65-6.63 (1H: H₇, J_{7,8} = 7.5 Hz, d), 6.97-6.95 (1H: H₈, J = 8.0 Hz, t), 7.37-

7.35 (1H: H₁₉, m), 7.44-7.42 (1H: H₁₆, bs), 7.59-7.55 (3H: 2xH₄, H₁₈, m), 8.03-8.01 (2H: 2xH₃, J_{3',4'} = 7.0 Hz, ad), 8.14-8.12 (1H: H₂₀, J_{20,19} = 8.5 Hz, ad), 8.49-8.48 (1H: H₁₇, J_{17,16} = 8.5 Hz, ad), 8.80-8.79 (1H: H₁₅, J_{15,16} = 6.5 Hz, J_{15,17} = 1.5 Hz, add), 11.10 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.49 (C_{4b}), 52.73 (C₁₁), 53.04 (C_{3b}), 54.10 (C₂), 91.20 (C₅), 109.00 (C₇), 109.25 (C_{10a}), 116.76 (C₃), 117.11 (C_{6a}), 121.02 (C₁₆), 121.69 (C₁₈), 122.49 (C₈), 126.89 (2xC₄), 127.40 (C₁₇), 128.12 (C₁₉, C_{17a}), 128.82 (C₄), 130.62 (2xC₃), 131.68 (C₂), 132.12 (C₂₀), 133.65 (C₉), 136.59 (C₂₁), 137.79 (C₅), 138.88 (C_{14a}), 143.09 (C₁₀), 148.81 (C₁₅), 157.59 (C_{4a}), 164.72 (C_{3a}), 167.54 (C₁₂), 188.13 (C₁). Anal. calcd. C₃₂H₂₅ClN₄O₆: C, 64.38; H, 4.22; N, 9.38; Found: C, 64.45; H, 4.16; N, 9.47.

dimethyl 1-(4-methylbenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5c**)

White powder (precipitated with dichloromethane/diethylether); mp 191-192 °C; IR (KBr) v/cm⁻¹: 3298, 3004, 2986, 1702, 1553; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 2.38 (3H: *p*-CH₃, s), 3.40 (3H: H_{3b}, s), 3.78 (3H: H_{4b}, s), 4.05-4.02 (1H: H_{11b}, J_{11b,11a} = 17.5 Hz, d), 4.17-4.14 (1H: H_{11a}, J_{11a,11b} = 17.5 Hz, d), 4.67-4.66 (1H: H₂, J_{2,5} = 2.5 Hz, ad), 5.656-5.651 (1H: H₅, J_{5,2} = 2.5 Hz, ad), 6.60-6.55 (2H: H₁₀, H₉, m), 6.64-6.62 (1H: H₇, J_{7,8} = 7.5 Hz, d), 6.94-6.91 (1H: H₈, J = 8.0 Hz, t), 7.20 (2H: (2H: 2xH₄, bs), 7.37-7.32 (1H: H₁₉, m), 7.46-7.42 (2H: H₁₆, H₁₈, m), 7.986-7.981 (2H: 2xH₃, J_{3',4'} = 2.5 Hz, ad), 8.14-8.12 (1H: H₂₀, J_{20,19} = 8.0 Hz, d), 8.56 (1H: H₁₇, bs), 8.79-8.78 (1H: H₁₅, J_{15,16} = 5.5 Hz, d), 11.14 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 21.34 (*p*-CH₃), 51.56 (C_{4b}), 52.61 (C₁₁), 53.06 (C_{3b}), 57.98 (C₂), 90.85 (C₅), 108.54 (C₇, C_{17a}), 109.21 (C_{10a}), 116.48 (C₃), 117.02 (C_{6a}), 121.02 (C₁₆), 121.78 (C₁₈), 122.51 (C₈), 127.67 (C₁₇), 128.13 (C₁₉), 128.93 (2xC₄), 129.09 (C₄), 129.36 (2xC₃), 130.70 (C₂), 132.04 (C₂₀), 133.62 (C₉), 135.94 (C₂₁), 138.90 (C_{14a}), 142.81 (C₅), 143.14 (C₁₀), 148.86 (C₁₅), 157.69 (C_{4a}), 164.67 (C_{3a}), 167.49 (C₁₂), 188.07 (C₁). Anal. calcd. C₃₃H₂₈N₄O₆: C, 68.74; H, 4.89; N, 9.72; Found: C, 68.81; H, 4.79; N, 9.78.

dimethyl 1-(4-cyanobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5d**)

White powder (precipitated with dichloromethane/diethylether); mp 205-207 °C; IR (KBr) v/cm⁻¹: 3327, 3012, 2959, 2231, 1698, 1624, 1532; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.39 (3H: H_{3b}, s), 3.79 (3H: H_{4b}, s), 4.05-4.02 (1H: H_{11b}, J_{11b,11a} = 17.5 Hz, d), 4.18-4.15 (1H: H_{11a}, J_{11a,11b} = 17.5 Hz, d), 4.63-4.62 (1H: H₂, J_{2,5} = 2.5 Hz, ad), 5.655-5.650 (1H: H₅, J_{5,2} = 2.5 Hz, ad), 6.52-6.50 (1H: H₁₀, J_{10,9} = 7.5 Hz, d), 6.61-6.58 (1H: H₉, J = 8.0 Hz, t), 6.67-6.65 (1H: H₇, J_{7,8} = 7.5 Hz, d), 6.98-6.95 (1H: H₈, J = 8.0 Hz, t), 7.37-7.35 (1H: H₁₉, m), 7.48-7.46 (1H: H₁₆, H₁₈, m), 7.68-7.66 (2H: 2xH₄, J_{4',3'} = 7.5 Hz, ad), 7.88 (2H: 2xH₃, bs), 8.43-8.41 (1H: H₂₀, J_{20,19} = 8.0 Hz, d), 8.66-8.64 (1H: H₁₇, J_{17,16} = 8.5 Hz, d), 8.82-8.80 (1H: H₁₅, J_{15,16} = 6.5 Hz, J_{15,17} = 2.0 Hz, add), 11.06 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.56 (C_{4b}), 52.59 (C₁₁), 53.04 (C_{3b}), 57.95 (C₂), 90.61 (C₅), 108.57 (C₇, C_{17a}), 109.19 (C_{10a}), 116.44 (C₃), 117.13 (C_{6a}), 117.65 (C₅), 118.26 (*p*-CN), 121.11 (C₁₆), 122.01 (C₁₈), 122.51 (C₈), 127.72 (C₁₇), 128.09 (C₁₉), 129.13 (C₄), 129.50 (2xC₃), 132.04 (C₂₀), 132.59 (2xC₄), 133.59 (C₉), 135.94 (C₂₁), 137.89 (C₂), 138.82 (C_{14a}), 143.10 (C₁₀), 148.91 (C₁₅), 157.42 (C_{4a}), 164.52 (C_{3a}), 168.50 (C₁₂), 187.35 (C₁). Anal. calcd. C₃₃H₂₅N₅O₆: C, 67.46; H, 4.29; N, 11.92; Found: C, 67.51; H, 4.20; N, 11.96.

dimethyl 1-(4-fluorobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5e**)

White powder (precipitated with dichloromethane/diethylether); mp 208-210 °C; IR (KBr) v/cm⁻¹: 3297, 3018, 2960, 1691, 1597, 1237; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.41 (3H: H_{3b}, s), 3.79 (3H: H_{4b}, s), 4.07-4.03 (1H: H_{11b}, J_{11b,11a} = 17.5 Hz, d), 4.19-4.15 (1H: H_{11a}, J_{11a,11b} = 17.5 Hz, d), 4.646-4.641 (1H: H₂, J_{2,5} = 2.5 Hz, ad), 5.658-5.653 (1H: H₅, J_{5,2} = 2.5 Hz, ad), 6.54-6.53 (1H: H₁₀, J_{10,9} = 7.0 Hz, d), 6.61-6.58 (1H: H₉, J = 7.5 Hz, t), 6.65-6.64 (1H: H₇, J_{7,8} = 7.5 Hz, d), 6.96-6.93 (1H: H₈, J = 8.0 Hz, t), 7.06 (2H:

2xH₄, bs), 7.37-7.34 (1H: H₁₉, m), 7.48-7.44 (1H: H₁₆, H₁₈, m), 8.15 (3H: 2xH₃, H₂₀, bs), 8.52 (1H: H₁₇, bs), 8.81-8.76 (1H: H₁₅, $J_{15,16}$ = 5.5 Hz, d), 11.12 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.54 (C_{4b}), 52.60 (C₁₁), 53.06 (C_{3b}), 57.89 (C₂), 89.98 (C₅), 108.56 (C₇), 109.12 (C_{17a}), 109.21 (C_{10a}), 115.02 (2xC₄, J_{C4-F} = 24.40 Hz, d), 116.39 (C₃), 117.12 (C_{6a}), 121.12 (C₁₆), 122.06 (C₁₈), 122.50 (C₈), 127.72 (C₁₇), 128.12 (C₁₉), 129.21 (C₄), 129.35 (C₂, J_{C2-F} = 2.44 Hz, d), 130.40 (2xC₃, J_{C3-F} = 8.22 Hz, d), 132.04 (C₂₀), 133.59 (C₉), 135.91 (C₂₁), 138.74 (C_{14a}), 141.91 (C₁₀), 148.90 (C₁₅), 157.60 (C_{4a}), 164.76 (C_{3a}), 167.30 (C₅, J_{C5-F} = 252.12 Hz, d), 168.51 (C₁₂), 187.40 (C₁). Anal. calcd. C₃₂H₂₅FN₄O₆: C, 66.20; H, 4.34; N, 9.65; Found: C, 66.11; H, 4.38; N, 9.59.

dimethyl 1-(4-bromobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5f**)

White powder (precipitated with dichloromethane/diethylether); mp 213-215 °C; IR (KBr) v/cm⁻¹: 3285, 3008, 2975, 1702, 1544, 1237, 673; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.40 (3H: H_{3b}, s), 3.78 (3H: H_{4b}, s), 4.04-4.01 (1H: H_{11b}, $J_{11b,11a}$ = 17.5 Hz, d), 4.17-4.13 (1H: H_{11a}, $J_{11a,11b}$ = 17.5 Hz, d), 4.645-4.640 (1H: H₂, $J_{2,5}$ = 2.5 Hz, ad), 5.64-5.63 (1H: H₅, $J_{5,2}$ = 2.5 Hz, ad), 6.54-6.53 (1H: H₁₀, $J_{10,9}$ = 7.0 Hz, ad), 6.65-6.60 (2H: H₉, H₇, m), 6.96-6.92 (1H: H₈, J = 8.0 Hz, t), 7.37-7.35 (1H: H₁₉, m), 7.47-7.43 (2H: H₁₆, H₁₈, m), 7.83 (2H: 2xH₄, bs), 7.95-7.93 (2H: 2xH₃, $J_{3,4}$ = 7.5 Hz, ad), 8.22-8.20 (1H: H₂₀, $J_{20,19}$ = 8.0 Hz, d), 8.50-8.48 (1H: H₁₇, $J_{17,16}$ = 8.0 Hz, d), 8.80-8.78 (1H: H₁₅, $J_{15,16}$ = 6.5 Hz, $J_{15,17}$ = 2.5 Hz, add), 11.14 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.74 (C_{4b}), 52.75 (C₁₁), 53.18 (C_{3b}), 57.89 (C₂), 91.52 (C₅), 108.55 (C₇), 109.12 (C_{17a}), 109.20 (C_{10a}), 116.40 (C₃), 117.11 (C_{6a}), 121.16 (C₁₆), 122.44 (C₁₈), 122.50 (C₈), 126.87 (C₅), 127.69 (C₁₇), 128.14 (C₁₉), 129.84 (2xC₃), 130.06 (C₄), 131.53 (2xC₄), 132.05 (C₂₀), 132.61 (C₂), 133.59 (C₉), 135.91 (C₂₁), 138.75 (C_{14a}), 141.91 (C₁₀), 148.94 (C₁₅), 157.71 (C_{4a}), 164.79 (C_{3a}), 168.49 (C₁₂), 187.46 (C₁). Anal. calcd. C₃₂H₂₅BrN₄O₆: C, 59.92; H, 3.93; N, 8.73; Found: C, 60.05; H, 3.89; N, 8.80.

dimethyl 1-([1,1'-biphenyl]-4-carbonyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5g**)

White powder (precipitated with dichloromethane/diethylether); mp 198-201 °C; IR (KBr) v/cm⁻¹: 3321, 3007, 2977, 1687, 1538, 1183; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.41 (3H: H_{3b}, s), 3.79 (3H: H_{4b}, s), 4.06-4.02 (1H: H_{11b}, $J_{11b,11a}$ = 17.5 Hz, d), 4.19-4.15 (1H: H_{11a}, $J_{11a,11b}$ = 17.5 Hz, d), 4.688-4.683 (1H: H₂, $J_{2,5}$ = 2.5 Hz, ad), 5.675-5.670 (1H: H₅, $J_{5,2}$ = 2.5 Hz, ad), 6.60 (2H: H₁₀, H₉, bs), 6.65-6.64 (1H: H₇, $J_{7,8}$ = 8.0 Hz, d), 6.96-6.93 (1H: H₈, J = 8.0 Hz, t), 7.36-7.34 (1H: H₁₉, m), 7.50 (5H: H₁₆, H₁₆, 2xH₈, H₉, bs), 7.80 (4H: 2xH₄, 2xH₇, bs), 8.07 (2H: 2xH₃, bs), 8.45-8.40 (1H: H₂₀, m), 8.65-8.62 (1H: H₁₇, $J_{17,16}$ = 8.5 Hz, ad), 8.80-8.79 (1H: H₁₅, $J_{15,16}$ = 6.5 Hz, $J_{15,17}$ = 2.0 Hz, add), 11.11 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.55 (C_{4b}), 52.62 (C₁₁), 53.08 (C_{3b}), 56.07 (C₂), 90.52 (C₅), 108.61 (C₇, C_{17a}), 109.19 (C_{10a}), 116.57 (C₃), 117.13 (C_{6a}), 121.17 (C₁₆), 122.11 (C₁₈), 122.49 (C₈), 127.76 (C₁₇), 127.84 (2xC₄, C₉), 128.15 (C₁₉), 129.50 (2xC₃, 2xC₇), 129.84 (2xC₈), 130.03 (C₄), 132.02 (C₂₀), 132.45 (C₂), 133.61 (C₉), 135.94 (C₂₁), 138.82 (C_{14a}), 140.81 (C₆), 143.11 (C₁₀), 145.20 (C₅), 148.92 (C₁₅), 157.40 (C_{4a}), 164.48 (C_{3a}), 168.50 (C₁₂), 187.31 (C₁). Anal. calcd. C₃₈H₃₀N₄O₆: C, 71.46; H, 4.73; N, 8.77; Found: C, 71.51; H, 4.64; N, 8.83.

dimethyl 1-benzoyl-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole-2,3-dicarboxylate (**5h**)

White powder (precipitated with dichloromethane/diethylether); mp 177-179 °C; IR (KBr) v/cm⁻¹: 3284, 3014, 2973, 1695, 1684, 1183; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.40 (3H: H_{3b}, s), 3.78 (3H: H_{4b}, s), 4.06-4.03 (1H: H_{11b}, $J_{11b,11a}$ = 17.5 Hz, d), 4.19-4.16 (1H: H_{11a}, $J_{11a,11b}$ = 17.5 Hz, d), 4.687-4.682 (1H: H₂, $J_{2,5}$ = 2.5 Hz, ad), 5.676-5.671 (1H: H₅, $J_{5,2}$ = 2.5 Hz, ad), 6.60 (2H: H₁₀, H₉, m), 6.66-6.64 (1H: H₇, $J_{7,8}$ = 8.0 Hz, d), 6.96-6.93 (1H: H₈, J = 8.0 Hz, t), 7.38-7.36 (1H: H₁₉, m), 7.50-7.44 (2H: H₁₆, H₁₈, m), 7.64

(3H: 2xH₄['], H₁₀['], bs), 8.04 (2H: 2xH₃['], bs), 8.45-8.41 (1H: H₂₀, m), 8.66-8.63 (1H: H₁₇, $J_{17,16}$ = 8.5 Hz, ad), 8.81-8.80 (1H: H₁₅, $J_{15,16}$ = 6.5 Hz, $J_{15,17}$ = 2.0 Hz, add), 11.07 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.50 (C_{4b}), 52.64 (C₁₁), 53.12 (C_{3b}), 54.24 (C₂), 91.07 (C₅), 108.56 (C₇), 108.84 (C_{17a}), 109.20 (C_{10a}), 116.41 (C₃), 117.07 (C_{6a}), 120.82 (C₁₆), 121.79 (C₁₈), 122.52 (C₈), 127.45 (C₁₇), 128.19 (C₁₉), 128.64 (2xC₄[']), 128.89 (2xC₃[']), 129.26 (C₄), 132.18 (C₂₀), 133.63 (C₉), 133.74 (C₅[']), 134.56 (C₂[']), 136.60 (C₂₁), 138.89 (C_{14a}), 143.11 (C₁₀), 148.79 (C₁₅), 157.56 (C_{4a}), 164.57 (C_{3a}), 167.53 (C₁₂), 188.30 (C₁[']). Anal. calcd. C₃₂H₂₆N₄O₆: C, 68.32; H, 4.66; N, 9.96; Found: C, 68.41; H, 4.58; N, 10.02.

dimethyl 1-(4-methoxybenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-3a,4-dihydro-1H-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**5i**)

White powder (precipitated with dichloromethane/diethylether); mp 194-196 °C; IR (KBr) v/cm⁻¹: 3281, 3031, 2972, 1707, 1483, 1374, 1127; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.41 (3H: H_{3b}, s), 3.78 (3H: H_{4b}, s), 3.82 (3H: *p*-OCH₃, s), 4.06-4.03 (1H: H_{11b}, $J_{11b,11a}$ = 17.5 Hz, d), 4.18-4.14 (1H: H_{11a}, $J_{11a,11b}$ = 17.5 Hz, d), 4.66-4.65 (1H: H₂, $J_{2,5}$ = 2.5 Hz, ad), 5.65-5.64 (1H: H₅, $J_{5,2}$ = 2.5 Hz, ad), 6.59 (2H: 2xH₄['], bs), 6.64-6.62 (1H: H₇, $J_{7,8}$ = 7.5 Hz, d), 6.94-6.91 (3H: H₈, H₉, H₁₀, m), 7.38-7.36 (1H: H₁₉, m), 7.59-7.55 (2H: H₁₆, H₁₈, m), 8.06 (2H: 2xH₃['], bs), 8.15-8.14 (1H: H₁₇, $J_{17,16}$ = 8.0 Hz, d), 8.58 (1H: H₂₀, bs), 8.79 (1H: H₁₅, bs), 11.15 (1H: H₁₃, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 51.51 (C_{4b}), 52.65 (C₁₁), 53.09 (C_{3b}), 54.11 (C₂), 55.69 (*p*-OCH₃), 91.19 (C₅), 108.56 (C₇, C_{17a}), 109.22 (C_{10a}), 114.42 (2xC₄[']), 116.44 (C₃), 117.07 (C_{6a}), 120.93 (C₁₆), 121.72 (C₁₈), 122.48 (C₈), 126.63 (2xC₃[']), 127.38 (C₁₇), 128.14 (C₁₉), 128.94 (C₄), 132.09 (C₂₀), 133.63 (C₉), 132.68 (C₂[']), 135.92 (C₂₁), 138.80 (C_{14a}), 143.10 (C₁₀), 148.82 (C₁₅), 157.56 (C_{4a}), 164.19 (C₅[']), 164.67 (C_{3a}), 167.49 (C₁₂), 188.07 (C₁[']). Anal. calcd. C₃₃H₂₈N₄O₇: C, 66.88; H, 4.76; N, 9.45; Found: C, 66.79; H, 4.83; N, 9.38.

dimethyl 1-(4-nitrobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4H-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6a**):

Yellow powder (precipitated with methanol); mp 268-271 °C; IR (KBr): v/cm⁻¹: 3335, 3007, 2982, 1732, 1691, 1624, 1539, 1494, 1342, 1226; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm}: 3.31 (3H: H_{2b}, s), 3.77 (3H: H_{3b}, s), 5.84 (2H: H₁₀, s), 7.39-7.36 (1H: H₇, J = 8.0 Hz, t), 7.55-7.45 (4H: H₈, H₁₅, H₁₇, H₁₈, m), 7.59-7.57 (1H: H₉, $J_{9,8}$ = 8.0 Hz, d), 7.91-7.90 (2H: 2xH₃['], $J_{3',4'}$ = 8.5 Hz, d), 8.18-8.17 (1H: H₁₆, $J_{16,15}$ = 8.0 Hz, d), 8.32-8.30 (2H: 2xH₄['], $J_{4',3'}$ = 9.0 Hz, d), 8.67-8.63 (2H: H₆, H₁₉, m), 8.74-8.73 (1H: H₁₄, $J_{14,15}$ = 3.5 Hz, ad), 10.36 (1H: H₁₂, s); ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm}: 49.57 (C₁₀), 52.18 (C_{3b}), 52.41 (C_{2b}), 92.72 (C₂), 110.49 (C₉), 117.22 (C₆, C₁₉), 118.58 (C₃), 121.90 (C₁₅), 122.57 (C₁₇), 122.78 (C₇), 123.31 (2xC₄[']), 125.88 (C₈), 126.84 (C₁₈), 127.59 (C_{16a}), 128.17 (C_{5a}), 129.95 (2xC₃[']), 132.74 (C₄), 133.63 (C₁₆, C₂₀), 137.11 (C_{9a}, C_{13a}), 142.74 (C_{1a}), 144.77 (C₂[']), 148.21 (C₁₄), 149.60 (C₅[']), 163.14 (C_{3a}), 164.86 (C_{2a}), 165.05 (C₁₁), 182.57 (C₁[']). Anal. calcd. C₃₂H₂₃N₅O₈: C, 63.47; H, 3.83; N, 11.57; Found: C, 63.57; H, 3.88; N, 11.42.

dimethyl 1-(4-chlorobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4H-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6b**)

Yellow powder (precipitated with methanol); mp 206-208 °C; IR (KBr): v/cm⁻¹: 3320, 3010, 2970, 1730, 1689, 1630, 1301, 1210, 750; ¹H-NMR (500 MHz, DMSO-*d*6): δ_{ppm}: 3.29 (3H: H_{2b}, s), 3.62 (3H: H_{3b}, s), 5.94 (2H: H₁₀, s), 7.39-7.37 (1H: H₇, J = 7.5 Hz, t), 7.56-7.49 (2H: H₈, H₁₅, m), 7.60-7.58 (2H: 2xH₄['], $J_{4',3'}$ = 8.0 Hz, d), 7.73-7.67 (4H: 2xH₃['], H₁₇, H₁₈, m), 7.85-7.84 (1H: H₉, $J_{9,8}$ = 8.0 Hz, d), 8.38-8.37 (1H: H₁₆, $J_{16,15}$ = 8.0 Hz, d), 8.45-8.43 (1H: H₆, $J_{6,7}$ = 8.0 Hz, d), 8.52-8.50 (1H: H₁₉, $J_{19,18}$ = 7.5 Hz, d), 9.00-8.99 (1H: H₁₄, $J_{14,15}$ = 2.5 Hz, ad), 10.75 (1H: H₁₂, s); ¹³C{¹H}-NMR (125 MHz, DMSO-*d*6): δ_{ppm}: 48.32 (C₁₀), 51.62 (C_{3b}), 51.98 (C_{2b}), 90.91 (C₂), 110.01 (C₉), 115.92 (C₆), 116.97 (C₁₉), 117.84 (C₃), 121.74 (C₁₅), 122.26 (C₇), 122.35 (C₁₇), 125.29 (C_{5a}), 125.56 (C₈), 126.94 (C₁₈), 127.94 (C_{16a}), 128.22 (2xC₄[']), 130.44 (2xC₃[']), 131.51 (C₄), 134.25 (C₂₀), 136.67 (C₂[']), 136.85 (C₁₆), 137.13 (C_{9a}), 137.40 (C₅[']), 138.22 (C_{13a}),

142.02 (C_{1a}), 148.98 (C₁₄), 161.97 (C_{3a}), 164.16 (C_{2a}), 166.05 (C₁₁), 182.87 (C_{1'}). Anal. calcd. C₃₂H₂₃ClN₄O₆: C, 64.60; H, 3.90; N, 9.42; Found: C, 64.70; H, 3.98; N, 9.24.

dimethyl 1-(4-methylbenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6c**)

Yellow powder (precipitated with methanol); mp 195-196 °C; IR (KBr): ν/cm^{-1} : 3300, 3023, 2980, 1735, 1675, 1640, 1310, 1215; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 2.43 (3H: *p*-CH₃, s), 3.30 (3H: H_{2b}, s), 3.77 (3H: H_{3b}, s), 5.84 (2H: H₁₀, s), 7.27-7.26 (2H: 2xH_{4'}, $J_{4',3'} = 6.5$ Hz, d), 7.32-7.29 (1H: H₇, $J_{7,6} = 8.0$ Hz, $J_{7,8} = 7.5$ Hz, t), 7.44-7.41 (1H: H₈, $J_{8,7} = 7.5$ Hz, $J_{8,9} = 8.0$ Hz, t), 7.50 (1H: H₁₅, bs), 7.56-7.54 (3H: H₉, H₁₈, H₁₇, m), 7.72-7.70 (2H: 2xH_{3'}, $J_{3',4'} = 8.0$ Hz, d), 8.24 (1H: H₁₆, bs), 8.43-8.41 (1H: H₆, $J_{6,7} = 8.5$ Hz, d), 8.75-8.70 (2H: H₁₄, H₁₉, m), 10.52 (1H: H₁₂, bs); ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 21.81 (*p*-CH₃), 49.66 (C₁₀), 51.92 (C_{3b}), 52.18 (C_{2b}), 91.33 (C₂), 110.32 (C₉), 116.84 (C₆, C₁₉), 119.50 (C₃), 121.75 (C₁₅), 122.44 (C₇), 122.59 (C₁₇), 125.45 (C₈), 126.76 (C_{5a}), 127.89 (C_{16a}, C₁₈), 128.31 (C₂₀), 128.93 (2xC_{4'}), 129.34 (2xC_{3'}), 130.92 (C₄), 133.54 (C_{13a}), 136.52 (C_{2'}), 137.19 (C_{9a}, C₁₆), 142.43 (C_{1a}), 142.89 (C_{5'}), 147.81 (C₁₄), 163.51 (C_{3a}), 165.19 (C_{2a}), 165.62 (C₁₁), 185.17 (C_{1'}). Anal. calcd. C₃₃H₂₆N₄O₆: C, 68.98; H, 4.56; N, 9.75; Found: C, 68.88; H, 4.51; N, 9.85.

dimethyl 1-(4-cyanobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6d**)

Yellow powder (precipitated with methanol); mp 241-243 °C; IR (KBr): ν/cm^{-1} : 3310, 3020, 2946, 2240, 1723, 1678, 1610, 1316, 1220; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.31 (3H: H_{2b}, s), 3.77 (3H: H_{3b}, s), 5.84 (2H: H₁₀, s), 7.37-7.36 (1H: H₇, $J = 7.5$ Hz, at), 7.58-7.47 (5H: H₈, H₉, H₁₅, H₁₇, H₁₈, m), 7.76-7.75 (2H: 2xH_{4'}, $J_{4',3'} = 7.0$ Hz, d), 7.85-7.83 (2H: 2xH_{3'}, $J_{3',4'} = 7.5$ Hz, d), 8.18 (1H: H₁₆, bs), 8.61-8.59 (1H: H₆, $J_{6,7} = 8.0$ Hz, d), 8.67-8.66 (1H: H₁₉, $J_{19,18} = 6.0$ Hz, ad), 8.73 (1H: H₁₄, bs), 10.38 (1H: H₁₂, bs); ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 49.57 (C₁₀), 52.15 (C_{3b}), 52.37 (C_{2b}), 92.56 (C₂), 110.48 (C₉), 115.13 (C_{5'}), 117.15 (C₆, C₁₉), 118.25 (C_{2'}), 118.55 (C₃), 121.89 (C₁₅), 122.55 (C₁₇), 122.73 (C₇), 125.83 (C₈), 126.80 (C_{5a}), 127.56 (C₁₈), 128.15 (C_{16a}, C₂₀), 129.52 (2xC_{4'}), 131.94 (2xC_{3'}), 132.55 (C₄), 133.64 (C_{13a}), 137.10 (C_{9a}, C₁₆), 142.69 (C_{1a}), 143.09 (*p*-CN), 148.22 (C₁₄), 163.16 (C_{3a}), 164.87 (C_{2a}), 165.06 (C₁₁), 182.91 (C_{1'}). Anal. calcd. C₃₃H₂₃N₅O₆: C, 67.69; H, 3.96; N, 11.96; Found: C, 67.81; H, 4.01; N, 11.79.

dimethyl 1-(4-fluorobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6e**)

Yellow powder (precipitated with methanol); mp 195-196 °C; IR (KBr): ν/cm^{-1} : 3281, 3022, 2960, 1745, 1693, 1597, 1233, 1218, 1153; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.36 (3H: H_{2b}), 3.77 (3H: H_{3b}), 5.79 (2H: H₁₀, s), 7.16-7.12 (2H: 2xH_{4'}, $J_{4',3'} = 8.0$ Hz, $J_{4',F} = 8.5$ Hz, t), 7.34-7.31 (1H: H₇, $J = 7.5$ Hz, t), 7.50-7.41 (4H: H₈, H₁₅, H₁₇, H₁₈, m), 7.56-7.54 (1H: H₉, $J_{9,8} = 8.5$ Hz, d), 7.84-7.81 (2H: 2xH_{3'}, $J_{3',4'} = 7.0$ Hz, $J_{3',F} = 5.5$ Hz, t), 8.14-8.12 (1H: H₁₆, $J_{16,15} = 8.0$ Hz, d), 8.45-8.44 (1H: H₆, $J_{6,7} = 8.0$ Hz, d), 8.67-8.66 (1H: H₁₉, $J_{19,18} = 6.0$ Hz, d), 8.706-8.701 (1H: H₁₄, $J_{14,15} = 2.5$ Hz, ad), 10.34 (1H: H₁₂, s); ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 49.71 (C₁₀), 52.02 (C_{3b}), 52.32 (C_{2b}), 91.67 (C₂), 110.42 (C₉), 115.36 (2xC_{4'}, $J_{C4'-F} = 22.50$ Hz, d), 116.83 (C₆), 117.05 (C₁₉), 119.01 (C₃), 121.89 (C₁₅), 122.41 (C₁₇), 122.56 (C₇), 125.60 (C₈), 126.71 (C_{5a}), 127.35 (C₁₈), 128.03 (C_{16a}), 131.37 (C₄), 131.66 (2xC_{3'}, $J_{C3'-F} = 8.75$ Hz, d), 133.86 (C₂₀), 135.42 (C_{2'}, $J_{C2'-F} = 2.50$ Hz, d), 136.46 (C₁₆), 137.14 (C_{9a}), 138.51 (C_{13a}), 142.42 (C_{1a}), 148.51 (C₁₄), 163.41 (C_{3a}), 165.11 (C_{2a}), 165.18 (C₁₁), 165.25 (C_{5'}, $J_{C5'-F} = 252.50$ Hz, d), 183.78 (C_{1'}). Anal. calcd. C₃₂H₂₃FN₄O₆: C, 66.43; H, 4.01; N, 9.68; Found: C, 66.53; H, 4.06; N, 9.53.

dimethyl 1-(4-bromobenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6f**)

Yellow powder (precipitated with methanol); mp 204-206 °C; IR (KBr): ν/cm^{-1} : 3326, 3032, 2950, 1730, 1689, 1620, 1299, 1210, 678; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ_{ppm} : 3.35 (3H: $\text{H}_{2\text{b}}$), 3.77 (3H: $\text{H}_{3\text{b}}$, s), 5.87 (2H: H_{10} , s), 7.34-7.31 (1H: H_7 , $J_{7,6} = 8.0$ Hz, $J_{7,8} = 7.5$ Hz, t), 7.45-7.42 (1H: H_8 , $J_{8,7} = 7.5$ Hz, $J_{8,9} = 8.0$ Hz, t), 7.57-7.54 (4H: H_9 , H_{15} , H_{17} , H_{18} , m), 7.61-7.59 (2H: $2\times\text{H}_{4'}$, $J_{4',3'} = 8.5$ Hz, d), 7.67-7.65 (2H: $2\times\text{H}_{3'}$, $J_{3',4'} = 8.5$ Hz, d), 8.26 (1H: H_{16} , bs), 8.50-8.48 (1H: H_6 , $J_{6,7} = 8.5$ Hz, d), 8.71-8.70 (1H: H_{19} , $J_{19,18} = 6.0$ Hz, ad), 8.77 (1H: H_{14} , bs), 10.54 (1H: H_{12} , bs); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ_{ppm} : 49.61 (C_{10}), 52.10 ($\text{C}_{3\text{b}}$), 52.35 ($\text{C}_{2\text{b}}$), 91.88 (C_2), 110.52 (C_9), 116.94 (C_6 , C_{19}), 118.92 (C_3), 121.80 (C_{15}), 122.56 (C_7), 122.65 (C_{17}), 125.63 (C_8), 126.74 ($\text{C}_{5\text{a}}$, C_{18}), 126.89 ($\text{C}_{5'}$), 127.88 ($\text{C}_{16\text{a}}$), 128.32 (C_{20}), 130.66 ($2\times\text{C}_{3'}$), 131.47 ($2\times\text{C}_{4'}$), 131.71 (C_4), 137.13 ($\text{C}_{9\text{a}}$, C_{16}), 138.03 ($\text{C}_{2'}$, $\text{C}_{13\text{a}}$), 142.55 ($\text{C}_{1\text{a}}$), 147.77 (C_{14}), 163.33 ($\text{C}_{3\text{a}}$), 165.06 ($\text{C}_{2\text{a}}$), 165.44 (C_{11}), 183.93 ($\text{C}_{1'}$). Anal. calcd. $\text{C}_{32}\text{H}_{23}\text{BrN}_4\text{O}_6$: C, 60.10; H, 3.63; N, 8.76; Found: C, 60.20; H, 3.68; N, 8.61.

dimethyl 1-([1,1'-biphenyl]-4-carbonyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6g**)

Yellow powder (precipitated with methanol); mp 175-177 °C; IR (KBr) ν/cm^{-1} : 3320, 3010, 2930, 1736, 1670, 1630, 1310, 1230, 1050; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ_{ppm} : 3.31 (3H: $\text{H}_{2\text{b}}$, s), 3.77 (3H: $\text{H}_{3\text{b}}$, s), 5.86 (2H: H_{10} , s), 7.34-7.31 (1H: H_7 , $J_{7,6} = 8.0$ Hz, $J_{7,8} = 7.5$ Hz, t), 7.53-7.39 (5H: H_8 , H_{15} , $2\times\text{H}_{8'}$, $\text{H}_{9'}$, m), 7.57-7.56 (3H: H_9 , H_{17} , H_{18} , m), 7.67-7.65 (2H: $2\times\text{H}_{7'}$, $J_{7',8'} = 8.5$ Hz, d), 7.71-7.69 (2H: $2\times\text{H}_{4'}$, $J_{4',3'} = 8.5$ Hz, d), 7.89-7.87 (2H: $2\times\text{H}_{3'}$, $J_{3',4'} = 8.0$ Hz, d), 8.24 (1H: H_{16} , bs), 8.50-8.48 (1H: H_6 , $J_{6,7} = 8.0$ Hz, d), 8.72-8.71 (1H: H_{19} , $J_{19,18} = 6.5$ Hz, $J_{19,17} = 2.0$ Hz, add), 8.76-8.75 (1H: H_{14} , $J_{14,15} = 3.5$ Hz, ad), 10.53 (1H: H_{12} , bs); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ_{ppm} : 49.62 (C_{10}), 51.97 ($\text{C}_{3\text{b}}$), 52.25 ($\text{C}_{2\text{b}}$), 91.59 (C_2), 110.53 (C_9), 116.92 (C_6 , C_{19}), 119.41 (C_3), 121.75 (C_{15}), 122.50 (C_7), 122.63 (C_{17}), 125.53 (C_8), 126.79 ($\text{C}_{5\text{a}}$, C_{18}), 126.87 ($2\times\text{C}_{7'}$), 127.38 ($2\times\text{C}_{8'}$), 128.26 ($\text{C}_{16\text{a}}$, C_{20}), 129.12 ($2\times\text{C}_{4'}$, $\text{C}_{9'}$), 129.77 ($2\times\text{C}_{3'}$), 131.34 (C_4), 137.18 ($\text{C}_{9\text{a}}$, C_{16}), 137.98 ($\text{C}_{2'}$), 140.19 (C_6 , $\text{C}_{13\text{a}}$), 142.52 ($\text{C}_{1\text{a}}$), 144.90 ($\text{C}_{5'}$), 147.71 (C_{14}), 163.47 ($\text{C}_{3\text{a}}$), 165.17 ($\text{C}_{2\text{a}}$), 165.61 (C_{11}), 184.86 ($\text{C}_{1'}$). Anal. calcd. $\text{C}_{38}\text{H}_{28}\text{N}_4\text{O}_6$: C, 71.69; H, 4.43; N, 8.80; Found: C, 71.80; H, 4.48; N, 8.64.

dimethyl 1-benzoyl-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6h**)

Yellow powder (precipitated with methanol); mp 190-193 °C; IR (KBr) ν/cm^{-1} : 3320, 3010, 2920, 1740, 1667, 1610, 1310, 1292; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ_{ppm} : 3.27 (3H: $\text{H}_{2\text{b}}$, s), 3.77 (3H: $\text{H}_{3\text{b}}$, s), 5.81 (2H: H_{10} , s), 7.34-7.31 (1H: H_7 , $J_{7,6} = 8.0$ Hz, $J_{7,8} = 7.5$ Hz, t), 7.56-7.42 (8H: $2\times\text{H}_{4'}$, $\text{H}_{5'}$, H_8 , H_9 , H_{15} , H_{17} , H_{18} , m), 7.80-7.78 (2H: $2\times\text{H}_{3'}$, $J_{3',4'} = 8.0$ Hz, d), 8.16-8.14 (1H: H_{16} , $J_{16,15} = 8.0$ Hz, d), 8.50-8.48 (1H: H_6 , $J_{6,7} = 8.5$ Hz, d), 8.69-8.67 (1H: H_{19} , $J_{19,18} = 7.0$ Hz, $J_{19,17} = 2.0$ Hz, dd), 8.714-8.710 (1H: H_{14} , $J_{14,15} = 2.0$ Hz, ad), 10.38 (1H: H_{12} , bs); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ_{ppm} : 49.69 (C_{10}), 51.99 ($\text{C}_{3\text{b}}$), 52.18 ($\text{C}_{2\text{b}}$), 91.59 (C_2), 110.38 (C_9), 116.95 (C_6 , C_{19}), 119.36 (C_3), 121.81 (C_{15}), 122.50 (C_7 , C_{17}), 125.53 (C_8), 126.80 (C_{18}), 127.60 ($\text{C}_{16\text{a}}$), 128.24 ($2\times\text{C}_{4'}$), 129.13 ($2\times\text{C}_{3'}$), 131.46 (C_4), 132.14 ($\text{C}_{5'}$), 133.60 (C_{20}), 137.15 ($\text{C}_{2'}$, $\text{C}_{9\text{a}}$, C_{16}), 139.20 ($\text{C}_{13\text{a}}$), 142.46 ($\text{C}_{1\text{a}}$), 148.10 (C_{14}), 163.45 ($\text{C}_{3\text{a}}$), 165.08 ($\text{C}_{2\text{a}}$), 165.26 (C_{11}), 185.28 ($\text{C}_{1'}$). Anal. calcd. $\text{C}_{32}\text{H}_{24}\text{N}_4\text{O}_6$: C, 68.56; H, 4.32; N, 9.99; Found: C, 68.66; H, 4.38; N, 9.82.

dimethyl 1-(4-methoxybenzoyl)-4-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (**6i**)

Yellow powder (precipitated with methanol); mp 193-195 °C; IR (KBr): ν/cm^{-1} : 3313, 3005, 2971, 1738, 1574, 1376, 1213, 1030; $^1\text{H-NMR}$ (500 MHz, CDCl_3): δ_{ppm} : 3.37 (3H: *p*- OCH_3 , s), 3.77 (3H: $\text{H}_{2\text{b}}$, s), 3.88 (3H: $\text{H}_{3\text{b}}$, s), 5.78 (2H: H_{10} , s), 6.96-6.94 (2H: $2\times\text{H}_{4'}$, $J_{4',3'} = 8.5$ Hz, d), 7.30-7.27 (1H: H_7 , $J_{7,6} = 8.0$ Hz, $J_{7,8} = 7.5$ Hz, t), 7.43-7.40 (2H: H_8 , H_{15} , m), 7.54-7.49 (3H: H_9 , H_{17} , H_{18} , m), 7.83-7.81 (2H: $2\times\text{H}_{3'}$, $J_{3',4'} = 8.5$ Hz, d), 8.13-8.11 (1H: H_{16} , $J_{16,15} = 7.5$ Hz, d), 8.34-8.32 (1H: H_6 , $J_{6,7} = 8.5$ Hz, d), 8.69-8.66 (2H: H_{14} , H_{19} , m), 10.36 (1H: H_{12} , s); $^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, CDCl_3): δ_{ppm} : 49.80 (C_{10}), 51.92 ($\text{C}_{2\text{b}}$), 52.30 (*p*-

OCH₃), 55.64 (C_{3b}), 91.08 (C₂), 110.36 (C₉), 113.58 (2xC_{4'}), 116.63 (C₆), 117.02 (C₁₉), 119.41 (C₃), 121.86 (C₁₅), 122.36 (C₁₇), 122.43 (C₇), 125.43 (C₈), 126.66 (C_{5a}), 127.32 (C₁₈), 128.01 (C_{16a}), 130.30 (C₄), 131.52 (2xC_{3'}), 131.76 (C_{2'}), 133.90 (C₂₀), 136.41 (C₁₆), 137.19 (C_{9a}), 138.52 (C_{13a}), 142.26 (C_{1a}), 148.51 (C₁₄), 163.20 (C_{5'}), 163.58 (C₁₁), 165.28 (C_{3a}), 165.35 (C_{2a}), 184.28 (C_{1'}). Anal. calcd. C₃₃H₂₆N₄O₇: C, 67.11; H, 4.44; N, 9.49; Found: C, 67.22; H, 4.49; N, 9.32.

dimethyl 4-hydroxy-4-(4-nitrophenyl)-5-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (**7a**)

Yellowish powder (precipitated with ethyl acetate/*n*-hexan); mp 184-186 °C; IR (KBr): ν/cm^{-1} : 3267, 3214, 3015, 2974, 1718, 1667, 1538, 1329, 1236, 1081; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.61 (3H: H_{2b}, s), 3.85 (3H: H_{3b}, s), 3.91-3.88 (1H: H_{10b}, $J_{10b,10a}$ = 17.5 Hz, d), 4.36-4.33 (1H: H_{10a}, $J_{10a,10b}$ = 17.5 Hz, d), 6.95-6.94 (1H: H₆, $J_{6,7}$ = 8.0 Hz, d), 7.01-6.98 (1H: H₈, J = 7.5 Hz, t), 7.21-7.18 (1H: H₇, J = 8.0 Hz, t), 7.41-7.39 (1H: H₁₅, m), 7.50-7.46 (3H: 2xH_{2'}, H₁₈, m), 7.60-7.55 (2H: H₉, -OH, m), 7.68-7.66 (1H: H₁₇, $J_{17,18}$ = 9.0 Hz, d), 7.92 (1H: H₁, s), 8.17-8.11 (3H: H₁₆, 2xH_{2'}, m), 8.68-8.63 (2H: H₁₄, H₁₉, m), 10.75 (1H: H₁₂, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 50.39 (C₁₀), 51.96 (C_{2b}), 52.50 (C_{3b}), 84.75 (C₄), 113.5 (C₂), 114.26 (C₈), 115.44 (C₉), 117.10 (C₁₉), 117.64 (C_{3a}), 119.05 (C₁), 120.21 (C₆), 121.74 (C₁₅), 122.34 (C₁₇), 122.46 (C_{9a}), 123.77 (2xC_{3'}), 127.30 (C₇), 128.06 (C₁₈), 128.65 (2xC_{2'}), 130.55 (C_{16a}), 133.41 (C₃), 133.87 (C_{5a}), 134.06 (C₂₀), 136.29 (C₁₆), 138.84 (C_{13a}), 143.14 (C_{1'}), 146.21 (C_{4'}), 148.75 (C₁₄), 163.73 (C_{3'a}), 166.42 (C_{2'a}), 168.95 (C₁₁). Anal. calcd. C₃₂H₂₅N₅O₈: C, 63.26; H, 4.15; N, 11.53; Found: C, 63.34; H, 4.09; N, 11.58.

dimethyl 4-(4-chlorophenyl)-4-hydroxy-5-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (**7b**)

Pale pink powder (precipitated with ethyl acetate/*n*-hexan); mp 179-180°C; IR (KBr): ν/cm^{-1} : 3265, 3209, 3017, 2944, 1716, 1658, 1533, 1237, 1074, 824; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.57 (3H: H_{2b}, s), 3.84 (3H: H_{3b}, s), 3.94-3.90 (1H: H_{10b}, $J_{10b,10a}$ = 17.5 Hz, d), 4.34-4.30 (1H: H_{10a}, $J_{10a,10b}$ = 17.5 Hz, d), 6.98-6.92 (2H: H₆, H₈, m), 7.18-7.15 (1H: H₇, J = 7.5 Hz, t), 7.26-7.24 (3H: 2xH_{3'}, H₁₈, m), 7.39-7.37 (1H: H₁₅, m), 7.51-7.47 (4H: 2xH_{2'}, H₁₇, -OH, m), 7.54-7.52 (1H: H₉, $J_{9,8}$ = 8.0 Hz, d), 7.90 (1H: H₁, s), 8.11-8.09 (1H: H₁₆, $J_{16,15}$ = 8.5 Hz, $J_{16,14}$ = 1.5 Hz, dd), 8.67-8.65 (2H: H₁₄, H₁₉, m), 10.71 (1H: H₁₂, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 50.42 (C₁₀), 51.98 (C_{2b}), 52.49 (C_{3b}), 84.68 (C₄), 113.58 (C₂), 114.28 (C₈), 115.40 (C₉), 117.10 (C₁₉), 117.64 (C_{3a}), 118.32 (C₁), 120.18 (C₆), 121.77 (C₁₅), 122.29 (C₁₇), 122.46 (C_{9a}), 127.29 (C₇), 128.08 (C₁₈), 128.19 (2xC_{2'}), 128.97 (2xC_{3'}), 130.56 (C_{16a}), 133.42 (C₃), 133.88 (C_{5a}), 134.00 (C₂₀), 134.89 (C_{4'}), 136.35 (C₁₆), 138.85 (C_{13a}), 140.63 (C_{1'}), 148.74 (C₁₄), 163.75 (C_{3'a}), 166.28 (C_{2'a}), 168.92 (C₁₁). Anal. calcd. C₃₂H₂₅ClN₄O₆: C, 64.38; H, 4.22; N, 9.38; Found: C, 64.31; H, 4.30; N, 9.42.

dimethyl 4-(4-cyanophenyl)-4-hydroxy-5-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (**7d**)

Beige powder (precipitated with ethyl acetate/*n*-hexan); mp 150-154°C; IR (KBr): ν/cm^{-1} : 3217, 3200, 3003, 2952, 2229, 1713, 1537, 1228, 1061; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.60 (3H: H_{2b}, s), 3.85 (3H: H_{3b}, s), 3.94-3.91 (1H: H_{10b}, $J_{10b,10a}$ = 17.5 Hz, d), 4.32-4.29 (1H: H_{10a}, $J_{10a,10b}$ = 17.5 Hz, d), 6.94-6.93 (1H: H₆, $J_{6,7}$ = 8.0 Hz, d), 7.00-6.97 (1H: H₈, J = 8.5 Hz, t), 7.20-7.17 (1H: H₇, J = 8.5 Hz, t), 7.41-7.38 (1H: H₁₅, m), 7.50-7.49 (2H: 2xH_{3'}, $J_{3',2'}$ = 6.5 Hz, d), 7.58-7.54 (4H: 2xH_{2'}, H₉, H₁₈, m), 7.64-7.62 (2H: H₁₇, -OH, $J_{17,18}$ = 8.5 Hz, ad), 7.91 (1H: H₁, s), 8.12-8.10 (1H: H₁₆, $J_{16,15}$ = 8.0 Hz, $J_{16,14}$ = 1.5 Hz, dd), 8.67-8.64 (2H: H₁₄, H₁₉, m), 10.74 (1H: H₁₂, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 51.02 (C₁₀), 51.94 (C_{2b}), 52.65 (C_{3b}), 84.75 (C₄), 111.89 (C_{4'}), 113.63 (C₂), 114.22 (C₈), 115.44 (C₉), 117.16 (C₁₉), 117.65 (C_{3a}), 118.45 (C₁), 120.17 (C₆), 121.78 (C₁₅), 122.17 (C₁₇), 122.45 (C_{9a}), 127.16 (C₇), 128.09 (C₁₈), 128.24 (2xC_{2'}), 130.56 (C_{16a}), 132.09 (2xC_{3'}), 133.50 (C₃), 133.88 (C_{5a}), 134.09 (C₂₀), 136.35

(C₁₆), 138.85 (C_{13a}), 141.40 (C_{1'}), 148.70 (C₁₄), 163.67 (C_{3'a}), 166.85 (C_{2'a}), 168.50 (C₁₁). Anal. calcd. C₃₃H₂₅N₅O₆: C, 67.46; H, 4.29; N, 11.92; Found: C, 67.35; H, 4.21; N, 11.84.

dimethyl 4-(4-fluorophenyl)-4-hydroxy-5-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (**7e**)

Beige powder (precipitated with ethyl acetate/*n*-hexan); mp 189-191 °C; IR (KBr): ν/cm^{-1} : 3291, 3196, 3052, 2987, 1705, 1543, 1324, 1233, 1160; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.54 (3H: H_{2b}, s), 3.81 (3H: H_{3b}, s), 3.95-3.92 (1H: H_{10b}, $J_{10b,10a}$ = 17.5 Hz, d), 4.33-4.30 (1H: H_{10a}, $J_{10a,10b}$ = 17.5 Hz, d), 6.97-6.92 (2H: H₆, H₈, m), 7.18-7.15 (1H: H₇, J = 8.5 Hz, t), 7.22-7.20 (2H: 2xH_{3'}, $J_{3',2'}$ = 6.5 Hz, d), 7.40-7.36 (3H: H₁₅, 2xH_{2'}, m), 7.58-7.56 (2H: H₉, H₁₈, m), 7.66-7.63 (2H: H₁₇, -OH, m), 7.90 (1H: H₁, s), 8.15-8.13 (1H: H₁₆, $J_{16,15}$ = 8.0 Hz, d), 8.69-8.66 (2H: H₁₄, H₁₉, m), 10.72 (1H: H₁₂, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 51.26 (C₁₀), 52.03 (C_{2b}), 52.65 (C_{3b}), 84.88 (C₄), 113.63 (C₂), 114.26 (C₈), 115.39 (C₉), 115.96 (2xC_{3'}, $J_{C3'-F}$ = 22.1 Hz, d), 117.22 (C₁₉), 117.65 (C_{3a}), 119.03 (C₁), 120.13 (C₆), 121.80 (C₁₅), 122.15 (C₁₇), 122.45 (C_{9a}), 127.20 (C₇), 128.10 (C₁₈), 128.71 (2x C_{2'}, $J_{C2'-F}$ = 8.1 Hz, d), 130.56 (C_{16a}), 133.51 (C₃), 133.87 (C_{5a}), 134.16 (C₂₀), 135.80 (C_{1'}, $J_{C1'-F}$ = 2.4 Hz, d), 136.32 (C₁₆), 138.84 (C_{13a}), 148.70 (C₁₄), 161.20 (C_{4'}, $J_{C4'-F}$ = 244.5 Hz, d), 163.70 (C_{3'a}), 167.01 (C_{2'a}), 168.54 (C₁₁). Anal. calcd. C₃₂H₂₅FN₄O₆: C, 66.20; H, 4.34; N, 9.65; Found: C, 66.29; H, 4.26; N, 9.71.

dimethyl 4-(4-bromophenyl)-4-hydroxy-5-(2-oxo-2-(quinolin-8-ylamino)ethyl)-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (**7f**)

Peach powder (precipitated with ethyl acetate/*n*-hexan); mp 177-179°C; IR (KBr): ν/cm^{-1} : 3272, 3201, 3012, 2948, 1716, 1658, 1533, 1237, 1074, 675; ¹H-NMR (500 MHz, CDCl₃): δ_{ppm} : 3.56 (3H: H_{2b}, s), 3.83 (3H: H_{3b}, s), 3.94-3.92 (1H: H_{10b}, $J_{10b,10a}$ = 17.5 Hz, d), 4.33-4.30 (1H: H_{10a}, $J_{10a,10b}$ = 17.5 Hz, d), 6.97-6.91 (2H: H₆, H₈, m), 7.17-7.14 (1H: H₇, J = 8.0 Hz, t), 7.39-7.37 (1H: H₁₅, m), 7.43-7.41 (4H: 2xH_{3'}, H₁₈, -OH, m), 7.49-7.48 (3H: 2xH_{2'}, H₁₇, m), 7.53-7.51 (1H: H₉, $J_{9,8}$ = 8.0 Hz, d), 7.89 (1H: H₁, s), 8.10-8.09 (1H: H₁₆, $J_{16,15}$ = 8.0 Hz, d), 8.67-8.64 (2H: H₁₄, H₁₉, m), 10.71 (1H: H₁₂, s). ¹³C{¹H}-NMR (125 MHz, CDCl₃): δ_{ppm} : 50.43 (C₁₀), 51.97 (C_{2b}), 52.50 (C_{3b}), 84.71 (C₄), 113.57 (C₂), 114.28 (C₈), 115.40 (C₉), 117.08 (C₁₉), 117.60 (C_{3a}), 118.31 (C₁), 120.19 (C₆), 121.76 (C₁₅), 122.29 (C₁₇), 122.46 (C_{9a}), 123.15 (C_{4'}), 127.27 (C₇), 128.05 (C₁₈), 128.50 (2xC_{2'}), 130.58 (C_{16a}), 131.51 (2xC_{3'}), 133.28 (C₃), 133.84 (C_{5a}), 133.97 (C₂₀), 136.33 (C₁₆), 141.10 (C_{13a}), 138.82 (C_{1'}), 148.73 (C₁₄), 163.73 (C_{3'a}), 166.24 (C_{2'a}), 168.90 (C₁₁). Anal. calcd. C₃₂H₂₅BrN₄O₆: C, 59.92; H, 3.93; N, 8.73; Found: C, 60.02; H, 3.95; N, 8.80.

For each series of compounds a representative was chosen (3a-i → **3f**, 3'a-i → **3'd**, 5a-i → **5i**, 6a-i → **6e**, 7a-i → **7b**), whose NMR spectrum is presented.

NMR Spectra of compounds

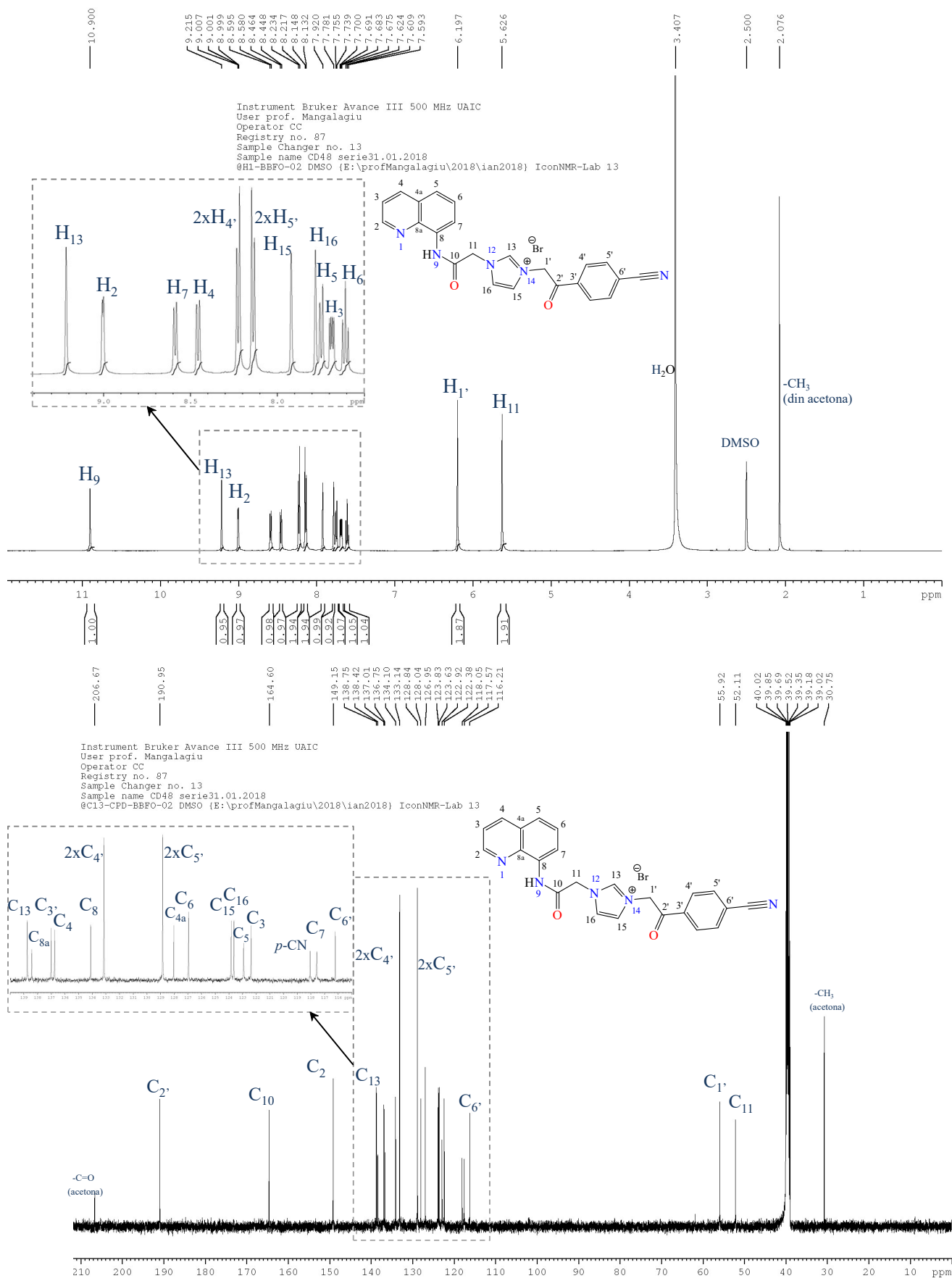


Figure 1. ¹H-NMR and ¹³C{¹H}-NMR Spectra for compound 3'd.

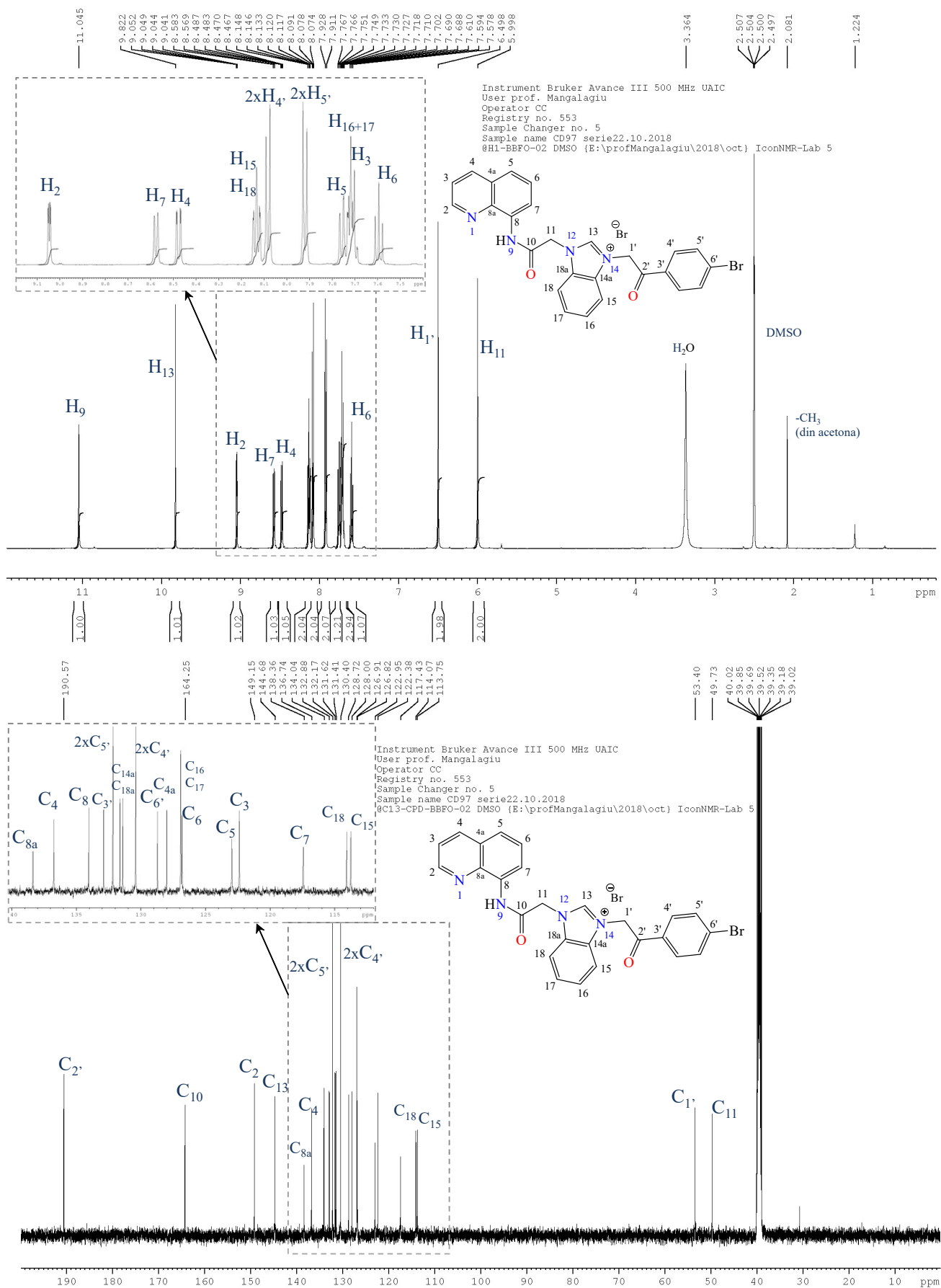


Figure 2. ¹H-NMR and ¹³C{¹H}-NMR Spectra for compound 3f.

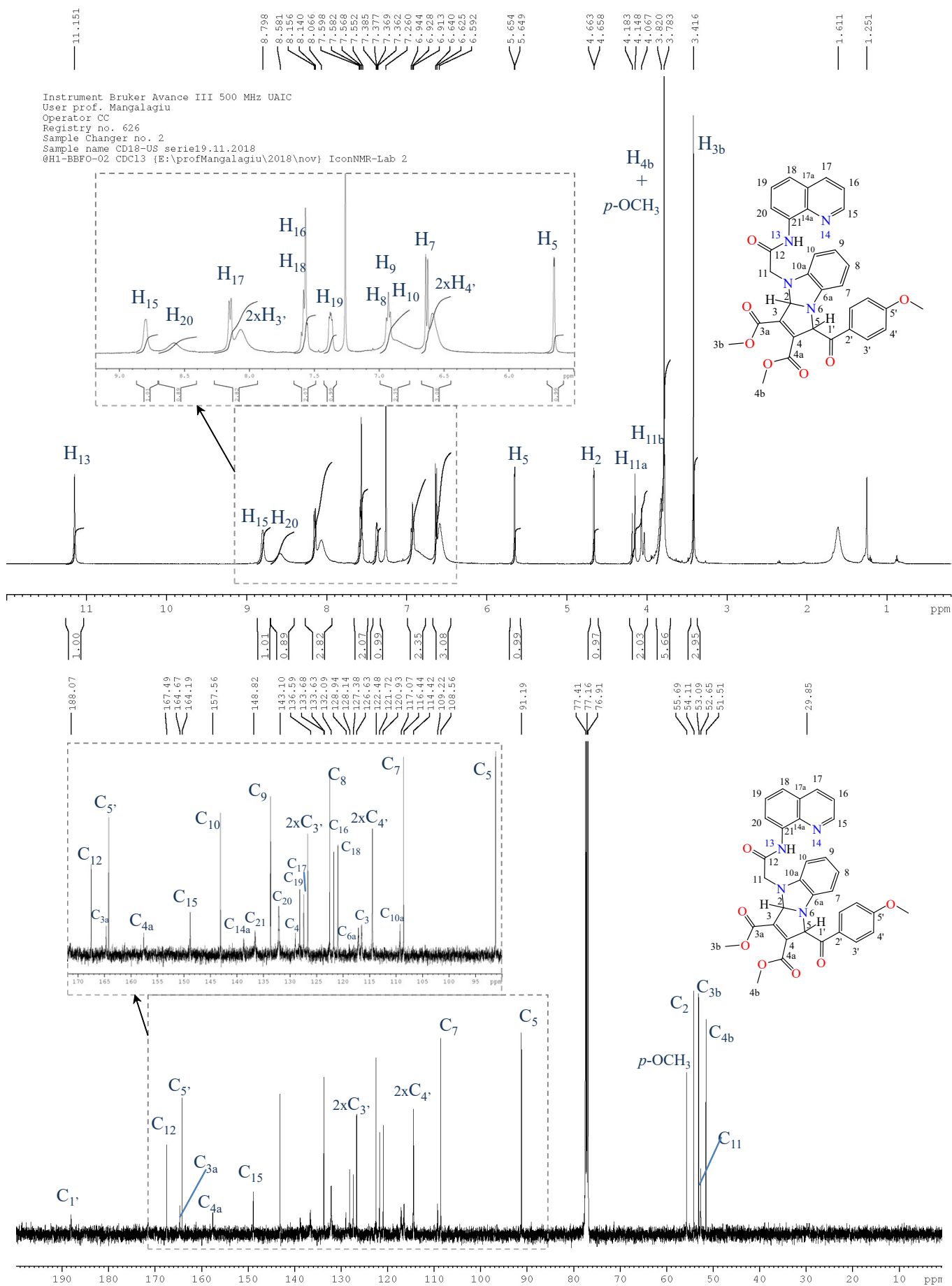


Figure 3. $^1\text{H-NMR}$ and $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ Spectra for compound **5i**.

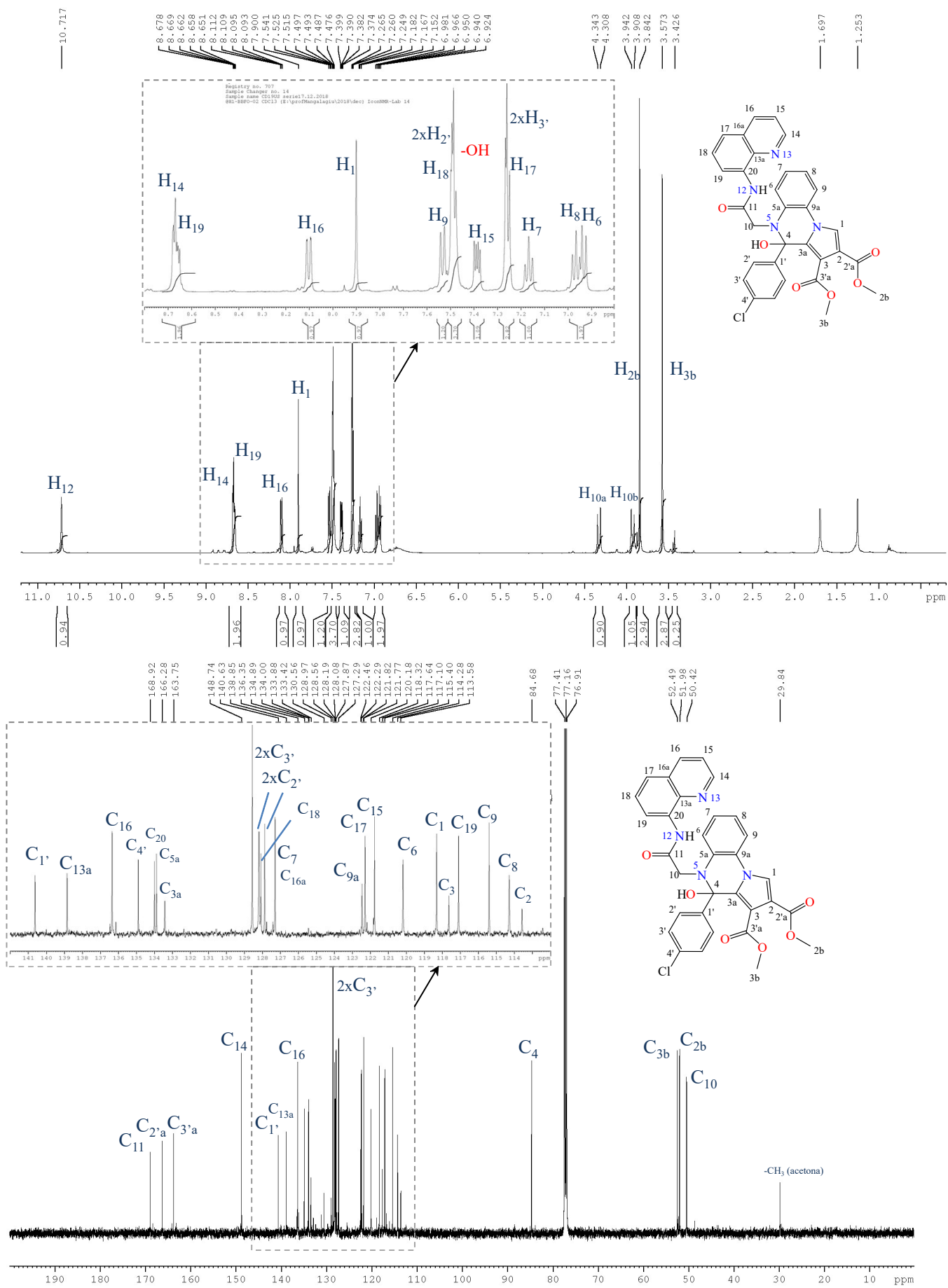


Figure 4. ¹H-NMR and ¹³C{¹H}-NMR Spectra for compound 7b.

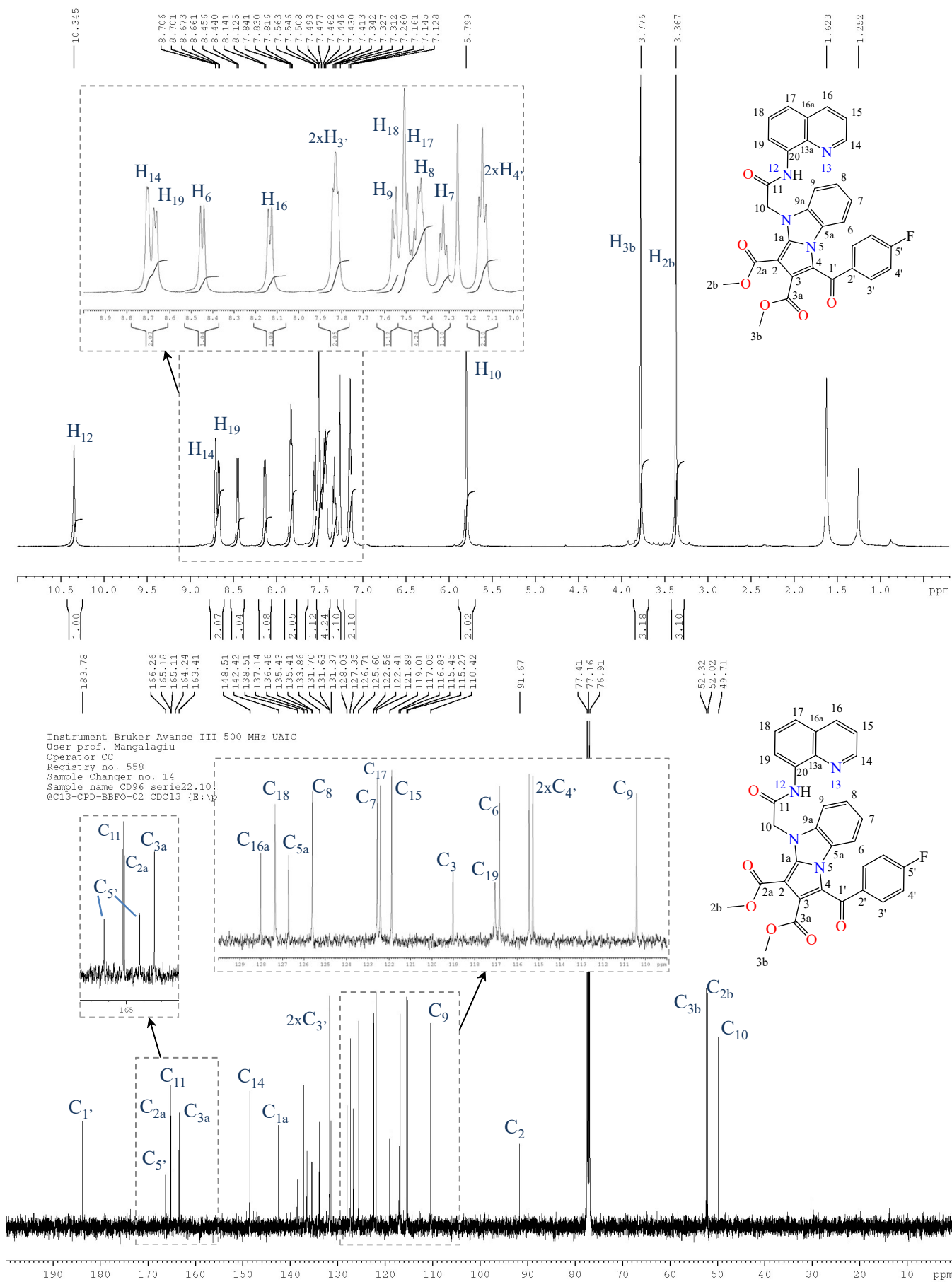


Figure 5. ^1H -NMR and $^{13}\text{C}\{^1\text{H}\}$ -NMR Spectra for compound **6e**.