Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of 4(3*H*)Quinazolinimines by Reaction of (*E*)-*N*-(Aryl)-Acetimidoyl or -benzimidoyl chloride with Amines

Supporting Information

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Experimental Section

General

All manipulations were performed in air. Reagent-grade solvents were obtained from E. Merck. Toluene was distilled from benzophenone ketyl. The compounds 2-aminobenzonitrile, aniline, *p*-phenylendiamine, 4-aminobenzonitrile, *p*-anisidine, (*R*)-(+)-α-methyl benzilamine, ethylenediamine, 1,3-diaminopropane, 2-picolinamina, piperonylamine and 2,5-dimethoxyaniline were purchased commercially. The imidoyl chlorides (*E*)-N-(2,6-diisopropylphenyl)acetimidoyl chloride[1] and (*E*)-*N*-(2,6-diisopropylphenyl)benzimidoyl chloride[2] were prepared according to published procedures. The compound (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride was prepared according to a modified literature procedure.[3] The following instruments were used for the physical characterization of the compounds. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts and the coupling constants are reported in parts per million ($SiMe_4$ as standard) and Hertz, respectively. Most of the NMR assignments were supported by additional 2D experiments and the numbers of scans used for ^{13}C NMR were ranged from 0.5–8K depending on the sample concentration. FT-IR spectra were recorded on a Bruker Vector-22 spectrophometer using KBr pellets and the infrared frequencies are reported in cm^{-1}. Mass spectra were acquired using a Micro Tof (Bruker) or a Clarus SQ 8T GC/MS (PerkinElmer) or a AB SCIEX Triple Quad 4500 LC/MS/MS.

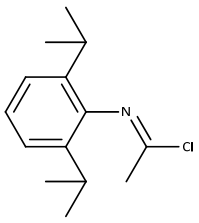
X-ray crystal structure analyses: For compounds **1**, **2**, **4**, **9** and **13** data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (Nonius B.V., 1998); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

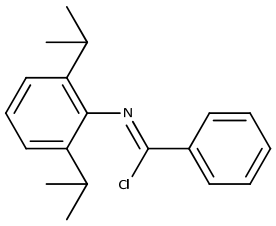
Exceptions and special features: For compound **2** a half badly disordered dichloromethane molecule was found in the asymmetrical unit and could not be satisfactorily refined. Compound **5** crystallized with one badly disordered over tree positions methanol molecule. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically

the effect of the solvents. The quoted formula and derived parameters are not included the squeezed solvent molecules.

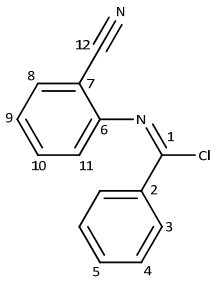
Crystallographic data for **1**, **2**, **4**, **5**, **9** and **13** have been deposited with Cambridge Crystallographic Data Centre, CCDC numbers 1008256, 1008257, 1008258, 1008259, 1008260 and 1057208. These data can be obtained free at www.ccdc.cam.ac.uk/conts/rtrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

Chart S1. Structures of imidoyl chlorides compounds





***(E)*-*N*-(2,6-diisopropylphenyl)acetimidoyl chloride** **(*E*)-*N*-(2,6-diisopropylphenyl)benzimidoyl chloride**



***N*-(2-cyanophenyl)benzimidoyl chloride**

***(E)*-*N*-(2-cyanophenyl)benzimidoyl chloride:** A mixture of *N*-(cyanophenyl)benzamide[3] (1.20 g, 5.40 mmol) and an excess of thionyl chloride (2 mL, 27 mmol) was stirred for 8 hour under reflux. The remainder thionyl chloride was distilled off raising temperature to 120 °C. The residues were removed under vacuum to give yellow solid (1.17 g, 90%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 8.21 (d, *J* = 7.8 Hz, 2H, H_3), 7.69 (d, *J* = 7.8 Hz, 1H, H_8), 7.66 – 7.55 (m, 2H, $H_{10,\ 5}$), 7.49 (t, *J* = 7.8 Hz, 2H, H_4), 7.27 (t, *J* = 7.7 Hz, 1H, H_9), 7.11 (d, *J* = 8.1 Hz, 1H, H_{11}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 150.6 (C_6), 147.6 (C_1), 134.6 (C_2), 133.5 (C_{10}), 133.0 (C_5), 133.0 (C_8), 129.9 (C_3), 128.7 (C_4), 125.2 (C_9), 120.9 (C_{11}), 116.7 (C_{12}), 104.9 (C_7).

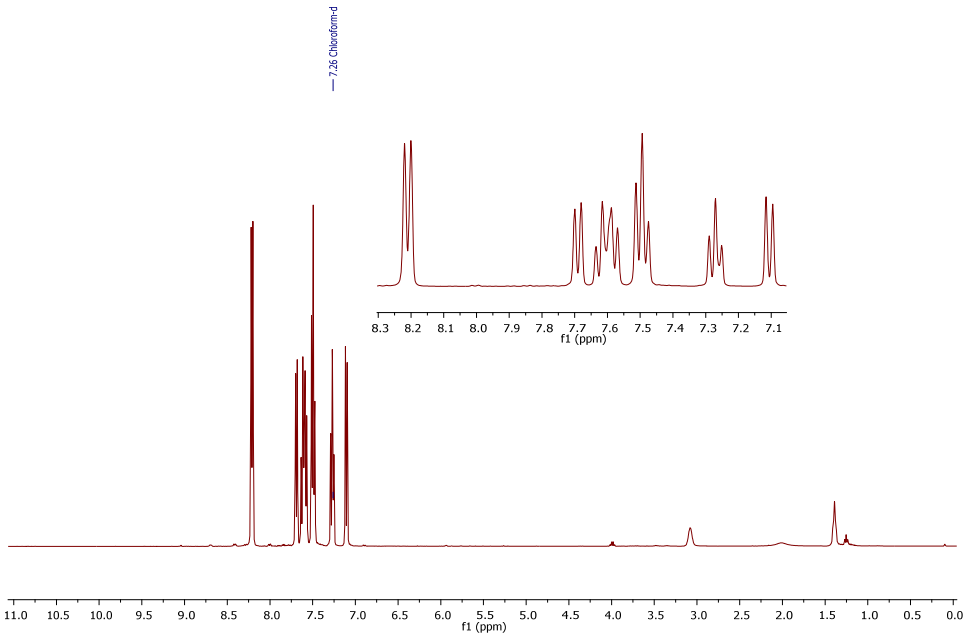
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.21 / 147.6, 133.0 (H_3 / $C_{1,5}$), 7.69 / 150.6, 133.5, 116.7 (H_8 / $C_{6,10,12}$), 7.66 – 7.55 / 150.6, 133.0 (H_{10} / $C_{6,8}$), 7.66 – 7.55 / 129.9 (H_5 / C_3), 7.49 / 134.6 (H_4 / C_2), 7.27 / 120.9, 104.9 (H_9 / $C_{11,7}$), 7.11 / 125.2, 104.9 (H_{11} / $C_{9,7}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.21 / 129.9 (H_3 / C_3), 7.69 / 133.0 (H_8 / C_8), 7.66 – 7.55 / 133.5 (H_{10} / C_{10}), 7.66 – 7.55 / 133.0 (H_5 / C_5), 7.49 / 128.7 (H_4 / C_4), 7.27 / 125.2 (H_9 / C_9), 7.11 / 120.9 (H_{11} / C_{11}).

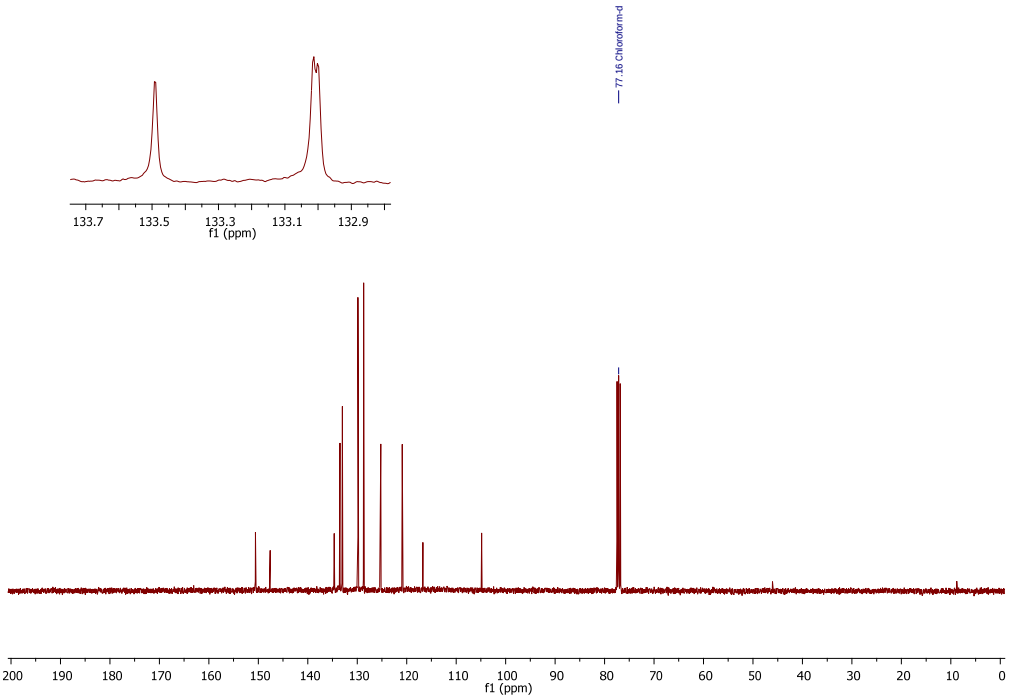
COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 8.21 / 7.49 (H_3 / H_4), 7.49 / 7.66 – 7.55 (H_4 / H_5), 7.69 / 7.27 (H_8 / H_9), 7.27 / 7.66 – 7.55 (H_9 / H_{10}), 7.66 – 7.55 / 7.11 (H_{10} / H_{11}).

FT-IR (KBr): ν / cm^{-1} = 3055, 3052, 2230 (CN), 1681, 1666, 1590, 1579, 1567, 1547, 1518, 1488, 1478, 1446, 1336, 1315, 1301, 1281, 1254, 1211, 1191, 1172, 1095, 1076, 1041, 1028, 1000, 979, 956, 925, 890, 869, 838, 764, 749, 734, 703, 682, 653, 633, 617, 604, 588, 561, 540, 504.

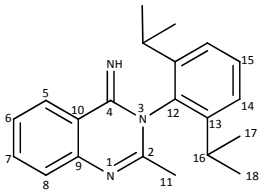
MS (ESI) for $C_{14}H_9ClN_2$ $[M]^+$: m/z calcd: 240, found: 240.



***N*-(2-cyanophenyl)benzimidoyl chloride. ^{1}H NMR** (400 MHz, $CDCl_3$, 298 K).



***N*-(2-cyanophenyl)benzimidoyl chloride. ^{13}C NMR** (100 MHz, $CDCl_3$, 298 K).



Compound 1

Synthesis of 3-(2,6)-diisopropylphenyl)-2-methylquinazolin-4(3*H*)-imine (1):

(*E*)-*N*-(2,6-diisopropylphenyl)acetimidoyl chloride (0.48 g, 2.03 mmol) was added to a solution of 2-aminobenzonitrile (0.24 g, 2.03 mmol) and trietylamine (0.31 mL, 2.23 mmol) in 30 mL of toluene and the reaction mixture was stirred for 6 hours under reflux. All volatiles were removed under vacuum. The solid residue was dissolved in 30 mL of CH_2Cl_2 and washed twice with 15 mL of water. The solution was evaporated to dryness and the crude product was crystallized from methanol to give colorless crystals (0.43 g, 66%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 8.30 (br. s, 1H, H_5), 7.58 (t, *J* = 7.6 Hz, 1H, H_7), 7.48 (m, 2H, $H_{8,15}$), 7.32 (m, 3H, $H_{6,14}$), 6.10 (br. s, 1H, NH), 2.69 (hept, *J* = 6.8 Hz, 2H, H_{16}), 1.99 (s, 3H, H_{11}), 1.17 (d, *J* = 6.9 Hz, 6H, H_{17}), 1.11 (d, *J* = 6.9 Hz, 6H, H_{18}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 154.4 (C_4), 153.6 (C_2), 146.6 (C_{13}), 144.6 (C_9), 132.8 (C_7), 131.4 (C_{12}), 130.6 (C_{15}), 126.4 (C_8), 126.4 (C_5 Not Clear), 126.2 (C_6), 125.4 (C_{14}), 120.6 (C_{10}), 28.4 (C_{16}), 25.0(C_{18}), 24.0 (C_{11}), 23.5 (C_{17}).

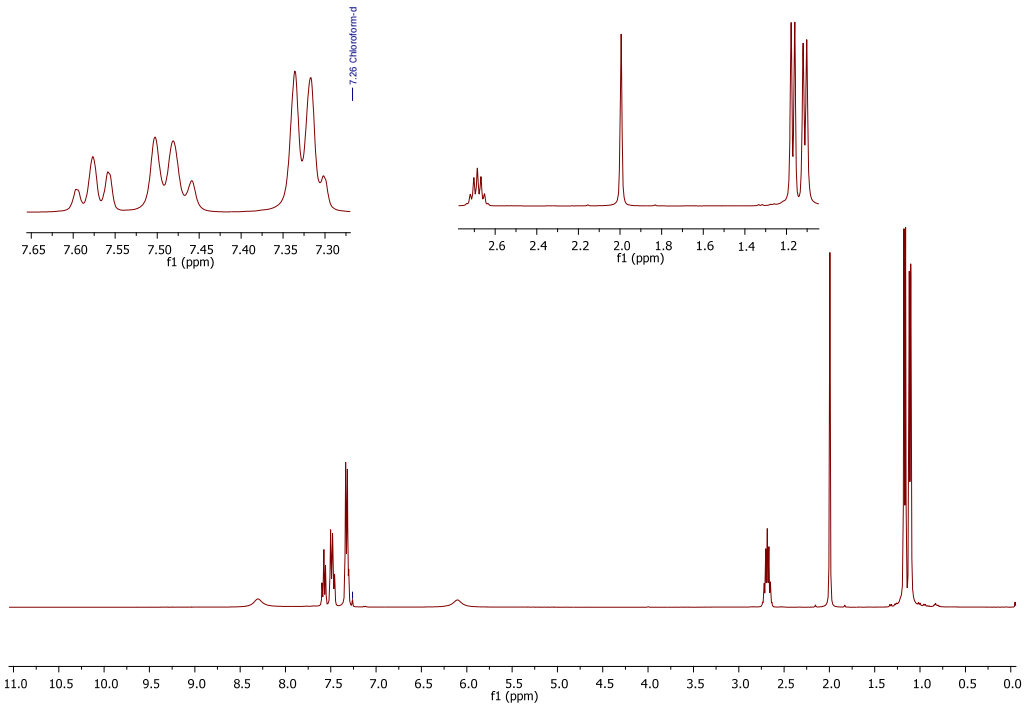
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 7.58 / 144.6, 126.4 (H_7 / $C_{9,5}$), 7.48 / 126.2, 120.6 (H_8 / $C_{6,10}$), 7.48 / 146.6 (H_{15} / C_{13}), 7.32 / 126.4, 120.6 (H_6 / $C_{8,10}$), 7.32 / 131.4, 28.4 (H_{14} / $C_{12,16}$), 2.7 / 131.4, 125.4 (H_{16} / $C_{12,14}$), 1.99 / 153.6 (H_{11} / C_2), 1.17 / 146.6, 25.0 (H_{17} / $C_{13,18}$), 1.11 / 146.6, 23.5 (H_{18} / $C_{13,17}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.30 / 126.4 (H_5 / C_5), 7.58 / 132.8 (H_7 / C_7), 7.48 / 130.6 (H_{15} / C_{15}), 7.48 / 126.4 (H_8 / C_8), 7.32 / 126.2 (H_6 / C_6), 7.32 / 125.4 (H_{14} / C_{14}), 2.69 / 28.4 (H_{16} / C_{16}), 1.99 / 24.0 (H_{11} / C_{11}), 1.17 / 23.5 (H_{17} / C_{17}), 1.11 / 25.0 (H_{18} / C_{18}).

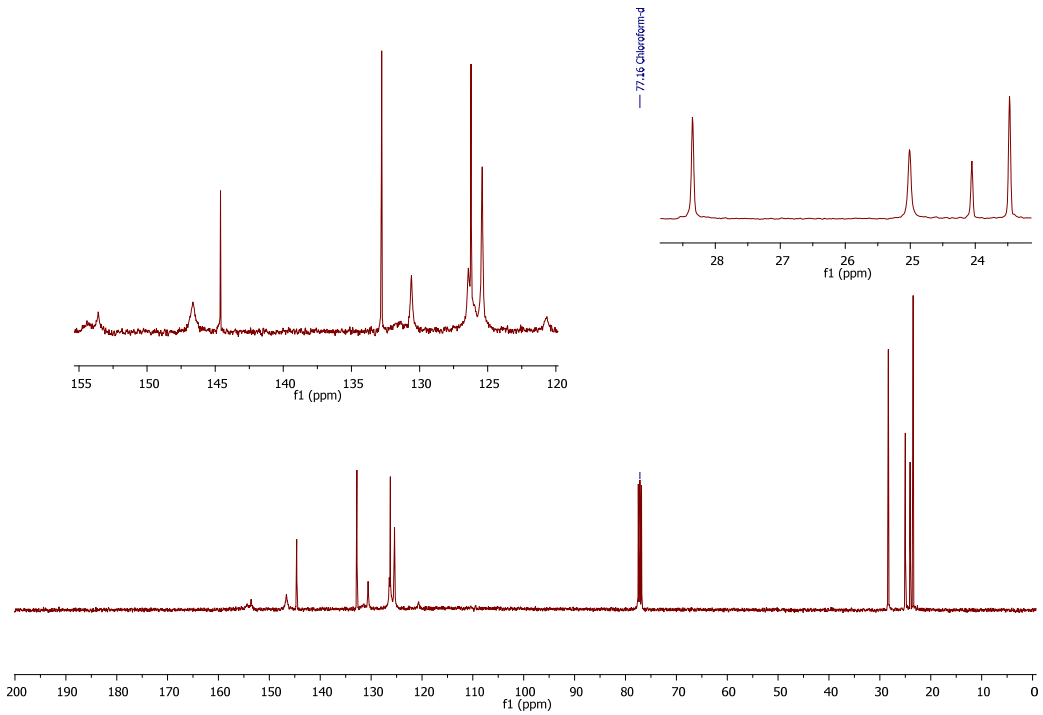
COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) $\delta(^1H)$ / $\delta(^1H)$ = 8.30 / 7.32 (H_5 / H_6), 7.32 / 7.58 (H_6 / H_7), 7.58 / 7.48 (H_7 / H_8), 7.48 / 7.32 (H_{15} / H_{14}), 2.69 / 1.17 (H_{16} / H_{17}), 2.69 / 1.11(H_{16} / H_{18}).

FT-IR (KBr): ν / cm^{-1} = 3442, 3288, 3078, 3061, 3034, 3009, 2963, 2929, 2870, 1630, 1594, 1582, 1466, 1379, 1364, 1352, 1306, 1276, 1249, 1230, 1207, 1178, 1144, 1058, 1030, 870, 838, 8.15, 766, 662, 643, 627, 615, 560, 544.

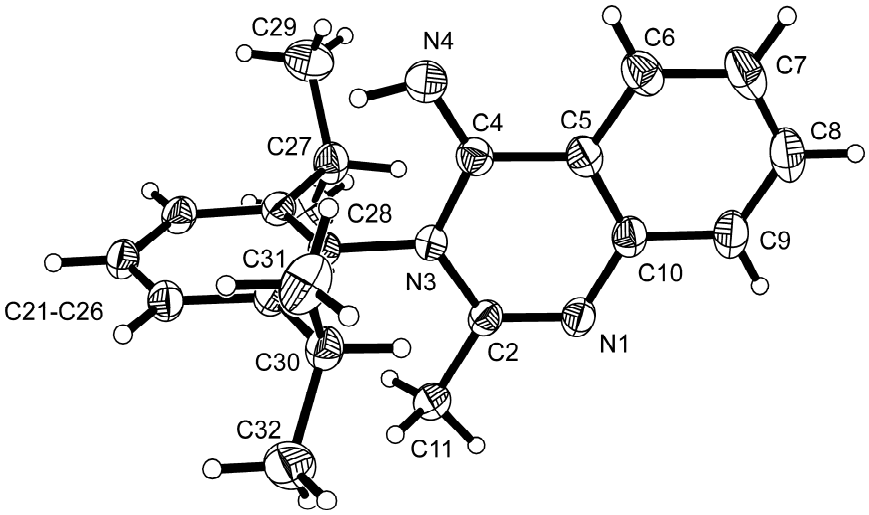
HRMS (ESI) for $C_{21}H_{26}N_3$ $[M+H]^+$: m/z calcd: 320.212, found: 320.212.



Compound 1. ^1H NMR (400 MHz, $CDCl_3$, 298 K).



Compound 1. ^{13}**C NMR** (100 MHz, $CDCl_3$, 298 K).



Crystal structure of compound 1 Selected bond lengths (Å) and angles (°): C4-N4, 1.276(2); C4-N3, 1.408(2); N3-C2, 1.389(2); C2-N1, 1.290(2); N1-C10, 1.391(2); C5-C4, 1.468(2); C4-N3-C21, 117.7(1); C2-N3-C21, 119.8(1); C2-N3-C4, 122.5(1). Only one molecule (molecule "A") of two found in the asymmetric unit is shown.

X-ray crystal structure analysis of 1: formula $C_{21}H_{25}N_3$, *M* = 319.44 colourless crystal, 0.38 x 0.35 x 0.15 mm, *a* = 11.8867(3), *b* = 12.5284(6), *c* = 13.0514(4) Å, α = 79.096(4), *β* = 89.444(2), γ = 77.230(5)°, *V* = 1860.3(1) $Å^3$, ρ_{calc} = 1.141 gcm^{-3}, μ = 0.521 mm^{-1}, empirical absorption correction (0.826 ≤ T ≤ 0.925), *Z* = 4, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, *T* = 223(2) K, ω and ϕ scans, 21856 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 $Å^{-1}$, 6335 independent (R_{int} = 0.037) and 5970 observed reflections [*I*>2σ(*I*)], 441 refined parameters, *R* = 0.045, wR^2 = 0.118, max. (min.) residual electron density 0.15 (-0.16) e.$Å^{-3}$, the hydrogen atoms at N4A and N4B were refined freely, but with N-H distance restraints (SADI); others were calculated and refined as riding atoms.

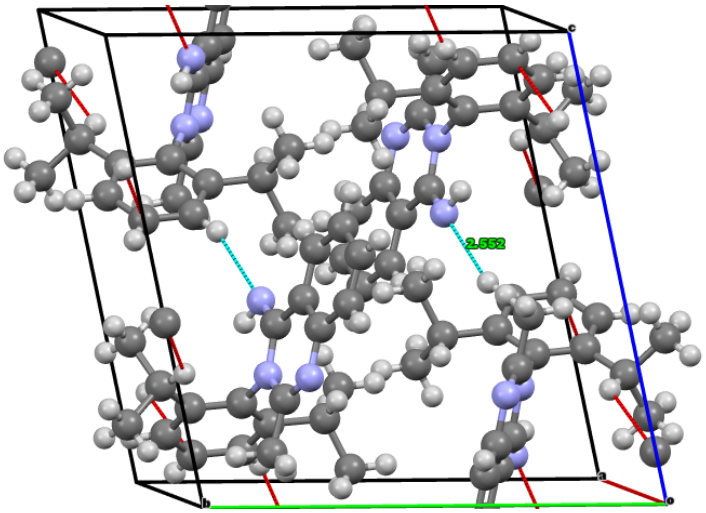
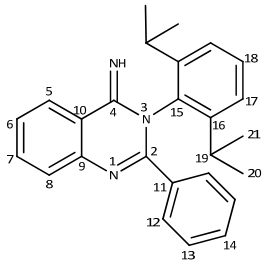


Figure S1. Interaction



Compound 2

Synthesis of 3-(2,6-diisopropylphenyl)-2-phenylquinazolin-4(3*H*)-imine (2):

(*E*)-*N*-(2,6-diisopropylphenyl)benzimidoyl chloride (0.84 g, 2.80 mmol) was added to a solution of 2-aminobenzonitrile (0.33 g, 2.80 mmol) and trietylamine (0.43 mL, 3.08 mmol) in 30 mL of toluene and the reaction mixture was stirred for 36 hours under reflux. All volatiles were removed under vacuum and the residue was dissolved in 30 mL CH_2Cl_2 and washed twice with 15 mL of water. After removal of solvent and drying, the crude product was crystallized from ethyl acetate to give colorless crystals (0.73 g, 68 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ/ppm = 8.36 (br. s, 1H, H_5), 7.67 (m, 2H, $H_{7,8}$), 7.44 (m, 2H, $H_{6,18}$), 7.34 - 7.12 (m, 7H, $H_{17,12,13,14}$), 6.33 (br. s, 1H, NH), 2.86 (hept, *J* = 6.7 Hz, 2H, H_{19}), 1.14 (d, *J* = 6.7 Hz, 6H, H_{20}), 1.00 (d, *J* = 6.8 Hz, 6H, H_{21}).

^{13}C NMR (100 MHz, CD_2Cl_2, 298 K) δ/ppm = 155.0 (C_4, Not Clear), 154.9 (C_2), 147.7 (C_{16}), 145.5 (C_9), 136.2 (C_{11}), 133.2 (C_7), 132.4 (C_{15}), 131.0 (C_{18}), 129.78 (C_{14}), 129.7 (C_{13}), 127.9 (C_{12}), 127.9 (C_8), 127.2 (C_6), 126.5 (C_5), 125.6 (C_{17}), 121.8 (C_{10}), 29.2 (C_{19}), 25.8 (C_{20}), 23.1 (C_{21}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K) δ(^{1}H) / δ(^{13}C) = 8.36 / 133.2 (H_5 / C_7), 7.67 / 145.5, 126.5 (H_7 / $C_{9,5}$), 7.67 / 127.2, 121.8 (H_8 / $C_{6,10}$), 7.44 / 127.8, 121.8 (H_6 / $C_{8,10}$), 7.44 / 147.6 (H_{18} / C_{16}), 7.34 – 7.12 / 154.9, 129.8 (H_{12} / $C_{2,14}$), 7.34 – 7.12 / 136.2 (H_{13} / C_{11}), 7.34 – 7.12 / 127.9 (H_{14} / C_{12}), 7.34 – 7.12 / 132.4, 29.2 (H_{17} / $C_{15,19}$), 2.86 / 132.4, 125.6 (H_{19} / $C_{15,17}$), 1.14 / 147.6, 23.1 (H_{20} / $C_{16,21}$), 1.00 / 147.6, 25.8 (H_{21} / $C_{16,20}$).

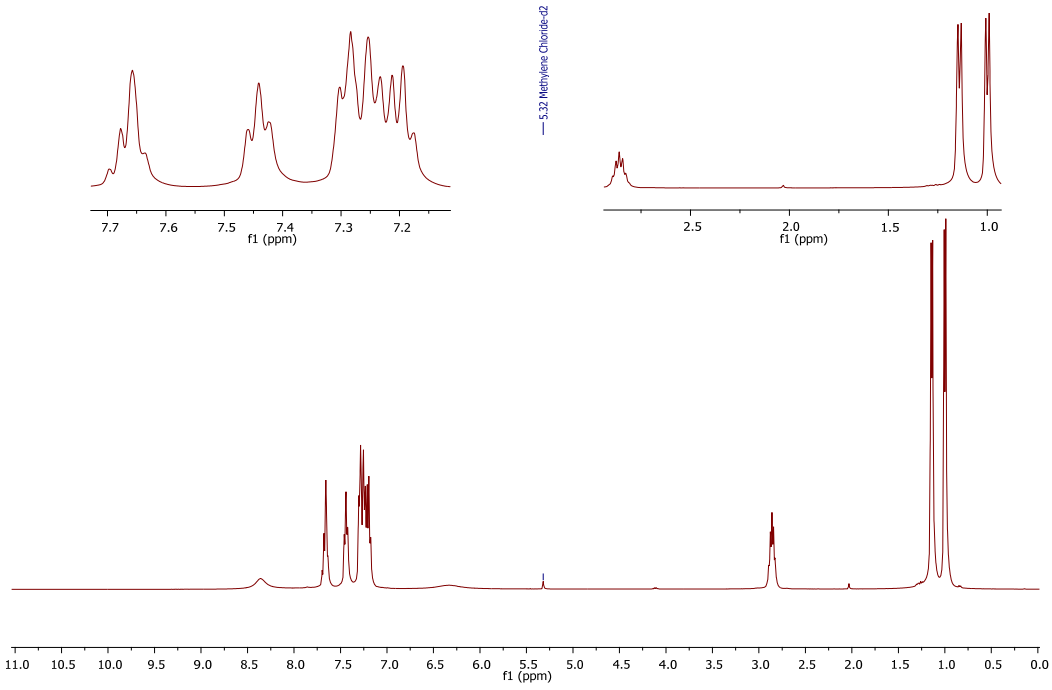
^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K) δ(^{1}H) / δ(^{13}C) = 8.36 / 126.5 (H_5 / C_5), 7.67 / 133.2 (H_7 / C_7), 7.67 / 127.8 (H_8 / C_8), 7.44 / 131.0 (H_{18} / C_{18}), 7.44 / 127.2 (H_6 / C_6), 7.34 - 7.12 / 129.8 (H_{14}

/ C_{14}), 7.34 - 7.12 / 129.7 (H_{13} / C_{13}), 7.34 - 7.12 / 127.9 (H_{12} / C_{12}), 7.34 - 7.12 / 125.6 (H_{17} / C_{17}), 2.86 / 29.2 (H_{19} / C_{19}), 1.14 / 25.8 (H_{20} / C_{20}), 1.00 / 23.1 (H_{21} / C_{21}).

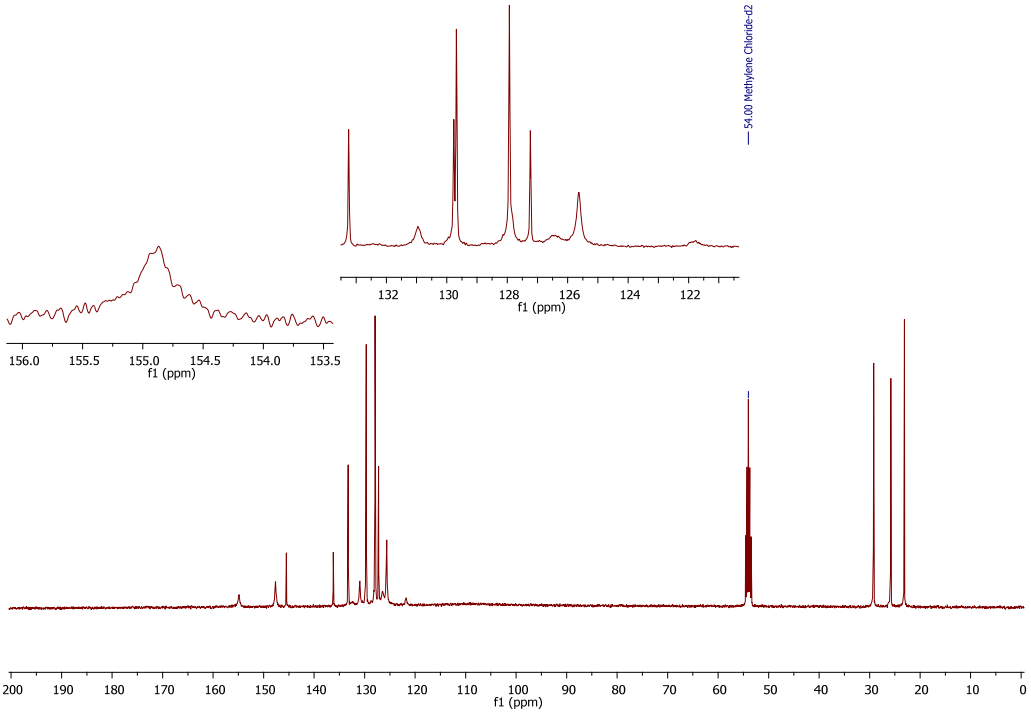
COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K) $\delta(^1H)$ / $\delta(^1H)$ = 8.36 / 7.44 (H_5 / H_6), 7.44 / 7.67 (H_6 / H_7), 7.67 (H_7 / H_8), 7.44 / 7.34 – 7.12 (H_{18} / H_{17}), 7.34 – 7.12 (H_{14} / H_{13}), 2.69 / 1.14, (H_{19} / H_{20}), 2.69 / 1.00 (H_{19} / H_{21}).

FT-IR (KBr): ν / cm^{-1} = 3448, 3301, 3258, 3064, 2960, 2927, 2865, 1744, 1625, 1608, 1557, 1494, 1474, 1444, 1384, 1360, 1322, 1297, 1248, 1235, 1205, 1177, 1154, 1142, 1050, 1031, 1020, 900, 873, 819, 800, 768, 757, 730, 704, 696, 671, 637.

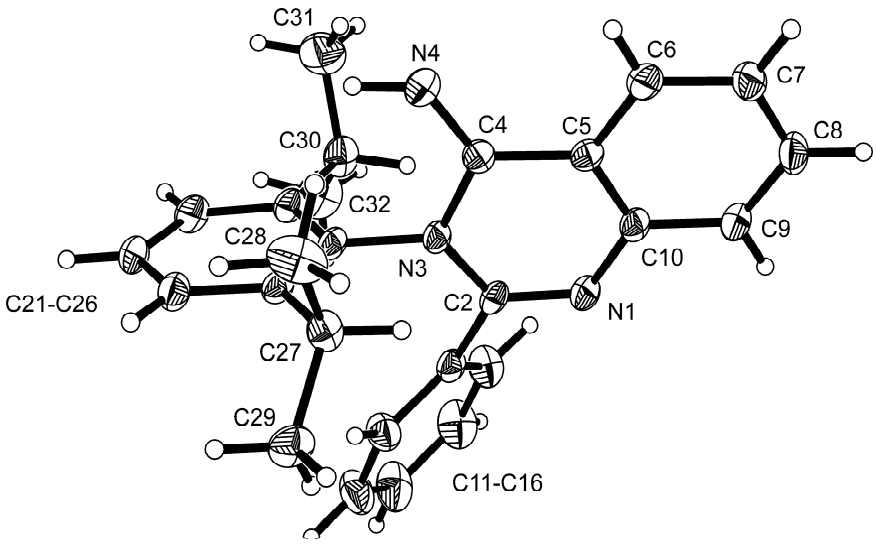
HRMS (ESI) for $C_{26}H_{28}N_3$ $[M+H]^+$: m/z calcd: 382.228, found: 382,228.



Compound 2. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K).



Compound 2. ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K).



Crystal structure of compound 2 . Selected bond lengths (Å) and angles (°): C4-N4, 1.281(4); C4-N3, 1.418(4); N3-C2, 1.399(4); C2-N1, 1.290(2); N1-C10, 1.391(4); C5-C4, 1.457(4); C4-N3-C21, 117.3(2); C2-N3-C21, 121.5(2); C2-N3-C4, 120.8(2).

X-ray crystal structure analysis of 2: formula $C_{26}H_{27}N_3$, M = 381.51 colourless crystal, 0.23 x 0.15 x 0.03 mm, a = 16.4490(8), b = 16.4490(8), c = 8.4714(4) Å, V = 2292.1(2) Å^3, ρ_{calc} = 1.106 gcm^{-3}, μ = 0.502 mm^{-1}, empirical absorption correction (0.893 ≤ T ≤ 0.985), Z = 4, tetragonal, space group P-4 (No. 81), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 8679 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 3410 independent (R_{int} = 0.058) and 2945 observed reflections [I>2σ(I)], 269 refined parameters, R = 0.059, wR^2 = 0.162, max. (min.) residual electron density 0.19 (-0.23) e.Å^{-3}, the hydrogen at N3 atom was refined freely, but with N-H distance restraints (DFIX and U-fixed value); others were calculated and refined as riding atoms.

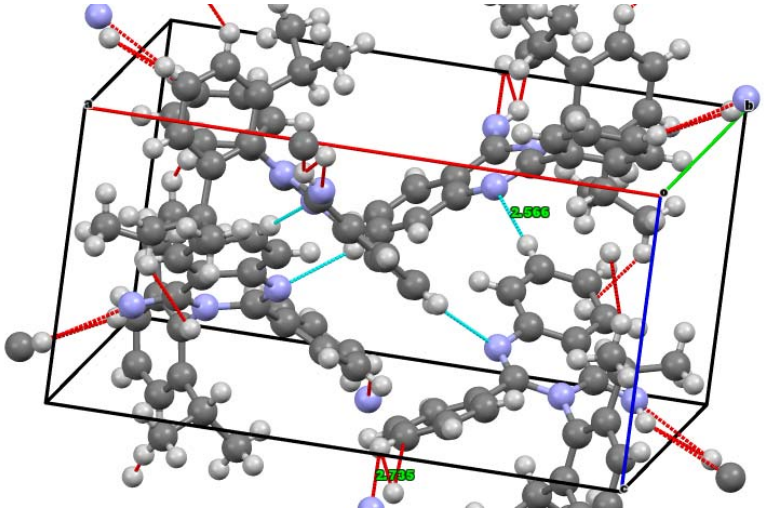
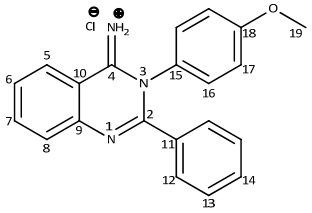


Figure S2. Interaction

The primary structure shows hydrogen bond interactions in the crystal lattice involving the lone pair of the nitrogen N1 from the cyclic imine ring with the hydrogen from C8 atom (N1---H8-C8 2.566 Å). These interactions result in the formation of tetramers in the unit cell (Figure S1 and S2). A second hydrogen bond interaction was observed between the tetramers and involves the exocyclic imine moiety (N4---H14-C14 2.735 Å).



Compound 3

Synthesis of 3-(4-methoxyphenyl)-2-phenylquinazolin-4(3*H*)-iminium chloride (3):

(*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.12 g, 0.49 mmol) was added to a solution of *p*-anisidine (0.06 g, 0.49 mmol) in 30 mL of toluene and the reaction mixture was stirred for 36 hours under reflux. All volatiles were removed under vacuum and the crude product was washed with acetone and dried to give yellow solid (0.14 g, 80 %).

^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$ (97:3), 298 K) δ/ppm = 8.65 (d, *J* = 7.8 Hz, 1H, H_5), 8.36 (d, *J* = 7.6 Hz, 2H, H_{12}), 8.29 (d, *J* = 8.0 Hz, 1H, H_8), 7.77 (d, *J* = 8.4 Hz, 2H, H_{16}), 7.58 (t, *J* = 7.2 Hz, 1H, H_{14}), 7.54 – 7.45 (m, 3H, $H_{13,7}$), 7.32 (t, *J* = 7.3 Hz, 1H, H_6), 6.93 (d, *J* = 8.5 Hz, 2H, H_{17}), 3.83 (s, 3H, H_{19}).

^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$ (97:3), 298 K) δ/ppm = 158.3 (C_{18}), 158.2 (C_4), 157.2 (C_2), 138.8 (C_9), 135.4 (C_7), 134.0 (C_{13}), 130.2 (C_{11}), 129.5 (C_{12}), 129.4 (C_{14}), 129.3 (C_{15}), 128.2 (C_6), 125.7 (C_{16}), 124.6 (C_5), 119.8 (C_8), 114.0 (C_{17}), 112.0 (C_{10}), 55.6 (C_{19}).

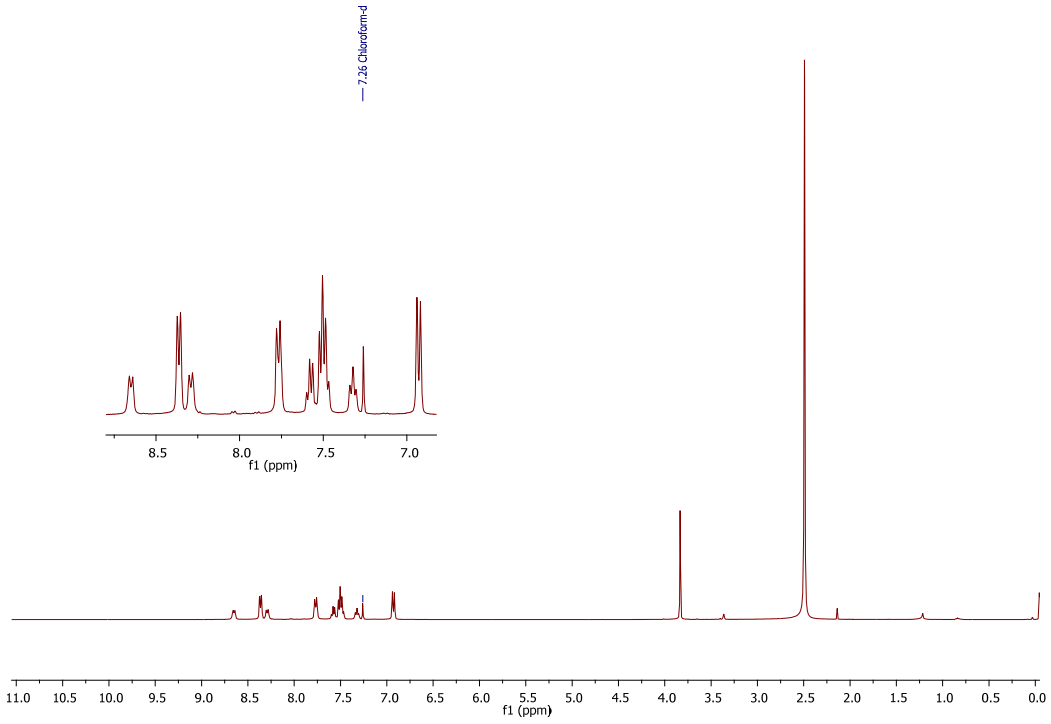
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3/CD_3OD$ (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.65 / 158.2, 138.8, 135.4 (H_5 / $C_{4,9,7}$), 8.36 / 157.2, 129.4 (H_{12} / $C_{2,14}$), 8.29 / 128.2, 112.0 (H_8 / $C_{6,10}$), 7.77 / 158.3 (H_{16} / C_{18}), 7.58 / 129.5 (H_{14} / C_{12}), 7.54 – 7.45 / 130.2 (H_{13} / C_{11}), 7.54 – 7.45 / 138.8, 124.6 (H_7 / $C_{9,5}$), 7.32 / 119.8, 112.0 (H_6 / $C_{8,10}$), 6.93 / 129.3 (H_{17} / C_{15}), 3.83 / 158.3 (H_{19} / C_{18}).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3/CD_3OD$ (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.65 / 124.6 (H_5 / C_5), 8.36 / 129.5 (H_{12} / C_{12}), 8.29 / 119.8 (H_8 / C_8), 7.77 / 125.7 (H_{16} / C_{16}), 7.58 / 129.4 (H_{14} / C_{14}), 7.54 – 7.45 / 134.0 (H_{13} / C_{13}), 7.54 – 7.45 / 135.4 (H_7 / C_7), 7.32 / 128.2 (H_6 / C_6), 6.93 / 114.0 (H_{17} / C_{17}), 3.83 / 55.6 (H_{19} / C_{19}).

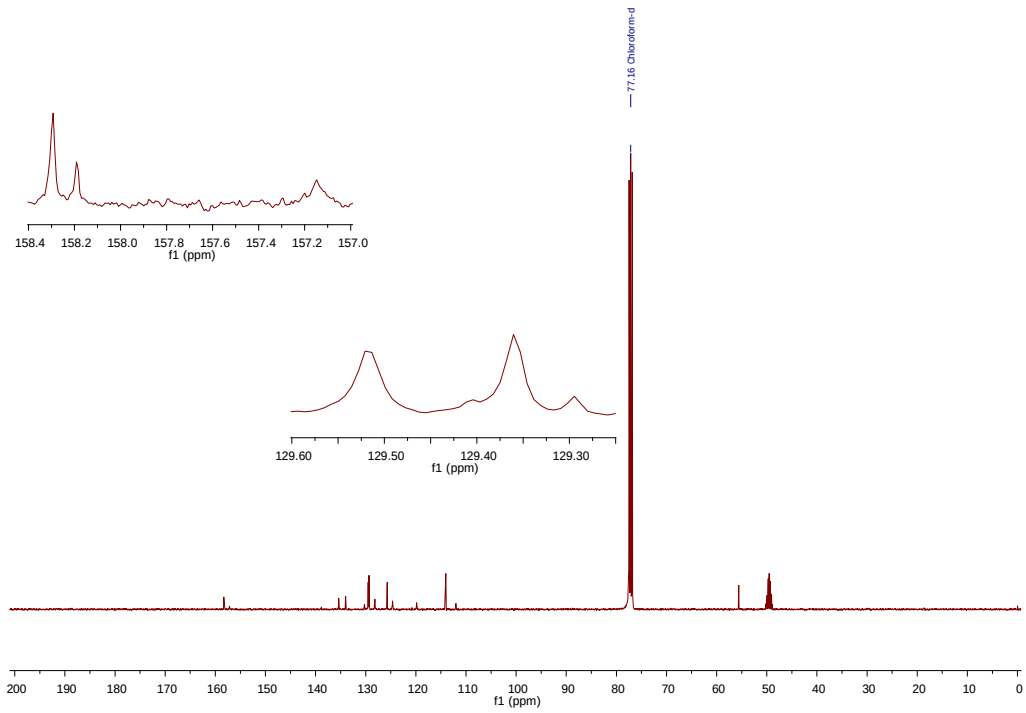
COSY (400 MHz, $CDCl_3/CD_3OD$ (97:3), 298 K) $\delta(^1H)$ / $\delta(^1H)$ = 8.65 / 7.32 (H_5 / H_6), 7.32 / 7.54 – 7.45 (H_6 / H_7), 7.54 – 7.45 / 8.29 (H_7 / H_8), 8.36 / 7.54 – 7.45 (H_{12} / H_{13}), 7.54 – 7.45 / 7.58 (H_{13} / H_{14}), 7.77 / 6.93 (H_{16} / H_{17}).

FT-IR (KBr): ν / cm^{-1} = 3288, 3066, 3048, 3004, 2955, 2934, 2910, 2836, 1734, 1634, 1600, 1561, 1508, 1458, 1431, 1416, 1380, 1366, 1331, 1296, 1252, 1236, 1175, 1156, 1109, 1081, 1032, 1002, 933, 827, 801, 768, 704, 675, 581, 529, 513.

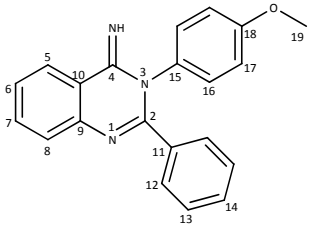
HRMS (ESI) for $C_{21}H_{18}N_3O^+$: m/z calcd: 328.144, found: 328.144.



Compound 3. ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K).



Compound 3. ^{13}C NMR (100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K).



Compound 4

Synthesis of 3-(4-methoxyphenyl)-2-phenylquinazolin-4(3*H*)-imine (4):

(*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.12 g, 0.49 mmol) was added to a solution of *p*-anisidine (0.06 g, 0.49 mmol) in 30 mL of toluene and the reaction mixture was stirred for 36 hours under reflux. All volatiles were removed under vacuum and the residue was dissolved in 30 mL CH_2Cl_2 and washed twice with 15 mL of 25% aqueous NH_3 solution. After removal of solvent and drying, the crude product was crystallized from ethyl acetate to give colorless crystals (0.12 g, 75 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ/ppm = 8.30 (br. s, 1H, H_5), 7.64 (t, *J* = 7.4 Hz, 1H, H_7), 7.57 (d, *J* = 7.9 Hz, 1H, H_8), 7.41 (t, *J* = 7.5 Hz, 1H, H_6), 7.32 – 7.18 (m, 5H, $H_{12,13,14}$), 7.07 (d, *J* = 8.8 Hz, 2H, H_{16}), 6.87 (d, *J* = 8.7 Hz, 2H, H_{17}), 6.66 (br. s, 1H, NH), 3.76 (s, 3H, H_{19}).

^{13}C NMR (100 MHz, CD_2Cl_2, 298 K) δ/ppm = 160.2 (C_{18}), 155.4 (C_4 Not Clear), 155.4 (C_2), 145.2 (C_9), 137.1 (C_{11}), 133.2 (C_7), 131.6 (C_{16}), 130.8 (C_{15}), 129.2 (C_{14}), 129.2 (C_{13}), 128.3 (C_{12}), 127.8 (C_8), 127.2 (C_6), 126.1 (C_5), 122.0 (C_{10}), 115.5 (C_{17}), 56.0 (C_{19}).

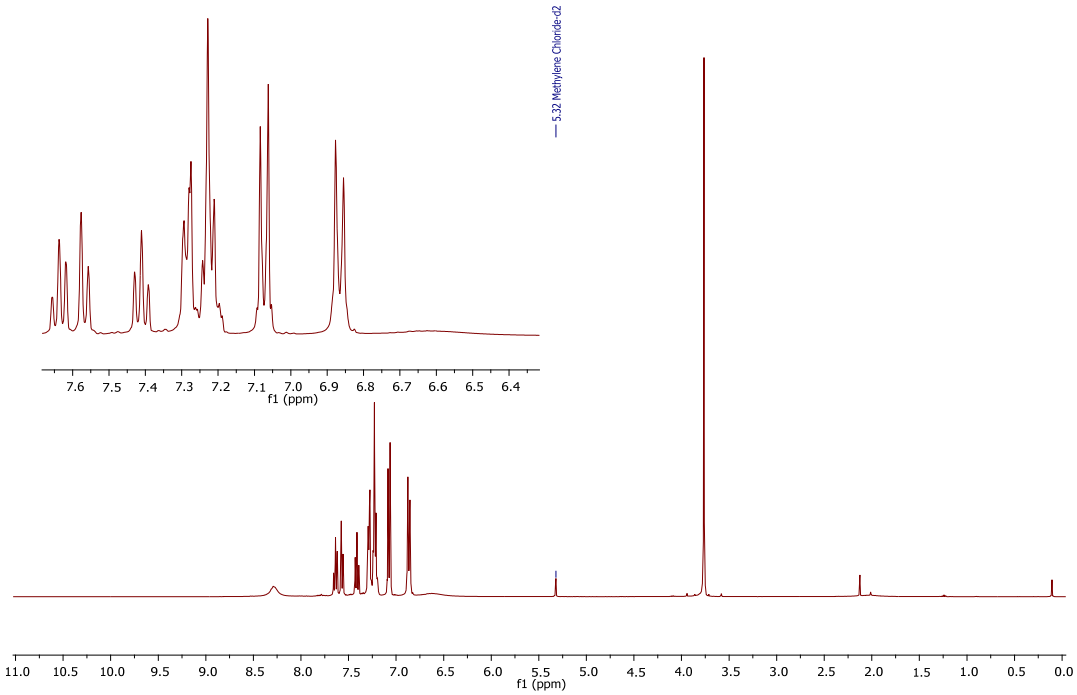
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2, 298 K) δ(^{1}H) / δ(^{13}C) = 8.30 / 145.2 (H_5 / C_9 Not clear), 7.64 / 145.2, 126.1 (H_7 / $C_{9,5}$), 7.57 / 127.2, 122.0 (H_8 / $C_{6,10}$), 7.41 / 127.8, 122.0 (H_6 / $C_{8,10}$), 7.32 – 7.18 / 155.4, 129.2 (H_{12} / $C_{2,14}$), 7.32 – 7.18 / 137.1 (H_{13} / C_{11}), 7.32 – 7.18 / 128.3 (H_{14} / C_{12}), 7.07 / 160.2 (H_{16} / C_{18}), 6.87 / 130.8 (H_{17} / C_{15}), 3.76 / 160.2 (H_{19} / C_{18}).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2, 298 K) δ(^{1}H) / δ(^{13}C) = 8.30 / 126.1 (H_5 / C_5), 7.64 / 133.2 (H_7 / C_7), 7.57 / 127.8 (H_8 / C_8), 7.41 / 127.2 (H_6 / C_6), 7.32 – 7.18 / 128.3 (H_{12} / C_{12}), 7.32 – 7.18 / 129.2 (H_{13} / C_{13}), 7.32 – 7.18 / 129.2 (H_{14} / C_{14}), 7.07 / 131.6 (H_{16} / C_{16}), 6.87 / 115.5 (H_{17} / C_{17}), 3.76 / 56.0 (H_{19} / C_{19}).

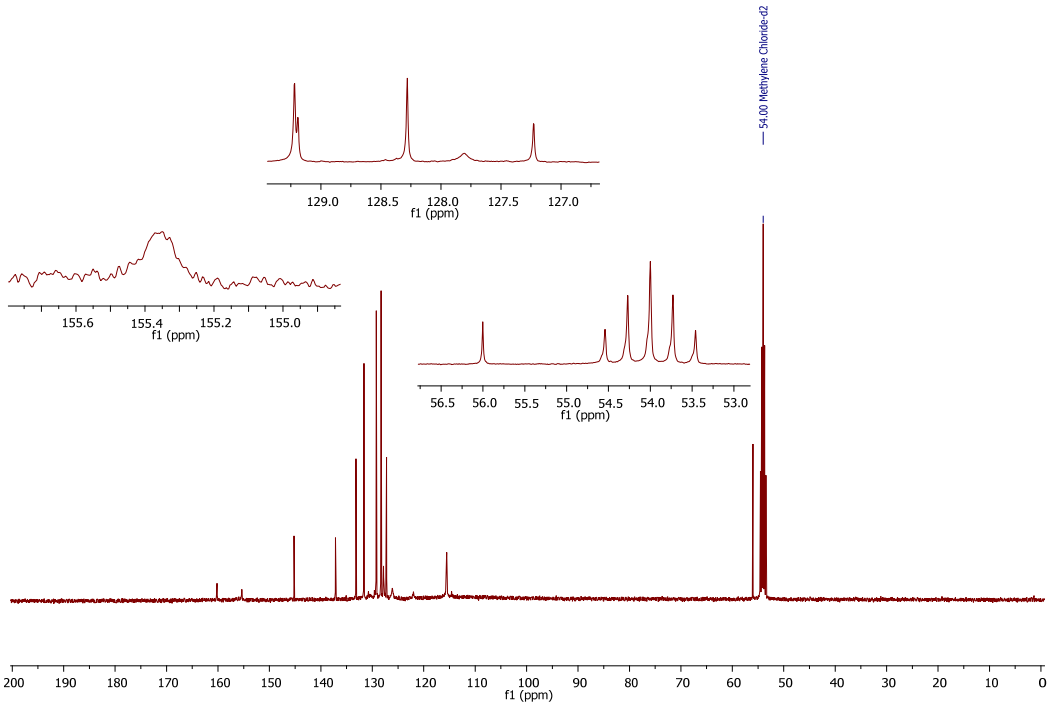
COSY (400 MHz / 400 MHz, CD_2Cl_2, 298 K) δ(^{1}H) / δ(^{1}H) = 8.30 / 7.41 (H_5 / H_6), 7.41 / 7.64 (H_6 / H_7), 7.64 / 7.57 (H_7 / H_8), 7.32 – 7.18 (H_{12} / H_{13}), 7.07 / 6.87 (H_{16} / H_{17}).

FT-IR (KBr): ν / cm^{-1} = 3311, 3297, 3060, 3033, 3002, 2859, 2936, 2909, 2835, 1678, 1632, 1606, 1584, 1565, 1508, 1473, 1463, 1442, 1362, 1317, 1298, 1251, 1176, 1152, 1136, 1108, 1075, 1053, 1029, 949, 916, 887, 875, 839, 821, 806, 766, 725, 698, 673, 656, 631, 583, 543, 481.

HRMS (ESI) for $C_{21}H_{18}N_3O$ $[M+H]^+$: m/z calcd: 328.144, found: 328.144.



Compound 4. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K).



Compound 4. ^{13}C NMR (100 MHz, CD_2Cl_2, 298 K).

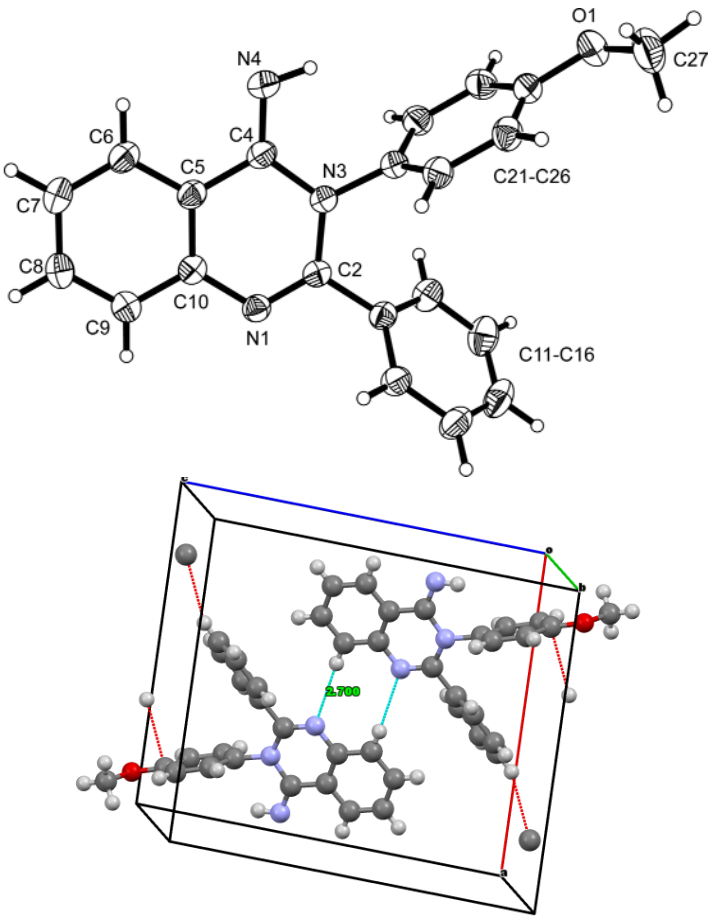
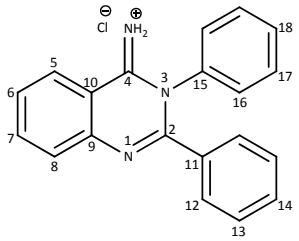


Figure S3. Crystal structure of compound 4. Selected bond lengths (Å) and angles (°): C4-N4, 1.271(2); C4-N3, 1.417(2); N3-C2, 1.389(2); C2-N1, 1.293(2); N1-C10, 1.396(2); C5-C4, 1.461(2); C4-N3-C21, 116.3(1); C2-N3-C21, 121.7(1); C2-N3-C4, 121.4(1). Only one of three molecules found in the asymmetric unit is shown (Up). Intermolecular interactions (Down).

X-ray crystal structure analysis of 4: formula $C_{21}H_{17}N_3O$, M = 327.38 colourless crystal, 0.40 x 0.15 x 0.04 mm, a = 12.9137(5), b = 14.1902(4), c = 14.6060(6) Å, α = 107.781(2), β = 90.352(2), γ = 98.594(2)°, V = 2516.2(2) Å^3, ρ_{calc} = 1.296 gcm^{-3}, μ = 0.649 mm^{-1}, empirical absorption correction (0.781 ≤ T ≤ 0.974), Z = 6, triclinic, space group $P\bar{1}$ (No. 2), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 34337 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 8764 independent (R_{int} = 0.040) and 7650 observed reflections [I>2σ(I)], 691 refined parameters, R = 0.038, wR^2 = 0.104, max. (min.) residual electron density 0.04 (-0.10) e.Å^{-3}, the hydrogen atoms at N4A, N4B and N4C were refined freely; others were calculated and refined as riding atoms.

Regarding the intermolecular interactions in the unit cell, the formation of two different parts of dimers between the three independent molecules (“A”, “B” and “C”) found in the asymmetric unit was observed. One symmetrical dimer is formed between two molecules “A” including the lone pairs of the imino nitrogen atom and the hydrogen atom at C9 of the neighbouring quinazolinimin moiety (N1A---H9A-C9A 2.700 Å). The second dimer is formed between the molecule “B” and “C” with the unsymmetrical distance N---H-C (N1B---H9C-C9C 2.615 Å and N1C---H9B-C9B 2.868 Å, respectively). The symmetrical dimer is linked to the unsymmetrical dimer over a hydrogen bond interaction involving the exocyclic imine moiety (N4A---H13B-C13B 2.666 Å). Additionally, two more hydrogen bonds involving the methoxy groups of the unsymmetrical dimmer were found in the packing diagram (O1B---H12A-C12A 2.700 Å and O1C---H16B-C16B 2.707 Å).



Compound 5

Synthesis of 2,3-Diphenylquinazolin-4(3*H*)-iminium chloride (5):

(*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.21 g, 0.86 mmol) was added to a solution of aniline (0.08 g, 0.86 mmol) in 30 mL of toluene and the reaction mixture was stirred for 36 hours under reflux. All volatiles were removed under vacuum and the light yellow solid was washed with acetone and crystallized from chloroform/methanol to give light yellow crystals (0.20 g, 70 %).

^{1}H NMR (400 MHz, $CDCl_3$/MeOH*, 298 K) δ/ppm = 9.17 (d, *J* = 8.2 Hz, 1H, H_5), 7.98 (t, *J* = 7.6 Hz, 1H, H_7), 7.89 (d, *J* = 8.0 Hz, 1H, H_8), 7.76 (t, *J* = 7.5 Hz, 1H, H_6), 7.48 (m, 3H, $H_{17,18}$), 7.34 – 7.19 (m,7H, $H_{16,12,13,14}$).

^{13}C NMR (100 MHz, $CDCl_3$/MeOH*, 298 K) δ/ppm = 157.4 (C_4), 152.1 (C_2), 145.7 (C_9), 137.6 (C_7), 134.4 (C_{15}), 133.2 (C_{11}), 131.4 (C_{18}), 131.2 (C_{17}), 130.2 (C_{14}), 120.0 (C_6), 129.0 (C_{16}), 128.6 (C_8), 128.5 (C_{13}), 128.2 (C_{12}), 127.7 (C_5), 113.2 (C_{10}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$/MeOH*, 298 K) $\delta(^{1}H)$ / $\delta(^{13}C)$ = 9,17 / 157.4, 145.7, 137.6 (H_5 / $C_{4,9,7}$), 7.98 / 145.7, 127.7 (H_7 / $C_{9,5}$), 7.89 / 130.0, 113.2 (H_8 / $C_{6,10}$), 7.76 / 128.6, 113.2 (H_6 / $C_{8,10}$), 7.48 / 134.4 (H_{17} / C_{15}), 7.48 / 129.0 (H_{18} / C_{16}), 7.34 – 7.19 / 131.4 (H_{16} / C_{18}), 7.34 – 7.19 / 152.1, 130.2 (H_{12} / $C_{2,14}$), 7.34 – 7.19 / 133.2 (H_{13} / C_{11}), 7.34 – 7.19 / 128.2 (H_{14} / C_{12}).

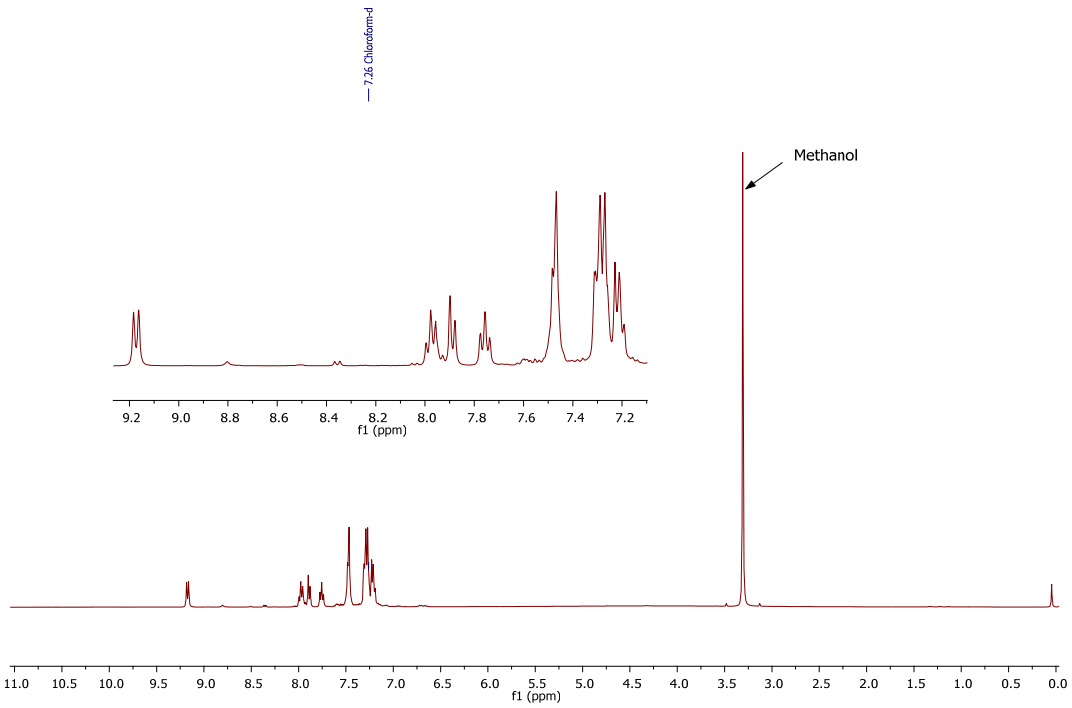
^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$/MeOH*, 298 K) $\delta(^{1}H)$ / $\delta(^{13}C)$ = 9.17 / 127.7 (H_5 / C_5), 7.98 / 137.6 (H_7 / C_7), 7.89 / 128.6 (H_8 / C_8), 7.76 / 130.0 (H_6 / C_6), 7.48 / 131.4 (H_{18} / C_{18}), 7.48 / 131.2 (H_{17} / C_{17}), 7.34 – 7.19 / 129.0 (H_{16} / C_{16}), 7.34 – 7.19 / 128.2 (H_{12} / C_{12}), 7.34 – 7.19 / 128.5 (H_{13} / C_{13}), 7.34 – 7.19 / 130.2 (H_{14} / C_{14}).

COSY (400 MHz / 400 MHz, $CDCl_3$/MOH*, 298 K) $\delta(^{1}H)$ / $\delta(^{1}H)$ = 9.17 / 7.76 (H_5 / H_6), 7.76 / 7.98 (H_6 / H_7), 7.98 / 7.89 (H_7 / H_8), 7.48 / 7.34 – 7.19 (H_{17} / H_{16}), 7.34 – 7.19 (H_{13} / H_{14}).

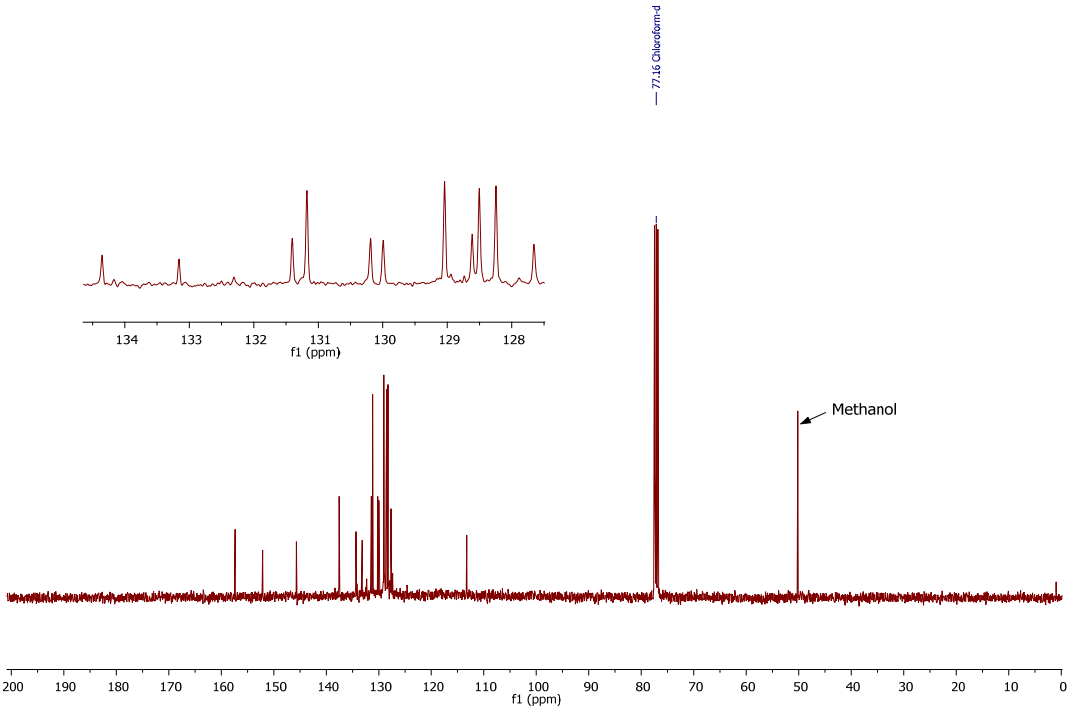
***Note**: A small drop of methanol HPLC (MeOH*) was added to the RMN sample ($CDCl_3$) to increase the solubility of the product.*

FT-IR (KBr): ν / cm^{-1} = 3378, 3201, 3052, 3027, 2940, 2780, 1654, 1606, 1595, 1570, 1536, 1489, 1472, 1458, 1444, 1338, 1308, 1291, 1280, 1222, 1156, 1076, 1037, 1017, 999, 972, 953, 923, 891, 873, 850, 773, 698, 677, 630, 614, 581, 560, 537, 522, 487.

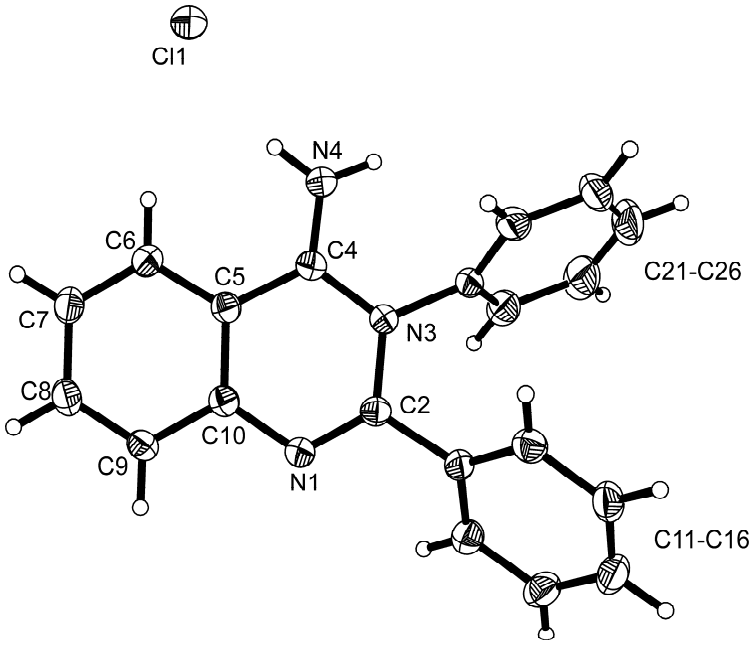
HRMS (ESI) for $C_{20}H_{16}N_3^+$: m/z calcd: 298.134, found: 298.134.



Compound 5. ^{1}H NMR (400 MHz, $CDCl_3$/MeOH*, 298 K).



Compound 5. ^{13}C NMR (100 MHz, $CDCl_3$/MeOH*, 298 K).



Crystal structure of compound 5. Selected bond lengths (Å) and angles (°): N4-C4, 1.307(2); C4-N3, 1.370(2); N3-C2, 1.398(2); C2-N1, 1.290(2); N1-C10, 1.387(2); C5-C4, 1.438(2); C4-N3-C21, 119.2(1); C2-N3-C21, 119.4(1); C2-N3-C4, 121.2(1).

X-ray crystal structure analysis of 5: formula $C_{20}H_{16}NClN_3$, M = 333.81 pale yellow crystal, 0.38 x 0.28 x 0.18 mm, a = 14.6582(9), b = 17.3558(12), c = 7.0639(7) Å, β = 98.146(3) °, V = 1779.0(2) Å^3, ρ_{calc} = 1.246 gcm^{-3}, μ = 0.220 mm^{-1}, Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71703 Å, T = 297(2) K, ω and ϕ scans, 14711 reflections collected (±h, ±k, ±l), 3634 independent (R_{int} = 0.053) and 2634 observed reflections [I>2σ(I)], 225 refined parameters, R = 0.041, wR^2 = 0.112, max. (min.) residual electron density 0.36 (-0.16) e.Å^{-3}, the hydrogen atoms at N4 were refined freely, but with N-H distance restraints (SADI); others were calculated and refined as riding atoms.

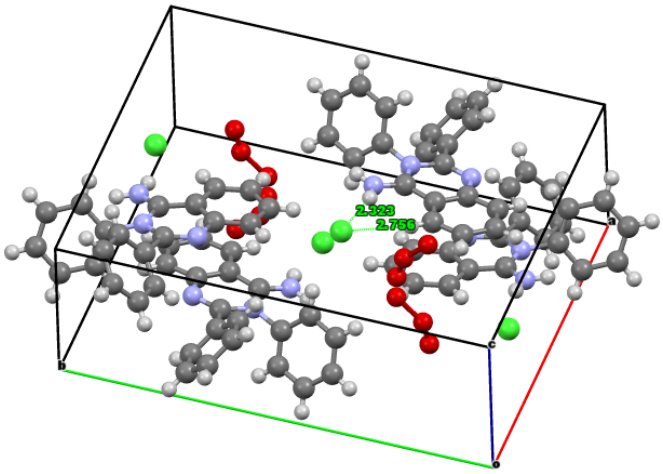
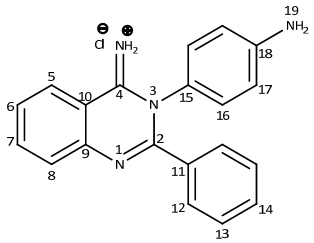


Figure S4. Interaction

The C26-C21-N3-C4 and C16-C11-C2-N1 dihedral angles are -107.7(2)° and 50.9(2)°, respectively, indicating that both phenyl substituents at N3 and C2 are perpendicularly rotated relative to the plane of the heteronuclear ring. The N4-C4, C4-N3, N3-C2 and C2-N1 bond lengths in **5** are 1.307(2), 1.370(2), 1.398(2) and 1.290(2) Å, which are close to those of molecular compounds **1-3**, as well as the angles at N3. Through hydrogen bond interactions (Cl1---H01-N4 2.296 Å and Cl1---H02-N4 2.450 Å) a dimeric unsymmetrical structure with bridged chlorine anions is formed.



Compound 6

Synthesis of 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-iminium chloride (6):

(*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.11g, 0.46 mmol) was added to a solution of *p*-phenylenediamine (0.05 g, 0.46 mmol) in 30 mL of toluene and the reaction mixture was stirred

for 18 hours under reflux. Light brown solid was formed, which were filtered and dried under vacuum (0.11 g, 69 %).

^{1}H NMR (400 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ/ppm = 8.77 (d, *J* = 8.2 Hz, 1H, H_5), 8.08 (t, *J* = 7.6 Hz, 1H, H_7), 7.96 (d, *J* = 8.3 Hz, 1H, H_8), 7.83 (t, *J* = 7.6 Hz, 1H, H_6), 7.37 – 7.25 (m, 5H, $H_{12,13,14}$), 6.96 (d, *J* = 8.0 Hz, 2H, H_{17}), 6.70 (d, *J* = 8.0 Hz, 2H, H_{16}), 3.74 (br. s, 2H, H_{19}, Not clear).

^{13}C NMR (100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ/ppm = 159.1 (C_4), 154.0 (C_2), 150.8 (C_{15}), 146.6 (C_9), 138.4 (C_7), 134.2 (C_{11}), 130.6 (C_{14}), 130.5 (C_6), 129.7 (C_{13}), 129.5 (C_{17}), 129.5 (C_8), 128.7 (C_{12}), 126.7 (C_5), 123.5 (C_{18}) , 116.5 (C_{16}), 113.5 (C_{10}).

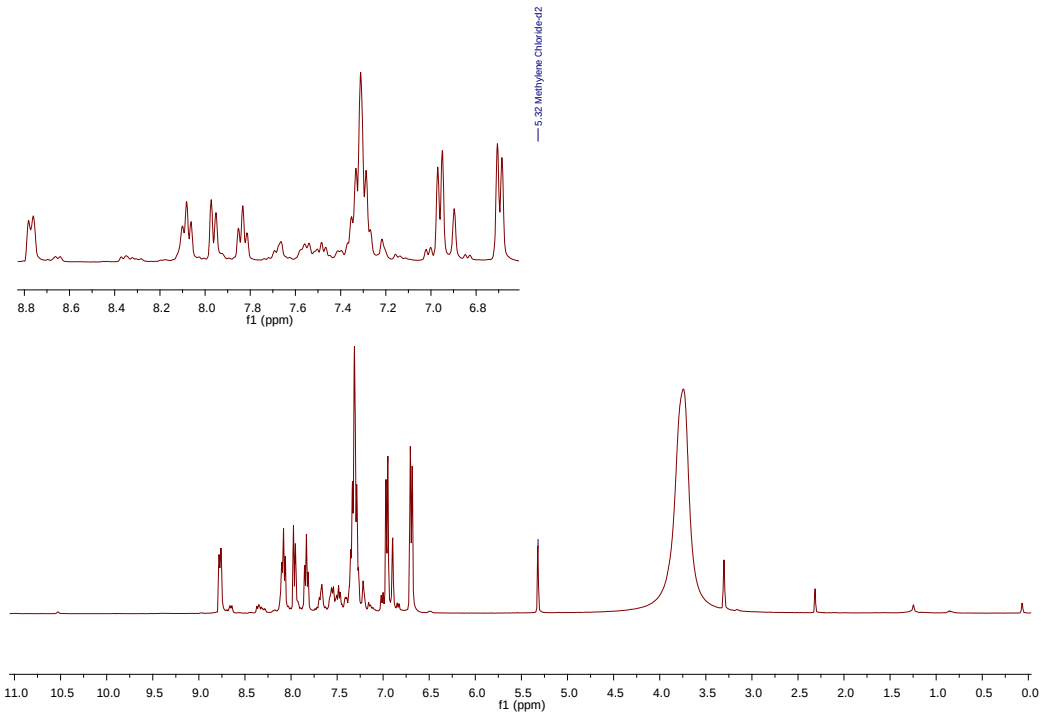
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.77 / 159.1, 146.6, 138.4 (H_5 / $C_{4,9,7}$), 8.08 / 146.6, 126.7 (H_7 / $C_{9,5}$), 7.96 / 130.5, 113.5 (H_8 / $C_{6,10}$), 7.83 / 129.5, 113.5 (H_6 / $C_{8,10}$), 7.37 – 7.25 / 154.0, 130.6 (H_{12} / $C_{2,14}$), 7.37 – 7.25 / 134.2 (H_{13} / C_{11}), 7.37 – 7.25 / 128.7 (H_{14} / C_{12}), 6.96 / 150.8 (H_{17} / C_{15}), 6.70 / 123.5 (H_{16} / C_{18}).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.77 / 126.7 (H_5 / C_5), 8.08 / 138.4 (H_7 / C_7), 7.96 / 129.5 (H_8 / C_8), 7.83 / 130.5 (H_6 / C_6), 7.37 – 7.25 / 128.7 (H_{12} / C_{12}), 7.37 – 7.25 / 129.7 (H_{13} / C_{13}), 7.37 – 7.25 / 130.6 (H_{14} / C_{14}), 6.96 / 129.5 (H_{17} / C_{17}), 6.70 / 116.5 (H_{16} / C_{16}).

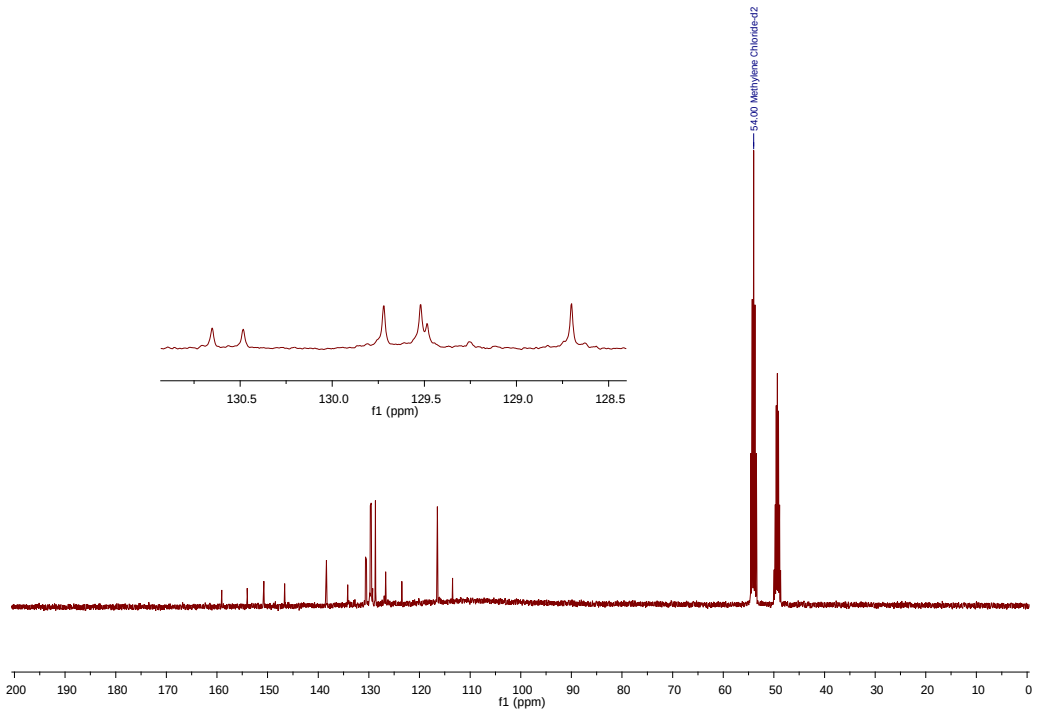
COSY (400 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{1}H) = 8.77 / 7.83 (H_5 / H_6), 7.83 / 8.08 (H_6 / H_7), 8.08 / 7.96 (H_7 / H_8), 7.37 – 7.25 (H_{13} / H_{14}), 6.96 / 6.70 (H_{17} / H_{16}).

FT-IR (KBr): ν / cm^{-1} = 3411, 3328, 3224, 3181, 3026, 2950, 2881, 2675, 2603, 2563, 1649, 1628, 1613, 1577, 1506, 1445, 1338, 1311, 1292, 1198, 1178,1159, 1113, 1031, 954, 825, 769, 708, 696, 677, 623, 593, 584, 540, 511.

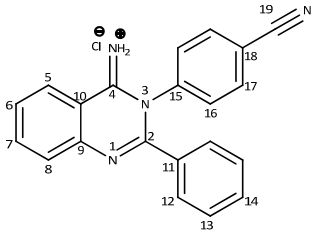
HRMS (ESI) for $C_{20}H_{17}N_4^+$: m/z calcd: 313.145, found: 313.145.



Compound 6. ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K).



Compound 6. ^{13}C NMR (100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K).



Compound 7

Synthesis of 3-(4-cyanophenyl)-2-phenylquinazolin-4-(3*H*)-iminium chloride (7):

(*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.12g, 0.51mmol) was added to a solution of 4-aminobenzonitrile (0.06g, 0.51mmol) in 30 mL of toluene and the reaction mixture was stirred for 96 hours under reflux. All volatiles were removed under vacuum and the crude product was washed with acetone and dried to give light yellow solid (0.12 g, 65 %).

^{1}H NMR (400 MHz, D_2O/CD_3OD (97:3), 298 K) δ/ppm = 8.43 (d, *J* = 8.4 Hz, 1H, H_5), 8.19 (t, *J* = 7.7 Hz, 1H, H_7), 7.96 (d, *J* = 8.3 Hz, 1H, H_8), 7.90 (m, 3H, $H_{6,17}$), 7.68 (d, *J* = 8.4 Hz, 2H, H_{16}), 7.43 – 7.28 (m, 5H, $H_{12,13,14}$).

^{13}C NMR (100 MHz, D_2O/CD_3OD (97:3), 298 K) δ/ppm = 158.9 (C_4), 153.8 (C_2), 145.9 (C_9), 139.4 (C_{15}), 139.3 (C_7), 136.1 (C_{17}), 133.0 (C_{11}), 131.5 (C_{14}), 131.1 (C_6), 130.8 (C_{16}), 129.9 (C_{13}), 129.4 (C_{12}), 128.9 (C_8), 125.9 (C_5), 118.7 (C_{19}), 115.5 (C_{18}), 113.8 (C_{10}).

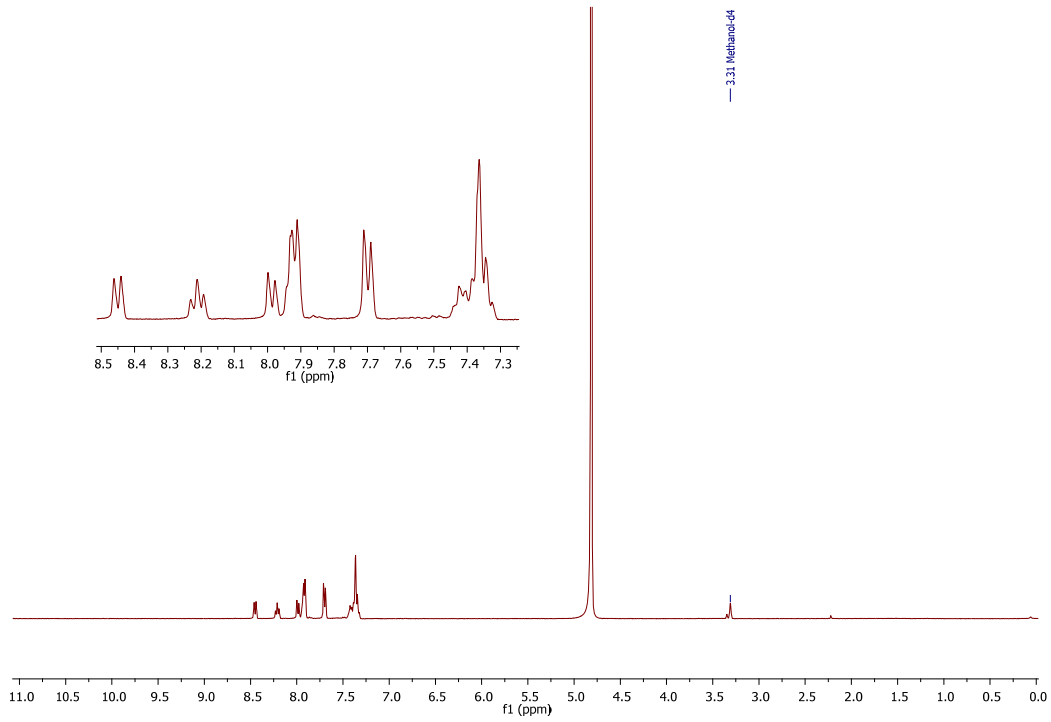
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, D_2O/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.43 / 158.9, 145.9, 139.3 (H_5 / $C_{4,9,7}$), 8.19 / 145.9, 125.9 (H_7 / $C_{9,5}$), 7.96 / 131.1, 113.8 (H_8 / $C_{6,10}$), 7.90 / 128.9, 113.8 (H_6 / $C_{8,10}$), 7.90 / 139.4, 118.7 (H_{17} / $C_{15,19}$), 7.68 / 115.5 (H_{16} / C_{18}), 7.43 – 7.28 / 153.8, 131.5 (H_{12} / $C_{2,14}$), 7.43 – 7.28 / 133.0 (H_{13} / C_{11}), 7.43 – 7.28 / 129.4 (H_{14} / C_{12}).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, D_2O/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 8.43 / 125.9 (H_5 / C_5), 8.19 / 139.3 (H_5 / C_5), 7.96 / 128.9 (H_8 / C_8), 7.90 / 131.1 (H_6 / C_6), 7.90 / 136.1 (H_{17} / C_{17}), 7.68 / 130.8 (H_{16} / C_{16}, 7.43 – 7.28 / 129.4 (H_{12} / C_{12}), 7.43 – 7.28 / 129.9 (H_{13} / C_{13}), 7.43 – 7.28 / 131.5 (H_{14} / C_{14}).

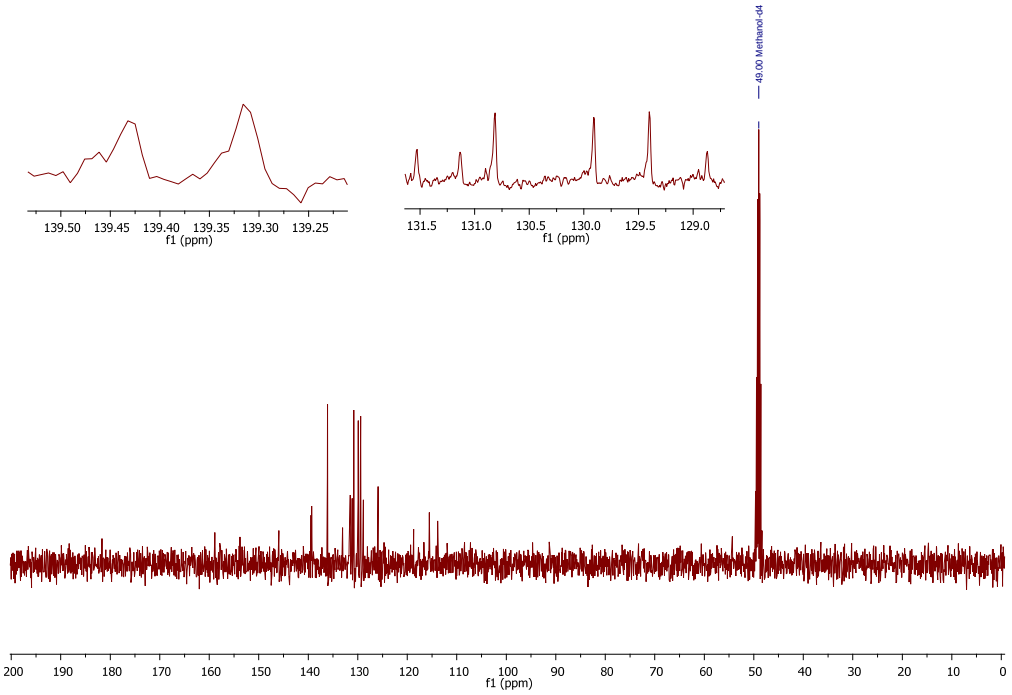
COSY (400 MHz / 400 MHz, D_2O/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{1}H) = 8.43 / 7.90 (H_5 / H_6), 7.90 / 8,19 (H_5 / H_6), 8.19 / 7.96 (H_7 / H_8), 7.90 / 7.68 (H_{17} / H_{16}), 7.43 – 7.28 (H_{13} / H_{14}).

FT-IR (KBr): ν / cm^{-1} = 3396, 3213, 3091, 3031, 2963, 2237 (CN), 1632, 1604, 1578, 1549, 1506, 1480, 1459, 1444, 1432, 1411, 1383, 1338, 1318, 1292, 1261, 1160, 1097, 1021, 956, 928, 864, 800, 734, 699, 673, 627, 583, 564, 546, 521.

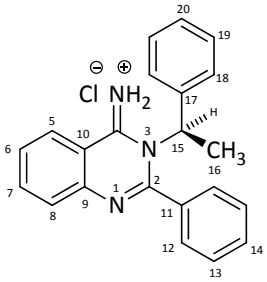
HRMS (ESI) for $C_{21}H_{15}N_4^+$: m/z calcd: 323.129, found: 323.129.



Compound 7. ^{1}**H NMR** (400 MHz, D_2O/CD_3OD (97:3), 298 K).



Compound 7. ^{13}C NMR (100 MHz, D_2O/CD_3OD (97:3), 298 K).



Compound 8

Synthesis of 2-Phenyl-3-(1-phenyl-ethyl)-(3*H*)-quinazolin-4-ylidene-iminium chloride (8):

Compound **8** was prepared by reaction of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.15 g, 0.59 mmol) with (*R*)-(+)-α-methyl benzilamine (0.08 mL, 0.59 mmol) in 20 mL of toluene. The was added at 0°C and stirred at this temperature for 2 hours. Then the reaction mixture was stirred for 48 hours at room temperature. The precipitate was filtrated and discarded. All volatiles were removed under vacuum from the solution; the product was separated by a short column of silica gel, using ethyl acetate and then chloroform. The chloroform was removed under vacuum and the

light yellow oil was obtained. Crystals of this compound were acquired from solution chloroform/ethyl acetate to give light yellow crystals (0.16 g, 70 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 7.80 (d, *J* = 8.0 Hz, 1H, H_5), 7.51 – 7.47 (m, 2H, $H_{7,\ 14}$), 7.41 – 7.39 (m, 2H, H_{12}), 7.32 – 7.31 (m, 3H, $H_{13,8}$), 7.26 – 7.22 (m, 1H, H_6), 7.20 – 7.19 (m, 2H, H_{19}), 7.16 – 7.10 (m, 3H, $H_{18,\ 20}$), 5.57 (q, *J* = 6.8 Hz, 1H, H_{15}), 1.82 (d, *J* = 7.2 Hz, 3H, H_{16}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 156.8 (C_2), 154.9 (C_4), 143.7 (C_{10}), 139.8 (C_{17}), 136.8 (C_9), 132.3 (C_7), 129.4 (C_8), 128.7 (C_{13}), 128.5 (C_{19}), 127.4 (C_{14}), 127.2 (C_{12}), 126.8 (C_{20}), 126.5 (C_6), 125.6 (C_{18}), 124.0 (C_5), 121.2 (C_{11}), 57.4 (C_{15}), 16.2 (C_{16}).

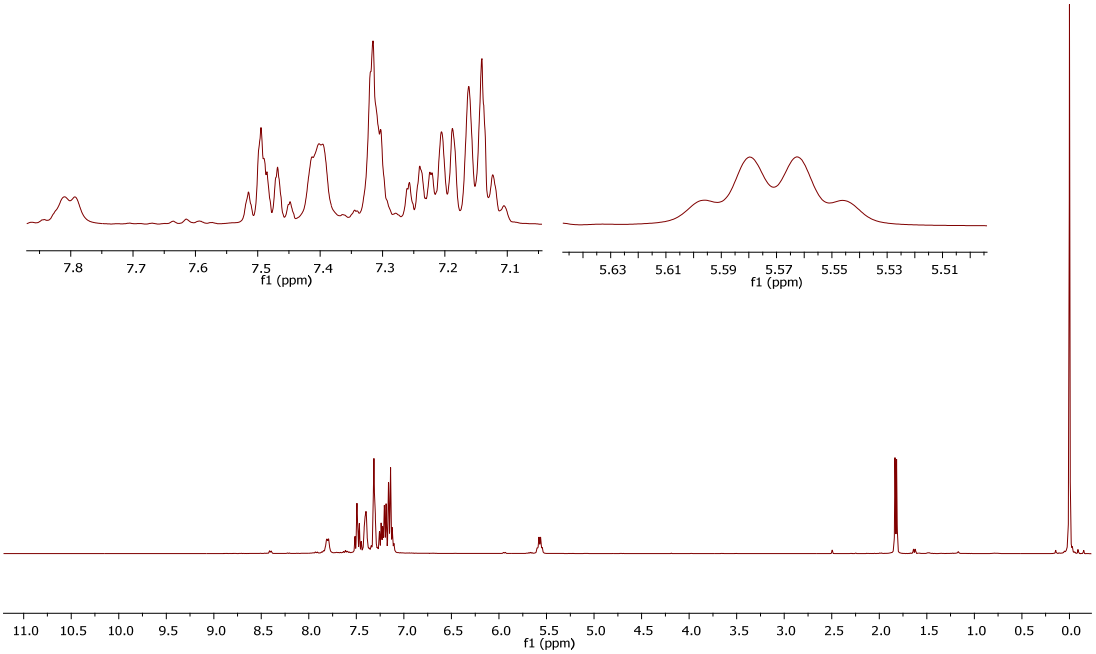
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 7.80 / 143.7, 132.3 (H_5 / $C_{10,\ 7}$), 7.51 – 7.47 / 143.7, 124.0 (H_7 / $C_{10,\ 5}$), 7.32 – 7.31 / 136.8 (H_8 / C_9), 7.20 – 7.19 / 139.8 (H_{19} / C_{17}), 5.57 / 156.8, 139.8, 125.6, 16.2 (H_{15} / $C_{2,\ 17,\ 18,\ 16}$), 1.82 / 139.8, 57.4.

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 7.80 / 124.0 (H_5 / C_5), 7.51 – 7.47 / 132.3, 127.4 ($H_{7,\ 14}$ / $C_{7,\ 14}$), 7.41 – 7.39 / 127.2 (H_{12} / C_{12}), 7.32 – 7.31 / 129.4, 128.7 ($H_{13,\ 8}$ / $C_{8,\ 13}$), 7.26 – 7.22 / 126.5 (H_6 / C_6), 7.20 – 7.19 / 128.5 (H_{19} / C_{19}), 7.16 – 7.10 / 126.8, 125.6 ($H_{18,\ 20}$ / $C_{20,\ 18}$), 5.57/ 57.4 (H_{15} / C_{15}), 1.82 / 16.2 (H_{16} / C_{16}).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 7.80 / 7.26 – 7.22 (H_5 / H_6), 7.26 – 7.22 / 7.51 – 7.47 (H_6 / H_7), 5.57 / 1.82 (H_{15} / H_{16}).

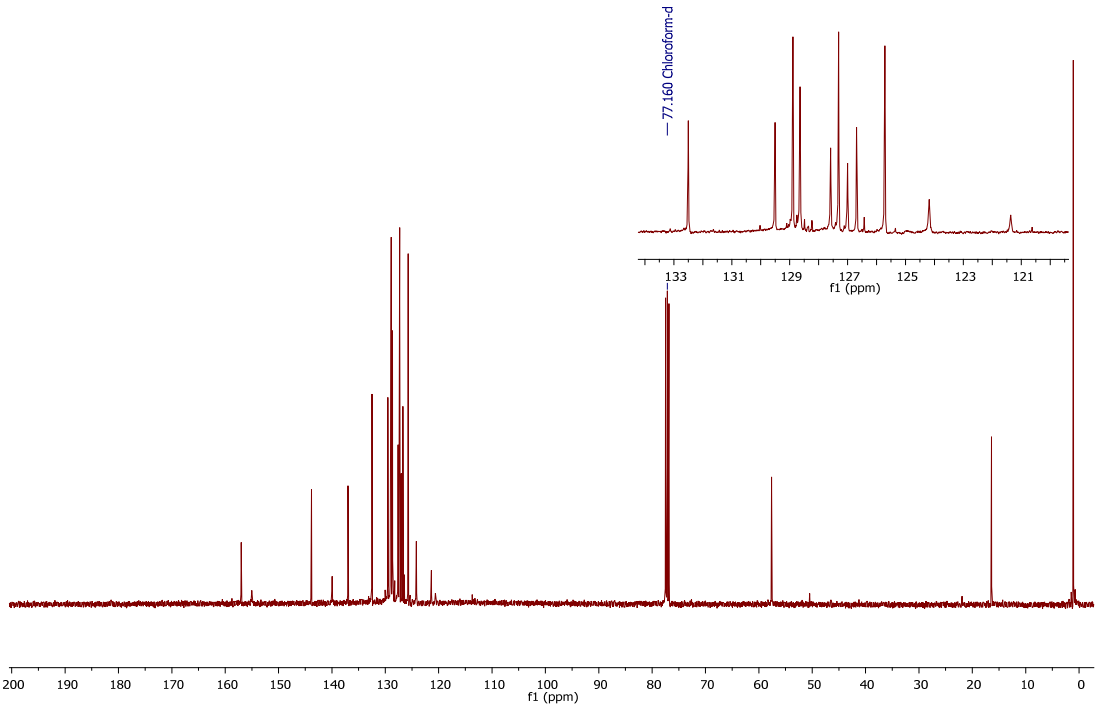
FTIR (KBr): ν / cm^{-1} = 3059, 3028, 2964, 2906, 2362, 2027, 1919, 1622, 1604, 1566, 1523, 1494, 1476, 1460, 1446, 1414, 1391, 1357, 1319, 1262, 1209, 1096, 1025, 875, 800, 698, 670, 642, 594, 539, 520, 394, 297.

HRMS (ESI) for $C_{20}H_{20}N_3^+$: m/z calcd: 326.165, found: 326.165

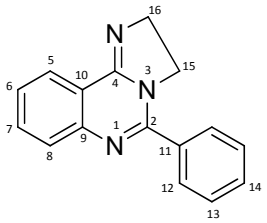


Compound 8. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

Note: Reference to $Si(CH_3)_4$.



Compound 8. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)



Compound 9

Synthesis of 5-phenyl-2,3-dihydroimidazo[1,2-*c*] quinazoline (9):

Compound **9** was prepared by reaction of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.15 g, 0.59 mmol) with ethylenediamine (0.04 mL, 0.59 mmol) in 20 mL of toluene. The ethylendiamine was added at 0°C and stirred at this temperature for 2 hours. Then the reaction mixture was stirred for 48 hours at room temperature. The precipitate was filtrated and discarded. All volatiles were removed under vacuum from the solution; the product was separated by a short column of silica gel, using ethyl acetate and then chloroform. The chloroform was removed under vacuum and the light yellow oil was obtained. Crystals of this compound were acquired from a solution chloroform/ethyl acetate to give light yellow crystals (0.09 g, 57 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 8.04 (d, *J* = 7.6 Hz, 1H, H_5), 7.64 – 7.61 (m, 2H, H_{13}), 7.58 (d, *J* = 1.2 Hz, 1H, H_8), 7.56 (br. s, 1H, H_7), 7.50 (d, *J* = 2.4 Hz, 2H, H_{12}), 7.48 (d, *J* = 1.2 Hz, 1H, H_{14}), 7.33 – 7.31 (m, 1H, H_6), 4.12 – 3.99 (m, 1H, $H_{15,\,16}$).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 155.5 (C_4), 153.8 (C_{11}), 146.7 (C_9), 135.1 (C_2), 133.1 (C_7), 130.2 (C_{14}), 128.7 (C_{12}), 127.7 (C_{13}), 127.2 (C_8), 126.5 (C_6), 125.2 (C_5), 117.9 (C_{10}), 53.4 (C_{15}), 48.9 (C_{16}).

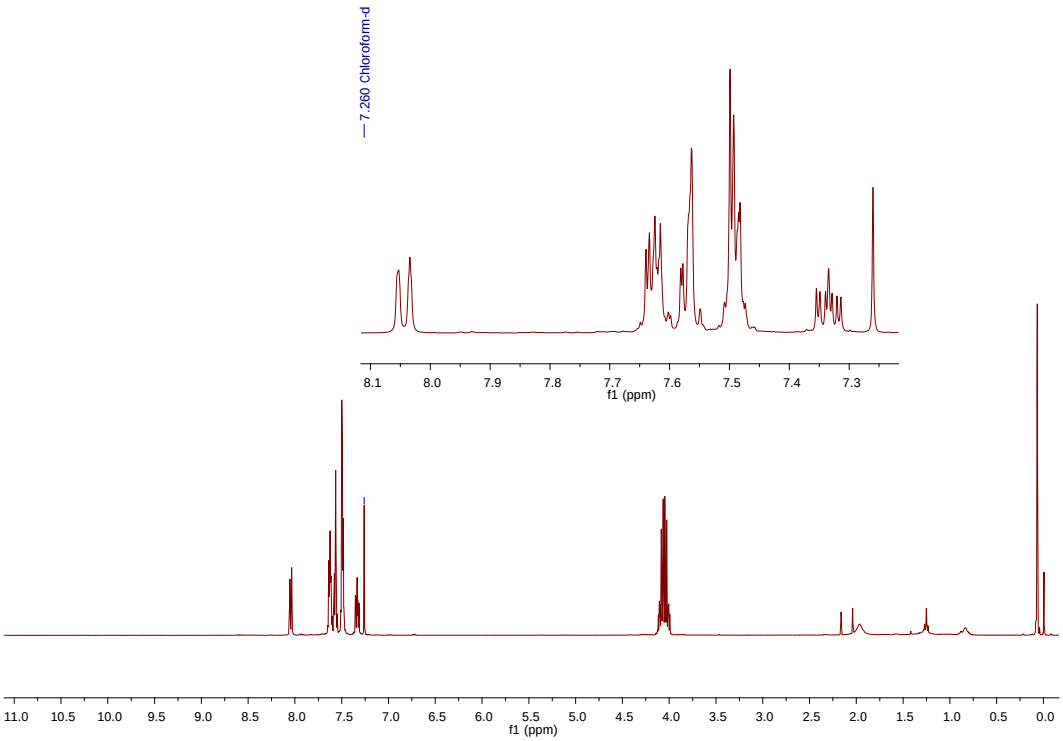
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.04 / 155.5, 146.7, 133.1, (H_5 / $C_{4,\,9,\,7}$), 7.64 – 7.61 / 153.8, 130.2 (H_{13} / $C_{11,\,14}$), 7.56 / 146.7, 125.2 (H_7 / $C_{9,\,5}$), 7.50 / 135.1, 127.7 (H_{12} / $C_{2,\,13}$), 7.33 – 7.31 / 127.2, 117.9 (H_6 / $C_{8,\,10}$), 4.12 – 3.99 / 53.4, 48.9 ($H_{15,\,16}$ / $C_{15,16}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.04 / 125.2 (H_5 / C_5), 7.64 – 7.61 / 127.7 (H_{13} / C_{13}), 7.58 / 127.2 (H_8 / C_8), 7.56 / 133.1 (H_7 / C_7), 7.50 / 128.7 (H_{12} / C_{12}), 7.48 / 130.2 (H_{14} / C_{14}), 7.33 – 7.31 / 126.5 (H_6 / C_6), 4.12 – 3.99 / 53.4, 48.9 ($H_{15,\,16}$ / $C_{15,\,16}$).

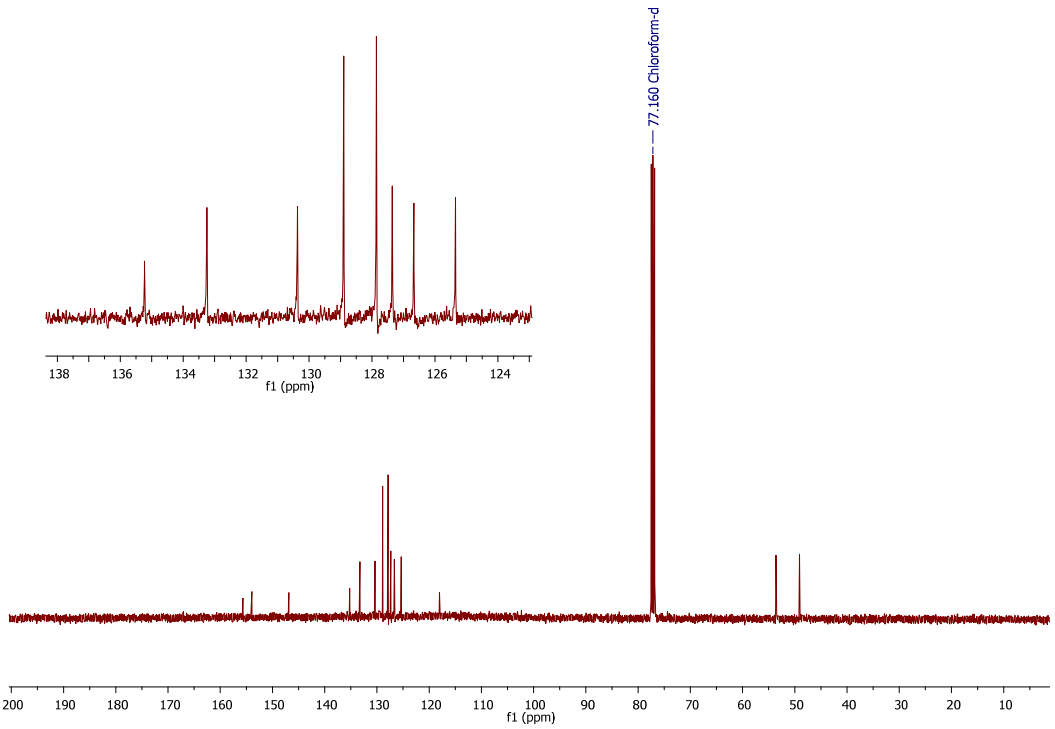
COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) $\delta(^1H)$ / $\delta(^1H)$ = 8.04 / 7.33 – 7.31 (H_5 / H_6), 7.33 – 7.31 / 7.56 (H_6 / H_7), 7.64 – 7.61 / 7.50 (H_{13} / H_{12}), 4.12 – 3.99 (H_{15} / H_{16}).

FTIR (KBr): ν / cm^{-1} = 3423, 3332, 3233, 3065, 2952, 2873, 1647, 1614, 1601, 1582, 1550, 1498, 1478, 1467, 1447, 1405, 1352, 1297, 1277, 1242, 1179, 1154, 1076, 1044, 1028, 1001, 979, 919, 856, 841, 779, 712, 701, 683, 670, 640, 586, 542, 435, 347, 297.

HRMS (ESI) for $C_{16}H_{14}N_3$ $[M+H]^+$: m/z calcd: 248.118 , found: 248.118.



Compound 9. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



Compound 9. ^{13}**C NMR** (100 MHz, $CDCl_3$, 298 K)

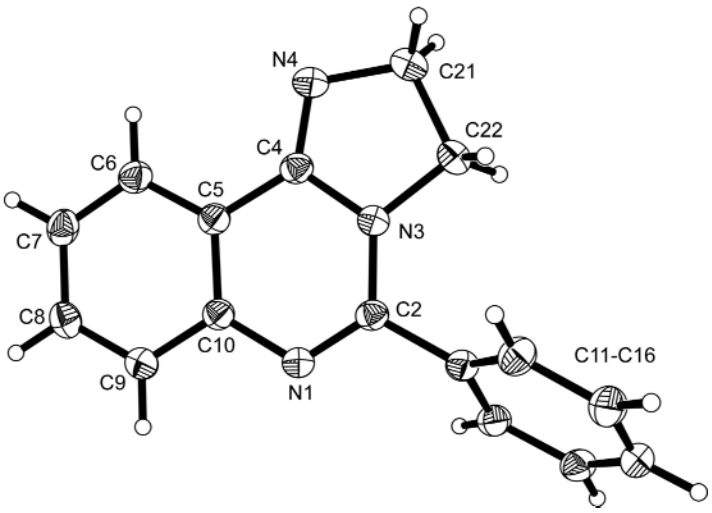
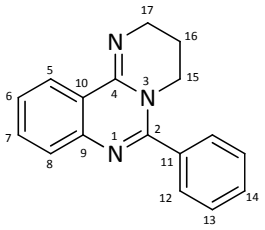


Figure S5. Crystal structure of compound 9. Selected bond lengths (Å): N1-C2, 1.304(2); C2-N3, 1.360 (2); N3-C4, 1.399(2); C21-N4, 1.278(2); N3-C22, 1.474(2); C21-C22, 1.531(2); C4-C5, 1.452(2). Selected angles (°): C10-N1-C2, 117.8(1); C2-N3-C4, 123.0(1); C2-N3-C22, 128.6(1); C4-N3-C22, 107.9(1); N3-C4-N4, 115.8(1). Selected torsion angles (°): N1-C2-N3-C22, -173.9(2); N3-C4-N4-C21, 1.0(2).

X-ray crystal structure analysis of 9: formula $C_{16}H_{13}N_3 \cdot H_2O$, M = 265.31 colourless crystal, 0.30 x 0.20 x 0.18 mm, a = 8.9276(2), b = 9.0785(2), c = 16.8687(3) Å, β = 96.058(2) °, V = 1359.6(1) Å^3, ρ_{calc} = 1.296 gcm^{-3}, μ = 0.084 mm^{-1}, empirical absorption correction (0.975 ≤ T ≤ 0.985), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 8031 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.62 Å^{-1}, 2695 independent (R_{int} = 0.033) and 2386 observed reflections [I>2σ(I)], 189 refined parameters, R = 0.044, wR^2 = 0.110, max. (min.) residual electron density 0.18 (-0.15) e.Å^{-3}, the hydrogen atoms at O1 were refined freely; others were calculated and refined as riding atoms.

Since the structure of this compound (**9**) has not been reported, a detailed analysis of its structural parameters (Figure S5) shows an extension of the planarity that includes the aliphatic ring (torsion angle N1-C2-N3-C22, -173.9(2)°; N3-C4-N4-C21, 1.0(2)°). Furthermore, the bond lengths of the aromatic heterocycle, in agreement with what was seen in compounds **1**-**3** (manuscript), show a marked double bond character of the imine bond (N1-C2, 1.304(2) Å and C21-N4, 1.278(2) Å, while the intermediate bonds between them, C2-N3 and N3-C4, have intermediate values between double and single bonds, 1.360(2) Å and 1.399(2) Å, respectively. It is important to point out that the bonds that connect with the aromatic ring, C4-C5 and N1-C10, have values of 1.452(2) Å and 1.402(2) Å. This difference may be due to the higher electronegativity of N, which makes the ring's conjugation extend to the heterocycle. Finally, and as expected, the phenyl ring is orthogonal to the fused heterocycles. The water molecule links two molecules of compound **9** via two strong N---H-O hydrogen bonds (N4---H01-O1 2.019 Å and N4---H02-O1 1.960 Å). Additionally, one more hydrogen bond is formed between the water oxygen and the hydrogen at C6 atom from the aromatic ring system (O1---H6-C6 2.490 Å).



Compound 10

6-phenyl-3,4-dihydro-2*H*-pyrimido[1,2-*c*] quinazoline (10). Compound **10** was prepared by reaction of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.15 g, 0.59 mmol) with 1,3-diaminopropane (0.05 mL, 0.59 mmol) in 20 mL of toluene. The reaction mixture was stirred for 48 hours under reflux. The precipitate was filtrated and discarded. All volatiles were removed under vacuum from the solution and the crude product was crystallized from diethyl ether to give light yellow crystals (0.09 g, 60 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 8.17 (d, *J* = 7.6 Hz, 1H, H_5), 7.51 – 7.45 (m, 7H, $H_{7,8,12,13,14}$), 7.32 (t, *J* = 7.2 Hz, 1H, H_6), 3.69 – 3.64 (m, 4H, $H_{15,17}$), 1.92 – 1.86 (m, 2H, H_{16}).

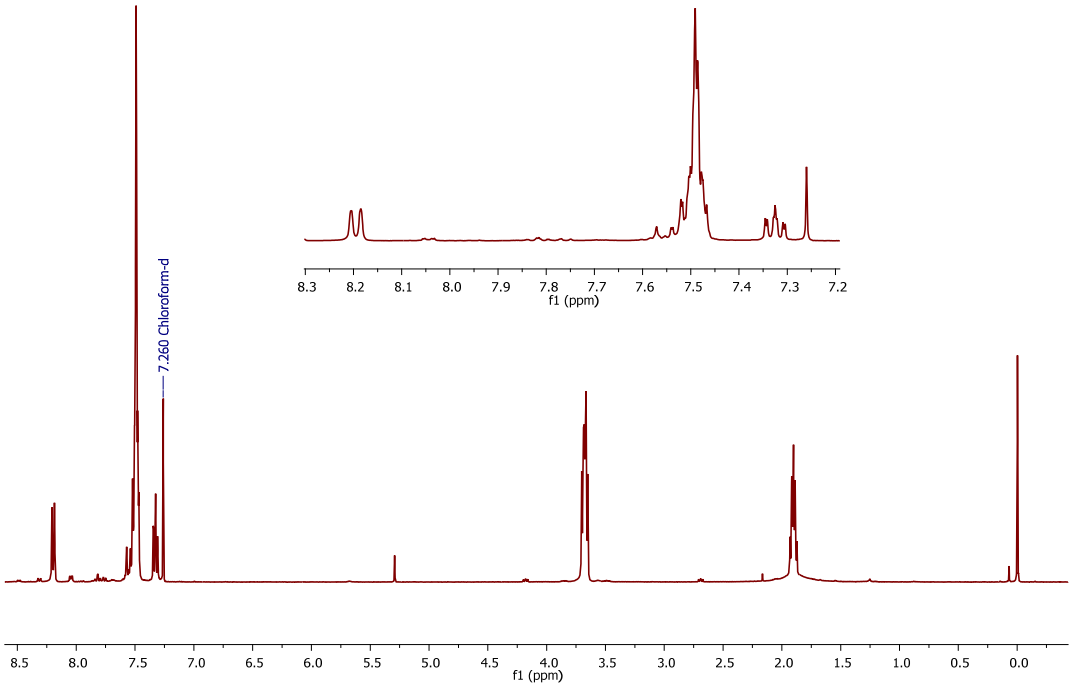
^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 155.5, 146.6, 144.0, 135.6, 122,66 ($C_{2,4,9,10,11}$), 132.0, 129.8, 129.00, 127.9, 127.0 ($C_{7,8,12,13,14}$), 126.8 (C_6), 124.6 (C_5), 47.7, 44.6 ($C_{15,17}$), 20.8 (C_{16}).

^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 1.92 – 1.86 / 47.7, 44.6 (H_{16} / $C_{15,17}$), 3.69 – 3.64 / 20.8 ($H_{15,17}$ / C_{16}).

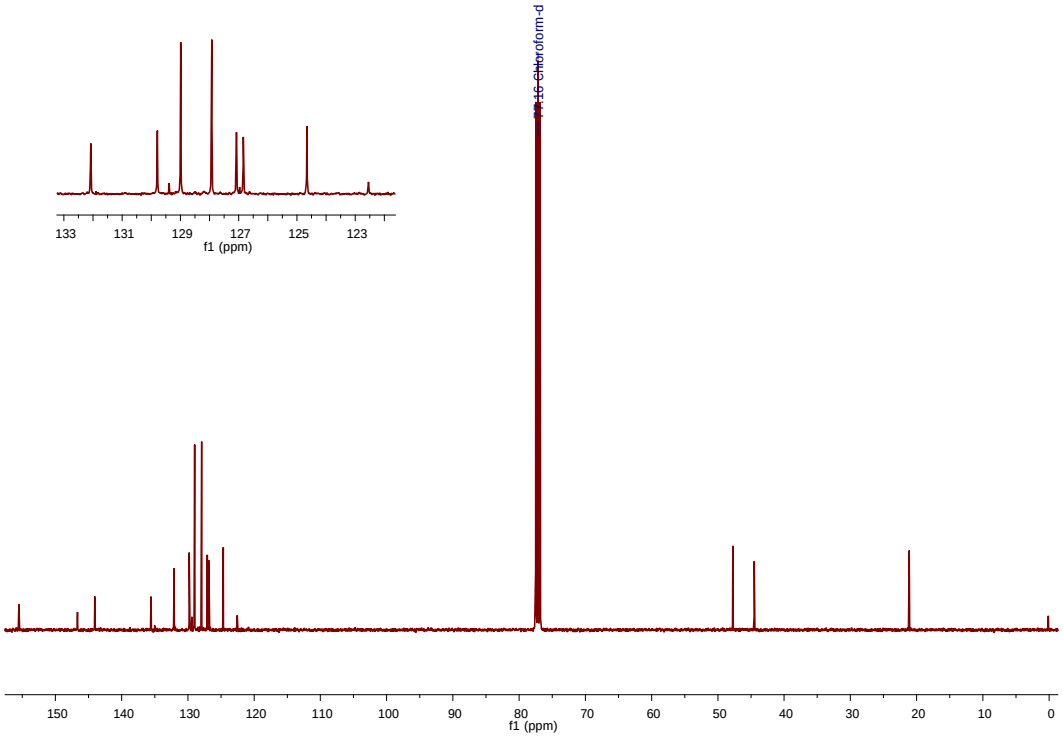
^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.17 / 124.6 (H_5 / C_5), 7.51 – 7.45 / 132.0, 129.8, 129.00, 127.9, 127.0 ($H_{7,8,12,13,14}$ / $C_{7,8,12,13,14}$), 7.32 / 126.8 (H_6 / C_6), 3.69 – 3.64 / 47.7, 44.6 ($H_{15,17}$ / $C_{15,17}$), 1.92 – 1.86 / 20.8 (H_{16} / C_{16}).

COSY (400 MHz / 400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 8.17 / 7.32 (H_5 / H_6), 3.69 – 3.64 / 1.92 – 1.86 ($H_{15,17}$ / H_{16}).

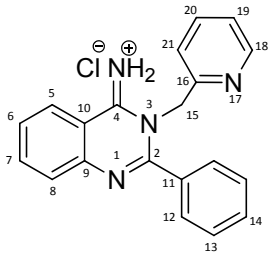
FTIR (KBr): ν / cm^{-1} = 3424, 3332, 3223, 3073, 2932, 2857, 1635, 1600, 1585, 1564, 1493, 1479, 1461, 1443, 1378, 1352, 1287, 1242, 1174, 1146, 1075, 1036, 1007, 956, 772, 718, 706, 672, 594, 542, 408, 348, 297.



Compound 10. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K)



Compound 10. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)



Compound 11

Synthesis of 2-phenyl-3-(pyridin-2-ylmethyl)quinazolin-4(3H)-iminium chloride (11):

2-picolinamina (0.22 g, 2.08 mmol) was added to a solution of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.50g, 2.08 mmol) in 20 mL of toluene and the reaction mixture was stirred for 26 hours under reflux. The precipitate was filtrated and discarded and from the solution a white solid was precipited from, which were filtered and dried under vacuum (0.32 g, 45 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 10.21 (br. s. 1H, NH), 8.81 (d, *J* = 8.4, 1H, H_5), 8.60 – 8.51 (m, 4H, $H_{6, 7, 8, 18}$), 7.72 – 7.69 (m, 2H, $H_{19, 20}$), 7.53 – 7.44 (m, 5H, $H_{12, 13, 14}$), 7.24 – 7.23 (m, 1H, H_{21}), 5.15 (s, 2H, H_{15}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 160.07 (C_4), 157.86, 155.36, 130.85, 120.30 ($C_{2, 9, 11, 16}$), 148.67, 129.90, 123.69 ($C_{6, 7, 8}$), 137.72, 135.49 ($C_{19, 20}$), 133.65, 129.06, 122.42 ($C_{12, 13, 14}$), 128.21 (C_{18}), 123.09 (C_{21}), 121.72 (C_5), 46.41 (C_{15}).

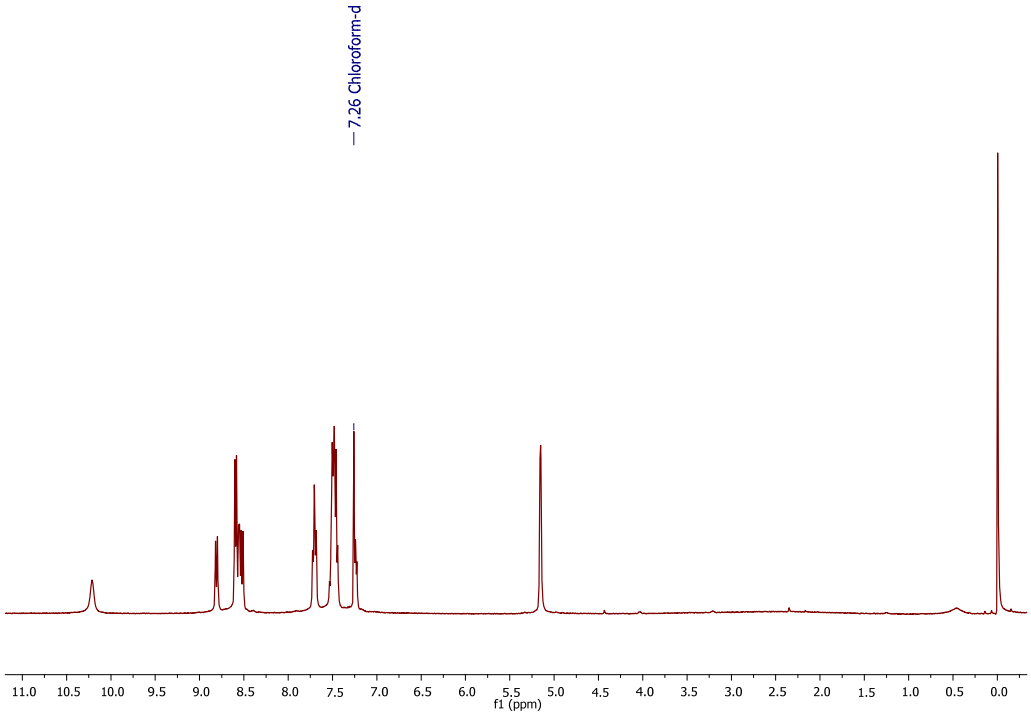
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.81 / 160.07 (H_5 / C_4), 7.24 – 7.23 / 137.72, 135.49 (H_{21} / $C_{19, 20}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 8.81 / 121.72 (H_5 / C_5), 8.60 – 8.51 / 148.67, 129.90, 128.21, 123.69 ($H_{6, 7, 8, 18}$ / $C_{6, 7, 8, 18}$), 7.72 – 7.69 / 137.72, 135.49 ($H_{19, 20}$ / $C_{19, 20}$), 7.53 – 7.44 / 133.65, 129.06, 122.42 ($H_{12, 13, 14}$ / $C_{12, 13, 14}$), 7.24 – 7.23 / 123.09 (H_{21} / C_{21}), 5.15 / 46.41 (H_{15} / C_{15}).

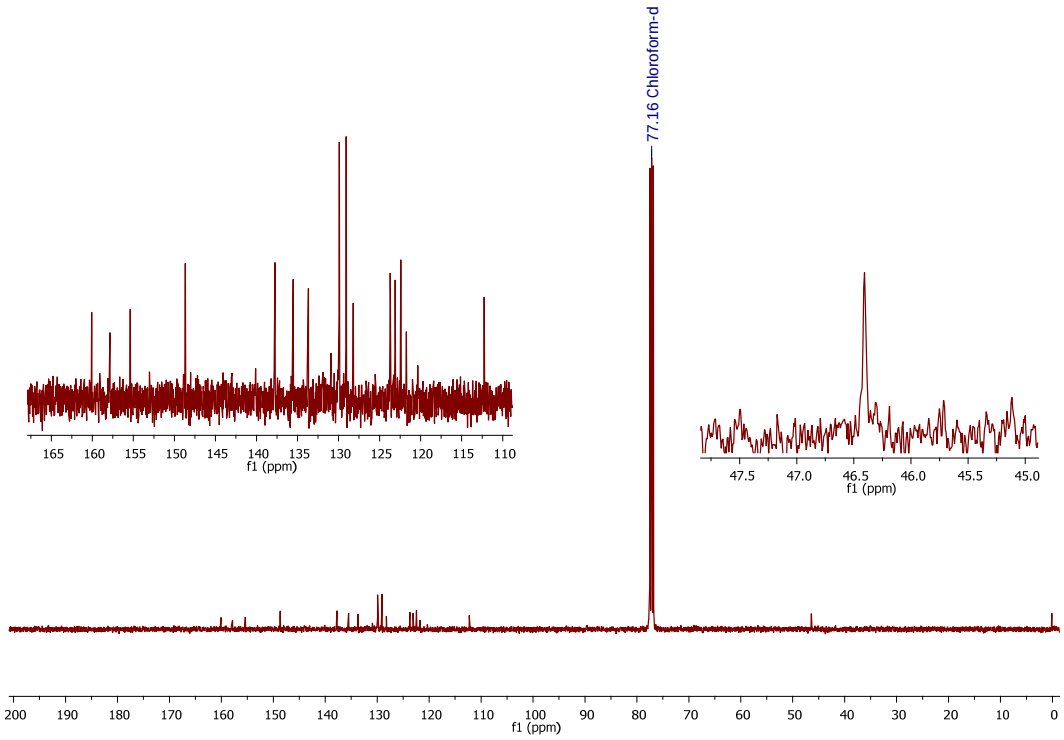
COSY (400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 8.81 / 8.60 – 8.51 (H_5 / $H_{6, 7, 8}$).

FT-IR (KBr): ν / cm^{-1} = 3302, 3062, 2851, 1632, 1616, 1563, 1519, 1504, 1477, 1458, 1431, 1404, 1383, 1330, 1288, 1274, 1213, 1189, 1153, 1117, 1030, 1018, 995, 966, 930, 881, 821, 767, 702, 678, 628, 581.

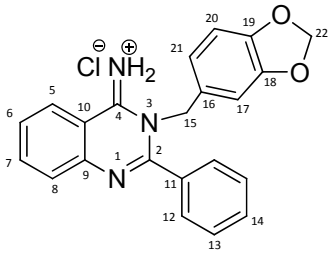
HRMS (ESI) for $C_{20}H_{17}N_4^+$: m/z calcd: 313.15 , found: 313.



Compound 11. ^{1}**H NMR** (400 MHz, $CDCl_3$, 298 K).



Compound 11. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K)



Compound 12

Synthesis of 3-(benzo[d][1,3]dioxol-5-ylmethyl)-2-phenylquinazolin-4(3H)-iminium chloride (12):

Piperonylamine (0.31 g, 2.08 mmol) was added to a solution of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.50g, 2.08 mmol) in 20 mL of toluene and the reaction mixture was stirred for 24 hours under reflux. Pale yellow solid was formed, which were filtered and dried under vacuum (0.44 g, 55 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 11.49 (br. s. 1H, HCl), 10.55 (br. s. 1H, NH), 9.44 (d, *J* = 8.2 Hz, 1H, H_5), 8.00 – 7.85 (m, 2H, $H_{7,\ 8}$), 7.77 (t, *J* = 7.5 Hz, 1H, H_6), 7.61 – 7.51 (m, 5H, $H_{12,\ 13,\ 14}$), 6.64 – 6.61 (m, 3H, $H_{17,\ 20,\ 21}$), 5.98 (s, 2H, H_{15}), 5.84 (s, 2H, H_{22}).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 157.16 (C_4), 154.08 (C_2), 148.30 (C_{19}), 147.88 (C_{18}), 145.55 (C_9), 137.14, 128.53 ($C_{7,\ 8}$), 133.72 (C_{15}), 131.20 (C_{14}), 129.81 (C_6), 129.31, 128.74 ($C_{12,\ 13}$), 127.70 (C_5), 126.55 (C_{11}), 120.93, 108.76, 107.42 ($C_{17,\ 20,\ 21}$), 114.30 (C_{10}), 101.30 (C_{22}), 53.40 (C_{15}).

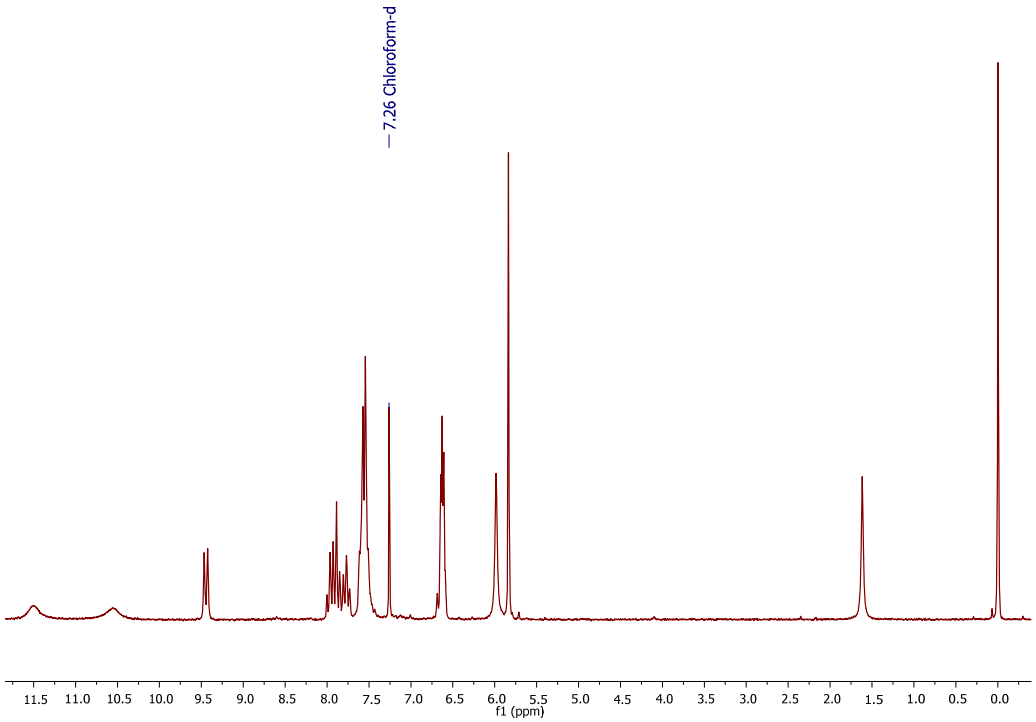
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 9.44 / 157.16, 145.55 (H_5 / $C_{4,\ 9}$), 8.00 – 7.85 / 145.55, 129.81, 127,70, 114.30 ($H_{7,\ 8}$ / $C_{5,\ 6,\ 9,\ 10}$), 7.77 / 137.14, 128.53, 114.30 (H_6 / $C_{7,\ 8,\ 10}$), 7.61 – 7.51 / 154.08, 126.55 ($H_{12,\ 13,\ 14}$ / $C_{2,\ 11}$), 5.98 / 120.93, 108.76, 107.42 (H_{15} / $C_{17,\ 20,\ 21}$), 5.84 / 148.30, 147.88 (H_{22} / $C_{19,\ 18}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 9.44 / 127.70 (H_5 / C_5), 8.00 – 7.85 / 137.14, 128.53 ($H_{7,\ 8}$ / $C_{7,\ 8}$), 7.77 / 129.81 (H_6/ C_6), 7.61 – 7.51 / 131.20, 129.31, 128.74 ($H_{12,\ 13,\ 14}$ / $C_{12,\ 13,\ 14}$), 6.64 – 6.61 / 120.93, 108.76, 107.42 ($H_{17,\ 20,\ 21}$ / $C_{17,\ 20,\ 21}$), 5.98 / 53.40 (H_{15} / C_{15}), 5.84 / 101.30 (H_{22} / C_{22}).

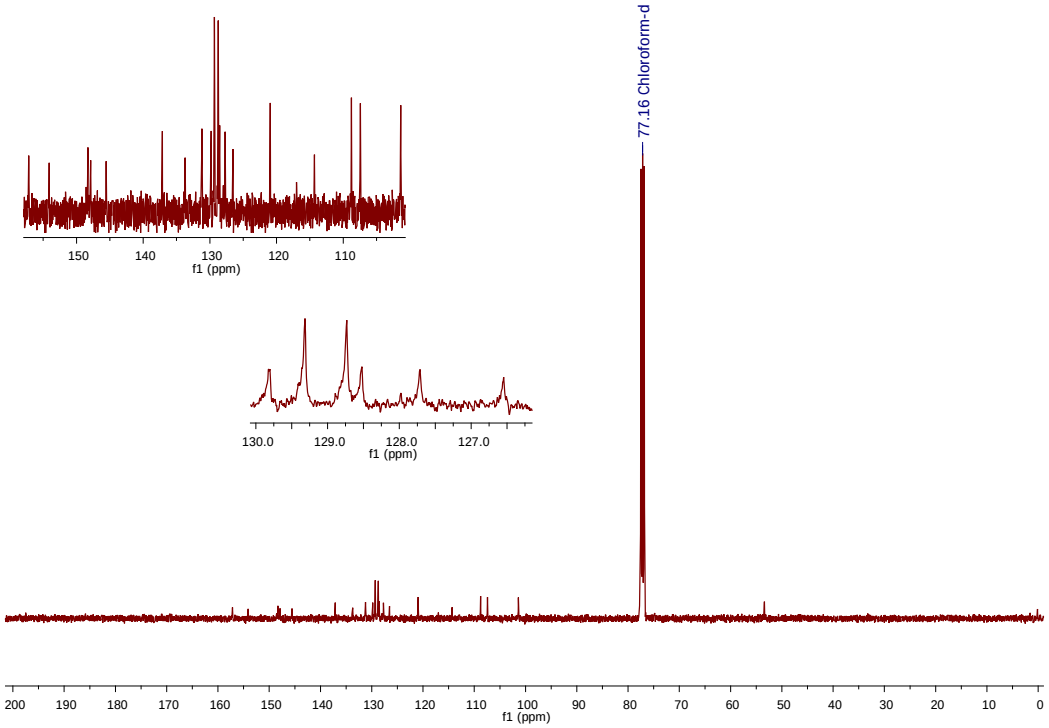
COSY (400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 9.44 / 7.77 (H_5 / H_6), 7.77 / 8.00 – 7.85 (H_6 / $H_{7,\ 8}$).

FT-IR (KBr): ν / cm^{-1} = 3425, 2995, 2875, 2782, 2560, 2057, 1854, 1695, 1613, 1599, 1585, 1500, 1486, 1467, 1445, 1388, 1358, 1322, 1275, 1249, 1206, 1189, 1154, 1132, 1118, 1105, 1089, 1043, 970, 939, 915, 892, 812, 772, 727, 711, 700, 675, 631, 614, 600, 585, 517, 498, 448, 425, 388, 318.

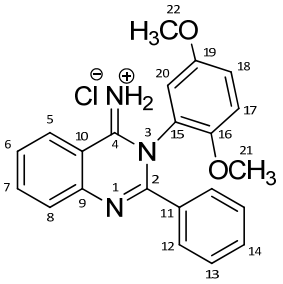
HRMS (ESI) for $C_{22}H_{18}N_3O_2^+$: m/z calcd: 356.14 , found: 356.



Compound 12. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).



Compound 12. ^{13}C NMR (100 MHz, $CDCl_3$, 298 K).



Compound 13

Synthesis of 3-(2,5-dimethoxyphenyl)-2-phenylquinazolin-4(3H)-iminium chloride (13):

2,5-dimethoxyaniline (0.32 g, 2.08 mmol) was added to a solution of (*E*)-*N*-(2-cyanophenyl)benzimidoyl chloride (0.50g, 2.08 mmol) in 20 mL of toluene and the reaction mixture was stirred for 24 hours under reflux. Gray solid was formed, which were filtered and dried under vacuum (0.53 g, 65 %).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ/ppm = 13.01 (s, 1H, NH), 9.54 (d, *J* = 8.1 Hz, 1H, H_5), 8.09 – 7.82 (m, 3H, $H_{6,\ 7,\ 8}$), 7.39 – 7.28 (m, *5*H, $H_{12,\ 13,\ 14}$), 7.04 – 6.89 (m, 2H, $H_{17,\ 18}$), 6.79 (br. s, 1H, H_{20}), 3.74 – 3.72 (m, 6H, $H_{21,\ 22}$).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ/ppm = 157.03 (C_4), 154.35, 152.32, 132.94, 121.98 ($C_{2,\ 11,\ 15,\ 19}$) 147,62 (C_{16}), 145.86 (C_9), 137.78 (C_7), 130.42 (C_{14}), 130.06 (C_6), 128.54 (C_5), 128.50 (C_8), 128.27, 128.05 ($C_{12,\ 13}$) , 118.75, 114.10 ($C_{17,\ 18}$), 114.45 (C_{20}) , 112.78 (C_{10}), 56.13 , 56.12 ($C_{21,\ 22}$).

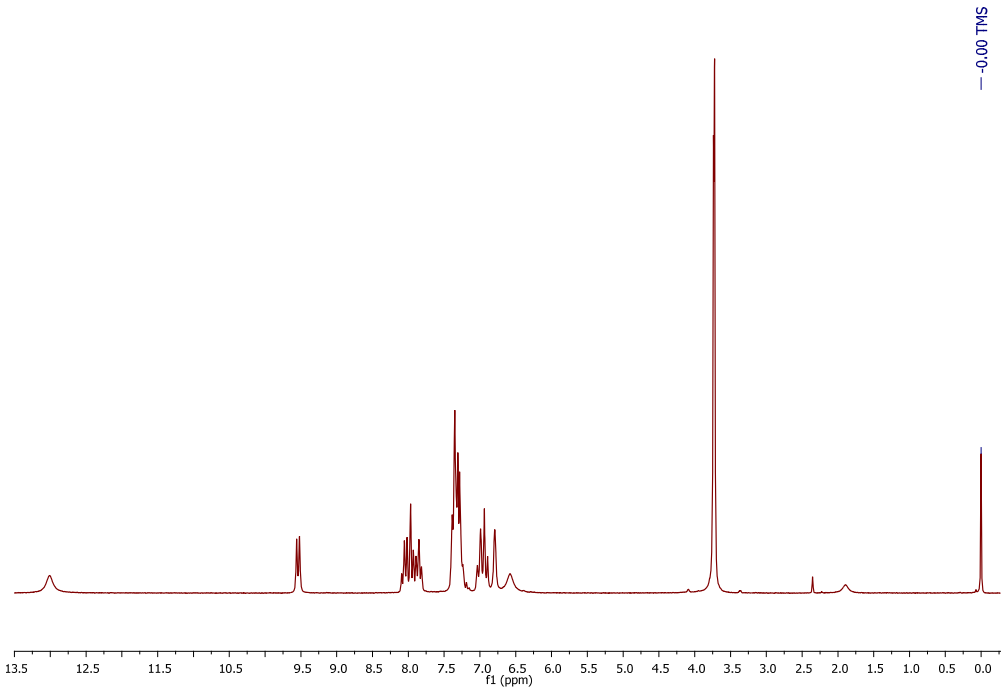
^{1}H, ^{13}C-HMBC (400 MHz / 100 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{13}C) = 9.54 / 157.03, 145.86, 137.78 (H_5 / $C_{4,9,7}$), 6.79 / 147.62 (H_{20} / C_{16}), 8.09 – 7.82 / 137.78, 130.06, 128.50 ($H_{6,\ 7,\ 8}$ / $C_{6,\ 7,\ 8}$).

^{1}H, ^{13}C-HSQC (400 MHz / 100 MHz, CD_2Cl_2/CD_3OD (97:3), 298 K) δ(^{1}H) / δ(^{13}C) = 9.54 / 128.54 (H_5 / C_5), 8.09 – 7.82 / 137.78, 130.06, 128.50 ($H_{6,\ 7,\ 8}$ / $C_{6,\ 7,\ 8}$), 7.39 – 7.28 / 128.27, 128.05, 130.42 ($H_{12,\ 13,\ 14}$ / $C_{12,\ 13,\ 14}$), 6.79 /114.45 (H_{20} / C_{20}), 3.74 – 3.72 / 56.13 , 56.12 ($H_{21,\ 22}$ / $C_{21,\ 22}$).

COSY (400 MHz, $CDCl_3$, 298 K) δ(^{1}H) / δ(^{1}H) = 9.54 / 8.09 – 7.82 (H_5 / $H_{6,\ 7,\ 8}$).

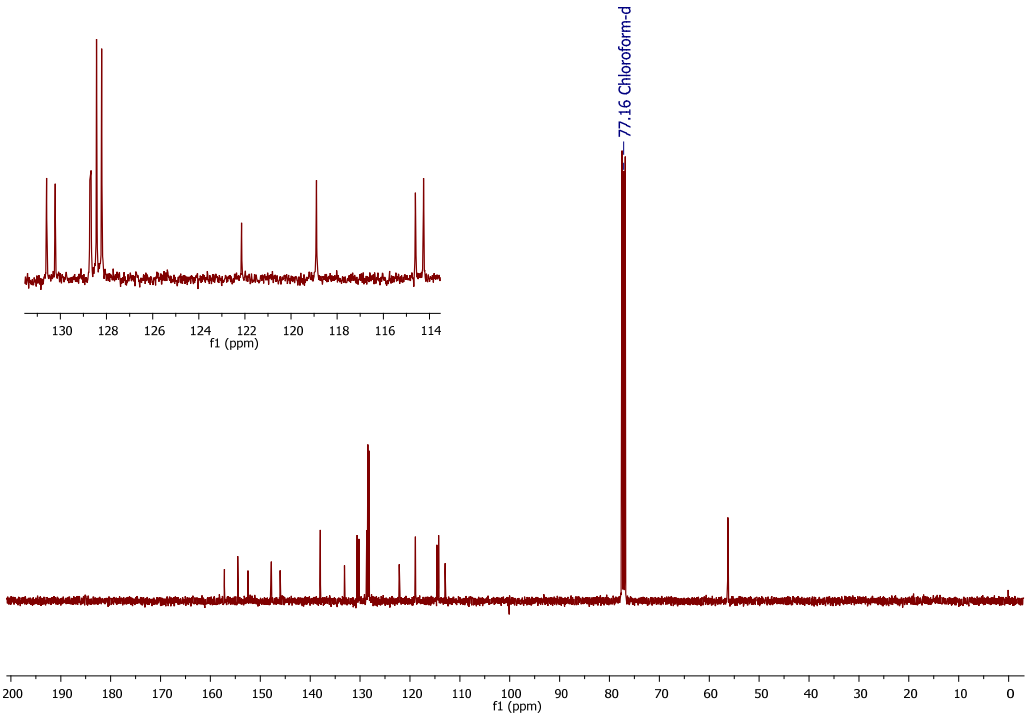
FT-IR (KBr): ν / cm^{-1} = 3393, 3029, 3000, 2938, 2834, 2745, 2663, 2012, 1830, 1658, 1625, 1599, 1573, 1530, 1506, 1479, 1465, 1446, 1340, 1314, 1298, 1275, 1234, 1204, 1160, 1144, 1117, 1078, 1041, 1016, 964, 935, 904, 887, 858, 808, 796, 779, 737, 726, 706, 678, 642, 586, 519, 492, 397, 355.

HRMS (ESI) for $C_{22}H_{20}N_3O_2^+$: m/z calcd: 358.16 , found: 359.

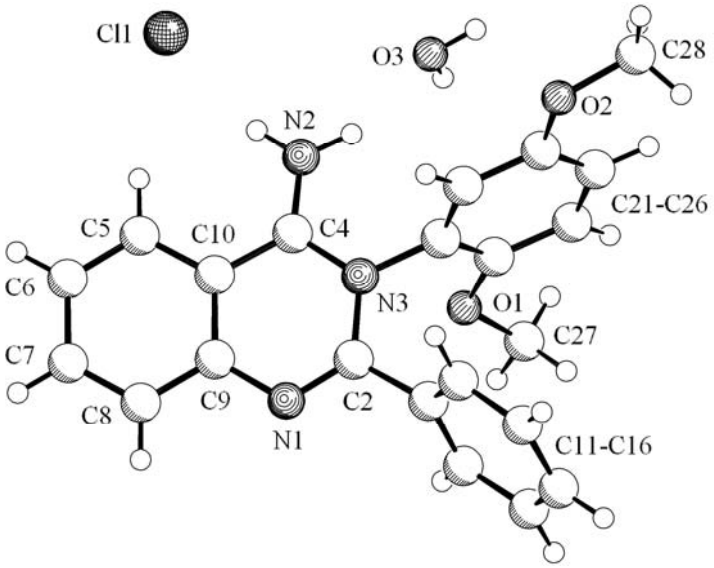


Compound 13. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K).

Note: Reference to $Si(CH_3)_4$.



Compound 13. ^{13}**C NMR** (100 MHz, $CDCl_3$, 298 K)



Crystal structure of compound 13. Selected bond lengths (Å): N1-C2, 1.286(2); C2-N3, 1.403 (2); N3-C4, 1.365(2); N4-C4, 1.313(2); N1-C9, 1.387(2). Selected angles (º)C4-N3-C21, 120.09(14); C2-N3-C21, 119.10(14); C2-N3-C4, 120.64(16); C9-N1-C2, 118.03(16).

Table S1. Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, **4**, **5** and **9**.

	1	**2**	**4**	**5**	**9**	**13**
	NH	**NH**	**NH**	**NH (HCl)**	**NH**	**NH (HCl)**
			Bond lengths (Å)			
C9-N1	1.391(19)	1.391(4)	1.396(17)	1.388(2)	1.402(17)	1.387(2)
N1-C2	1.290(17)	1.290(4)	1.293(17)	1.286(2)	1.304(18)	1.286(2)
C2-N3	1.389(16)	1.399(4)	1.389(17)	1.407(2)	1.360(17)	1.403(2)
N3-C4	1.408(17)	1.418(4)	1.417(17)	1.364(3)	1.399(18)	1.365(2)
C4-NH (HCl)	1.275(19)	1.280(4)	1.271(19)	1.308(2)	1.278(18)	1.313(2)
C4-C10	1.468(19)	1.458(4)	1.461(2)	1.436(3)	1.452(2)	1.440(3)
C10-C9	1.392(2)	1.397(4)	1.395(19)	1.408(3)	1.406(19)	1.409(3)
			Angles(°)			
C9-N1-C2	117.80(12)	118.80(3)	117.94(11)	118.13(17)	117.79(11)	118.03(16)
C2-N3-C4	122.48(11)	120.80(2)	121.41(11)	119.16(16)	123.04(12)	120.64(16)
C2-N3-C(Ar)	119.79(10)	121.50(2)	121.72(11)	121.14(16)	128.63(12)	119.10(14)
C(Ar)-N3-C4	117.72(10)	117.30(2)	116.29(11)	119.46(16)	107.87(11)	120.09(14)

References:

[1] (a) Boeré, R. T., Klassen, V., Wolmershäuser G. J. Chem. Soc., Dalton Trans., 1998, 4147 - 4154. **(b)** Masuda, J. D., and Sthephan D. W. Dalton Trans., 2006, 17, 2089 – 2097.

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[3] Fathalla W. M., Čajan M., Marek J., Pazdera, P. Molecules 2001, 6, 574 – 587.