Electronic Supplementary Information

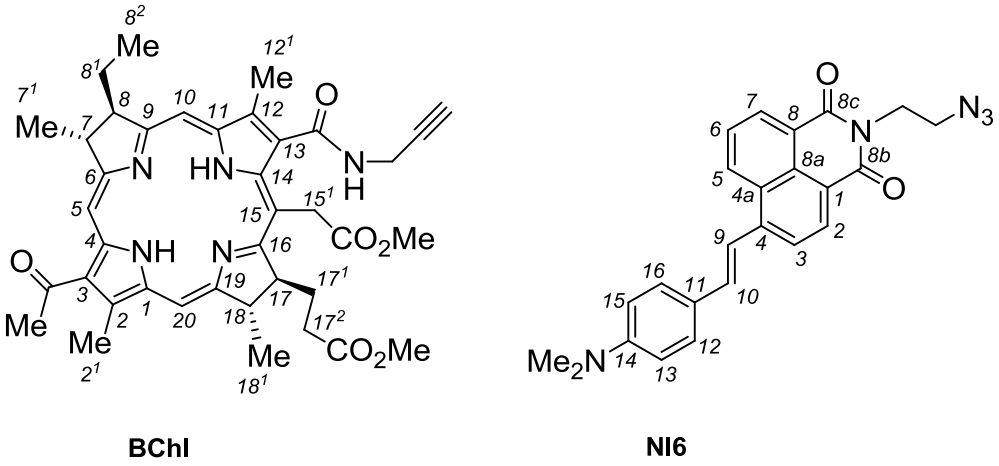
Novel Bacteriochlorin–Styrylnaphthalimide Conjugate for Simultaneous Photodynamic Therapy and Fluorescence Imaging

Pavel A. Panchenko, Mikhail A. Grin, Olga A. Fedorova, Marina A. Zakharko, Dmitriy A. Pritmov, Andrey F. Mironov, Antonina N. Arkhipova, Yuri V. Fedorov, Gediminas Jonusauskas, Raisa I. Yakubovskaya, Natalia B. Morozova, Anastasia A. Ignatova and Alexey V. Feofanov

CONTENTS

1. Synthesis of the compounds

General analytical methods. ^{1}H and ^{13}C NMR spectra were recorded on an Avance 400, Avance 500 and Avance 600 spectrometers (Bruker) operating at 400.13, 500.13, 600.22 MHz (for ^{1}H) and 100.61, 125.76, 150.93 MHz (for ^{13}C) respectively. The chemical shifts were determined with an accuracy of 0.01 ppm relative to residual solvent signals and translated to the internal standard (TMS), coupling constants were measured with an accuracy of 0.1 Hz. The numbering of carbon atoms in the naphthalimide and bacteriochlorin fragments used for the description of the ^{1}H NMR spectra of the synthesized compounds is shown in Scheme S1. In the case of conjugate **BChl-NI**, carbon atoms of naphthalimide are marked with a prime. The assignment of ^{1}H and ^{13}C signals is based on 2D NMR experiments (HMBC, HSQC, ^{1}H COSY), which were performed using standard pulse sequences from the Bruker library. 2D NMR spectra are presented in section 2.



Scheme S1. Numbering of the carbon atoms in **BChl** and **NI6**

Melting points were measured on Melt-temp melting point electrothermal apparatus and were uncorrected. The reaction course and purity of the final products was followed by TLC on silica gel (DC-Alufolien Kieselgel 60 F254, Sigma-Aldrich). Column chromatography was conducted over silica gel (Kieselgel, particle size 40-60 μm, Acros Organics). Preparative TLC was performed on silica gel 60 (Merck) using 20×20 cm plates with a layer thickness of 1 mm. IR spectra were recorded on a Bruker EQUINOX 55 spectrometer and on Magna-IR 750 Nicolet spectrometer with potassium bromide pellets. Electron impact (EI) (70 eV) mass spectra were obtained from Finnigan Polaris Q instrument (ion-trap) in standard conditions. The mass-spectra of **BChl** and **BChl-NI** were obtained by MALDI method on time-offlight mass-spectrometer Bruker Ultraflex TOF/TOF using dihydroxybenzene matrix. *m/z*: 1997.68 (M^{+}). Elemental analyses were carried out in the Microanalysis Laboratory of the A.N. Nesmeyanov Institute of Organoelement Compounds.

4-(4-*N*,*N*-dimethylaminostyryl)-*N*-(2-hydroxyethyl)-1,8-naphthalimide (NI3). A solution of compound **NI1** (0.90 g, 2.81 mmol), $Pd(OAc)_2$ (8 mg, 0.04 mmol), tris-(*ortho*-tolyl)phosphine (47 mg, 0.155 mmol), triethylamine (5.4 ml) and 4-*N*,*N*-dimethylaminostyrene (0.50 g, 3.37 mmol) in dry DMF (30 ml) was stirred at 110 °C during 13 h under argon atmosphere. The mixture was cooled to ambient temperature then diluted with water and exctracted with $CHCl_3$. The organic layer was dried with Na_2SO_4 and evaporated in vacuum. The residue was subjected to chromatography on a silica gel by using gradient mixture dichloromethane – methanol and then recrystallized from ethanol to give 0.27 g (yield 25%) of a dark red solid. M.p. 217 °C (decomp.). ^{1}H NMR (400.13 MHz, DMSO-d_6, 27 °C): δ = 2.99 (s, 6H, $N(CH_3)_2$), 3.58–3.69 (m, 2H, $C\underline{H}_2OH$), 4.16 (t, 2H, $C\underline{H}_2CH_2OH$, J = 6.3), 4.82 (m, 1H, OH, J = 6.3), 6.77 (d, 2H, H(13), H(15), J = 8.8), 7.54 (d, 1H, H(9), J = 15.9), 7.70 (d, 2H, H(12), H(16), J = 8.8), 7.87 (m, 1H, H(6), J = 7.3, J = 8.8), 7.94 (d, 1H, H(10), J = 15.9), 8.19 (d, 1H, H(3), J = 8.2), 8.44 (d, 1H, H(7), J = 7.3), 8.53 (d, 1H, H(5), J = 8.8), 8.99 (d, 1H, H(2), J = 8.2). ^{13}C NMR (100.61 MHz, DMSO-d_6, 27 °C): δ = 40.12 ($N(CH_3)_2$), 41.79 ($\underline{C}H_2CH_2OH$), 57.83 ($\underline{C}H_2OH$), 112.00 (C(13), C(15)), 117.49 (C(9)), 119.54 (C(1)), 122.21 (C(3)), 122.51 (C(8)), 124.42 (C(11)), 126.57 (C(6)), 128.34 (C(8a)), 128.78 (C(4a)), 128.98 (C(12), C(16)), 130.61 (C(2)), 130.70 (C(7)), 130.78 (C(5)), 135.77 (C(10)), 141.97 (C(4)), 150.76 (C(14)), 163.38 (C(8b)), 163.69 (C(8c)). FT-IR (KBr)/cm^{-1}: 3489 (ν_{OH}); 2923, 2865 (ν_{CH}); 1695, 1646 ($\nu_{C=O}$). EI-MS, *m/z* (*I, %*): 387 (27), 386 (100) $[M]^+$, 387 (27), 355 (17), 343 (58), 341 (29), 327 (15), 255 (19), 228 (16), 162 (16). Elemental analysis: calculated (%) for $C_{24}H_{22}N_2O_3$ (MW 386.44): C 74.59, H 5.74, N 7.25, O 12.42; found C 74.30, H 5.82, N 7.06.

4-(4-*N*,*N*-dimethylaminostyryl)-*N*-(2-chloroethyl)-1,8-naphthalimide (NI5). A mixture of **NI3** (0.06 g, 0.155 mmol) and $POCl_3$ (1.1ml, 0.012 mol) was stirred at 85°C for 2 h. The excess of $POCl_3$ was removed under reduced pressure, the residue was dissolved in $CHCl_3$ and then, washed sequentially with 5% aqueous solution of Na_2CO_3 and distilled water. The organic layer was dried with $MgSO_4$ and evaporated in vacuum. The residue was chromatographed on SiO_2 using dichloromethane – methanol gradient mixture to give 56 mg (89% yield) of **NI5**. M.p. 187–189 °C. ^{1}H NMR (600.17 MHz, DMSO-d_6, 30 °C): δ = 3.00 (s, 6H, $N(CH_3)_2$), 3.83-3.92 (m, 2H, $C\underline{H}_2CH_2Cl$), 4.41 (m, 2H, CH_2Cl, J = 6.9), 6.78 (d, 2H, H(13), H(15), J = 8.8), 7.56 (d, 1H, H(10), J = 16.0), 7.71 (d, 2H, H(12), H(16), J = 8.8), 7.86-7.93 (m, 1H, H(6)), 7.95 (d, 1H, H(9), J = 16.0), 8.21 (d, 1H, H(3), J = 8.1), 8.46 (d, 1H, H(2), J = 8.1), 8.55 (d, 1H, H(7), J = 7.1), 9.02 (d, 1H, H(5), J = 8.2). ^{13}C NMR (150.93 MHz, DMSO-d_6, 30 °C): δ = 40.03 ($N(CH_3)_2$), 40.77 (CH_2Cl), 52.88 ($\underline{C}H_2CH_2Cl$), 112.13 (C(13), C(15)), 117.51 (C(9)), 119.13 (C(1)), 122.09 (C(3)), 122.30 (C(8), C(11)), 124.42 (C(11)), 126. 70 (C(6)),

128.38 (C(8a)), 128.81 (C(4a)), 129.01 (C(12), C(16)), 130.86 (C(2)), 130.97 (C(7)), 131.12 (C(5)), 135.97 (C(10)), 142.32 (C(4)), 149.39 (C(14)), 163.19 (C(8b)), 163.53 (C(8c)). EI-MS, *m/z* (*I, %*): 406 (35), 404 (100) $[M]^+$, 386 (22), 369 (16), 342 (41), 341 (25), 298 (12), 255 (15), 162 (18), 113 (32). Elemental analysis: calculated (%) for $C_{24}H_{21}ClN_2O_2$ (MW 404.89): C 71.19, H 5.23, Cl 8.76, N 6.92, O 7.90; found C 70.92, H 5.28, N 6.85.

4-(4-*N*,*N*-dimethylaminostyryl)-*N*-(2-azidoethyl)-1,8-naphthalimide (NI6). To a solution of compound **NI5** (50 mg, 0.12 mmol) in DMF (3.5 ml) NaN_3 (48 mg, 0.74 mmol) was added. The reaction mixture was stirred at 100 °C for 7 h under argon atmosphere and then, chloroform (20 ml) was added. The resulting solution was washed with water and dried with $MgSO_4$. After removing of a solvent, 28 mg (55% yield) of a pure product was obtained. M.p. 148 °C (decomp.). ^{1}H NMR (400.13 MHz, DMSO-d_6, 30 °C): δ = 3.00 (s, 6H, $N(CH_3)_2$), 3.63 (m, 2H, CH_2N_3, J = 6.0), 4.31 (m, 2H, $CH_2CH_2N_3$, J = 6.0), 6.78 (d, 2H, H(15), H(13), J = 8.8), 7.54 (d, 1H, H(10), J = 15.9), 7.71 (d, 2H, H(12), H(16), J = 8.8), 7.86-7.93 (m, 2H, H(6)), 7.92-7.99 (m, 1H, H(9)), 8.20 (d, 1H, H(3), J = 7.9), 8.46 (d, 1H, H(2), J = 7.9), 8.55 (d, 1H, H(7), J = 7.3), 9.00 (d, 1H, H(5), J = 8.7).^{13}C NMR (100.61 MHz, DMSO-d_6, 30°C): δ = 38.53 ($CH_2CH_2N_3$), 40.05 ($N(CH_3)_2$), 48.35 (CH_2N_3), 112.02 (C(13), C(15)), 117.44 (C(9)), 119.12 (C(1)), 122.10 (C(3)), 122.31 (C(8)), 124.39 (C(11)), 126.74 (C(6)), 128.39 (C(8a)), 128.83 (C(4a)), 129.04 (C(12), C(16)), 130.90 (C(2)), 131.00 (C(7)), 131.12 (C(5)), 136.03 (C(10)), 142.36 (C(4)), 150.83 (C14)), 163.35 (C(8b)), 163.69 (C(8c)). EI-MS, *m/z* (*I, %*): 411 (9) $[M]^+$, 353 (66), 352 (100), 342 (69), 341 (43), 328 (36), 327 (28), 253 (28), 226 (28), 57 (31). Elemental analysis: calculated (%) for $C_{24}H_{21}N_5O_2$ (MW 411.46): C 70.06, H 5.14, N 17.02, O 7.78; found C 70.17, H 5.22, N 16.98.

Propargyl-15^2,17^3-dimethoxy-13^1-amide of bacterichlorin *e* (BChl). To a solution of 50 mg (0.08 mmol) of methyl ether of bacteriopheophorbide (**BPheid**) in pyridine (4 ml) propargylamine (0.3 ml, 4.5 mmol) was added. The reaction mixture was stirred at room temperature for 28 h and then, diluted with chloroform. The resulting solution was washed sequentially with 0.1N HCl, aqueous $NaHCO_3$ and water. Organic layer was dried with Na_2SO_4 and evaporated in vacuum. The residue was purified by column chromatography on SiO_2 using chloroform–methanol mixture (v/v=100/2) to give 41mg (76% yield) of **BChl**. M.p. 162 °C (decomp.). ^{1}H NMR (500.13 MHz, CD_2Cl_2, 25 °C): δ = –1.31 (s, 1H, NH, pyrrole), –1.26 (s, 1H, NH, pyrrole), 1.08 (t, 3H, H(8^2), J = 7.4), 1.62 (d, 3H, H(18^1), J = 7.3), 1.66-1.75 (m, 1H, H(17^1)), 1.87 (d, 3H, H(7^1), J = 7.3), 2.05-2.16 (m, 2H, H(17^1), H(8^1)), 2.19-2.25 (m, 1H, H(17^2)), 2.36-2.43 (m, 1H, H(8^1)), 2.46 (t, 1H, C≡CH, J = 2.6), 2.53-2.60 (m, 1H, CH_2(17^2)), 3.17 (s, 3H, $COCH_3$), 3.34 (s, 3H, H(12^1)), 3.56-3.62 (m, 6H, C(17^2)–$COOCH_3$, H(2^1)), 3.79 (s, 3H, C(15^1)–$COOCH_3$), 4.17-4.21 (m, 2H, H(8), H(17)), 4.28 (q, 1H, H(18), J = 7.3), 4.35 (dq,

1H, H(7), *J* = 3.2, *J* = 7.3), 4.45 (ddd, 1H, NHC$\underline{H}_2$, *J* = 17.4, *J* = 5.5, *J* = 2.6), 4.53 (ddd, 1H, NHC$\underline{H}_2$, *J* = 17.4, *J* = 5.5, *J* = 2.6), 5.12 (d, 1H, H(15^1), *J* = 19.2), 5.30 (d, 1H, H(15^1), *J* = 19.2), 6.69 (t, 1H, NHCO, *J* = 5.5), 8.65 (s, 1H, H(10)), 8.76 (s, 1H, H(20)), 9.30 (s, 1H, H(5)).^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 11.06 (C(8^2)), 12.00 (C(12^1)), 13.99 (C(2^1)), 23.44 (C(18^1), 23.95 (C(7^1)), 29.87 (C(17^1)), 30.57 (C(8^1)), 30.68 ($\underline{C}H_2$NHCO), 31.48 (C≡$\underline{C}$H), 33.56 (CO$\underline{C}H_3$), 38.15 (C(15^1)), 47.35 (C(7)), 48.60 (C(18)), 51.99 (C(17^2)–COO$\underline{C}H_3$), 52.79 (C(15^1)–COO$\underline{C}H_3$), 53.64 (C(17)), 57.78 (C(8)), 79.68 ($\underline{C}$≡CH), 97.17 (C(10)), 98.01 (C(20)), 98.66 (C(5)), 105.09 (C(14)), 129.05 (C(11)), 129.46 (C(3)), 132.30 (C(12)), 132.64 (C(2)), 133.00 (C(1)), 133.56 (C(15)), 134.13 (C(13)), 135.38 (C(4)), 164.25 (C(19)), 165.78 (C(9)), 166.31 (C(16)), 169.10 (C(6)), 169.18 (CONH), 173.95 (C(17^2)–$\underline{C}$OOCH$_3$), 174.16 (C(15^1)–$\underline{C}$OOCH$_3$), 198.87 ($\underline{C}$OCH$_3$). FT-IR (KBr)/cm^{-1}: 3287 ($\nu_{\equiv C\text{-}H}$); 2120 ($\nu_{C\equiv C}$); 1736 ($\nu_{C=O}$); 1657, 1511($\nu_{NH\text{-}C=O}$). Elemental analysis: calculated (%) for $C_{39}H_{45}N_5O_6$ (MW 679.80): C 68.90, H 6.67, N 10.30, O 14.12; found C 68.81, H 6.75, N 10.22. Mass (MALDI): 679.2 (M^+).

Conjugate BChl-NI. A mixture of **BChl** (20 mg, 0.03 mmol), **NI6** (14 mg, 0.033 mmol), diisopropylethylamine (10.5 μl, 0.06 mmol), copper (I) iodide (1 mg, 0.005 mmol) and chloroform (3.0 ml) was stirred at room temperature for 3 h. Then, the reaction mixture was concentrated in vacuum and the product was isolated by the preparative thin layer chromatography on SiO_2 using dichloromethane–methanol mixture (v/v=25/1) as an eluent. Yield of **BChl-NI** is 20 mg (61%). M.p. 135 °C (decomp.). ^{1}H NMR (600.13 MHz, CD_2Cl_2, 23 °C): δ = –1.36 (s, 1H, NH, pyrrole), –1.34 (s, 1H, NH, pyrrole), 1.06 (t, 3H, H(8^2), *J* = 7.2), 1.61 (d, 3H, H(18^1), *J* = 7.2), 1.64-1.72 (m, 1H, H(17^1)), 1.87 (d, 3H, H(7^1), *J* = 7.3), 2.01-2.16 (m, 2H, H(8^1), H(17^1)), 2.17-2.26 (m, 1H, H(17^2)), 2.35-2.42 (m, 1H, H(8^1)), 2.52-2.58 (m, 1H, H(17^2)), 3.01 (s, 6H, N(CH_3)$_2$), 3.16 (s, 6H, 2×COOCH$_3$), 3.56 (s, 3H, COCH$_3$), 3.57 (s, 3H, H(12^1)), 3.68 (s, 1H, H(2^1)), 4.11-4.19 (m, 2H, H(8), H(17)), 4.26 (q, 1H, H(7), *J* = 7.3), 4.29-4.36 (m, 1H, H(18)), 4.53-4.67 (m, 2H, triazole–C$\underline{H}_2$CH$_2$), 4.71-4.80 (m, 2H, triazole–CH$_2$C$\underline{H}_2$), 4.80-4.84 (m, 1H, C$\underline{H}_2$NHCO), 4.98-5.02 (m, 1H, C$\underline{H}_2$NHCO), 5.06 (d, 1H, H(15^1), *J* = 19.2), 5.29 (d, 1H, H(15^1), *J* = 19.2), 6.66 (d, 2H, H(13′), H (15′), *J* = 8.3), 7.02 (d, 1H, H(10′), *J* = 15.3), 7.15-7.17 (m, 1H, NHCO), 7.31-7.37 (m, 3H, H(9′), H(12′), H(16′)), 7.50-7.60 (m, 1H, H(6′)), 7.60-7.70 (m, 1H, H(3′)), 7.98 (s, 1H, triazole), 8.23-8.34 (m, 1H, H(2′)), 8.38-8.44 (m, 2H, H(5′), H(7′)), 8.52 (s, 1H, H(10)), 8.72 (s, 1H, H(5)), 9.27 (s, 1H, H (20)). ^{13}C NMR (125.76 MHz, CD_2Cl_2, 25 °C): δ = 11.08 (C(8^2)), 12.41 (C(12^1)), 14.00 (C(2^1)), 23.49 (C(18^1), 23.89 (C(7^1)), 29.85 (C(17^1)), 30.43 (C(8^1)), 32.11 (C(17^2)), 33.54 ($\underline{C}$H$_3$CO), 36.52 ($\underline{C}$H$_2$NHCO), 38.08 (C(15^1)), 40.12 (triazole–CH$_2$$\underline{C}H_2$), 40.58 (N($CH_3$)$_2$), 47.17 (C(7)), 48.38 (C(18)), 48.48 (triazole–$\underline{C}$H$_2$CH$_2$), 51.95 (C(17^2)–COO$\underline{C}$H$_3$), 52.68 (C(15^1)–COO$\underline{C}$H$_3$), 53.55 (C(17)), 57.75 (C(8)), 96.77 (C(10)), 98.03 (C(20)), 98.54 (C(5)), 105.20 (C(14)), 112.46 (C(13′), C(15′)),

117.88 (C(9′)), 119.72 (C(1′)), 122.67 (C(8′)), 122.81 (C(3′)), 123.86 (triazole(CH)), 124.86 (C(11'), 126.59 (C(6′)), 128.84 (C(3)), 128.92 (C(12′), C(16′)), 129.01 (C(8a′)), 129.55 (C(11)), 129.83 (C(4a′)), 130.73 (C(7′)), 131.49 (C(5′)), 131.58 (C(2′)), 132.22 (C(12)), 132.33 (C(2)), 132.59 (C(1)), 133.93 (C(15)), 134.34 (C(13)), 135.18 (C(4)), 136.10 (C(10')), 143.02 (C(4′)), 144.82 ($NHCH_2\underline{C}$), 151.50 (C(14′)), 163.79 (C(8b′)), 164.19 (C(19)), 164.54 (C(8a′)), 165.92(C(9)), 166.60(C(16)), 168.69(C(6)), 169.21(NHCO), 173.87($C(17^2)$–$\underline{C}OOCH_3$), 173.93 ($C(15^1)$–$\underline{C}OOCH_3$), 198.73 ($CH_3\underline{C}O$). FT-IR (KBr)/cm^{-1}: 1733 ($\nu_{C=O}$); 1695 ($\nu_{C=C}$); 1654, 1524($\nu_{NH\text{-}C=O}$), 1434 ($\nu_{N=N}$). Elemental analysis: calculated (%) for $C_{63}H_{66}N_{10}O_8$ (MW 1091.26): C 69.34, H 6.10, N 12.84, O 11.73, found C 69.25, H 6.18, N 12.76. Mass (MALDI): 1091.32 (M^+).

2. 2D NMR spectra of NI3, BChl and BChl-NI

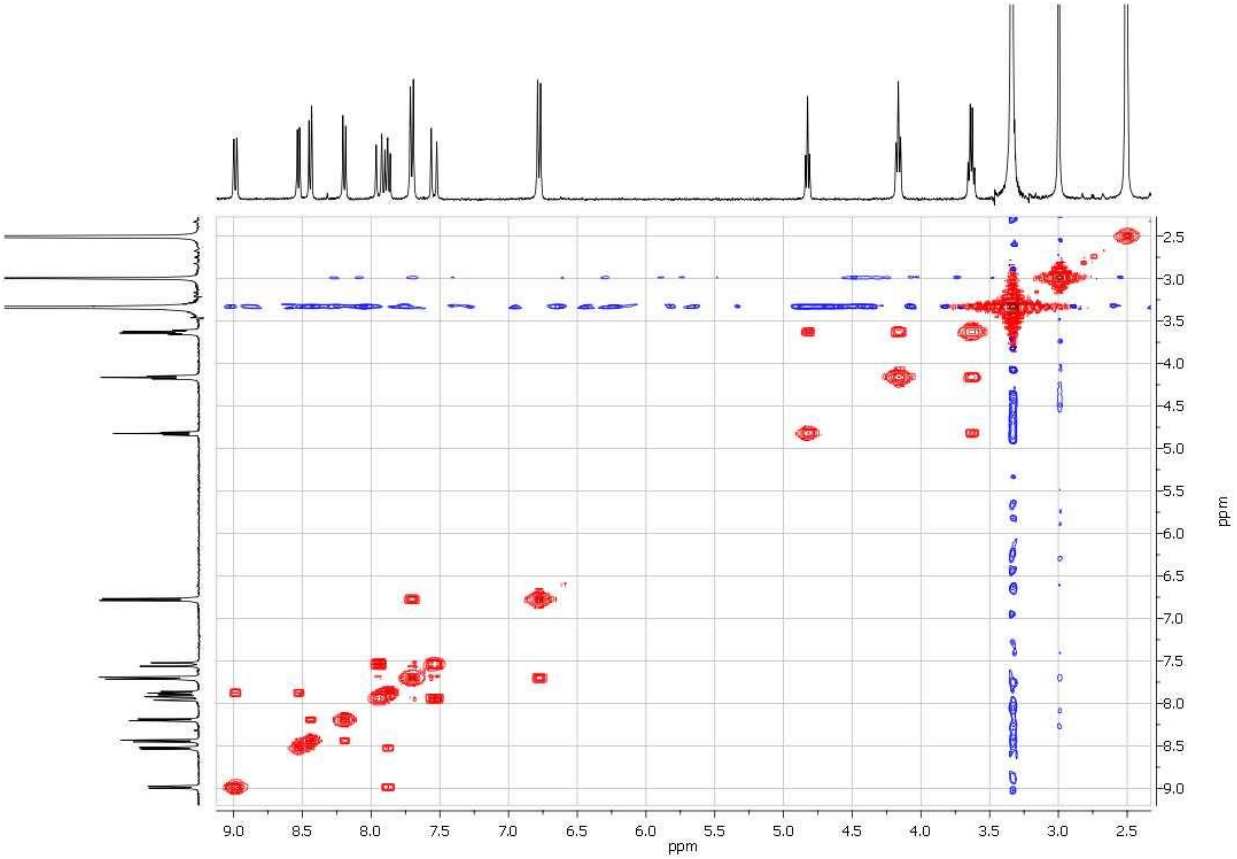


Fig.S1. COSY spectrum of compound **NI3** in DMSO-d_6.

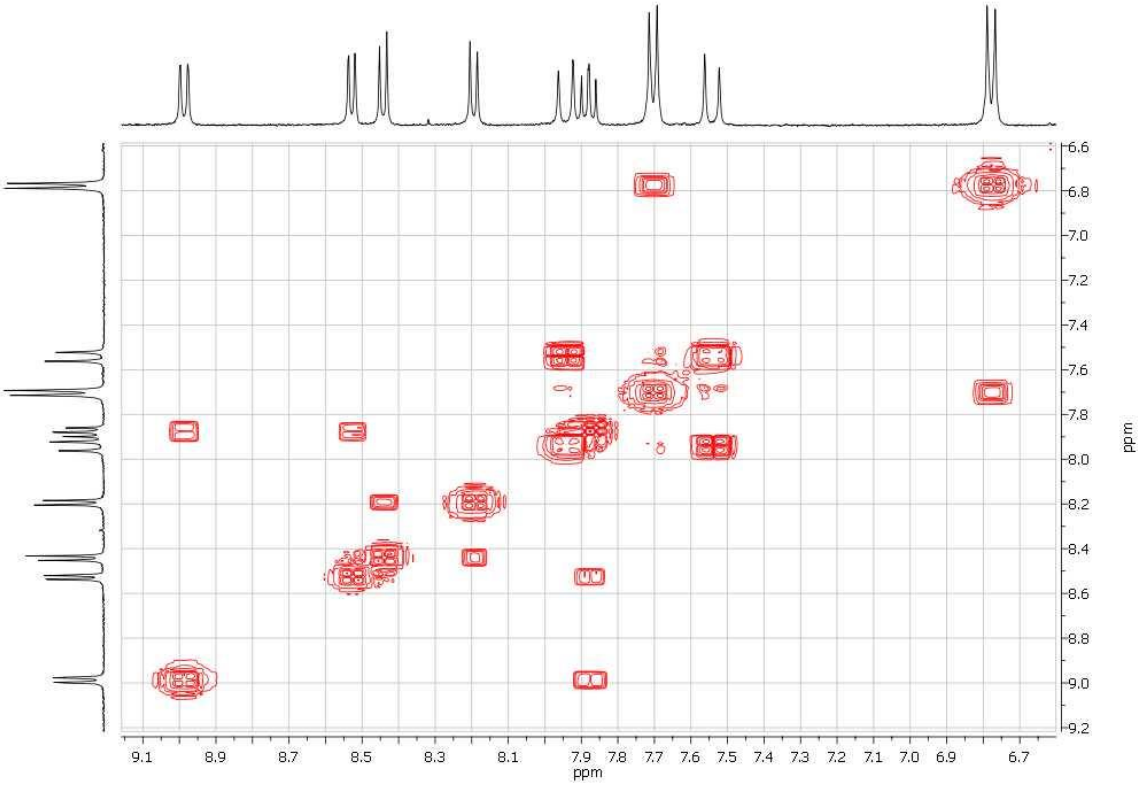


Fig.S2. Aromatic part of COSY spectrum of compound **NI3** in DMSO-d_6.

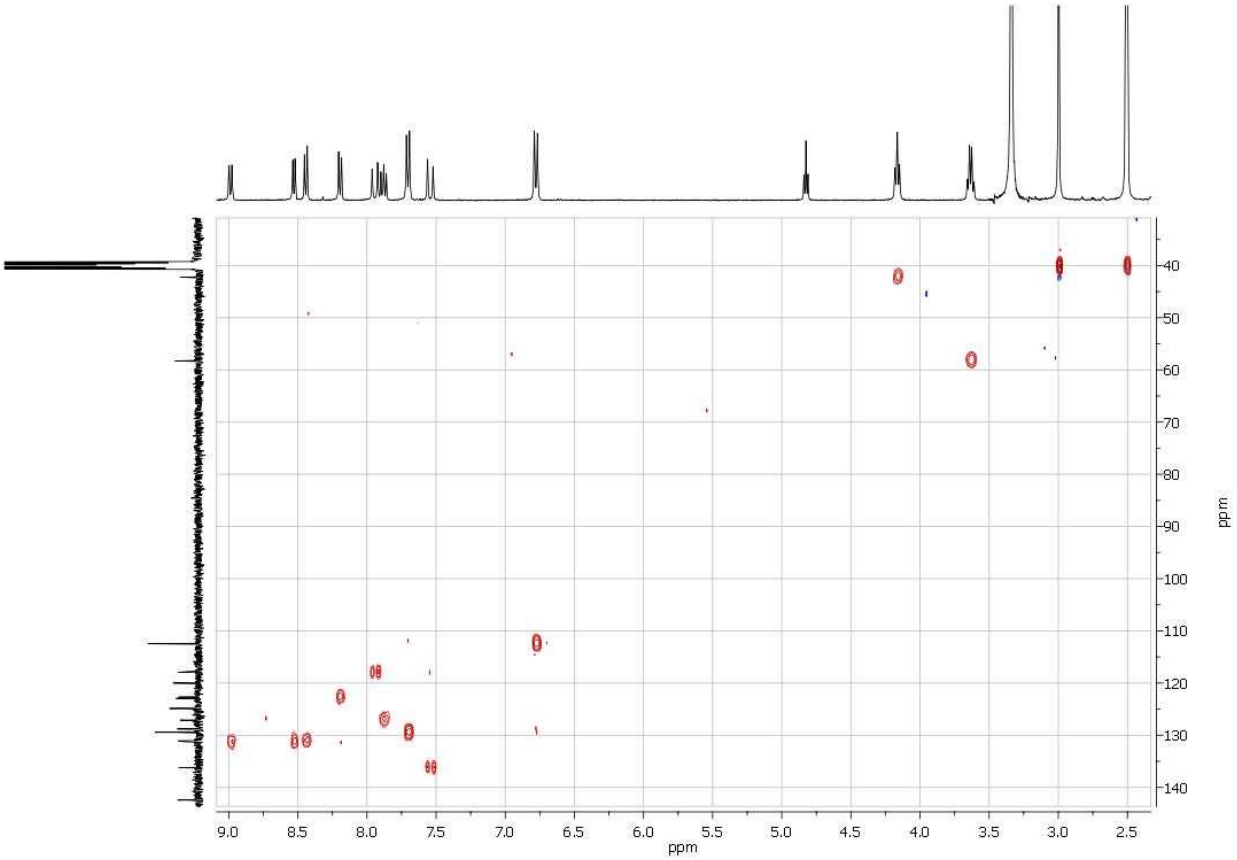


Fig.S3. HSQC spectrum of compound **NI3** in DMSO-d_6.

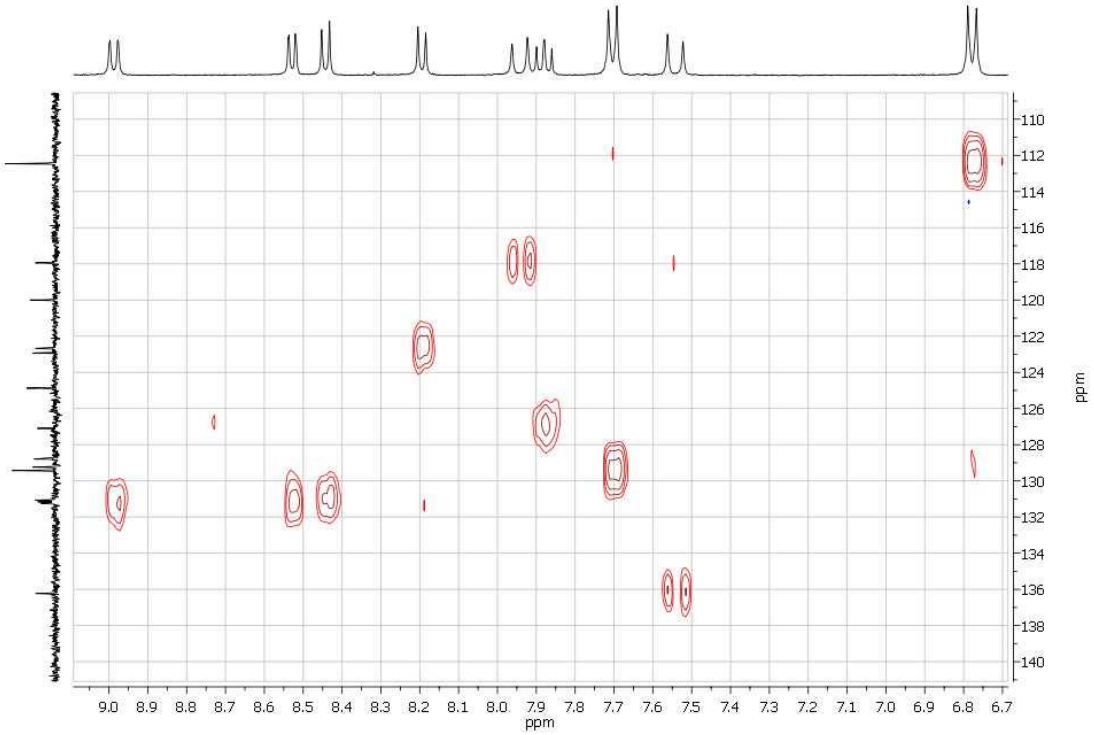


Fig.S4. Aromatic part of HSQC spectrum of compound **NI3** in DMSO-d_6.

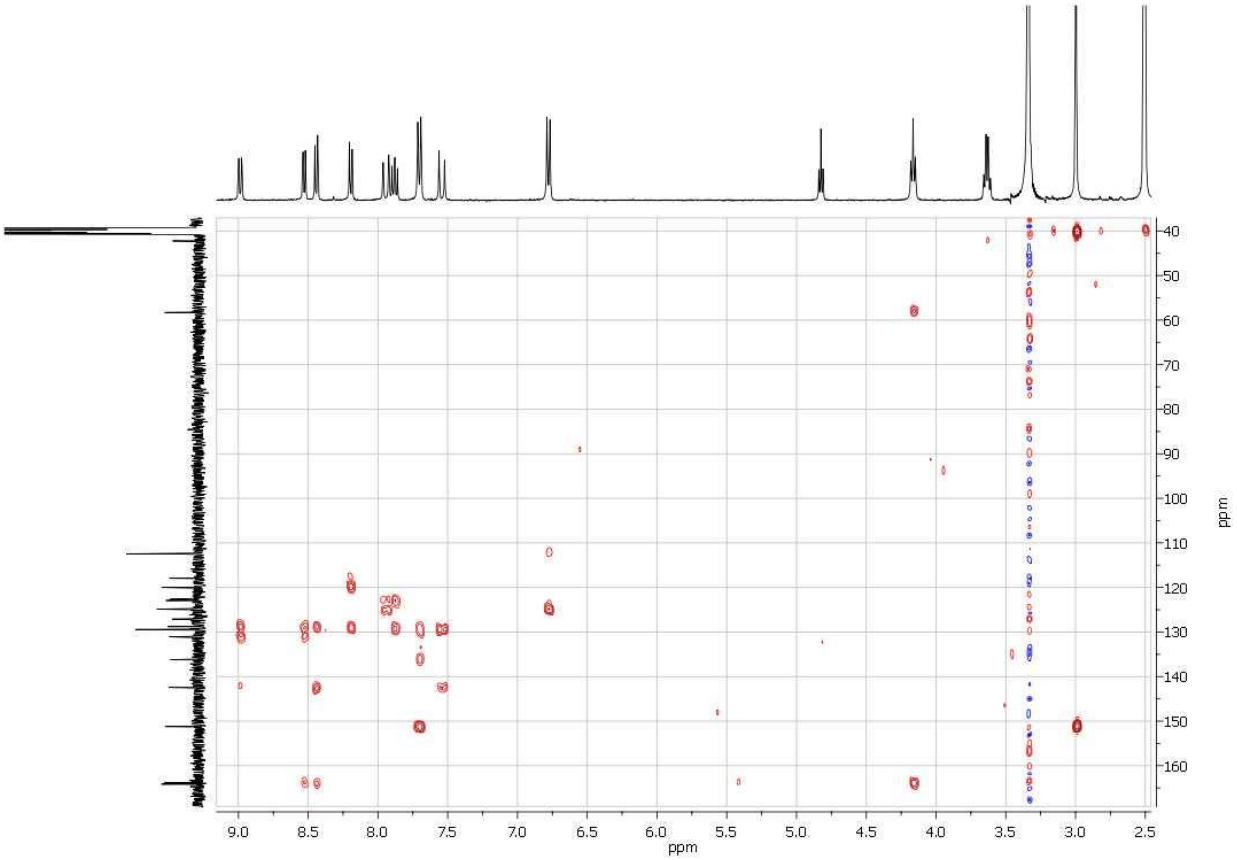


Fig.S5. HMBC spectrum of compound **NI3** in DMSO-d_6.

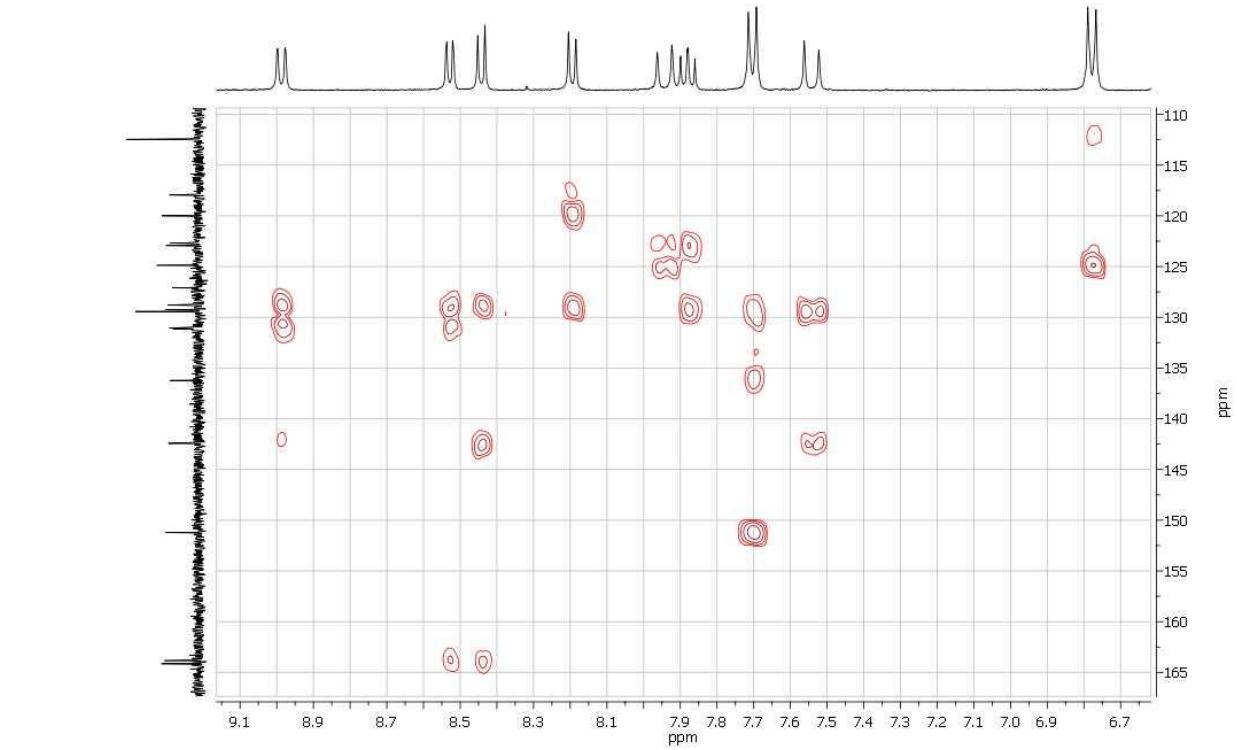


Fig.S6. Aromatic part of HMBC spectrum of compound **NI3** in DMSO-d_6.

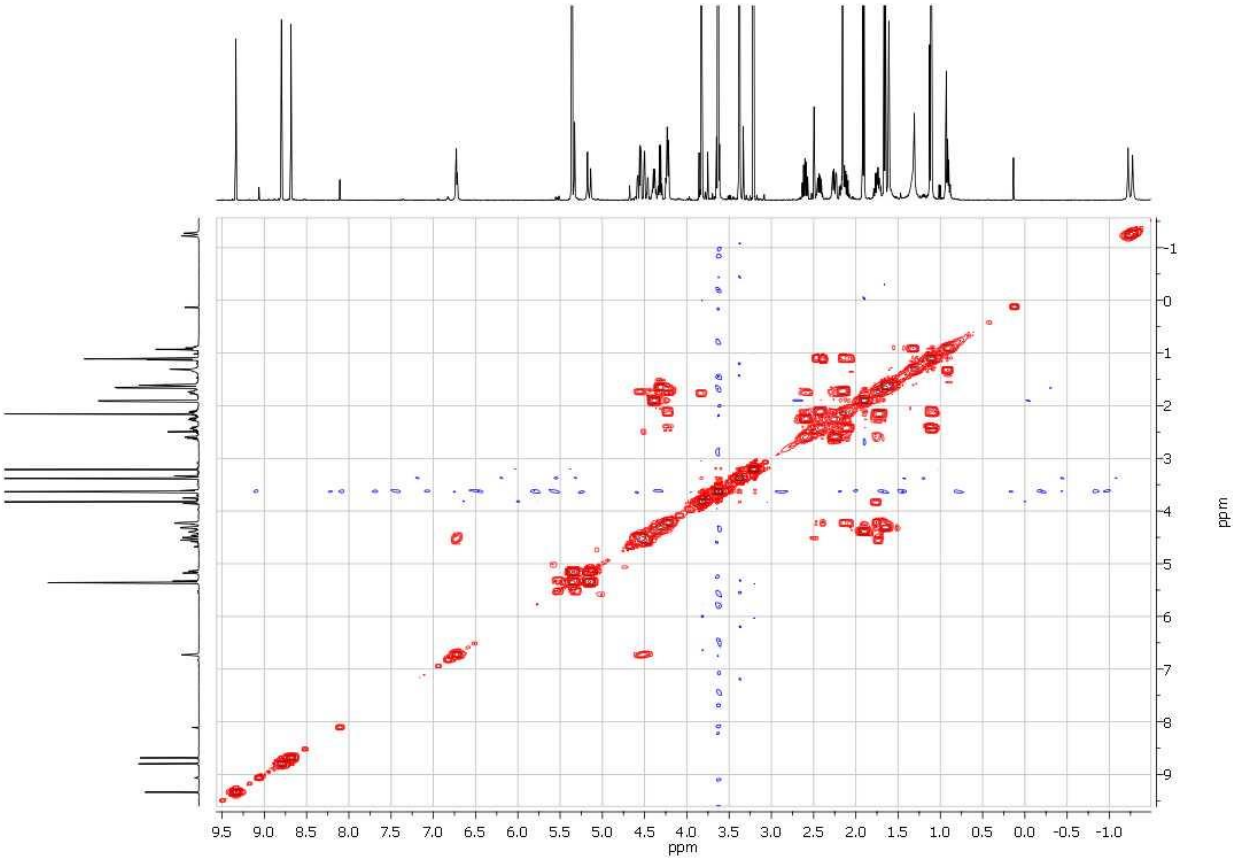


Fig.S7. COSY spectrum of compound **BChl** in CD_2Cl_2.

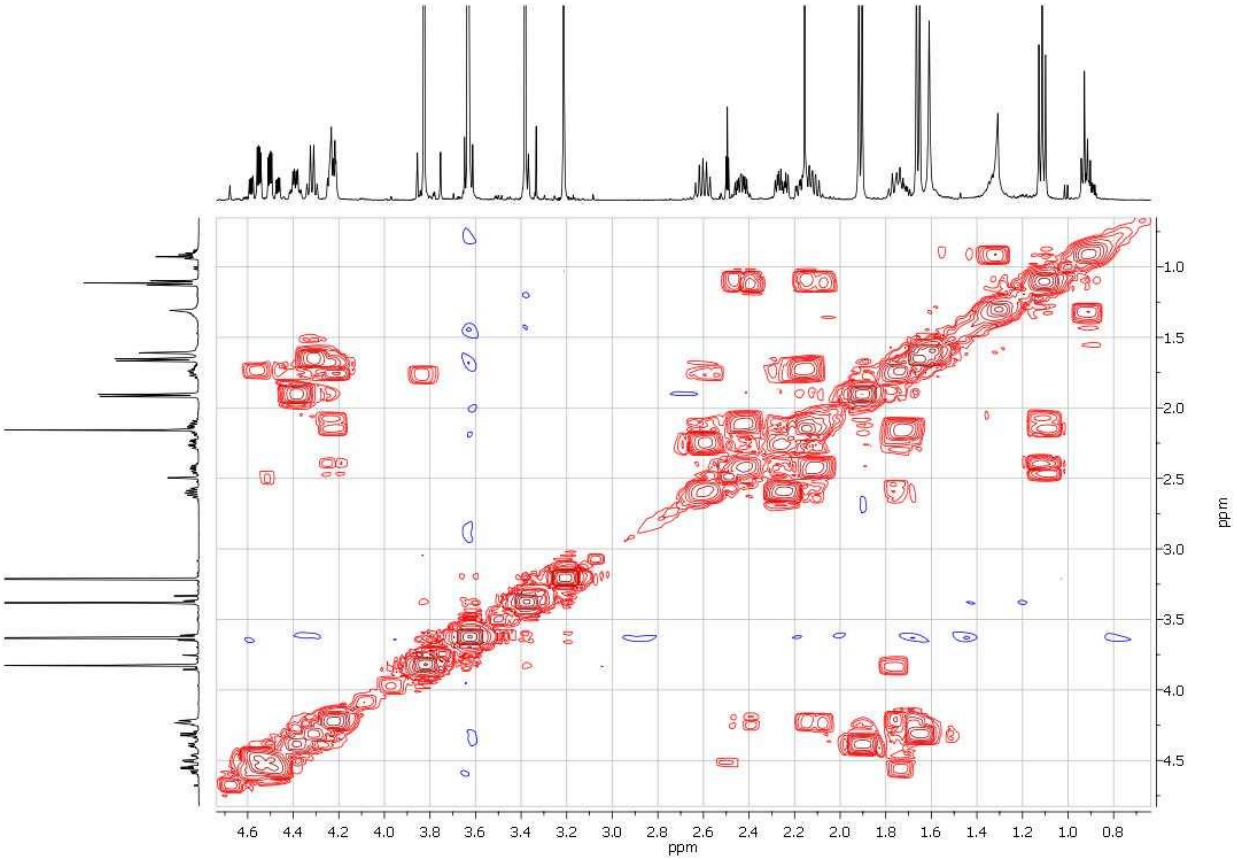


Fig.S8. Aliphatic part of COSY spectrum of compound **BChl** in CD_2Cl_2.

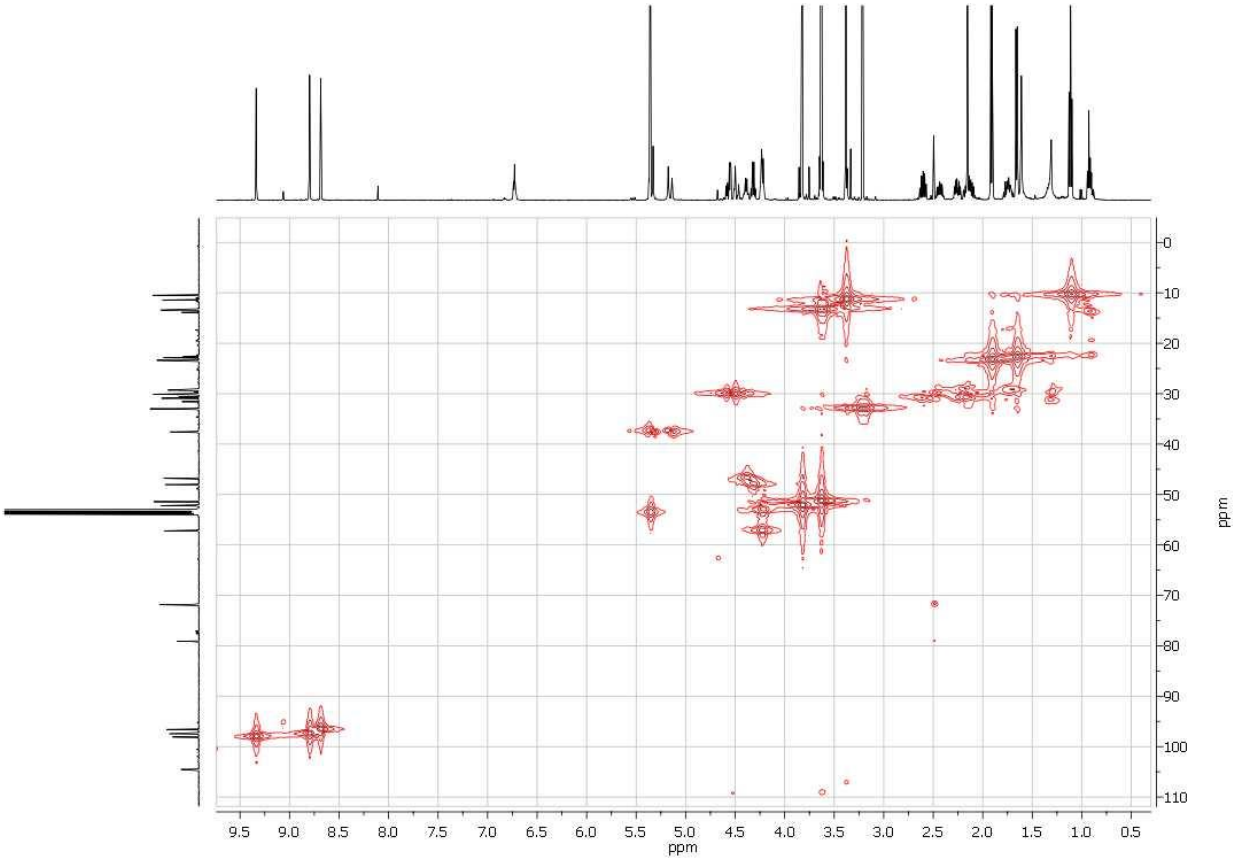


Fig.S9. HSQC spectrum of compound **BChl** in CD_2Cl_2.

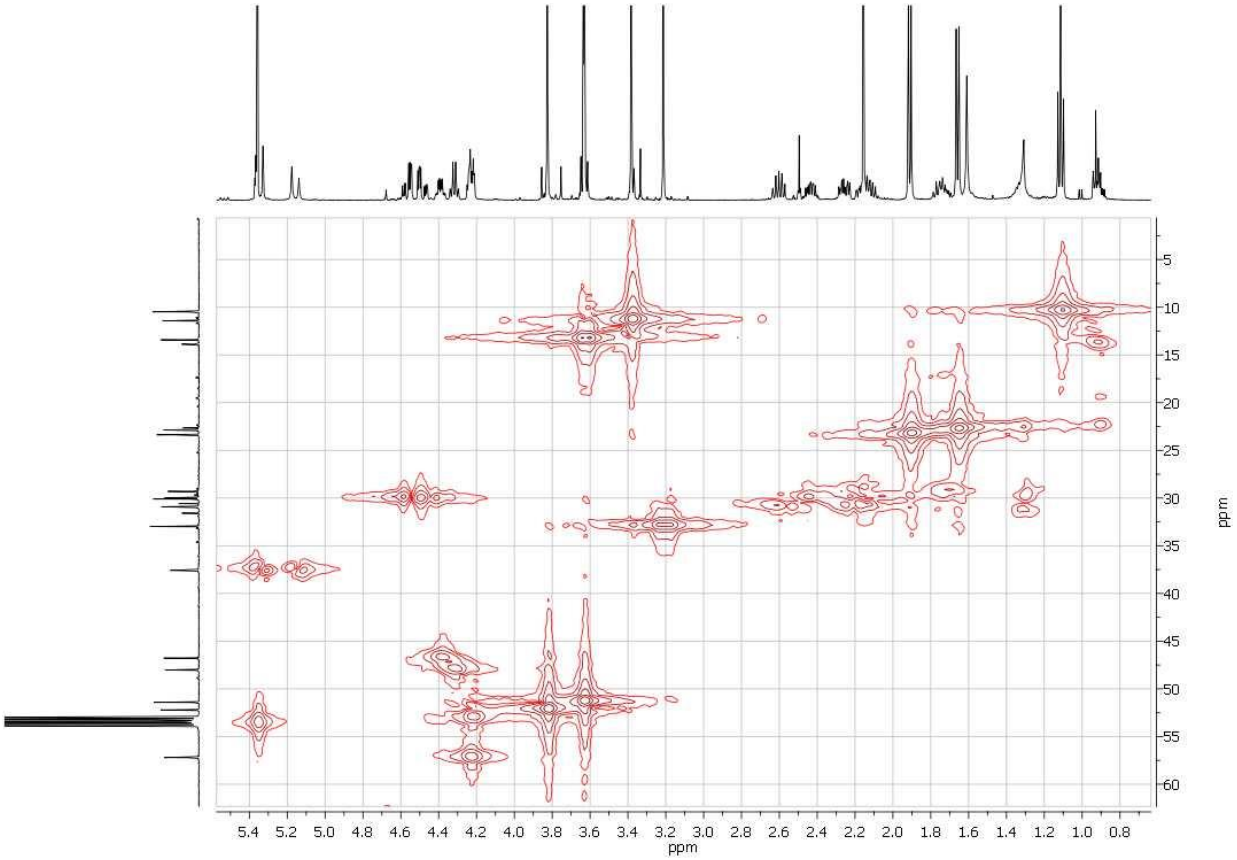


Fig.S10. Aliphatic part of HSQC spectrum of compound **BChl** in CD_2Cl_2.

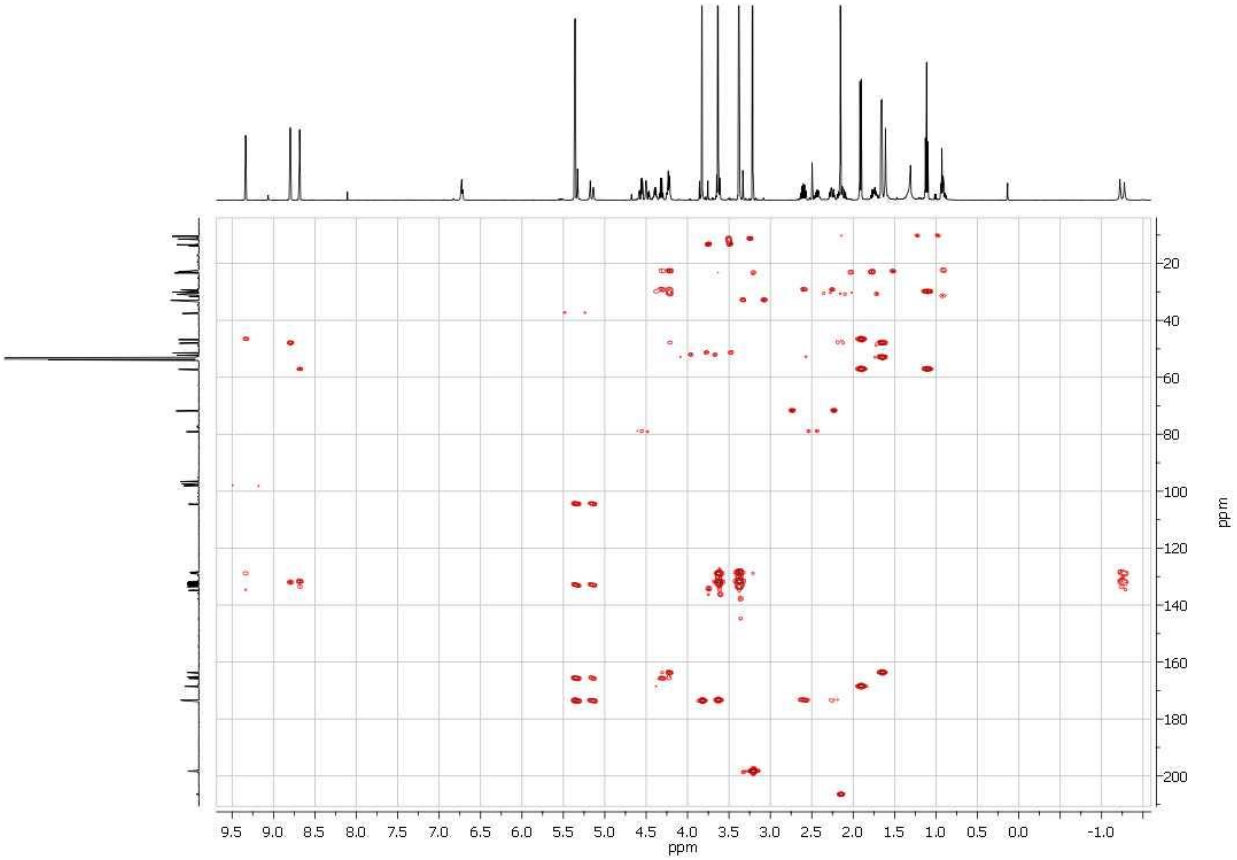


Fig.S11. HMBC spectrum of compound **BChl** in CD_2Cl_2.

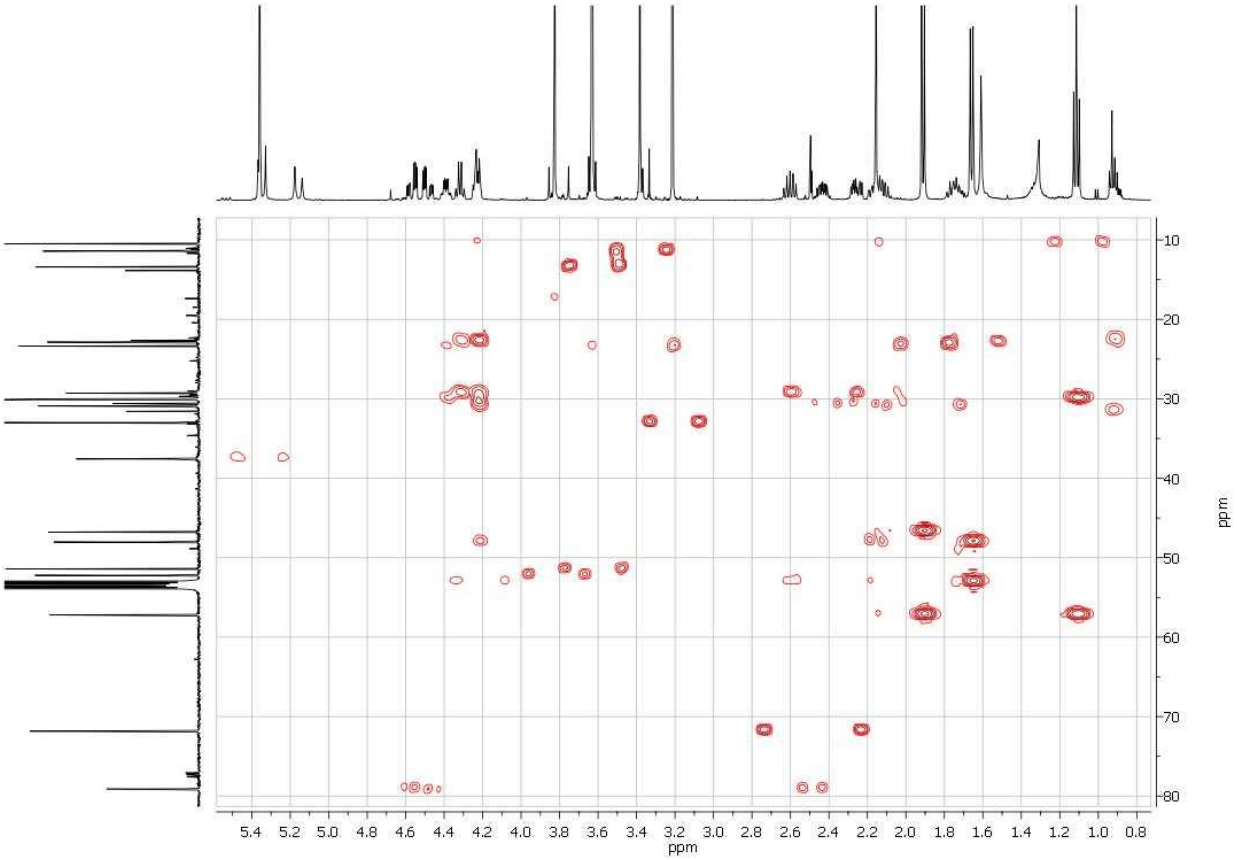


Fig.S12. Aliphatic part of HMBC spectrum of compound **BChl** in CD_2Cl_2.

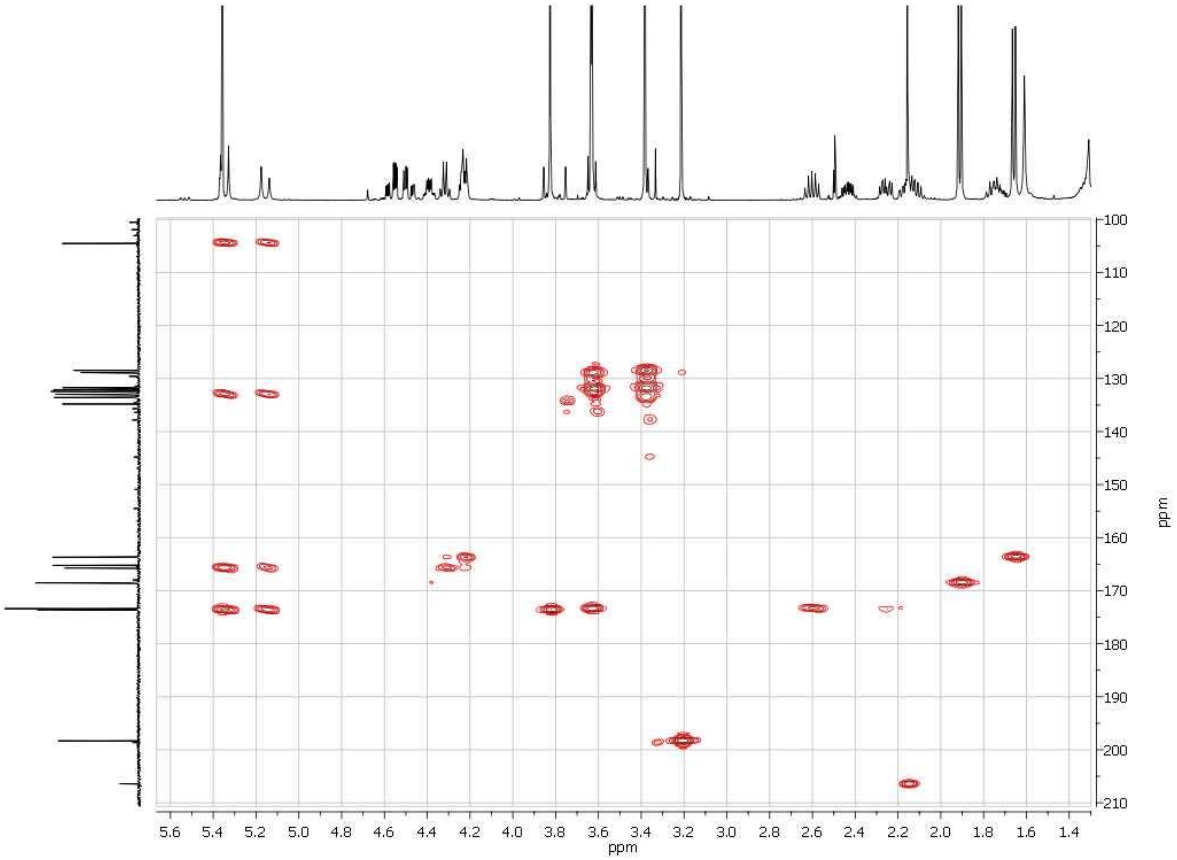


Fig.S13. Aliphatic part of HMBC spectrum of compound **BChl** in CD_2Cl_2.

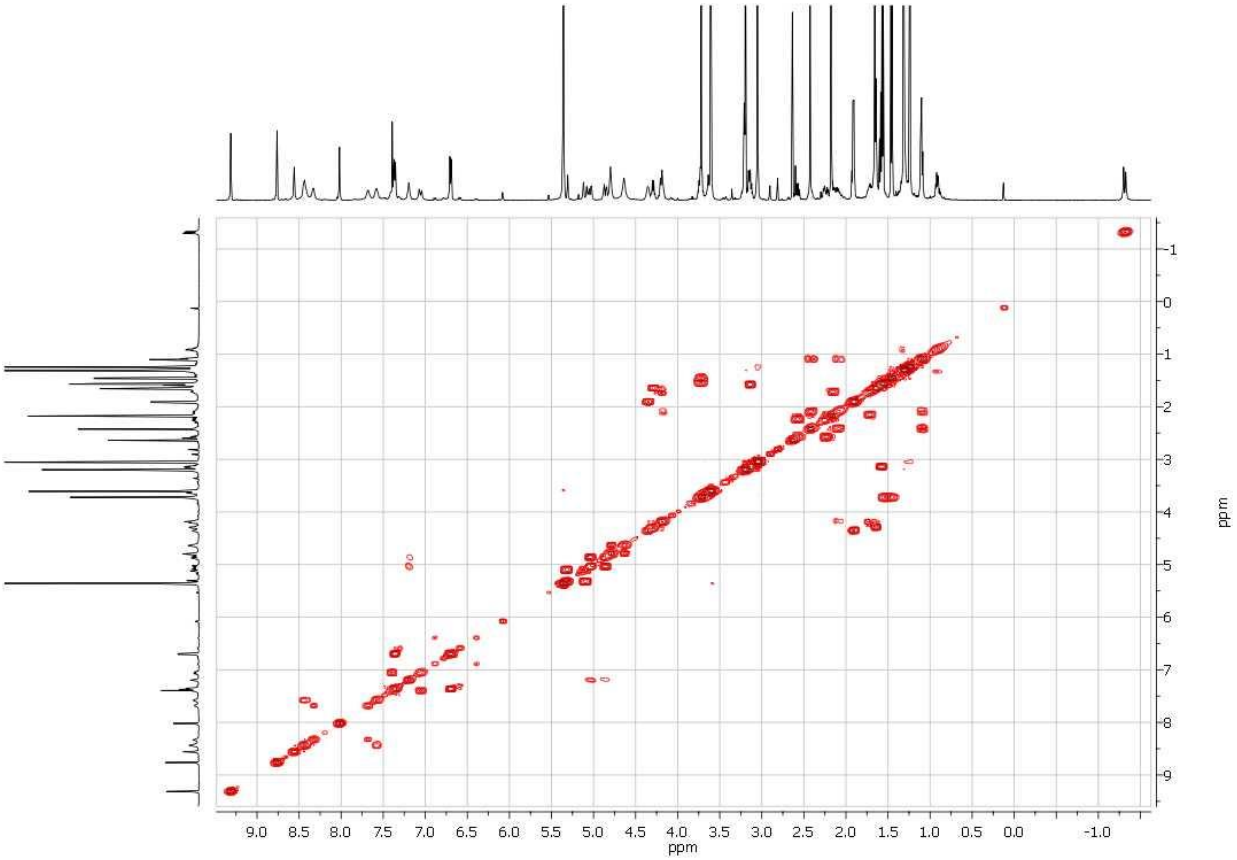


Fig.S14. COSY spectrum of compound **BChl-NI** in CD_2Cl_2.

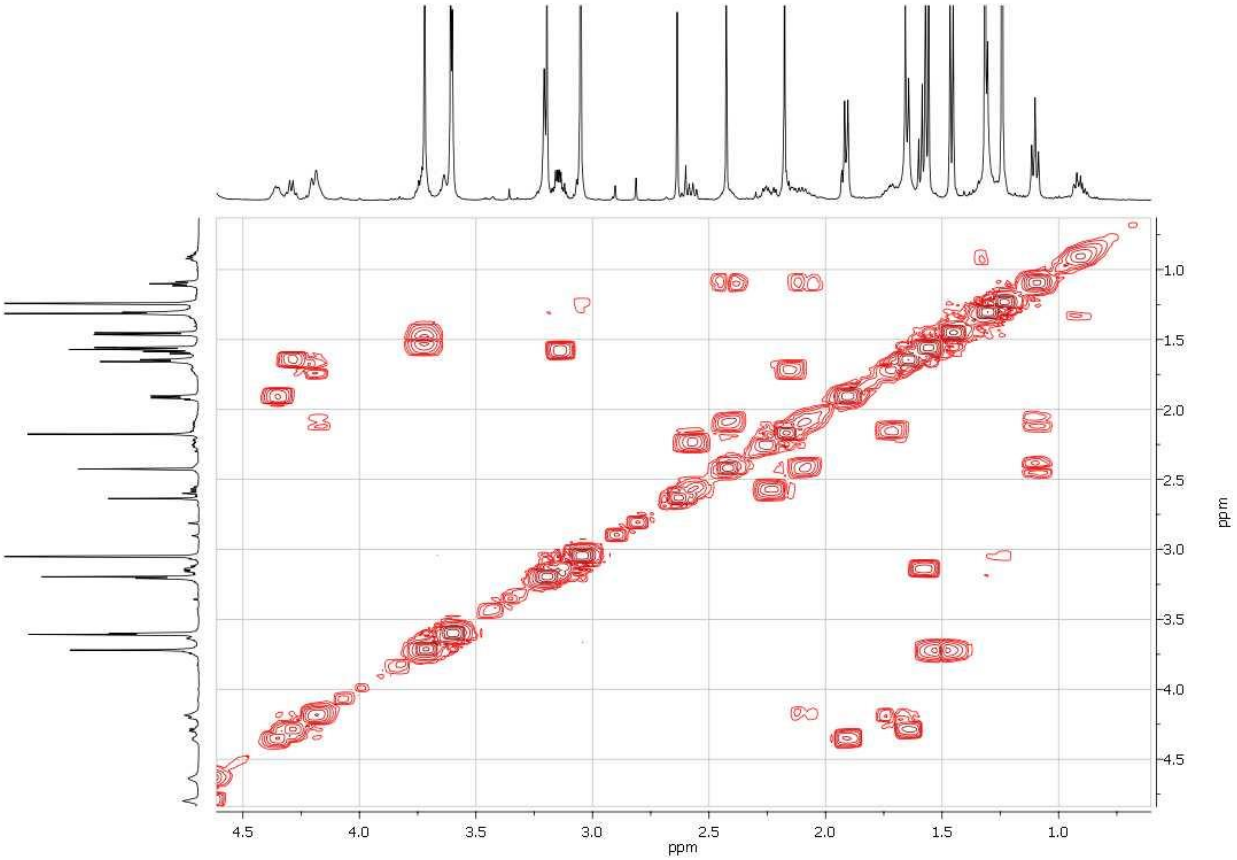


Fig.S15. Aliphatic part of COSY spectrum of compound **BChl-NI** in CD_2Cl_2.

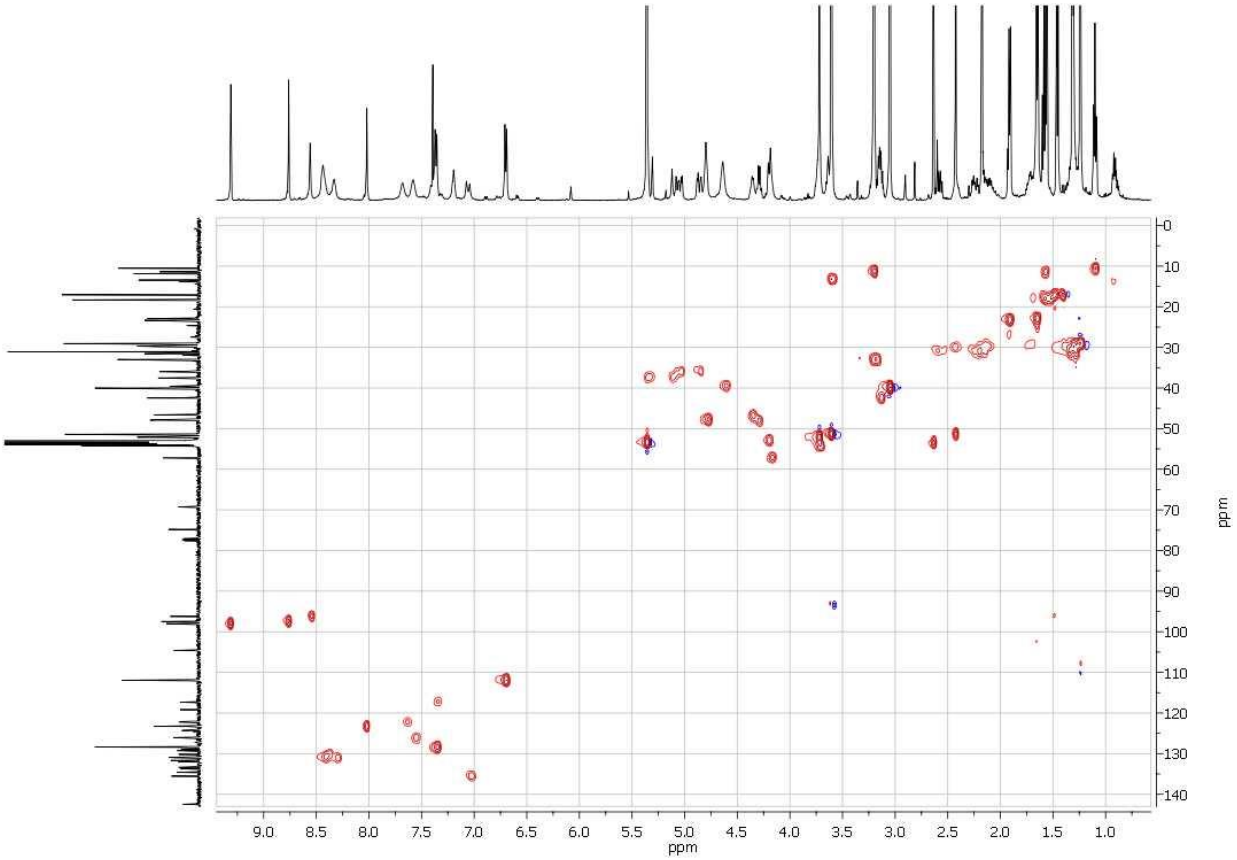


Fig.S16. HSQC spectrum of compound **BChl-NI** in CD_2Cl_2.

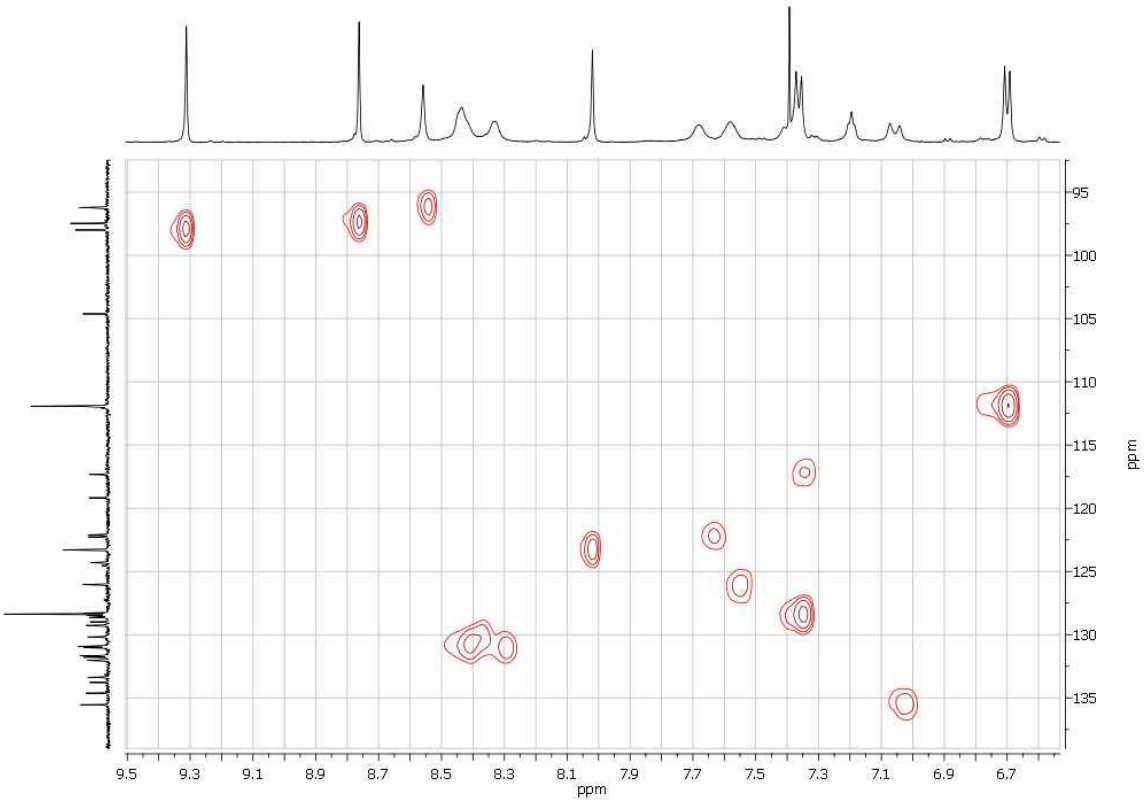


Fig.S17. Aromatic part of HSQC spectrum of compound **BChl-NI** in CD_2Cl_2.

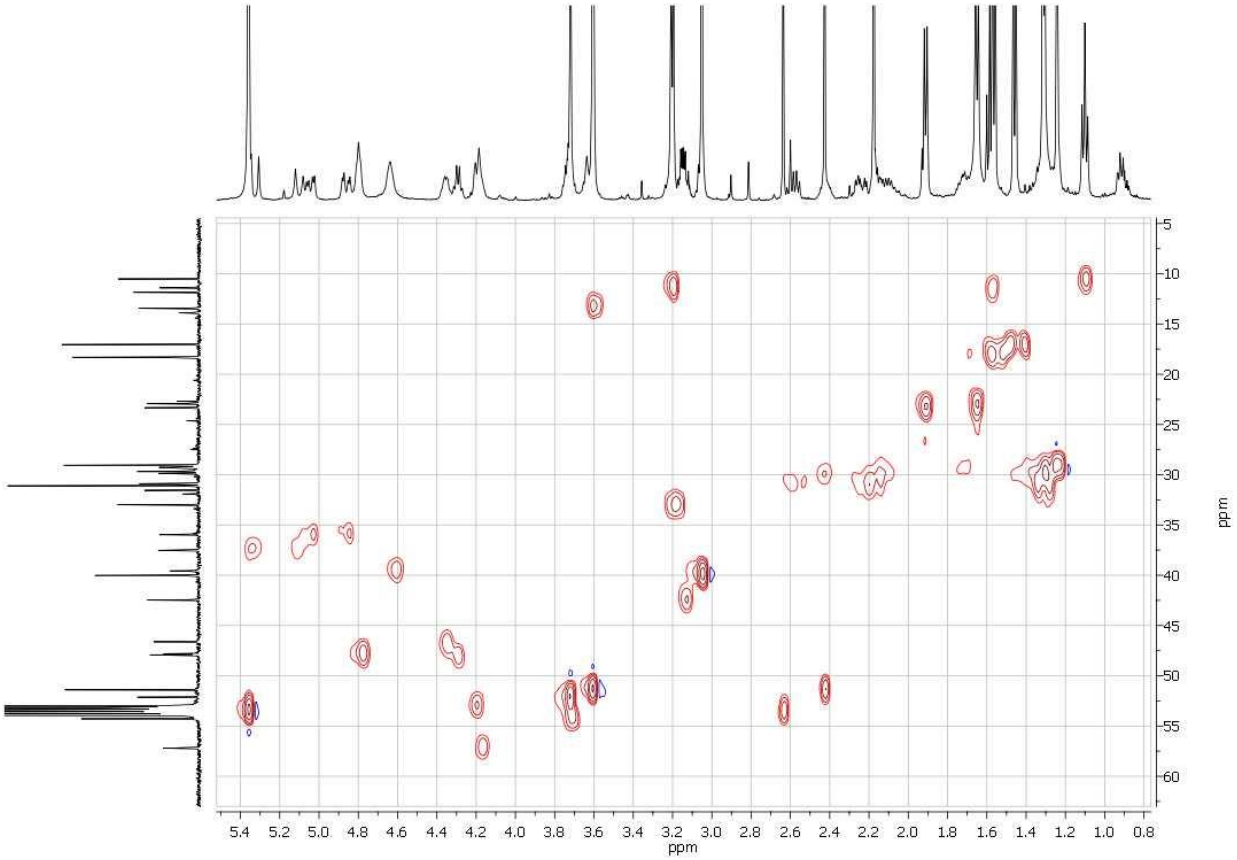


Fig.S18. Aliphatic part of HSQC spectrum of compound **BChl-NI** in CD_2Cl_2.

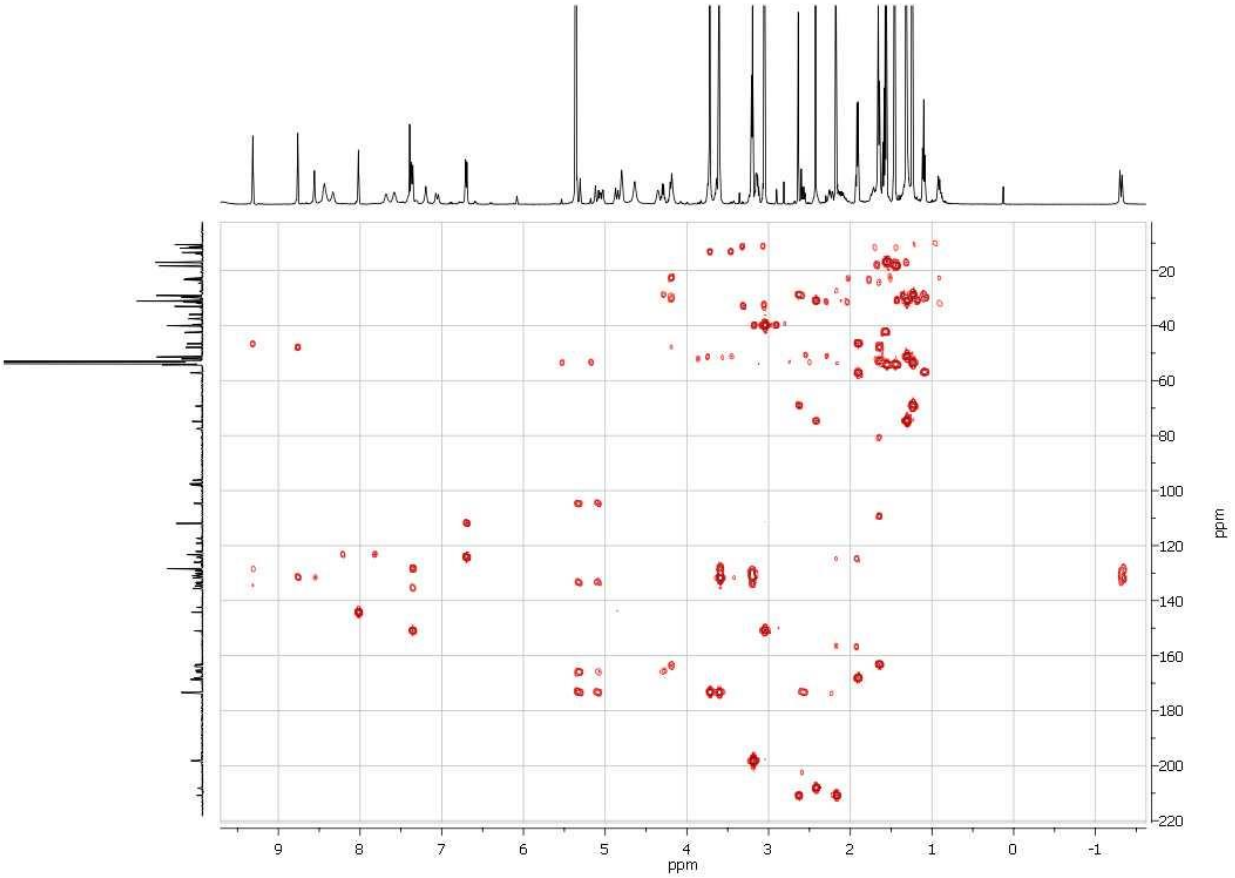


Fig.S19. HMBC spectrum of compound **BChl-NI** in CD_2Cl_2.

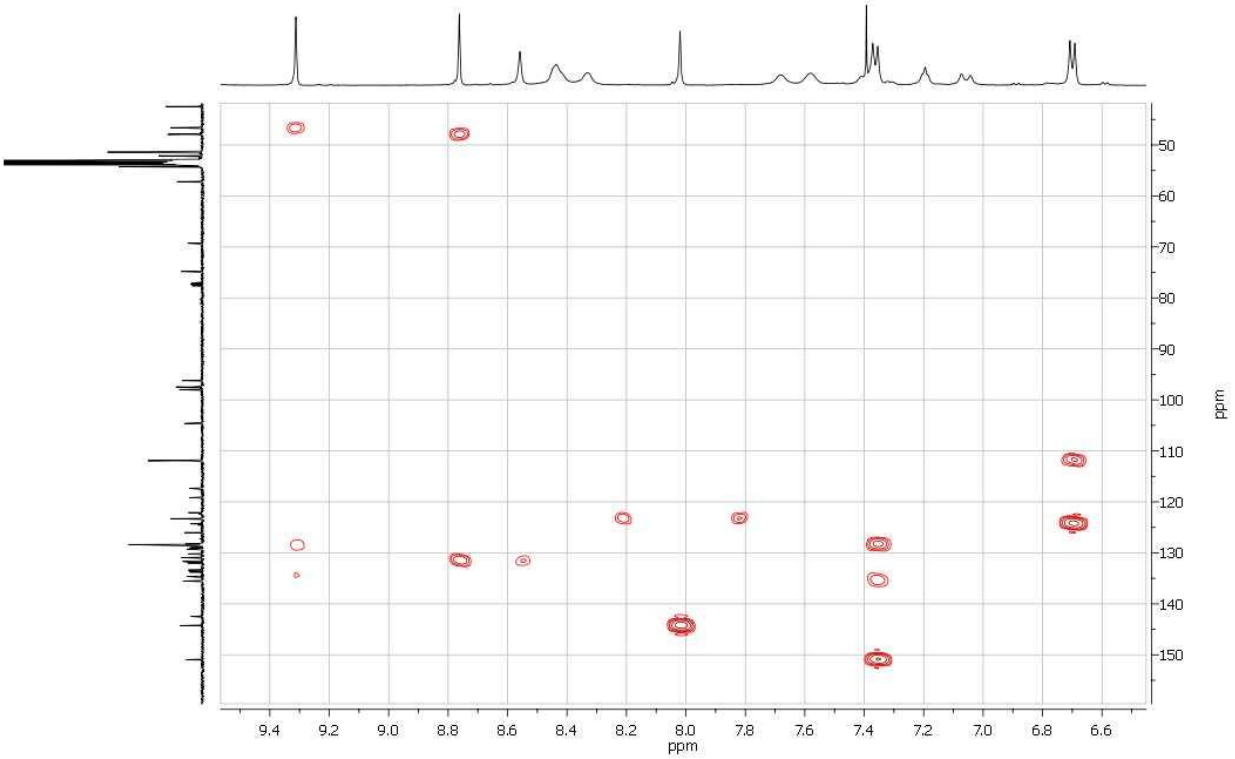


Fig.S20. Aromatic part of HMBC spectrum of compound **BChl-NI** in CD_2Cl_2.

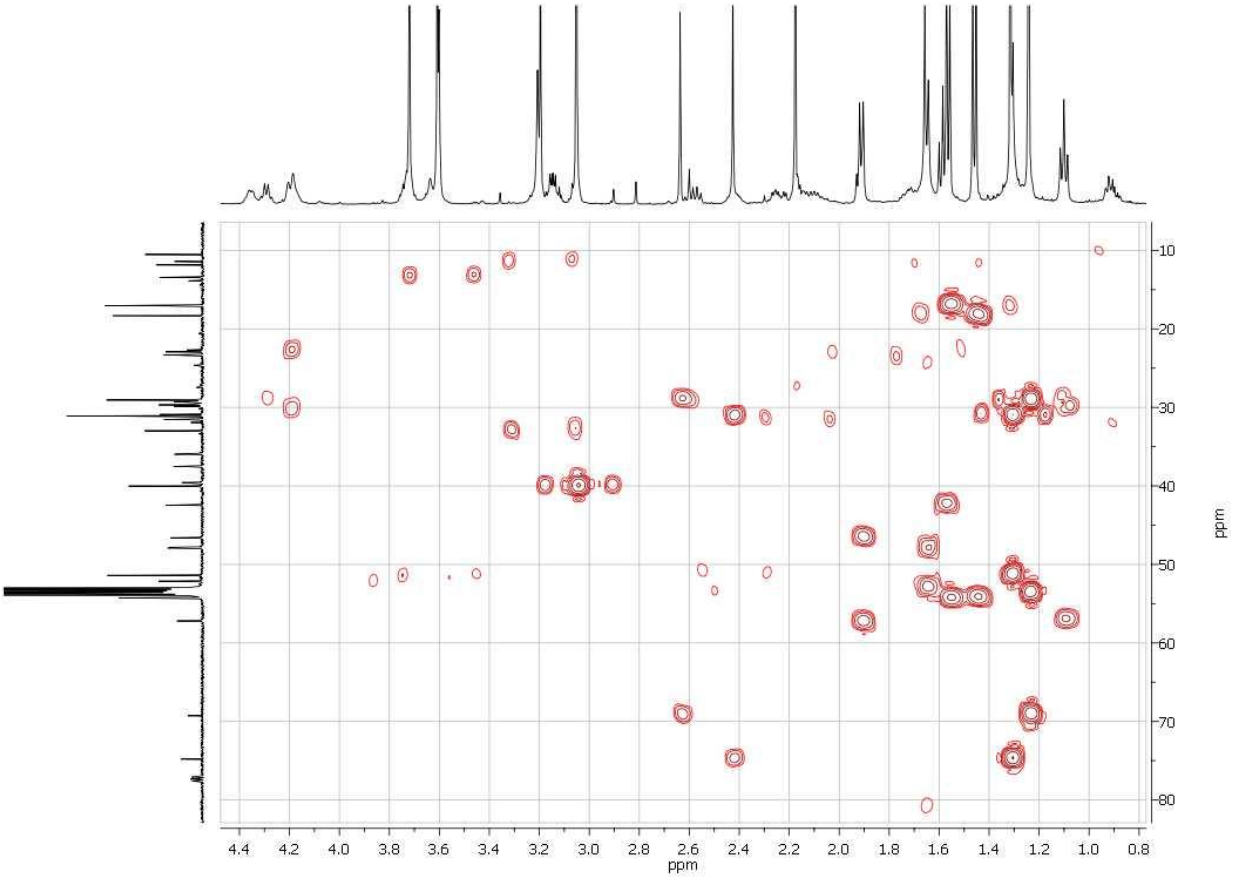


Fig.S21. Aliphatic part of HMBC spectrum of compound **BChl-NI** in CD_2Cl_2.

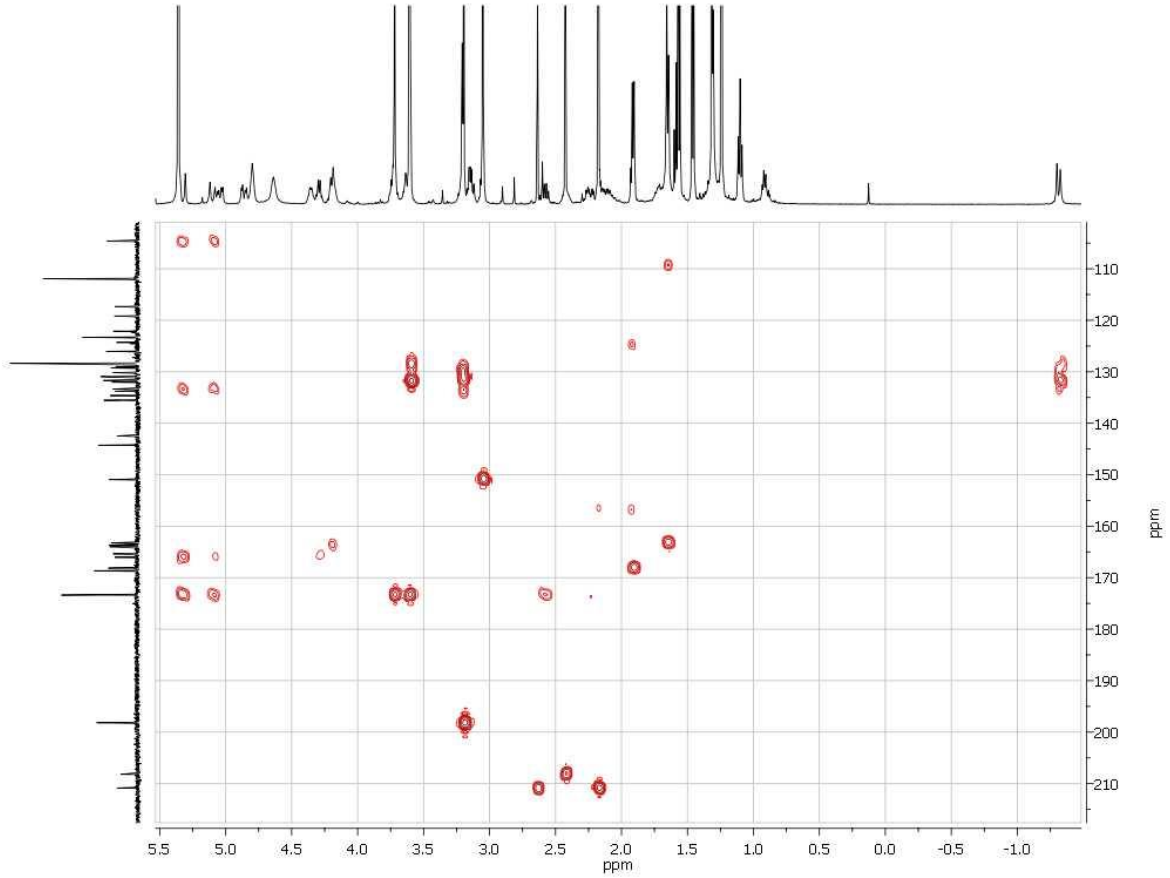


Fig.S22. Aliphatic part of HMBC spectrum of compound **BChl-NI** in CD_2Cl_2.

3. Evaluation of Different Parameters for RET process

Energy transfer efficiency value Φ_{RET1} for the conjugate **BChl-NI** was calculated using the expression shown in Eq. (S1),

$$\Phi_{RET1} = \frac{k_{RET1}}{k_{RET1} + \tau_{D,0}^{-1}} \quad \text{(S1)}$$

where $\tau_{D,0}$ is the 4-styrylnaphthalimide donor chromophore excited state lifetime in the absence of RET acceptor ($\tau_{D,0}$ = 0.38 ns, the lifetime of **NI4**), and k_{RET1} – energy transfer rate constant. According to Förster resonance theory, estimation of k_{RET1} was done following Eq. (S2),

$$k_{RET1} = \frac{1}{\tau_{D,0}}\left(\frac{R_0}{r}\right)^6 \quad \text{(S2)}$$

where r is the distance between the donor and acceptor chromophores (15.06 Å) which was obtained from the PM6 optimized ground state geometry of **BChl-NI** (Fig.S23), and R_0 is the critical Förster distance. To calculate R_0 we used Eq. (S3),

$$R_0^6 = \frac{9000 \ln 10\, \kappa^2 \varphi^{fl}}{128\, \pi^2 N_A n^4} \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda \quad \text{(S3)}$$

where κ^2 denotes a factor which describes the relative orientations of the donor and acceptor (κ^2 = 2/3 for a random orientation), φ^{fl} is the donor emission quantum yield in the absence of the acceptor (the quantum yield of compound **NI4**, φ^{fl} = 0.032), n is the refractive index of the medium (n = 1.344 for acetonitrile), N_A is Avogadro constant ($N_A = 6.02 \cdot 10^{23}$ mol^{-1}) and the integral defines the amount of overlap between the normalized emission spectrum of the donor $F_D(\lambda)$ and the acceptor absorption spectrum $\varepsilon_A(\lambda)$.

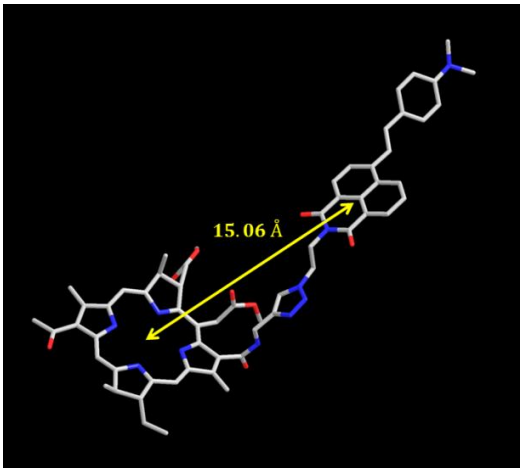


Fig.S23. Optimized ground state geometry of **BChl-NI** obtained by MOPAC 2012 using PM6 Hamiltonian. The solvent effect was included in geometry optimizations following the «COnductorlike Screening Model» (COSMO) implemented in MOPAC 2012. A dielectric constant of ε = 20 and a refraction index of solvent (n) such that n^2 = 2 were used.

4. Changes in the absorption spectra of mixed solutions containing BChl, NI3 and DPBF

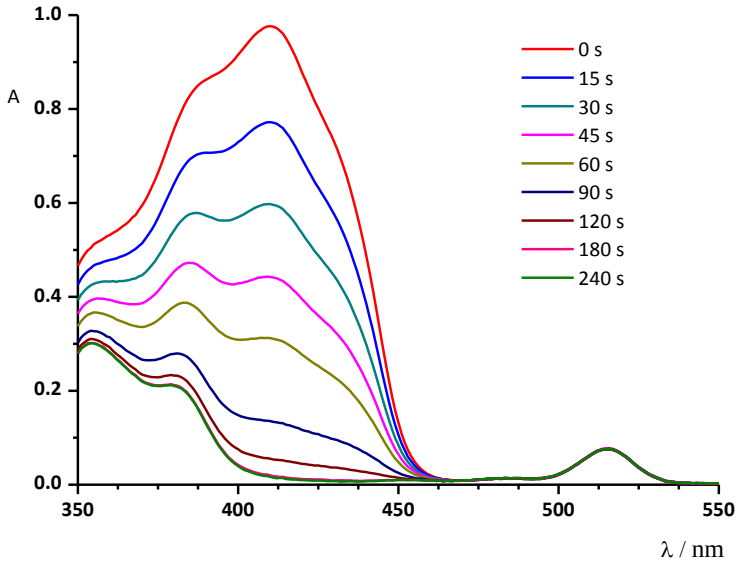


Fig.S24. Changes in the UV/Vis absorption spectrum of a mixed solution containing the conjugate **BChl** ($3.8 \cdot 10^{-6}$ M) and DPBF ($4.0 \cdot 10^{-5}$ M) in acetone upon irradiation at 510 nm.

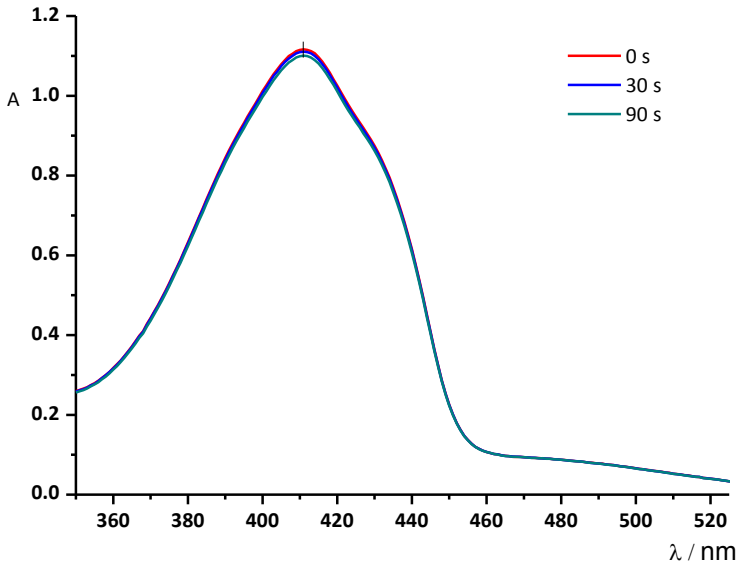


Fig.S25. Changes in the UV/Vis absorption spectrum of a mixed solution containing the compound **NI3** ($5.2 \cdot 10^{-6}$ M) and DPBF ($4.0 \cdot 10^{-5}$ M) in acetone upon irradiation at 490 nm.

5. Steady-state spectra of the conjugate and individual chromophores in rabbit blood serum

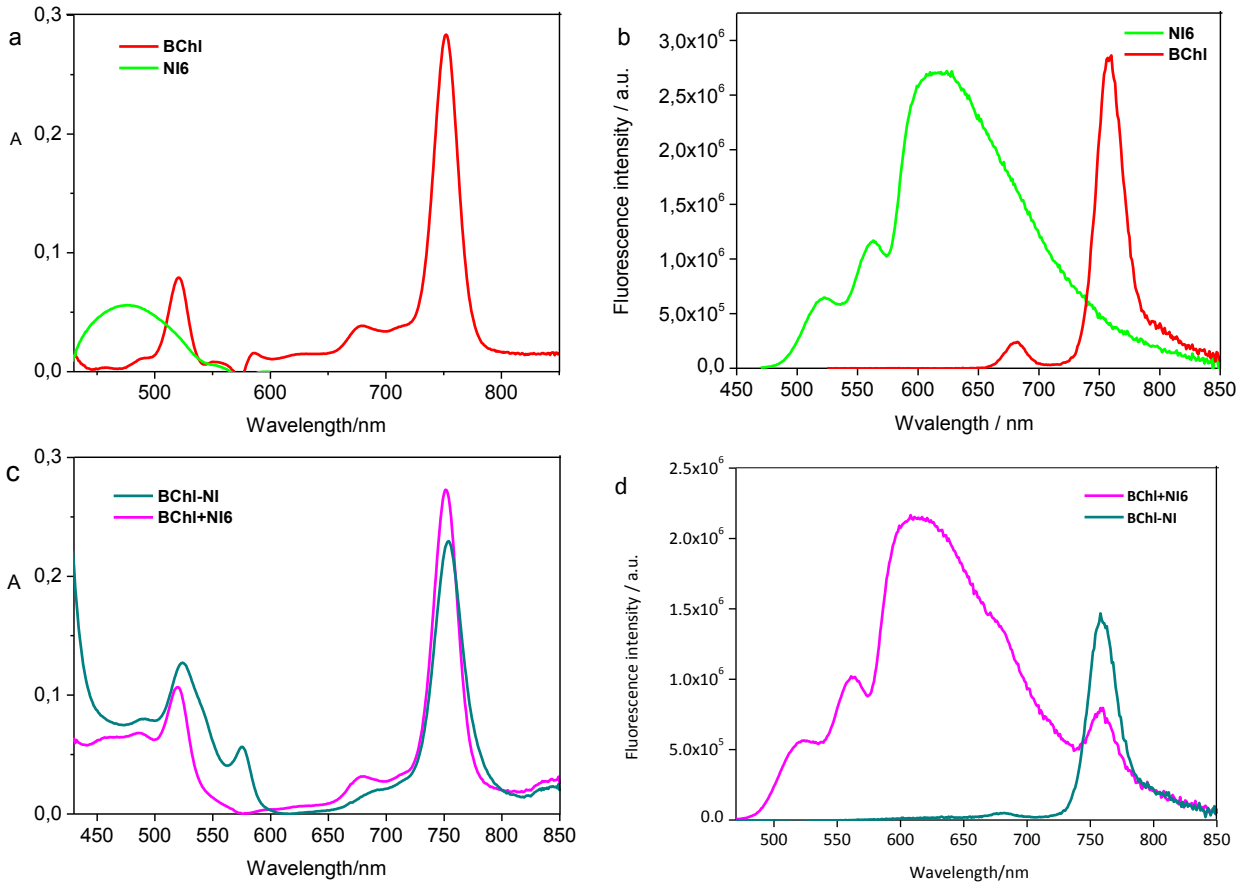


Fig.S26. UV/Vis absorption (a,c) and fluorescence emission (b, d) spectra of compounds **BChl**, **NI6**, **BChl-NI** and equimolar mixture of **BChl** and **NI6** (denoted as «**BChl** + **NI6**») in rabbit blood serum. Excitation wavelength is 460 nm for **NI6**, **BChl-NI**, **BChl+NI6** and 515 nm for **BChl**. Concentration of all compounds – $4.7 \cdot 10^{-5}$ M.