Supplementary Information

Design and Engineering of a Dual-Mode Absorption/Emission Molecular Switch for All-Optical Encryption

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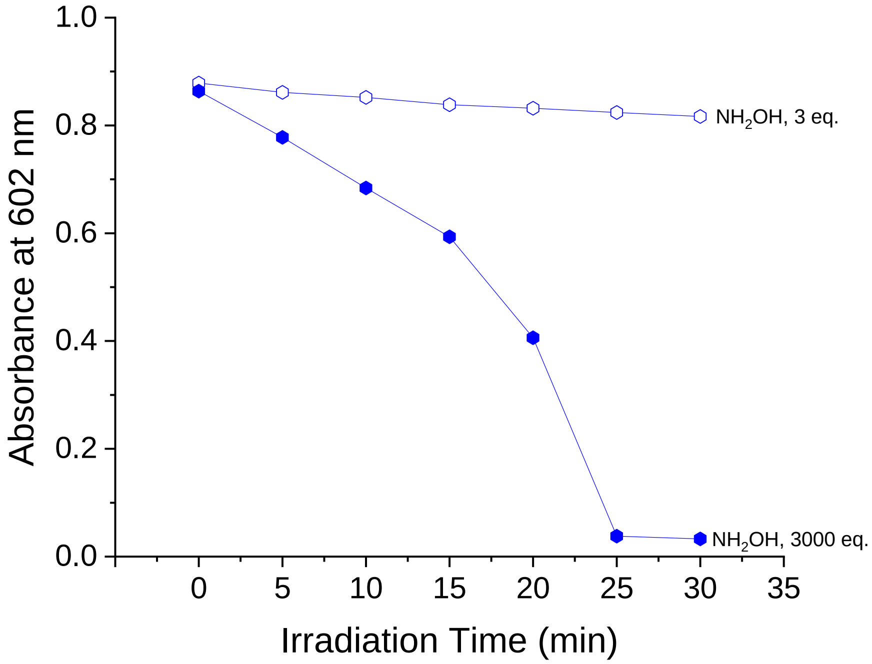

Figure S1. Evolution of the absorbance recorded at 602 nm of an aqueous solution of **RZ** (18 µM, 20 ºC) before and after irradiation at 525 nm (0 – 30 min, 5 min irradiation intervals) in the presence of 3000 (filled dots) or 3 (empty dots) equivalents of NH_2OH.

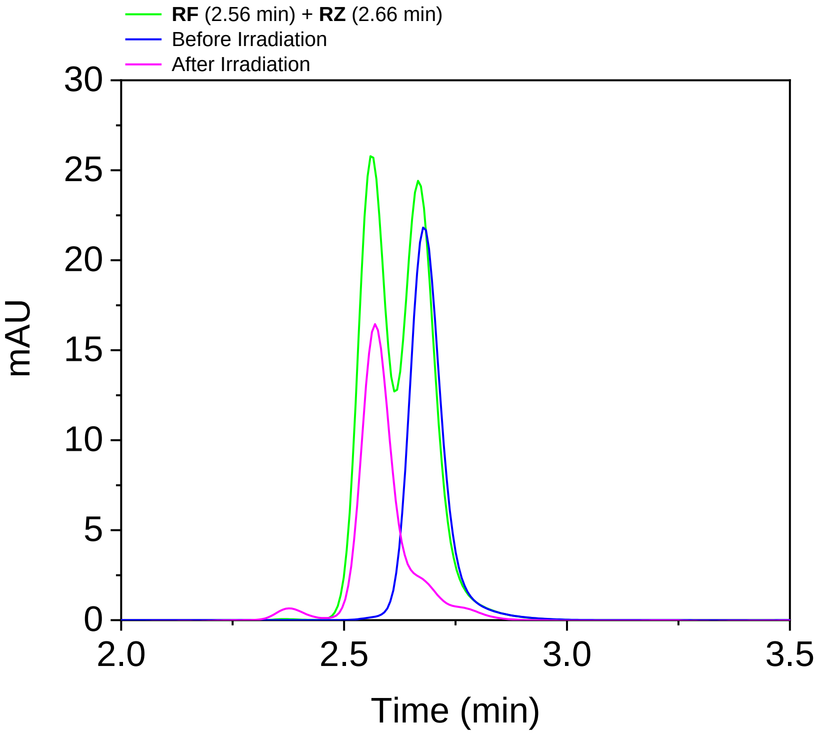

Figure S2. HPLC chromatograms of a solution of **RZ** (20 ºC, NH_2OH 3000 eq.) before (blue trace) and after (pink trace) irradiation at 525 nm. The green trace is a mixture of commercial **RZ** and **RF** standards.

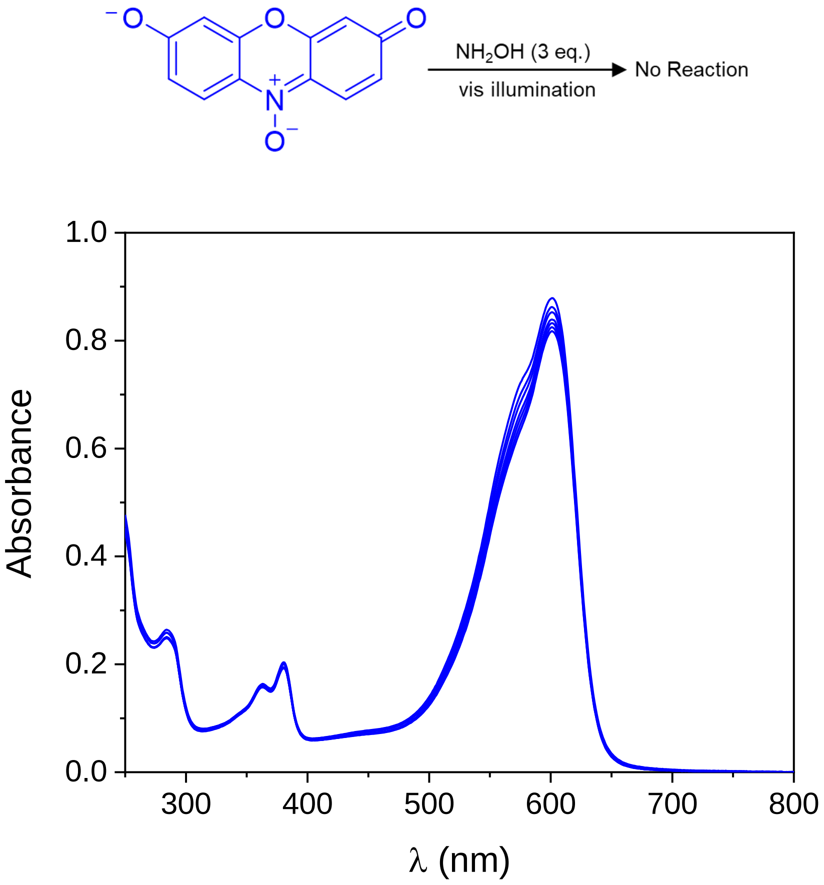

Figure S3. Absorption spectra of an aqueous solution of **RZ** (18 μM, 20 ºC, NH$_2$OH 3 eq.) before and after irradiation at 525 nm (0 – 30 min, 5 min irradiation intervals).

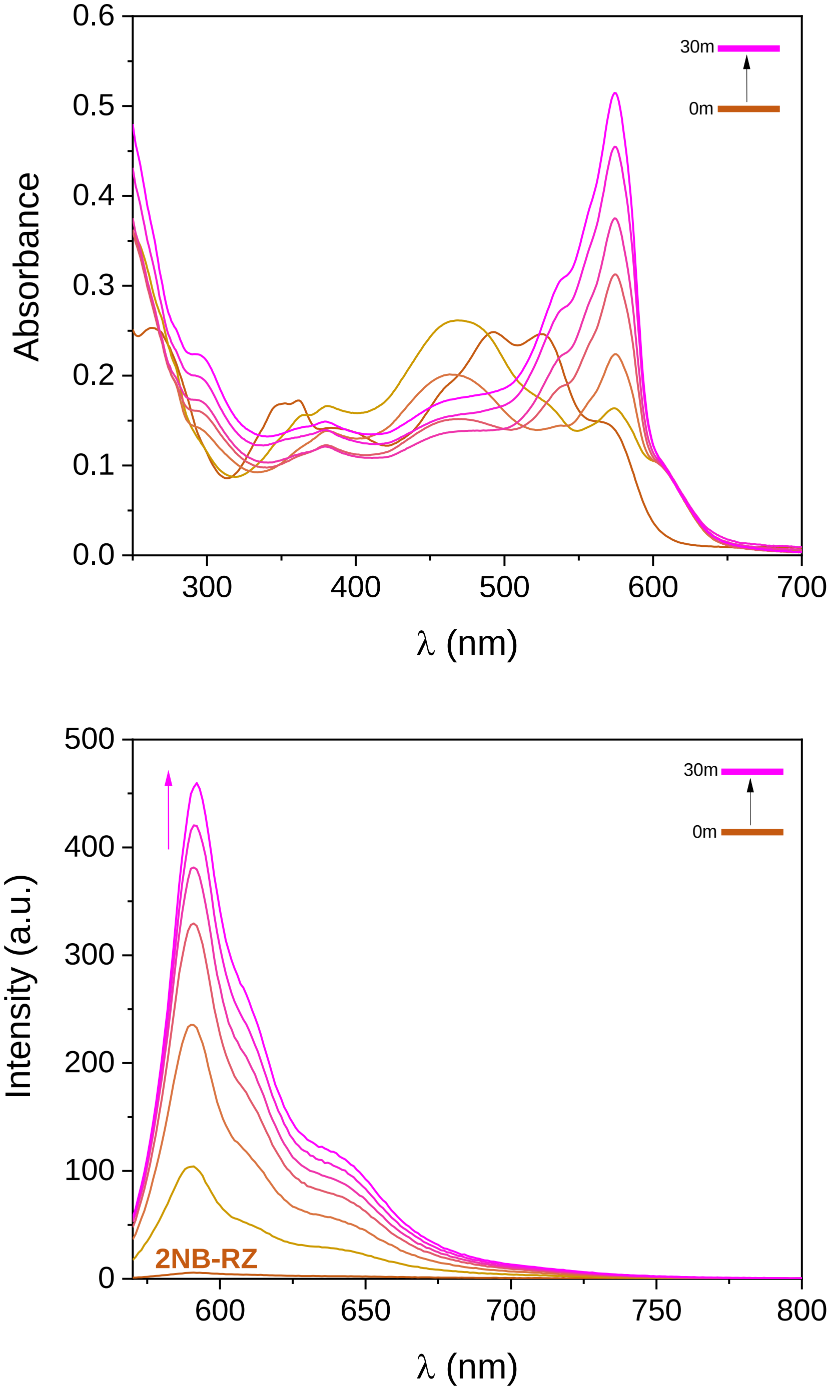

Figure S4. Absorption (top panel) and emission (bottom panel, λ_{Ex} = 550 nm) spectra of a solution of **2NB-RZ** (18 μM, 20 ºC, CH_3OH, NH_2OH 3000 eq.) before and after irradiation at 365 nm (0 – 30 min, 5 min irradiation intervals).

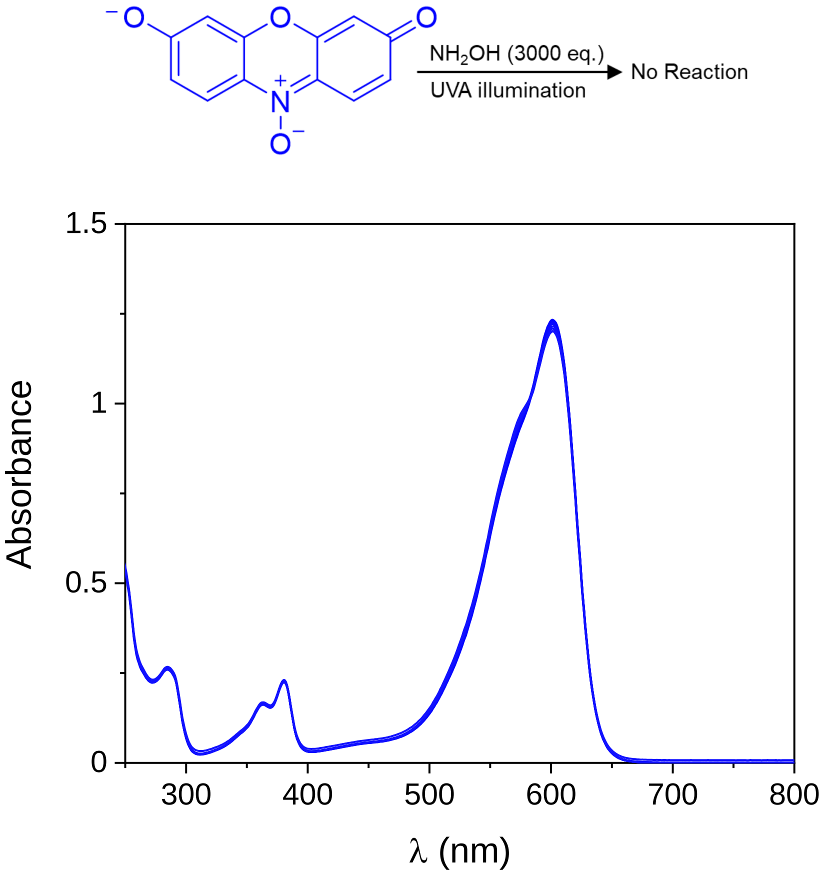

Figure S5. Absorption spectra of an aqueous solution of **RZ** (25 µM, 20 ºC, NH_2OH 3000 eq.) before and after irradiation at 365 nm (0 – 30 min).

Materials and Methods

Chemicals were purchased from Sigma-Aldrich, Fisher Scientific and ACP Chemicals. Solvents were purchased from ACP Chemicals. N,N'-dimethylformamide (DMF) was dried under nitrogen with 3Å molecular sieves. All other reagents were used as received. Ultrapure deionized water (MilliΩ, 18.2 MΩ) was obtained from a Millipore Purification System. Reactions were monitored by thin layer chromatography using aluminum backed sheets coated with 200 μm silica (60, F_{254}). SiliaFlash® P60, 40-63 mm (230-400 mesh) silica gel from SiliCycle was used for purification of compounds by column chromatography. NMR spectra were collected at room temperature with a Bruker Avance 400 spectrometer. Steady-state absorption spectra were recorded with an Agilent Cary 60 UV-visible spectrometer, using quartz cells with a path length of 1 cm. Steady-state emission spectra were recorded with an Agilent Cary Eclipse spectrometer. FTIR Diamond ATR spectra were recorded with a Cary 630 spectrometer by Agilent Technologies. Electrospray Ionization Mass Spectrometry (ESI-MS) was performed using an Advion Expression compact mass spectrometer. Illumination at 365 nm was done using a laboratory TLC lamp (Mineralight UVGL 25, 0.4 mW cm^{-2}). Illumination at 525 nm was performed using an in-house designed illumination setup consisting of a set of three light-emitting diodes (LEDs, LEDEngin LZ4-00G108 green) each connected to a heat sink and diaphragm-based active cooling system (Nuventix SynJet). A DC Power Supply provided a current of 700 mA. According to manufacturer specifications these conditions deliver an average radiant flux of 3.3 W per LED. The temperature of the irradiated solution is 21.2 °C, recorded using a thermocouple. Absorption and emission spectra were recorded immediately after irradiation. HPLC was conducted using an Agilent 1260 Infinity system consisting of a quat pump with a photodiode array detector. 50 μL samples were injected into a Fisher Scientific Acclaim 120 C18 column (120Å beads, 5 μm pore size, 2.1 × 250 mm). Samples eluted isocratically using a phosphate buffer (pH 6.8)-acetonitrile-methanol solvent system (52%:3%:45% v/v). The flow rate was kept at 0.4 mL/min. The products were monitored at 600 nm.

Synthetic Protocols

Synthesis of 2NB-RZ. To a clean, oven-dried 100 mL two-necked round-bottom flask equipped with a magnetic stir bar, 10 mL of dry DMF, resazurin sodium salt (252.6 mg, 1 mmol) and K_2CO_3 (277.7 mg, 2 mmol) were added. The flask was sealed and purged with N_2 for 15 min. In a separate flask, 331.8 mg (1.5 mmol) of 2-nitrobenzyl bromide were dissolved in 2 mL of dry DMF and sonicated until all solid was dissolved. The 2-nitrobenzyl bromide solution was added dropwise to the solution containing resazurin over the course of 20 minutes. The resulting solution was stirred for 1 week at room temperature under N_2. The reaction mixture was precipitated using 100 mL of cold CH_3OH, vacuum filtered and washed three times with 10 mL of cold CH_3OH affording **2NB-RZ** (87%) as a rust coloured solid. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d,1H), 8.20 (d, 1H), 8.05 (d, 1H), 7.83 (d, 1H), 7.74 (t, 1H), 7.58 (t, 1H), 7.07 (dd, 1H), 6.98 (d, 1H), 6.77 (dd, 1H), 6.29 (d, 1H), 5.63 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.0, 162.6, 152.7, 148.8, 147.0, 134.3, 132.9, 131.7, 131.2, 129.2, 128.4, 125.5, 124.9, 122.8, 122.2, 113.8, 105.8, 101.8, 67.9. FTIR-ATR: 3080, 2922 cm^{-1} (ν_s, C–H); 1728 cm^{-1} (ν_s, C=O); 1587, 1416 cm^{-1} (ν_s, C=C); 1520, 1345 cm^{-1} (ν_s, N=O); 1470 cm^{-1} (ν_s, N–O); 1282 cm^{-1} (ν_s, C–N aromatic); 1121, 1099 cm^{-1} (ν_s, C–O).

Synthesis of 2NB-RF. To a clean and oven-dried two-necked 100 mL round bottom flask equipped with a magnetic stir bar, resorufin sodium salt (235 mg, 1 mmol) and K_2CO_3 (691 mg, 5 mmol) were dissolved in acetone (65 mL). 2-nitrobenzyl bromide (216 mg, 1 mmol) was added to the flask, which was then attached to a reflux condenser and degassed for 15 min under N_2 atmosphere. The reaction was refluxed overnight under N_2. The crude mixture was concentrated under reduced pressure and dissolved in CH_2Cl_2 (20 mL). The mixture was extracted first with 0.1 M NaOH (3 × 20 mL), followed by a wash with brine (20 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude compound was purified by column chromatography [SiO_2:Hexanes/EtOAc 1:1 (v/v)] to yield **2NB-RF** (73%) as an orange solid. ESI-MS: *m/z* = 349.2 $[M]^+$; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, 1H), 7.86-7.84 (d, 1H), 7.77-7.69 (m, 2H), 7.58-7.52 (m, 1H), 7.43 (d, 1H), 7.07-7.04 (d, 1H), 6.92 (s, 1H), 6.86-6.83 (d, 1H), 6.33 (s, 1H), 5.61 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 186.4, 162.8, 149.7, 146.9, 146.2, 145.6, 134.8, 134.5, 134.2, 132.5, 132.2, 131.8, 129.0, 128.4, 125.4, 113.9, 106.9, 101.4, 67.7. FTIR-ATR: 3082, 2918 cm^{-1} (ν_s, C–H); 1718 cm^{-1} (ν_s, C=O); 1647, 1438 cm^{-1} (ν_s, C=C); 1521, 1338 cm^{-1} (ν_s, N=O); 1502 cm^{-1} (ν_s, N–O); 1248 cm^{-1} (ν_s, C–N aromatic); 1095, 1017 cm^{-1} (ν_s, C–O).

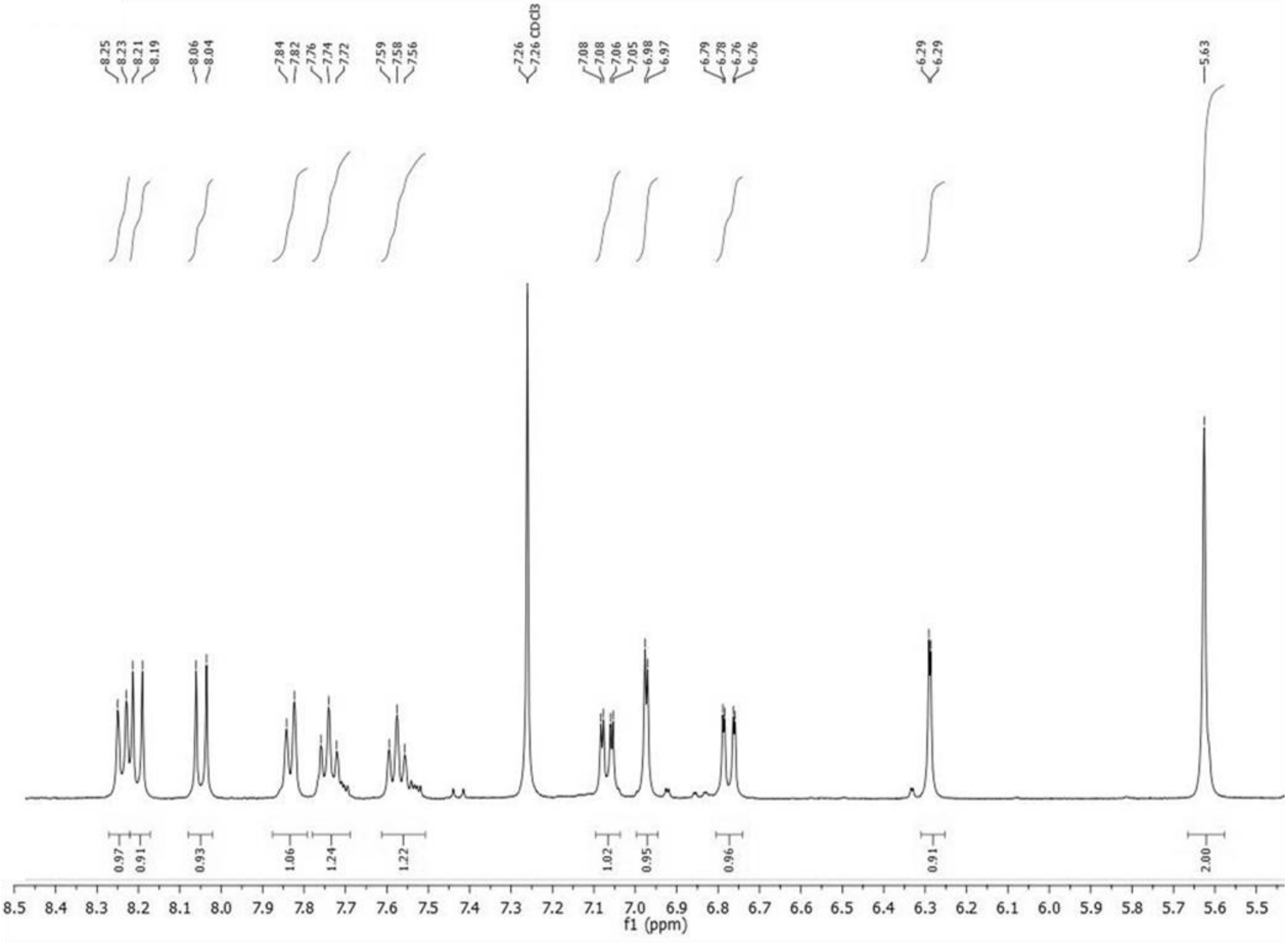

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 20 °C, 400 MHz) of **2NB-RZ**.

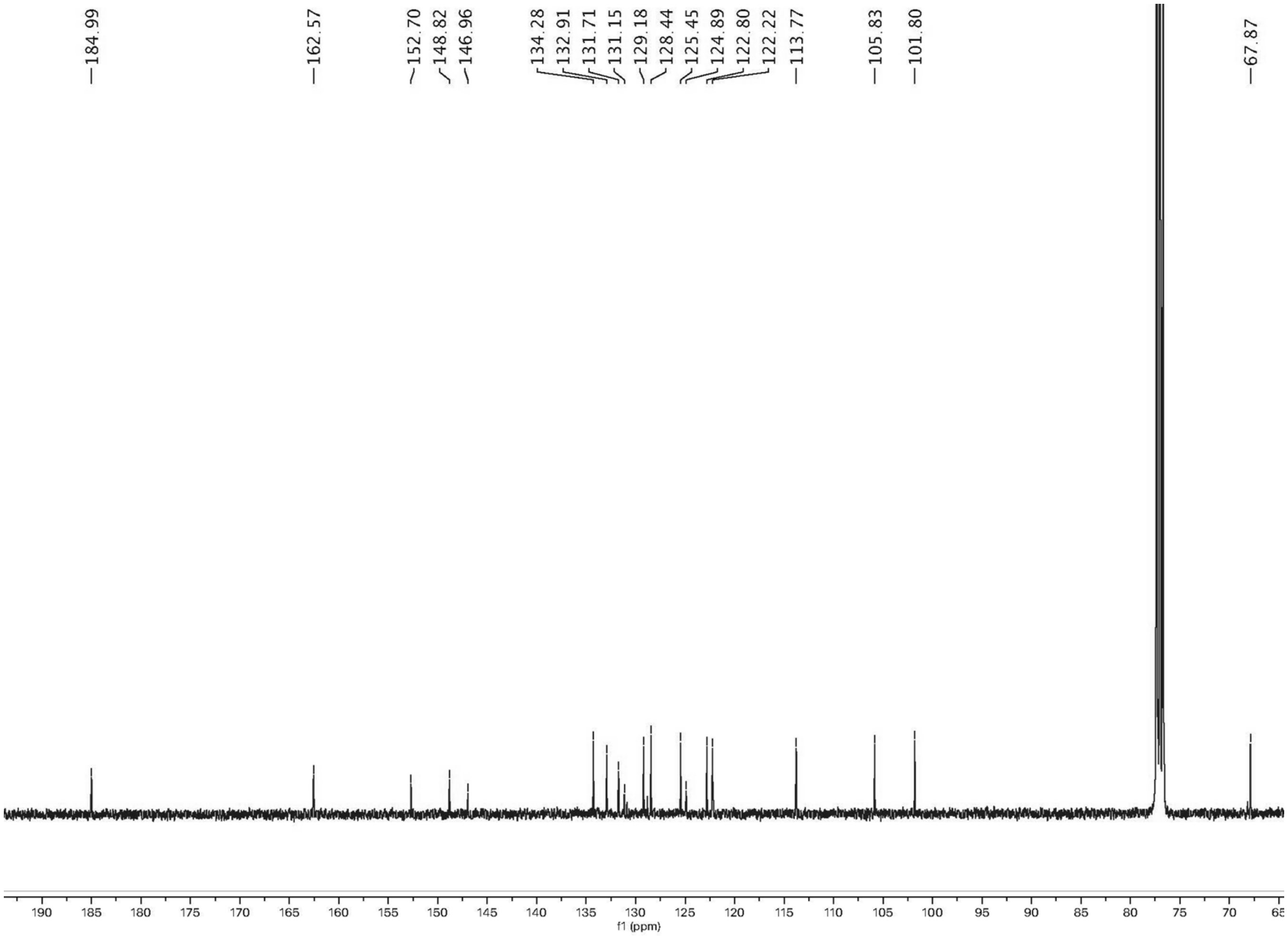

Figure S7. ^{13}C NMR spectrum (CDCl$_3$, 20 °C, 100 MHz) of **2NB-RZ**.

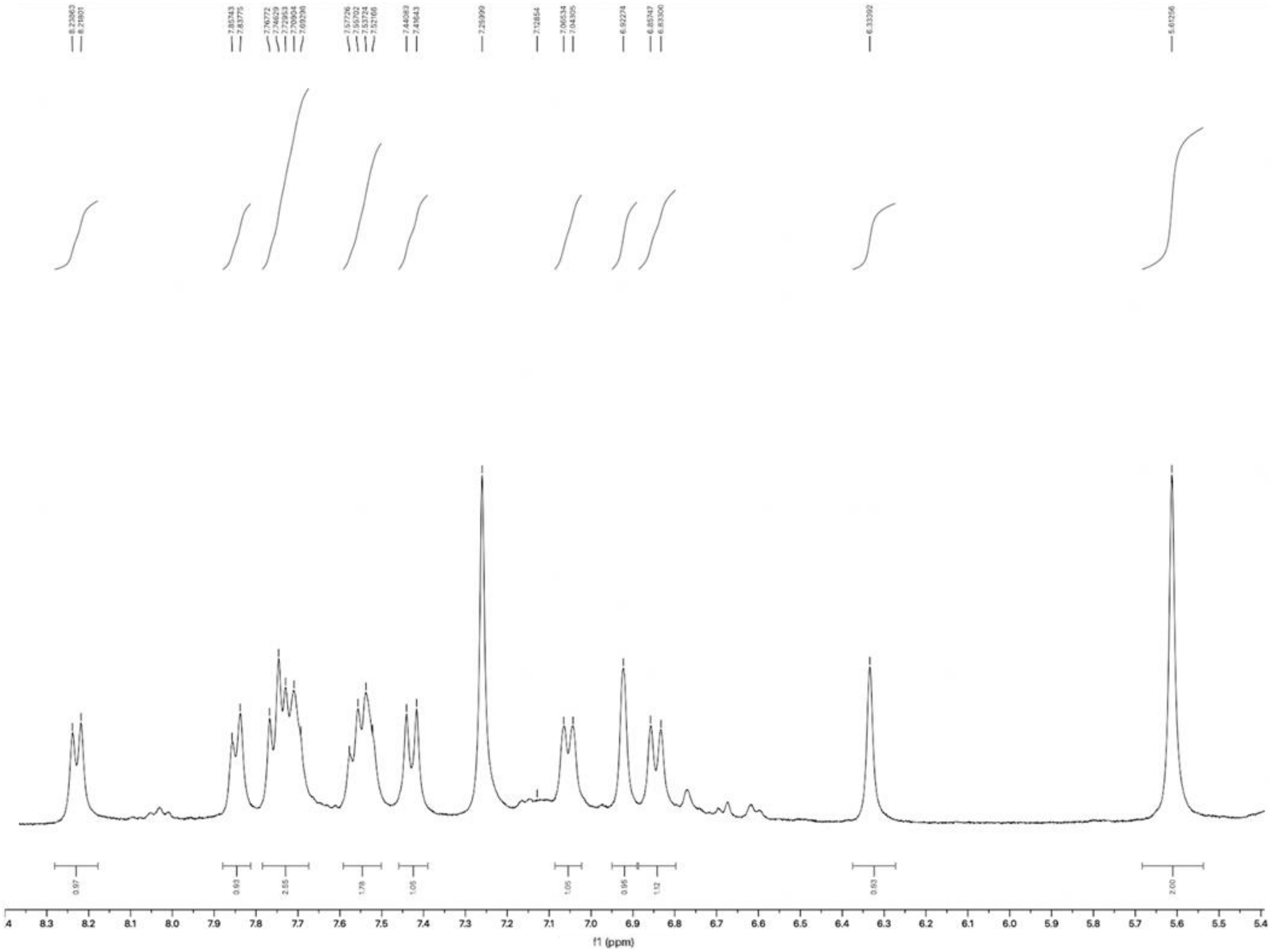

Figure S8. ^{1}H NMR spectrum (CDCl$_3$, 20 °C, 400 MHz) of **2NB-RF**.

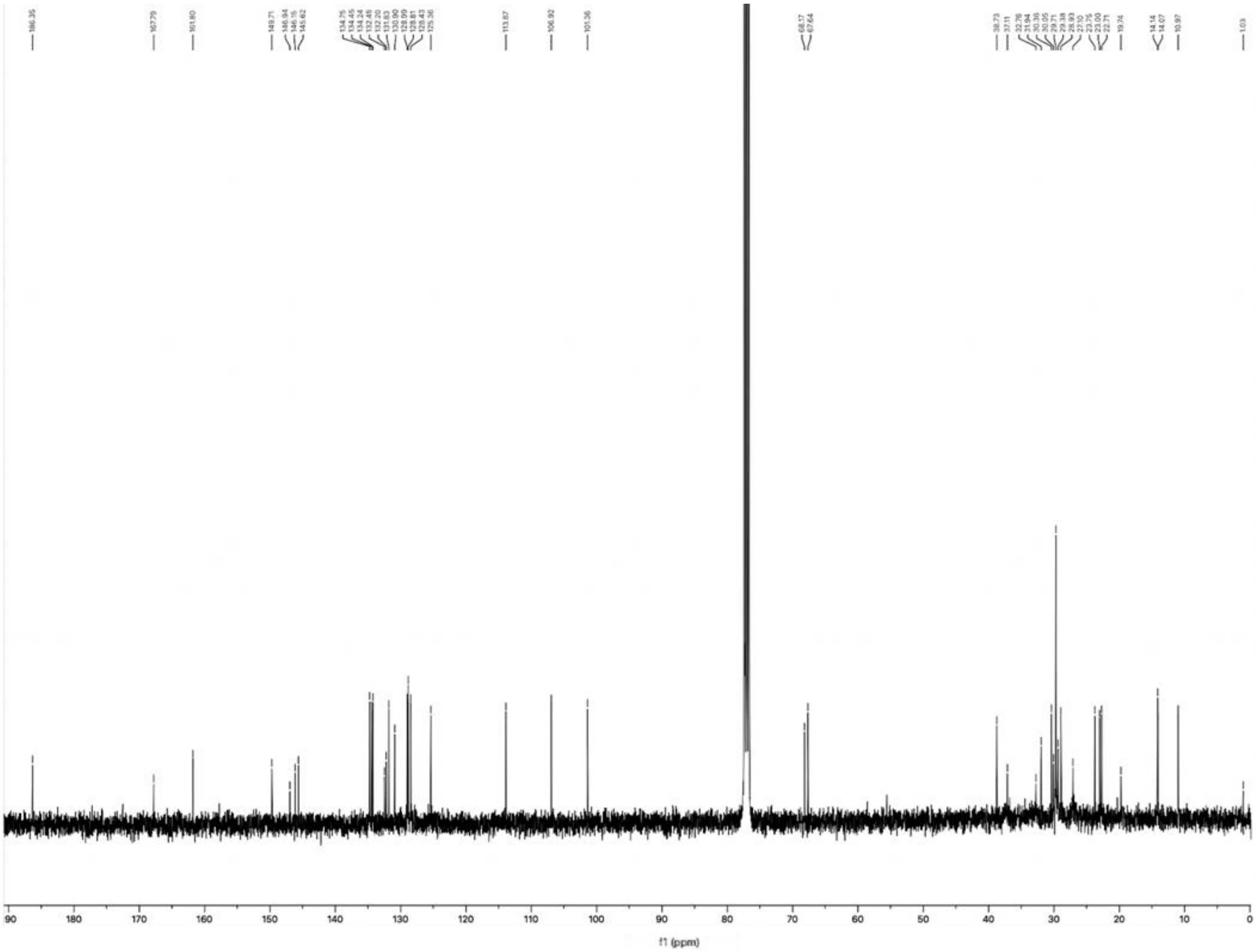

Figure S9. ^{13}C NMR spectrum (CDCl$_3$, 20 °C, 100 MHz) of **2NB-RF**.