

Nitration of 2,3-dihydroimidazo[1,2-*a*]benzimidazole and its *N*⁹-substituted derivatives

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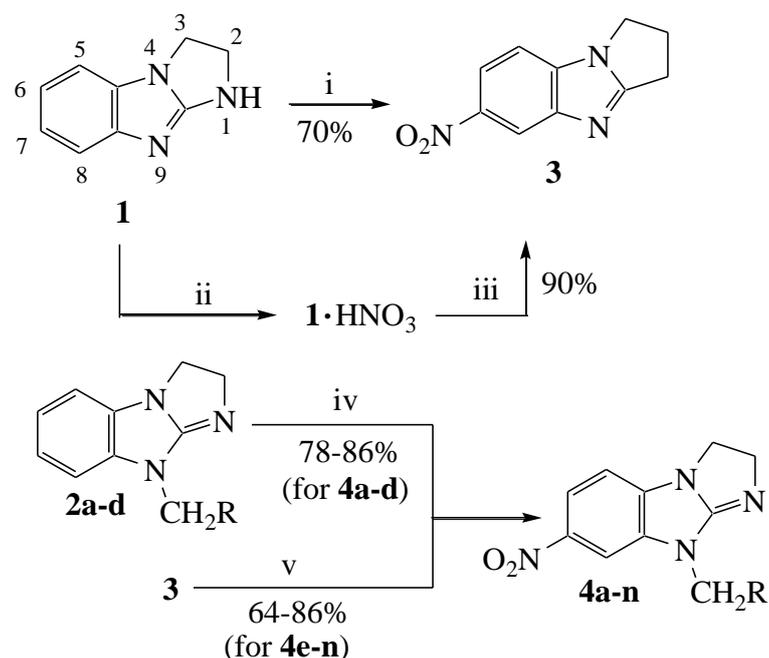
S1. General Information

The solvents were purified according to standard procedures. NMR spectra for ¹H, ¹³C and ¹⁵N were recorded on spectrometer Bruker Avance 600 in DMSO-*d*₆ or CDCl₃ at 600, 150 and 61 MHz, respectively. Chemical shifts of nuclei ¹H and ¹³C were measured relatively the signals of deuterated solvent: δ = 2.50 (2.49) ppm for residual protons and 39.09 (39.28) ppm for carbon (DMSO-*d*₆), δ = 7.26 (7.25) ppm for residual protons and 77.0 (76.9) ppm for carbon (CDCl₃) for 30 (50)°C [S1], ¹⁵N chemical shifts were given relatively ¹⁵NH₃. Coupling constants (*J*) are reported in Hz. Melting points were determined by using Fisher-Johns Melting Point Apparatus (Fisher Scientific) and are uncorrected. Elemental analysis was performed by the classical method of microanalysis [S2]. The reaction and purity of the obtained compounds were monitored by TLC (plates with Al₂O₃ III activity grade, eluent CHCl₃, development of TLC plates by exposition to iodine vapors in iodine chamber).

The DFT geometry optimization calculations (B3LYP/6-311G**) were performed using quantum chemical program package Firefly 8.0 [S3], which is partially based on the GAMESS (US) [S4] source code. Chemical shifts were calculated by deMon2k program, PW91-PW91/IGLO-II level [S5].

Starting compounds **1** [S6], **2a,c,d** [S7], **2b** [S8] were synthesized as described previously.

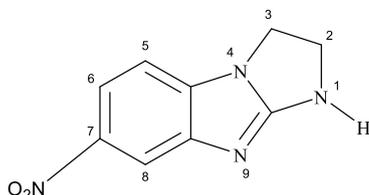
S2. Characterization of the compounds.



- | | |
|--|--|
| a R = H | h R = PhOCH ₂ |
| b R = Et ₂ NCH ₂ | i R = 4-MeOC ₆ H ₄ OCH ₂ |
| c R = morpholinomethyl | j R = 4-ClC ₆ H ₄ OCH ₂ |
| d R = piperidinomethyl | k R = PhC(O) |
| e R = 4-Bu ^t C ₆ H ₄ | l R = 3,4-(MeO) ₂ C ₆ H ₃ C(O) |
| f R = 4-ClC ₆ H ₄ | m R = 4-FC ₆ H ₄ C(O) |
| g R = 4-F ₃ CC ₆ H ₄ | n R = 4-ClC ₆ H ₄ C(O) |

Scheme S1 Reagents and conditions: i, KNO₃/H₂SO₄, -5 °C; ii, HNO₃, Me₂CO; iii, H₂SO₄, -5 °C; iv, CF₃COOH, HNO₃, 30-35 °C, 2-3 h. v, RCH₂Br, DMF, reflux, 6 h.

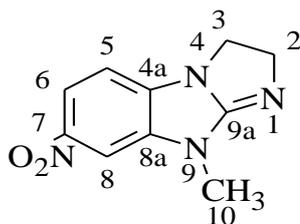
7-Nitro-2,3-dihydro-1H-imidazo[1,2-a]benzimidazole (3).



The starting compound was 2,3-dihydro-1H-imidazo[1,2-a]benzimidazole (1). The yield was 1.8 g (90%), yellow powder crystals, mp 261-263 °C (EtOH) (lit [S9] 262-263 °C (EtOH)). ¹H NMR (DMSO-*d*₆), δ: 4.03 (t, *J* 7.4, 2H, H-3), 4.22 (t, *J* 7.4, 2H, H-2), 7.25 (d, *J* 8.7, 1H, H-5), 7.52 (s, 1H, NH), 7.88 (dd, *J* 8.7, 2.4, 1H, H-6), 7.94 (d, *J* 2.1, 1H, H-8). ¹³C NMR (DMSO-*d*₆), δ: 41.36 (C-2), 47.50 (C-3), 106.91 (C-5), 110.39 (C-8), 115.63 (C-6), 137.4 (C-4a), 141.35 (C-7), 148.7 (C-8a), 164.70 (C-9a). ¹⁵N NMR (DMSO-*d*₆), δ, (from ¹⁵N – ¹H HMBC spectrum): 137.18 (N-4), 158.22 (N-1), 184.78 (N-9), 373.28 (NO₂). ¹³C – ¹H HMBC

spectrum, δ^H , δ^C , multiplicity, J^{C-H} , integral (cross-peak assignment): 4.03, 41.36, t, 79.58 (H-3, C-2), 4.03, 47.50, dt, J 150.0, 4.14 (H-3, C-3), 4.03, 164.70, t, 60.56 (H-3, C-9a), 4.22, 41.36, dt, J 144.0, 88.41 (H-2, C-2), 4.22, 47.50, t, 57.74 (H-2, C-3), 4.22, 164.70, t, 90.83 (H-2, C-9a), 7.25, 106.91, dd, J 168, 269.12 (H-5, C-5), 7.25, 110.39, d, 30.21 (H-5, C-8), 7.25, 115.63, d, 5.03 (H-5, C-6), 7.25, 137.4, d, 5.05 (H-5, C-4a), 7.25, 141.35, t, 175.62 (H-5, C-7), 7.25, 148.7, t, 142.27 (H-5, C-8a), 7.88, 110.39, br.d, 42.76 (H-6, C-5), 7.88, 115.63, dd, J 167.6, 221.75 (H-6, C-6), 7.88, 137.40, sym.m, 91.1, (H-6, C-4a), 7.88, 141.35, dd, 52.47 (H-6, C-7), 7.88, 148.7, d, 3.37 (H-6, C-8a), 7.94, 106.91, s, 9.37 (H-8, C-5), 7.94, 110.39, d, J 167.9, 211.95 (H-8, C-8), 7.94, 115.63, d, 122.94 (H-8, C-6), 7.94, 137.40, br.d, 81.11 (H-8, C-4a), 7.94, 141.35, d, 71.75 (H-8, C-7), 7.94, 148.70, s, 44.37 (H-8, C-8a). $^{15}N - ^1H$ HMBC spectrum, δ^H , δ^N , multiplicity, J^{C-H} , integral (cross-peak assignment): 4.03, 137.18, m, 287.35 (H-3, N-4), 4.22, 60.61, m, 158.22 (H-2, N-1), 4.22, 137.81, m, 271.83 (H-2, N-4), 7.25, 137.81, d, 212.54 (H-5, N-4), 7.25, 373.28, d, 133.84 (H-5, NO₂), 7.52, 60.61, d, J 96.0, 417.26 (H-1, N-1), 7.52, 137.81, s, 122.35 (H-1, N-4), 7.52, 373.28, d, 428.94 (H-1, NO₂), 7.94, 137.81, s, 36.03 (H-8, N-4), 7.94, 184.78, s, 36.99 (H-8, N-9), 7.94, 373.28, d, 348.31 (H-8, NO₂). Found (%): C, 52.68; H, 4.21; N, 27.63. Calc. for C₉H₈N₄O₂ (%): C, 52.94; H, 3.95; N, 27.44.

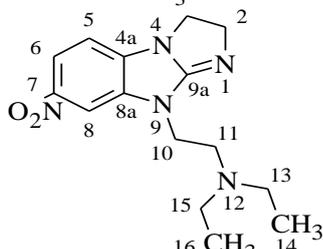
9-Methyl-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (4a).



The starting compound was 9-methyl-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**2a**). The yield was 1.9 g (86%), yellow powder, mp 206-208°C (C₆H₅CH₃). 1H NMR (CDCl₃), δ : 3.38 (s, 3H, H-10), 3.92 (t, J 8.3, 2H, H-3), 4.32 (t, J 8.2, 2H, H-2), 6.62 (d, J 8.5, 1H, H-5), 7.56 (d, J 2.1, 1H, H-8), 7.94 (dd, J 8.6, 2.2, 1H, H-6). ^{13}C NMR (CDCl₃), δ : 28.73 (C-10), 44.53 (C-3), 58.78 (C-2), 101.98 (C-8), 104.31 (C-5), 119.16 (C-6), 135.76 (C-4a), 138.19 (C-8a), 141.52 (C-7), 161.48 (C-9a). ^{15}N NMR (CDCl₃), δ (from $^{15}N - ^1H$ HMBC spectrum): 96.67 (N-9), 132.13 (N-4), 146.72 (N-1), 373.41 (NO₂). $^{13}C - ^1H$ HMBC spectrum, δ^H , δ^C , multiplicity, J^{C-H} , integral (cross-peak assignment): 3.38, 28.73, d, J 138.0, 181.14 (H-10, C-10), 3.38, 138.19, d, 137.28 (H-10, C-8a), 3.38, 161.48, d, 138.41 (H-10, C-9a), 3.92, 44.53, dt, J 156.0, 19.29 (H-3, C-3), 3.92, 58.78, t, 27.98 (H-3, C-2), 3.92, 161.48, t, 27.93 (H-3, C-9a), 4.32, 44.53, t, 10.98 (H-2, C-3), 4.32, 161.48, m, 61.12 (H-2, C-9a), 6.62, 104.31, dd, J 168.0, 76.62 (H-5, C-5), 6.62, 138.19, t, 16.97 (H-5, C-8a), 6.62, 141.52, t, 23.21 (H-5, C-7), 7.56, 101.98, d, J 168.0, 69.20 (H-8, C-8), 7.56, 119.16, s, 5.19 (H-8, C-6), 7.56, 135.76, d, 6.18 (H-8, C-4a), 7.56, 138.19, d, 4.22 (H-8, C-8a), 7.56, 141.52, d, 7.74 (H-8, C-7), 7.94, 101.98, m, 50.03 (H-6, C-8), 7.94, 119.16, dd, J 162, 319.18 (H-6, C-6), 7.94, 135.76, dd, 68.72 (H-6, C-4a), 7.94, 141.52, m, 51.90 (H-6, C-7). $^{15}N - ^1H$ HMBC spectrum, δ^H , δ^N , multiplicity, J^{C-H} , integral (cross-peak assignment): 3.38, 96.67, d, (H-10, N-9), 4.32, 132.13, t, (H-2, N-4), 4.32, 146.72, d, (H-2, N-1), 6.62, 96.67, d, (H-5, N-9), 6.62, 132.13, d, (H-5, N-4), 6.62, 146.72, d, (H-5, N-1), 7.56, 96.67, d, (H-8, N-9), 7.56, 373.41,

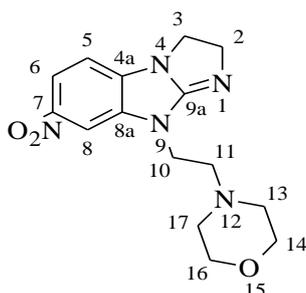
d, (H-8, NO₂), 7.94, 373.41, d, (H-6, NO₂). Found (%): C, 55.10; H, 4.59; N, 25.61. Calc. for C₁₀H₁₀N₄O₂ (%): C, 55.04; H, 4.62; N, 25.68.

N,N-Diethyl-2-(7-nitro-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazol-9-yl)ethan-1-amine (**4b**).



The starting compound was 2-(2,3-dihydro-9*H*-imidazo[1,2-*a*]benzimidazol-9-yl)-*N,N*-diethylethan-1-amine (**2b**). The yield was 2.4 g (78%), orange crystals, mp 85-86°C (*isooctane*:PhMe, 9:1). ¹H NMR (DMSO-*d*₆), δ: 0.85 (t, *J* 7.1, 6H, H-14, H-16), 2.47 (q, *J* 7.1, 4H, H-13, H-15), 2.68 (t, *J* 6.3, 2H, H-10), 3.82 (t, *J* 6.3, 2H, H-11), 3.90 (t, *J* 8.2, 2H, H-3), 4.14 (t, *J* 8.2, 2H, H-2), 6.85 (d, *J* 8.6, 1H, H-5), 7.75 (d, *J* 2.2, 1H, H-8), 7.88 (dd, *J* 8.6, 2.2, 1H, H-6). ¹³C NMR (DMSO-*d*₆) δ: 11.85, 41.01, 44.09, 46.54, 49.85, 58.42, 102.28, 104.61, 118.59, 135.96, 138.01, 140.27, 160.14. Found (%): C, 59.57; H, 6.84; N, 23.11. Calc. for C₁₅H₂₁N₅O₂ (%): C, 59.39; H, 6.98; N, 23.09.

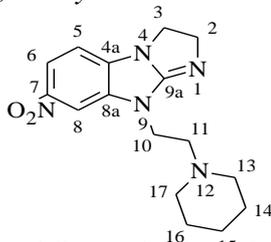
9-[2-(Morpholin-4-yl)ethyl]-7-nitro-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazole (**4c**).



The starting compound was 9-[2-(morpholin-4-yl)ethyl]-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazole (**2c**). The yield was 2.6 g (81%), red-orange crystals, mp 125-126°C (*isooctane*-PhMe, 3:2). ¹H NMR (CDCl₃), δ: 2.50 (t, *J* 4.5, 4H, H-13, H-17), 2.69 (t, *J* 6.5, 2H, H-11), 3.63 (t, *J* 4.7, 4H, H-14, H-16), 3.87 (t, *J* 6.5, 2H, H-10), 3.91 (t, *J* 8.3, 2H, H-3), 4.30 (t, *J* 8.6, 2H, H-2), 6.61 (d, *J* 8.5, 1H, H-5), 7.67 (d, *J* 2.2, 1H, H-8), 7.93 (dd, *J* 8.5, 2.2, 1H, H-6). ¹³C NMR (CDCl₃) δ: 40.66 (C-10), 44.40 (C-3), 53.75 (C-13, C-17), 56.06 (C-11), 58.83 (C-2), 66.85 (C-14, C-16), 102.74 (C-8), 104.34 (C-5), 119.08 (C-6), 135.78 (C-4a), 137.80 (C-8a), 141.42 (C-7), 161.09 (C-9a). ¹⁵N NMR (CDCl₃), δ (from ¹⁵N – ¹H HMBC spectrum): 41.21 (N-12), 102.26 (N-9), 128.88 (N-4), 147.76 (N-1), 370.36 (NO₂). ¹³C – ¹H HMBC spectrum, δ^H, δ^C, multiplicity, *J*^{C-H}, integral (cross-peak assignment): 2.50, 53.75, tm, *J* 66.0, 198.34 (H-13,17, C-13,17), 2.50, 56.06, t, 42.17 (H-13, C-11), 2.50, 66.85, d, 50.94 (H-13, C-14), 2.69, 40.66, td, 417.02 (H-11, C-10), 2.69, 53.75, m, 893.35 (H-11, C-13), 2.69, 56.06, d.t, *J* 132.0, 711.08 (H-11, C-11), 3.62, 53.75, t, 178.24 (H-14, C-13), 3.62, 66.85, tm, *J* 66.0, 711.08 (H-14, C-14), 3.87, 40.66, dt, *J* 138.0, 507.91 (H-10, C-10), 3.87, 56.06, t, 498.28 (H-10, C-11), 3.87, 137.80, t, 281.22 (H-10, C-8a), 3.87, 161.09, m, 296.97 (H-10, C-9a), 3.91, 44.40, dt, *J* 144.0, 252.07 (H-3, C-3), 3.91, 58.83, t, 364.35 (H-3, C-2), 3.91, 161.09, t, 381.02 (H-3, C-9a), 4.30, 44.40, t, 178.79 (H-2, C-3), 4.30, 58.83, dt, *J* 144.0, 252.07 (H-2, C-2), 4.30, 161.09, m, 593.81 (H-2, C-9a),

6.61, 102.74, d, 65.04 (H-5, C-8), 6.61, 104.34, dd, J 168.0, 711.84 (H-5, C-5), 6.61, 137.80, t, 330.22 (H-5, C-8a), 6.61, 141.42, t, 391.18 (H-5, C-7), 7.67, 102.64, d, J 168.0, 448.23 (H-8, C-8), 7.67, 104.40, s, 20.30 (H-8, C-5), 7.67, 119.08, t, 153.98 (H-8, C-6), 7.67, 135.78, d, 288.19 (H-8, C-4a), 7.67, 137.80, d, 61.02 (H-8, C-8a), 7.67, 141.42, t, 130.26 (H-8, C-7), 7.93, 102.74, m, 155.13 (H-6, C-8), 7.93, 119.08, dd, J 168.0, 401.97 (H-6, C-6), 7.93, 135.78, t, 231.72 (H-6, C-4a), 7.93, 141.42, d, 156.92 (H-6, C-7), $^{15}\text{N} - ^1\text{H}$ HMBC spectrum, δ^{H} , δ^{N} , multiplicity, $J^{\text{C-H}}$, integral (cross-peak assignment): 2.69, 102.26, t, 54.63, (H-11, N-9), 3.62, 41.21, d, 58.27, (H-14,16, N-12), 3.87, 41.21, t, 42.75, (H-10, N-12), 3.87, 102.26, t, 18.14, (H-10, N-9), 3.91, 128.88, t, 5.65, (H-3, N-4), 3.91, 147.76, t, 0.89, (H-3, N-1), 4.30, 128.88, t, 18.69, (H-2, N-4), 4.30, 147.76, t, 16.21, (H-2, N-1), 6.61, 102.26, d, 3.27, (H-5, N-9), 6.61, 128.88, d, 9.69, (H-5, N-4), 6.61, 370.36, d, 1.99, (H-5, NO₂), 7.67, 102.26, s, 11.29, (H-8, N-9), 7.67, 128.88, s, 2.27, (H-8, N-4), 7.67, 370.36, s, 17.16, (H-8, NO₂), 7.93, 128.88, s, 2.20, (H-6, N-4), 7.93, 370.36, dd, 14.96, (H-6, NO₂). Found (%): C, 56.84; H, 6.18; N, 22.24. Calc. for C₁₅H₁₉N₅O₃ (%): C, 56.77; H, 6.03; N, 22.07.

7-Nitro-9-[2-(piperidin-1-yl)ethyl]-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4d**).

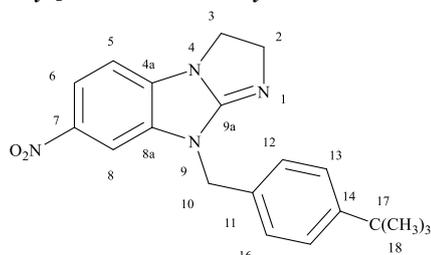


The starting compound was 9-[2-(piperidin-1-yl)ethyl]-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**2d**). The yield was 2.5 g (79%), orange crystals, mp 106-107°C (isooctane:PhMe, 9:1). ^1H NMR (CDCl₃), δ : 1.36-1.39 (m, 2H, H-15), 1.49-1.53 (m, 4H, H-14, H-16), 2.43 (br.s., 4H, H-13, H-17), 2.63 (t, J 6.6, 2H, H-11), 3.86 (t, J 6.6, 2H, H-10), 3.90 (t, J 8.4, 2H, H-3), 4.30 (t, J 8.3, 2H, H-2), 6.60 (d, J 8.52, 1H, H-5), 7.72 (d, J 2.1, 1H, H-8), 7.91 (dd, J 8.5, 2.1, 1H, H-6). ^{13}C NMR (CDCl₃), δ : 24.17 (C-15), 25.91 (C-14, C-16), 41.19 (C-10), 44.38 (C-3), 54.85 (C-13, C-17), 56.57 (C-11), 58.83 (C-2), 103.11 (C-8), 104.22 (C-5), 118.94 (C-6), 135.72 (C-4a), 138.01 (C-8a), 141.44 (C-7), 161.13 (C-9a). ^{15}N NMR (CDCl₃), δ (from $^{15}\text{N} - ^1\text{H}$ HMBC spectrum): 45.65 (N-12), 103.13 (N-9), 128.94 (N-4), 147.00 (N-1), 370.61 (NO₂). $^{13}\text{C} - ^1\text{H}$ HMBC spectrum, δ^{H} , δ^{C} , multiplicity, $J^{\text{C-H}}$, integral (cross-peak assignment): 1.38, 25.91, dm, J 30.0, 9.72 (H-15, C-15), 1.38, 54.85, m, 38.55 (H-15, C-13, C-17), 1.51, 24.17, m, 92.91 (H-14, H-16, C-15), 1.51, 25.91, tm, J 61.4, 131.3 (H-14, H-16, C-14, C-16), 1.51, 54.85, m, 231.83 (H-14, H-16, C-13, C-17), 2.63, 41.19, t, 249.16 (H-11, C-10), 2.63, 56.57, dt, 254.51 (H-11, C-11), 3.86, 41.19, dt, J 156.0, 384.1 (H-10, C-10), 3.86, 56.57, t, 329.40 (H-10, C-11), 3.86, 138.01, m, 319.33 (H-10, C-8a), 3.86, 161.13, m, 296.45 (H-10, C-9a), 3.90, 44.38, dt, J 144.0, 153.8 (H-3, C-3), 3.90, 58.83, t, 253.18 (H-3, C-2), 3.90, 161.13, t, 180.54 (H-3, C-9a), 4.30, 44.38, t, 131.99 (H-2, C-3), 4.30, 58.83, dt, J 144.0, 11.1 (H-2, C-2), 4.30, 161.13, m, 464.17 (H-2, C-9a), 6.60, 103.11, d, 33.54 (H-5, C-8), 6.60, 104.22, dd, J 156.0, 498.4 (H-5, C-5), 6.60, 138.01, t, 230.97 (H-5, C-8a), 6.60, 141.44, t, 268.70 (H-5, C-7), 7.72, 103.11, d, J 168.0, 340.18 (H-8, C-8), 7.72, 118.94, t, 89.55 (H-8, C-6), 7.72, 135.72, q, 252.59 (H-8, C-4a), 7.72, 138.01, d, 67.58 (H-8, C-8a), 7.72, 141.44, t, 132.66 (H-8, C-7), 7.91, 103.11, dd, 110.83 (H-6, C-8), 7.91, 118.94, dd, J 168.0, 302.25 (H-6, C-6), 7.91, 135.72, t, 129.92 (H-6, C-4a), 7.91, 141.44, br.d, 95.31 (H-6, C-7). $^{15}\text{N} - ^1\text{H}$ HMBC spectrum, δ^{H} , δ^{N} , multiplicity, $J^{\text{C-H}}$, integral

(cross-peak assignment): 1.51, 103.13, br.s, 93.21, (H-14, H-16, N-9), 2.63, 103.13, t, 88.85, (H-11, N-9), 3.86, 45.65, t, 61.90, (H-10, N-12), 3.86, 103.13, t, 28.54, (H-10, N-9), 3.90, 128.94, t, 5.65, (H-3, N-4), 4.30, 128.94, t, 29.87, (H-2, N-4), 4.30, 147.00, t, 28.17, (H-2, N-1), 6.60, 103.13, d, 3.02, (H-5, N-9), 6.60, 128.94, d, 14.09, (H-5, N-4), 6.60, 370.61, d, 3.43, (H-5, NO₂), 7.72, 103.13, br.s, 12.36, (H-8, N-9), 7.72, 370.61, br.s, 17.02, (H-8, NO₂), 7.91, 370.61, dd, 15.44, (H-6, NO₂). Found (%): C, 60.61; H, 6.65; N, 22.29. Calc. for C₁₆H₂₁N₅O₂ (%): C, 60.94; H, 6.71; N, 22.21.

7-Nitro-9-benzyl(2-aryloxyethyl)dihydroimidazobenzimidazoles 4e-j. A solution of compound **3** (1.02 g, 5 mmol) and the corresponding benzyl- or 2-aryloxyethyl bromide (5 mmol) in DMF (8-10 ml) was refluxed for 6 h. The solution was cooled down, and diethyl ether (5-10 ml) was added. The hydrobromide precipitate that separated was filtered off and washed with ether. To obtain the base, the salt was treated with conc. NH₄OH. The resulting yellow precipitate was filtered off and washed with water. Then it was purified by chromatography on a column with Al₂O₃, using CHCl₃ as the eluent.

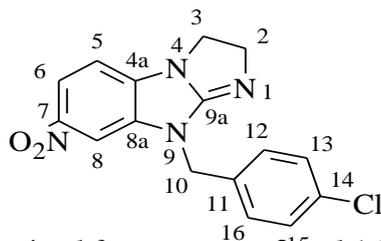
9-[4-tert-Butylphenyl)methyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (4e).



The compound was obtained from compound **3** and 1-bromomethyl-4-*tert*-butylbenzene. The yield was 1.47 g (68%), yellow powder, mp 187-189°C (PhMe). ¹H NMR (DMSO-*d*₆), δ: 1.23 (s, 9H, H-18), 3.95 (t, *J* 8.2, 2H, H-3), 4.17 (t, *J* 8.2, 2H, H-2), 5.00 (s, 2H, H-10), 6.89 (d, *J* 8.6, 1H, H-5), 7.32 (d, *J* 8.2, 2H, H-13, H-15 (or H-12, H-16)), 7.36 (d, *J* 8.2, 2H, H-12, H-16 (or H-13, H-15)), 7.72 (d, *J* 1.7, 1H, H-8), 7.90 (dd, *J* 8.5, 1.8, 1H, H-6). ¹³C NMR (DMSO-*d*₆) δ: 30.98, 44.25, 44.90, 58.41, 102.04, 104.89, 119.15, 125.35, 127.27, 133.23, 136.11, 137.18, 140.32, 150.02, 160.18. Found (%): C, 68.48; H, 6.36; N, 15.93. Calc. for C₂₀H₂₂N₄O₂ (%): C, 68.55; H, 6.33; N, 15.99.

9-[4-tert-Butylphenyl)methyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrobromide (4e·HBr), white with a yellow tint powder, mp 250-251°C (BuOH). ¹H NMR (DMSO-*d*₆), δ: 1.24 (s, 9H, H-18), 4.40 (t, *J* 8.3, 2H, H-3), 4.49 (t, *J* 8.6, 2H, H-2), 5.51 (s, 2H, H-10), 7.41 (s, 4H, H-12, H-13, H-15, H-16), 7.69 (d, *J* 8.8, 1H, H-5), 8.26 (dd, *J* 8.8, 2.0, 1H, H-6), 8.44 (d, *J* 1.9, 1H, H-8), 10.44 (br.s, 1H, ⁺NH). ¹³C NMR (DMSO-*d*₆) δ: 43.52, 43.78, 49.26, 55.47, 66.39, 110.09, 112.28, 113.76, 120.60, 121.72, 122.62, 123.74, 127.86, 134.79, 147.22, 148.95, 156.12. Found (%): C, 55.47; H, 5.29; Br, 18.71; N, 13.08. Calc. for C₂₀H₂₃N₄O₂Br (%): C, 55.69; H, 5.37; Br, 18.53; N, 12.99.

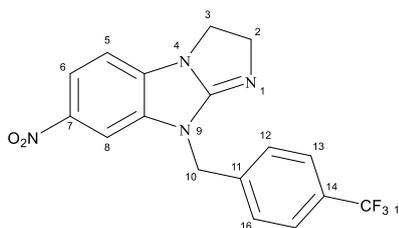
9-[(4-Chlorophenyl)methyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4f**).



The compound was obtained from reactant **3** and 1-bromomethyl-4-chlorobenzene. The yield was 1.4 g (66%), yellow powder, mp 186-187°C (PhMe). ¹H NMR (DMSO-*d*₆), δ: 3.96 (t, *J* 8.2, 2H, H-3), 4.17 (t, *J* 8.2, 2H, H-2), 5.04 (s, 2H, H-10), 6.90 (d, *J* 8.6, 1H, H-5), 7.41 (s, 4H, H-12, H-13, H-15, H-16), 7.73 (d, *J* 2.2, 1H, H-8), 7.91 (dd, *J* 8.6, 2.2, 1H, H-6). ¹³C NMR (DMSO-*d*₆) δ: 44.30, 44.58, 58.41, 102.12, 104.98, 119.28, 128.57, 129.44, 132.25, 135.23, 136.14, 137.01, 140.35, 160.15. Found (%): C, 58.51; H, 4.01; Cl, 10.83; N, 17.12. Calc. for C₁₆H₁₃N₄O₂Cl (%): C, 58.45; H, 3.99; Cl, 10.78; N, 17.04.

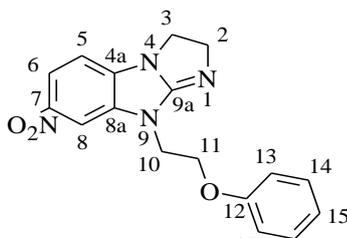
9-(4-Chlorophenylmethyl)-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrobromide (**4f**·HBr). White with a yellow tint powder, mp 259-261°C (EtOH). Found (%): C, 45.77; H, 3.31; Br+Cl, 27.32; N, 13.44. Calc. for C₁₆H₁₄N₄O₂ClBr (%): C, 46.91; H, 3.44; Br, 19.05; Cl, 8.65; N, 13.68.

7-Nitro-9-[(4-trifluoromethylphenyl)methyl]-2,9-dihydro-3H-imidazo[1,2-a]-benzimidazole (**4g**).



The compound was obtained from reactant **3** and 1-bromomethyl-4-(trifluoromethyl)benzene. The yield was 1.2 g (64%), yellow crystalline powder, mp 169-171°C (EtOAc). ¹H NMR (CDCl₃), δ: 3.98 (t, *J* 8.3, 2H, H-3), 4.37 (t, *J* 8.3, 2H, H-2), 5.03 (s, 2H, H-10), 6.67 (d, *J* 8.5, 1H, H-5), 7.47 (d, *J* 8.0, 2H, H-12, H-16), 7.49 (d, *J* 1.9, 1H, H-8), 7.60 (d, *J* 8.0, 2H, H-13, H-15), 7.96 (dd, *J* 8.5, 2.0, 1H, H-6). ¹³C NMR (CDCl₃) δ: 44.70, 46.15, 58.97, 102.58, 104.71, 119.71, 123.87 (q, *J* = 272.2 Hz, CF₃), 126.03 (q, *J* = 3.7 Hz, 13,15-C), 127.76, 130.55 (q, *J* = 32.7 Hz, 14-C), 135.90, 137.14, 139.03 (q, *J* = 1.3 Hz, 11-C), 141.61, 161.10. Found (%): N, 15.29. Calc. for C₁₇H₁₃N₄O₂F (%): N, 15.46.

7-Nitro-9-(2-phenoxyethyl)-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4h**).

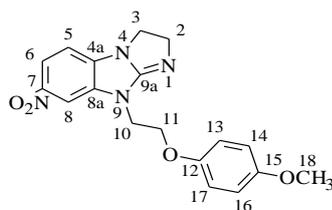


The compound was obtained from reactant **3** and 2-phenoxyethyl bromide. The yield was 1.1 g (67%), yellow crystals, mp 192-195°C (PrⁱOH). ¹H NMR (CDCl₃), δ: 3.91 (t, *J* 8.3, 2H, H-3), 4.19 (t, *J* 4.9, 2H, H-11), 4.29 (t, *J* 4.9, 2H, H-10), 4.32 (t, *J* 8.3, 2H, H-2), 6.61 (d, *J* 9.1, 1H, H-5), 6.82 (d, *J* 8.6, 2H, H-13, H-

17), 6.91 (t, J 7.4, 1H, H-15), 7.21 (t, J 8.6, 2H, H-14, H-16), 7.94-7.96 (m, 2H, H-6, H-8). ^{13}C NMR (CDCl_3), δ : 42.92 (C-10), 44.50 (C-3), 58.81 (C-2), 65.80 (C-11), 103.89 (C-8), 104.43 (C-5), 114.26 (C-13), 119.14 (C-6), 121.26 (C-15), 129.49 (C-14), 135.64 (C-4a), 138.19 (C-8a), 141.59 (C-7), 157.94 (C-12), 160.95 (C-9a). ^{15}N NMR (CDCl_3), δ : (from $^{15}\text{N} - ^1\text{H}$ HMBC spectrum): 101.11 (N-9), 128.2 (N-4), 147.01 (N-1), 370.1 (NO_2). $^{13}\text{C} - ^1\text{H}$ HMBC spectrum, δ^{H} , δ^{C} , multiplicity, $J^{\text{C-H}}$, integral (cross-peak assignment): 3.91, 44.50, d.t, J 144.0, 112.27 (H-3, C-3), 3.91, 58.81, t, 138.12 (H-3, C-2), 3.91, 160.95, m, 197.43 (H-3, C-9a), 4.19, 42.92, d. br. t, J 162.0, 264.12 (H-10, C-10), 4.19, 65.80, m, 180.93 (H-10, C-11), 4.19, 138.19, m, 199.05 (H-10, C-8a), 4.19, 160.95, m, 371.76 (H-10, C-9a), 4.29, 42.92, m, 124.94 (H-11, C-10), 4.29, 65.80, dt, J 144.0, 131.59 (H-11, C-11), 4.29, 157.94, m, 159.52 (H-11, C-12), 4.32, 44.50, t, 116.70 (H-2, C-3), 4.32, 58.81, dt, J 144.0, 131.59 (H-2, C-2), 4.32, 160.95, t, 132.68 (H-2, C-9a), 6.61, 103.89, d, 50.02 (H-5, C-8), 6.61, 104.43, dm, J 168.0, 336.32 (H-5, C-5), 6.61, 119.14, d, 4.17 (H-5, C-6), 6.61, 135.64, t, 2.55 (H-5, C-4a), 6.61, 138.19, t, 259.94 (H-5, C-8a), 6.61, 141.59, t, 313.80 (H-5, C-7), 6.82, 114.26, tm, J 84.0, 153.91 (H-13, C-13), 6.82, 121.26, m, 77.21 (H-13, C-15), 6.82, 129.49, d, 9.53 (H-13, C-14), 6.82, 157.94, dm, 42.79 (H-13, C-12), 6.91, 114.26, m, 122.59 (H-15, C-13), 6.91, 121.26, dm, J 156.0, 4.61 (H-15, C-15), 6.91, 129.49, m, 31.97 (H-15, C-14), 6.91, 157.94, d, 2.84 (H-15, C-12), 7.22, 114.26, m, 51.50 (H-14, C-13), 7.22, 121.26, m, 9.19 (H-14, C-15), 7.22, 129.49, dm, J 162.0, 7.14 (H-14, C-14), 7.22, 129.49, m, 132.66 (H-14, C-14), 7.22, 157.94, m, 260.34 (H-14, C-12), 7.95, 103.89, m, 88.39 (H-6, C-8), 7.94, 103.89, dm, J 174.0, 153.24 (H-8, C-8), 7.94, 119.14, m, 102.30 (H-8, C-6), 7.95, 119.14, dd, J 168.0, 322.89 (H-6, C-6), 7.94, 135.64, m, 341.51 (H-6, H-8, C-4a), 7.94, 138.19, m, 95.73 (H-8, C-8a), 7.94, 141.59, m, 311.77 (H-6, H-8, C-7). $^{15}\text{N} - ^1\text{H}$ HMBC spectrum, δ^{H} , δ^{N} , multiplicity, $J^{\text{C-H}}$, integral (cross-peak assignment): 3.91, 128.63, t, 5.03, (H-3, N-4), 4.19, 101.11, t, 17.26, (H-10, N-9), 4.29, 101.11, m, 84.16, (H-11, N-9), 4.32, 128.2, t, 19.07 (H-2, N-4), 4.32, 147.01, t, 14.63, (H-2, N-1), 6.61, 101.11, d, 2.13, (H-5, N-9), 6.61, 128.2, d, 11.74, (H-5, N-4), 6.61, 370.10, d, 3.05, (H-5, NO_2), 7.94, 101.11, d, 13.21, (H-8, N-9), 7.95, 128.2, m, 5.79, (H-6, H-8, N-4), 7.94, 370.10, m, 7.46, (H-6, H-8, NO_2). Found (%): C, 62.76; H, 4.78; N, 17.52. Calc. for $\text{C}_{17}\text{H}_{16}\text{N}_4\text{O}_3$ (%): C, 62.95; H, 4.97; N, 17.27.

7-Nitro-9-(2-phenoxyethyl)-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrochloride (**4h**·HCl) was obtained by dropping a solution of hydrogen chloride in Pr^iOH to a solution of the base **4h** in acetone. White with a yellow tint powder, mp 259-260°C (EtOH).

9-[2-(4-Methoxyphenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4i**).

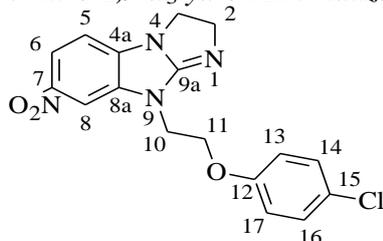


The compound was obtained from reactant **3** and 2-(4-methoxyphenoxy)ethyl bromide. The yield was 1.2 g (68%), yellow crystalline powder, mp 164-166°C (PhMe). ^1H NMR (CDCl_3), δ : 3.70 (s, 3H, OCH_3), 3.91 (t, J 8.3, 2H, H-2), 4.16 (t, J 4.9, 2H, H-11), 4.24 (t, J 4.9, 2H, H-10), 4.31 (t, J 8.3, 2H, H-3), 6.61 (d, J

8.5, 1H, H-5), 6.75 (s, 4H, H-13, H-14, H-16, H-17), 7.92 (d, *J* 2.1, 1H, H-8), 7.94 (dd, *J* 8.5, 2.1, 1H, H-6). ¹³C NMR (CDCl₃) δ: 43.01, 44.48, 55.67, 58.79, 66.39, 103.88, 104.42, 114.66, 114.68, 115.18, 115.29, 119.12, 135.63, 138.19, 141.58, 152.09, 154.18, 160.97. Found (%): C, 59.87; H, 5.01; N, 15.69. Calc. for C₁₈H₁₈N₄O₄ (%): C, 61.01; H, 5.12; N, 15.81.

9-[2-(4-Methoxyphenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrochloride (**4i**·HCl) was obtained by dropping a solution of hydrogen chloride in PrⁱOH to a solution of the base **4i** in acetone. White with a yellow tint powder, mp 255-257°C (EtOH).

9-[2-(4-Chlorophenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4j**).

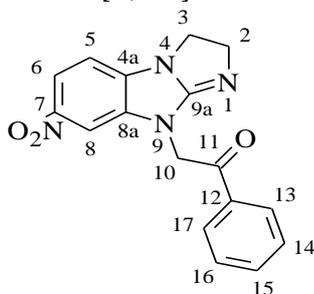


The compound was obtained from reactant **3** and 2-(4-chlorophenoxy)ethyl bromide. The yield was 1.67 g (65%), yellow crystals, mp 204-206°C (PhMe). Found (%): C, 56.90; H, 4.17; N, 15.66; Cl, 9.70. Calc. for C₁₇H₁₅N₄O₃Cl (%): C, 56.91; H, 4.21; N, 15.62; Cl, 9.88.

9-[2-(4-chlorophenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrochloride (**4j**·HCl) was obtained by dropping a solution of hydrogen chloride in PrⁱOH to a solution of base **4j** in acetone, mp 272-274°C (EtOH). ¹H NMR (DMSO-*d*₆) δ: 4.30-4.37 (m, 3H, H-2, H-3, H-10 (or H-11)), 4.64 (t, *J* 5.1, 2H, H-11 (or H-10)), 6.87-6.88 (m, 2H, H-13, H-17 (or H-14, H-16)), 7.27-7.31 (m, 3H, H-5, H-14, H-16 (or H-13, H-17)), 7.41-7.43 (m, 1H, H-6), 7.63-7.65 (m, 1H, H-8). ¹³C NMR (DMSO-*d*₆) δ: 43.54, 43.63, 49.32, 65.88, 110.28, 111.74, 116.34, 122.83, 123.85, 124.85, 127.95, 129.14, 134.82, 156.12, 156.67. Calc. for C₁₇H₁₆N₄O₃Cl₂ (%): C, 51.66; H, 4.08; N, 14.18; Cl, 17.94.

7-Nitro-9-acylmethyldihydroimidazobenzimidazoles **4k-n**. A solution of compound **3** (1.02 g, 5 mmol) and the corresponding ω-bromoacetophenone (5 mmol) in MeCN (20 ml) was refluxed for 8 h. The resulting precipitate of the hydrobromide was cooled, then filtered off and washed with ether. Bases **4k-n** were isolated similarly to compounds **4e-j**.

2-(7-Nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazol-9-yl)-1-phenylethan-1-one (**4k**).

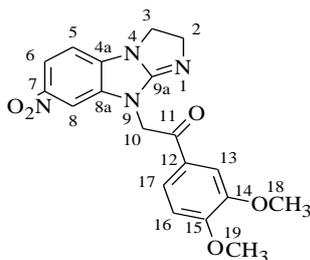


The compound was obtained from reactant **3** and 2-bromo-1-phenylethan-1-one. The yield was 1.2 g (72%), yellow crystals, mp 202-204°C (PhMe). ¹H NMR (DMSO-*d*₆) δ: 3.99 (t, *J* 8.2, 2H, H-3), 4.13 (t, *J* 8.2, 2H, H-2), 5.55 (s, 2H, H-10), 6.94 (d, *J* 8.7, 1H, H-5), 7.60 (t, *J* 7.5, 2H, H-14, H-16), 7.72 (t, *J* 7.4, 1H, H-

15), 7.90 (s, 1H, H-8), 7.94 (d, *J* 7.2, 1H, H-6), 8.07 (d, *J* 7.2, 2H, H-13, H-17). ¹³C NMR (DMSO-*d*₆) δ: 44.38, 48.86, 58.25, 102.82, 104.92, 119.13, 128.14, 128.79, 133.97, 134.4, 136.16, 138.13, 140.51, 160.29, 192.6. Found (%): C, 63.08; H, 4.43; N, 17.47; Calc. for C₁₇H₁₄N₄O₃ (%): C, 63.35; H, 4.38; N, 17.38.

2-(7-Nitro-2,3-dihydro-9H-imidazo[1,2-*a*]benzimidazol-9-yl)-1-phenylethan-1-one hydrochloride (**4k**·HCl) was obtained by dropping a solution of hydrogen chloride in 2-propanol to a solution **4k** in toluene, white with a yellow tint crystals, mp. 239-241°C (BuOH). Found (%): C, 56.87; H, 4.24; N, 15.58; Cl, 9.91. Calc. for C₁₇H₁₅N₄O₃Cl (%): C, 56.91; H, 4.21; N, 15.62; Cl, 9.88.

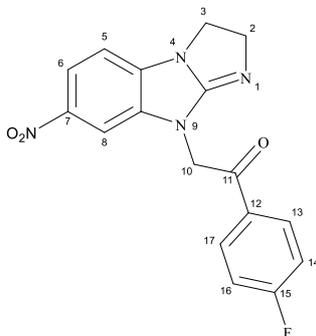
1-(3,4-Dimethoxyphenyl)-2-(7-nitro-2,3-dihydro-9H-imidazo[1,2-*a*]benzimidazol-9-yl)ethan-1-one (**4l**).



The compound was obtained from reactant **3** and 2-bromo-1-(3,4-dimethoxyphenyl)ethan-1-one. The yield was 1.32 g (69%), yellow crystals, mp 182-184°C (BuOH:DMF 5:1). ¹H NMR (DMSO-*d*₆) δ: 3.83 (s, 3H, H-18), 3.88 (s, 3H, H-19), 4.01 (t, *J* 8.3, 2H, H-3), 4.14 (t, *J* 8.3, 2H, H-2), 5.52 (s, 2H, H-10), 6.97 (d, *J* 8.6, 1H, H-5), 7.14 (d, *J* 8.5, 1H, H-16), 7.52 (d, *J* 2.0, 1H, H-13), 7.76 (dd, *J* 8.4, 2.0, 1H, H-17), 7.86 (d, *J* 2.2, 1H, H-8), 7.95 (dd, *J* 8.6, 2.2, 1H, H-6). ¹³C NMR (DMSO-*d*₆) δ: 44.32 (C-3), 48.62 (C-10), 55.55 (C-18), 55.80 (C-19), 57.87 (C-2), 102.88 (C-8), 105.14 (C-5), 110.47 (C-13), 111.00 (C-16), 119.15 (C-6), 122.96 (C-17), 127.10 (C-12), 136.01 (C-4a), 138.09 (C-8a), 140.56 (C-7), 148.61 (C-14), 153.70 (C-15), 160.24 (C-9a), 190.84 (C-11). ¹⁵N NMR (DMSO-*d*₆) δ (from ¹⁵N – ¹H HMBC spectrum): 96.11 (N-9), 130.39 (N-4), 150.15 (N-1), 370.96 (NO₂). ¹³C – ¹H HMBC spectrum, δ^H, δ^C, multiplicity, *J*^{C-H}, integral (cross-peak assignment): 3.83, 55.55, d, *J* 144.0, 6.81 (H-18, C-18), 3.83, 148.61, d, 138.12 (H-18, C-14), 3.88, 55.80, d, *J* 144.0, 10.55 (H-19, C-19), 3.88, 153.70, d, 92.65 (H-19, C-15), 4.02, 44.32, dt, *J* 120.0, 11.43 (H-3, C-3), 4.01, 57.87, d, 66.59 (H-3, C-2), 4.01, 160.24, t, 19.21 (H-3, C-9a), 4.14, 44.32, d, 59.22 (H-2, C-3), 4.14, 58.80, dt, *J* 122.0, 6.97 (H-2, C-2), 4.14, 160.24, t, 27.11 (H-2, C-9a), 5.52, 48.62, d, *J* 144.0, 59.31 (H-10, C-10), 5.52, 127.10, s, 2.61 (H-10, C-12), 5.52, 138.09, d, 123.67 (H-10, C-8a), 5.52, 160.26, d, 134.14 (H-10, C-9a), 5.52, 190.84, d, 128.96 (H-10, C-11), 6.97, 105.14, dd, *J* 174.0, 71.75 (H-5, C-5), 6.97, 138.09, t, 66.17 (H-5, C-8a), 6.97, 140.56, t, 79.64 (H-5, C-7), 7.14, 111.00, dd, *J* 168.0, 9.42 (H-16, C-16), 7.14, 127.10, t, 81.92 (H-16, C-12), 7.14, 148.61, t, 74.43 (H-16, C-14), 7.14, 153.70, t, 29.14 (H-16, C-15), 7.14, 190.84, s, 1.00 (H-16, C-11), 7.52, 122.96, m, 17.93 (H-13, C-17), 7.52, 127.10, d, 5.53 (H-13, C-12), 7.52, 148.61, t, 18.76 (H-13, C-14), 7.52, 153.70, dd, 44.91 (H-13, C-15), 7.52, 190.84, t, 24.77 (H-13, C-11), 7.76, 110.47, m, 3.90 (H-17, C-13), 7.76, 148.61, d, 1.40 (H-17, C-14), 7.76, 153.70, t, 21.44 (H-17, C-15), 7.76, 190.84, t, 8.97 (H-17, C-11), 7.86, 102.88, dd, *J* 174.0, 18.38 (H-13, C-13), 7.86, 136.01, d, 23.20 (H-8, C-4a), 7.86, 138.09, d, 4.11 (H-8, C-8a), 7.86, 140.56, t, 24.76 (H-8, C-7), 7.95, 102.88, t, 3.81 (H-6, C-8), 7.95, 119.15, dq, *J* 132.0, 26.52 (H-6, C-6), 7.95, 136.01, m, 12.90 (H-6, C-4a), 7.95, 140.56, m, 6.25 (H-6, C-7), ¹⁵N – ¹H

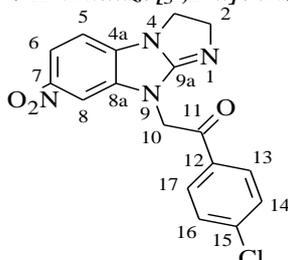
HMBC spectrum, δ^H , δ^N , multiplicity, J^{C-H} , integral (cross-peak assignment): 4.01, 130.39, m, 2.5, (H-3, N-4), 4.14, 130.39, m, 4.51, (H-2, N-4), 4.14, 150.15, m, 1.23, (H-2, N-1), 5.92, 96.11, s, 24.68, (H-10, N-9), 6.97, 96.11, d, 2.21, (H-5, N-9), 6.97, 130.39, d, 14.66, (H-5, N-4), 6.97, 370.96, d, 3.28, (H-5, NO₂), 7.86, 96.11, s, 17.06, (H-8, N-9), 7.86, 370.96, d, 22.78, (H-8, NO₂), 7.95, 370.96, dd, 27.93, (H-6, NO₂). Found (%): C, 59.92; H, 4.47; N, 14.89. Calc. for C₁₉H₁₈N₄O₅ (%): C, 59.68; H, 4.74; N, 14.65.

1-(4-Fluorophenyl)-2-(7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazol-9-yl)ethan-1-one (4m).



The compound was obtained from reactant **3** and 2-bromo-1-(4-fluorophenyl)ethan-1-one. The yield was 1.19 g (70%), yellow crystals, mp 191-192°C (EtOH). ¹H NMR (DMSO-*d*₆), δ : 3.99 (t, *J* 8.4, 2H, H-3), 4.12 (t, *J* 8.3, 2H, H-2), 5.54 (s, 2H, H-10), 6.95 (d, *J* 8.6, 1H, H-5), 7.43 (t, *J* 8.9, 2H, H-14, H-16), 7.89 (d, *J* 2.2, 1H, H-8), 7.94 (dd, *J* 8.6, 2.2, 1H, H-6), 8.14-8.16 (m, 2H, H-13, H-17). ¹³C NMR (DMSO-*d*₆), δ : 44.39, 48.82, 58.25, 102.83, 104.95, 115.89 (d, *J* = 22.0, C-14,16), 119.16, 131.09, 131.27 (d, *J* = 9.6, C-12,13), 136.16, 138.10, 140.50, 160.28, 165.43 (d, *J* = 253, C-15), . Found (%): N, 16.31. Calc. for C₁₇H₁₃N₄O₃F (%): N, 16.46.

1-(4-Chlorophenyl)-2-(7-nitro-2,3-dihydro-9H-imidazo[1,2-a]benzimidazol-9-yl)ethan-1-one (4n).



The compound was obtained from reactant **3** and 2-bromo-1-(4-chlorophenyl)ethan-1-one. The yield was 1.3 g (75%), yellow crystals, mp 214-216°C (PhMe). ¹H NMR (DMSO-*d*₆), δ : 3.97 (t, *J* 8.2, 2H, H-3), 4.12 (t, *J* 8.2, 2H, H-2), 5.53 (s, 2H, H-10), 6.92 (d, *J* 8.6, 1H, H-5), 7.66 (d, *J* 8.5, 2H, H-14, H-16), 7.89 (d, *J* 2.0, 1H, H-8), 7.93 (dd, *J* 8.5, 2.1, 1H, H-6), 8.07 (d, *J* 8.52, 2H, H-13, H-17). ¹³C NMR (DMSO-*d*₆), δ : 44.37, 48.88, 58.27, 102.83, 104.90, 119.16, 128.91, 130.06, 132.98, 136.12, 138.01, 138.91, 140.50, 160.22, 191.77. Found (%): C, 57.31; H, 3.61; Cl, 9.79; N, 15.77. Calc. for C₁₇H₁₃N₄O₃Cl (%): C, 57.23; H, 3.67; Cl, 9.94; N, 15.70.

S3. Data of quantum chemical calculations.

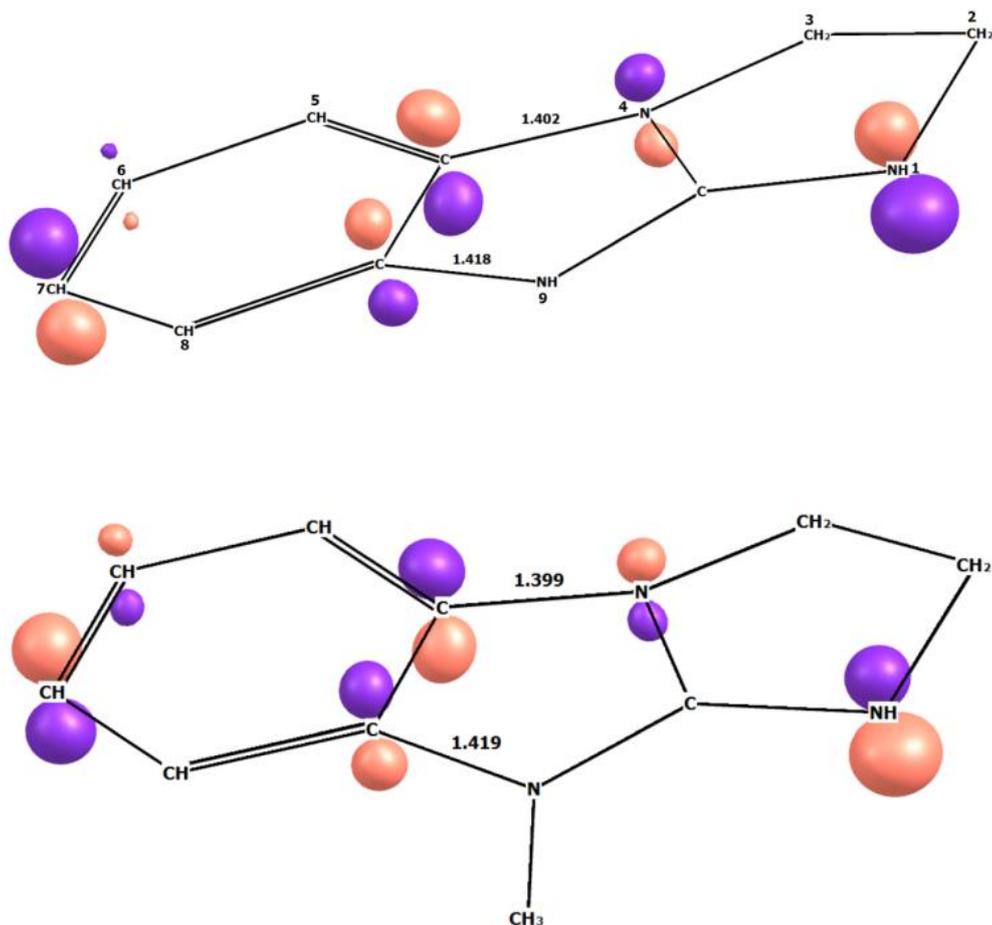


Figure 1 HOMO of protonated forms of 2,3-dihydroimidazo[1,2-*a*]benzimidazole (top) and 9-methyl-2,3-dihydroimidazo[1,2-*a*]benzimidazole (B3LYP/6-311G^{**}) (bottom).

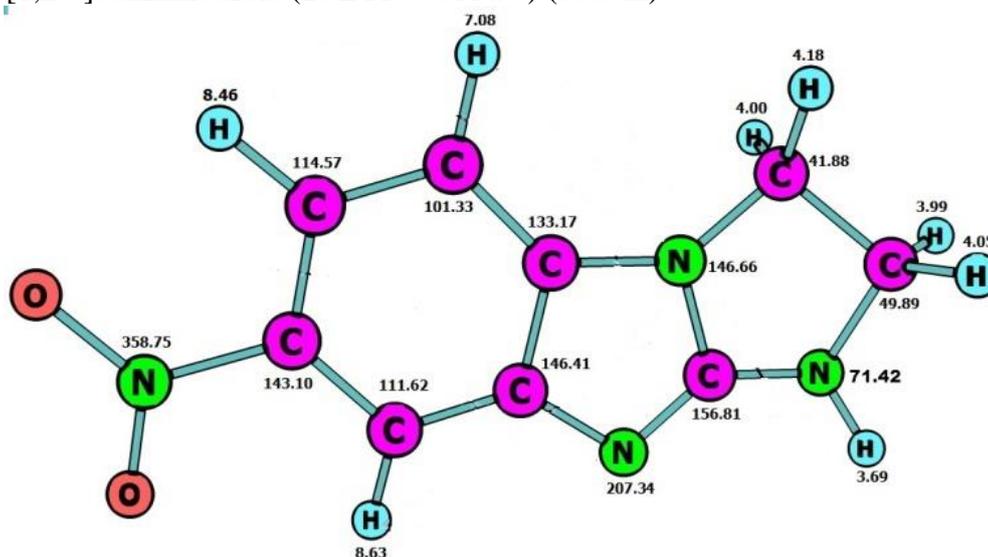


Figure 2 Calculated chemical shifts (¹H, ¹³C and ¹⁵N) for 9-*H*-7-nitro-2,3-dihydroimidazo[1,2-*a*]benzimidazole (B3LYP/6-311G^{**}//PW91-PW91/IGLO-II).

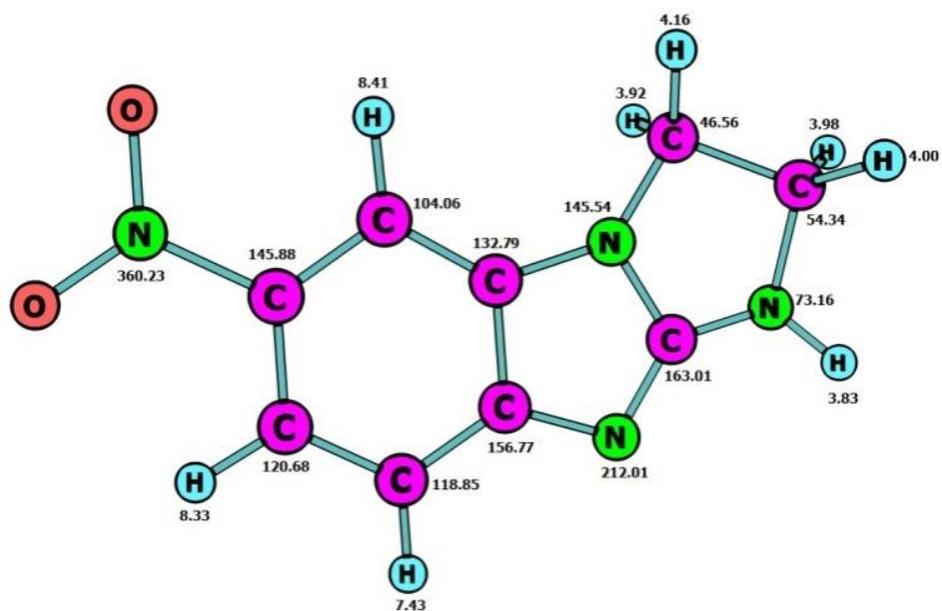
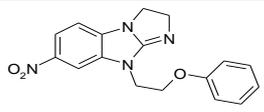
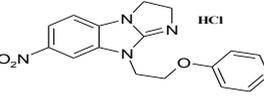
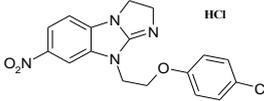
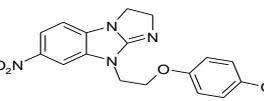
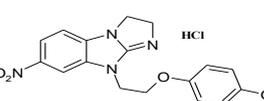
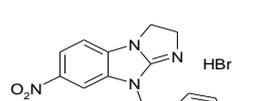
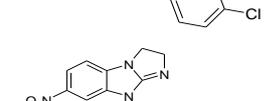
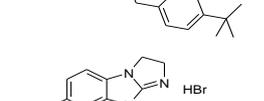
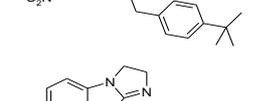


Figure 3 Calculated chemical shifts (^1H , ^{13}C and ^{15}N) for 9-*H*-6-nitro-2,3-dihydroimidazo-[1,2-*a*]benzimidazole.

S4. Antimicrobial activity of 9-substituted 7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazoles.

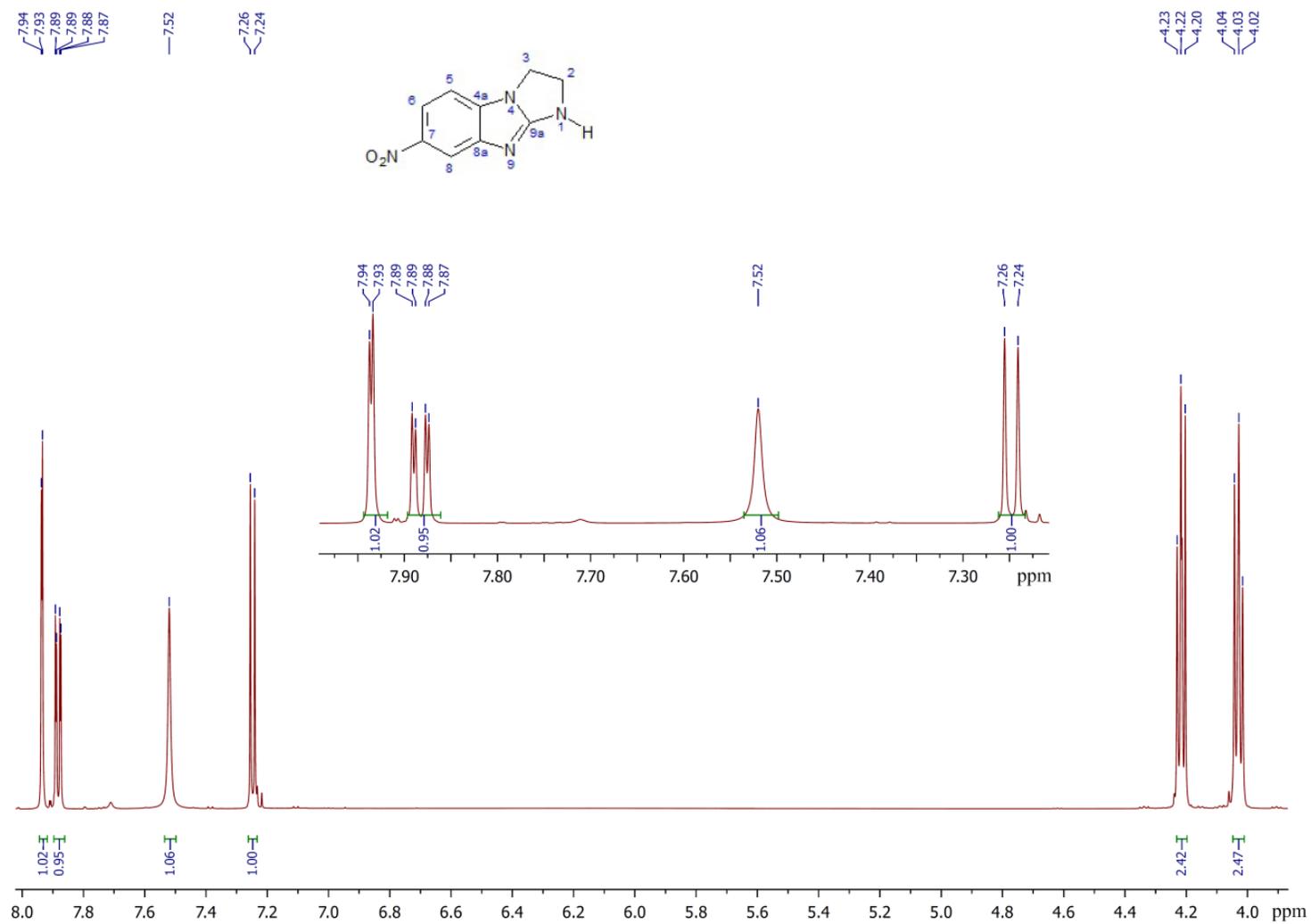
Compound	Structure	MIC/ $\mu\text{g ml}^{-1}$				
		<i>Colpoda steinii</i>	<i>P.italicum</i>	<i>St. aureus</i>	<i>E. coli</i>	
4h		62.5	0	0	10	
4h·HCl		15.6	0	0	10	
4j·HCl		1.9	12	12	15	
4i		31.25	0	0	0	
4i·HCl		3.9	0	10	0	
4f·HBr		3.9	0	0	15	
4e		31.25	0	12	0	
4e·HBr		1.98	14	0	12	
Comparison drugs	6*		1.9	12	8	22
	Toltrazuril		62.5	-	-	-
	Fundazol		-	35	-	-
	Furazolidon		-	-	25	28

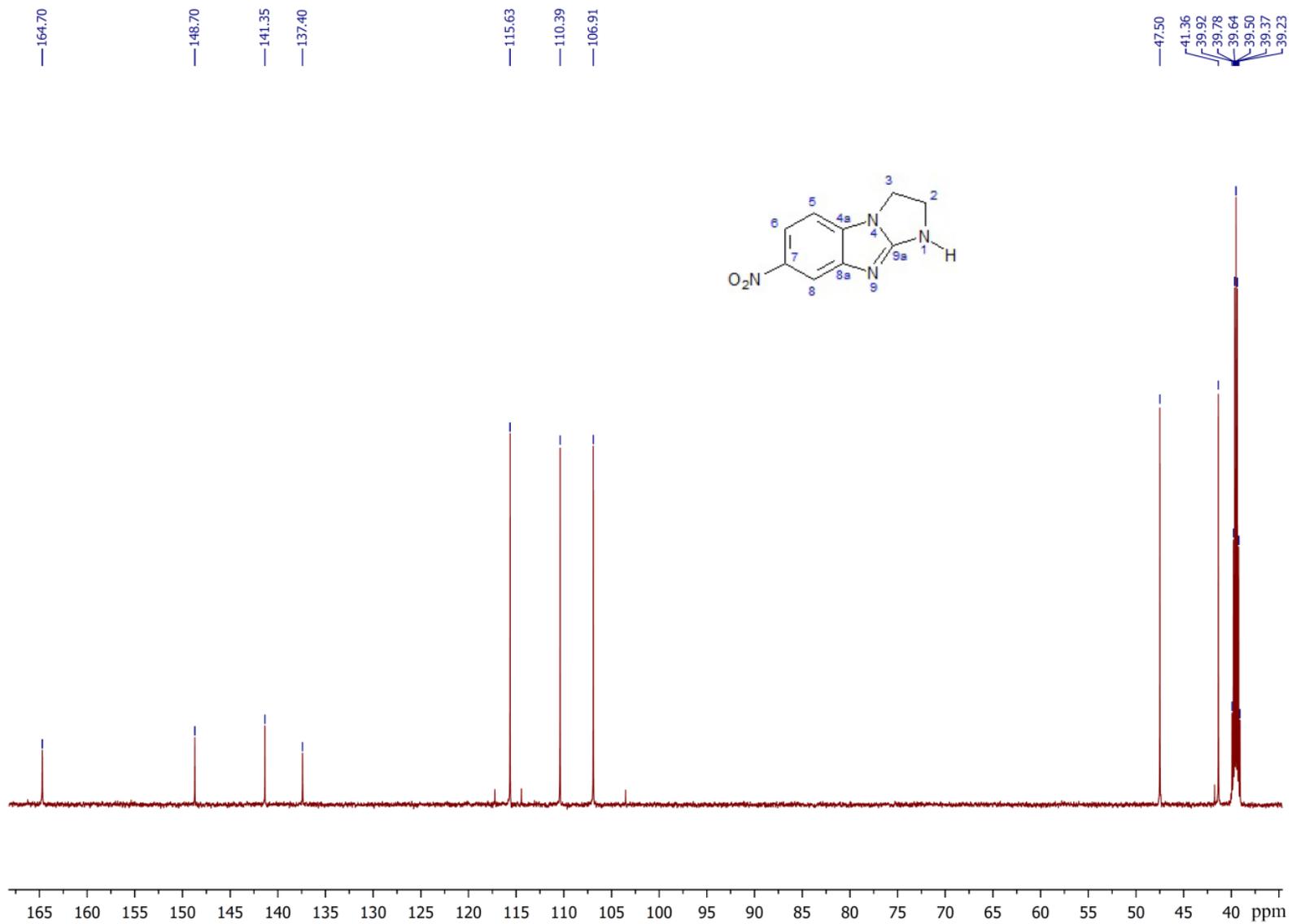
*Compound **6** was described in the article [S10]

S5. References

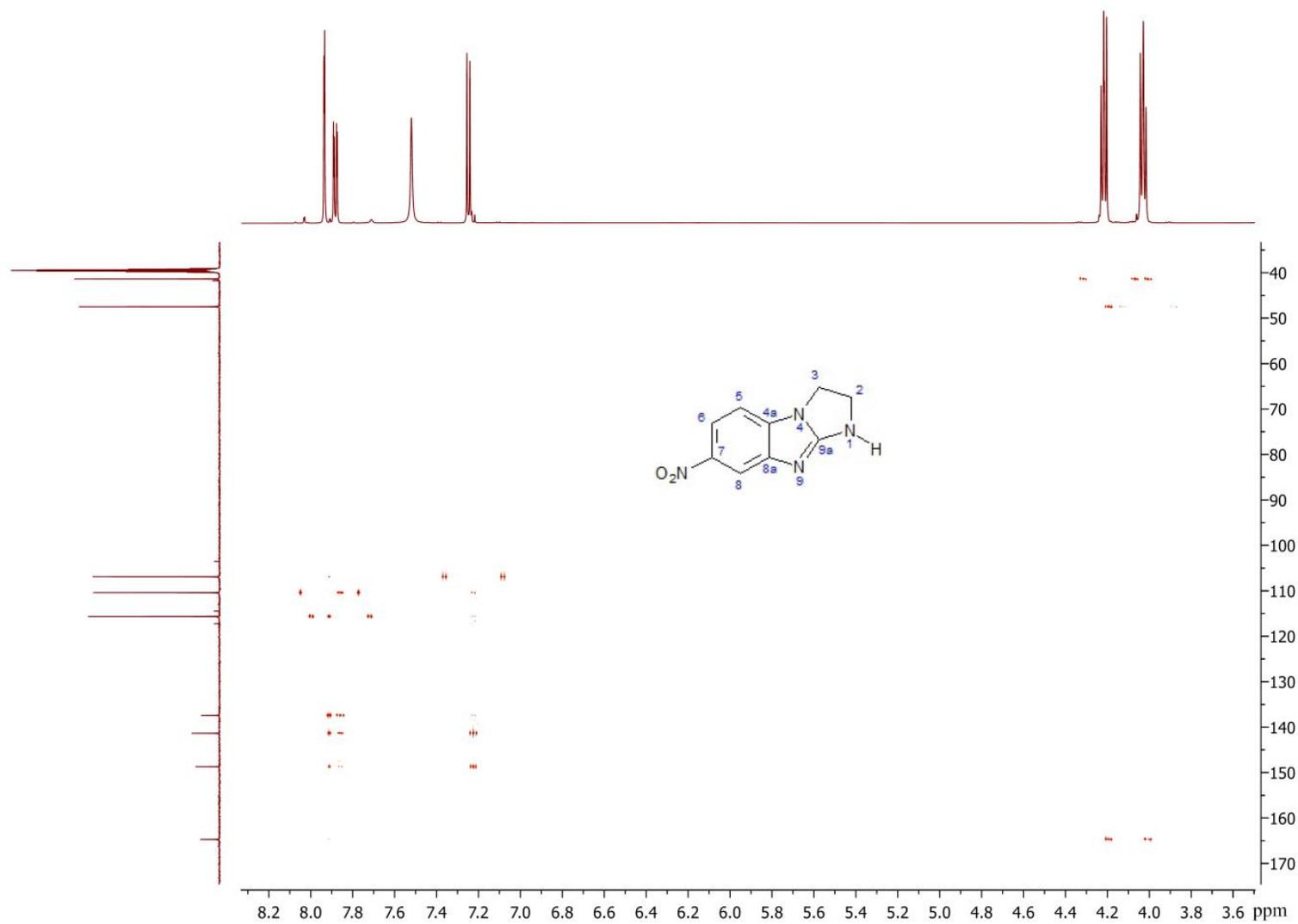
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S5. NMR spectra of compounds 3 and 4a-n.
7-Nitro-2,3-dihydro-1*H*-imidazo[1,2-*a*]benzimidazole (**3**).

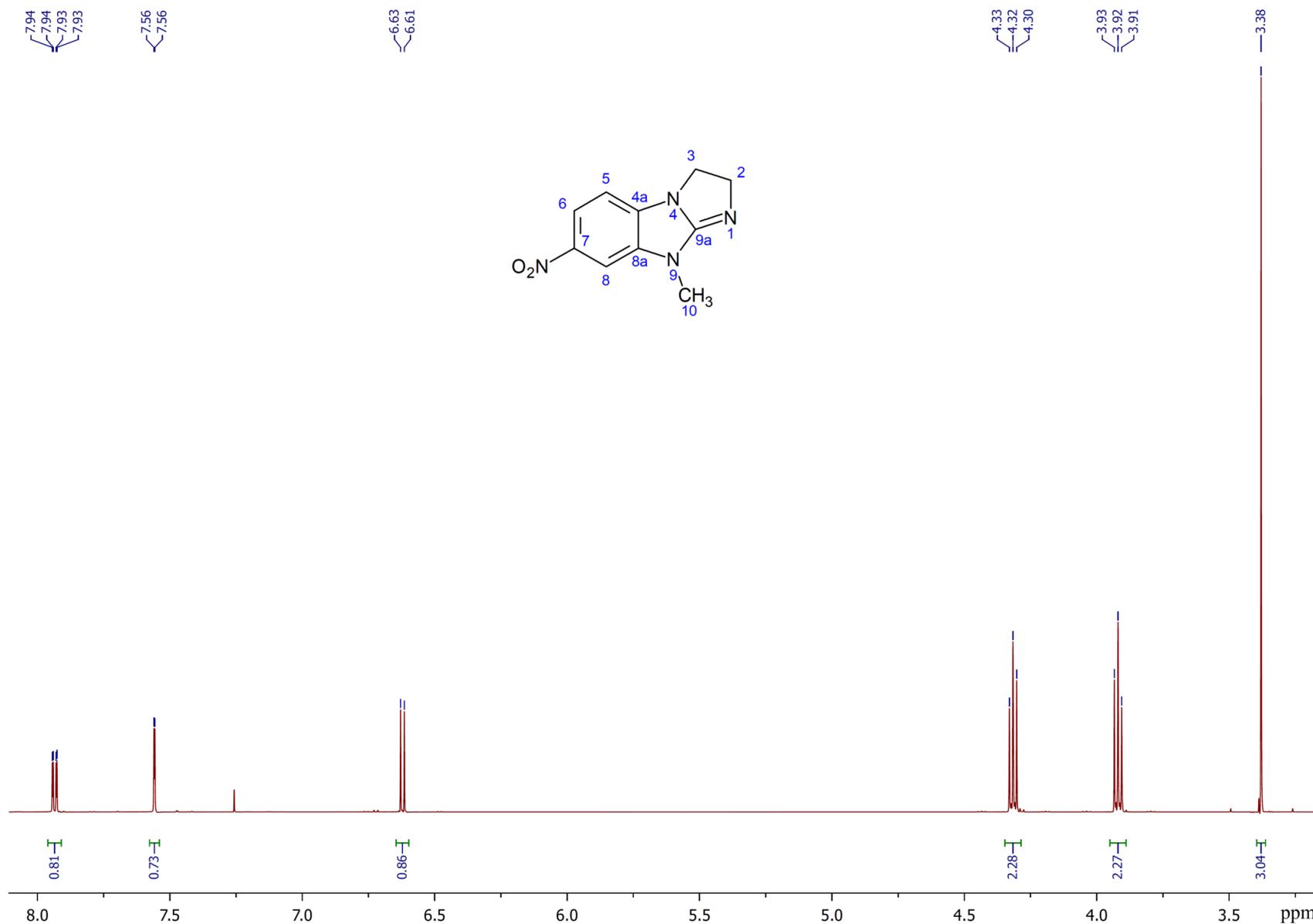


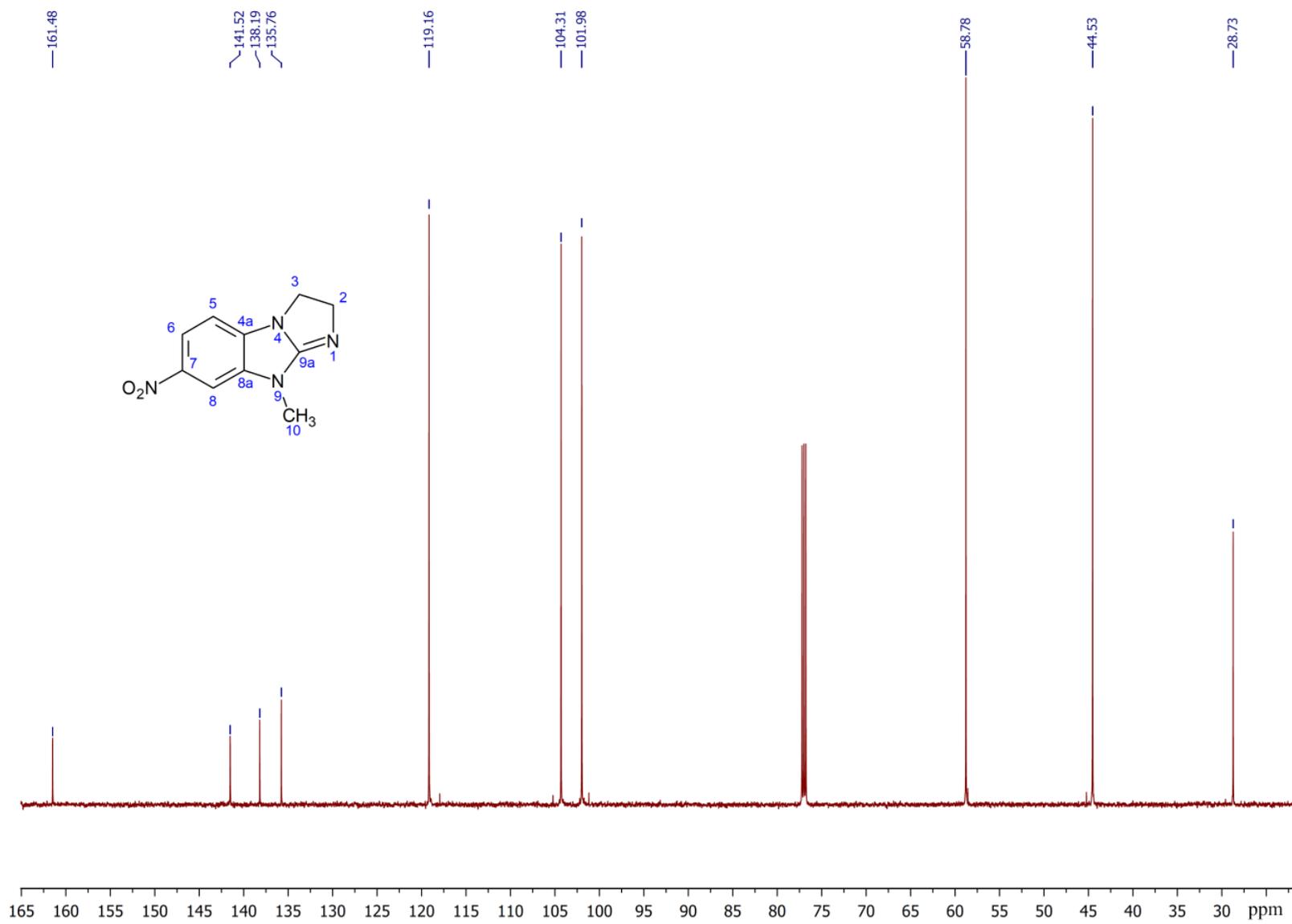


^1H - ^{13}C HMBC

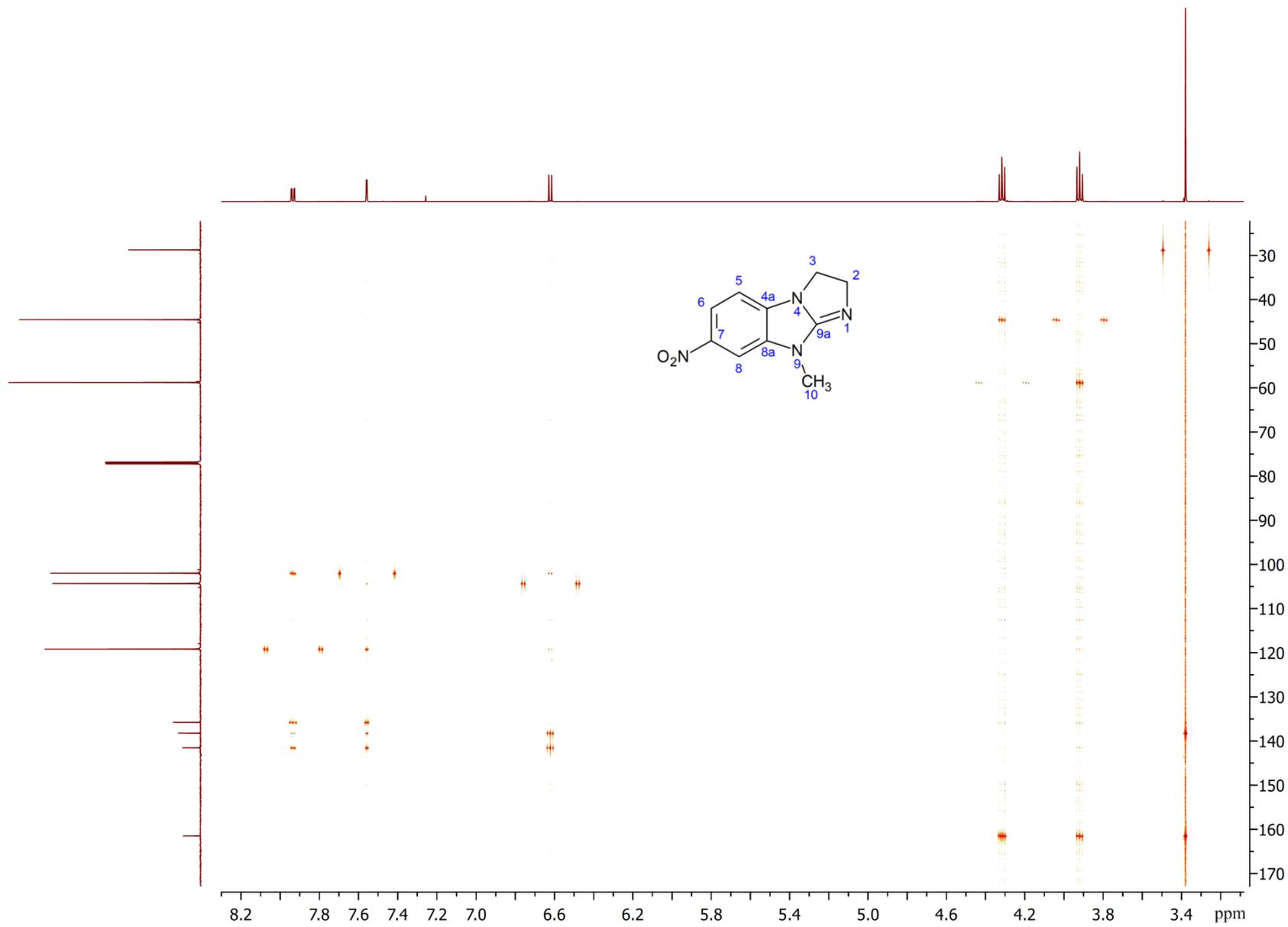


9-Methyl-7-nitro-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazole (**4a**).

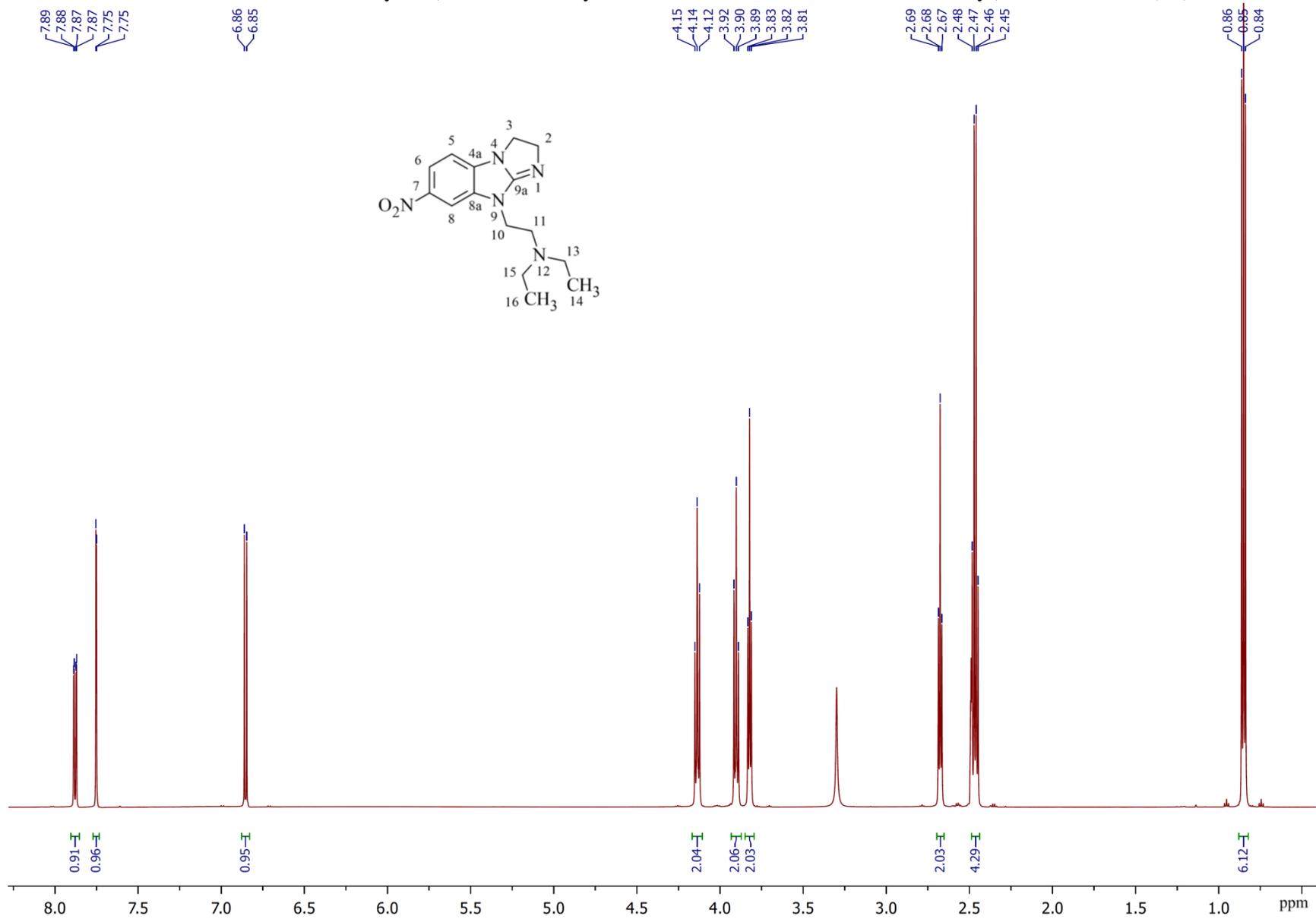


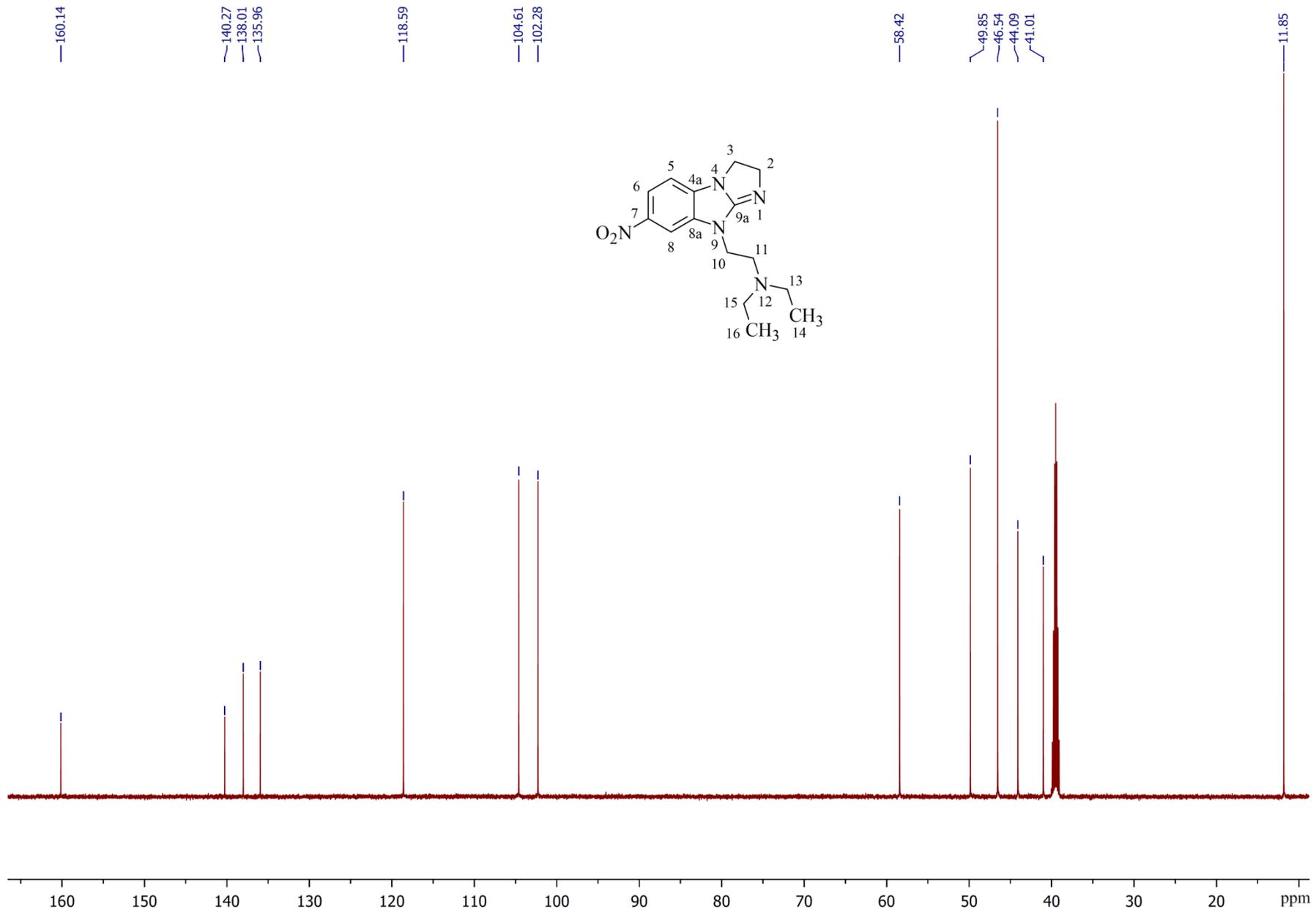


^1H - ^{13}C HMBC

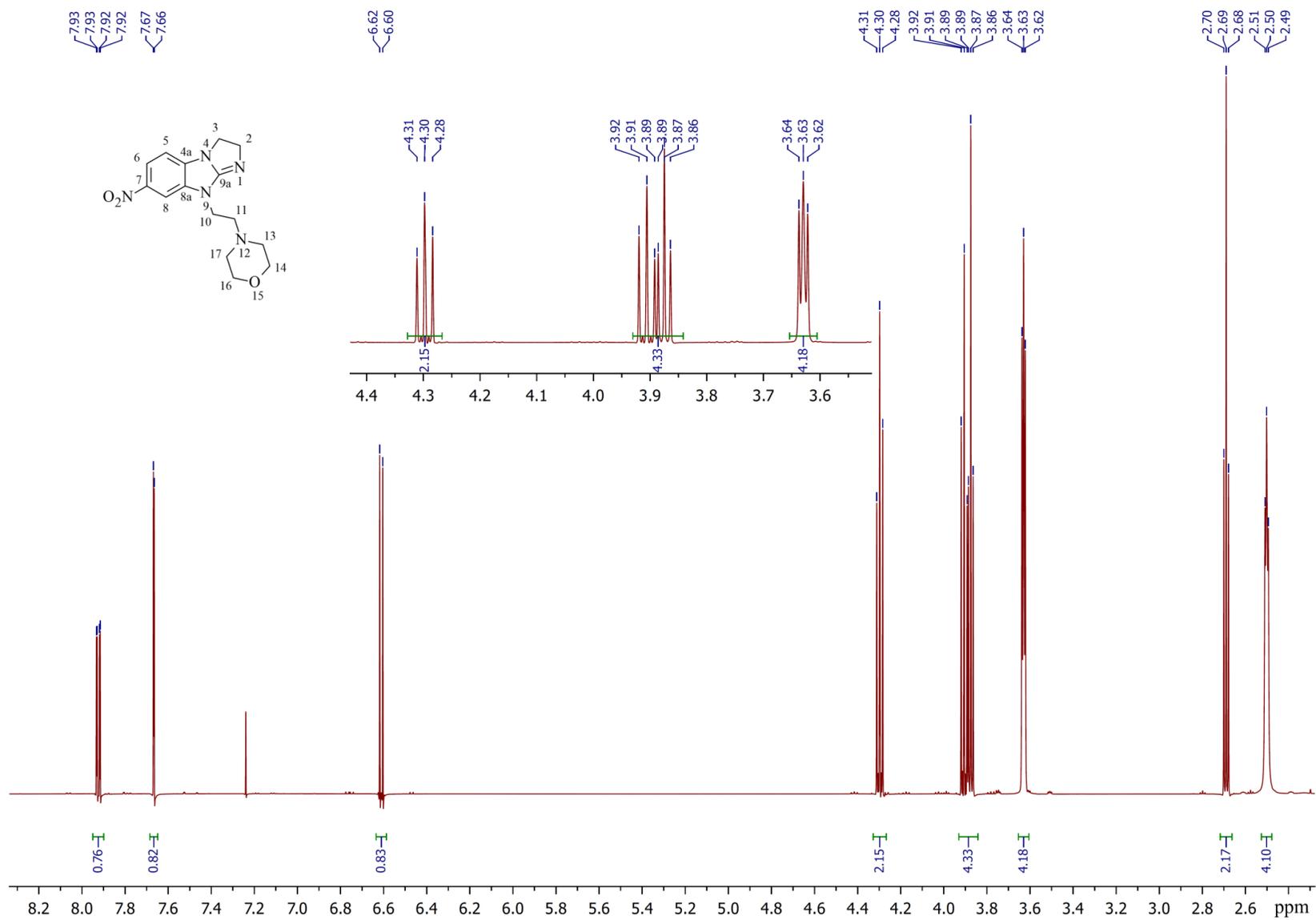


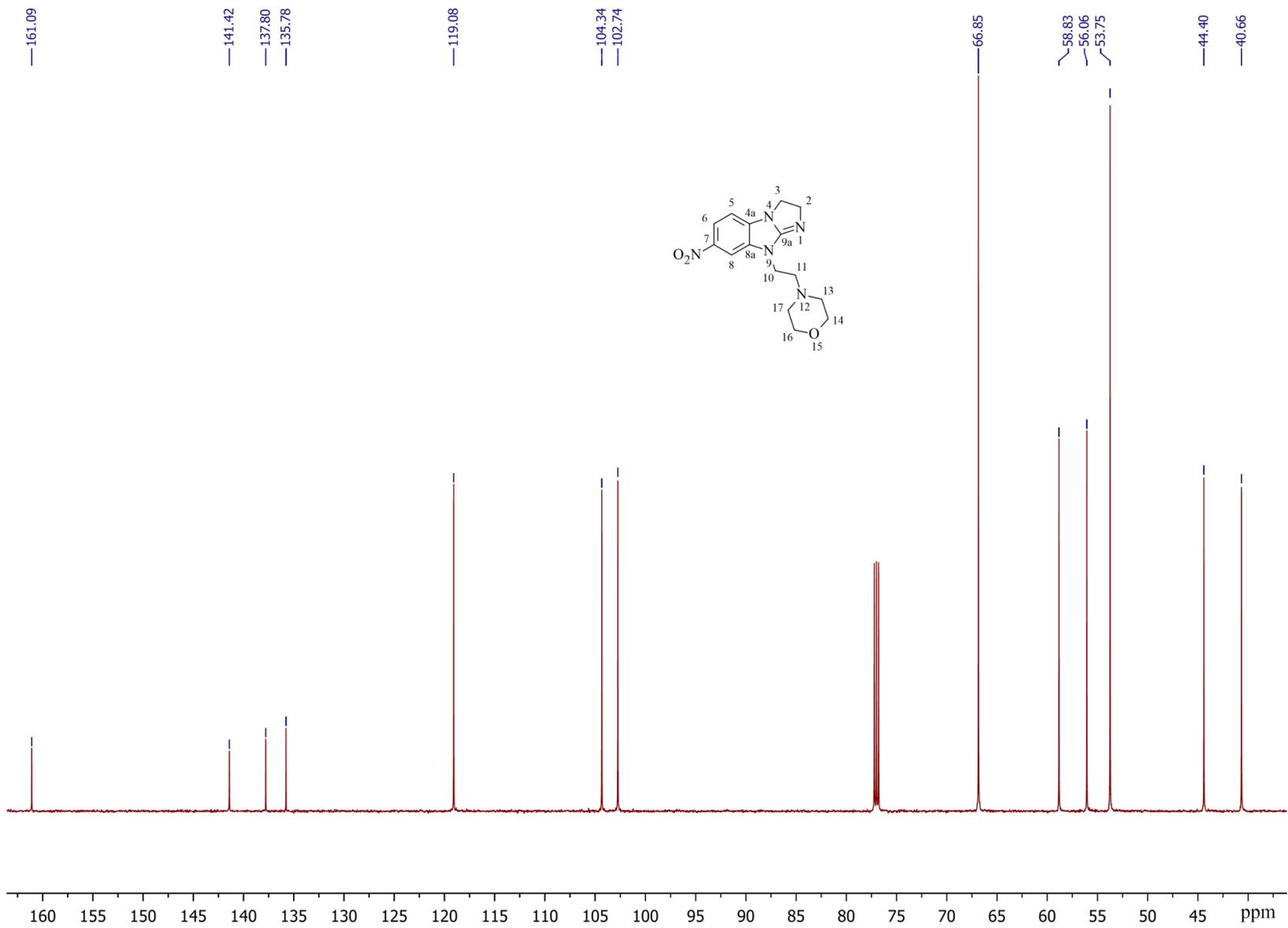
N,N-Diethyl-2-(7-nitro-2,3-dihydro-9*H*-imidazo[1,2-*a*]benzimidazol-9-yl)ethan-1-amine (**4b**).



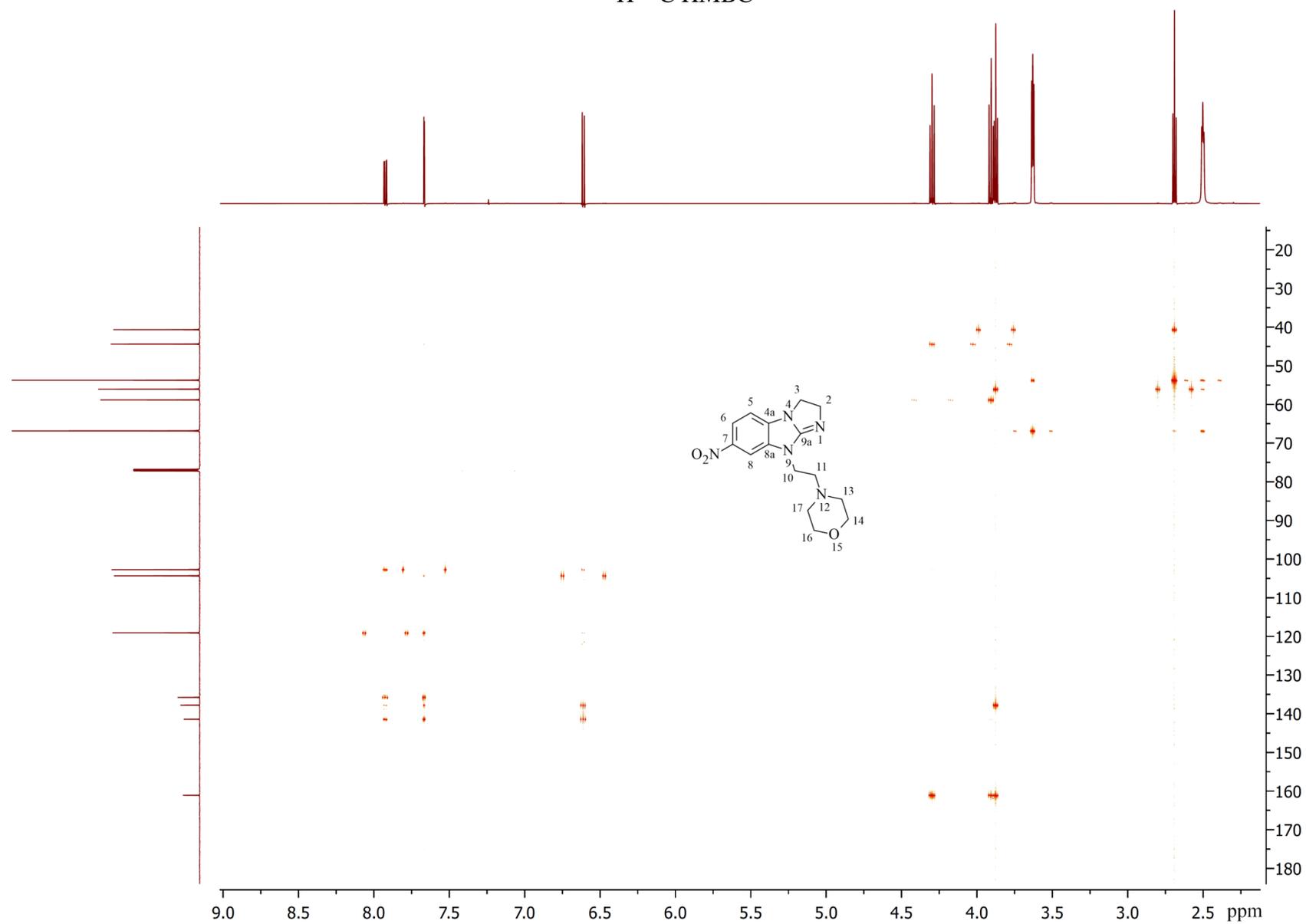


9-[2-(Morpholin-4-yl)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4c**).

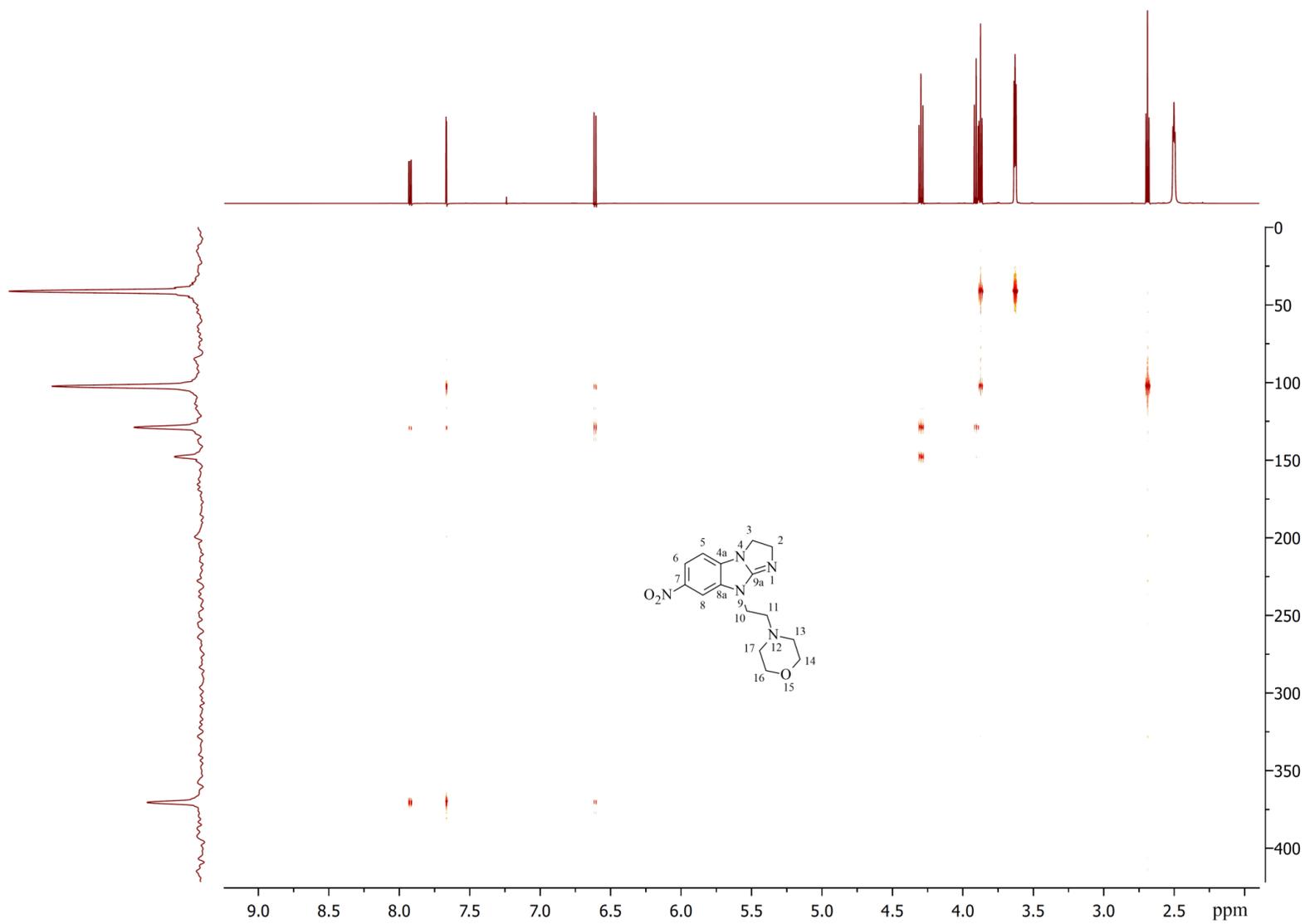




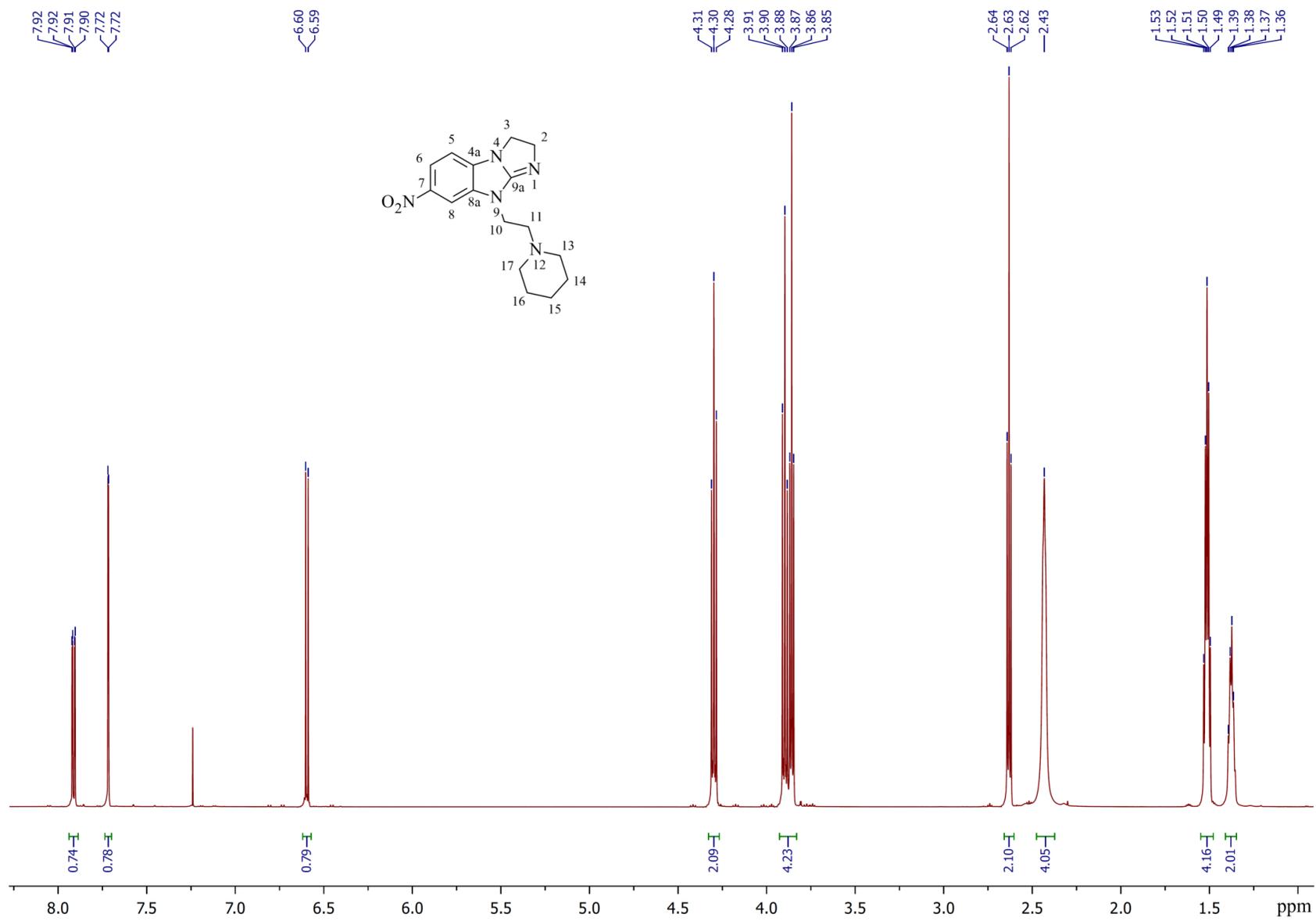
^1H - ^{13}C HMBC

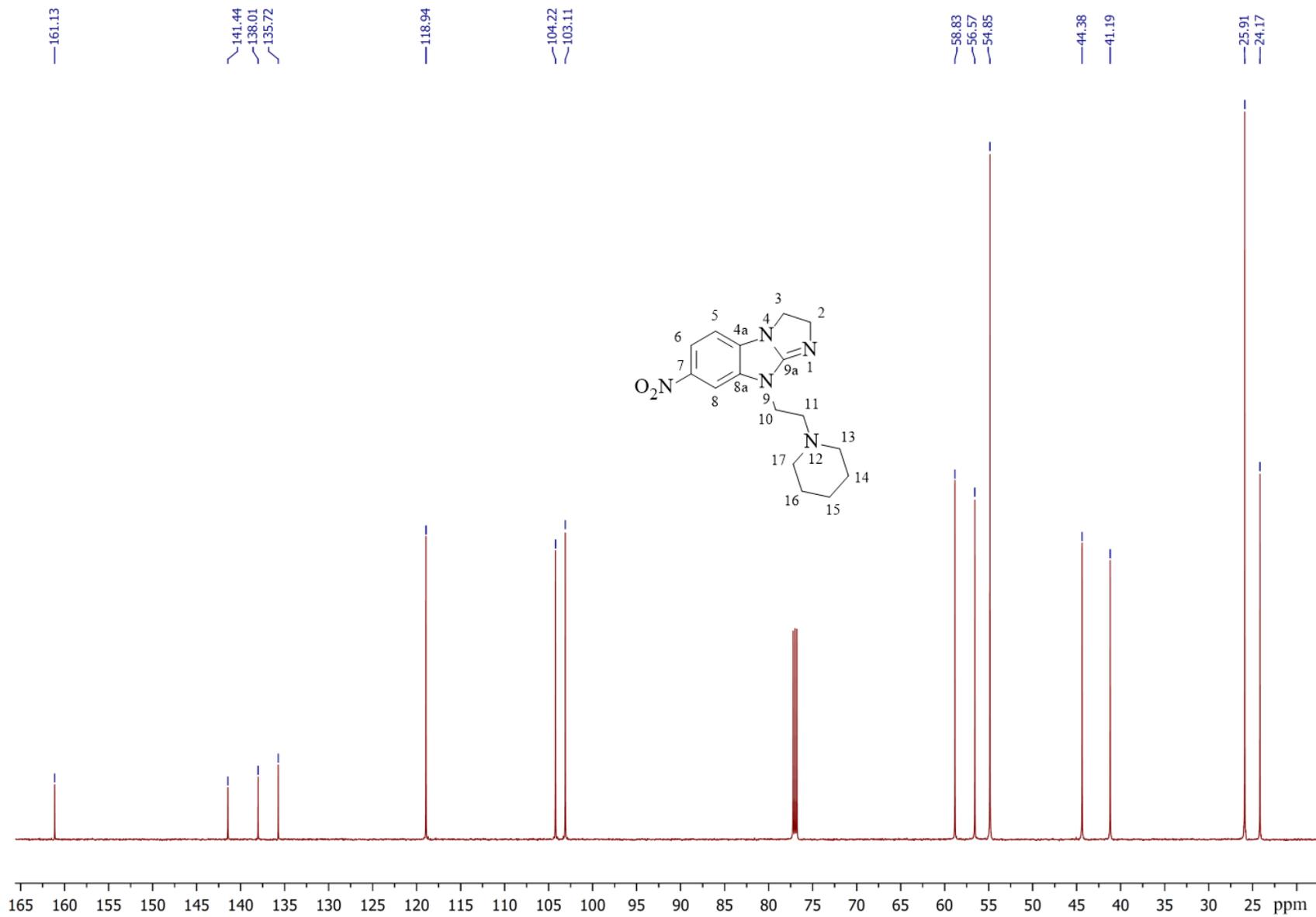


^1H - ^{15}N HMBC

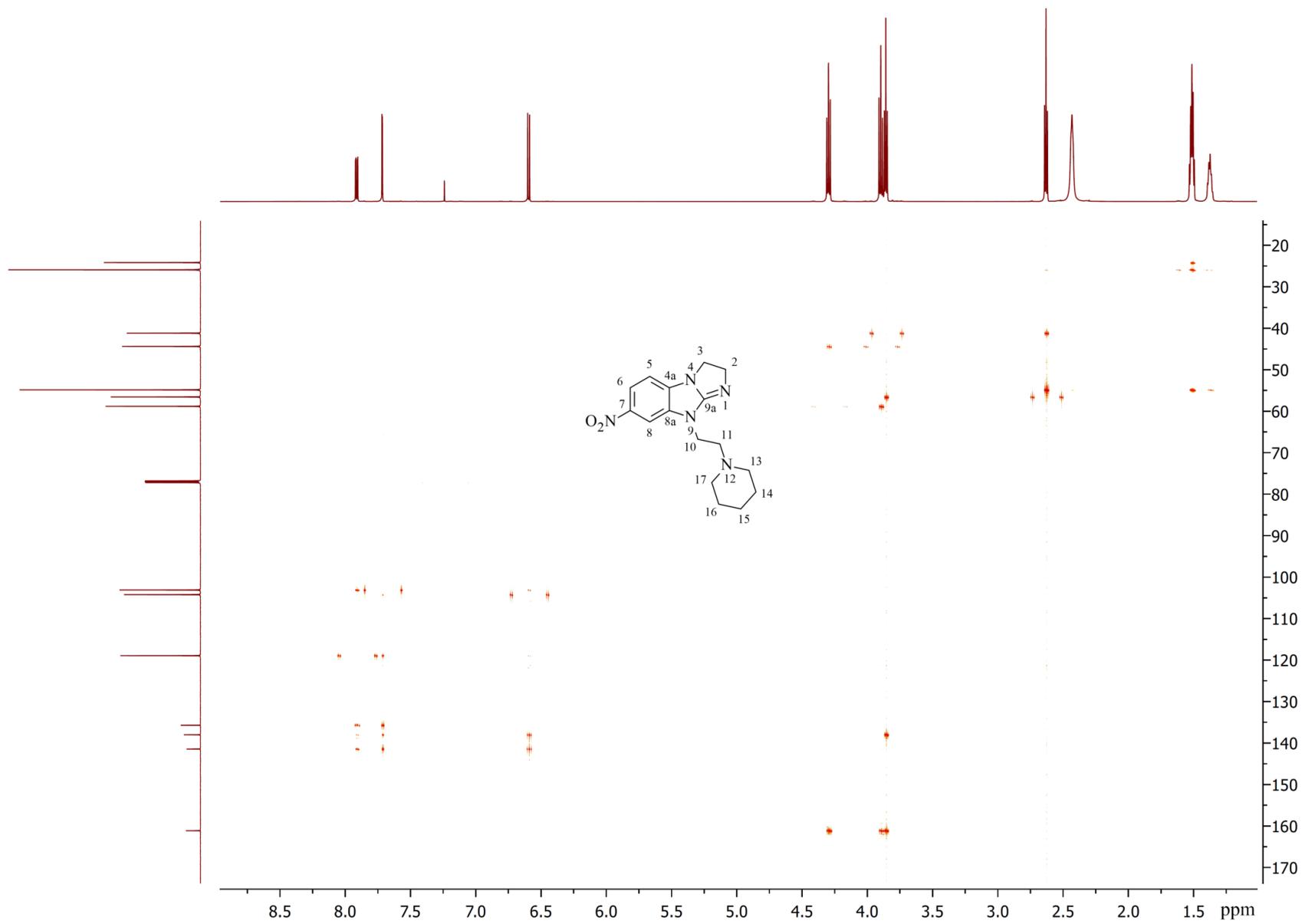


7-Nitro-9-[2-(piperidin-1-yl)ethyl]-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4d**).

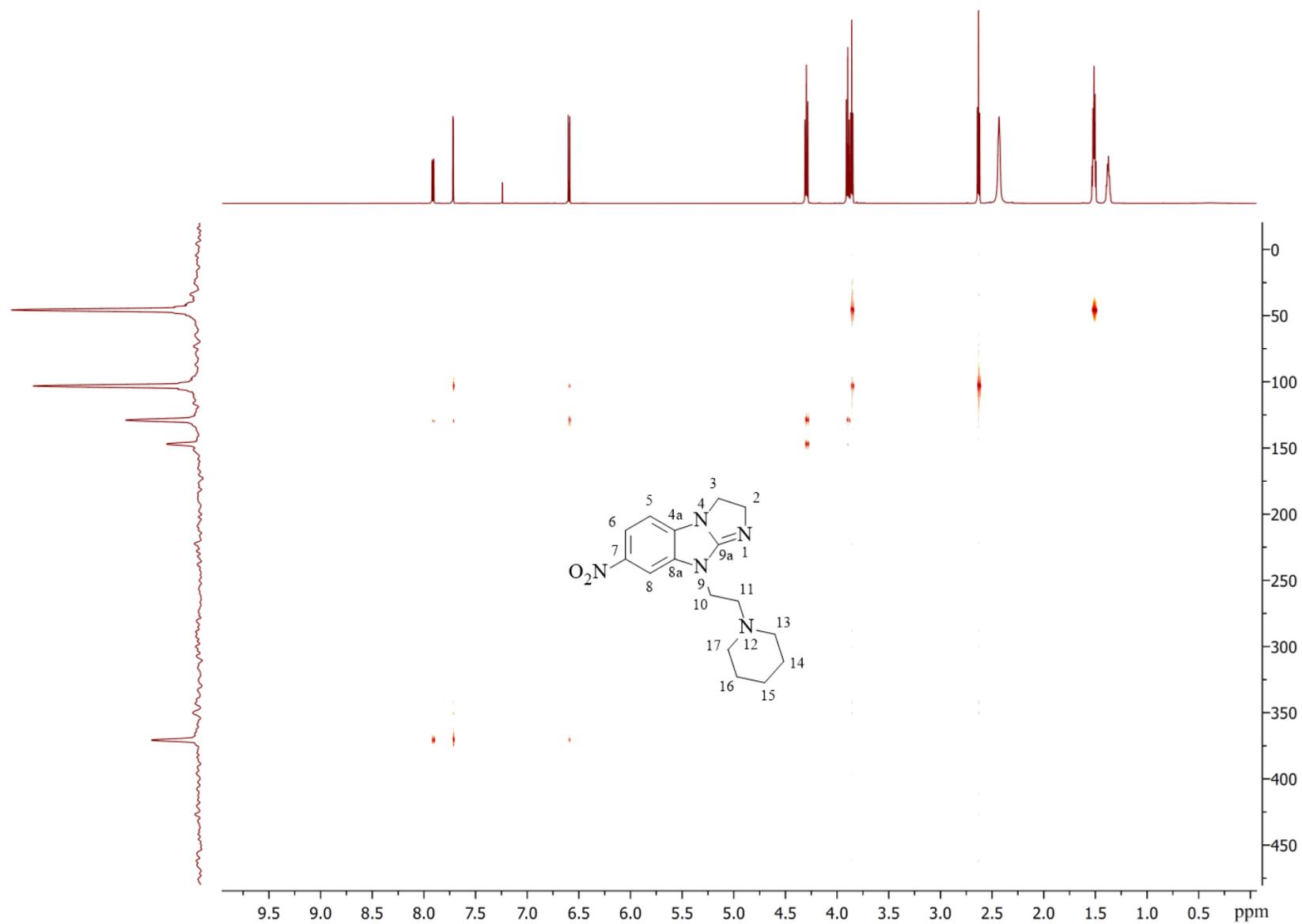




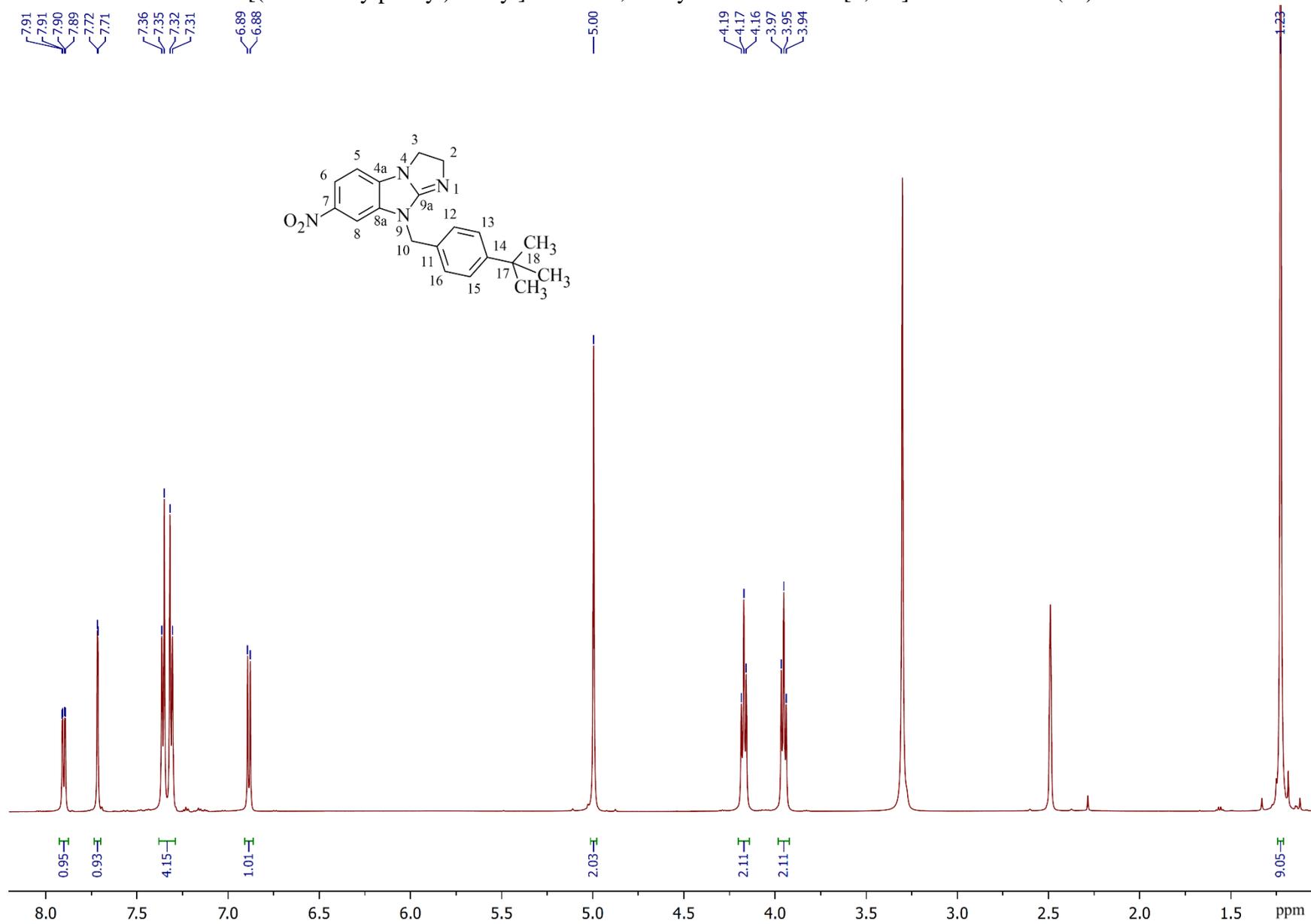
^1H - ^{13}C HMBC

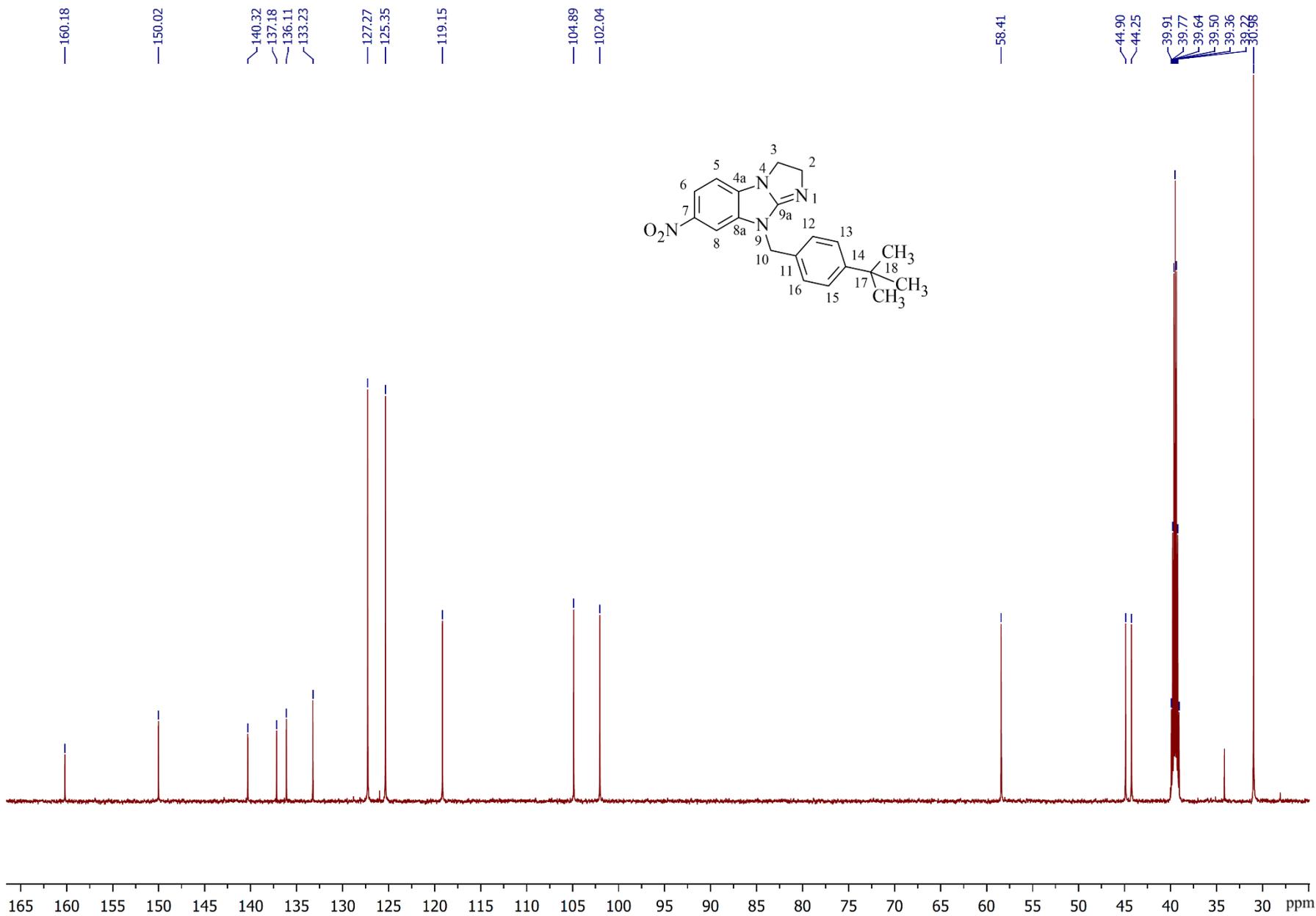


^1H - ^{15}N HMBC

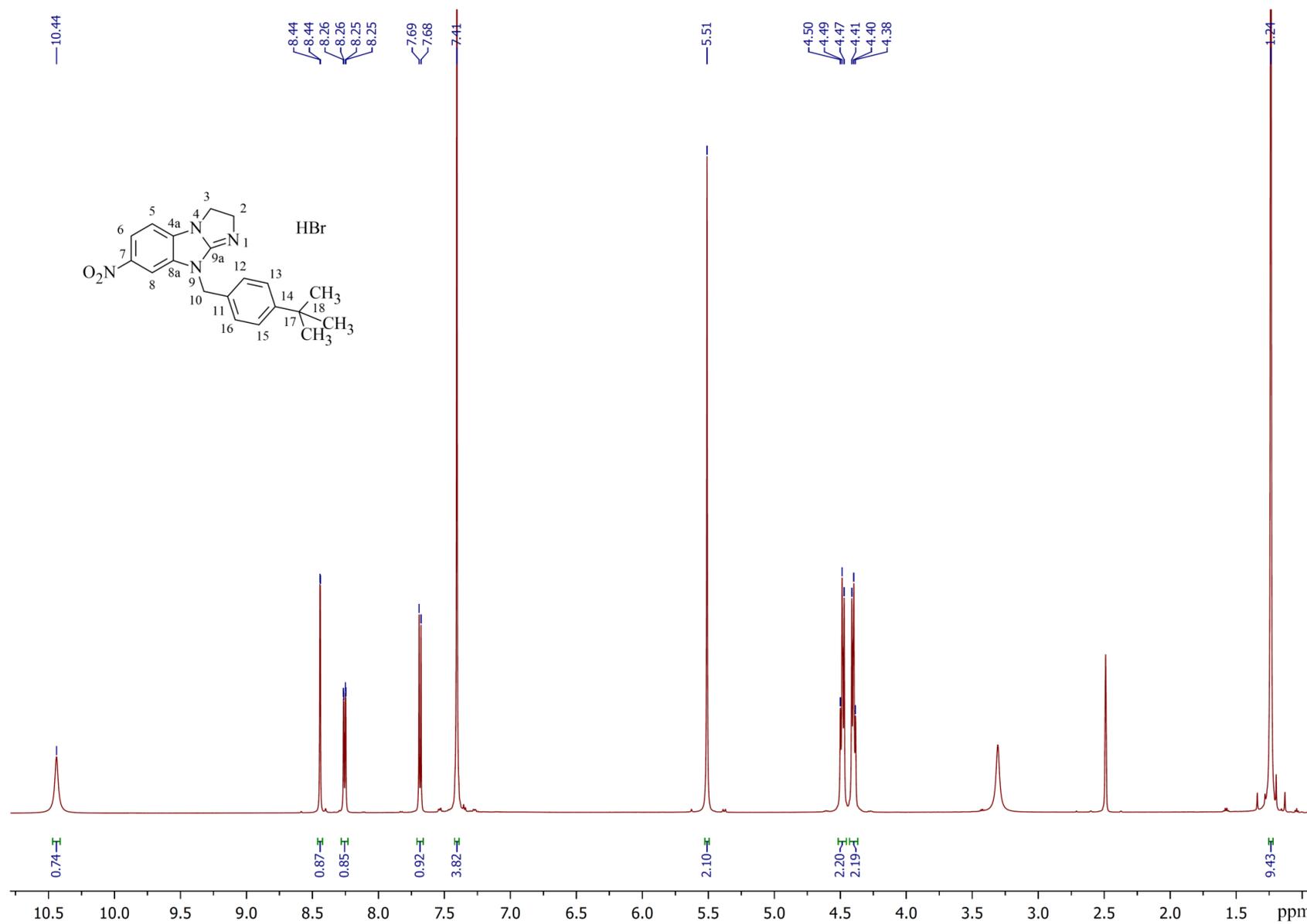


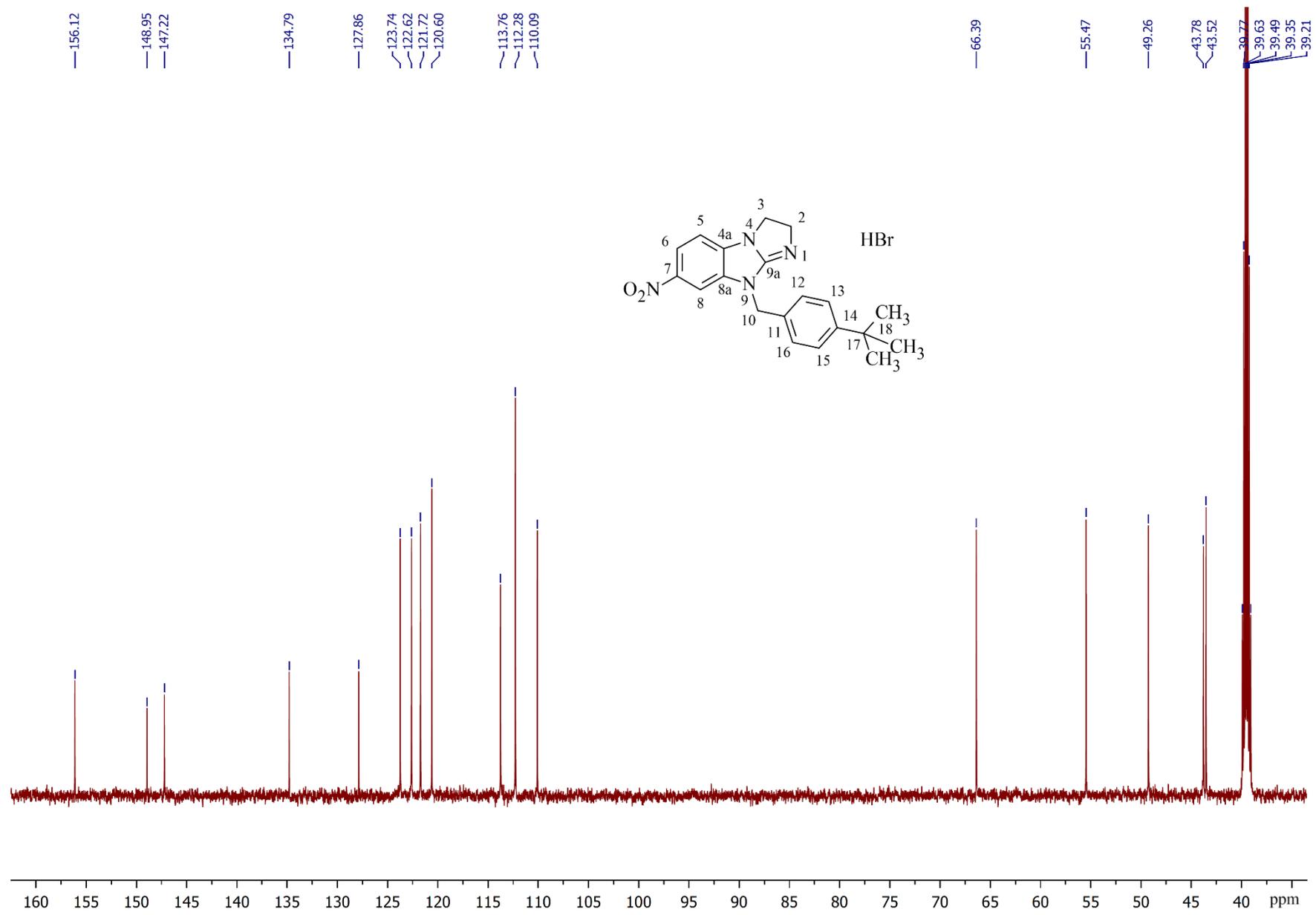
9-[(4-*tert*-Butylphenyl)methyl]-7-nitro-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazole (**4e**).



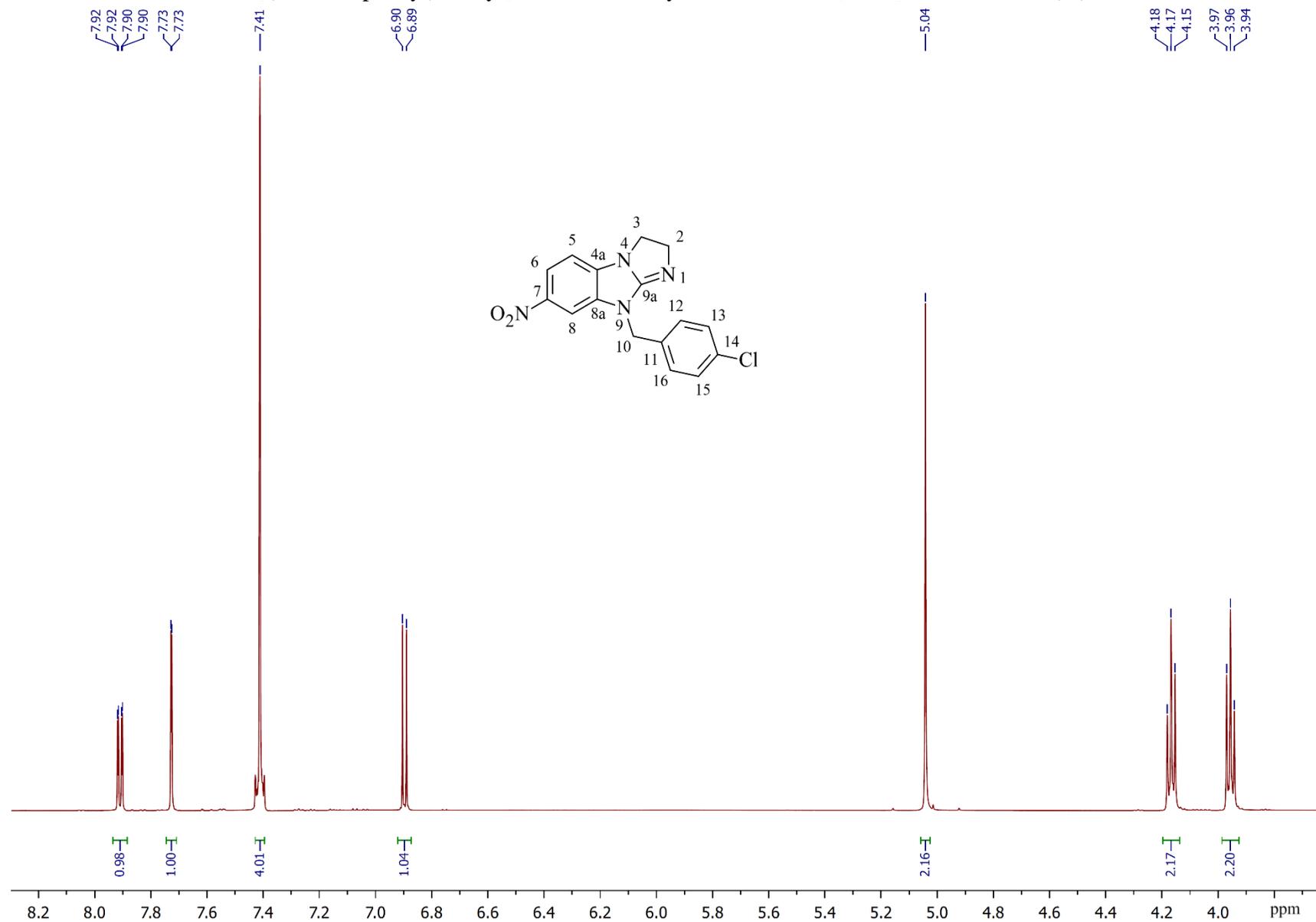


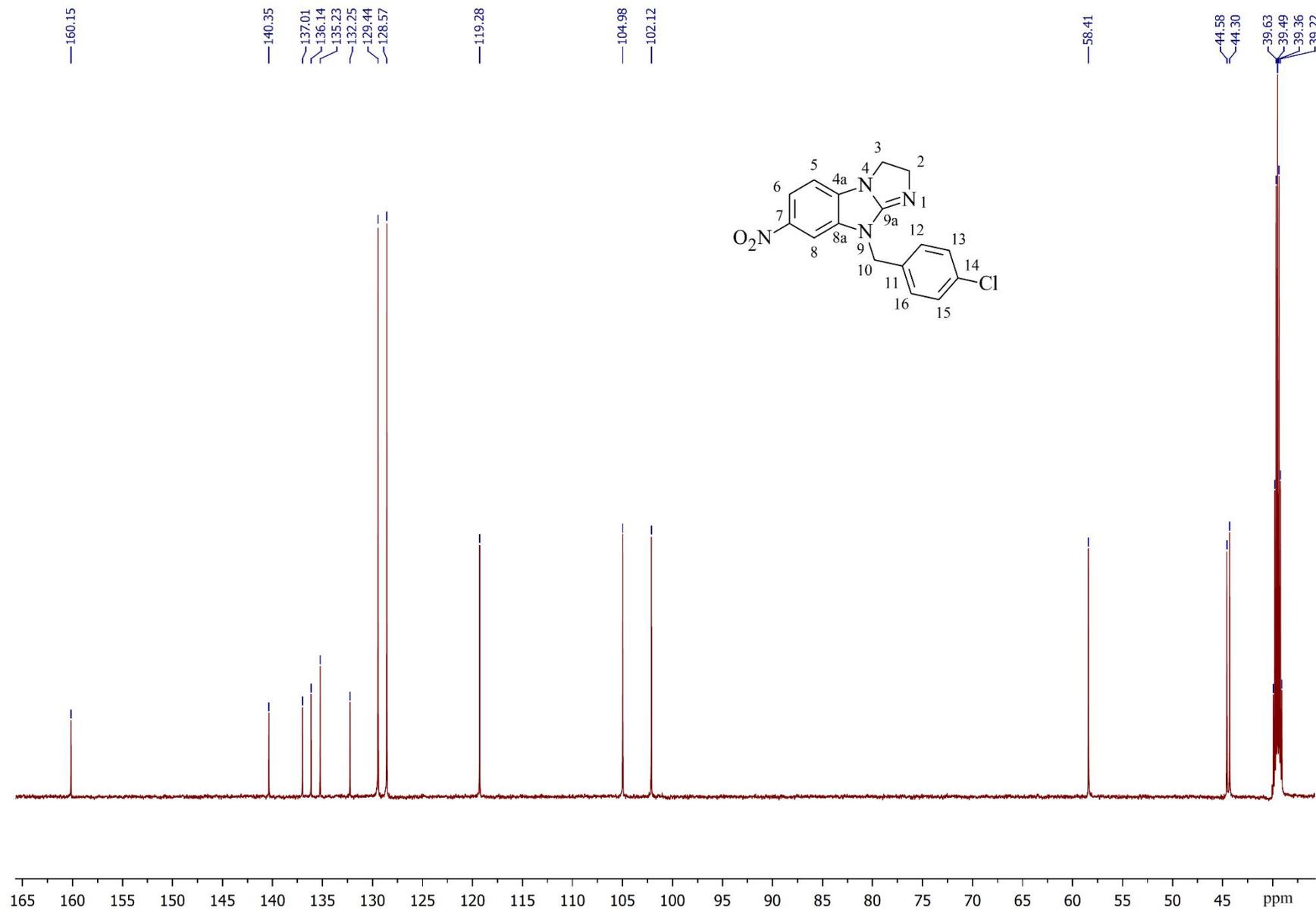
9-[(4-*tert*-Butylphenyl)methyl]-7-nitro-2,9-dihydro-3*H*-imidazo[1,2-*a*]benzimidazole hydrobromide (**4e**·HBr).



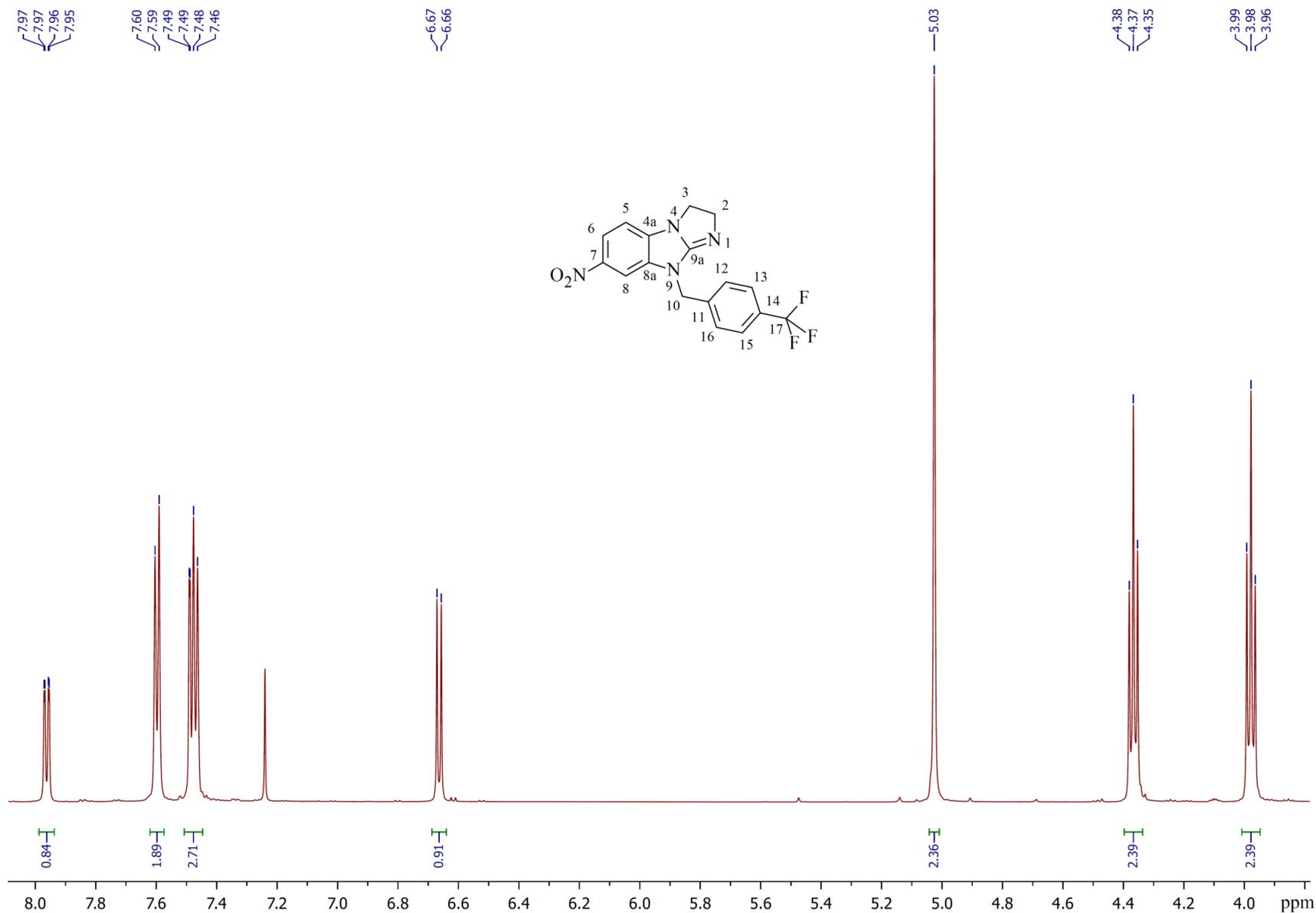


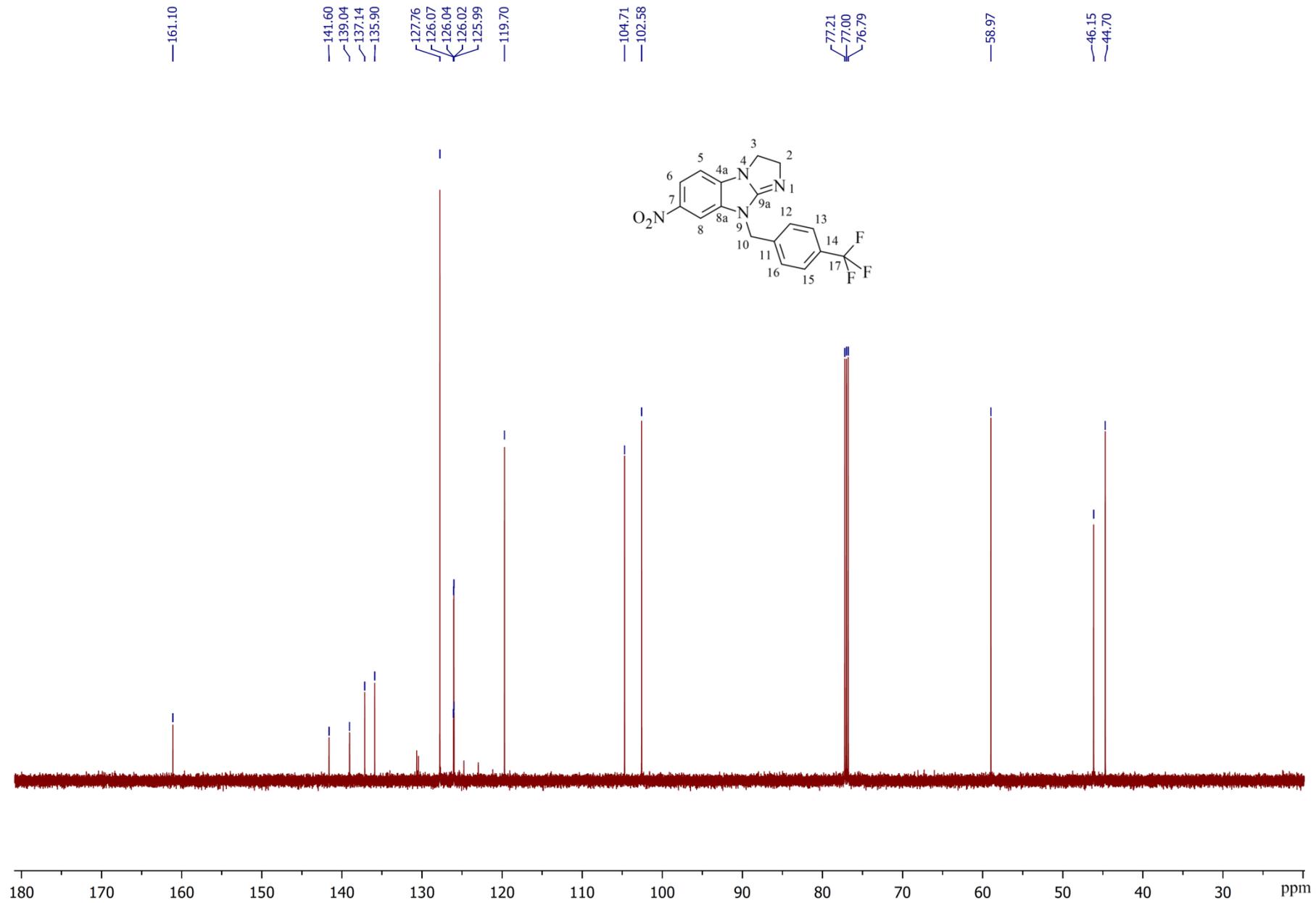
9-[(4-Chlorophenyl)methyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4f**).



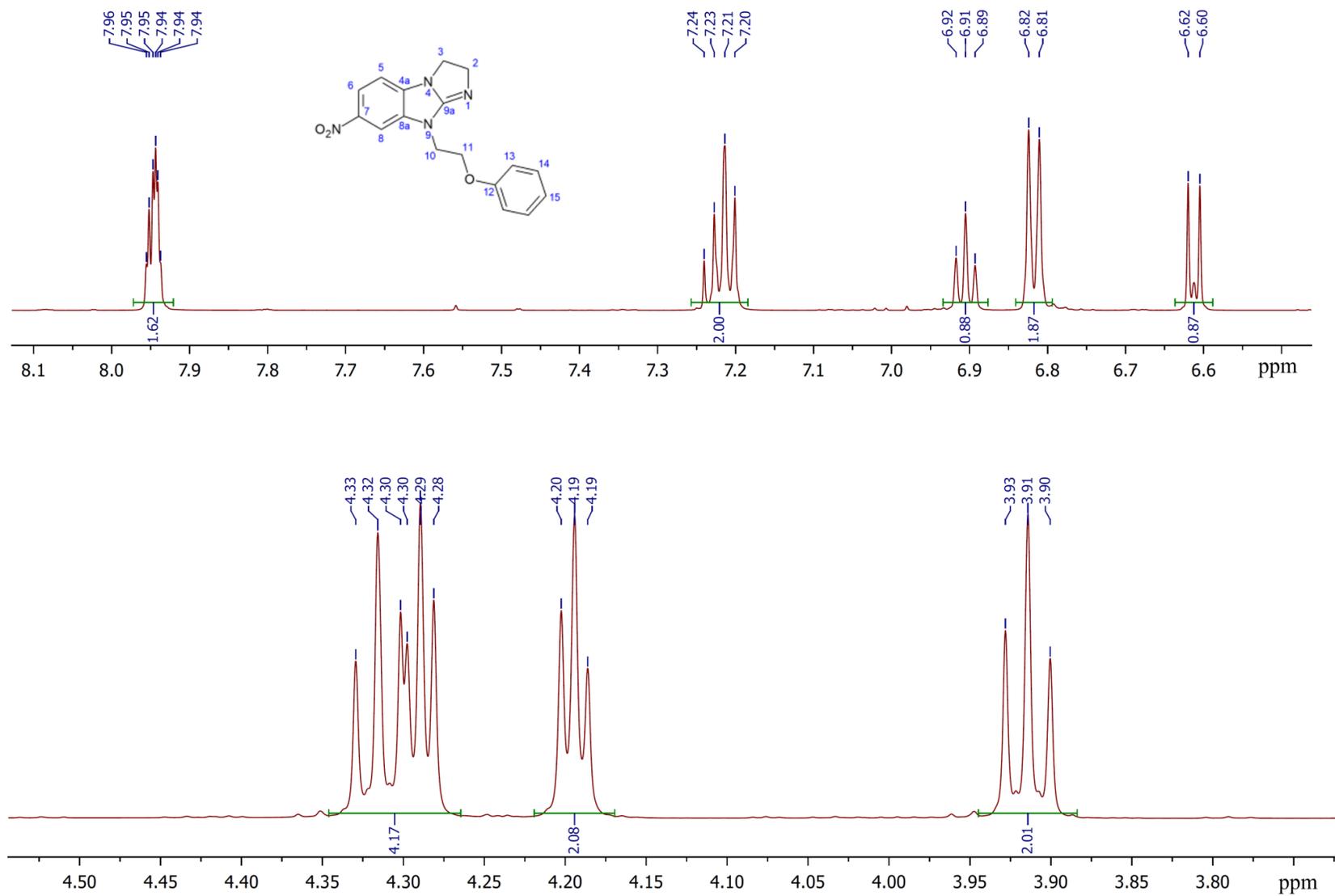


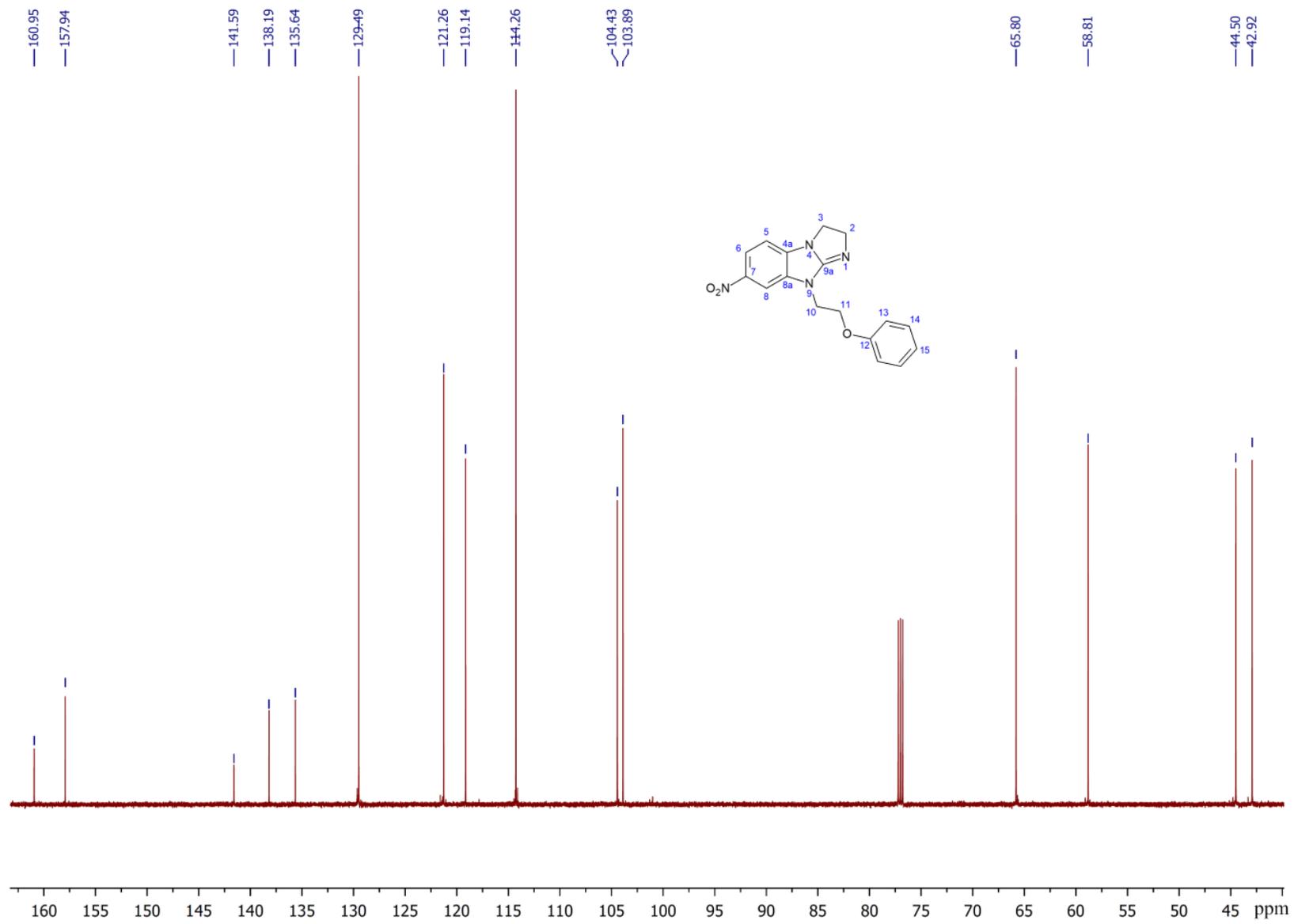
7-Nitro-9-{[4-(trifluoromethyl)phenyl]methyl}-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole (**4g**).



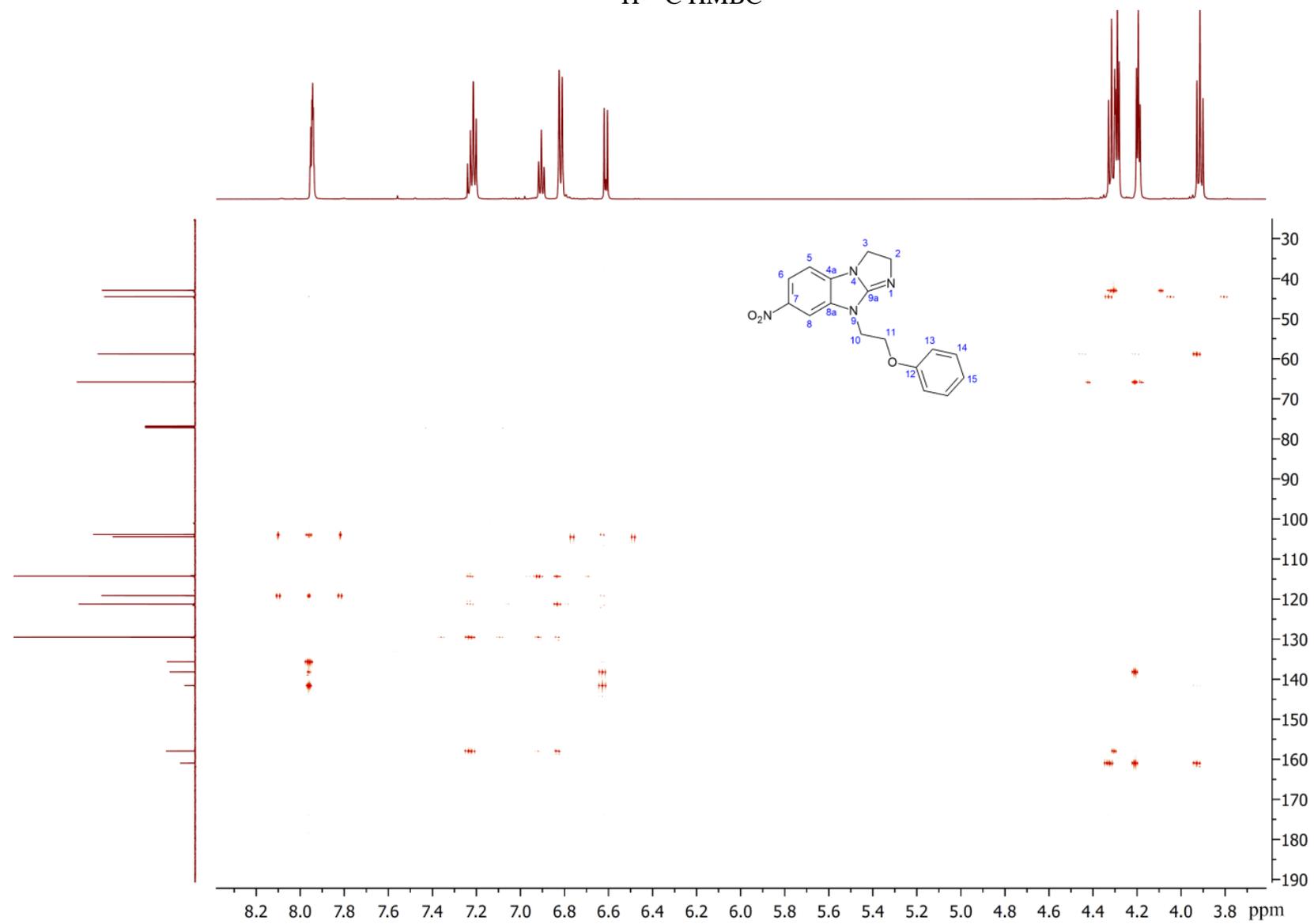


7-Nitro-9-(2-phenoxyethyl)-2,9-dihydro-3H-imidazo[1,2-*a*]benzimidazole (**4h**).

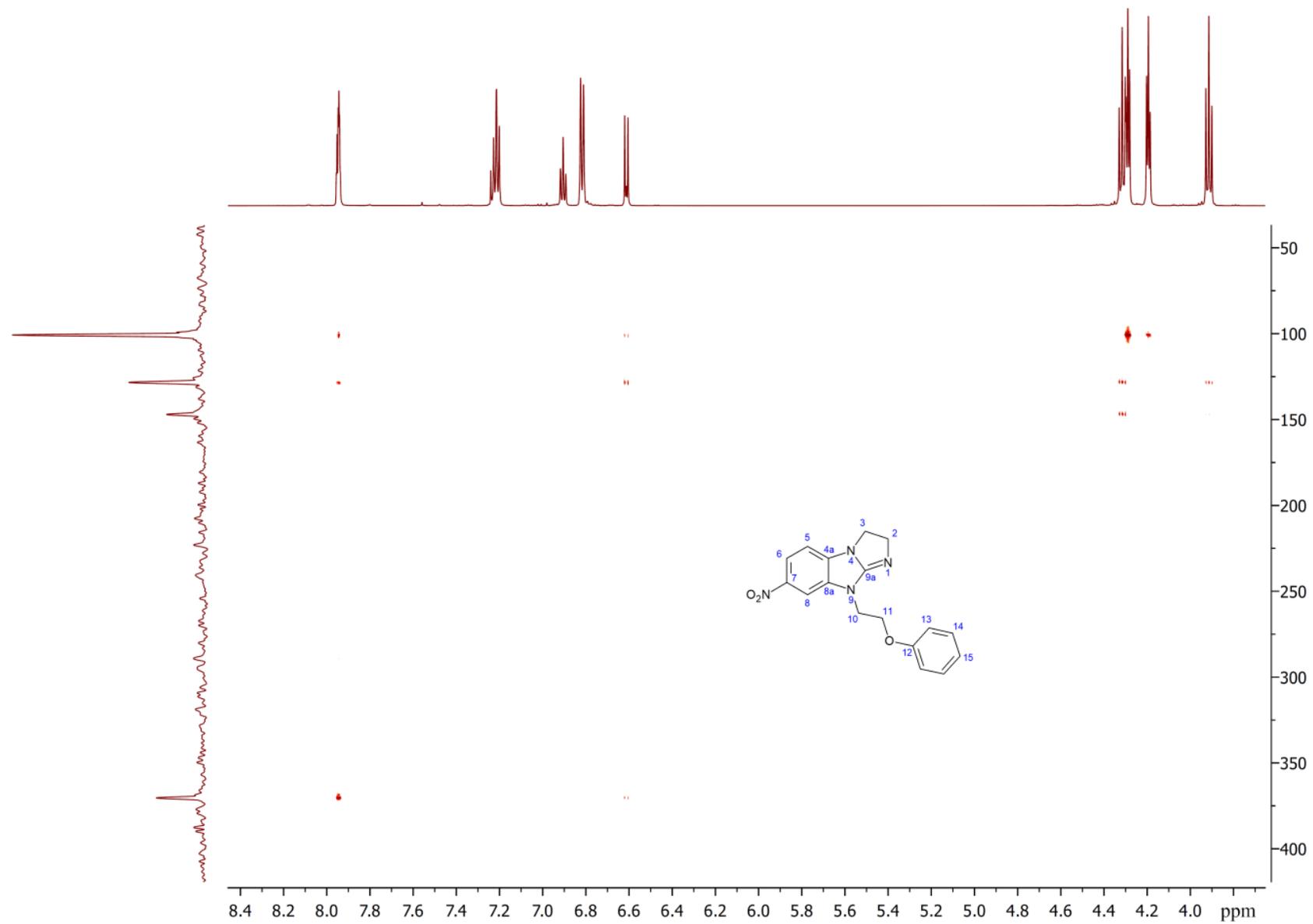




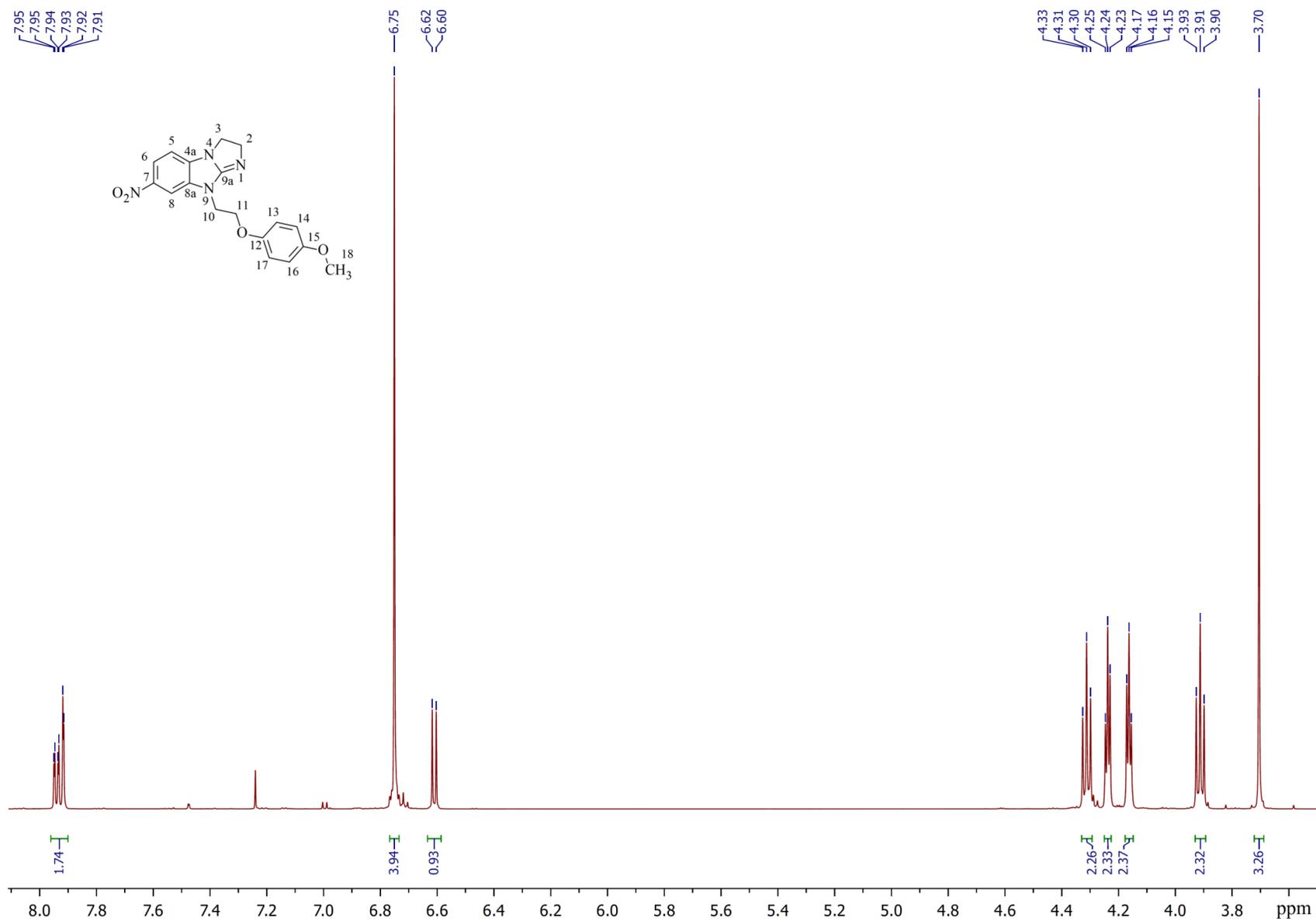
^1H - ^{13}C HMBC

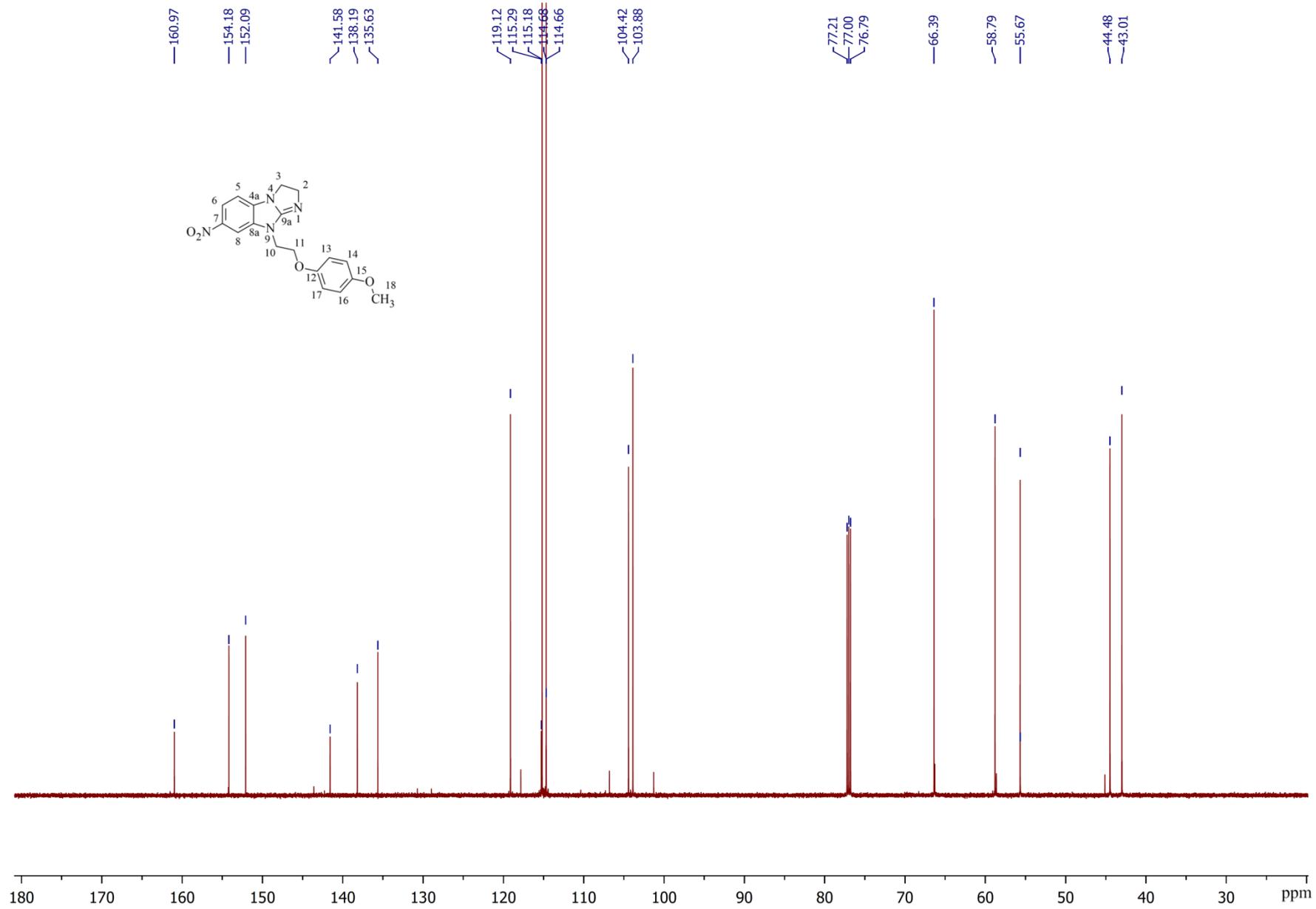


^1H - ^{15}N HMBC

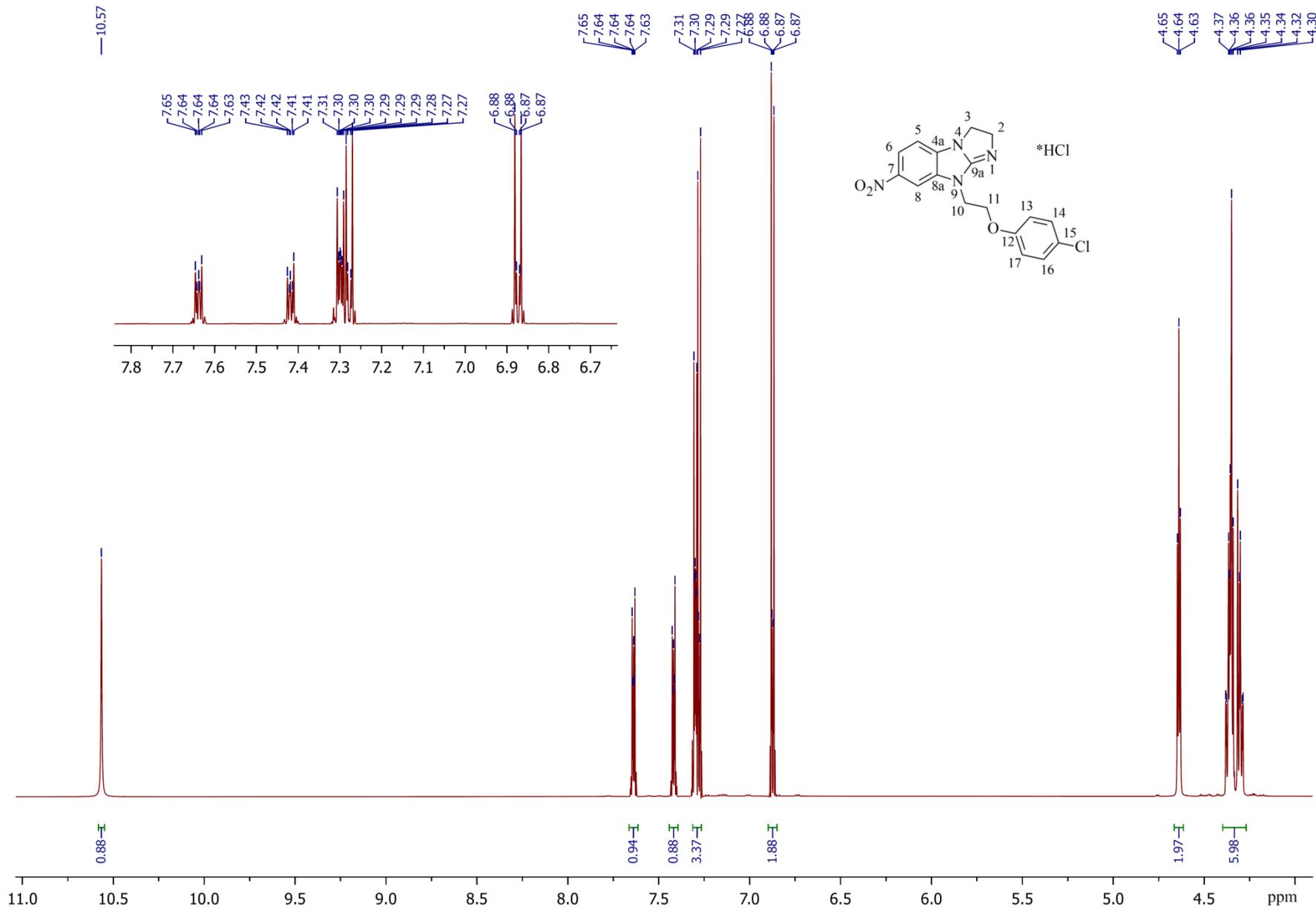


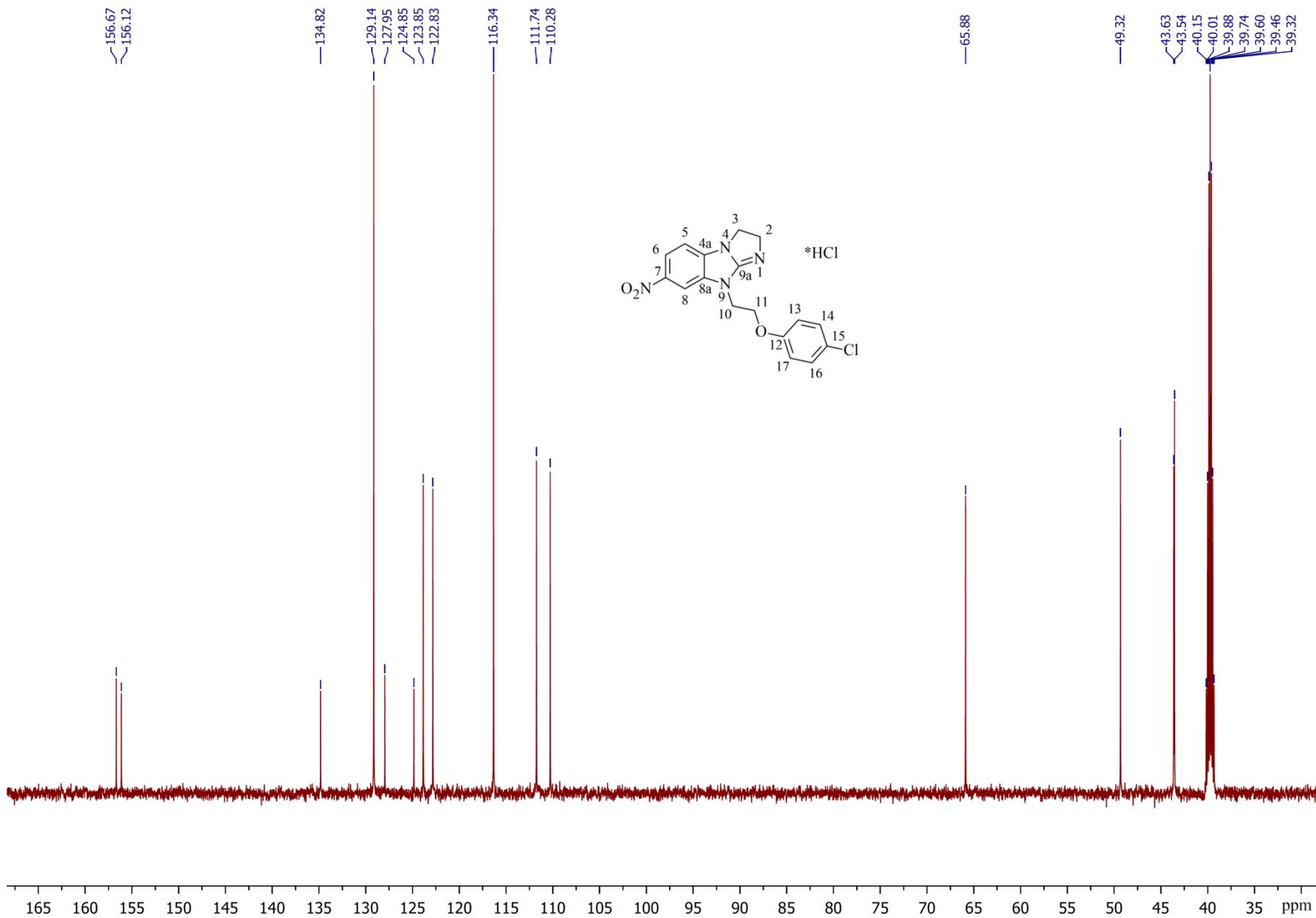
9-[2-(4-Methoxyphenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-*a*]benzimidazole (**4i**).



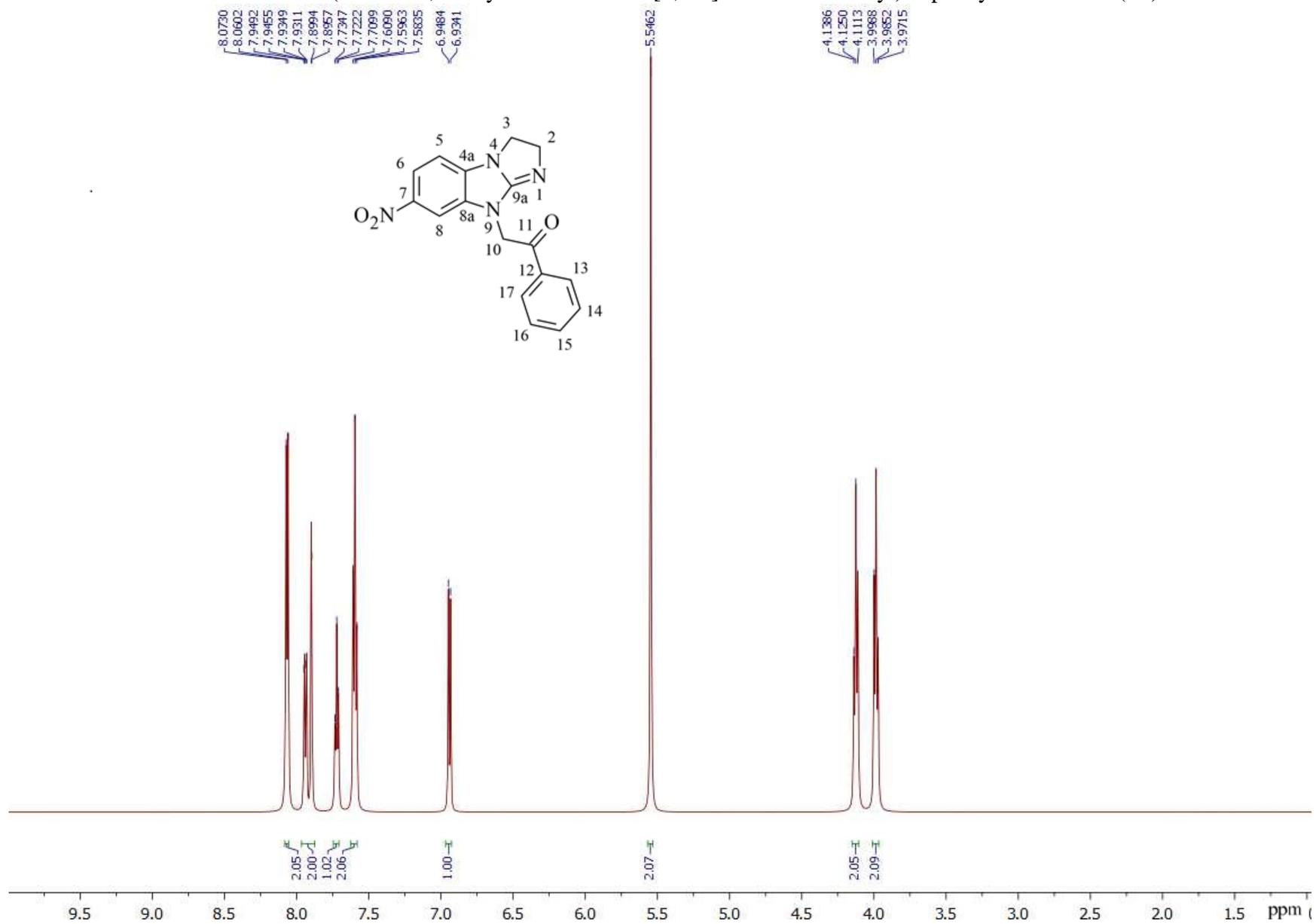


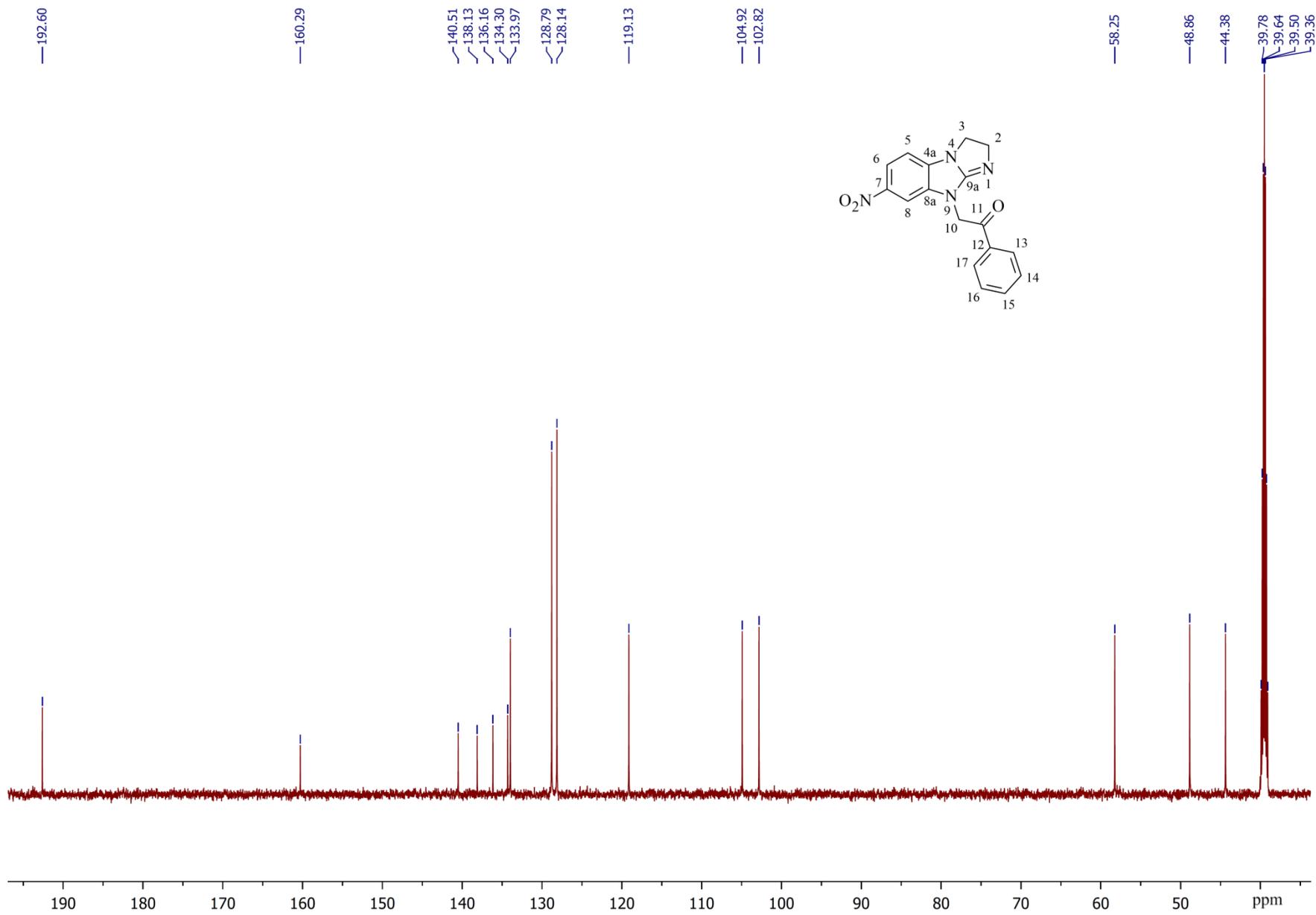
9-[2-(4-Chlorophenoxy)ethyl]-7-nitro-2,9-dihydro-3H-imidazo[1,2-a]benzimidazole hydrochloride (**4j**·HCl).



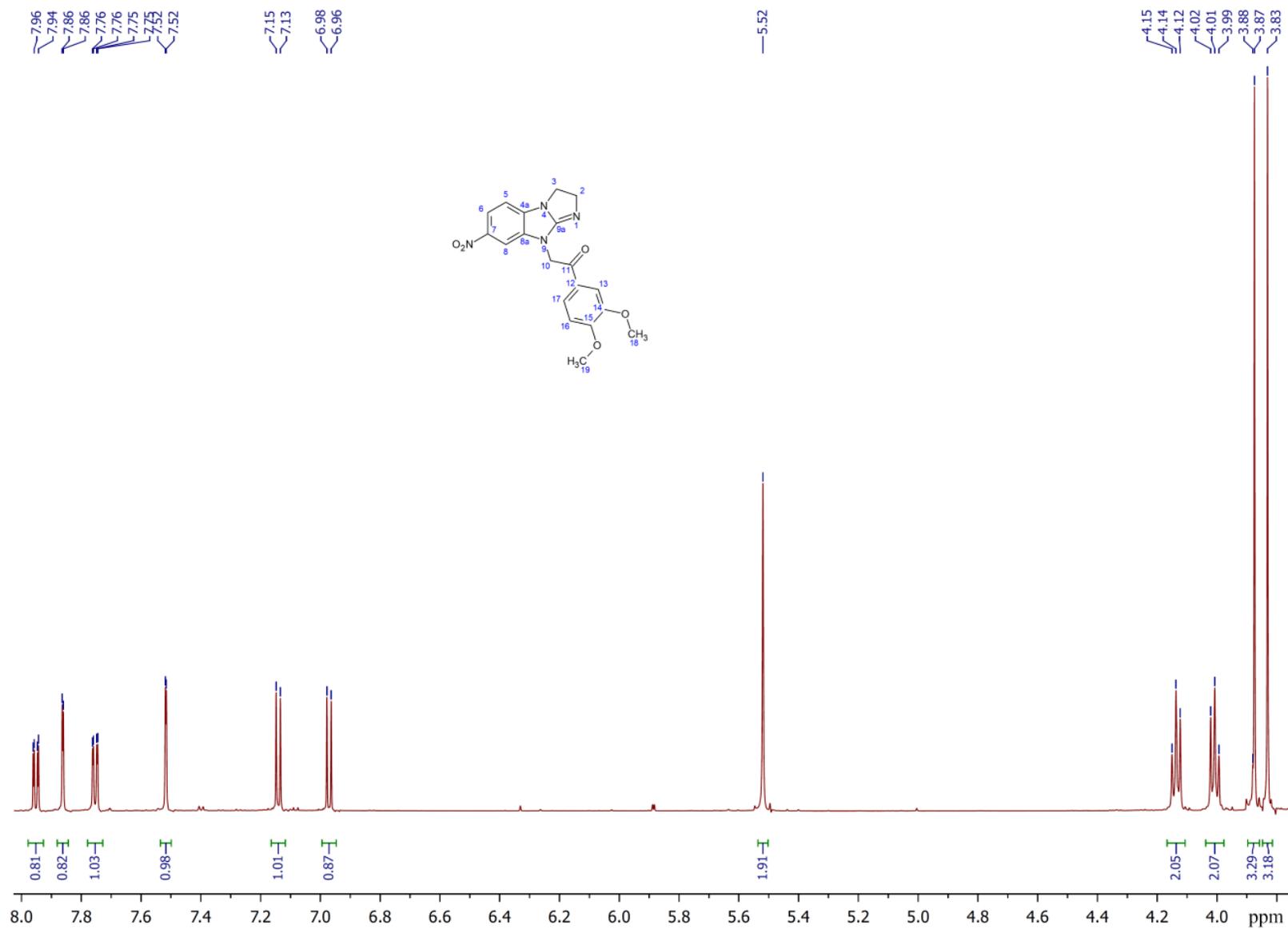


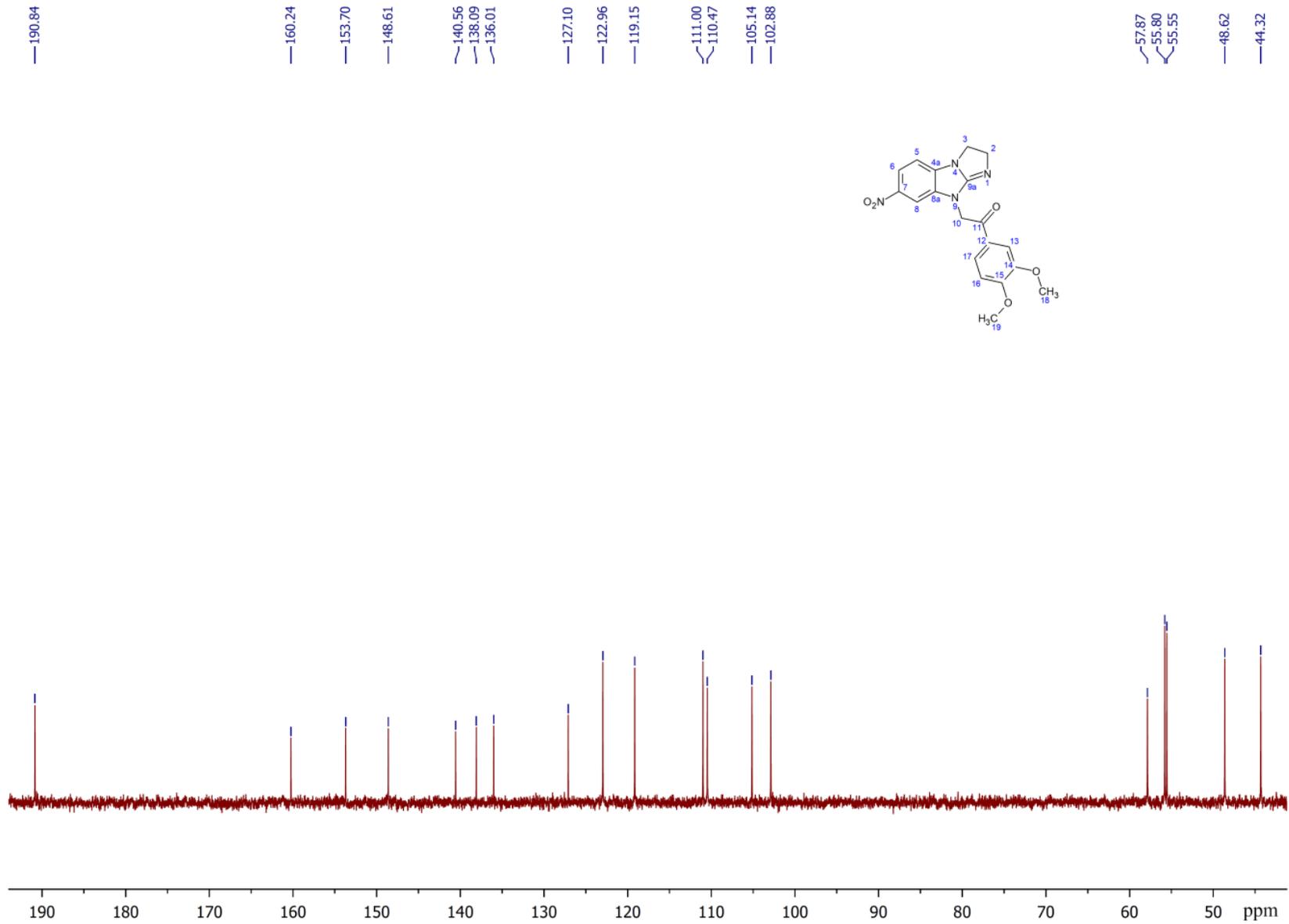
2-(7-Nitro-2,3-dihydro-9H-imidazo[1,2-a]benzimidazol-9-yl)-1-phenylethan-1-one (**4k**).



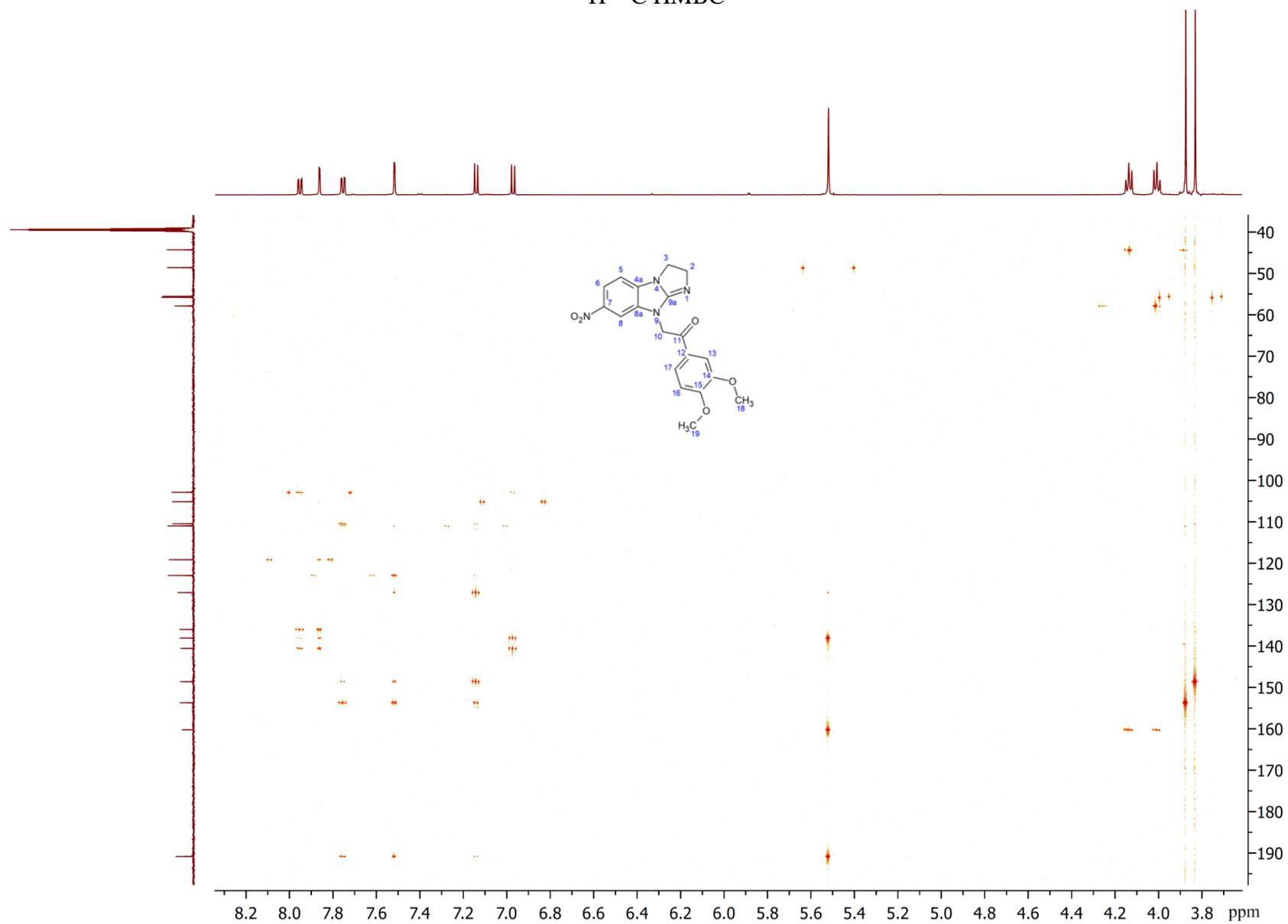


1-(3,4-Dimethoxyphenyl)-2-(7-nitro-2,3-dihydro-9H-imidazo[1,2-a]benzimidazol-9-yl)ethan-1-one (**41**).

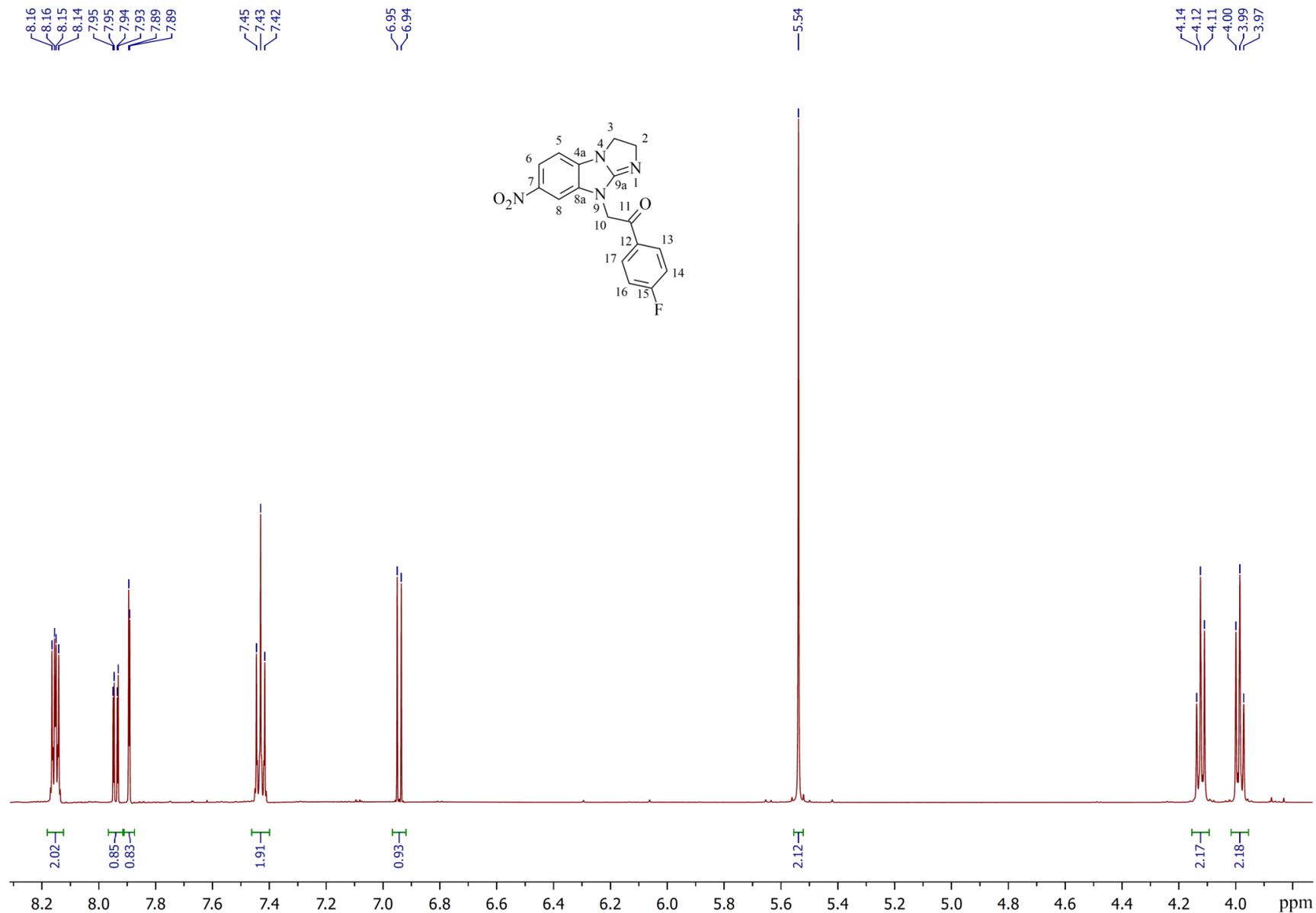


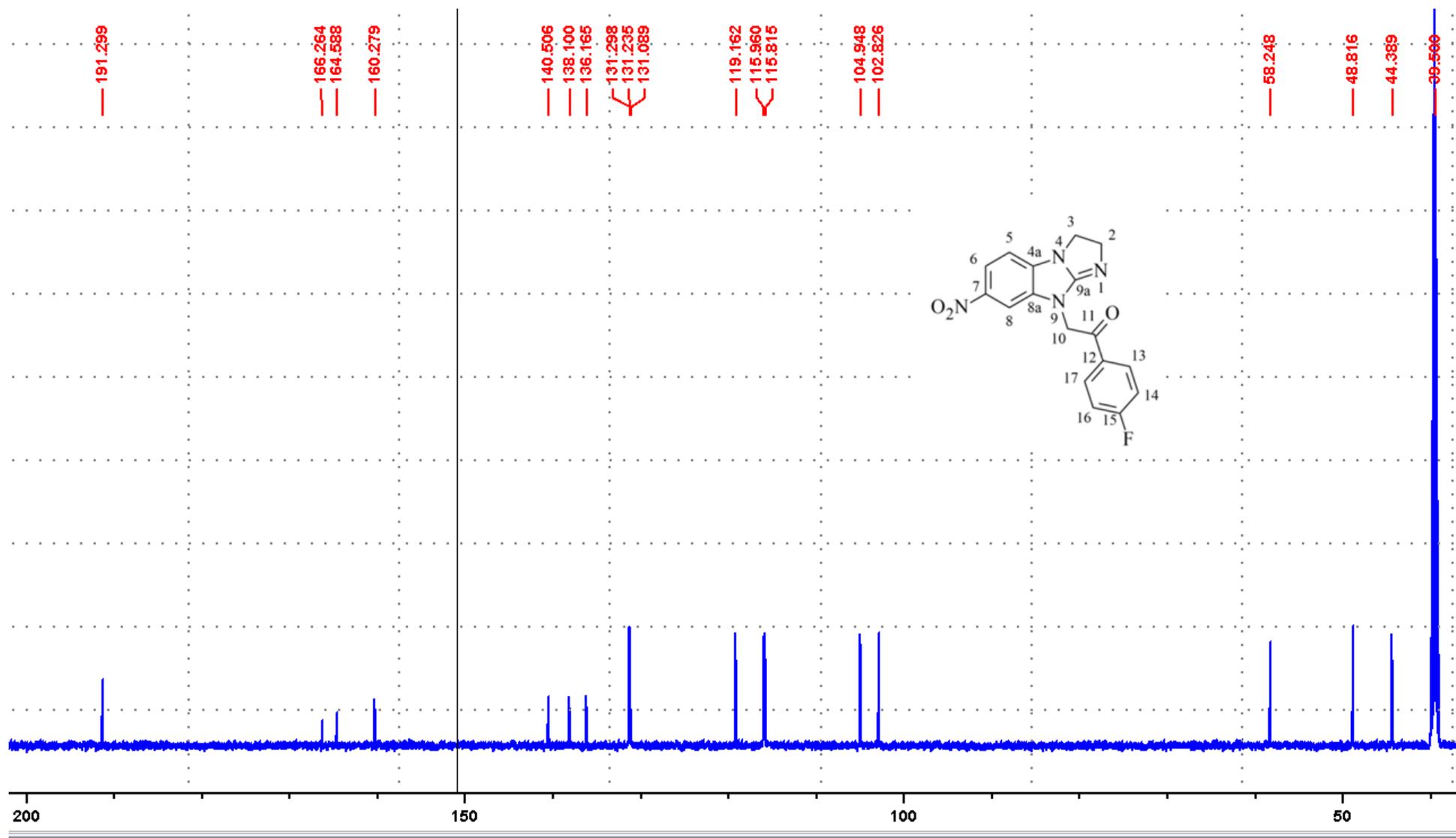


^1H - ^{13}C HMBC



1-(4-Fluorophenyl)-2-(7-nitro-2,3-dihydro-9H-imidazo[1,2-a]benzimidazol-9-yl)ethan-1-one (**4m**).





1-(4-Chlorophenyl)-2-(7-nitro-2,3-dihydro-9H-imidazo[1,2-a]benzimidazol-9-yl)ethan-1-one (**4n**).

