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A simple and convenient method for synthesizing dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione

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1. Experimental

The melting points of compounds **2-5** were determined on a PolyTherm A heating stage at a heating rate of 4 °C min^{-1} and were not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 instrument (the frequencies for ^{1}H were 500 MHz) in DMSO-d_6 at 303 K. Residual proton signals of DMSO-d_6 (δ 2.5) were used as internal standards. High resolution mass spectra were recorded on a MicrOTOF II instrument (Bruker Daltonics) using electrospray ionization.The mass scanning range (*m*/*z* 50) was 3000 Da; the compounds were injected with a syringe. MeCN and MeOH solvents were used; the solution flow rate was 4.0 μl min^{-1}.

Synthesis and Characterization of the Products

1,1'-(4,6-Dinitro-1,3-phenylene)dipyridinium dichloride 1 were obtained as described [Th. Zincke, G. Weispfenning, *J. prakt. Chem.*, 1910, **82**, 1].

***Dipyrido[1,2-a:1',2'-a']benzo[1,2-d:5,4-d]diimidazole* 2.** A solution of $SnCl_2 \cdot 2H_2O$ (11.57 g, 51.27 mmol) in 4% hydrochloric acid (42 ml) was added to a solution of compound **1** (4.50 g, 11.39 mmol) in 80% aqueous *i*-PrOH (60 ml). The reaction mixture was stirred at 40 °C for 15 min, then cooled, treated with 25% NH_3 solution to pH=7-8, and extracted with chloroform. Chloroform was distilled off to leave a yellowish-brown powder which was crystallized from a DMF + Pr^{i}OH mixture. Yield 2.59 g (88%), mp >300 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 7.04 (t, *J* 6.3 Hz, 2H, H^{2,10}), 7.59 (t, *J* 6.5 Hz, 2H, H^{3,9}), 7.66 (d, *J* 9.2 Hz, 2H, H^{4,8}), 8.06 (s, 1H, H^{6}), 9.01 (d, *J* 6.8 Hz, 2H, H^{1,11}), 9.20 (s, 1H, H^{13}). ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 93.75, 105.21, 109.70, 116.52, 125.11, 126.69, 130.63, 143.33, 148.99. ESI-HRMS: *m/z* calcd for $C_{16}H_{11}N_4$ $[M+H]^+$ 259.0984, found: 259.0978.

***6-Nitrodipyrido[1,2-a:1',2'-a']benzo[1,2-d:5,4-d]diimidazole* 3.** A solution of KNO_3 (0.94 g, 9.30 mmol) in conc. H_2SO_4 (15 ml) was added at 30 °C to a solution of compound **2** (2.00 g, 7.75 mmol) in sulfuric acid (15 ml). The mixture was stirred at 30 °C for 4 h, then cooled, poured onto ice, and treated with 25% NH_3 solution to pH=7-8. The resulting precipitate was filtered off, dried, and crystallized from DMF. Yield: 1.86 g (79%), mp >300 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 7.11 (t, *J* 6.7 Hz, 2H, $H^{2,10}$), 7.66-7.71 (m, 4H, $H^{3,4,8,9}$), 8.98 (d, *J* 6.2 Hz, 2H, $H^{1,11}$), 9.38 (s, 1H, H^{13}). ^{13}C NMR (DMSO-d_6, 125 MHz) *δ*: 100.19, 111.37, 116.85, 125.61, 126.65, 126.85, 132.42, 137.80, 150.95. ESI-HRMS: *m/z* calcd for $C_{16}H_{10}N_5O_2$ $[M+H]^+$ 304.0835, found: 304.0829.

***Dipyrido[1,2-a:1',2'-a']benzo[1,2-d:5,4-d]diimidazol-6-amine* 4a**. A solution of $SnCl_2 \cdot 2H_2O$ (2.61 g, 11.55 mmol) in 36% HCl (20 ml) was added at 60 °C to a solution of compound **3** (1.00 g, 3.30 mmol) in 36% HCl (30 ml), and the mixture was stirred for 0.5 h at 60 °C. The mixture was cooled, treated with a 25% NH_3 solution to pH=7-8, and extracted with chloroform. Chloroform was distilled off to leave a yellowish-orange powder that was crystallized from Pr^iOH. Yield: 0.78 g (87%), mp = 247-252 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 5.88 (s, 2H, NH_2), 6.88 (t, *J* 6.6 Hz, 2H, $H^{2,10}$), 7.43 (t, *J* 7.8 Hz, 2H, $H^{3,9}$), 7.59 (d, *J* 9.2 Hz, 2H, $H^{4,8}$), 8.12 (s, 1H, H^{13}), 8.78 (d, *J* 6.8 Hz, 2H, $H^{1,11}$). ^{13}C NMR (DMSO-d_6, 125 MHz) *δ*: 78.98, 109.25, 116.91, 126.40, 126.43, 128.89, 129.21, 129.83, 146.72. ESI-HRMS: *m/z* calcd for $C_{16}H_{12}N_5$ $[M+H]^+$ 274.1093, found: 274.1087.

***N-(Dipyrido[1,2-a:1',2'-a']benzo[1,2-d:5,4-d]diimidazole-6-yl)-propionamide* 4b.** Propionic anhydride (0.4 ml) was added at 70°C to a solution of compound **4a** (0.25 g, 0.92 mmol) in DMF (5 ml), and the mixture was stirred for 2 h at 90 °C. The mixture was cooled and poured into water. The precipitate that formed was filtered off. Yield: 0.25 g (84%), mp > 360 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.15 (m, 3H, CH_3), 2.49 (m, 2H, CH_2), 7.06 (t, *J* 6.2 Hz, 2H, $H^{2,10}$), 7.58 (t, *J* 7.8 Hz, 2H, $H^{3,9}$), 7.70 (d, *J* 9.3 Hz, 2H, $H^{4,8}$), 8.98 (d, *J* 6.8 Hz, 2H, $H^{1,11}$), 9.10 (s, 1H, H^{13}), 9.92 (s, 1H, NH). ESI-HRMS: *m/z* calcd for $C_{19}H_{16}N_5O$ $[M+H]^+$ 330.1356, found: 330.1349.

***Dipyrido[1,2-a:1',2'-a']benzo[1,2-d:5,4-d]diimidazole-6,13-dione* 5.** A solution of KNO_3 (0.24 g, 2.37 mmol) in conc. H_2SO_4 (10 ml) was added at 20 °C to a solution of compound **4** (0.50 g, 1.83 mmol) in conc. H_2SO_4 (10 ml), and the mixture was stirred at 20 °C for 10 h. The mixture was cooled, poured onto ice, and treated with 25% NH_3 solution to pH=7-8. The resulting precipitate was filtered off, dried, and crystallized from a DMF + Pr^iOH mixture. Yield: 0.39 g (74%), mp >300 °C. ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 7.42 (t, *J* 7.3 Hz, 2H, $H^{2,10}$), 7.66-7.73 (m, 2H, $H^{3,9}$), 7.95 (d, *J* 8.9 Hz, 2H, $H^{4,8}$), 9.25 (d, *J* 6.7 Hz, 2H, $H^{1,11}$). ^{13}C NMR (DMSO-d_6, 125 MHz) *δ*: 118.30, 119.70, 124.24, 127.97, 130.88, 145.57, 146.21, 164.51, 177.40. ESI-HRMS: *m/z* calcd for $C_{16}H_9N_4O_2$ $[M+H]^+$ 289.2739, found: 289.2720.

Table S1. Crystallographic data for compounds 2, 3 and 5

Compound	**2**	**3**	**5**
Formula	$C_{16}H_{10}N_4$	$C_{16}H_{11}N_5O_3$	$C_{16}H_8N_4O_2$
Formula weight	258.28	321.30	288.26
T, K	120	120	120
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	Pbca	$P2_1/n$	$P2_1/c$
Z / Z'	8 / 1	4 / 1	4 / 1
a, Å	8.3797(13)	7.9238(3)	11.549(3)
b, Å	13.613(2)	11.6203(5)	13.735(3)
c, Å	20.377(3)	15.1992(7)	7.7401(19)
β, °		102.9450(10)	91.390(5)
V, $Å^3$	2324.5(6)	1363.93(10)	1227.5(5)
d_{calc}, g cm^{-3}	1.476	1.565	1.560
μ, cm^{-1}	0.92	1.13	1.08
$2\theta_{max}$, °	52	60	56
Refl. collected / independent	13570 / 2319	20142 / 3981	13975 / 2971
Observed reflections [I>2σ(I)]	1522	3096	1838
R_1	0.0469	0.0452	0.0522
wR_2	0.1073	0.1235	0.1195
GOF	1.014	1.025	1.032
Residual density, e $Å^{-3}$ (d_{max}/d_{min})	0.202/-0.283	0.471/-0.242	0.250/-0.202

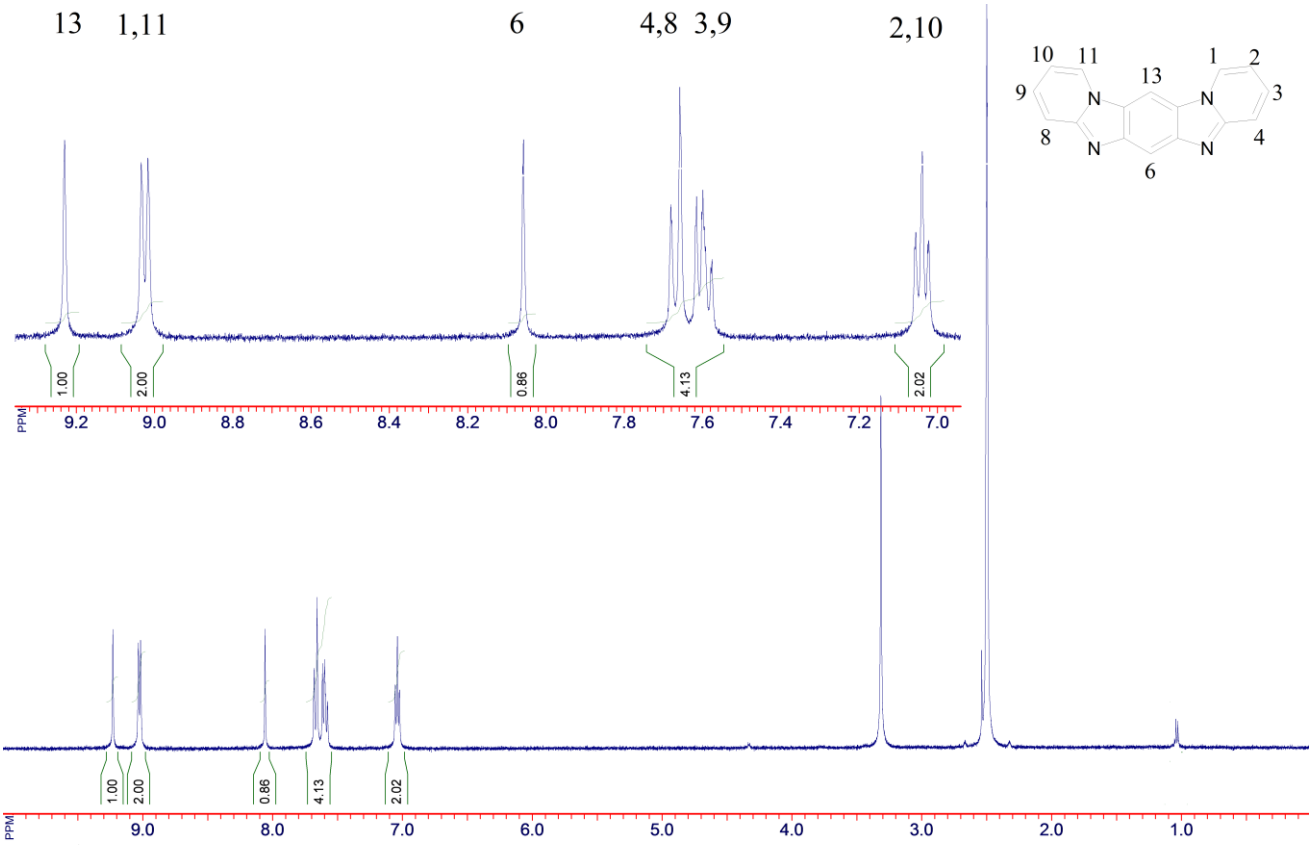
Table S2. Bond lengths (Å) in structures 2, 3 and 5

Bond	**2**	**3**	**5**
C6-C7	1.353(3)	1.358(2)	1.351(3)
C6-N5B	1.378(3)	1.3719(17)	1.373(2)
C7-C8	1.425(3)	1.418(2)	1.410(3)
C8-C9	1.357(3)	1.368(2)	1.348(3)
C9-C9A	1.414(3)	1.4127(19)	1.405(3)
C9A-N10	1.328(3)	1.3349(18)	1.333(3)
C9A-N5B	1.404(2)	1.3916(17)	1.392(3)
N10-C10A	1.387(3)	1.3728(17)	1.352(2)
C10A-C11	1.395(3)	1.4048(19)	1.480(3)
C10A-C5A	1.421(3)	1.4268(17)	1.377(3)
C11-C11A	1.394(3)	1.4051(18)	1.484(3)
C11A-N12	1.390(3)	1.3751(17)	1.353(2)
C11A-C4B	1.425(3)	1.4237(18)	1.380(3)
N12-C12A	1.331(3)	1.3358(17)	1.336(2)
C12A-N4A	1.398(3)	1.3902(17)	1.400(3)
C12A-C1	1.414(3)	1.4139(19)	1.401(2)
C1-C2	1.358(3)	1.367(2)	1.360(3)
C2-C3	1.425(3)	1.418(2)	1.409(3)
C3-C4	1.348(3)	1.362(2)	1.345(3)
C4-N4A	1.373(3)	1.3772(16)	1.376(2)
N4A-C4B	1.391(3)	1.3932(16)	1.377(2)
C4B-C5	1.382(3)	1.3850(18)	1.452(3)
C5-C5A	1.386(3)	1.3808(18)	1.449(3)
C5A-N5B	1.392(3)	1.3941(17)	1.375(2)
O1-N13		1.2300(16)	
O2-N13		1.2287(16)	
C11-N13		1.4439(17)	
O1-C11			1.218(2)
O2-C5			1.234(2)

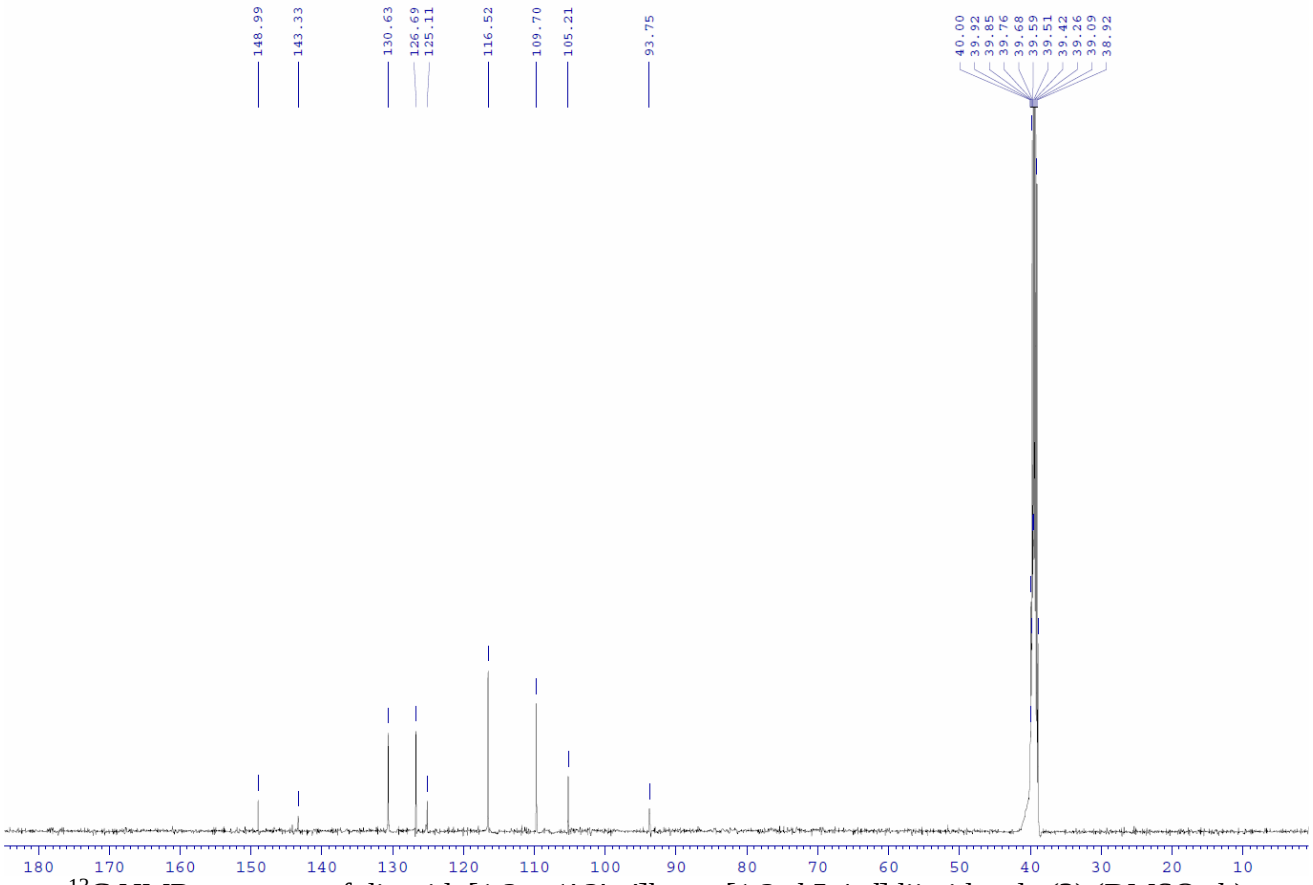
Table S3. Selected bond angles (°) in structures 2, 3 and 5

Bond angle	**2**	**3**	**5**
C10A-C11-C11A	116.45(19)	118.75(11)	112.65(16)
C4B-C5-C5A	113.23(18)	113.49(11)	110.41(17)
C5-C5A-N5B	130.54(18)	129.75(12)	128.60(18)
N4A-C4B-C5	130.87(18)	130.17(12)	128.48(17)
N12-C11A-C11	128.38(19)	130.22(12)	125.26(17)
N10-C10A-C11	128.36(18)	130.61(12)	125.05(18)
C6-N5B-C5A	130.69(17)	129.83(11)	131.52(18)
C4-N4A-C4B	130.64(17)	130.29(12)	131.64(16)
C12A-N12-C11A	104.63(17)	104.92(11)	104.24(16)
C9A-N10-C10A	104.82(17)	105.03(11)	104.16(17)
C10A-C5A-N5B	104.75(17)	104.58(11)	104.86(17)
C11A-C4B-N4A	104.66(17)	104.76(11)	105.00(16)

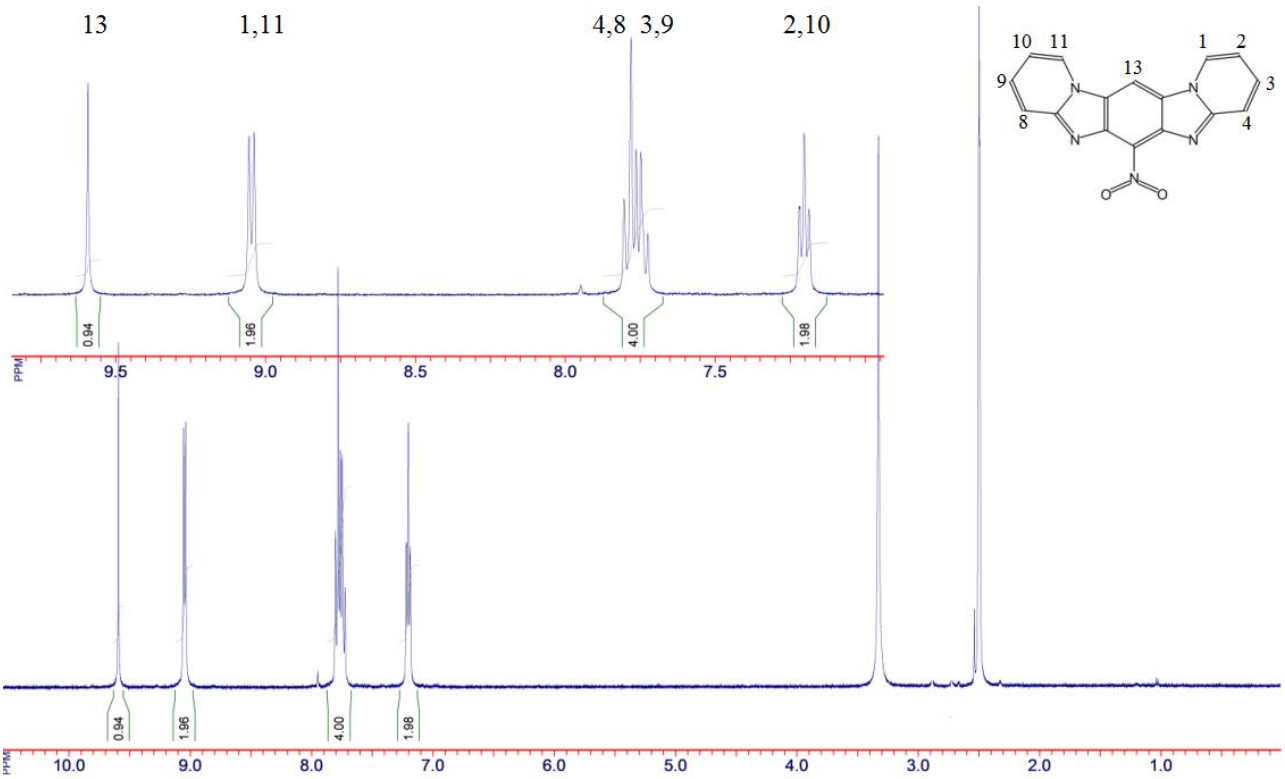
5. NMR spectra of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole and its derivatives



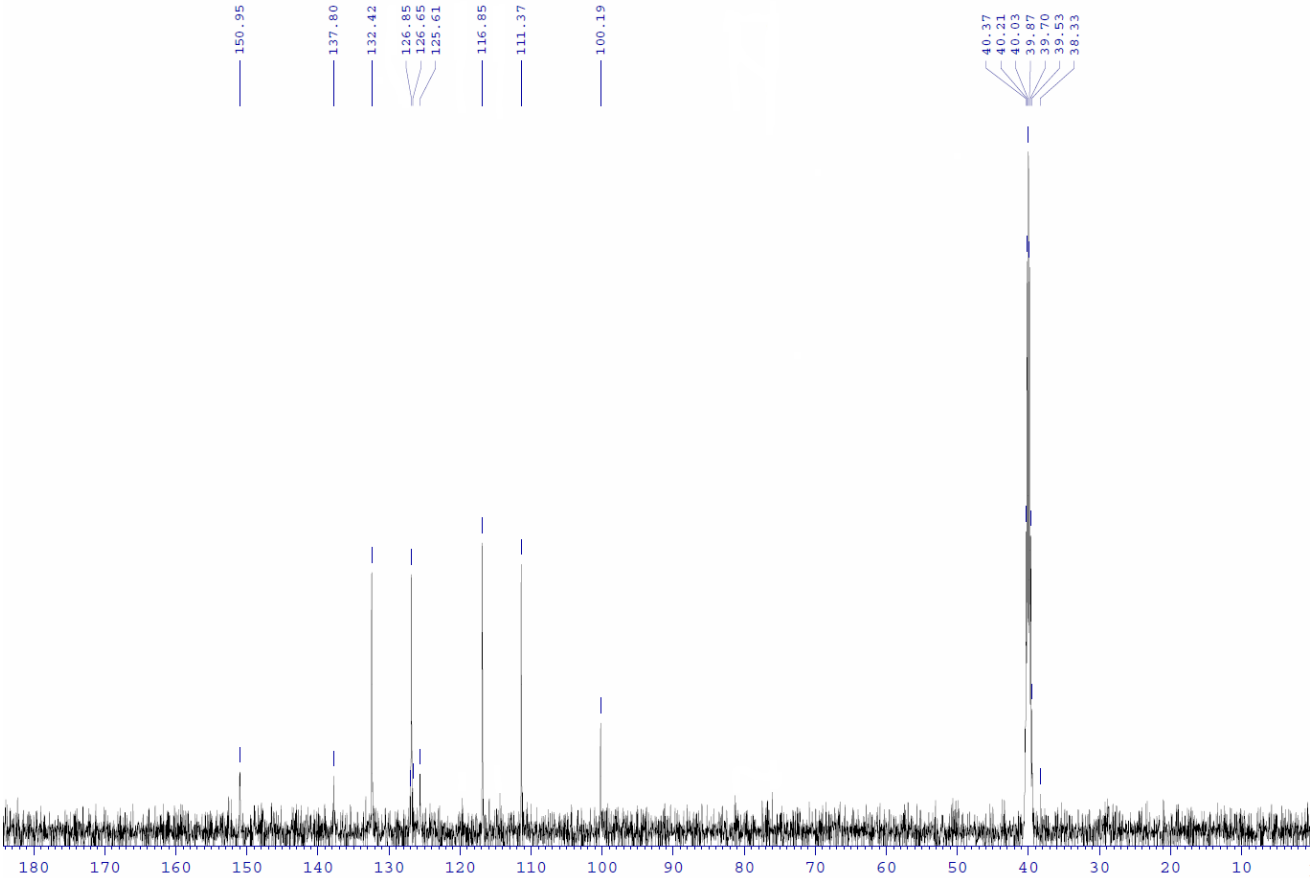
^{1}H NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**2**) (DMSO-d_6)



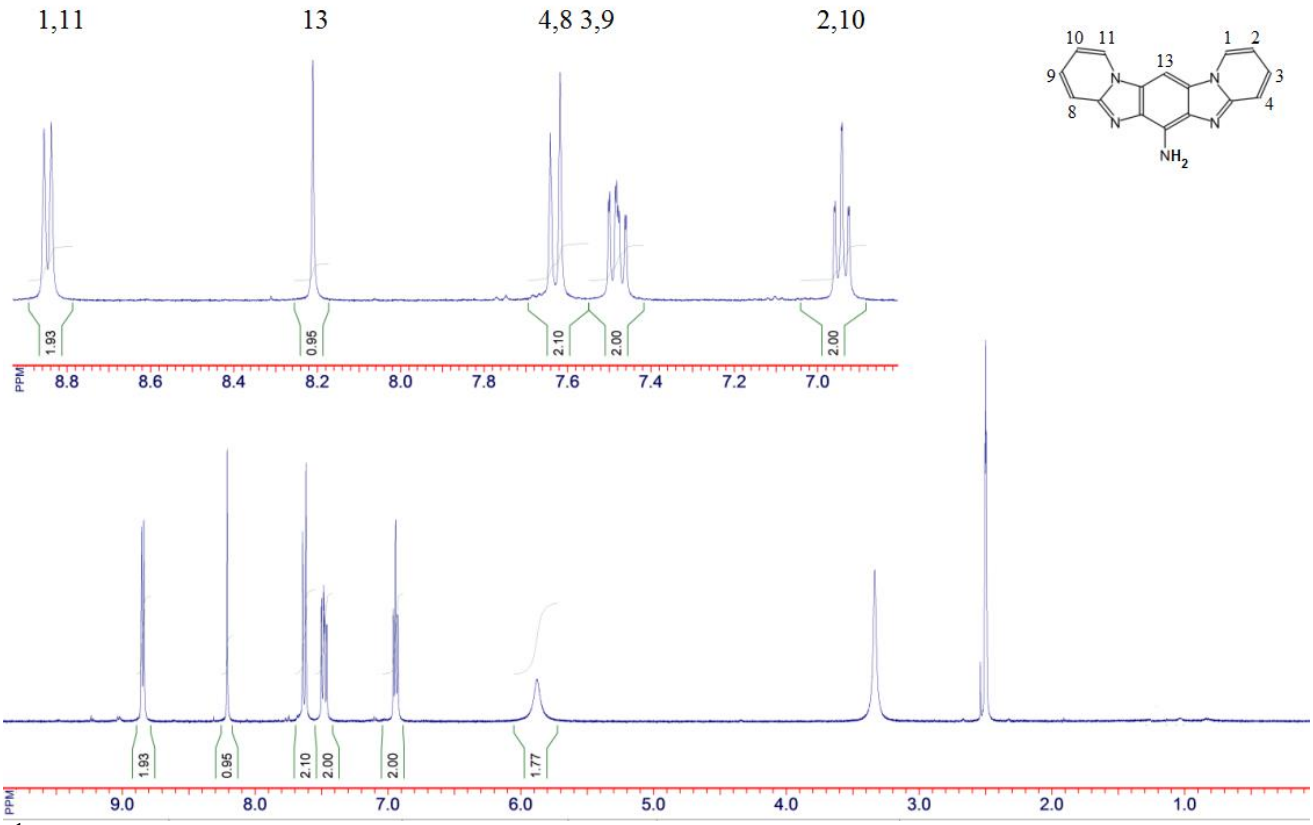
^{13}C NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**2**) (DMSO-d_6)



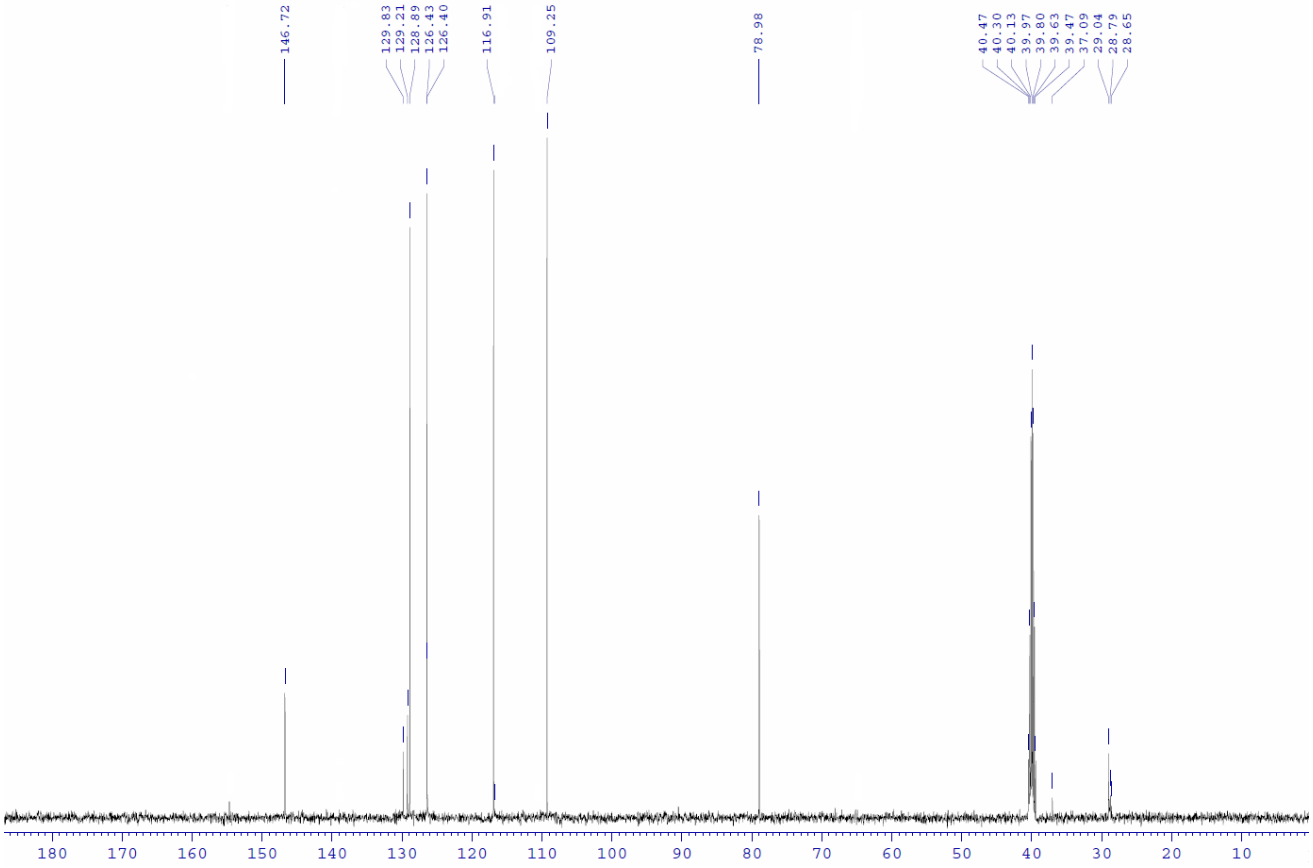
^{1}H NMR spectrum of 6-nitro-dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**3**) (DMSO-d_6)



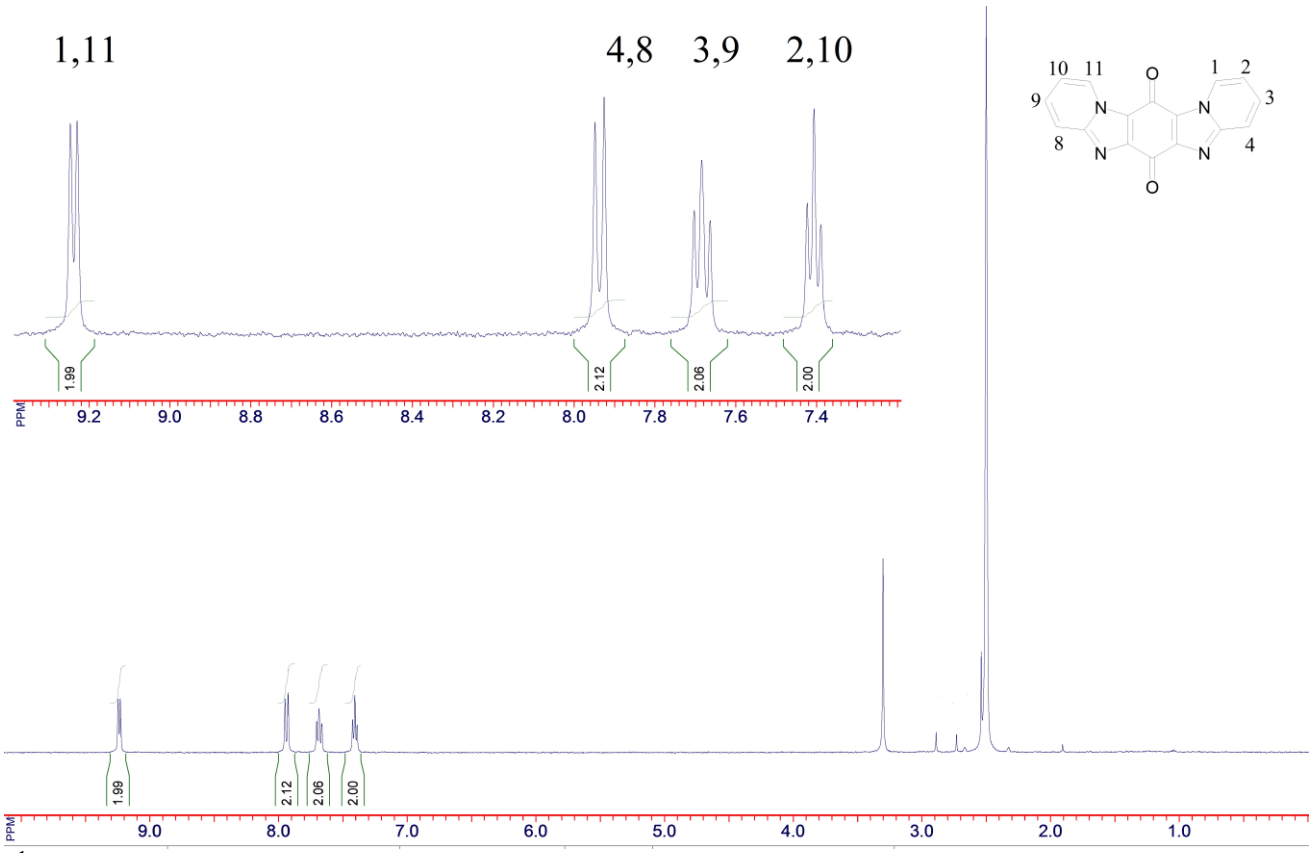
^{13}C NMR spectrum of 6-nitro-dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**3**) (DMSO-d_6)



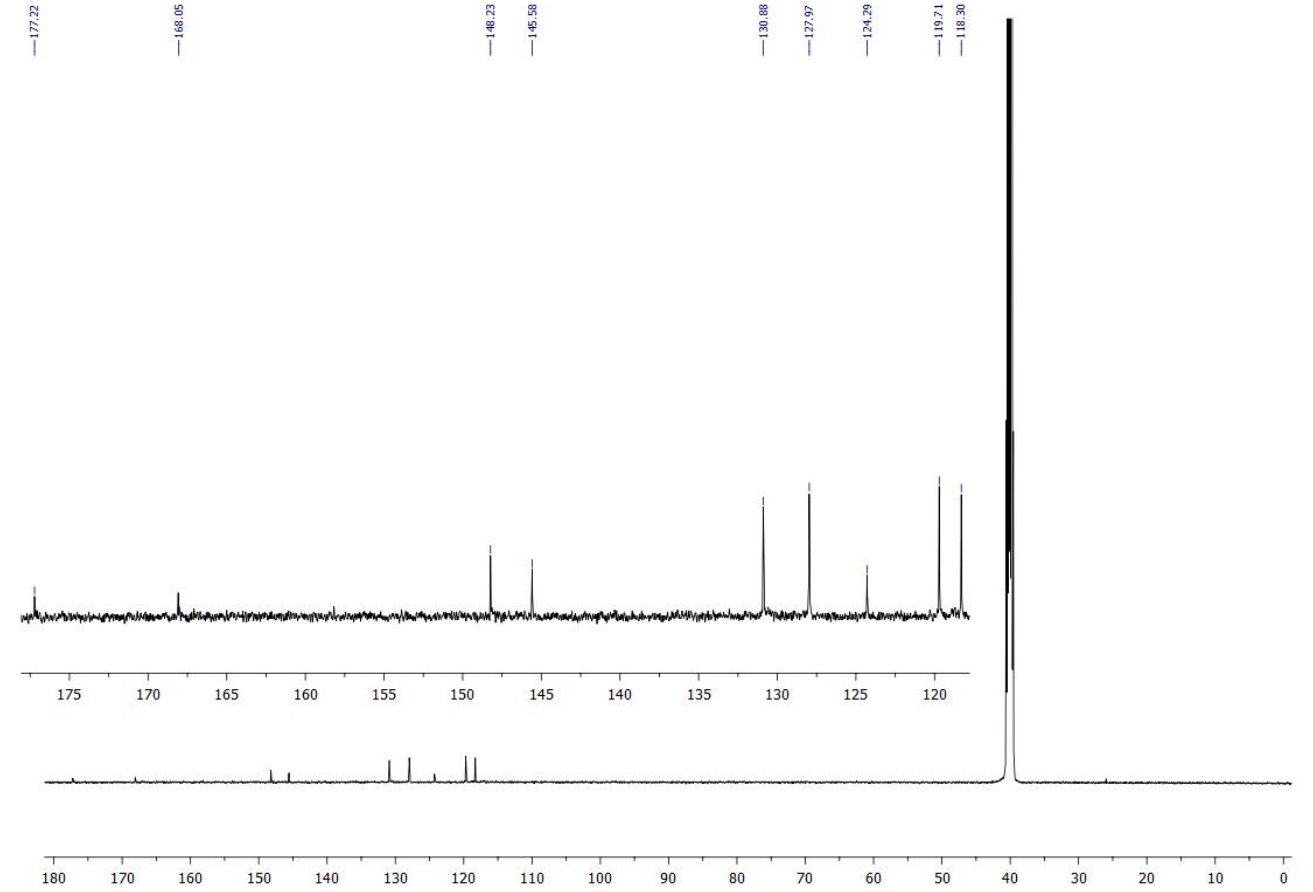
^{1}H NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazol-6-amine (**4a**) (DMSO-d_6)



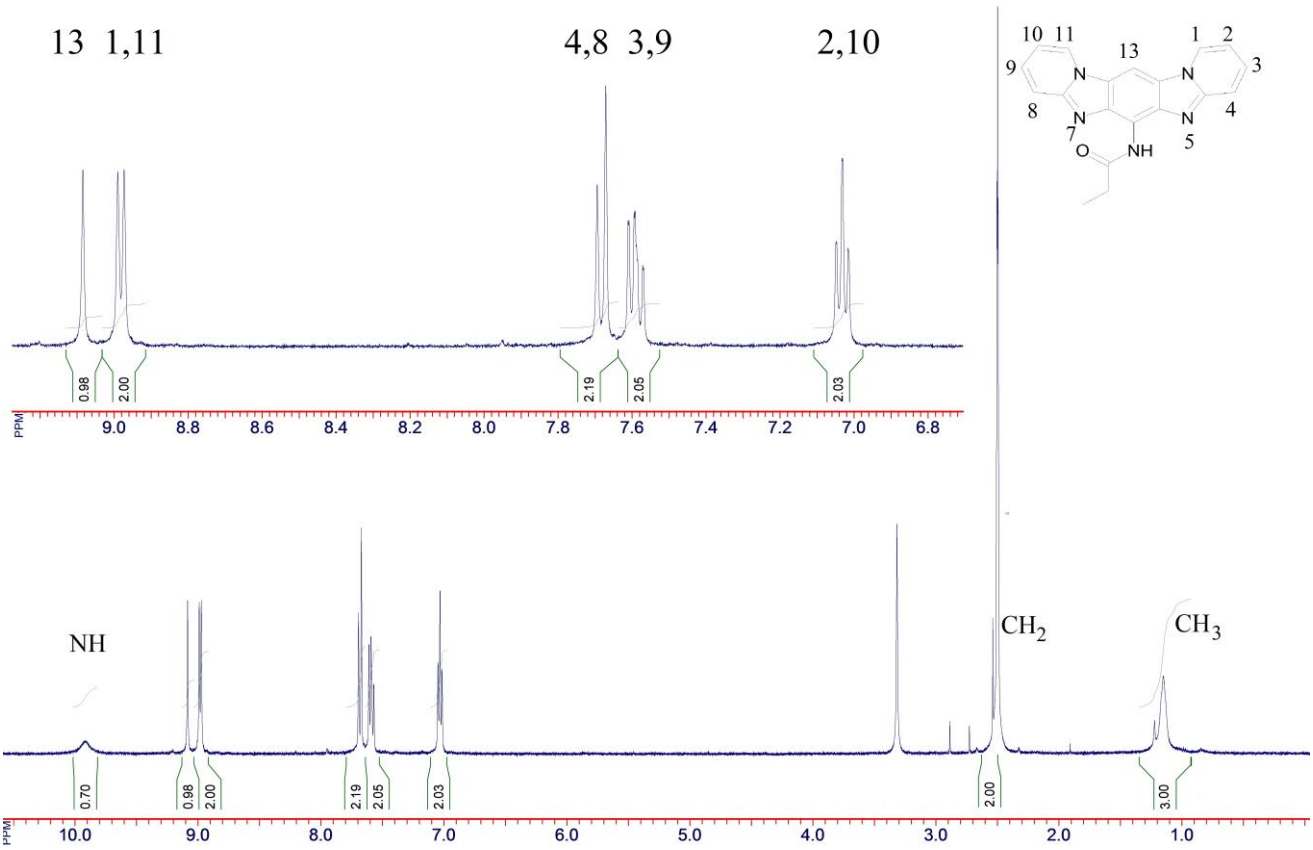
^{13}C NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazol-6-amine (**4a**) (DMSO-d_6)



^{1}H NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione (**5**) (DMSO-d_6)

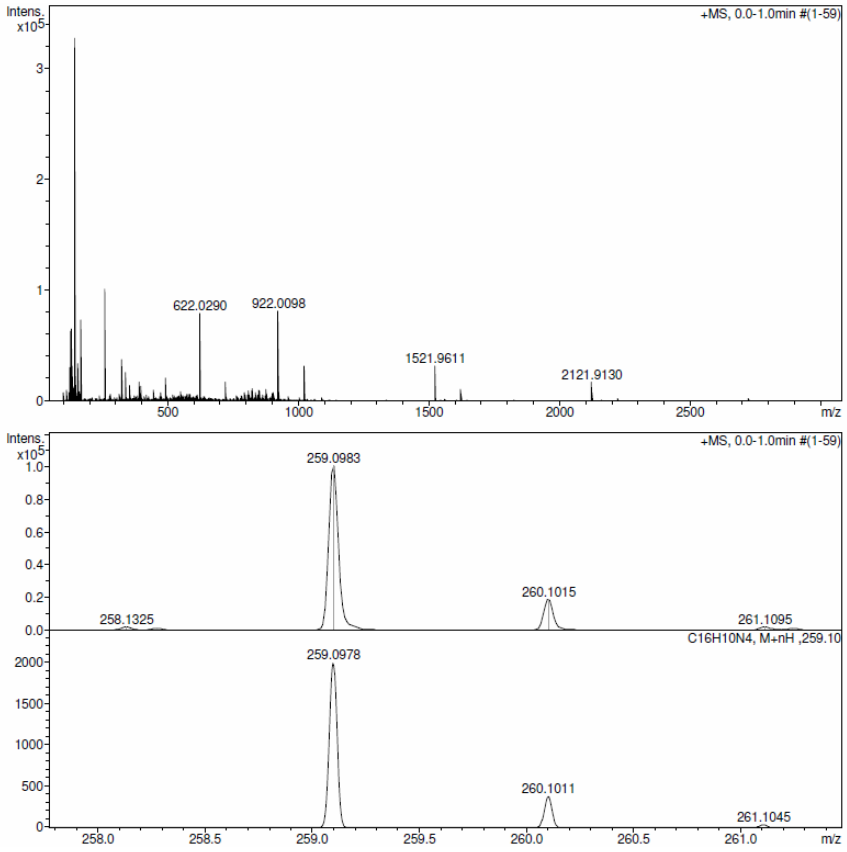


^{13}C NMR spectrum of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione (**5**) (DMSO-d_6)

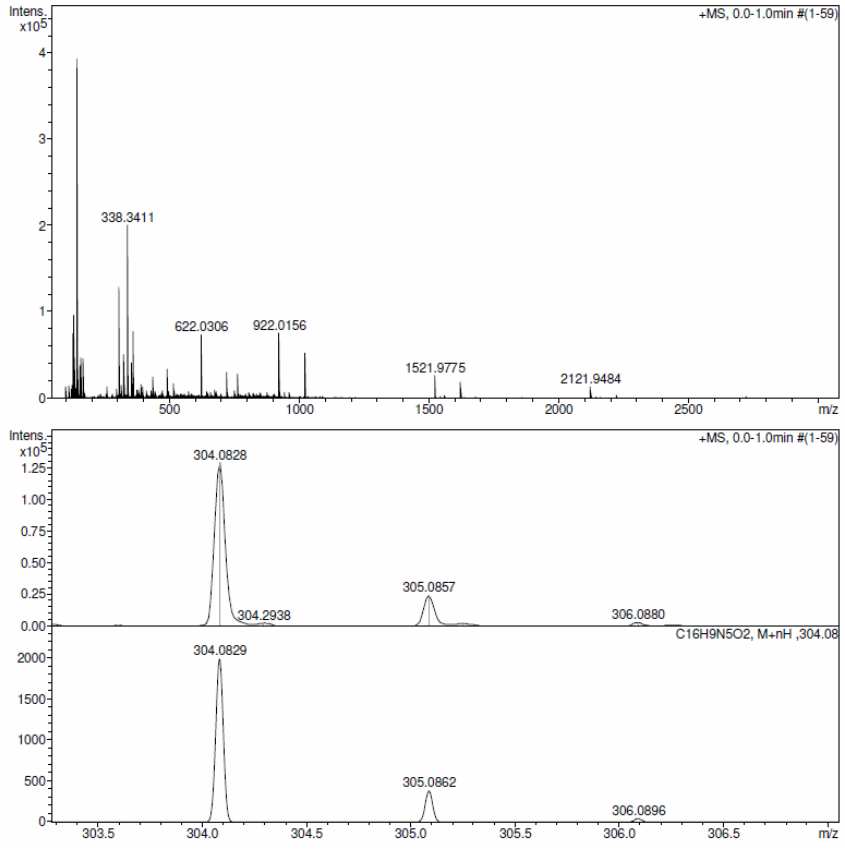


^{1}H NMR spectrum of N-(dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6-yl)-propionamide (**4b**) (DMSO-d_6)

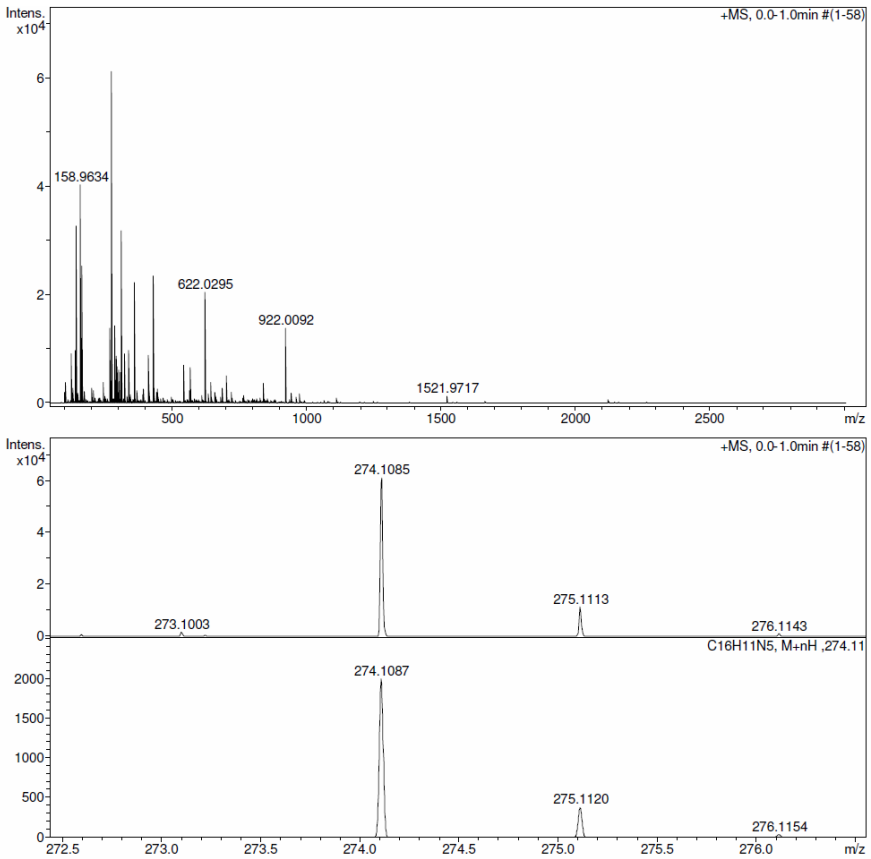
6. High resolution mass spectra of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole and its derivatives



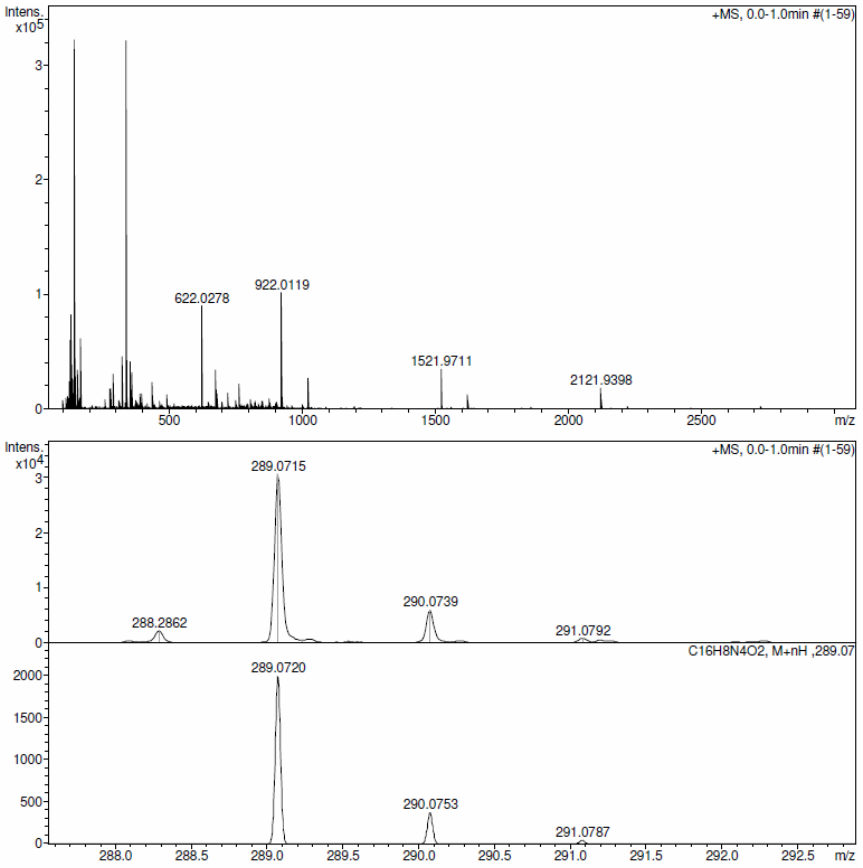
HRMS of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**2**)



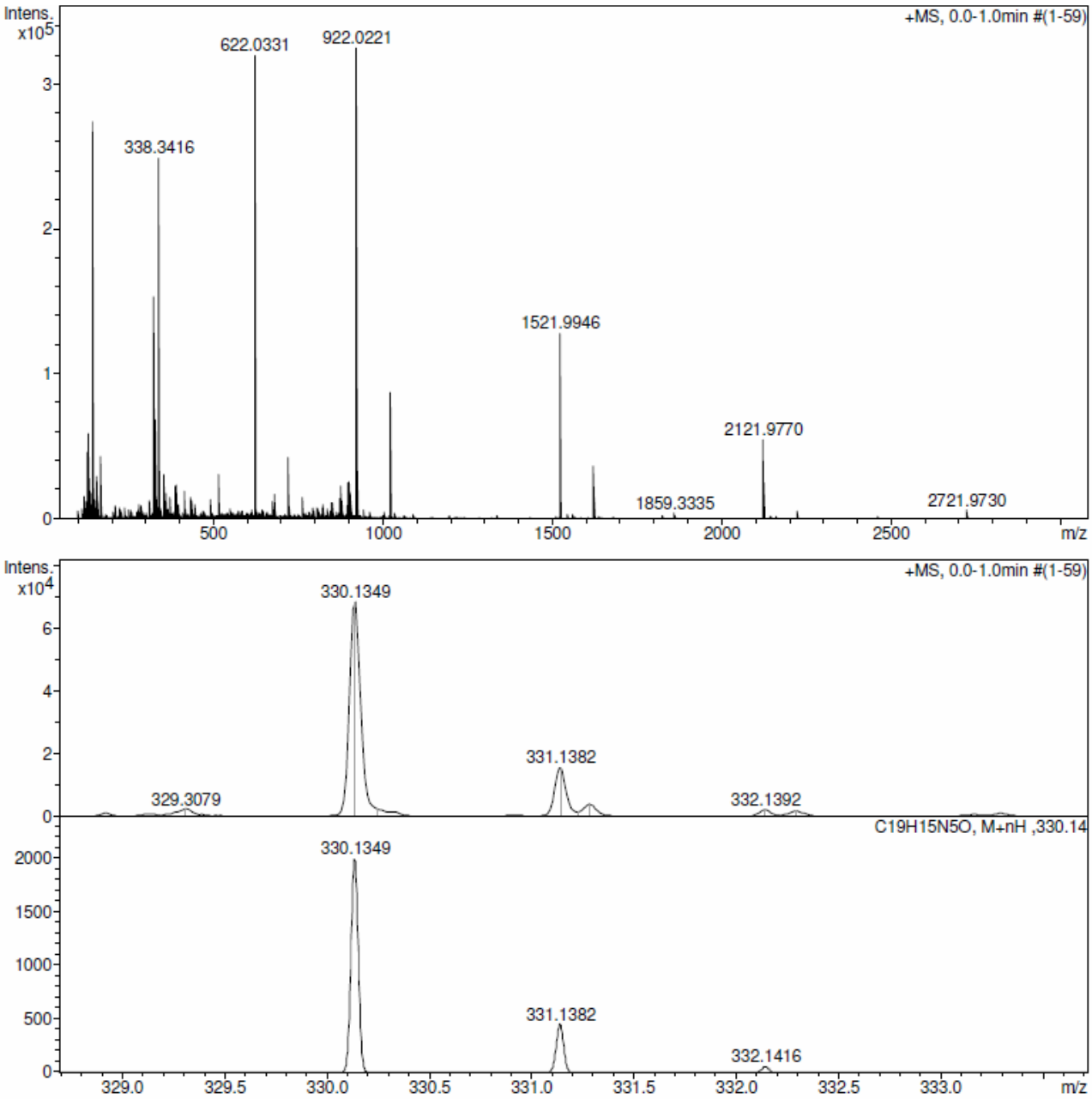
HRMS of 6-nitro-dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole (**3**)



HRMS of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazol-6-amine (**4a**)



HRMS of dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6,13-dione (**5**)



HRMS of N-(dipyrido[1,2-*a*:1',2'-*a*']benzo[1,2-*d*:5,4-*d*]diimidazole-6-yl)-propionamide (**4b**)