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Crystal structure and properties of new benzimidazopyrido[2,3-*b*]indole-6-carbonitriles

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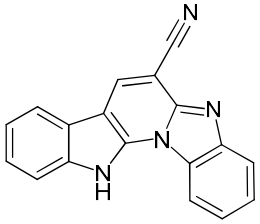
1. General information

Elemental analysis was performed on a PerkinElmer 240C instrument. ^{1}H and ^{13}C NMR spectra were acquired on a Bruker DPX-250 spectrometer (250 and 63 MHz respectively) in DMSO-d_6. IR spectra were recorded on a Varian 3100 FT-IR instrument from mulls in mineral oil. The mass spectrum was obtained by direct input on a Finnigan MAT INCOS 50 mass spectrometer. Absorption spectra and luminescence spectra of compounds **4c,d** were obtained in acetonitrile and dimethyl sulfoxide (DMSO) at room temperature using standard methods. Electronic absorption spectra were recorded on a Cary 50 Scan spectrophotometer (Varian). Luminescence spectra were recorded on a Cary Eclipse spectrofluorimeter. Fluorescence quantum yields were determined using the Parker-Rice method (C.A. Parker, Photoluminescence of Solutions: With Applications to Photochemistry and Analytical Chemistry, Elsevier, 1968) with an anthracene solution as a standard phosphor. The solvents used for measurements were purified and dried according to standard methods (Gordon A., Ford R. Chemist's Companion. M.: Mir. 1976. 536 p.).

Benzimidazopyridoindoles **4a-d** were synthesized similarly.[S1] Indole-3-carbaldehydes **5a,b**, from which compounds **6** were obtained, were synthesized according to work.[S2]

2. Characterization of compounds 4a-d.

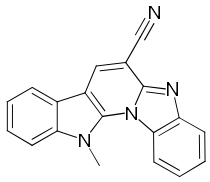
12*H*-Benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4a



Yellow crystals, yield 61%, mp 250-252°C. IR spectrum, ν_{max}, cm^{-1}: 3242, 2225, 1625, 1565, 1469. ^{1}H NMR (250 MHz, DMSO-d_6) δ: 13.13 (s, 1H), 9.12 (s, 1H), 8.89 (d, J =7.50 Hz, 1H), 8.17

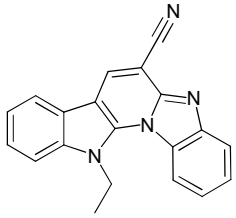
(d, *J* =7.50 Hz, 1H), 7.98 (d, *J* =7.50 Hz, 1H), 7.78 (d, *J* =7.50 Hz, 1H), 7.69 -7.36 (м, 4H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6) δ: 147.03, 143.32, 137.71, 136.93, 134.19, 127.65, 126.58, 125.44, 122.79, 122.28, 122.14, 119.89, 119.22, 117.72, 114.00, 113.35, 104.86, 88.79. Anal. Calcd (%) for $C_{18}H_{10}N_4$: C 76.61; H 3.54; N 19.84. Found: C 76.85; H 3.22; N 19.58.

12-Methyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4b



Yellow crystals, yield 65%, mp 220-222°C. IR spectrum, ν_{max}, cm^{-1}: 2212, 1615, 1591, 1566, 1506. ^{1}H NMR (250 MHz, DMSO-d_6) δ: 9.09 (s, 1H), 8.62 (d, *J* =7.50 Hz, 1H), 8.18 (d, *J* =7.50 Hz, 1H), 8.97 (d, *J* =7.50 Hz, 1H), 7.80 (d, *J* =7.50 Hz, 1H), 7.66 -7.40 (м, 4H), 4.38 (s, 3H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6) δ: 148.66, 144.47, 140.83, 139.58, 133.61, 128.85, 126.29, 125.55, 123.26, 122.38, 122.15, 119.88, 119.66, 117.70, 116.19, 112.14, 105.84, 90.17, 36.46. Anal. Calcd (%) for $C_{19}H_{12}N_4$: C 77.03; H 4.05; N 18.92. Found: C 77.35; H 3.97; N 18.58.

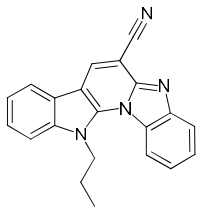
12-Ethyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4c



Yellow crystals, yield 62%, mp 258-260°C. IR spectrum, ν_{max}, cm^{-1}: 2215, 1616, 1577, 1499, 1473, 1438.^{1}H NMR (250 MHz, DMSO-d_6) δ: 9.09 (s, 1H), 8.41 (d, *J* =7.50 Hz, 1H), 8.19 (d, *J* =7.50 Hz, 1H), 7.98 (d, *J* =7.50 Hz, 1H), 7.89 (d, *J* =7.50 Hz, 1H), 7.67-7.39 (м, 4H), 4.92 (k, *J* = 7.50 Hz, 2H), 1.52 (t, *J* =7.50 Hz, 3H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6) δ: 148.92, 144.54, 140.26, 138.27, 133.46, 128.85, 126.35, 125.56, 123.31, 122.99, 122.38, 120.14, 119.80, 117.65,

115.43, 112.74, 106.37, 90.72, 42.54, 15.65. Anal. Calcd (%) for $C_{20}H_{14}N_4$: C 77.42; H 4.51; N 18.06. Found: C 77.35; H 3.49; N 18.18.

12-Propyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4d



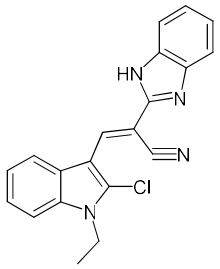
Yellow crystals, yield 60%, mp 272-274°C. IR spectrum, ν_{max}, cm^{-1}: 2222, 1614, 1567, 1469, 1451. ^1H NMR (250 MHz, DMSO-d_6) δ: 9.13 (s, 1H), 8.39 (d, J =7.50 Hz, 1H), 8.20 (d, J =7.50 Hz, 1H), 8.02-7.91 (м, 2H), 7.68-7.41 (м, 4H), 4.87 (t, J =7.60 Hz, 2H), 1.84 (k, J =7.60 Hz, 2H), 0.65 (t, J =7.60 Hz, 3H) ppm. ^{13}C NMR (63 MHz, DMSO-d_6) δ: 148.86, 144.57, 140.57, 138.57, 133.57, 128.83, 126.44, 125.53, 123.37, 122.93, 122.31, 120.17, 119.87, 117.59, 115.53, 113.08, 106.33, 90.83, 48.78, 23.17, 10.88. Anal. Calcd (%) for $C_{21}H_{16}N_4$: C 77.78; H 4.93; N 17.28. Found: C 77.49; H 4.89; N 17.18. M/z calcd for $C_{21}H_{16}N_4$: 325.25 $[M]^+$; found: 325.00.

3. General synthesis of compounds 5a,b.

A mixture of 2-chloro-1*H*-indole-3-carbaldehyde **6a,b** (0.001 mol) and 1*H*-benzimidazol-2-yl-acetonitrile (0.001 mol) in propan-2-ol (15 mL) was boiled for 1.5-2 h, and then stirred at room temperature for 8-10 h. The precipitate was filtered off, washed with petroleum ether, dried and then recrystallized from butan-1-ol.

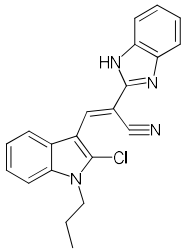
4. Characterization of compounds 5a,b

2-(1*H*-Benz[*d*]imidazol-2-yl)-3-(2-chloro-1-ethyl-1*H*-indol-3-yl)acrylonitrile 5a.



Yellow crystals, yield 67%, mp 235-237°C. IR spectrum, ν_{max}, cm^{-1}: 2651, 2215, 1624, 1595, 1535, 1488, 1425, 1393, 1347, 1237, 1046, 749. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ: 13.08 (s,1H), 8.40 (s, 1H), 8.02 (d, *J* =7.50 Hz, 1H), 7.71–7.61 (m, 3H), 7.40–7.21 (m, 4H), 4.41 (k, *J* =7.50 Hz, 2H), 1.33 (t, *J* =7.50 Hz, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d$_6$) δ: 148.69, 143.91, 137.72, 135.65, 135.41, 131.15, 123.99, 123.87, 123.69, 122.62, 122.17, 121.70, 119.38, 117.66, 111.90, 111.40, 107.71, 99.90, 40.05, 14.97. Anal. Calcd (%) for $C_{20}H_{15}N_4Cl$: C 69.28; H 4.33; N 16.16; Cl 10.23. Found: C 69.48; H 4.52; N 16.18; Cl 10.51.

2-(1*H*-Benz[*d*]imidazol-2-yl)-3-(2-chloro-1-propyl-1*H*-indol-3-yl)acrylonitrile 5b.



Yellow crystals, yield 67%, mp 242-244°C. IR spectrum, ν_{max}, cm^{-1}: 2961, 2215, 1596, 1468, 1425. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ: 13.06 (s,1H), 8.41 (s, 1H), 8.03 (d, *J* = 7.50 Hz, 1H), 7.73–7.67 (m, 2H), 7.55 (d, *J* =7.50 Hz, 1H), 7.40-7.19 (m, 4H), 4.35 (t, *J* =7.50 Hz, 2H), 1.80 (k, *J* =7.50 Hz, 2H), 0.91 (t, *J* =7.50 Hz, 3H) ppm. ^{13}C NMR (151 MHz, DMSO-d$_6$) δ: 148.65, 146.16, 137.93, 135.64, 131.32, 124.32, 124.03, 123.84, 123.59, 123.28, 122.20, 121.99, 121.69, 117.61, 115.58, 111.37, 107.72, 99.56, 39.64, 14.93. Anal. Calcd (%) for $C_{21}H_{17}N_4Cl$: C 69.91; H 4.71; N 15.53; Cl 9.84. Found: C 69.98; H 4.62; N 15.48; Cl 9.69.

5. X-Ray crystal data of CCDC 2189189 (4d)

$C_{21}H_{16}N_4$ (M_r = 324.38 g mol^{-1}): triclinic, space group *P*-1 (no. 2), a = 8.2387(2) Å, b = 9.5255(2) Å, c = 10.6889(2) Å, α = 106.482(2)°, β = 103.048(2)°, γ = 91.366(2)°, V = 780.13(3) Å^3, Z = 2, T = 100.00(10) K, μ(CuKα) = 0.664 mm^{-1}, *Dcalc* = 1.381 g/cm^3, 16359 reflections measured (8.894° ≤ 2Θ ≤ 152.036°), 3239 unique (R_{int} = 0.0273, R_{sigma} = 0.0162) which were used in all calculations. The final R_1 was 0.0445 (I > 2σ(I)) and wR_2 was 0.1248 (all data). The X-ray diffraction data set was recorded on an Agilent SuperNova diffractometer using a microfocus X-ray radiation source with copper anode and Atlas S2 two-dimensional CCD detector. The reflections were collected, unit cell parameters determined and refined using the specialized CrysAlisPro software suite (Rigaku Oxford Diffraction, 2015). The structures were solved using the ShelXT program (Sheldrick, 2015) and refined with the ShelXL program (Sheldrick, 2015). Molecular graphics and presentation of structures for the publication were performed with the Olex2 ver. 1.5 software suite.

The complete X-ray structural dataset for compound **4d** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 2189189).

6. Photochemical properties of benzimidazolepyridoindoles 4c,d and 5a,b.

Spectral parameters registered for solutions in acetonitrile and DMSO are collected in Table S1. The UV–Vis absorption and fluorescence spectra of compound **4c** in acetonitrile are shown in Figure S1.

Table S1 Optical data of compounds **4c,d** and **5a,b** in acetonitrile and DMSO

	CH_3CN			DMSO		
	λ_{max}, nm	ε, $M^{-1}cm^{-1}$	λ^{fl}_{max}, nm	λ_{max}, nm	ε, $M^{-1}cm^{-1}$	λ^{fl}_{max}, nm
4c	292	1,96e5	439; 460	296	1,48e5	442; 464
	397	5,07e4		400	3,68e4	
	417	4,75e4		419	3,64e4	
	φ=0. 0.97[a]; λ^{ex} =417 nm			φ=0.99; λ^{ex} =419 nm		
4d	293	1,85e5	440; 462	296	2,26e5	440; 464
	397	4,88e4		400	4,09e4	
	417	4,65e4		419	3,95e4	
	φ=0.90; λ^{ex} =417 nm			φ=0.94; λ^{ex} =419 nm		
5a	267	3,60e4		270	2,12e4	
	386	3,36e4		390	1,92e4	
	φ=0,031; λ^{ex} =385 nm			φ=0,055; λ^{ex} =390 nm		
5b	280-294	2,15e4	442	282-296	2,88e4	446
	386	2,92e4		390	3,17e4	
	φ=0,079; λ^{ex} =385 nm			φ=0,16; λ^{ex} =390 nm		

[a] Fluorescence quantum yields were determined using the method by Parker-Rice with a solution anthracene as a standard luminophore.

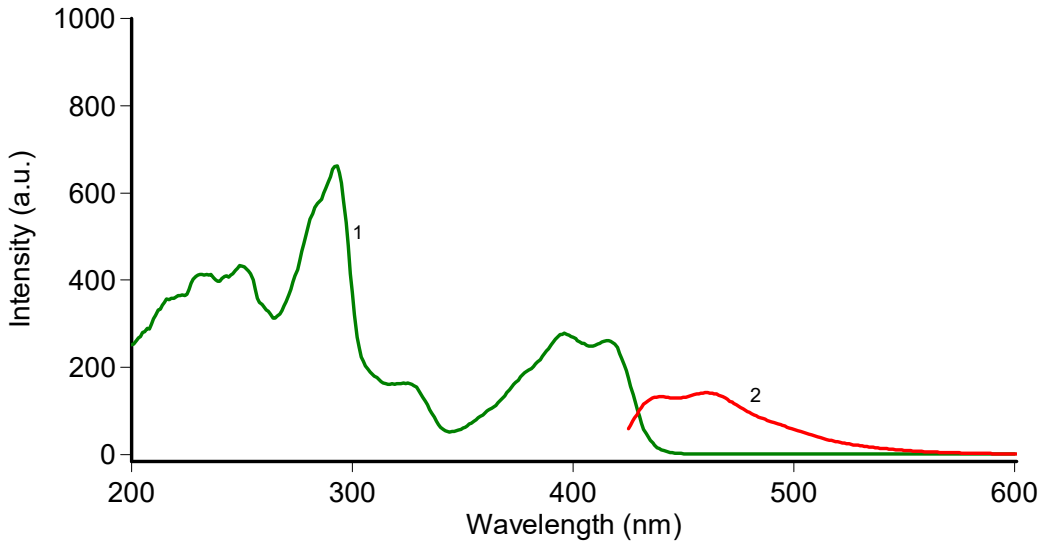


Figure S1 Electronic absorption spectra (1) and photoluminescence spectra (2) of compound **4c** in acetonitrile, 298 K (2.1.10-6 M).

The electronic absorption and photoluminescence spectra of the **4d** compound in acetonitrile, as well as the spectra of the **4c** and **4d** compounds in DMSO, have the similar appearance as in Figure S1.

7. References

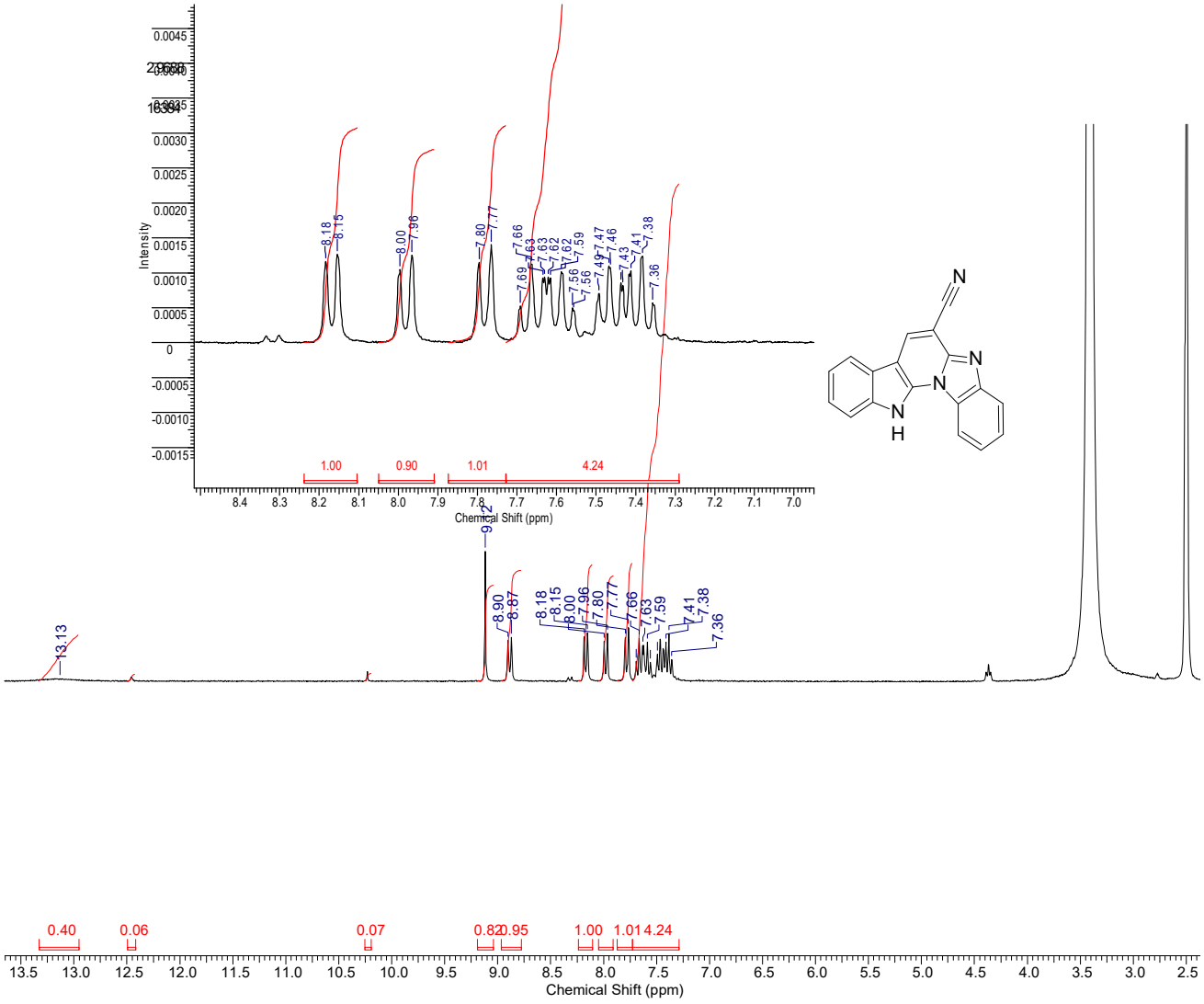
S1. N. I. Vikrishchuk, L. D. Popov and O. I. Askalepova, *RU Patent 2800553*, 2023.

S2. K. F. Suzdalev, N. I. Vikrishchuk, K. A. Prikhodko, E. Yu. Shasheva, S. V. Kurbatov, S. K. Bogus, P. A. Galenko-Yaroshevsky, *Chem. Heterocycl. Compd*., 2016, **52**, 303, https://doi.org/10.1007/s10593-016-1882-y.

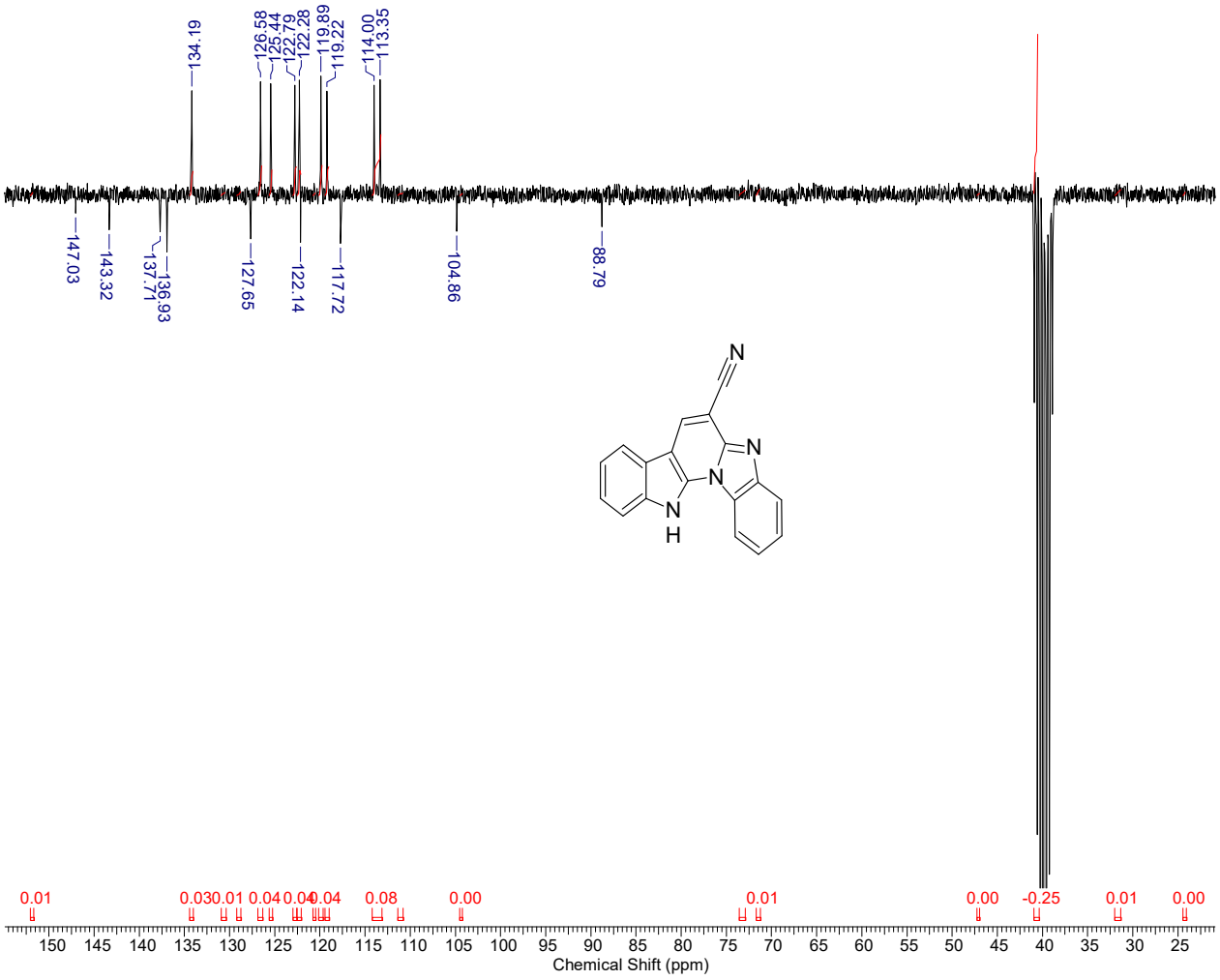
8. NMR spectra of compounds 4a-d and 5a,b.

12*H*-Benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*] indole-6-carbonitrile 4a.

^{1}H NMR spectrum

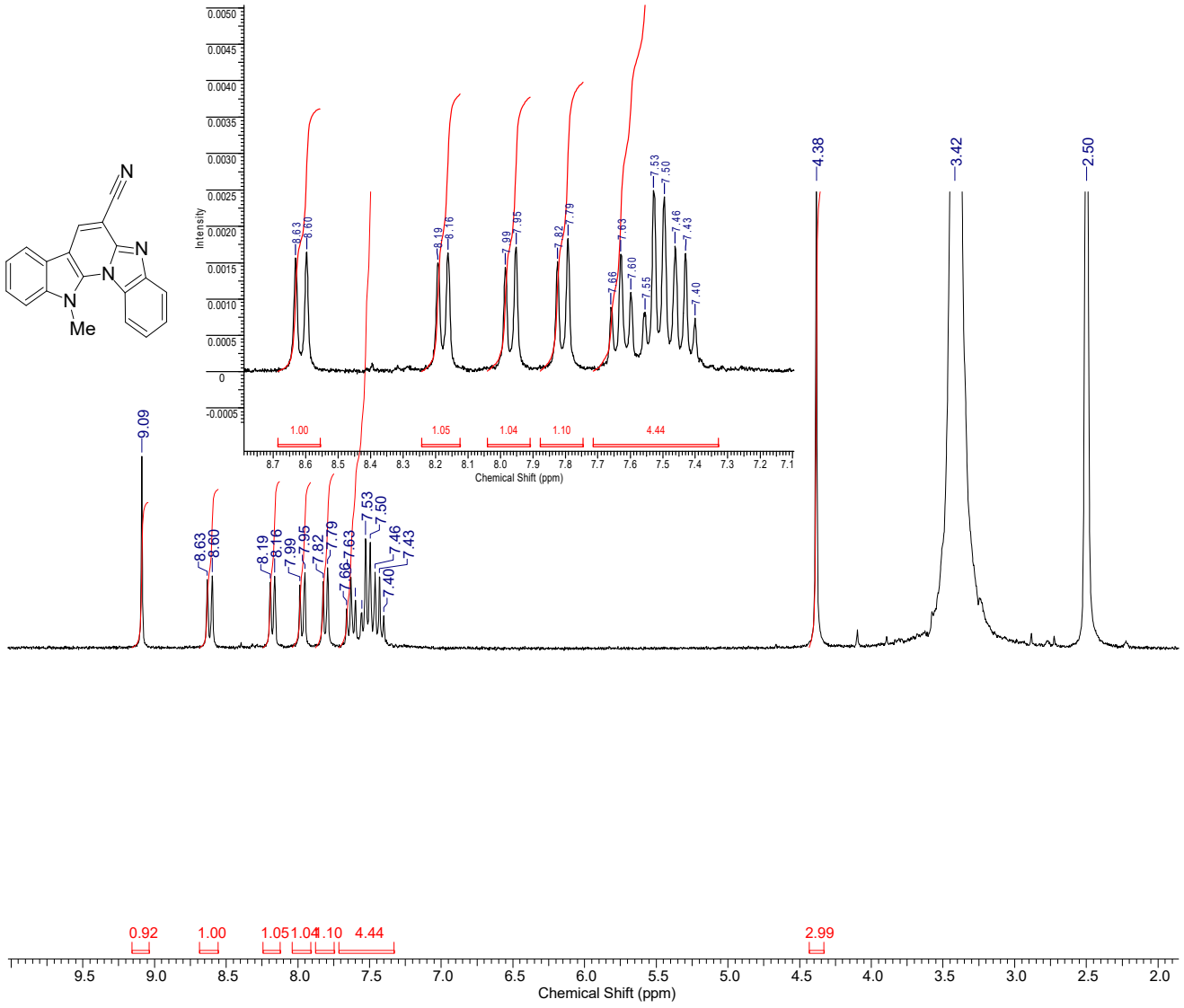


^{13}C NMR spectrum

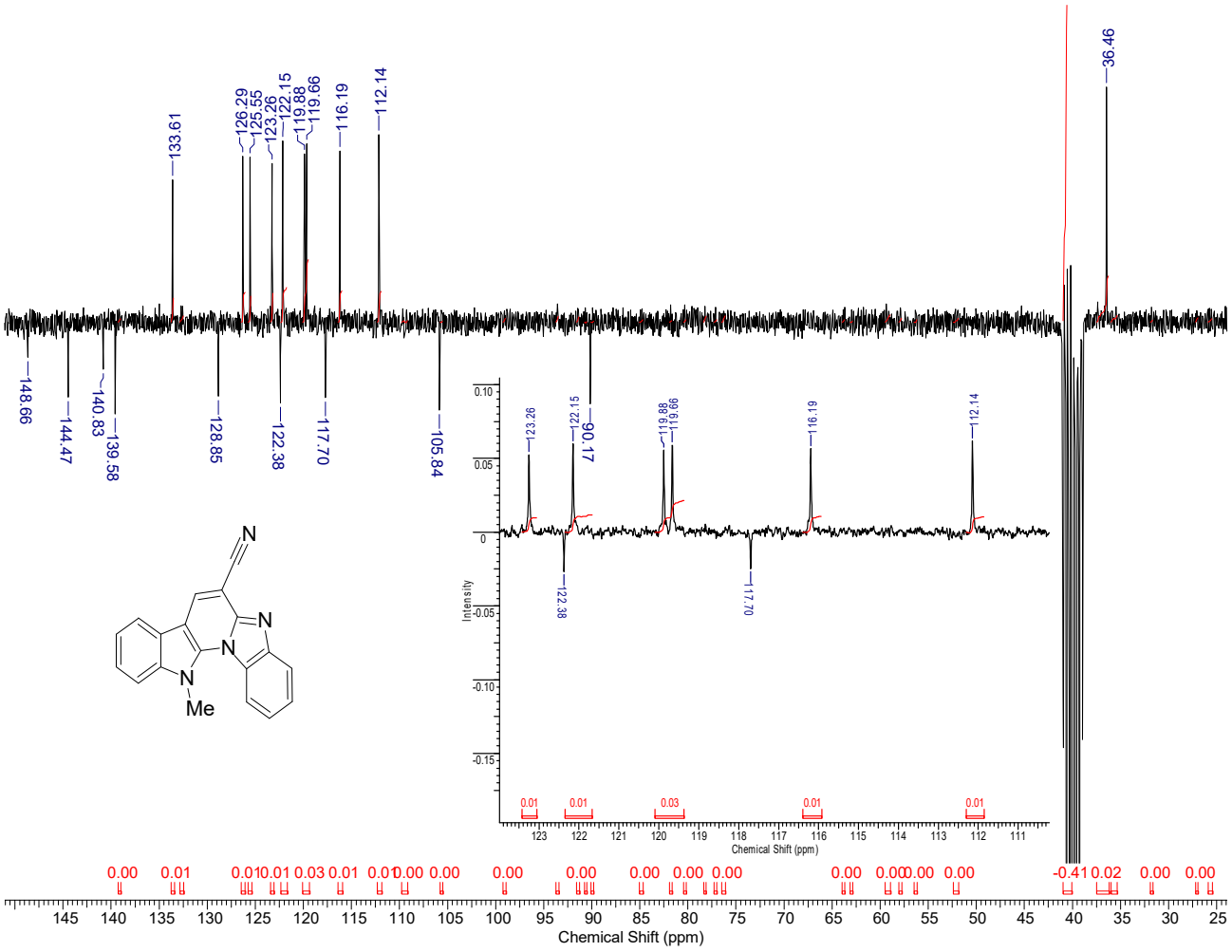


12-Methyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*] indole-6-carbonitrile 4b.

^{1}H NMR spectrum

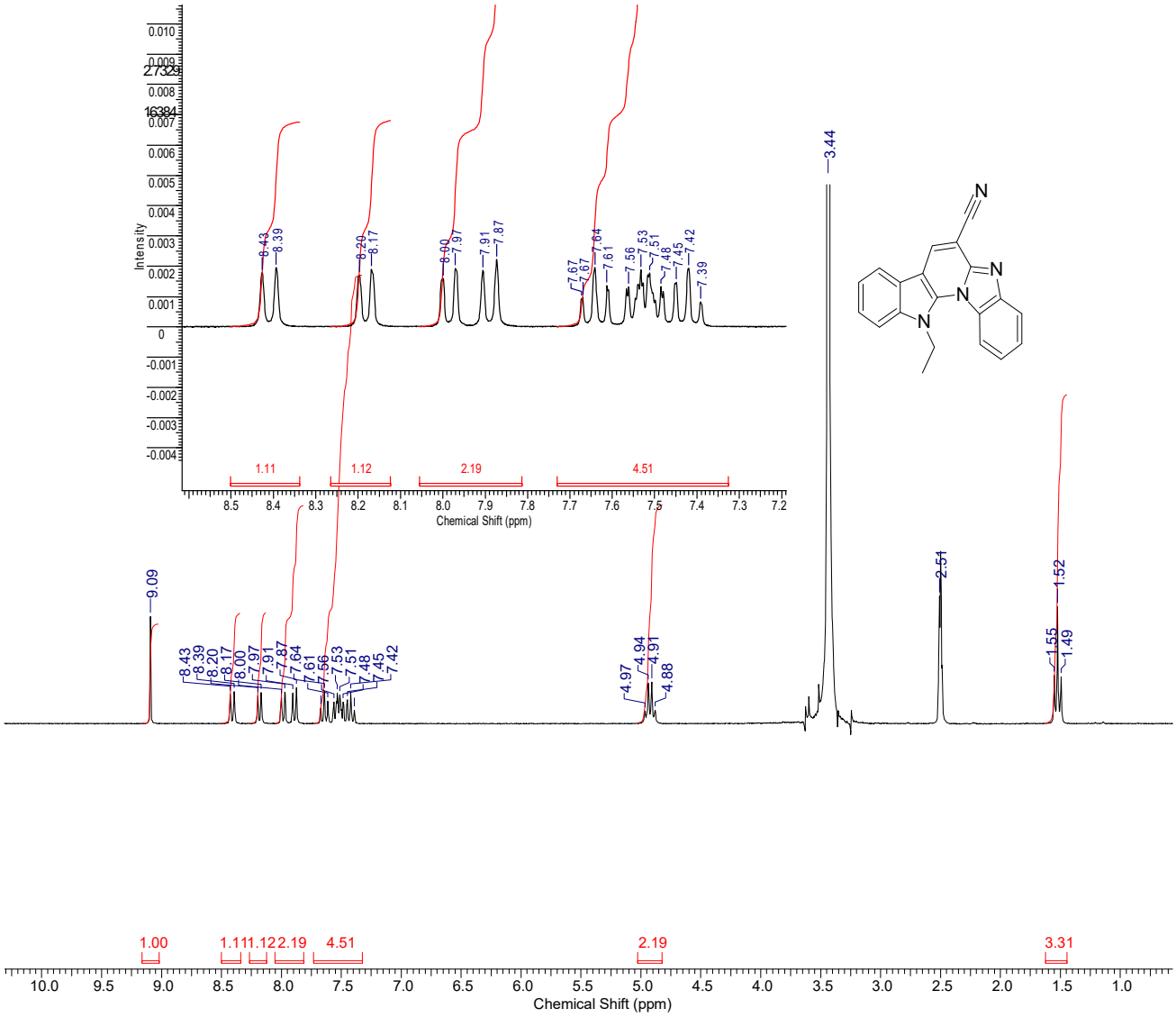


^{13}C NMR spectrum

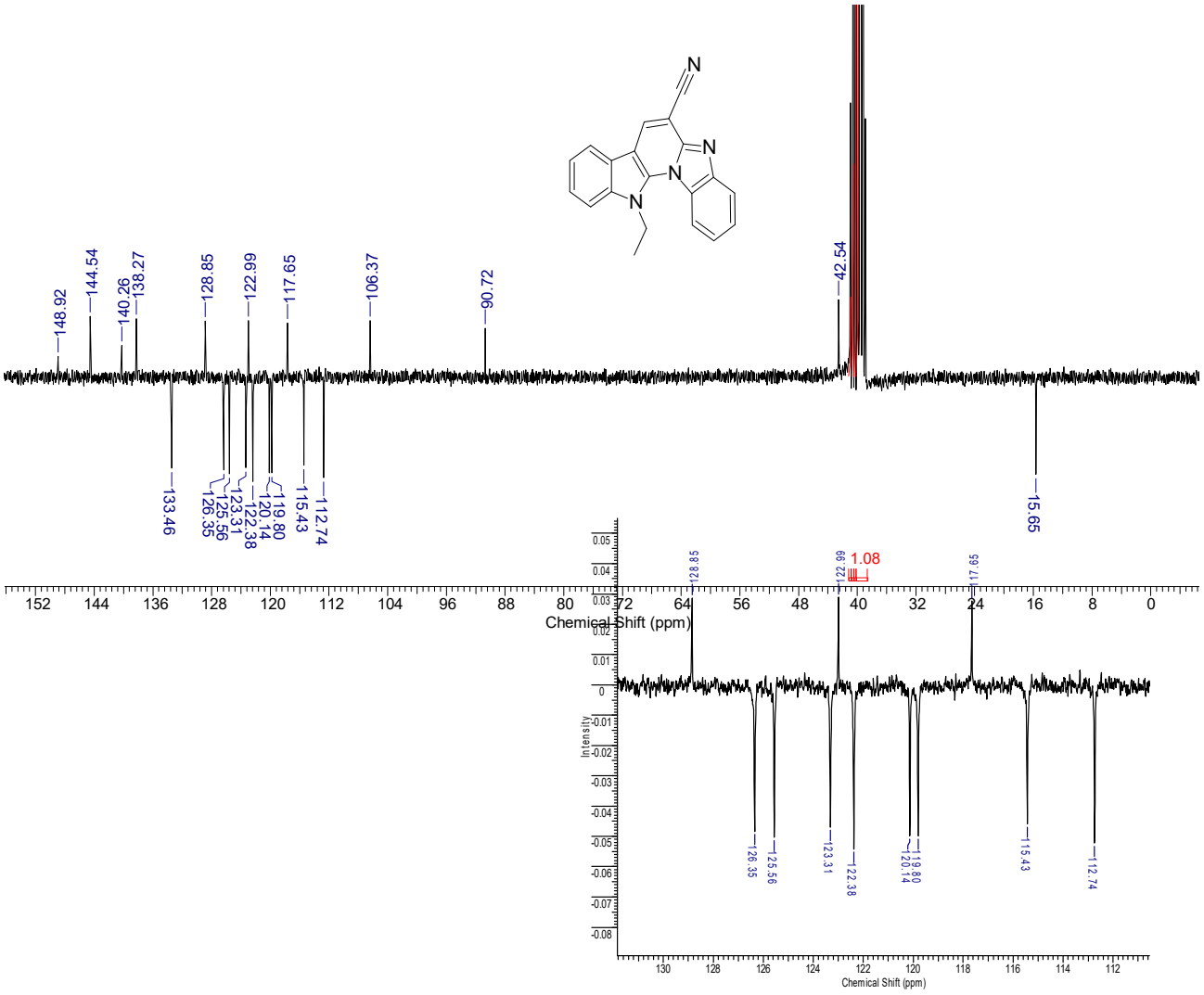


12-Ethyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4c

^{1}H NMR spectrum

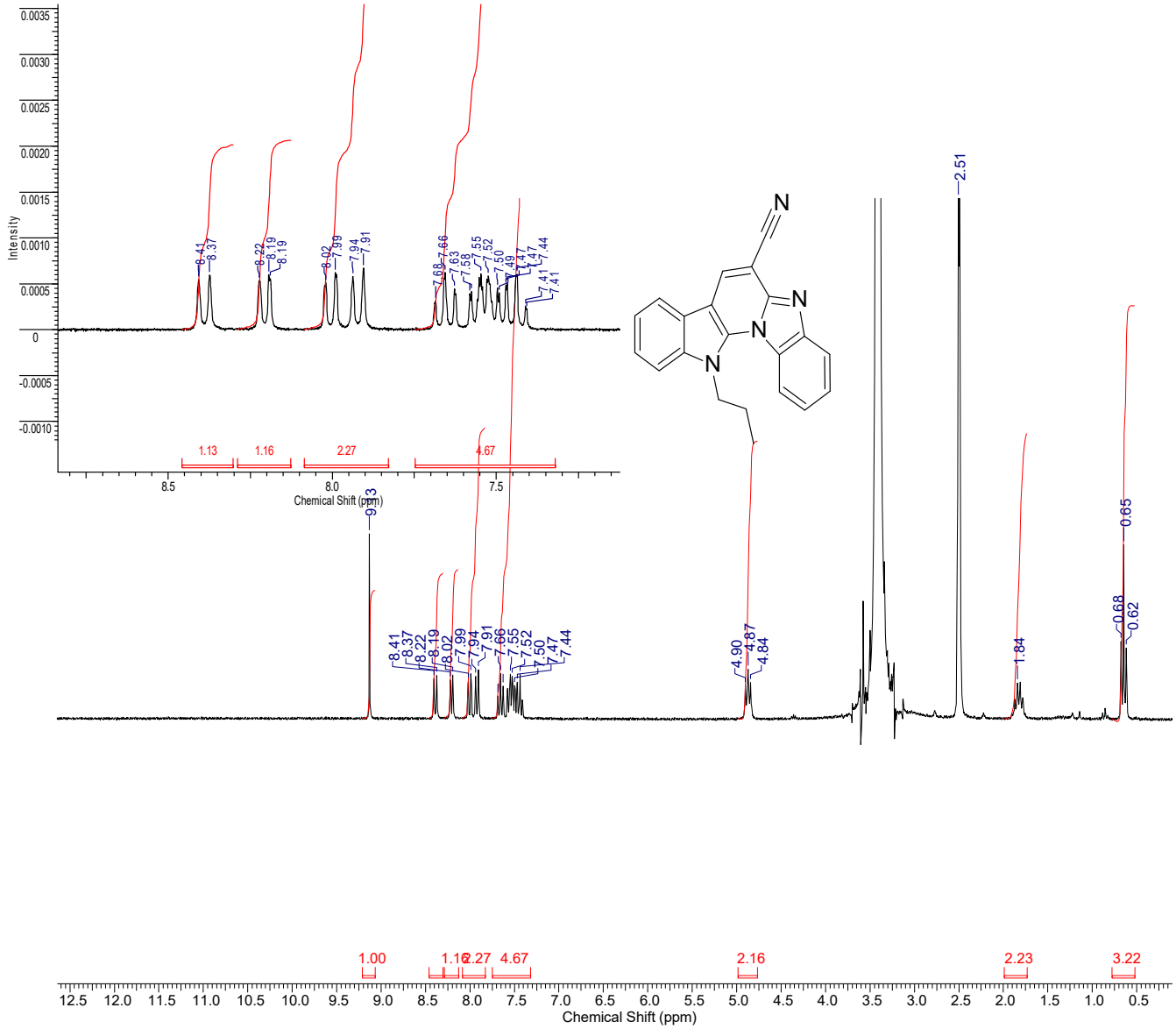


^{13}C NMR spectrum

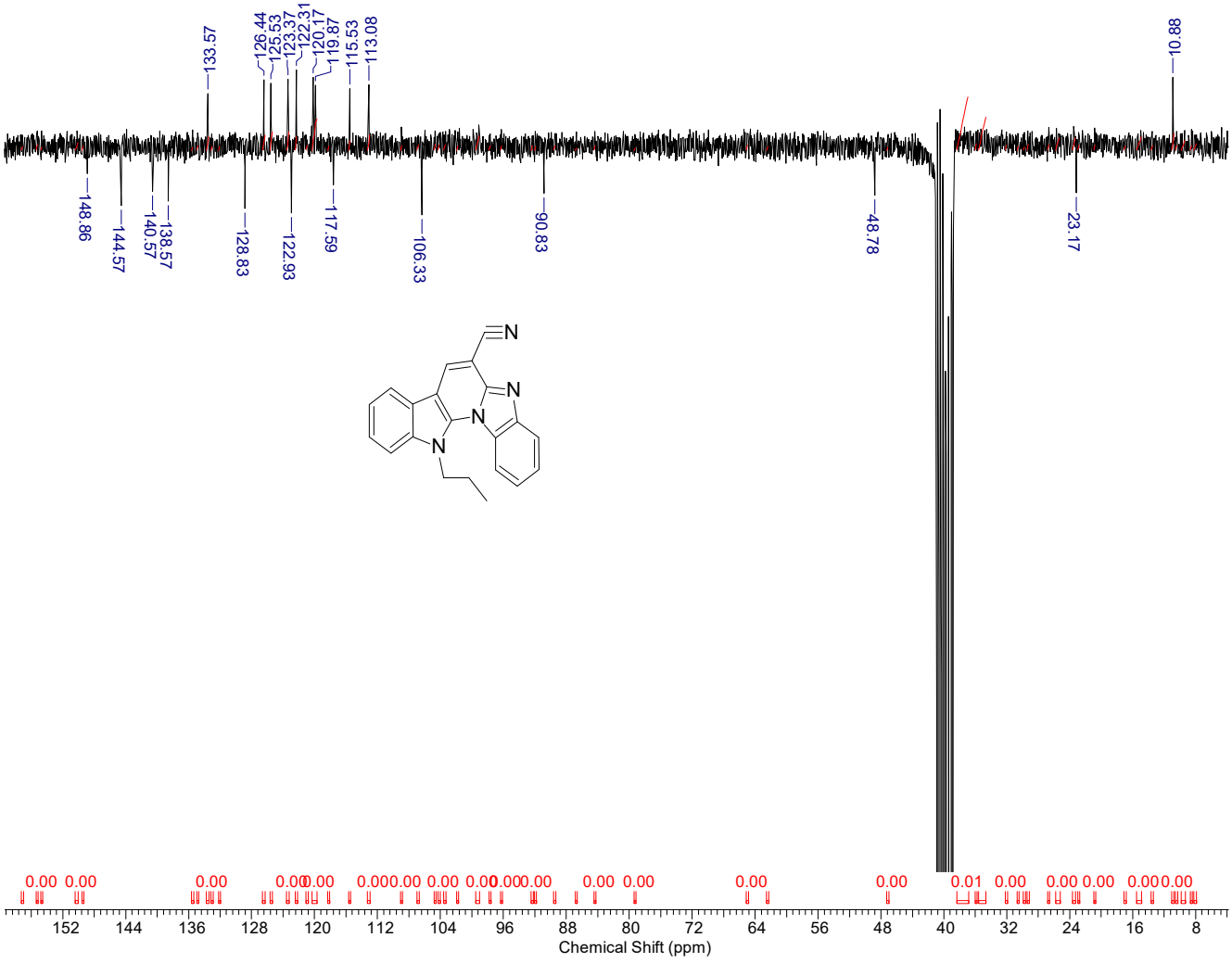


12-Propyl-12*H*-benz[4',5']imidazo[1',2':1,6]pyrido[2,3-*b*]indole-6-carbonitrile 4d

^{1}H NMR spectrum

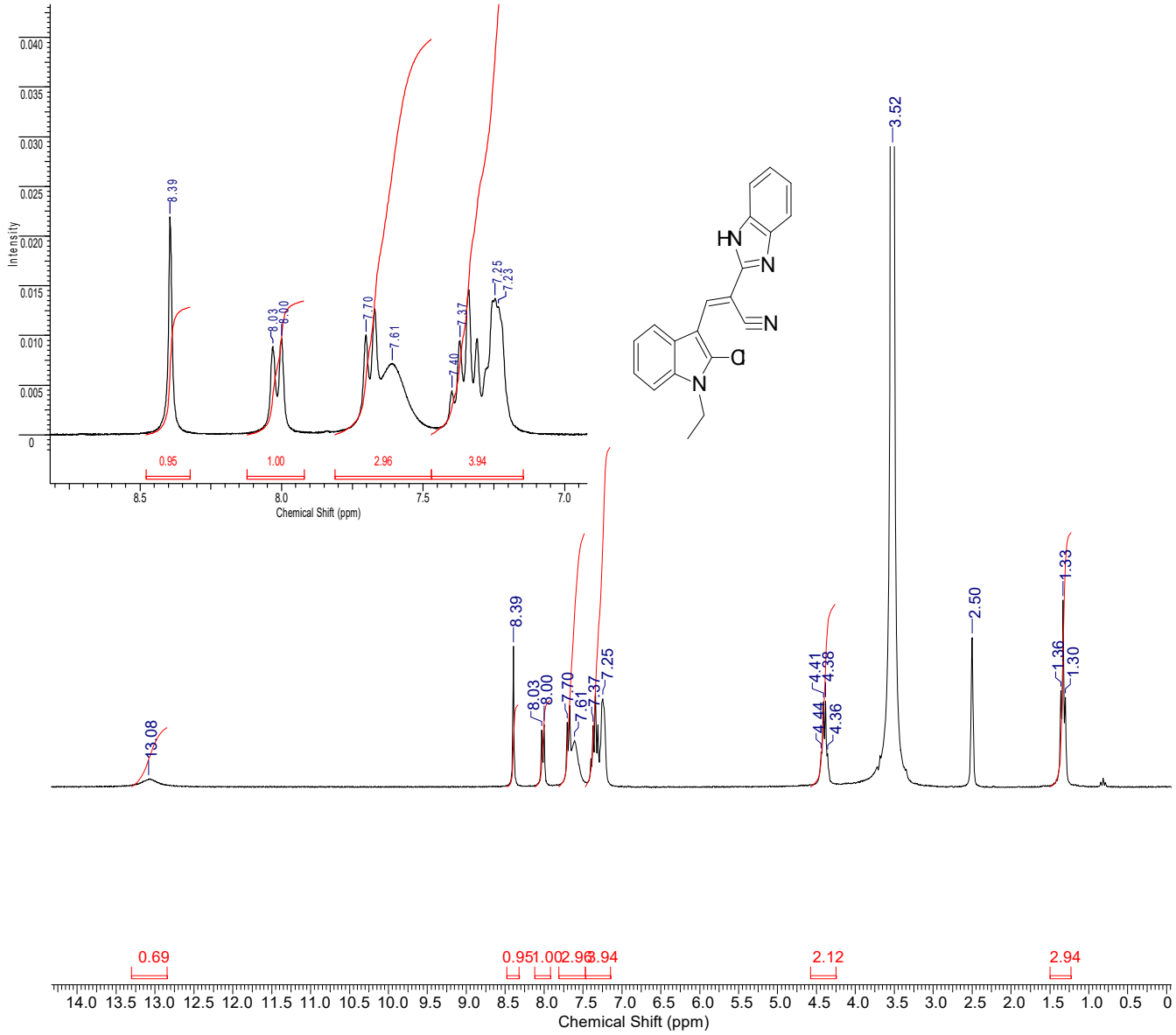


^{13}C NMR spectrum

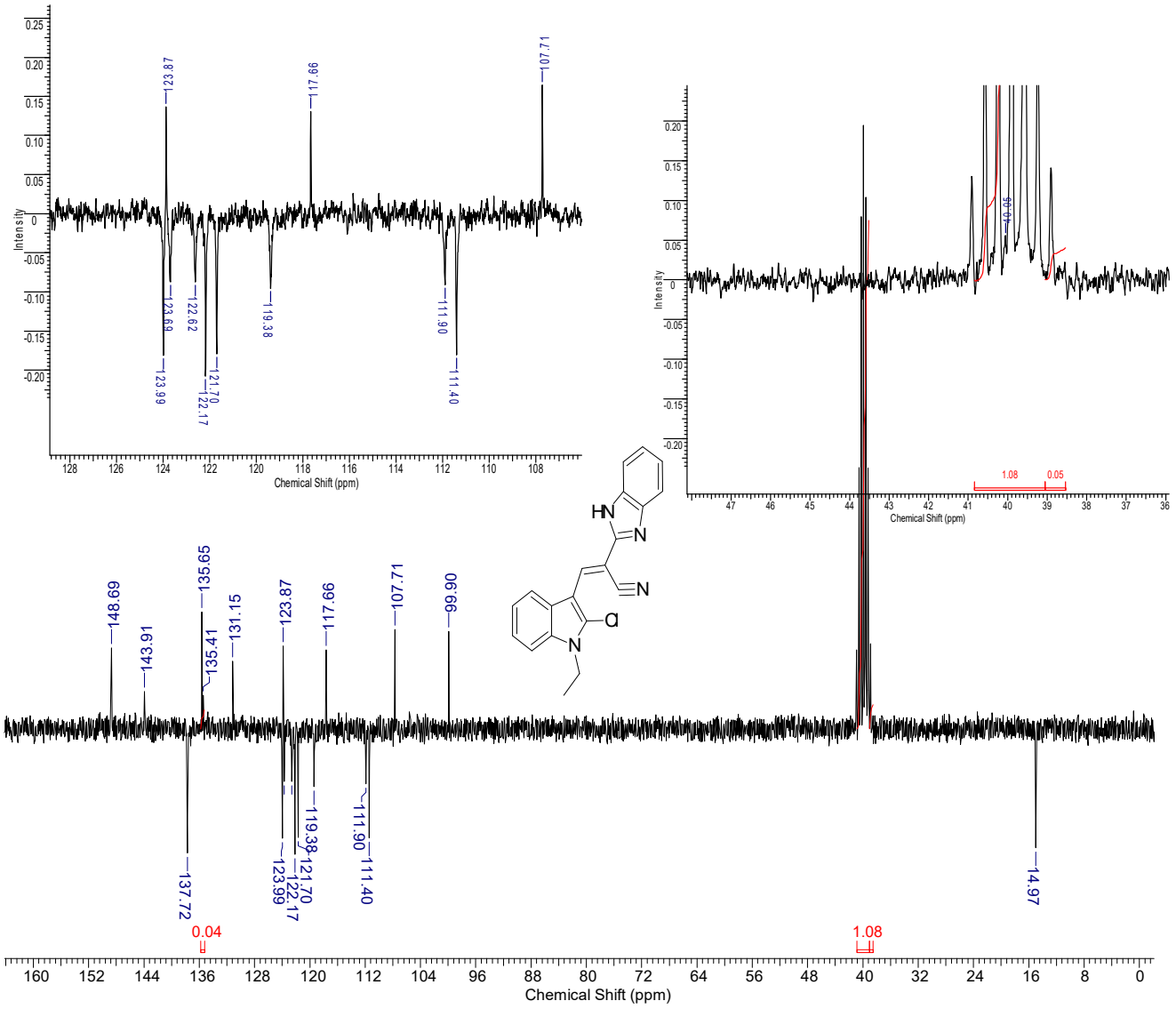


2-(1*H*-Benz[*d*]imidazol-2-yl)-3-(2-chloro-1-ethyl-1*H*-indol-3-yl)acrylonitrile 5a.

^{1}H NMR spectrum

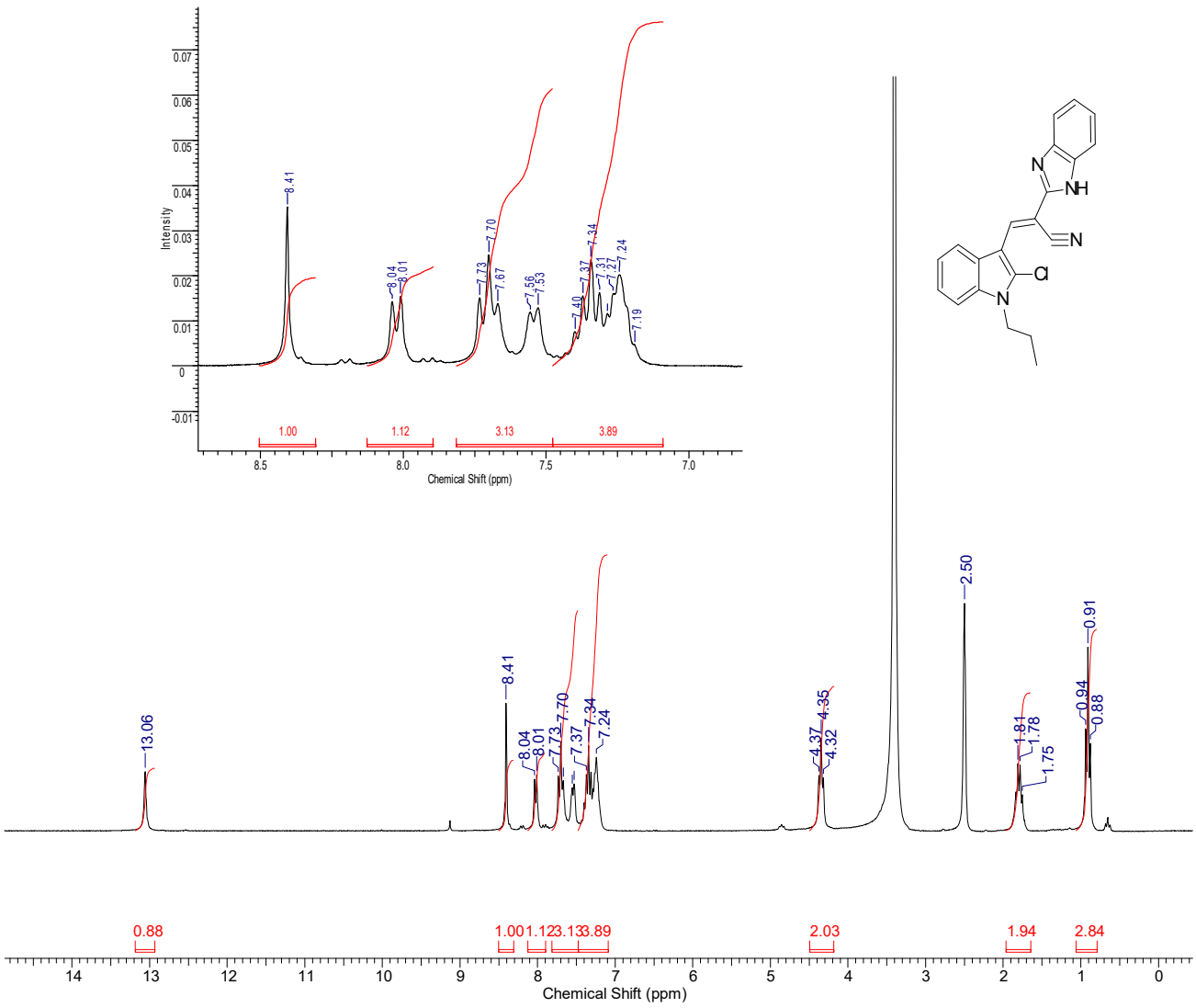


^{13}C NMR spectrum



2-(1*H*-Benz[*d*]imidazol-2-yl)-3-(2-chloro-1-propyl-1*H*-indol-3-yl)acrylonitrile 5b.

^{1}H NMR spectrum



^{13}C NMR spectrum