Supplementary Material

Synthesis of Pyrrole and Indole Quinoxalinone and Oxazinone Derivatives by Intramolecular Copper-Catalyzed Reactions

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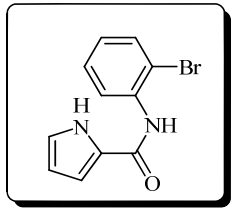
Contents

General

^{1}H NMR (400.16 MHz) and ^{13}C NMR (100.62 MHz) were conducted on a High Resolution Spectrometer Bruker Advance 400 in Cl_3CD or DMSO-*d6* as a solvent otherwise indicated, and referenced with residual solvent signal. Gas Chromatographic (GC) analyses were performed on an instrument with a flame ionization detector equipped with a VF-5ms column (30 m x 0.25 mm x 0.25 μm). Gas Chromatographic-Mass Spectrometer analyses were carried out on a GC/MS QP 5050 equipped with a quadrupole detector and a VF-5ms column (30 m x 0.25 mm x 0.25 μm). High Resolution Mass Spectra were performed in a MS/MS instrument in pure products. These data were obtained by ESI or APPI mode ionization and TOF detection. Melting points were performed with an electrical instrument and are uncorrected. MW-induced reactions were performed in a single mode instrument (CEM Focused Microwave™ Synthesis System, Model Discover) equipped with noncontact infrared sensor to measure the temperature, direct pressure control system by measurement of pressure of the reaction vessel contents and cooling system by compressed air. Quantification by GC was performed by the Internal Standard Method.

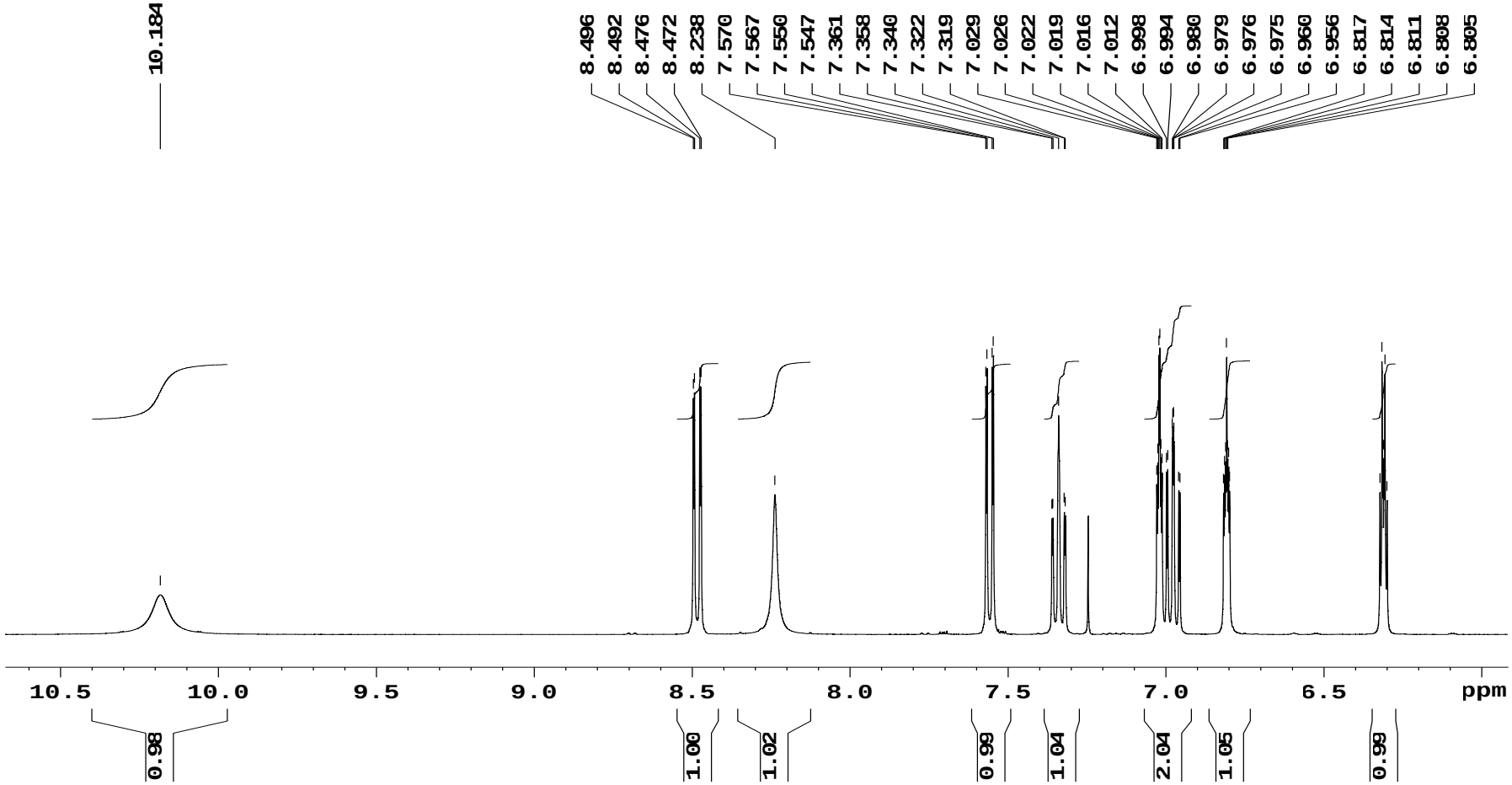
Materials

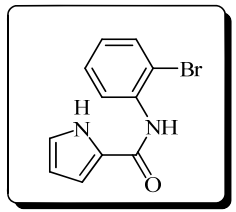
1*H*-pyrrole-2-carboxylic acid, 1*H*-indole-2-carboxylic acid, oxalyl chloride, 2-bromoaniline, 2-bromophenol, 2-iodophenol, 1,1´carbonyldiimidazole, 2-bromo-4-methylaniline, sodium hydride, potassium carbonate, potassium phosphate, cesium carbonate, L-proline, 1, 10 phenantroline, *N*,*N*-dimethylethylendiamine and CuI were commercially available and used as received from the supplier. 2-bromo-4-chloroaniline, 4-amino-3-bromobenzonitrile, 2-bromo-4nitroaniline and 1-bromo-2-naphthylamine were obtained by reported methods.[1] THF and DMF were dried and store under nitrogen, over molecular sieves (4 Å). The purification of compounds was carried out by chromatography column on silica gel or by radial thin layer chromatography. In all purifications analytical grade solvents were distilled before used.



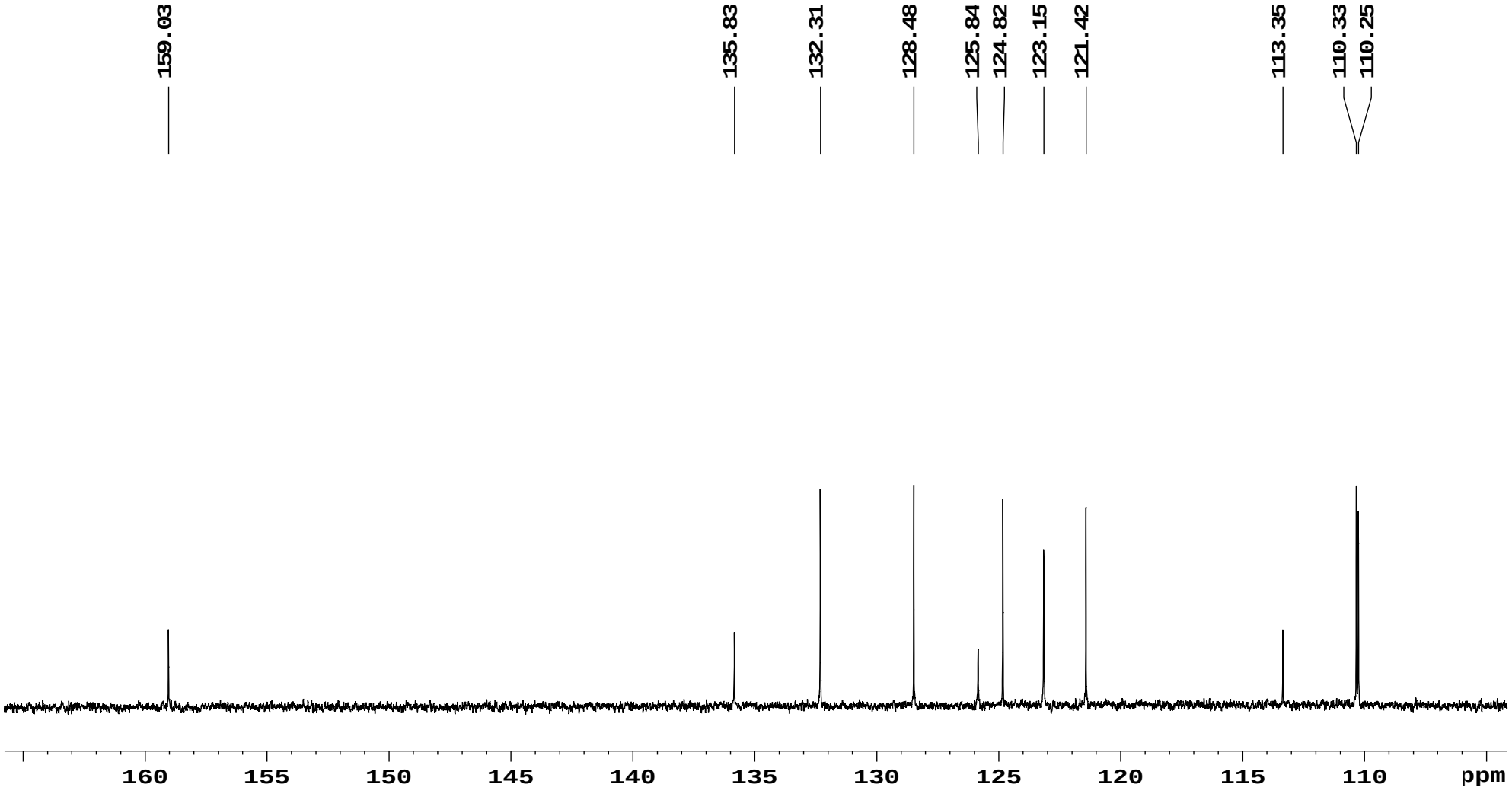
Spectra data of compounds 1a-g, 2a-d and 4a

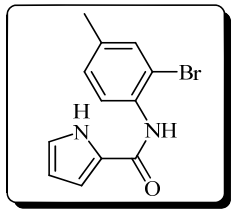
^{1}H NMR *N*-(2-bromophenyl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1a**



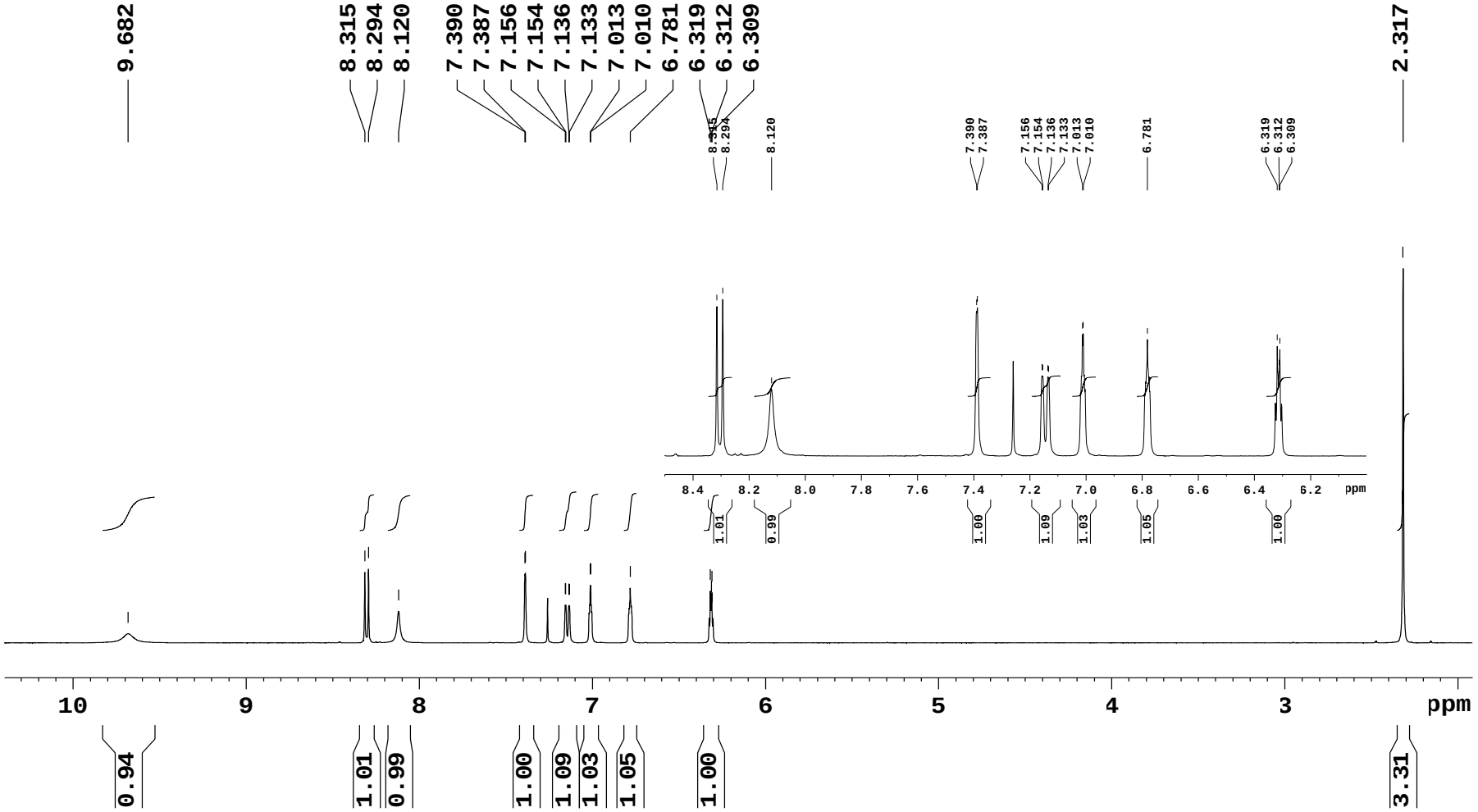


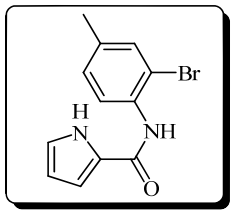
^{13}C NMR *N*-(2-bromophenyl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1a**



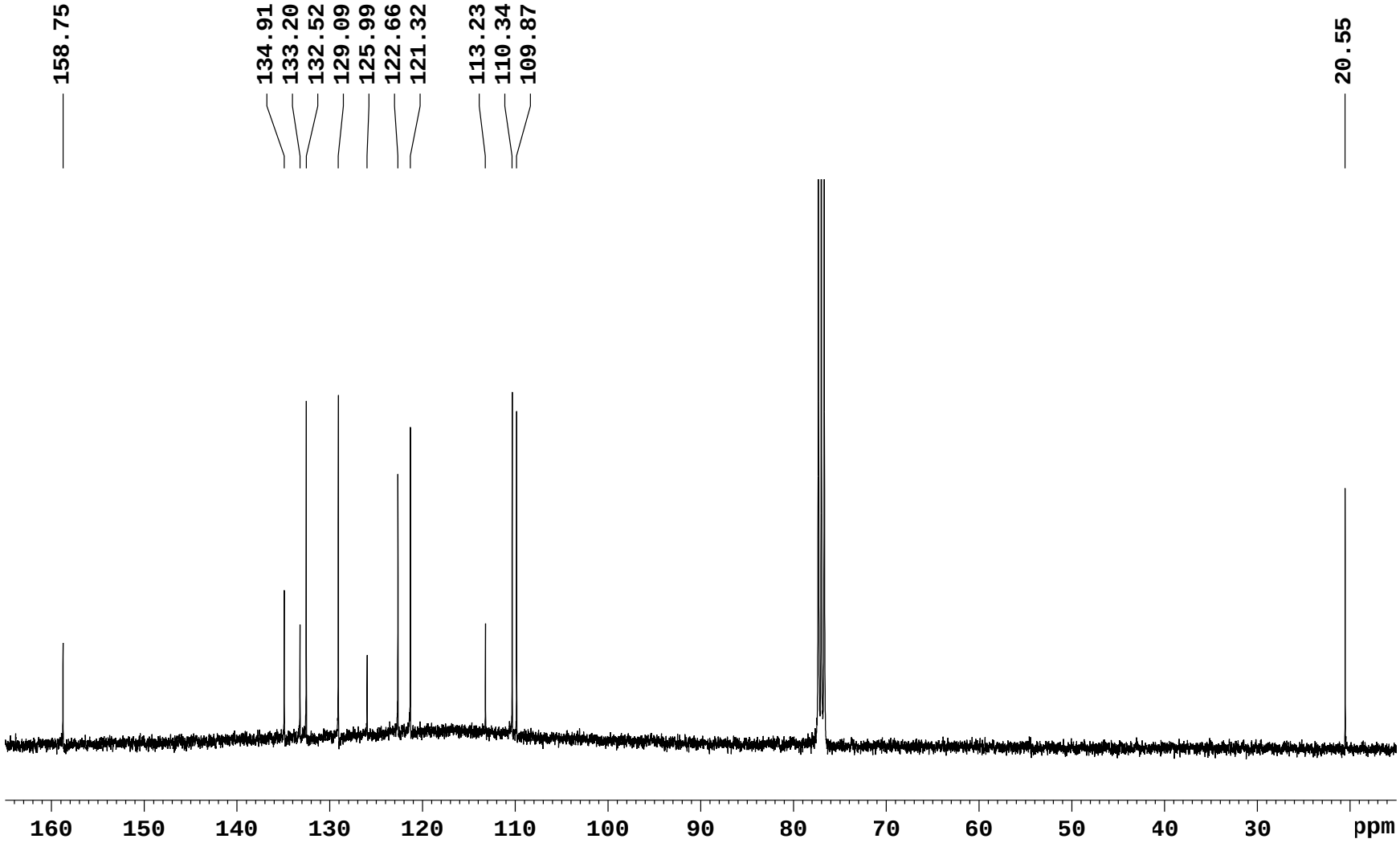


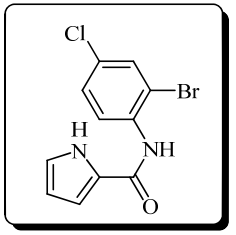
^{1}H NMR *N*-(2-bromo-4-methylphenyl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1b**





^{13}C NMR *N*-(2-bromo-4-methylphenyl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1b**





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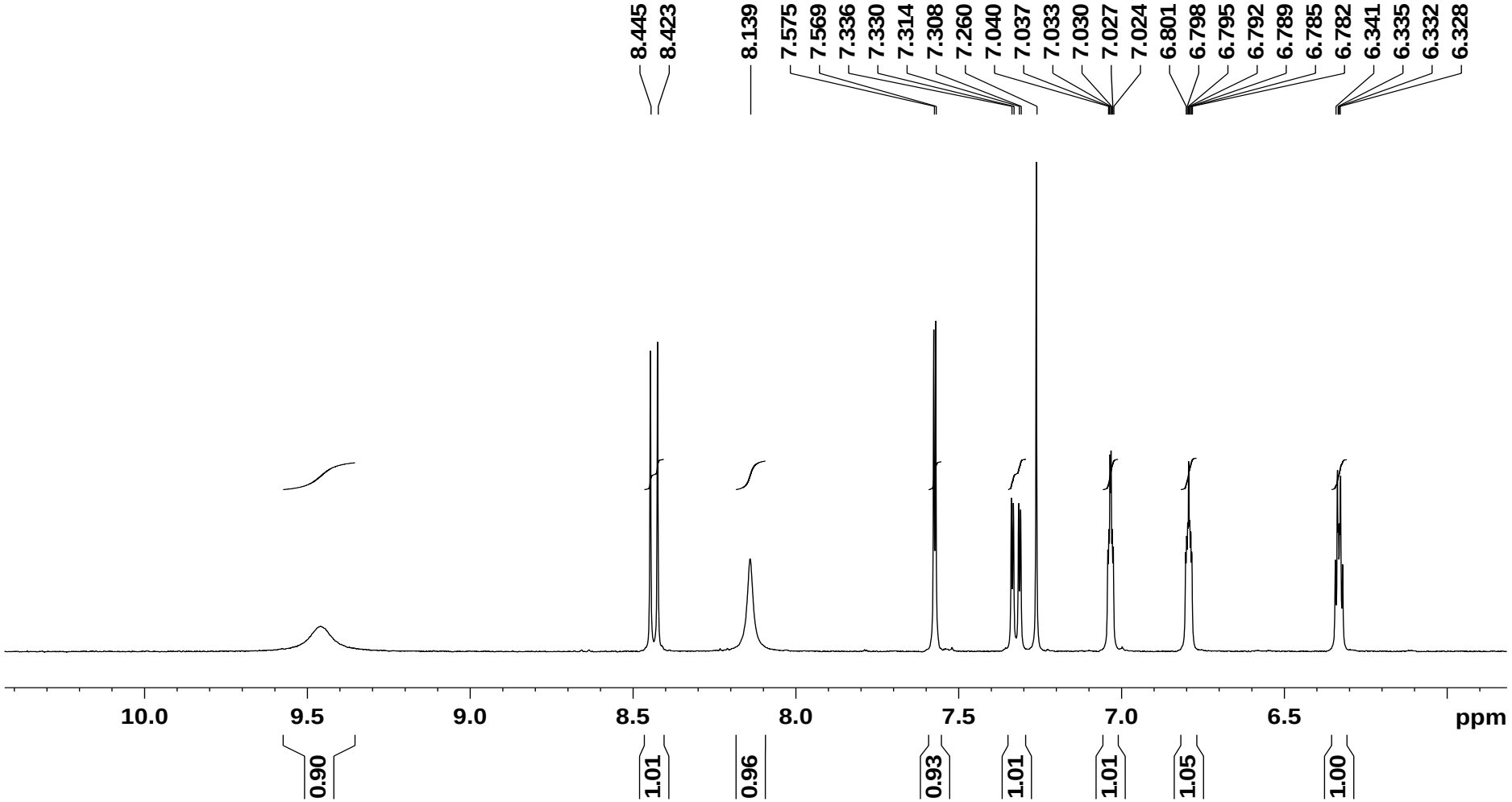
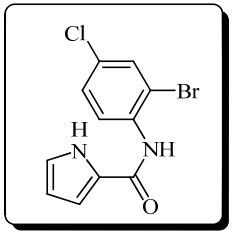
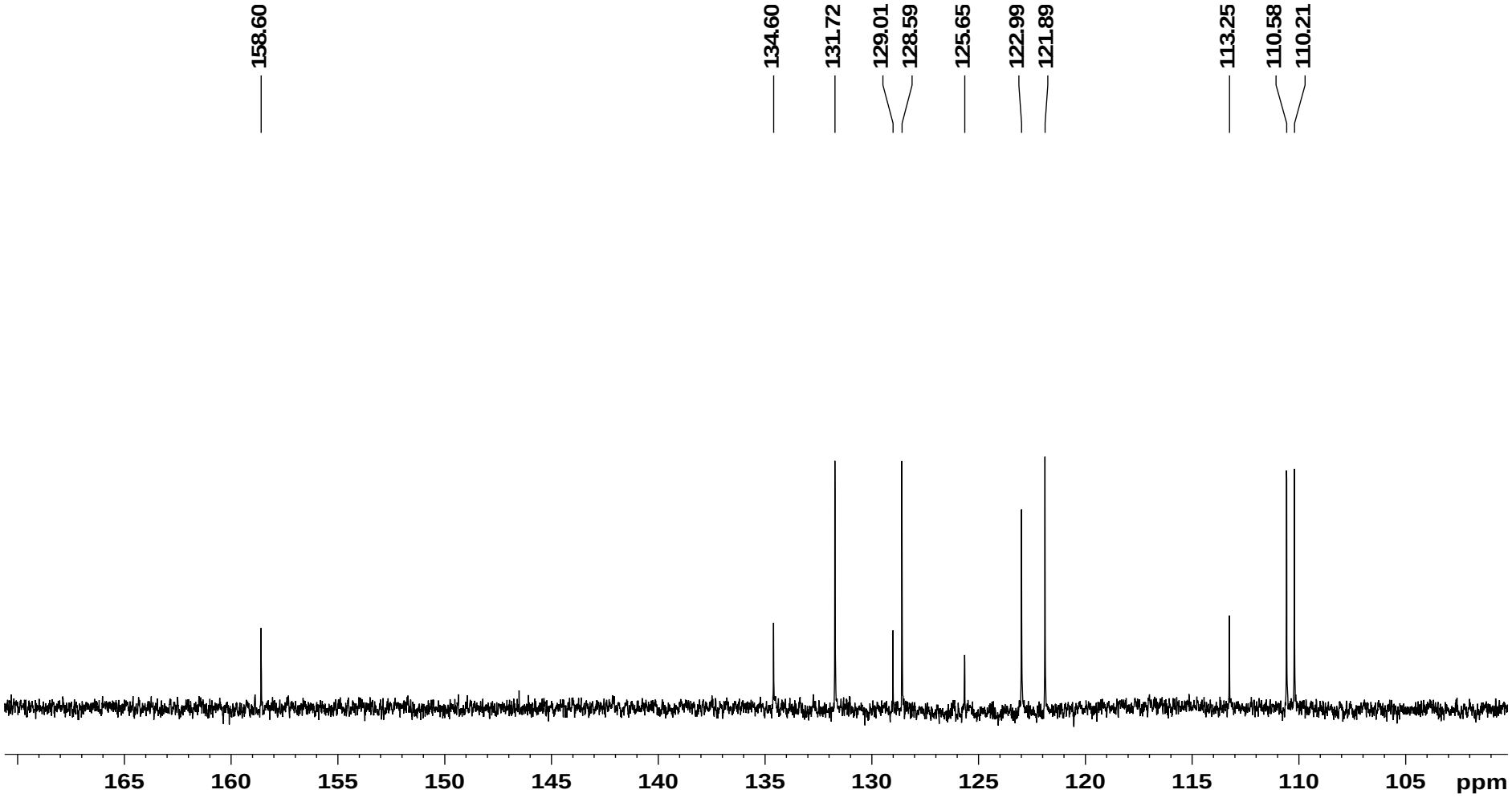
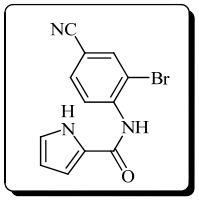




^{13}C NMR *N*-(2-bromo-4-chlorophenyl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1c**





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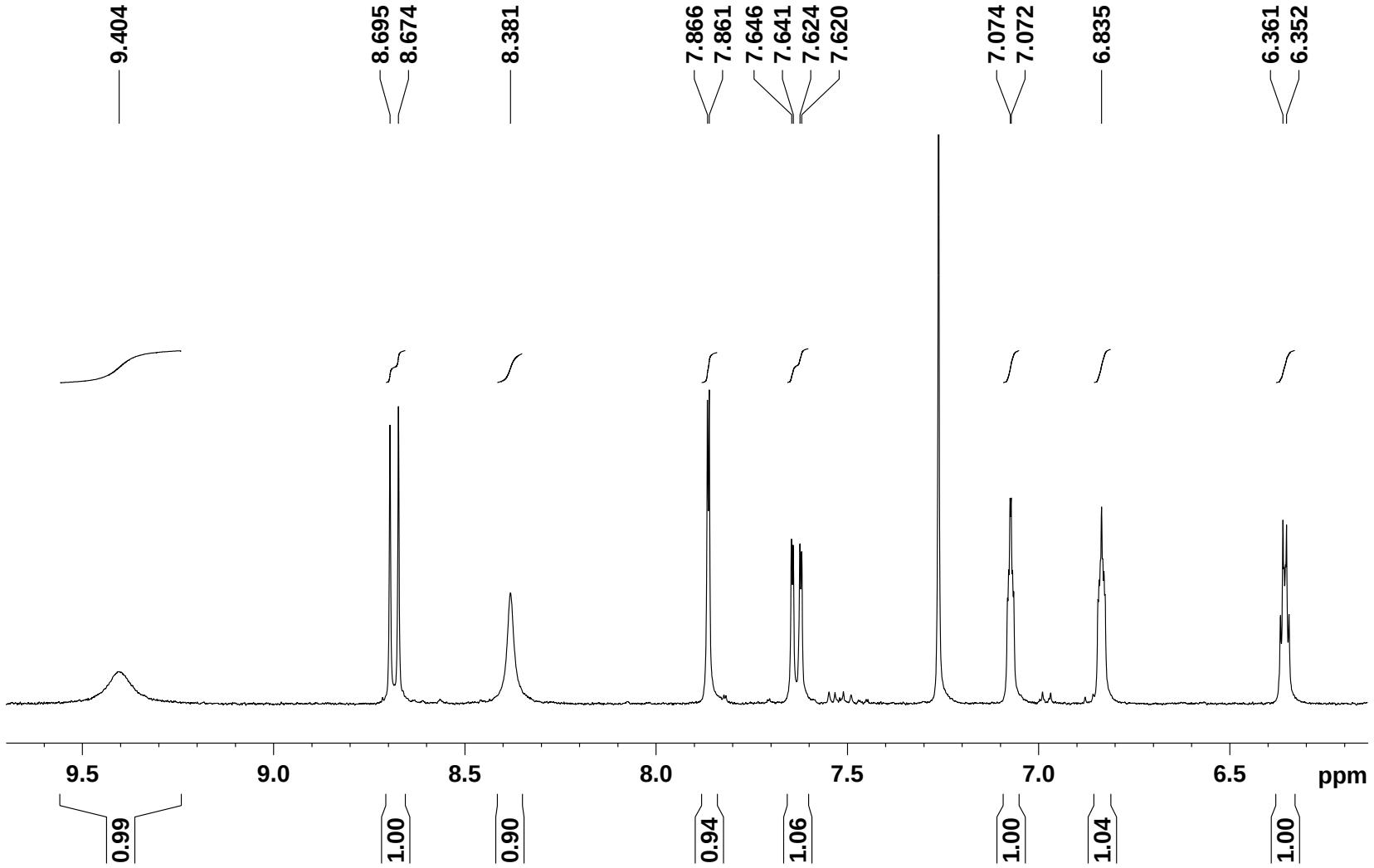
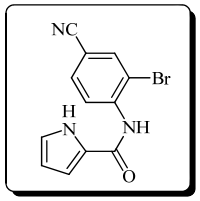
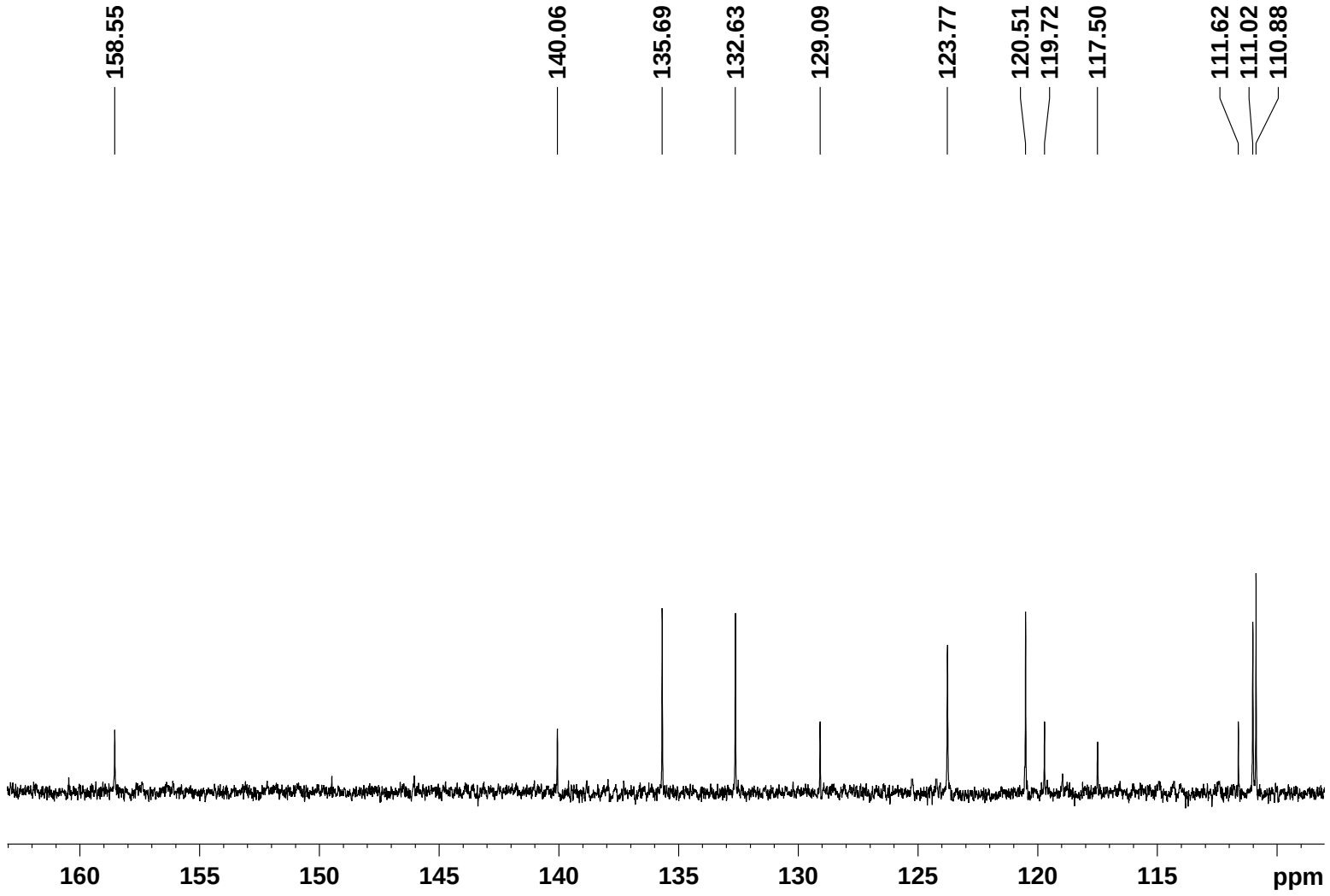
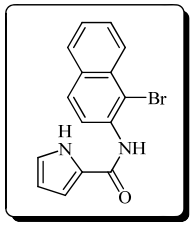


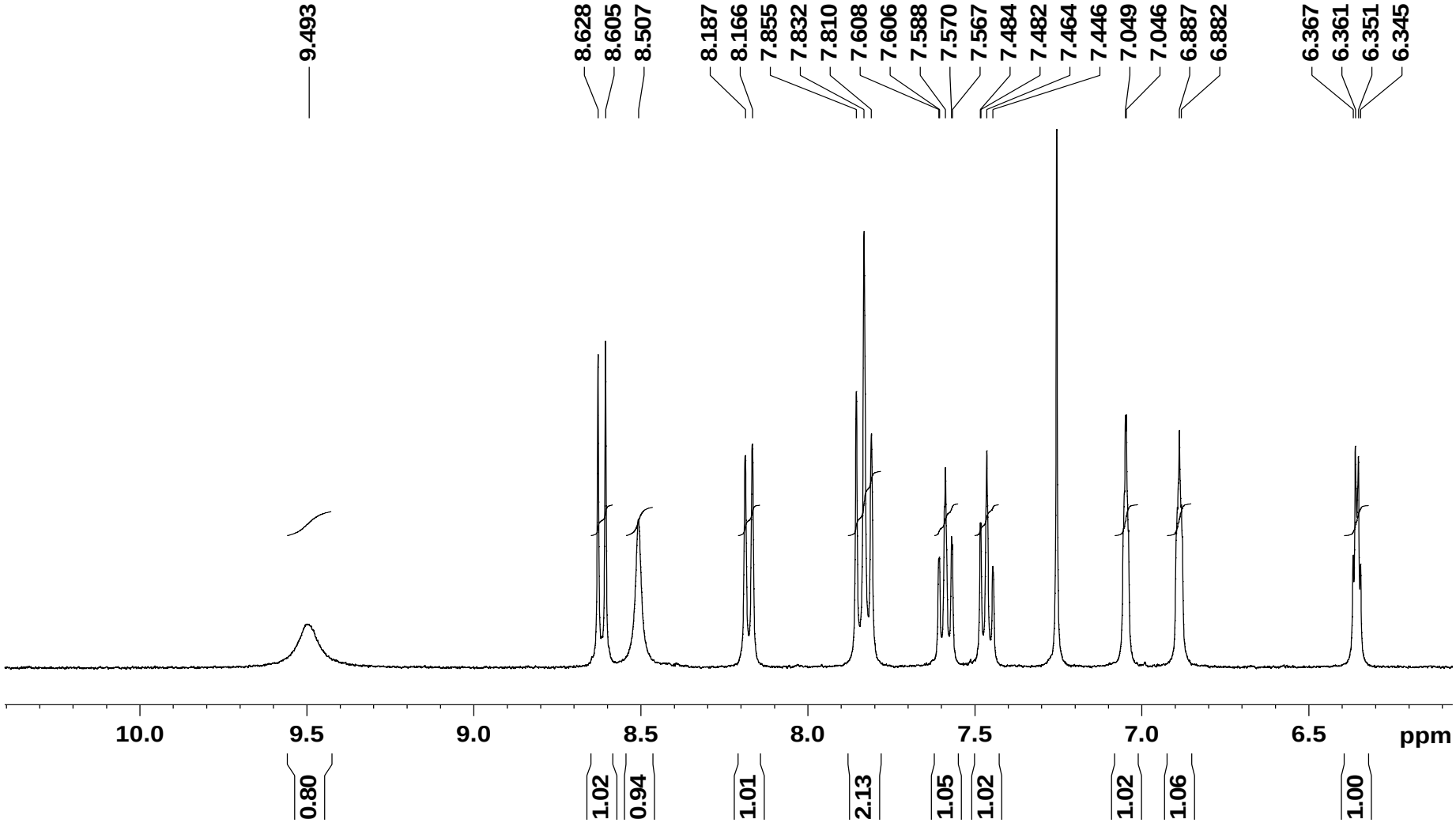


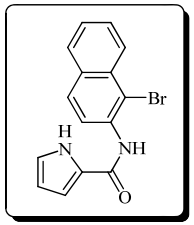
^{13}C NMR ***N*-(2-Bromo- 4-cyanophenyl)-1H-pyrrole-2-carboxamide** ($CDCl_3$) **1d**



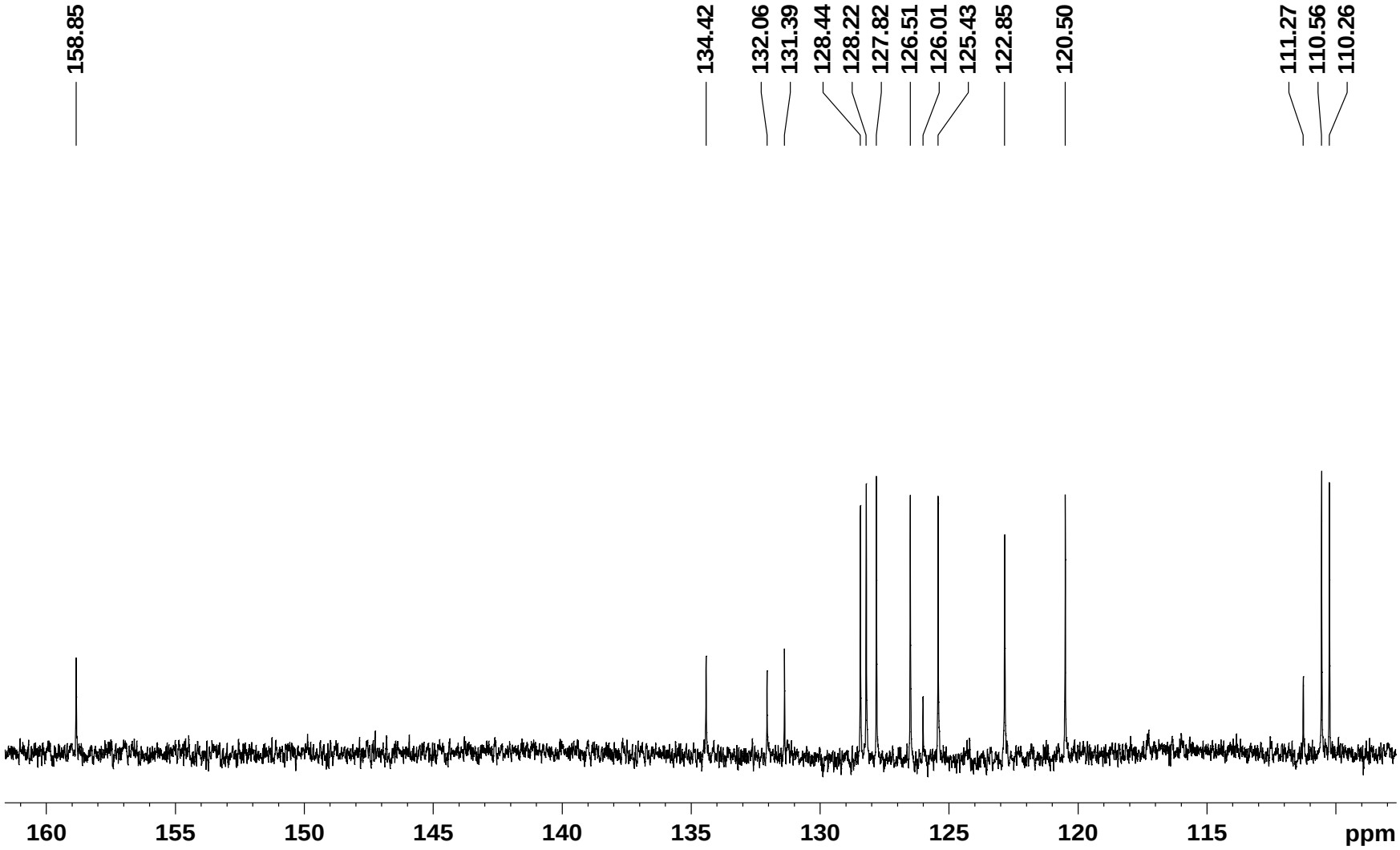


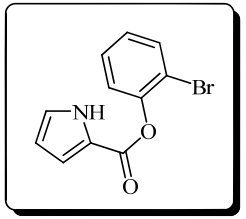
^{1}H NMR *N*-(1-bromonaphthalen-2-yl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1e**



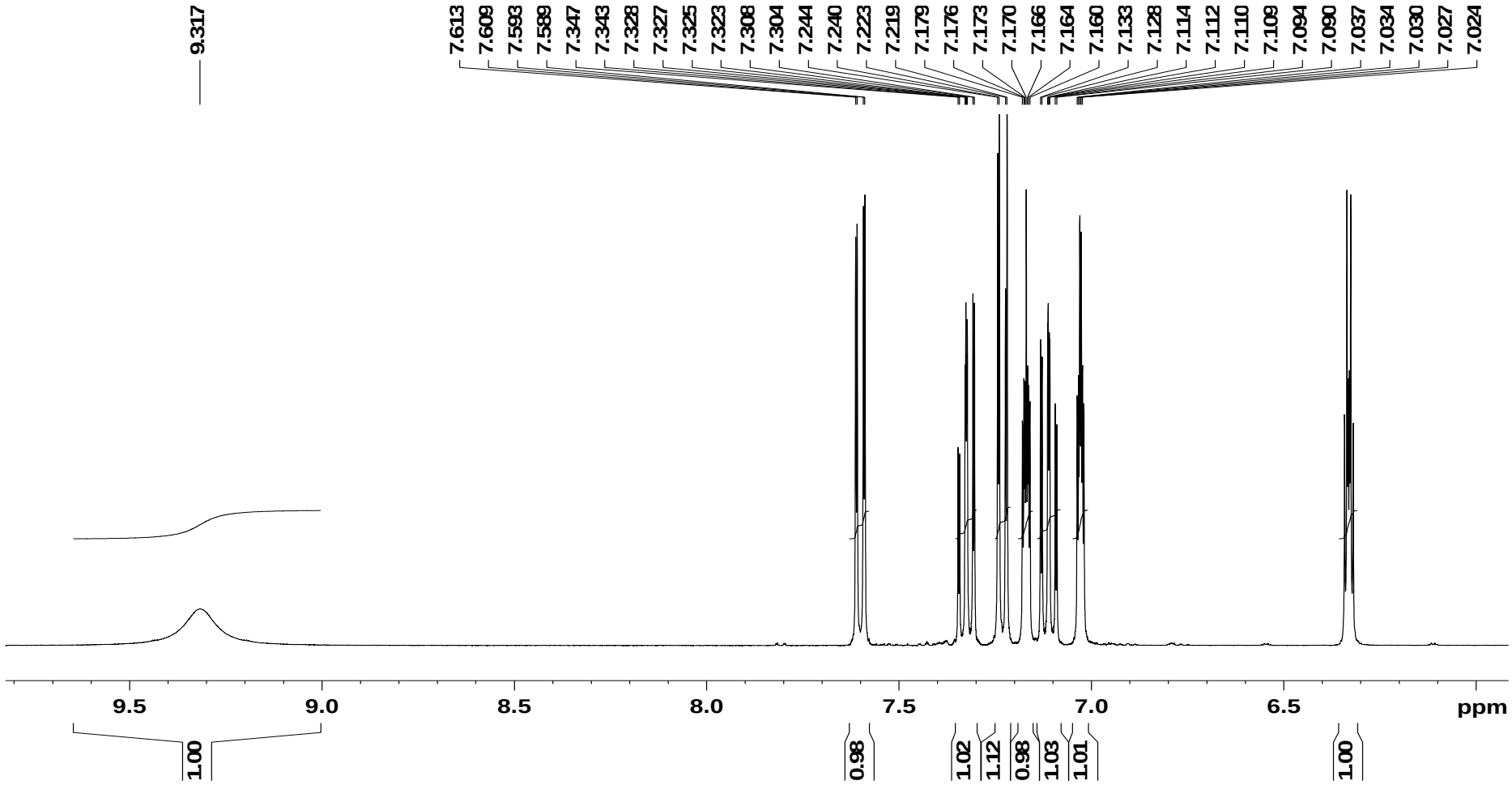


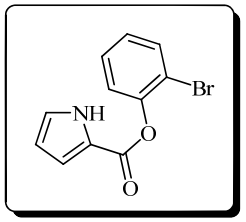
^{13}C NMR *N*-(1-bromonaphthalen-2-yl)-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **1e**



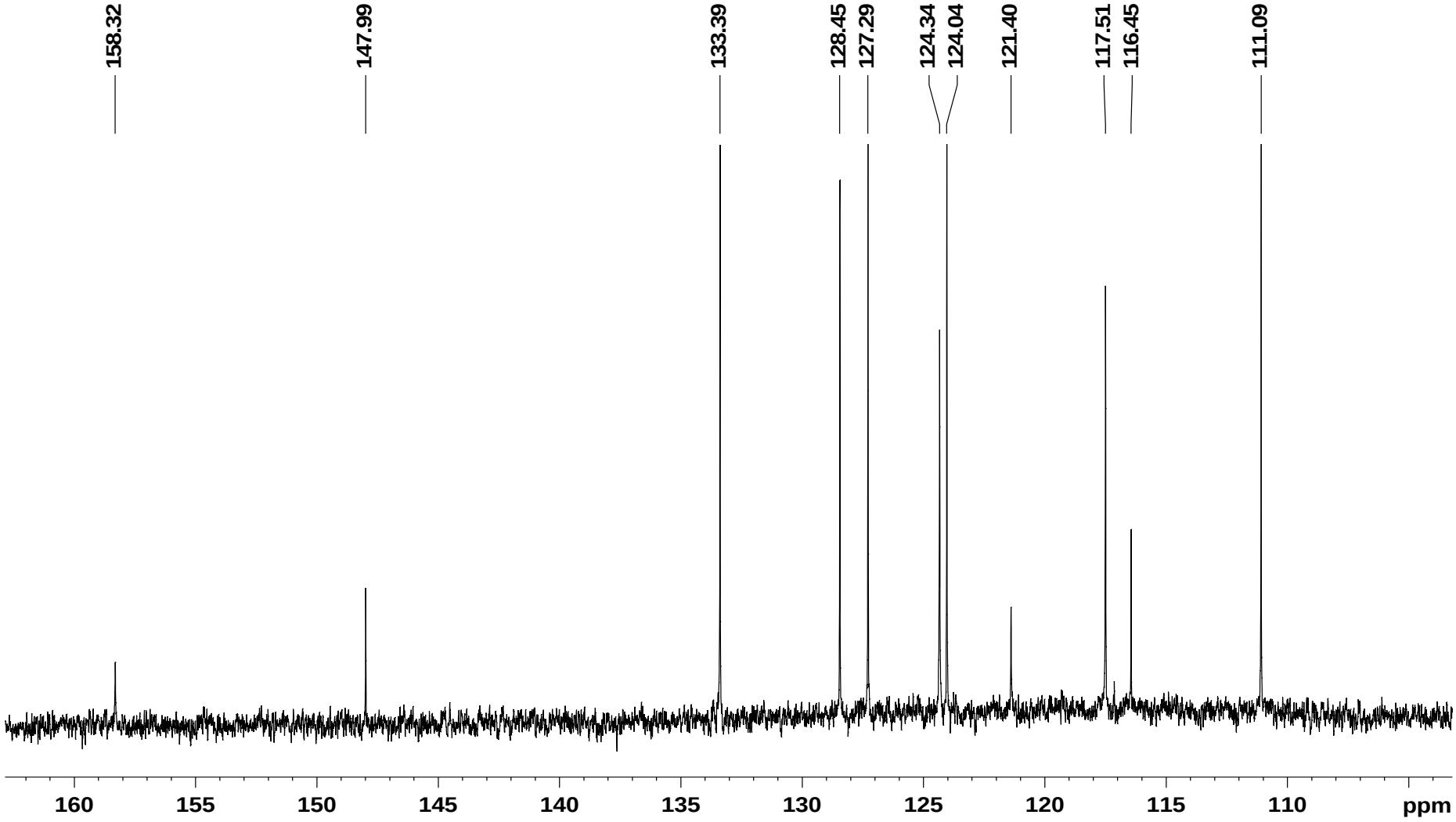


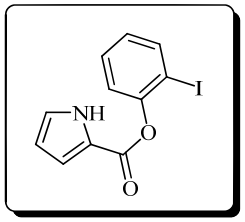
^{1}H NMR 2-bromophenyl-1*H*-pyrrole-2-carboxylate ($CDCl_3$) **1f**



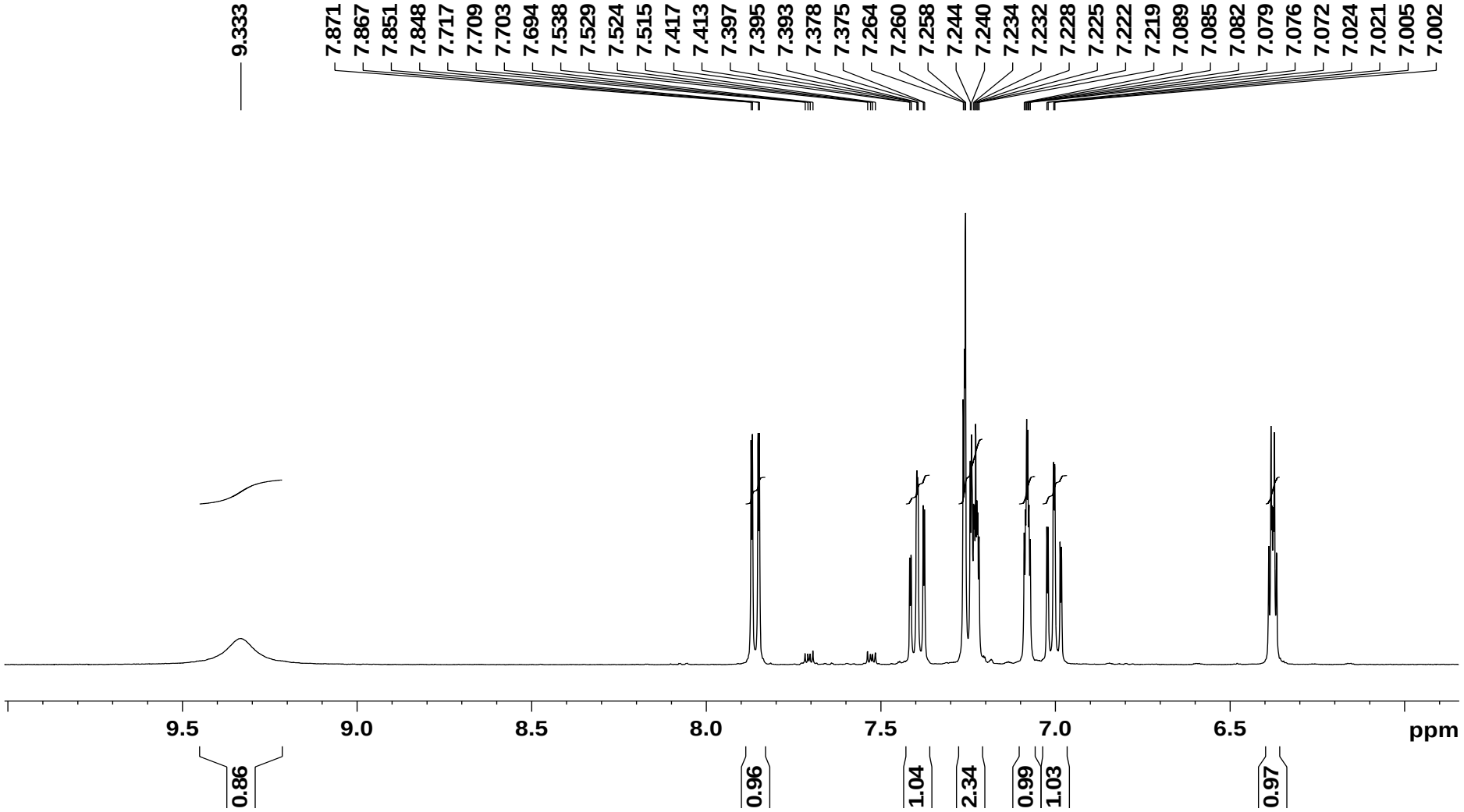


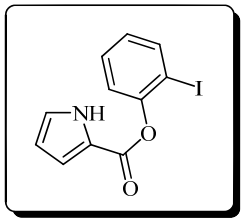
^{13}C NMR 2-bromophenyl-1*H*-pyrrole-2-carboxylate ($CDCl_3$) **1f**



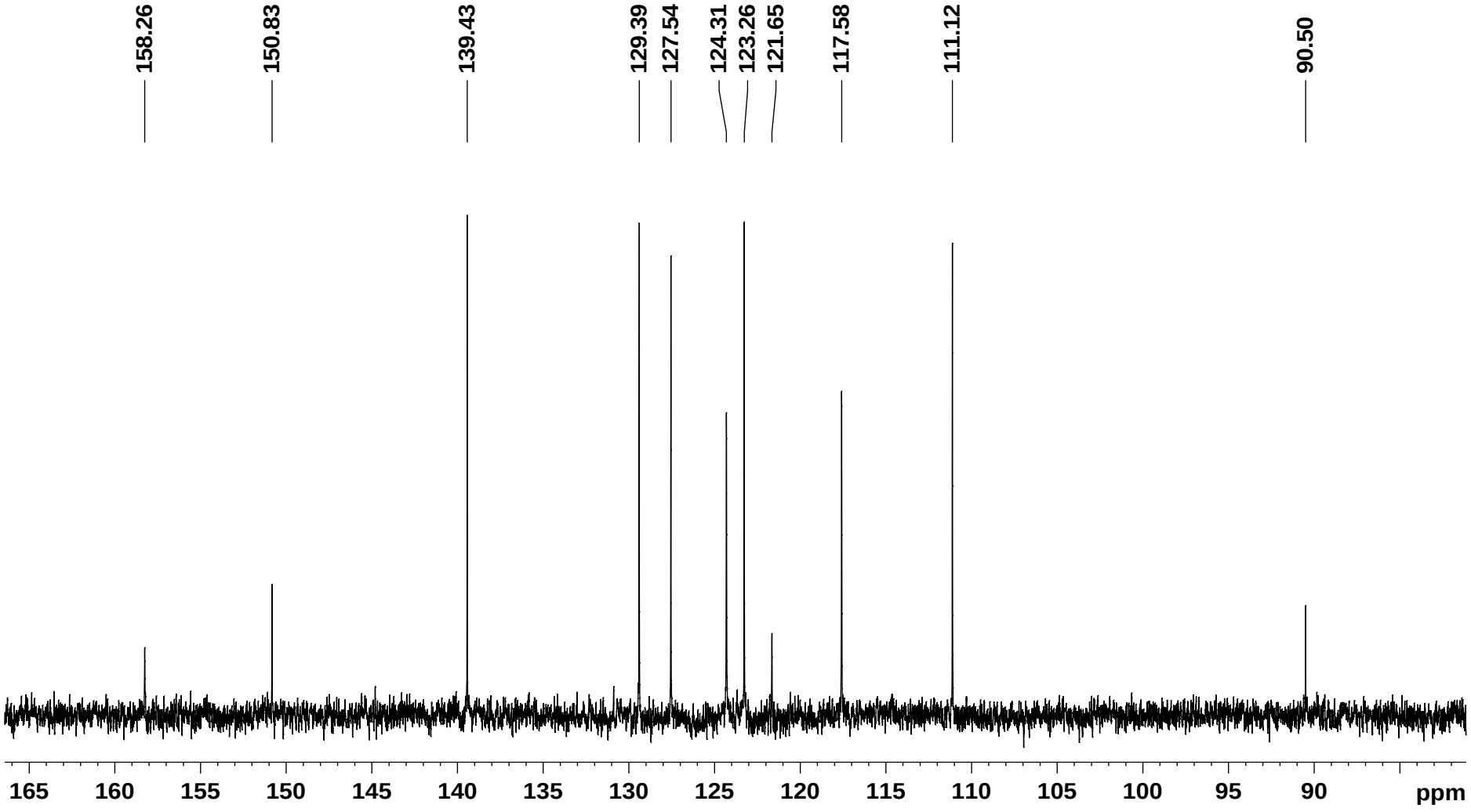


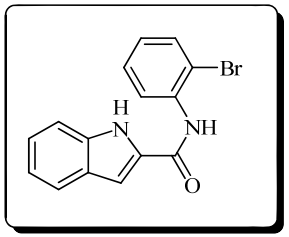
^{1}H NMR 2-iodophenyl-1*H*-pyrrole-2-carboxylate ($CDCl_3$) **1g**



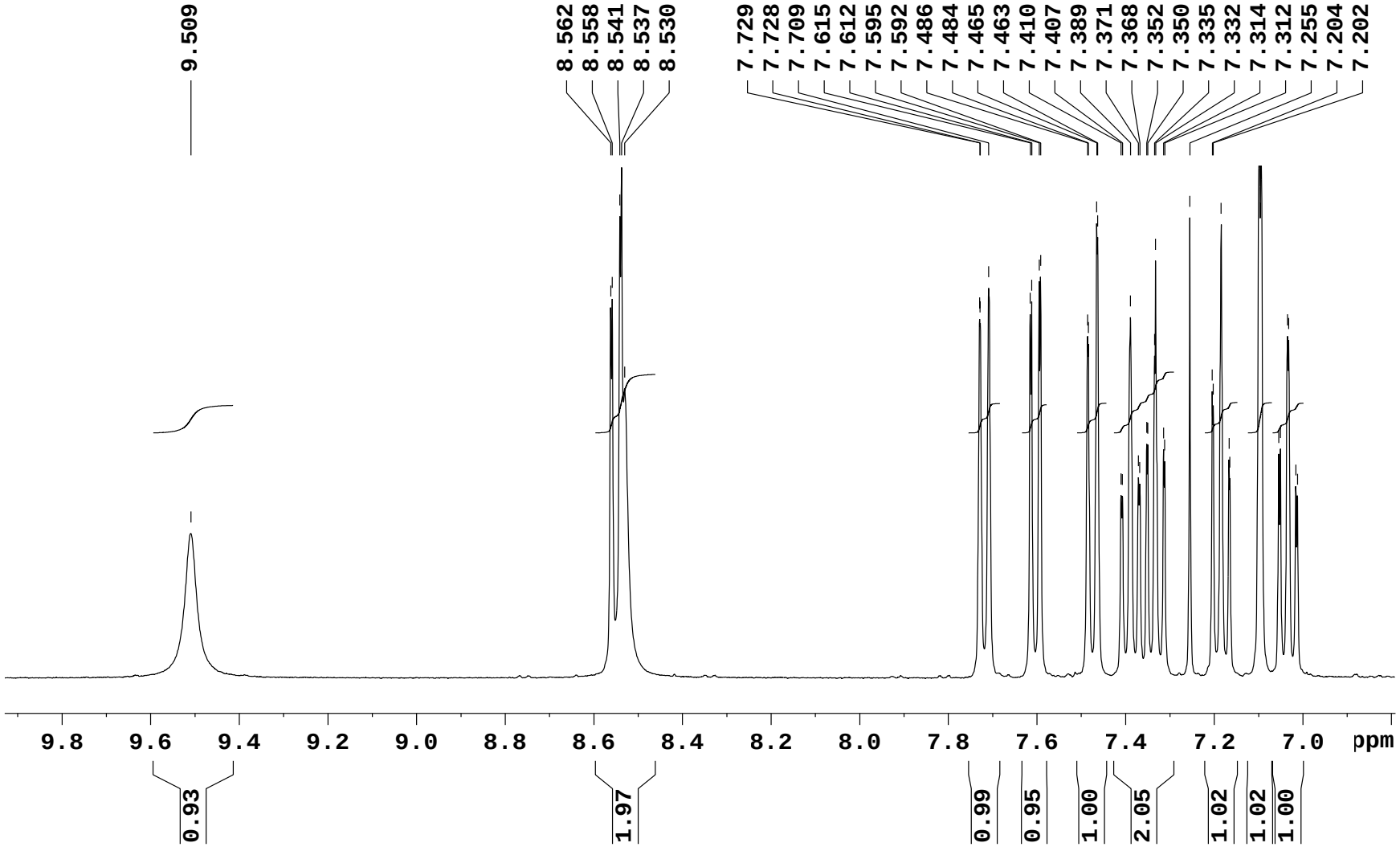


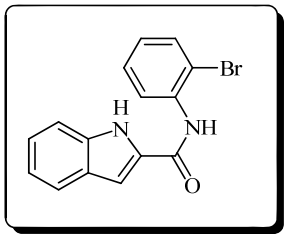
^{13}C NMR 2-iodophenyl-1*H*-pyrrole-2-carboxylate ($CDCl_3$) **1g**



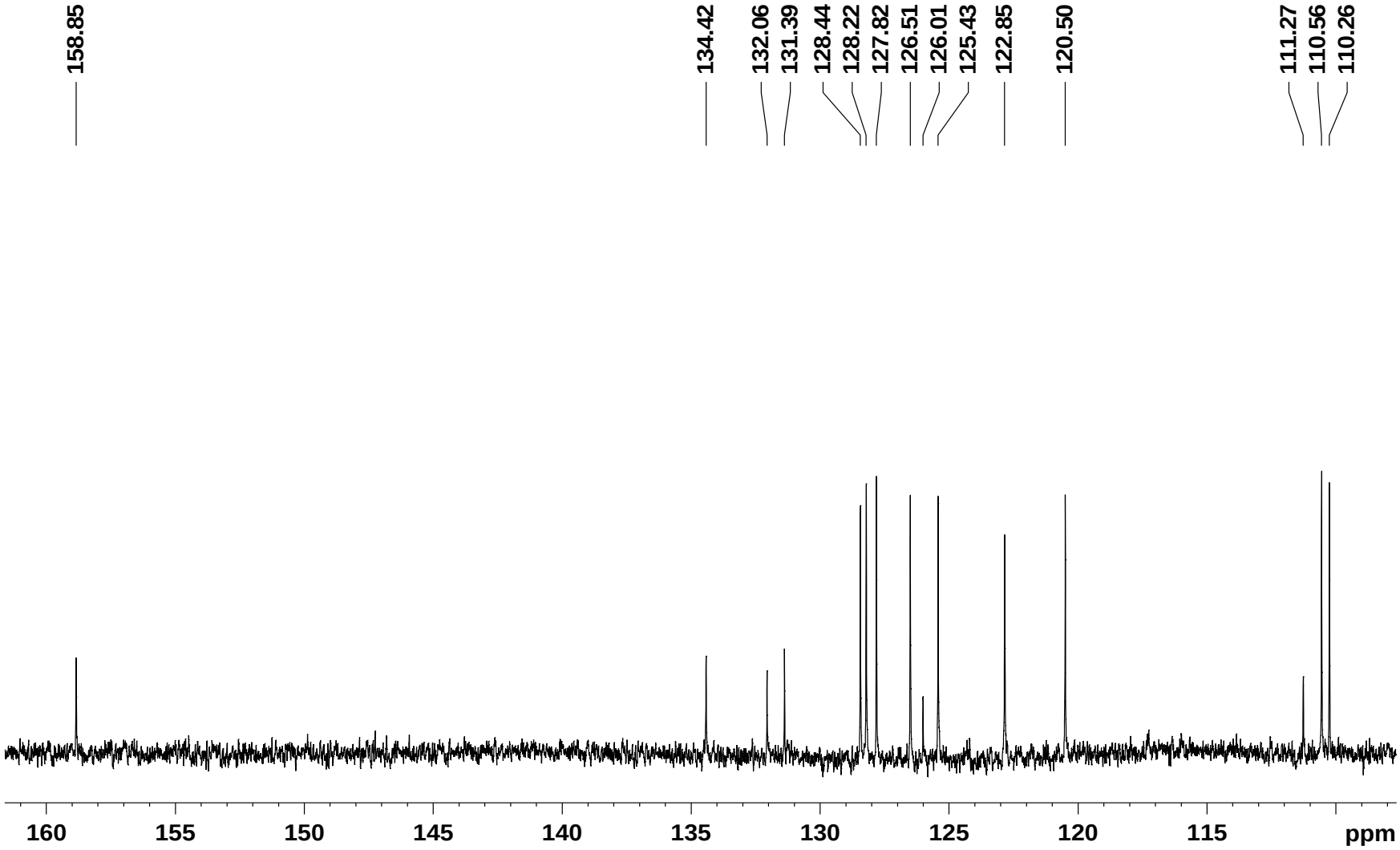


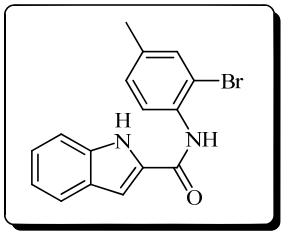
^{1}H NMR *N*-(2-bromophenyl)-1*H*-indole-2-carboxamide ($CDCl_3$) **2a**



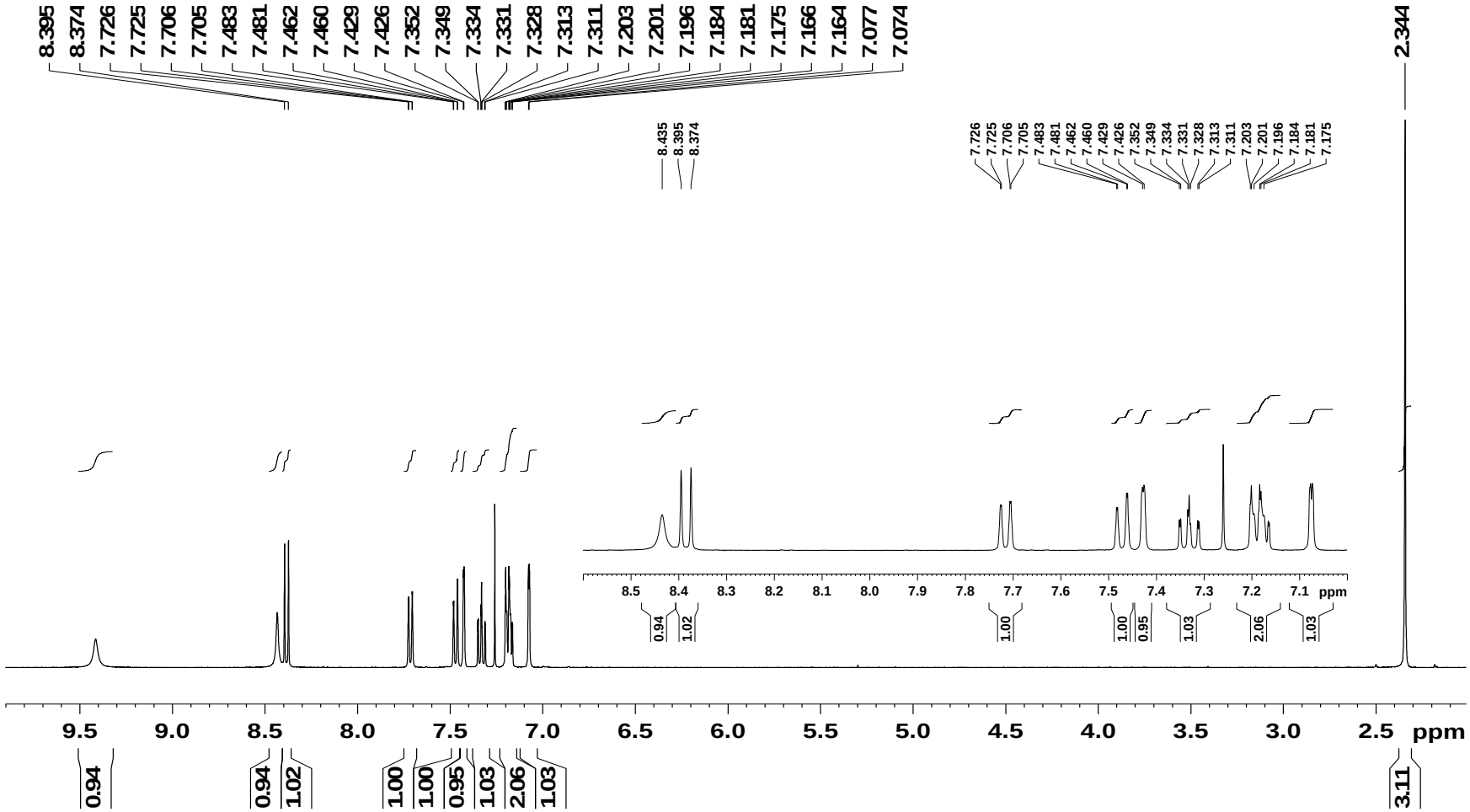


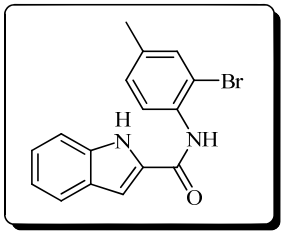
^{13}C NMR *N*-(2-bromophenyl)-1*H*-indole-2-carboxamide ($CDCl_3$) **2a**



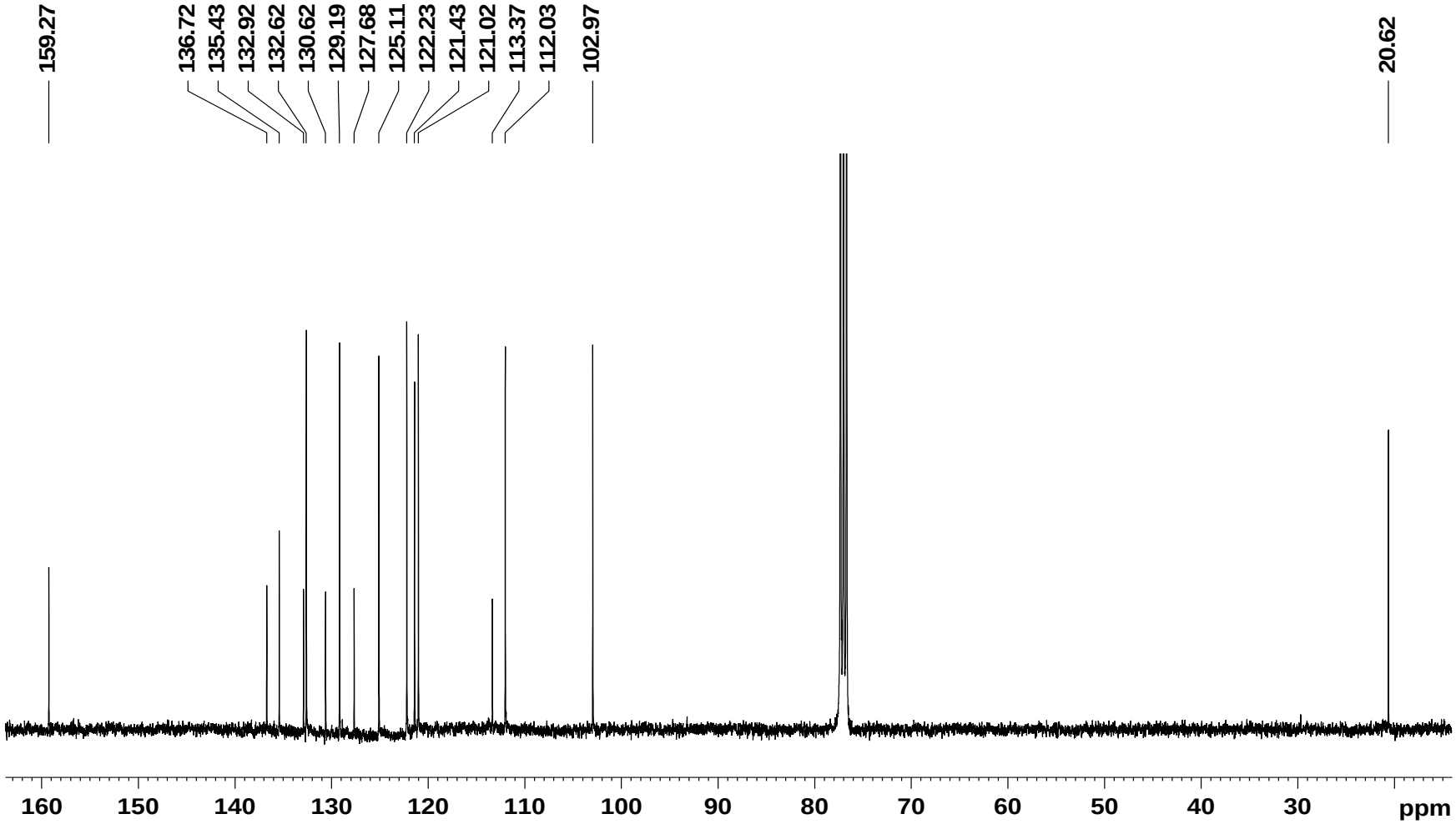


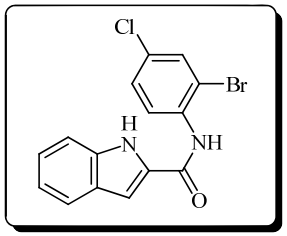
^{1}H NMR *N*-(2-bromo-4-methylphenyl)-1*H*-indole-2-carboxamide ($CDCl_3$) **2b**





^{13}C NMR *N*-(2-bromo-4-methylphenyl)-1*H*-indole-2-carboxamide ($CDCl_3$) **2b**





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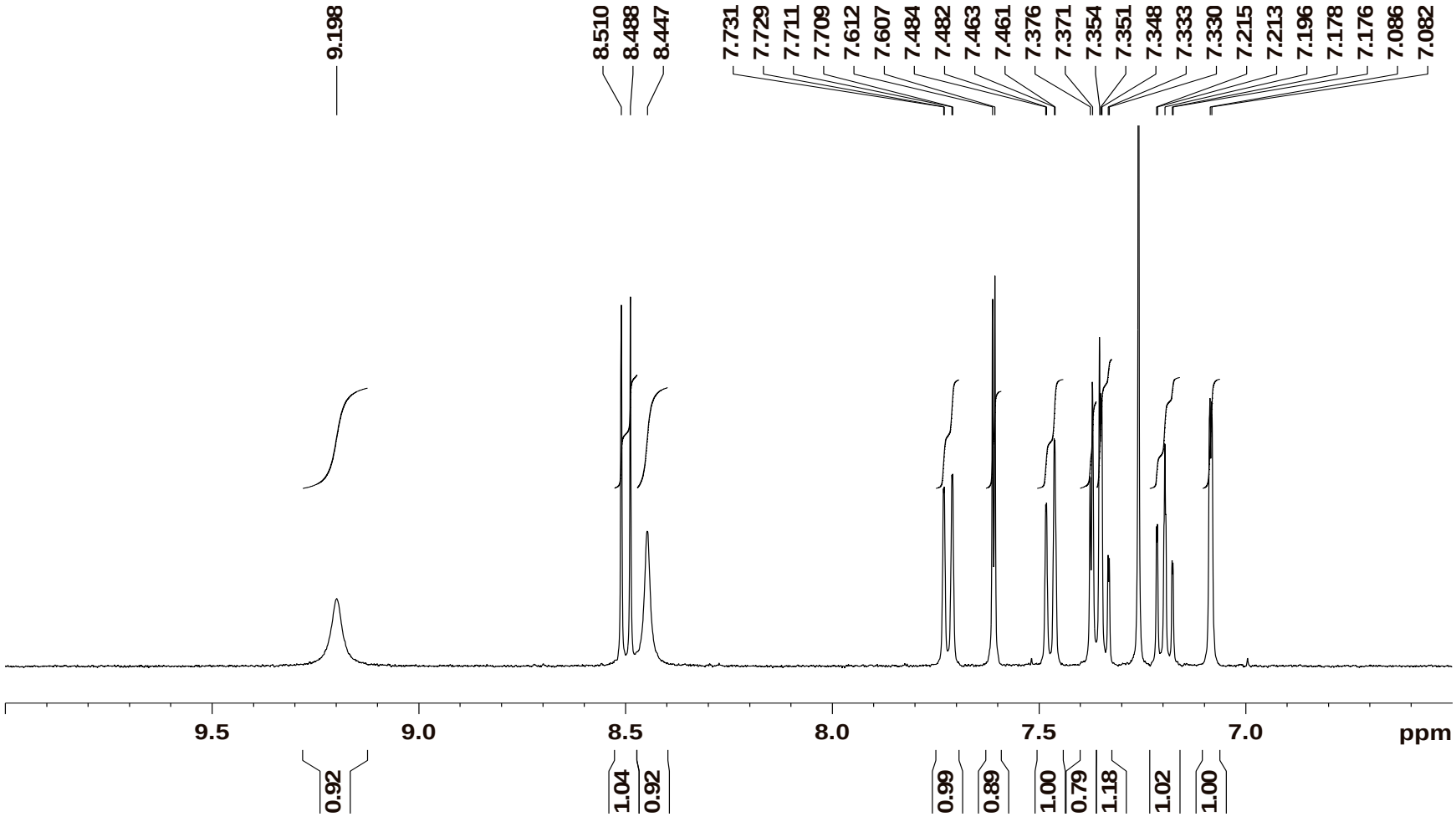
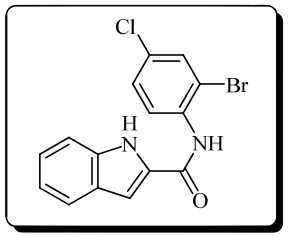
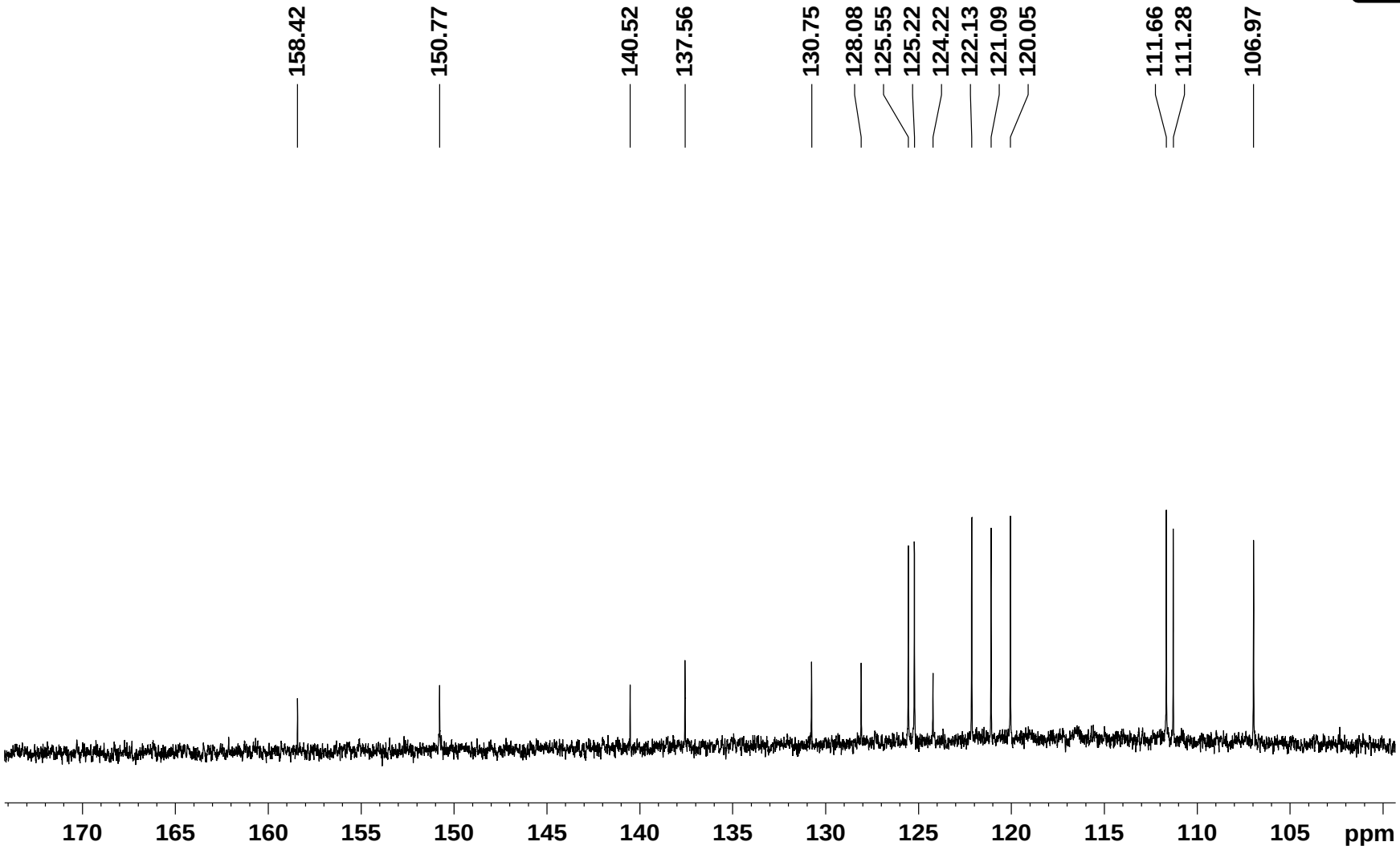
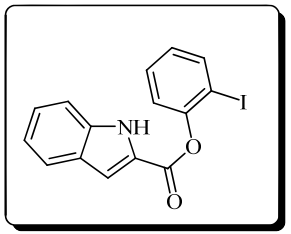


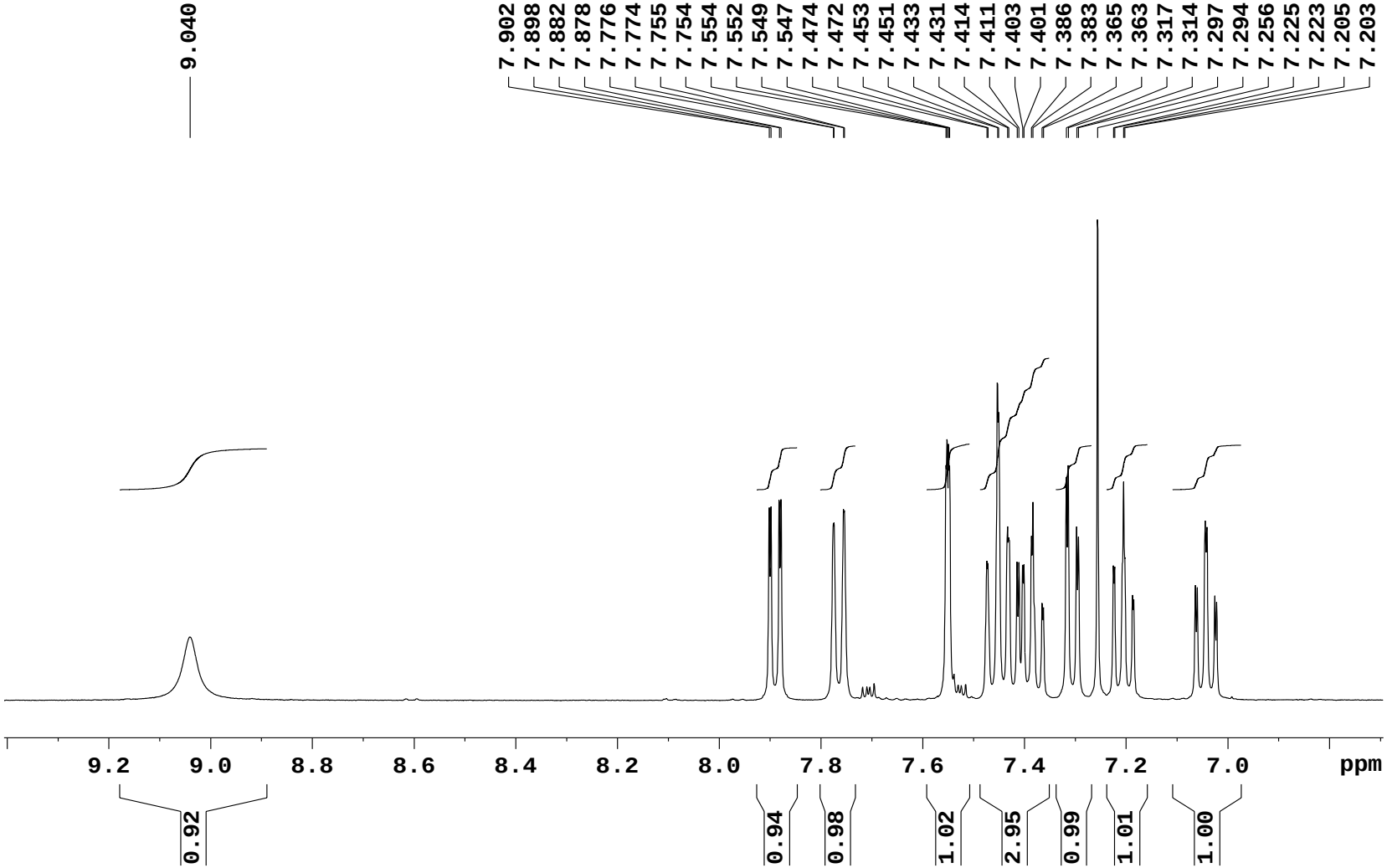


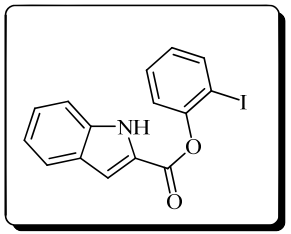
^{13}C NMR *N*-(2-bromo-4-chlorophenyl)-1*H*-indole-2-carboxamide ($CDCl_3$) **2c**



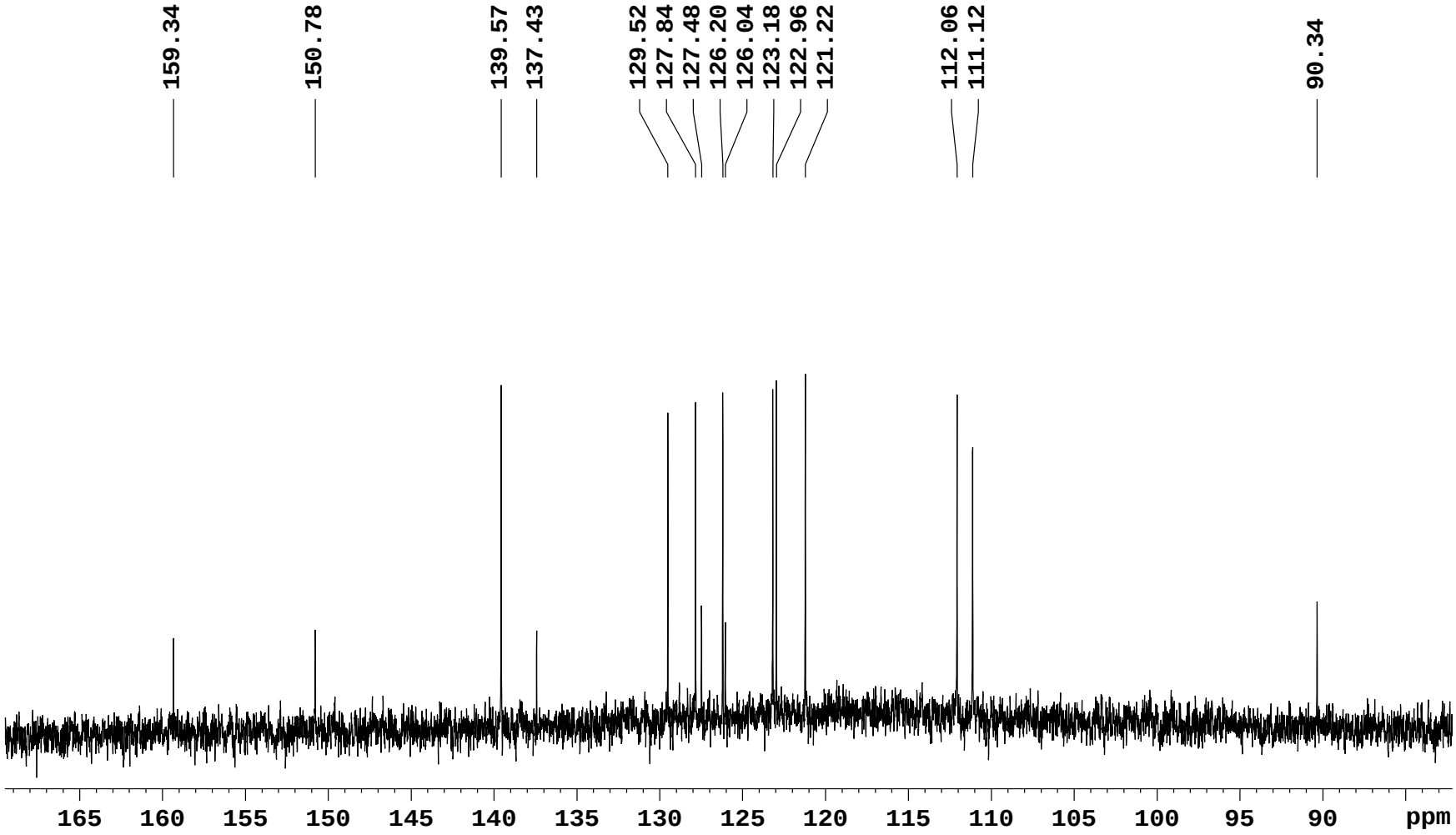


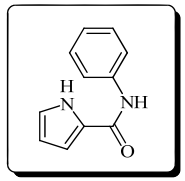
^{1}H NMR 2-iodophenyl-1*H*-indole-2-carboxylate ($CDCl_3$) **2d**



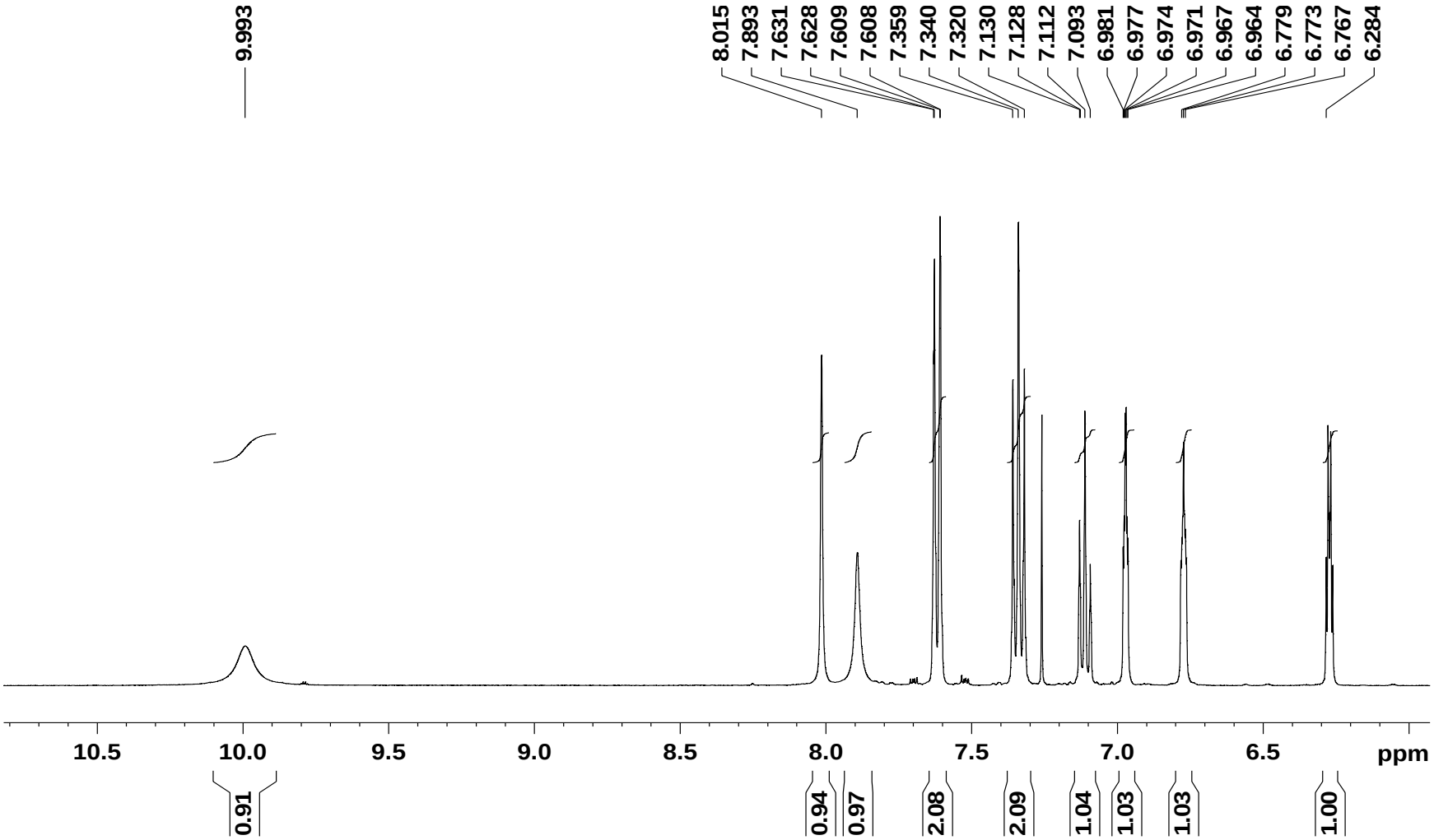


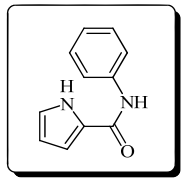
^{13}C NMR 2-iodophenyl-1*H*-indole-2-carboxylate ($CDCl_3$) **2d**



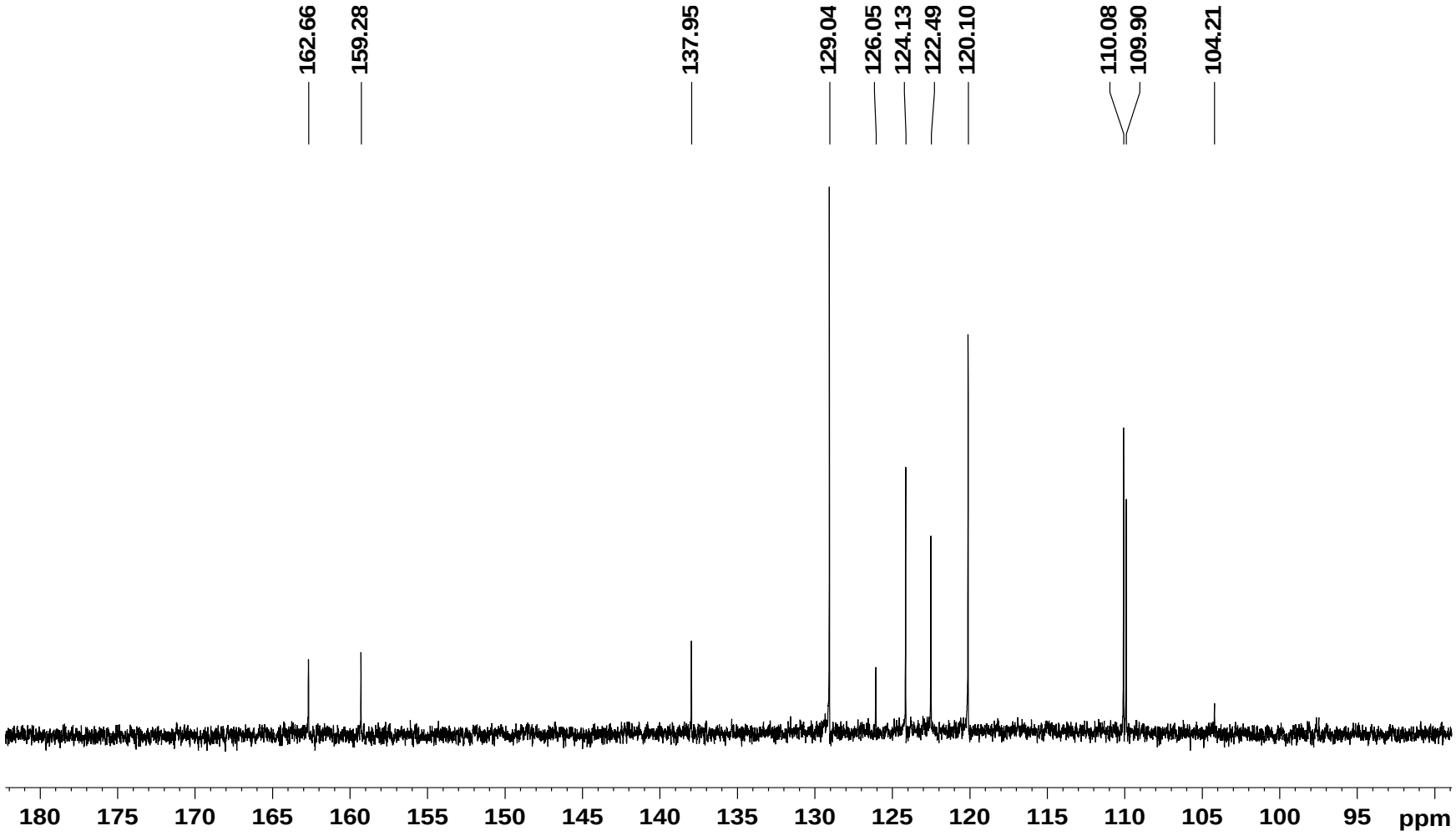


^{1}H NMR *N*-phenyl-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **4a**





^{13}C NMR N-phenyl-1*H*-pyrrole-2-carboxamide ($CDCl_3$) **4a**



***N*-(2-bromophenyl)-1*H*-pyrrole-2-carboxamide (1a)**.**^{1}H NMR (400 MHz, $CDCl_3$)** δ: 6.31 (m, 1H), 6.80 (m, 1H), 7.00 (m, 2H), 7.34 (m, 1H), 7.56 (dd, 1H, *J* = 8.0 Hz, 1.5 Hz), 8.24 (bs, 1H), 8.48 (dd, 1H, *J* = 8.3 Hz, 1.5 Hz), 10.18 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.2, 110.3, 113.4, 121.4, 123.2, 124.8, 125.8, 128.5, 132.3, 135.8, 159.0.

***N*-(2-bromo-4-methylphenyl)-1*H*-pyrrole-2-carboxamide (1b)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 2.32 (s, 3H), 6.31 (m, 1H), 6.78 (m, 1H), 7.01 (m, 1H), 7.15 (dd, 1H, *J* = 8.5 Hz, 1.0 Hz), 7.40 (d, 1H, *J* = 1.1 Hz), 8.12 (bs, 1H), 8.30 (d, 1H, *J* = 8.3 Hz), 9.69 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 20.5, 109.9, 110.3, 113.2, 121.3, 122.7, 126.0, 129.1, 132.5, 133.2, 134.0, 158.8.

***N*-(2-bromo-4-chlorophenyl)-1*H*-pyrrole-2-carboxamide (1c)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 6.33 (m, 1H), 6.79 (m, 1H), 7.32 (dd, 1H, *J* = 8.9 Hz, 2.5 Hz), 7.57 (d, 1H, *J* = 2.5 Hz), 8.14 (bs, 1H), 8.43 (d, 1H, *J* = 8.9 Hz), 9.46 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.2, 110.6, 113.3, 121.9, 123.0, 125.7, 128.6, 129.0, 131.7, 134.6, 158.6.

***N*-(2-Bromo- 4-cyanophenyl)-1H-pyrrole-2-carboxamide (1d). ^{1}H NMR (400 MHz, $CDCl_3$)** δ: 6.36 (m, 1H), 6.84 (m, 1H), 7.07 (m,1H), 7.63 (dd, 1H, *J*= 8.6 Hz, 1.9 Hz), 7.86 (d, 1H, *J*= 1.9 Hz), 8.38 (bs, 1H), 8.68 (d, 1H, *J*= 8.6 Hz), 9.40 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.9, 111.0, 111.6, 117.5, 119.7, 120.5, 123.8, 129.1, 132.6, 135.7, 140.1, 158.6.

***N*-(1-bromonaphthalen-2-yl)-1*H*-pyrrole-2-carboxamide (1e)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 6.36 (m, 1H), 6.89 (m, 1H), 7.05 (m, 1H), 7.46 (m, 1H), 7.59 (m, 1H), 7.83 (t, 2H, *J* = 8.9 Hz), 8.18 (d, 1H, *J* = 8.5), 8.50 (bs, 1H), 8.62 (d, 1H, *J* = 8.9 Hz), 9.49 (bs, 1H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.3, 110.6, 111.3, 120.5, 122.9, 125.4, 126.0, 126.5, 127.8, 128.2, 128.4, 131.4, 132.1, 134,4, 158.9.

2-bromophenyl -1*H*-pyrrole-2-carboxylate (1f). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.33 (m, 1H), 7.03 (m, 1H), 7.11 (m, 1H), 7.23 (dd, 1H, J = 8.1 Hz, 1.69 Hz), 7.33 (m, 1H), 7.60 (dd, 1H, J = 8.1 Hz, 1.54 Hz), 9.23 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 111.1, 116.5, 117.5, 121.4, 124.0, 124.3, 127.3, 128.5, 133.4, 148.0, 158.3.

2-iodophenyl-1*H*-pyrrole-2-carboxylate (1g). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (m, 1H), 7.00 (td, 1H, *J* = 7.6 Hz, 1.4 Hz), 7.08 (m, 1H), 7.21-7.26 (m, 2H), 7.40 (m, 1H), 7.86 (dd, 1H, *J* = 8.1 Hz, 1.44 Hz), 9.33 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 90.5, 111.1, 117.6, 121.7, 123.3, 124.3, 127.5, 129.4, 139.4, 150.8, 158.3.

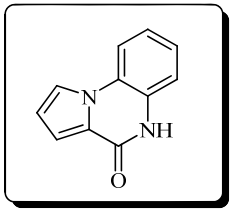
***N*-(2-bromophenyl)-1*H*-indole-2-carboxamide (2a)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.03 (td, 1H, J = 7.6 Hz, 1.5 Hz), 7.09 (d, 1H, *J* = 1.7 Hz), 7.18 (m, 1H), 7.36 (m, 2H), 7.48 (dd, 1H, *J* = 8.4 Hz, 0.7 Hz), 7.60 (dd, 1H, *J* = 8.1 Hz, 1.4 Hz), 7.72 (d, 1H, *J* = 8.1 Hz), 8.54 (m, 2H), 9.51 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 103.2, 112.1, 113.5, 121.1, 121.6, 122.3, 125.2, 125.3, 127.6, 128.6, 130.5, 132.4, 135.5, 136.8, 159.4.

***N*-(2-bromo-4-methylphenyl)-1*H*-indole-2-carboxamide (2b)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 2.34 (s, 3H), 7.08 (m, 1H), 7.19 (m, 2H), 7.33 (m, 1H), 7.43 (d, 1H, *J* = 1.3 Hz), 7.47 (dd, 1H, *J* = 8.3 Hz, 0.8 Hz), 7.72 (dd, 1H, *J* = 8.0 Hz, 0.7 Hz), 8.38 (d, 1H, *J* = 8.3 Hz), 8.43 (bs, 1H), 9.42 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 20.6, 103.0, 112.0, 113.4, 121.0, 121.4, 122.2, 125.1, 127.7, 129.2, 130.6, 132.6, 132.9, 135.4, 136.7, 159.3.

***N*-(2-bromo-4-chlorophenyl)-1*H*-indole-2-carboxamide (2c)**. **^{1}H NMR (400 MHz, $CDCl_3$)** δ: 7.08 (d, 1H, *J* = 1.5 Hz), 7.20 (m, 1H), 7.37 (m, 1H), 7.47 (dd, 1H, *J* = 8.3 Hz, 0.8 Hz), 7.61 (d, 1H, *J* = 2.3 Hz), 7.72 (dd, 1H, *J* = 8.0 Hz, 0.8 Hz), 8.44 (bs, 1H), 8.50 (d, 1H, *J* = 8.9 Hz), 9.20 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 107.0, 111.3, 111.7, 120.1, 121.1, 122.1, 124.2, 125.2, 125.6, 128.1, 130.8, 137.6, 140.5, 150.8, 158.4.

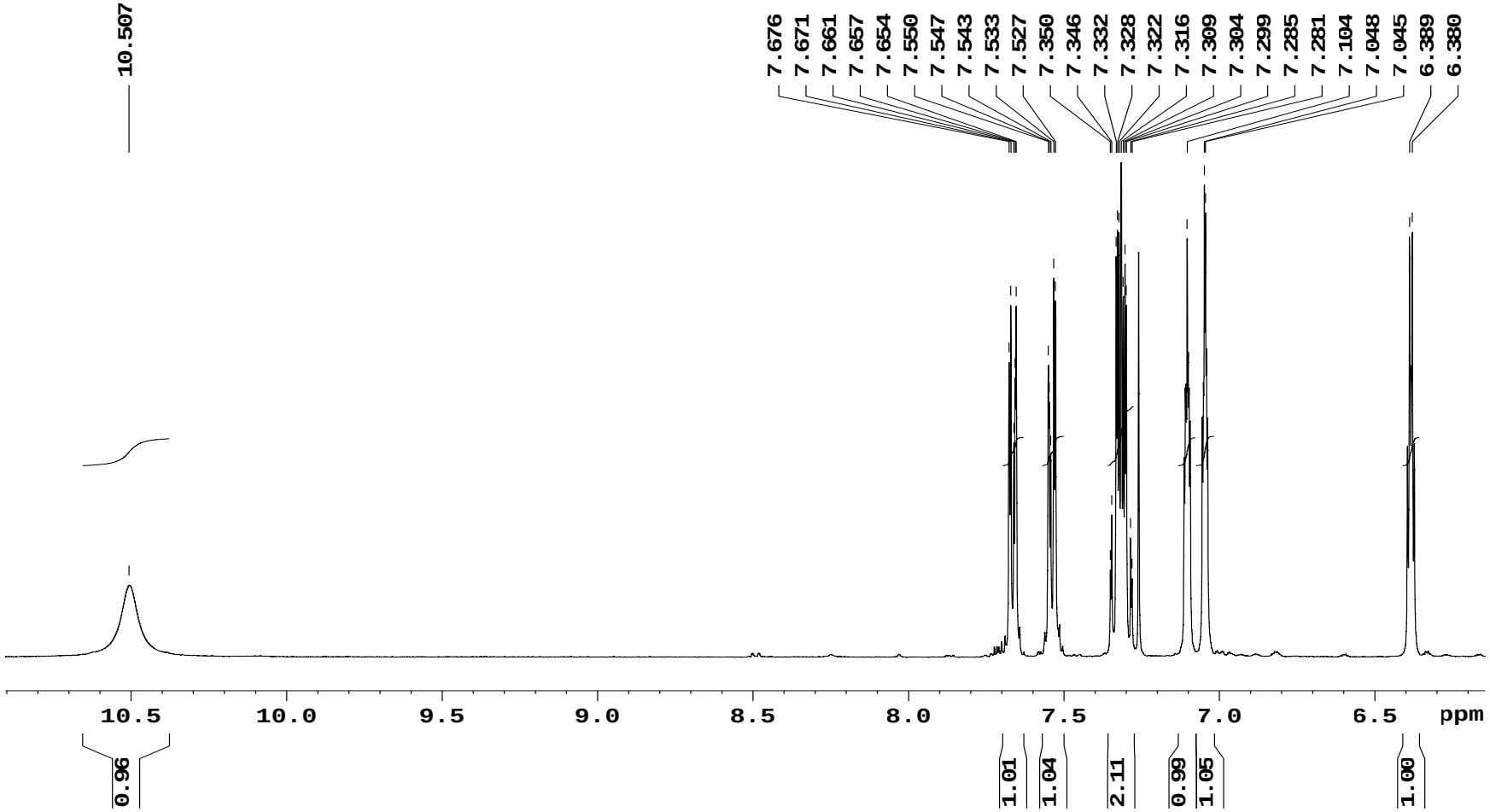
2-iodophenyl 1*H*-indole-2-carboxylate (2d). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04 (td, 1H, *J* = 7.6 Hz, 1.5 Hz), 7.20 (m, 1H), 7.30 (dd, 1H, *J* = 8.2 Hz, 1.3 Hz), 7.36-7.47 (m, 3H), 7.55 (m, 1H), 7.76 (dd., 1H, *J* = 8.1 Hz, 0.6 Hz), 7.89 (dd, 1H, *J* = 7.9 Hz, 1.5 Hz), 9.04 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 90.3, 111.1, 112.1, 121.2, 123.0, 123.2, 126.0, 126.2, 127.5, 127.8, 129.5, 137.4, 139.6, 150.8, 159.3.

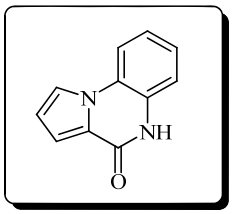
***N*-phenyl-1*H*-pyrrole-2-carboxamide (4a).^{1}H NMR (400 MHz, $CDCl_3$)** δ: 6.27 (m, 1H), 6.77 (m, 1H), 6.97 (m, 1H), 7.11 (m, 1H), 7.34 (m, 2H), 7.62 (m, 1H), 7.89 (bs, 1H), 8.02 (bs, 1H), 9.99 8bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 104.2, 109.9, 110.1, 120.1, 122.5, 124.1, 126.1, 129.0, 137.9, 159.3, 162.7.



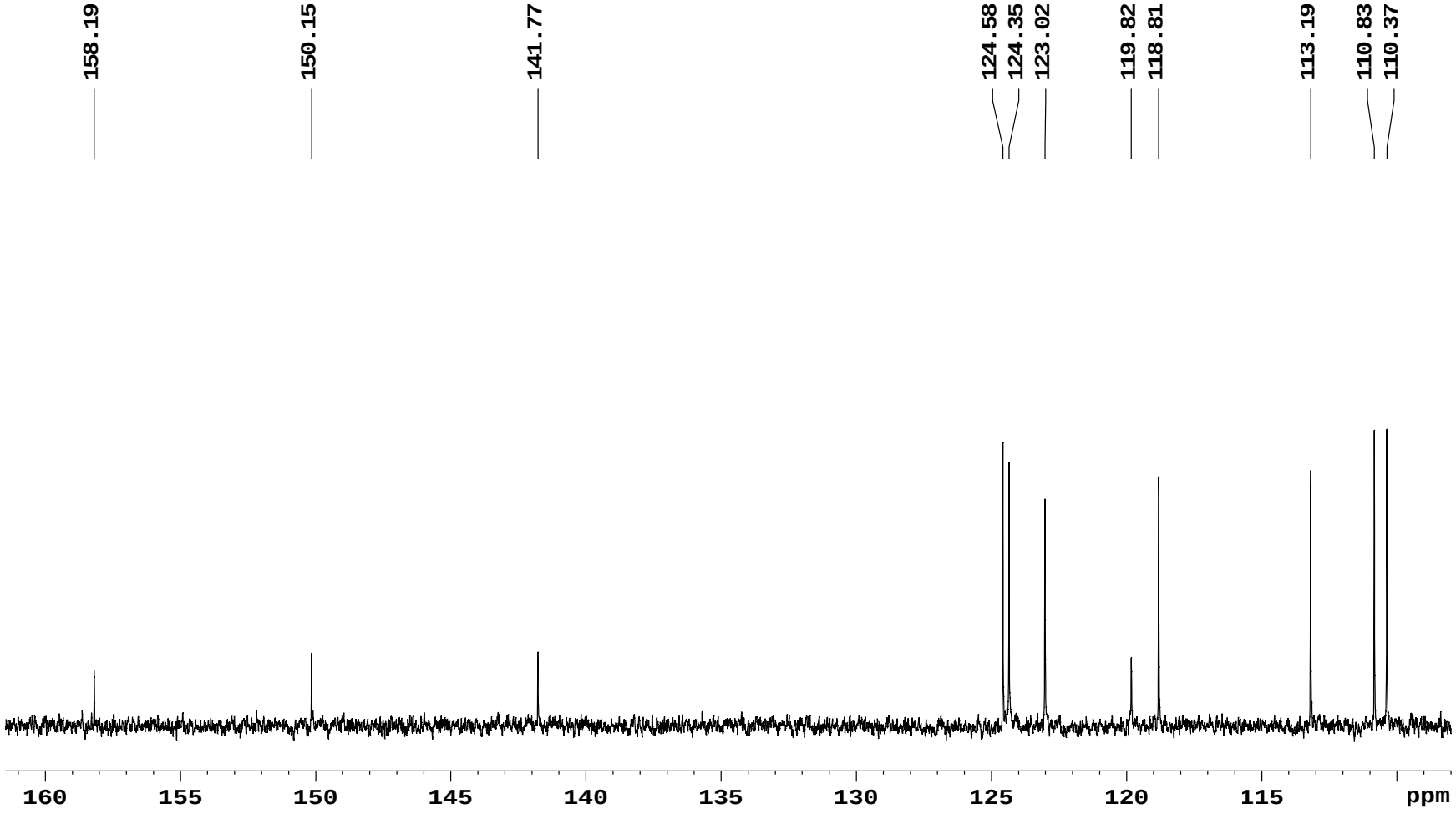
^{1}H , ^{13}C, COSY ^{1}H-^{1}H and HSQC ^{1}H-^{13}C spectra for compounds 3a-f and 5a-d

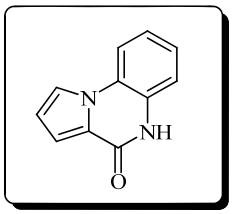
^{1}H NMR pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3a**



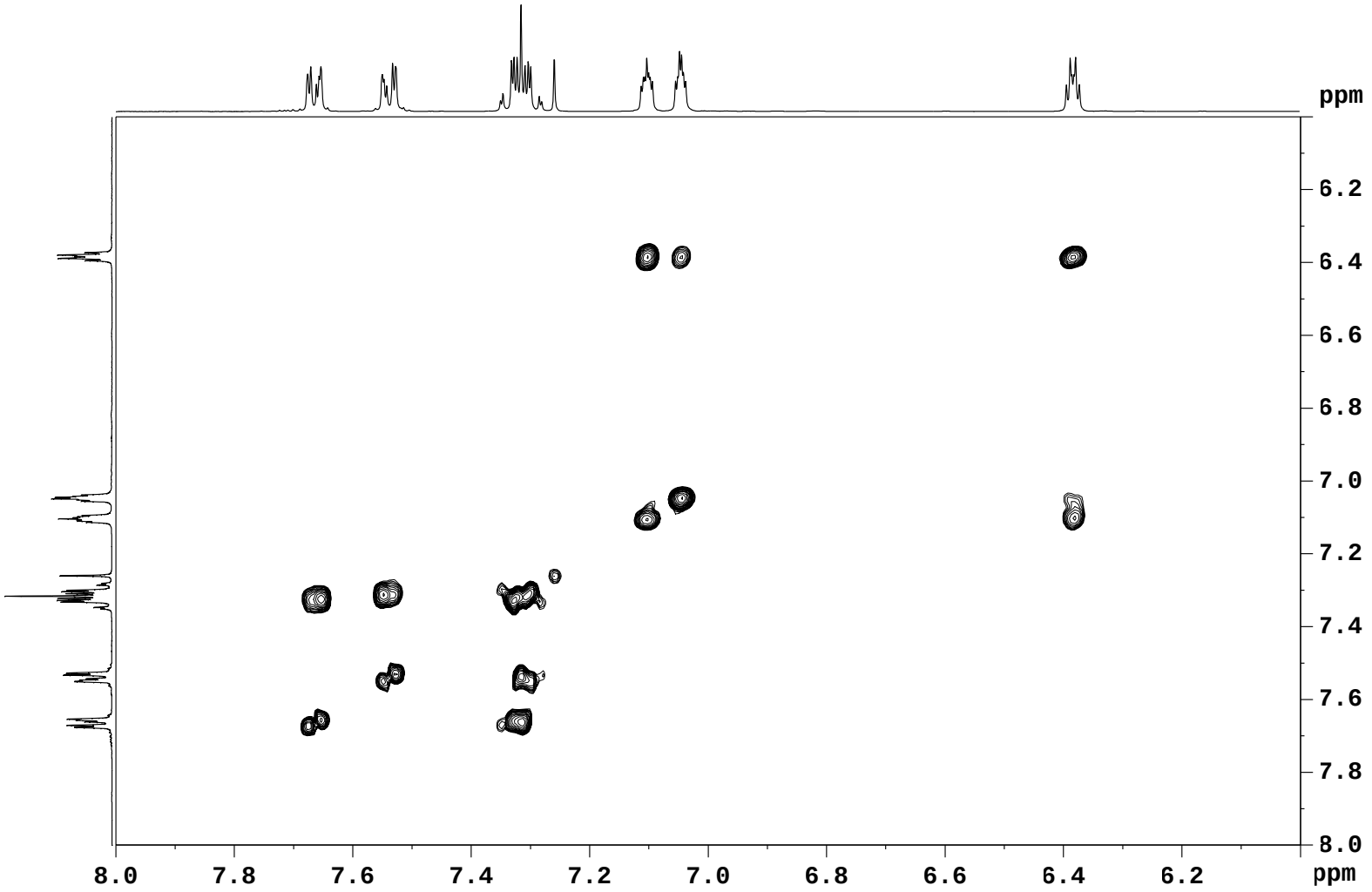


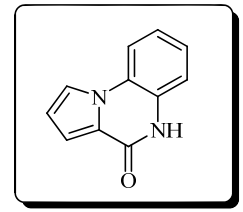
^{13}C NMR pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3a**



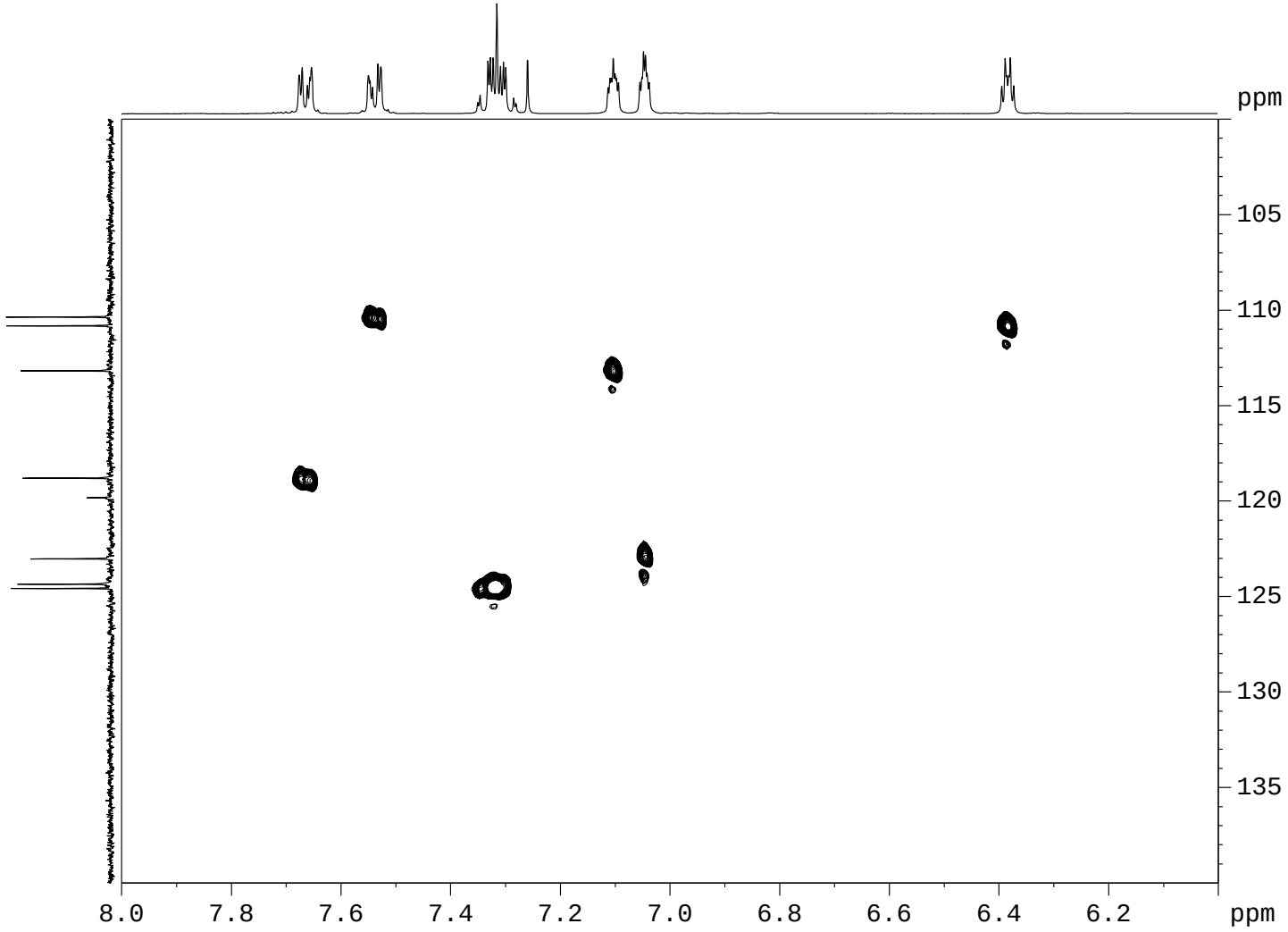


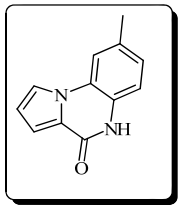
^{1}H-^{1}H COSY pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3a**



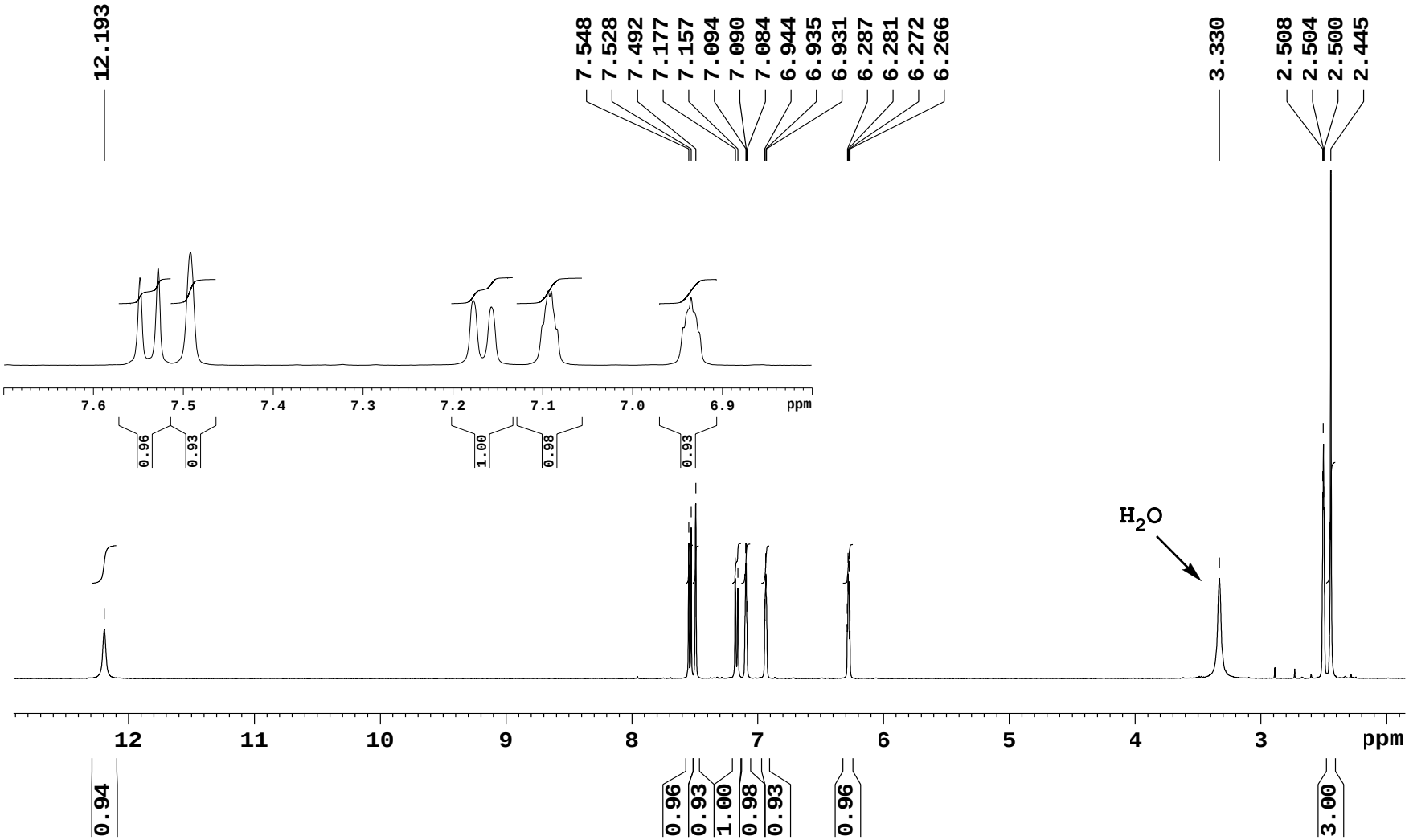


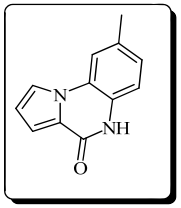
^{1}H-^{13}C HSQC pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3a**



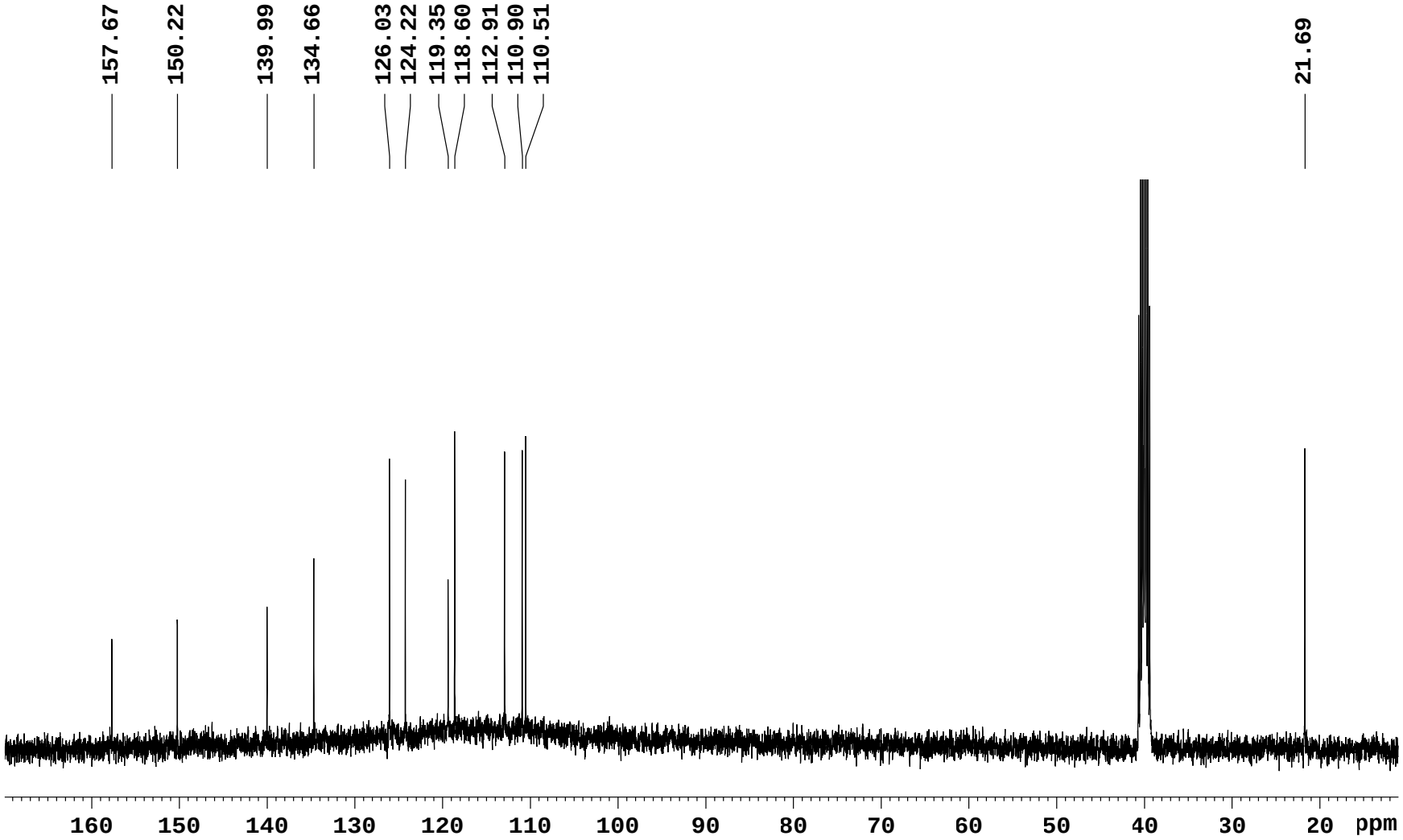


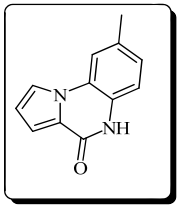
^{1}H NMR 8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3b**



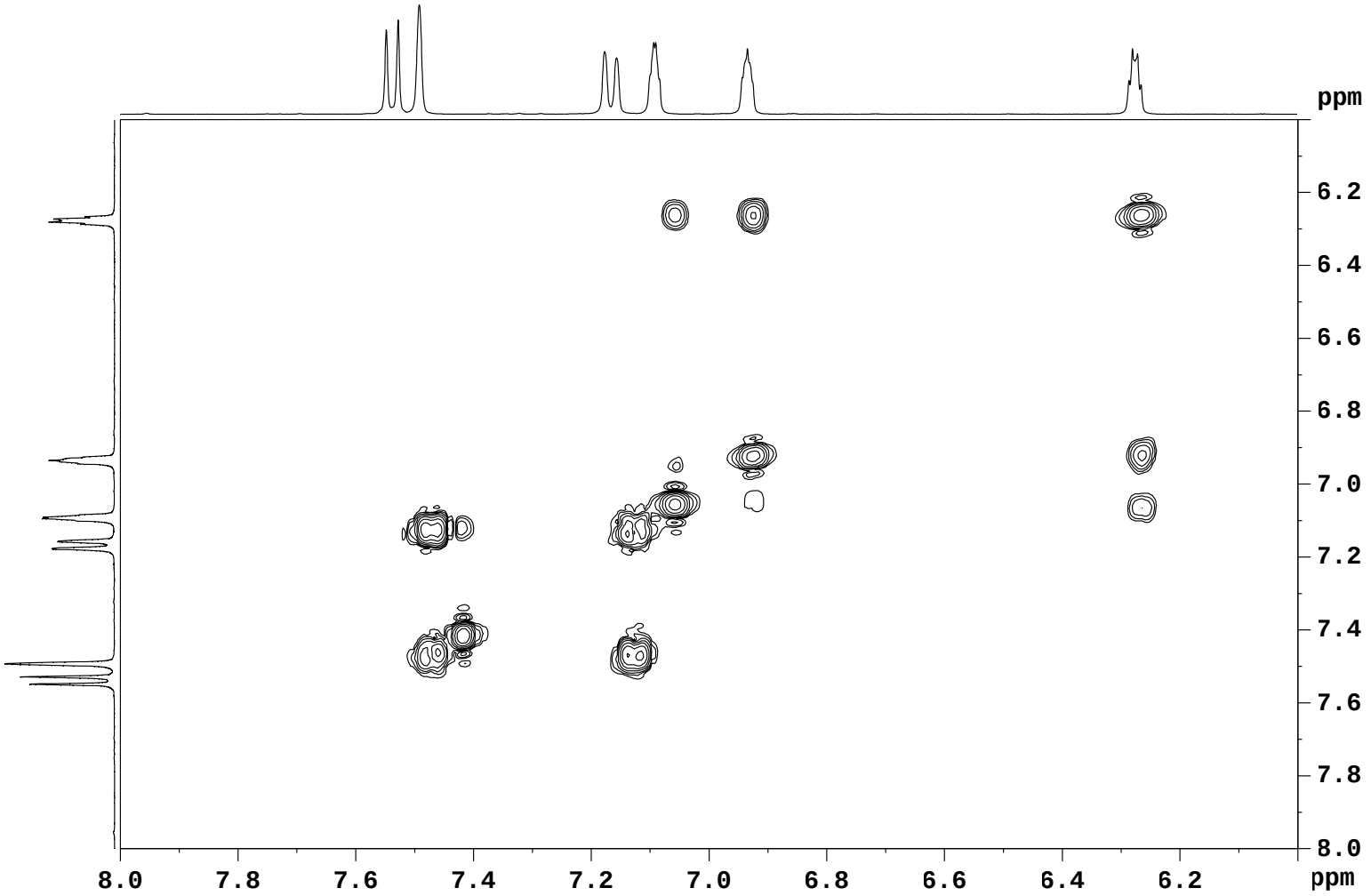


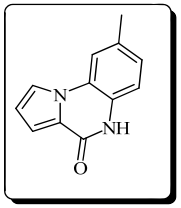
^{13}C NMR 8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3b**



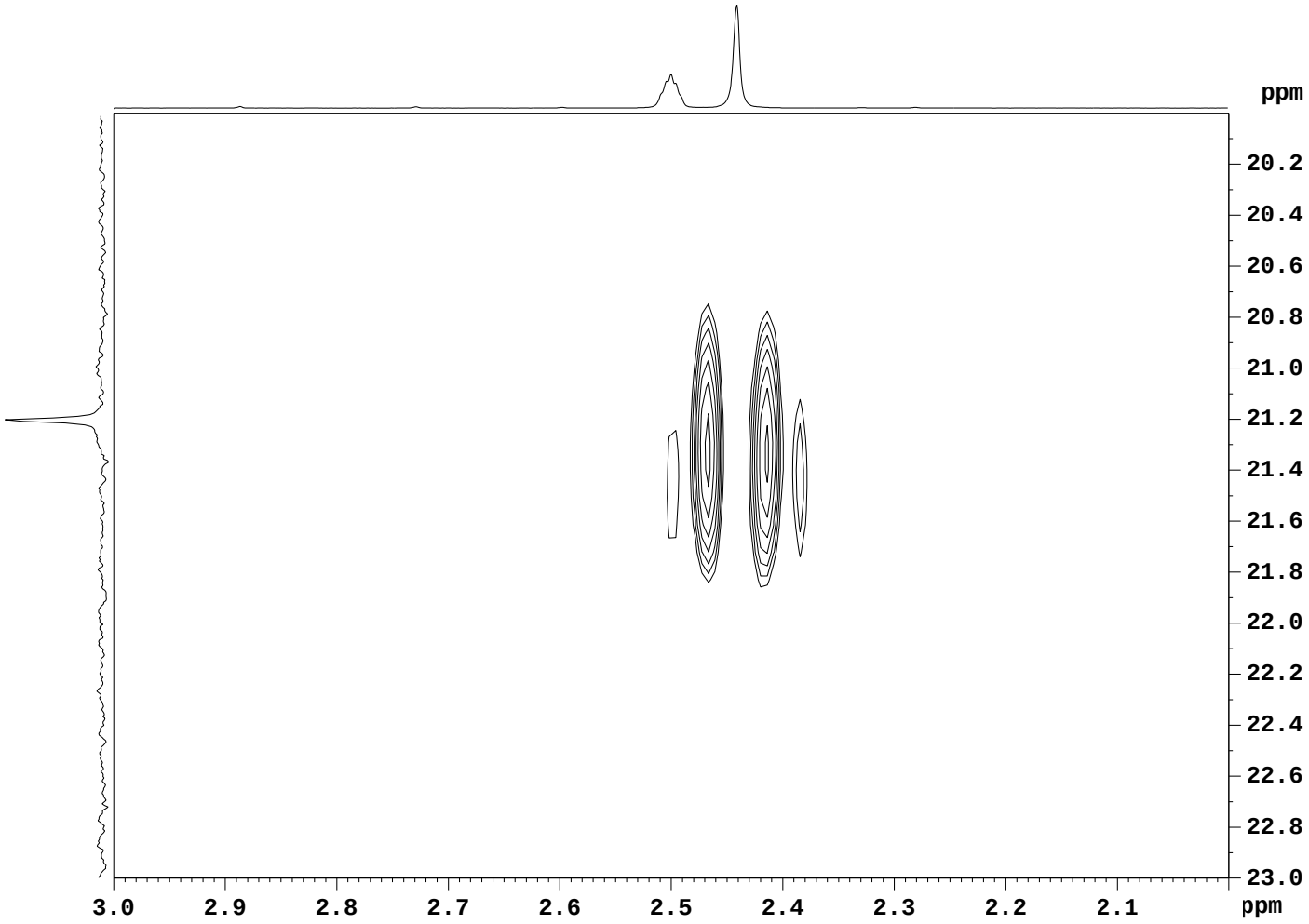


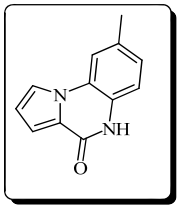
^{1}H-^{1}H COSY 8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3b**



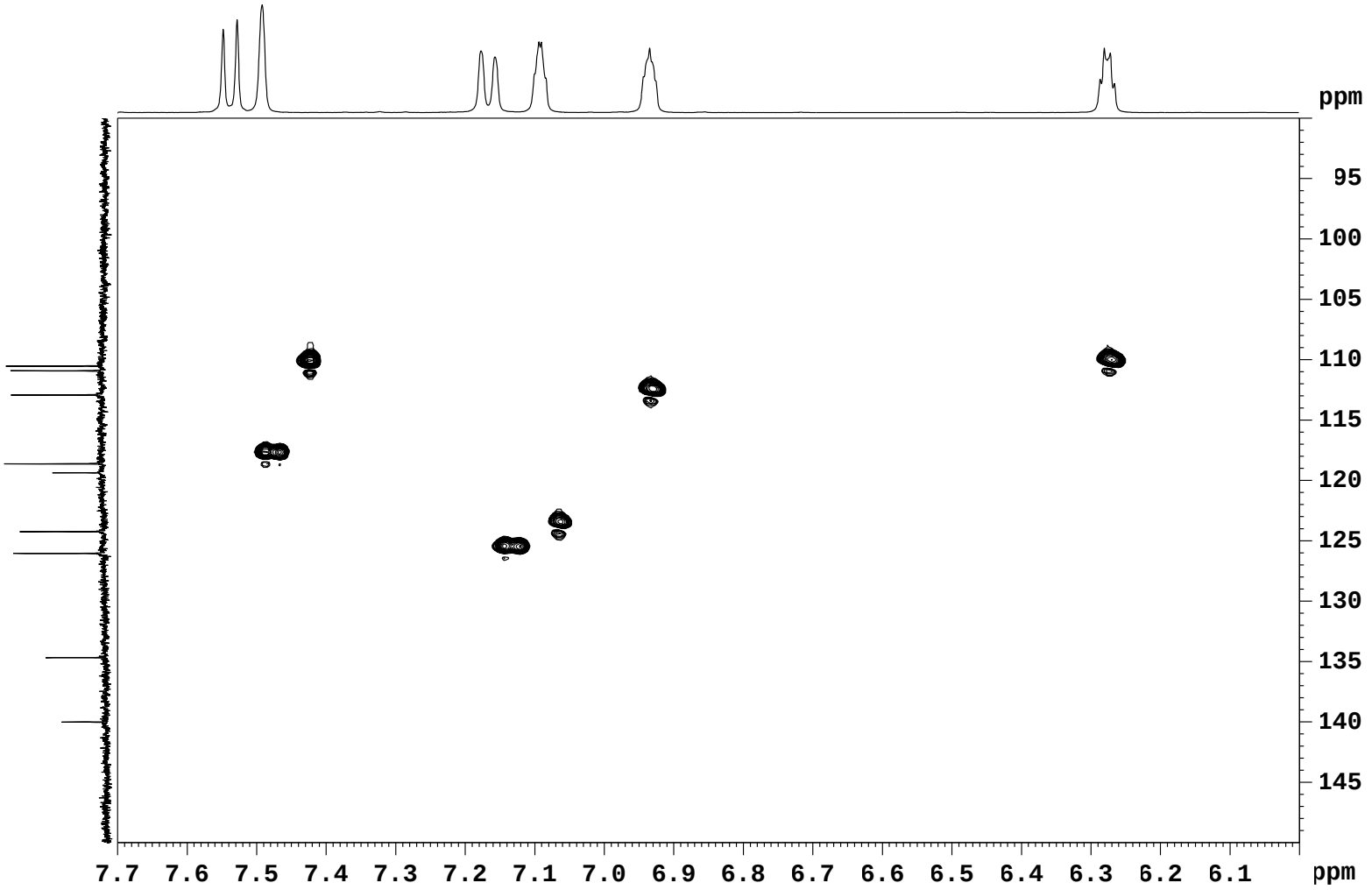


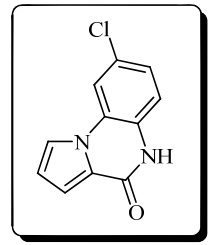
^{1}H-^{13}C HSQC 8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3b**



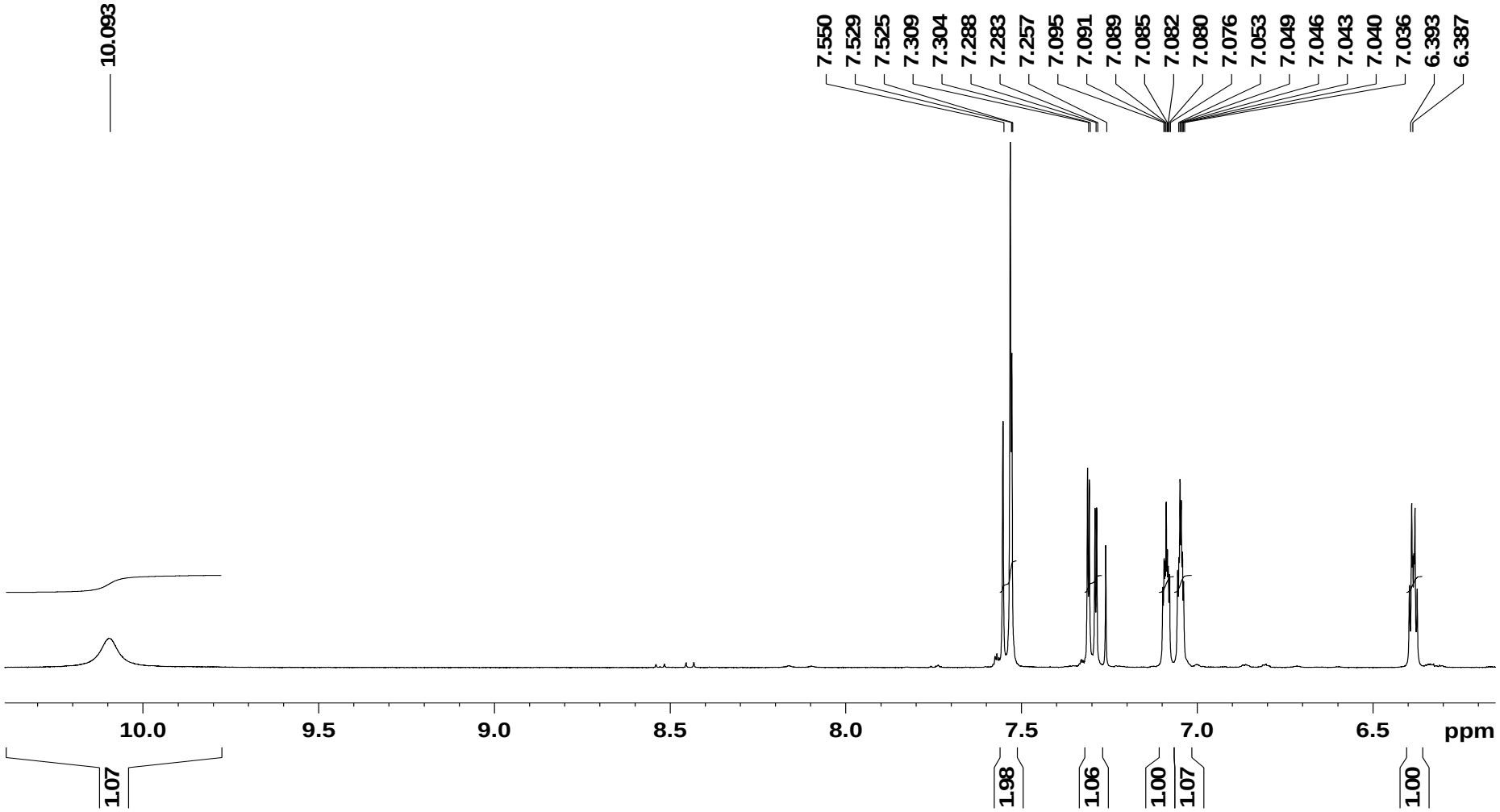


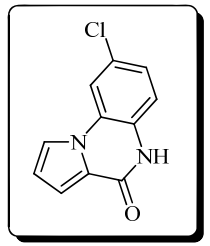
^{1}H-^{13}C HSQC 8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3b**



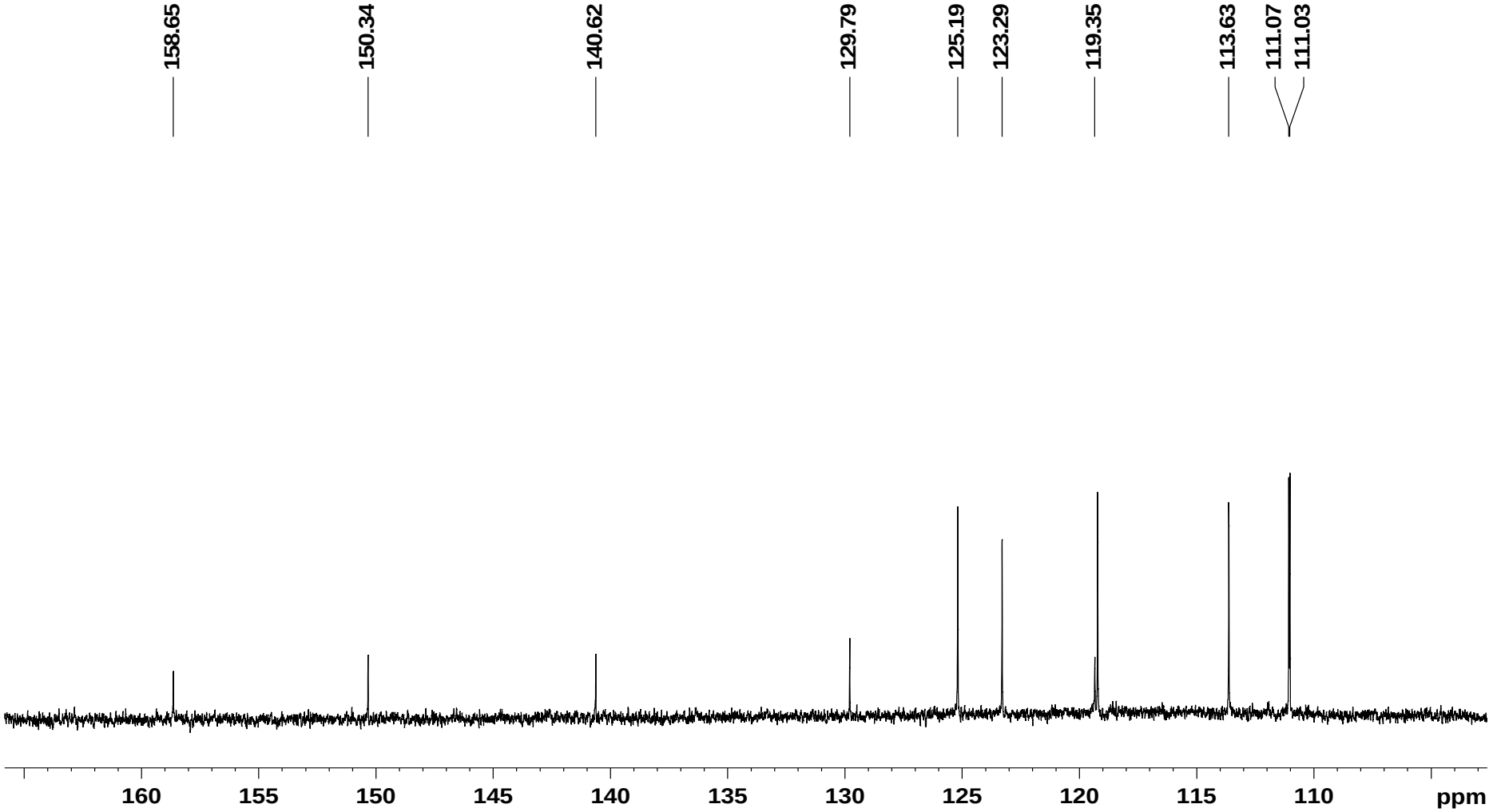


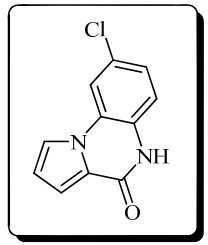
^{1}H NMR 8-chloropyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one.($CDCl_3$) **3c**



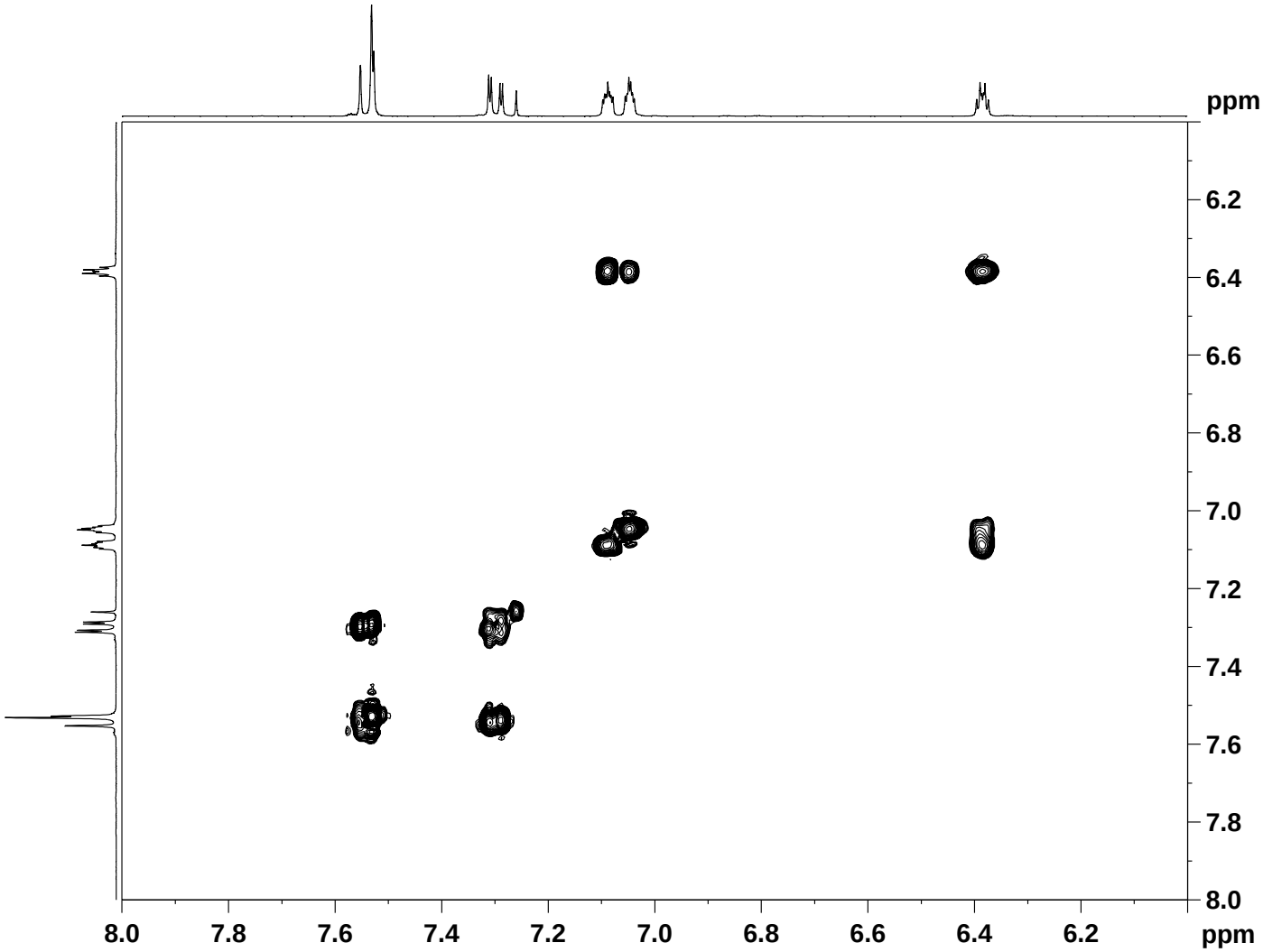


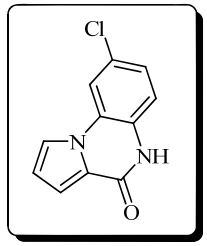
^{13}C NMR 8-chloropyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3c**



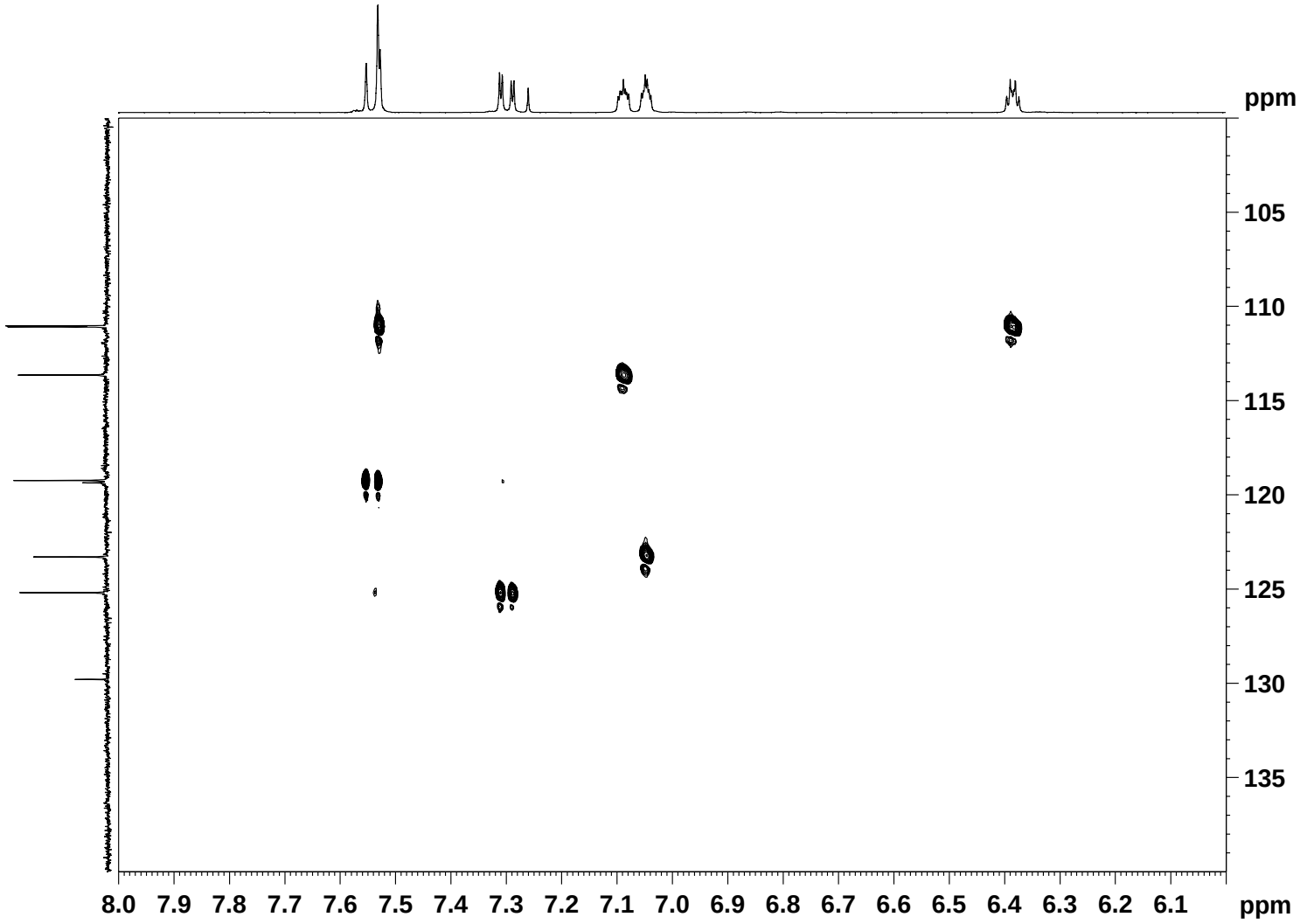


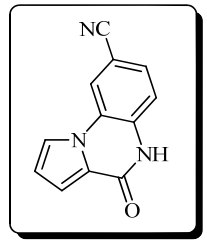
^{1}H-^{1}H COSY 8-chloropyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3c**



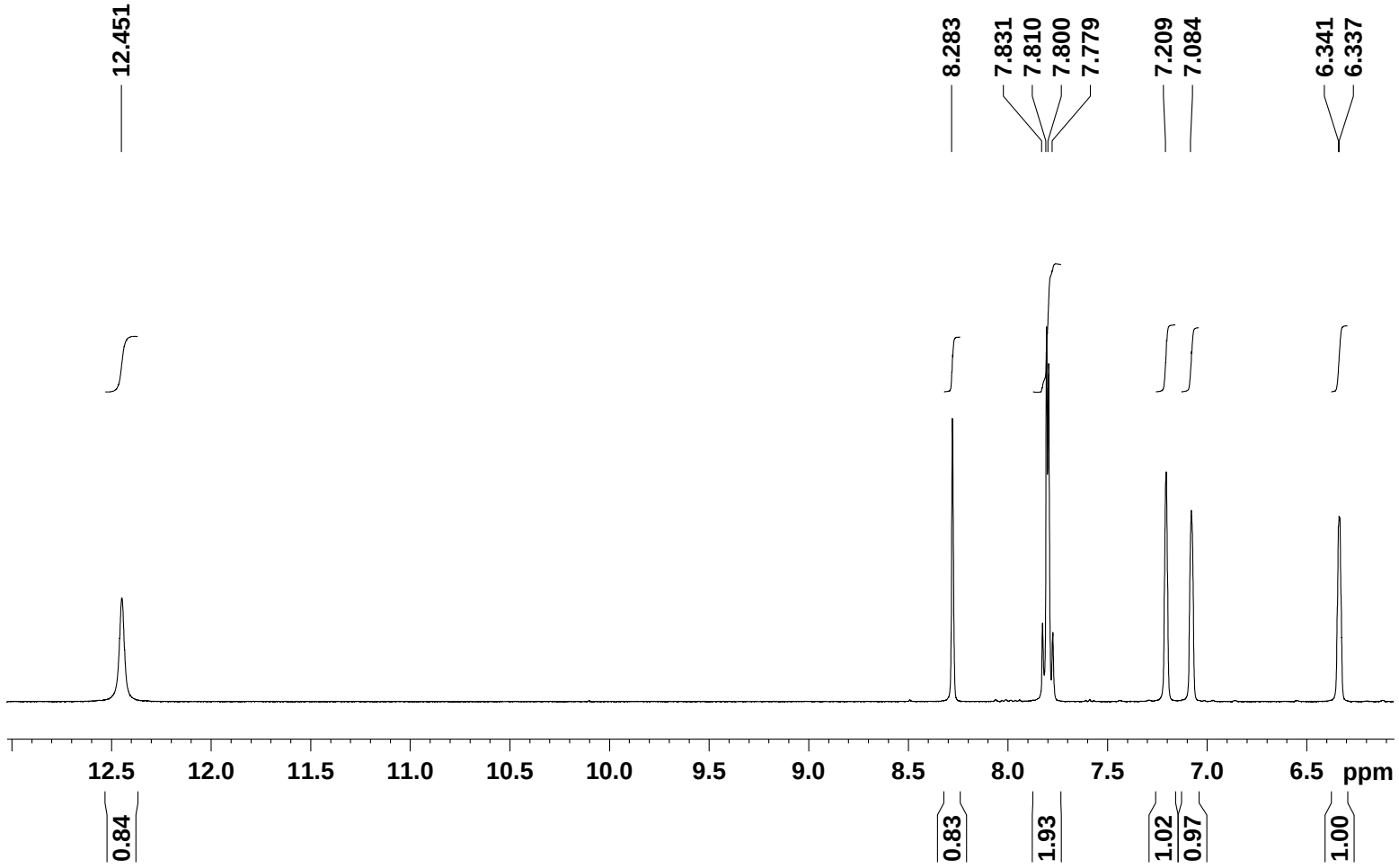


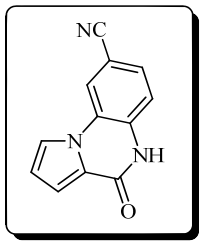
^{1}H-^{13}C HSQC 8-chloropyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3c**



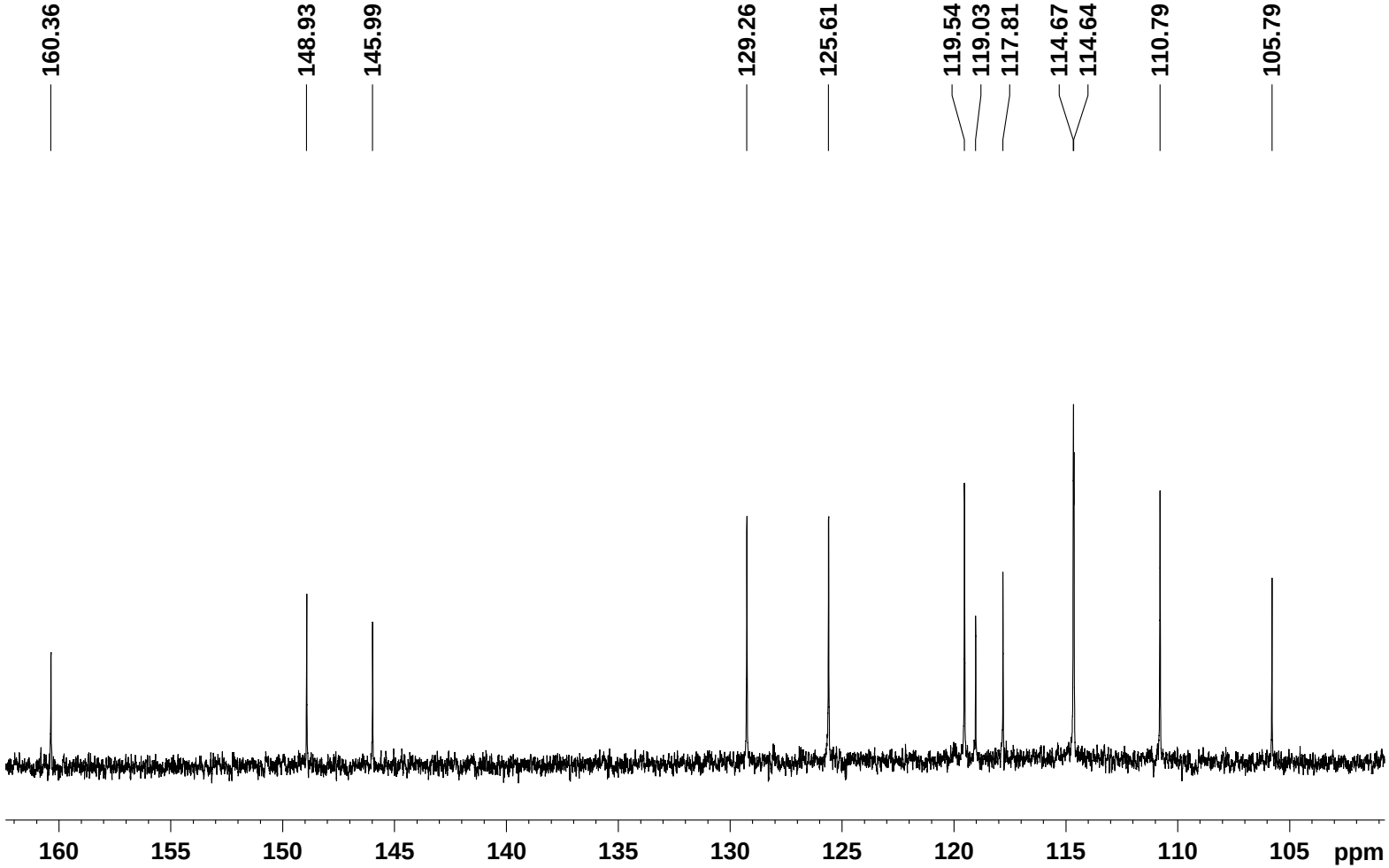


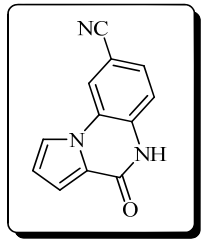
^{1}H NMR 8-cyanopyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3d**



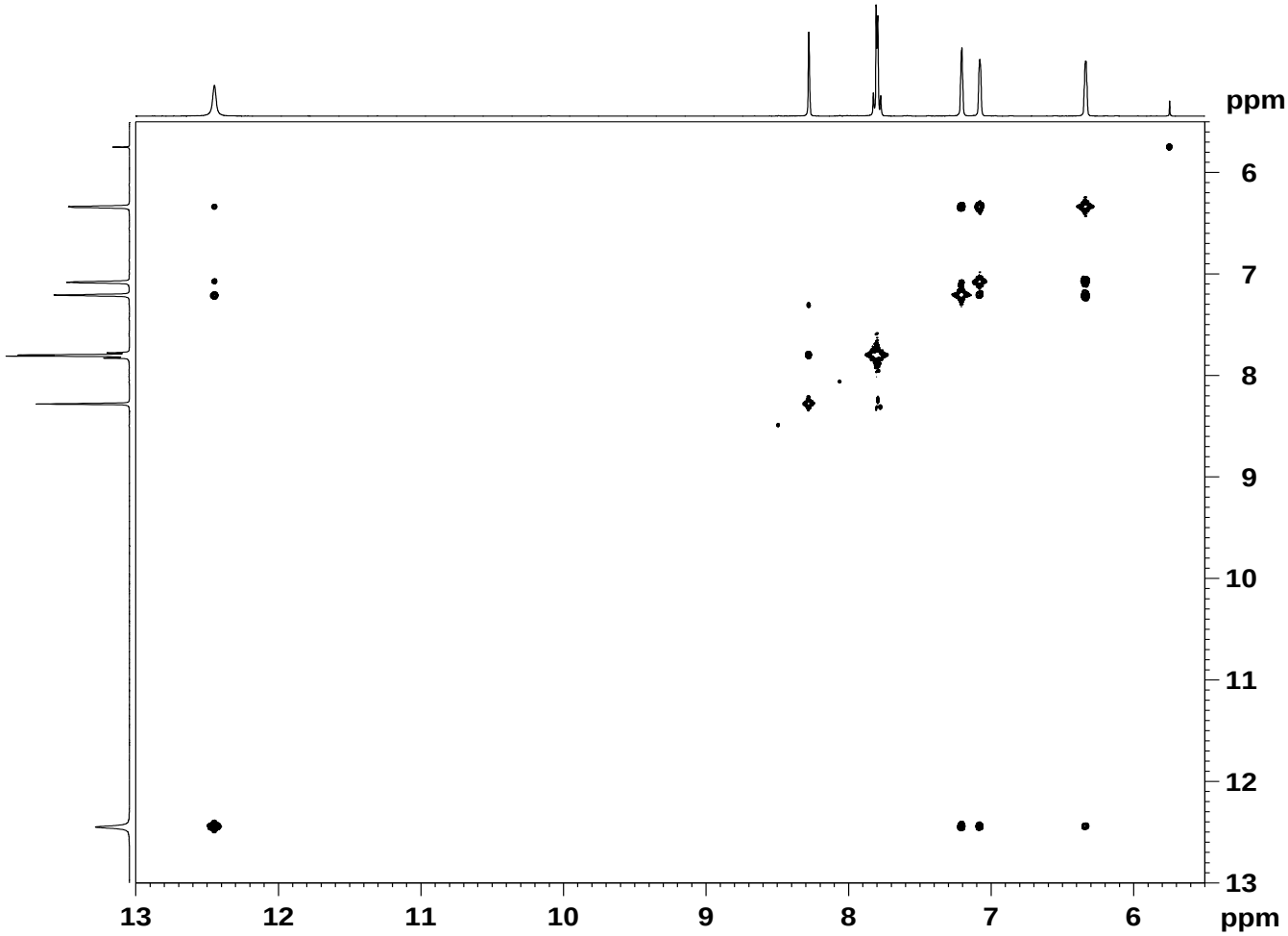


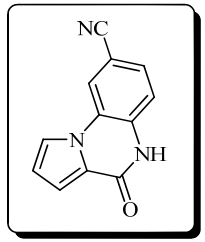
^{13} C NMR 8-cyanopyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3d**



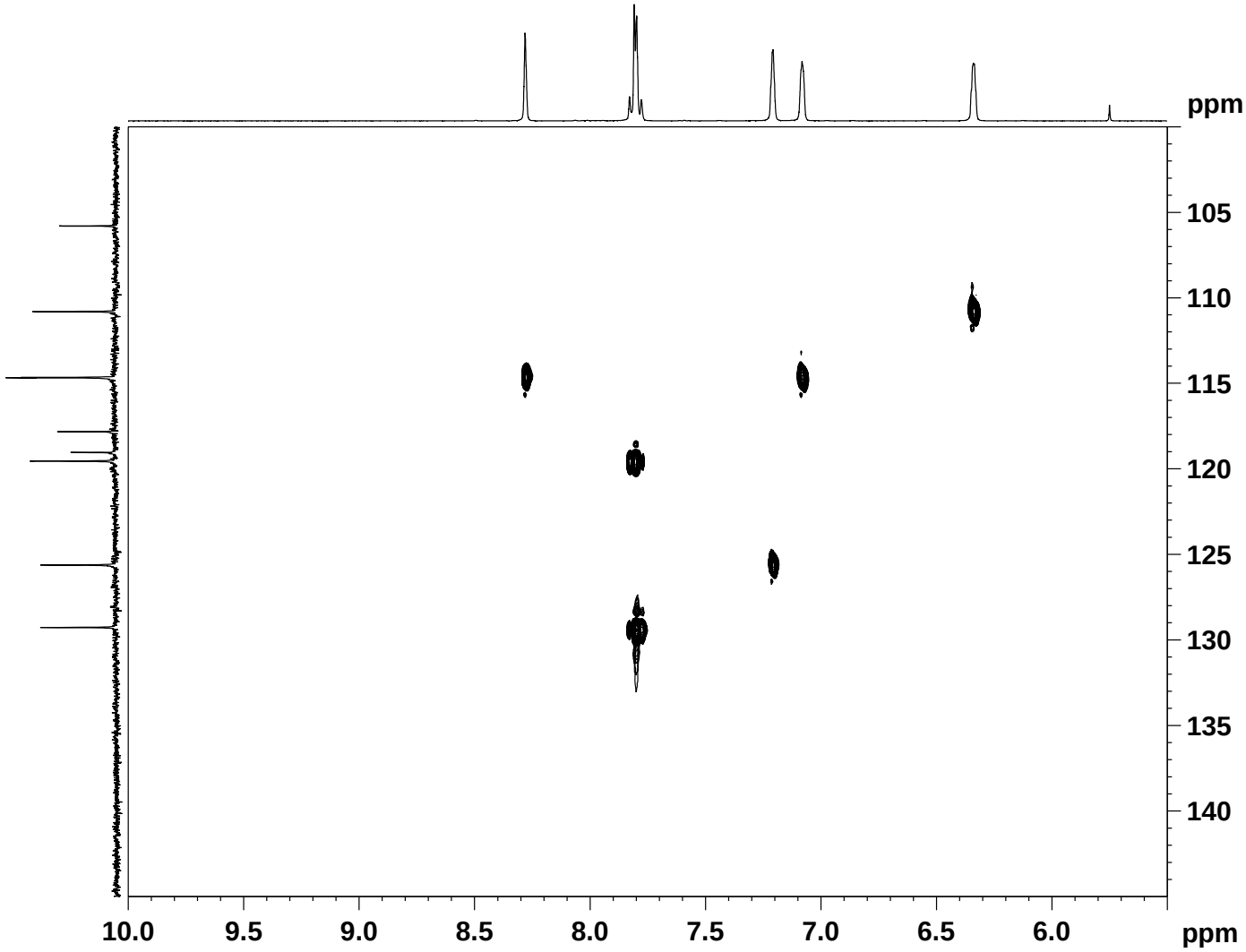


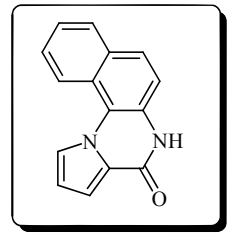
^{1}H-^{1}H COSY 8-cyanopyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3d**



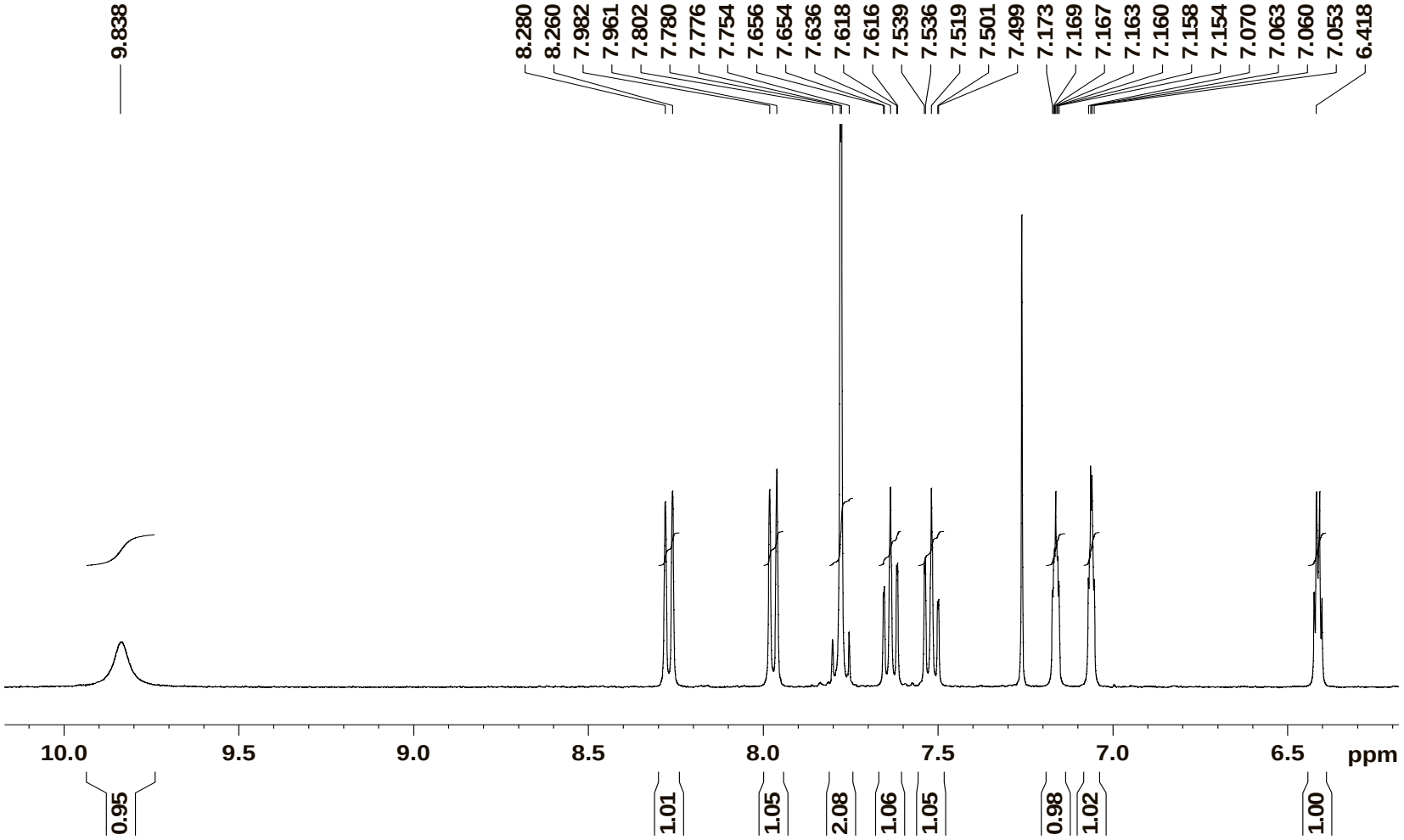


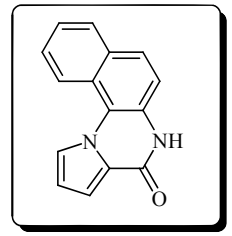
^{1}H-^{13} C HSQC 8-cyanopyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (DMSO-*d6*) **3d**



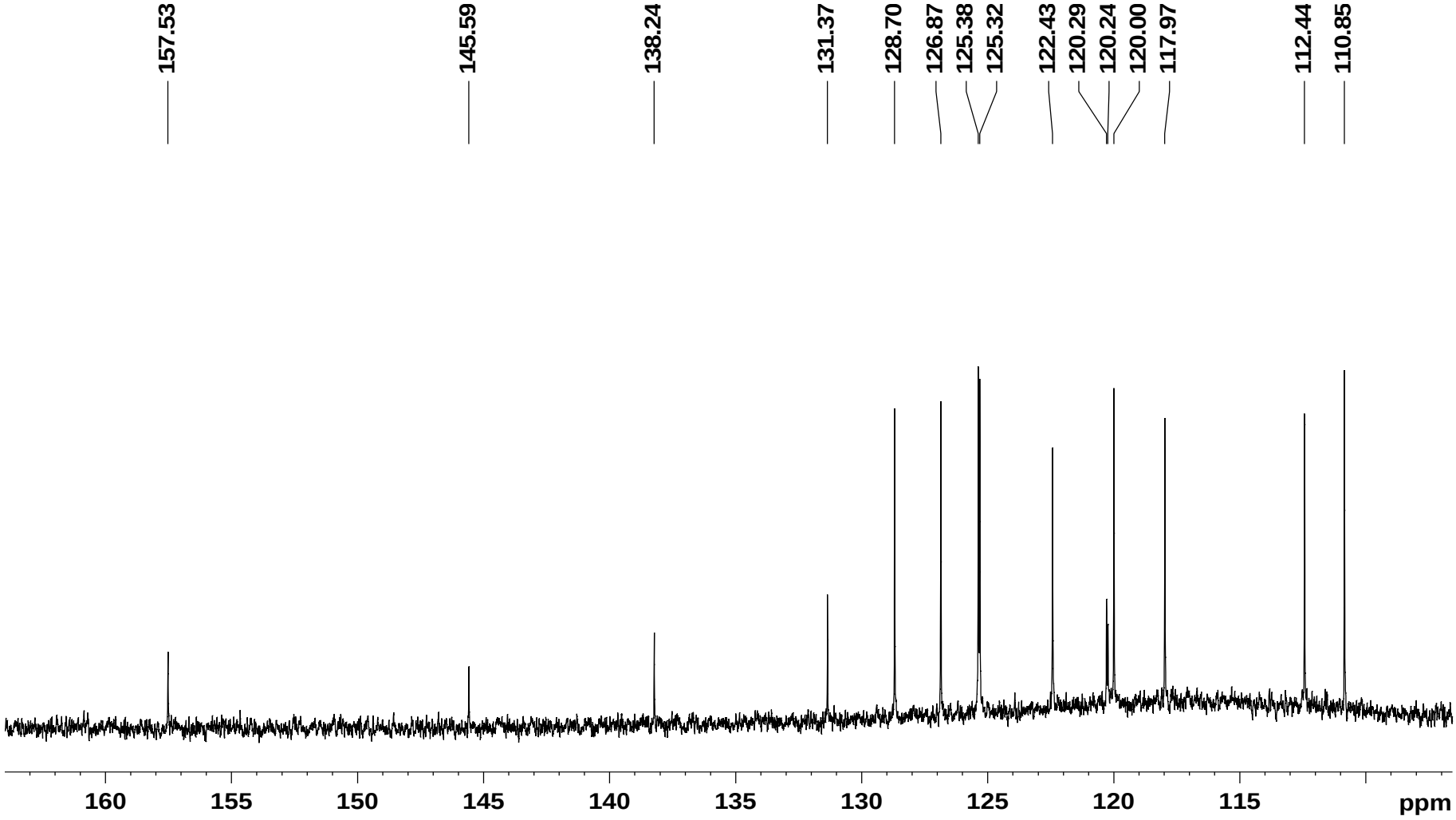


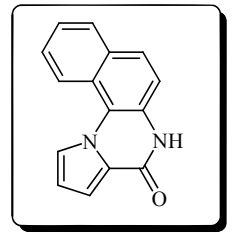
^{1}H NMR benzo[*h*]pyrrolo[1,2-**a**]quinoxalin-4(5*H*)-one ($CDCl_3$) **3e**



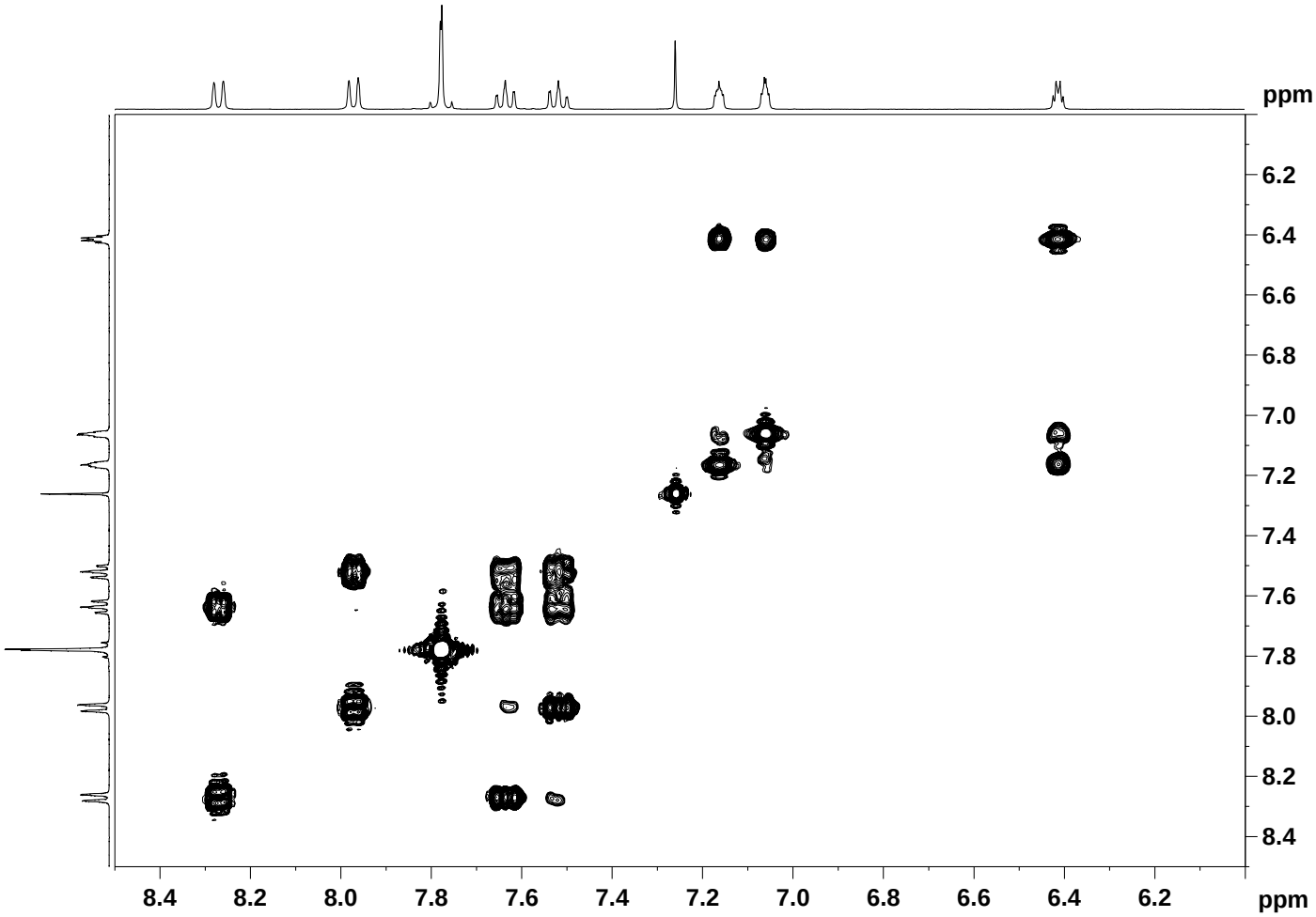


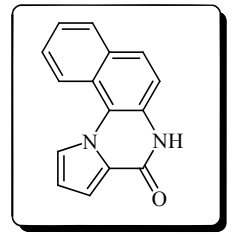
^{13}C NMR benzo[*h*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3d**



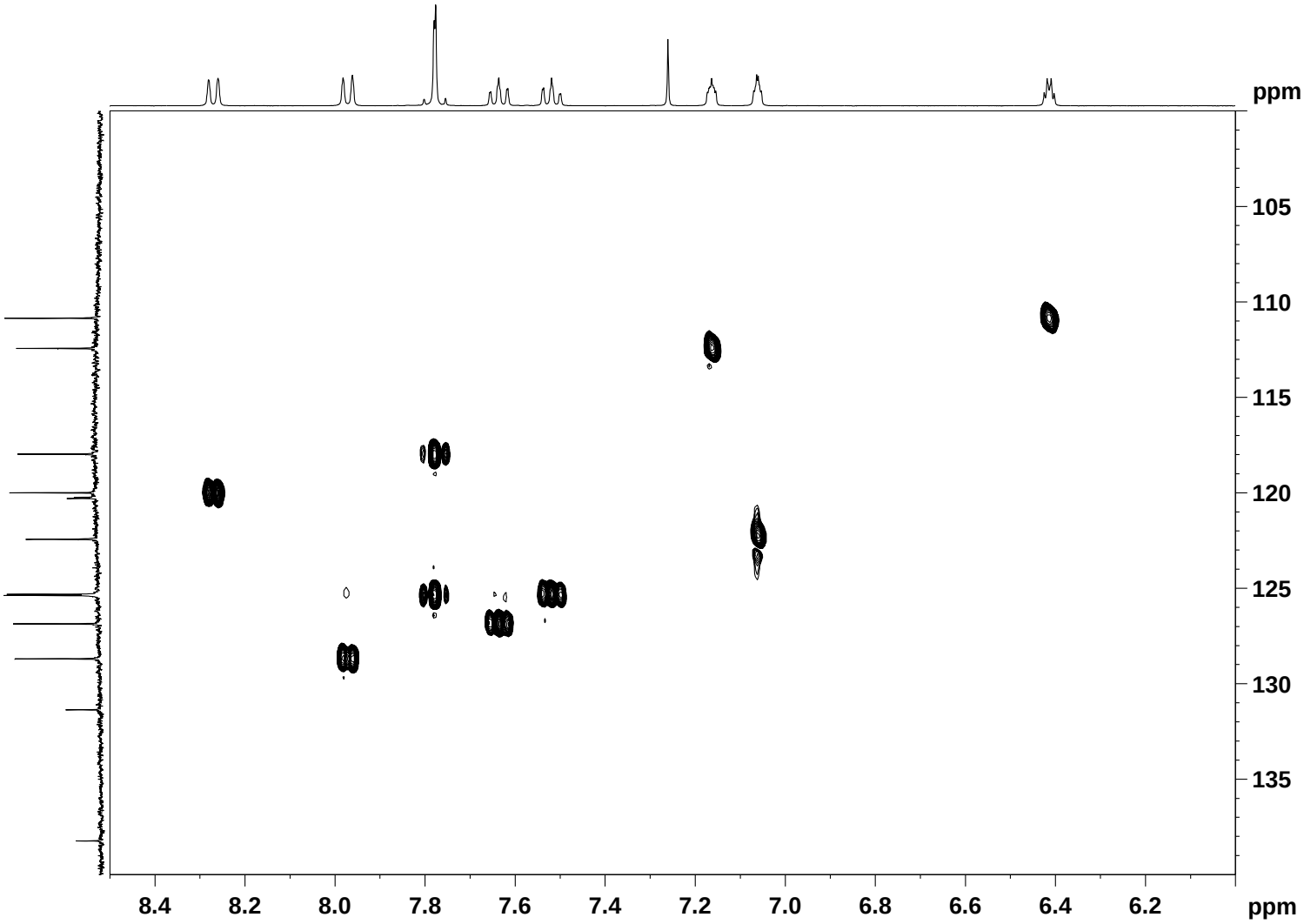


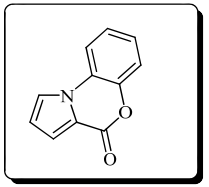
^{1}H-^{1}H COSY benzo[*h*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3d**



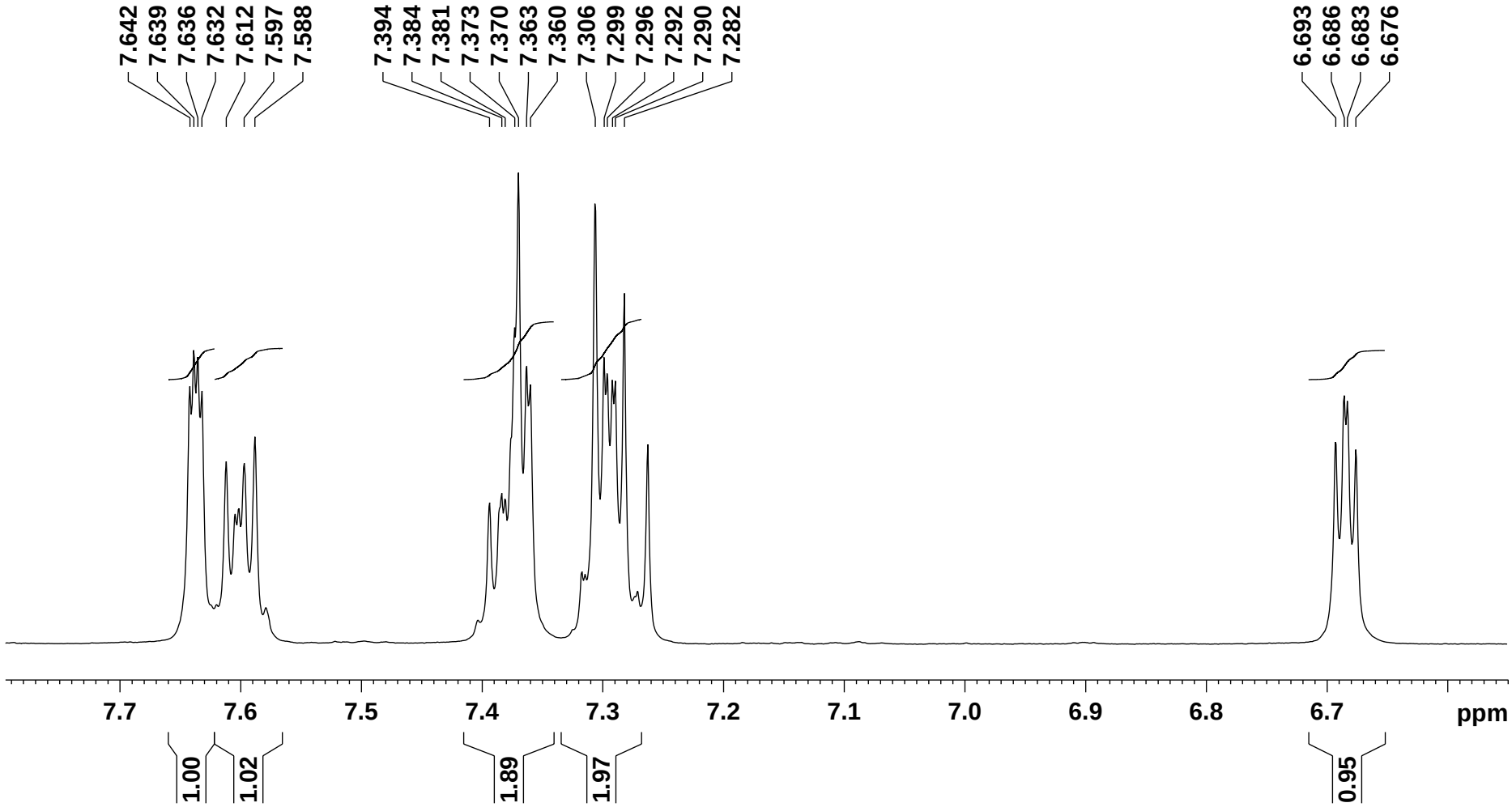


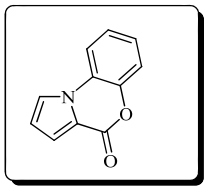
^{1}H-^{13}C HSQC benzo[*h*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one ($CDCl_3$) **3d**



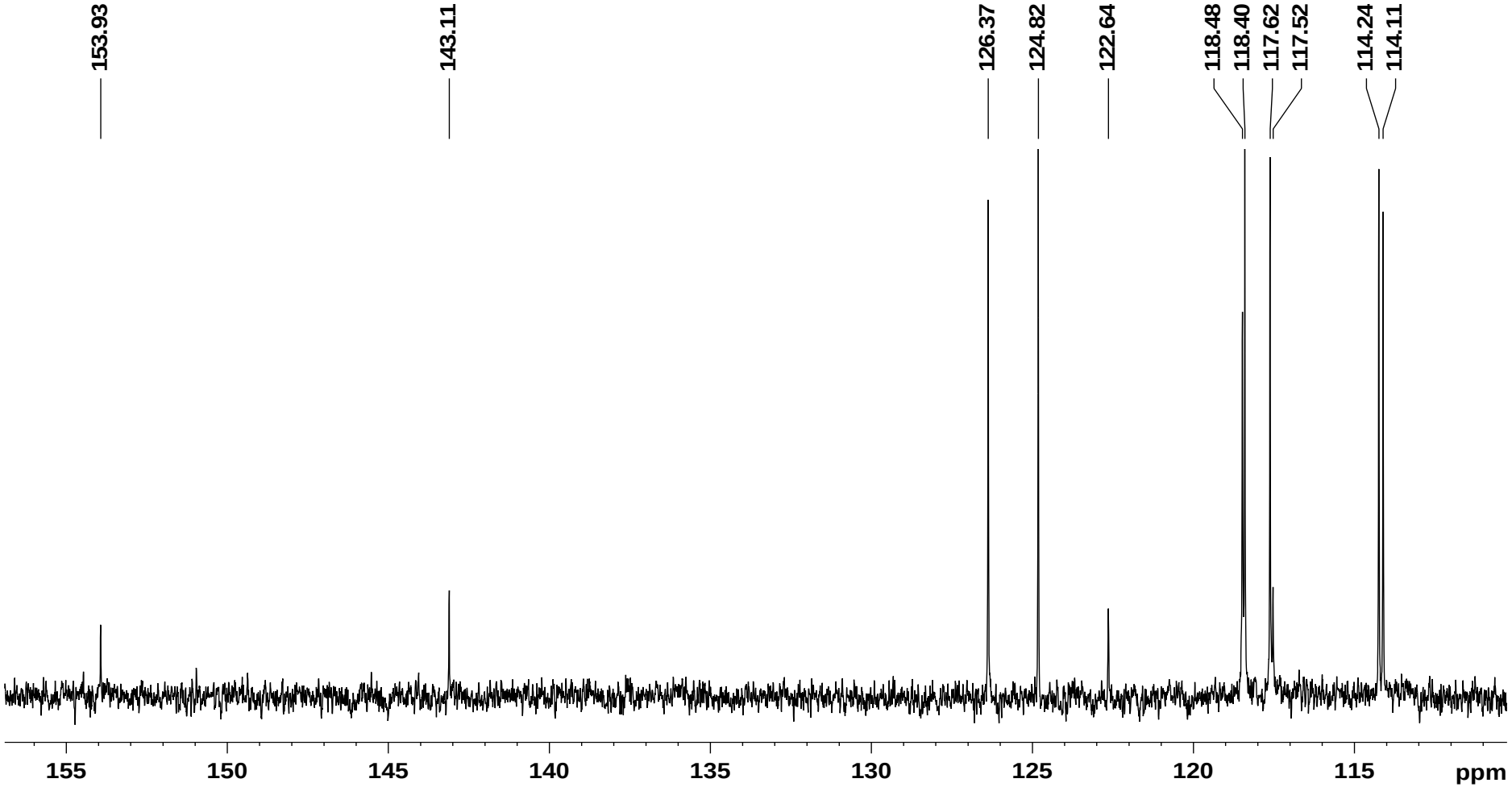


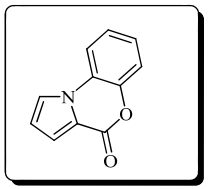
^{1}H NMR 4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **3e**



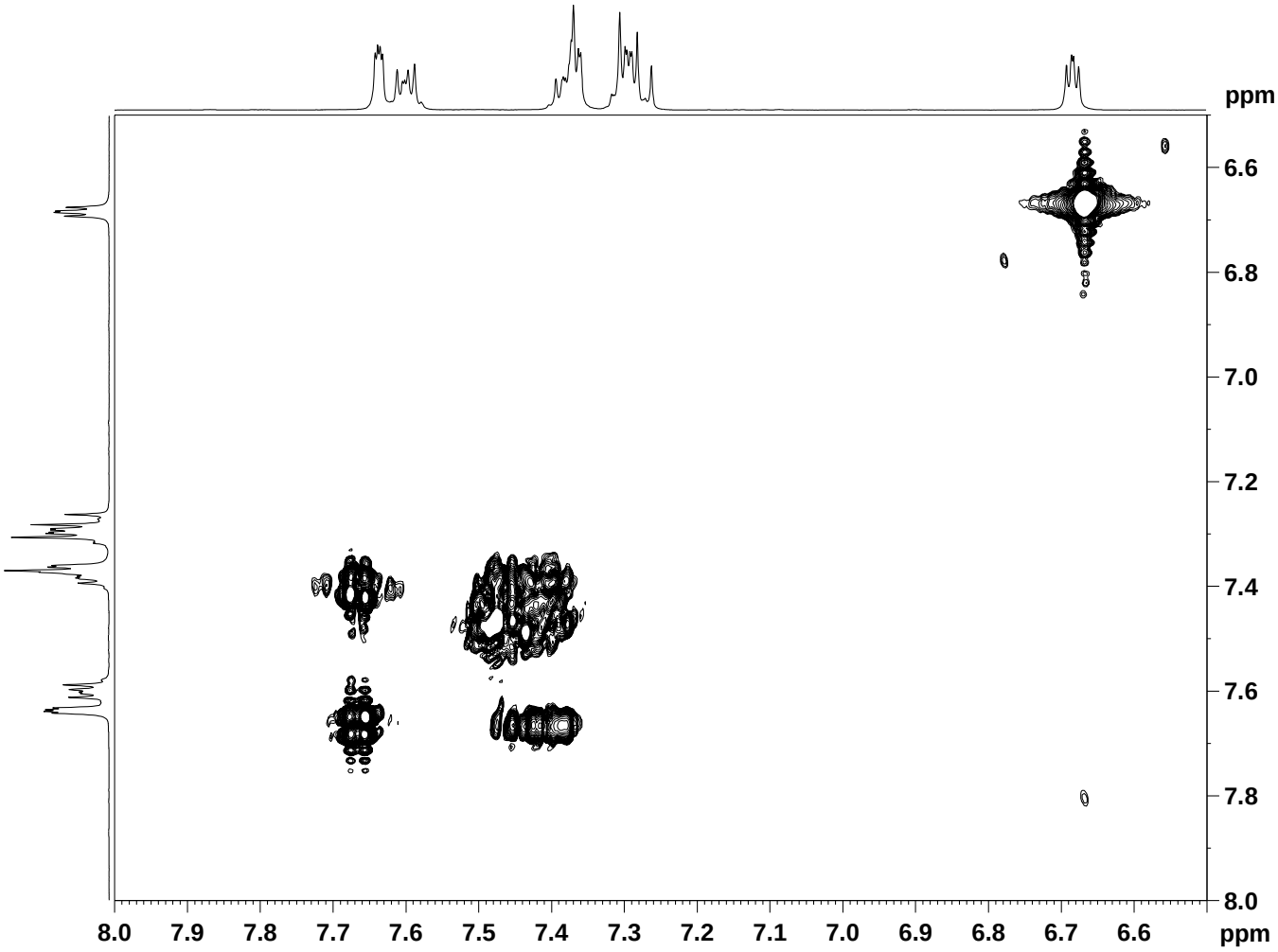


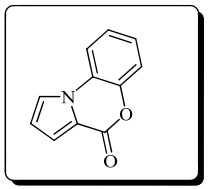
^{13}C NMR 4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **3e**



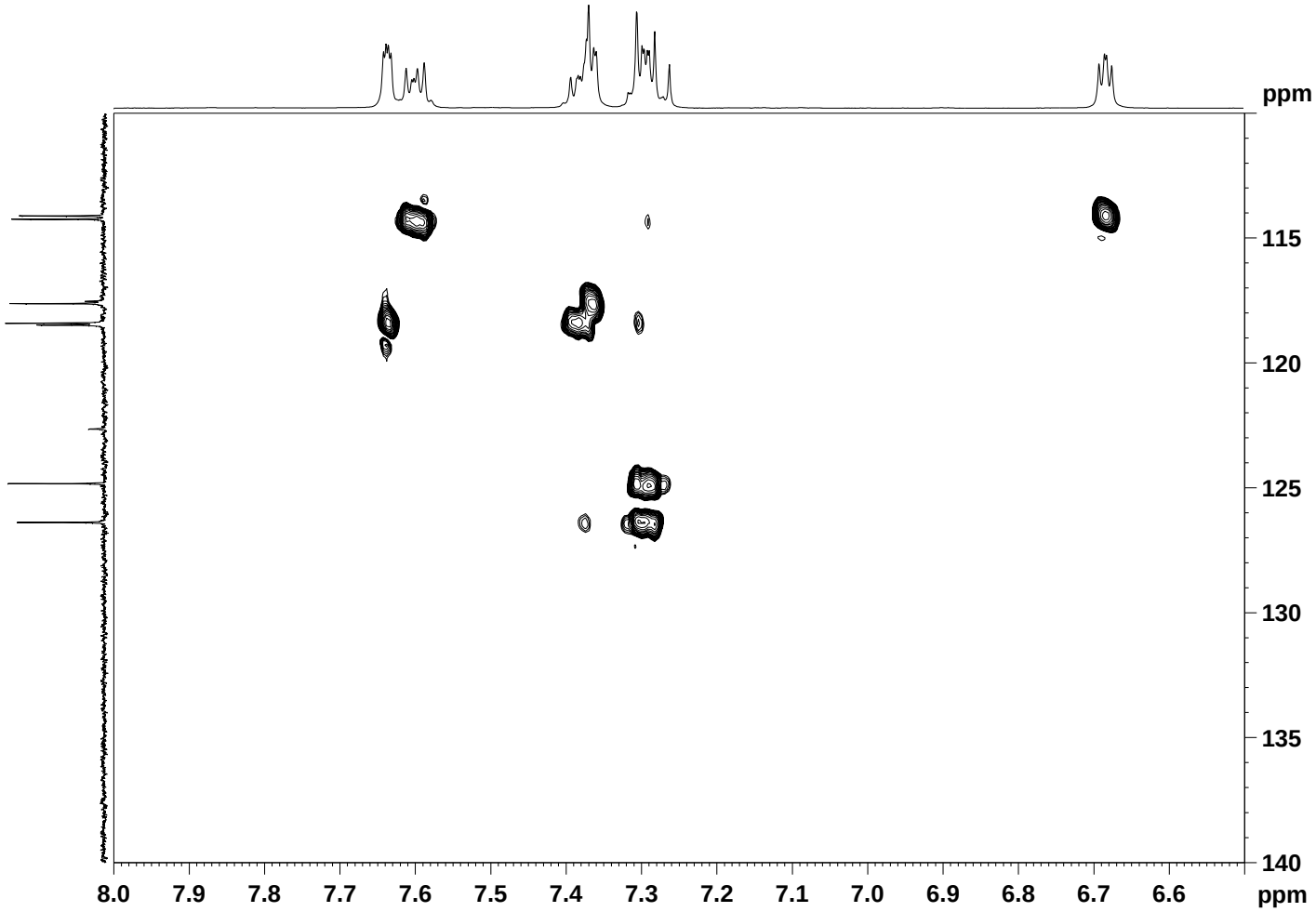


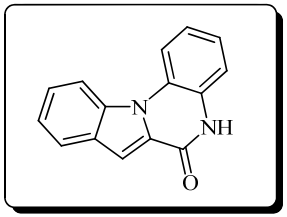
^{1}H-^{1}H COSY 4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **3e**



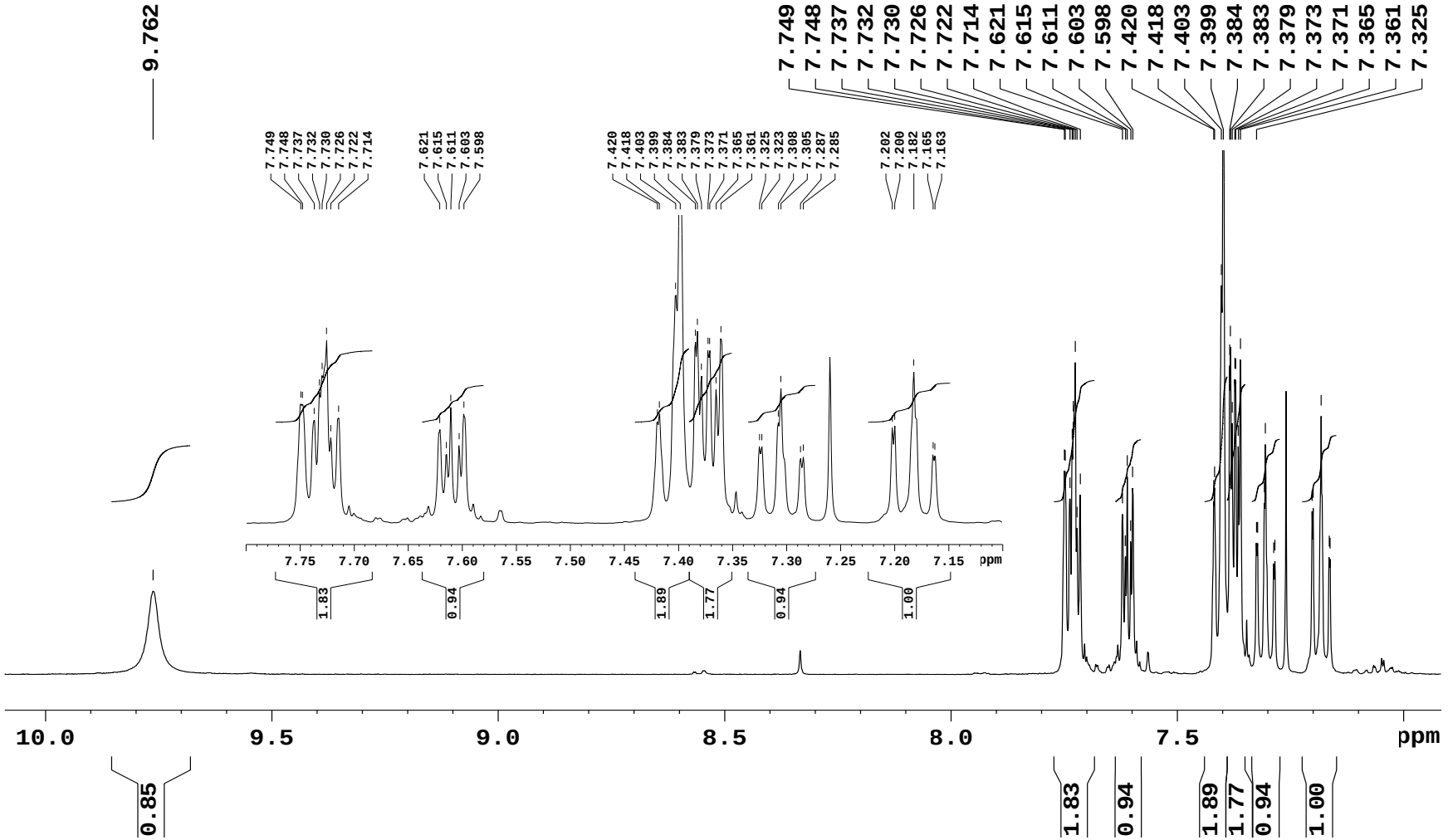


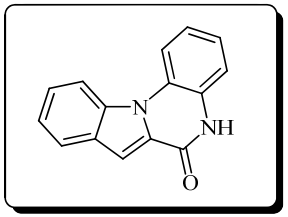
^{1}H-^{13}C HSQC 4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **3e**



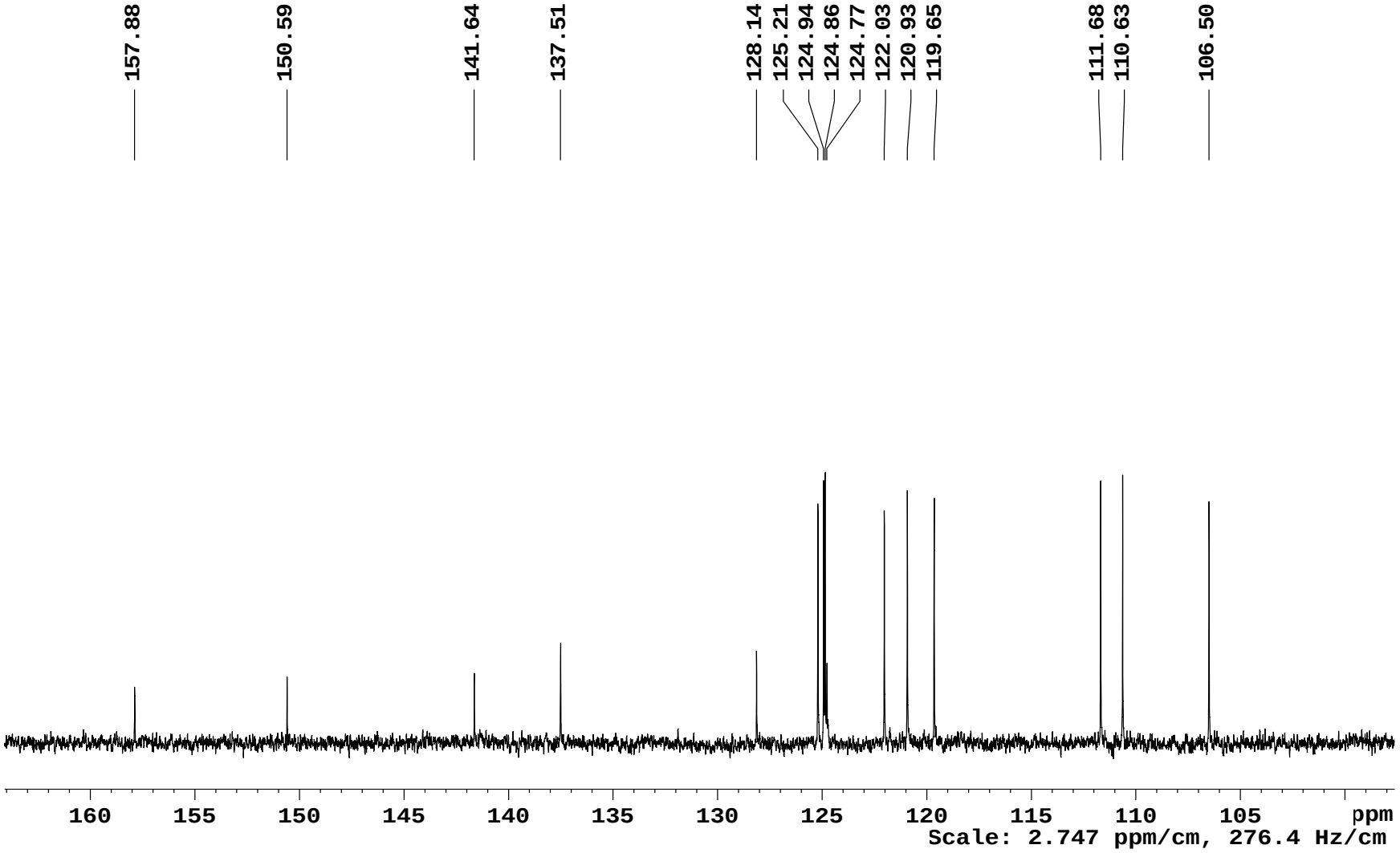


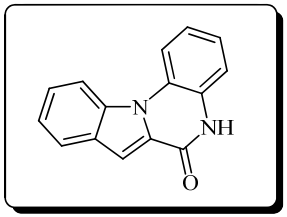
^{1}H NMR indolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5a**



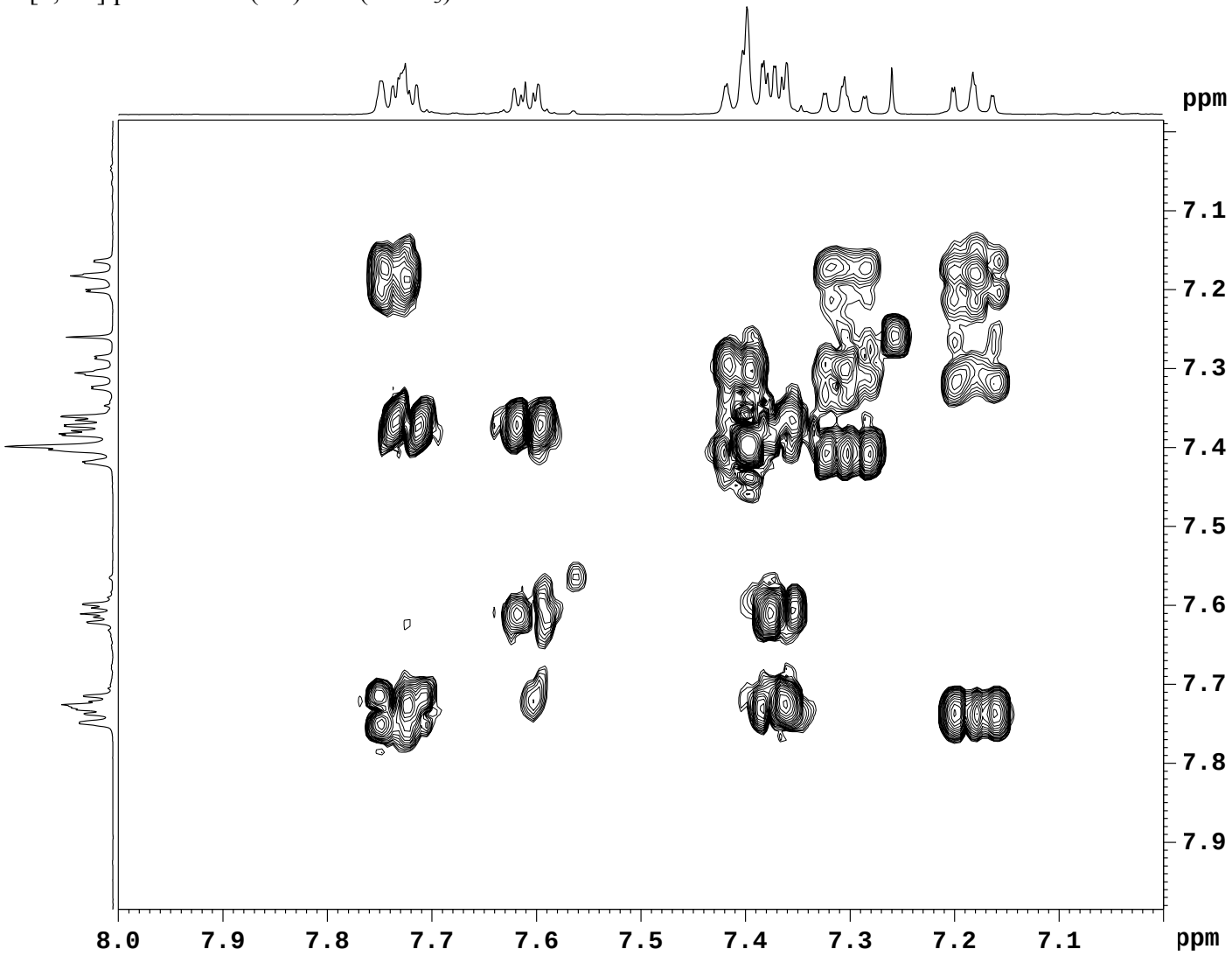


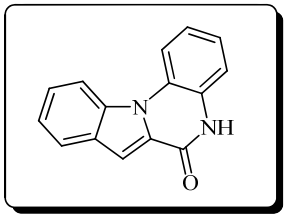
^{13}C NMR indolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5a**



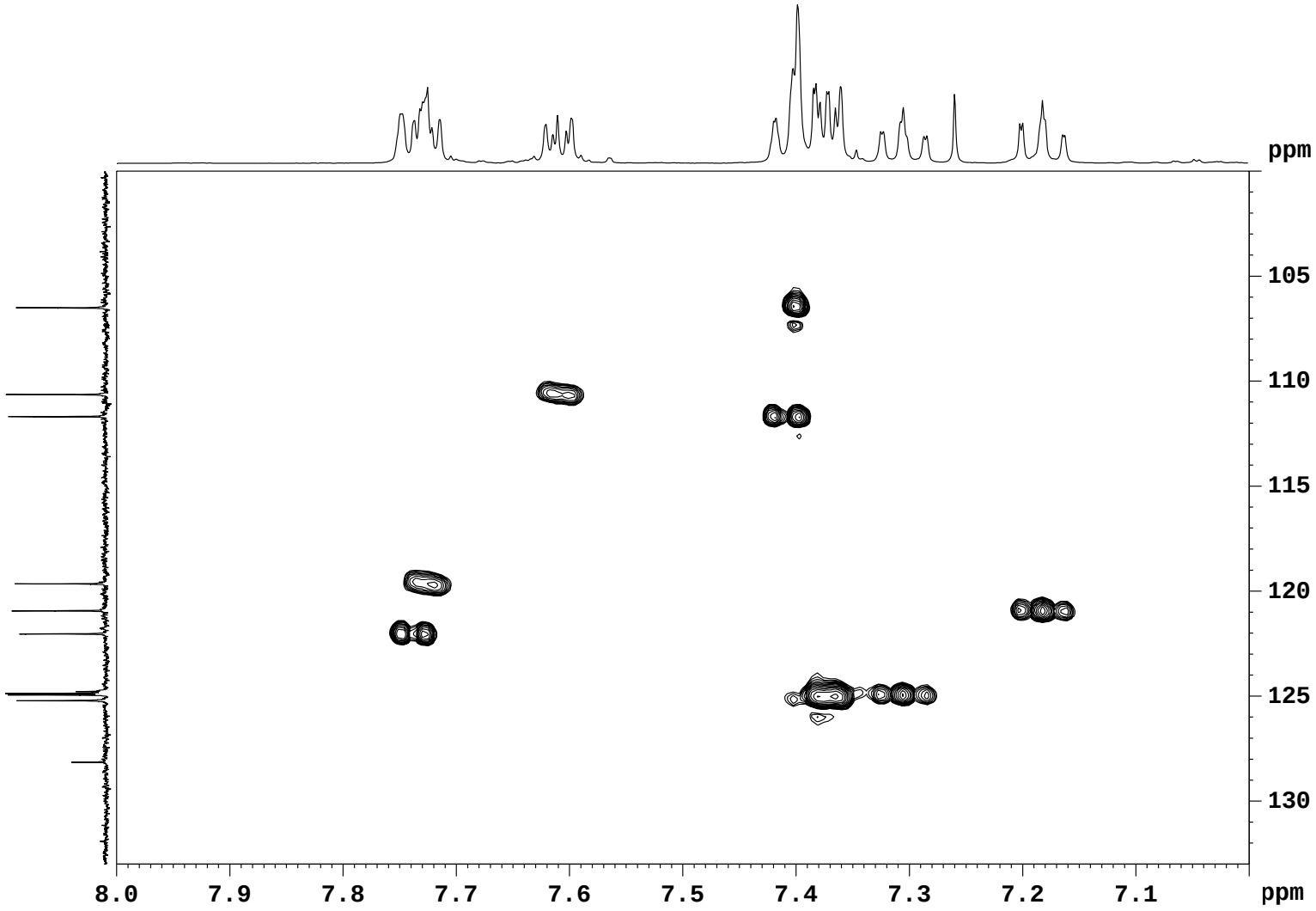


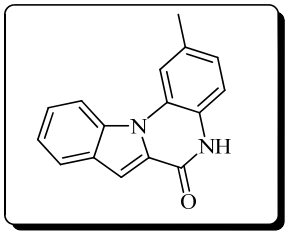
^{1}H-^{1}H COSY indolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5a**



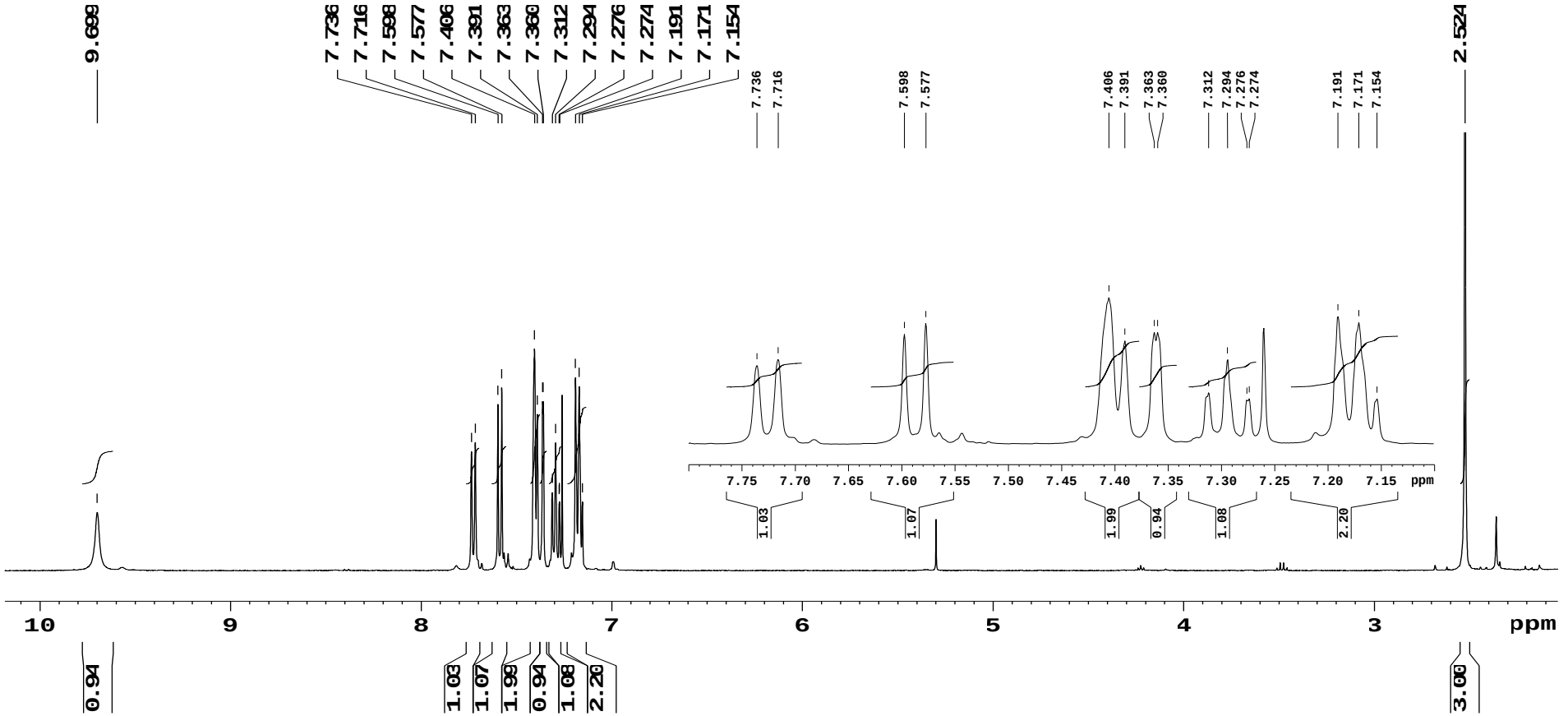


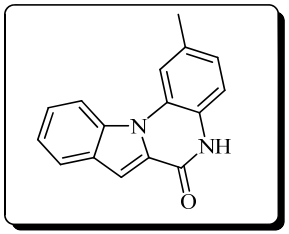
^{1}H-^{13}C HSQC indolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5a**



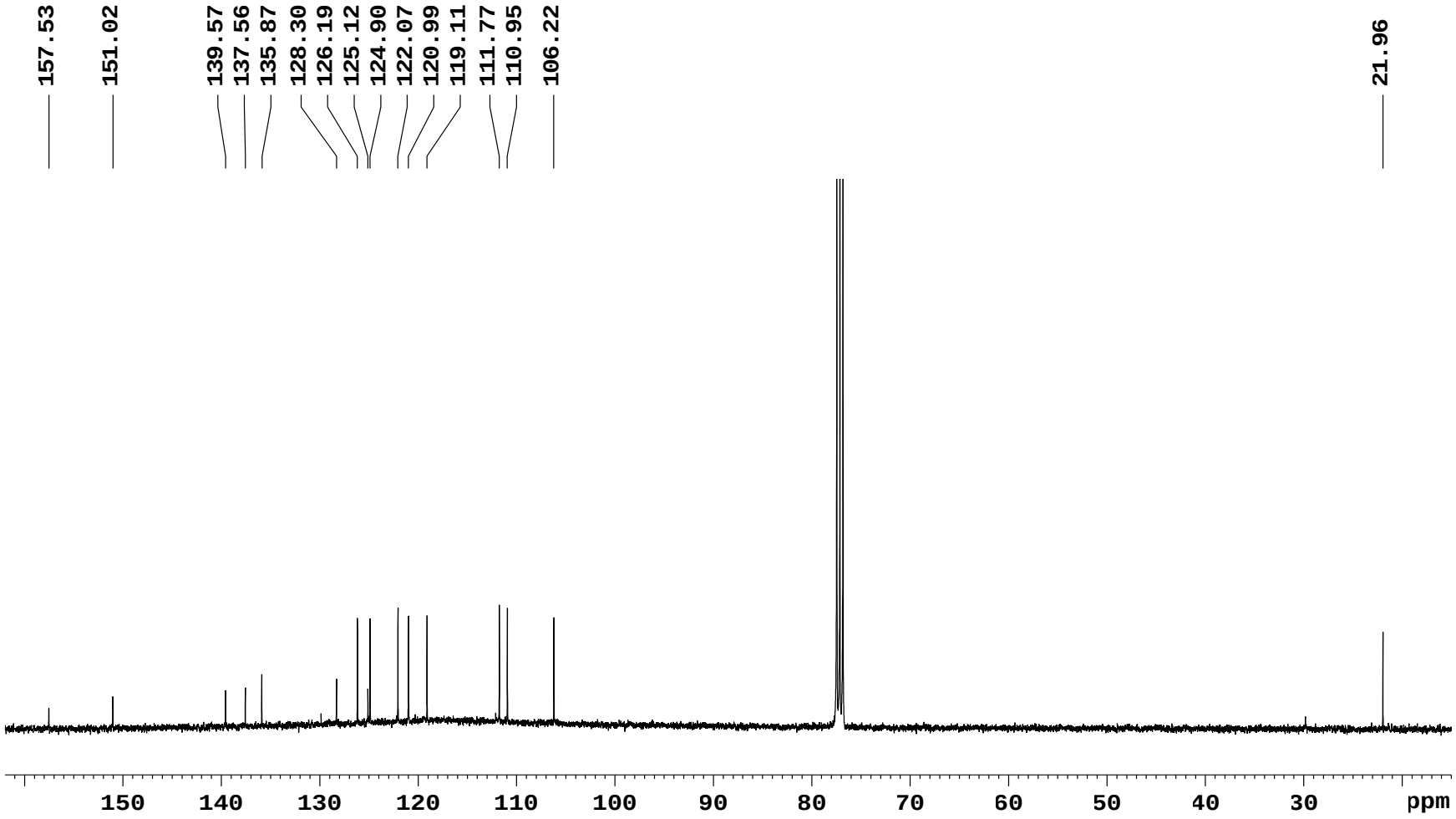


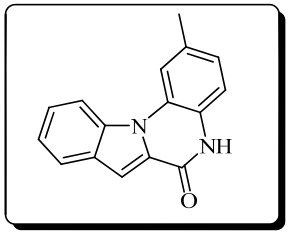
^{1}H NMR 2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5b**



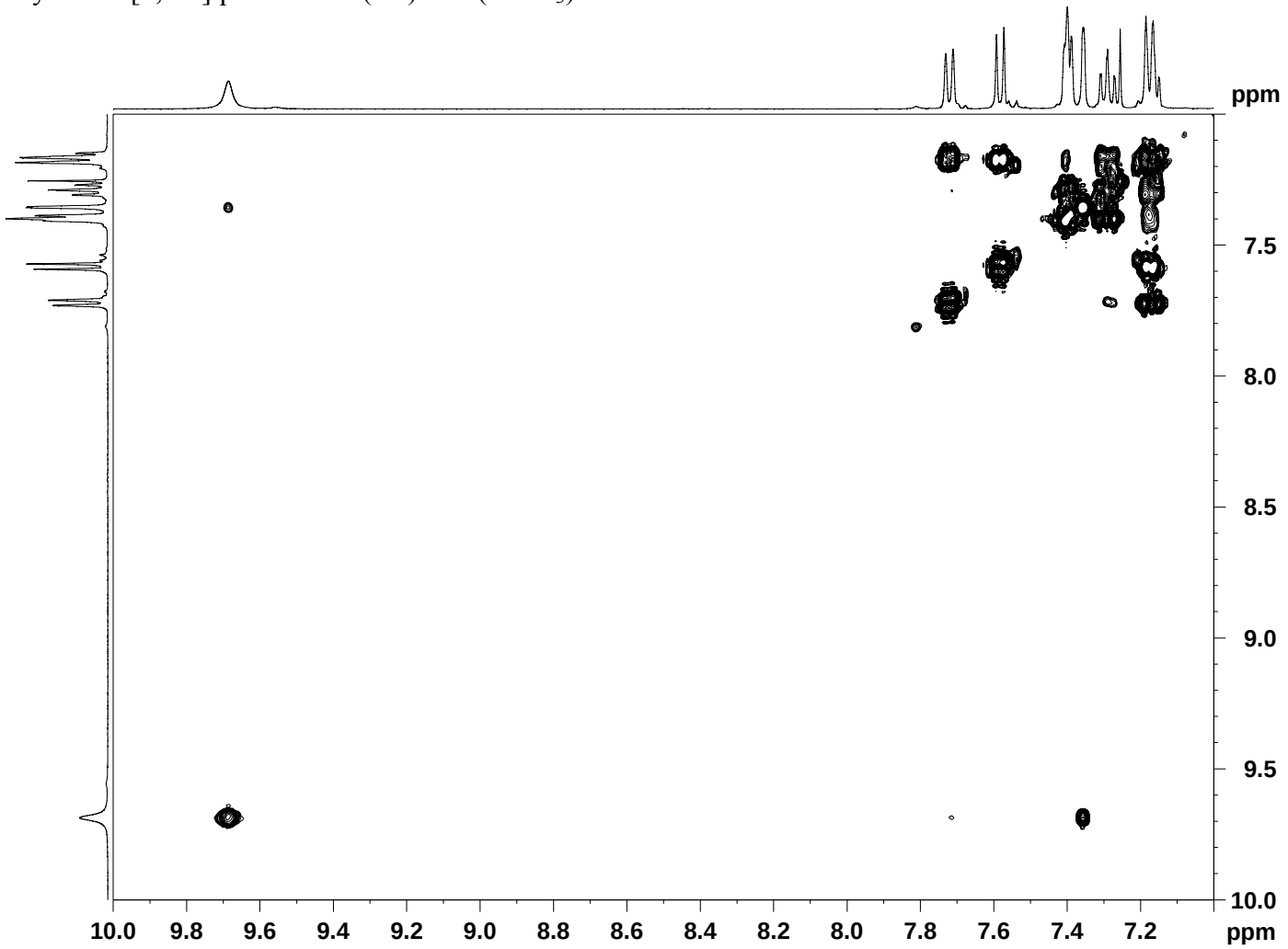


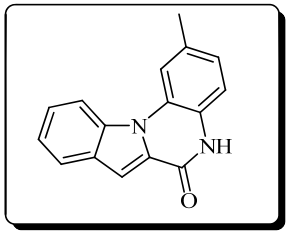
^{13}C NMR 2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5b**



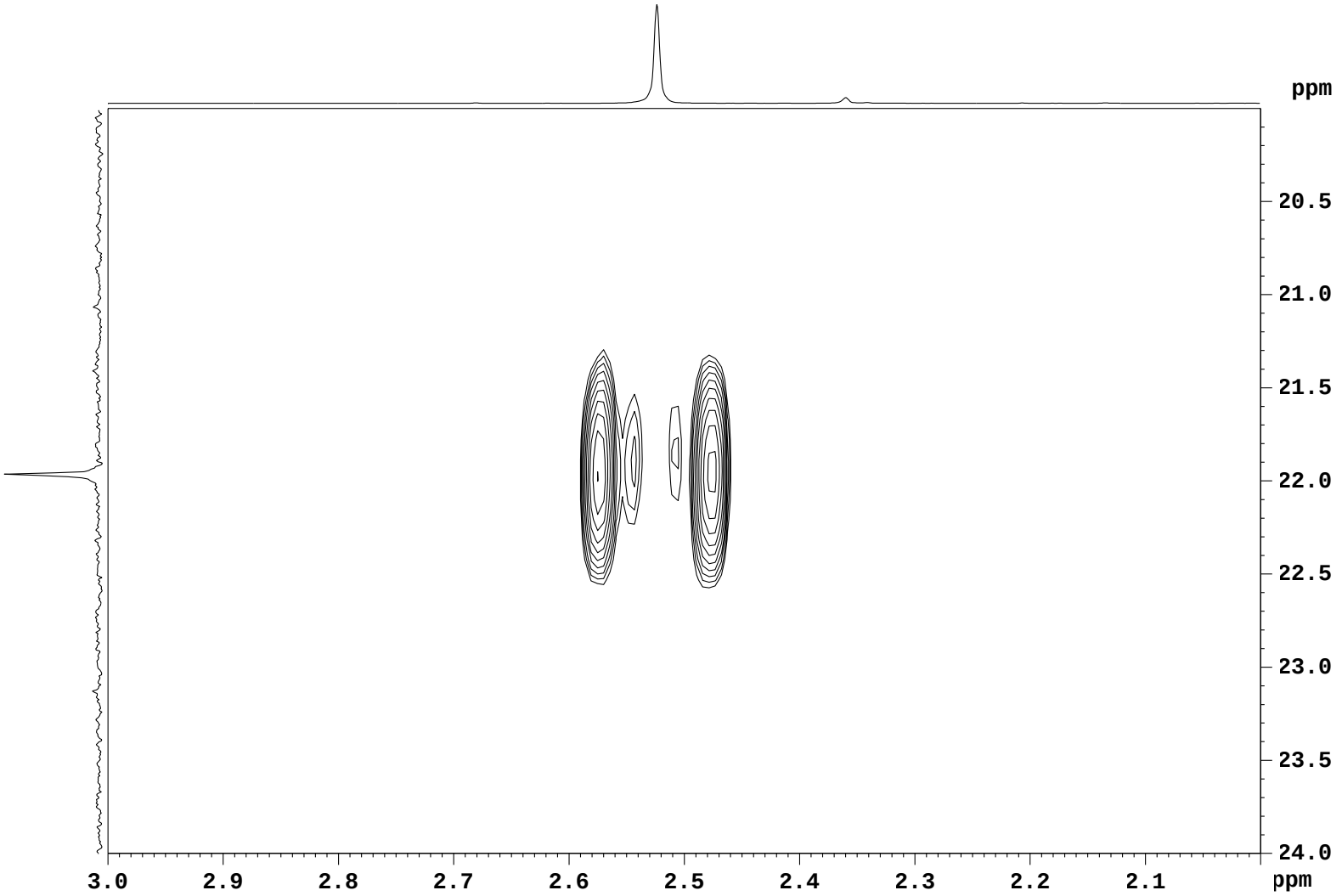


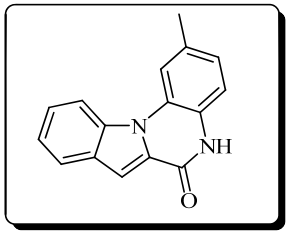
^{1}H-^{1}H COSY 2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5b**



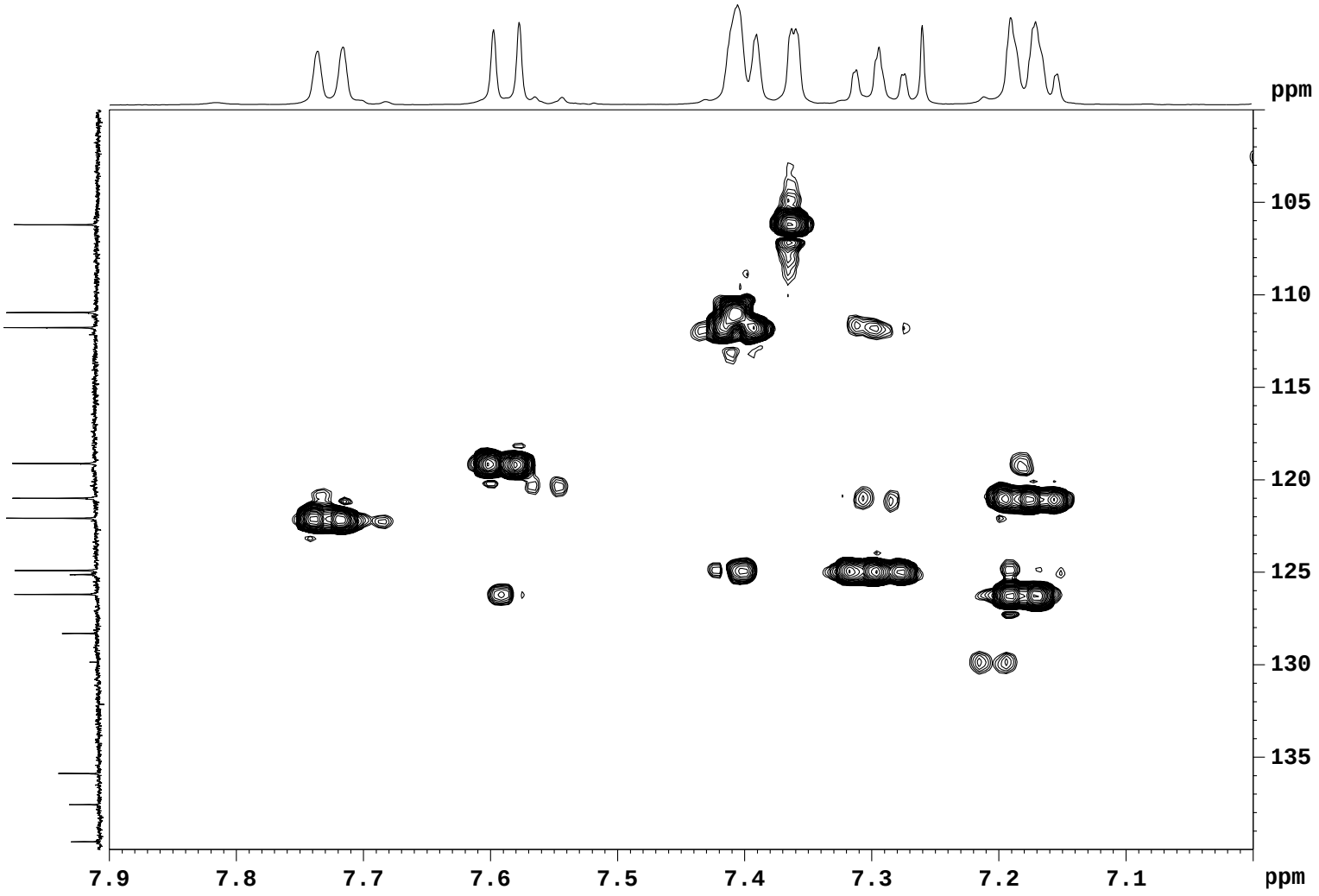


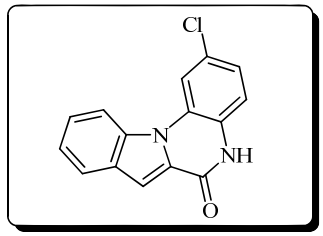
^{1}H-^{13}C HSQC 2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5b**



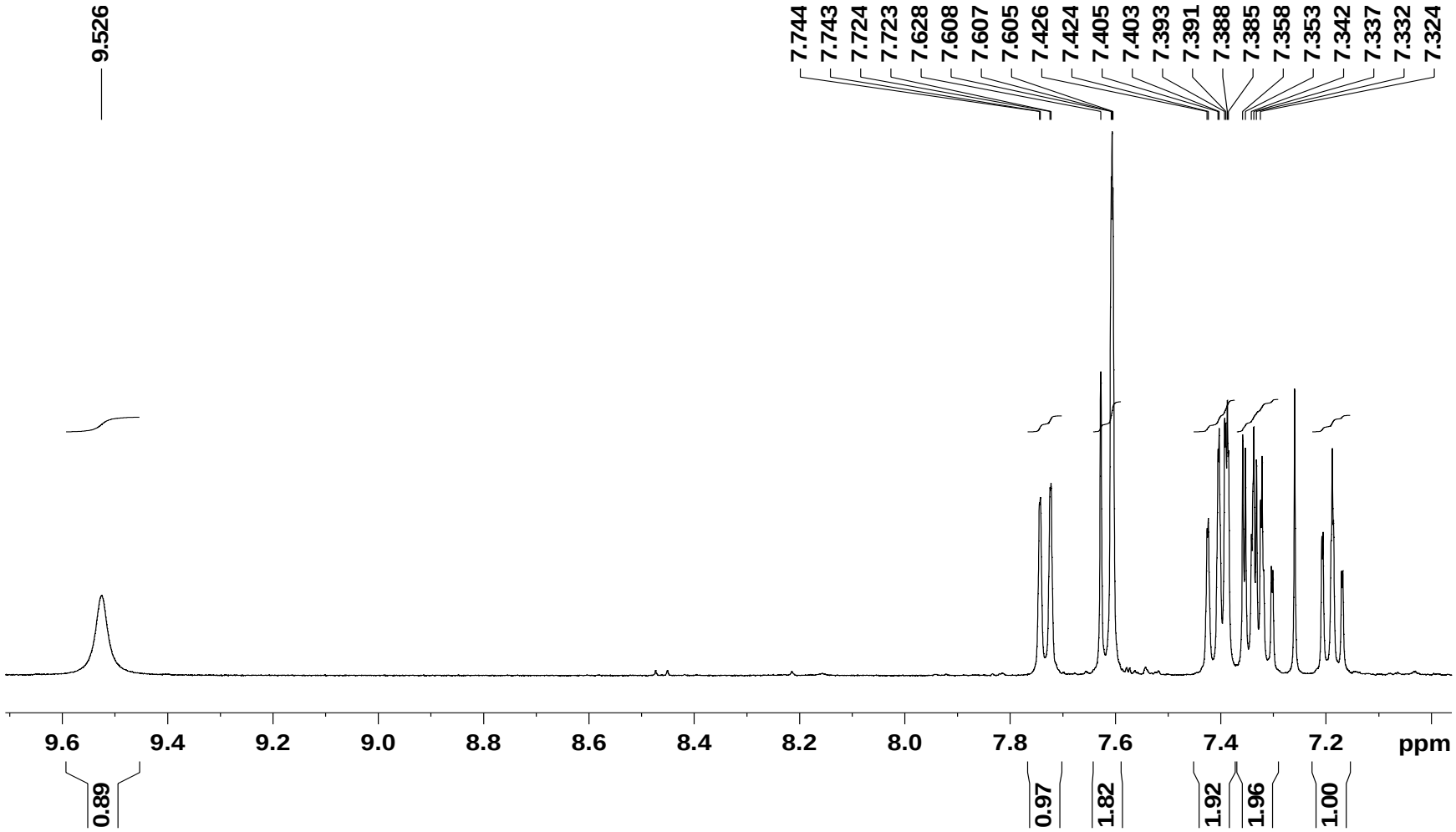


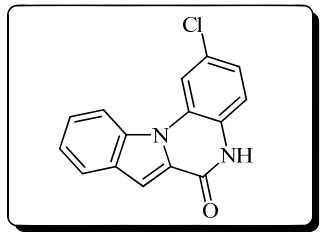
^{1}H-^{13}C HSQC 2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5b**



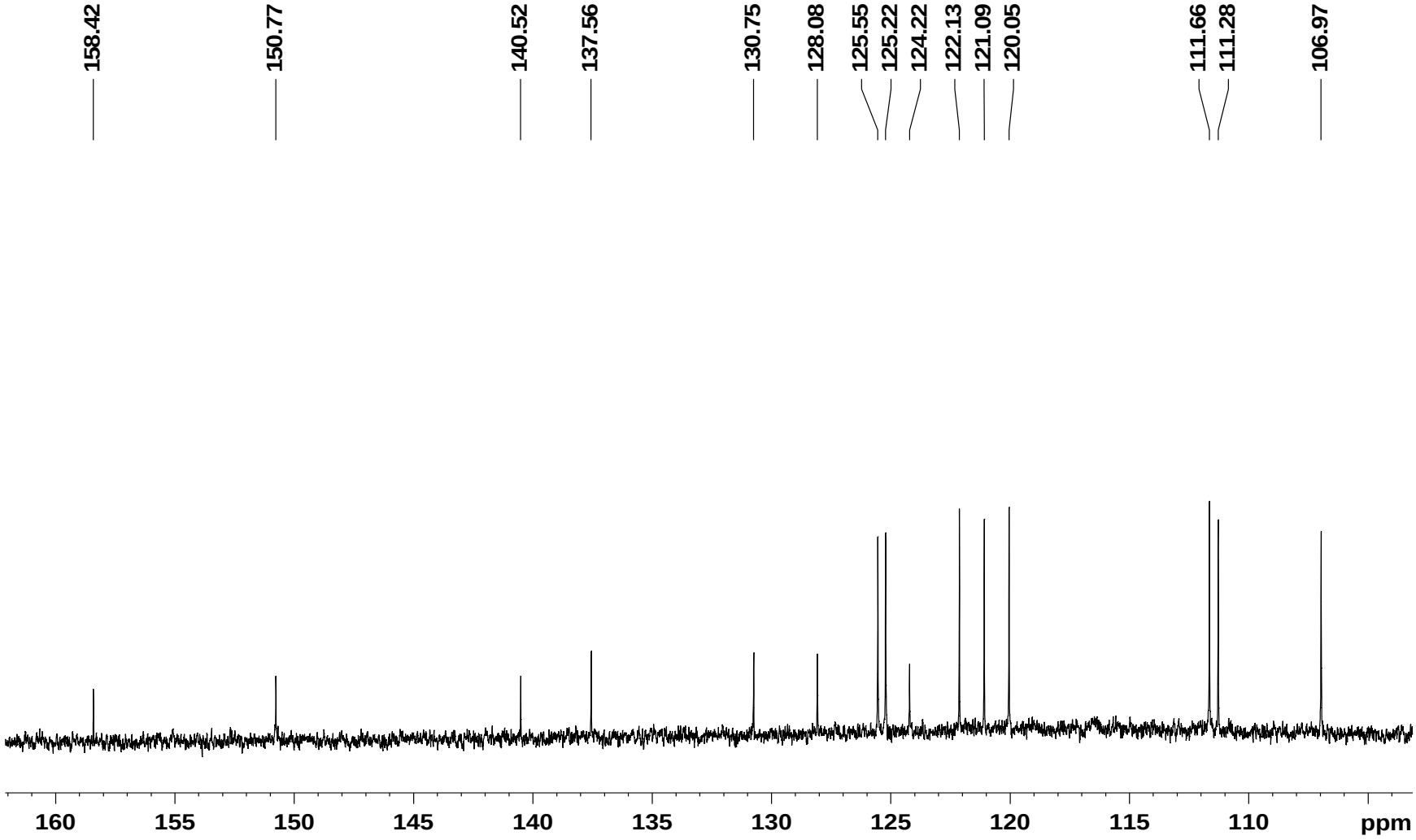


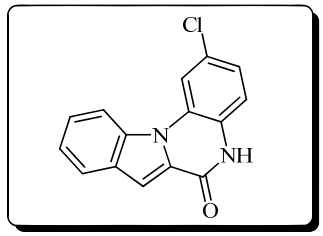
^{1}H NMR 2-chloroindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5c**



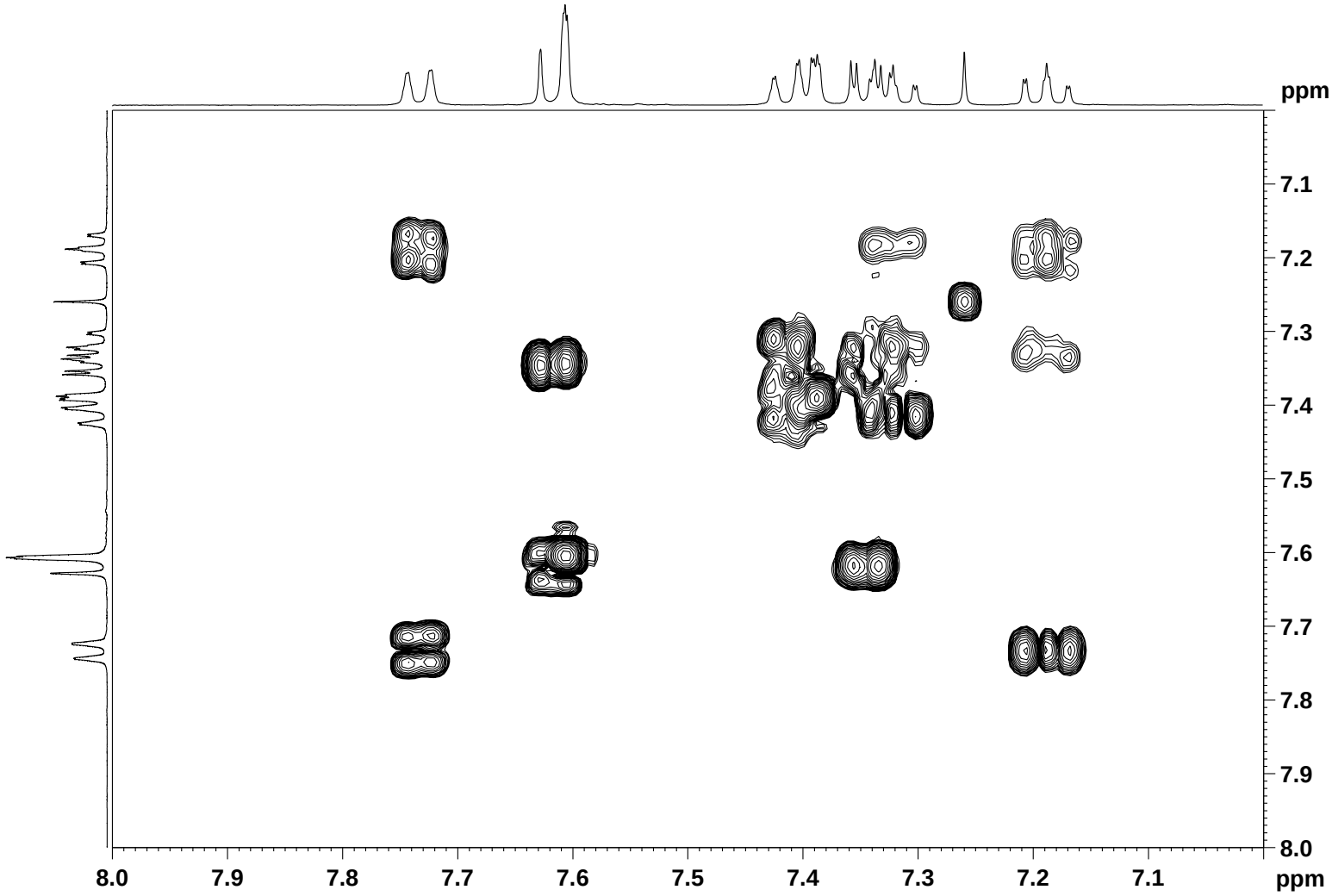


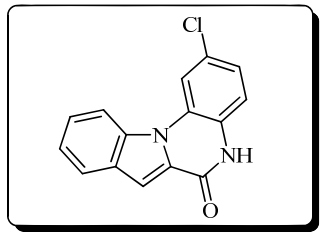
^{13}C NMR 2-chloroindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5c**



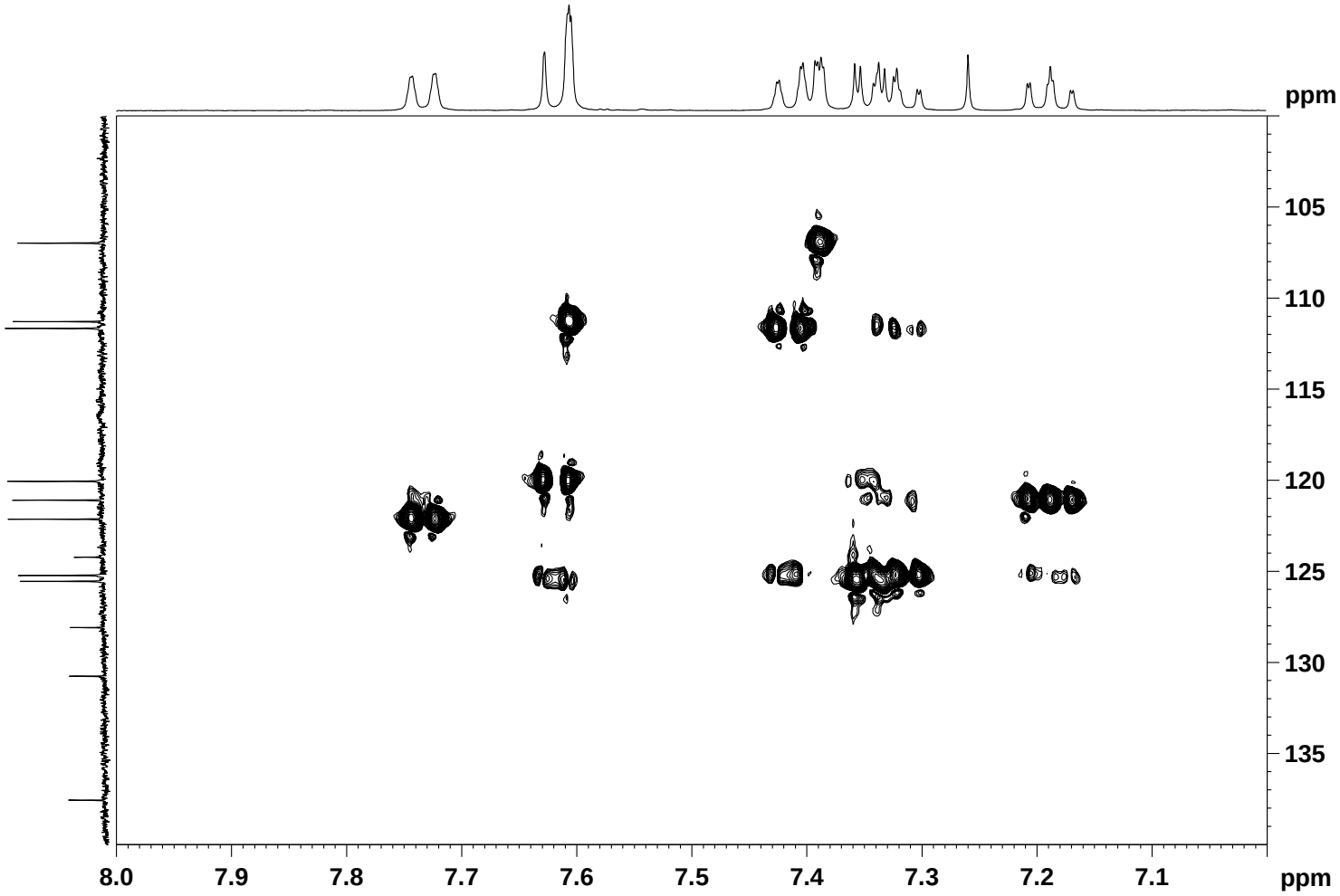


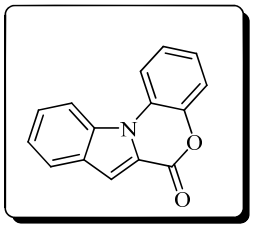
^{1}H-^{1}H COSY 2-chloroindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5c**



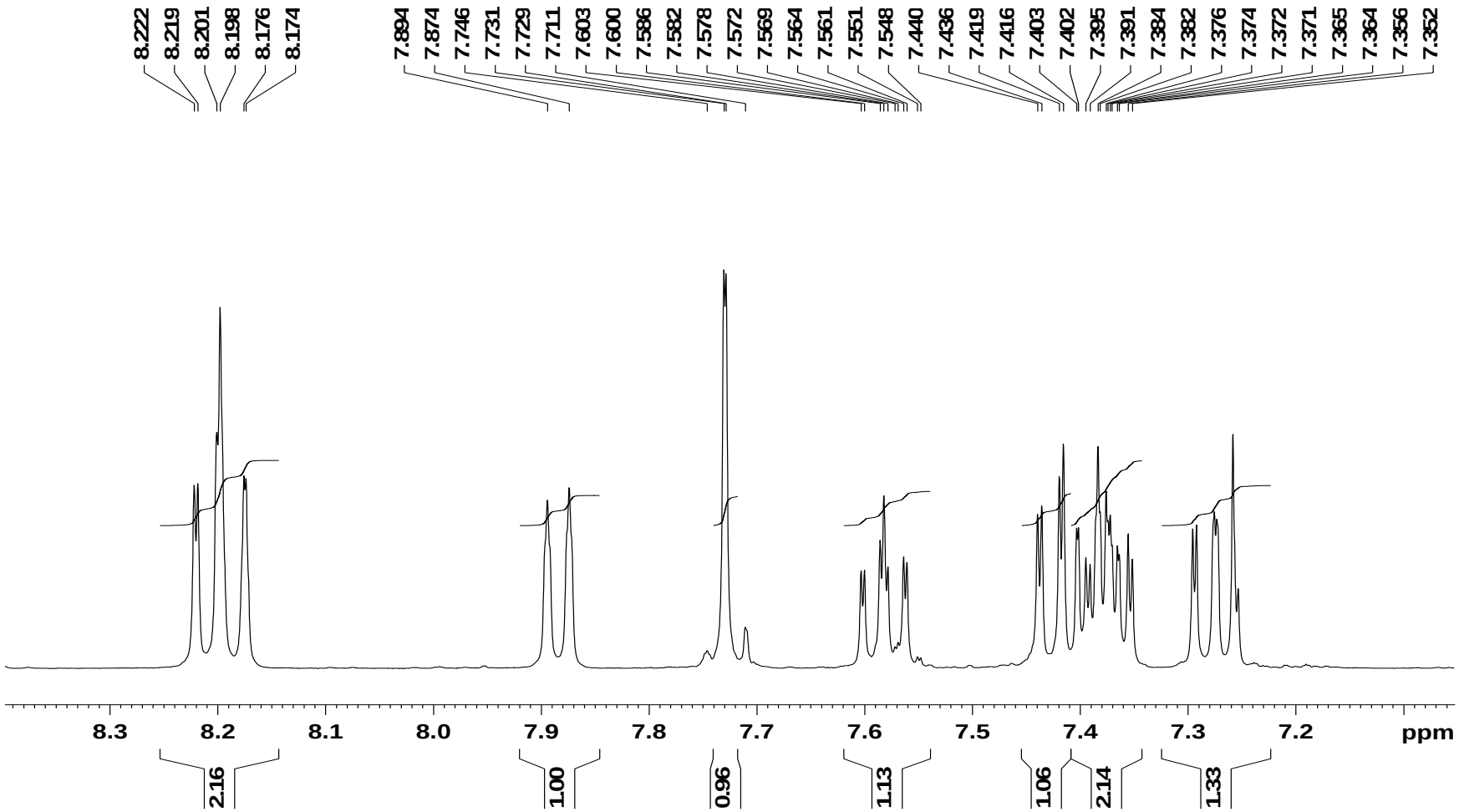


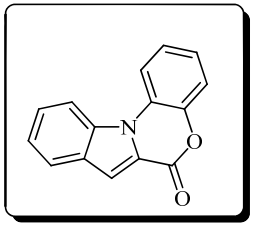
^{1}H-^{13}C HSQC 2-chloroindolo[1,2-*a*]quinoxalin-6(5*H*)-one ($CDCl_3$) **5c**



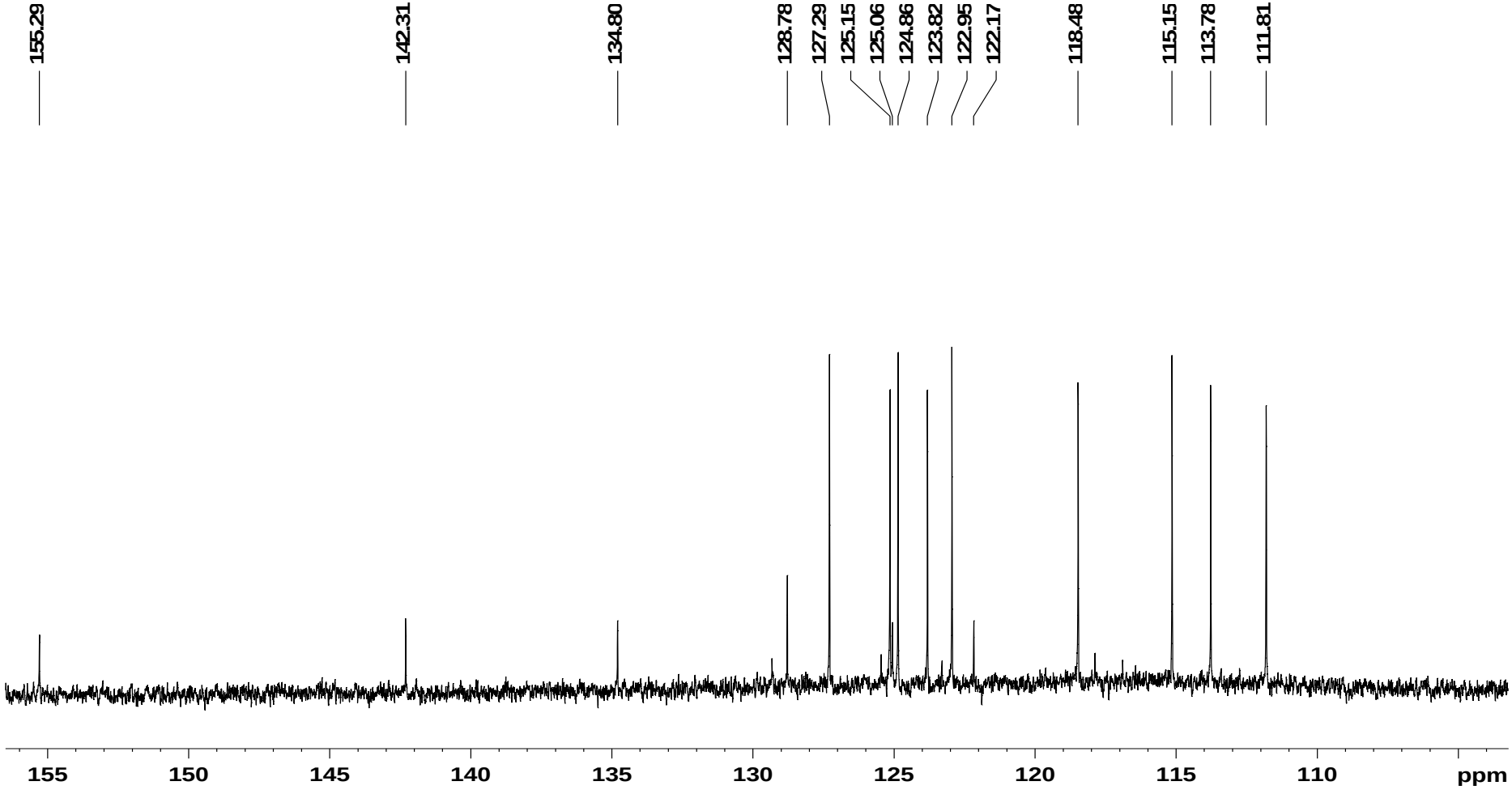


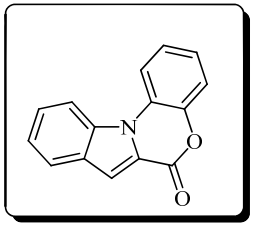
^{1}H NMR 4*H*-benzo[*b*]indolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **5d**



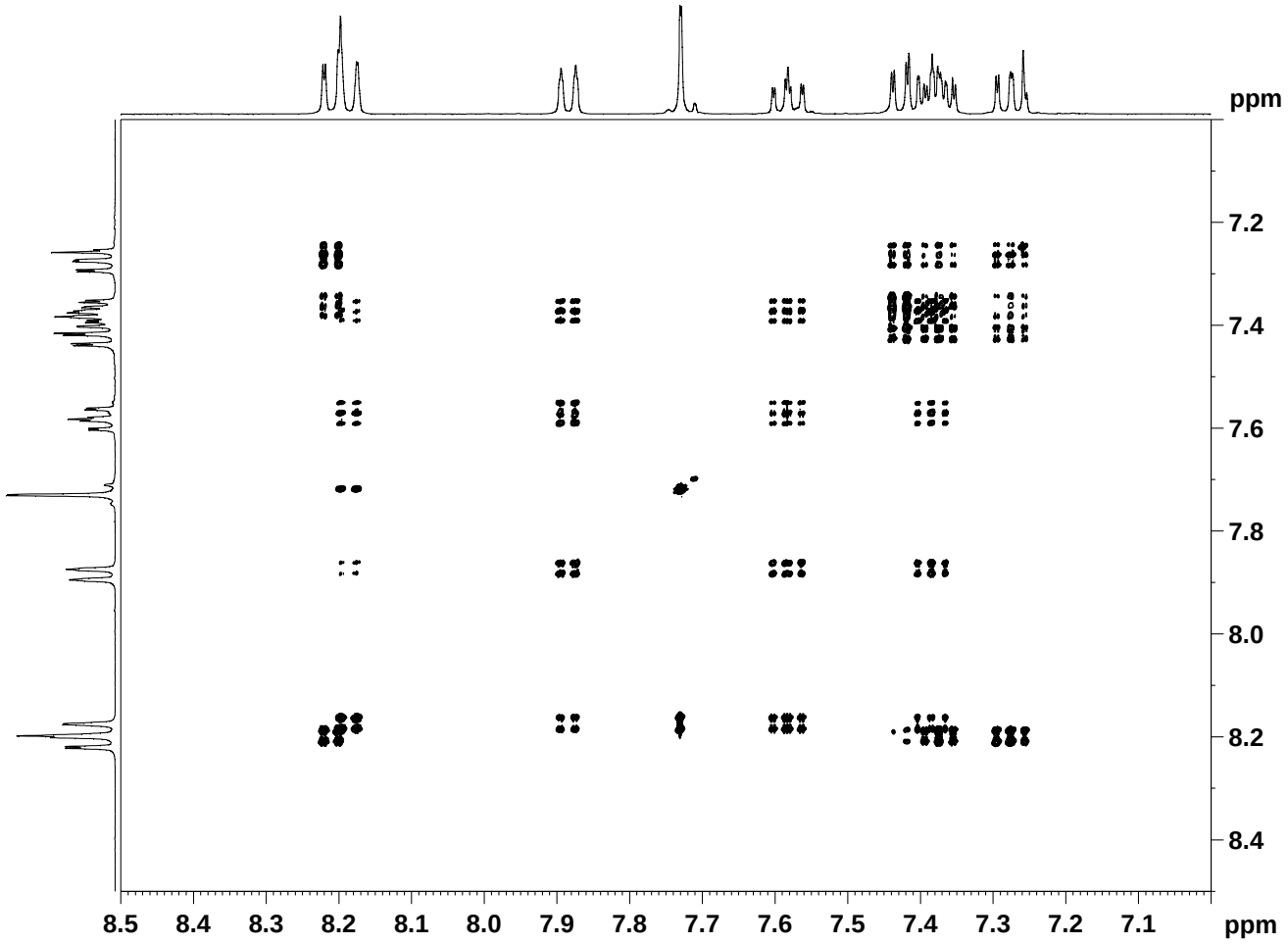


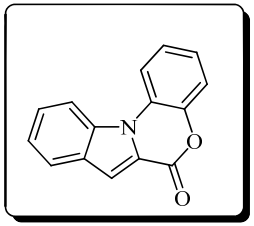
^{13}C NMR 4*H*-benzo[*b*]indolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **5d**



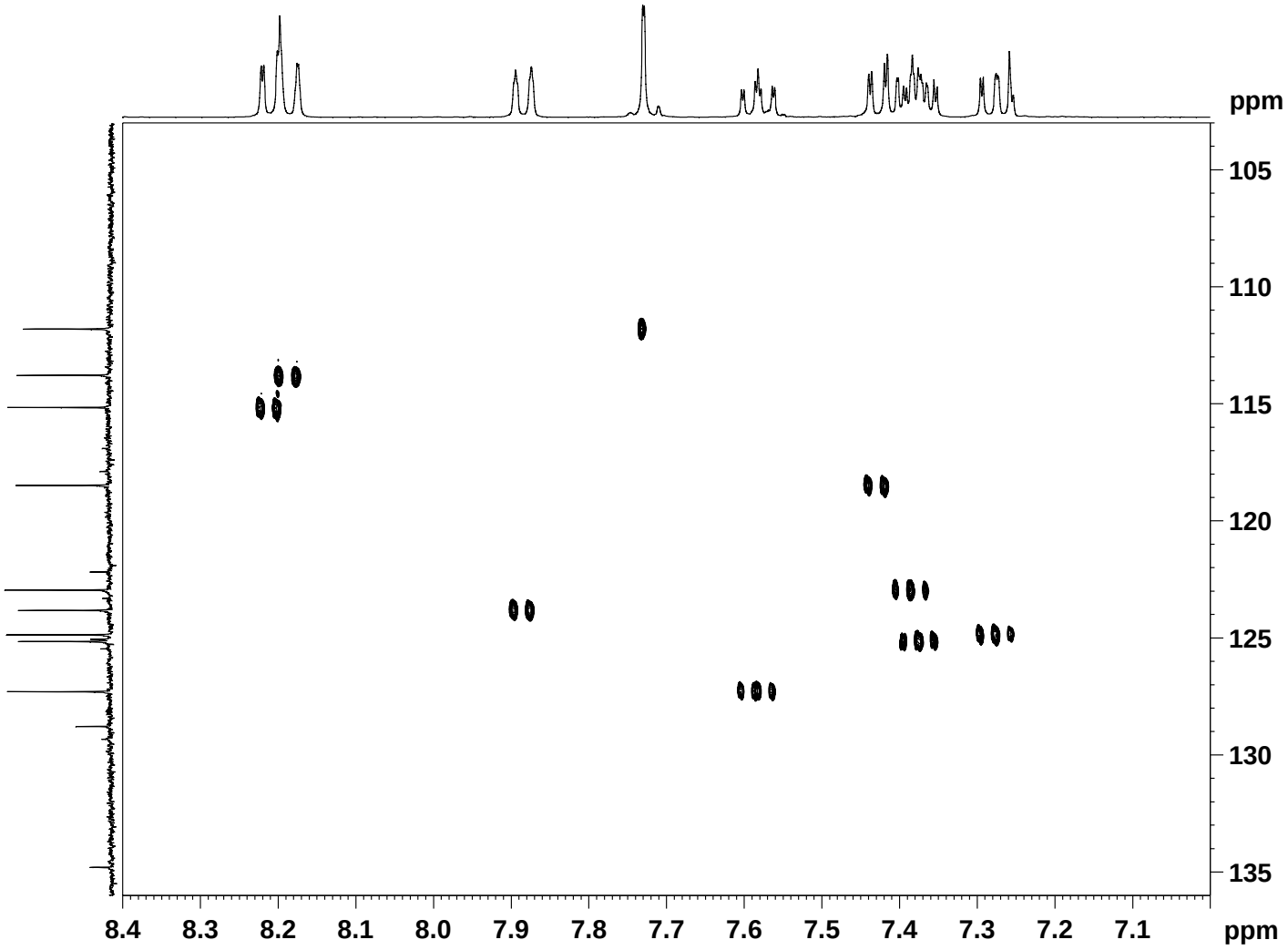


^{1}H-^{1}H COSY 4*H*-benzo[*b*]indolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **5d**





^{1}H-^{13}C HSQC 4*H*-benzo[*b*]indolo[1,2-*d*][1,4]oxazin-4-one ($CDCl_3$) **5d**



pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (3a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (m, 1H), 7.05 (m, 1H), 7.10 (m, 1H), 7.32 (m, 2H), 7.54 (m, 1H), 7.66 (m, 1H), 10.51 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.4, 110.8, 113.2, 118.8, 119.8, 123.0, 124.4, 124.6, 141.8, 150.2, 158.2.**^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H**: 6.38/7.05, 6.38/7.10, 7.30/7.54, 7.30/7.66. **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C** : 6.38/110.8, 7.05/123, 7.10/113.2, 7.32/124.4, 7.32/124.6, 7.54/110.4, 7.66/118.8.

8-methylpyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (3b). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.44 (s, 3H), 6.27 (m, 1H), 6.93 (m, 1H), 7.09 (m, 1H), 7.16 (d, 1H, *J* = 8.1 Hz), 7.49 (s, 1H), 7.53 (d, 1H, *J* = 8.1 Hz), 12.19 (bs, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ: 21.2, 110.0, 110.4, 112.4, 118.1, 118.9, 123.7, 125.5, 134.2, 139.5, 149.7, 157.2. **^{1}H-^{1}H COSY NMR (DMSO-d_6) δ_H-δ_H**: 6.27/6.93, 6.27/7.09, 7.16/7.49. **^{1}H-^{13}C HSQC NMR (DMSO-d_6) δ_H-δ_C**: 2.44/21.2, 6.27/110.4, 6.93/112.4, 7.09/123.7, 7.16/125.5, 7.49/110.0, 7.53/118.

8-chloropyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (3c). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.38 (m, 1H), 7.05 (m, 1H), 7.09 (m, 1H), 7.30 (dd, 1H, *J* = 8.4 Hz, 1.9 Hz), 7.54 (m, 2H), 10.10 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.0, 111.1, 113.6, 119.2, 119.4, 123.3, 125.2, 129.8, 140.6, 150.3, 158.7. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H**: 6.38/7.05, 6.38/7.09, 7.30/7.54. **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 6.39/111.1, 7.05/123.3, 7.09/113.6, 7.30/125.2, 7.53/111.0, 7.53/119.2.

8-cyanopyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (**3d**). **^{1}H NMR (400 MHz, DMSO-d_6)** δ: 6.34 (m, 1H), 7.08 (m, 1H), 7.21 (m, 1H), 7.80 (m, 2H), 8.23 (bs, 1H), 12.45 (bs, 1H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ: 105.8, 110.8, 114.6, 114.7, 117.8, 119.0, 119.5, 125.6, 129.3, 146.0, 148.9, 160.4. **^{1}H-^{1}H COSY NMR (DMSO-d_6) δ_H-δ_H**: 6.34/7.08, 6.34/7.21, 6.34/12.45, 7.08/7.21, 7.08/12.45, 7.21/12.45, 7.80/8.23. **^{1}H-^{13}C HSQC NMR (DMSO-d_6) δ_H-δ_C**: 6.34/110.8, 7.08/114.7, 7.21/125.6, 7.80/119.5, 7.80/129.3, 8.23/114.7.

benzo[*h*]pyrrolo[1,2-*a*]quinoxalin-4(5*H*)-one (3e). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.41 (m, 1H), 7.06 (m, 1H), 7.16 (m, 1H), 7.52 (m, 1H), 7.64 (m, 1H), 7.78 (d, 2H, *J* = 1.3 Hz), 7.97 (d, 1H, *J* = 8.3 Hz), 8.27 (d, 1H, *J* = 8.3 Hz), 9.84 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 110.9, 112.4, 118.0, 120.0, 120.2, 120.3, 122.4, 125.3, 125.4, 126.9, 128.7, 131.4, 138.2, 145.6, 157.5. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H:**

6.41/7.06, 6.41/7.16, 7.52/7.64, 7.52/7.97,7.52/8.27, 7.64/7.97, 7.64/8.27. **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C** : 6.41/110.9, 7.06/122.4, 7.16/112.4, 7.52/125.3, 7.64/126.9, 7.78/125.4, 7.97/128.7, 8.27/120.2.

4*H*-benzo[*b*]pyrrolo[1,2-*d*][1,4]oxazin-4-one (3f). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.68 (dd, 1H, *J* = 4.0 Hz, 2.8 Hz), 7.30 (m, 2H), 7.37 (m, 2H), 7.60 (m, 1H), 7.64 (dd, 1H, *J* = 2.7 Hz, 1.4 Hz). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 114.1, 114.2, 117.5, 117.6, 118.4, 118.5, 122.6, 124.8, 126.4, 143.1, 153.9. . **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H**: 6.68/7.37, 6.68/7.64, 7.30/7.37, 7.30/7.60. **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 6.68/114.1, 7.30/124.8, 7.30/126.4, 7.37/117.6, 7.37/118.5, 7.69/114.2, 7.64/118.5.

indolo[1,2-*a*]quinoxalin-6(5*H*)-one (5a). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (m, 1H), 7.31 (m, 1H), 7.37 (m, 2H), 7.41 (m, 2H), 7.61 (m, 1H), 7.73 (m, 2H), 9.76 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 106.5, 110.6, 111.7, 119.6, 120.9, 122.0, 124.8, 124.9, 124.9, 125.2, 128.1, 137.5, 141.64, 150.6, 157.9. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H**: 7.18/7.31, 7.18/7.73, 7.31/7.41, 7.37/7.61, 7.37/7.73. **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 7.18/120.9, 7.31/124.9, 7.37/124.9, 7.37/125.2, 7.41/106.5, 7.41/111.7, 7.61/110.6, 7.73/119.6, 7.73/122.0.

2-methylindolo[1,2-*a*]quinoxalin-6(5*H*)-one (5b). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.52 (s, 3H), 7.18 (m, 2H), 7.29 (m, 1H), 7.36 (d, 1H, *J* = 1.1 Hz), 7.40 (m, 2H), 7.59 (d, 1H, *J* = 8.2 Hz), 7.73 (d, 1H, *J* = 8.2 Hz), 9.69 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 22.0, 106.2, 110.9, 111.8, 119.1, 121.0, 122.1, 124.9, 125.1, 126.2, 128.3, 135.9, 137.6, 139.6, 151.0, 157.5. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H**: 7.18/7.59, 7.18/7.73, 7.29/7.40, 7.36/9.69 **^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 2.52/22.0, 7.18/121.0, 7.18/126.2, 7.29/124.9, 7.36/106.2,7.40/110.9, 7.40/111.8, 7.59/119.1, 7.73/122.1.

2-chloroindolo[1,2-*a*]quinoxalin-6(5*H*)-one (5c). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19 (m, 1H), 7.33 (m, 2H), 7.40 (m, 2H), 7.61 (m, 2H), 7.73 (dd, 1H, *J* = 8.0 Hz, 0.7 Hz), 9.53 (bs, 1H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ: 107.0, 111.3, 111.7, 120.0, 121.1, 122.1, 124.2, 125.2, 125.6, 128.1, 130.8, 137.6, 140.5, 150.8, 158.4. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H** : 7.19/7.33, 7.18/7.73, 7.33/7.40, 7.33/7.61.**^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 7.19/121.1, 7.33/125.2, 7,33/125.6, 7.40/107.0, 7.40/111.7, 7.61/111.3, 7.61/120.0, 7.73/122.1.

4*H*-benzo[*b*]indolo[1,2-*d*][1,4]oxazin-4-one (5d). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (m, 1H), 7.38 (m, 2H), 7.43 (dd, 1H, *J*= 8.0 Hz, 1.5 Hz), 7.58 (m, 1H), 7.73 (d, 1H, *J*= 0.8 Hz), 7.88 (m, 1H), 8.19 (m, 2H^{13} **C NMR (100 MHz, $CDCl_3$)** δ: 111.8, 113.8, 115.2, 118.5, 122.2, 122.9, 123.8, 124.9, 125.1, 125.2, 127.3, 128.8, 134.8, 142.3, 155.3. **^{1}H-^{1}H COSY NMR ($CDCl_3$) δ_H-δ_H** : 7.27/7.38, 7.27/7.43, 7.27/8.20, 7.38/7.43, 7.3877.58, 7.38/7.88, 7.38/8.20, 7.43/8.20, 7.58/7.88, 7.58/8.20, 7.73/8.20.**^{1}H-^{13}C HSQC NMR ($CDCl_3$) δ_H-δ_C**: 7.27/124.9, 7.38/125.2, 7.38/122.9, 7.43/118.5, 7.58/127.3, 7.73/111.8, 7.88/123.8, 8.20/113.8, 8.20/115.2.

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1 Beugelmans, R; Chbani, M. *Bull. Soc. Chim. Fr*. **1995**, *132*, 290-305.