SUPPORTING INFORMATION

FOR

Palladium Nanoparticle Catalyzed Synthesis of Indoles *via* intramolecular Heck Cyclisation

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S1. *General Information*

All the starting materials were purchased commercially and were used without further purification. All the Michael adducts were synthesized in 100 ml round bottom flasks. All reactions related to the synthesis of indoles were performed inside round bottom flasks (50 mL, Borosil^{TM}) and Sealed Tubes (VENSIL™) under ambient conditions. TLC plates (Silica gel 60-F254 coated on aluminium plates purchased from Merck) were visualized by either UV light or inside an iodine chamber. ^{1}H and ^{13}C NMR experiments were performed using JEOL ECS-400MHz and Bruker Avance III 500 MHz spectrometers. The chemical shifts were quoted in reference to tetramethyl silane (for ^{1}H) and $CDCl_3$ (for ^{13}C NMR) as internal standards.

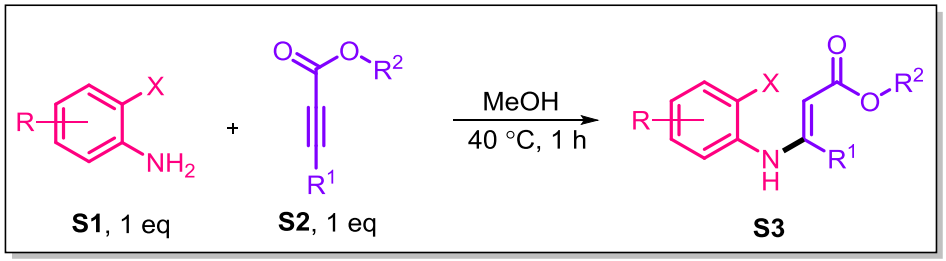
S2. *Single Crystal X-Ray Diffraction Studies of 2a*

Single crystal of ***2a*** suitable for diffraction measurement was used directly from the reaction mixtures. The diffraction data for the compounds were collected on a Bruker APEX-II CCD Diffractometer using MoKα radiation (λ=0.71073 Å) using φ and ω scans of narrow (0.5°) frames at 100 K. The structure was solved by direct methods using SHELXL-97 as implemented in the WinGX program system [1]. Anisotropic refinement was executed on all non-hydrogen atoms. The aliphatic and aromatic hydrogen atoms were placed on calculated positions but were allowed to ride on their parent atoms during subsequent cycles of refinements.

S3. *Experimental Section*

l. General procedure for the synthesis of 2-((2-iodophenyl)amino)maleate (S1) derivatives *via* Michael addition.

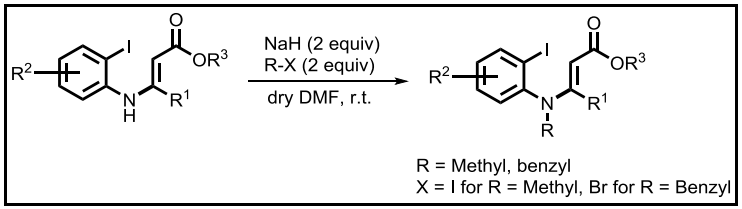
The 2-((2-halophenyl)amino)maleate (S3) derivatives were synthesized as per the following literature procedure.[1]



Scheme SI-1.

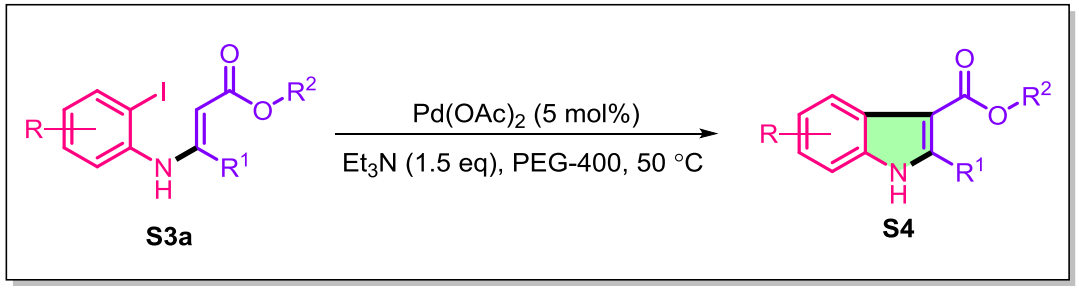
A thoroughly cleaned and oven dried round bottom flask (RB, 100 ml) was charged with 1 equivalent (5 mmol) of 2-haloanilines (**S1**) and 1 equivalent (5 mmol) of the propiolate esters (**S2**) in 20 ml methanol at room temperature under ambient aerial conditions. The reaction was allowed to stir at 40 °C for 1 hour (monitored using TLC). Upon completion (as indicated by TLC), methanol was evaporated under vacuum followed by extraction with ethyl acetate (3 x 20 ml). The combined organic layers were washed with brine, dried using anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified using silica gel column chromatograpy (1% - 3% EtOAc-Hexanes) as the eluent to afford the pure products.

2. General procedure for the alkylation and *N*-benzylation of 2-((2-iodophenyl)amino)maleate derivatives: 2-Iodoaniline and propiolate ester adducts were *N*-protected as per the following procedure (*Scheme SI-2*).



In a clean 100 mL round bottom flask 2 mmols of the Michael adduct, 2 equivalents of a non-nucleophilic base (NaH) and 2 equivalents of the alkyl/benzyl halide were taken in the presence of 15 mL dry DMF as solvent. The reaction mixture was stirred at room temperature and the reaction was monitored using thin layer chromatography. After completion, the reaction was poured into 250 mL ice water and was extracted with ethyl acetate several times. The combined organic layers were then washed with brine and dried with sodium sulfate. Subsequent column chromatography yielded the products.

2. General Procedure for the cyclisation of 2-((2-iodophenyl)amino)maleate (S3a) derivatives.

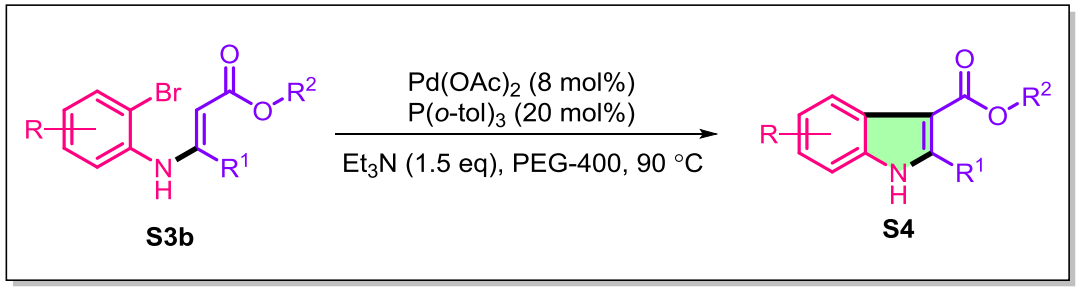


Scheme SI-2.

A thoroughly cleaned and round bottom flask was charged with 1 equivalent (0.1 mmol) of 2-((2-iodophenyl)amino)maleate, 5 mol% of Palladium acetate catalyst and 1.5 equivalents of triethyl amine (anhydrous) in PEG-400 solvent (1.5 ml). The reaction mixture was allowed to stir at 50 °C for 3 hours (monitored *via* TLC). Upon completion, the reaction was quenched with a saturated solution of ammonium chloride,

filtered through a plug of celite and was extracted with Ethyl acetate (3 x 20 ml). The combined organic layers were washed with brine and dried using anhydrous sodium sulphate and concentrated in vacuum to get the crude product. The crude mixture was purified using silica gel column chromatography (60-120 silica gel) in 10% - 20% EtOAc–Hexanes as the eluent to afford the pure indole products (**S4**).

3. General procedure for the cyclisation of 2-((2-bromophenyl)amino)maleate derivatives (S3b).

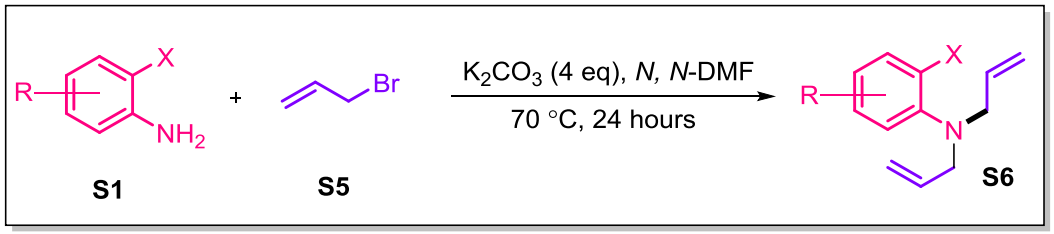


Scheme S1-3.

A thoroughly cleaned and dried sealed tube (VENSIL™) was charged with 1 equivalent (0.1 mmol) of 2-((2-bromophenyl)amino)maleates, 8 mol% of Palladium acetate catalyst, 20 mol% of tri-*o*-tolyl phosphine ligand and 1.5 equivalents of triethyl amine base in 1.5 ml PEG-400 solvent. The reaction mixture was allowed to stir at 80 °C for 3.5 hours (monitored *via* TLC). Upon completion, the reaction was quenched with saturated ammonium chloride solution, filtered through a plug of celite and extracted with Ethyl acetate (3 x 20 ml). The combined organic layers were washed with brine and dried with anhydrous sodium sulphate. The dried organic layers were then concentrated in vacuum to obtain the crude product. Purification of the crude product using silica gel column chromatography (60-120 silica gel) in 10% - 20% EtOAc – Hexanes as the eluent affords the pure indole products (**S4**).

4. General procedure for the synthesis of *N, N*-diallyl-2-haloanilines (S6).

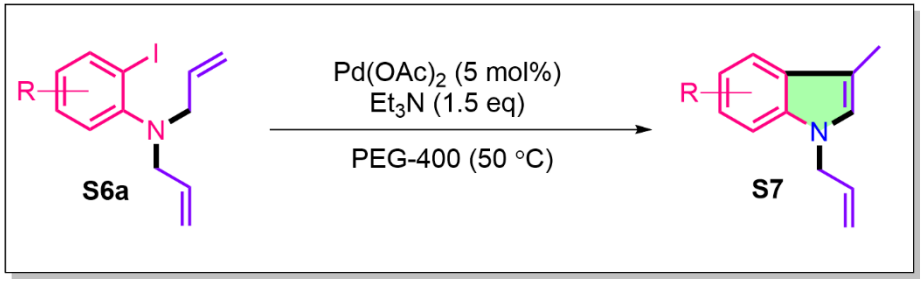
N, N-diallyl-2-haloanilines were synthesized as per the literature procedure.[2]



Scheme SI-4.

In a clean and dried round bottom flask, were taken 1 equivalent (5 mmol) of 2-haloanilines, 1.1 equivalents of allyl bromide, 4 equivalents of K_2CO_3 in 10 ml N, N-DMF solvent. The reaction mixture was allowed to stir for 5 hours at 50 °C (monitored using TLC). After completion of the reaction (as indicated by TLC), the reaction mixture was poured into 100 ml of ice water and was extracted with Ethyl acetate (5 x 20 ml). The combined organic layers were washed with brine and dried using anhydrous sodium sulphate. The dried organic layers were then concentrated in vacuum to obtain the crude product. The crude product was purified using silica gel column chromatography (100-200 silica gel) in hexanes to obtain the product **S6.**

5. General procedure for the cyclisation of *N, N*-diallyl-2-iodoanilines.



Scheme SI-5.

In a clean and dried sealed tube (VENSIL™), were added 1 equivalent (0.1 mmol) of *N, N*-diallyl-2-iodoanilines, 5 mol% of Palladium acetate, 1.5 equivalents of triethylamine and PEG-400 solvent. The reaction was allowed to stir at 50 ^{o}C for 3.5 hours (monitored *via* TLC). Upon completion, the reaction was quenched with water and was extracted with ethyl acetate (3 x 20 ml). The combined organic layers were washed with brine and dried using anhydrous sodium sulphate. Concentration of the dried organic layers under vacuum followed by column chromatography (100-200 silica gel) in hexane as eluent affords the desired products (**S7**).

Hydrogen Bonding Pattern of the Compound 2a

In ***2a,*** intermolecular hydrogen bonding is operative between the NH hydrogen atom (H11) and carbonyl oxygen atom of nearest neighbouring unit (O3#1). This eventually leads to formation of a one-dimensional network through establishment of a 10 membered ring (Figure 2).

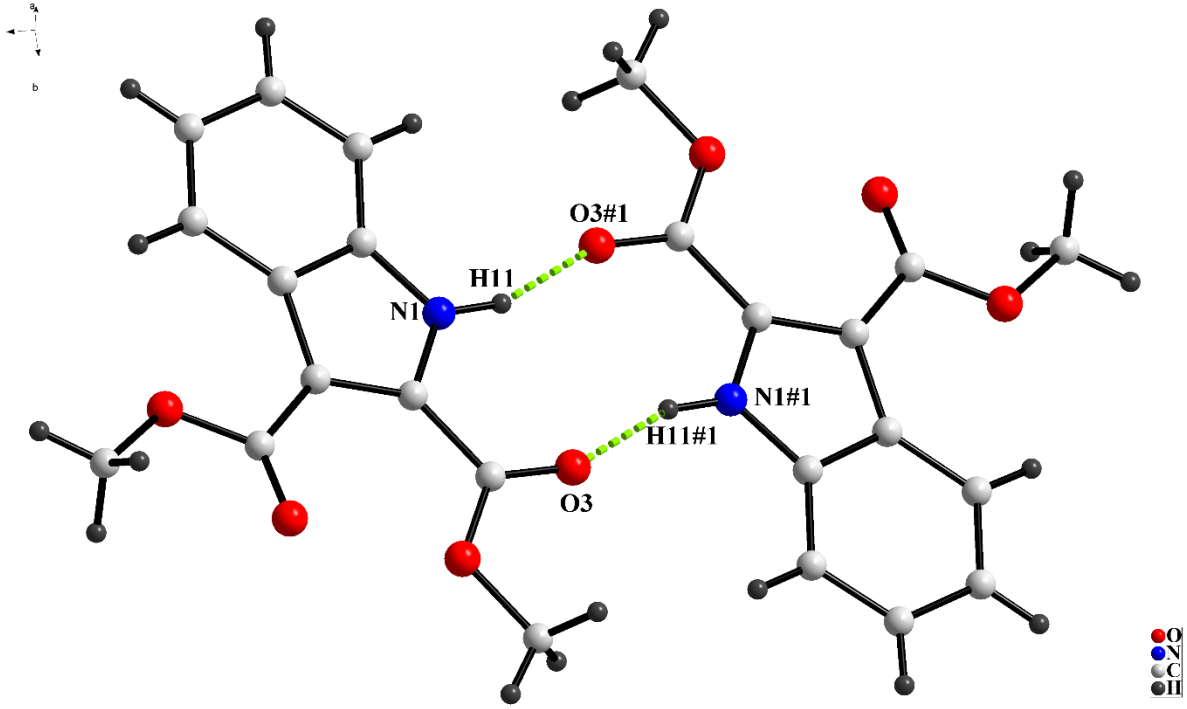


Figure **2**: Representative view of presence of intermolecular H-bonding in ***2a*.** The green dashed lines represent intermolecular H-bonding.

Table S1. Crystallographic data for ***2a.***

Empirical formula	$C_{12}H_{11}N_1O_4$
Formula weight	233.22
Temperature/K	100 (2)
Wavelength	0.71073 Å
CCDC	2299474
Crystal system	Trigonal
Space group	$R\bar{3}$
a/Å	33.45(2)
b/Å	33.45(2)
c/Å	5.541(4)
α/°	90
β/°	90
γ/°	120
Volume [$Å^3$]	5369(7)
Z	18
ρ_{calc} [Mg/m^3]	1.298
μ [mm^{-1}]	0.099
F(000)	504
Crystal size [mm^3]	0.28 x 0.13 x 0.10
Theta range for data collection	3.655 to 25.993°
Index ranges	-41<=h<=41, -41<=k<=41, -6<=l<=6
Reflections collected	51845
Independent reflections	2342 [R(int) = 0.2469]
Completeness to theta = 25.242°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2342 /0/159
Goodness-of-fit on F^2	1.071

Final R indices [I>2sigma(I)]	R1 = 0.0781, wR2 = 0.2172
R indices (all data)	R1 = 0.1260, wR2 = 0.2473

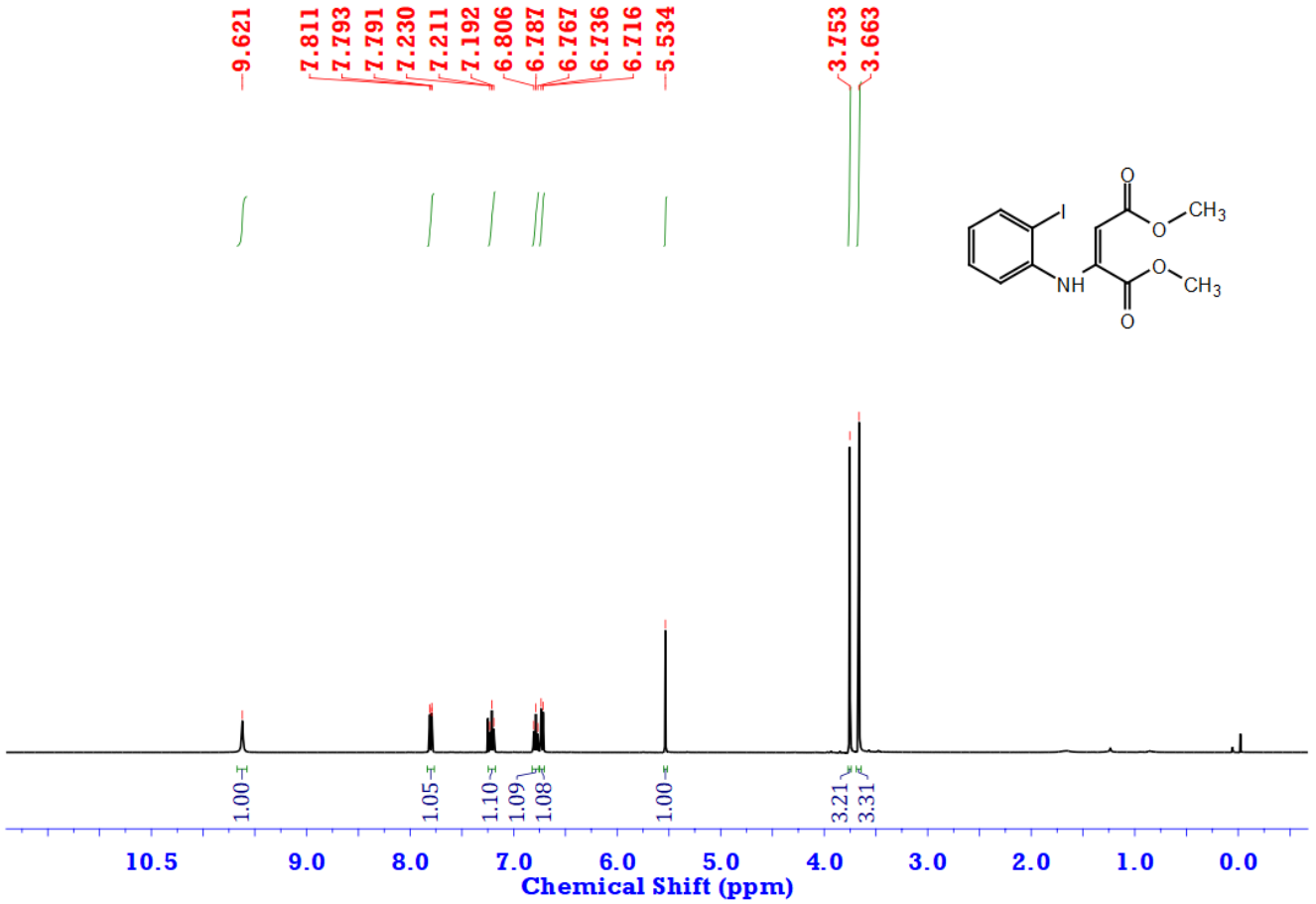
Table S2. Selected bond lengths [Å] and angles [°] for ***2a.***

Bond Length [Å]			
O(1)-C(9)	1.182(5)	C(1)-C(6)	1.403(5)
O(2)-C(9)	1.350(4)	C(2)-C(3)	1.403(5)
O(2)-C(11)	1.443(5)	C(3)-C(4)	1.376(5)
O(3)-C(12)	1.212(4)	C(4)-C(5)	1.418(5)
O(4)-C(12)	1.324(4)	C(5)-C(6)	1.404(5)
O(4)-C(10)	1.440(5)	C(5)-C(7)	1.445(5)
N(1)-C(8)	1.364(5)	C(7)-C(8)	1.401(5)
N(1)-C(6)	1.372(4)	C(7)-C(9)	1.470(5)
C(1)-C(2)	1.372(5)	C(8)-C(12)	1.474(5)
Bond angles [°]			
C(9)-O(2)-C(11)	116.2(3)	O(1)-C(9)-C(7)	128.3(4)
C(12)-O(4)-C(10)	115.8(3)	O(1)-C(9)-O(2)	120.9(4)
C(8)-N(1)-C(6)	109.9(3)	O(3)-C(12)-C(8)	121.9(3)
C(2)-C(1)-C(6)	116.6(4)	O(3)-C(12)-O(4)	123.6(3)
C(1)-C(2)-C(3)	121.3(4)	O(4)-C(12)-C(8)	114.5(3)

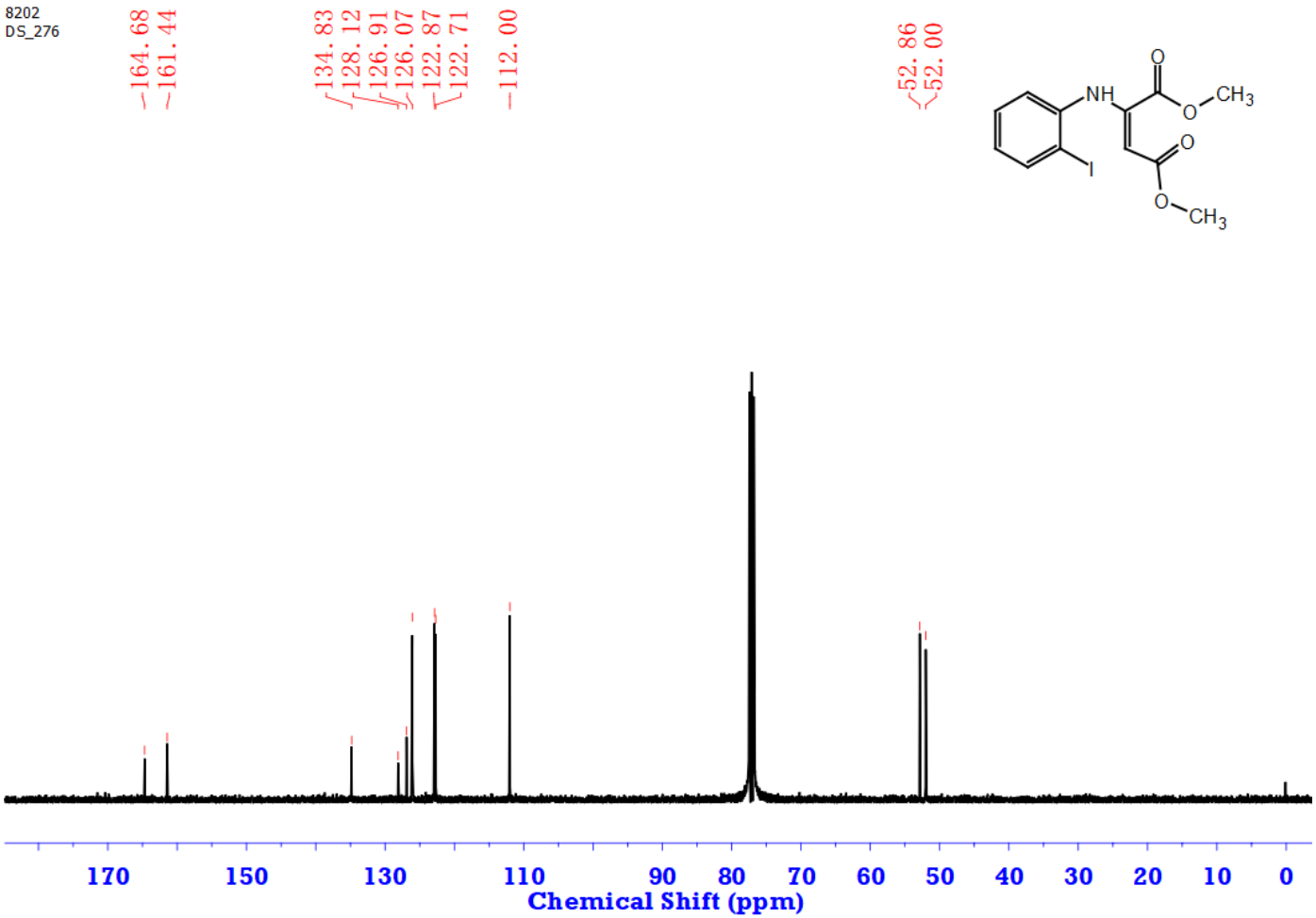
C(4)-C(3)-C(2)	122.2(3)	N(1)-C(8)-C(7)	109.2(3)

NMR Spectra of the Compounds

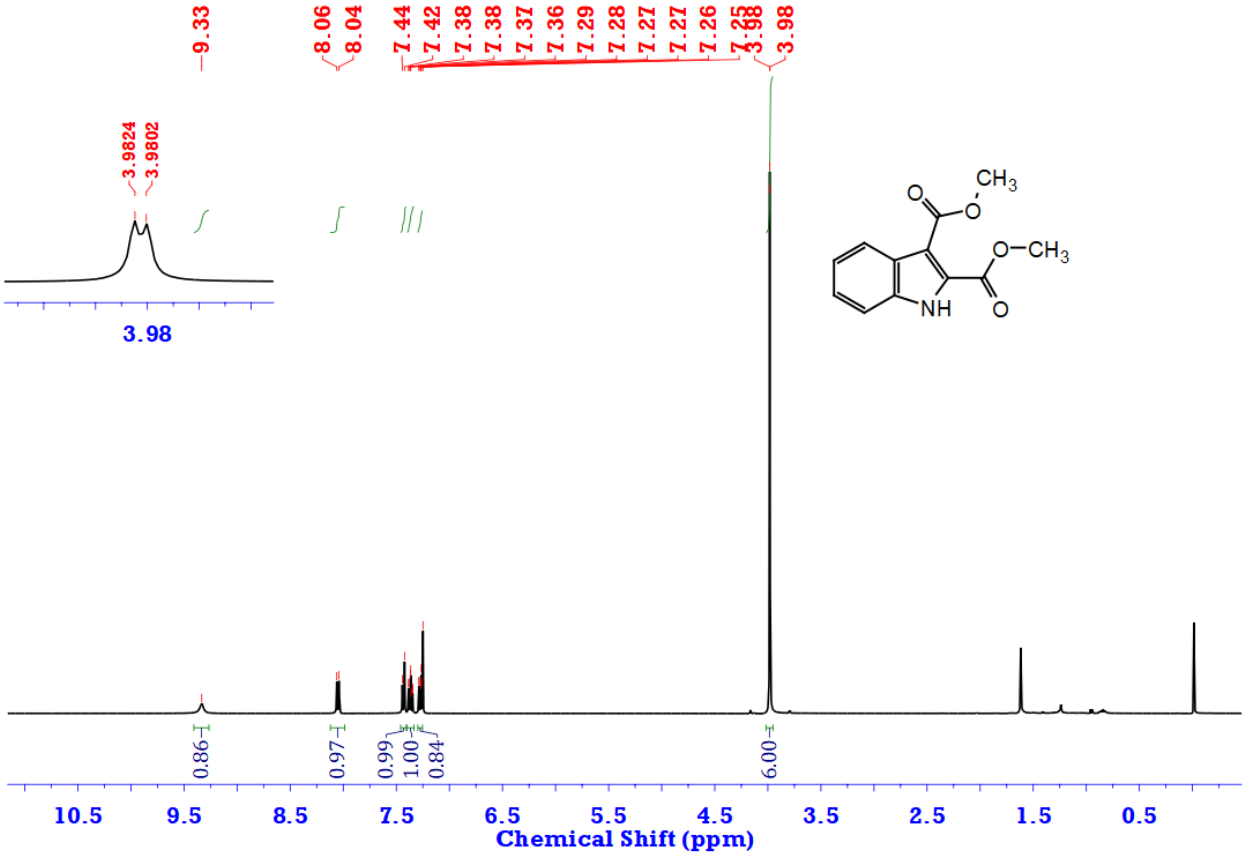
Sp(1). ^{1}H NMR Spectrum of *1a* (dimethyl 2-((2-iodophenyl)amino)maleate) (Yellow oily liquid) NMR (400 MHz, $CDCl_3$) δ (ppm) 9.62 , 7.80 (d, *J* = 8 Hz), 7.21 (t, *J* = 7.7 Hz), 6.79 (t, *J* = 7.7 Hz), 6.73 (d, *J* = 8.0 Hz), 3.75 , 3.66 . ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.4, 134.8, 128.1, 126.9, 126.0, 122.8. 122.7, 112.0, 52.8, 52.



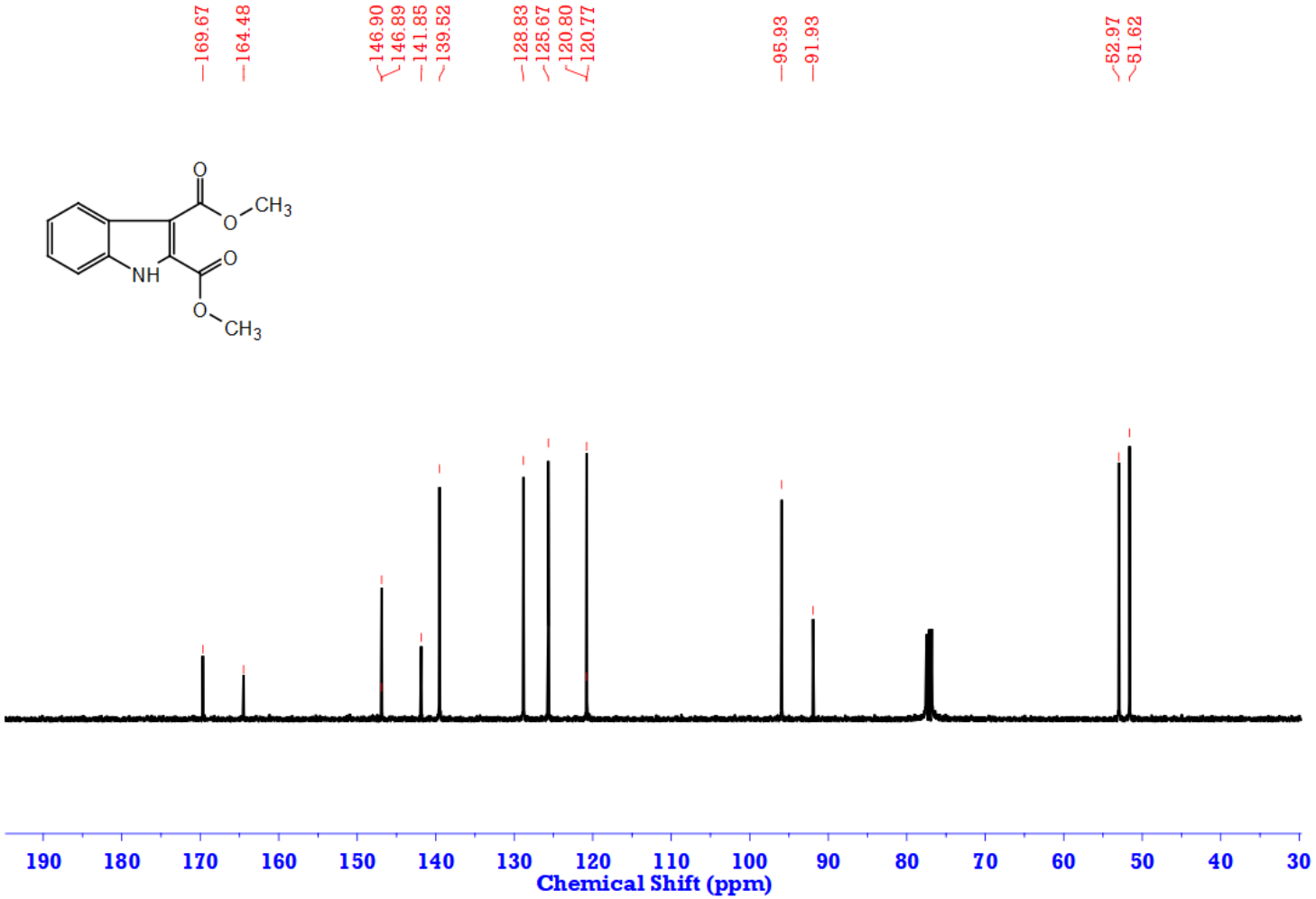
Sp(2). ^{13}C NMR Spectrum of *1a* (dimethyl 2-((2-iodophenyl)amino)maleate).



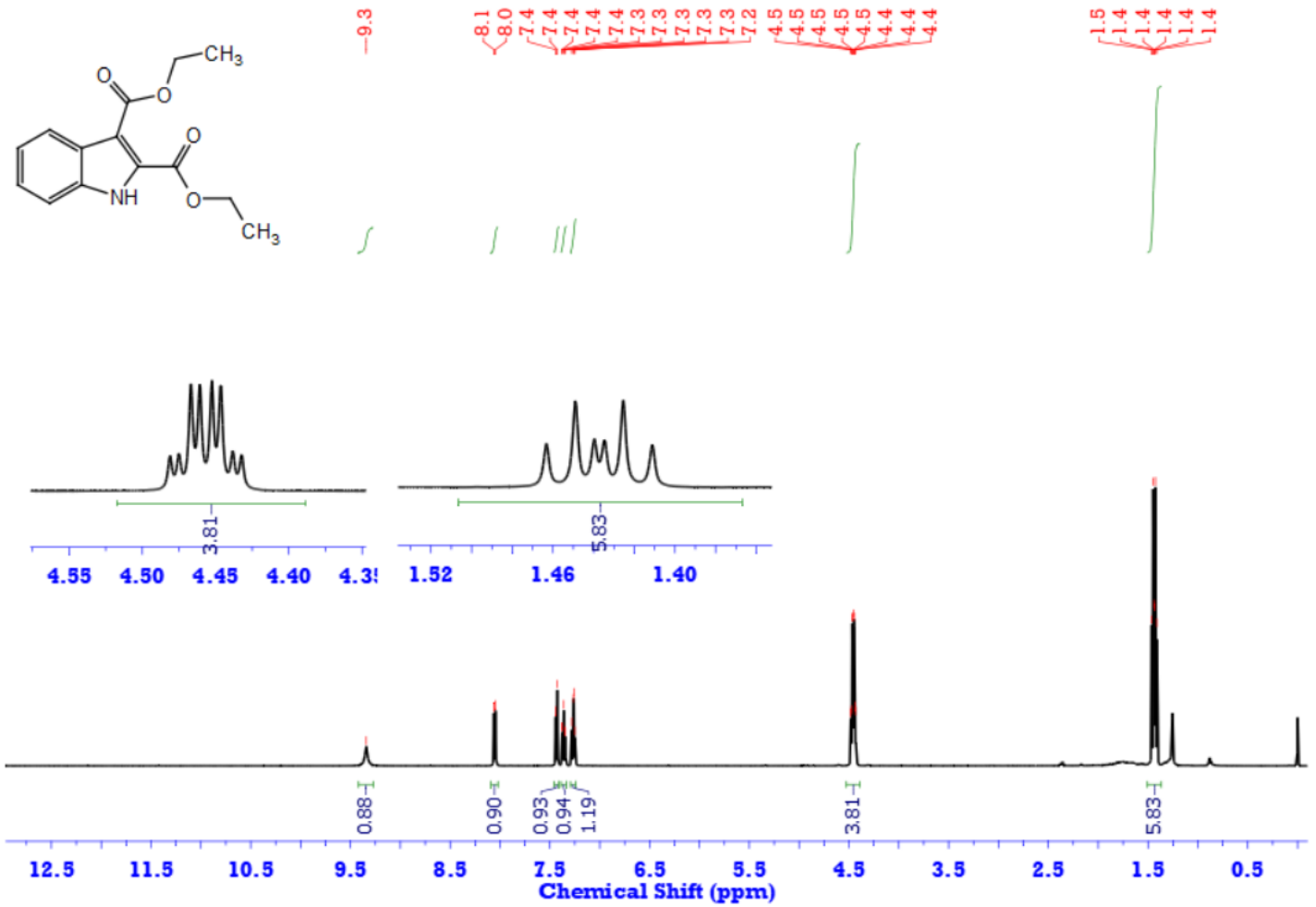
Sp(3). ^{1}H NMR Spectrum of 2a (dimethyl 1H-indole-2,3-dicarboxylate) (White crystalline solid, m.p. 113-114 ^{o}C) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.33 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.39 - 7.34 (m, 1 H), 7.30 – 7.26 (m, 1H), 3.98 (s, 3H), 3.98 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 169.6, 164.4, 146.9, 146.9, 146.8, 141.8, 139.5, 128.8, 125.6, 120.8, 120.7, 95.9, 91.9, 52.9.[3]



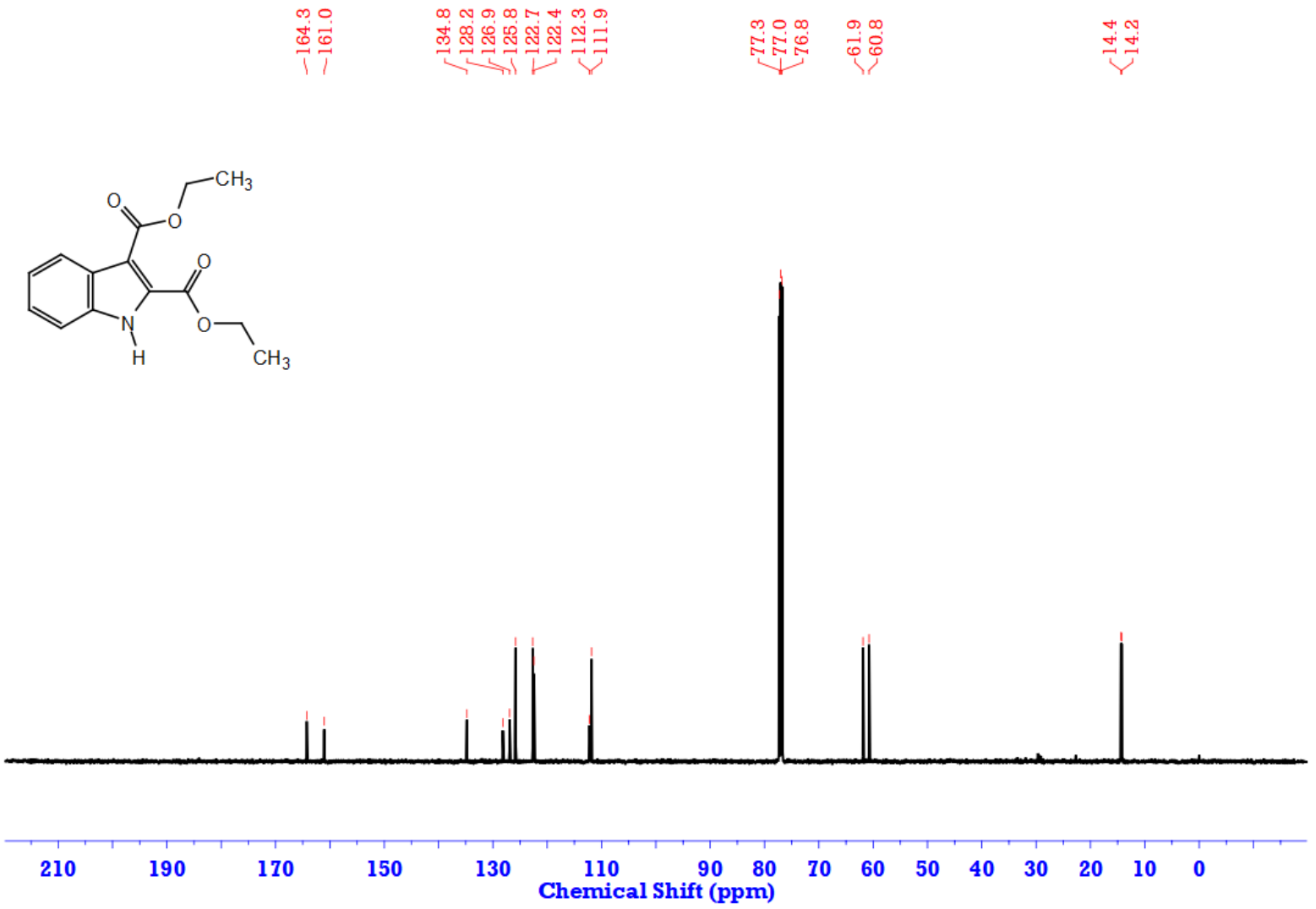
Sp(4). ^{13}C NMR Spectrum of 2a (dimethyl 1H-indole-2,3-dicarboxylate).



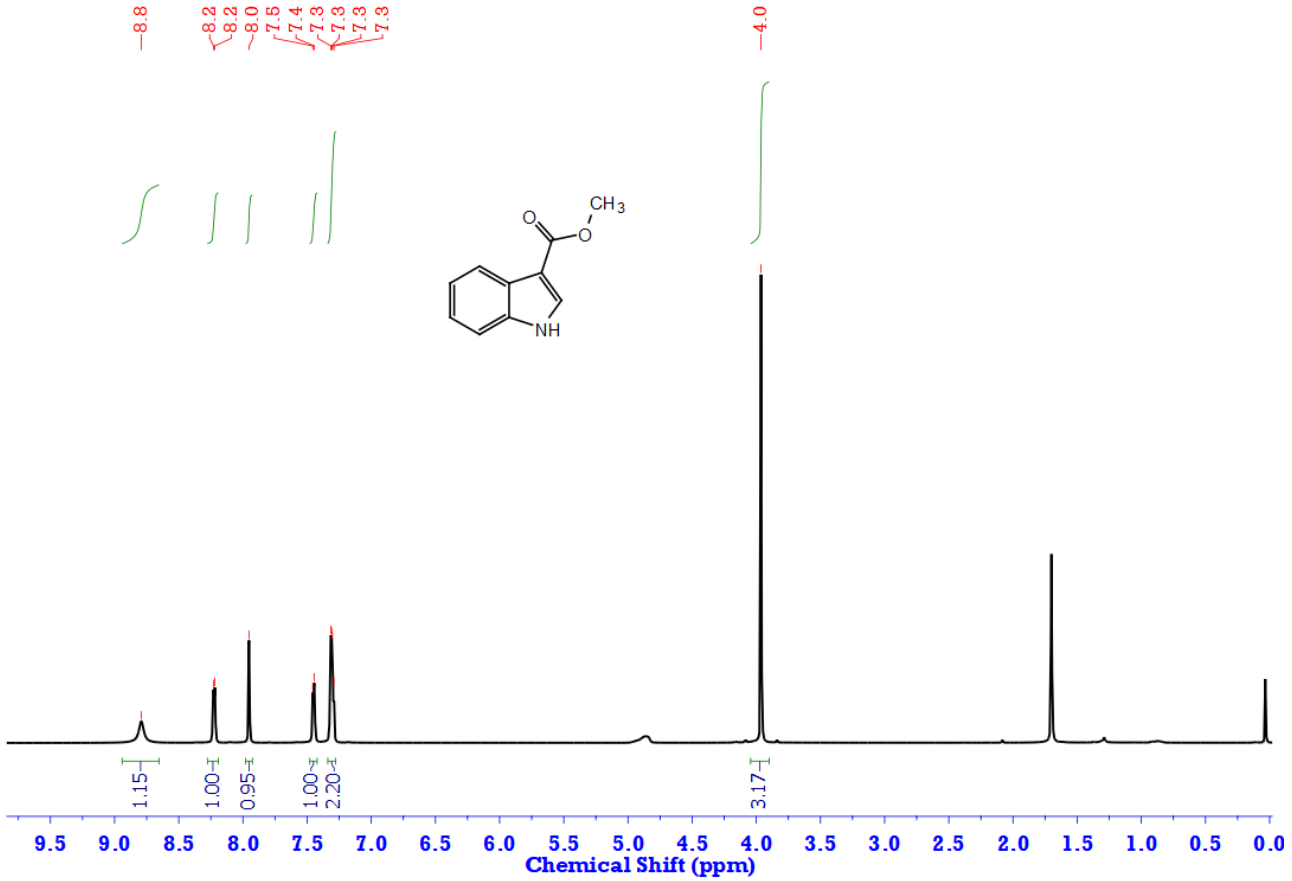
Sp(5). ^{1}H NMR Spectrum of *2b* (diethyl 1H-indole-2,3-dicarboxylate), (Colourless Oil**):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.36 (s, 1H), 7.29 – 7.24 (m, 1H), 4.46 (m, 4H), 1.44 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) 164.3, 161.0, 134.8, 128.2, 126.9, 125.8, 122.7, 122.4, 112.3, 111.9, 61.9, 60.8, 14.4, 14.2.[3]



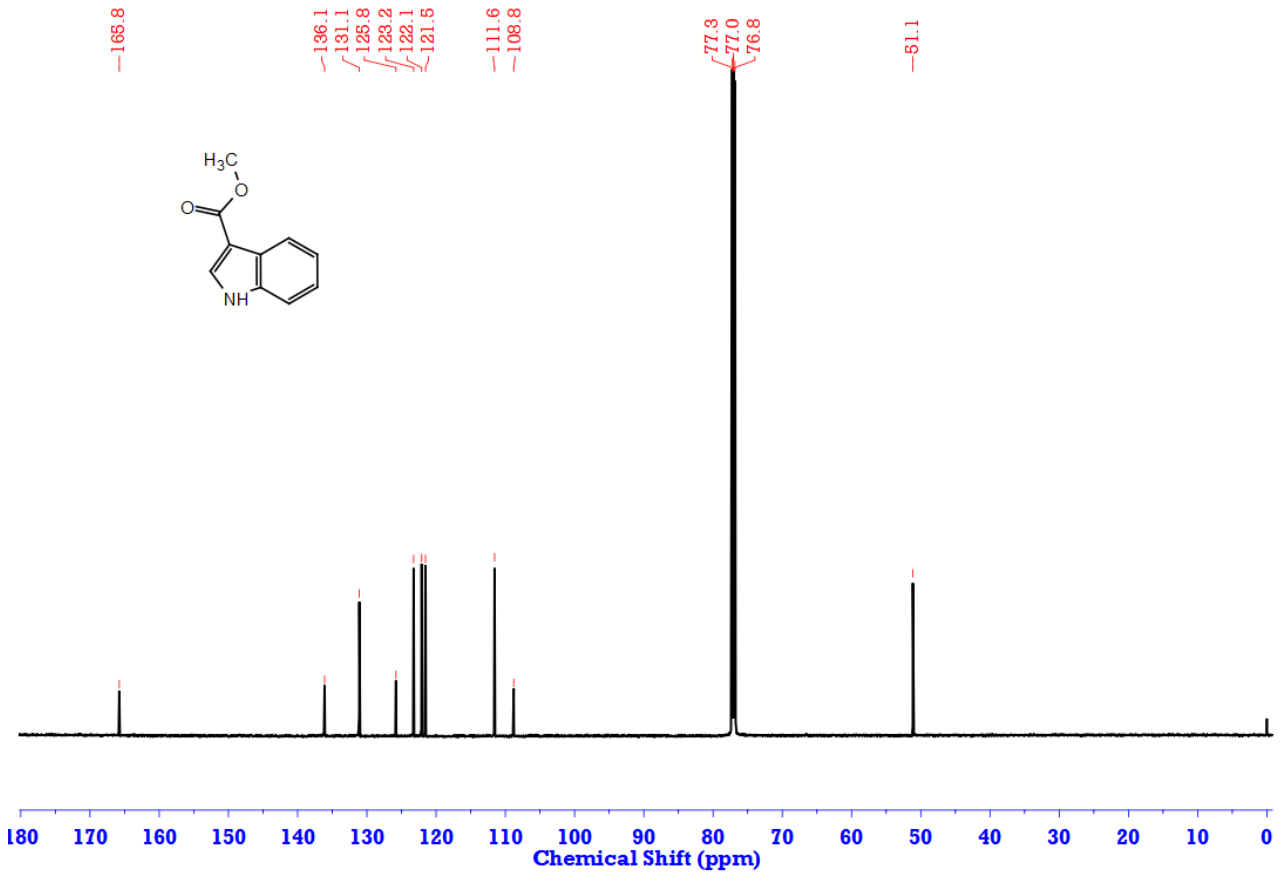
Sp(6). ^{13}C NMR Spectrum of *2b* (diethyl 1H-indole-2,3-dicarboxylate).



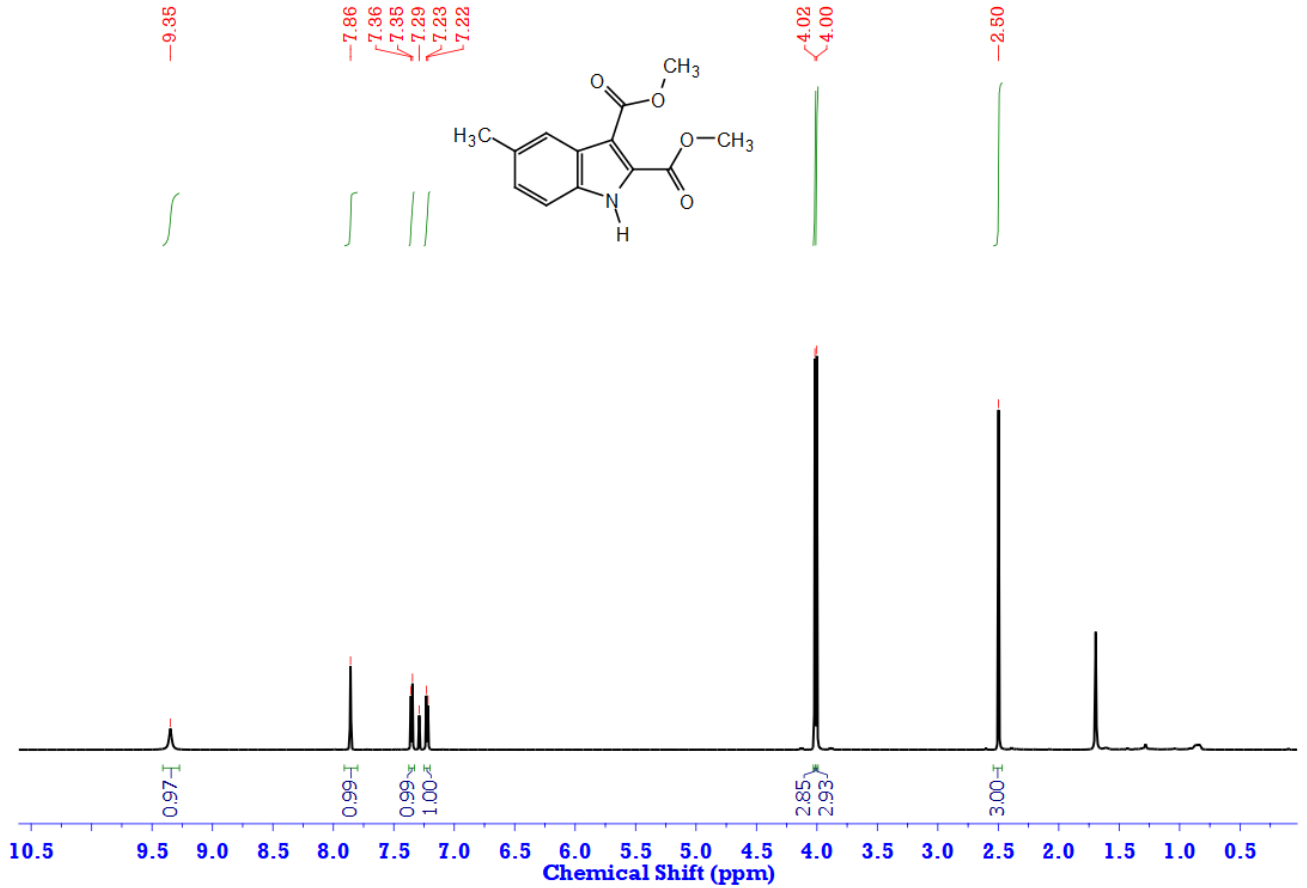
Sp(7). ^{1}H NMR Spectrum of *2c* (methyl 1H-indole-3-carboxylate) (White crystalline solid, m.p. 123-124 ^{o}C) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.22 (d, *J* = 6.0 Hz, 1H), 7.95 (s, 1H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 3.96 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ 165.8, 136.1, 131.1, 125.8, 123.2, 122.1, 121.6, 111.6, 108.8, 81.1.[4]



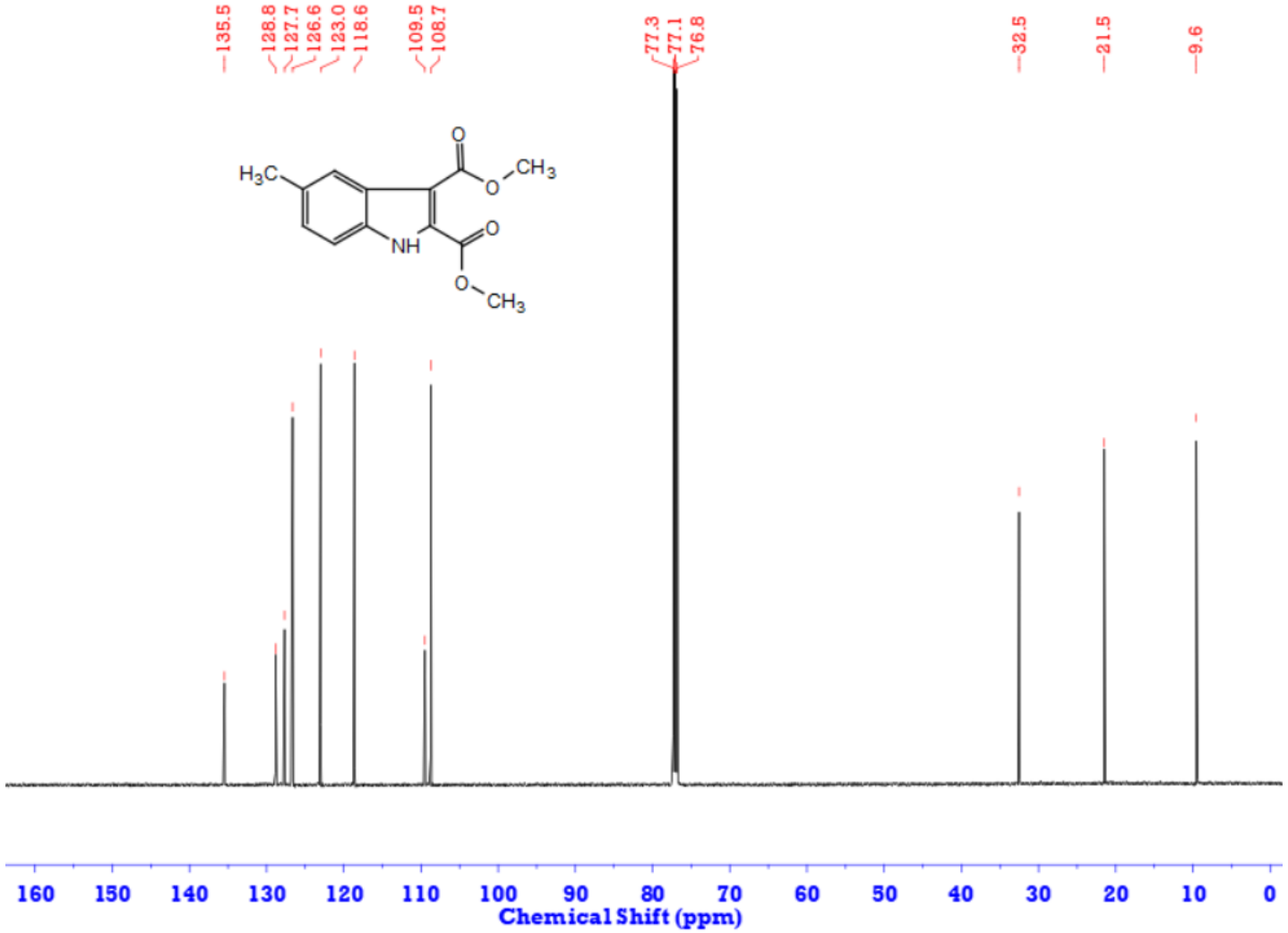
Sp(8). ^{13}C NMR Spectrum of *2c* (methyl 1H-indole-3-carboxylate).



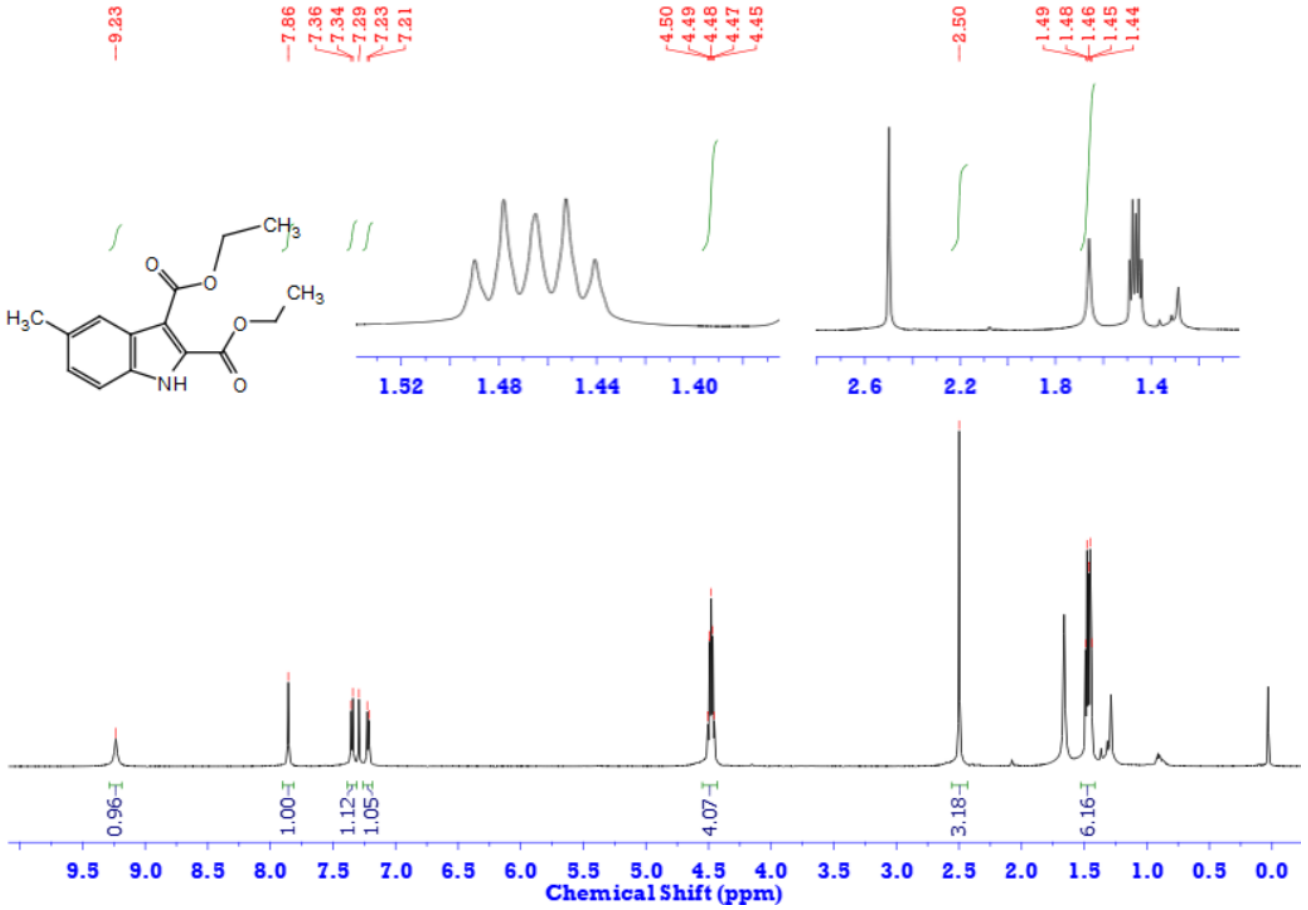
Sp(9). ^{1}H NMR Spectrum of dimethyl *2d* (5-methyl-1H-indole-2,3-dicarboxylate) (White solid, m.p. 128 ^{o}C) ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.86 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.8, 161.4, 133.2, 132.2, 127.9, 127.9, 127.1, 121.9, 111.6, 111.4, 52.7, 51.8, 21.6.[5]



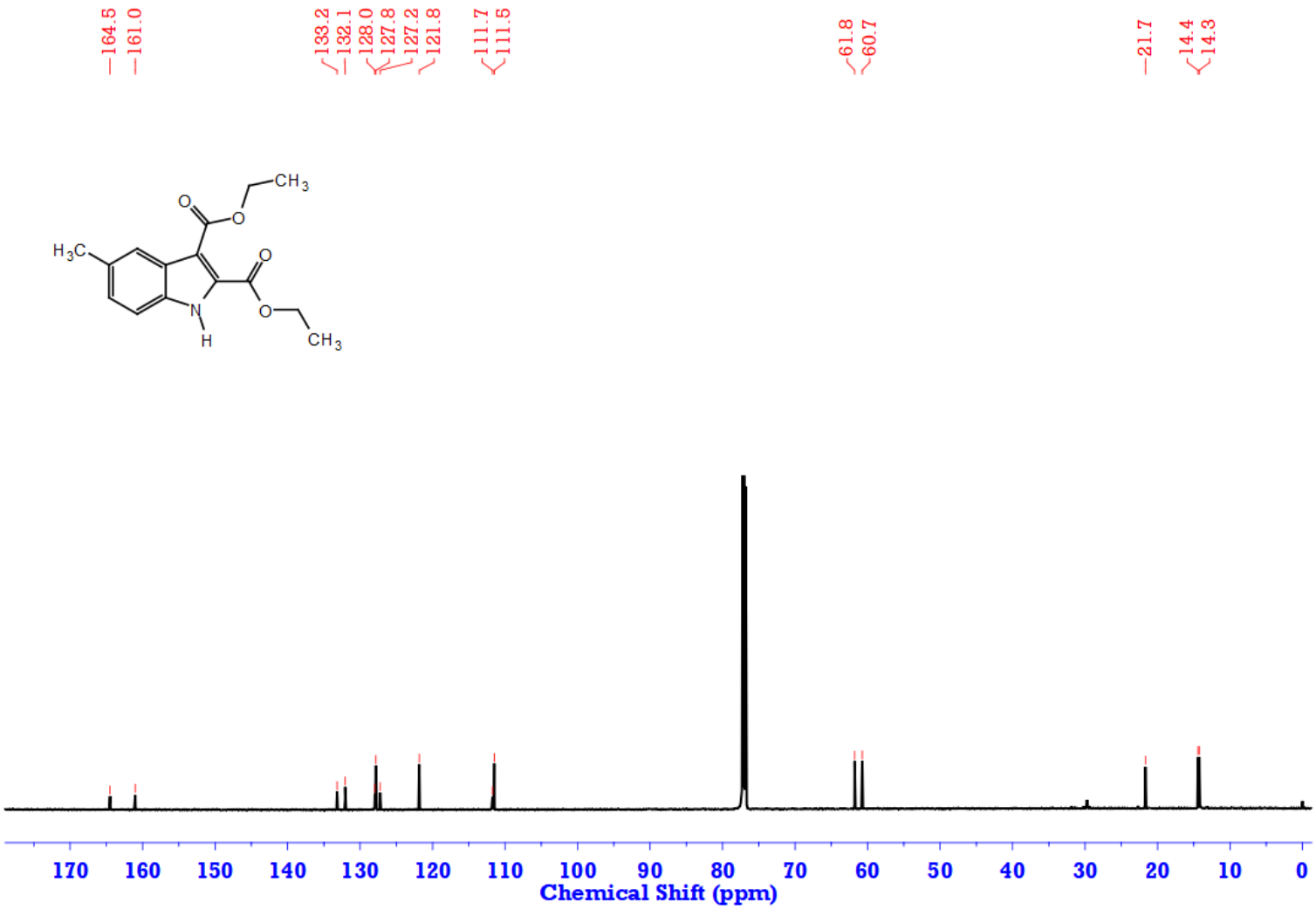
Sp(10). ^{13}C NMR Spectrum of dimethyl *2d* (5-methyl-1H-indole-2,3-dicarboxylate).



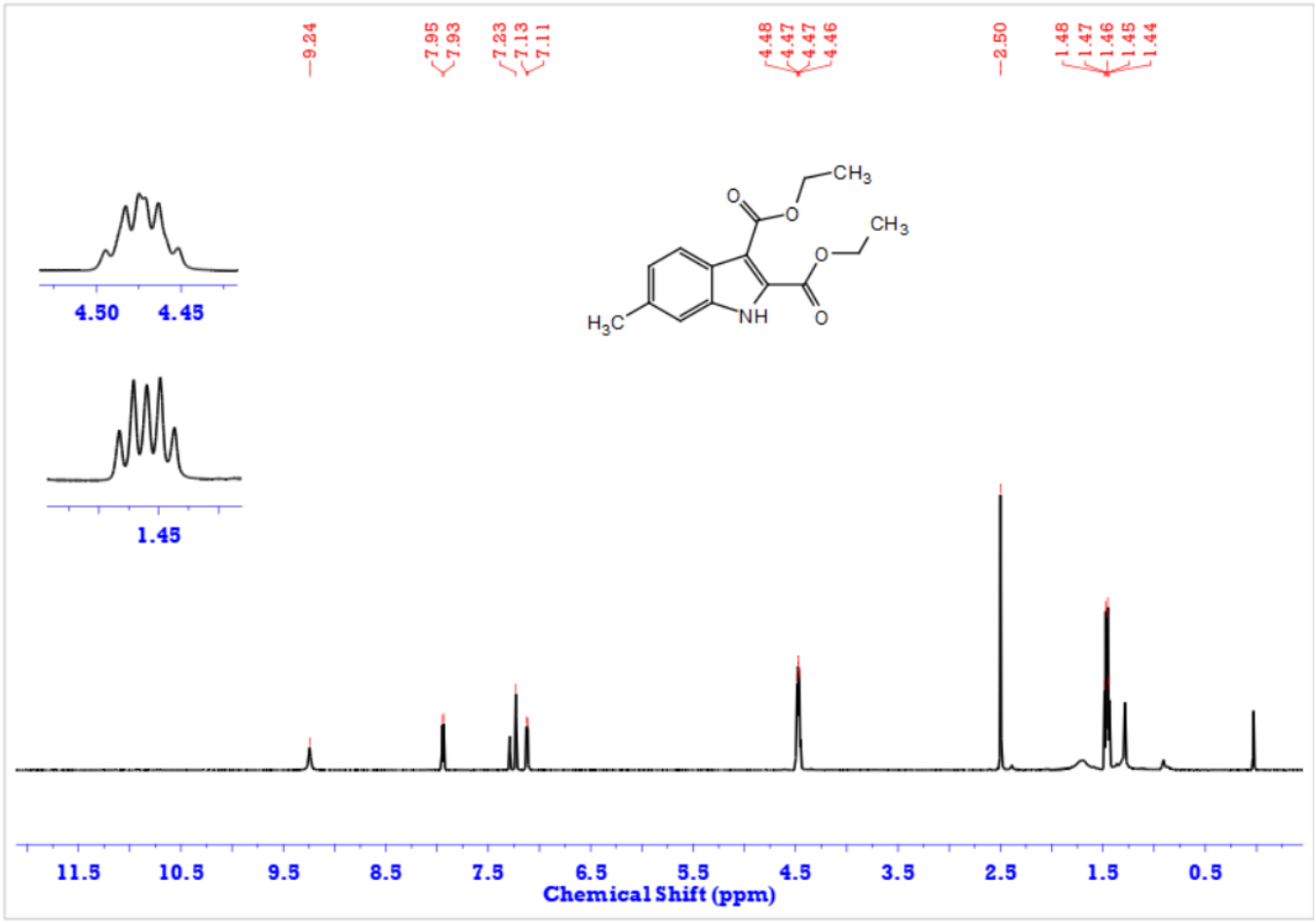
Sp(11). ^{1}H NMR Spectrum of *2e* (diethyl 5-methyl-1H-indole-2,3-dicarboxylate) (Colourless Oil): ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.86 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 1H), 4.52 – 4.44 (m, 3H), 2.50 (s, 3H), 1.5 - 1.43 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 161.0, 133.2, 132.1, 128.0, 127.8, 127.2, 121.8, 111.7, 111.5, 61.8, 60.7, 21.7, 14.4, 14.3.[6]



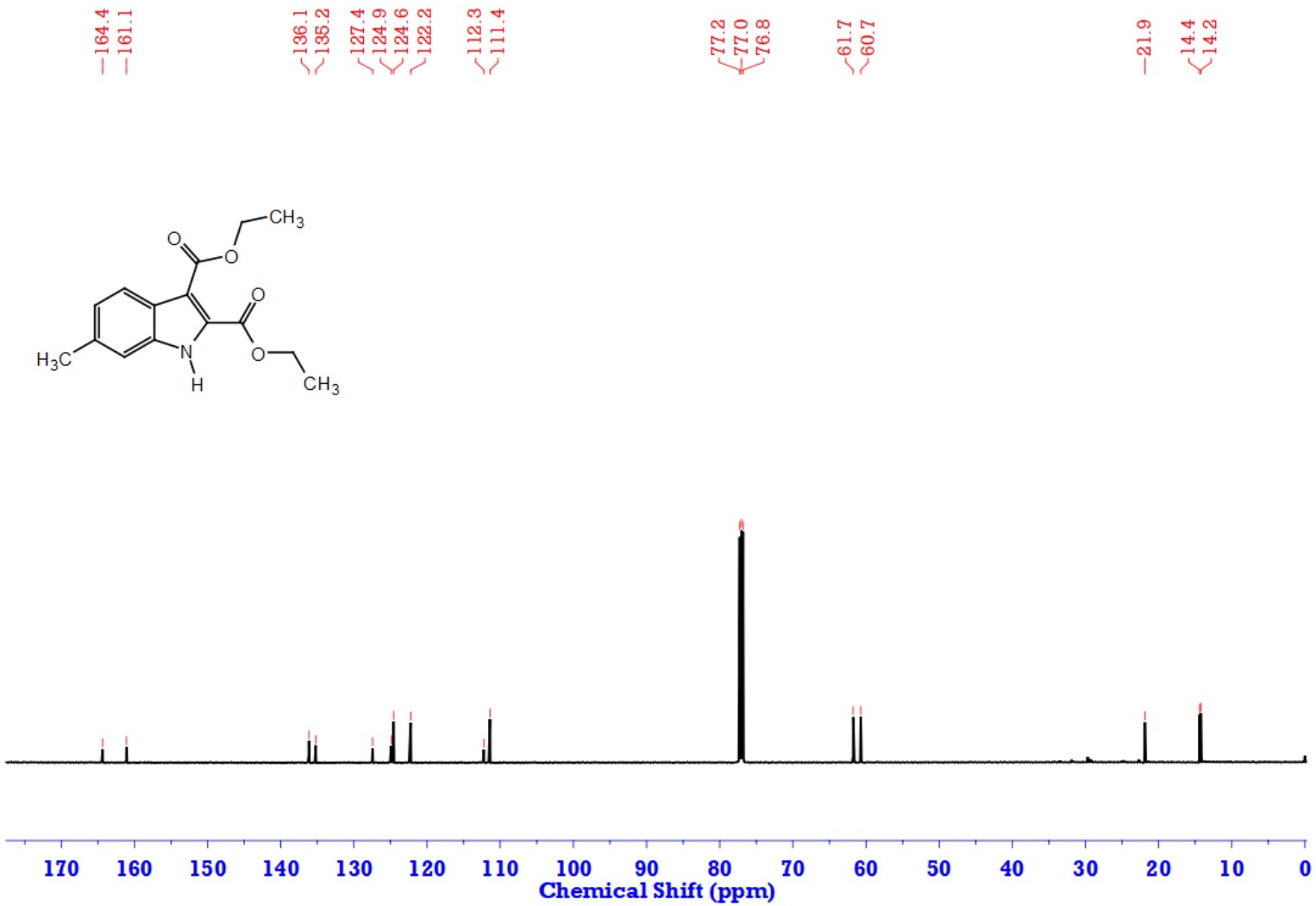
Sp(12). ^{13}C NMR Spectrum of *2e* (diethyl 5-methyl-1H-indole-2,3-dicarboxylate).



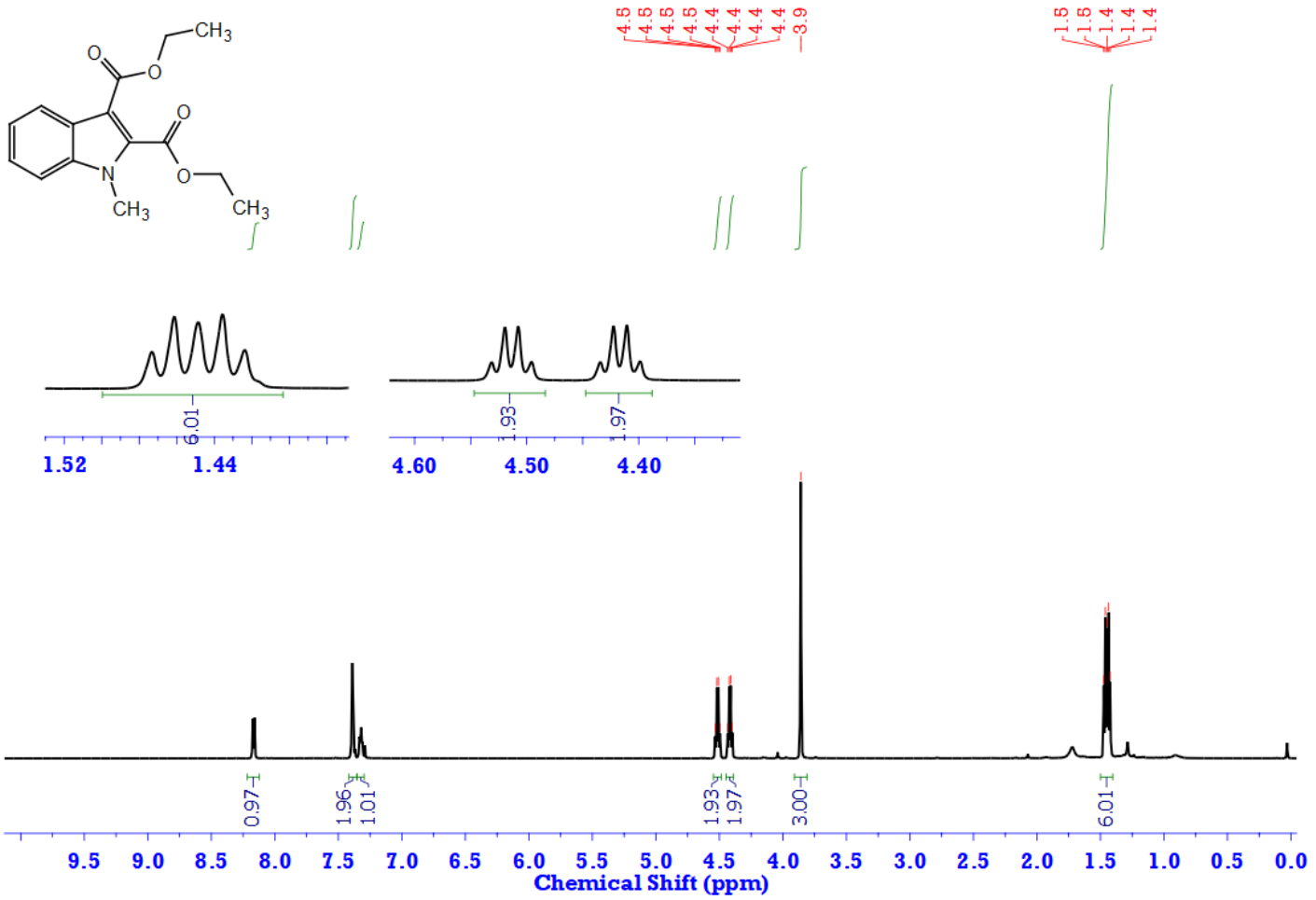
Sp(13). ^{1}H NMR Spectrum of *2f* (diethyl 6-methyl-1H-indole-2,3-dicarboxylate) (Colourless oil). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.23 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 4.53 – 4.41 (m, 4H), 2.50 (s, 3H), 1.48 - 1.44 (m, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.4, 161.1, 136.1, 135.2, 127.4, 124.9, 124.6, 122.2, 112.3, 112.3, 111.4, 61.7, 60.7, 21.9, 14.4, 14.2.[6]



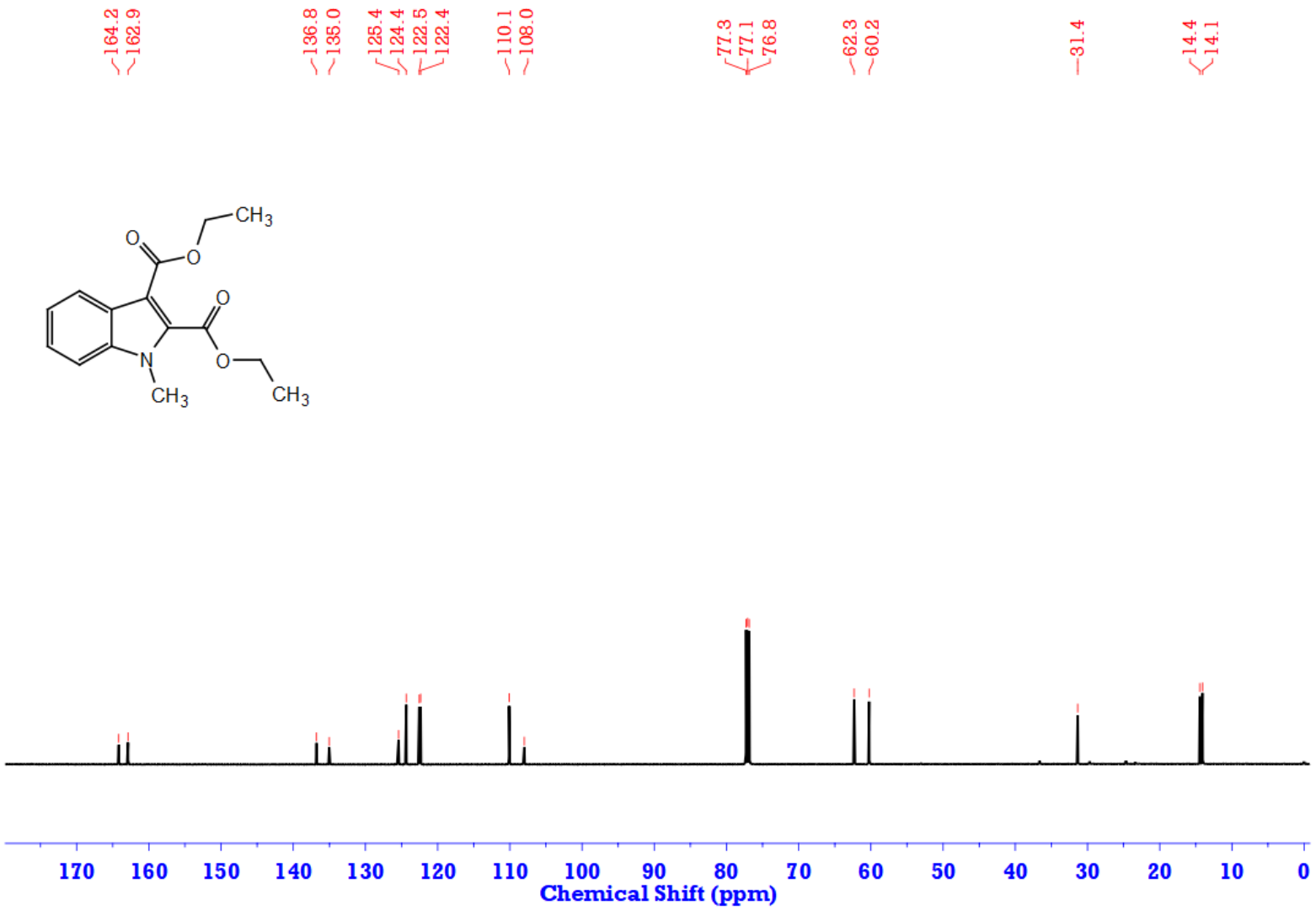
Sp(14). ^{13}C NMR Spectrum of *2f* (diethyl 6-methyl-1H-indole-2,3-dicarboxylate).



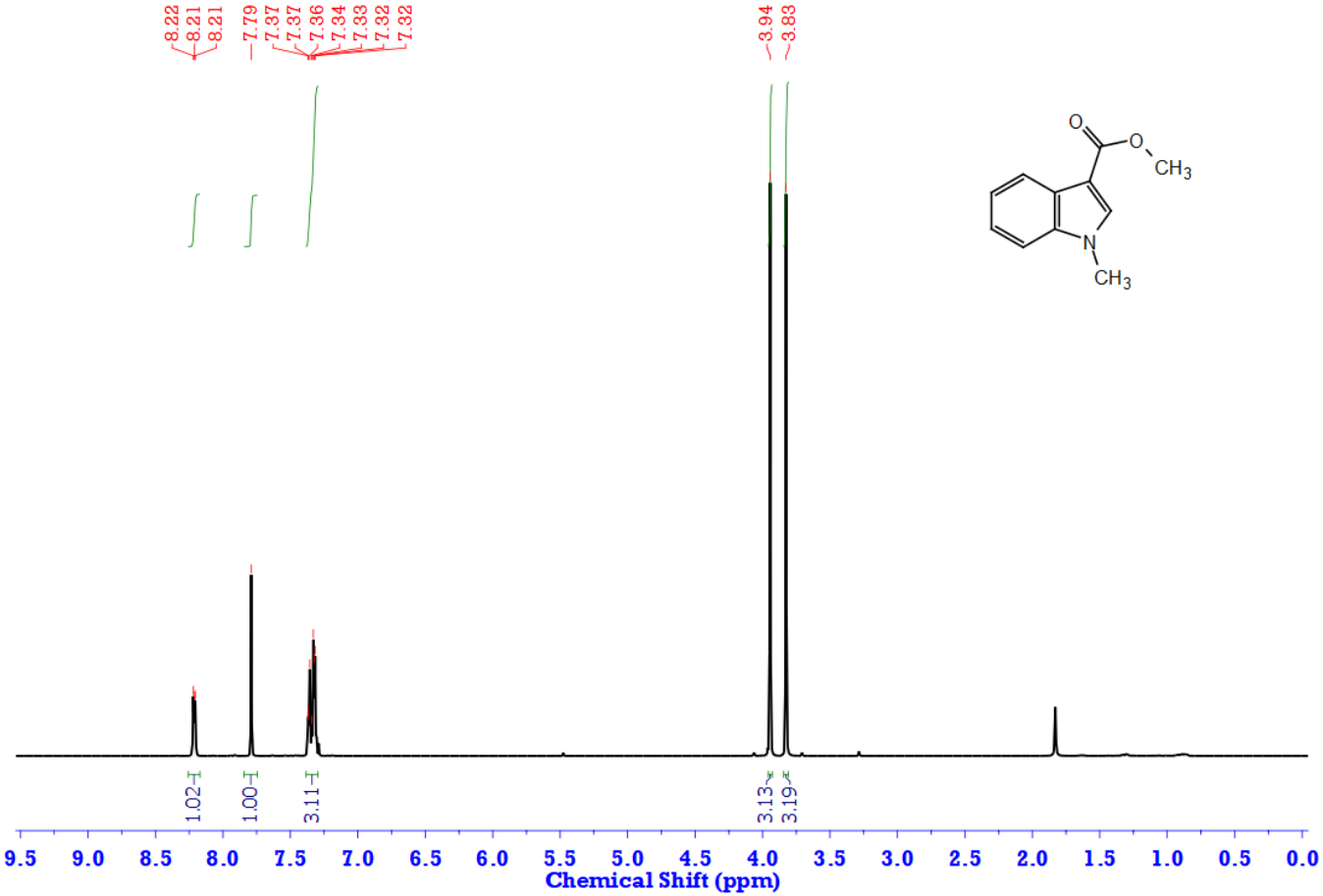
Sp(15). ^{1}H NMR Spectrum of *2s* (diethyl 1-methyl-1H-indole-2,3-dicarboxylate) (Yellow liquid) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, 1H), 7.38 (m, 1H), 7.35 – 7.29 (m, 1H), 4.51 (q, *J* = 7.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 1H), 1.50 – 1.40 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 162.9, 136.8, 135.0, 125.4, 124.4, 122.5, 122.4, 110.1, 108.0, 62.3, 60.2, 31.4, 14.4, 14.1.[7]



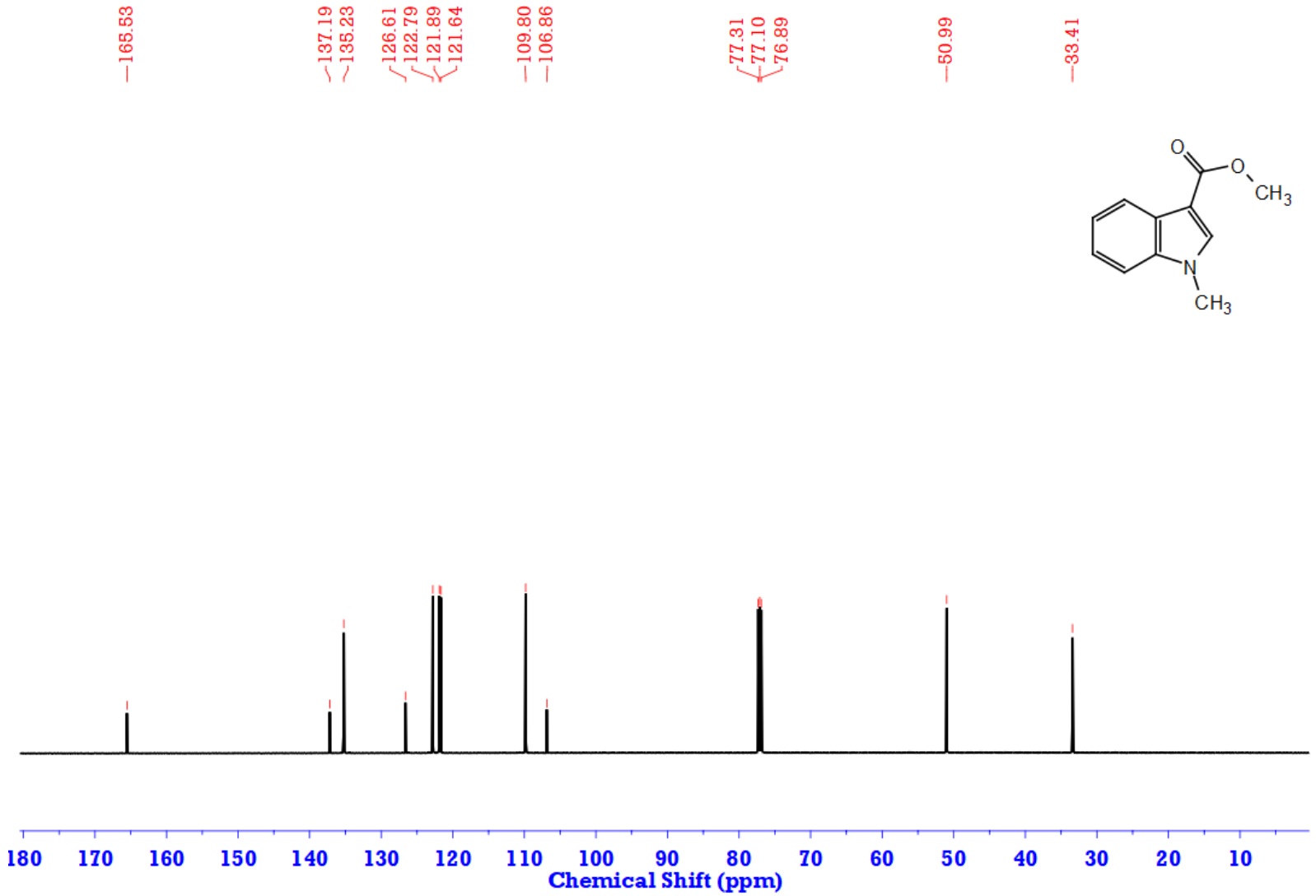
Sp(16). ^{13}C NMR Spectrum of *2s* (diethyl 1-methyl-1H-indole-2,3-dicarboxylate).



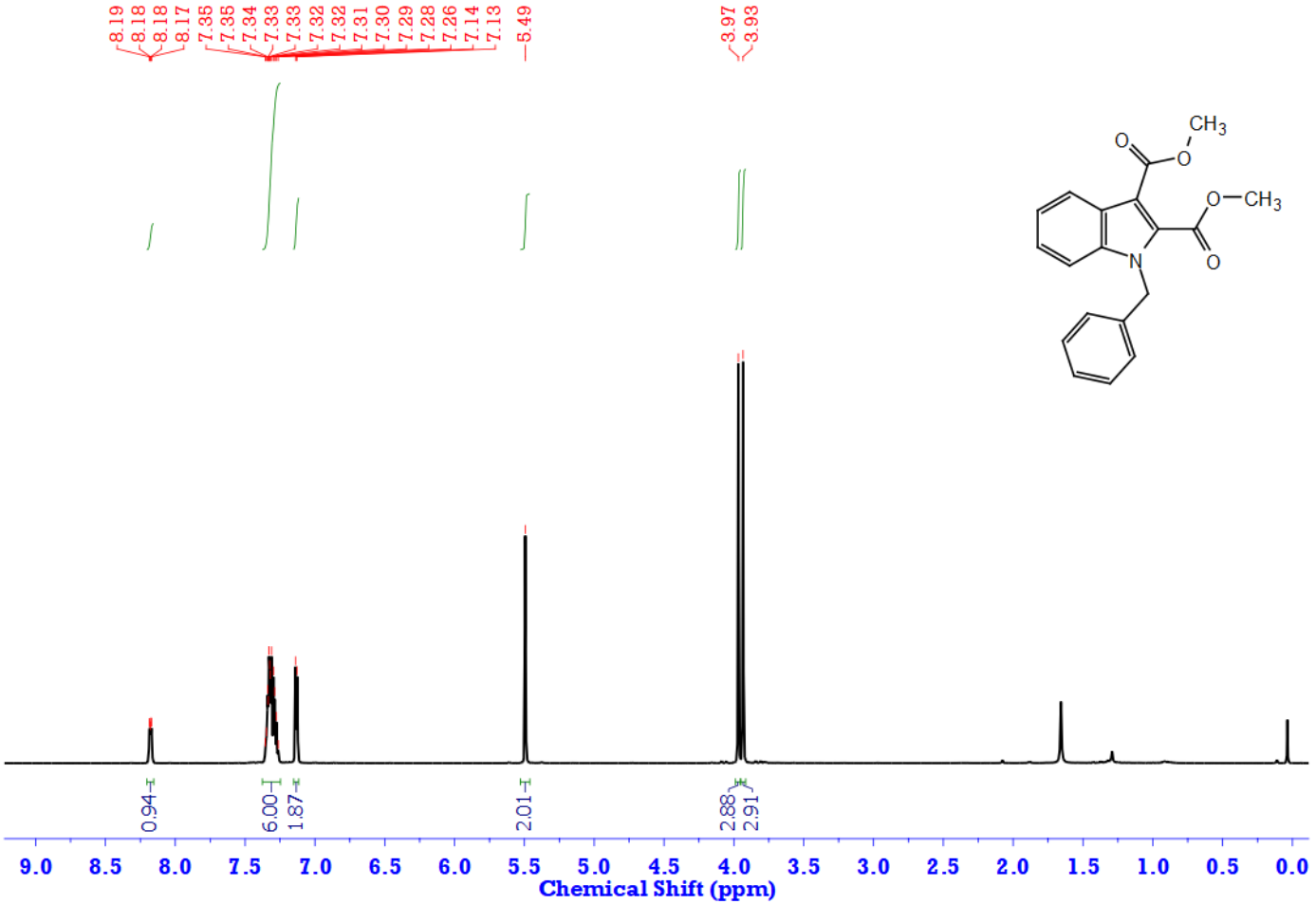
Sp(17). ^{1}H NMR Spectrum of *2t* (methyl 1-methyl-1H-indole-3-carboxylate) (Colourless oil**).** ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 – 8.17 (m, 1H), 7.79 (s, 1H), 7.40 – 7.27 (m, 3H), 3.94 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 137.2, 135.2, 126.6, 122.8, 121.9, 121.6, 109.8, 106.9, 51.0, 33.4.[8]



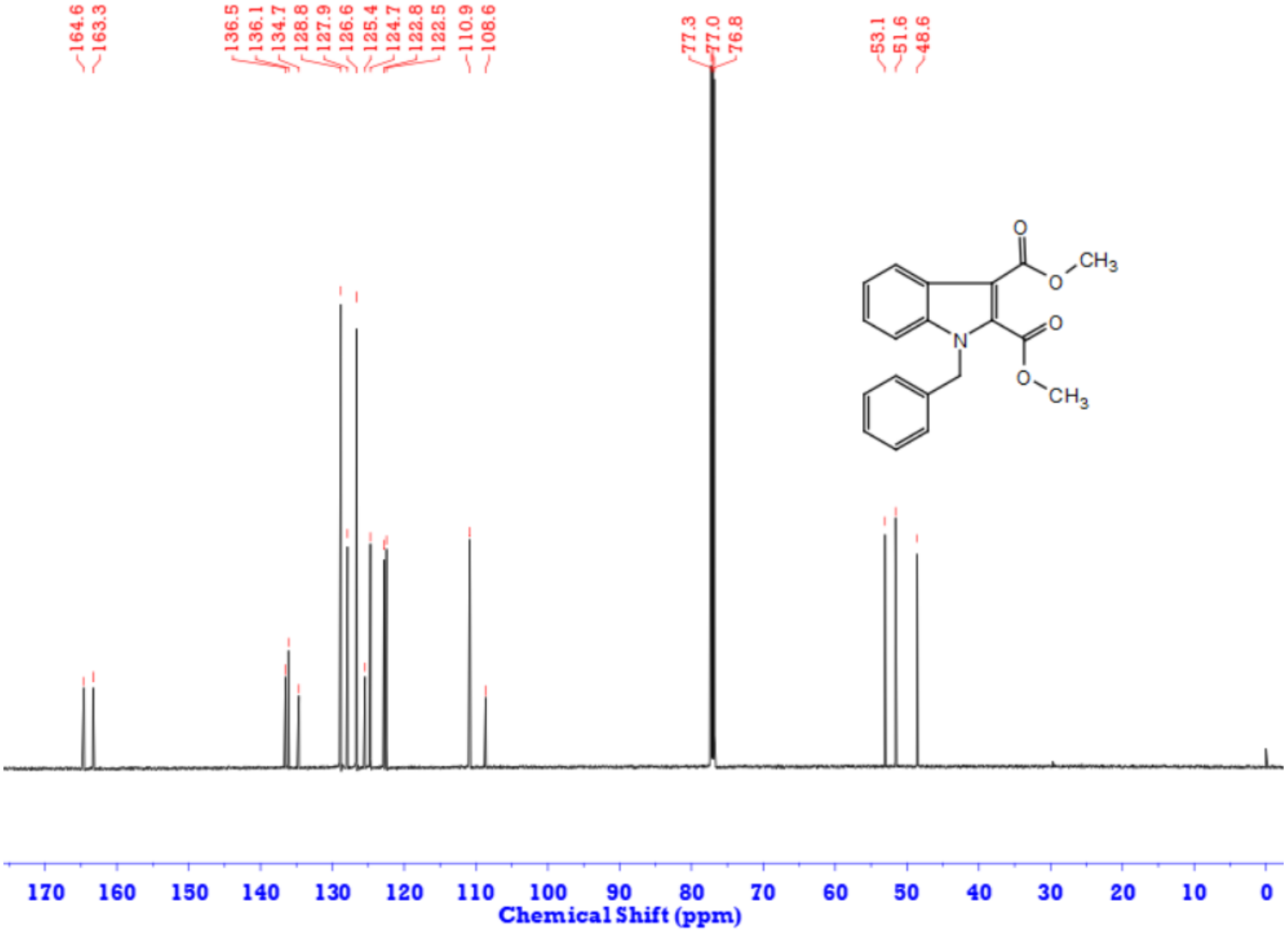
Sp(18). ^{13}C NMR Spectrum of *2t* (methyl 1-methyl-1H-indole-3-carboxylate).



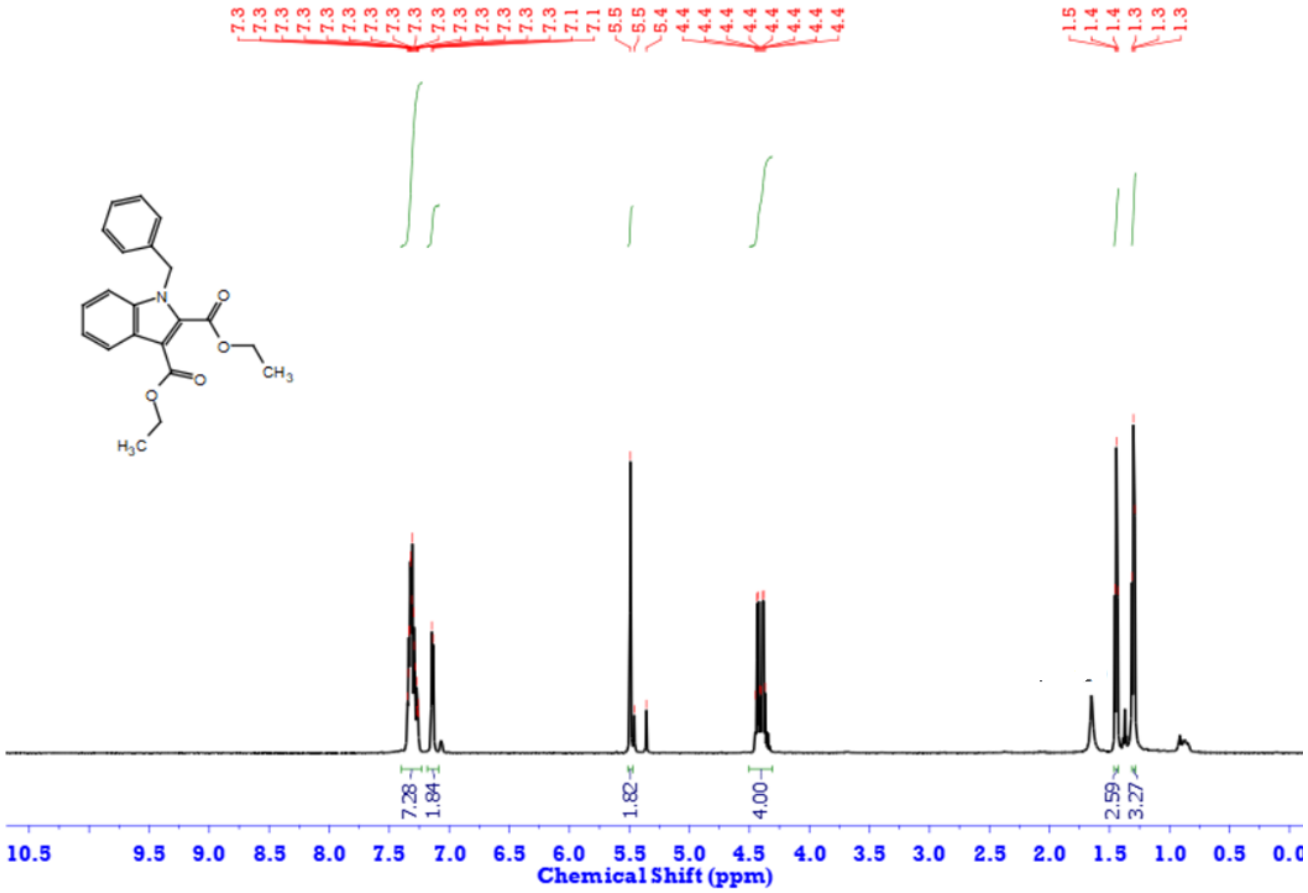
Sp(19). ^{1}H NMR Spectrum of *2u* (2,3-dimethyl 1-benzyl-1H-indole-2,3-dicarboxylate) (Colourless oil) ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 - 8.16 (1H), 7.37 – 7.25 (m, 2H), 7.13 (d, *J* = 7.3 Hz, 1H), 5.49 (s, 1H), 3.97 (s, 1H), 3.93 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 164.5, 163.3 , 136.5, 136.1, 134.6, 128.8, 127.9, 126.6, 125.4, 124.7, 122.8, 122.4, 110.8, 108.6, 53.0, 51.6, 48.5.[9]



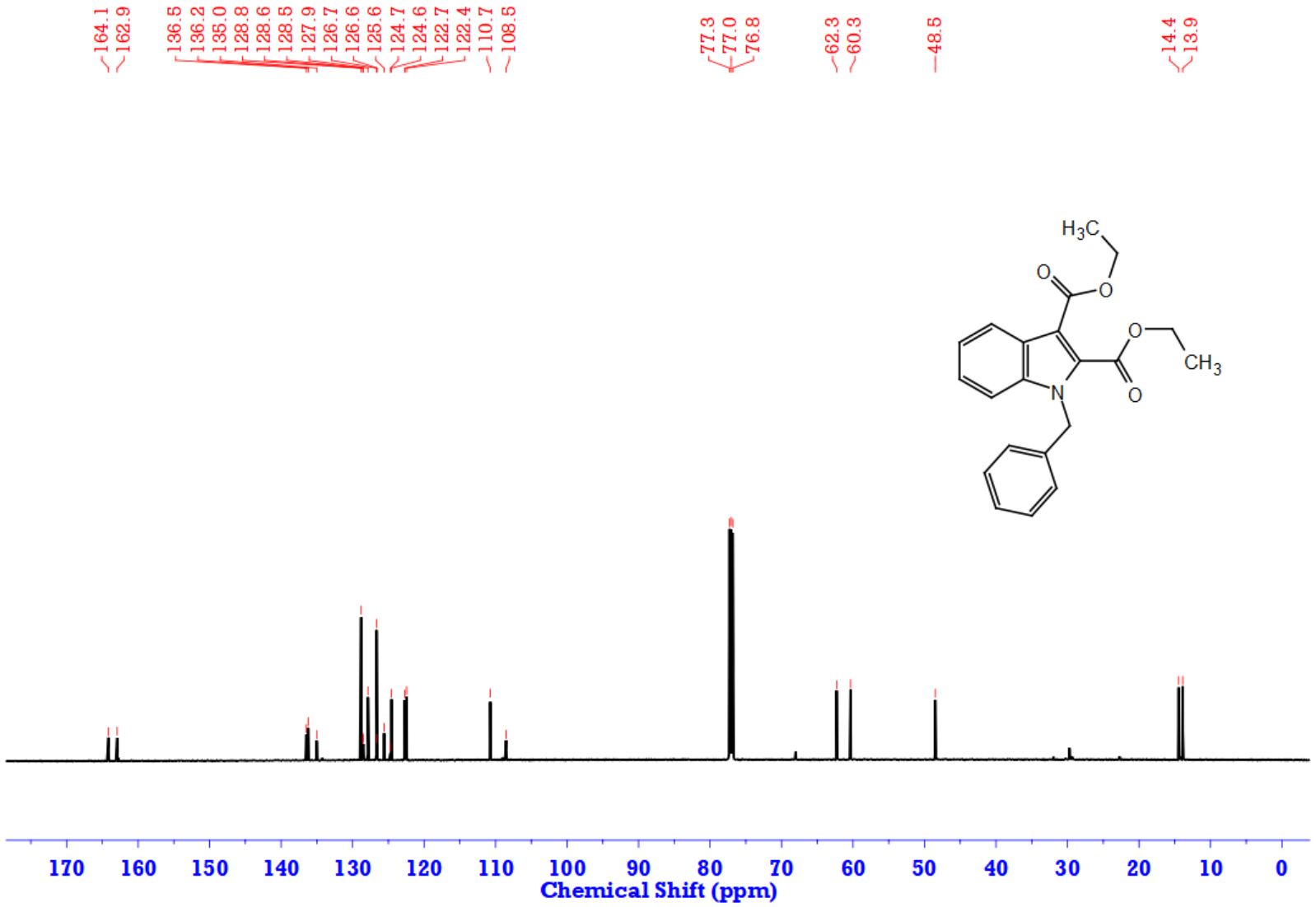
Sp(20). ^{13}C NMR Spectrum of *2u* (dimethyl 1-benzyl-1H-indole-2,3-dicarboxylate).



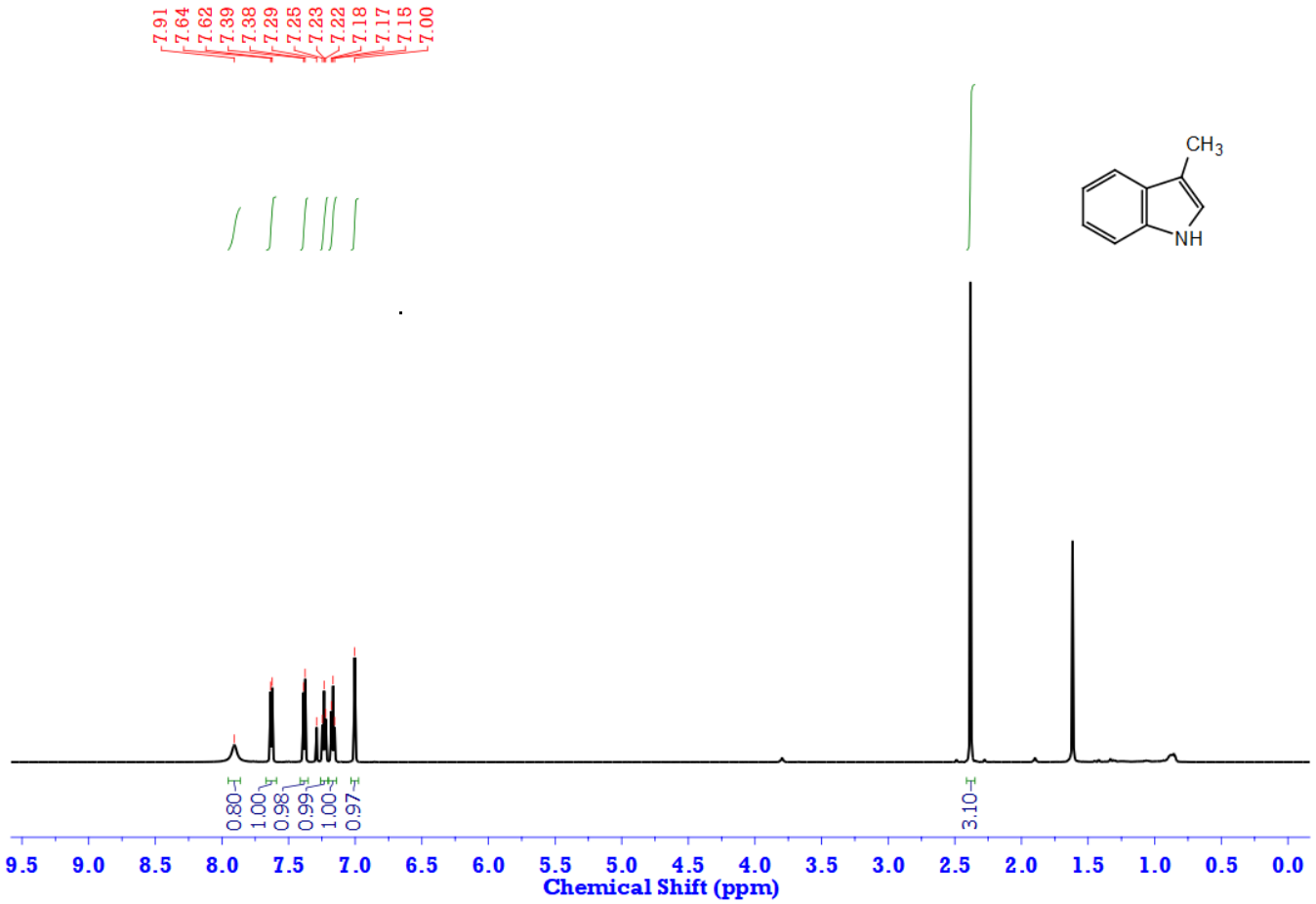
Sp(21). ^{1}H NMR Spectrum of *2v* (diethyl 1-benzyl-1H-indole-2,3-dicarboxylate) (Yellow oil) ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.19 (d, *J* = 2.8 Hz, 1H), 7.38 – 7.24 (m, 7H), 7.14 (d, *J* = 7.1 Hz, 2H), 5.49 (s, 2H), 4.41 (dq, *J* = 26.4, 7.1 Hz, 4H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 164.1, 162.9, 136.5, 136.2, 135.0, 128.8, 128.6, 127.9, 126.7, 126.6, 125.6, 124.6, 122.7, 122.4, 110.7, 108.5, 62.3, 60.3, 48.50, 14.4, 13.9.[9]



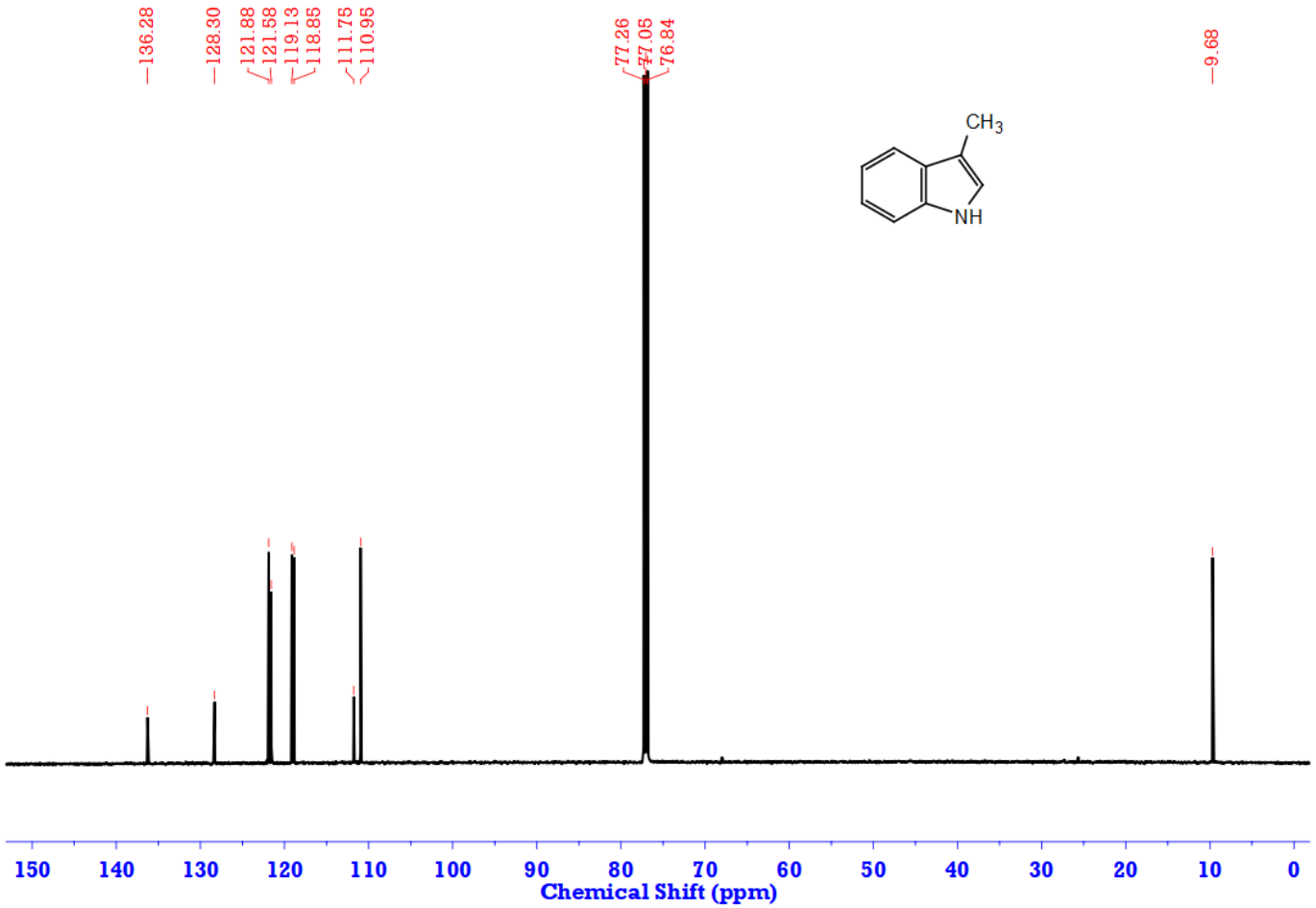
Sp(22). ^{13}C NMR Spectrum of *2v* (diethyl 1-benzyl-1H-indole-2,3-dicarboxylate)



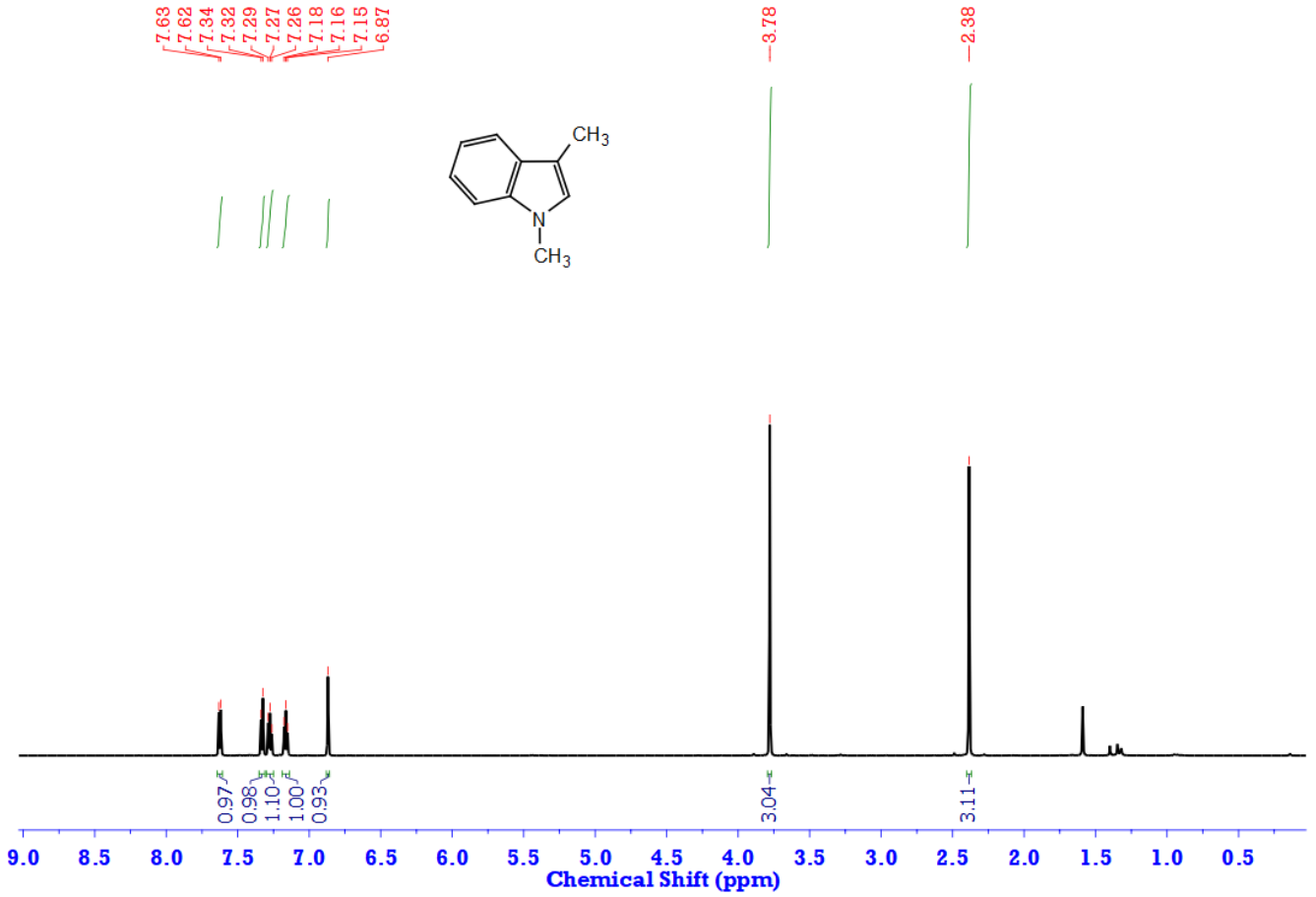
Sp(23). ^{1}H NMR Spectrum of *4a* (3-methyl-*1H*-indole) (White crystalline solid, m.p. 96 ^{o}C**).** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 2.38 (s, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 136.3, 128.3, 121.9, 121.6, 119.1, 118.8, 111.8, 111.0, 9.7.[10]



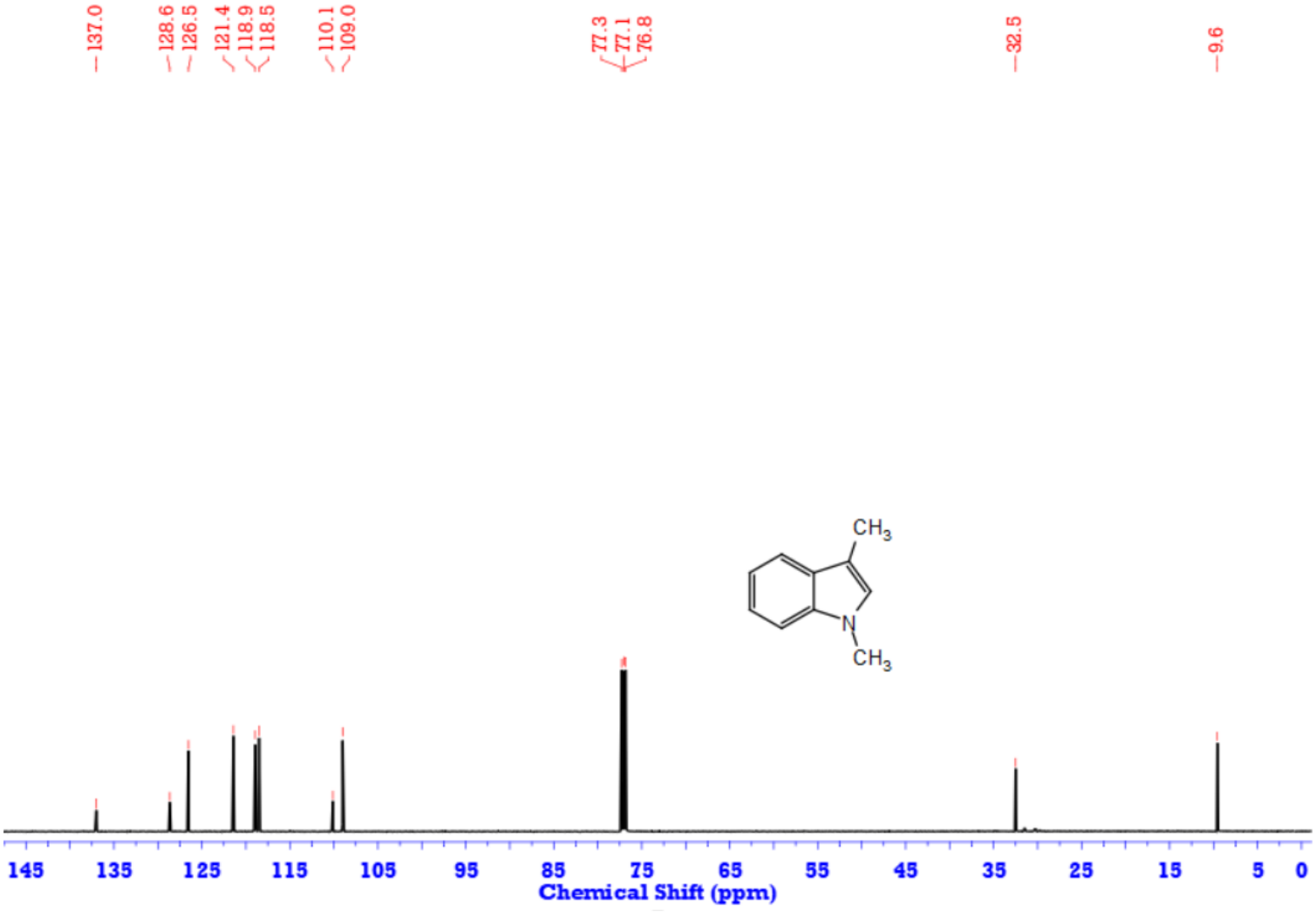
Sp(24). ^{13}C NMR Spectrum of *4a* (3-methyl-*1H*-indole).



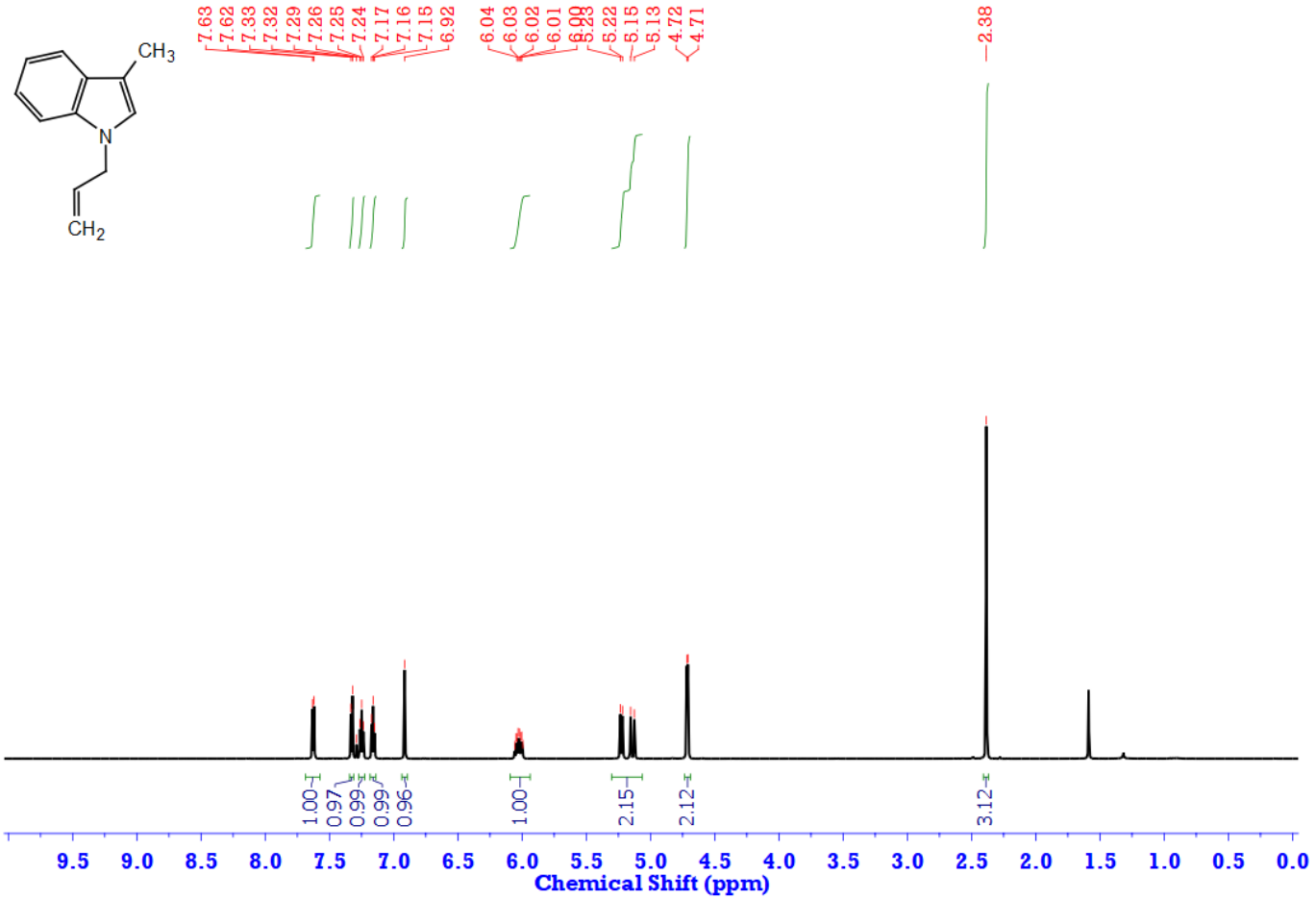
Sp(25). ^{1}H NMR Spectrum of *4b* (*N*-methyl-3-methyl-*1H*-indole) (Colourless oil) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.87 (s, 1H), 3.78 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.0, 128.6, 126.5, 121.4, 118.9, 118.5, 110.1, 109.0, 32.5, 9.6.[12]



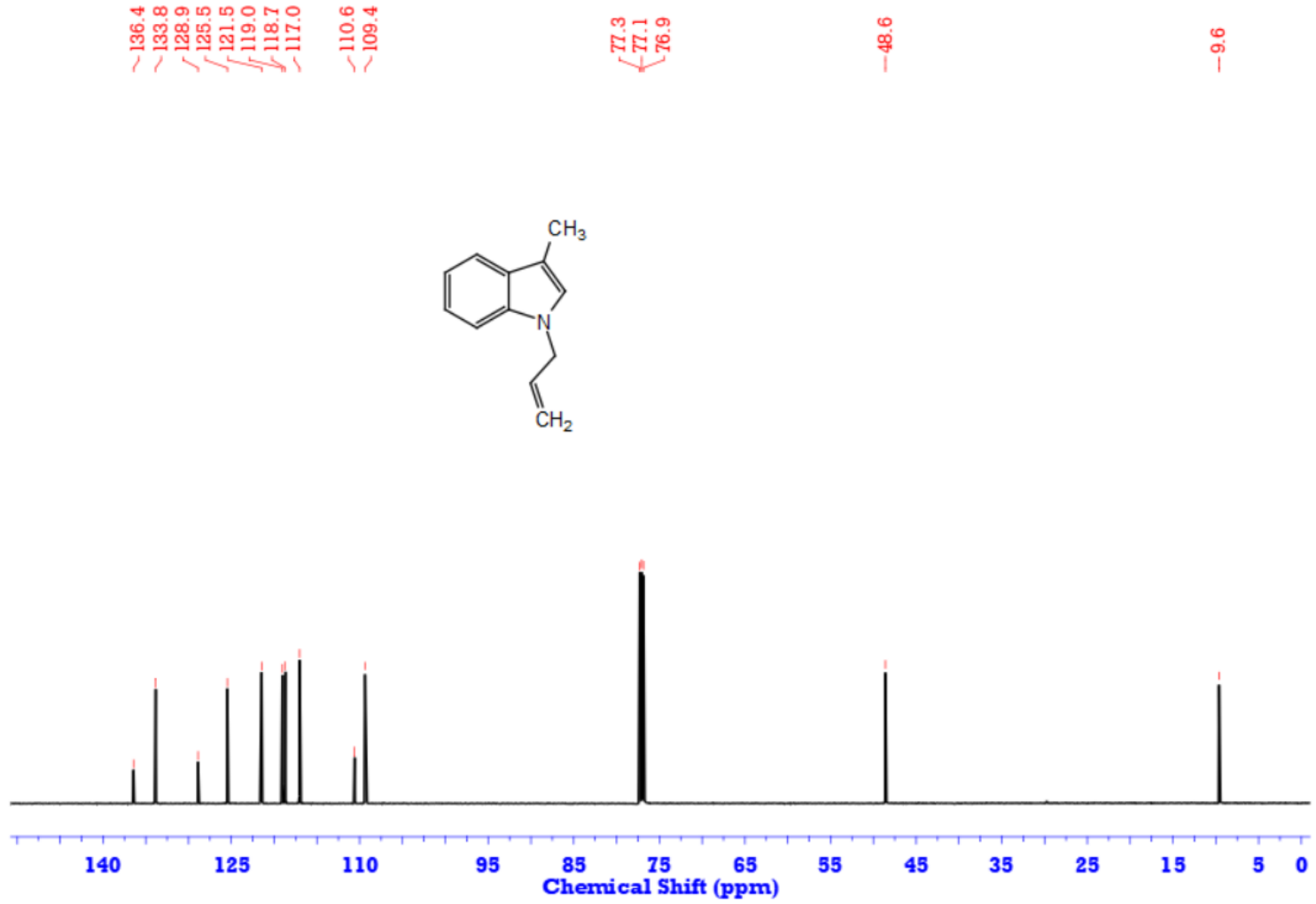
Sp(26). ^{13}C NMR Spectrum of *4b* (*N*-methyl-3-methyl-*1H*-indole).



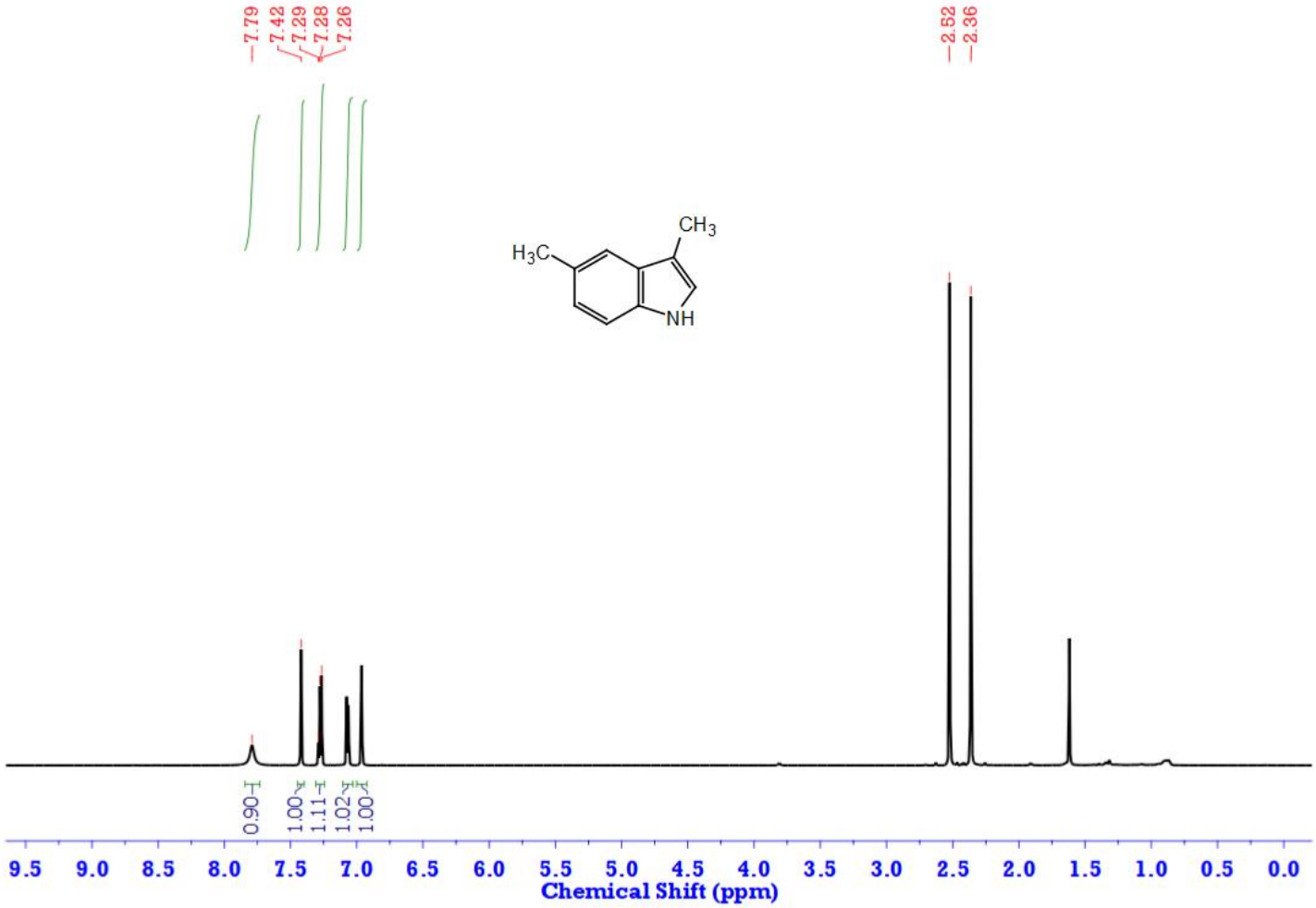
Sp(27). ^{1}H NMR Spectrum of *4c* (1-allyl-3-methyl-1H-indole) (Colourless oil) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.92 (s, 1H), 6.02 (ddd, *J* = 16.1, 10.5, 5.2 Hz, 1H), 5.18 (dd, *J* = 51.4, 13.6 Hz, 2H), 4.71 (d, *J* = 5.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.4, 133.8, 128.9, 125.5, 121.5, 119.0, 118.7, 117.0, 110.6, 109.4, 48.6, 9.6.[13, 16]



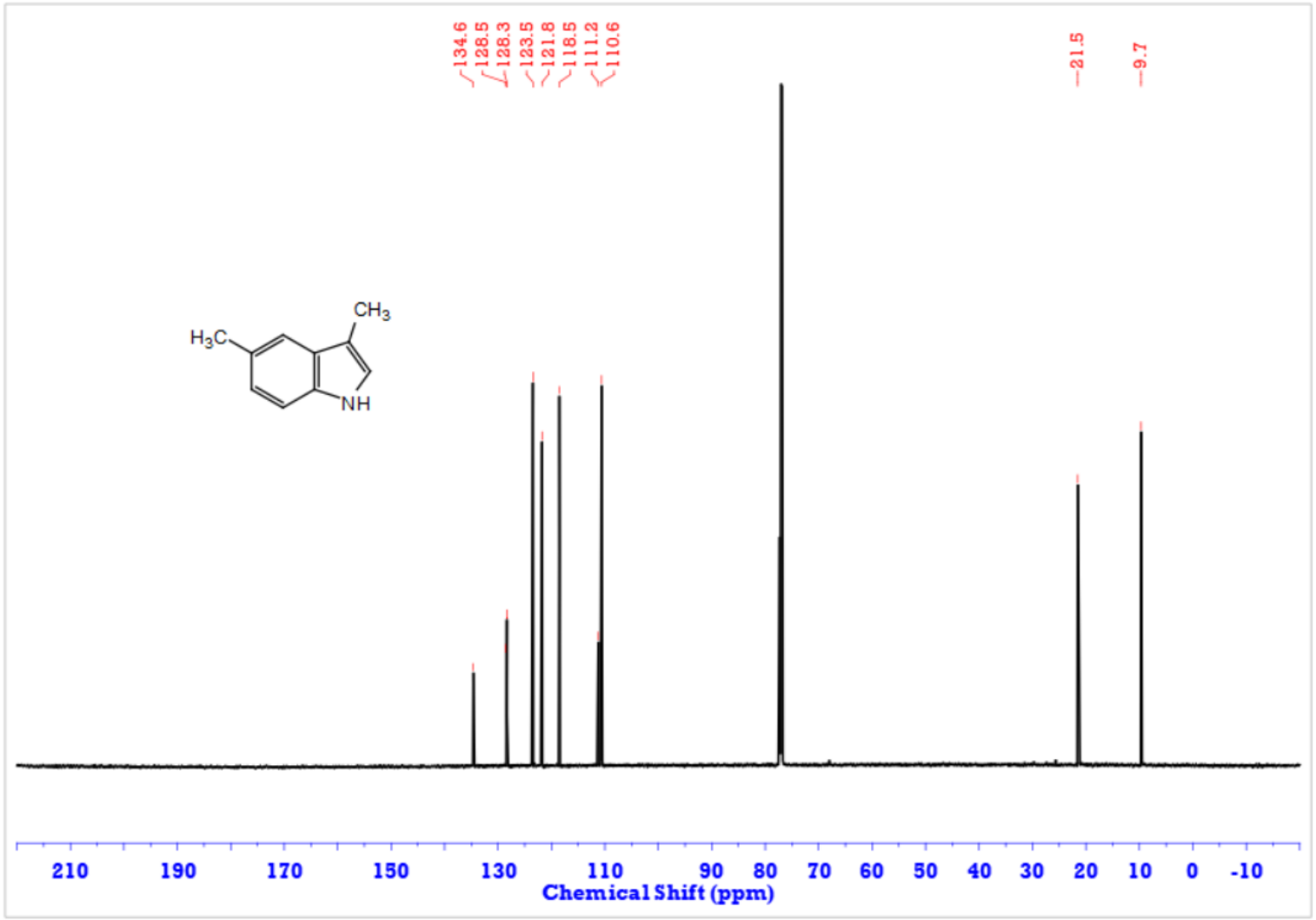
Sp(28). ^{13}C NMR Spectrum of *4c* (1-allyl-3-methyl-1H-indole).



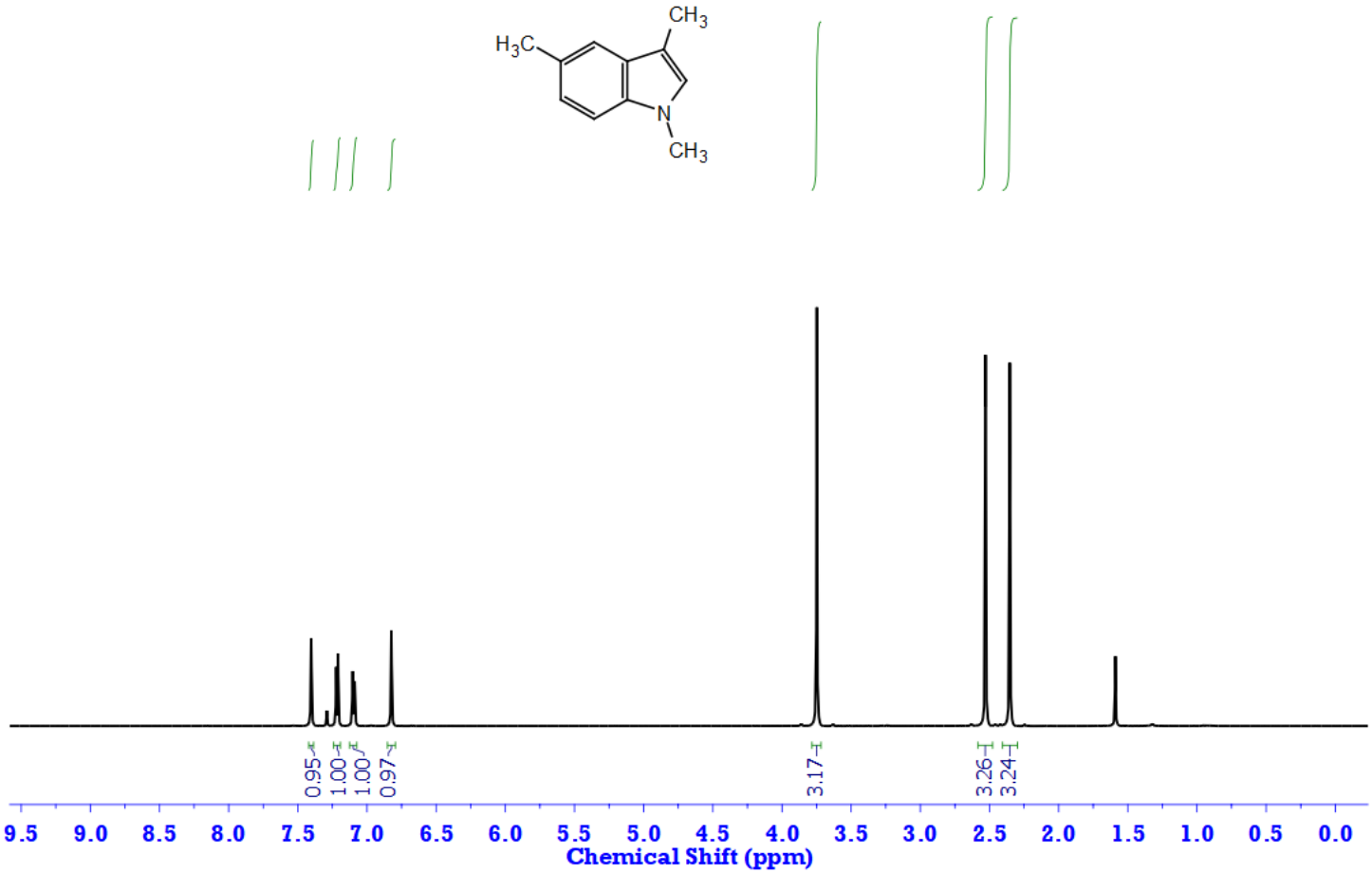
Sp(29). ^{1}H NMR Spectrum of *4e* (3,5-dimethyl-1H-indole) (White crystalline solid, m. p. 76 ^{o}C) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.42 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.96 (s, 1H), 2.52 (s, 1H), 2.36 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.6, 128.5, 128.3, 123.5, 121.8, 118.5, 111.2, 110.6, 21.5, 9.7.[14]



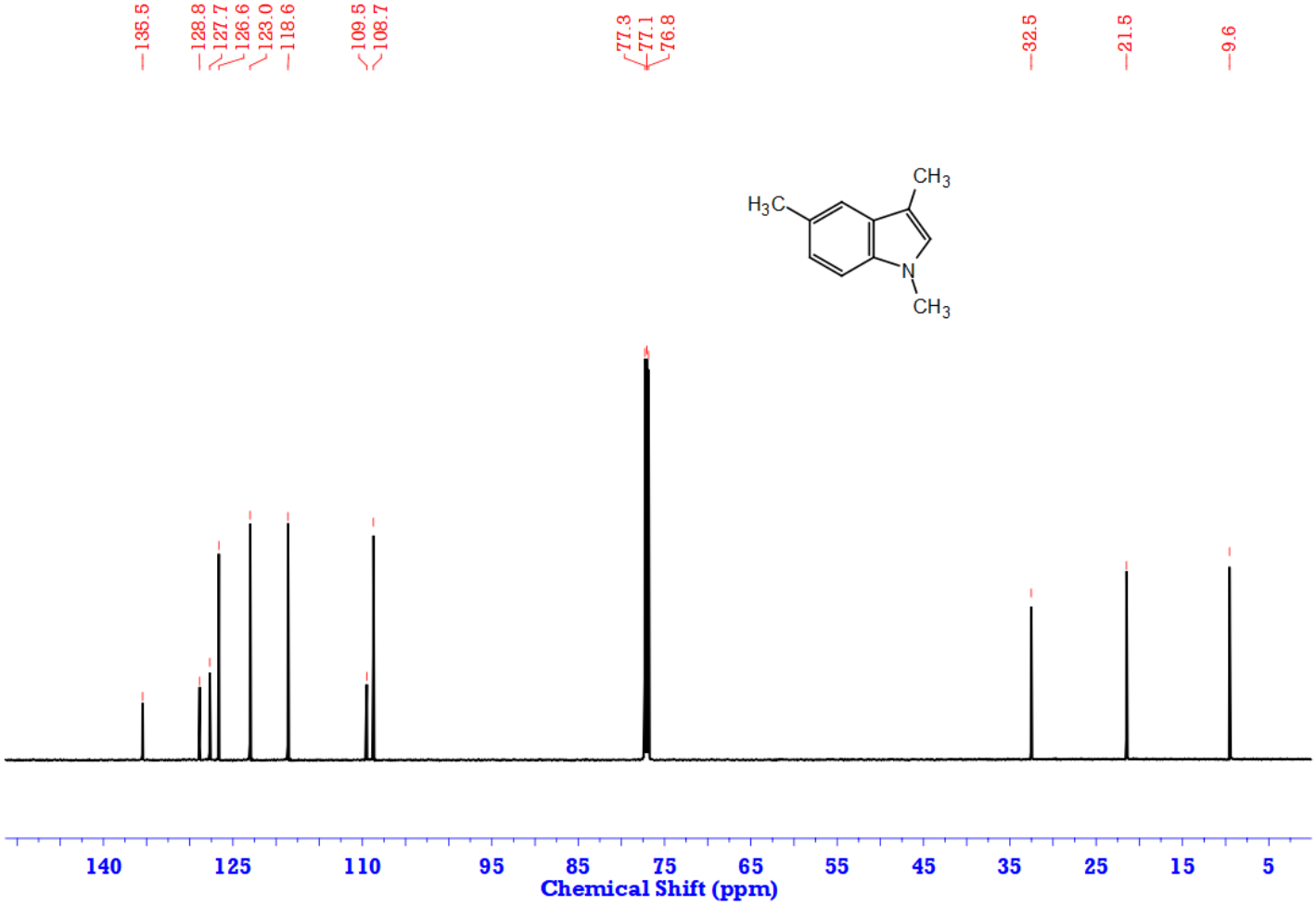
Sp(30). ^{13}C NMR Spectrum of *4e* (3,5-dimethyl-1H-indole).



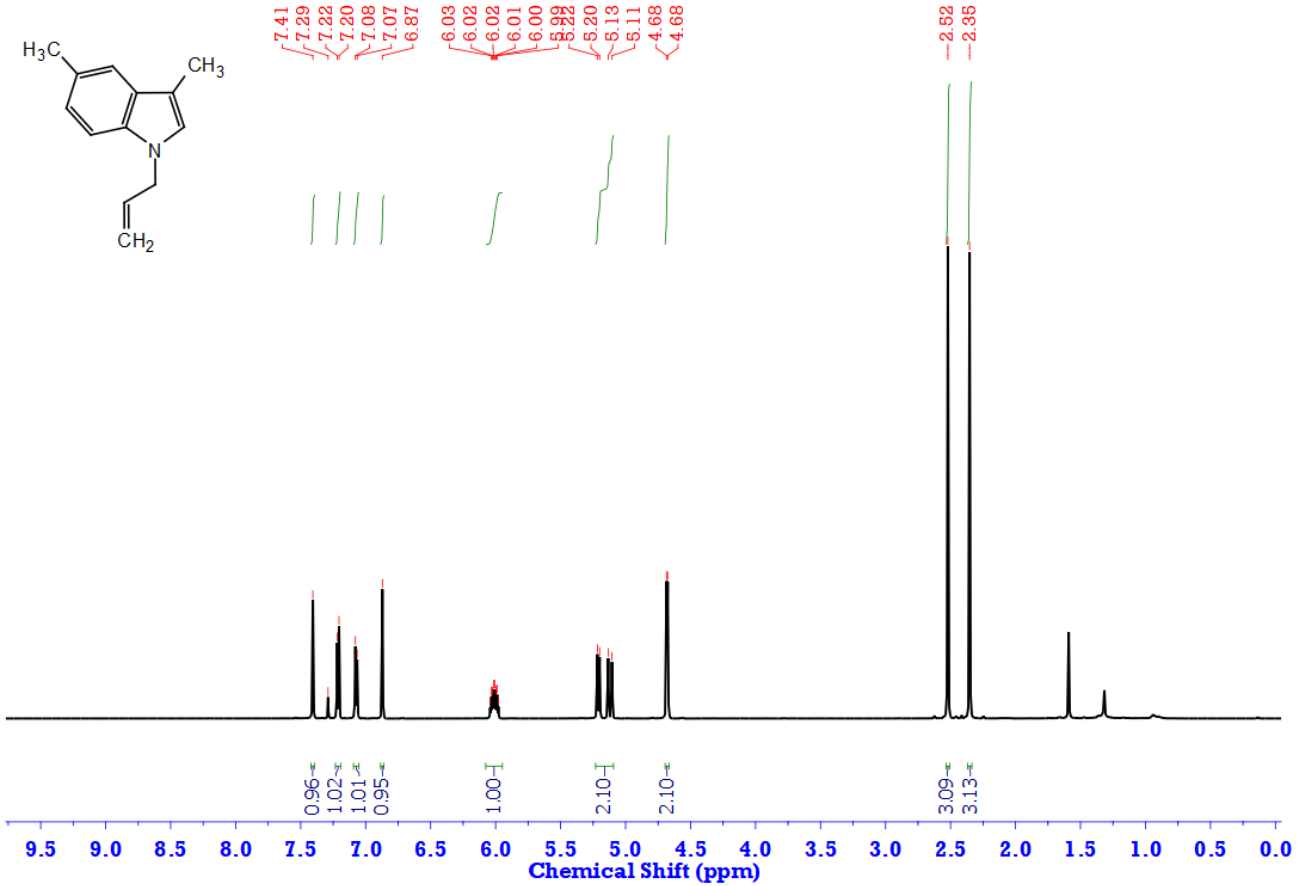
Sp(31). ^{1}H NMR Spectrum of *4f* (1,3,5-trimethyl-1H-indole) (Colourless liquid) ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.40 (s, 1H), 7.22 (d, *J* = 8.3 Hz, 1H), 7.10 (d, *J* = 8.2 Hz, 1H), 6.82 (s, 1H), 3.75 (s, 3H), 2.53 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) 135.5, 128.8, 127.7, 126.6, 123.0, 118.6, 109.5, 108.7, 32.5, 21.5, 9.6.



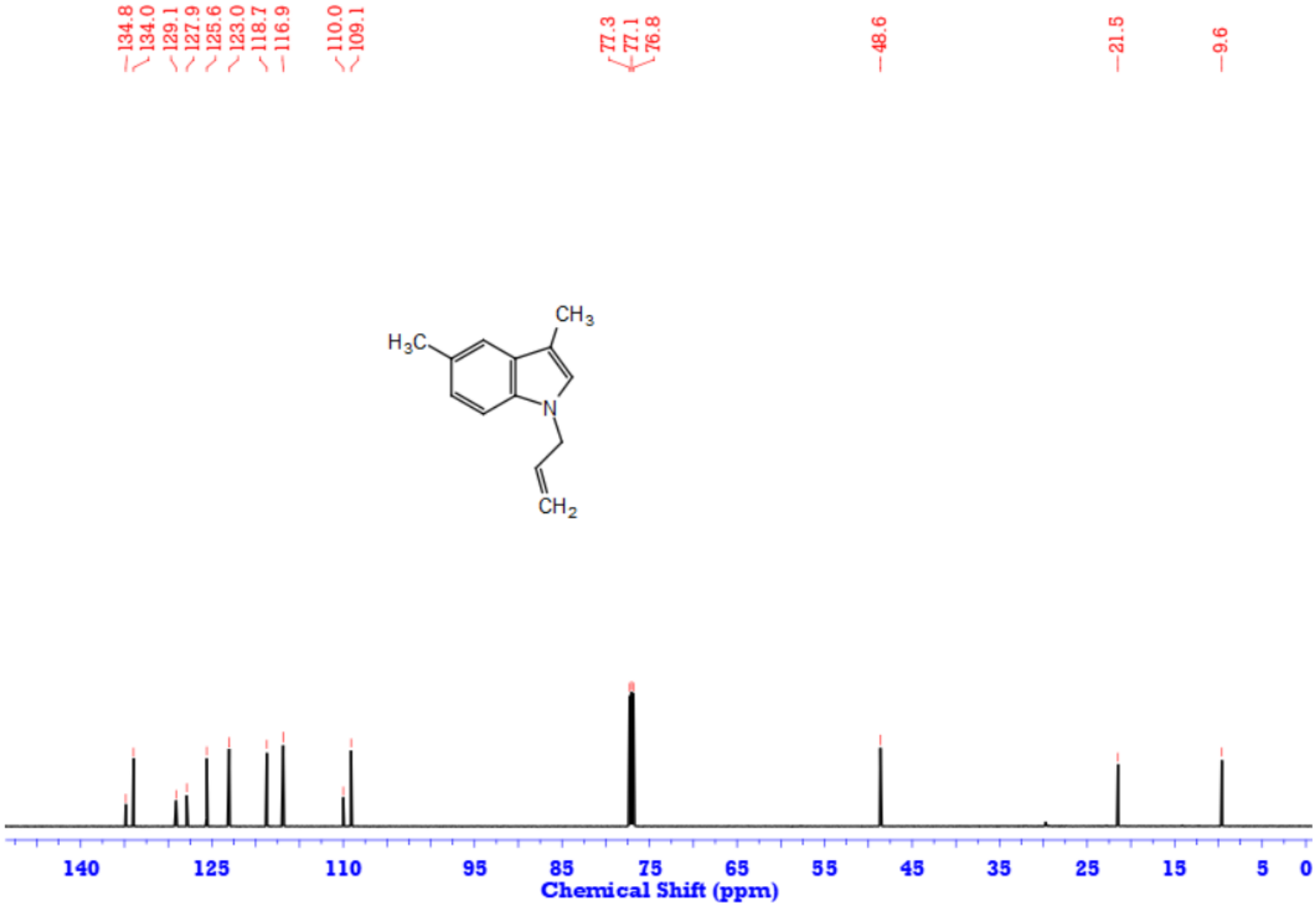
Sp(32). ^{13}C NMR Spectrum of *4f* (1,3,5-trimethyl-1H-indole).



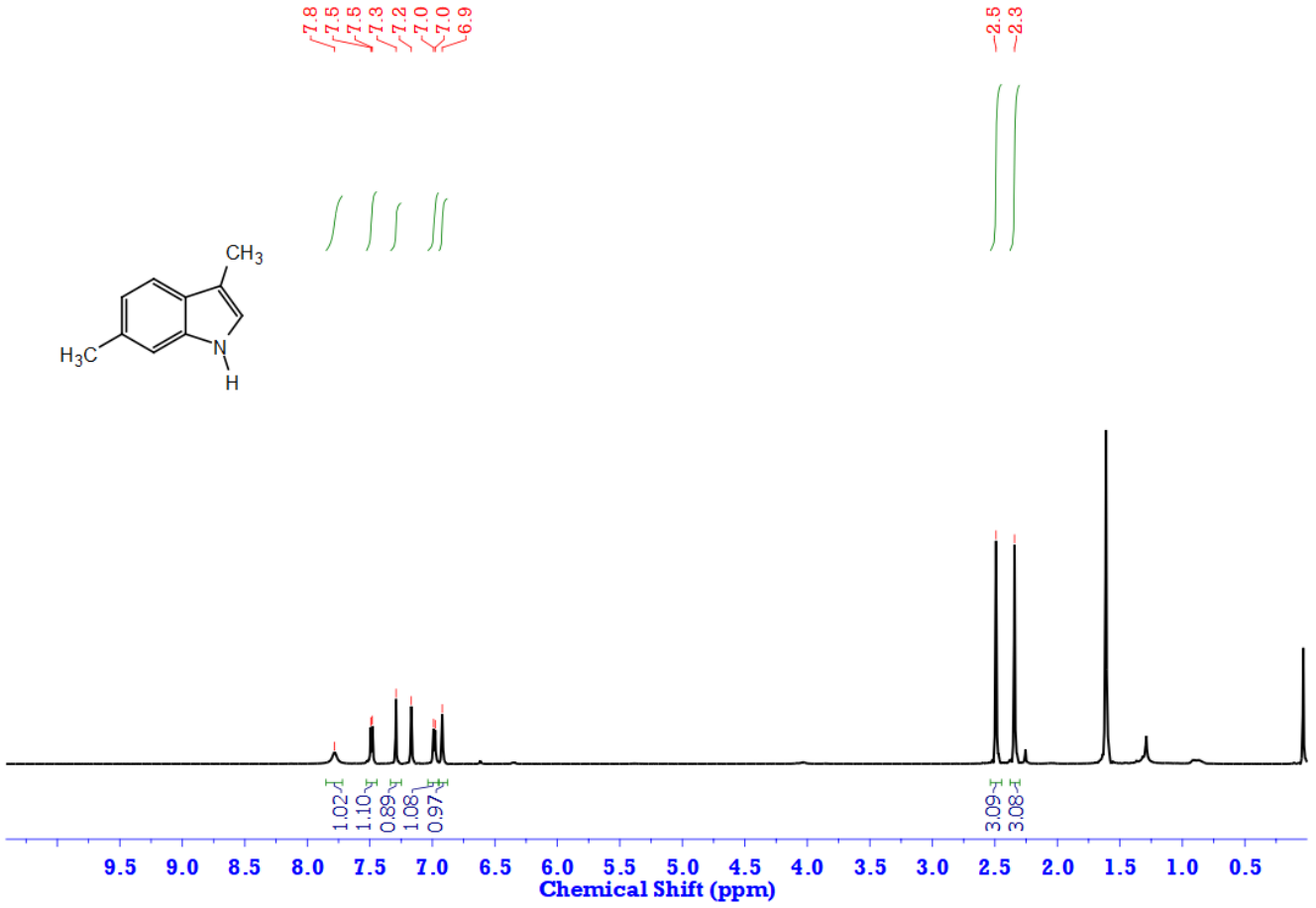
Sp(33). ^{1}H NMR Spectrum of *4g* (1-allyl-3,5-dimethyl-1H-indole) (Colourless Oil) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.87 (s, 1H), 6.01 (ddd, *J* = 22.2, 10.5, 5.4 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.12 (d, *J* = 17.1 Hz, 1H), 4.68 (d, *J* = 5.2 Hz, 2H), 2.52 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.8, 134.0, 129.1, 127.9, 125.6, 123.0, 118.7, 116.9, 110.0, 109.1, 48.6, 21.5, 9.6.



Sp(34). ^{13}C NMR Spectrum of *4g* (1-allyl-3,5-dimethyl-1H-indole).

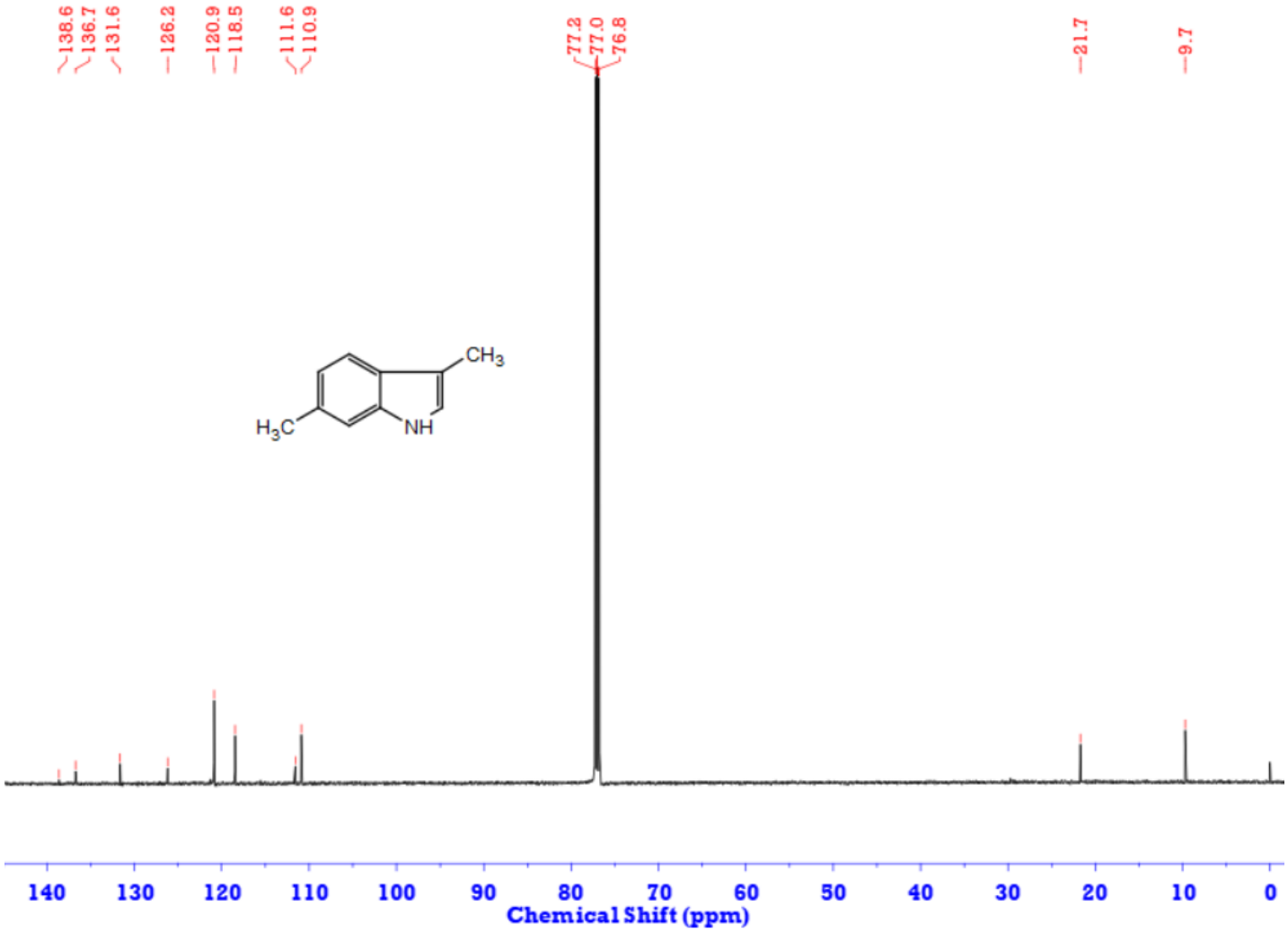


Sp(35). ^{1}H NMR Spectrum of *4h* (3,6-Dimethyl-*1H*-indole) (White crystalline solid, m. p. 92 ^{o}C) ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.29 (s, 1H), 6.98 (d, *J* = 7.9 Hz, 1H), 6.92 (s, 1H), 2.49 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 136.7, 131.6, 126.2, 120.9, 118.5, 111.6, 110.9, 21.7, 9.7.[15]

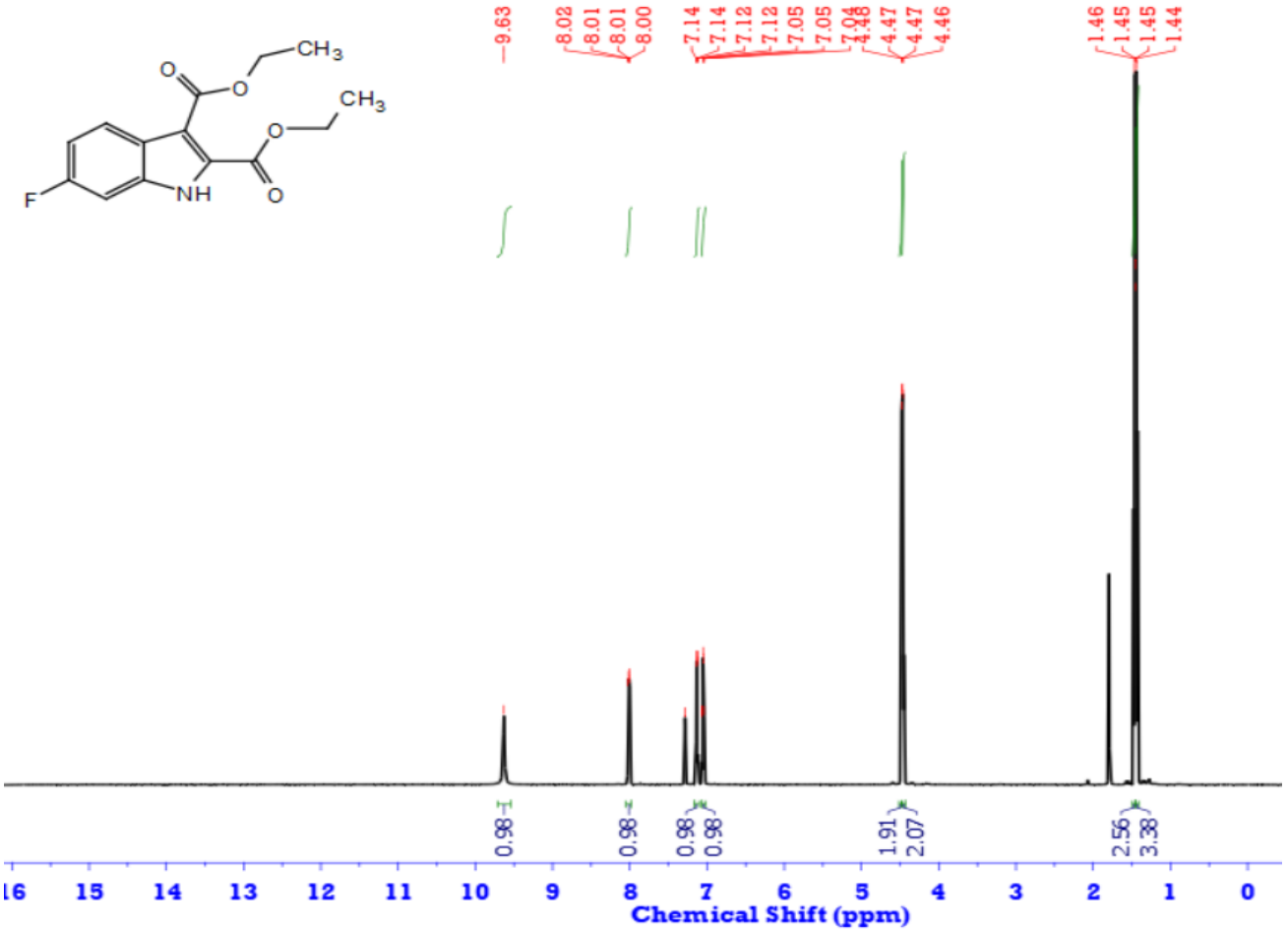


,

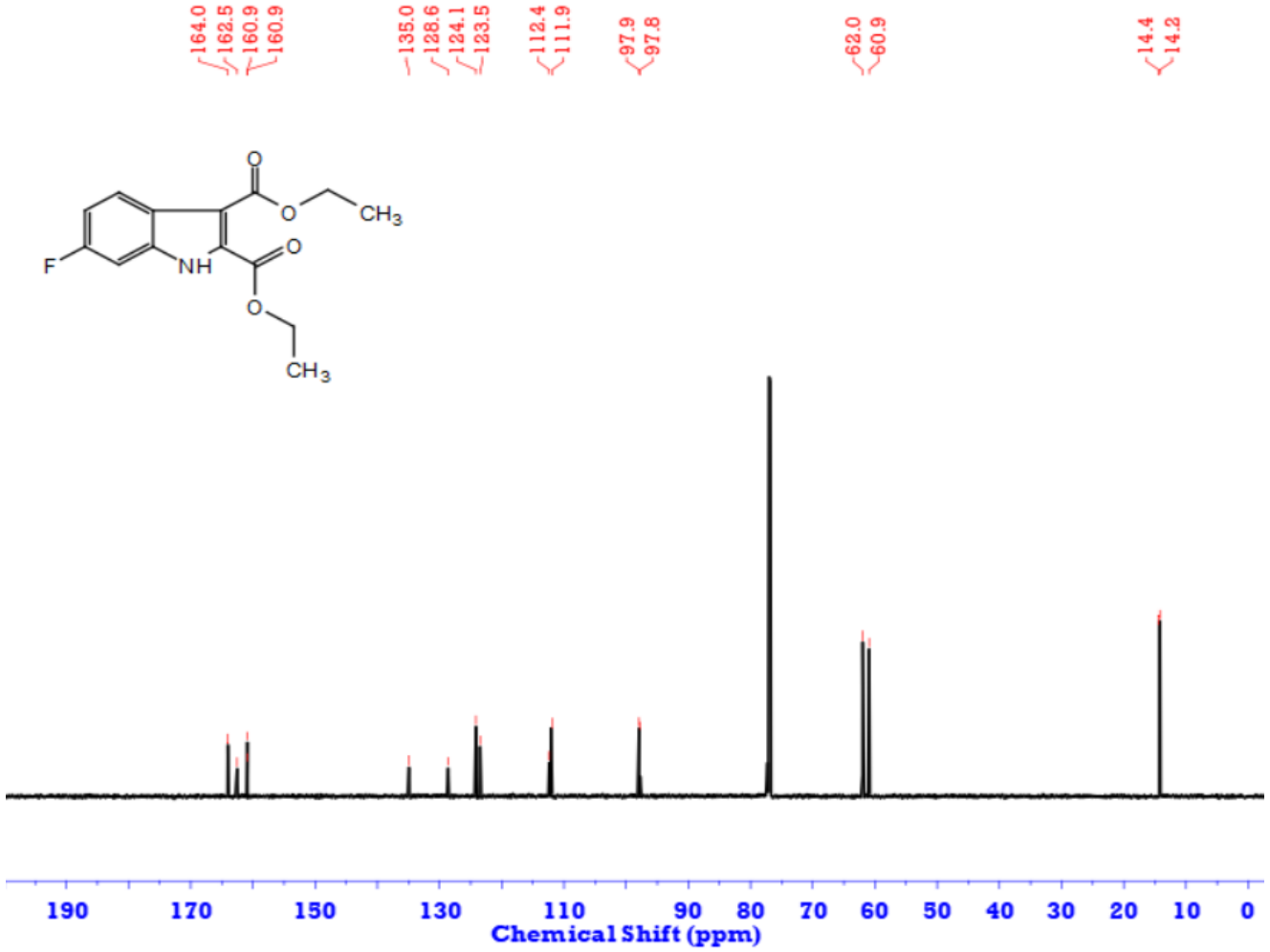
Sp(36). ^{13}C NMR Spectrum of *4h* (3,6-Dimethyl-*1H*-indole).



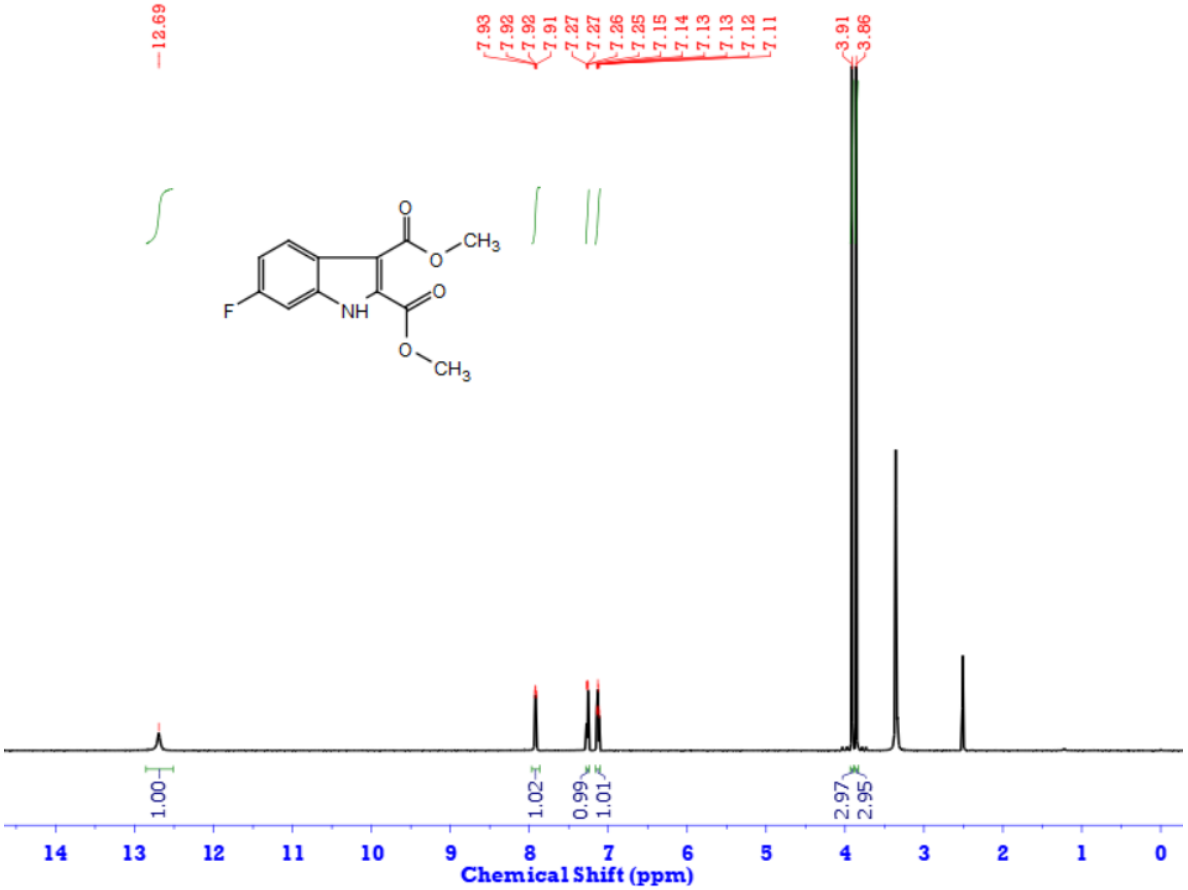
Sp(37). ^{1}H NMR Spectrum of *9h* (diethyl 5-fluoro-1H-indole-2,3-dicarboxylate). (White crystalline solid) ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.01 (dd, *J* = 8.9, 5.3 Hz, 1H), 7.13 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.07 – 7.01 (m, 1H), 4.48 (q, *J* = 3.3 Hz, 4H), 4.47 (q, *J* = 3.3 Hz, 4H), 1.46 (t, *J* = 6 Hz, 3H), 1.45 – 1.41 (t, *J* = 6 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.0, 162.5, 160.9 (d, *J* = 4.1 Hz), 135.0, 128.6, 124.1, 123.5, 112.4, 111.9, 97.9, 97.8, 62.0, 60.9, 14.4, 14.2.[5]



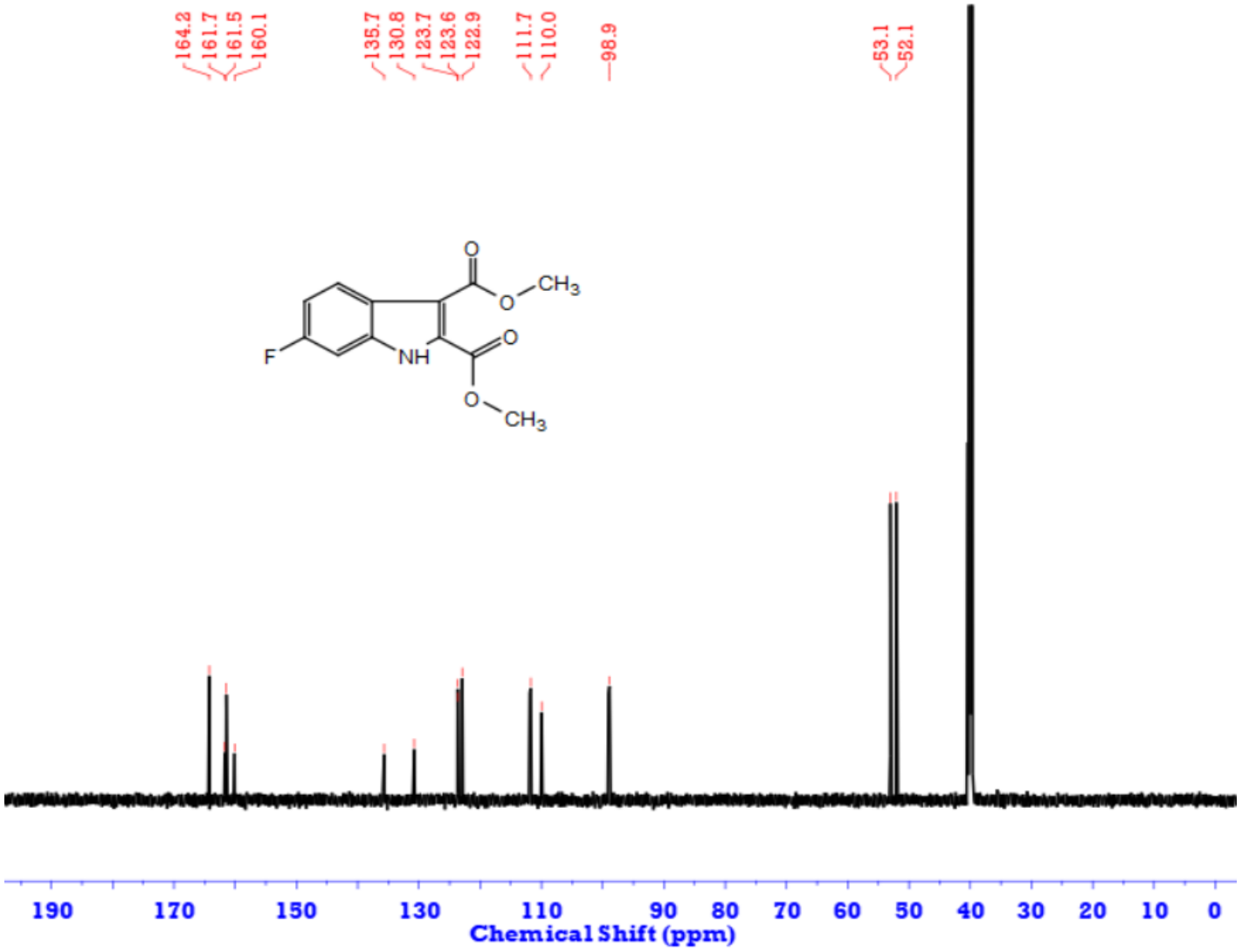
Sp(38). ^{13}C NMR Spectrum of *9h* (diethyl 5-fluoro-1H-indole-2,3-dicarboxylate)



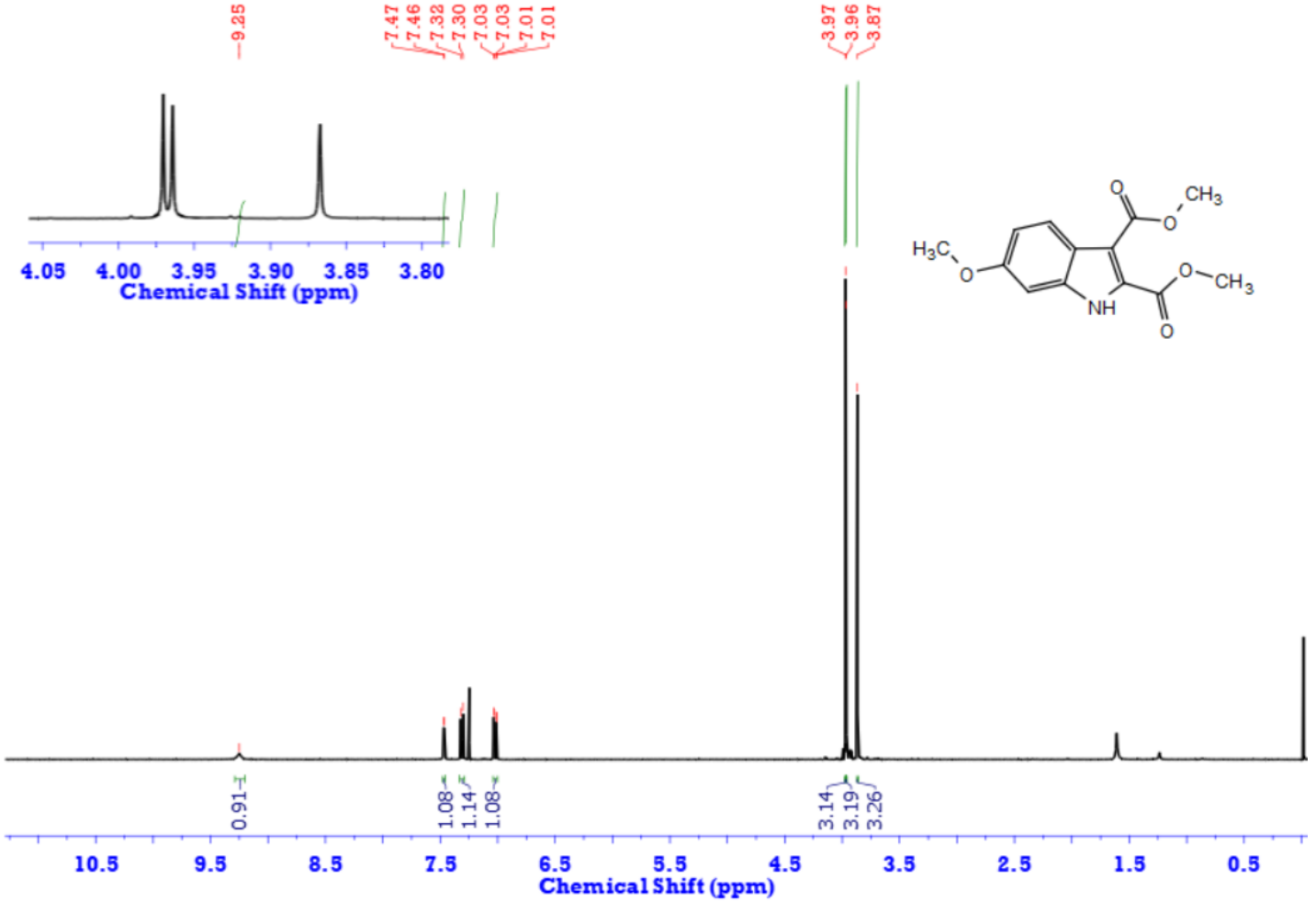
Sp(39). ^{1}H NMR Spectrum of *9g* (dimethyl 5-fluoro-1H-indole-2,3-dicarboxylate). (Pale yellow solid) ^{1}H NMR (600 MHz, DMSO) δ 12.69 (s, 1H), 7.92 (dd, *J* = 8.9, 5.4 Hz, 1H), 7.26 (dd, *J* = 9.4, 2.0 Hz, 1H), 7.13 (td, *J* = 9.6, 2.3 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (150 MHz, DMSO) δ 164.2, 161.7, 161.5, 160.1, 135.7, 130.8, 123.6 (d, *J* = 10.4 Hz), 122.9, 111.7, 110.0, 98.9, 53.1, 52.1.[5]



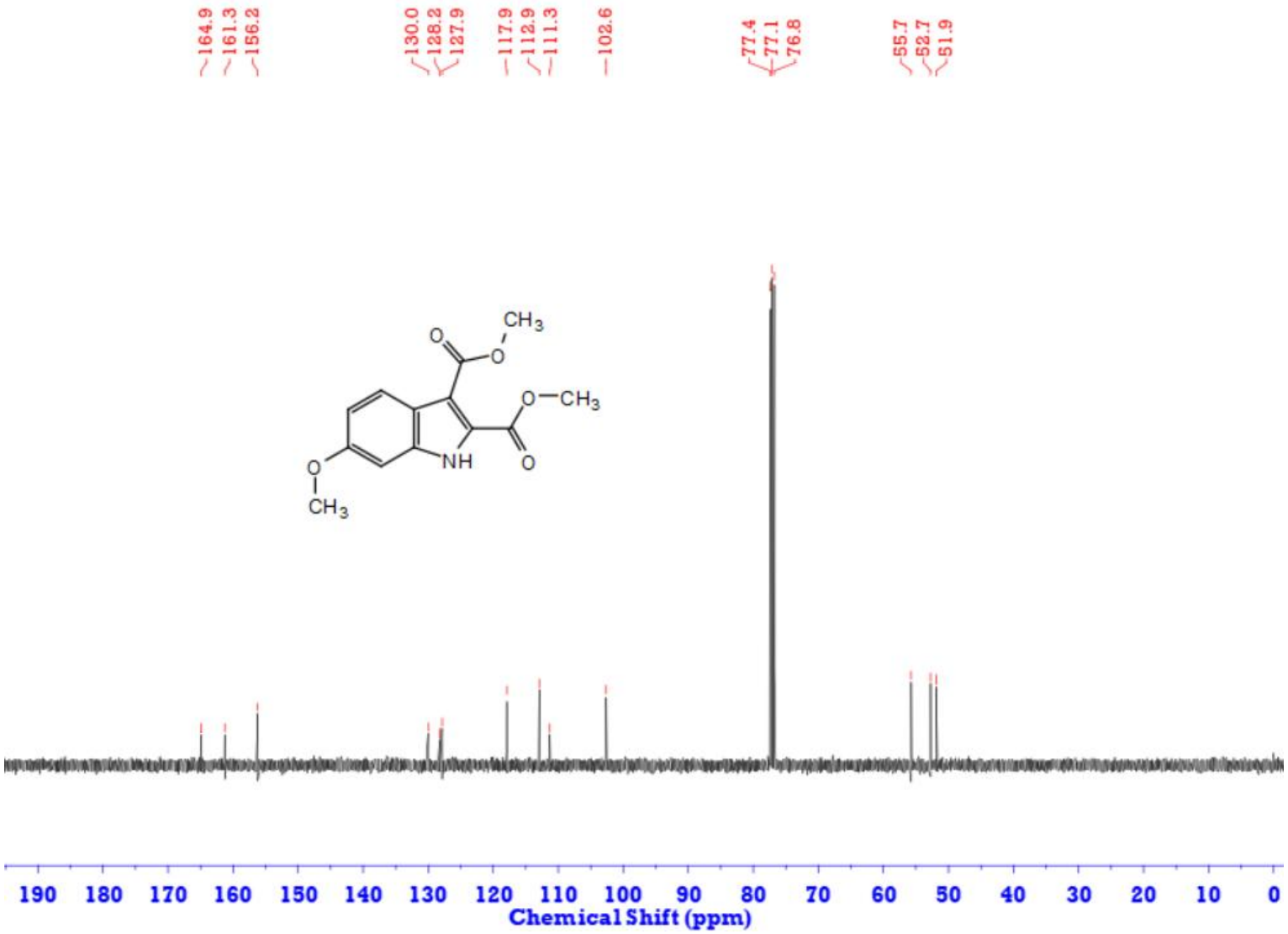
Sp(40). ^{13}C NMR Spectrum of *9g* (dimethyl 5-fluoro-1H-indole-2,3-dicarboxylate).


164.2
161.7
161.5
160.1
135.7
130.8
123.7
123.6
122.9
111.7
110.0
98.9
53.1
52.1
O
O
CH3
O
F
NH
O
CH3
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

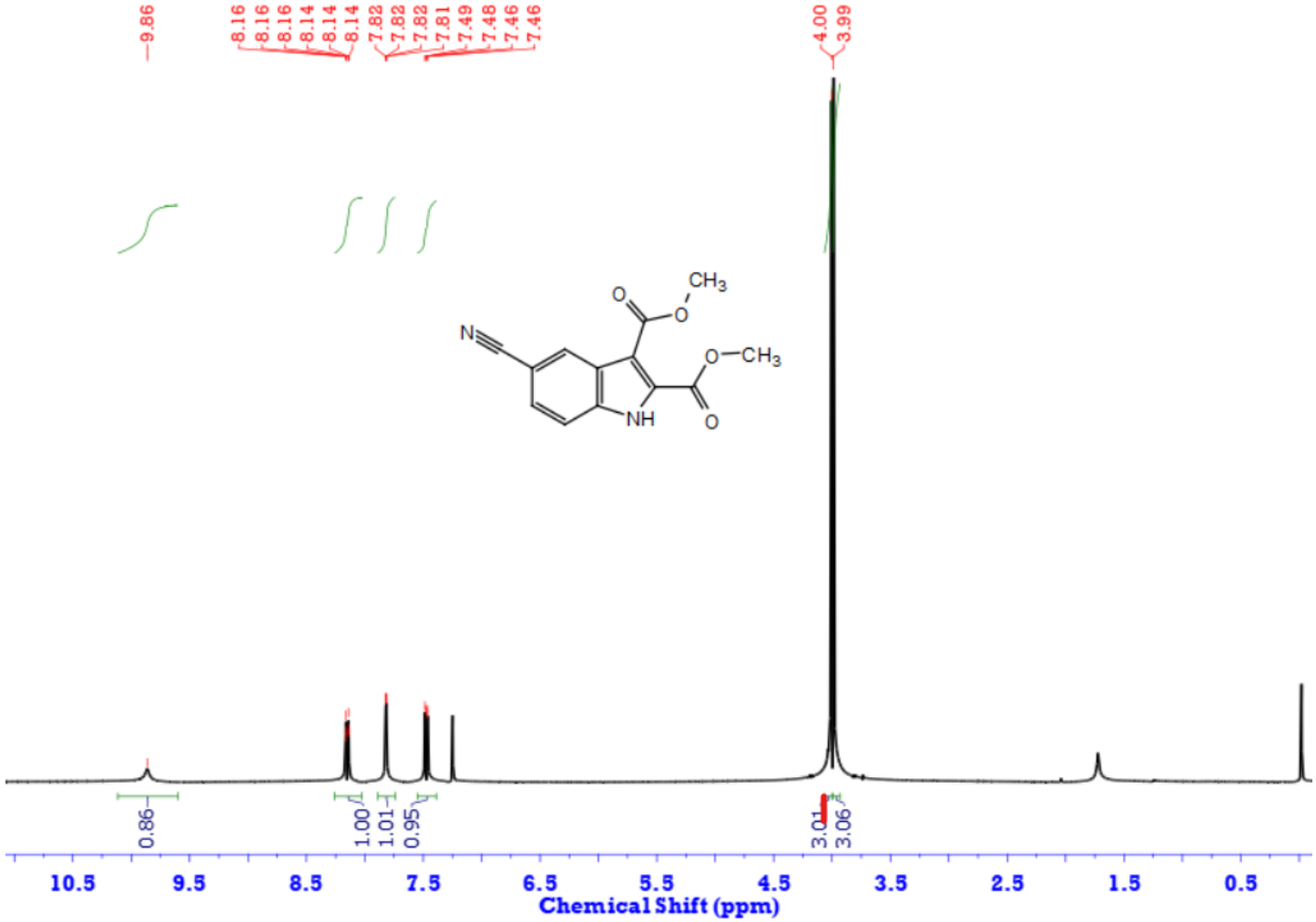
Sp(41). ^{1}NMR of 2m (dimethyl 5-methoxy-1H-indole-2,3-dicarboxylate) (White solid) (400 MHz, $CDCl_3$) δ 9.25 (s), 7.47 (d, *J* = 2.5 Hz), 7.31 (d, *J* = 9.0 Hz), 7.02 (dd, *J* = 9.0, 2.5 Hz), 3.97 (s), 3.96 (s), 3.87 (s). ^{13}C NMR (101 MHz , $CDCl_3$) δ 164.9, 161.3, 156.2, 130.0, 128.2, 127.9, 117.9, 112.9, 111.3, 102.6, 55.7, 52.7, 51.9.[5]



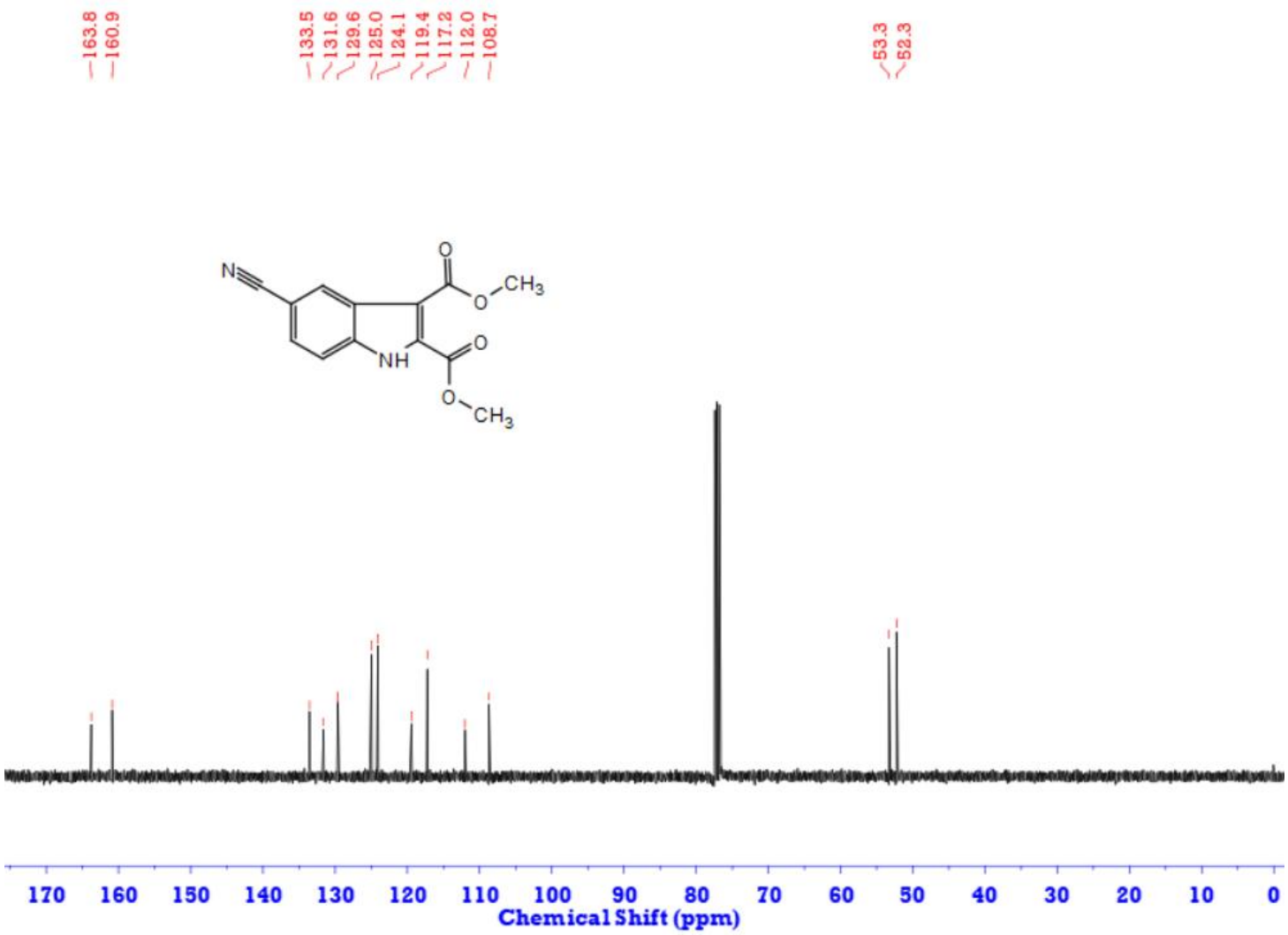
Sp42. ^{13}C NMR of 2m (dimethyl 5-methoxy-1H-indole-2,3-dicarboxylate)


164.9
161.3
156.2
130.0
128.2
127.9
117.9
112.9
111.3
102.6
77.4
77.1
76.8
55.7
52.7
51.9
CH3
O
O
O—CH3
NH
O
O
CH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

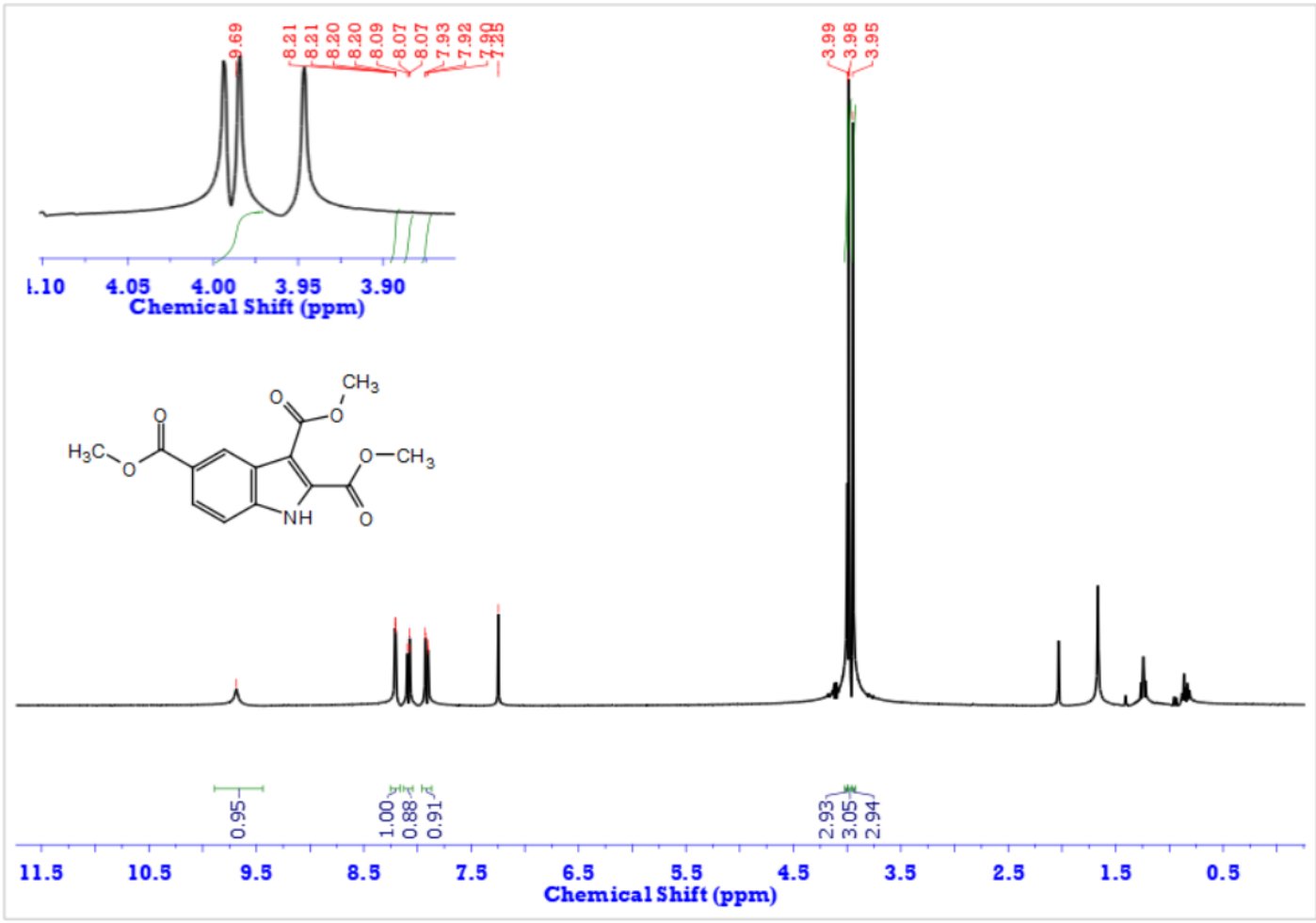
Sp43. ^{1}H NMR of *3n* (dimethyl 5-cyano-1H-indole-2,3-dicarboxylate, white solid) (400 MHz, $CDCl_3$) δ 9.86 (s), 8.15 (d, *J* = 8.6 Hz), 7.47 (dd, *J* = 8.5, 1.5 Hz), 4.00 (s), 3.99 (s). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.8, 160.9, 133.5, 131.6, 129.6, 125.0, 124.1, 119.4, 117.2, 112.0, 108.7, 53.3, 52.3. **Elemental Analysis (**Observed**) %N (**10.47%**), %C** (60.22%), %H (3.94%)., %O (25.37%).[17]



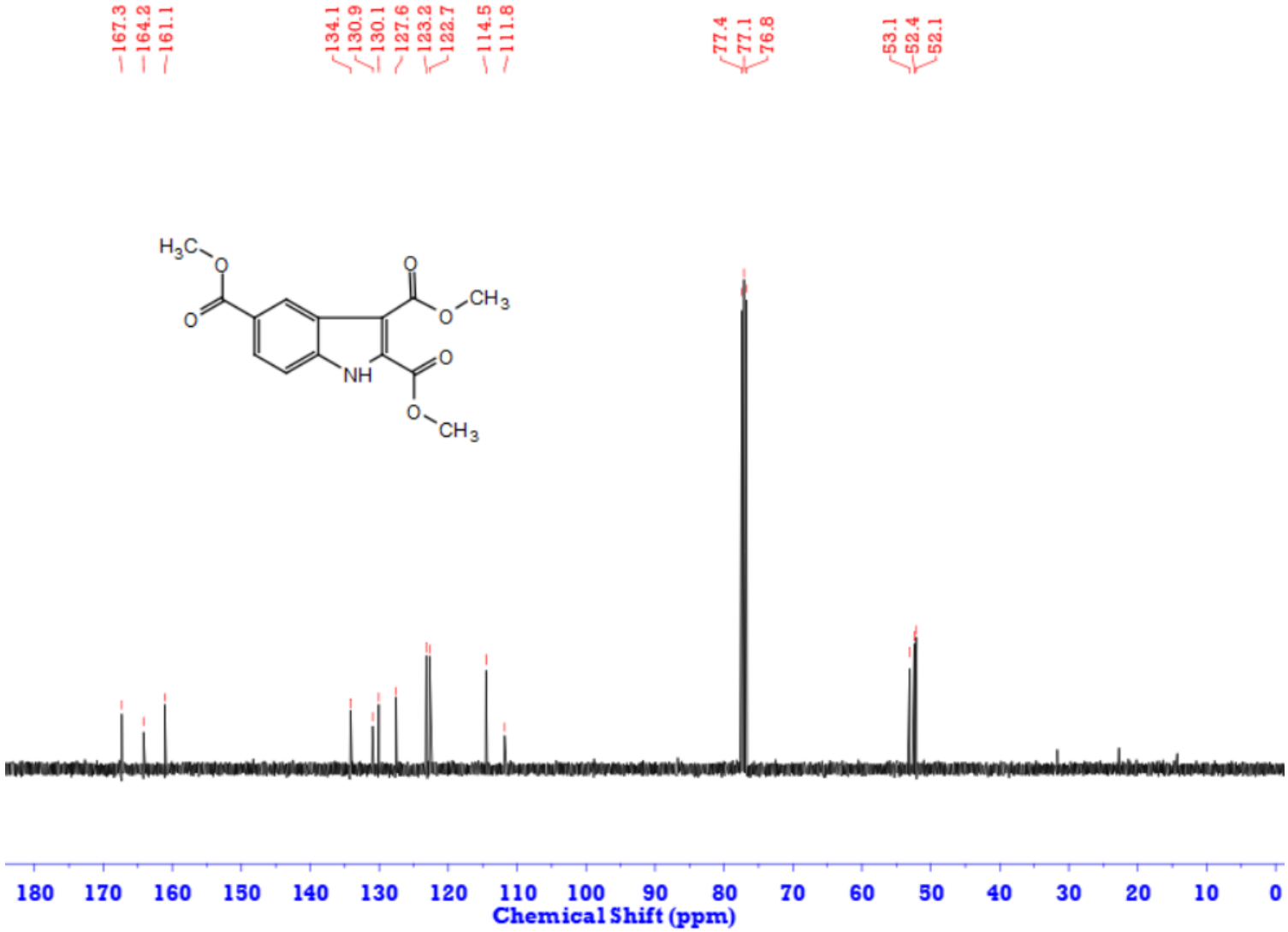
Sp44. ^{13}C NMR of *3n* (dimethyl 5-cyano-1H-indole-2,3-dicarboxylate.



Sp45. ^{1}H NMR of *3p* (trimethyl 1H-indole-2,3,5-tricarboxylate, white solid) (400 MHz, $CDCl_3$) δ 9.69 (s), 8.21 (dd, *J* = 1.6, 0.9 Hz), 8.14 – 8.05 (m), 7.91 (dd, *J* = 8.8, 1.7 Hz), 7.25 (s), 3.99 (s), 3.98 (s), 3.95 (s). ^{13}C NMR (101 MHz,) δ 167.3, 164.2 , 161.1, 134.1, 131.0, 130.1, 127.6, 123.2, 122.7, 114.5, 111.8, 53.1, 52.4, 52.1.[5]



Sp46. ^{13}C NMR of *3p* (trimethyl 1H-indole-2,3,5-tricarboxylate)



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