Supporting Information

An expedient route to tricyanovinylindoles and indolylmaleimides from *o*-alkynylanilines utilising DMSO as one-carbon synthon

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1. General information

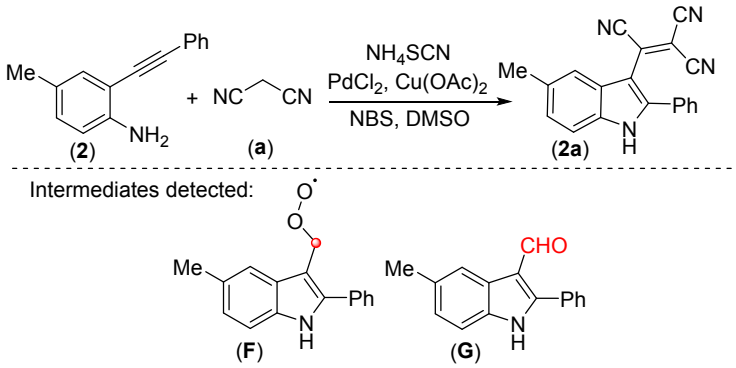
All the compounds were commercial grade and used without further purification. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ or DMSO with tetramethylsilane as an internal standard for ^1H NMR (400, 500 and 600 MHz) $CDCl_3$ solvent as an internal standard for ^{13}C NMR (100, 125 and 150 MHz). HRMS spectra were recorded using ESI mode (Q-TOF type Mass Analyser). IR spectra were recorded in KBr or neat. All UV experiments were performed at a probe concentration of 0.143 mM in 1 mL quartz cuvettes of path length 1 cm at 25 ^oC in UV/VIS Spectrometer. Photoluminescence were carried out at a concentration of 0.143 mM in 1 mL quartz cuvettes at 25 ^oC in Spectrofluorometer in HPLC grade acetonitrile solution.

2. Mechanistic Investigation

Analysis of reaction intermediates:

(A) *^1H NMR analysis*

To detect the intermediate species in the reaction mixture for this transformation ^1H NMR spectroscopy was performed. In this study (**2a**) was taken as a representative example. In a 5 mL oven-dried round bottom flask, 4-methyl-2-(phenylethynyl)aniline (**2**) (0.125 mmol, 26 mg), malanonitrile (**a**) (0.5 mmol, 33 mg), ammonium thiocyanate (0.25 mmol, 19 mg), $PdCl_2$ (7 mol%, 1.5 mg), $Cu(OAc)_2$ (7 mol%, 1.5mg) and *N*-bromosuccinimide (0.125 mmol, 22 mg) were taken in DMSO (1.0 mL) and was stirred on a preheated oil bath at 110 ^oC. Small aliquots of the reaction mixture were withdrawn at 10, 20, and 30 minutes. The crude product so obtained was used for ^1H NMR study in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H NMR (400 MHz).



Inference: In the ^1H NMR spectra, there is clear evidence of intermediates (**F**) and (**G**) from peaks at δ ~3.9 and ~12.6 ppm respectively. Moreover, as the reaction proceeds peak at ~3.9

ppm diminishes with a simultaneous increase in the peak at ~12.6 ppm. This confirms that the reaction is proceeding *via* the formation of (**F**) followed by (**G**).

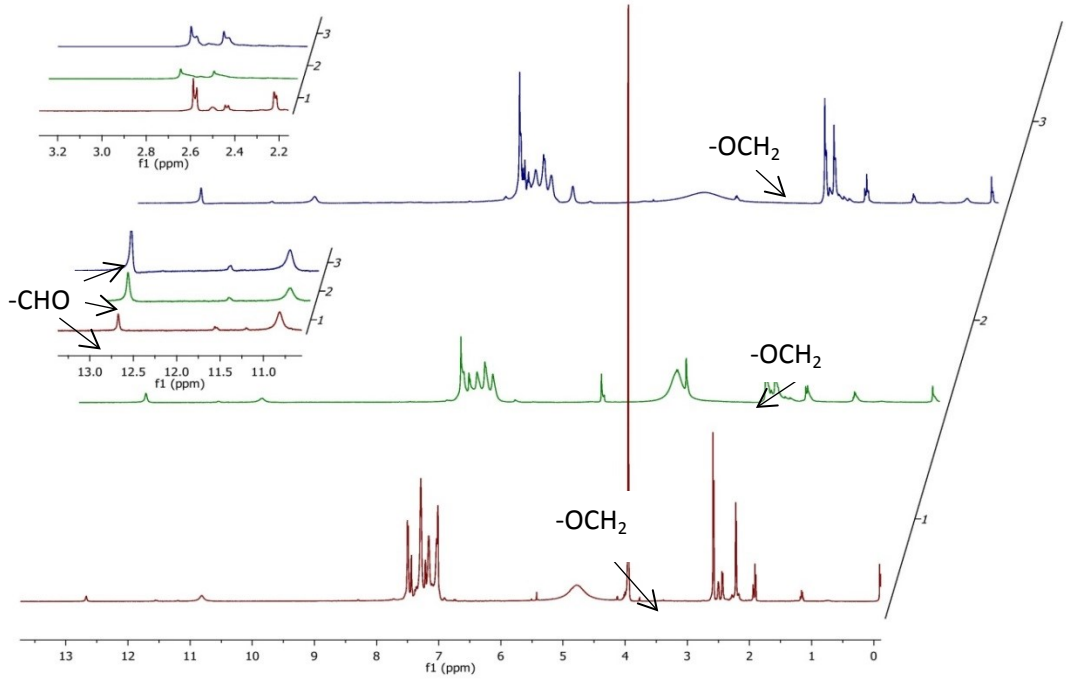


Fig. S1 ^{1}H NMR analysis of reaction mixture at (1) 10 min; red (2) 20 min; green (3) 30 min.; blue.

(B) ***IR analysis of reaction mixture***

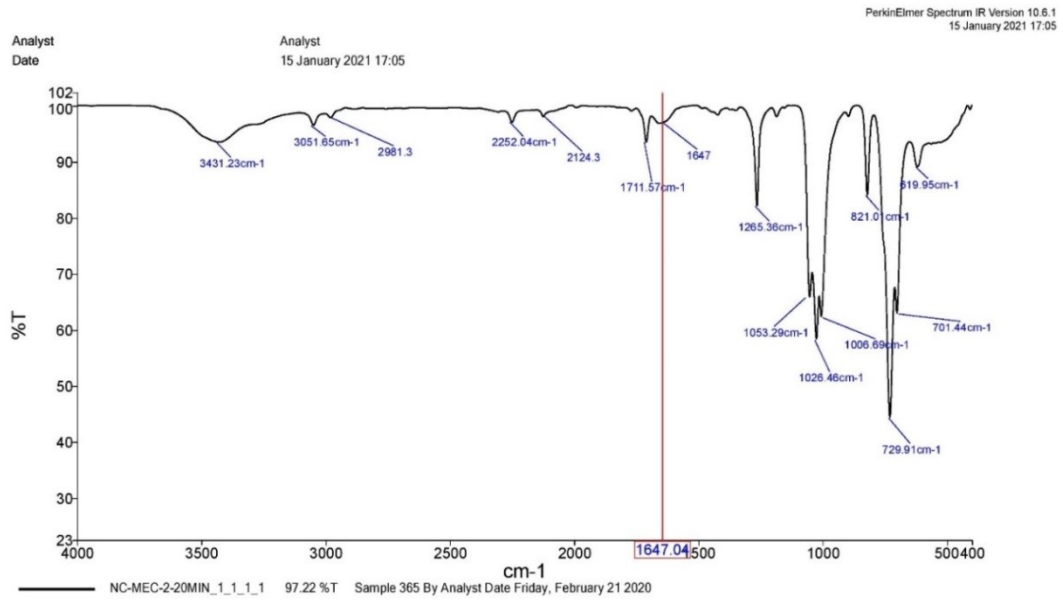


Fig. S2 IR analysis of reaction mixture

Inference: The appearance of a peak at 1711 cm^{-1} in the IR spectrum taken during the course of the reaction indicates the involvement of carbonyl moiety in the intermediates.

(C) *ESI-MS analysis*

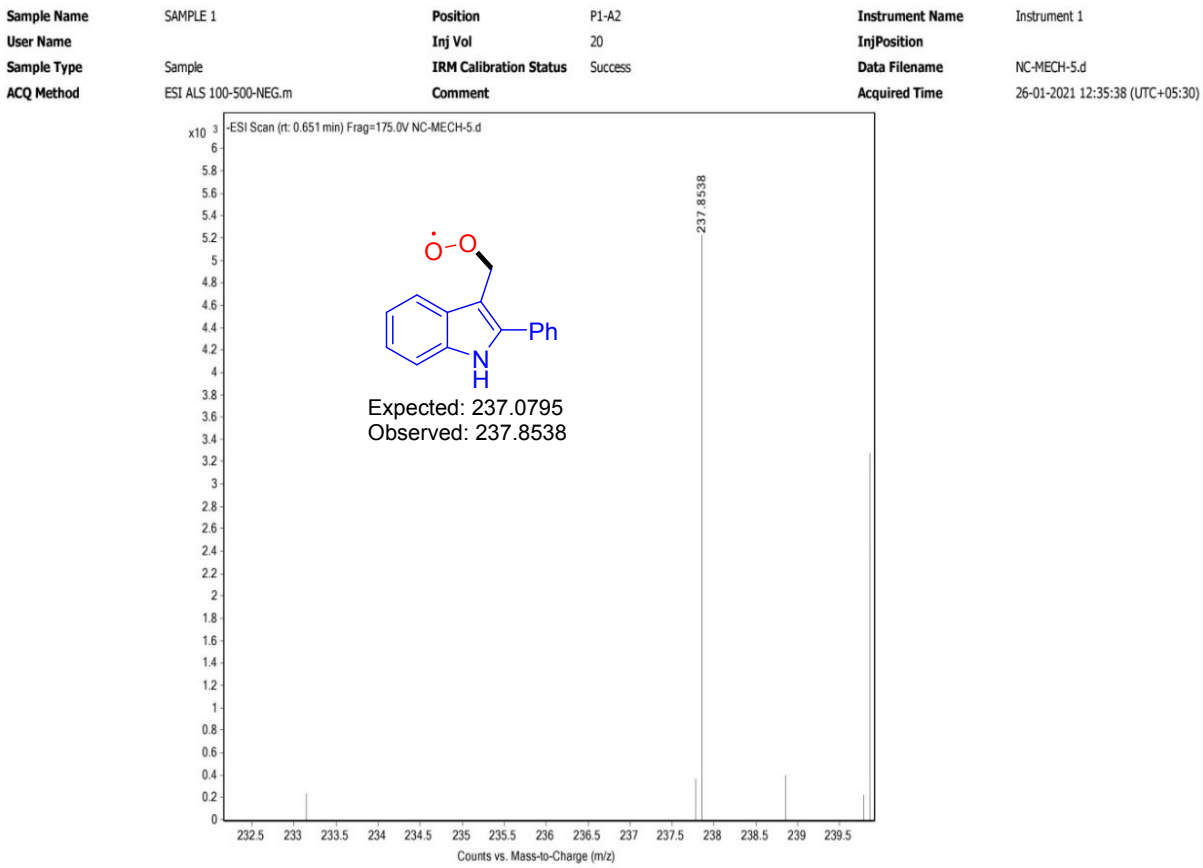
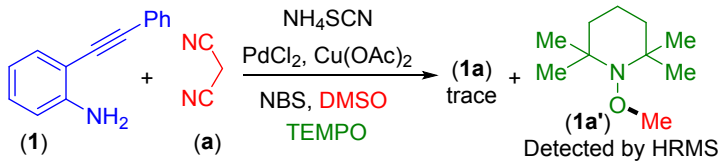


Fig. S3 ESI-MS analysis of reaction intermediate

(D) *Radical-trapping experiment*:



In a 5 mL oven-dried round bottom flask, 2-(phenylethynyl)aniline (**1**) (0.125 mmol, 24 mg), malanonitrile (**a**) (0.5 mmol, 33 mg), ammonium thiocyanate (0.25 mmol, 19 mg), $PdCl_2$ (7 mol%, 1.5 mg), $Cu(OAc)_2$ (7 mol%, 1.5 mg), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 2 equiv., 39 mg), and *N*-bromosuccinimide (0.125 mmol, 22 mg) were taken in DMSO (1 mL) and was stirred on a preheated oil bath at 110 °C. A small aliquot of the reaction mixture was withdrawn at 1 h and diluted with 60:40 acetonitrile : water mixture (1 mL) and subjected to HRMS. The HRMS analysis of this reaction aliquot shows HRMS values for methylated-TEMPO adduct (**1b'**). This observation infers the generation of methyl radical in the reaction which is expected to arise from DMSO.

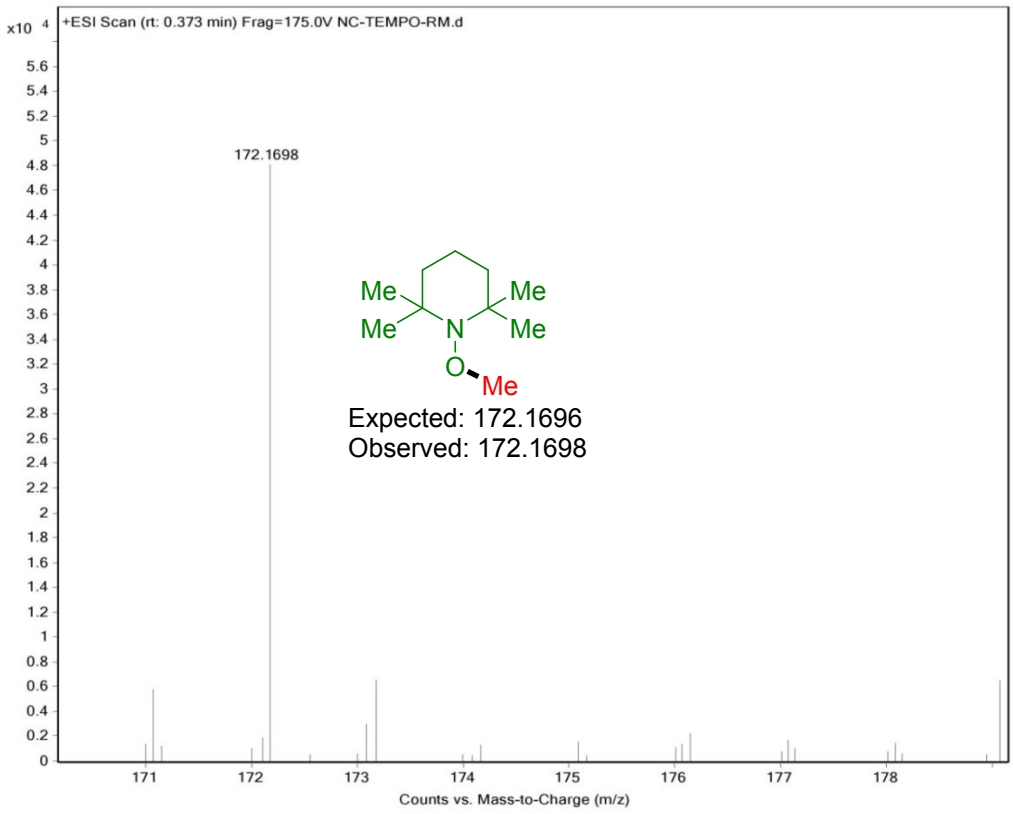
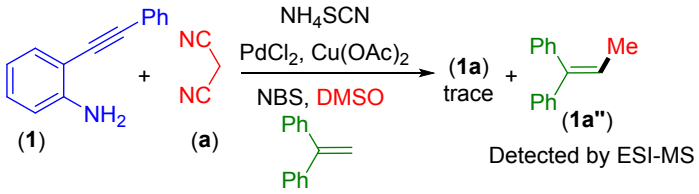


Fig. S4 HRMS analysis of methylated-TEMPO adduct



In a 5 mL oven-dried round bottom flask, 2-(phenylethynyl)aniline (**1**) (0.125 mmol, 24 mg), malanonitrile (**a**) (0.5 mmol, 33 mg), ammonium thiocyanate (0.25 mmol, 19 mg), $PdCl_2$ (7 mol%, 1.5 mg), $Cu(OAc)_2$ (7 mol%, 1.5 mg), 1,1-diphenylethylene (1 equiv., 22.5 mg), and *N*-bromosuccinimide (0.125 mmol, 22 mg) were taken in DMSO (1 mL) and was stirred on a preheated oil bath at 110 ^oC. A small aliquot of the reaction mixture was withdrawn at 1 h and diluted with 60:40 acetonitrile : water mixture (1 mL) and subjected to ESI-MS. The ESI-MS analysis of this reaction aliquot shows ESI-MS values for methylated-1,1-diphenylethylene adduct (**1a"**). This observation infers the generation of methyl radical in the reaction which is expected to arise from DMSO.

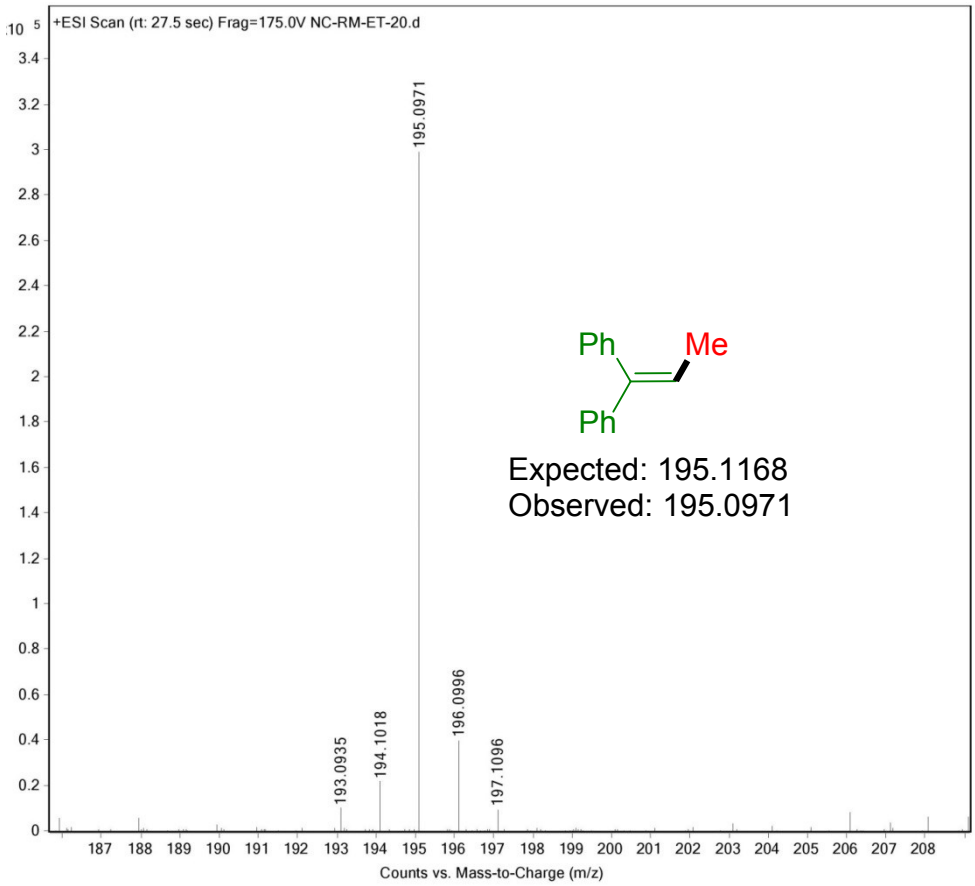


Fig. S5. HRMS analysis of methylated-1,1-diphenylethylene adduct

3. Crystallographic Description:

Diffraction data were collected at 292 K with MoKα radiation (λ = 0.71073 Å) using a Bruker Nonius SMART APEX CCD diffractometer equipped with a graphite monochromator and Apex CD camera. The SMART software was used for data collection and for indexing the reflections and determining the unit cell parameters. Data reduction and cell refinement were performed using SAINT1,2 software and the space groups of these crystals were determined from systematic absences by XPREP and further justified by the refinement results. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL-973 software. All the non-H atoms were refined in the anisotropic approximation against F2 of all reflections.

1. G. M. Sheldrick, SADABS, 1996, based on the method described in: R. H. Blessing, *Acta Crystallogr.* 1995, **A51**, 33–38.

2. SMART and SAINT, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.

3. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112–122.

Crystallographic description of 2-(5-fluoro-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (19a)

M.F. = $C_{20}H_{11}FN_4$, crystal dimensions 0.26 x 0.22 x 0.24 mm, M_r = 326.33, monoclinic space, group P 21/c, a = 11.4106 (7), b = 14.3958 (14), c = 9.9664 (5) Å, α = 90°, β = 94.167° (6) , γ = 90°, V = 1632.8 (2) Å^3, Z = 4, ρ_{calcd} = 1.327 g/cm^3, μ = 0.090 mm^{-1}, F(000) = 672.0, refinement method = full-matrix least-squares on F^2, final R indices [$I > 2\sigma(I)$]: R_1 = 0.0521 (1842), wR_2 = 0.1383 (3709), goodness of fit = 1.000. CCDC No = 2051416 for 2-(5-fluoro-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile **(19a)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

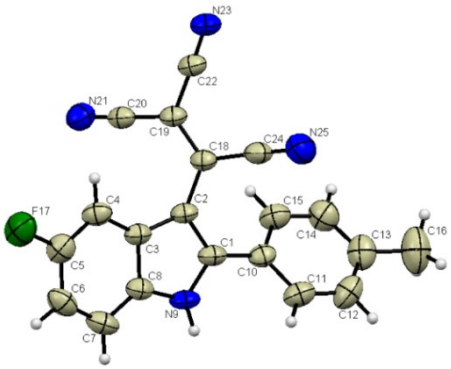


Fig. S6 ORTEP diagram of (**19a**) (CCDC 2051416).

4. Photophysical Studies:

Photophysical studies such as UV-vis and photoluminescence were conducted on few selected compounds. The absorption λ_{abs} and the emission λ_{em} spectra of the compounds were measured in 0.143 mM acetonitrile solution. The UV-vis and fluorescence emission spectra of these compounds (**2a**, **8a**, **9a**, **13a**, **22a**, **23a**, **25a**) are presented in Fig. 1 and their results are described in Table S2. As evident from the UV-vis spectra, most compounds exhibit three distinct absorption maxima. The fluorescence emission spectra infer that the compounds **25a**, **8a** and **9a** show maximum fluorescence intensity, thus they may find potential application in various fields of research.

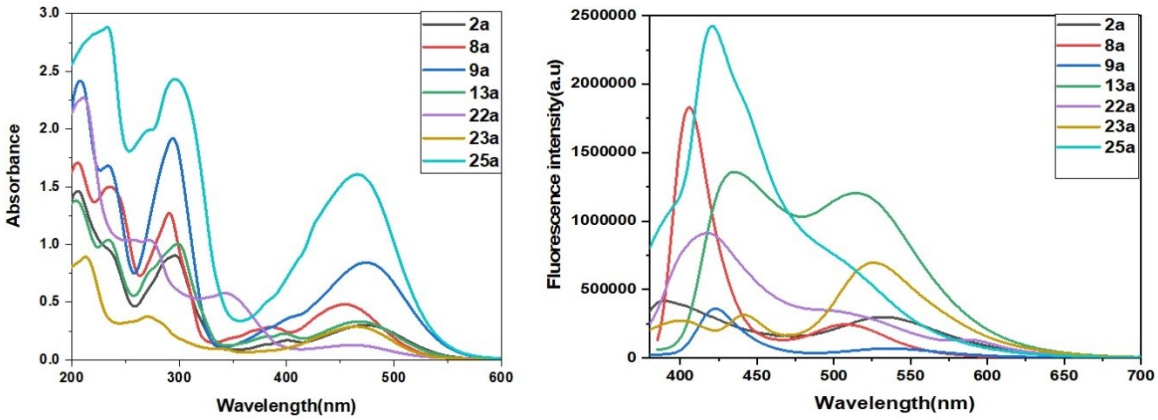
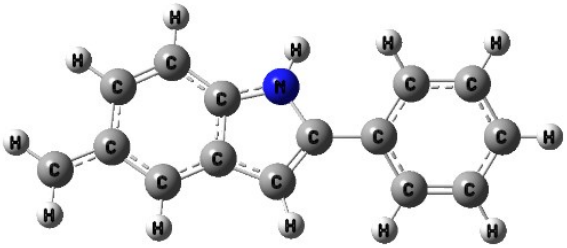


Fig. S7 UV-vis spectra (left) and Photoluminescence spectra (right) of **2a**, **8a**, **9a**, **13a**, **22a**, **23a**, **24a** in 0.143 mM CH_3CN solution.

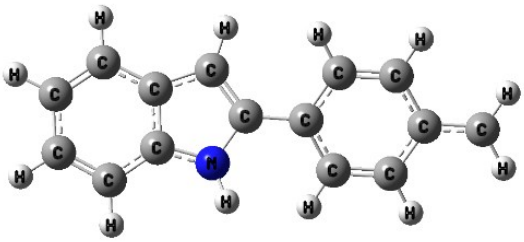
Table S2 UV-vis and Photoluminescence Parameters

Entry	**Compound**	**Colour under UV lamp (365 nm)**	**λ_{abs} (nm)**	**$\varepsilon \times 10^3$ (L mol^{-1} cm^{-1})**	**λ_{em} (nm)**
1	**2a**	Yellow	296, 399, 475	6.33, 1.17, 2.10	533
2	**8a**	Blue	233, 291, 454	10.48, 9.14, 3.36	410
3	**9a**	Orange red	234, 294, 474	11.85, 13.49, 5.90	422, 538
4	**13a**	Greenish yellow	233, 298, 468	7.27, 7.03, 2.32	435, 515
5	**22a**	Greenish yellow	272, 343, 464	7.37, 4.08, 0.89	417, 510
6	**23a**	Green	271, 465	2.66, 2.06	526
7	**25a**	Blue	233, 293, 462	20.13, 17.0, 11.18	421

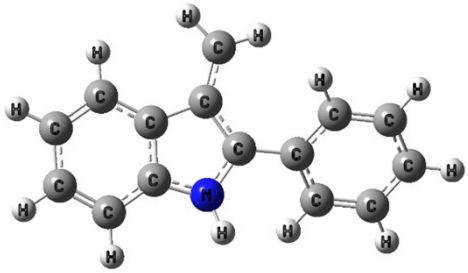
5. DFT calculation:



Radical_I: 28 atoms, 109 electrons, neutral, doublet



Radical_II: 28 atoms, 109 electrons, neutral, doublet



Radical_III: 28 atoms, 109 electrons, neutral, doublet

Fig. S8 Methyl substituted radical studied for DFT.

Table S3. Thermodynamic parameters for the three possible radical species

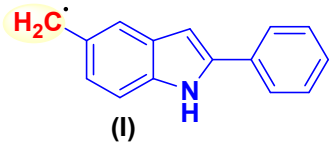
Species	Rel. E (kcal.mol^{-1})	Rel. H (kcal.mol^{-1})	Comment
Radical_I	0.00	0.00	Least stable
Radical_II	-1.56	-1.58	Gain stability
Radical_III	-2.51	-35.32	Most stable

The -Me group present in 3-methyl-2-phenyl indole intermediate (**D**) is selectively getting oxidised even in the presence of other methyl groups (present in the phenyl part of the indole and 2-phenyl ring as in substrates **2** and **7**). The resultant methyl radical in 3-methyl-2-phenyl indole (**D**) is more stable compared to the corresponding radicals originating from **2** and **7** which is confirmed by DFT calculations. From experimental results we can conclude

that out of the three radicals (Fig S5), radical_III is the one that has higher stability. In order to verify our results and to have a better understanding, we performed theoretical calculations using GAUSSIAN-16 program package.[1] The calculation has been performed with the help of the density functional theory approach along with the M06-2X functional and cc-pVTZ basis set for hydrogen, carbon and nitrogen atoms. The thermodynamics parameters for relative energy and enthalpy for these three radicals have been calculated and shown in Table S3, the values are expressed in kcal.mol^{-1}. As can be seen from the table, the relative energies, as well as the relative enthalpies, are the lowest for radical_III, signifying its greater stability.

Computational Details :

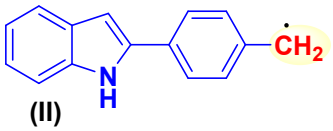
Radical I



(I)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.767212	1.057198	0.187799
2	6	0	2.524585	1.623091	0.284604
3	6	0	1.413325	0.786020	0.132350
4	6	0	1.544911	-0.600640	-0.101529
5	6	0	2.818134	-1.155426	-0.204445
6	6	0	3.954395	-0.339305	-0.061303
7	1	0	4.647548	1.676580	0.299410
8	1	0	2.406568	2.682543	0.469551
9	1	0	2.944273	-2.214442	-0.390338
10	6	0	-2.825218	1.073967	-0.363013
11	6	0	-4.211506	1.075949	-0.362726
12	6	0	-4.910920	-0.070792	-0.016651
13	6	0	-4.213059	-1.220459	0.331426
14	6	0	-2.828975	-1.221463	0.340517
15	6	0	-2.115212	-0.073897	-0.008698
16	1	0	-2.291936	1.963356	-0.673858
17	1	0	-4.745996	1.972978	-0.644249
18	1	0	-5.992071	-0.069928	-0.018228
19	1	0	-4.750937	-2.117212	0.607339
20	1	0	-2.287380	-2.109151	0.638437
21	6	0	0.216687	-1.129860	-0.182681
22	7	0	0.074428	1.072895	0.166699
23	1	0	-0.322549	1.951990	0.447326
24	6	0	-0.653149	-0.089315	-0.006043
25	6	0	5.252693	-0.870982	-0.156812
26	1	0	5.408178	-1.922709	-0.344042
27	1	0	6.120978	-0.239602	-0.045056
28	1	0	-0.061089	-2.149184	-0.389960

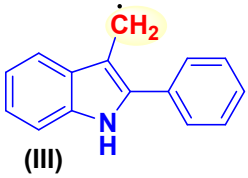
Radical II



(II)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.584023	-0.792331	0.126402
2	6	0	-3.362595	-1.427249	0.220821
3	6	0	-2.219831	-0.641478	0.093604
4	6	0	-2.282711	0.754335	-0.112003
5	6	0	-3.537997	1.367551	-0.211778
6	6	0	-4.671207	0.592773	-0.091242
7	1	0	-5.492091	-1.371928	0.219265
8	1	0	-3.296045	-2.494613	0.383791
9	1	0	-3.613563	2.434021	-0.377176
10	6	0	2.016952	-1.136197	-0.261411
11	6	0	3.388962	-1.195527	-0.256411
12	6	0	4.175237	-0.044024	0.002605
13	6	0	3.476896	1.167456	0.252774
14	6	0	2.107393	1.215680	0.249066
15	6	0	1.339878	0.066729	-0.006821
16	1	0	1.454493	-2.029776	-0.500376
17	1	0	3.890241	-2.132141	-0.463968
18	1	0	4.048775	2.063000	0.459258
19	1	0	1.601351	2.146528	0.466853
20	6	0	-0.936287	1.224287	-0.172133
21	7	0	-0.893273	-0.990671	0.130386
22	1	0	-0.543644	-1.891631	0.402746
23	6	0	-0.110841	0.139934	-0.011362
24	1	0	-5.646437	1.053957	-0.163404
25	6	0	5.569401	-0.098298	0.009731
26	1	0	6.158358	0.784894	0.206779
27	1	0	6.090050	-1.024453	-0.182514
28	1	0	-0.613932	2.234993	-0.355003

Radical III



(III)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.158108	-1.021718	-0.181549
2	6	0	2.916657	-1.629478	-0.237965
3	6	0	1.800001	-0.813540	-0.103674

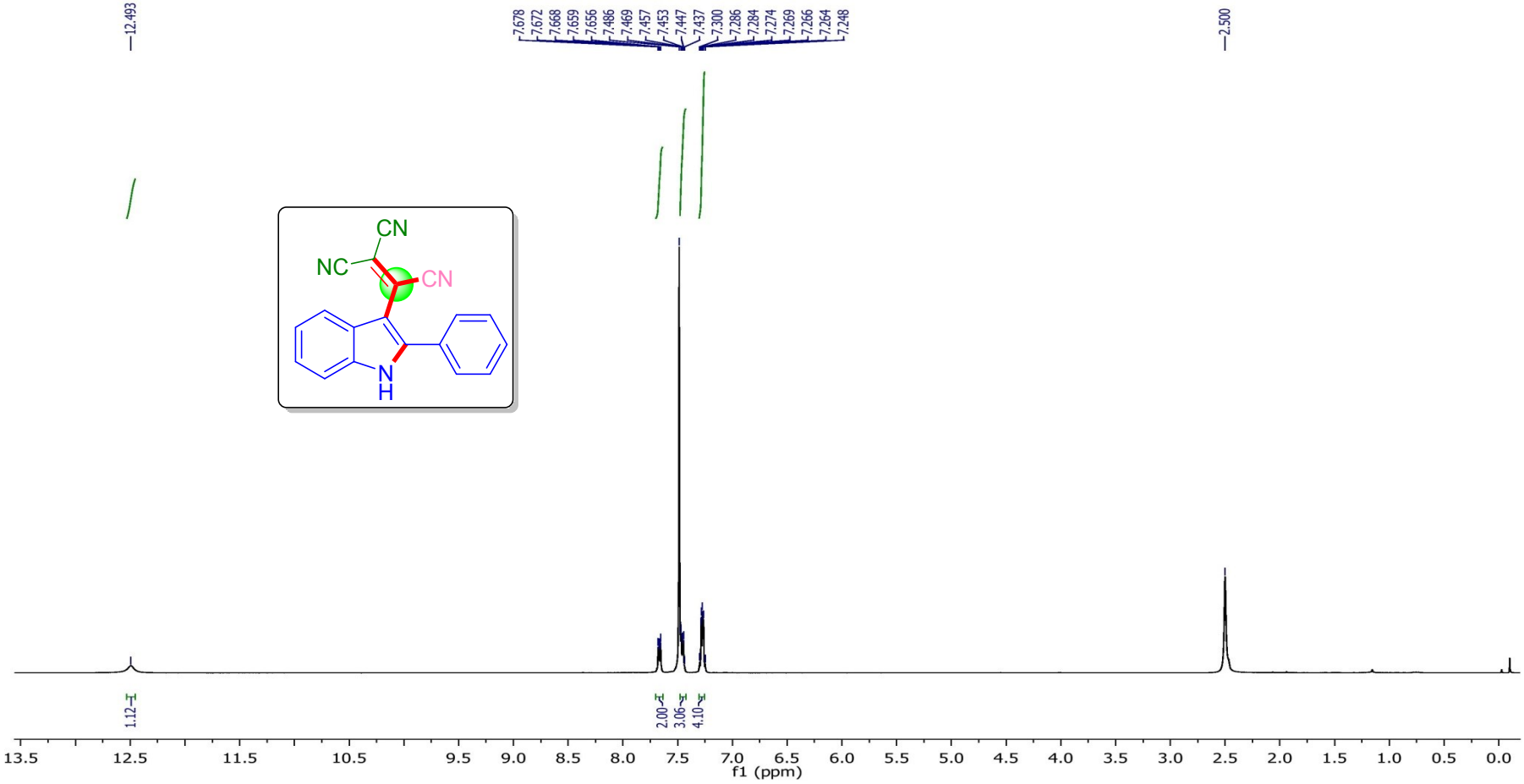
4	6	0	1.903402	0.573835	0.072293
5	6	0	3.162689	1.160926	0.136501
6	6	0	4.283014	0.359145	0.006928
7	1	0	5.048876	-1.626415	-0.282638
8	1	0	2.820672	-2.697768	-0.377442
9	1	0	3.264940	2.228734	0.279281
10	6	0	-2.407355	-1.225552	0.477108
11	6	0	-3.788148	-1.320482	0.449975
12	6	0	-4.551511	-0.277454	-0.057063
13	6	0	-3.918427	0.858642	-0.544324
14	6	0	-2.537690	0.956793	-0.524367
15	6	0	-1.757109	-0.082988	-0.006101
16	1	0	-1.824362	-2.028156	0.910710
17	1	0	-4.271364	-2.207468	0.836808
18	1	0	-4.504597	1.669380	-0.955465
19	1	0	-2.050396	1.824208	-0.946255
20	6	0	0.550361	1.113118	0.164095
21	7	0	0.459369	-1.139626	-0.106002
22	1	0	0.089404	-2.024308	-0.407712
23	6	0	0.222301	2.427774	0.434552
24	1	0	1.000779	3.165084	0.558807
25	1	0	-0.796575	2.744168	0.587847
26	6	0	-0.308202	0.000835	0.007517
27	1	0	5.268474	0.801340	0.049640
28	1	0	-5.629989	-0.350553	-0.075117

Reference

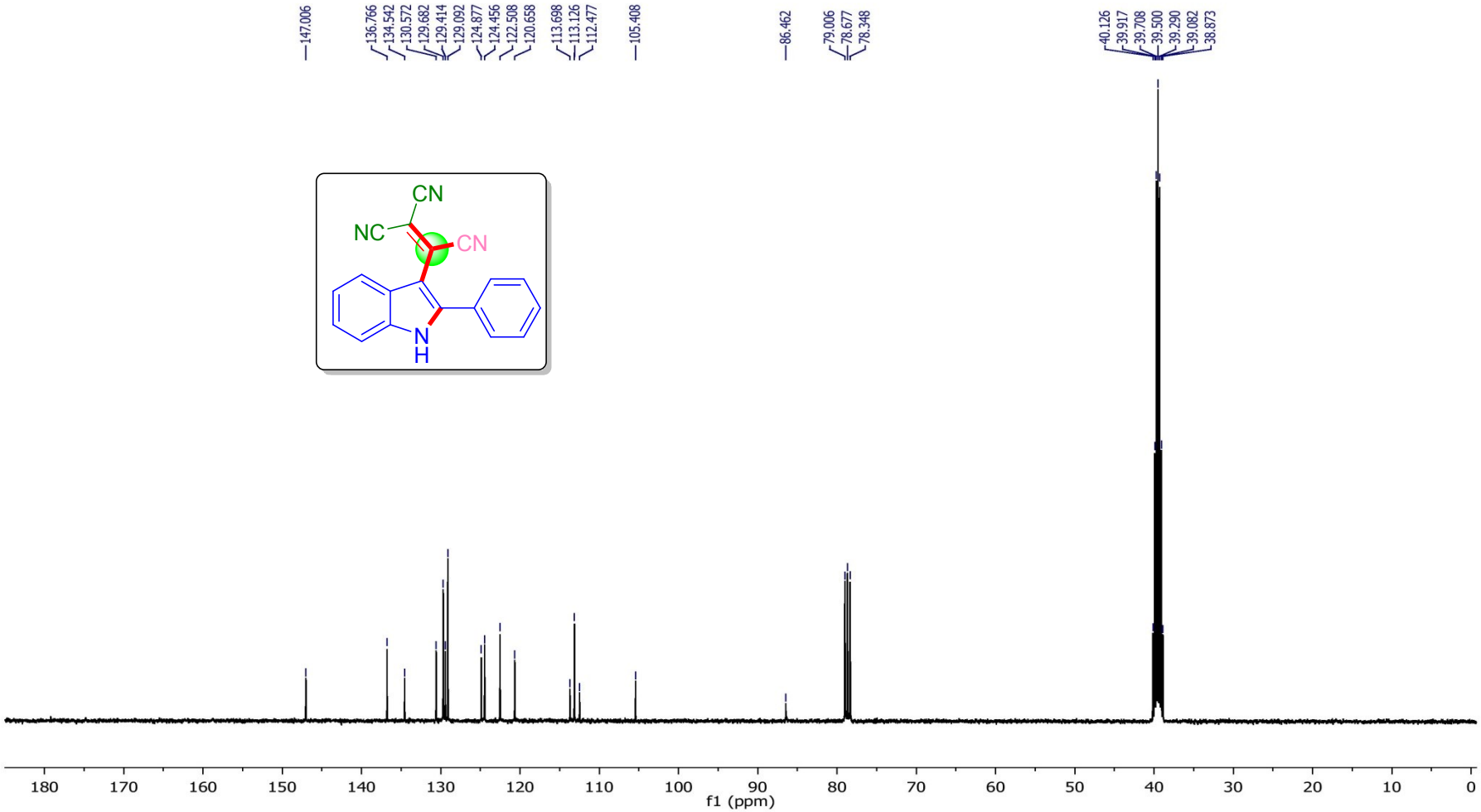
1. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

Spectra of all compounds

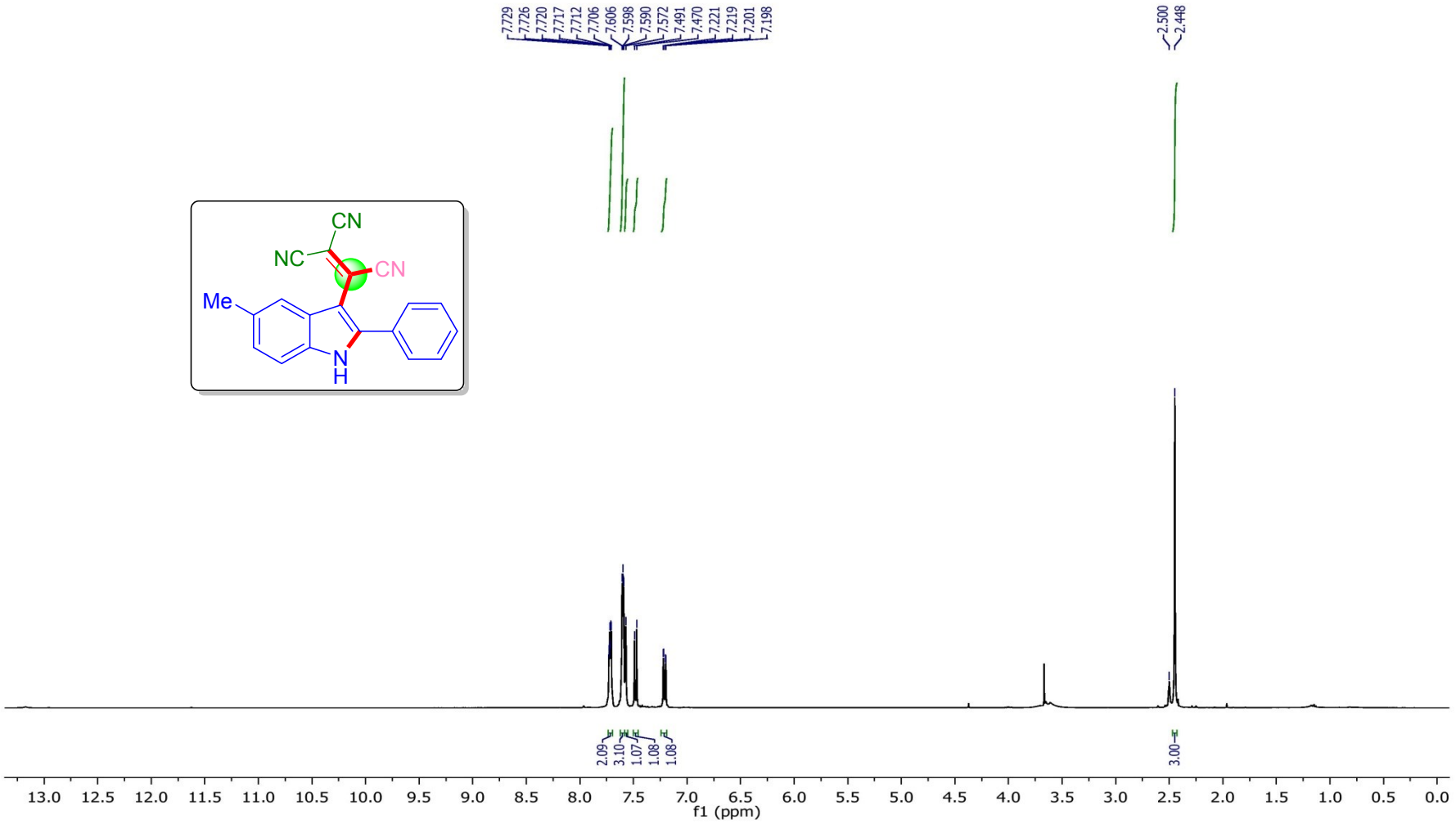
2-(2-Phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (1a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



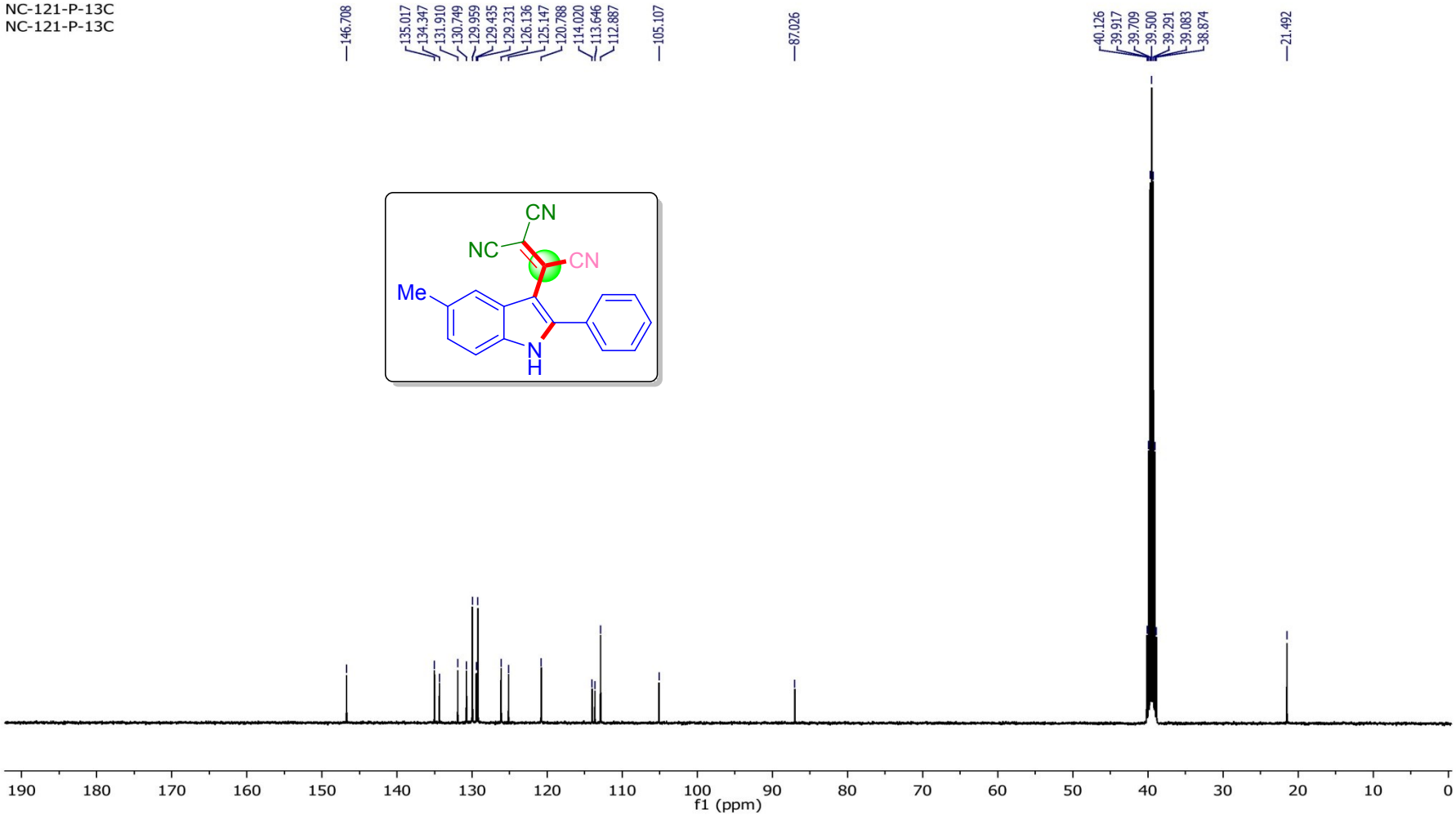
2-(2-Phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (1a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



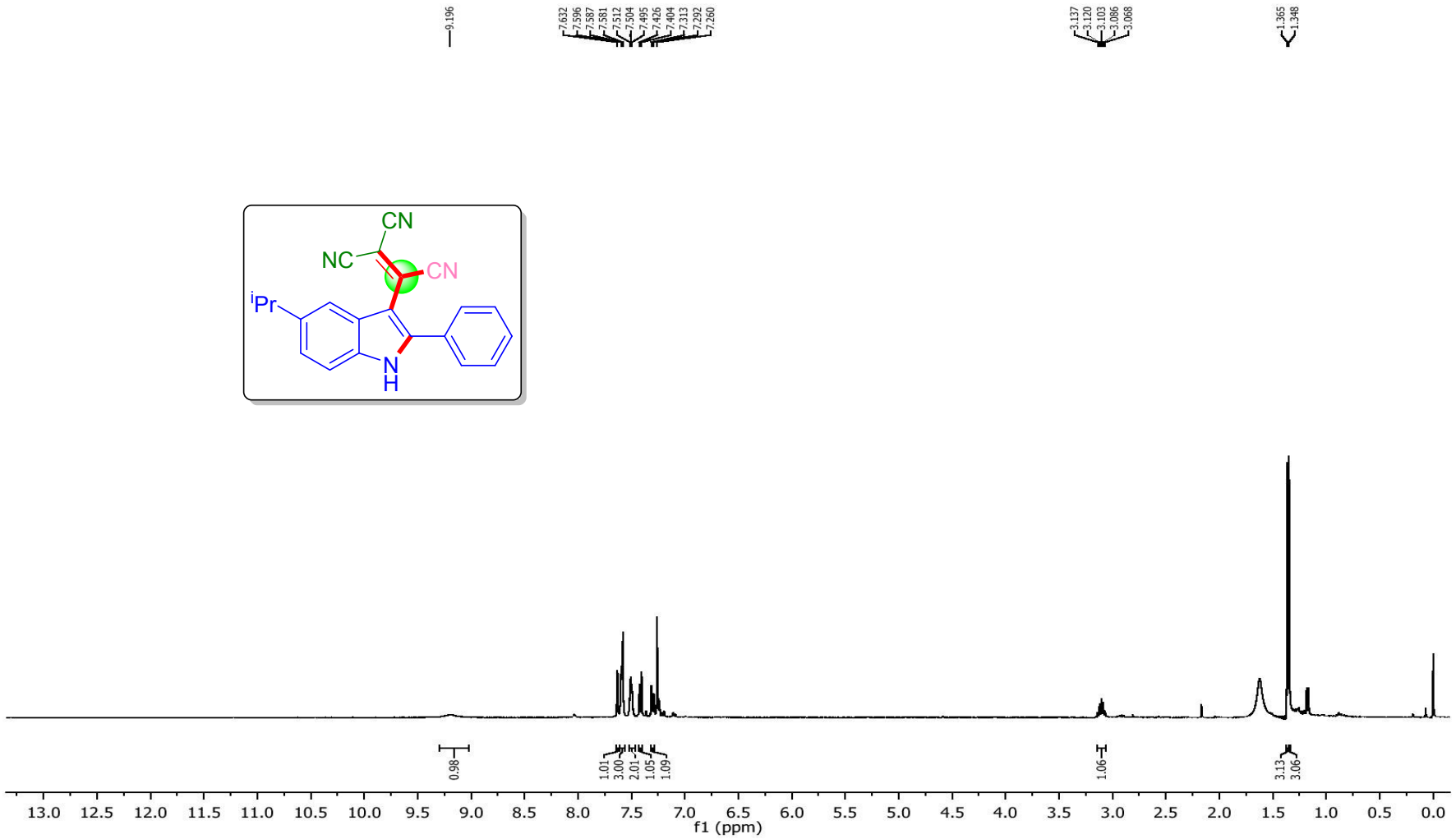
2-(5-Methyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (2a): ^{1}H NMR (400 MHz, DMSO)



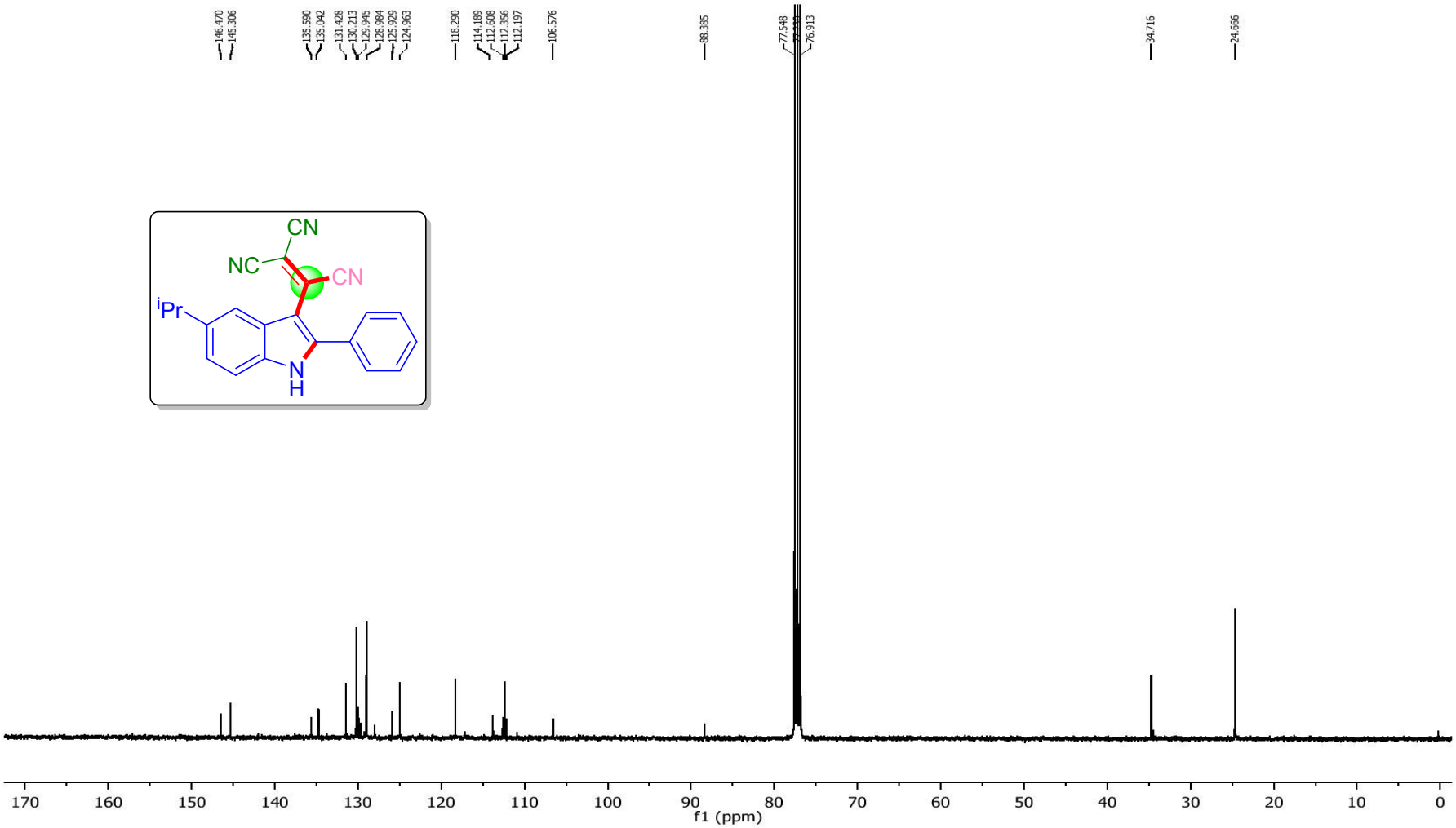
2-(5-Methyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (2a): ^{13}C NMR (100 MHz, DMSO)



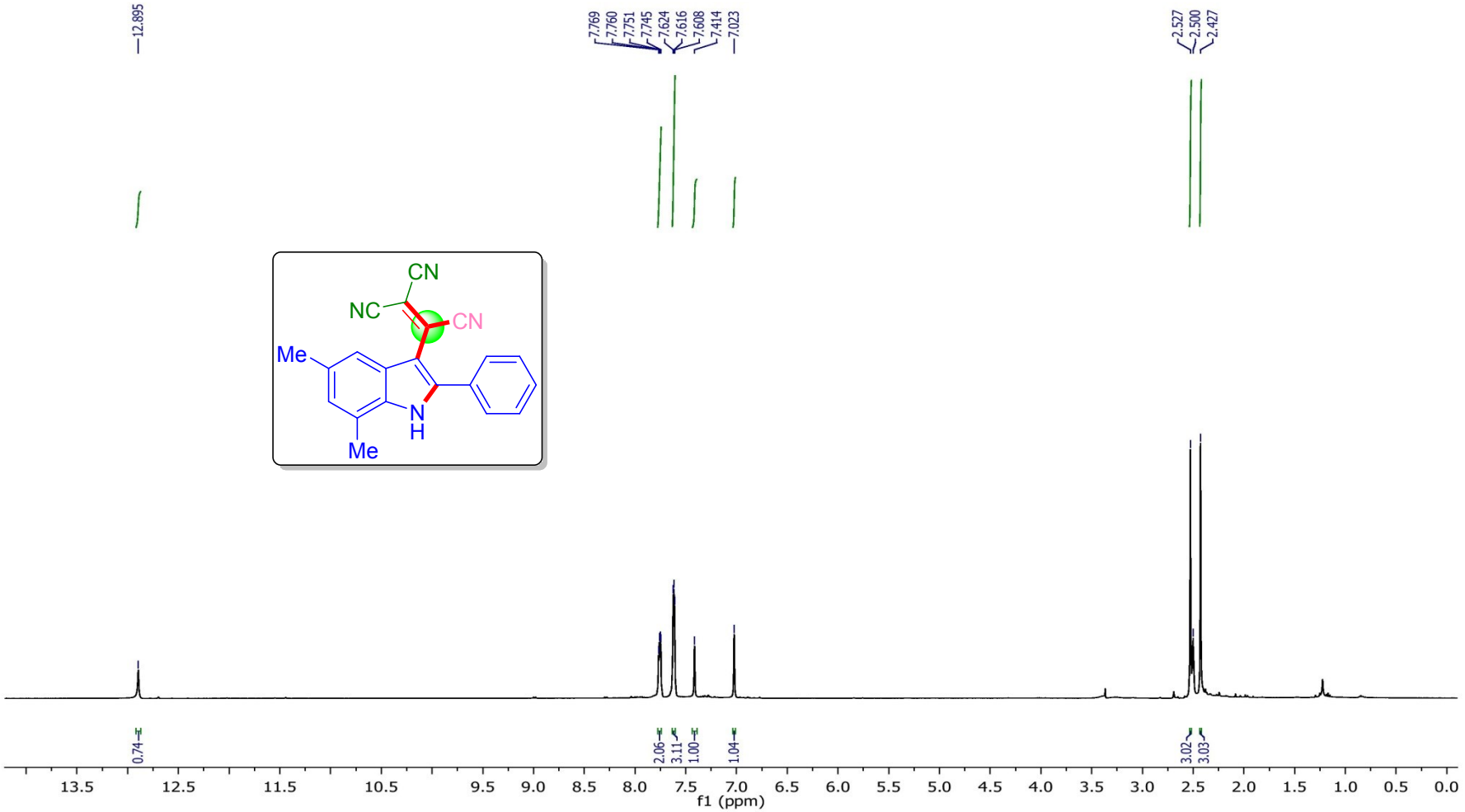
2-(5-Isopropyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (3a): ^{1}H NMR (400 MHz, $CDCl_3$)



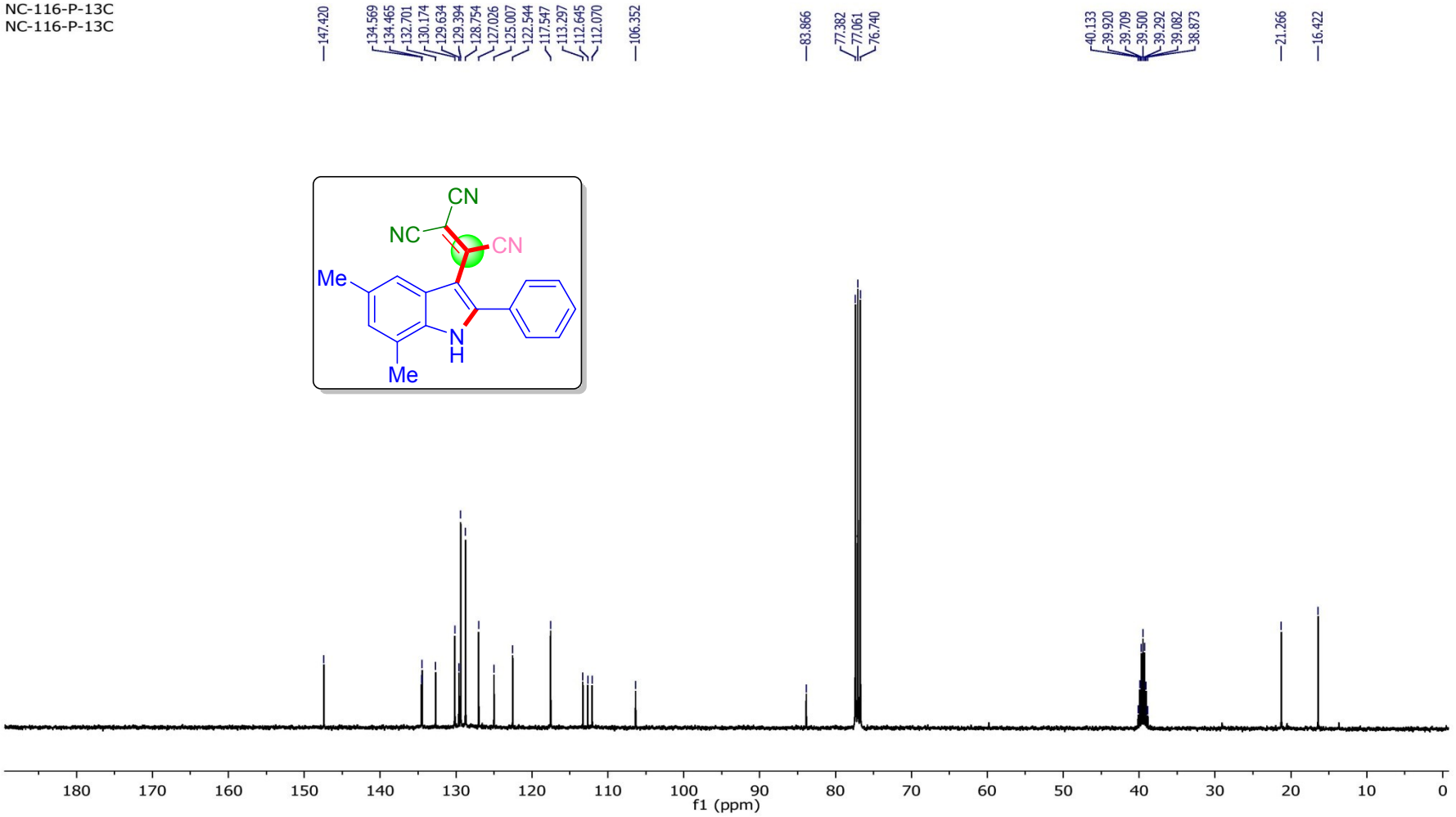
2-(5-Isopropyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (3a): ^{13}C NMR (100 MHz, $CDCl_3$)



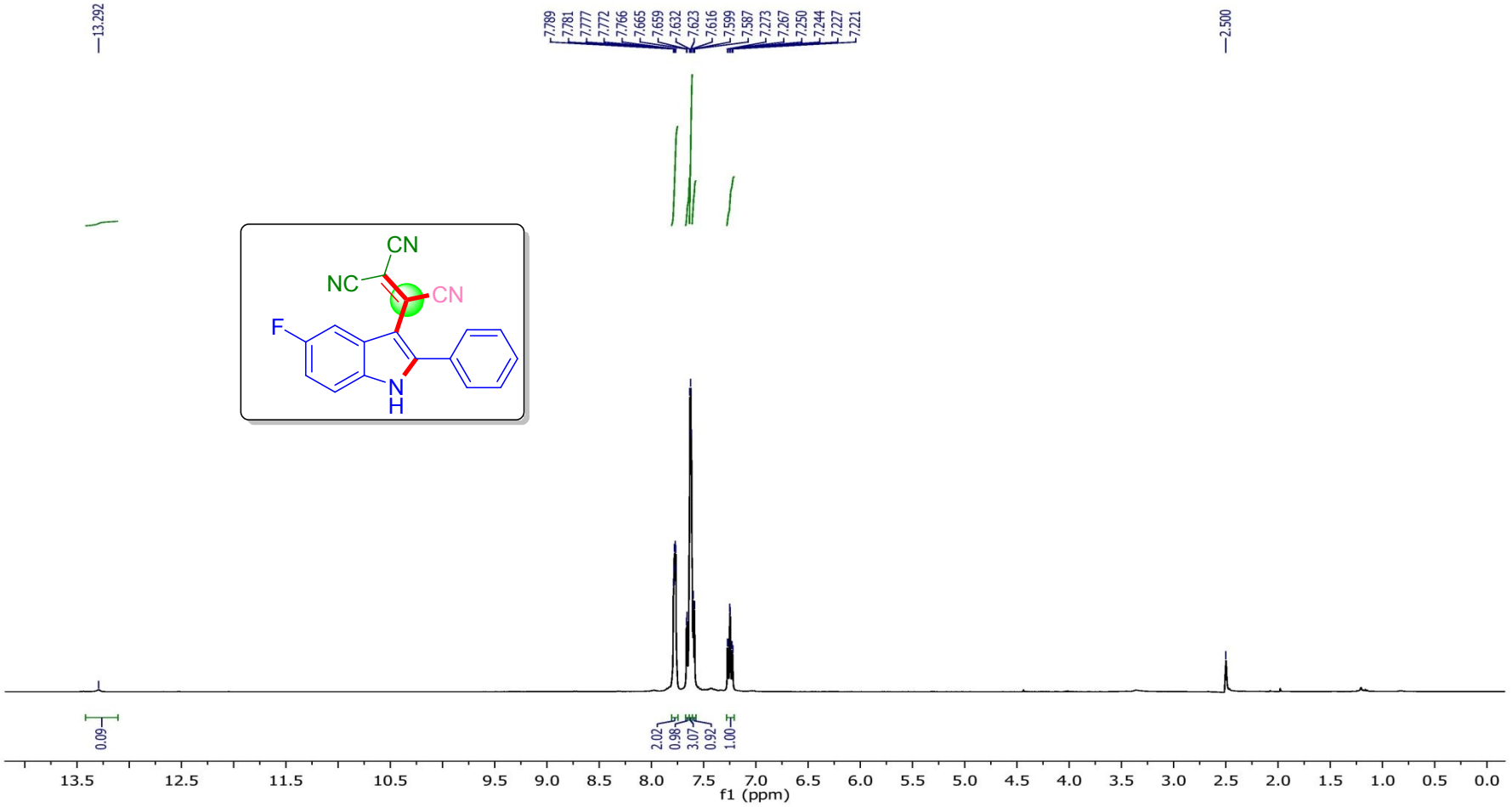
2-(5,7-Dimethyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (4a): ^{1}H NMR (400 MHz, $CDCl_3$ +DMSO)



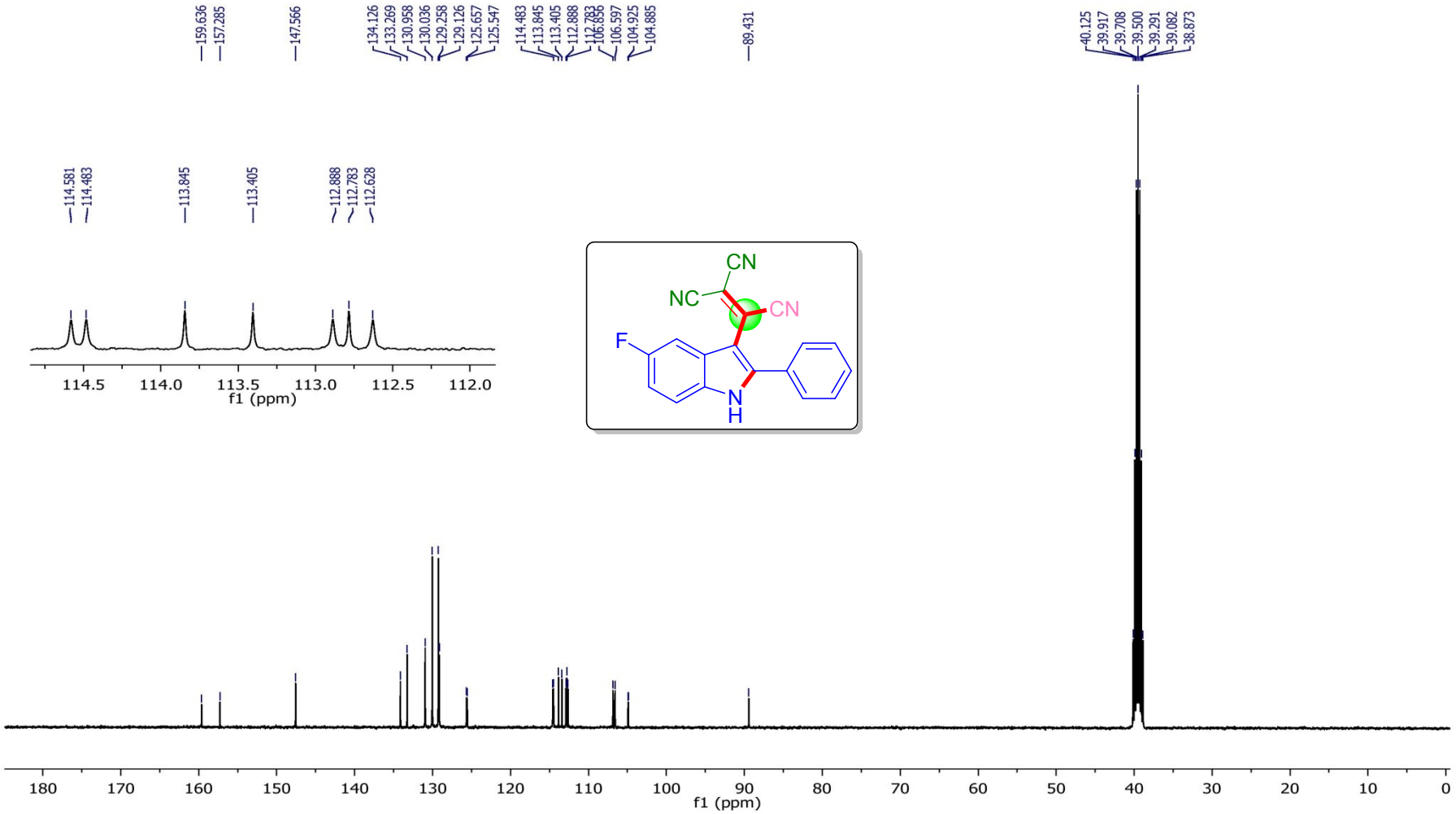
2-(5,7-Dimethyl-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (4a): ^{13}C NMR (100 MHz, $CDCl_3$ +DMSO)



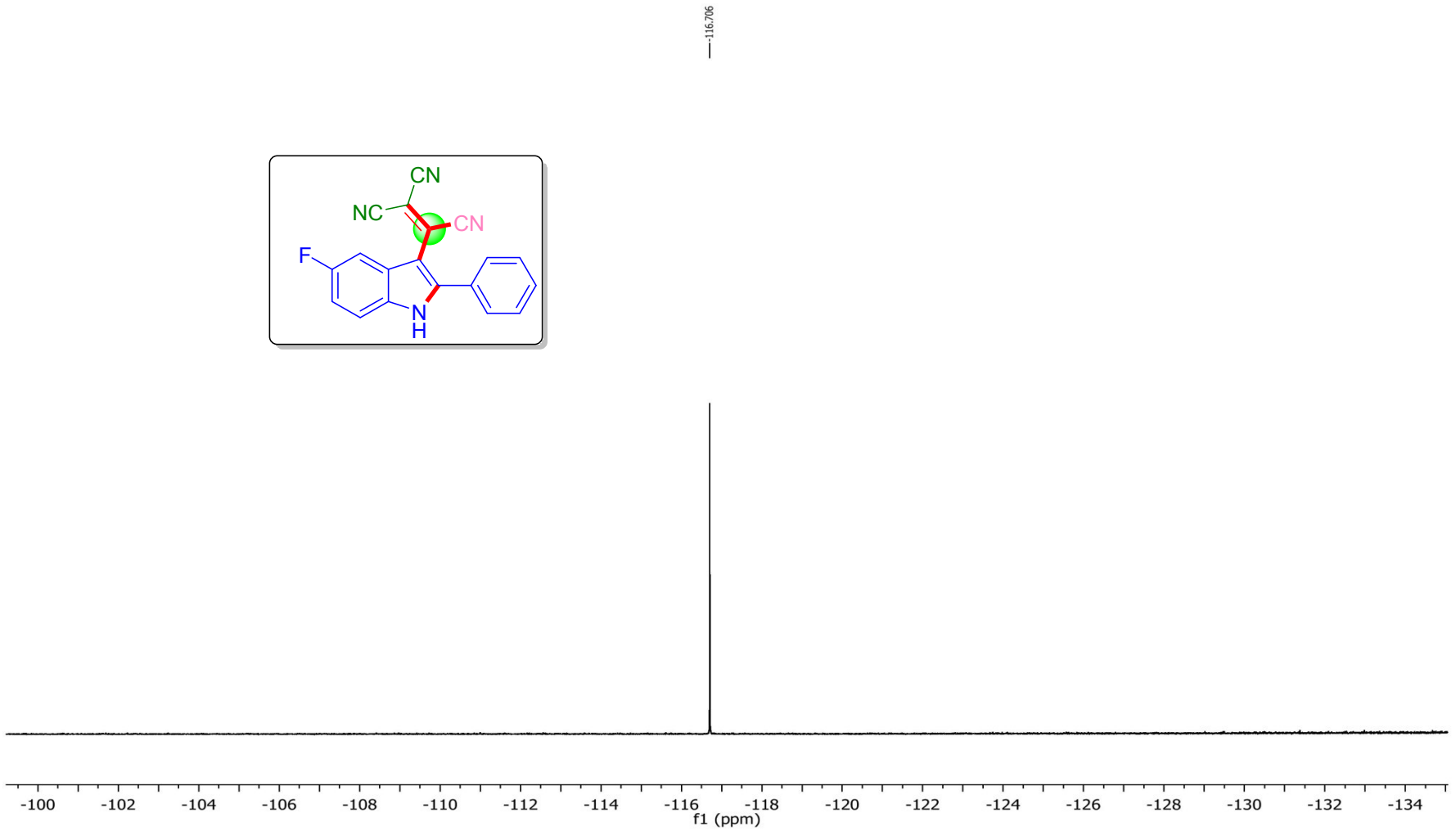
2-(5-Fluoro-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (5a): ^{1}H NMR (400 MHz, DMSO)



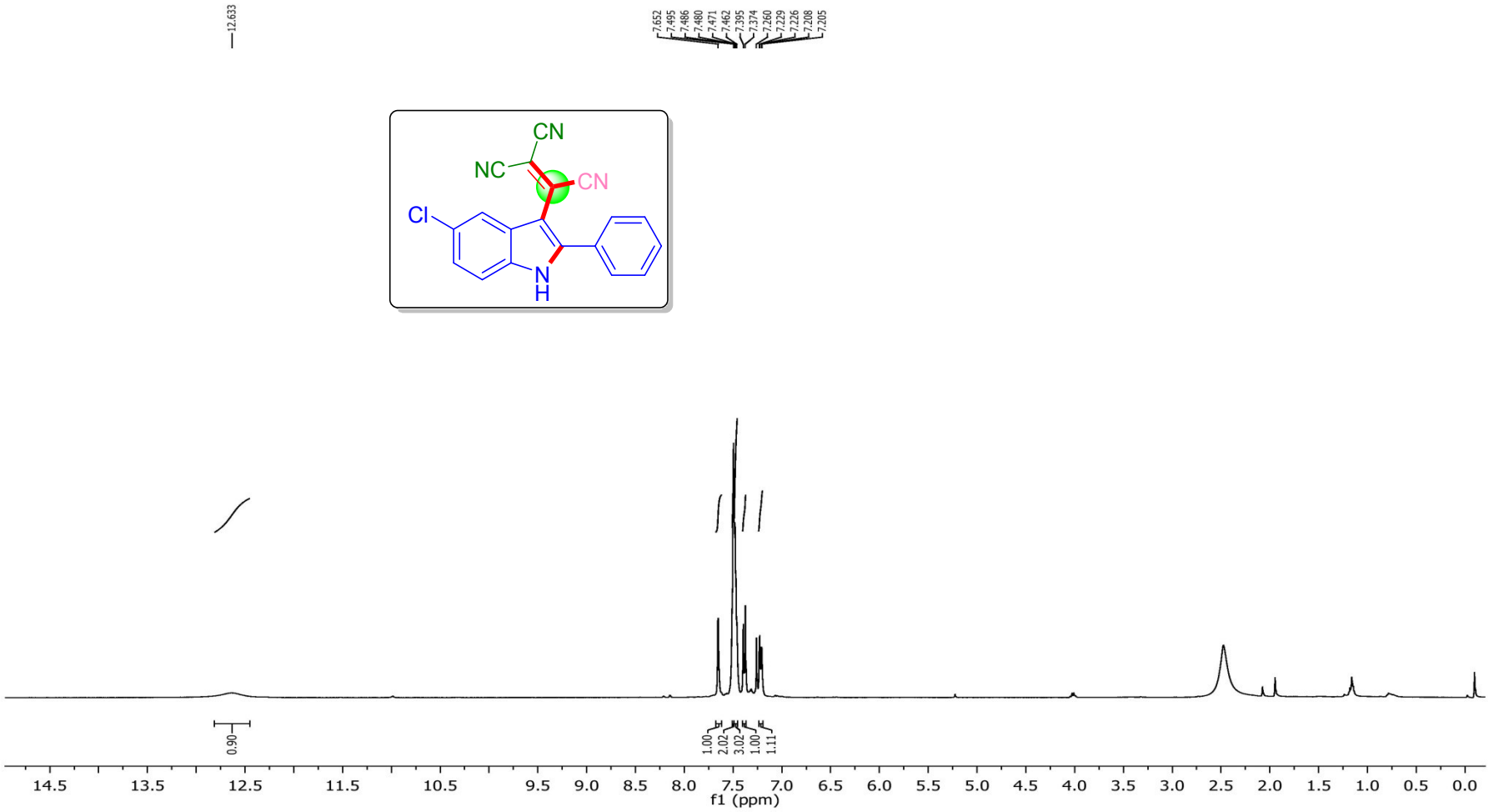
2-(5-Fluoro-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (5a): ^{13}C NMR (100 MHz, DMSO)



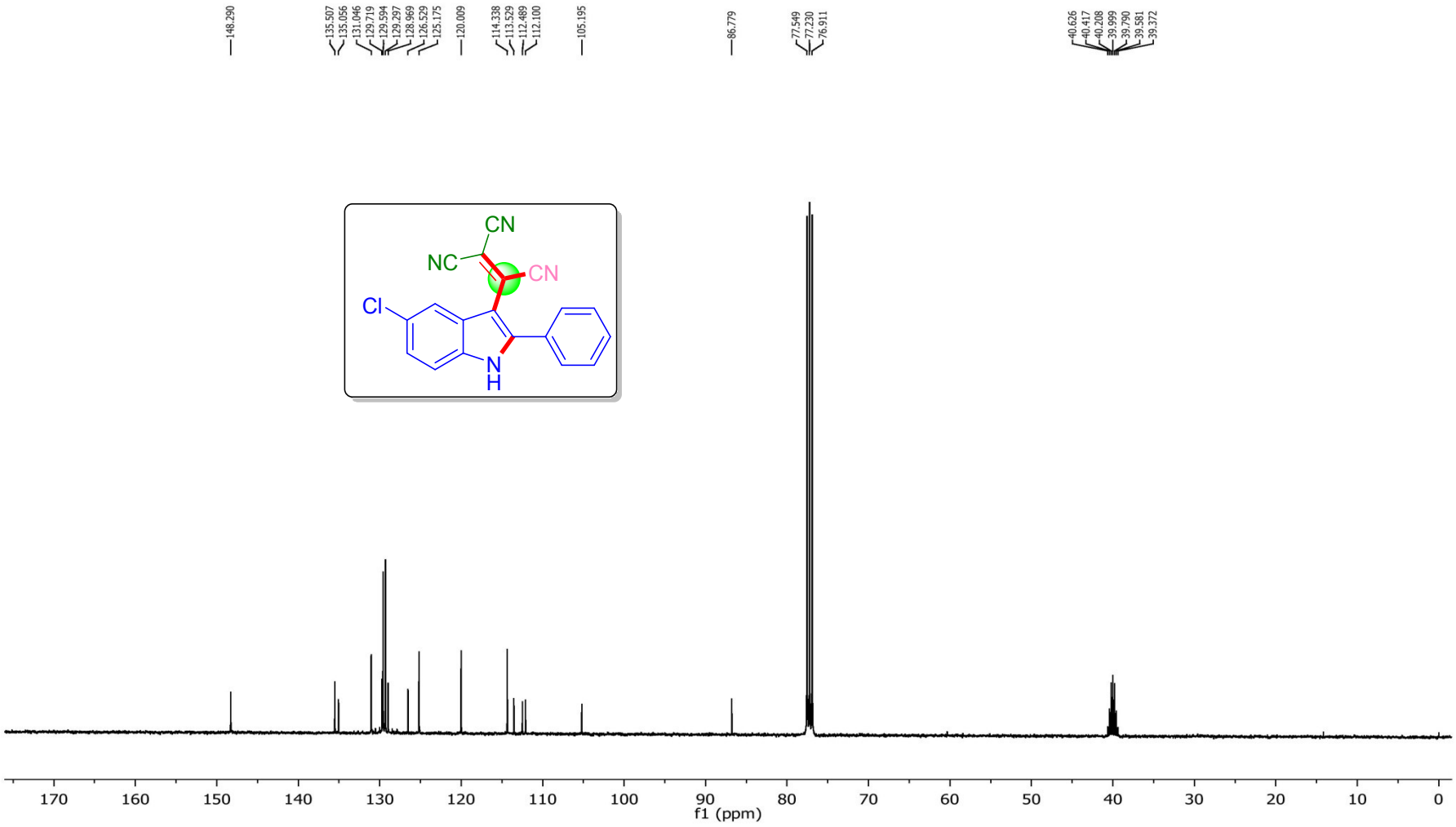
2-(5-Fluoro-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (5a): ^{19}F NMR (400 MHz, DMSO)



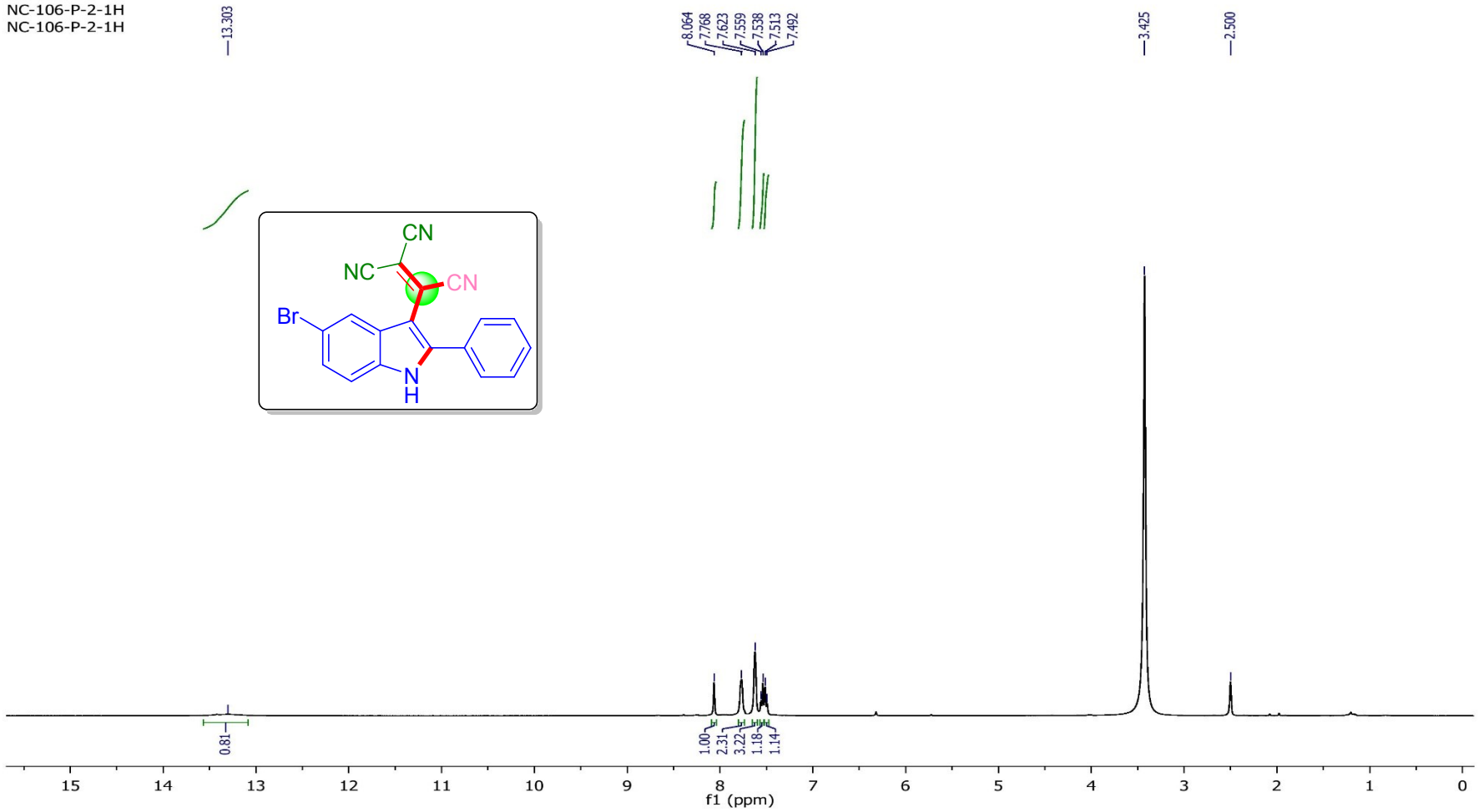
2-(5-Chloro-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (6a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



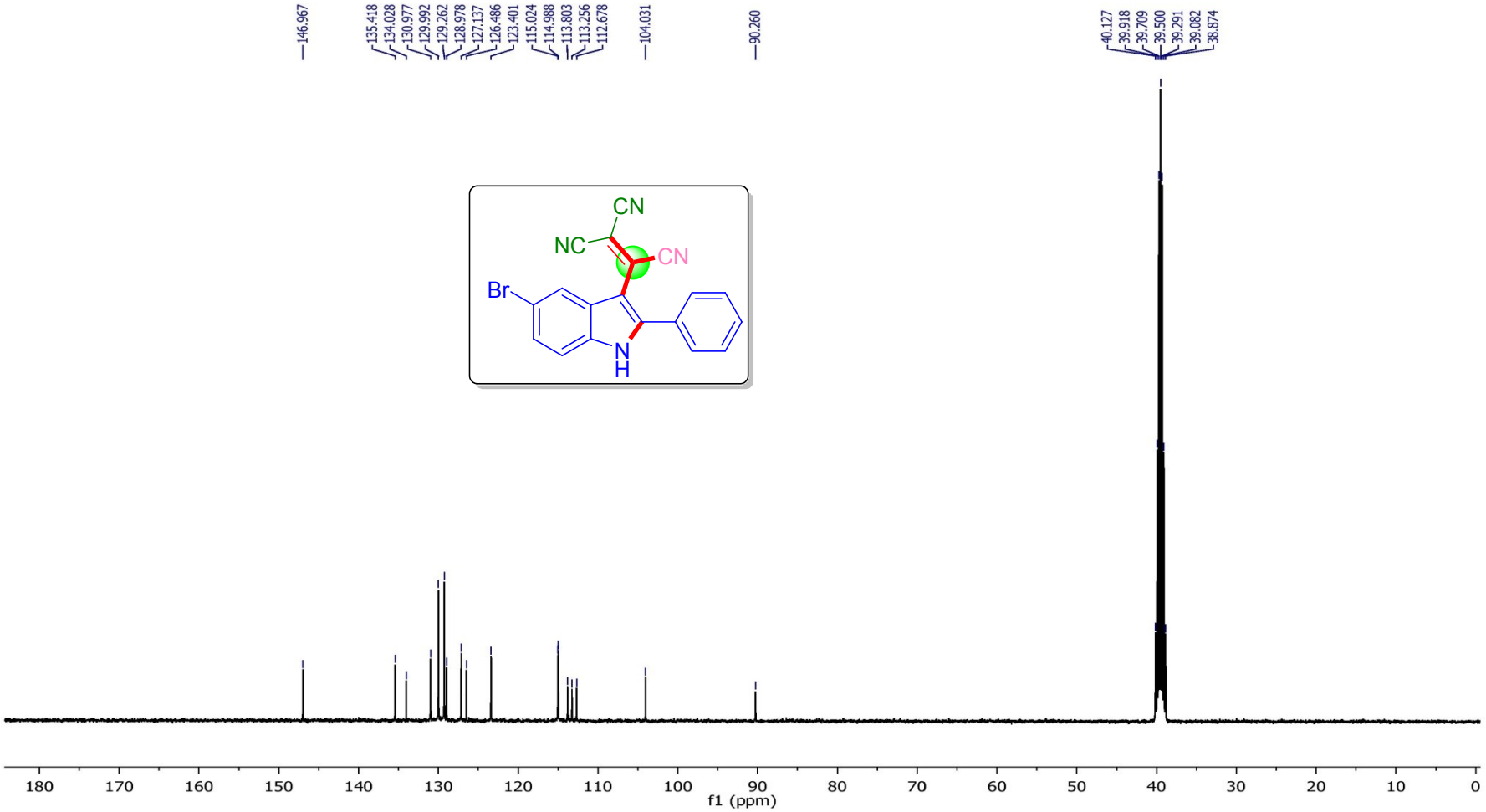
2-(5-Chloro-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (6a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



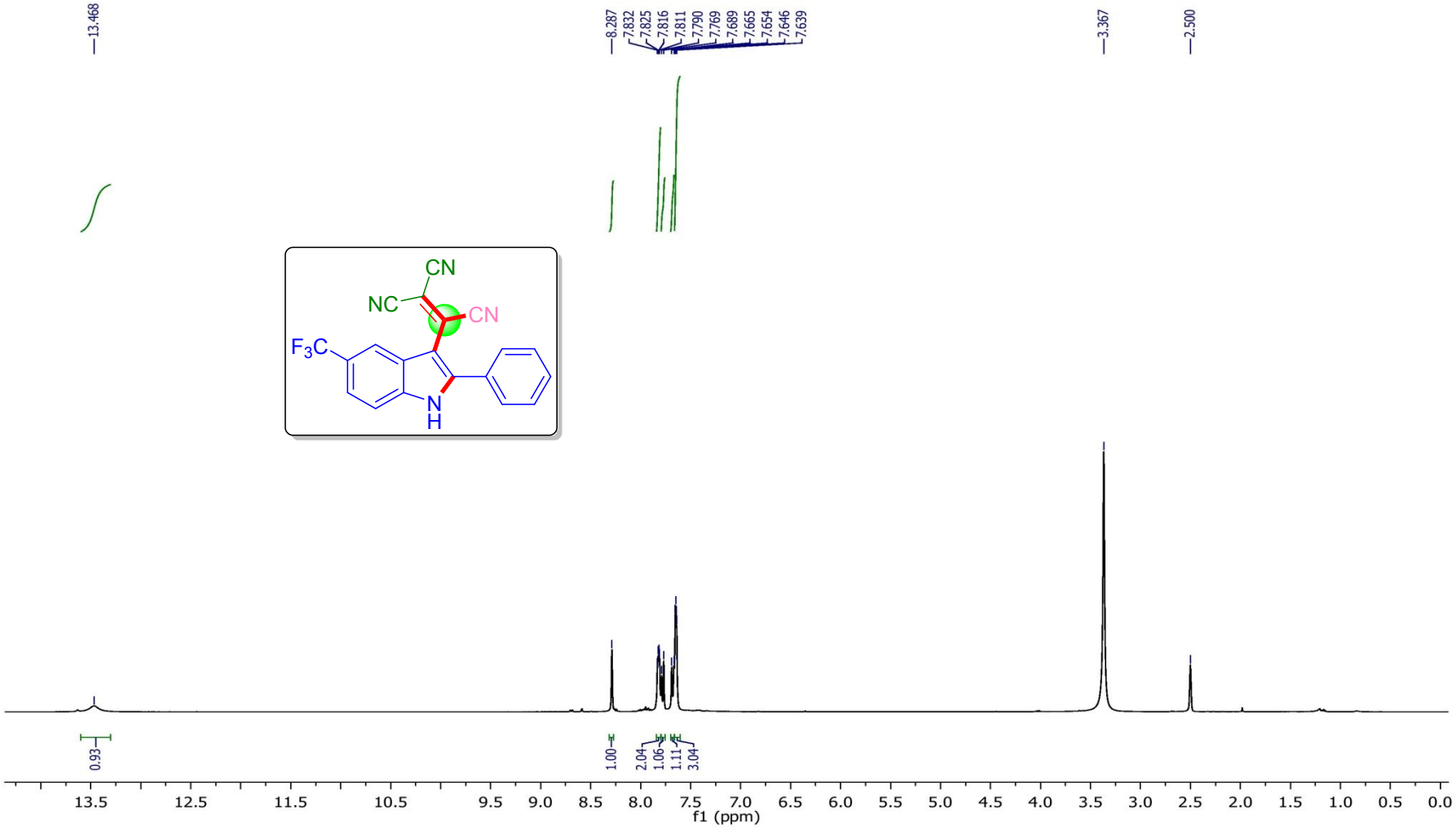
2-(5-Bromo-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (7a): ^{1}H NMR (400 MHz, DMSO)



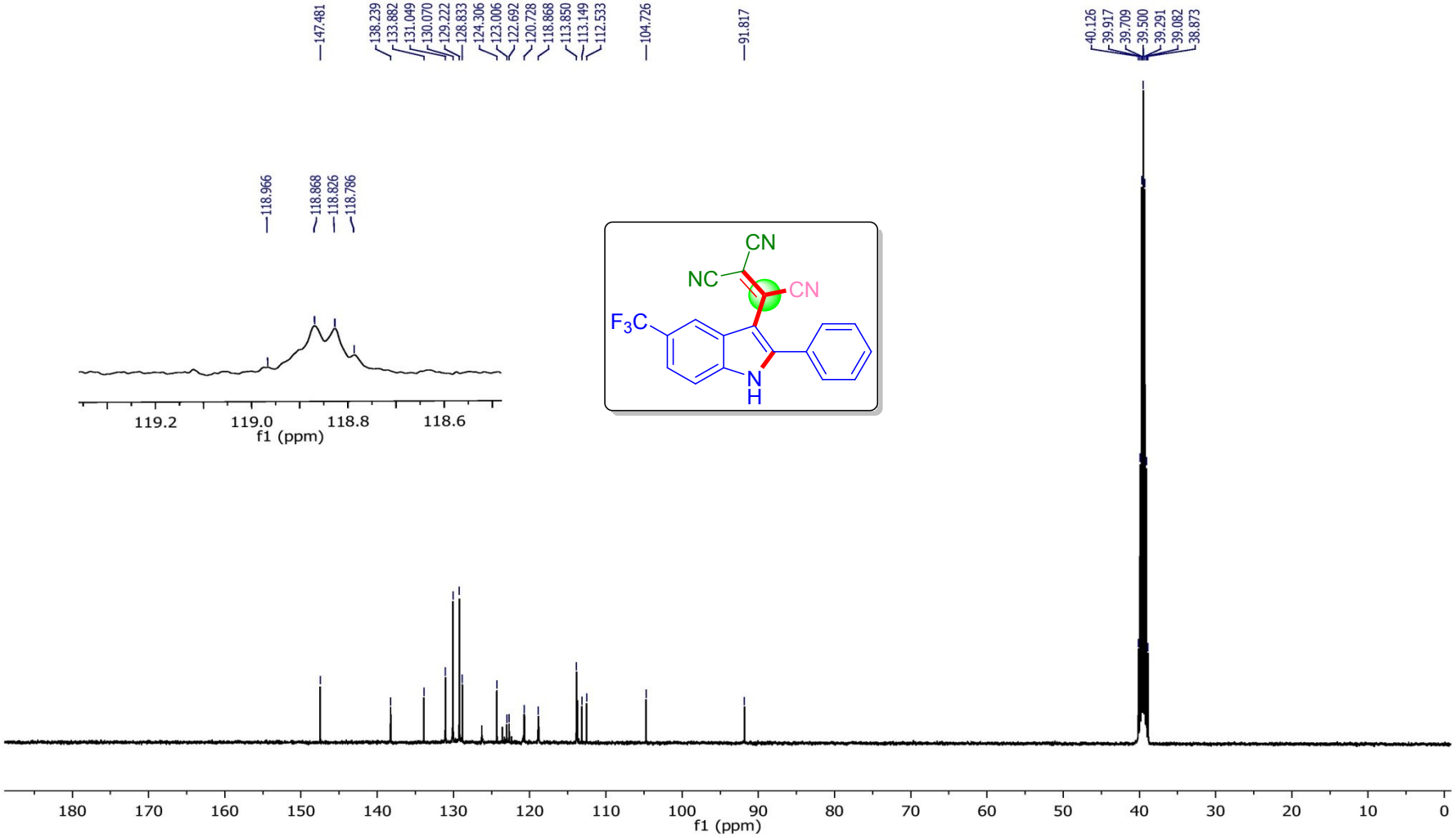
2-(5-Bromo-2-phenyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (7a): ^{13}C NMR (100 MHz, DMSO)



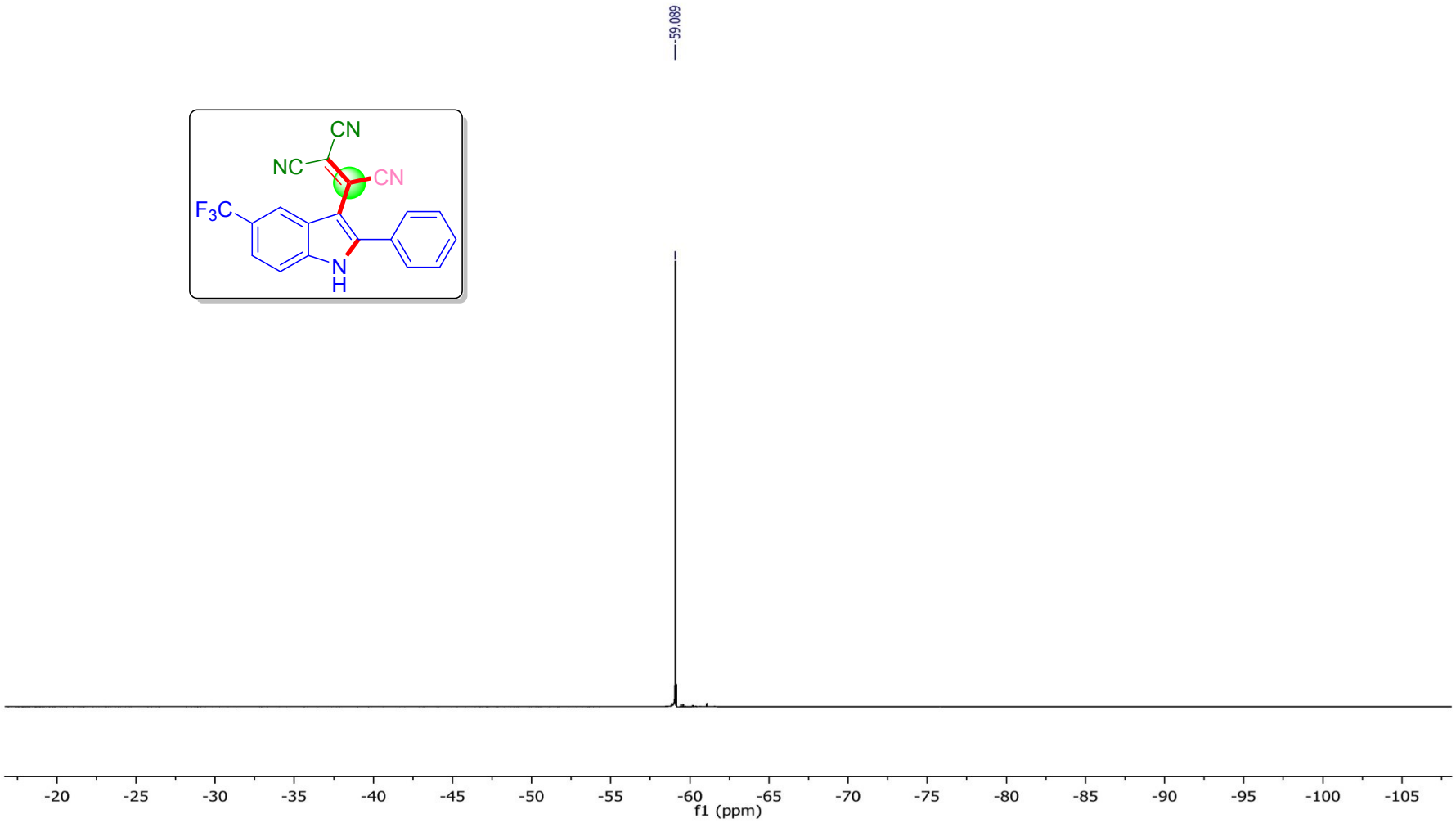
2-(2-Phenyl-5-trifluoromethyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (8a): ^{1}H NMR (400 MHz, DMSO)



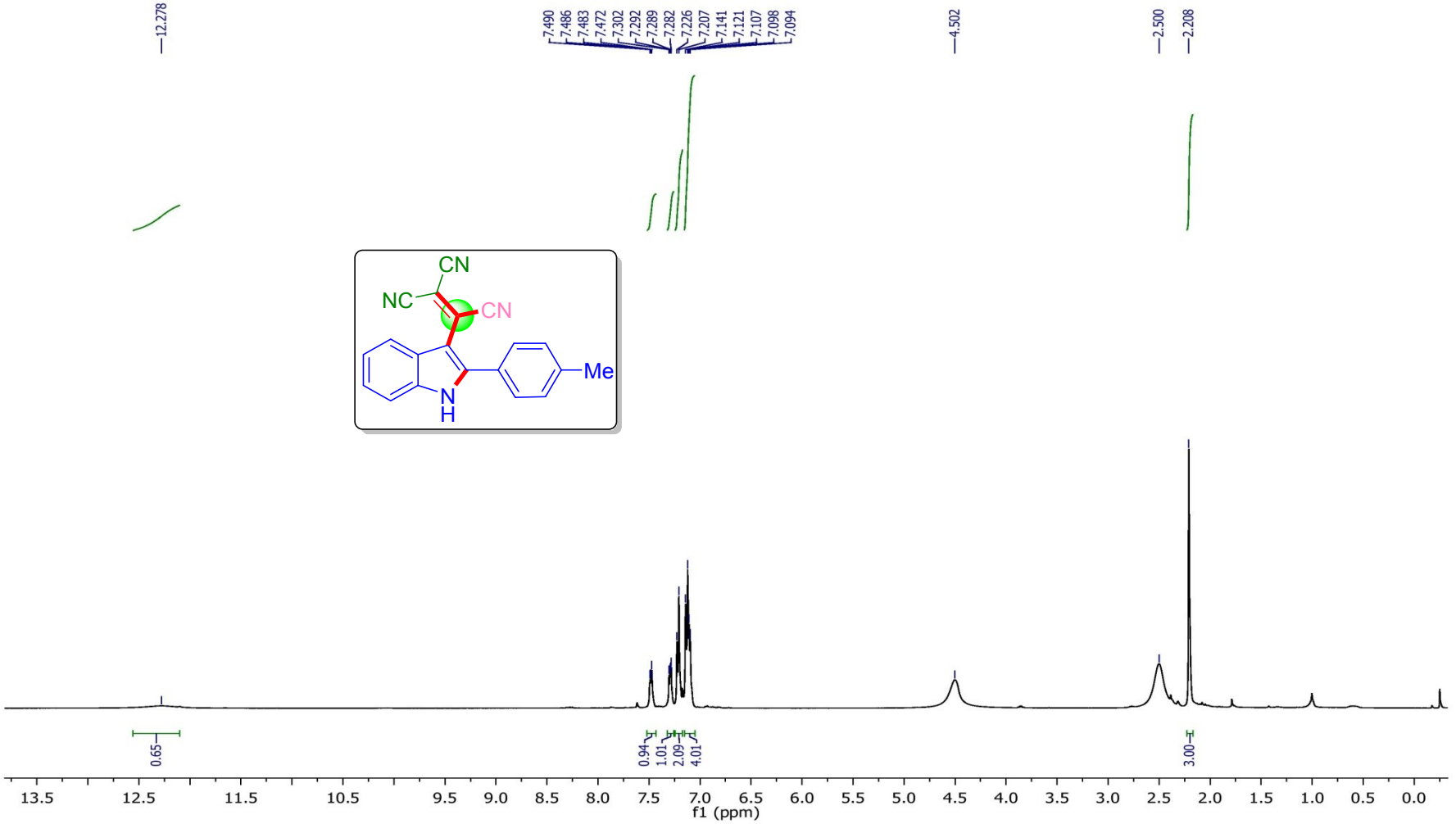
2-(2-Phenyl-5-trifluoromethyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (8a): ^{13}C NMR (100 MHz, DMSO)



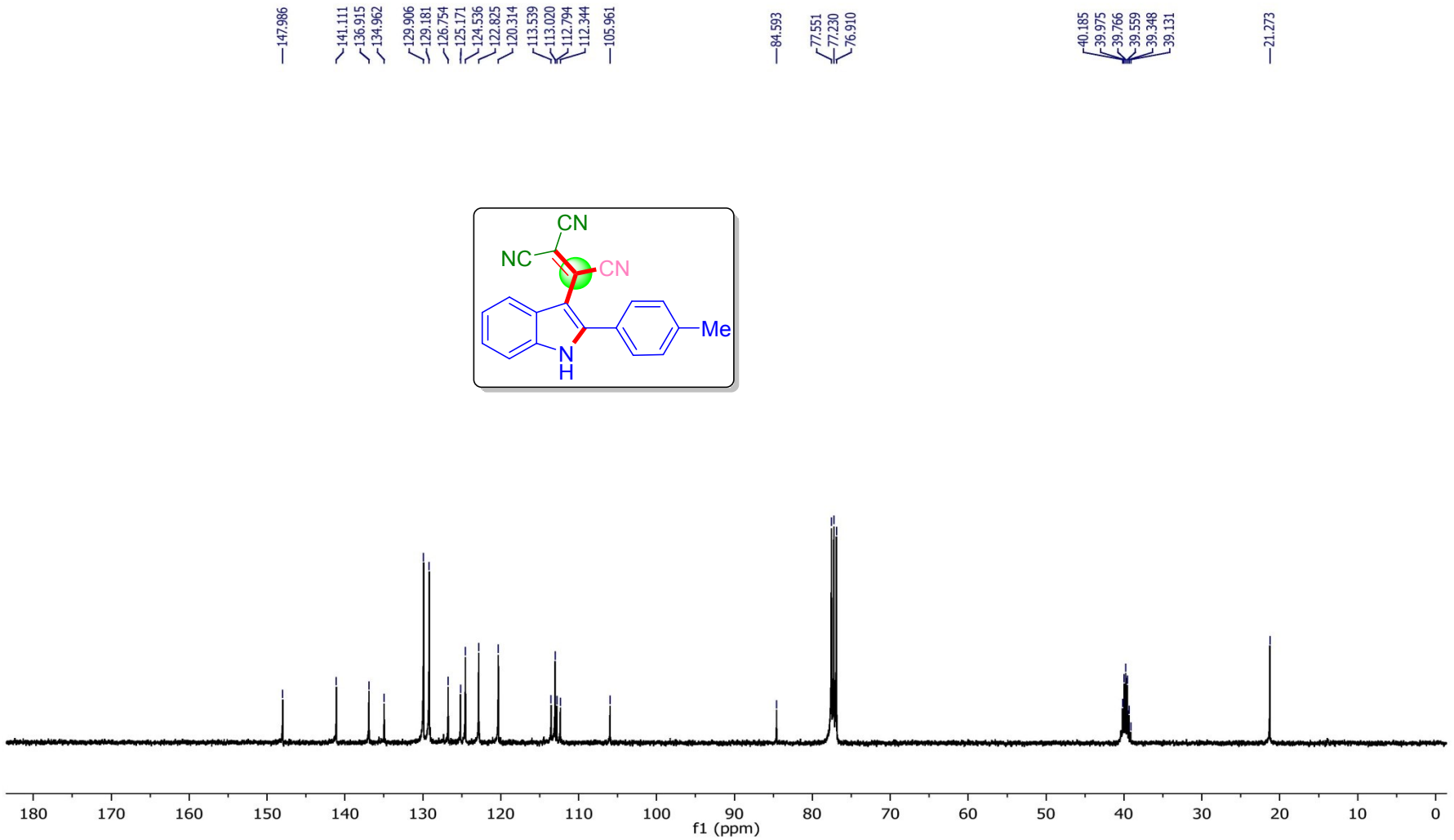
2-(2-Phenyl-5-trifluoromethyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (8a): ^{19}F NMR (400 MHz, DMSO)



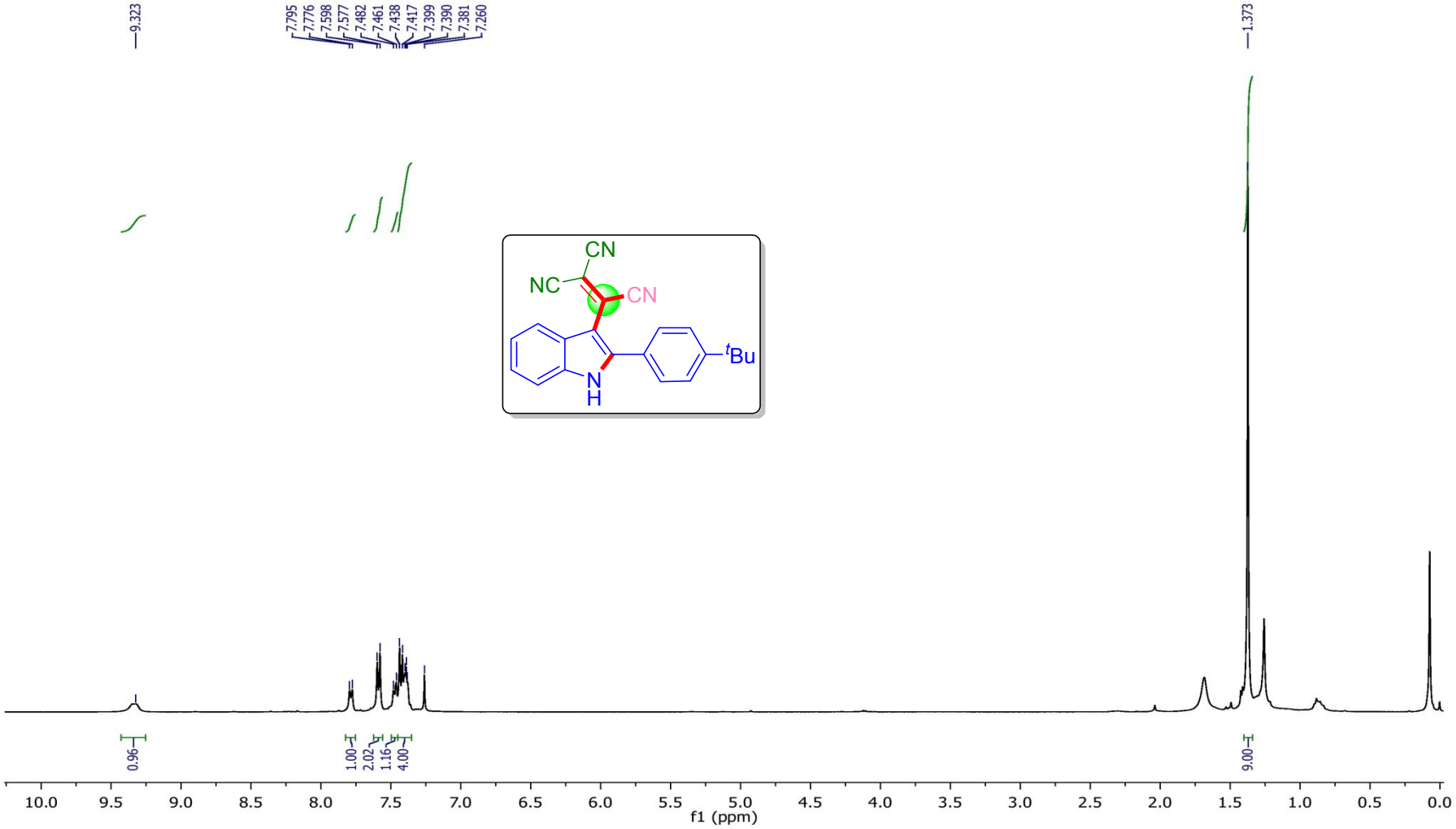
2-(2-(*p*-Tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (9a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



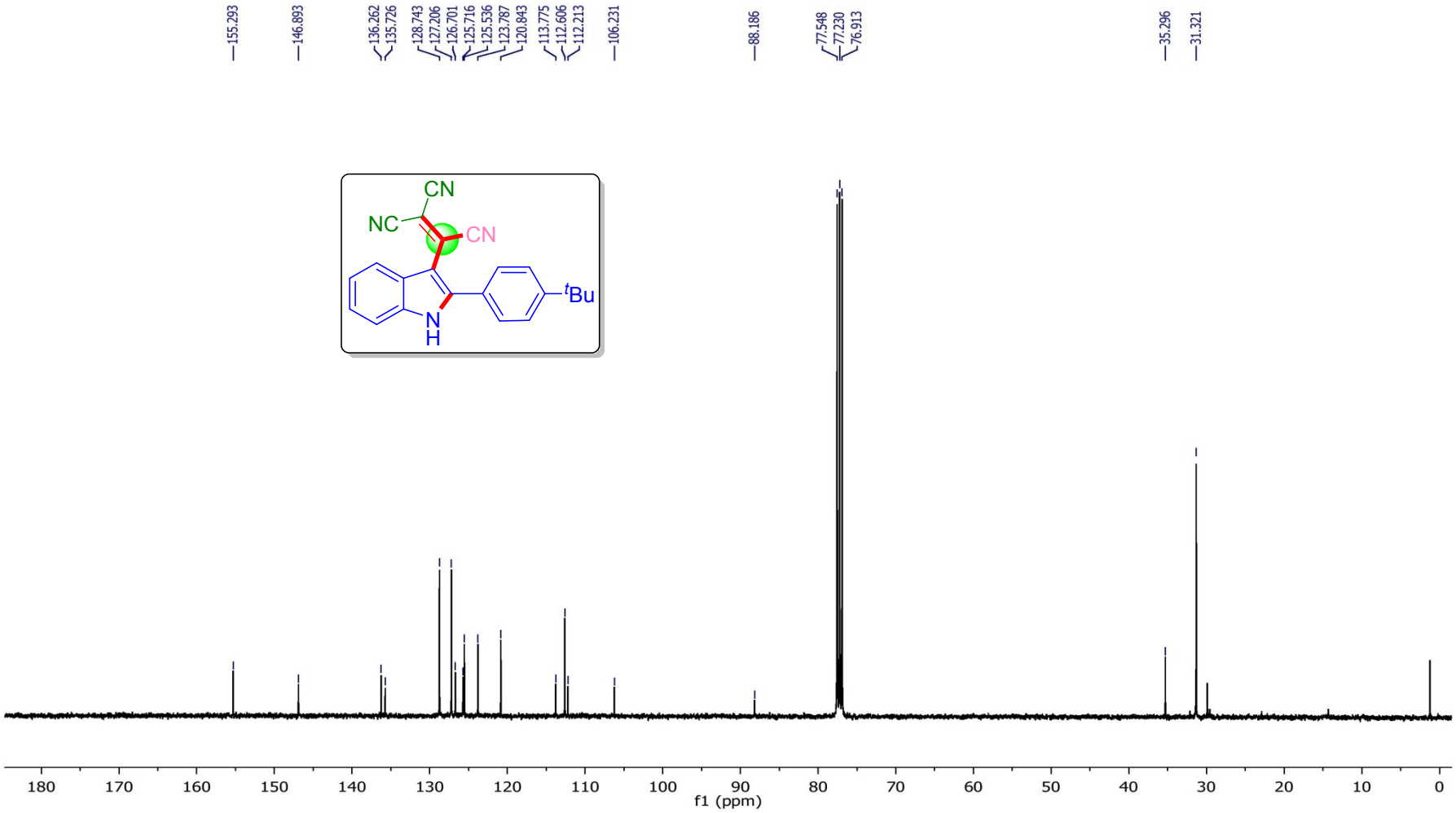
2-(2-(*p*-Tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (9a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



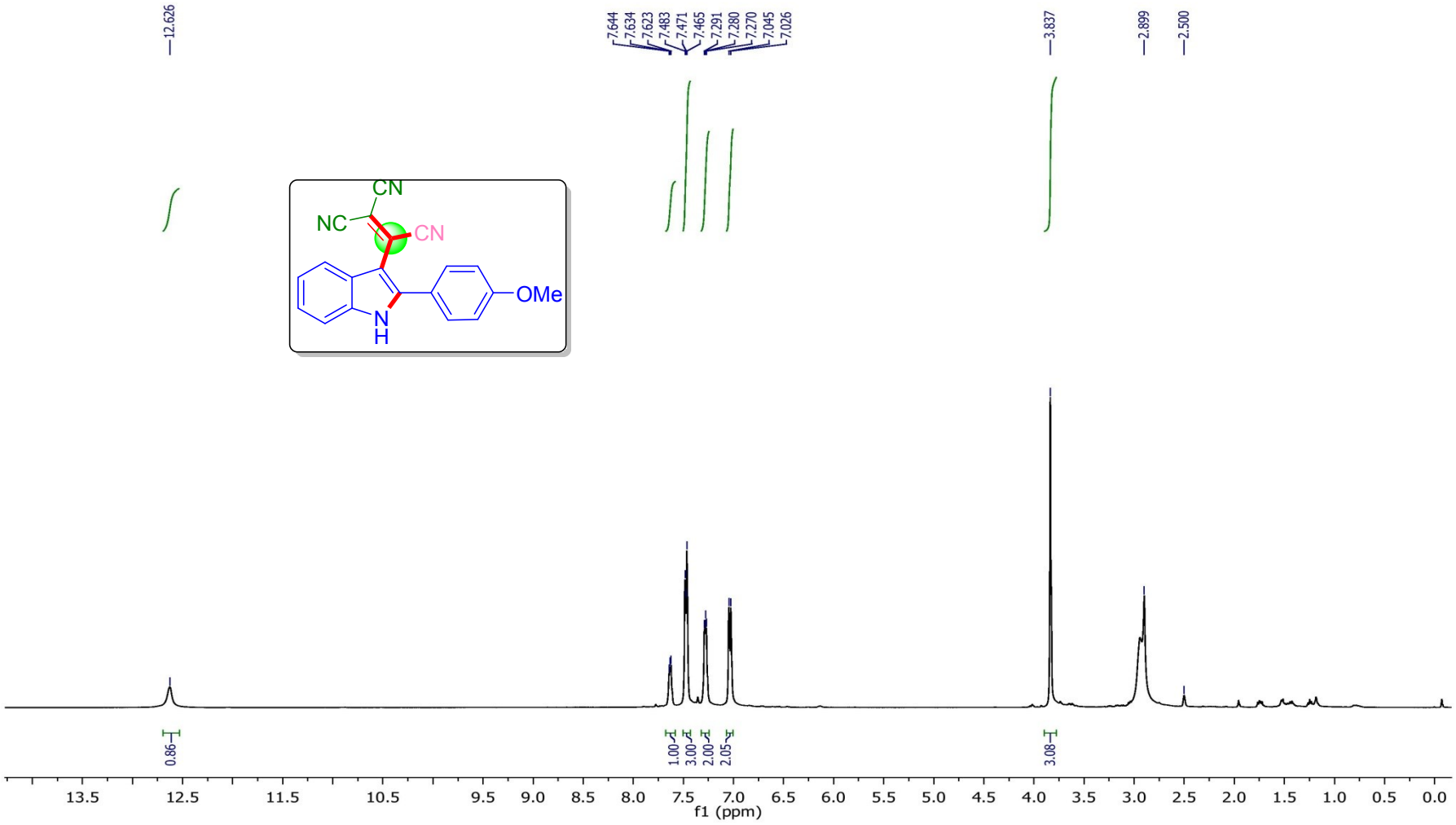
2-(2-(4-(*tert*-Butyl)phenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (10a): ^{1}H NMR (400 MHz, $CDCl_3$)



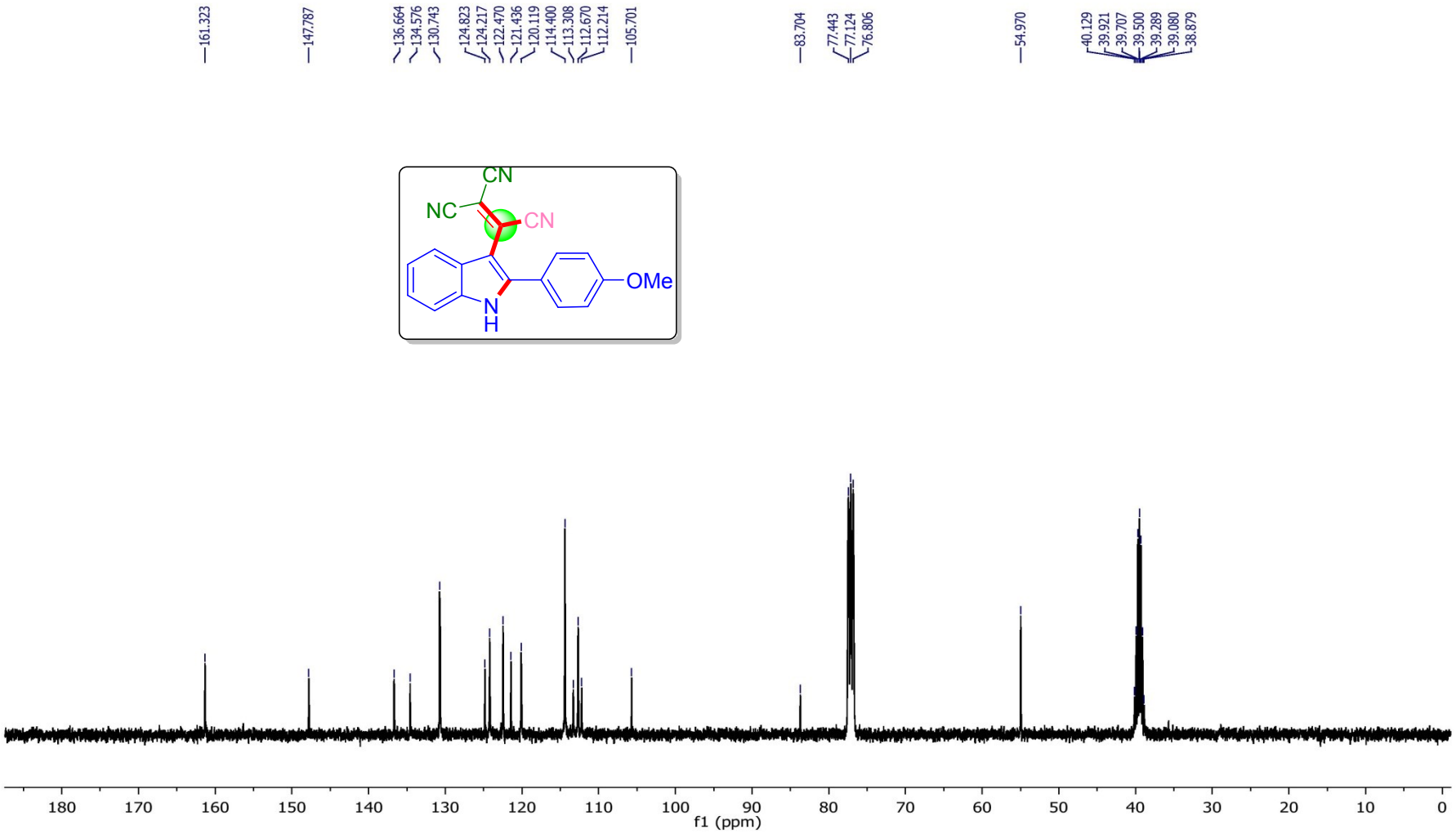
2-(2-(4-(*tert*-Butyl)phenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (10a): ^{13}C NMR (100 MHz, $CDCl_3$)



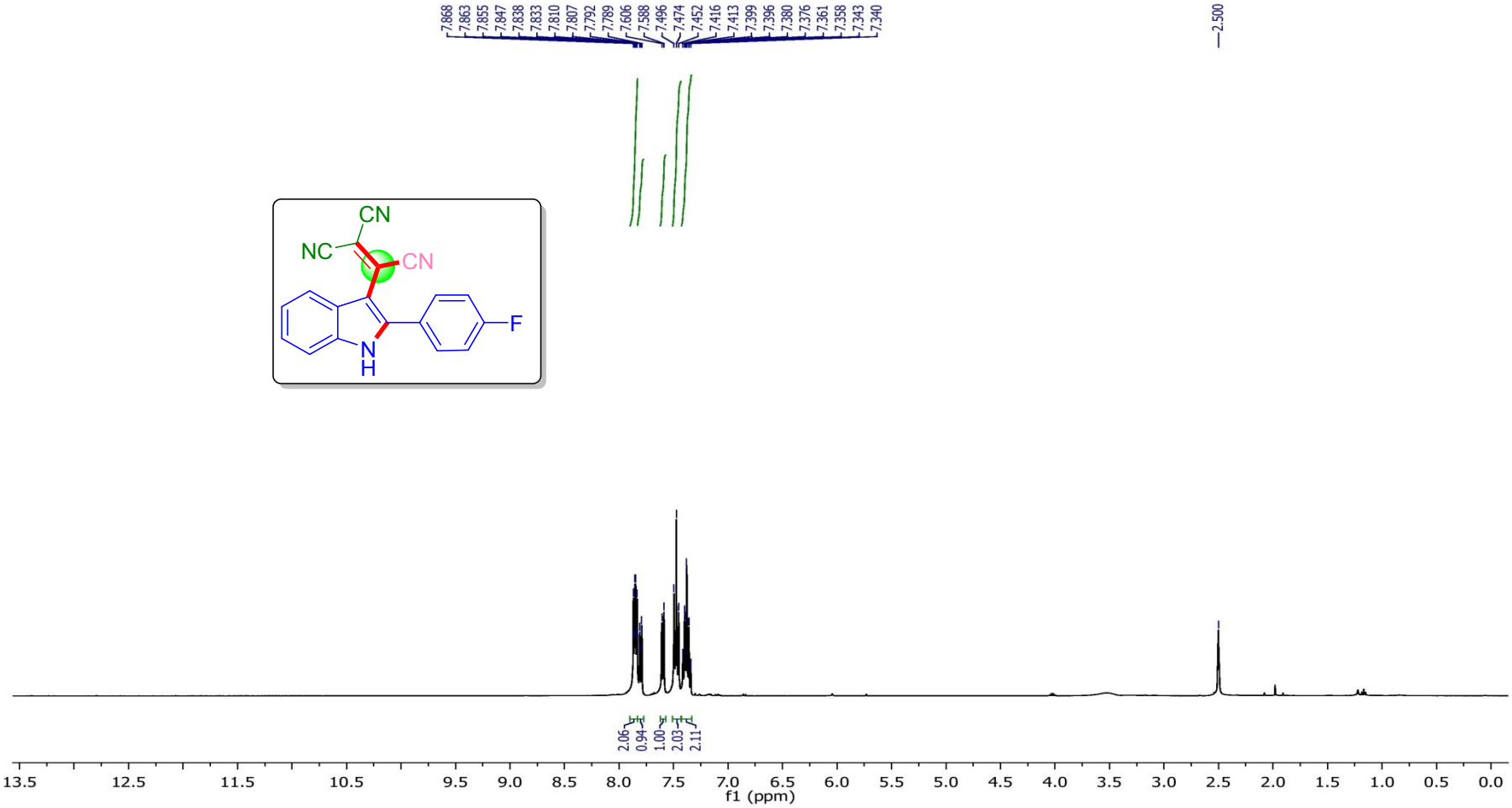
2-(2-(4-Methoxyphenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (11a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



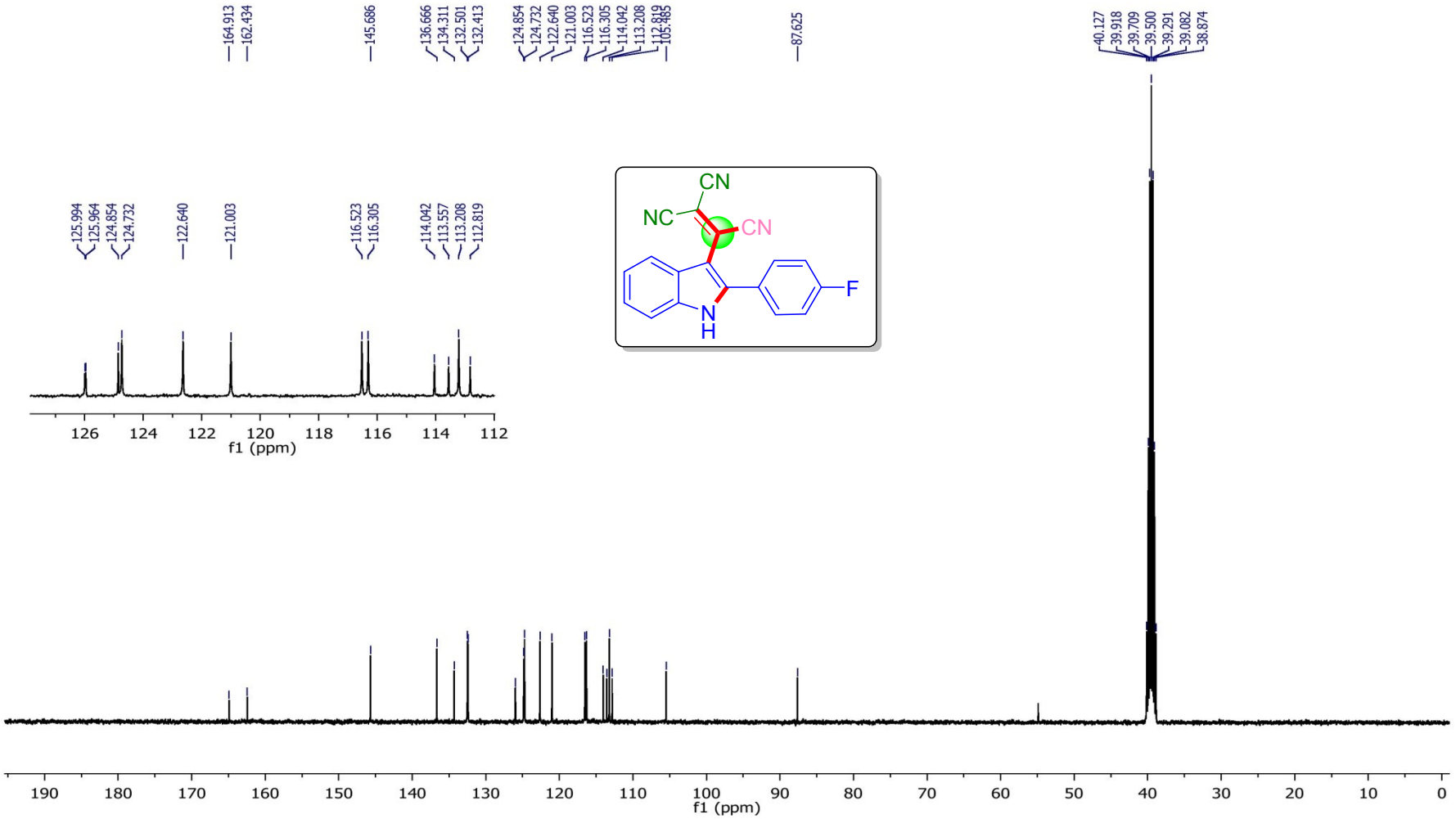
2-(2-(4-Methoxyphenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (11a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



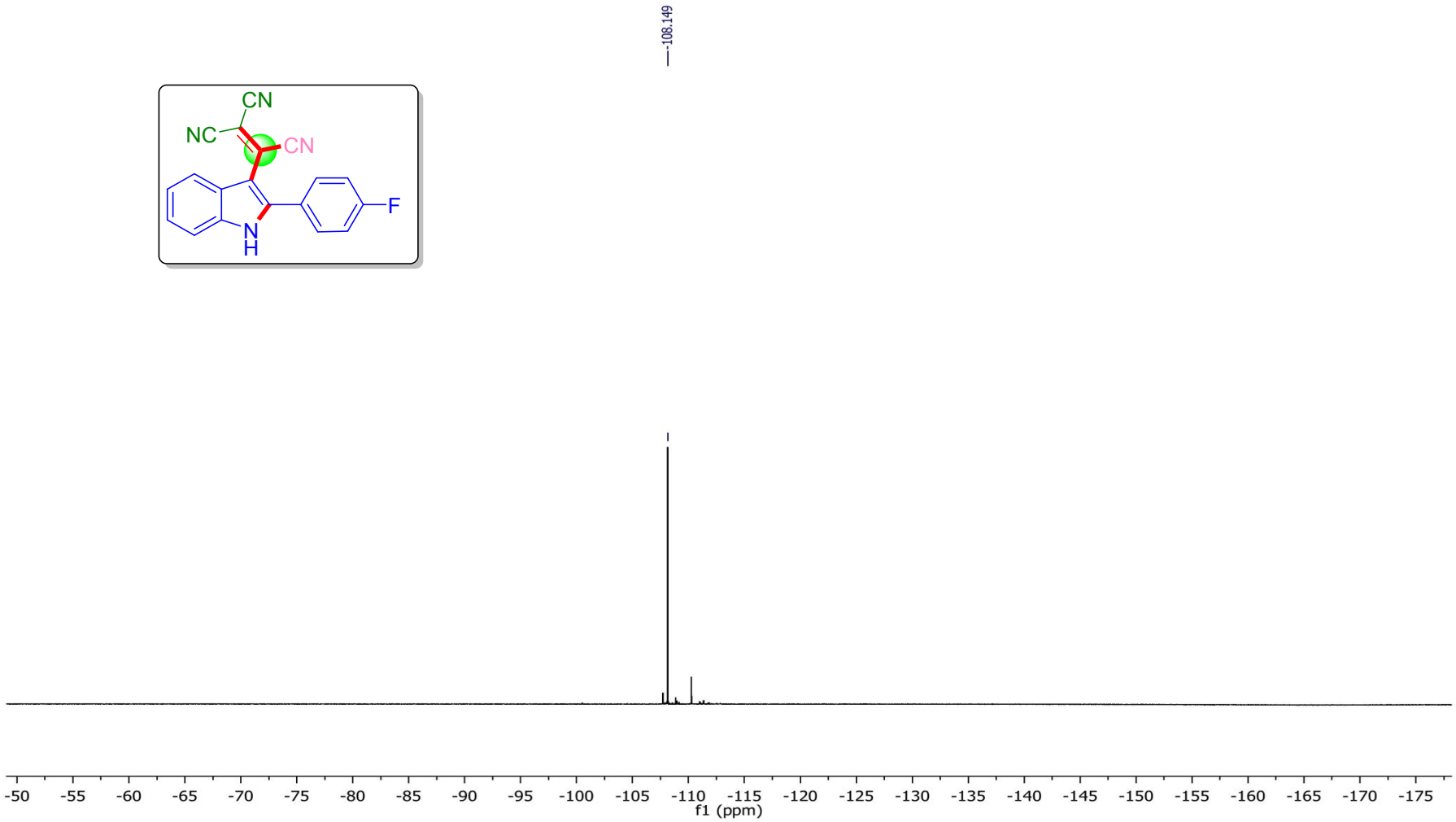
2-(2-(4-Fluorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (12a): ^{1}H NMR (400 MHz, DMSO)



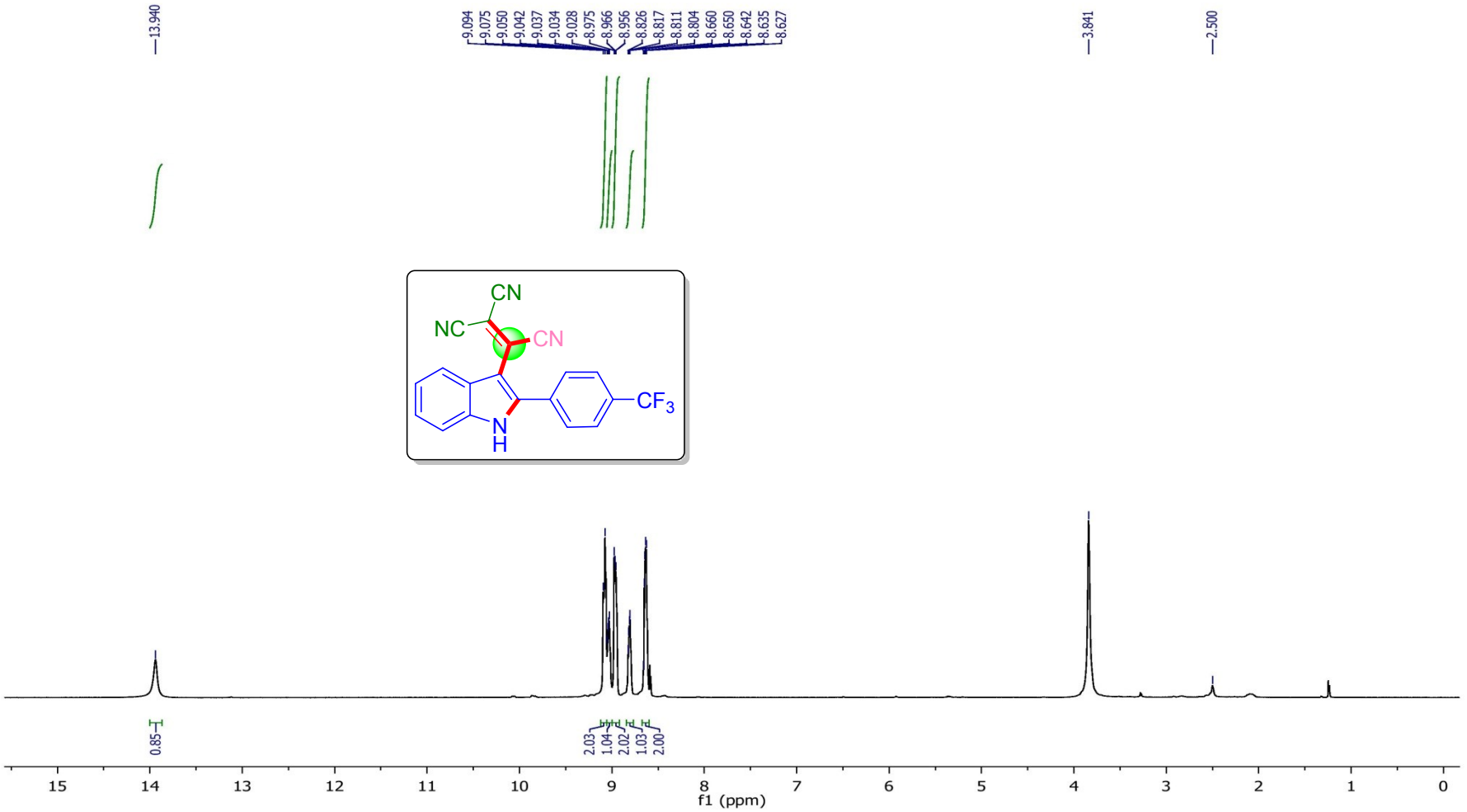
2-(2-(4-Fuorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (12a): ^{13}C NMR (100 MHz, DMSO)



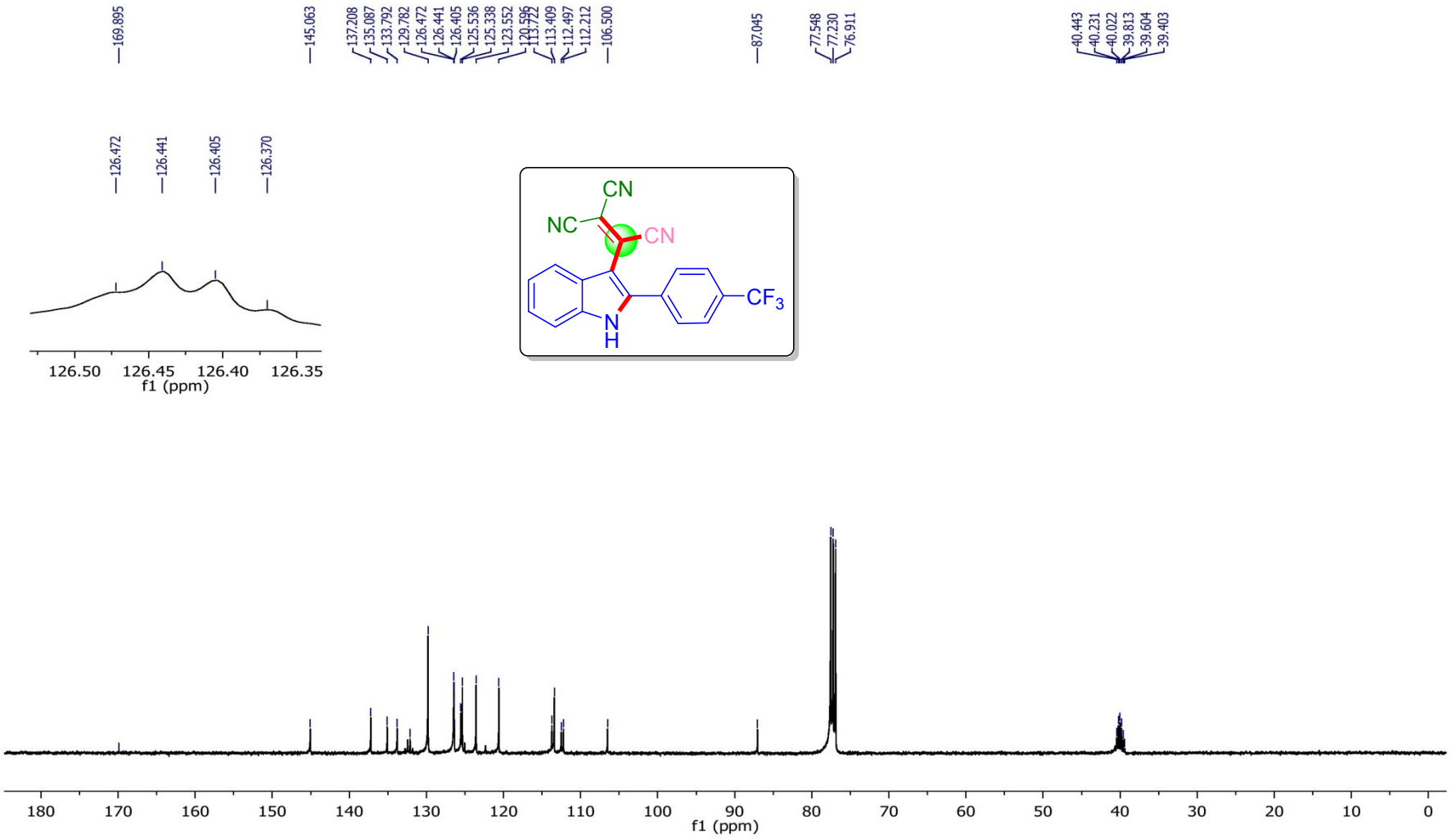
2-(2-(4-Fluorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (12a): ^{19}F NMR (400 MHz, DMSO)



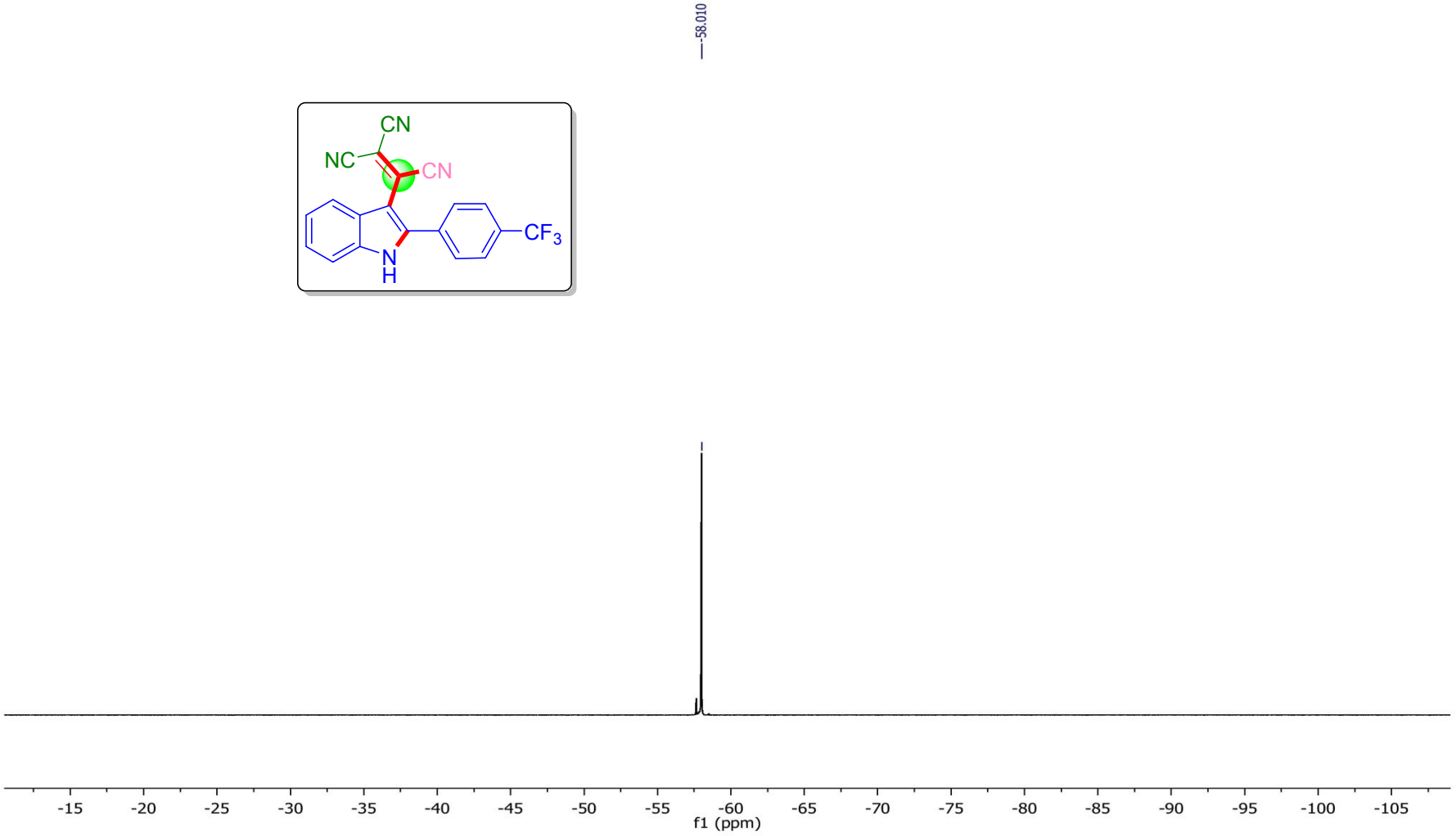
2-(2-(4-Trifluoromethylphenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (13a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



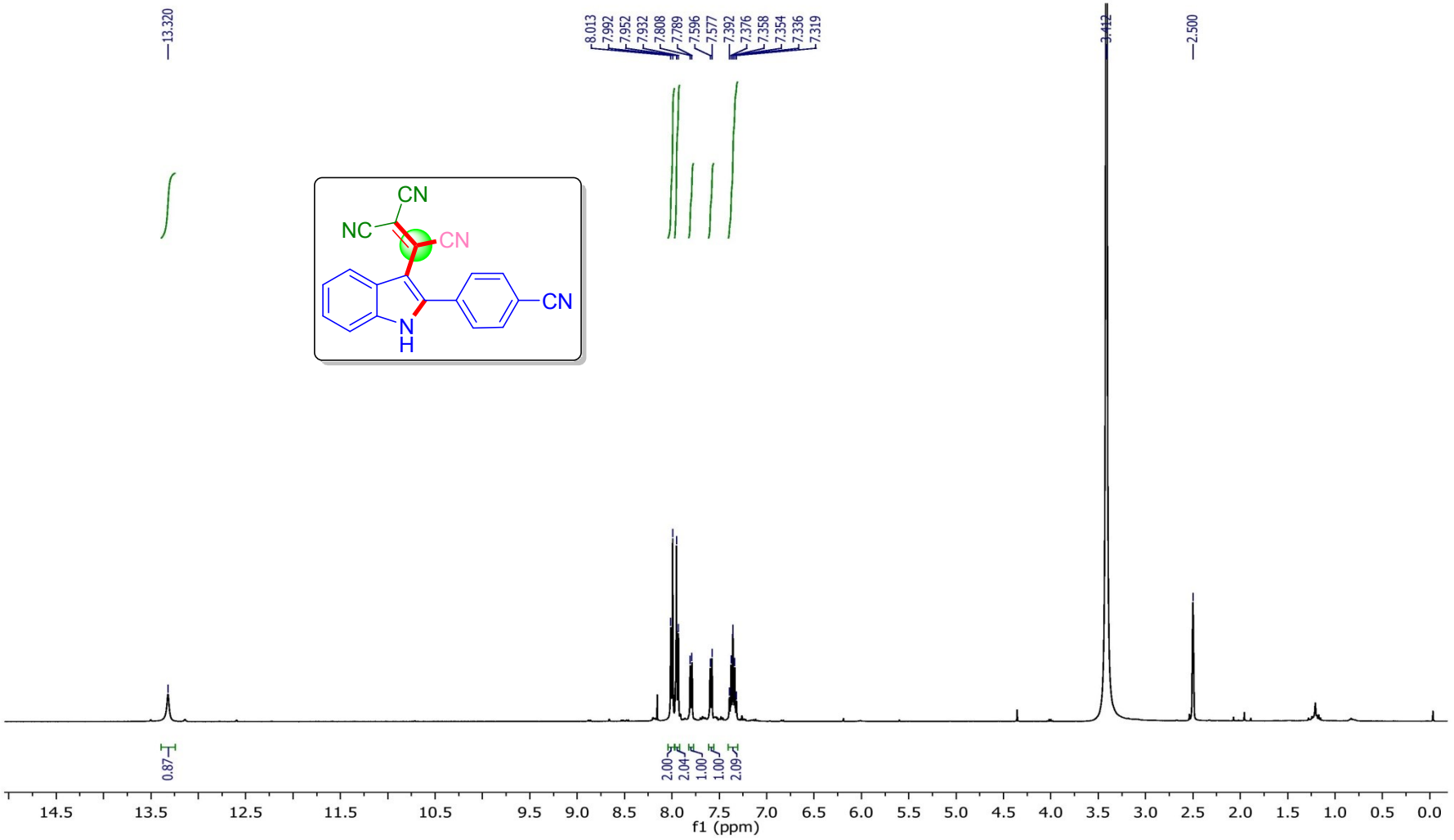
2-(2-(4-Trifluoromethylphenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (13a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



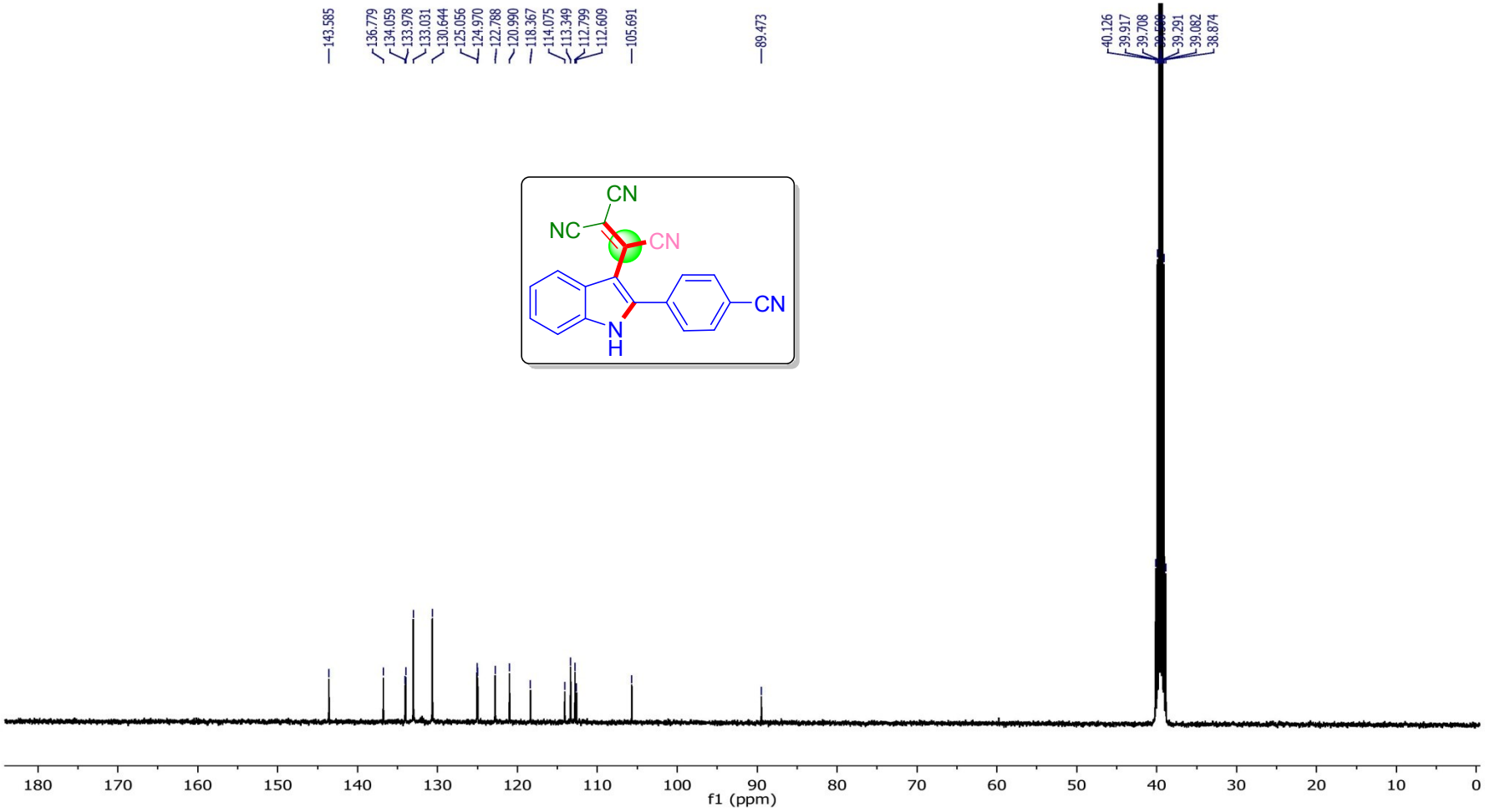
2-(2-(4-Trifluoromethylphenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (13a): ^{19}F NMR (400 MHz, $CDCl_3$ + DMSO)



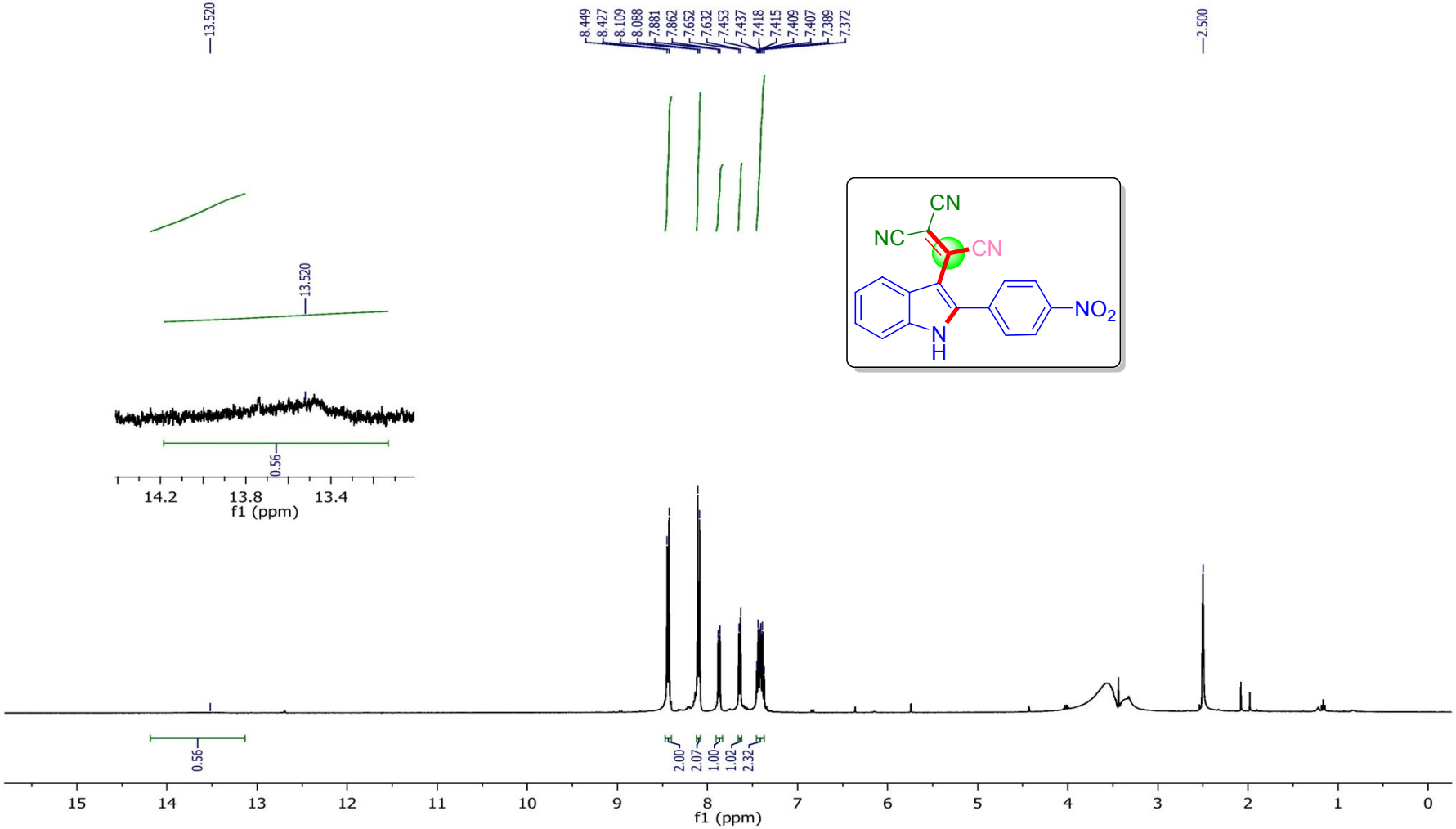
2-(2-(4-Cyanophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (14a): ^{1}H NMR (400 MHz, DMSO)



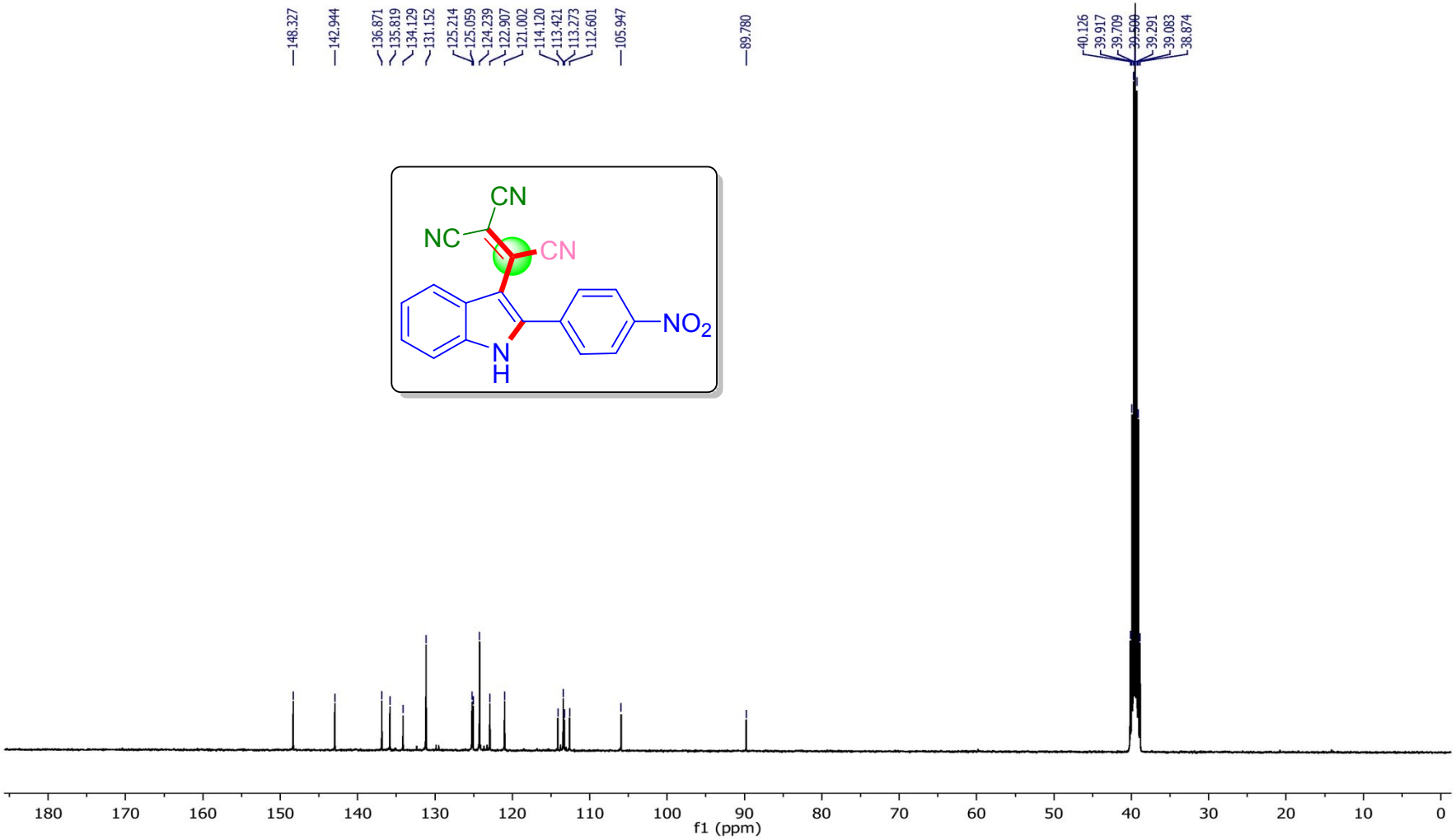
2-(2-(4-Cyanophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (14a): ^{13}C NMR (100 MHz, DMSO)



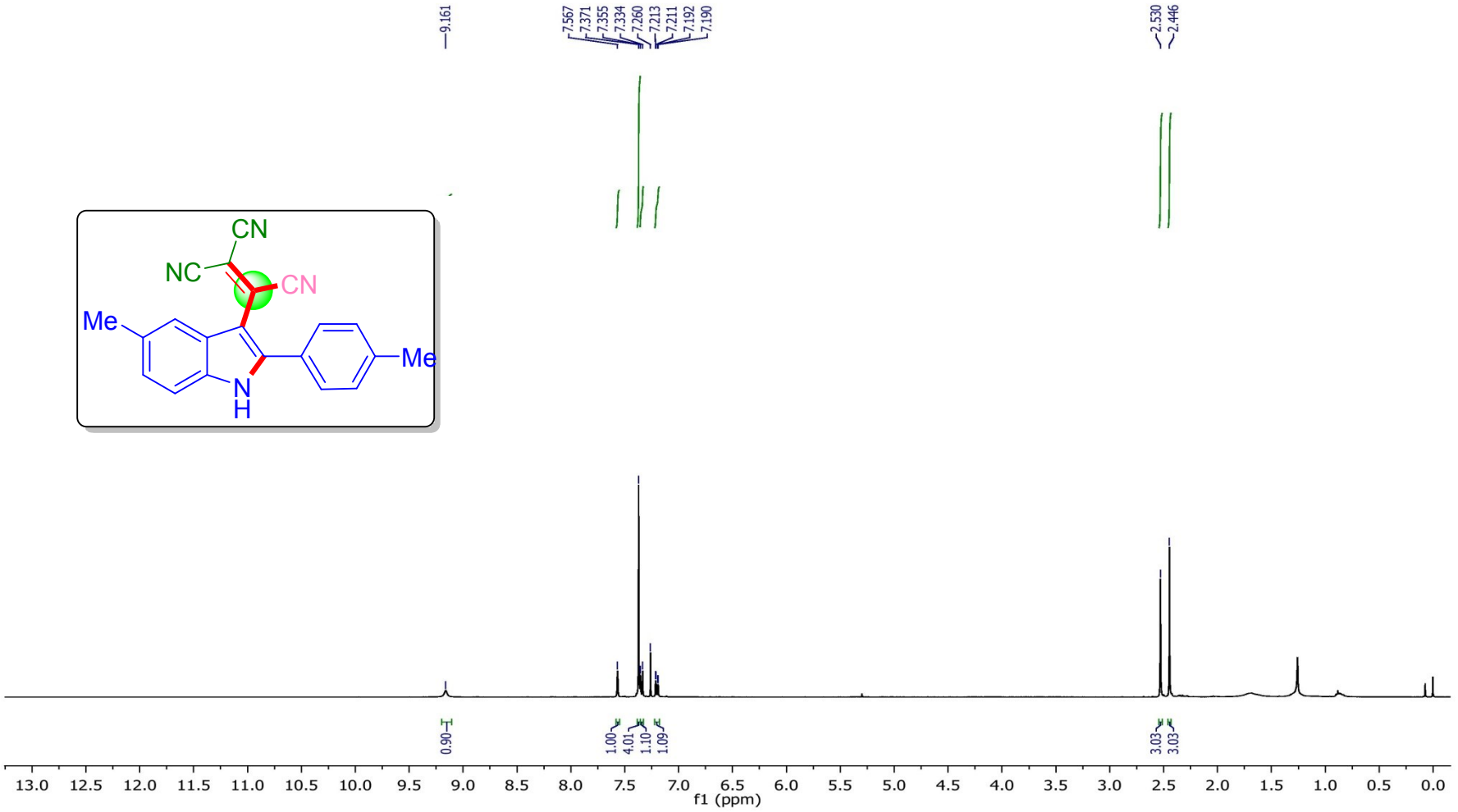
2-(2-(4-Nitrophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (15a): ^{1}H NMR (400 MHz, DMSO)



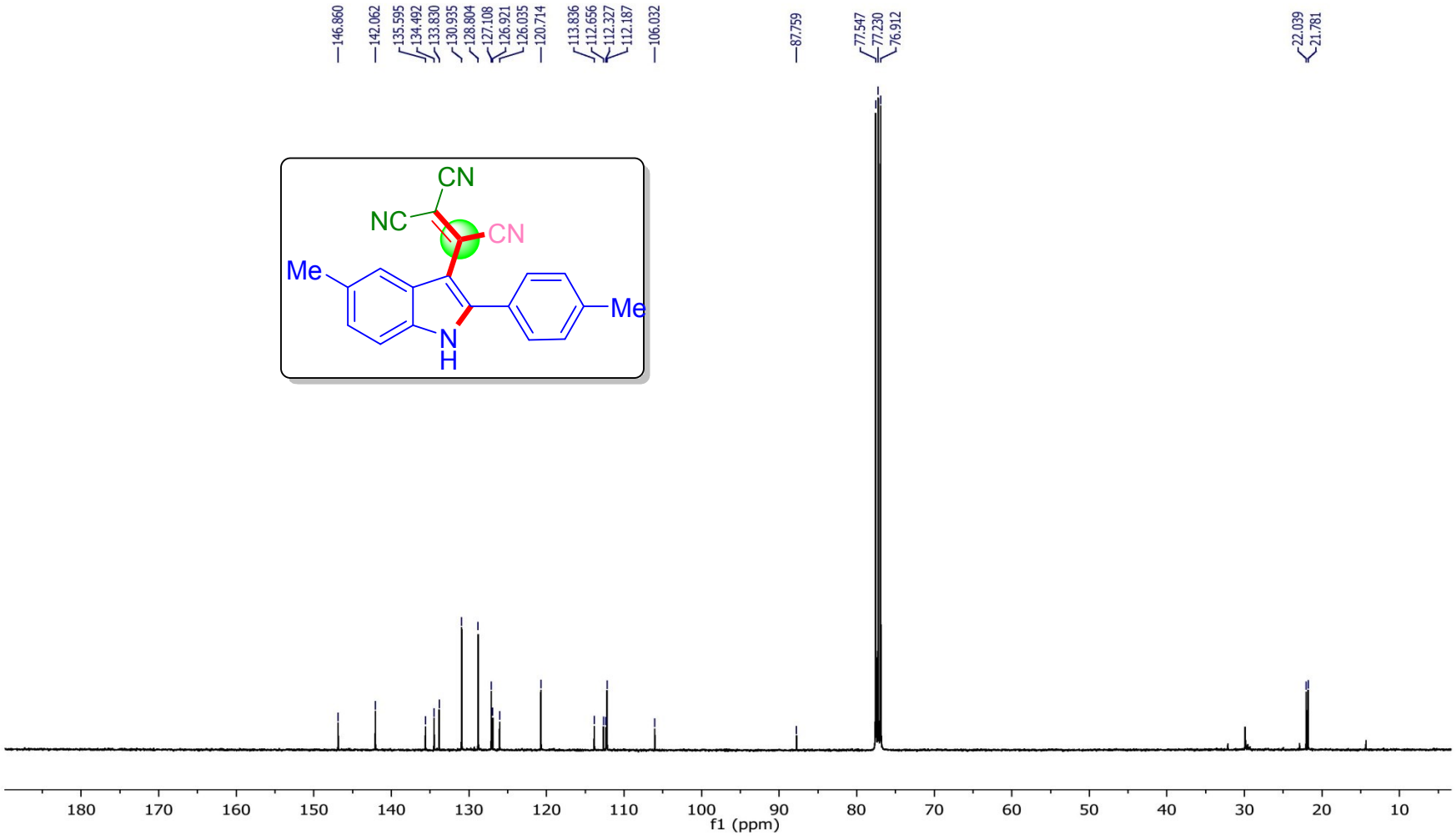
2-(2-(4-Nitrophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (15a): ^{13}C NMR (100 MHz, DMSO)



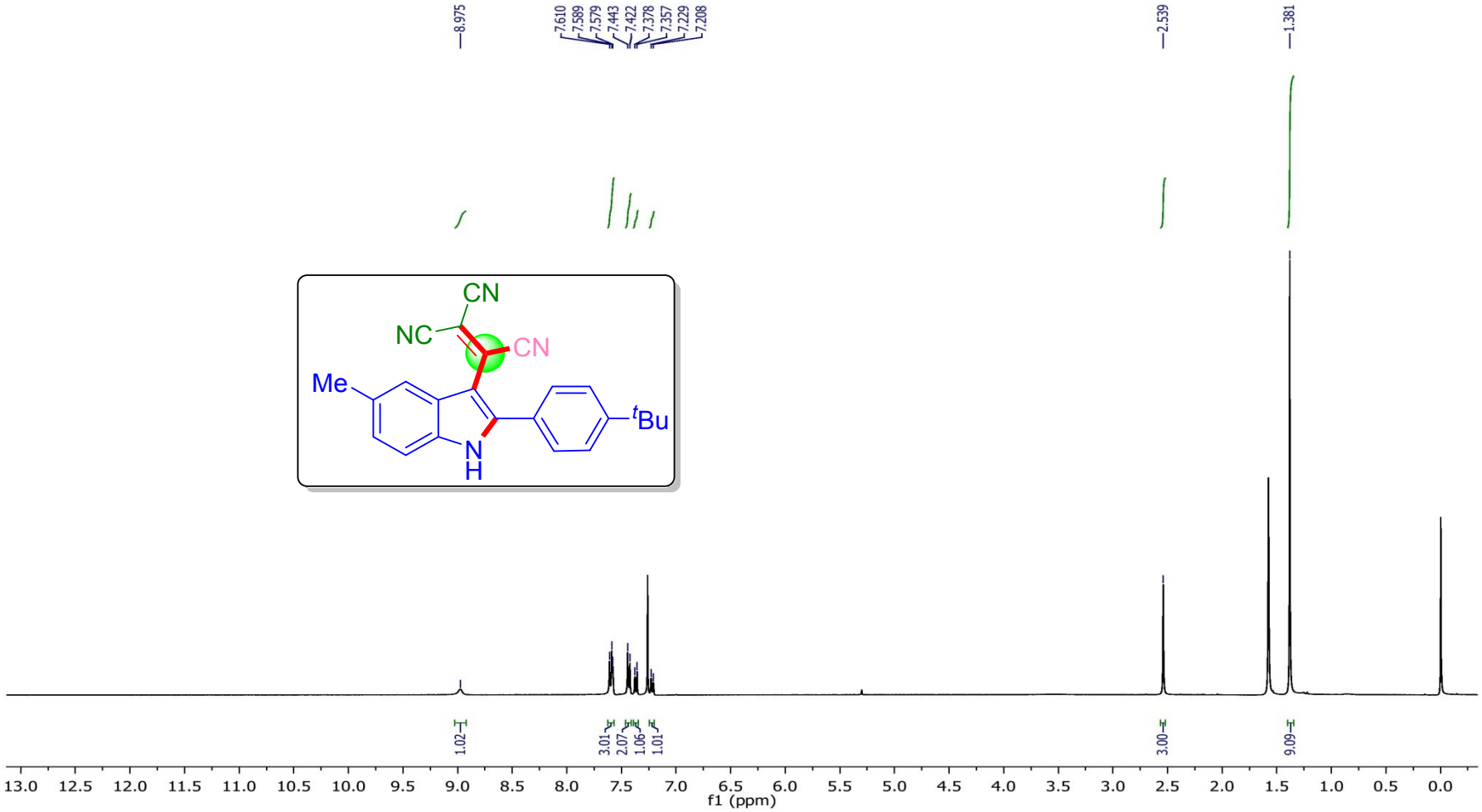
2-(5-Methyl-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (16a): ^{1}H NMR (400 MHz, $CDCl_3$)



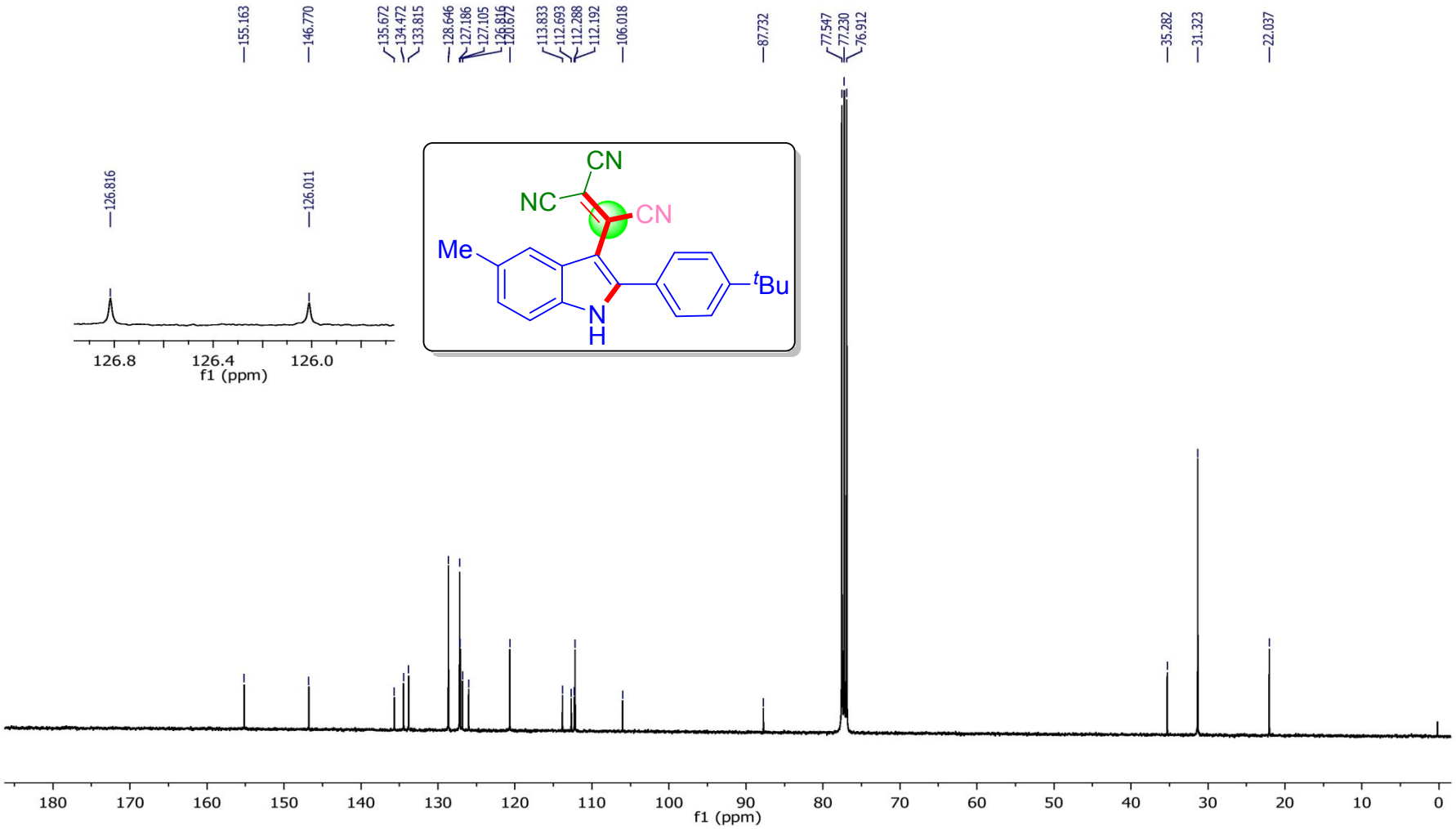
2-(5-Methyl-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (16a): ^{13}C NMR (100 MHz, $CDCl_3$)



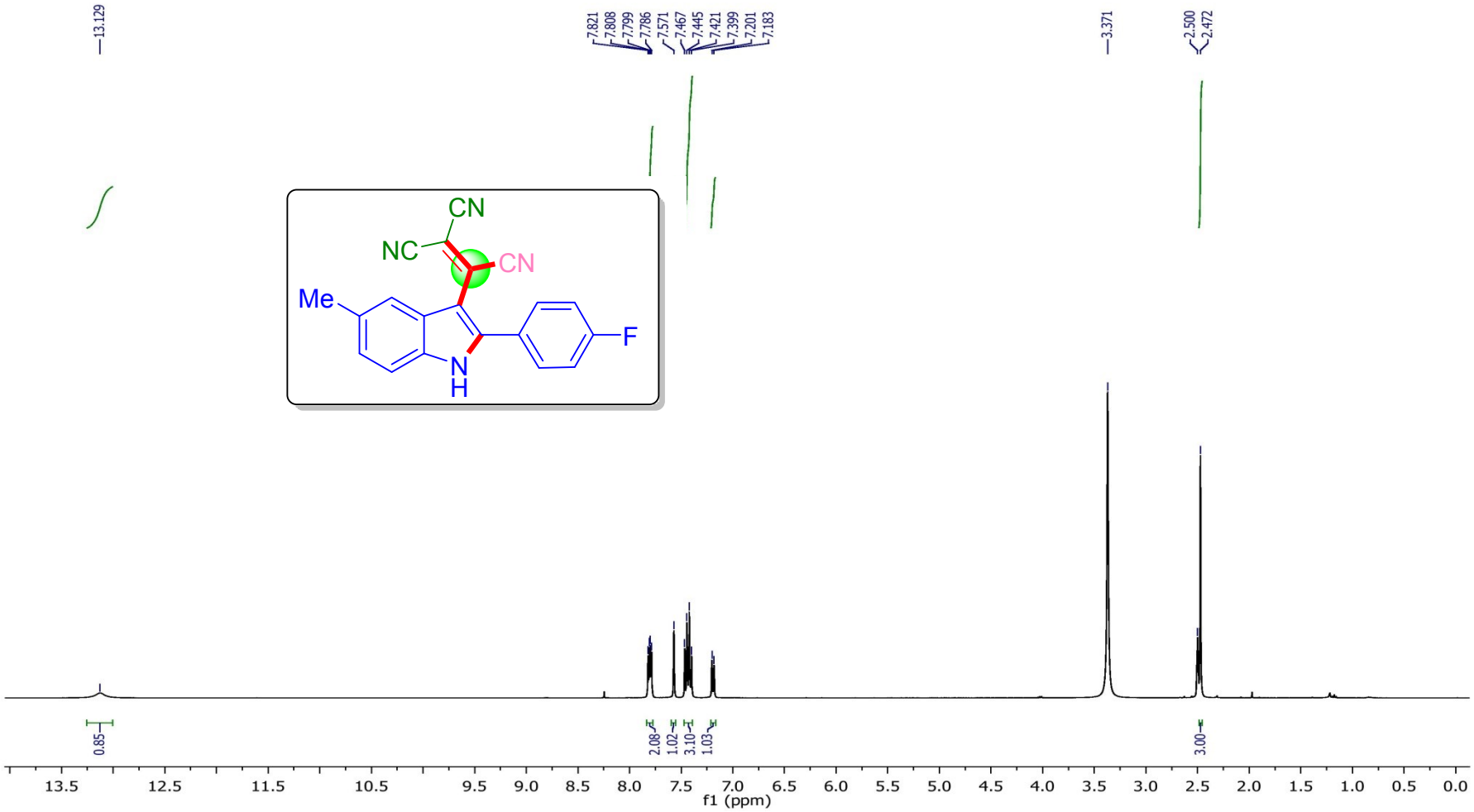
2-(2-(4-(*tert*-Butyl)phenyl)-5-methyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (17a): ^{1}H NMR (400 MHz, $CDCl_3$)



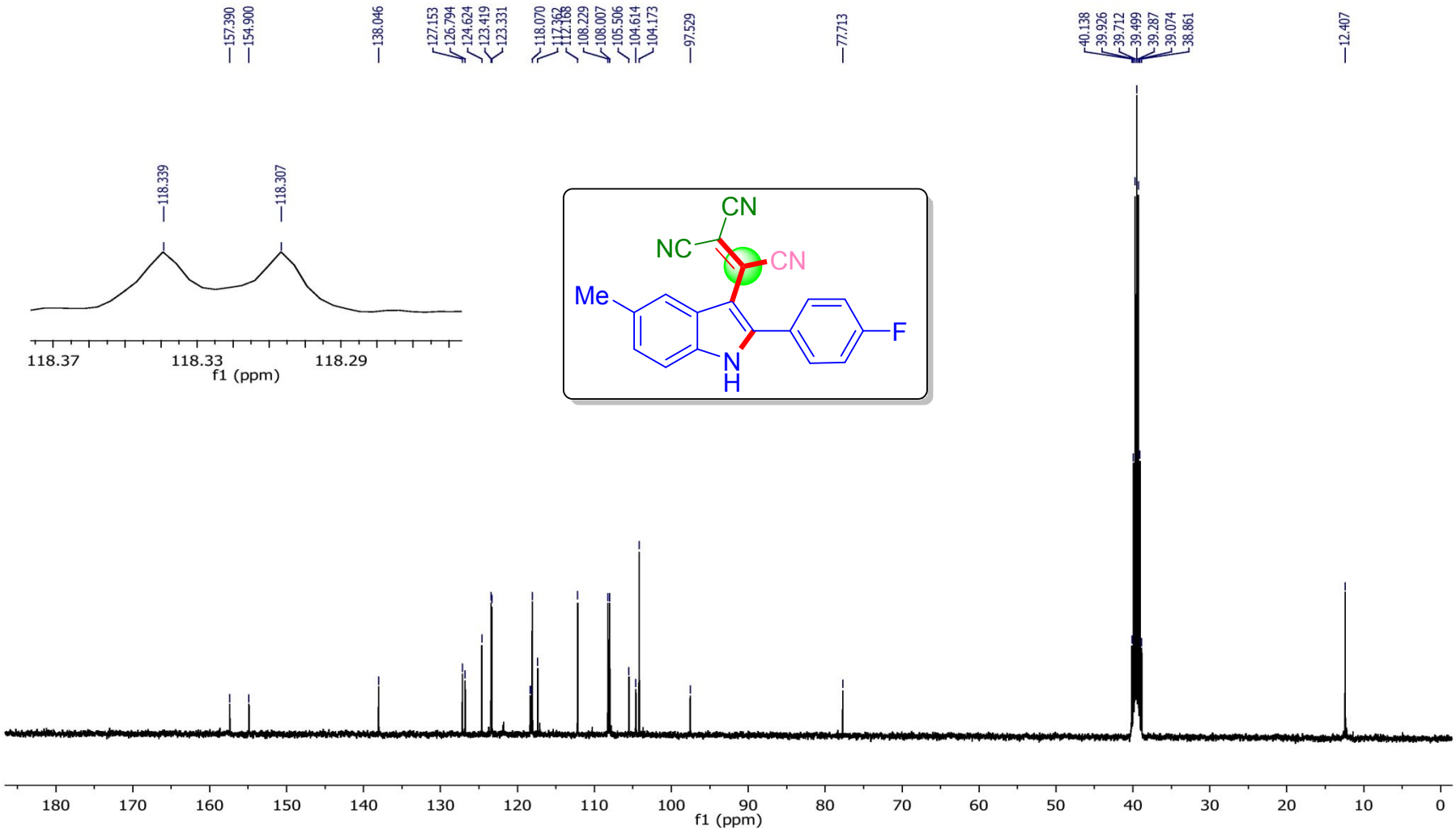
2-(2-(4-(*tert*-Butyl)phenyl)-5-methyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (17a): ^{13}C NMR (100 MHz, $CDCl_3$)



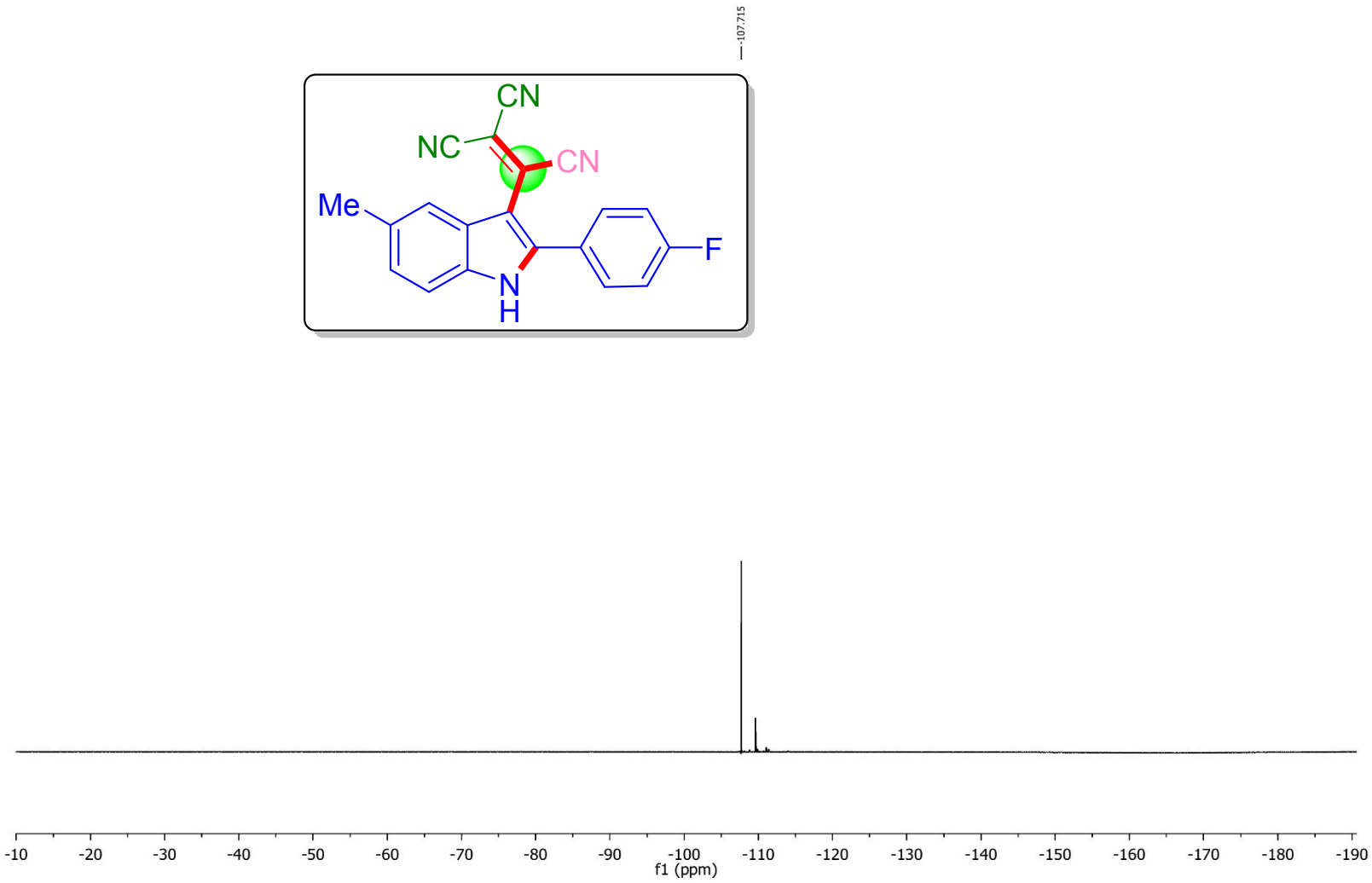
2-(2-(4-Fluorophenyl)-5-methyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (18a): ^{1}H NMR (400 MHz, DMSO)



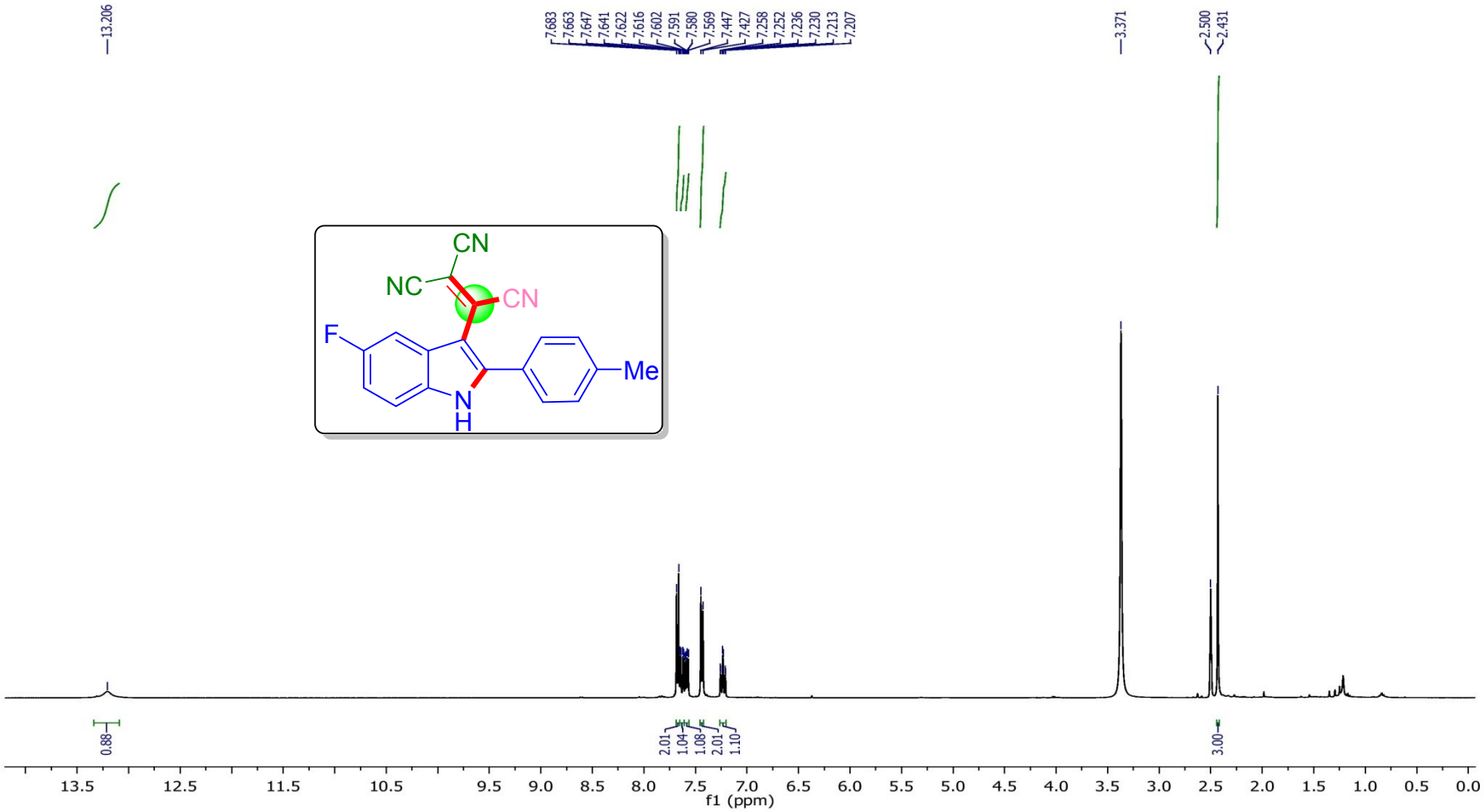
2-(2-(4-Fluorophenyl)-5-methyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (18a): ^{13}C NMR (100 MHz, DMSO)



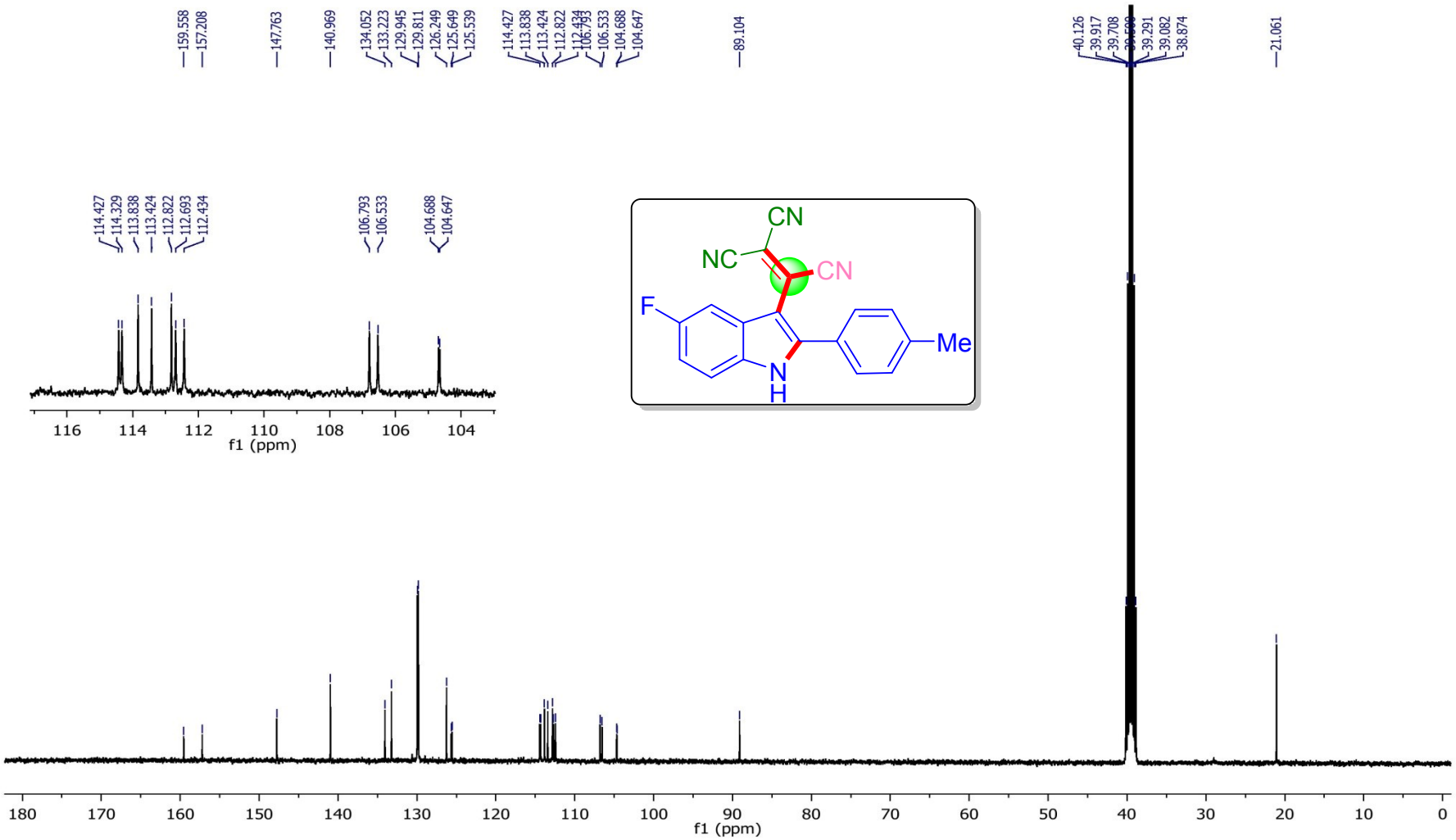
2-(2-(4-Fluorophenyl)-5-methyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (18a): ^{19}F NMR (400 MHz, DMSO)



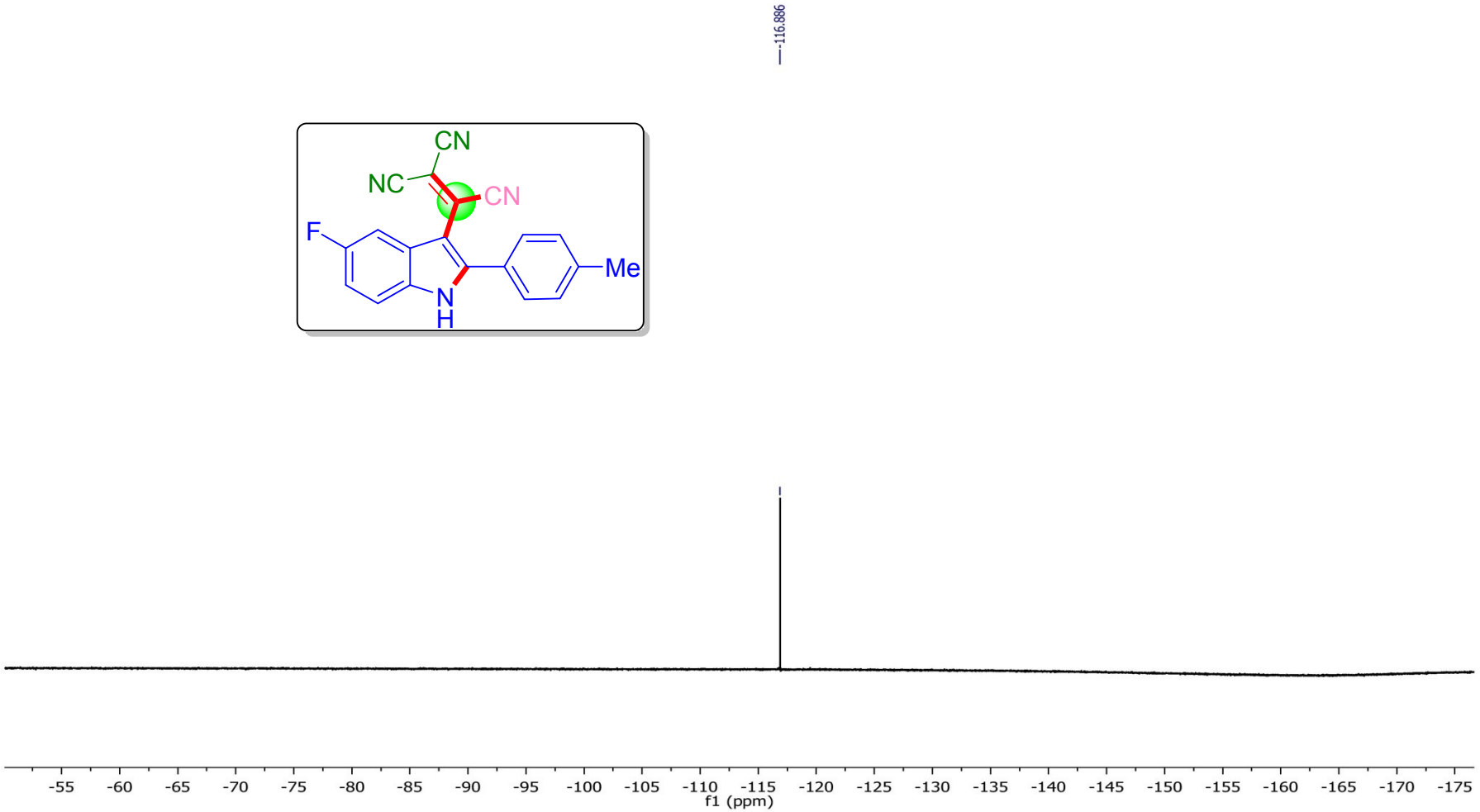
2-(5-Fluoro-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (19a): ^{1}H NMR (400 MHz, DMSO)



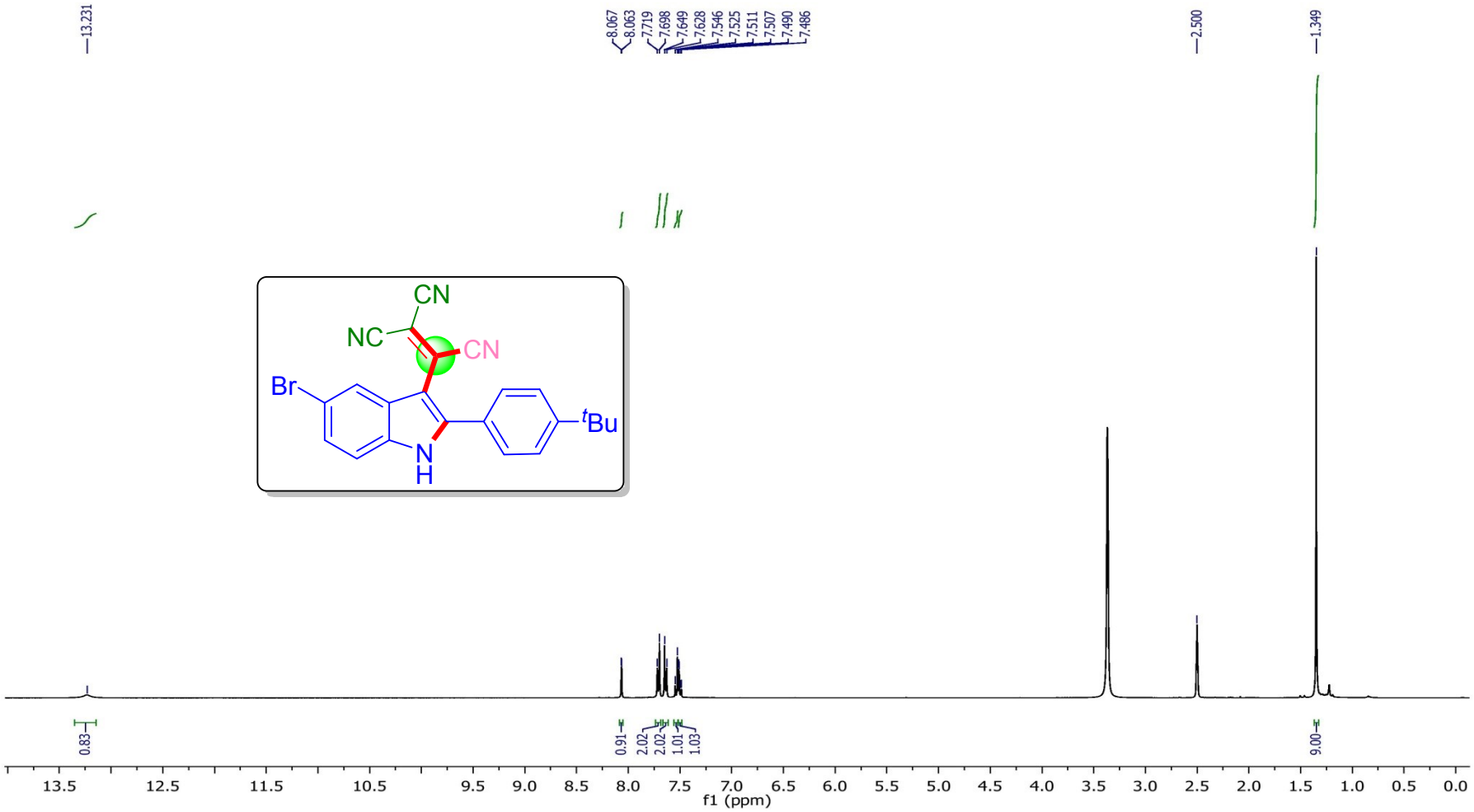
2-(5-Fluoro-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (19a): ^{13}C NMR (100 MHz, DMSO)



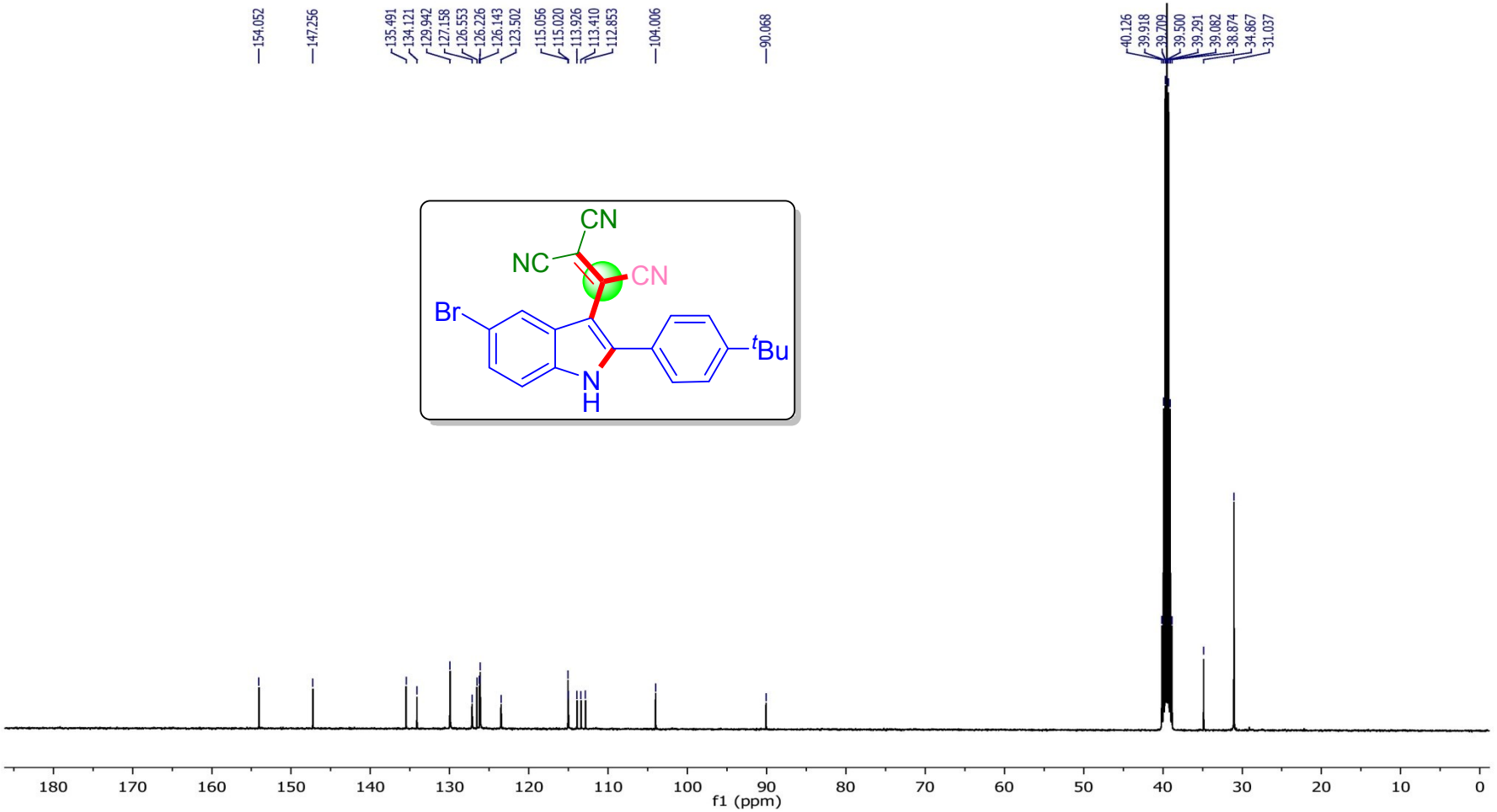
2-(5-Fluoro-2-(*p*-tolyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (19a): ^{19}F NMR (400 MHz, DMSO)



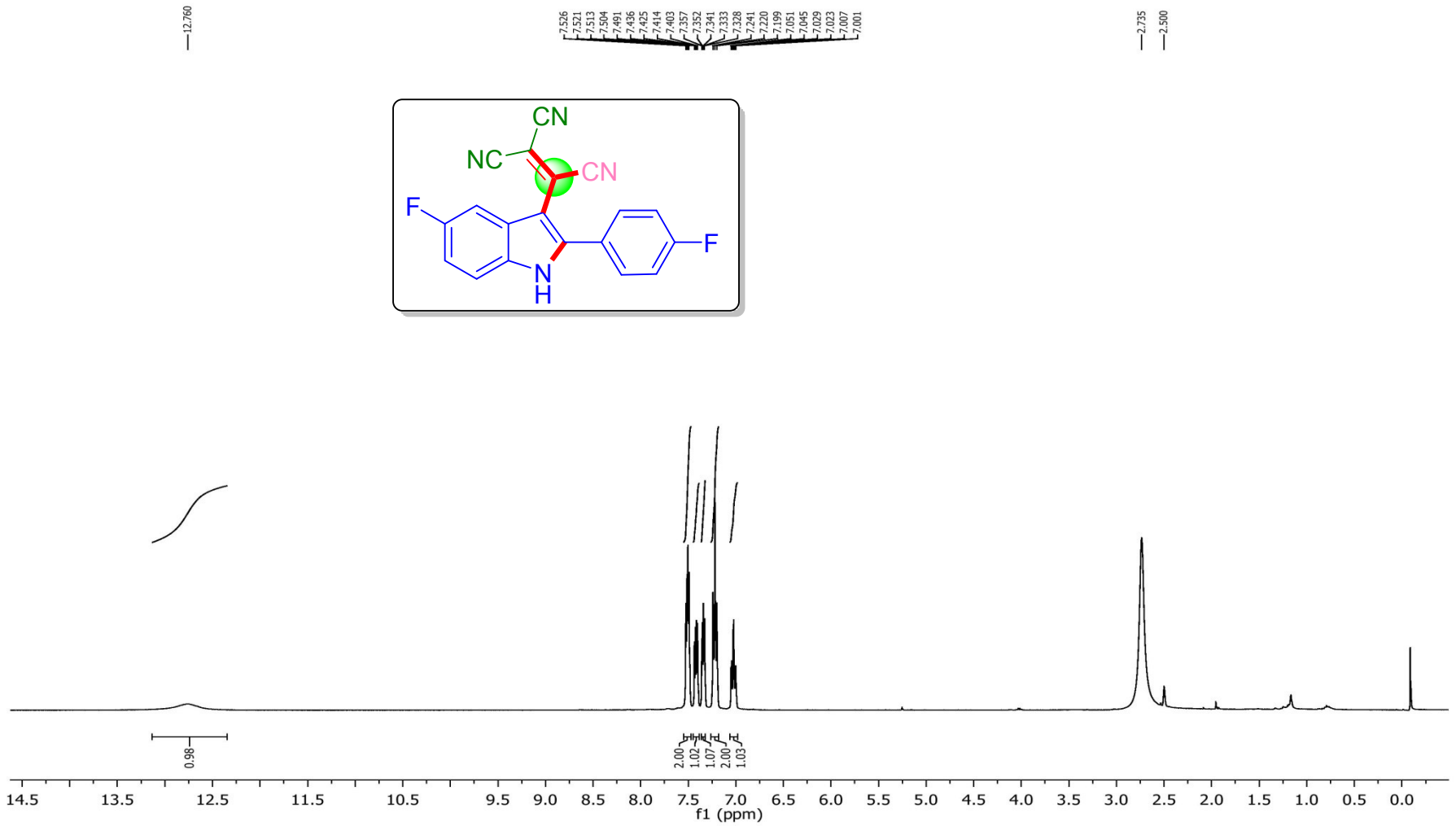
2-(5-Bromo-2-(4-(*tert*-butyl)phenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (20a): ^{1}H NMR (400 MHz, DMSO)



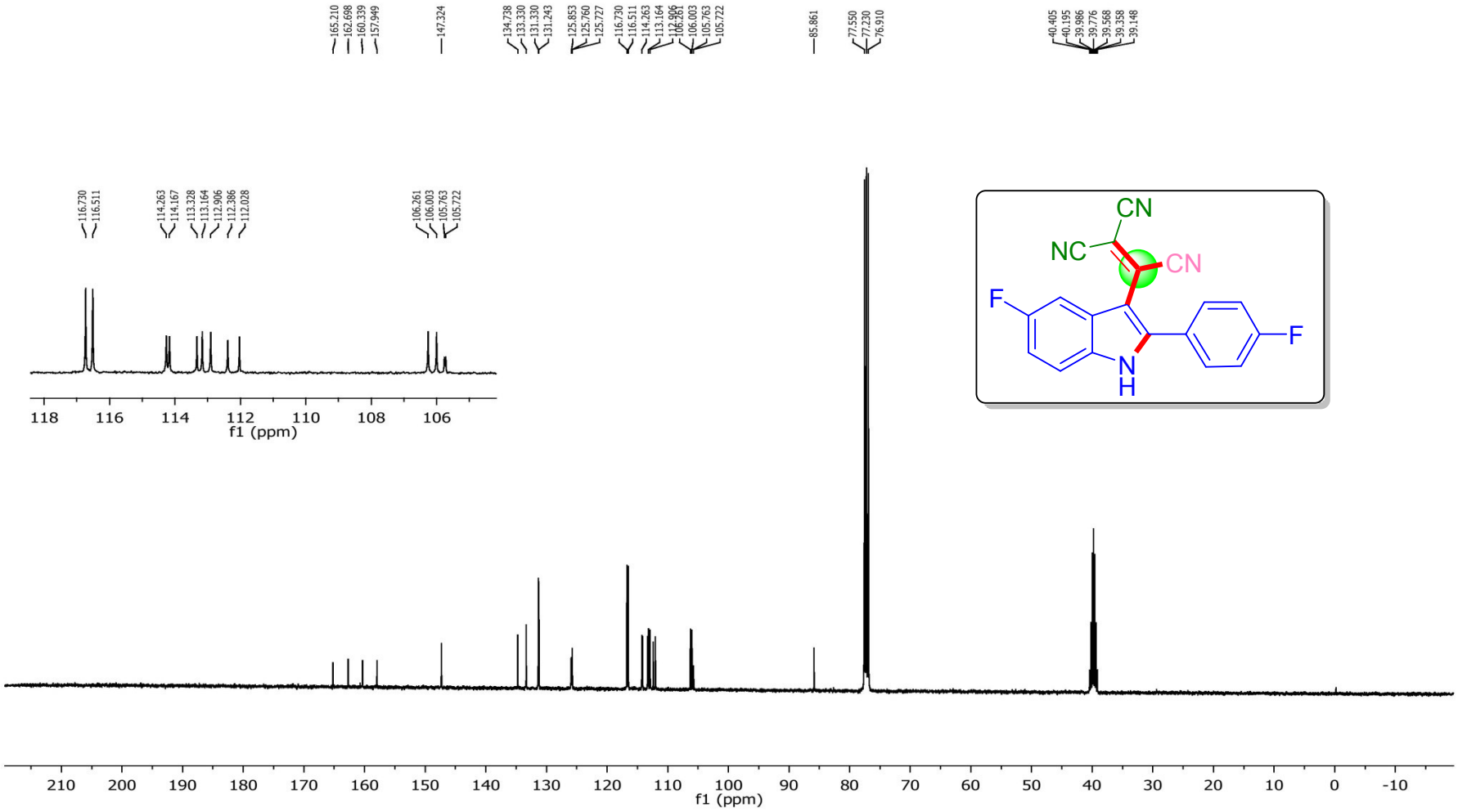
2-(5-Bromo-2-(4-(*tert*-butyl)phenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (20a): ^{13}C NMR (100 MHz, DMSO)



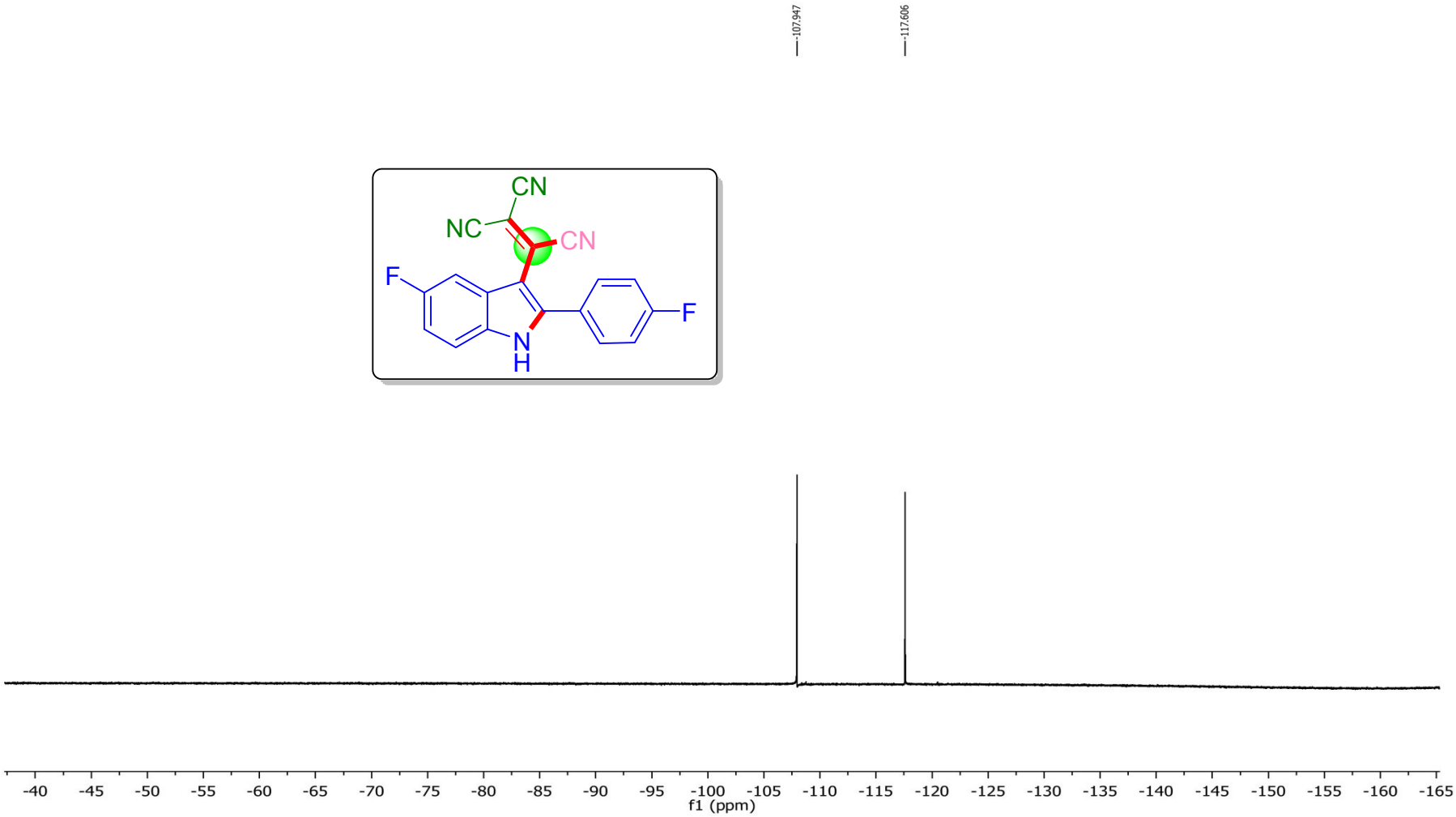
2-(5-Fluoro-2-(4-fluorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (21a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



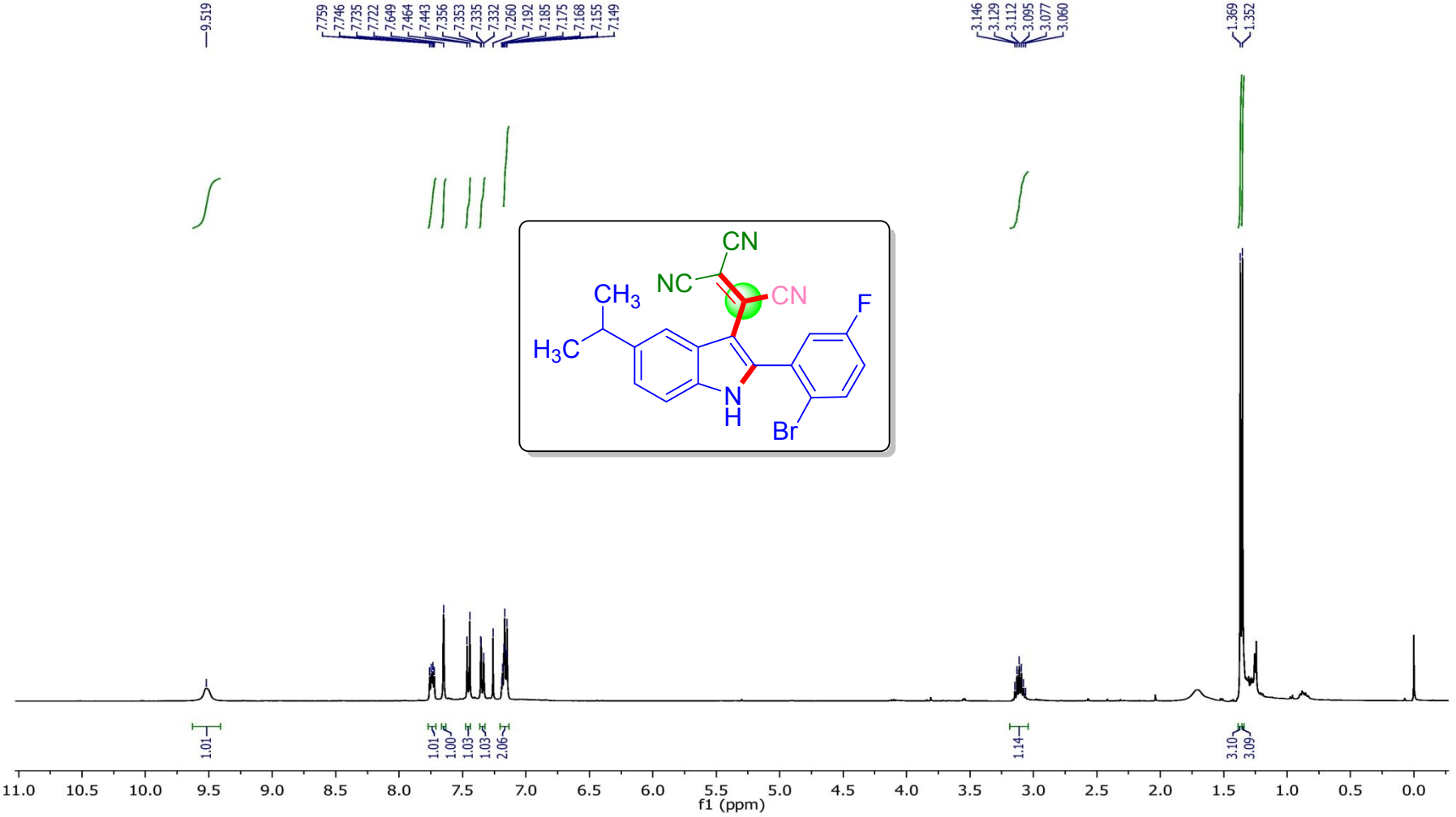
2-(5-Fluoro-2-(4-fluorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (21a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



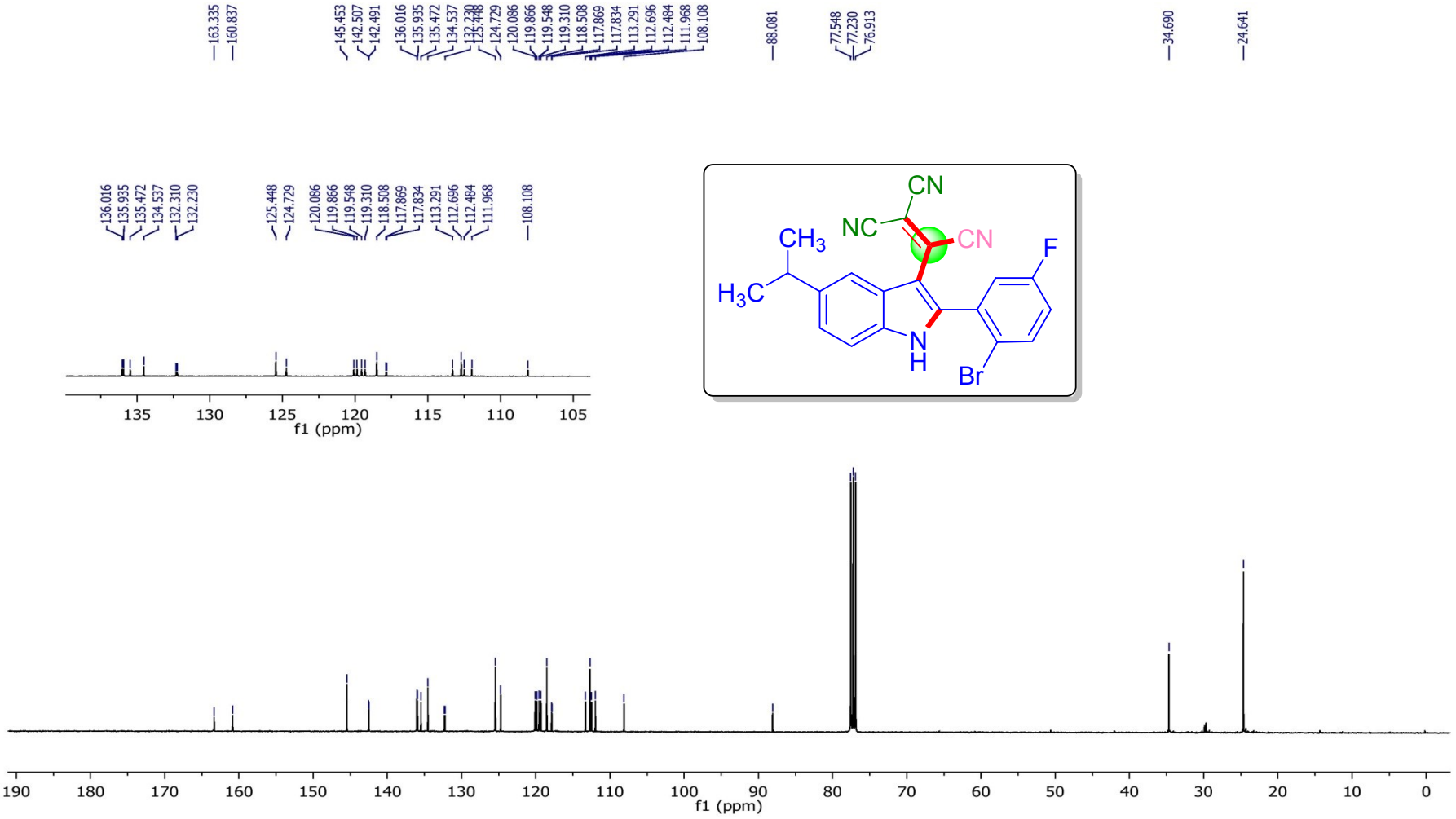
2-(5-Fluoro-2-(4-fluorophenyl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (21a): ^{19}F NMR (100 MHz, $CDCl_3$ + DMSO)



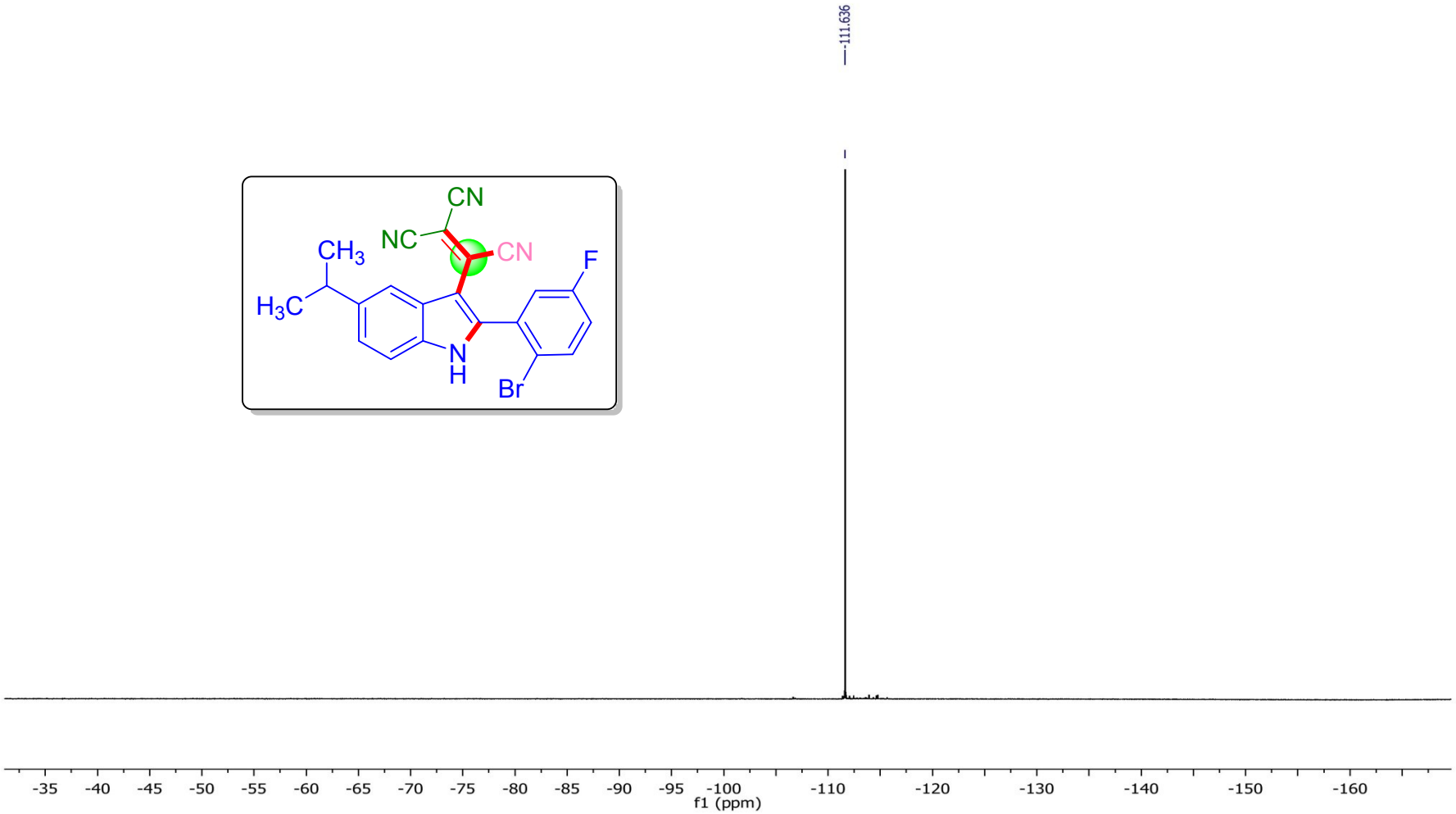
2-(2-(2-Bromo-5-fluorophenyl)5-isopropyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (22a): ^{1}H NMR (400 MHz, $CDCl_3$)



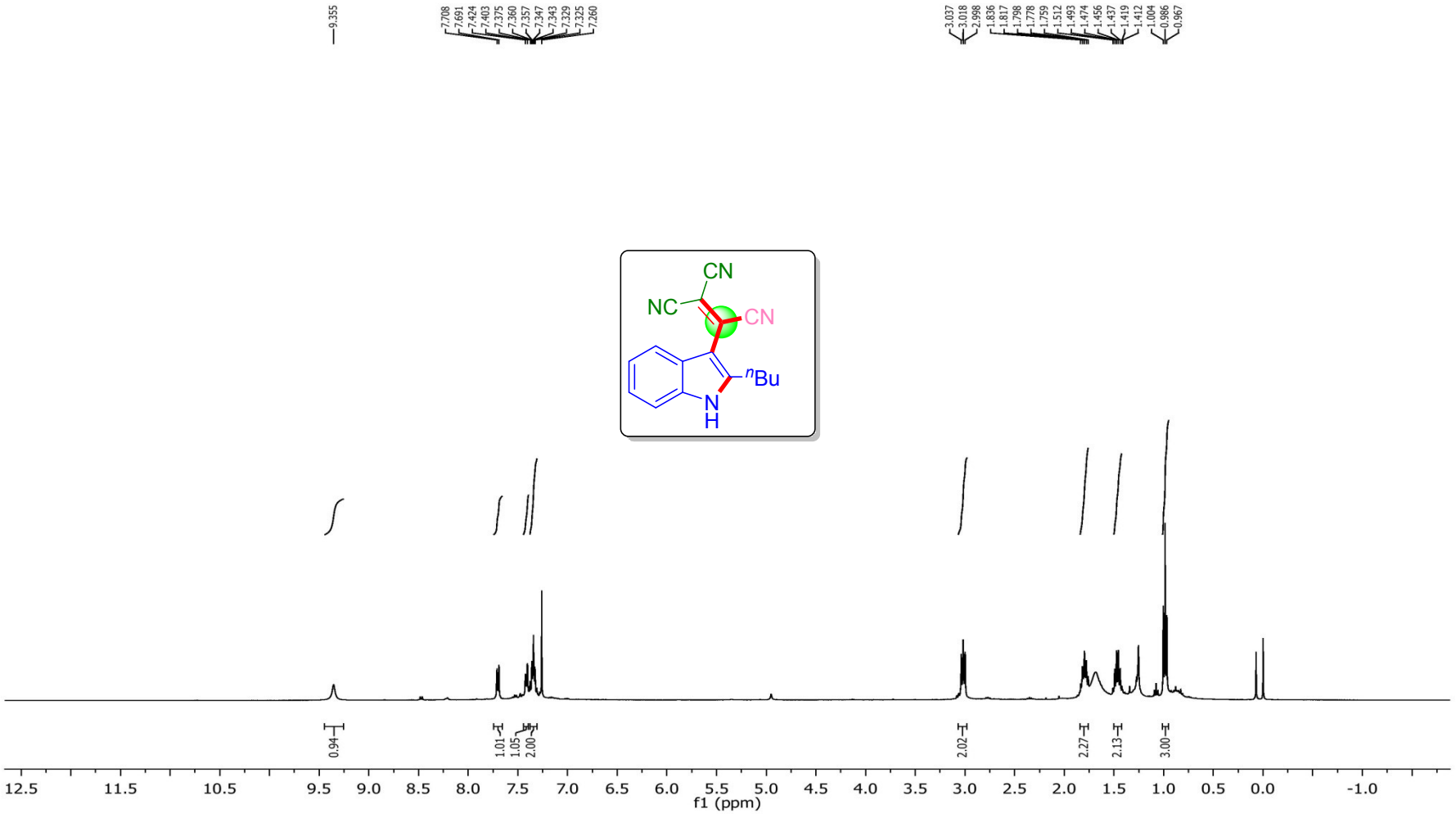
2-(2-(2-Bromo-5-fluorophenyl)5-isopropyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (22a): ^{13}C NMR (100 MHz, $CDCl_3$)



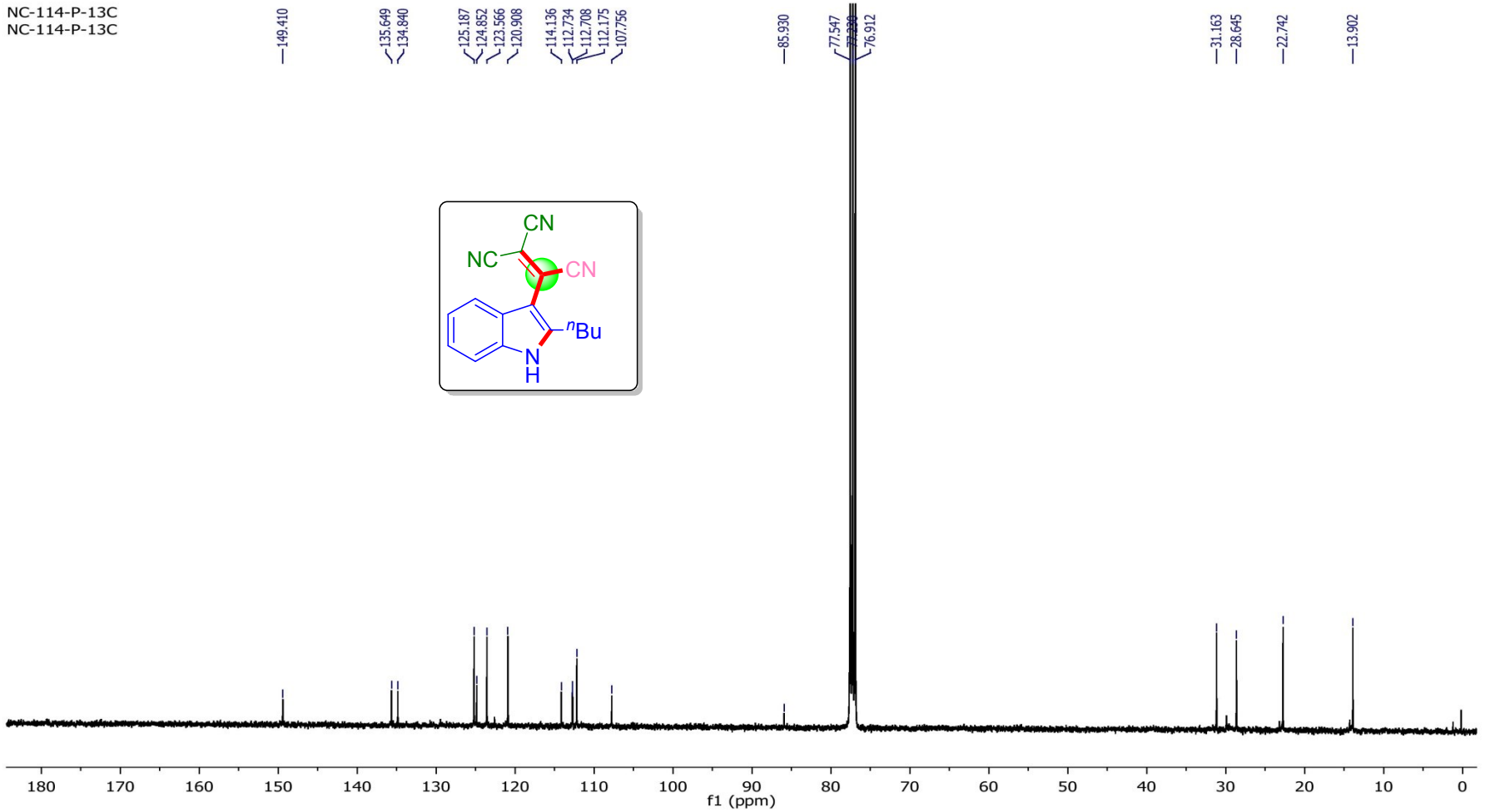
2-(2-(2-Bromo-5-fluorophenyl)5-isopropyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (22a): ^{19}F NMR (400 MHz, $CDCl_3$)



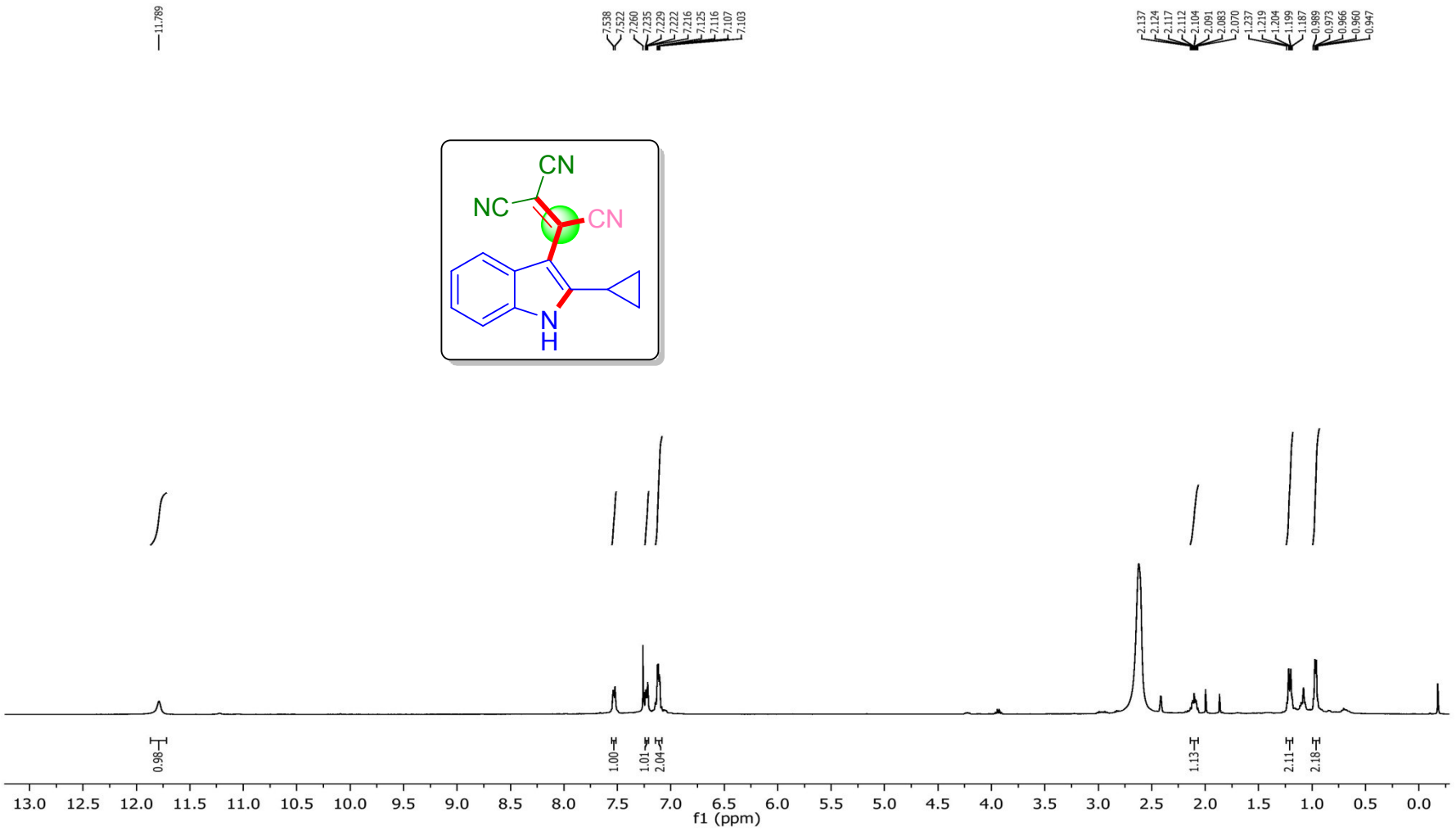
2-(2-Butyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (23a): ^{1}H NMR (400 MHz, $CDCl_3$)



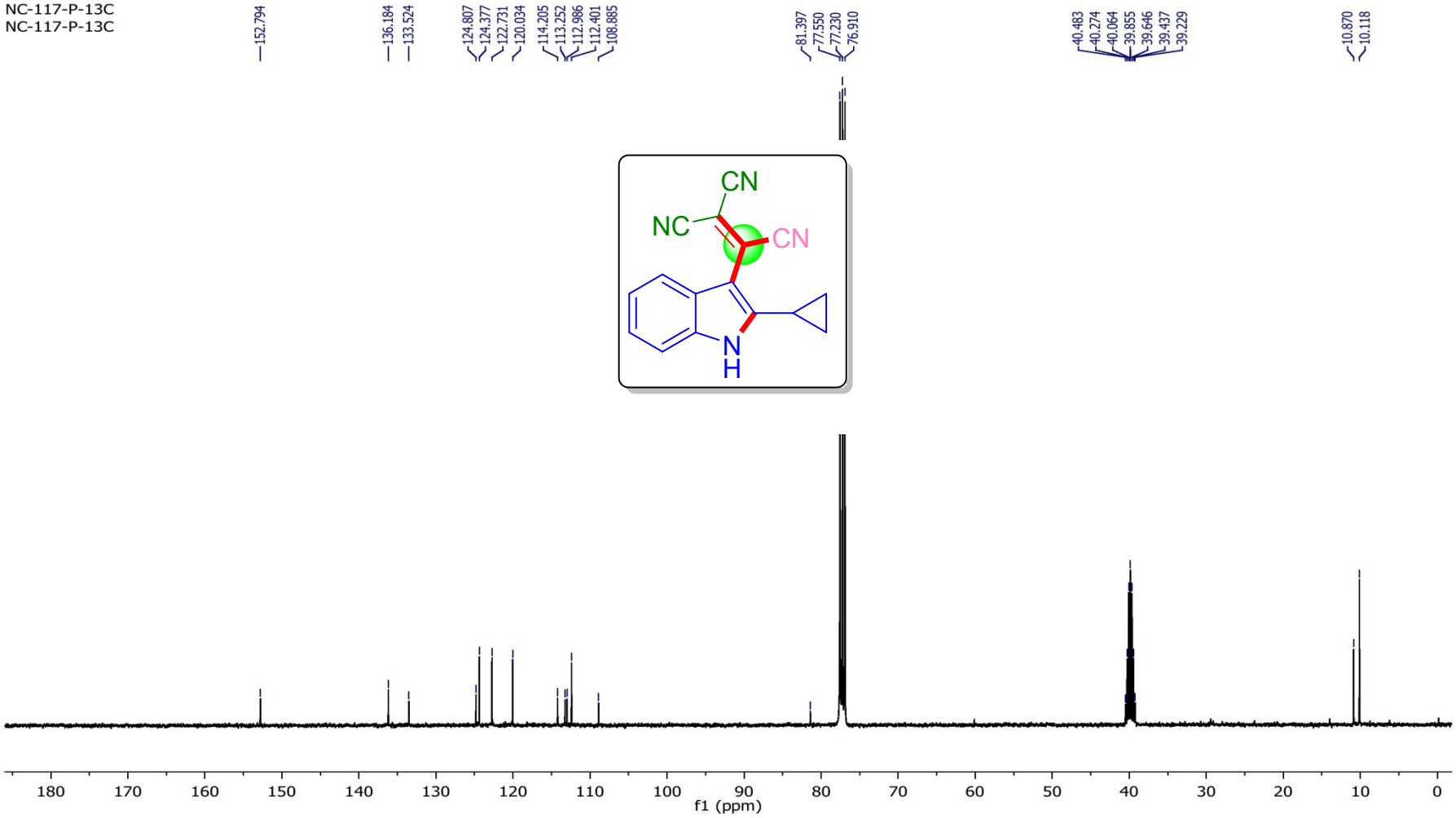
2-(2-Butyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (23a): ^{13}C NMR (100 MHz, $CDCl_3$)



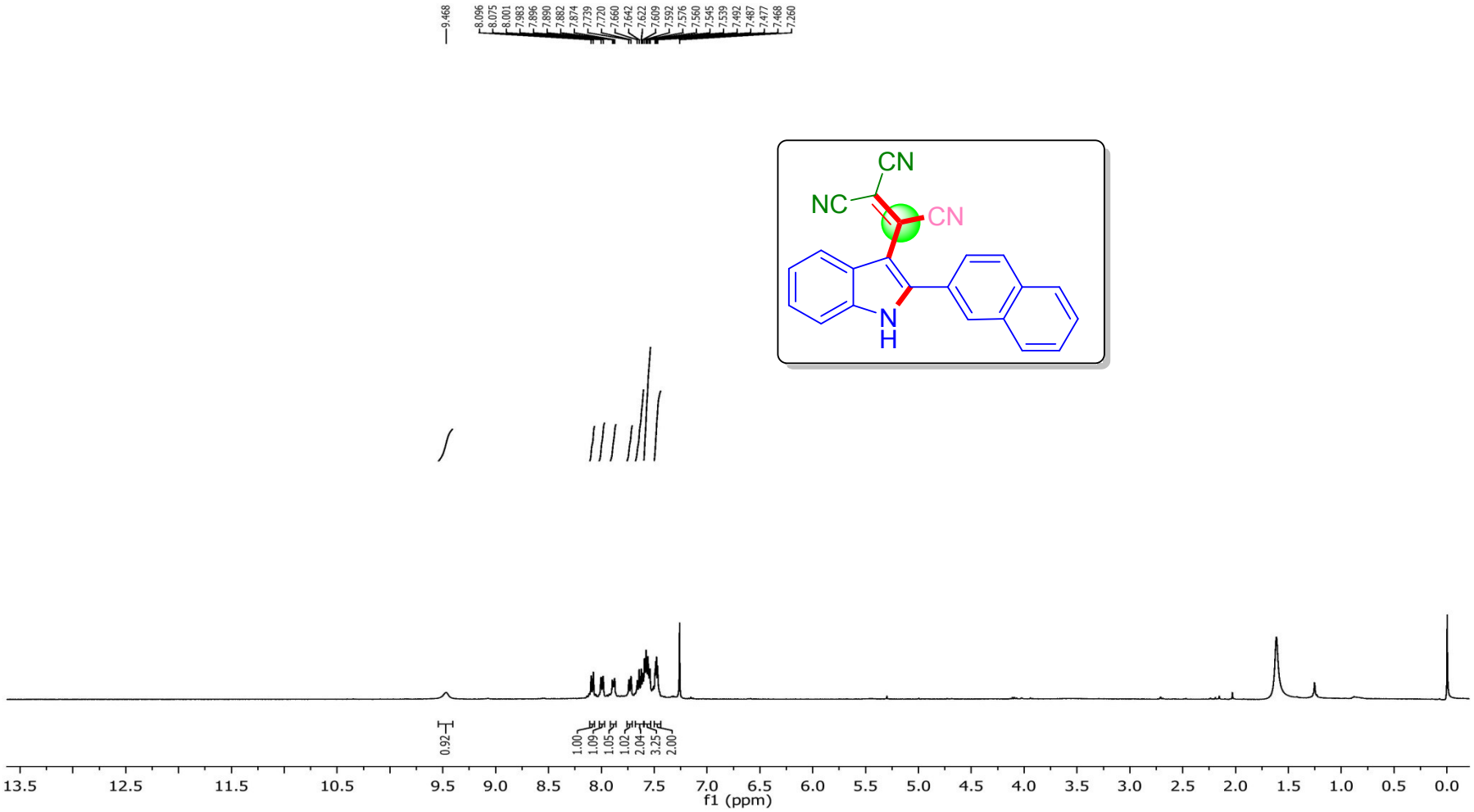
2-(2-Cyclopropyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (24a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



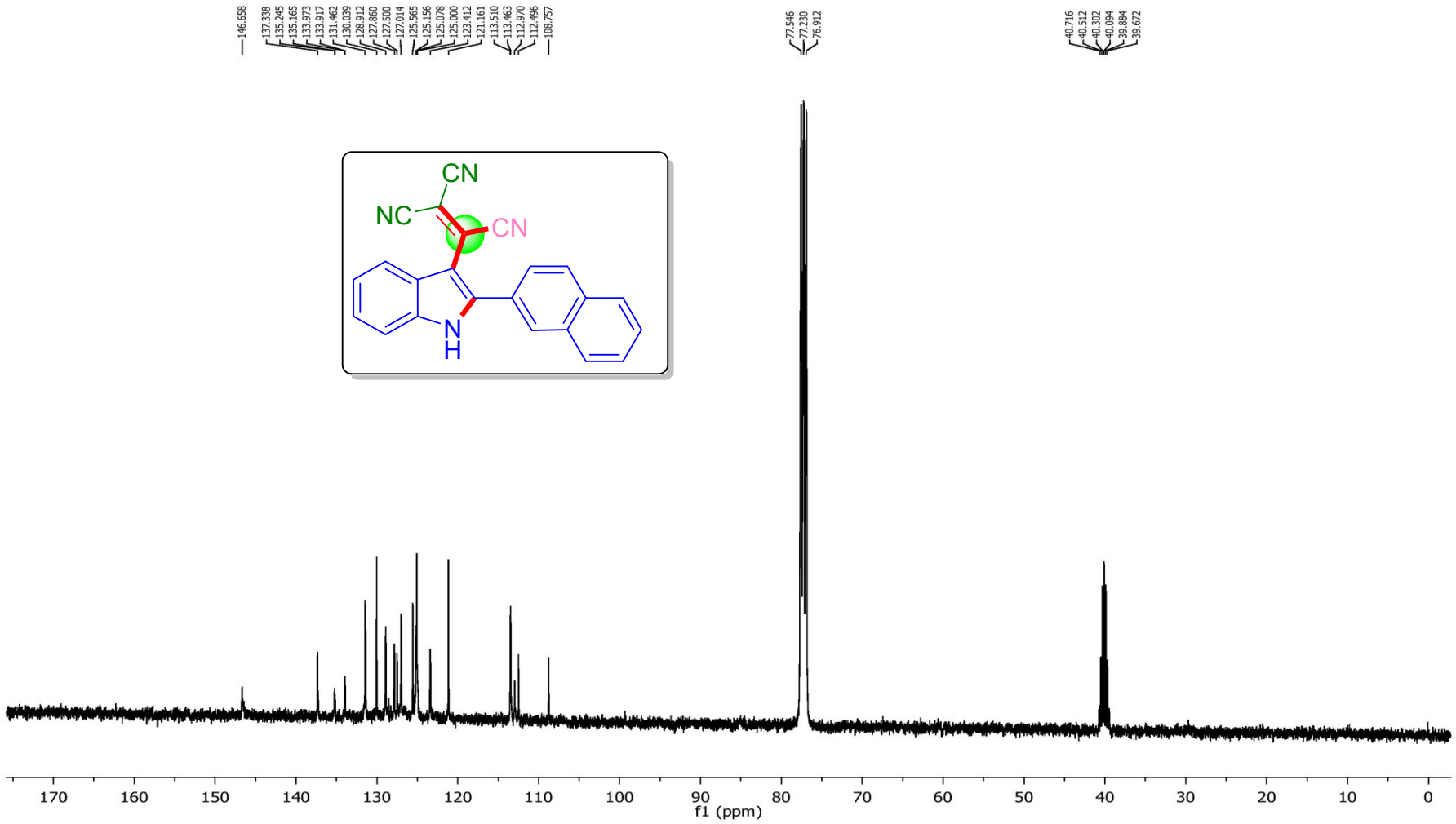
2-(2-Cyclopropyl-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (24a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



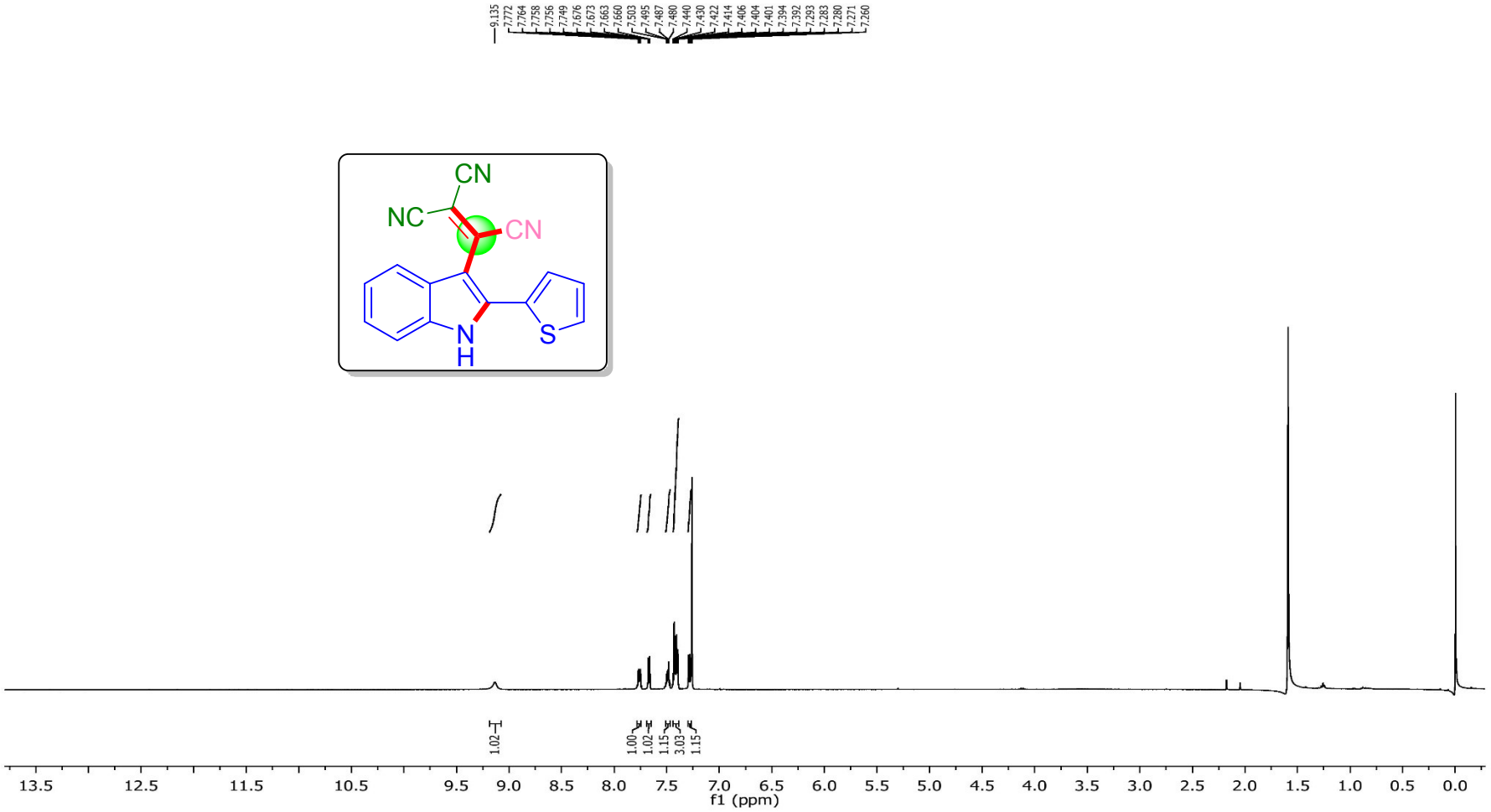
2-(2-(Naphthalen-2-yl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (25a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



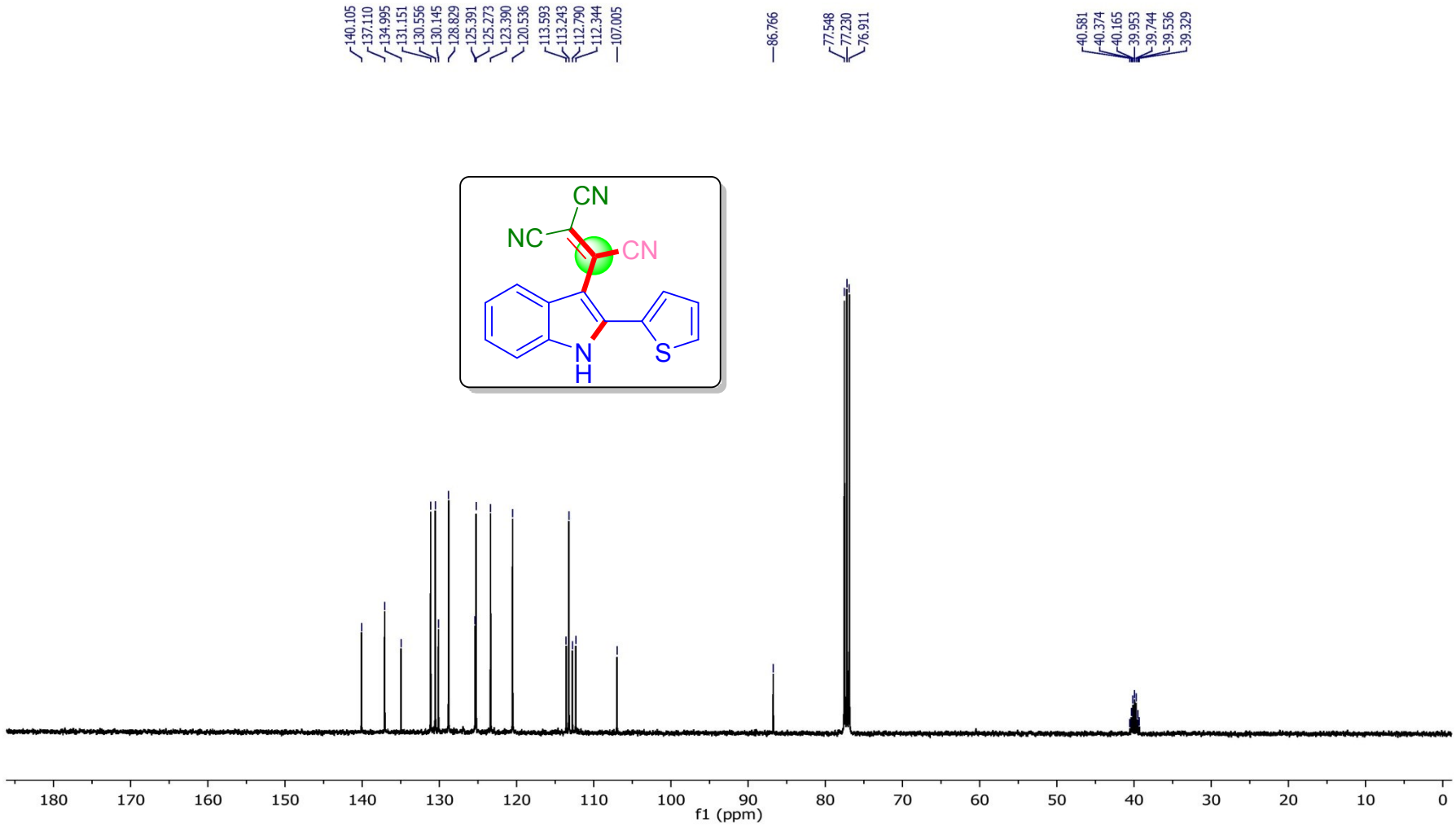
2-(2-(Naphthalen-2-yl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (25a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



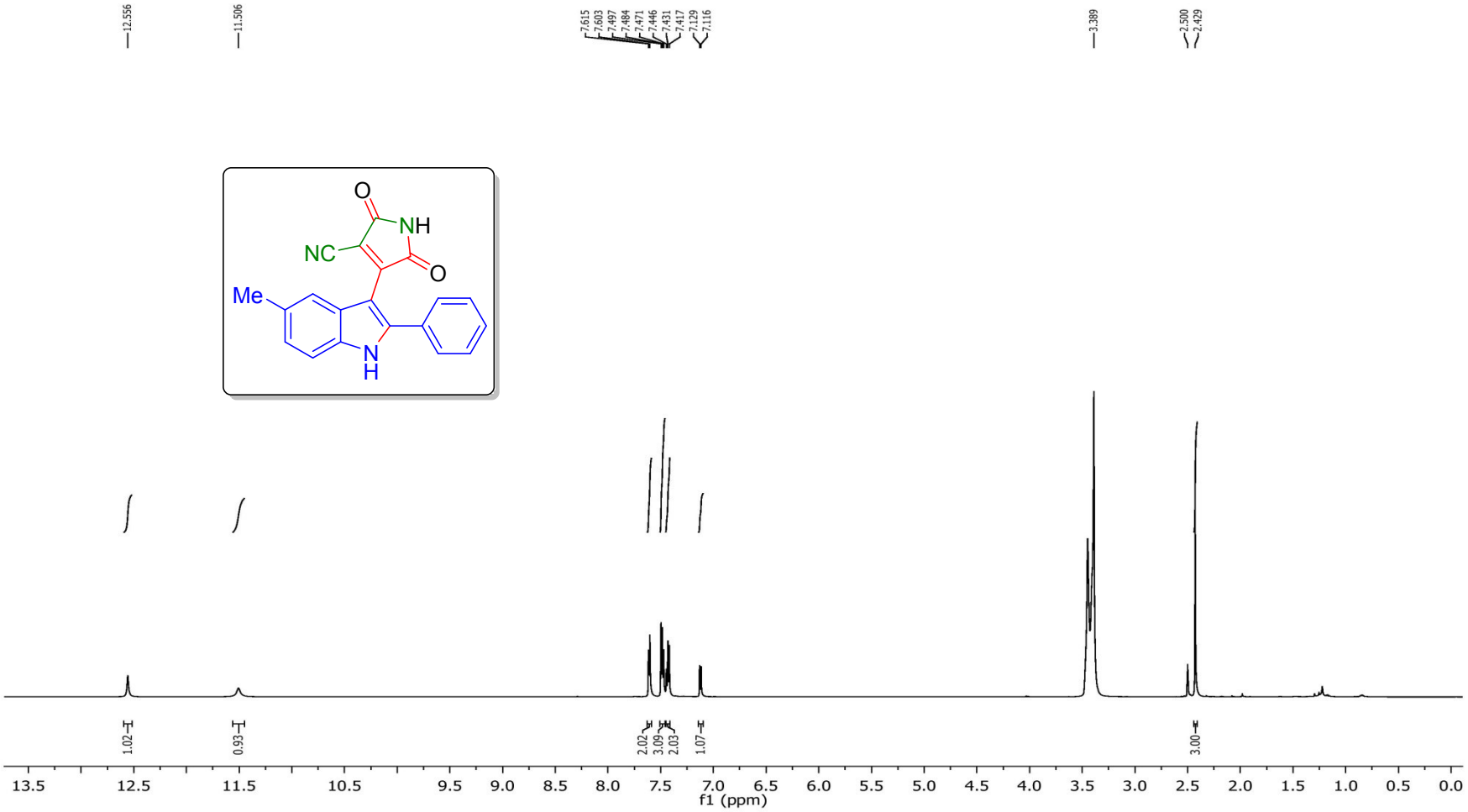
2-(2-(Thiophen-2-yl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (26a): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



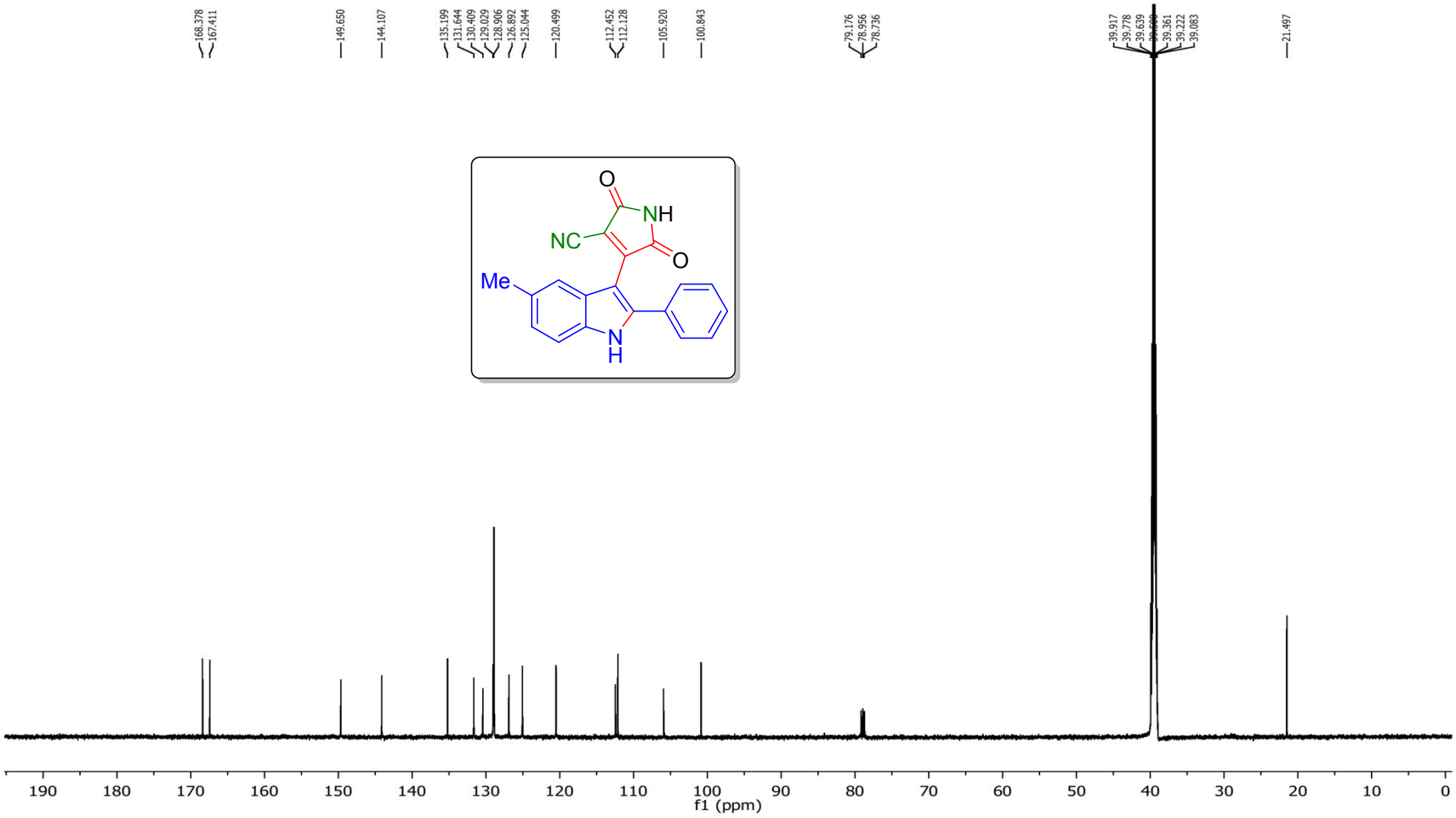
2-(2-(Thiophen-2-yl)-1*H*-indol-3-yl)ethene-1,1,2-tricarbonitrile (26a): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



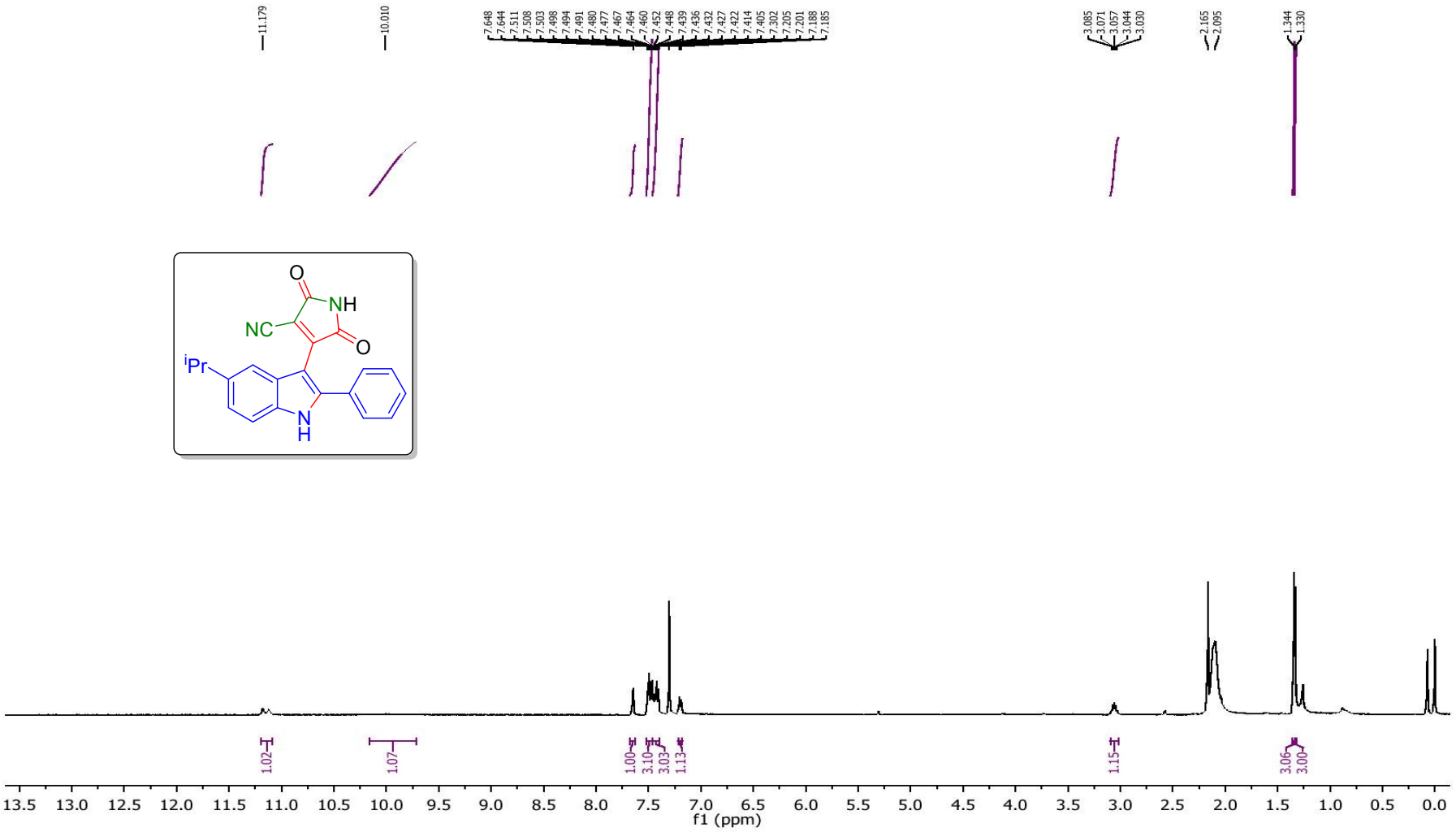
4-(5-Methyl-2-phenyl-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (2ab): ^{1}H NMR (600 MHz, $CDCl_3$ + DMSO)



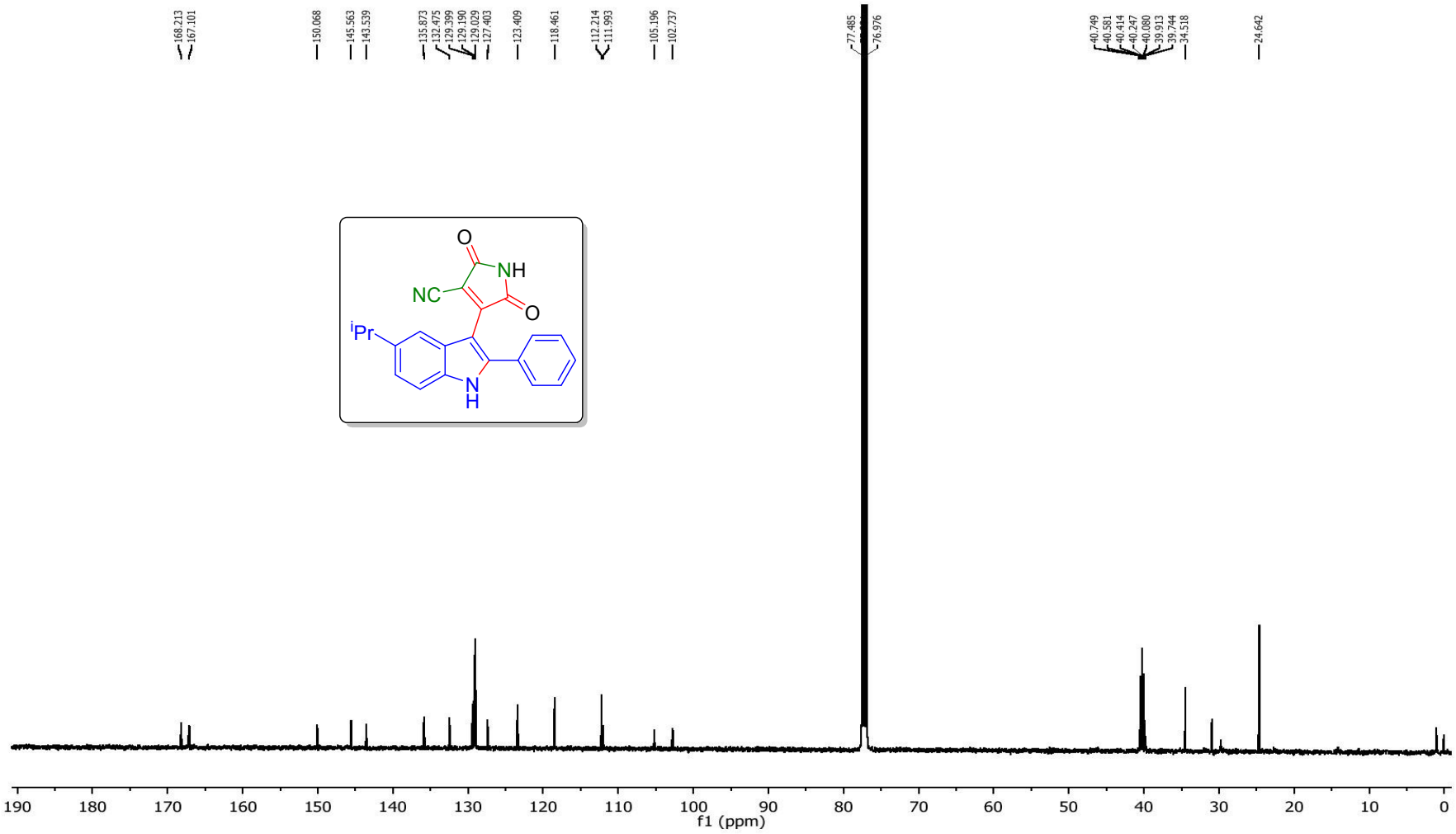
4-(5-Methyl-2-phenyl-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (2ab): ^{13}C NMR (150 MHz, $CDCl_3$ + DMSO)



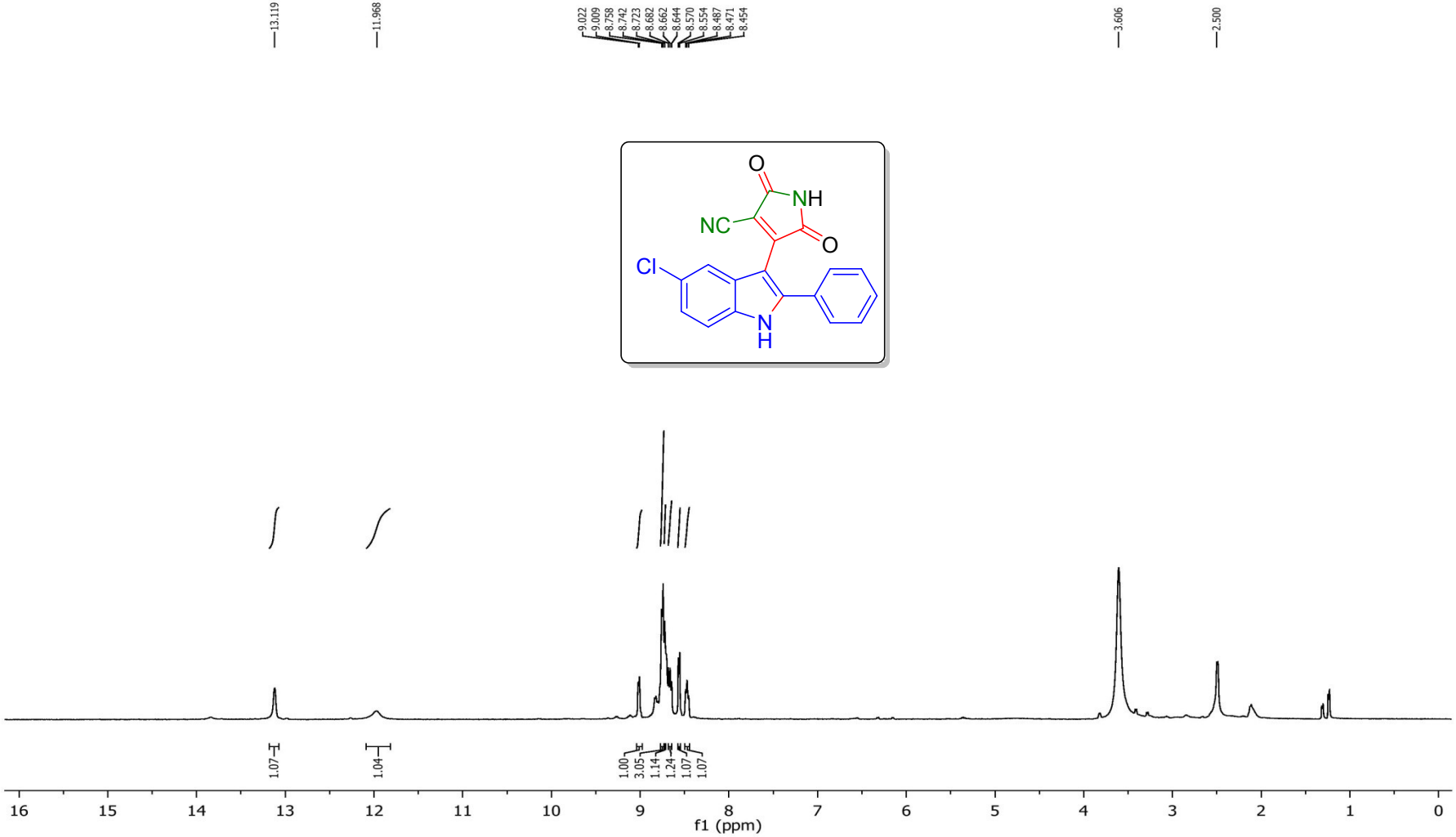
4-(5-Isopropyl-2-phenyl-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (3ab): **^{1}H NMR (500 MHz, $CDCl_3$ + DMSO)**



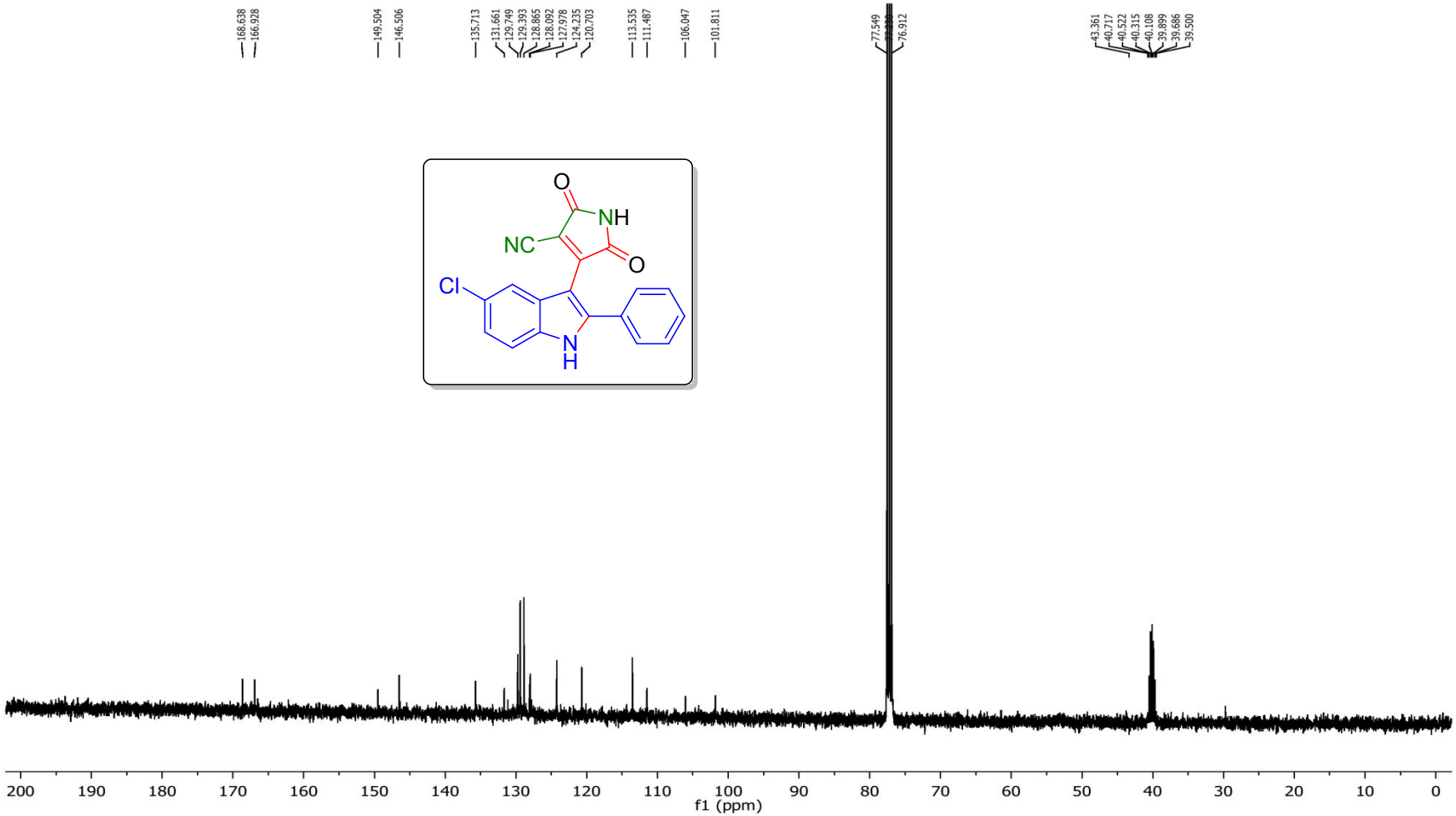
4-(5-Isopropyl-2-phenyl-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (3ab): **^{13}C NMR (125 MHz, $CDCl_3$ + DMSO)**



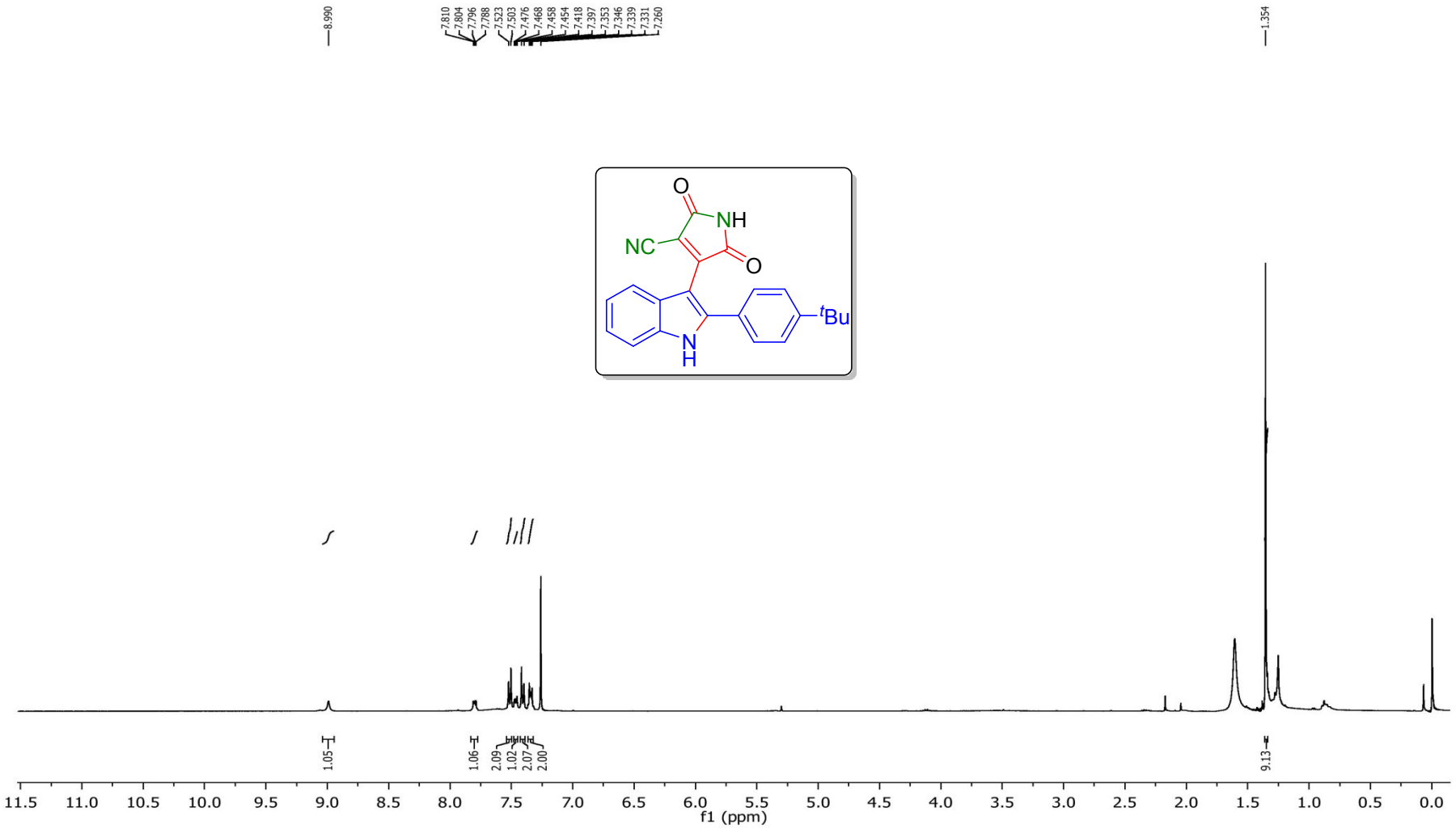
4-(5-Chloro-2-phenyl-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (6ab): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



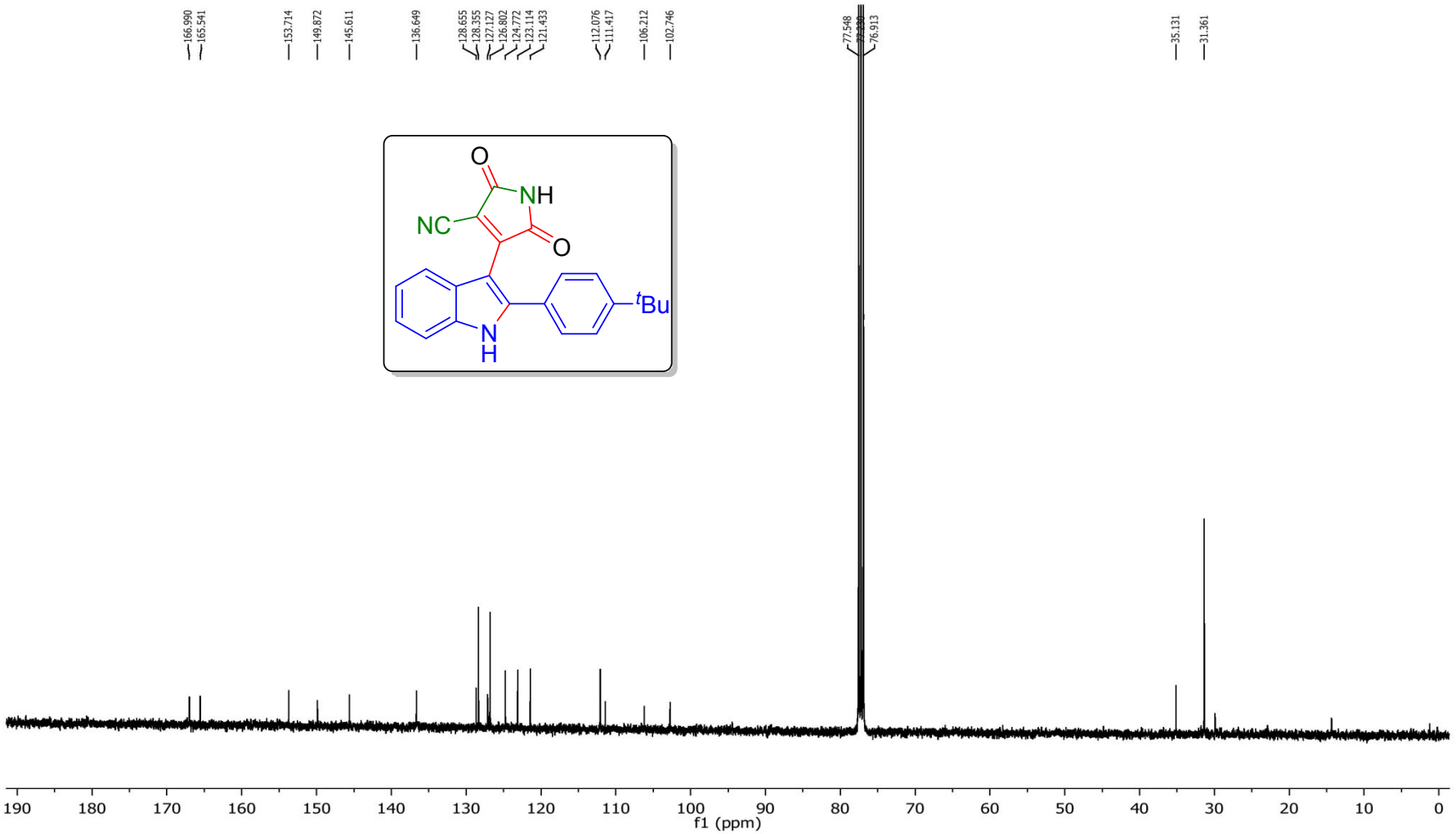
4-(5-Chloro-2-phenyl-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (6ab): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



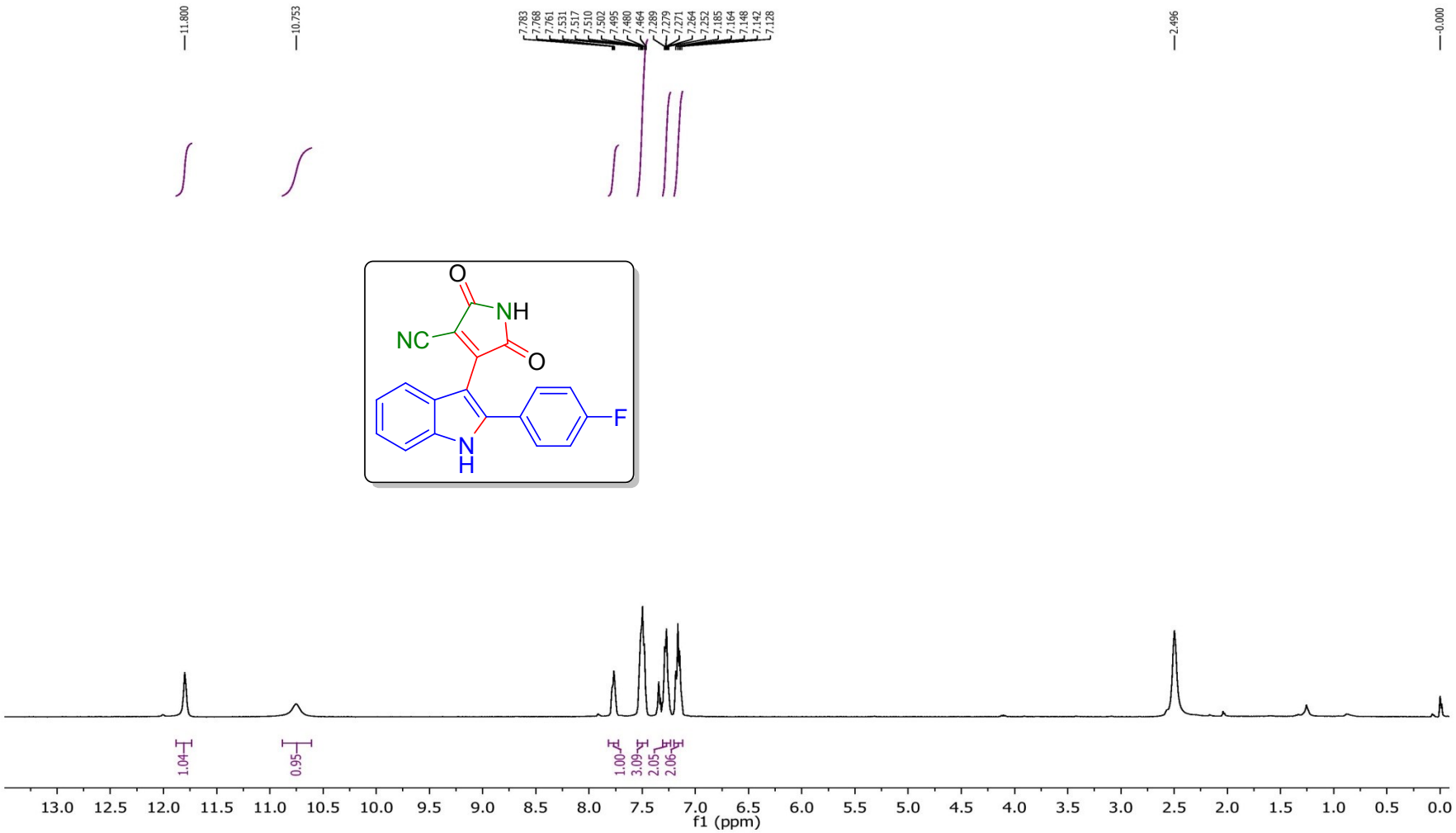
4-(2-(4-(*tert*-Butyl)phenyl)-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (10ab): ^{1}H NMR (400 MHz, $CDCl_3$)



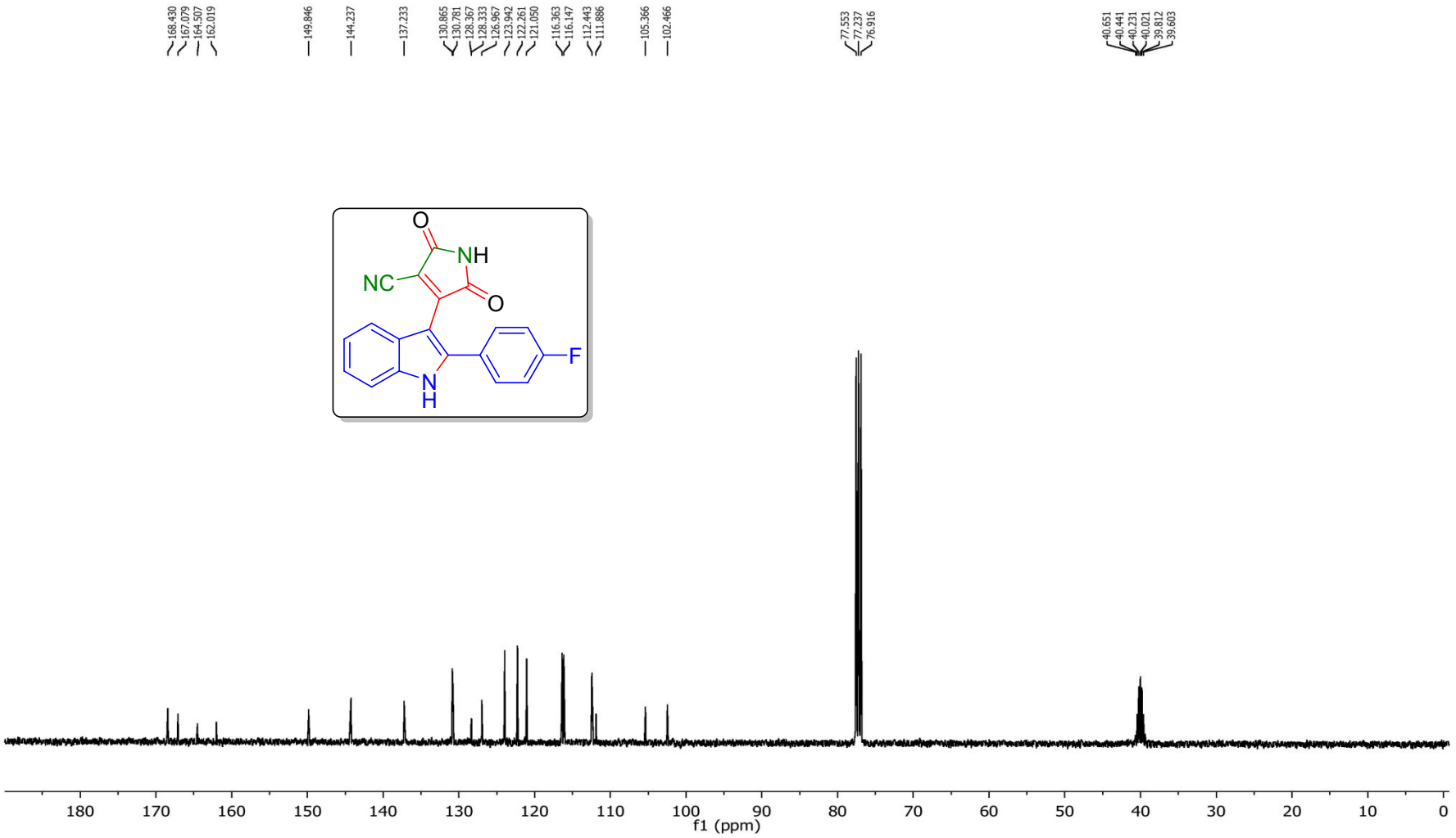
4-(2-(4-(*tert*-Butyl)phenyl)-1*H*-indol-3-yl)-2,5-dioxo-2,5-dihydro-1*H*-pyrrole-3-carbonitrile (10ab): ^{13}C NMR (100 MHz, $CDCl_3$)



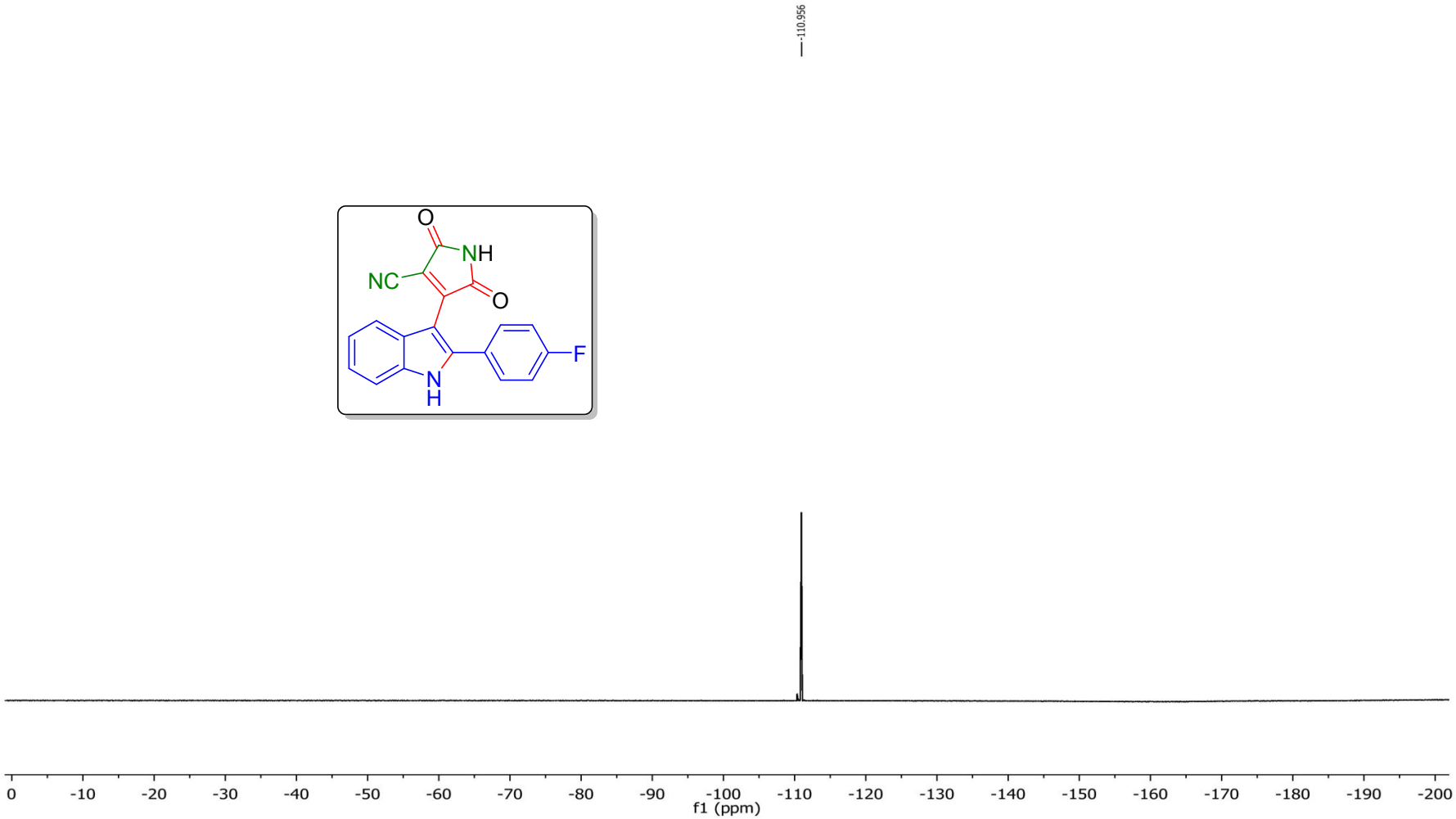
4-(2-(4-Fluorophenyl)-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (12ab): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



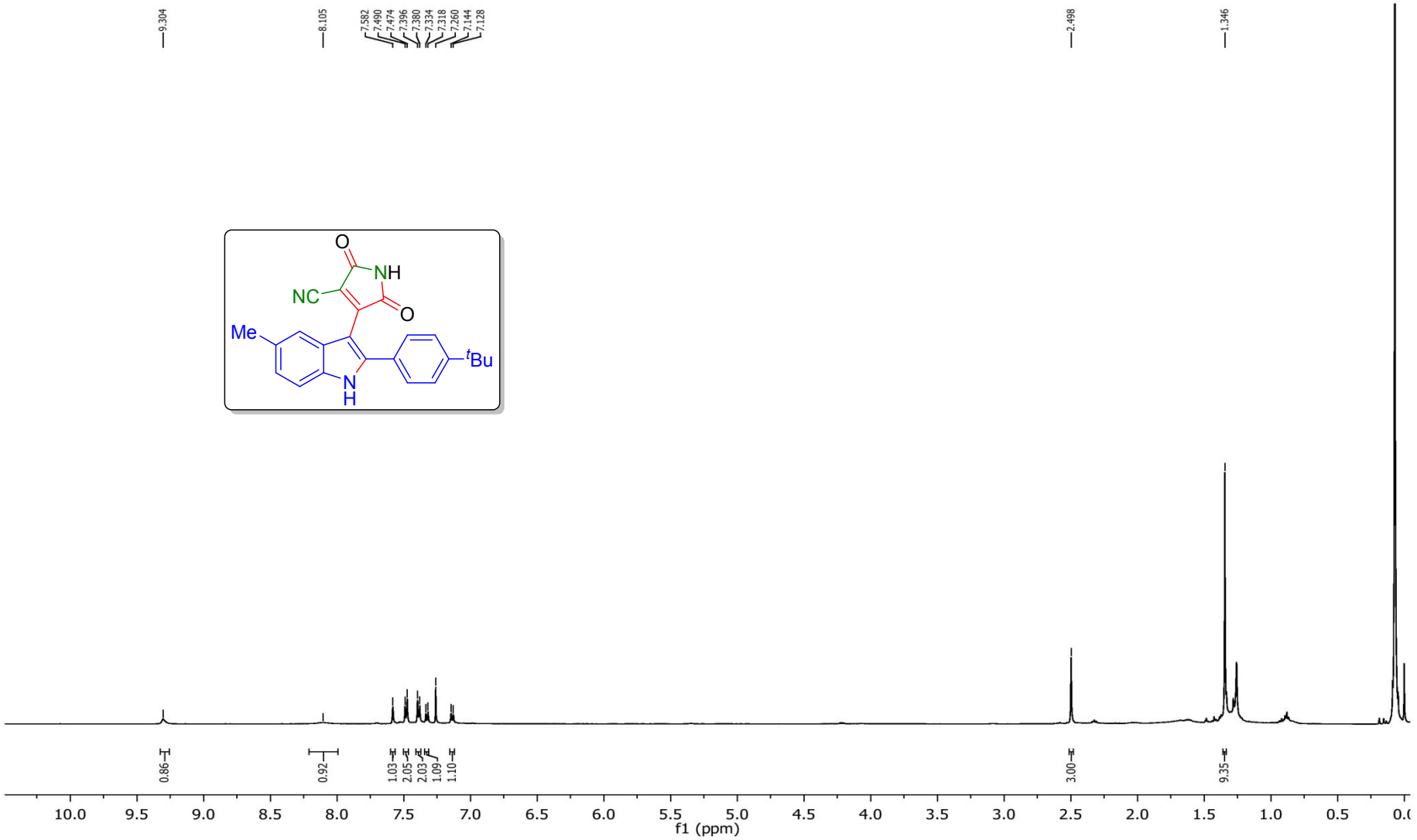
4-(2-(4-Fluorophenyl)-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (12ab): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



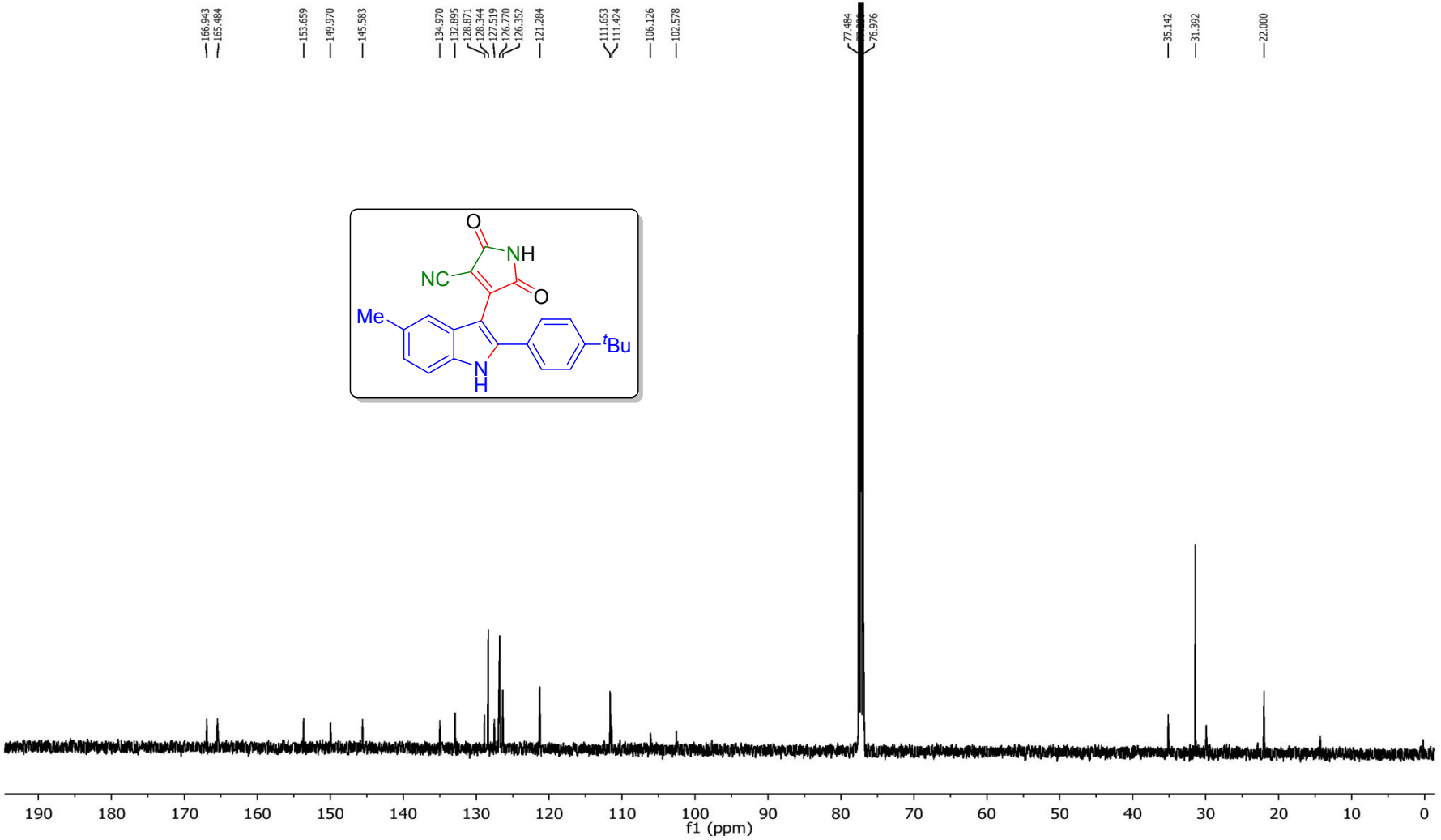
4-(2-(4-Fluorophenyl)-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (12ab): ^{19}F NMR (400 MHz, $CDCl_3$ + DMSO)



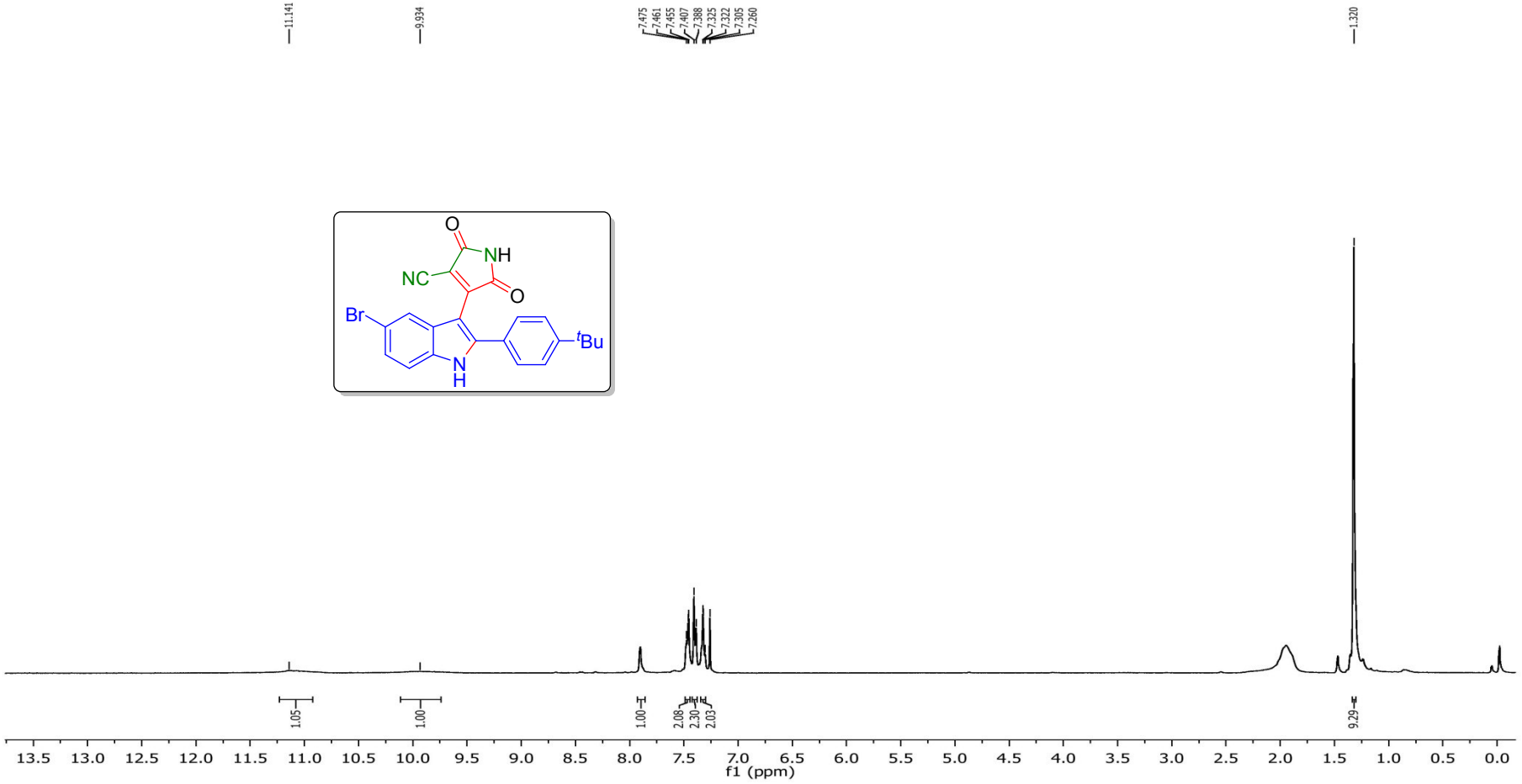
4-(2-(4-(tert-Butyl)phenyl)-5-methyl-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (17ab): ^{1}H NMR (500 MHz, $CDCl_3$)



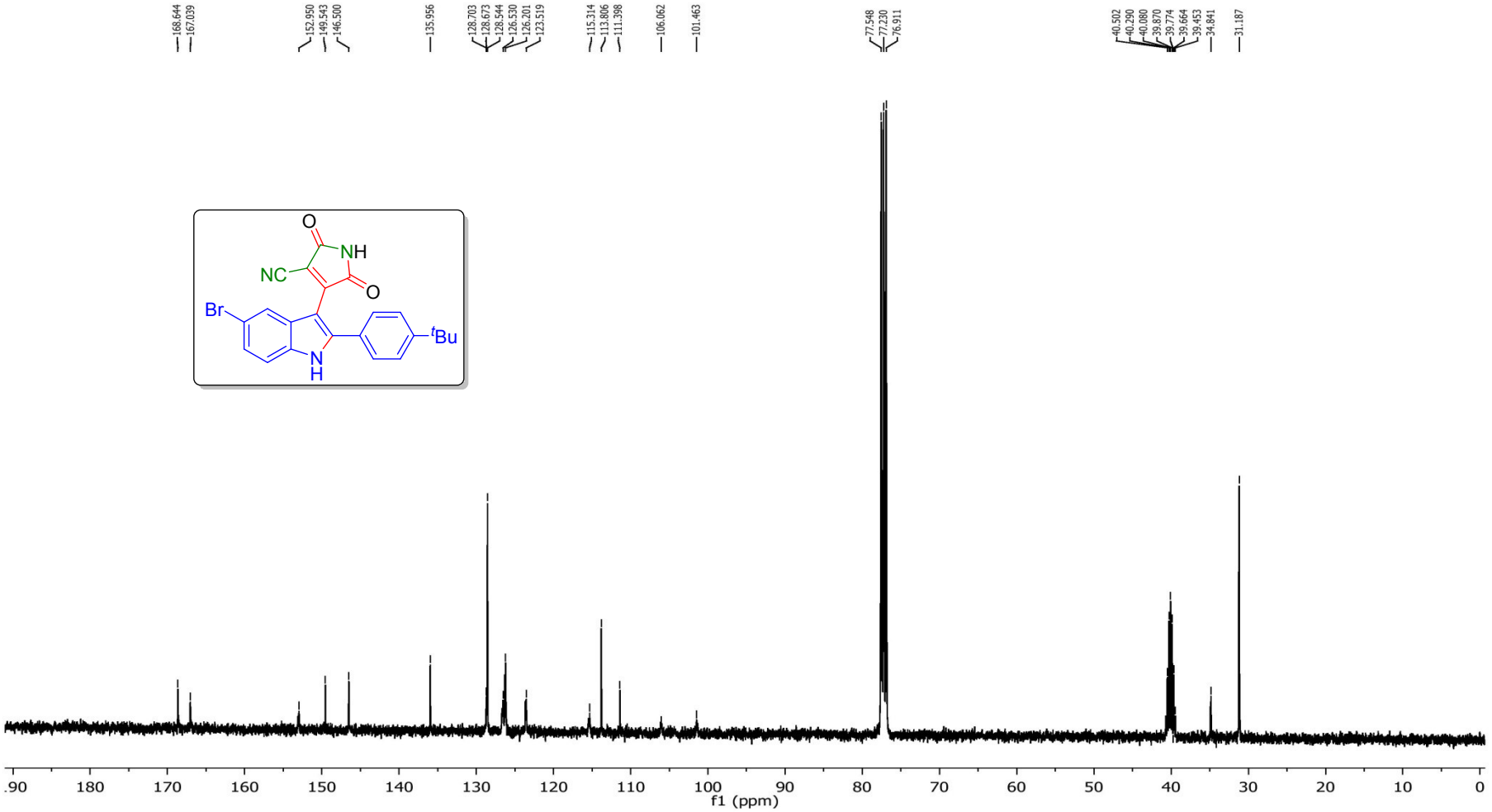
4-(2-(4-(tert-Butyl)phenyl)-5-methyl-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (17ab): ^{13}CNMR (125 MHz, $CDCl_3$)



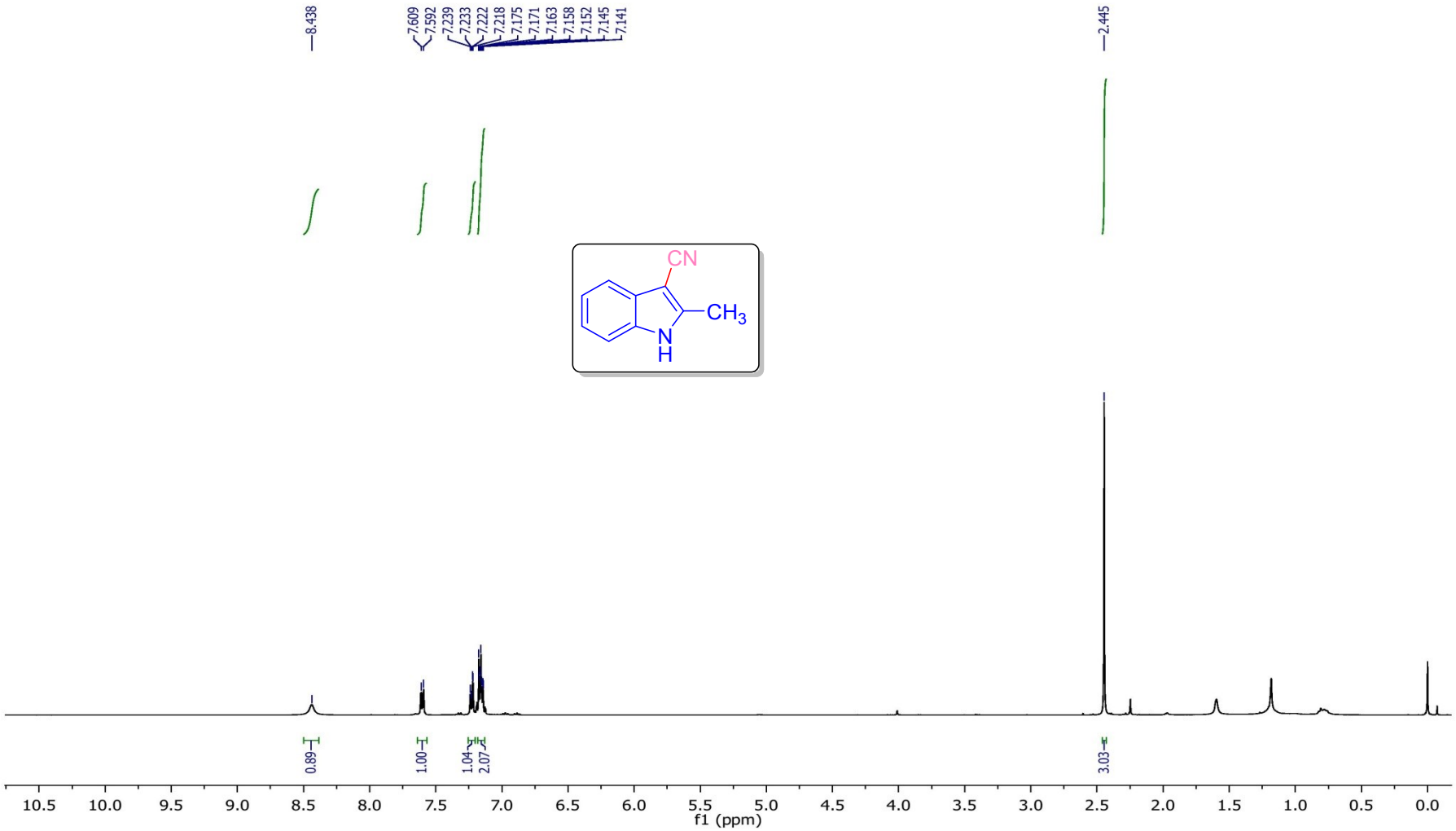
4-(5-Bromo-2-(4-(tert-butyl)phenyl)-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (20ab): ^{1}H NMR (400 MHz, $CDCl_3$ + DMSO)



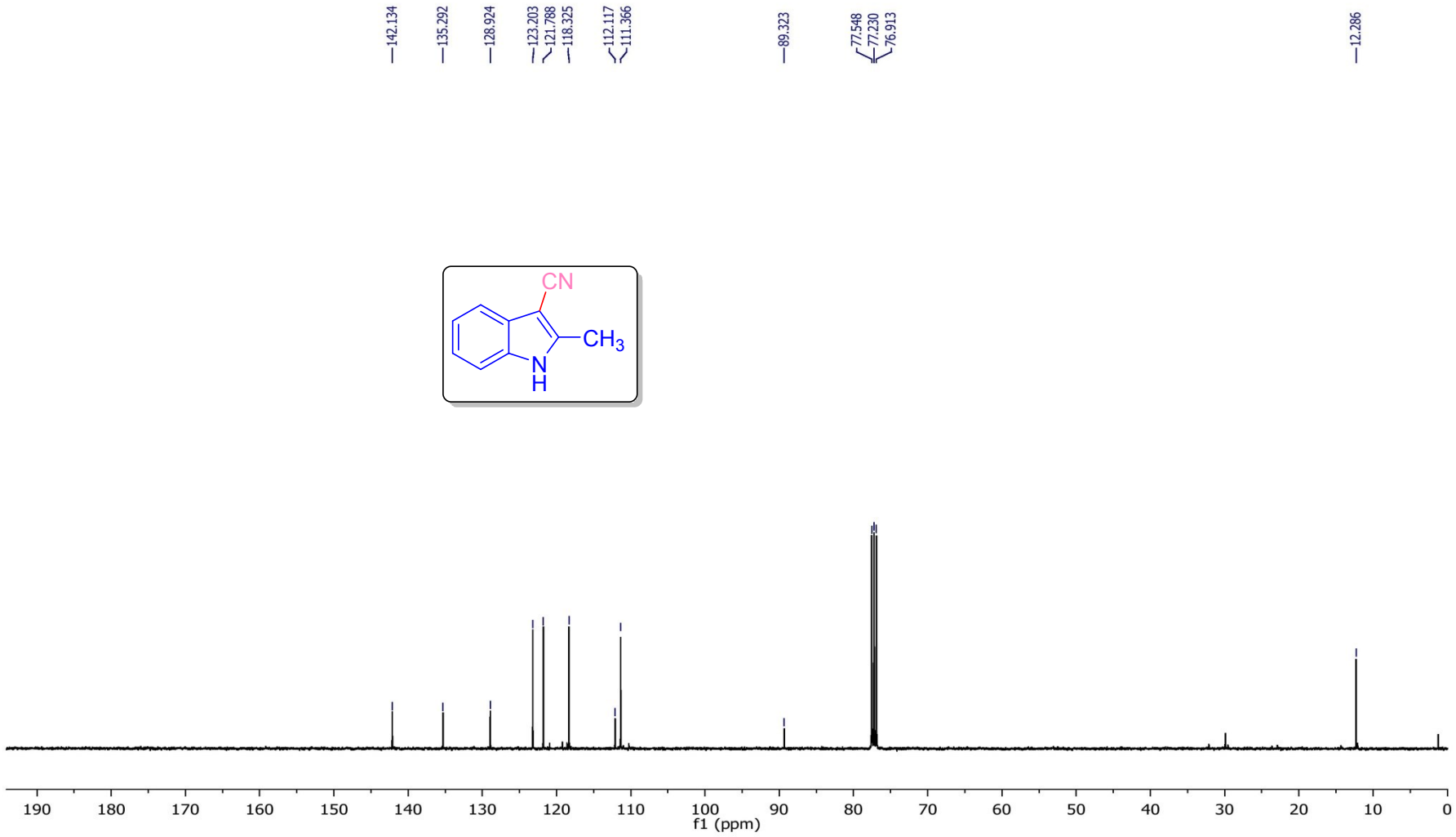
4-(5-Bromo-2-(4-(tert-butyl)phenyl)-1H-indol-3-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrole-3-carbonitrile (20ab): ^{13}C NMR (100 MHz, $CDCl_3$ + DMSO)



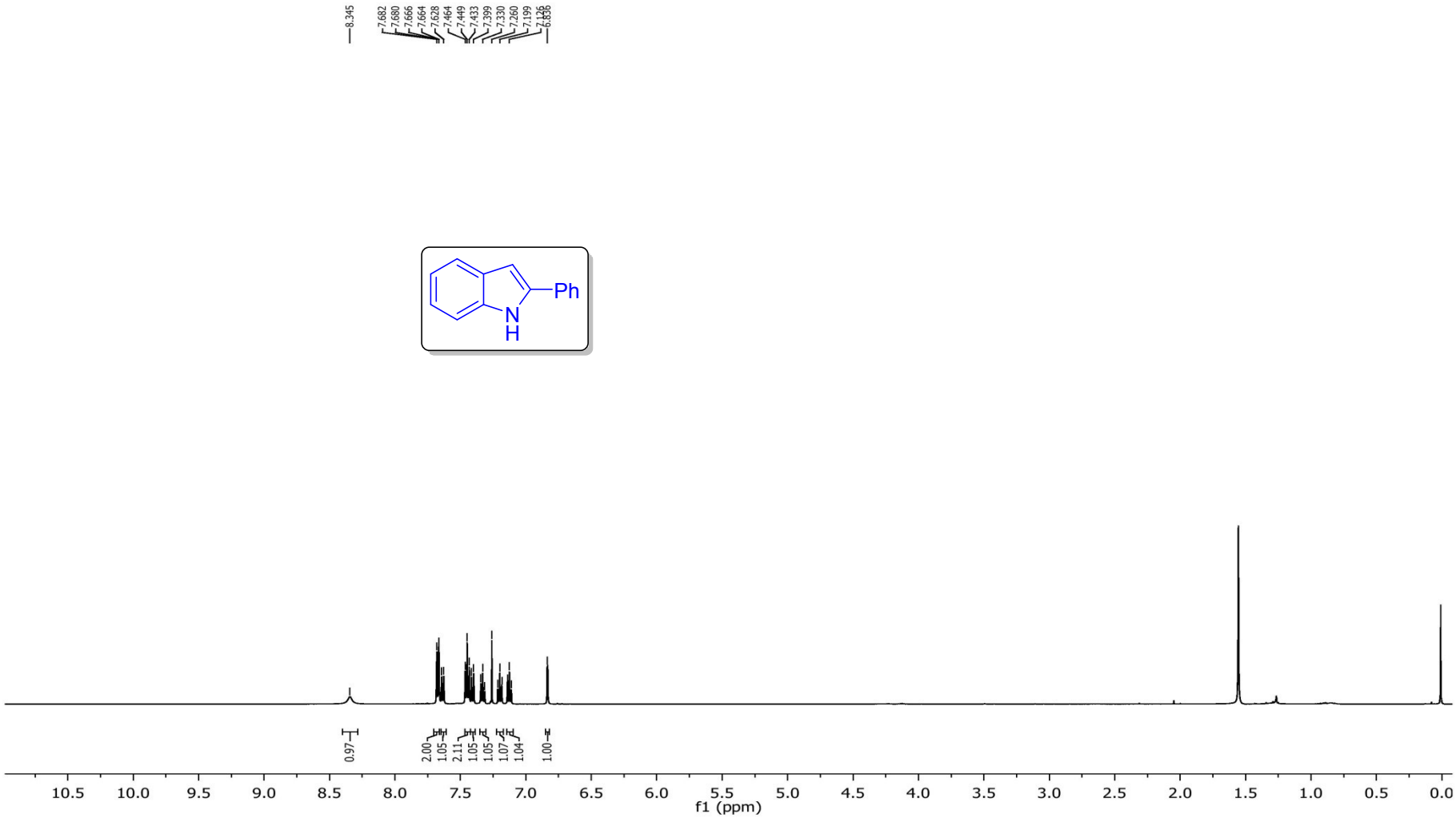
2-Methyl-1*H*-indole-3-carbonitrile (30b): ^{1}H NMR (400 MHz, $CDCl_3$)



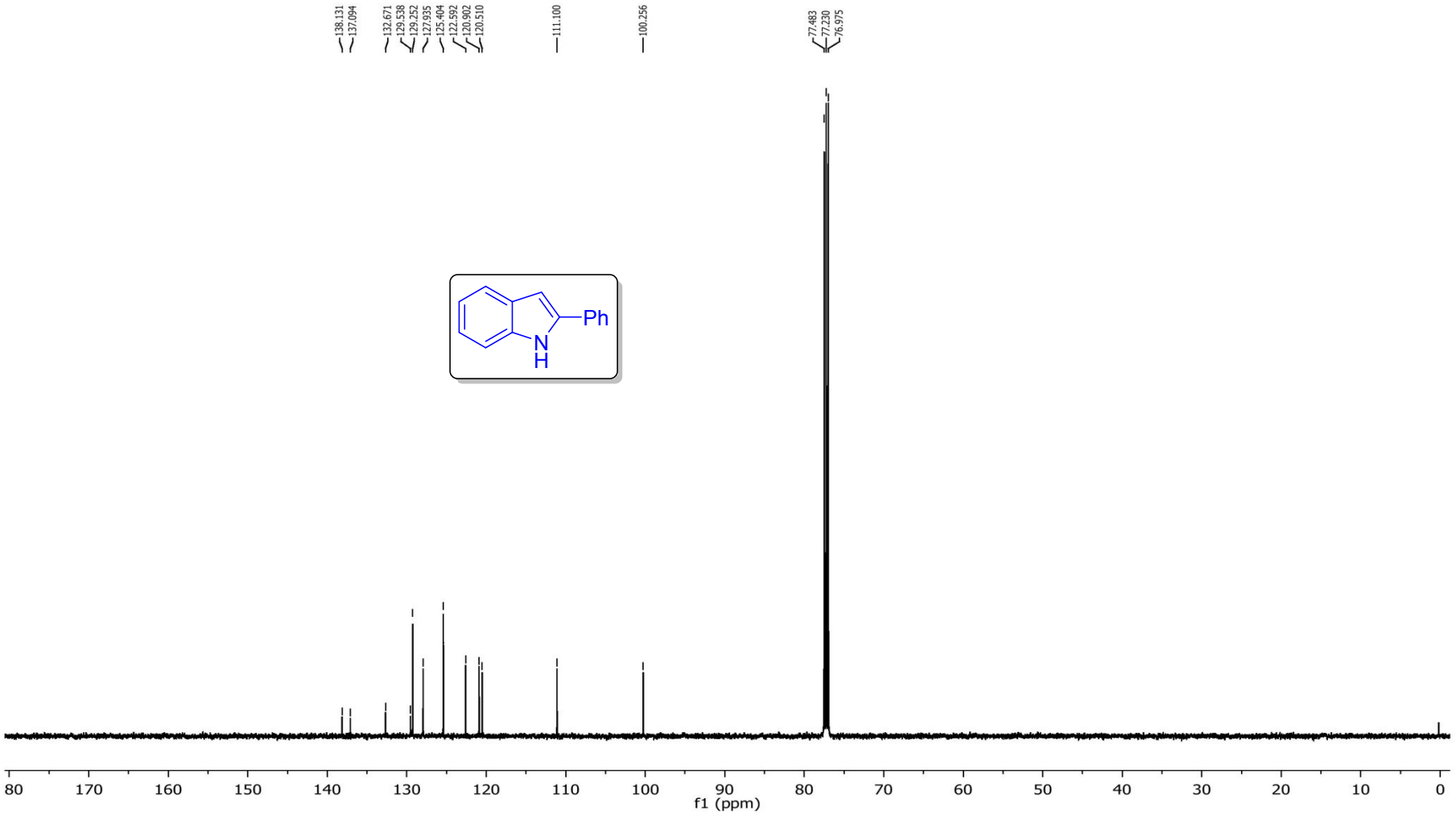
2-Methyl-1*H*-indole-3-carbonitrile (30b): ^{13}C NMR (100 MHz, $CDCl_3$)



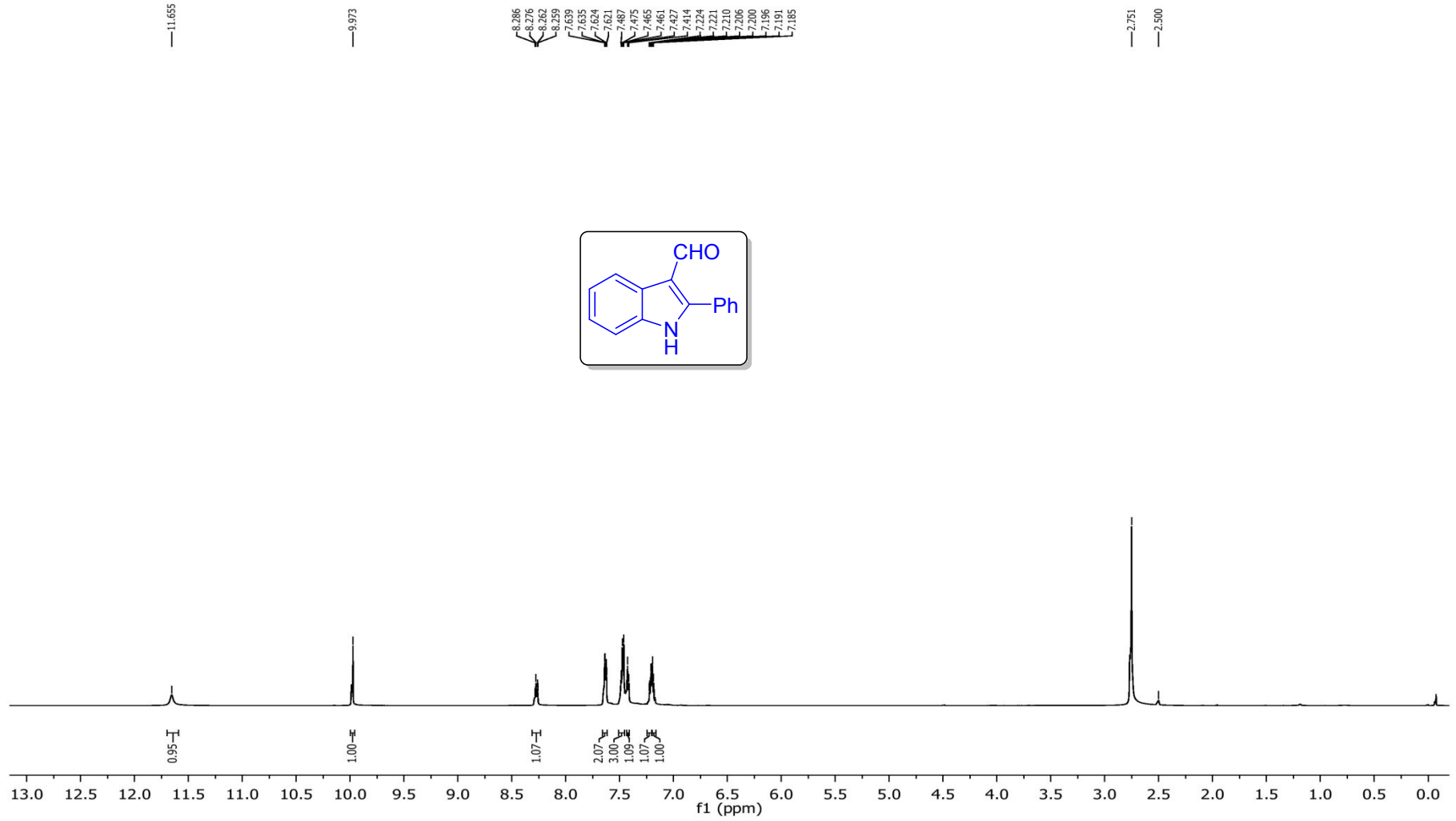
2-Phenyl-1*H*-indole (B): ^{1}H NMR (500 MHz, $CDCl_3$)



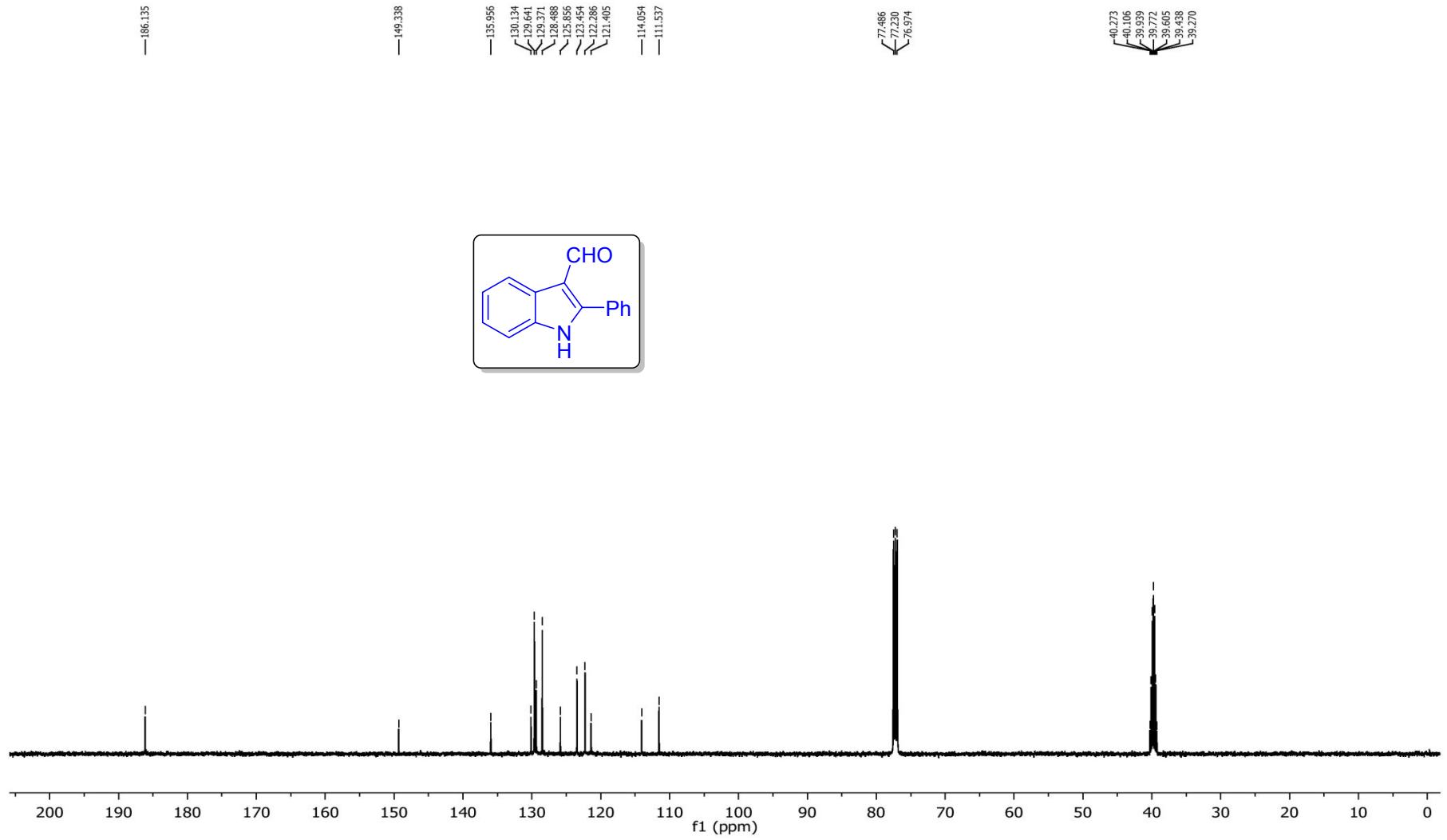
2-Phenyl-1*H*-indole (B): ^{13}C NMR (125 MHz, $CDCl_3$)



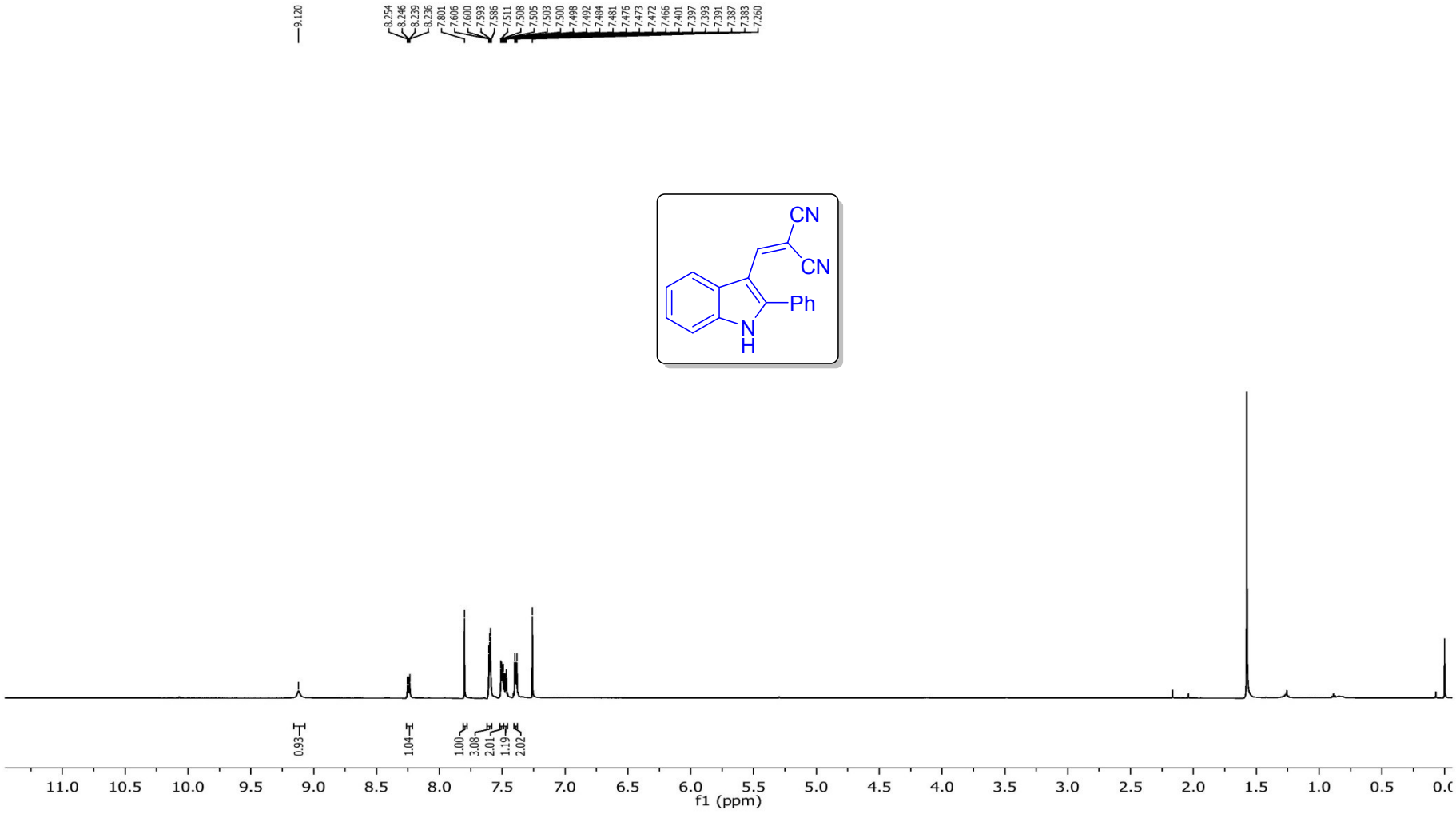
2-Phenyl-1*H*-indole-3-carbaldehyde (G): ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO)



2-Phenyl-1*H*-indole-3-carbaldehyde (G): ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO)



2-((2-Phenyl-1*H*-indol-3-yl)methylene)malononitrile (H): ^{1}H NMR (500 MHz, $CDCl_3$)



2-((2-Phenyl-1*H*-indol-3-yl)methylene)malononitrile (H): ^{13}C NMR (125 MHz, $CDCl_3$)