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The general Remarks

All the reactions, that involve the use of reagents sensitive to oxygen or hydrolysis, were carried out under a nitrogen atmosphere. The glassware was previously dried with a heating gun and set with cycles of vacuum and nitrogen. Syringes, used to transfer reagents and solvents, were previously set under a nitrogen atmosphere. All chemicals and solvents are commercially available and were used without further purification. The chromatographic column separations were performed by flash technique, using silica gel (pore size 60., particle size 230–400 mesh, Merck Grade 9385). For thin-layer chromatography (TLC), Silica on TLC Alu foils with a fluorescent indicator (254 nm) was employed and the detection was performed by irradiation with UV light (λ = 254 nm and/or 366 nm).

^{1}H NMR analyses were performed with 300 MHz or 400 MHz spectrometers at room temperature. The coupling constants (J) are expressed in Hertz (Hz), and the chemical shifts (δ) in ppm. The multiplicity of the proton spectra was described by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), dt (double triplet), dd (double doublet), m (multiplet), br (broad). ^{13}C NMR analyses were performed with the same instruments at 74.45 MHz MHz or 101 MHz; the APT sequence was used to distinguish the methine and methyl carbon signals from those arising from methylene and quaternary carbon atoms. All ^{13}C NMR spectra were recorded with complete proton decoupling. Low-resolution MS spectra were recorded with an electron impact source and electrospray/ion trap instruments, using a syringe pump device to directly inject sample solutions. The values are expressed as mass-charge ratio and the relative intensities of the most significant peaks are shown in brackets. Elemental analyses were recorded in the analytical laboratories of Università degli Studi di Milano. High-resolution mass spectra (HR-MS) were acquired on a Synapt G2-S*i* QTof mass spectrometer (Waters, Milford, MA, USA) equipped with a Zspray ESI-probe (Waters) for electrospray ionization in positive polarity and full scan mode. Data were processed using MassLynx v4.2 software (Waters). Microwave-enhanced reactions were performed with the single-mode microwave synthesizer "Biotage® Initiator Classic".

Employed DESs are known mixtures that were prepared according to literature procedures.[1]

Compounds **1a,e,h** are known compounds and were prepared according to literature procedures.[2]

All unknown starting materials and final products have been fully characterized through NMR spectroscopy, mass spectrometry, and HRMS or elemental analysis.

The amount of water in the DES selected for this study (+CAS/CAM) has been evaluated by Karl-Fischer titration: water content = 5.2 % w/w

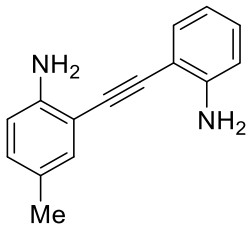
[1] a) V. De Santi, F. Cardellini, L. Brinchi, R. Germani, *Tetrahedron Lett*. **2012**, *53*, 5151; b) F. Cardellini, M. Tiecco, R. Germani, G. Cardinali, L. Corte, L. Roscini, N. Spreti, *RSC Adv.* **2014**, *4*, 55990; c) R. Germani, M. Orlandini, M. Tiecco, T. Del Giacco, *J. Mol. Liq.* **2017**, *240*, 233; d) T. Palomba, G. Ciancaleoni, T. Del Giacco, R. Germani, F. Ianni, M. Tiecco, *J. Mol. Liq.* **2018**, *262*, 285.

[2]) a) J. Yu, D. Zhang-Negrerie, Y. Du, *Org. Lett.* **2016**, *18*, 3322; b) G. Abbiati, A. Arcadi, M. Chiarini, F. Marinelli, E. Pietropaolo, E. Rossi, *Org. Biomol. Chem.* **2012**, *10*, 7801; c) Jung, K. Y.; Vanommeslaeghe, K.; Lanning, M. E.; Yap, J. L.; Gordon, C.; Wilder, P. T.; MacKerell, A. D., Jr.; Fletcher, S, *Org. Lett.* **2013**, *15*, 3234.

The general procedure for the synthesis of 2,2'-(ethyne-1,2-diyl)dianiline 1b-d,f,g,i-k

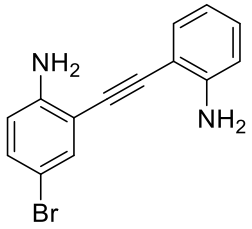
Under a nitrogen atmosphere, to a stirred solution of trans-dichlorobis-(triphenylphosphine)palladium(II) (1 mol%) and the corresponding 2-iodoaniline (1 equiv.) in anhydrous TEA (0.3 M) 2-ethynylaniline (1 or 1.5 equiv.) was added. The reaction was stirred at rt for 5 min, and then CuI (1 mol%) was added. The reaction mixture was stirred at rt until no more starting product was detected by TLC analysis. The reaction mixture was filtered through celite and the solvent was removed at reduced pressure. The crude material was purified by flash chromatography over silica gel to yield the desired product **1b-d,f,g,i-k.**

2-((2-aminophenyl)ethynyl)-4-methylaniline 1b



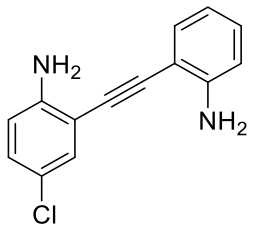
The general procedure was followed using: 2-iodo-4-methylaniline (200 mg, 0.85 mmol), 2-ethynylaniline (150 mg, 1.27 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (6 mg, 0.0085 mmol) and CuI (1.6 mg, 0.0085 mmol). Reaction time: 3 h. Purification of the crude by column chromatography (SiO_2, Hex/DCM 1:1) yielded **1b** (168 mg, 89%) as a brownish solid.
^{1}H NMR (300 MHz, $CDCl_3$): 7.37 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.20 (dd, *J* = 1.4, 0.7 Hz, 1H), 7.15 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 6.97 (ddd, *J* = 8.2, 2.1, 0.7 Hz, 1H), 6.79 – 6.68 (m, 2H), 6.66 (d, *J* = 8.2 Hz, 1H), 4.07 (bs, 4H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 147.6 (C), 145.3 (C), 132.1 (CH), 132.0 (CH), 130.6 (CH), 129.7 (CH), 127.3 (C), 118.0 (CH), 114.6 (CH), 114.4 (CH), 108.2 (C), 108.1(C), 91.3 (C), 90.8 (C), 20.3 (CH_3). ESI(+)-MS: m/z (%)= 223 (100) $[M+1]^+$. Elemental analysis calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60; found C, 81.19; H, 6.38; N, 12.59.

2-((2-aminophenyl)ethynyl)-4-bromoaniline 1c



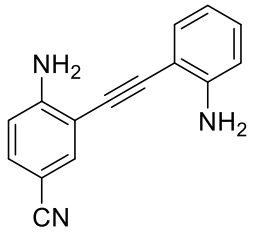
The general procedure was followed using: 4-bromo-2-iodoaniline (200 mg, 0.67 mmol), 2-ethynylaniline (79 mg, 0.67 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (5 mg, 0.0067 mmol) and CuI (1 mg, 0.0067 mmol). Reaction time: 3 h. Purification of the crude by column chromatography (SiO_2, Hex/Et_2O 2:1 to 1:1) yielded **1c** (169 mg, 88%) as a brownish solid.
^{1}H NMR (300 MHz, $CDCl_3$): 7.47 (dd, *J* = 2.4, 0.3 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.22 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.16 (ddd, *J* = 8.2, 7.4, 1.6 Hz, 1H), 6.80 – 6.66 (m, 2H), 6.61 (dd, *J* = 8.6, 0.4 Hz, 1H), 4.23 (bs, 4H).
^{13}C NMR (75 MHz, $CDCl_3$): 147.7 (C), 146.6 (C), 134.0 (CH), 132.4 (CH), 132.1 (CH), 130.1 (CH), 118.1 (CH), 115.8 (CH), 114.5 (CH), 109.9 (C), 109.0 (C), 107.5 (C), 92.2 (C), 89.7 (C). ESI(-)-MS: m/z (100 %)= 288 (100) $[M-1]^-$. Elemental analysis calcd for $C_{14}H_{11}BrN_2$: C, 58.56; H, 3.86; N, 9.76; found C, 58.47; H, 3.87; N, 9.79.

2-((2-aminophenyl)ethynyl)-4-chloroaniline 1d



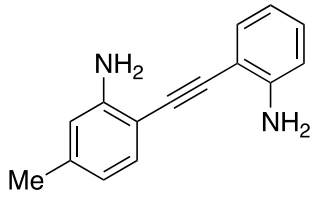
The general procedure was followed using: 4-chloro-2-iodoaniline (200 mg, 0.79 mmol), 2-ethynylaniline (138 mg, 1.18 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (5.5 mg, 0.0079 mmol) and CuI (1.5 mg, 0.0079 mmol). Reaction time: 2 h. Purification of the crude by column chromatography (SiO_2, DCM/Hex 1:2 to 3:1) yielded **1d** (159 mg, 83%) as a pale yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.19 (td, *J* = 8.0, 1.6 Hz, 1H), 7.12 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.79 – 6.73 (m, 2H), 6.68 (d, *J* = 8.6 Hz, 1H), 4.21 (bs, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 147.7 (C), 146.2 (C), 132.1 (CH), 131.2 (CH), 130.1 (CH), 129.7 (CH), 122.3 (C), 118.1 (CH), 115.5 (CH), 114.6 (CH), 109.5 (C), 107.6 (C), 92.2 (C), 89.7 (C). ESI(+)-MS: m/z (100 %)= 243 (100) $[M+1]^+$. Elemental analysis calcd for $C_{14}H_{11}ClN_2$: C, 69.28; H, 4.57; N, 11.54; found C, 69.17; H, 4.56; N, 11.56.

4-amino-3-((2-aminophenyl)ethynyl)benzonitrile 1f



The general procedure was followed using: 4-amino-3-iodobenzonitrile (200 mg, 0.81 mmol), 2-ethynylaniline (142 mg, 1.21 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (6 mg, 0.0081 mmol) and CuI (1.5 mg, 0.0081 mmol). The reaction was conducted at rt Reaction time: 1,5 h. Purification of the crude by column chromatography (SiO_2, DCM/Hex 2:1 to 3:1) yielded **1f** (153 mg, 81%) as a yellow solid. 1H NMR (300 MHz, $CDCl_3$): 7.63 (dd, *J* = 1.9, 0.4 Hz, 1H), 7.36 (td, *J* = 8.3, 1.7 Hz, 2H), 7.18 (m, 1H), 6.78 – 6.69 (m, 3H), 4.46 (bs, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 150.9 (C), 147.8 (C), 136.2 (CH), 133.2 (CH), 132.2 (CH), 130.4 (CH), 119.3 (C), 118.16 (CH), 114.6 (CH), 114.0 (CH), 108.3 (C), 107.0 (C), 100.2 (C), 92.8 (C), 88.5 (C). ESI(+)-MS: m/z (%)= 234 (100) $[M+1]^+$. Elemental analysis calcd for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01; found C, 77.38; H, 4.76; N, 18.05.

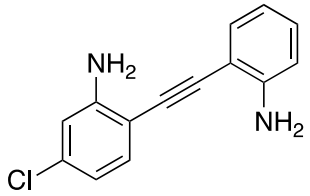
2-((2-aminophenyl)ethynyl)-5-methylaniline 1i



The general procedure was followed using: 5-methyl-2-iodoaniline (200 mg, 0.86 mmol), 2-ethynylaniline (100 mg, 0,86 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (6 mg, 0.0086 mmol) and CuI (1.6 mg, 0.0086 mmol). The reaction was conducted at r.t, and after 2h heated to 45 °C. Reaction time: 3 h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 4:1 to 3:1) yielded **1i** (150 mg, 78%) as a pale-yellow solid.

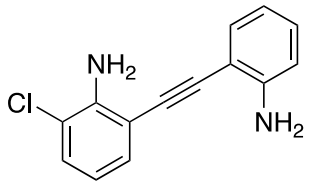
^{1}H NMR (400 MHz, $CDCl_3$): 7.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.17 (m, 1H), 6.79 – 6.72 (m, 2H), 6.62 – 6.55 (m, 2H), 4.30 (bs, 2H), 4.26 (bs, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 147.65 (C), 147.63 (C), 140.2 (C), 132.0 (CH), 131.9 (CH), 129.6 (CH), 119.2 (CH), 118.0 (CH), 115.1 (CH), 114.4 (CH), 108.4 (C), 105.3 (C), 91.4 (C), 90.5 (C), 21.7 (CH_3). ESI(+)-MS: m/z (%)= 223 (100) $[M+1]^+$. Elemental analysis calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60; found C, 80.88; H, 6.37; N, 12.57.

2-((2-aminophenyl)ethynyl)-5-chloroaniline 1j



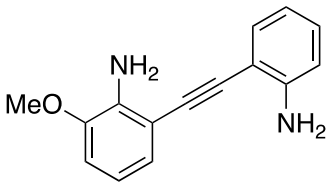
The general procedure was followed using: 5-chloro-2-iodoaniline (300 mg, 1.17 mmol), 2-ethynylaniline (138 mg, 1.17 mmol), trans-dichlorobis-(triphenylphosphine)palladium(II) (8 mg, 0.012 mmol) and CuI (2 mg, 0.012 mmol). The reaction was heated to 50 °C. Reaction time: 1,5 h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 4:1 + 1% Et_3N to 3:1 + 1% Et_3N) yielded **1j** (226 mg, 80%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 7.38 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.18 (m, 1H), 6.80 – 6.69 (m, 4H), 4.16 (bs, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 148.5 (C), 147.7 (C), 135.3 (C), 133.0 (CH), 132.1 (CH), 130.0 (CH), 118.2 (CH), 118.1 (CH), 114.5 (CH), 114.2 (CH), 107.8 (C), 106.6 (C), 91.9 (C), 90.1 (C). HRMS (ESI) calculated for $C_{14}H_{12}ClN_2$ $[M+H]^+$ requires *m/z* = 243.0684, found *m/z* 243.0694.

2-((2-aminophenyl)ethynyl)-6-chloroaniline 1k



The general procedure was followed using: 6-chloro-2-iodoaniline (200 mg, 0,79 mmol), 2-ethynylaniline (93 mg, 0,97 mmol), *trans*-dichlorobis-(triphenylphosphine)palladium(II) (6 mg, 0.0079 mmol) and CuI (1,5 mg, 0.0079 mmol). The reaction was heated to 50 °C. Reaction time: 1,5 h. Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **1k** (152 mg,79%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 7.39 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.29 (ddd, *J* = 16.4, 7.8, 1.3 Hz, 2H), 7.19 (td, *J* = 8.1, 1.5 Hz, 1H), 6.77 (dt, *J* = 6.9, 3.0 Hz, 2H), 6.68 (t, *J* = 7.8 Hz, 1H), 4,49 (bs, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): 147.8 (C), 144.3 (C), 132.1 (CH), 130.4 (CH), 130.1 (CH), 129.7 (CH), 118.8 (C), 118.1 (CH), 117.9 (CH), 114.5 (CH), 109.3 (C), 107.6 (C), 91.9 (C), 90.3 (C). HRMS (ESI) calculated for $C_{14}H_{12}ClN_2$ $[M+H]^+$ requires *m/z* = 243.0684, found *m/z* 243.0695.

Procedure for the synthesis of 2-((2-aminophenyl)ethynyl)-2-methoxyaniline 1g

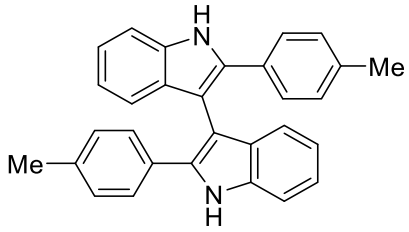


Step 1: Under a nitrogen atmosphere, to a stirred solution of 2-bromo-6-methoxyaniline (300 mg, 1.48 mmol) in anhydrous toluene (0.25 M), CuI (3 mg, 0.015 mmol), triphenylphosphine (12 mg, 0.044 mmol) and triethylamine (2,6 ml) were added. The reaction was stirred at rt for 5 min, then trans-dichlorobis-(triphenylphosphine)palladium(II) (11 mg, 0.015 mmol) and trimethylsilylacetylene (218 mg, 2.22 mmol) in a solution of TEA (2.22 M) was added. The reaction mixture was stirred at 100 °C until no more starting product was detected by TLC analysis. The reaction mixture was quenched with EtOAc (100 ml), NaCl ss (40 ml) was added and the crude was extracted with EtOAc (3x). Combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum.
The crude was dissolved in MeOH (0.2 M), K_2CO_3 (300 mg, 2.22 mmol) was added, and the reaction mixture was stirred at rt for 30 min. After evaporation of most of the solvent, the crude material was diluted in EtOAc (50 mL), and washed with H_2O and brine. The organic layer was collected, dried over anhydrous Na_2SO_4, filtered, concentrated and purified by flash chromatography over silica gel to yield the desired 2-ethynylaniline.
Purification of the crude by column chromatography (SiO_2, Hex/EtOAc 99:1) yielded 2-ethynyl-6-methoxyaniline (164 mg, 75%) as an orange liquid.
Step 2: To a stirred solution of 2-iodoaniline (238 mg, 1.09 mmol) in anhydrous TEA (0.3 M), trans-dichlorobis-(triphenylphosphine)palladium(II) (8 mg, 0.011 mmol) and 2-ethynyl-6-methoxyaniline (160 mg, 1.09 mmol) were added. The reaction was stirred at rt for 5 min, and then CuI (2 mg, 0.011 mmol) was added. The reaction mixture was stirred at rt until no more starting product was detected by TLC analysis. The reaction mixture was filtered through celite and the solvent was removed at reduced pressure. The crude material was purified by flash chromatography (SiO_2, Hex/EtOAc 9:1) to yield **1g** (147 mg, 56%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): 7.40 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.17 (m, 1H), 7.04 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.85 – 6.66 (m, 4H), 4.25 (bs, 4H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 147.6 (C), 146.8 (C), 138.2 (C), 132.1 (CH), 129.7 (CH), 123.8 (CH), 118.0 (CH), 117.3 (CH), 114.4 (CH), 110.5 (CH), 108.2 (C), 107.8 (C), 91.12 (C), 91.08 (C), 55.7 (CH_3). ESI(+)-MS: m/z (%)= 239 (100) $[M+1]^+$. Elemental analysis calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76; O, 6.71 found C, 75.82; H, 5.88; N, 11.74.

General procedure for the synthesis of bis-indole 3a-z

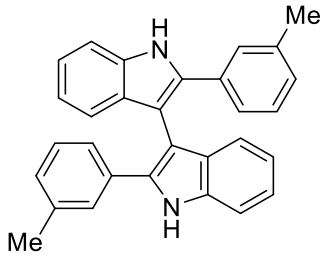
In a microwave test tube, the appropriate 2,2'-(ethyne-1,2-diyl)dianiline **1a-k** (0.2 mmol) and the aldehyde (3 equiv.) **2a-p** were added to the selected DES (0.5 mL). The mixture was heated at 70 °C under microwave heating for 5 minutes. Then, water was added to the mixture and extracted with EtOAc. The organic layers were dried with Na_2SO_4, filtered and evaporated under reduced pressure. The crude material was purified by flash column chromatography over silica gel to yield the corresponding 2,2'-disubstituted 3,3'-biindoles **3a-z**.

2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3a



The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3a** (63 mg, 76%) as a pale-yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.48 (s, 2H), 7.46 – 7.39 (m, 6H), 7.05 (dd, *J* = 8.1, 6.7 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 4H), 6.84 (d, *J* = 7.7 Hz, 2H), 6.82 – 6.74 (m, 2H), 2.17 (s, 6H).
Spectral data are in good agreement with literature values.[3]

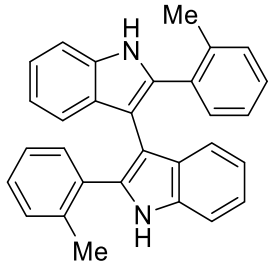
2,2'-di-*m*-tolyl-1*H*,1'*H*-3,3'-biindole 3b



The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 3-methylbenzaldehyde **2b** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3b** (62 mg, 75%) as a pale-yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.49 (s, 2H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.39 (s, 2H), 7.21 (d, *J* = 7.7 Hz, 2H), 7.07 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 2H), 6.95 – 6.88 (m, 4H), 6.81 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H), 2.15 (s, 6H).
Spectral data are in good agreement with literature values.[4]

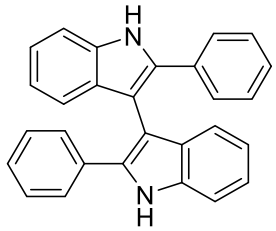
[3] A. Arcadi, M. Chiarini, G. D'Anniballe, F. Marinelli, E. Pietropaolo, *Org. Lett.* **2014**, *16*, 1736.
[4] T. Niu, Y. Zhang, *Tetrahedron Letters*, **2010**, 51, 52, 6847

2,2'-di-*o*-tolyl-1*H*,1'*H*-3,3'-biindole 3c



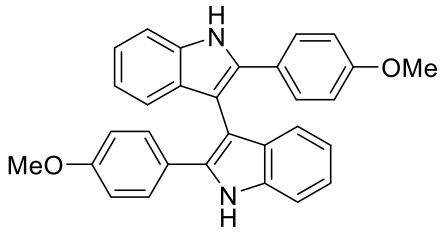
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 2-methylbenzaldehyde **2c** (72 mg, 0.6 mmol). Reaction time 10 minutes instead of 5 minutes. Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 95:5) yielded **3c** (53 mg, 64%) as a dark yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.06 (s, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.16 – 7.03 (m, 4H), 7.00 – 6.95 (m, 4H), 6.83 (t, *J* = 7.4 Hz, 2H), 6.57 (dd, *J* = 7.7, 1.4 Hz, 2H), 1.68 (s, 6H).
Spectral data are in good agreement with literature values.[4]

2,2'-diphenyl-1*H*,1'*H*-3,3'-biindole 3d



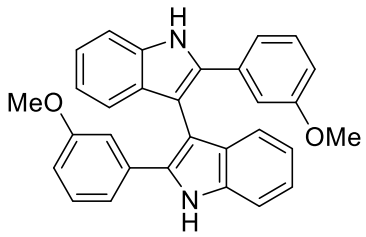
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and benzaldehyde **2d** (64 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1 to 7:1) yielded **3d** (50 mg, 65%) as a yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.55 (s, 2H), 7.56 – 7.46 (m, 4H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.12 (m, 4H), 7.16 – 7.02 (m, 4H), 6.90 (d, *J* = 7.9 Hz, 2H), 6.81 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H).
Spectral data are in good agreement with literature values.[4]

2,2'-bis(4-methoxyphenyl)-1*H*,1'*H*-3,3'-biindole 3e



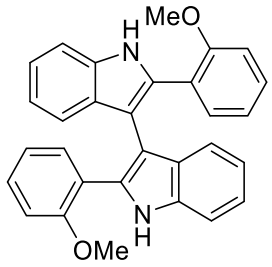
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 4-methoxybenzaldehyde **2e** (82 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1 to 3:1) yielded **3e** (51 mg, 58%) as an orange solid.
^{1}H NMR (300 MHz, DMSO): 11.42 (s, 2H), 7.47 (d, *J* = 8.8 Hz, 4H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.04 (ddd, *J* = 7.8, 6.5, 1.2 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.82 – 6.73 (m, 6H), 3.65 (s, 6H).
Spectral data are in good agreement with literature values.[4]

2,2'-bis(3-methoxyphenyl)-1*H*,1'*H*-3,3'-biindole 3f



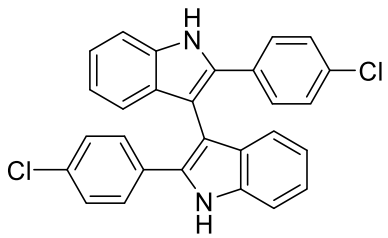
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 3-methoxybenzaldehyde **2f** (82 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 6:1) yielded **3f** (69 mg, 78%) as a light pink solid.
^{1}H NMR (300 MHz, DMSO): 11.59 (s, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.22 – 7.04 (m, 8H), 6.94 (d, *J* = 7.8 Hz, 2H), 6.84 (ddd, *J* = 7.9, 6.9, 1.0 Hz, 2H), 6.68 (ddd, *J* = 7.8, 2.6, 1.4 Hz, 2H), 3.42 (s, 6H). ^{13}C NMR (75 MHz, DMSO): 159.5 (2xC), 136.8 (2xC), 134.8 (2xC), 134.5 (2xC), 130.0 (2xC), 129.9 (2xCH), 122.4 (2xCH), 119.7 (2xCH), 119.6 (2xCH), 119.0 (2xCH), 113.2 (2xCH), 112.0 (2xCH), 111.7 (2xCH), 107.0 (2xC), 55.0 (2xCH_3). ESI(+)-MS: m/z (%)= 445 (55) $[M+1]^+$. Elemental analysis calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30; found C, 88.27; H, 5.45; N 6.27.

2,2'-bis(2-methoxyphenyl)-1H,1'H-3,3'-biindole 3g



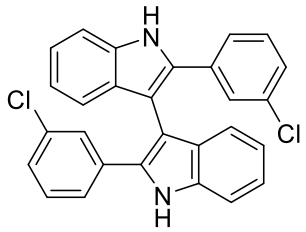
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 2-methoxybenzaldehyde **2g** (82 mg, 0.6 mmol). Reaction time 10 minutes instead of 5 minutes. Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 8:1 to 6:1) yielded **3g** (52 mg, 59%) as an orange solid.
^{1}H NMR (300 MHz, DMSO): 11.03 (s, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.06 (m, 4H), 7.07 – 6.95 (m, 4H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.78 (td, *J* = 7.5, 1.0 Hz, 2H), 6.64 (td, *J* = 7.5, 1.0 Hz, 2H), 3.59 (s, 6H). ^{13}C NMR (75 MHz, DMSO): 157.0 (2xC), 136.4 (2xC), 132.8 (2xC), 131.1 (2xCH), 129.0 (2xCH), 128.6 (2xC), 122.6 (2xC), 121.2 (2xCH), 120.4 (2xCH), 119.6 (2xCH), 118.7 (2xCH), 111.8 (2xCH), 111.5 (2xCH), 107.7 (2xC), 55.7 (2xCH_3). ESI(+)-MS: m/z (%)= 445 (95) $[M+1]^+$. Elemental analysis calcd for $C_{30}H_{24}N_2O_2$: C, 81.06; H, 5.44; N, 6.30; found C, 87.93; H, 5.42; N 6.26.

2,2'-bis(4-chlorophenyl)-1*H*,1'*H*-3,3'-biindole 3h



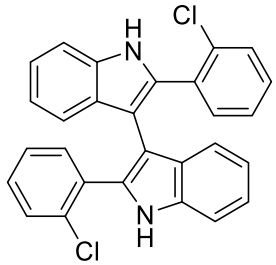
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 4-chlorobenzaldehyde **2h** (84 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 95:5 to 9:1) yielded **3h** (57 mg, 63%) as a yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.64 (s, 2H), 7.48 – 7.40 (m, 6H), 7.31 – 7.22 (m, 4H), 7.10 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.84 (ddd, *J* = 7.9, 6.8, 1.0 Hz, 2H).
Spectral data are in good agreement with literature values.[4]

2,2'-bis(3-chlorophenyl)-1*H*,1'*H*-3,3'-biindole 3i



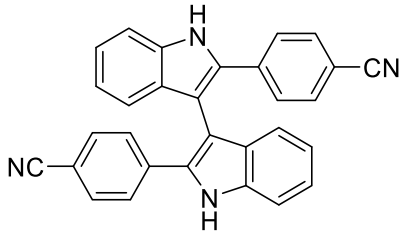
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 3-chlorobenzaldehyde **2i** (84 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3i** (45 mg, 50%) as a pale-yellow solid.
^{1}H NMR (400 MHz, DMSO): 11.72 (s, 2H), 7.53 – 7.48 (m, 4H), 7.38 – 7.31 (m, 2H), 7.24 – 7.13 (m, 6H), 7.04 (d, *J* = 7.9 Hz, 2H), 6.92 (ddd, *J* = 8.0, 6.9, 1.0 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): 137.1 (2xC), 135.3 (2xC), 133.6 (2xC), 133.4 (2xC), 130.6 (2xCH), 129.4 (2xC), 127.1 (2xCH), 126.4 (2xCH), 125.4 (2xCH), 122.9 (2xCH), 120.0 (2xCH), 119.9 (2xCH), 112.1 (2xCH), 107.3 (2xC). HRMS (ESI) calculated for $C_{28}H_{18}Cl_2N_2Na$ $[M+Na]^+$ requires *m/z* = 475.0745, found *m/z* 475.0742.

2,2'-bis(2-chlorophenyl)-1*H*,1'*H*-3,3'-biindole 3j



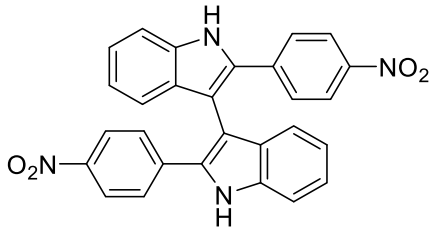
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 2-chlorobenzaldehyde **2j** (84 mg, 0.6 mmol). Reaction time 10 minutes instead of 5 minutes. Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3j** (63 mg, 70%) as a pale-yellow solid.
^{1}H NMR (400 MHz, DMSO): 11.29 (s, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.33 (dd, *J* = 8.1, 1.2 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.19 (m, 2H), 7.12 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 2H), 7.06 (td, *J* = 7.5, 1.3 Hz, 2H), 6.99 – 6.89 (m, 4H). ^{13}C NMR (101 MHz, DMSO): 136.6 (2xC), 133.1 (2xC), 133.1 (2xC), 132.7 (2xC), 132.6 (2xCH), 130.0 (2xCH), 129.5 (2xCH), 128.4 (2xC), 127.1 (2xCH), 121.9 (2xCH), 120.1 (2xCH), 119.2 (2xCH), 111.8 (2xCH), 108.2 (2xC). ESI(-)-MS: m/z (%)= 452 (100) $[M-1]^-$. Elemental analysis calcd for $C_{28}H_{18}Cl_2N_2$: C, 74.18; H, 4.00; N, 6.18; found C, 74.02; H, 4.00; N, 6.17.

4,4'-(1*H*,1'*H*-[3,3'-biindole]-2,2'-diyl)dibenzonitrile 3k



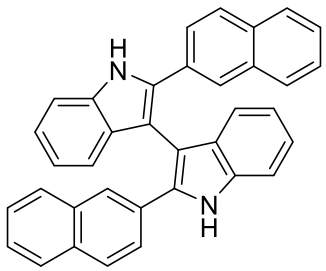
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 4-formylbenzonitrile **2k** (79 mg, 0.6 mmol). Purification of the crude by crystallization from dichloromethane yielded **3k** (65 mg, 75%) as a yellow solid.
^{1}H NMR (400 MHz, DMSO): 11.88 (s, 2H), 7.66 (d, *J* = 8.3 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): 137.6 (2xC), 137.6 (2xC), 133.1 (2xC), 132.8 (4xCH), 129.0 (2xC), 127.3 (4xCH), 123.5 (2xCH), 120.2 (2xCH), 120.2, 119.3 (2xC), 112.3 (2xCH), 109.4 (2xC), 108.5 (2xC). HRMS (ESI) calculated for $C_{30}H_{18}N_4Na$ $[M+Na]^+$ requires *m/z* = 457.1429, found *m/z* 457.1437.

2,2'-bis(4-nitrophenyl)-1*H*,1'*H*-3,3'-biindole 3l



The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 4-nitrobenzaldehyde **2l** (90 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, CH_2Cl_2/Hex 1.5:1 + 2% EtOAc) yielded **3l** (69 mg, 73%) as a dark red solid.
^{1}H NMR (300 MHz, DMSO): 11.99 (s, 2H), 8.04 (d, *J* = 9.1 Hz, 4H), 7.66 (d, *J* = 9.0 Hz, 4H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.24 – 7.13 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.95 – 6.84 (m, 2H). ^{13}C NMR (75 MHz, DMSO): 146.0 (2xC), 139.6 (2xC), 137.8 (2xC), 132.9 (2xC), 128.9 (2xC), 127.5 (4xCH), 124.22 (4xCH), 123.8 (2xCH), 120.4 (2xCH), 120.3 (2xCH), 112.4 (2xCH), 109.1 (2xC). ESI(-)-MS: m/z (%)= 474 (100) $[M-1]^-$. Elemental analysis calcd for $C_{28}H_{18}N_4O_4$: C, 70.88; H, 3.82; N, 11.81; found C, 70.94; H, 3.84; N, 11.82.

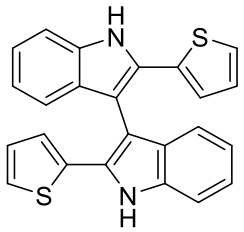
2,2'-di(naphthalen-2-yl)-1*H*,1'*H*-3,3'-biindole 3m



The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and 2-naphthaldehyde **2m** (93 mg, 0.6 mmol). Reaction time 10 minutes instead of 5 minutes. Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3m** (73 mg, 75%) as a brown solid.

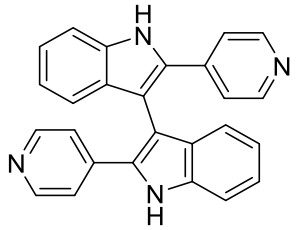
^{1}H NMR (300 MHz, DMSO): 11.78 (s, 2H), 8.15 (s, 2H), 7.7-7.59 (m, 8H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.45 – 7.34 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.81 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, DMSO): 137.2 (2xC), 135.2 (2xC), 133.3 (2xC), 132.2 (2xC), 131.1 (2xC), 129.9 (2xC), 128.2 (2xCH), 128.1 (2xCH), 127.9 (2xCH), 126.8 (2xCH), 126.4 (2xCH), 125.3 (2xCH), 125.2 (2xCH), 122.5 (2xCH), 119.8 (2xCH), 119.6 (2xCH), 111.9 (2xCH), 107.4 (2xC). ESI(+)-MS: m/z (%)= 486 (95) $[M+1]^+$. Elemental analysis calcd for $C_{36}H_{24}N_2$: C, 89.23; H, 4.99; N, 5.78; found C, 89.41; H, 4.98; N, 5.76.

2,2'-di(thiophen-2-yl)-1*H*,1'*H*-3,3'-biindole 3n



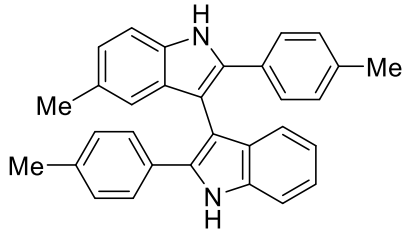
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and thiophene-2-carbaldehyde **2n** (67 mg, 0.6 mmol). Reaction time 10 minutes instead of 5 minutes. Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 7:1) yielded **3n** (59 mg, 57%) as a brown solid. ^{1}H NMR (300 MHz, DMSO): 11.71 (s, 2H), 7.48 – 7.41 (m, 4H), 7.19 (dd, *J* = 5.0, 1.2 Hz, 2H), 7.11 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 2H), 6.99 – 6.92 (m, 4H), 6.91 – 6.83 (m, 2H). ^{13}C NMR (101 MHz, DMSO): 137.1 (2xC), 135.0 (2xC), 131.9 (2xC), 130.0 (2xC), 127.1 (2xCH), 126.6 (2xCH), 124.1 (2xCH), 122.5 (2xCH), 119.8 (2xCH), 119.4 (2xCH), 111.5 (2xCH), 105.4 (2xC). ESI(-)-MS: m/z (%)= 395 (100) $[M-1]^-$. Elemental analysis calcd for $C_{24}H_{16}N_2S_2$: C, 72.70; H, 4.07; N, 7.06; found C, 72.67; H, 4.07; N, 7.03.

2,2'-di(pyridin-4-yl)-1*H*,1'*H*-3,3'-biindole 3o



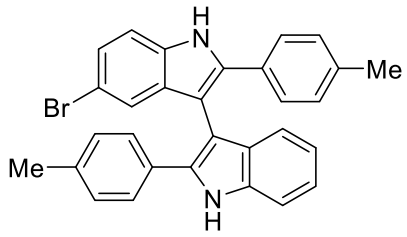
The general procedure was followed using: 2,2'-(ethyne-1,2-diyl)dianiline **1a** (42 mg, 0.2 mmol) and isonicotinaldehyde **2o** (64 mg, 0.6 mmol). Extracted with $NaHCO_3$ ss. and CH_2Cl_2, instead of H_2O and EtOAc. Purification of the crude by flash column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) yielded **3o** (23 mg, 30%) as a brown solid.
^{1}H NMR (400 MHz, DMSO): 11.99 (s, 2H), 8.37 (d, *J* = 5.3 Hz, 4H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 5.9 Hz, 4H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO): 150.0 (4xCH), 140.2 (2xC), 137.5 (2xC), 131.9 (2xC), 129.1 (2xC), 123.8 (2xCH), 120.7 (4xCH), 120.3 (2xCH), 120.2 (2xCH), 112.4 (2xCH), 109.1 (2xC). HRMS (ESI) calculated for $C_{26}H_{19}N_4$ $[M+H]^+$ requires *m/z* = 387.1610, found *m/z* 387.1614.

5-methyl-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3q



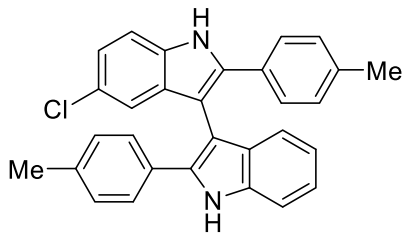
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-4-methylaniline **1b** (44 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 95:5 to 9:1) yielded **3q** (63 mg, 74%) as a pale yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.48 (s, 1H), 11.36 (s, 1H), 7.51 – 7.39 (m, 5H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.07 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.02 – 6.94 (m, 4H), 6.93 – 6.86 (m, 2H), 6.81 (ddd, *J* = 7.9, 6.7, 1.0 Hz, 1H), 6.67 (s, 1H), 2.16 (s, 9H). ^{13}C NMR (75 MHz, DMSO): 136.8 (C), 136.6 (C), 136.5 (C), 135.2 (C), 135.13 (C), 135.08 (C), 130.7 (C), 130.6 (C), 130.5 (C), 130.2 (C), 129.43 (2xCH), 129.39 (2xCH), 127.8 (C), 126.5 (2xCH), 126.4 (2xCH), 123.7 (CH), 122.0 (CH), 119.6 (CH), 119.4 (CH), 119.1 (CH), 111.6 (CH), 111.4 (CH), 106.6 (C), 105.9 (C), 21.6 (CH_3), 21.1 (2xCH_3). ESI(+)-MS: m/z (%)= 427 (60) $[M+1]^+$. Elemental analysis calcd for $C_{31}H_{26}N_2$: C, 87.29; H, 6.14; N, 6.57; found C, 87.01; H, 6.15; N, 6.60.

5-bromo-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3r



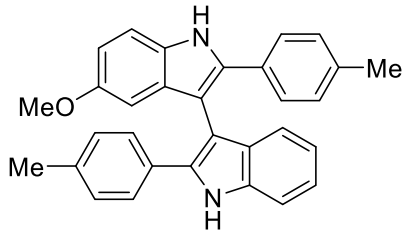
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-4-bromoaniline **1c** (58 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, CH_2Cl_2/Hex 1:3) yielded **3r** (50 mg, 51%) as a pale-yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.74 (s, 1H), 11.55 (s, 1H), 7.50 – 7.36 (m, 6H), 7.17 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.07 (ddd, *J* = 8.1, 6.5, 1.6 Hz, 1H), 7.01 (dd, *J* = 8.2, 2.6 Hz, 4H), 6.91 (d, *J* = 1.9 Hz, 1H), 6.88 – 6.77 (m, 2H), 2.18 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, DMSO): 137.2 (C), 136.87 (C), 136.85 (C), 136.8 (C), 135.44 (C), 135.36 (C), 131.8 (C), 130.4 (C), 130.0 (C), 129.76 (C), 129.5 (4xCH), 126.7 (2xCH), 126.6 (2xCH), 124.4 (CH), 122.1 (CH), 121.4 (CH), 119.6 (CH), 119.4 (CH), 113.7 (CH), 112.0 (C), 111.8 (CH), 105.9 (C), 105.3 (C), 21.1 (2xCH_3). ESI(+)-MS: m/z (%)= 492 (65) $[M+1]^+$. Elemental analysis calcd for $C_{30}H_{23}BrN_2$: C, 73.32; H, 4.72; N, 5.70; found C, 73.39; H, 4.74; N, 5.66.

5-chloro-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3s



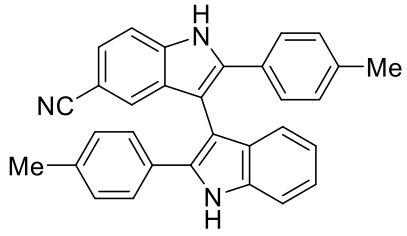
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-4-chloroaniline **1d** (49 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3s** (69 mg, 77%) as a white solid.
^{1}H NMR (300 MHz, DMSO): 11.73 (s, 1H), 11.55 (s, 1H), 7.57 – 7.28 (m, 6H), 7.12 – 6.97 (m, 6H), 6.94 – 6.48 (m, 3H), 2.17 (s, 6H).
^{13}C NMR (75 MHz, DMSO): 137.2 (C), 137.0 (C), 136.7 (C), 136.8 (C), 135.4 (C), 135.2 (C), 131.1 (C), 130.4 (C), 130.1 (C), 129.8 (C), 129.5 (4xCH), 126.7 (2xCH), 126.6 (2xCH), 124.0 (C), 122.1 (CH), 121.9 (CH), 119.6 (CH), 119.4 (CH), 118.3 (CH), 113.3 (CH), 111.8 (CH), 106.1 (C), 105.4 (C), 21.1 (2xCH3). ESI(+)-MS: m/z (%)= 447 (100) $[M+1]^+$. Elemental analysis calcd for $C_{30}H_{23}ClN_2$: C, 80.61; H, 5.19; N, 6.27; found C, 80.48; H, 5.20; N, 6.30.

5-methoxy-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3t



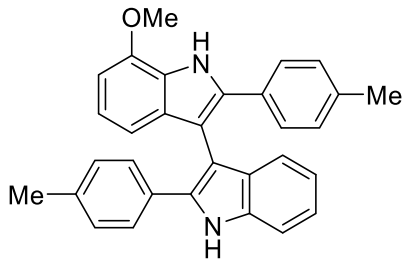
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-4-methoxyaniline**1e** (48 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3t** (56 mg, 64%) as a pale-yellow solid.
^{1}H NMR (300 MHz, DMSO): 11.48 (s, 1H), 11.32 (s, 1H), 7.49 – 7.39 (m, 5H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.09 – 6.95 (m, 5H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.79 (dd, *J* = 7.1, 1.0 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.27 (d, *J* = 2.5 Hz, 1H), 3.41 (s, 3H), 2.19 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (75 MHz, DMSO): 153.7 (C), 136.8 (C), 136.6 (C), 136.5 (C), 135.8 (C), 135.2 (C), 131.9 (C), 130.8 (2xC), 130.1 (C), 129.6 (C), 129.42 (2xCH), 129.40 (2xCH), 126.8 (2xCH), 126.5 (2xCH), 122.0 (CH), 119.7 (CH), 119.4 (CH), 112.3 (CH), 112.1 (CH), 111.7 (CH), 106.5 (C), 106.1 (C), 101.1 (CH), 55.4 (CH_3), 21.14 (CH_3), 21.12 (CH_3). ESI(+)-MS: m/z (%)= 443 (100) $[M+1]^+$. Elemental analysis calcd for $C_{31}H_{26}N_2O$: C, 84.13; H, 5.92; N, 6.33; found C, 84.03; H, 5.92; N, 6.34.

2,2'-di-*p*-tolyl-1*H*,1'*H*-[3,3'-biindole]-5-carbonitrile 3u



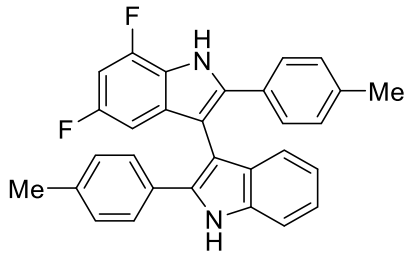
The general procedure was followed using: 4-amino-3-((2-aminophenyl)ethynyl)benzonitrile **1f** (47 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 5:1) yielded **3u** (68 mg, 78%) as a yellow solid.
^{1}H NMR (300 MHz, DMSO): 12.15 (s, 1H), 11.61 (s, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.37 (m, 6H), 7.22 (d, *J* = 1.6 Hz, 1H), 7.12 – 6.98 (m, 5H), 6.92 – 6.76 (m, 2H), 2.18 (s, 6H). ^{13}C NMR (75 MHz, DMSO): 138.6 (C), 137.8 (C), 137.7 (C), 137.0 (C), 136.9 (C), 135.7 (C), 130.3 (C), 129.6 (2xCH), 129.6 (2xCH), 129.5 (C), 126.9 (2xCH), 126.8 (2xCH), 124.8 (CH), 124.6 (CH), 122.2 (CH), 121.0 (C), 119.7 (CH), 119.3 (CH), 113.0 (CH), 111.8 (CH), 107.1 (C), 104.6 (C), 101.5 (C), 21.2 (CH_3), 21.1 (CH_3). 2 quaternary carbon are missing, probably overlapped. ESI(+)-MS: m/z (%)= 438 (100) $[M+1]^+$. Elemental analysis calcd for $C_{31}H_{23}N_3$: C, 85.10; H, 5.30; N, 9.60; found C, 85.37; H, 5.29; N, 9.63.

7-methoxy-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3v



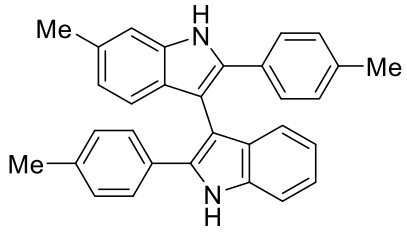
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-6-methoxyaniline**1e** (48 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3v** (50 mg, 57%) as a brown solid.
^{1}H NMR (400 MHz, DMSO): 11.48 (s, 1H), 11.43 (s, 1H), 7.60 – 7.40 (m, 5H), 7.08 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.76 (t, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.8 Hz, 1H), 3.98 (s, 3H), 2.20 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, DMSO): 146.5 (C), 136.8 (C), 136.6 (C), 136.4 (C), 135.6 (C), 135.2 (C), 131.5 (C), 130.7 (C), 130.6 (C), 130.1 (C), 129.4 (2xCH), 129.2 (2xCH), 127.3 (2xCH), 126.9 (C), 126.6 (2xCH), 122.0 (CH), 120.0 (CH), 119.6 (CH), 119.4 (CH), 112.5 (CH), 111.6 (CH), 107.1 (C), 106.6 (C), 102.7 (CH), 55.6 (CH_3), 21.2 (CH_3), 21.1 (CH_3). HRMS (ESI) calculated for $C_{31}H_{26}N_2NaO$ $[M+Na]^+$ requires *m/z* = 465.1943, found *m/z* 465.1952.

5,7-difluoro-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3w



The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-4,6-difluoroaniline**1g** (49 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/CH_2Cl_2 4:1 to 3:1) yielded **3w** (52 mg, 60%) as a white solid.
^{1}H NMR (300 MHz, Acetone-d_6): 11.01 (s, 1H), 10.71 (s, 1H), 7.59 – 7.39 (m, 5H), 7.12 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 7.08 – 6.98 (m, 5H), 6.89 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.79 (ddd, *J* = 11.1, 9.6, 2.2 Hz, 1H), 6.55 (dd, *J* = 9.3, 2.2 Hz, 1H), 2.22 (s, 6H).
Spectral data are in good agreement with literature values.[3]

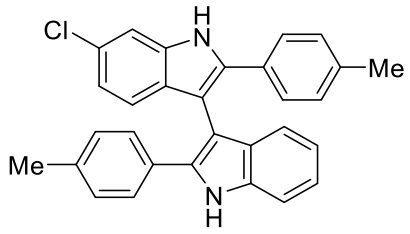
6-methyl-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3x



The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-5-methylaniline **1i** (45 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3x** (55 mg, 64%) as a yellow solid.

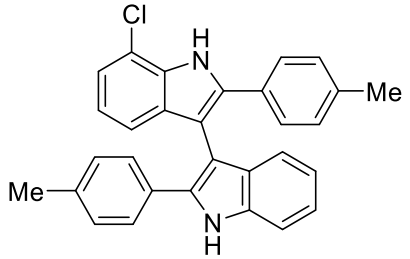
^{1}H NMR (300 MHz, DMSO): 11.46 (s, 1H), 11.31 (s, 1H), 7.48 – 7.38 (m,5H), 7.21 (m, 1H), 7.05 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.03 – 6.94 (m, 4H), 6.85 (m, 1H), 6.79 (dd, *J* = 6.8, 1.0 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.62 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.36 (s, 3H), 2.17 (s, 3H), 2.16 (s, 3H).
^{13}C NMR (75 MHz, DMSO): 137.2 (C), 136.8 (C), 136.6 (C), 136.3 (C), 135.0 (C), 134.4 (C), 131.1 (C), 130.8 (C), 130.6 (C), 129.9 (C), 129.41 (2xCH), 129.38 (2xCH), 127.9 (C), 126.6 (2xCH), 126.4 (2xCH), 122.0 (CH), 121.2 (CH), 119.6 (CH), 119.4 (2xCH), 111.6 (CH), 111.5 (CH), 106.5 (C), 106.2 (C), 21.9 (CH_3), 21.12 (CH_3), 21.11 (CH_3).HRMS (ESI) calculated for $C_{31}H_{26}N_2Na$ $[M+Na]^+$ requires *m/z* = 449.1994, found *m/z* 449.1999.

6-chloro-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3y



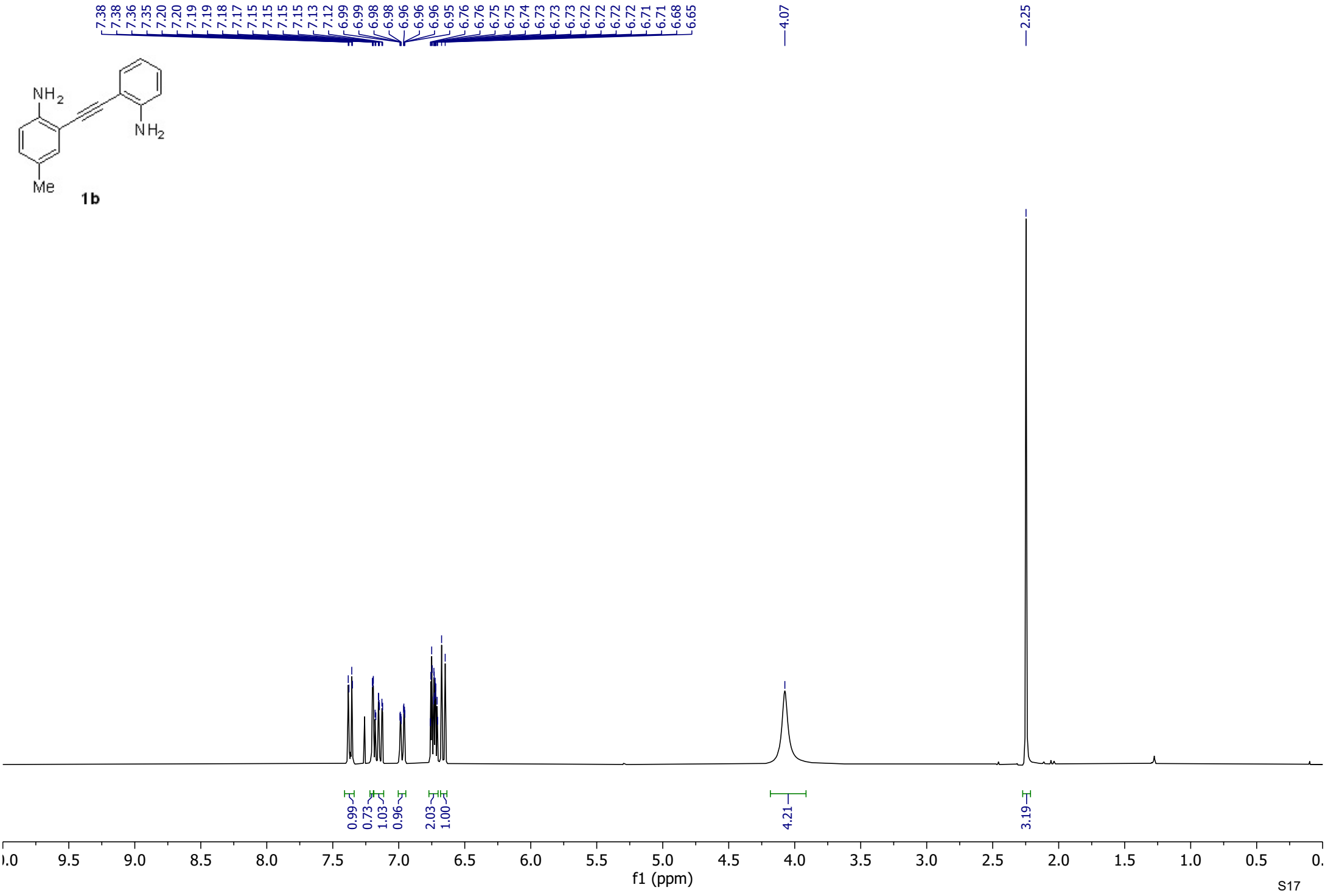
The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-5-chloroaniline **1j** (48 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3y** (67 mg, 75%) as a pale-yellow solid.
^{1}H NMR (400 MHz, DMSO): 11.68 (s, 1H), 11.54 (s, 1H), 7.48 –7.41 (m, 6H), 7.08 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 4H), 6.93 – 6.79 (m, 4H), 2.20 (s, 6H). ^{13}C NMR (101 MHz, DMSO): 137.2 (C), 137.1 (C), 136.8 (C), 136.8 (C), 136.2 (C), 135.4 (C), 130.5 (C), 130.2 (C), 129.7 (C), 129.5 (2xCH), 129.5 (2xCH), 128.7 (C), 126.7 (4xCH), 126.5 (C), 122.1 (CH), 120.9 (CH), 119.8 (CH), 119.5 (CH), 119.5 (CH), 111.7 (CH), 111.2 (CH), 106.6 (C), 105.6 (C), 21.2 (2xCH_3). HRMS (ESI) calculated for $C_{30}H_{23}ClN_2Na$ $[M+Na]^+$ requires *m/z* = 469.1447, found *m/z* 469.1451.

7-chloro-2,2'-di-*p*-tolyl-1*H*,1'*H*-3,3'-biindole 3z

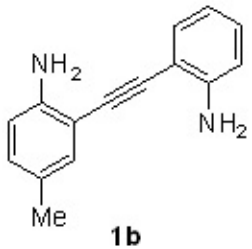


The general procedure was followed using: 2-((2-aminophenyl)ethynyl)-6-chloroaniline**1h** (49 mg, 0.2 mmol) and 4-methylbenzaldehyde **2a** (72 mg, 0.6 mmol). Purification of the crude by flash column chromatography (SiO_2, Hex/EtOAc 9:1) yielded **3z** (72 mg, 80%) as a white solid.
^{1}H NMR (400 MHz, DMSO): 11.57 (s, 1H), 11.53 (s, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.39 (m, 3H), 7.15 (dd, *J* = 6.6, 1.9 Hz, 1H), 7.08 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.06 – 7.00 (m, 4H), 6.92 – 6.78 (m, 4H), 2.20 (s, 6H).
^{13}C NMR (101 MHz, DMSO): 137.4 (C), 137.2 (C), 136.81 (C), 136.77 (C), 135.5 (C), 133.8 (C), 131.8 (C), 130.5 (C), 129.9 (C), 129.8 (C), 129.5 (2xCH), 129.2 (2xCH), 127.8 (2xCH), 126.7 (2xCH), 122.1 (CH), 121.7 (CH), 120.6 (CH), 119.6 (CH), 119.4 (CH), 118.5 (CH), 116.2 (C), 111.7 (CH), 107.8 (C), 105.6 (C), 21.2 (2xCH_3). HRMS (ESI) calculated for $C_{30}H_{23}ClN_2Na$ $[M+H]^+$ requires *m/z* = 469.1447, found *m/z* 469.1454.

^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



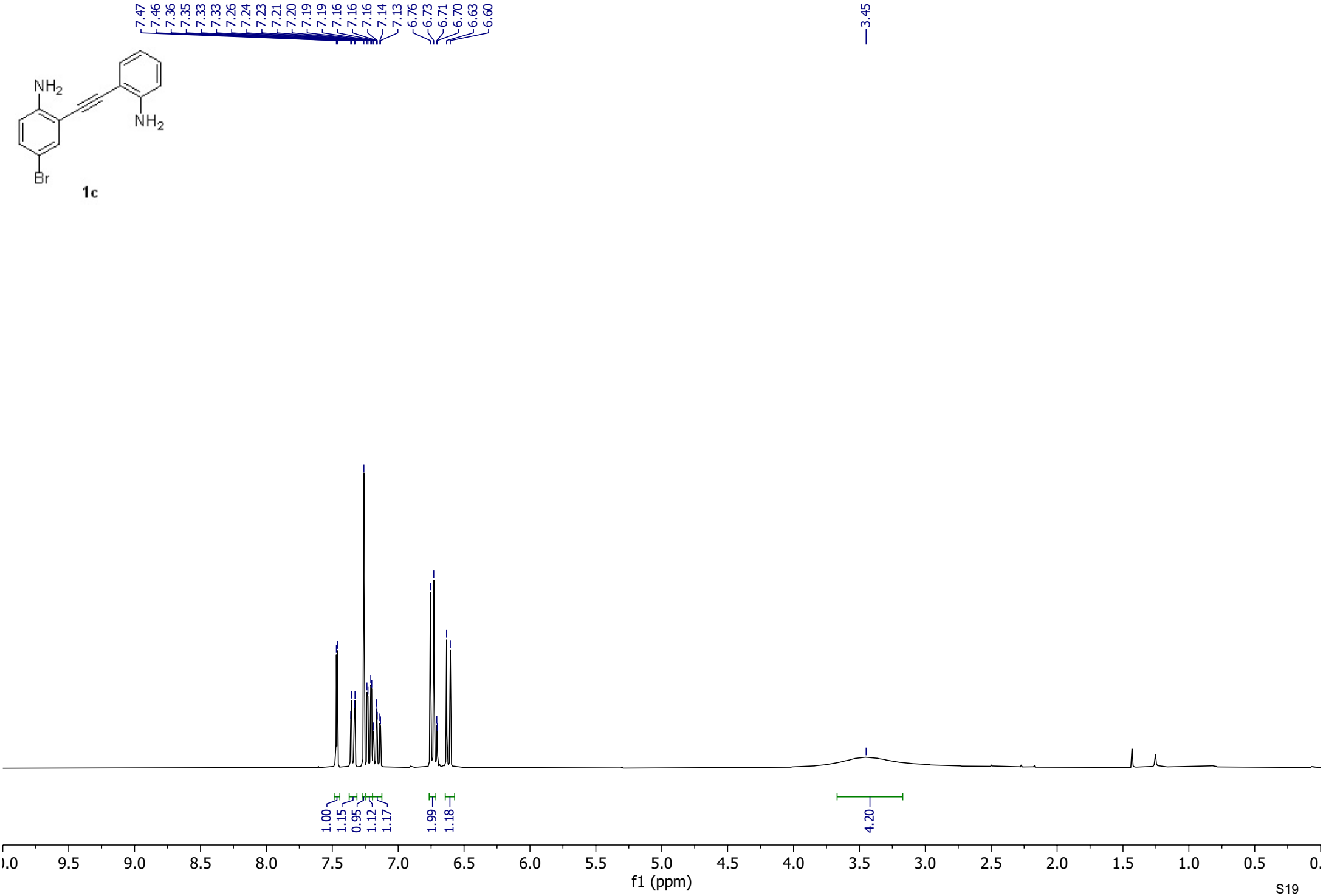
1b

147.62
145.28
132.13
132.01
130.60
129.68
127.30
118.01
114.65
114.41
108.19
108.14
91.34
90.83
20.29

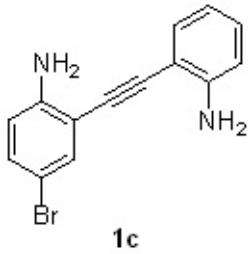
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

^{1}H NMR (300 MHz, $CDCl_3$)

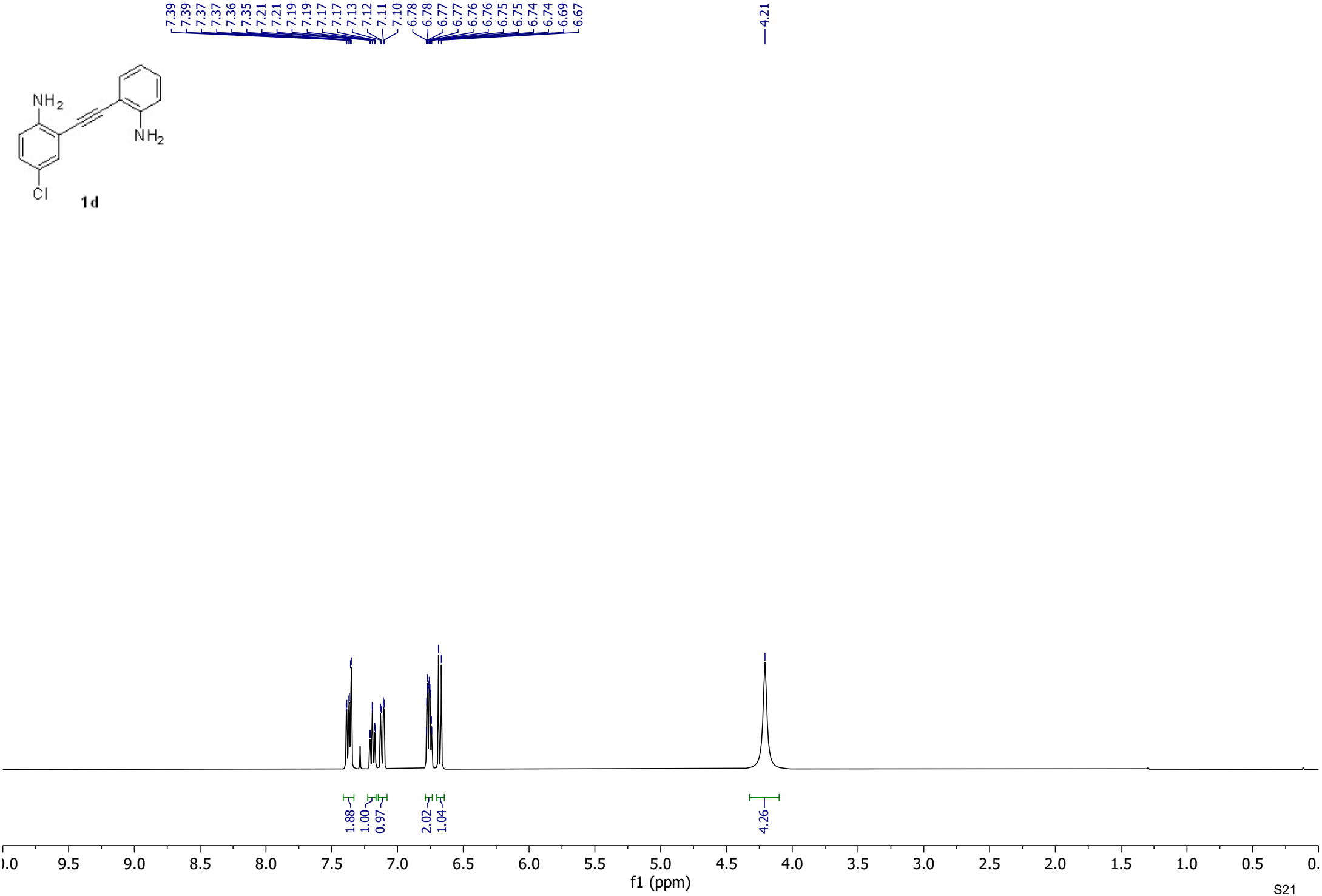


^{13}C NMR (75 MHz, $CDCl_3$)

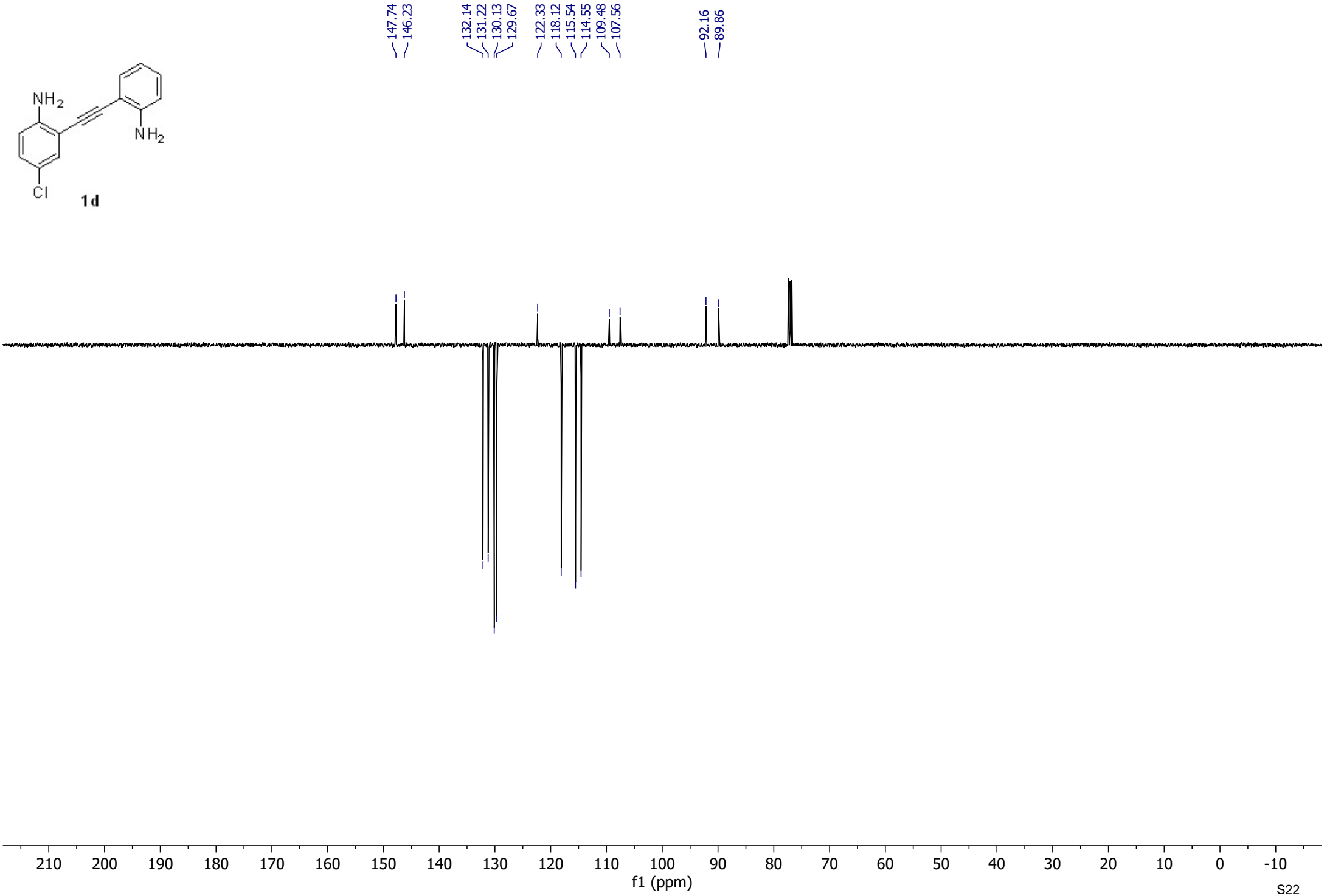


1c

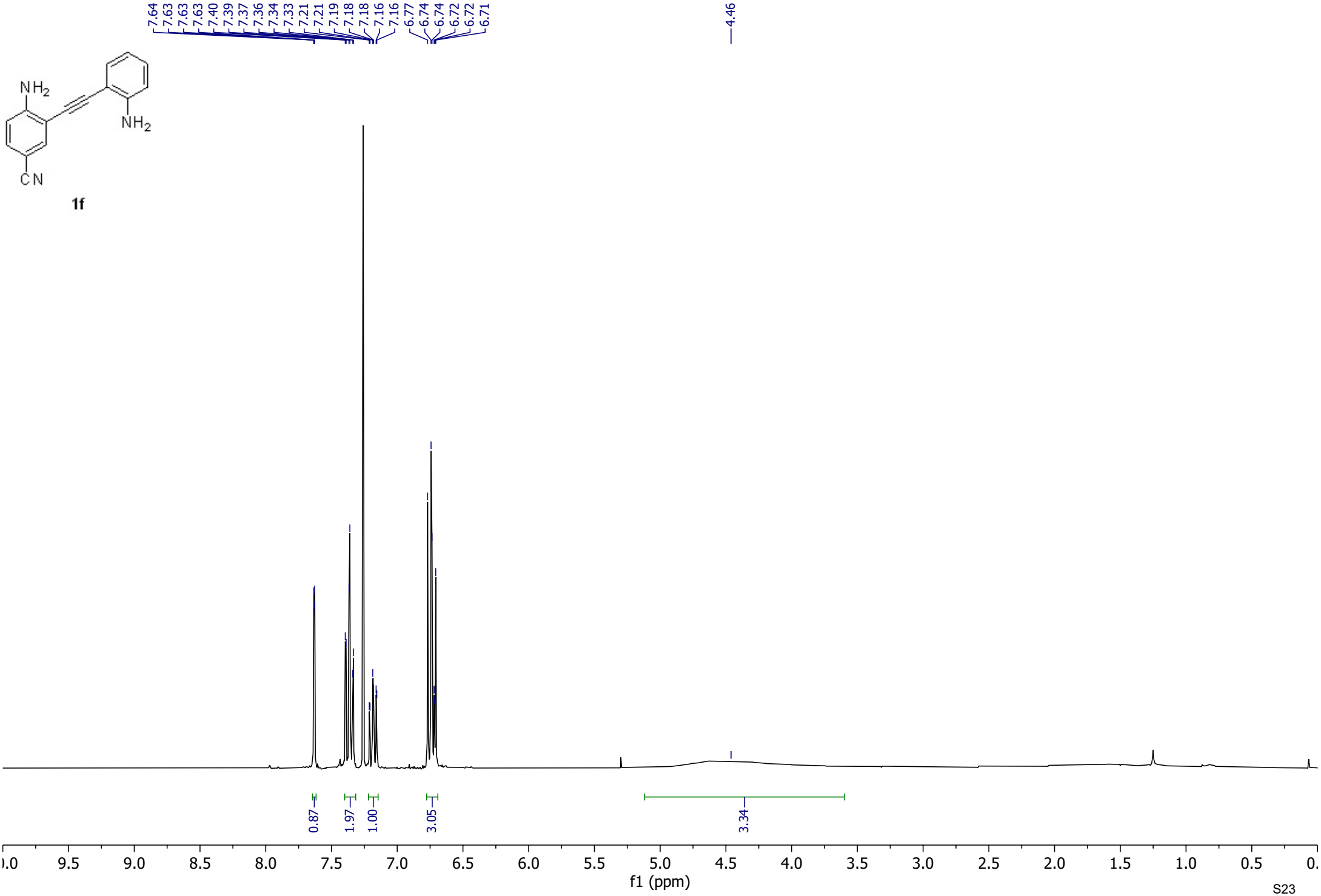
^{1}H NMR (400 MHz, $CDCl_3$)



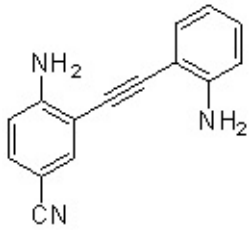
^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)

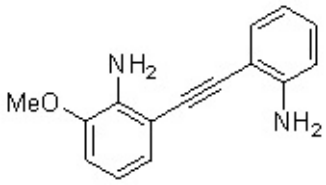


^{13}C NMR (75 MHz, $CDCl_3$)



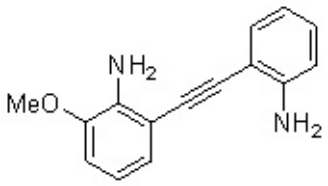
1f

^{1}H NMR (400 MHz, $CDCl_3$)



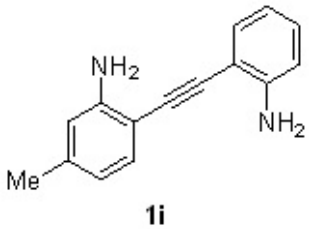
1g

^{13}C NMR (101 MHz, $CDCl_3$)



1g

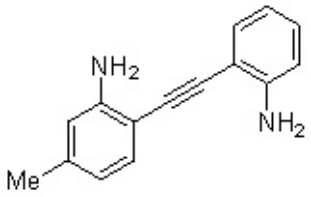
^{1}H NMR (400 MHz, $CDCl_3$)



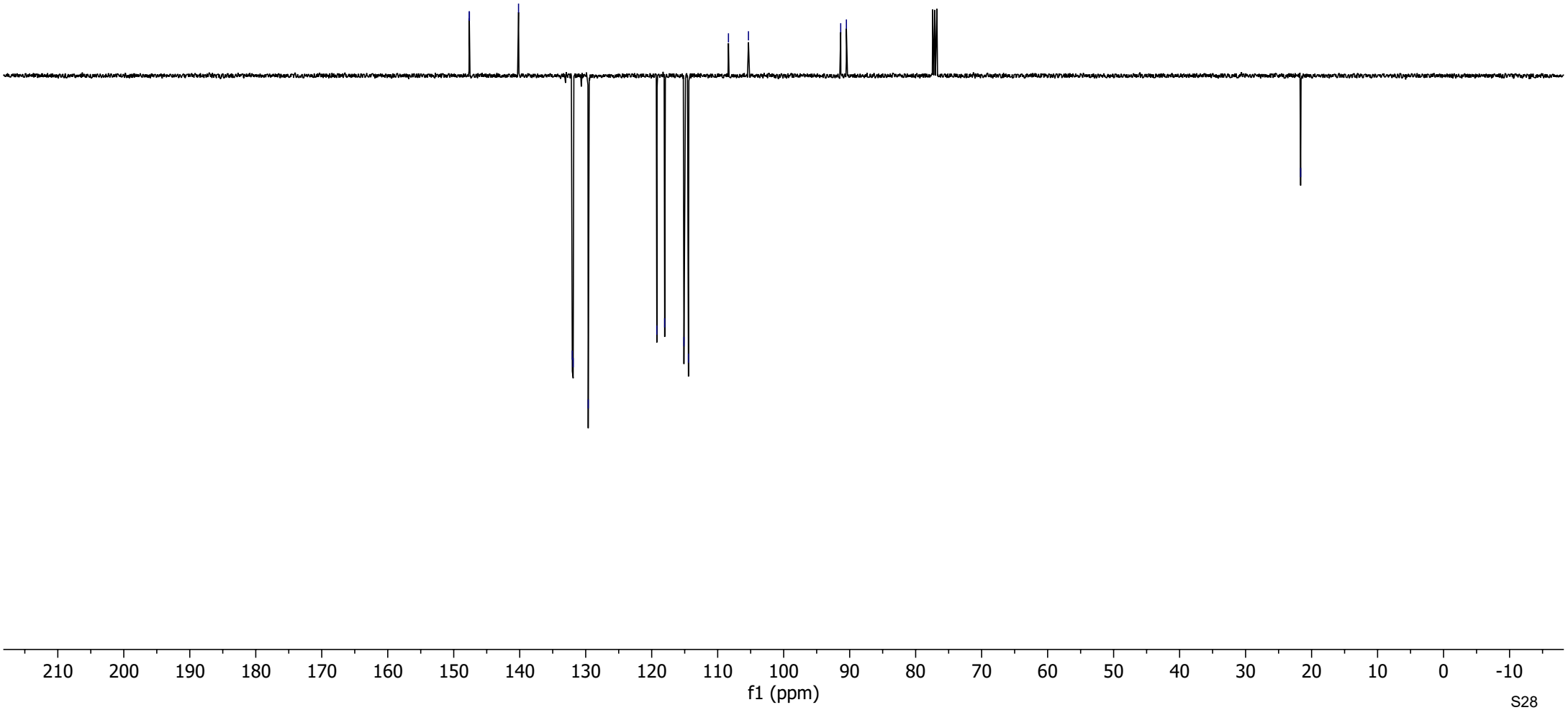
1i

^{13}C NMR (101 MHz, $CDCl_3$)

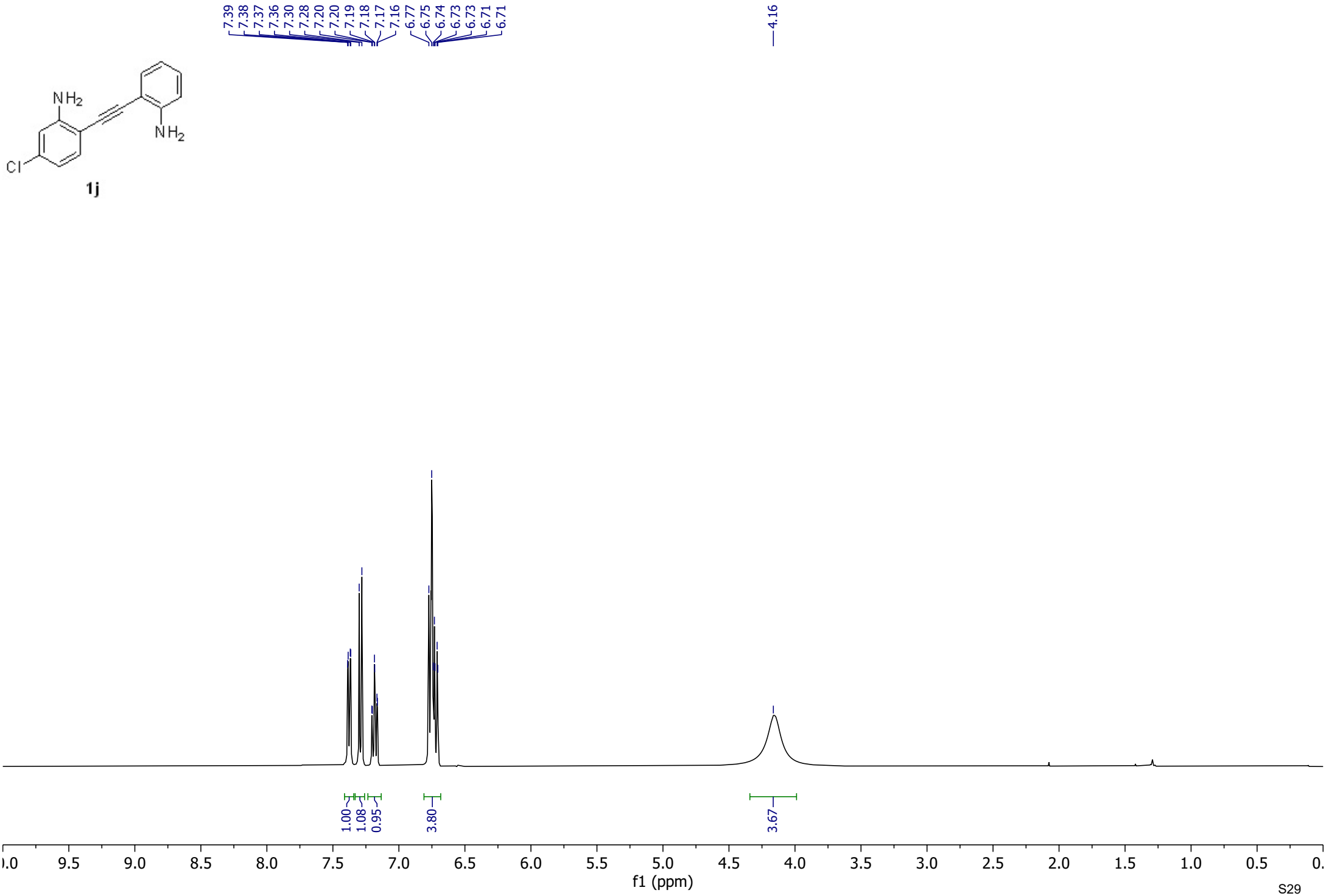
147.65
147.63
140.18
132.03
131.90
129.62
119.23
118.03
115.11
114.43
108.37
105.34
91.36
90.50
21.66



1i

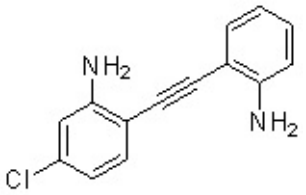


^{1}H NMR (400 MHz, $CDCl_3$)

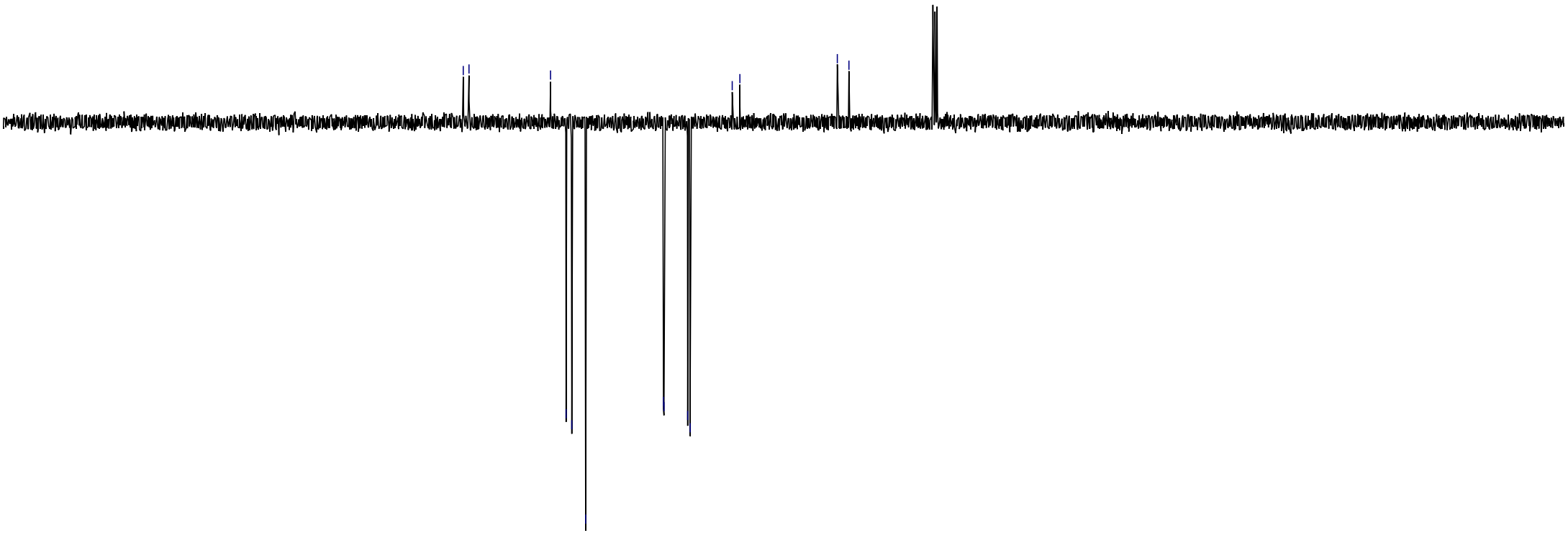


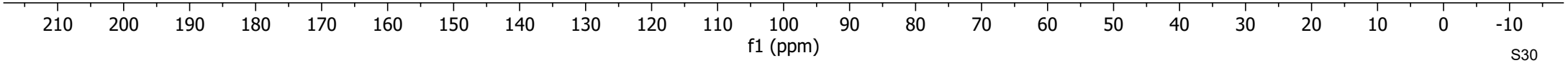
^{13}C NMR (101 MHz, $CDCl_3$)

148.54
147.67
135.32
132.96
132.09
129.99
118.20
118.13
114.53
114.16
107.79
106.62
91.86
90.10

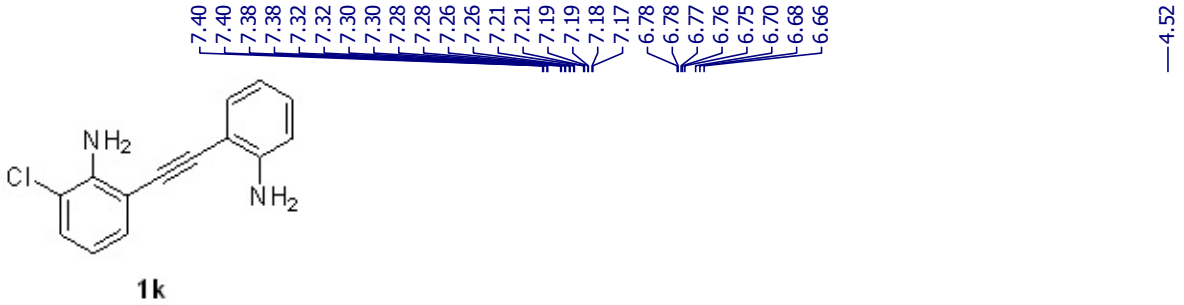


1j

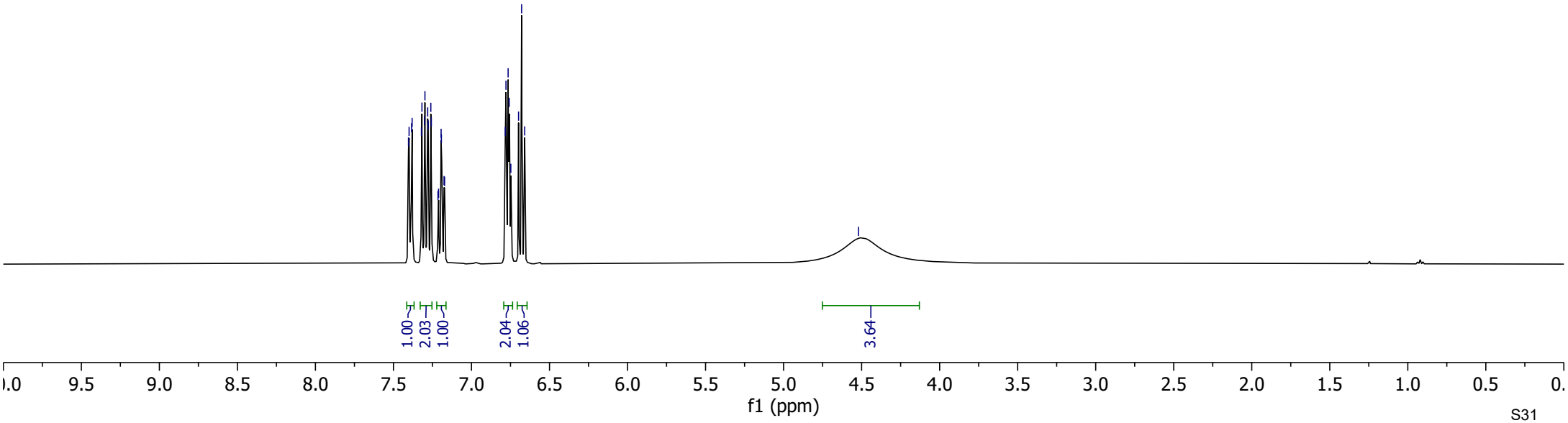




^{1}H NMR (400 MHz, $CDCl_3$)

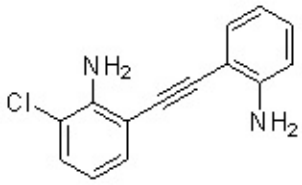


1k

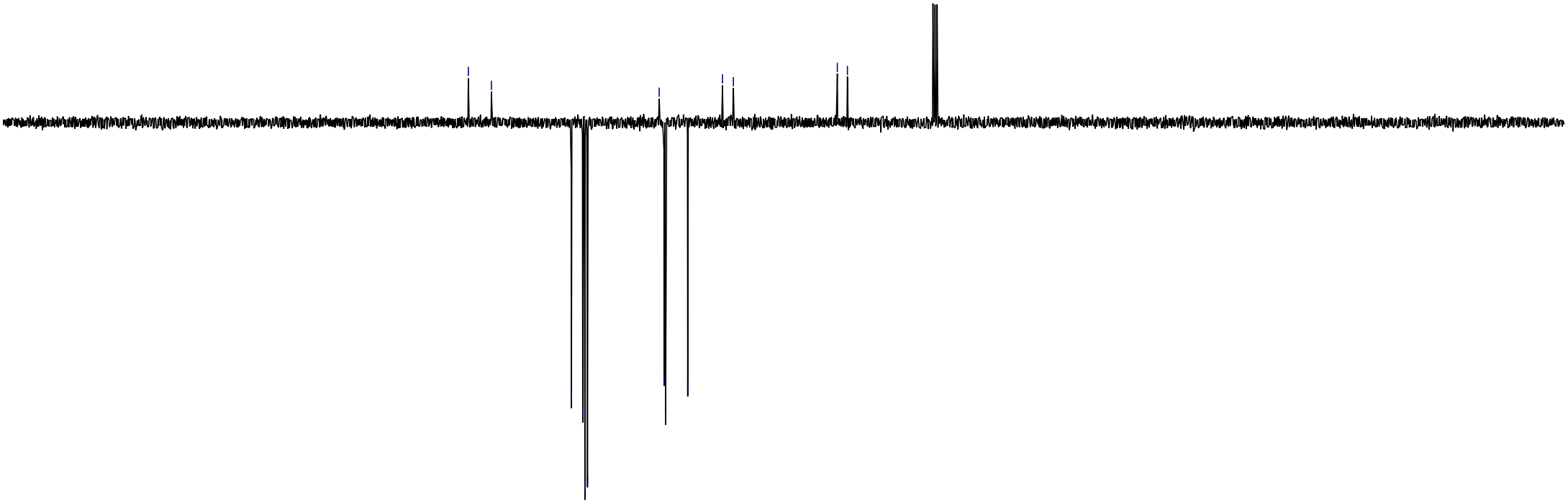


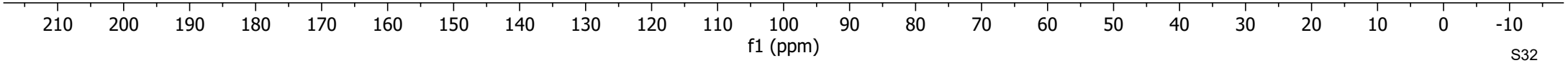
^{13}C NMR (101 MHz, $CDCl_3$)

147.77
144.28
132.15
130.44
130.10
129.72
118.85
118.11
117.88
114.53
109.26
107.61
91.86
90.33

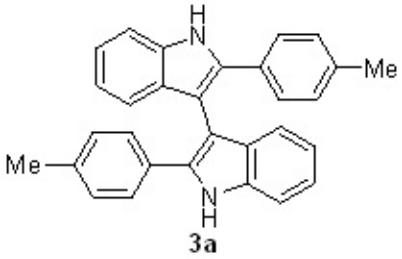


1k



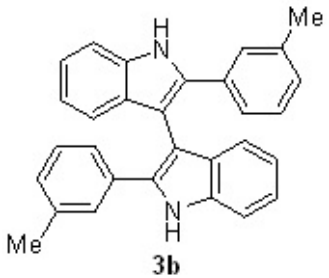


^{1}H NMR (300 MHz, DMSO



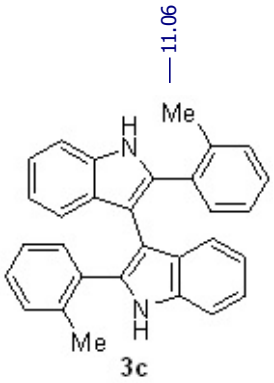
3a

^{1}H NMR (300 MHz, DMSO)



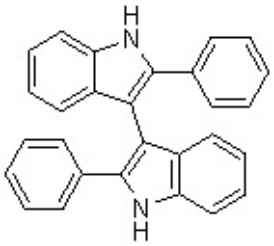
3b

^{1}H NMR (300 MHz, DMSO)



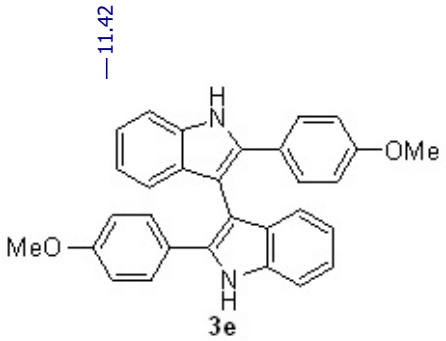
3c

^{1}H NMR (300 MHz, DMSO)



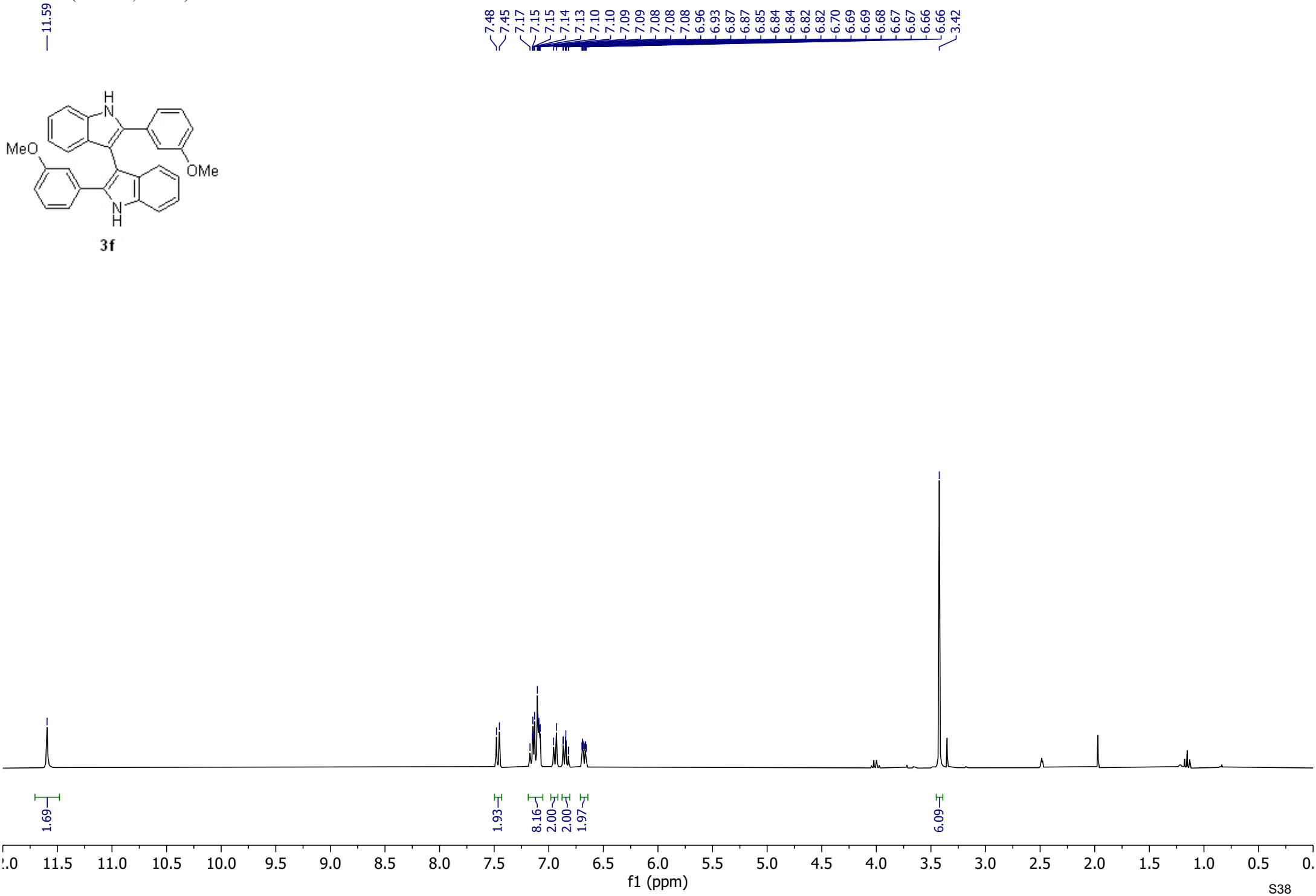
3d

^{1}H NMR (300 MHz, DMSO)



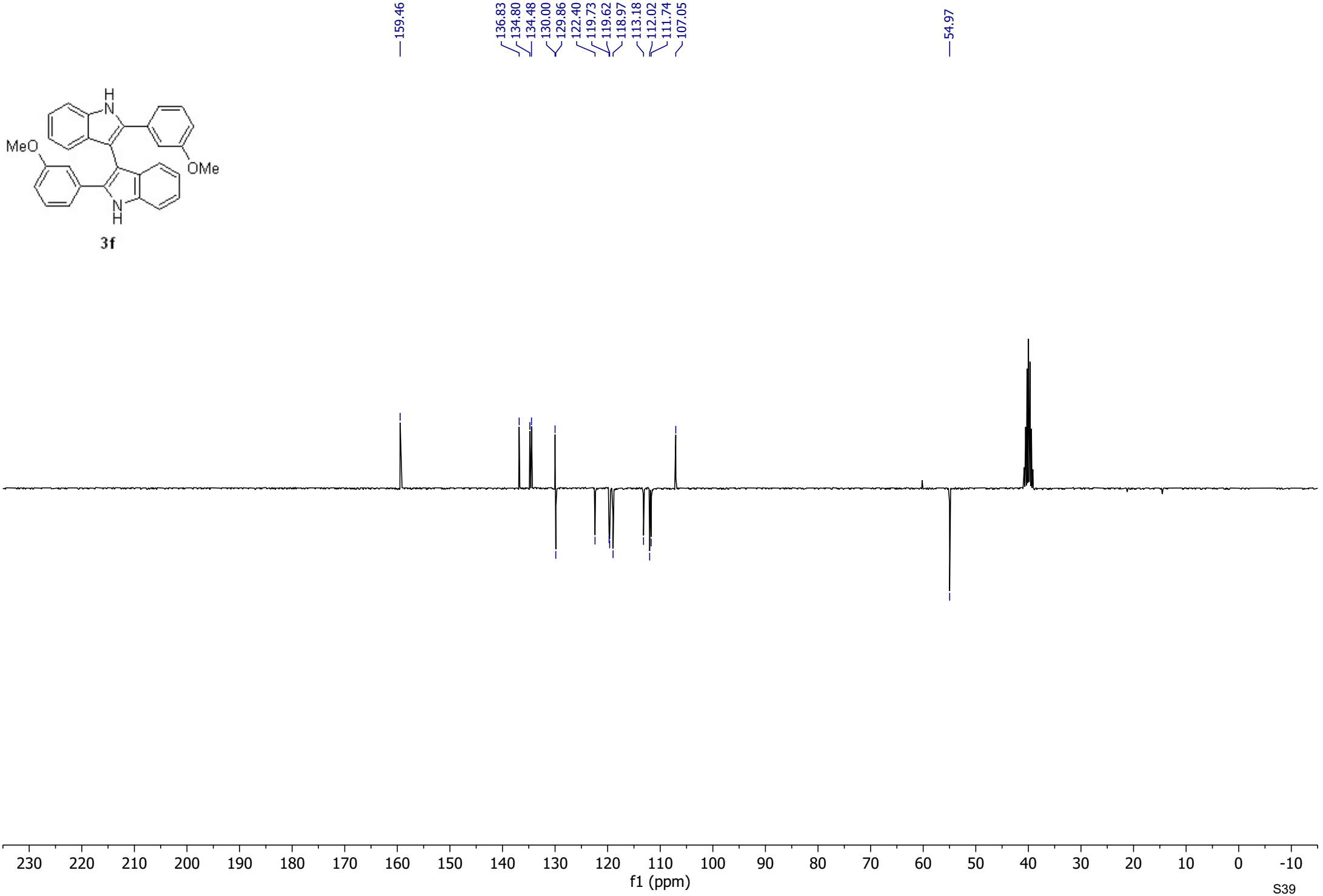
3e

^{1}H NMR (300 MHz, DMSO)

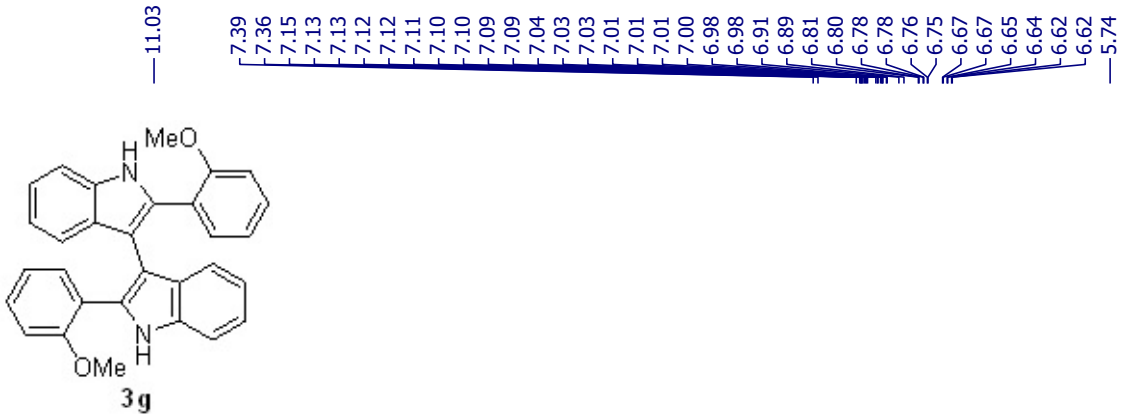


3f

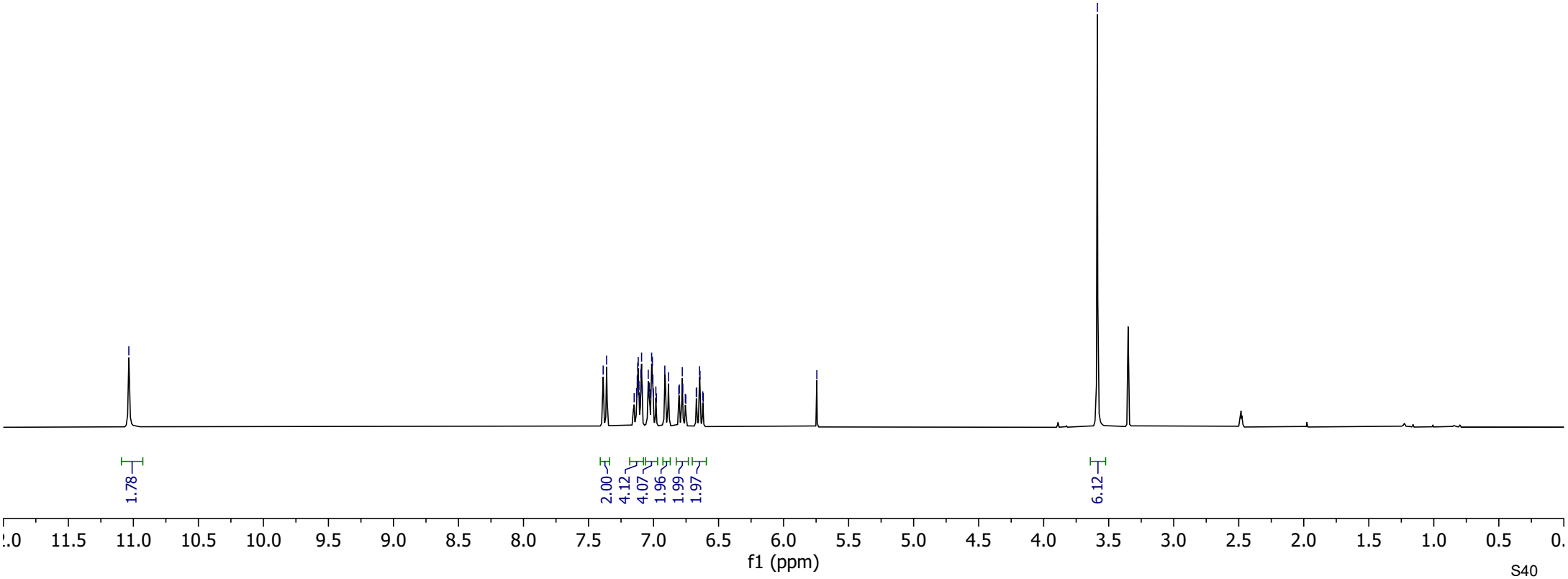
^{13}C NMR (75 MHz, DMSO)



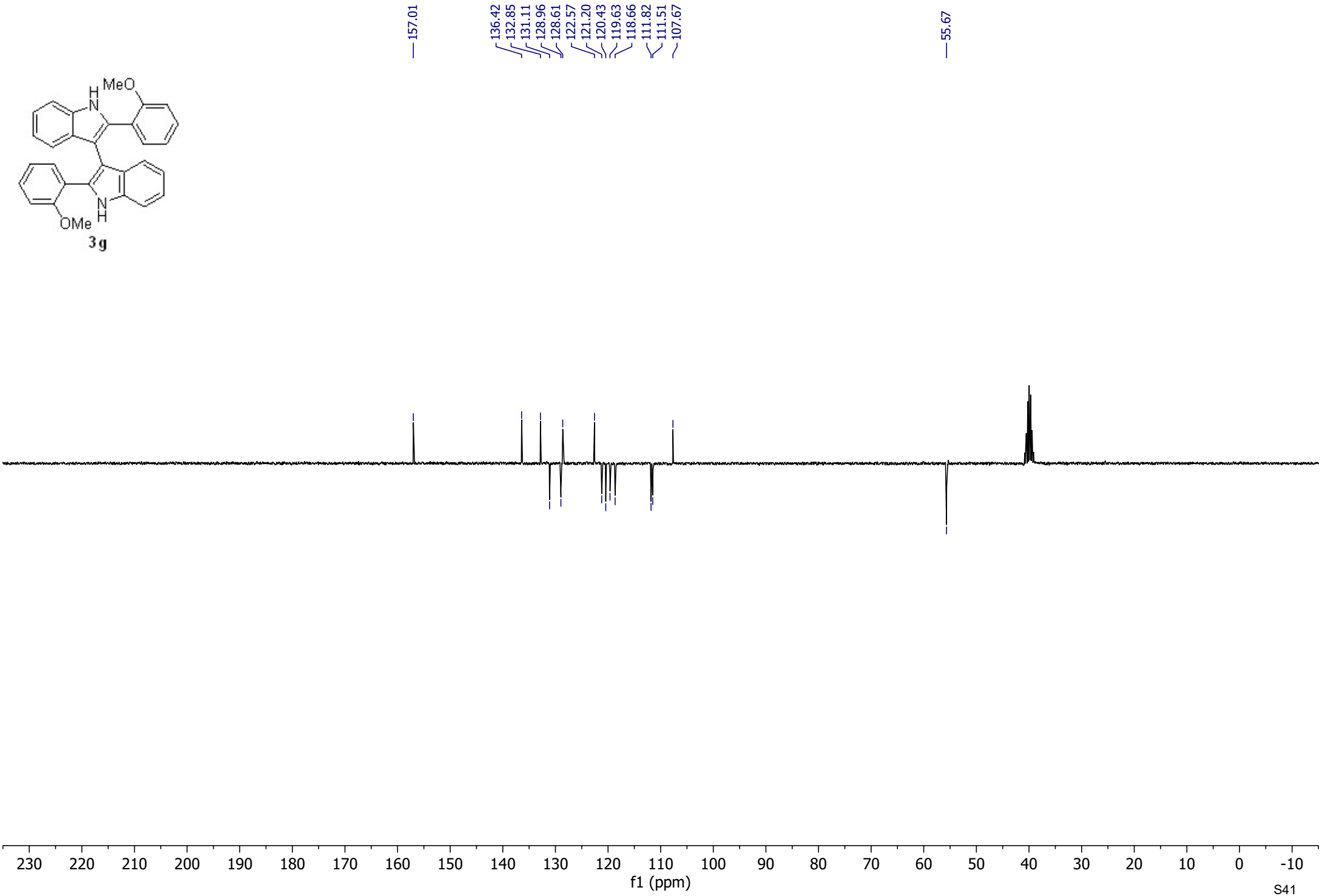
^{1}H NMR (300 MHz, DMSO)



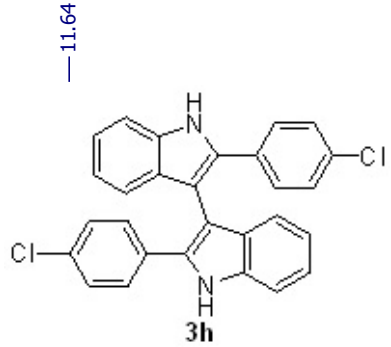
3g



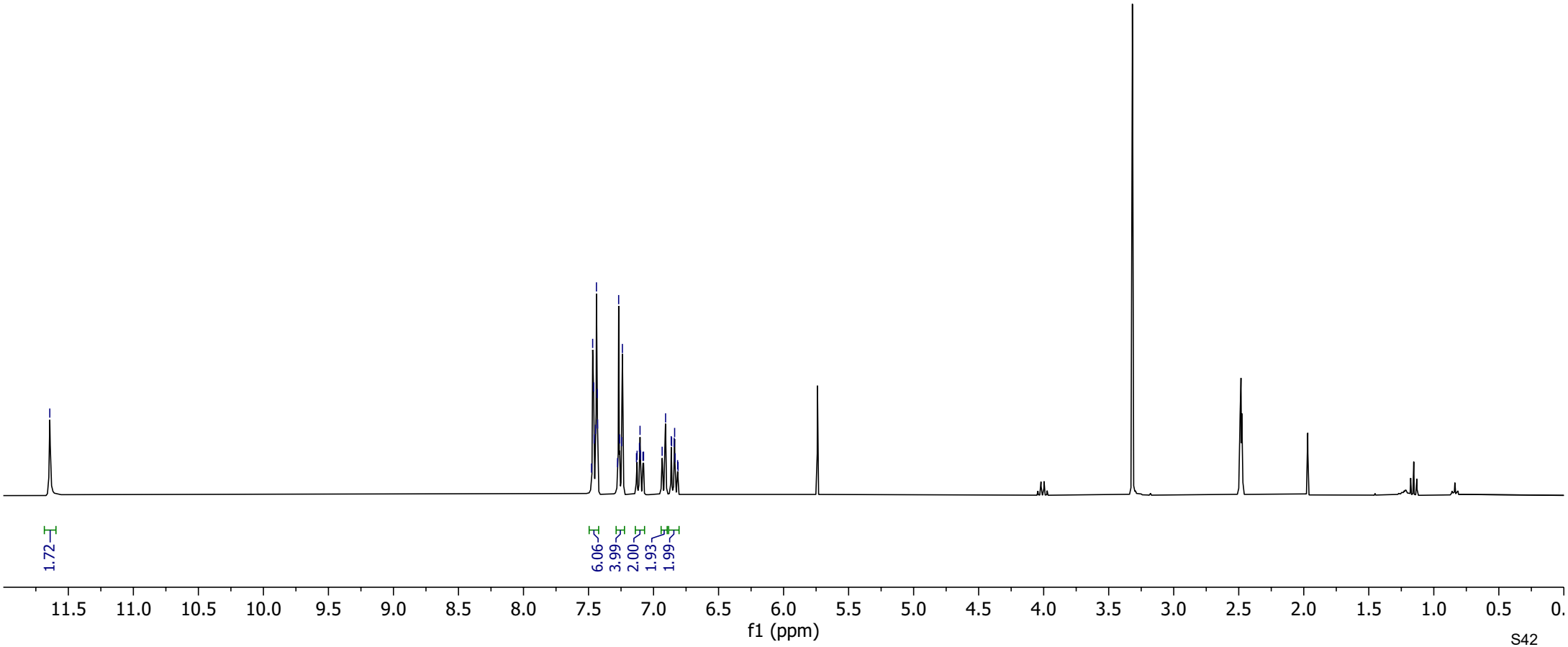
^{13}C NMR (75 MHz, DMSO)



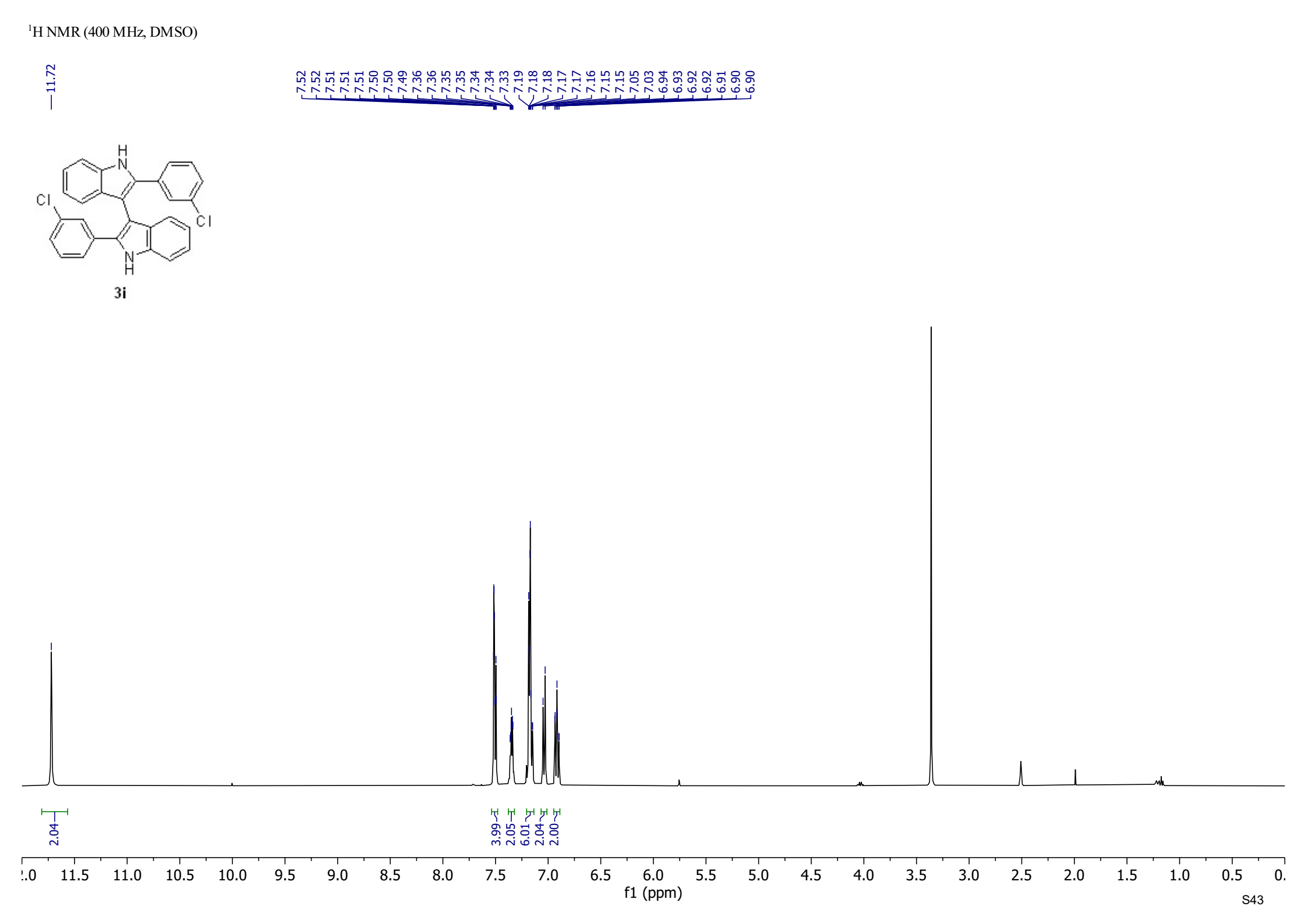
^{1}H NMR (300 MHz, DMSO)



3h

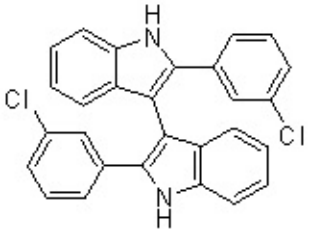


^{1}H NMR (400 MHz, DMSO)

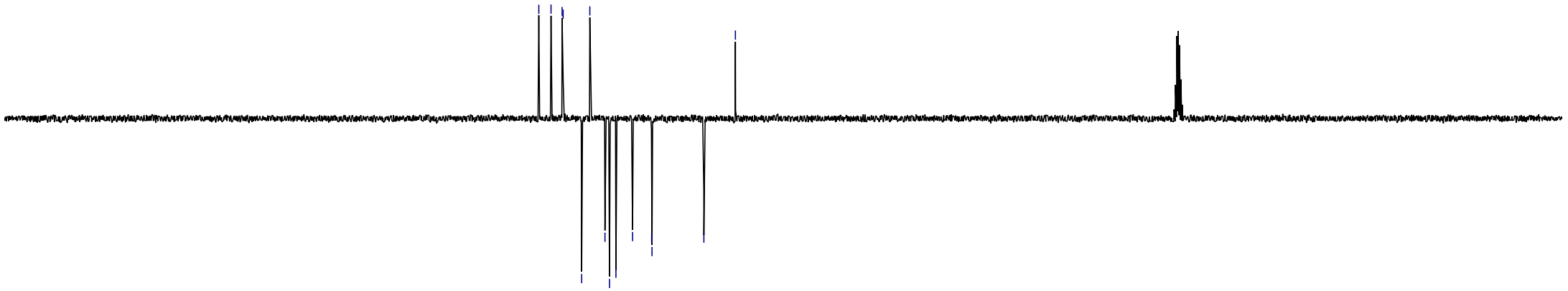


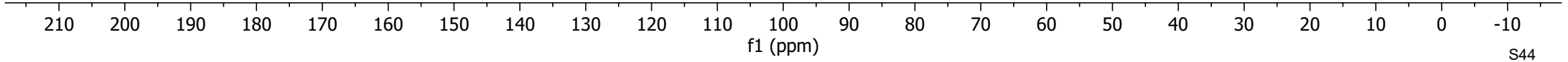
^{13}C NMR (101 MHz, DMSO)

137.12
135.27
133.59
133.43
130.62
129.37
127.08
126.39
125.41
122.88
119.98
119.93
112.05
107.27

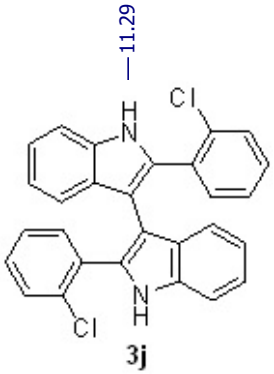


3i

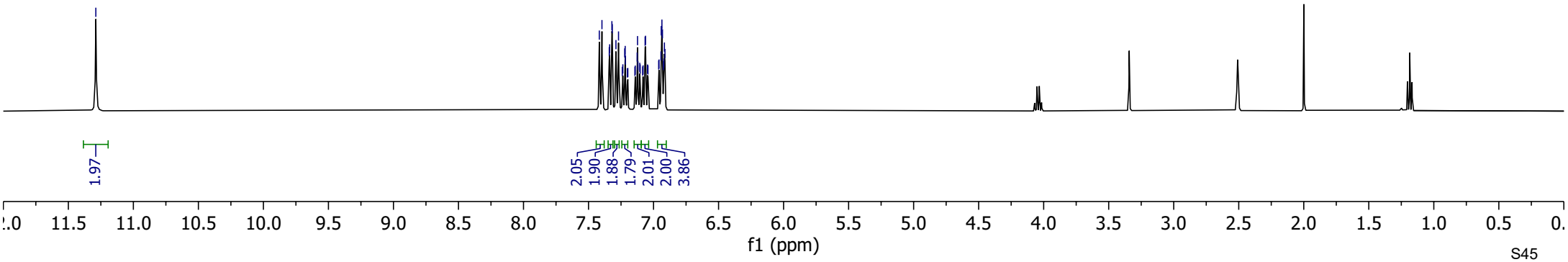




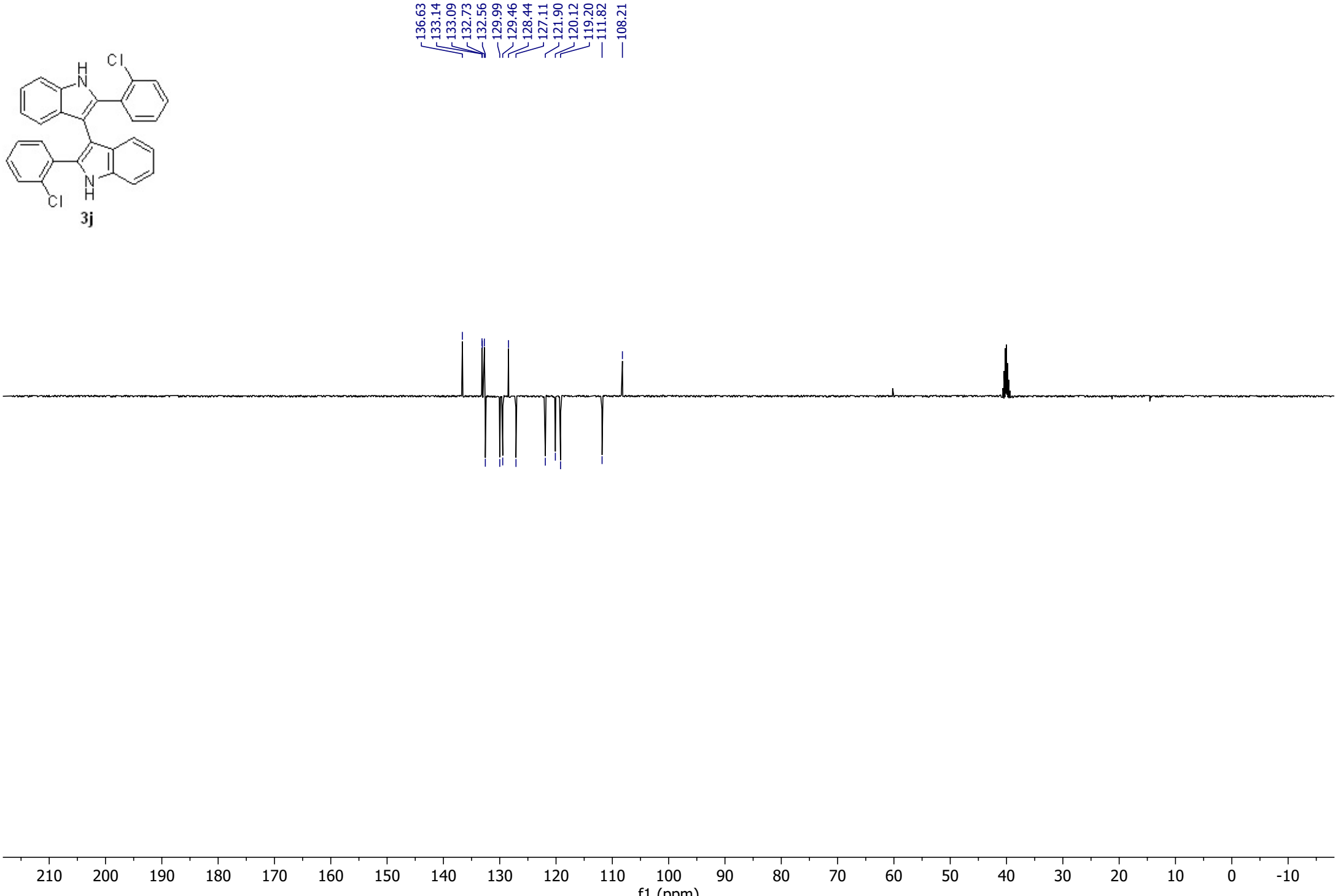
^{1}H NMR (400 MHz, DMSO)



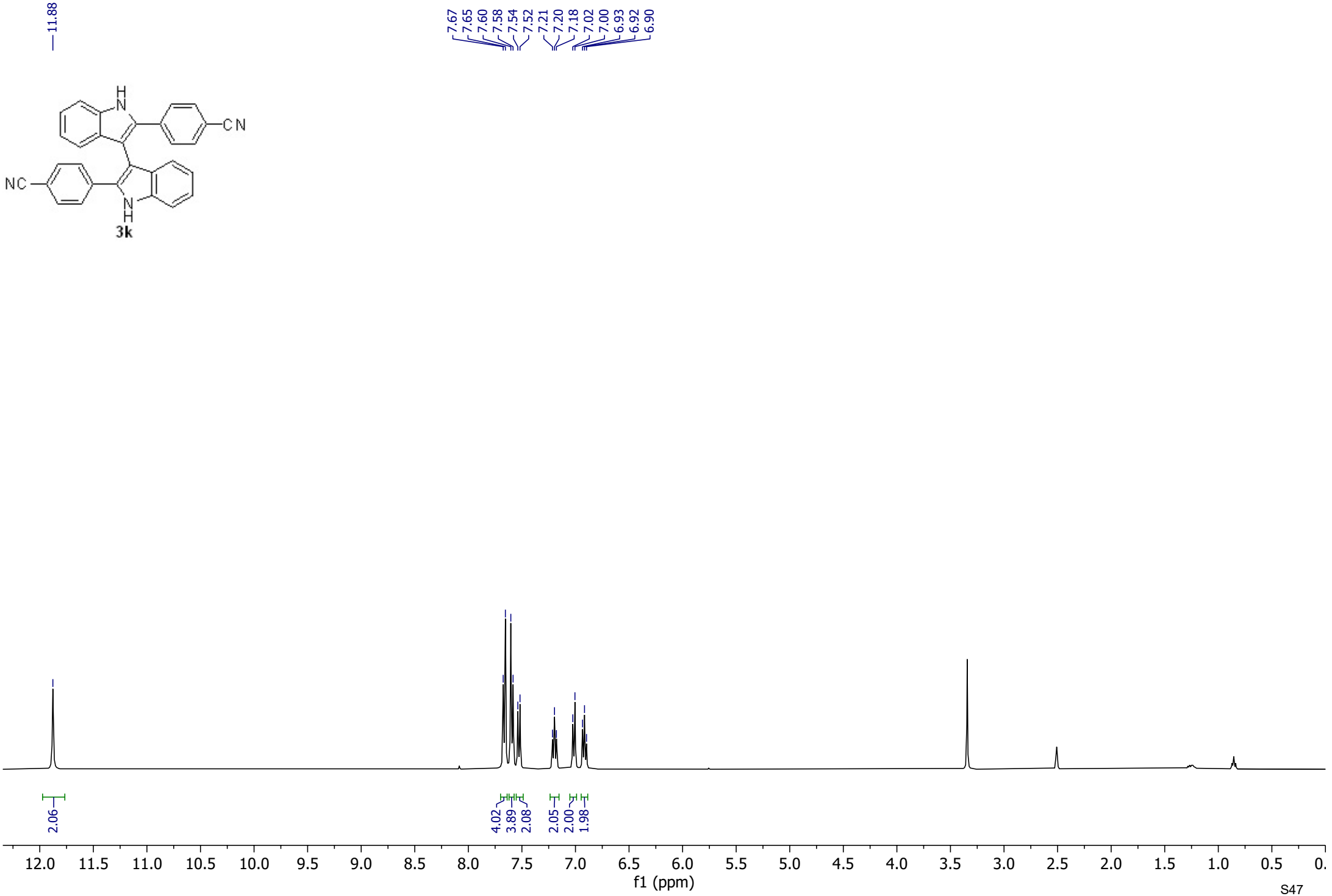
3j



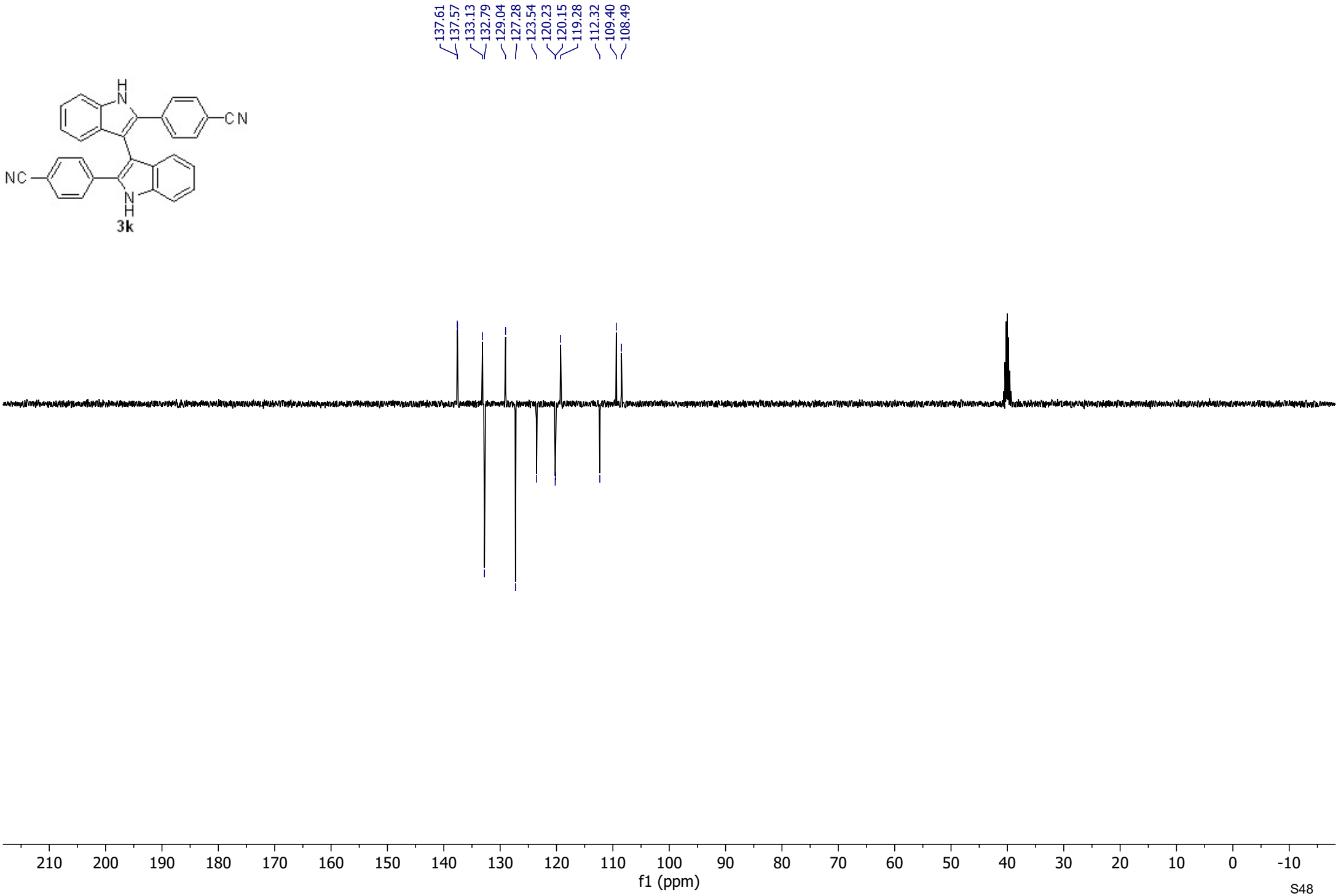
^{13}C NMR (101 MHz, DMSO)



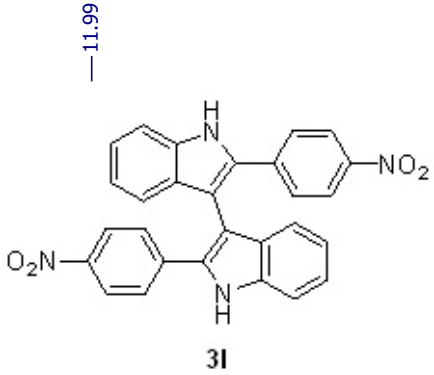
^{1}H NMR (400 MHz, DMSO)



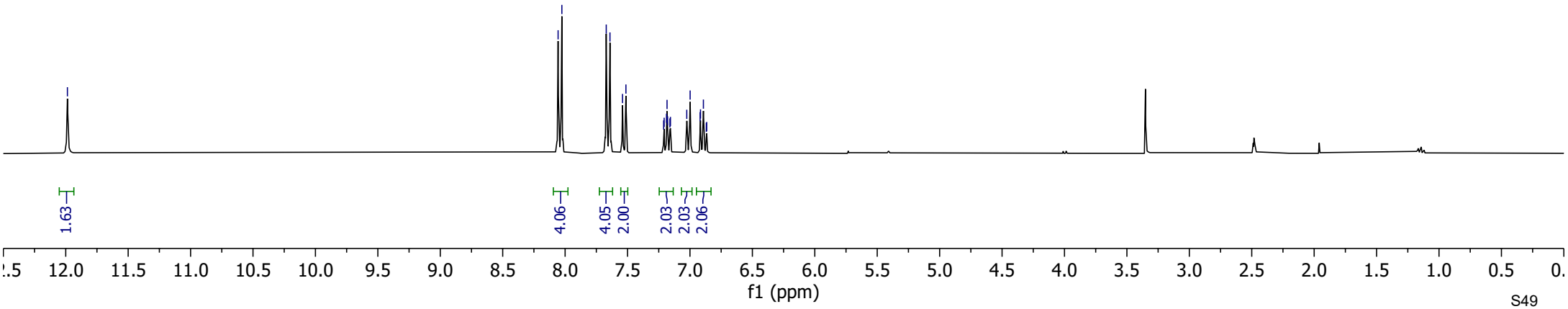
^{13}C NMR (101 MHz, DMSO)



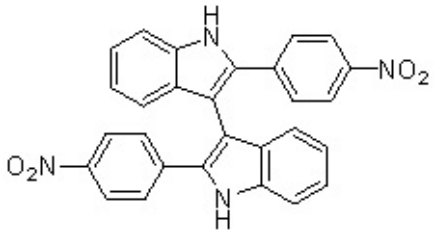
^{1}H NMR (300 MHz, DMSO)



3l

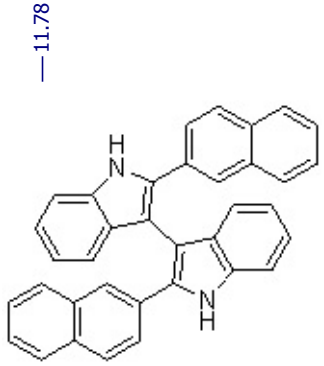


^{13}C NMR (75 MHz, DMSO)



3l

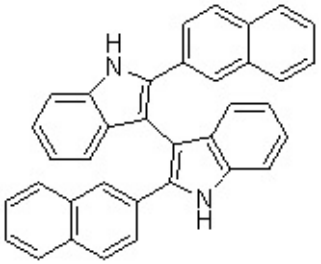
^{1}H NMR (300 MHz, DMSO)



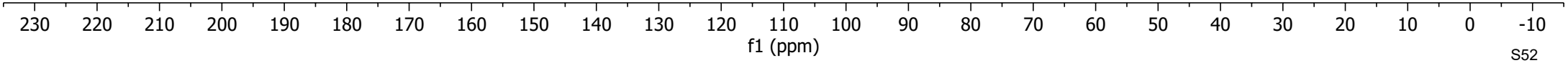
3m

^{13}C NMR (75 MHz, DMSO)

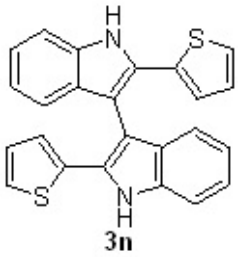
137.19
135.18
133.32
132.24
131.10
129.92
128.17
128.11
127.88
126.84
126.39
125.27
125.22
122.48
119.84
119.64
111.87
107.41



3m



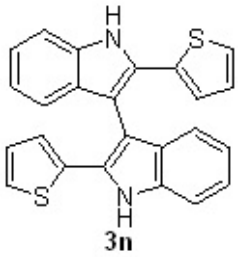
^{1}H NMR (300 MHz, DMSO)



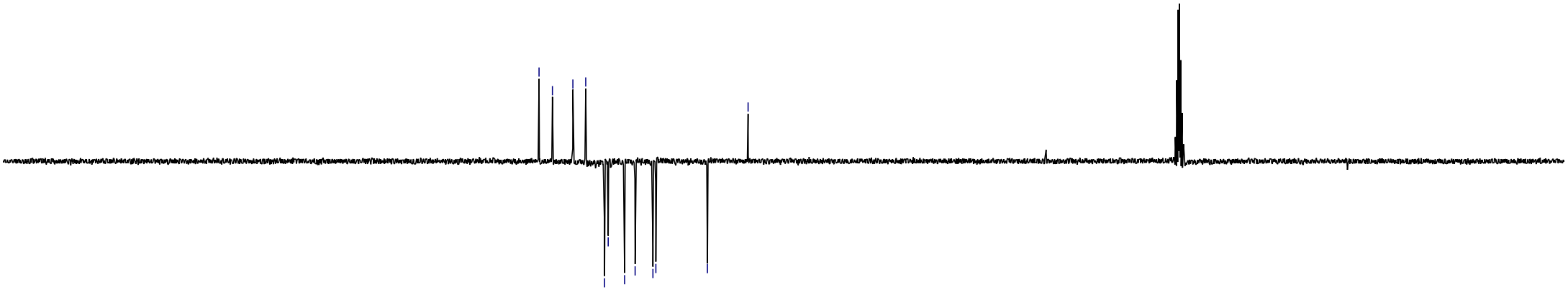
3n

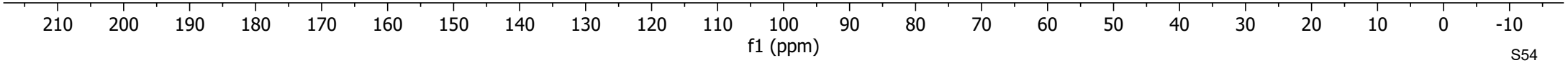
^{13}C NMR (101 MHz, DMSO)

137.06
135.03
131.93
129.98
127.13
126.58
124.09
122.50
119.80
119.35
111.54
105.38

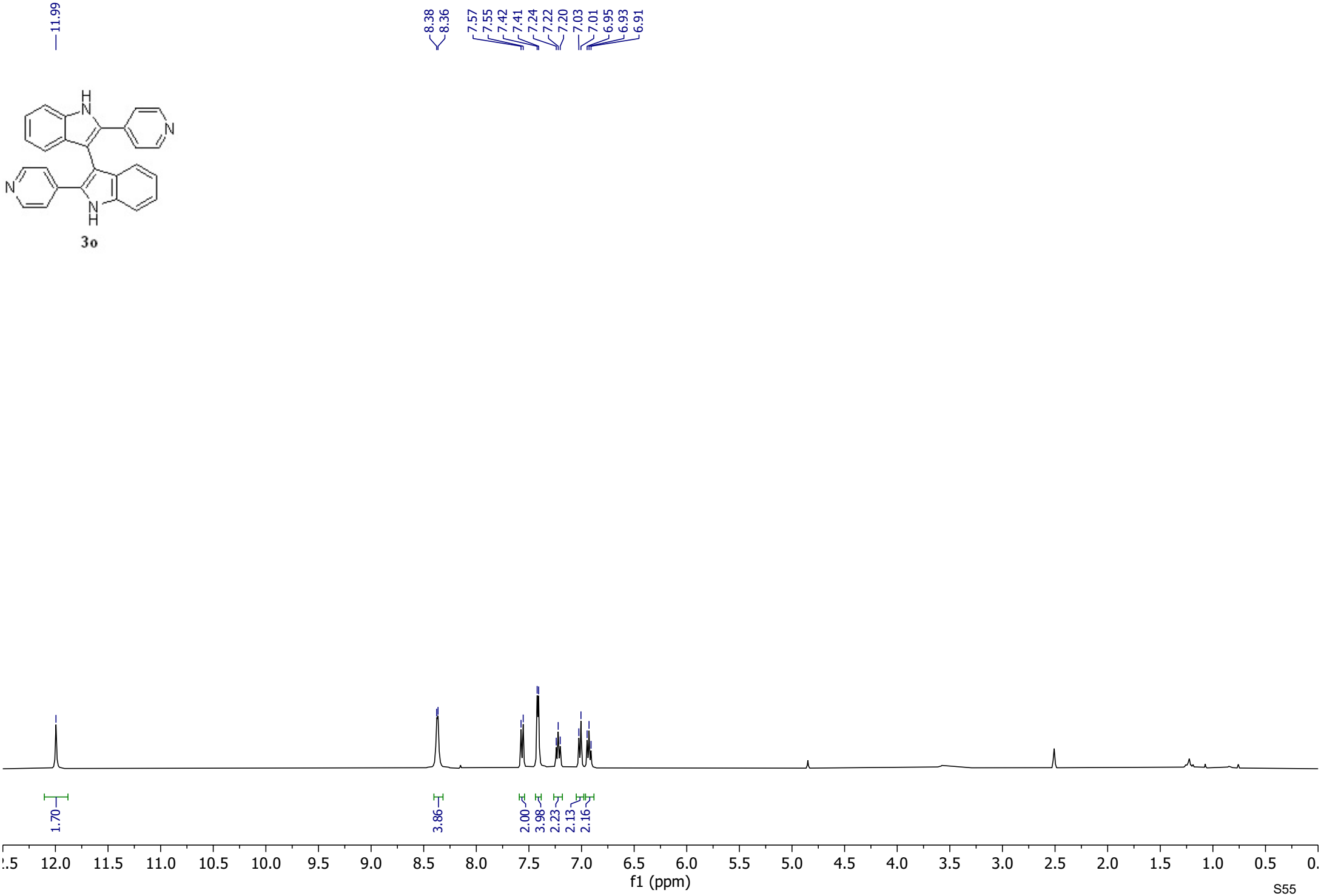


3n

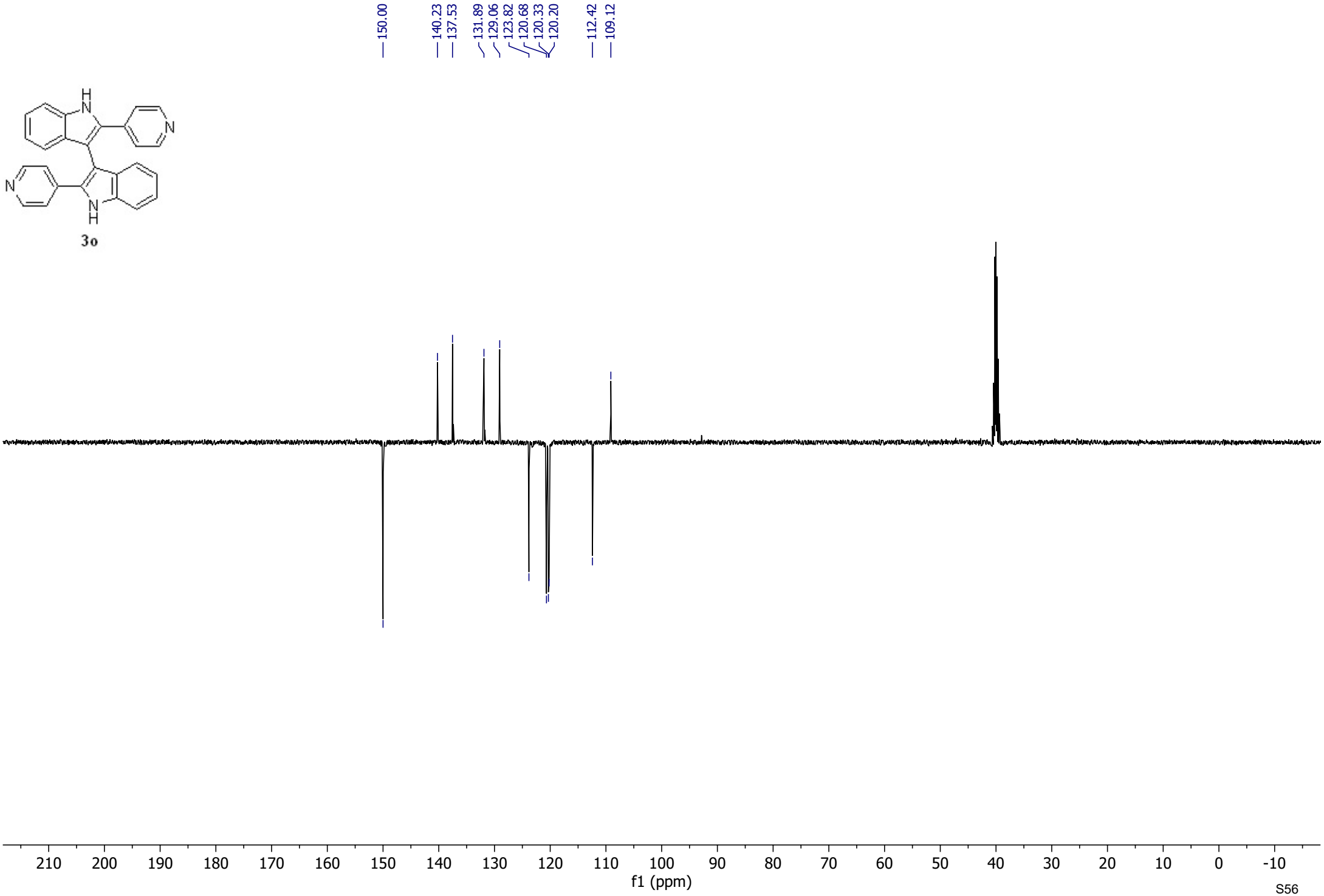




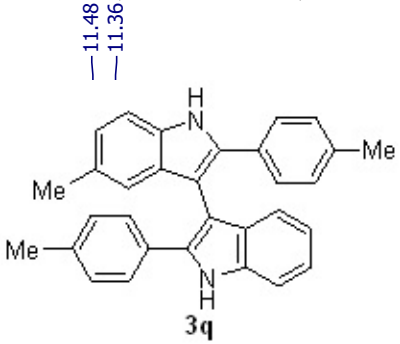
^{1}H NMR (400 MHz, DMSO)



^{3}C NMR (101 MHz, DMSO)

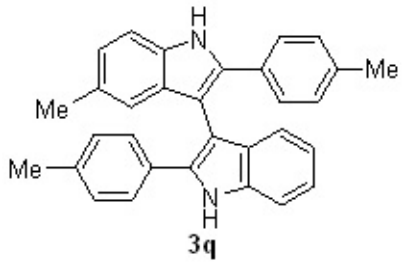


^{1}H NMR (300 MHz, DMSO)

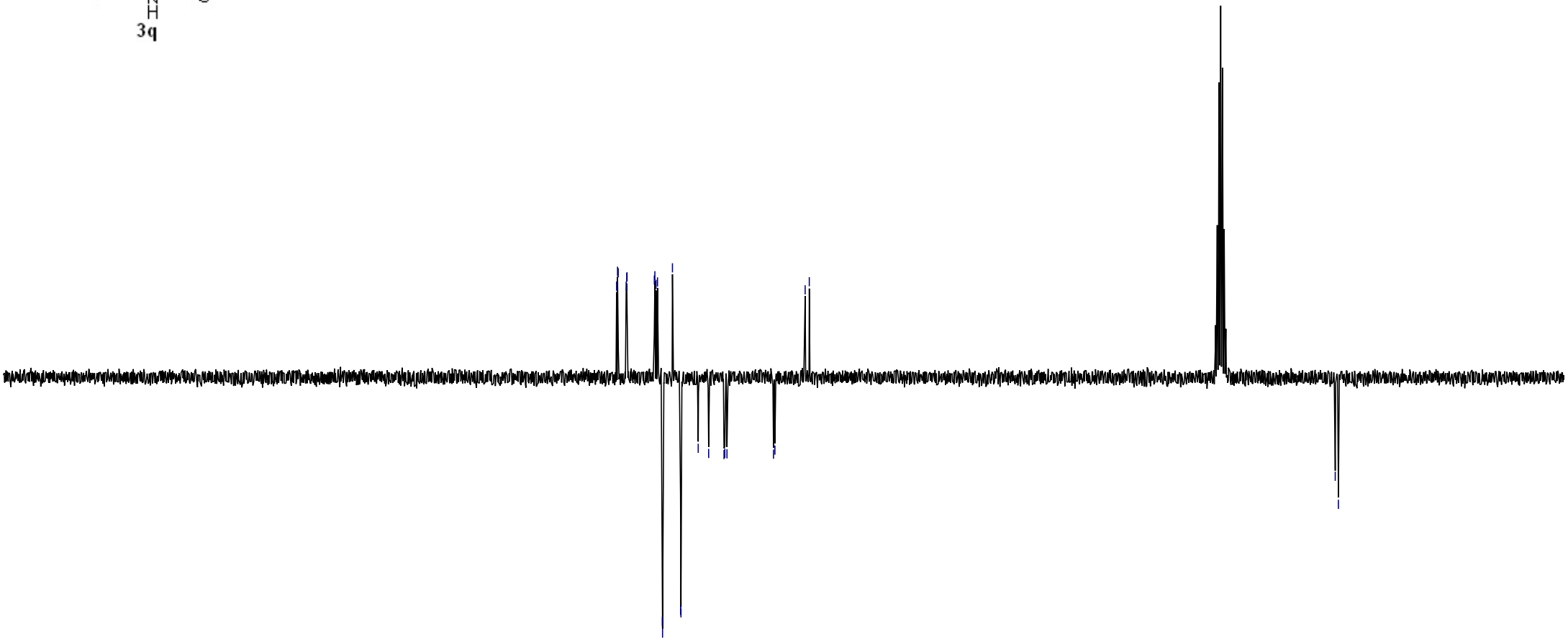


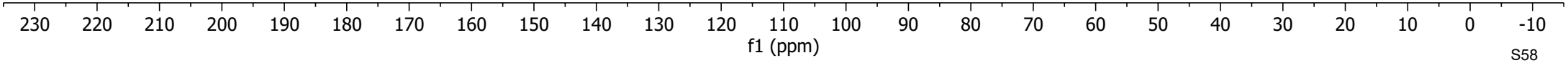
3q

^{13}C NMR (75 MHz, DMSO)

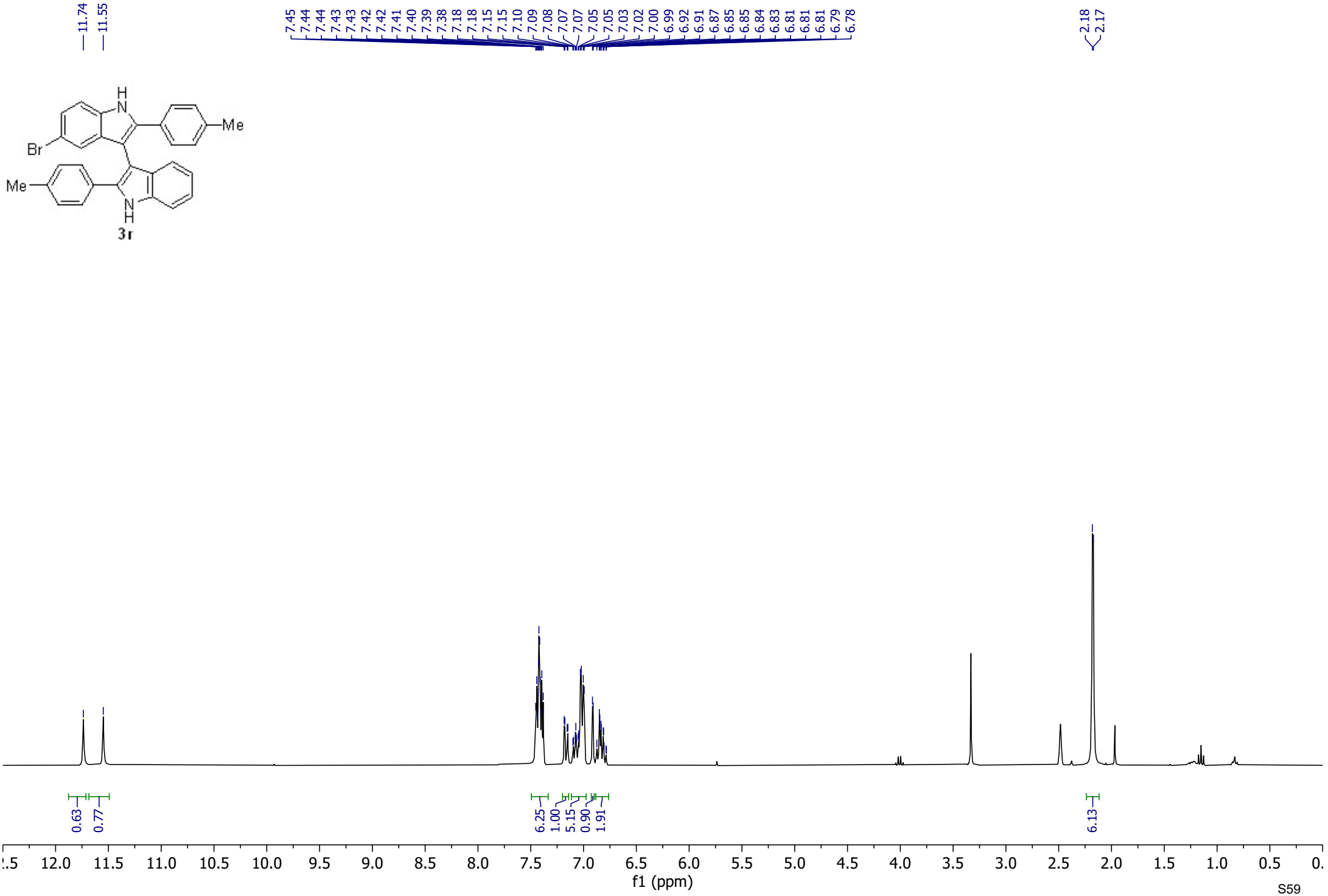


3q

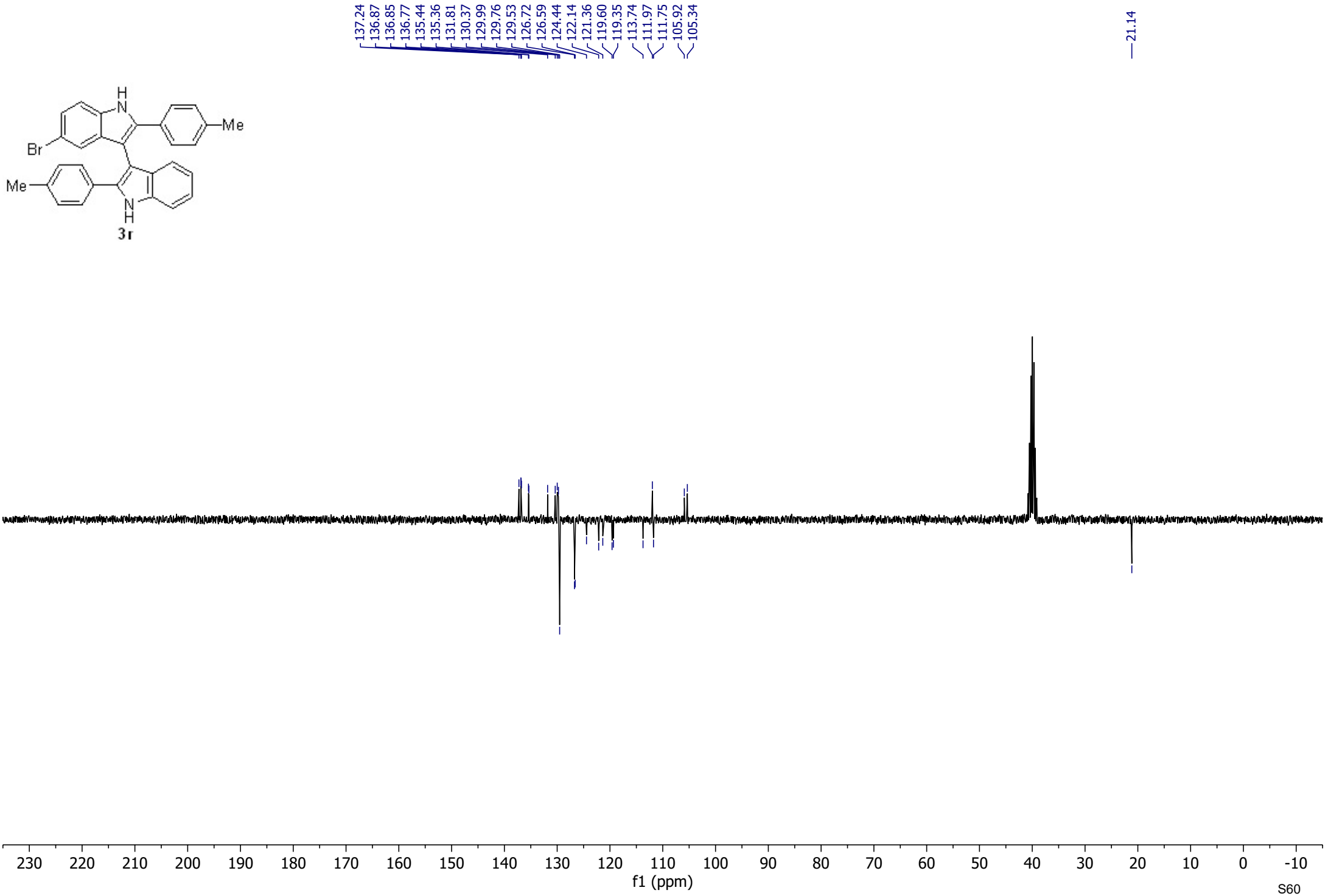




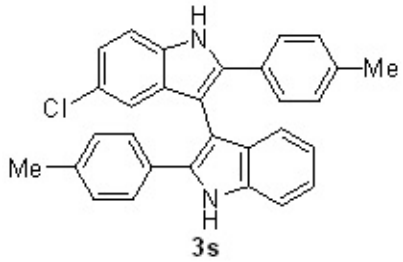
^{1}H NMR (300 MHz, DMSO)



^{13}C NMR (75 MHz, DMSO)

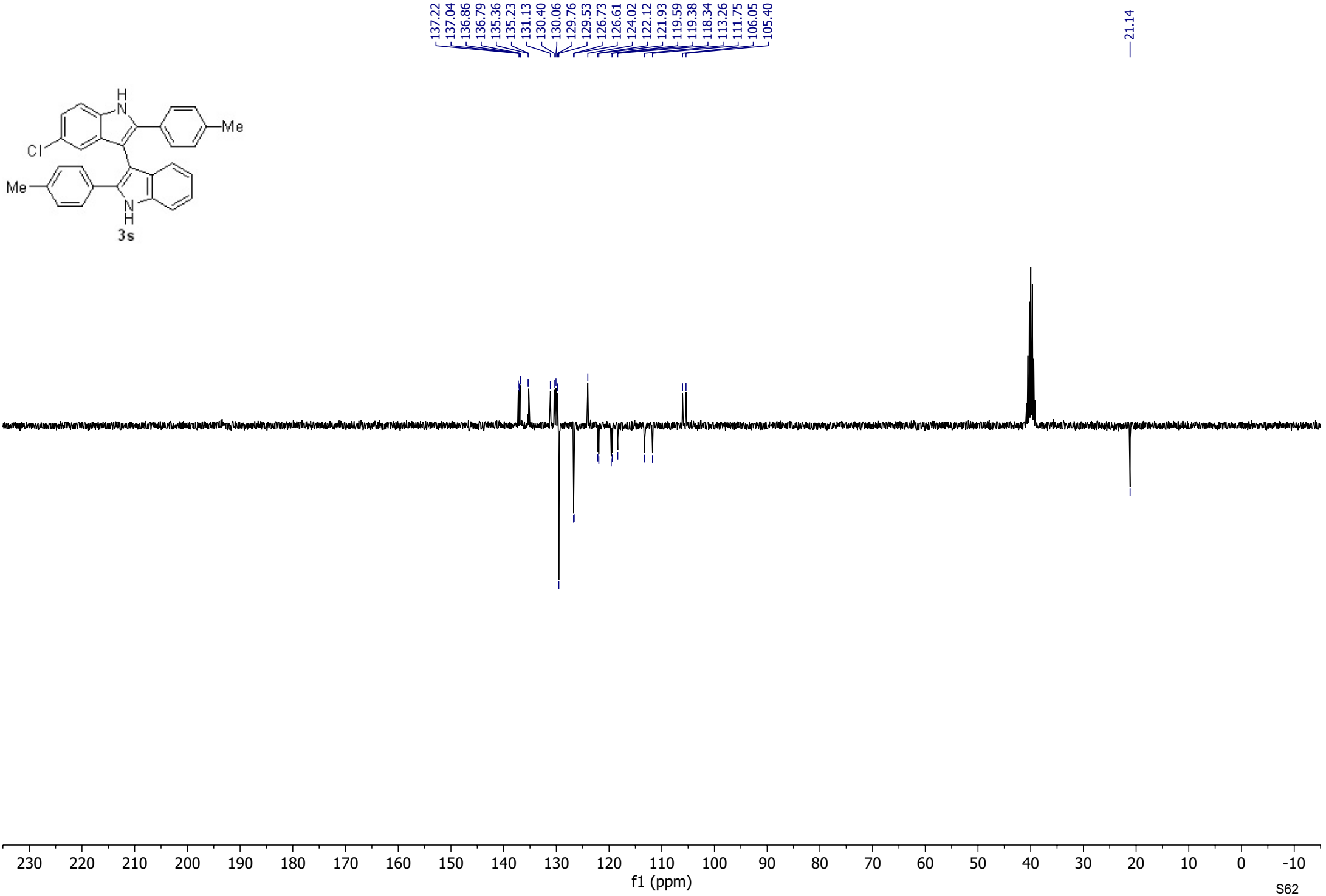


^{1}H NMR (300 MHz, DMSO)

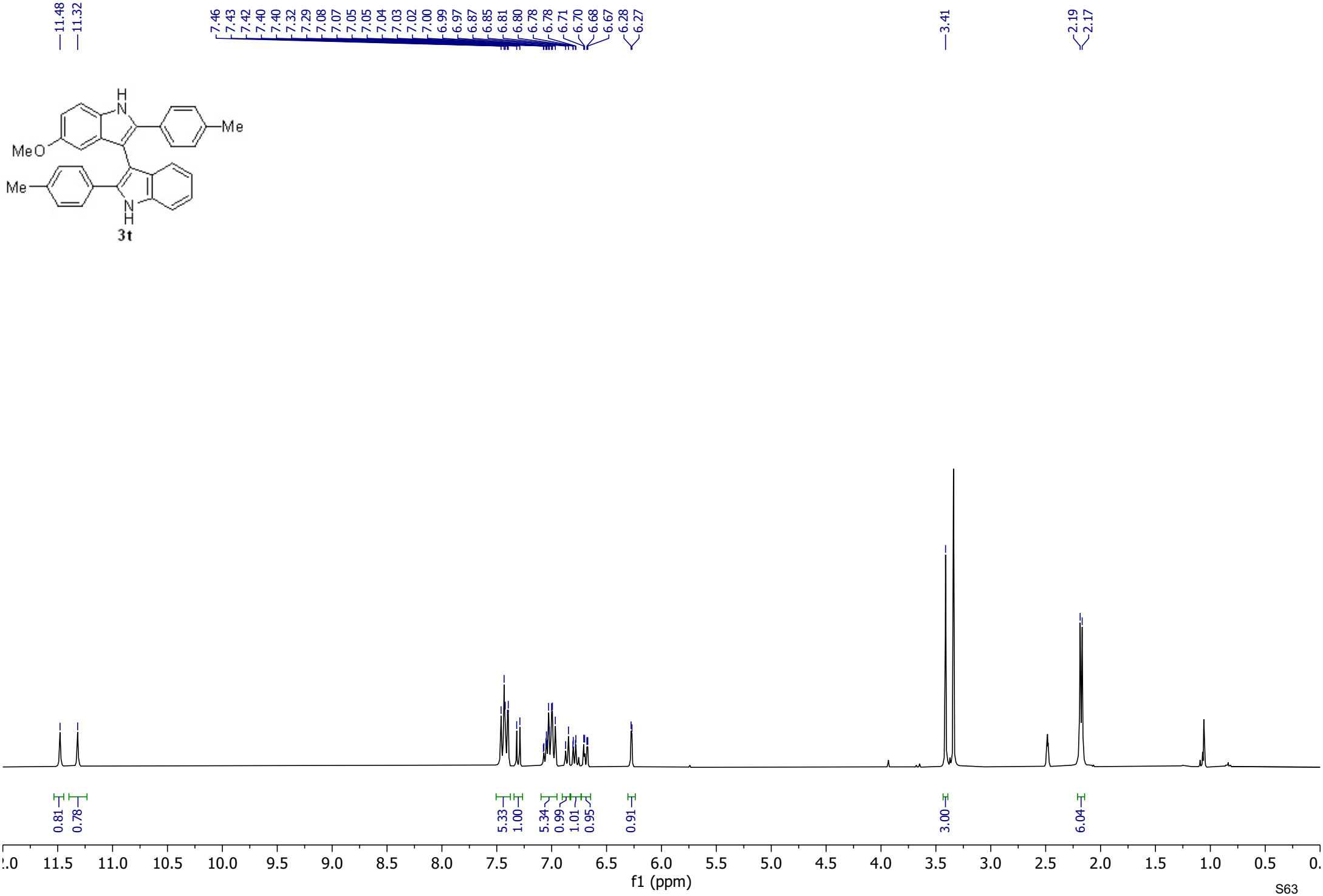


3s

^{13}C NMR (75 MHz, DMSO)

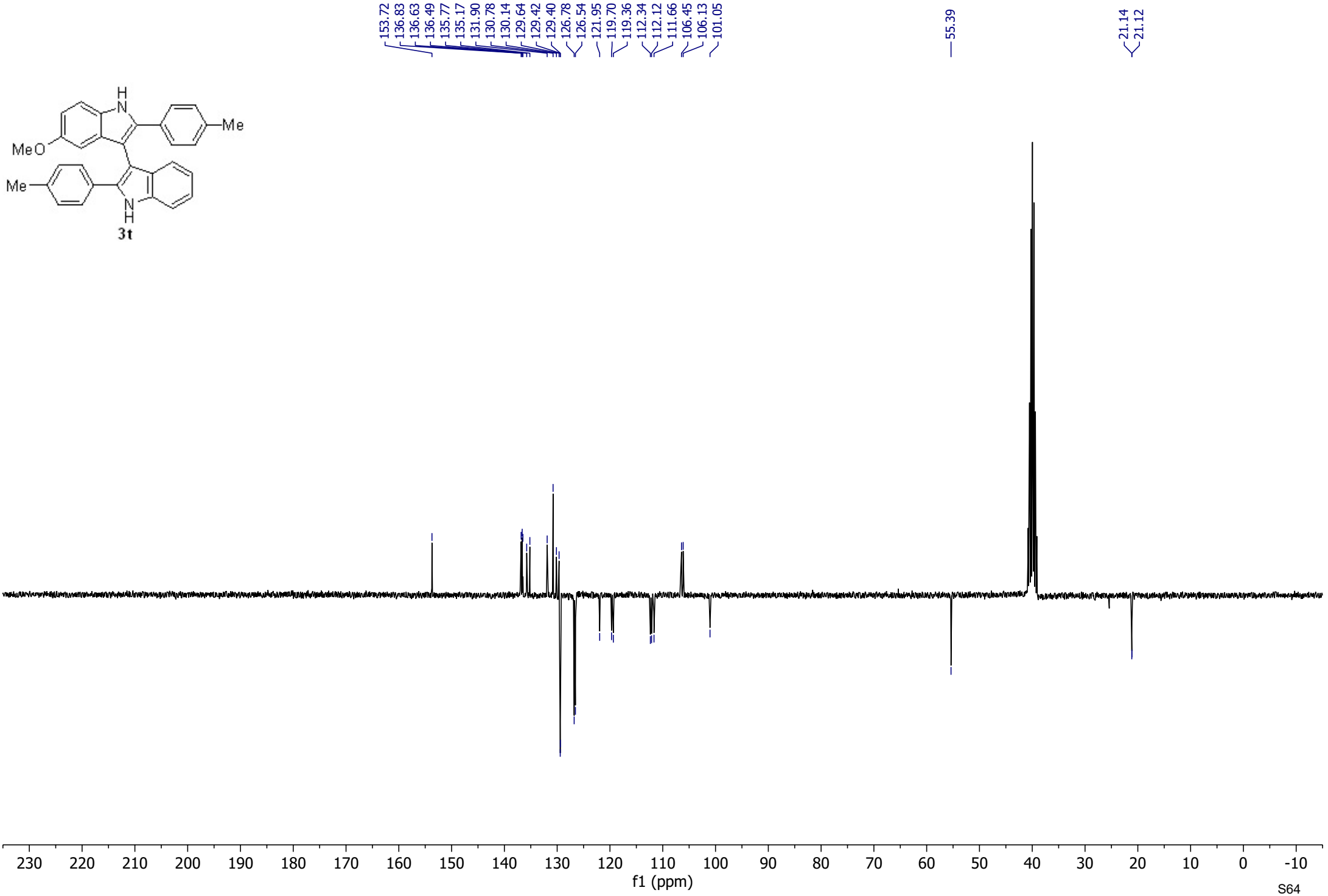


^{1}H NMR (300 MHz, DMSO)

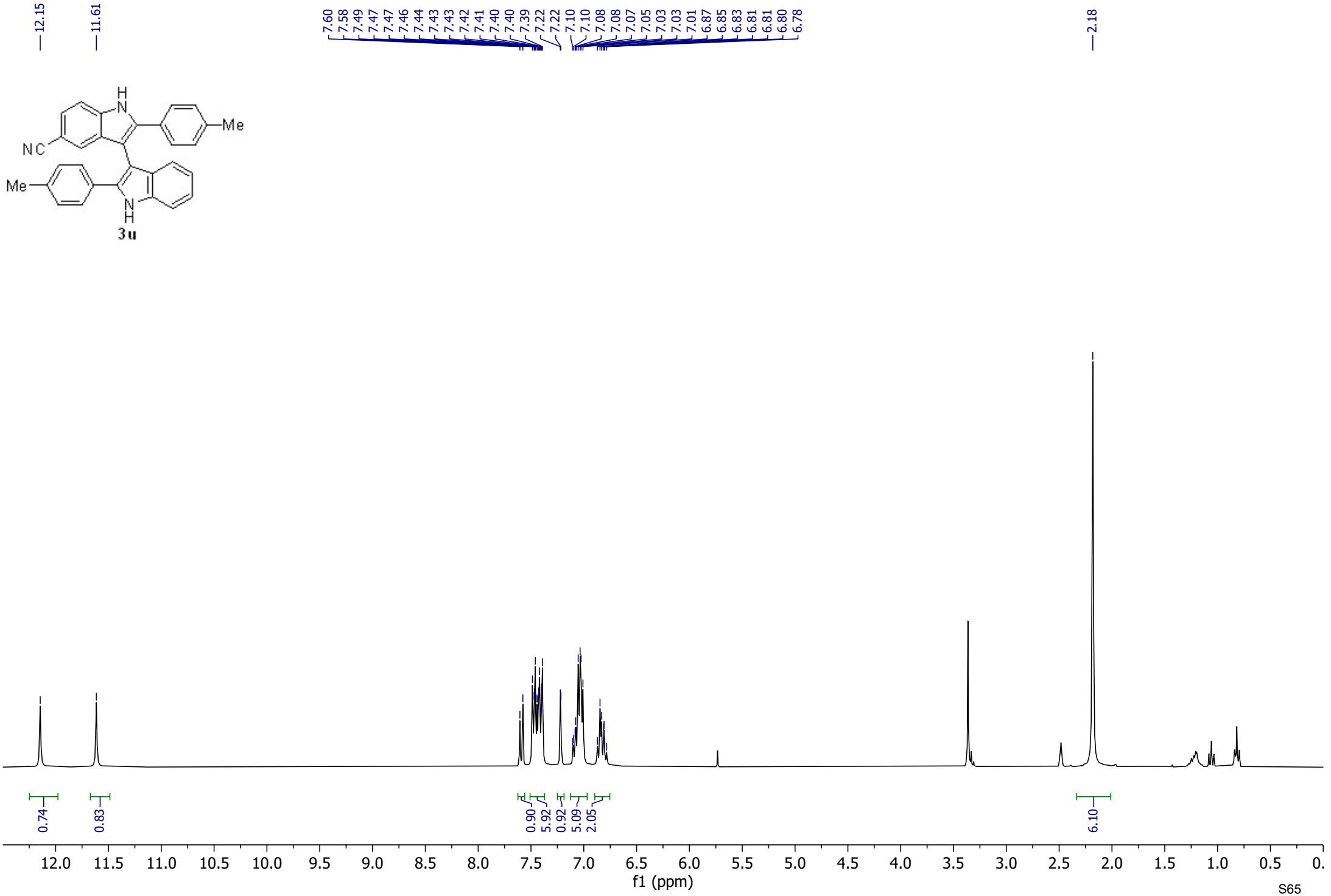


3t

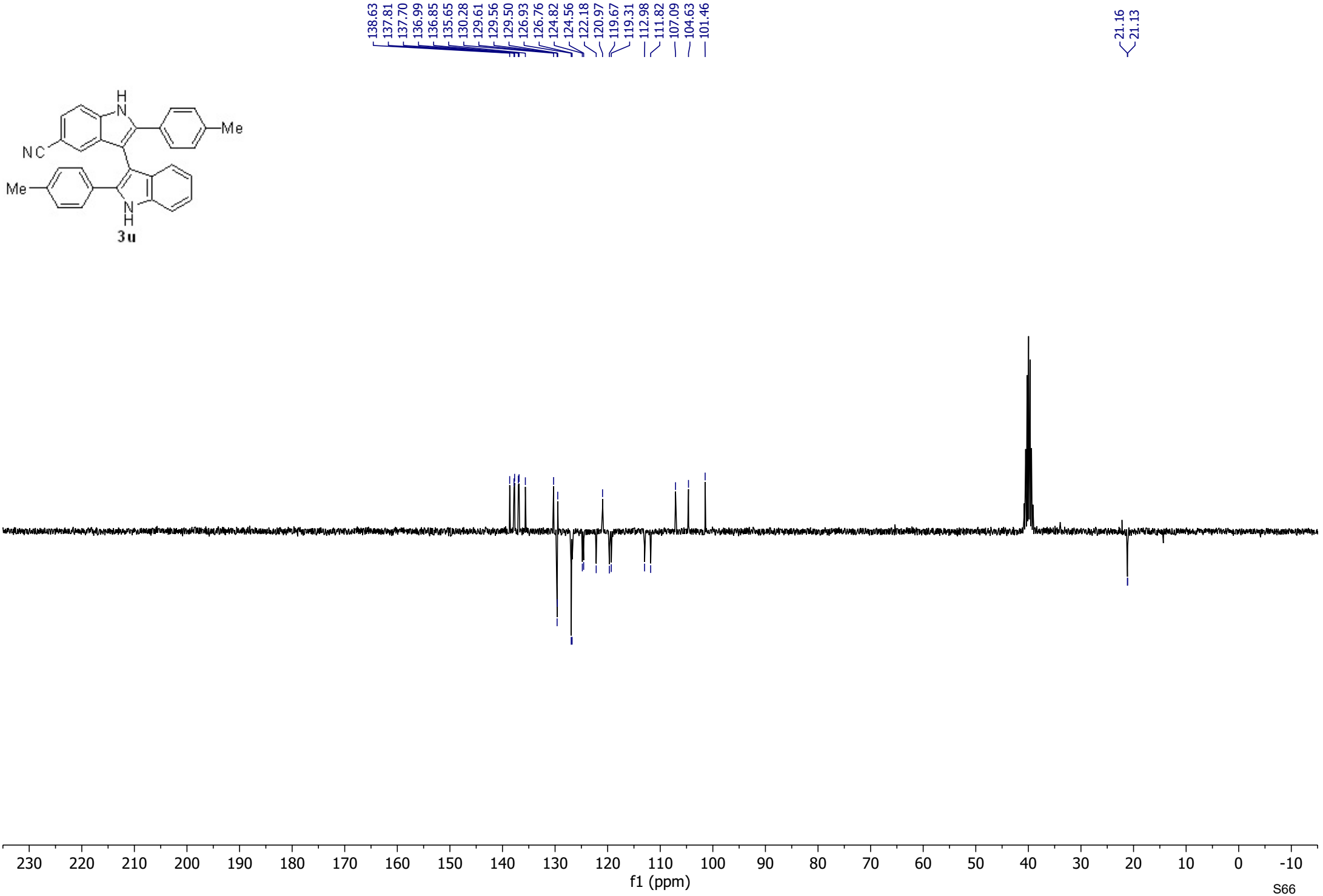
^{13}C NMR (75 MHz, DMSO)



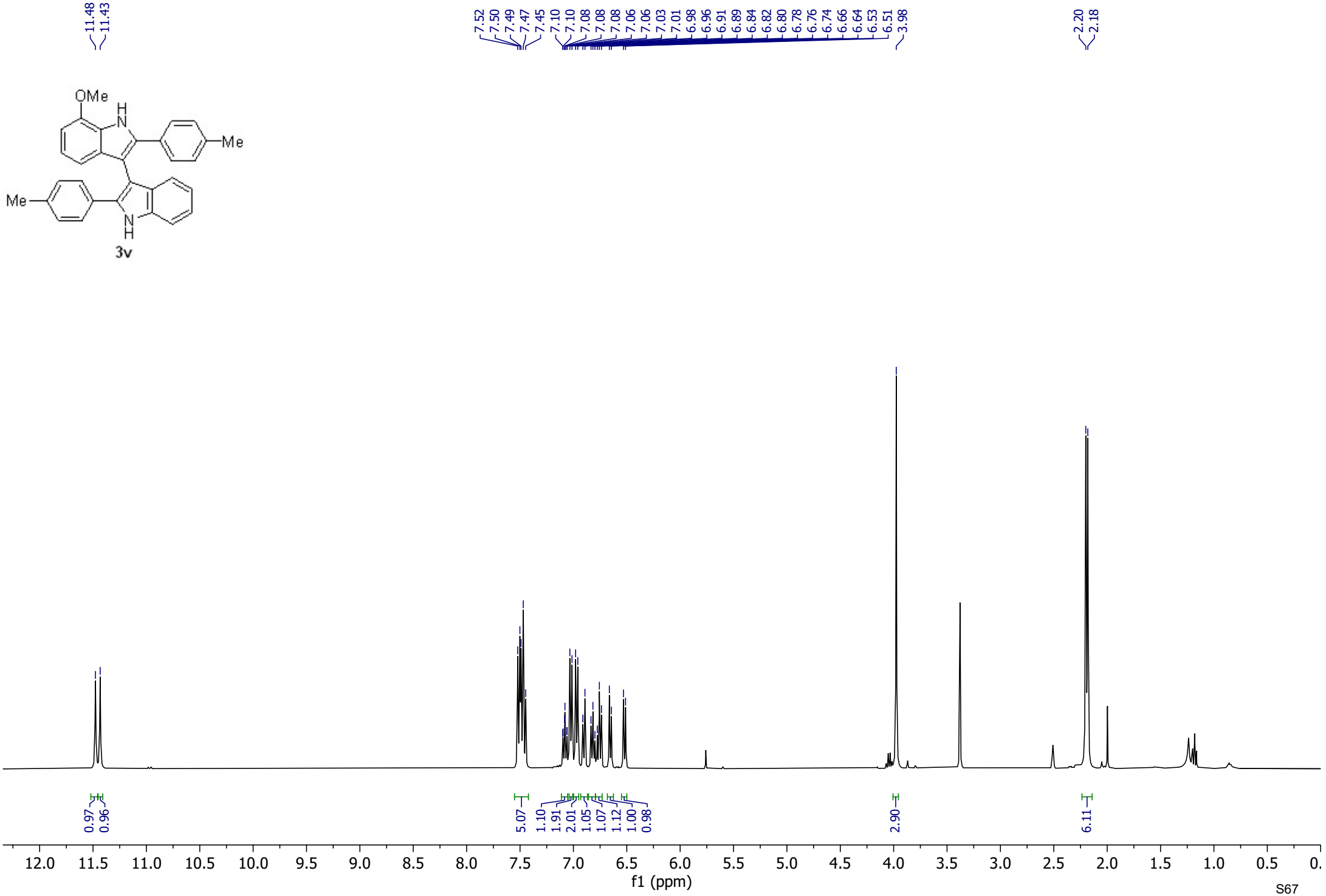
^{1}H NMR (300 MHz, DMSO)



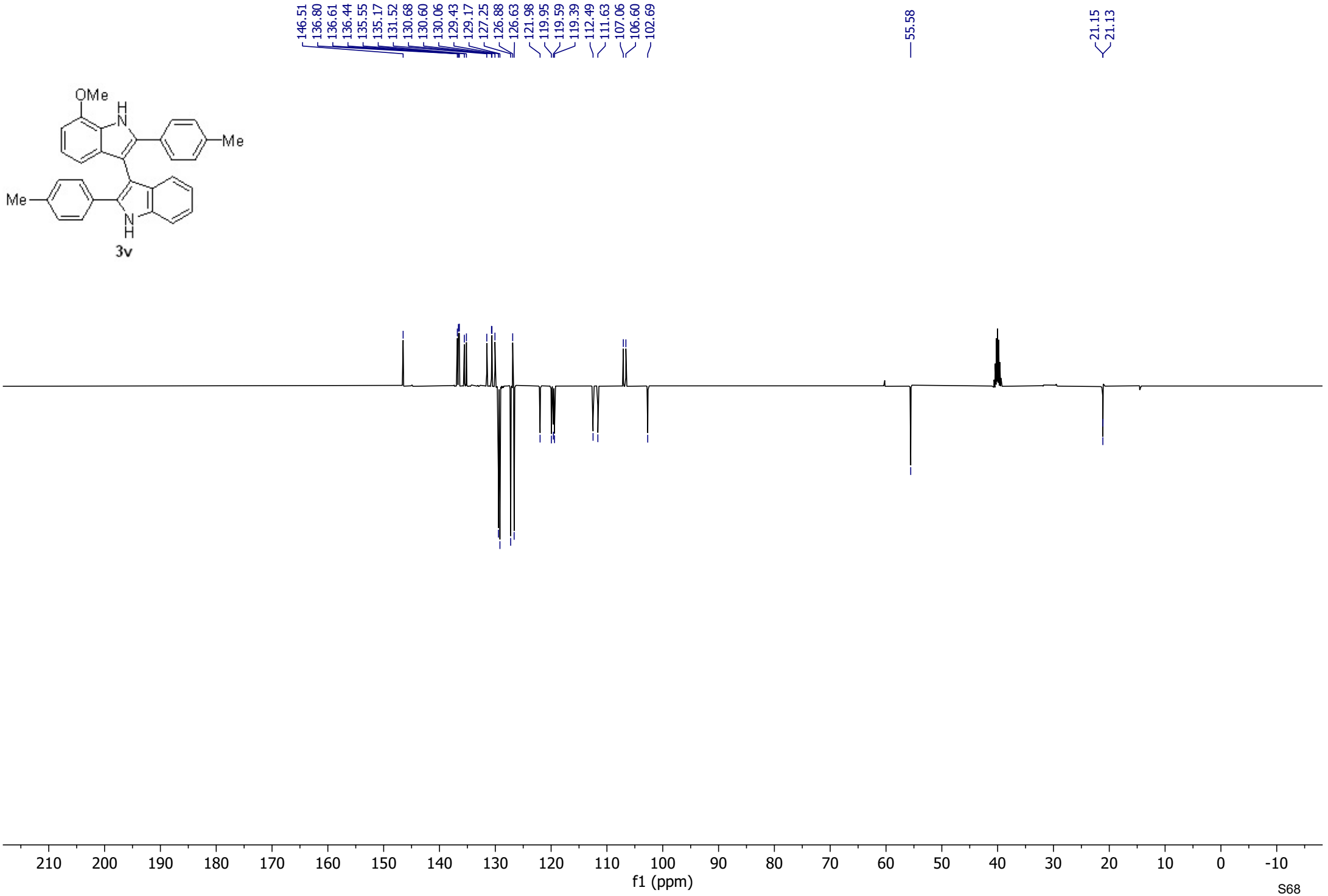
^{13}C NMR (75 MHz, DMSO)



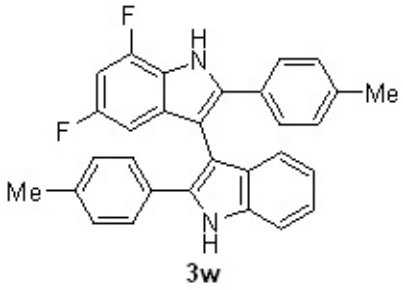
^{1}H NMR (400 MHz, DMSO)



^{13}C NMR (101 MHz, DMSO)

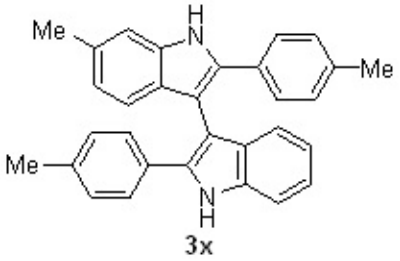


^{1}H NMR (300 MHz, Acetone)



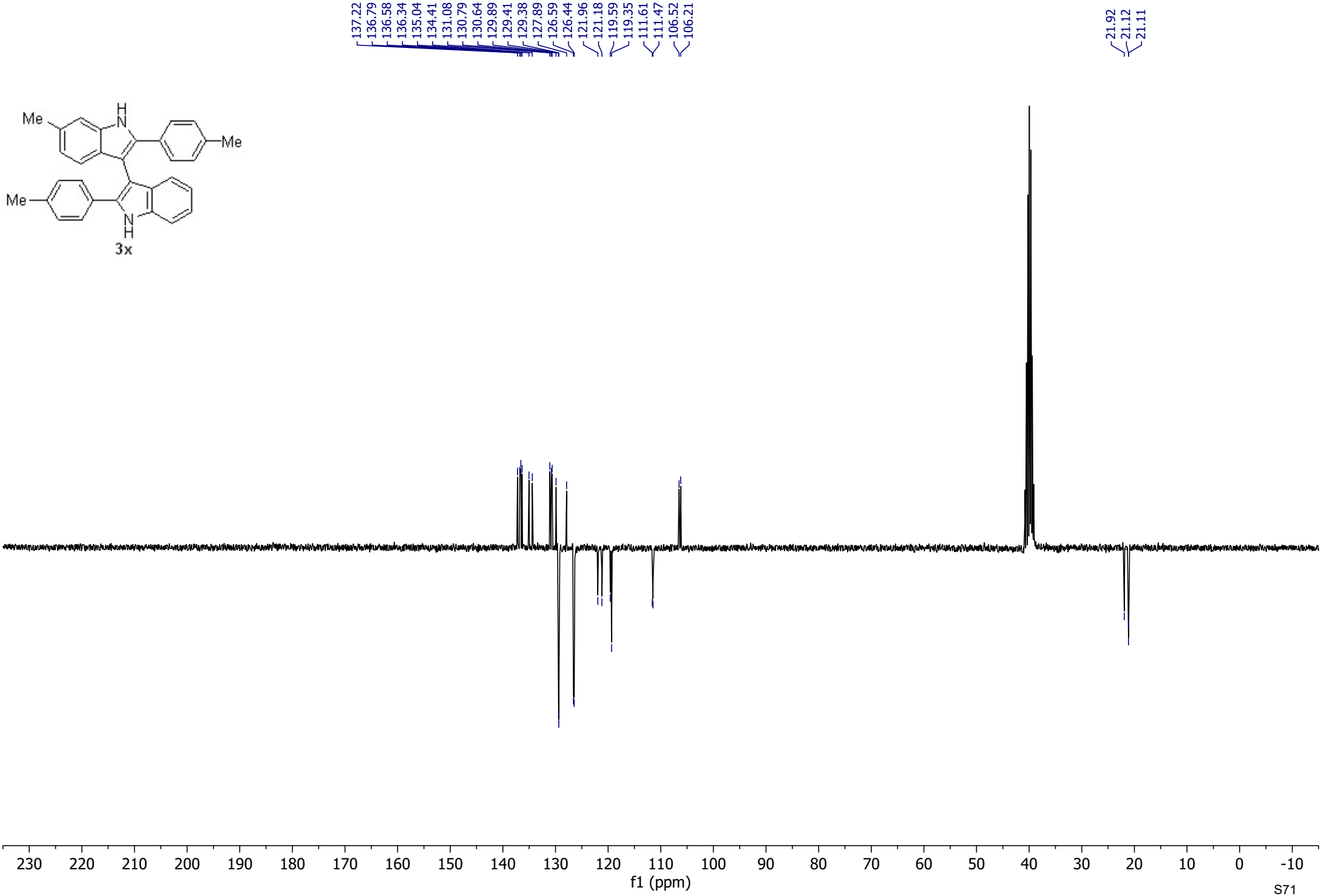
3w

^{1}H NMR (300 MHz, DMSO)

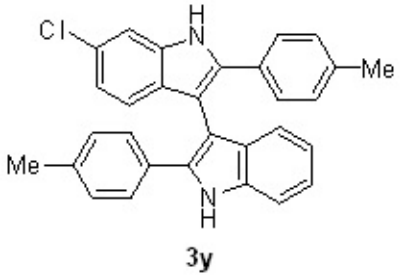


3x

^{13}C NMR (75 MHz, DMSO)

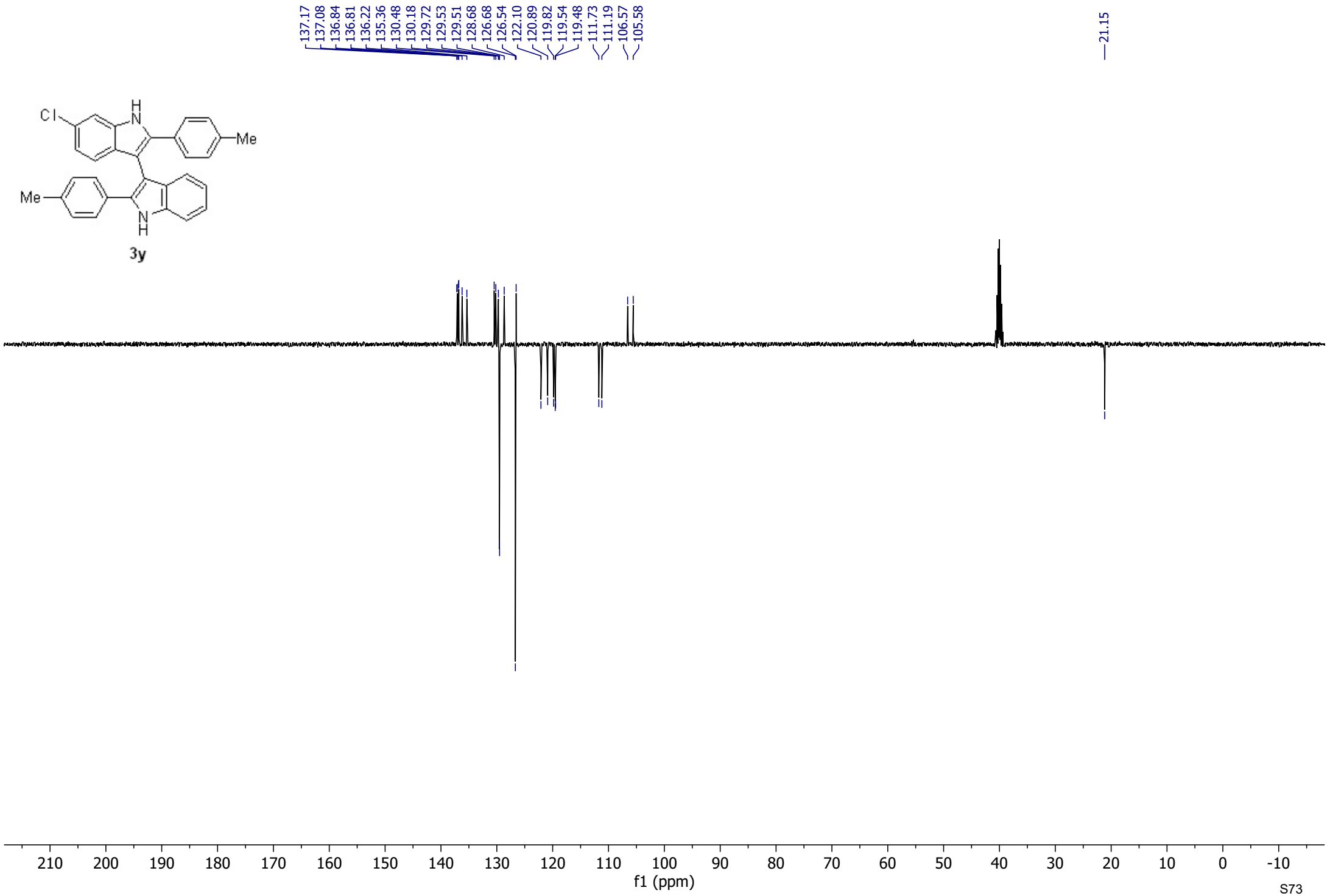


^{1}H NMR (400 MHz, DMSO)

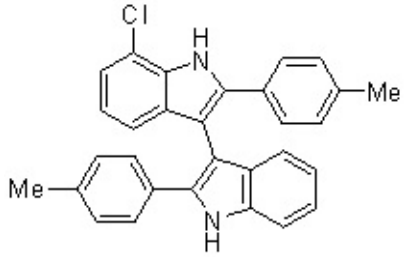


3y

^{13}C NMR (101 MHz, DMSO)



^{1}H NMR (400 MHz, DMSO)

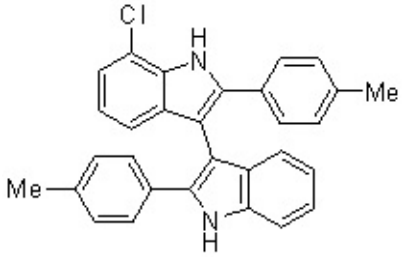


3z

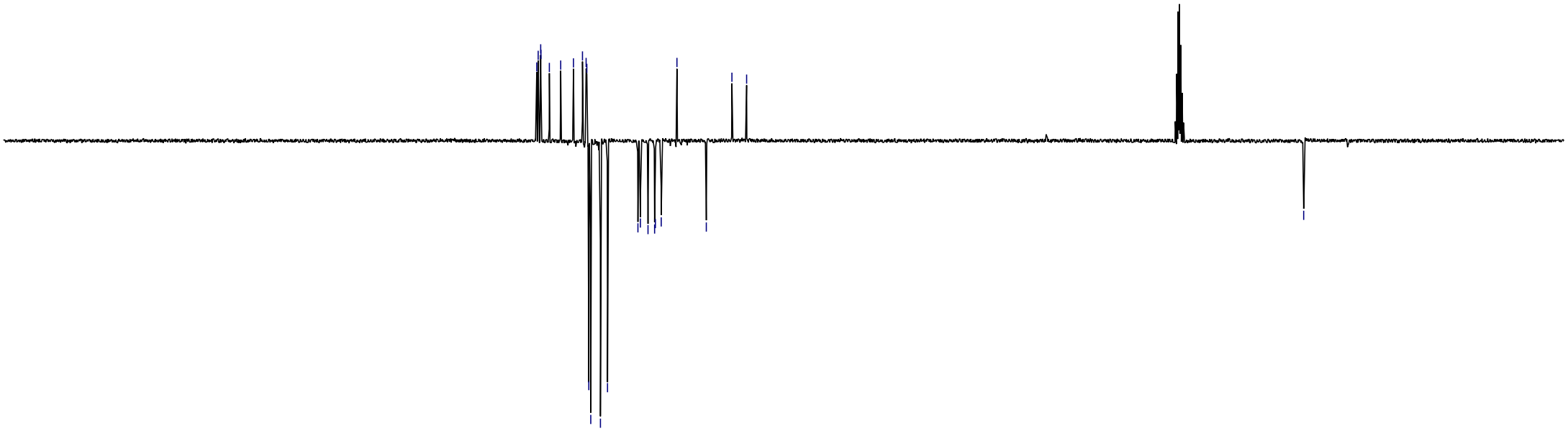
^{13}C NMR (101 MHz, DMSO)

137.41
137.19
136.81
136.77
135.49
133.77
131.84
130.48
129.92
129.81
129.52
129.22
127.75
126.68
122.07
121.70
120.55
119.55
119.43
118.54
116.16
111.71
107.83
105.60

21.19



3z



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f1 (ppm)