Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Electronic Supplementary Information

for

Gold Catalysed Regio- and Chemoselective Azo Coupling of 1,2- and 1,4-Diazoquinones with 1*H*-Indoles

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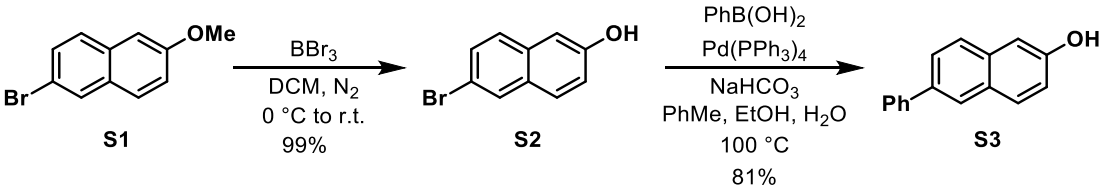
1. General information

Unless otherwise specified all gold(I) complexes, reagents, 1*H*-indoles (**2a, 2b**, **2d–g**, **2m**, **2n**, **2p**, **2w**), substrates (**S1**, **S4**, **S8**, **S10**, **S12–S14**, **S16–S18**, **S20**, **S22**, **S23**, **S27**) and solvents were purchased from commercial sources and used as received. Dichloromethane, toluene and tetrahydrofuran were dried and distilled following standard literature procedures and dimethyl sulfoxide was dried over 4 Å molecular sieves.[S1] Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel F_{254} plates. Visualisation was achieved by UV light (254 nm) and/or using a vanillin or potassium permanganate stain. Flash column chromatography was performed using silica gel (60 Å, 230–400 mesh) and a gradient solvent system (dichloromethane/ethyl acetate/60–80 °C petroleum ether as eluent). Melting points (m.p.) were measured in an open glass capillary using a melting point apparatus and are uncorrected. Unless otherwise stated, ^{1}H, ^{13}C, ^{19}F, and ^{31}P nuclear magnetic resonance (NMR) spectra were recorded on a 400 or 600 MHz NMR spectrometer at 298 K. All ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with ^{1}H-decoupling. Chemical shifts (ppm) are reported as follows: chemical shift (δ) in ppm (multiplicity, coupling constant, number of protons) using the residual deuterated solvent signal as the internal reference in ^{1}H NMR spectra ($CDCl_3$ = 7.26 ppm; CD_2Cl_2 = 5.32 ppm; DMSO-d_6 = 2.50 ppm; acetone-d_6 = 2.05 ppm; CD_3OD = 3.31 ppm) and ^{13}C NMR spectra ($CDCl_3$ = 77.16 ppm; CD_2Cl_2 = 53.84 ppm; DMSO-d_6 = 39.52 ppm; acetone-d_6 = 206.26 ppm; CD_3OD = 49.00 ppm). ^{19}F and ^{31}P NMR spectra were indirectly referenced relative to the solvent residual signal. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), sext (sextet), dd (doublet of doublets), dt (doublet of triplets), td (triplet of doublets), tsep (triplet of septets) or m (multiplet). Coupling constants (*J*) are reported in Hertz (Hz) and the number of protons (*n*) for a given resonance is indicated by *n*H. Infrared spectra were recorded on a FTIR spectrometer with ATR sampling module and selected absorption bands reported in wavenumbers (ν, cm^{-1}). High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI) and reported in units of mass to charge ratio (*m/z*). Diffraction data were collected on an X-ray diffractometer fitted with a hybrid photon counting detector, using CuKα radiation (λ = 1.54184 Å) with the data processed with CrysAlisPro and structures solved and refined by standard methods using the SHELX software suite.[S2]

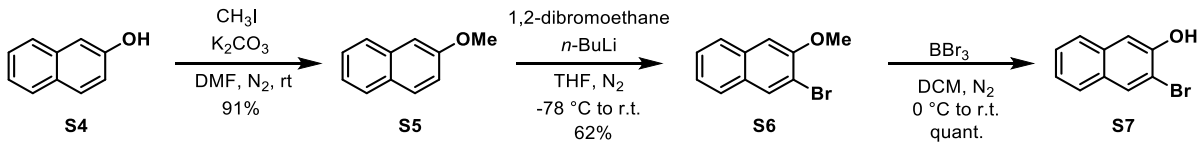
2. Experimental procedures

2.1. Procedures for the preparation of 2-naphthols S3, S7 and S9



6-Bromo-2-naphthol (S2).[S3,S4] To a round bottom flask equipped with a magnetic stirrer bar was added 2-bromo-6-methoxynaphthalene **S1** (500.0 mg, 2.10 mmol, 1.00 equiv.). Then three vacuum-refill cycles with nitrogen were carried out followed by the addition of dry dichloromethane (4.0 mL). The solution was cooled to 0 °C, and BBr_3 (2.1 mL, 1 M in dichloromethane, 2.10 mmol, 1.00 equiv.) was added. The reaction mixture was stirred vigorously at 0 °C for 2 h, and then additional BBr_3 (1.2 mL, 1 M in dichloromethane, 1.20 mmol, 0.57 equiv.) was added. The reaction mixture was allowed to warm to room temperature and stirred for a further 15 h. On completion, the reaction mixture was quenched by addition of ice (50 g), diluted with dichloromethane (50 mL) and the aqueous phase was extracted with dichloromethane (2 × 20 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give **S2** as a grey solid (470.0 mg, 99%) which was used in the next step without further purification; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.91 (s, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.77–7.71 (m, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.47 (dd, J = 8.8, 2.1 Hz, 1H), 7.17–7.11 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 155.8, 133.2, 129.3, 128.9, 128.9, 128.7, 128.3, 119.8, 115.2, 108.8.

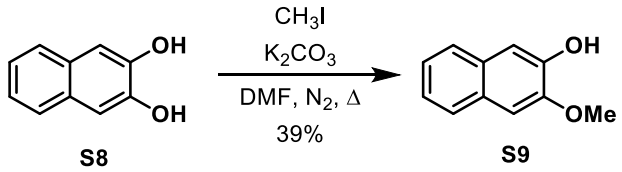
6-Phenyl-2-naphthol (S3).[S5,S6] To a two-neck round bottom flask equipped with a magnetic stirrer bar and reflux condenser was added 6-bromo-2-naphthol **S2** (300.0 mg, 1.34 mmol, 1.00 equiv.) and $Pd(PPh_3)_4$ (77.7 mg, 67.00 µmol, 5 mol %). Three vacuum-refill cycles with nitrogen were carried out. Then, toluene (15.0 mL), a solution of sodium bicarbonate (338.0 mg, 4.02 mmol, 3.00 equiv.) in water (4.0 mL) and a solution of phenyl boronic acid (213.0 mg, 1.75 mmol, 1.30 equiv.) in ethanol (4.5 mL) were added sequentially. The reaction mixture was stirred vigorously for 10 min at room temperature, then heated to 100 °C for 24 h. On cooling to room temperature, the reaction mixture was quenched by addition of water (20 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5) to give **S3** as a light-yellow solid (243.0 mg, 81%); ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 8.71 (s, 1H), 8.07 (s, 1H), 7.87 (d, J = 8.8 Hz, 1H), 7.82–7.68 (m, 4H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 2.4 Hz, 1H), 7.19 (dd, J = 8.8, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 156.7, 142.2, 136.5, 135.4, 131.0, 129.9, 129.9, 128.0, 127.9, 127.9, 126.6, 126.5, 119.9, 109.8.



2-Methoxynaphthalene (S5).[S7] To a two-neck round bottom flask equipped with a magnetic stirrer bar was added 2-naphthol **S4** (8.65 g, 60.00 mmol, 1.00 equiv.) and K_2CO_3 (12.44 g, 90.00 mmol, 1.50 equiv.). Three vacuum-refill cycles with nitrogen were carried out. Then, dry dimethylformamide (60.0 mL) was added, followed by the dropwise addition of iodomethane (5.7 mL, 90.00 mmol, 1.50 equiv.). The reaction mixture was stirred vigorously at room temperature for 24 h. Upon completion the reaction mixture was quenched by addition of a saturated aqueous ammonium chloride solution (100 mL) and stirred for a further 30 min, then extracted with a mixture of diethyl ether/hexane (3 × 100 mL, 2:1 v/v). The combined organic phase was washed with brine (3 × 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give **S5** as a pale beige powder (9.36 g, 98%) which was used in the next step without further purification; ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 7.86–7.74 (m, 3H), 7.44 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.33 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.29 (d, J = 2.6 Hz, 1H), 7.14 (dd, J = 9.0, 2.5 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 158.7, 135.8, 130.1, 129.9, 128.4, 127.6, 127.2, 124.4, 119.5, 106.6, 55.6.

3-Bromo-2-methoxynaphthalene (S6).[S8] To a round bottom flask equipped with a magnetic stirrer bar was added 2-methoxynaphthalene **S5** (6.33 g, 40.00 mmol, 1.00 equiv.). Then, three vacuum-refill cycles with nitrogen were carried out followed by the addition of dry tetrahydrofuran (48.0 mL). The solution was cooled to –78 °C, and *n*-BuLi (17.0 mL, 2.5 M in hexanes, 42.50 mmol, 1.06 equiv.) was added dropwise. The resulting solution was allowed to warm to room temperature and stirred for a further 2 h. On cooling again to –78 °C, 1,2-dibromoethane (3.9 mL, 44.00 mmol, 1.10 equiv.) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred vigorously overnight (*ca.* 14 h), and then quenched by addition of a saturated aqueous ammonium chloride solution (100 mL) and extracted with diethyl ether (3 × 100 mL). The combined organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by recrystallisation from *n*-hexane (twice) to give **S6** as a white solid (5.88 g, 62%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.06 (s, 1H), 7.73 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.1 Hz, 1H), 7.46 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.36 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.16 (s, 1H), 4.01 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 153.7, 133.7, 132.4, 129.6, 126.9, 126.8, 126.7, 124.6, 113.5, 106.8, 56.4.

3-Bromo-2-naphthol (S7).[S8] Prepared following the procedure for the synthesis of compound **S2** with 3-bromo-2-methoxynaphthalene **S6** (14.76 mmol scale). The compound **S7** was obtained as a grey solid (3.29 g, quant.) which was used in the next step without further purification; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 1H), 7.69 (m, 2H), 7.46 (ddd, J = 8.2, 6.8, 1.2 Hz, 1H), 7.40 (s, 1H), 7.36 (ddd, J = 8.2, 6.8, 1.1 Hz, 1H), 5.68 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 149.5, 134.1, 131.3, 129.6, 127.0, 126.9, 126.7, 124.6, 112.6, 110.8.

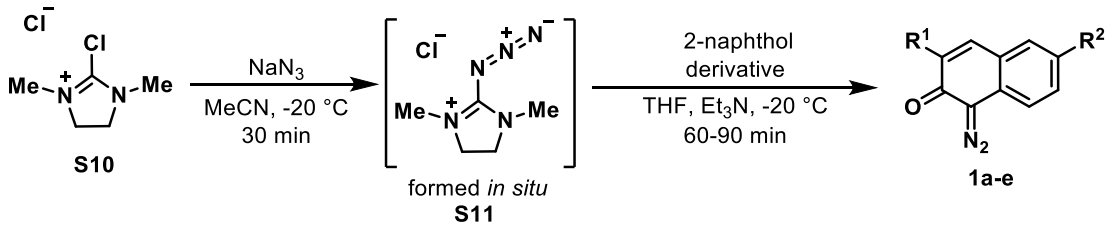


S8 **S9**

3-Methoxynaphthalen-2-ol (S9).[S9] To a round bottom flask equipped with a magnetic stirrer bar were added 2,3-dihydroxynapthalene **S8** (1.00 g, 6.26 mmol, 1.00 equiv.) and K_2CO_3 (1.81 g, 13.12 mmol, 2.10 equiv.). Three vacuum-refill cycles with nitrogen were carried out. Then, dry dimethylformamide (20.0 mL) was added and the heterogeneous mixture was heated to 100 °C for 30 min. The reaction mixture was allowed to cool to room temperature, then iodomethane (0.4 mL, 6.26 mmol, 1.00 equiv.) was added dropwise and the reaction mixture was stirred for a further 20 h. Upon completion, the reaction mixture was quenched by addition of water (100 mL) and extracted with diethyl ether (3 × 40 mL). The combined organic phase was washed with water (100 mL), brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:0 to 95:5).

At this stage, a mixture of mono- and dialkylated compounds was obtained. Therefore, the following purification method was carried out: To the residue, a solution of KOH (6.40 g) in water (15.0 mL) was added and the mixture stirred until no further dissolution was observed. The aqueous phase was washed with diethyl ether (2 × 15 mL) to remove the dialkylated side-product, then a solution of HCl (6 M) was added dropwise until precipitation of a solid was observed (pH < 7). The aqueous phase was then extracted with diethyl ether (3 × 15 mL). The combined organic phase was washed with water (3 × 20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give **S9** as a light orange solid (424.0 mg, 39%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63–7.55 (m, 2H), 7.28–7.20 (m, 2H), 7.18 (s, 1H), 7.04 (s, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 147.5, 145.8, 129.8, 129.1, 126.6, 126.5, 124.5, 124.0, 109.5, 105.9, 56.0.

2.2. General procedure for the preparation of 1,2-diazonaphthoquinones 1a–e[S10,S11]

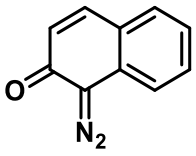


Caution 1: *Although no incidients were experienced in handling azidoimidazolinium salt* ***S10****, it is potentially explosive. Therefore, precaution should be taken in preparation. Synthesis was typically carried out between 1-2 mmol scale. In the case of the 2-diazonaphthalen-1(2H)-one (****1a****), a 9 mmol scale reaction could be carried out safely.*

Caution 2: *Diazonaphthoquinones (****1****) are also potentially explosive. Many of these compounds are sensitive to heat, light, shock, and metal catalysts. Therefore, precaution should be taken in preparation, storage (in the dark, under 5* °C*) and use.*

To a round bottom flask equipped with a magnetic stirrer bar was added 2-chloro-1,3-dimethylimidazolinium chloride **S10** (1.50 equiv.) and acetonitrile (2.0 mL/mmol of naphthol derivative). The solution was cooled to –20 °C, then sodium azide (1.67 equiv.) and 15-crown-5 ether (0.33 equiv.) were added sequentially. The reaction mixture was stirred for 30 min, after which a solution containing naphthol (1.00 equiv.) and triethylamine (2.00 equiv.) in tetrahydrofuran (4.0 mL/mmol of naphthol derivative) was added dropwise. The reaction progress was monitored by TLC (0.5–2 h). On completion, the reaction mixture was quenched with water (20 mL for up to 2 mmol scale) and extracted with dichloromethane (3 × 30 mL). The combined organic phase was washed with water (20 mL), brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to furnish the title compound. All diazoquinones **1a–e** were obtained as solids, and stored in the dark under anhydrous conditions at 5 ºC.

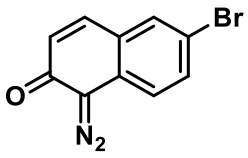
1-Diazonaphthalen-2(1*H*)-one (1a).[S11]



1a

Prepared following the general procedure with 2-naphthol **S4** (1.25 mmol scale). Reaction time: 0.5 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) to give **1a** as a brown solid (170.2 mg, 80%); ^{1}H NMR (600 MHz, CD_3OD) δ (ppm): 7.80 (d, J = 9.7 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.56 (ddd, J = 8.3, 7.3, 1.3 Hz, 1H), 7.46–7.43 (m, 1H), 7.32–7.28 (m, 1H), 6.60 (d, J = 9.7 Hz, 1H); ^{13}C NMR (151 MHz, CD_3OD) δ (ppm): 182.1, 142.5, 131.2, 131.2, 128.4, 126.8, 126.0, 125.8, 121.2, 79.8.

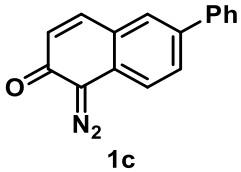
6-Bromo-1-diazonaphthalen-2(1*H*)-one (1b).[S11]



1b

Prepared following the general procedure using 6-bromo-2-naphthol **S2** (1.00 mmol scale). Reaction time: 1 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) to give **1b** as a green-brown solid (189.4 mg, 76%); ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 7.91 (d, J = 2.1 Hz, 1H), 7.79 (d, J = 9.8 Hz, 1H), 7.69 (dd, J = 8.6, 2.1 Hz, 1H), 7.52 (d, J = 8.6 Hz, 1H), 6.62 (d, J = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm):179.4, 139.6, 133.1, 132.9, 127.9, 127.6, 123.3, 117.7.

1-Diazo-6-phenylnaphthalen-2(1*H*)-one (1c).

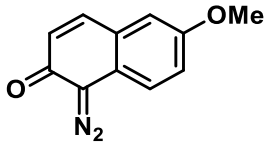


1c

Prepared following the general procedure with 6-phenyl-2-naphthol **S3** (1.06 mmol scale). Reaction time: 1.5 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 70:30) to give **1c** as a light brown solid (198.7 mg, 76%); ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 8.02 (d, J = 2.0 Hz, 1H), 7.90 (d, J = 9.7 Hz, 1H), 7.88 (dd, J = 8.3, 2.0 Hz, 1H), 7.76–7.71 (m, 2H), 7.63 (d, J = 8.3 Hz, 1H), 7.52–7.46 (m, 2H), 7.42–7.36 (m, 1H), 6.61 (d, J = 9.7 Hz, 1H); ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 180.0, 141.1, 140.7, 138.1, 129.9, 129.2, 128.9, 128.4, 127.6,

127.3, 126.9, 126.7, 122.1; IR (ATR, neat, ν, cm^{-1}): 2092 (ν_{as}, C=N=N), 1626, 1289, 1250, 1188, 1152, 829, 762, 696; HRMS (ESI–TOF) calcd. for $C_{16}H_{11}N_2O$ $[M+H]^+$: 247.0866, found 247.0891.

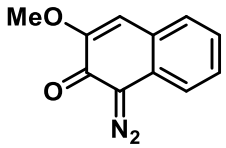
1-Diazo-6-methoxynaphthalen-2(1*H*)-one (1d).[S12]



1d

Prepared following the general procedure with 6-methoxy-2-naphthol **S12** (1.25 mmol scale). Reaction time: 1.5 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:20 to 70:30) to give **1d** as a black solid (113.3 mg, 45%); ^{1}H NMR (400 MHz, acetone-d_6) δ(ppm): 7.73 (d, J = 9.8 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.28 (d, J = 2.6 Hz, 1H), 7.18 (dd, J = 8.7, 2.6 Hz, 1H), 6.54 (d, J = 9.8 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ(ppm): 180.3, 158.0, 140.6, 127.5, 126.6, 122.7, 120.6, 119.0, 113.6, 55.9.

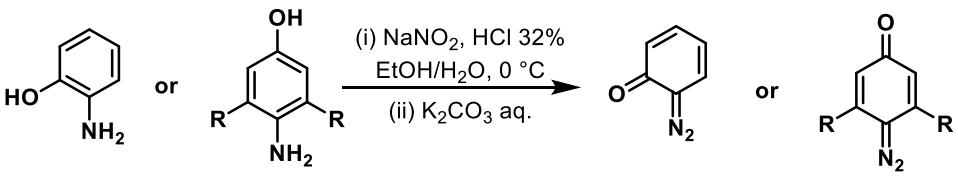
1-Diazo-3-methoxynaphthalen-2(1*H*)-one (1e).



1e

Prepared following the general procedure with 3-methoxy-2-naphthol **S9** (1.25 mmol scale). Reaction time: 50 min. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 70:30 to 50:50) to give **1e** as an orange solid (204.6 mg, 82%); ^{1}H NMR (400 MHz, acetone-d_6) δ(ppm): 7.59 (d, J = 7.8 Hz, 1H), 7.44–7.35 (m, 2H), 7.25 (ddd, J = 7.8, 6.2, 2.3 Hz, 1H), 7.10 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ(ppm): 174.9, 152.8, 128.9, 127.6, 126.5, 125.6, 123.4, 120.7, 113.5, 56.0; IR (ATR, neat, ν, cm^{-1}): 2087 (ν_{as}, C=N=N), 1584, 1283, 1219, 1180, 1121, 765; HRMS (ESI–TOF) calcd. for $C_{11}H_9N_2O_2$ $[M+H]^+$: 201.0659, found 201. 0667.

2.3. General procedure for the preparation of 1,2- and 1,4-diazoquinones 1f–h[S13]

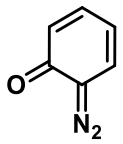


S13 **1f-h**

Caution: *Diazoquinones are potentially explosive. Many of these compounds are sensitive to heat, light, shock and metal catalysts. Therefore, precaution should be taken in preparation, storage (in the dark, under 5* °C*) and use.*

To a round bottom flask equipped with a magnetic stirrer bar was added aminophenol derivative **S13** (10.00 mmol, 1.00 equiv.) and ethanol (60.0 mL). The solution was cooled to 0 ºC and HCl (8.4 mL, 12 M, 100.0 mmol, 10.00 equiv.) was slowly added. The reaction mixture was stirred at 0 ºC for 10 min, then an ice-cold solution of $NaNO_2$ (2.07 g, 30.00 mmol, 3.00 equiv.) in water (4 mL) was added dropwise over 10 min. The resulting mixture was stirred for a further 2 h at 0 ºC, then cold dichloromethane (200 mL) and crushed ice (30 g) were added sequentially. Upon vigorous stirring, a cold solution of K_2CO_3 (9.30 g, 67.00 mmol, 6.70 equiv.) in water (10 mL) was added dropwise. The organic phase was collected, and the aqueous phase was extracted with dichloromethane (100 mL). The combined organic phase was washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to give the title compound, which were used without further purification unless otherwise stated. All diazoquinones **1f–h** were obtained as solids, and stored in the dark under anhydrous conditions at 5 ºC.

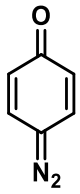
6-Diazocyclohexa-2,4-dien-1-one (1f).[S14]



1f

Prepared following the general procedure with 2-aminophenol **S13a**. Compound **1f** was obtained as a black solid (0.95 g, 79%) and used without further purification; ^{1}H NMR (600 MHz, CD_3OD) δ (ppm): 7.50 (ddd, J = 8.7, 1.9, 0.7 Hz, 1H), 7.45 (ddd, J = 9.4, 6.7, 1.9 Hz, 1H), 6.64 (dt, J = 9.4, 0.7 Hz, 1H), 6.41 (ddd, J = 8.7, 6.7, 0.9 Hz, 1H); ^{13}C NMR (151 MHz, CD_3OD) δ (ppm): 179.9, 141.3, 127.0, 124.5, 116.4, 90.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.24 (ddd, J = 9.4, 6.7, 1.8 Hz, 1H), 7.16 (dd, J = 8.8, 1.8 Hz, 1H), 6.61 (d, J = 9.4 Hz, 1H), 6.24 (ddd, J = 8.8, 6.7, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.1, 138.6, 123.8, 123.7, 115.8, 88.5.

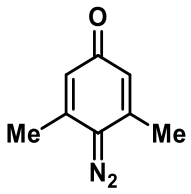
4-Diazocyclohexa-2,5-dien-1-one (1g).[S14]



1g

Prepared following the general procedure with 4-aminophenol **S13b**. Compound **1g** was obtained as a brown solid (0.63 g, 52%) and used without further purification; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.44–7.38 (m, 2H), 6.68–6.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.4, 130.1, 127.4.

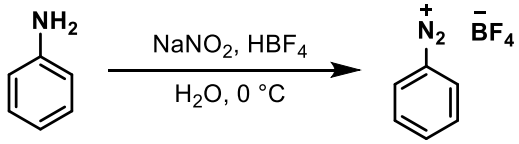
4-Diazo-3,5-dimethylcyclohexa-2,5-dien-1-one (1h).[S15]



1h

Prepared following the general procedure with 4-amino-3,5-dimethylphenol **S13c**. Purified by flash column chromatography on silica gel (eluent: *n*-hexane/dichloromethane/methanol = 50:50:0 to 0:80:20). The solid obtained was redissolved in dichloromethane (50 mL), vacuum filtered through a pad of Celite (eluent: dichloromethane, 3 × 25 mL) and concentrated *in vacuo* to give **1h** as an orange solid (1.40 g, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.16 (s, 2H), 2.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 182.3, 139.7, 125.9, 18.4.

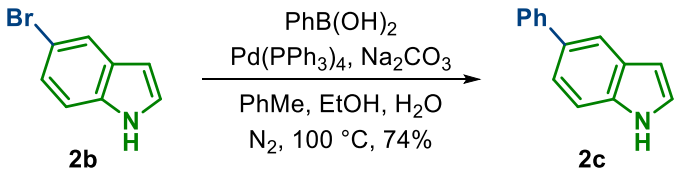
2.4. Procedure for the preparation of benzenediazonium tetrafluoroborate (S15).[S16]



S14 **S15**

Tetrafluoroboronic acid (5.25 mL, 41.86 mmol, 50% in water, 2.60 equiv.) was dissolved in water (10.00 mL) and cooled down to 0 °C. To this solution, aniline **S14** (1.48 mL, 16.10 mmol, 1.00 equiv.) was added at 0 °C and the ensuing reaction mixture was stirred for 60 minutes. Sodium nitrite (1.00 equiv.) in 1.50 mL of water was added dropwise and the resulting mixture was stirred for 30 minutes. The precipitated white solid was collected by vacuum filtration, dissolved in a minimum amount of acetone and precipitated with diethyl ether to afford the title compound **S15** as a white solid (2.32 g, 75%); ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.52 – 8.46 (m, 2H), 8.26 (tt, J = 7.7, 1.2 Hz, 1H), 7.98 – 7.88 (m, 2H); ^{13}C NMR (101 MHz, CD_3CN) δ (ppm): 143.0, 133.4, 132.8; ^{19}F NMR (376 MHz, CD_3CN) δ (ppm): –151.35.

2.5. Procedure for the preparation of 5-Phenyl-1*H*-indole (2c).[S17]

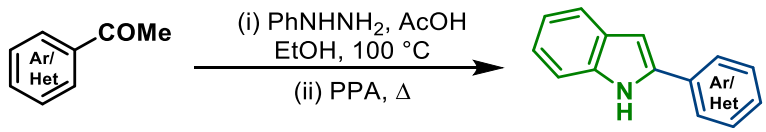


2b **2c**

To a two-neck round bottom flask equipped with a magnetic stirrer bar and reflux condenser was added 5-bromo-1*H*-indole **2b** (196.0 mg, 1.00 mmol, 1.00 equiv.) and phenyl boronic acid (244.0 mg, 2.00 mmol, 2.00 equiv.). Three vacuum-refill cycles with nitrogen were carried out. Then, a solution of toluene/ethanol (3.0 mL, 1:1 v/v) was added and the reaction mixture was stirred vigorously. To the

resulting mixture was added a solution of sodium carbonate (265.0 mg, 2.50 mmol, 2.50 equiv.) in water (3.0 mL), followed by a solution of $Pd(PPh_3)_4$ (58.0 mg, 0.05 mmol, 5 mol %) in toluene/ethanol (3.0 mL, 1:1 v/v). The reaction mixture was heated to 100 °C for 1 h, then additional $Pd(PPh_3)_4$ (58.0 mg, 0.05 mmol, 5 mol %) in toluene/ethanol (3.0 mL, 1:1 v/v) solution was added, then the reaction mixture stirred at 100 ºC for a further 24 h (*note: **2b** and **2c** have a similar R_f by TLC analysis)*. On cooling to room temperature, the reaction mixture was quenched by the addition of water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 80:20) to give **2c** as a light-yellow solid (145.1 mg, 74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.12 (s, 1H), 7.92–7.87 (m, 1H), 7.75–7.66 (m, 2H), 7.52–7.42 (m, 4H), 7.38–7.32 (m, 1H), 7.24 (dd, J = 3.2, 2.4 Hz, 1H), 6.64 (ddd, J = 3.2, 2.0, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 142.7, 135.4, 133.5, 128.8, 128.5, 127.5, 126.4, 125.0, 122.0, 119.4, 111.4, 103.1.

2.6. General procedure for the preparation of 2-(hetero)aryl-1*H*-indoles 2h–l.[S18]

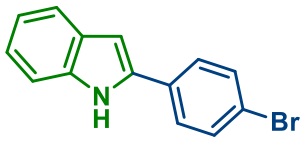


S16 **2h-l**

Step one: To a round bottom flask equipped with a magnetic stirrer bar was added (hetero)aryl ketone derivative **S16** (10.00 mmol, 1.00 equiv.), phenylhydrazine (1.30 g, 12.00 mmol, 1.20 equiv.) and ethanol (6.0 mL). The reaction mixture was heated to 100 °C, and under vigorous stirring glacial acetic acid (1.2 mL, 40.00 mmol, 4.00 equiv.) was added. The reaction progress was monitored by TLC (0.5–2 h). On completion, the reaction mixture was cooled to room temperature and the solvent was removed *in vacuo* to give a colourful solid which was used in the next step without further purification.

Step two: Unless otherwise stated, polyphosphoric acid (12.5 g) was added to a beaker and heated to 120 ºC, then the crude hydrazone was added with constant manual stirring (with the aid of a glass stirring rod). The reaction mixture was stirred for 15 min at the same temperature then the beaker was removed from the heat. To the hot reaction mixture, a mixture of ice/water (50 g) was added, and then stirred vigorously for a further 30 min. The solid obtained was collected by vacuum filtration, washed with cold water (100 mL) and ethanol (20 mL). The resulting solid was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) and recrystallised from hot ethanol to give the title compound.

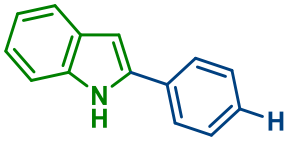
2-(4-Bromophenyl)-1*H*-indole (2h).[S19]



2h

Prepared following the general procedure with 4'-bromoacetophenone **S16a**. Reaction time for step one = 1.5 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5) and recrystallised from hot ethanol to give **2h** as a white solid (1.54 g, 56%); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 11.58 (s, 1H), 7.86–7.78 (m, 2H), 7.68–7.62 (m, 2H), 7.53 (d, J = 7.8 Hz, 1H), 7.41–7.38 (m, 1H), 7.11 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.00 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.94 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 137.2, 136.4, 131.8, 131.5, 128.5, 126.9, 121.9, 120.3, 120.2, 119.5, 111.4, 99.4.

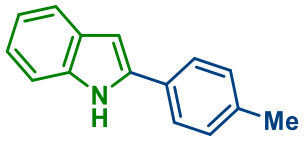
2-Phenyl-1*H*-indole (2i).[S19]



2i

Prepared following the general procedure with acetophenone **S16b**. Reaction time for step one = 0.5 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5) and recrystallised from hot ethanol to give **2i** as a white solid (0.79 g, 41%); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.52 (s, 1H), 7.86 (dd, J = 8.3, 1.2 Hz, 2H), 7.53 (dd, J = 7.8, 1.0 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.41 (dd, J = 8.1, 1.0 Hz, 1H), 7.34–7.27 (m, 1H), 7.10 (ddd, J = 8.1, 7.0, 1.2 Hz, 1H), 7.00 (ddd, J = 7.9, 7.0, 1.0 Hz, 1H), 6.90 (dd, J = 2.2, 1.0 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 137.6, 137.1, 132.2, 128.9, 128.6, 127.4, 125.0, 121.6, 120.0, 119.4, 111.3, 98.7.

2-(*p*-Tolyl)-1*H*-indole (2j).[S19]

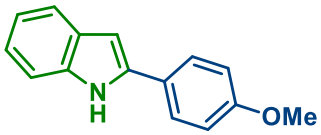


2j

Prepared following the general procedure with 4'-methylacetophenone **S16c**. Reaction time for step one = 1 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10) and recrystallised from hot ethanol to give **2j** as a white solid (1.37 g, 66%); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.46 (s, 1H), 7.78–7.70 (m, 2H), 7.51 (dd, J = 8.0, 1.1 Hz, 1H), 7.39 (dd, J = 8.0, 1.2 Hz, 1H), 7.31–7.22 (m, 2H), 7.08 (ddd, J = 8.0, 7.0, 1.2 Hz, 1H), 6.99 (ddd, J = 8.0, 7.0, 1.0 Hz,

1H), 6.83 (d, J = 1.7 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 137.8, 137.0, 136.8, 129.5, 128.7, 124.9, 121.3, 119.9, 119.3, 111.2, 98.0, 20.8.

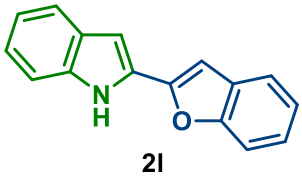
2-(4-Methoxyphenyl)-1*H*-indole (2k).[S20]



2k

Prepared following the general procedure with 4'-methoxyacetophenone **S16d**. Reaction time for step one = 1 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) and recrystallised from hot ethanol to give **2k** as a light-yellow solid (0.89 g, 40%); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 11.39 (s, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.48 (d, J = 7.9 Hz, 1H), 7.36 (dd, J = 8.0, 1.1 Hz, 1H), 7.08–7.00 (m, 3H), 6.96 (ddd, J = 7.9, 7.0, 1.1 Hz, 1H), 6.75 (d, J = 1.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 158.8, 137.8, 136.9, 128.8, 126.4, 124.9, 121.0, 119.6, 119.2, 114.3, 111.0, 97.3, 55.2.

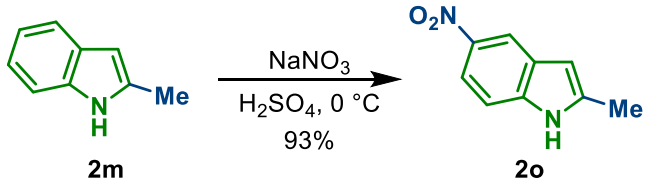
2-(Benzofuran-2-yl)-1*H*-indole (2l).[S21]



2l

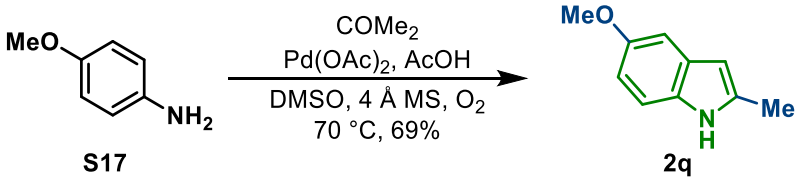
Prepared following the general procedure with benzofuranyl methyl ketone **S16e**. Reaction time for step one = 1.5 h *[note: for the second step, the quenched reaction mixture was neutralised with a saturated aqueous sodium bicarbonate solution (50 mL) and extracted with ethyl acetate (5 × 20 mL)]*. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5) and recrystallised from hot ethanol to give **2l** as a beige solid (0.44 g, 19%); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 11.83 (s, 1H), 7.69 (ddd, J = 7.6, 1.4, 0.7 Hz, 1H), 7.63 (dq, J = 8.3, 0.9 Hz, 1H), 7.60 (dt, J = 7.9, 1.0 Hz, 1H), 7.45 (dd, J = 8.1, 0.9 Hz, 1H), 7.35–7.30 (m, 2H), 7.28 (td, J = 7.4, 1.0 Hz, 1H), 7.17 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.05 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.97 (s, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 154.1, 149.8, 137.2, 128.7, 128.4, 128.1, 124.5, 123.4, 122.6, 121.1, 120.6, 119.8, 111.5, 111.0, 101.6, 100.4.

2-Methyl-5-nitro-1*H*-indole (2o).[S22]



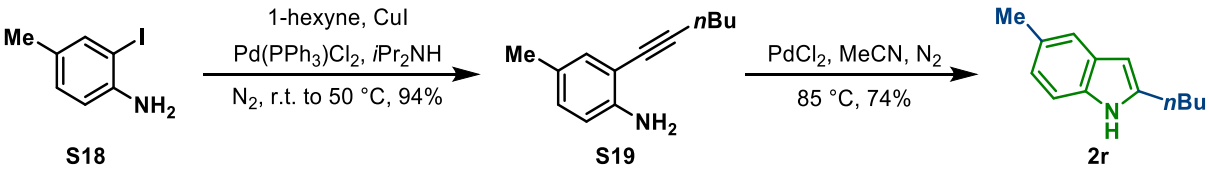
To a round bottom flask equipped with a magnetic stirrer bar was added 2-methyl-1*H*-indole **2m** (1.00 g, 7.62 mmol, 1.00 equiv.) and sulfuric acid (6.0 mL). The solution was cooled to 0 ºC, and a solution of $NaNO_3$ (0.69 g, 8.07 mmol, 1.06 equiv.) in sulfuric acid (6.5 mL) was added dropwise. Ice (50 g) was added, and the reaction mixture stirred vigorously for 30 min. The solid formed was collected by vacuum filtration and washed with water (20 × 10 mL) until a neutral pH was reached, then dried under high vacuum to give **2o** as a yellow solid (1.26 g, 94%); ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 11.70 (s, 1H), 8.41 (d, J = 2.3 Hz, 1H), 7.91 (dd, J = 8.9, 2.3 Hz, 1H), 7.42 (d, J = 8.9 Hz, 1H), 6.42 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm): 140.4, 139.9, 139.4, 127.9, 115.8, 115.6, 110.7, 101.6, 13.4; ^{1}H NMR (600 MHz, $CDCl_3$) δ(ppm): 8.46 (d, J = 2.2 Hz, 1H), 8.30 (br s, 1H), 8.03 (dd, J = 8.9, 2.2 Hz, 1H), 7.31 (d, J = 8.9 Hz, 1H), 6.39 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 142.0, 139.3, 138.7, 128.6, 117.0, 116.8, 110.1, 102.8, 13.9.

5-Methoxy-2-methyl-1*H*-indole (2q).[S23]



To a round bottom flask equipped with a magnetic stirrer bar was added 4-methoxyaniline **S17** (1.23 g, 10.00 mmol, 1.00 equiv.), $Pd(OAc)_2$ (0.22 g, 1.00 mmol, 10 mol %), and powdered 4 Å MS (1.00 g). Three vacuum-refill cycles with oxygen were carried out. Then, acetone (3.7 mL, 50.00 mmol, 5.00 equiv.), glacial acetic acid (0.6 mL, 10.00 mmol, 1.00 equiv.) and dimethyl sulfoxide (100.0 mL) were added. The reaction mixture was heated to 70 °C and stirred vigorously for 24 h. On cooling to room temperature, the reaction mixture was quenched by addition of ethyl acetate (200 mL) and brine (100 mL). The resulting mixture was vacuum filtered through a pad of Celite (eluent: ethyl acetate, 3 × 50 mL). The organic phase was collected, and the aqueous phase extracted with ethyl acetate (50 mL). The combined organic phase was washed with brine (2 × 100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:0 to 99:1) to give **2q** as a light-yellow solid (1.11 g, 69%); ^{1}H NMR (400 MHz, DMSO-d_6) δ(ppm): 10.69 (s, 1H), 7.14 (d, J = 8.7 Hz, 1H), 6.90 (d, J = 2.5 Hz, 1H), 6.62 (dd, J = 8.7, 2.5 Hz, 1H), 6.03 (dt, J = 2.0, 1.0 Hz, 1H), 3.72 (s, 3H), 2.35 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ(ppm): 153.1, 136.1, 131.2, 129.1, 111.0, 109.5, 101.2, 99.0, 55.2, 13.5; ^{1}H NMR (600 MHz, $CDCl_3$) δ(ppm): 7.74 (br s, 1H), 7.15 (d, J = 8.7 Hz, 1H), 7.03 (d, J =

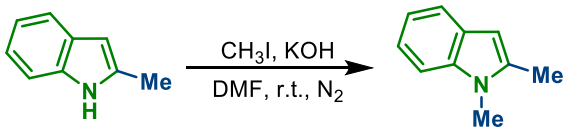
2.5 Hz, 1H), 6.80 (dd, J = 8.7, 2.5 Hz, 1H), 6.17 (br s, 1H), 3.87 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 154.2, 136.1, 131.3, 129.6, 111.0, 110.7, 102.0, 100.4, 56.0, 13.8.



2-(Hex-1-yn-1-yl)-4-methylaniline (S19).[S24,S25] To a two-neck round bottom flask equipped with a magnetic stirrer bar and reflux condenser was added 2-iodo-4-methylaniline **S18** (1.17 g, 5.00 mmol, 1.00 equiv.), CuI (95.2 mg, 0.50 mmol, 10 mol %) and $Pd(PPh_3)_2Cl_2$ (175.5 mg, 0.25 mmol, 5 mol %). Three vacuum-refill cycles with nitrogen were carried out. Then, iPr$_2$NH (10.0 mL) was added and the reaction mixture stirred at room temperature for 5 min, after which 1-hexyne (0.9 mL, 7.50 mmol, 1.50 equiv.) was added dropwise. The reaction mixture was heated to 50 °C for 24 h (*note: **S18** and **S19** have similar R_f based on TLC analysis)*. On cooling to room temperature, the reaction mixture was quenched by addition of a saturated aqueous ammonium chloride solution (30 mL) and extracted with dichloromethane (3 × 30 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 99:1) to give **S19** as a dark-brown oil (0.88 g, 94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.08 (d, J = 2.1 Hz, 1H), 6.90 (dd, J = 8.1, 2.1 Hz, 1H), 6.61 (d, J = 8.1 Hz, 1H), 4.03 (br s, 2H), 2.48 (t, J = 6.9 Hz, 2H), 2.21 (s, 3H), 1.69–1.57 (m, 2H), 1.57–1.43 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.3, 132.3, 129.6, 127.1, 114.4, 109.1, 95.5, 77.2, 31.2, 22.1, 20.3, 19.4, 13.7.

2-Butyl-5-methyl-1*H*-indole (2r).[S26,S27] To a two-neck round bottom flask equipped with a magnetic stirrer bar and reflux condenser was added 2-(hex-1-yn-1-yl)-4-methylaniline **S19** (0.80 g, 4.27 mmol, 1.00 equiv.) and $PdCl_2$ (38.2 mg, 0.21 mmol, 5 mol %). Three vacuum-refill cycles with nitrogen were carried out. Then, acetonitrile (11.0 mL) was added and the reaction mixture was heated to 85 °C for 24 h. On cooling to room temperature, the solvent was removed *in vacuo* and the resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether) to give **2r** as a yellow solid (0.60 g, 74%); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 10.69 (s, 1H), 7.17–7.15 (m, 1H), 7.13 (d, J = 8.2 Hz, 1H), 6.79 (dd, J = 8.2, 1.7 Hz, 1H), 6.01 (dd, J = 2.1, 1.0 Hz, 1H), 2.67 (t, J = 7.6 Hz, 2H), 2.33 (s, 3H), 1.70–1.56 (m, 2H), 1.40–1.28 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 140.2, 134.3, 128.6, 126.7, 121.3, 118.7, 110.2, 97.6, 30.9, 27.3, 21.8, 21.2, 13.7; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.70 (br s, 1H), 7.37–7.35 (m, 1H), 7.19 (d, J = 8.2 Hz, 1H), 6.98 (ddd, J = 8.2, 1.6, 0.6 Hz, 1H), 6.19 (dd, J = 2.2, 1.0 Hz, 1H), 2.74 (t, J = 7.7 Hz, 2H), 2.47 (s, 3H), 1.79–1.64 (m, 2H), 1.53–1.39 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 140.2, 134.2, 129.3, 128.8, 122.5, 119.6, 110.0, 99.1, 31.4, 28.1, 22.5, 21.6, 14.0.

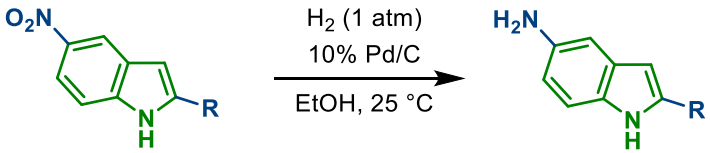
1,2-Dimethyl-1*H*-indole (2s).[S28,S29]



2m **2s**

To a two-neck round bottom flask equipped with a magnetic stirrer bar was added 2-methyl-1*H*-indole **2m** (1.31g, 10.00 mmol, 1 equiv.), potassium hydroxide (2.81 g, 50.00 mmol, 5 equiv.) and dry *N*,*N*-dimethylformamide (30.0 mL) under a nitrogen atmosphere. Iodomethane (1.25 mL, 20.00 mmol, 2 equiv.) was added dropwise and the reaction mixture stirred vigorously at room temperature for 30 min. The resulting mixture was vacuum filtered through a pad of silica (eluent: ethyl acetate, 4 × 25 mL). Water (200 mL) was added, and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 99:1) to give **2s** as a light-yellow solid (1.35 g, 93%); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 7.45–7.39 (m, 1H), 7.37–7.33 (m, 1H), 7.05 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H), 6.95 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 6.19 (t, J = 1.0 Hz, 1H), 3.64 (s, 3H), 2.39 (d, J = 1.0 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 137.0, 137.0, 127.5, 119.9, 119.0, 118.8, 109.1, 99.0, 29.2, 12.4.

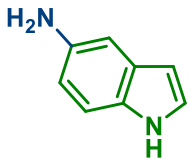
2.7. General procedure for the synthesis of 5-amino-1*H*-indole derivatives S21.[S30]



2o or S20 **S21**

To a two-neck round bottom flask equipped with a magnetic stirrer was added 5-nitro-1*H*-indole derivative **2o** or **S20** (3.00 mmol, 1.00 equiv.). A septum was fitted and three vacuum-refill cycles with nitrogen were carried out, followed by the addition of ethanol (12.5 mL) and 10% Pd/C (137 mg) at 25 °C. The mixture was purged with nitrogen and subsequently subjected to hydrogen atmosphere (1 atm, using a balloon). Following completion as indicated by TLC, the mixture was filtered through Celite (eluent: MeOH, 3 × 5 mL), concentrated *in vacuo* and dried under high vacuum to afford the aminoindoles **S21**.

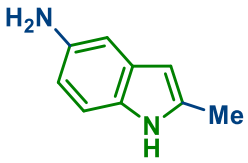
1*H*-indol-5-amine (S21a).[S31]



S21a

Prepared following the general procedure with 5-nitro-1*H*-indole **S20**. The compound was isolated and used without further purification in the next step. The amine **S21a** was obtained as a light brown solid (353.0 mg, 89%); ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 7.17 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 3.1 Hz, 1H), 6.95 (d, J = 2.2 Hz, 1H), 6.66 (dd, J = 8.6, 2.2 Hz, 1H), 6.25 (d, J = 3.1 Hz, 1H); ^{13}C NMR (101 MHz, CD_3OD) δ (ppm): 139.6, 132.9, 130.1, 125.9, 114.2, 112.4, 107.4, 101.3.

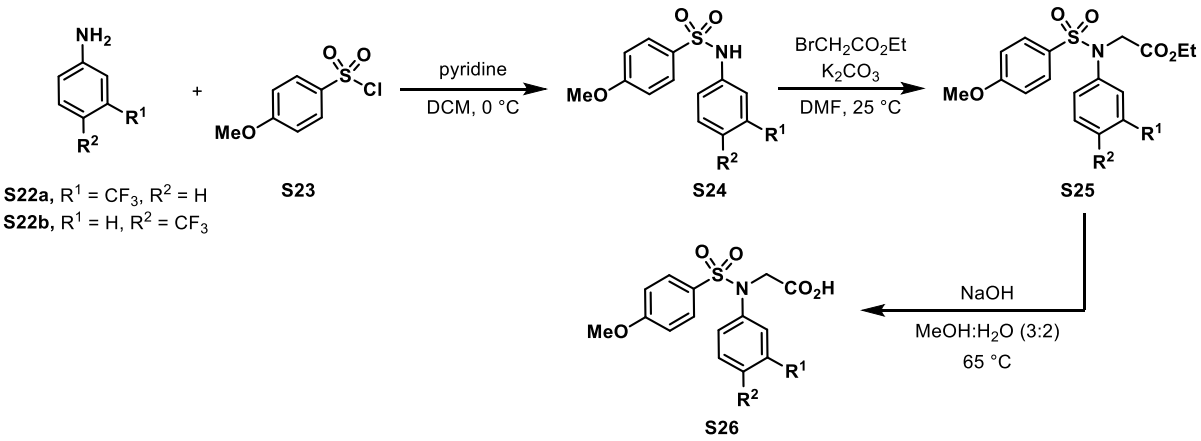
2-Methyl-1*H*-indol-5-amine (S21b).[S32]



S21b

Prepared following the general procedure with 5-nitro-2-methyl-1*H*-indole **2o**. The compound was isolated and used without further purification in the next step. The amine **S21b** was obtained as a light brown solid (434.2 mg, 99%); ^{1}H NMR (400 MHz, CD_3OD) δ (ppm): 7.04 (dt, J = 8.4, 0.8 Hz, 1H), 6.82 (d, J = 2.1 Hz, 1H), 6.57 (dd, J = 8.4, 2.1 Hz, 1H), 5.92 (t, J = 0.8 Hz, 1H), 2.35 (d, J = 0.8 Hz, 3H); ^{13}C NMR (101 MHz, CD_3OD) δ (ppm): 139.4, 137.0, 133.3, 131.3, 112.8, 111.6, 107.0, 99.5, 13.5.

2.8. General procedure for the synthesis of glycine derivatives S26.[S33,S34]



S22a, R^1 = CF_3, R^2 = H
S22b, R^1 = H, R^2 = CF_3

S23 **S24** **S25** **S26**

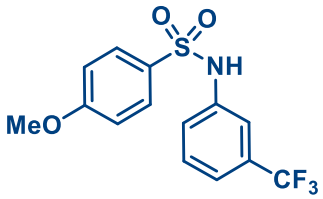
Step one: To a stirring solution of *m*- or *p*-(trifluoromethyl)aniline **S22a** and **S22b** (0.822 g, 5.10 mmol, 1.02 equiv.) in dry dichloromethane (4.0 mL) was added pyridine (0.81 mL, 10 mmol, 2.00 equiv.) at room temperature. The resulting mixture was cooled to 0 °C, after which a solution of 4-methoxybenzenesulfonyl chloride **S23** (1.033 g, 5.00 mmol, 1.00 equiv.) in dry dichloromethane (4.0

mL) was added. The reaction mixture was stirred for 2 h at 0 °C, then diluted with a mixture of diethyl ether/*n*-hexane (40.0 mL, v/v = 1:1), quenched by the addition of HCl solution (20 mL, 6 M), transferred to a separatory funnel and the organic layer was collected. The aqueous layer was then extracted with a mixture of diethyl ether/*n*-hexane (1 × 40.0 mL, v/v = 1:1). The combined organic layers were washed with HCl solution (2 × 20 mL, 6 M) and water (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to provide the *N*-arylbenzenesulfonamide **S24**.

Step two: To a solution of benzenesulfonamide **S24** (1.491 g, 4.50 mmol, 1.00 equiv.) in dry dimethylformamide (12.0 mL) was added K_2CO_3 (1.866 g, 13.50 mmol, 3.00 equiv.) followed by the dropwise addition of ethyl bromoacetate (1.25 mL, 11.50 mmol, 2.50 equiv.). After stirring for 15 h at 25 °C, the reaction mixture was diluted with water (30 mL), quenched by the addition of HCl solution (0.5 mL, 6 M, pH ~ 5), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (2 × 20 mL) and brine (2 × 20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to provide the ethyl *N*-sulfonyl-*N*-arylglycinate **S25**.

Step three:[S34] To a solution of NaOH (8.000 g, 200.00 mmol, 50.00 equiv.) in a mixture of methanol/water (75.0 mL, v/v = 3:2) was added the ethyl *N*-sulfonyl-*N*-arylglycinate **S25** (1.700 g, 4.00 mmol, 1.00 equiv.). The reaction mixture was heated at 65 °C and stirred for 6 h, and then cooled to room temperature, quenched with HCl solution (2 M) to pH 2 and diluted with water (150 mL). The precipitate was collected by vacuum filtration, washed with water (5 × 10 mL) and dried overnight in a vacuum desiccator over KOH pellets to provide the glycine derivative **S26**.

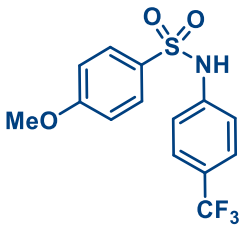
4-Methoxy-*N*-(3-(trifluoromethyl)phenyl)benzenesulfonamide (S24a).



S24a

Prepared following the general procedure step 1 with 3-(trifluoromethyl)aniline **S22a** and 4-methoxybenzenesulfonyl chloride **S23**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 70:30) to give **S24a** as a light yellow wax (1.595 g, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.81 – 7.74 (m, 2H), 7.55 (s, 1H), 7.38 – 7.31 (m, 3H), 7.29 (dt, J = 7.3, 2.2 Hz, 1H), 6.95 – 6.88 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.6, 137.6, 131.9 (q, J = 32.9 Hz), 130.1, 130.0, 129.6, 124.0, 123.7 (q, J = 272.5 Hz), 121.7 (q, J = 3.8 Hz), 117.6 (q, J = 3.9 Hz), 114.56, 55.75; ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$) δ (ppm): –62.87.

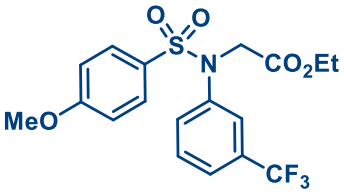
4-Methoxy-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (S24b).[S33]



S24b

Prepared following the general procedure step 1 with 4-(trifluoromethyl)aniline **S22b** and 4-methoxybenzenesulfonyl chloride **S23**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 70:30) to give **S24b** as a light yellow wax (1.557 g, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.82 – 7.78 (m, 2H), 7.58 (s, 1H), 7.48 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 6.96 – 6.88 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 163.6, 140.2, 130.2, 129.6, 126.8 (q, J = 3.8 Hz), 126.7 (q, J = 32.8 Hz), 124.1 (q, J = 271.6 Hz), 119.71, 114.63, 55.77; ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$) δ (ppm): –62.25.

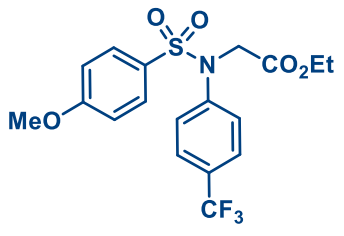
Ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycinate (S25a).



S25a

Prepared following the general procedure step 2 with benzenesulfonamide **S24a**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5 to 80:20) to give **S25a** as a yellow oil (1.634 g, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.61 – 7.57 (m, 2H), 7.55 – 7.52 (m, 1H), 7.48 – 7.40 (m, 3H), 6.95 – 6.90 (m, 2H), 4.40 (s, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 168.6, 163.5, 140.8, 132.4, 131.7 (q, J = 32.7 Hz), 130.1, 130.0, 129.9, 125.5 (q, J = 3.7 Hz), 124.9 (q, J = 3.9 Hz), 123.5 (q, J = 272.3 Hz), 114.2, 61.8, 55.8, 52.6, 14.1; ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$) δ (ppm): –62.76.

Ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycinate (S25b).

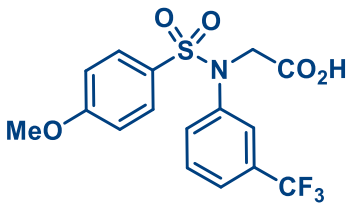


S25b

Prepared following the general procedure step 2 with benzenesulphonamide **S24b**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5 to 85:15) to give

S25b as a light-yellow oil (1.784 g, 95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.66 – 7.59 (m, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.98 – 6.88 (m, 2H), 4.42 (s, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.85 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.6, 163.5, 143.4, 130.1, 130.1, 129.8 (q, J = 32.8 Hz), 128.3, 126.4 (q, J = 3.6 Hz), 123.9 (q, J = 272.3 Hz), 114.3, 61.8, 55.7, 52.3, 14.2; ^{19}F{^{1}H} NMR (376.5 MHz, $CDCl_3$) δ (ppm): –62.62.

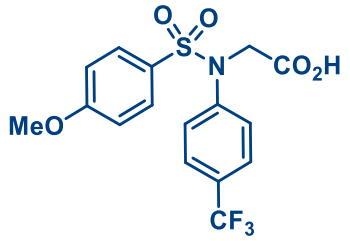
***N*-((4-Methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycine (S26a).**



S26a

Prepared following the general procedure step 3 with ethyl glycinate **S25a**. The compound was isolated and used without further purification in the next step. The carboxylic acid **S26a** was obtained as a light yellow solid (560.6 mg g, 36%); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 12.94 (br s, 1H), 7.68 – 7.63 (m, 1H), 7.61 – 7.54 (m, 3H), 7.51 (t, J = 2.0 Hz, 1H), 7.47 (dt, J = 8.1, 1.5 Hz, 1H), 7.12 – 7.05 (m, 2H), 4.48 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 169.9, 162.9, 140.6, 131.5, 130.3, 129.6, 129.6, 129.5 (q, J = 32.1 Hz), 124.5 (q, J = 3.9 Hz), 124.1 (q, J = 3.8 Hz), 123.7 (q, J = 272.4 Hz), 114.5, 55.8, 51.6; ^{19}F{^{1}H} NMR (376.5 MHz, DMSO-d_6) δ (ppm): –61.24.

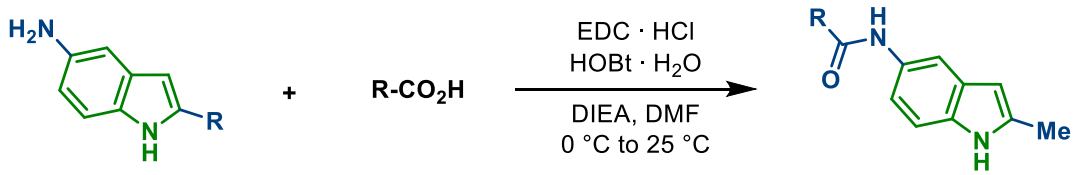
***N*-((4-Methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycine (S26b).**



S26b

Prepared following the general procedure step 3 with ethyl glycinate **S25b**. The compound was isolated and used without further purification in the next step. The carboxylic acid **S26b** was obtained as a white solid (716.4 mg, 46%); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.98 (br s, 1H), 7.71 (d, J = 8.4 Hz, 2H), 7.67 – 7.61 (m, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.14 – 7.05 (m, 2H), 4.50 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 169.8, 162.9, 143.7, 129.7, 129.6, 127.1, 127.1 (q, J = 32.2 Hz), 126.1 (q, J = 3.8 Hz), 124.9 (q, J = 272.2 Hz), 114.6, 55.7, 51.4; ^{19}F{^{1}H} NMR (376.5 MHz, DMSO-d_6) δ (ppm): –60.92.

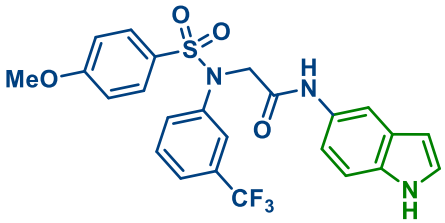
2.9. General procedure for the synthesis of the indolyl amides 2t–v.



S21 **S26 or S27** **2t-v**

To a solution of the carboxylic acid **S26** or ibuprofen **S27** (0.50 mmol, 1.00 equiv.) in dry dimethylformamide (2.50 mL) was added *N*,*N*-diisopropylethylamine (0.27 mL, 1.50 mmol, 3.00 equiv.). The resulting mixture was cooled to 0 °C, and then *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (143.8 mg, 0.75 mmol, 1.50 equiv.), 1-hydroxybenzotriazole monohydrate (114.9 mg, 0.75 mmol, 1.50 equiv.) and 1*H*-indol-5-amine derivative **S21** (0.75 mmol, 1.50 equiv.) were added sequentially. The reaction mixture was stirred at 0 °C for 10 min and then allowed to warm to 25 °C and stirred for a further 24 h. The mixture was quenched by the addition of water (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with HCl solution (4 × 5 mL, 6 M), a saturated solution of $NaHCO_3$ (2 × 20 mL), brine (20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The resulting residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to provide the title compound.

***N*-(1*H*-Indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (2t).**[S35]

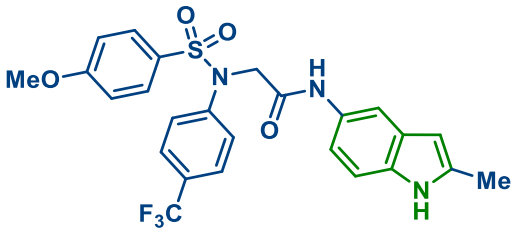


2t

Prepared following the general procedure with 1*H*-indol-5-amine **S21a** and glycine derivative **S26a**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:20 to 60:40) to give **2t** as a beige solid (225.6 mg, 90%); m.p. = 154–156 °C; ^{1}H NMR (600 MHz, acetone-d_6) δ (ppm): 10.18 (br s, 1H), 9.24 (br s, 1H), 7.94 – 7.90 (m, 1H), 7.80 – 7.78 (m, 1H), 7.68 – 7.58 (m, 4H), 7.59 – 7.53 (m, 1H), 7.33 (dt, J = 8.7, 0.8 Hz, 1H), 7.29 (t, J = 2.8 Hz, 1H), 7.25 (dd, J = 8.7, 2.1 Hz, 1H), 7.09 – 7.04 (m, 2H), 6.42 (ddd, J = 3.1, 2.0, 0.9 Hz, 1H), 4.59 (s, 2H), 3.87 (s, 3H); ^{13}C NMR analysis shows two sets of signals, which indicate the presence of rotamers (denoted as α and β); ^{13}C NMR (151 MHz, acetone-d_6) δ (ppm): 166.0 (α), 165.9 (β), 164.4 (α), 142.3 (α), 134.4 (α), 134.2 (β), 132.4 (α), 131.5 (α), 131.4 (β), 131.4 (q, J = 32.5 Hz, α), 131.0 (α), 130.8 (α), 130.3 (α), 128.9 (α), 128.9 (β), 126.4 (α), 126.3 (β), 126.1 (q, J = 3.9 Hz, α), 125.0 (q, J = 3.8 Hz, α), 124.8 (q, J = 271.8 Hz, α), 116.3 (α), 116.2 (β), 115.1 (α), 112.6 (α), 112.5 (β), 111.9 (α), 111.9 (β), 102.5 (α), 102.4 (β),

56.2 (α), 55.1 (α), 55.0 (β); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, acetone-d_6) δ (ppm): –63.01; IR (ATR, neat, ν, cm^{-1}): 3390, 1674, 1588, 1478, 1325, 1258, 1156, 1126, 1086, 886, 804.

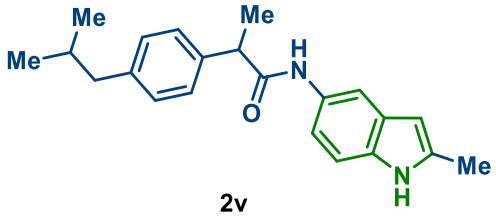
2-((4-Methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide (2u).



2u

Prepared following the general procedure with 2-methyl-1*H*-indol-5-amine **S21b** and glycine derivative **S26b**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:20 to 60:40) to give **2u** as a beige solid (204.0 mg, 78%); m.p. = 176–178 °C; ^{1}H NMR (600 MHz, acetone-d_6) δ (ppm): 9.92 (br s, 1H), 9.12 (br s, 1H), 7.76 – 7.74 (m, 1H), 7.72 – 7.69 (m, 2H), 7.69 – 7.66 (m, 2H), 7.62 – 7.58 (m, 2H), 7.19 (dt, J = 8.6, 0.8 Hz, 1H), 7.15 (dd, J = 8.6, 2.1 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.09 (dt, J = 2.0, 1.0 Hz, 1H), 4.58 (s, 2H), 3.88 (s, 3H), 2.39 (d, J = 1.0 Hz, 3H); ^{13}C NMR analysis shows two sets of signals, which indicate the presence of rotamers (denoted as α and β); ^{13}C NMR (151 MHz, acetone-d_6) δ (ppm): 165.9 (α), 165.8 (β), 164.4 (α), 145.1 (α), 137.3 (α), 137.1 (β), 134.7 (α), 134.7 (β), 134.5 (α), 131.4 (α), 131.3 (β), 131.0 (α), 130.5 (β), 130.5 (α), 130.0 (α), 130.0 (β), 129.1 (q, J = 32.5 Hz, α), 128.5 (α), 126.8 (q, J = 3.7 Hz, α), 125.1 (q, J = 271.4 Hz, α), 115.1 (α), 115.0 (α), 114.9 (β), 111.7 (α), 111.6 (β), 111.0 (α), 110.9 (β), 100.6 (α), 100.6 (β), 56.1 (α), 54.7 (α), 55.7 (β), 13.6 (α), 13.5 (β); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, acetone-d_6) δ (ppm): –62.86; IR (ATR, neat, ν, cm^{-1}): 3396, 1665, 1566, 1350, 1324, 1263, 1165, 1120, 866, 836, 786, 720; HRMS (ESI–QTOF) calcd. for $C_{25}H_{23}F_3N_3O_4S$ $[M+H]^+$: 518.1361, found 518.1352.

2-(4-Isobutylphenyl)-*N*-(2-methyl-1*H*-indol-5-yl)propenamide (2v).

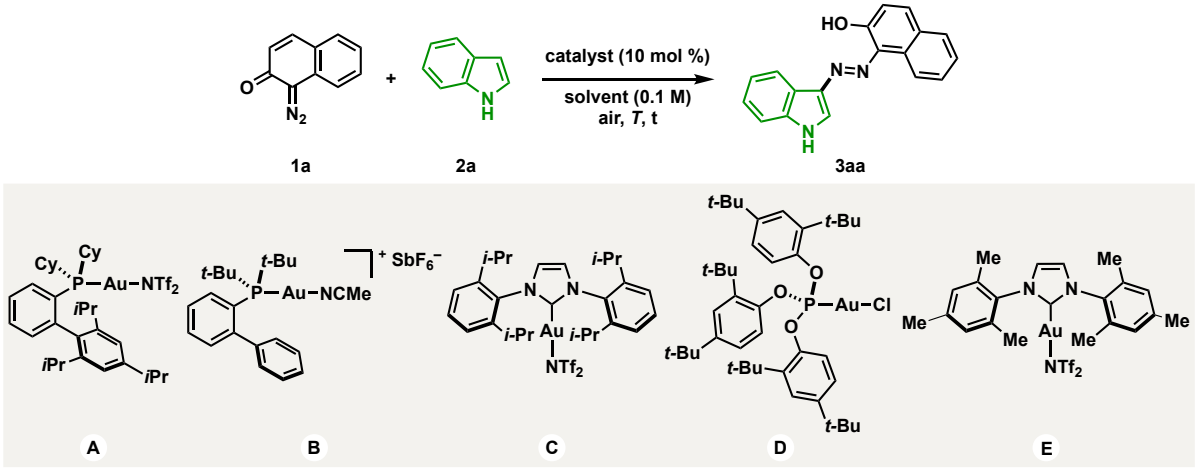


2v

Prepared following the general procedure with 2-methyl-1*H*-indol-5-amine **S21b** and ibuprofen **S27**. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 85:15 to 70:30) to give **2v** as a light-yellow solid (154.9 mg, 92%); m.p. = 61–63 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.20 (br s, 1H), 7.63 – 7.54 (m, 1H), 7.33 – 7.27 (m, 3H), 7.19 – 7.14 (m, 2H), 7.06 – 6.99 (m, 2H), 6.08 (br s, 1H), 3.72 (q, J = 7.2 Hz, 1H), 2.49 (d, J = 7.2 Hz, 2H), 2.33 (s, 3H), 1.89 (thept,

J = 7.2, 6.8 Hz, 1H), 1.61 (d, J = 7.2 Hz, 3H), 0.93 (d, J = 6.7 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 172.9, 140.9, 138.6, 136.4, 133.7, 130.2, 129.8, 129.2, 127.6, 115.0, 111.7, 110.4, 100.3, 47.6, 45.1, 30.3, 22.5, 18.7, 13.7; IR (ATR, $CDCl_3$, ν, cm^{-1}): 3400, 3291, 2954, 1656, 1479, 1231, 776, 734; HRMS (ESI–QTOF) calcd. for $C_{22}H_{27}N_2O$ $[M+H]^+$: 335.2123, found 335.2155.

2.10. General procedure for the optimisation of the reaction conditions



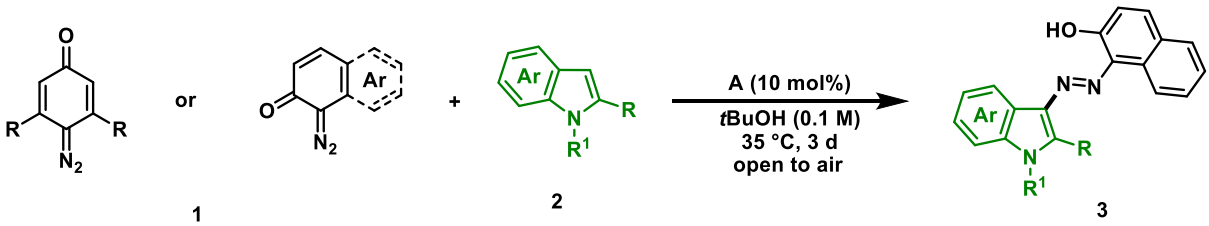
To a 5 mL glass screw cap reaction tube equipped with a magnetic stirrer bar was added 1-diazonaphthalen-2(1*H*)-one **1a** (17.0 mg, 0.10 mmol, 1.00 equiv.), 1*H*-indole **2a** (17.6 mg, 0.15 mmol, 1.50 equiv.), the Brønsted or Lewis acid at the stated catalyst loading and the solvent (1 mL, 0.1 M). The reaction tube was sealed and the mixture was stirred vigorously at the noted temperature and time. On completion, the reaction mixture was diluted with acetone (9 mL), vacuum filtered through a short pad of silica gel (eluent: acetone, 3 × 15 mL) and concentrated *in vacuo*. The resulting mixture was analysed by ^{1}H NMR spectroscopy using 2-(bromomethyl)naphthalene (11.1 mg, 0.05 mmol) as the internal standard in DMSO-d_6 (700 µL, 0.07 M).

Table S1. Additional Catalytic Systems Tested for the Optimisation of the Reaction Conditions[a]

Entry	Catalyst	Yield (%)[b]
1	$Sc(OTf)_2$	–[c]
2	$FeCl_3$	–[c]
3	TFA	–[c]
4	AcOH	–[c]
5	$PTSA{\cdot}H_2O$	–[c]
6	$Cu(OAc)_2$	–[c]
7	$Cu(OTf)_2$	–[c]
8	$Zn(OTf)_2$	–[c]
9	$AgNTf_2$	11
10[d]	**E**	–[e,f]
11[g]	**A**	–[f]
12[g]	–	–[f]

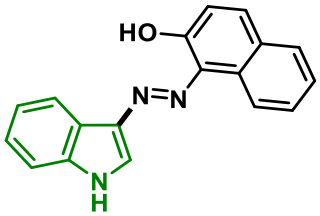
Unless otherwise stated, all reactions were performed with **1a** (0.10 mmol, 1.00 equiv) and **2a** (0.15 mmol, 1.50 equiv), 10 mol % of the Brønsted or Lewis acid in non-distilled solvent (0.1 M, 1.0 mL) open to air at 35 °C for 3 d. Yield determined by ^{1}H NMR measurements with 2-(bromomethyl)naphthalene as the internal standard. No reaction detected by TLC analysis and ^{1}H NMR measurements of the crude reaction mixture. [d] Reaction performed with 5 mol % of NHC-gold(I) complex **E**, di-*tert*-butyl peroxide (1.20 equiv) and 3 Å molecular sieves (50 mg) in dichloromethane (0.1 M) at 25 °C for 3 d. A 5% conversion of **1a** was detected by ^{1}H NMR measurements of the crude reaction mixture. Complex mixture of unknown decomposition products detected based on TLC analysis and ^{1}H NMR measurements of the crude reaction mixture. Reaction performed with benzenediazonium tetrafluoroborate **S15** in place of **1a**. Tf = trifluoromethanesulfonyl; PTSA = *p*-toluenesulfonic acid; TFA = 2,2,2-trifluoroacetic acid.

2.11. General procedure for the preparation of (*E*)-arylazoindoles



Unless otherwise stated, to a 5 mL glass screw cap reaction tube equipped with a magnetic stirrer bar was added diazoquinone **1** (0.10 mmol, 1.00 equiv.), 1*H*-indole **2** (0.15 mmol, 1.50 equiv.) and $XPhosAuNTf_2$ **A** (9.6 mg, 0.01 mmol, 10 mol %) followed by *t*-BuOH (1.0 mL, 0.1 M). The reaction tube was sealed and the mixture stirred vigorously at 35 °C for 3 d. On completion, the reaction mixture was concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate) to deliver the title compound **3**.

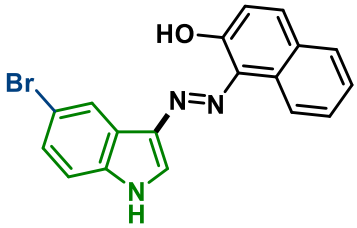
(*E*)-1-((1*H*-Indol-3-yl)diazenyl)naphthalen-2-ol (3aa).



3aa

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 1*H*-indole **2a**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 80:20 to 60:40) to give **3aa** as a dark red solid (24.3 mg, 85%); m.p. = 233–235 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.26 (s, 1H), 12.25 (s, 1H), 8.77 (d, J = 8.4 Hz, 1H), 8.52 (s, 1H), 8.49 (dd, J = 6.9, 1.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.75–7.69 (m, 1H), 7.60–7.53 (m, 1H), 7.52–7.45 (m, 1H), 7.42–7.32 (m, 2H), 7.23 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.0, 137.0, 133.1, 132.1, 131.8, 131.7, 129.1, 128.3, 128.2, 127.7, 124.2, 124.1, 122.9, 121.7, 121.3, 119.8, 118.0, 112.7; IR (ATR, acetone, ν, cm^{-1}): 3393, 1620, 1570, 1525, 1417, 1377, 1243, 1100, 813, 742; HRMS (ESI–TOF) calcd. for $C_{18}H_{14}N_3O$ [M+H]$^+$: 288.1137, found 288.1148.

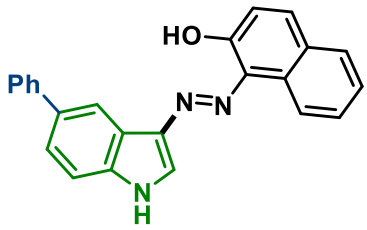
(*E*)-1-((5-Bromo-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ab).



3ab

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-bromo-1*H*-indole **2b**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 80:20:0 to 75:25:5) to give **3ab** as a violet solid (14.7 mg, 40%); m.p. = 245–247 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.04 (s, 1H), 12.40 (s, 1H), 8.65 (d, J = 8.4 Hz, 1H), 8.60 (d, J = 2.0 Hz, 1H), 8.58 (s, 1H), 7.93 (t, J = 8.1 Hz, 2H), 7.70 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.54 (d, J = 8.6 Hz, 1H), 7.51–7.44 (m, 2H), 7.24 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.1, 135.6, 132.8, 132.3, 132.3, 131.6, 129.1, 128.5, 128.2, 127.7, 126.6, 124.2, 123.8, 120.8, 119.8, 119.6, 115.1, 114.8; IR (ATR, acetone, ν, cm^{-1}): 3403, 2922, 1527, 1460, 1420, 1380, 1229, 1178, 813, 745; HRMS (ESI–TOF) calcd. for $C_{18}H_{13}BrN_3O$ [M+H]$^+$: 366.0242, found 366.0242.

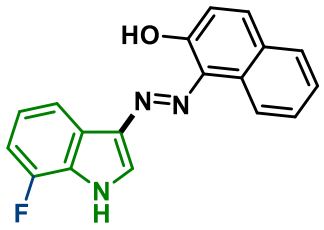
(*E*)-1-((5-Phenyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ac).



3ac

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-phenyl-1*H*-indole **2c**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 80:20:0 to 80:15:5) to give **3ac** as a dark red solid (19.9 mg, 55%); m.p. = 233–235 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.13 (s, 1H), 12.31 (s, 1H), 8.84 (s, 1H), 8.81 (d, J = 8.4 Hz, 1H), 8.55 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 7.4 Hz, 2H), 7.70–7.62 (m, 3H), 7.57 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.0, 141.2, 136.4, 135.1, 133.6, 132.4, 131.9, 131.8, 129.1, 129.1, 128.4, 128.2, 127.4, 127.0, 126.7, 124.18, 123.2, 121.1, 120.0, 119.8, 118.8, 113.2; IR (ATR, acetone, ν, cm^{-1}): 3273, 1524, 1463, 1424, 1240, 816, 743, 696; HRMS (ESI–TOF) calcd. for $C_{24}H_{18}N_3O$ $[M+H]^+$: 364.1450, found 364.1454.

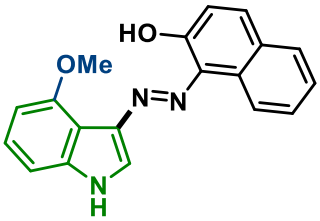
(*E*)-1-((7-Fluoro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ad).



3ad

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 7-fluoro-1*H*-indole **2d**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 80:20:0 to 85:10:5) to give **3ad** as a dark red solid (16.7 mg, 55%); m.p. = 268–270 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.12 (s, 1H), 12.76 (s, 1H), 8.74 (dd, J = 8.4, 1.1 Hz, 1H), 8.61 (s, 1H), 8.28 (dd, J = 7.9, 0.8 Hz, 1H), 7.93 (dt, J = 8.0, 0.6 Hz, 1H), 7.92 (d, J = 8.9 Hz, 1H), 7.72 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.49 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.37 (td, J = 7.9, 4.8 Hz, 1H), 7.24 (d, J = 8.9 Hz, 1H), 7.22 (ddd, J = 11.3, 7.9, 0.8 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 150.2, 149.1 (d, J = 245.8 Hz), 133.6 (d, J = 2.3 Hz), 132.6, 132.3, 131.7, 129.1, 128.3, 128.2, 127.8, 124.7 (d, J = 13.7 Hz), 124.2, 123.5 (d, J = 6.0 Hz), 121.5 (d, J = 4.6 Hz), 121.3, 119.8, 117.8 (d, J = 3.5 Hz), 109.2 (d, J = 15.7 Hz); ^{19}F{^{1}H} NMR (376.5 MHz, DMSO-d_6) δ (ppm): –132.36; IR (ATR, acetone, ν, cm^{-1}): 3259, 1586, 1453, 1231, 1174, 1126, 814, 779, 745; HRMS (ESI–TOF) calcd. for $C_{18}H_{13}FN_3O$ $[M+H]^+$: 306.1048, found 306.1051.

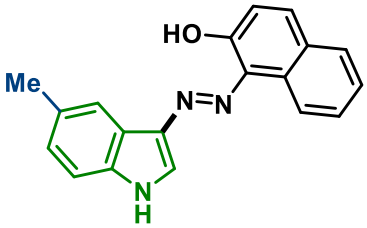
(*E*)-1-((4-Methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ae).



3ae

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 4-methoxy-1*H*-indole **2e**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 70:30:0 to 68:30:2) to give **3ae** as a brown solid (9.6 mg, 30%); m.p. = 216–219 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 15.09 (s, 1H), 12.18 (s, 1H), 8.82 (dd, J = 8.4, 1.3 Hz, 1H), 8.19 (s, 1H), 7.92–7.83 (m, 2H), 7.60 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.44 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.11 (dd, J = 8.2, 0.8 Hz, 1H), 6.77 (dd, J = 7.7, 0.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 153.5, 152.4, 137.2, 132.5, 131.9, 131.8, 129.3, 128.1, 127.9, 127.3, 124.19, 123.8, 121.5, 120.3, 114.3, 113.1, 105.9, 102.2, 55.3; IR (ATR, acetone, ν, cm^{-1}): 3288, 2931, 1595, 1509, 1424, 1363, 1329, 1085, 822, 734; HRMS (ESI–TOF) calcd. for $C_{19}H_{16}N_3O_2$ $[M+H]^+$: 318.1243, found 318.1257.

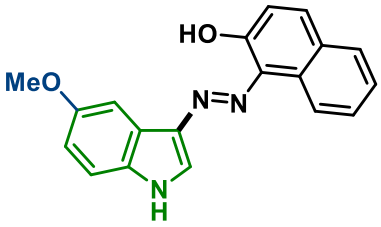
(*E*)-1-((5-Methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3af).



3af

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-methyl-1*H*-indole **2f**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 70:30:0 to 70:28:2) to give **3af** as a dark red solid (23.6 mg, 78%); m.p. = 217–219 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.25 (s, 1H), 12.15 (s, 1H), 8.76 (d, J = 8.5 Hz, 1H), 8.45 (d, J = 3.1 Hz, 1H), 8.28 (s, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.72 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.47 (ddd, J = 8.1, 6.8, 1.0 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.18 (dd, J = 8.2, 1.0 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.0, 135.3, 132.9, 131.9, 131.7, 131.7, 131.6, 129.1, 128.3, 128.2, 127.6, 125.5, 124.0, 121.4, 121.3, 119.7, 118.3, 112.4, 21.6; IR (ATR, acetone, ν, cm^{-1}): 3310, 1525, 1467, 1423, 1379, 1251, 812, 787, 739; HRMS (ESI–TOF) calcd. for $C_{19}H_{16}N_3O$ $[M+H]^+$: 302.1293, found 302.1317.

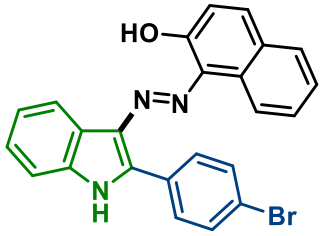
(*E*)-1-((5-Methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ag).



3ag

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-methoxy-1*H*-indole **2g**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 70:30 to 50:50) to give **3ag** as a red solid (28.0 mg, 88%); m.p. = 210–212 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.15 (s, 1H), 12.15 (s, 1H), 8.75 (d, J = 8.5 Hz, 1H), 8.45 (s, 1H), 8.03 (d, J = 2.6 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.68 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.52–7.40 (m, 2H), 7.23 (d, J = 9.0 Hz, 1H), 6.99 (dd, J = 8.8, 2.6 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 156.1, 149.9, 133.2, 132.2, 131.7, 131.6, 131.5, 129.0, 128.3, 128.2, 127.5, 124.0, 121.1, 119.7, 118.5, 113.5, 113.5, 103.7, 55.2; IR (ATR, acetone, ν, cm^{-1}): 3403, 1524, 1468, 1420, 1264, 1240, 1209, 1104, 812, 745; HRMS (ESI–TOF) calcd. for $C_{19}H_{16}N_3O_2$ $[M+H]^+$: 318.1243, found 318.1256.

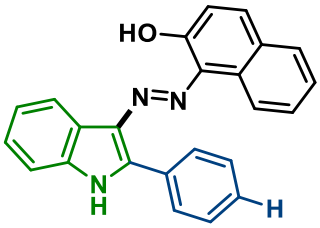
(*E*)-1-((2-(4-Bromophenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ah).



3ah

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-(4-bromophenyl)-1*H*-indole **2h**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 100:0 to 90:10) to give **3ah** as a brown red solid (34.2 mg, 77%); m.p. = 245–247 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.26 (s, 1H), 12.61 (s, 1H), 8.76 (d, J = 8.5 Hz, 1H), 8.57 (dd, J = 8.0, 1.3 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.9 Hz, 1H), 7.90–7.83 (m, 4H), 7.73 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.60–7.57 (m, 1H), 7.49 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.42 (td, J = 7.4, 1.5 Hz, 2H), 7.18 (d, J = 8.9 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm):149.4, 140.4, 136.4, 132.2, 132.1, 131.6, 130.9, 129.7, 129.6, 129.4, 128.4, 128.2, 127.8, 124.9, 124.2, 123.4, 123.3, 122.2, 121.3, 119.5, 118.7, 112.5; IR (ATR, acetone, ν, cm^{-1}): 3402, 1480, 1452, 1429, 1373, 1243, 819, 746; HRMS (ESI–TOF) calcd. for $C_{24}H_{17}BrN_3O$ $[M+H]^+$: 442.0555, found 442.0560.

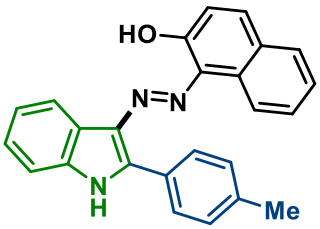
(*E*)-1-((2-Phenyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ai).



3ai

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-phenyl-1*H*-indole **2i**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 95:5 to 90:10) to give **3ai** as a brown solid (29.2 mg, 80%); m.p. = 139–141 °C; ^{1}H NMR (600 MHz, acetone-d_6) δ (ppm): 14.27 (s, 1H), 11.45 (s, 1H), 8.93 (d, J = 8.4 Hz, 1H), 8.75 (dd, J = 6.8, 2.2 Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.67–7.56 (m, 4H), 7.47 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H), 7.45–7.37 (m, 2H), 7.14 (d, J = 8.9 Hz, 1H); ^{13}C NMR (151 MHz, acetone-d_6) δ (ppm): 150.9, 142.4, 137.6, 133.4, 132.9, 131.7, 131.1, 131.1, 130.5, 130.1, 129.9, 129.6, 129.1, 128.3, 125.5, 124.9, 124.0, 123.7, 122.7, 120.6, 120.5, 113.0; IR (ATR, acetone-d_6, ν, cm^{-1}): 3401, 3303, 2924, 1456, 1420, 1374, 1244, 818, 746, 696; HRMS (ESI–TOF) calcd. for $C_{24}H_{18}N_3O$ $[M+H]^+$: 364.1450, found 364.1482.

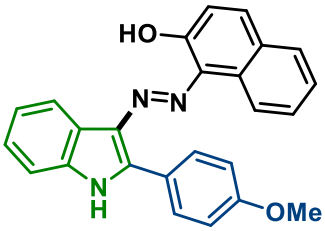
(*E*)-1-((2-(4-Methylphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aj).



3aj

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-(4-methylphenyl)-1*H*-indole **2j**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 100:0 to 90:10) to give **3aj** as a green-red metallic luster solid (36.2 mg, 96%); m.p. = 234–236 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.32 (s, 1H), 12.50 (s, 1H), 8.77 (d, J = 8.5 Hz, 1H), 8.58 (dd, J = 6.6, 1.7 Hz, 1H), 7.92 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.77–7.68 (m, 1H), 7.57 (dd, J = 6.8, 1.9 Hz, 1H), 7.51–7.34 (m, 5H), 7.17 (d, J = 8.9 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 149.3, 142.1, 139.6, 136.3, 131.8, 131.6, 129.7, 129.7, 129.3, 128.9, 128.3, 128.2, 127.7, 127.3, 124.6, 124.1, 123.2, 122.1, 121.3, 119.6, 118.9, 112.4, 21.0; IR (ATR, acetone, ν, cm^{-1}): 3397, 3298, 2954, 2922, 1494, 1453, 1430, 1370, 1243, 817, 747; HRMS (ESI–TOF) calcd. for $C_{25}H_{20}N_3O$ $[M+H]^+$: 378.1607, found 378.1602.

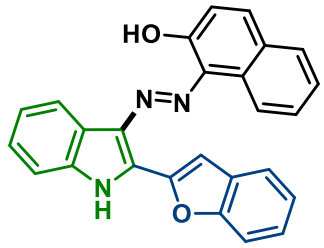
(*E*)-1-((2-(4-Methoxyphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ak).



3ak

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-(4-methoxylphenyl)-1*H*-indole **2k**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 90:10 to 80:20) to give **3ak** as a red solid (39.3 mg, 99%); m.p. = 204–206 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.32 (s, 1H), 12.44 (s, 1H), 8.77 (d, J = 8.4 Hz, 1H), 8.57 (dd, J = 7.0, 1.8 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 7.90–7.84 (m, 3H), 7.72 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.55 (dd, J = 6.8, 1.5 Hz, 1H), 7.48 (ddd, J = 8.1, 6.8, 1.1 Hz, 1H), 7.45–7.33 (m, 2H), 7.21 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 8.9 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 160.5, 149.2, 142.1, 136.3, 131.6, 131.6, 130.4, 129.7, 129.1, 128.3, 128.2, 127.6, 124.5, 124.0, 123.1, 122.4, 122.0, 121.3, 119.6, 119.0, 114.7, 112.3, 55.5; IR (ATR, acetone, ν, cm^{-1}): 3399, 3314, 2924, 1609, 1493, 1454, 1371, 1248, 1178, 818, 747; HRMS (ESI–TOF) calcd. for $C_{25}H_{20}N_3O_2$ $[M+H]^+$: 394.1556, found 394.1556.

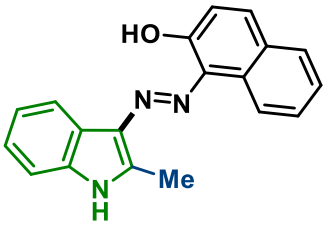
(*E*)-1-((2-(Benzofuran-2-yl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3al).



3al

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-(benzofuran-2-yl)-1*H*-indole **2l**. Reaction time: 3 d. Purified twice by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 90:10:0 to 70:29:1) to give **3al** as a dark red solid (19.7 mg, 49%); m.p. = 246–248 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.85 (s, 1H), 12.79 (s, 1H), 8.80 (d, J = 8.3 Hz, 1H), 8.61–8.58 (m, 1H), 7.97–7.93 (m, 2H), 7.86 (dt, J = 7.7, 1.0 Hz, 1H), 7.75 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.72–7.69 (m, 2H), 7.62–7.58 (m, 1H), 7.50 (dtd, J = 8.3, 6.7, 1.2 Hz, 2H), 7.46–7.42 (m, 2H), 7.38 (ddd, J = 7.9, 7.3, 1.0 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 155.1, 150.2, 147.6, 137.3, 132.6, 131.9, 130.2, 130.0, 129.6, 128.4, 128.2, 127.8, 127.7, 126.2, 125.6, 124.2, 124.0, 123.4, 122.6, 122.1, 121.3, 120.0, 118.3, 112.4, 111.2, 106.9; IR (ATR, acetone, ν, cm^{-1}): 3389, 3058, 2920, 1566, 1431, 1368, 1243, 849, 813, 739; HRMS (ESI–TOF) calcd. for $C_{26}H_{18}N_3O_2$ $[M+H]^+$: 404.1399, found 404.1399.

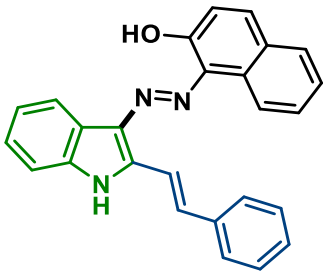
(*E*)-1-((2-Methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3am).



3am

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-methyl-1*H*-indole **2m**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 50:50 to 0:100) to give **3am** as a red solid (29.9 mg, 99%); m.p. = 255–258 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.53 (s, 1H), 12.21 (s, 1H), 8.76 (d, J = 8.4 Hz, 1H), 8.44 (d, J = 7.6 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.70 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.49–7.44 (m, 2H), 7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.29 (td, J = 7.6, 1.4 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.0, 142.5, 135.8, 131.6, 131.2, 129.7, 129.4, 128.2, 128.2, 127.5, 124.0, 123.6, 122.8, 121.4, 121.1, 119.6, 118.7, 111.9, 11.4; IR (ATR, acetone, ν, cm^{-1}): 3385, 2923, 1548, 1459, 1423, 1375, 1245, 957, 814, 744; HRMS (ESI–QTOF) calcd. for $C_{19}H_{16}N_3O$ $[M–H]^-$: 300.1137, found 300.1216.

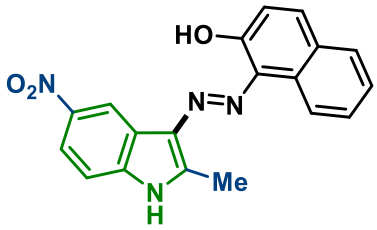
1-((*E*)-(2-((*E*)-Styryl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3an).



3an

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and (*E*)-2-styryl-1*H*-indole **2n**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 90:10:0 to 70:28:2) to give **3an** as a dark red solid (38.4 mg, 98%); m.p. = 223–225 °C (decomp.); ^{1}H NMR (600 MHz, DMSO) δ (ppm): 14.70 (s, 1H), 12.43 (s, 1H), 8.77 (d, J = 7.4 Hz, 1H), 8.51–8.47 (m, 1H), 7.94–7.90 (m, 2H), 7.73 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.69–7.65 (m, 2H), 7.62 (d, J = 16.5 Hz, 1H), 7.56 (d, J = 16.5 Hz, 1H), 7.54–7.47 (m, 4H), 7.44–7.36 (m, 3H), 7.28 (d, J = 8.9 Hz, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 150.4, 139.0, 137.4, 136.0, 133.2, 132.1, 131.6, 130.8, 130.0, 129.2, 129.1, 128.4, 128.3, 127.8, 126.9, 125.4, 124.2, 123.0, 122.1, 121.3, 119.6, 118.5, 114.2, 112.1; IR (ATR, acetone, ν, cm^{-1}): 3392, 3051, 1520, 1457, 1238, 945, 813, 745, 693; HRMS (ESI–TOF) calcd. for $C_{26}H_{20}N_3O$ $[M+H]^+$: 390.1606, found 390.1560.

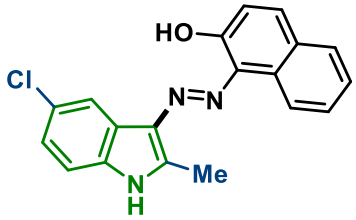
(*E*)-1-((2-Methyl-5-nitro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ao).



3ao

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-methyl-5-nitro-1*H*-indole **2o**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 80:20 to 60:40) to provide **3ao** as a red solid (14.0 mg, 40%); m.p. = 296–298 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.20 (s, 1H), 12.77 (s, 1H), 9.33 (d, J = 2.4 Hz, 1H), 8.76 (d, J = 8.4 Hz, 1H), 8.17 (dd, J = 8.9, 2.4 Hz, 1H), 7.99–7.91 (m, 2H), 7.71 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 7.65 (d, J = 8.9 Hz, 1H), 7.51 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.26 (d, J = 9.0 Hz, 1H), 2.77 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.4, 145.0, 142.8, 138.7, 132.5, 131.6, 130.2, 129.3, 128.4, 128.2, 127.6, 124.2, 120.9, 119.6, 118.7, 118.0, 117.4, 112.3, 11.5; IR (ATR, acetone, ν, cm^{-1}): 3256, 1619, 1559, 1458, 1331, 1303, 1246, 842, 812, 737; HRMS (ESI–TOF) calcd. for $C_{19}H_{15}N_4O_3$ $[M+H]^+$: 347.1144, found 347.1153.

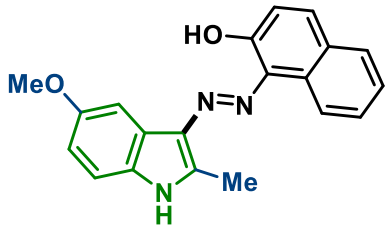
(*E*)-1-((5-Chloro-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ap).



3ap

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-chloro-2-methyl-1*H*-indole **2p**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) to give **3ap** as a red solid (33.0 mg, 98%); m.p. = 238–240 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.32 (s, 1H), 12.39 (s, 1H), 8.65 (d, J = 8.3 Hz, 1H), 8.38 (d, J = 2.1 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.9 Hz, 1H), 7.71 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.48 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.31 (dd, J = 8.5, 2.1 Hz, 1H), 7.24 (d, J = 8.9 Hz, 1H), 2.72 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 150.1, 143.8, 134.2, 131.7, 131.5, 129.3, 129.0, 128.4, 128.2, 127.6, 126.9, 124.1, 123.4, 120.9, 120.1, 119.7, 119.6, 113.6, 11.5; IR (ATR, acetone, ν, cm^{-1}): 3390, 2922, 1468, 1446, 1424, 1376, 1239, 817, 799, 748; HRMS (ESI–TOF) calcd. for $C_{19}H_{15}ClN_3O$ $[M+H]^+$: 336.0904, found 336.0904.

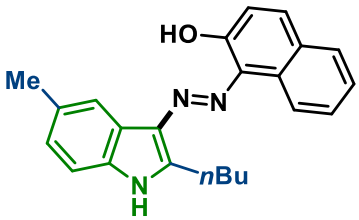
(*E*)-1-((5-Methoxy-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aq).



3aq

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 5-methoxy-2-methyl-1*H*-indole **2q**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 90:10:0 to 90:7:3) to give **3aq** as a red solid (32.9 mg, 99%); m.p. = 224–226 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.41 (s, 1H), 12.11 (s, 1H), 8.74 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 2.6 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.67 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H), 7.46 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.23 (d, J = 8.9 Hz, 1H), 6.92 (dd, J = 8.7, 2.6 Hz, 1H), 3.92 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 156.0, 149.8, 142.6, 131.5, 130.9, 130.4, 129.8, 129.3, 128.3, 128.2, 127.3, 123.9, 121.1, 119.6, 119.2, 112.6, 112.2, 103.8, 55.2, 11.4; IR (ATR, acetone, ν, cm^{-1}): 3378, 2924, 1591, 1468, 1434, 1374, 1267, 1208, 813, 747; HRMS (ESI–TOF) calcd. for $C_{20}H_{18}N_3O_2$ $[M+H]^+$: 332.1399, found 332.1412.

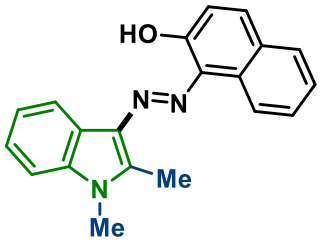
(*E*)-1-((2-Butyl-5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ar).



3ar

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-butyl-5-methyl-1*H*-indole **2r**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100:0 to 99:1) to give **3ar** as a red solid (35.4 mg, 99%); m.p. = 192–193 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.56 (s, 1H), 12.09 (s, 1H), 8.75 (d, J = 8.4 Hz, 1H), 8.25 (s, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.71 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.47 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H), 7.36 (d, J = 8.2 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.13 (dd, J = 8.2, 1.7 Hz, 1H), 3.07 (t, J = 7.5 Hz, 2H), 2.52 (s, 3H), 1.88–1.73 (m, 2H), 1.41 (sext, J = 7.4 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 149.9, 146.4, 134.1, 131.5, 131.5, 131.0, 129.4, 129.1, 128.2, 128.2, 127.4, 124.9, 123.9, 121.3, 121.2, 119.6, 118.9, 111.7, 30.9, 25.4, 21.9, 21.6, 13.6; ; IR (ATR, acetone, ν, cm^{-1}): 3361, 2919, 1537, 1459, 1431, 1376, 1240, 1181, 1017, 823, 799, 738; HRMS (ESI–TOF) calcd. for $C_{23}H_{24}N_3O$ $[M+H]^+$: 358.1919, found 358.1932.

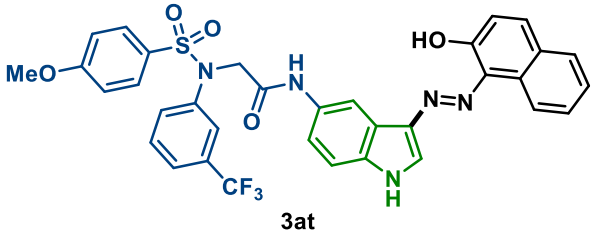
(*E*)-1-((1,2-Dimethyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3as).



3as

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 1,2-dimethyl-1*H*-indole **2s**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 80:20) to give **3as** as a red solid (15.1 mg, 48%); m.p. = 236–238 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ(ppm): 14.49 (s, 1H), 8.73 (d, J = 8.4 Hz, 1H), 8.48–8.44 (m, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.69 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.46 (ddd, J = 8.0, 6.8, 1.2 Hz, 1H), 7.39 (td, J = 7.4, 1.2 Hz, 1H), 7.35 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.21 (d, J = 8.9 Hz, 1H), 3.80 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ(ppm): 149.9, 143.8, 137.2, 131.5, 131.2, 129.5, 129.4, 128.3, 128.2, 127.5, 124.0, 123.7, 123.2, 121.4, 121.2, 119.6, 118.1, 110.6, 30.2, 10.2; IR (ATR, acetone, ν, cm^{-1}): 3052, 2923, 1530, 1469, 1408, 1366, 1327, 1253, 1064, 818, 735; HRMS (ESI–TOF) calcd. for $C_{20}H_{18}N_3O$ [M+H]$^+$: 316.1444, found 316.1462.

(*E*)-*N*-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (3at).

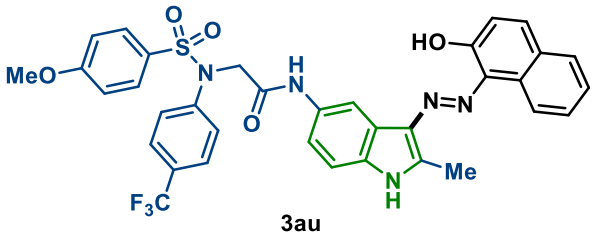


3at

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and *N*-(1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido) acetamide **2t**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate/dichloromethane = 90:10:0 to 70:30:0 then to 40:30:30) to give **3at** as a red solid (30.6 mg, 45%); m.p. = 224–226 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ(ppm): 14.21 (s, 1H), 12.18 (br s, 1H), 10.25 (s, 1H), 9.19 (d, J = 1.8 Hz, 1H), 9.01 – 8.96 (m, 1H), 8.47 (s, 1H), 7.92 – 7.85 (m, 2H), 7.78 (t, J = 2.0 Hz, 1H), 7.69 – 7.65 (m, 4H), 7.64 – 7.59 (m, 1H), 7.49 (dd, J = 8.7, 0.6 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.27 (dd, J = 8.7, 2.1 Hz, 1H), 7.22 (d, J = 8.9 Hz, 1H), 7.08 – 7.04 (m, 2H), 4.70 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 165.6, 162.9, 149.9, 141.2, 134.3, 133.4, 133.3, 132.3, 131.7, 131.2, 130.2, 129.7, 129.6 (q, J = 32.0 Hz), 129.5, 129.1, 128.1, 128.0, 127.5, 124.5 (q, J = 3.9 Hz), 124.0 (q, J = 3.8 Hz), 123.9, 123.7 (q, J = 272.5 Hz), 122.4, 119.6, 118.0, 116.7, 114.5, 112.7, 112.4, 55.7, 53.5;

$^{19}F\{^{1}H\}$ NMR (376.5 MHz, DMSO-d_6) δ(ppm): –61.14; IR (ATR, methanol, ν, cm^{-1}): 3367,3303, 1676, 1594, 1333, 1262, 1150, 1127, 1092, 809; HRMS (ESI–QTOF) calcd. for $C_{34}H_{27}F_3N_5O_5S$ $[M+H]^+$: 674.1685, found 674.1703.

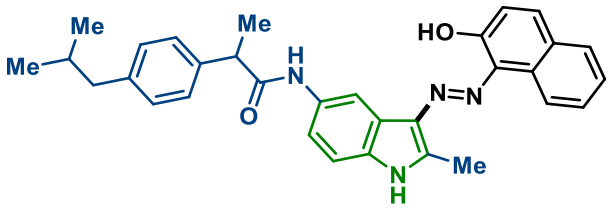
(*E*)-*N*-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (3au).



3au

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide **2u**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 80:20 to 50:50) to give **3au** as an orange solid (60.6 mg, 88%); m.p. = 276–278 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ(ppm): 14.46 (s, 1H), 12.15 (s, 1H), 10.23 (s, 1H), 9.18 – 9.08 (m, 1H), 9.03 – 8.93 (m, 1H), 7.93 – 7.87 (m, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.9 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.46 – 7.38 (m, 3H), 7.29 – 7.18 (m, 2H), 7.11 – 7.04 (m, 2H), 4.71 (s, 2H), 3.78 (s, 3H), 2.70 (s, 3H); ^{13}C NMR analysis shows two sets of signals, which indicate the presence of rotamers (denoted as α and β); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 165.4 (α), 165.3 (β), 162.9 (α), 149.9 (α), 149.3 (β), 144.2 (α), 142.8 (β), 142.7 (α), 134.2 (α), 134.1 (β), 132.1 (α), 131.6 (β), 131.6 (α), 131.1 (α), 131.1 (β), 130.2 (β), 129.9 (α), 129.7 (α), 129.6 (α), 129.4 (α), 129.4 (β), 128.2 (β), 128.1 (α), 127.9 (α), 127.4 (α), 127.1 (α), 126.9 (q, J = 32.0 Hz, α), 126.0 (q, J = 3.7 Hz, α), 124.0 (q, J = 272.0 Hz, α), 123.8 (α), 122.5 (β), 122.4 (α), 119.5 (α), 119.3 (β), 118.7 (α), 118.7 (β), 115.9 (α), 115.8 (β), 114.6 (α), 112.1 (α), 112.0 (β), 111.9 (α), 55.7 (α), 53.0 (α), 52.9 (β), 11.4 (α); $^{19}F\{^{1}H\}$ NMR (376.5 MHz, DMSO-d_6) δ (ppm): –60.81; IR (ATR, acetone, ν, cm^{-1}): 3286, 3249, 1687, 1662, 1333, 1261, 1152, 1124, 878; HRMS (ESI–TOF) calcd. for $C_{35}H_{29}F_3N_5O_5S$ $[M+H]^+$: 688.1841, found 688.1814.

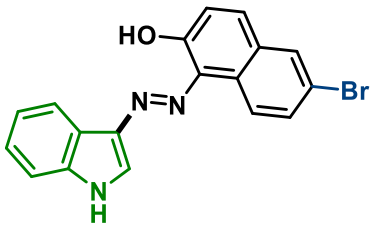
(*E*)-*N*-(3-((2-Hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-(4-isobutylphenyl)propanamide (3av).



3av

Prepared following the general procedure with 1-diazonaphthalen-2(1*H*)-one **1a** and 2-(4-isobutylphenyl)-*N*-(2-methyl-1*H*-indol-5-yl)propenamide **2v**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 90:10 to 70:30) to give **3av** as a red solid (41.2 mg, 82%); m.p. = 237–239 °C (decomp.); ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.46 (s, 1H), 12.12 (br s, 1H), 10.12 (s, 1H), 9.13 (d, J = 2.1 Hz, 1H), 9.06 (d, J = 8.5 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.9 Hz, 1H), 7.68 (ddd, J = 8.5, 6.8, 1.4 Hz, 1H), 7.50 (t, J = 7.4 Hz, 1H), 7.42 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 7.27 (dd, J = 8.7, 2.1 Hz, 1H), 7.22 (d, J = 8.7 Hz, 1H), 7.13 (d, J = 7.8 Hz, 2H), 3.88 (q, J = 7.0 Hz, 1H), 2.70 (s, 3H), 2.39 (d, J = 7.1 Hz, 2H), 1.78 (tsep, J = 7.1, 6.7 Hz, 1H), 1.51 (d, J = 7.0 Hz, 3H), 0.82 (d, J = 6.7 Hz, 6H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 172.0, 149.8, 142.5, 139.6, 139.4, 134.7, 131.9, 131.6, 131.1, 130.0, 129.4, 128.9, 128.2, 128.0, 127.4, 127.1, 124.0, 122.6, 119.5, 118.7, 116.3, 112.5, 111.7, 45.7, 44.2, 29.6, 22.2, 19.0, 11.4; IR (ATR, acetone, ν, cm^{-1}): 3232, 2955, 1655, 1467, 1426, 1374, 1244, 1025, 1008, 817, 751; HRMS (ESI–TOF) calcd. for $C_{32}H_{33}N_4O_2$ [M+H]$^+$: 505.2604, found 505.2599.

(*E*)-1-((1*H*-Indol-3-yl)diazenyl)-6-bromonaphthalen-2-ol (3ba).

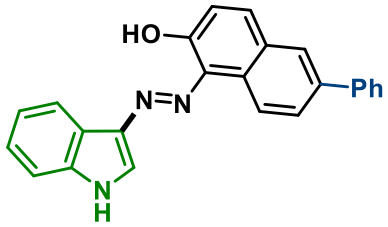


3ba

Prepared following the general procedure with 6-bromo-1-diazonaphthalen-2(1*H*)-one **1b** and 1*H*-indole **2a**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 70:30 to 50:50) to give **3ba** as a violet solid (28.8 mg, 79%); m.p. = 254–255 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.21 (s, 1H), 12.30 (s, 1H), 8.67 (d, J = 9.0 Hz, 1H), 8.54 (s, 1H), 8.48–8.40 (m, 1H), 8.19 (d, J = 2.1 Hz, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.80 (dd, J = 9.0, 2.1 Hz, 1H), 7.59–7.52 (m, 1H), 7.42–7.33 (m, 2H), 7.28 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.2, 137.0, 133.1, 132.7, 130.7, 130.3, 130.3, 130.0, 129.4, 129.1, 124.3, 123.8, 123.0, 121.7, 121.1, 118.0, 116.9, 112.8; IR (ATR, acetone, ν, cm^{-1}): 3309, 1586, 1527,

1430, 1387, 1244, 976, 817, 741; HRMS (ESI–TOF) calcd. for $C_{18}H_{13}BrN_3O$ $[M+H]^+$: 366.0237, found 366.0215.

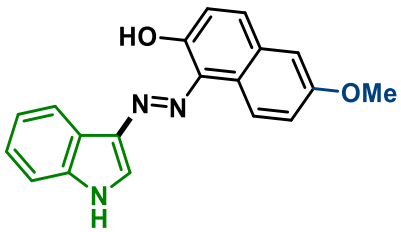
(*E*)-1-((1*H*-Indol-3-yl)diazenyl)-6-phenylnaphthalen-2-ol (3ca).



3ca

Prepared following the general procedure with 1-diazo-6-phenylnaphthalen-2(1*H*)-one **1c** and 1*H*-indole **2a**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 70:30 to 50:50) to give **3ca** as a black solid (15.5 mg, 43%); m.p. = 254–257 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 14.25 (s, 1H), 12.28 (s, 1H), 8.84 (d, J = 8.8 Hz, 1H), 8.57–8.49 (m, 2H), 8.24 (d, J = 2.0 Hz, 1H), 8.06 (dd, J = 8.8, 2.0 Hz, 1H), 7.98 (d, J = 8.9 Hz, 1H), 7.89–7.82 (m, 2H), 7.57 (dd, J = 6.8, 1.2 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.44–7.34 (m, 3H), 7.27 (d, J = 8.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 150.2, 139.8, 137.0, 135.6, 133.2, 132.2, 132.2, 130.9, 129.1, 129.0, 128.5, 127.4, 126.7, 126.6, 125.8, 124.2, 122.9, 122.1, 121.7, 120.2, 118.0, 112.8; IR (ATR, acetone, ν, cm^{-1}): 3211, 1434, 1398, 1294, 1240, 1151, 1121, 805, 755, 729, 689; HRMS (ESI–TOF) calcd. for $C_{24}H_{18}N_3O$ $[M+H]^+$: 364.1444, found 364.1465.

(*E*)-1-((1*H*-Indol-3-yl)diazenyl)-6-methoxynaphthalen-2-ol (3da).

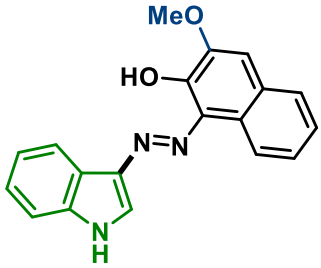


3da

Prepared following the general procedure with 1-diazo-6-methoxynaphthalen-2(1*H*)-one **1d** and 1*H*-indole **2a**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 80:20:0 to 60:35:5) to give **3da** as a black solid (14.3 mg, 45%); m.p. = 221–223 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 13.94 (s, 1H), 12.24 (s, 1H), 8.67 (d, J = 8.9 Hz, 1H), 8.50 (s, 1H), 8.46 (dd, J = 6.5, 1.8 Hz, 1H), 7.80 (d, J = 9.0 Hz, 1H), 7.55 (dd, J = 7.7, 1.5 Hz, 1H), 7.44–7.31 (m, 4H), 7.19 (d, J = 9.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 156.0, 148.2, 137.0, 133.2, 132.1, 130.7, 129.5, 129.2, 126.7, 124.2, 123.0, 122.8, 121.7, 120.1, 119.5, 118.0, 112.70, 107.1, 55.2; IR (ATR, acetone, ν, cm^{-1}): 3324, 1596, 1526, 1425,

1241, 1159, 1116, 1031, 822, 734; HRMS (ESI–TOF) calcd. for $C_{19}H_{16}N_3O_2$ $[M+H]^+$: 318.1237, found 318.1184.

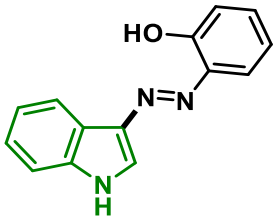
(*E*)-1-((1*H*-Indol-3-yl)diazenyl)-3-methoxynaphthalen-2-ol (3ea).



3ea

Prepared following the general procedure with 1-diazo-3-methoxynaphthalen-2(1*H*)-one **1e** and 1*H*-indole **2a**. Reaction time: 3 d. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 47.5:50:2.5 to 40:50:10) to give **3ea** as a dark brown solid (10.4 mg, 33%); m.p. = 248–249 °C; ^{1}H NMR (600 MHz, DMSO-d_6) δ (ppm): 14.71 (s, 1H), 12.27 (s, 1H), 8.64 (d, J = 8.3 Hz, 1H), 8.52 (d, J = 3.1 Hz, 1H), 8.46 (dd, J = 7.3, 0.9 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.59–7.53 (m, 2H), 7.47–7.42 (m, 2H), 7.42–7.33 (m, 2H), 3.97 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ (ppm): 148.6, 143.0, 137.0, 132.7, 132.0, 129.2, 127.6, 127.0, 126.9, 125.1, 124.4, 124.2, 122.9, 121.6, 121.0, 118.0, 112.8, 109.3, 55.9; IR (ATR, acetone, ν, cm^{-1}): 3304, 1471, 1414, 1267, 1240, 1106, 825, 740, 714; HRMS (ESI–TOF) calcd. for $C_{19}H_{16}N_3O_2$ $[M+H]^+$: 318.1237, found 318.1286.

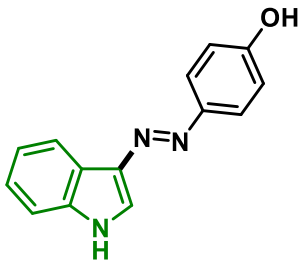
(*E*)-2-((1*H*-Indol-3-yl)diazenyl)phenol (3fa).[S36]



3fa

Prepared following the general procedure with 6-diazocyclohexa-2,4-dien-1-one **1f** and 1*H*-indole **2a**. Reaction time: 3 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane = 80:20 to 50:50) to give **3fa** as a red solid (21.2 mg, 89%); m.p. = 170–171 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.14 (br s, 1H), 11.87 (br s, 1H), 8.44–8.40 (m, 2H), 7.78 (dd, J = 7.9, 1.7 Hz, 1H), 7.50 (dd, J = 7.5, 1.3 Hz, 1H), 7.30 (td, J = 7.2, 1.4 Hz, 1H), 7.25 (td, J = 7.7, 1.6 Hz, 2H), 7.04–6.95 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 152.1, 138.2, 136.7, 133.7, 132.5, 130.3, 126.83, 124.0, 122.6, 122.2, 119.7, 118.2, 117.6, 112.4; IR (ATR, acetone, ν, cm^{-1}): 3394, 1524, 1480, 1424, 1390, 1268, 1245, 1103, 746; HRMS (ESI–TOF) calcd. for $C_{14}H_{12}N_3O$ $[M+H]^+$: 238.0975, found 238.0985.

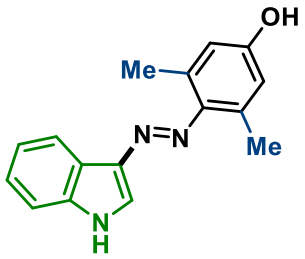
(*E*)-4-((1*H*-Indol-3-yl)diazenyl)phenol (3ga).[S36]



3ga

Prepared following the general procedure with 4-diazocyclohexa-2,5-dien-1-one **1g**, 1*H*-indole **2a** and XPhosAuNTf$_2$ **A** (4.8 mg, 5 mol %). Reaction time: 2 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 72.5:25:2.5 to 65:25:10) to give **3ga** as a dark brown solid (21.1 mg, 88%); m.p. = 211–214 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 11.90 (s, 1H), 9.87 (s, 1H), 8.38 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 3.0 Hz, 1H), 7.74–7.65 (m, 2H), 7.50–7.43 (m, 1H), 7.25 (td, J = 8.1, 7.6, 1.5 Hz, 1H), 7.20 (td, J = 7.5, 1.3 Hz, 1H), 6.92–6.86 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 158.6, 146.3, 136.5, 135.1, 131.6, 123.5, 123.0, 122.2, 122.0, 118.3, 115.6, 112.1; IR (ATR, acetone, ν, cm^{-1}): 3248, 1581, 1500, 1386, 1230, 1125, 1107, 834, 744, 673; HRMS (ESI–TOF) calcd. for $C_{14}H_{12}N_3O$ $[M+H]^+$: 238.0975, found 238.0992.

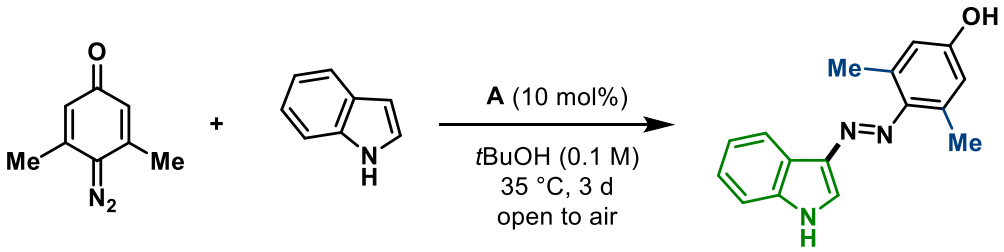
(*E*)-4-((1*H*-Indol-3-yl)diazenyl)-3,5-dimethylphenol (3ha).



3ha

Prepared following the general procedure with 4-diazo-3,5-dimethylcyclohexa-2,5-dien-1-one **1h**, 1*H*-indole **2a** and XPhosAuNTf$_2$ **A** (4.8 mg, 5 mol %). Reaction time: 3 h. Purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) to give **3ha** as a dark orange solid (26.4 mg, 99%); m.p. = 194–196 °C (decomp.); ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 10.91 (br s, 1H), 8.45–8.39 (m, 1H), 8.34 (s, 1H), 8.14 (d, J = 3.0 Hz, 1H), 7.55–7.48 (m, 1H), 7.24 (pd, J = 7.1, 1.4 Hz, 2H), 6.64 (s, 2H), 2.45 (s, 6H); ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 157.1, 145.7, 137.7, 137.5, 134.0, 131.6, 124.4, 123.2, 123.0, 119.5, 116.6, 112.7, 20.4; IR (ATR, acetone-d_6, ν, cm^{-1}): 3367, 3212, 2922, 1400, 1311, 1245, 1191, 1092, 1027, 856, 751, 718; HRMS (ESI–TOF) calcd. for $C_{16}H_{16}N_3O$ $[M+H]^+$: 266.1288, found 266.1260.

2.7. Procedure for the 2 mmol scale preparation of (*E*)-4-((1*H*-indol-3-yl)diazenyl)-3,5-dimethylphenol (3ha)

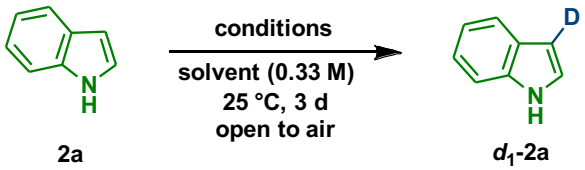


1h (2.00 mmol) **2a** (3.00 mmol) **3ha** (1.66 mmol, 442.1 mg)

To a round bottom flask equipped with a magnetic stirrer bar was added 4-diazo-3,5-dimethylcyclohexa-2,5-dien-1-one **1h** (296.3 mg, 2.00 mmol, 1.00 equiv.), 1*H*-indole **2a** (351.5 mg, 3.00 mmol, 1.50 equiv.) and XPhosAuNTf$_2$ **A** (19.1 mg, 0.02 mmol, 1 mol %), followed by *t*-BuOH (20.0 mL, 0.1 M). The reaction flask was sealed and the mixture was stirred vigorously at 35 °C for 3 d. On completion, the reaction mixture was concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 90:10 to 80:20) to give **3ha** as a dark orange solid (442.1 mg, 83%).

3. Control experiments

3.1. Deuterium-labelling studies with gold(I) phosphine complex A and 1*H*-indole 2a.



Set-up: to a 5 mL round-bottom flask equipped with a magnetic stirrer was added 1*H*-indole (23.5 mg, 0.20 mmol, 1.00 equiv.) and XPhosAuNTf$_2$ **A** (9.5 mg, 0.01 mmol, 5 mol %) followed by CD_3OD (0.5 mL). The reaction mixture was stirred vigorously at 25 °C and the reaction progress was monitored by ^{1}H NMR measurements. After 3 d, the solvent was removed *in vacuo* and the resulting crude residue was redissolved in dichloromethane (5 mL), vacuum filtered through a short pad of silica gel (eluent: dichloromethane, 3 mL). The filtrate was concentrated *in vacuo* and purified by silica gel flash column chromatography (eluent: petroleum ether/ethyl acetate = 90:10) to give the deuterated product ***d*$_1$-2a**. The degree of deuteration was determined by ^{1}H NMR integration of the 1*H*-indolyl C3 proton at 6.59 ppm relative to the non-exchangeable signal at 7.68 ppm, wich showed 70% deuterium incorporation. The reaction was also run in CD_2Cl_2 and $CDCl_3$ in place of CD_3OD, but no deuterium exchange was detected by ^{1}H NMR analysis. The reaction was performed a further two times but in the absence of the group 11 metal complex in CD_3OD (0.5 mL) and in a mixture of $CDCl_3/D_2O$ (0.5 mL, v/v = 1:1). Under these latter two reaction conditions, no deuterium incorporation could be observed by ^{1}H NMR measurements.

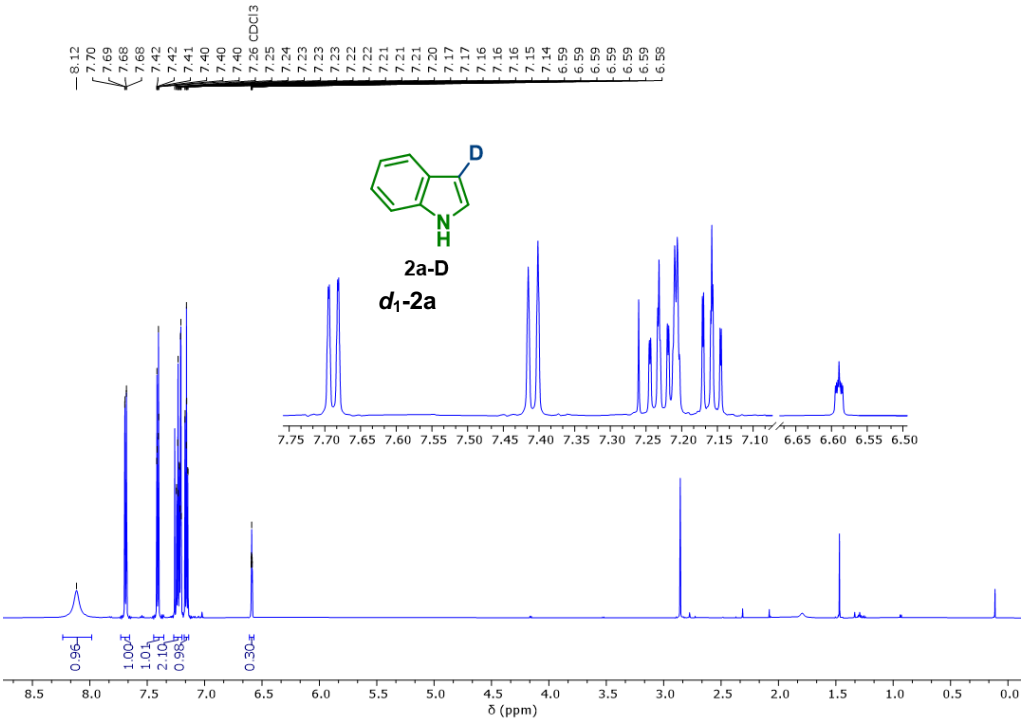


Figure S1. ^{1}H NMR spectrum of 1*H*-indole ***d*$_1$-2a**.

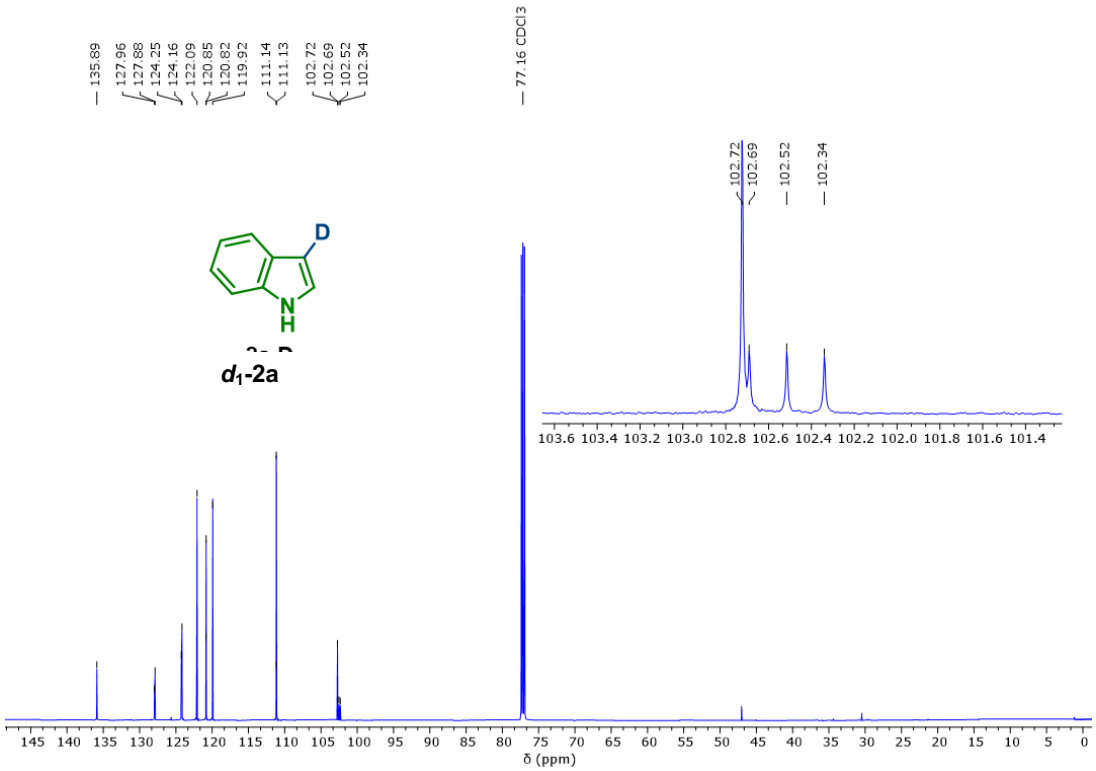


Figure S2. [1] C NMR spectrum of 1*H*-indole ***d*$_1$-2a**.

3.2. General procedures for the NMR measurement experiments.

General procedure A (for sealed capillary set-up): A melting point capillary tube was charged with a solution of dibromomethane in CD_3OD (50 μL, 2 M) and then the open end was sealed by using a flame torch to give an enclosed solution in the capillary tube for use as an external standard for quantification in ^1H NMR measurements. A solution of $XPhosAuNTf_2$ **A** in CD_3OD (0.05 M) was used instead for external standard referencing in $^{31}P\{^1H\}$ NMR measurements.

General procedure B (for stoichiometric reaction set-up): To an Eppendorf tube was added 1*H*-indole **2a** (1.2 mg, 0.01 mmol, 1.00 equiv.) and $XPhosAuNTf_2$ **A** (9.6 mg, 0.01 mmol, 1.00 equiv.) followed by CD_3OD (0.3 mL). The mixture was homogenised, then transferred to an NMR tube using a Pasteur pipette, and the Eppendorf tube was rinsed with an additional portion of CD_3OD (0.1 mL). Then, a sealed capillary tube charged with the external standard (dibromomethane or $XPhosAuNTf_2$ **A**) was added and the NMR tube was sealed.

^1H NMR measurements: The NMR tube was transferred to the bore of a 400 MHz NMR instrument at 298.2 K and the progress of the reaction was monitored over time.

$^{31}P\{^1H\}$ VT-NMR measurements: In the absence of an external standard, the NMR tube was transferred to the bore of a 400 MHz NMR instrument at 298.2 K. The lock and sweep were both disabled and

shimming of the sample was completed using the ^{1}H NMR signal of CD_3OD. ^{1}H and $^{31}P\{^{1}H\}$ spectra were both obtained at 298.2 K. This was followed by slowly cooling the sample to 193.2 K inside the bore of the magnet. The aforementioned shimming procedure was repeated and the ^{1}H and $^{31}P\{^{1}H\}$ spectra were acquired at this temperature. Then, the sealed capillary tube charged with the solution of gold(I) phosphine complex **A** in CD_3OD (0.05 M) was added to the NMR tube, and the ^{1}H and $^{31}P\{^{1}H\}$ spectra were acquired at 193.2 K.

3.3. ^{1}H NMR measurements of gold(I) phosphine complex A, 1*H*-indole (2a) and stoichiometric mixture of the group 11 metal salt and *N*-heterocycle in CD_3OD.

The control experiments were performed following general procedures A and B using mixtures of **2a**:gold(I) phosphine complex **A** and dibromomethane as the internal standard. After the second day, the homogeneous solution displayed a colour change from colourless to pink and a black precipitate was visible at the bottom of the NMR tube.

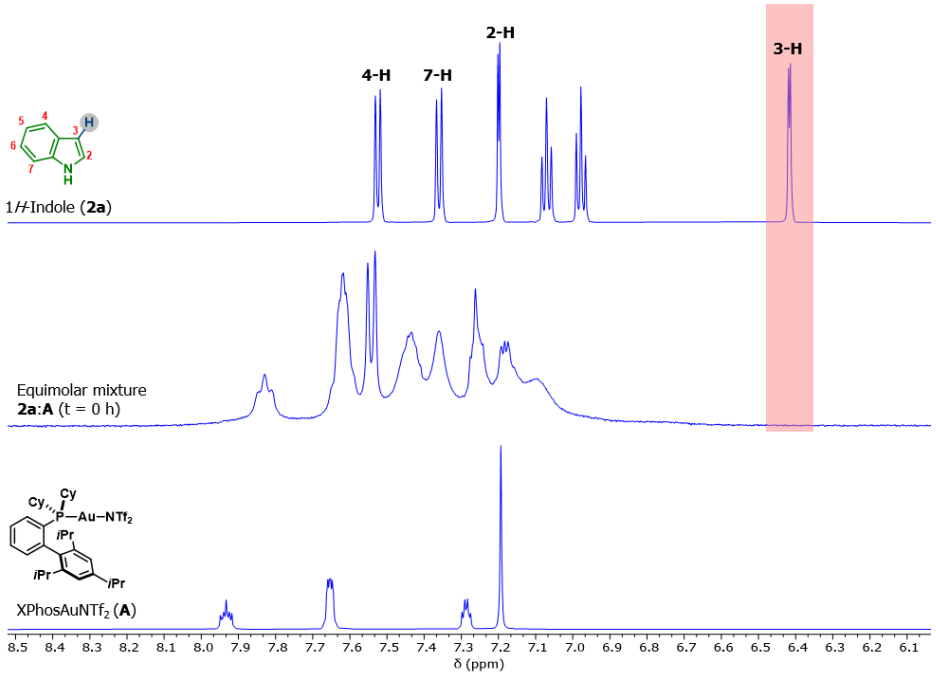


Figure S3. ^{1}H NMR spectra of the aromatic region of 1*H*-indole **2a** (top), gold(I) phosphine complex **A** (bottom) and an equimolar mixture of **2a**:**A** (middle) in CD OD at 298.2 K. Red highlights proton of interest in **2a**.

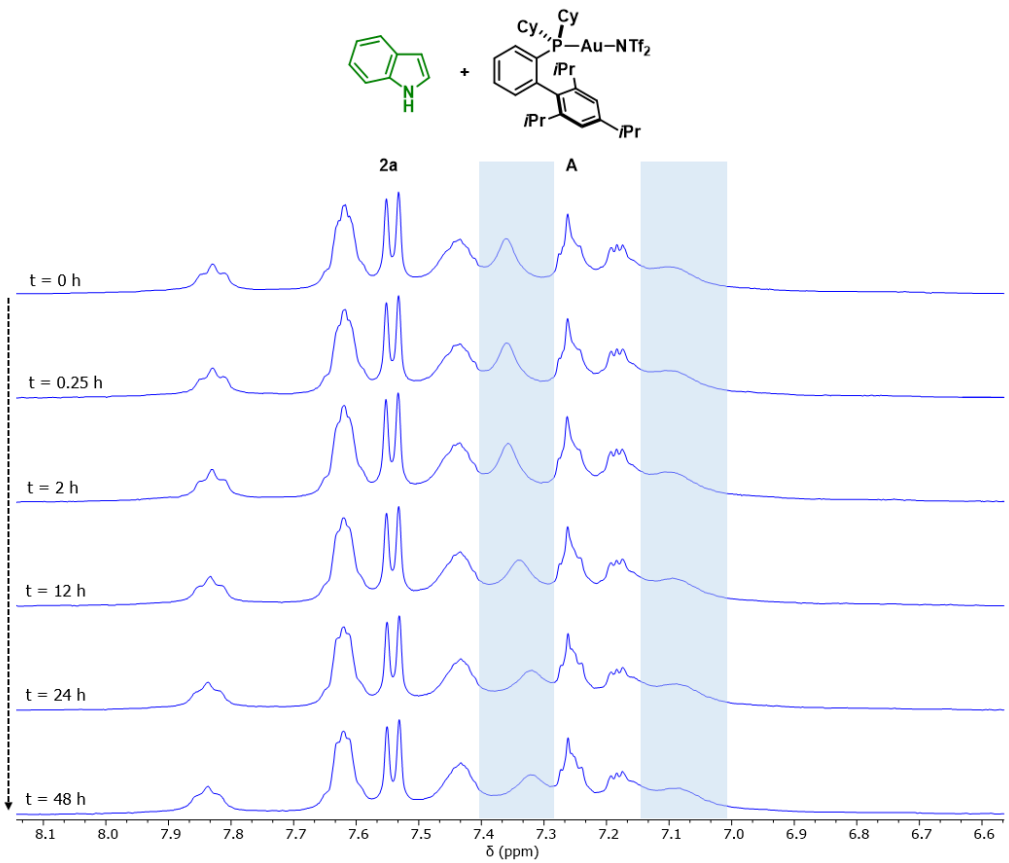


Figure S4. ^{1}H NMR spectra of the aromatic region of the of the equimolar mixture of **2a**:**A** in CD OD monitored over time at 298.2 K. Blue highlights protons that changed over time.

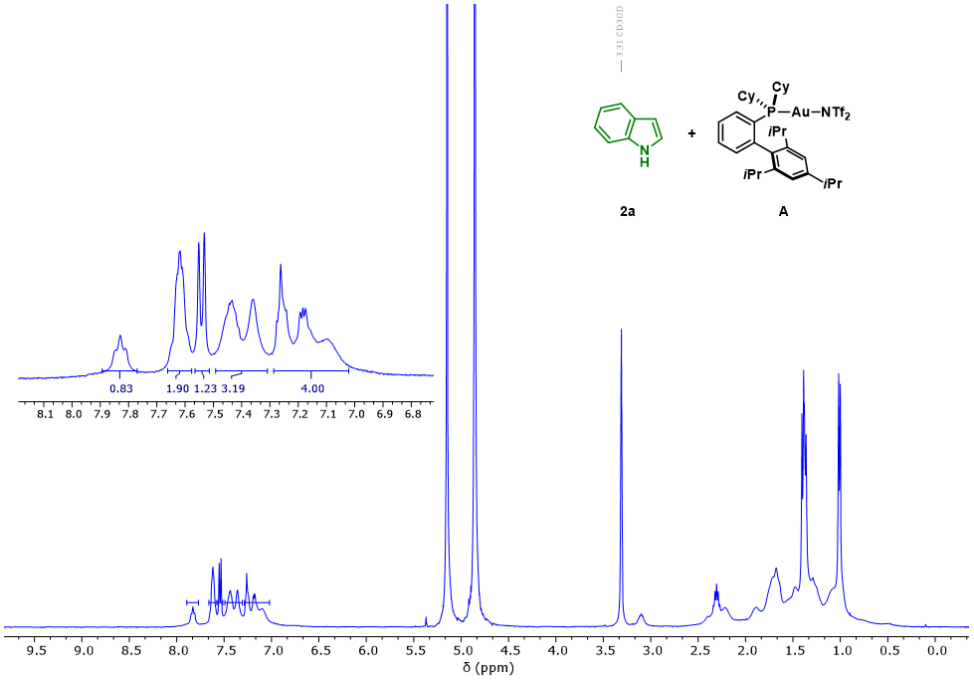


Figure S5. ^{1}H NMR spectrum of the equimolar mixture of **2a**:**A** in CD OD after 2 d at 298.2 K.

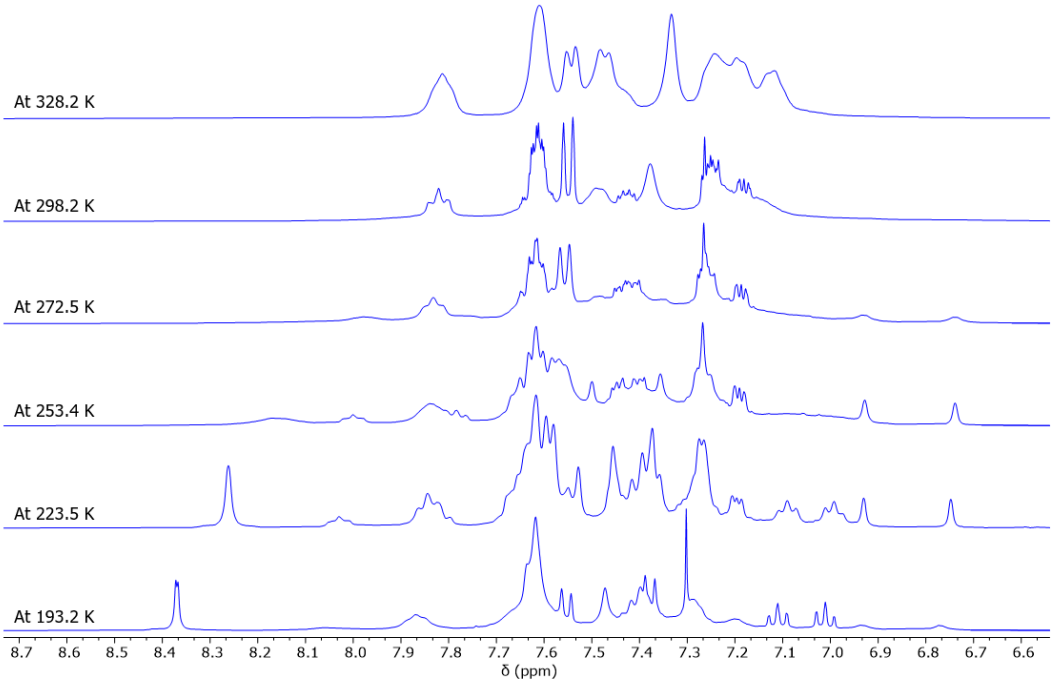


Figure S6. Variable temperature ^{1}H NMR experiment of an equimolar mixture of **2a**:**A** in CD OD.

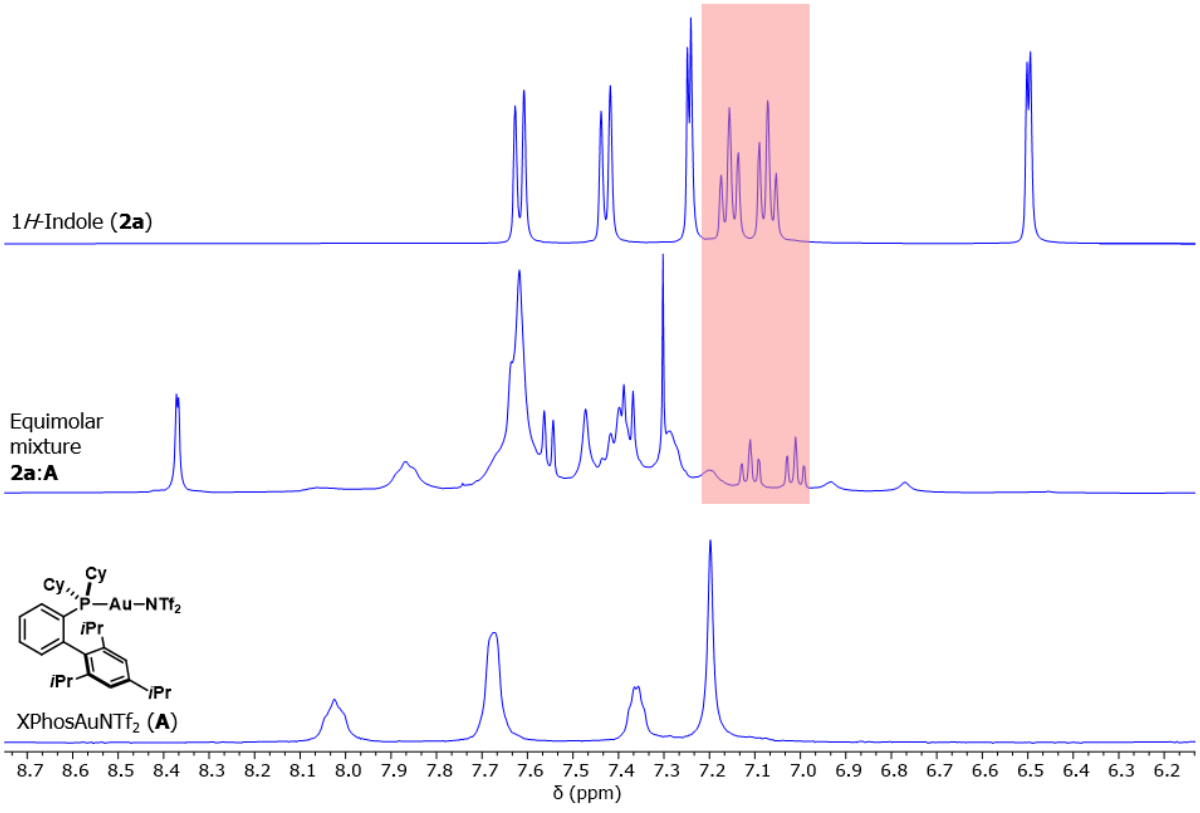


Figure S7. ^{1}H NMR spectra of the aromatic region of 1*H*-indole **2a** (top), an equimolar mixture of **2a**:gold(I) phosphine complex **A** in CD OD (t = 2 days; middle), and gold(I) phosphine complex **A** (bottom). Experiment run at 193.2 K. Red highlights the protons of interest in **2a**.

3.4. ^{31}P{^{1}H} NMR measurements of gold(I) phosphine complex A, 1*H*-indole (2a) and stoichiometric mixture of the group 11 metal salt and *N*-heterocycle in CD_3OD.

The control experiment was performed following to general procedure A and B using mixtures of **2a**:**A**. The homogenised equimolar mixture of **2a**:gold(I) phosphine complex **A** was allowed to react for 2 d, after which time VT NMR experiments were performed. The $^{31}P\{^{1}H\}$ NMR experiment recorded at 193.2 K showed three distinct resonances at 41.5, 41.0 and 33.3 ppm. In the equimolar mixture of **2a**:**A**, the metal complex was found to be present in a negligible concentration (resonance of the catalyst appears at 32.5 ppm).[S37]

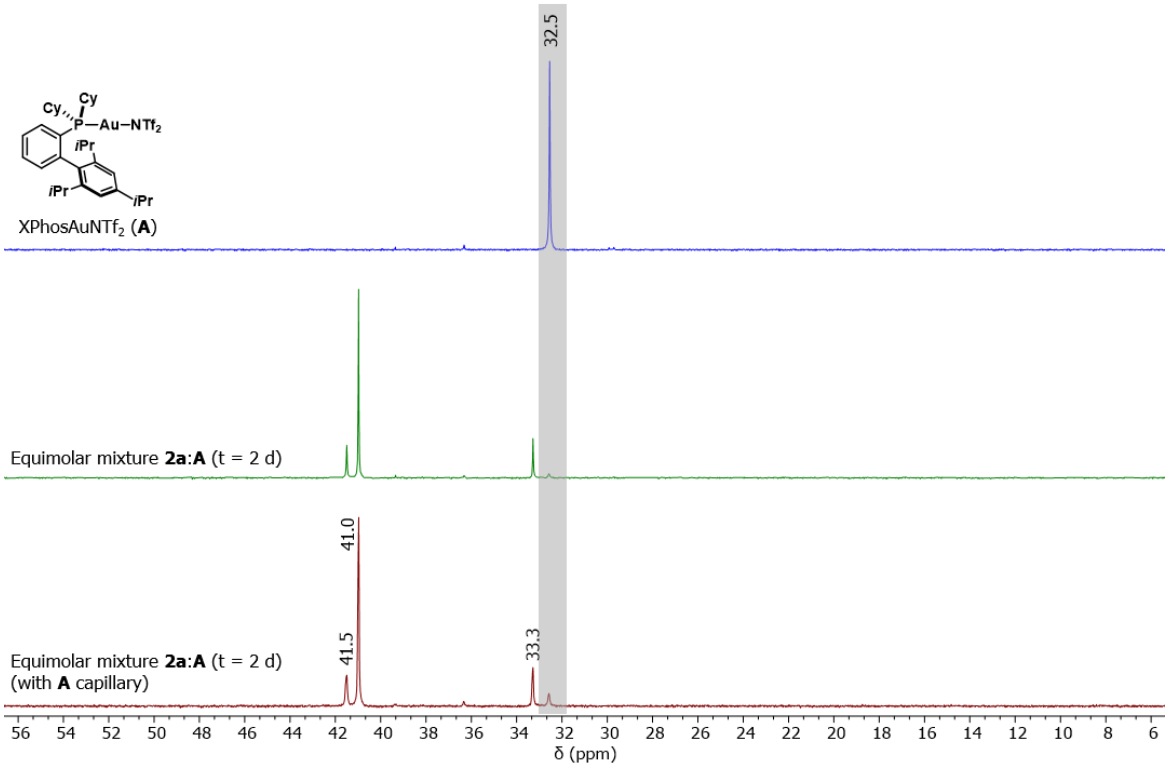
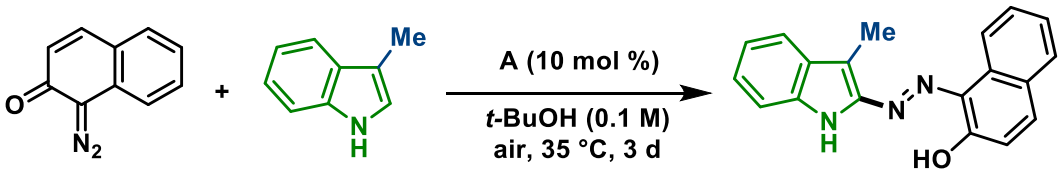


Figure S8. $^{1}P\{^{1}H\}$ NMR spectra of a CD OD solution of gold(I) phosphine complex **A** (top), an equimolar mixture of **2a**:**A** (middle), and an equimolar mixture of **2a**:**A** with the group 11 metal complex also contained in a sealed capillary tube (bottom), in the 6.0–56.0 ppm region at 193.2 K. Grey highlights the $^{1}P\{^{1}H\}$ resonance signal in gold(I) phosphine complex **A**.

3.5. Gold(I) phosphine complex A-catalysed reaction of 1-diazonaphthalen-2(1*H*)-one (1a) with 1*H*-indole (2w).



1a 2w 3aw

To a 5 mL glass screw cap reaction tube equipped with a magnetic stirrer bar was added 1-diazonaphthalen-2(1*H*)-one **1a** (17.0 mg, 0.10 mmol, 1.00 equiv.), 3-methyl-1*H*-indole **2w** (19.7 mg, 0.15 mmol, 1.50 equiv.) and $XPhosAuNTf_2$ **A** (9.5 mg, 0.01 mmol, 10 mol %) followed by *t*-BuOH (1.0 mL, 0.1 M). The reaction tube was sealed and the reaction mixture stirred vigorously at 35 °C for 3 d. On completion, the reaction mixture was diluted with acetone (9 mL), vacuum filtered through a short pad of silica gel (eluent: acetone, 3 × 15 mL) and concentrated *in vacuo*. The resulting mixture was analysed by ^{1}H NMR spectroscopy using 2-(bromomethyl)naphthalene (11.1 mg, 0.05 mmol) as the internal standard in DMSO-d_6 (700 μL, 0.07 M), which indicated partial decomposition of compound **1a** (26% conversion) and no formation of the target (*E*)-diazene product **3aw**.

3.6. Stoichiometric reaction of gold(I) phosphine complex A with 1-diazonaphthalen-2(1*H*)-one (1a) and 1*H*-indole (2a).

The control experiment was performed following general procedures A and B using mixtures of **2a**:**A** and dibromomethane as the internal standard. After 48 h, a solution of 1-diazonaphthalen-2(1*H*)-one **1a** (1.7 mg, 0.01 mmol, 1.00 equiv.) in CD_3OD (0.2 mL) was added and the progress of the reaction mixture was monitored over a 7 d period. No product formation was observed in the first 12 h upon the addition of **1a**. After 12 h, the peaks corresponding to the product **3aa** emerged at 8.83, 8.55 and 8.11 ppm along with the formation of a side-product arising from decomposition of **1a** detected at 7.96 ppm. Compound **1a** was almost fully consumed after 4 d, providing the azo compound **3aa** in 35% yield as determined by ^{1}H NMR measurements.

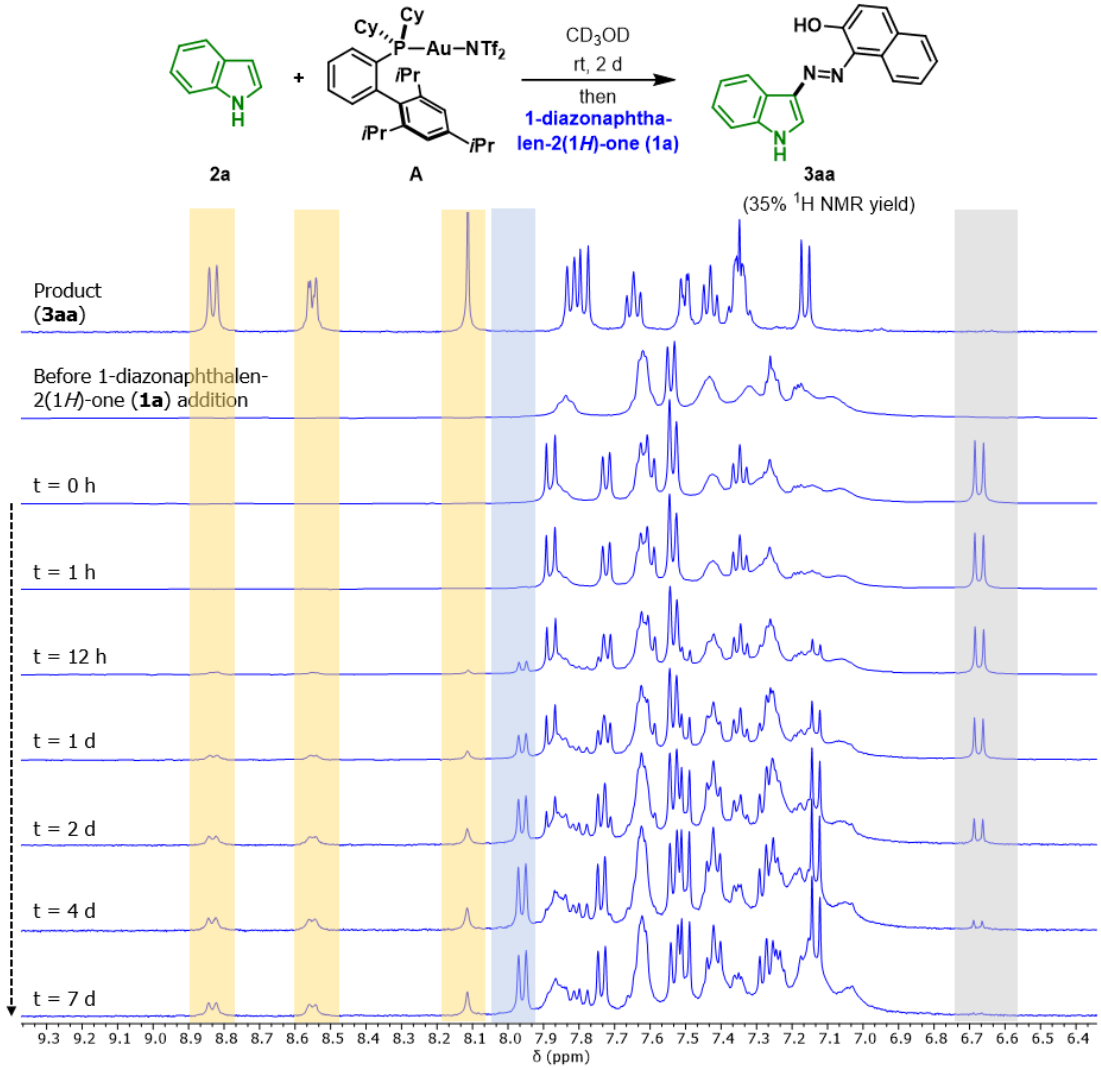


Figure S9. ^{1}H NMR spectra of the aromatic region following addition of **1a** in CD OD monitored over time at 298.2 K. Grey and yellow highlight the protons of interest in **1a** and **3aa**, respectively. Blue highlights the signal of the unknown side-product.

3.7. Gold(I) phosphine complex A-catalysed reactions of 1-diazonaphthalen-2(1*H*)-one (1a) and 1*H*-indole (2a) in the presence and absence of acetic acid.

To an Eppendorf tube was added 1-diazonaphtalen-2(1*H*)-one **1a** (17 mg, 0.10 mmol, 1.00 equiv.), 1*H*-indole **2a** (17.6 mg, 0.15 mmol, 1.50 equiv.), and gold(I) phosphine complex **A** (10 or 20 mol %), followed by CD_3OD (0.7 mL) and acetic acid (5.7 µL, 0.10 mmol, 1.00 equiv., if stated). The mixture was homogenised, then transferred to an NMR tube using a Pasteur pipette, and the Eppendorf tube was rinsed with an additional portion of CD_3OD (0.3 mL). Then, dibromomethane was added as external standard (see *general procedure A*) and the NMR tube was sealed. After 3 d, the reaction mixture was diluted with acetone (9 mL), vacuum filtered through a short pad of silica gel (eluent: acetone, 3 × 15 mL) and concentrated *in vacuo*. The resulting mixture was analysed by ^{1}H NMR spectroscopy using 2-(bromomethyl)naphthalene as the internal standard in DMSO-d_6 (700 µL, 0.07 M).

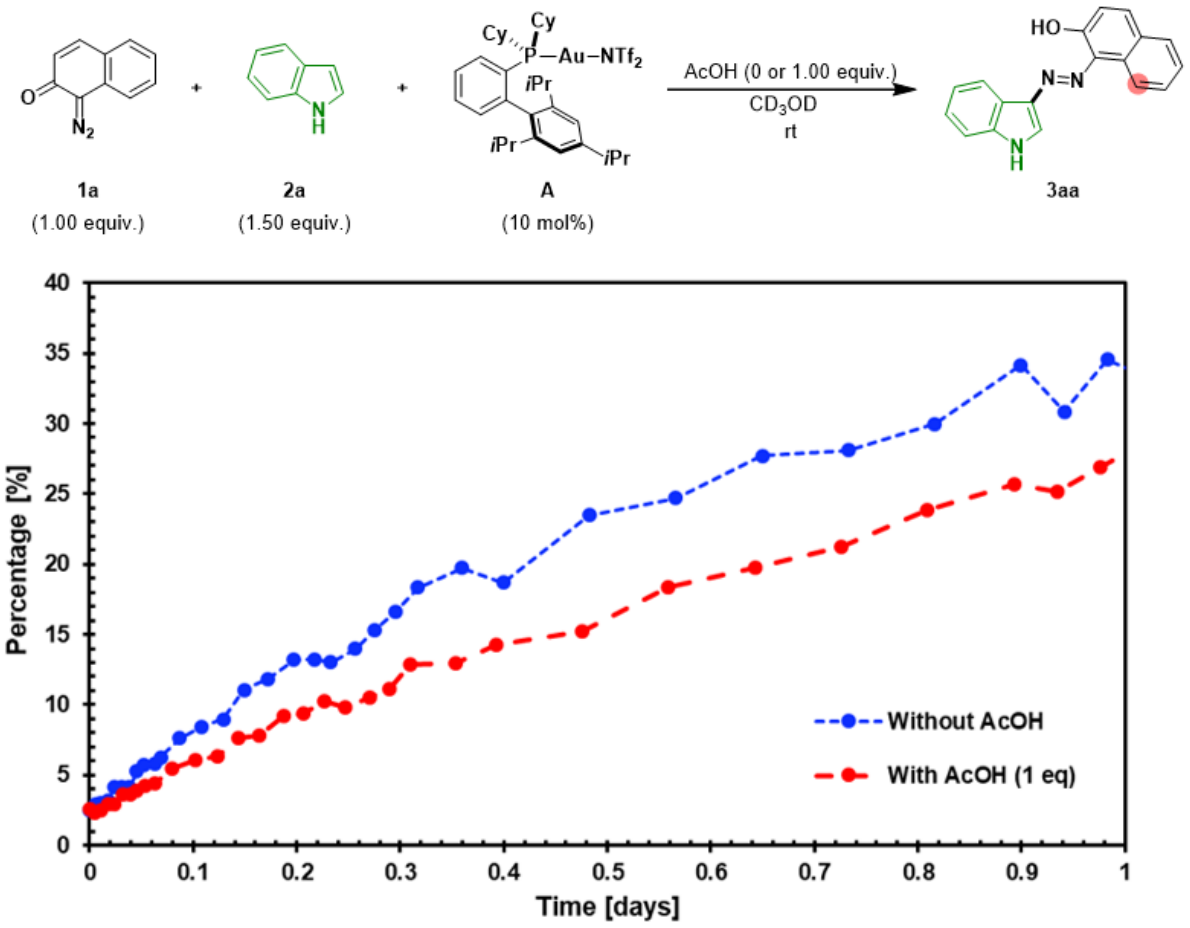


Figure S10. Comparison of the reaction progress for the formation of **3aa** in the presence and absence of acetic acid. Experiment run at 298.2 K.

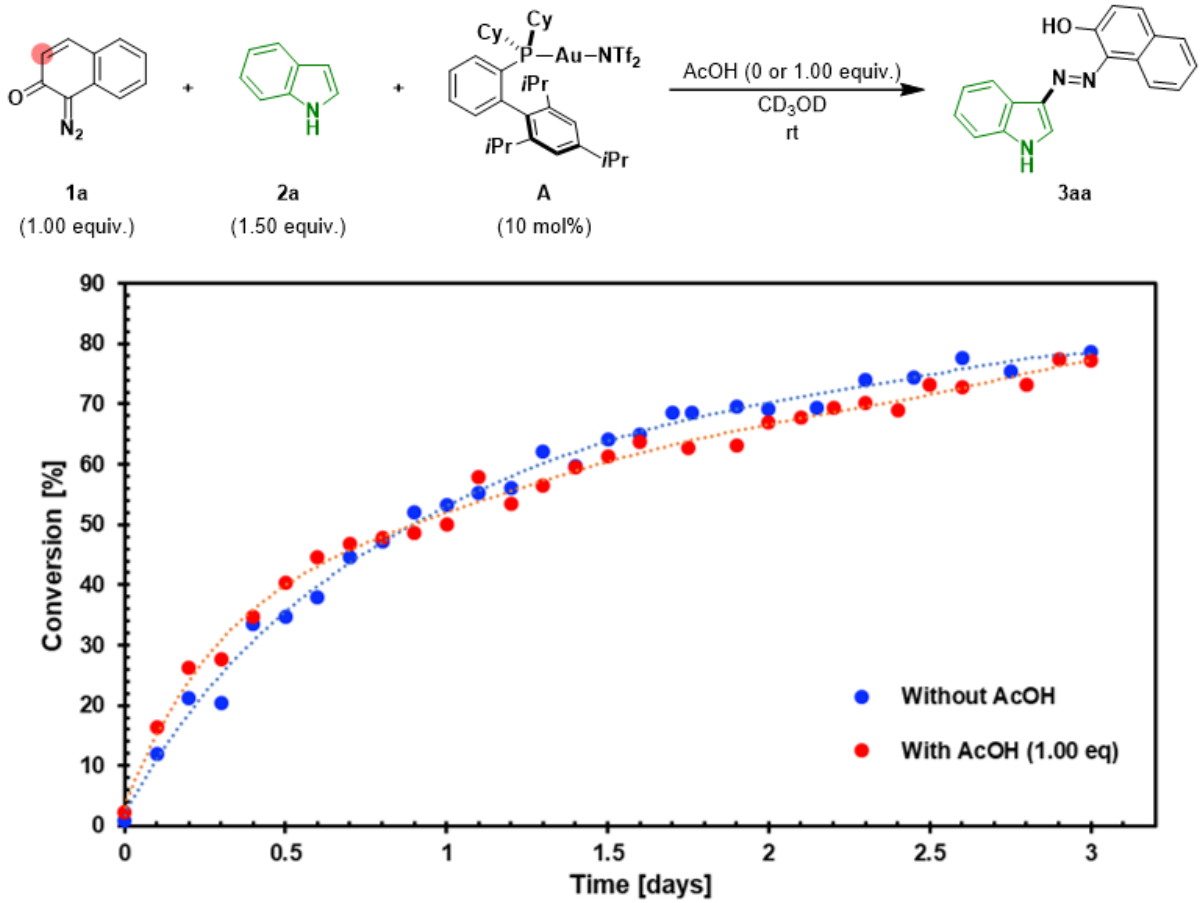
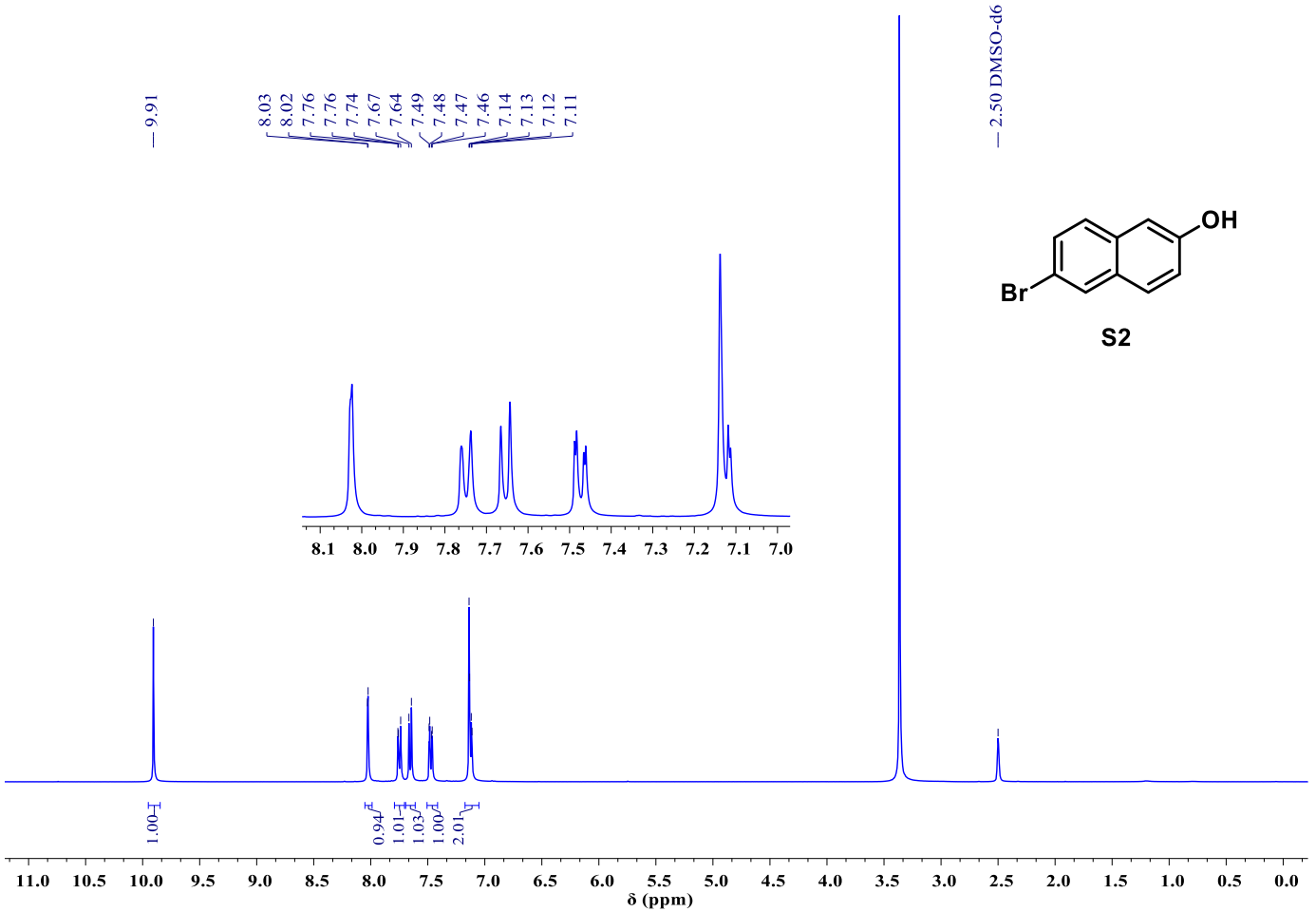


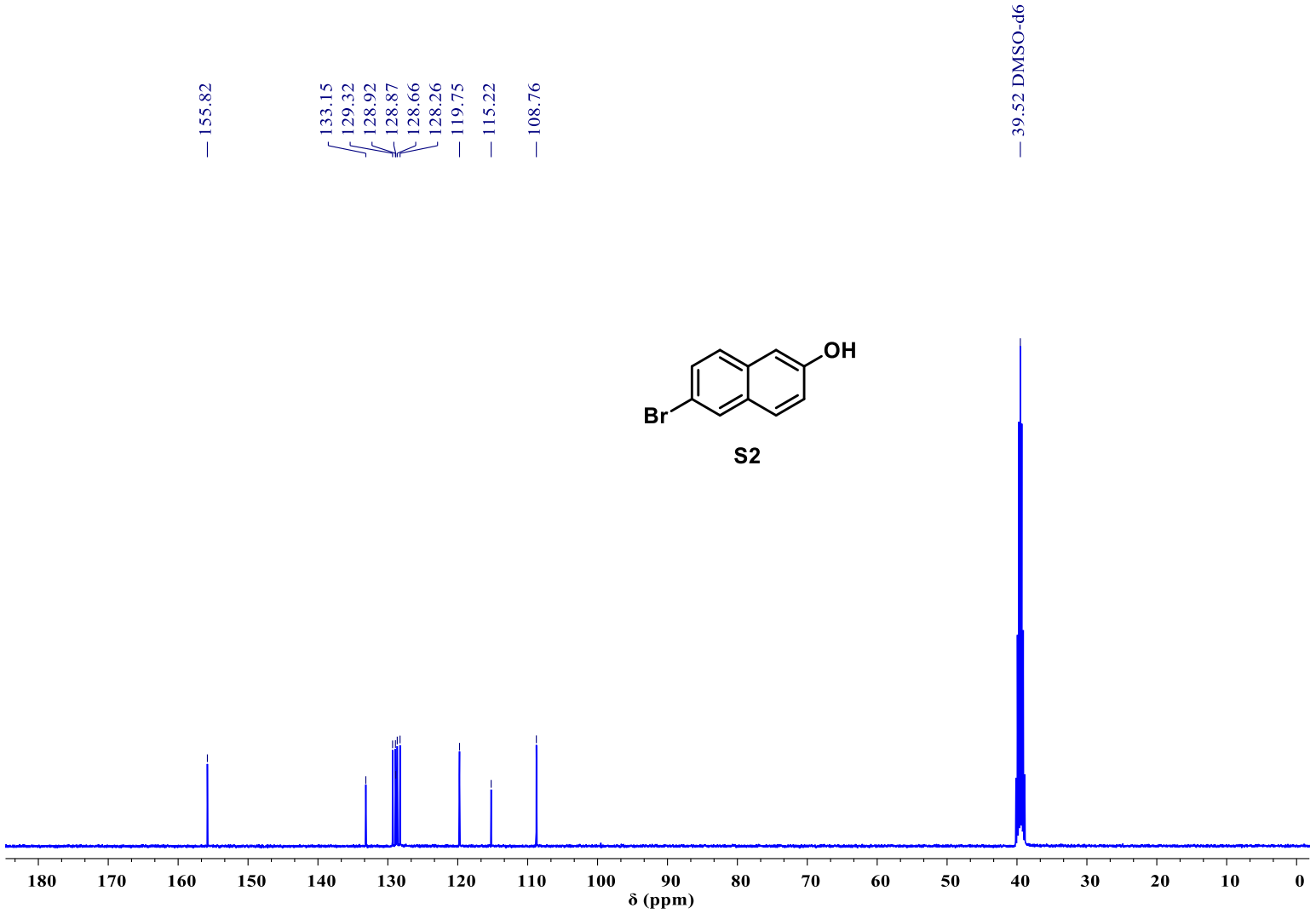
Figure S11. Comparison of the reaction progress for the conversion of **1a** in the presence and absence of AcOH. Experiment run at 298.2 K.

4. ^{1}H, ^{13}C, ^{19}F NMR and IR spectra

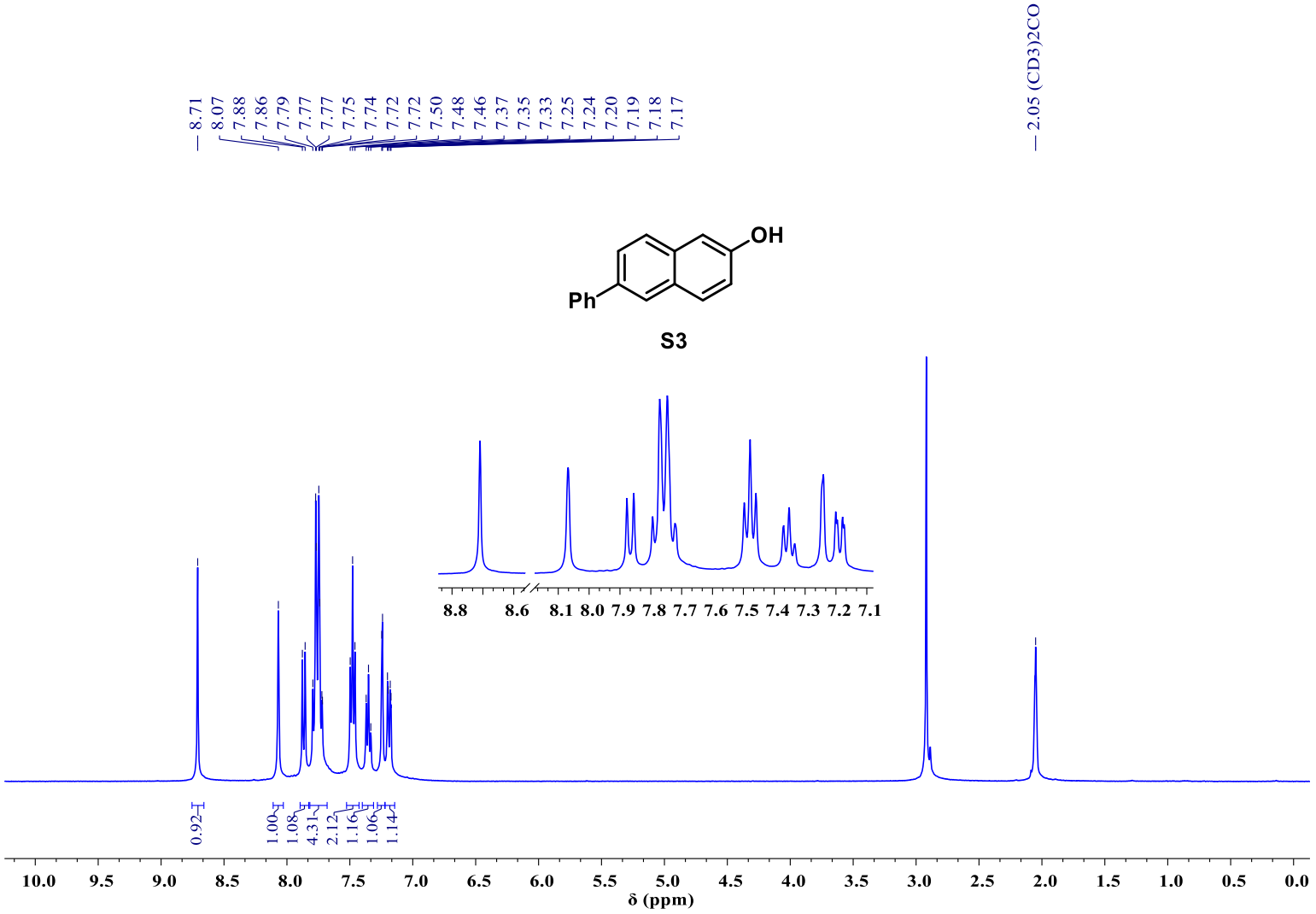
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 6-bromo-2-naphthol (S2).



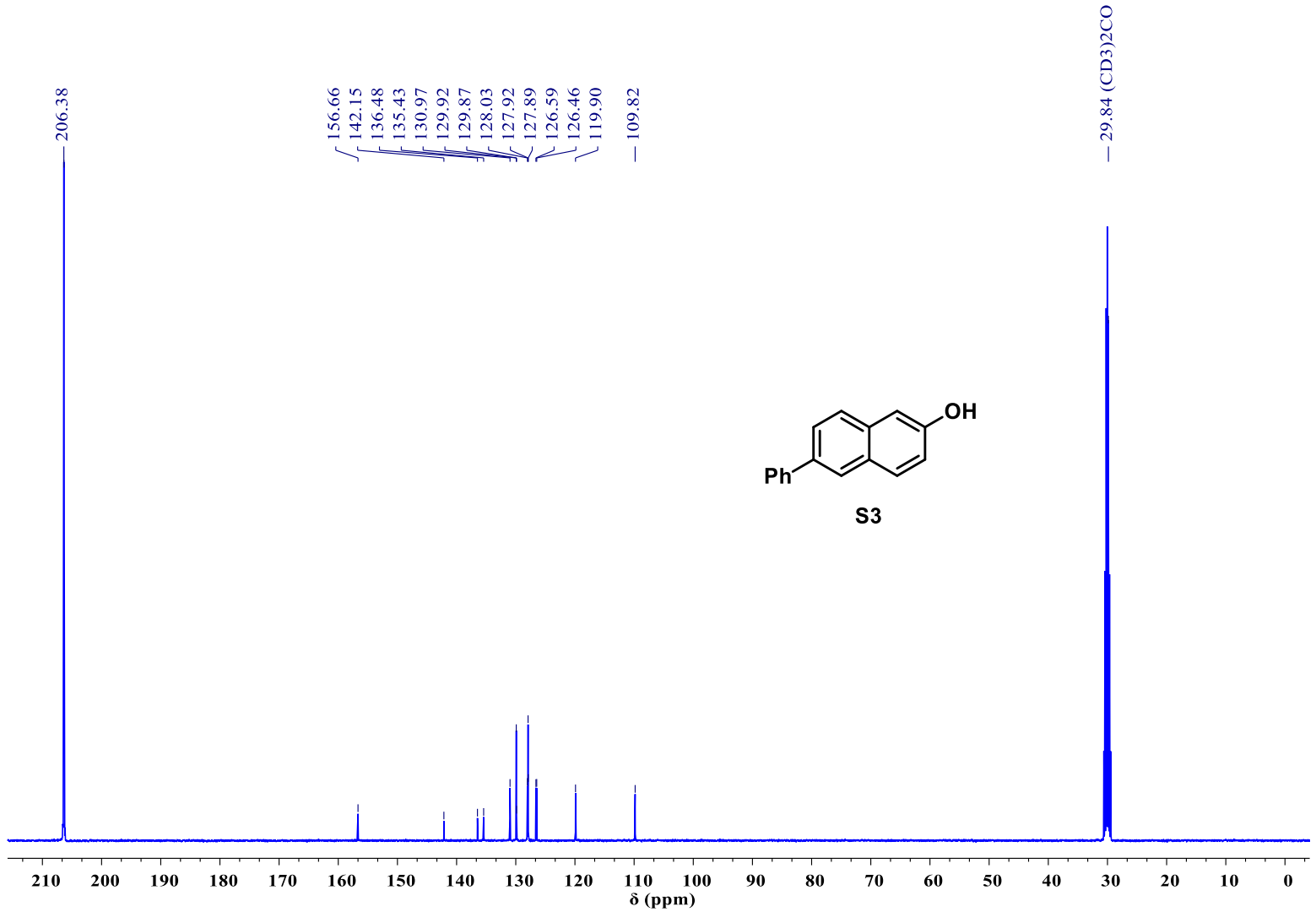
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 6-bromo-2-naphthol (S2).



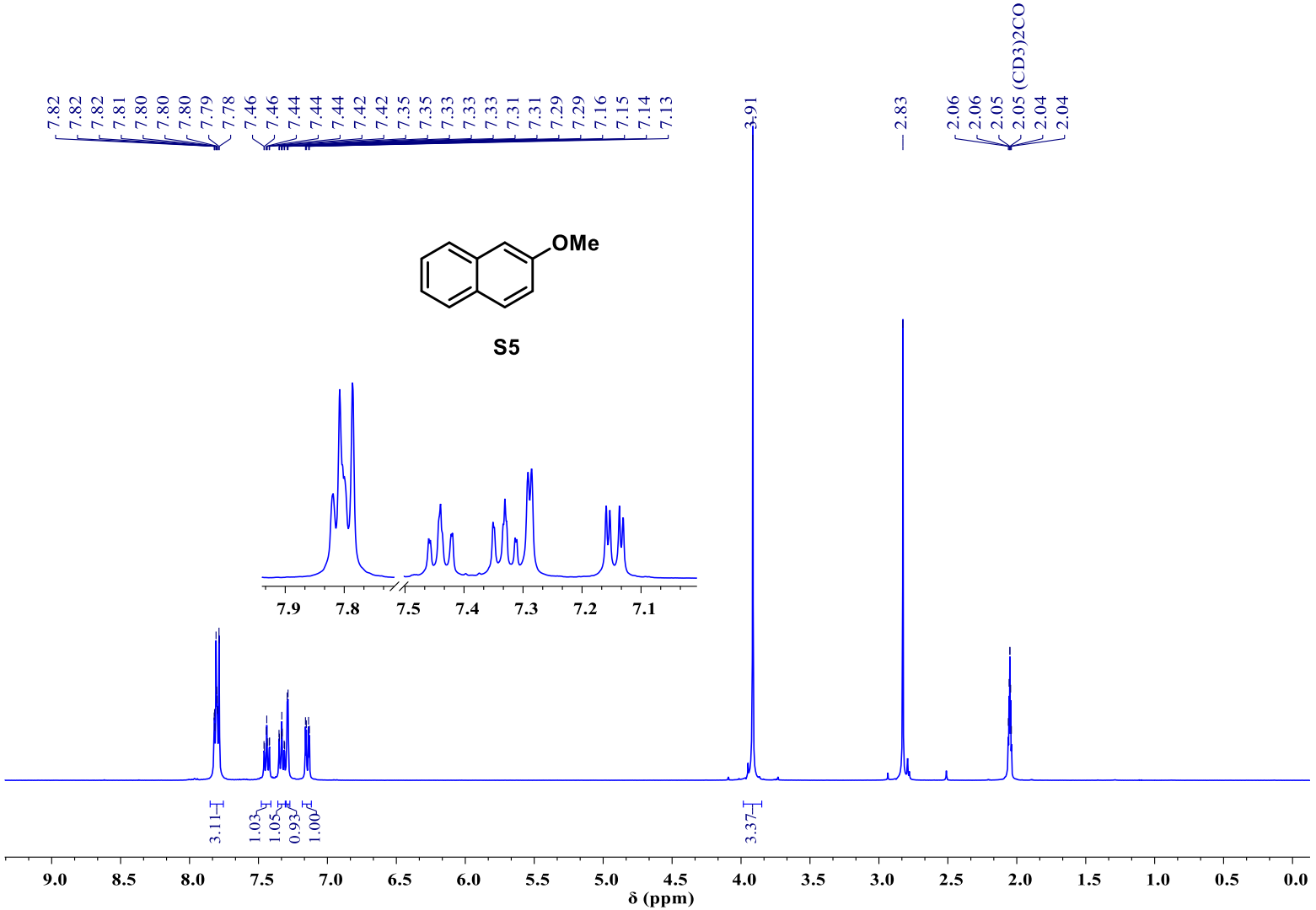
^{1}H NMR (400 MHz, acetone-d_6) spectrum of 6-phenyl-2-naphthol (S3).



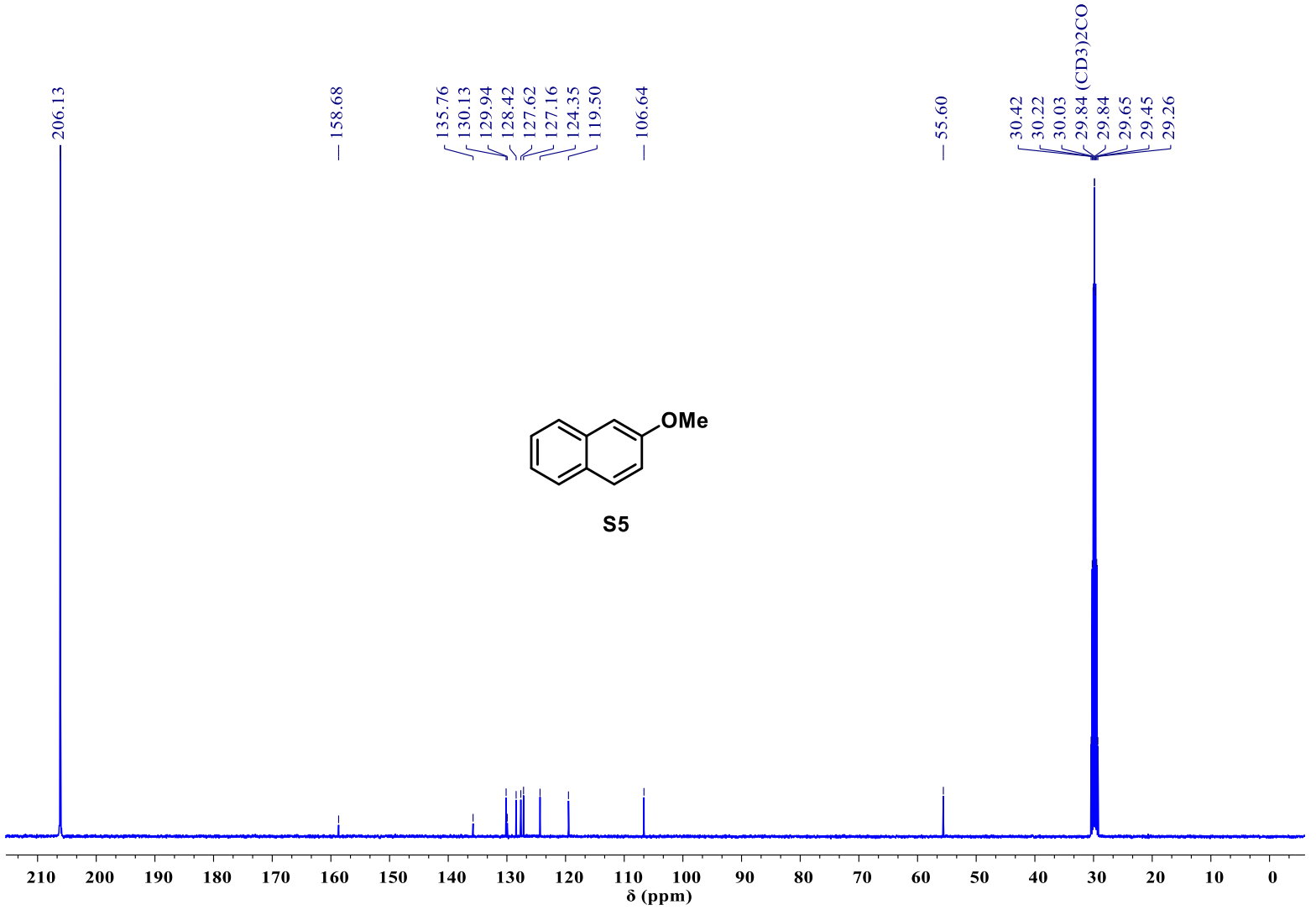
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 6-phenyl-2-naphthol (S3).



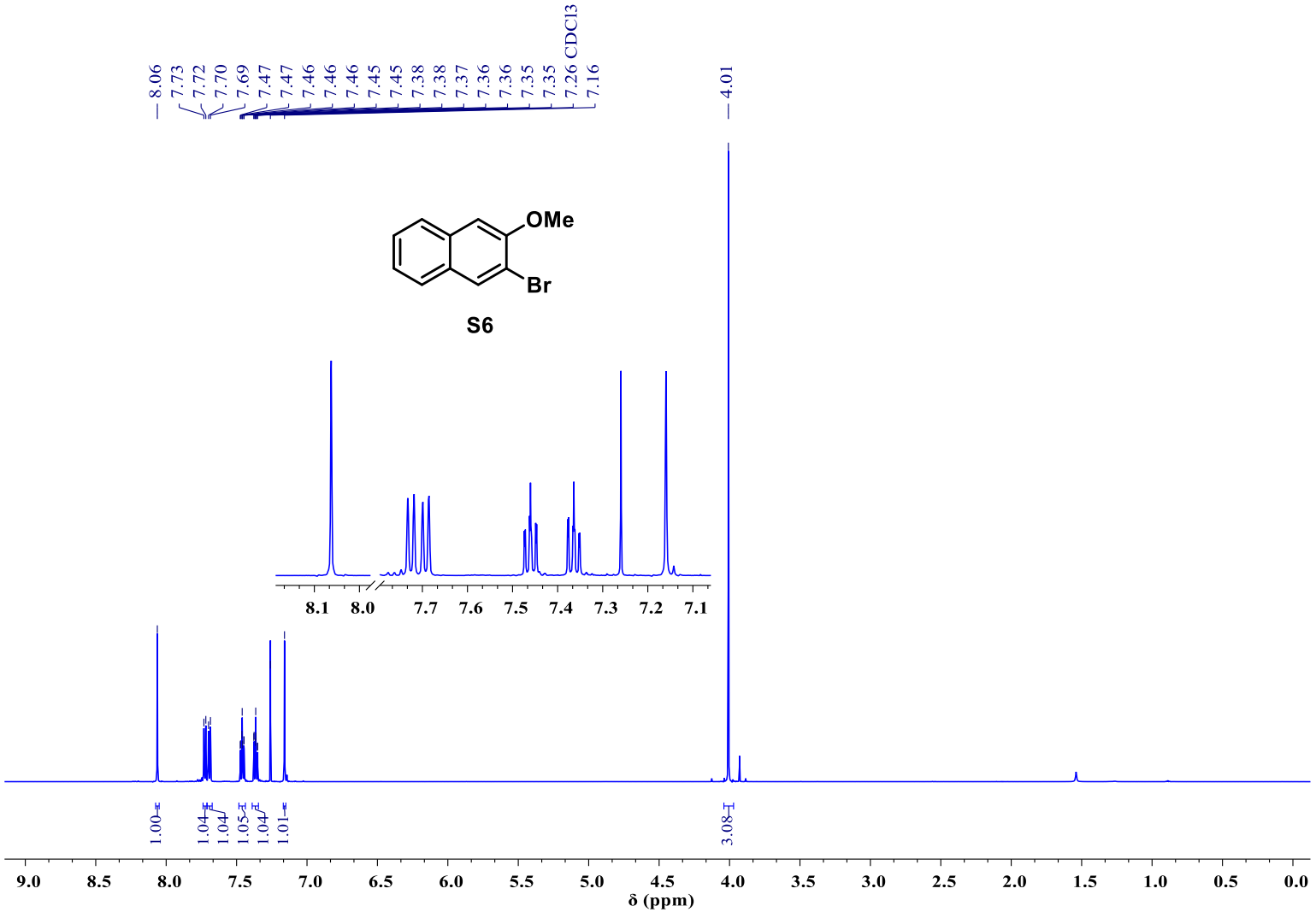
[1]H NMR (400 MHz, acetone-d_6) spectrum of 3-methoxynaphthalene (S5).



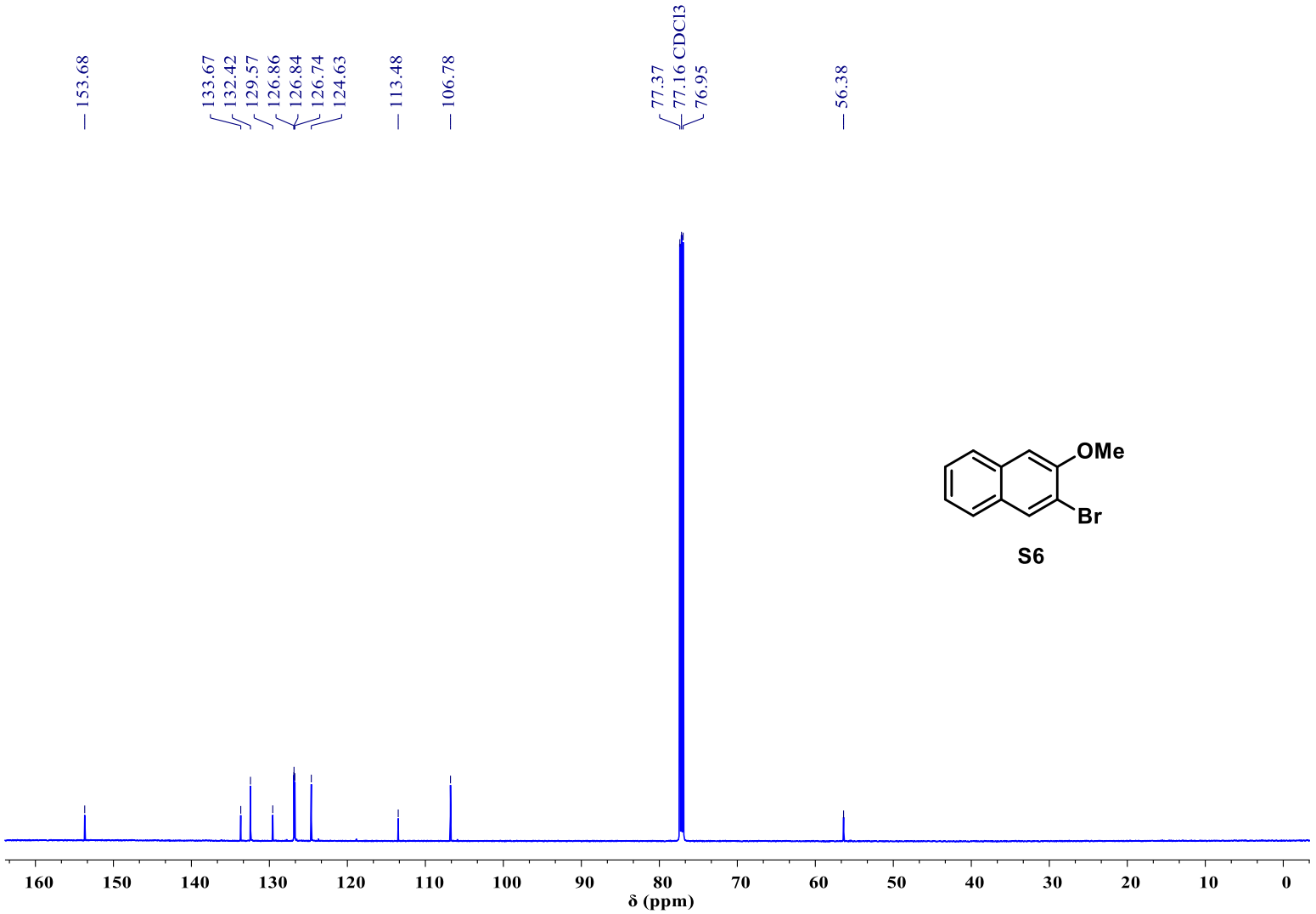
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 3-methoxynaphthalene (S5).



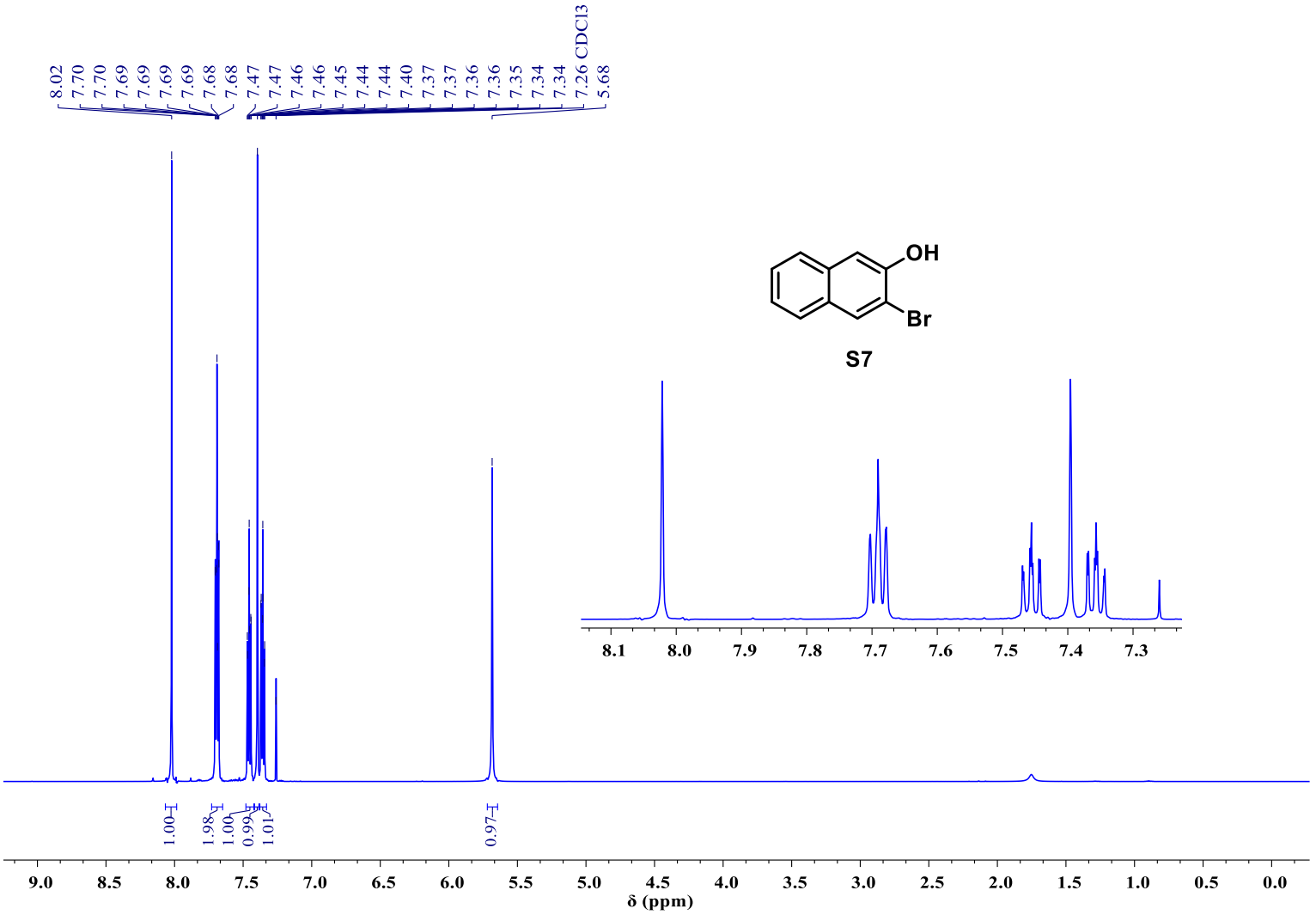
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-bromo-2-methoxynaphthalene (S6).



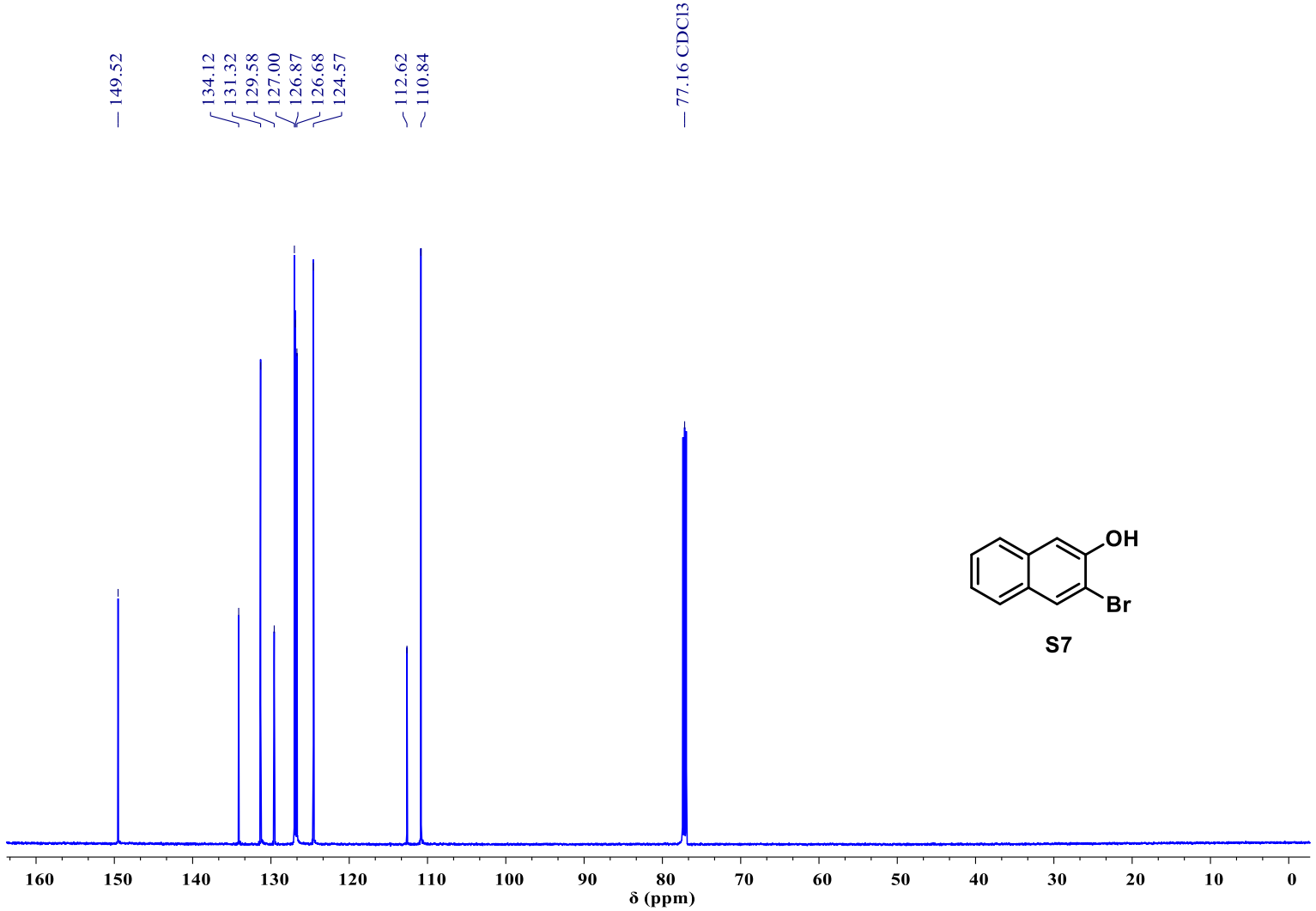
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 3-bromo-2-methoxynaphthalene (S6).



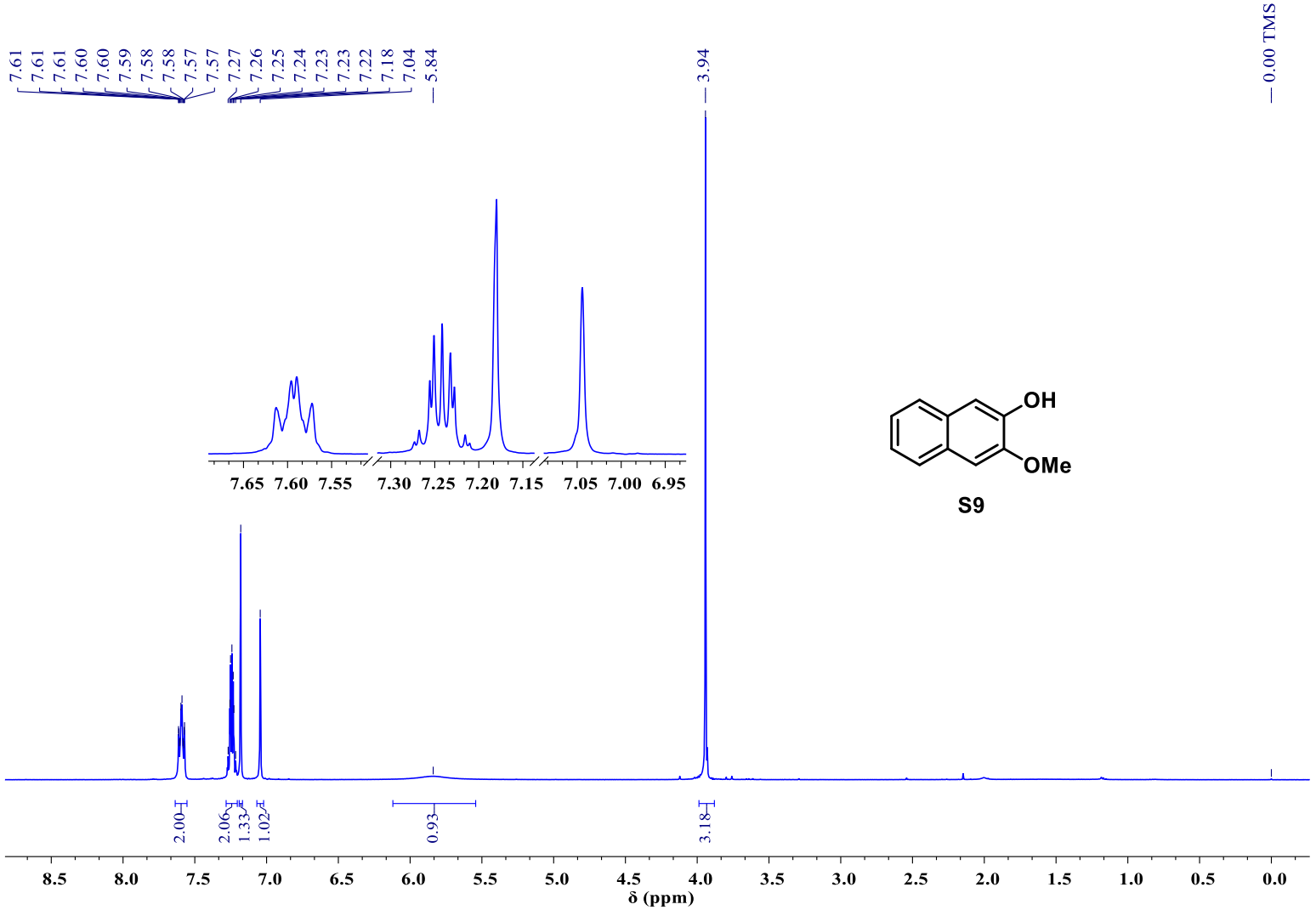
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 3-bromo-2-naphthol (S7).



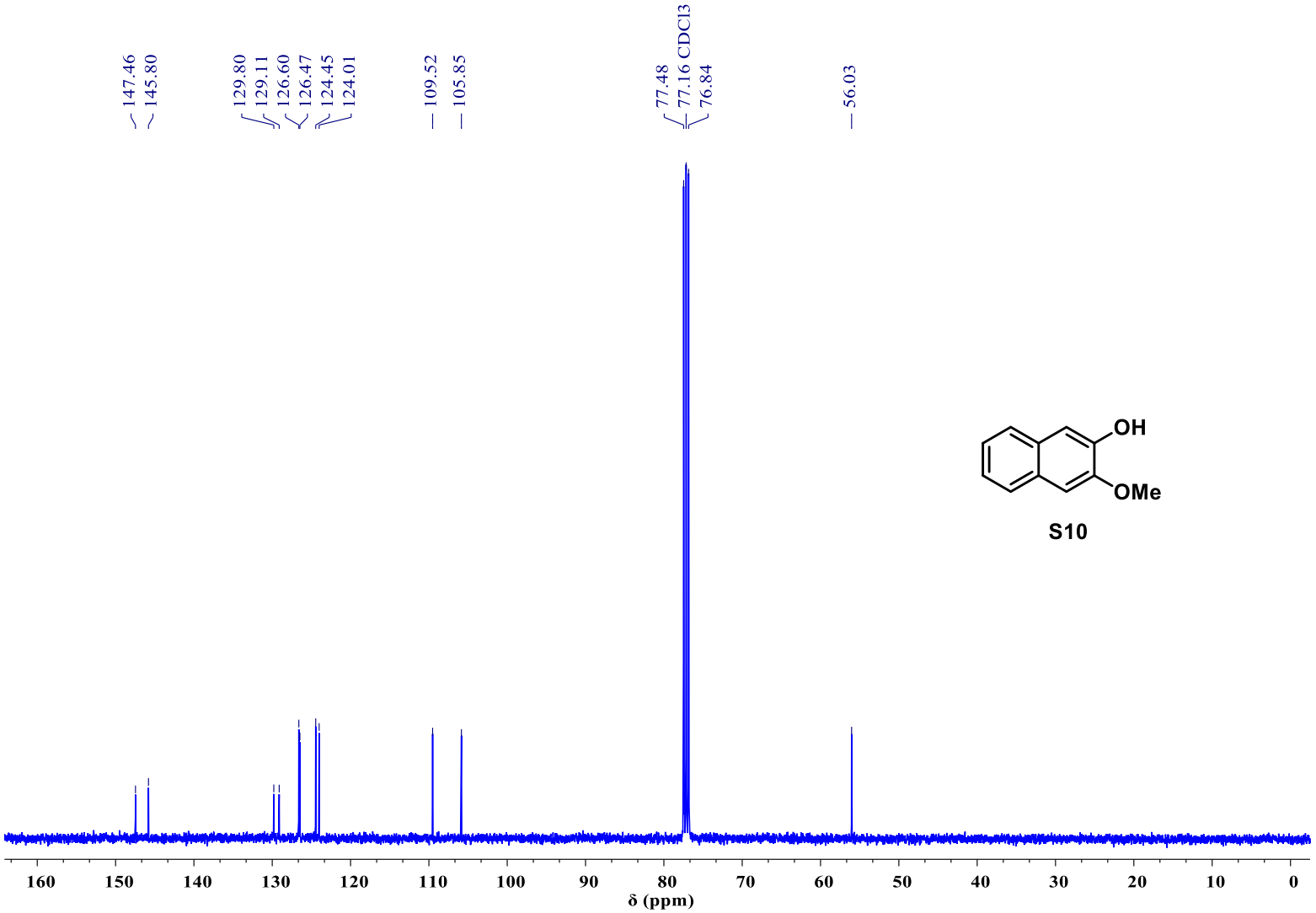
^{13}C NMR (151 MHz, acetone-d_6) spectrum of 3-bromo-2-naphthol (S7).



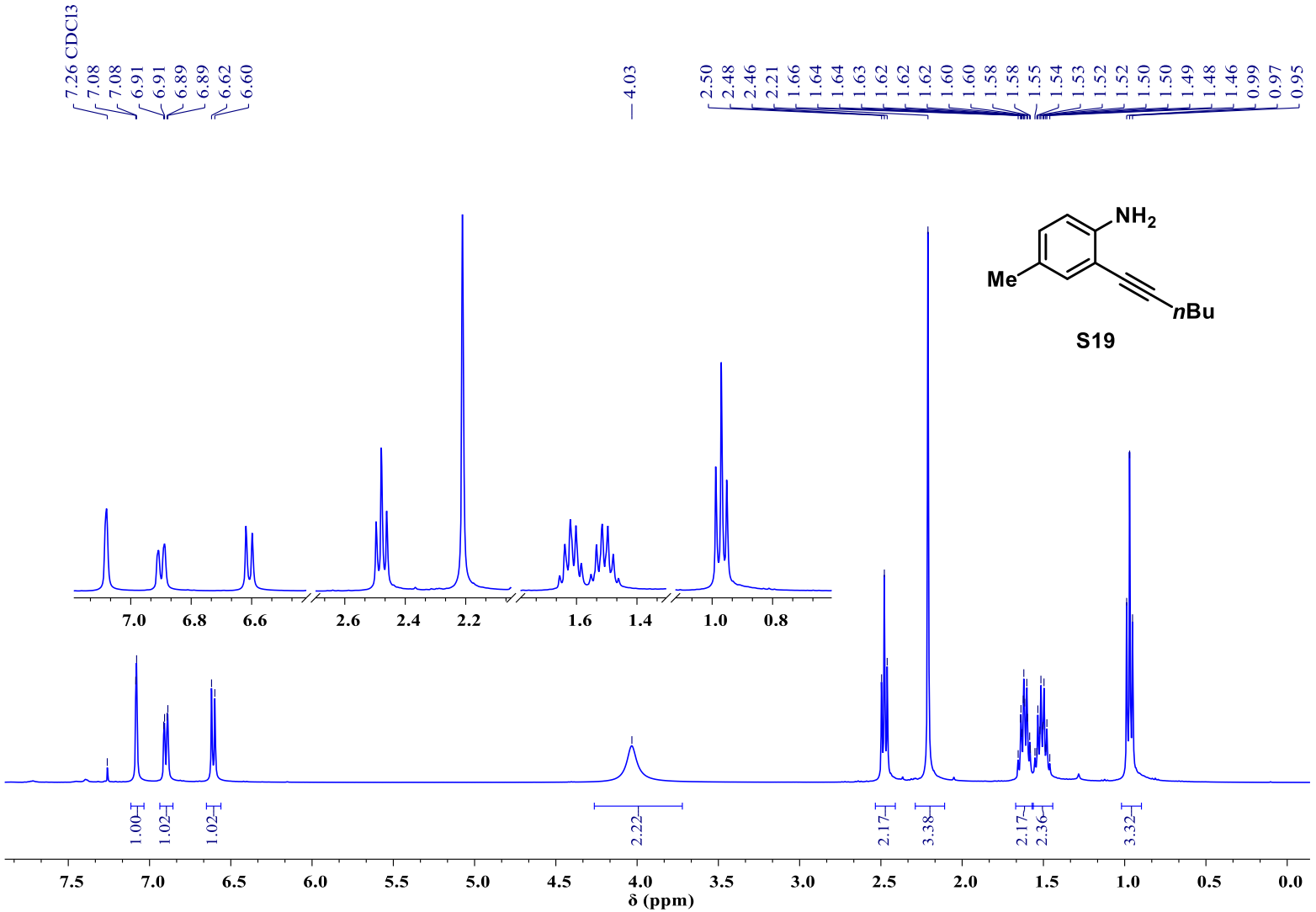
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 3-methoxynaphthalen-2-ol (S9).



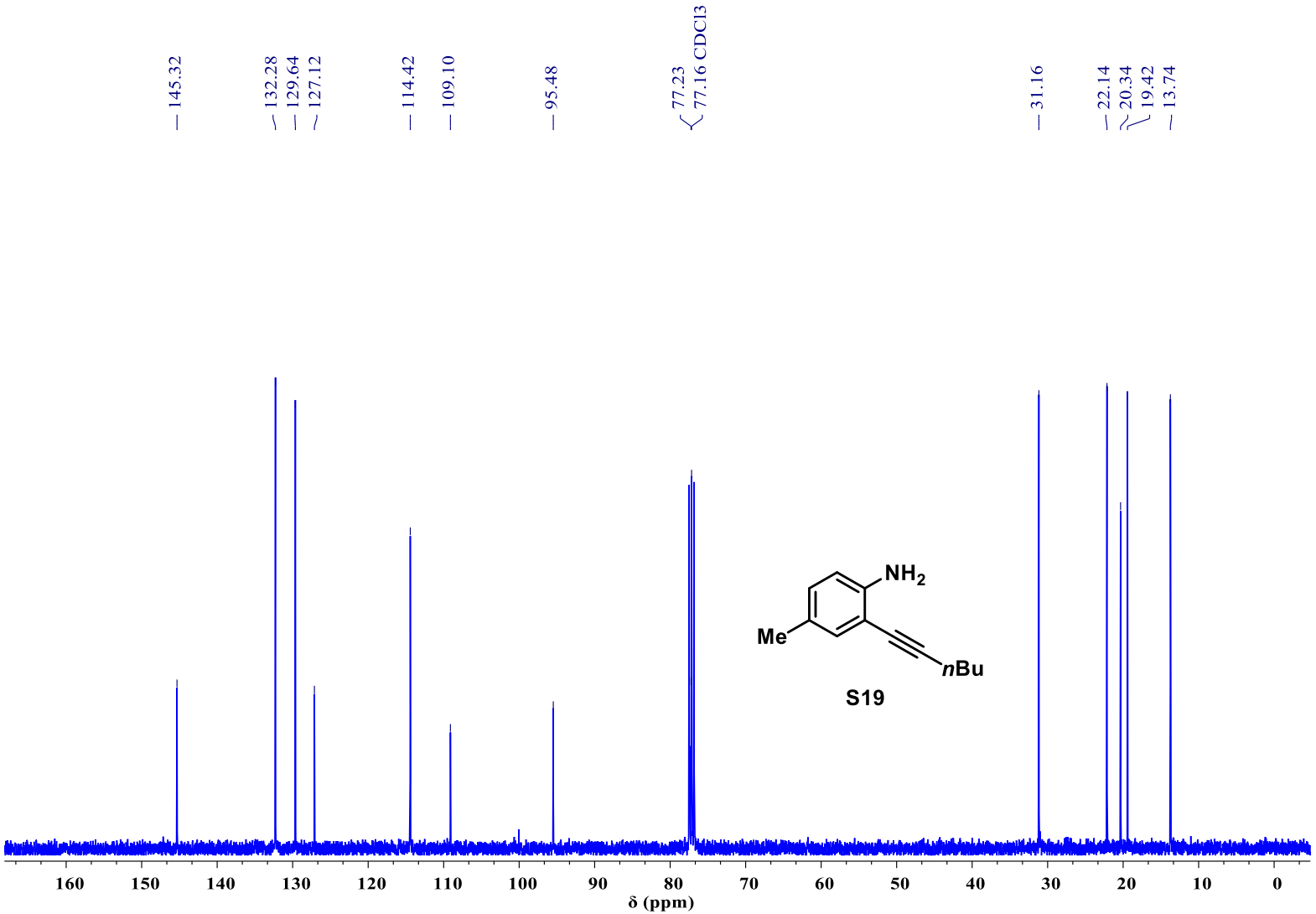
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 3-methoxynaphthalen-2-ol (S9).



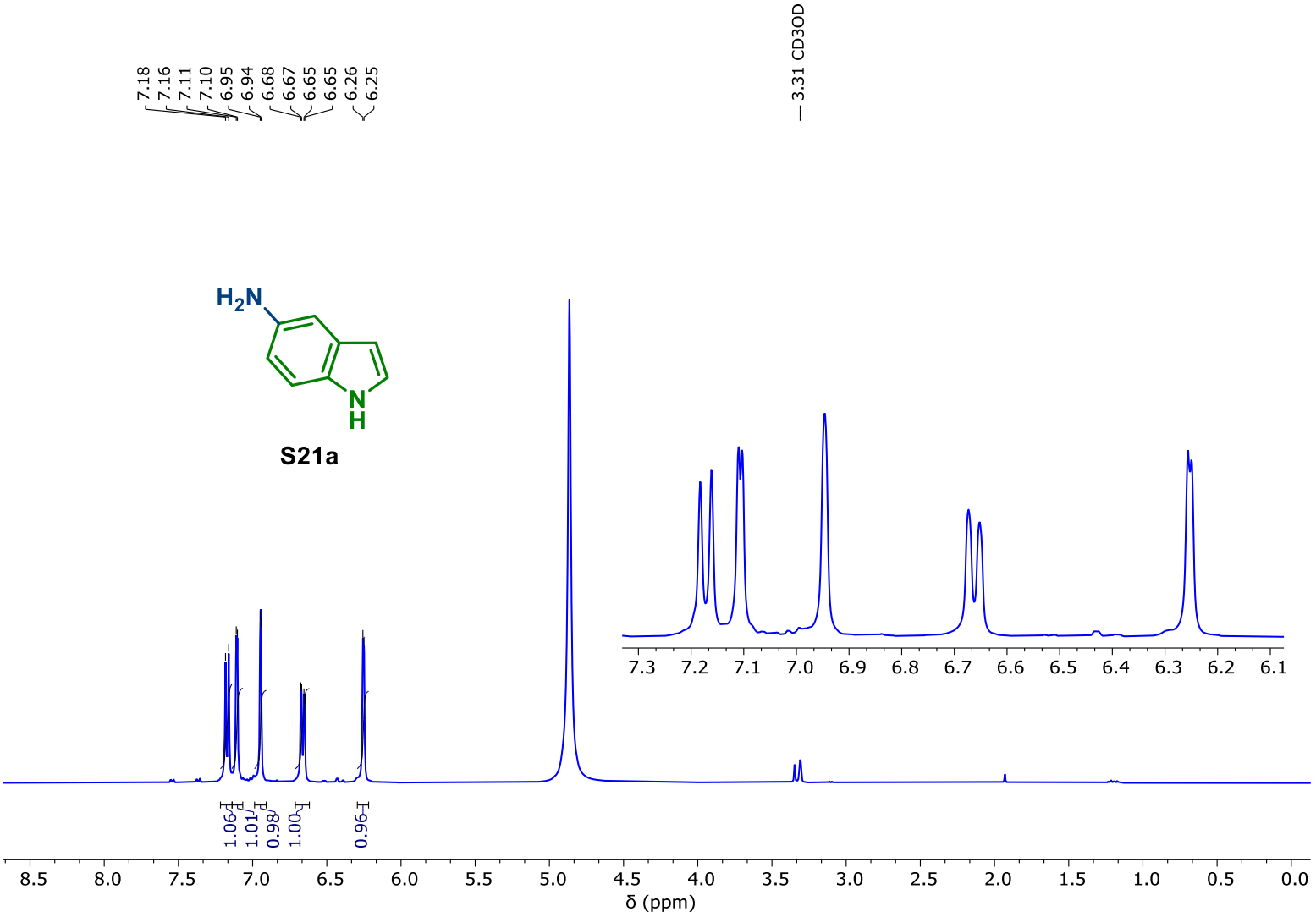
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-(hex-1-yn-1-yl)-4-methylaniline (S19).



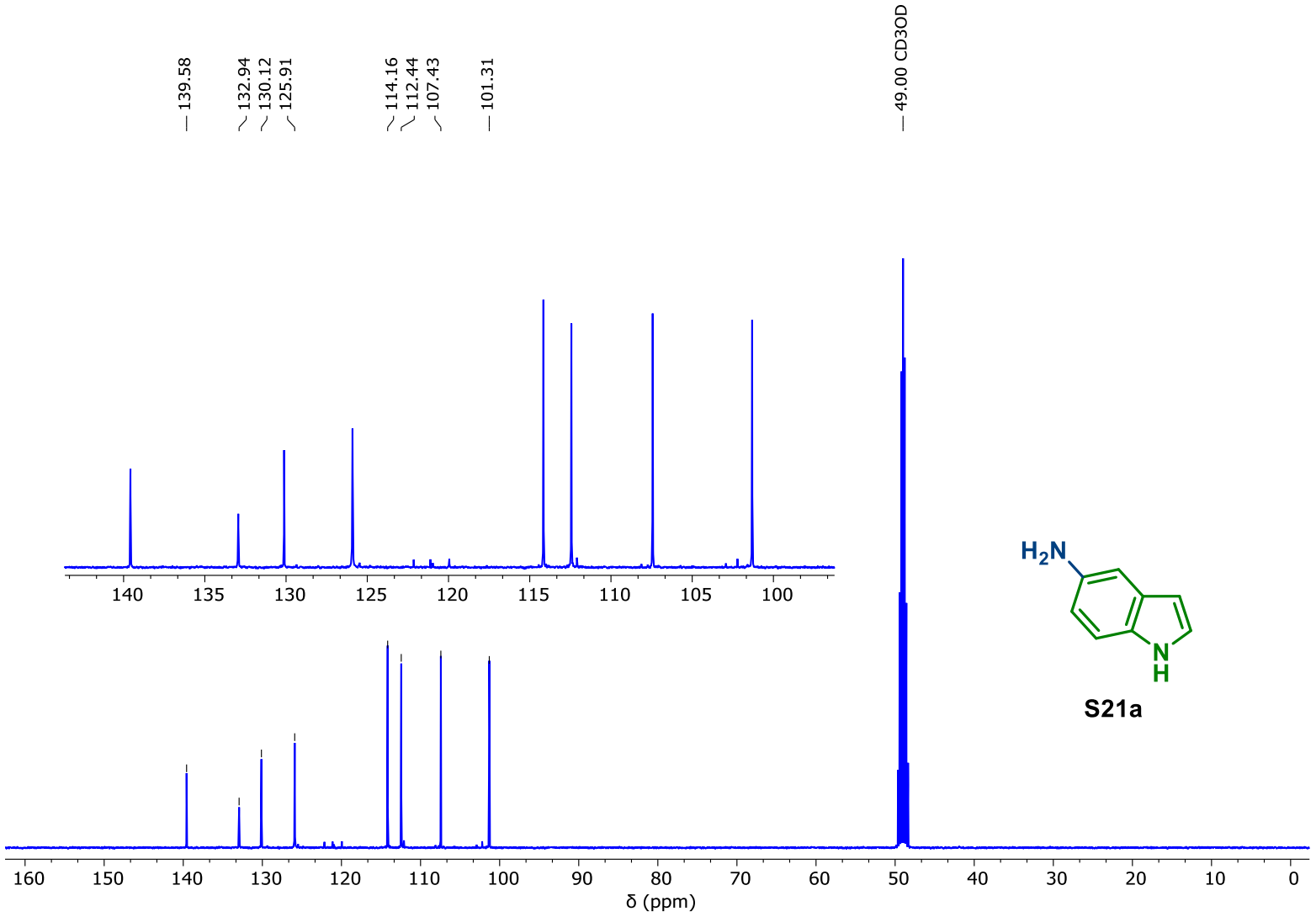
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-(hex-1-yn-1-yl)-4-methylaniline (S19).



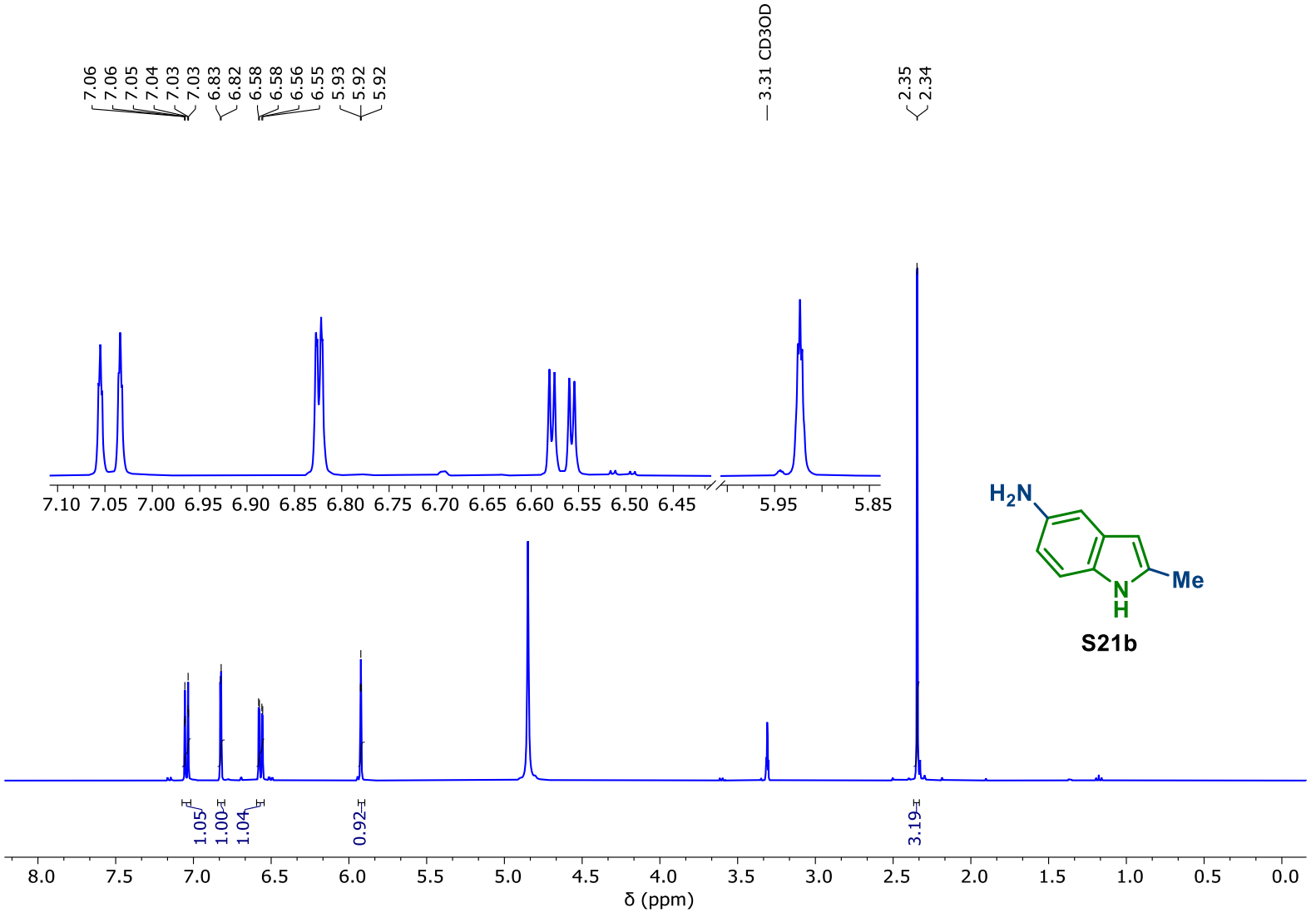
^{1}H NMR (400 MHz, CD_3OD) spectrum of 1*H*-indol-5-amine (S21a).



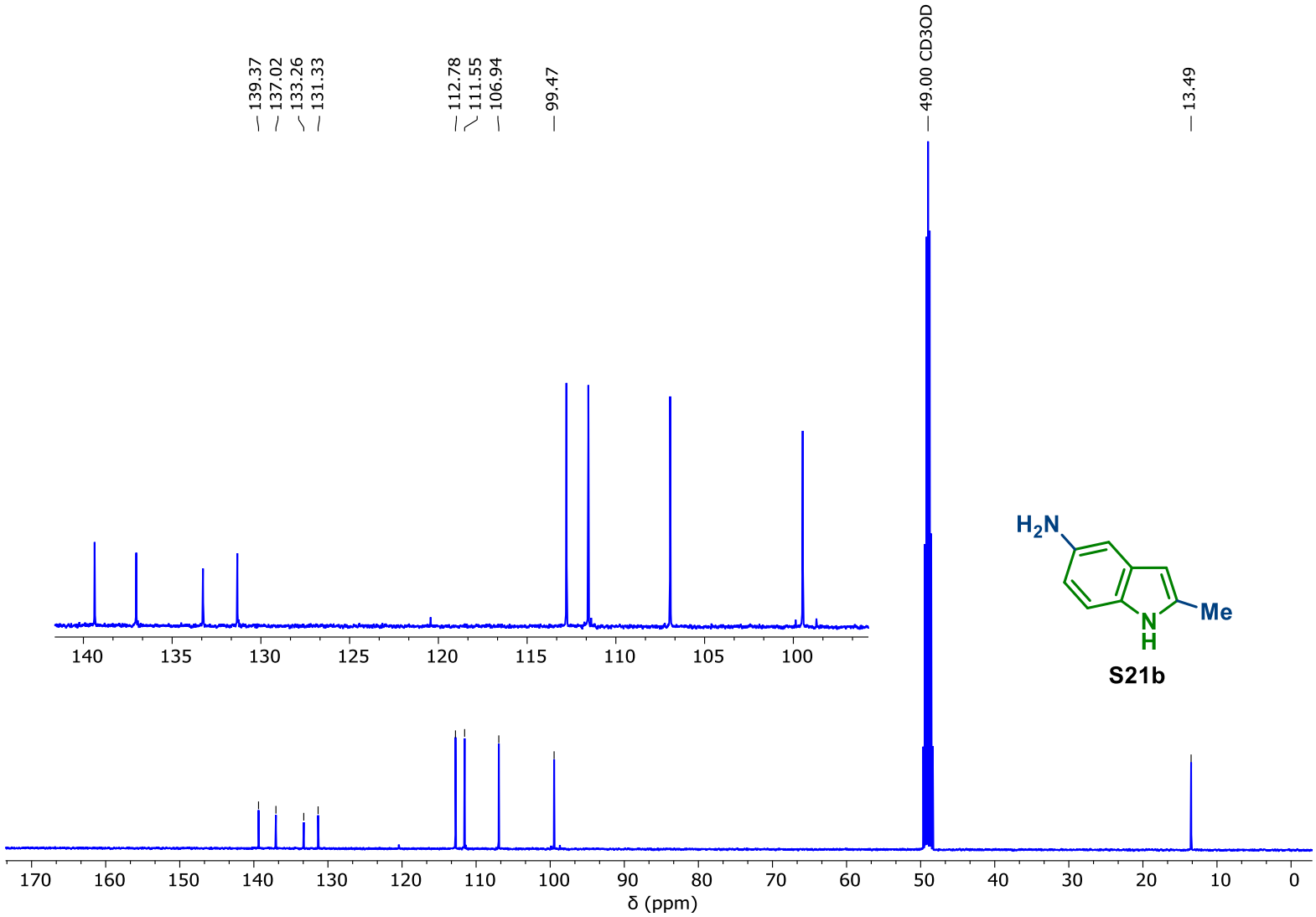
^{13}C NMR (100 MHz, CD_3OD) spectrum of 1*H*-indol-5-amine (S21a).



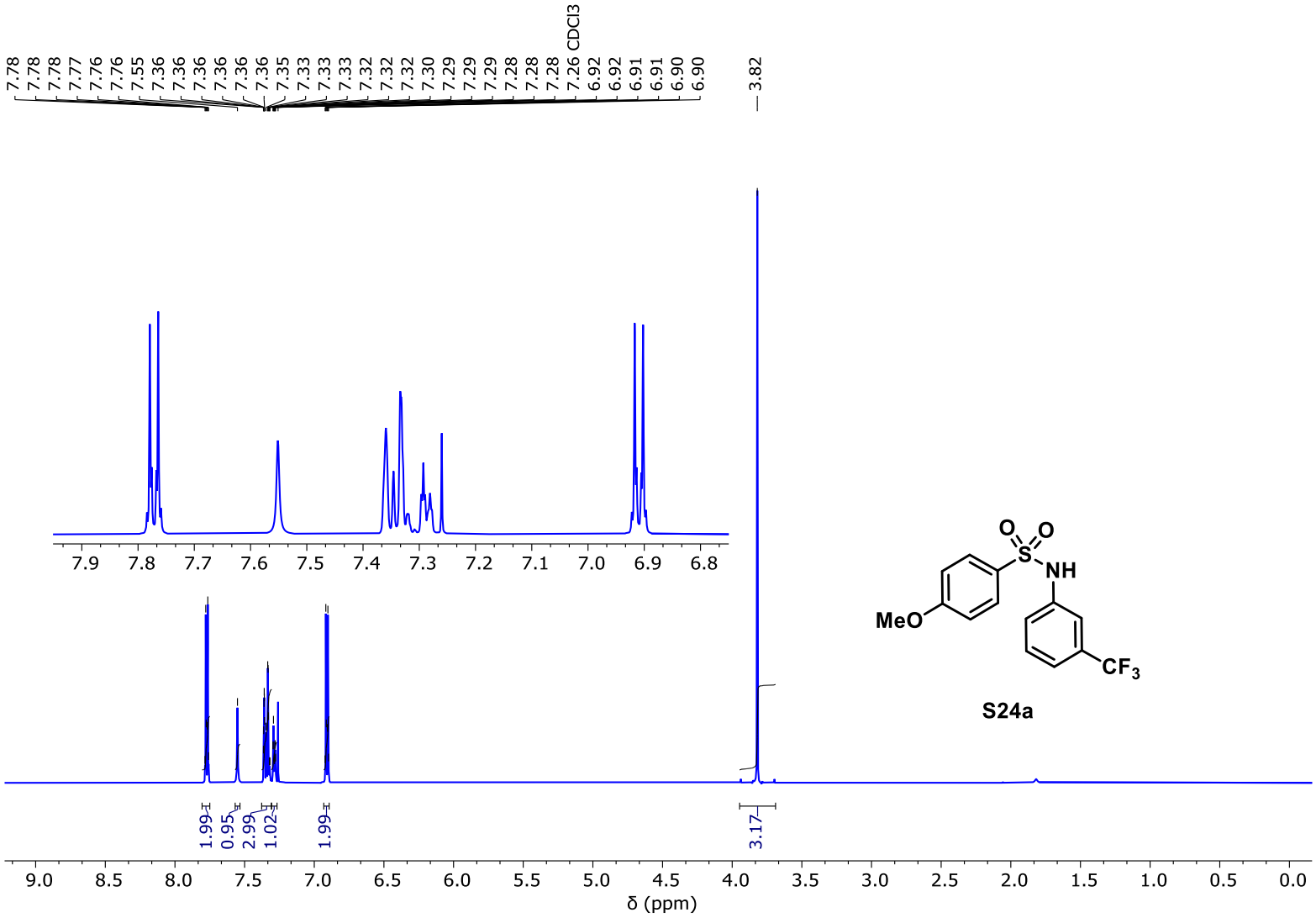
^{1}H NMR (400 MHz, CD_3OD) spectrum of 2-methyl-1*H*-indol-5-amine (S21b).



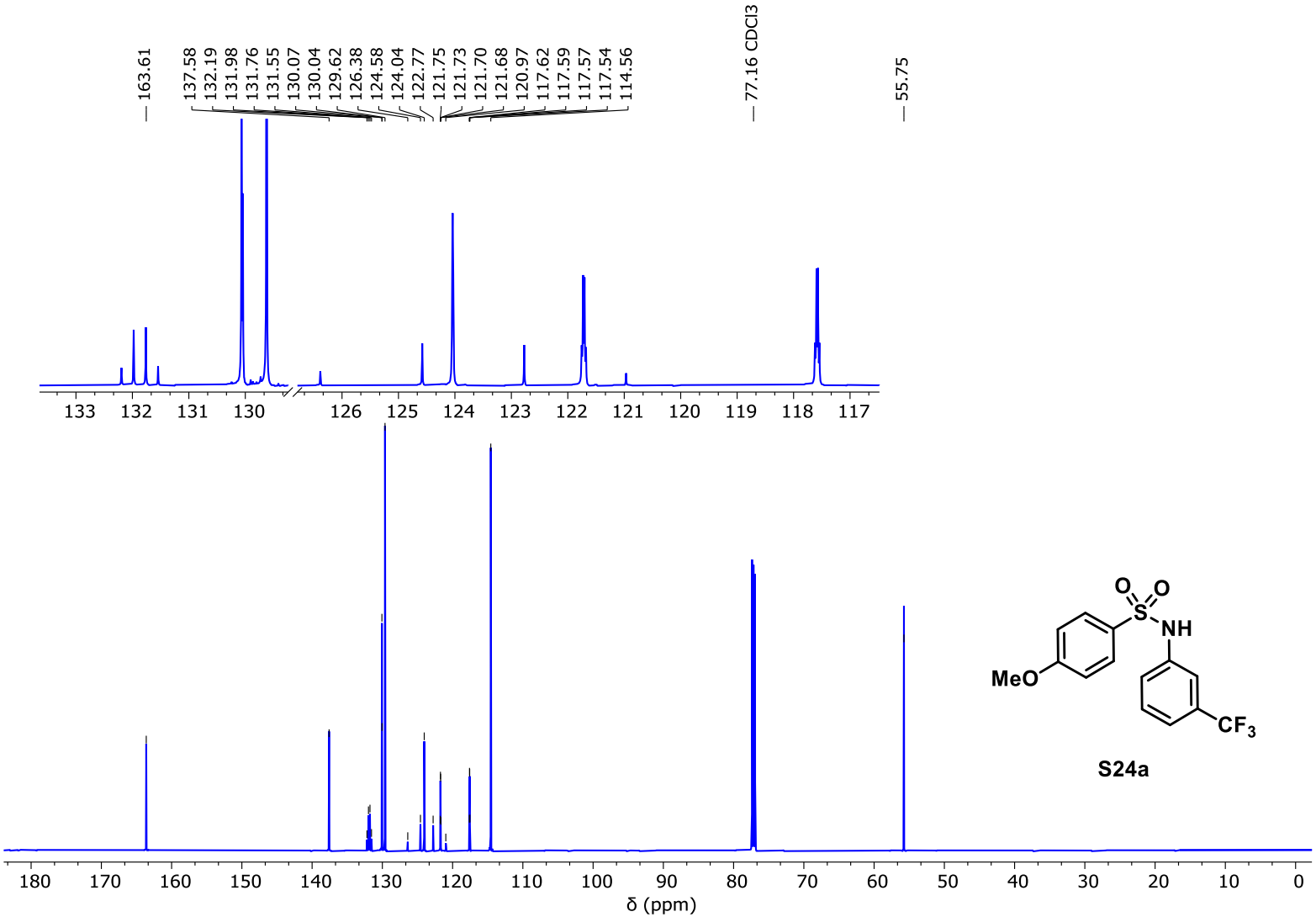
^{13}C NMR (100 MHz, CD_3OD) spectrum of 2-methyl-1*H*-indol-5-amine (S21b).



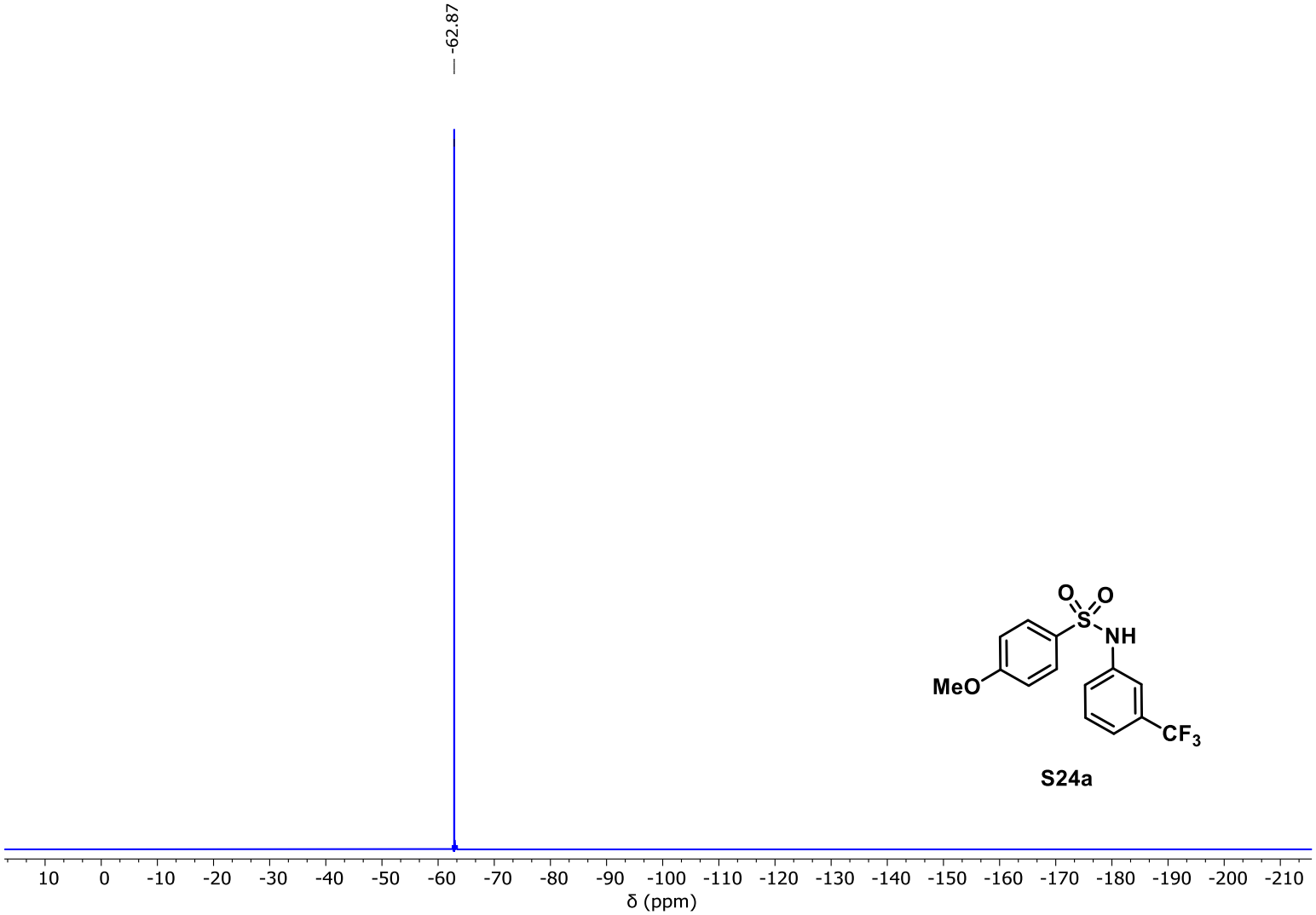
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(3-(trifluoromethyl)phenyl)benzenesulfonamide (S24a).



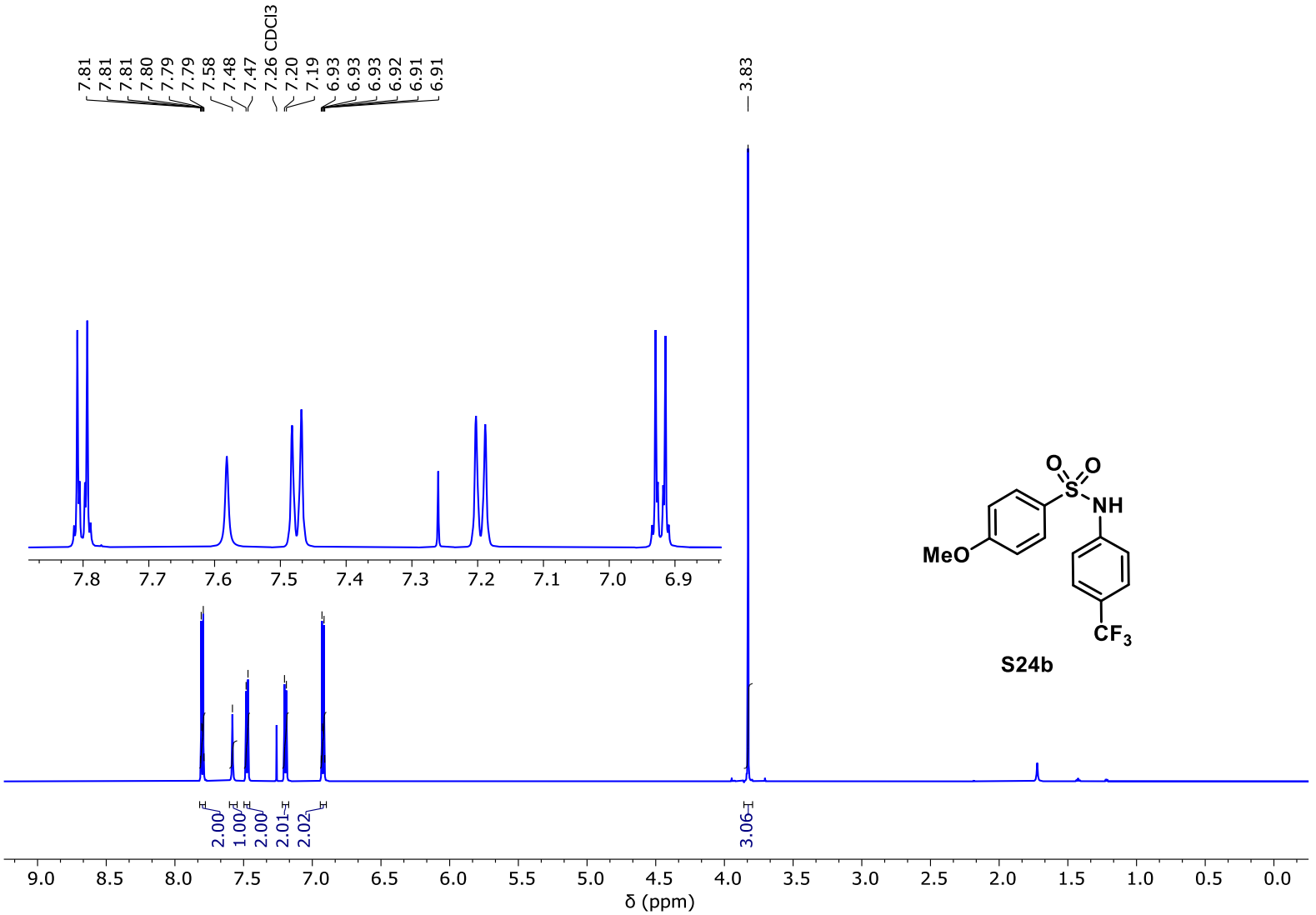
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(3-(trifluoromethyl)phenyl)benzenesulfonamide (S24a).



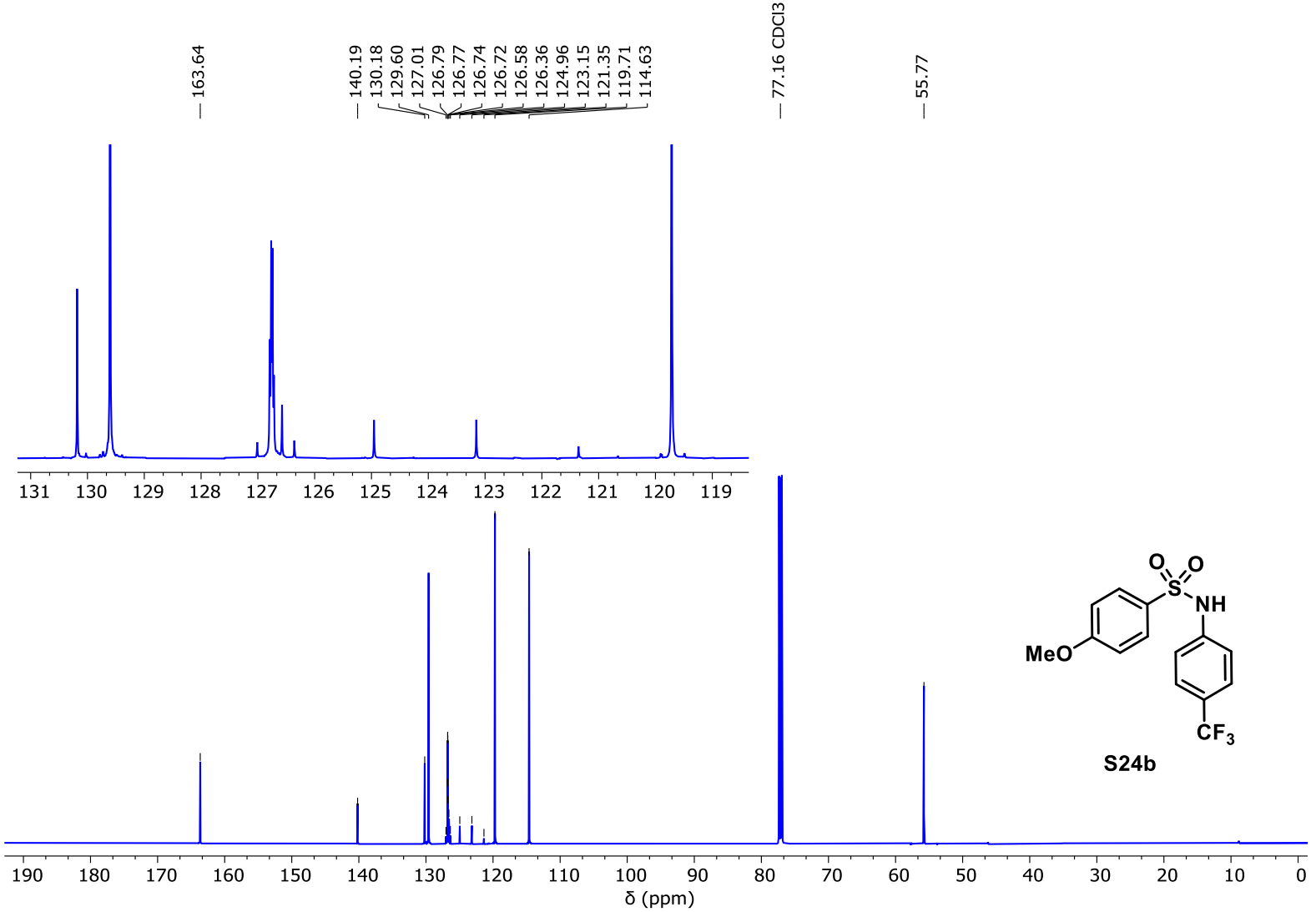
^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(3-(trifluoromethyl)phenyl)benzenesulfonamide (S24a).



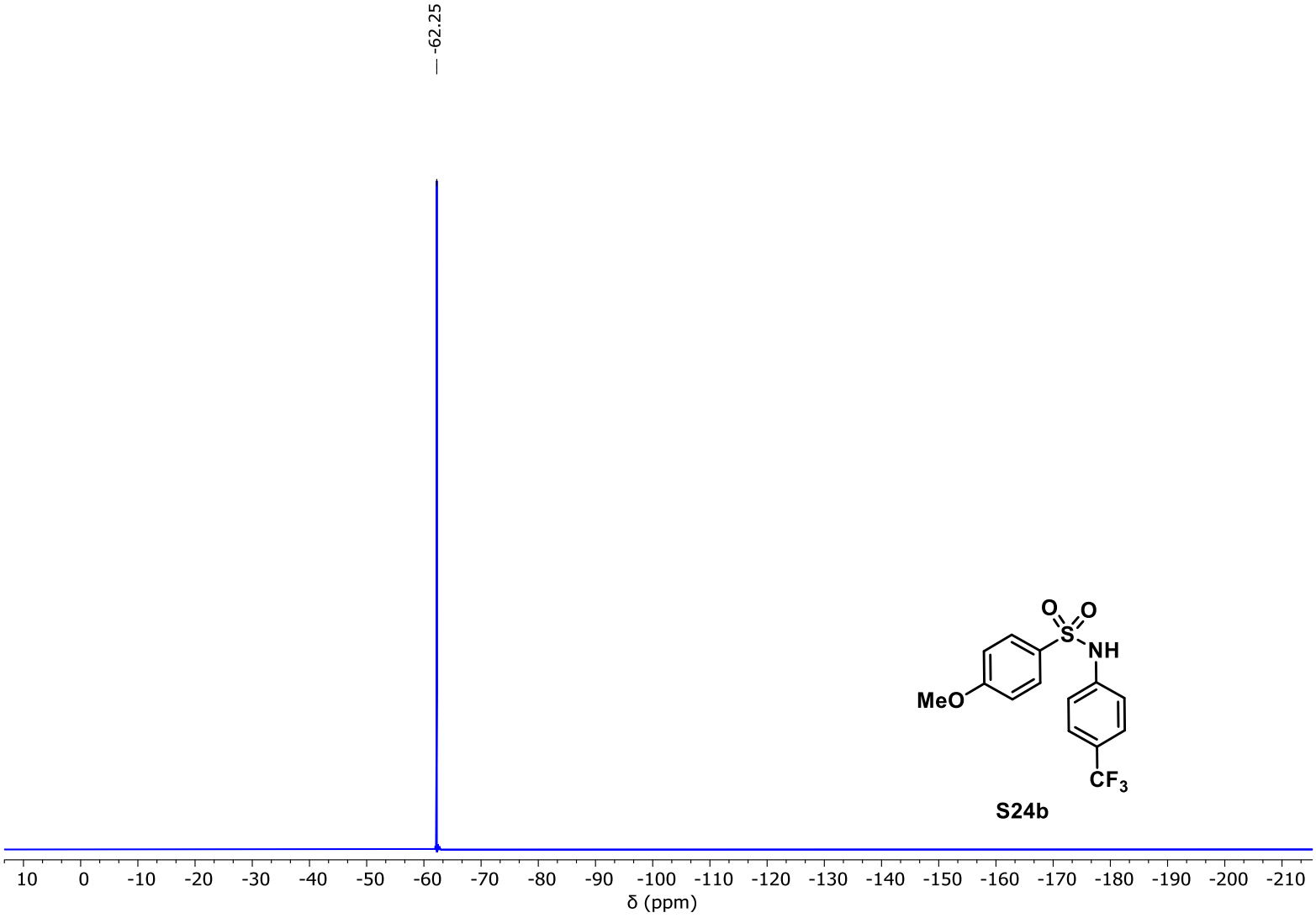
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (S24b).



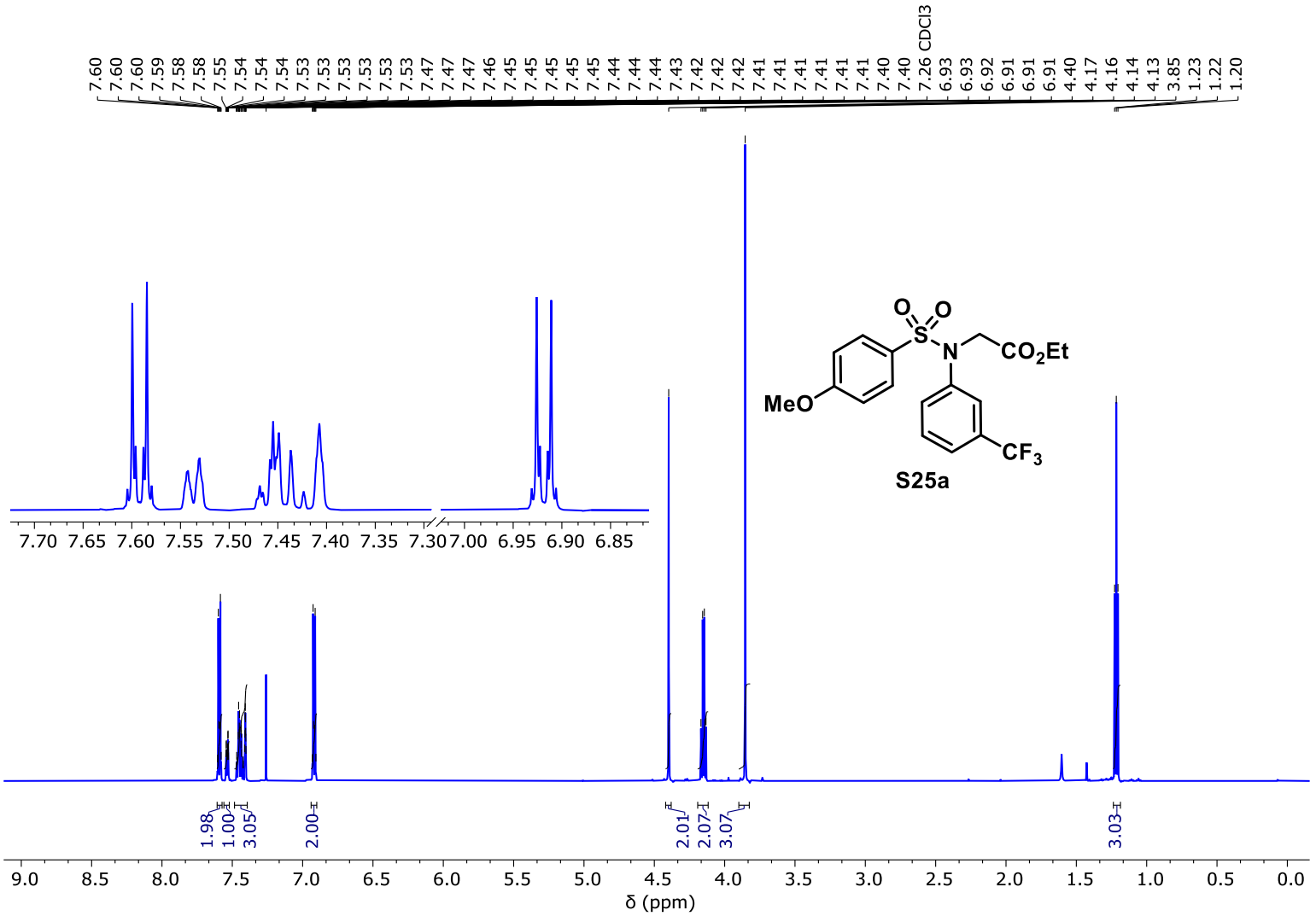
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (S24b).



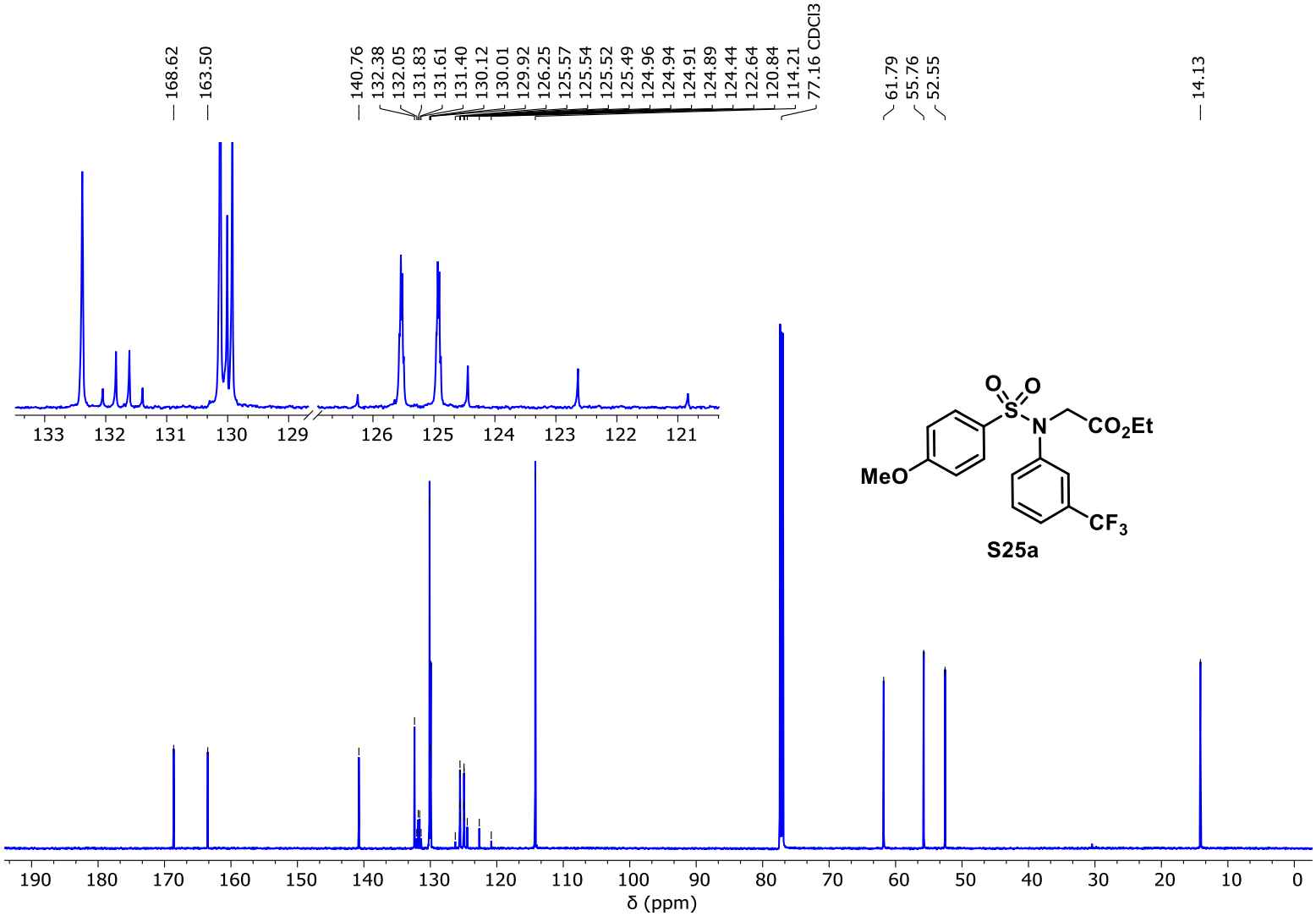
^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of 4-methoxy-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (S24b).



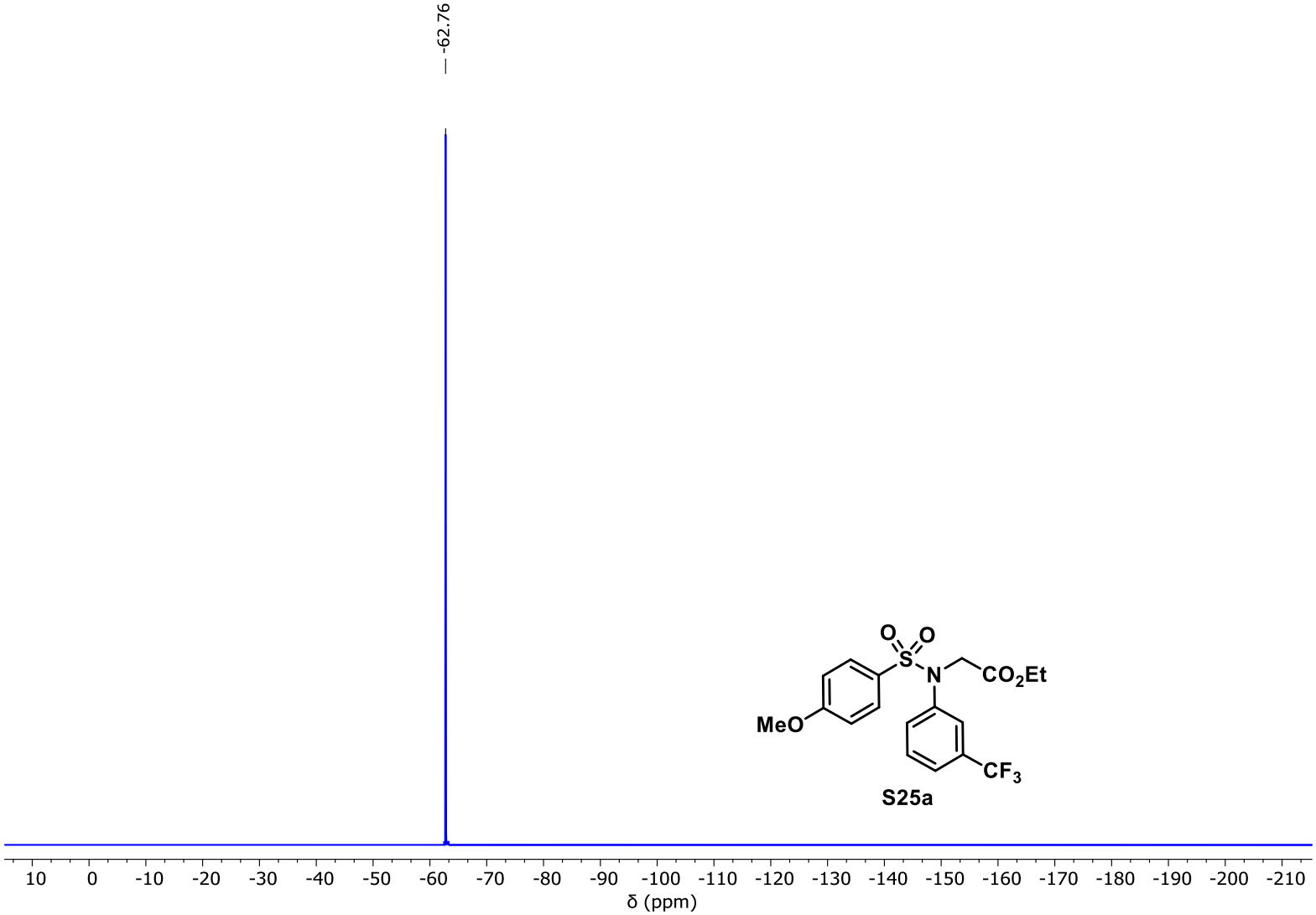
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycinate (S25a).



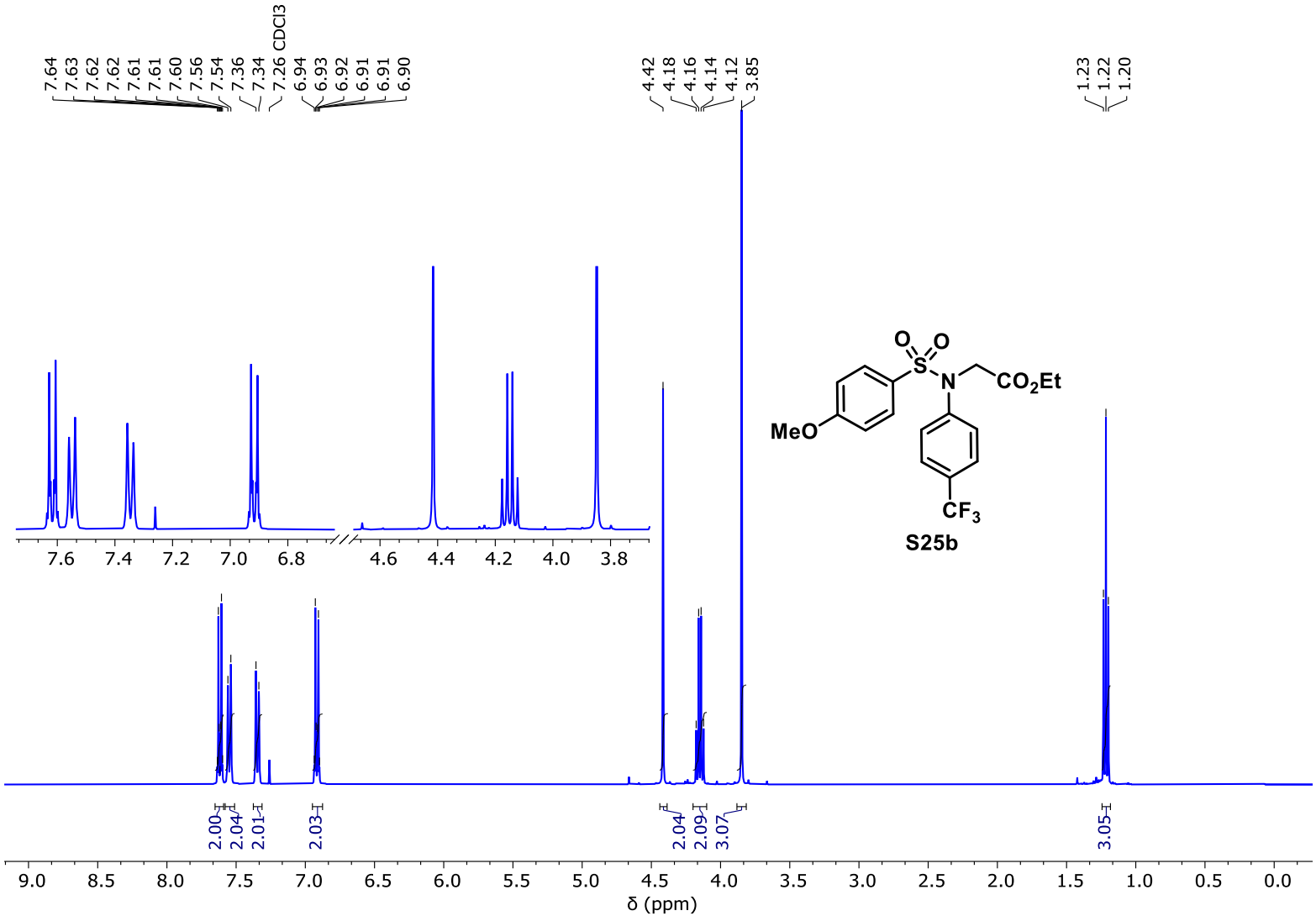
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycinate (S25a).



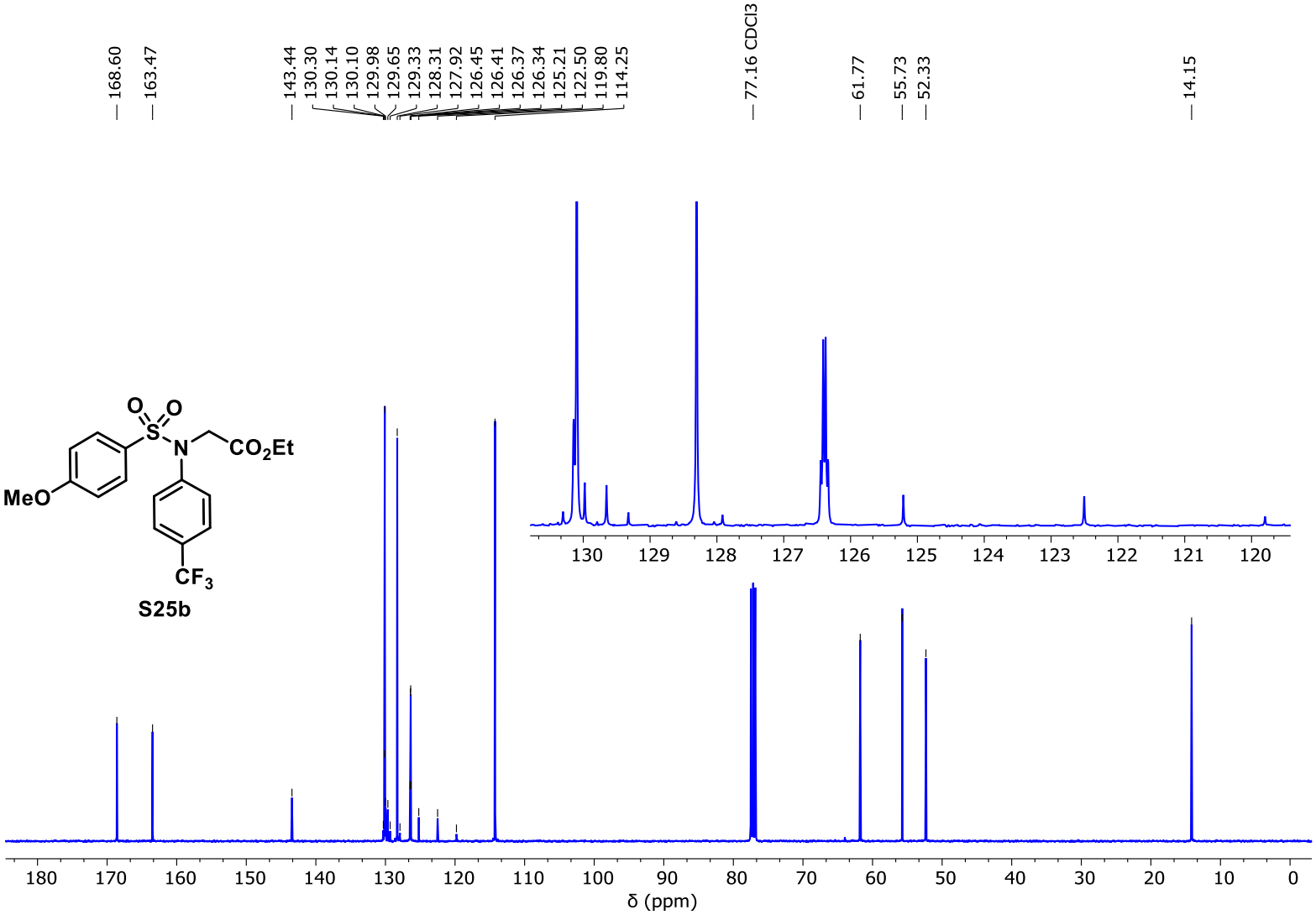
^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycinate (S25a).



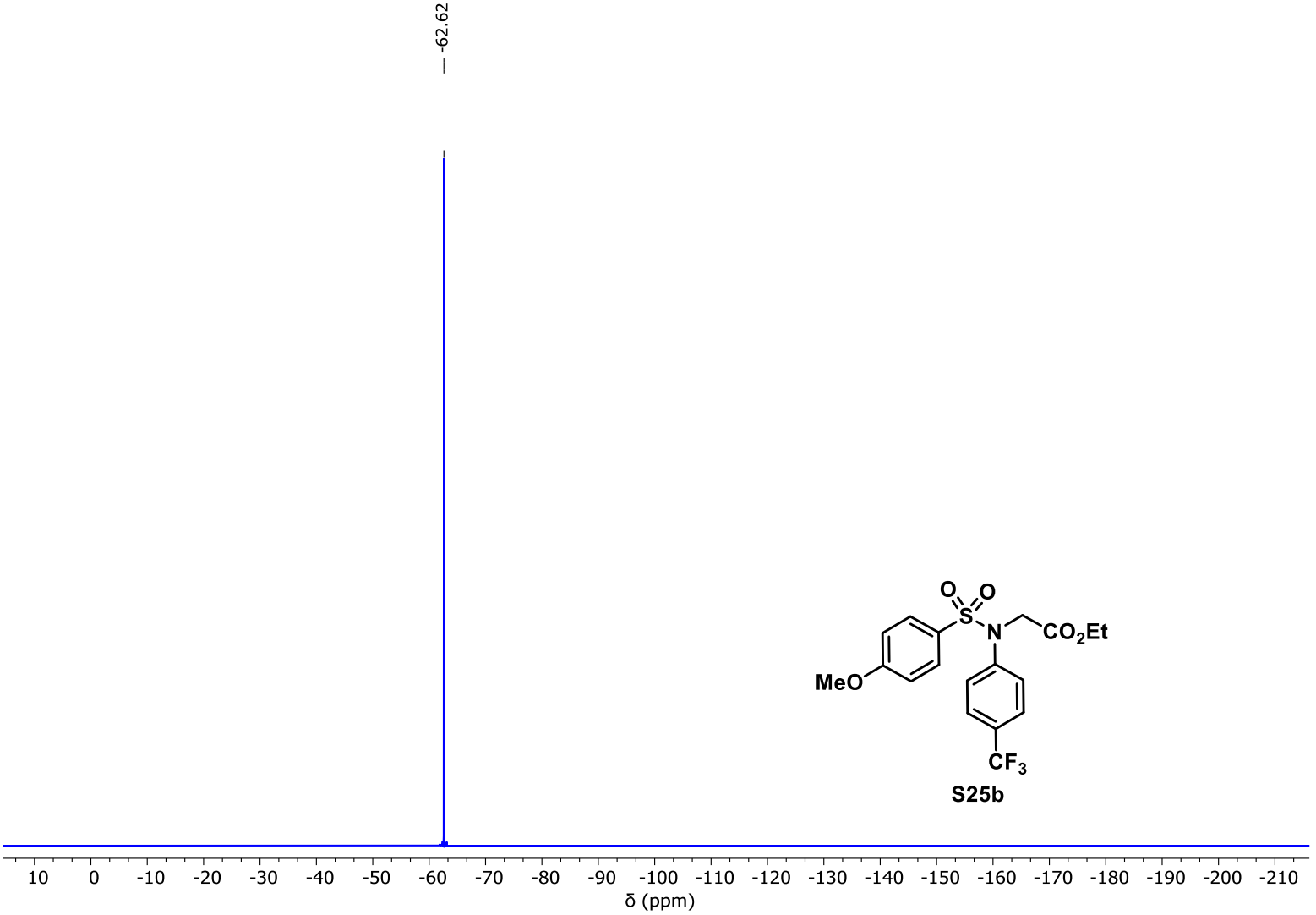
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycinate (S25b).



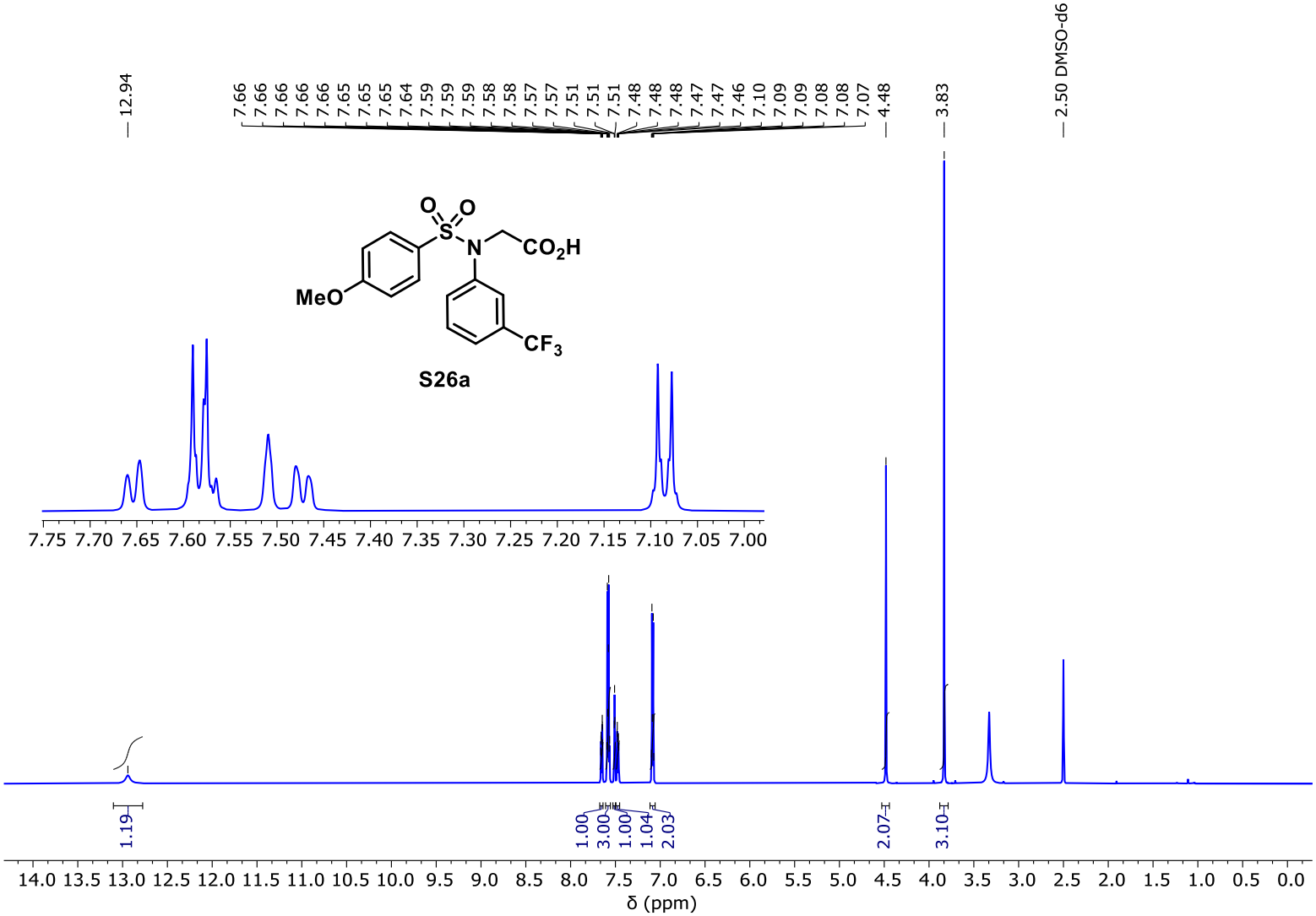
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycinate (S25b).



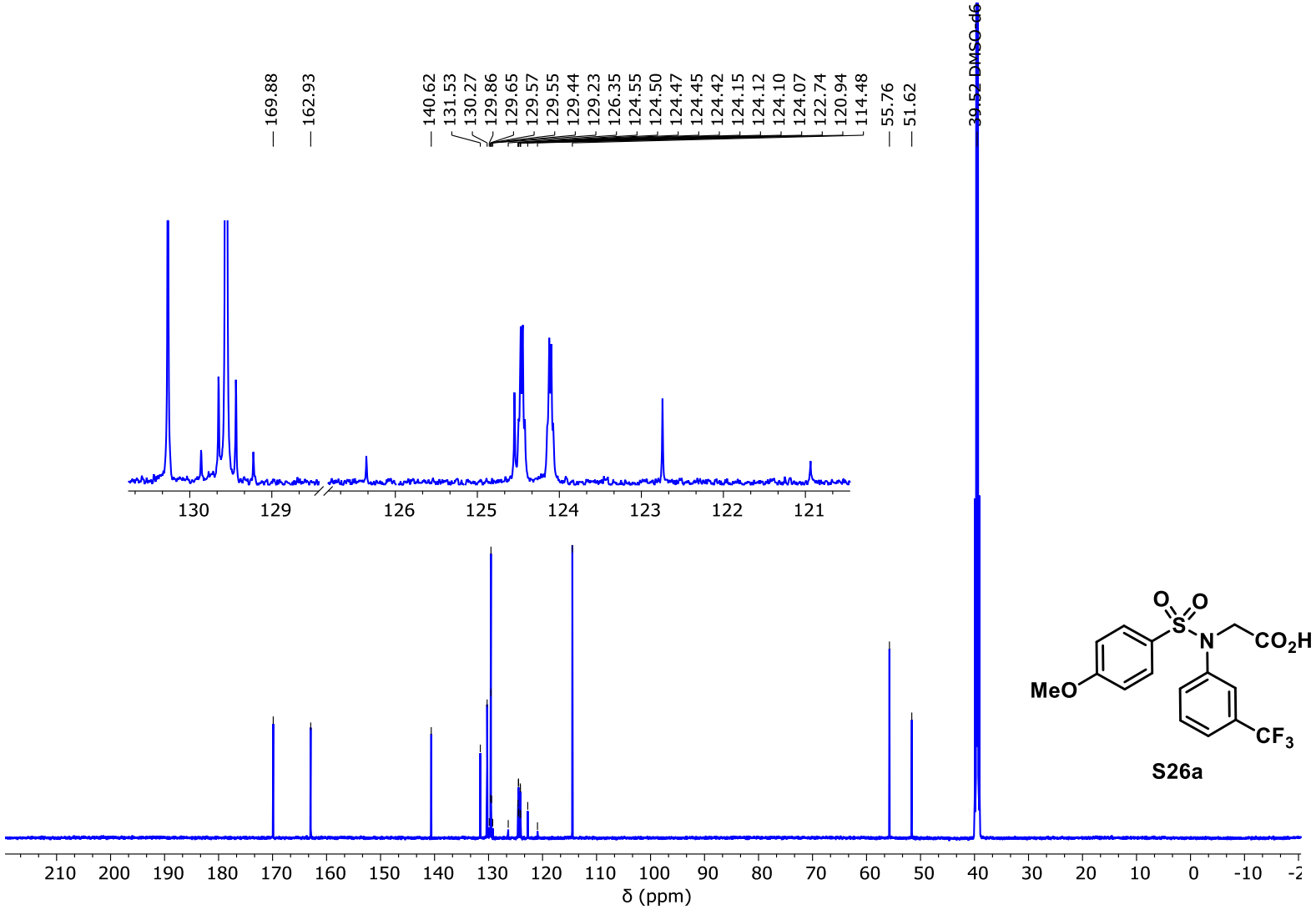
^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of ethyl *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycinate (S25b).



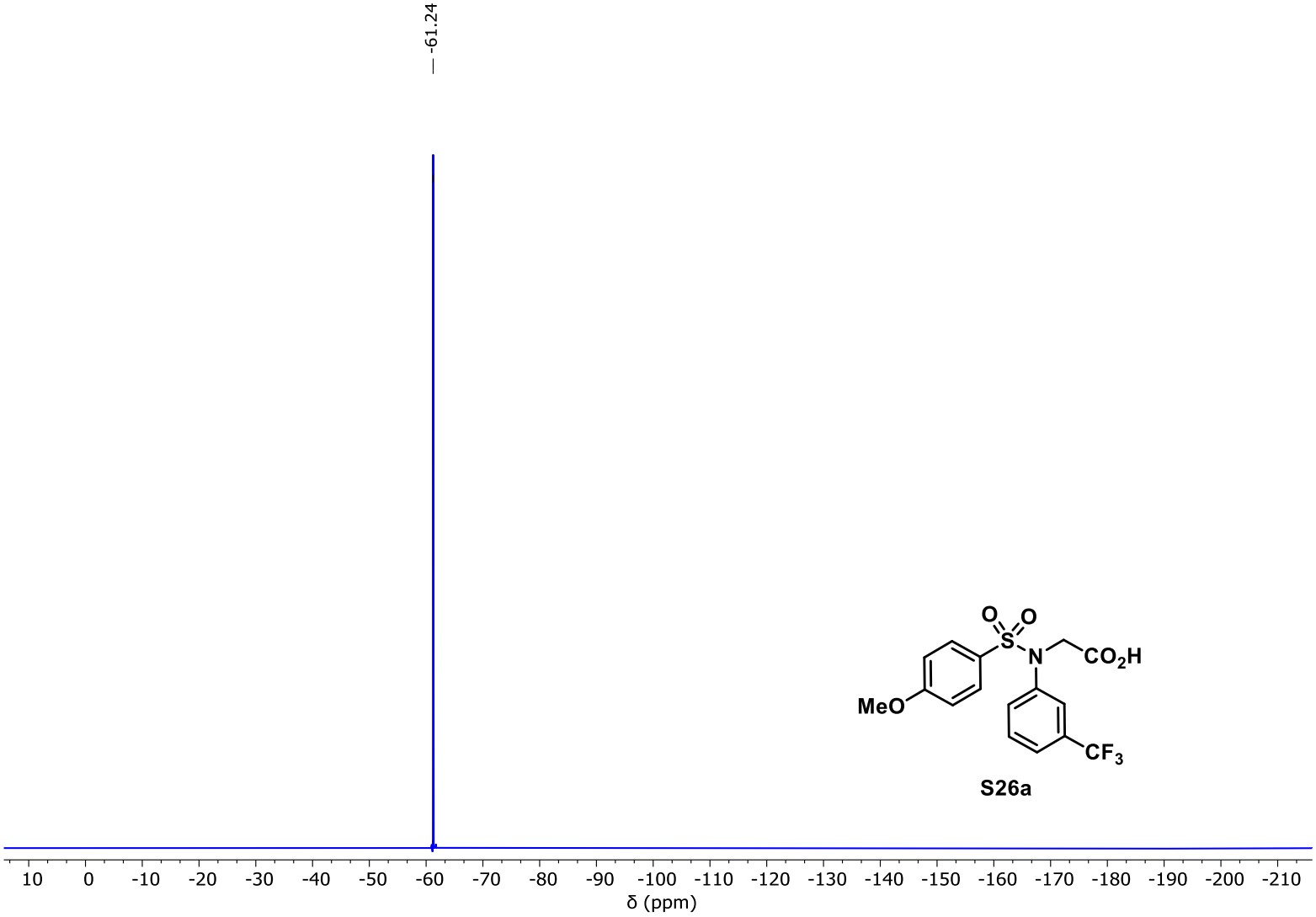
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycine (S26a).



^{13}C NMR (151 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycine (S26a).

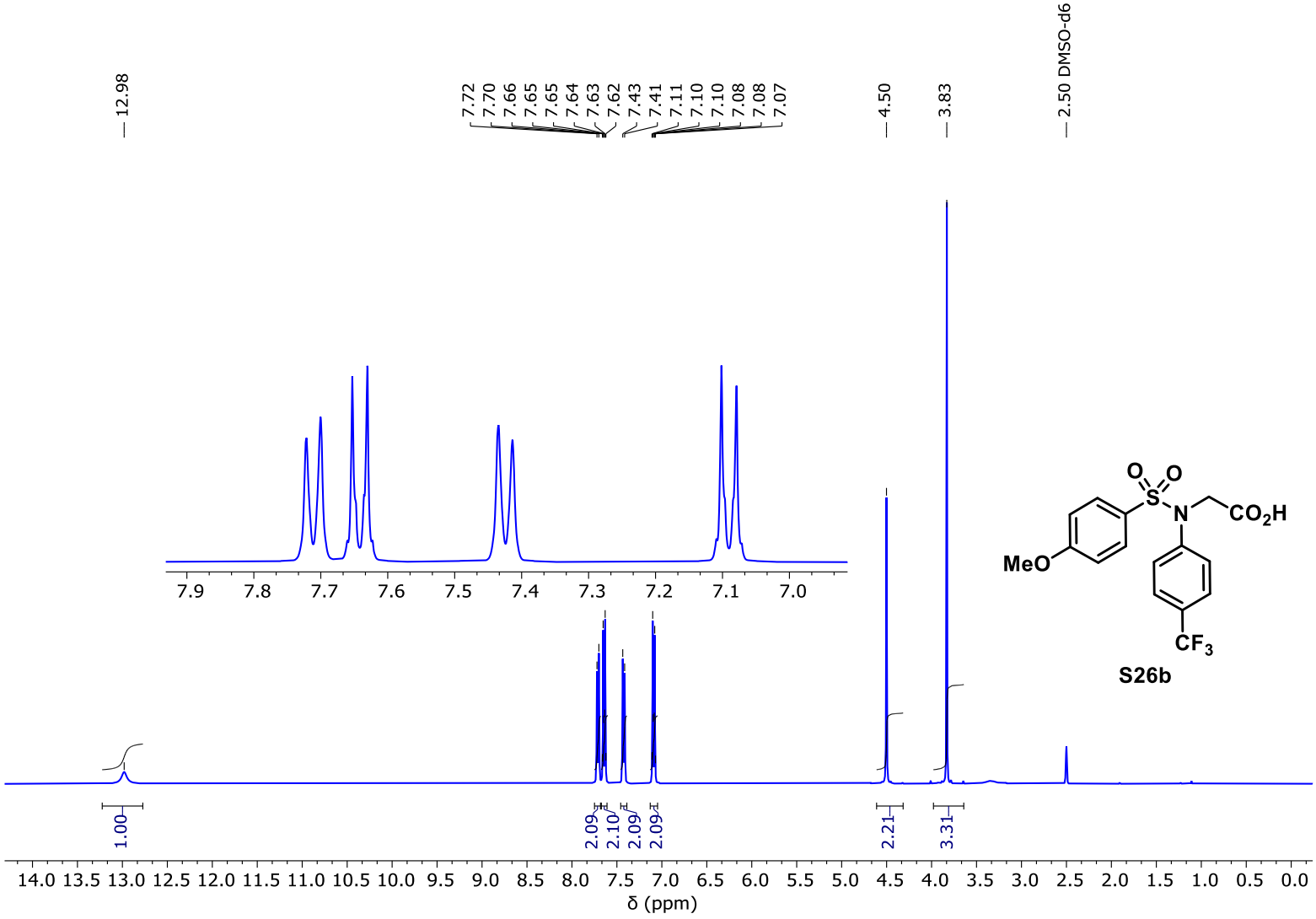


^{19}F NMR (376.5 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(3-(trifluoromethyl)phenyl)glycine (S26a).

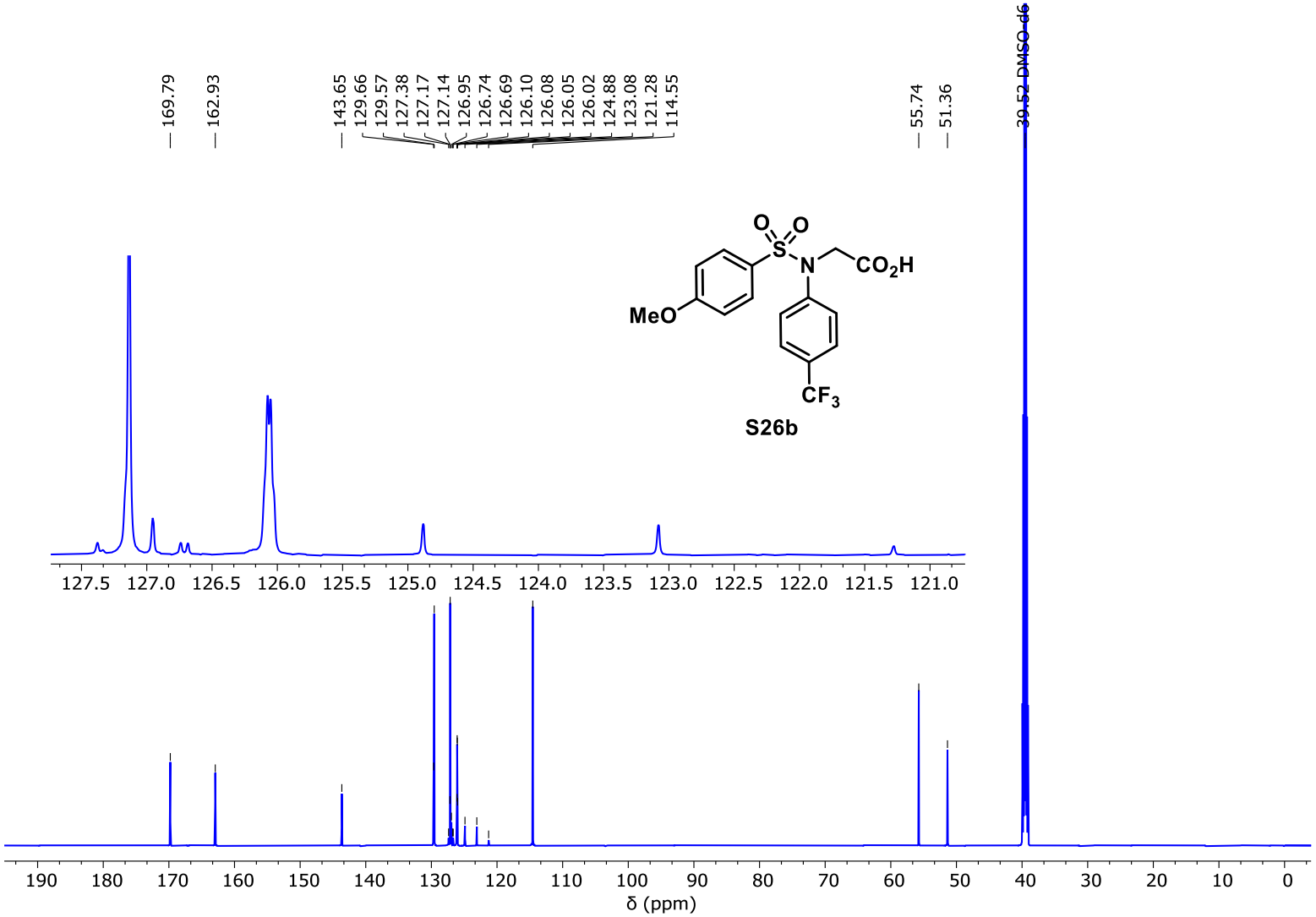


S26a

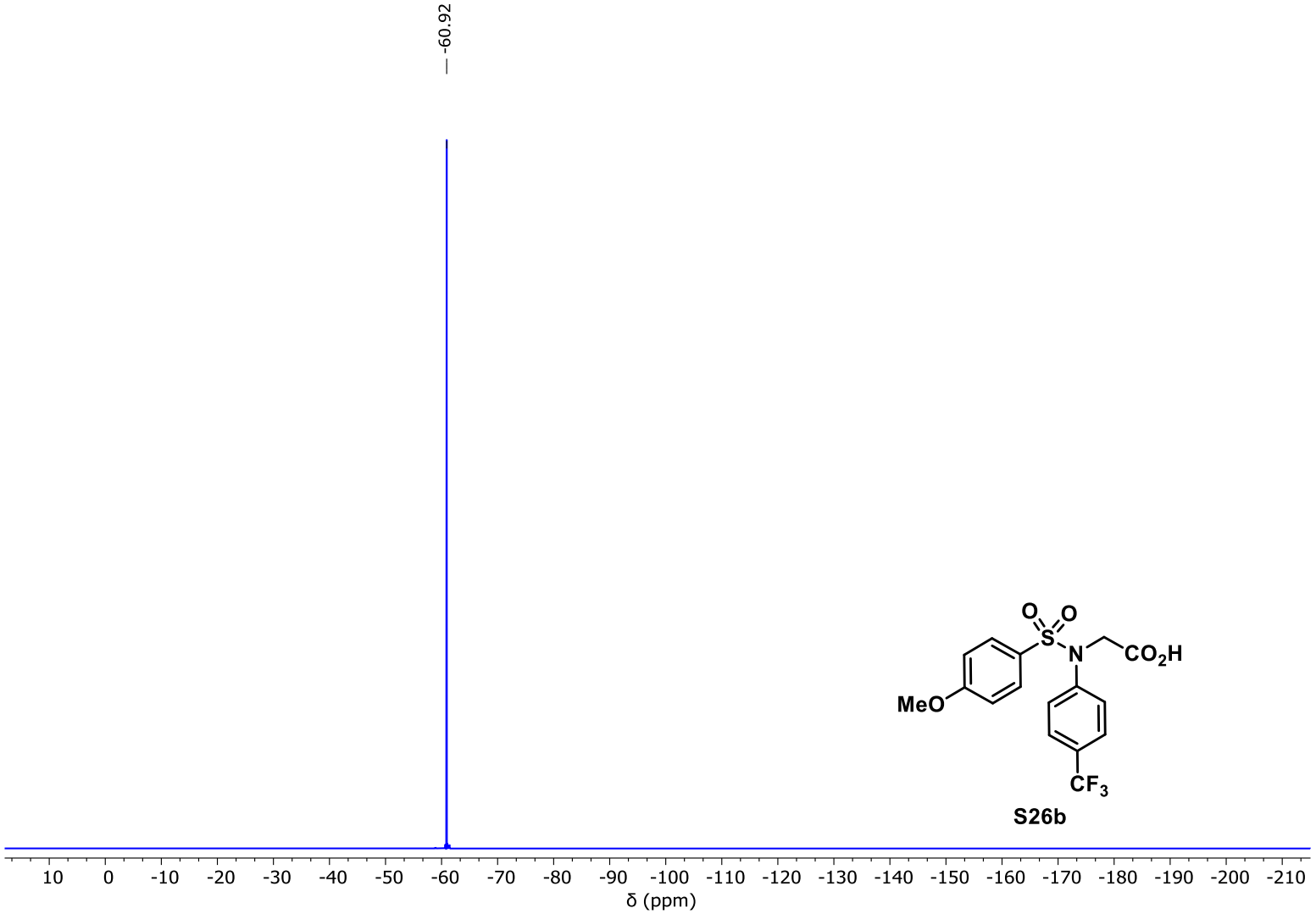
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycine (S26b).



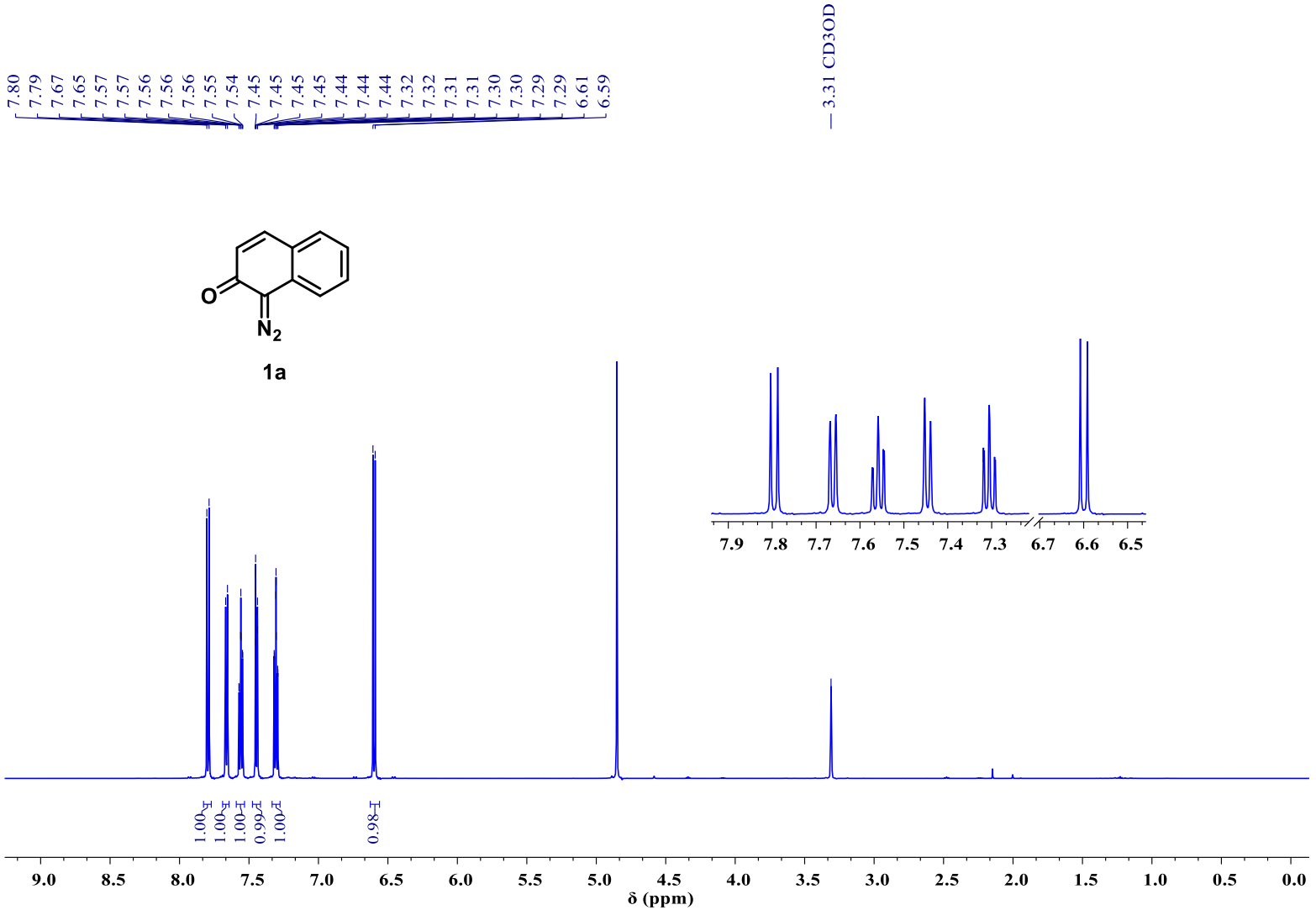
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycine (S26b).



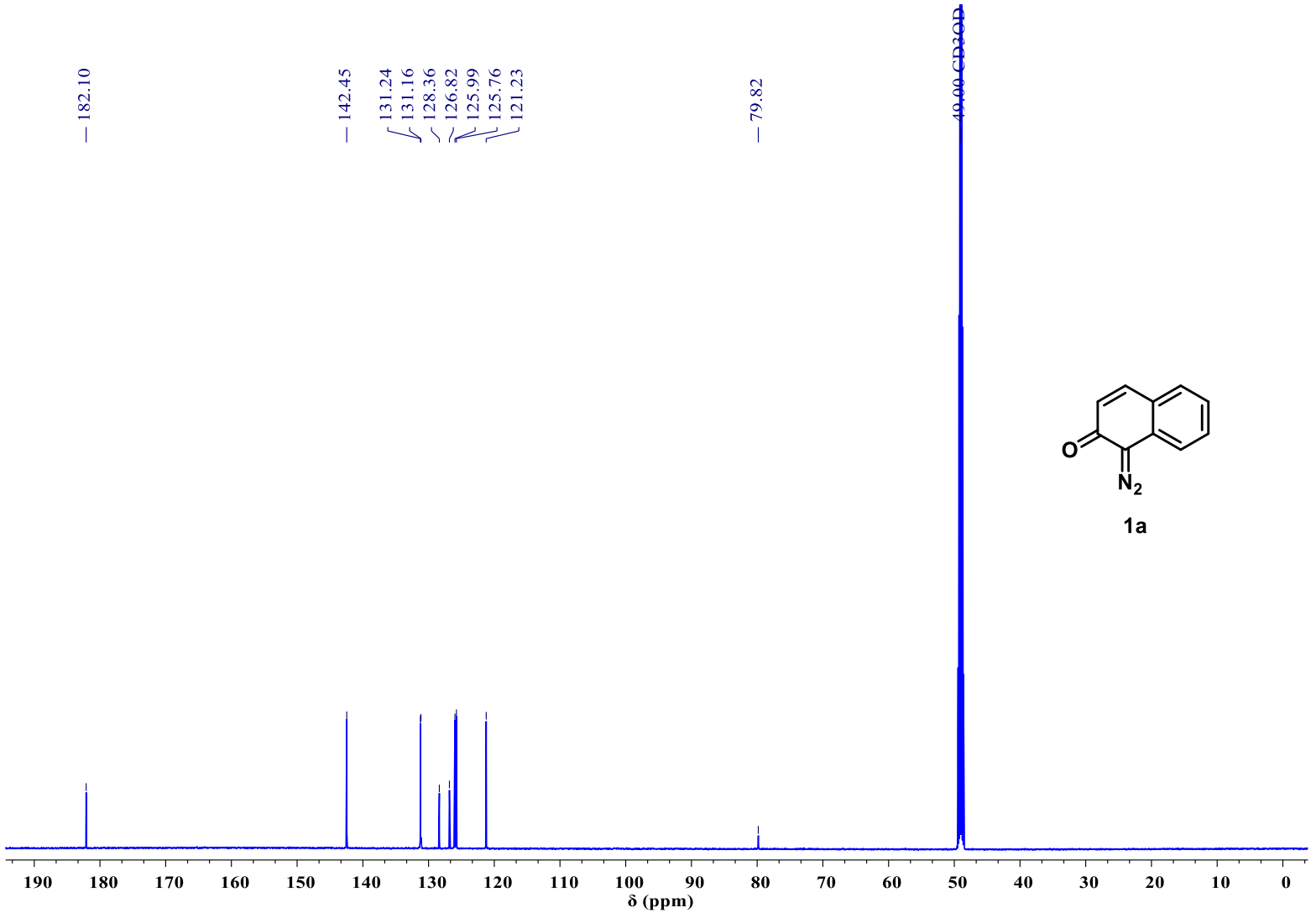
^{19}F NMR (376.5 MHz, DMSO-d_6) spectrum of *N*-((4-methoxyphenyl)sulfonyl)-*N*-(4-(trifluoromethyl)phenyl)glycine (S26b).



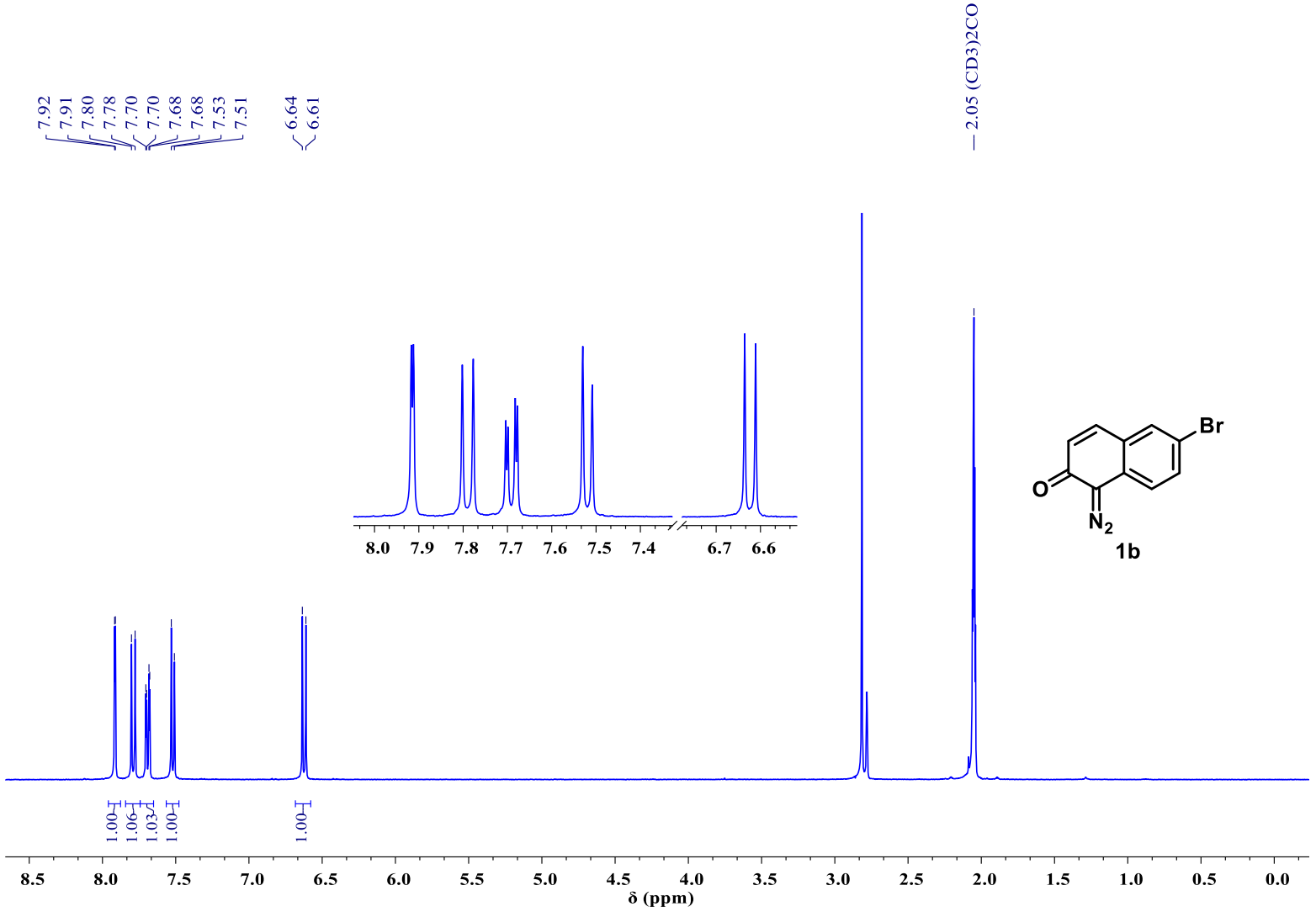
^{1}H NMR (600 MHz, CD_3OD) spectrum of 1-diazonaphthalen-2(1*H*)-one (1a).



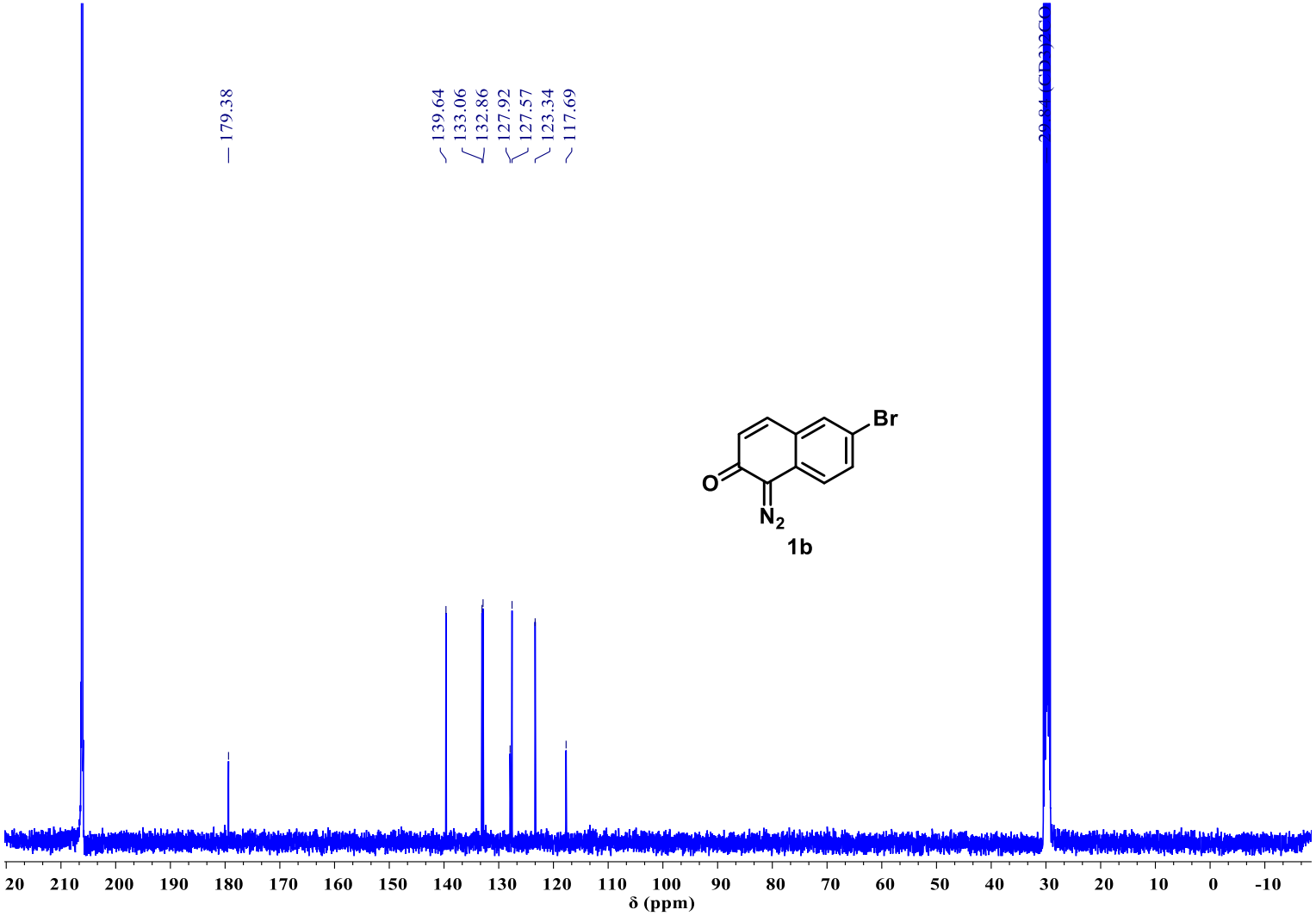
^{13}C NMR (151 MHz, CD_3OD) spectrum of 1-diazonaphthalen-2(1*H*)-one (1a).



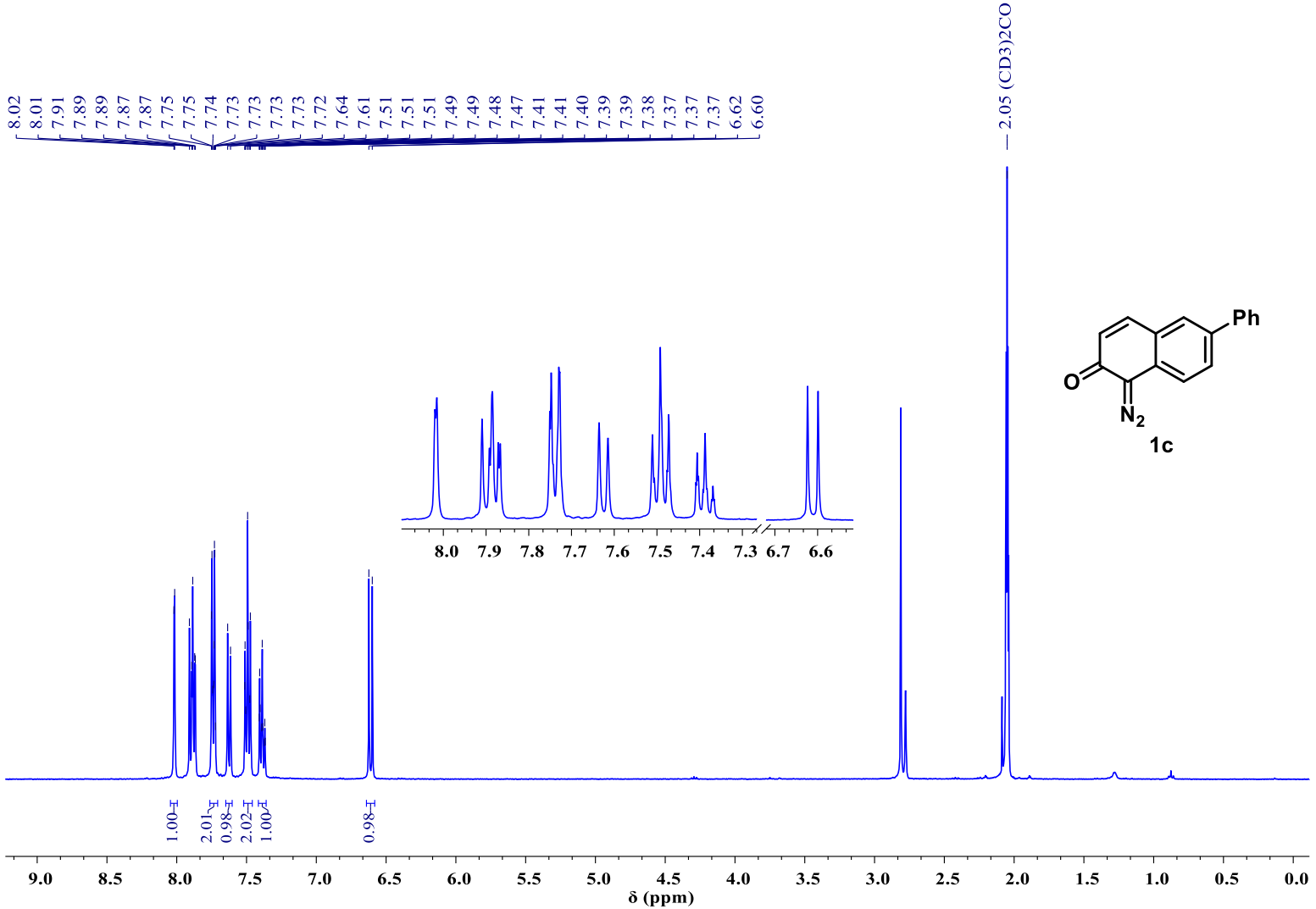
^{1}H NMR (400 MHz, acetone-d_6) spectrum of 6-bromo-1-diazonaphthalen-2(1*H*)-one (1b).



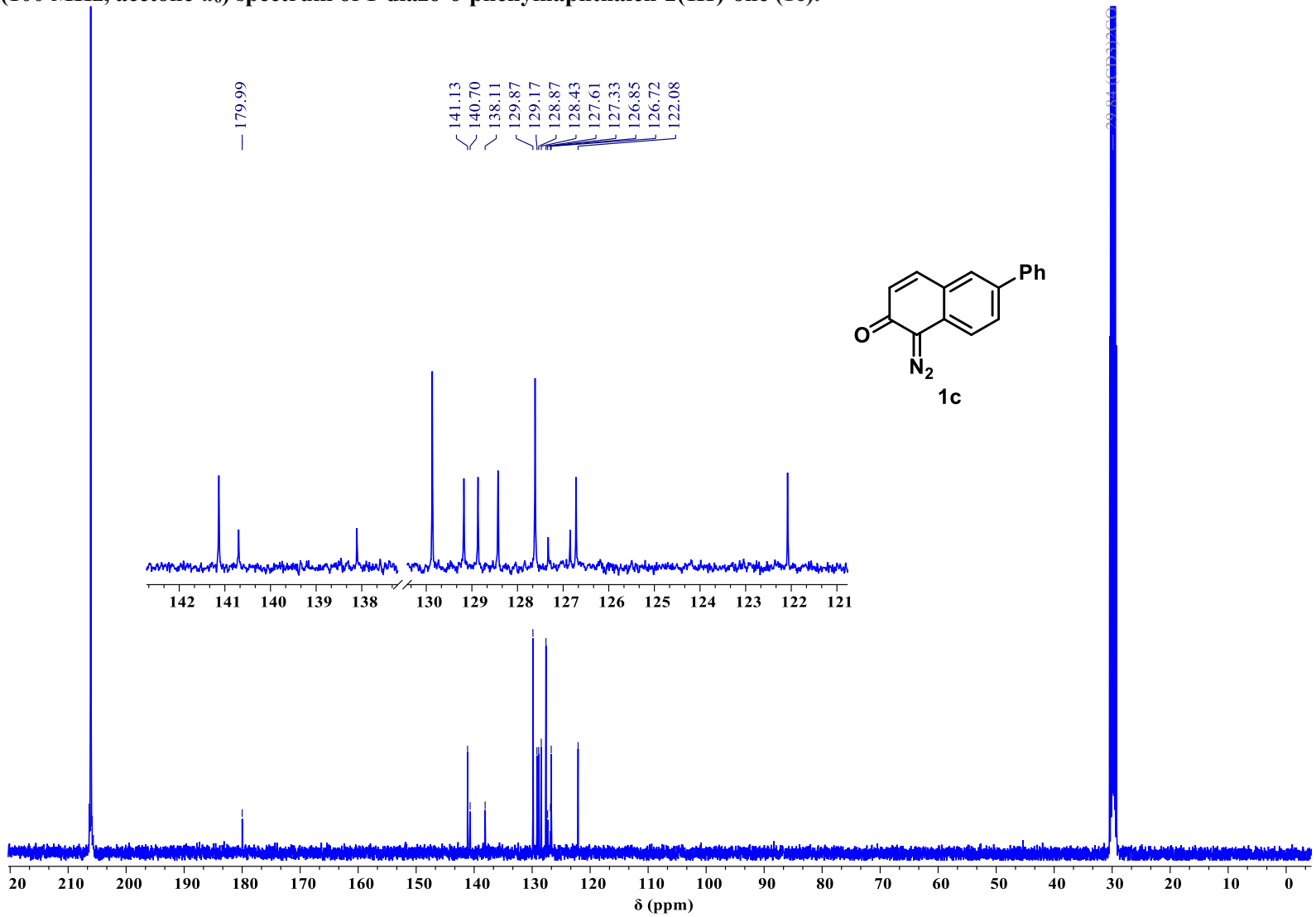
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 6-bromo-1-diazonaphthalen-2(1*H*)-one (1b).



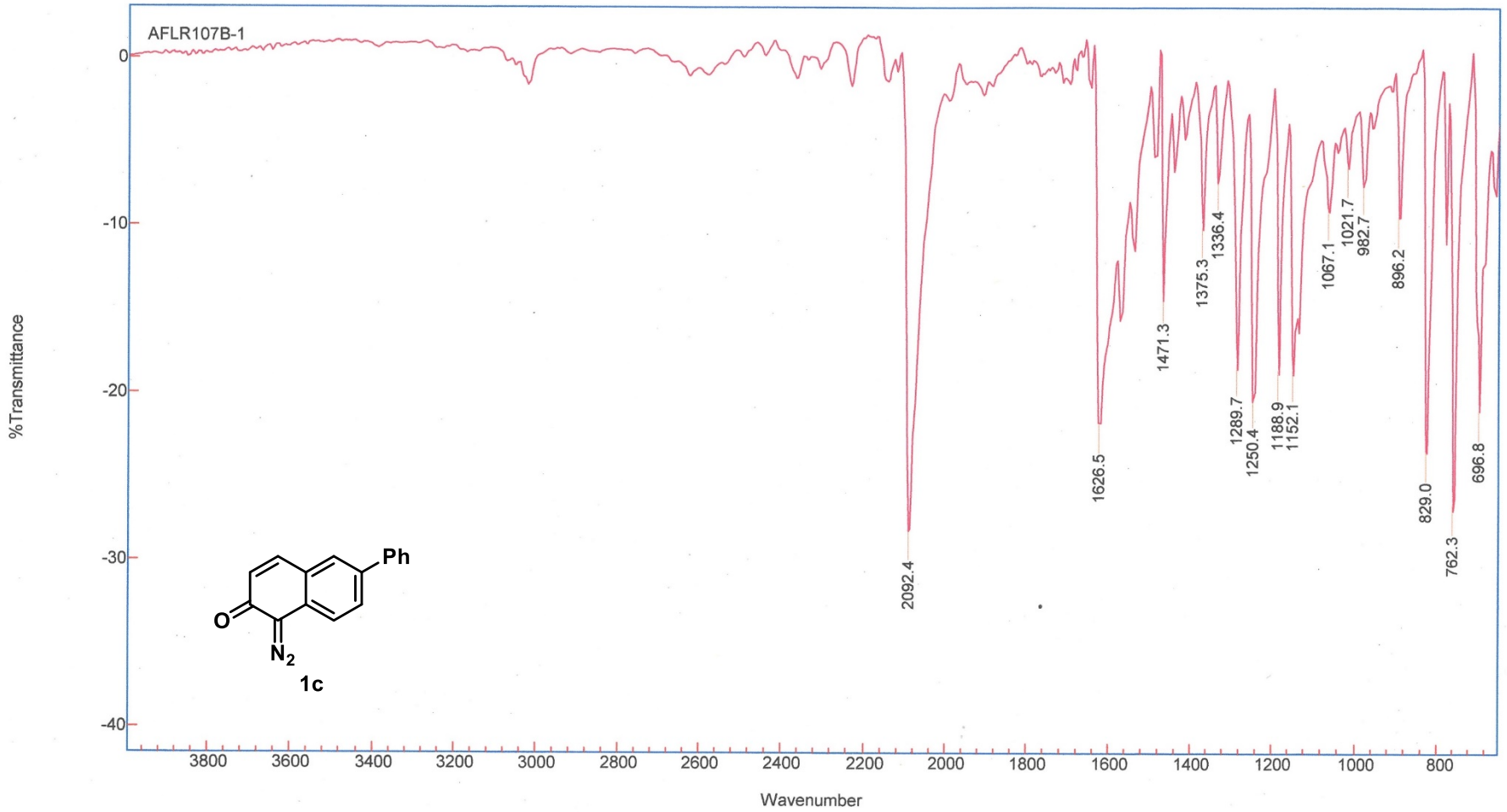
^{1}H NMR (400 MHz, acetone-d_6) spectrum of 1-diazo-6-phenylnaphthalen-2(1*H*)-one (1c).



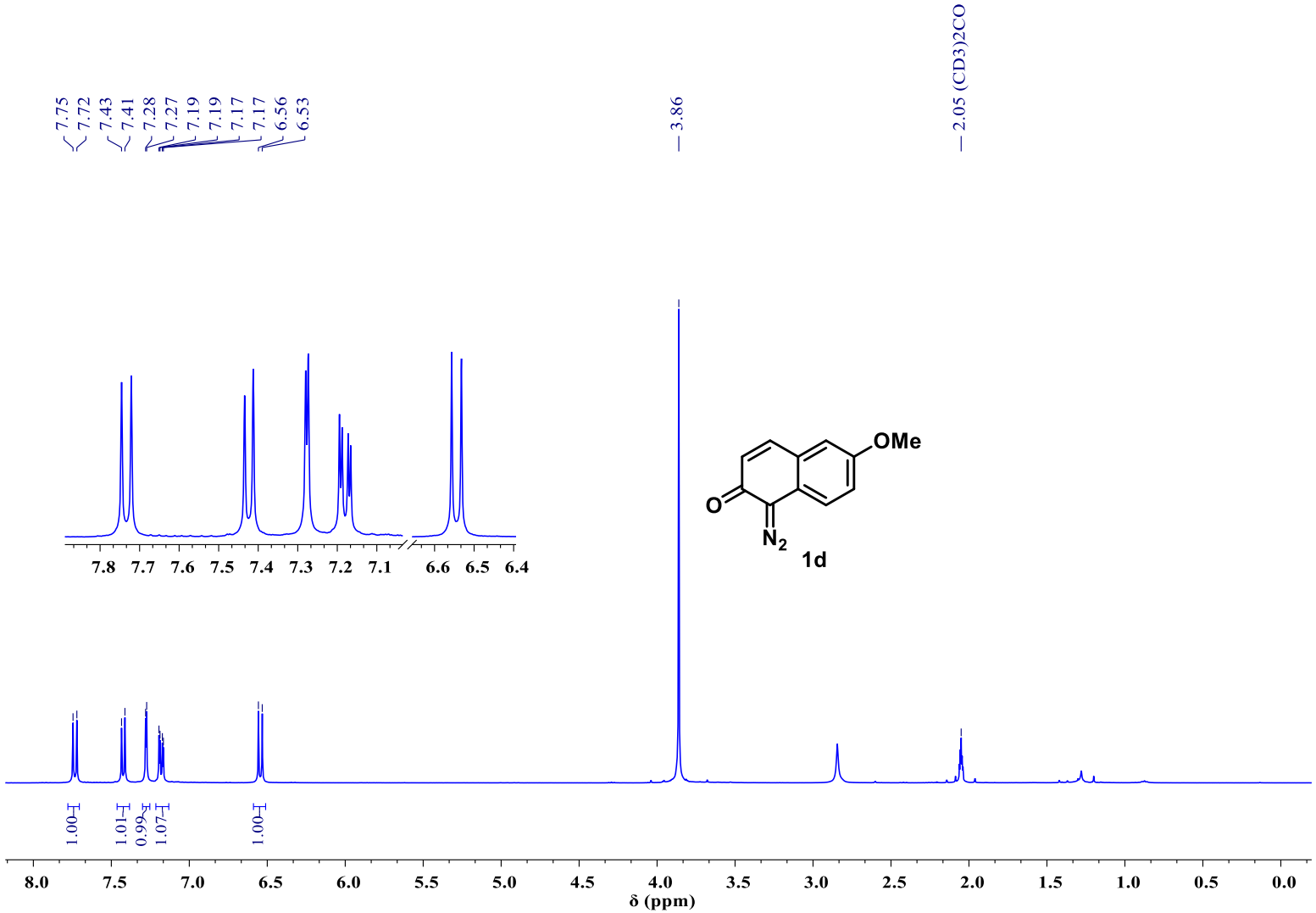
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 1-diazo-6-phenylnaphthalen-2(1*H*)-one (1c).



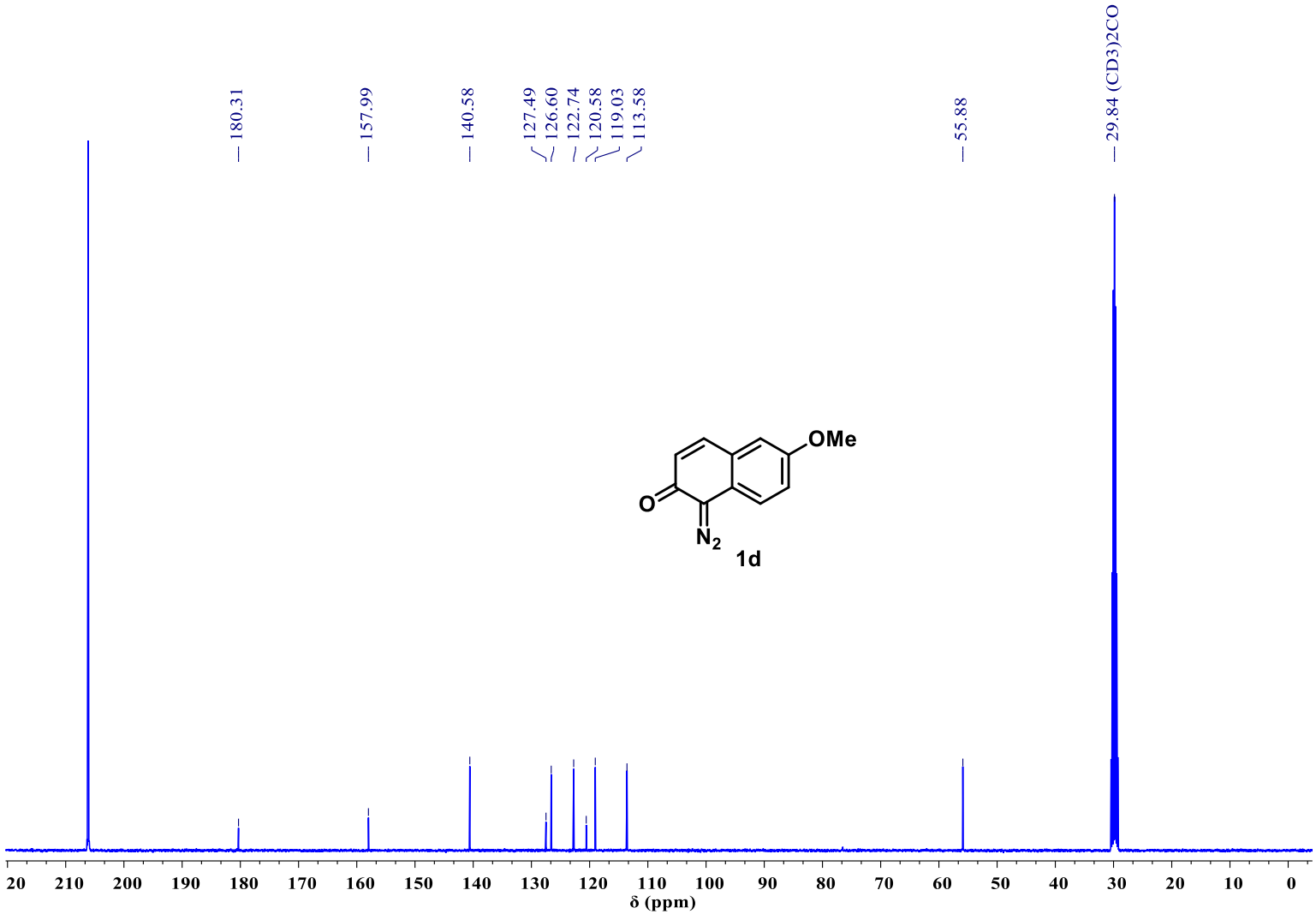
ATR-IR spectrum of 1-diazo-6-phenylnaphthalen-2(1*H*)-one (1c).



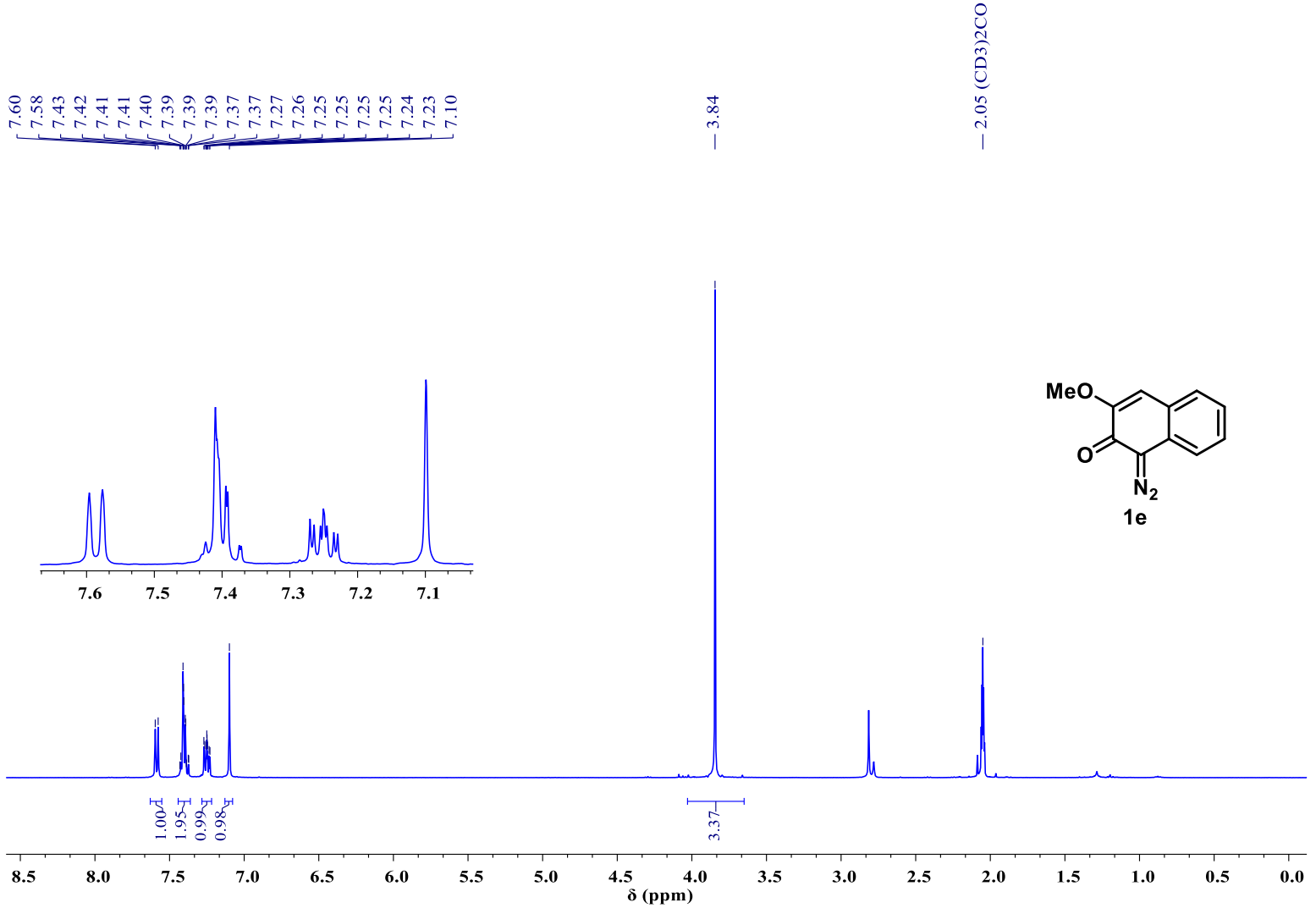
^{1}H NMR (400 MHz, acetone-d_6) spectrum of 1-diazo-6-methoxynaphthalen-2(1*H*)-one (1d).



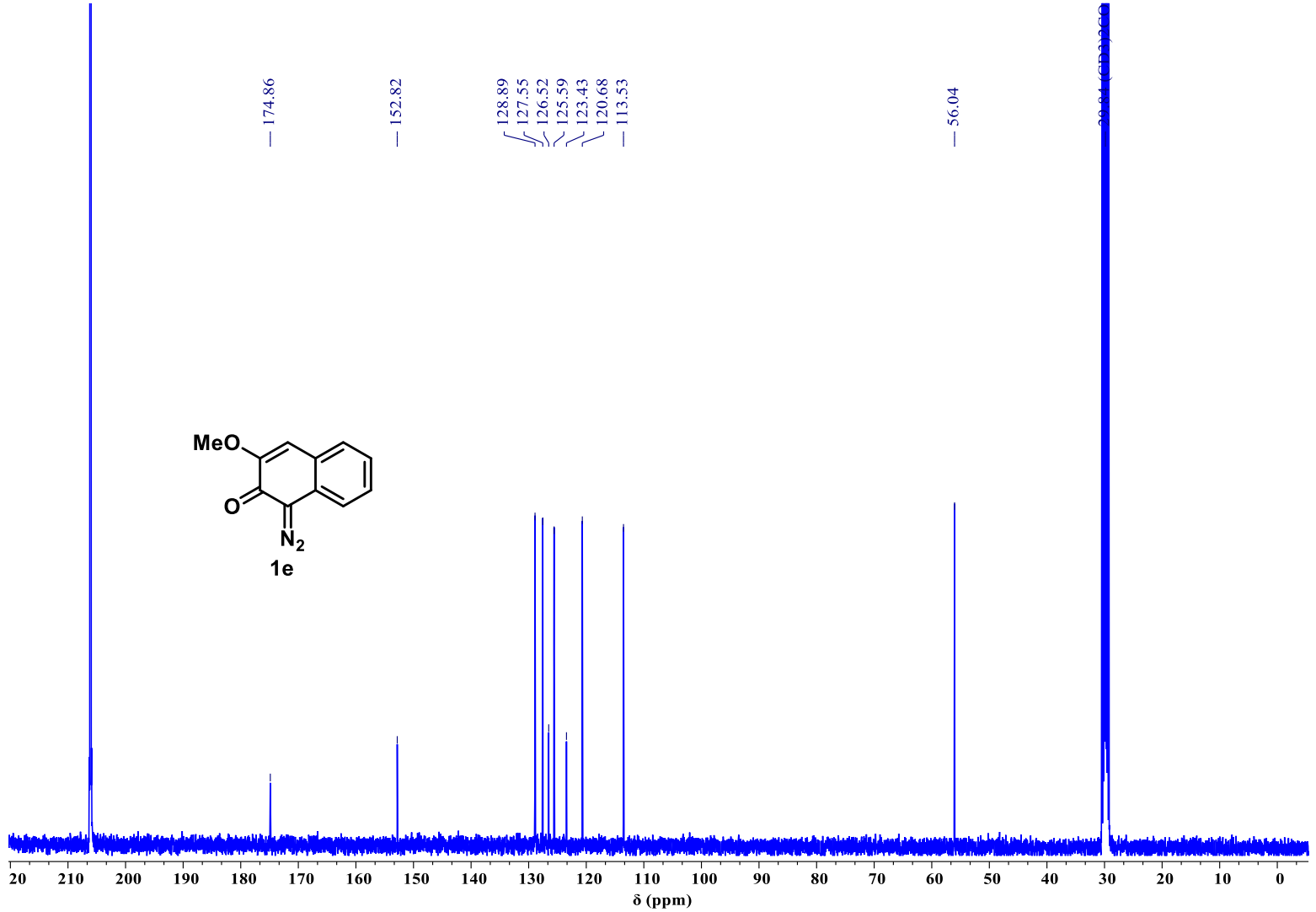
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 1-diazo-6-methoxynaphthalen-2(1*H*)-one (1d).



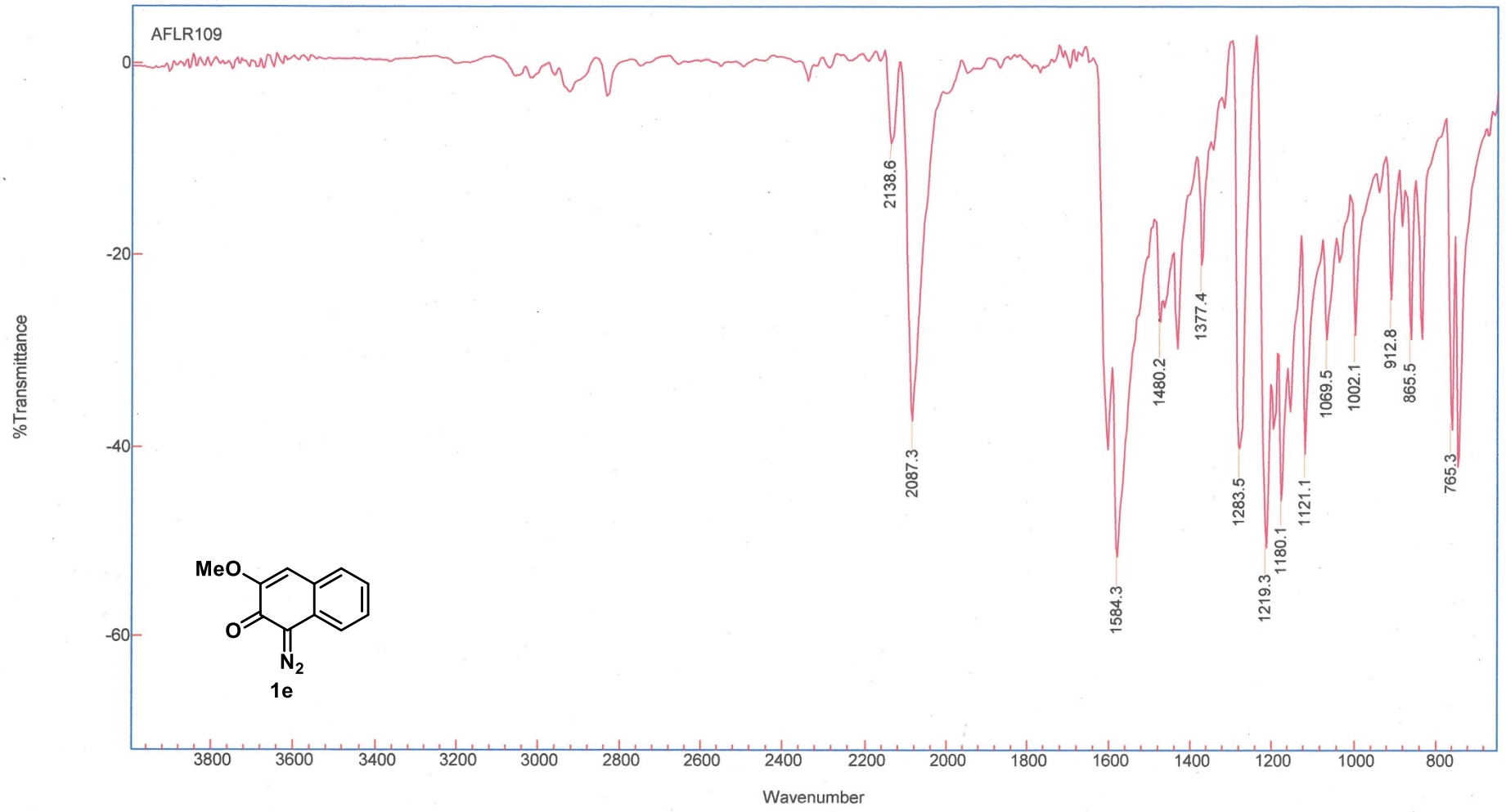
[1]H NMR (400 MHz, acetone-d_6) spectrum of 1-diazo-3-methoxynaphthalen-2(1*H*)-one (1e).



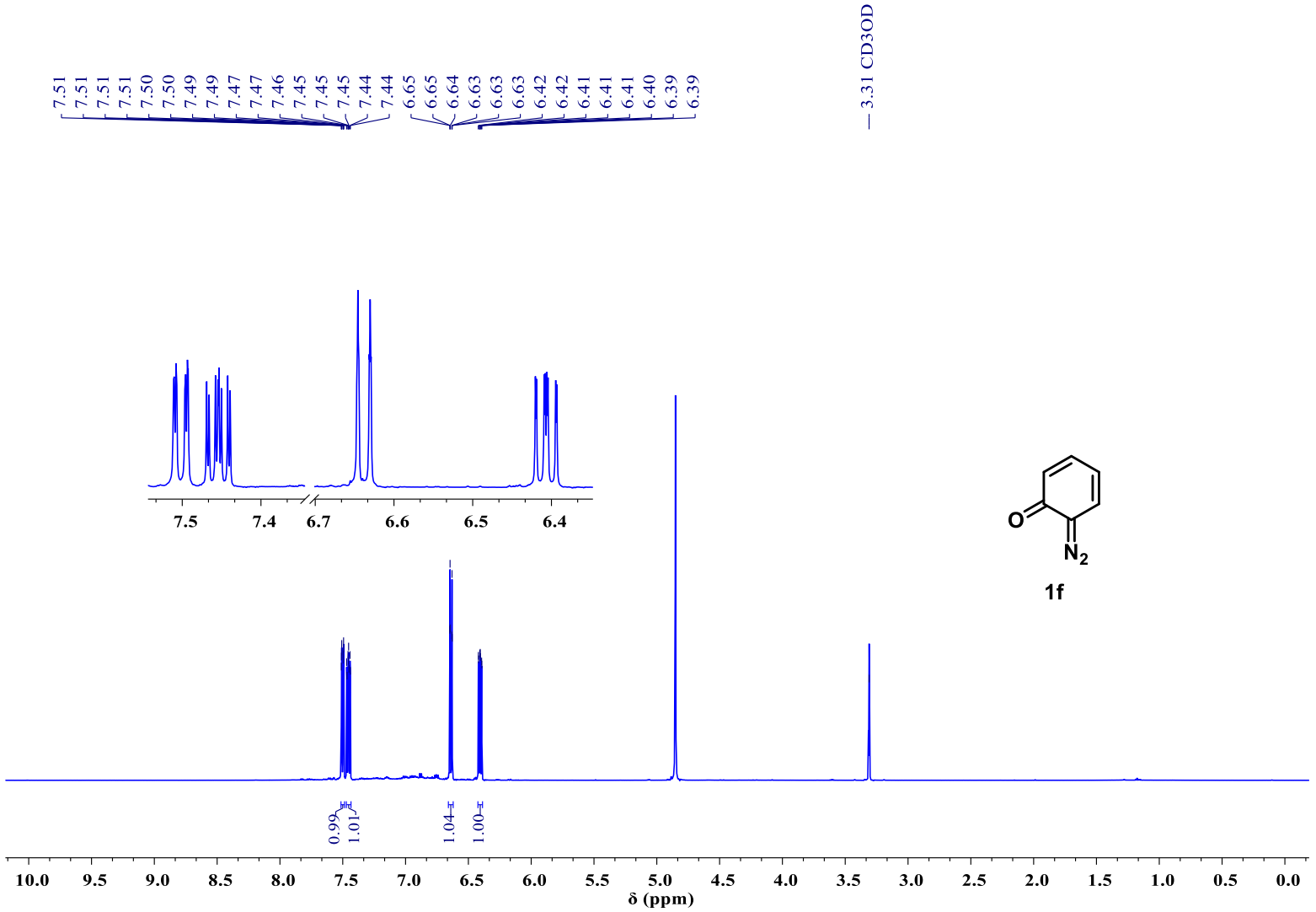
^{13}C NMR (100 MHz, acetone-d_6) spectrum of 1-diazo-3-methoxynaphthalen-2(1*H*)-one (1e).



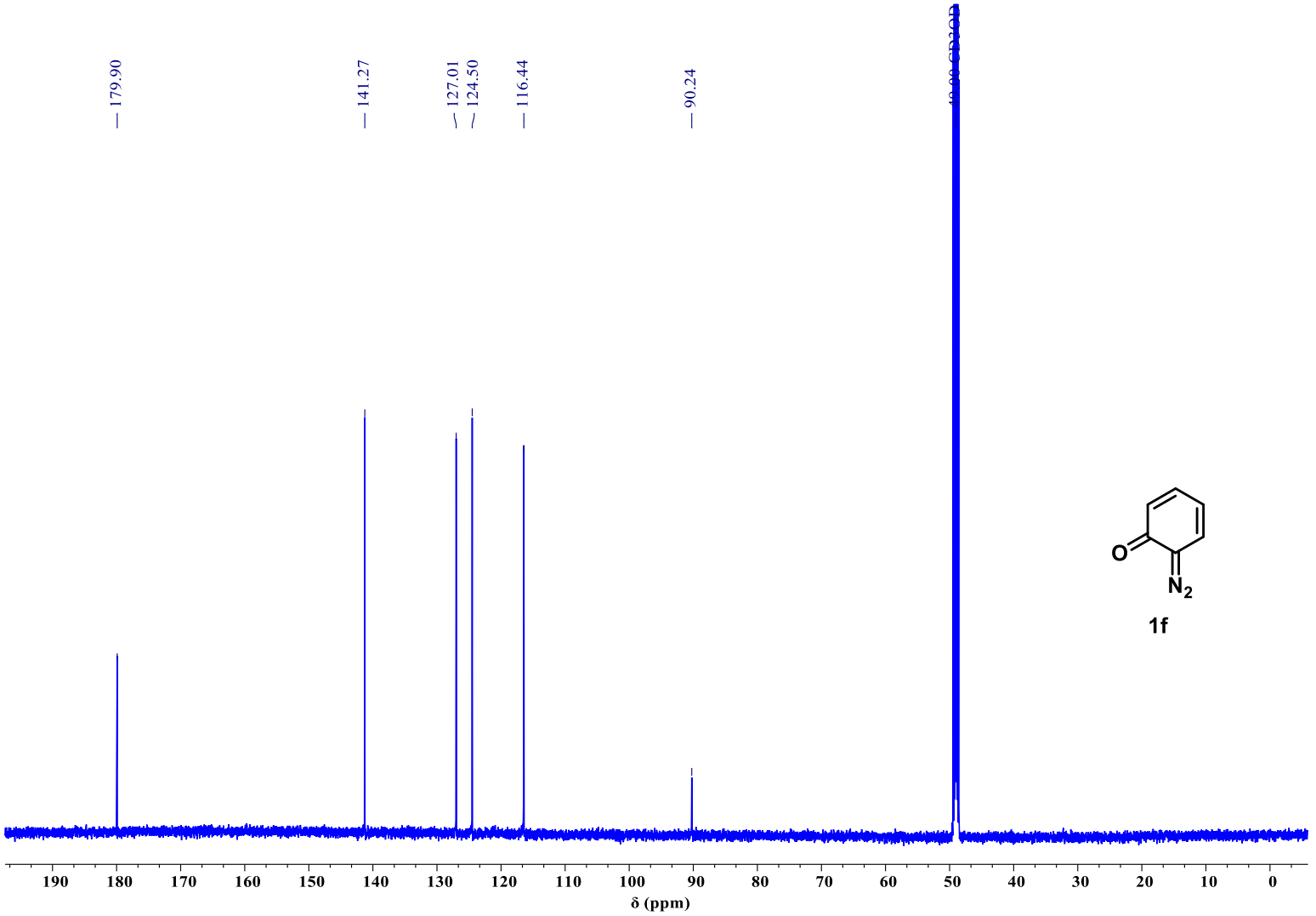
ATR-IR spectrum of 1-diazo-3-methoxynaphthalen-2(1*H*)-one (1e).



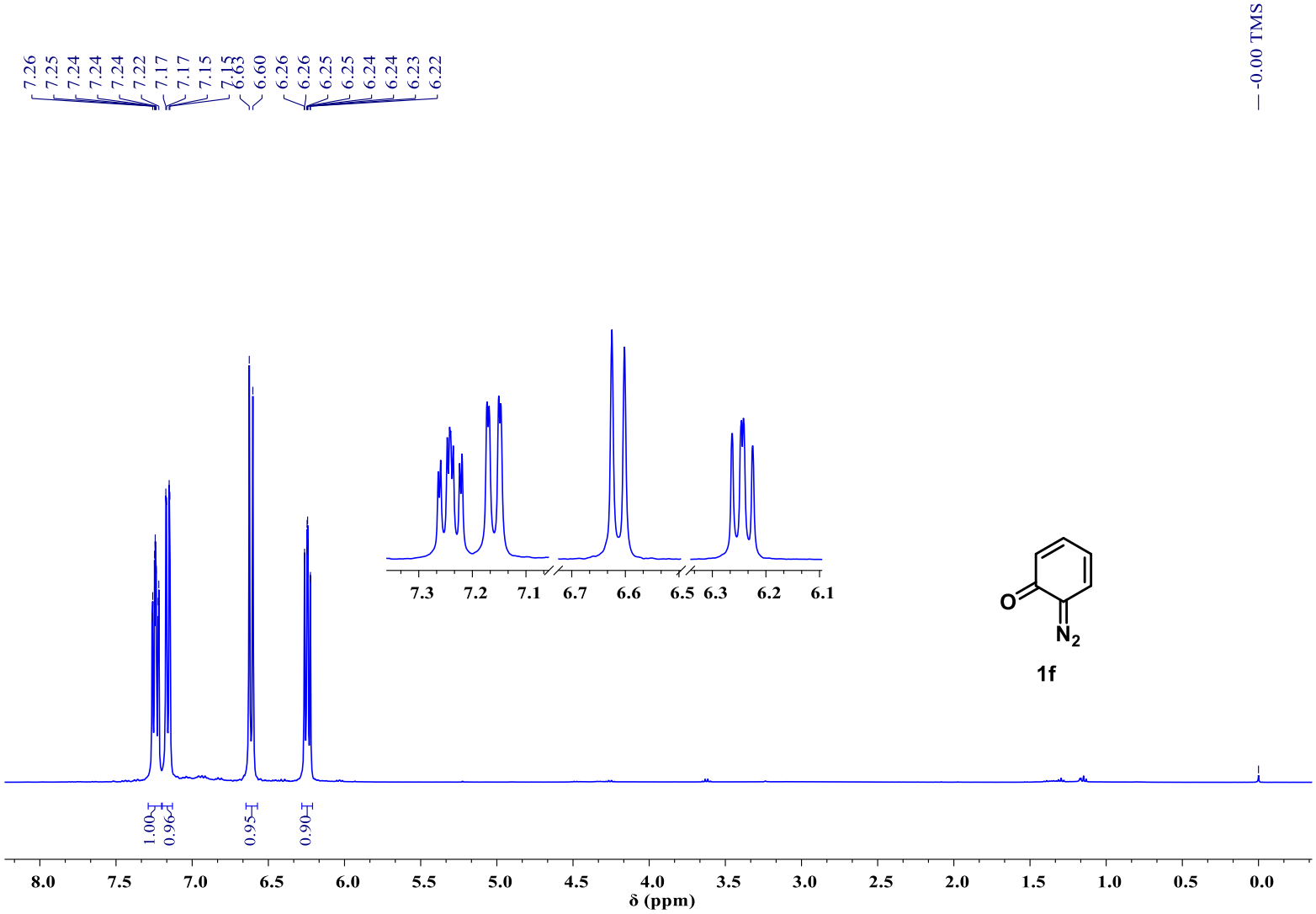
^{1}H NMR (600 MHz, CD_3OD) spectrum of 6-diazocyclohexa-2,4-dien-1-one (1f).



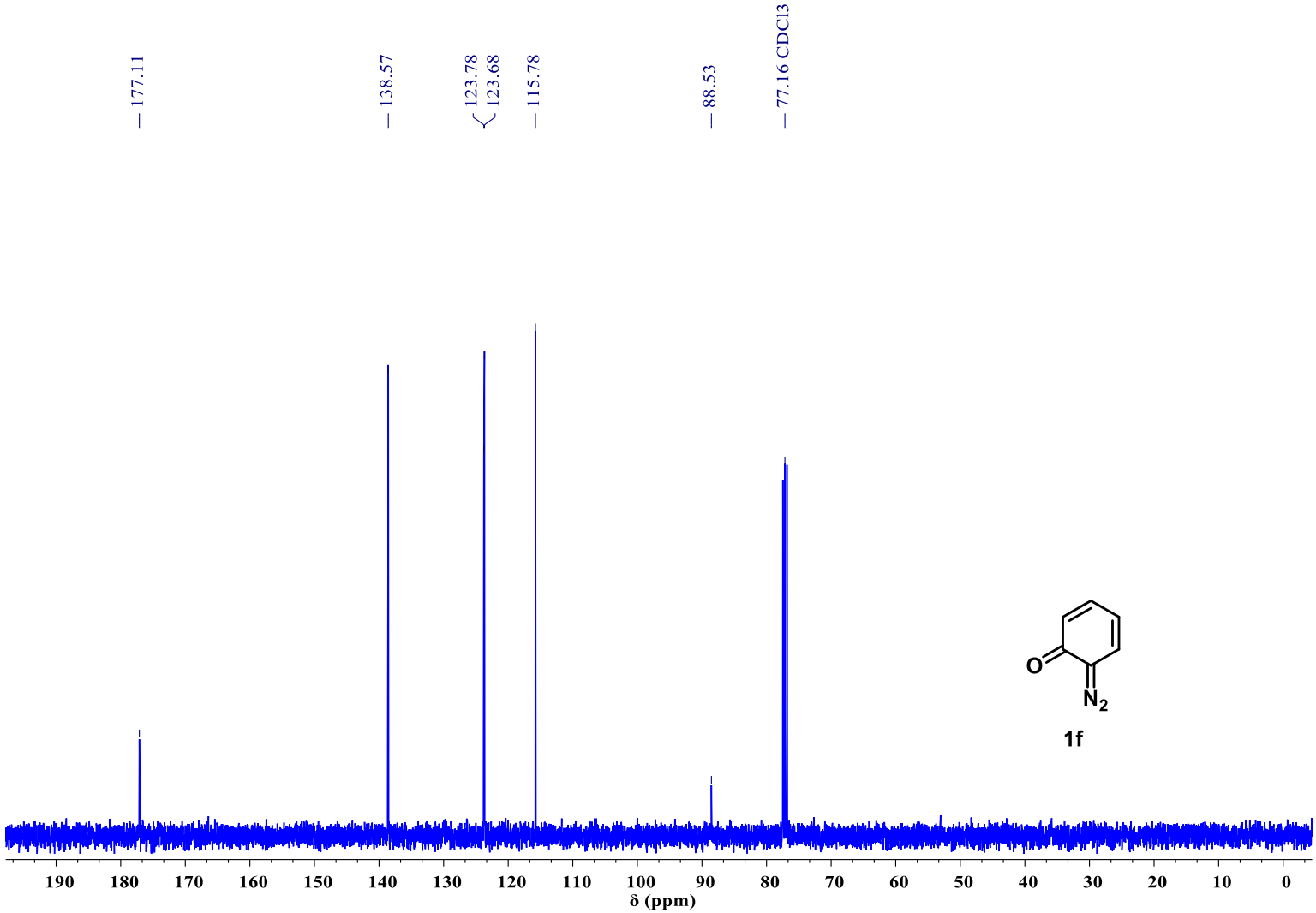
^{13}C NMR (151 MHz, CD_3OD) spectrum of 6-diazocyclohexa-2,4-dien-1-one (1f).



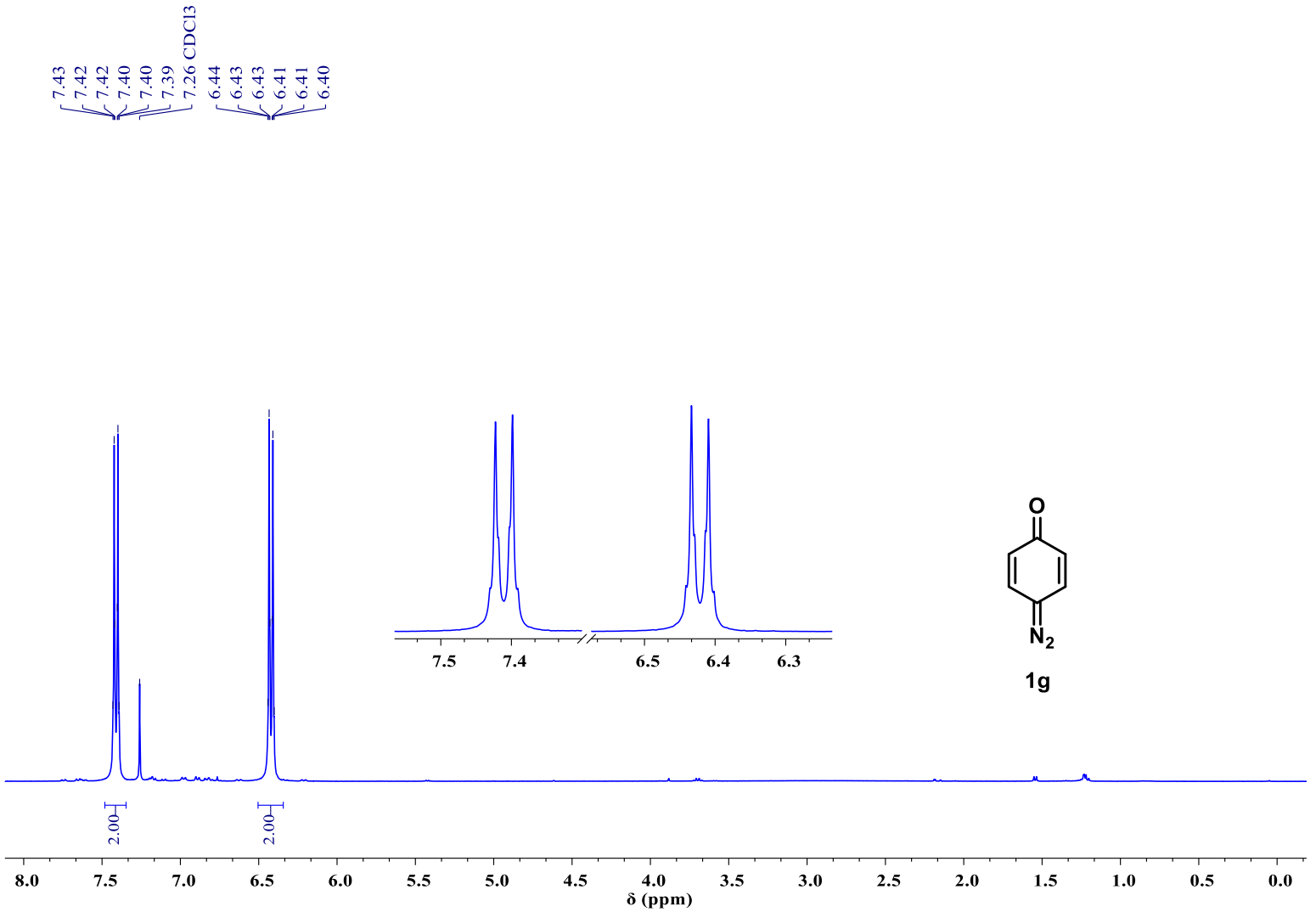
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 6-diazocyclohexa-2,4-dien-1-one (1f).



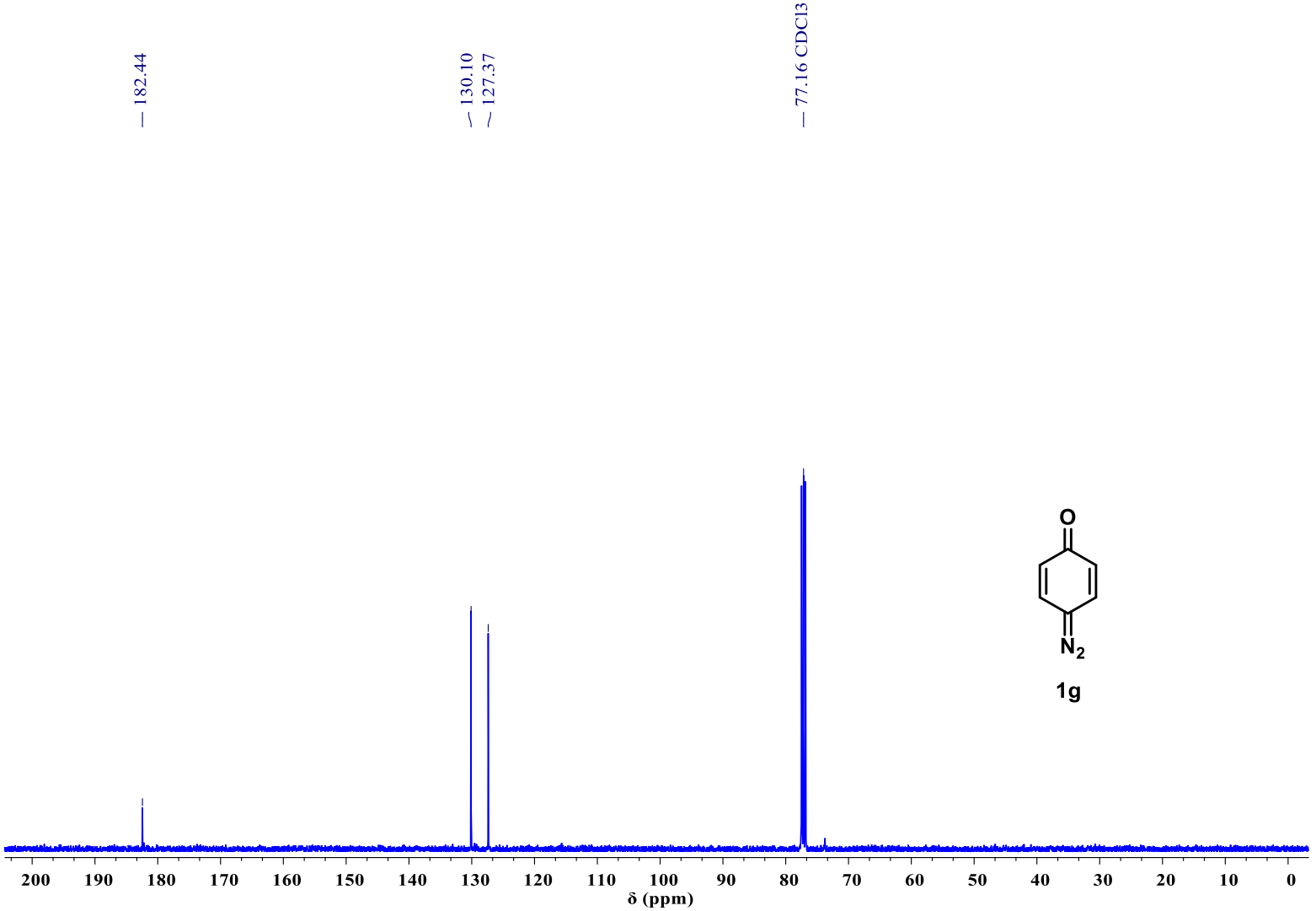
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 6-diazocyclohexa-2,4-dien-1-one (1f).



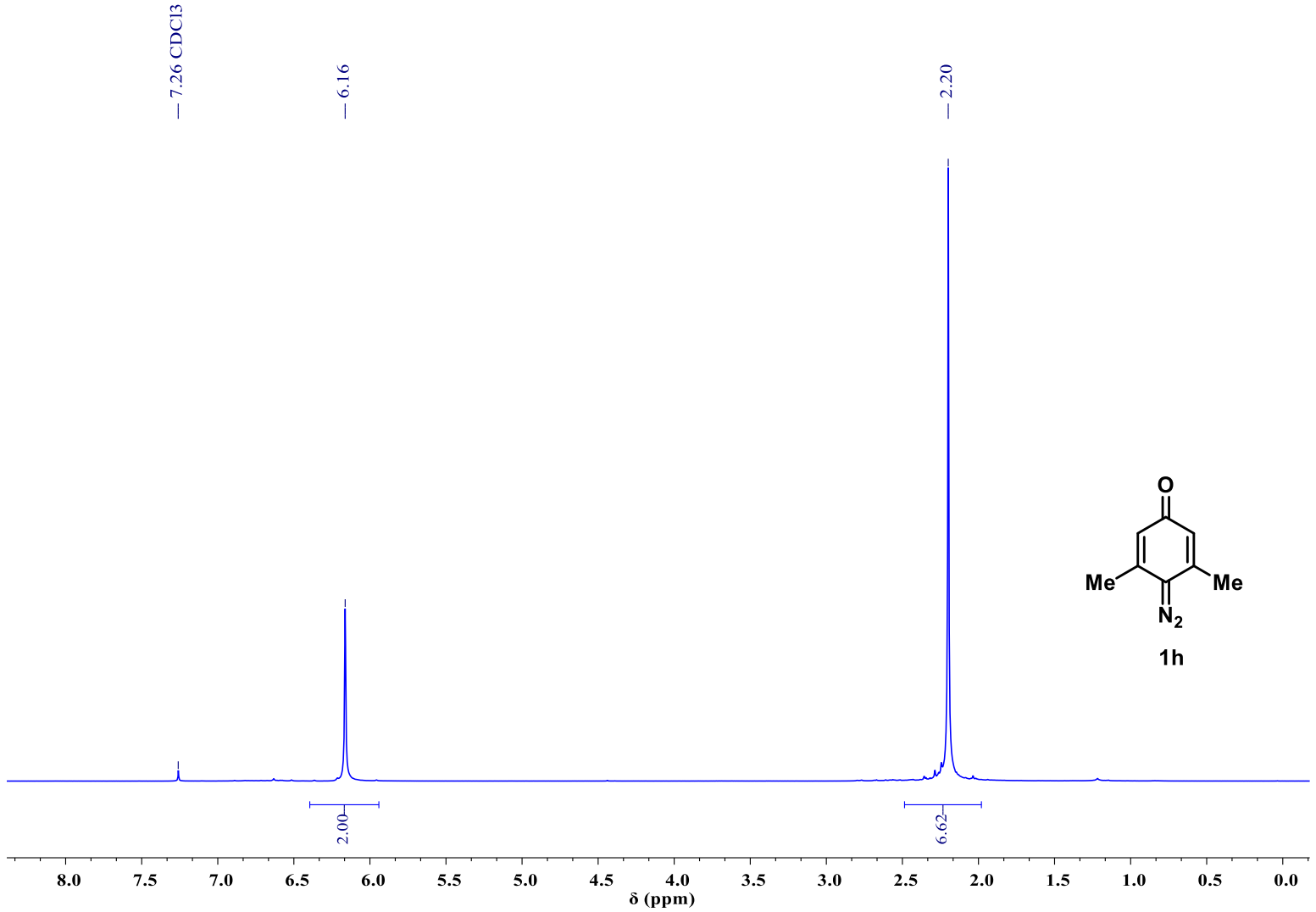
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-diazocyclohexa-2,5-dien-1-one (1g).



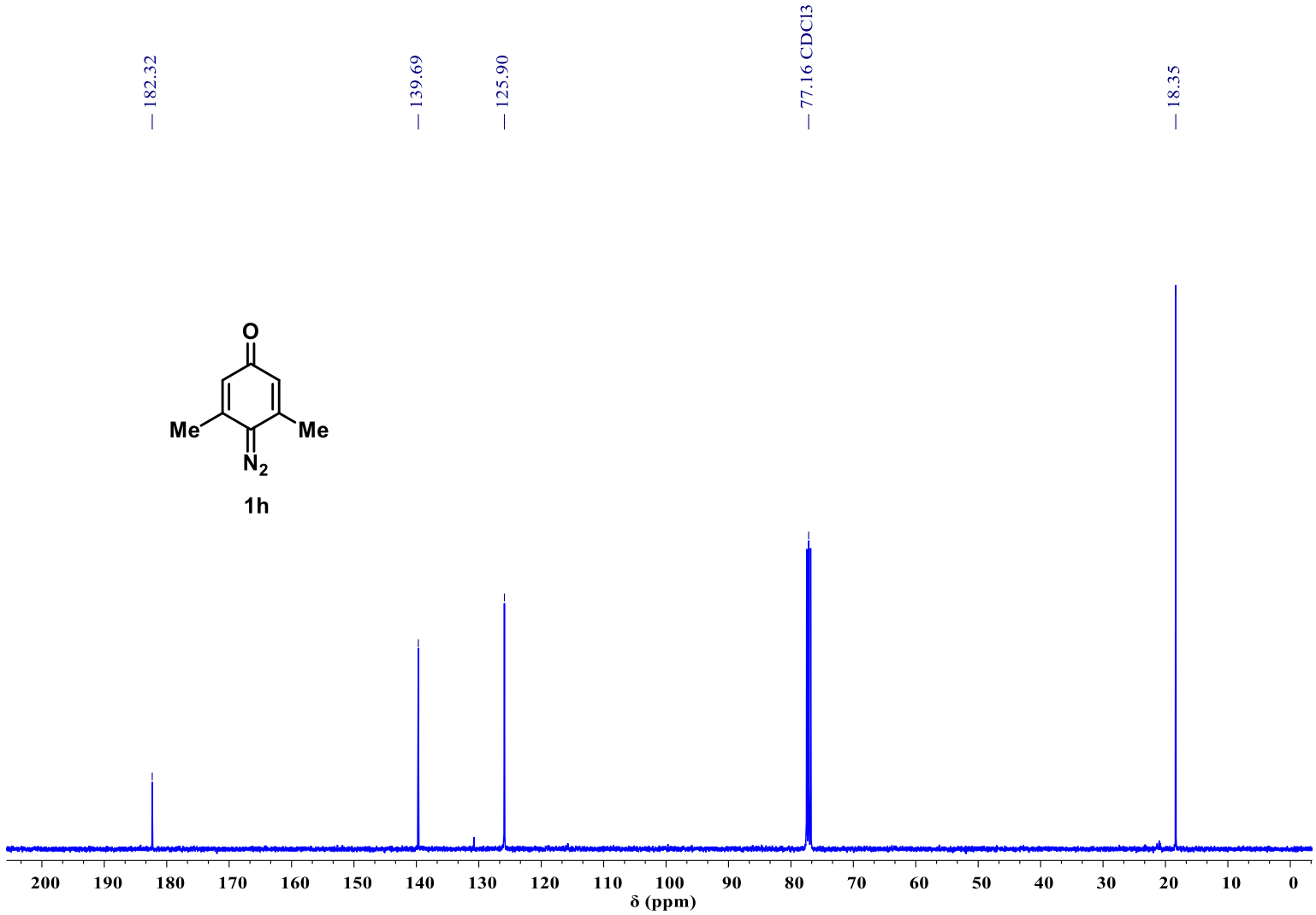
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4-diazocyclohexa-2,5-dien-1-one (1g).



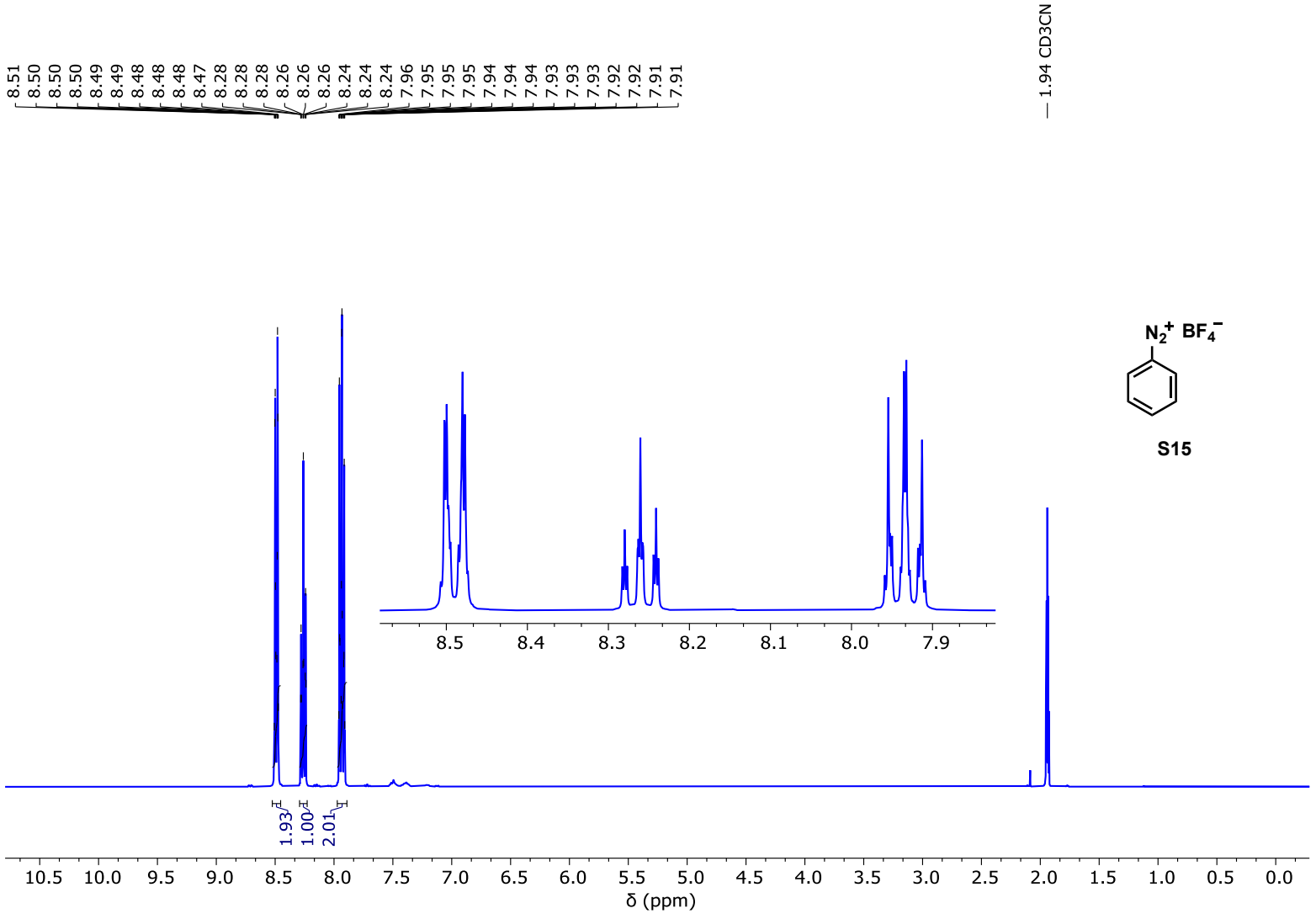
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4-diazo-3,5-dimethylcyclohexa-2,5-dien-1-one (1h).



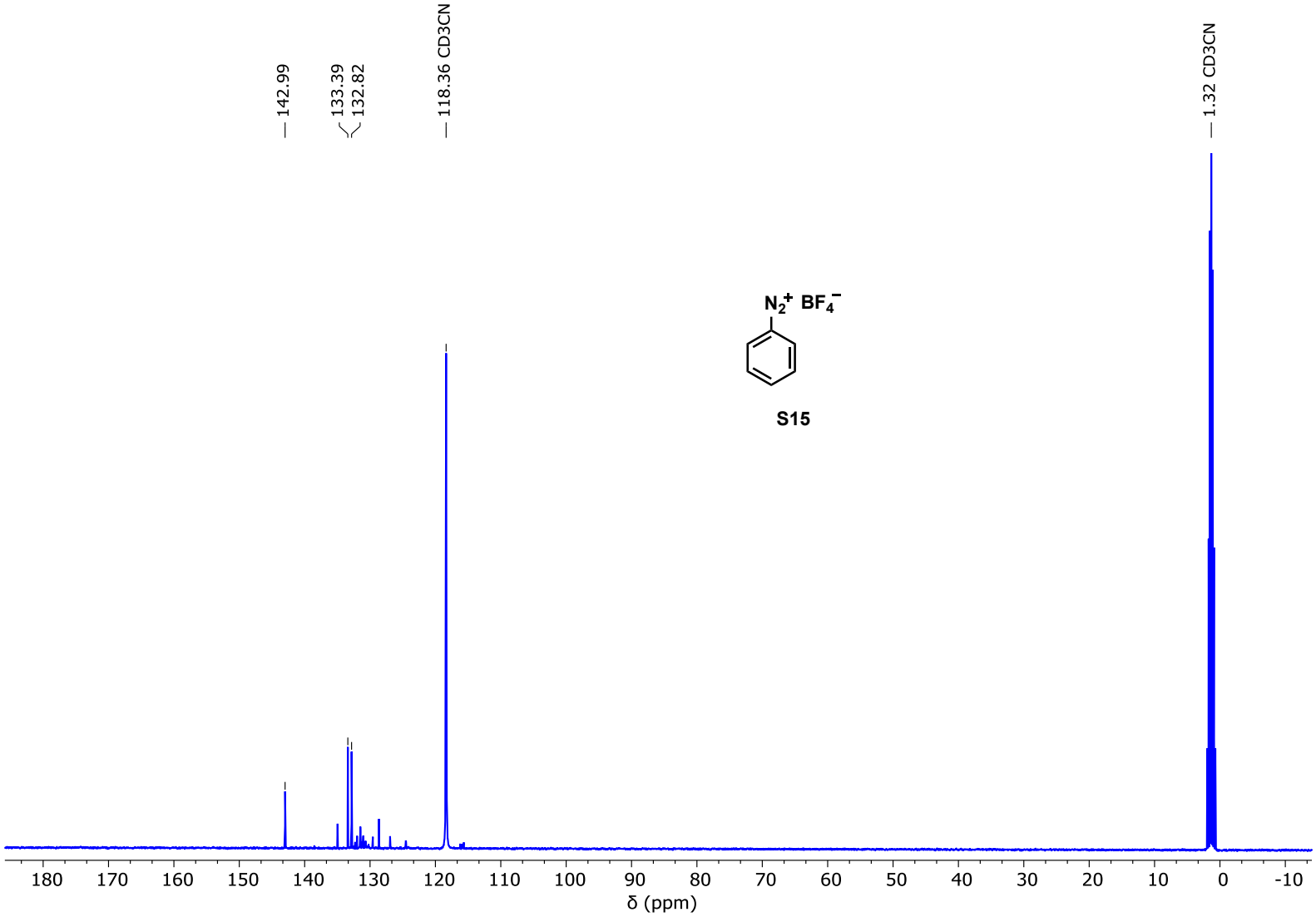
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4-diazo-3,5-dimethylcyclohexa-2,5-dien-1-one (1h).



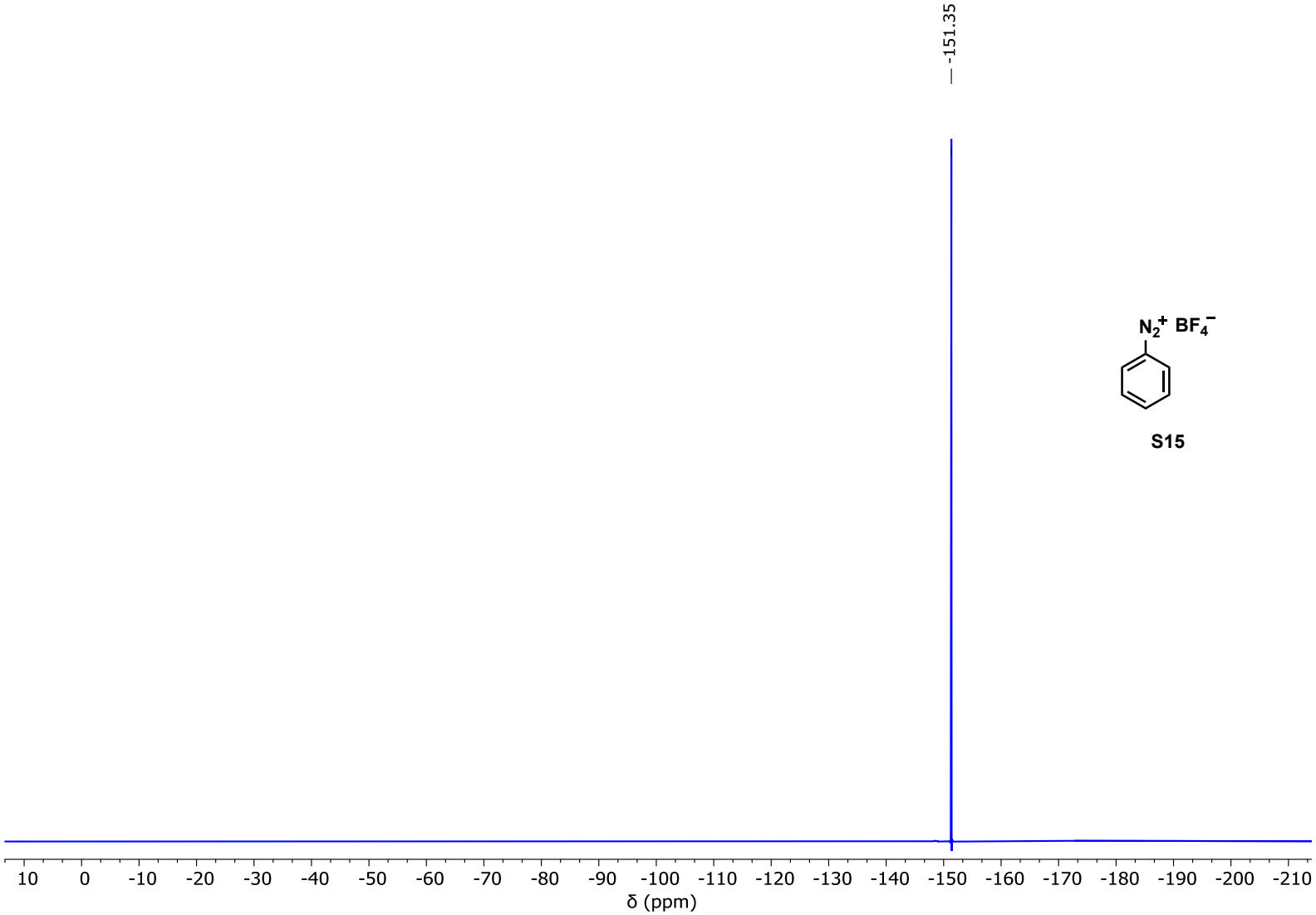
^{1}H NMR (400 MHz, CD_3CN) spectrum of benzenediazonium tetrafluoroborate (S15).



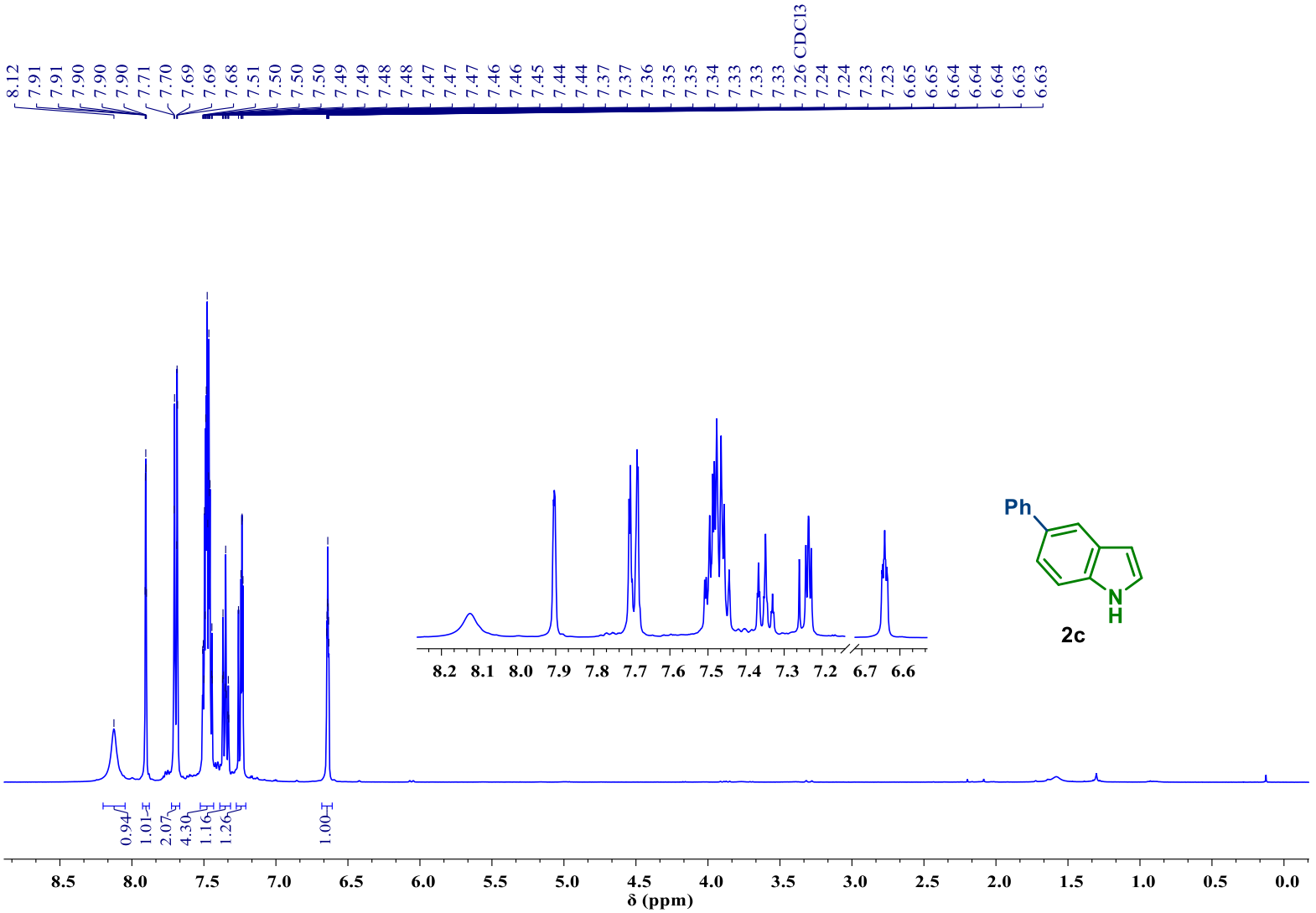
^{13}C NMR (101 MHz, CD_3CN) spectrum of benzenediazonium tetrafluoroborate (S15).



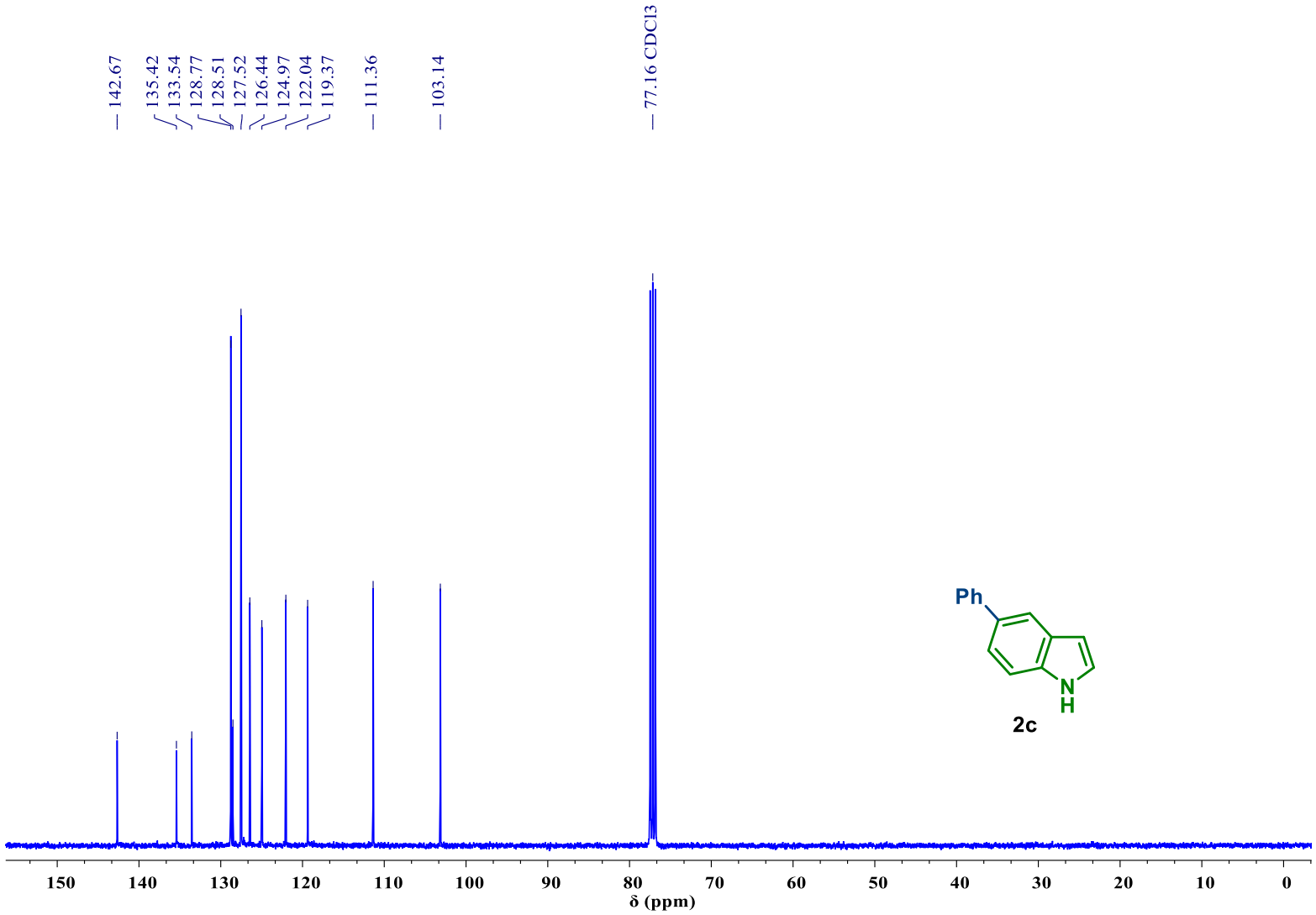
^{19}F NMR (376 MHz, CD_3CN) spectrum of benzenediazonium tetrafluoroborate (S15).



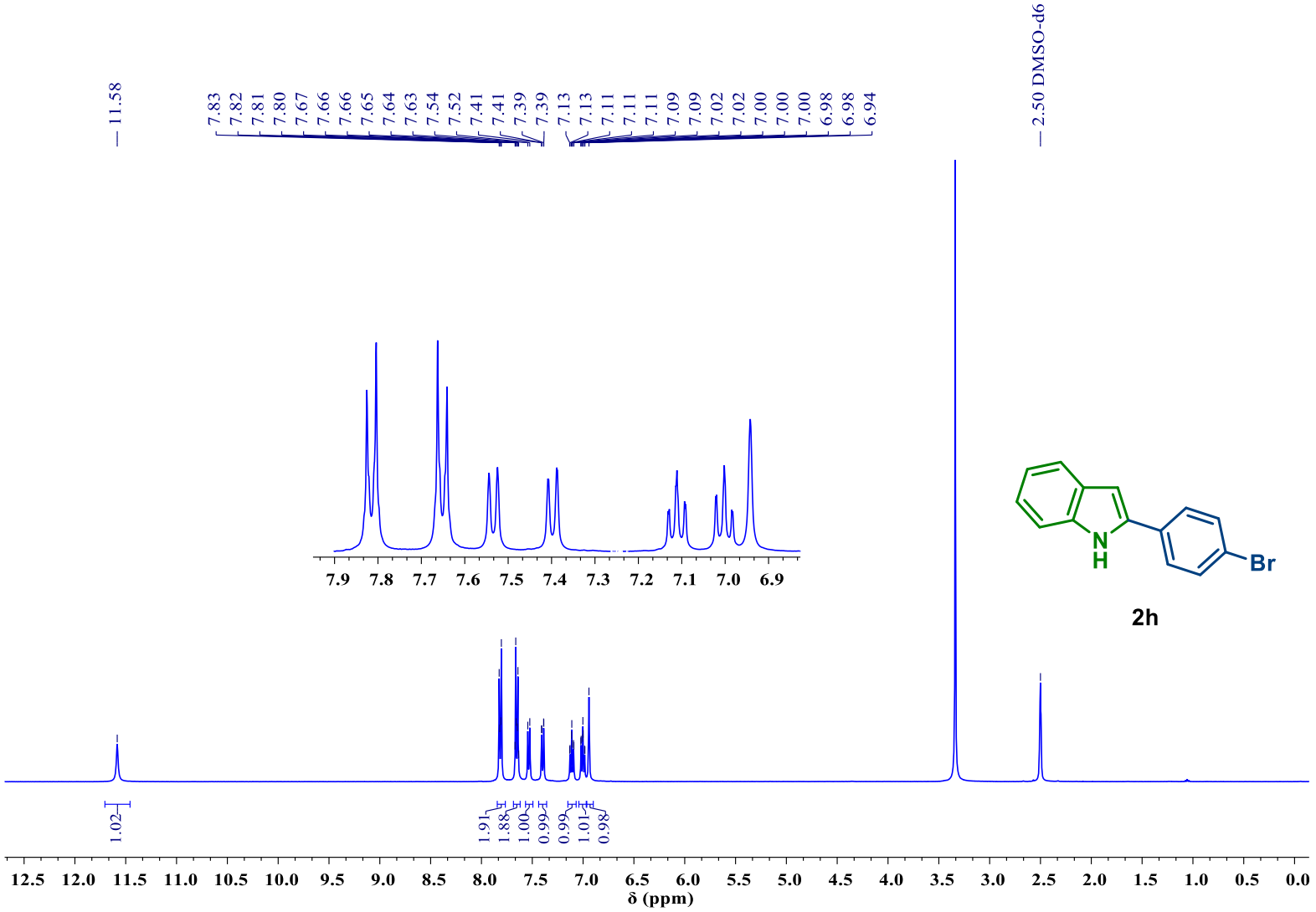
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 5-phenyl-1*H*-indole (2c).



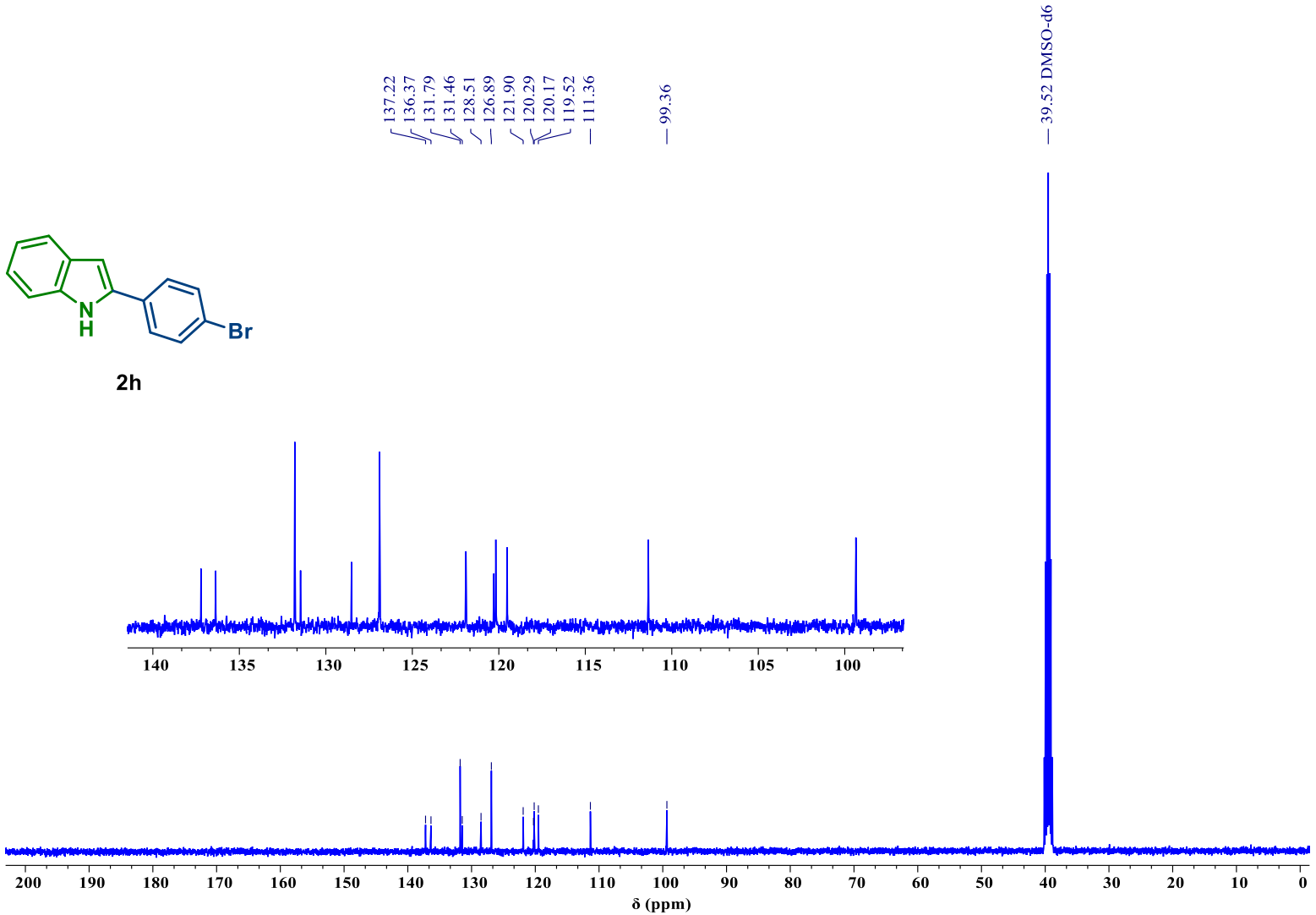
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5-phenyl-1*H*-indole (2c).



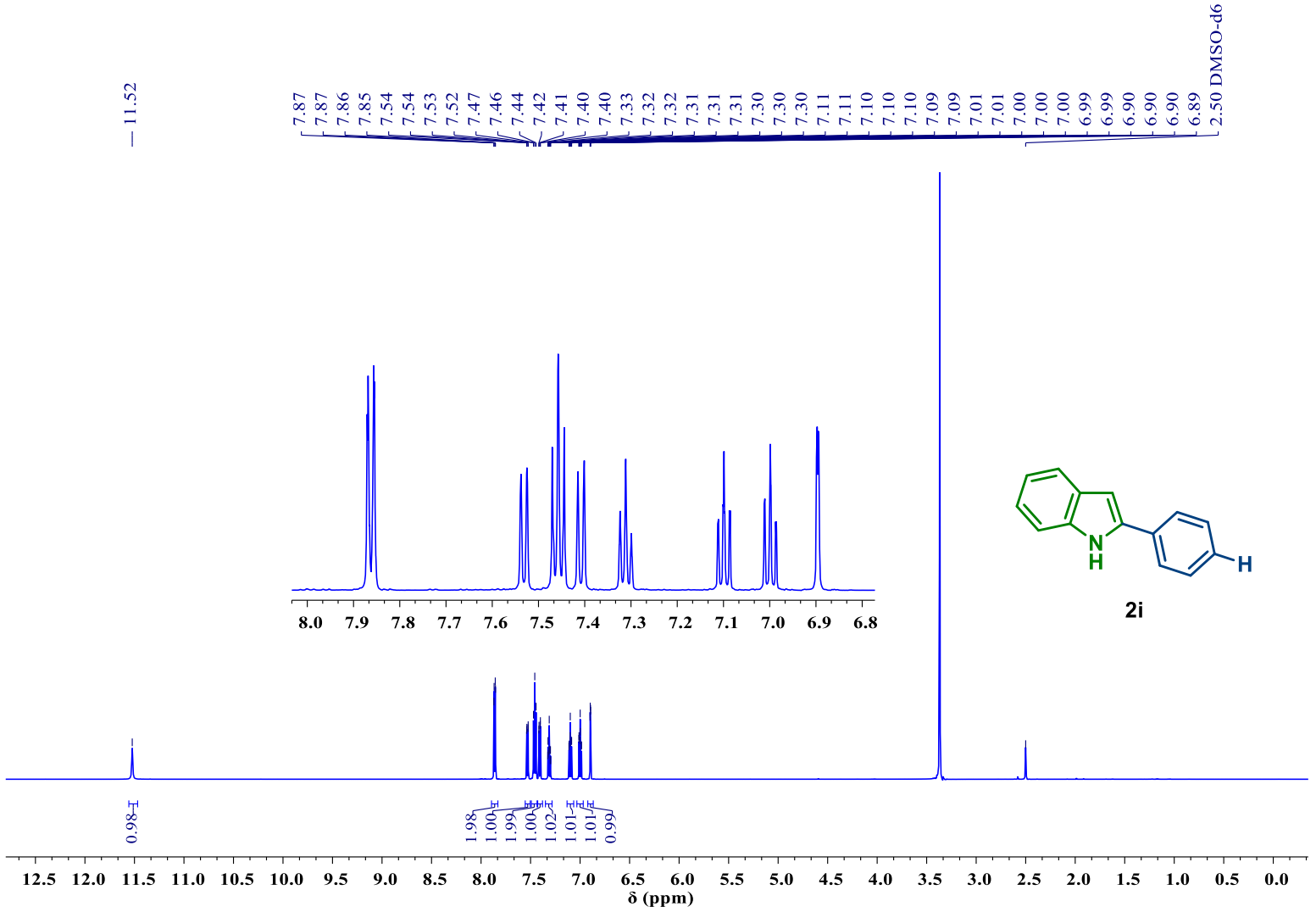
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2-(4-bromophenyl)-1*H*-indole (2h).



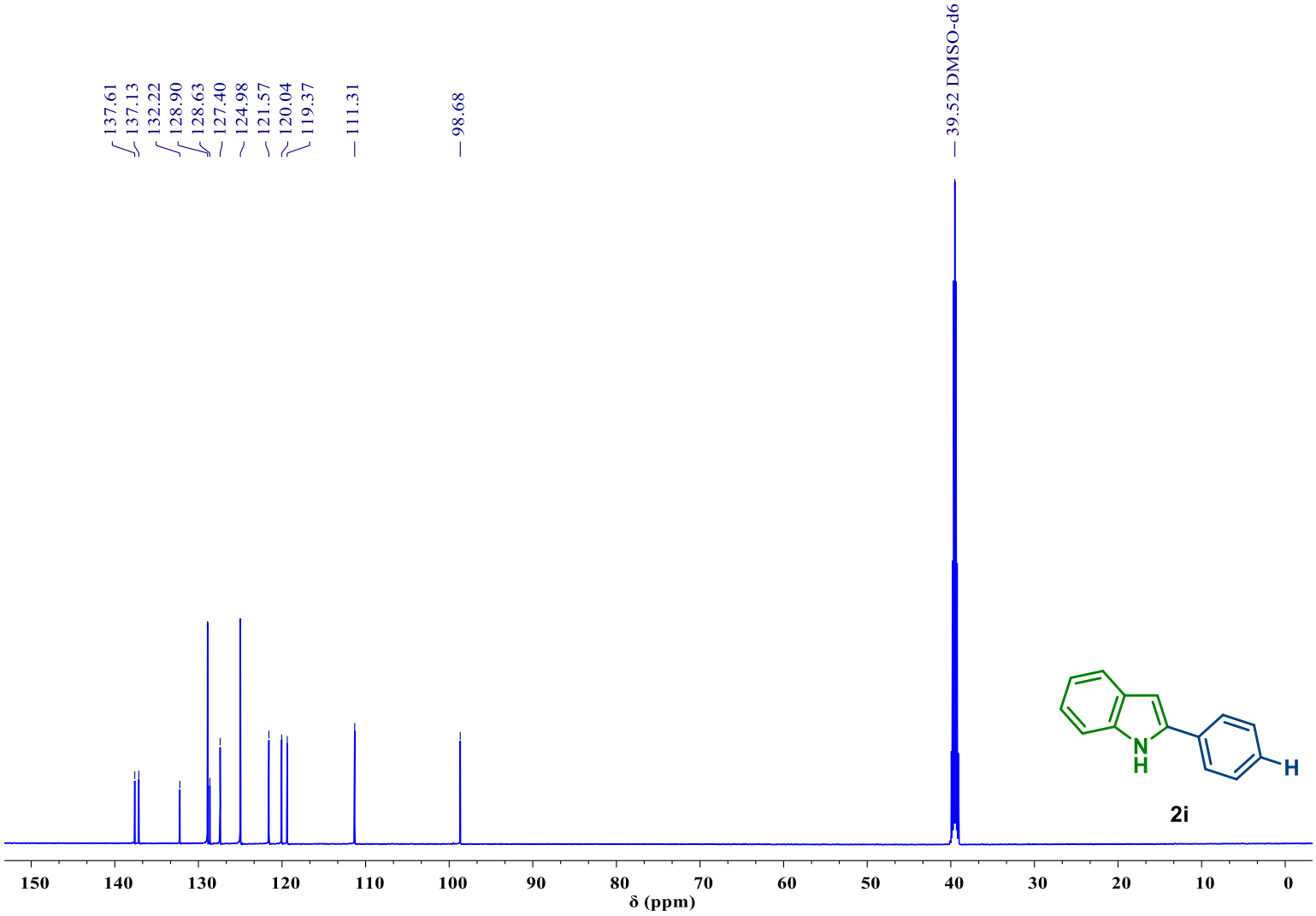
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2-(4-bromophenyl)-1*H*-indole (2h).



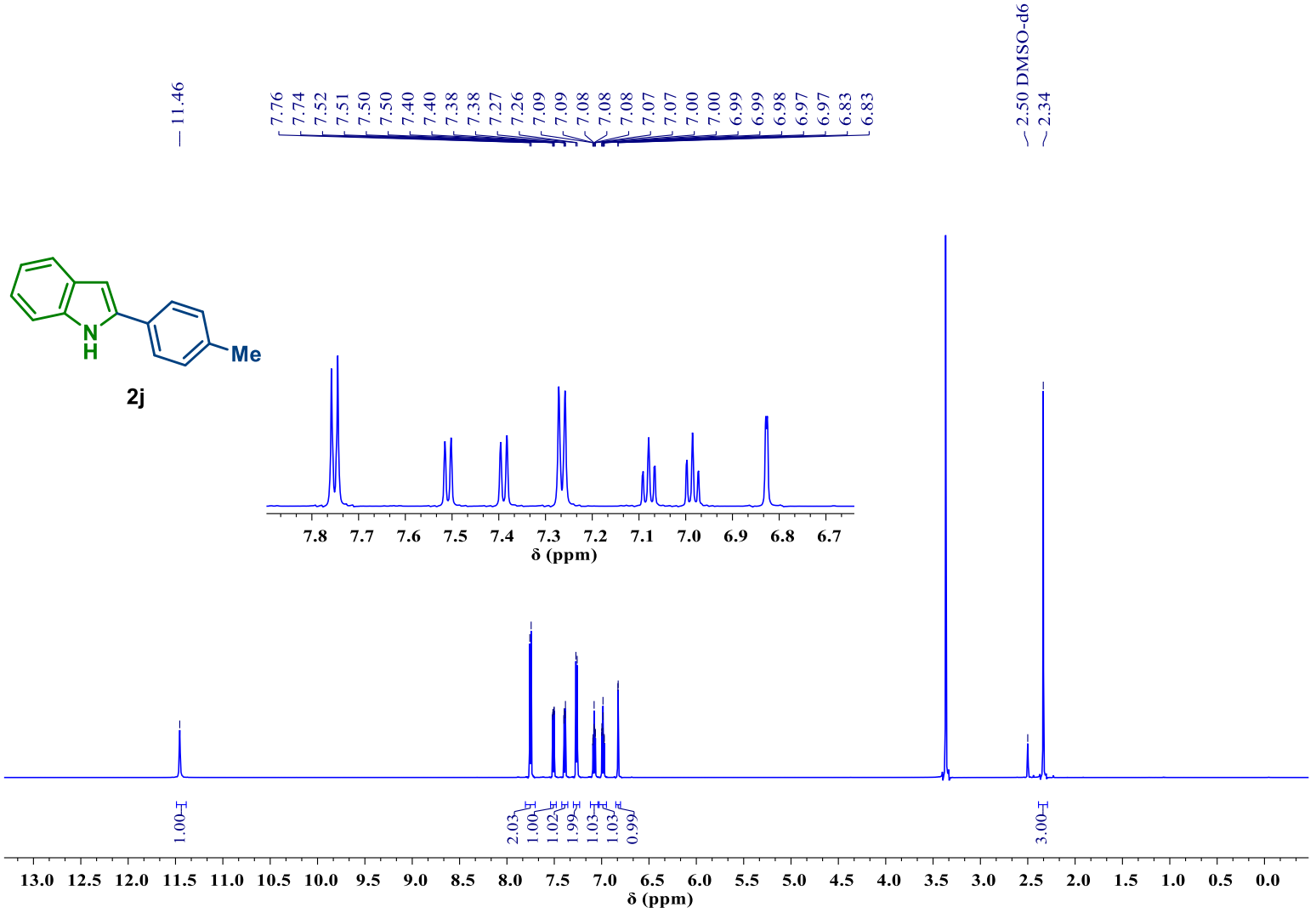
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of 2-phenyl-1*H*-indole (2i).



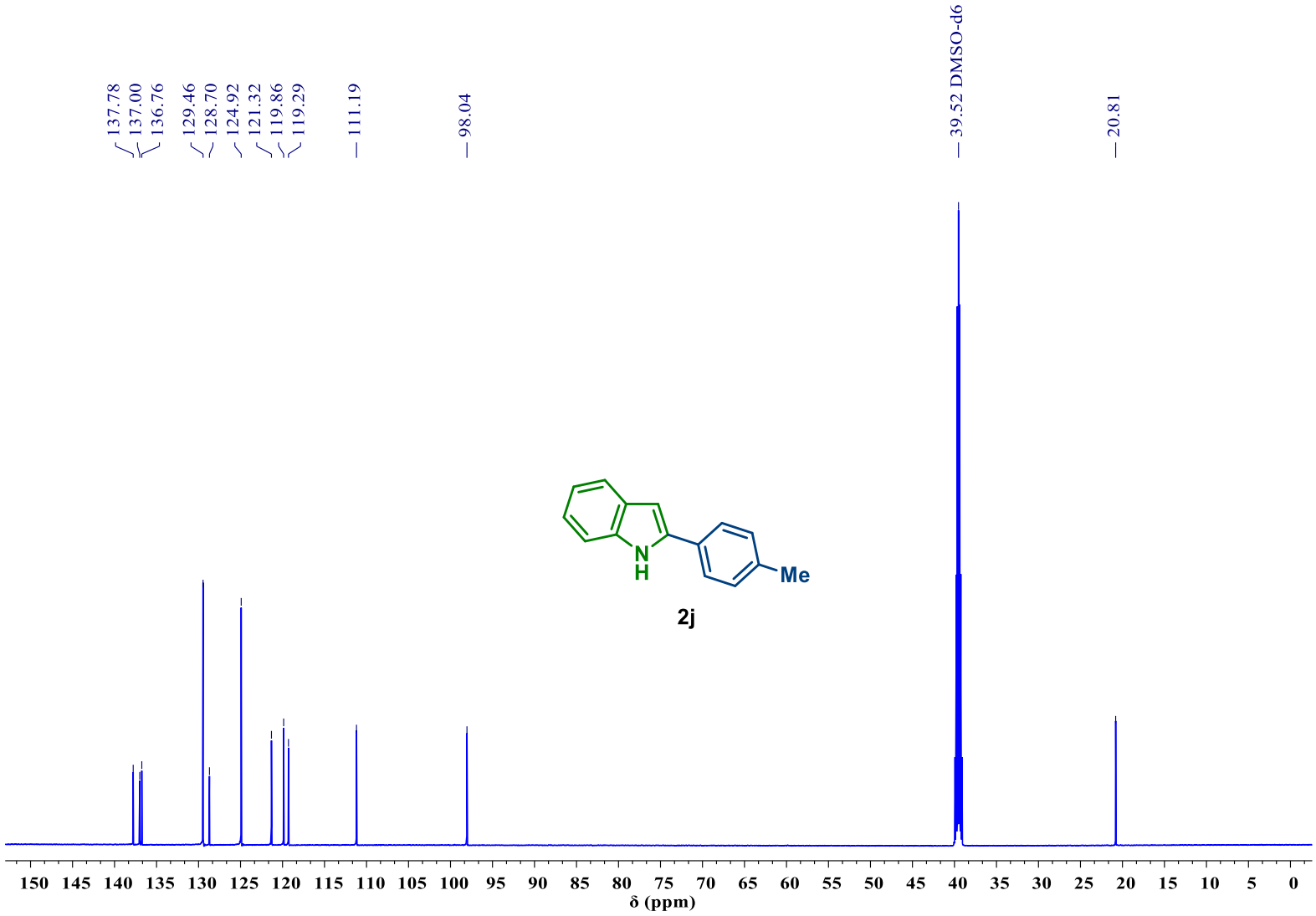
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of 2-phenyl-1*H*-indole (2i).



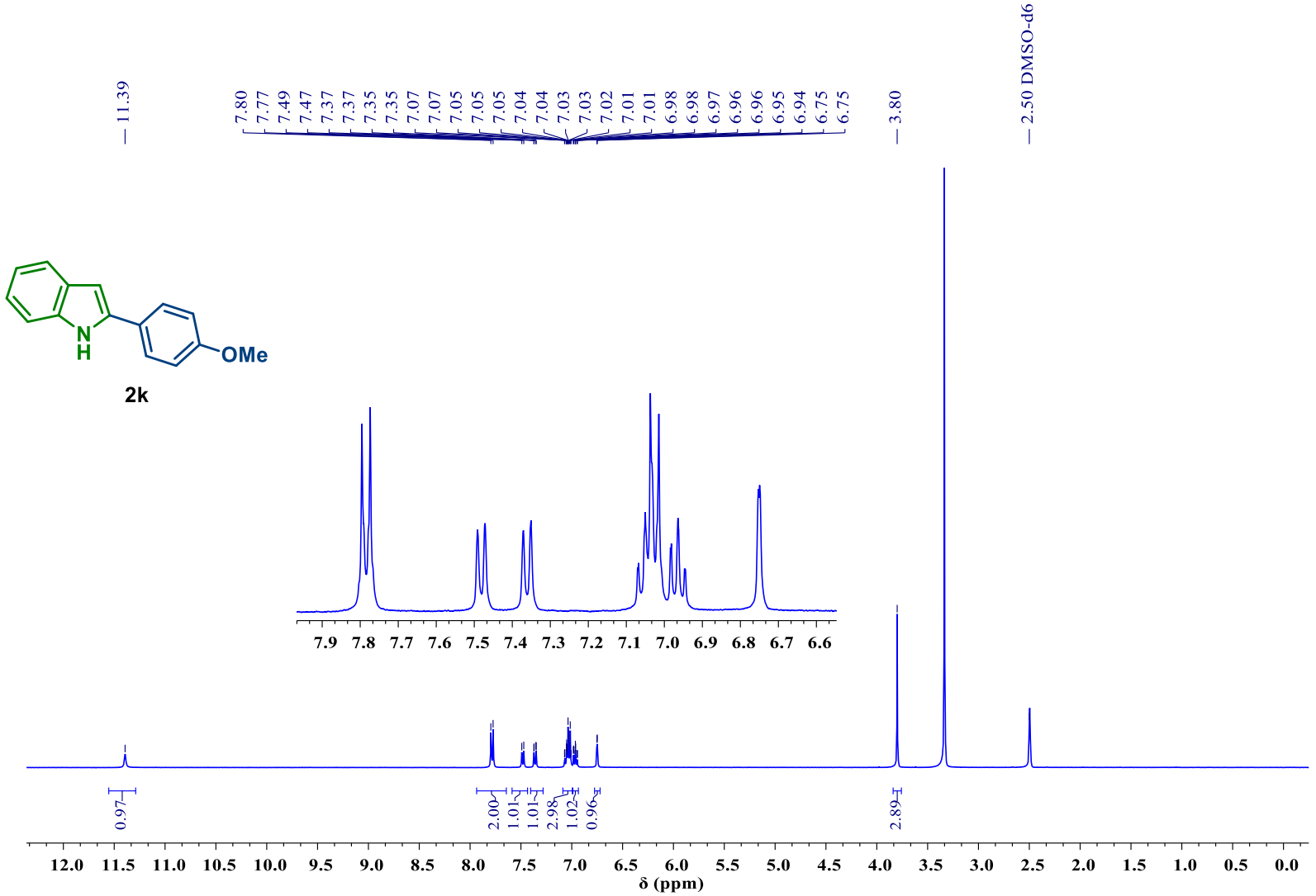
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of 2-(*p*-tolyl)-1*H*-indole (2j).



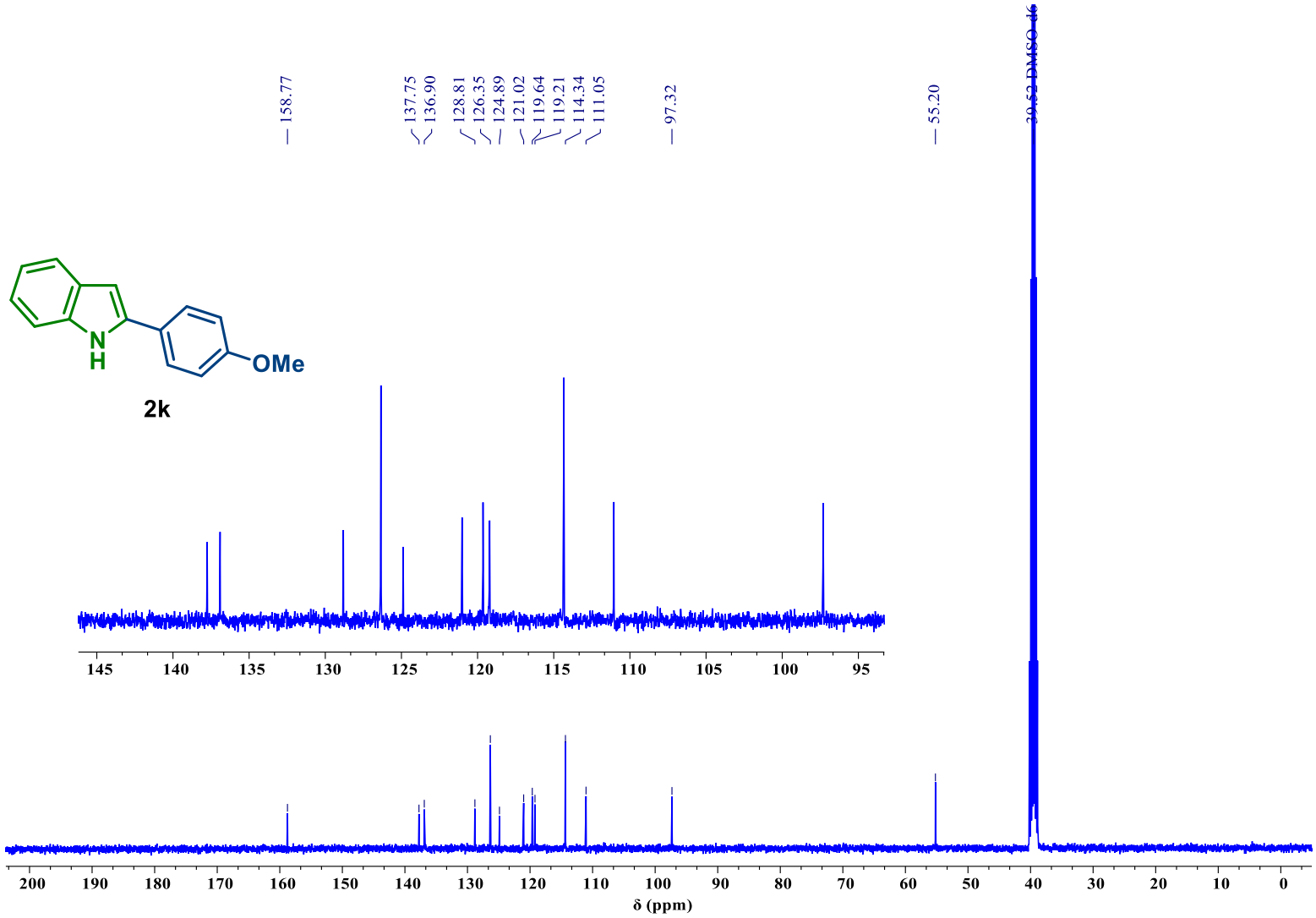
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2-(*p*-tolyl)-1*H*-indole (2j).



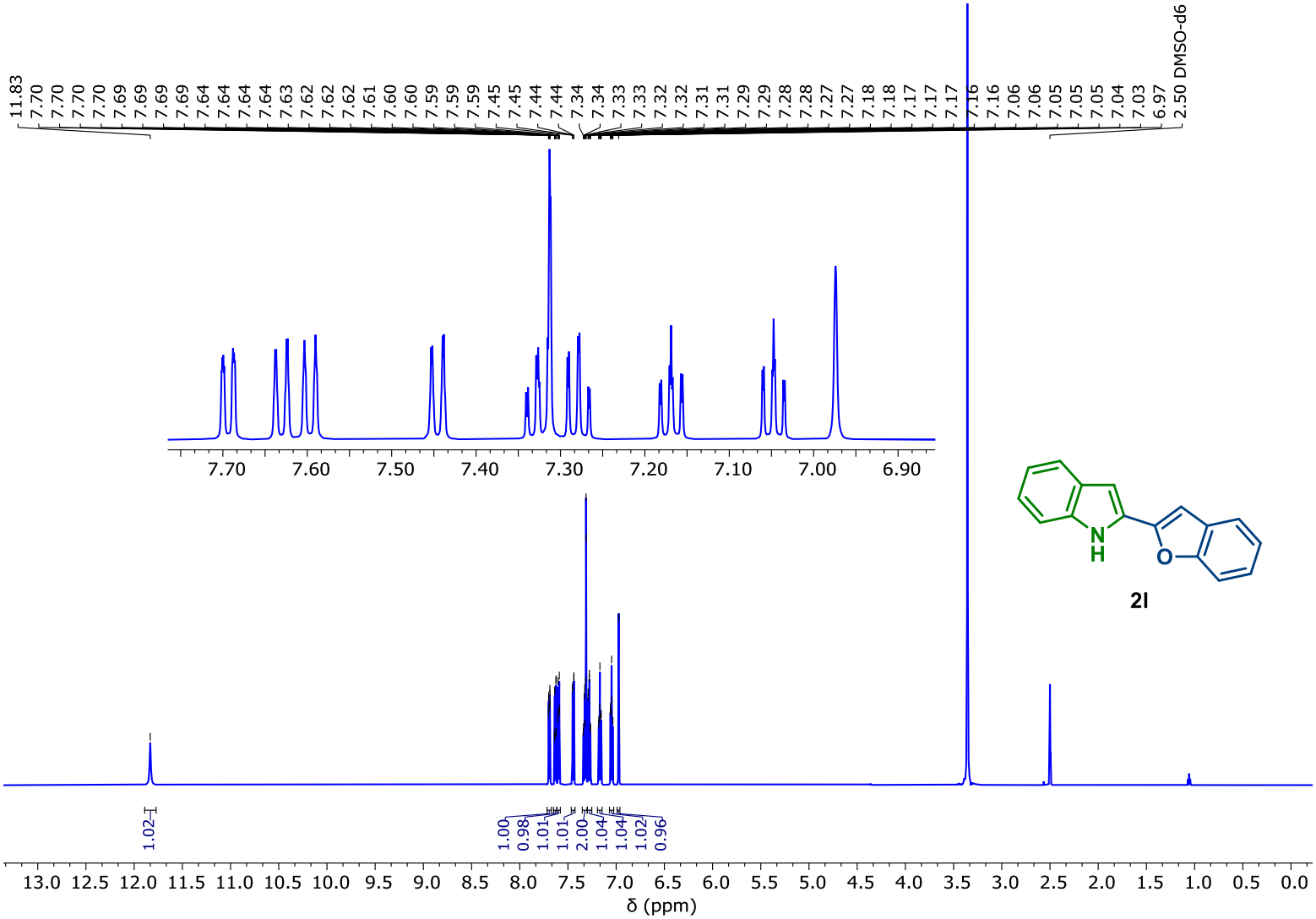
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2-(4-methoxyphenyl)-1*H*-indole (2k).



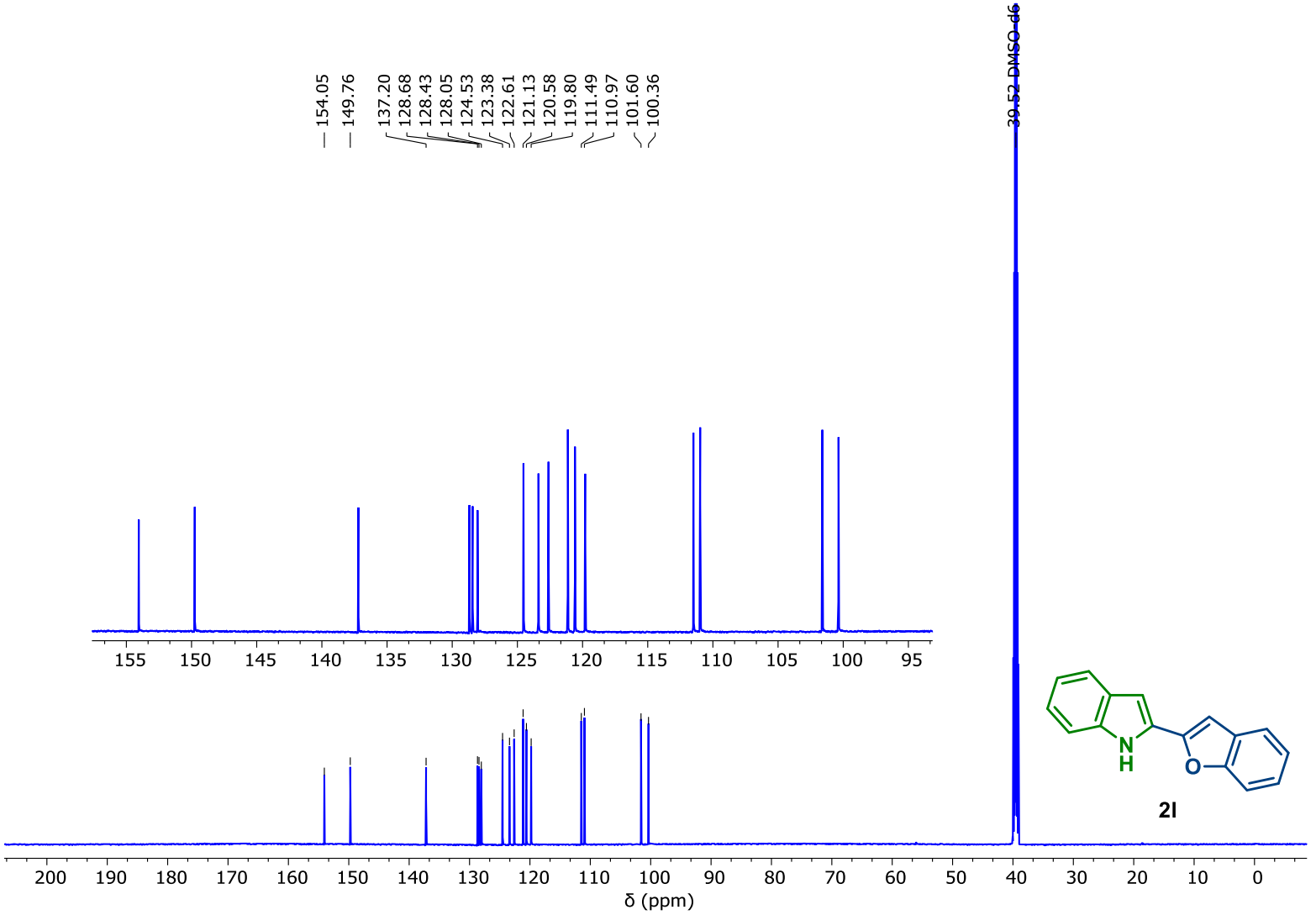
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2-(4-methoxyphenyl)-1*H*-indole (2k).



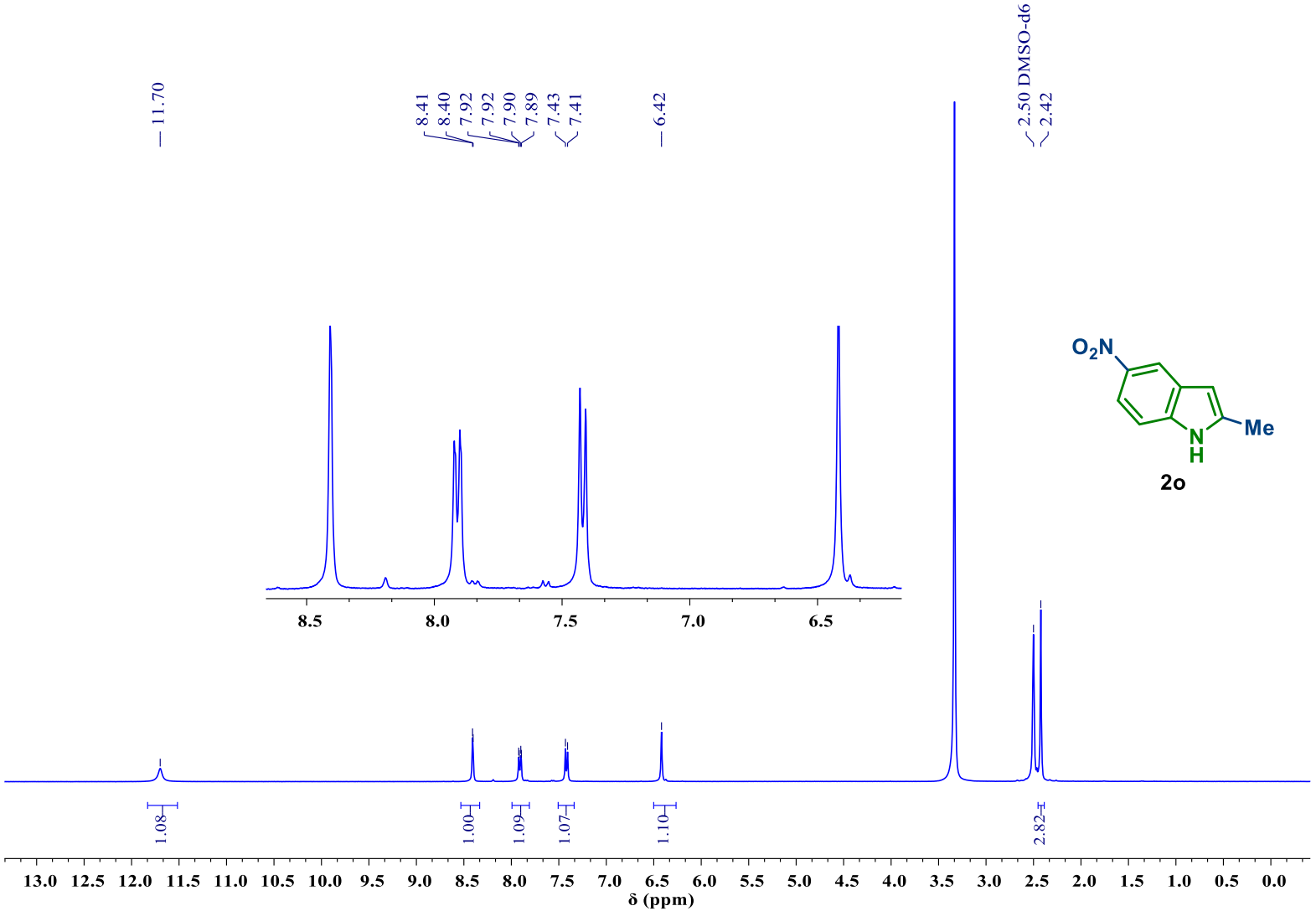
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of 2-(benzofuran-2-yl)-1*H*-indole (2l).



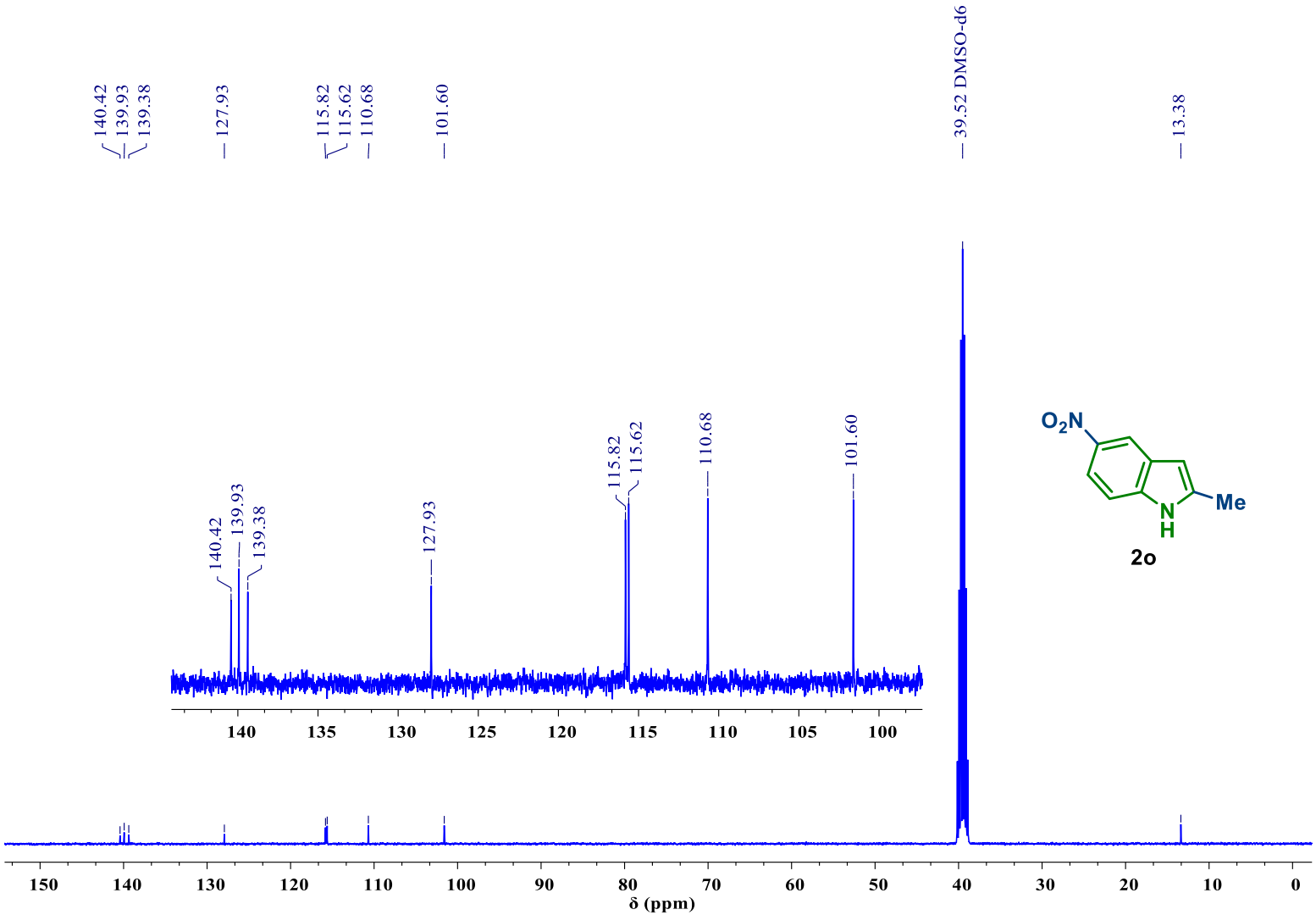
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of 2-(benzofuran-2-yl)-1*H*-indole (2l).



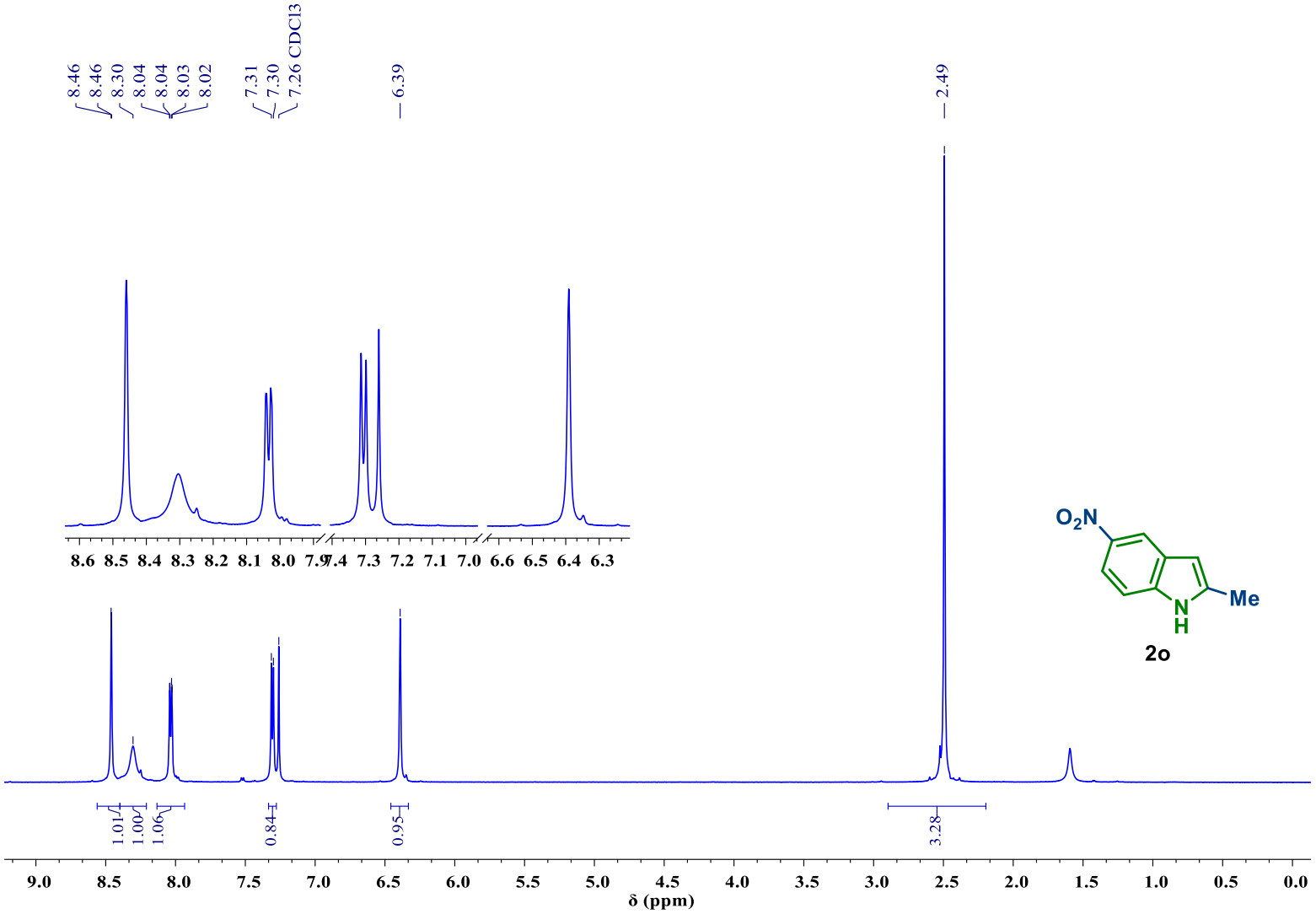
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2-methyl-5-nitro-1*H*-indole (2o).



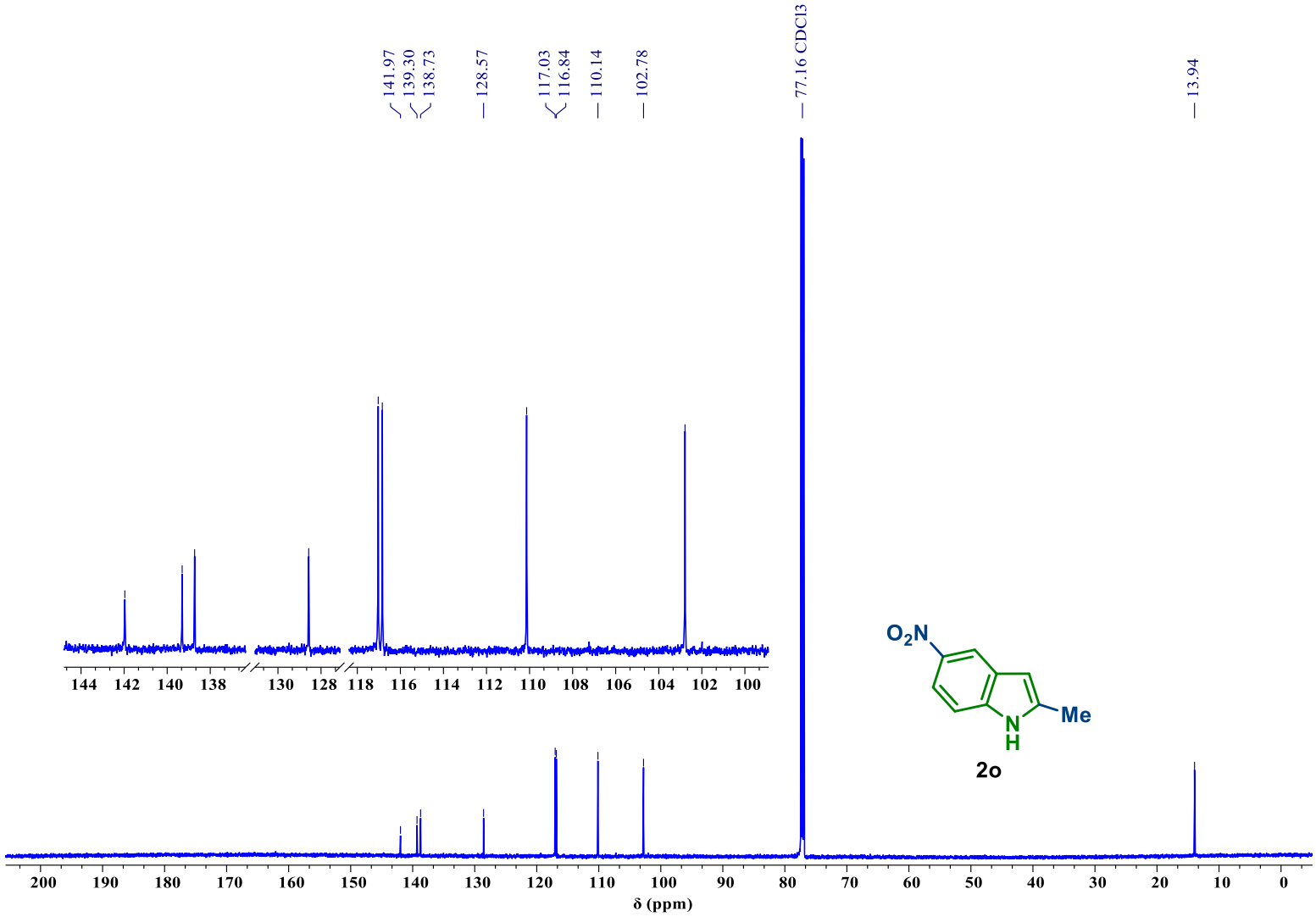
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2-methyl-5-nitro-1*H*-indole (2o).



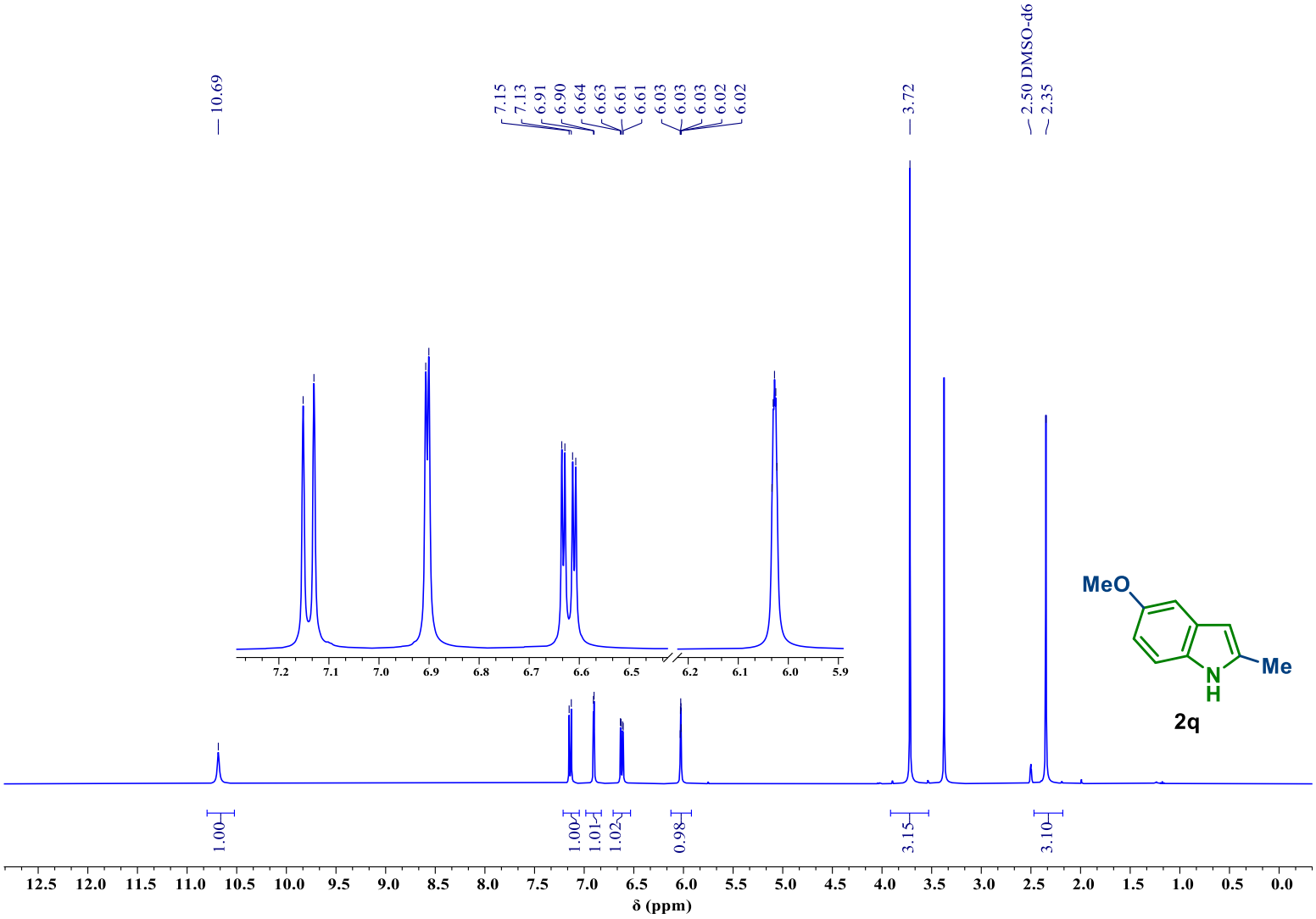
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 2-methyl-5-nitro-1*H*-indole (2o).



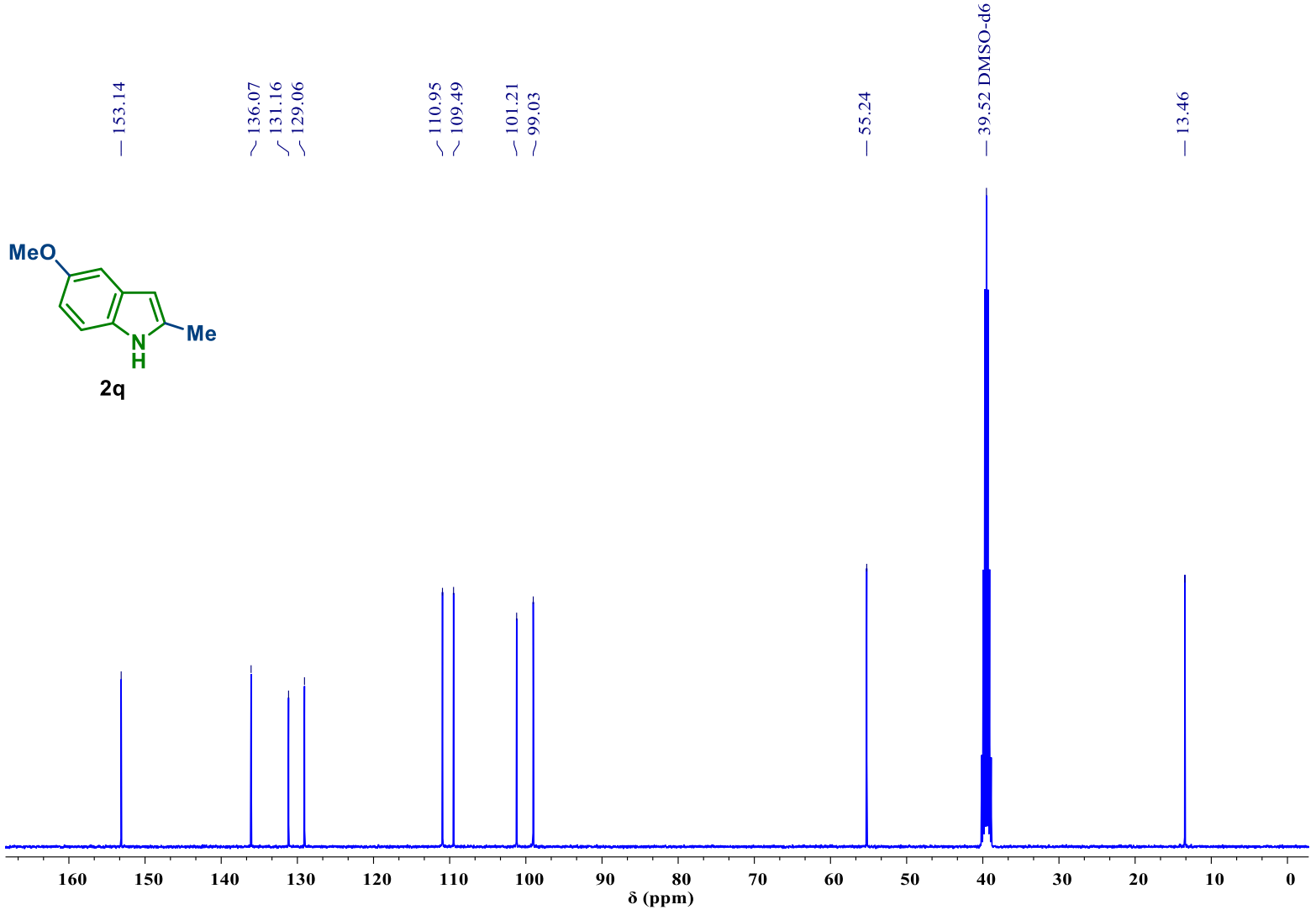
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 2-methyl-5-nitro-1*H*-indole (2o).



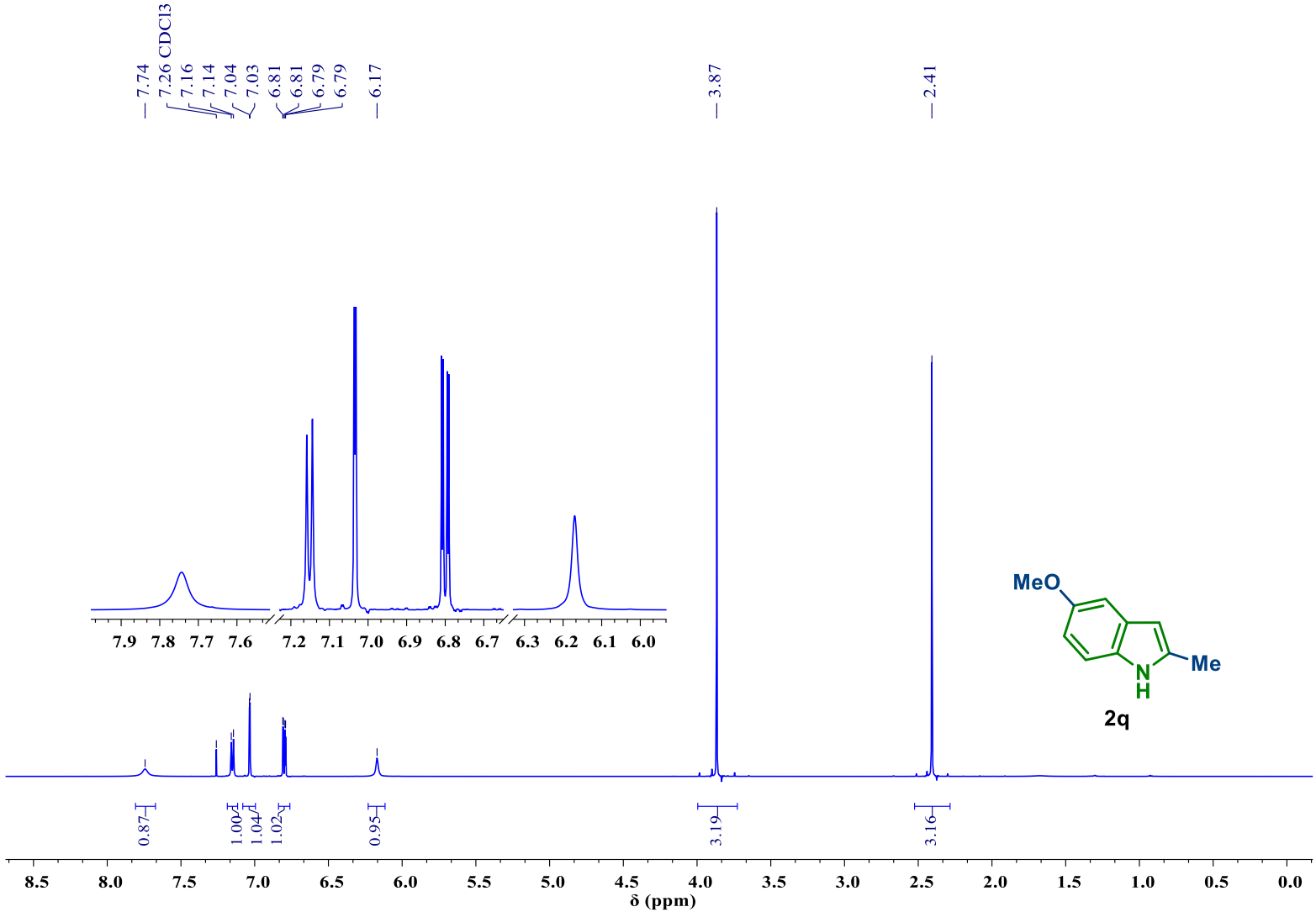
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 5-methoxy-2-methyl-1*H*-indole (2q).



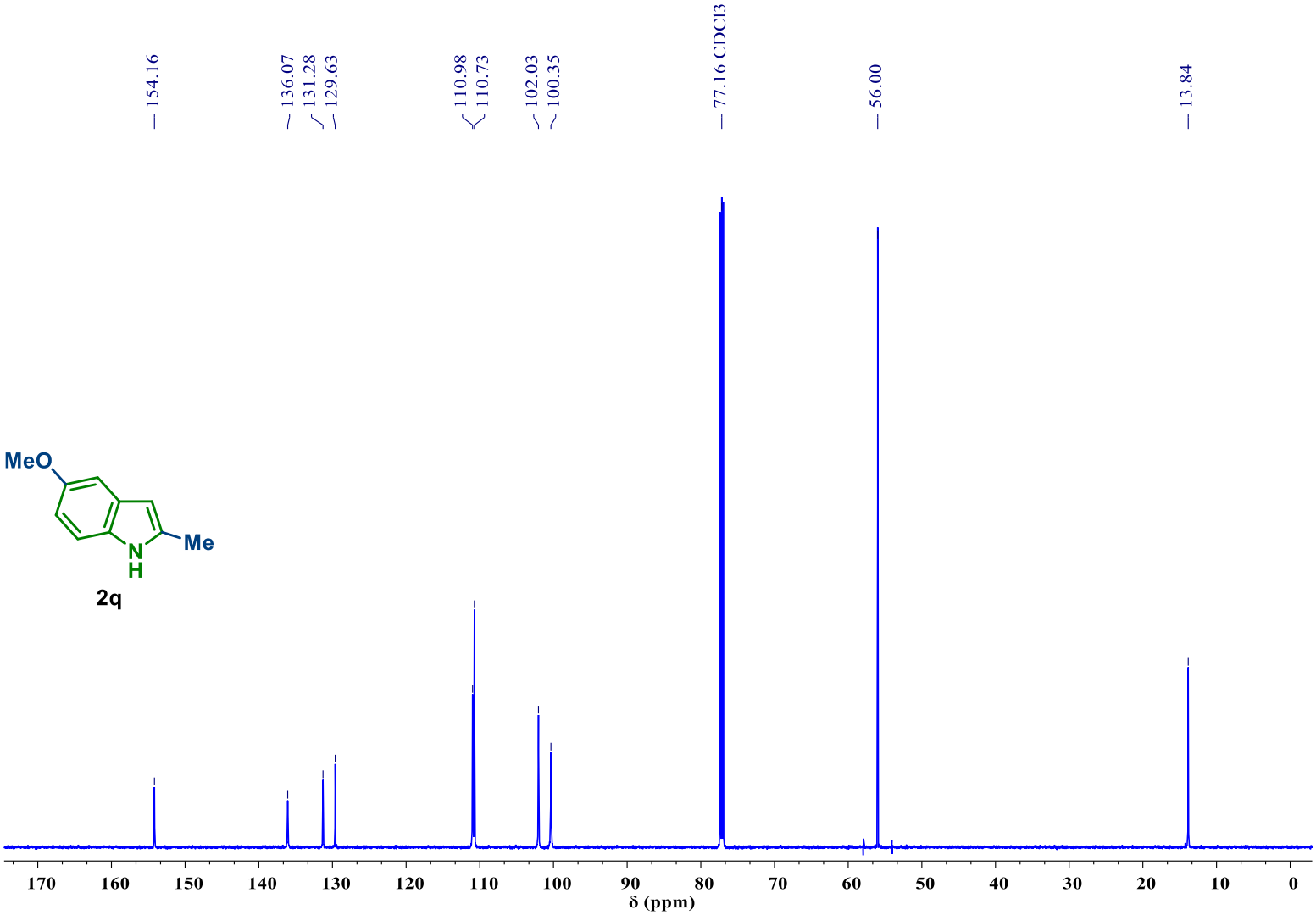
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 5-methoxy-2-methyl-1*H*-indole (2q).



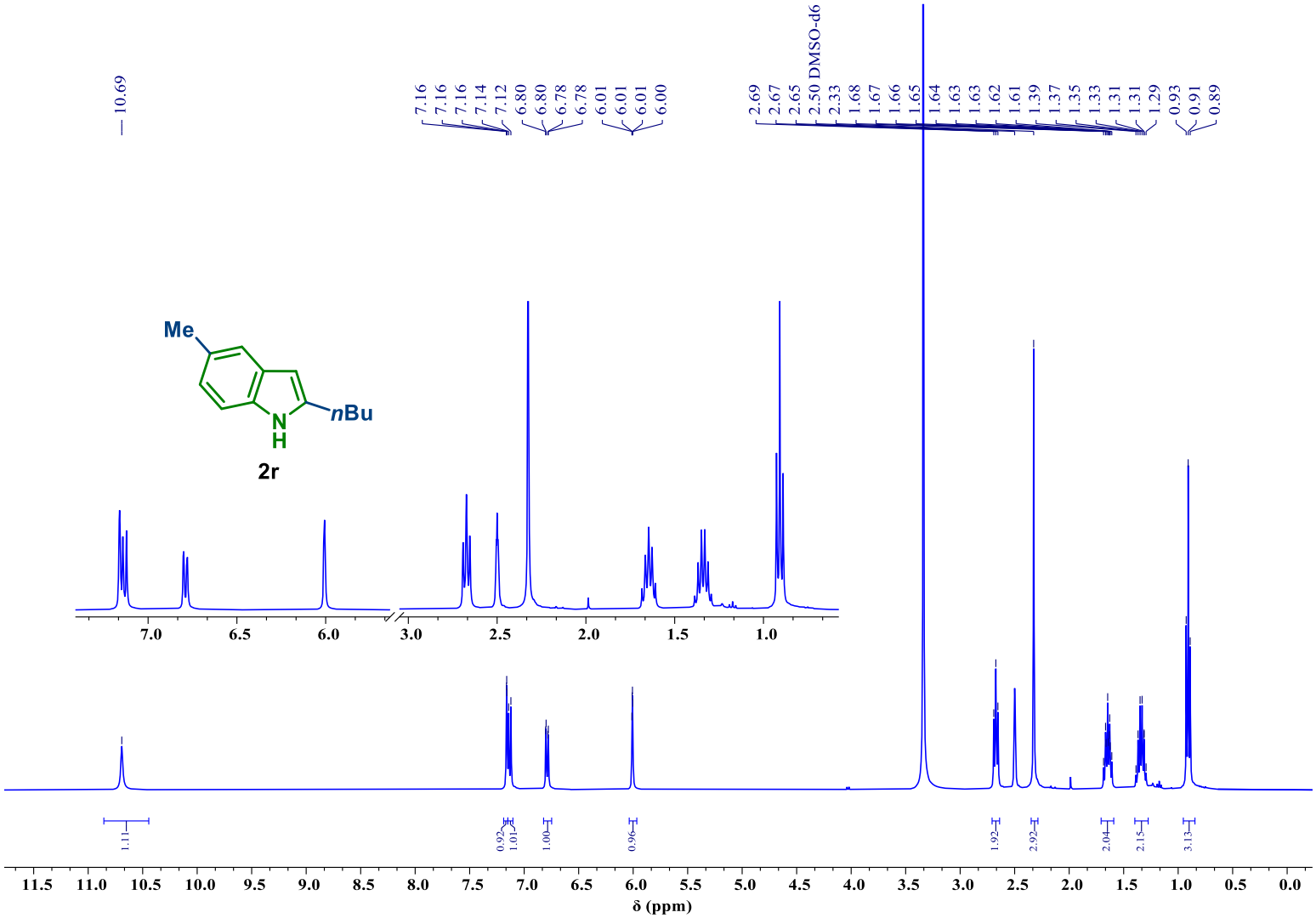
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of 5-methoxy-2-methyl-1*H*-indole (2q).



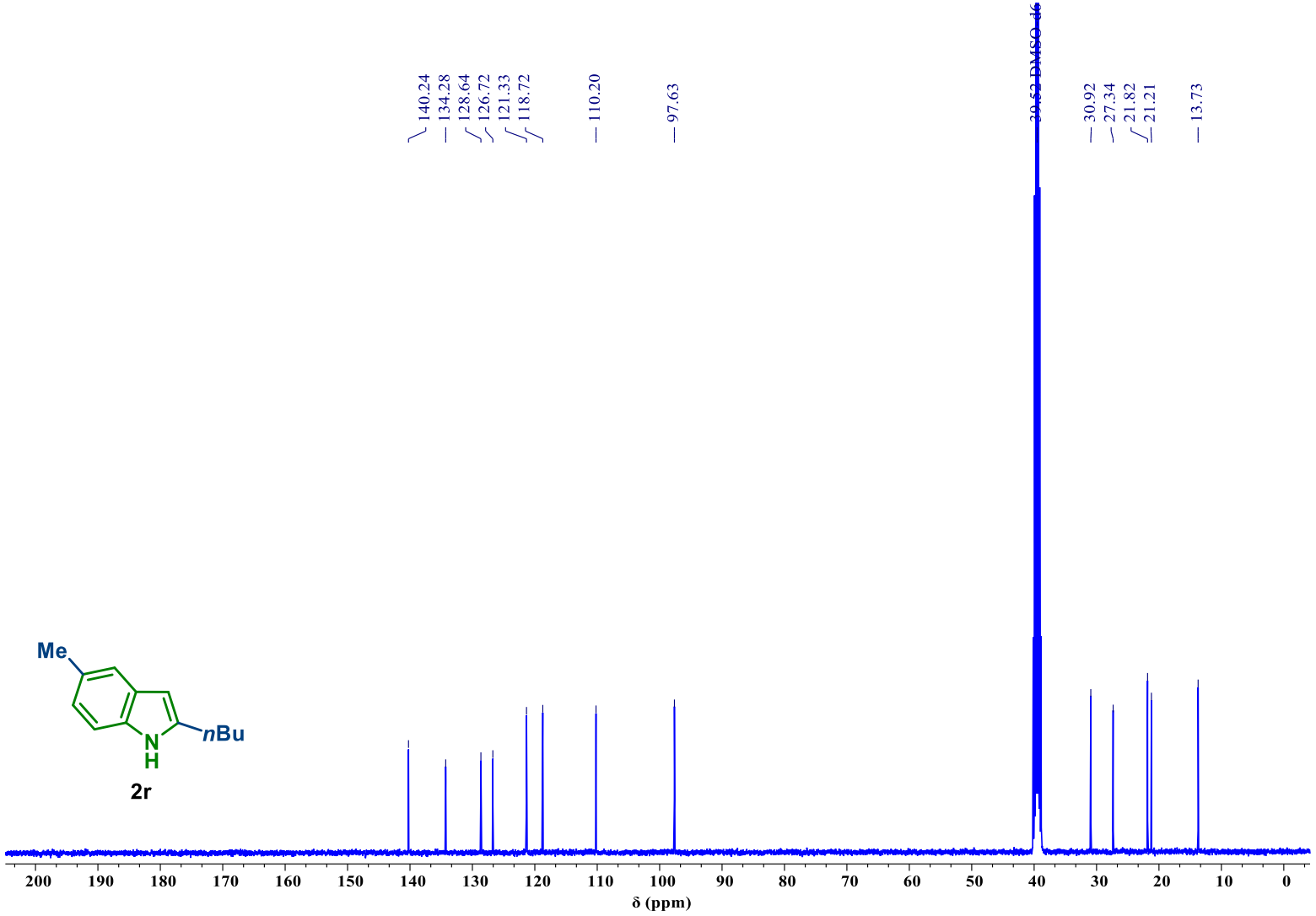
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 5-methoxy-2-methyl-1*H*-indole (2q).



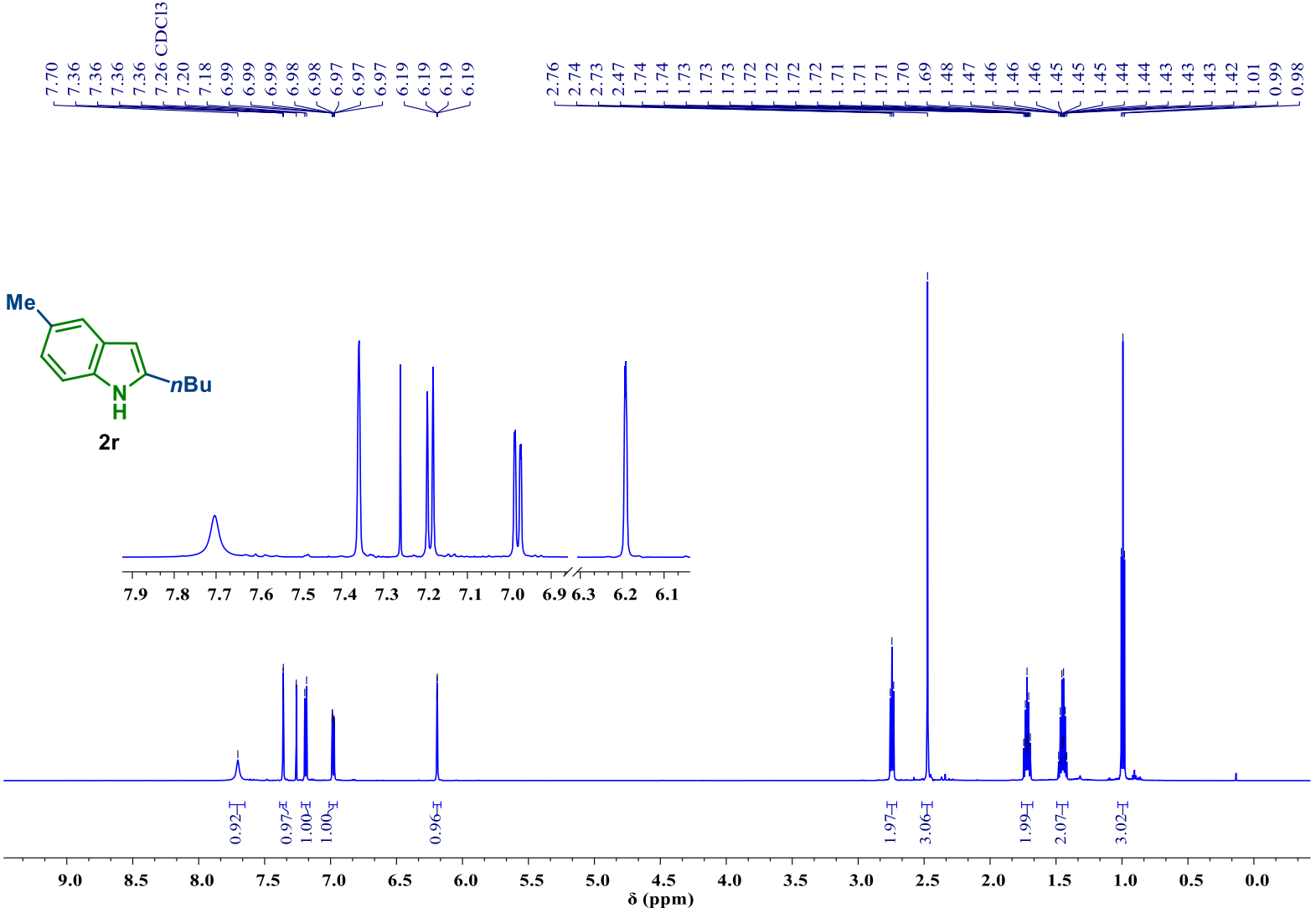
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of 2-butyl-5-methyl-1*H*-indole (2r).



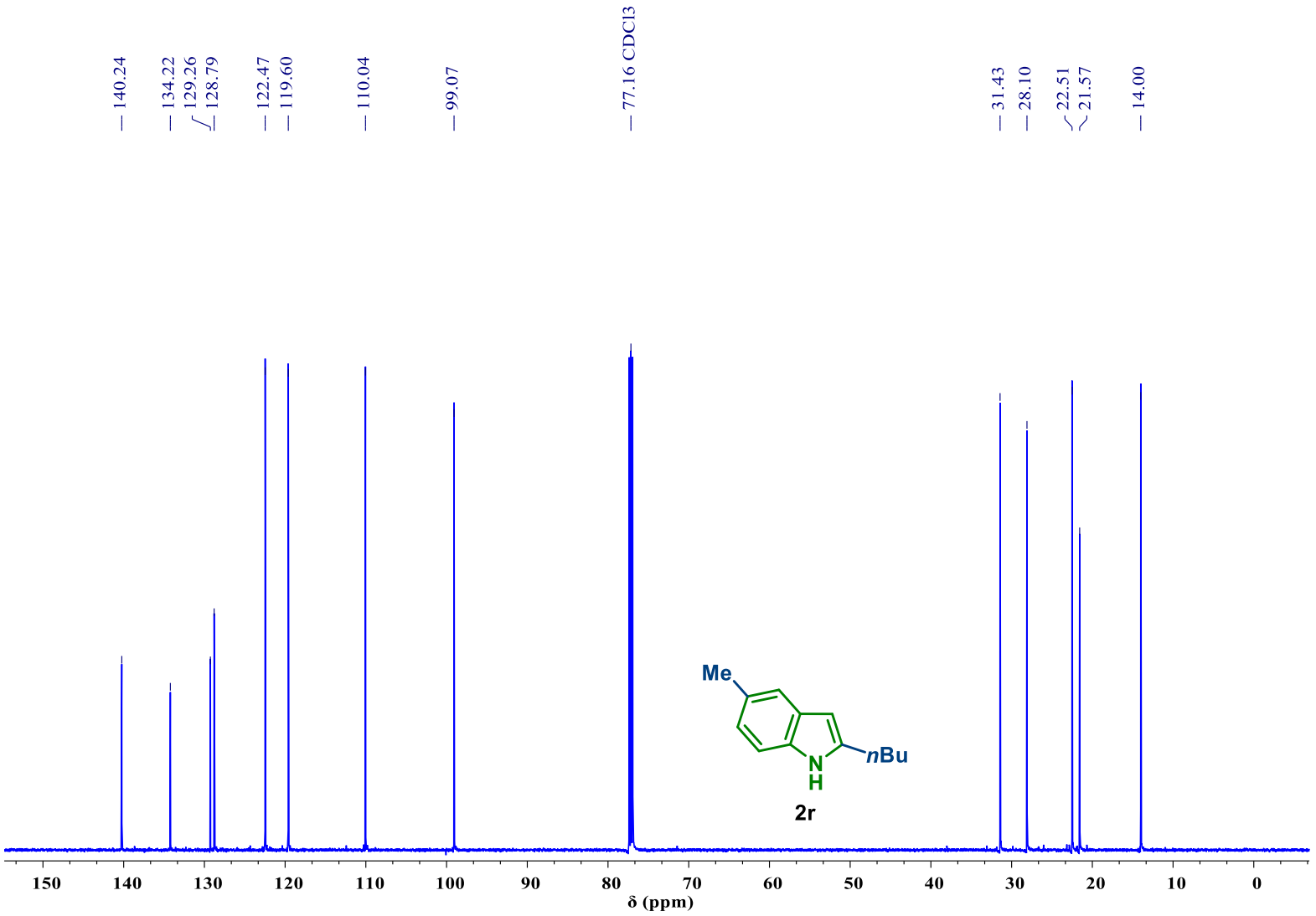
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 2-butyl-5-methyl-1*H*-indole (2r).



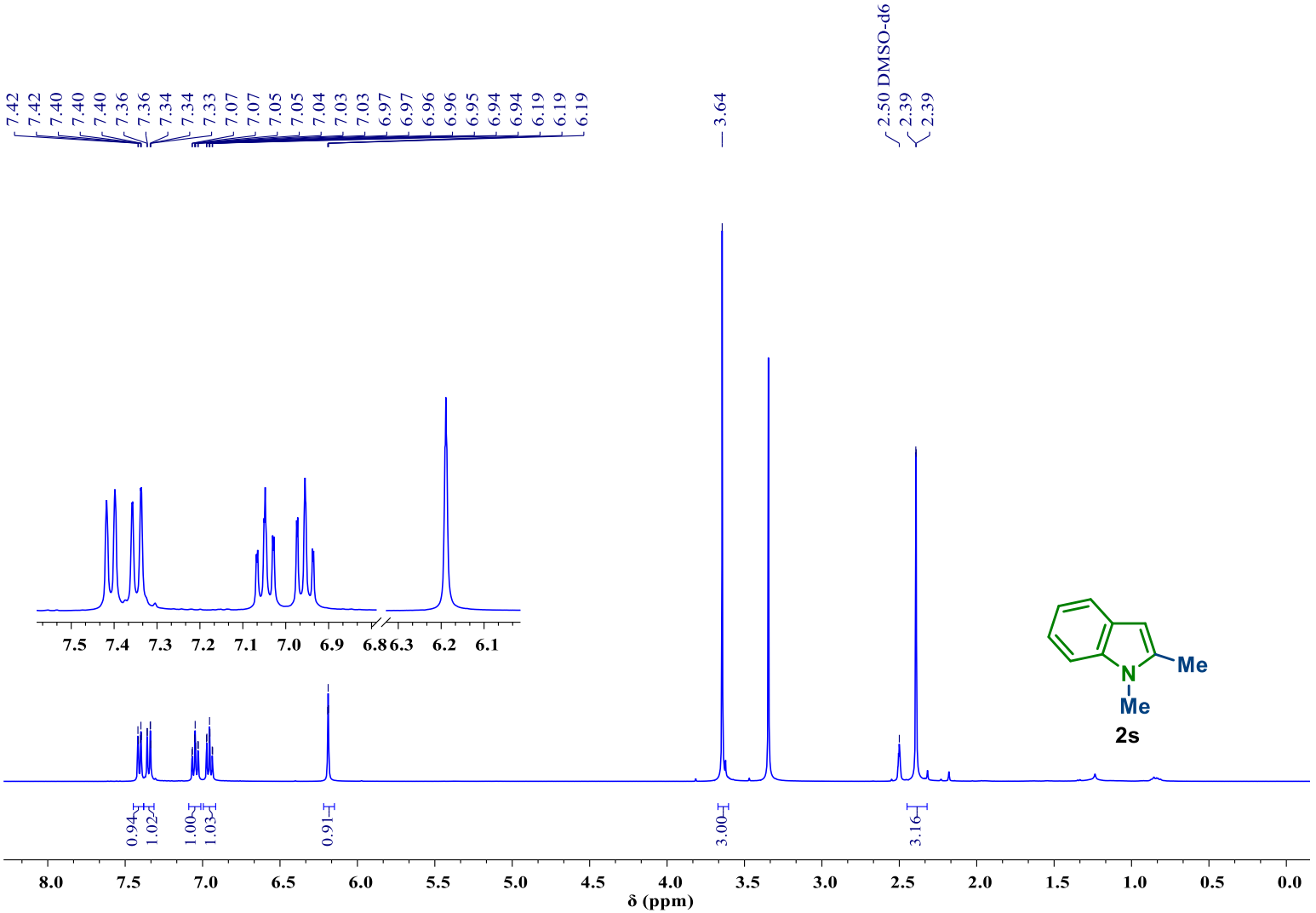
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-butyl-5-methyl-1*H*-indole (2r).



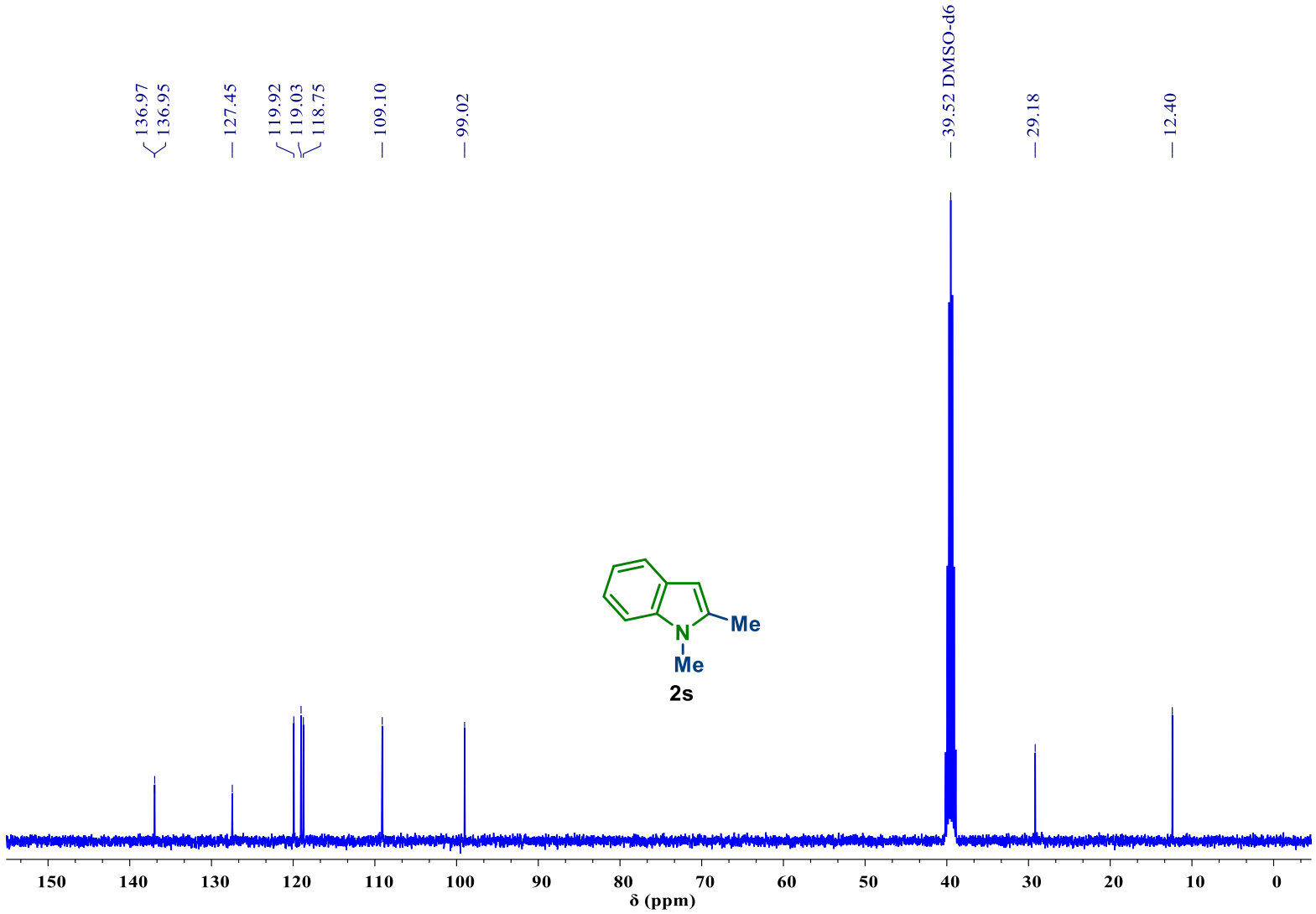
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-butyl-5-methyl-1*H*-indole (2r).



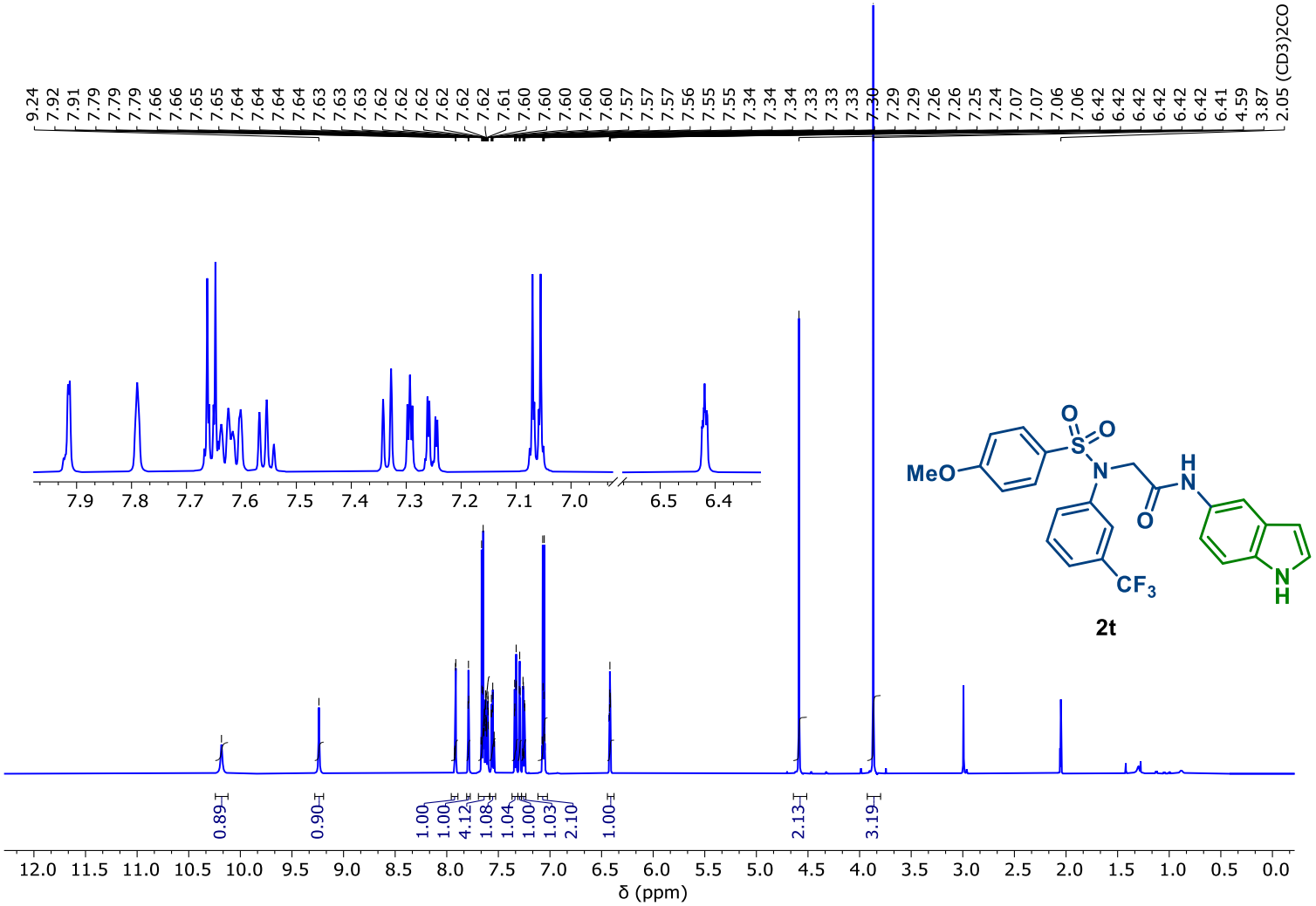
[1]H NMR (400 MHz, DMSO-d_6) spectrum of 1,2-dimethyl-1*H*-indole (2s).



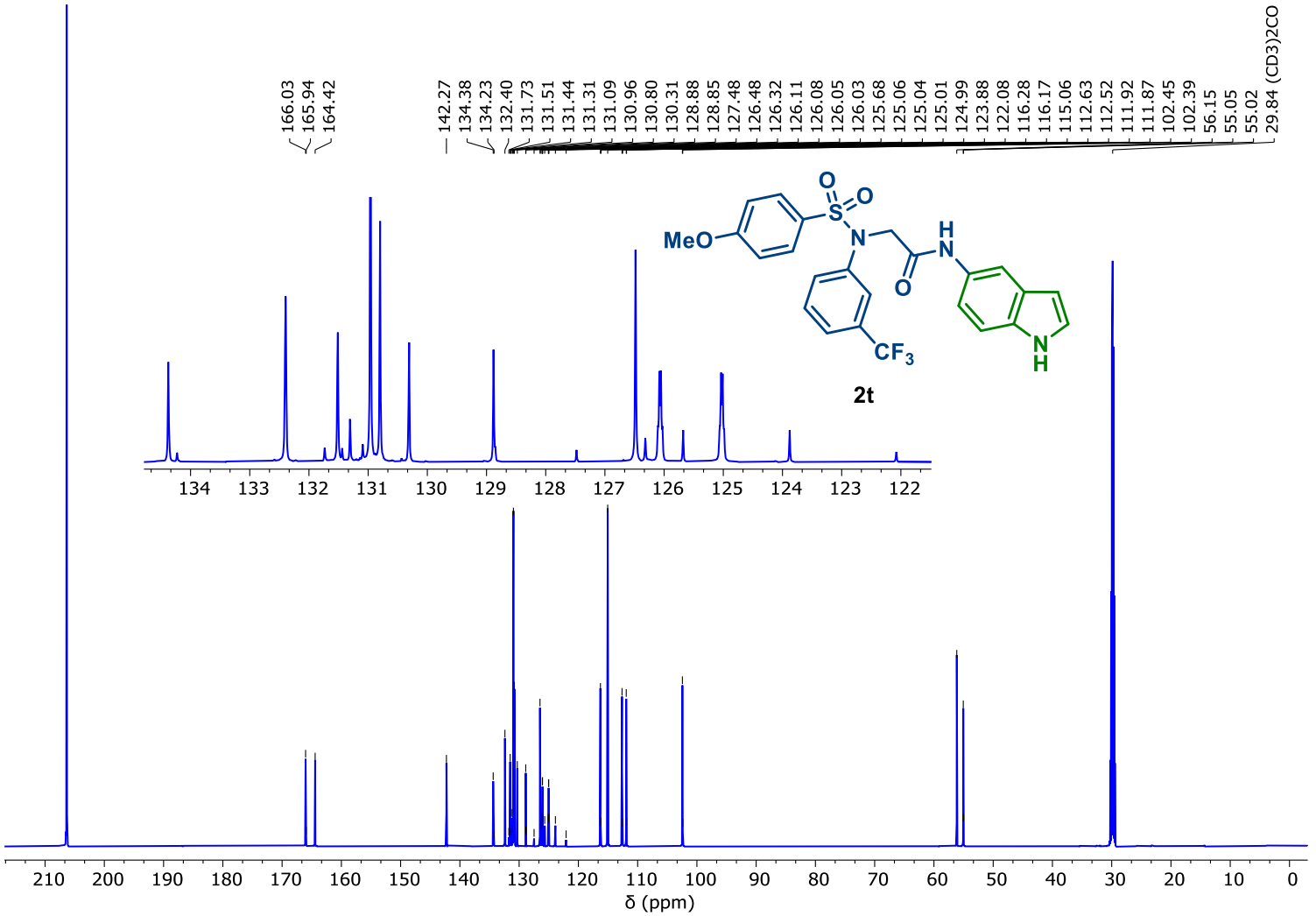
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of 1,2-dimethyl-1*H*-indole (2s).



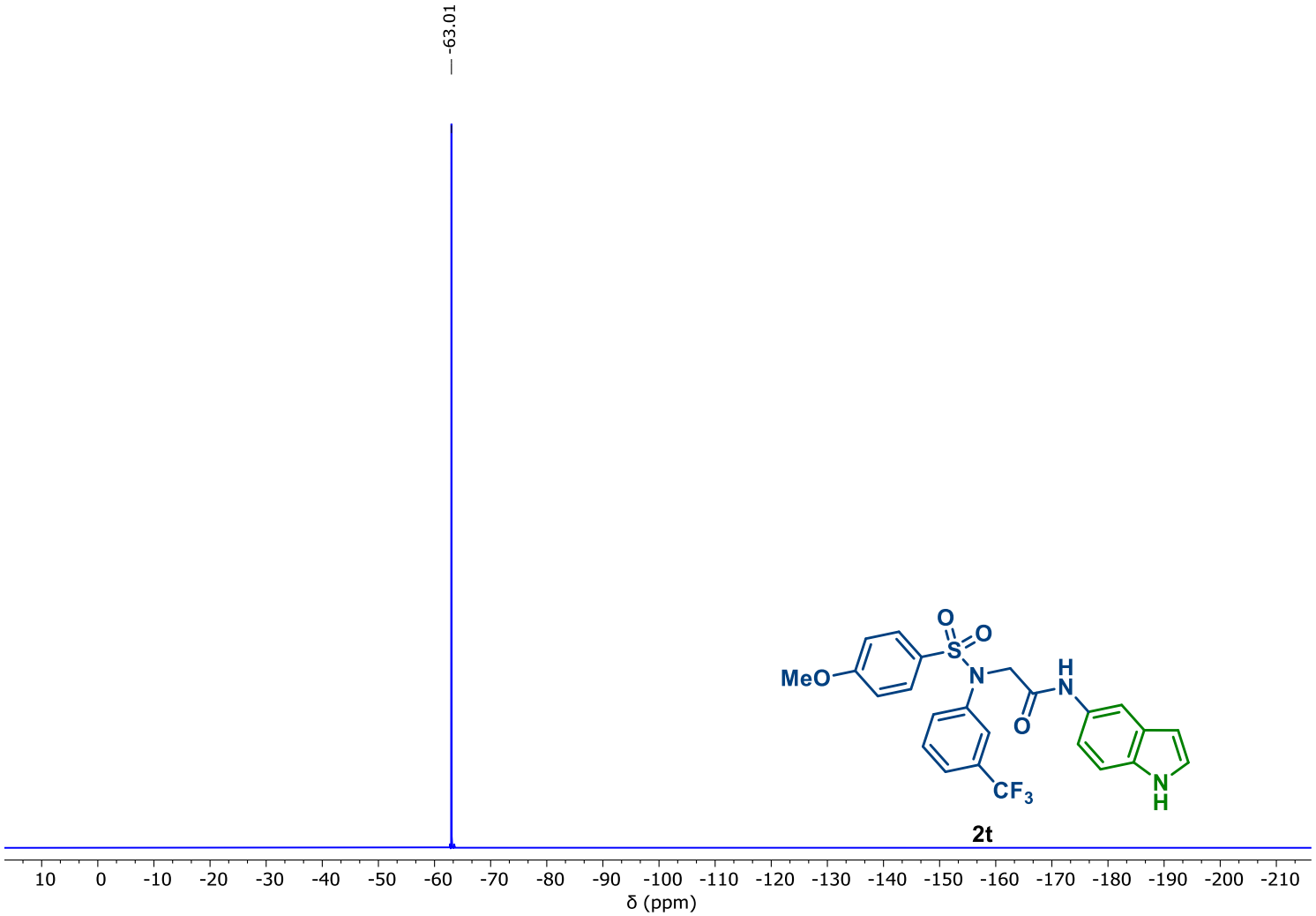
[1]H NMR (600 MHz, acetone-d_6) spectrum of *N*-(1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido) acetamide (2t).



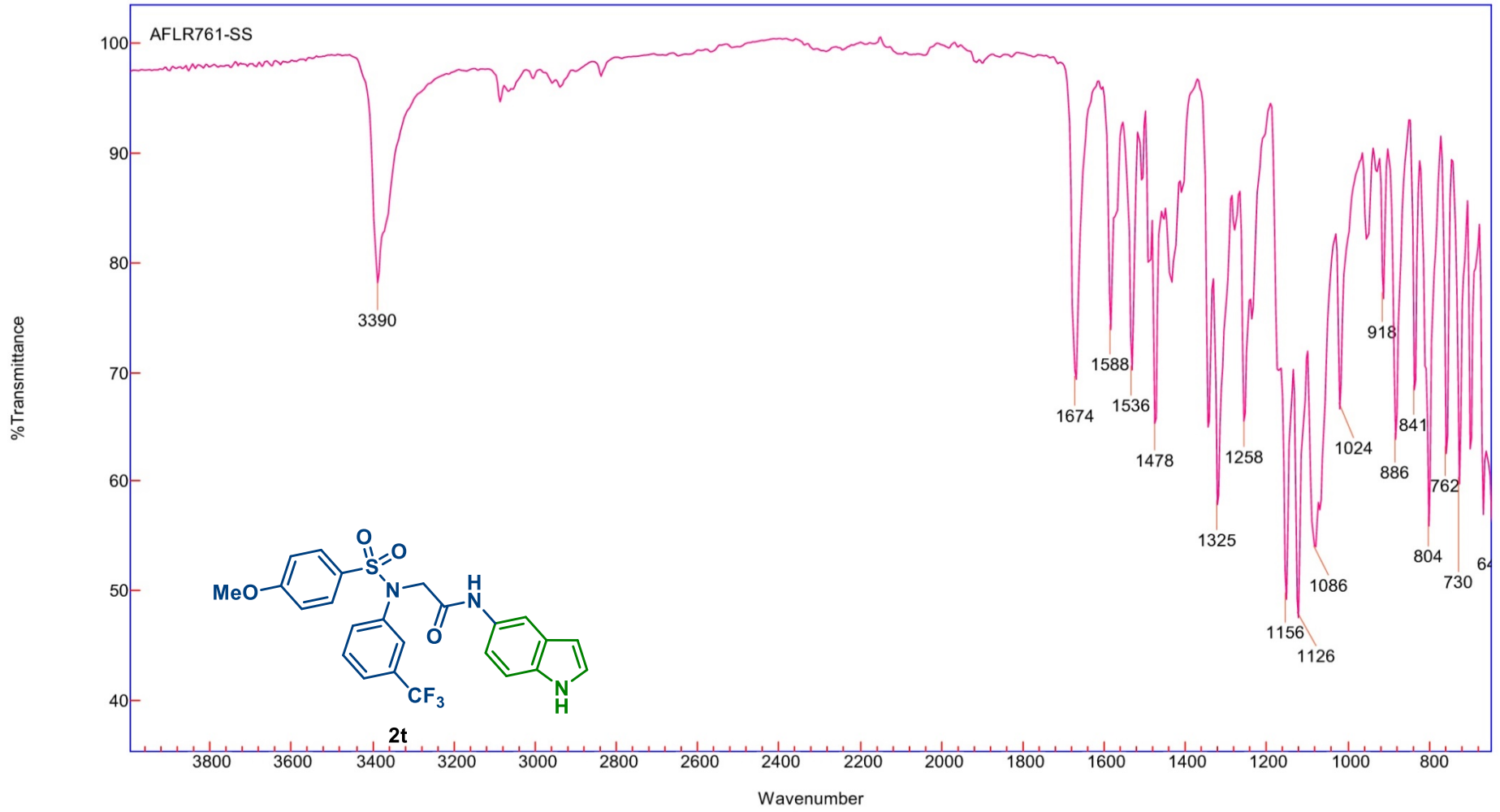
^{13}C NMR (151 MHz, acetone-d_6) spectrum of *N*-(1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido) acetamide (2t).



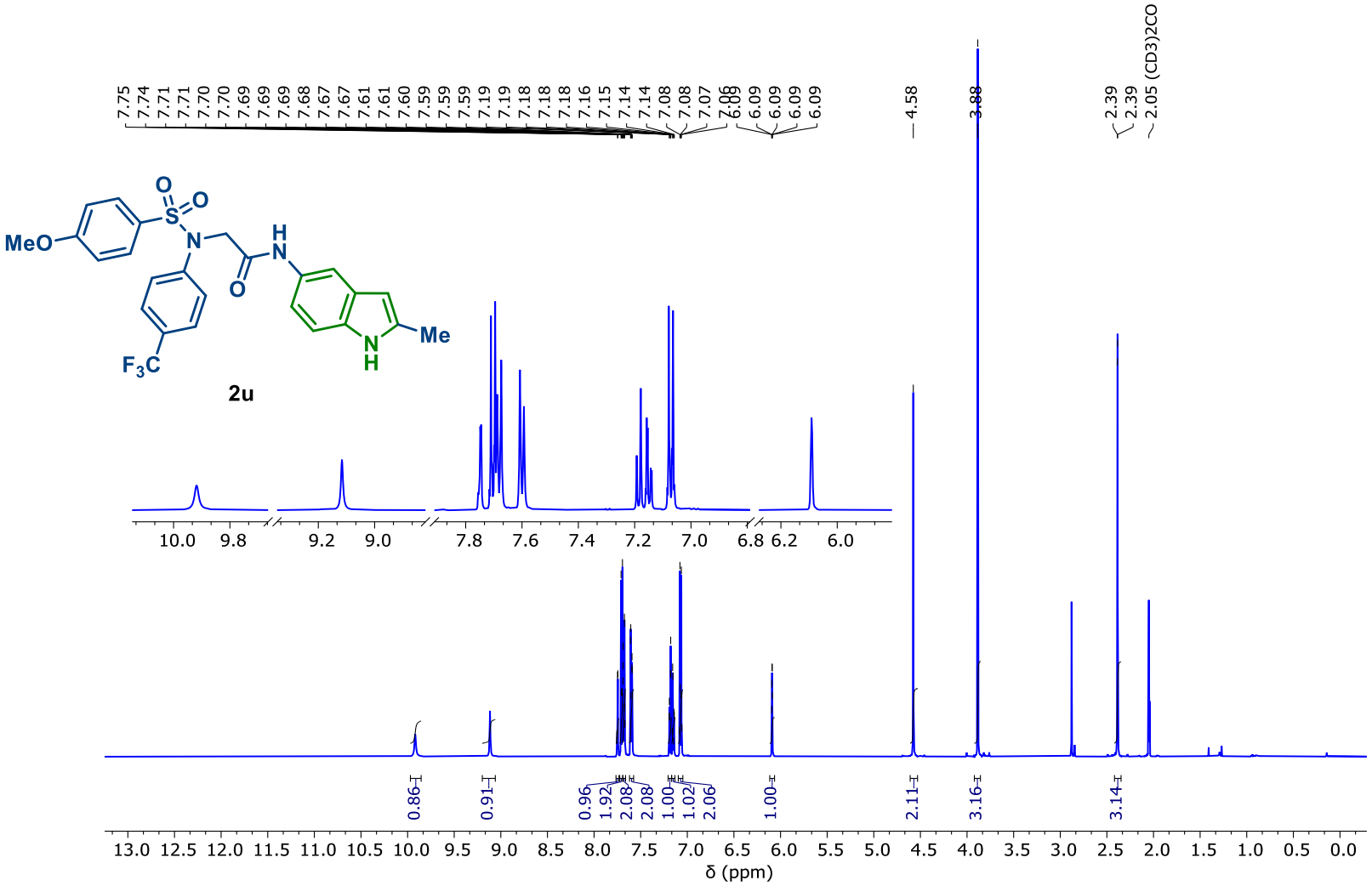
^{19}F NMR (376.5 MHz, acetone-d_6) spectrum of *N*-(1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido) acetamide (2t).



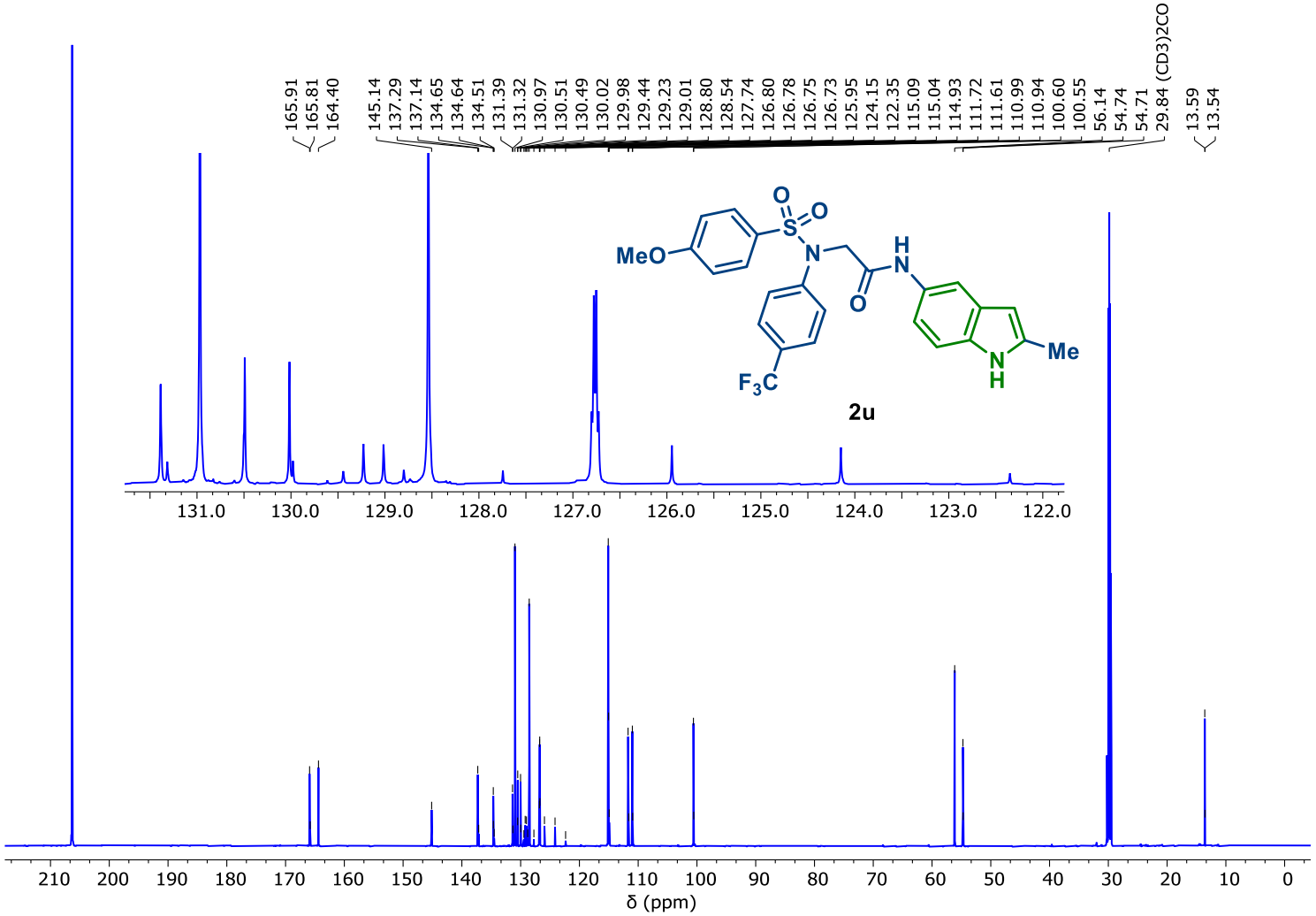
ATR-IR spectrum of (*N*-(1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl)sulfonamido) acetamide (2t).



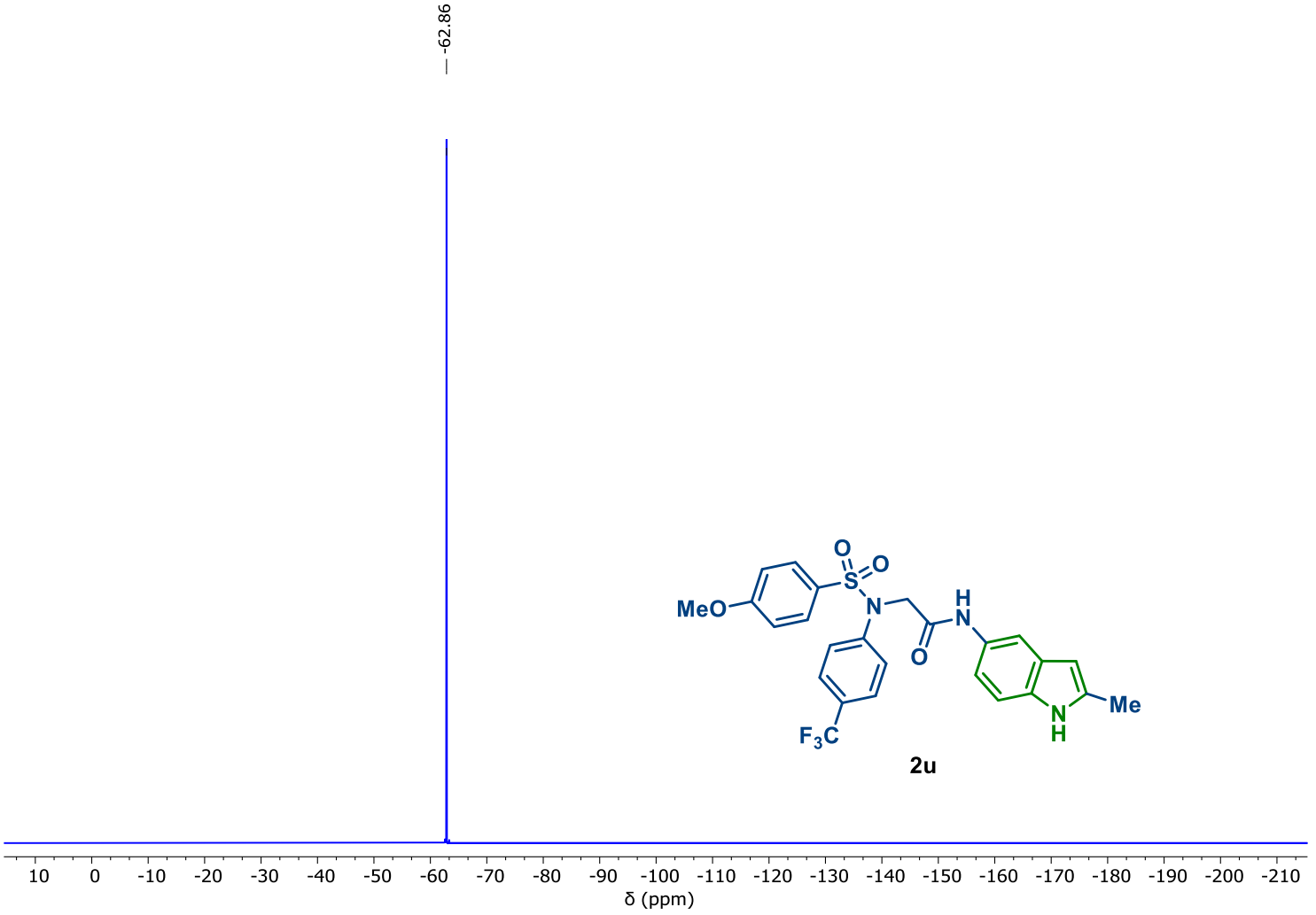
^{1}H NMR (600 MHz, acetone-d_6) spectrum of 2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide (2u).



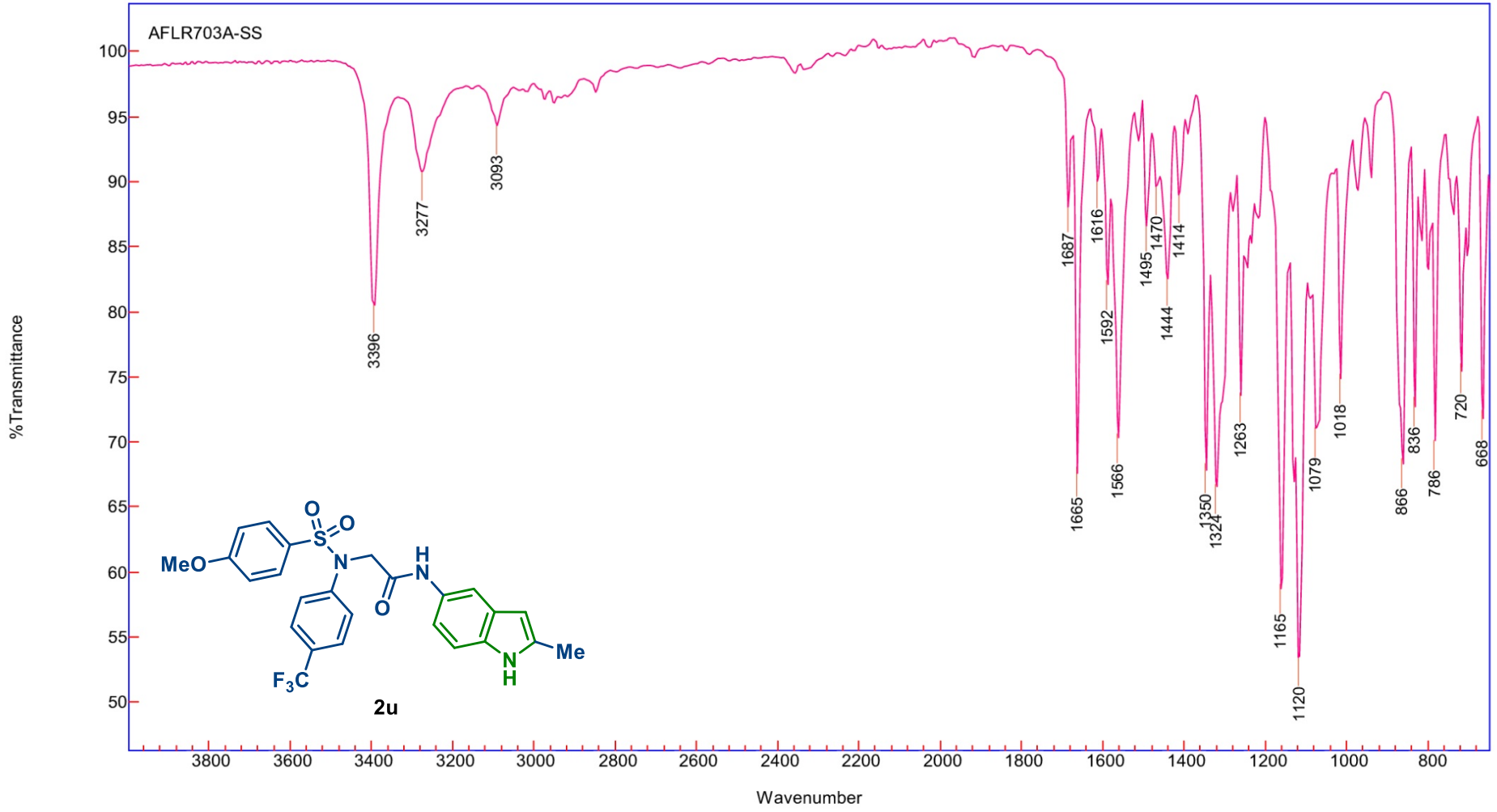
^{13}C NMR (151 MHz, acetone-d_6) spectrum of 2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide (2u).



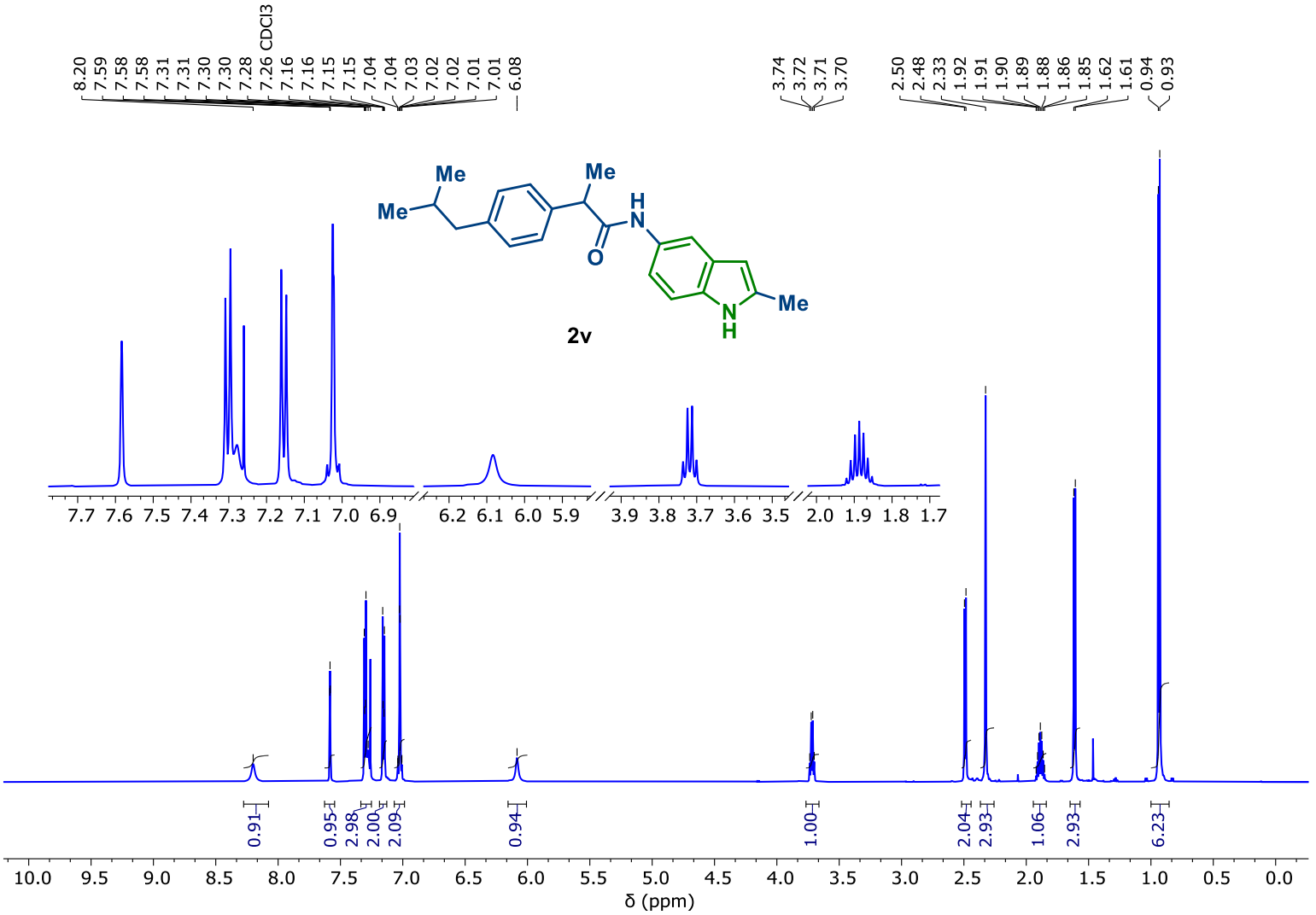
^{19}F NMR (376.5 MHz, acetone-d_6) spectrum of 2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide (2u).



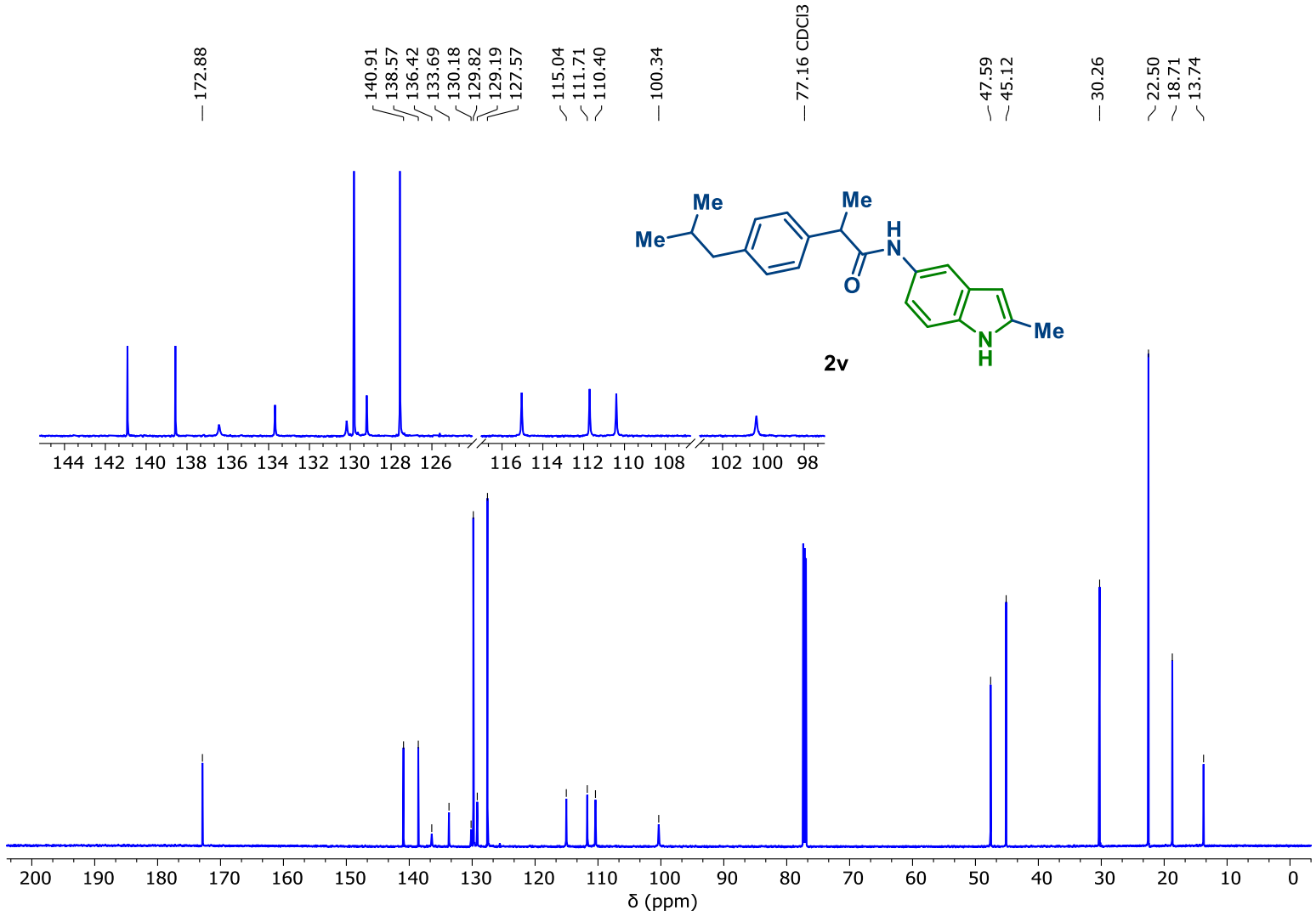
ATR-IR spectrum of 2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)-*N*-(2-methyl-1*H*-indol-5-yl)acetamide (2u).



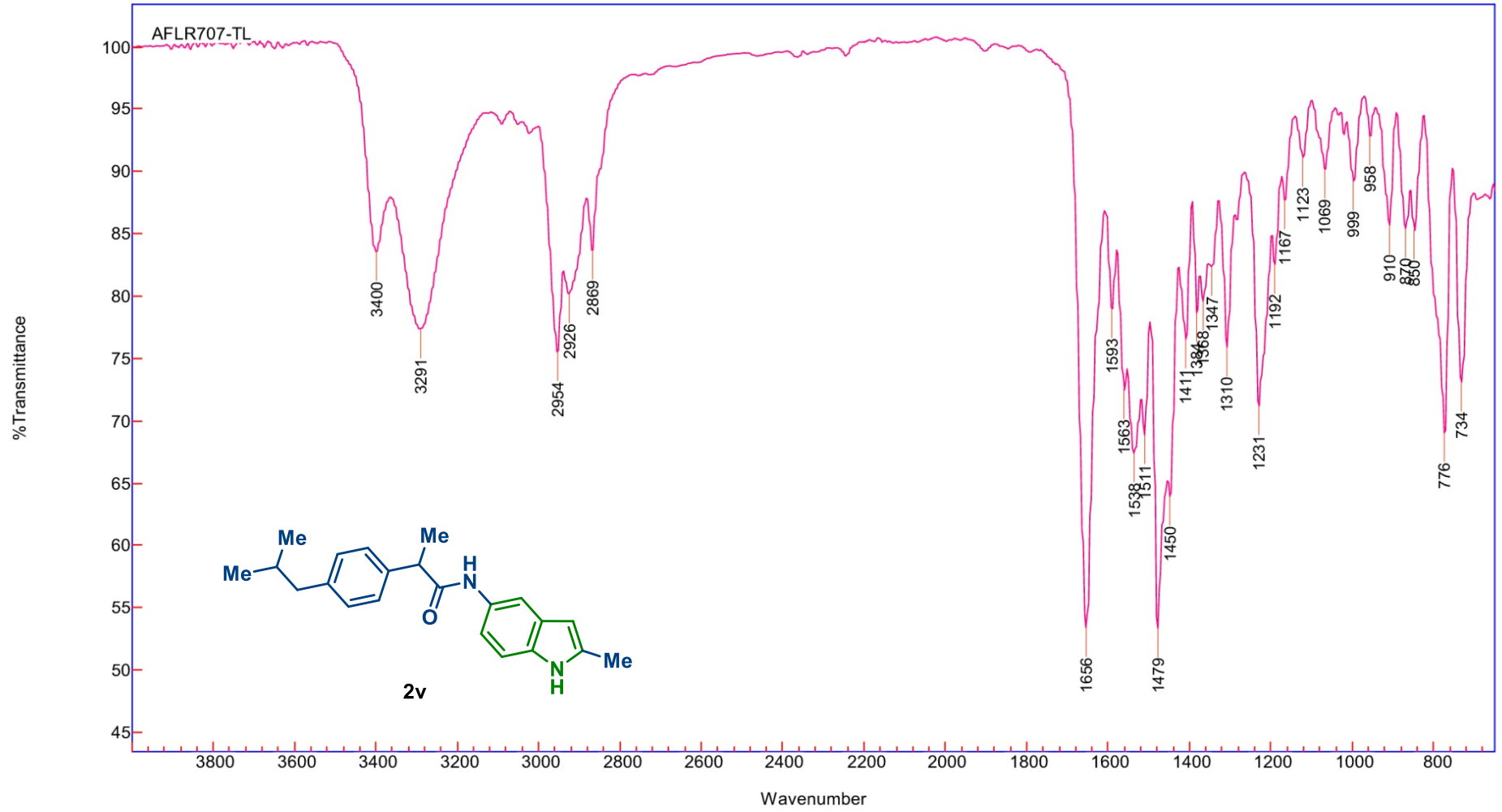
[1]H NMR (600 MHz, $CDCl_3$) spectrum of 2-(4-isobutylphenyl)-*N*-(2-methyl-1*H*-indol-5-yl)propanamide (2v).



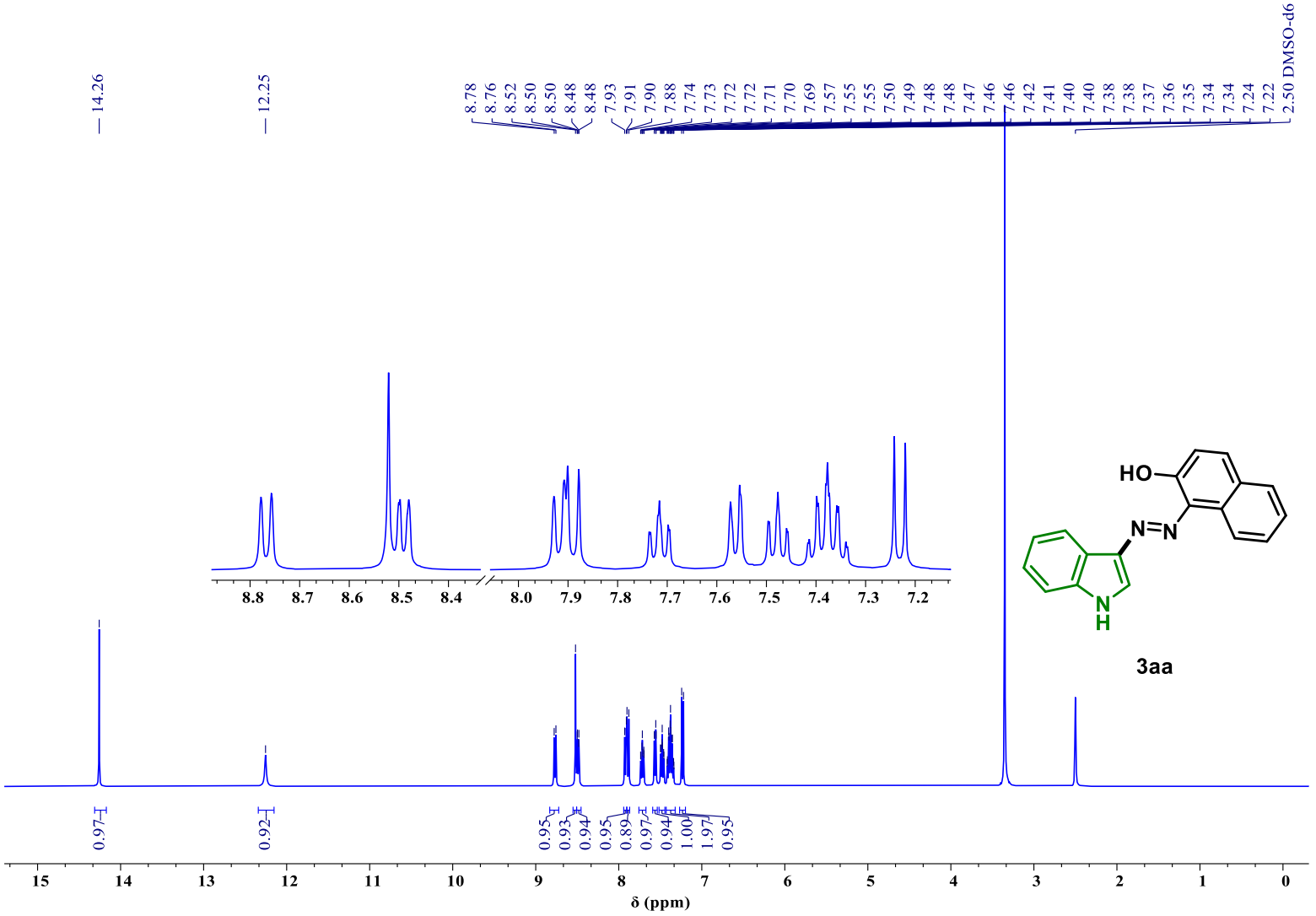
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of 2-(4-isobutylphenyl)-*N*-(2-methyl-1*H*-indol-5-yl)propanamide (2v).



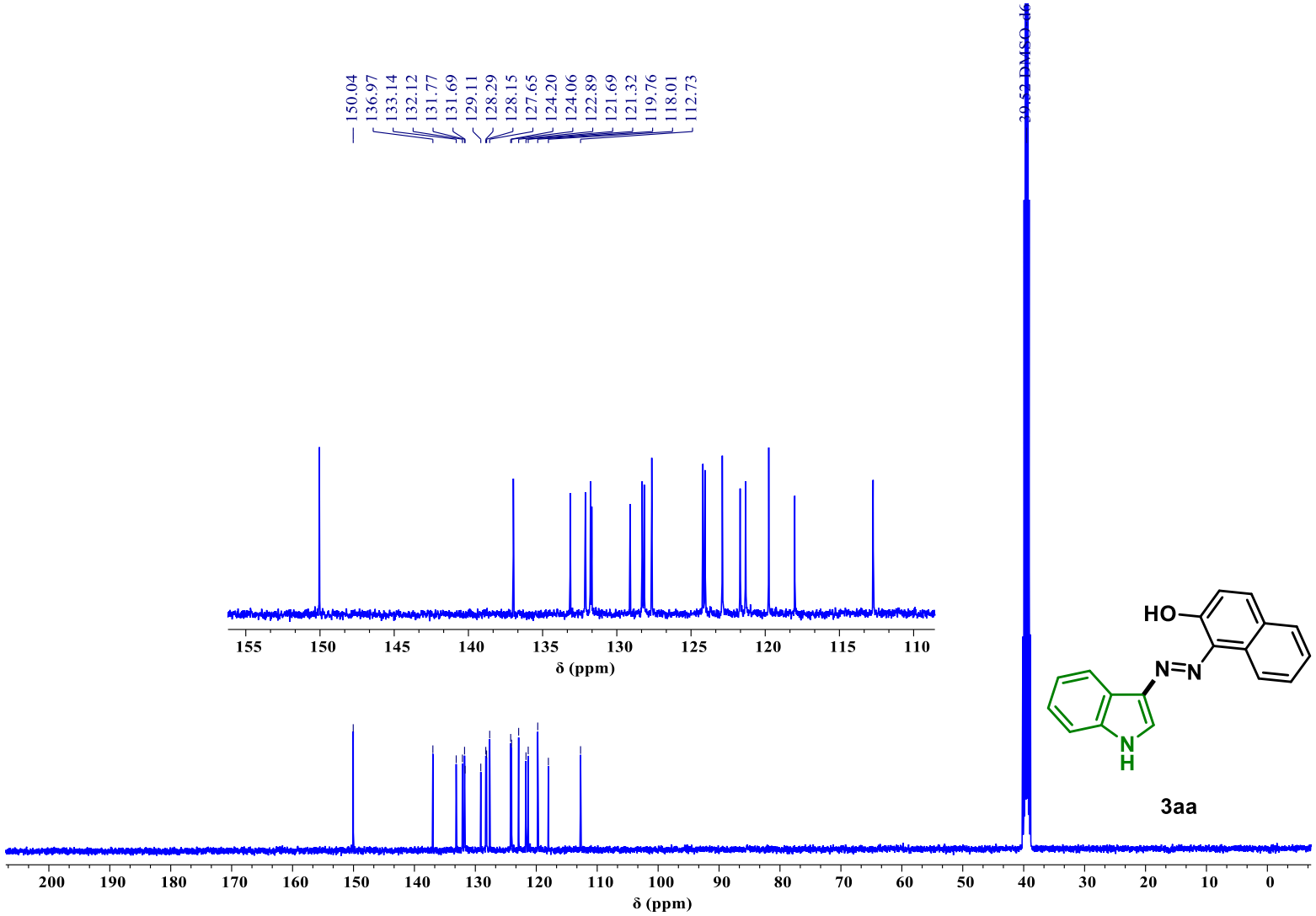
ATR-IR spectrum of 2-(4-isobutylphenyl)-*N*-(2-methyl-1*H*-indol-5-yl)propanamide (2v).



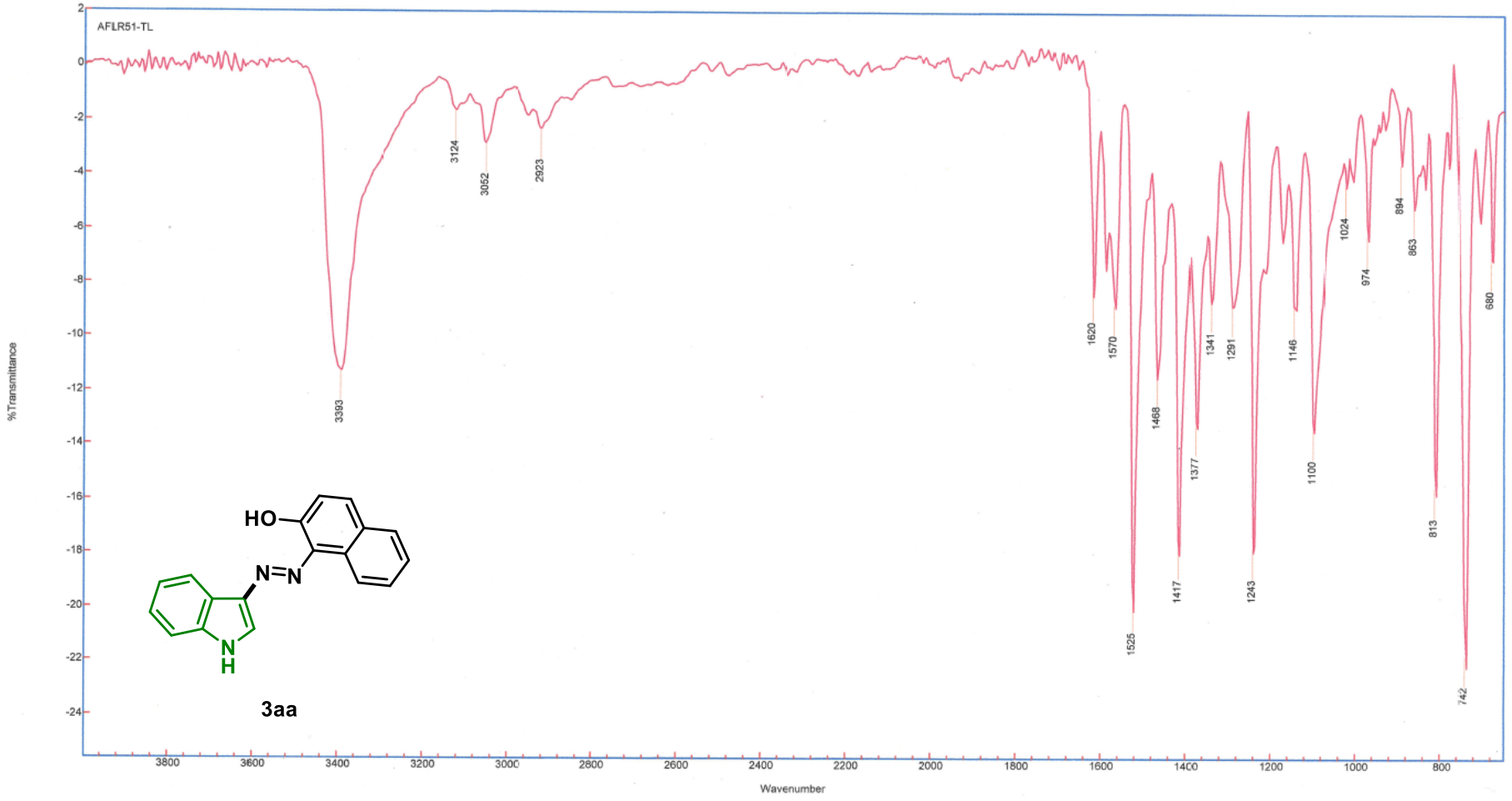
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aa).



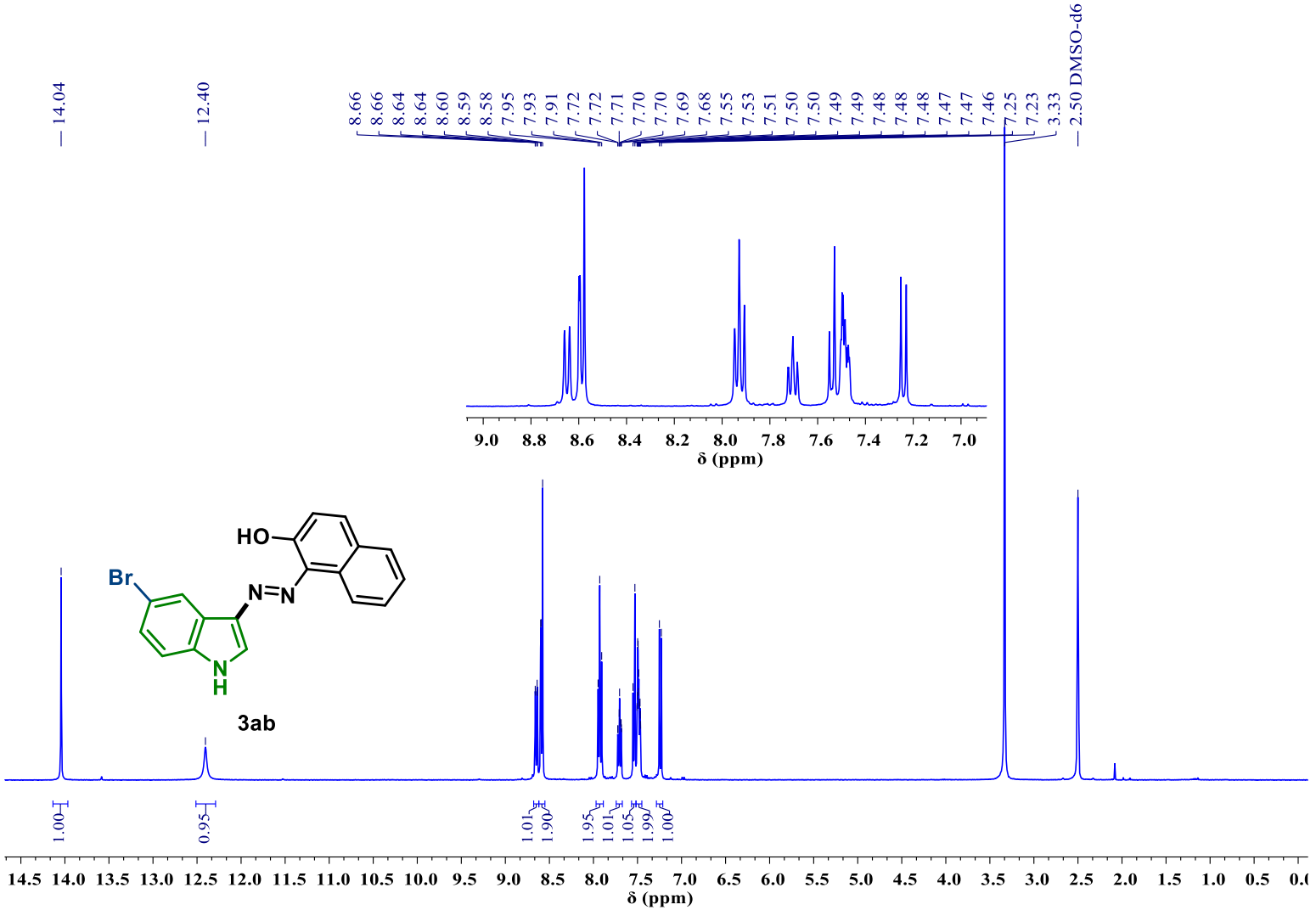
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aa).



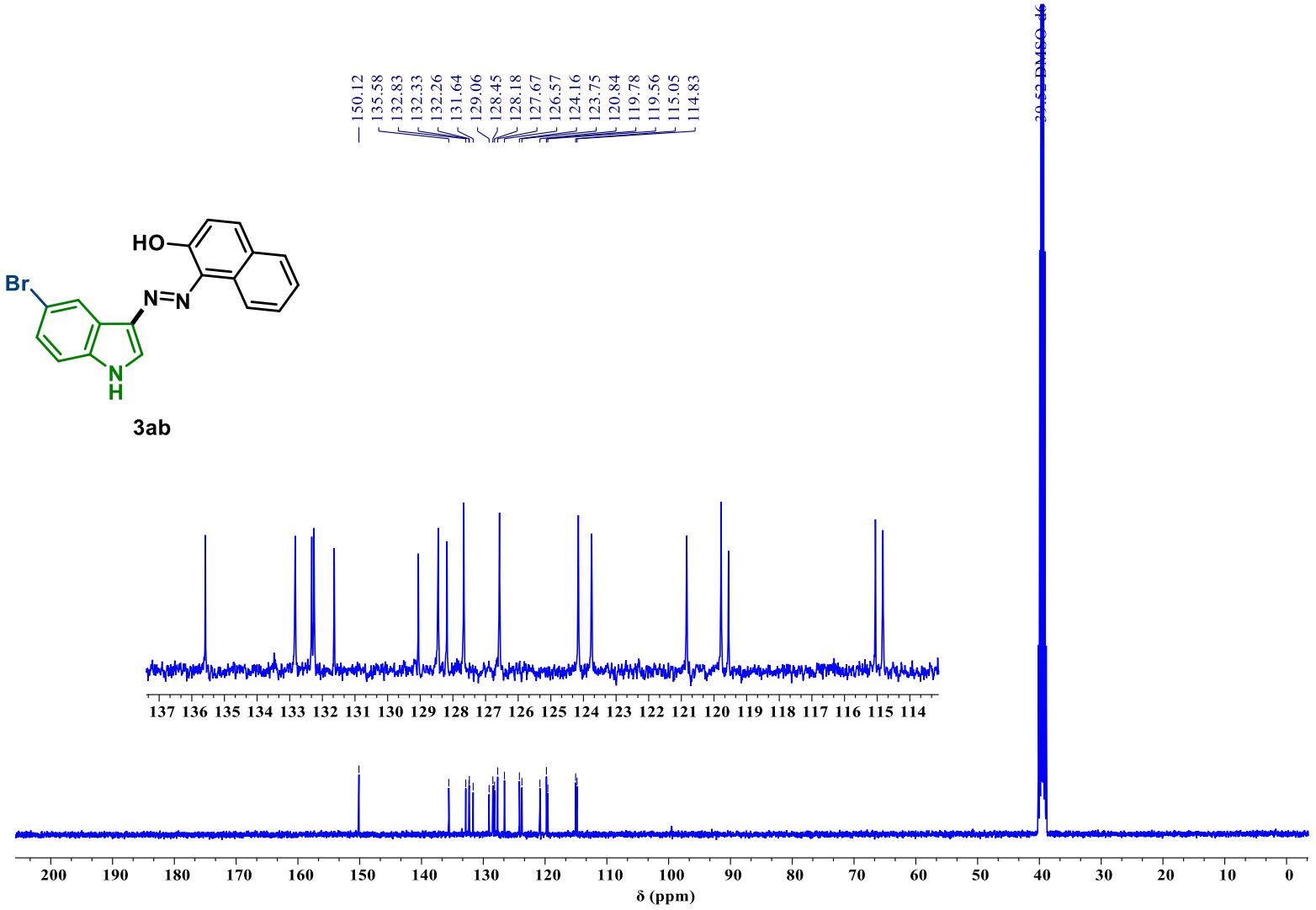
ATR-IR spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aa).



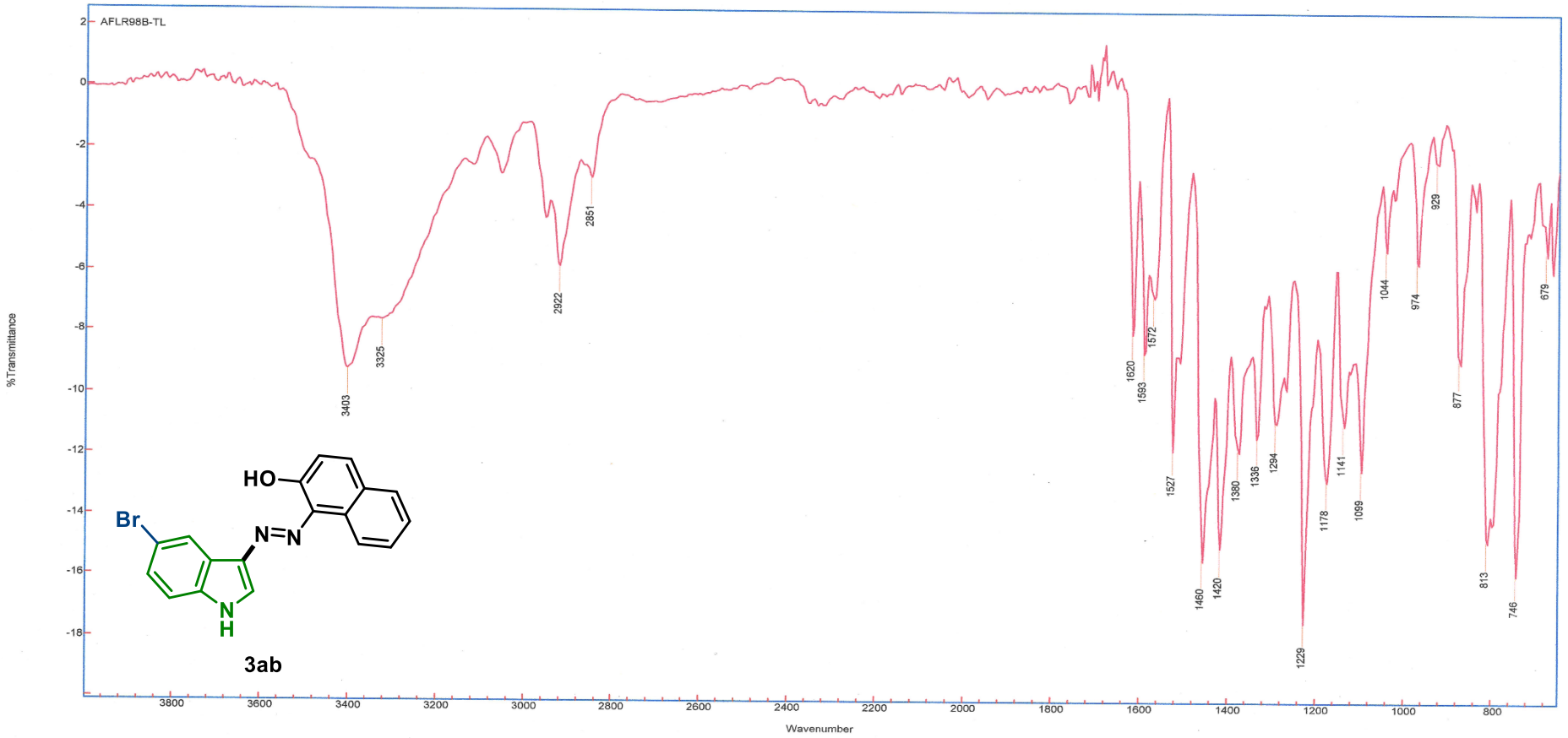
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-bromo-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ab).



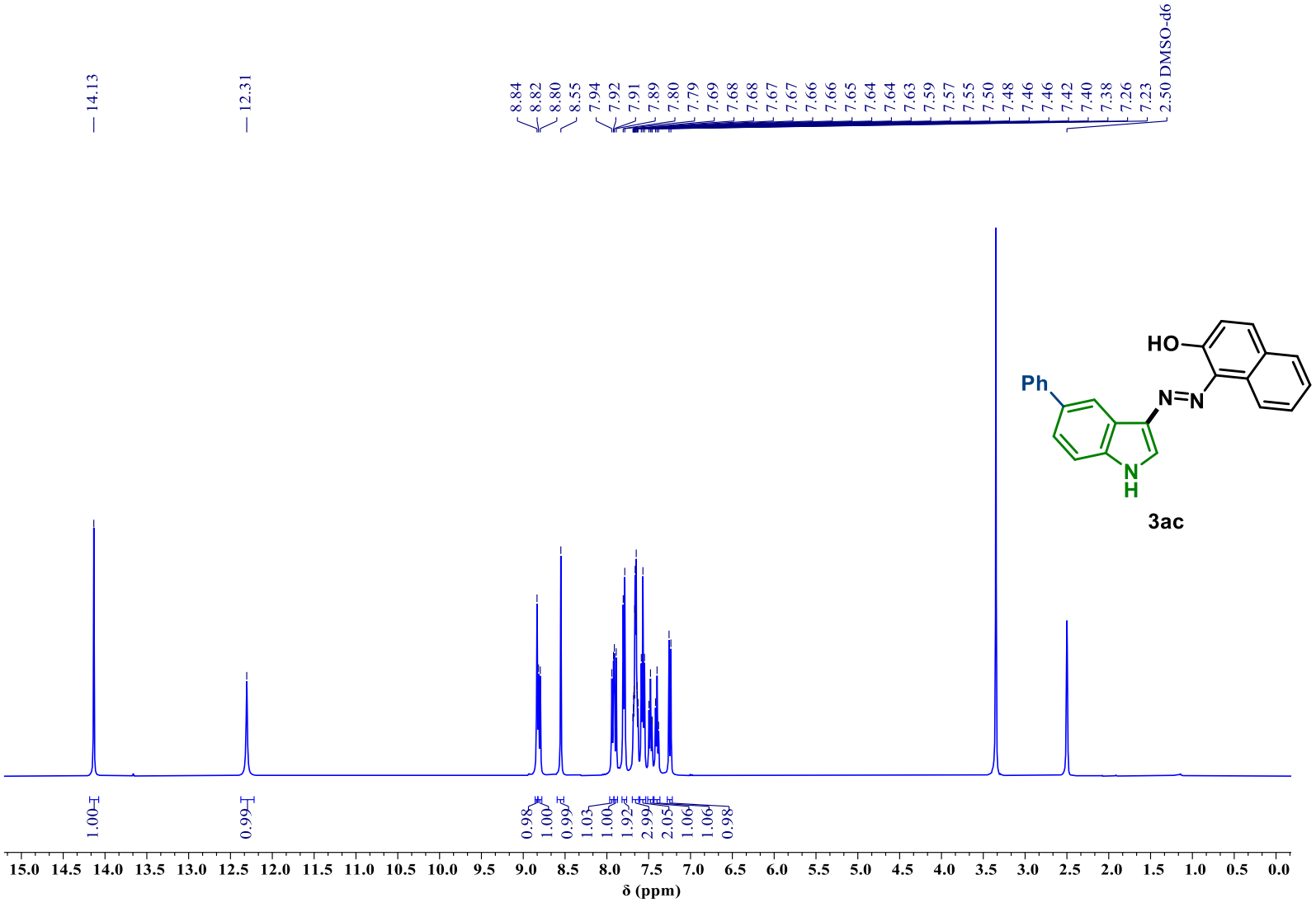
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-bromo-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ab).



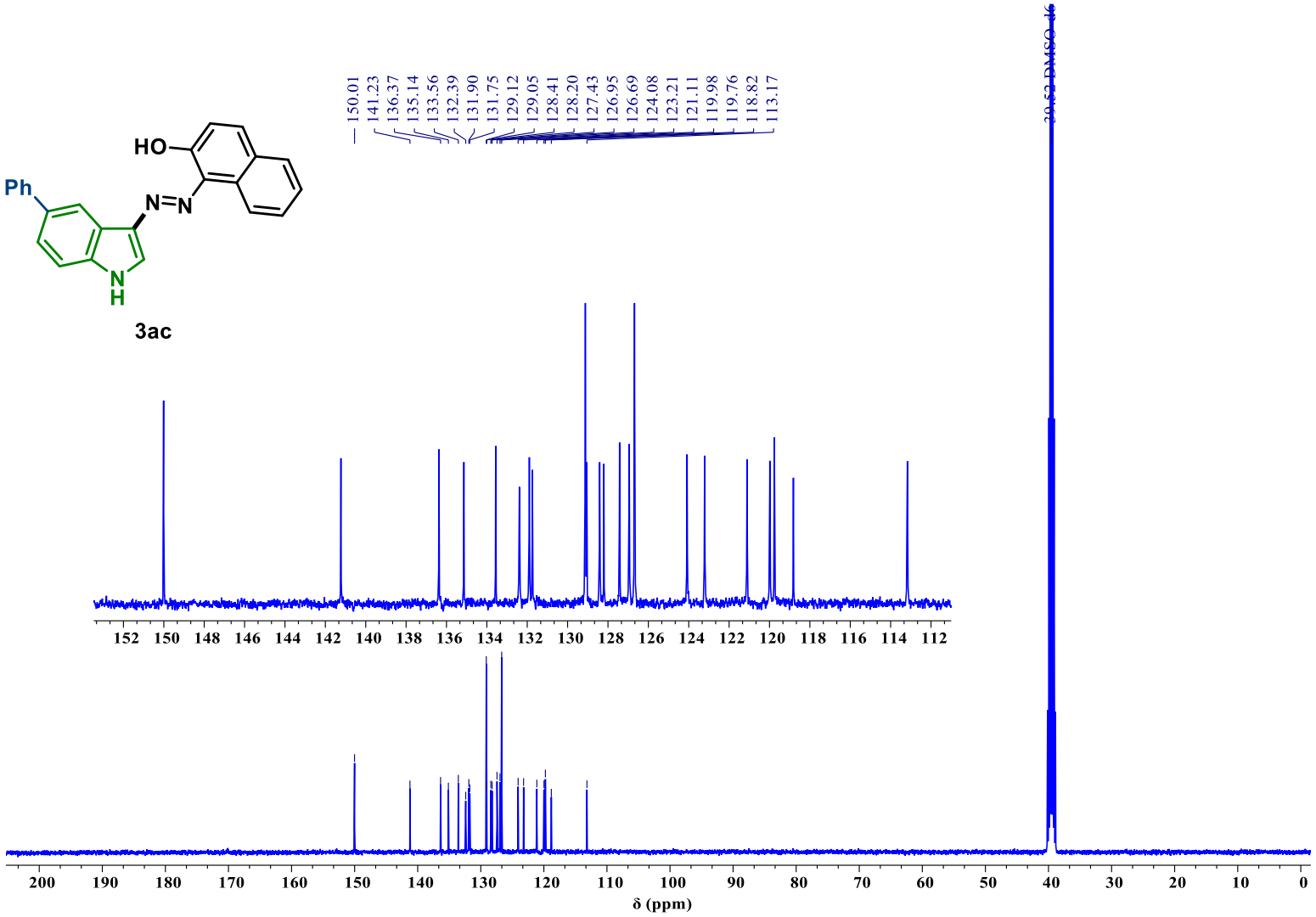
ATR-IR spectrum of (*E*)-1-((5-bromo-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ab).



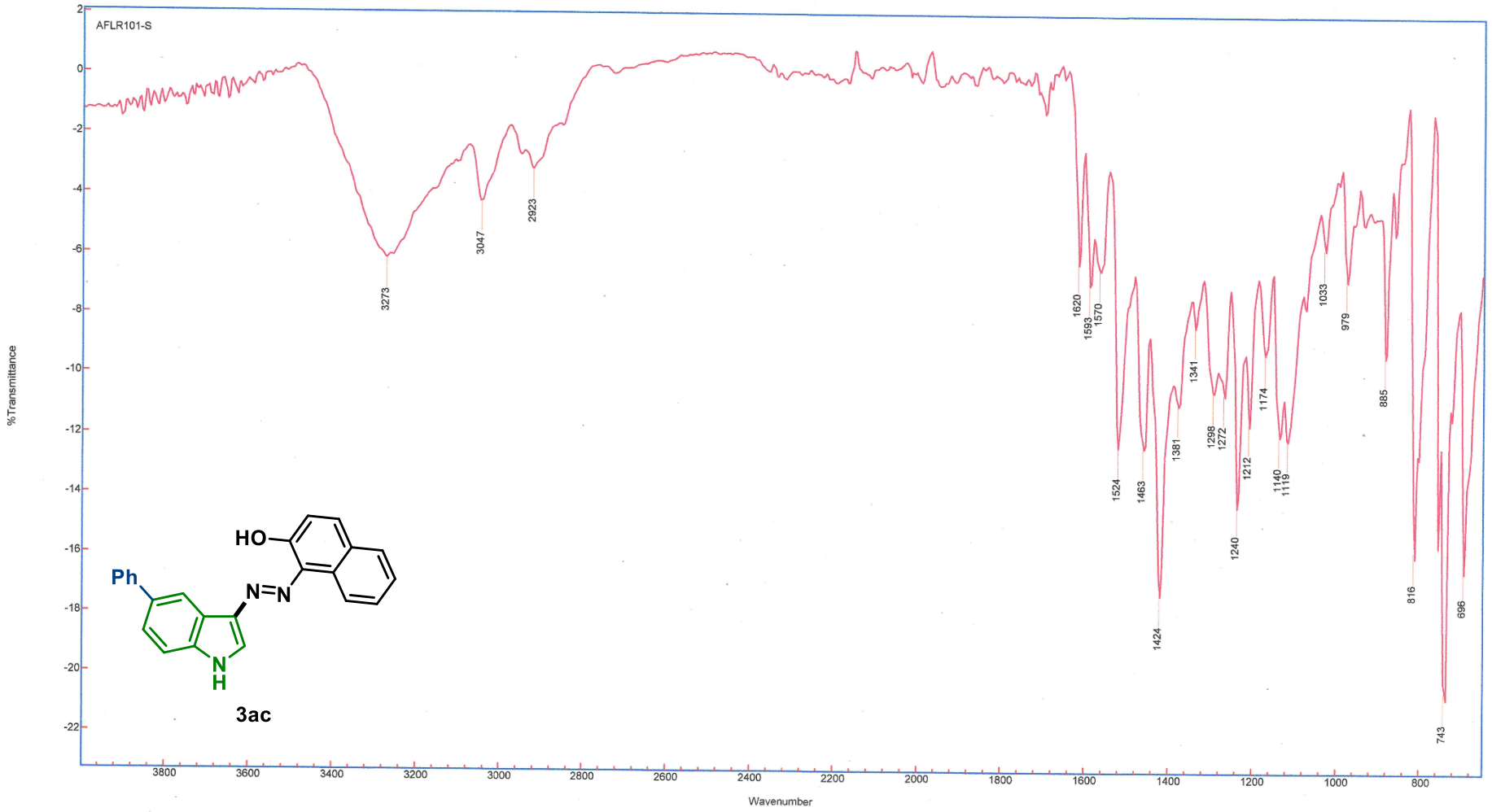
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-phenyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ac).



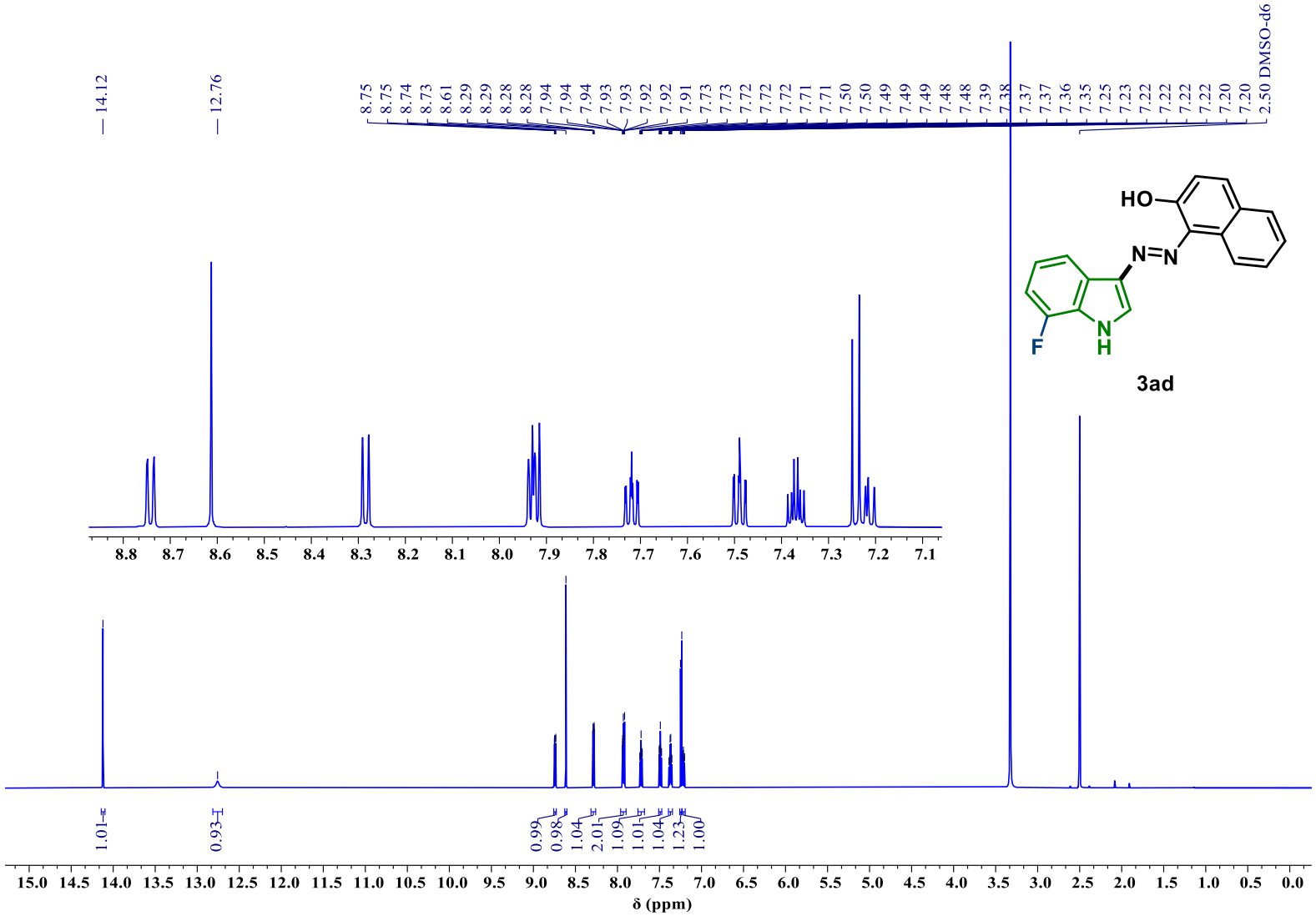
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-phenyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ac).



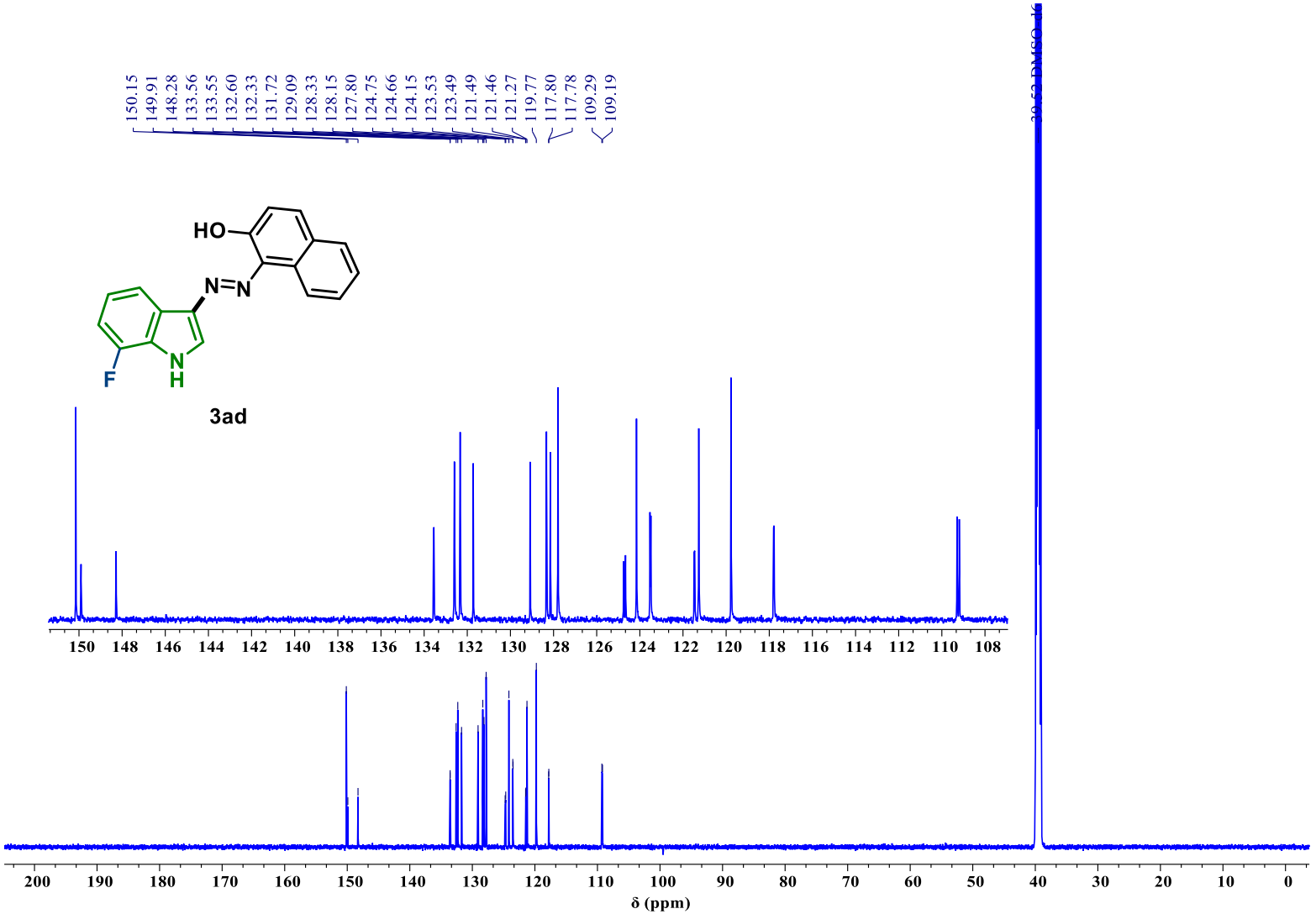
ATR-IR spectrum of (*E*)-1-((5-phenyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ac).



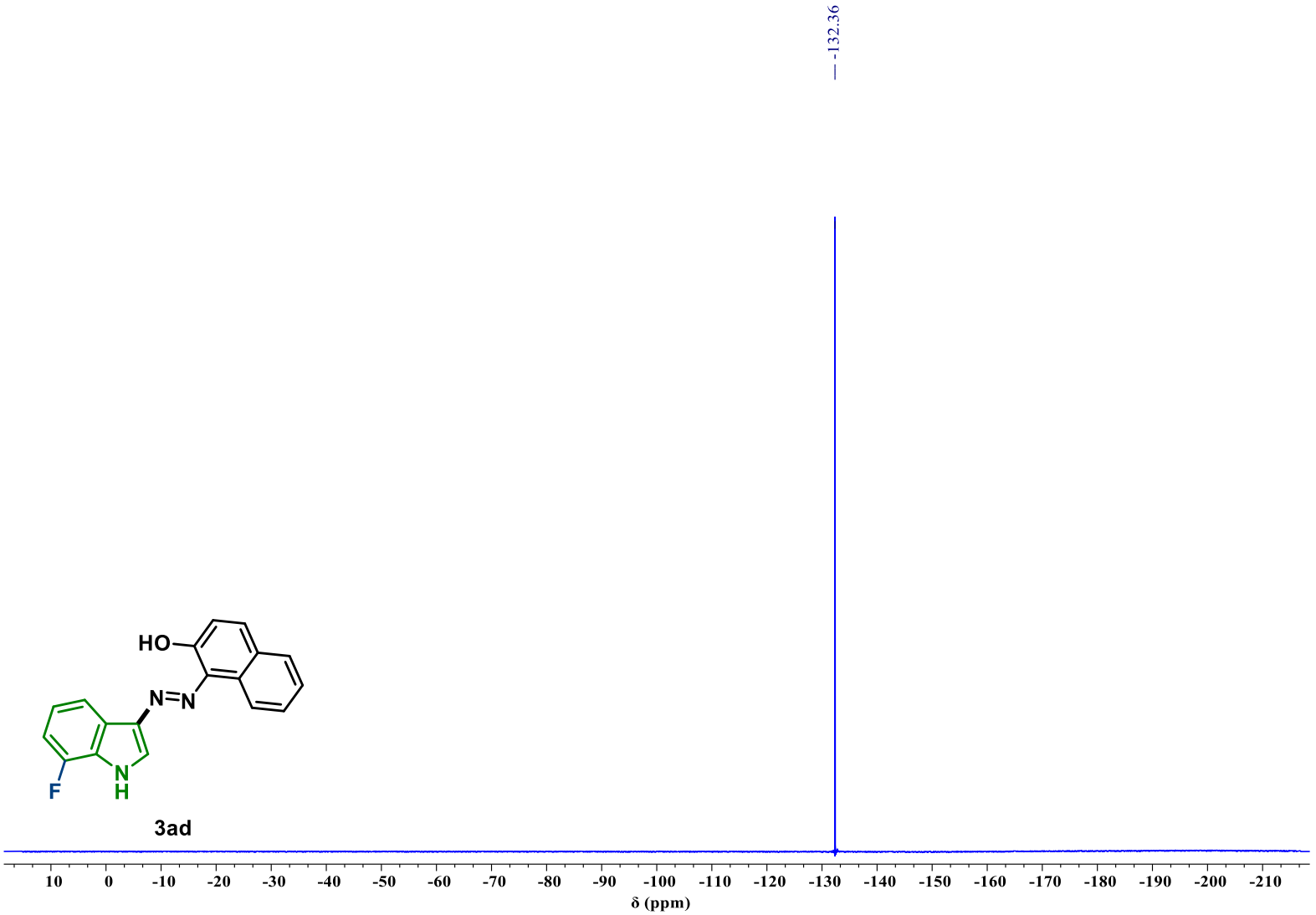
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*E*)-1-((7-fluoro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ad).



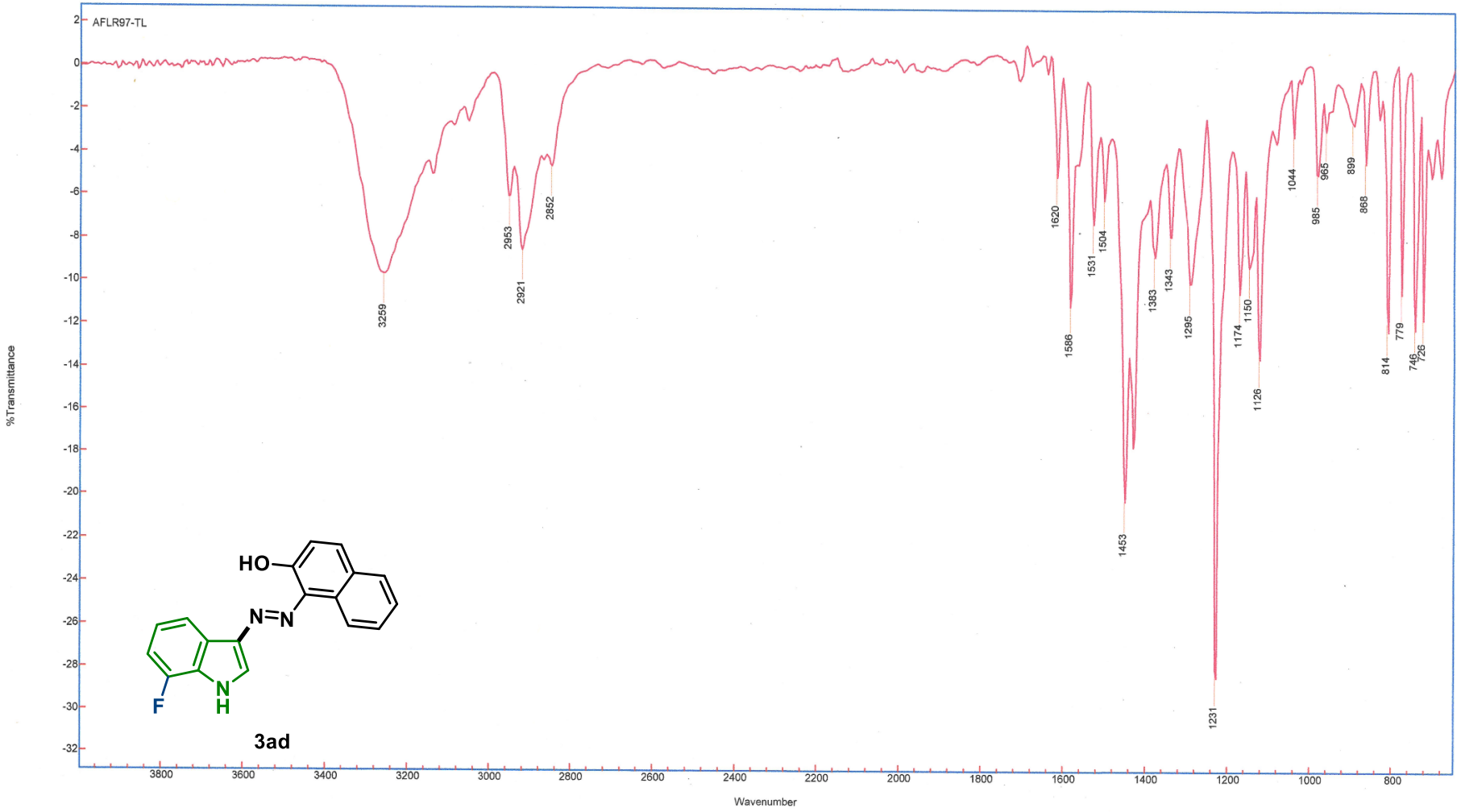
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of (*E*)-1-((7-fluoro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ad).



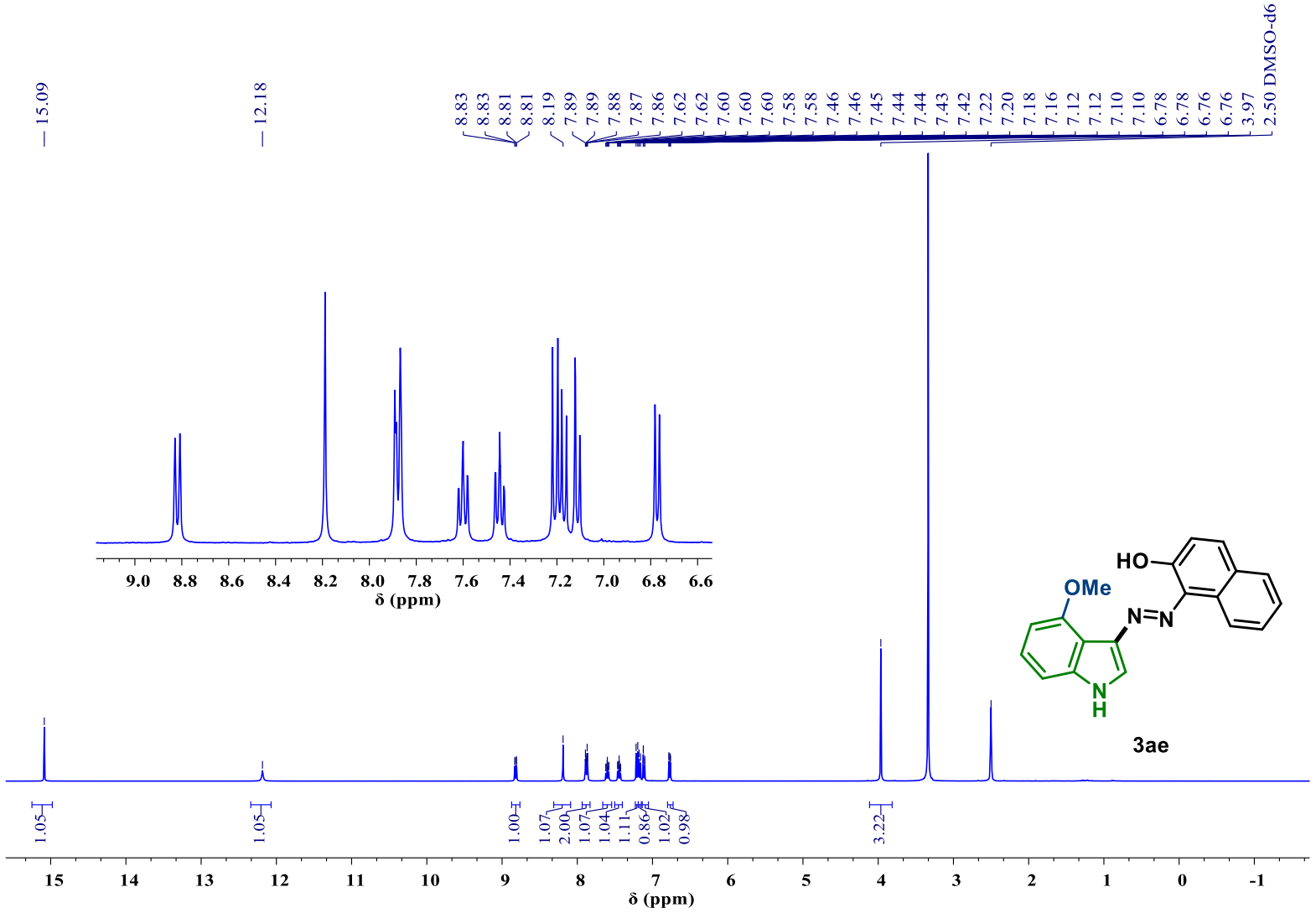
^{19}F {^{1}H} NMR (376.5 MHz, DMSO-d_6) spectrum of (*E*)-1-((7-fluoro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ad).



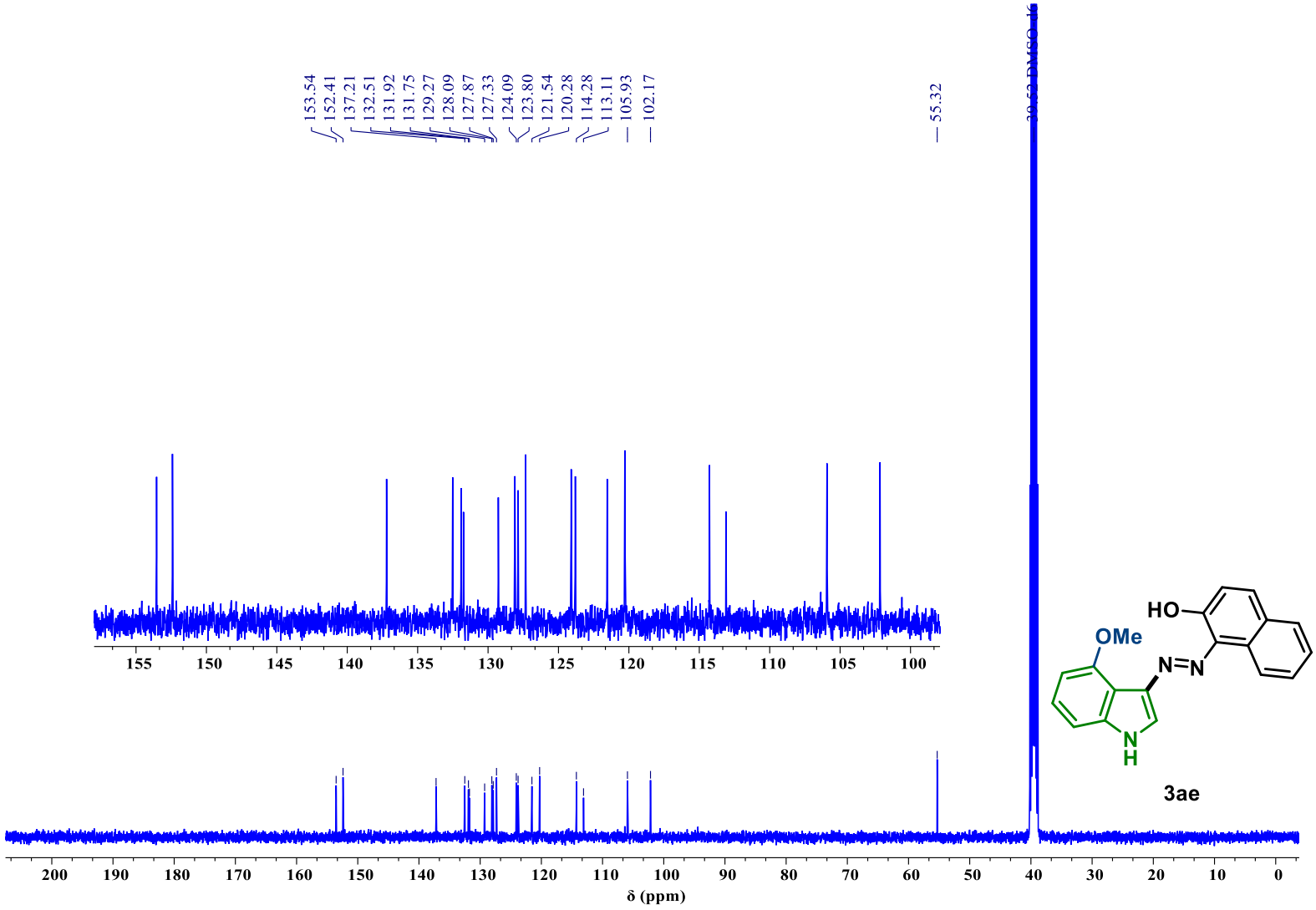
ATR-IR spectrum of (*E*)-1-((7-fluoro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ad).



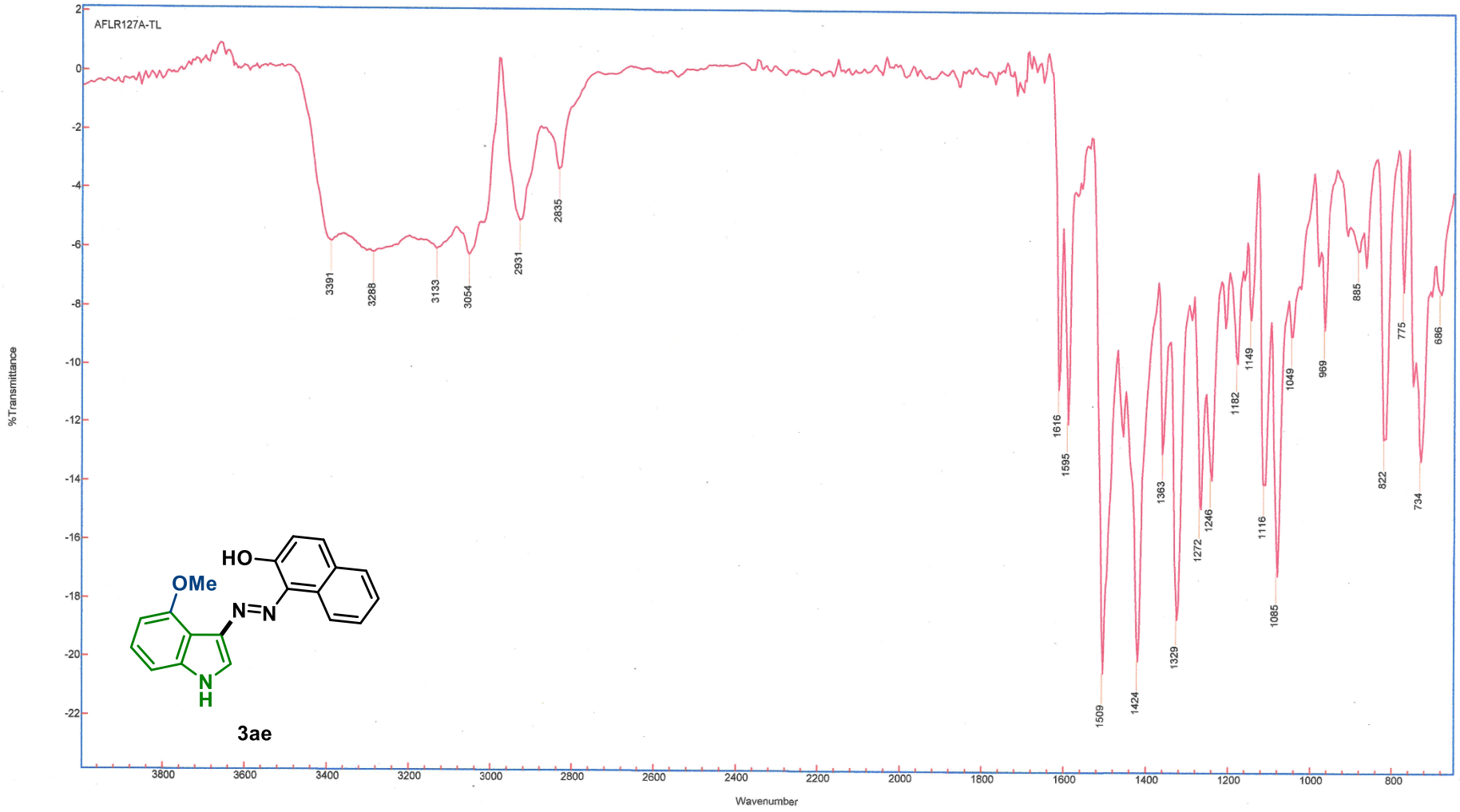
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((4-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ae).



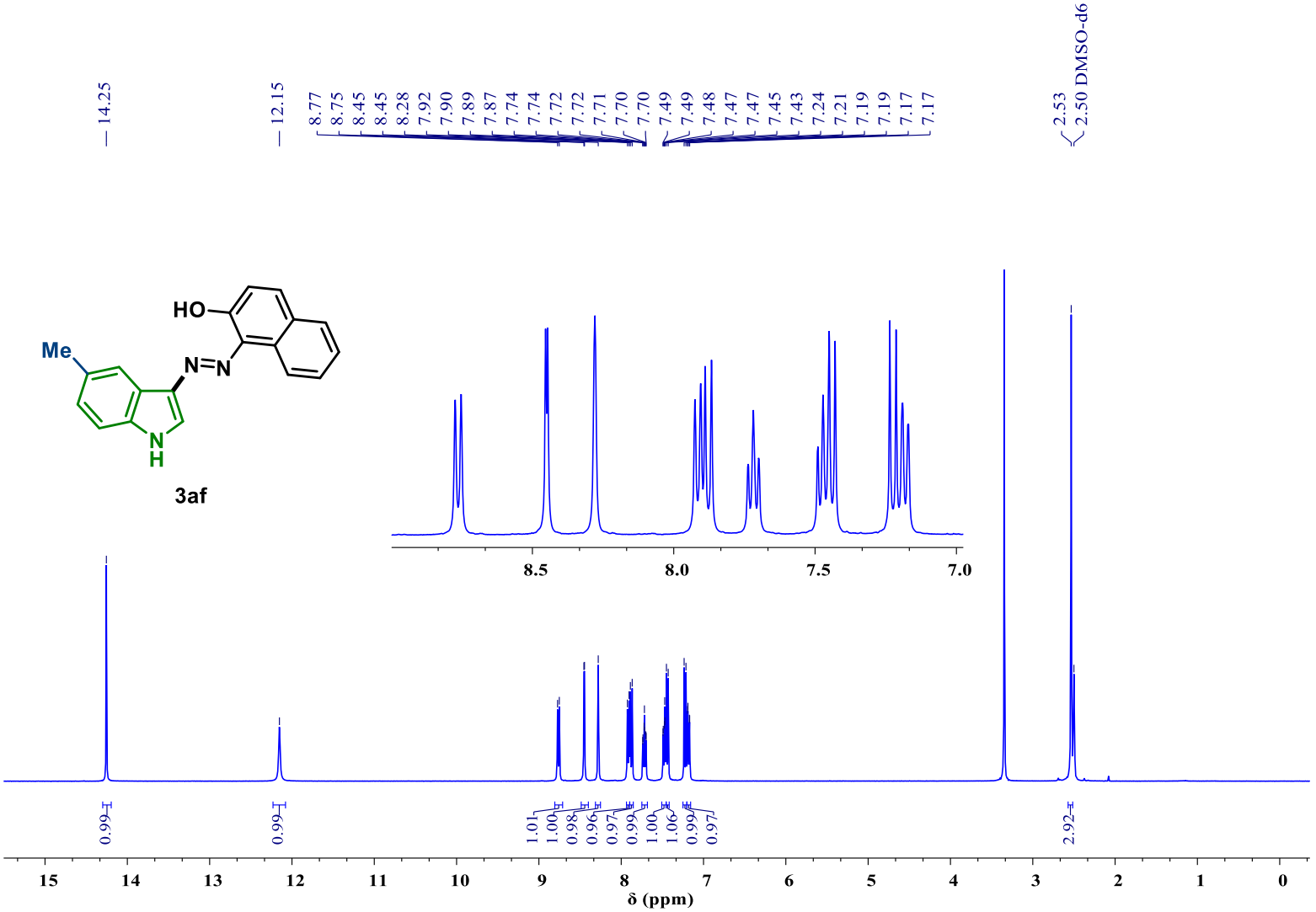
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((4-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ae).



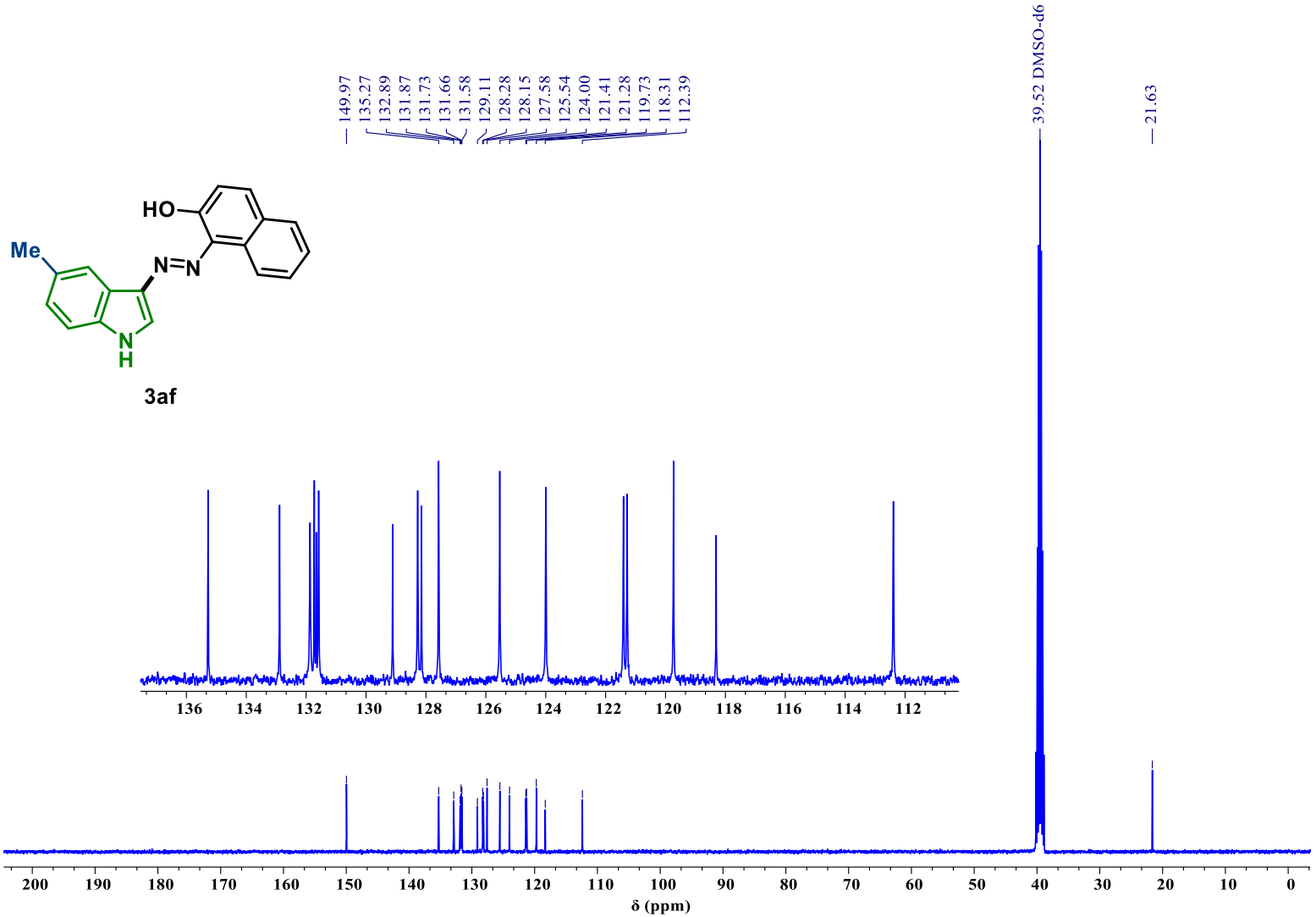
ATR-IR spectrum of (*E*)-1-((4-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ae).



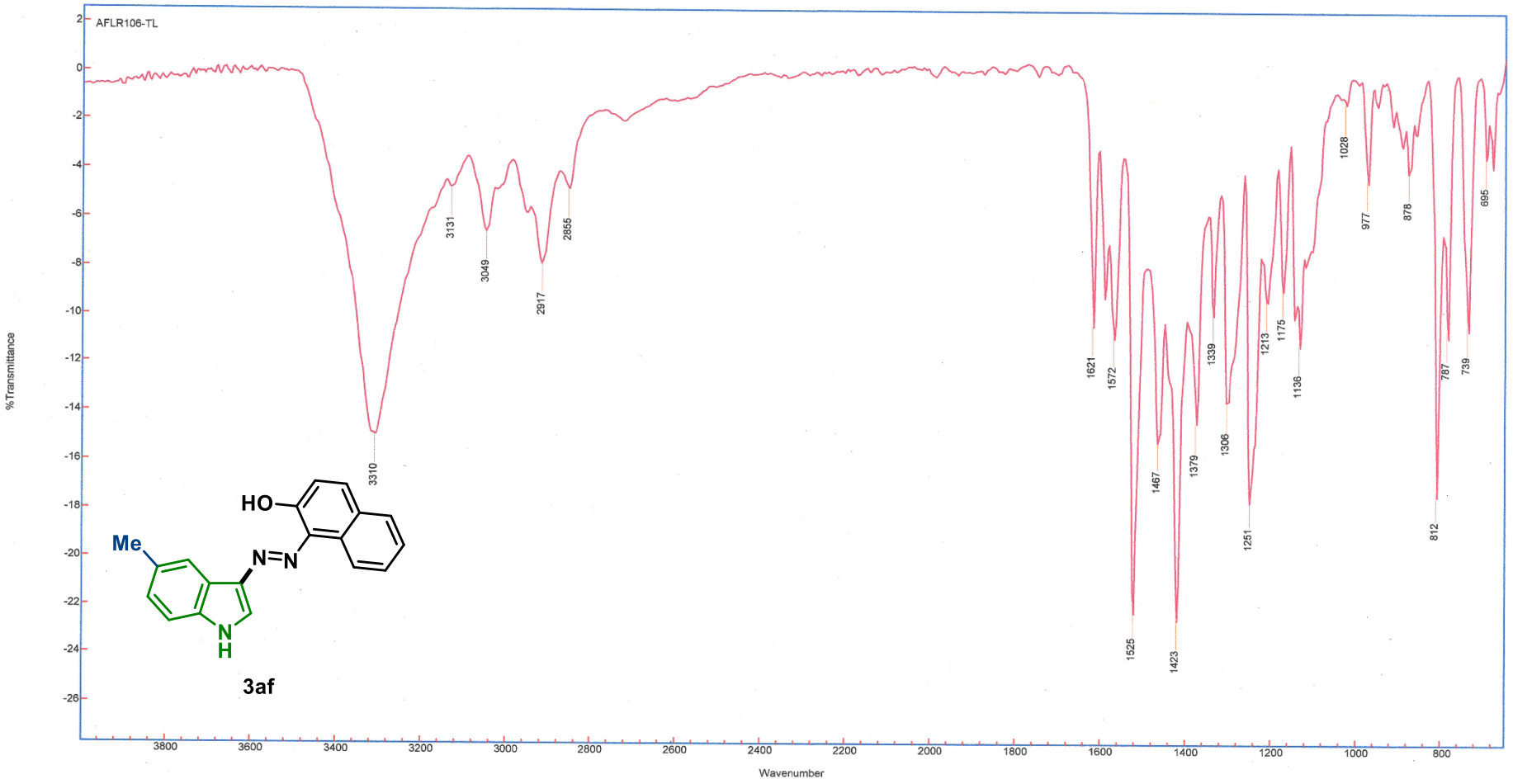
[1]H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3af).



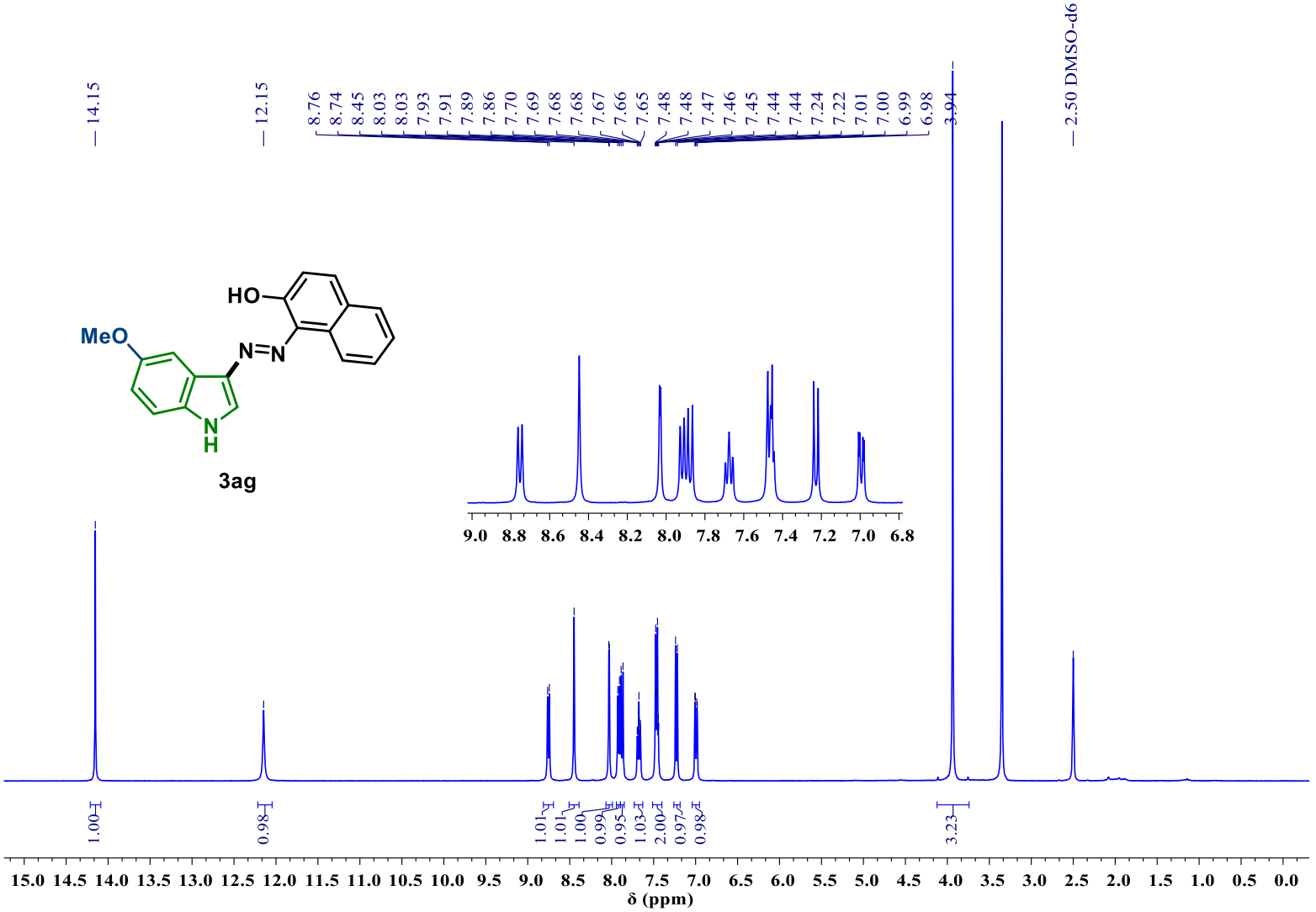
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3af).



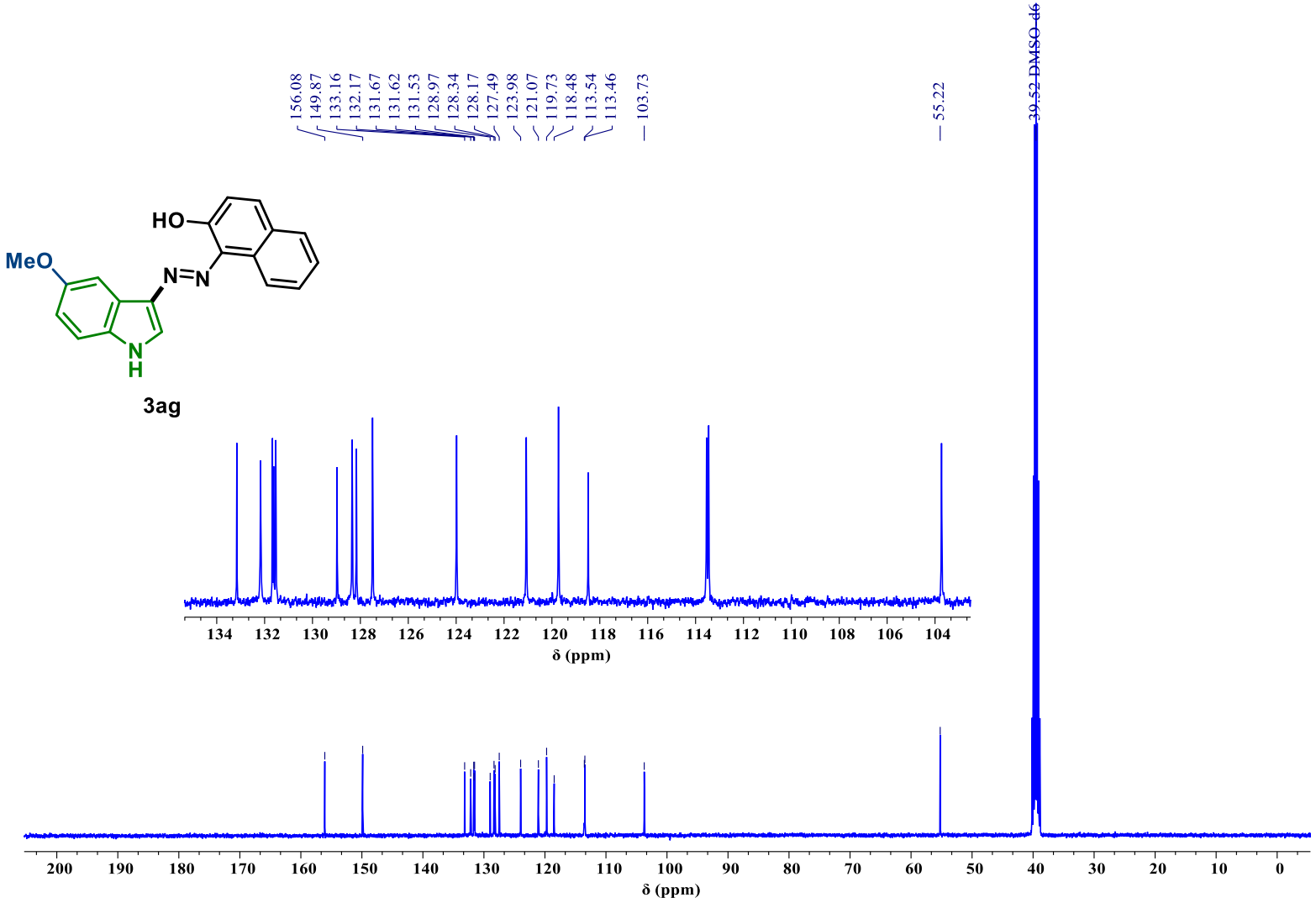
ATR-IR spectrum of (*E*)-1-((5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3af).



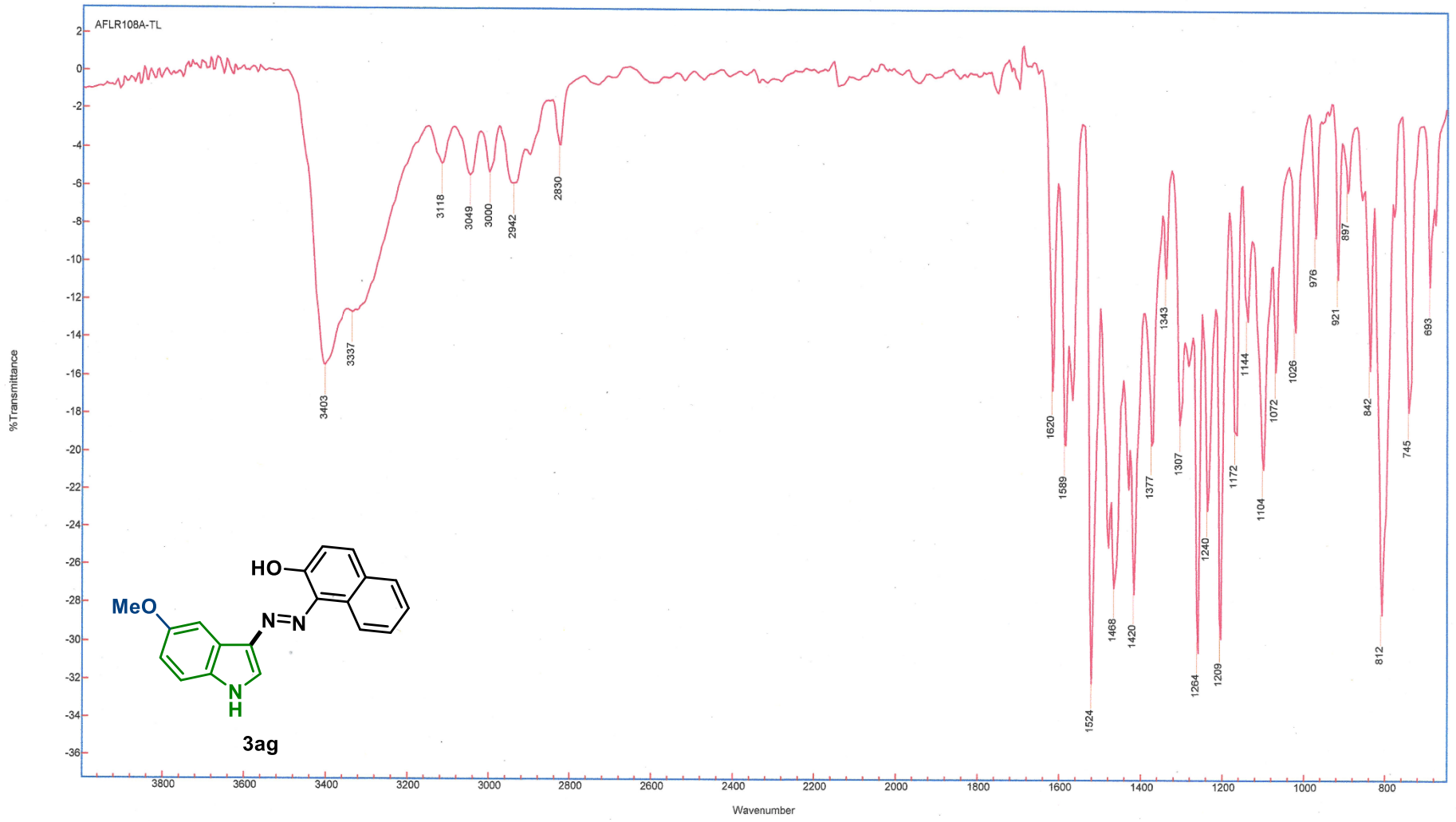
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ag).



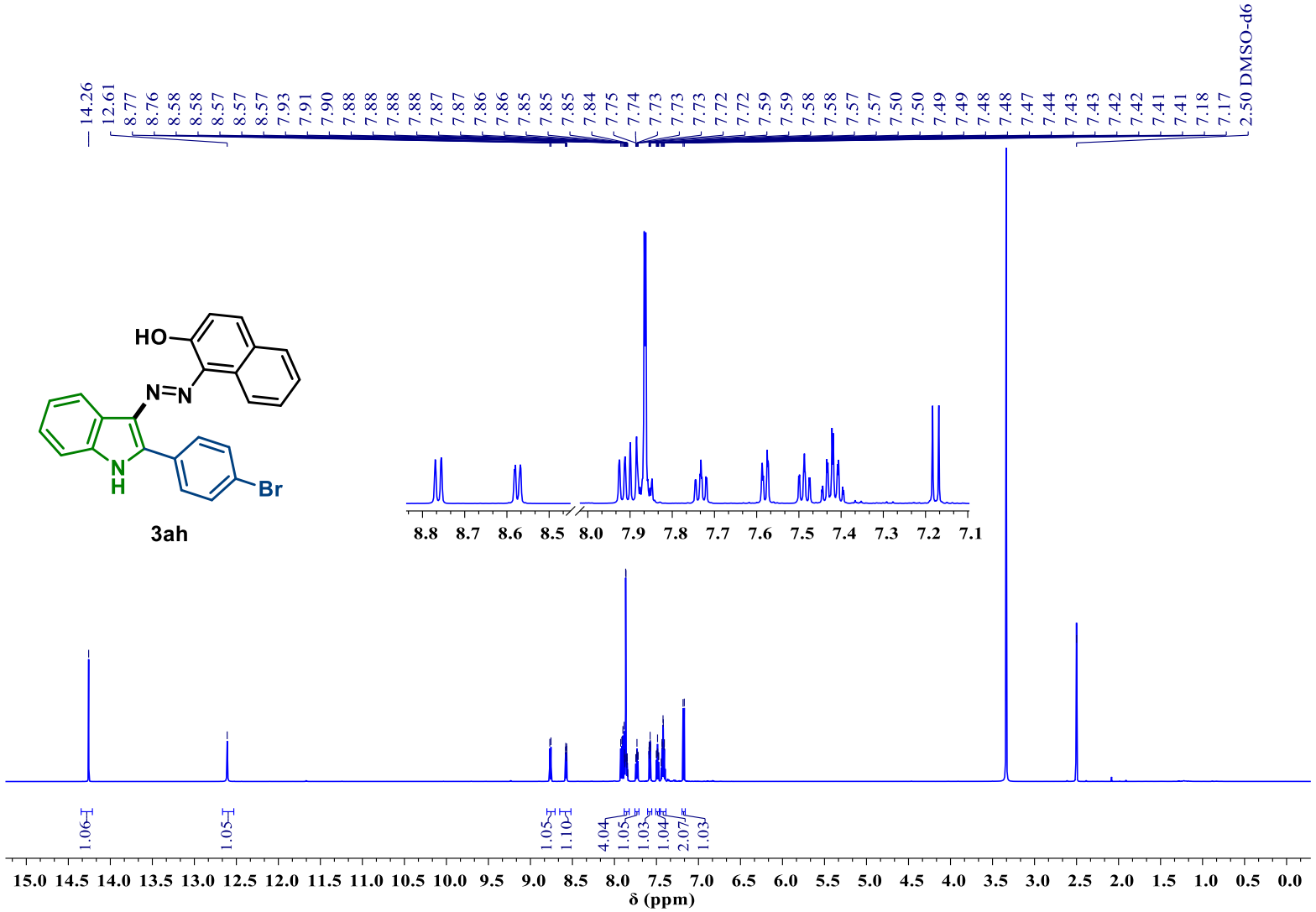
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ag).



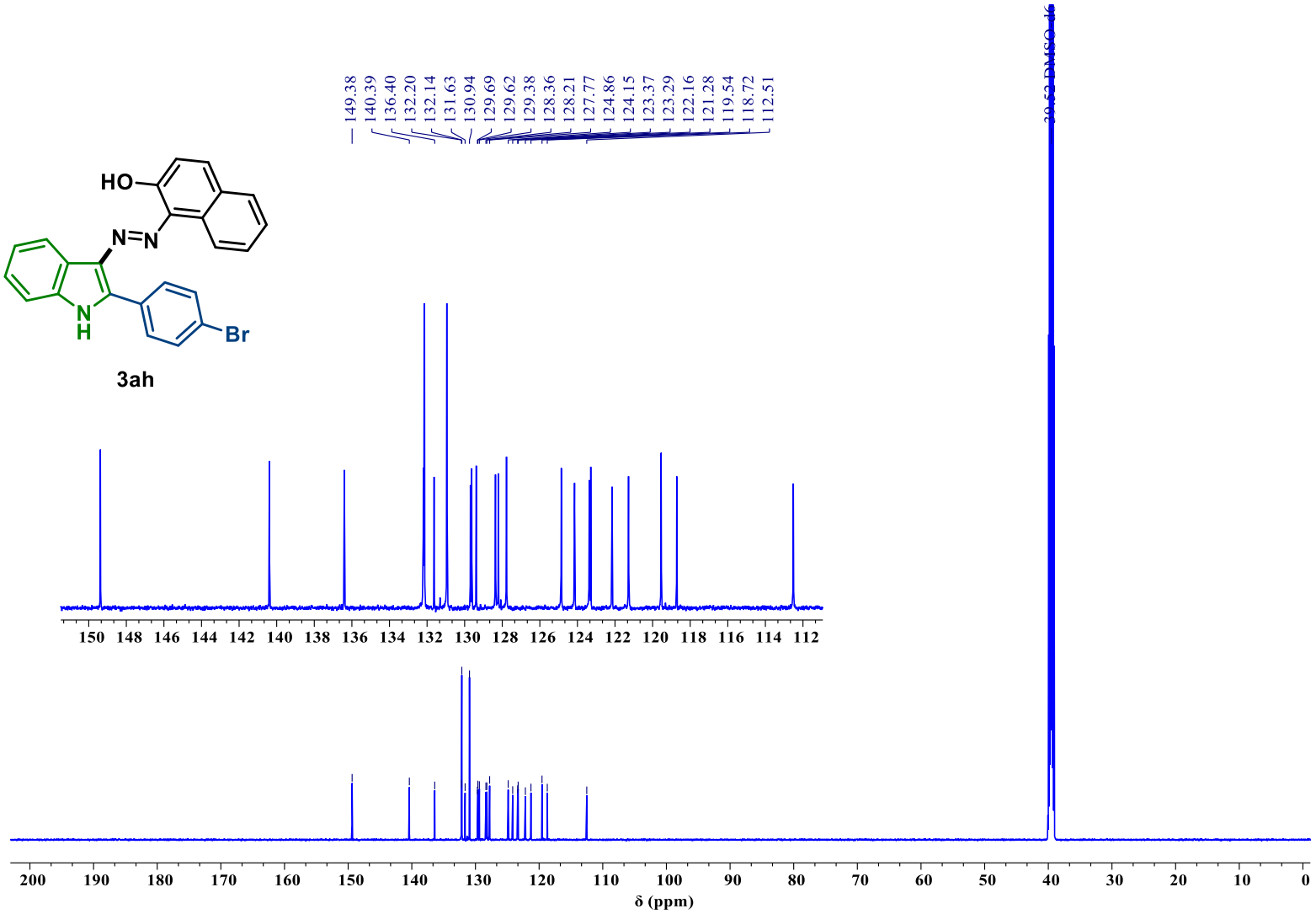
ATR-IR spectrum of (*E*)-1-((5-methoxy-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ag).



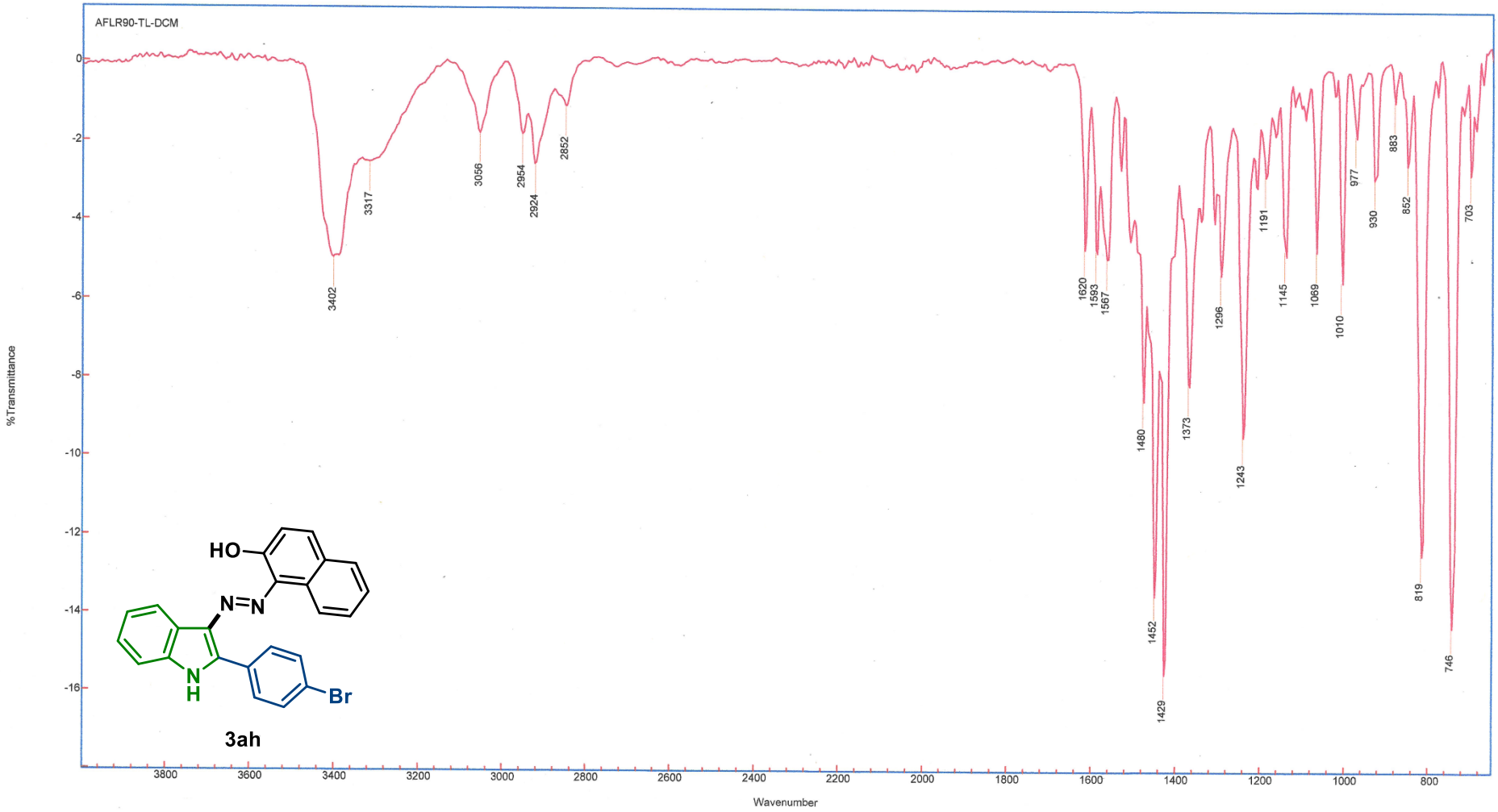
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-bromophenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ah).



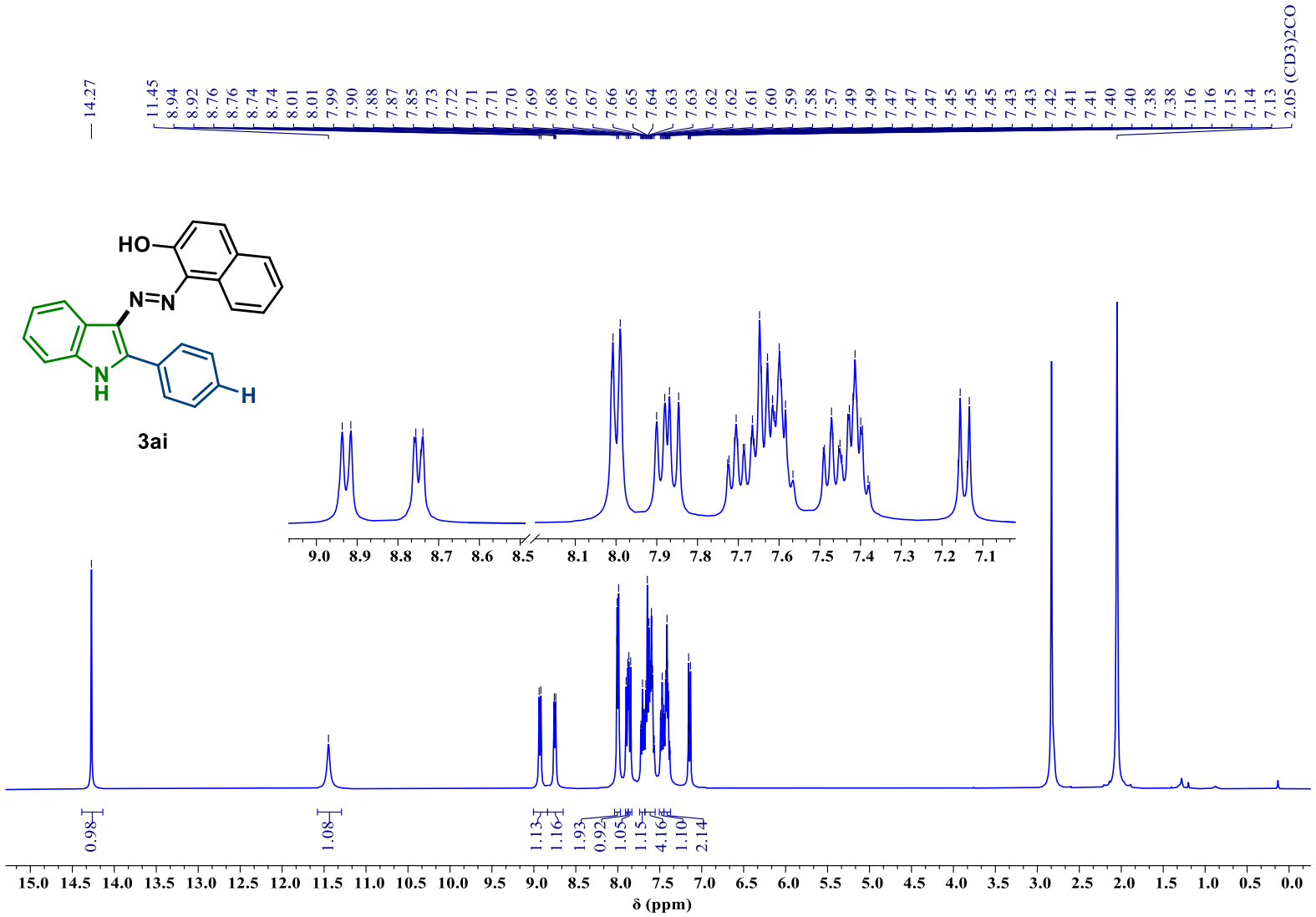
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-bromophenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ah).



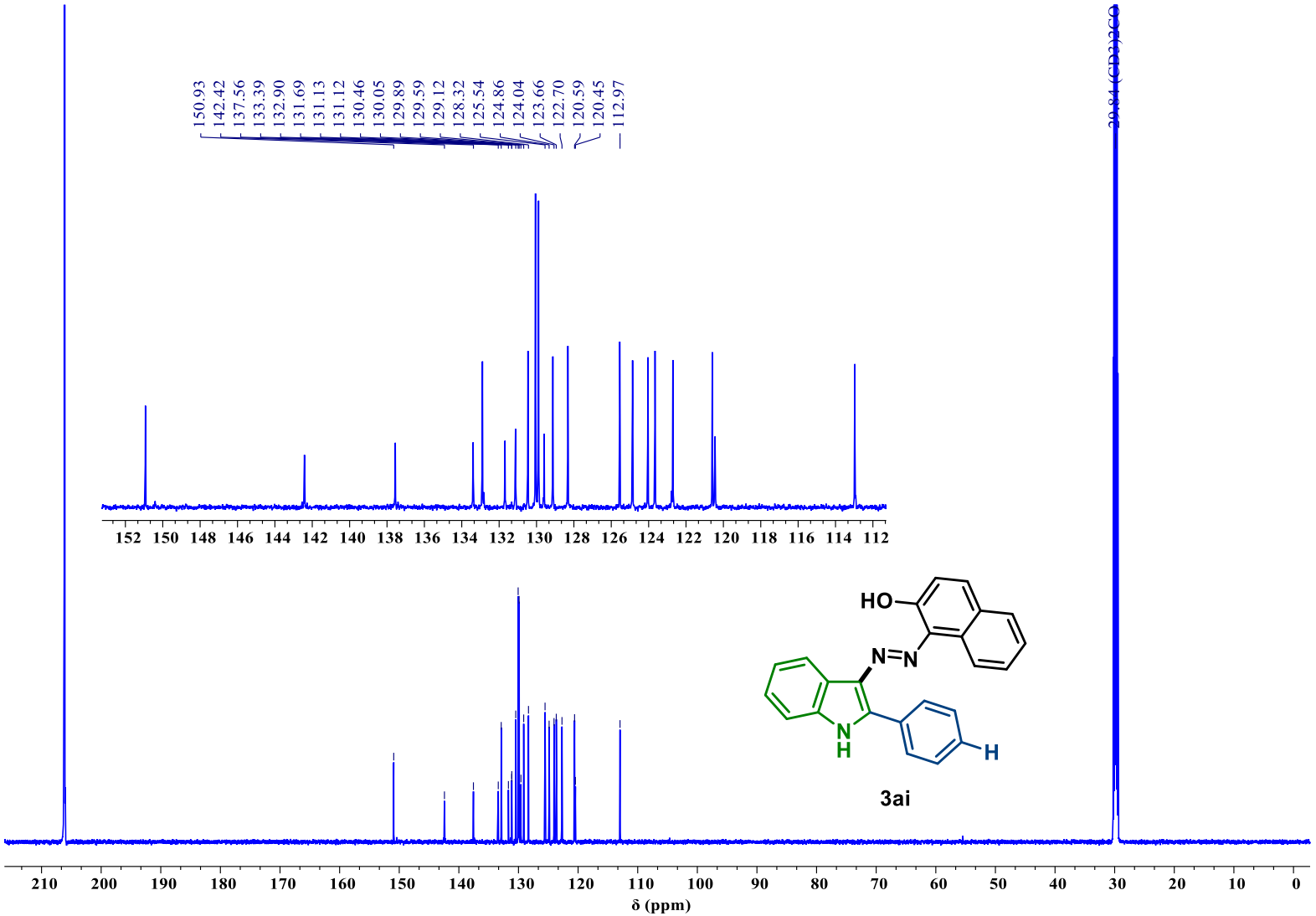
ATR-IR spectrum of (*E*)-1-((2-(4-bromophenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ah).



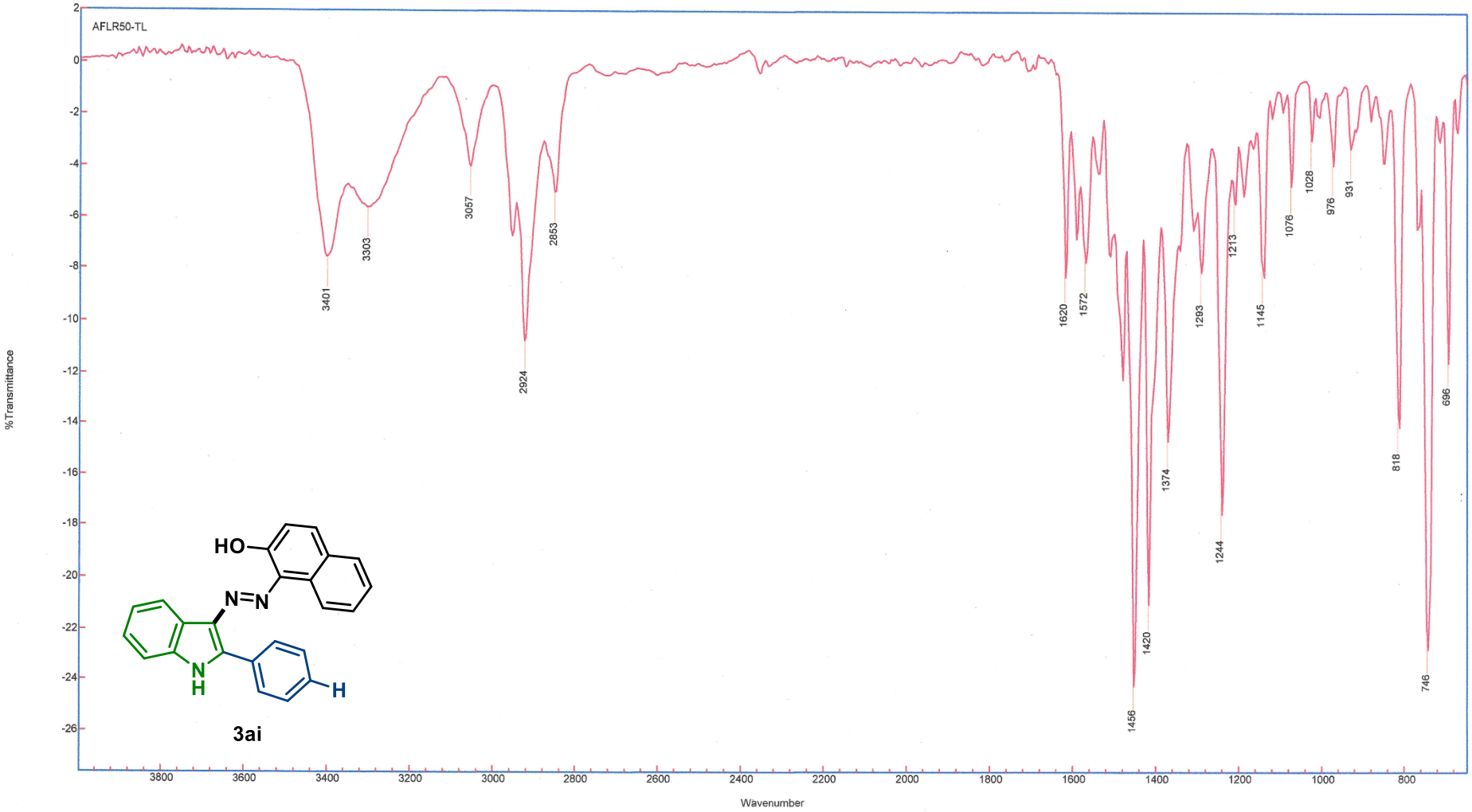
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-phenyl-*1H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ai).



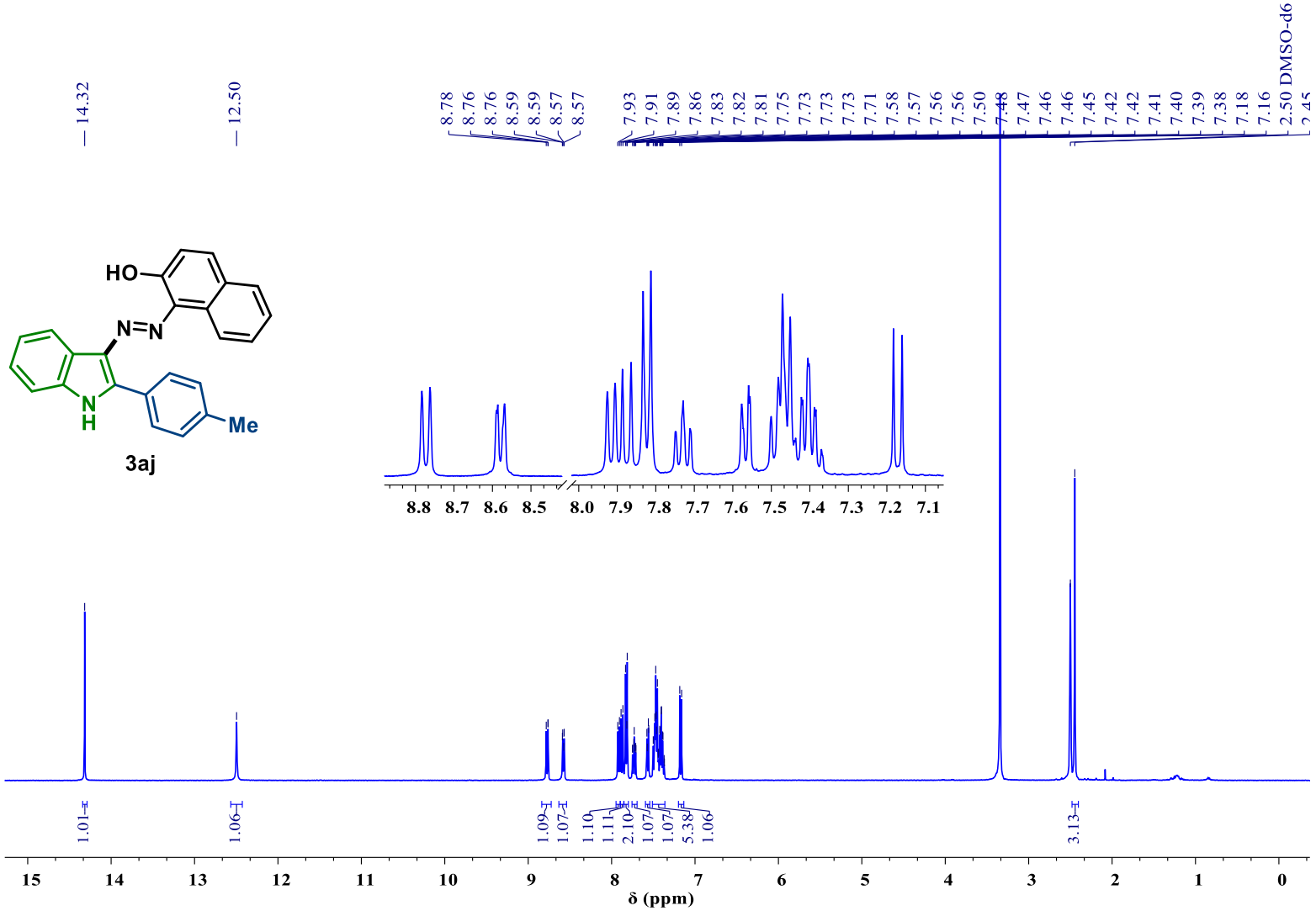
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-phenyl-*1H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ai).



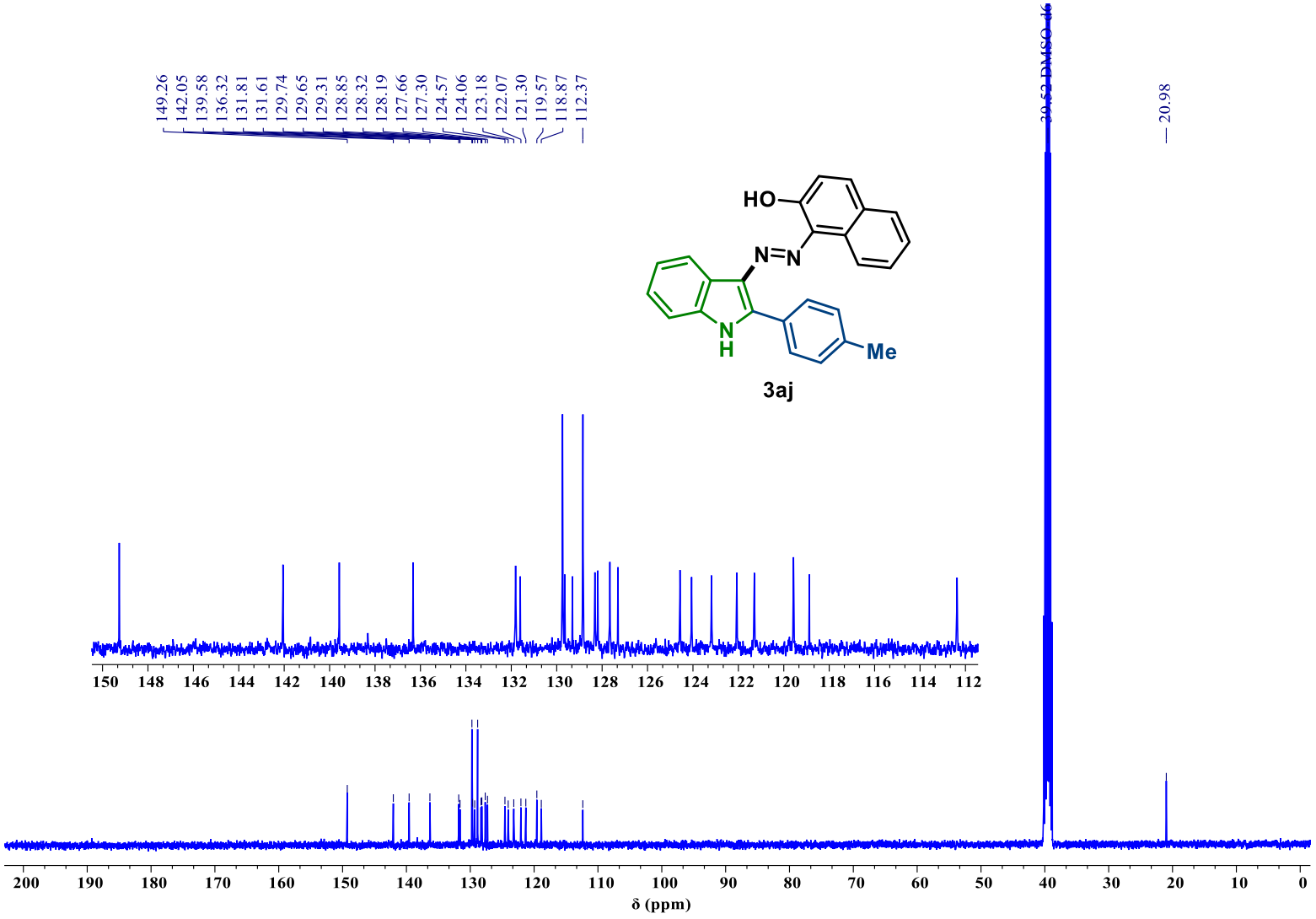
ATR-IR spectrum of (*E*)-1-((2-phenyl-*1H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ai).



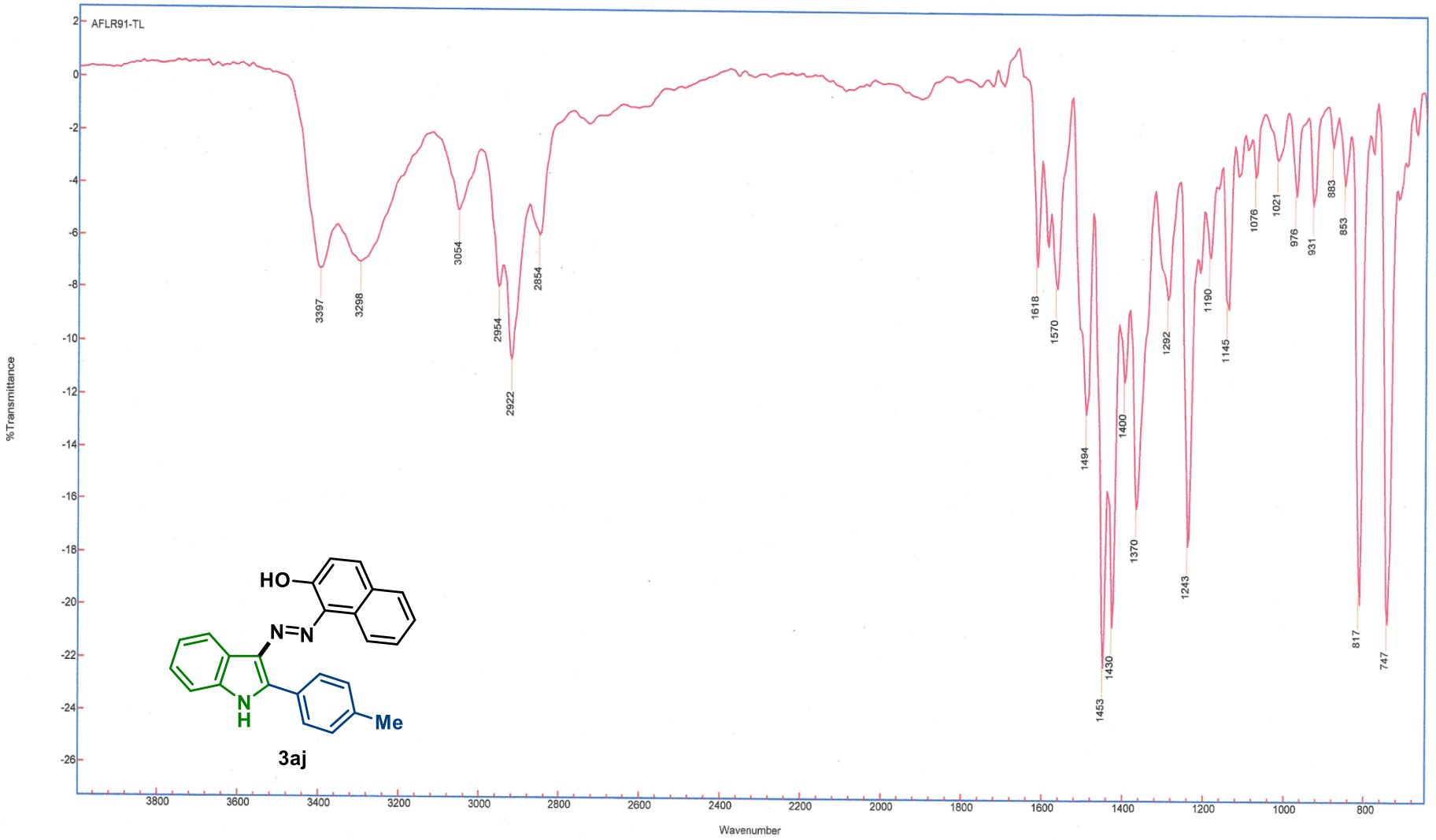
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-methylphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aj).



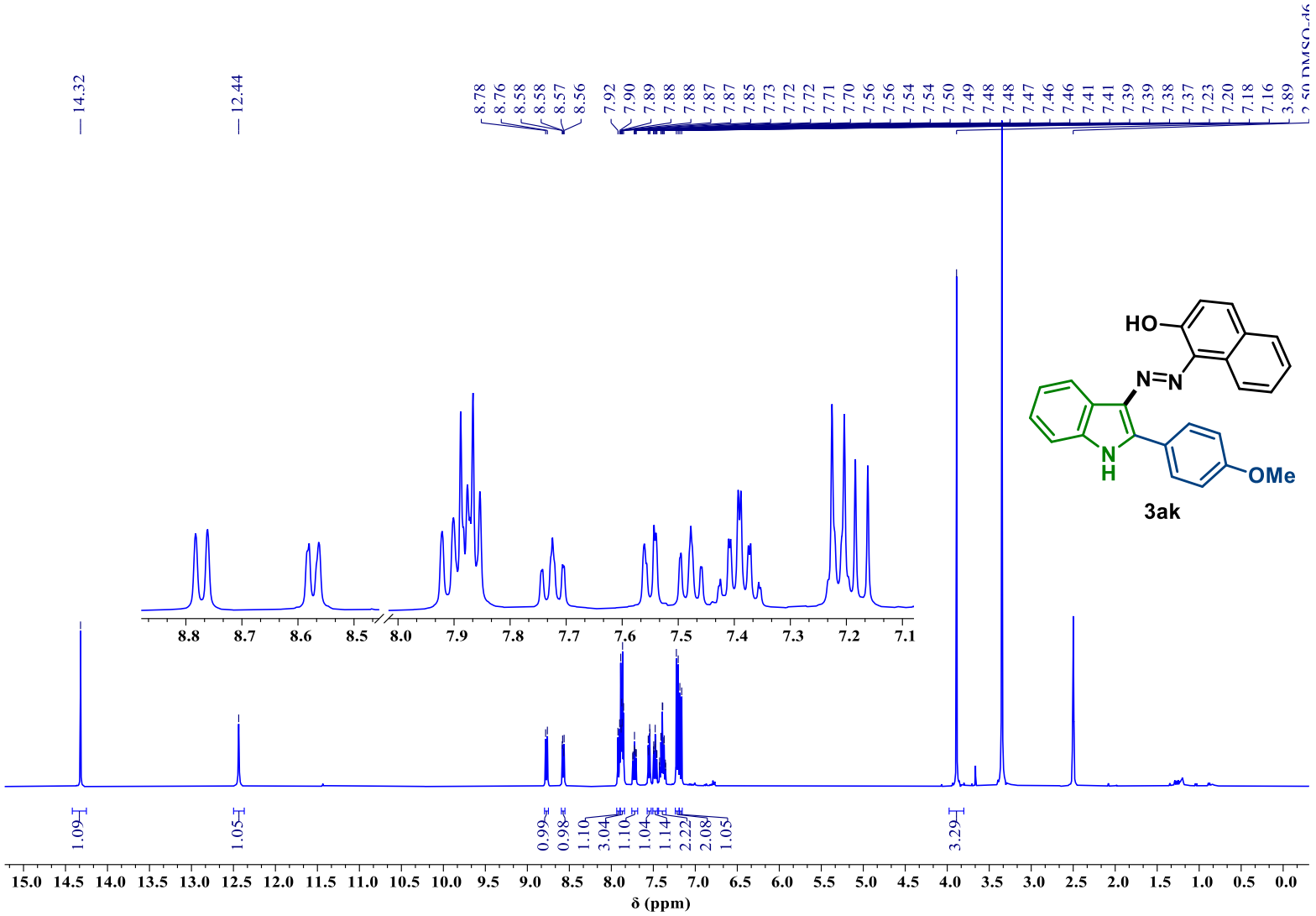
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-methylphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aj).



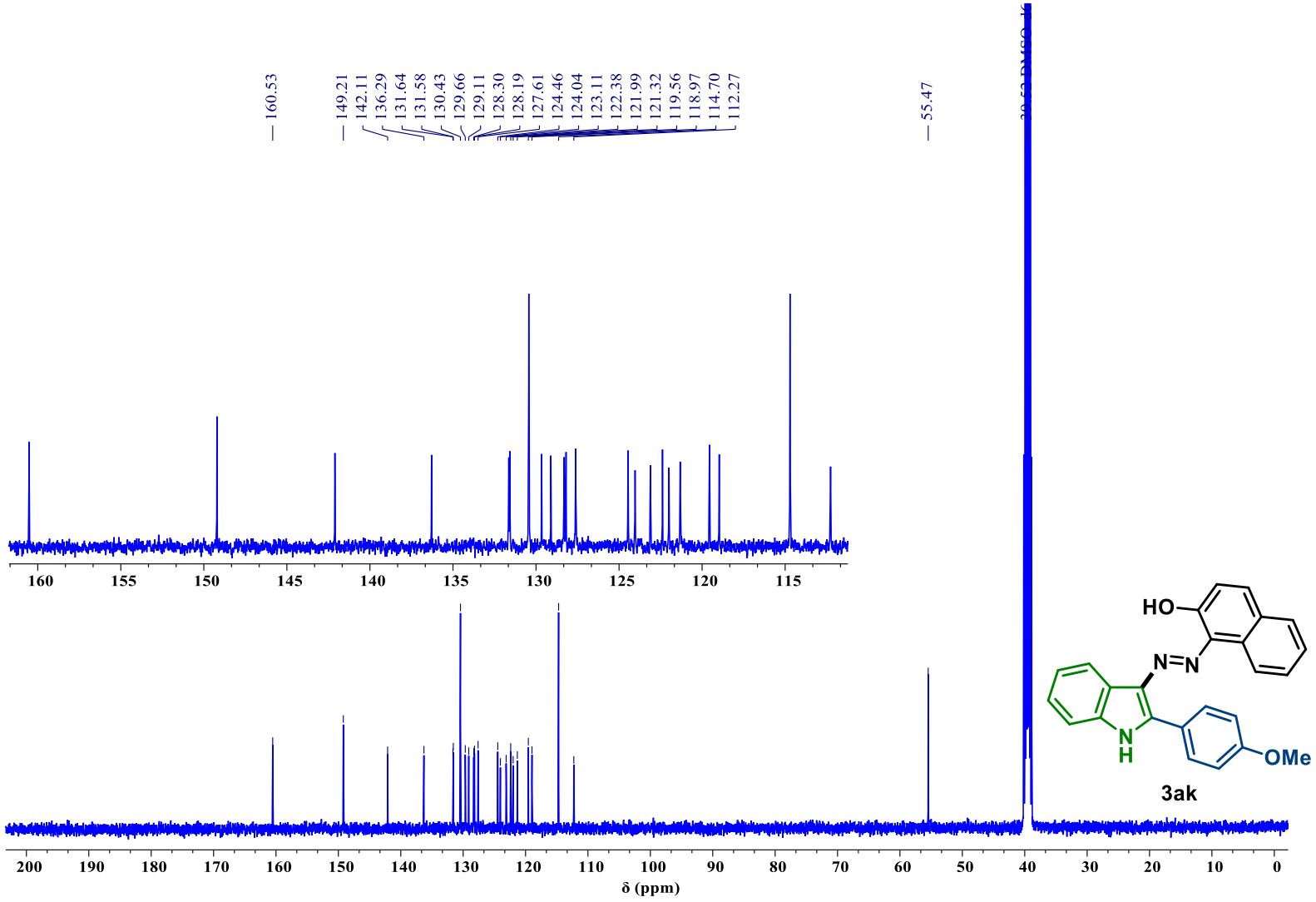
ATR-IR spectrum of (*E*)-1-((2-(4-methylphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aj).



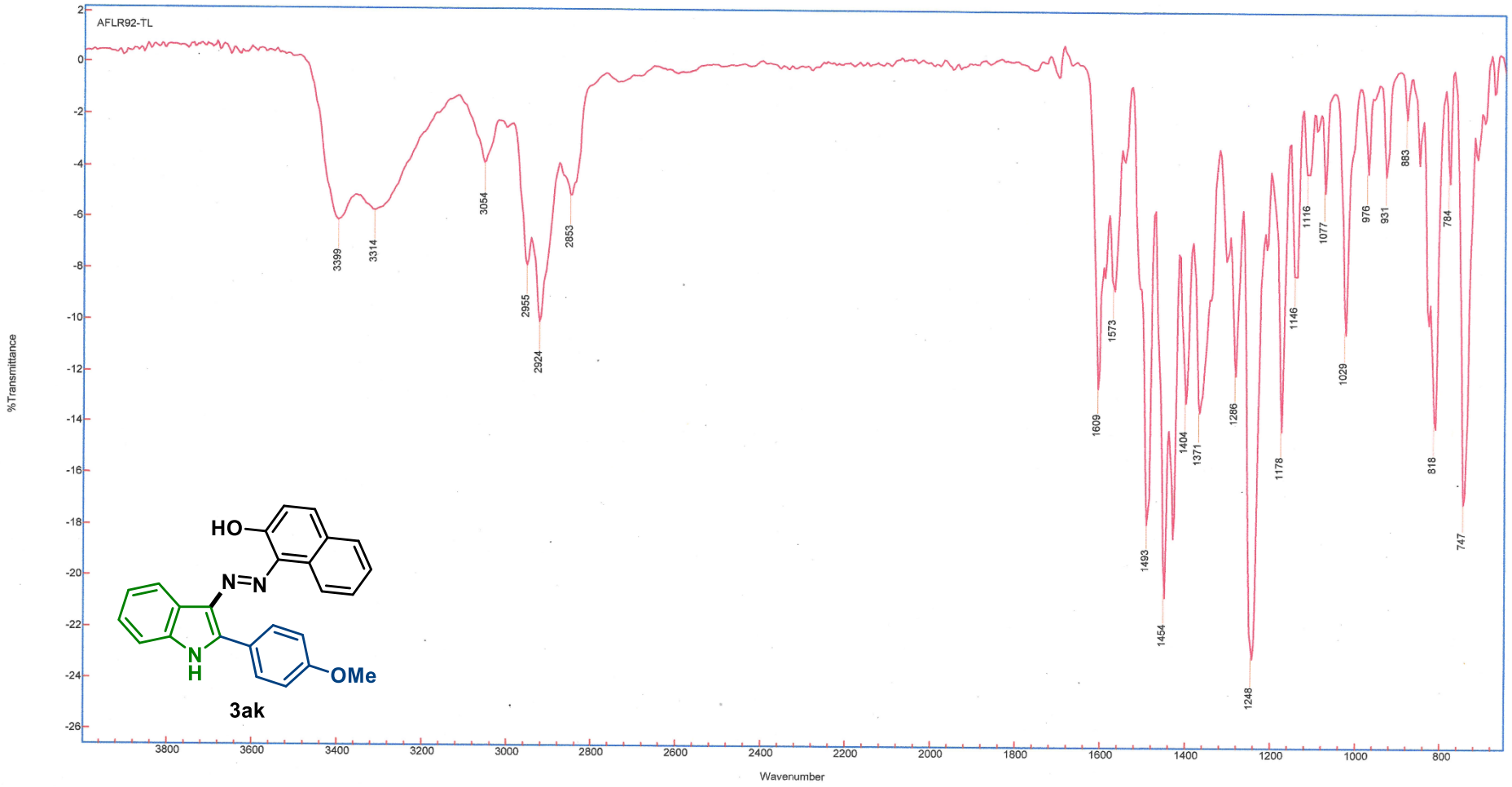
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-methoxyphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ak).



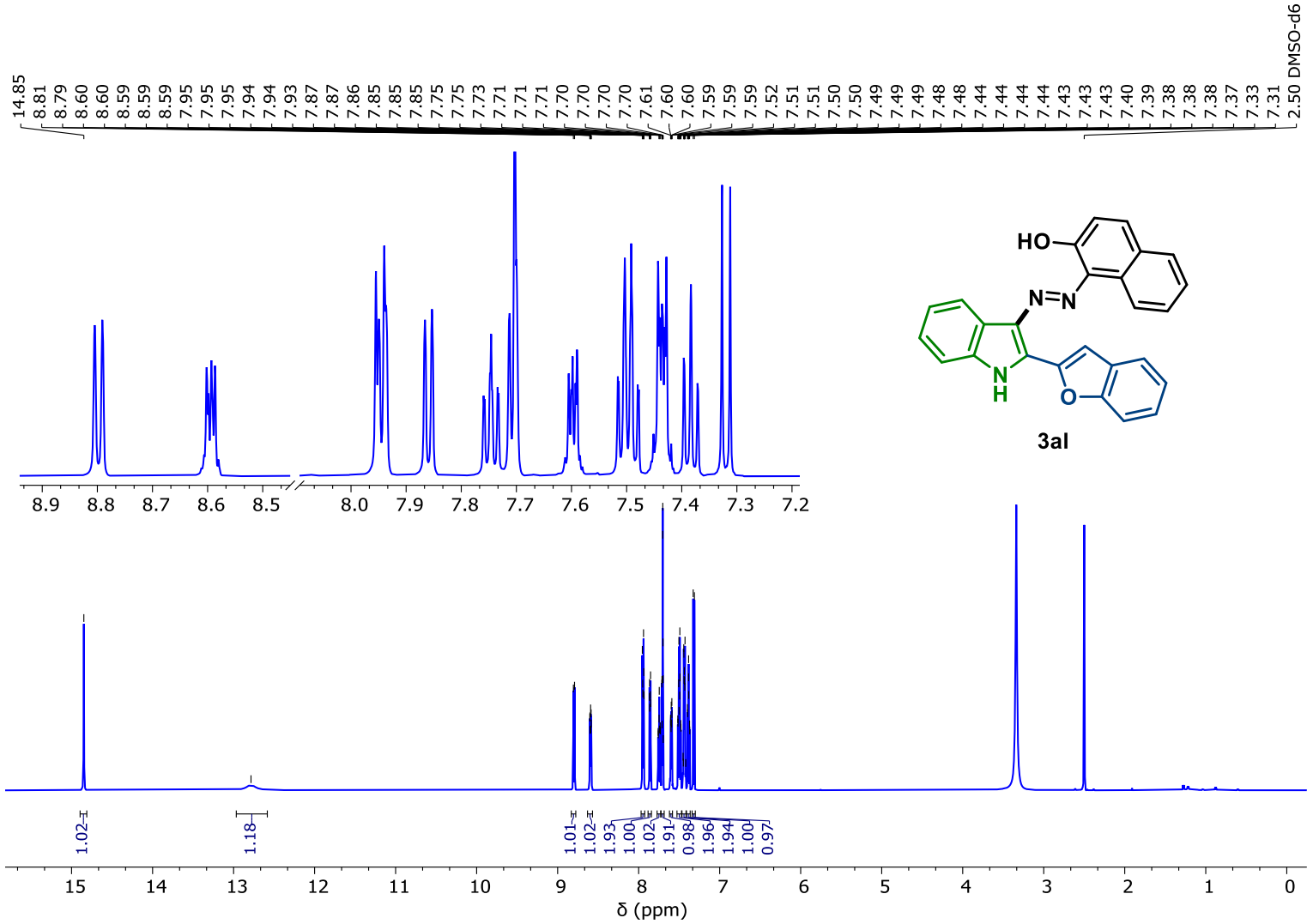
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(4-methoxyphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ak).



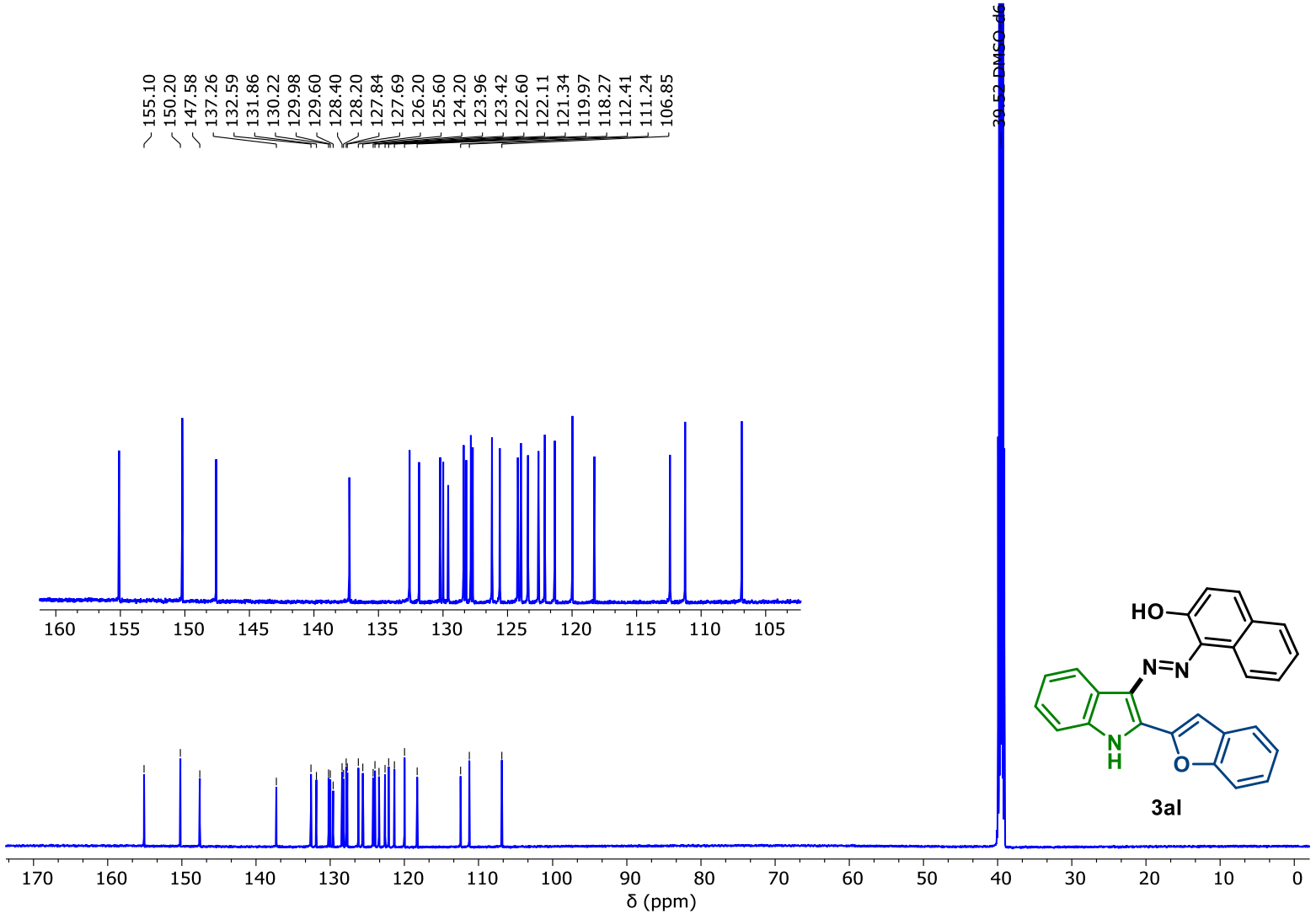
ATR-IR spectrum (*E*)-1-((2-(4-methoxyphenyl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ak).



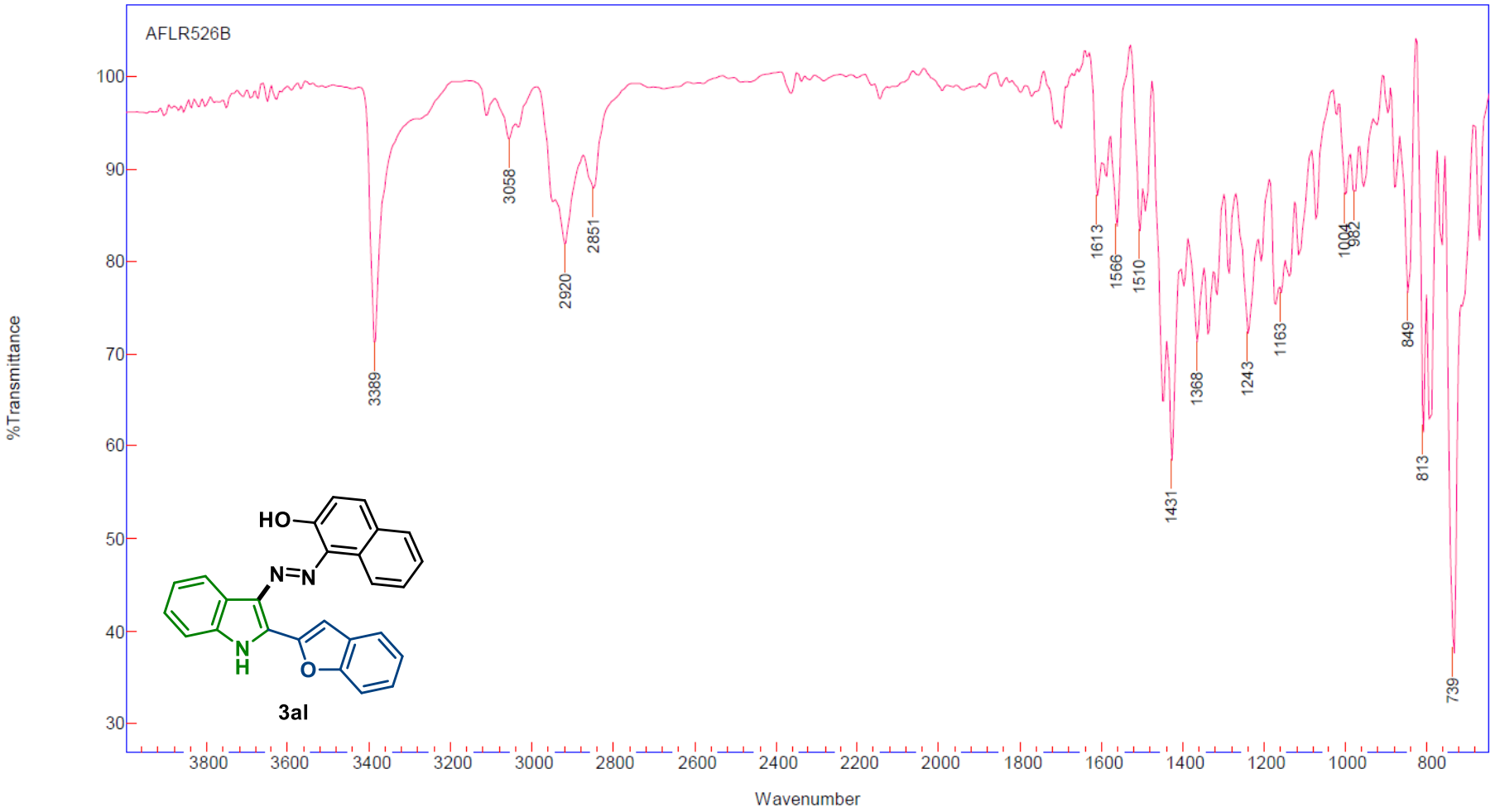
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(benzofuran-2-yl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3al).



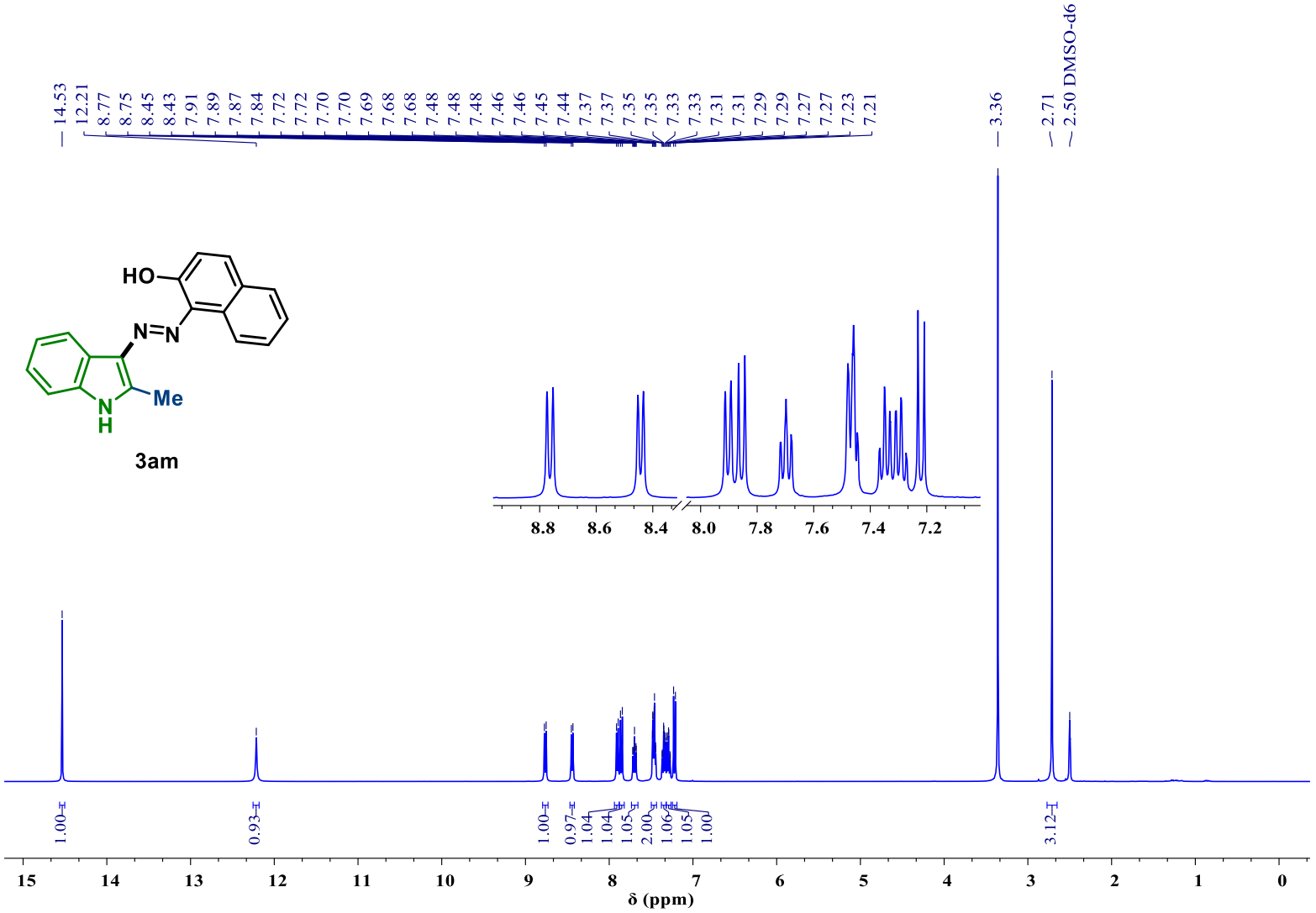
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-(benzofuran-2-yl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3al).



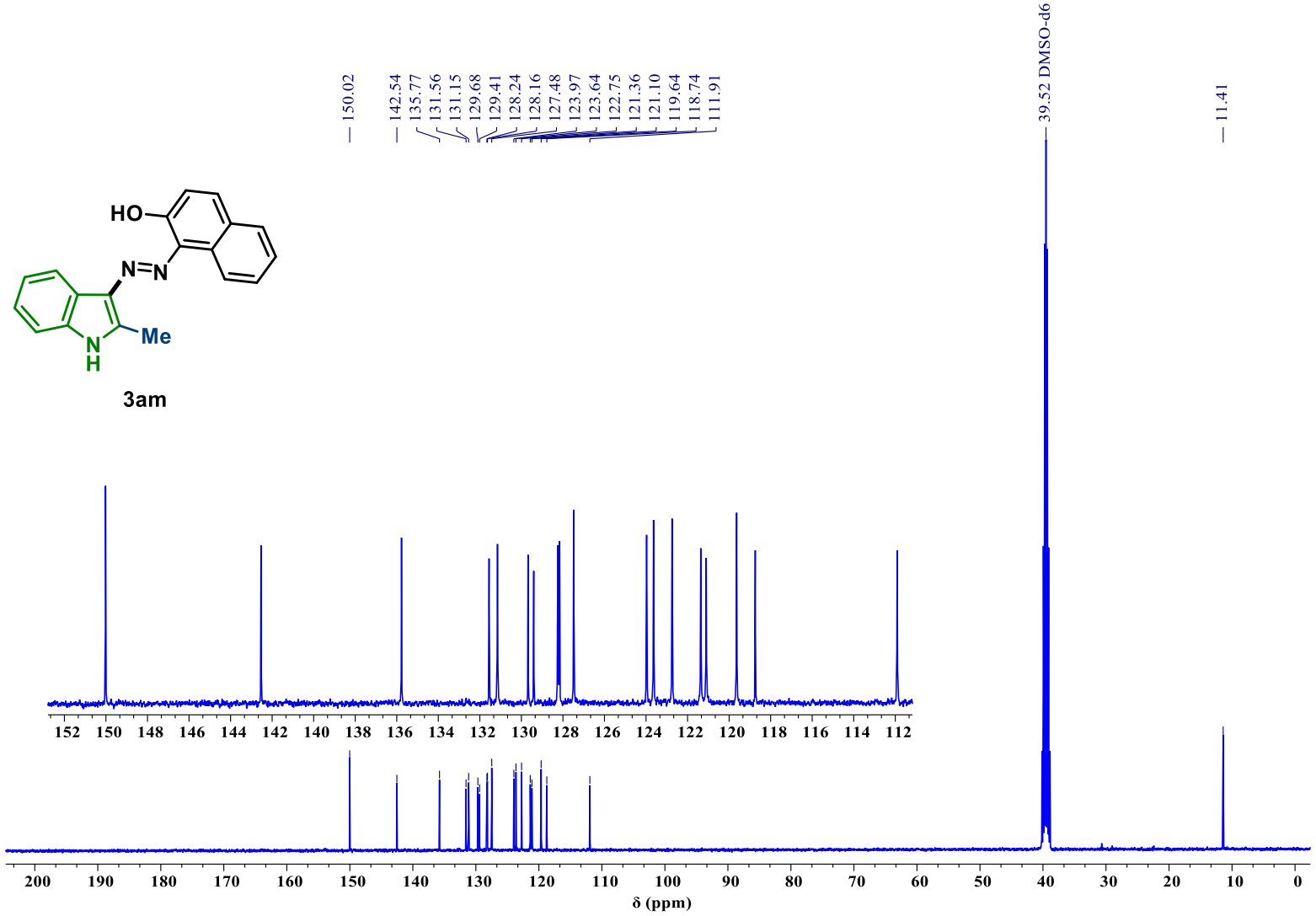
ATR-IR spectrum of (*E*)-1-((2-(benzofuran-2-yl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3al).



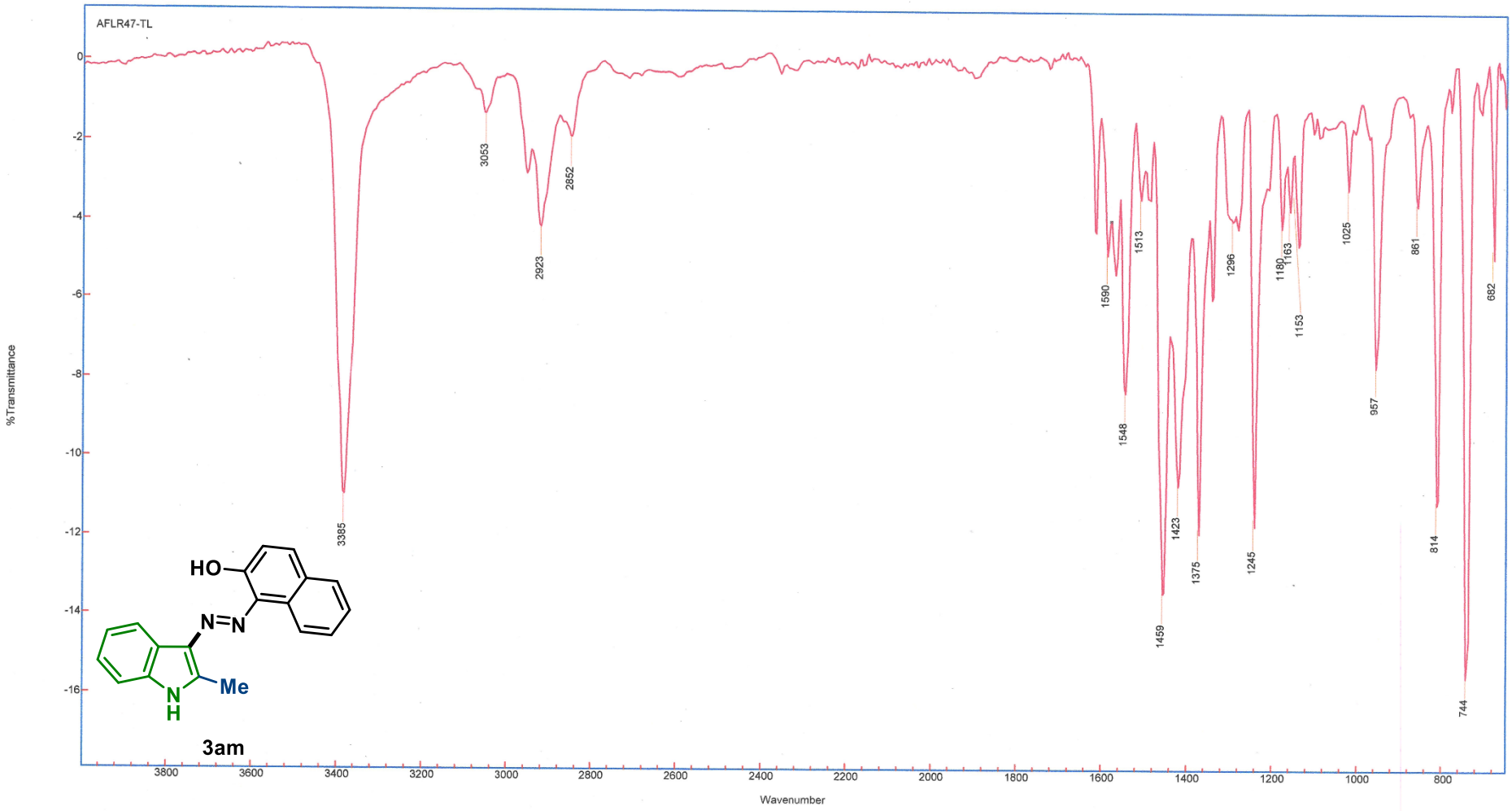
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3am).



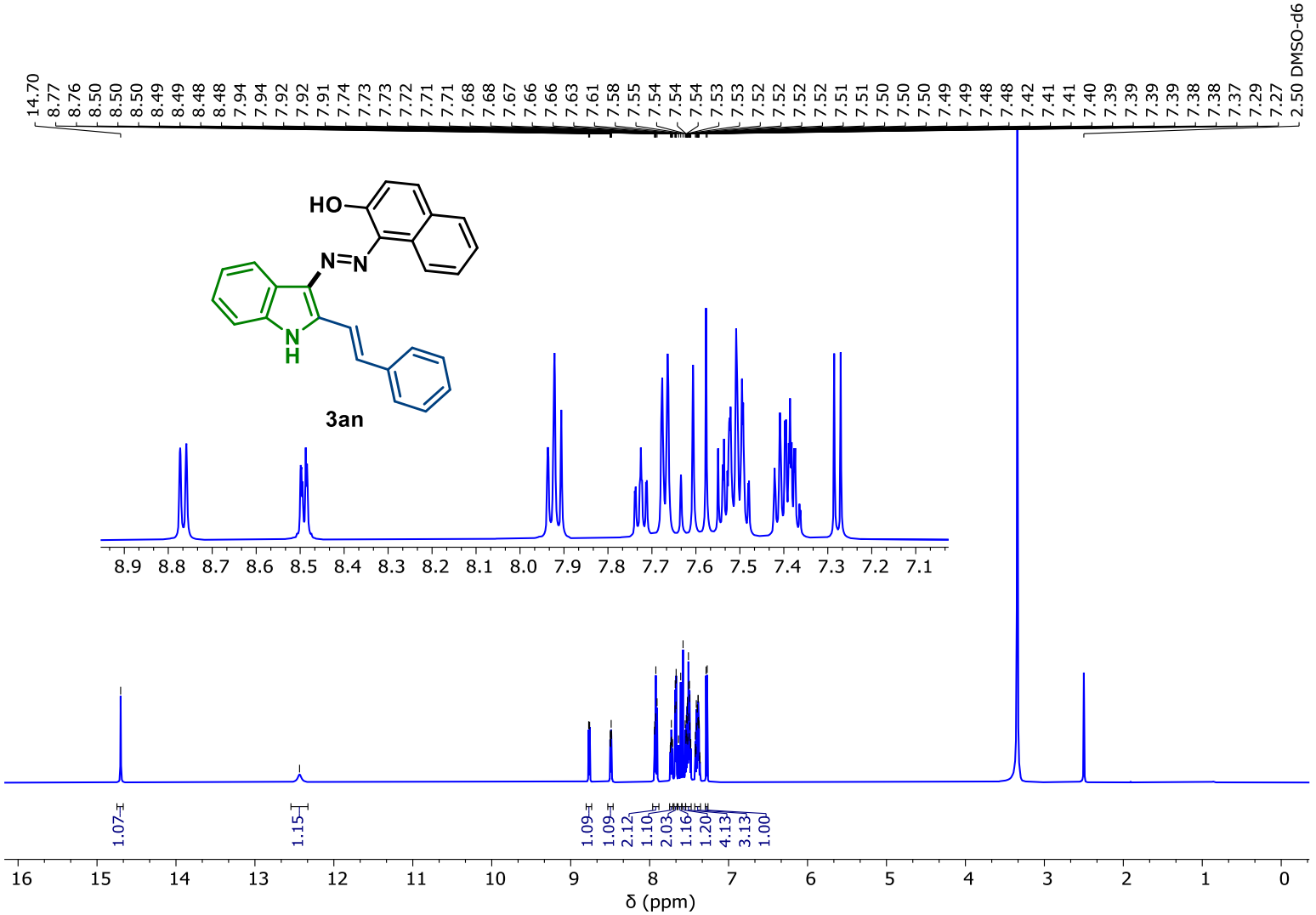
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3am).



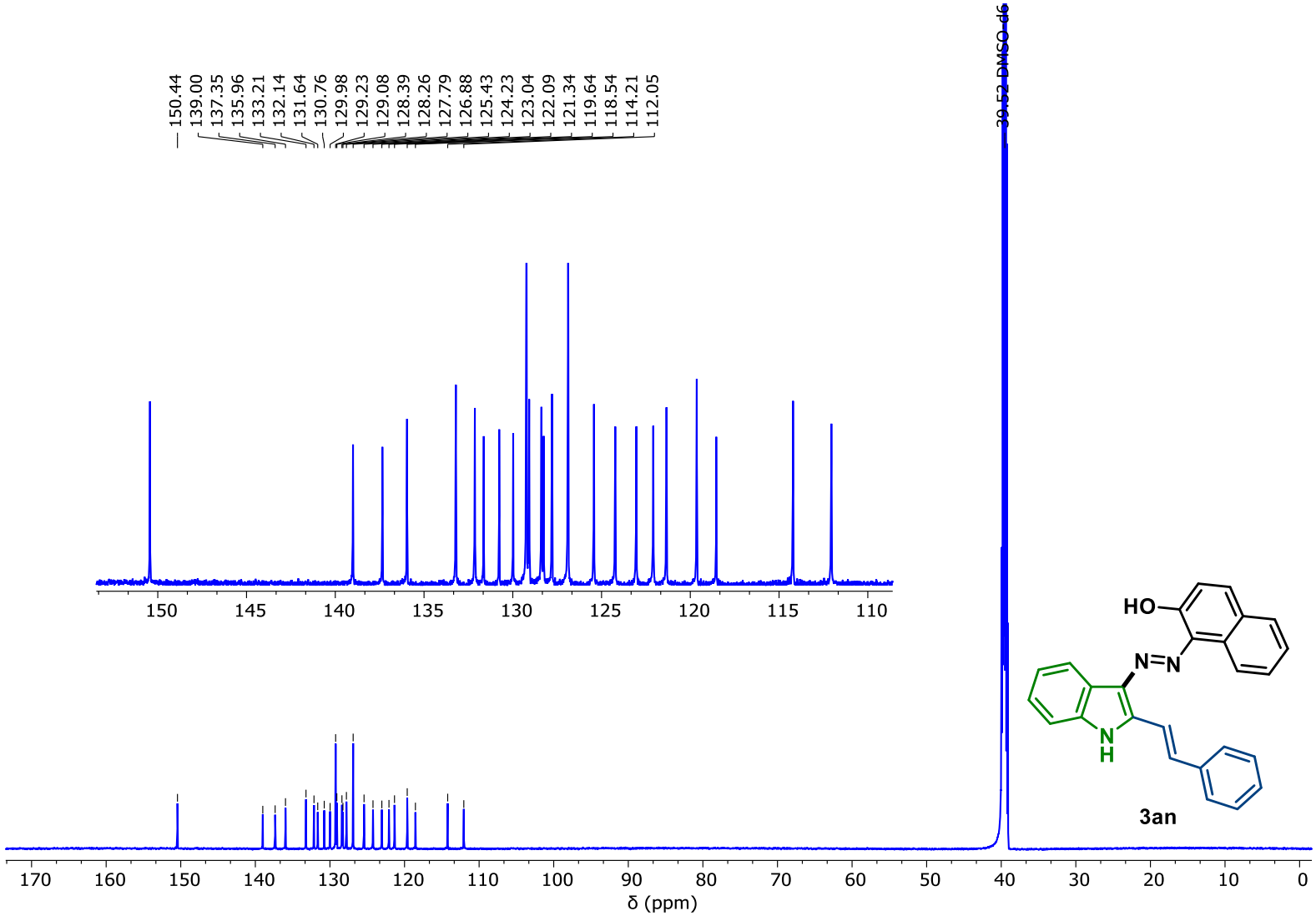
ATR-IR spectrum (*E*)-1-((2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3am).



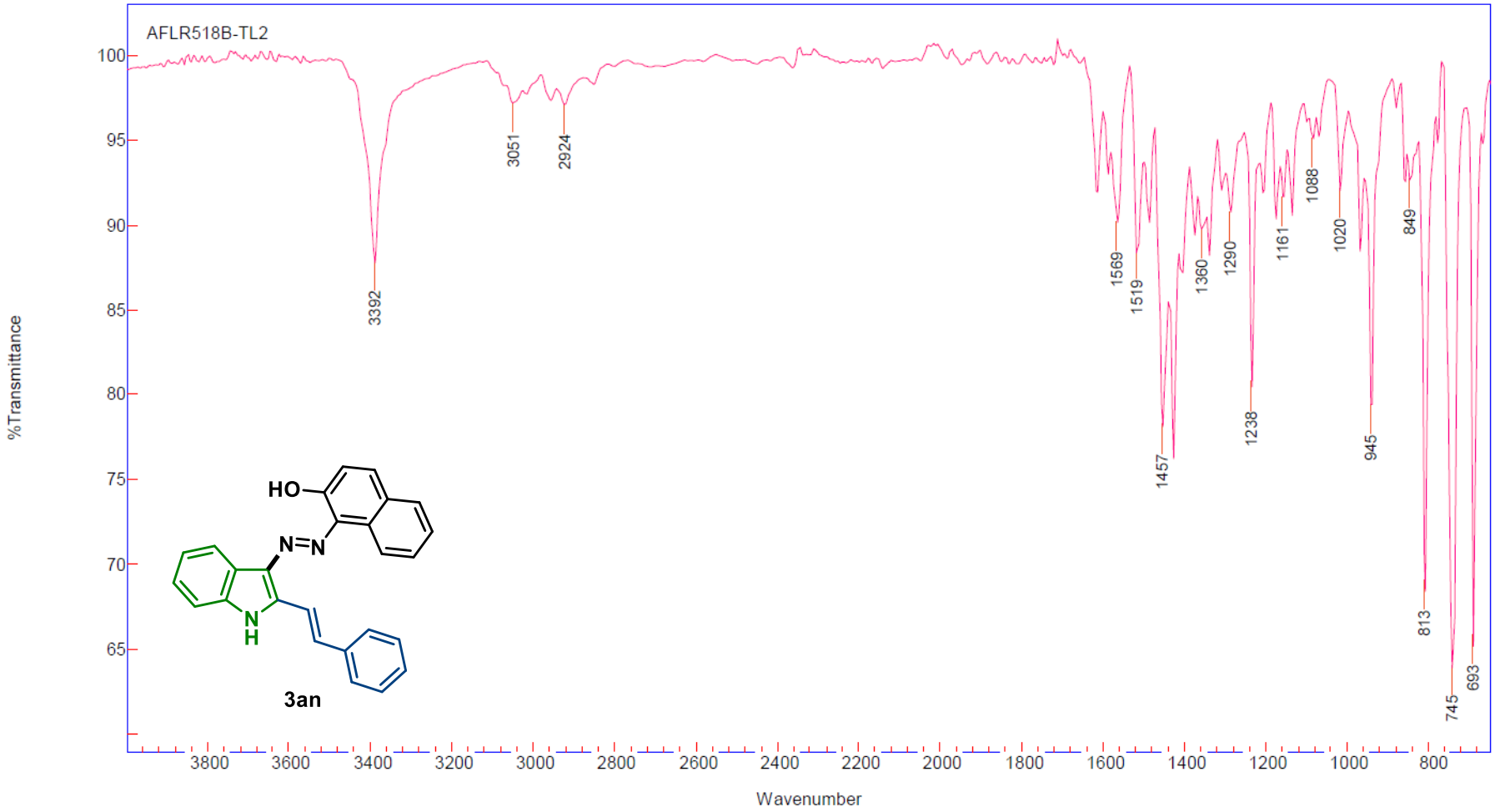
[1]H NMR (600 MHz, DMSO-d_6) spectrum of 1-((*E*)-(2-((*E*)-styryl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3an).



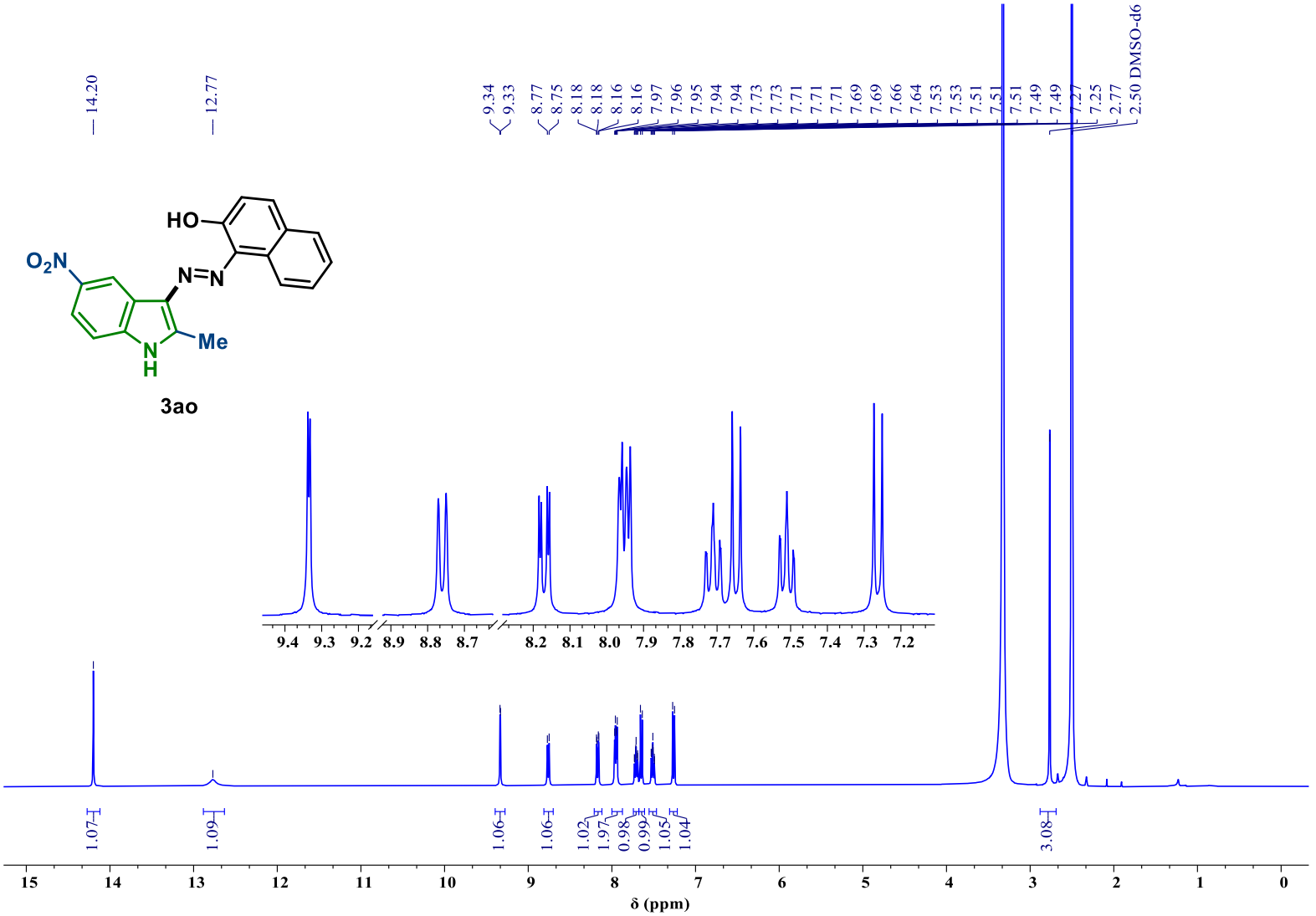
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of 1-((*E*)-(2-((*E*)-styryl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3an).



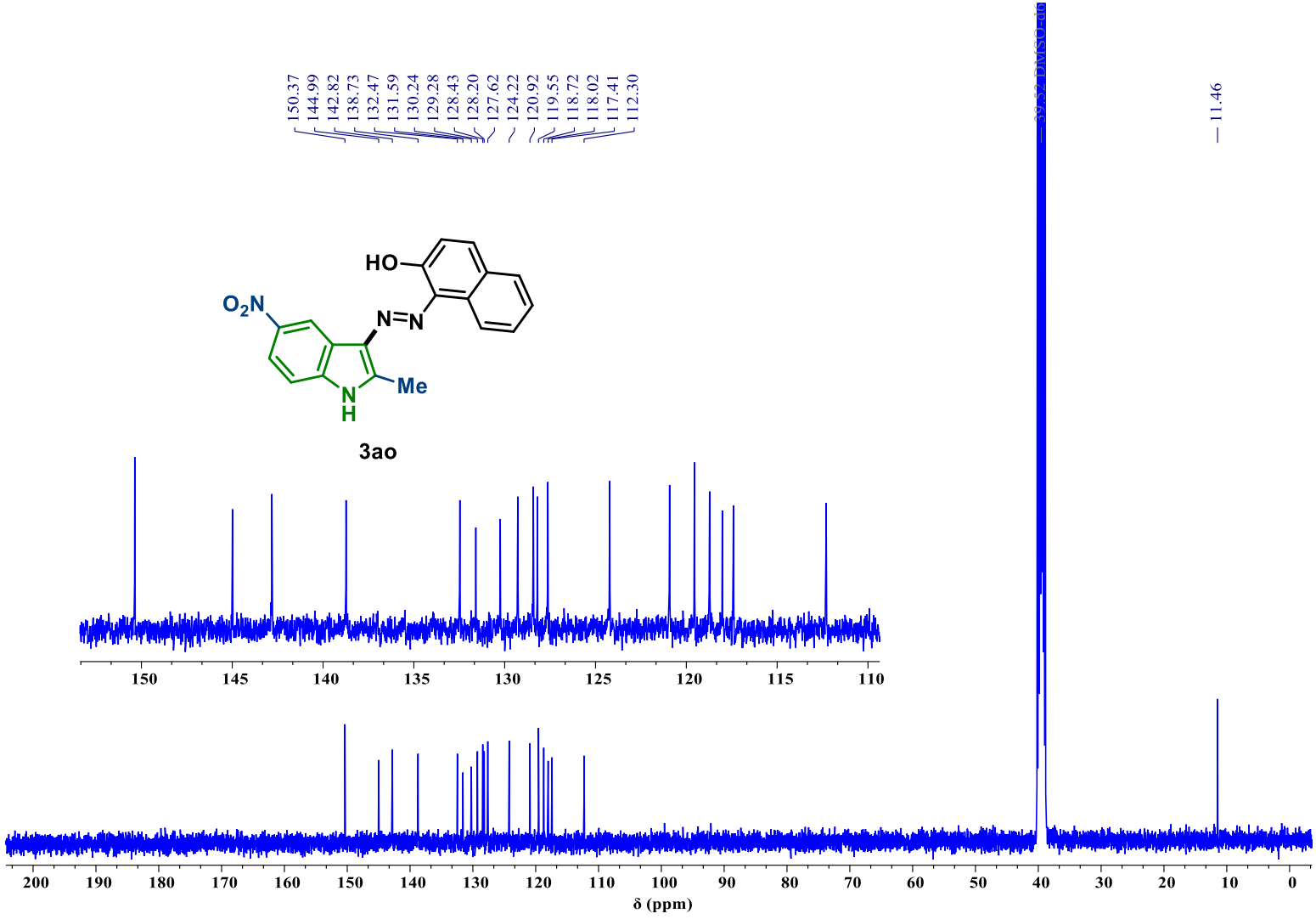
ATR-IR spectrum of 1-((*E*)-(2-((*E*)-styryl)-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3an).



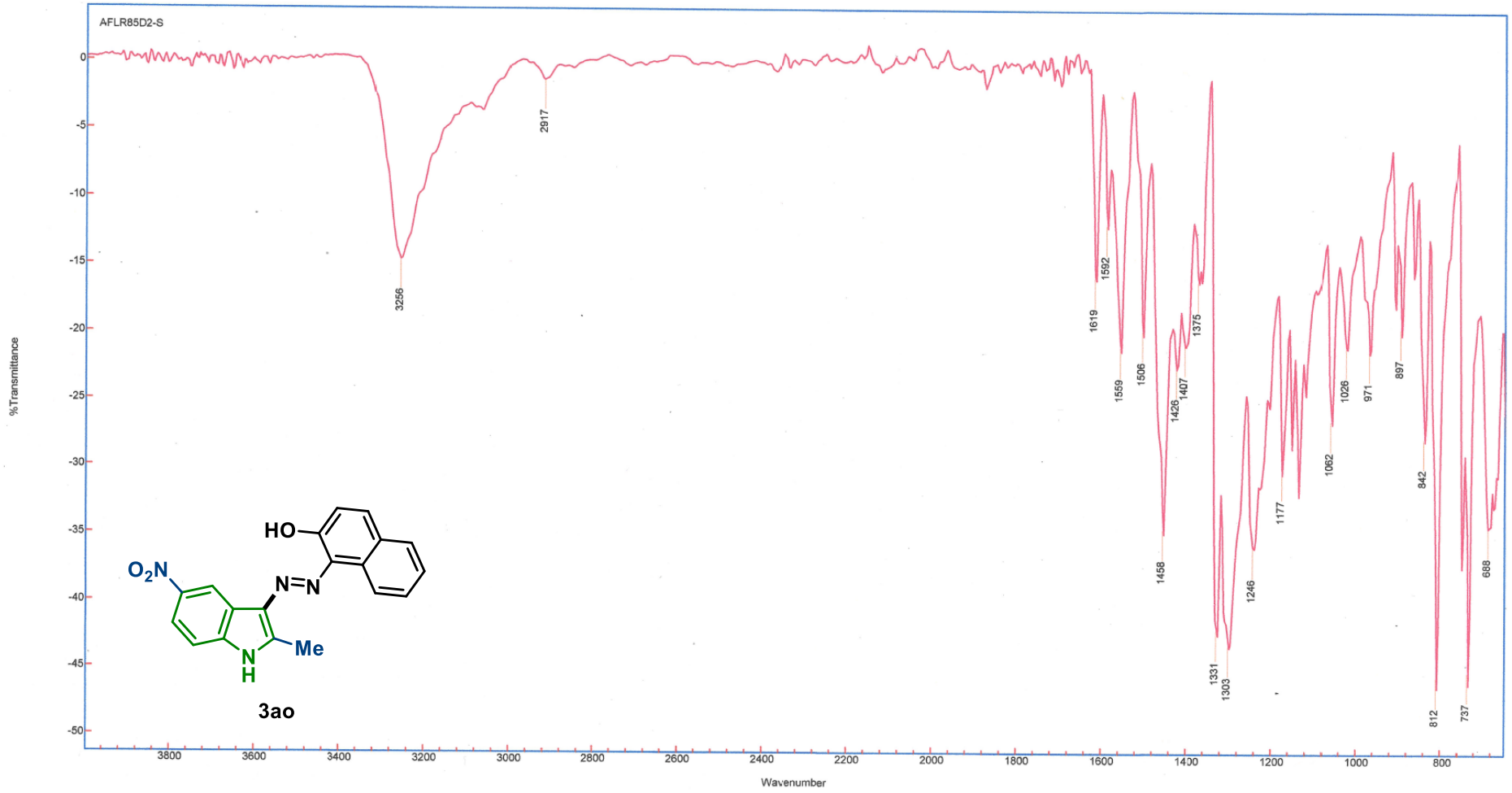
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-methyl-5-nitro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ao).



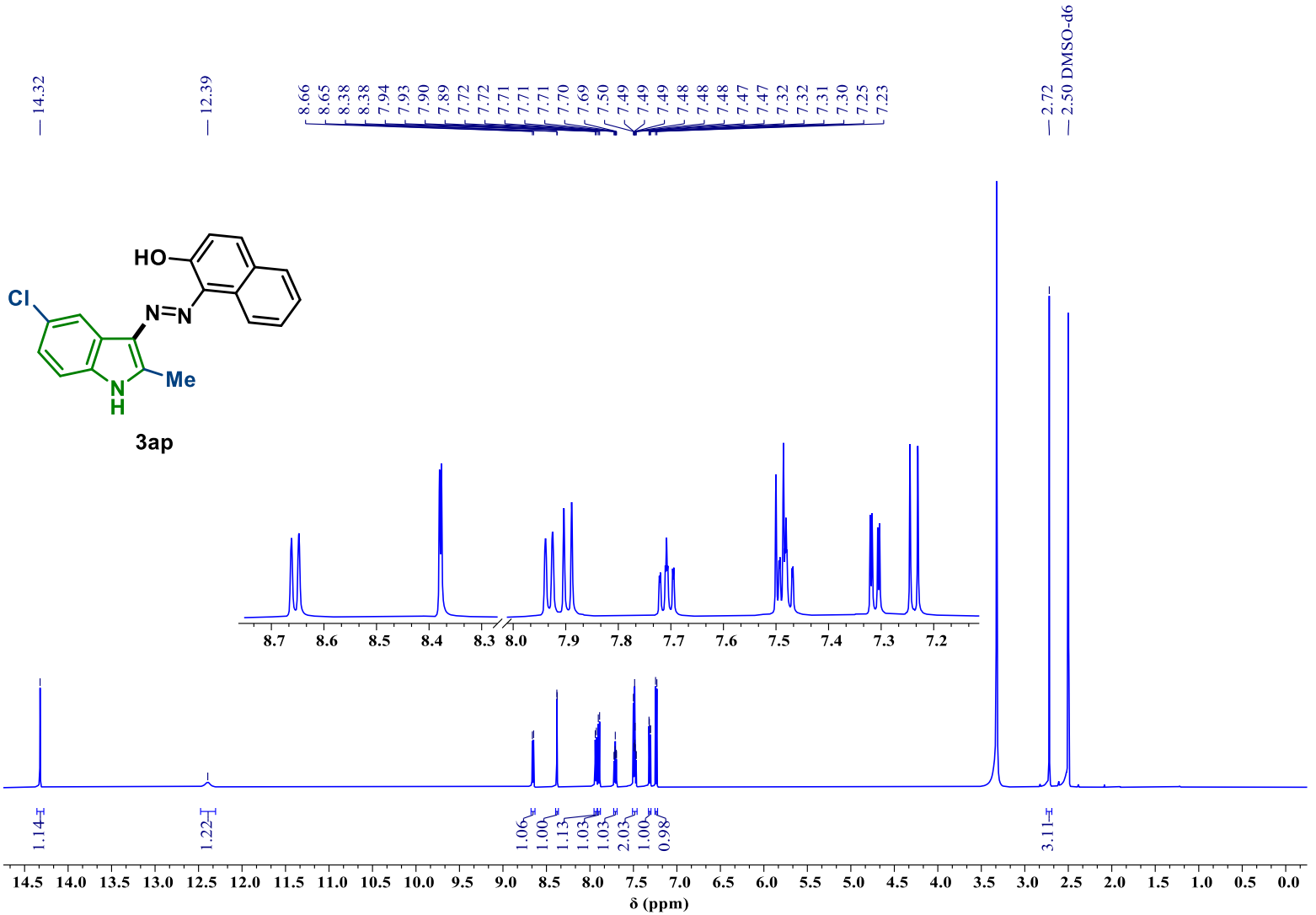
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-methyl-5-nitro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ao).



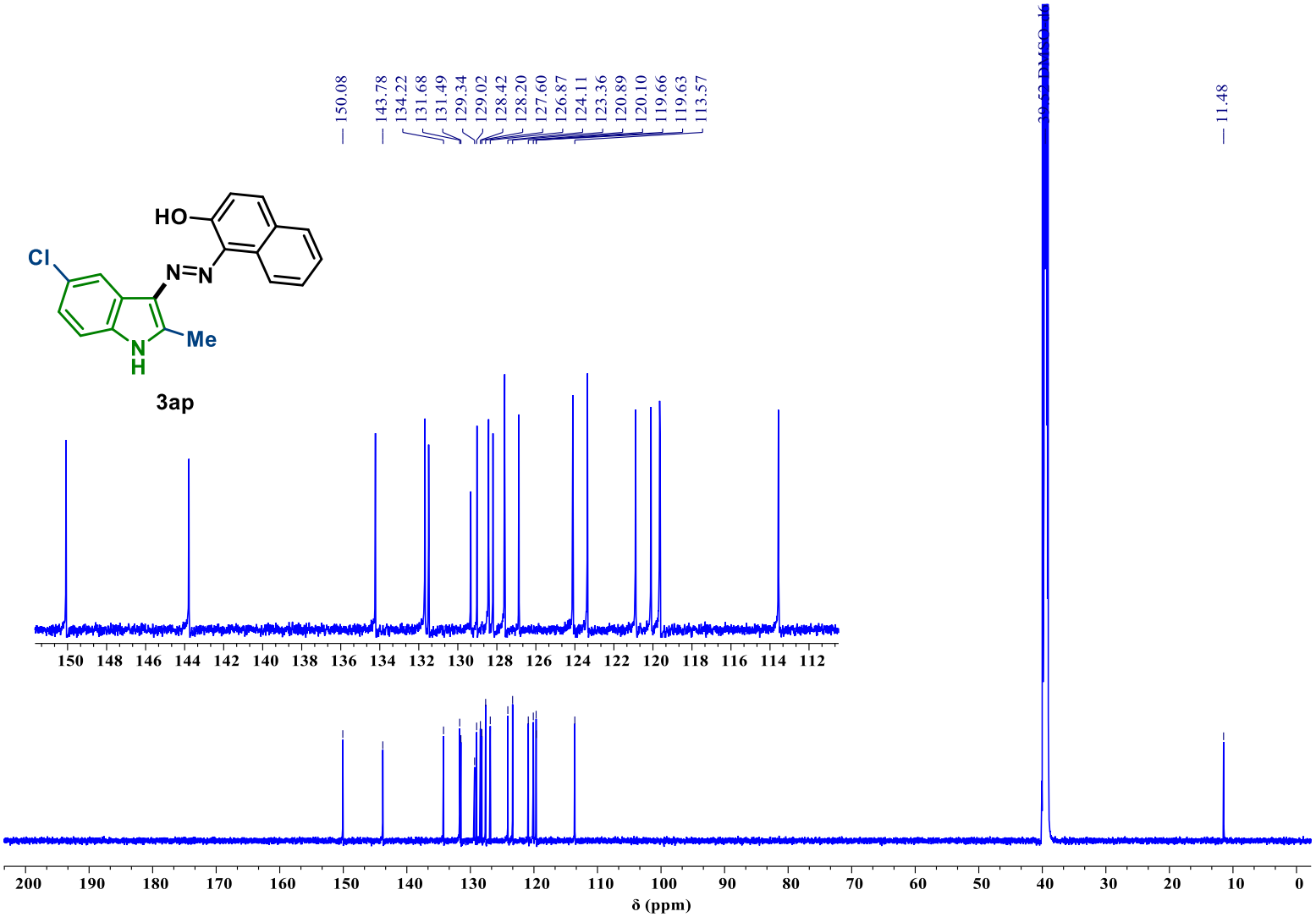
ATR-IR spectrum of (*E*)-1-((2-methyl-5-nitro-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ao).



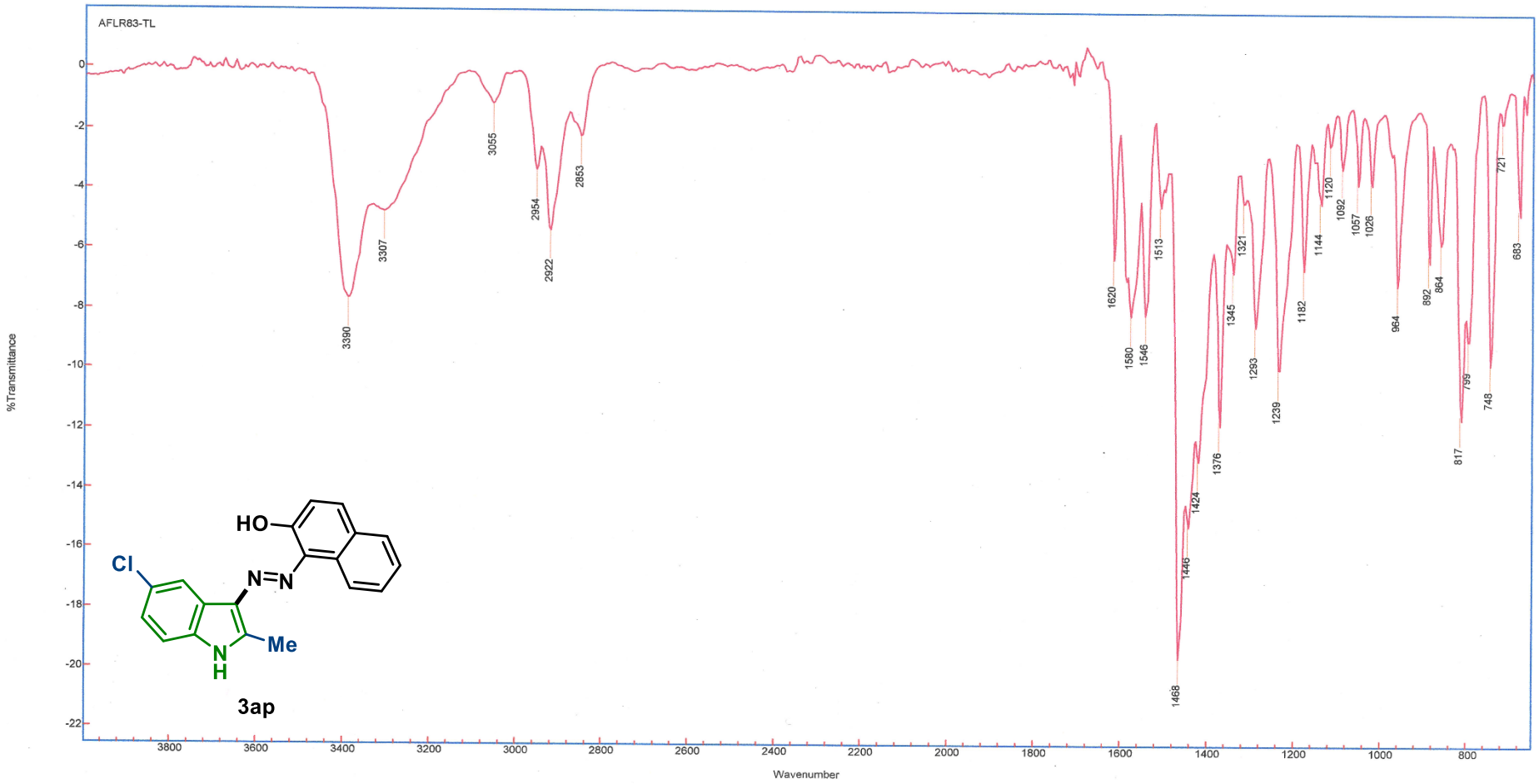
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-chloro-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ap).



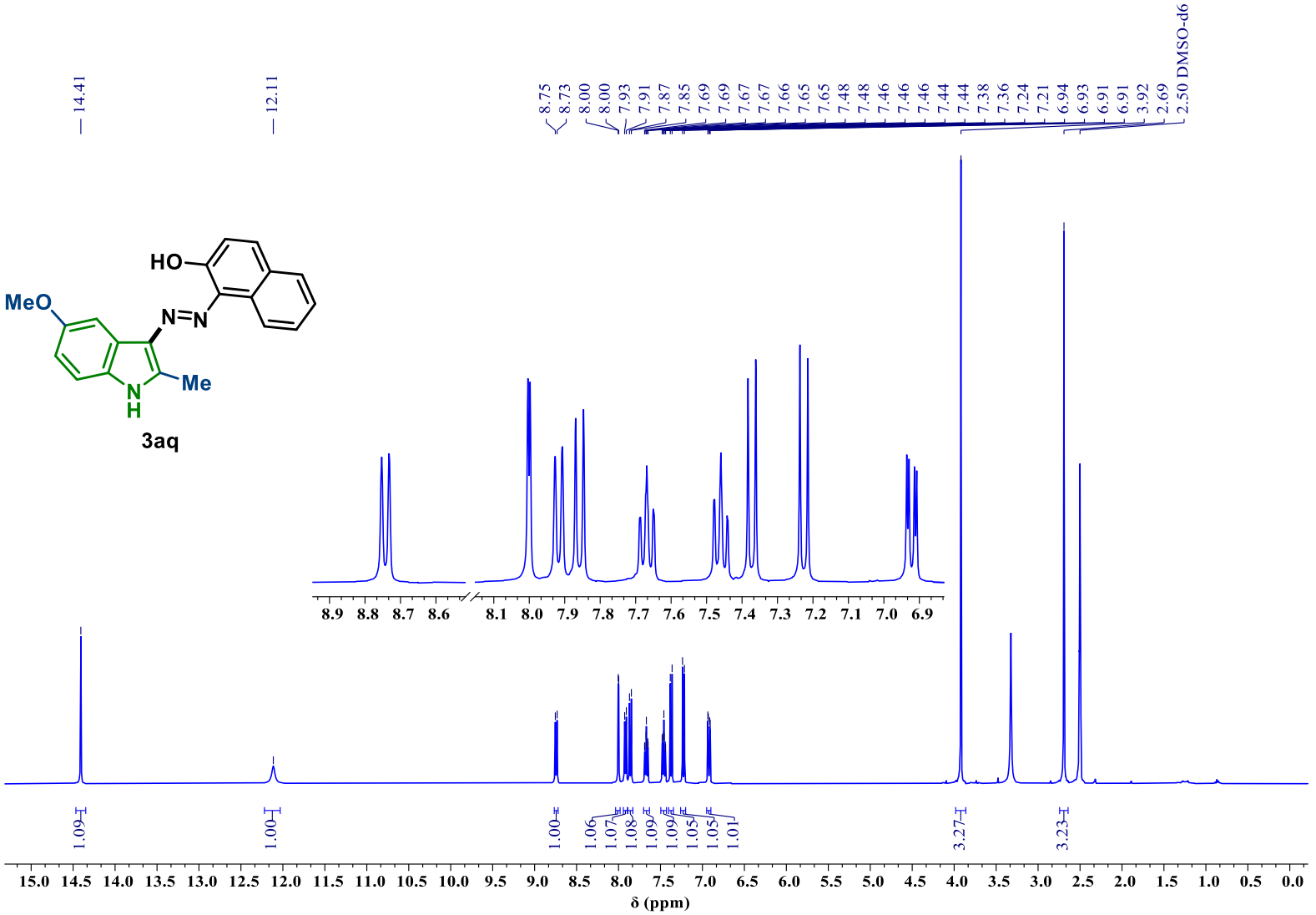
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-chloro-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ap).



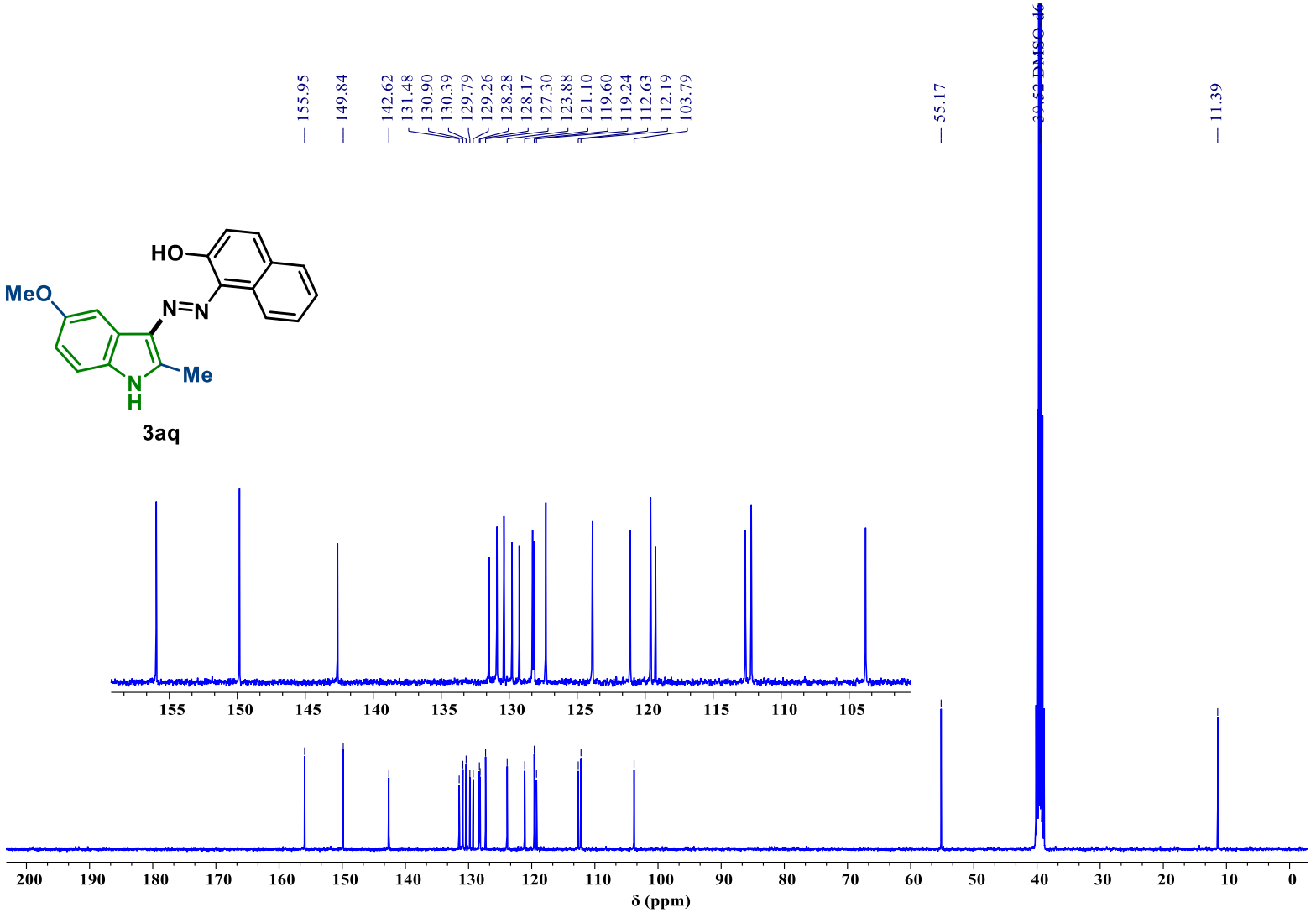
ATR-IR spectrum of (*E*)-1-((5-chloro-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ap).



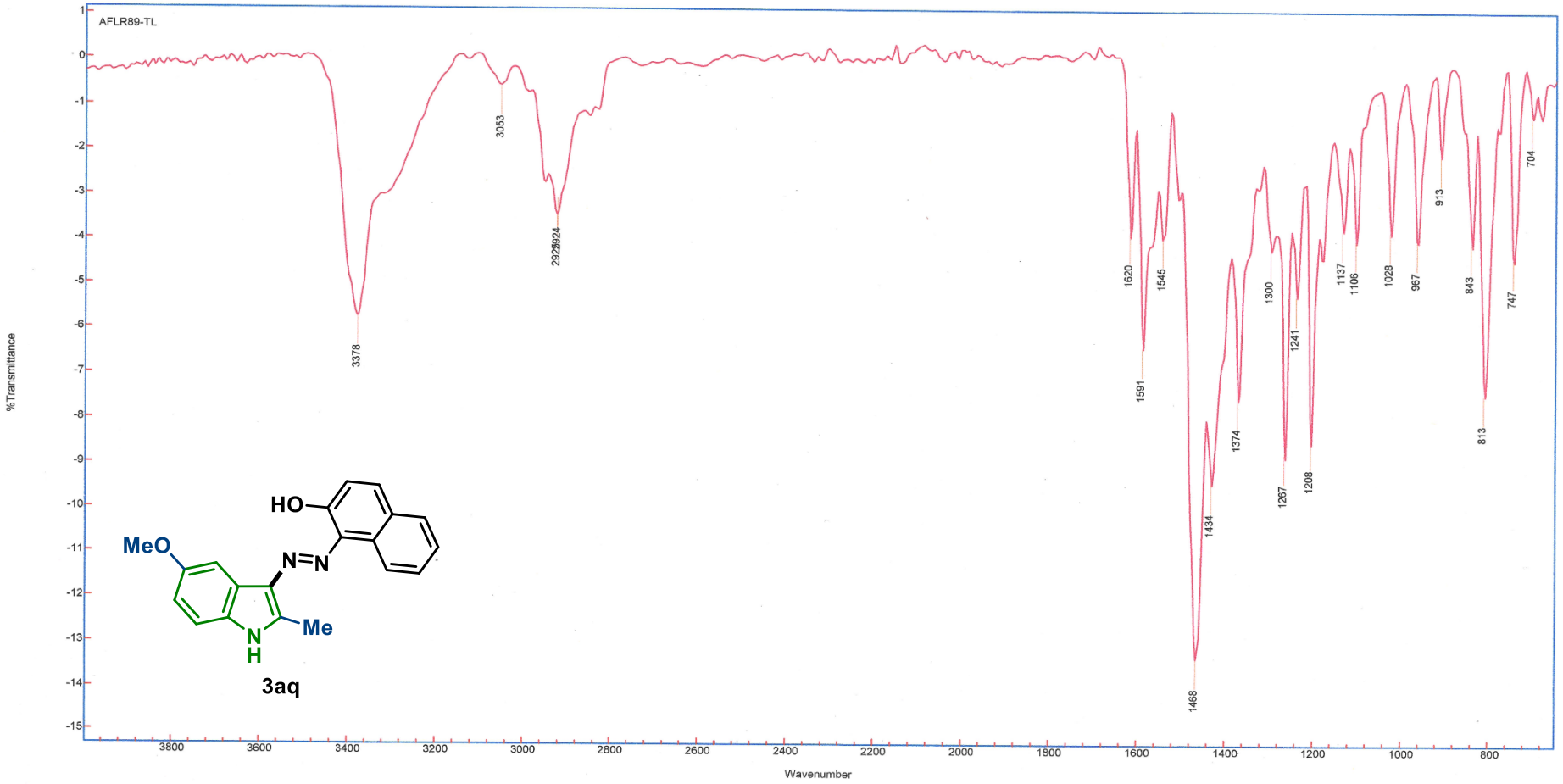
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methoxy-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aq).



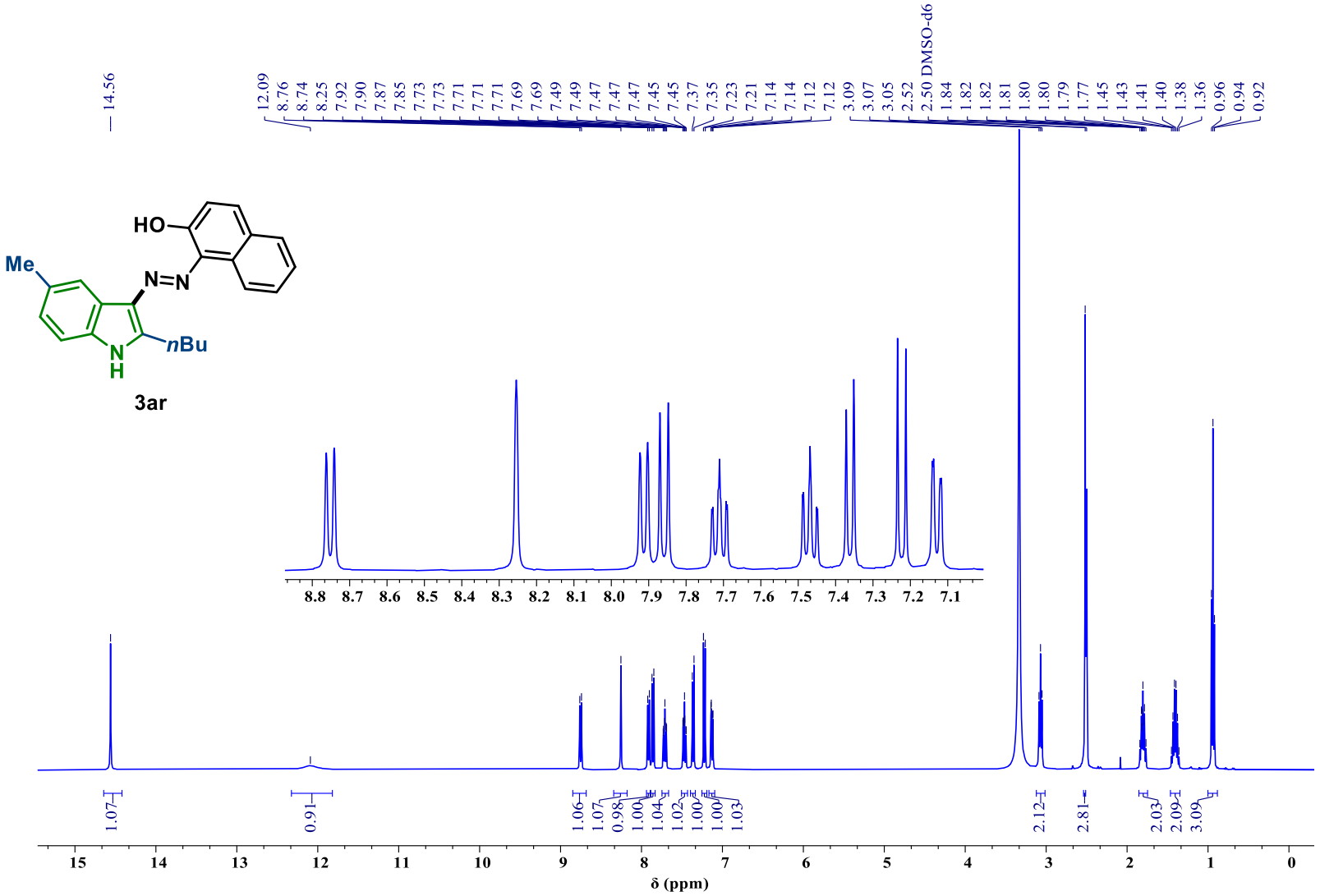
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((5-methoxy-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aq).



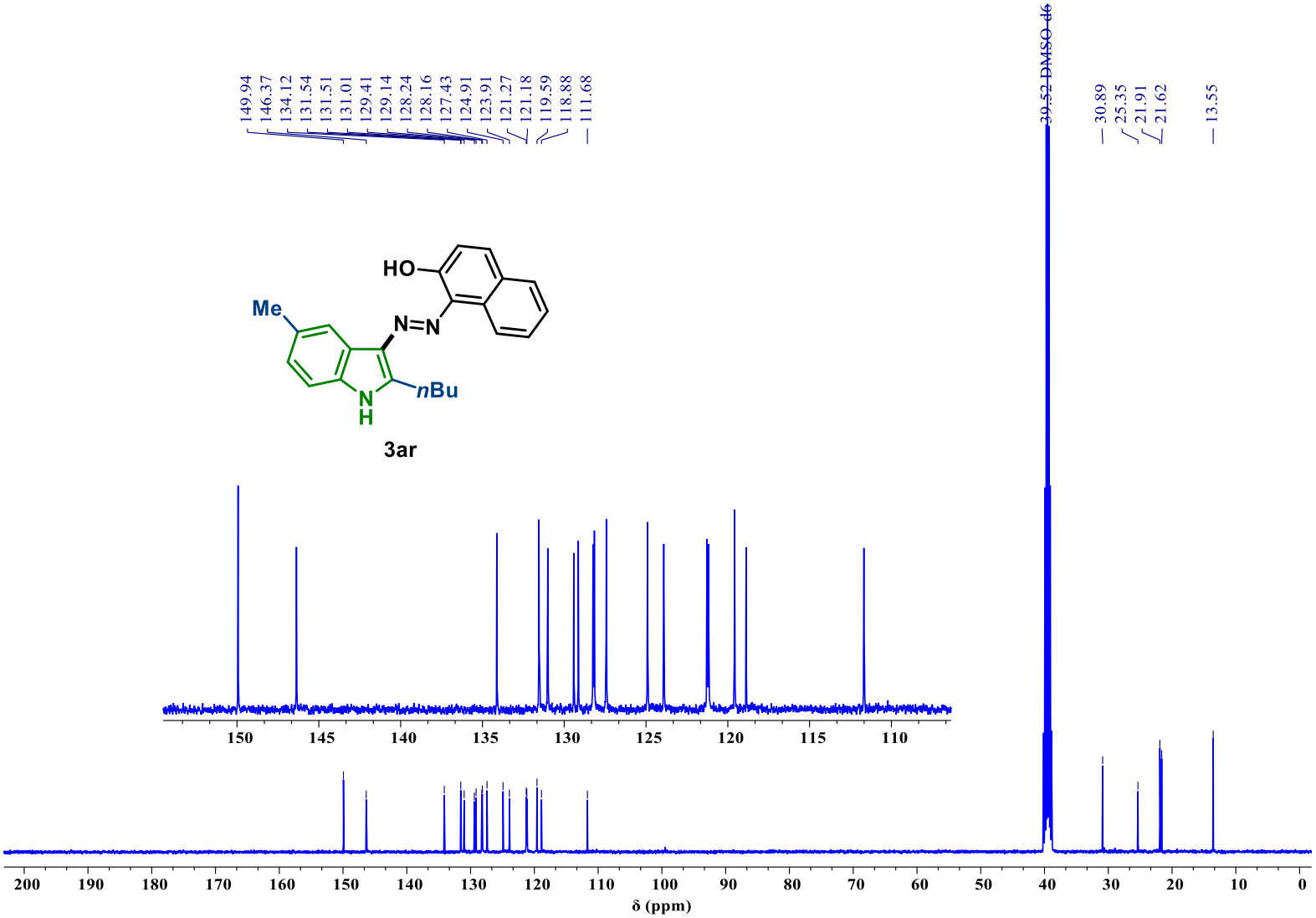
ATR-IR spectrum of (*E*)-1-((5-methoxy-2-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3aq).



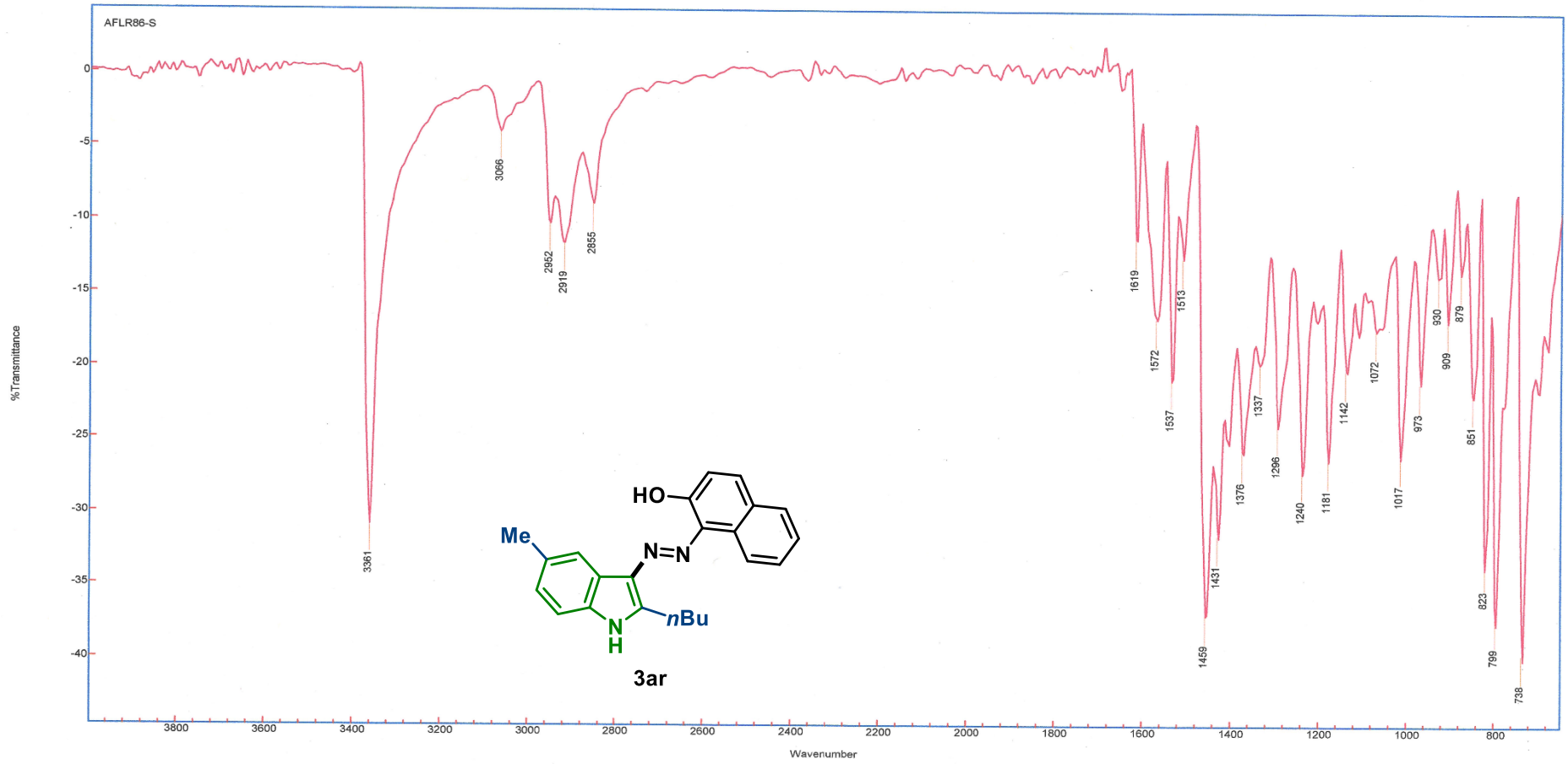
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-butyl-5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ar).



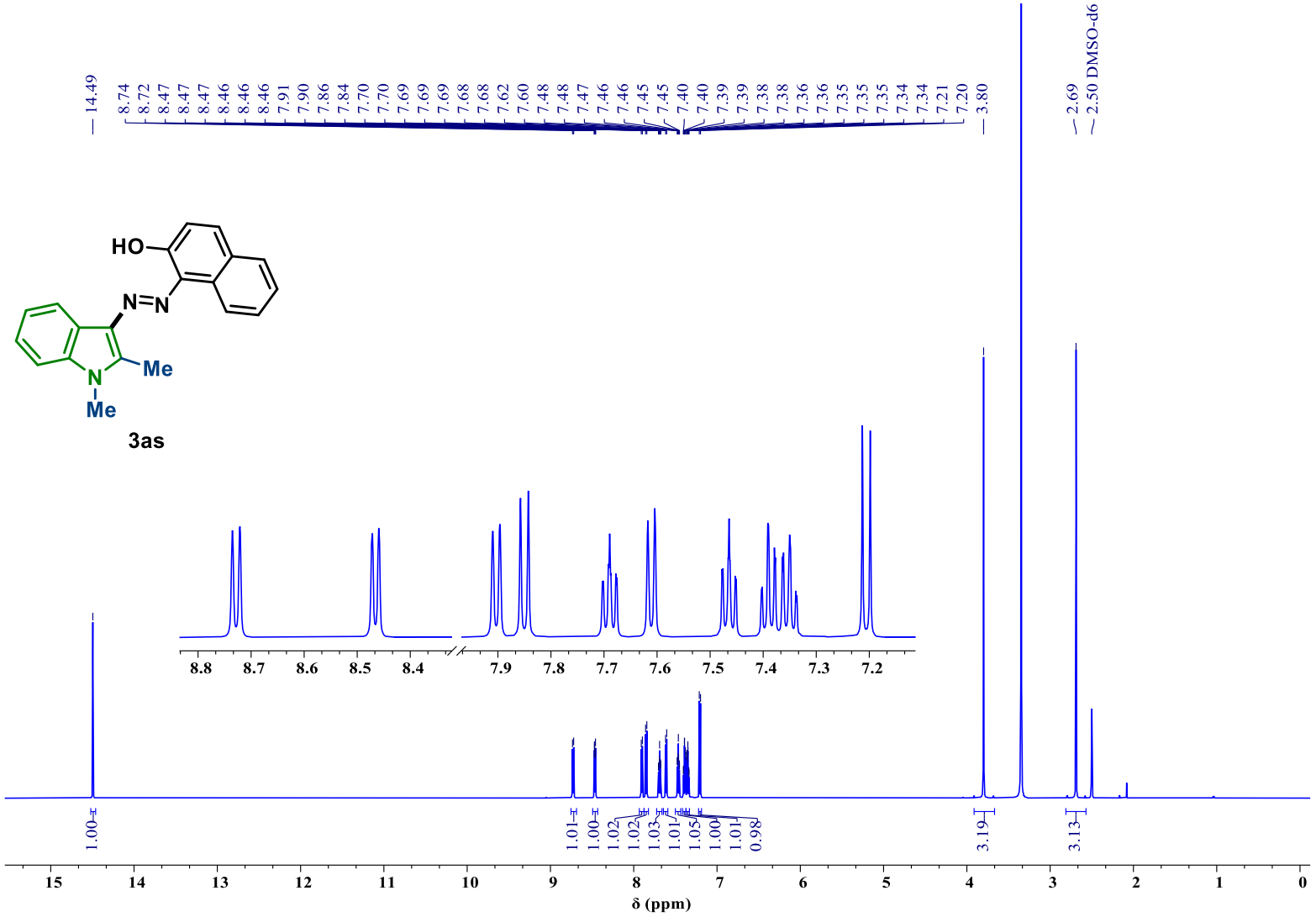
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((2-butyl-5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ar).



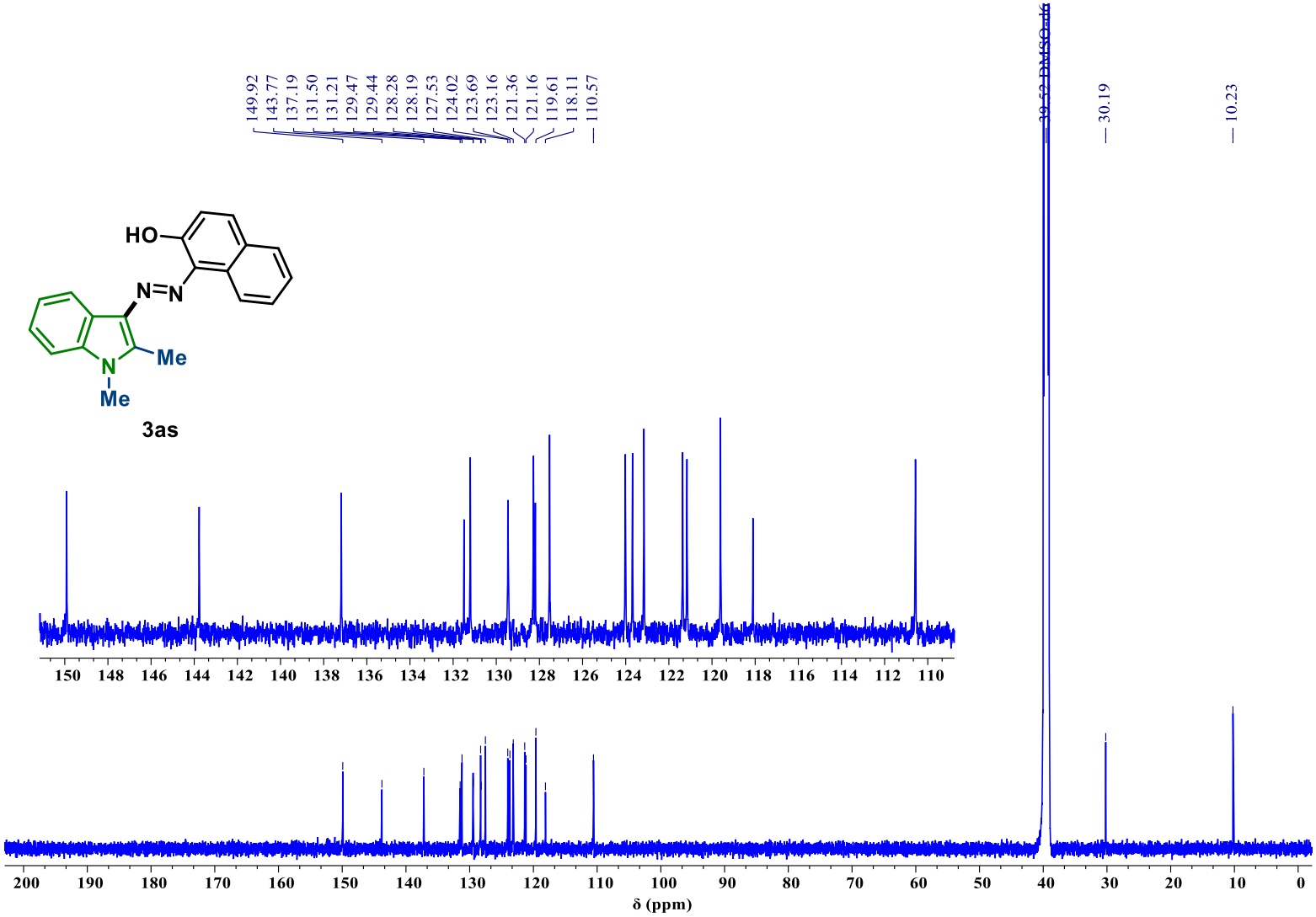
ATR-IR spectrum of (*E*)-1-((2-butyl-5-methyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3ar).



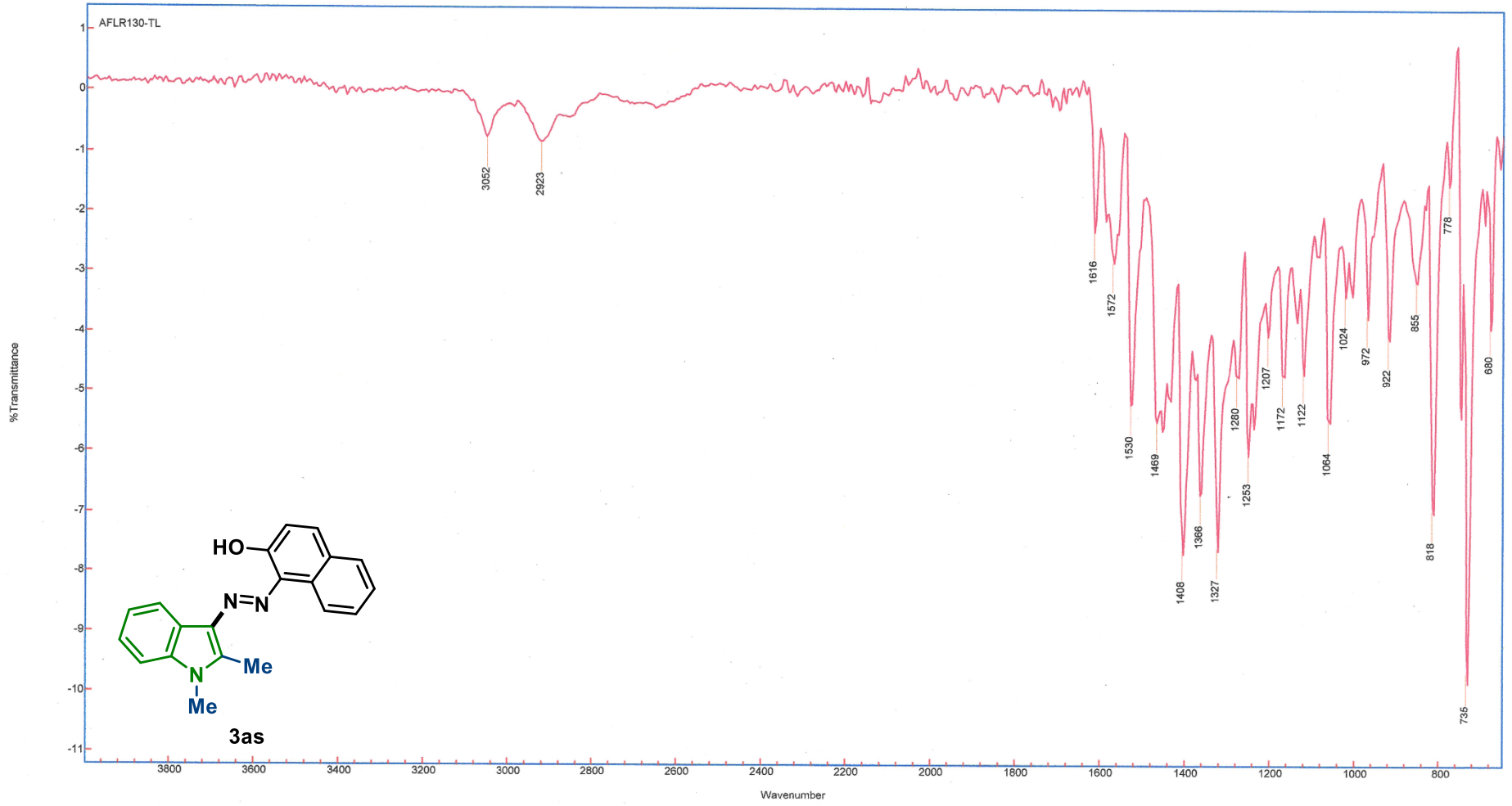
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*E*)-1-((1,2-dimethyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3as).



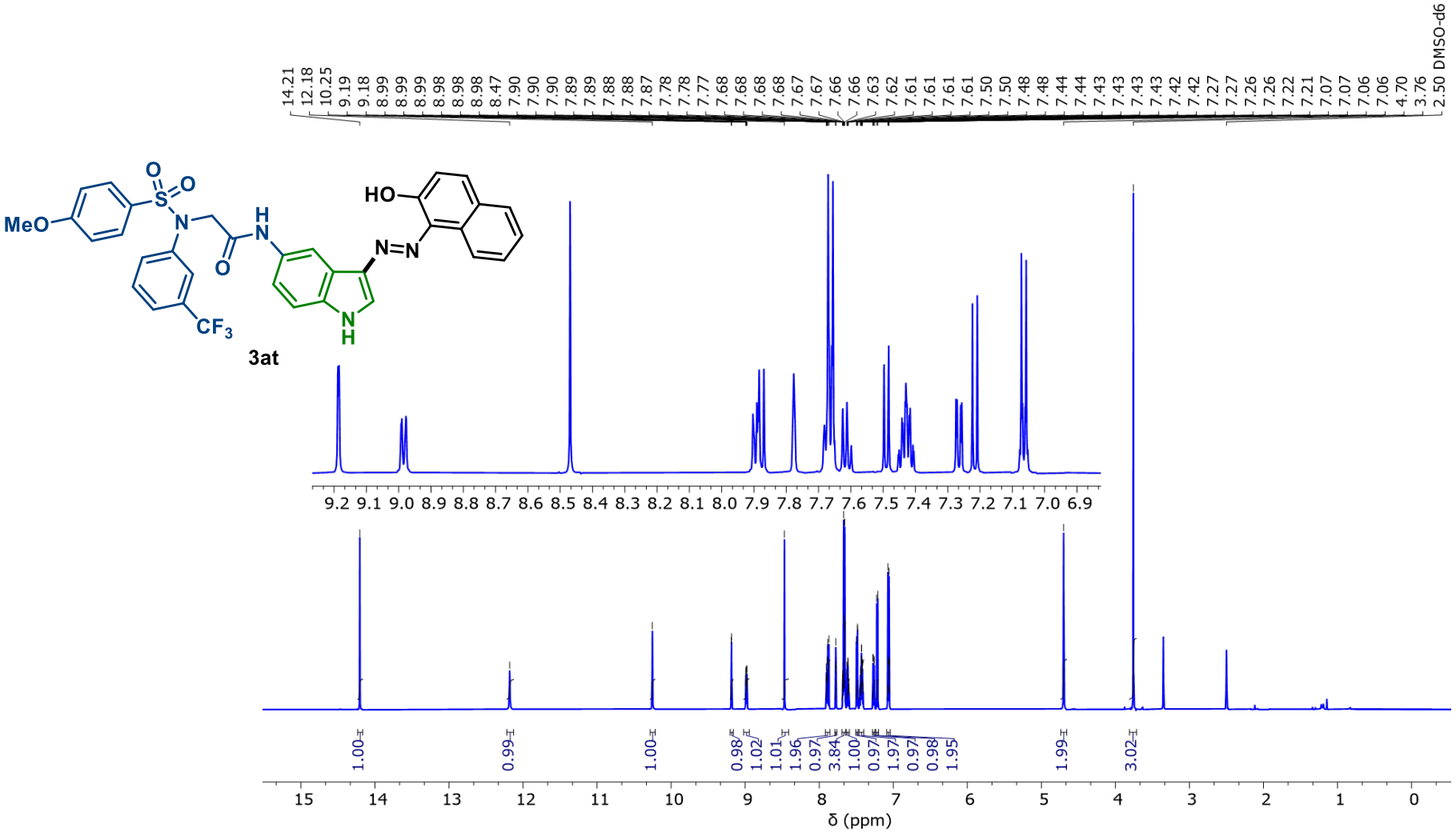
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of (*E*)-1-((1,2-dimethyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3as).



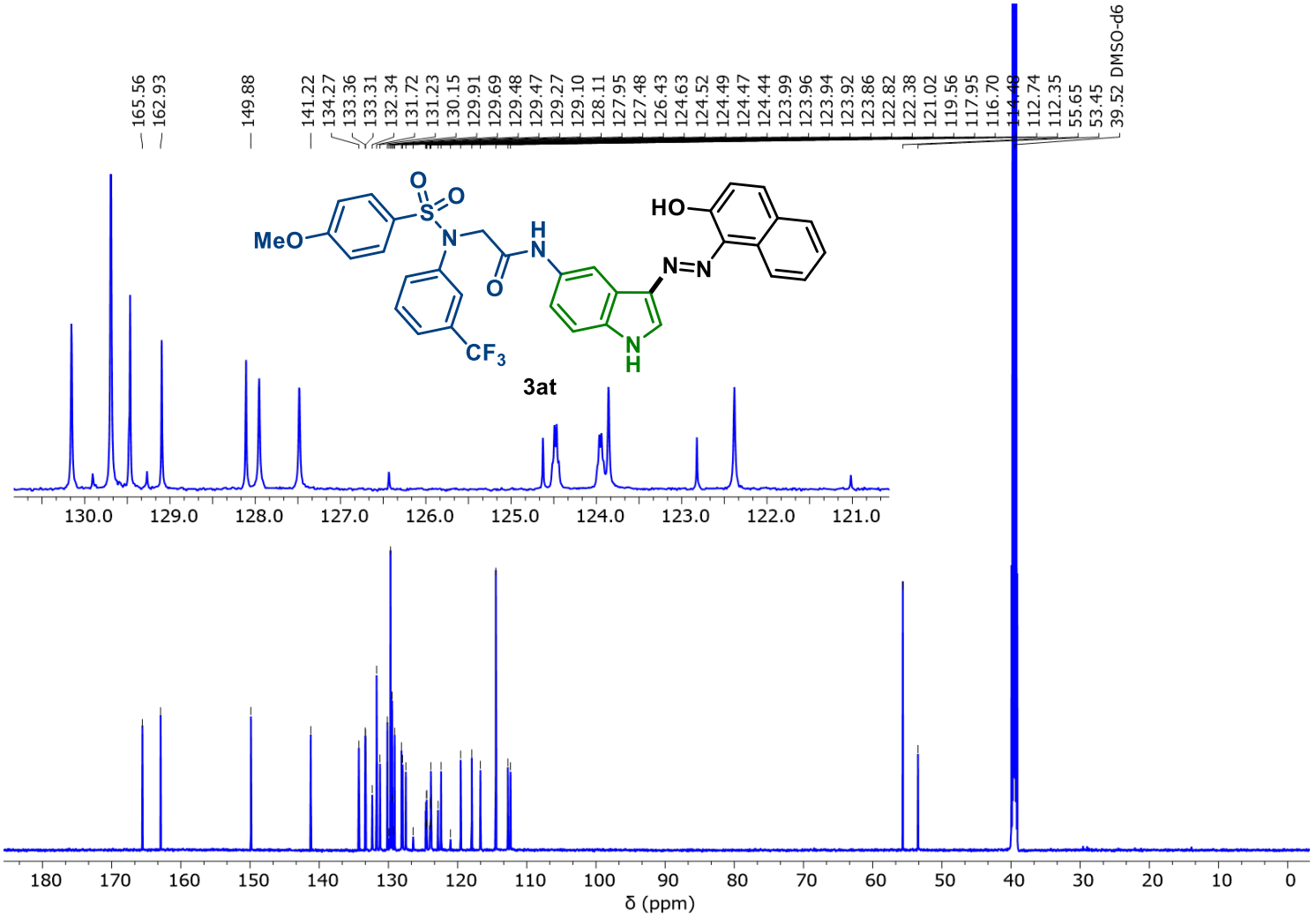
ATR-IR spectrum of (*E*)-1-((1,2-dimethyl-1*H*-indol-3-yl)diazenyl)naphthalen-2-ol (3as).



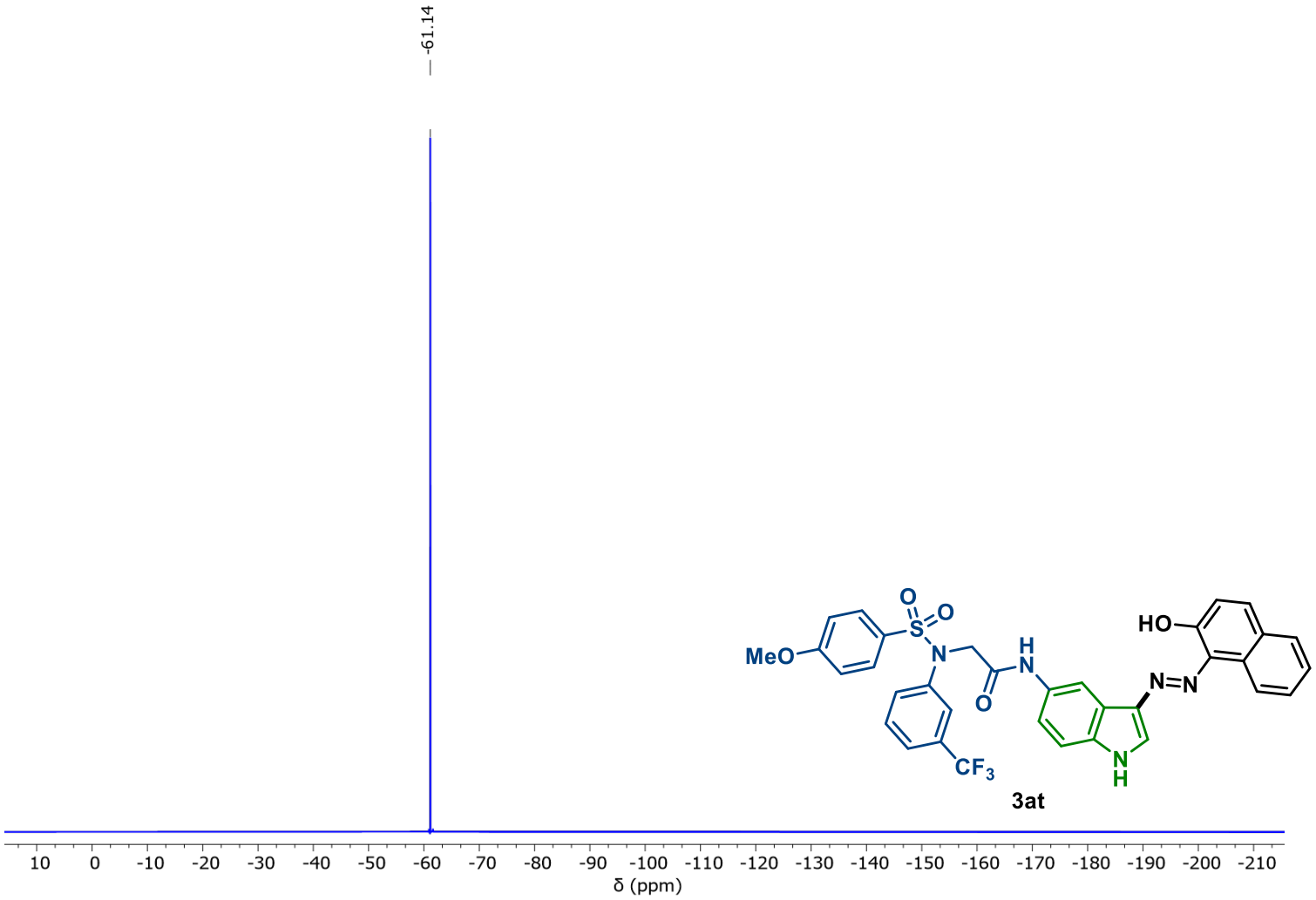
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoro methyl)phenyl)phenyl)sulfonamido)acetamide (3at).



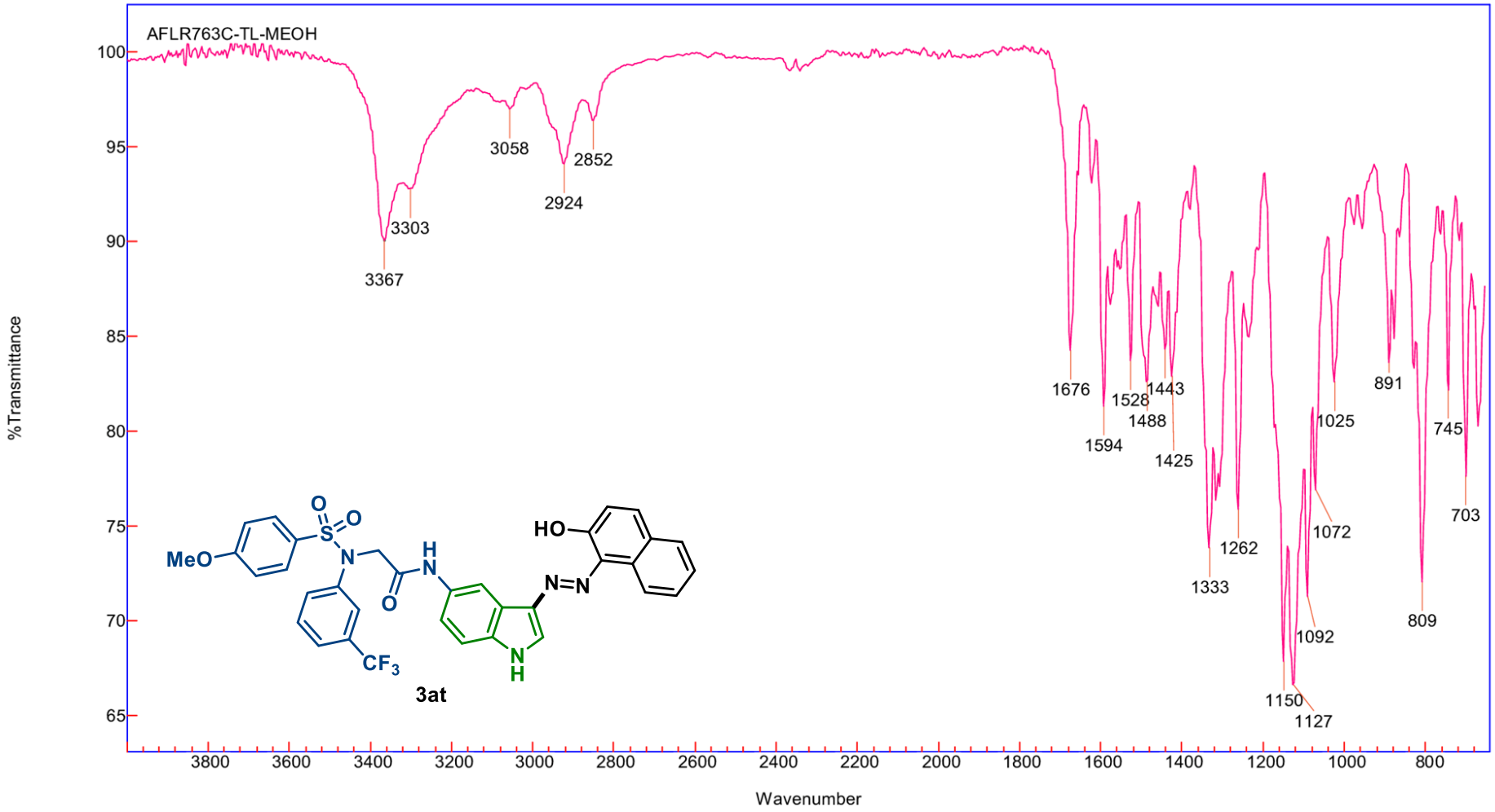
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoro methyl)phenyl)phenyl)sulfonamido)acetamide (3at).



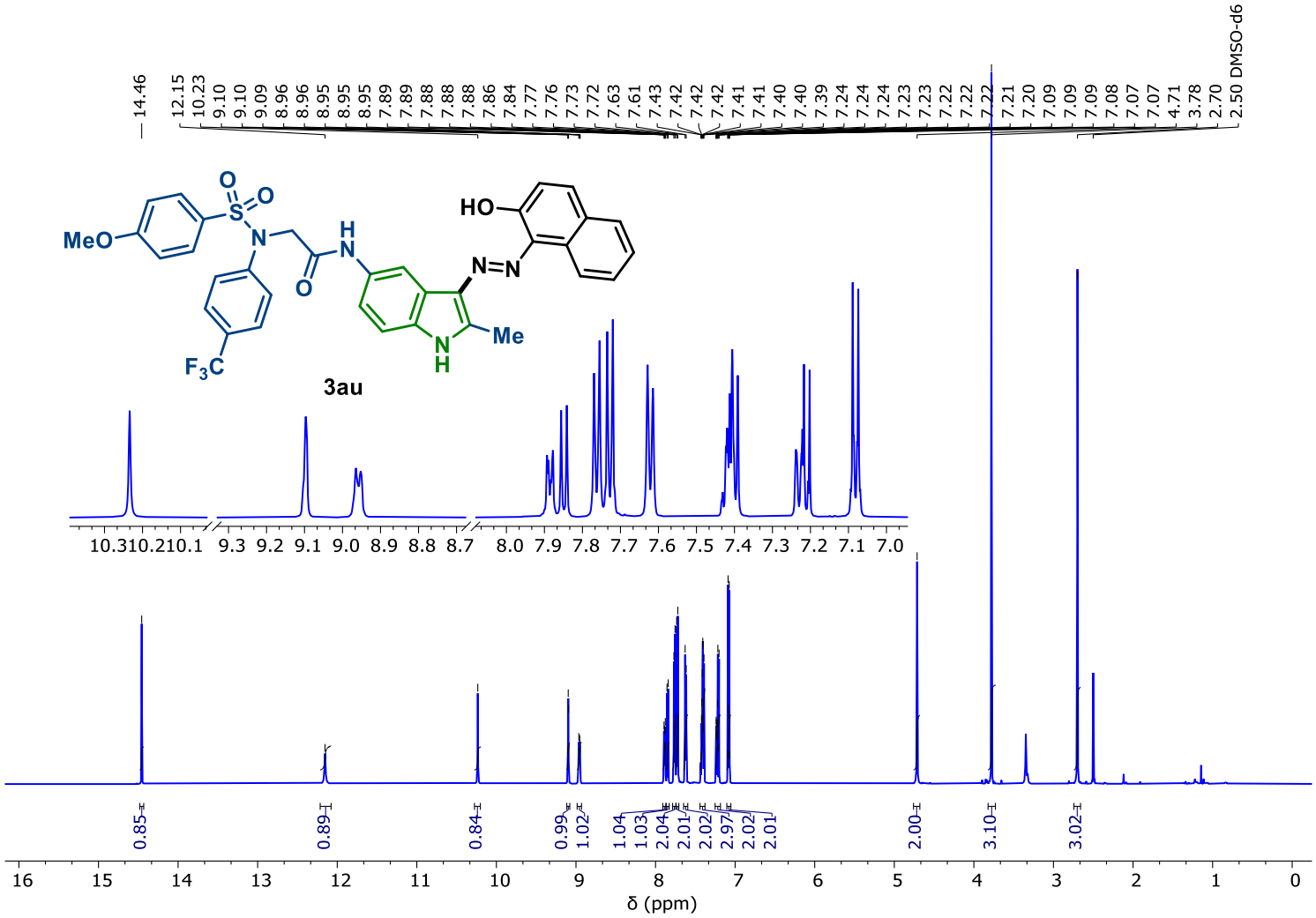
^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoro methyl)phenyl)phenyl)sulfonamido)acetamide (3at).



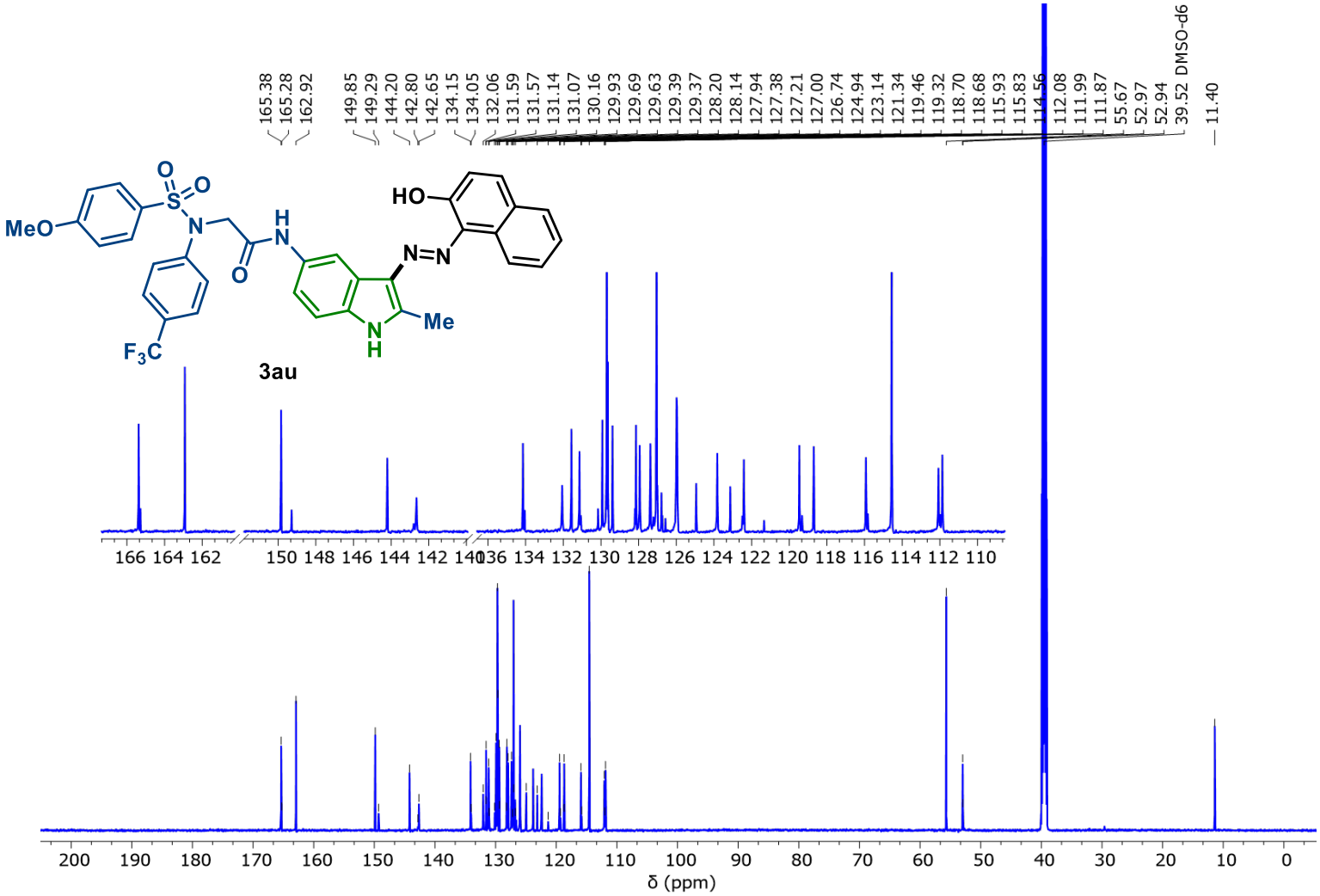
ATR-IR spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(3-(trifluoromethyl)phenyl)phenyl) sulfonamido)acetamide (3at).



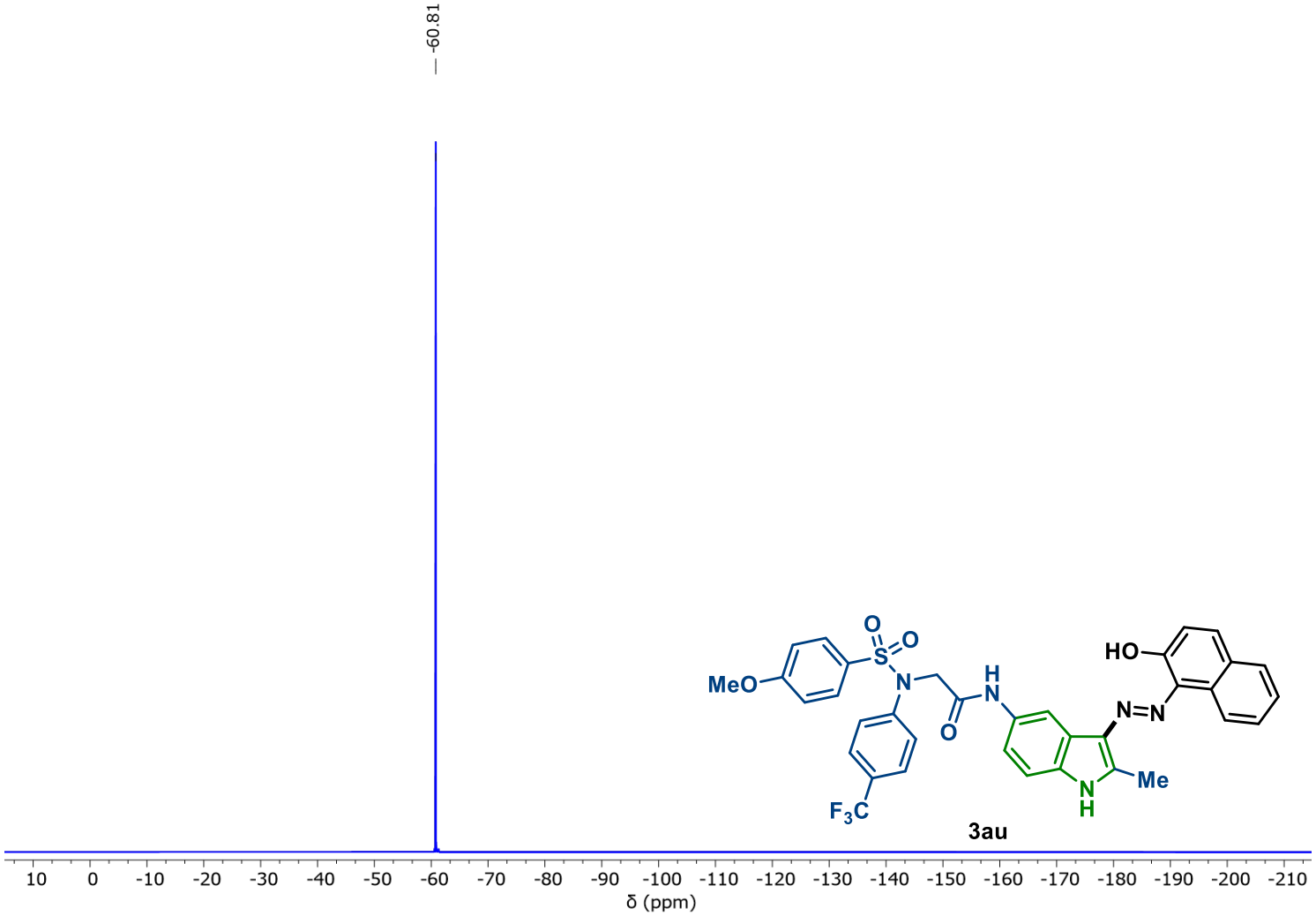
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*E*)-N-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (3au).



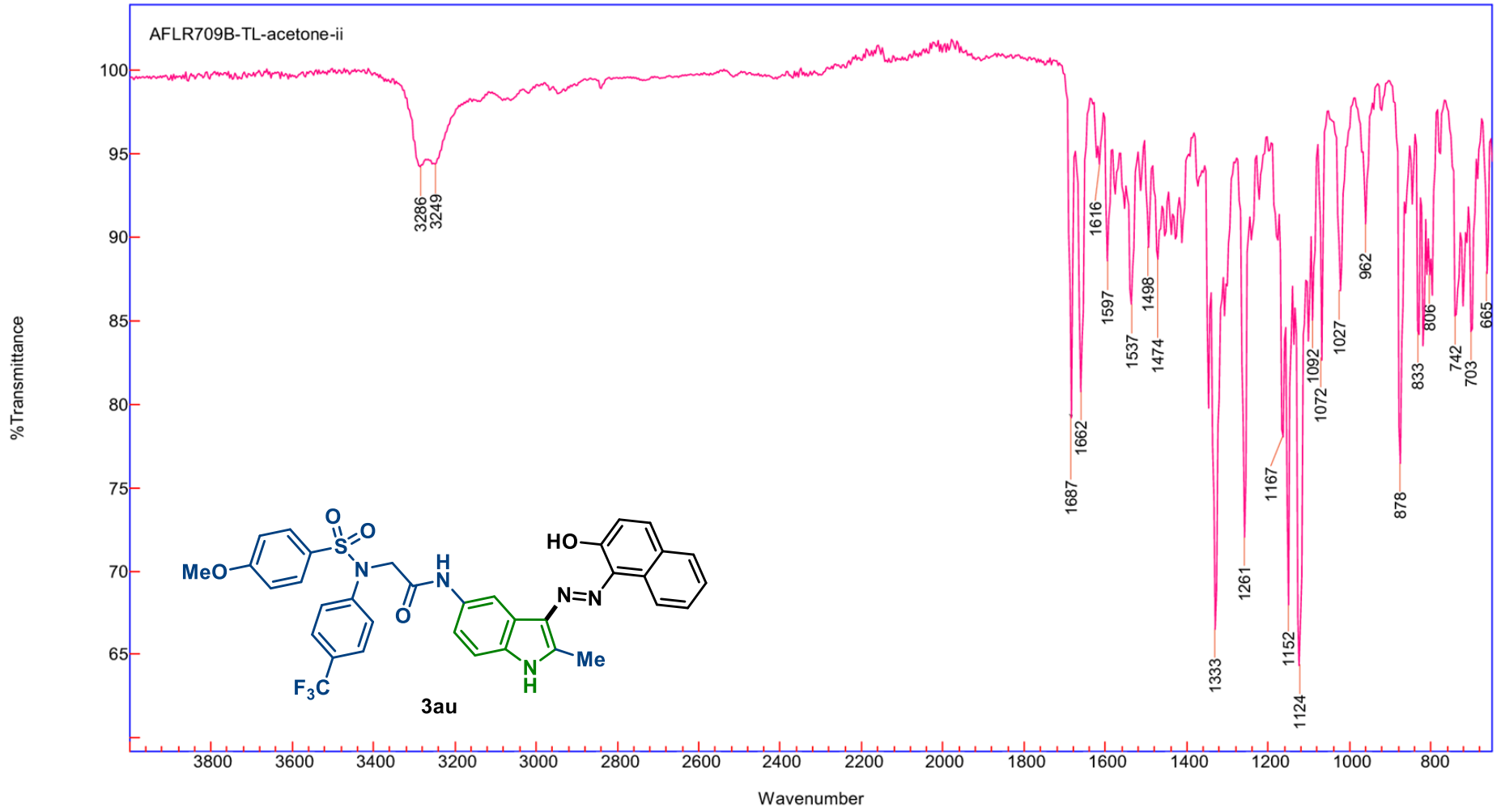
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (3au).



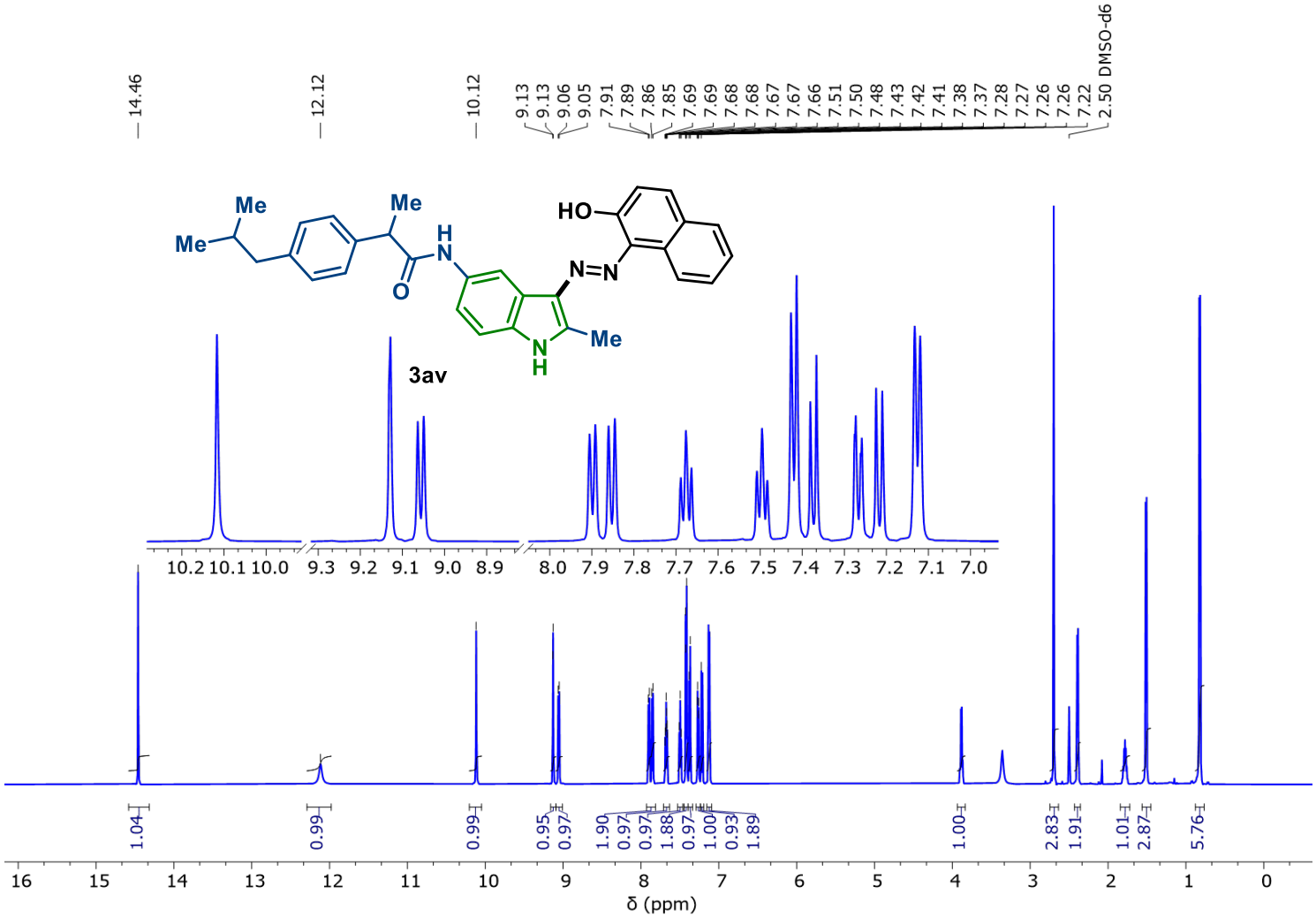
^{19}F NMR (376.5 MHz, DMSO-d_6) spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(4-(trifluoromethyl)phenyl)phenyl)sulfonamido)acetamide (3au).



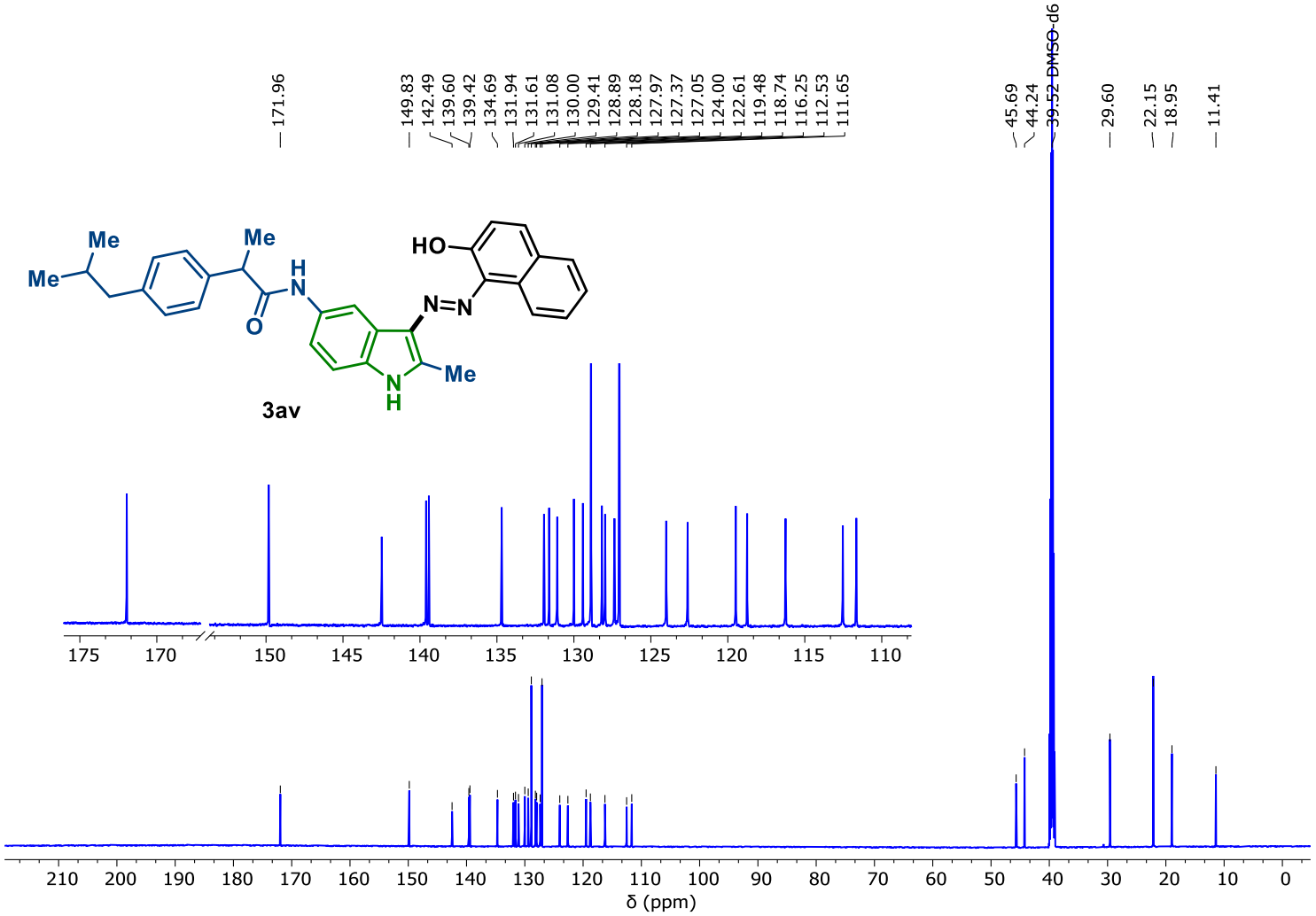
ATR-IR spectrum of (*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-((4-methoxy-*N*-(4-(trifluoromethyl) phenyl)phenyl)sulfonamido)acetamide (3au).



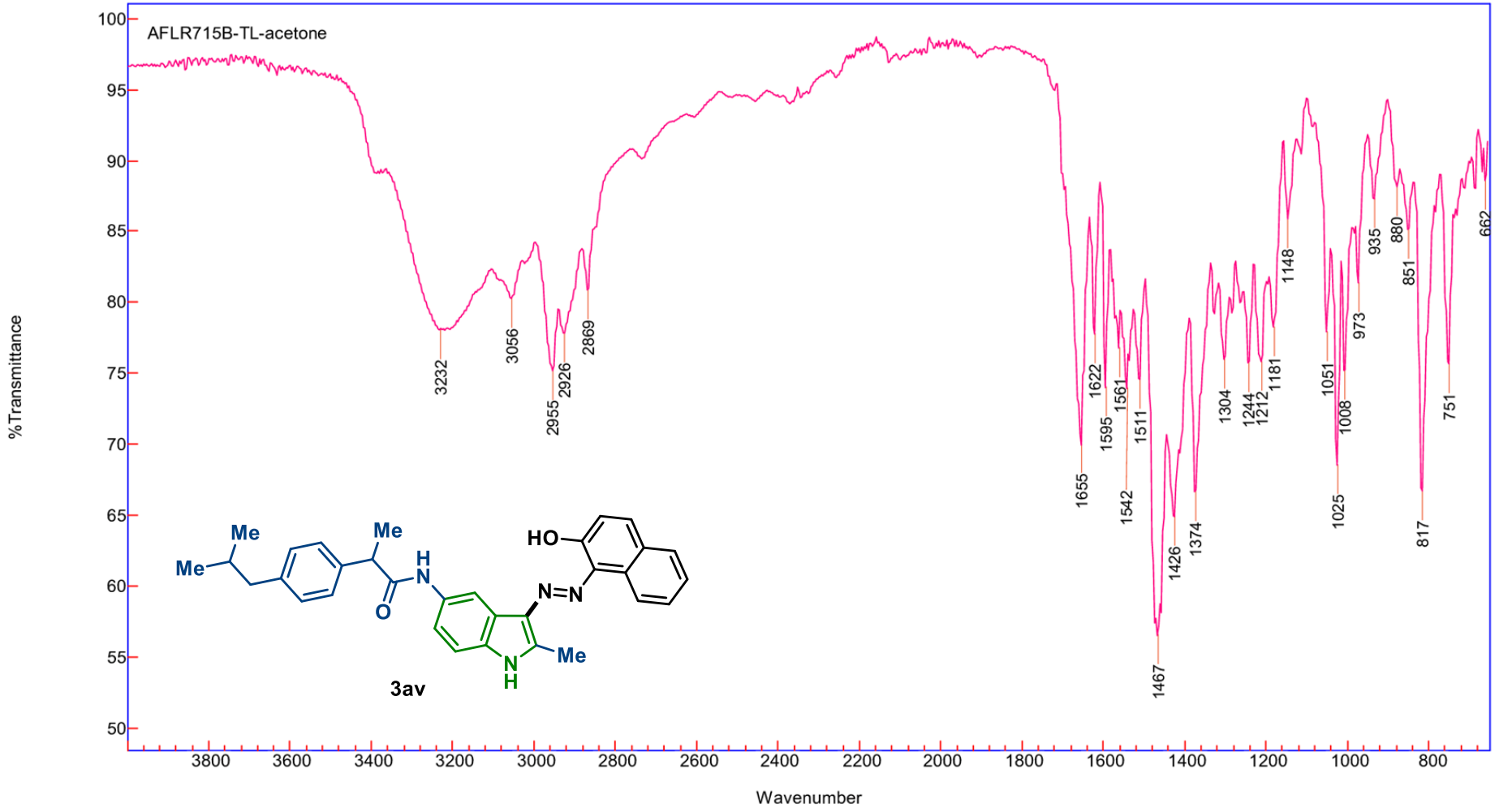
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of ((*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-(4-isobutylphenyl)propanamide (3av).



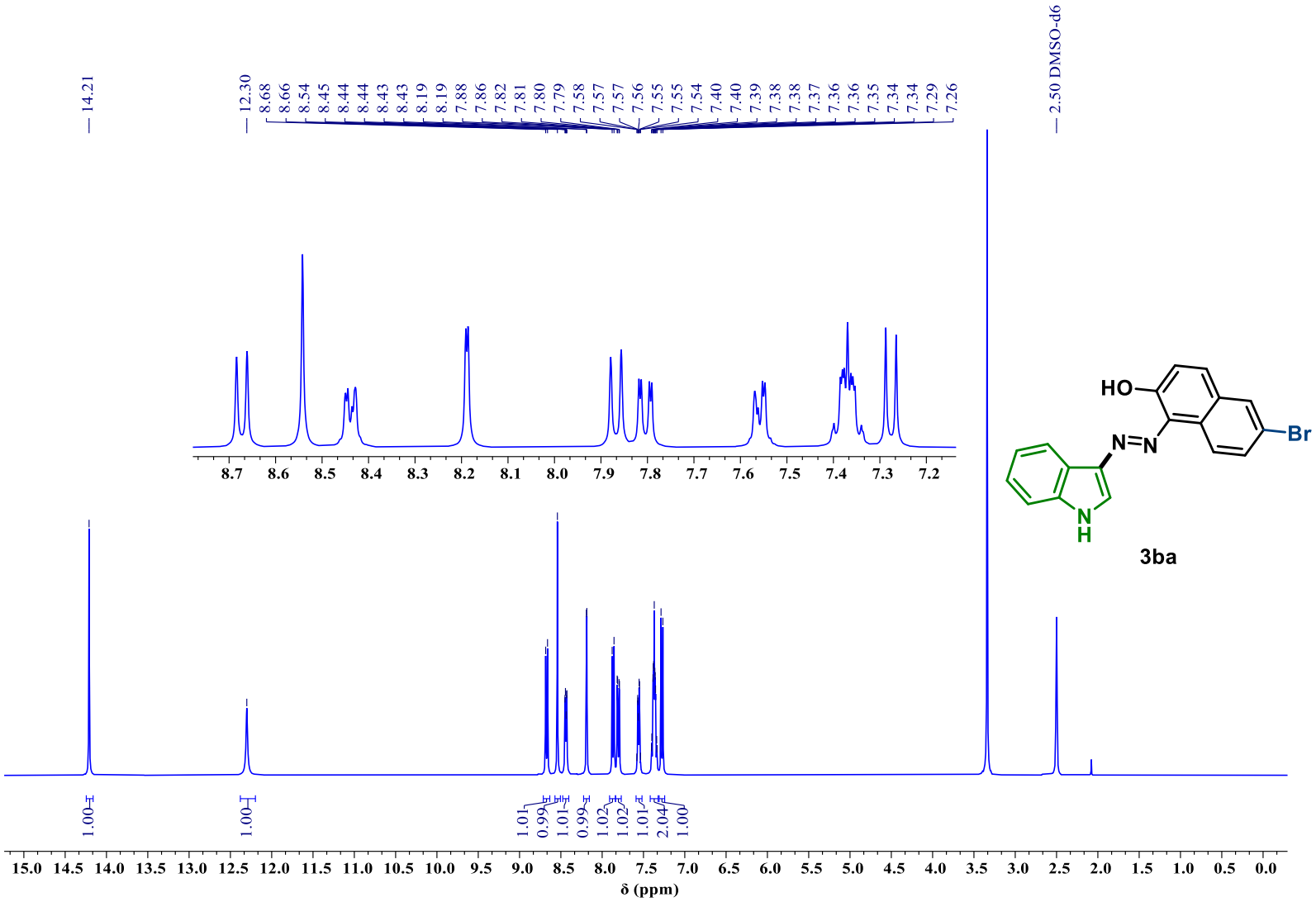
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of ((*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-(4-isobutylphenyl)propanamide (3av).



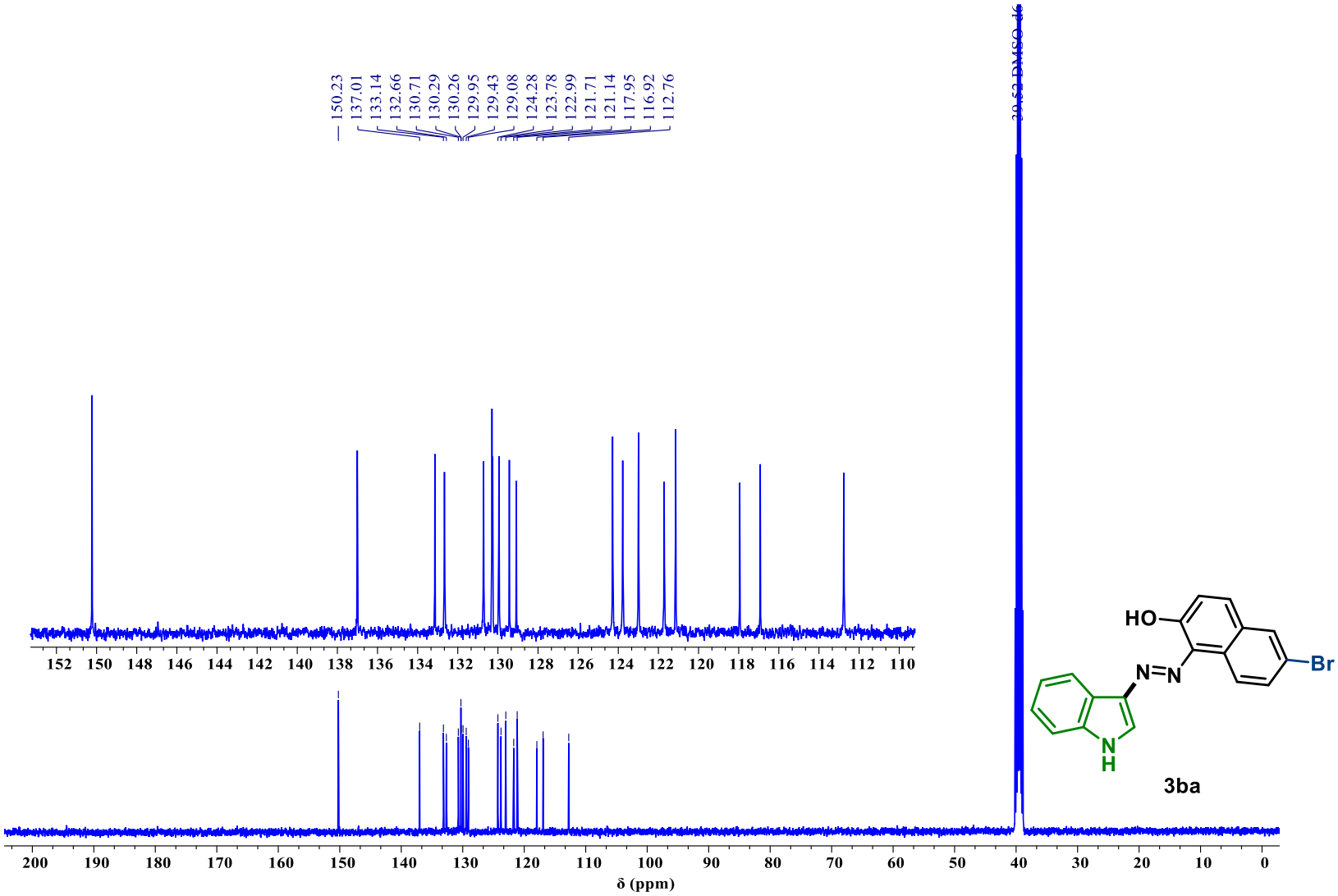
ATR-IR spectrum of ((*E*)-*N*-(3-((2-hydroxynaphthalen-1-yl)diazenyl)-2-methyl-1*H*-indol-5-yl)-2-(4-isobutylphenyl)propanamide (3av).



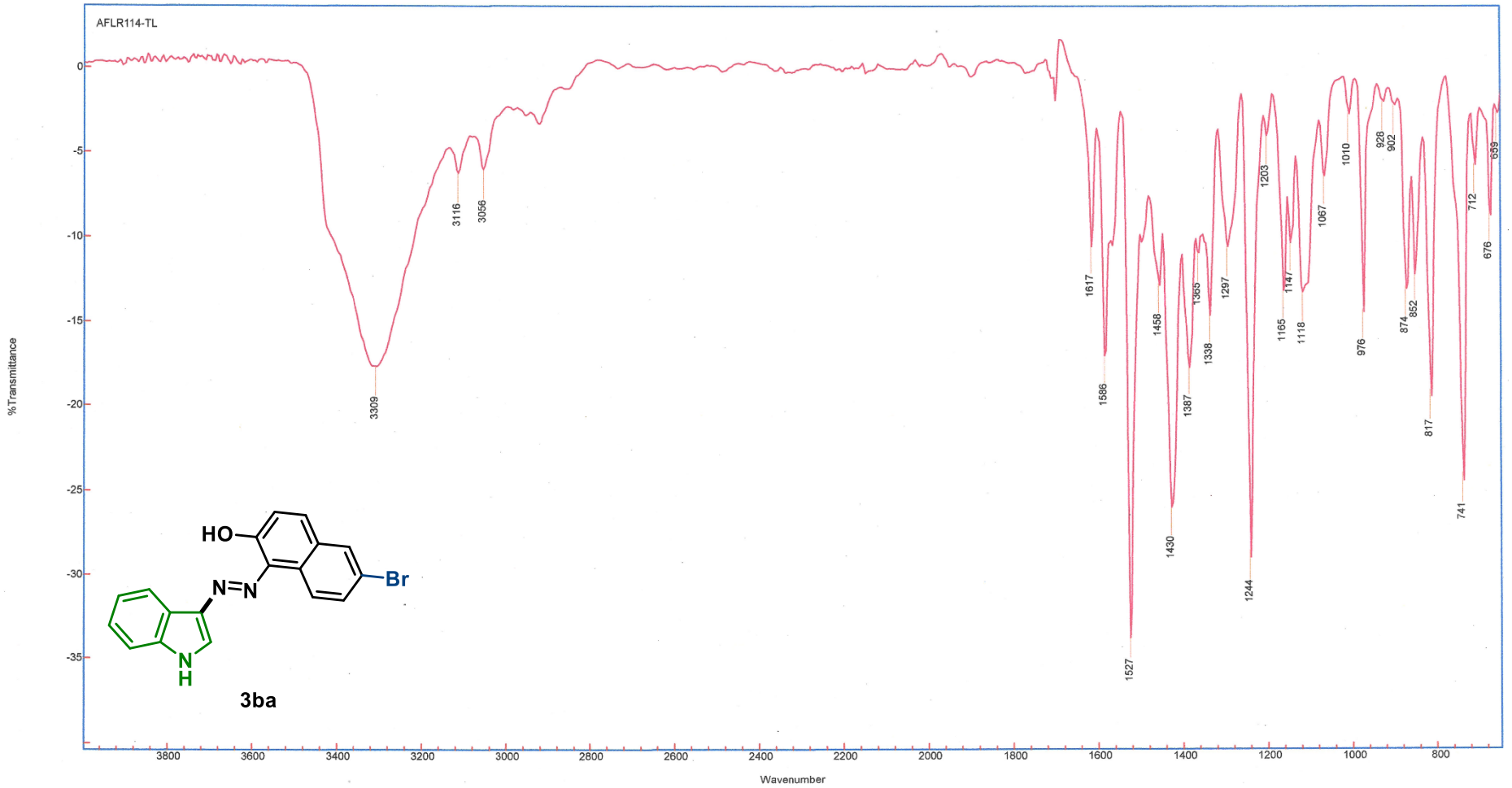
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-Indol-3-yl)diazenyl)-6-bromonaphthalen-2-ol (3ba).



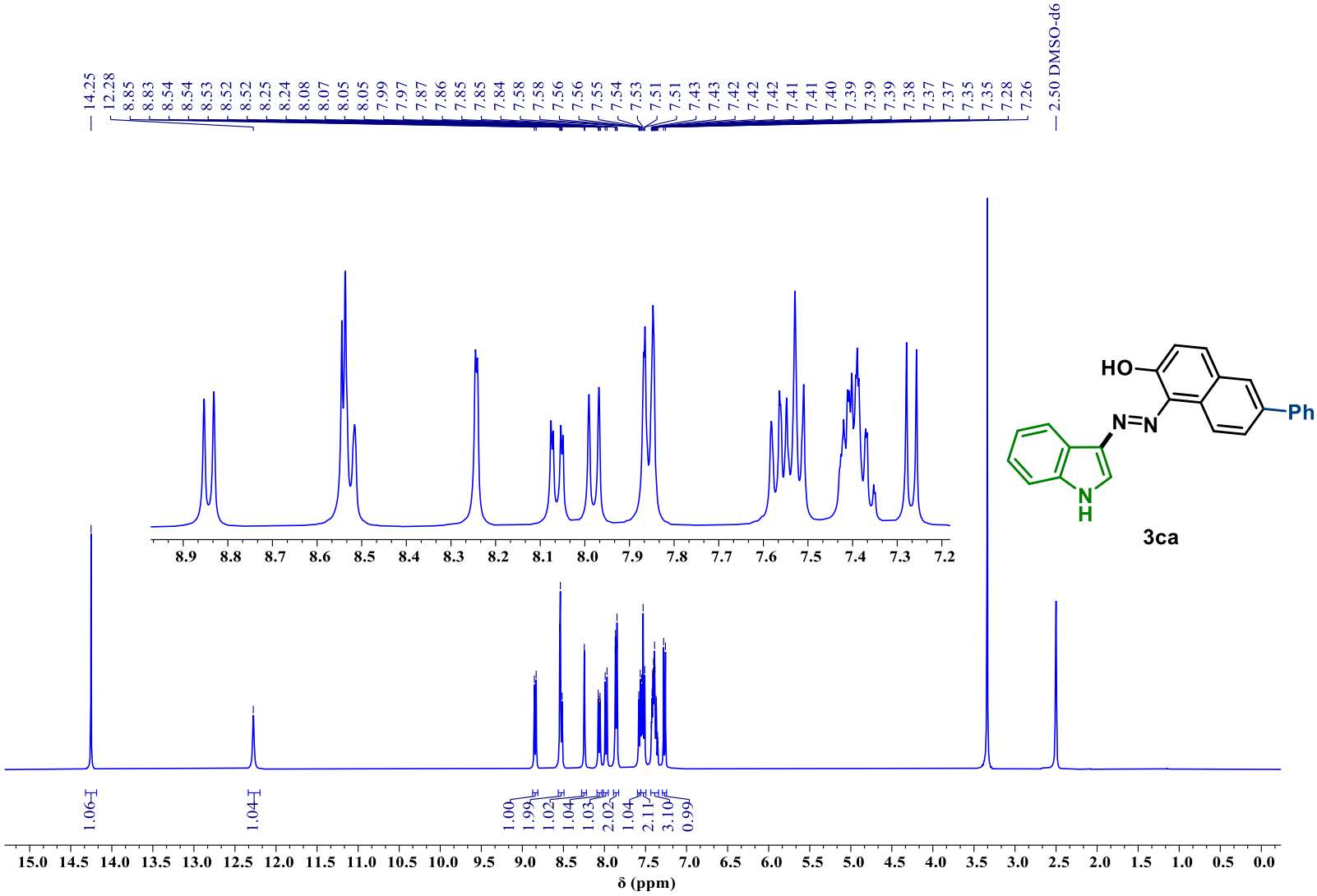
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-bromonaphthalen-2-ol (3ba).



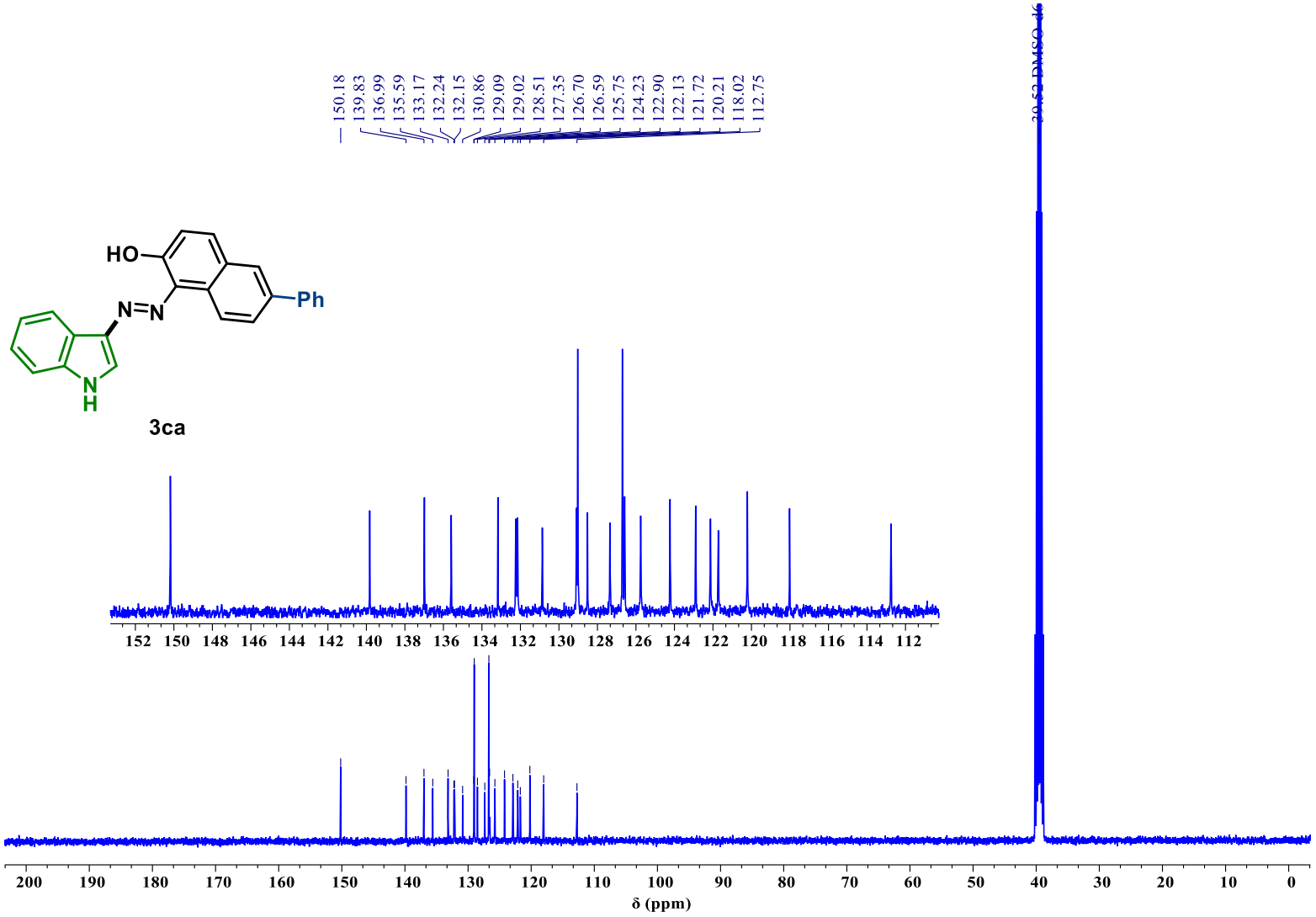
ATR-IR spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-bromonaphthalen-2-ol (3ba).



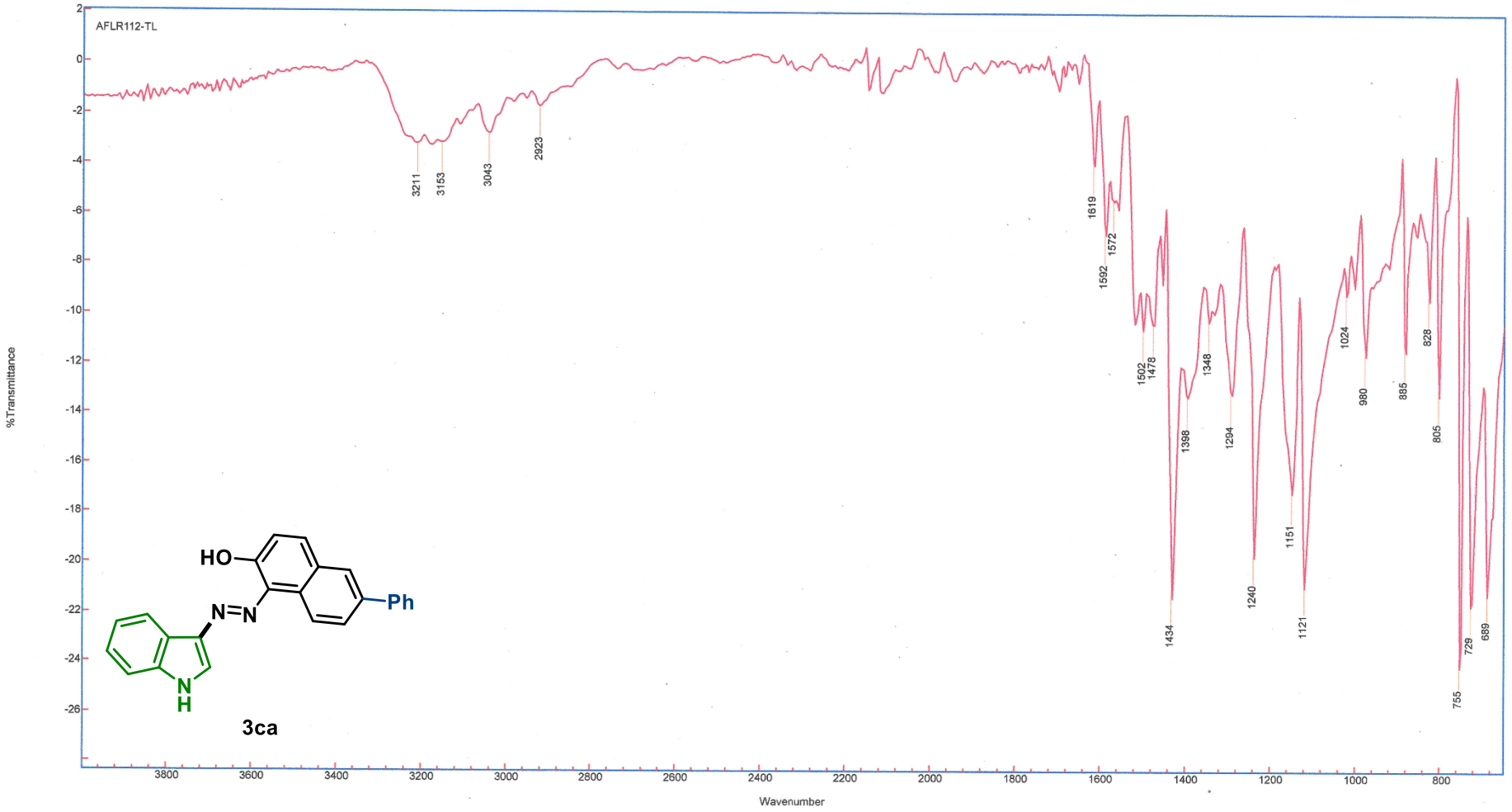
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-phenylnaphthalen-2-ol (3ca).



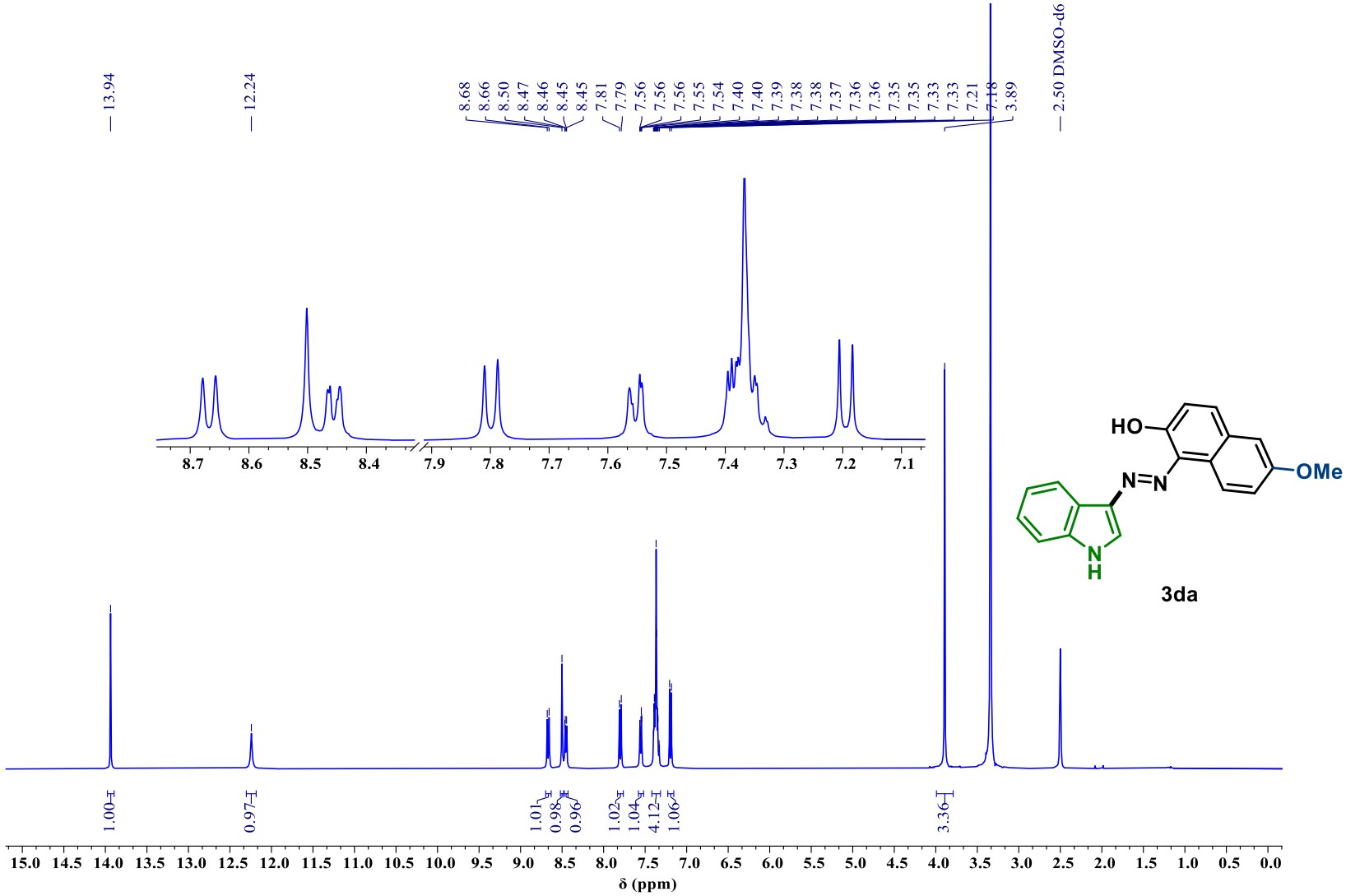
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-phenylnaphthalen-2-ol (3ca).



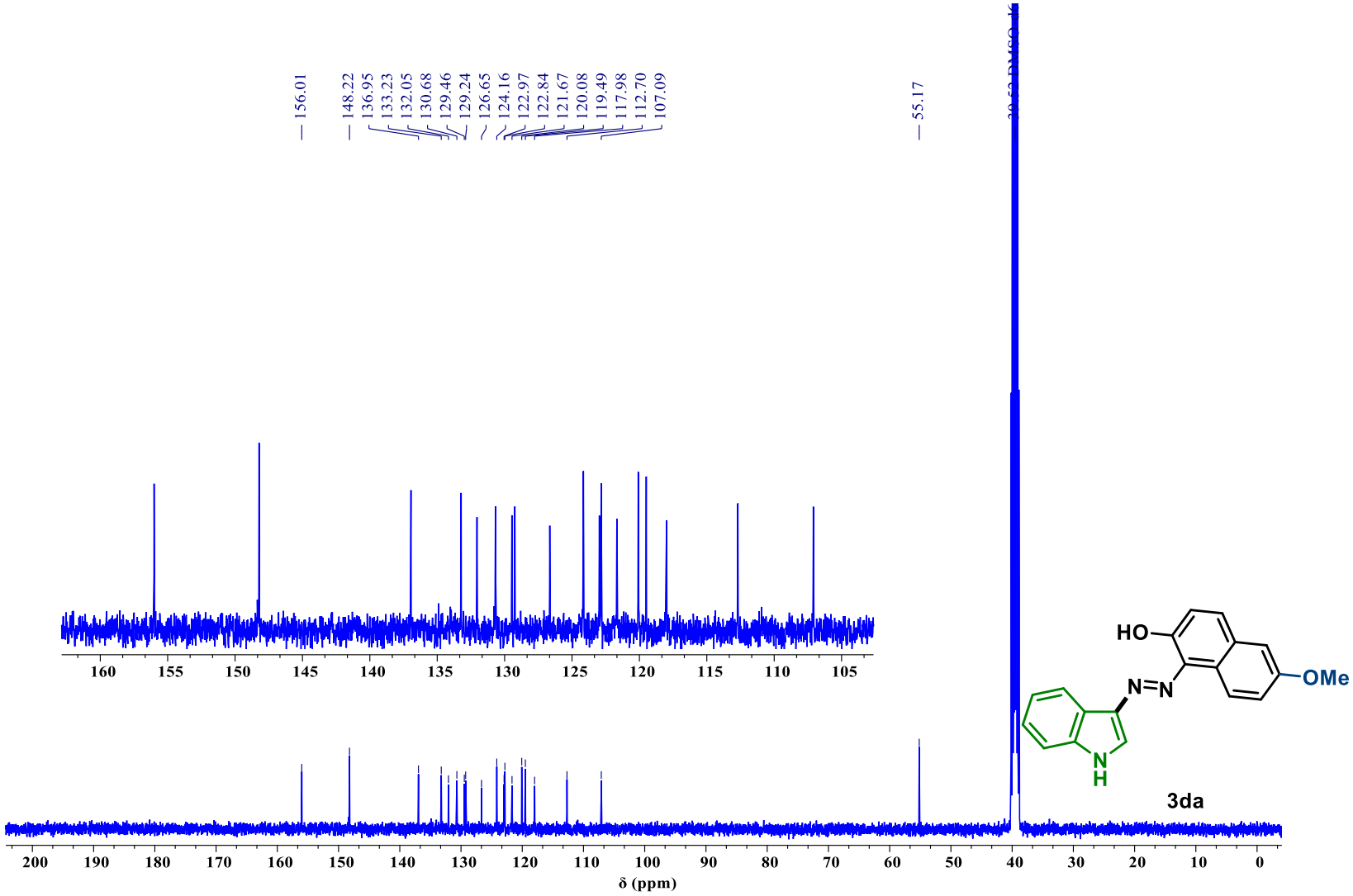
ATR-IR spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-phenylnaphthalen-2-ol (3ca).



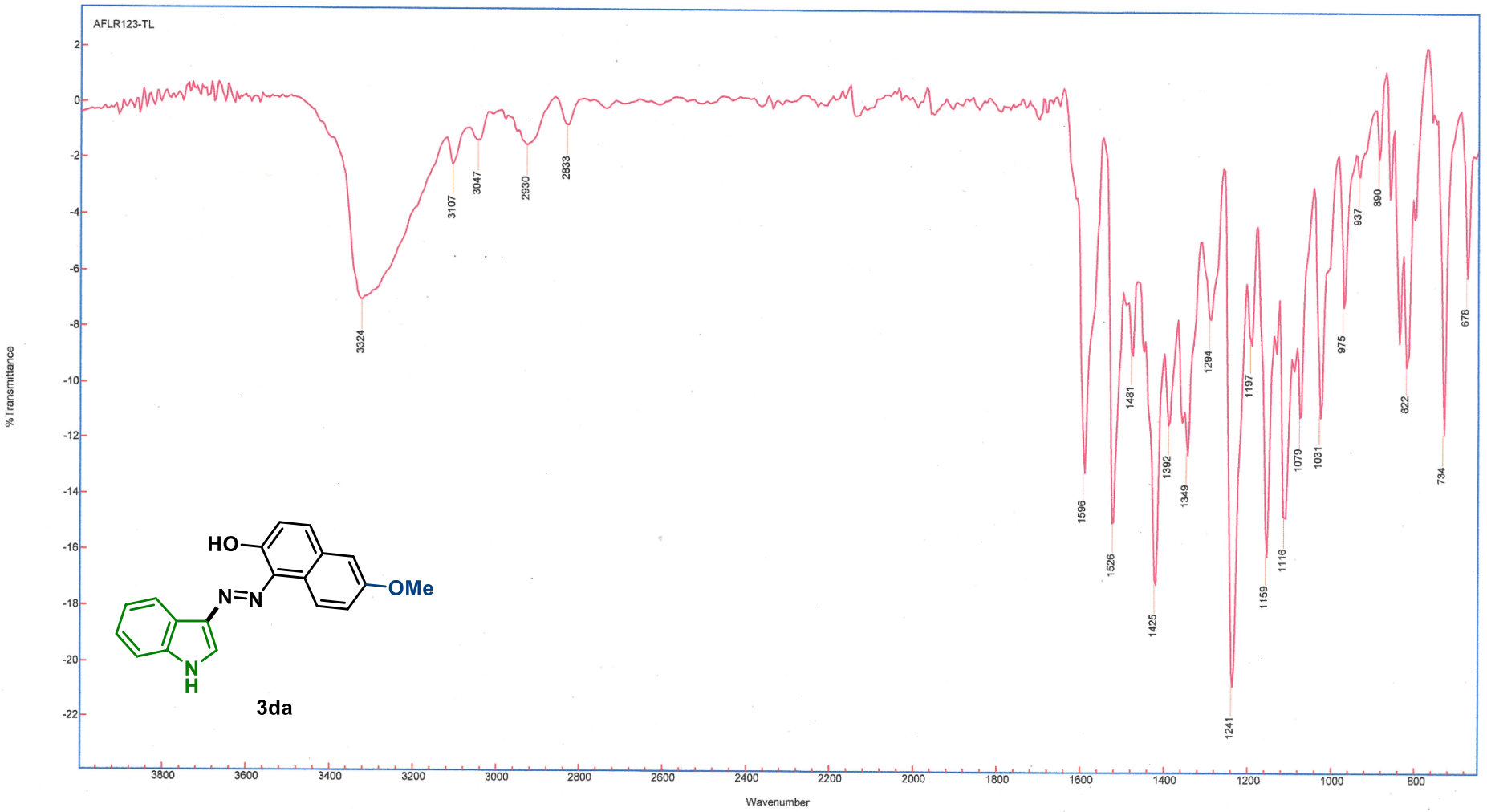
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-methoxynaphthalen-2-ol (3da).



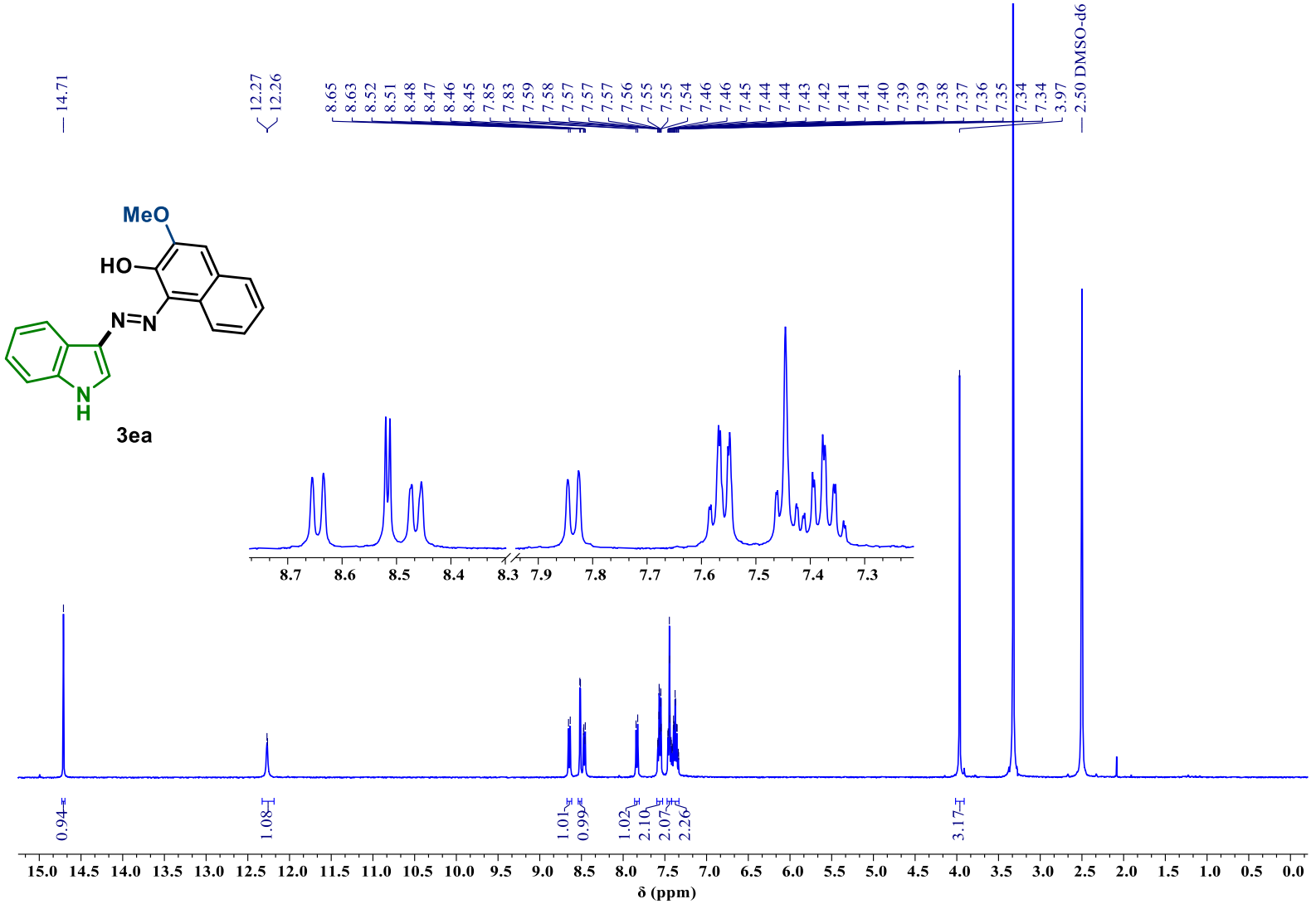
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-methoxynaphthalen-2-ol (3da).



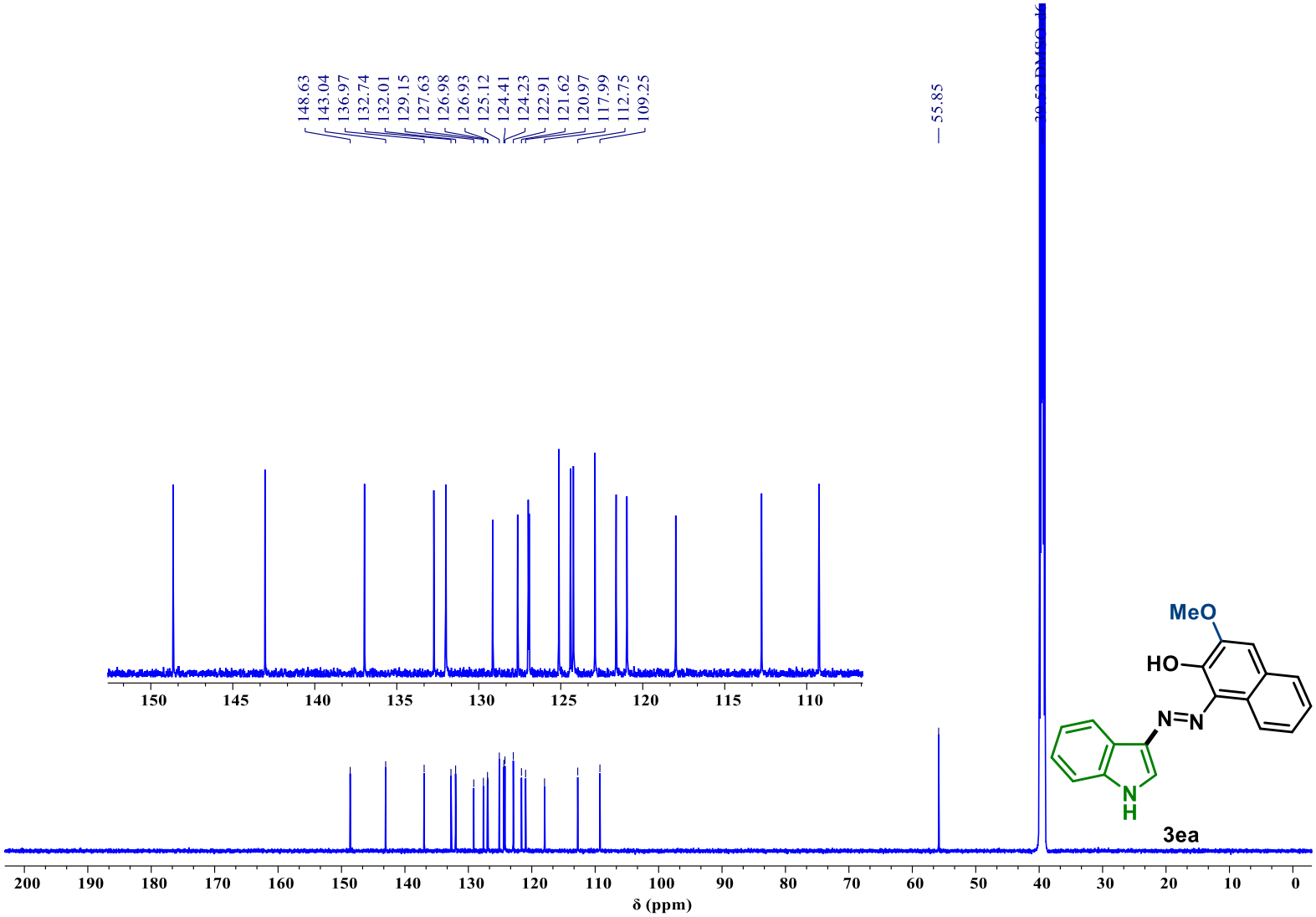
ATR-IR spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-6-methoxynaphthalen-2-ol (3da).



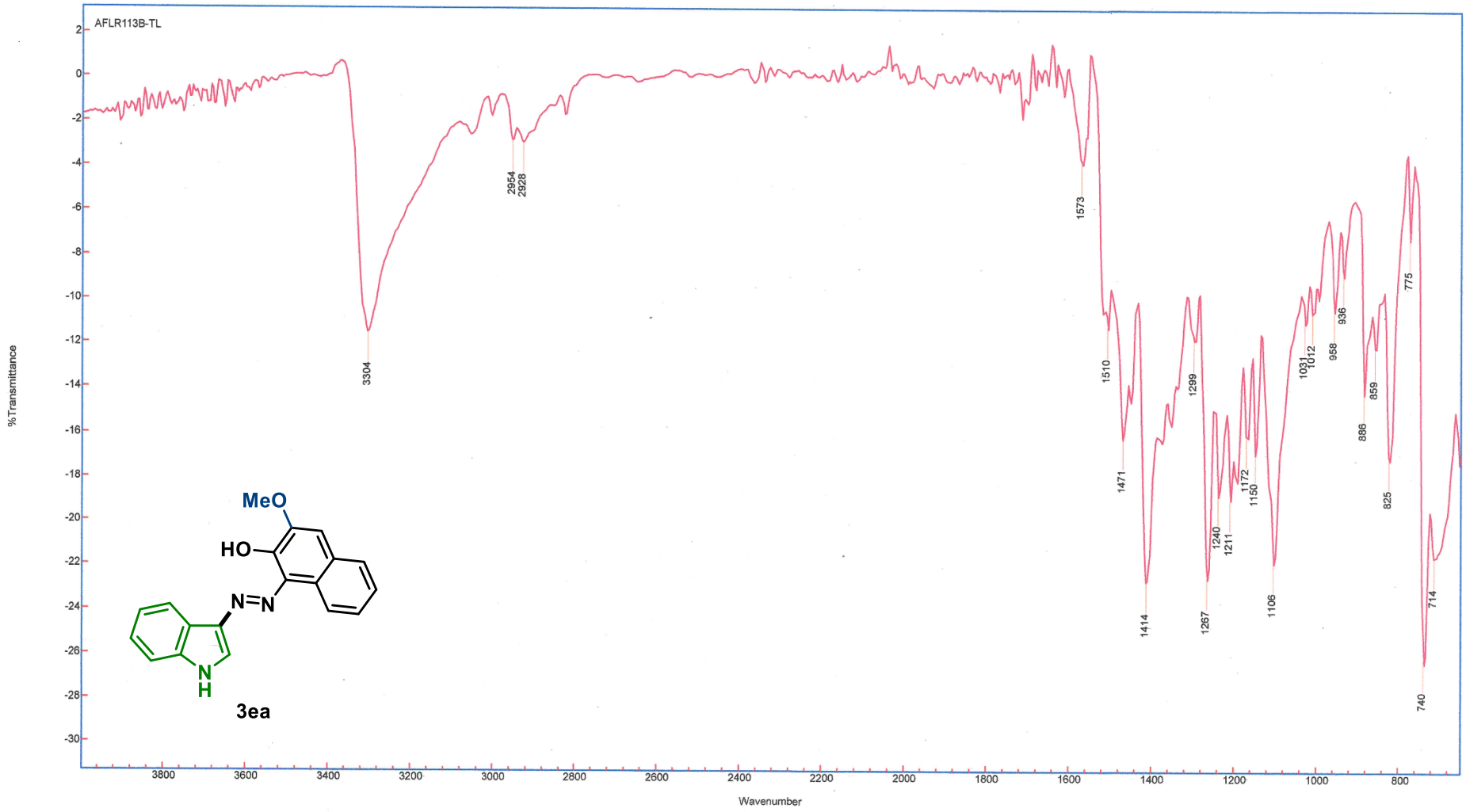
^{1}H NMR (600 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-3-methoxynaphthalen-2-ol (3ba).



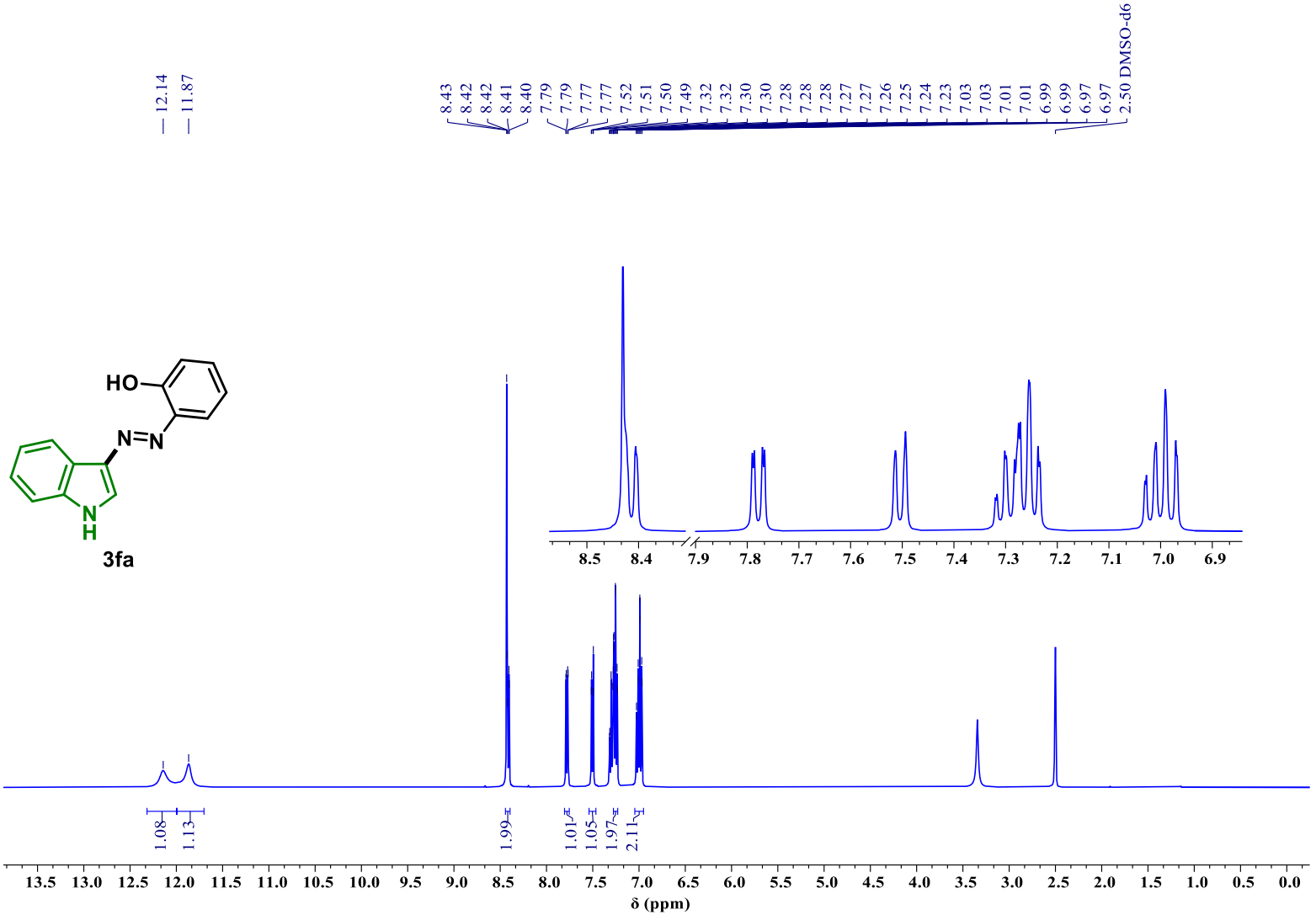
^{13}C NMR (151 MHz, DMSO-d_6) spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-3-methoxynaphthalen-2-ol (3ba).



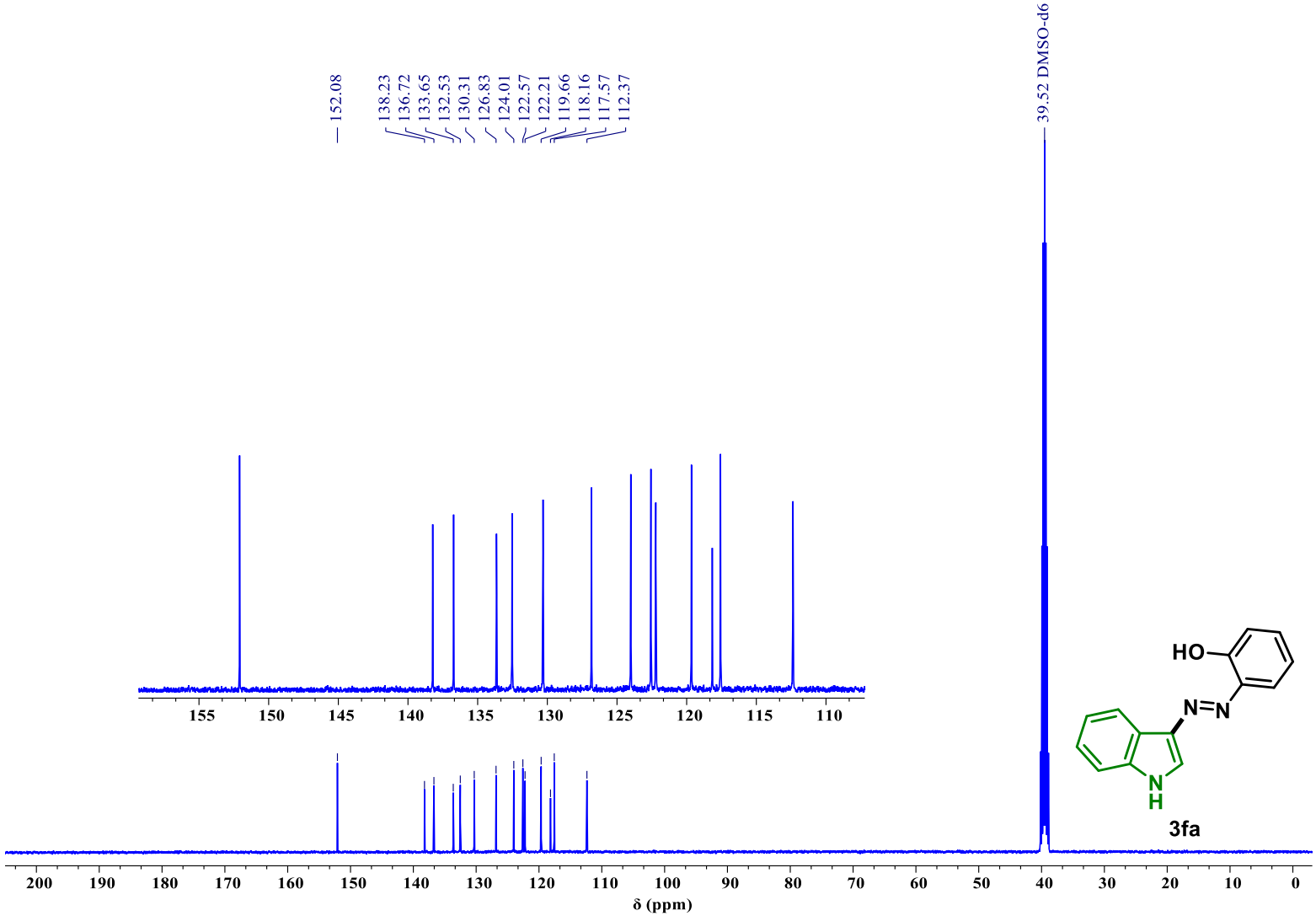
ATR-IR spectrum of (*E*)-1-((1*H*-indol-3-yl)diazenyl)-3-methoxynaphthalen-2-ol (3ba).



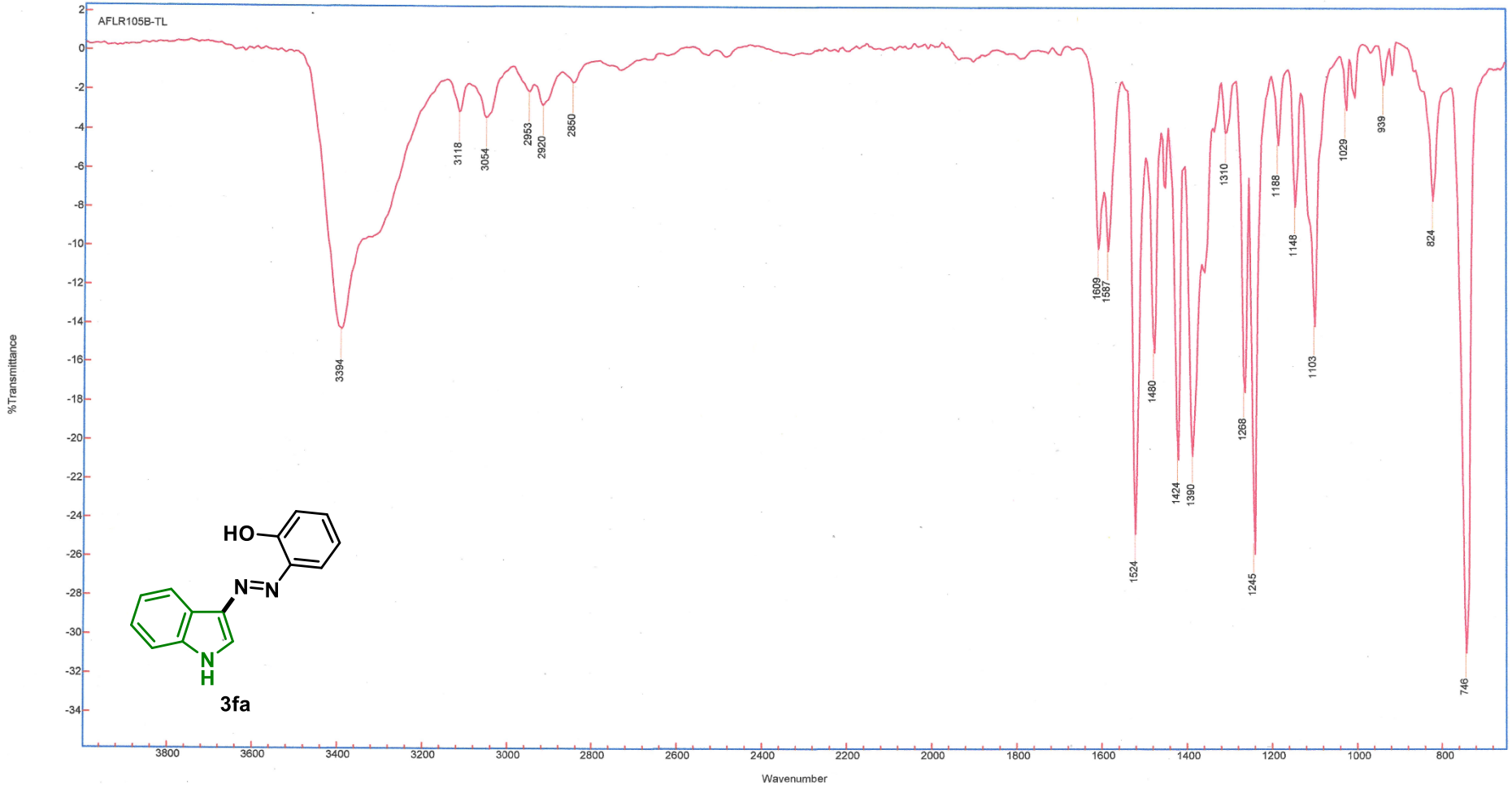
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-2-((1*H*-indol-3-yl)diazenyl)phenol (3fa).



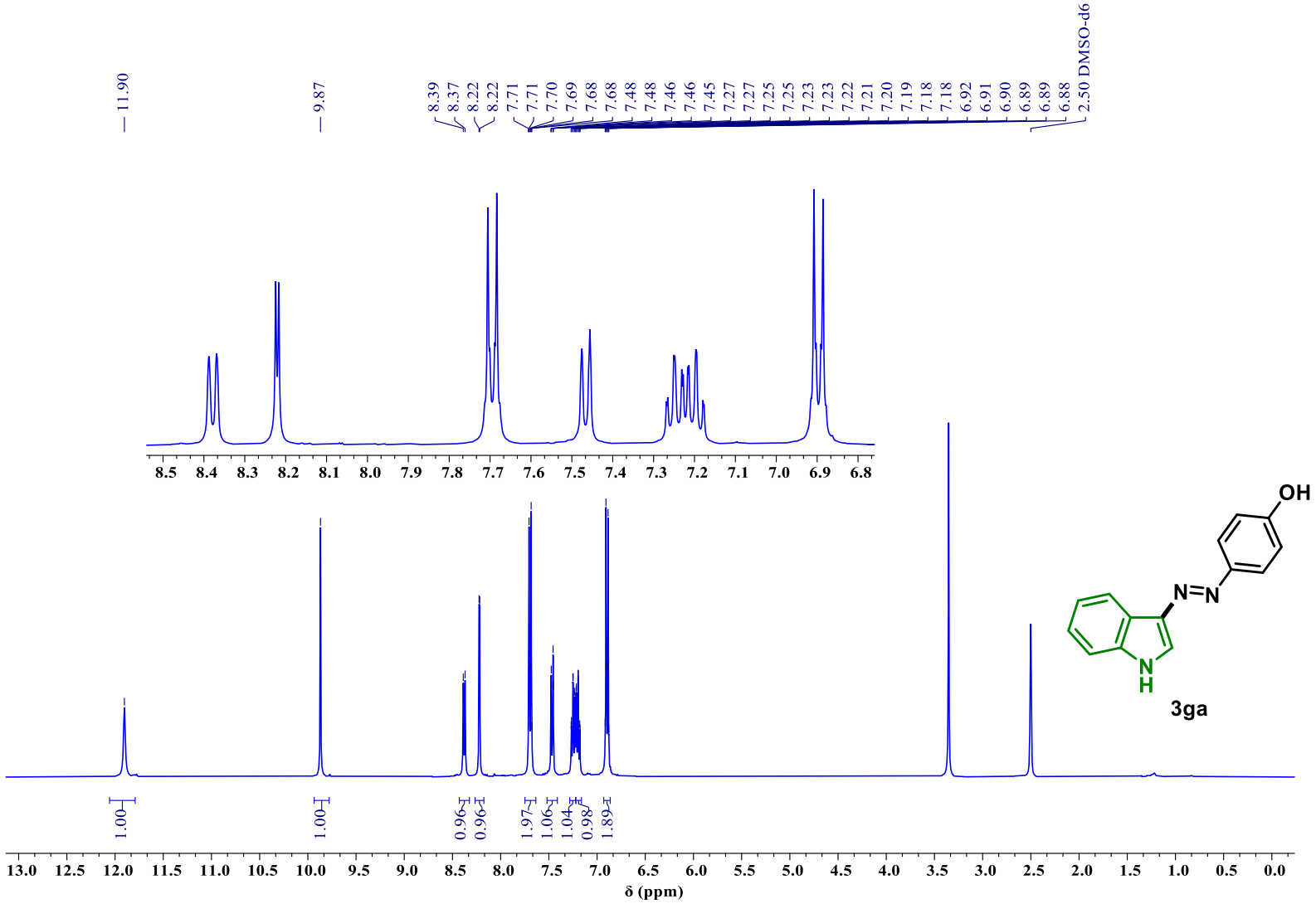
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-2-((1*H*-indol-3-yl)diazenyl)phenol (3fa).



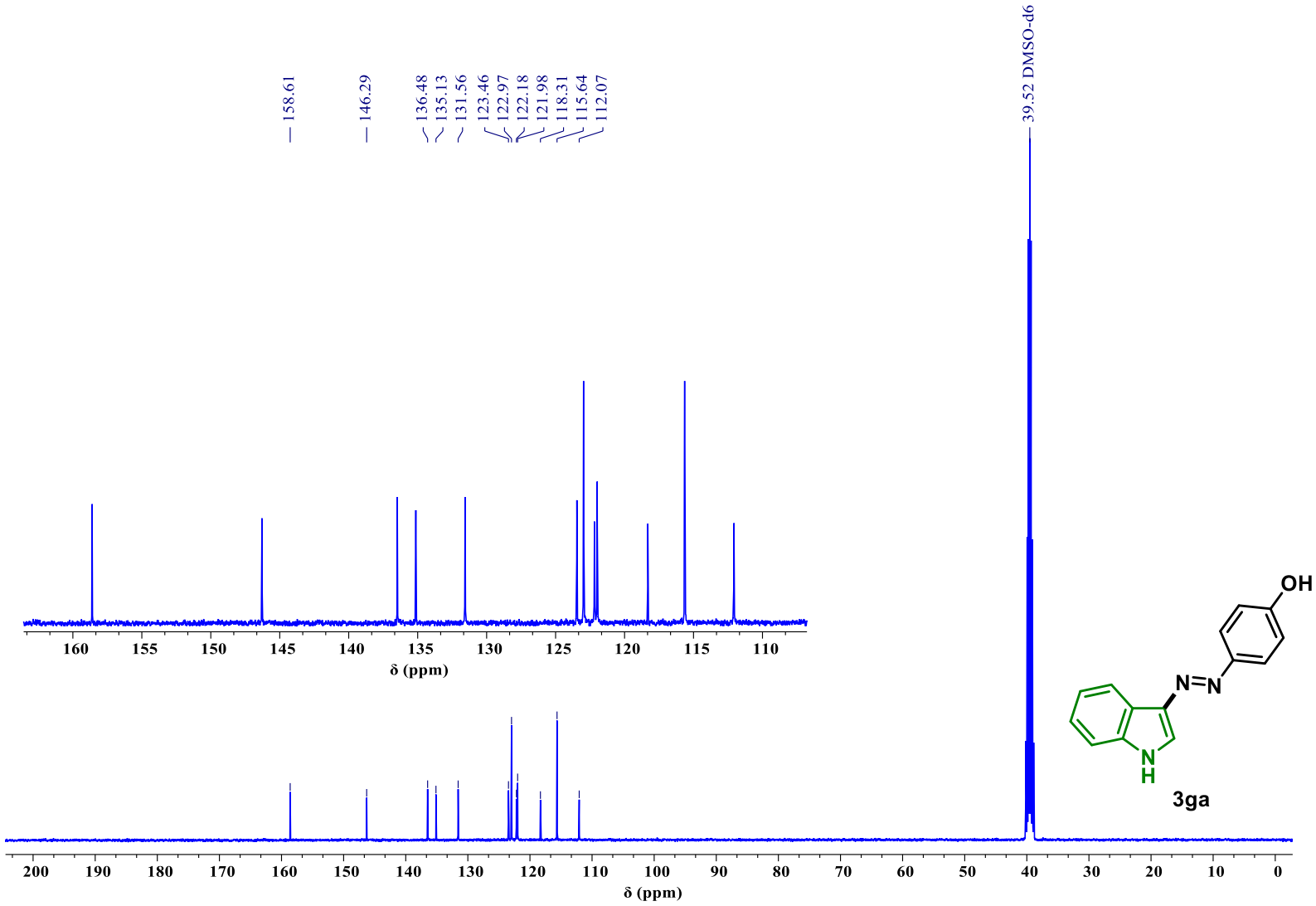
ATR-IR spectrum of (*E*)-2-((1*H*-indol-3-yl)diazenyl)phenol (3fa).



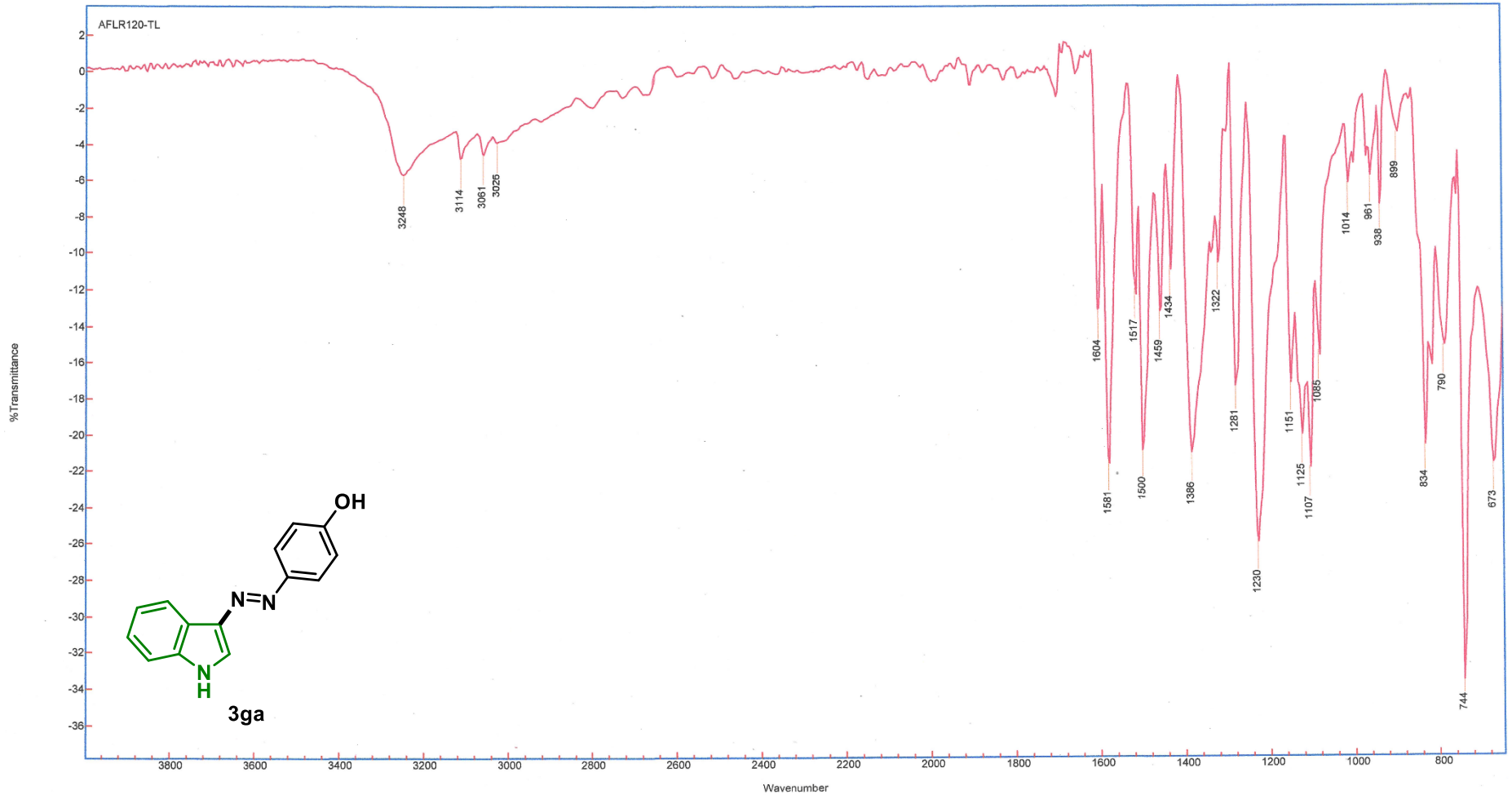
^{1}H NMR (400 MHz, DMSO-d_6) spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)phenol (3ga).



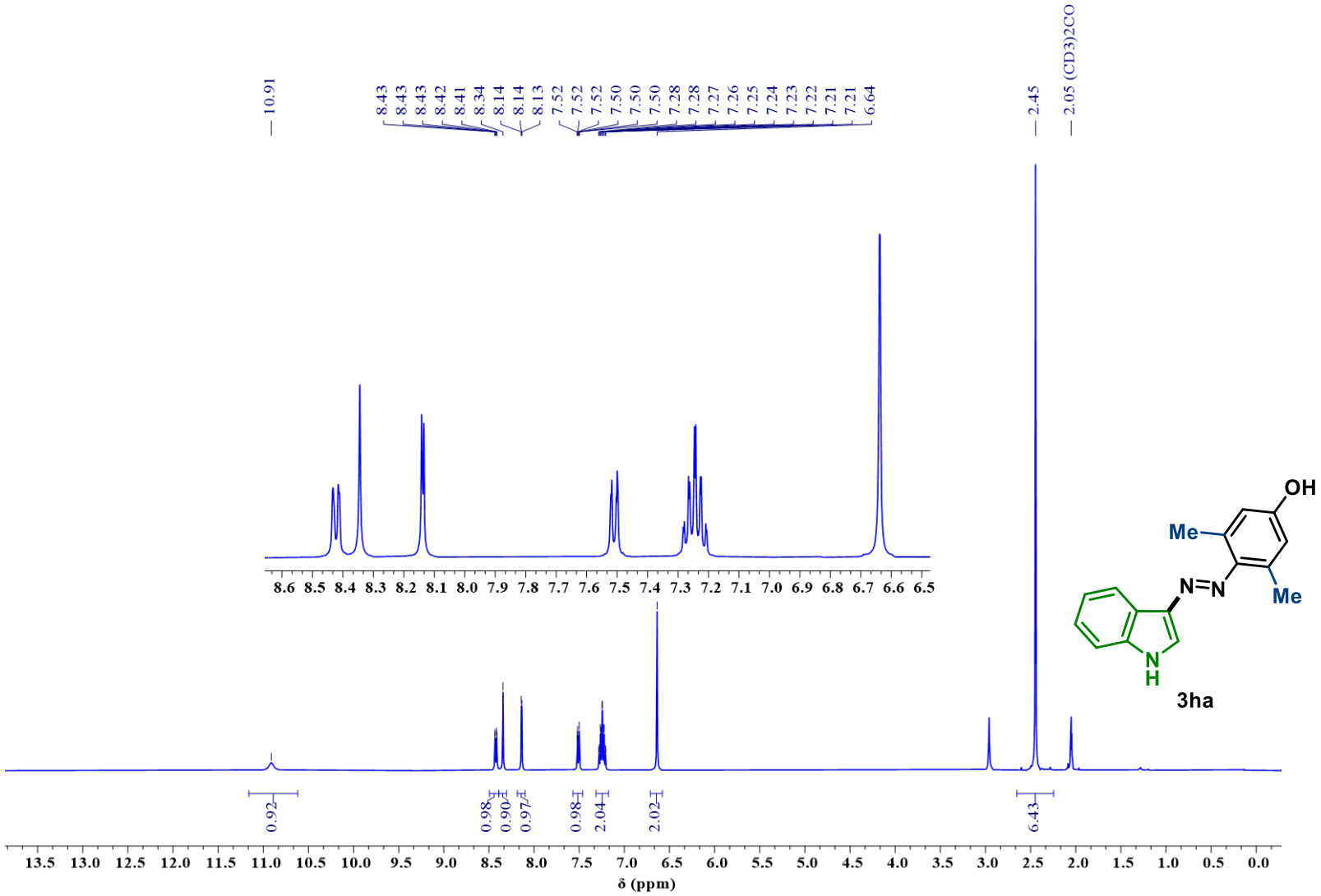
^{13}C NMR (100 MHz, DMSO-d_6) spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)phenol (3ga).



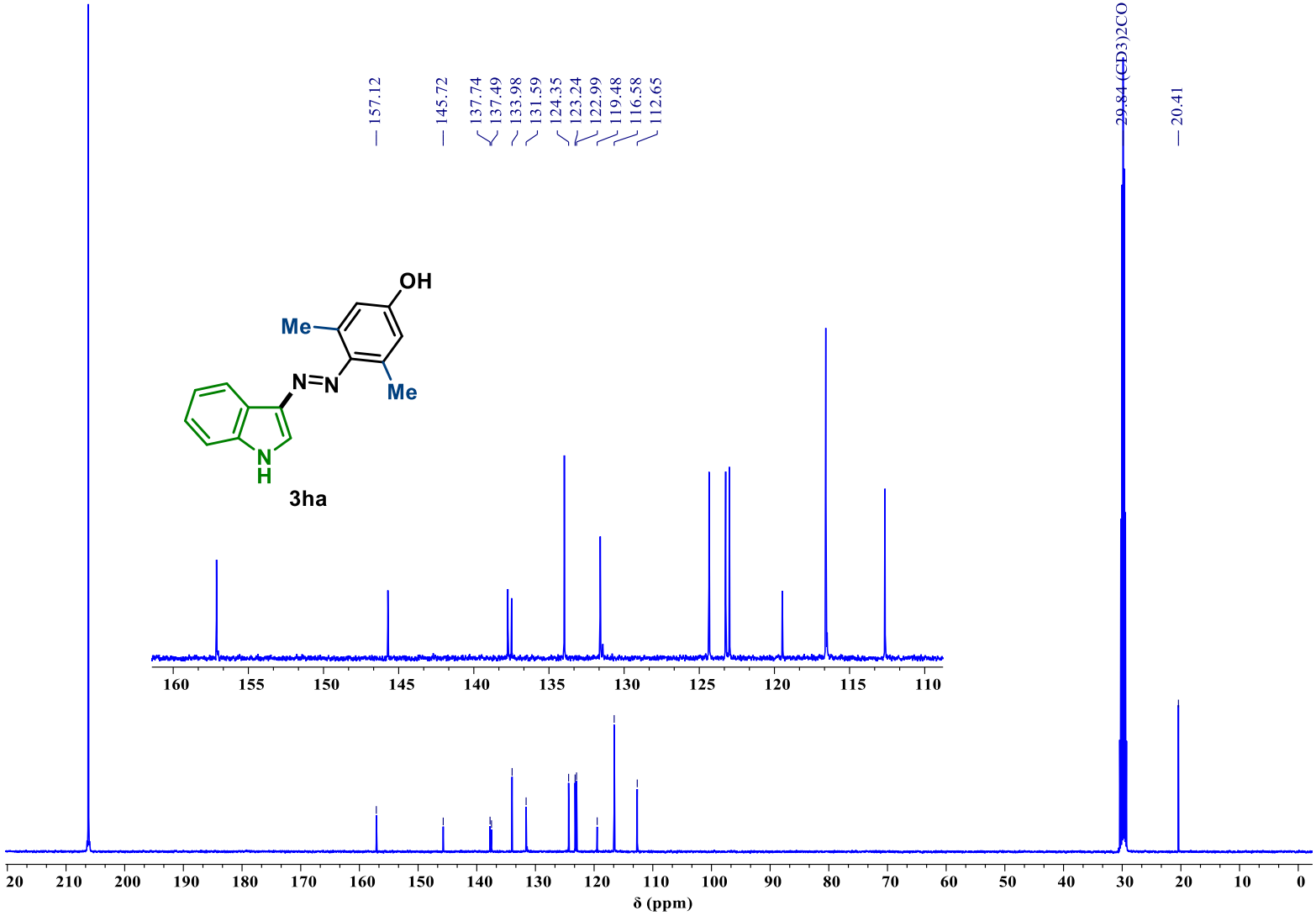
ATR-IR spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)phenol (3ga).



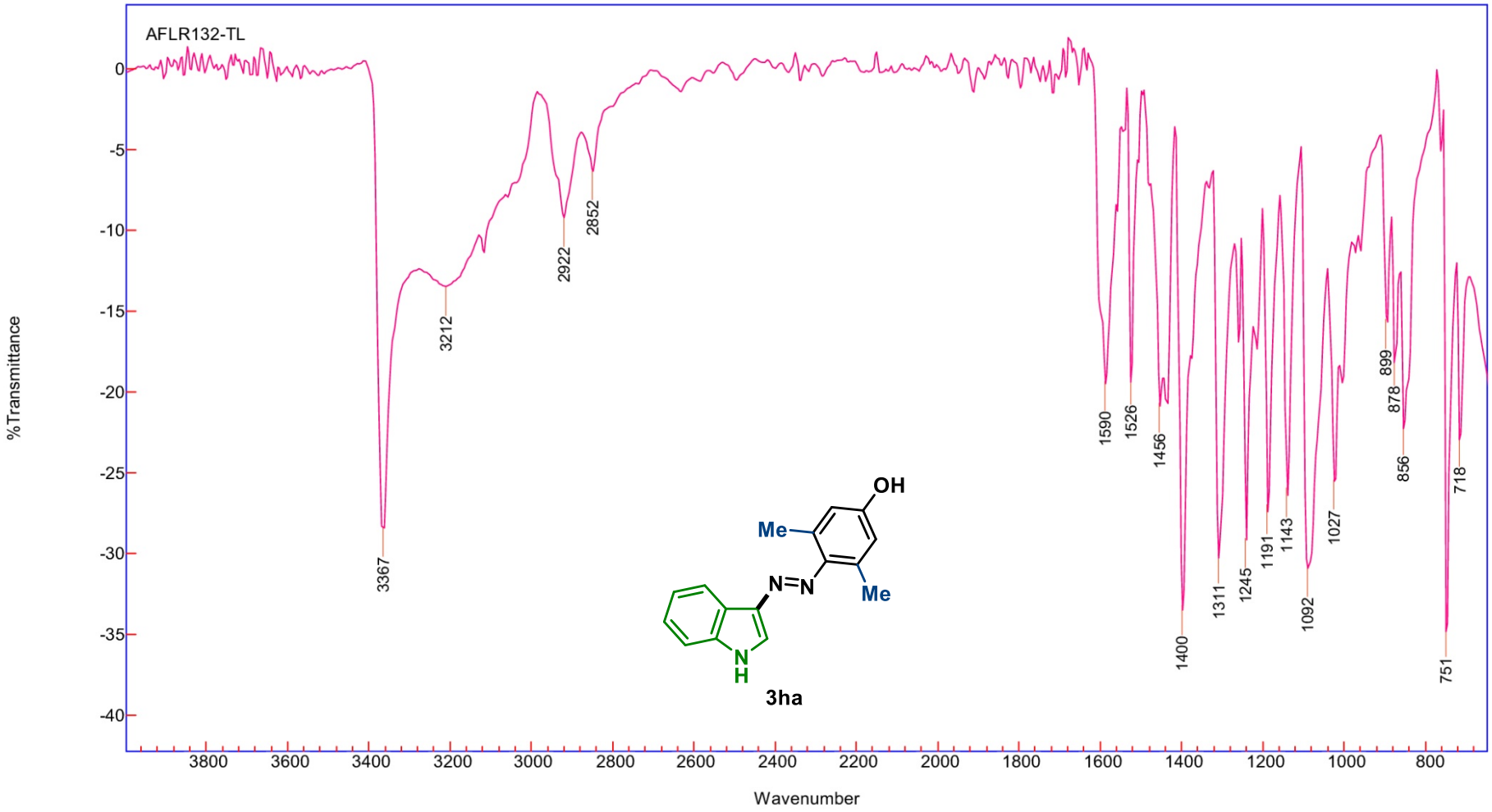
^{1}H NMR (400 MHz, acetone-d_6) spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)-3,5-dimethylphenol (3ha).



^{13}C NMR (100 MHz, acetone-d_6) spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)-3,5-dimethylphenol (3ha).



ATR-IR spectrum of (*E*)-4-((1*H*-indol-3-yl)diazenyl)-3,5-dimethylphenol (3ha).



5. X-Ray crystal drawings of 3ar and 3ba

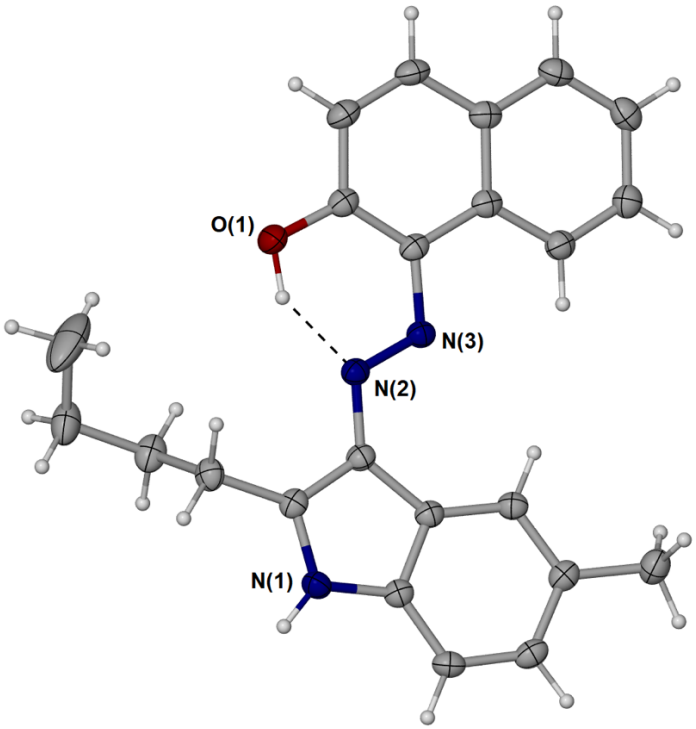


Figure S12. X-ray crystal structure drawing of **3ar** with thermal ellipsoids at 50% probability levels. [8]

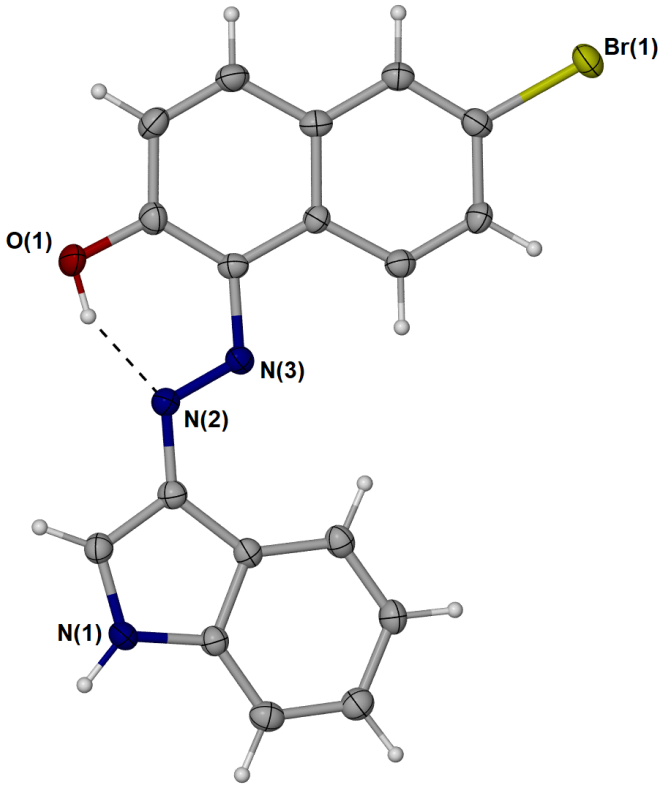


Figure S13. X-ray crystal structure drawing of **3ba** with thermal ellipsoids at 50% probability levels.

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S38 CCDC 2251735 (**3ar**) 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.

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