

Supplementary Information

Metal-free Synthesis of 3,3'-Bisindolylmethanes in Water Using $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ as Pre-catalyst

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1. General information

All chemicals were purchased from J&K Scientific or Bidepharm unless otherwise specified. $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was purchased from Energy Chemical. Anhydrous solvents were purchased from J&K Scientific and directly used. Unless otherwise noted, reagents were commercially available and used as purchased. All reactions were conducted under a nitrogen atmosphere or air by using standard Schlenk or vacuum line techniques. All glassware and vials were oven-dried prior to use. All work-up and purification procedures were carried out with reagent-grade solvents. Analytical thin-layer chromatography (TLC) was performed using glass plates precoated with 0.25 mm Kiesegel 60 F₂₅₄(Merck). The developed chromatography was analyzed by UV lamp (254 nm and 365 nm). Flash chromatography was performed on 200-400 mesh silica gel with the indicated eluents. GC-MS analysis was conducted on an Agilent 7890A GC System with an Agilent 5975C MSD or Bruker SCION TQ with Bruker 456 GC System. Proton Nuclear magnetic resonance (¹H NMR) spectra were recorded at 400 MHz in indicated deuterated solvents and coupling constants (*J*) were reported in Hertz (Hz). Splitting patterns were designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; dd, doublet of doublets, *etc.* The chemical shifts were reported on the δ scale (*ppm*). Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded at 101 MHz and the chemical shifts were accurate to one decimal place or two decimal places to help distinguish overlapping peaks. High resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (Xevo G2-XS QTof) using electrospray ionization (ESI) in positive mode.

2. Starting materials

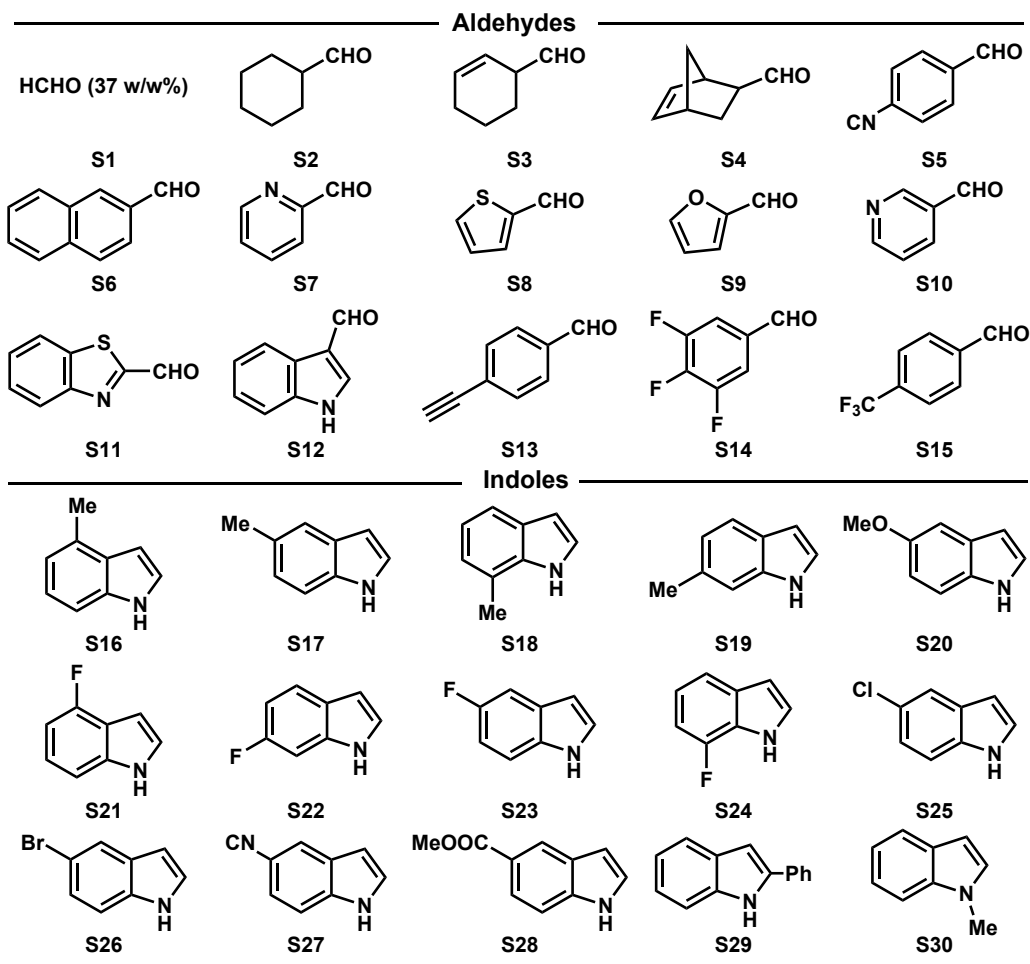


Figure S1. The structure of aldehydes and indoles

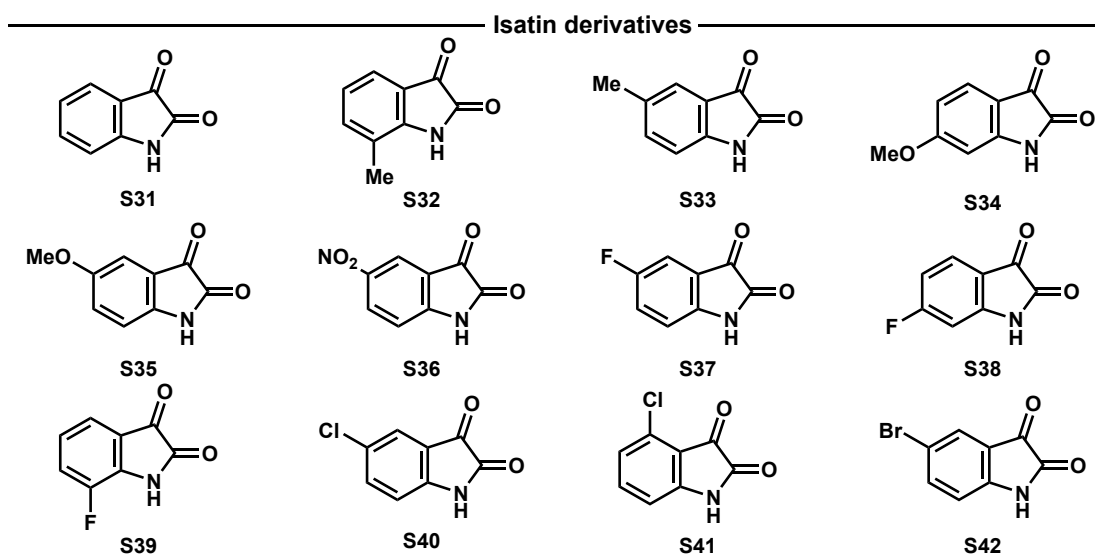
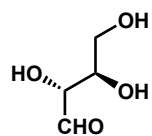
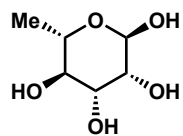


Figure S2. The structure of isatins

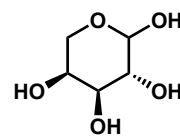
Carbohydrates



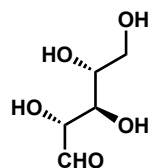
S43
D-(-)-Erythrose



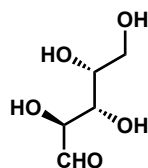
S44
 α -L-Rhamnopyranose
monohydrate



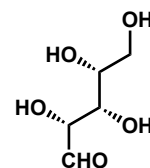
S45
L-(+)-Arabinose



S46
D-Ribose

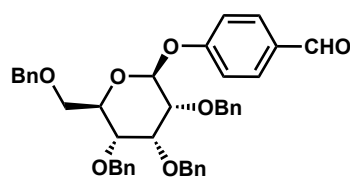


S47
D-Lyxose

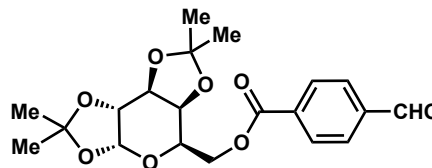


S48
D-(+)-Xylose

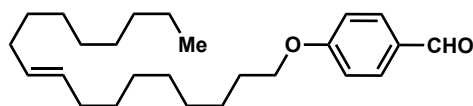
----- **Late-stage natural complex and drugs** -----



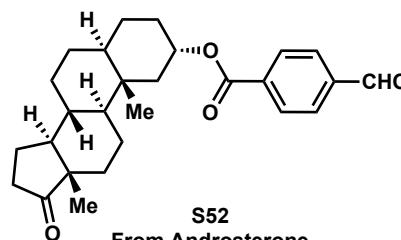
S49
From Helicid



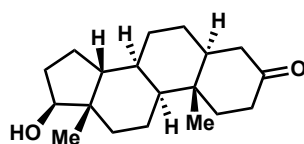
S50
From Galactose



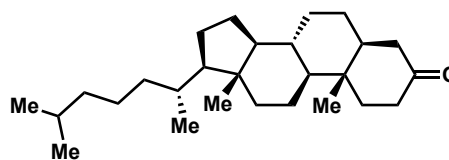
S51
From Oleyl alcohol



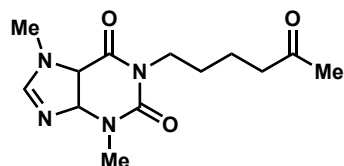
S52
From Androsterone



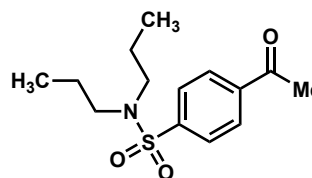
S53
Stanolone



S54
Dihydrocholesterol



S55
Pentoxifylline



S56
From Probenecid

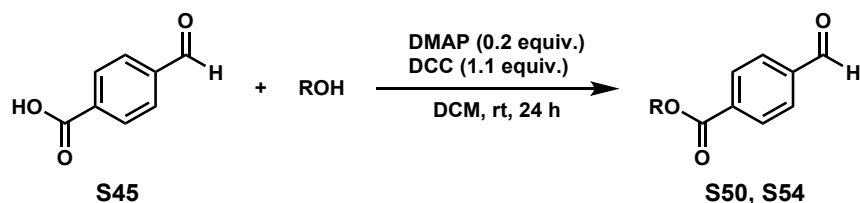
Figure S3. The structure of carbohydrates, natural complex and drugs

3. Synthesis and characterization of substrates

Substrates S1-S49, S51-S53 and S55 in Figures S1-S3 are commercially available.

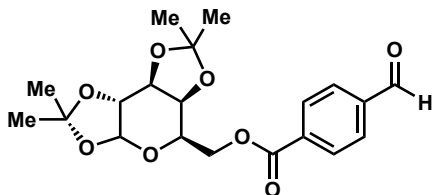
Preparation of S50, S54 and S56

Substrates S50 and S54 in Supplementary Figure S3 were prepared according to the method below.¹⁻⁷



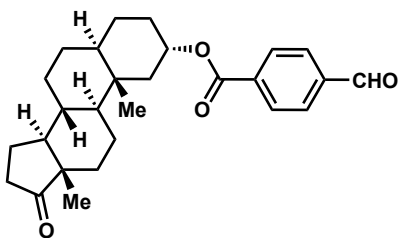
To a suspension of 4-formylbenzoic acid S45 (0.5 g, 3.33 mmol) in dichloromethane (8 mL) were added *N,N*-dimethyl-4-aminopyridine (DMAP, 81.4 mg, 0.67 mmol), alcohol (1.13 g, 4.33 mmol) and *N,N'*-dicyclohexylcarbodiimide (DCC, 0.756 g, 3.66 mmol). The mixture was stirred at room temperature for 24 h then diethyl ether (20 mL) was added. The precipitate was filtered through celite and the filtrate was successively washed with a 1 N aqueous solution of HCl (2 × 20 mL), saturated aqueous NaHCO₃ solution (2 × 20 mL) and brine (2 × 20 mL). The organic phase was then dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography (PE/EA, 10:1, v/v) to yield the corresponding ester.

(5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl 4-formylbenzoate (S50)



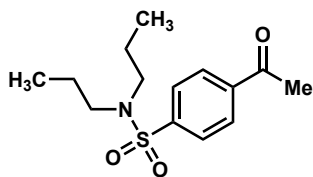
White solid: R_f 0.40 (PE/EA, 5:1, v/v); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.08 (s, 1H), 8.18 (d, $J = 8.3$ Hz, 2H), 7.93 (d, $J = 8.3$ Hz, 2H), 5.55 (d, $J = 5.0$ Hz, 1H), 4.65 (dd, $J = 7.9$, 2.5 Hz, 1H), 4.54 (dd, $J = 11.6$, 4.6 Hz, 1H), 4.45 (dd, $J = 11.6$, 7.7 Hz, 1H), 4.36 – 4.29 (m, 2H), 4.20 – 4.15 (m, 1H), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.78, 165.52, 139.25, 135.07, 130.39, 129.61, 109.85, 108.93, 96.39, 77.47, 77.15, 76.83, 71.17, 70.79, 70.53, 66.14, 64.60, 26.09, 26.05, 25.03, 24.56. Data in accordance with the literature.¹

(2*S*,5*S*,8*R*,9*S*,10*S*,13*S*,14*S*)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta [*a*]phenanthrene-2-yl 4-formylbenzoate (S52)



White solid: R_f 0.63 (100% DCM); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.11 (s, 1H), 8.20 (d, $J = 8.3$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 2H), 5.32 (1H), 2.45 (dd, $J = 19.3$, 8.6 Hz, 1H), 2.12-2.03 (m, 1H), 1.98-1.88 (m, 2H), 1.83-1.75 (m, 3H), 1.72-1.69 (m, 1H), 1.66-1.56 (m, 6H), 1.54-1.48 (m, 1H), 1.41-1.23 (m, 6H), 1.09-0.99 (m, 1H), 0.88 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 221.5, 191.8, 165.0, 139.1, 136.2, 130.2, 129.6, 71.6, 54.5, 51.5, 47.9, 40.6, 36.2, 35.9, 35.1, 33.2, 33.0, 31.6, 30.8, 28.1, 26.3, 21.8, 26.3, 13.9, 11.5.

4-acetyl-*N,N*-dipropylbenzenesulfonamide (S56)⁸



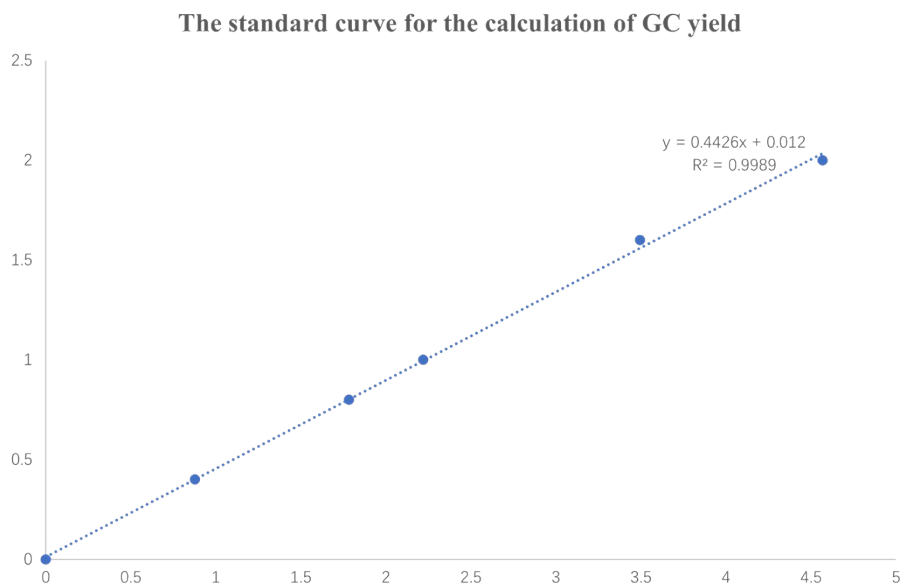
The synthesis of S56: A mixture of 4-acetylbenzenesulfonyl chloride (400 mg, 1.84 mmol), dipropylamine (2 M in THF, 1.0 mL, 2.0 mmol), and triethylamine (370 mg, 3.66 mmol) in anhydrous THF (10 mL) was stirred at room temperature overnight. Brine was added, and the reaction mixture was extracted with EA (3 times). The combined organic layer was washed with brine (30 mL), dried over anhydrous Na₂SO₄, and filtered. Removal of solvent in vacuo gave **S56** as an off-white solid (304 mg, 73%).

Off-white solid: *R_f* 0.50 (PE/EA, 2:1, v/v); ¹H NMR (400 MHz, CDCl₃) δ 8.10-8.02 (m, 2H), 7.93-7.86 (m, 2H), 3.14-3.06 (m, 4H), 2.65 (s, 3H), 1.55 (dq, *J* = 14.9, 7.3 Hz, 4H), 0.87 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 196.98, 144.32, 139.70, 128.96, 127.36, 50.01, 26.96, 22.04, 11.25.

4. General procedure

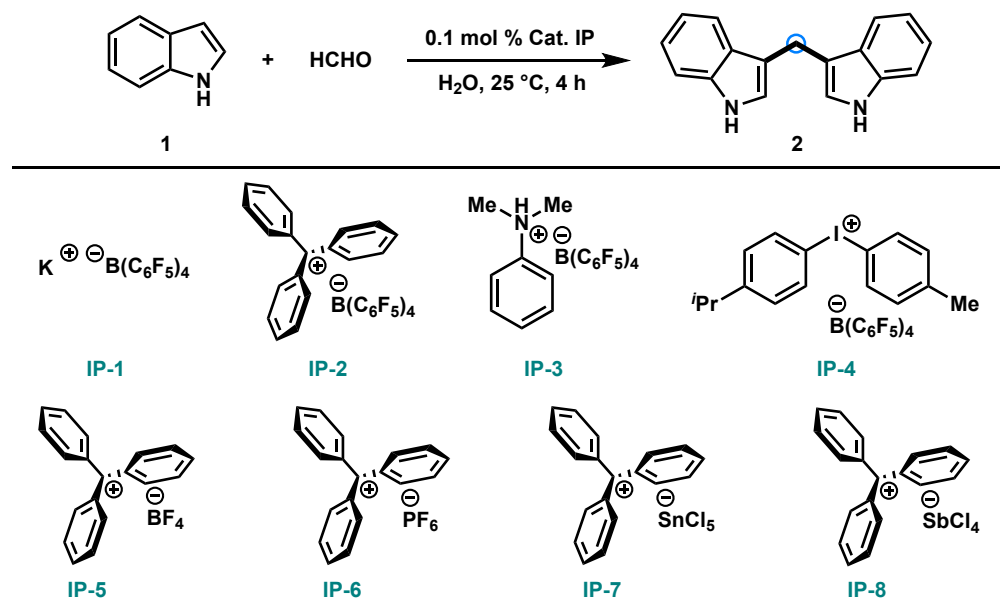
General procedure for bisindolylmethanes (BIMs): To a well-dried flask (25 mL) equipped with a magnetic stir bar, $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (0.01M Pre-stored solution in H_2O , 40.0 μL), tryptamines derivatives (0.5 mmol, 1.0 equiv.), aldehydes (0.3 mmol, 0.6 equiv.) were added. Then, 2.5 mL pure water was added *via* syringe. The resulting solution was heated in an oil bath at 80 °C and stirred vigorously for 8 hours. When the reaction was complete, the mixture was diluted with EA (1 mL), and extracted with EA (3 \times 5 mL), and the organic phase was dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, and the crude mixture was purified by preparative thin layer chromatography or flash column chromatography.

Product Calibration



5. Optimization of the reaction conditions.

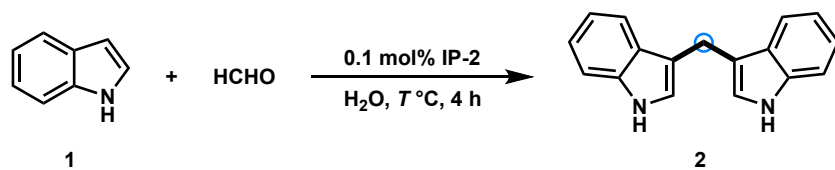
Table S1. Screening Ion-pairs as catalyst.



Entry	Cat.	2 Yield (%) ^a
1	--	n.d.
2	IP-1	5
3	IP-2	41
4	IP-3	11
5	IP-4	9
6	IP-5	10
7	IP-6	13
8	IP-7	15
9	IP-8	15

Reactions were performed on 0.5 mmol scale in 2.0 mL deionized H₂O. ^aYield based on **1** and was determined by GC analysis by using anisole as an internal standard. n.d.: not detected.

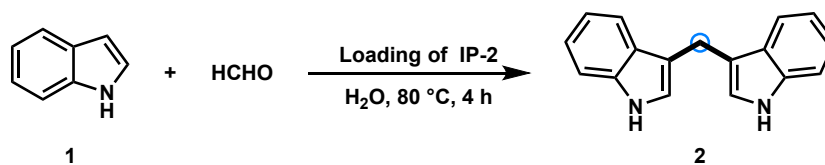
Table S2. Screening reaction temperature.



Entry	T (°C)	2 Yield (%) ^a
1	30	42
2	40	62
3	50	76
4	60	80
5	70	82
6	80	86
7	90	84

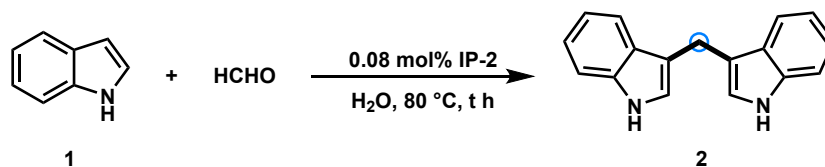
Reactions were performed on 0.5 mmol scale in 2.0 mL deionized H₂O. ^aYield based on **1** and was determined by GC analysis by using anisole as an internal standard.

Table S3. Screening loading of catalyst.



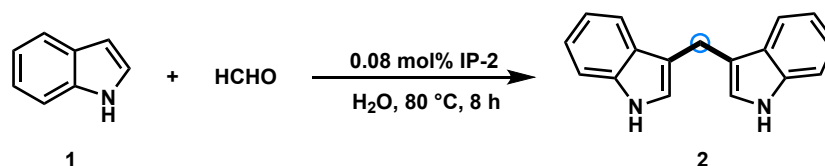
Entry	Loading of Cat. IP-2 (%)	3 Yield (%) ^a
1	0.05	62
2	0.06	65
3	0.07	68
4	0.08	84
5	0.09	86
6	0.1	88

Reactions were performed on 0.5 mmol scale in 2.0 mL deionized H₂O. ^aYield based on **1** and was determined by GC analysis by using anisole as an internal standard.

Table S4. Screening reaction time.

Entry	t (h)	2 Yield (%) ^a
1	1	72
2	2	77
3	4	84
4	6	92
5	8	99 (98) ^b
6	10	99
7	12	98

Reactions were performed on 0.5 mmol scale in 2.0 mL deionized H₂O. ^aYield based on **1** and was determined by GC analysis by using anisole as an internal standard. ^bIsolated yield.

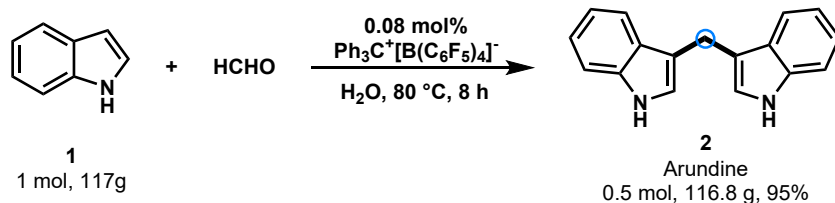
Table S5. Screening the volume of H₂O.

Entry	Volume of H ₂ O (mL)	2 Yield (%) ^a
1	0.5	92
2	1.0	97
3	1.5	98
4	2.0	98
5	2.5	99 (98) ^b
6	3.0	99

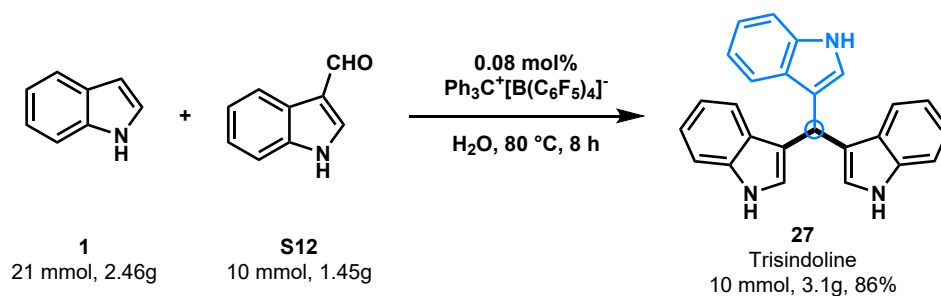
Reactions were performed on 0.5 mmol scale in deionized H₂O. ^aYield based on **1** and was determined by GC analysis by using anisole as an internal standard. ^bIsolated yield.

6. Synthetic application

Scheme S1: 100 gram-scale synthesis of Arundine



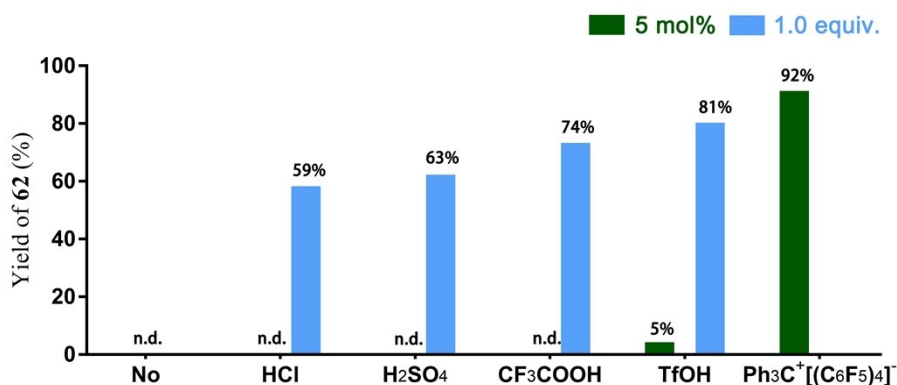
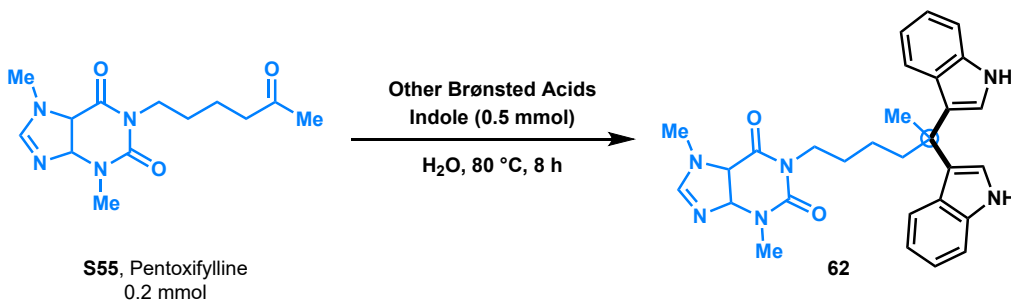
Procedure for the 100 gram-scale synthesis of Arundine: To a 1000 mL well-dried round bottom flask equipped with a mechanical stir bar, $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (720 mg), indole (117 g, 1 mol, 1.0 equiv.), formaldehydes in water (37% w/w, 50 mL, 0.6 mol, 0.6 equiv.) were added. Then, 200 mL pure water was added. The mixture was heated in an oil bath at 80 °C and stirred vigorously for 8 hours. When the reaction was complete, the mixture was filtered through Buchner funnel, and the residue was washed with PE (200 mL). The residue was further purified by recrystallization in PE/EA (5:1) to obtain the product (yellow solid, 116.8 g, 95%).



Procedure for the gram-scale synthesis of Trisindoline: To a 100 mL well-dried round bottom flask equipped with a magnetic stir bar, $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (184.5 mg, 0.008 mmol), indole (2.46 g, 21 mmol), indole-3-carboxaldehyde (1.45 g, 10 mmol) were added. Then, 20 mL pure water was added. The mixture was heated in an oil bath at 80 °C and stirred vigorously for 8 hours. When the reaction was complete, the mixture was filtered through Buchner funnel, and the residue was washed with PE (50 mL). The residue was further purified by recrystallization in EA to obtain the product (yellowish solid, 3.1 g, 86%).

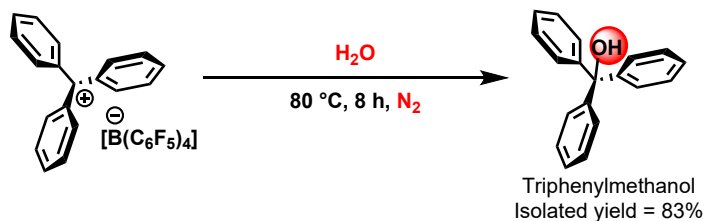
7. Mechanistic studies

7.1 Comparison with other Brønsted acids



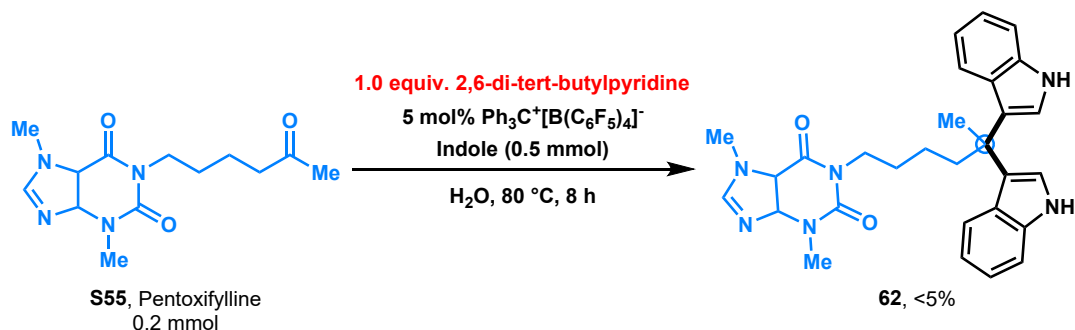
Procedure: To an over-dried reaction tube (25 mL) equipped with a magnetic stir bar, pentoxifylline (55.6 mg, 0.2 mmol), indole (58.5 mg, 0.5 mmol) and Brønsted acids (0.01 M pre-stored solution in H₂O, 5 mol% or 1 equiv.) were added. Then, 2.5 mL pure water was charged *via* syringe. The resulting solution was heated in an oil bath at 80 °C and stirred vigorously for 8 h. When the reaction was complete, the mixture was diluted with EA (1 mL), filtered through a short pad of silica gel, and washed with EA (3×5 mL). The filtrate was concentrated under reduced pressure and the residue was analyzed by ¹H NMR.

7.2 Hydrolysis of $\text{Ph}_3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in H_2O



Procedure: To an over-dried Schlenk tube (25 mL) equipped with a magnetic stir bar, $\text{Ph}_3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (36.8 mg, 0.04 mmol) was added. Then, 2.5 mL pure water was charged *via* syringe. The resulting solution was heated in an oil bath at $80\text{ }^\circ\text{C}$ and stirred vigorously for 8 h. When the reaction was complete, the mixture was diluted with EA (1 mL), filtered through a short pad of silica gel, and washed with EA (10 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by silica gel column chromatography (PE/EA, 20/1, v/v) to give triphenylmethanol as a white solid, 8.6 mg, 83%. $^1\text{H NMR}$ (400 MHz, CDCl_3 -*d*) δ 7.35 - 7.22 (m, 15H), 2.86 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3 -*d*) δ 146.95, 128.04, 128.05, 127.39, 82.12.

7.3 Proton scavenging experiment



Procedure: To an over-dried reaction tube (25 mL) equipped with a magnetic stir bar, pentoxifylline (0.2 mmol, 55.6 mg), indole (58.5 mg, 0.5 mmol), 2,6-di-tert-butylpyridine (38.2 mg, 0.2 mmol) and $\text{Ph}_3\text{C}^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (5 mol%, 9.2 mg, 0.01 mmol) were added. Then, 2.5 mL pure water was charged *via* syringe. The resulting solution was heated in an oil bath at 80 °C and stirred vigorously for 8 h. When the reaction was complete, the mixture was diluted with EA (1 mL), filtered through a short pad of silica gel, and washed with EA (3×5 mL). The filtrate was concentrated under reduced pressure and the residue was analyzed by ^1H NMR.

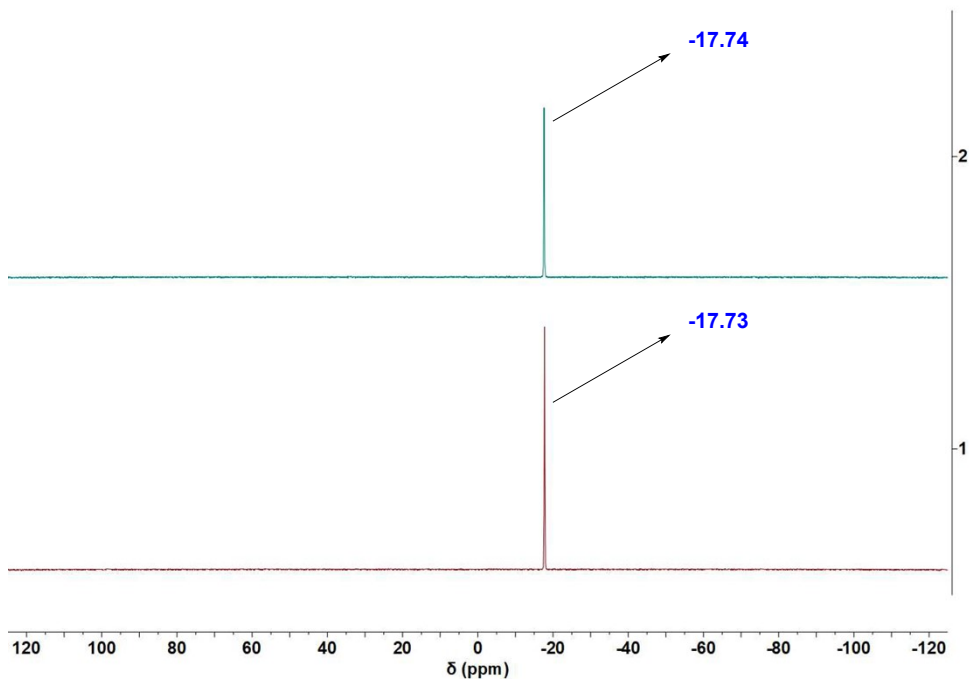


Figure S4. ^{11}B -NMR (400 MHz, CDCl_3 -*d*) spectra of $\text{Ph}_3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ before and after reaction under standard conditions.

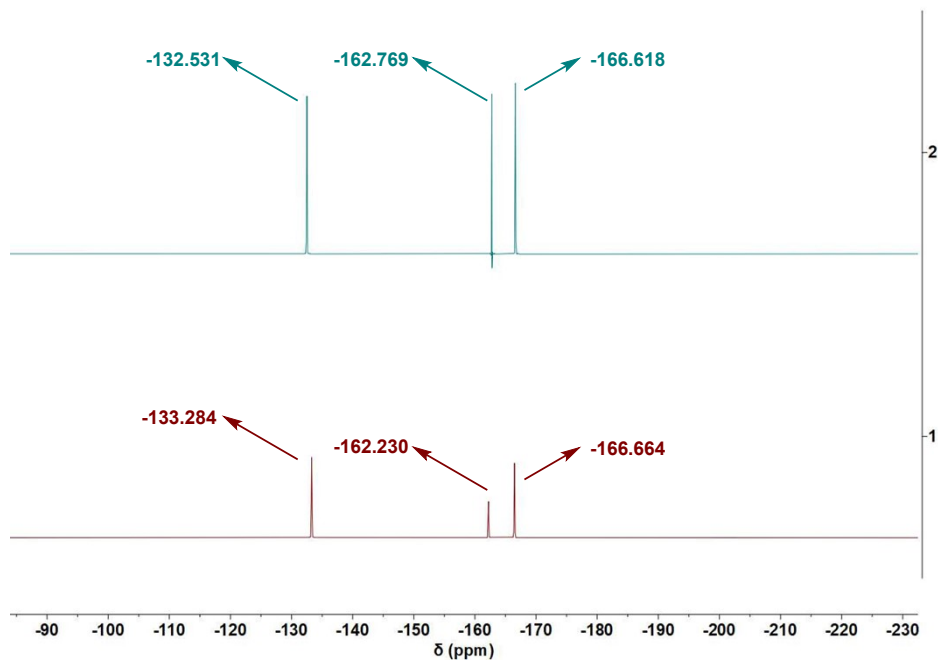


Figure S5. ^{19}F -NMR (400 MHz, CDCl_3 -*d*) spectra of $\text{Ph}_3^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ before and after reaction under standard conditions.

8. X-ray data of compound 53

Table S5 Crystal data and structure refinement for 53.

Identification code	53
Empirical formula	C ₂₁ H ₂₄ N ₂ O ₅
Formula weight	384.42
Temperature/K	170.00(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	6.4858(3)
b/Å	10.2602(5)
c/Å	14.1368(6)
α/°	90
β/°	96.740(4)
γ/°	90
Volume/Å ³	934.24(7)
Z	2
ρ _{calc} /cm ³	1.367
μ/mm ⁻¹	0.807
F(000)	408.0
Crystal size/mm ³	0.14 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.296 to 142.916
Index ranges	-5 ≤ h ≤ 7, -12 ≤ k ≤ 12, -17 ≤ l ≤ 14
Reflections collected	5076
Independent reflections	2956 [R _{int} = 0.0204, R _{sigma} = 0.0281]
Data/restraints/parameters	2956/1/267
Goodness-of-fit on F ²	1.195
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0464, wR ₂ = 0.1350
Final R indexes [all data]	R ₁ = 0.0510, wR ₂ = 0.1470
Largest diff. peak/hole / e Å ⁻³	0.24/-0.32
Flack parameter	0.0(3)

Crystal structure determination of [53]

Crystal Data for C₂₁H₂₄N₂O₅ (*M* = 384.42 g/mol): monoclinic, space group P2₁ (no. 4), *a* = 6.4858(3) Å, *b* = 10.2602(5) Å, *c* = 14.1368(6) Å, β = 96.740(4)°, *V* = 934.24(7) Å³, *Z* = 2, *T* = 170.00(10) K, μ(Cu Kα) = 0.807 mm⁻¹, *D*_{calc} = 1.367 g/cm³, 5076 reflections measured (6.296° ≤ 2θ ≤ 142.916°), 2956 unique (*R*_{int} = 0.0204, *R*_{sigma} = 0.0281) which were used in all calculations. The final *R*₁ was 0.0464 (*I* > 2σ(*I*)) and *wR*₂ was 0.1470 (all data).

Refinement model description

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 53. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
O1	7323(5)	7223(4)	2915(2)	30.6(8)
O2	3575(5)	6885(3)	4569(2)	28.5(8)
O3	7509(5)	6866(4)	5793(2)	27.7(8)
O4	8296(5)	9564(3)	5303(2)	30.3(8)
O5	11202(5)	9222(4)	4130(3)	41.2(10)
N1	8535(6)	3074(4)	3124(3)	29.3(9)
N2	4276(6)	6404(5)	-13(3)	33.8(10)
C1	5190(7)	3137(5)	2491(3)	22.8(10)
C2	3316(8)	2591(5)	2085(3)	27.5(10)
C3	3176(9)	1253(5)	1975(4)	33.3(12)
C4	4883(9)	446(5)	2261(3)	36.1(13)
C5	6746(9)	953(5)	2655(3)	34.5(12)
C6	6894(7)	2296(5)	2770(3)	26.8(10)
C7	7903(7)	4356(5)	3080(3)	27.4(10)
C8	5866(7)	4455(5)	2705(3)	23.2(10)
C9	4503(7)	5649(5)	2571(3)	23.0(10)
C10	5344(6)	6823(5)	3165(3)	22.3(9)
C11	5517(7)	6564(5)	4245(3)	23.5(10)
C12	7200(7)	7345(4)	4828(3)	20.8(9)
C13	6672(7)	8789(5)	4822(3)	27.5(11)
C14	4040(7)	6069(5)	1545(3)	24.6(10)
C15	5104(8)	5755(5)	793(3)	31.9(11)
C16	2653(7)	7168(5)	202(3)	26.1(10)
C17	2463(6)	6988(5)	1180(3)	22.6(9)
C18	917(7)	7678(5)	1583(3)	26.4(10)
C19	-362(8)	8507(6)	1020(4)	32.7(11)
C20	-134(8)	8678(6)	49(4)	33.3(11)
C21	1359(8)	8008(6)	-368(3)	32.7(11)

Table S7 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 53. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	35.1(18)	36(2)	20.8(17)	-3.4(16)	4.6(14)	-9.6(15)
O2	29.6(16)	28.8(18)	28.3(16)	-0.2(15)	7.9(13)	-0.7(15)
O3	33.4(17)	32(2)	17.6(15)	1.2(14)	1.1(13)	2.2(16)
O4	26.0(16)	27.1(19)	36.7(19)	-8.5(15)	-1.5(14)	-2.6(14)

Table S7 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 53. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*^2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O5	31.2(19)	33(2)	60(3)	-3(2)	6.2(18)	-0.5(16)
N1	26.2(19)	33(2)	27(2)	-0.8(18)	-2.6(16)	7.1(18)
N2	39(2)	44(3)	19.2(19)	1.3(18)	6.9(17)	11(2)
C1	27(2)	24(2)	17(2)	0.5(18)	1.8(17)	-0.2(19)
C2	32(2)	28(3)	22(2)	0.2(19)	0.5(18)	-0.8(19)
C3	45(3)	31(3)	24(2)	-1(2)	5(2)	-10(2)
C4	60(4)	23(3)	26(2)	2(2)	9(2)	1(2)
C5	49(3)	29(3)	26(2)	6(2)	5(2)	8(2)
C6	33(2)	32(3)	16(2)	0(2)	3.2(18)	2(2)
C7	30(2)	26(3)	25(2)	-5(2)	-0.8(18)	4(2)
C8	25(2)	24(3)	19(2)	0.9(19)	0.8(17)	-2.4(19)
C9	22(2)	27(2)	19(2)	0.4(18)	-0.8(17)	-3.6(18)
C10	24(2)	22(2)	20(2)	0.0(19)	0.1(16)	-2.5(19)
C11	27(2)	23(3)	20(2)	-0.6(18)	3.0(17)	-0.1(18)
C12	28(2)	18(2)	16(2)	-2.3(17)	1.7(16)	5.1(18)
C13	25(2)	27(3)	28(2)	-7(2)	-4.9(19)	0.9(19)
C14	24(2)	28(3)	21(2)	1.5(19)	-0.6(17)	-2.9(19)
C15	31(2)	39(3)	25(2)	2(2)	-0.2(19)	8(2)
C16	30(2)	29(3)	19(2)	1(2)	-0.7(18)	0(2)
C17	23(2)	22(2)	22(2)	-1.0(19)	-0.4(16)	0.6(18)
C18	28(2)	32(3)	19(2)	1.1(19)	1.1(17)	-2(2)
C19	31(3)	36(3)	31(3)	-1(2)	0(2)	3(2)
C20	34(3)	32(3)	32(2)	1(2)	-6(2)	7(2)
C21	39(3)	38(3)	20(2)	3(2)	-3(2)	0(2)

Table S8 Bond Lengths for 53.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
O1	C10	1.431(5)	C7	C8	1.369(6)
O2	C11	1.429(5)	C8	C9	1.509(7)
O3	C12	1.442(5)	C9	C10	1.532(6)
O4	C13	1.426(6)	C9	C14	1.510(6)
N1	C6	1.377(6)	C10	C11	1.540(6)
N1	C7	1.378(6)	C11	C12	1.517(6)
N2	C15	1.373(6)	C12	C13	1.521(7)
N2	C16	1.374(6)	C14	C15	1.372(7)
C1	C2	1.399(7)	C14	C17	1.441(6)
C1	C6	1.421(7)	C16	C17	1.414(6)

Table S8 Bond Lengths for 53.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C8	1.443(7)	C16	C21	1.392(7)
C2	C3	1.383(7)	C17	C18	1.402(6)
C3	C4	1.403(8)	C18	C19	1.375(7)
C4	C5	1.373(8)	C19	C20	1.408(7)
C5	C6	1.390(8)	C20	C21	1.376(8)

Table S9 Bond Angles for 53.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	N1	C7	108.9(4)	O2	C11	C10	108.3(3)
C15	N2	C16	109.2(4)	O2	C11	C12	108.0(3)
C2	C1	C6	118.7(4)	C12	C11	C10	114.3(4)
C2	C1	C8	133.6(4)	O3	C12	C11	110.2(4)
C6	C1	C8	107.7(4)	O3	C12	C13	110.1(4)
C3	C2	C1	119.1(5)	C11	C12	C13	111.4(4)
C2	C3	C4	120.9(5)	O4	C13	C12	112.8(4)
C5	C4	C3	121.4(5)	C15	C14	C9	128.0(4)
C4	C5	C6	117.9(5)	C15	C14	C17	106.1(4)
N1	C6	C1	107.0(4)	C17	C14	C9	125.7(4)
N1	C6	C5	131.1(5)	C14	C15	N2	110.2(4)
C5	C6	C1	121.9(5)	N2	C16	C17	107.3(4)
C8	C7	N1	110.9(4)	N2	C16	C21	130.6(4)
C1	C8	C9	125.1(4)	C21	C16	C17	122.1(4)
C7	C8	C1	105.5(4)	C16	C17	C14	107.2(4)
C7	C8	C9	129.3(4)	C18	C17	C14	134.1(4)
C8	C9	C10	113.8(4)	C18	C17	C16	118.7(4)
C8	C9	C14	113.5(4)	C19	C18	C17	119.2(4)
C14	C9	C10	108.7(4)	C18	C19	C20	121.1(5)
O1	C10	C9	111.2(4)	C21	C20	C19	121.0(5)
O1	C10	C11	109.4(3)	C20	C21	C16	117.9(5)
C9	C10	C11	112.8(4)				

Table S10 Torsion Angles for 53.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C10	C11	O2	148.0(4)	C8	C1	C6	C5	-179.9(4)
O1	C10	C11	C12	27.5(5)	C8	C9	C10	O1	61.1(5)
O2	C11	C12	O3	70.2(4)	C8	C9	C10	C11	-62.2(5)

Table S10 Torsion Angles for 53.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O2	C11	C12	C13	-52.3(5)	C8	C9	C14	C15	-19.6(7)
O3	C12	C13	O4	62.0(5)	C8	C9	C14	C17	166.2(4)
N1	C7	C8	C1	-0.6(5)	C9	C10	C11	O2	-87.7(5)
N1	C7	C8	C9	176.5(4)	C9	C10	C11	C12	151.9(4)
N2	C16	C17	C14	-0.5(5)	C9	C14	C15	N2	-175.8(5)
N2	C16	C17	C18	179.3(4)	C9	C14	C17	C16	176.0(4)
N2	C16	C21	C20	-178.7(5)	C9	C14	C17	C18	-3.7(9)
C1	C2	C3	C4	-0.3(8)	C10	C9	C14	C15	108.2(6)
C1	C8	C9	C10	159.2(4)	C10	C9	C14	C17	-66.0(6)
C1	C8	C9	C14	-75.8(6)	C10	C11	C12	O3	-169.2(4)
C2	C1	C6	N1	178.7(4)	C10	C11	C12	C13	68.3(5)
C2	C1	C6	C5	-0.5(7)	C11	C12	C13	O4	-175.5(4)
C2	C1	C8	C7	-178.5(5)	C14	C9	C10	O1	-66.5(5)
C2	C1	C8	C9	4.2(8)	C14	C9	C10	C11	170.2(4)
C2	C3	C4	C5	-0.2(8)	C14	C17	C18	C19	179.6(5)
C3	C4	C5	C6	0.3(7)	C15	N2	C16	C17	0.0(6)
C4	C5	C6	N1	-178.9(4)	C15	N2	C16	C21	179.1(5)
C4	C5	C6	C1	0.0(7)	C15	C14	C17	C16	0.7(5)
C6	N1	C7	C8	0.1(6)	C15	C14	C17	C18	-179.0(5)
C6	C1	C2	C3	0.6(7)	C16	N2	C15	C14	0.4(6)
C6	C1	C8	C7	0.8(5)	C16	C17	C18	C19	-0.1(7)
C6	C1	C8	C9	-176.5(4)	C17	C14	C15	N2	-0.7(6)
C7	N1	C6	C1	0.4(5)	C17	C16	C21	C20	0.2(7)
C7	N1	C6	C5	179.5(5)	C17	C18	C19	C20	-0.4(8)
C7	C8	C9	C10	-17.4(7)	C18	C19	C20	C21	0.8(8)
C7	C8	C9	C14	107.7(5)	C19	C20	C21	C16	-0.7(8)
C8	C1	C2	C3	179.8(5)	C21	C16	C17	C14	-179.6(5)
C8	C1	C6	N1	-0.7(5)	C21	C16	C17	C18	0.1(7)

Table S11 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 53.

Atom	x	y	z	U(eq)
H2	2935.21	6213.61	4653.64	43
H4	9342.88	9490.65	5033.12	45
H5A	11942.82	9896.26	4081.26	62
H5B	11982.53	8555.68	4215.36	62
H1A	9756.31	2803.11	3337.65	35
H2A	4704.86	6342.98	-563.79	41

Table S11 Hydrogen Atom Coordinates ($\text{\AA} \times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 53.

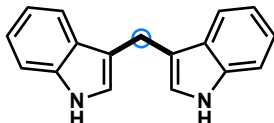
Atom	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
H2B	2180.37	3119.77	1890.89	33
H3A	1933.05	882.75	1707.35	40
H4A	4748.69	-451.17	2181	43
H5	7874.66	413.79	2840.72	41
H7	8747.15	5060.67	3279.39	33
H9	3170.87	5417.3	2789.54	28
H10	4373.26	7547.38	3022.94	27
H11	5789.59	5634.03	4358.14	28
H12	8498.48	7233.61	4545.48	25
H13A	6390.83	9084.42	4167.8	33
H13B	5419.69	8914.41	5124.75	33
H15	6224.04	5184.47	824.54	38
H18	758.31	7577.03	2224.42	32
H19	-1393.77	8962.29	1284.27	39
H20	-1007.19	9252.36	-315.57	40
H21	1500.41	8113.35	-1010.77	39
H3	6330(80)	6920(50)	6060(30)	21(12)
H1	7240(100)	7210(80)	2370(50)	60(20)

Experimental

Single crystals of $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_5$ [53]: A suitable crystal was selected on a **XtaLAB AFC12 (RINC): Kappa single** diffractometer. The crystal was kept at 170.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

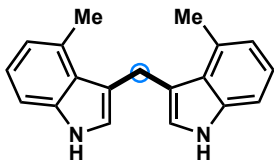
9. Compound characterization data

3,3'-bisindolylmethane (Arundine) 2



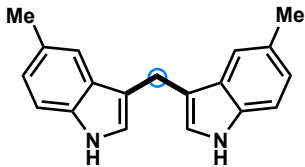
As a brown solid: R_f 0.3 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (s, 2H), 7.64 (d, $J = 7.8$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.21 (t, $J = 7.6$ Hz, 2H), 7.11 (t, $J = 7.8$ Hz, 2H), 6.92 (d, $J = 1.9$ Hz, 2H), 4.26 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.54, 127.66, 122.31, 121.99, 119.32, 119.27, 115.76, 111.15, 77.45, 77.13, 76.82, 21.30. Data in accordance with the literature.⁹

bis(4-methyl-1H-indol-3-yl)methane 3



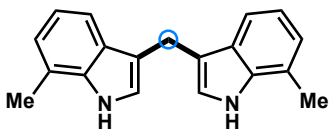
As a milky solid: R_f 0.32 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (s, 2H), 7.19 (d, $J = 8.1$ Hz, 2H), 7.10 (t, $J = 7.7$ Hz, 2H), 6.87 (d, $J = 7.5$ Hz, 2H), 6.67 (s, 2H), 4.57 (s, 2H), 2.68 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.08, 131.44, 126.01, 123.08, 122.11, 120.82, 117.59, 109.12, 25.88, 20.21. Data in accordance with the literature.⁹

bis(5-methyl-1H-indol-3-yl)methane 4



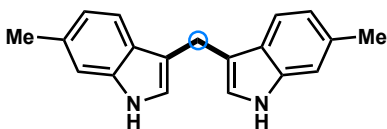
As a milky solid: R_f 0.35 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (s, 2H), 7.25 (d, $J = 1.6$ Hz, 1H), 7.23 (s, 1H), 7.06 (d, $J = 2.5$ Hz, 2H), 6.90 (d, $J = 2.3$ Hz, 2H), 6.85 (dd, $J = 8.8, 2.5$ Hz, 2H), 4.16 (s, 2H), 3.81 (s, 6H), 2.17 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 134.88, 128.46, 127.87, 123.57, 122.56, 118.96, 115.23, 110.84, 21.65, 21.26. Data in accordance with the literature.⁹

bis(7-methyl-1H-indol-3-yl)methane 5



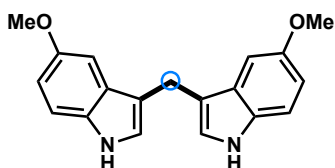
As a pale yellow solid: R_f 0.40 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (s, 1H), 7.50 (t, $J = 5.6$ Hz, 1H), 7.09 – 6.98 (m, 2H), 6.91 (d, $J = 2.4$ Hz, 1H), 4.24 (d, $J = 4.7$ Hz, 1H), 2.49 (d, $J = 4.7$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.09, 127.18, 122.49, 122.03, 120.30, 119.48, 117.07, 116.32, 21.55, 16.73. Data in accordance with the literature.⁹

bis(6-methyl-1H-indol-3-yl)methane 6



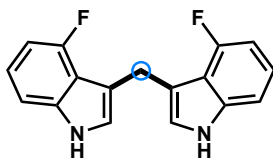
As a pale yellow solid: R_f 0.38 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.53 (d, $J = 8.0$ Hz, 1H), 7.12 (s, 1H), 6.97 (dd, $J = 8.0, 1.4$ Hz, 1H), 6.82 – 6.77 (m, 1H), 4.21 (s, 1H), 2.50 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.99, 131.72, 125.56, 121.69, 121.02, 119.01, 115.65, 111.16, 21.86, 21.40. Data in accordance with the literature.⁹

bis(5-methoxy-1H-indol-3-yl)methane 7



As a brown solid: R_f 0.35 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (s, 2H), 7.46 (s, 2H), 7.24 (d, $J = 8.3$ Hz, 2H), 7.06 (dd, $J = 8.3, 1.7$ Hz, 2H), 6.83 (d, $J = 2.3$ Hz, 2H), 4.21 (s, 2H), 2.48 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 153.89, 131.68, 127.99, 123.18, 115.33, 112.14, 111.90, 101.07, 56.02, 21.39. Data in accordance with the literature.⁹

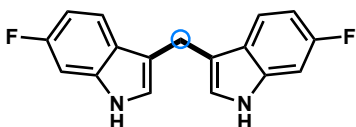
bis(4-fluoro-1H-indol-3-yl)methane 8



As a milky solid: R_f 0.25 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (s, 2H), 7.12 – 7.02 (m, 4H), 6.94 (s, 2H), 6.75 (ddd, $J = 11.1, 7.0, 1.6$ Hz, 2H), 4.44 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.29 (d, $J = 222.4$ Hz), 139.29, 122.41, 122.34 (t, $J = 2.2$

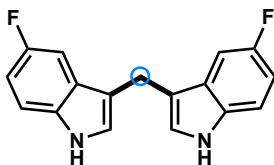
Hz), 116.19, 115.30 (d, $J = 3.4$ Hz), 107.28 (d, $J = 3.8$ Hz), 104.65, 23.32. ^{19}F NMR (376 MHz, CDCl_3) δ -122.80 (d, $J = 11.7$ Hz). Data in accordance with the literature.⁹

bis(6-fluoro-1H-indol-3-yl)methane 9



As a milky solid: R_f 0.30 (PE: EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.02 (td, $J = 7.8, 4.8$ Hz, 2H), 6.98 – 6.89 (m, 4H), 4.23 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.08 (d, $J = 237.6$ Hz), 136.41 (d, $J = 12.4$ Hz), 124.18, 122.46, 119.95 (d, $J = 10.1$ Hz), 115.63, 108.08 (d, $J = 24.5$ Hz), 97.46 (d, $J = 26.1$ Hz), 21.33. ^{19}F NMR (376 MHz, CDCl_3) δ -121.11 – 121.40 (m). Data in accordance with the literature.⁹

bis(5-fluoro-1H-indol-3-yl)methane 10

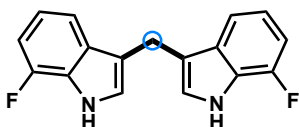


As a milky solid: R_f 0.25 (PE: EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.91 (s, 2H), 7.25 (q, $J = 4.5$ Hz, 2H), 7.20 (dd, $J = 9.6, 2.5$ Hz, 2H), 7.00 (s, 2H), 6.92 (td, $J = 9.1, 2.5$ Hz, 2H), 4.13 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.72 (d, $J = 234.2$ Hz), 133.05, 127.89 (d, $J = 9.8$ Hz), 124.02, 115.50 (d, $J = 4.9$ Hz), 111.76 (d, $J = 9.7$ Hz), 110.42 (d,

$J = 26.4$ Hz), 104.18 (d, $J = 23.3$ Hz), 21.40. ^{19}F NMR (376 MHz, CDCl_3) δ -124.70.

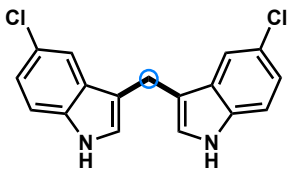
Data in accordance with the literature.⁹

bis(7-fluoro-1H-indol-3-yl)methane 11



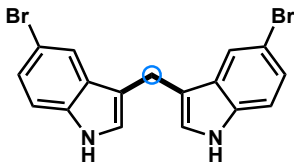
As a milky solid: R_f 0.30 (PE: EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (s, 2H), 7.37 (d, $J = 7.9$ Hz, 2H), 7.02 (td, $J = 7.8, 4.8$ Hz, 2H), 6.98 – 6.89 (m, 4H), 4.23 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 149.70 (d, $J = 243.7$ Hz), 131.30 (d, $J = 5.9$ Hz), 124.83 (d, $J = 13.4$ Hz), 123.02 (d, $J = 1.5$ Hz), 119.64 (d, $J = 6.2$ Hz), 116.31 (d, $J = 2.4$ Hz), 115.07 (d, $J = 3.4$ Hz), 106.95 (d, $J = 16.0$ Hz), 21.43. ^{19}F NMR (376 MHz, CDCl_3) δ -135.27, -135.28, -135.30, -135.31. Data in accordance with the literature.⁹

bis(5-chloro-1H-indol-3-yl)methane 12



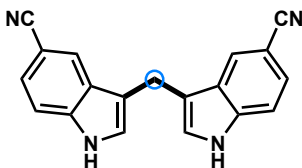
As a brown solid: R_f 0.20 (PE: EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 2H), 7.54 (d, $J = 1.9$ Hz, 2H), 7.26 (d, $J = 8.6$ Hz, 2H), 7.14 (dd, $J = 8.6, 2.0$ Hz, 2H), 6.96 (d, $J = 2.4$ Hz, 2H), 4.14 (s, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 134.91, 128.60, 125.07, 123.69, 122.38, 118.73, 115.04, 112.24, 21.20. Data in accordance with the literature.⁹

bis(5-bromo-1H-indol-3-yl)methane 13



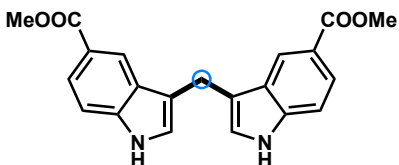
As a brown solid: R_f 0.25 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (s, 1H), 7.69 (s, 1H), 7.24 (q, $J = 8.6$ Hz, 2H), 6.93 (d, $J = 2.3$ Hz, 1H), 4.12 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.16, 129.25, 124.93, 123.51, 121.83, 114.94, 112.68, 112.64, 21.19. Data in accordance with the literature.⁹

3,3'-methylenebis(1H-indole-5-carbonitrile) 14



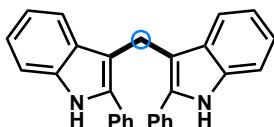
As a pale yellow solid: R_f 0.3 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.40 (s, 2H), 8.09 (s, 2H), 7.55 – 7.45 (m, 4H), 7.38 (dd, $J = 8.5, 1.6$ Hz, 2H), 4.21 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 138.62, 127.36, 126.24, 124.93, 124.15, 121.47, 115.58, 113.22, 100.73, 20.68. Data in accordance with the literature.¹⁰

dimethyl 3,3'-methylenebis(1H-indole-5-carboxylate) 15



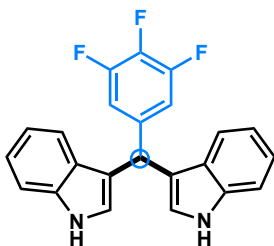
As a pale yellow solid: R_f 0.4 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.19 (s, 2H), 7.66 (d, $J = 8.6$ Hz, 2H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.20 (s, 2H), 4.20 (s, 2H), 3.76 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 167.81, 139.58, 127.19, 125.29, 122.48, 121.83, 120.19, 115.95, 111.92, 52.13, 21.10. Data in accordance with the literature.¹⁰

bis(2-phenyl-1H-indol-3-yl)methane 16



As a milky solid: R_f 0.25 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.99 (s, 2H), 7.60 – 7.52 (m, 4H), 7.40 (t, $J = 7.4$ Hz, 4H), 7.30 (dd, $J = 18.8, 7.7$ Hz, 4H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.11 – 7.02 (m, 2H), 6.89 – 6.81 (m, 2H), 4.56 (s, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 135.98, 134.59, 133.40, 129.44, 128.80, 128.43, 127.61, 122.05, 120.11, 119.52, 112.13, 110.61, 21.40. Data in accordance with the literature.¹¹

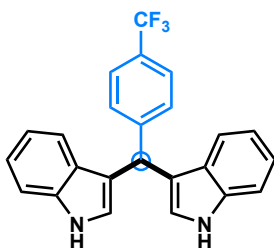
3,3'-((3,4,5-trifluorophenyl)methylene)bis(1H-indole) 17



As a fuchsia solid: R_f 0.50 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.97 (s, 2H), 7.41 – 7.34 (m, 4H), 7.24 – 7.18 (m, 2H), 7.09 – 7.02 (m, 2H), 6.95 (dd, $J = 8.7, 6.6$ Hz,

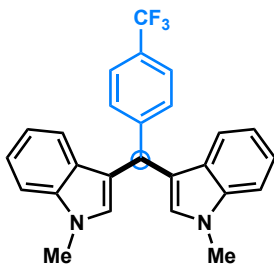
2H), 6.66 (d, $J = 2.6$ Hz, 2H), 5.82 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.18 (dd, $J = 249.0, 11.0$ Hz), 140.69, 139.51 (dt, $J = 252.0, 20.0$ Hz), 136.80, 126.73, 123.74, 122.45, 119.72, 118.26, 112.71 (d, $J = 5.3$ Hz), 112.56 (d, $J = 5.3$ Hz), 111.46, 39.71. ^{19}F NMR (376 MHz, CDCl_3) δ -134.77 (d, $J = 31.5$ Hz), -163.57 (d, $J = 26.0$ Hz). Data in accordance with the literature.¹⁷

3,3'-((4-(trifluoromethyl)phenyl)methylene)bis(1H-indole) 18



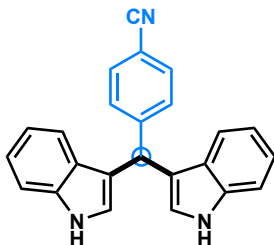
As a red solid: R_f 0.45 (PE: EA = 5:1); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (s, 2H), 7.54 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 2H), 7.37 (dd, $J = 7.7, 3.6$ Hz, 4H), 7.20 (t, $J = 7.6$ Hz, 2H), 7.06 – 7.00 (m, 2H), 6.65 (d, $J = 2.5$ Hz, 2H), 5.95 (s, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.24, 136.77, 129.11, 126.91, 125.35, 125.30, 123.77, 122.28, 119.83, 119.54, 118.86, 111.27, 40.17. ^{19}F NMR (376 MHz, CDCl_3) δ -62.05. Data in accordance with the literature.¹⁵

3,3'-((4-(trifluoromethyl)phenyl)methylene)bis(1-methyl-1H-indole) 19



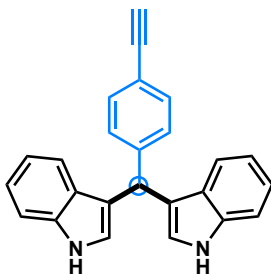
As a red solid: R_f 0.25 (PE: EA = 50:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.54 (d, $J = 8.0$ Hz, 2H), 7.46 (d, $J = 7.8$ Hz, 2H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.32 (d, $J = 8.2$ Hz, 1H), 7.25 – 7.20 (m, 2H), 7.05 – 7.00 (m, 2H), 6.53 (s, 1H), 5.94 (s, 1H), 3.70 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.72, 137.54, 129.08, 128.41, 127.33, 125.32 (q, $J = 4.1$ Hz), 121.77, 119.93, 118.97, 117.40, 109.33, 40.09, 32.82. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -61.97. Data in accordance with the literature.¹⁶

4-(di(1H-indol-3-yl)methyl)benzonitrile 20



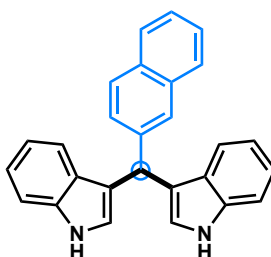
As a pink solid: R_f 0.5 (PE: EA = 2:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO}-d_6$) δ 10.98 (d, $J = 2.5$ Hz, 2H), 7.83 (d, $J = 7.8$ Hz, 1H), 7.62 – 7.54 (m, 1H), 7.42 (dd, $J = 24.5, 7.1$ Hz, 4H), 7.25 (d, $J = 8.0$ Hz, 2H), 7.07 (t, $J = 8.2$ Hz, 2H), 6.94 – 6.88 (m, 2H), 6.85 (s, 2H), 6.16 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO}-d_6$) δ 148.74, 137.13, 133.70, 133.52, 129.74, 127.62, 126.83, 124.68, 121.73, 119.13, 118.63, 116.56, 112.23, 111.76, 38.77. Data in accordance with the literature.¹⁴

3,3'-((4-ethynylphenyl)methylene)bis(1H-indole) 21



As a red solid: R_f 0.25 (PE: EA = 5:1); $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.78 (s, 1H), 7.44 (d, $J = 8.3$ Hz, 3H), 7.40 (d, $J = 7.9$ Hz, 2H), 7.35 – 7.29 (m, 6H), 7.21 (ddd, $J = 8.2, 7.0, 1.2$ Hz, 3H), 7.05 (ddd, $J = 8.1, 7.0, 1.1$ Hz, 3H), 6.57 (d, $J = 1.4$ Hz, 2H), 5.89 (s, 2H), 3.08 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 145.21, 136.76, 132.27, 128.88, 127.02, 123.81, 122.18, 119.95, 119.89, 119.47, 119.10, 112.43, 85.01, 40.21. Data in accordance with the literature.¹⁷

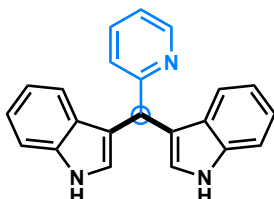
3,3'-((naphthalen-2-yl)methylene)bis(1H-indole) 22



As a red solid: R_f 0.30 (PE: EA = 5:1); $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.83 (t, $J = 4.7$ Hz, 3H), 7.79 – 7.75 (m, 2H), 7.74 – 7.67 (m, 1H), 7.53 (dd, $J = 8.6, 1.7$ Hz, 1H), 7.46 – 7.41 (m, 4H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.21 – 7.15 (m, 2H), 7.04 – 6.98 (m, 2H), 6.62 (d, $J = 1.5$ Hz, 2H), 6.07 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 141.70, 136.77, 133.70,

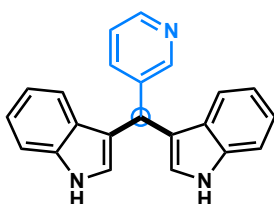
132.45, 128.03, 127.87, 127.69, 127.18, 126.85, 125.82, 125.41, 123.93, 122.07, 120.06, 119.58, 119.39, 111.19, 40.38. Data in accordance with the literature.¹⁴

3,3'-(pyridin-2-ylmethylene)bis(1H-indole) 23



As a white solid: R_f 0.35 (PE: EA = 2:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 10.96 (s, 2H), 8.49 (d, $J = 5.1$ Hz, 1H), 7.66 (t, $J = 7.7$ Hz, 1H), 7.41 – 7.28 (m, 5H), 7.17 (t, $J = 7.1$ Hz, 1H), 7.03 (t, $J = 6.6$ Hz, 2H), 6.94 (s, 2H), 6.86 (t, $J = 8.5$ Hz, 2H), 5.92 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 164.60, 149.30, 137.02, 136.99, 127.25, 124.17, 123.04, 121.82, 121.41, 119.51, 118.78, 117.43, 112.69, 43.20. Data in accordance with the literature.¹⁴

3,3'-(pyridin-3-ylmethylene)bis(1H-indole) 24

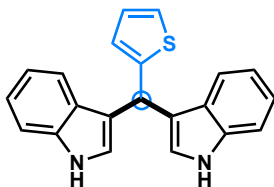


As a purple solid: R_f 0.45 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}D_6$) δ 10.92, 8.62, 8.62, 8.40, 8.40, 8.39, 8.38, 7.71, 7.69, 7.38, 7.36, 7.31, 7.30, 7.29, 7.27, 7.07, 7.05, 7.03, 6.90, 6.88, 6.86, 5.92. $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 150.19, 147.69, 140.81,

137.13, 136.15, 126.91, 124.22, 123.85, 121.59, 119.50, 118.88, 117.67, 112.10, 37.62.

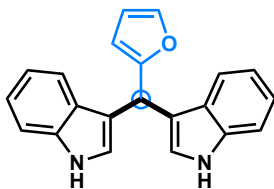
Data in accordance with the literature.¹⁴

3,3'-(thiophen-2-ylmethylene)bis(1H-indole) 25



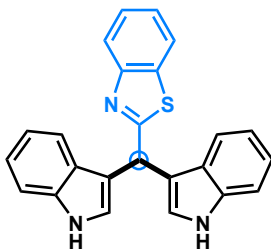
As an orange solid: R_f 0.35 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (s, 2H), 7.47 (d, $J = 7.3$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.22 – 7.12 (m, 3H), 7.04 (t, $J = 7.5$ Hz, 2H), 6.95 – 6.88 (m, 2H), 6.83 (d, $J = 1.5$ Hz, 2H), 6.17 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.71, 136.64, 126.82, 126.54, 125.24, 123.73, 123.30, 122.12, 119.86, 119.76, 119.46, 111.24, 35.37. Data in accordance with the literature.¹⁴

3,3'-(furan-2-ylmethylene)bis(1H-indole) 26



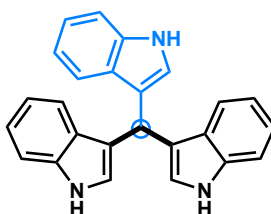
As an orange solid: R_f 0.40 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.94 (s, 2H), 7.49 (d, $J = 7.9$ Hz, 2H), 7.35 (d, $J = 8.2$ Hz, 3H), 7.21 – 7.15 (m, 2H), 7.07 – 7.02 (m, 2H), 6.86 (d, $J = 1.5$ Hz, 2H), 6.31 (dd, $J = 3.2, 1.8$ Hz, 1H), 6.06 (d, $J = 4.2$ Hz, 1H), 5.95 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 157.88, 141.36, 136.61, 126.85, 123.18, 122.07, 119.78, 119.46, 117.64, 111.25, 110.26, 106.73, 34.19. Data in accordance with the literature.¹⁵

2-(di(1H-indol-3-yl)methyl)benzo[d]thiazole 27



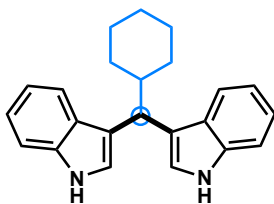
As a brown solid: R_f 0.30 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.06 (s, 1H), 7.94 (t, $J = 7.6$ Hz, 2H), 7.46 (d, $J = 8.1$ Hz, 3H), 7.38 (dd, $J = 12.7, 7.9$ Hz, 3H), 7.23 (d, $J = 2.4$ Hz, 2H), 7.11 – 7.03 (m, 2H), 6.92 (t, $J = 7.6$ Hz, 2H), 6.39 (d, $J = 6.0$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 176.93, 153.51, 136.97, 135.61, 126.86, 126.43, 125.26, 124.59, 122.95, 122.63, 121.75, 119.46, 119.18, 115.81, 111.71. **HRMS** (EI) Calcd for $\text{C}_{24}\text{H}_{17}\text{N}_3\text{S}$: $[\text{M}+\text{H}]^+$ 380.1221. Found: m/z 380.1219.

tri(1H-indol-3-yl)methane 28



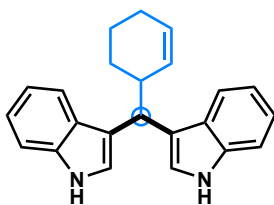
As a white solid: R_f 0.45 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 10.75 (d, $J = 2.4$ Hz, 3H), 7.41 (d, $J = 7.9$ Hz, 3H), 7.34 (d, $J = 8.1$ Hz, 3H), 7.02 (t, $J = 7.5$ Hz, 3H), 6.95 (d, $J = 2.3$ Hz, 3H), 6.90 – 6.81 (m, 3H), 6.06 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}D_6$) δ 137.09, 127.28, 123.74, 121.17, 119.84, 118.77, 118.48, 111.91, 31.44. Data in accordance with the literature.¹⁶

3,3'-(cyclohexylmethylene)bis(1H-indole) 29



As a brown solid: R_f 0.25 (PE: EA = 5:1); $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.71 (s, 2H), 7.69 (s, 1H), 7.28 – 7.23 (m, 2H), 7.17 (td, $J = 8.1, 7.5, 1.3$ Hz, 2H), 7.10 (ddd, $J = 8.0, 6.9, 1.2$ Hz, 2H), 6.99 (d, $J = 2.4$ Hz, 2H), 4.29 (d, $J = 8.8$ Hz, 1H), 2.27 (dddd, $J = 14.6, 11.6, 7.7, 3.2$ Hz, 1H), 1.86 (d, $J = 11.7$ Hz, 2H), 1.72 (d, $J = 13.6$ Hz, 3H), 1.34 – 1.21 (m, 2H), 1.17 – 1.02 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.33, 127.88, 121.70, 119.87, 119.80, 119.08, 111.12, 43.04, 40.23, 32.48, 26.83, 26.78. Data in accordance with the literature.¹²

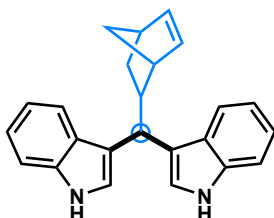
3,3'-(cyclohex-2-en-1-ylmethylene)bis(1H-indole) 30



As a brown solid: R_f 0.35 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (d, $J = 7.8$ Hz, 2H), 7.69 (d, $J = 7.9$ Hz, 2H), 7.30 (dd, $J = 7.9, 3.5$ Hz, 2H), 7.18 – 7.03 (m, 6H), 5.72 – 5.59 (m, 2H), 4.35 (d, $J = 9.4$ Hz, 1H), 2.67 – 2.54 (m, 1H), 2.18 – 2.02 (m, 3H), 1.98 – 1.83 (m, 2H), 1.43 – 1.31 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 136.36, 136.33, 127.85, 127.67, 127.12, 127.01, 121.79, 121.73, 121.59, 119.71, 119.53, 119.48, 119.16,

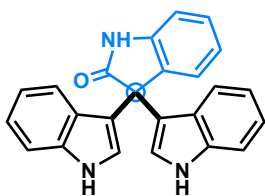
111.16, 39.38, 38.88, 30.96, 27.35, 25.25. **HRMS** (EI) Calcd for C₂₃H₂₂N₂: [M+H]⁺ 327.1861. Found: m/z 327.1856. Data in accordance with the literature.¹³

3,3'-(bicyclo[2.2.1]hept-5-en-2-ylmethylene)bis(1H-indole) 31



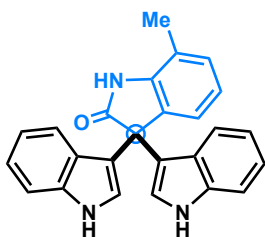
As a pale brown solid: R_f 0.35 (PE: EA = 5:1); **¹H NMR** (400 MHz, CDCl₃) δ 7.84 (s, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.19 (s, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.05 (d, *J* = 9.0 Hz, 2H), 7.00 – 6.95 (m, 1H), 6.28 – 6.23 (m, 1H), 6.13 (d, *J* = 8.7 Hz, 1H), 3.87 (d, *J* = 11.9 Hz, 1H), 3.21 – 3.12 (m, 1H), 2.82 (s, 1H), 2.65 (s, 1H), 1.98 (td, *J* = 8.6, 8.2, 4.5 Hz, 1H), 1.56 (s, 1H), 1.44 – 1.32 (m, 2H), 0.81 (d, *J* = 11.8 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 137.56, 136.53, 136.37, 133.10, 127.65, 126.97, 121.72, 121.63, 121.45, 121.21, 120.59, 120.48, 119.92, 119.63, 119.00, 111.25, 111.11, 49.63, 45.58, 44.48, 43.18, 38.82, 32.92. **HRMS** (EI) Calcd for C₂₄H₂₂N₂: [M+H]⁺ 339.1861. Found: m/z 339.1867.

1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 32



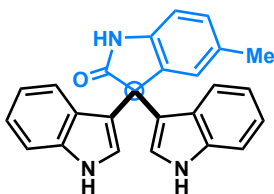
As a white solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.01 (s, 1H), 10.64 (s, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 3H), 7.04 – 6.98 (m, 1H), 6.93 (t, $J = 7.0$ Hz, 0H), 6.86 (d, $J = 2.5$ Hz, 2H), 6.80 (t, $J = 8.1$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.31, 141.86, 137.45, 135.14, 128.38, 126.23, 125.44, 124.83, 122.01, 121.48, 121.31, 118.76, 115.19, 112.15, 110.76, 53.09. Data in accordance with the literature.¹⁹

7'-methyl-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 33



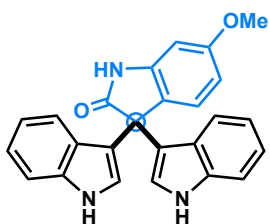
As a white solid: R_f 0.4 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 10.95 (s, 2H), 10.64 (s, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 7.02 (dd, $J = 18.0, 7.8$ Hz, 4H), 6.87 – 6.76 (m, 5H), 2.31 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 180.90, 140.40, 137.45, 134.77, 129.56, 126.28, 124.76, 122.79, 121.91, 121.41, 119.36, 118.72, 115.01, 112.10, 80.22, 53.33, 16.76. Data in accordance with the literature.¹⁹

5'-methyl-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 34



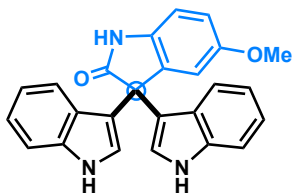
As a lavender solid: R_f 0.4 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 10.93 (d, J = 2.6 Hz, 2H), 10.49 (s, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.1 Hz, 2H), 7.02 – 6.95 (m, 4H), 6.85 (d, J = 7.6 Hz, 1H), 6.81 (d, J = 2.5 Hz, 2H), 6.80 – 6.74 (m, 2H), 2.15 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.34, 139.43, 137.45, 135.17, 130.71, 128.97, 126.24, 124.82, 121.46, 118.75, 114.92, 112.12, 109.93, 53.14, 21.35. Data in accordance with the literature.¹⁹

6'-methoxy-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 35



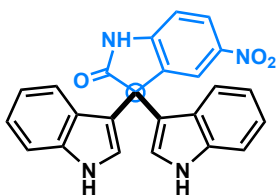
As a milky solid: R_f 0.25 (PE: EA = 2:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 10.90 (s, 2H), 10.52 (s, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.2 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.81 (s, 2H), 6.77 (t, J = 7.6 Hz, 2H), 6.52 (s, 1H), 6.45 (d, J = 8.3 Hz, 1H), 3.71 (d, J = 1.7 Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.80, 159.08, 142.98, 137.48, 127.18, 126.26, 126.08, 124.75, 121.43, 121.34, 118.73, 115.26, 112.11, 106.88, 96.80, 54.79, 53.39. Data in accordance with the literature.¹⁹

5'-methoxy-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 36



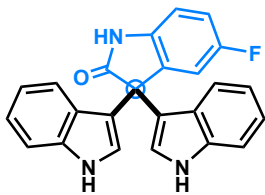
As a pale pink solid: R_f 0.25 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.00 (s, 1H), 10.48 (s, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.02 (t, $J = 8.2$ Hz, 1H), 6.92 (d, $J = 8.9$ Hz, 1H), 6.88 (d, $J = 2.5$ Hz, 2H), 6.81 (dt, $J = 8.1, 3.7$ Hz, 3H), 3.61 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 178.57, 154.71, 137.45, 136.49, 135.22, 126.20, 124.90, 121.48, 121.31, 118.77, 114.76, 112.62, 112.57, 112.16, 110.41, 55.82, 52.77. Data in accordance with the literature.¹⁹

5'-nitro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 37



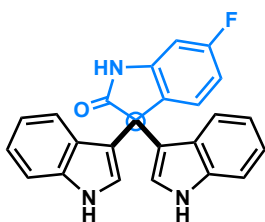
As a pale yellow solid: R_f 0.25 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.39 (s, 1H), 11.14 (s, 2H), 8.24 (dd, $J = 8.6, 2.4$ Hz, 1H), 7.98 (d, $J = 2.4$ Hz, 1H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.22 (dd, $J = 8.4, 3.0$ Hz, 3H), 7.04 (t, $J = 7.6$ Hz, 2H), 6.96 (d, $J = 2.6$ Hz, 2H), 6.84 (t, $J = 7.5$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 180.61, 148.36, 143.68, 137.56, 135.81, 126.01, 125.92, 125.15, 121.74, 120.86, 120.62, 119.12, 113.83, 112.40, 109.33, 54.79. Data in accordance with the literature.¹⁹

5'-fluoro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 38



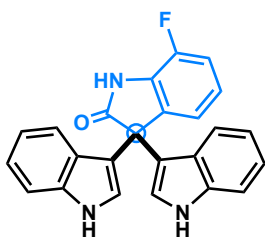
As a milky solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 10.98 (s, 2H), 10.62 (s, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.08 – 6.92 (m, 5H), 6.87 (s, 2H), 6.79 (t, $J = 7.5$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.22, 158.40 (d, $J = 236.6$ Hz), 138.10, 137.48, 136.87 (d, $J = 7.5$ Hz), 126.08, 124.98, 121.58, 121.14, 118.92, 114.76 (d, $J = 23.1$ Hz), 114.19, 112.97 (d, $J = 24.3$ Hz), 112.24, 110.90 (d, $J = 8.2$ Hz), 53.64. $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO-}d_6$) δ -121.45 (td, $J = 8.9, 4.4$ Hz). Data in accordance with the literature.¹⁹

6'-fluoro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 39



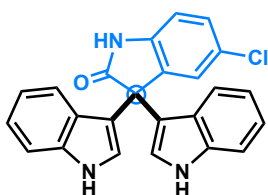
As a pale pink solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.00 (s, 2H), 10.77 (s, 1H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 8.1$ Hz, 3H), 7.02 (t, $J = 7.0$ Hz, 2H), 6.86 (d, $J = 2.5$ Hz, 2H), 6.84 – 6.79 (m, 3H), 6.77 – 6.70 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.51, 162.34 (d, $J = 232.2$ Hz), 143.40 (d, $J = 12.2$ Hz), 137.48, 130.99, 126.66 (d, $J = 9.9$ Hz), 126.12, 124.85, 121.51, 121.17, 118.83, 114.55, 112.20, 108.06 (d, $J = 21.8$ Hz), 98.24 (d, $J = 26.6$ Hz), 52.68. $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO-}d_6$) δ -113.23 – -113.32 (m). **HRMS** (EI) Calcd for $\text{C}_{24}\text{H}_{16}\text{FN}_3\text{O}$: $[\text{M}+\text{H}]^+$ 382.1365. Found: m/z 382.1356.

7'-fluoro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 40



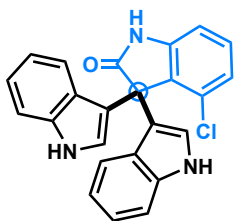
As a milky solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 11.09 (s, 1H), 10.98 (s, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.19 (d, $J = 8.0$ Hz, 2H), 7.12 (t, $J = 9.3$ Hz, 1H), 7.05 (d, $J = 5.6$ Hz, 1H), 6.99 (t, $J = 7.6$ Hz, 2H), 6.91 (q, $J = 7.7, 6.5$ Hz, 1H), 6.83 (s, 2H), 6.81 – 6.73 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.06, 147.01 (d, $J = 242.3$ Hz), 138.01, 137.47, 128.92 (d, $J = 12.4$ Hz), 126.09, 124.93, 122.87 (d, $J = 5.9$ Hz), 121.57, 121.14, 118.91, 115.37 (d, $J = 17.2$ Hz), 114.23, 112.23, 53.44. $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO-}d_6$) δ -132.49 (dd, $J = 10.4, 4.7$ Hz). Data in accordance with the literature.¹⁹

5'-chloro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 41



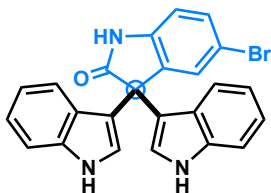
As a milky solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 11.03 (s, 2H), 10.77 (s, 1H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.30 (d, $J = 8.3$ Hz, 1H), 7.24 – 7.16 (m, 3H), 7.08 – 6.98 (m, 3H), 6.90 (s, 2H), 6.86 – 6.79 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 178.93, 140.82, 137.48, 137.15, 128.39, 126.04, 125.98, 125.22, 124.97, 121.61, 121.06, 118.97, 114.04, 112.29, 111.67, 53.98. Data in accordance with the literature.¹⁹

4'-chloro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 42



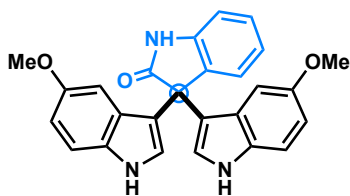
As a white solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 10.99 (s, 2H), 10.77 (s, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.25 (dd, $J = 22.3, 9.2$ Hz, 4H), 7.04 – 6.95 (m, 3H), 6.88 (s, 2H), 6.85 – 6.79 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.50, 144.28, 137.26, 131.54, 130.50, 126.40, 125.97, 123.39, 121.43, 121.08, 118.85, 112.21, 111.16, 109.13, 77.20, 53.97. **HRMS** (EI) Calcd for $\text{C}_{24}\text{H}_{16}\text{ClN}_3\text{O}$: $[\text{M}+\text{H}]^+$ 398.1060. Found: m/z 398.1057.

5'-bromo-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 43



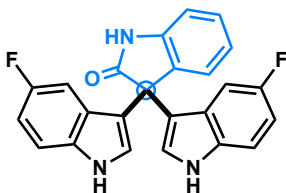
As a milky solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 11.00 (s, 2H), 10.75 (s, 1H), 7.36 (dd, $J = 19.2, 8.1$ Hz, 3H), 7.26 (s, 1H), 7.17 (d, $J = 7.9$ Hz, 2H), 7.00 (t, $J = 7.6$ Hz, 2H), 6.94 (d, $J = 8.2$ Hz, 1H), 6.86 (s, 2H), 6.79 (t, $J = 7.6$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.80, 141.23, 137.53, 137.48, 131.24, 127.89, 126.03, 124.97, 121.62, 121.04, 118.97, 114.04, 113.68, 112.30, 112.23, 54.28. Data in accordance with the literature.¹⁹

5,5''-dimethoxy-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 44



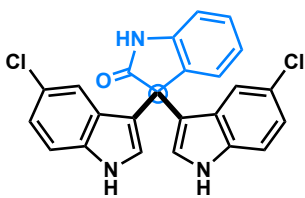
As a white solid: R_f 0.3 (PE: EA = 2:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 10.77 (s, 2H), 10.57 (s, 1H), 7.20 (dd, $J = 17.4, 6.9$ Hz, 4H), 6.97 (d, $J = 6.7$ Hz, 1H), 6.94 – 6.88 (m, 1H), 6.82 (s, 2H), 6.66 (d, $J = 10.9$ Hz, 4H), 3.49 (d, $J = 1.9$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.31, 153.33, 142.39, 135.08, 132.34, 128.38, 126.65, 125.71, 125.52, 122.04, 114.16, 112.61, 110.96, 109.98, 103.84, 55.64, 53.04. Data in accordance with the literature.¹⁹

5,5''-difluoro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 45



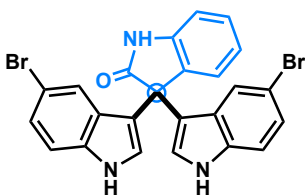
As a milky solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 11.01 (s, 2H), 10.61 (s, 1H), 7.17 (m, 4H), 7.10 (d, $J = 10.1$ Hz, 2H), 6.96 (d, $J = 7.7$ Hz, 1H), 6.91 (t, $J = 7.5$ Hz, 1H), 6.82 (s, 2H), 6.70 – 6.61 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.05, 159.18 (d, $J = 234.9$ Hz), 141.77, 137.34 (d, $J = 12.6$ Hz), 134.65, 128.57, 125.37, 123.01, 122.24, 122.15, 114.99, 110.28, 107.43 (d, $J = 24.1$ Hz), 98.02 (d, $J = 25.4$ Hz), 52.87. $^{19}\text{F NMR}$ (376 MHz, $\text{DMSO-}d_6$) δ -121.75 – -122.07 (m). Data in accordance with the literature.¹⁹

5,5''-dichloro-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 46



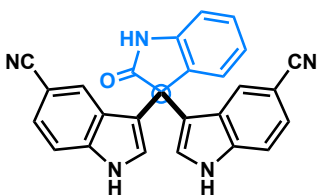
As a milky solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.24 (s, 2H), 10.76 (s, 1H), 7.40 (d, $J = 8.6$ Hz, 2H), 7.27 (t, $J = 7.7$ Hz, 1H), 7.19 (d, $J = 10.0$ Hz, 3H), 7.07 – 7.01 (m, 3H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.94 (d, $J = 2.4$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 178.10, 141.74, 136.00, 134.18, 128.79, 127.11, 126.67, 125.42, 123.50, 122.37, 121.66, 120.16, 114.43, 113.91, 110.39, 53.39. Data in accordance with the literature.¹⁹

5,5''-dibromo-1H,1''H-[3,3':3'',3''-terindol]-2'(1'H)-one 47



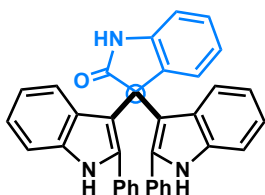
As a milky solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, $\text{DMSO-}d_6$) δ 11.19 (d, $J = 2.7$ Hz, 2H), 10.70 (s, 1H), 7.32 (dd, $J = 5.3, 3.3$ Hz, 4H), 7.23 (td, $J = 7.7, 1.3$ Hz, 1H), 7.11 (dd, $J = 8.7, 2.0$ Hz, 3H), 6.96 (dd, $J = 18.0, 7.5$ Hz, 2H), 6.87 (d, $J = 2.6$ Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 178.10, 141.74, 136.22, 134.12, 128.82, 127.79, 126.53, 125.42, 124.18, 123.19, 122.38, 114.39, 114.33, 111.60, 53.17. Data in accordance with the literature.¹⁹

2'-oxo-1',2'-dihydro-1H,1''H-[3,3':3'',3''-terindole]-5,5''-dicyanitrile 48



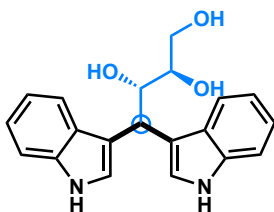
As a brown solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.63 (s, 2H), 10.82 (s, 1H), 7.53 (d, $J = 8.6$ Hz, 4H), 7.36 (dd, $J = 8.3, 1.6$ Hz, 2H), 7.29 – 7.21 (m, 2H), 7.08 (d, $J = 2.5$ Hz, 2H), 7.01 (d, $J = 7.7$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 179.50, 141.68, 139.35, 133.68, 129.07, 127.62, 126.33, 125.73, 125.57, 124.39, 122.63, 121.20, 115.59, 113.91, 110.64, 101.15, 52.58. Data in accordance with the literature.¹⁹

2,2''-diphenyl-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one 49



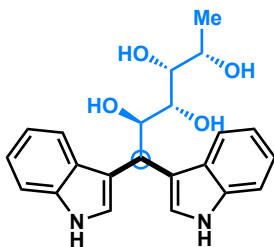
As a lavender solid: R_f 0.3 (PE: EA = 1:1); $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 11.05 (s, 1H), 10.74 (s, 1H), 10.46 (s, 1H), 7.39 – 7.14 (m, 7H), 6.90-7.07 (m, 10H), 6.84 (t, $J = 7.5$ Hz, 1H), 6.65 (dt, $J = 23.9, 7.6$ Hz, 3H), 6.31 (s, 1H). $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 177.98, 141.49, 136.07, 136.02, 135.34, 134.66, 133.99, 129.48, 129.22, 128.36, 128.06, 127.85, 127.73, 127.58, 127.16, 126.37, 125.94, 122.03, 121.80, 121.05, 120.74, 118.86, 118.48, 112.16, 111.43, 111.11, 110.93, 109.66, 53.88. Data in accordance with the literature.²⁰

(2R,3R)-4,4-di(1H-indol-3-yl)butane-1,2,3-triol 50



As a pale yellow solid: R_f 0.3 (DCM: CH_3OH = 20:1); $^1\text{H NMR}$ (401 MHz, CD_3OD) δ 7.70 (d, J = 7.9 Hz, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.19 (s, 1H), 7.07 – 7.00 (m, 2H), 6.97 – 6.88 (m, 2H), 5.07 (d, J = 3.9 Hz, 1H), 4.39 (dd, J = 7.7, 4.0 Hz, 1H), 3.81 (dd, J = 11.3, 3.2 Hz, 1H), 3.66 (dd, J = 11.2, 6.3 Hz, 1H), 3.61 – 3.51 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 128.35, 127.05, 123.70, 122.77, 120.79, 120.68, 119.04, 118.70, 118.09, 118.02, 117.39, 114.10, 110.77, 110.63, 75.16, 72.53, 63.85, 35.36. **HRMS** (EI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$ 337.1552. Found: m/z 337.1566.

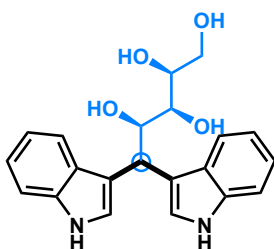
(2S,3R,4R,5R)-1,1-di(1H-indol-3-yl)hexane-2,3,4,5-tetraol 51



As a reddish solid: R_f 0.25 (DCM: CH_3OH = 20:1); $^1\text{H NMR}$ (401 MHz, CD_3OD) δ 7.70 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.36 – 7.27 (m, 3H), 7.17 (s, 1H), 7.04 (dd,

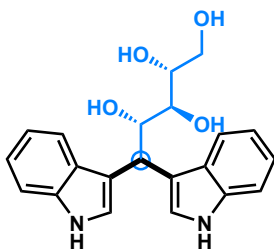
$J = 8.2, 7.0$ Hz, 2H), 6.93 (qd, $J = 8.0, 1.0$ Hz, 2H), 5.15 (d, $J = 3.3$ Hz, 1H), 4.52 (dd, $J = 8.5, 3.3$ Hz, 1H), 3.82 (d, $J = 9.6$ Hz, 1H), 3.80 – 3.75 (m, 1H), 3.66 (d, $J = 7.5$ Hz, 1H), 1.17 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 136.88, 136.45, 128.45, 127.09, 123.87, 120.76, 120.66, 119.12, 118.76, 118.07, 117.97, 117.72, 113.86, 110.76, 110.62, 100.08, 74.61, 73.78, 70.44, 67.82, 35.20, 19.19. HRMS (EI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$ 381.1814. Found: m/z 381.1814. Data in accordance with the literature.²¹

(2S,3S,4R)-5,5-di(1H-indol-3-yl)pentane-1,2,3,4-tetraol 52



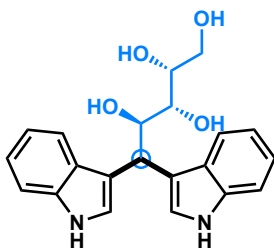
As a reddish solid: R_f 0.3 (DCM: $\text{CH}_3\text{OH} = 10:1$); ^1H NMR (401 MHz, CD_3OD) δ 7.68 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 6.8$ Hz, 1H), 7.32 (s, 3H), 7.28 (t, $J = 7.4$ Hz, 5H), 7.20 (s, 3H), 7.06 – 6.98 (m, 4H), 6.92 (dd, $J = 17.2, 7.5$ Hz, 3H), 4.88 (s, 2H), 4.80 (d, $J = 8.7$ Hz, 1H), 4.64 (s, 5H), 3.76 (d, $J = 9.3$ Hz, 3H), 3.62 – 3.48 (m, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 138.15, 138.00, 129.16, 128.51, 123.78, 123.61, 122.08, 120.32, 119.40, 119.30, 117.99, 117.69, 112.06, 74.12, 71.53, 65.09, 38.59. HRMS (EI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$ 367.1658. Found: m/z 367.1654. Data in accordance with the literature.¹¹

(2R,3R,4R)-5,5-di(1H-indol-3-yl)pentane-1,2,3,4-tetraol 53



As a reddish solid: R_f 0.25 (DCM: CH_3OH = 10:1); $^1\text{H NMR}$ (401 MHz, CD_3OD) δ 7.65 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 9.1 Hz, 1H), 7.38 (s, 1H), 7.31 (t, J = 7.8 Hz, 2H), 7.12 (s, 1H), 7.07 – 7.01 (m, 2H), 6.94 (t, J = 7.5 Hz, 2H), 5.15 (d, J = 3.1 Hz, 1H), 4.64 (s, 2H), 4.41 (dd, J = 8.5, 3.2 Hz, 1H), 3.91 – 3.84 (m, 1H), 3.79 (dd, J = 11.4, 3.7 Hz, 1H), 3.71 – 3.60 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 138.14, 137.59, 129.70, 128.26, 125.14, 124.45, 122.06, 121.94, 120.23, 119.88, 119.36, 119.30, 118.54, 114.96, 112.07, 111.89, 77.98, 75.97, 73.66, 63.93, 37.08. **HRMS** (EI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$ 367.1658. Found: m/z 367.1663. Data in accordance with the literature.¹¹

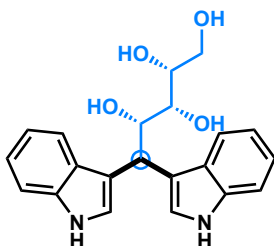
(2R,3S,4S)-5,5-di(1H-indol-3-yl)pentane-1,2,3,4-tetraol 54



As a pale yellow solid: R_f 0.2 (DCM: CH_3OH = 10:1); $^1\text{H NMR}$ (401 MHz, CD_3OD) δ 7.69 (d, J = 8.0 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.18 (s, 1H), 7.09 – 6.99 (m, 3H), 6.97 – 6.88 (m, 1H), 5.13 (d, J = 3.1 Hz, 2H), 4.64 (s, 2H), 4.50 (dd, J = 8.6, 3.2 Hz, 2H), 4.00 (t, J = 6.2 Hz, 1H), 3.63 – 3.45 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, CD_3OD) δ 138.14, 137.68, 129.72, 128.35, 125.16, 124.18, 122.05, 121.95, 120.37,

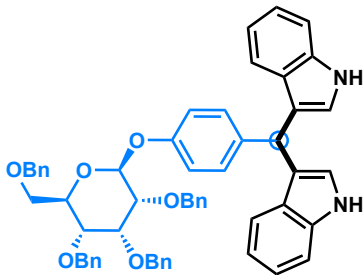
120.01, 119.37, 119.26, 118.95, 115.04, 112.04, 111.91, 75.38, 73.01, 72.06, 65.85, 37.18. **HRMS** (EI) Calcd for $C_{21}H_{22}N_2O_4$: $[M+H]^+$ 367.1658. Found: m/z 367.1660. Data in accordance with the literature.¹¹

(2R,3S,4R)-5,5-di(1H-indol-3-yl)pentane-1,2,3,4-tetraol 55



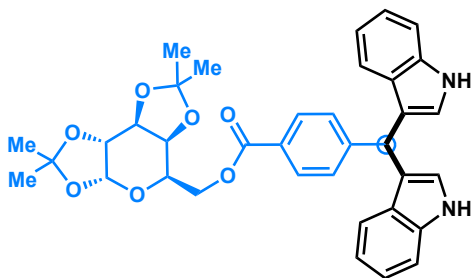
As a pale yellow solid: R_f 0.2 (DCM: CH_3OH = 10:1); **1H NMR** (400 MHz, CD_3OD) δ 7.71 (d, J = 7.7 Hz, 1H), 7.59 (d, J = 8.8 Hz, 2H), 7.38 (s, 2H), 7.32 – 7.25 (m, 4H), 7.11 (s, 2H), 7.03 (q, J = 6.7 Hz, 4H), 6.98 – 6.87 (m, 4H), 4.63 (s, 1H), 3.80 (q, J = 5.1, 4.7 Hz, 1H), 3.66 (t, J = 3.7 Hz, 2H), 3.56 (t, J = 5.2 Hz, 4H). **^{13}C NMR** (101 MHz, CD_3OD) δ 138.05, 137.88, 129.16, 128.28, 124.09, 123.94, 122.08, 122.00, 120.17, 120.10, 119.38, 119.32, 117.88, 116.77, 112.08, 111.99, 76.70, 74.97, 72.40, 65.03, 39.18. **HRMS** (EI) Calcd for $C_{21}H_{22}N_2O_4$: $[M+H]^+$ 367.1658. Found: m/z 367.1651. Data in accordance with the literature.¹¹

3-((3a,7a-dihydro-1H-indol-3-yl)(4-(((2S,3R,4R,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)cyclohexa-2,4-dien-1-yl)methyl)-1H-indole 56



As an orange solid: R_f 0.2 (PE: EA = 5:1); $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.89 (s, 2H), 7.42 – 7.30 (m, 15H), 7.29 – 7.26 (m, 2H), 7.25 (d, $J = 1.9$ Hz, 2H), 7.24 – 7.21 (m, 4H), 7.20 – 7.14 (m, 5H), 7.03 – 6.98 (m, 4H), 6.57 (t, $J = 2.5$ Hz, 3H), 5.84 (s, 1H), 5.51 (d, $J = 7.9$ Hz, 1H), 4.96 – 4.88 (m, 2H), 4.82 (d, $J = 11.9$ Hz, 1H), 4.73 (d, $J = 12.1$ Hz, 1H), 4.58 (d, $J = 12.1$ Hz, 1H), 4.53 – 4.46 (m, 2H), 4.39 (d, $J = 11.5$ Hz, 1H), 4.24 – 4.17 (m, 2H), 3.80 (dd, $J = 10.8, 1.9$ Hz, 1H), 3.69 (dd, $J = 10.8, 4.9$ Hz, 1H), 3.59 – 3.50 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 156.02, 138.95, 138.66, 138.36, 138.08, 137.94, 136.79, 129.66, 128.55, 128.52, 128.40, 128.33, 128.16, 127.90, 127.87, 127.76, 127.58, 127.18, 123.90, 121.90, 120.07, 119.88, 119.23, 116.57, 111.19, 99.44, 78.84, 75.66, 74.85, 74.62, 73.47, 73.29, 72.67, 71.73, 69.28, 39.50. **HRMS** (EI) Calcd for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_3$: $[\text{M}+\text{H}]^+$ 861.3904. Found: m/z 861.3901.

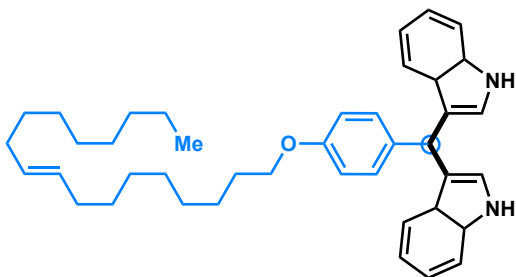
((3aS,4R,8aS,8bS)-2,2,7,7-tetramethylhexahydrobenzo[1,2-d:3,4-d']bis([1,3]dioxole)-4-yl)methyl 4-(di(1H-indol-3-yl)methyl)benzoate 57



As a red solid: R_f 0.35 (PE: EA = 2:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 – 7.94 (m, 4H), 7.42 – 7.33 (m, 6H), 7.18 (t, $J = 7.1$ Hz, 2H), 7.01 (t, $J = 7.0$ Hz, 2H), 6.61 – 6.58 (m, 2H), 5.92 (s, 1H), 5.58 (d, $J = 4.9$ Hz, 1H), 4.66 (dd, $J = 7.9, 2.5$ Hz, 1H), 4.47 (qd, $J = 11.5, 6.2$ Hz, 2H), 4.34 (ddd, $J = 9.8, 6.5, 2.2$ Hz, 2H), 4.20 (ddd, $J = 7.1, 5.1, 1.8$ Hz, 1H), 1.50 (d, $J = 13.4$ Hz, 6H), 1.35 (d, $J = 10.6$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.69, 149.78, 136.75, 129.92, 128.87, 128.05, 126.95, 123.83, 122.16, 119.85, 119.45, 118.82, 111.28, 109.79, 108.96, 96.42, 71.20, 70.79, 70.60, 66.21, 63.83, 40.35, 26.17, 26.09, 25.09, 24.59. **HRMS** (EI) Calcd for $\text{C}_{43}\text{H}_{58}\text{N}_2$: $[\text{M}+\text{H}]^+$ 609.2601. Found: m/z 609.2608.

(E)-3,3'-((4-(octadec-9-en-1-yloxy)phenyl)methylene)bis(3a,7a-dihydro-1H-indole)

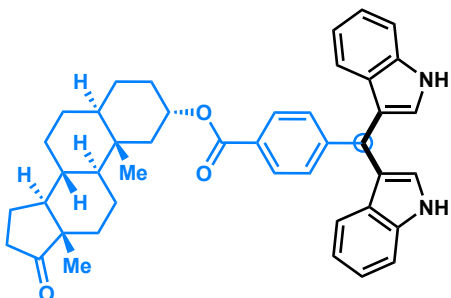
58



As an orange solid: R_f 0.35 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (s, 2H), 7.42 (d, $J = 7.9$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.19 (t, $J =$

7.5 Hz, 2H), 7.03 (t, $J = 7.5$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 2H), 6.59 (s, 2H), 5.85 (s, 1H), 5.42 – 5.38 (m, 1H), 3.94 (t, $J = 6.5$ Hz, 2H), 2.06 (d, $J = 6.3$ Hz, 3H), 1.79 (p, $J = 6.8$ Hz, 2H), 1.48 (s, 2H), 1.33 (d, $J = 19.2$ Hz, 23H), 0.97 – 0.89 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 157.59, 136.78, 136.11, 130.12, 130.00, 129.69, 127.17, 123.68, 121.98, 120.13, 119.28, 114.24, 111.16, 68.48, 39.43, 32.06, 29.91, 29.86, 29.68, 29.63, 29.56, 29.53, 29.48, 29.40, 27.36, 26.25, 22.85, 14.30. **HRMS** (EI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$ 593.4471. Found: m/z 593.4463.

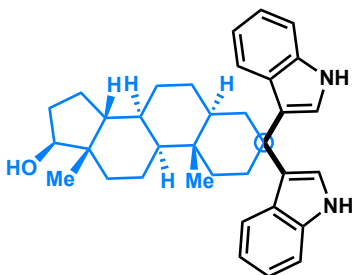
(2S,5S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a]phenanthren-2-yl 4-(di(1H-indol-3-yl)methyl)benzoate 59



As a red solid: R_f 0.35 (PE: EA = 2:1); ^1H NMR (401 MHz, CDCl_3) δ 8.07 (d, $J = 2.5$ Hz, 2H), 7.99 (d, $J = 8.3$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.37 (t, $J = 8.1$ Hz, 4H), 7.18 (ddd, $J = 8.1, 7.0, 1.2$ Hz, 2H), 7.06 – 6.98 (m, 2H), 6.68 – 6.62 (m, 2H), 5.95 (s, 1H), 5.28 (s, 1H), 2.45 (dd, $J = 19.2, 8.6$ Hz, 1H), 2.07 (dt, $J = 18.3, 9.0$ Hz, 1H), 1.98 – 1.65 (m, 7H), 1.64 – 1.44 (m, 6H), 1.41 – 1.19 (m, 7H), 1.02 (qd, $J = 12.0, 5.6$ Hz, 1H), 0.87 (d, $J = 3.9$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 221.88, 166.15, 149.57, 136.79, 129.74, 129.11, 128.87, 126.97, 123.83, 123.79, 122.16, 119.86, 119.43, 118.84, 111.30, 70.42, 54.49, 51.52, 47.96, 40.52, 40.36, 36.14, 36.00, 35.10, 33.27, 33.06, 31.62, 30.82,

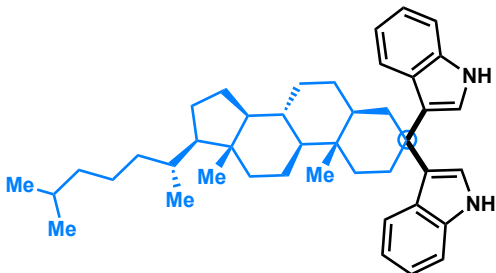
28.14, 26.39, 21.84, 20.19, 13.94, 11.52. **HRMS** (EI) Calcd for C₄₃H₄₆N₂O₃: [M+H]⁺ 639.3587. Found: m/z 639.3587.

(5S,8S,9S,10S,13S,14R,17S)-3,3-di(1H-indol-3-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-ol 60



As a white solid: *R_f* 0.30 (PE: EA = 2:1); **¹H NMR** (400 MHz, DMSO-*d*₆) δ 10.74 (s, 1H), 10.61 (s, 1H), 7.42 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 6.84 (q, *J* = 7.5, 7.0 Hz, 2H), 6.64 (t, *J* = 7.1 Hz, 2H), 4.38 (d, *J* = 4.8 Hz, 1H), 3.31 (d, *J* = 2.3 Hz, 1H), 2.75 (d, *J* = 13.5 Hz, 1H), 2.40 (d, *J* = 13.3 Hz, 1H), 2.02 (q, *J* = 11.7, 11.0 Hz, 2H), 1.75 (dt, *J* = 9.4, 5.4 Hz, 1H), 1.66 (d, *J* = 12.5 Hz, 1H), 1.59 – 1.50 (m, 2H), 1.46 (d, *J* = 11.2 Hz, 1H), 1.36 (s, 2H), 1.35 – 1.24 (m, 3H), 1.18 (d, *J* = 12.7 Hz, 3H), 1.11 – 1.01 (m, 1H), 0.86 (s, 4H), 0.78 (dd, *J* = 11.2, 7.3 Hz, 1H), 0.73 – 0.63 (m, 1H), 0.58 (s, 3H), 0.54 – 0.45 (m, 1H). **¹³C NMR** (101 MHz, DMSO-*d*₆) δ 137.51, 137.41, 126.64, 126.16, 125.91, 124.16, 121.11, 120.89, 120.76, 120.62, 120.56, 119.53, 118.01, 117.91, 111.85, 82.47, 80.58, 55.02, 51.10, 43.08, 42.07, 39.47, 38.98, 37.08, 36.57, 35.81, 35.66, 33.14, 31.84, 30.34, 28.78, 23.57, 20.69, 12.91, 11.88. **HRMS** (EI) Calcd for C₃₅H₄₂N₂O: [M+H]⁺ 507.3375. Found: m/z 507.3369.

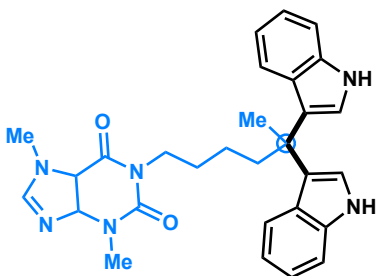
3,3'-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene-3,3'-diyl)bis(1H-indole) 61



As a brown solid: R_f 0.2 (PE: EA = 10:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (s, 1H), 7.73 (s, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 8.1$ Hz, 1H), 7.31 (d, $J = 7.7$ Hz, 2H), 7.24 (d, $J = 6.4$ Hz, 1H), 7.10 – 7.01 (m, 2H), 6.96 – 6.79 (m, 3H), 2.70 (d, $J = 11.3$ Hz, 1H), 2.44 – 2.24 (m, 3H), 1.95 (dt, $J = 12.6, 3.4$ Hz, 1H), 1.85 – 1.71 (m, 1H), 1.69 – 1.56 (m, 2H), 1.56 – 1.40 (m, 6H), 1.38 – 1.28 (m, 5H), 1.23 (t, $J = 13.2$ Hz, 3H), 1.12 (d, $J = 39.5$ Hz, 4H), 1.05 (s, 6H), 0.93 – 0.84 (m, 9H), 0.79 (d, $J = 4.7$ Hz, 1H), 0.65 (s, 3H), 0.62 – 0.55 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 137.21, 137.03, 126.86, 125.98, 123.16, 121.90, 121.31, 121.27, 121.18, 121.05, 120.79, 118.66, 118.62, 111.25, 111.09, 56.64, 56.38, 54.61, 42.70, 41.93, 40.14, 40.04, 39.61, 38.83, 36.46, 36.28, 35.92, 35.67, 35.59, 32.79, 32.06, 28.84, 28.36, 28.11, 24.27, 23.97, 22.94, 22.68, 21.04, 18.78, 12.88, 12.19. **HRMS** (EI) Calcd for $\text{C}_{43}\text{H}_{58}\text{N}_2$: $[\text{M}+\text{H}]^+$ 603.4678. Found: m/z 603.4670.

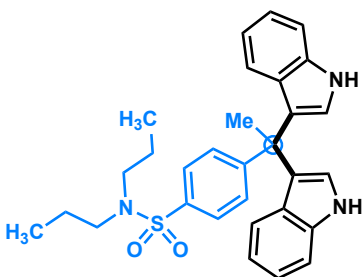
1-(5,5-di(1H-indol-3-yl)hexyl)-3,7-dimethyl-3,4,5,7-tetrahydro-1H-purine-2,6-dione

62



As a grey solid: R_f 0.35 (PE: EA = 1:1); $^1\text{H NMR}$ (401 MHz, CDCl_3) δ 7.98 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 4.8$ Hz, 1H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.03 (t, $J = 8.1$ Hz, 4H), 6.82 (t, $J = 8.1$ Hz, 2H), 3.97 – 3.86 (m, 5H), 3.54 (s, 3H), 2.45 – 2.37 (m, 2H), 1.83 (s, 3H), 1.62 (q, $J = 7.7$ Hz, 2H), 1.31 – 1.19 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 154.84, 151.53, 148.74, 141.43, 137.11, 126.49, 124.24, 121.34, 118.65, 111.05, 107.76, 41.56, 40.25, 38.48, 33.62, 29.76, 28.61, 27.06, 22.19. **HRMS** (EI) Calcd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4$: $[\text{M}+\text{H}]^+$ 497.2665. Found: m/z 497.2668.

4-(1,1-di(1H-indol-3-yl)ethyl)-N,N-dipropylbenzenesulfonamide 63

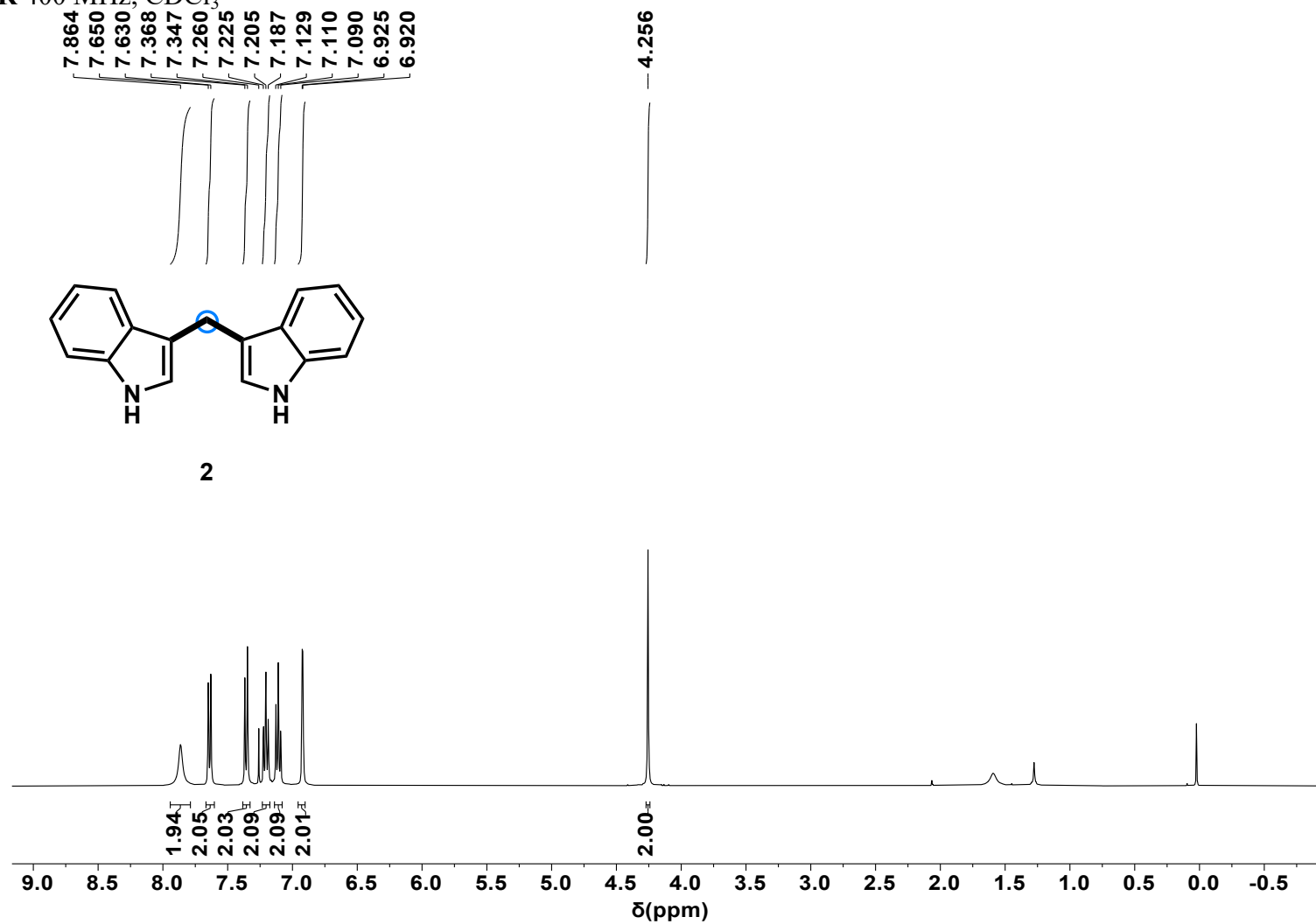


As a brown solid: R_f 0.2 (PE: EA = 5:1); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (s, 2H), 7.67 (d, $J = 8.6$ Hz, 2H), 7.52 (d, $J = 8.6$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 9.1$ Hz, 2H), 7.18 – 7.12 (m, 2H), 6.98 – 6.90 (m, 2H), 6.61 (d, $J = 2.4$ Hz, 2H), 3.11 – 3.02 (m, 4H), 2.36 (s, 3H), 1.51 (h, $J = 7.4$ Hz, 4H), 0.83 (t, $J = 7.4$ Hz, 6H). $^{13}\text{C NMR}$

(101 MHz, CDCl₃) δ 153.01, 137.64, 137.20, 128.87, 126.73, 126.19, 123.71, 123.51, 121.85, 121.81, 119.20, 111.44, 49.83, 44.47, 28.78, 22.36, 11.29. **HRMS** (EI) Calcd for C₃₀H₃₃N₃O₂S: [M+H]⁺ 500.2372. Found: m/z 500.2373.

10. Spectra for compounds

^1H NMR 400 MHz, CDCl_3

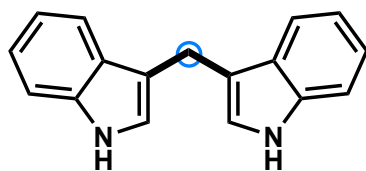


^{13}C NMR 101 MHz, CDCl_3

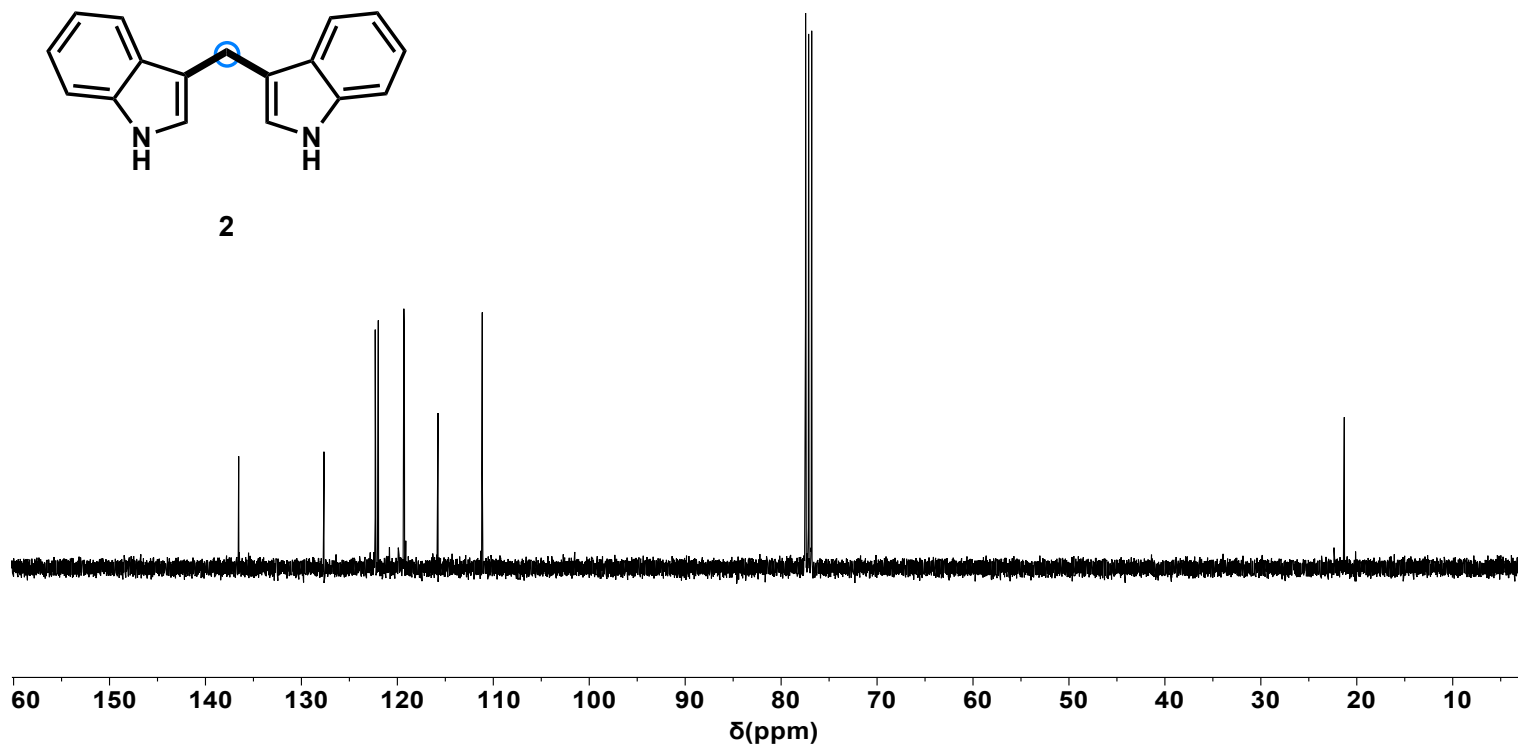
136.538
127.655
122.306
121.987
119.324
119.271
115.762
111.149

77.450
77.134
76.815

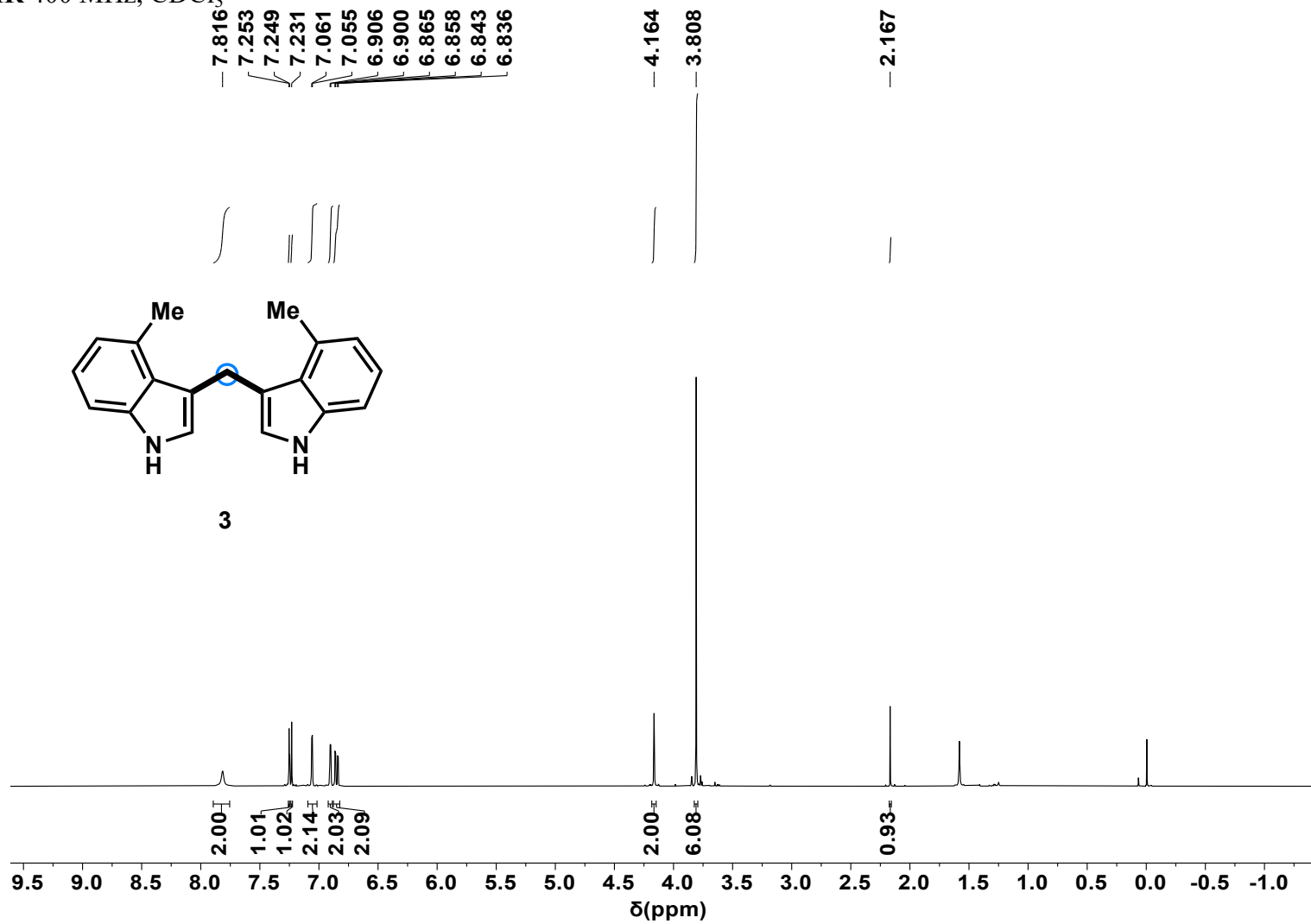
21.302



2



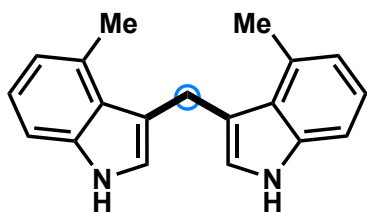
^1H NMR 400 MHz, CDCl_3



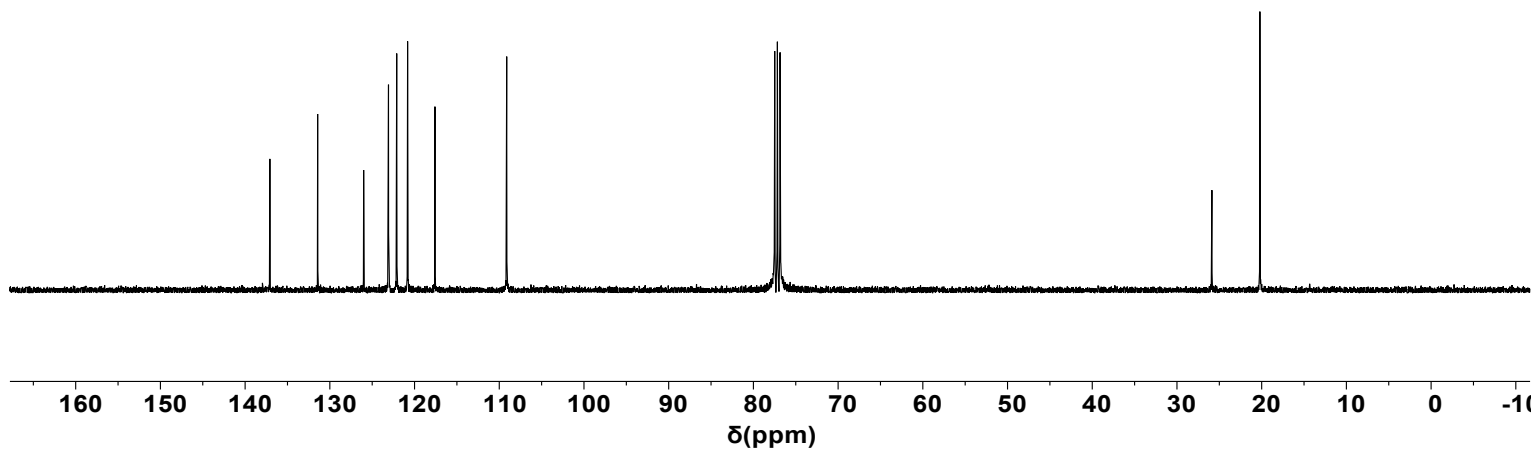
^{13}C NMR 101 MHz, CDCl_3

137.0783
131.437
126.005
123.075
122.105
120.819
117.592
109.123

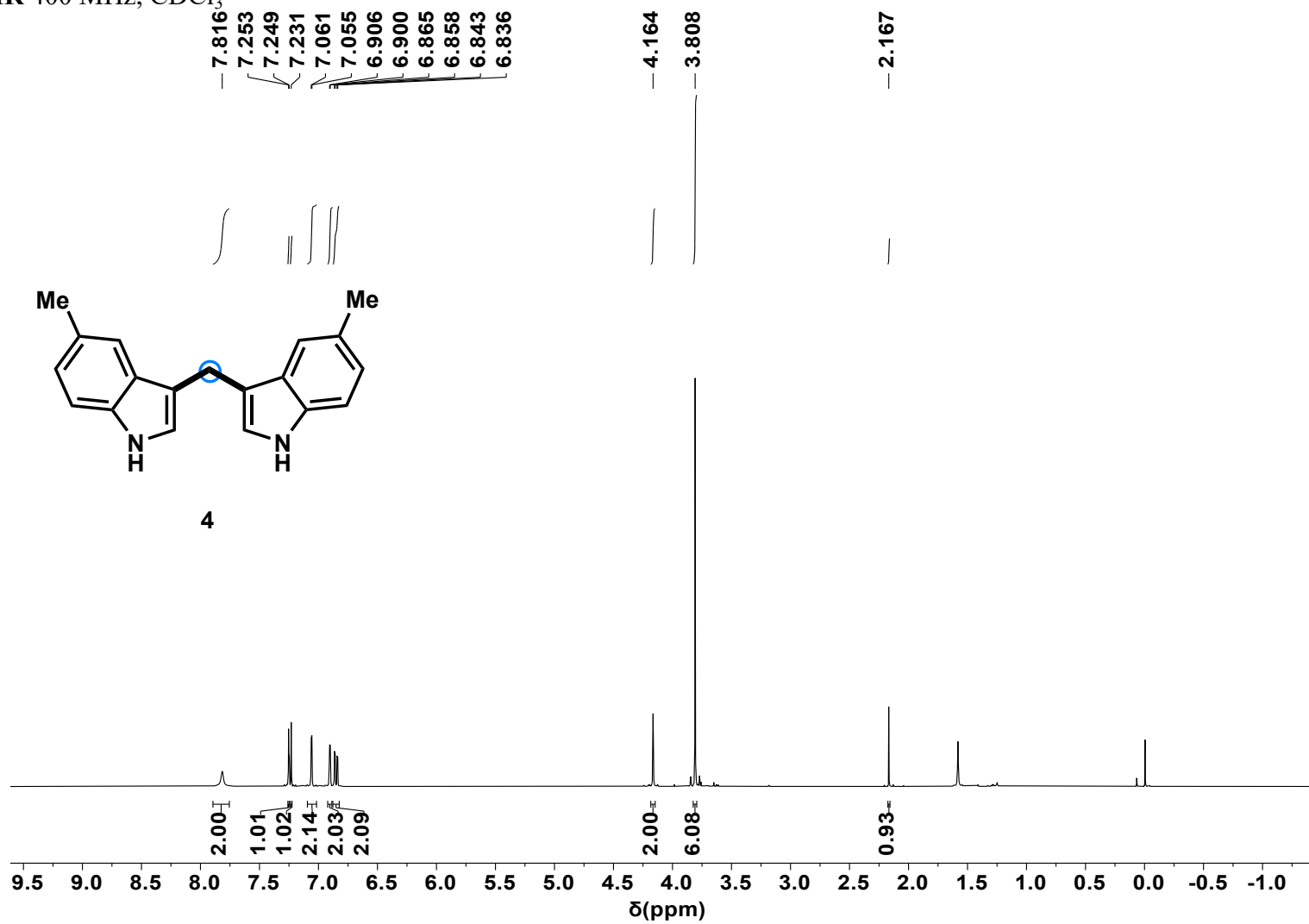
25.876
20.212



3



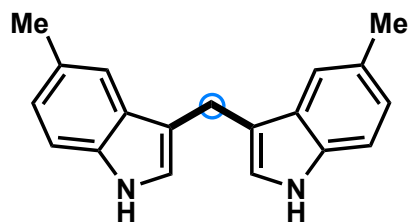
^1H NMR 400 MHz, CDCl_3



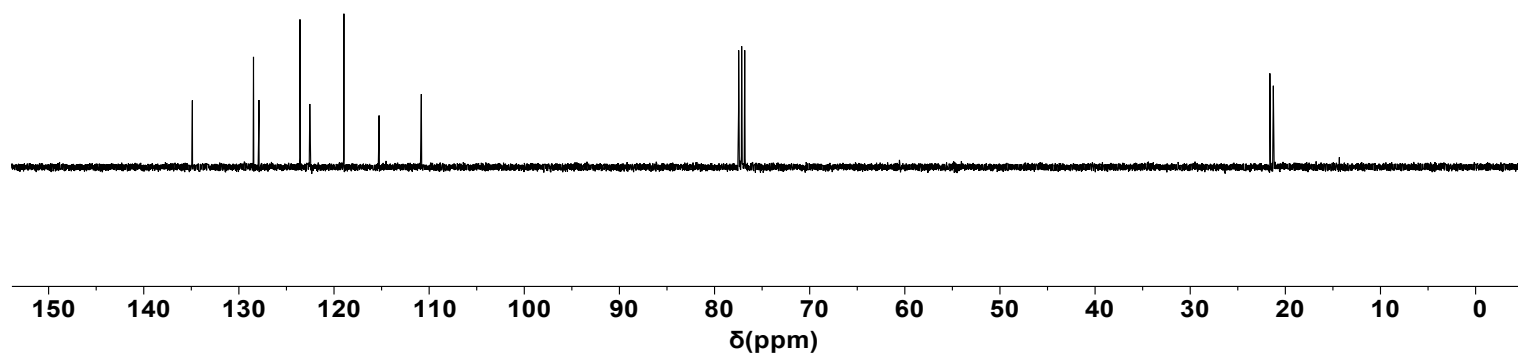
^{13}C NMR 101 MHz, CDCl_3

134.890
128.463
127.896
123.577
122.546
118.960
115.264
110.824

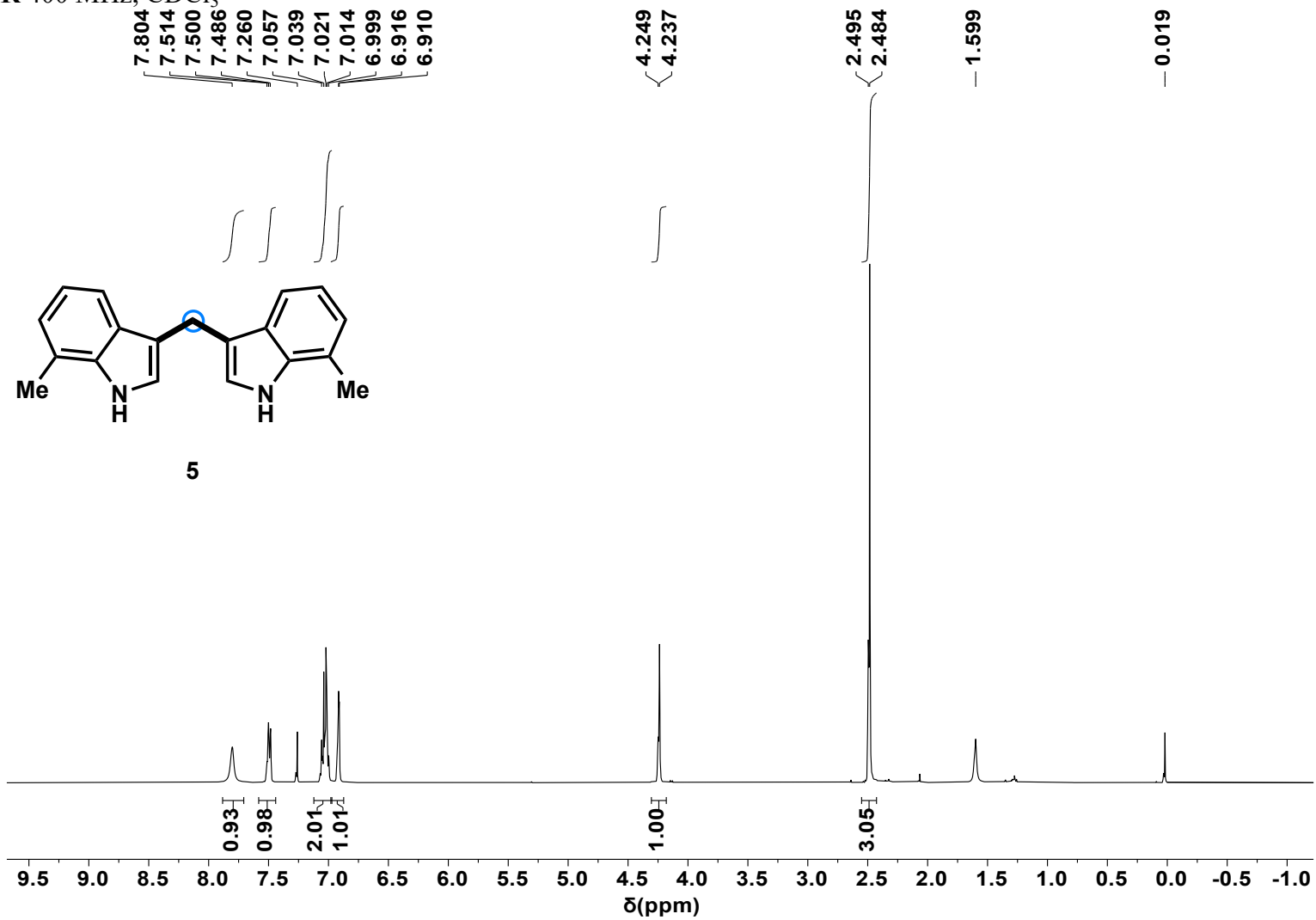
21.626
21.264



4



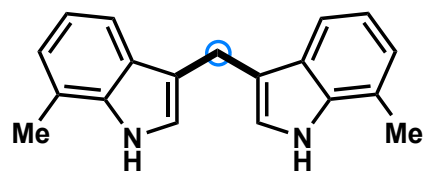
^1H NMR 400 MHz, CDCl_3



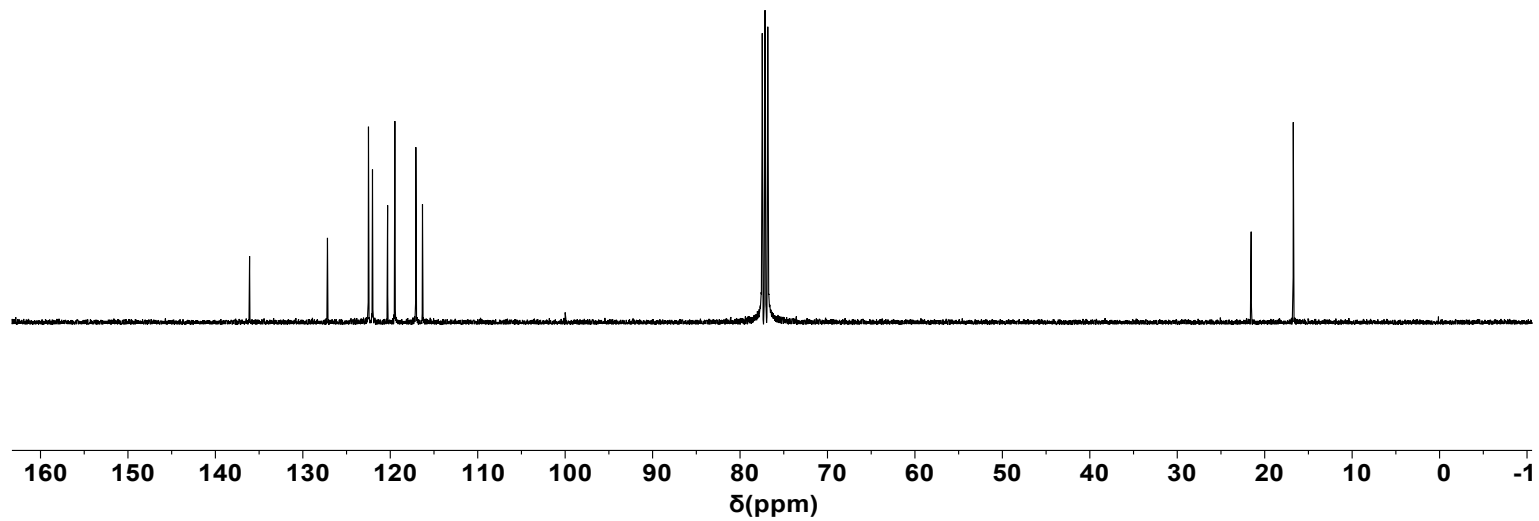
^{13}C NMR 101 MHz, CDCl_3

136.089
127.179
122.493
122.033
120.303
119.477
117.072
116.317

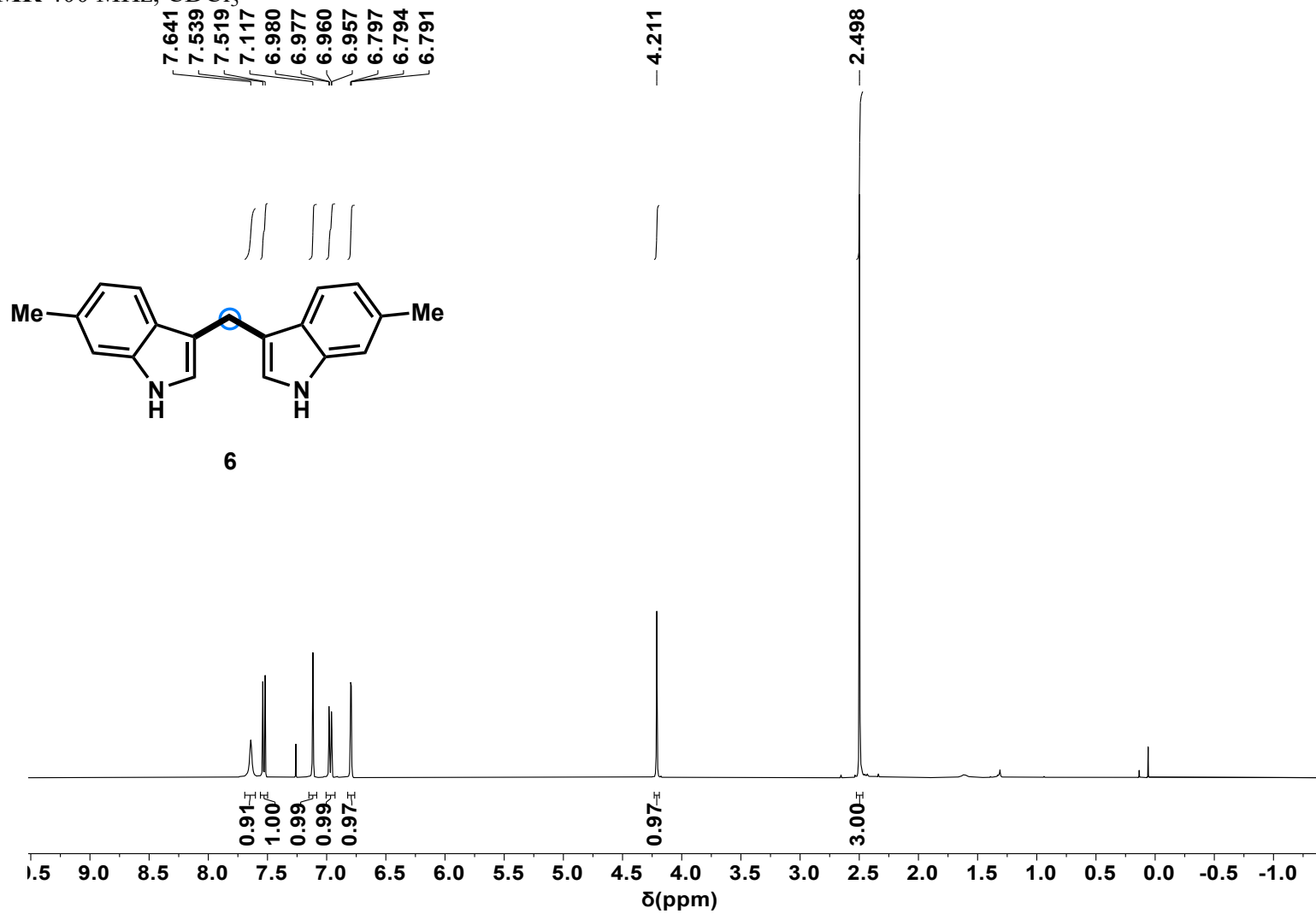
21.546
16.730



5



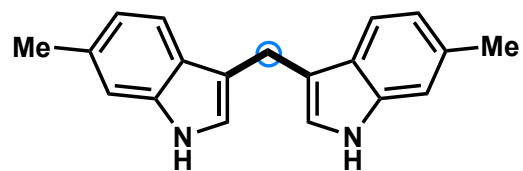
^1H NMR 400 MHz, CDCl_3



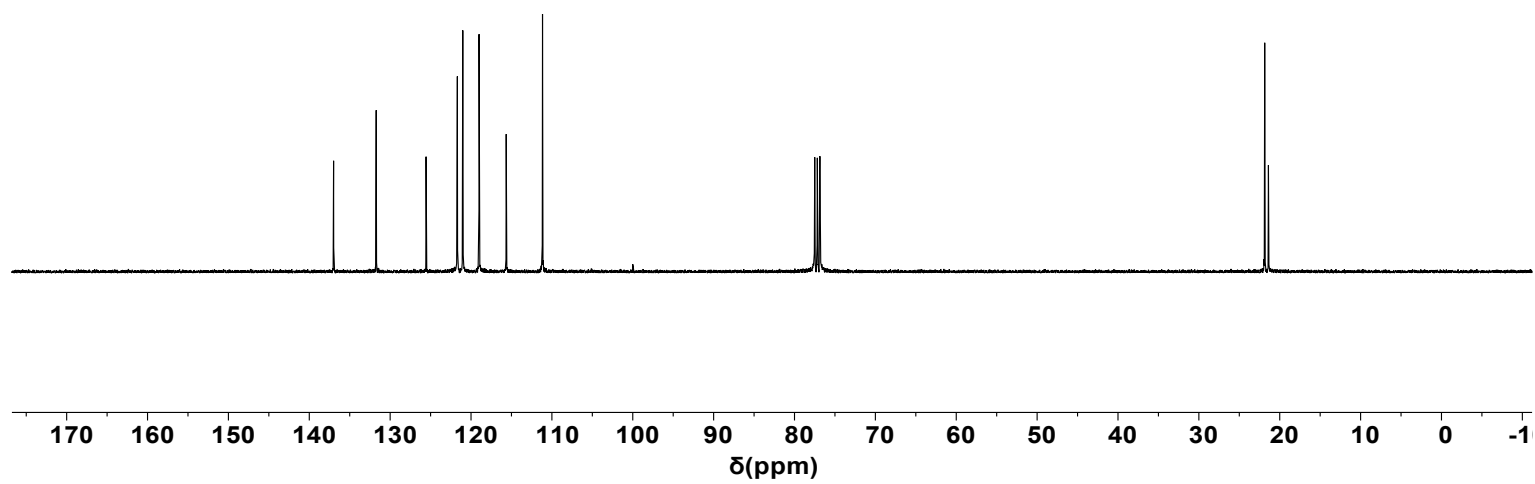
^{13}C NMR 101 MHz, CDCl_3

136.994
131.723
125.557
121.694
121.019
119.009
115.650
111.159

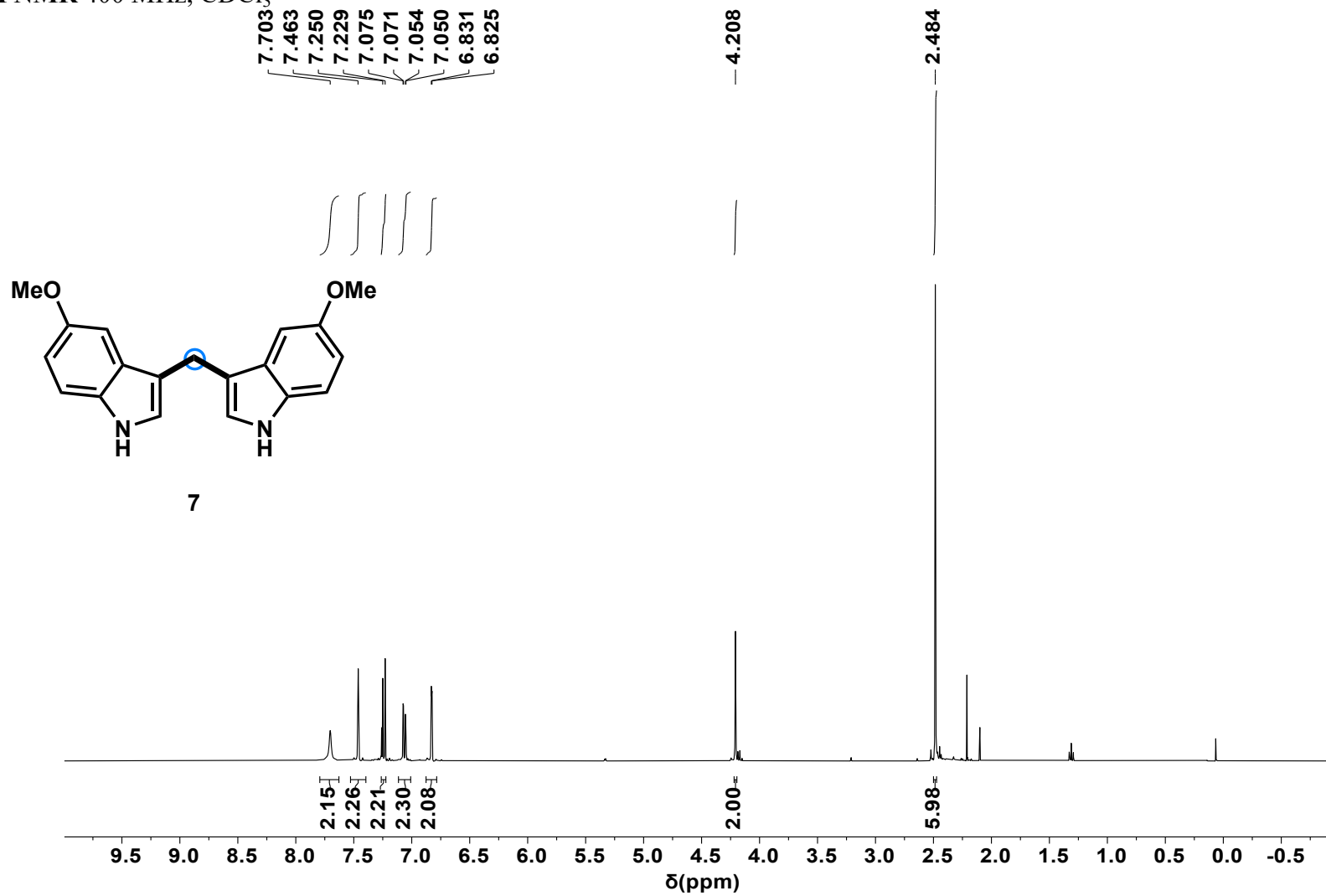
21.857
21.397



6



^1H NMR 400 MHz, CDCl_3



^{13}C NMR 101 MHz, CDCl_3

— 153.886

— 131.676

— 127.992

— 123.184

— 115.334

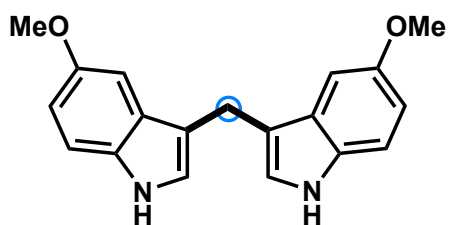
— 112.144

— 111.901

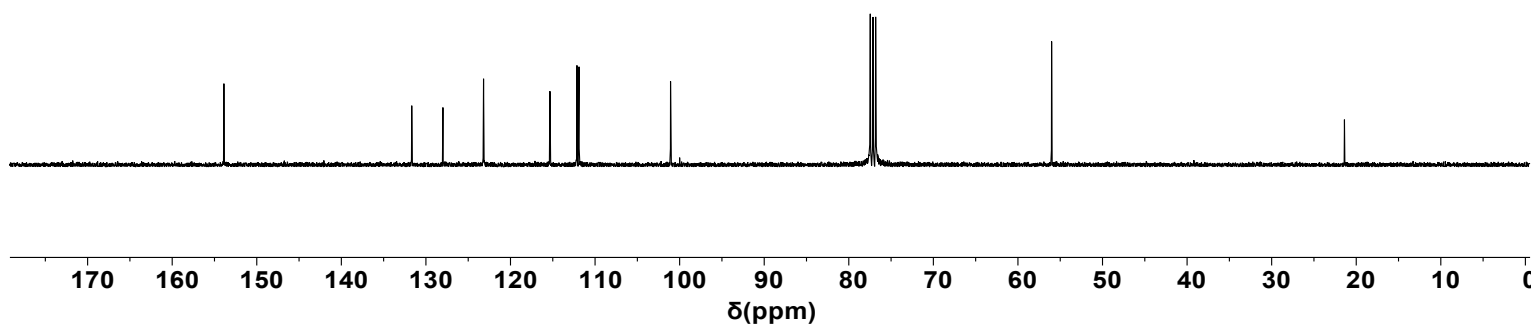
— 101.073

— 56.020

— 21.392

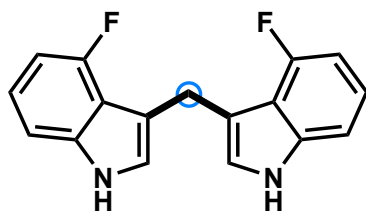


7

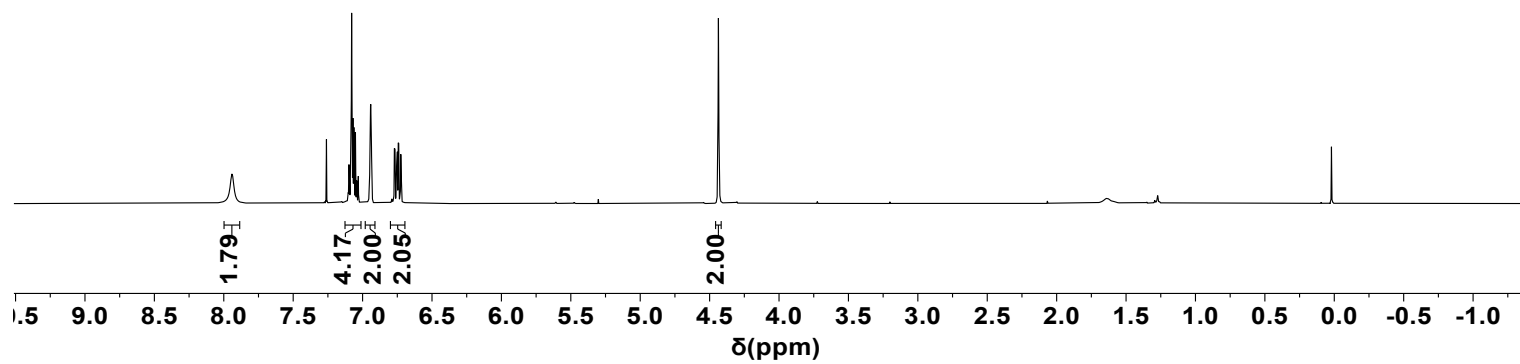


^1H NMR 400 MHz, CDCl_3

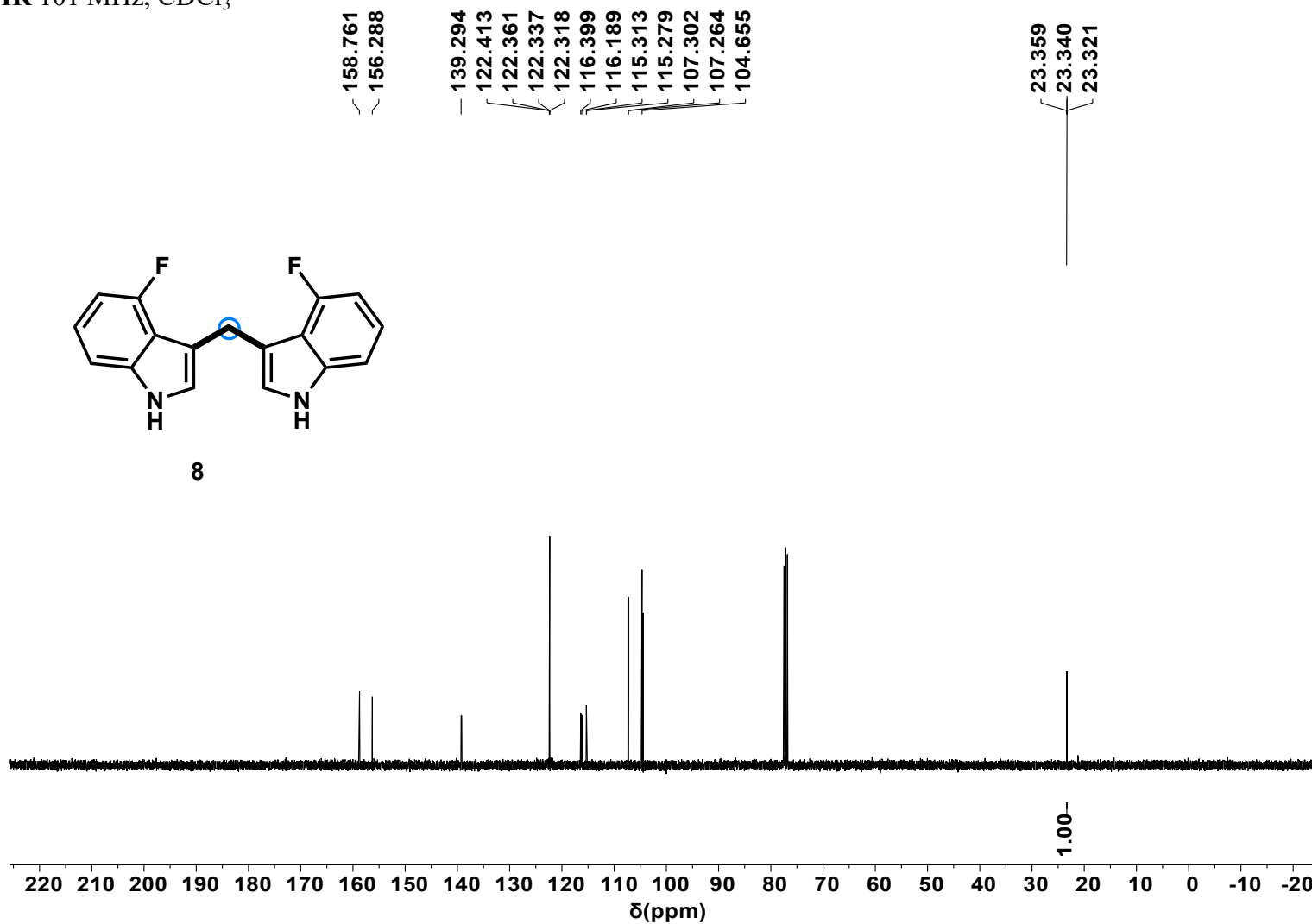
7.941
7.099
7.096
7.083
7.079
7.070
7.063
7.051
7.043
7.031
6.945
6.771
6.766
6.754
6.749
6.743
6.740
6.725
6.722
4.437



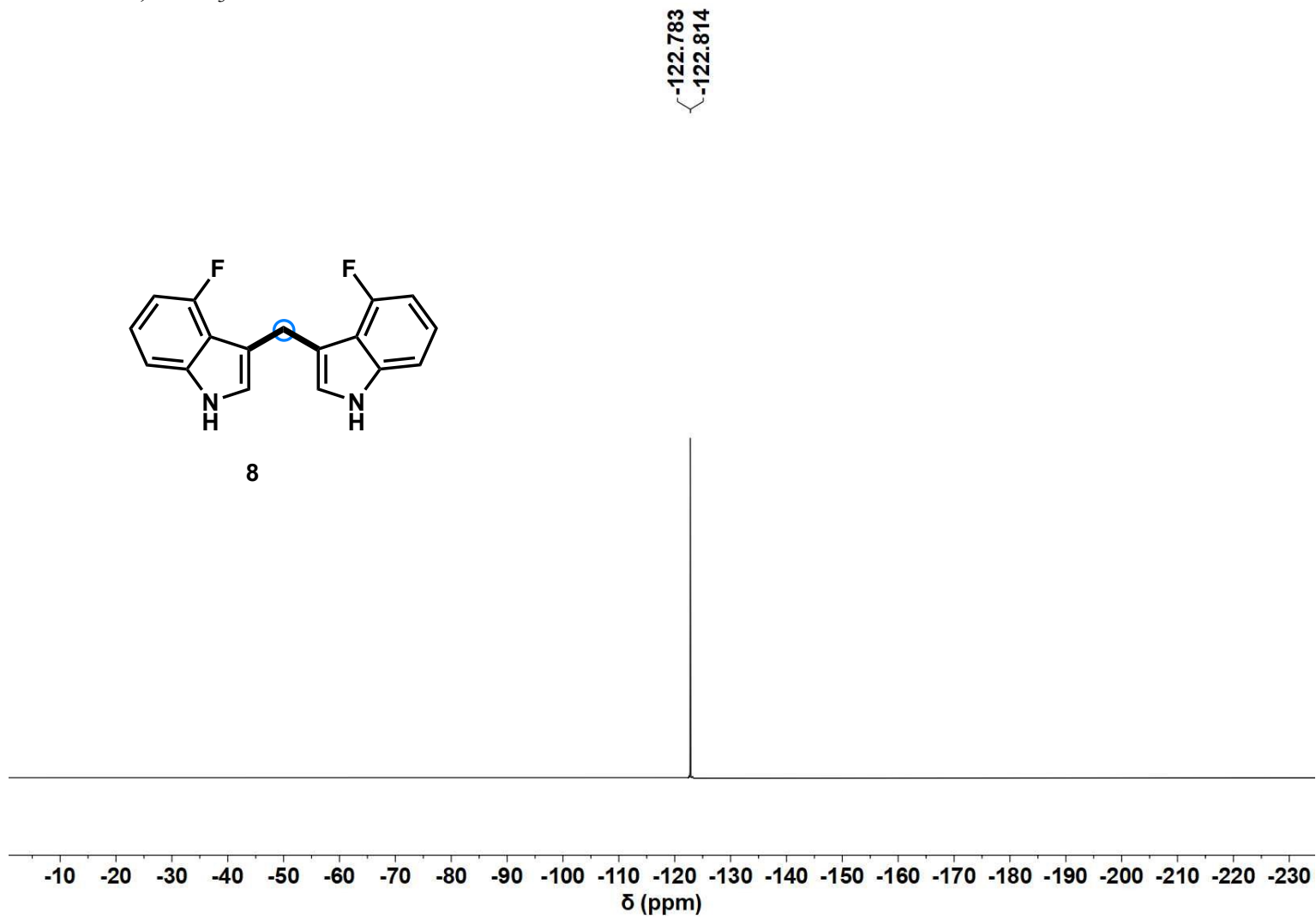
8



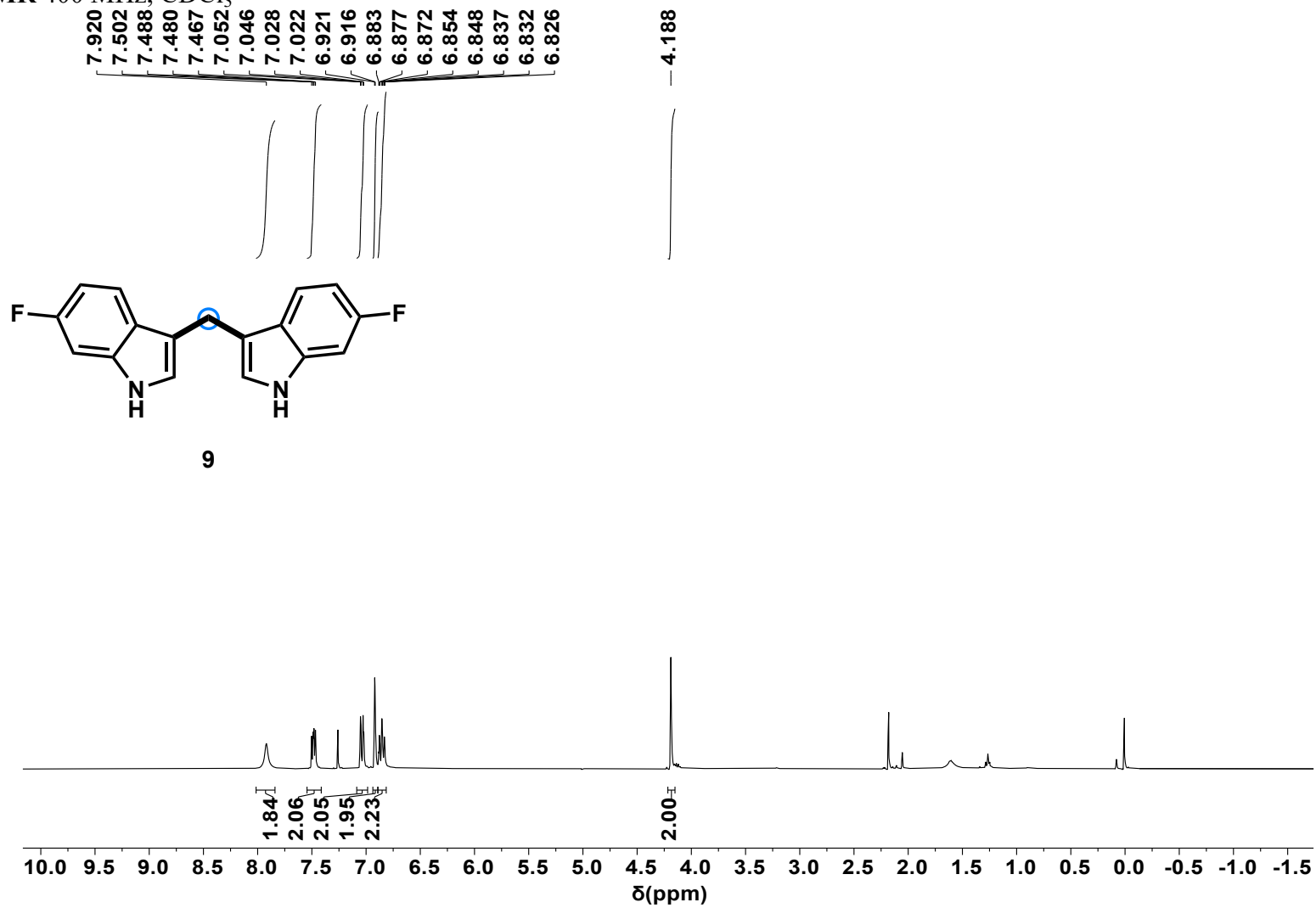
^{13}C NMR 101 MHz, CDCl_3



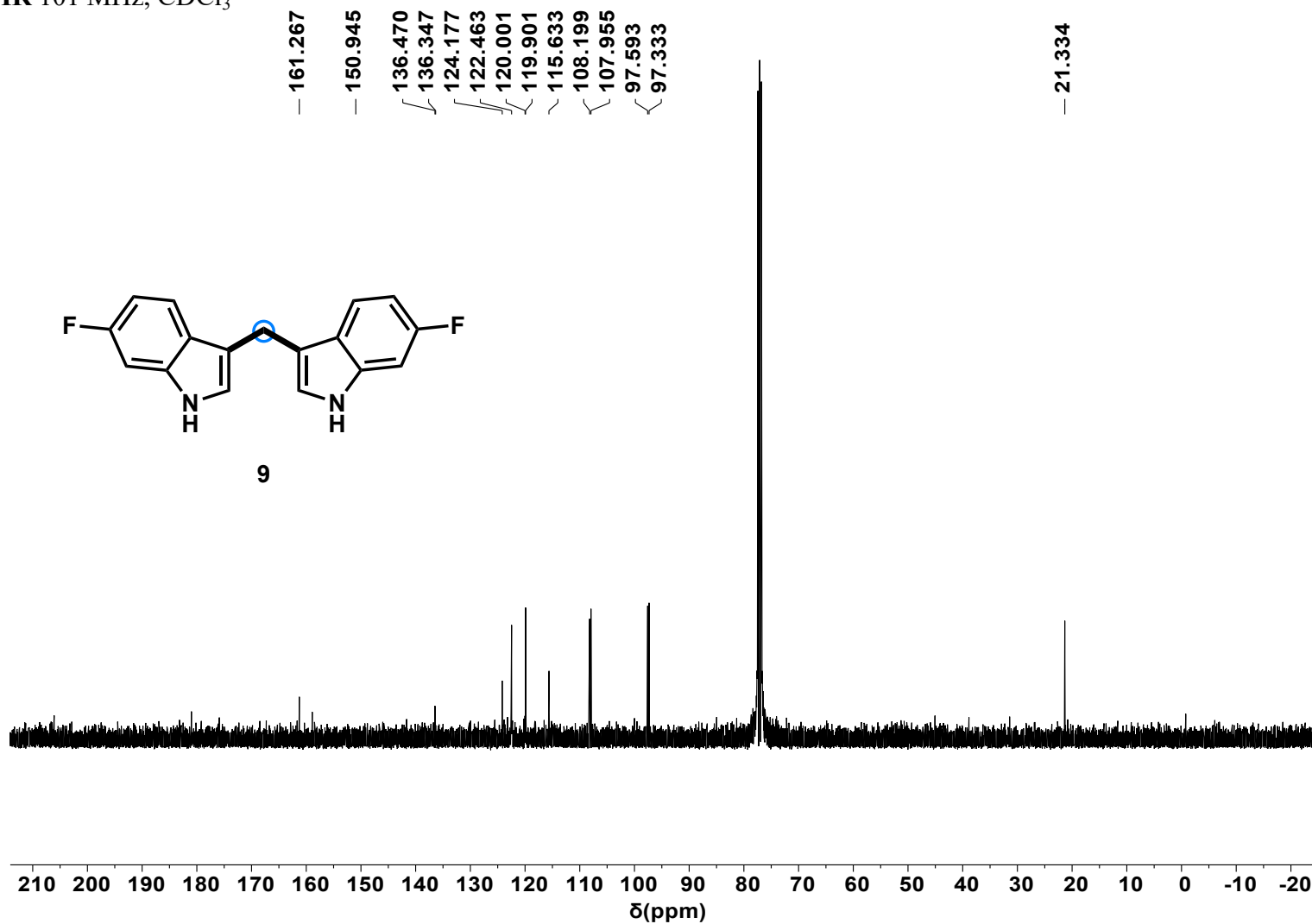
^{19}F NMR 376 MHz, CDCl_3



^1H NMR 400 MHz, CDCl_3

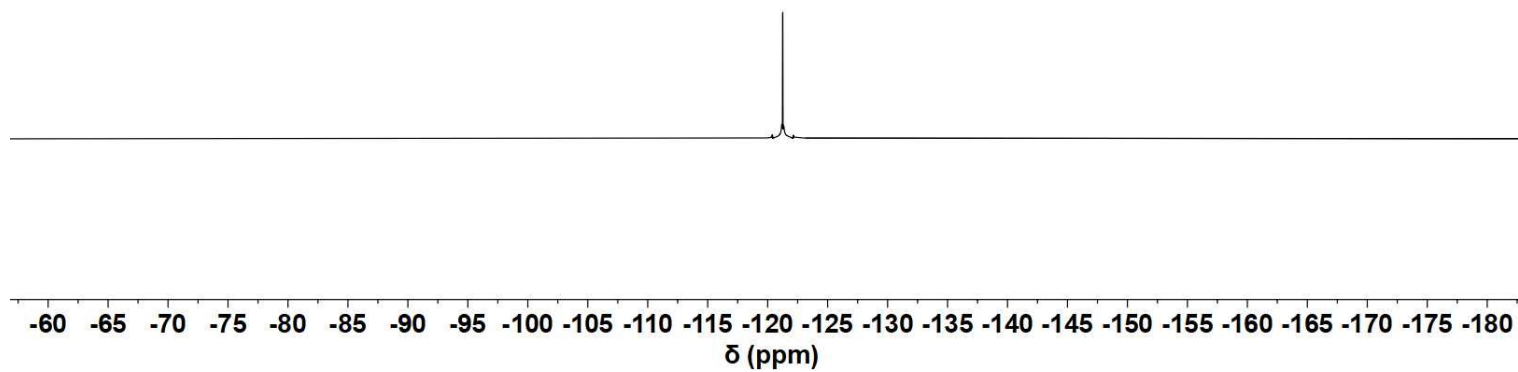
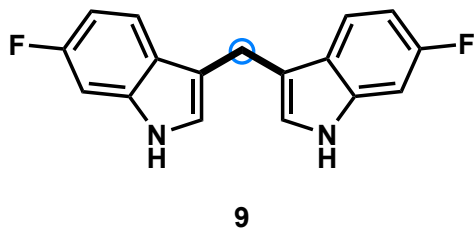


^{13}C NMR 101 MHz, CDCl_3

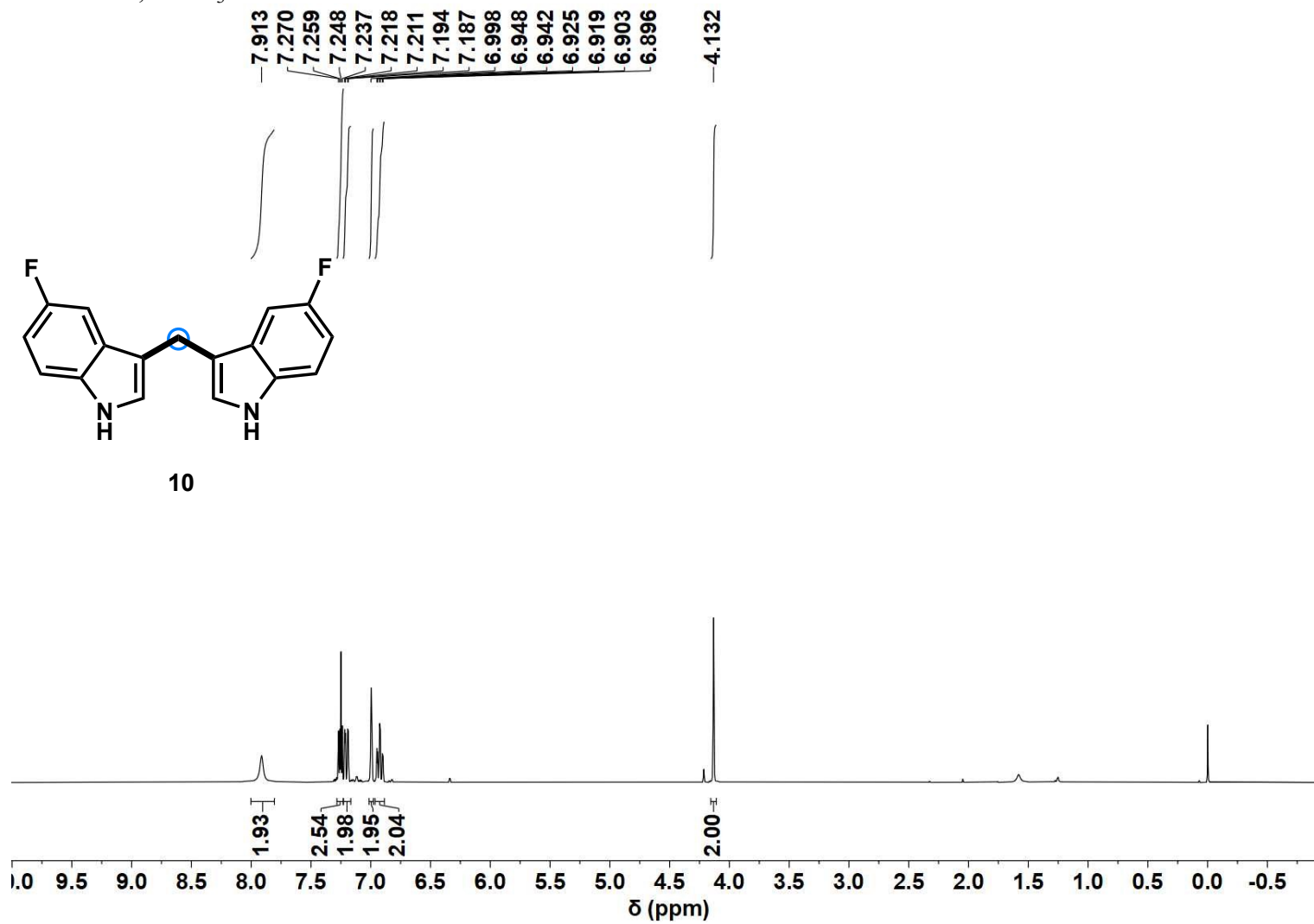


^{19}F NMR 376 MHz, CDCl_3

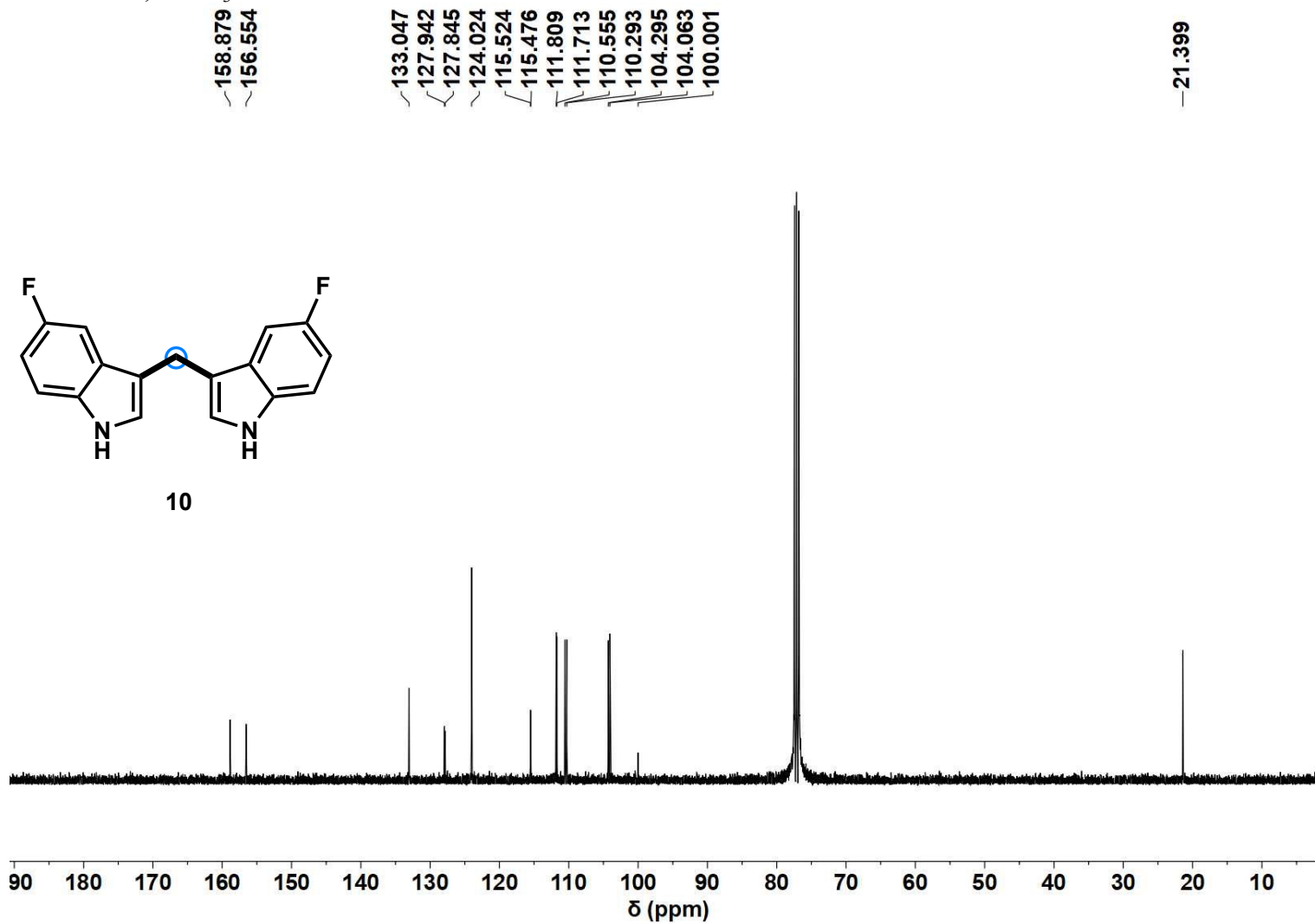
-121.219
-121.234
-121.246
-121.262
-121.289



^1H NMR 400 MHz, CDCl_3

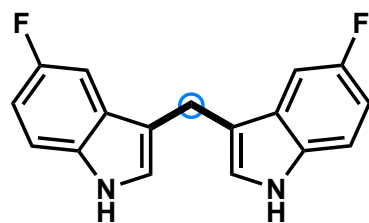


^{13}C NMR 101 MHz, CDCl_3

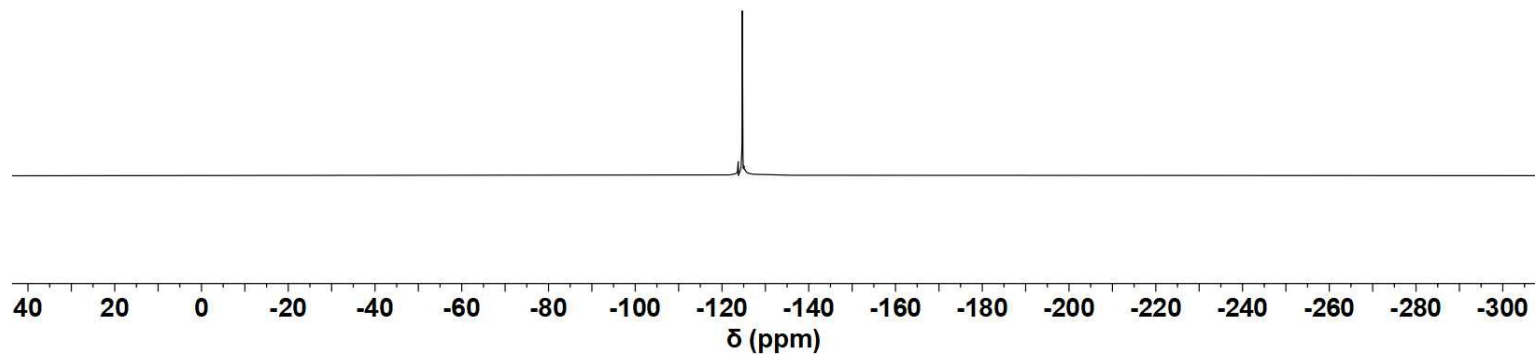


^{19}F NMR 376 MHz, CDCl_3

---124.697

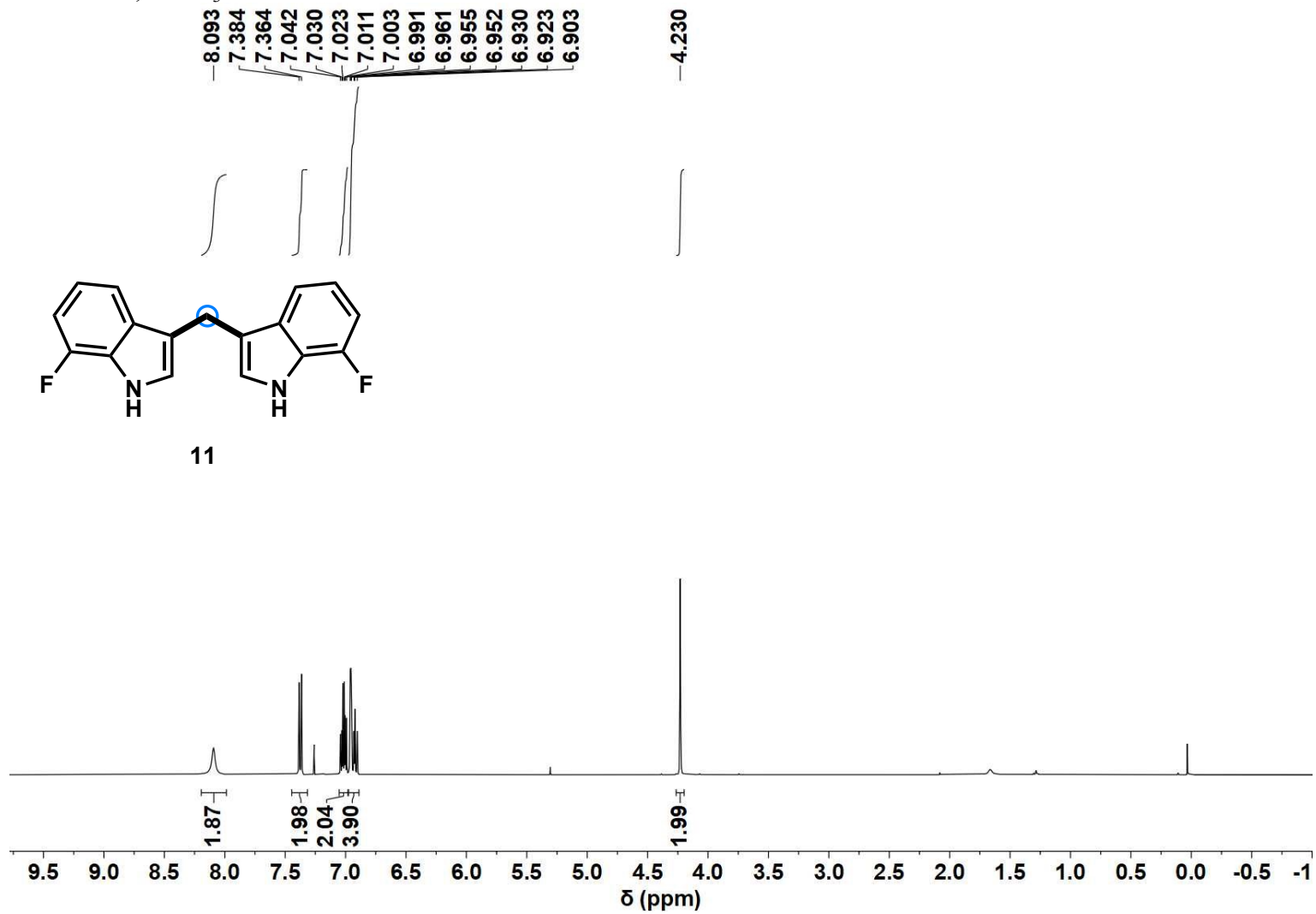


10



S81

^1H NMR 400 MHz, CDCl_3

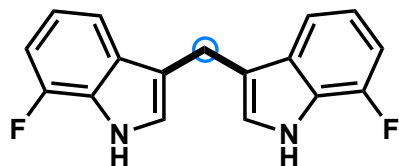


^{13}C NMR 101 MHz, CDCl_3

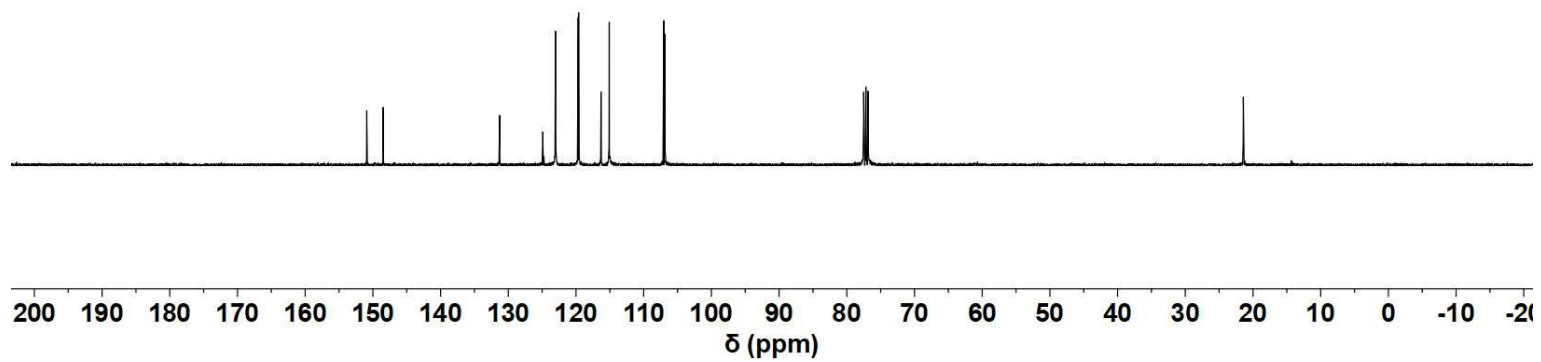
^{19}F NMR 376 MHz,

150.908
148.484
131.328
131.269
124.896
124.763
123.027
123.013
119.673
119.611
116.324
116.300
115.084
115.050
107.033
106.875

21.447
21.426
21.412

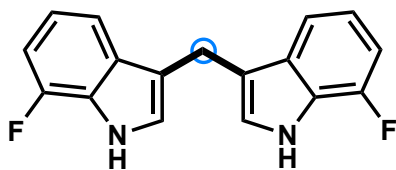


11

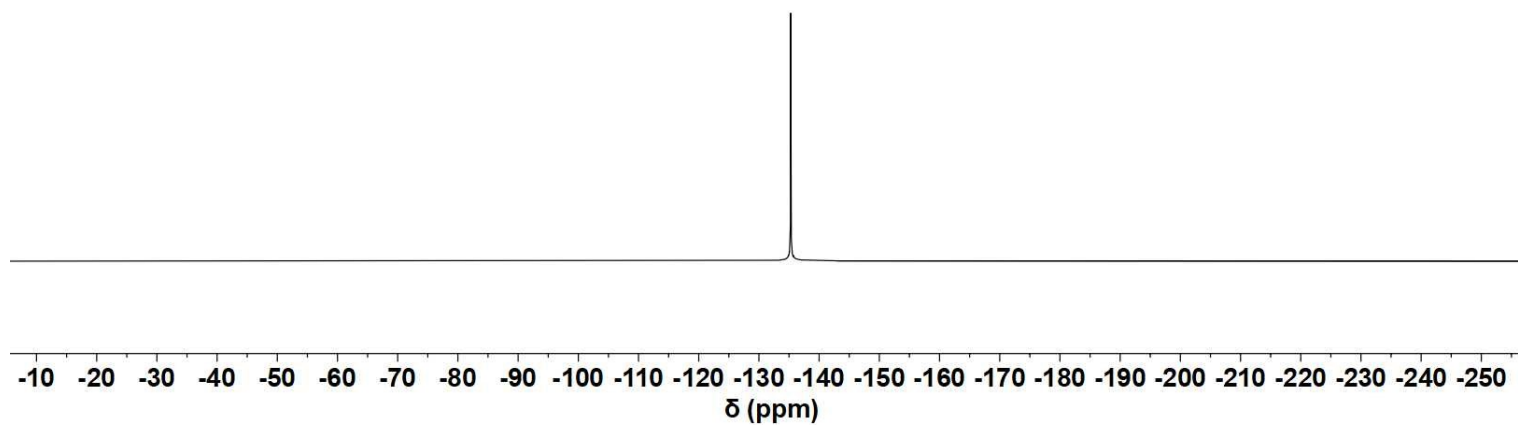


^{19}F NMR 376 MHz, CDCl_3

-135.268
-135.282
-135.299
-135.312

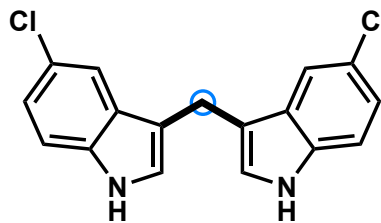
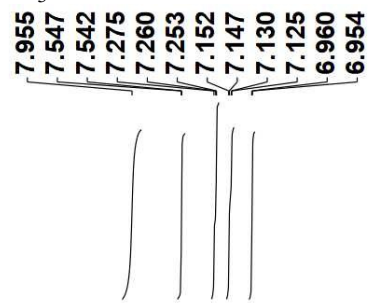


11

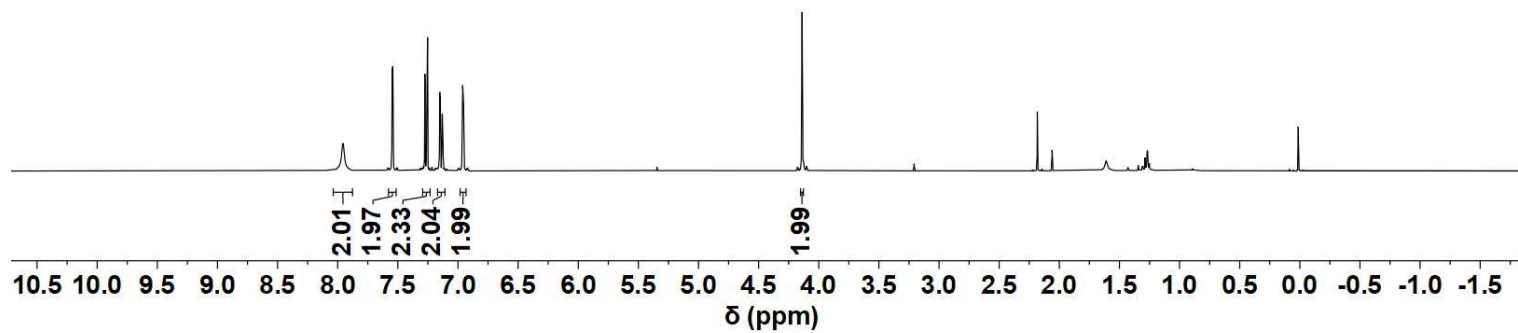


S84

^1H NMR 400 MHz, CDCl_3



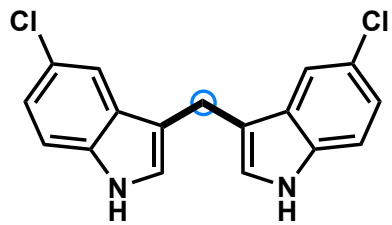
12



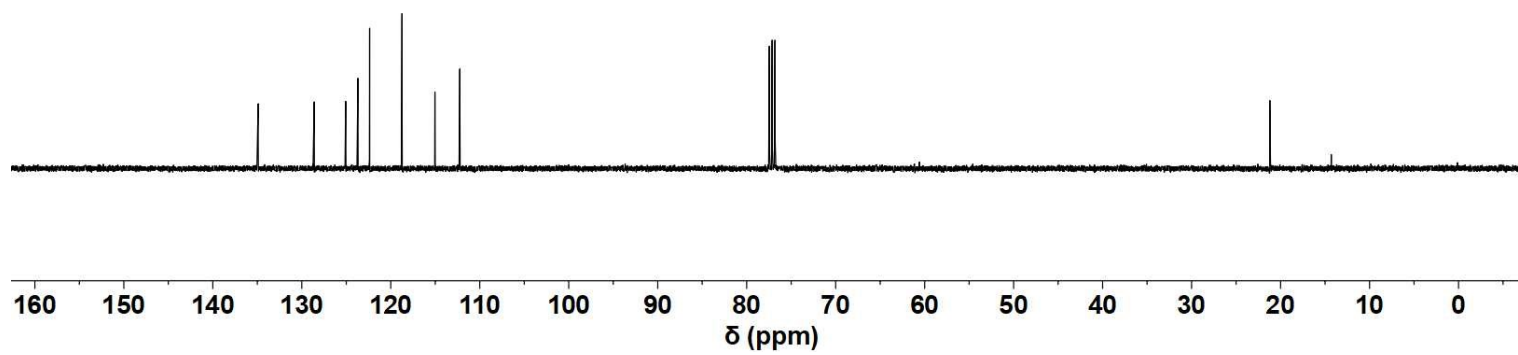
^{13}C NMR 101 MHz, CDCl_3

134.908
128.603
125.065
123.693
122.379
118.735
115.041
112.244

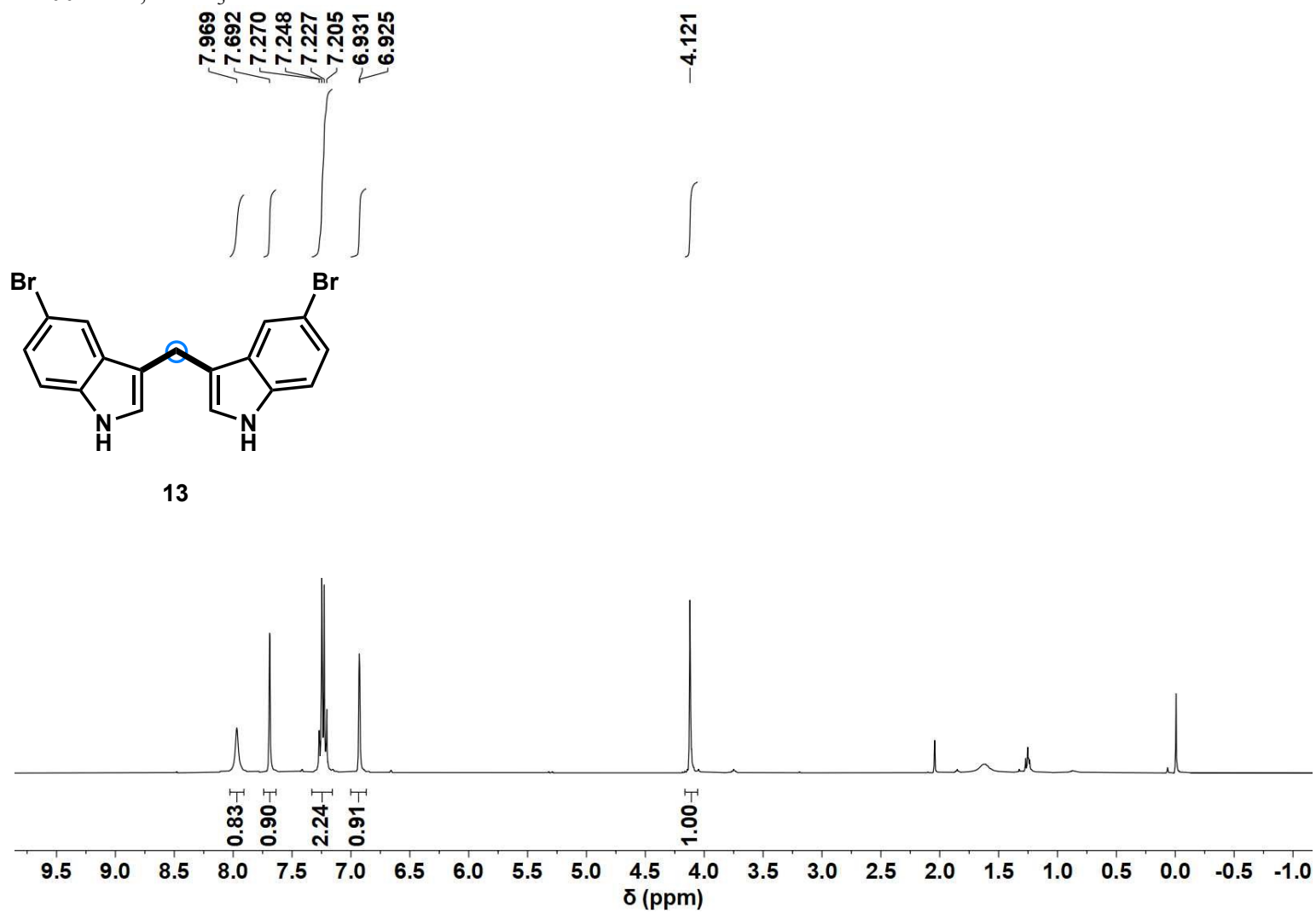
21.205



12



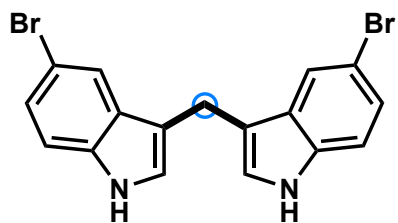
$^1\text{H NMR}$ 400 MHz, CDCl_3



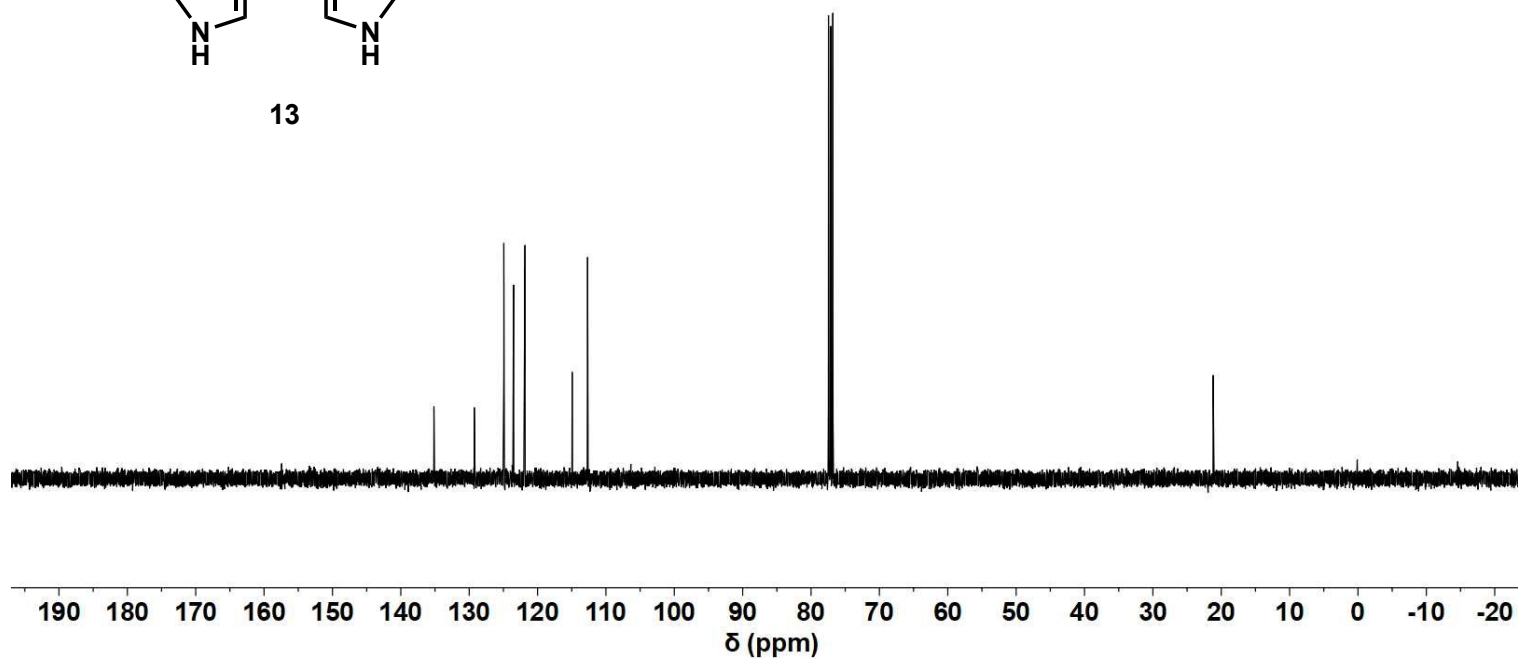
^{13}C NMR 101 MHz, CDCl_3

135.160
129.253
124.933
123.512
121.833
114.940
112.681
112.641

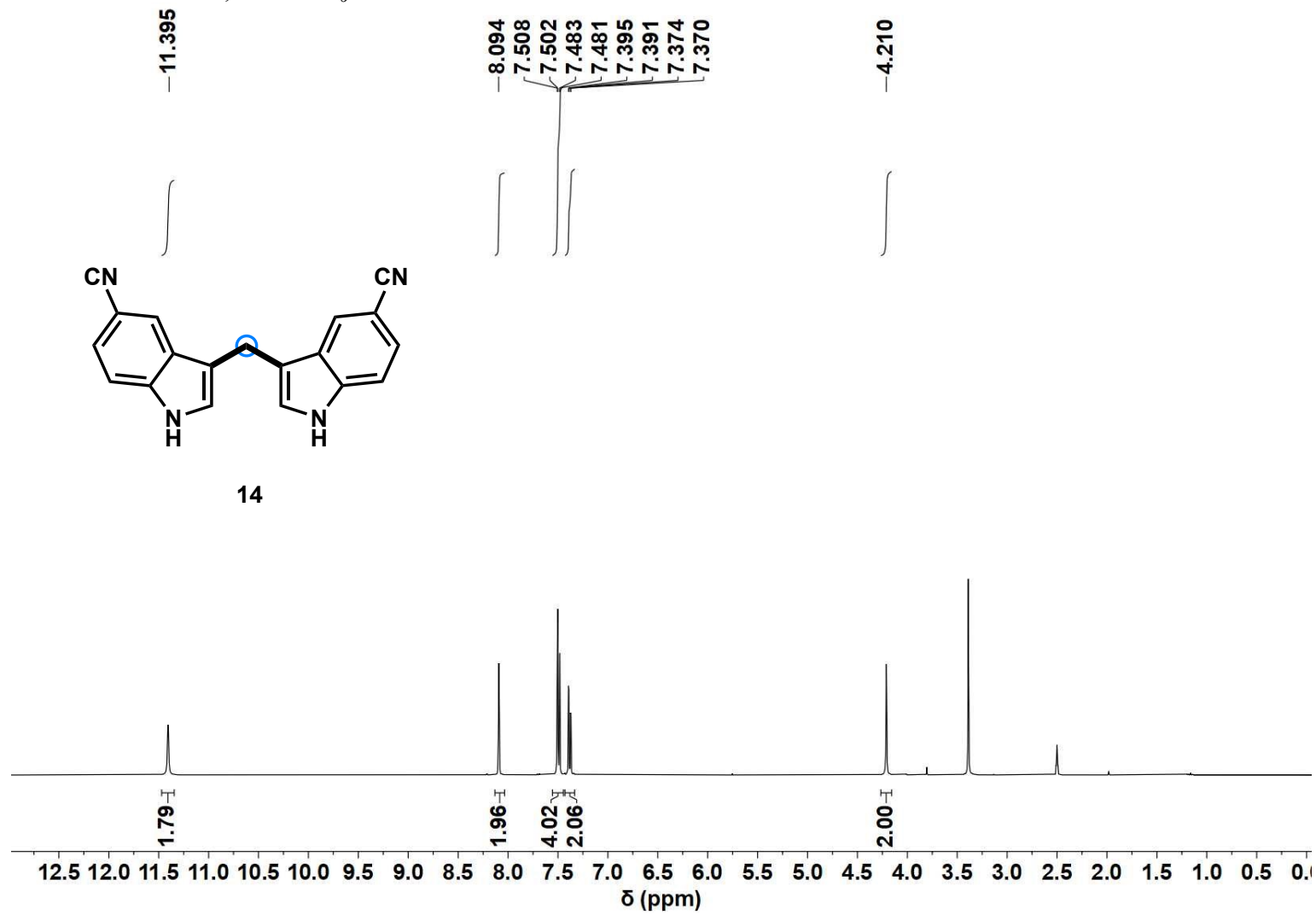
21.187



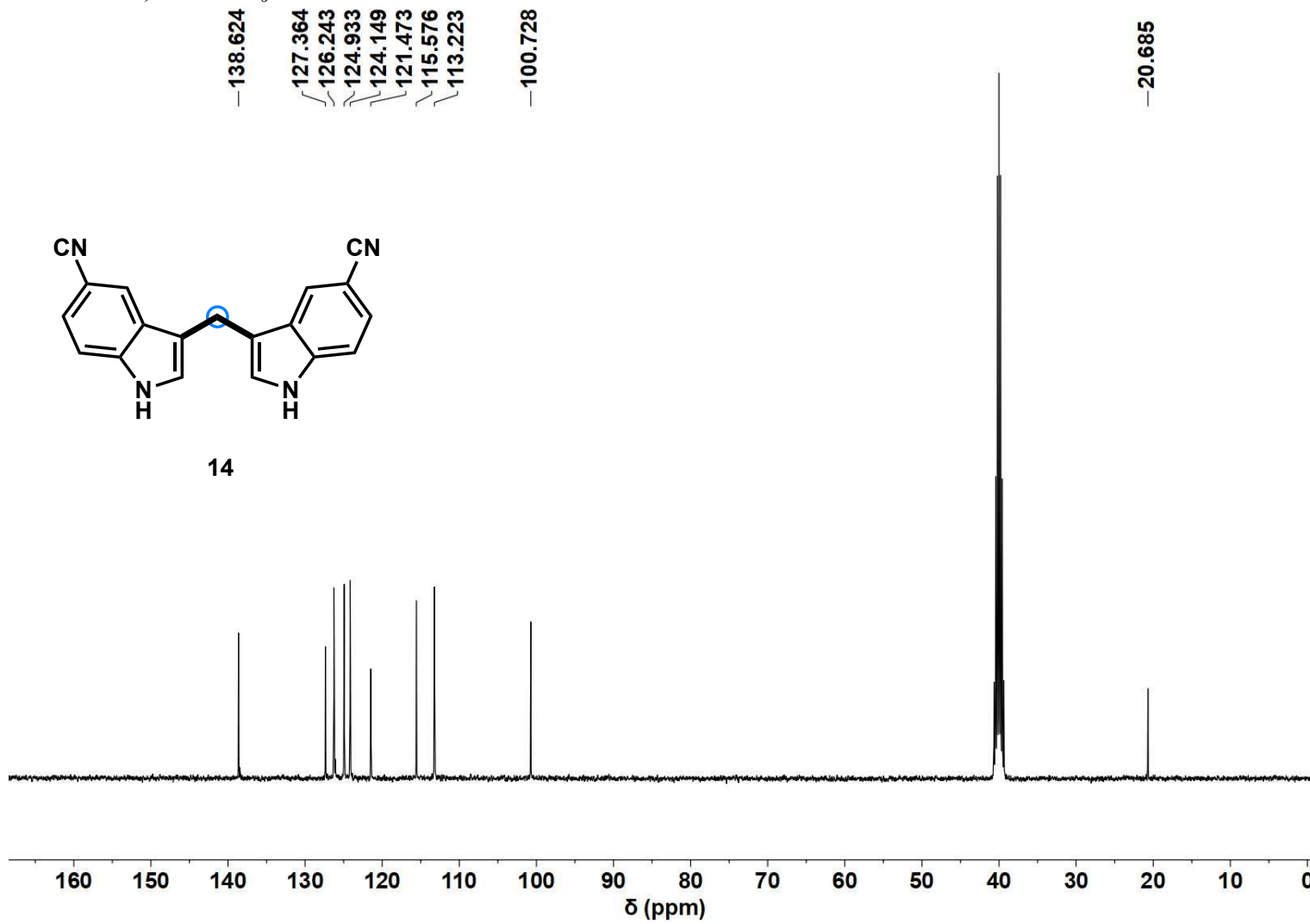
13



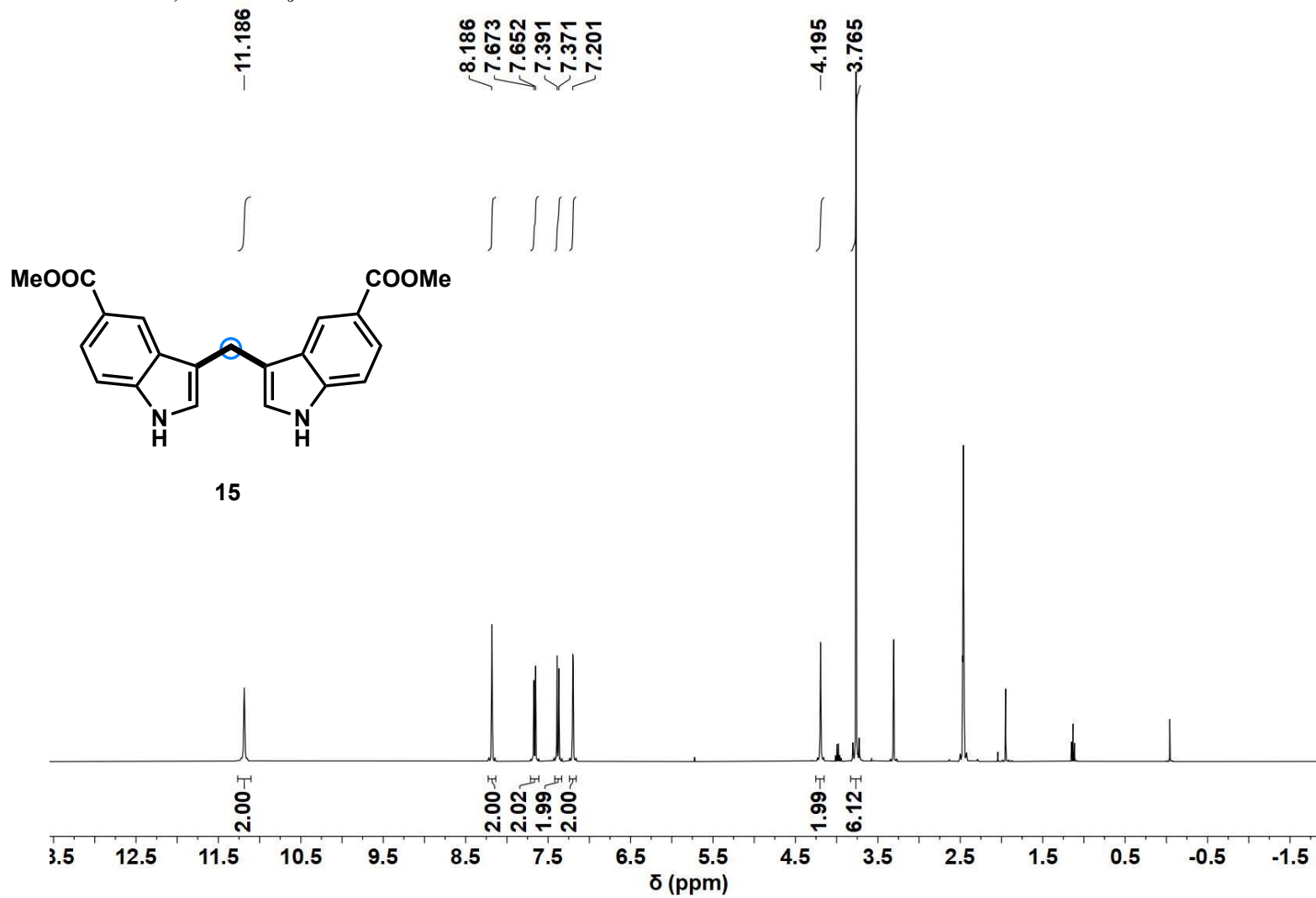
^1H NMR 400 MHz, $\text{DMSO-}d_6$



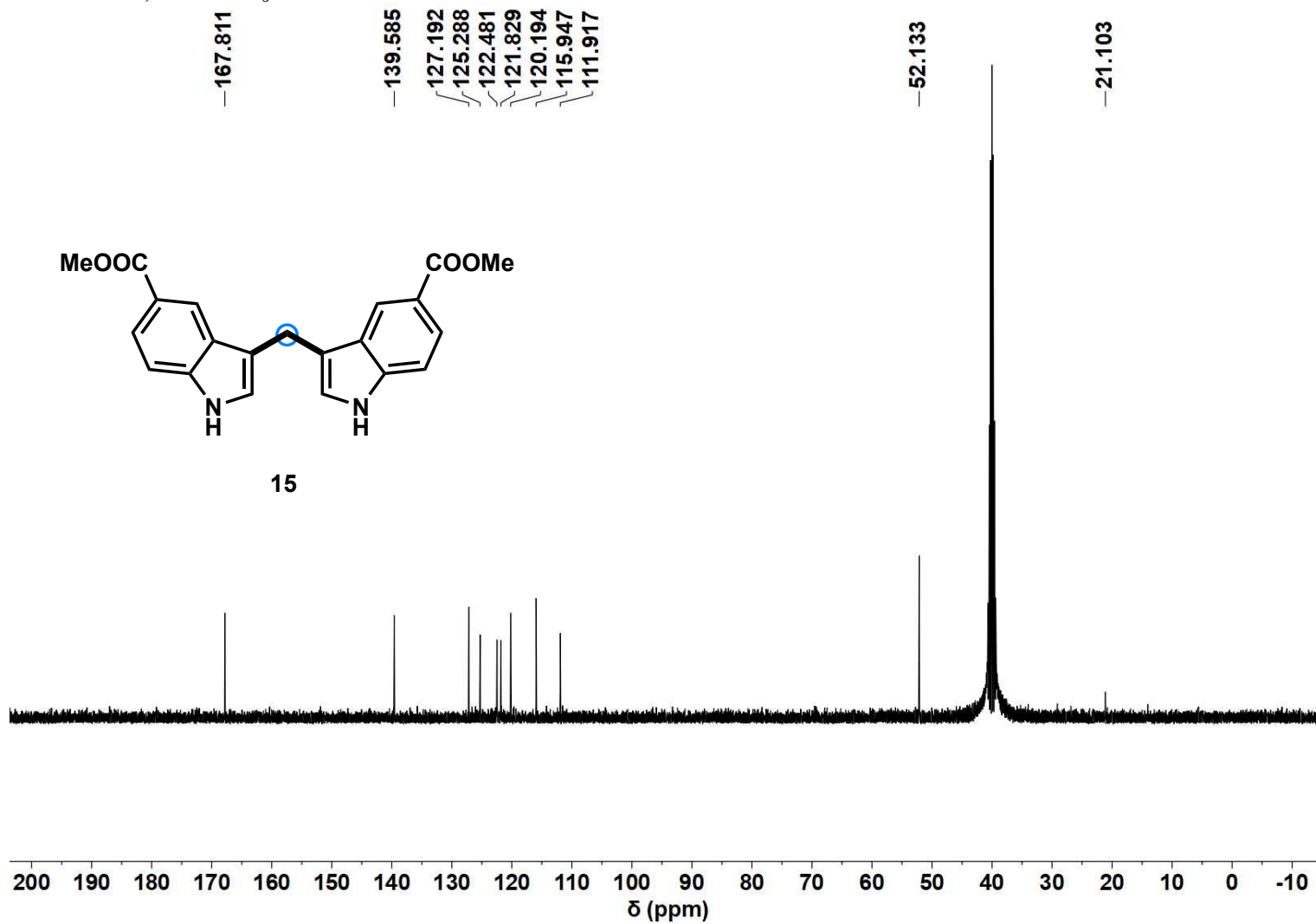
¹³C NMR 101 MHz, DMSO-*d*₆



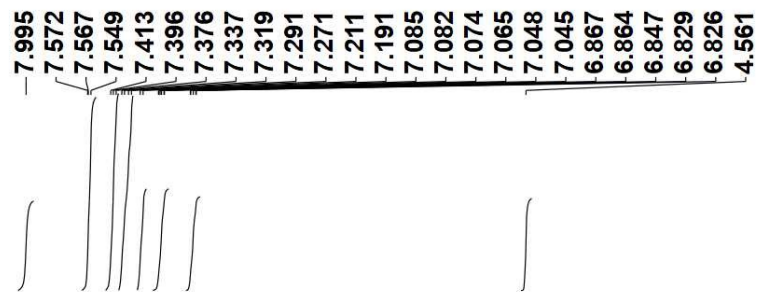
^1H NMR 400 MHz, $\text{DMSO-}d_6$



^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

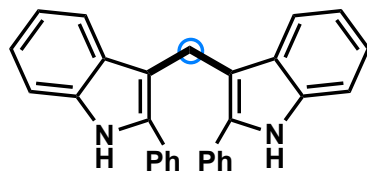


^1H NMR 400 MHz, CDCl_3

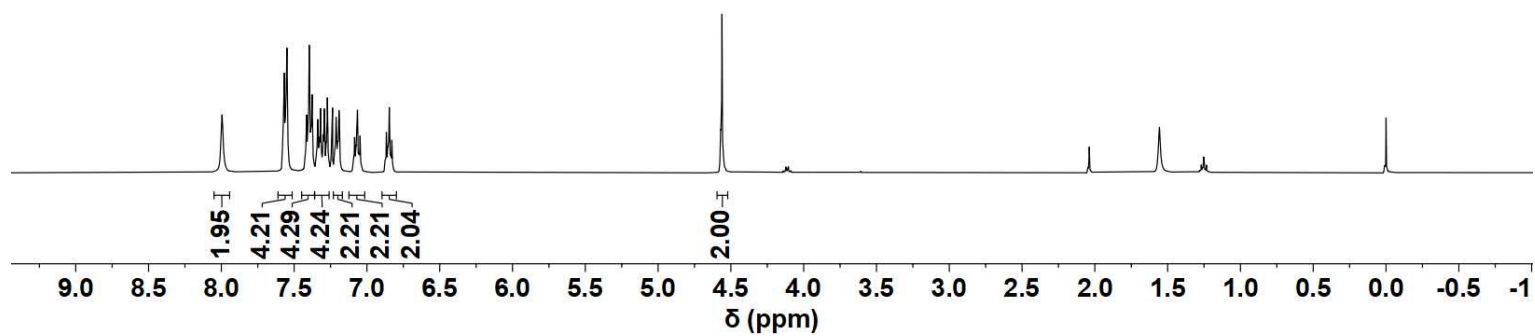


1.556

-0.000



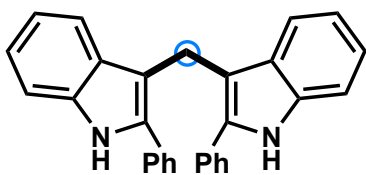
16



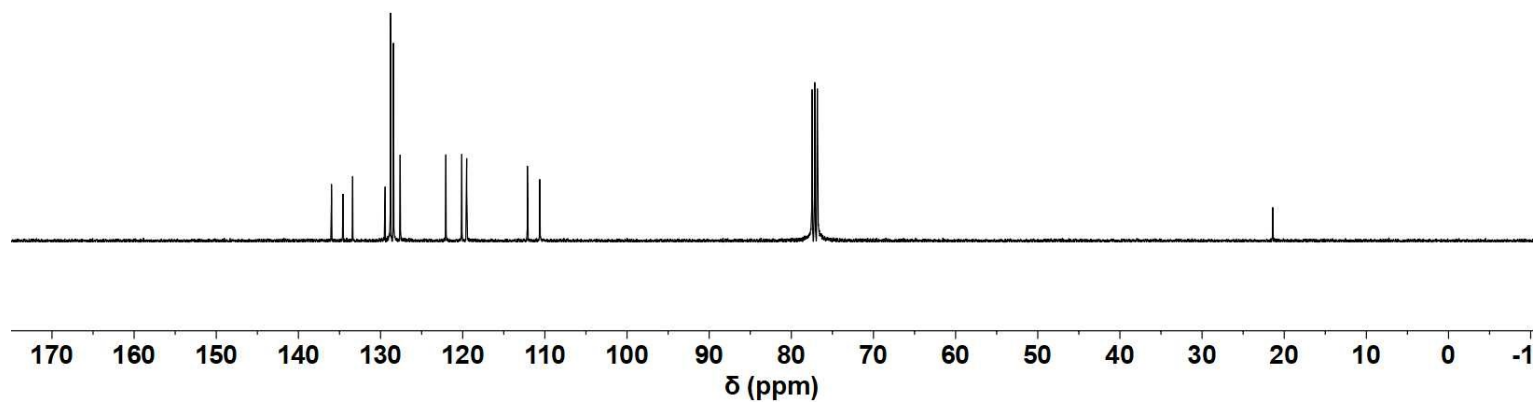
¹³C NMR 101 MHz, CDCl₃

135.979
134.585
133.399
129.437
128.799
128.429
127.614
122.049
120.114
119.520
112.127
110.608

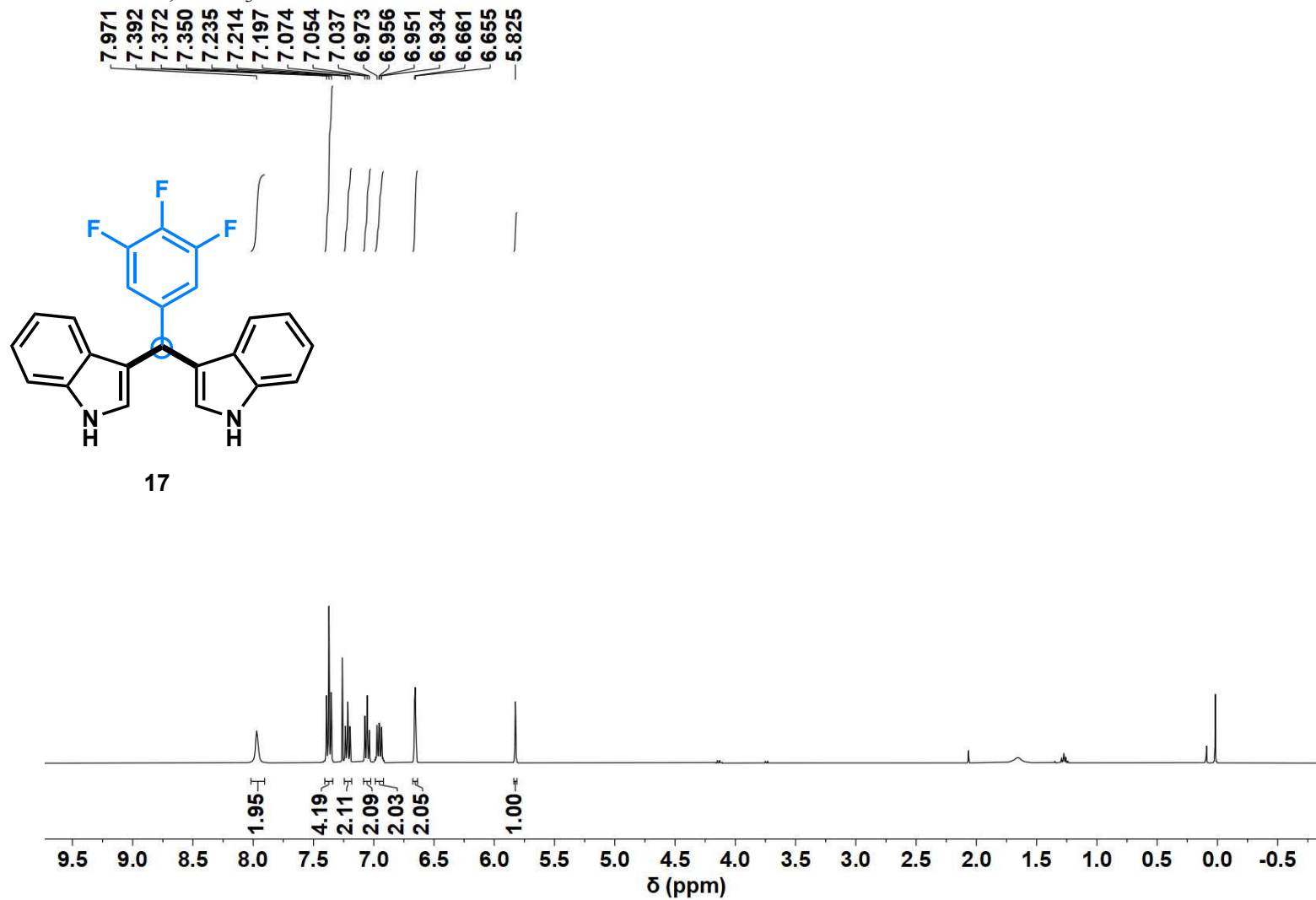
21.401



16

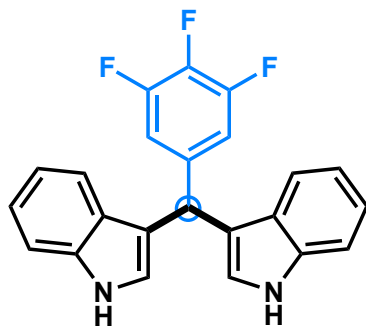


¹H NMR 400 MHz, CDCl₃

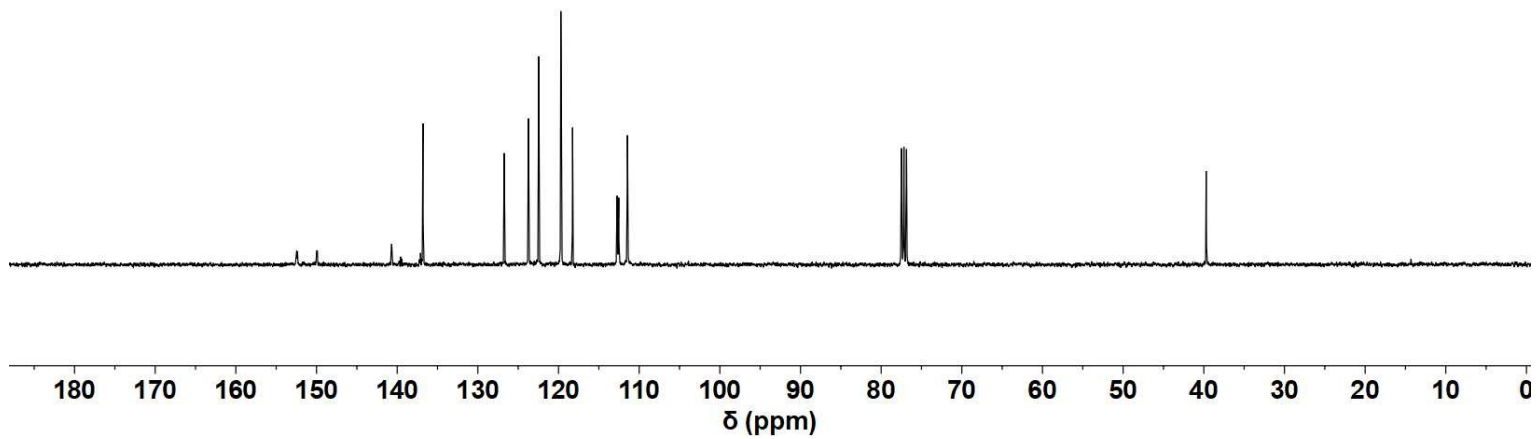


^{13}C NMR 101 MHz, CDCl_3

152.471
152.364
150.001
149.890
140.687
136.803
126.734
123.737
122.452
119.716
118.258
112.740
112.687
112.582
112.529
111.457
40.861



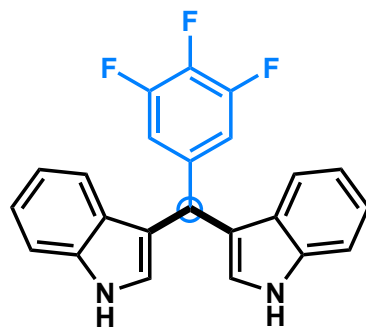
17



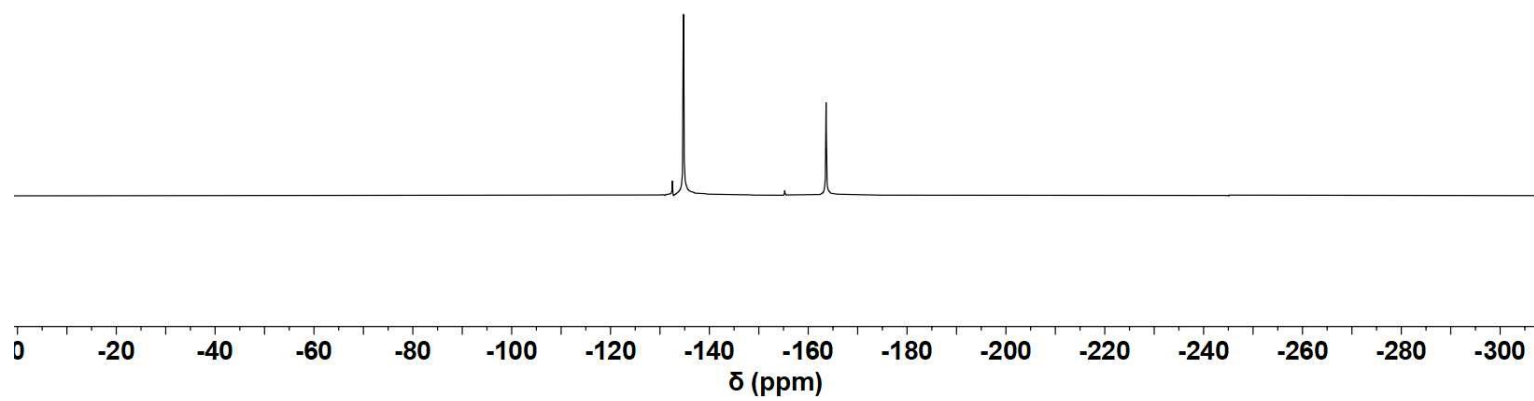
^{19}F NMR 376 MHz, CDCl_3

-134.724
-134.808

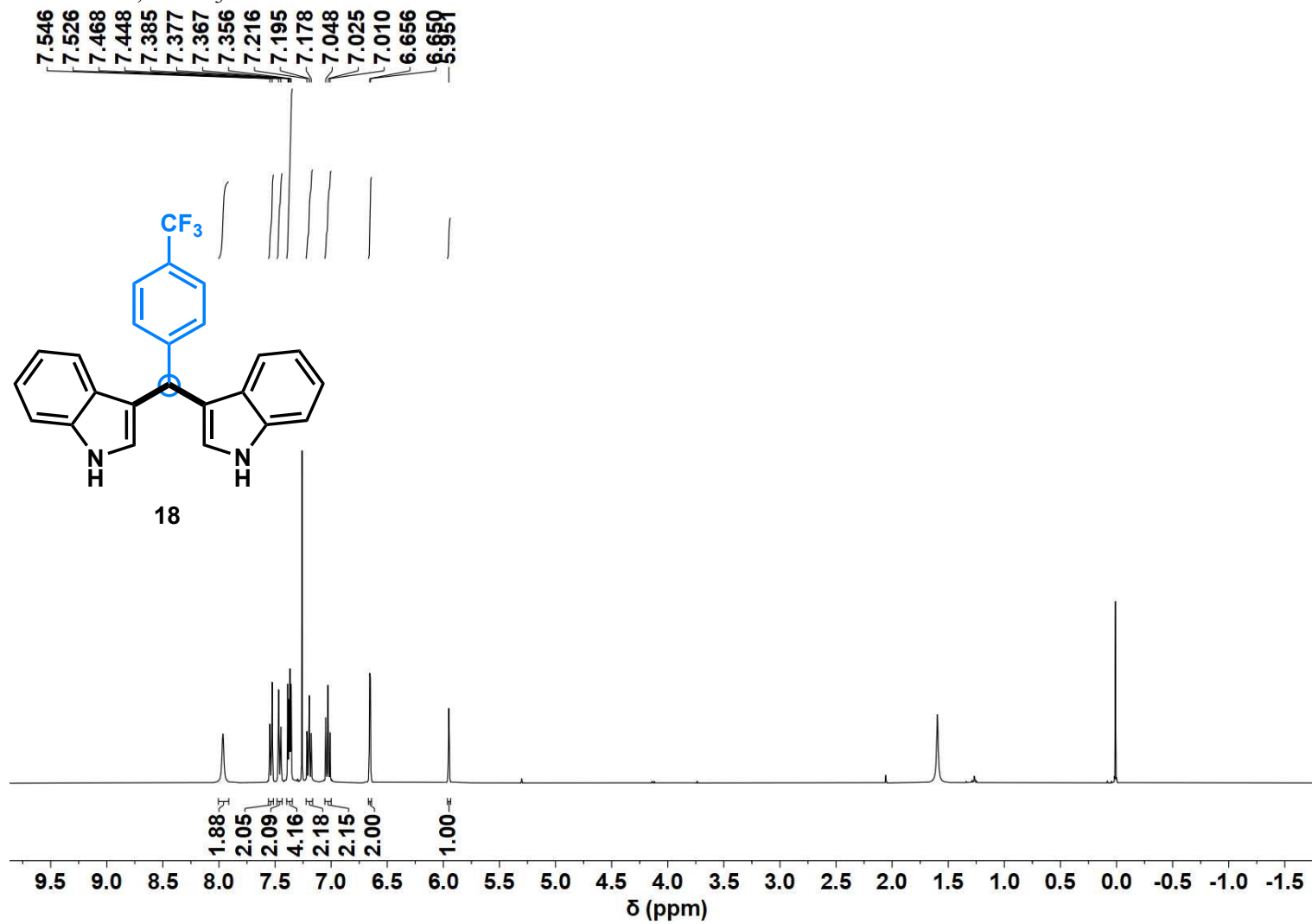
-163.531
-163.600
-163.674



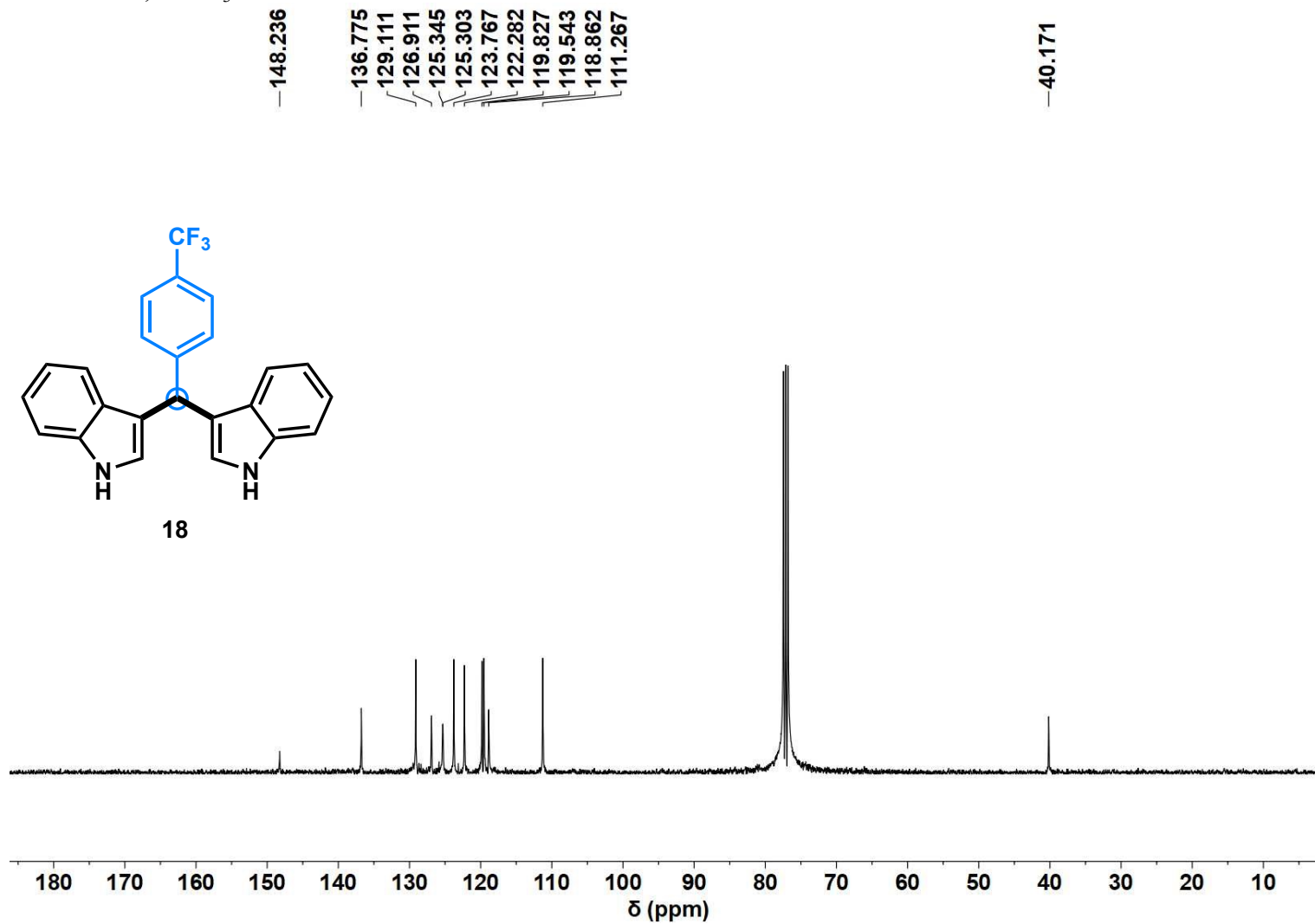
17



^1H NMR 400 MHz, CDCl_3

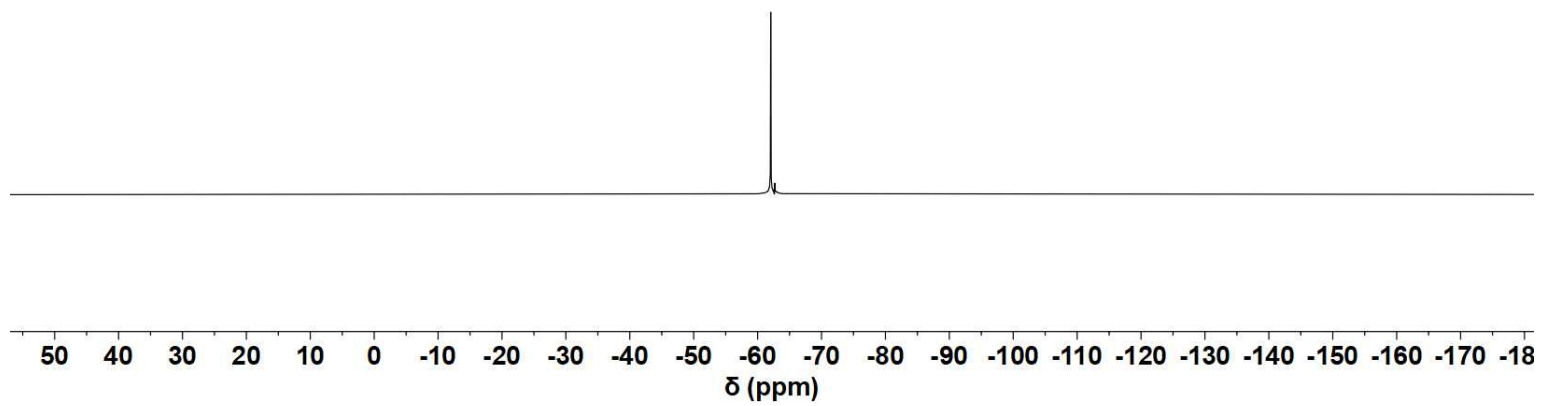
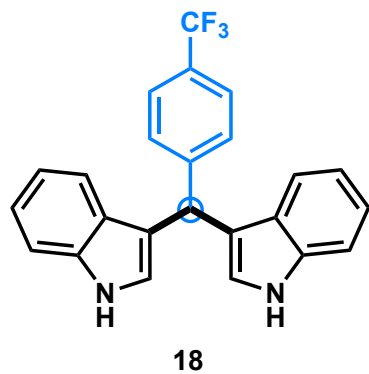


^{13}C NMR 101 MHz, CDCl_3



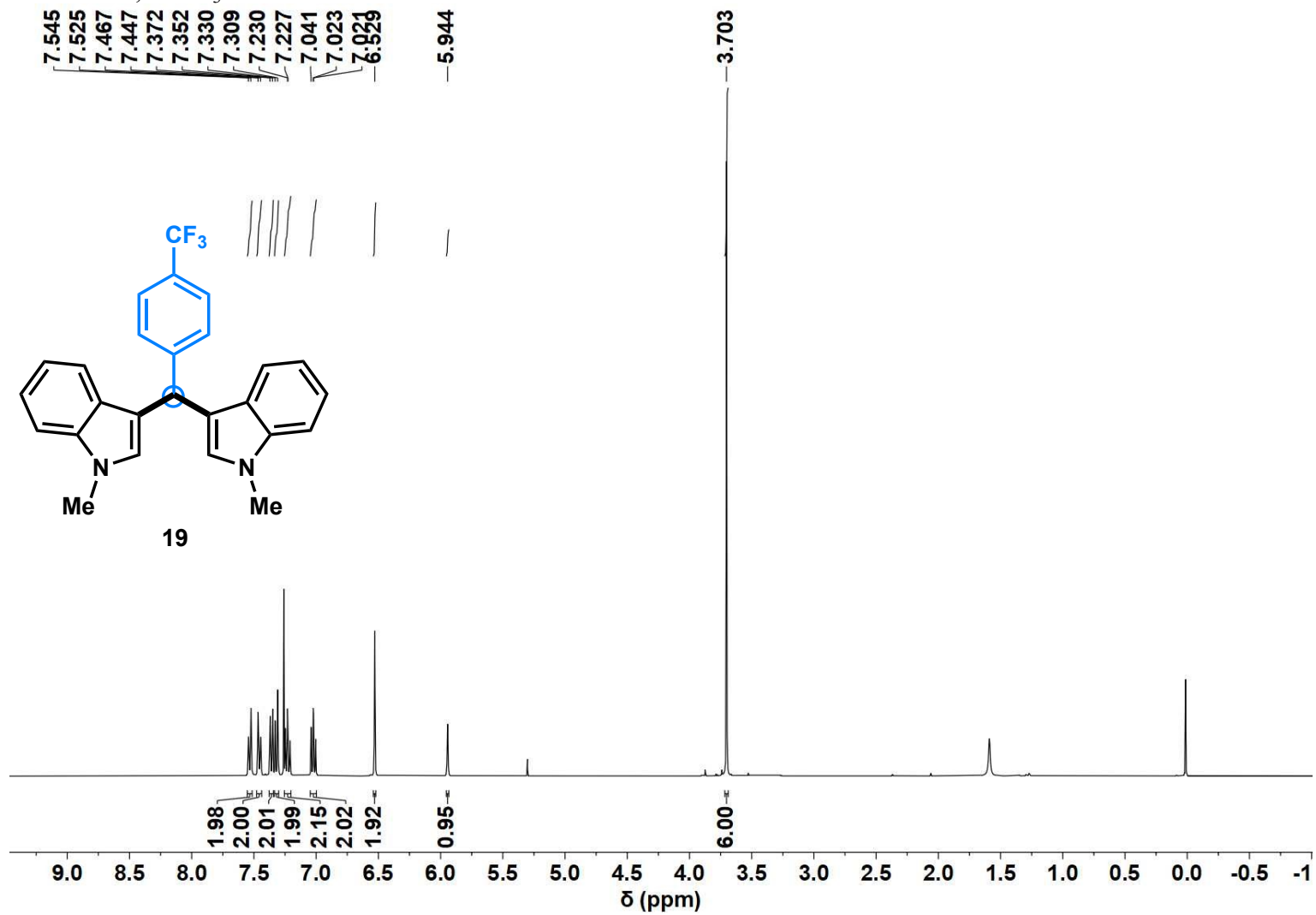
^{19}F NMR 376 MHz, CDCl_3

---62.054

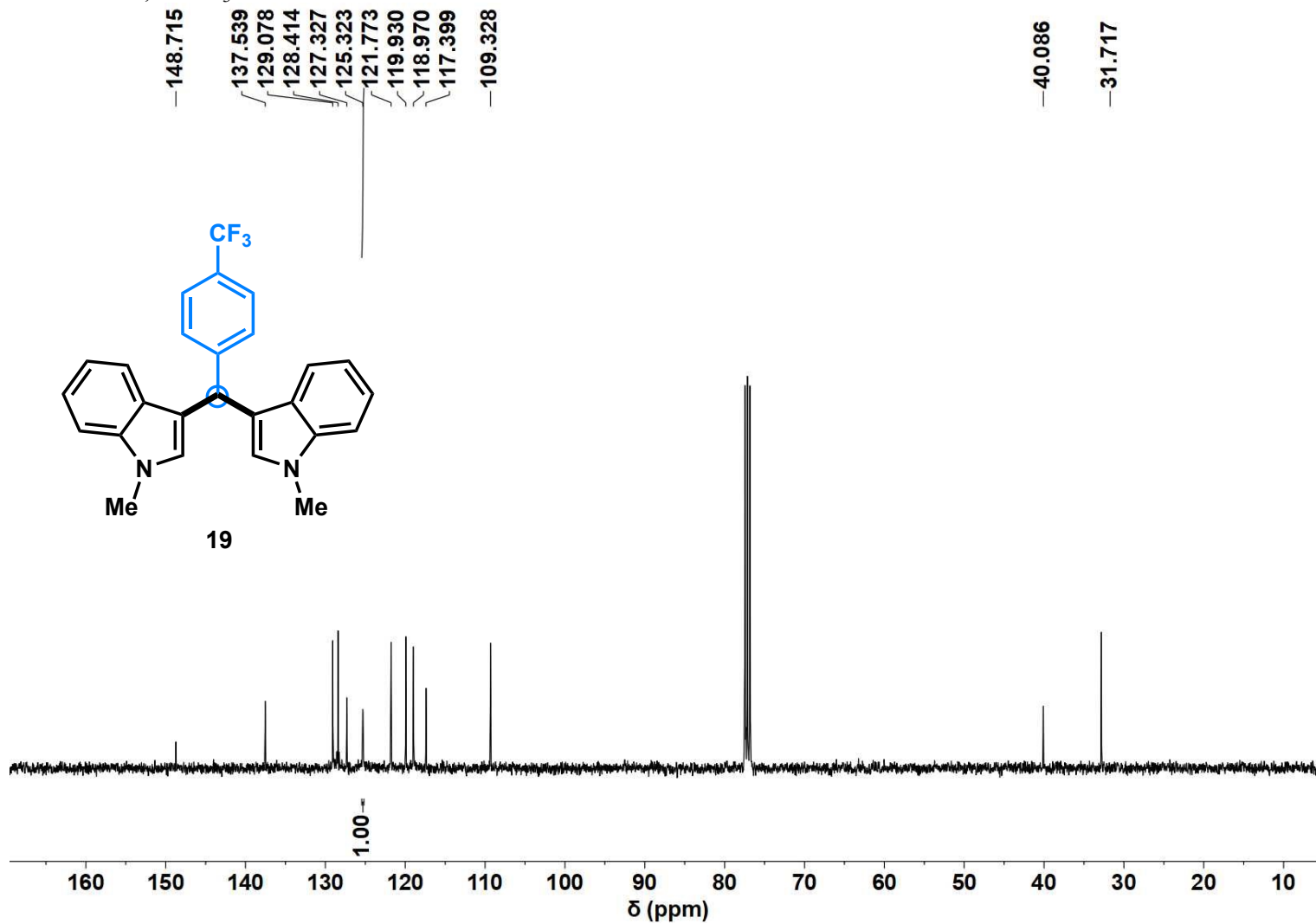


S100

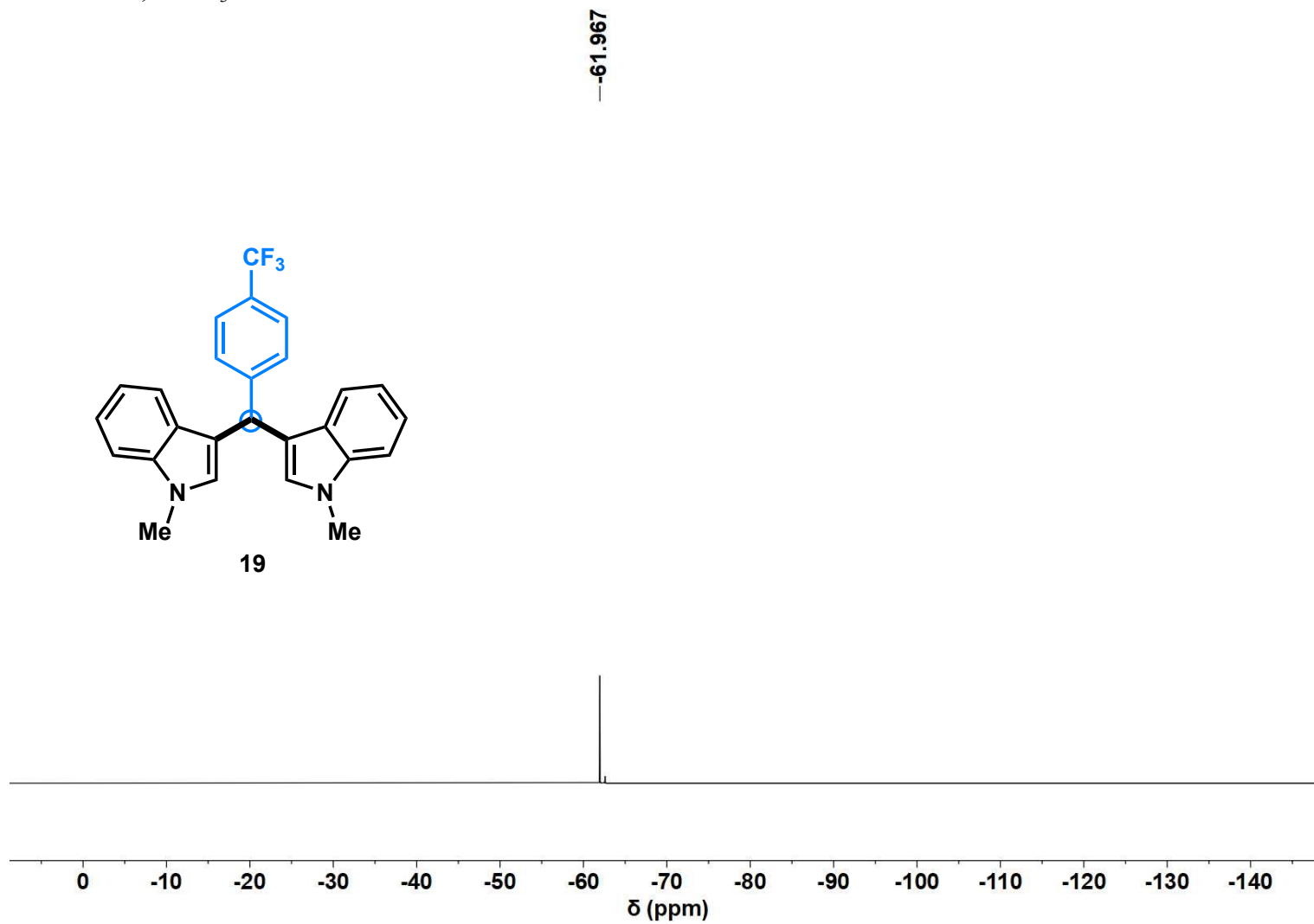
^1H NMR 400 MHz, CDCl_3



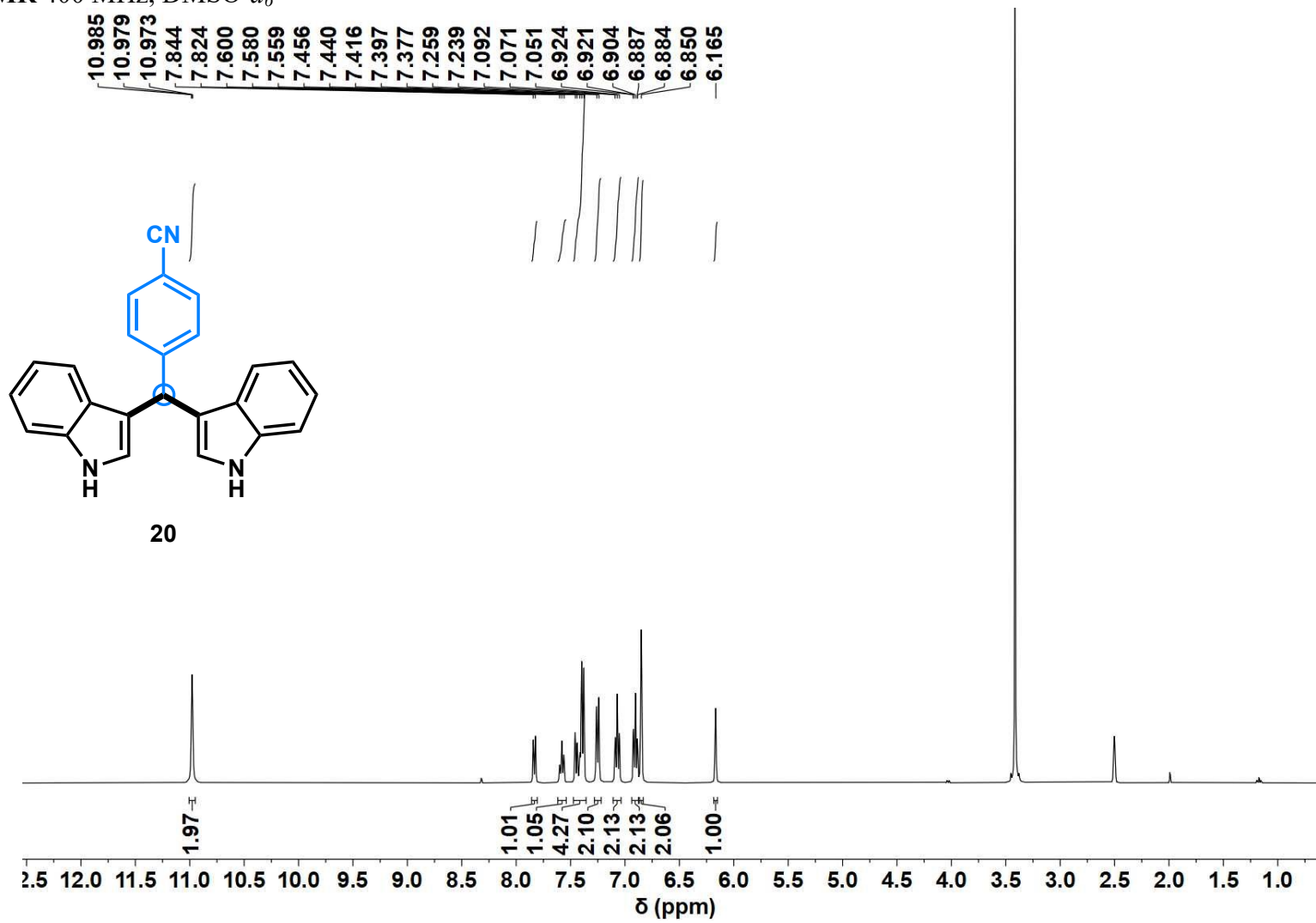
¹³C NMR 101 MHz, CDCl₃



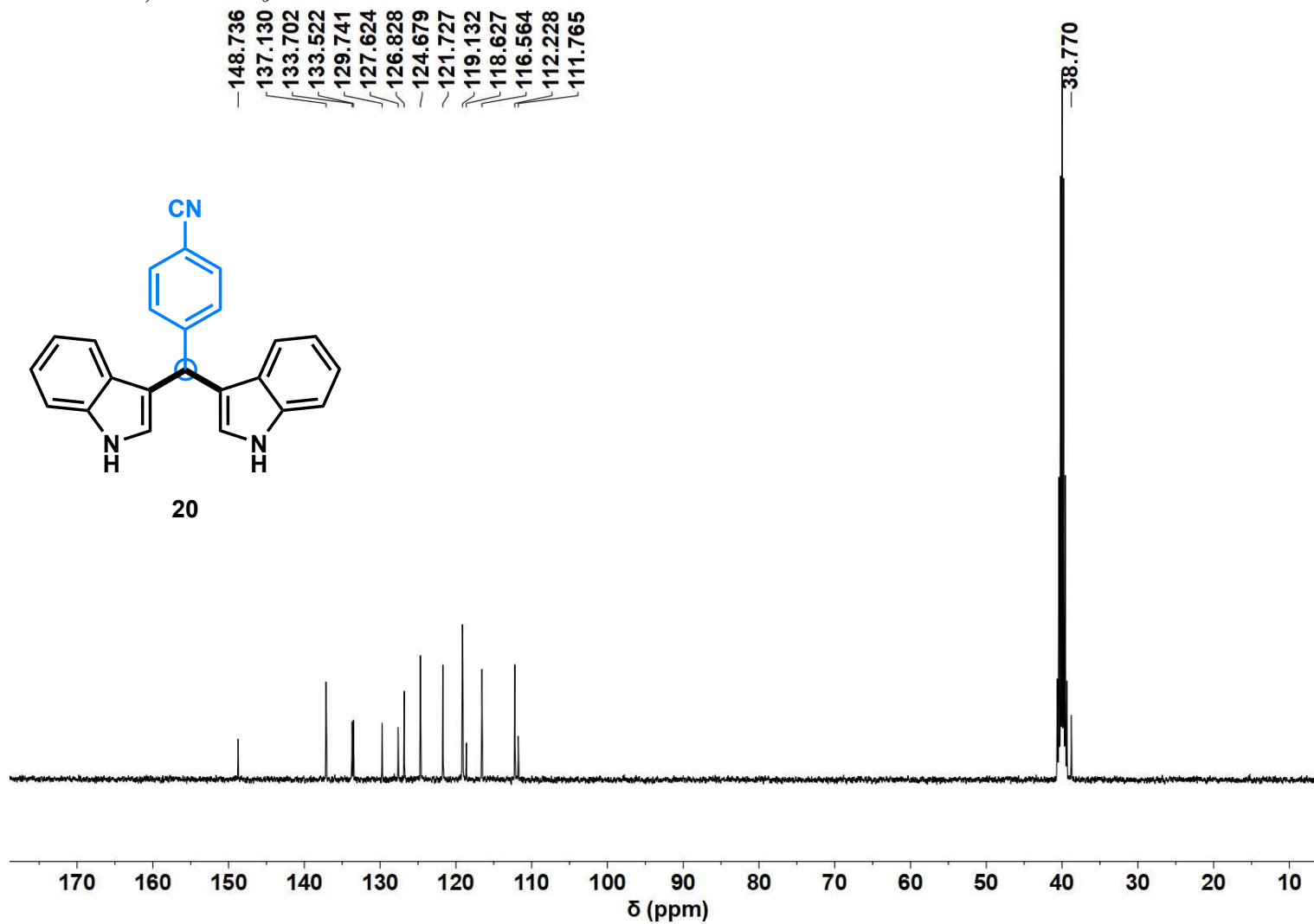
^{19}F NMR 376 MHz, CDCl_3



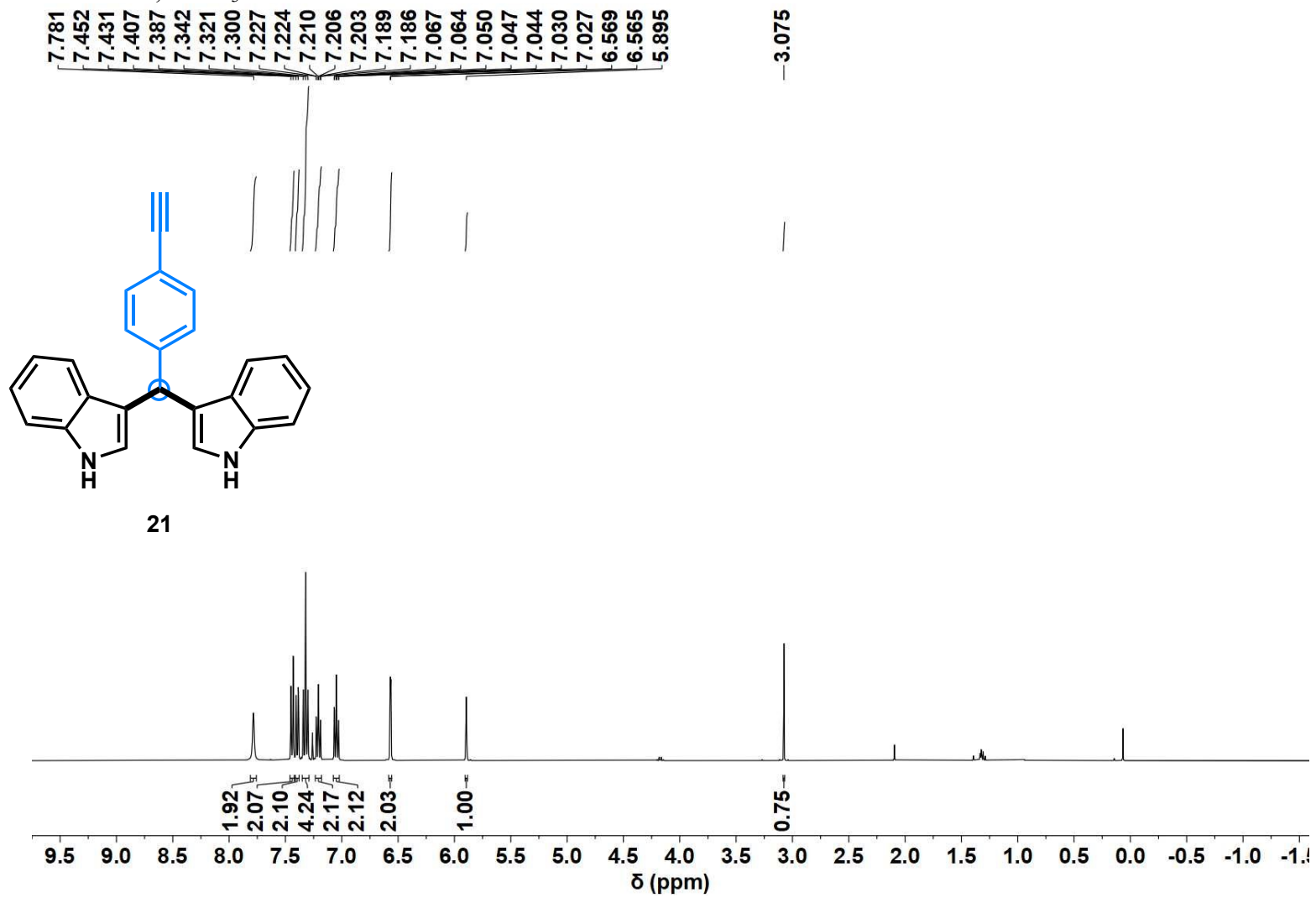
^1H NMR 400 MHz, $\text{DMSO-}d_6$



¹³C NMR 101 MHz, DMSO-*d*₆



^1H NMR 400 MHz, CDCl_3

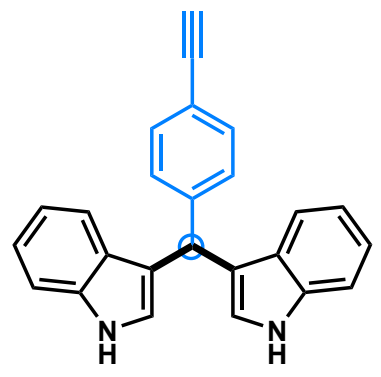


¹³C NMR 101 MHz, CDCl₃

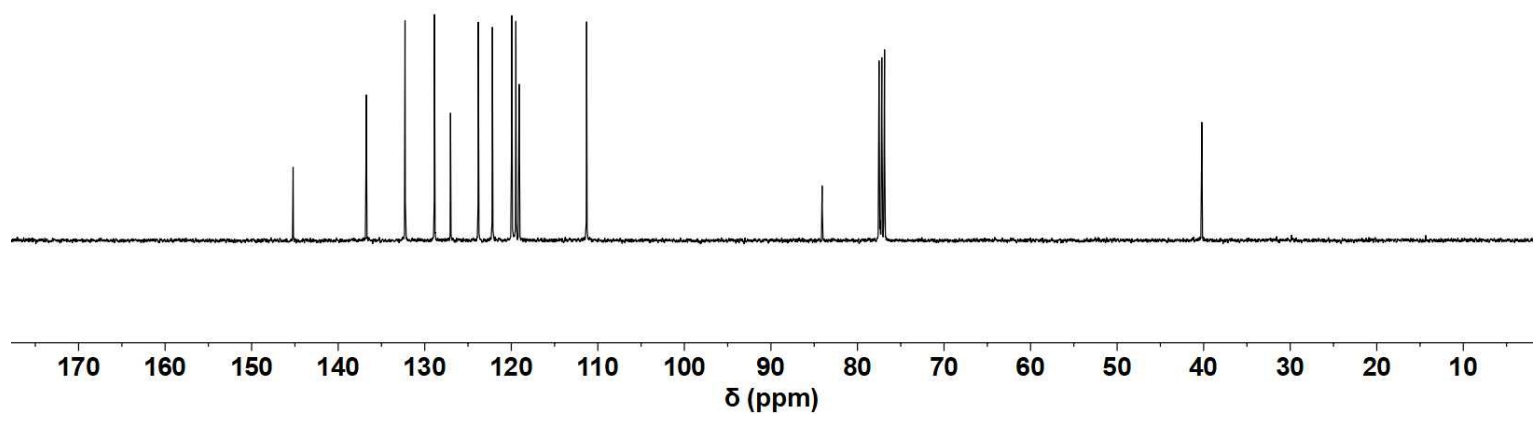
145.210
136.761
132.274
128.876
127.021
123.809
122.181
119.945
119.888
119.468
119.095
112.429

85.011

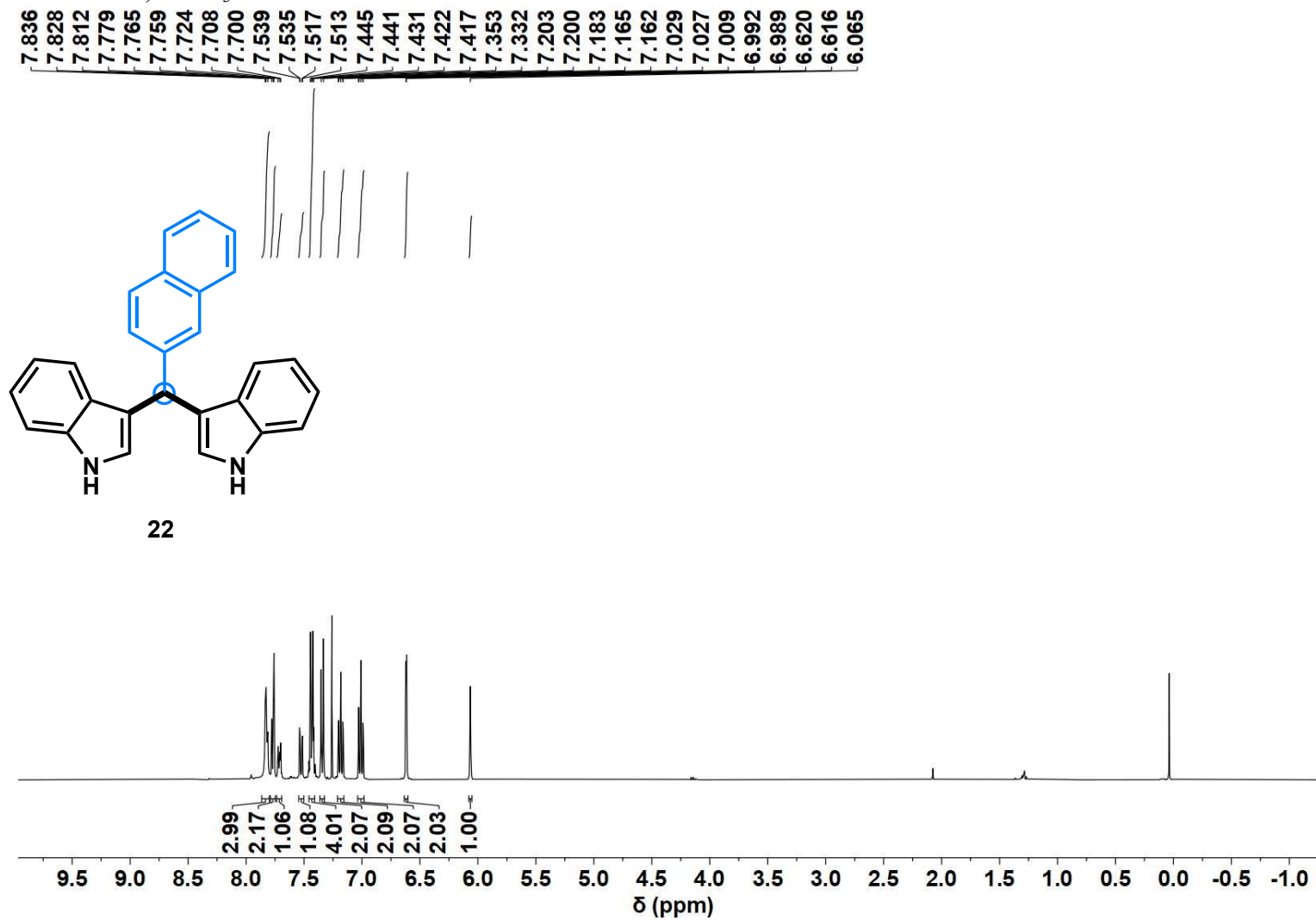
40.214



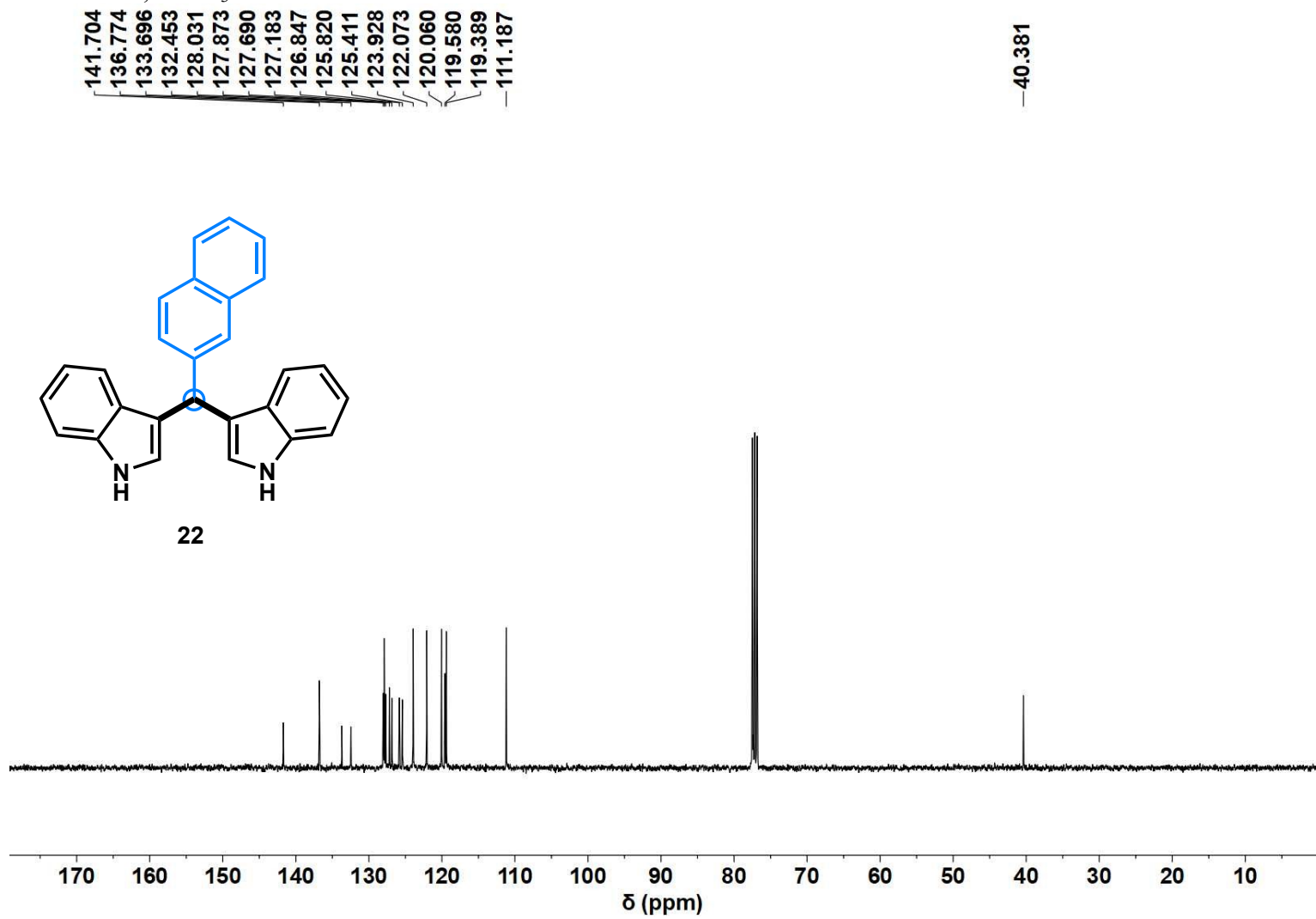
21



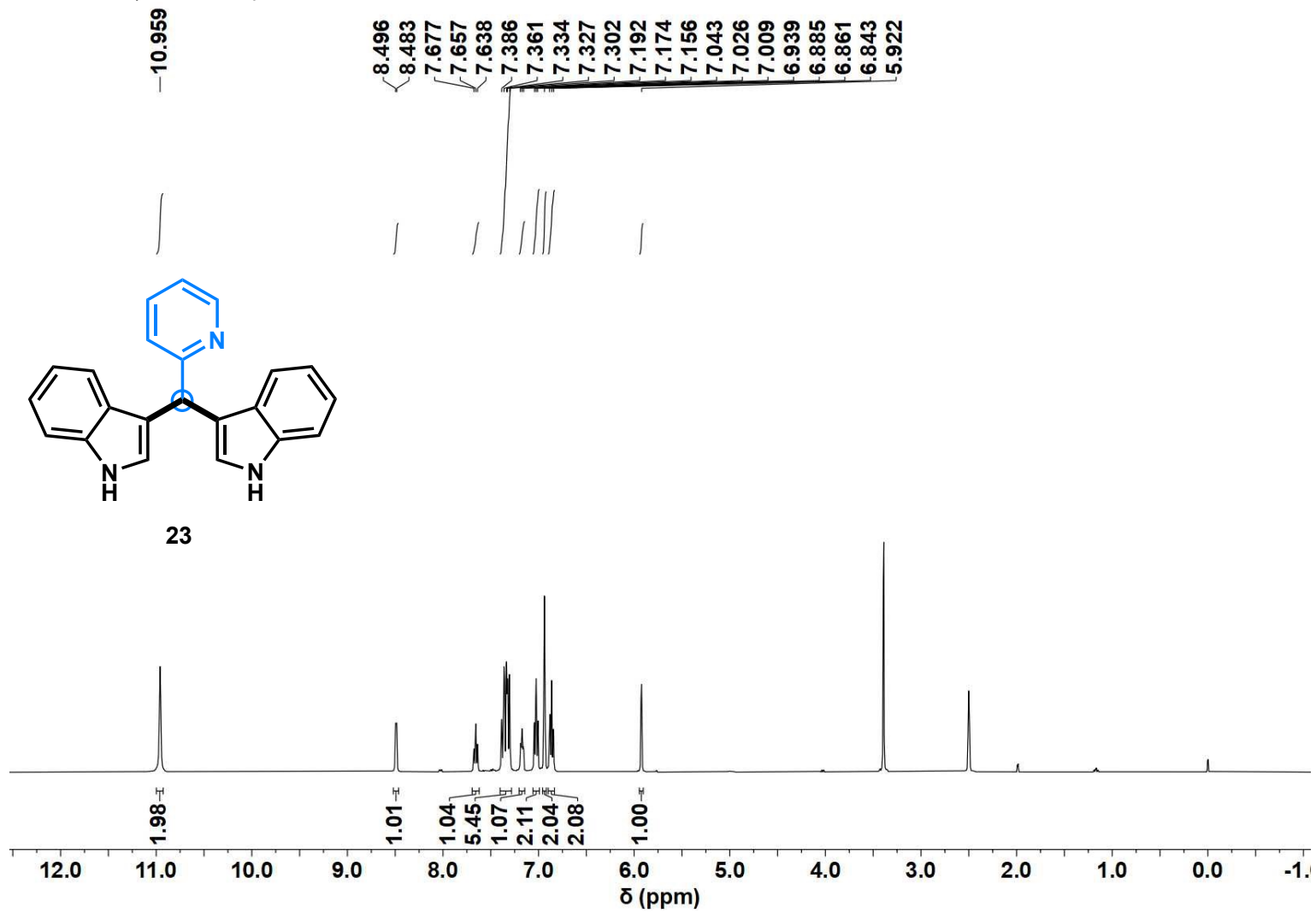
¹H NMR 400 MHz, CDCl₃



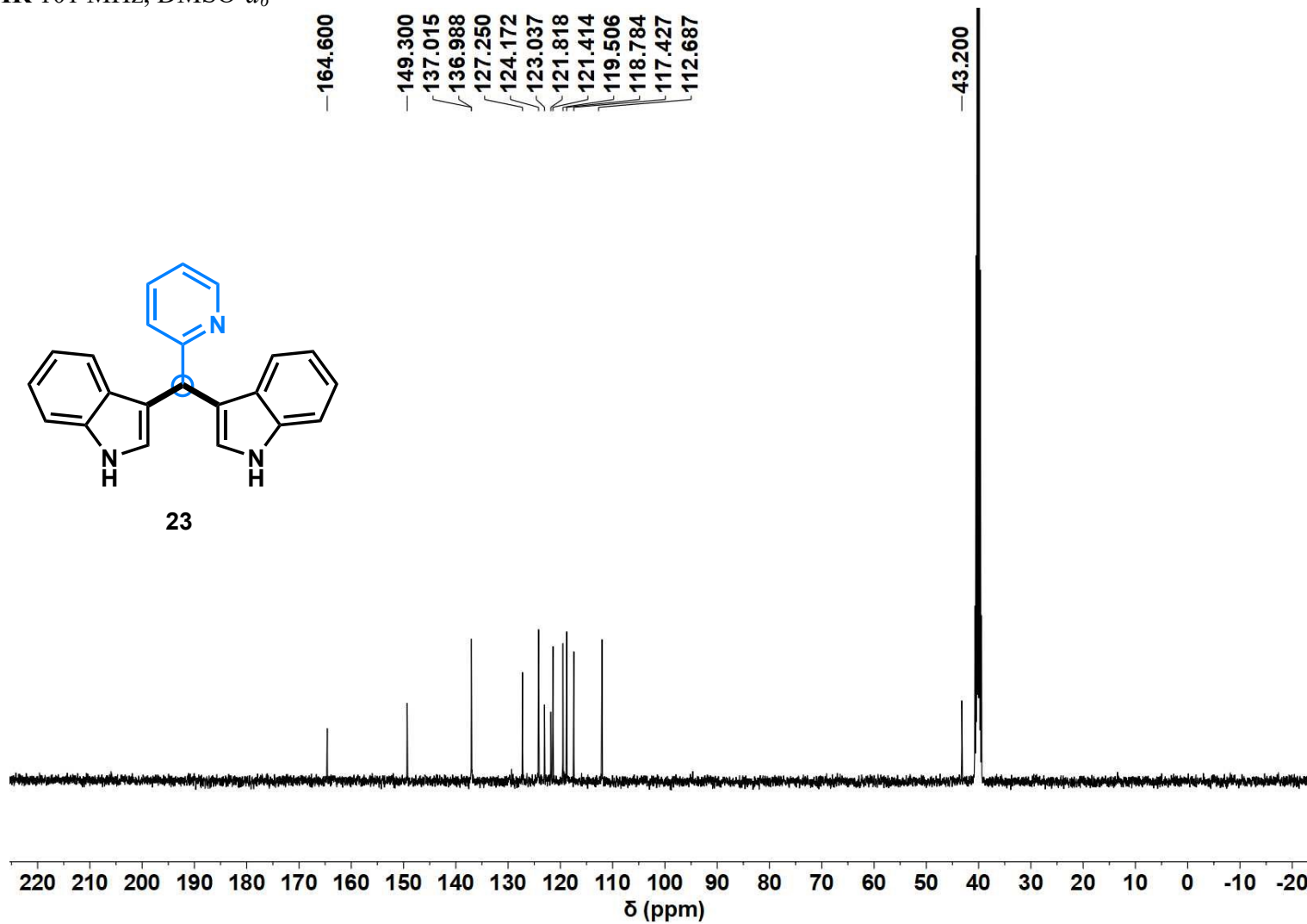
¹³C NMR 101 MHz, CDCl₃



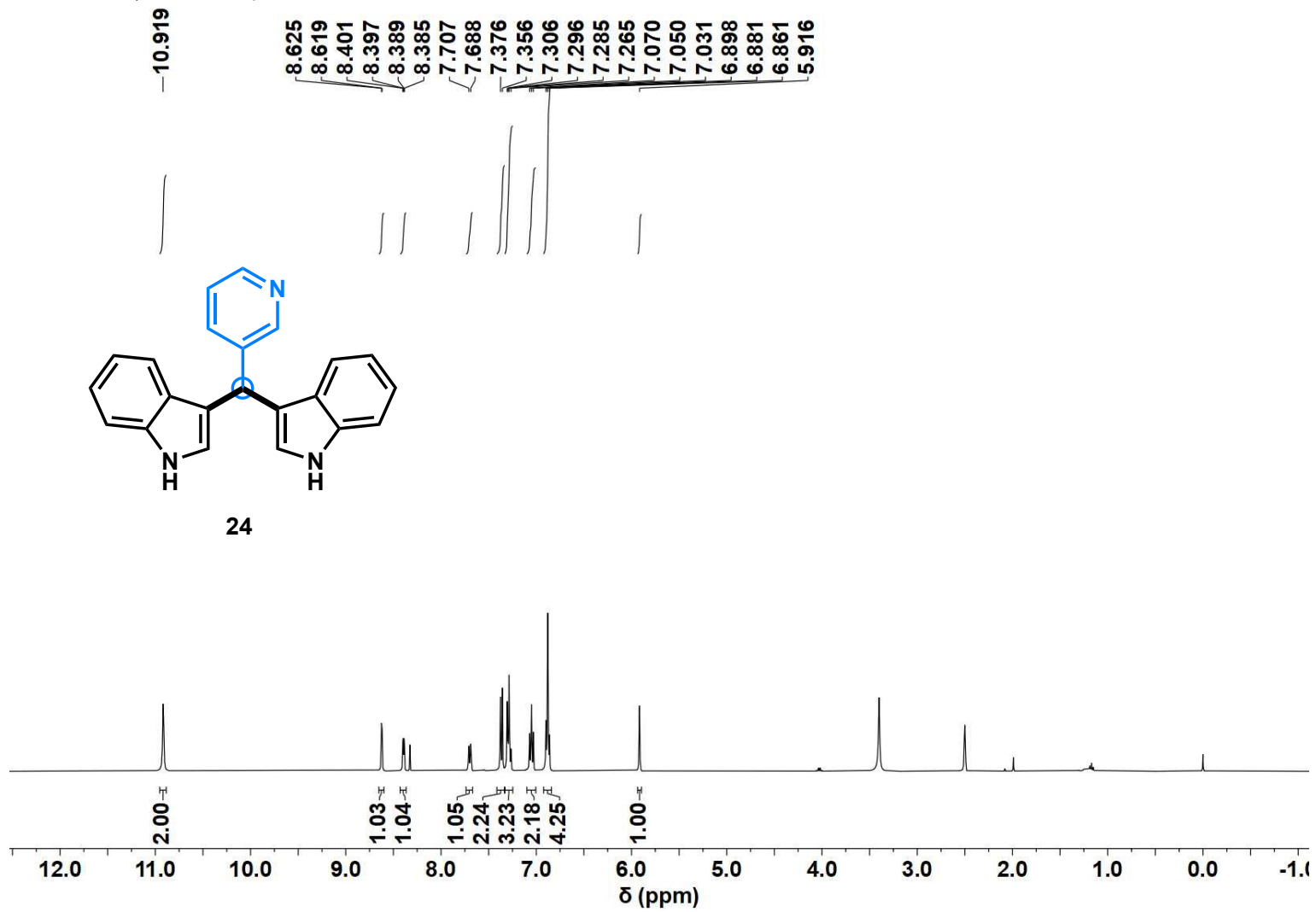
^1H NMR 400 MHz, DMSO- d_6



^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

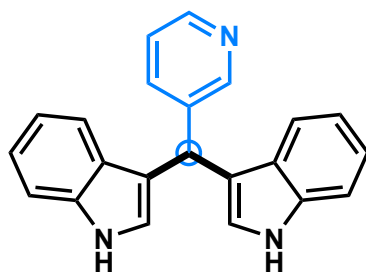


^1H NMR 400 MHz, DMSO- d_6

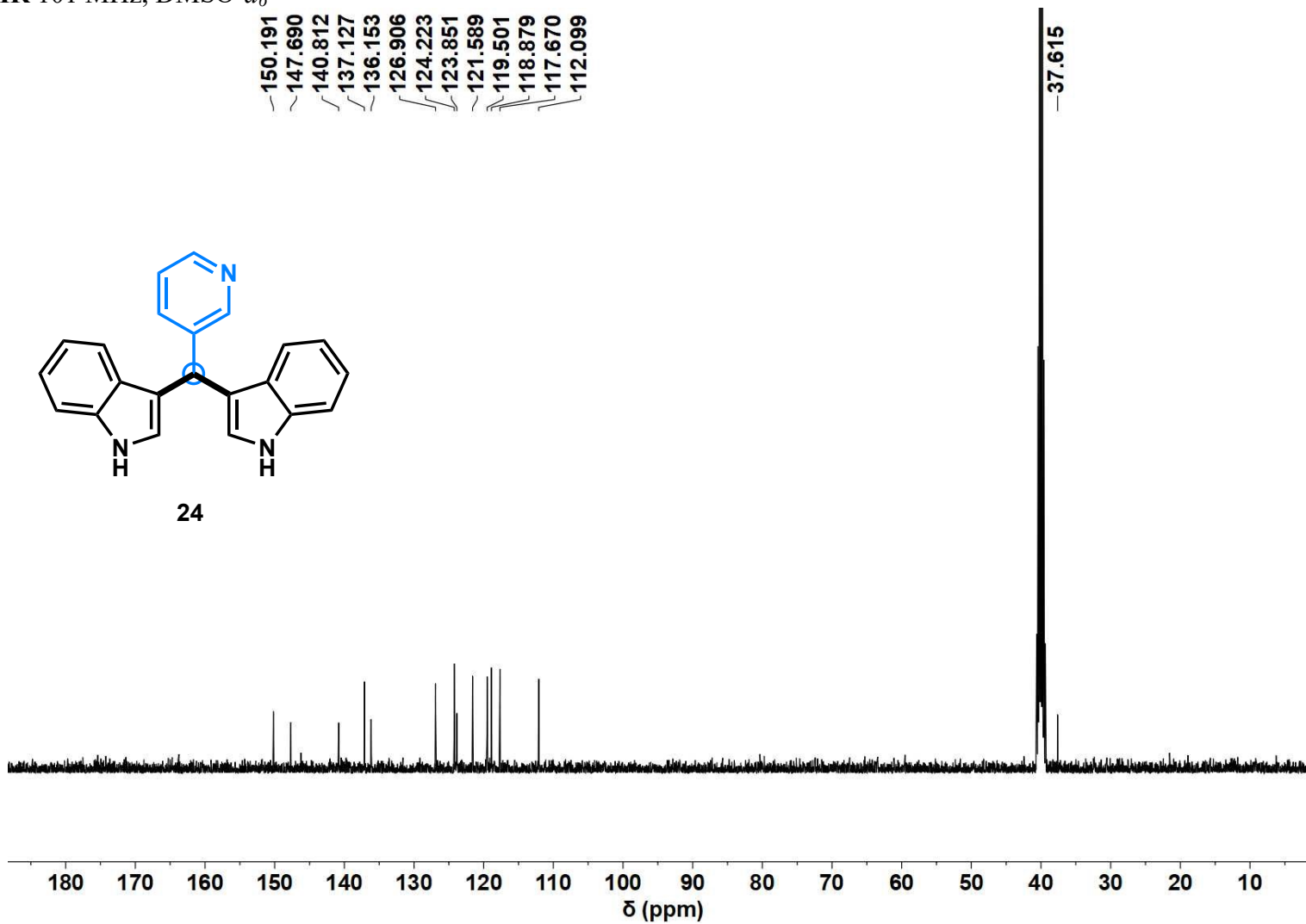


¹³C NMR 101 MHz, DMSO-*d*₆

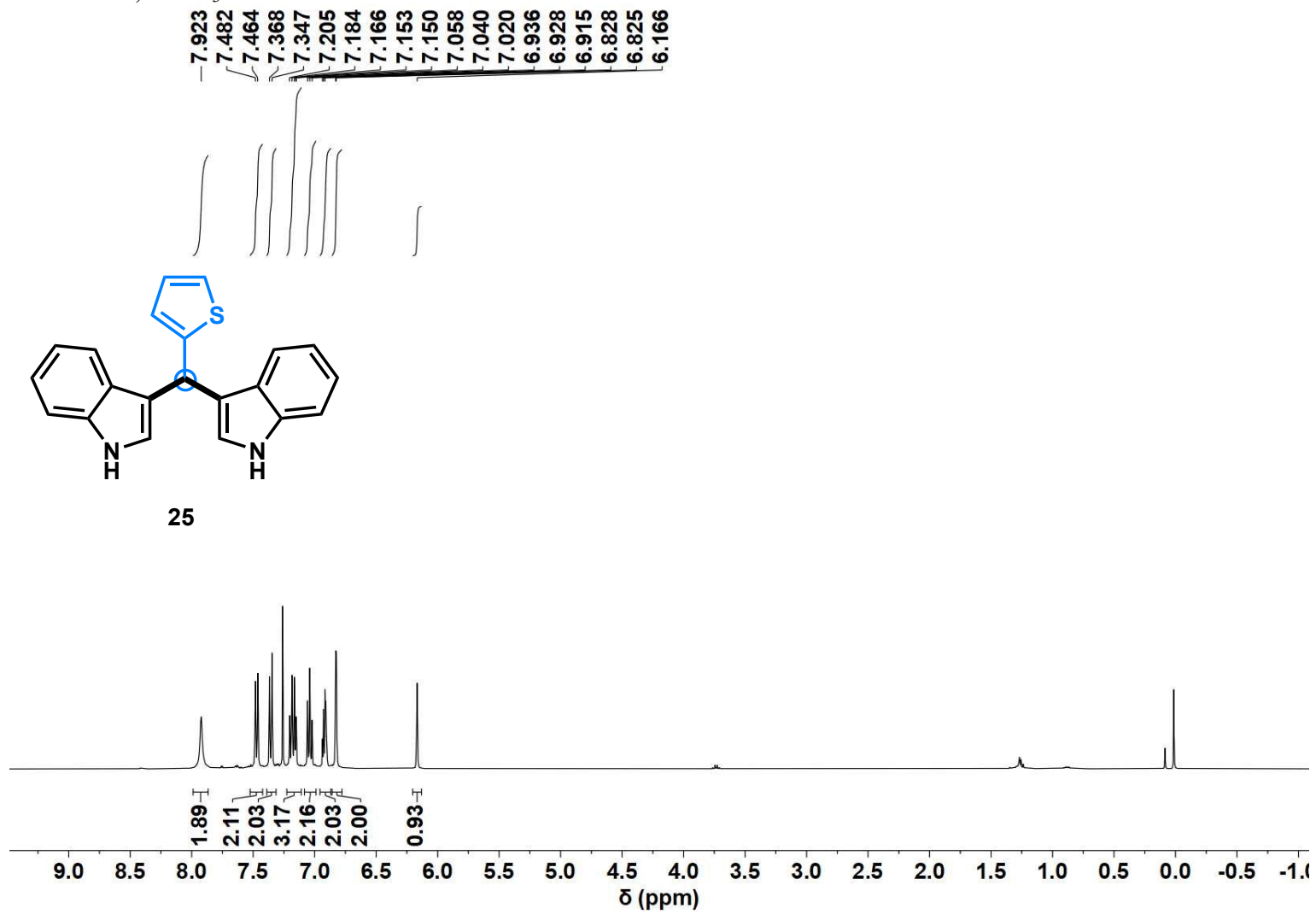
150.191
147.690
140.812
137.127
136.153
126.906
124.223
123.851
121.589
119.501
118.879
117.670
112.099



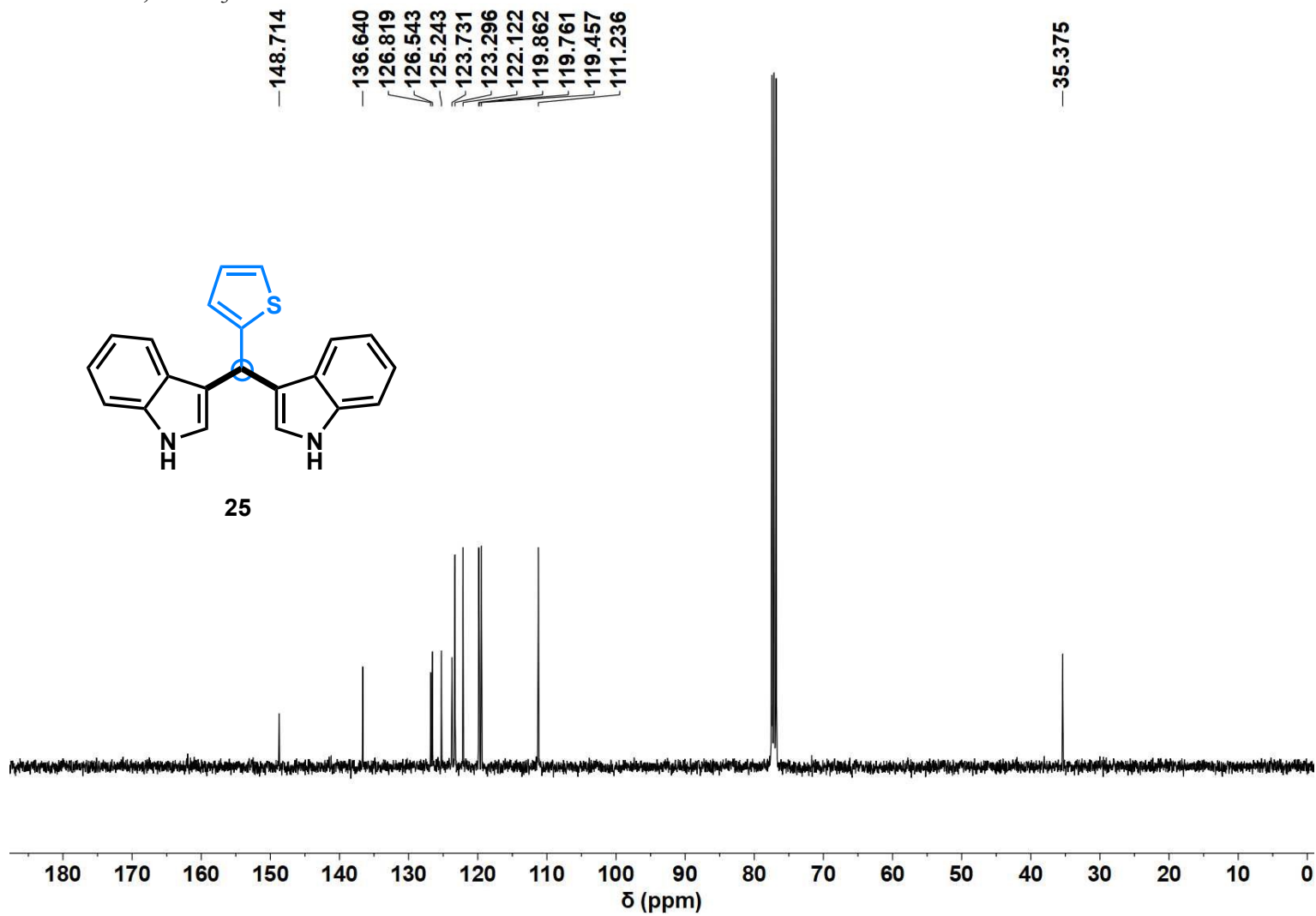
24



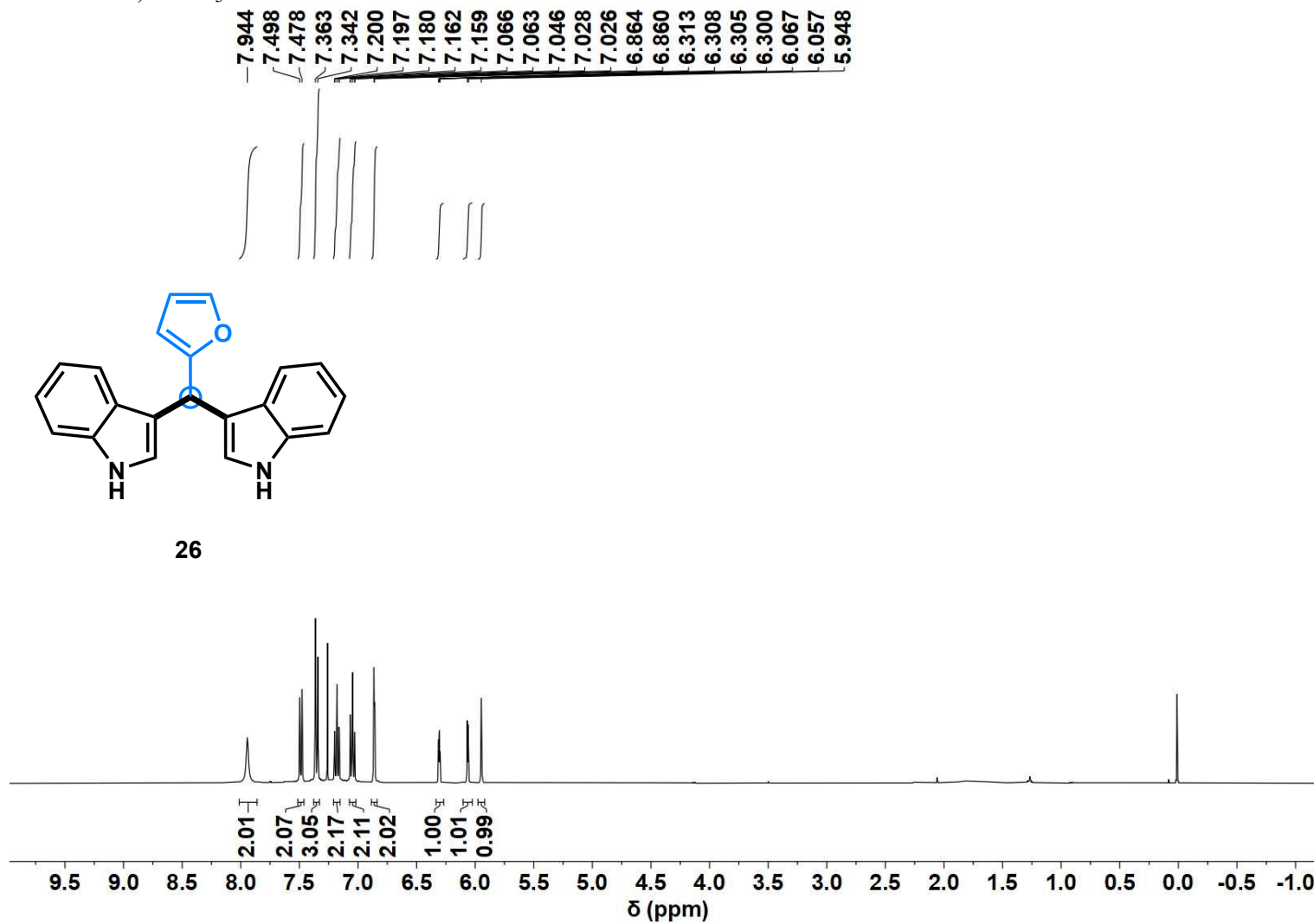
^1H NMR 400 MHz, CDCl_3



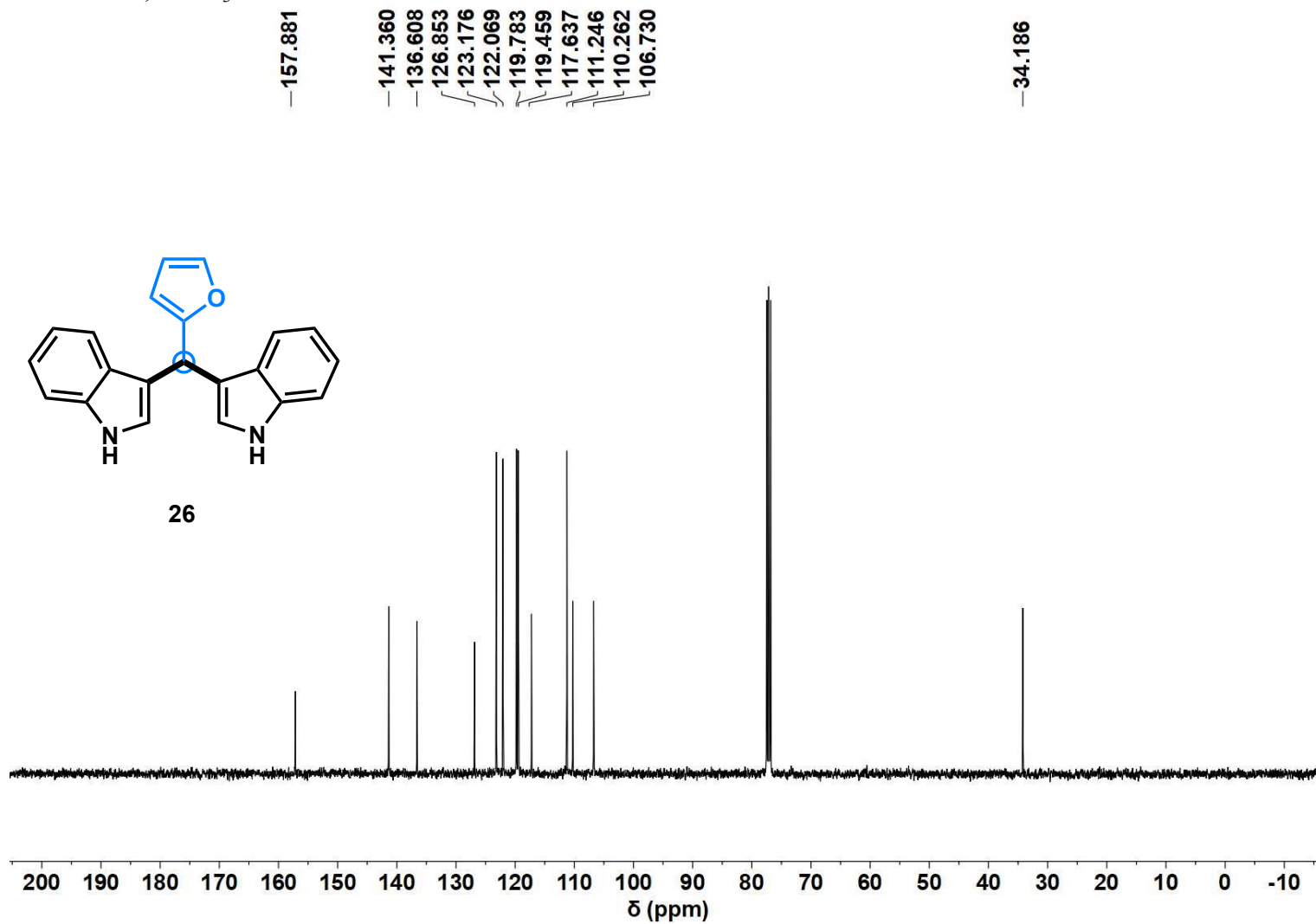
^{13}C NMR 101 MHz, CDCl_3



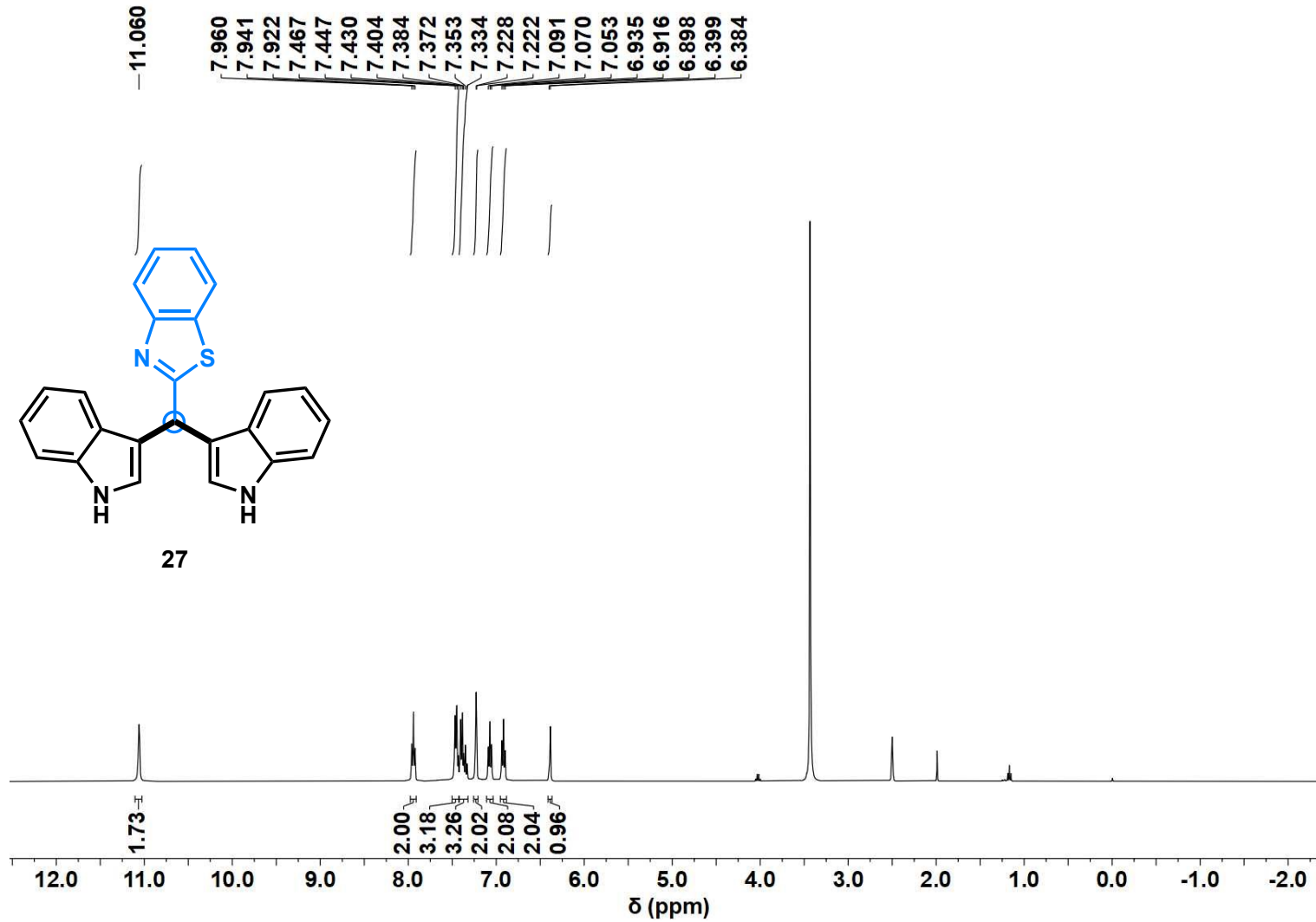
^1H NMR 400 MHz, CDCl_3



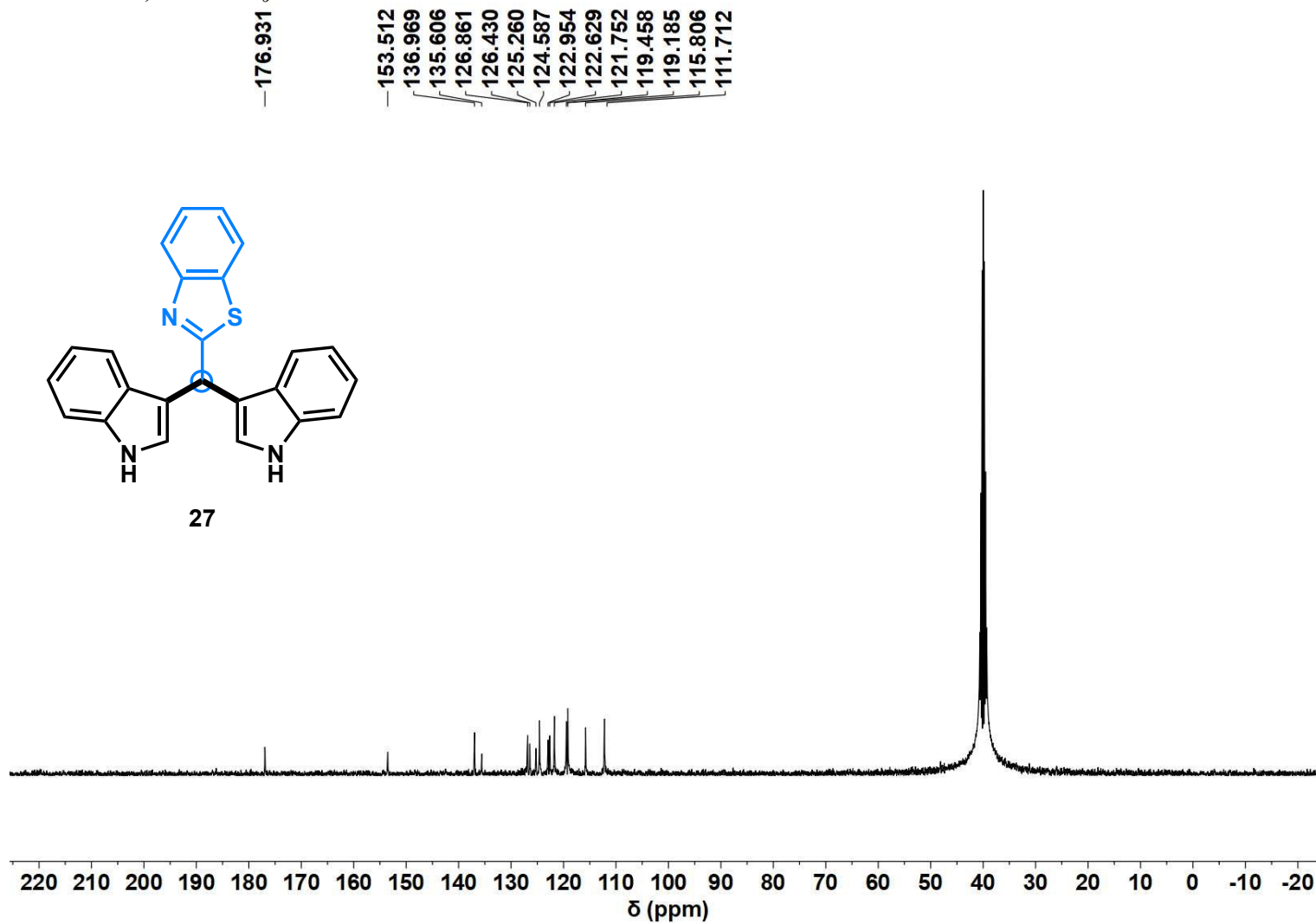
^{13}C NMR 101 MHz, CDCl_3



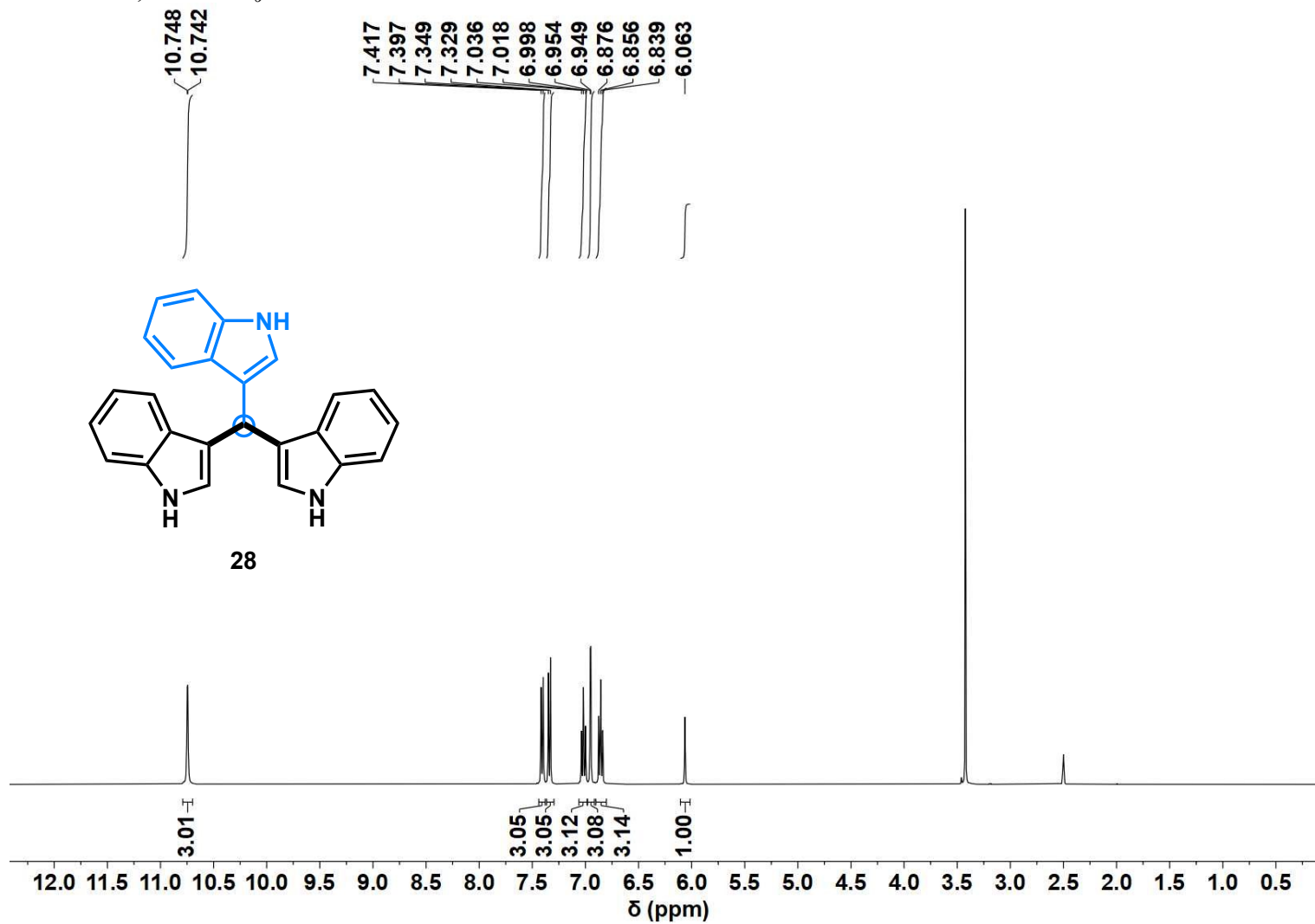
^1H NMR 400 MHz, $\text{DMSO-}d_6$



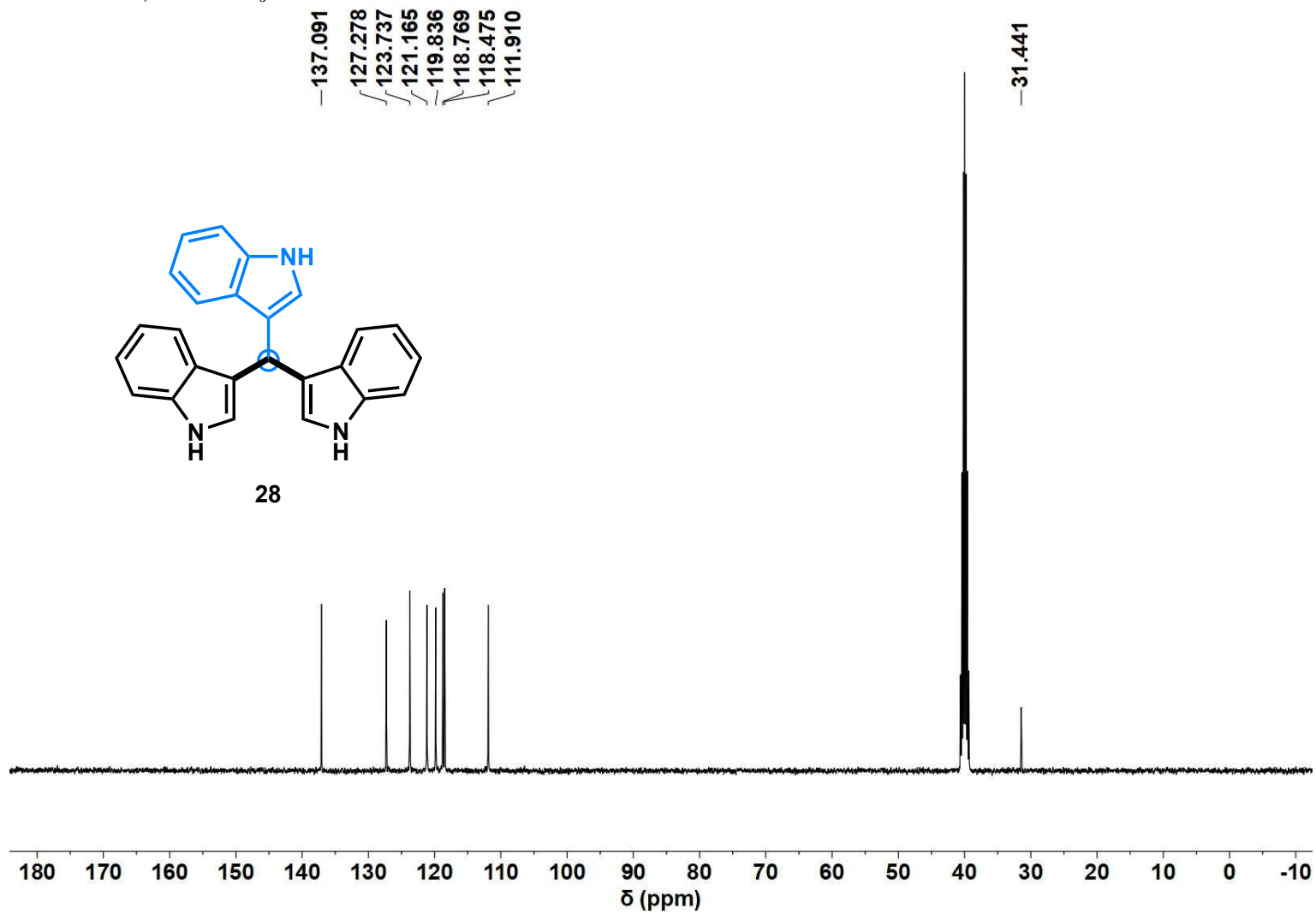
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



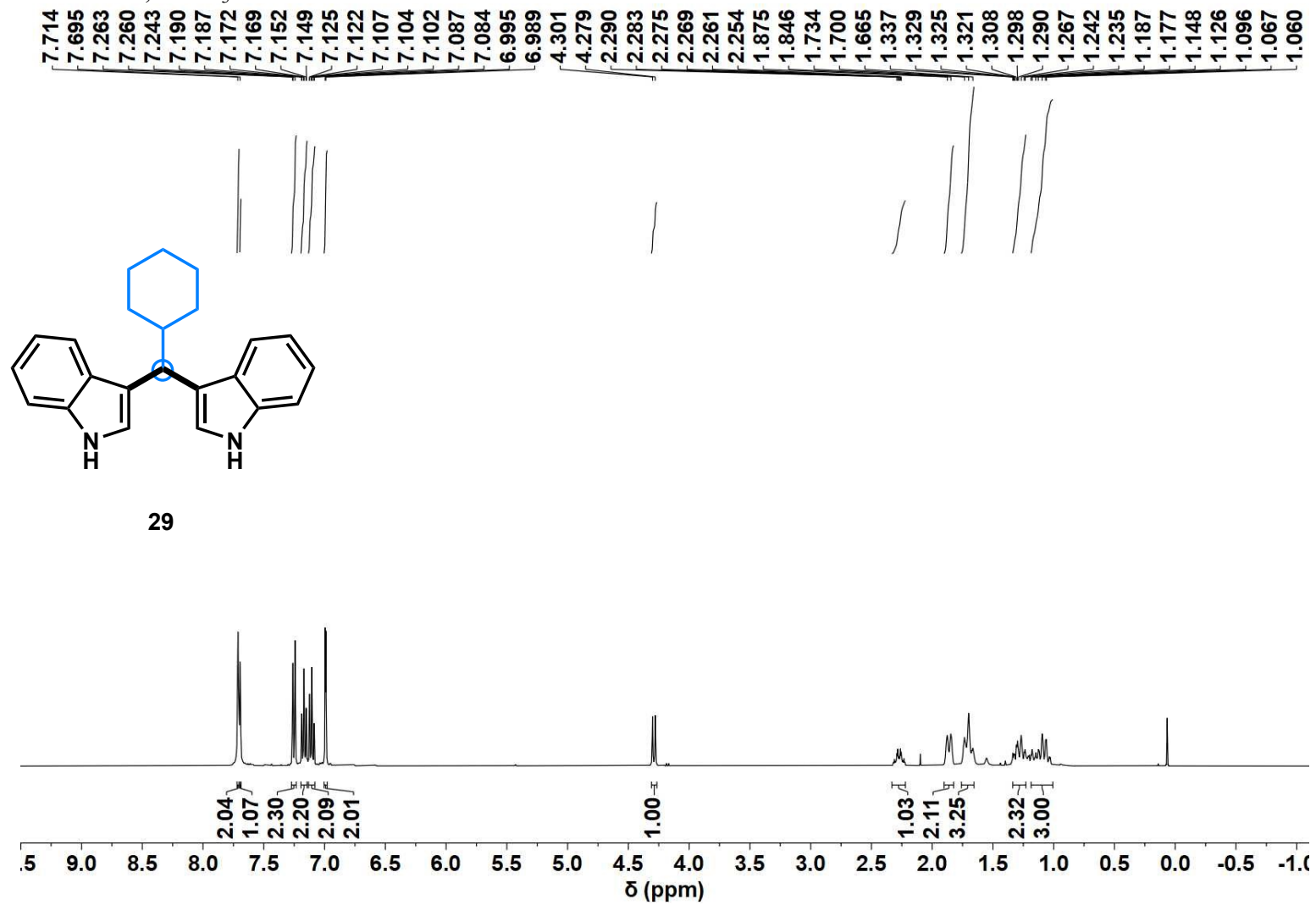
^1H NMR 400 MHz, $\text{DMSO-}d_6$



^{13}C NMR 400 MHz, $\text{DMSO-}d_6$



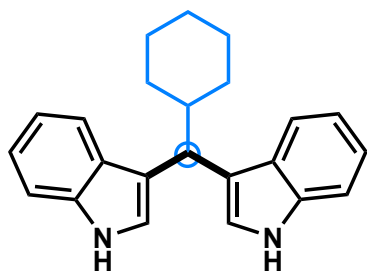
¹H NMR 400 MHz, CDCl₃



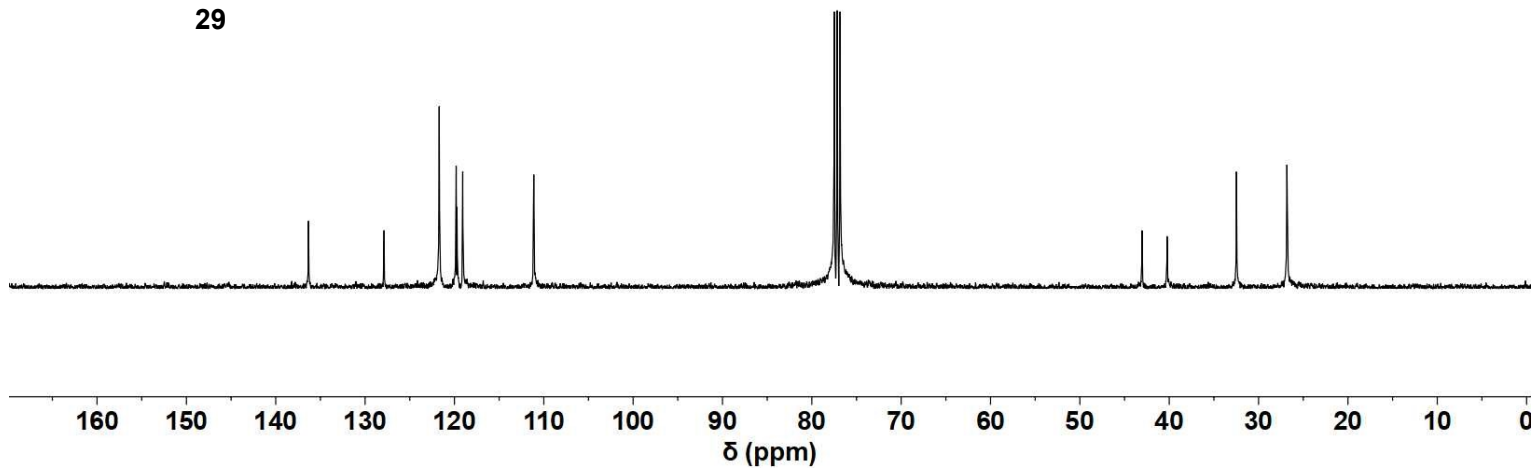
^{13}C NMR 101 MHz, CDCl_3

136.334
127.877
121.701
119.869
119.803
119.075
111.121

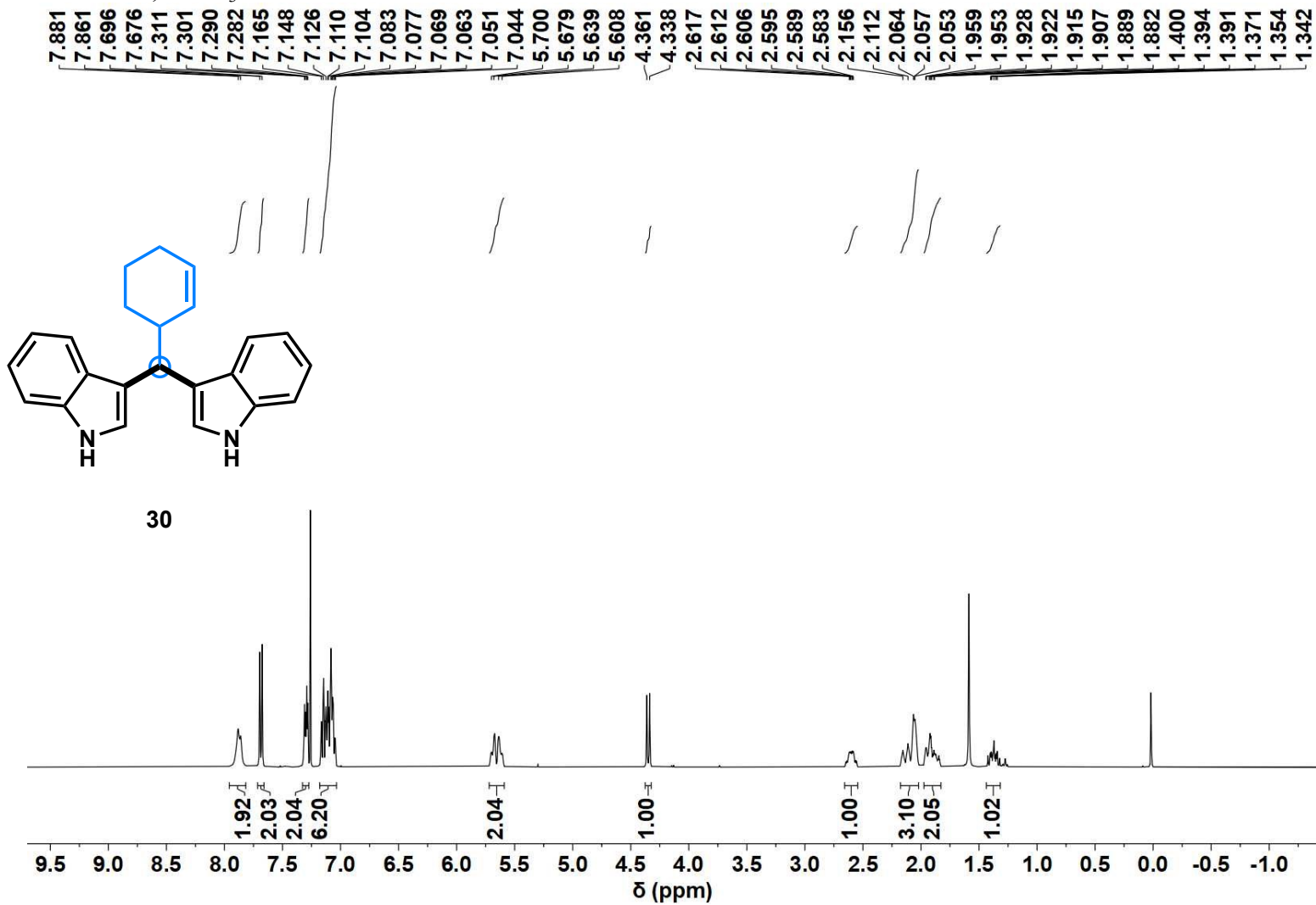
43.044
40.234
32.477
26.827
26.784



29



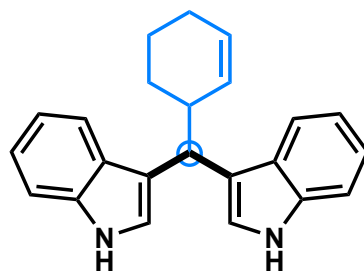
¹H NMR 400 MHz, CDCl₃



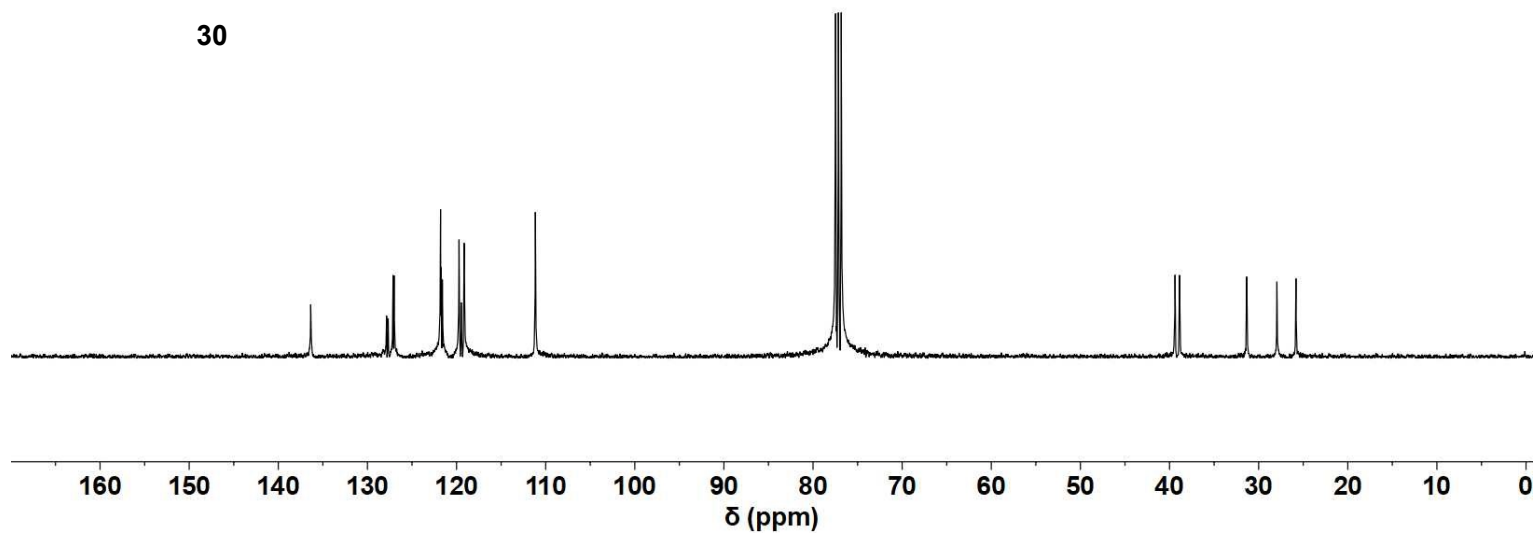
^{13}C NMR 101 MHz, CDCl_3

136.363
136.330
127.848
127.670
127.122
127.012
121.791
121.733
121.595
119.712
119.533
119.479
119.156
111.157

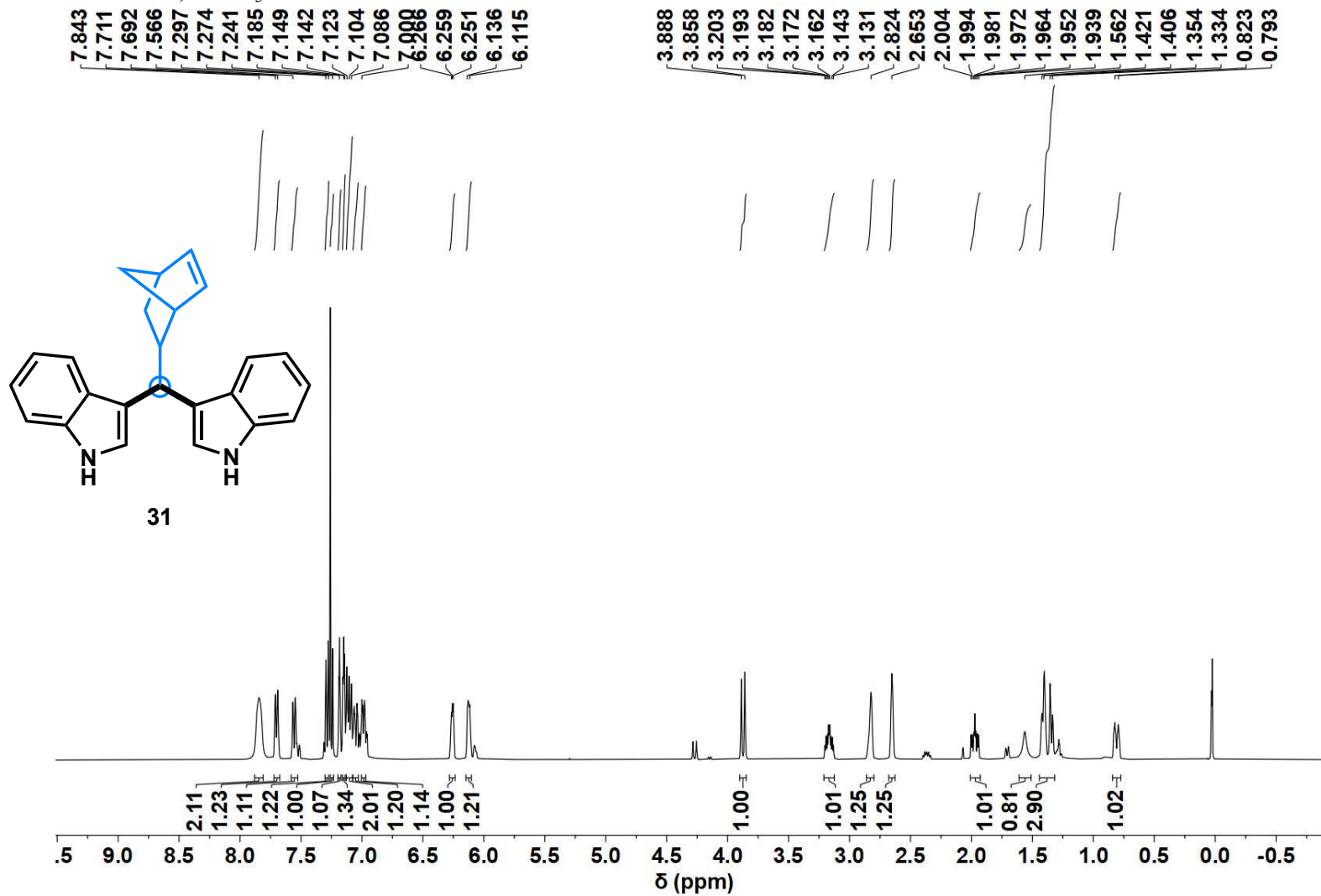
39.380
38.880
30.964
27.351
25.247



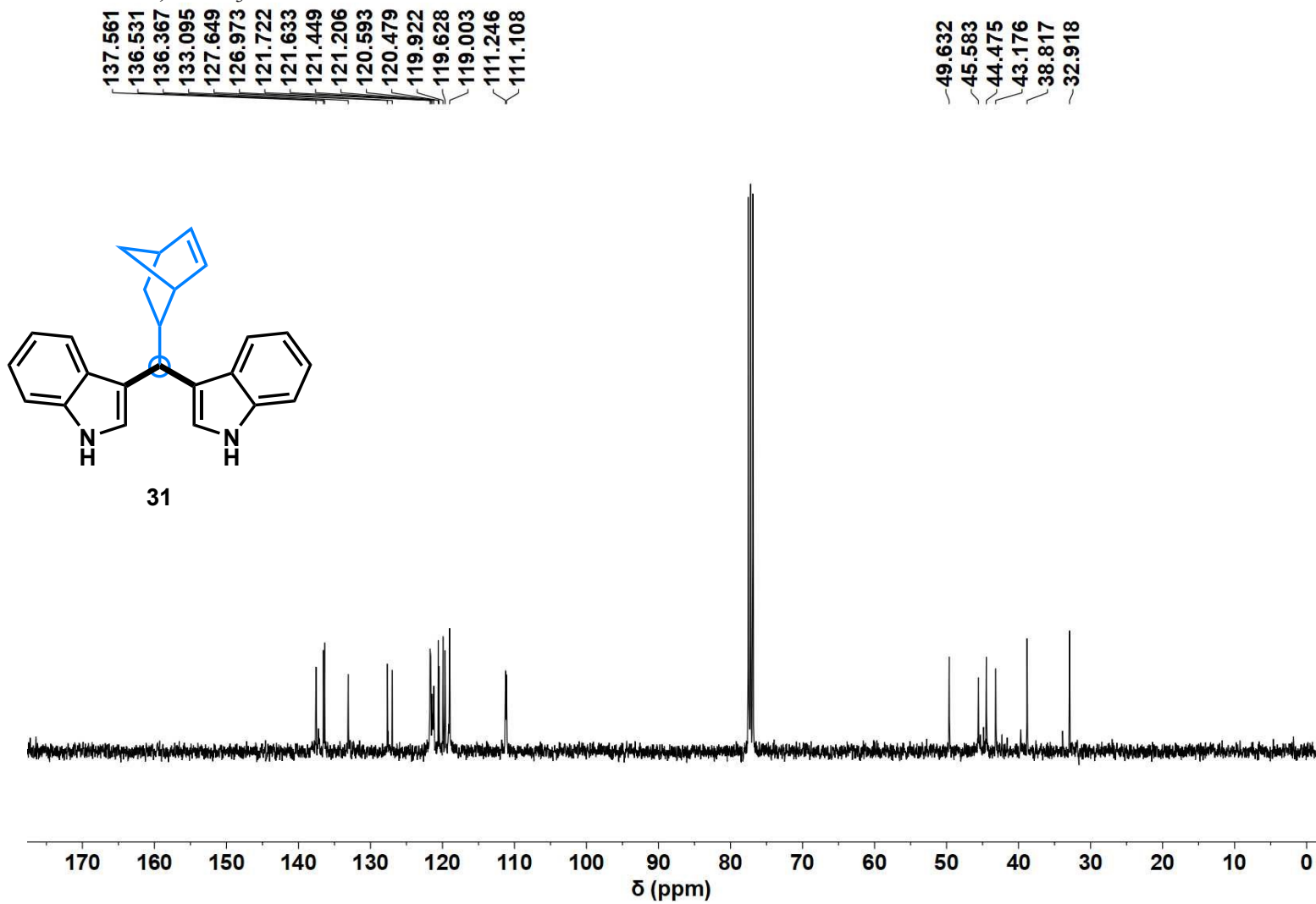
30



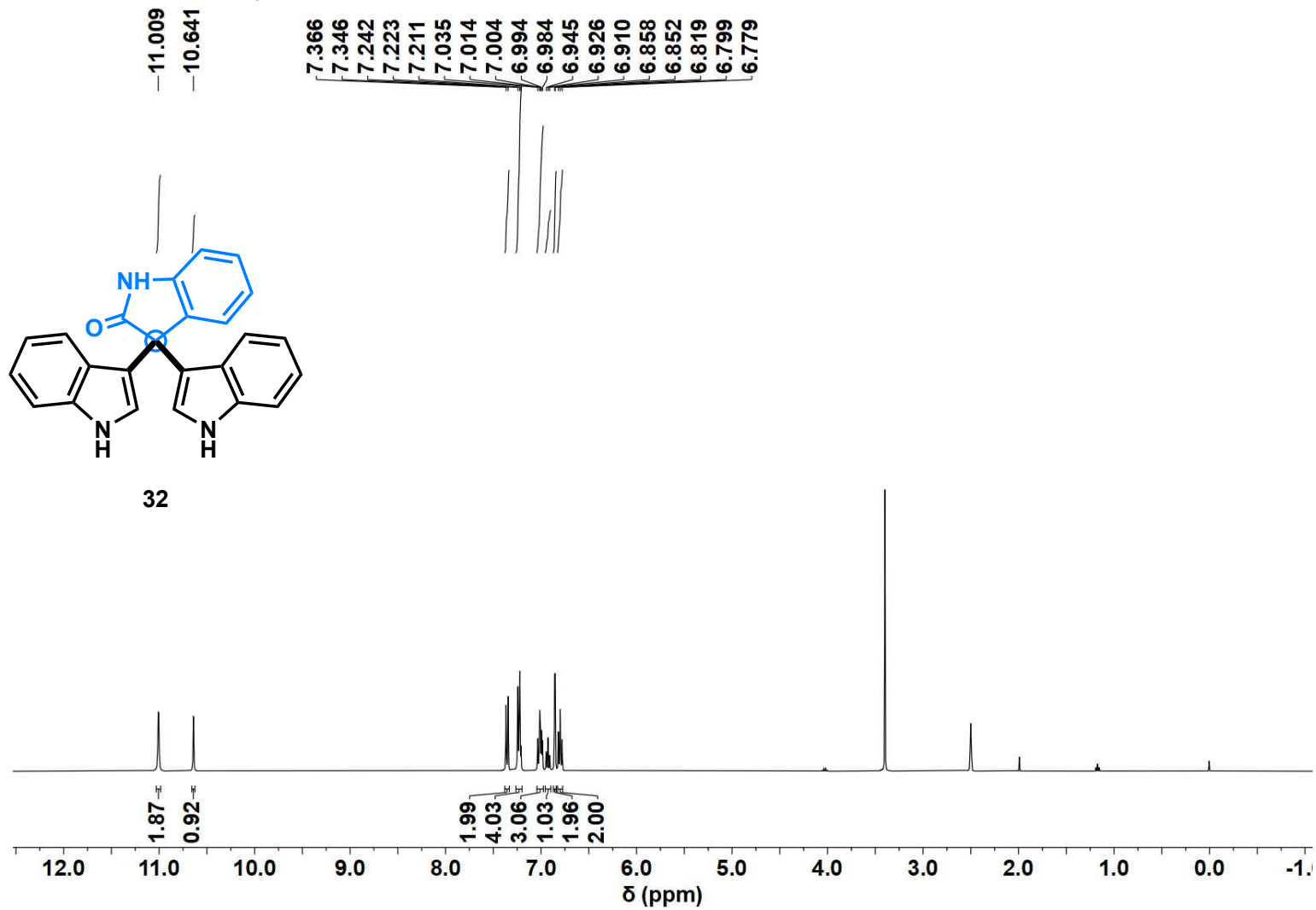
¹H NMR 400 MHz, CDCl₃



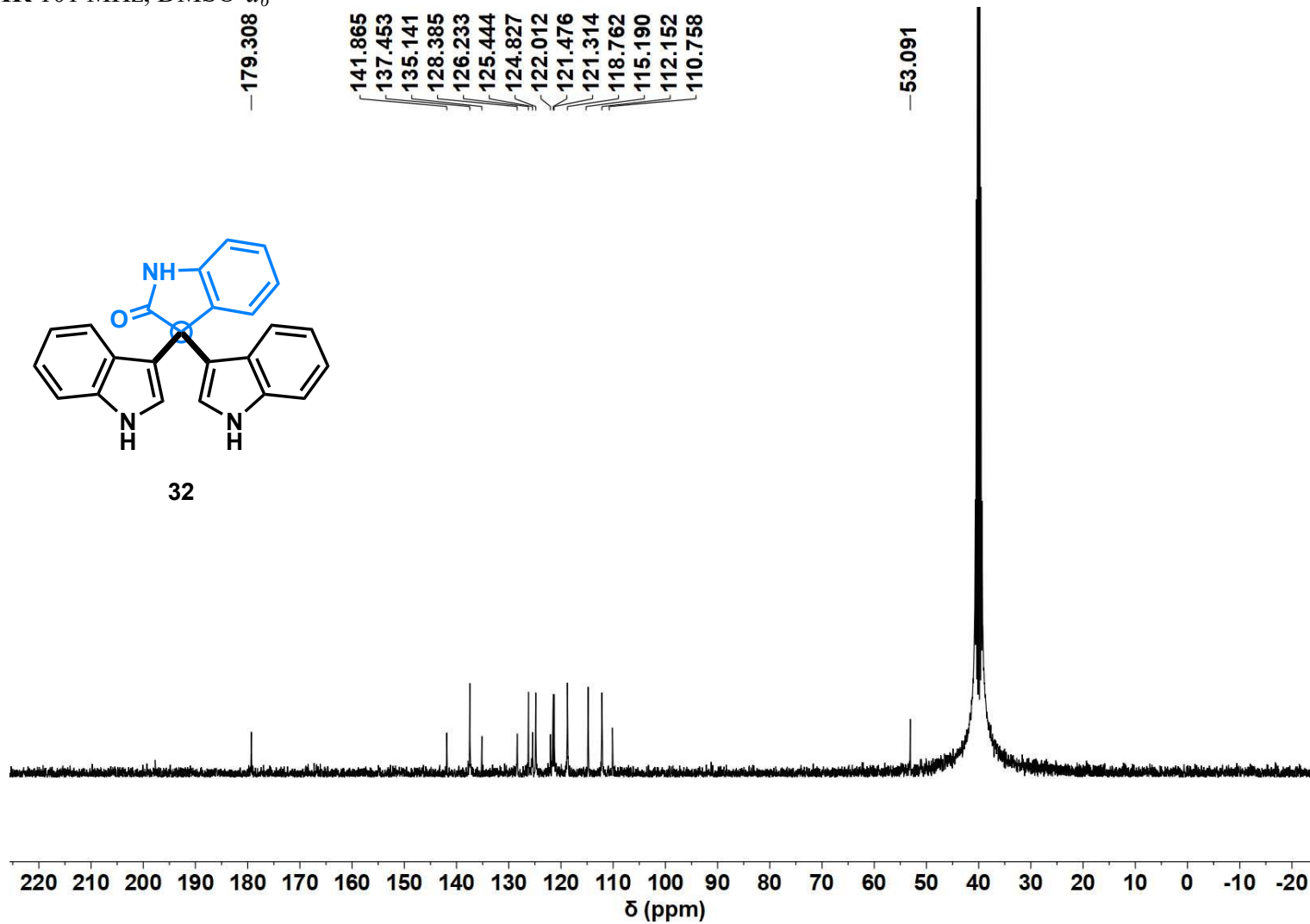
^{13}C NMR 101 MHz, CDCl_3



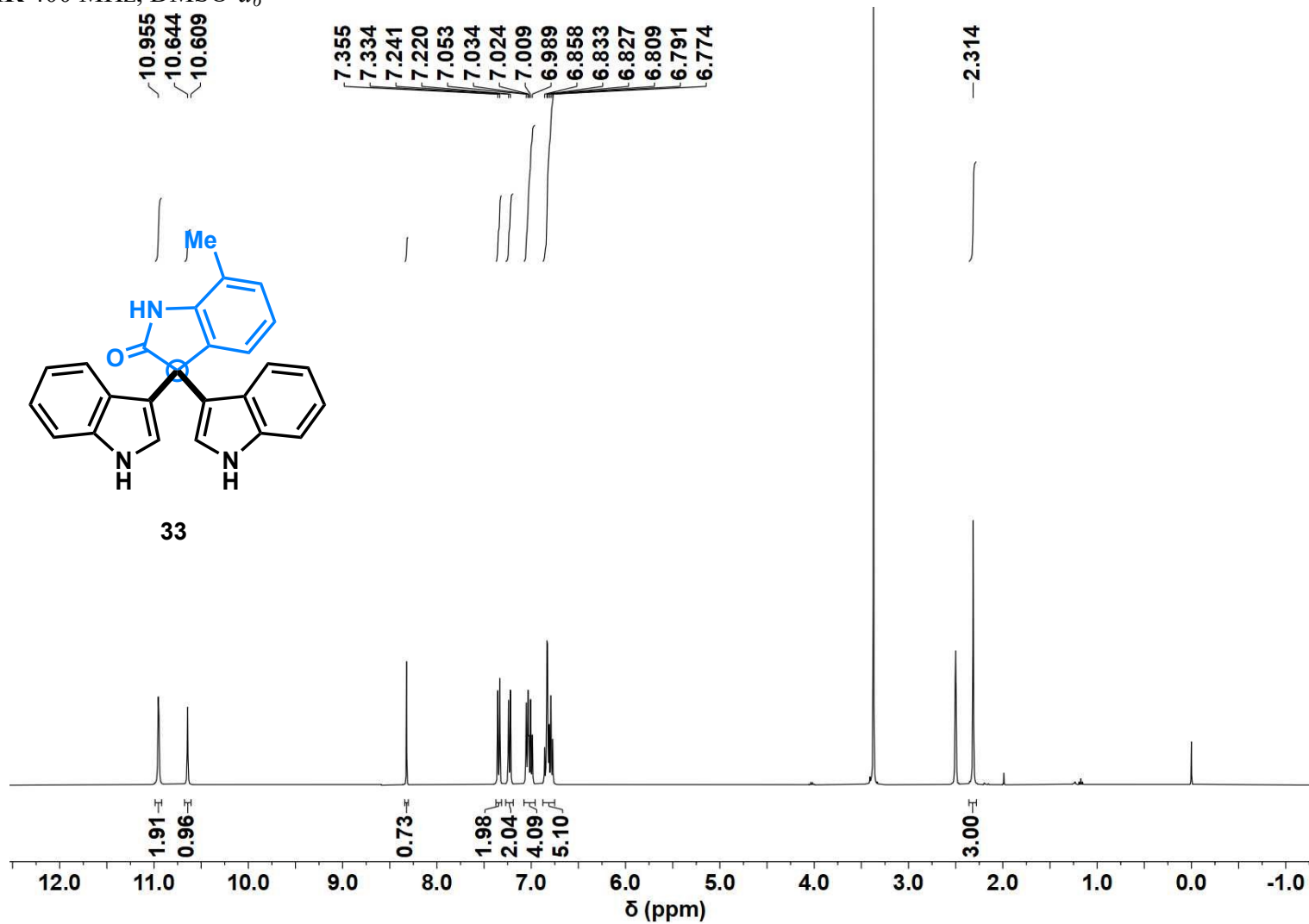
^1H NMR 400 MHz, $\text{DMSO-}d_6$



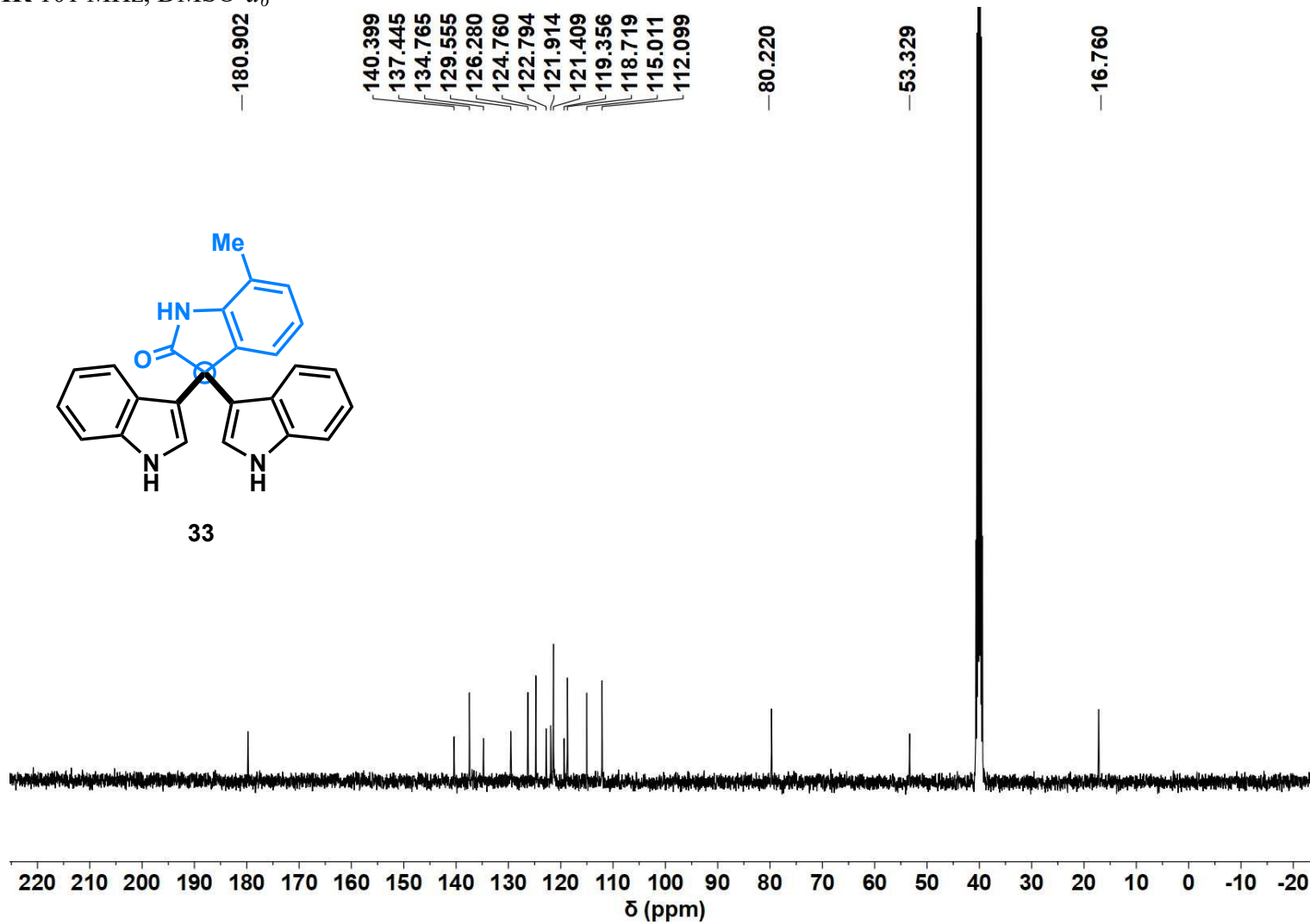
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



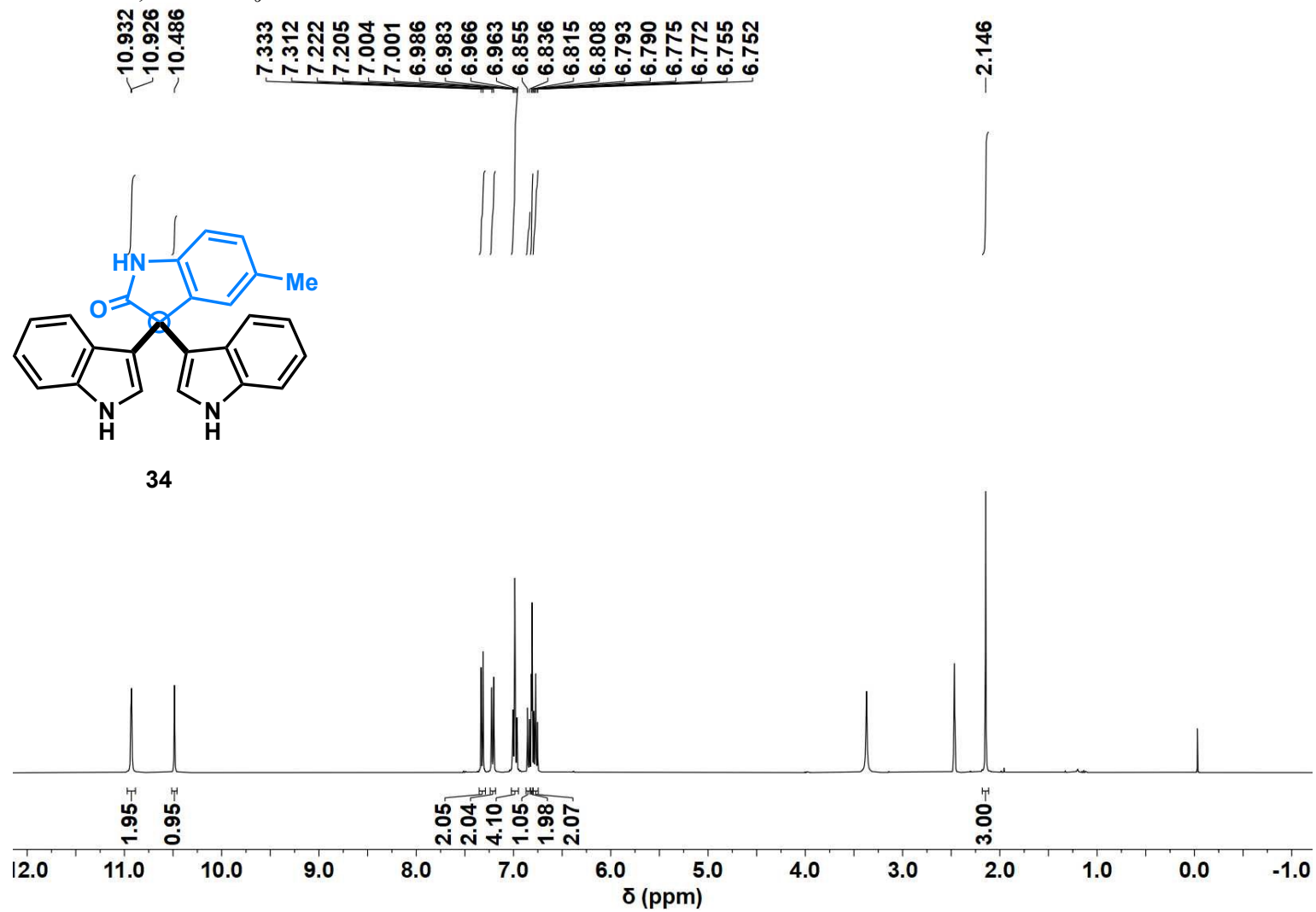
^1H NMR 400 MHz, $\text{DMSO-}d_6$



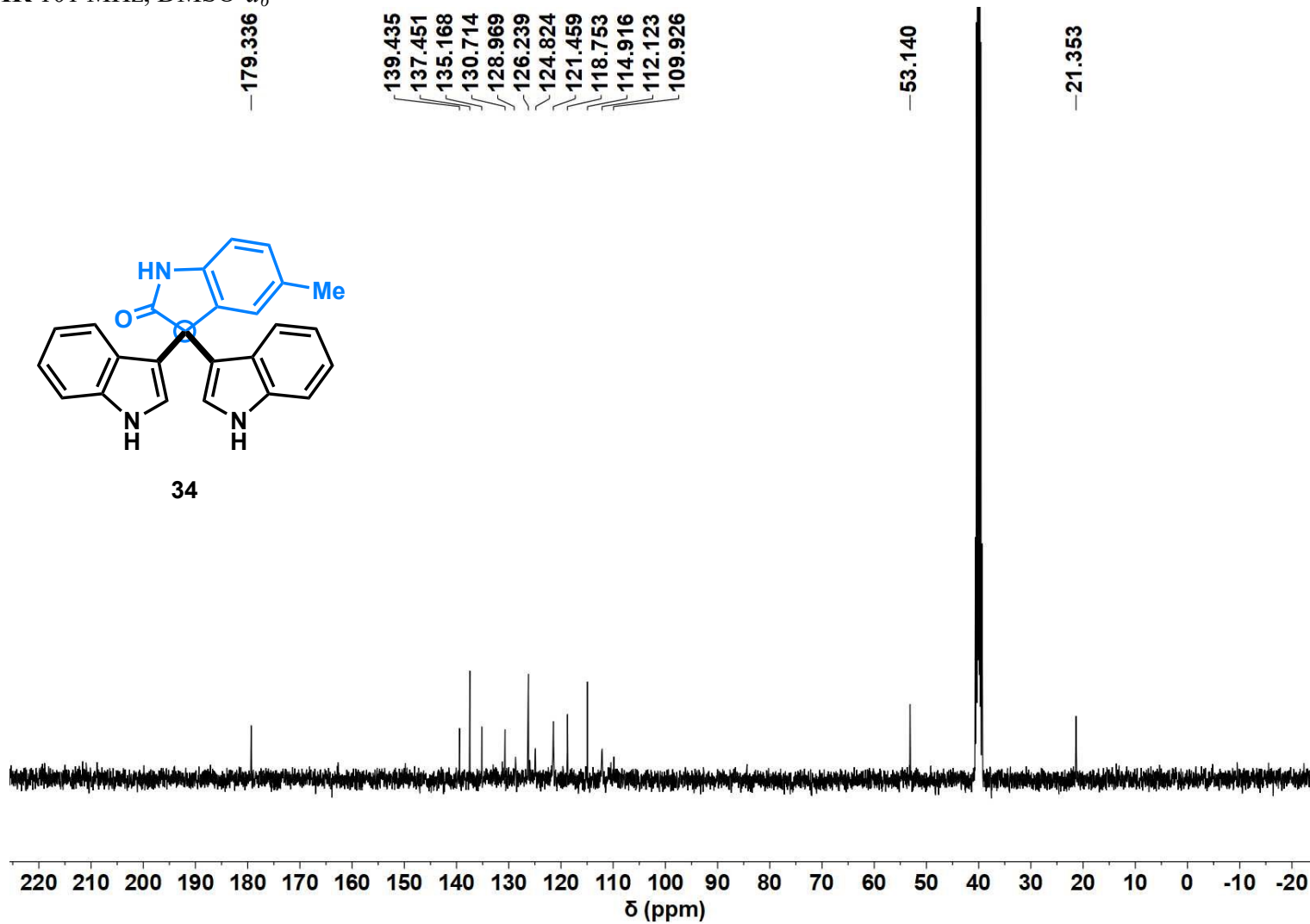
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



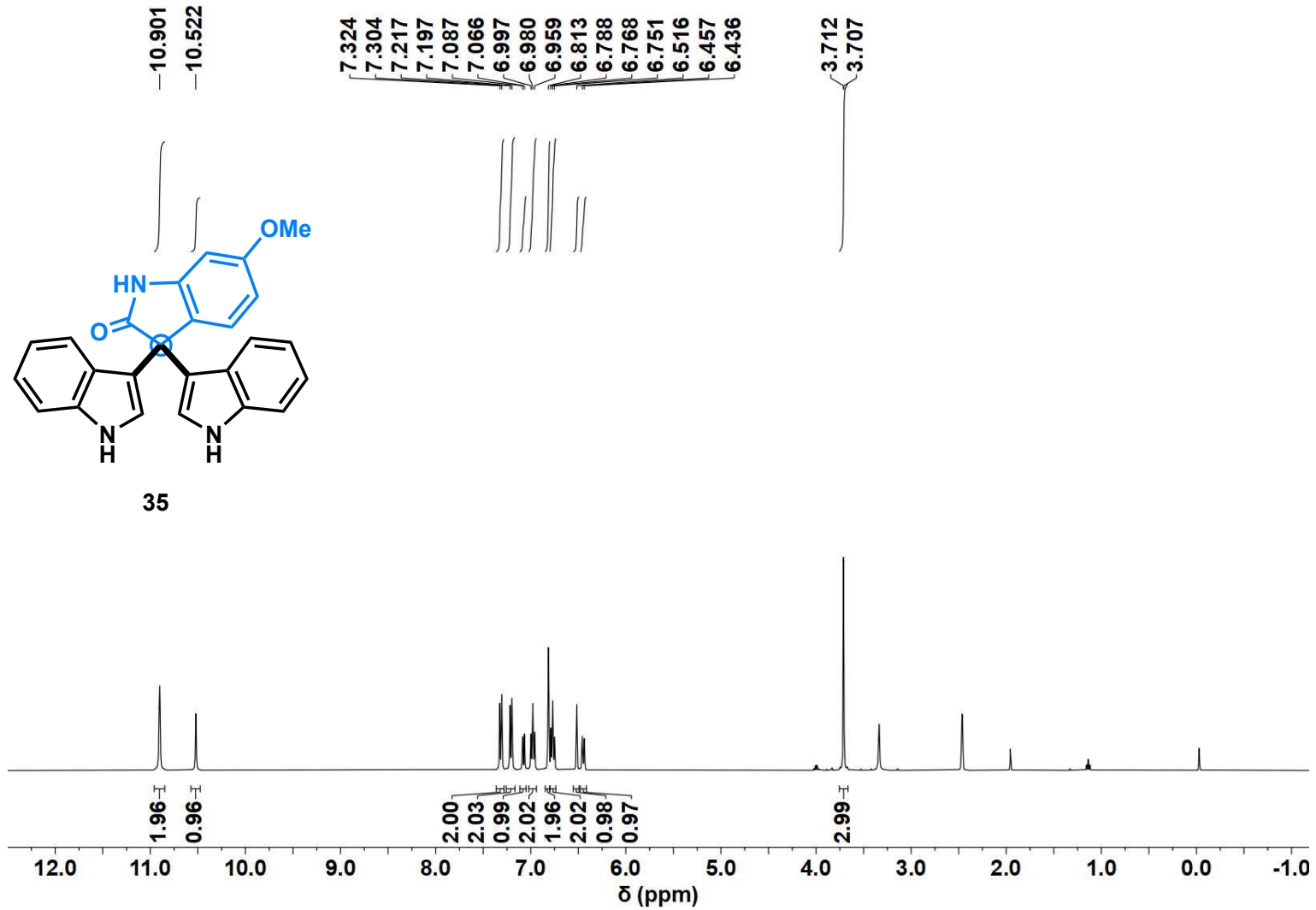
^1H NMR 400 MHz, $\text{DMSO-}d_6$



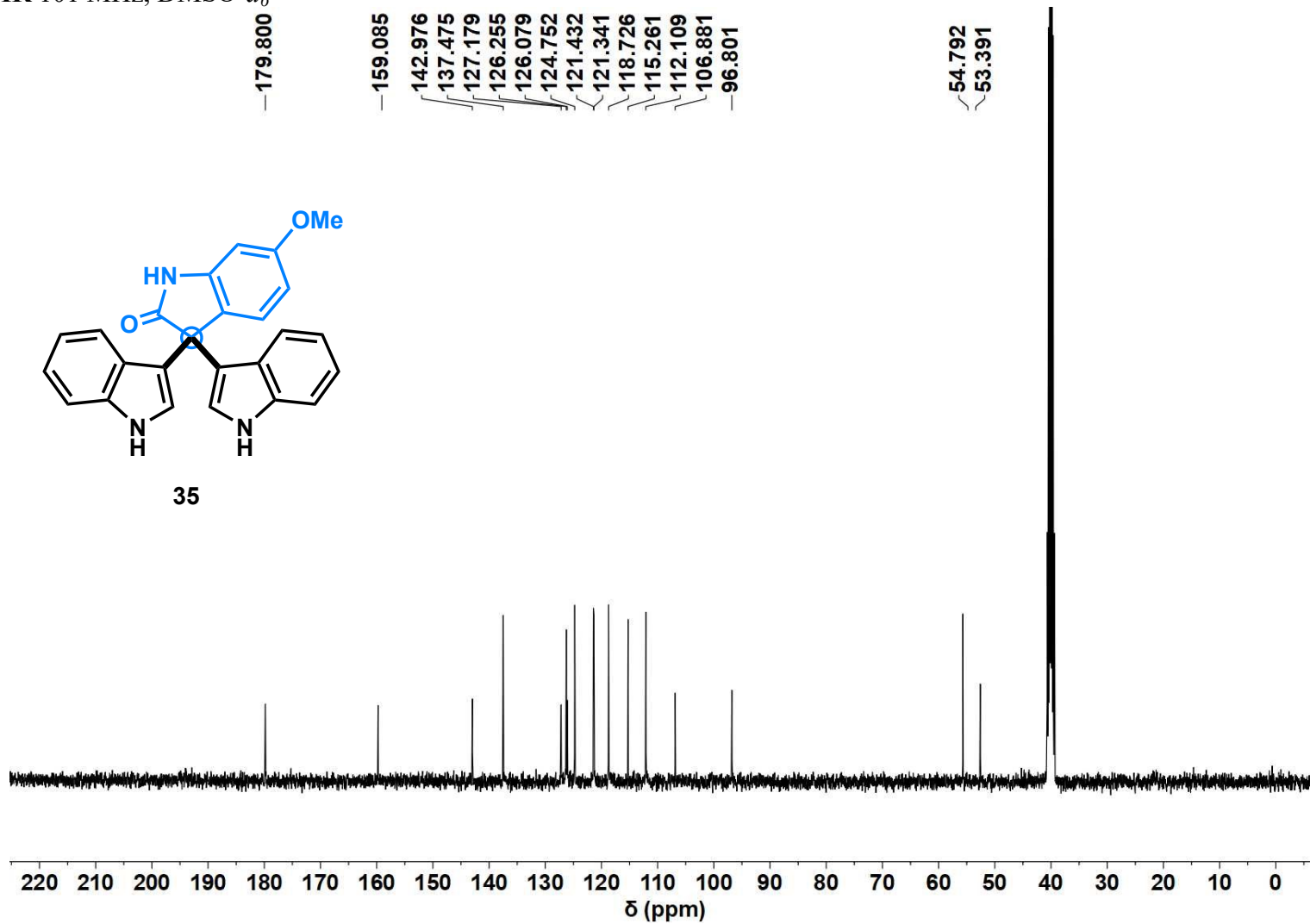
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



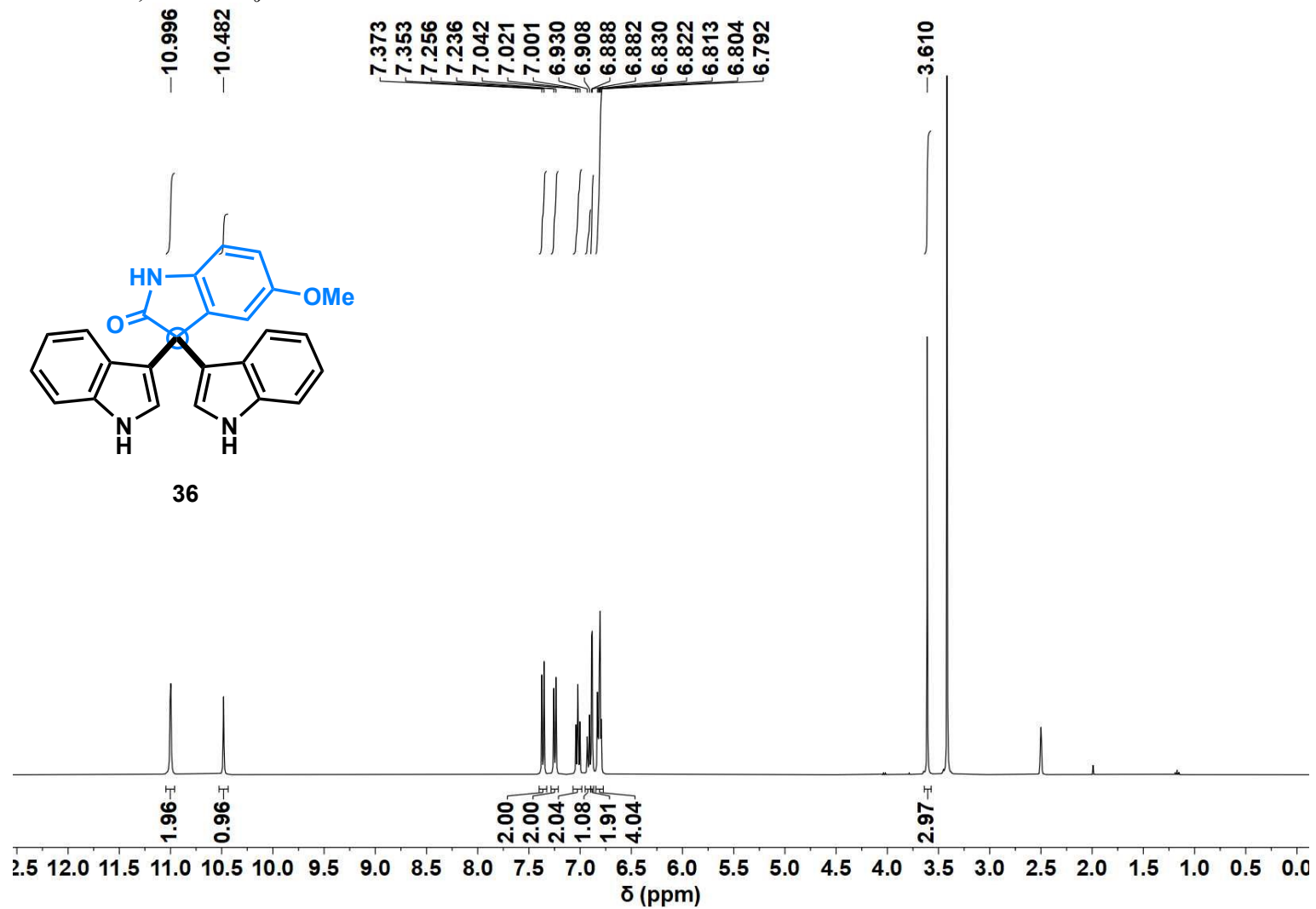
^1H NMR 400 MHz, $\text{DMSO-}d_6$



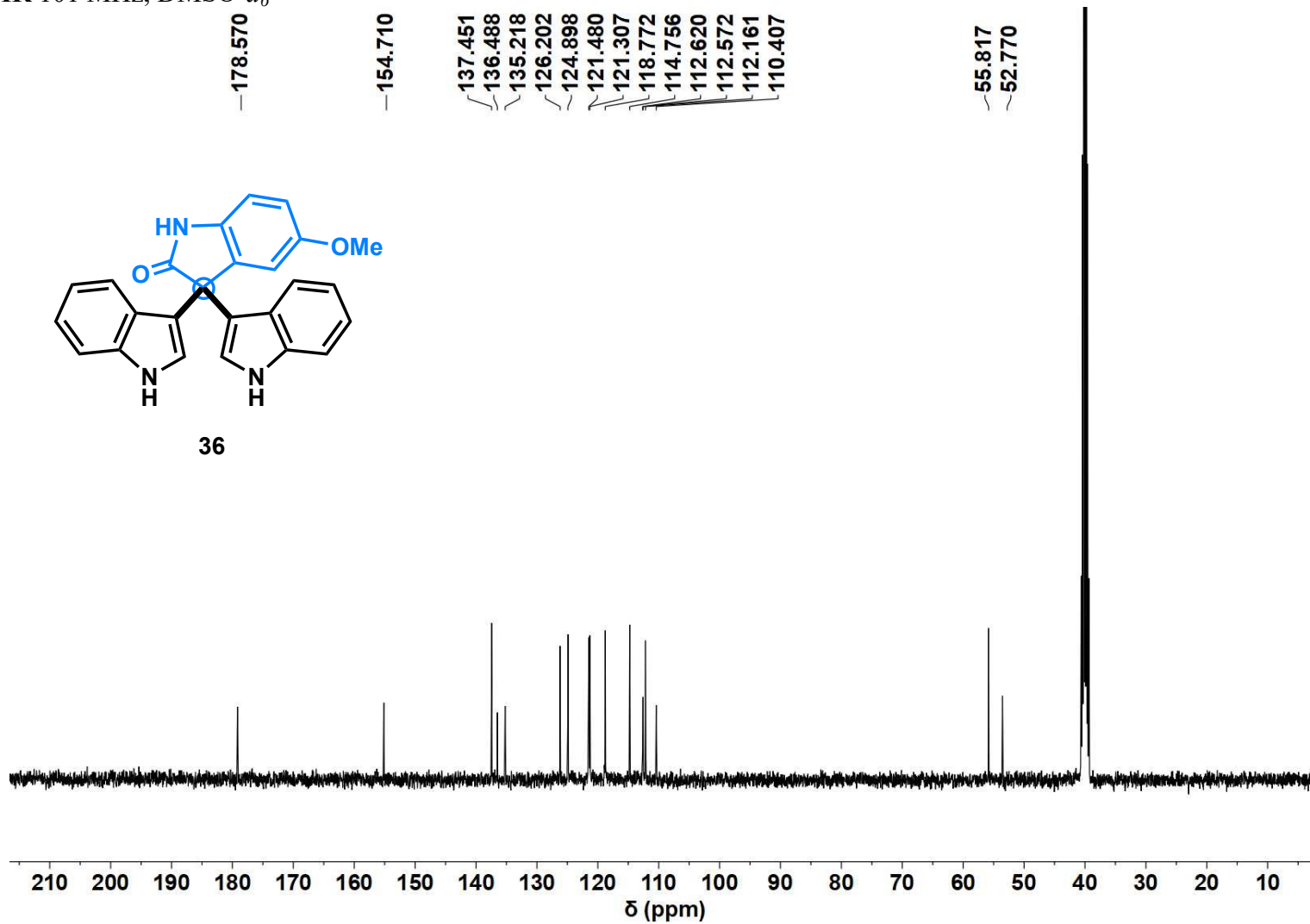
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



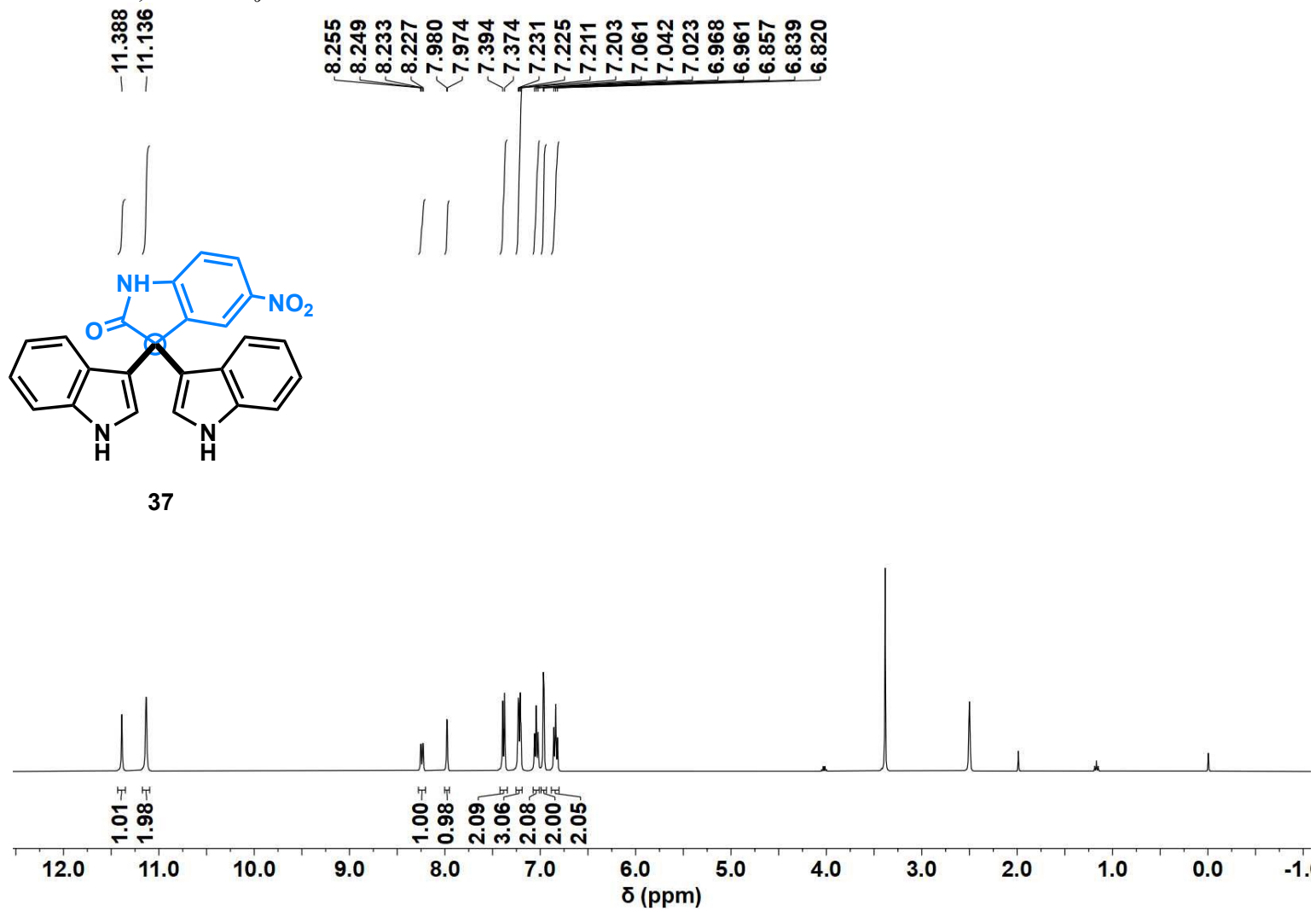
^1H NMR 400 MHz, $\text{DMSO-}d_6$



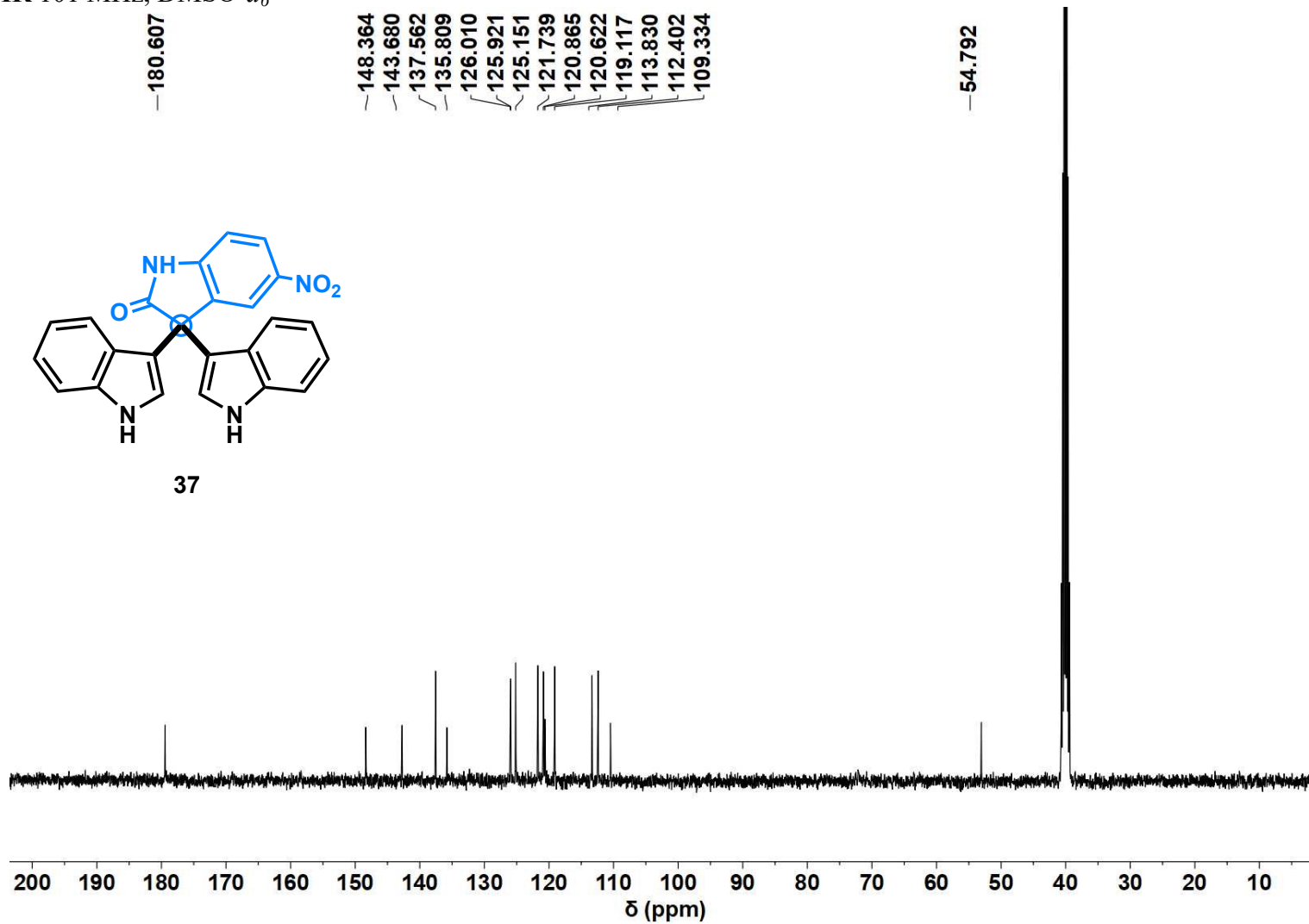
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



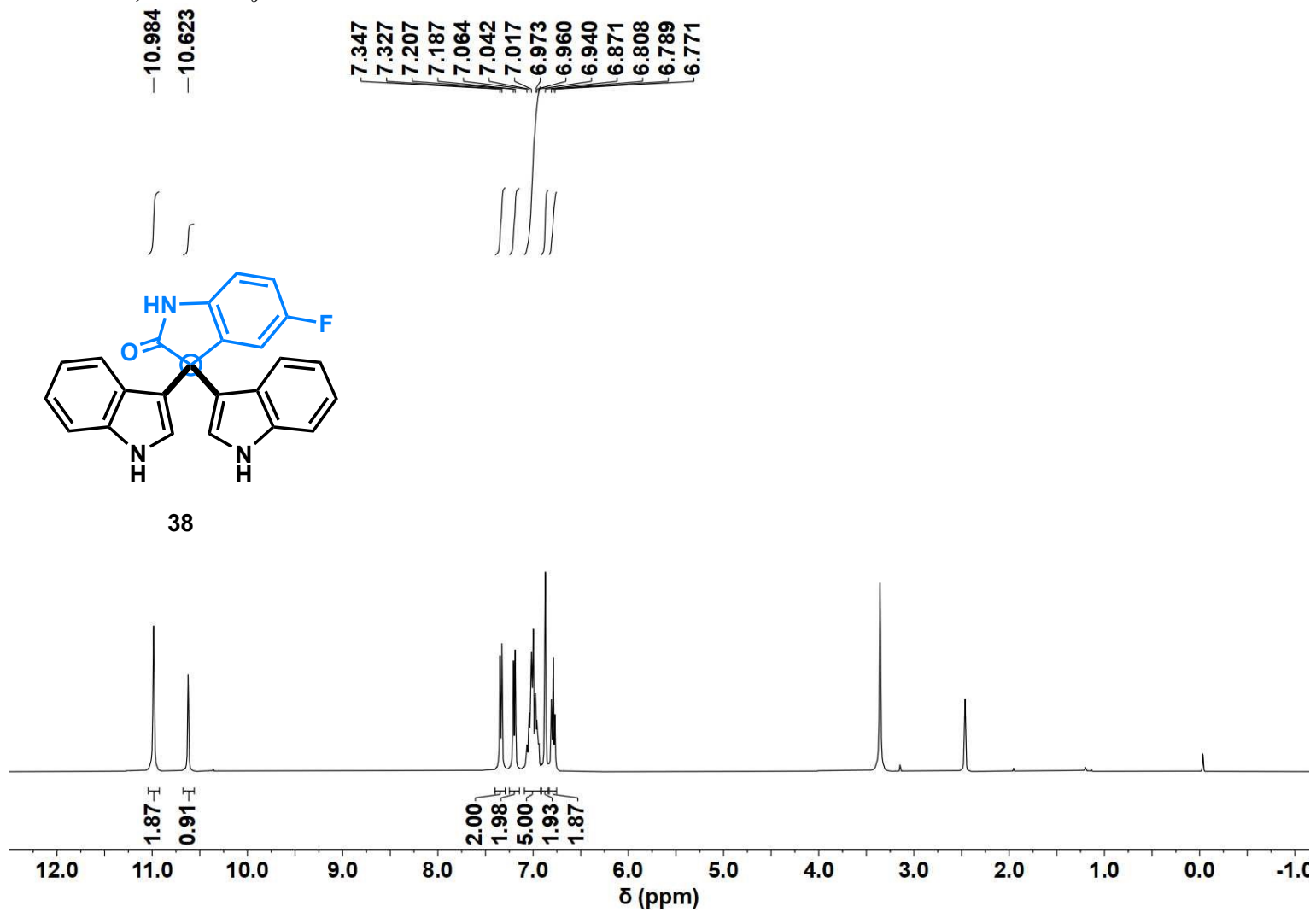
^1H NMR 400 MHz, $\text{DMSO-}d_6$



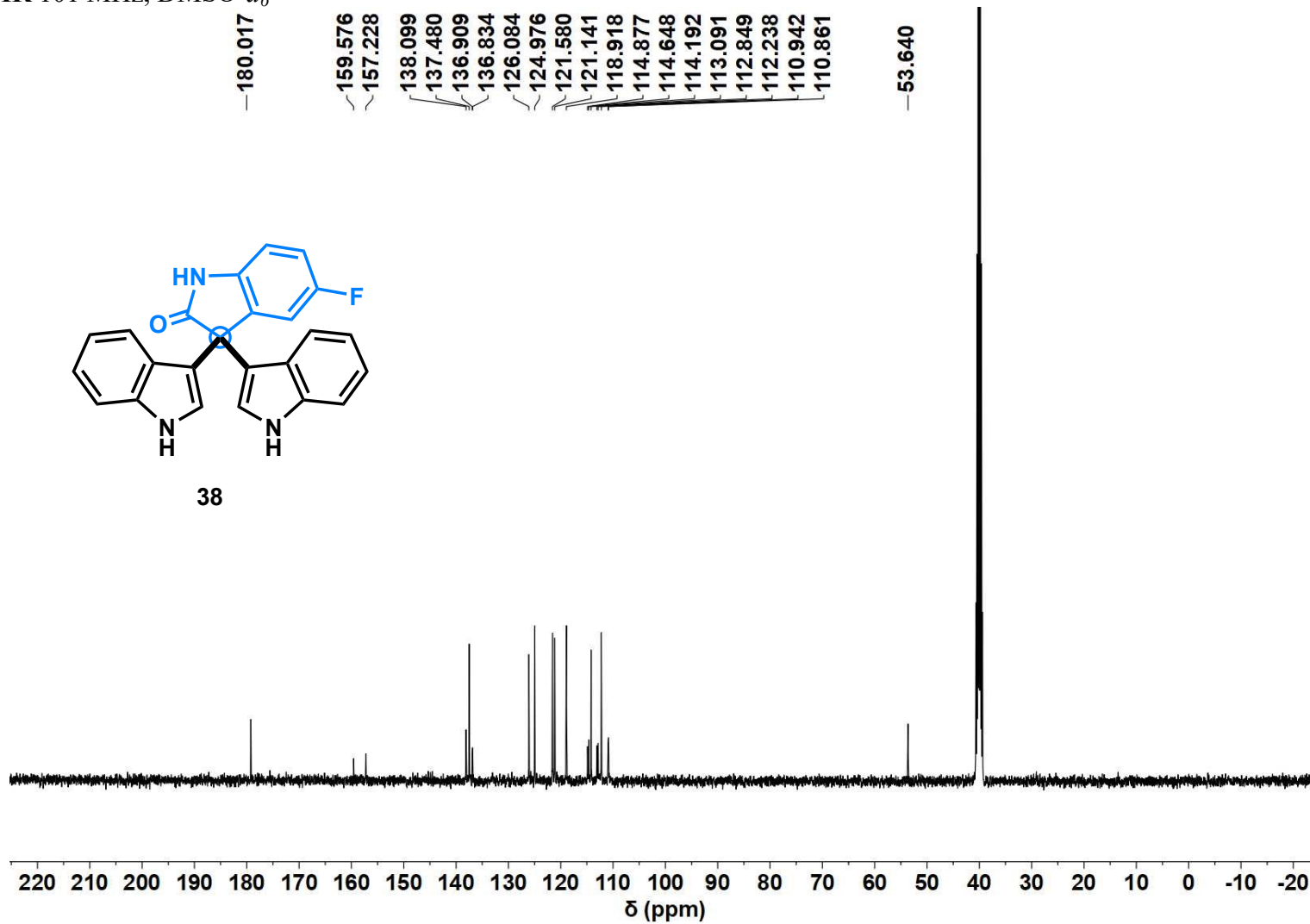
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



^1H NMR 400 MHz, $\text{DMSO-}d_6$

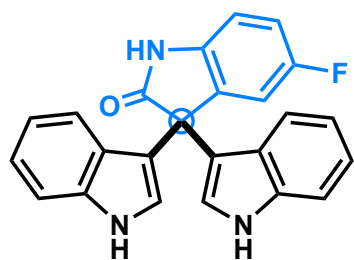


^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

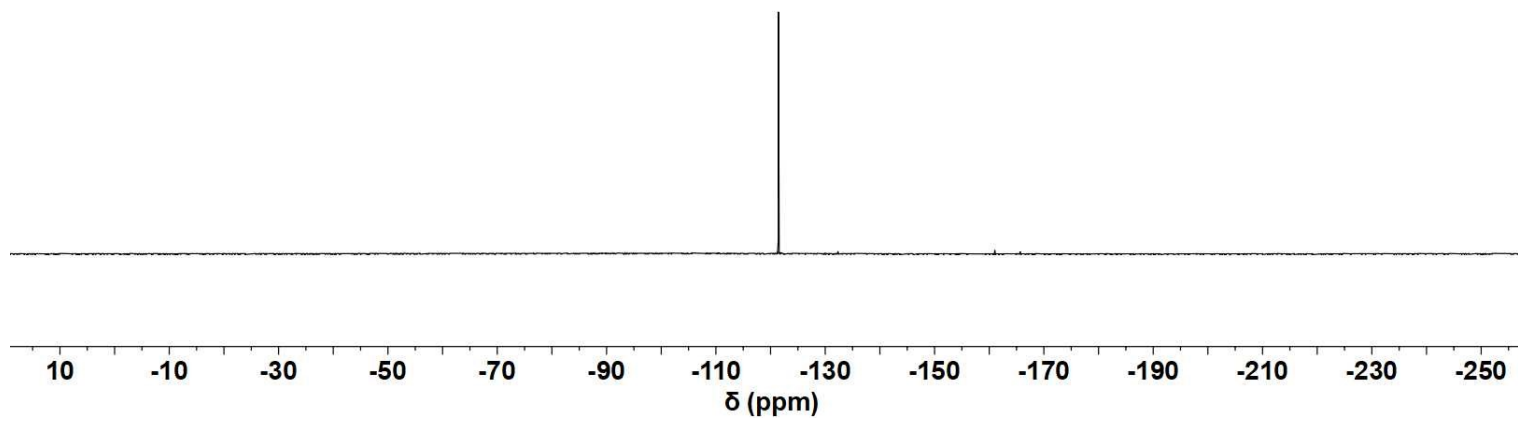


^{19}F NMR 376 MHz, $\text{DMSO-}d_6$

-121.417
-121.428
-121.440
-121.452
-121.464
-121.476

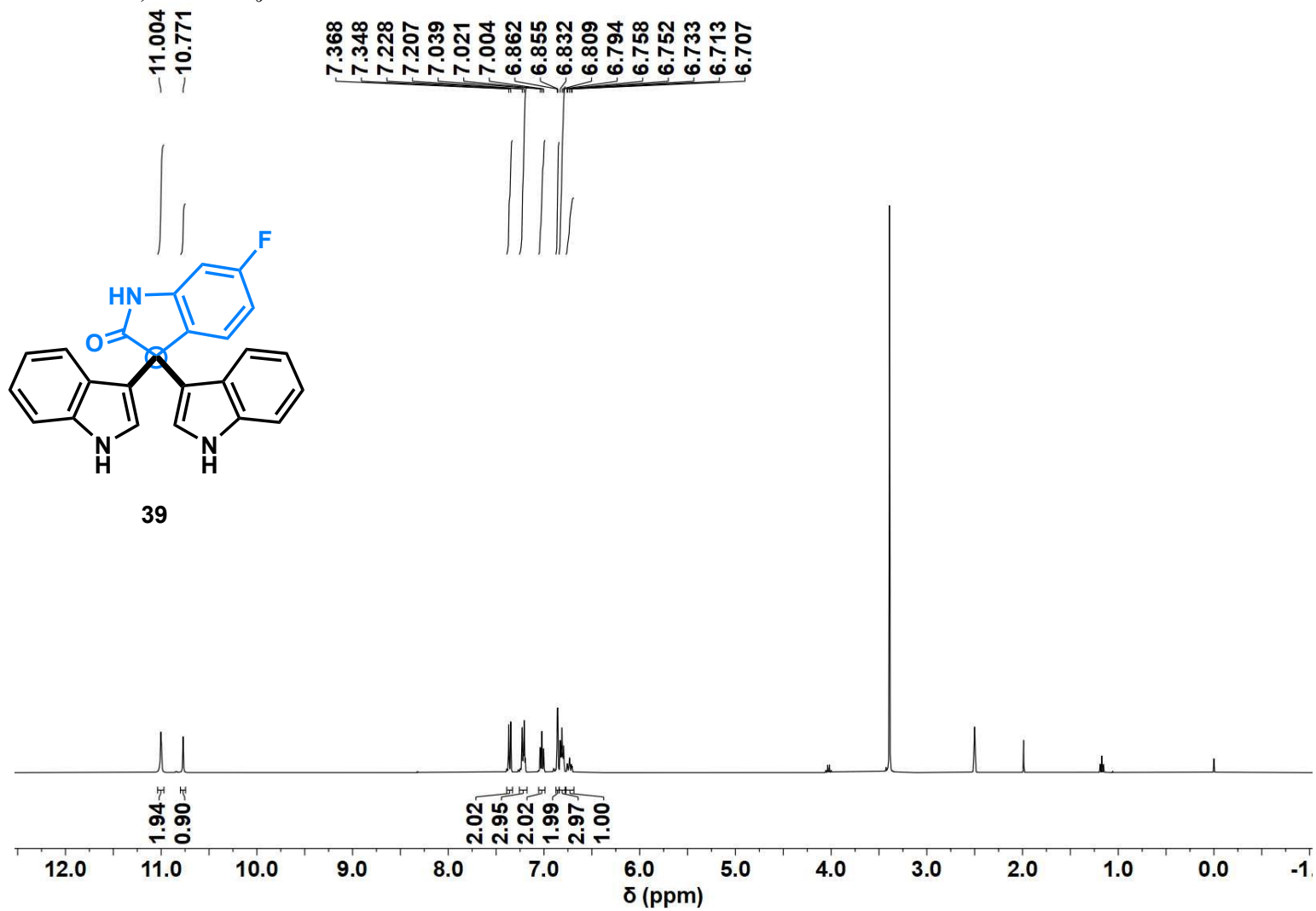


38

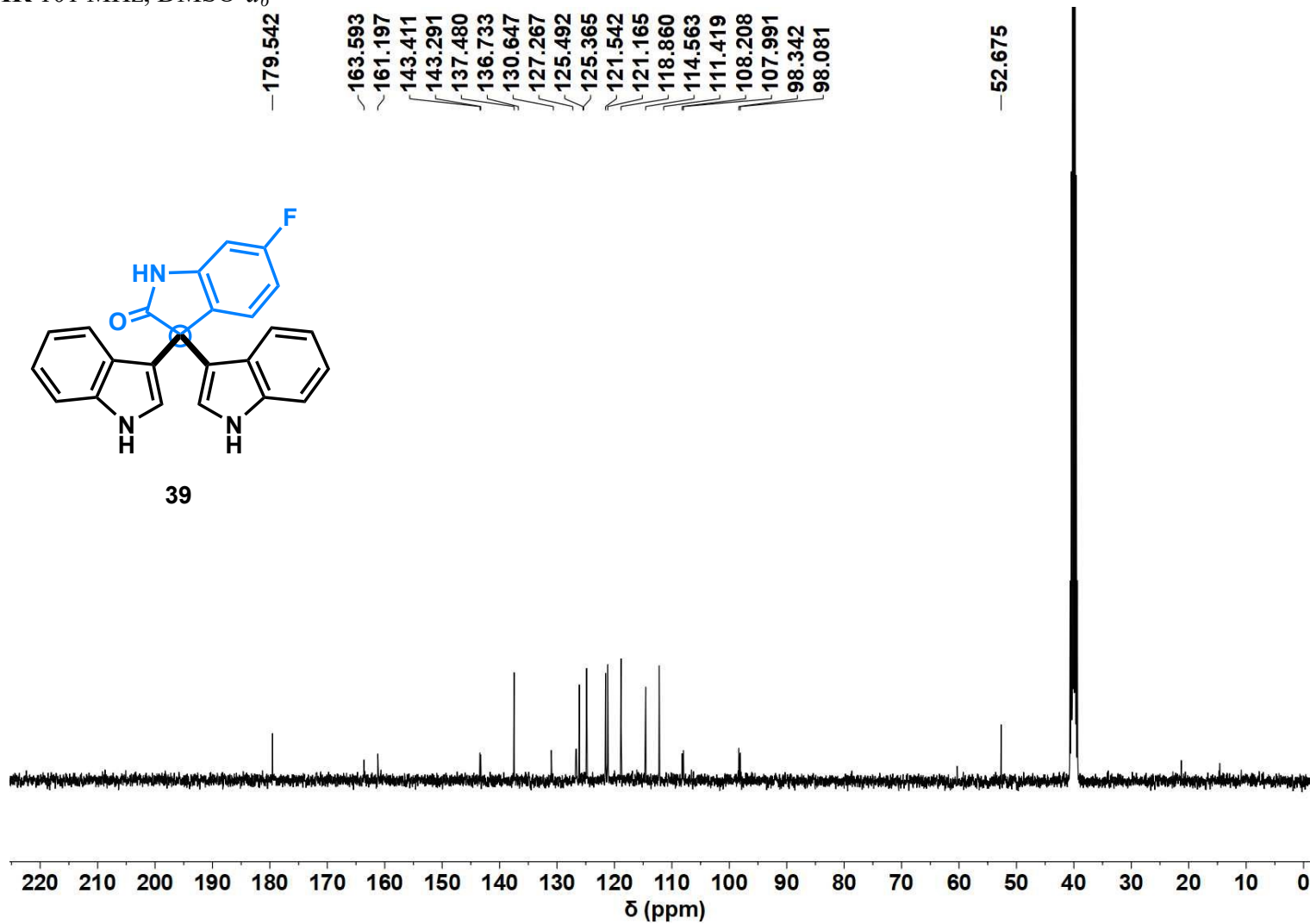


S142

^1H NMR 400 MHz, $\text{DMSO-}d_6$

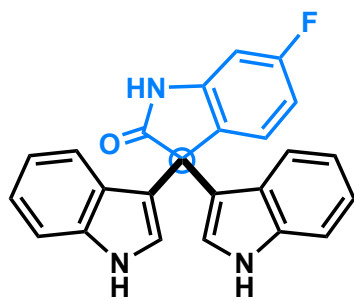


^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

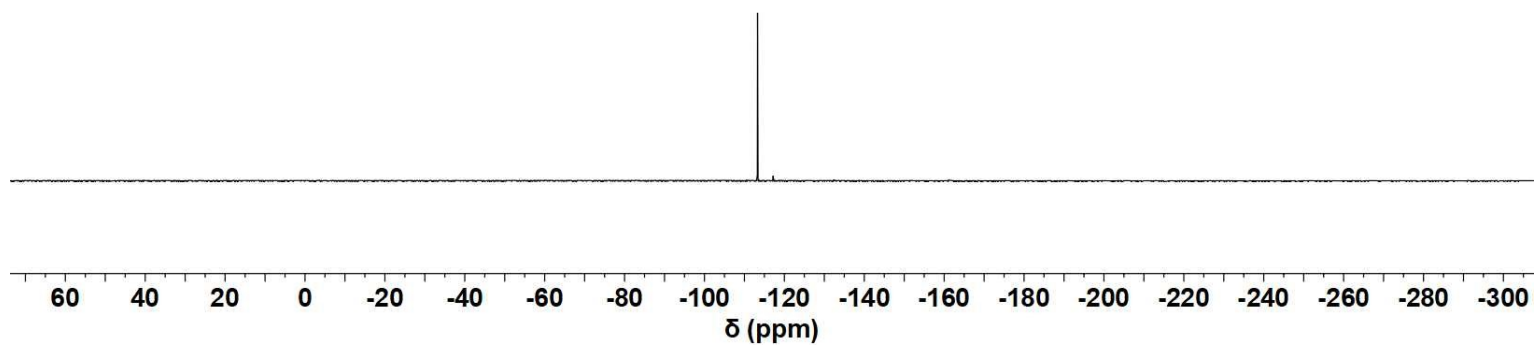


^{19}F NMR 376 MHz, $\text{DMSO-}d_6$

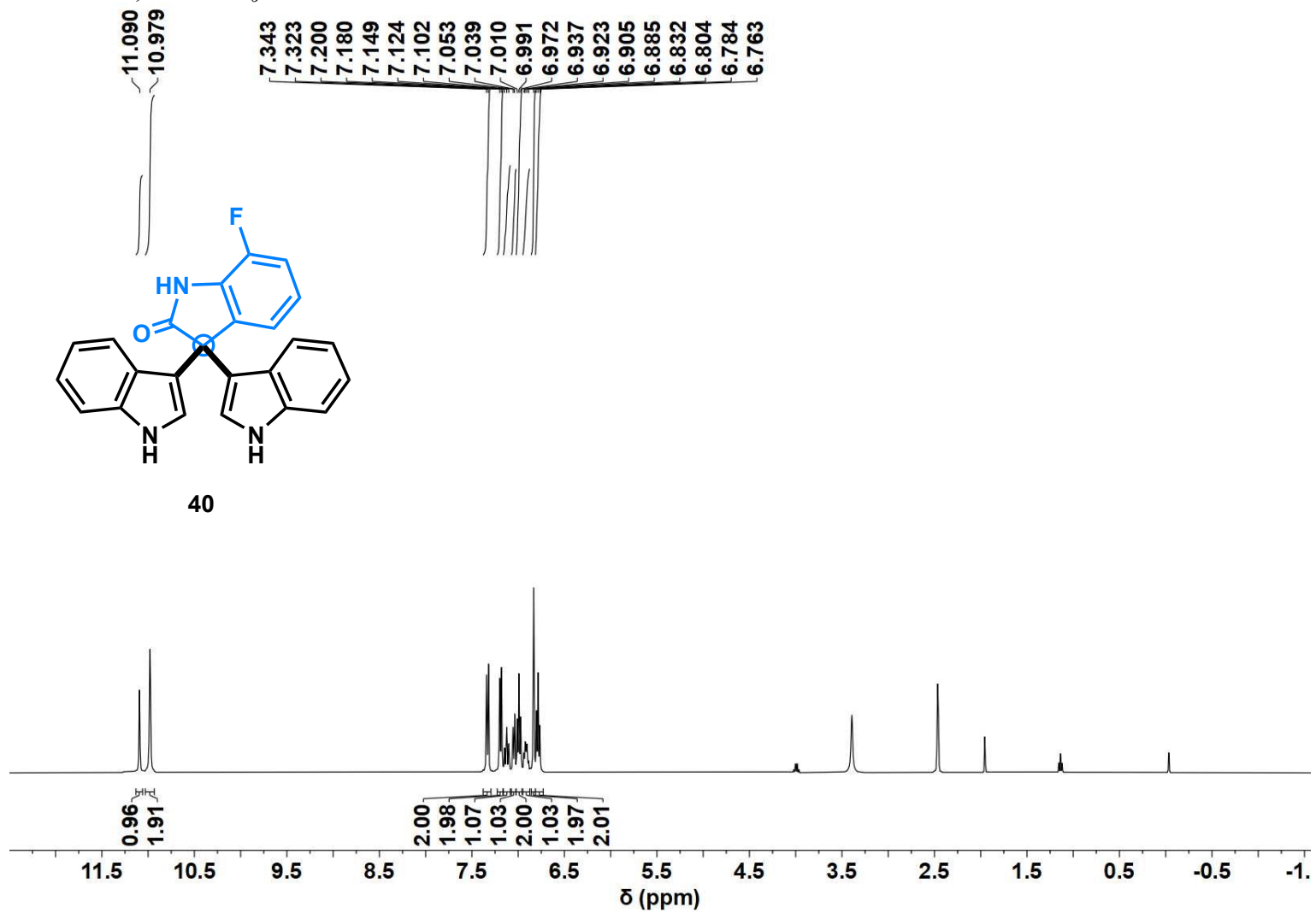
-113.246
-113.271
-113.285
-113.297
-113.310



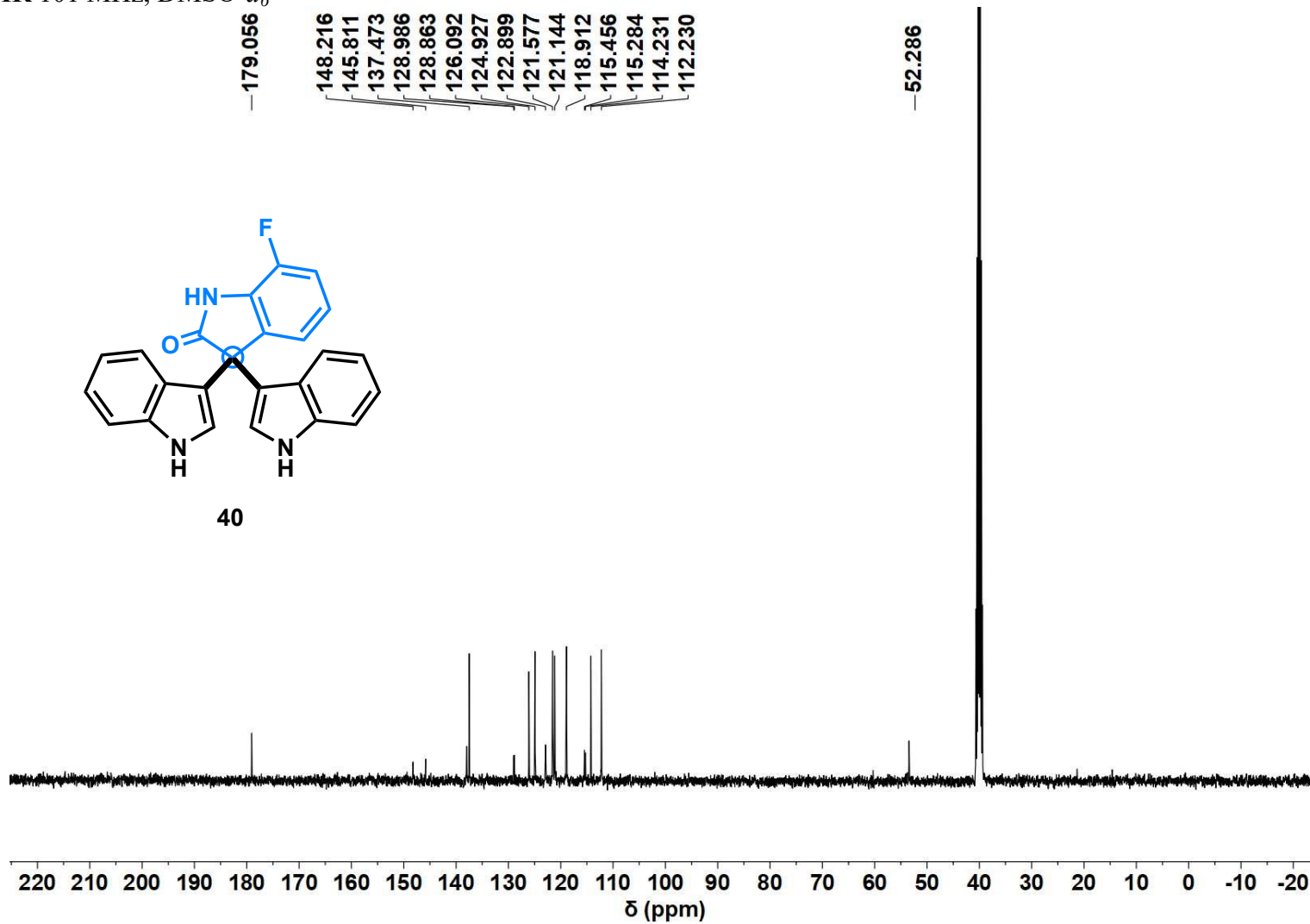
39



^1H NMR 400 MHz, $\text{DMSO-}d_6$

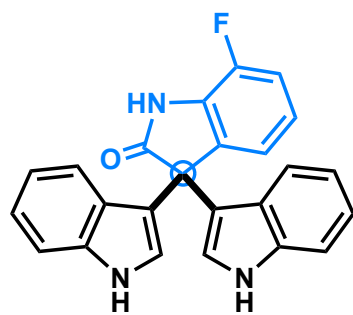


^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

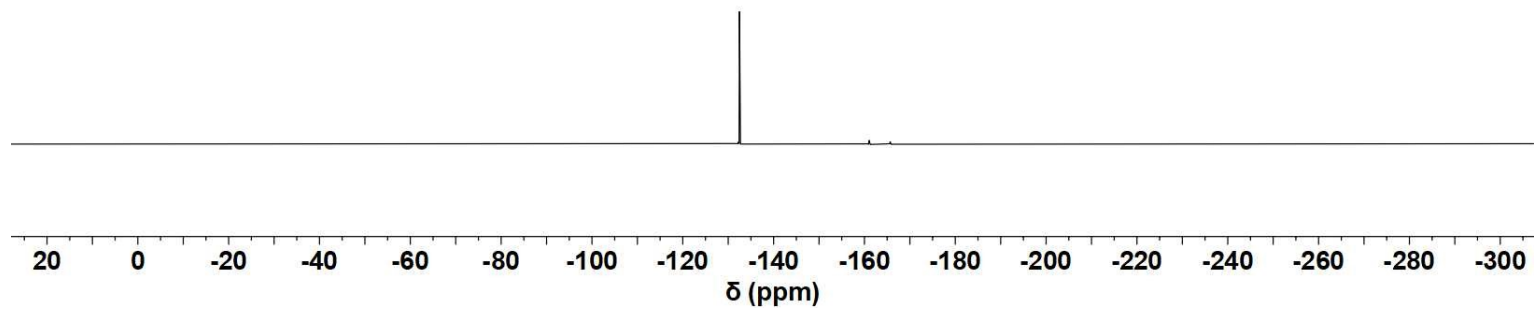


^{19}F NMR 376 MHz, $\text{DMSO-}d_6$

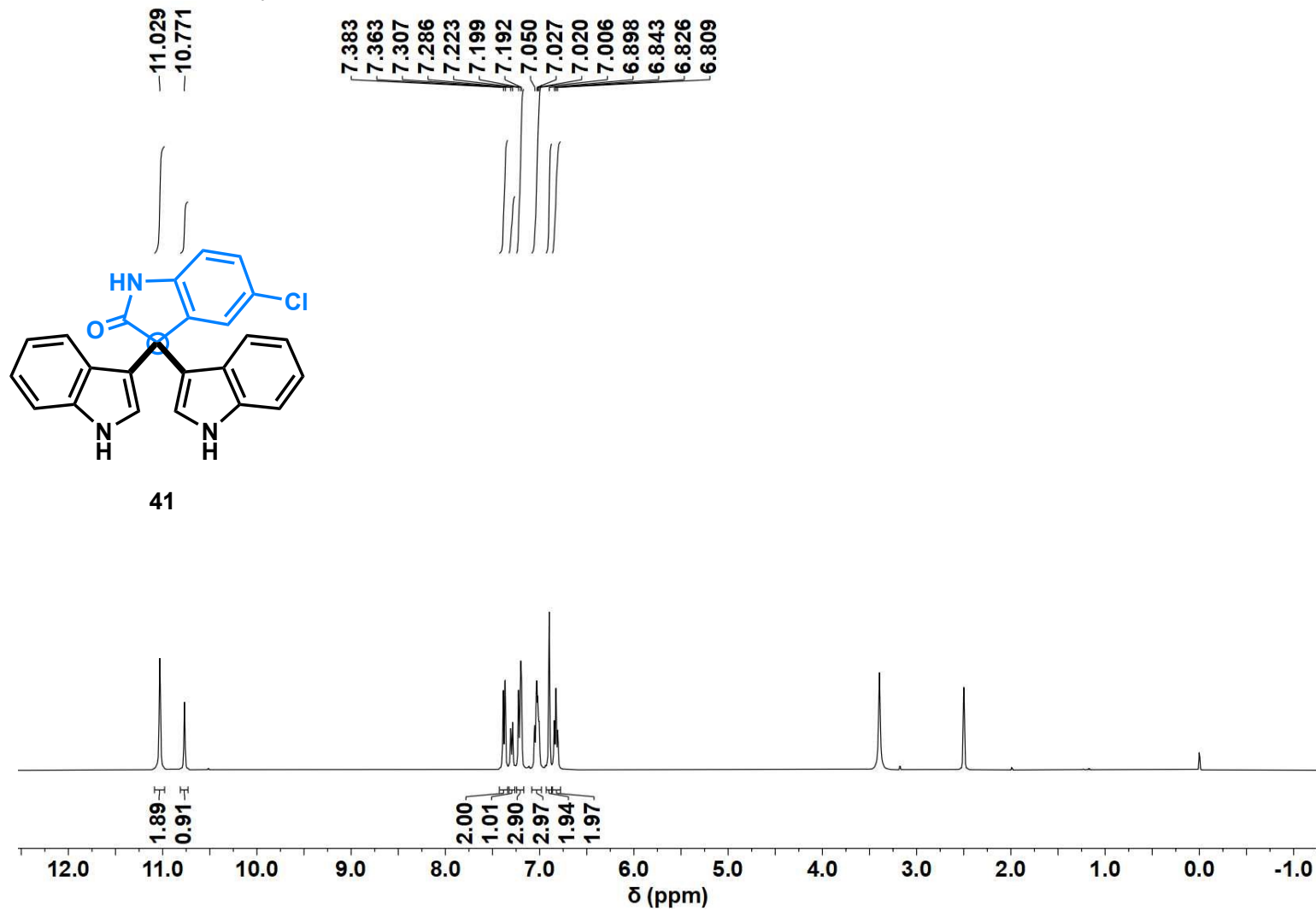
-132.475
-132.487
-132.502
-132.515



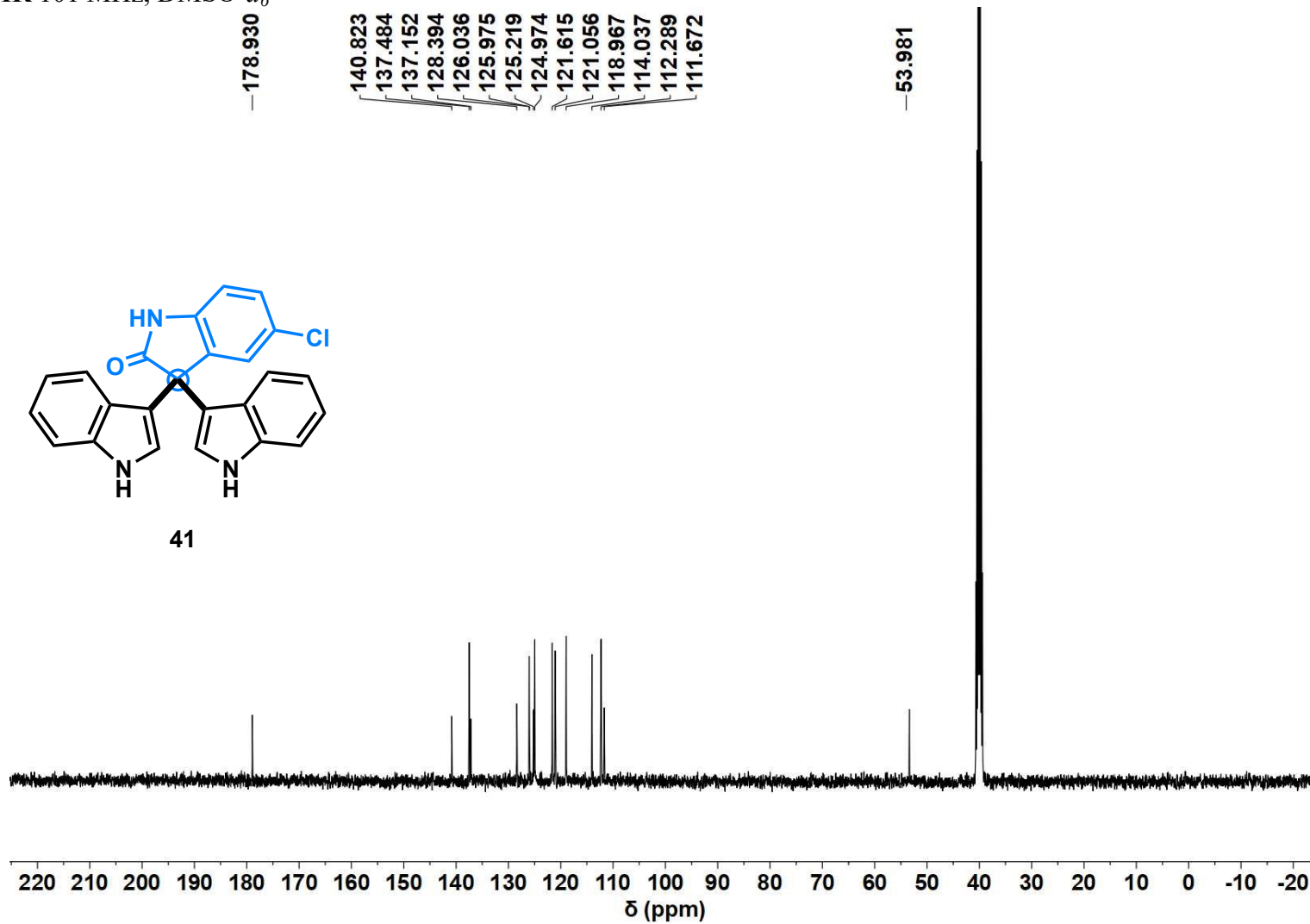
40



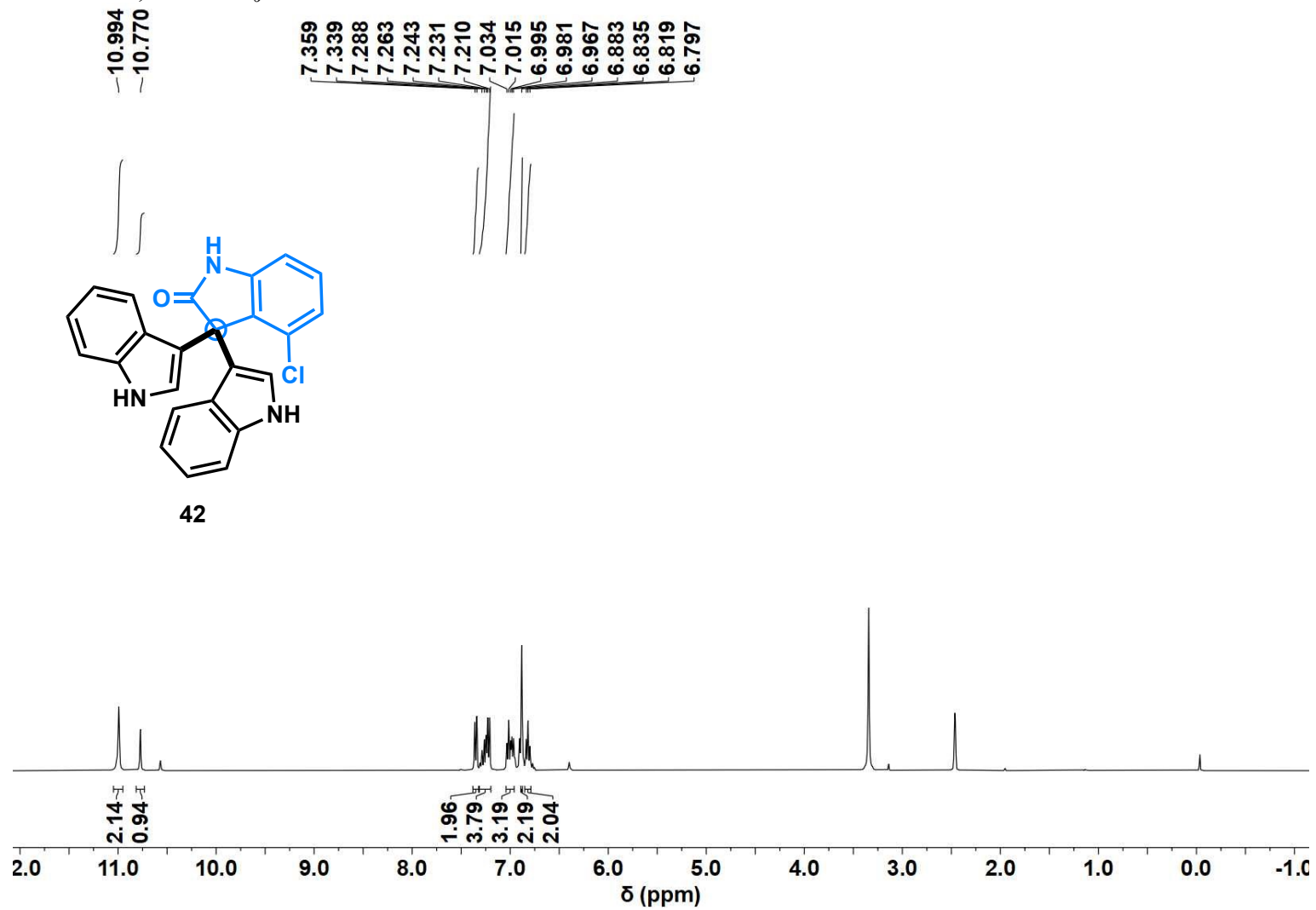
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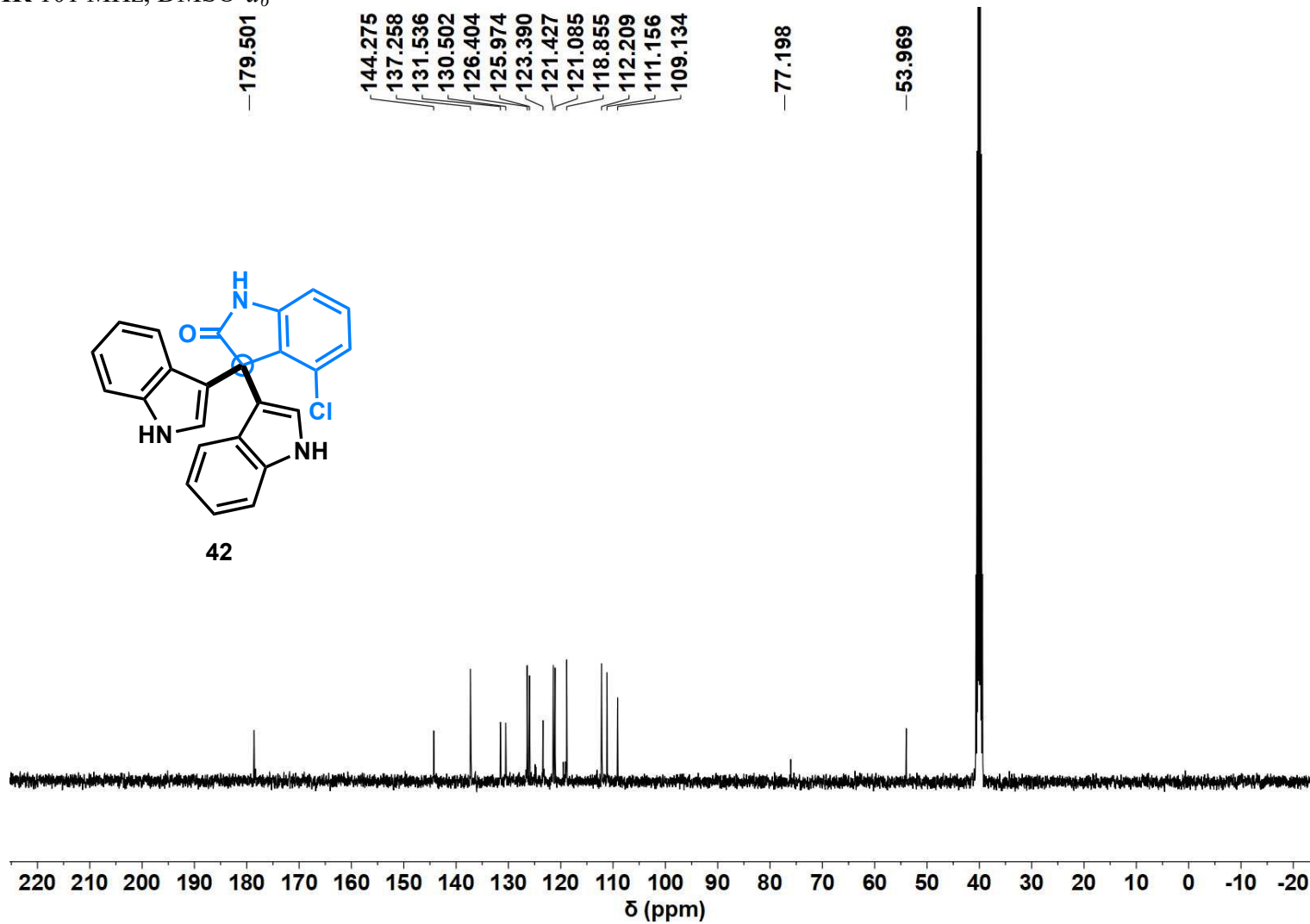
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



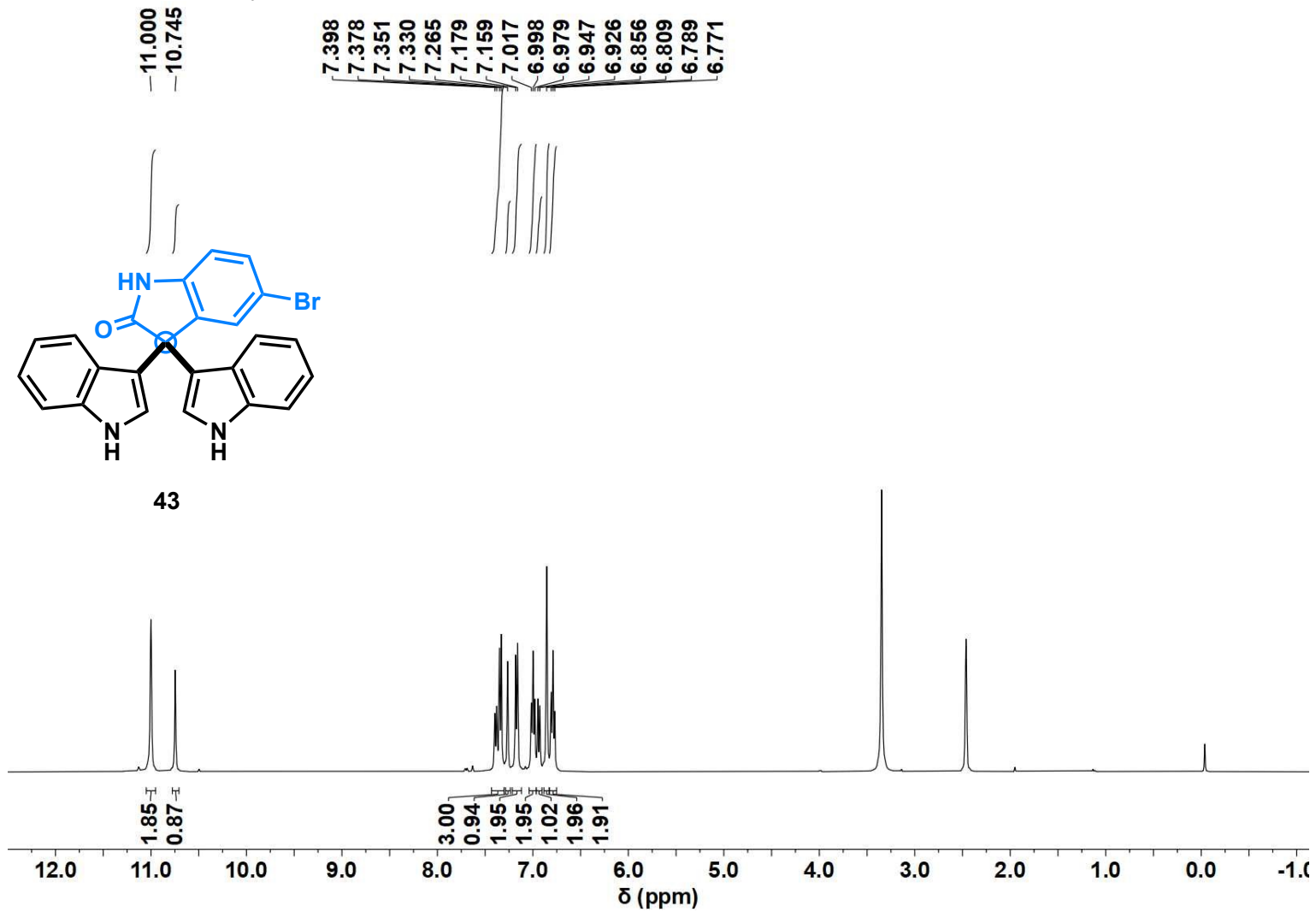
^1H NMR 400 MHz, $\text{DMSO-}d_6$



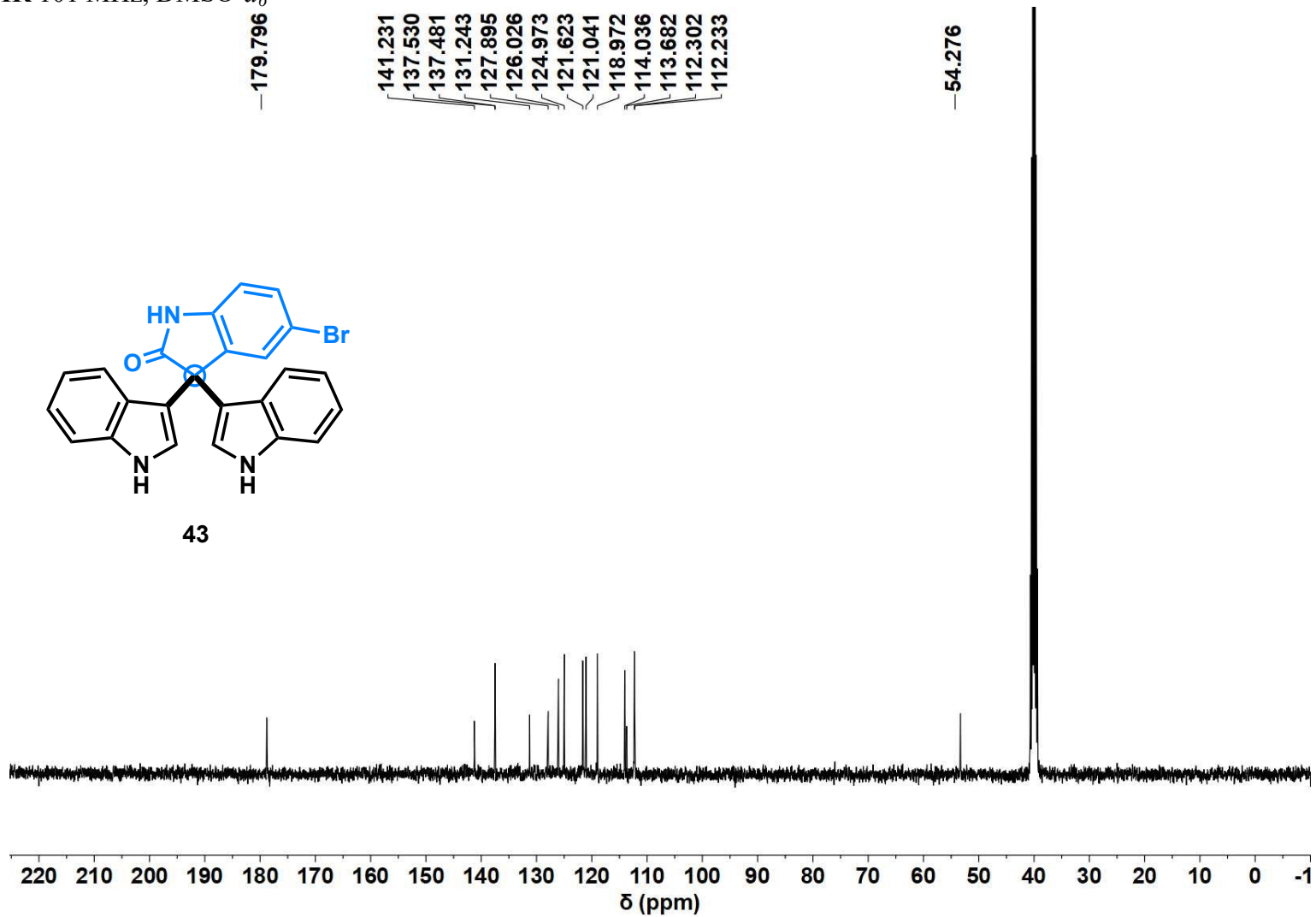
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



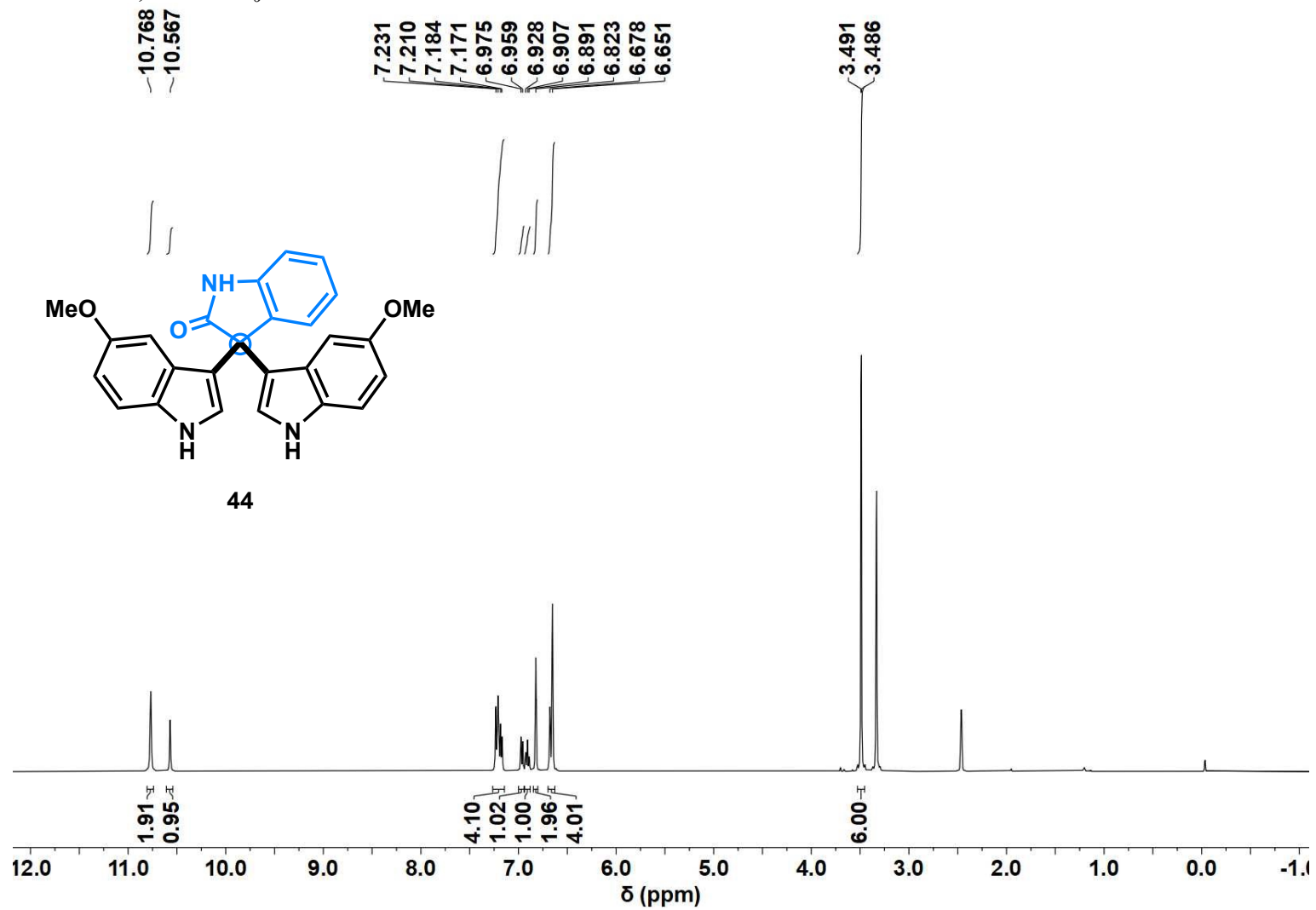
^1H NMR 400 MHz, $\text{DMSO-}d_6$



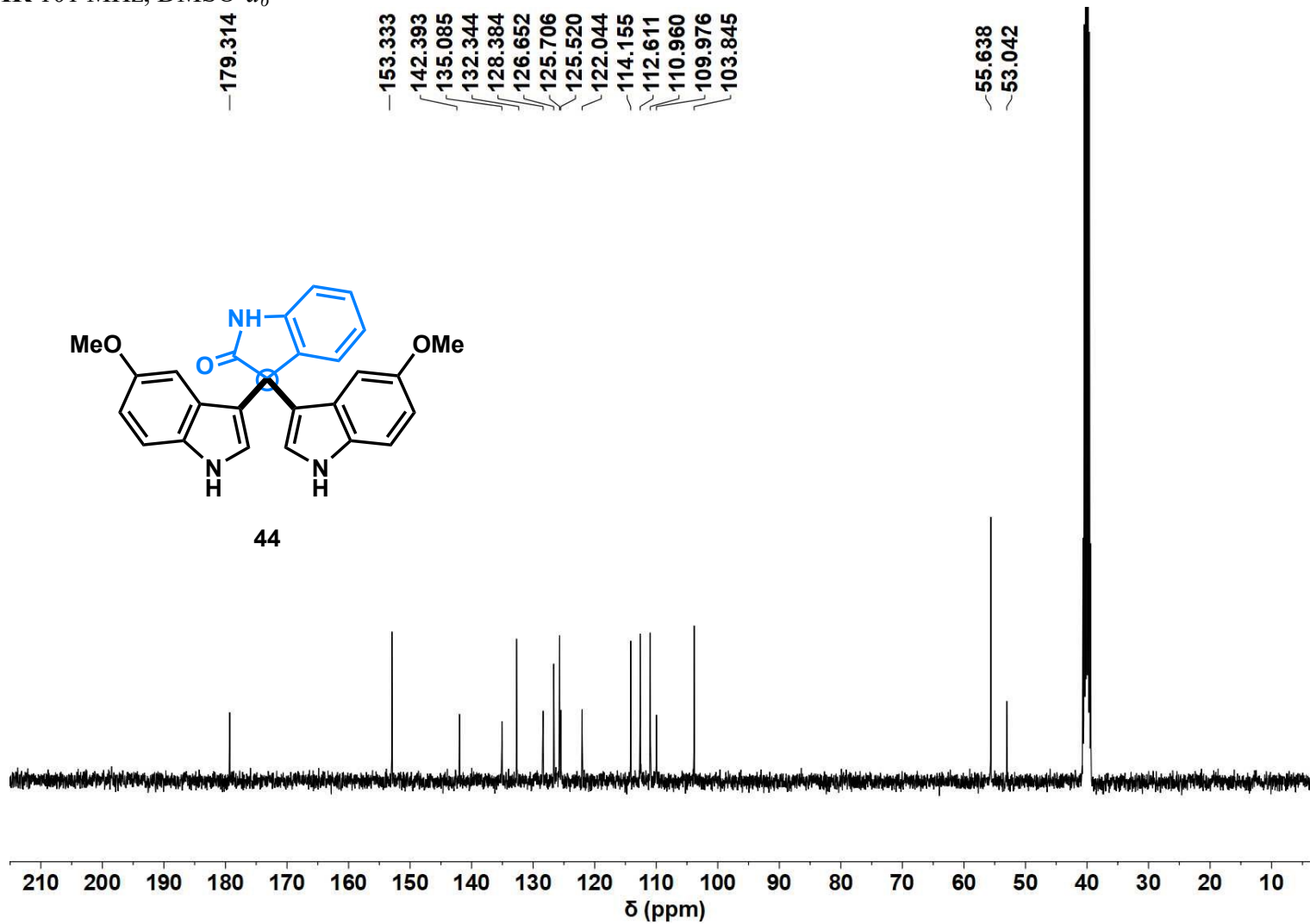
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



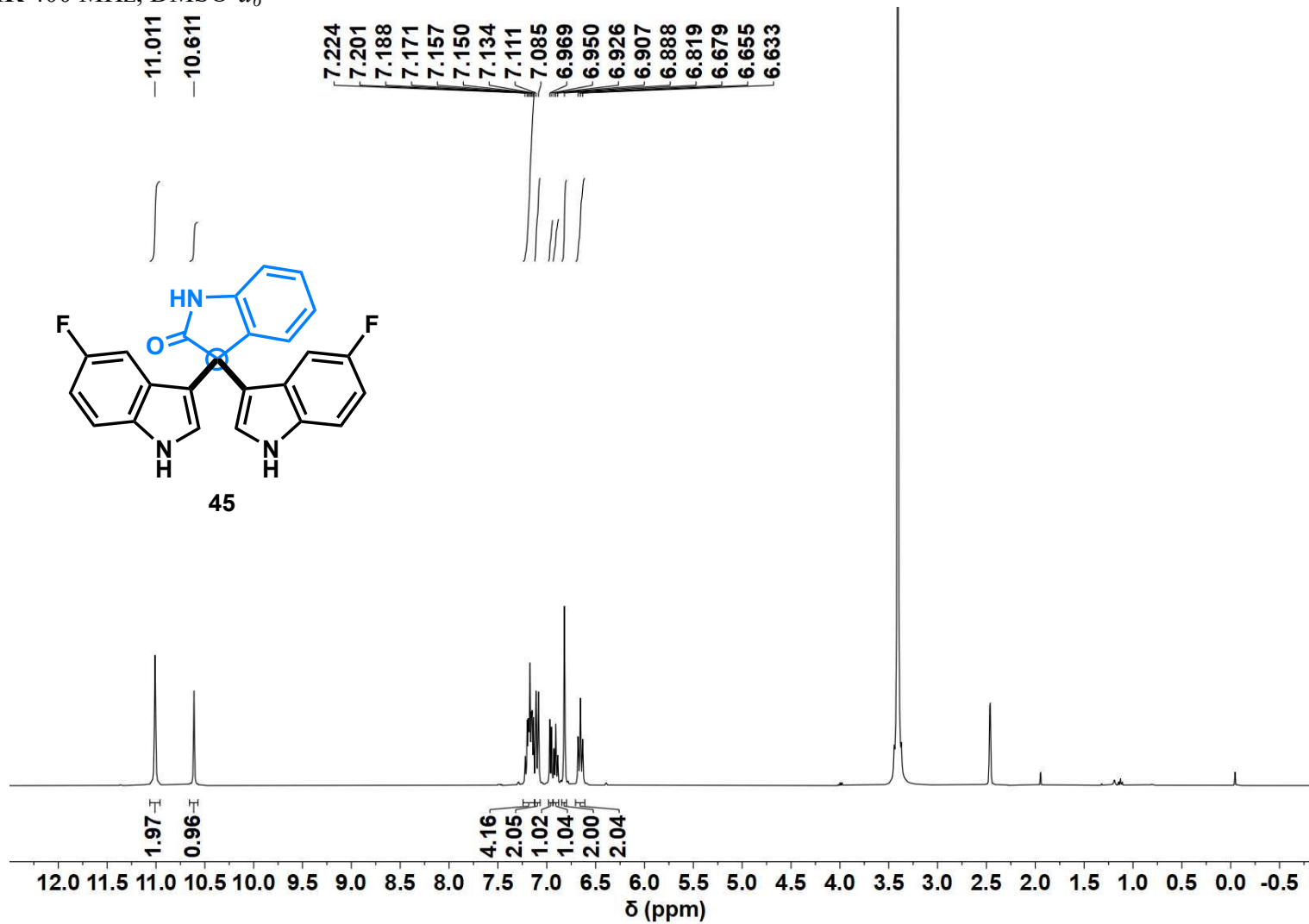
^1H NMR 400 MHz, $\text{DMSO-}d_6$



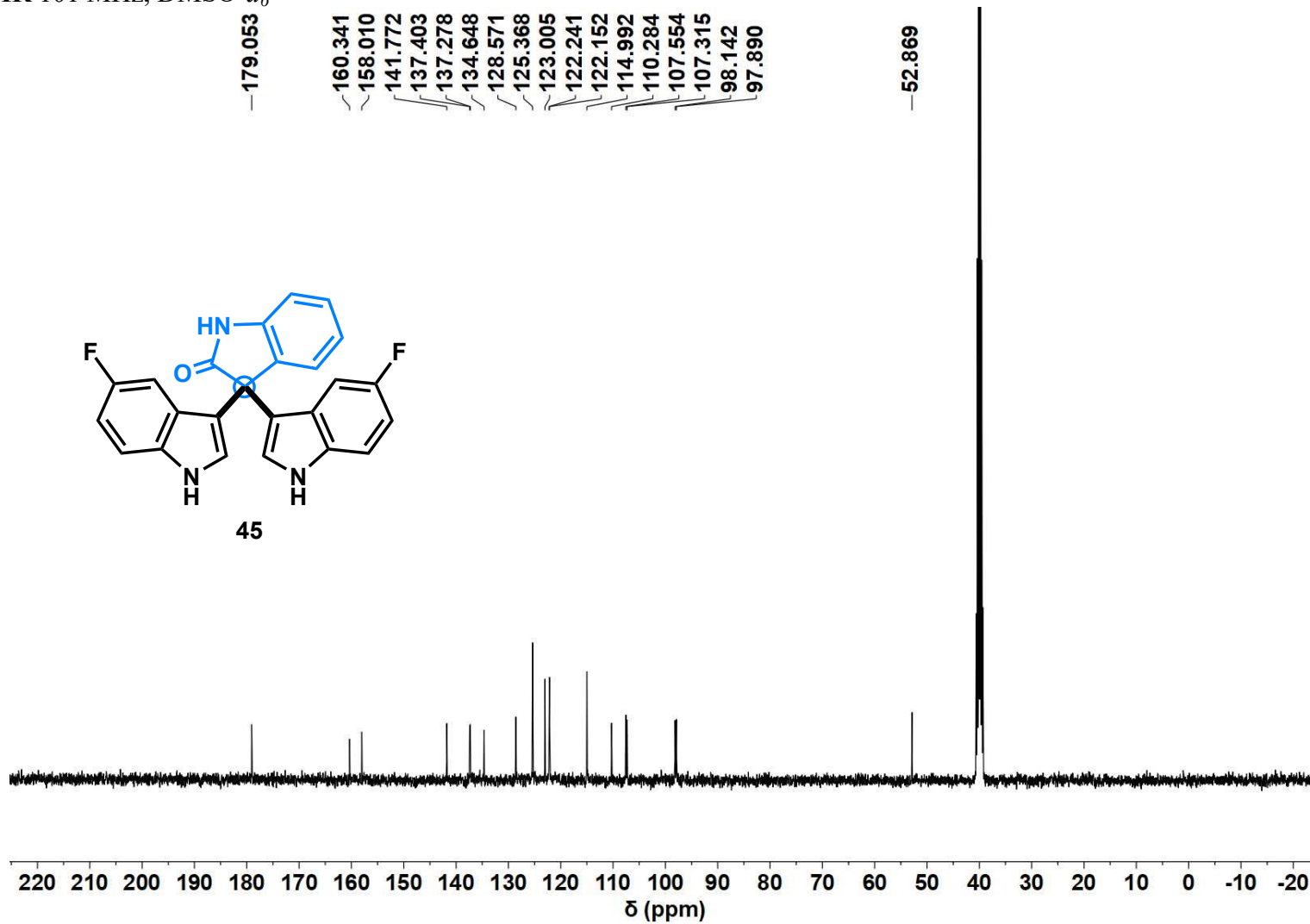
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^1H NMR 400 MHz, $\text{DMSO-}d_6$

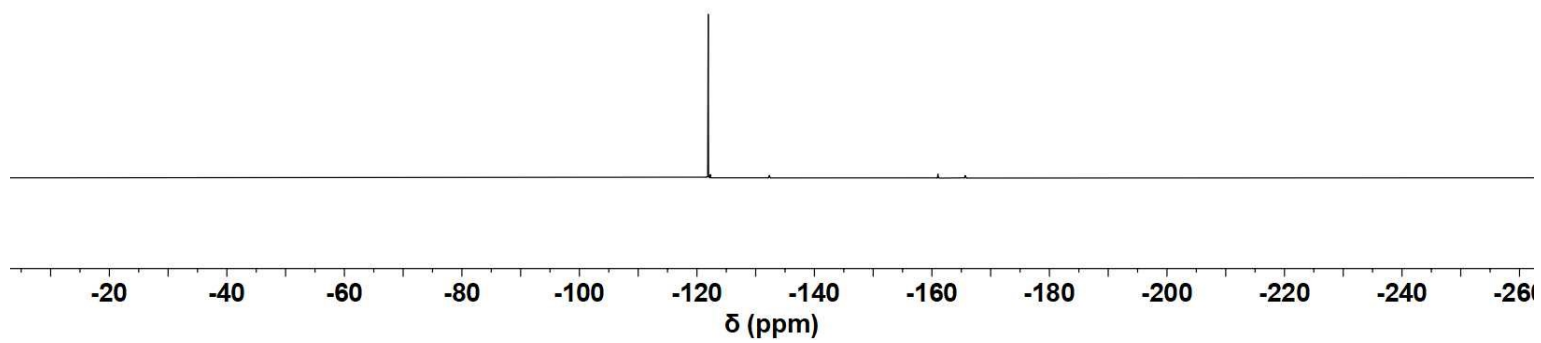
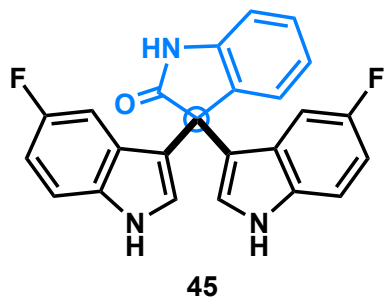


^{13}C NMR 101 MHz, $\text{DMSO-}d_6$

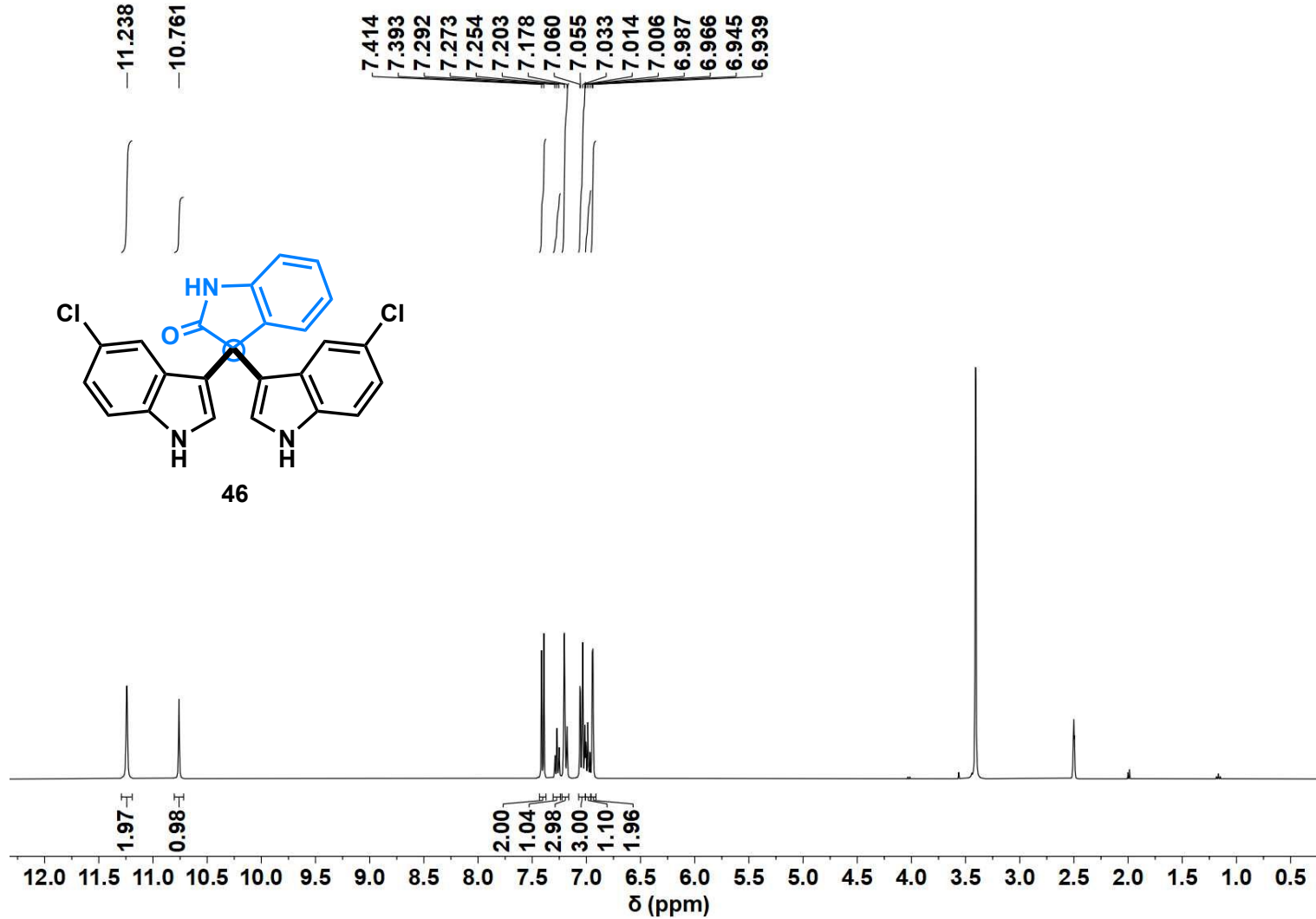


^{19}F NMR 376 MHz, $\text{DMSO-}d_6$

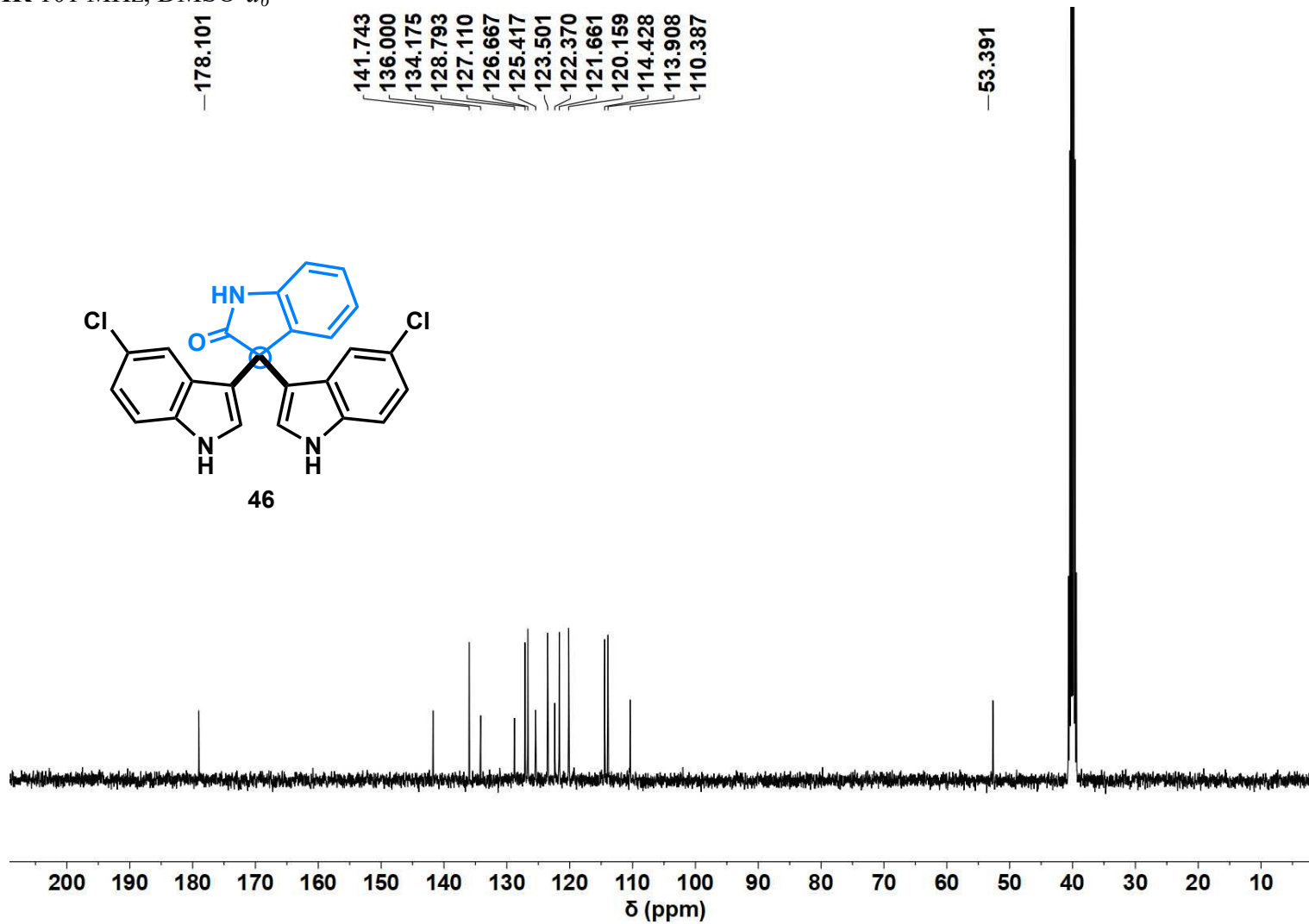
-121.884
-121.908
-121.924
-121.935
-121.951
-121.979



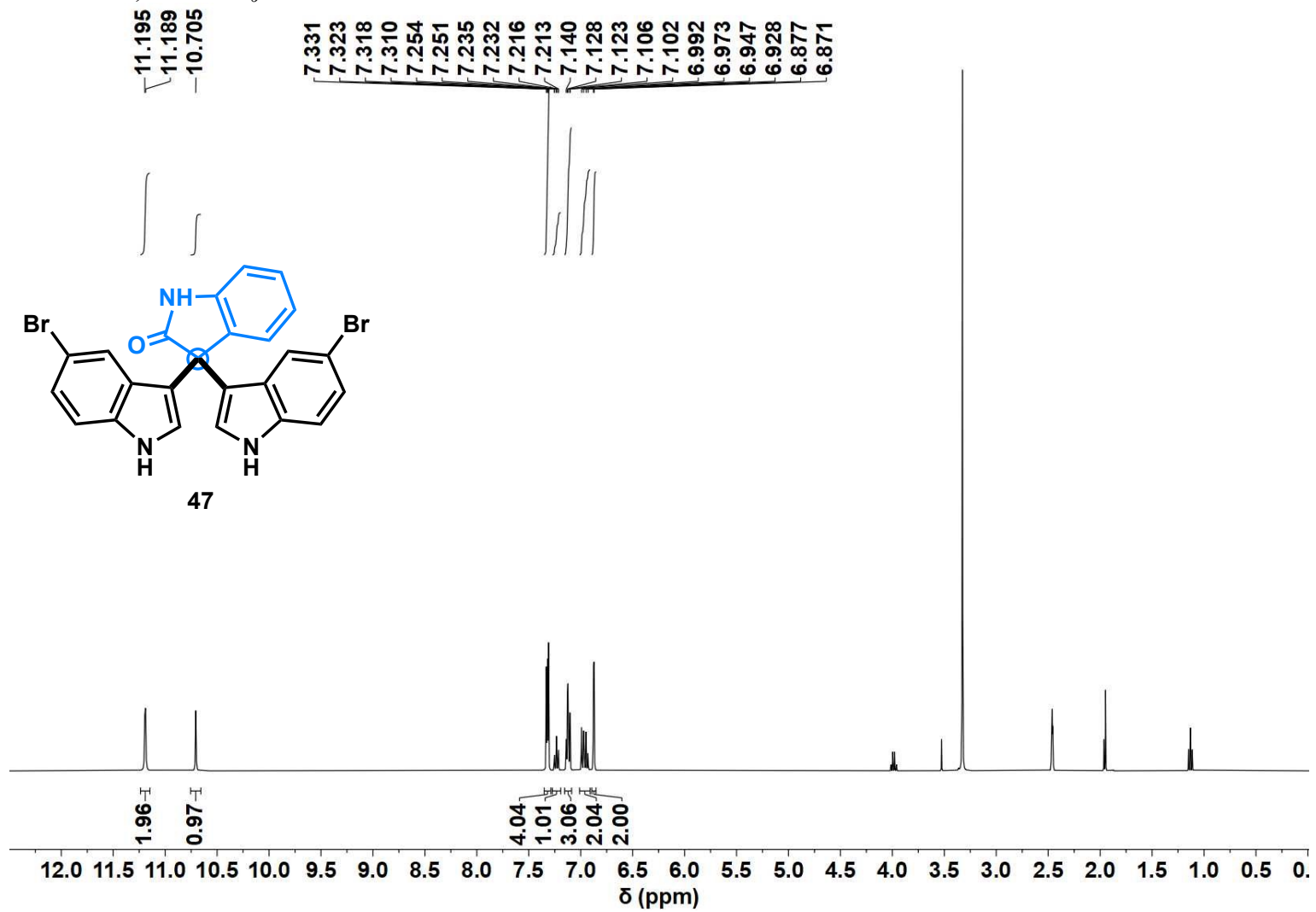
^1H NMR 400 MHz, $\text{DMSO-}d_6$



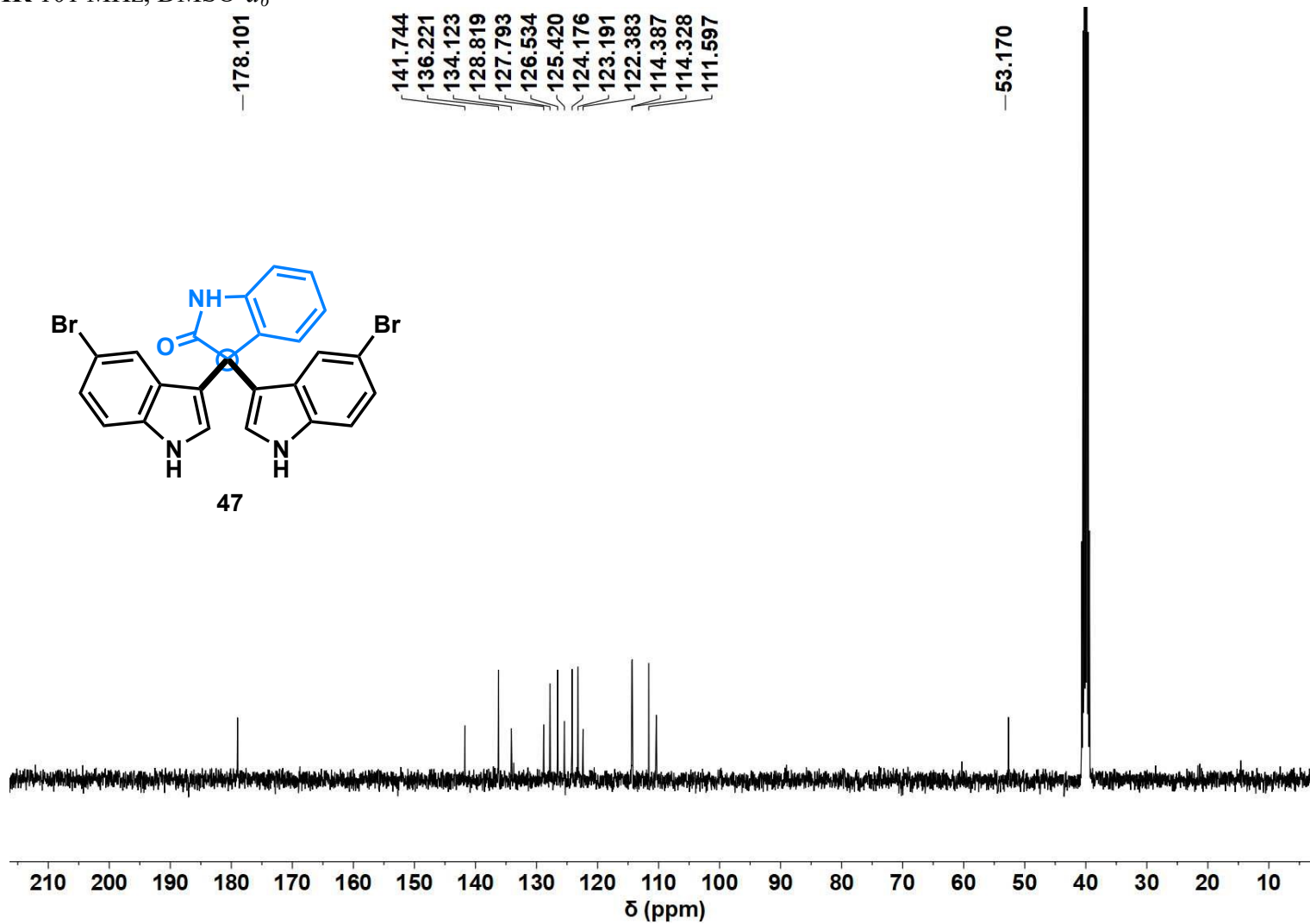
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



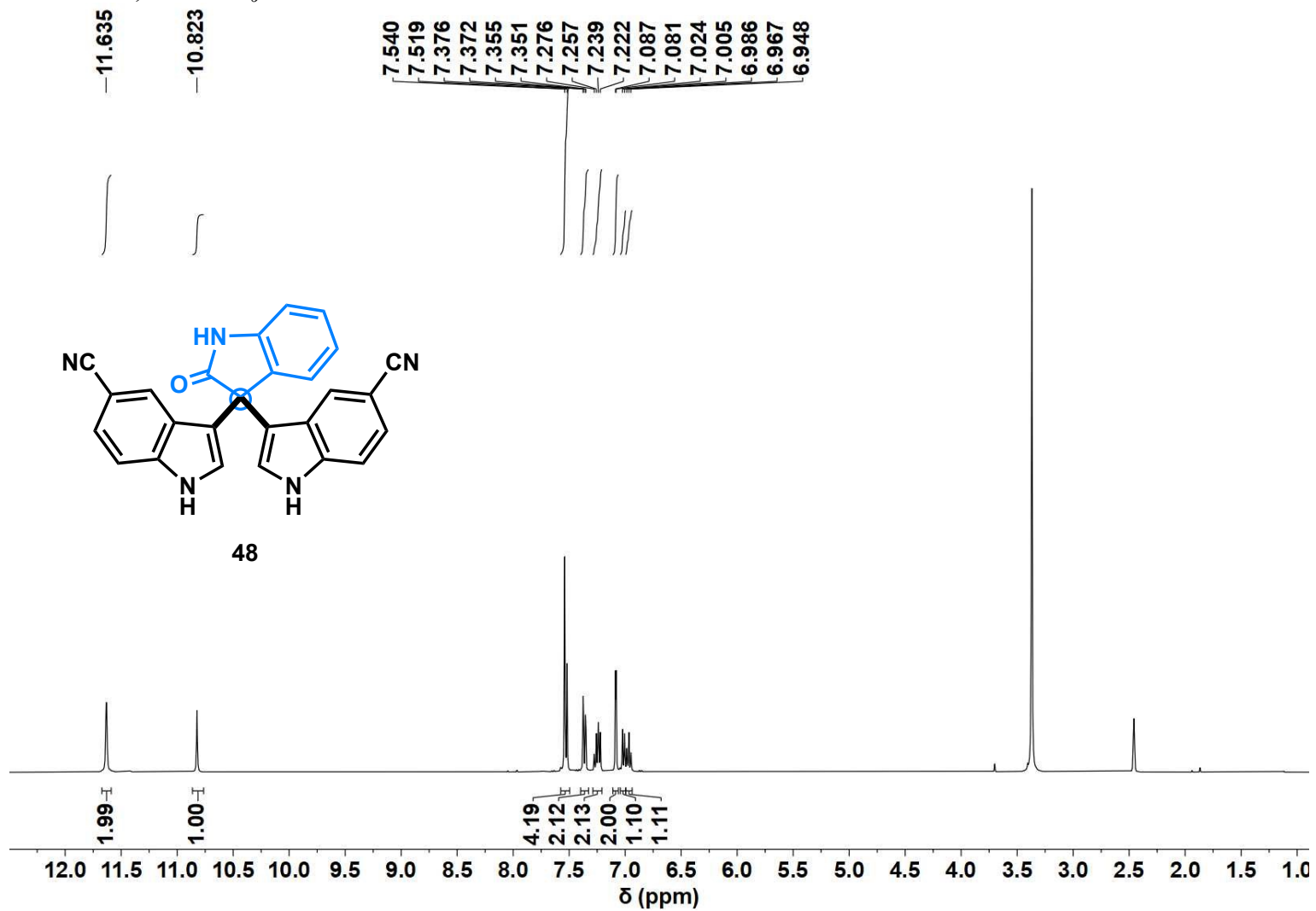
^1H NMR 400 MHz, $\text{DMSO-}d_6$



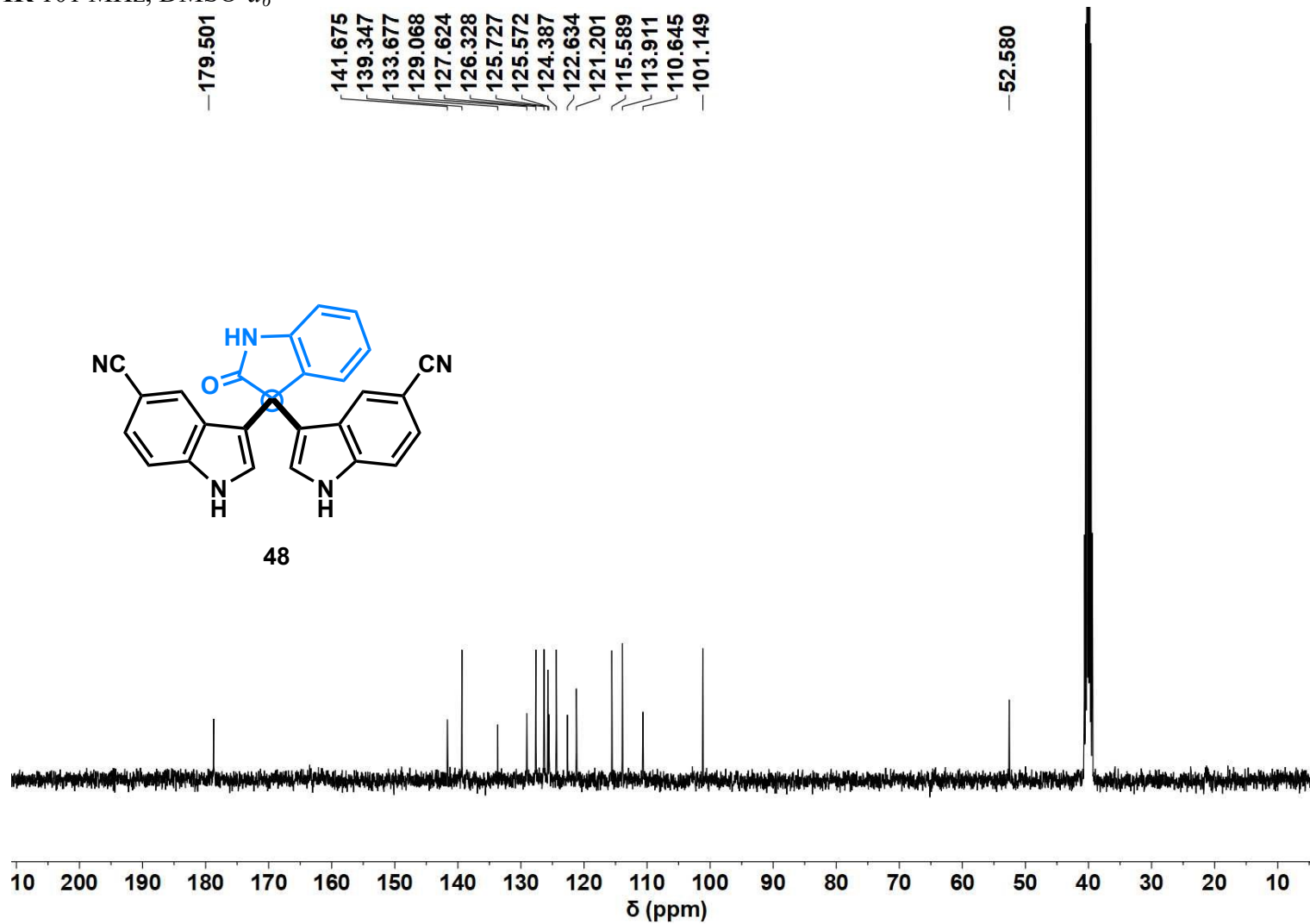
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



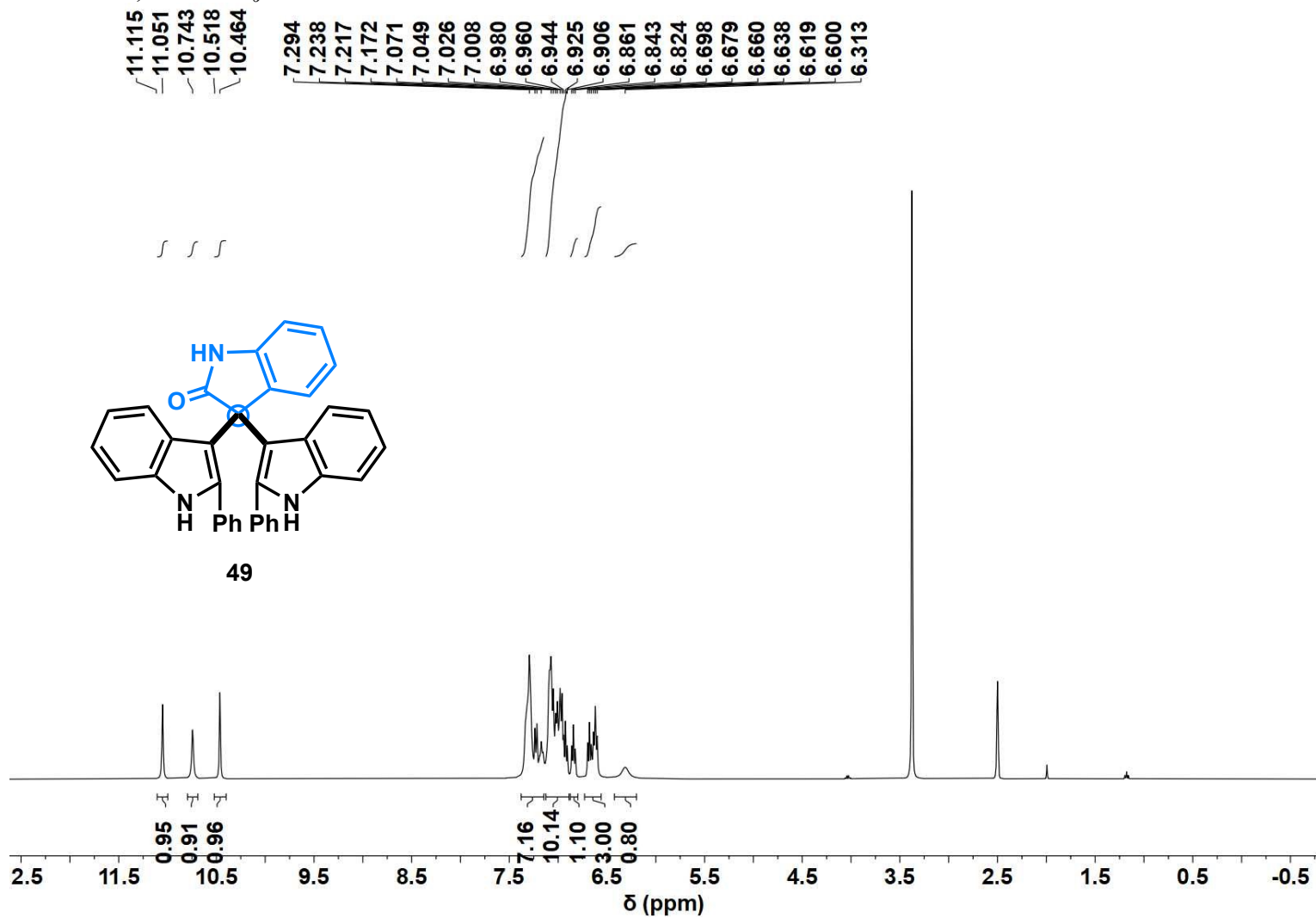
^1H NMR 400 MHz, $\text{DMSO-}d_6$



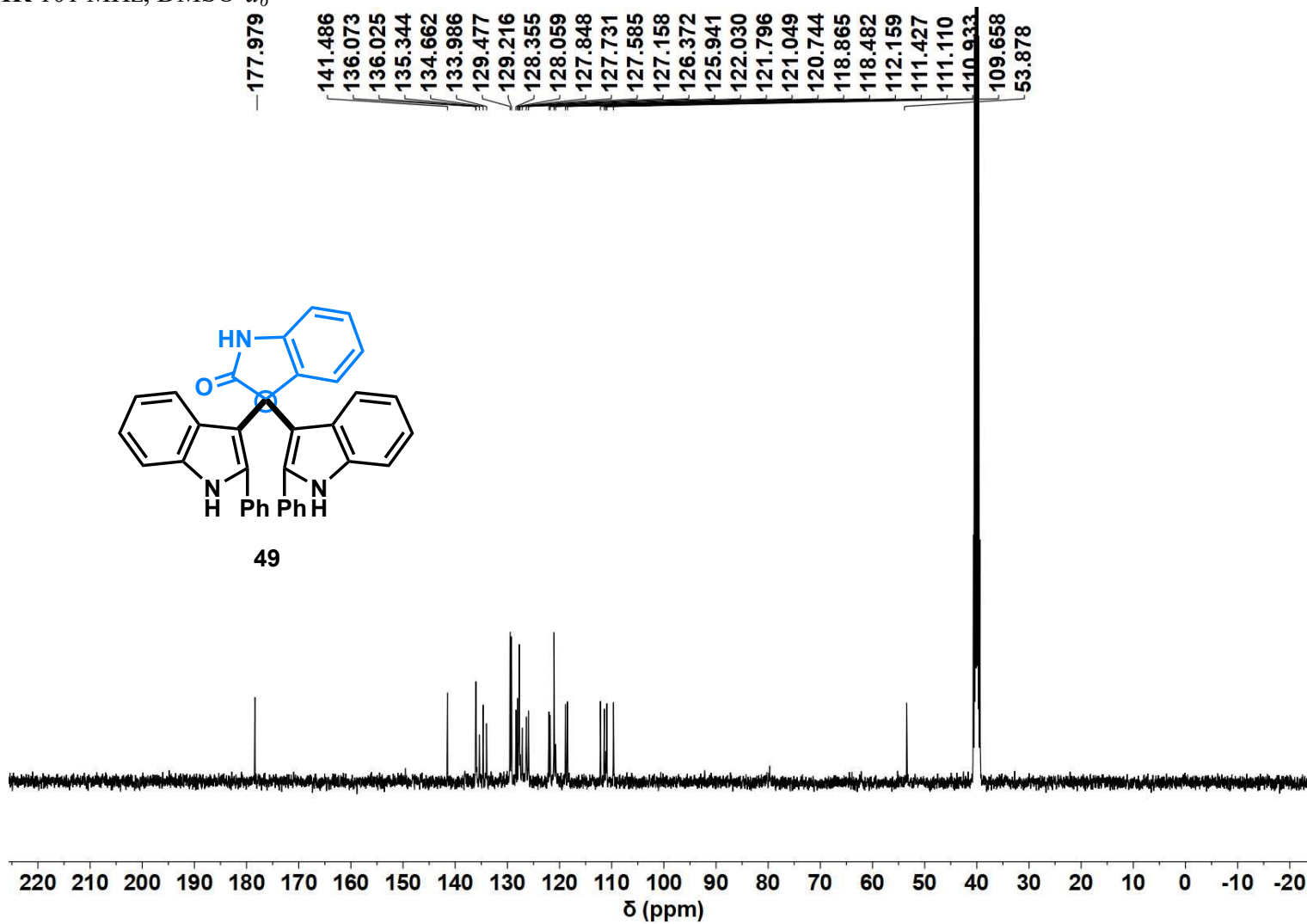
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



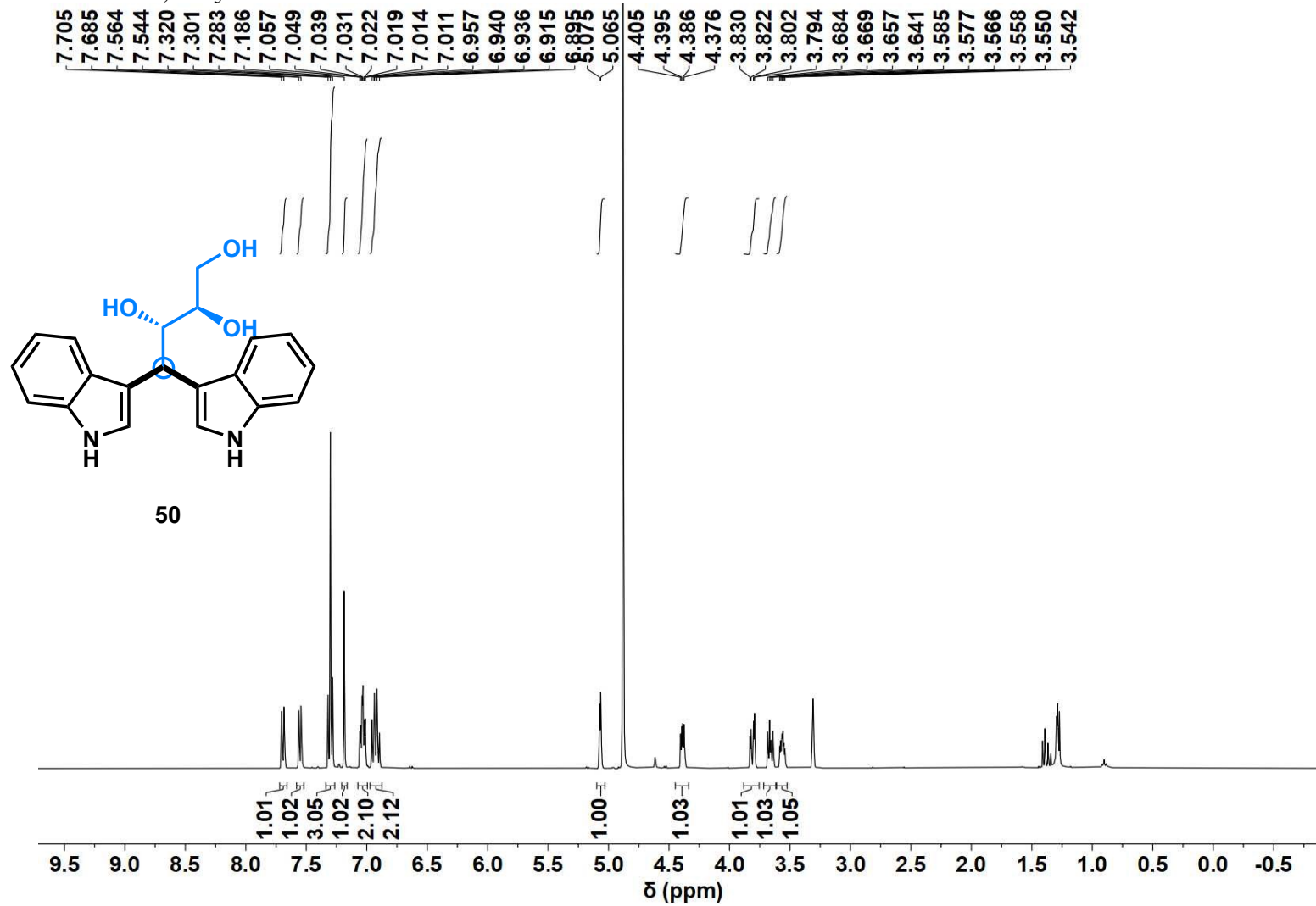
^1H NMR 400 MHz, $\text{DMSO-}d_6$



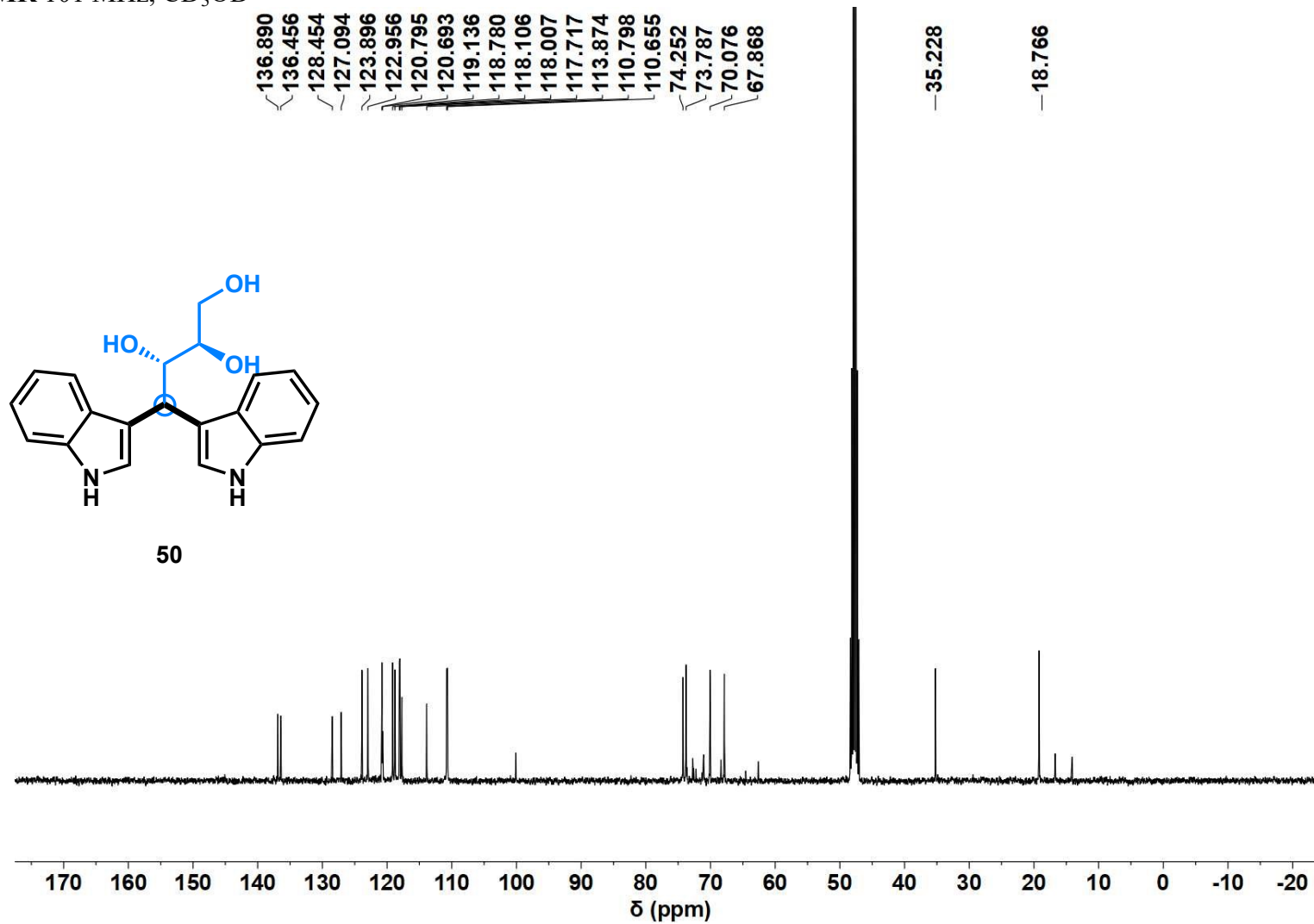
^{13}C NMR 101 MHz, $\text{DMSO-}d_6$



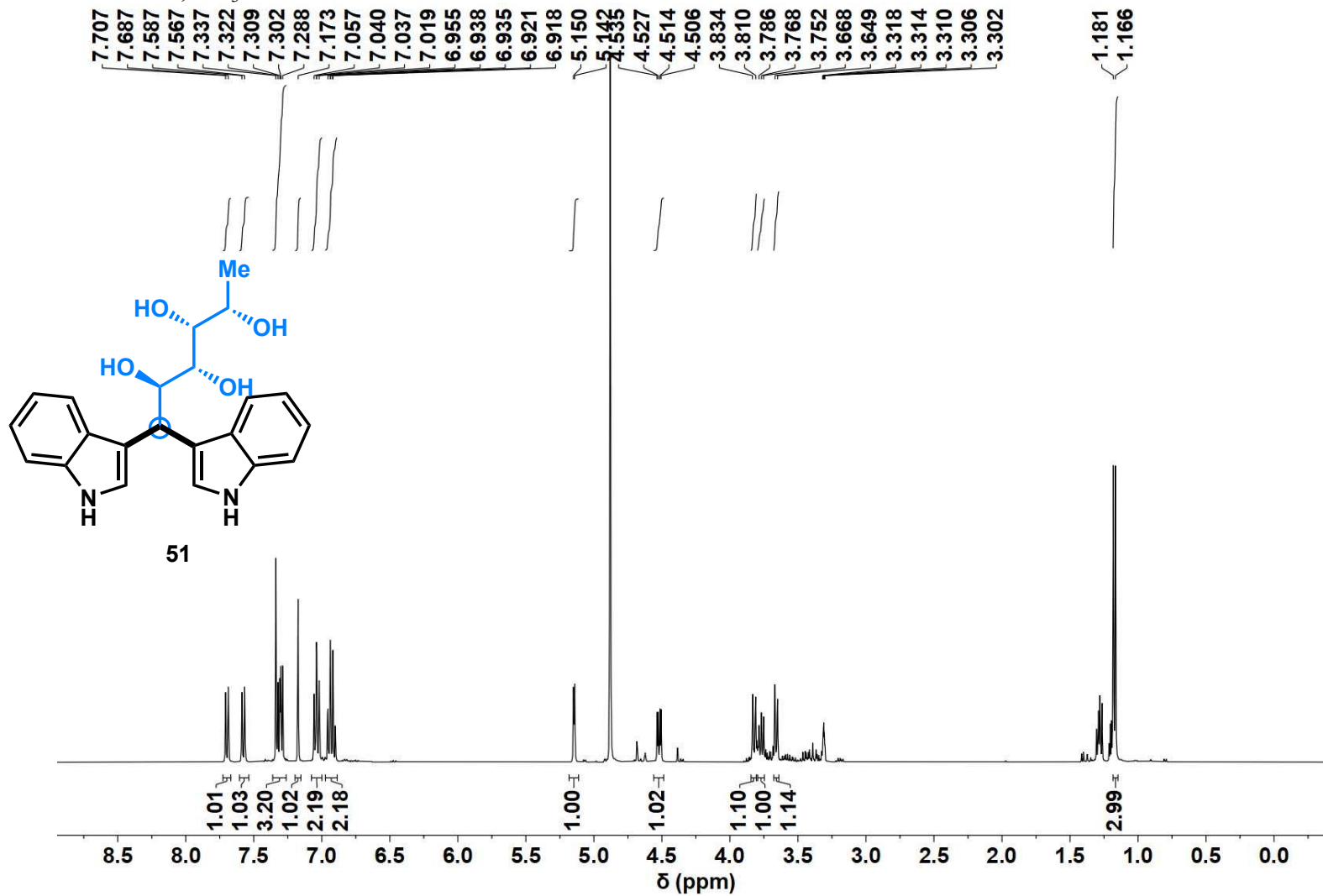
^1H NMR 400 MHz, CD_3OD



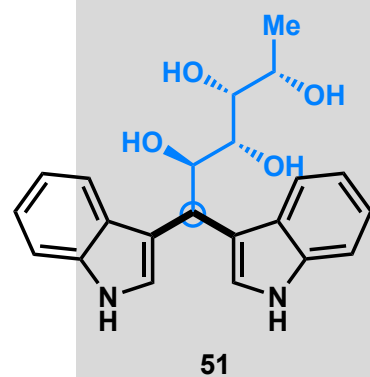
^{13}C NMR 101 MHz, CD_3OD



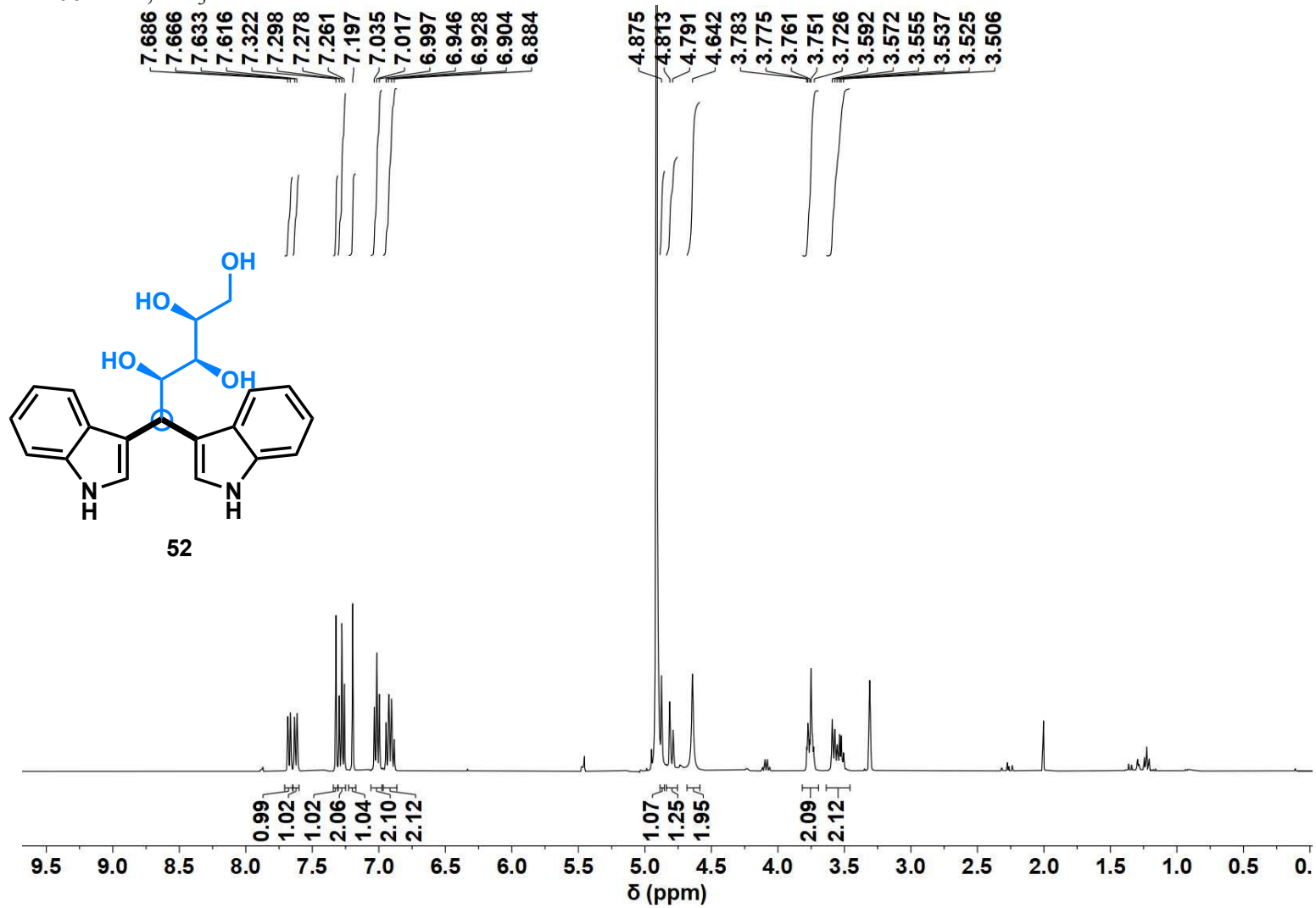
¹H NMR 400 MHz, CD₃OD



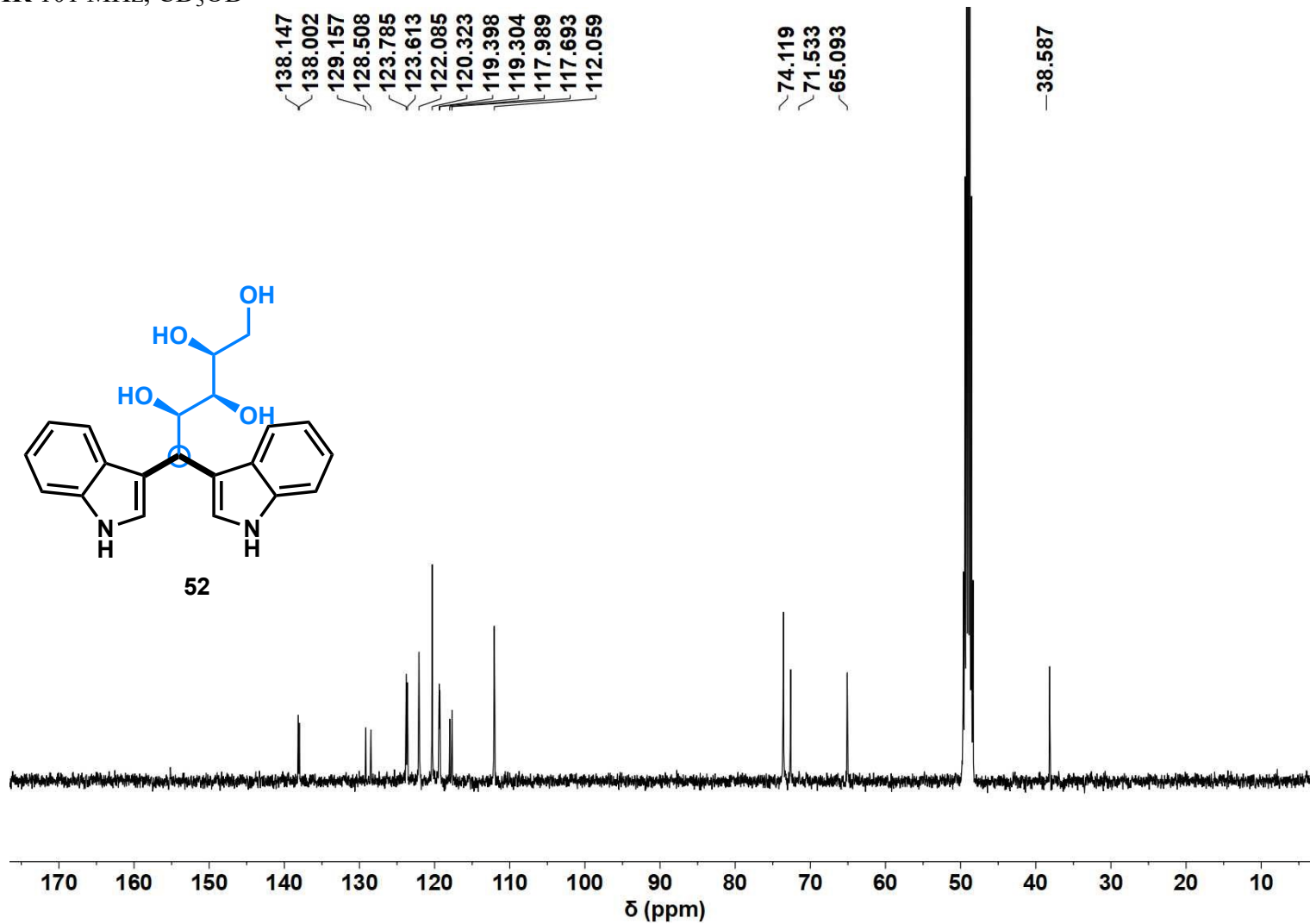
^{13}C NMR 101 MHz, CD_3OD



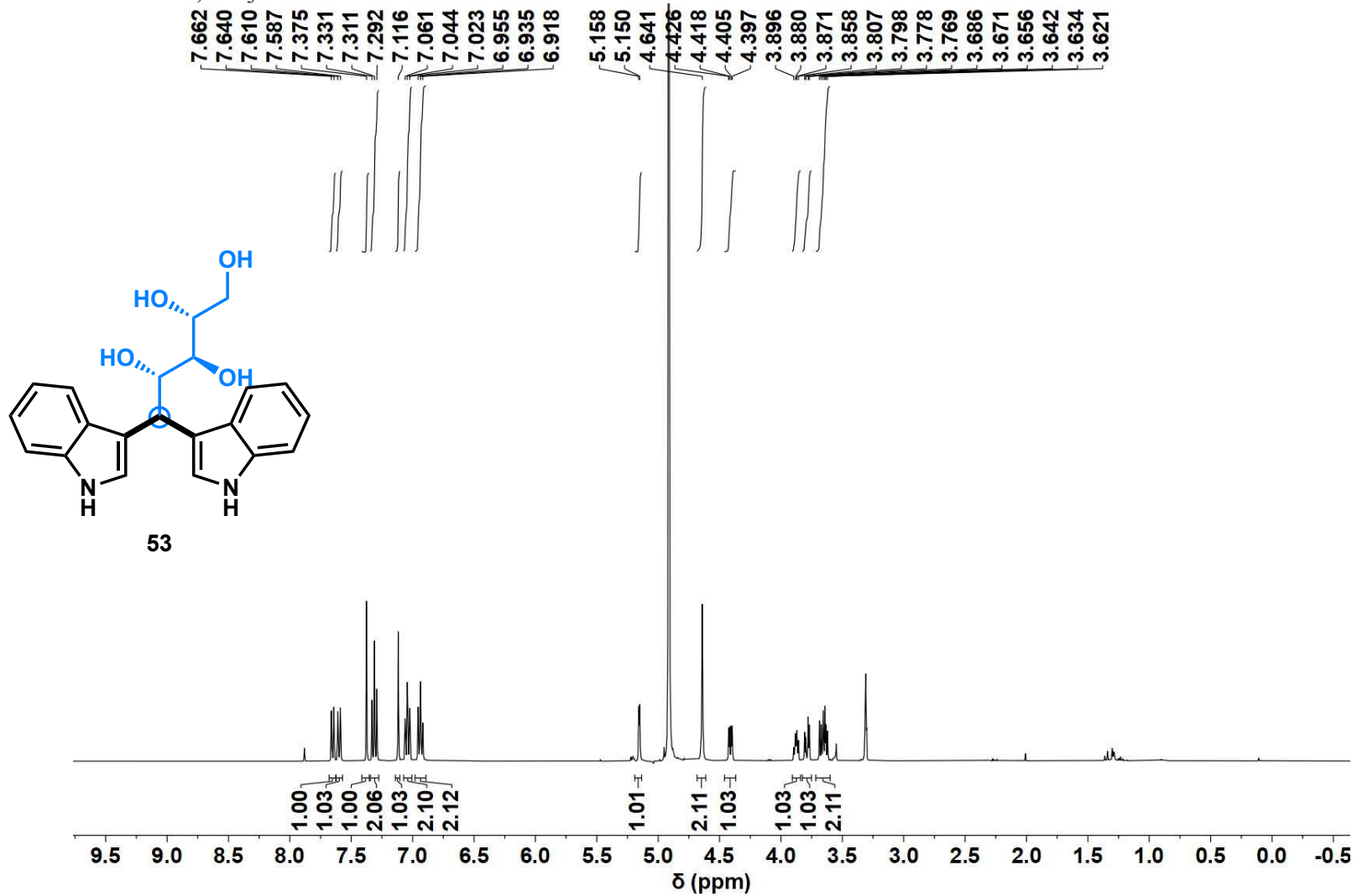
^1H NMR 400 MHz, CD_3OD



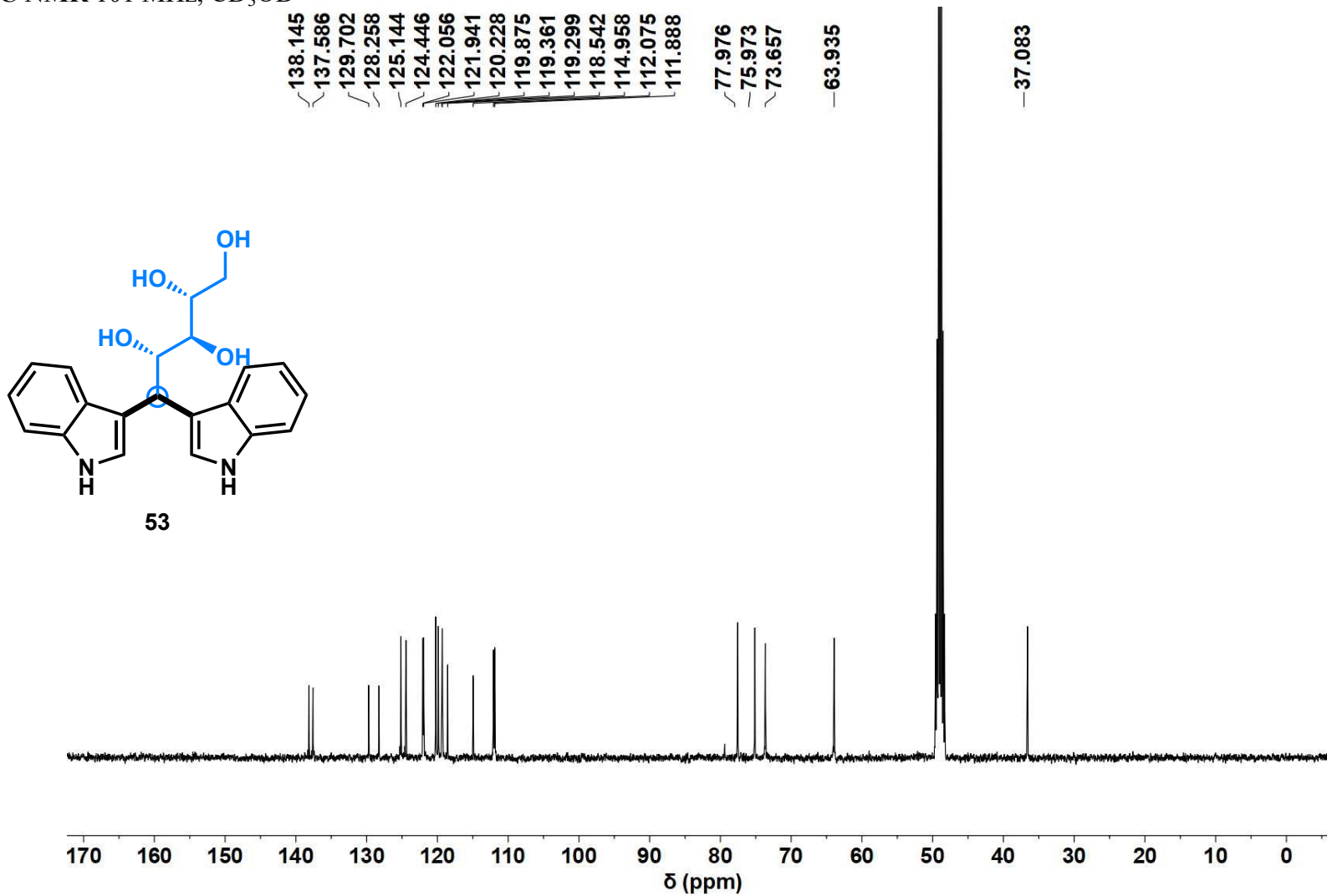
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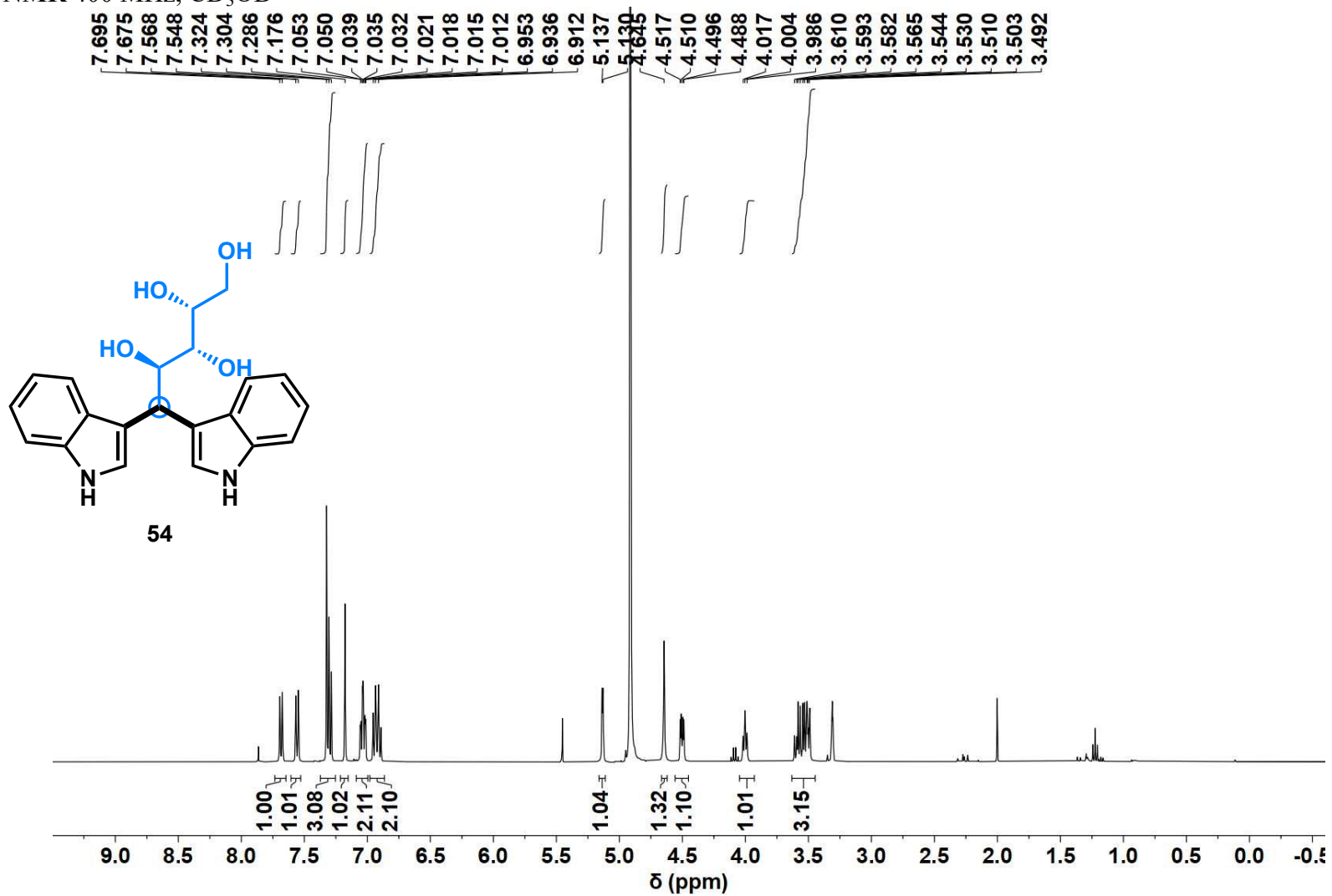
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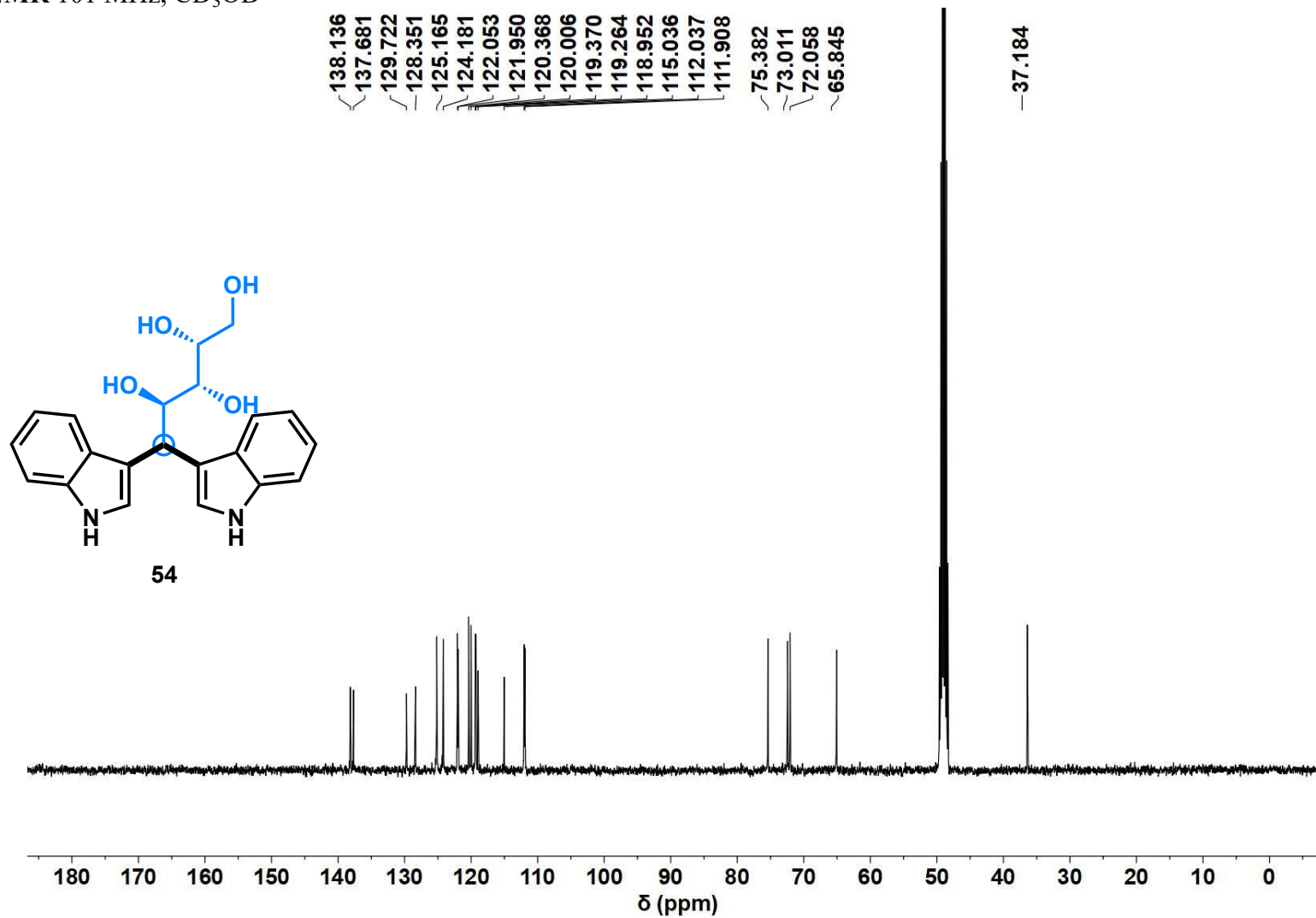
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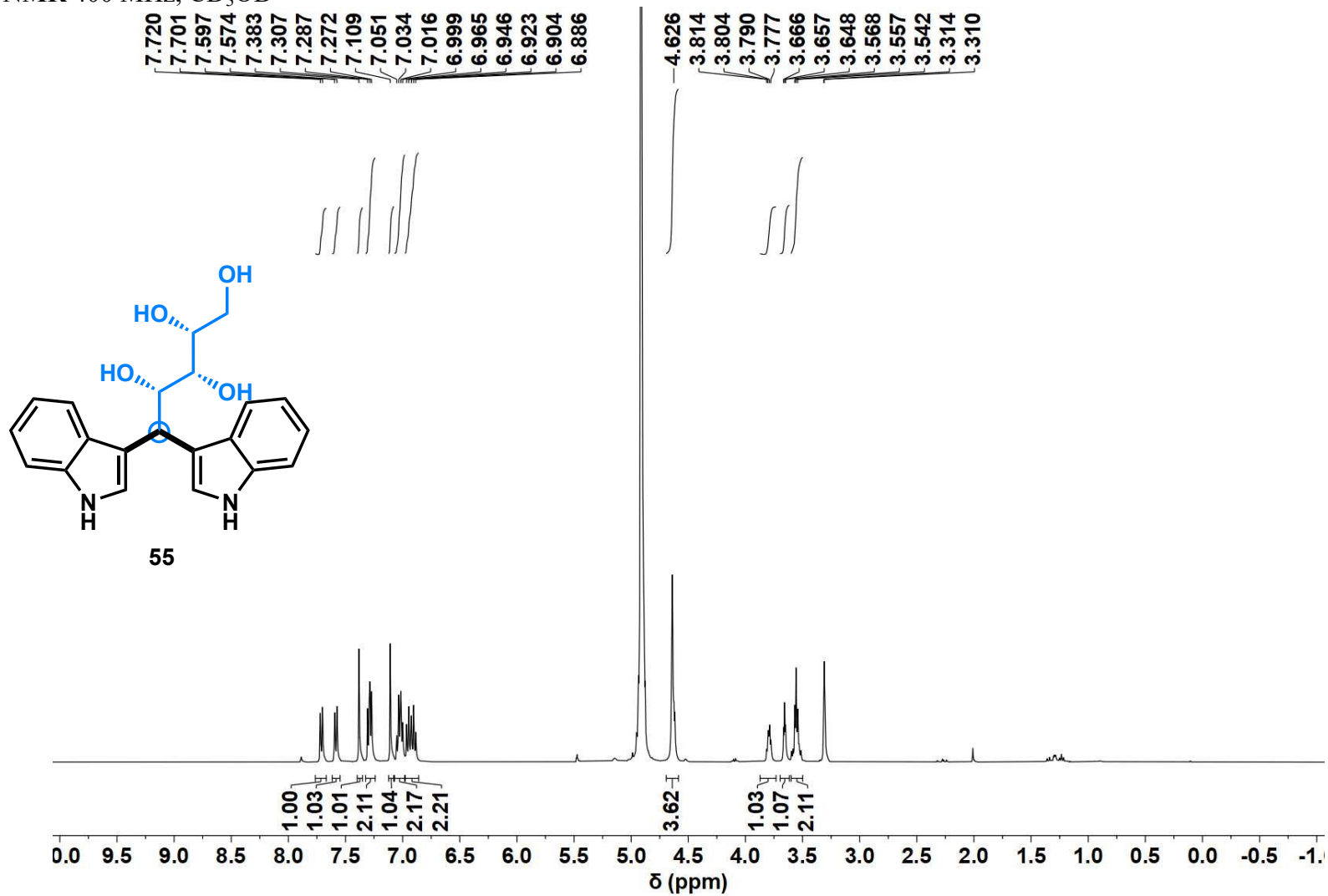
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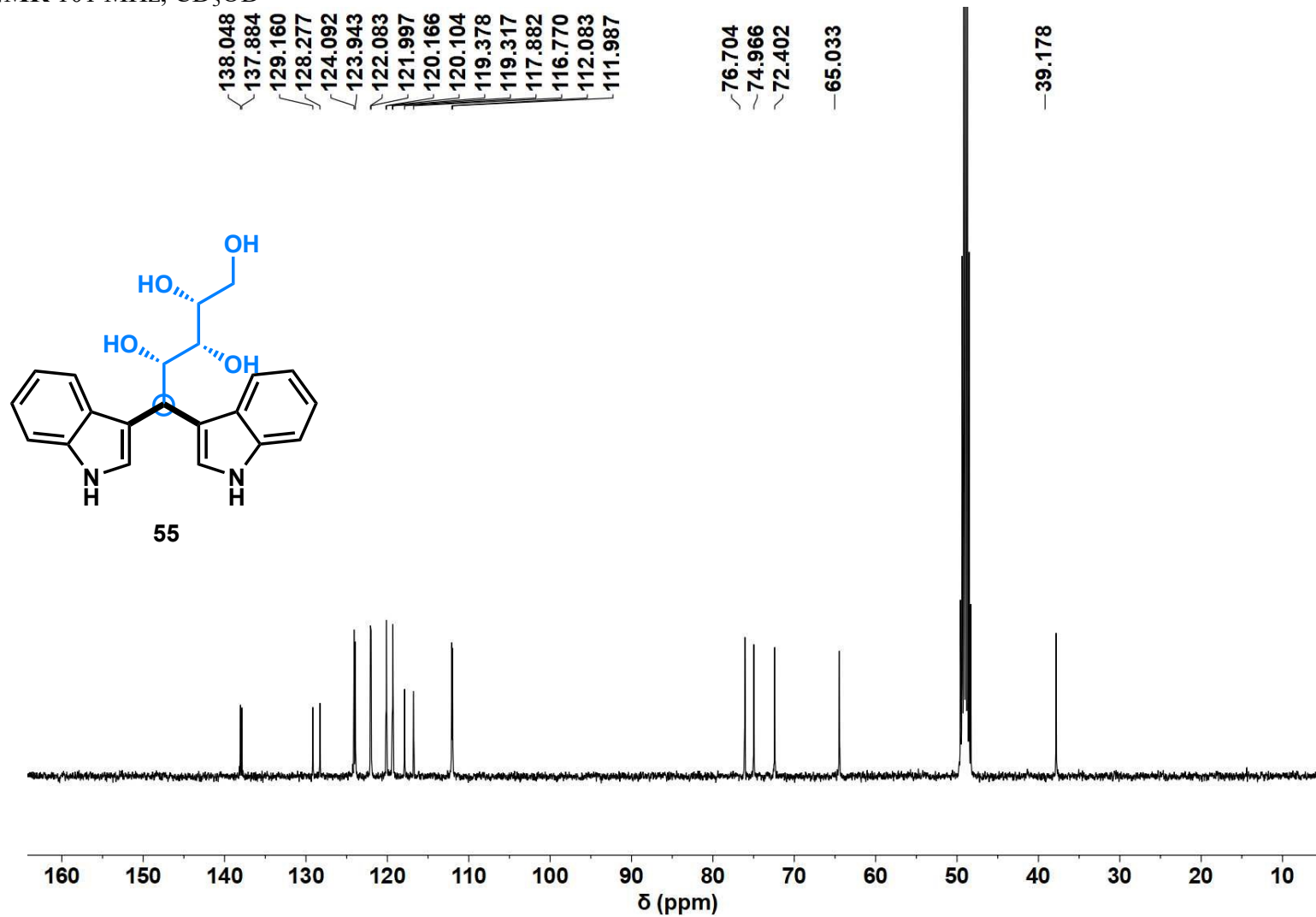
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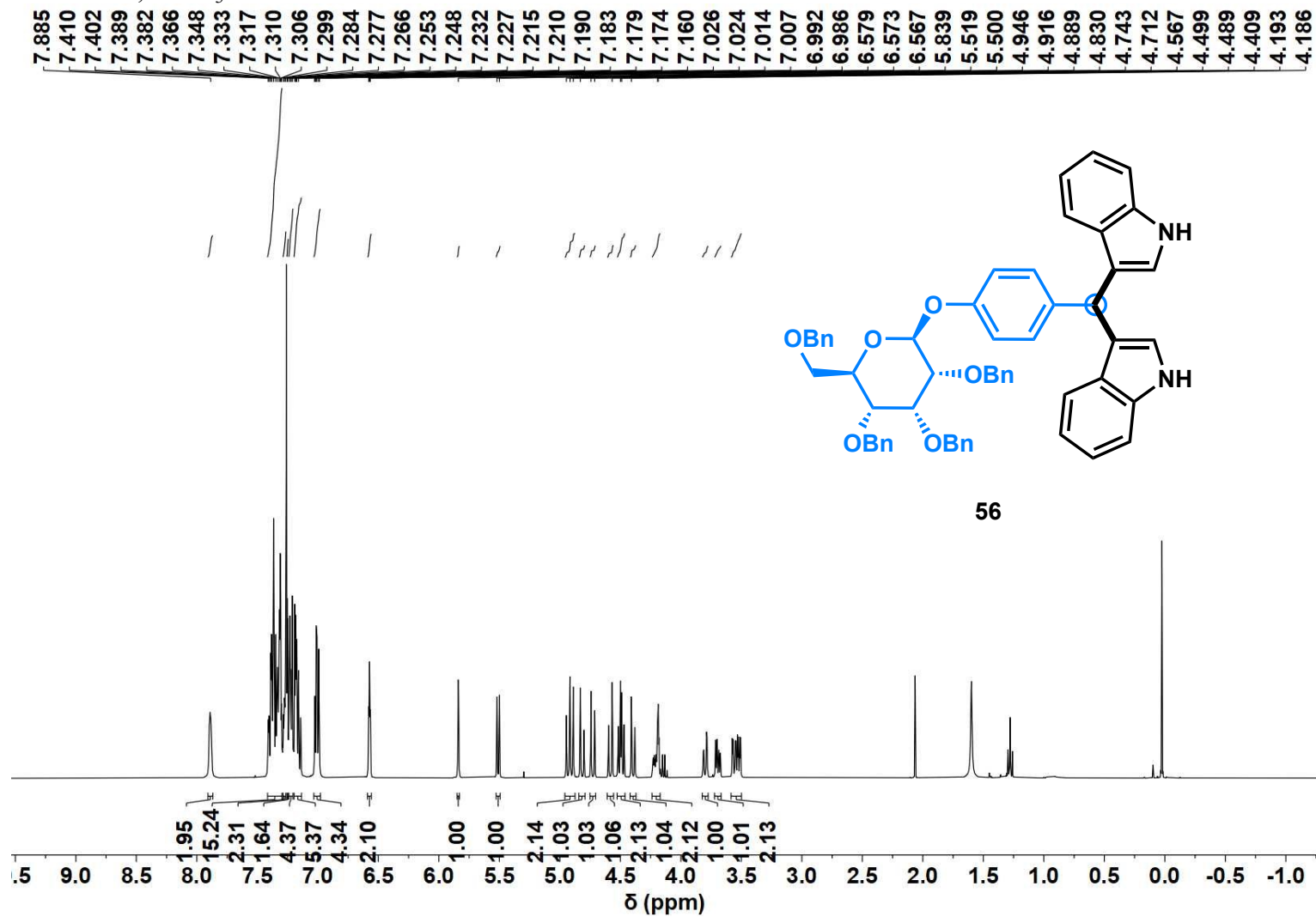
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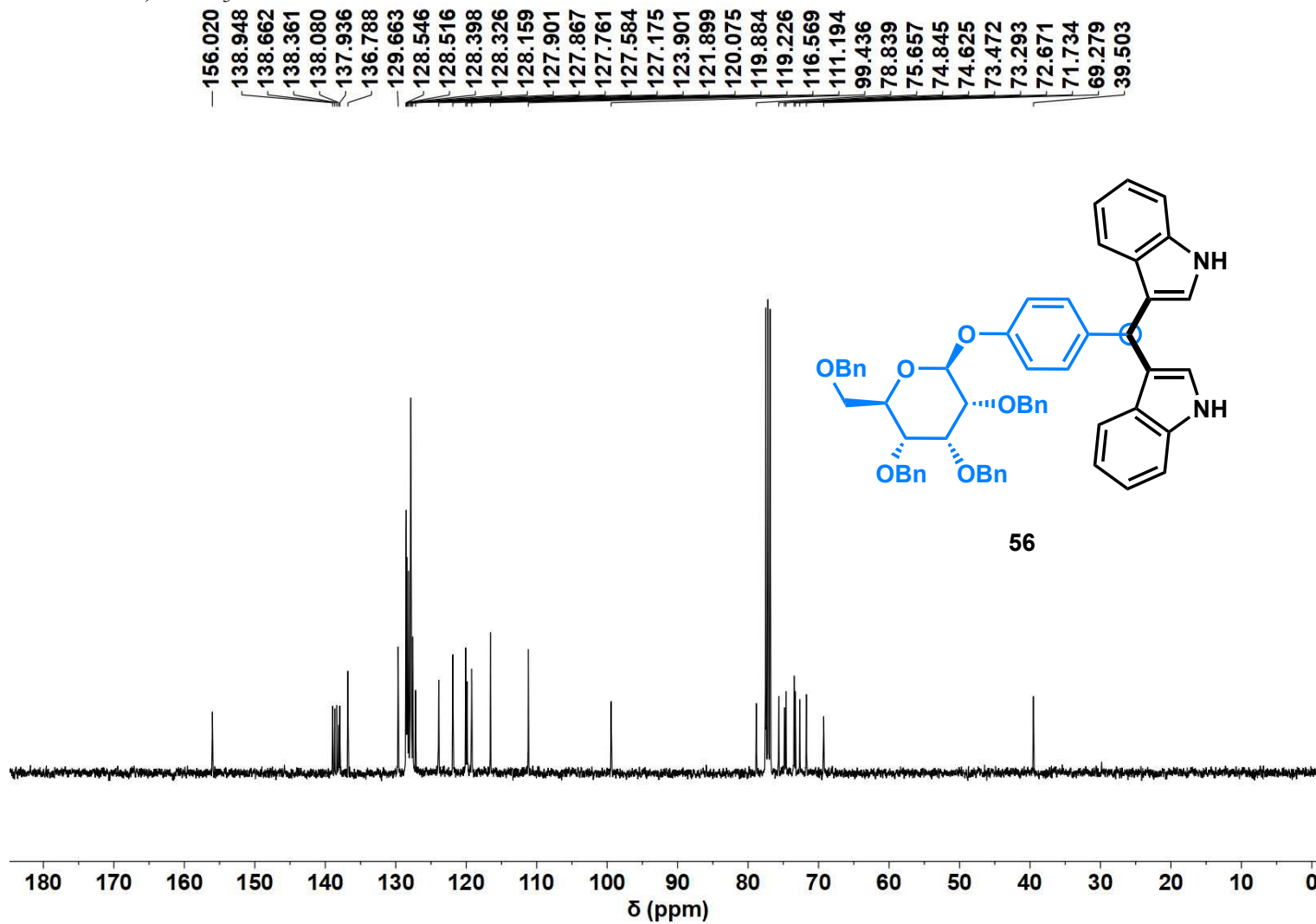
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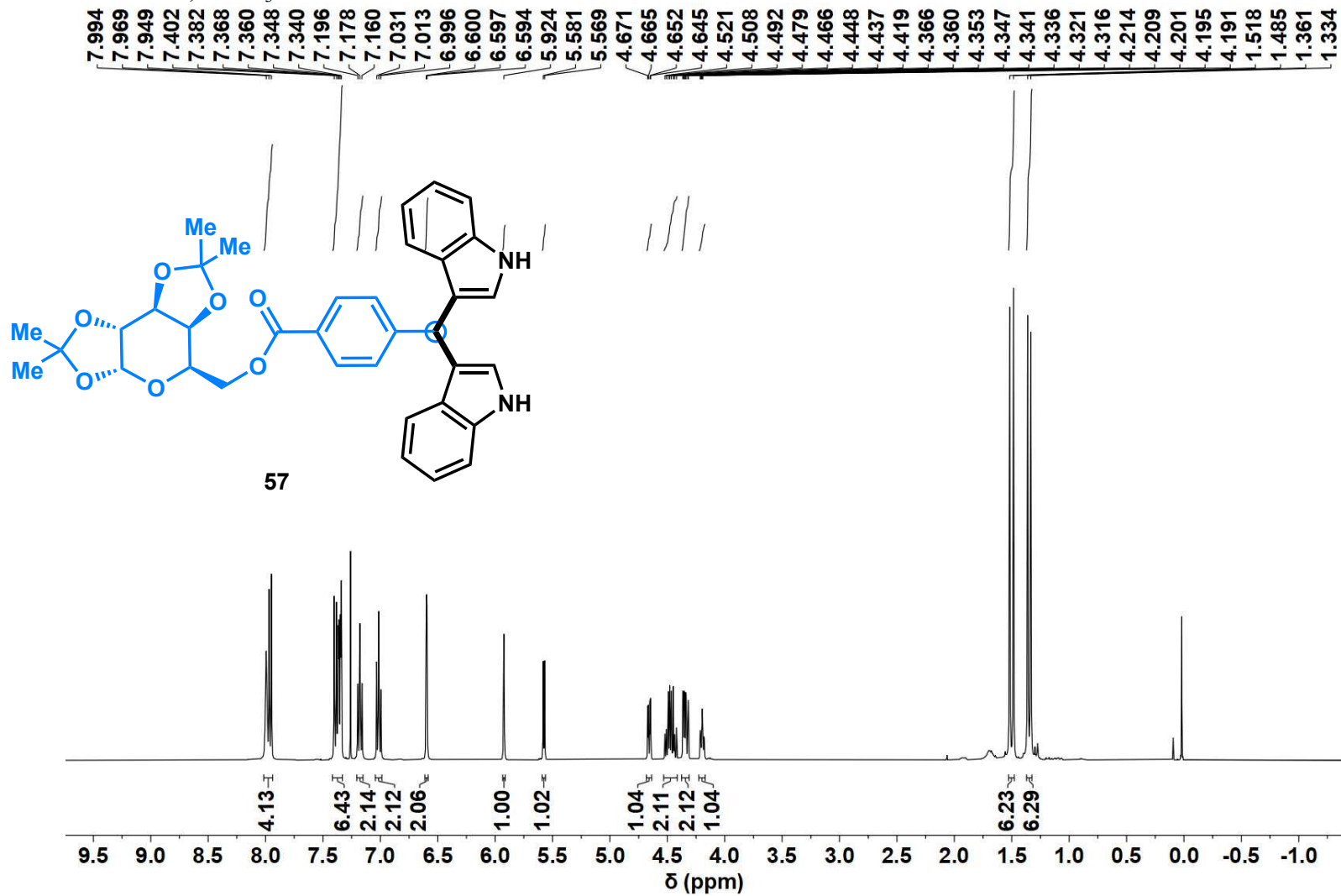
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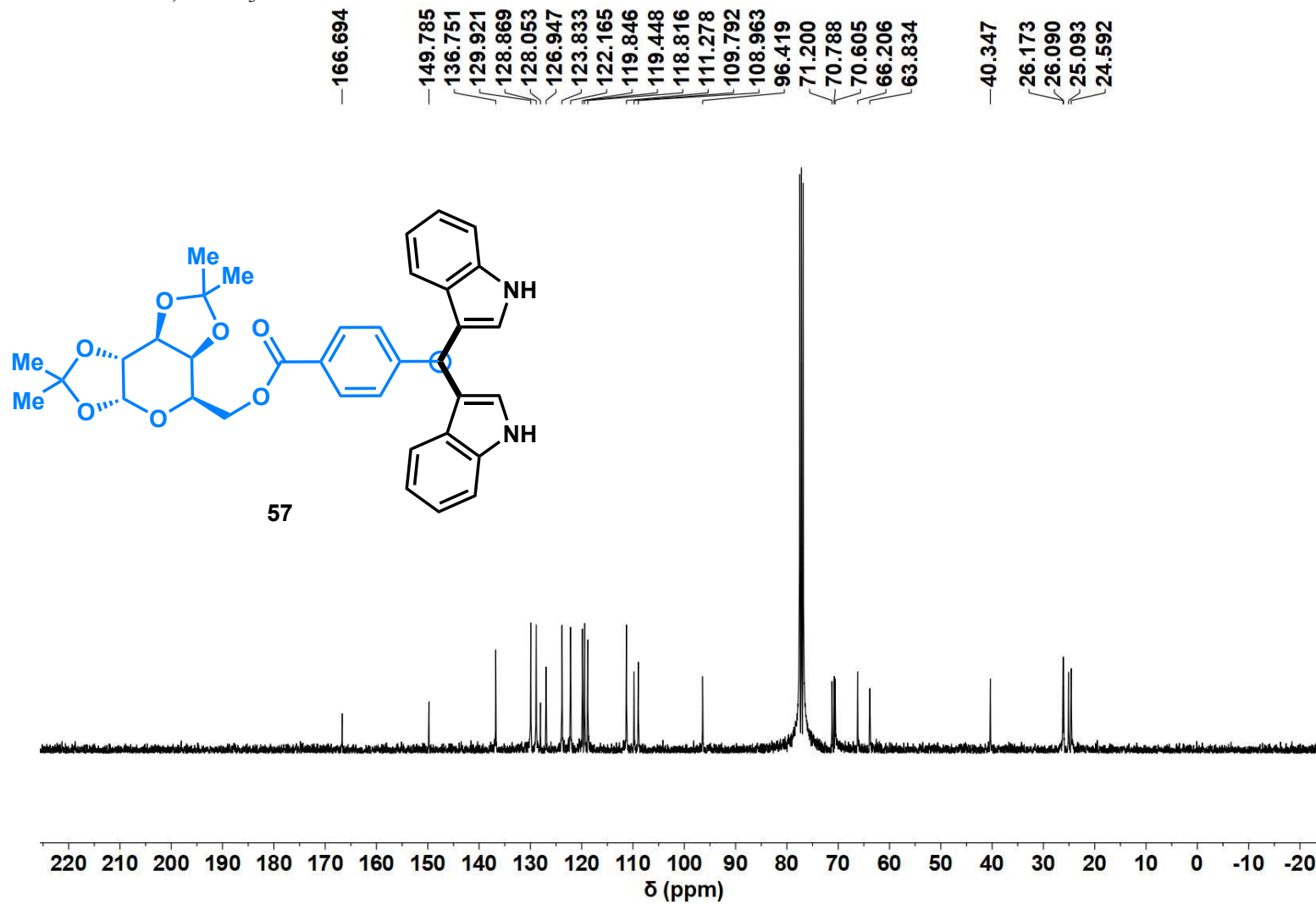
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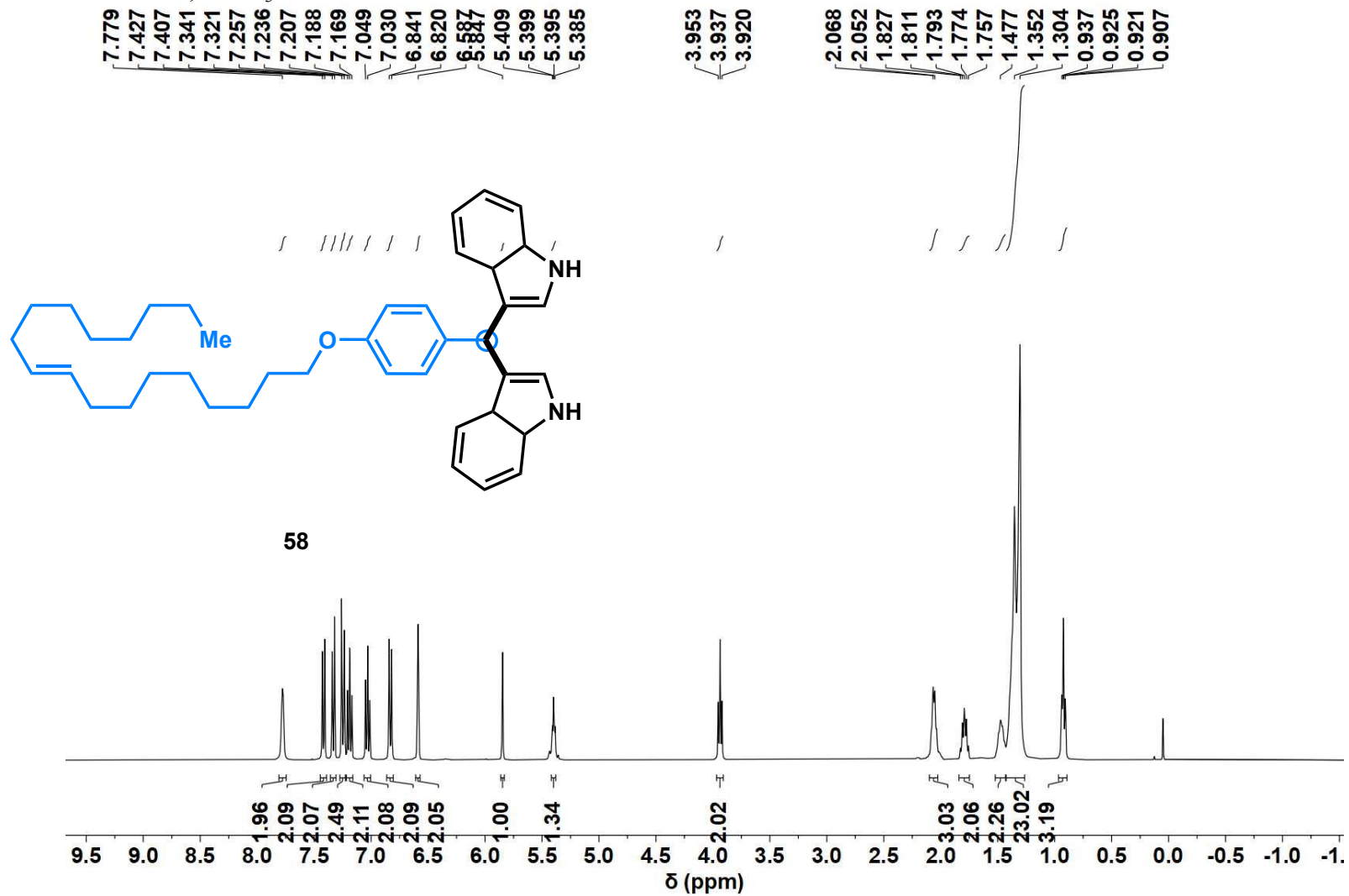
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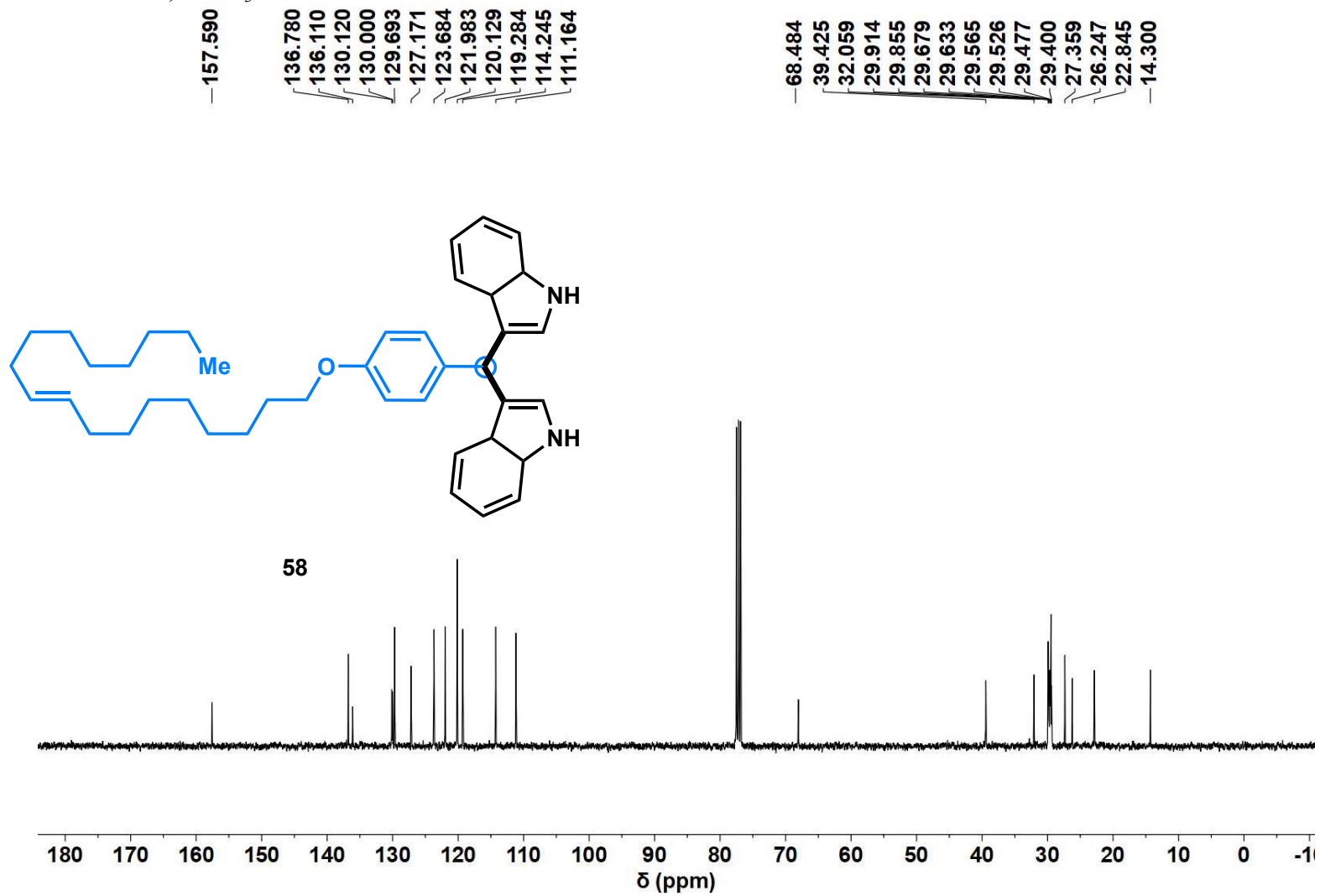
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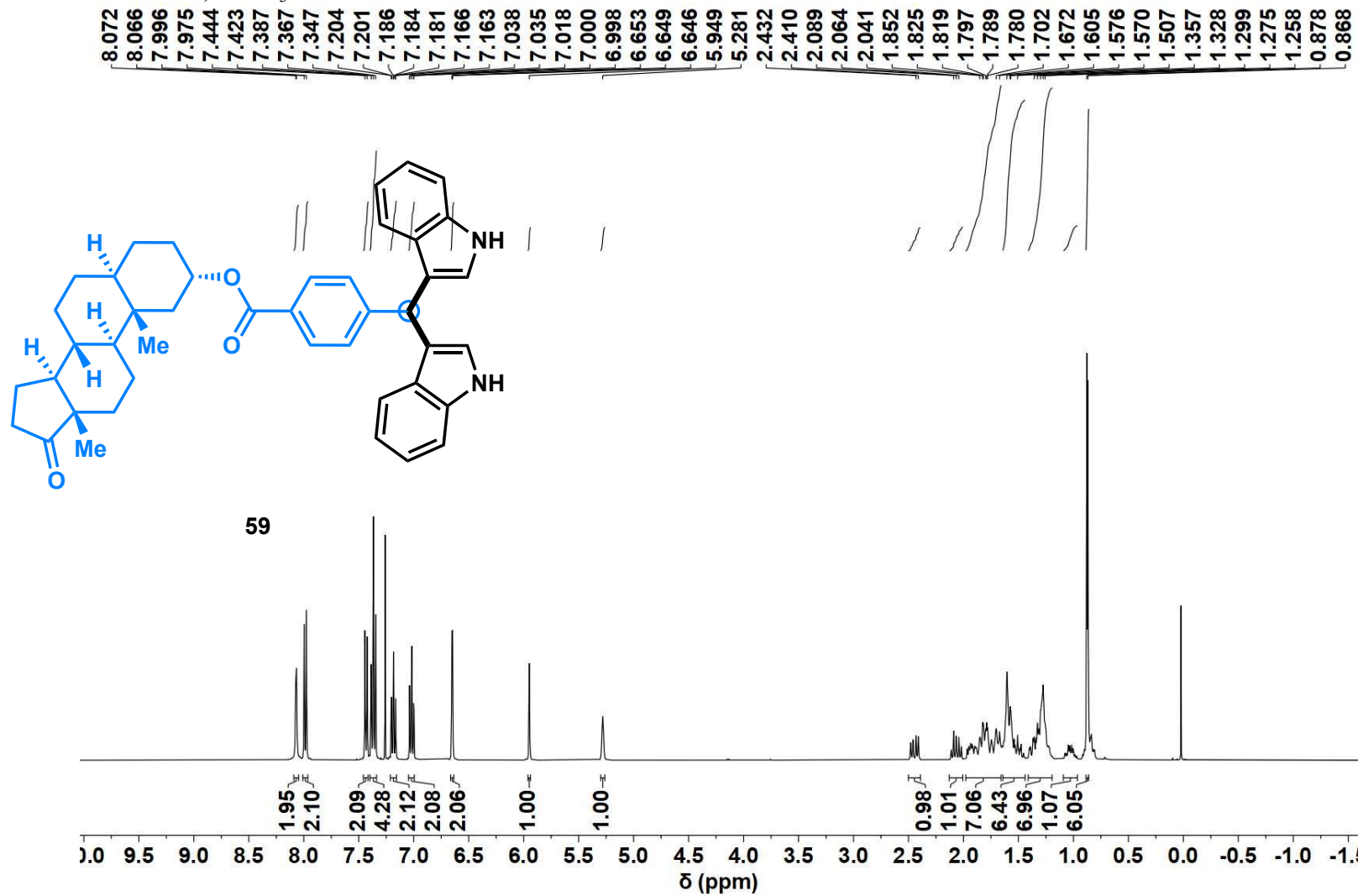
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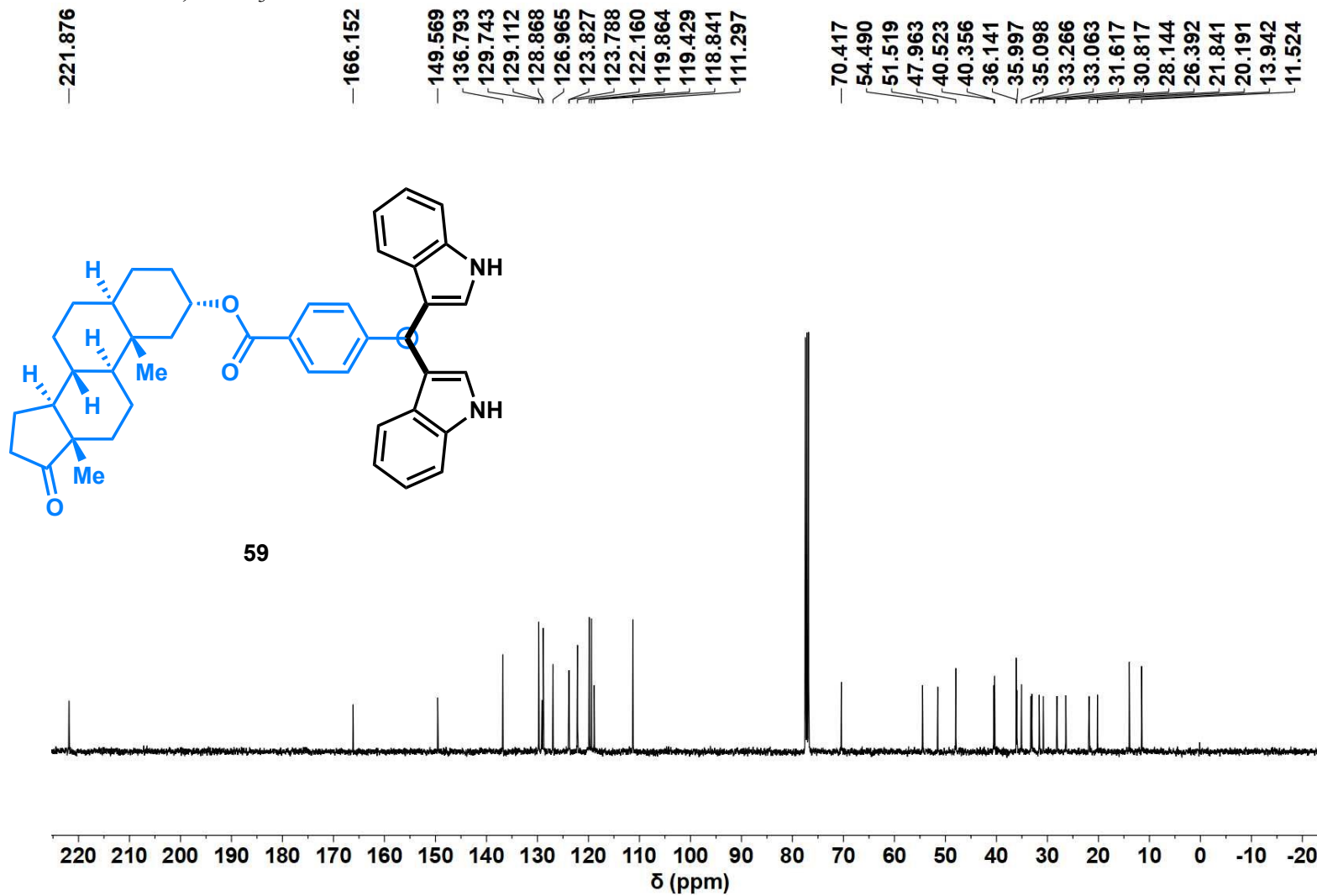
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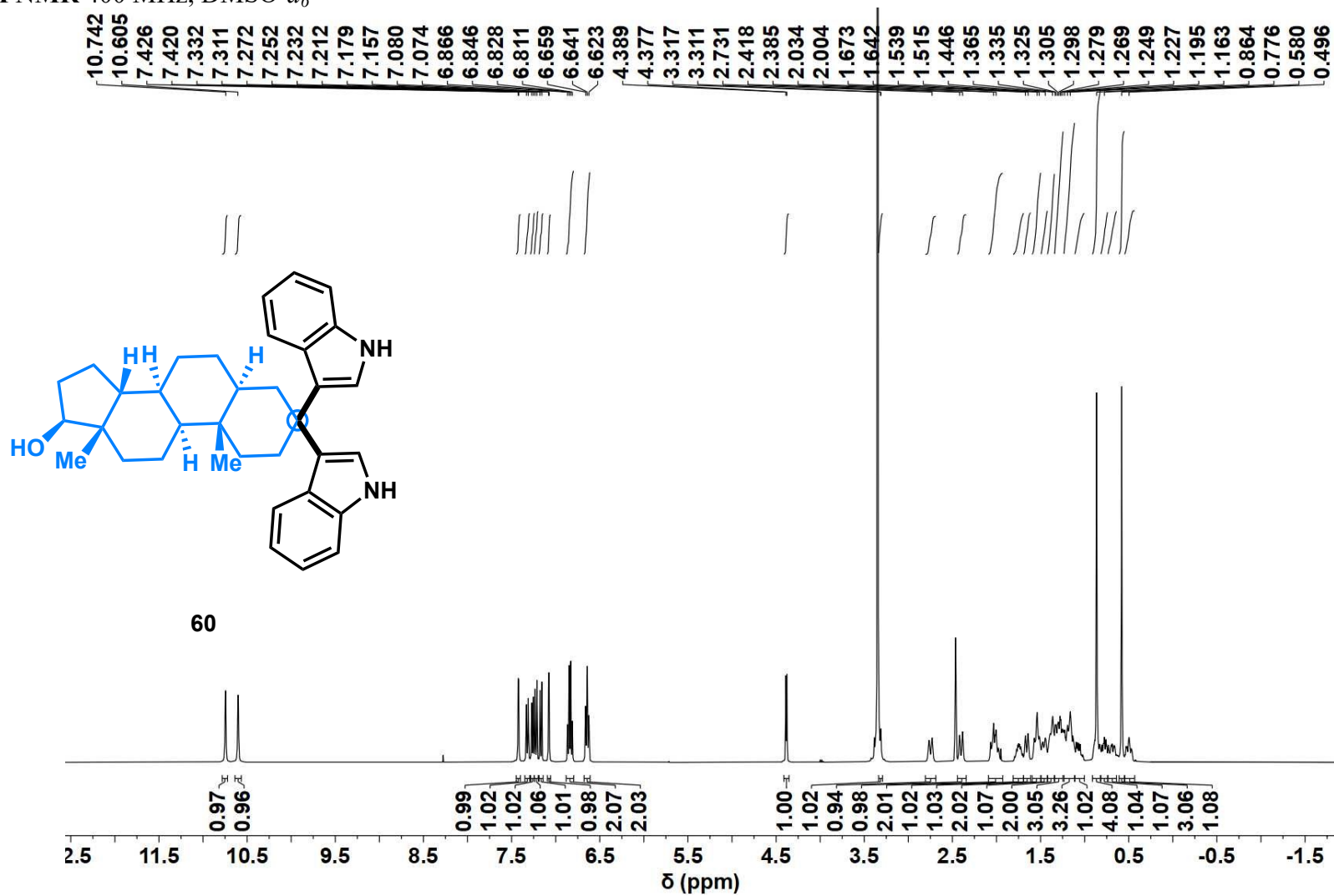
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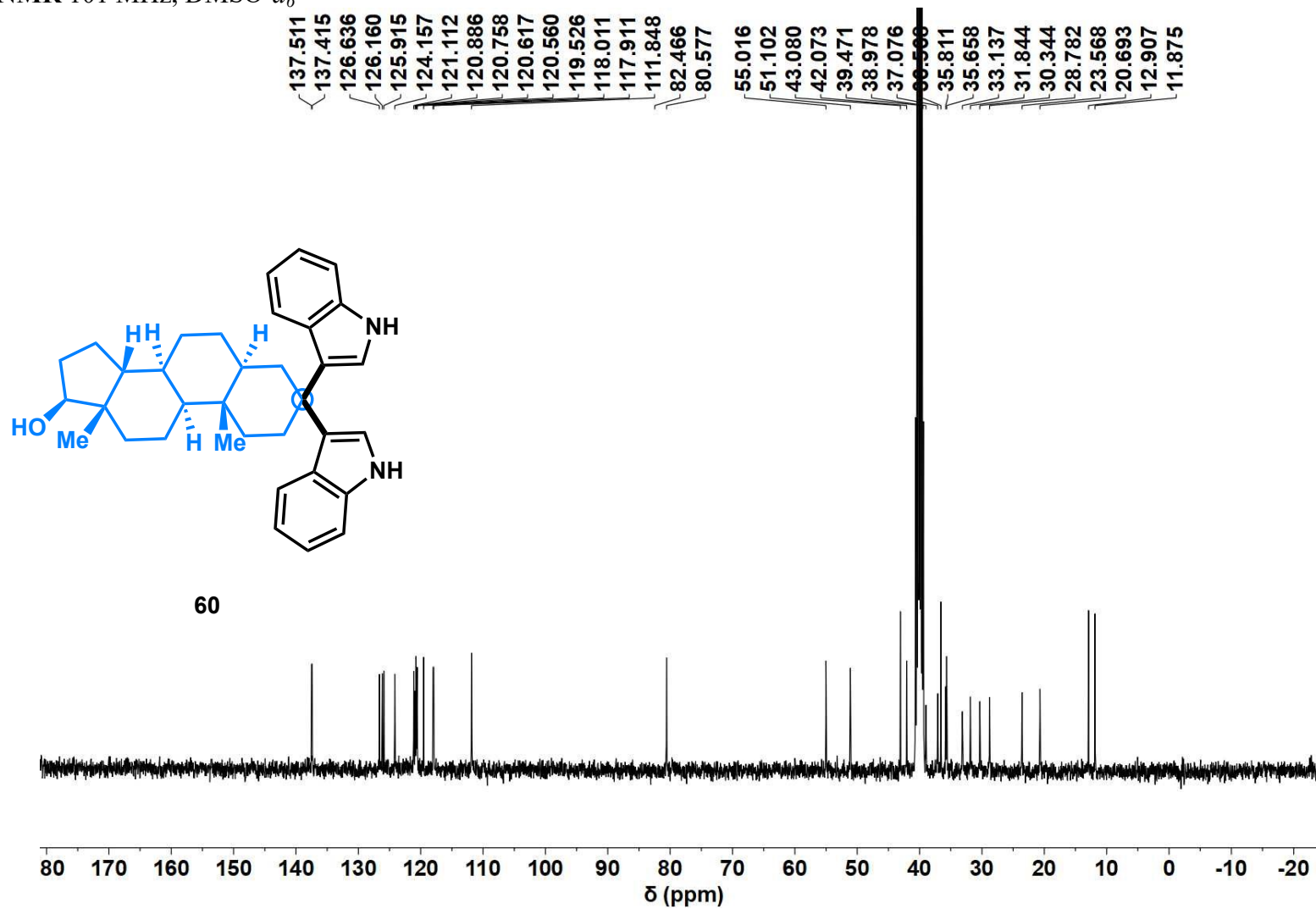
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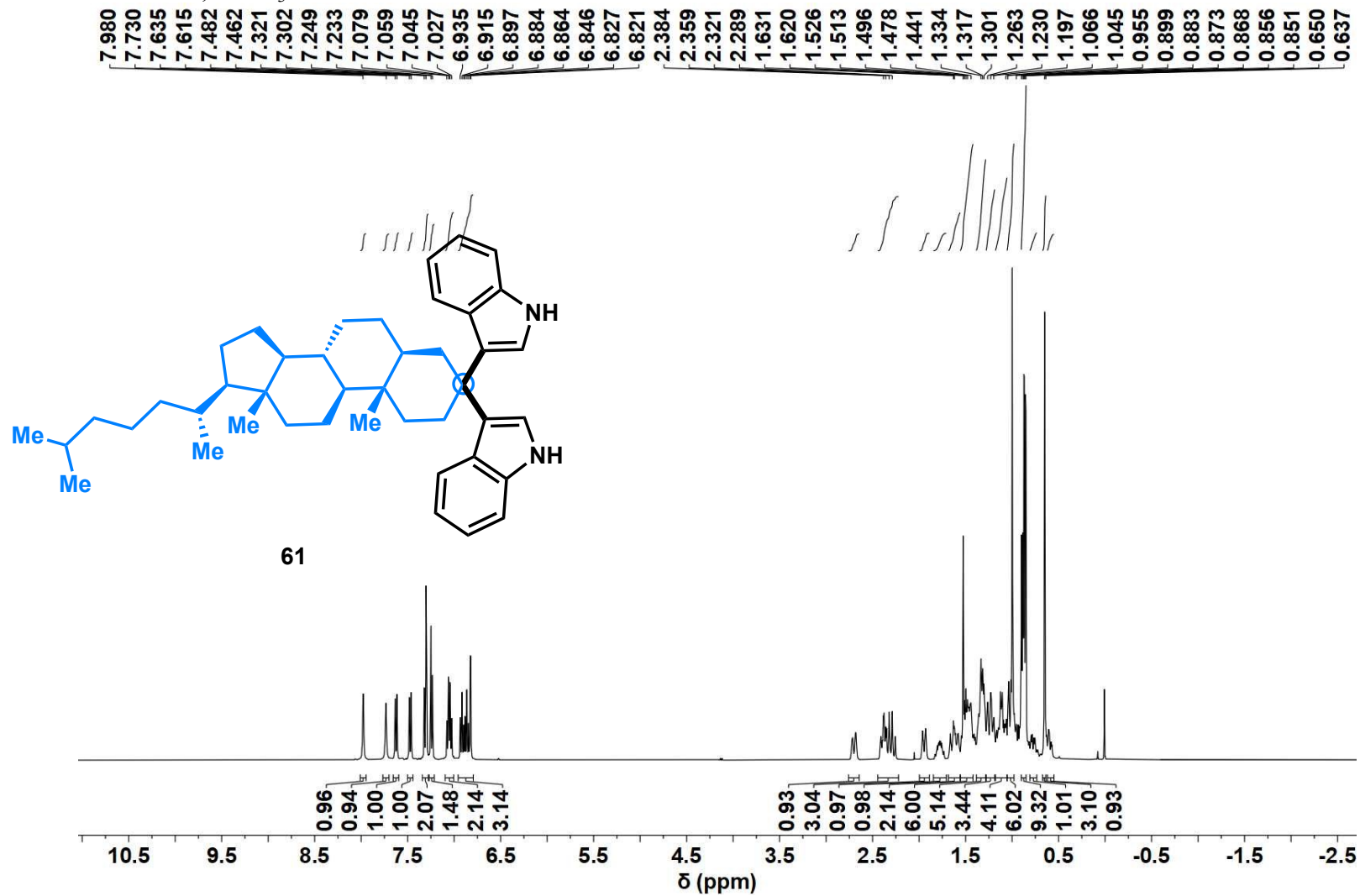
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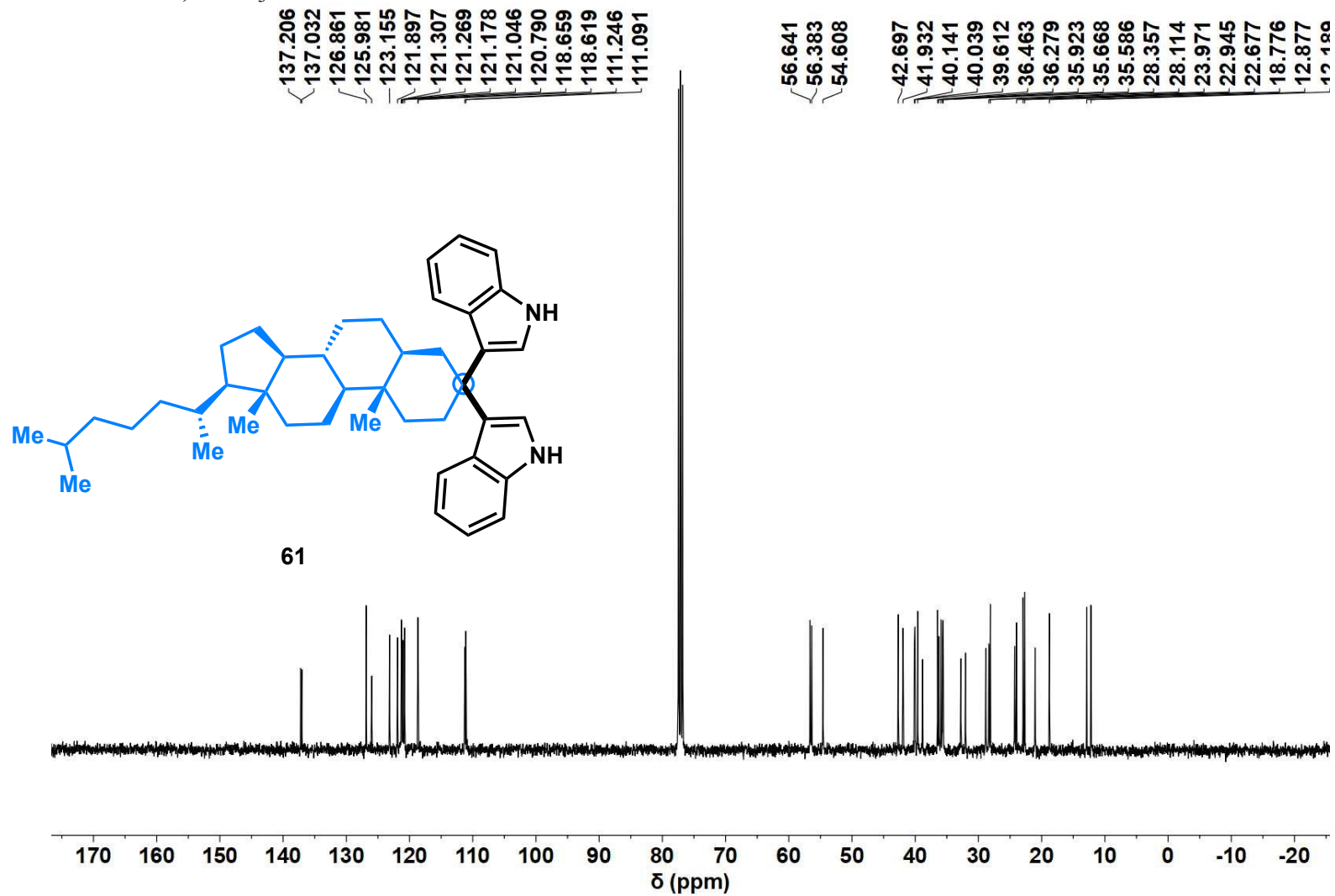
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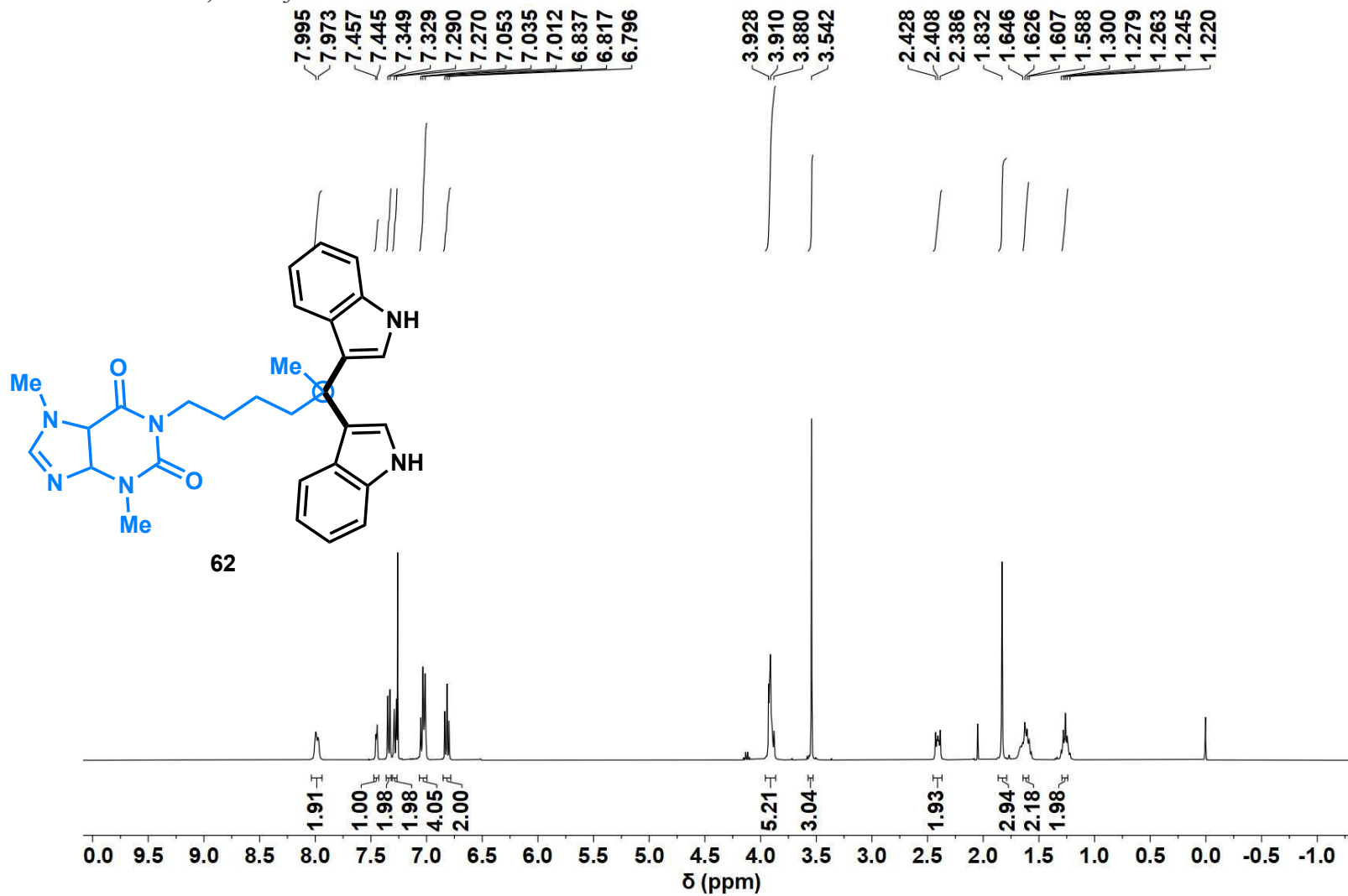
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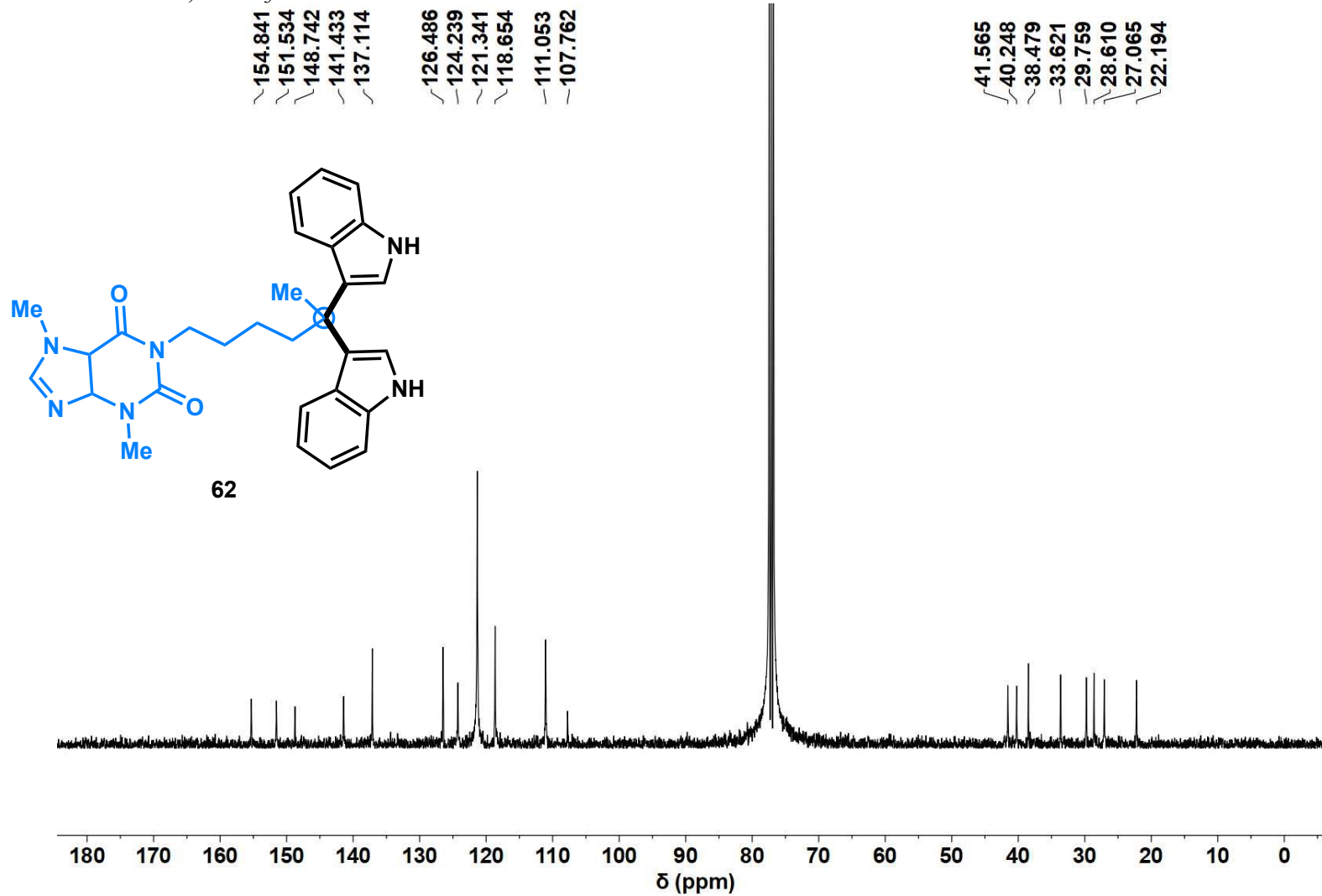
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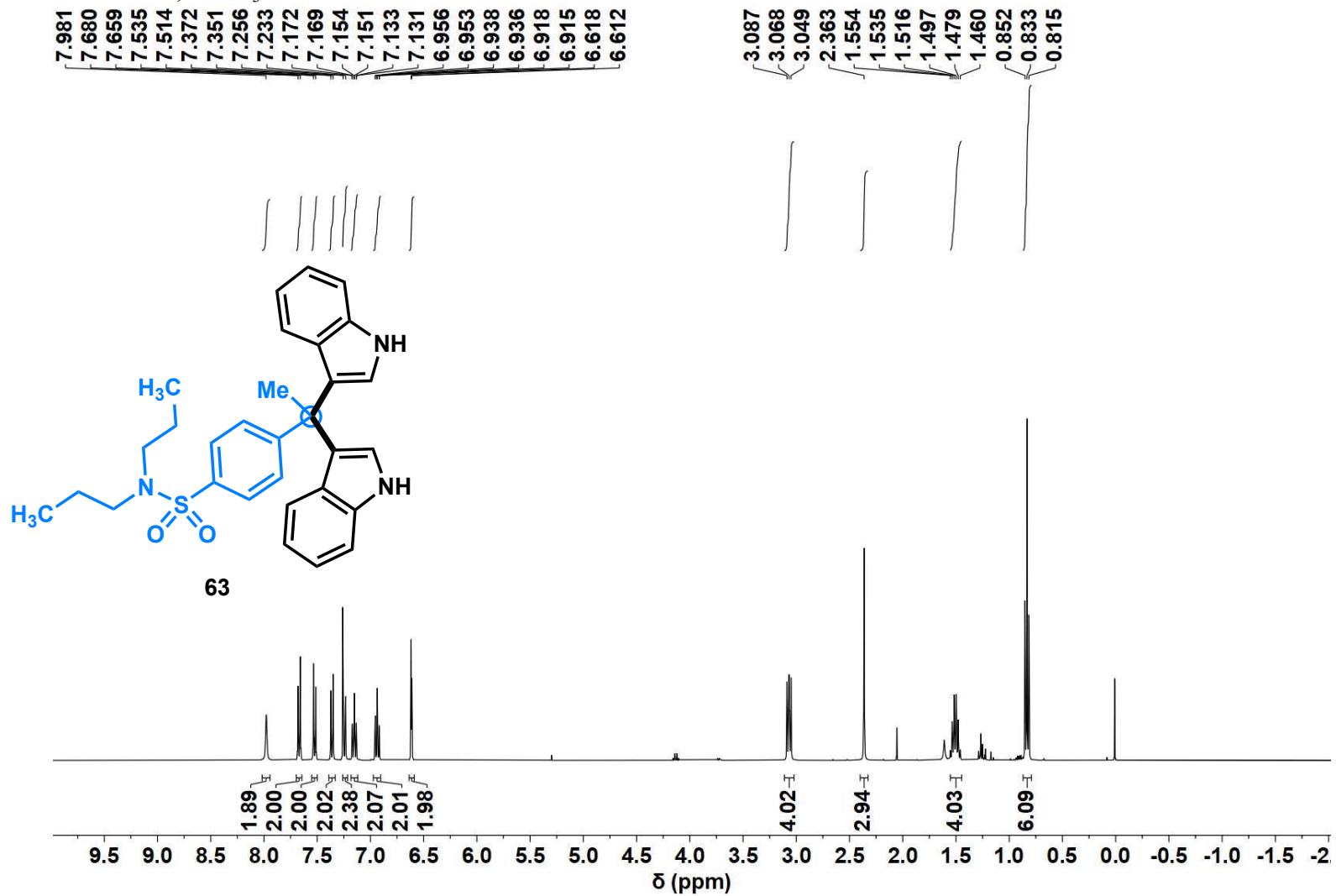
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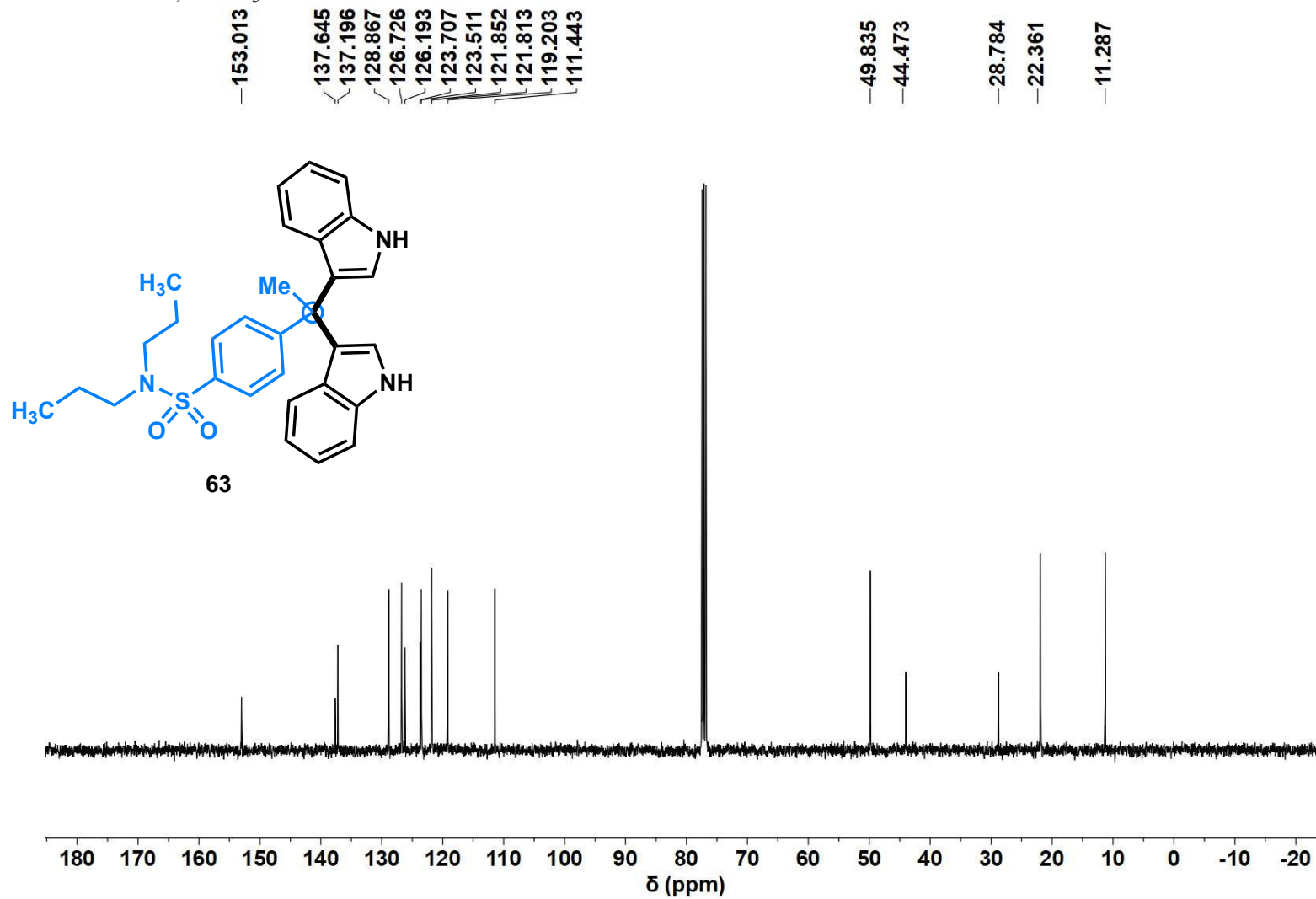
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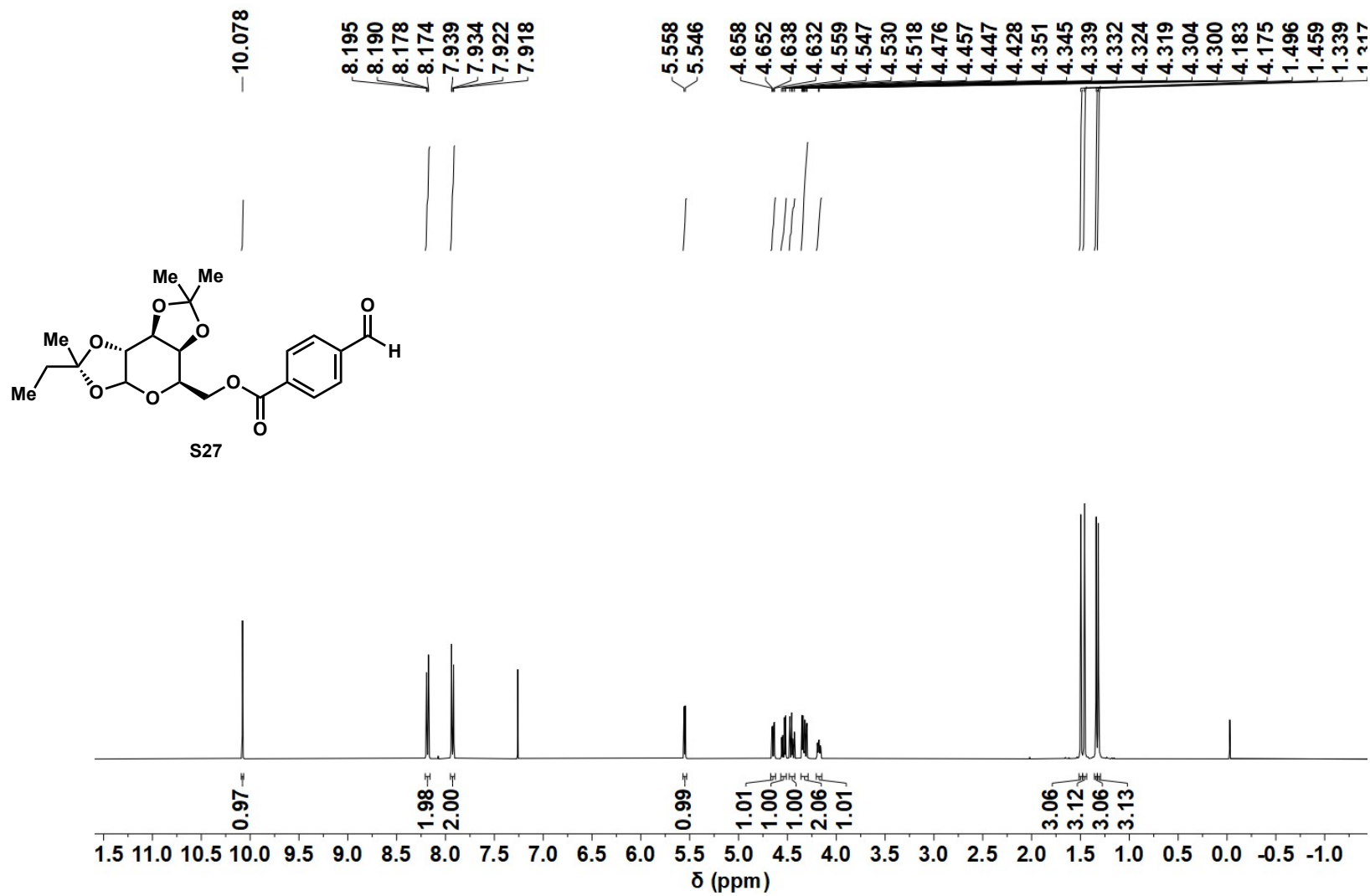
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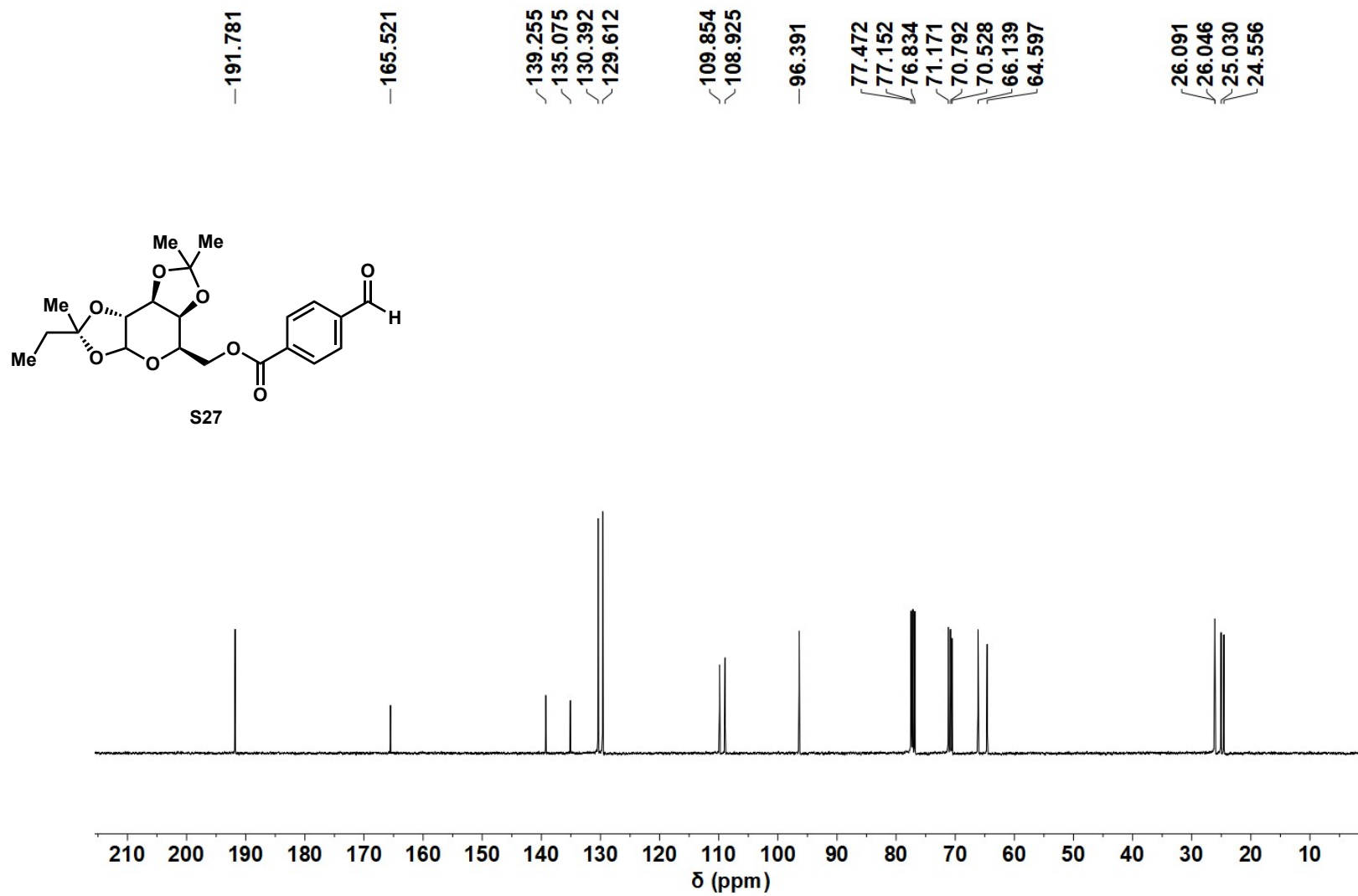
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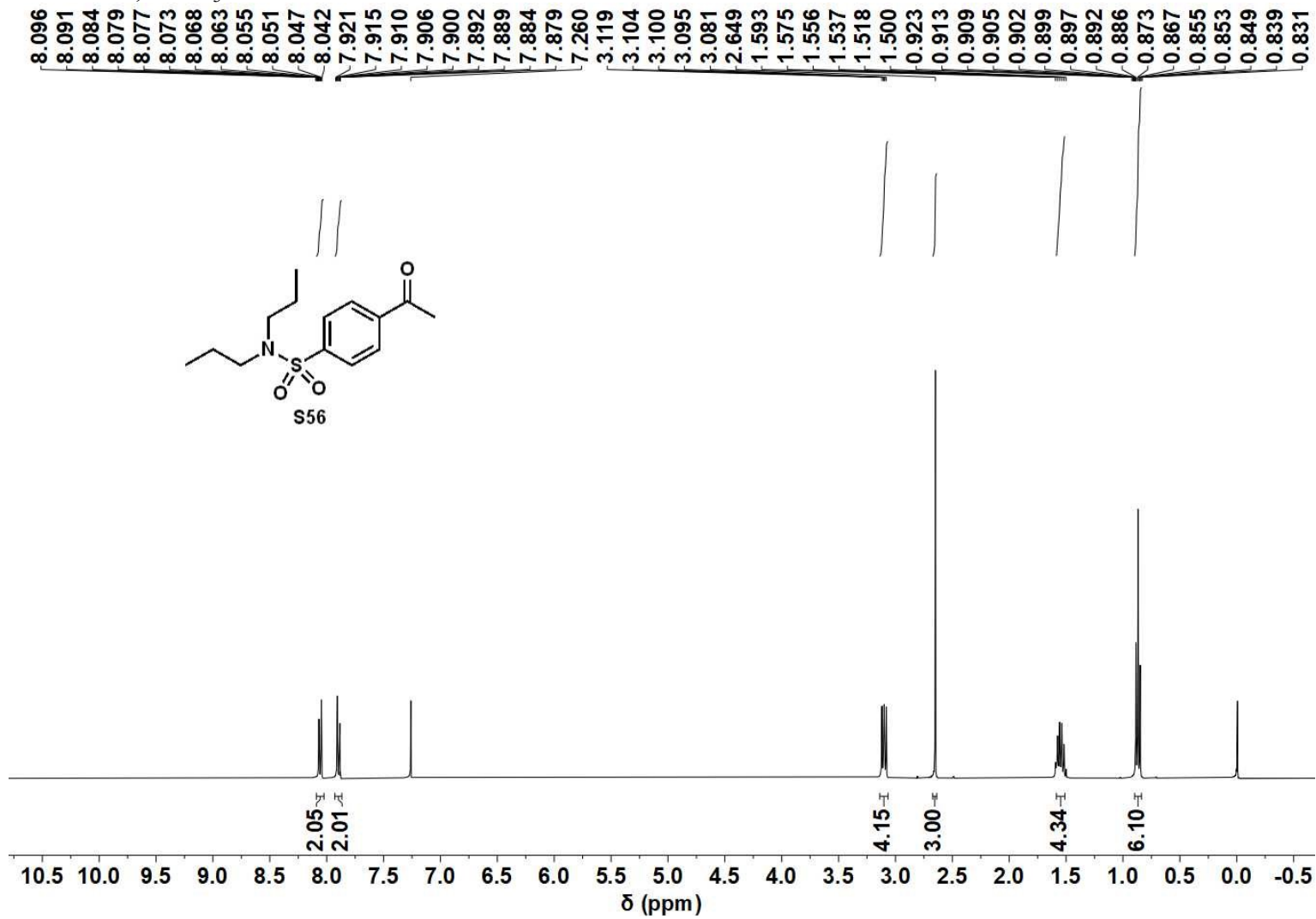
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¹³C NMR 100 MHz, CDCl₃



¹H NMR 400 MHz, CDCl₃



^{13}C NMR 100 MHz, CDCl_3

—196.979

—144.318

—139.704

—128.958

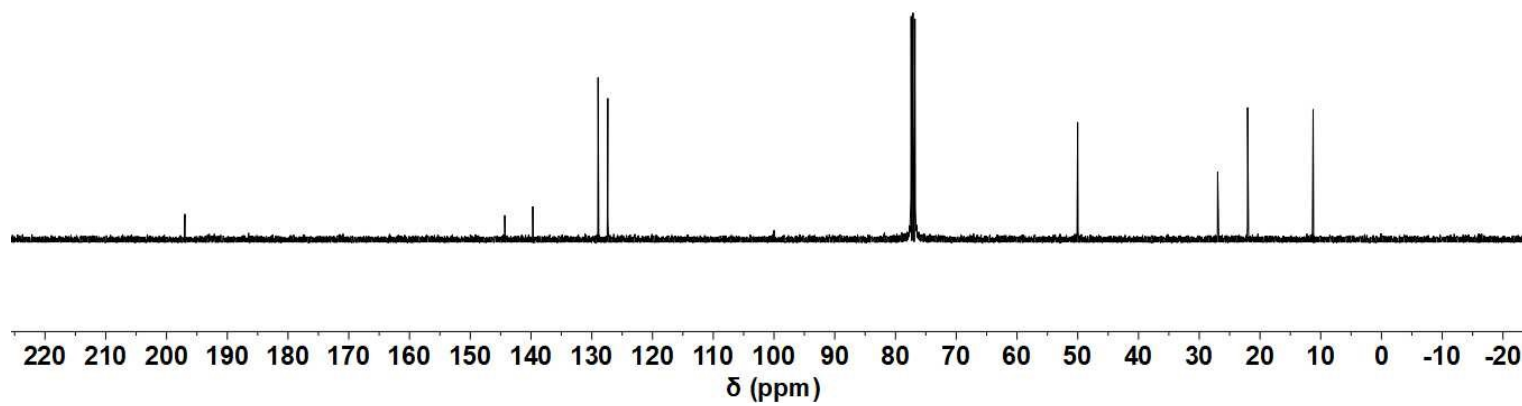
—127.361

—50.015

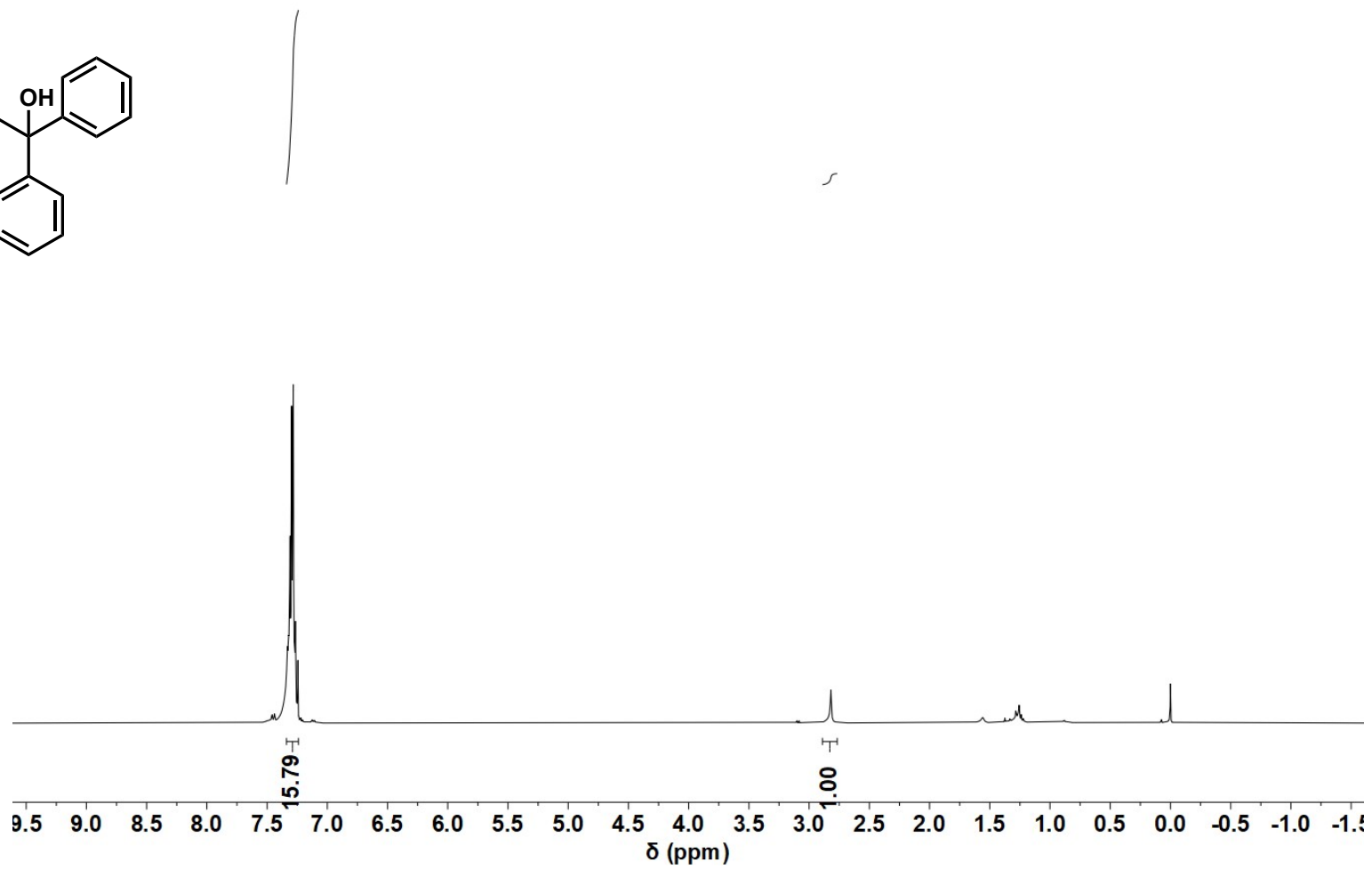
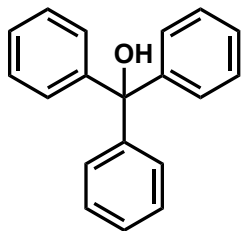
—26.965

—22.035

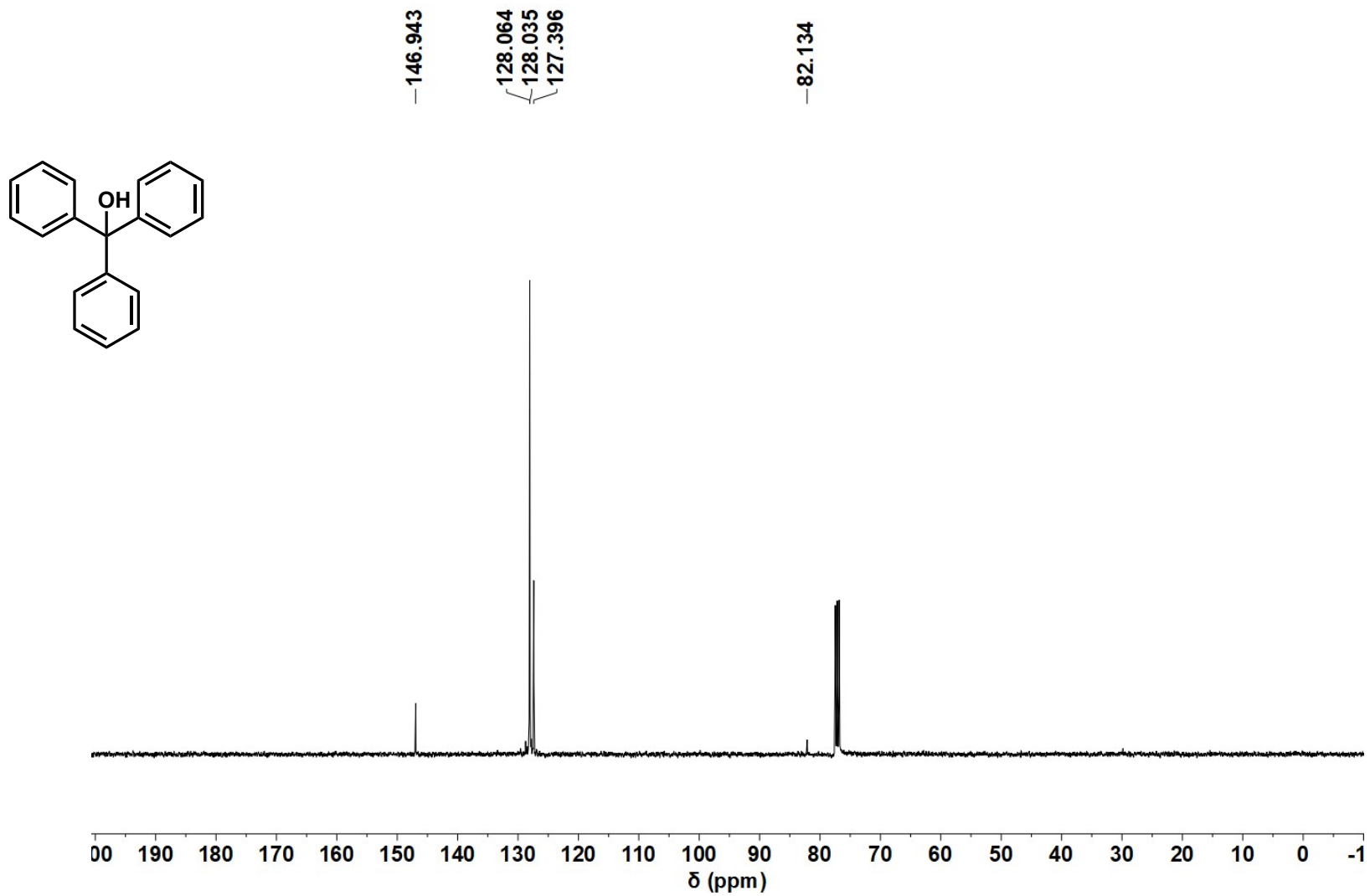
—11.252



^1H NMR 400 MHz, CDCl_3



^{13}C NMR 100 MHz, CDCl_3



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