Brønsted Acid Controlled Selective Site-Activation of Isatins with Enaminones: Divergent Cascade One-Pot Synthesis of Pyrrolo[3,4-c]quinolin-1-ones and Spirooxindoles

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Supporting Information

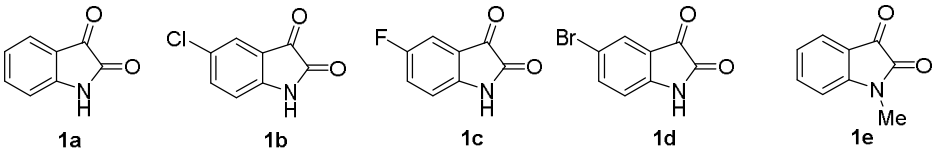
Content

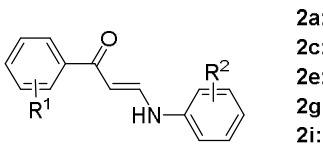
1. General Information

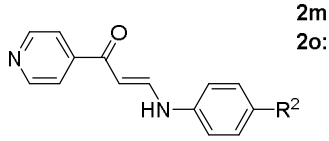
All compounds were fully characterized by spectroscopic data. The NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), Bruker DRX500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) and Bruker DRX500 (^{1}H: 600 MHz, ^{13}C: 150 MHz), chemical shifts (δ) are expressed in ppm, and J values are given in Hz, and deuterated $CDCl_3$, Acetone-d_6 and DMSO-d_6 were used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF_{254}. The melting points were determined on XT-4A melting point apparatus and are uncorrected. HRMs were performed on a Agilent LC/MS TOF instrument.

All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh).

The material **1a–d** was purchased from Aldrich Corporation Limited. Compound **1e** were prepared according to the literature[1]. Compounds **2a–n** were prepared according to the literature[2].







2a: R^1 = 4-OMe, R^2 = 4-Me; **2b:** R^1 = 4-Me, R^2 = 4-F;
2c: R^1 = H, R^2 = 4-OMe; **2d:** R^1 = 4-OMe, R^2 = 4-Cl;
2e: R^1 = 4-Me, R^2 = 4-Cl; **2f:** R^1 = 4-Me, R^2 = H;
2g: R^1 = 4-F, R^2 = 4-OMe; **2h:** R^1 = H, R^2 = 2-Cl;
2i: R^1 = H, R^2 = 4-Me; **2j:** R^1 = H, R^2 = 4-Cl;
2k: R^1 = 2-Cl, R^2 = H; **2l:** R^1 = 4-Cl, R^2 = 4-F;
2m: R^1 = 4-NO_2, R^2 = 4-Me; **2n:** R^1 = 4-OMe, R^2 = 4-NO_2;
2o: R^1 = 2-Cl, R^2 = 4-NHAc;

2p: R^2 = OMe;
2q: R^2 = H

Fig. S1 the structures of **1** and **2**

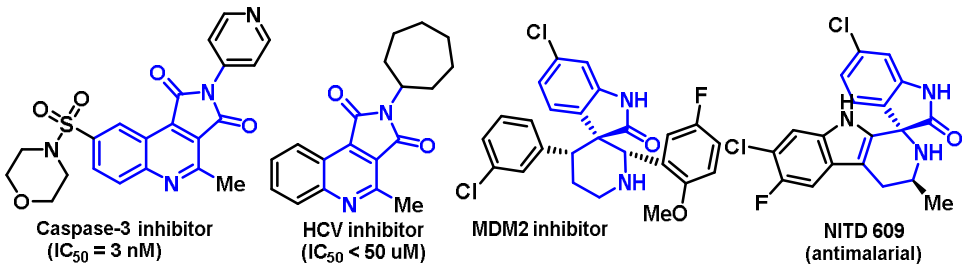
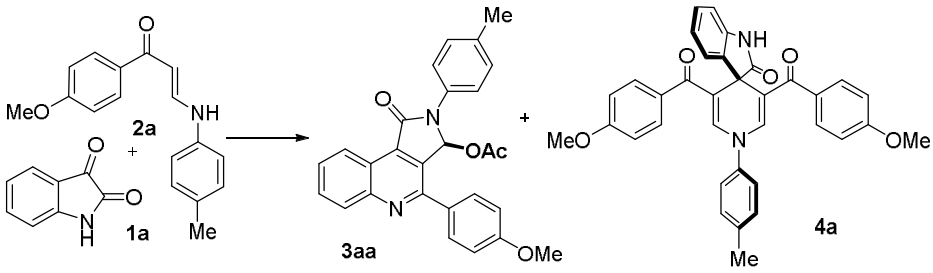


Fig. S2. Representative biologically active pyrroloquinolines and spirooxindoles.

2. Optimization of the reaction conditions

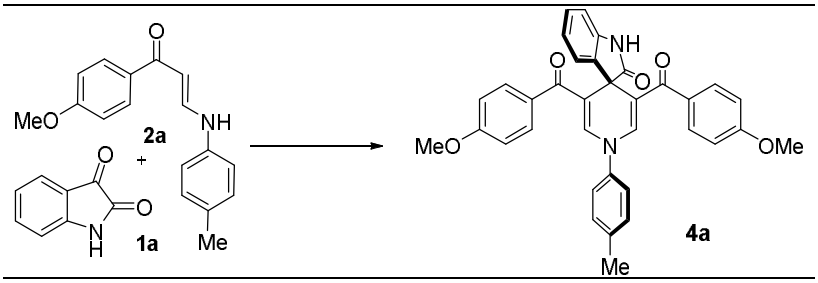
Table S1 Synthesis of 3-acetyl pyrroloquinolines:[a]



Entry	Solvent	Catalyst [equiv]	*T* [°C]	Time [h]	Yield [%][b]	
					3aa	**4a**
1	Toluene	AcOH (1.0)	110	2.0	14	17
2	Xylene	AcOH (1.0)	110	2.0	16	27
3	Acetonitrile	AcOH (1.0)	110	2.0	17	13
4	1,4-Dioxane	AcOH (1.0)	110	2.0	24	18
5	1,4-Dioxane	AcOH (3.0)	110	2.0	44	17
6	1,4-Dioxane	AcOH (5.0)	110	2.0	53	11
7	**1,4-Dioxane**	**AcOH (10.0)**	**110**	**2.0**	**65**	**trace**
8	1,4-Dioxane	AcOH (20.0)	110	2.0	57	trace
9	-	AcOH (30.0)	110	2.0	15	26
10	Xylene	Et_3N (1.0)	110	2.0	-	-
11	Xylene	Piperidine (1.0)	110	2.0	-	-
12	Xylene	K_2CO_3 (1.0)	110	2.0	-	-

[a]Reaction condition: isatin **1a** (0.5 mmol) and enaminone **2a** (0.5 mmol) in solvent (1.0 mL); [b]Isolated yield.

Table S2 Synthesis of spirooxindoles:[a]

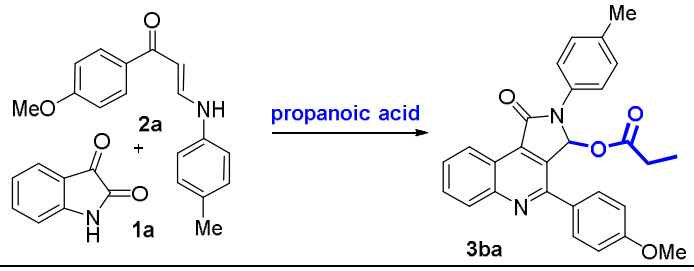


Entry	Solvent	Catalyst [equiv]	*T* [°C]	Time [h]	Yield [%][b]
1	Xylene	$ZnCl_2$ (1.0)	110	2.0	36
2	Xylene	LiCl (1.0)	110	2.0	25
3	Xylene	$FeCl_3$ (1.0)	110	2.0	26
4	Xylene	$CoCl_2$ (1.0)	110	2.0	30
5	Xylene	$NiCl_2$ (1.0)	110	2.0	23
6	Xylene	$CeCl_3$ (1.0)	110	2.0	34
7	Xylene	$CuSO_4$ (1.0)	110	2.0	19
8	Xylene	$MgBr_2$ (1.0)	110	2.0	26
9	Xylene	Oxone (1.0)	110	2.0	36
10	Xylene	$(NH_4)_2S_2O_8$ (1.0)	110	2.0	30
11	Xylene	$K_2S_2O_8$ (1.0)	110	2.0	38
12	Xylene	$Na_2S_2O_8$ (1.0)	110	2.0	31
13	Xylene	TBHP (1.0)	110	2.0	-
14	Xylene	CAN (1.0)	110	2.0	-
15	Xylene	$NaHSO_4$ (1.0)	110	2.0	36

16	Xylene	$KHSO_4$ (1.0)	110	2.0	43
16	Xylene	$KHSO_4$ (1.0)	110	8.0	64
17	Xylene	$KHSO_4$ (0.5)	110	8.0	47
18	Xylene	$KHSO_4$ (2.0)	110	8.0	73
19	Xylene	$KHSO_4$ (3.0)	110	8.0	72
20	Xylene	$KHSO_4$ (2.0)	120	8.0	79
21	**Xylene**	**$KHSO_4$ (2.0)**	**130**	**8.0**	**88**
22	Xylene	$KHSO_4$ (2.0)	140	8.0	87
23	Toluene	$KHSO_4$ (2.0)	130	8.0	76
24	1,4-Dioxane	$KHSO_4$ (2.0)	130	8.0	68

[a]Reaction condition: isatin **1a** (0.5 mmol), enaminone **2a** (1.0 mmol) and in solvent (1.0 mL); [b]Isolated yield.

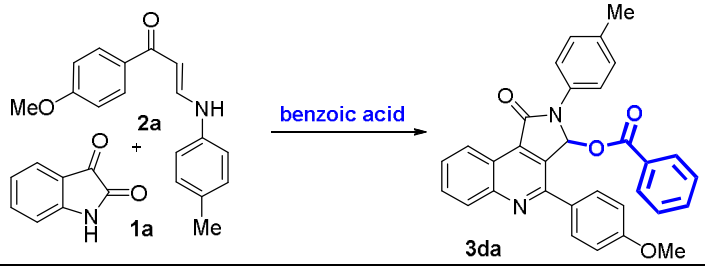
Table S3 Synthesis of 3-propionyl pyrroloquinolines:[a]



Entry	Solvent	propanoic acid [equiv]	*T* [°C]	Time [h]	Yield [%][b]
1	1,4-Dioxane	3.0	110	2.0	56
2	1,4-Dioxane	5.0	110	2.0	70
3	1,4-Dioxane	10.0	110	2.0	71
4	Toluene	5.0	110	2.0	62
5	Xylene	5.0	110	2.0	65

[a]Reaction condition: isatin **1a** (0.5 mmol) and enaminone **2a** (0.5 mmol) in solvent (1.0 mL); [b]Isolated yield.

Table S4 Synthesis of 3-benzoyl pyrroloquinolines:[a]

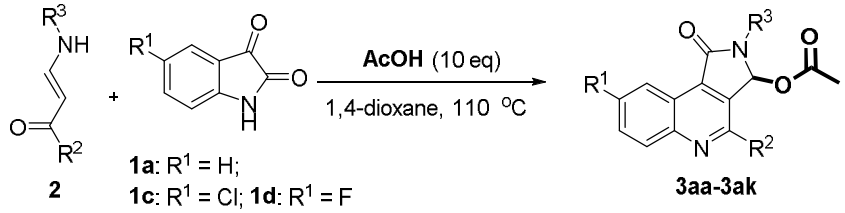


Entry	Solvent	benzonic acid [equiv]	*T* [°C]	Time [h]	Yield [%][b]
1	1,4-Dioxane	2.0	110	2.0	38
2	1,4-Dioxane	3.0	110	2.0	46
3	1,4-Dioxane	5.0	110	2.0	46
4	Toluene	3.0	110	2.0	49
5	Xylene	3.0	110	2.0	51
6	Xylene	3.0	120	2.0	56
7	Xylene	3.0	130	2.0	54

[a]Reaction condition: isatin **1a** (0.5 mmol) and enaminone **2a** (0.5 mmol) in solvent (1.0 mL); [b]Isolated yield.

3. General Procedure

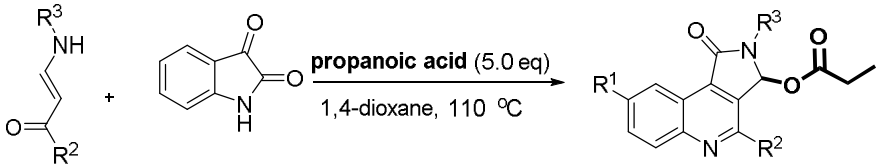
3.1 Synthesis of 3-acetoxy-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-ones.



2 **1a**: R^1 = H; **1c**: R^1 = Cl; **1d**: R^1 = F **3aa-3ak**

Isatins **1** (0.5 mmol), *N*-aryl enaminones **2** (0.5 mmol), acetic acid (10.0 equiv), and 1,4-dioxane (1.0 mL) were charged into a 10 mL ace glass pressure tube, and the mixture was stirred at 110 °C for 2.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3aa–3ak**.

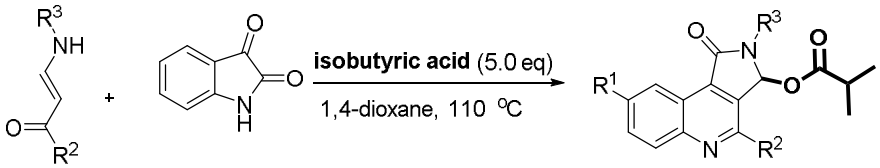
3.2 Synthesis of 3-propiony-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-ones.



2 **1a** **3ba-3be**

Isatin **1a** (0.5 mmol), *N*-aryl enaminones **2** (0.5 mmol), propanoic acid (5.0 equiv) and 1,4-dioxane (1.0 mL) were charged into a 10 mL ace glass pressure tube, and the mixture was stirred at 110 °C for 4.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3ba–3be**.

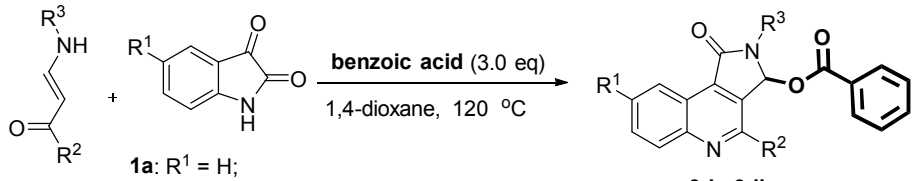
3.3 Synthesis of 3-isobutyra-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-ones.



2 **1a** **3ca-3cf**

Isatin **1a** (0.5 mmol), *N*-aryl enaminones **2** (0.5 mmol), isobutyric acid (5.0 equiv) and 1,4-dioxane (1.0 mL) were charged into a 10 mL ace glass pressure tube, and the mixture was stirred at 110 °C for 4.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3ca–3cf**.

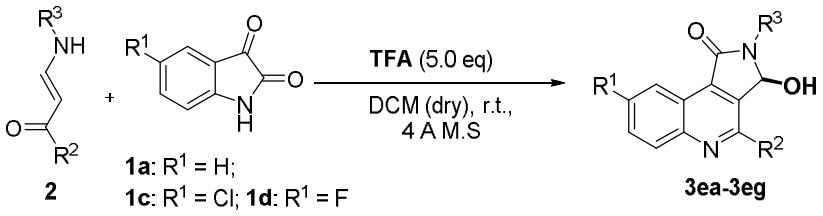
3.4 Synthesis of 3-benzoy-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-ones.



2 **1a**: R^1 = H; **1c**: R^1 = Cl; **1d**: R^1 = F **3da-3di**

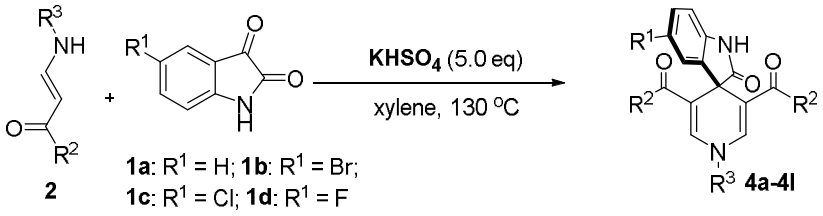
Isatins **1** (0.5 mmol), *N*-aryl enaminones **2** (0.5 mmol), benzoic acid (3.0 equiv) and xylene (1.0 mL) were charged into a 10 mL ace glass pressure tubes, and the mixture was stirred at 120 °C for 8.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3da–3di**.

3.5 Synthesis of 3-hydroxy-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-ones.



Isatins **1** (0.5 mmol), *N*-aryl enaminones **2** (0.5 mmol), trifluoroacetic acid (5.0 equiv), 4Å M.S. (30 mg), and freshly distilled dichloromethane (1.0 mL) were charged into a 10 mL ace glass pressure tube, and the mixture was stirred at room temperature for 2.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then dichloromethane (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3ea–3eg**.

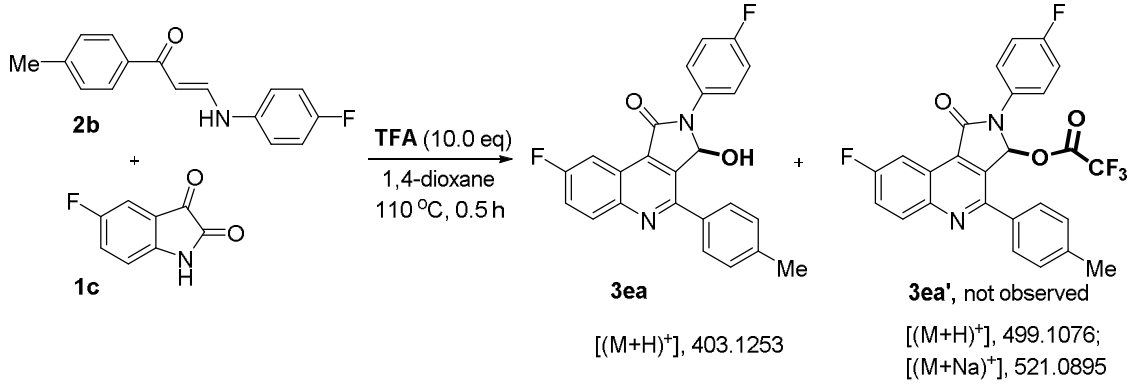
3.6 Synthesis of the symmetrical structure of spirooxindoles.



Isatins **1** (0.5 mmol), *N*-aryl enaminones **2** (1.0 mmol), $KHSO_4$ (2.0 equiv), and xylene (1.0 mL) were charged into a 10 mL ace glass pressure tube, and the mixture was stirred at 130 °C for 8.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **4a–4l**.

4. Additional experiments

4.1 The LC-MS analysis of the crude extract of **3ea.**



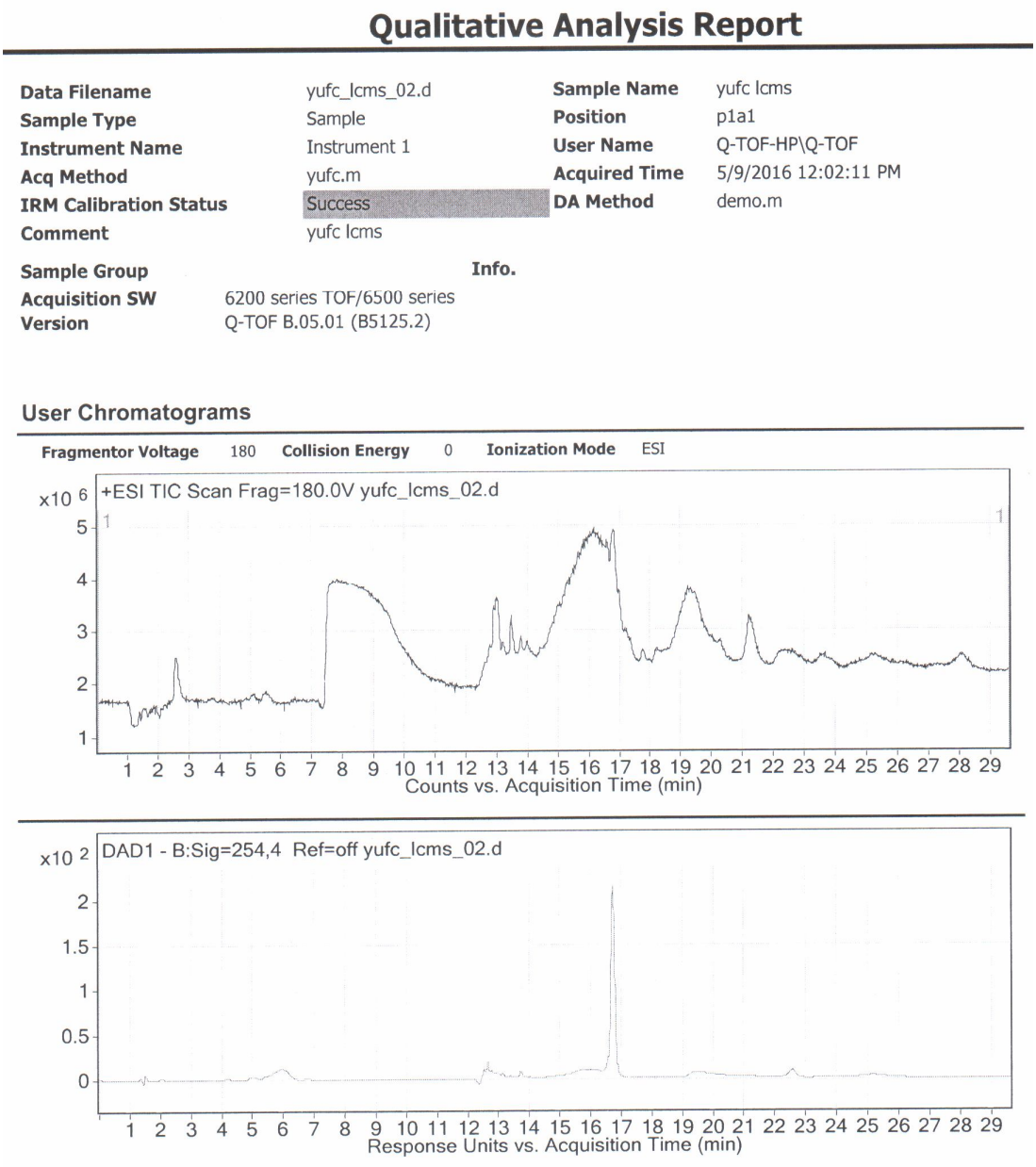
Trifluoroacetylation product **3ea′** was not observed in the crude extract of **3ea,** which has been tested through

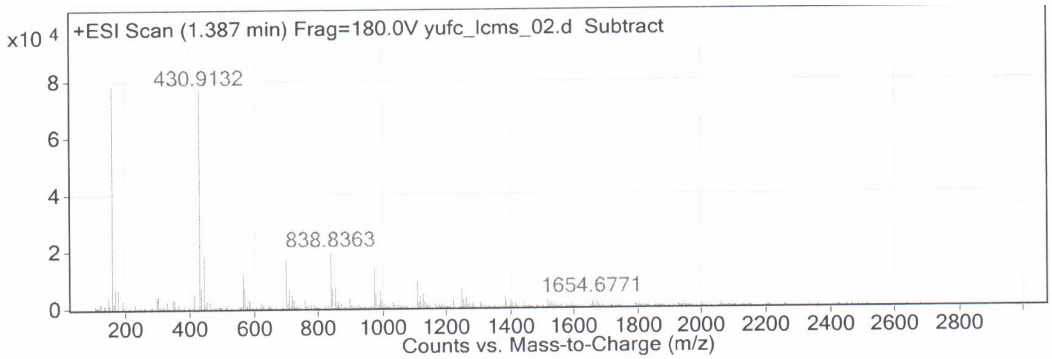
LC-MS. We found the molecular ion peak of **3ea** ([(M+H)$^+$], 403.1253; found, 403.1252) in the spectra, but not **3ea′** ([(M+H)$^+$], 499.1076 and [(M+Na)$^+$], 521.0895).

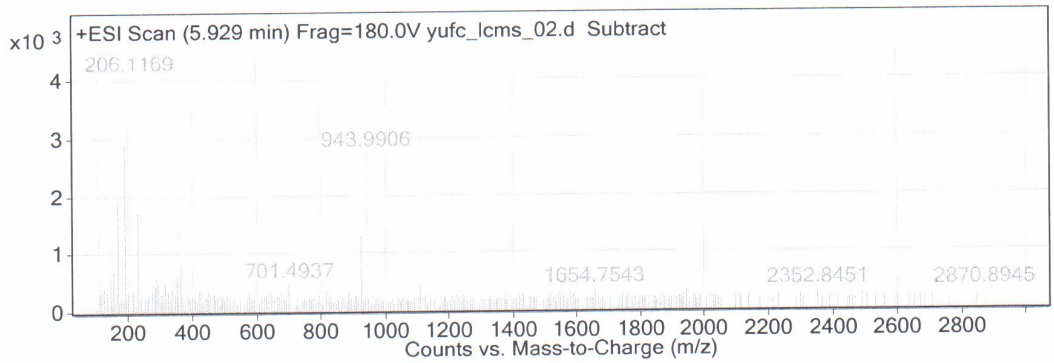
Operating Conditions :

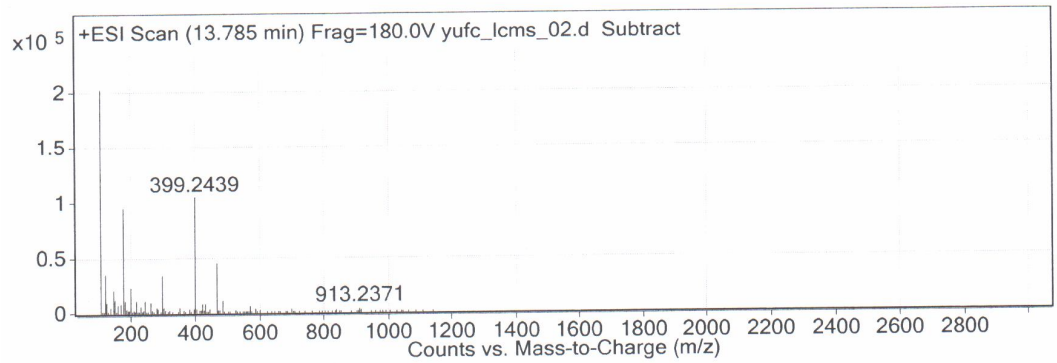
The LC-MS analysis was performed on an Agilent 1260-6530B LC/MS TOF instrument. All organic solvents were of high performance liquid chromatography (HPLC) grade and were obtained from Fisher (Suwanee, GA). Chromatographic separation was performed at 35 ^oC using a Zorbax SB-C18 column (5 µm particle size, 4.6×150 mm, Agilent) was used for the chromatographic separation. The injection volume was 10 µL. The HPLC mobile phase consists of H_2O (A) and MeOH (B). The equicontinuity conditions were: starting at 70% A and 30% B, changing linearly to 22% A and 78% B in 35 min. The detection wavelength was 254 nm.

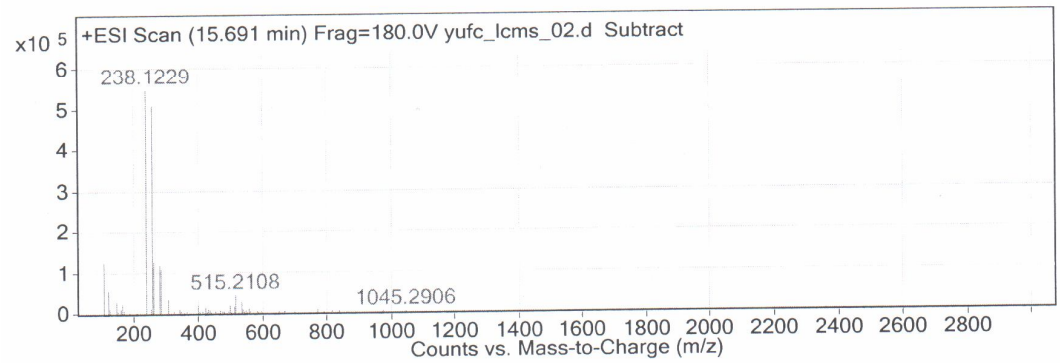
The ESI source worked in negative mode, and the operating parameters were as follows : drying gas (N_2) flow rate, 10.0 L/min; drying gas temperature, 350 °C; nebulizer, 40 psig; capillary, 4000 V; OCT RF V, 750 V; fragmentor voltage, 180 V; skimmer voltage, 65 V.

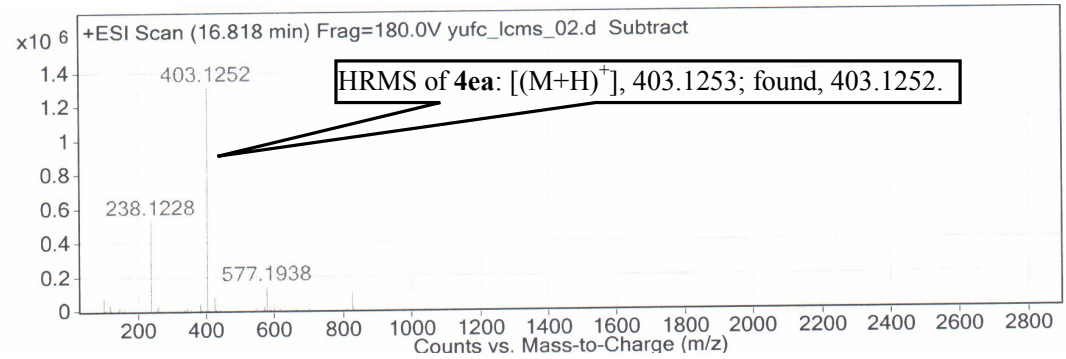












HRMS of **4ea**: [(M+H)$^+$], 403.1253; found, 403.1252.

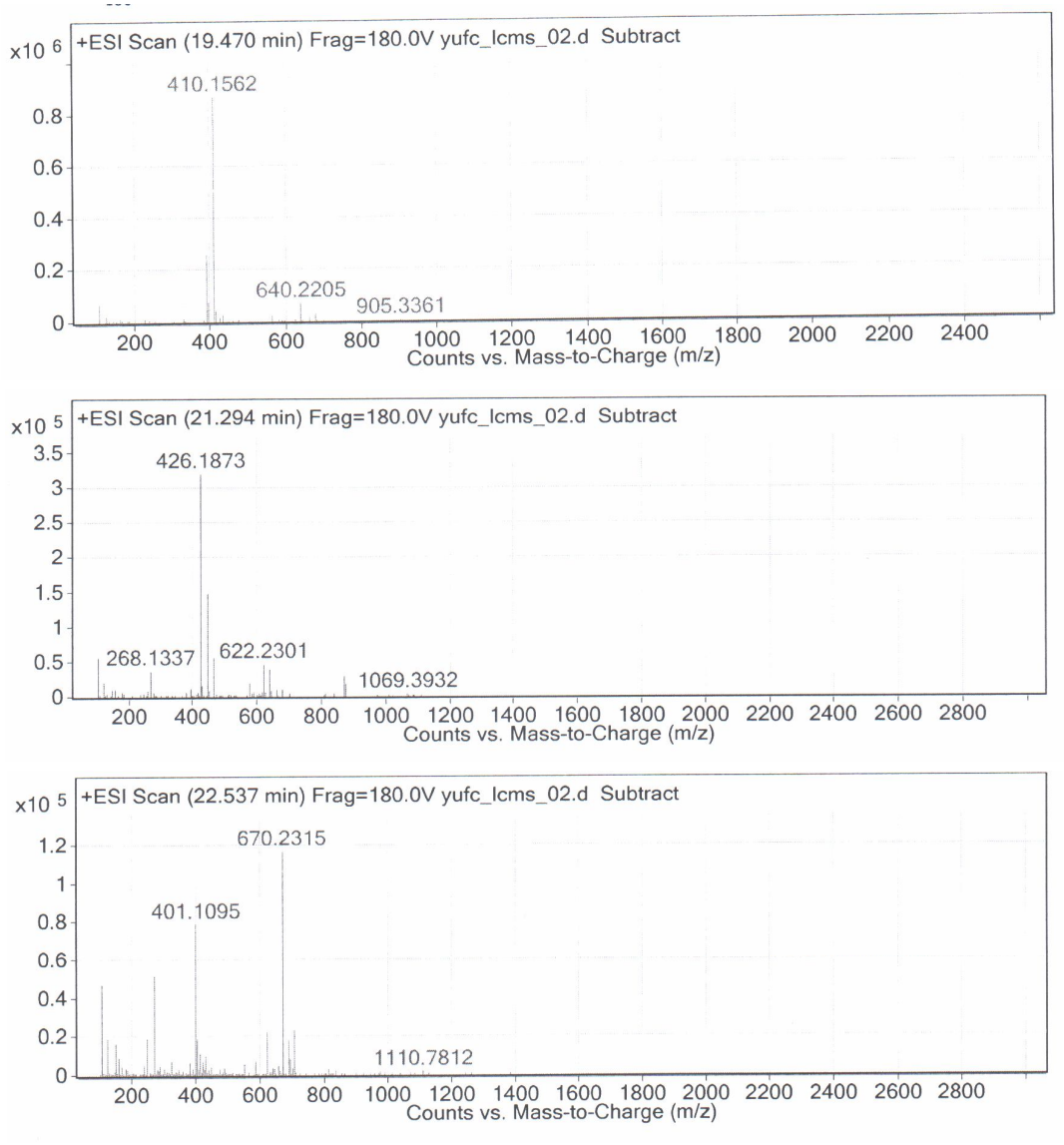
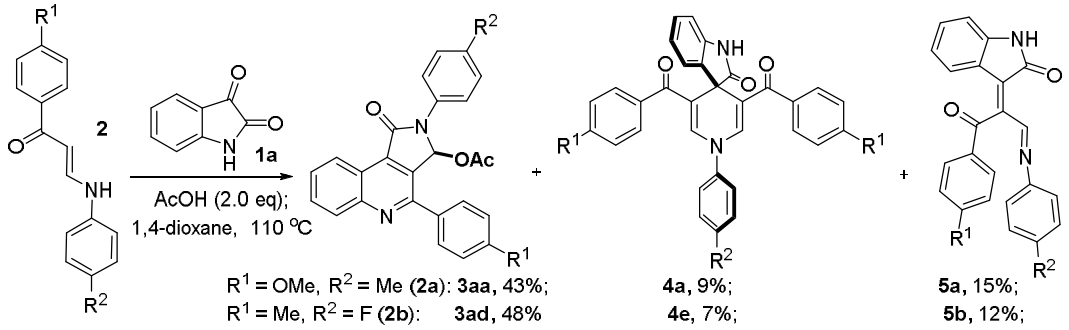


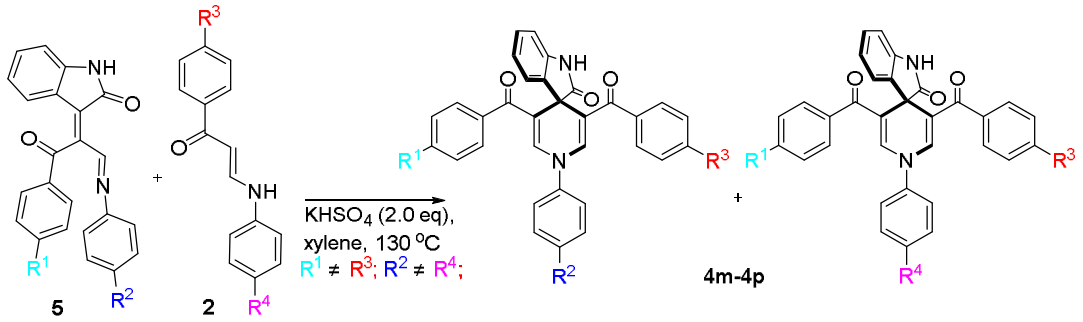
Fig. S3. LC-MS analysis of the crude extract of **3ea**.

4.1 Synthesis of intermediate 5.



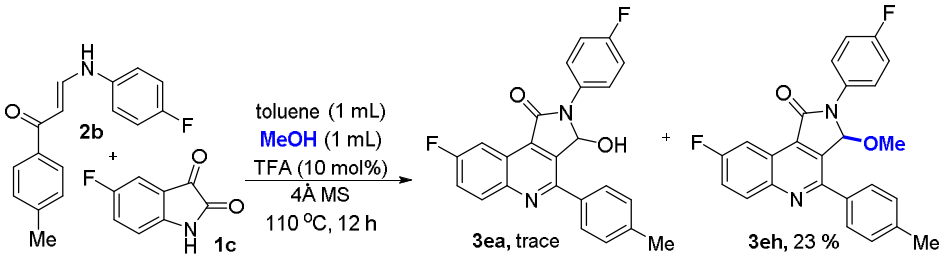
Isatin **1a** (2.0 mmol), *N*-Aryl enaminones **2a**/**2b** (2.0 mmol), acetic acid (2.0 equiv), and 1,4-dioxane (4.0 mL) were charged into a 25 mL round-bottom flask, and the mixture was stirred at 110 °C for 2.0 hours. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give **3aa** (43%)/**3ad** (48%), **4a** (9%)/**4e** (7%), and *α*,*β*-unsaturated 2-oxindoles **5a** (15%)/**5b** (12%).

4.2 Synthesis of the unsymmetrical structure of spirooxindoles.



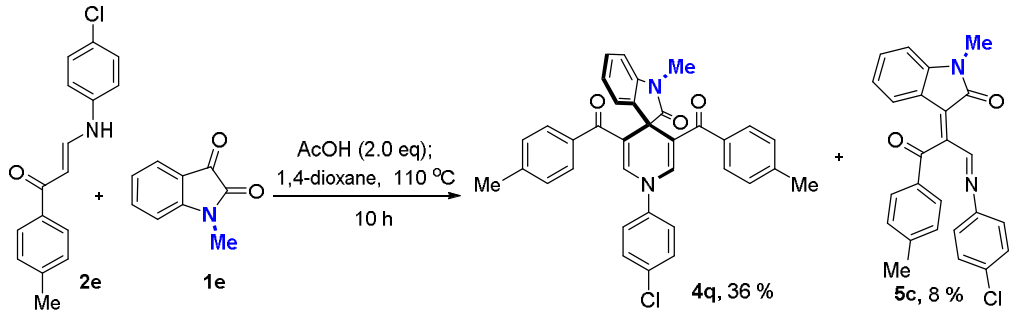
Pathway A: *α,β*-Unsaturated 2-oxindoles **5** (0.05 mmol), *N*-aryl enaminones **2** (0.05 mmol), $KHSO_4$ (2.0 equiv), and xylene (1.0 mL) were charged into a 5 mL ace glass pressure tube, and the mixture was stirred at 130 °C for 5.0 hours (followed by TLC). The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (5 mL × 2) were added. The organic phase was washed with water (5 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **4m–4p**.

4.3 Synthesis of 3-methoxyl-pyrrolo[3,4-*c*]quinolin-1-one 3el.



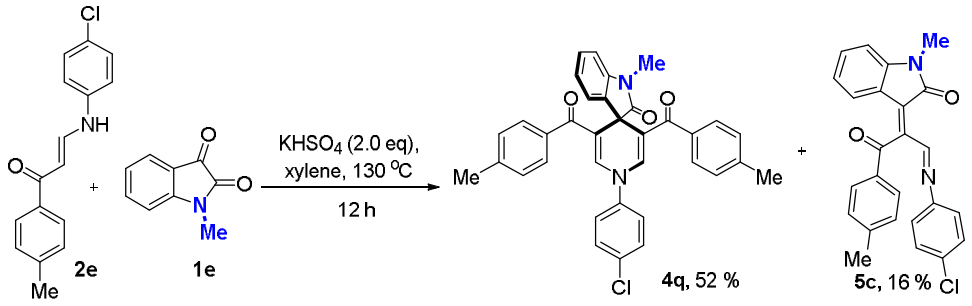
Isatins **1a** (1.0 mmol), *N*-aryl enaminones **2b** (1.0 mmol), trifluoroacetic acid (0.1 equiv), 4Å M.S. (60 mg), xylene (1.0 mL) and MeOH (1.0 mL) were charged into a 10 mL round-bottom flask, and the mixture was stirred at 110 °C for 12.0 hours. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then dichloromethane (15 mL × 2) were added. The organic phase was washed with water (10 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **3eh** (23%).

4.4 Procedures for N-methylisatin in cascade cyclizations experiment

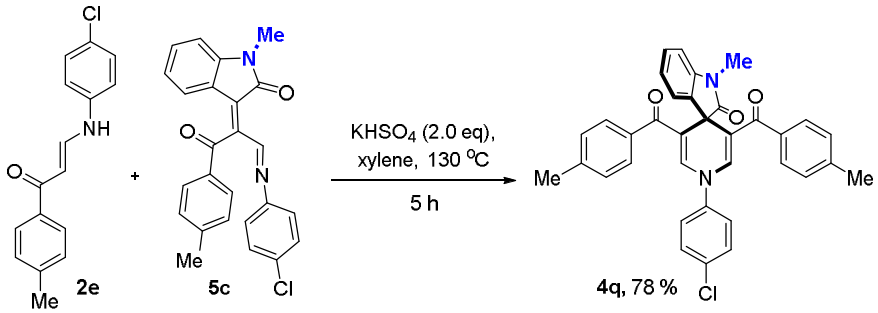


Pathway A: N-Methylisatin **1e** (1.0 mmol), *N*-Aryl enaminones **2e** (1.0 mmol), acetic acid (1.0 equiv), and 1,4-dioxane (4.0 mL) were charged into a 25 mL round-bottom flask, and the mixture was stirred at 110 °C for 10.0 hours. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over

Na_2SO_4, concentrated and purified by flash column chromatography to give **4q** (36%) and *α*,*β*-unsaturated 2-oxindoles **5c** (8%).



Pathway B: N-Methylisatin **1e** (1.0 mmol), *N*-aryl enaminones **2e** (1.0 mmol), $KHSO_4$ (2.0 equiv), and xylene (4.0 mL) were charged into a 25 mL round-bottom flask, and the mixture was stirred at 130 °C for 12.0 hours. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (30 mL × 2) were added. The organic phase was washed with water (20 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give **4q** (52%) and *α*,*β*-unsaturated 2-oxindoles **5c** (16%).

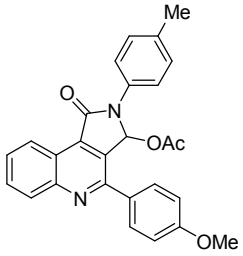


Pathway C: *N*-Aryl enaminones **2e** (0.05 mmol),*α*,*β*-unsaturated 2-oxindoles **5c** (0.05 mmol), $KHSO_4$ (2.0 equiv), and xylene (1.0 mL) were charged into a 5 mL ace glass pressure tube, and the mixture was stirred at 130 °C for 5.0 hours. The mixture was cooled to room temperature, neutralized with a saturated solution of Na_2CO_3 to pH 8–9, and then EtOAc (5 mL × 2) were added. The organic phase was washed with water (5 mL), dried over Na_2SO_4, concentrated and purified by flash column chromatography to give the product **4q** (78%).

5. Characterization of products

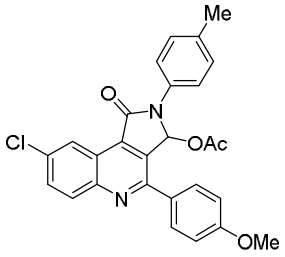
5.1 pyrrolo[3,4-*c*]quinolin-1-ones 3

4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3aa).



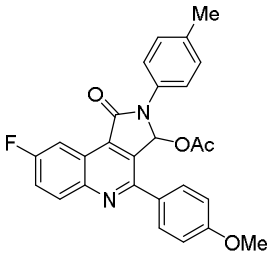
Pale yellow solid; mp 222.5–224.5 °C; IR (KBr): 3444, 1755, 1718, 1614, 1512, 1422, 1254, 1152, 1016, 894, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3H, $COCH_3$), 2.38 (s, 3H, $ArCH_3$), 3.88 (s, 3H, $ArOCH_3$), 7.03 (d, J = 8.8 Hz, 2H, ArH), 7.25 (d, J = 8.8 Hz, 2H, ArH), 7.43 (d, J = 8.0 Hz, 2H, ArH), 7.69–7.73 (m, 1H, ArH), 7.76 (d, J =8.8 Hz, 2H, ArH), 7.83–7.87 (m, 1H, ArH), 8.08 (s, 1H, C–CH–N), 8.26 (d, J = 8.4 Hz, 1H, ArH), 9.09 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 21.3, 55.6, 79.8, 114.4, 114.4, 122.1, 124.2, 125.4, 125.4, 128.5, 129.8, 130.0, 130.0, 130.1, 130.1, 130.5, 131.2, 132.2, 132.3, 136.0, 137.4, 149.8, 154.1, 160.9, 166.5, 169.6; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{23}N_2O_4$ [$(M+H)^+$], 439.1652; found, 439.1657.

8-chloro-4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ab).



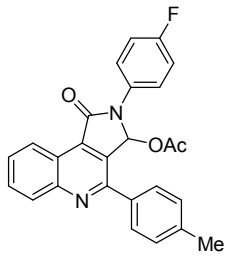
White solid; mp 233–234 °C; IR (KBr): 3445, 1755, 1705, 1605, 1506, 1254, 1173, 1016, 829, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 3H, $COCH_3$), 2.38 (s, 3H, $ArCH_3$), 3.88 (s, 3H, $ArOCH_3$), 7.03 (d, J = 8.8 Hz, 2H, ArH), 7.25 (d, J = 8.4 Hz, 2H, ArH), 7.42 (d, J = 8.4 Hz, 2H, ArH), 7.74–7.79 (m, 3H, ArH), 8.07 (s, 1H, C–CH–N), 8.17 (d, J = 9.2 Hz, 1H, ArH), 9.08 (d, J = 2.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 21.3, 55.6, 79.7, 114.4, 114.4, 122.5, 123.2, 125.3, 125.3, 130.0, 130.0, 130.1, 130.1, 130.1, 131.2, 132.1, 132.3, 133.1, 134.7, 135.3, 137.5, 148.1, 154.2, 161.0, 166.0, 169.6; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{22}ClN_2O_4$ [$(M+H)^+$], 473.1263; found, 473.1261.

8-fluoro-4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ac).



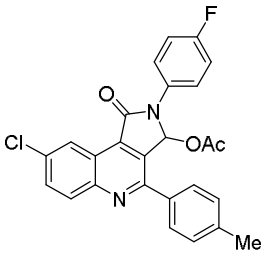
Pale yellow solid; mp 214–216 °C; IR (KBr): 3444, 1757, 1718, 1613, 1508, 1376, 1252, 1186, 1138, 1021, 834 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.57 (s, 3H, $COCH_3$), 2.38 (s, 3H, $ArCH_3$), 3.88 (s, 3H, $ArOCH_3$), 7.03 (d, J = 8.8 Hz, 2H, ArH), 7.25 (d, J = 8.0 Hz, 2H, ArH), 7.42 (d, J = 8.4 Hz, 2H, ArH), 7.59–7.64 (m, 1H, ArH), 7.74 (d, J =8.8 Hz, 2H, ArH), 8.07 (s, 1H, C–CH–N), 8.24 (dd, J = 9.2 Hz, 1H, ArH), 8.71 (dd, J = 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.2, 21.2, 55.6, 79.7, 107.9 (d, J = 23.8 Hz), 114.4, 114.4, 121.6 (d, J = 25.9 Hz), 122.8 (d, J = 11.7 Hz), 125.3, 125.3, 130.0, 130.0, 130.0, 130.0, 130.2, 132.1, 132.3 (d, J = 9.2 Hz), 133.0, 135.7 (d, J = 6.1 Hz), 137.5, 146.9, 153.3, 160.9, 161.8 (d, J = 249.9 Hz), 166.1, 169.6; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{22}FN_2O_4$ [$(M+H)^+$], 457.1558; found, 457.1559.

2-(4-fluorophenyl)-1-oxo-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ad).



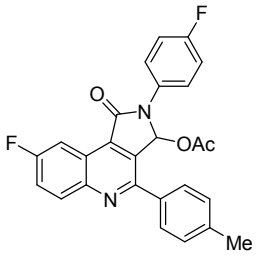
White solid; mp 183–184 °C; IR (KBr): 3445, 1754, 1720, 1512, 1385, 1224, 1153, 1013, 835, 779 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 3H, $COCH_3$), 2.43 (s, 3H, $ArCH_3$), 7.12–7.16 (m, 2H, ArH), 7.31–7.33 (m, 2H, ArH), 7.51–7.54 (m, 2H, ArH), 7.65–7.67 (m, 2H, ArH), 7.71–7.75 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 8.04 (s, 1H, C–CH–N), 8.27–8.29 (m, 1H, ArH), 9.06–9.08 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 21.7, 79.9, 116.4, 116.6, 122.3, 124.3, 127.6, 127.7, 128.7, 128.7, 129.0, 129.8, 129.8, 130.2, 131.0, 131.5, 132.6, 135.3, 135.8, 140.0, 150.0, 154.8, 161.8 (d, J = 245.8 Hz), 166.7, 169.9; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{20}FN_2O_3$ [$(M+H)^+$], 427.1452; found, 427.1452.

8-chloro-2-(4-fluorophenyl)-1-oxo-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ae).



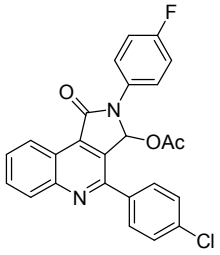
White solid; mp 271.5–273 °C; IR (KBr): 3442, 1755, 1706, 1593, 1512, 1223, 1180, 1157, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.52 (s, 3H, $COCH_3$), 2.43 (s, 3H, $ArCH_3$), 7.11–7.16 (m, 2H, ArH), 7.30–7.32 (m, 2H, ArH), 7.49–7.53 (m, 2H, ArH), 7.64–7.66 (m, 2H, ArH), 7.77–7.80 (m, 1H, ArH), 8.04 (s, 1H, C–CH–N), 8.17–8.20 (m, 1H, ArH), 9.04–9.05 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 21.7, 79.8, 116.5, 116.7, 122.8, 123.3, 127.5, 127.6, 128.6, 128.6, 129.9, 129.9, 130.8, 131.5, 132.6, 133.4, 134.9, 135.1, 135.3, 140.3, 148.3, 154.9, 161.8 (d, J = 246.1 Hz), 166.2, 169.8; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{19}ClFN_2O_3$ [$(M+H)^+$], 461.1063; found, 461.1060.

8-fluoro-2-(4-fluorophenyl)-1-oxo-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3af).



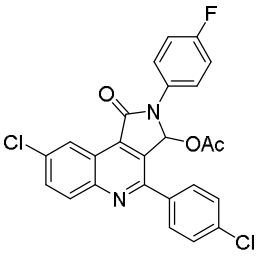
White solid; mp 215–216 °C; IR (KBr): 3444, 1760, 1722, 1620, 1508, 1373, 1192, 1134, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 3H, $COCH_3$), 2.43 (s, 3H, $ArCH_3$), 7.12–7.16 (m, 2H, ArH), 7.30–7.32 (m, 2H, ArH), 7.50–7.53 (m, 2H, ArH), 7.59–7.65 (m, 3H, ArH), 8.03 (s, 1H, C–CH–N), 8.25–8.28 (m, 1H, ArH), 8.66–8.69 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1, 21.5, 79.6, 107.9 (d, J = 23.8 Hz), 116.3, 116.5, 121.8 (d, J = 26.0 Hz), 122.9 (d, J = 11.8 Hz), 127.4, 127.5, 128.4, 128.4, 129.7, 129.7, 130.3 (d, J = 2.9 Hz), 132.5 (d, J = 9.5 Hz), 133.2, 134.8, 135.3 (d, J = 6.2 Hz), 139.9, 147.0, 153.8 (d, J = 2.9 Hz), 161.6 (d, J = 246.0 Hz), 161.8 (d, J = 250.4 Hz), 166.2, 169.6; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{19}F_2N_2O_3$ [$(M+H)^+$], 445.1358; found, 445.1357.

4-(4-chlorophenyl)-2-(4-fluorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ag).



White solid; mp 200–201 °C; IR (KBr): 3443, 1510, 1387, 1221, 1151, 1094, 1015, 961, 895, 837, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.58 (s, 3H, $COCH_3$), 7.12–7.16 (m, 2H, ArH), 7.49–7.52 (m, 4H, ArH), 7.73–7.76 (m, 3H, ArH), 7.86–7.90 (m, 1H, ArH), 8.03 (s, 1H, C–CH–N), 8.26 (d, J = 8.4 Hz, 1H, ArH), 9.07 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 79.7, 116.5, 116.7, 122.5, 124.3, 127.6, 127.7, 129.4, 129.4, 129.4, 130.2, 130.2, 130.2, 130.9, 131.8, 132.3, 136.1, 136.2, 136.5, 149.9, 153.3, 161.8 (d, J = 246.1 Hz), 166.5, 169.8; HRMS (TOF ES^+): *m/z* calcd for $C_{25}H_{17}ClFN_2O_3$ [$(M+H)^+$], 447.0906; found, 447.0902.

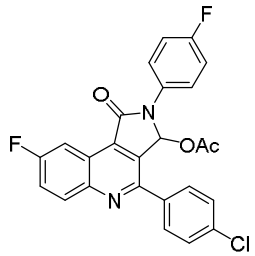
8-chloro-4-(4-chlorophenyl)-2-(4-fluorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ah).



White solid; mp 265–266 °C; IR (KBr): 3431, 1755, 1709, 1595, 1512, 1180, 1093, 1015, 831, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59 (s, 3H, $COCH_3$), 7.13–7.17 (m, 2H, ArH), 7.48–7.51 (m, 4H, ArH), 7.73–7.75 (m, 2H, ArH), 7.79–7.81 (m, 1H, ArH), 8.04 (s, 1H, C–CH–N), 8.17–8.19 (m, 1H, ArH), 9.05–9.06

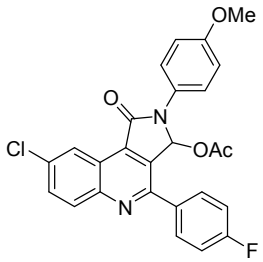
(m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 79.6, 116.6, 116.8, 122.9, 123.3, 127.5, 127.6, 129.5, 129.5, 130.2, 130.2, 130.7, 131.6, 132.9, 133.1, 135.4, 135.7, 136.1, 136.5, 148.3, 153.4, 161.9 (d, J = 246.4 Hz), 166.0, 169.8; HRMS (TOF ES$^+$): *m/z* calcd for $C_{25}H_{16}Cl_2FN_2O_3$ [(M+H)$^+$], 481.0517; found, 481.0509.

4-(4-chlorophenyl)-8-fluoro-2-(4-fluorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ai).



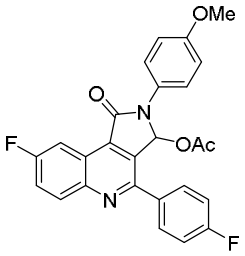
White solid; mp 208.5–210.5 °C; IR (KBr): 3444, 1754, 1711, 1511, 1409, 1224, 1195, 1016, 838, 779 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.60 (s, 3H, $COCH_3$), 7.36–7.41 (m, 2H, ArH), 7.64–7.68 (m, 4H, ArH), 7.90–7.96 (m, 3H, ArH), 8.31 (s, 1H, C–CH–N), 8.33–8.37 (m, 1H, ArH), 8.50–8.53 (m, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.6, 81.1, 107.5 (d, J = 23.6 Hz), 116.8, 117.0, 122.6, 122.9, 122.9 (d, J =20.7 Hz), 129.0, 129.1, 129.6, 129.6, 131.2, 131.2, 131.9, 133.6 (d, J = 9.5 Hz), 134.8, 135.4 (d, J = 6.0 Hz), 135.6, 136.8, 146.9, 153.0, 160.8 (d, J = 353.0 Hz), 163.3 (d, J = 405.0 Hz), 166.3, 170.0; HRMS (TOF ES$^+$): *m/z* calcd for $C_{25}H_{16}ClF_2N_2O_3$ [(M+H)$^+$], 465.0812; found, 465.0808.

8-chloro-4-(4-fluorophenyl)-2-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3aj).



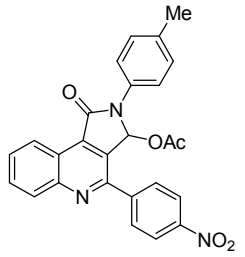
White solid; mp 224.5–226.5 °C; IR (KBr): 3442, 1751, 1714, 1600, 1517, 1153, 1126, 1181, 957, 835, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (s, 3H, $COCH_3$), 3.84 (s, 3H, $ArOCH_3$), 6.97 (d, J = 8.8 Hz, 2H, ArH), 7.21–7.23 (m, 2H, ArH), 7.40 (d, J = 8.8 Hz, 2H, ArH), 7.77–7.81 (m, 3H, ArH), 8.00 (s, 1H, C–CH–N), 8.19 (d, J = 8.8 Hz, 1H, ArH), 9.08–9.09 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.4, 55.8, 79.9, 115.0, 116.3 (d, J = 21.6 Hz), 123.0, 123.4, 127.4, 130.8 (d, J = 8.5 Hz), 131.5, 132.8, 133.3, 134.0, 135.5, 135.8, 148.3, 153.6, 159.2, 164.0 (d, J = 248.9 Hz), 166.1, 169.7; HRMS (TOF ES$^+$): *m/z* calcd for $C_{26}H_{19}ClFN_2O_4$ [(M+H)$^+$], 477.1012; found, 477.1028.

8-fluoro-4-(4-fluorophenyl)-2-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3ak).



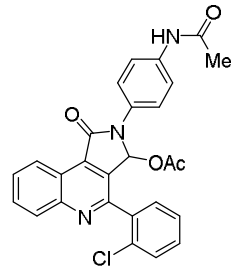
Pale yellow solid; mp 215.5–217 °C; IR (KBr): 3446, 1756, 1720, 1614, 1513, 1367, 1238, 1197, 1137, 1014, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.59 (s, 3H, $COCH_3$), 3.83 (s, 3H, $ArOCH_3$), 6.97 (d, J = 8.8 Hz, 2H, ArH), 7.19–7.23 (m, 2H, ArH), 7.40 (d, J = 8.8 Hz, 2H, ArH), 7.61–7.66 (m, 1H, ArH), 7.76–7.80 (m, 2H, ArH), 8.00 (s, 1H, C–CH–N), 8.24–8.28 (m, 1H, ArH), 8.70–8.73 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3, 55.8, 79.9, 108.2 (d, J = 23.9 Hz), 115.0, 116.3 (d, J = 21.6 Hz), 122.2 (d, J = 26.0 Hz), 123.2, 123.4, 127.5, 130.8 (d, J = 8.4 Hz), 132.6 (d, J = 9.3 Hz), 133.2, 134.1, 136.2 (d, J = 6.1 Hz), 147.1, 152.8, 159.2, 162.3 (d, J = 250.6 Hz), 163.9 (d, J = 248.5 Hz), 166.3, 169.7; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{19}F_2N_2O_4$ $[(M+H)^+]$, 461.1307; found, 461.1305.

4-(4-nitrophenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3al).



White solid; mp 250–252 °C; IR (KBr): 2962, 1717, 1514, 1363, 1149, 1011, 959, 856, 740, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 1.63 (s, 3H, C–CH_3), 2.43 (s, 3H, $ArCH_3$), 7.30 (d, J = 9.84 Hz, 2H, ArH), 7.45 (d, J = 10.02 Hz, 2H, ArH), 7.83–7.86 (m, 1H, ArH), 7.96–7.99 (m, 1H, ArH), 8.06 (d, J = 10.44 Hz, 2H, ArH), 8.14 (s, 1H, C–CH), 8.33–8.35 (m, 1H, ArH), 8.43 (d, J = 10.38 Hz, 2H, ArH), 9.18 (d, J = 9.84 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.5, 21.5, 79.6, 122.9, 124.3, 124.3, 124.6, 124.6, 125.5, 125.5, 130.0, 130.1, 130.1, 130.3, 130.4, 130.4, 132.1, 132.2, 132.4, 136.8, 138.0, 144.2, 148.8, 150.0, 152.0, 166.2, 169.7; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{20}N_3O_5$ $[(M+H)^+]$, 454.1397; found, 454.1401.

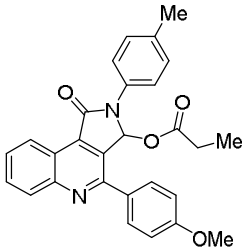
2-(4-acetamidophenyl)-4-(2-chlorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl acetate (3am).



Yellow solid; mp 254–256 °C; IR (KBr): 3358, 1754, 1697, 1515, 1152, 1076, 1007, 838, 794, 725, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3H, C–CH_3), 2.06 (s, 3H, C–CH_3), 7.44 (d, J = 10.26 Hz, 2H, ArH), 7.51–7.53 (m, 1H, ArH), 7.55–7.58 (m, 1H, ArH), 7.64–7.66 (m, 4H, ArH), 7.73 (s, 1H, C–CH), 7.91–7.94 (m,

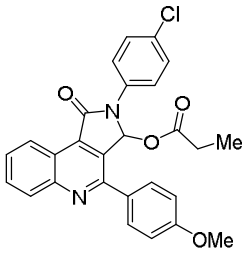
1H, ArH), 8.00–8.03 (m, 1H, ArH), 8.27 (d, J = 10.08 Hz, 1H, ArH), 8.98 (d, J = 9.72 Hz, 1H, ArH), 10.07 (s, 1H, NH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.5, 24.8, 80.0, 120.3, 120.3, 121.4, 122.6, 123.6, 124.0, 126.5, 126.5, 128.2, 130.4, 130.5, 130.6, 131.6, 131.8, 132.4, 134.6, 135.3, 136.8, 139.1, 149.4, 153.7, 166.3, 169.3, 169.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{27}H_{21}ClN_3O_4$ [(M+H)$^+$], 486.1215; found, 486.1220.

4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl propionate (3ba).



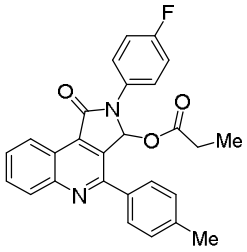
White solid; mp 211–212 °C; IR (KBr): 1751, 1719, 1610, 1514, 1390, 1295, 1249, 1178, 1128, 1077, 1030, 957, 885, 831, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66–0.70 (m, 3H, C–CH_3), 1.69–1.76 (m, 1H, C–CH_2–C), 1.85–1.89 (m, 1H, C–CH_2–C), 2.37 (s, 3H, $ArCH_3$), 3.87 (s, 3H, $ArOCH_3$), 7.01–7.04 (m, 2H, ArH), 7.23–7.26 (m, 2H, ArH), 7.43 (d, J = 8.4 Hz, 2H, ArH), 7.69–7.73 (m, 1H, ArH), 7.76 (d, J = 8.8 Hz, 2H, ArH), 7.83–7.87 (m, 1H, ArH), 8.13 (s, 1H, C–CH–N), 8.26 (d, J = 8.4 Hz, 1H, ArH), 9.10 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ =8.6, 21.3, 27.2, 55.6, 79.6, 114.3, 114.3, 122.1, 124.2, 125.4, 125.4, 128.5, 129.8, 130.30, 130.0, 130.1, 130.1, 130.5, 131.2, 132.2, 132.4, 136.0, 137.3, 149.7, 154.0, 160.9, 166.5, 173.1; HRMS (TOF ES$^+$): *m/z* calcd for $C_{28}H_{25}N_2O_4$ [(M+H)$^+$], 453.1809; found, 453.1809.

2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl propionate (3bb).



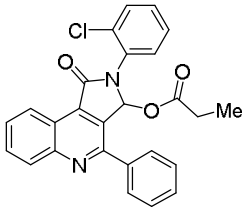
Yellow solid; mp 206–208 °C; IR (KBr): 1752, 1721, 1611, 1384, 1295, 1250, 1178, 1125, 1075, 1011, 955, 884, 834, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67–0.71 (m, 3H, C–CH_3), 1.69–1.75 (m, 1H, C–CH_2–C), 1.85–1.90 (m, 1H, C–CH_2–C), 3.87 (s, 3H, $ArOCH_3$), 7.03 (d, J = 6.8 Hz, 2H, ArH), 7.40–7.43 (m, 2H, ArH), 7.54–7.57 (m, 2H, ArH), 7.69–7.76 (m, 3H, ArH), 7.84–7.88 (m, 1H, ArH), 8.15 (s, 1H, C–CH–N), 8.26 (d, J = 8.4 Hz, 1H, ArH), 9.06 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6, 27.1, 55.6, 79.2, 114.4, 114.4, 121.9, 124.0, 126.2, 126.2, 128.6, 129.5, 129.5, 129.8, 130.1, 130.1, 130.4, 131.3, 132.3, 132.7, 133.5, 135.6, 149.8, 154.0, 160.9, 166.4, 173.2; HRMS (TOF ES$^+$): *m/z* calcd for $C_{27}H_{22}ClN_2O_4$ [(M+H)$^+$], 473.1263; found, 473.1262.

2-(4-fluorophenyl)-1-oxo-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl propionate (3bc).



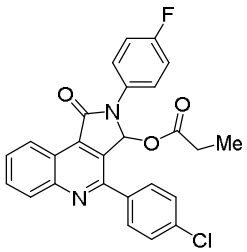
White solid; mp 170–171 °C; IR (KBr): 1747, 1722, 1509, 1386, 1222, 1151, 1065, 1004, 979, 886, 835, 822, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.64–0.68 (m, 3H, C–CH_3), 1.64–1.70 (m, 1H, C–CH_2–C), 1.82–1.88 (m, 1H, C–CH_2–C), 2.42 (s, 3H, ArCH_3), 7.11–7.16 (m, 2H, ArH), 7.31 (d, J = 8.0 Hz, 2H, ArH), 7.51–7.54 (m, 2H, ArH), 7.67 (d, J = 8.0 Hz, 2H, ArH), 7.70–7.74 (m, 1H, ArH), 7.85–7.88 (m, 1H, ArH), 8.09 (s, 1H, C–CH–N), 8.28 (d, J = 8.0 Hz, 1H, ArH), 9.07 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.5, 21.4, 27.1, 79.5, 116.3 (d, J = 22.5 Hz), 116.3 (d, J = 22.5 Hz), 122.1, 124.1, 127.4 (d, J = 8.5 Hz), 127.4 (d, J = 8.5 Hz), 128.5, 128.5, 128.7, 129.6, 129.6, 129.9, 130.8 (d, J = 3.1 Hz), 131.3, 132.5, 135.1, 135.5, 139.7, 149.8, 154.5, 161.5 (d, J = 245.8 Hz), 166.5, 173.1; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{22}FN_2O_3$ [$(M+H)^+$], 441.1609; found, 441.1610.

2-(2-chlorophenyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl propionate (3bd).



Yellow solid; mp 164–166 °C; IR (KBr): 1753, 1721, 1603, 1484, 1369, 1356, 1153, 1129, 1075, 1050, 1009, 981, 884, 768, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.64–0.68 (m, 3H, C–CH_3), 1.65–1.75 (m, 1H, C–CH_2–C), 1.81–1.91 (m, 1H, C–CH_2–C), 7.28–7.39 (m, 3H, ArH), 7.41–7.48 (m, 3H, ArH), 7.50–7.58 (m, 1H, ArH), 7.73–7.81 (m, 3H, ArH), 7.87–7.91 (m, 1H, ArH), 7.99 (s, 1H, C–CH–N), 8.31 (d, J = 8.4 Hz, 1H, ArH), 9.08 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.57, 27.0, 79.5, 122.4, 124.2, 127.9, 127.9, 128.5, 128.5, 128.5, 128.9, 129.0, 129.0, 129.5, 130.0, 130.5, 130.7, 131.4, 132.6, 133.2, 134.5, 135.4, 138.1, 149.8, 154.5, 173.0; HRMS (TOF ES^+): *m/z* calcd for $C_{26}H_{20}ClN_2O_3$ [$(M+H)^+$], 443.1157; found, 443.1159.

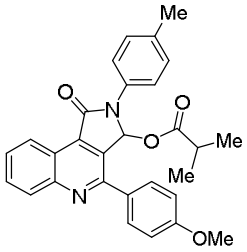
4-(4-chlorophenyl)-2-(4-fluorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl propionate (3be).



White solid; mp 192–193 °C; IR (KBr): 1595, 1512, 1493, 1386, 1226, 1155, 1131, 1099, 1079, 1013, 952, 885, 836, 826, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.68–0.72 (m, 3H, C–CH_3), 1.69–1.79 (m, 1H, C–CH_2–C), 1.85–1.92 (m, 1H, C–CH_2–C), 7.12–7.17 (m, 2H, ArH), 7.48–7.53 (m, 4H, ArH), 7.73–7.77 (m, 3H, ArH), 7.86–7.91 (m, 1H, ArH), 8.09 (s, 1H, C–CH–N), 8.27 (d, J = 8.4 Hz, 1H, ArH), 9.08 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.6, 27.1, 79.3, 116.4 (d, J = 22.8 Hz), 116.4 (d, J = 22.8 Hz), 122.3, 124.1, 127.4 (d, J = 8.4 Hz), 127.4 (d, J = 8.4 Hz), 129.2, 129.2, 129.9, 130.0, 130.0, 130.0, 130.7 (d, J = 3.0 Hz),

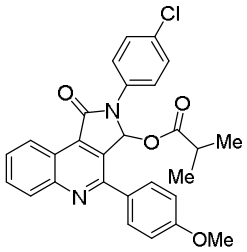
131.6, 132.2, 135.9, 136.0, 136.3, 149.7, 153.0, 161.6 (d, J = 246.0 Hz), 166.3, 173.2; HRMS (TOF ES$^+$): *m/z* calcd for $C_{26}H_{19}ClFN_2O_3$ [(M+H)$^+$], 461.1063; found, 461.1064.

4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3ca).



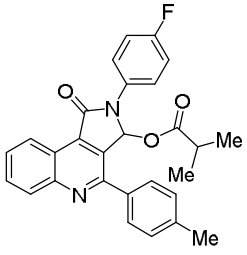
Pale yellow solid; mp 188–190 °C; IR (KBr): 1745, 1718, 1609, 1515, 1507, 1391, 1297, 1249, 1179, 1110, 1089, 1033, 966, 902, 834, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (d, J = 7.2 Hz, 3H, C–CH_3), 0.66 (d, J = 6.0 Hz, 3H, C–CH_3), 2.05–2.07 (m, 1H, C–CH–C), 2.37 (s, 3H, ArCH_3), 3.86 (s, 3H, ArCH_3), 7.01 (d, J = 8.8 Hz, 2H, ArH), 7.23–7.26 (m, 2H, ArH), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.69–7.73 (m, 1H, ArH), 7.78–7.80 (m, 2H, ArH), 7.83–7.87 (m, 1H, ArH), 8.16 (s, 1H, C–CH–N), 8.26 (d, J = 8.4 Hz, 1H, ArH), 9.10 (d, J = 7.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 18.3, 21.3, 33.9, 55.6, 79.4, 114.4, 114.4, 122.1, 124.2, 125.6, 125.6, 128.4, 129.7, 129.9, 129.9, 130.2, 130.2, 130.6, 131.2, 132.1, 132.4, 136.2, 137.4, 149.8, 153.9, 160.9, 166.5, 175.6; HRMS (TOF ES$^+$): *m/z* calcd for $C_{29}H_{27}N_2O_4$ [(M+H)$^+$], 467.1965; found, 467.1971.

2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3cb).



Yellow solid; mp 208.5–210 °C; IR (KBr): 1746, 1720, 1611, 1498, 1385, 1253, 1178, 1131, 1095, 1036, 957, 902, 832, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (d, J = 6.8 Hz, 3H, C–CH_3), 0.66 (d, J = 6.8 Hz, 3H, C–CH_3), 2.03–2.07 (m, 1H, C–CH–C), 3.86 (s, 3H, ArOCH_3), 7.01 (d, J = 8.8 Hz, 2H, ArH), 7.40 (d, J = 8.4 Hz, 2H, ArH), 7.53 (d, J = 8.4 Hz, 2H, ArH), 7.70–7.72 (m, 1H, ArH), 7.77 (d, J = 8.4 Hz, 2H, ArH), 7.83–7.87 (m, 1H, ArH), 8.19 (s, 1H, C–CH–N), 8.25 (d, J = 8.4 Hz, 1H, ArH), 9.06 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 18.3, 33.8, 55.6, 79.0, 114.4, 114.4, 122.0, 124.0, 126.4, 126.4, 128.6, 129.4, 129.4, 129.8, 130.2, 130.2, 130.4, 131.3, 132.2, 133.4, 135.7, 149.8, 153.9, 161.0, 166.4, 175.7; HRMS (TOF ES$^+$): *m/z* calcd for $C_{28}H_{24}ClN_2O_4$ [(M+H)$^+$], 487.1419; found, 487.1419.

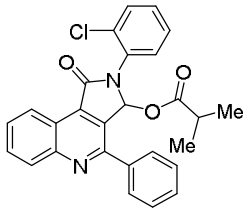
2-(4-fluorophenyl)-1-oxo-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3cc).



White solid; mp 203–205 °C; IR (KBr): 1749, 1722, 1511, 1388, 1223, 1123, 1098, 1041, 961, 835, 823, 779,

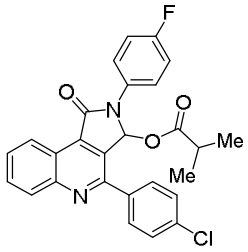
747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.57 (d, J = 6.8 Hz, 3H, C–CH_3), 0.64 (d, J = 7.2 Hz, 3H, C–CH_3), 1.99–2.05 (m, 1H, C–CH–C), 2.41 (s, 3H, ArCH_3), 7.11–7.15 (m, 2H, ArH), 7.29–7.31 (m, 2H, ArH), 7.48–7.52 (m, 2H, ArH), 7.68 (d, J = 8.4 Hz, 2H, ArH), 7.73–7.75 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 8.14 (s, 1H, C–CH–N), 8.28 (d, J = 8.8 Hz, 1H, ArH), 9.08 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 18.3, 21.4, 33.8, 79.3, 116.2 (d, J = 22.8 Hz), 116.2 (d, J = 22.8 Hz), 122.2, 124.1, 127.7 (d, J = 8.5 Hz), 127.7 (d, J = 8.5 Hz), 128.6, 128.6, 128.7, 129.6, 129.6, 129.9, 130.8 (d, J = 3.0 Hz), 131.3, 132.5, 135.2, 135.8, 139.8, 149.8, 154.4, 161.6 (d, J = 245.9 Hz), 166.5, 175.6; HRMS (TOF ES^+): *m/z* calcd for $C_{28}H_{24}FN_2O_3$ [$(M+H)^+$], 455.1765; found, 455.1765.

2-(2-chlorophenyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3cd).



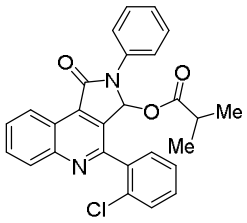
White solid; mp 175–177 °C; IR (KBr): 1747, 1725, 1483, 1403, 1126, 1095, 1049, 967, 867, 776, 750, 711, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.59 (d, J = 7.2 Hz, 3H, C–CH_3), 0.65 (d, J = 6.8 Hz, 3H, C–CH_3), 1.99–2.06 (m, 1H, C–CH–C), 7.37–7.39 (m, 3H, ArH), 7.43–7.52 (m, 3H, ArH), 7.54–7.57 (m, 1H, ArH), 7.73–7.77 (m, 1H, ArH), 7.81–7.83 (m, 2H, ArH), 7.87–7.91 (m, 1H, ArH), 8.06 (s, 1H, C–CH–N), 8.31 (d, J = 6.8 Hz, 1H, ArH), 9.09 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.2, 18.3, 33.8, 79.5, 122.4, 124.2, 127.8, 127.8, 128.6, 128.6, 128.9, 129.0, 129.0, 129.6, 130.0, 130.6, 130.6, 130.6, 131.4, 132.5, 133.2, 134.2, 135.6, 138.2, 149.8, 154.4, 175.5; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{22}ClN_2O_3$ [$(M+H)^+$], 457.1313; found, 457.1315.

4-(4-chlorophenyl)-2-(4-fluorophenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3ce).



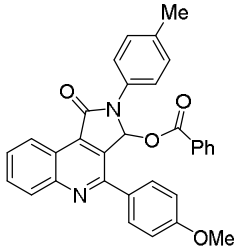
White solid; mp 229–231 °C; IR (KBr): 1747, 1722, 1511, 1386, 1355, 1235, 1154, 1092, 1043, 841, 825, 778cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.61 (d, J = 6.8 Hz, 3H, C–CH_3), 0.66 (d, J = 6.8 Hz, 3H, C–CH_3), 2.04–2.07 (m, 1H, C–CH–C), 7.12–7.16 (m, 2H, ArH), 7.46–7.51 (m, 4H, ArH), 7.73–7.77 (m, 3H, ArH), 7.86–7.89 (m, 1H, ArH), 8.13 (s, 1H, C–CH–N), 8.27 (d, J = 8.4 Hz, 1H, ArH), 9.08 (dd, J = 7.6 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 18.3, 33.8, 79.1, 116.3 (d, J = 22.6 Hz), 116.3 (d, J = 22.6 Hz), 122.3, 124.1, 127.6 (d, J = 8.5 Hz), 127.6 (d, J = 8.5 Hz), 129.1, 129.2, 129.2, 129.9, 130.0, 130.0, 130.6 (d, J = 3.0 Hz), 131.6, 132.2, 136.0, 136.1, 136.3, 149.7, 152.9, 161.6 (d, J = 246.0 Hz), 166.3, 175.7; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{21}ClFN_2O_3$ [$(M+H)^+$], 475.1219; found, 475.1213.

4-(2-chlorophenyl)-1-oxo-2-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl isobutyrate (3cf).



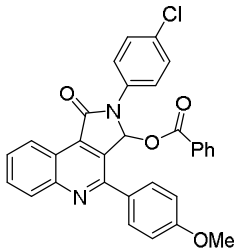
White solid; mp 184–186 °C; IR (KBr): 1760, 1713, 1596, 1502, 1391, 1356, 1271, 1110, 1094, 964, 774, 746, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 0.65 (d, J = 6.8 Hz, 3H, C–CH_3), 0.68 (d, J = 6.8 Hz, 3H, C–CH_3), 2.03–2.07 (m, 1H, C–CH–C), 7.25–7.28 (m, 1H, ArH), 7.39–7.48 (m, 4H, ArH), 7.50–7.51 (m, 1H, ArH), 7.54–7.60 (m, 3H, ArH), 7.79–7.81 (m, 1H, ArH), 7.83–7.93 (m, 1H, ArH), 8.02 (s, 1H, C–CH–N), 8.30 (d, J = 8.4 Hz, 1H, ArH), 9.15 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 18.7, 33.6, 78.7, 122.7, 124.1, 124.1, 124.2, 126.9, 127.2, 129.3, 129.3, 129.3, 130.0, 130.2, 130.7, 130.7, 131.4, 132.8, 133.6, 135.0, 135.5, 136.8, 149.5, 153.1, 166.1, 175.1; HRMS (TOF ES^+): *m/z* calcd for $C_{27}H_{22}ClN_2O_3$ [$(M+H)^+$], 457.1313; found, 457.1315.

4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3da).



White solid; mp 220–222 °C; IR (KBr): 1718, 1609, 1508, 1389, 1252, 1176, 1157, 1085, 1067, 1027, 959, 835, 779, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, $ArCH_3$), 3.67 (s, 3H, $ArOCH_3$), 6.79–7.81 (m, 2H, ArH), 7.20–7.27 (m, 4H, ArH), 7.43–7.47 (m, 3H, ArH), 7.58 (d, J = 8.0 Hz, 2H, ArH), 7.68 (d, J = 7.2 Hz, 2H, ArH), 7.69–7.75 (m, 1H, ArH), 7.85–7.89 (m, 1H, ArH), 8.26 (s, 1H, C–CH–N), 8.29 (d, J = 8.4 Hz, 1H, ArH), 9.14 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 55.4, 80.6, 114.3, 114.3, 122.2, 124.2, 125.4, 125.4, 128.3, 128.3, 128.5, 128.6, 129.7, 129.7, 129.8, 129.9, 129.9, 130.0, 130.0, 130.3, 131.3, 132.4, 132.7, 133.5, 136.0, 137.4, 149.8, 154.5, 160.6, 165.4, 166.7; HRMS (TOF ES^+): *m/z* calcd for $C_{32}H_{25}N_2O_4$ [$(M+H)^+$], 501.1809; found, 501.1810.

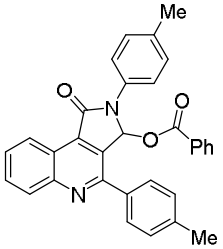
2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1-oxo-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3db).



White solid; mp 229–230 °C; IR (KBr): 1723, 1607, 1496, 1386, 1250, 1177, 1155, 1078, 1063, 1025, 960, 835, 775, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.67 (s, 3H, $ArOCH_3$), 6.79 (d, J = 8.4, Hz, 2H, ArH), 7.24–7.28 (m, 2H, ArH), 7.38 (d, J = 8.8 Hz, 2H, ArH), 7.45–7.47 (m, 1H, ArH), 7.58–7.61 (m, 4H, ArH), 7.66 (d, J = 8.8 Hz, 2H, ArH), 7.73–7.75 (m, 1H, ArH), 7.86–7.89 (m, 1H, ArH), 8.26 (d, J = 8.4 Hz, 1H, ArH), 8.28 (s, 1H, C–CH–N), 9.10 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 80.2, 114.3, 114.3,

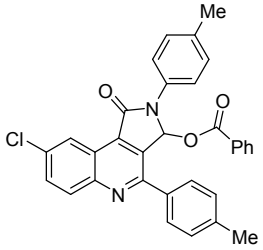
122.0, 124.1, 126.3, 126.3, 128.3, 128.3, 128.7, 129.5, 129.5, 129.7, 129.7, 129.9, 129.9, 129.9, 130.2, 131.4, 132.5, 132.8, 133.6, 133.7, 135.6, 149.8, 154.5, 160.7, 165.4, 166.5; HRMS (TOF ES^+): *m/z* calcd for $C_{31}H_{22}ClN_2O_4$ [$(M+H)^+$], 521.1263; found, 521.1264.

1-oxo-2,4-di-*p*-tolyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3dc).



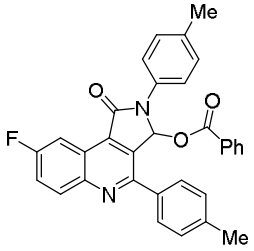
White solid; mp 211–213 °C; IR (KBr): 1720, 1514, 1389, 1270, 1252, 1157, 1084, 1066, 1026, 960, 826, 778, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 7.19–7.26 (m, 4H, ArH), 7.43–7.47 (m, 3H, ArH), 7.55–7.59 (m, 4H, ArH), 7.72–7.76 (m, 1H, ArH), 7.86–7.89 (m, 1H, ArH), 8.24 (s, 1H, C–CH–N), 8.29 (d, *J* = 8.4 Hz, 1H, ArH), 9.14 (d, *J* = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.2, 80.5, 122.3, 124.2, 125.4, 125.4, 128.2, 128.2, 128.3, 128.3, 128.6, 128.6, 129.5, 129.5, 129.7, 129.7, 129.9, 130.0, 130.0, 131.3, 132.4, 132.8, 133.5, 135.0, 136.0, 137.3, 139.4, 149.8, 155.0, 165.3, 166.6; HRMS (TOF ES^+): *m/z* calcd for $C_{32}H_{25}N_2O_3$ [$(M+H)^+$], 485.1860; found, 485.1858.

8-chloro-1-oxo-2,4-di-*p*-tolyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3dd).



White solid; mp 249–250 °C; IR (KBr): 1728, 1704, 1593, 1517, 1495, 1406, 1272, 1248, 1081, 1063, 1027, 967, 825, 752, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 7.07 (d, *J* = 7.6 Hz, 2H, ArH), 7.19–7.26 (m, 5H, ArH), 7.44–7.46 (m, 3H, ArH), 7.54–7.59 (m, 4H, ArH), 7.78–7.81 (m, 1H, ArH), 8.20 (s, 1H, C–CH–N), 8.23 (d, *J* = 8.4 Hz, 1H, ArH), 9.14 (d, *J* = 6.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.3, 80.4, 122.7, 123.2, 125.3, 125.3, 125.3, 128.2, 128.2, 128.3, 128.3, 128.5, 129.5, 129.5, 129.7, 129.7, 130.0, 130.0, 130.0, 131.3, 132.2, 132.3, 133.5, 133.6, 134.6, 134.9, 135.3, 137.4, 139.7, 148.1, 155.1, 165.2, 166.1; HRMS (TOF ES^+): *m/z* calcd for $C_{32}H_{24}ClN_2O_3$ [$(M+H)^+$], 519.1470; found, 519.1469.

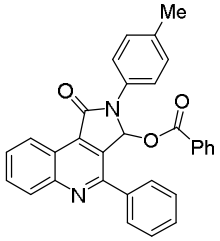
8-fluoro-1-oxo-2,4-di-*p*-tolyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3de).



White solid; mp 205.5–207 °C; IR (KBr): 1726, 1706, 1604, 1518, 1507, 1405, 1358, 1271, 1234, 1201, 1140, 1083, 1065, 1082, 972, 881, 826, 807, 770, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 3H, $ArCH_3$),

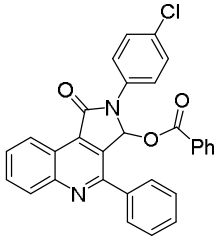
2.34 (s, 3H, $ArCH_3$), 7.08 (d, J = 7.6 Hz, 2H, ArH), 7.21–7.28 (m, 4H, ArH), 7.45–7.47 (m, 3H, ArH), 7.56–7.60 (m, 4H, ArH), 7.64–7.66 (m, 1H, ArH), 8.25 (s, 1H, C–CH–N), 8.30 (dd, J = 9.2 Hz, 1H, ArH), 8.78 (d, J = 9.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 21.2, 80.4, 108.0 (d, J = 23.8 Hz), 121.7 (d, J = 26.0 Hz), 123.0 (d, J = 11.7 Hz), 125.3, 125.3, 128.2, 128.2, 128.3, 128.3, 128.5, 128.6, 129.5, 129.5, 129.7, 129.7, 130.0, 130.0, 130.3, 132.3 (d, J = 11.1 Hz), 132.4, 133.5, 133.6, 134.6, 135.7 (d, J = 6.4 Hz), 137.4, 139.5, 147.0, 154.3 (d, J = 2.8 Hz), 161.9 (d, J = 249.8 Hz), 165.2, 166.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{32}H_{24}FN_2O_3$ [(M+H)$^+$], 503.1765; found, 503.1764.

1-oxo-4-phenyl-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3df).



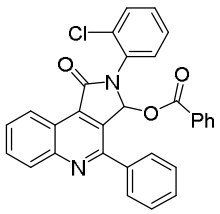
White solid; mp 259–261 °C; IR (KBr): 1721, 1606, 1515, 1387, 1357, 1272, 1250, 1155, 1087, 1066, 1025, 953, 821, 780, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3H, $ArCH_3$), 7.11–7.23 (m, 7H, ArH), 7.34–7.39 (m, 3H, ArH), 7.47 (d, J = 8.4 Hz, 2H, ArH), 7.62 (d, J = 7.6 Hz, 2H, ArH), 7.67–7.70 (m, 1H, ArH), 7.79–7.83 (m, 1H, ArH), 8.18 (s, 1H, C–CH–N), 8.23 (d, J = 8.8 Hz, 1H, ArH), 9.08 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 80.2, 122.3, 124.1, 125.2, 125.2, 128.2, 128.2, 128.3, 128.3, 128.4, 128.7, 128.7, 129.2, 129.5, 129.5, 129.8, 129.9, 129.9, 131.3, 132.3, 132.7, 133.4, 136.0, 137.2, 149.7, 154.9, 165.1, 166.5; HRMS (TOF ES$^+$): *m/z* calcd for $C_{31}H_{23}N_2O_3$ [(M+H)$^+$], 471.1703; found, 471.1707.

2-(4-chlorophenyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3dg).



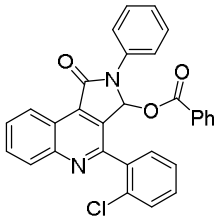
White solid; mp 292–294 °C; IR (KBr): 1721, 1498, 1384, 1357, 1248, 1156, 1082, 1065, 1024, 959, 831, 780, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.32 (m, 5H, ArH), 7.39 (d, J = 8.4 Hz, 3H, ArH), 7.45–7.47 (m, 1H, ArH), 7.56 (d, J = 7.6 Hz, 2H, ArH), 7.60 (d, J = 8.4 Hz, 2H, ArH), 7.69 (d, J = 7.6 Hz, 2H, ArH), 7.79–7.81 (m, 1H, ArH), 7.90–7.93 (m, 1H, ArH), 8.29 (s, 1H, C–CH–N), 8.32 (d, J = 8.4 Hz, 1H, ArH), 9.14 (d, J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.9, 122.3, 124.1, 126.2, 126.2, 128.2, 128.3, 128.3, 128.4, 128.4, 128.9, 128.9, 129.0, 129.4, 129.5, 129.5, 129.7, 129.7, 130.1, 131.5, 132.7, 132.8, 133.6, 133.7, 135.7, 137.6, 149.8, 155.0, 165.2, 166.5; HRMS (TOF ES$^+$): *m/z* calcd for $C_{30}H_{20}ClN_2O_3$ [(M+H)$^+$], 491.1157; found, 491.1159.

2-(2-chlorophenyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3dh).



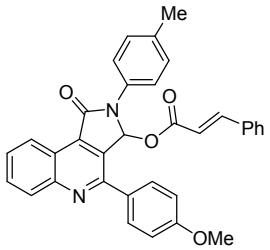
Yellow solid; mp 165–167 °C; IR (KBr): 1723, 1601, 1485, 1404, 1263, 1249, 1162, 1084, 1064, 1024, 964, 769, 712, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.39 (m, 3H, ArH), 7.43–7.52 (m, 3H, ArH), 7.54–7.57 (m, 1H, ArH), 7.73–7.77 (m, 1H, ArH), 7.81–7.83 (m, 2H, ArH), 7.87–7.91 (m, 1H, ArH), 8.06 (s, 1H, C–CH–N), 8.31 (d, J = 6.8 Hz, 1H, ArH), 9.09 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 80.5, 122.4, 124.3, 128.0, 128.3, 128.3, 128.4, 128.9, 128.9, 128.9, 129.4, 129.6, 129.6, 130.0, 130.6, 131.5, 132.7, 133.4, 133.6, 135.5, 137.8, 149.8, 154.9, 165.3; HRMS (TOF ES^+): *m/z* calcd for $C_{30}H_{20}ClN_2O_3$ [$(M+H)^+$], 491.1157; found, 491.1159.

2-(2-chlorophenyl)-1-oxo-4-phenyl-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl benzoate (3di).



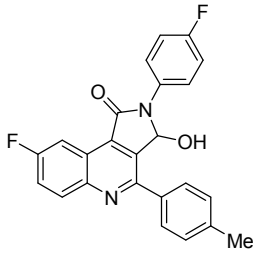
White solid; mp 232–233 °C; IR (KBr): 1732, 1719, 1601, 1504, 1386, 1273, 1256, 1156, 1082, 1062, 1024, 953, 776, 748, 697 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.99–7.01 (m, 1H, ArH), 7.19–7.30 (m, 5H, ArH), 7.37–7.41 (m, 3H, ArH), 7.46–7.50 (m, 1H, ArH), 7.61 (d, J = 7.6 Hz, 2H, ArH), 7.66 (d, J = 7.6 Hz, 2H, ArH), 7.81–7.85 (m, 1H, ArH), 7.91–7.95 (m, 1H, ArH), 8.17 (s, 1H, C–CH–N), 8.31 (d, J = 8.8 Hz, 1H, ArH), 9.09 (d, J = 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 79.4, 122.6, 123.6, 123.6, 124.2, 126.7, 127.0, 128.1, 128.2, 128.2, 1292., 129.3, 129.3, 129.7, 129.7, 129.9, 130.0, 130.4, 131.4, 132.5, 133.5, 135.2, 136.3, 149.5, 153.2, 164.3, 166.2; HRMS (TOF ES^+): *m/z* calcd for $C_{30}H_{20}ClN_2O_3$ [$(M+H)^+$], 491.1157; found, 491.1159.

4-(4-methoxyphenyl)-1-oxo-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-3-yl cinnamate (3dj).



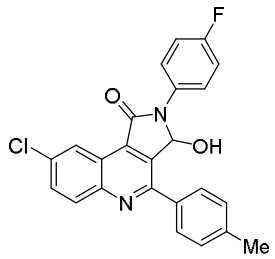
White solid; mp 222–223.5 °C; IR (KBr): 2962, 1713, 1607, 1450, 1388, 1355, 1268, 1192, 1030, 1006 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ = 2.35 (s, 3H, $ArCH_3$), 3.70 (s, 3H, $ArOCH_3$), 5.97 (d, J = 15.96 Hz, 1H, C=CH), 6.94 (d, J = 8.70 Hz, 2H, ArH), 7.23–7.28 (m, 3H, C=CH+ArH), 7.31–7.34 (m, 5H, ArH), 7.46 (d, J = 8.34 Hz, 2H, ArH), 7.70–7.72 (m, 1H, ArH), 7.75 (d, J = 8.70 Hz, 2H, ArH), 7.85–7.87 (m, 1H, ArH), 8.17 (s, 1H, C–CH), 8.27 (d, J = 8.46 Hz, 1H, ArH), 9.13 (d, J = 8.22 Hz, 1H, ArH); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 21.1, 55.3, 80.1, 114.3, 114.3, 116.0, 122.0, 124.1, 125.3, 125.3, 128.2, 128.2, 128.4, 128.9, 128.9, 129.7, 129.8, 129.9, 129.9, 129.9, 129.9, 130.4, 130.7, 131.1, 132.3, 133.8, 135.9, 137.2, 146.2, 149.7, 154.2, 160.7, 165.3, 166.5; HRMS (TOF ES^+): *m/z* calcd for $C_{34}H_{27}N_2O_4$ [$(M+H)^+$], 527.1965; found, 527.1966.

8-fluoro-2-(4-fluorophenyl)-3-hydroxy-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3ea).



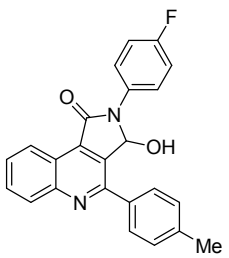
Pale yellow solid; mp 274–276 °C; IR (KBr): 3088, 1709, 1695, 1611, 1508, 1379, 1228, 1197, 1118, 880, 821, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ = 2.54 (s, 3H, $ArCH_3$), 6.01 (d, J = 10.4 Hz, 1H, OH), 6.18 (d, J = 10.8 Hz, 1H, C–CH–N), 6.40–6.44 (m, 2H, ArH), 6.51–6.53 (m, 2H, ArH), 6.88–6.93 (m, 1H, ArH), 7.04–7.07 (m, 2H, ArH), 7.27 (d, J = 7.6 Hz, 2H, ArH), 7.40–7.44 (m, 1H, ArH), 7.82–7.85 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ = 19.4, 80.6, 105.2 (d, J = 23.6 Hz), 113.6, 113.8, 119.1 (d, J = 25.9 Hz), 120.5 (d, J = 11.5 Hz), 123.0, 123.1, 127.3, 127.3, 127.4, 127.4, 130.6 (d, J = 9.8 Hz), 131.3 (d, J = 2.8 Hz), 132.6 (d, J = 6.0 Hz), 133.3, 134.7, 137.4, 144.0, 151.5 (d, J = 2.5 Hz), 158.0 (d, J = 242.2 Hz), 159.3 (d, J = 247.4 Hz), 163.1; HRMS (TOF ES^+): *m/z* calcd for $C_{24}H_{17}F_2N_2O_2$ [$(M+H)^+$], 403.1253; found, 403.1254.

8-chloro-2-(4-fluorophenyl)-3-hydroxy-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3eb).



Yellow solid; mp 248–249 °C; IR (KBr): 3443, 1695, 1637, 1508, 1378，1229, 1104, 1081, 821, 743 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+Acetone-d_6): δ = 2.44 (s, 3H, $ArCH_3$), 5.93 (dd, J = 10.4 Hz, 1H, OH), 6.87 (dd, J = 10.6 Hz, 1H, C–CH–N), 7.12–7.17 (m, 2H, ArH), 7.30–7.31 (m, 2H, ArH), 7.73–7.75 (m, 1H, ArH), 7.83–7.87 (m, 2H, ArH), 8.00–8.02 (m, 2H, ArH), 8.09–8.12 (m, 1H, ArH), 9.05 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$+Acetone-d_6): δ = 20.9, 82.4, 115.3, 115.5, 122.2, 122.4, 122.6, 124.4, 128.8, 129.0, 129.0, 129.0, 130.9, 131.2, 132.7, 133.8, 134.1, 134.8, 135.5, 139.4, 147.2, 154.2, 160.1 (d, J = 243.3 Hz), 164.9; HRMS (TOF ES^+): *m/z* calcd for $C_{24}H_{17}ClFN_2O_2$ [$(M+H)^+$], 419.0957; found, 419.0953.

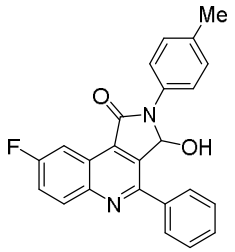
2-(4-fluorophenyl)-3-hydroxy-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3ec).



White solid; mp 232–235 °C; IR (KBr): 3068, 1702, 1600, 1508, 1388, 1228, 1162, 1117, 1039, 900, 824, 772, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ = 2.52 (s, 3H, $ArCH_3$), 5.92 (d, J = 9.2 Hz, 1H, OH), 6.16

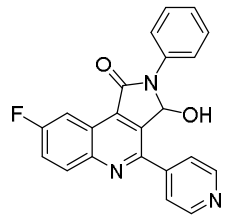
(d, J = 8.8 Hz, 1H, C–CH–N), 6.39–6.43 (m, 2H, ArH), 6.50–6.52 (m, 2H, ArH), 6.88–6.92 (m, 1H, ArH), 7.01–7.07 (m, 3H, ArH), 7.27 (d, J = 7.6 Hz, 2H, ArH), 7.35 (d, J = 8.8 Hz, 1H, ArH), 8.23 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ = 19.4, 80.6, 113.6, 113.8, 119.9, 121.7, 123.1, 123.2, 126.4, 127.3, 127.3, 127.5, 127.7, 128.8, 131.5 (d, J = 2.8 Hz), 132.9, 133.6, 134.1, 137.3, 146.8, 152.1, 157.8 (d, J = 241.8 Hz), 163.4; HRMS (TOF ES$^+$): *m/z* calcd for $C_{24}H_{18}FN_2O_2$ [(M+H)$^+$], 385.1347; found, 385.1347.

8-fluoro-3-hydroxy-4-phenyl-2-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3ed).



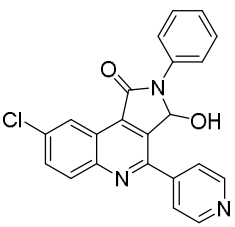
Pale yellow solid; mp 227–228 °C; IR (KBr): 3428, 1667, 1511, 1388, 1235, 1185, 1106, 854, 809 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.38 (s, 3H, $ArCH_3$), 6.82 (d, J = 10.8 Hz, 1H, OH), 7.17 (d, J = 10.4 Hz, 1H, C–CH–N), 7.32–7.34 (m, 2H, ArH), 7.58–7.64 (m, 3H, ArH), 7.76–7.78 (m, 2H, ArH), 7.87–7.92 (m, 1H, ArH), 8.22–8.23 (m, 2H, ArH), 8.33–8.37 (m, 1H, ArH), 8.71 (m, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5, 82.9, 107.6 (d, J = 23.5 Hz), 121.9 (d, J = 25.7 Hz), 123.0, 123.1, 123.6, 123.6, 129.4, 129.4, 130.0, 130.0, 130.2, 130.2, 130.4, 133.4 (d, J = 9.2 Hz), 135.0, 135.3, 135.6, 137.7, 138.7, 146.5, 154.3, 161.9 (d, J = 246.9 Hz), 165.4; HRMS (TOF ES$^+$): *m/z* calcd for $C_{24}H_{18}FN_2O_2$ [(M+H)$^+$], 385.1347; found, 385.1348.

8-fluoro-3-hydroxy-2-phenyl-4-(pyridin-4-yl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3ee).



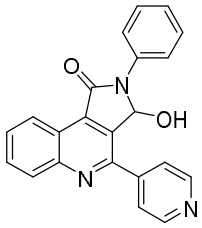
Pale yellow solid; mp 320–321 °C; IR (KBr): 3093, 1698, 1603, 1500, 1377, 1360, 1234, 1191, 1113, 1066, 881, 834, 757, 689 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.01 (d, J = 10.8 Hz, 1H, OH), 6.35 (d, J = 10.4 Hz, 1H, C–CH–N), 6.40–6.43 (m, 1H, ArH), 6.61–6.65 (m, 2H, ArH), 6.98–7.04 (m, 3H, ArH), 7.27 (d, J = 6.0 Hz, 2H, ArH), 7.48 (dd, J = 9.4 Hz, 1H, ArH), 7.79 (dd, J = 9.6 Hz, 1H, ArH), 7.92 (d, J = 6.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 82.5, 107.7 (d, J = 23.8 Hz), 122.4 (d, J = 26.1 Hz), 123.6, 123.6, 123.8, 124.3, 124.3, 126.5, 129.9, 129.9, 133.8 (d, J = 9.8 Hz), 135.5 (d, J = 6.2 Hz), 137.5, 137.8, 145.6, 146.5, 151.0, 151.0, 151.9 (d, J = 2.7 Hz), 162.4 (d, J = 248.3 Hz), 165.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{22}H_{15}FN_3O_2$ [(M+H)$^+$], 372.1143; found, 372.1143.

8-chloro-3-hydroxy-2-phenyl-4-(pyridin-4-yl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3ef).



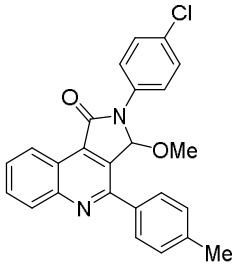
Pale yellow solid; mp 316–318 °C; IR (KBr): 3090, 1683, 1598, 1502, 1394, 1324, 1278, 1169, 1120, 1097, 833, 755, 731, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ = 2.44 (s, 3H, $ArCH_3$), 6.19 (m, 2H, C–CH–N+OH), 6.41–6.44 (m, 1H, ArH), 6.60–6.64 (m, 2H, ArH), 6.99–7.04 (m, 3H, ArH), 7.31–7.39 (m, 3H, ArH), 7.91–7.93 (m, 2H, ArH), 8.23–8.24 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ = 80.3, 121.2, 121.2, 121.2, 121.2, 121.4, 122.0, 124.1, 127.4, 127.4, 127.4, 127.4, 130.1, 130.2, 133.1, 133.2, 135.2, 143.4, 145.5, 148.4, 148.6, 150.3, 163.1; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{15}ClN_3O_2$ [$(M+H)^+$], 388.0847; found, 388.0848.

3-hydroxy-2-phenyl-4-(pyridin-4-yl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3eg).



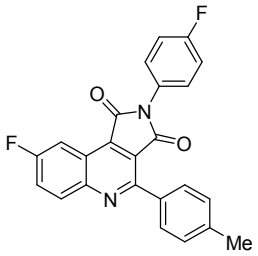
Pale yellow solid; mp 286–287 °C; IR (KBr): 3047, 1716, 1603, 1501, 1391, 1369, 1317, 1138, 1067, 1008, 849, 772, 736, 688 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 6.04 (d, *J* = 10.8 Hz, 1H, OH), 6.36 (d, *J* = 10.4 Hz, 1H, C–CH–N), 6.40–6.44 (m, 1H, ArH), 6.62–6.66 (m, 2H, ArH), 6.99–7.01 (m, 3H, ArH), 7.08–7.12 (m, 1H, ArH), 7.30 (d, *J* = 6.0 Hz, 2H, ArH), 7.42 (d, *J* = 8.8 Hz, 1H, ArH), 7.94 (d, *J* = 5.2 Hz, 2H, ArH), 8.22 (d, *J* = 8.8 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 82.5, 123.0, 123.7, 123.7, 123.3, 124.4, 124.4, 126.4, 129.8, 129.8, 130.4, 130.7, 132.1, 135.8, 137.2, 137.6, 145.9, 149.3, 151.0, 152.5, 165.7; HRMS (TOF ES^+): *m/z* calcd for $C_{22}H_{16}N_3O_2$ [$(M+H)^+$], 354.1237; found, 354.1236.

2-(4-chlorophenyl)-3-methoxy-4-(*p*-tolyl)-2,3-dihydro-1*H*-pyrrolo[3,4-*c*]quinolin-1-one (3eh).



Yellow solid; mp 185–187 °C; IR (KBr): 2923, 1710, 1495, 1339, 1307, 1241, 1183, 1139, 1078, 1014, 860, 829, 770, 738 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.19 (s, 3H, $ArCH_3$), 3.11 (s, 3H, C-OCH_3), 7.00 (d, *J* = 7.9 Hz, 2H, ArH), 7.18 (d, *J* = 6.6 Hz, 2H, ArH), 7.22 (d, *J* = 8.05 Hz, 2H, ArH), 7.70–7.73 (m, 1H, ArH), 7.77–7.80 (m, 1H, ArH), 8.14 (d, *J* = 8.35 Hz, 1H, ArH), 8.75 (s, 1H, C-CH), 9.07 (d, *J* = 8.15 Hz, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5, 51.3, 96.8, 116.6, 123.0, 124.7, 125.1, 125.1, 126.4, 126.4, 129.3, 129.3, 129.4, 129.5, 130.0, 130.0, 130.3, 131.2, 131.7, 133.2, 134.3, 135.1, 138.5, 139.3, 145.5, 149.6, 167.4; HRMS (TOF ES^+): *m/z* calcd for $C_{25}H_{20}ClN_2O_2$ [$(M+H)^+$], 415.1208; found, 415.1211.

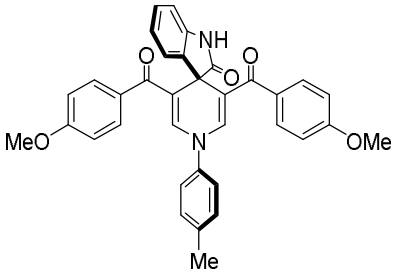
8-fluoro-2-(4-fluorophenyl)-4-(*p*-tolyl)-1*H*-pyrrolo[3,4-*c*]quinoline-1,3(2*H*)-dione (3ei).



Yellow solid; mp 259–261 °C; IR (KBr): 1767, 1722, 1602, 1552, 1511, 1388, 1348, 1235, 1193, 1162, 1111, 1090, 877, 837, 806, 757 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$+DMSO-d_6): δ = 2.42 (s, 3H, $ArCH_3$), 7.34–7.40 (m, 4H, ArH), 7.53–7.56 (m, 2H, ArH), 7.89–7.91 (m, 2H, ArH), 7.95–7.98 (m, 1H, ArH), 8.32–8.34 (m, 1H, ArH), 8.43–8.45 (m, 1H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$+DMSO-d_6): δ = 21.9, 108.4 (d, J = 22.5 Hz), 116.7 (d, J = 22.5 Hz), 116.7 (d, J = 22.5 Hz), 121.6 (d, J = 11.25 Hz), 122.9, 124.4 (d, J = 26.25 Hz), 128.6, 129.3, 129.3, 130.5 (d, J = 8.75 Hz), 130.5 (d, J = 8.75 Hz), 130.9, 130.9, 133.7 (d, J = 10.0 Hz), 134.4, 137.7 (d, J = 6.25 Hz), 140.5, 148.9, 154.7, 162.4 (d, J = 243.8 Hz), 162.4 (d, J = 248.8 Hz), 166.9, 167.5; HRMS (TOF ES^+): *m/z* calcd for $C_{24}H_{15}F_2N_2O_2$ [$(M+H)^+$], 401.1096; found, 401.1098.

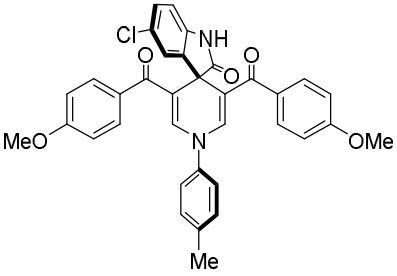
5.2 spirooxindoles 4

(2-oxo-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-methoxyphenyl)methanone) (4a).



Yellow solid; mp 240–242 °C; IR (KBr): 3426, 2922, 1718, 1608, 1257, 1163, 1013, 839, 752, 604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, $ArCH_3$), 3.81 (s, 6H, $ArOCH_3$), 6.81–6.94 (m, 6H, ArH), 7.03–7.05 (m, 2H, ArH), 7.10–7.13 (m, 1H, ArH), 7.18–7.20 (m, 2H, ArH), 7.25–7.26 (m, 1H, ArH), 7.35 (s, 2H, C=CH), 7.59–7.62 (m, 5H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 50.9, 55.5, 55.5, 109.3, 113.7, 113.7, 113.7, 113.7, 118.7, 118.7, 121.0, 121.0, 121.0, 122.3, 123.2, 128.6, 130.7, 130.7, 130.7, 131.4, 131.4, 131.4, 131.4, 131.4, 135.9, 137.2, 140.3, 140.3, 142.1, 162.6, 162.6, 180.4, 192.4, 192.4; HRMS (TOF ES^+): *m/z* calcd for $C_{35}H_{29}N_2O_5$ [$(M+H)^+$], 557.2071; found, 557.2067.

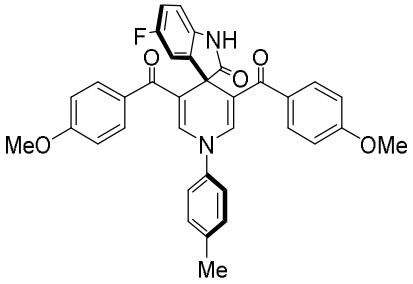
(5-chloro-2-oxo-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-methoxyphenyl)methanone) (4b).



Yellow solid; mp 207–208 °C; IR (KBr): 3442, 1722, 1609, 1509, 1469, 1256, 1015, 820, 761, 604 cm^{-1}; ^1H

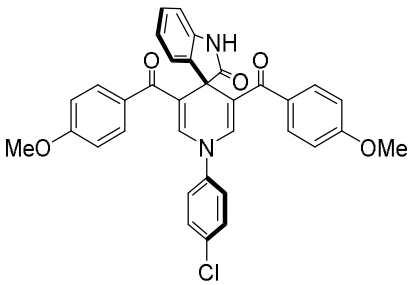
NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, $ArCH_3$), 3.81 (s, 6H, $ArOCH_3$), 6.75 (d, J = 8.0 Hz, 1H, ArH), 6.87 (d, J = 8.8 Hz, 4H, ArH), 7.03–7.09 (m, 3H, ArH), 7.17–7.21 (m, 3H, ArH), 7.39 (s, 2H, C=CH), 7.61 (d, J = 8.8 Hz, 4H, ArH), 7.97 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 51.1, 55.5, 55.5, 110.4, 113.8, 113.8, 113.8, 113.8, 118.3, 118.3, 121.1, 121.1, 123.5, 127.2, 128.6, 130.8, 130.8, 131.1, 131.1, 131.4, 131.4, 131.4, 131.4, 137.4, 137.5, 140.2, 140.8, 140.8, 141.0, 162.6, 162.6, 180.0, 180.0, 192.3, 192.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{35}H_{28}ClN_2O_5$ [(M+H)$^+$], 591.1681; found, 591.1679.

(5-fluoro-2-oxo-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-methoxyphenyl)methanone) (4c).



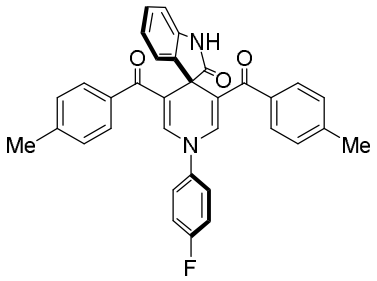
Yellow solid; mp 249–250 °C; IR (KBr): 3442, 1717, 1632, 1496, 1259, 1171, 1007, 806, 759, 609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.33 (s, 3H, $ArCH_3$), 3.81 (s, 6H, $ArOCH_3$), 6.73–6.76 (m, 1H, ArH), 6.78–6.83 (m, 1H, ArH), 6.87 (d, J = 8.8 Hz, 4H, ArH), 6.98–7.00 (m, 1H, ArH), 7.04 (d, J = 8.4 Hz, 2H, ArH), 7.19 (d, J = 8.0 Hz, 2H, ArH), 7.38 (s, 2H, C=CH), 7.60 (d, J = 8.8 Hz, 4H, ArH), 7.87 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 51.4, 55.5, 55.5, 109.8 (d, J = 7.7 Hz), 111.1 (d, J = 24.3 Hz), 113.8, 113.8, 113.8, 113.8, 114.8 (d, J = 23.1 Hz), 118.3, 118.3, 121.1, 121.1, 130.8, 130.8, 131.2, 131.4, 131.4, 131.4, 131.4, 137.1 (d, J = 6.7 Hz), 137.4, 138.3, 140.2, 140.7, 140.7, 159.3 (d, J = 237.7 Hz), 162.6, 162.6, 180.3, 192.3, 192.3; HRMS (TOF ES$^+$): *m/z* calcd for $C_{35}H_{28}FN_2O_5$ [(M+H)$^+$], 575.1977; found, 575.1979.

(1'-(4-chlorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-methoxyphenyl)methanone) (4d).



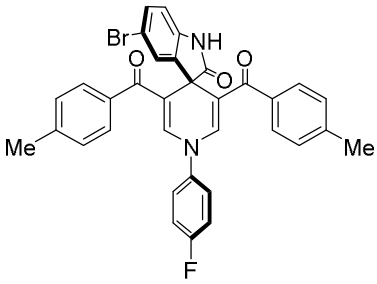
Yellow solid; mp 294–295 °C; IR (KBr): 1712, 1625, 1600, 1558, 1493, 1251, 1176, 1145, 1016, 1000, 841, 752 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 3.80 (s, 6H, $2ArOCH_3$), 6.69–6.71 (m, 1H, ArH), 6.77–6.79 (m, 1H, ArH), 6.98–6.99 (m, 5H, ArH), 7.35–7.37 (m, 1H, ArH), 7.38 (s, 2H, C=CH), 7.42–7.44 (m, 2H, ArH), 7.46–7.48 (m, 2H, ArH), 7.61 (d, J = 7.2 Hz, 4H, ArH), 10.26 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 51.3, 56.4, 56.4, 109.2, 114.7, 114.7, 114.7, 114.7, 118.9, 118.9, 121.9, 123.7, 123.7, 124.4, 128.9, 130.7, 130.7, 131.6, 132.0, 132.0, 132.2, 132.2, 132.2, 132.2, 136.9, 140.2, 140.2, 142.1, 144.4, 163.2, 163.2, 180.5, 192.5, 192.5; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{26}ClN_2O_5$ [(M+H)$^+$], 577.1525; found, 577.1527.

(1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(*p*-tolylmethanone) (4e).



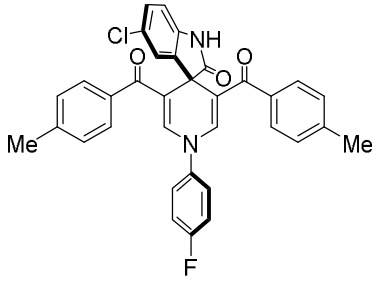
Yellow solid; mp 303–305 °C; IR (KBr): 3434, 1716, 1633, 1563, 1506, 1326, 1265, 1142, 1008, 834, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6H, $ArCH_3$), 6.85–6.87 (m, 1H, ArH), 6.93–6.97 (m, 1H, ArH), 7.07–7.15 (m, 5H, ArH), 7.16–7.20 (m, 4H, ArH), 7.27–7.29 (m, 1H, ArH), 7.33 (s, 2H, C=CH), 7.51–7.53 (m, 4H, ArH), 7.78 (br, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 50.6, 109.3, 117.1 (d, J = 23.1 Hz), 117.1 (d, J = 23.1 Hz), 119.0, 119.0, 122.2, 123.0, 123.1, 123.2 (d, J = 8.4 Hz), 123.2 (d, J = 8.4 Hz), 128.6, 129.0, 129.0, 129.0, 129.0, 129.2, 129.2, 129.2, 129.2, 135.5, 135.8, 135.8, 138.8, 140.5, 140.5, 142.1, 142.3, 142.3, 161.5, 180.1, 193.1, 193.1; HRMS (TOF ES^+): *m/z* calcd for $C_{34}H_{25}FN_2O_3Na$ [$(M+Na)^+$], 551.1741; found, 551.1742.

(5-bromo-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(*p*-tolylmethanone) (4f).



Yellow solid; mp 352–354 °C; IR (KBr): 3449, 1715, 1634, 1471, 1261, 1143, 999, 824, 748, 596 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.49 (s, 6H, $ArCH_3$), 5.83–5.85 (m, 1H, ArH), 6.37–6.46 (m, 7H, ArH), 6.50 (s, 2H, C=CH), 6.61–6.69 (m, 6H, ArH), 6.79 (s, 1H, ArH), 9.61 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.0, 22.0, 51.2, 111.0, 113.5, 117.5 (d, J = 22.9 Hz), 117.5 (d, J = 22.9 Hz), 118.1, 118.1, 124.8 (d, J = 9.8 Hz), 124.8 (d, J = 9.8 Hz), 127.2, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 131.5, 136.8, 136.8, 139.2, 139.9, 142.3, 142.9, 142.9, 143.8, 161.4 (d, J = 242.9 Hz), 180.1, 193.5, 193.5; HRMS (TOF ES^+): *m/z* calcd for $C_{34}H_{25}BrFN_2O_3$ [$(M+H)^+$], 607.1027; found, 607.1027.

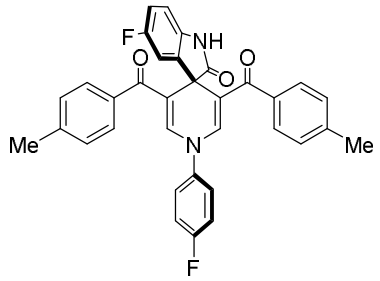
(5-chloro-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(*p*-tolylmethanone) (4g).



Yellow solid; mp 325–326 °C; IR (KBr): 1715, 1636, 1607, 1560, 1509, 1474, 1325, 1267, 1182, 1143, 1007, 825, 755, 706 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 1.46 (s, 6H, $ArCH_3$), 5.85 (d, J = 8.0 Hz, 1H, ArH),

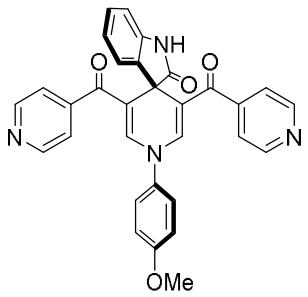
6.22–6.25 (m, 1H, ArH), 6.38–6.44 (m, 6H, ArH), 6.47 (s, 2H, C=CH), 6.59–6.62 (m, 2H, ArH), 6.65–6.67 (m, 5H, ArH), 9.58 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.0, 22.0, 51.3, 111.4, 117.6 (d, J = 22.9 Hz), 117.6 (d, J = 22.9 Hz), 118.2, 118.2, 124.6, 124.9 (d, J = 8.7 Hz), 124.9 (d, J = 8.7 Hz), 125.9, 128.7, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 130.0, 136.8, 136.8, 138.8, 139.9 (d, J = 2.3 Hz), 142.3, 142.9, 142.9, 143.4, 161.5 (d, J = 242.4 Hz), 180.3, 193.5, 193.5; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{25}ClFN_2O_3$ [(M+H)$^+$], 563.1532; found, 563.1536.

(5-fluoro-1'-(4-fluorophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(*p*-tolylmethanone) (4h).



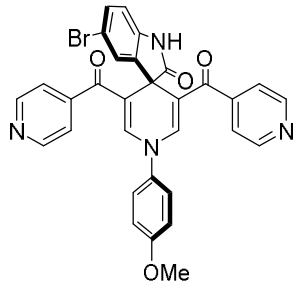
Yellow solid; mp 332–333 °C; IR (KBr): 3444, 1715, 1639, 1508, 1485, 1267, 1184, 1007, 806, 759, 606 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6H, $ArCH_3$), 6.77–6.82 (m, 2H, ArH), 6,98–7.00 (m, 1H, ArH), 7.07–7.19 (m, 8H, ArH), 7.32 (s, 2H, C=CH), 7.48–7.50 (m, 4H, ArH), 7.94 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 21.6. 51.2, 109.9 (d, J = 7.7 Hz), 111.0 (d, J = 24.2 Hz), 114.9 (d, J = 22.9 Hz), 117.2 (d, J = 23.1 Hz), 117.2 (d, J = 23.1 Hz), 118.8, 118.8, 123.4 (d, J = 8.5 Hz), 123.4 (d, J = 8.5 Hz), 129.2, 129.2, 129.2, 129.2, 129.2, 129.3, 129.3, 129.3, 129.3, 135.8, 135.8, 136.9 (d, J = 6.8 Hz), 138.5, 138.8, 141.0, 141.0, 142.5, 142.5, 159.2 (d, J = 205.0 Hz), 161.4 (d, J = 246.7 Hz), 180.1, 193.1, 193.1; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{25}F_2N_2O_3$ [(M+H)$^+$], 547.1828; found, 547.1825.

(1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(pyridin-4-ylmethanone) (4i).



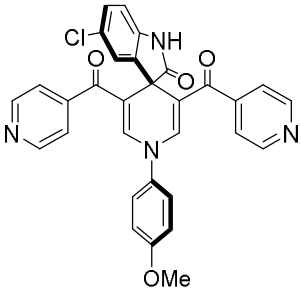
Yellow solid; mp 360–361 °C; IR (KBr): 3438, 1712, 1639, 1551, 1512, 1330, 1277, 1083, 1021, 836, 657 cm^{-1}; ^{1}H NMR (400 MHz, Acetone-d_6+DMSO-d_6): δ = 3.77 (s, 3H, $ArOCH_3$), 6.82–6.84 (m, 1H, ArH), 6.89–6.93 (m, 1H, ArH), 6.96–6.98 (m, 2H, ArH), 7.11–7.15 (m, 1H, ArH), 7.39–7.42 (m, 2H, ArH), 7.45–7.48 (m, 7H, C=CH+ArH), 8.66–8.67 (m, 4H, ArH); ^{13}C NMR (100 MHz, Acetone-d_6+DMSO-d_6): δ = 60.1, 65.5, 118.8, 125.2, 125.2, 128.4, 131.4, 132.5, 132.5, 132.5, 132.5, 133.8, 133.9, 133.9, 138.4, 138.4, 146.1, 146.1, 153.5, 153.5, 153.5, 154.0, 156.1, 156.1, 160.4, 160.4, 160.4, 160.4, 169.0, 189.5, 201.7, 201.7; HRMS (TOF ES$^+$): *m/z* calcd for $C_{31}H_{23}N_4O_4$ [(M+H)$^+$], 515.1714; found, 515.1712.

(5-bromo-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(pyridin-4-ylmethanone) (4j).



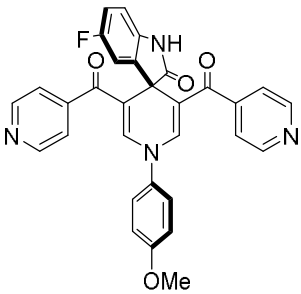
Yellow solid; mp 335–337 °C; IR (KBr): 3443, 1722, 1639, 1545, 1510, 1327, 1277, 1245, 1020, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$+DMSO-d_6): δ = 3.37 (s, 3H, $ArOCH_3$), 6.45–6.50 (m, 1H, ArH), 6.46–6.51 (m, 2H, ArH), 6.75–6.79 (m, 2H, ArH), 6.84–6.87 (m, 2H, ArH), 6.95–6.99 (m, 6H, ArH+C=CH), 8.24–7.27 (m, 4H, ArH), 10.10 (s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6): δ = 49.3, 54.8, 109.9, 113.1, 114.5, 114.5, 117.1, 117.1, 121.4, 121.4, 121.4, 121.4, 122.6, 122.6, 125.3, 130.5, 134.4, 136.3, 141.8, 142.5, 142.5, 144.6, 144.6, 149.3, 149.3, 149.5, 149.5, 158.3, 178.5, 190.5, 190.5; HRMS (TOF ES^+): *m/z* calcd for $C_{31}H_{22}BrN_4O_4$ [$(M+H)^+$], 593.0819; found, 593.0820.

(5-chloro-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(pyridin-4-ylmethan one) (4k).



Yellow solid; mp 360–361 °C; IR (KBr): 3446, 1714, 1643,1549, 1510, 1273, 1150, 1020, 829, 654 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 3.78 (s, 3H, $ArOCH_3$), 6.80 (d, *J* = 8.4 Hz, 1H, ArH), 7.02 (d, *J* = 8.8 Hz, 1H, ArH), 7.18–7.21 (m, 1H, ArH), 7.42–7.43 (m, 4H, C=CH+ArH), 7.51 (d, *J* = 6.4 Hz, 4H, ArH), 7.58 (d, *J* = 6.0 Hz, 1H, ArH), 8.72 (d, *J* = 6.4 Hz, 4H, ArH), 10.61 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 60.1, 65.5, 118.8, 125.2, 125.2, 128.4, 131.4, 132.5, 132.5, 132.5, 132.5, 133.8, 133.9, 133.9, 138.4, 138.4, 146.1, 146.1, 153.5, 153.5, 153.5, 154.0, 156.1, 156.1, 160.4, 160.4, 160.4, 160.4, 169.0, 189.5, 201.7, 201.7; HRMS (TOF ES^+): *m/z* calcd for $C_{31}H_{22}ClN_4O_4$ [$(M+H)^+$], 549.1324; found, 549.1325.

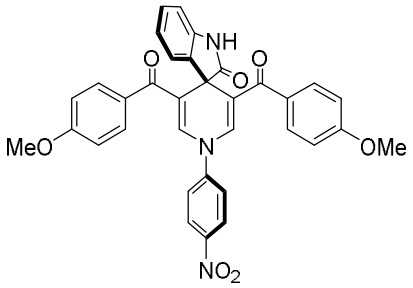
(5-fluoro-1'-(4-methoxyphenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(pyridin-4-ylmethan one) (4l).



Pink solid; mp 225.5–227 °C; IR (KBr): 3439, 1715, 1638,1512, 1481, 1326, 1275, 1022, 802, 656 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 3.77 (s, 3H, $ArOCH_3$), 6.75–6.78 (m, 1H, ArH), 6.94–7.00 (m, 1H, ArH), 7.02 (d, *J* = 8.8 Hz, 1H, ArH), 7.41 (s, 1H, C=CH), 7.42–7.44 (m, 4H, ArH), 7.51 (dd, *J* = 8.8 Hz, 4H, ArH), 8.72 (d,

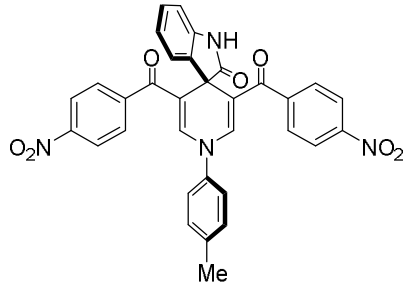
J = 4.4 Hz, 4H, ArH), 10.49 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 50.9, 56.4, 109.5 (d, J = 7.9 Hz), 112.4 (d, J = 24.3 Hz), 115.1 (d, J = 23.2 Hz), 115.8, 115.8, 117.9, 117.9, 123.2, 123.2, 123.2, 123.2, 124.6, 124.6, 136.4, 137.6 (d, J = 7.1 Hz), 140.5, 144.5, 144.5, 146.3, 146.3, 151.1, 151.1, 151.1, 151.1, 158.5, 159.3, 180.0, 192.4, 192.4; HRMS (TOF ES$^+$): *m/z* calcd for $C_{31}H_{22}FN_4O_4$ [(M+H)$^+$], 533.1620; found, 533.1617.

(1'-(4-nitrophenyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-methoxyphenyl)methanone) (4m).



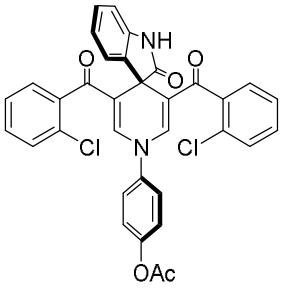
Yellow solid; mp 303–305 °C; IR (KBr): 3249, 1709, 1617, 1592, 1509, 1273, 1248, 1161, 999, 775, 760 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.82 (s, 6H, ArOCH$_3$), 6.67–6.70 (m, 1H, ArH), 7.76–7.78 (m, 1H, ArH), 7.00–7.04 (m, 4H, ArH), 7.37 (d, J = 7.26 Hz, 1H, ArH), 7.57 (s, 2H, C=CH), 7.60–7.61 (m, 2H, ArH), 7.67–7.69 (m, 4H, ArH), 8.26 (d, J = 9.00 Hz, 1H, ArH), 10.30 (s, 1H, NH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 50.9, 55.9, 55.9, 108.8, 114.3, 114.3, 114.3, 114.3, 114.3, 119.4, 120.9, 120.9, 121.4, 123.9, 125.9, 125.9, 128.5, 131.3, 131.3, 131.9, 131.9, 131.9, 131.9, 135.8, 138.1, 138.1, 144.0, 144.8, 147.2, 162.9, 162.9, 179.5, 192.0, 192.0; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{26}N_3O_7$ [(M+H)$^+$], 588.1765; found, 588.1770.

(2-oxo-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis((4-nitrophenyl)methanone)(4n).



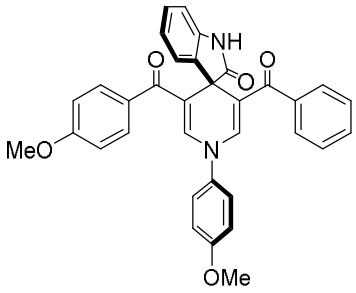
Yellow solid; mp 302–304 °C; IR (KBr): 3077, 1707, 1513, 1263, 1142, 1006, 854, 787, 718, 705, 683 cm^{-1}; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 2.27 (s, 3H, ArCH$_3$), 6.75–6.77 (m, 1H, ArH), 6.88–6.90 (m, 1H, ArH), 7.10–7.13 (m, 1H, ArH), 7.23 (d, J = 8.04 Hz, 2H, ArH), 7.31 (d, J = 8.16 Hz, 2H, ArH), 7.43–7.44 (m, 3H, C=CH+ArH), 7.78 (d, J = 8.46 Hz, 4H, ArH), 8.27 (d, J = 8.40 Hz, 4H, ArH), 10.44 (s, 1H, NH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 20.8, 50.2, 108.8, 118.4, 118.4, 121.7, 122.1, 122.1, 122.1, 123.9, 124.1, 124.1, 124.1, 128.6, 130.3. 130.3, 130.3, 130.7, 130.7, 130.7, 135.9, 137.3, 140.2, 143.1, 143.1, 143.8, 144.7, 144.7, 149.4, 149.4, 179.5, 191.8, 191.8; HRMS (TOF ES$^+$): *m/z* calcd for $C_{33}H_{23}N_4O_7$ [(M+H)$^+$], 587.1561; found, 587.1567.

***N*-(4-(3',5'-bis(2-chlorobenzoyl)-2-oxo-1'*H*-spiro[indoline-3,4'-pyridin]-1'-yl)phenyl)acetamide (4o).**



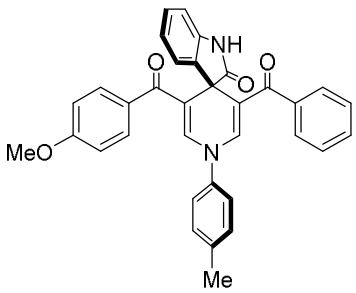
Yellow solid; mp >360 °C; IR (KBr): 3330, 1721, 1658, 1515, 1272, 1153, 1033, 1006, 839, 761, 697 cm^{-1}; ^1H NMR (600 MHz, DMSO-d_6): δ = 2.02 (s, 3H, C–CH_3), 6.78 (d, J = 9.18 Hz, 1H, ArH), 6.91–6.93 (m, 1H, ArH), 7.07 (s, 2H, C=CH), 7.15–7.17 (m, 3H, ArH), 7.27 (d, J = 8.46 Hz, 2H, ArH), 7.34 (d, J = 8.76 Hz, 1H, ArH), 7.38–7.40 (m, 2H, ArH), 7.44–7.48 (m, 4H, ArH), 7.59 (d, J = 10.50 Hz, 2H, ArH), 10.11 (s, 1H, NH), 10.43 (s, 1H, NH); ^{13}C NMR (150 MHz, DMSO-d_6): δ = 24.8, 50.0, 109.1, 120.1, 120.1, 121.0, 121.0, 121.8, 123.1, 123.1, 123.1, 124.8, 128.1, 128.1, 128.9, 129.9, 129.9, 130.8, 130.8, 132.1, 132.1, 135.5, 137.8, 138.6, 138.6, 139.6, 143.9, 143.9, 144.3, 144.3, 169.3, 179.6, 191.4, 191.4; HRMS (TOF ES^+): *m/z* calcd for $C_{34}H_{24}Cl_2N_3O_4$ [$(M+H)^+$], 608.1138; found, 608.1137.

3'-benzoyl-5'-(4-methoxybenzoyl)-1'-(4-methoxyphenyl)-1'*H*-spiro[indoline-3,4'-pyridin]-2-one (4p).



Yellow solid; mp 255–257 °C; IR (KBr): 3061, 1709, 1626, 1601, 1470, 1330, 1243, 1184, 1146, 1003, 833, 750, 701 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 3.73 (s, 3H, $ArOCH_3$), 3.79 (s, 3H, $ArOCH_3$), 6.72 (d, J = 7.65 Hz, 1H, ArH), 6.82–6.85 (m, 1H, ArH), 6.98 (d, J = 8.4 Hz, 4H, ArH), 7.05–7.08 (m, 1H, ArH), 7.27 (d, J = 5.7 Hz, 2H, ArH), 7.34 (d, J = 8.2 Hz, 2H, ArH), 7.39 (d, J = 7.3 Hz, 1H, ArH), 7.44–7.47 (m, 2H, ArH), 7.52–7.60 (m, 5H, ArH+C=CH), 10.30 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 51.0, 56.3, 56.3, 109.1, 114.4, 114.4, 115.9, 115.9, 118.2, 118.6, 121.8, 123.9, 123.9, 124.2, 128.7, 129.3, 129.3, 129.5, 129.5, 131.9, 131.9, 132.3, 136.6, 137.0, 139.7, 141.1, 142.7, 144.2, 158.9, 162.9, 180.5, 180.5; HRMS (TOF ES^+): *m/z* calcd for $C_{34}H_{27}N_2O_5$ [$(M+H)^+$], 543.1914; found, 543.1919.

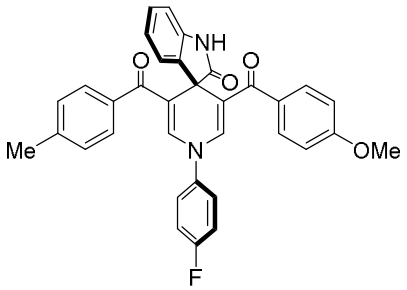
3'-benzoyl-5'-(4-methoxybenzoyl)-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyridin]-2-one (4q).



Yellow solid; mp 270–272 °C; IR (KBr): 3270, 1711, 1632, 1598, 1556, 1510, 1470, 1328, 1248, 1145, 1003, 841, 745, 701, 654 cm^{-1}; ^1H NMR (500 MHz, DMSO-d_6): δ = 2.31 (s, 3H, $ArCH_3$), 3.83 (s, 3H, $ArOCH_3$), 6.74 (d, J = 7.6 Hz, 1H, ArH), 6.86–6.87 (m, 1H, ArH), 7.02 (d, J = 8.75 Hz, 2H, ArH), 7.08–7.09 (m, 1H, ArH),

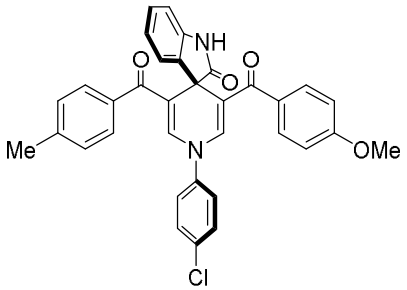
7.26–7.29 (m, 3H, ArH), 7.36 (d, J = 6.2 Hz, 2H, ArH), 7.49–7.50 (m, 3H, ArH), 7.57–7.64 (m, 5H, ArH+C=CH), 10.33 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.2, 51.1, 56.3, 109.1, 114.6, 114.6, 118.6, 118.8, 121.2, 121.2, 128.7, 129.5, 129.5, 129.6, 130.9, 131.3, 131.3, 131.3, 131.9, 131.9, 132.0, 132.4, 132.4, 136.9, 137.2, 139.6, 140.5, 140.9, 142.2, 144.2, 163.0, 180.4, 180.4; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{27}N_2O_4$ [(M+H)$^+$], 527.1965; found, 527.1973.

1'-(4-fluorophenyl)-3'-(4-methoxybenzoyl)-5'-(4-methylbenzoyl)-1'*H*-spiro[indoline-3,4'-pyridin]-2-one (4r).



Yellow solid; mp 318–320 °C; IR (KBr): 3255, 1708, 1629, 1600, 1558, 1507, 1469, 1325, 1248, 1177, 1142, 1001, 947, 836, 745, 698 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.36 (s, 3H, $ArCH_3$), 3.83 (s, 3H, $ArOCH_3$), 6.74 (d, J = 8.55 Hz, 1H, ArH), 6.83–6.86 (m, 1H, ArH), 7.02 (d, J = 8.55 Hz, 2H, ArH), 7.07–7.10 (m, 1H, ArH), 7.29–7.32 (m, 4H, ArH), 7.36 (s, 2H, C=CH), 7.42 (d, J = 7.30 Hz, 1H, ArH), 7.48–7.50 (m, 2H, ArH), 7.54 (d, J = 7.85 Hz, 2H, ArH), 7.64 (d, J = 8.55 Hz, 2H, ArH), 10.31 (s, 1H, NH); ^{13}C NMR (125 MHz, DMSO-d_6): δ = 21.9, 51.0, 56.3, 109.1, 114.6, 114.6, 117.5 (d, J = 22.5 Hz), 117.5 (d, J = 22.5 Hz), 118.5, 118.7, 121.8, 124.2, 124.4, 124.5, 124.5, 128.7, 129.8, 129.8, 129.8, 129.8, 131.9, 132.0, 132.0, 136.8, 136.9, 139.8, 140.6, 141.6, 142.6, 144.2, 161.2 (d, J = 242.5 Hz), 163.0, 180.4, 180.4,; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{26}FN_2O_4$ [(M+H)$^+$], 545.1871; found, 545.1871.

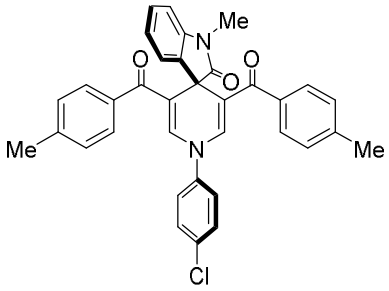
1'-(4-chlorophenyl)-3'-(4-methoxybenzoyl)-5'-(4-methylbenzoyl)-1'*H*-spiro[indoline-3,4'-pyridin]-2-one (4s).



Yellow solid; mp 318–319 °C; IR (KBr): 1713, 1630, 1602, 1509, 1493, 1325, 1254, 1182, 1146, 1013, 1003, 843, 745 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.34 (s, 3H, $ArCH_3$), 3.80 (s, 3H, $ArOCH_3$), 6.70 (d, J = 7.6 Hz, 1H, ArH), 6.78–6.82 (m, 1H, ArH), 6.98 (d, J = 8.0 Hz, 2H, ArH), 7.03–7.07 (m, 1H, ArH), 7.26 (d, J = 7.6 Hz, 2H, ArH), 7.36 (m, 3H, ArH+C=CH), 7.41 (d, J = 8.2 Hz, 2H, ArH), 7.48–7.52 (m, 4H, ArH), 7.62 (d, J = 8.0 Hz, 2H, ArH), 10.28 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5, 50.7, 55.9, 108.7, 114.2, 114.2, 118.3, 118.5, 121.4, 123.3, 123.3, 123.3, 123.9, 128.3, 129.5, 129.5, 129.5, 130.2, 130.2, 130.2, 131.2, 131.4, 131.7, 131.7, 136.4, 139.6, 140.6, 141.6, 142.3, 143.8, 162.7, 179.9, 192.0, 193.0; HRMS (TOF ES$^+$): *m/z* calcd for $C_{34}H_{26}ClN_2O_4$ [(M+H)$^+$], 561.1576; found, 561.1576.

(1'-(4-chlorophenyl)-1-methyl-2-oxo-1'*H*-spiro[indoline-3,4'-pyridine]-3',5'-diyl)bis(*p*-tolylmethanone)

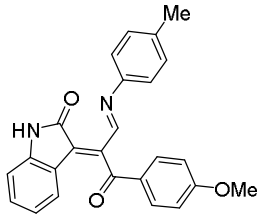
(4t).



Yellow solid; mp 165–167 °C; IR (KBr): 1711, 1631, 1607, 1563, 1492, 1327, 1263, 1143, 1081, 1008, 829, 747, 692 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.33 (s, 3H, $ArCH_3$), 2.33 (s, 3H, $ArCH_3$), 3.22 (s, 3H, N–CH_3), 6.87–6.92 (m, 2H, ArH), 7.14–7.18 (m, 1H, ArH), 7.24–7.26 (m, 4H, ArH), 7.39 (s, 2H, C=CH), 7.41–7.51 (m, 9H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5, 21.5, 27.0, 49.9, 107.5, 118.3, 118.3, 122.2, 123.5, 123.5, 123.7, 128.6, 129.5, 129.5, 129.5, 129.5, 129.5, 129.5, 129.5, 129.5, 130.2, 130.2, 131.4, 135.4, 136.2, 136.2, 140.8, 140.8, 141.6, 142.4, 142.4, 145.2, 178.5, 193.0, 193.0; HRMS (TOF ES^+): *m/z* calcd for $C_{35}H_{28}ClN_2O_3$ [$(M+H)^+$], 559.1783; found, 559.1786.

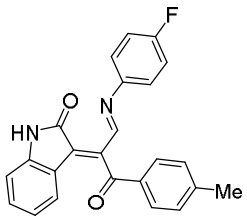
4.3 *α,β*-unsaturated 2-oxindoles 5

3-(1-(4-methoxyphenyl)-1-oxo-3-(*p*-tolylimino)propan-2-ylidene)indolin-2-one (5a).



Red solid; mp 181–183 °C; IR (KBr): 3261, 1737, 1702, 1616, 1592, 1569, 1467, 1422, 1308, 1269, 1205, 1165, 1105, 1025, 992, 845, 741 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3H, $ArCH_3$), 3.92 (s, 3H, $ArOCH_3$), 6.82–6.87 (m, 2H, ArH), 6.95–7.02 (m, 3H, ArH), 7.07–7.11 (m, 1H, ArH), 7.16–7.39 (m, 4H, ArH), 8.07–8.08 (m, 2H, ArH), 8.29 (s, 1H, C–CH=N), 10.14 (s, 1H, NH); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.6, 55.9, 110.4, 114.7, 114.7, 121.6, 122.1, 122.2, 122.2, 123.1, 125.9, 128.9, 129.4, 129.5, 130.1, 130.1, 131.5, 132.3, 132.3, 138.4, 142,0, 146.2, 148.8, 156.2, 164.8, 169.1, 194.6; HRMS (TOF ES^+): *m/z* calcd for $C_{25}H_{21}N_2O_3$ [$(M+H)^+$], 397.1547; found, 397.1545.

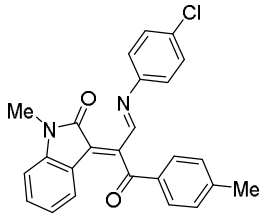
3-(3-((4-fluorophenyl)imino)-1-oxo-1-(*p*-tolyl)propan-2-ylidene)indolin-2-one (5b).



Red solid; mp 272–273 °C; IR (KBr): 3362, 1704, 1677, 1661, 1604, 1496, 1468, 1337, 1227, 1202, 1179, 1147, 993, 844, 823, 760, 740 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ = 2.36 (s, 3H, $ArCH_3$),6.74–6.86 (m, 3H, ArH), 7.18–7.23 (m, 5H, ArH), 7.35 (d, *J* = 8.0 Hz, 2H, ArH), 7.93 (d, *J* = 8.0 Hz, 2H, ArH), 9.96 (s, 1H, C–CH=N), 10.98 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.3, 111.5, 117.2 (d, *J* = 22.7 Hz), 117.2 (d, *J* = 22.7

Hz), 121.2, 122.8, 124.2 (d, J = 8.5 Hz), 124.2 (d, J = 8.5 Hz), 125.3, 130.3, 130.3, 130.9, 130.9, 131.1, 132.9, 133.8, 144.2, 144.7, 146.4, 148.0 (d, J = 3.0 Hz), 158.3, 162.4 (d, J = 243.7 Hz), 168.9, 195.5; HRMS (TOF ES$^+$): *m/z* calcd for $C_{24}H_{18}FN_2O_2$ [(M+H)$^+$], 385.1347; found, 385.1345.

3-(3-((4-chlorophenyl)imino)-1-oxo-1-(*p*-tolyl)propan-2-ylidene)-1-methylindolin-2-one (5c).



Red solid; mp 144–146 °C; IR (KBr): 1698, 1663, 1601, 1472, 1375, 1332, 1262, 1172, 1090, 976, 834, 743, 730 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.40 (s, 3H, $ArCH_3$), 3.26 (s, 3H, N–CH_3), 6.76–6.81 (m, 2H, ArH), 7.02–7.04 (m, 1H, ArH), 7.12–7.14 (m, 2H, ArH), 7.22–7.29 (m, 5H, ArH), 7.92–9.94 (m, 2H, ArH), 10.13 (s, 1H, C–CH=N); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.9, 26.0, 108.4, 120.2, 122.8, 123.1, 123.1, 125.2, 129.2, 129.2, 129.4, 129.4, 129.5, 129.5, 129.8, 129.8, 131.5, 133.3, 133.4, 144.5, 144.6, 145.4, 149.3, 157.4, 167.0, 195.2; HRMS (TOF ES$^+$): *m/z* calcd for $C_{25}H_{20}ClN_2O_2$ [(M+H)$^+$], 415.1208; found, 415.1204.

6. X-ray Structure and Data[3] of 3ak (CCDC 1409628)

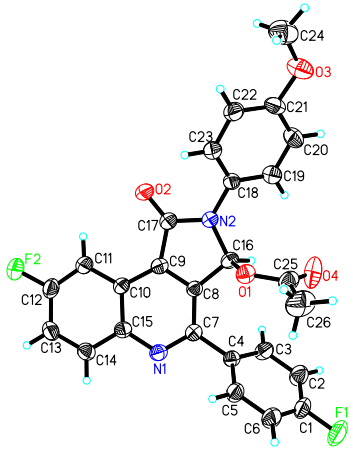


Fig. S4 X-Ray crystal structure of **3ak**

Table S5 Crystal data and structure refinement for **3ak**

Empirical formula	$C_{26}H_{18}F_2N_2O_4$
Formula weight	460.42
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 6.0426(10) A alpha = 78.111(2) deg.
	b = 12.222(2) A beta = 79.431(2) deg.
	c = 15.374(3) A gamma = 87.801(3) deg.
Volume	1092.2(3) A^3
Z, Calculated density	2, 1.400 Mg/m^3
Absorption coefficient	0.107 mm^-1
F(000)	476
Crystal size	0.48x 0.32 x 0.18 mm
Theta range for data collection	1.38 to 25.15 deg.
Limiting indices	-7<=h<=7, -14<=k<=14, -18<=l<=18
Completeness to theta = 25.15	99.6%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9506 and 0.9811
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3897 / 0 / 309
Goodness-of-fit on F^2	0.986
Final R indices [I>2sigma(I)]	R1 = 0.1311, wR2 = 0.1826
R indices (all data)	R1 = 0.0556, wR2 = 0.1383
Extinction coefficient	0.0052(5)
Largest diff. peak and hole	0.384 and -0.185 e.A^-3

7. X-ray Structure and Data[4] of 4l (CCDC 1431049)

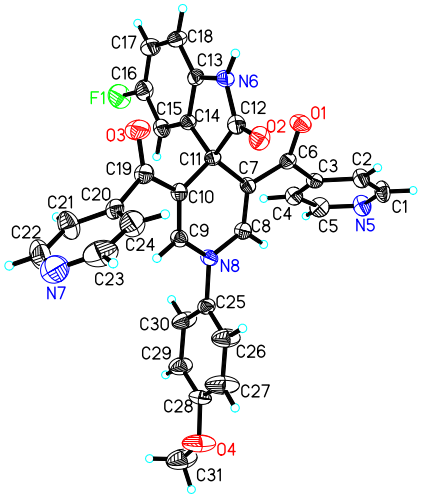


Fig. S5 X-Ray crystal structure of **4l**

Table S6 Crystal data and structure refinement for **4l**

Empirical formula	$C_{31}H_{21}FN_4O_4$
Formula weight	532.52
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, Cc
Unit cell dimensions	a = 6.522(3) A alpha = 90.00 deg.
	b = 19.035(8) A beta = 92.660(6) deg.
	c = 20.250(8) A gamma = 90.00 deg.
Volume	2511.2(17) A^3
Z, Calculated density	4, 1.408 Mg/m^3
Absorption coefficient	0.100 mm^-1
F(000)	1104
Crystal size	0.30x 0.18 x 0.16 mm
Theta range for data collection	2.36 to 18.57 deg.
Limiting indices	-7<=h<=7, -22<=k<=22, -24<=l<=24
Reflection collected/unique	9923/2431[R(int) =0.0730]
Completeness to theta = 25.15	98.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9705 and 0.9841
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4444 / 2/ 363
Goodness-of-fit on F^2	0.987
Final R indices [I>2sigma(I)]	R1 = 0.1205, wR2 = 0.1328
R indices (all data)	R1 = 0.0554, wR2 = 0.1024
Extinction coefficient	0.0052(5)
Largest diff. peak and hole	0.187 and -0.174 e.A^-3

8. NMR spectra (^{1}H NMR and ^{13}C NMR)

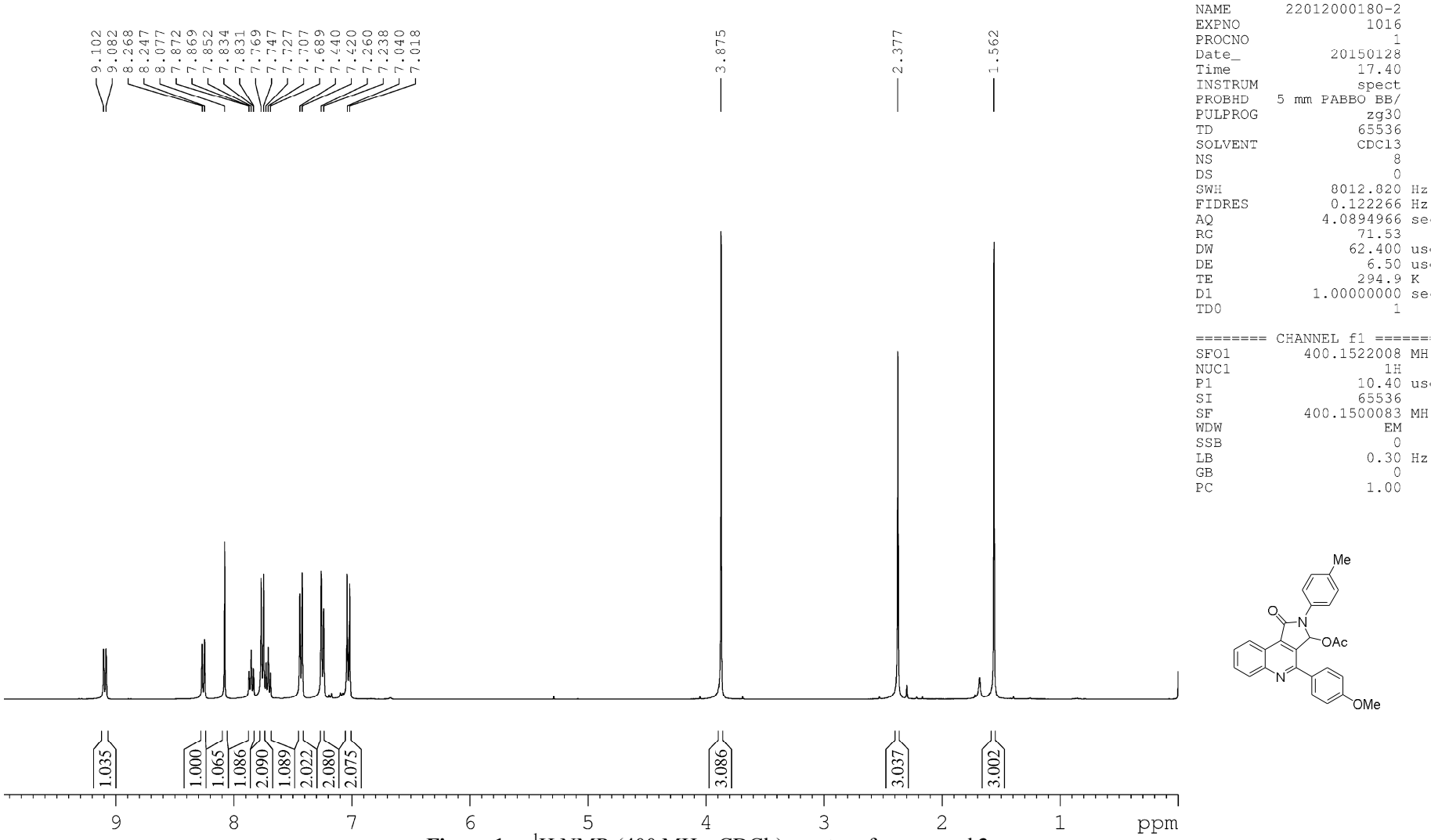


Figure 1. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3aa**

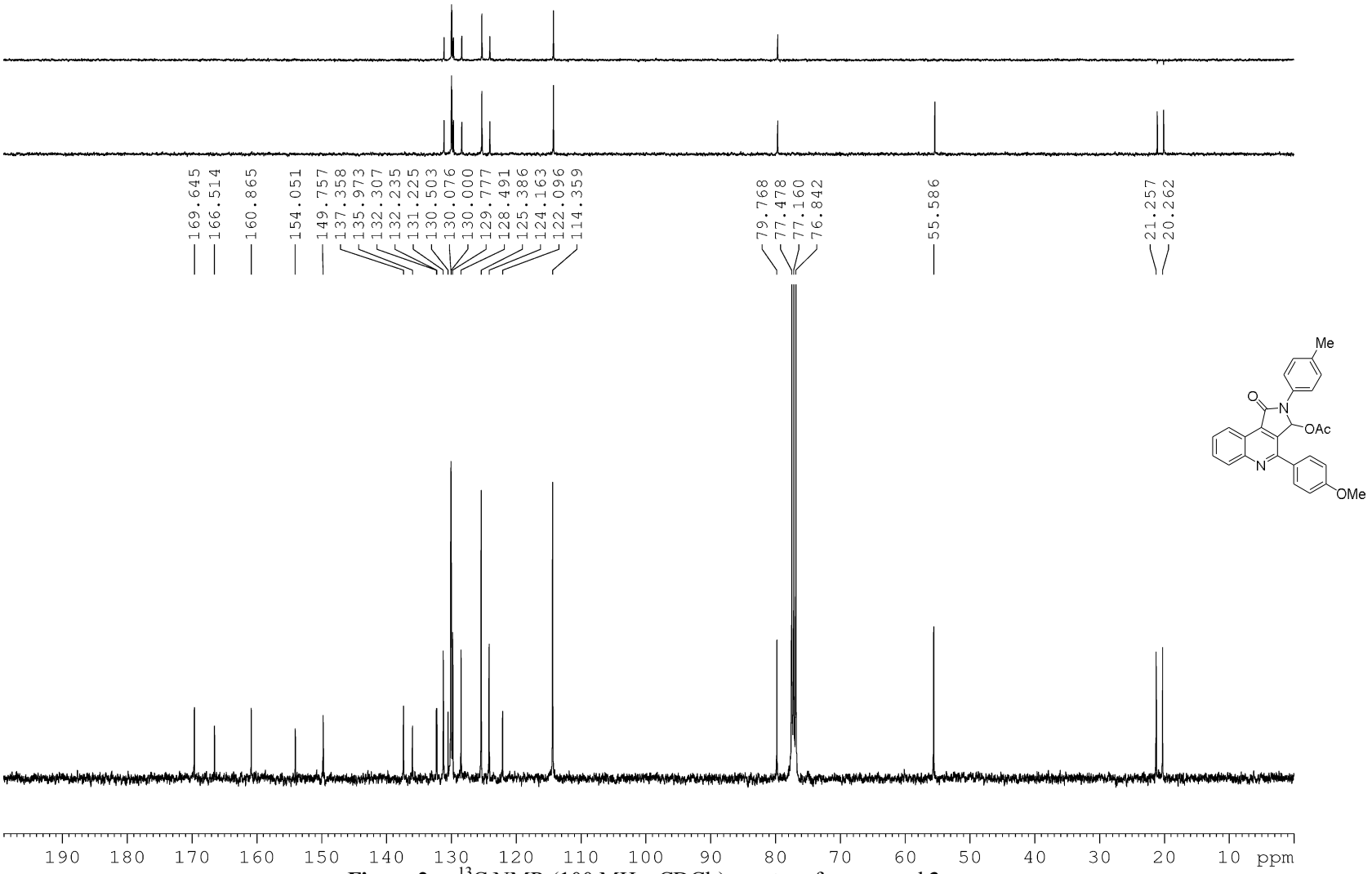


Figure 2. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3aa**

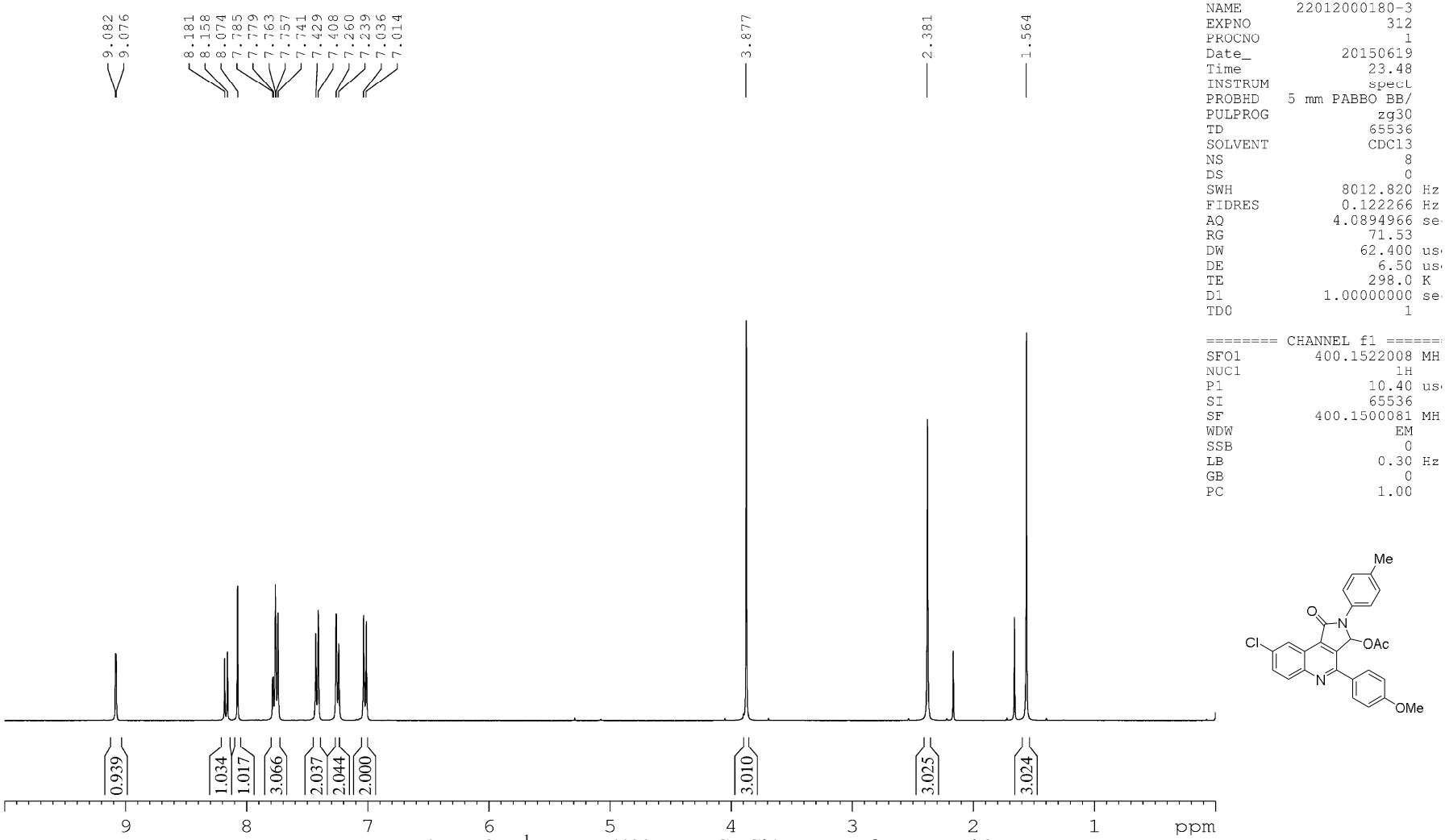


Figure 3. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ab**

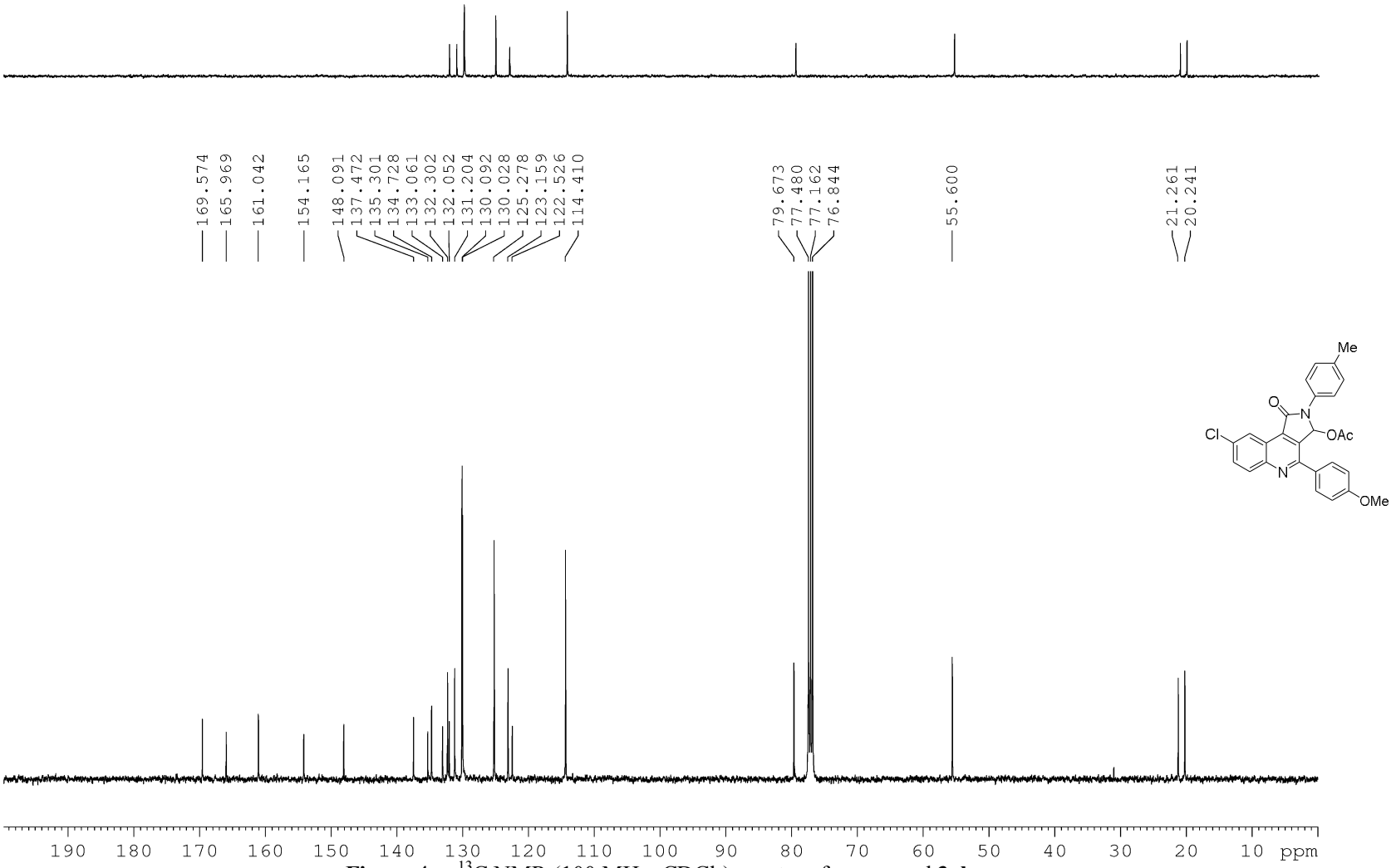


Figure 4. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ab**

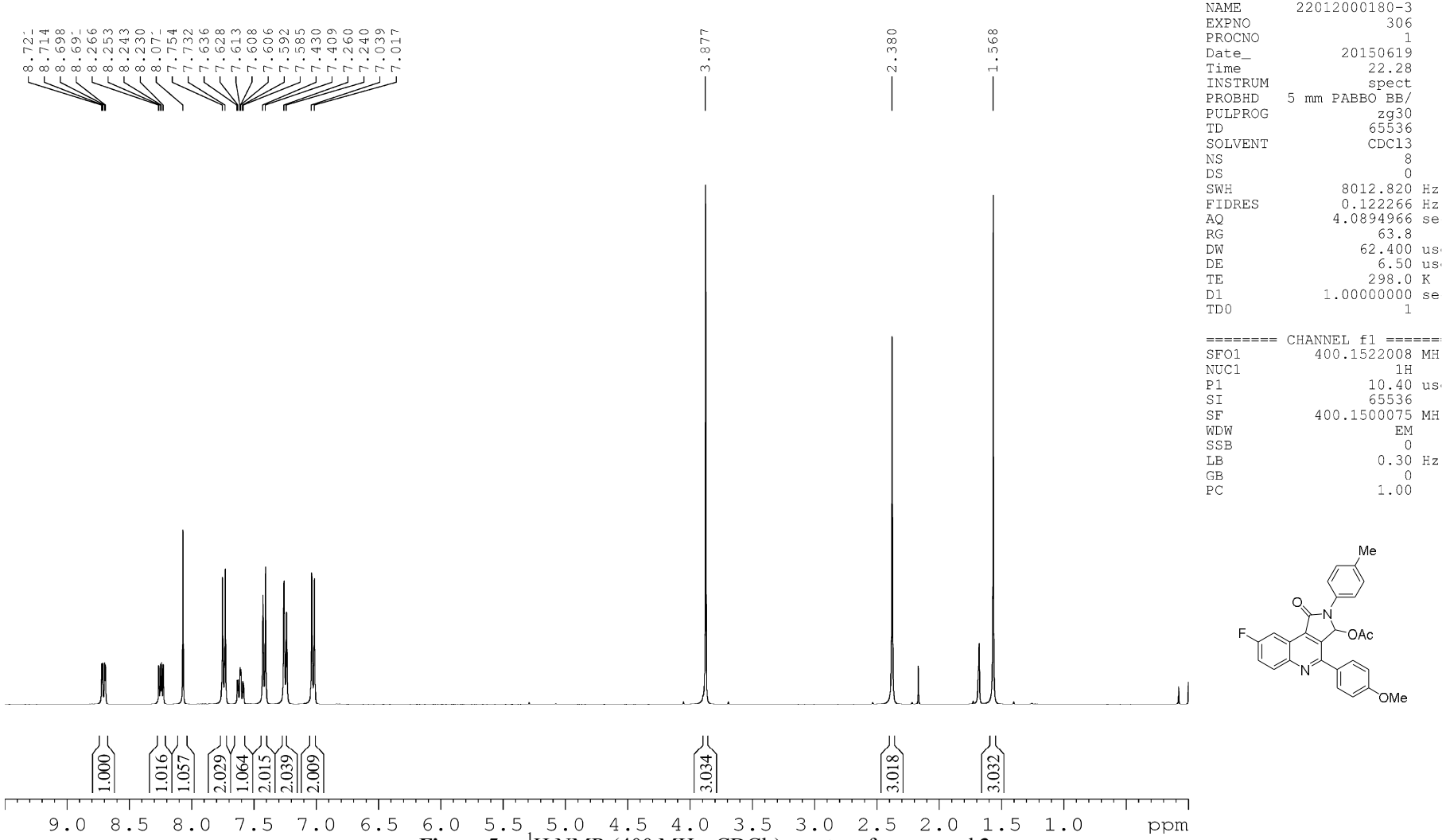


Figure 5. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ac**

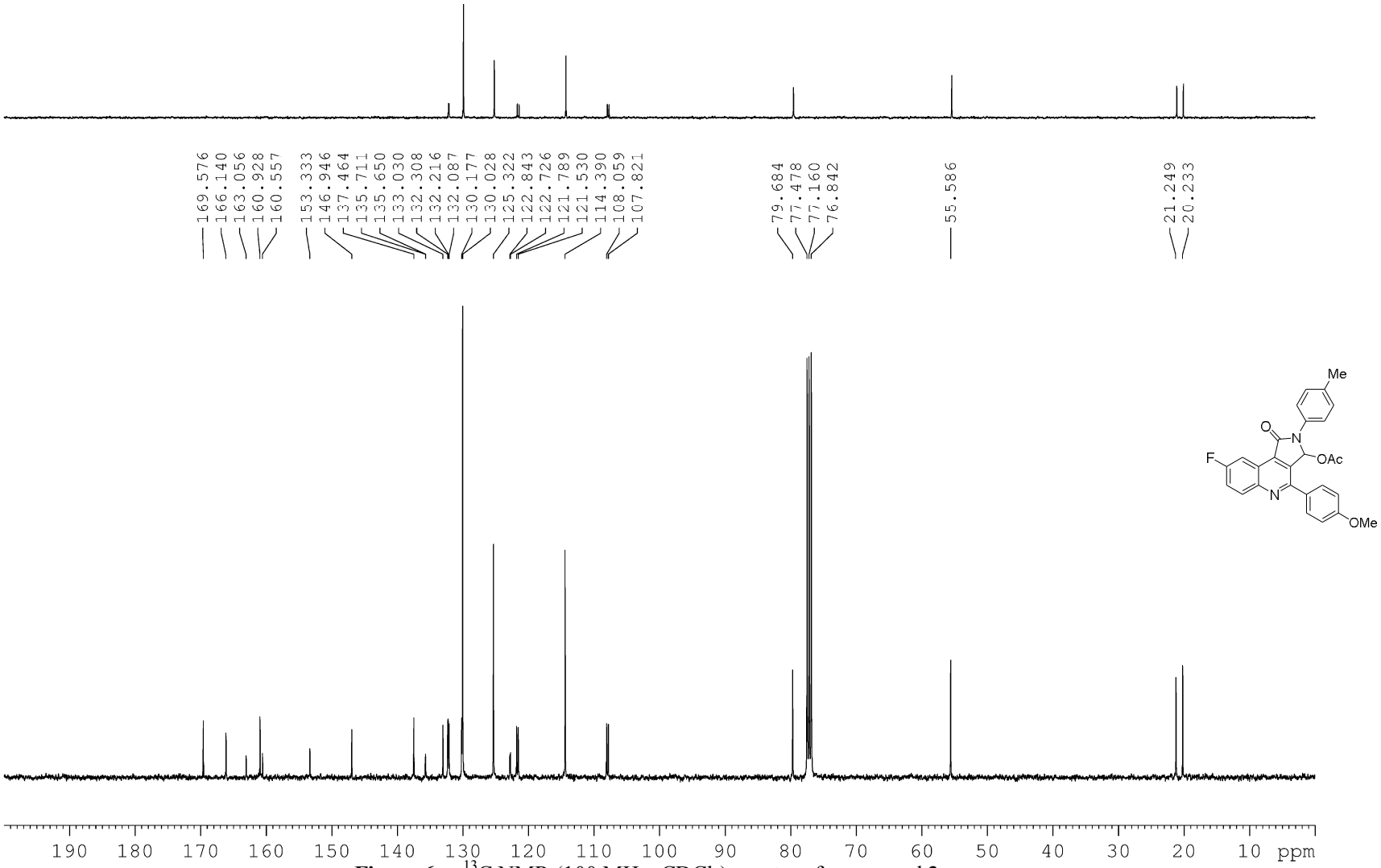


Figure 6. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ac**

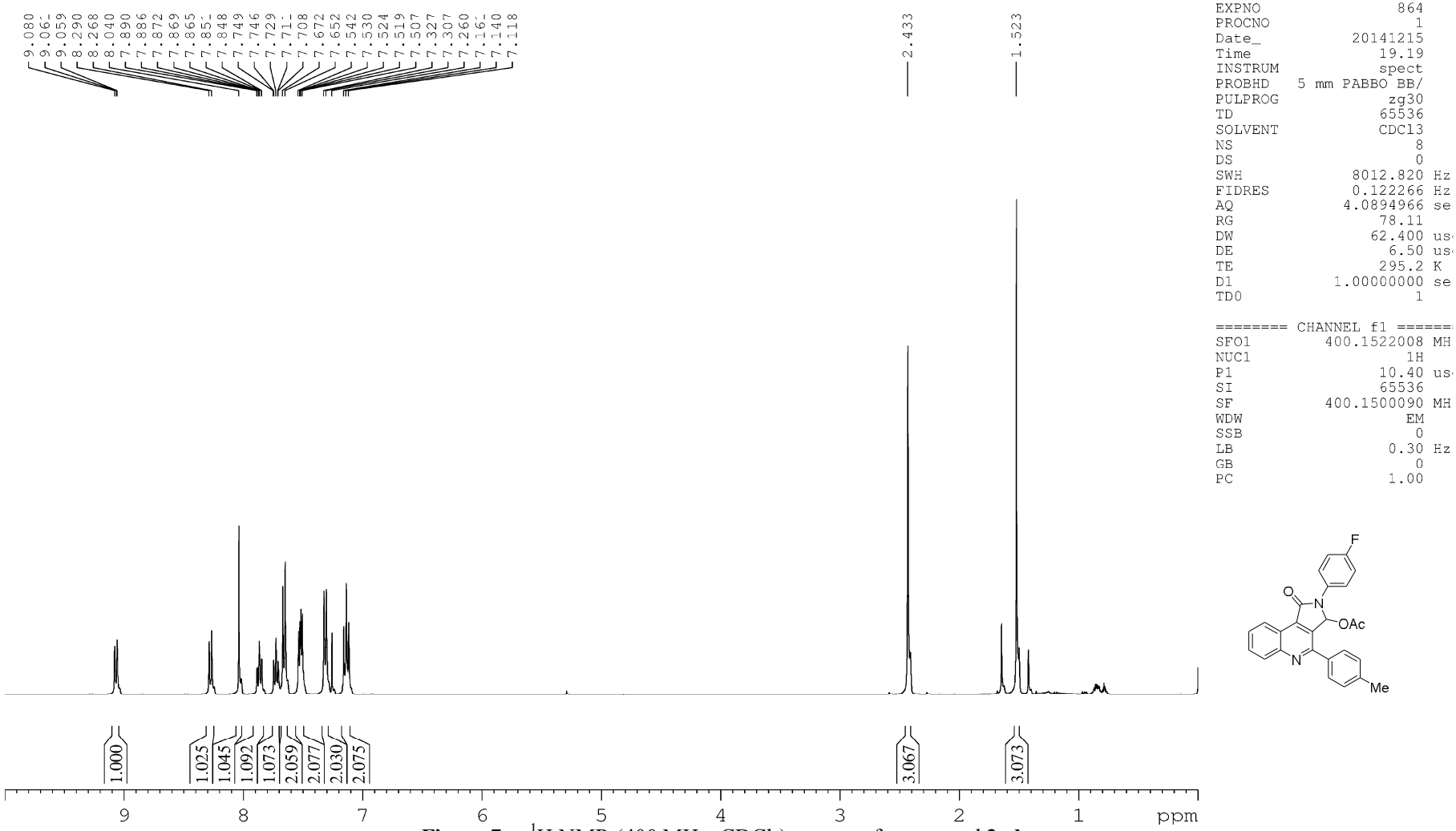


Figure 7. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ad**

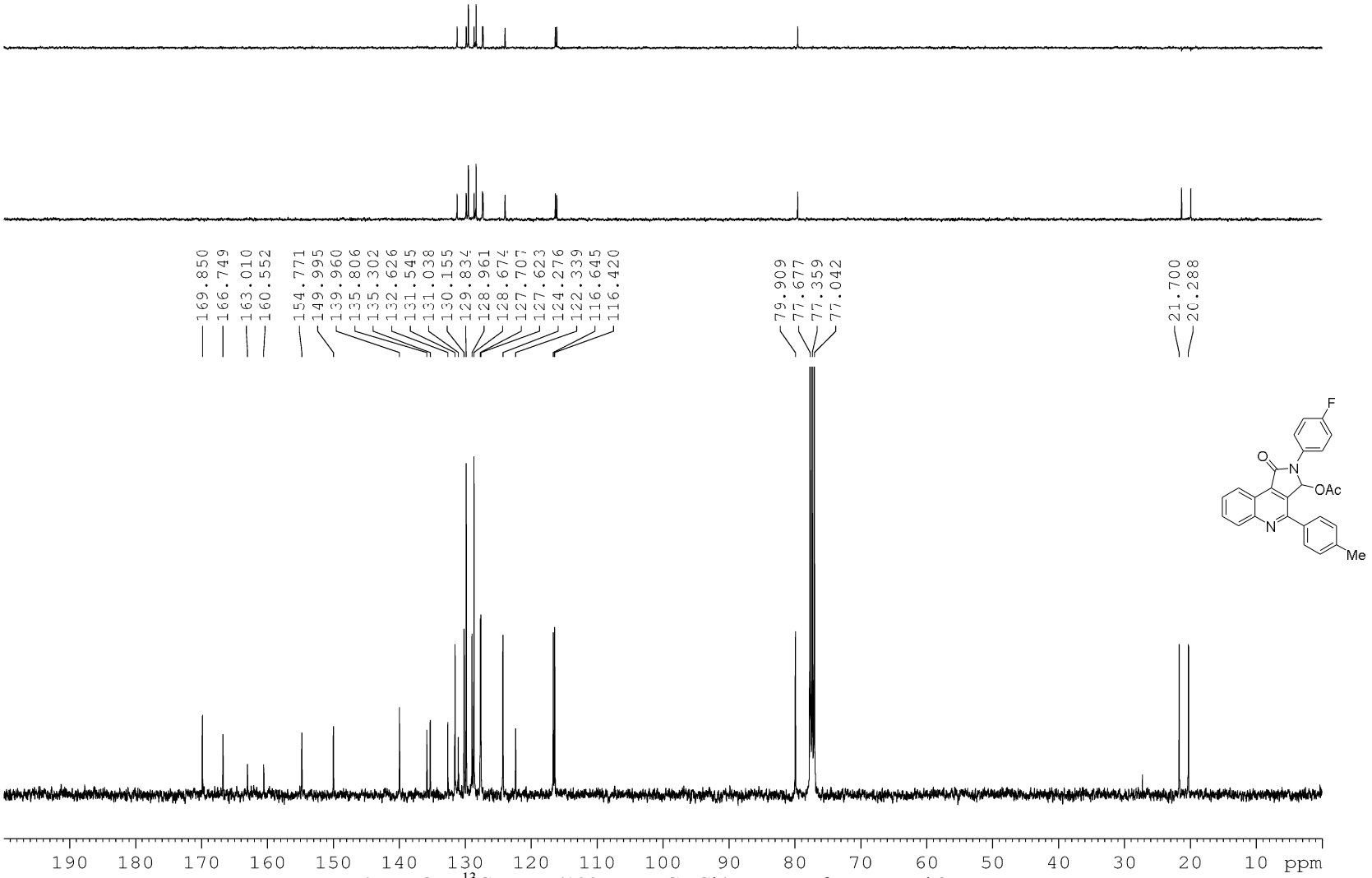


Figure 8. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ad**

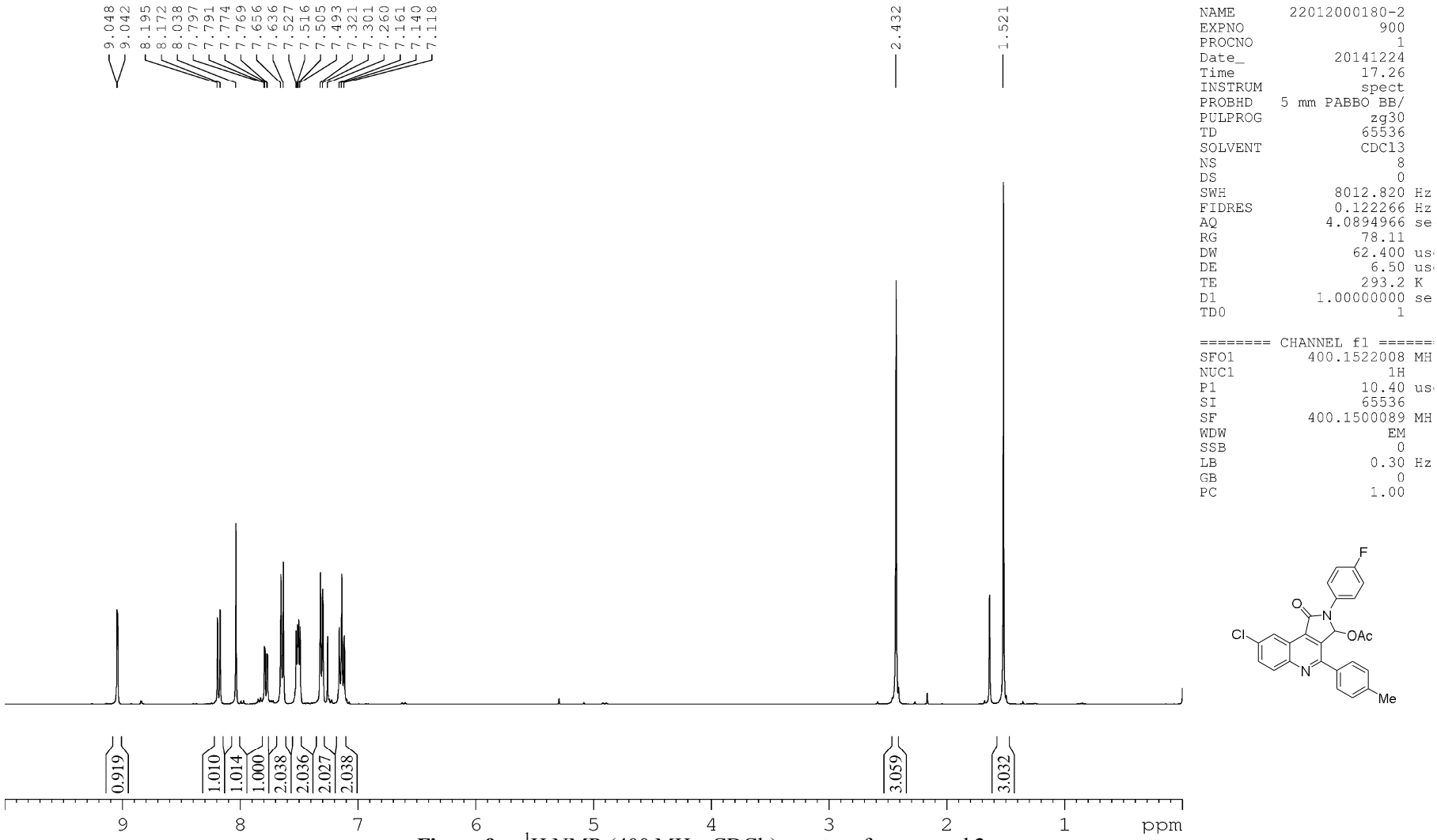


Figure 9. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ae**

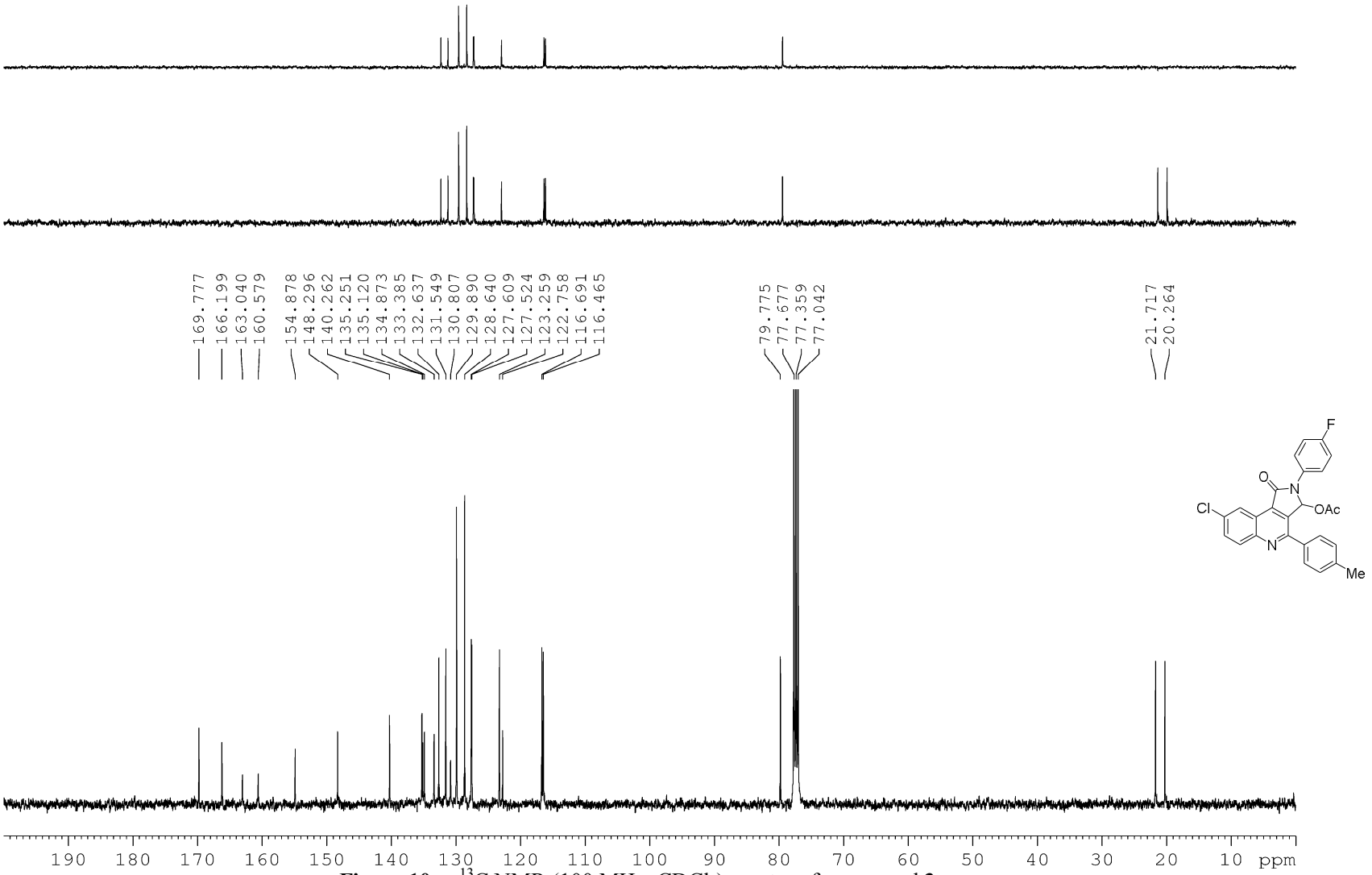


Figure 10. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ae**

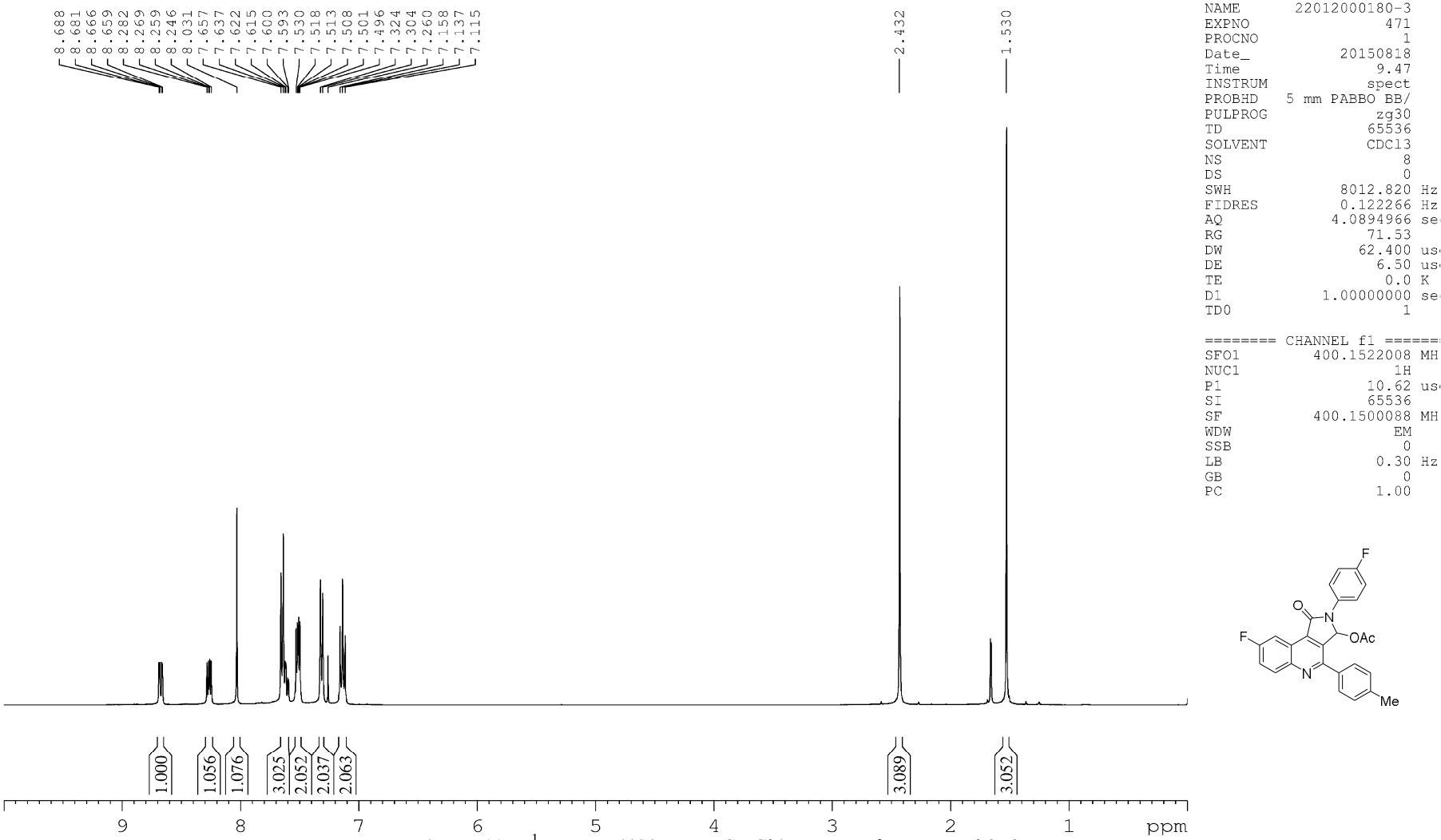


Figure 11. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3af**

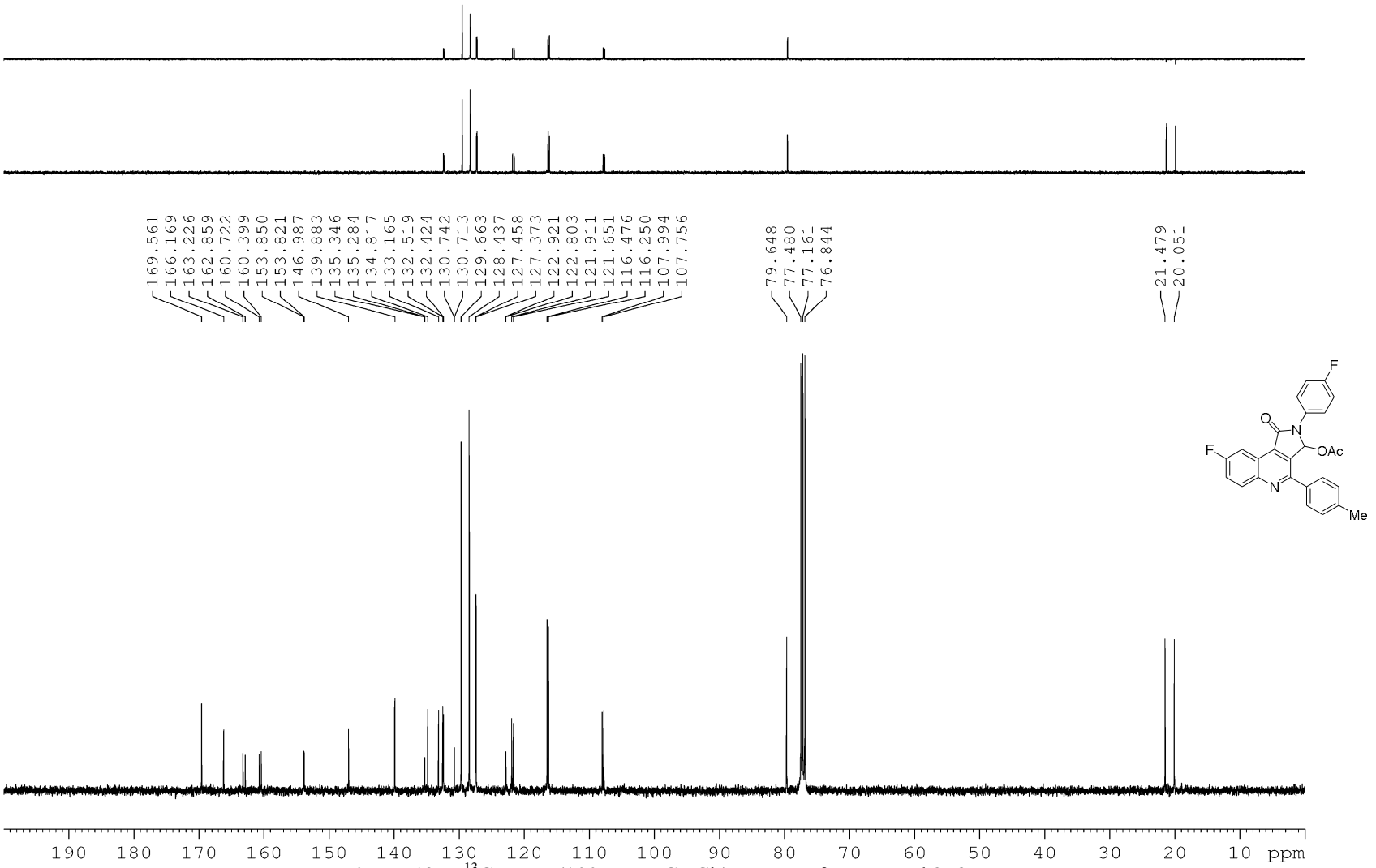


Figure 12. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3af**

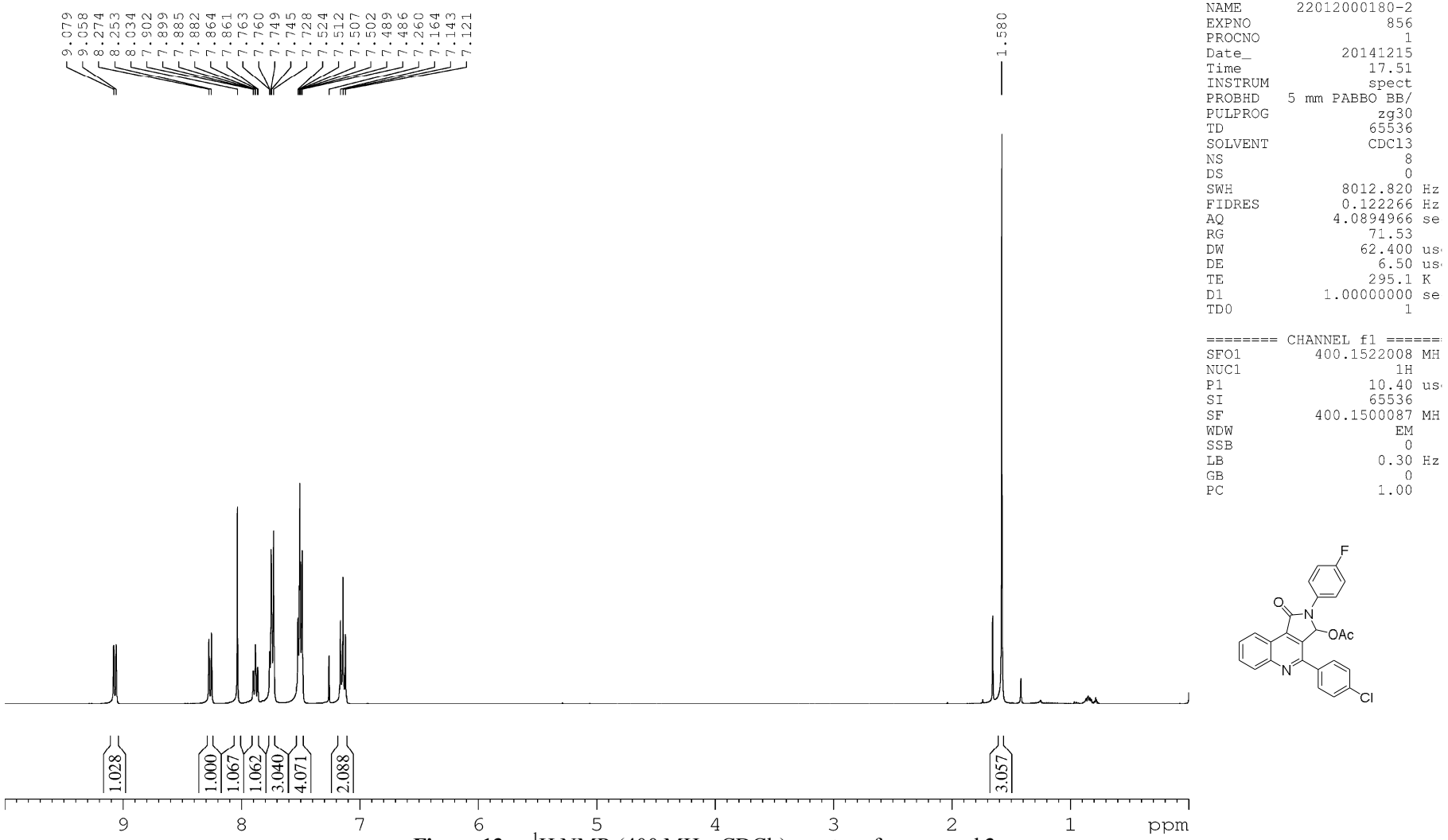


Figure 13. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ag**

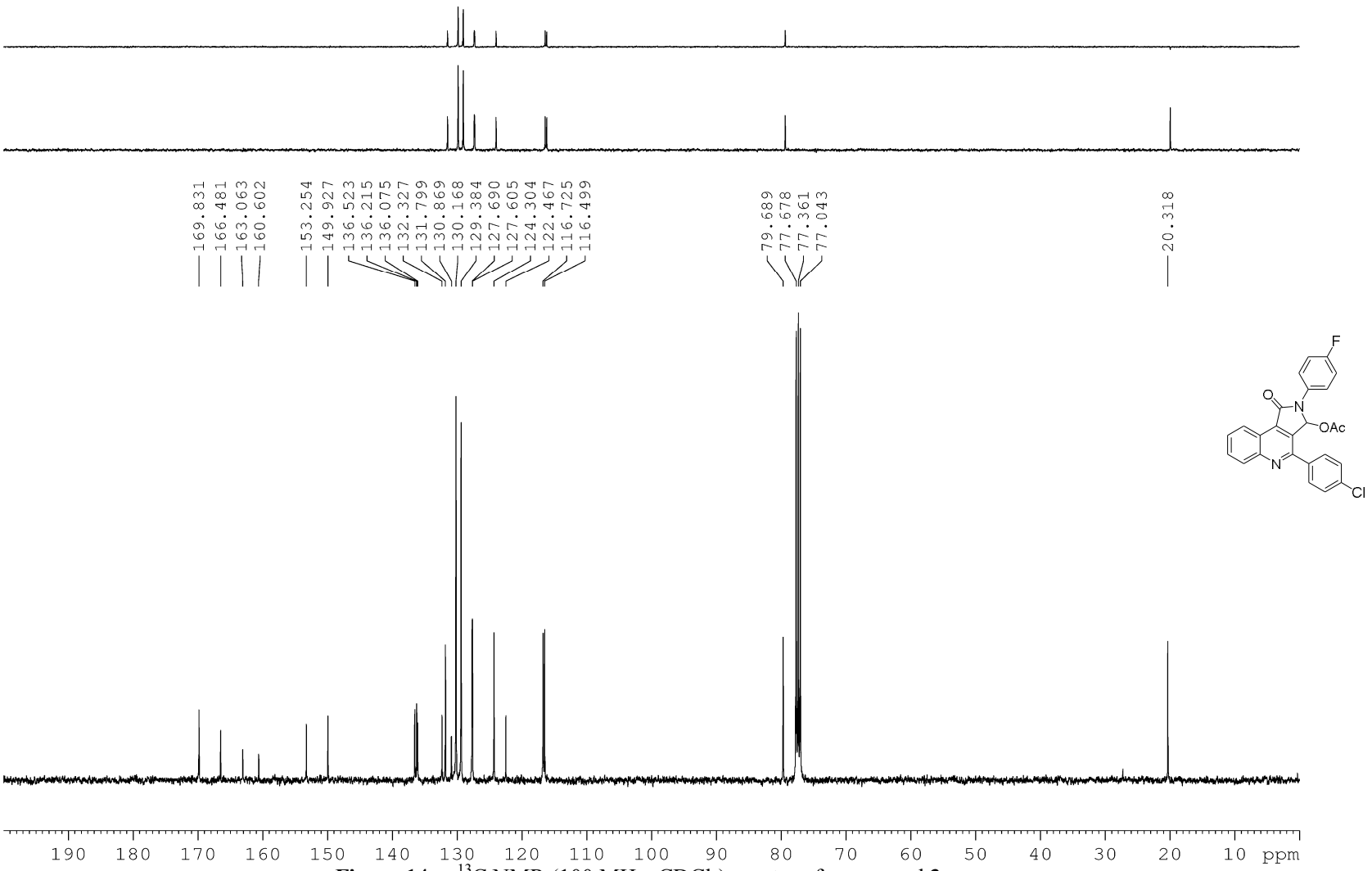


Figure 14. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ag**

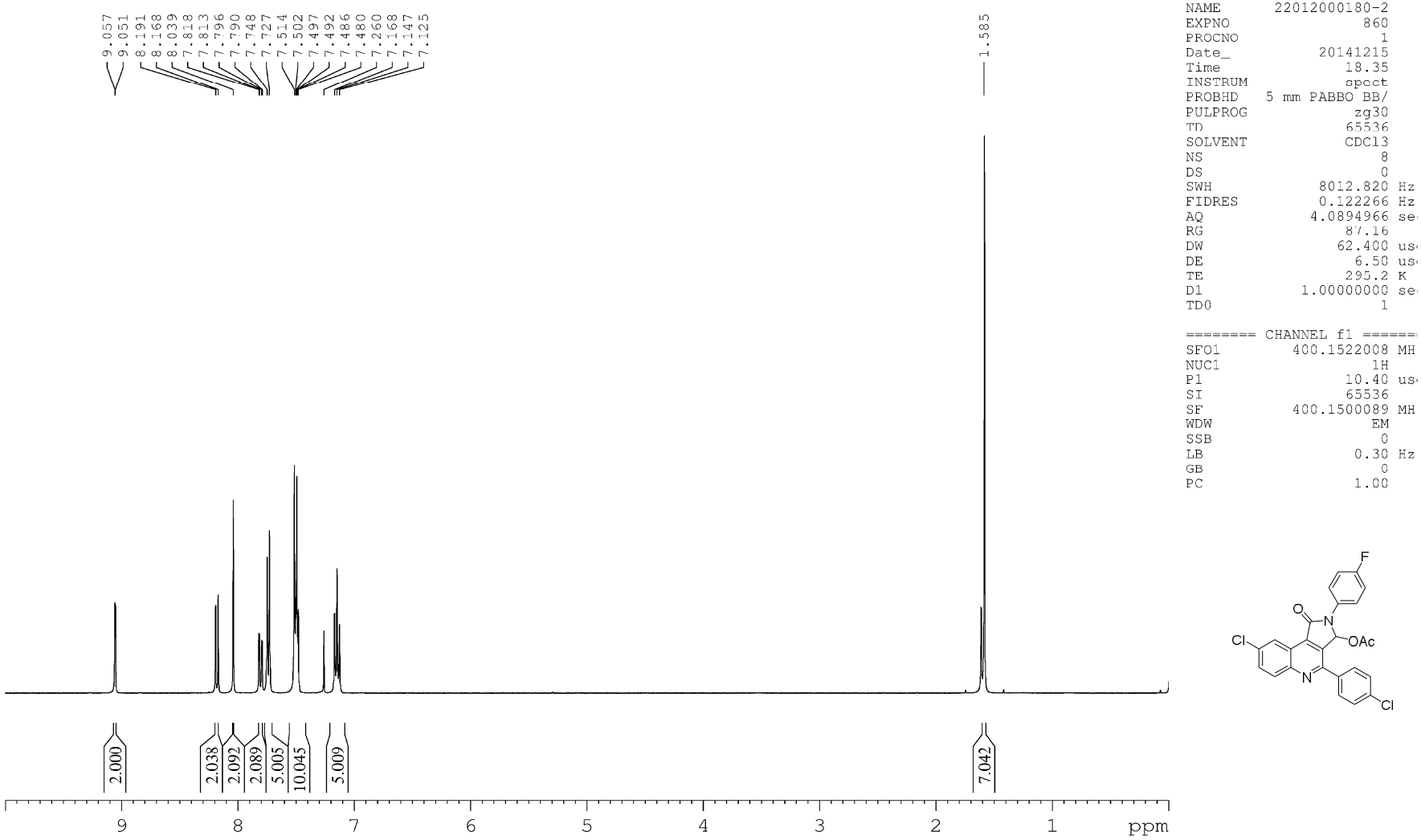


Figure 15. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ah**

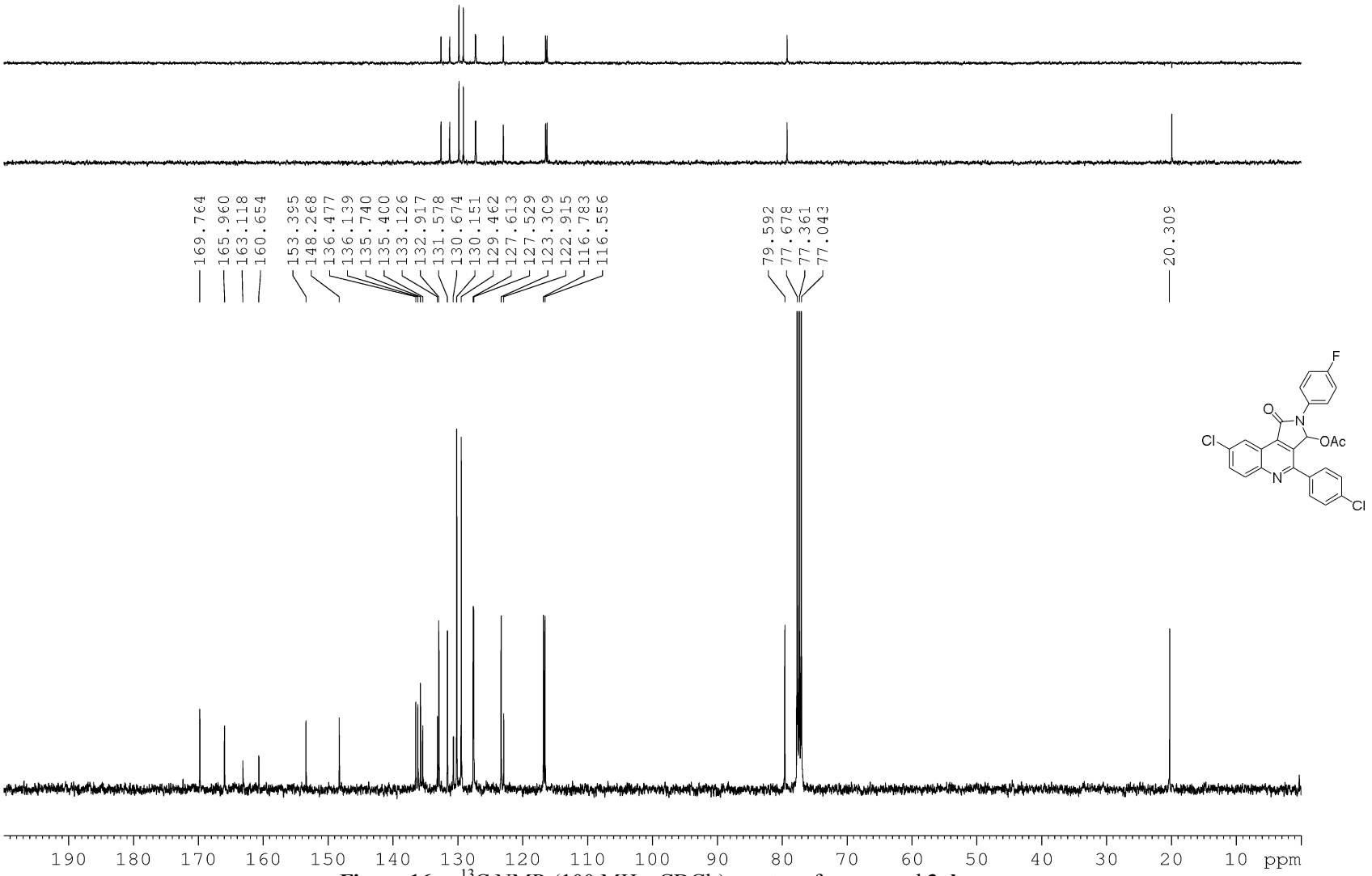


Figure 16. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ah**

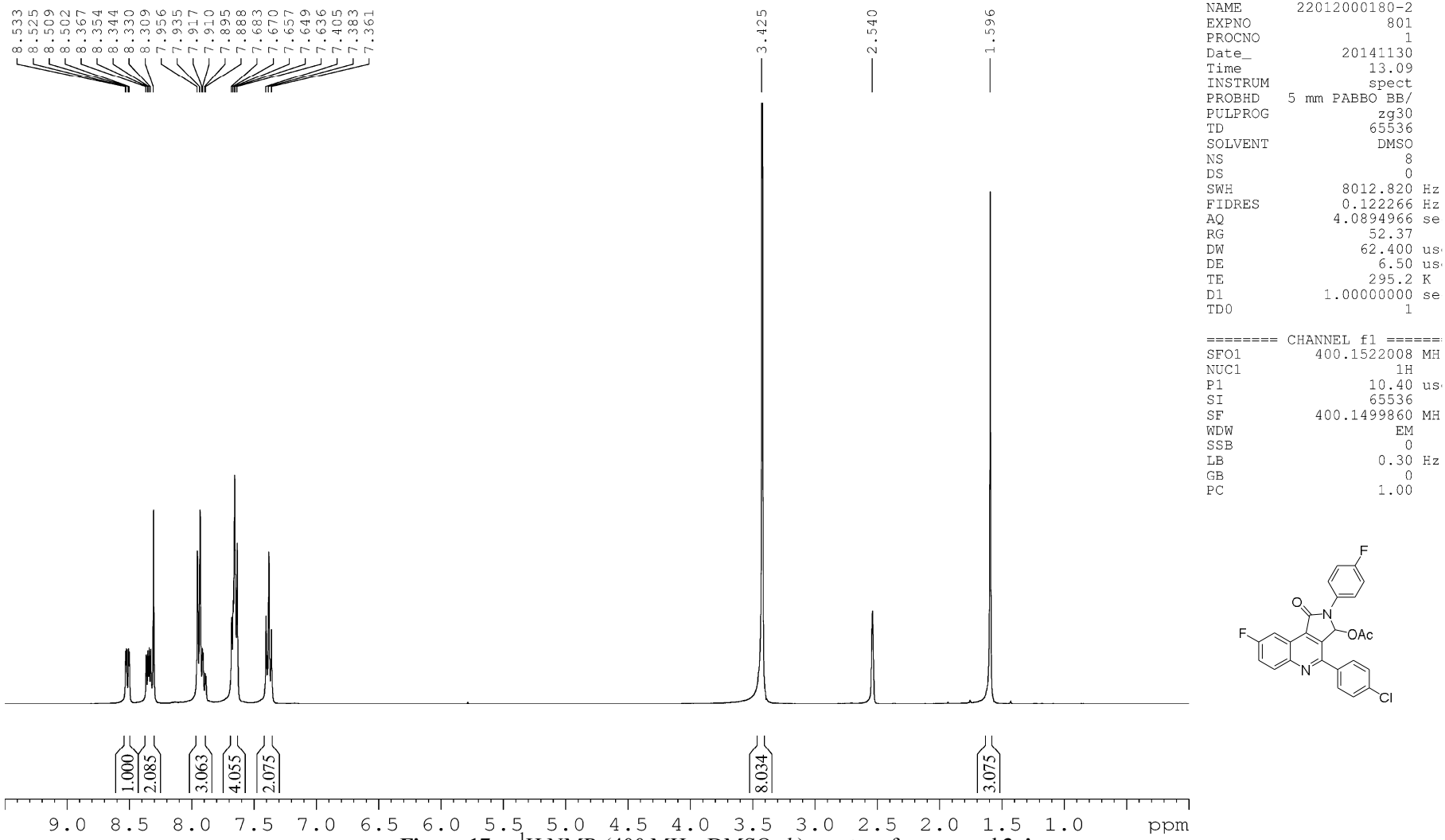


Figure 17. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3ai**

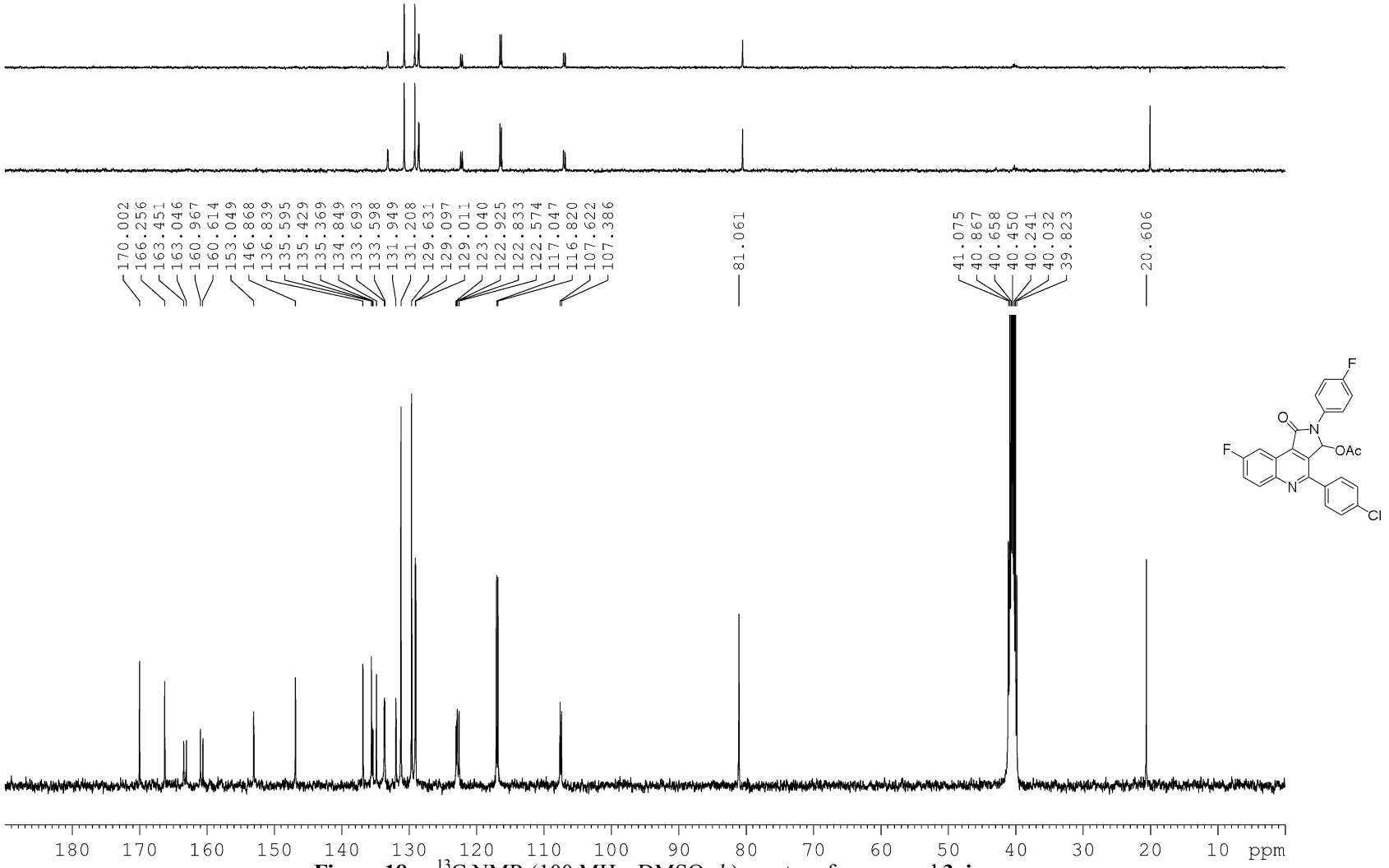


Figure 18. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **3ai**

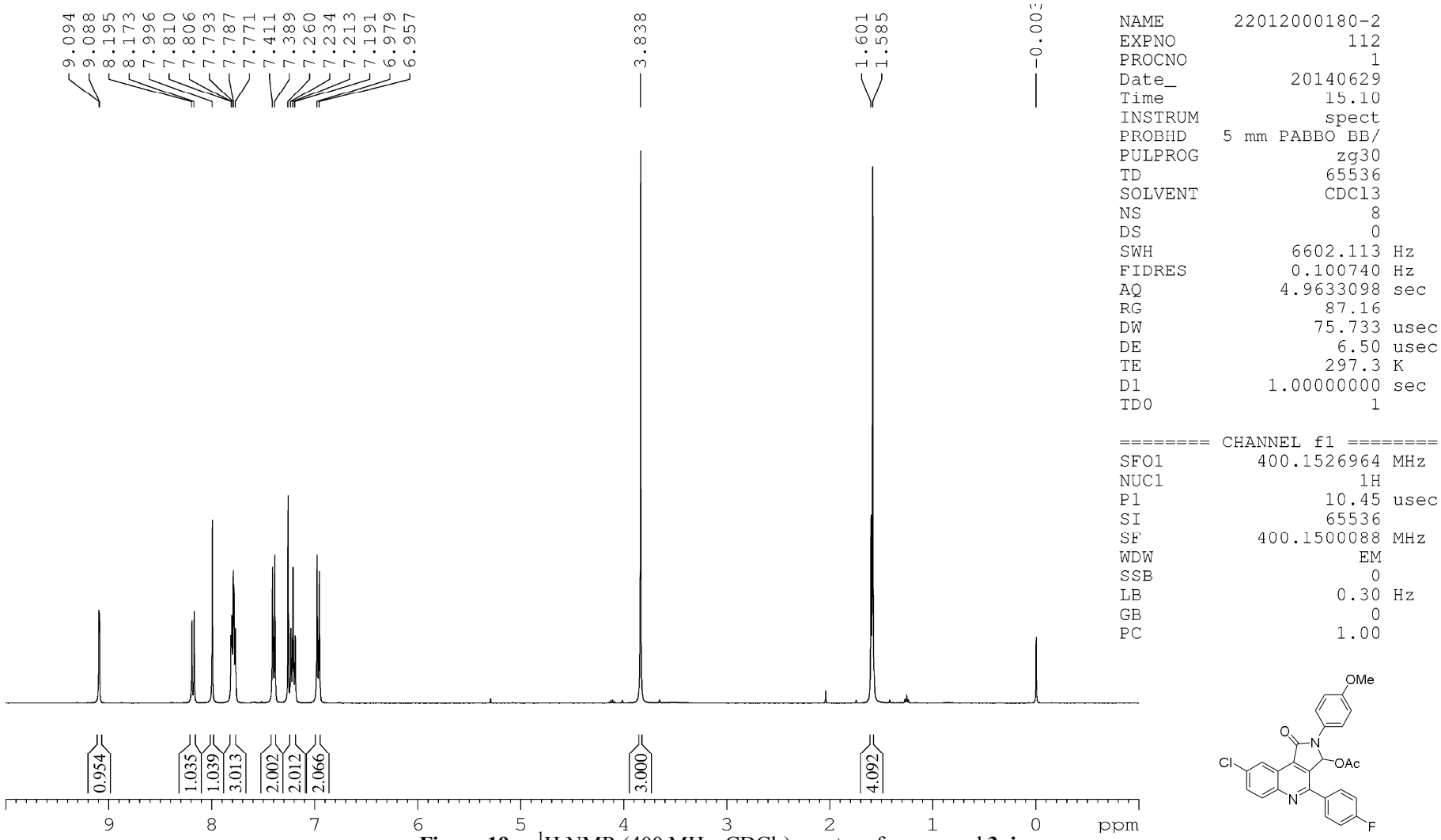


Figure 19. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3aj**

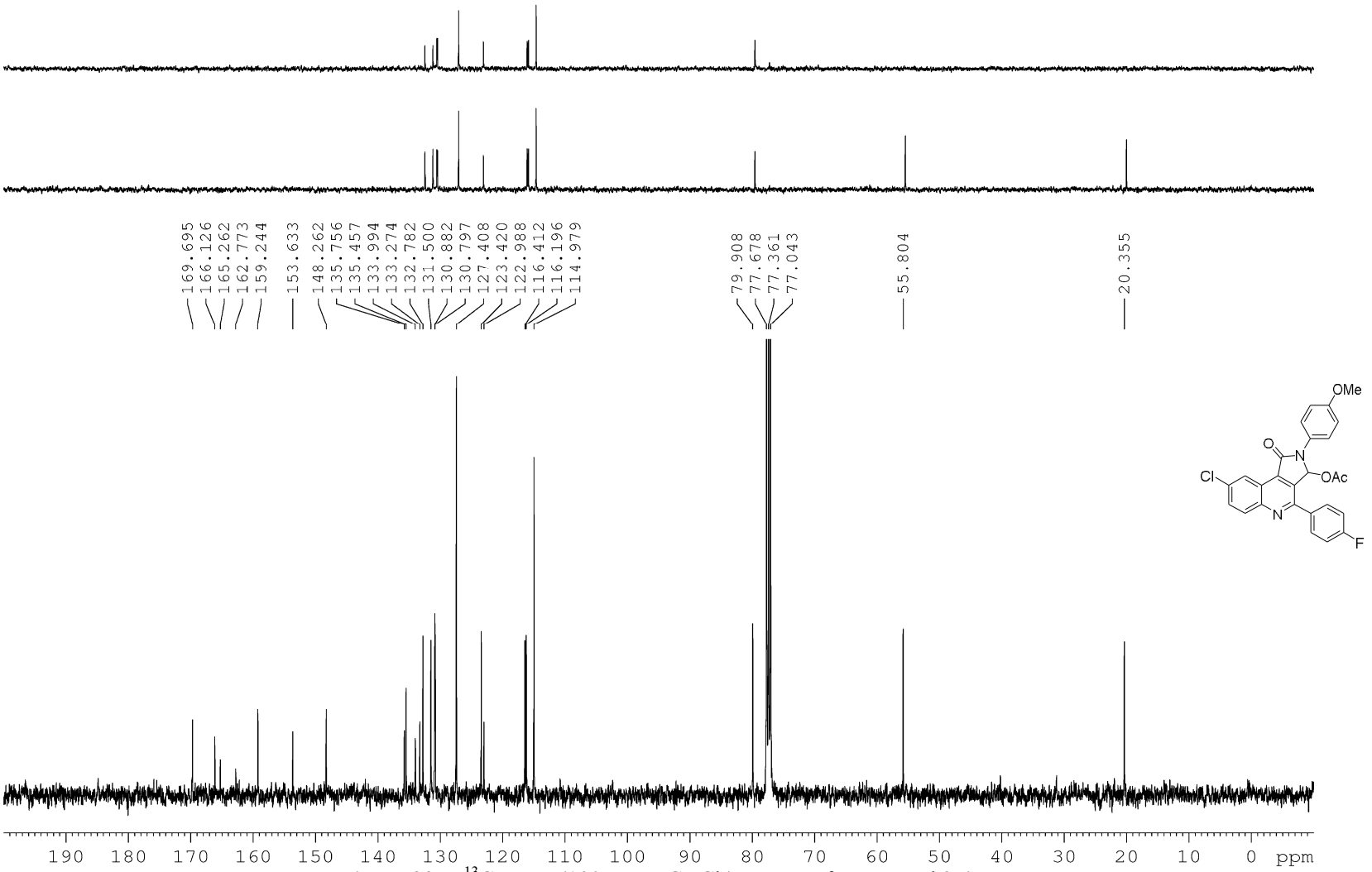


Figure 20. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3aj**

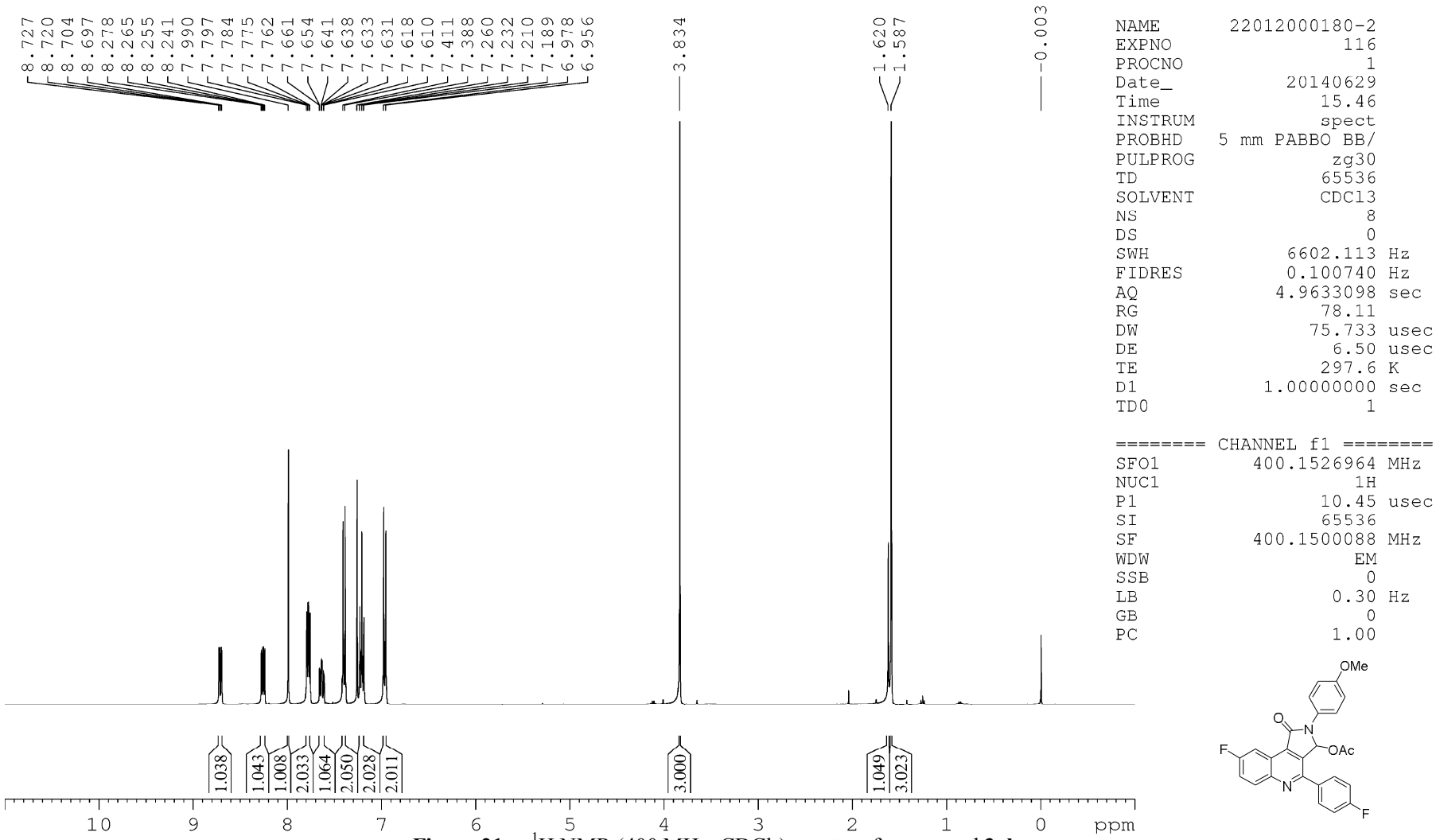


Figure 21. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ak**

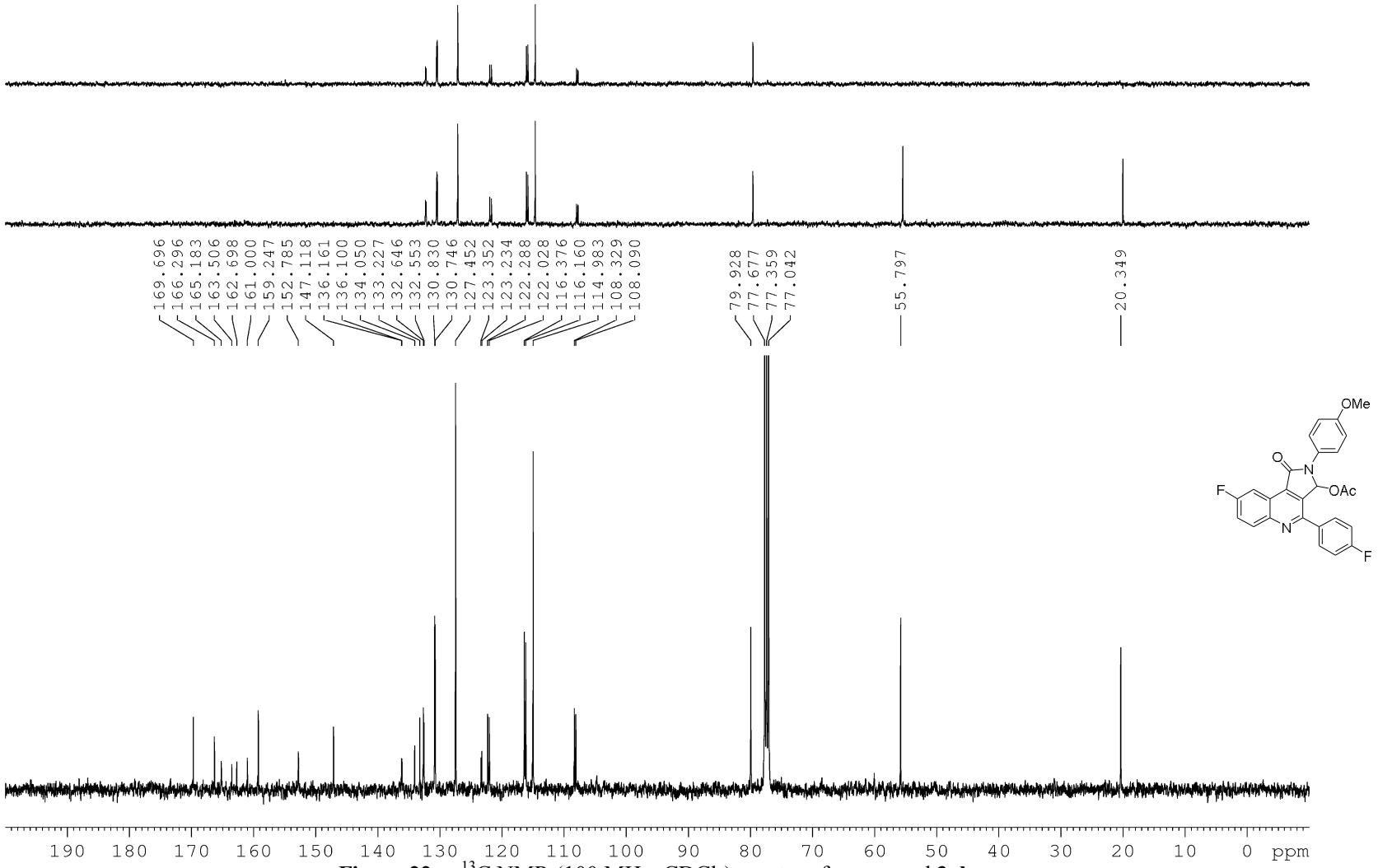


Figure 22. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ak**

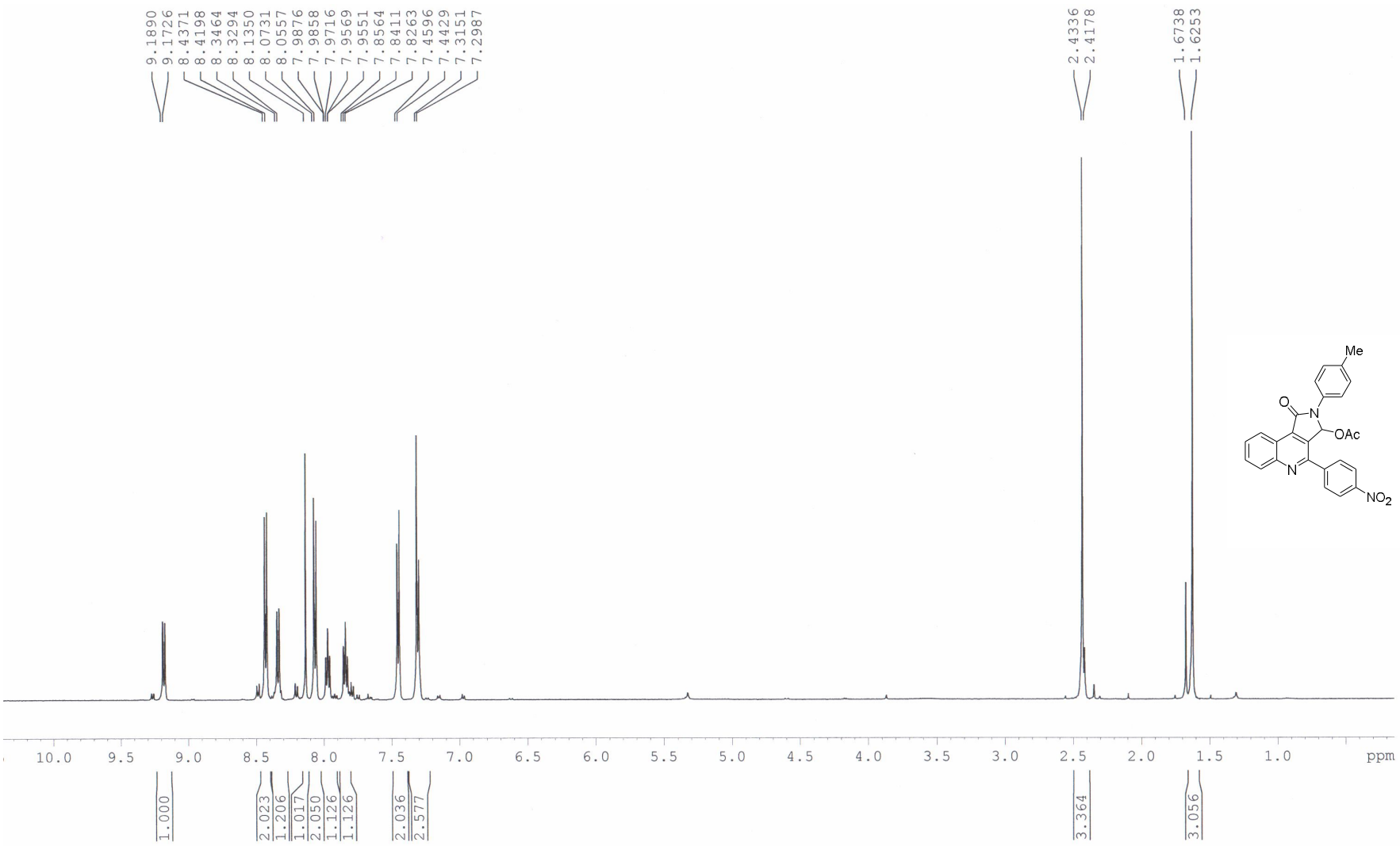


Figure 23. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3al**

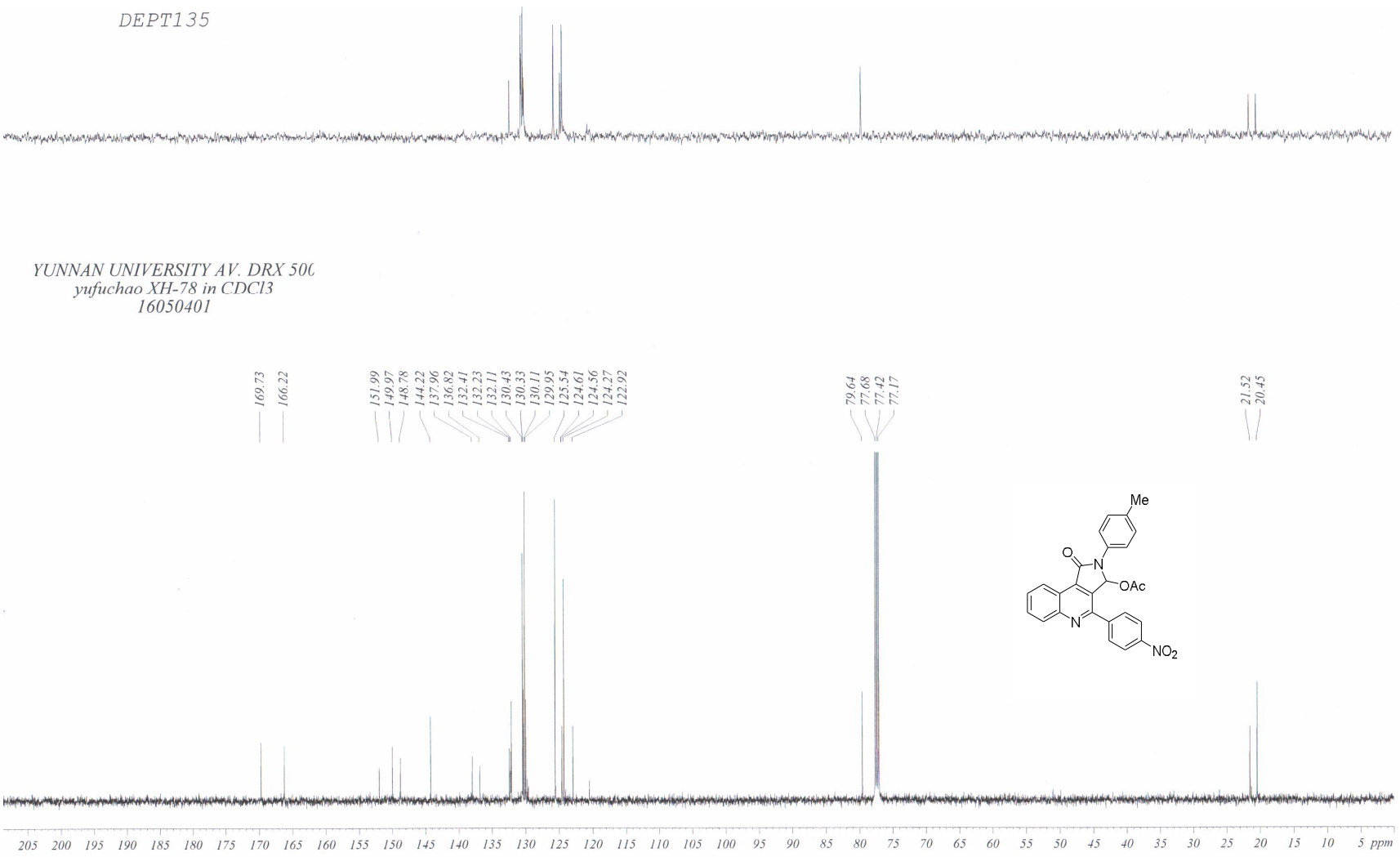


Figure 24. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3al**

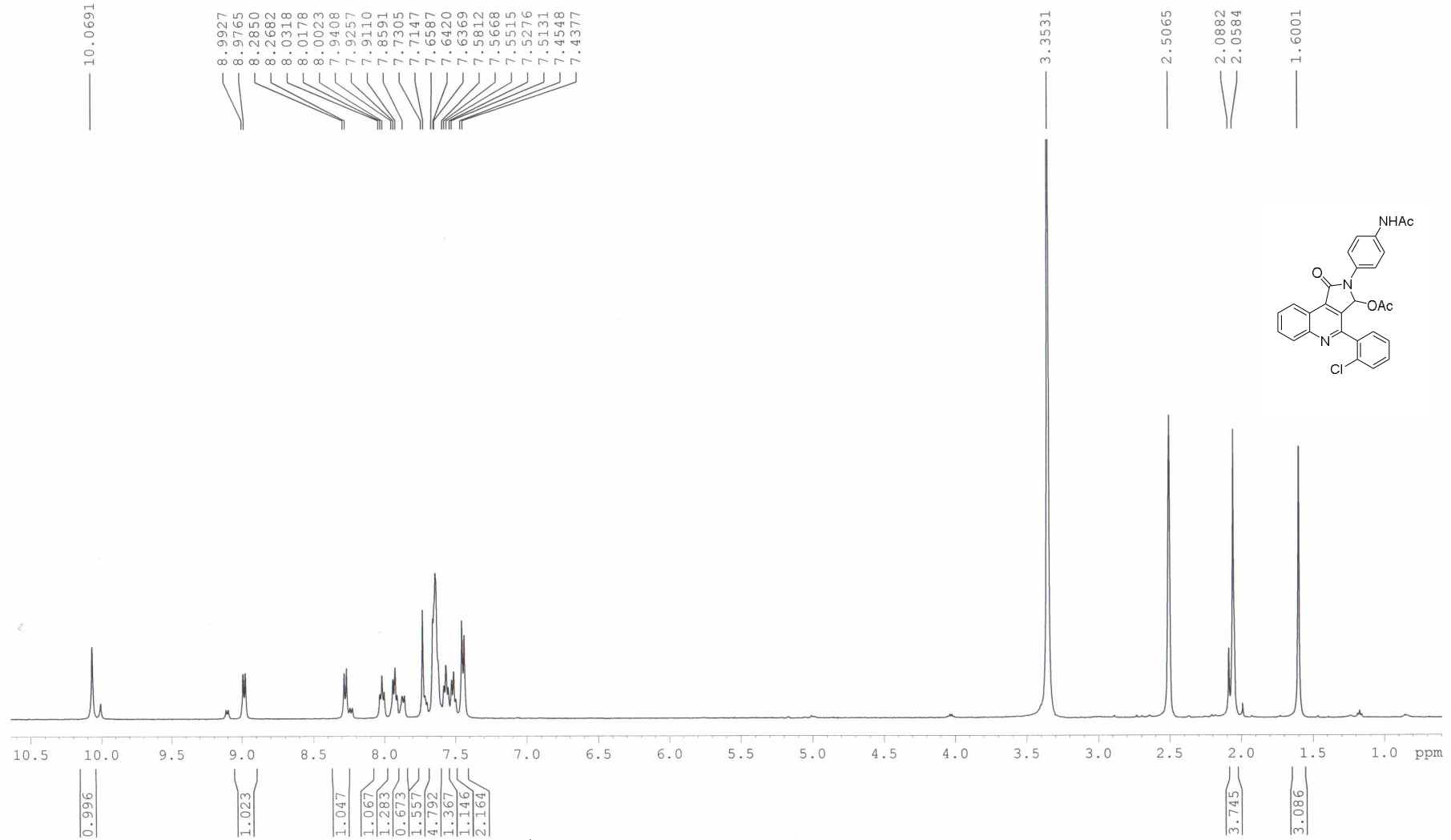


Figure 25. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **3am**

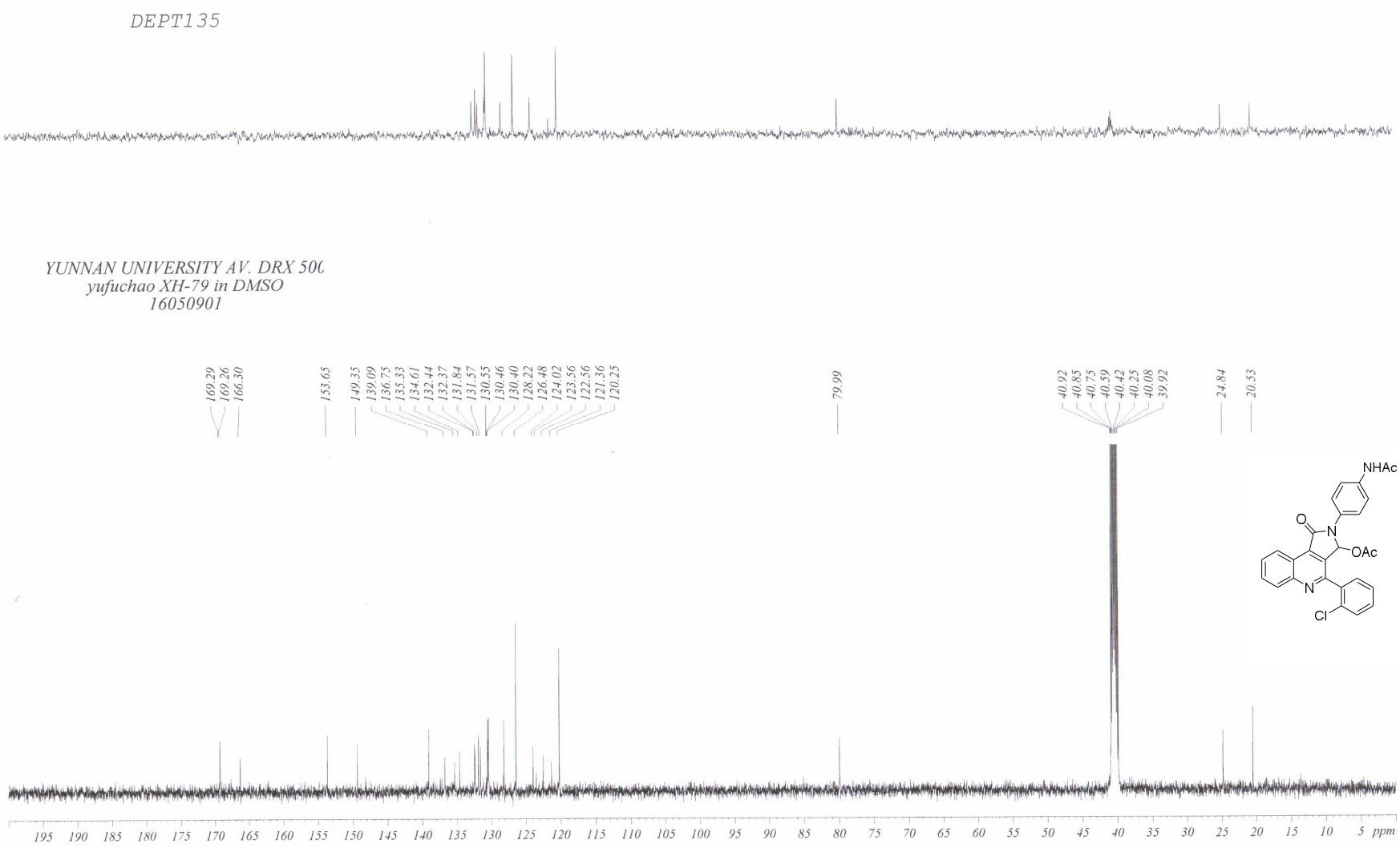


Figure 26. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **3am**

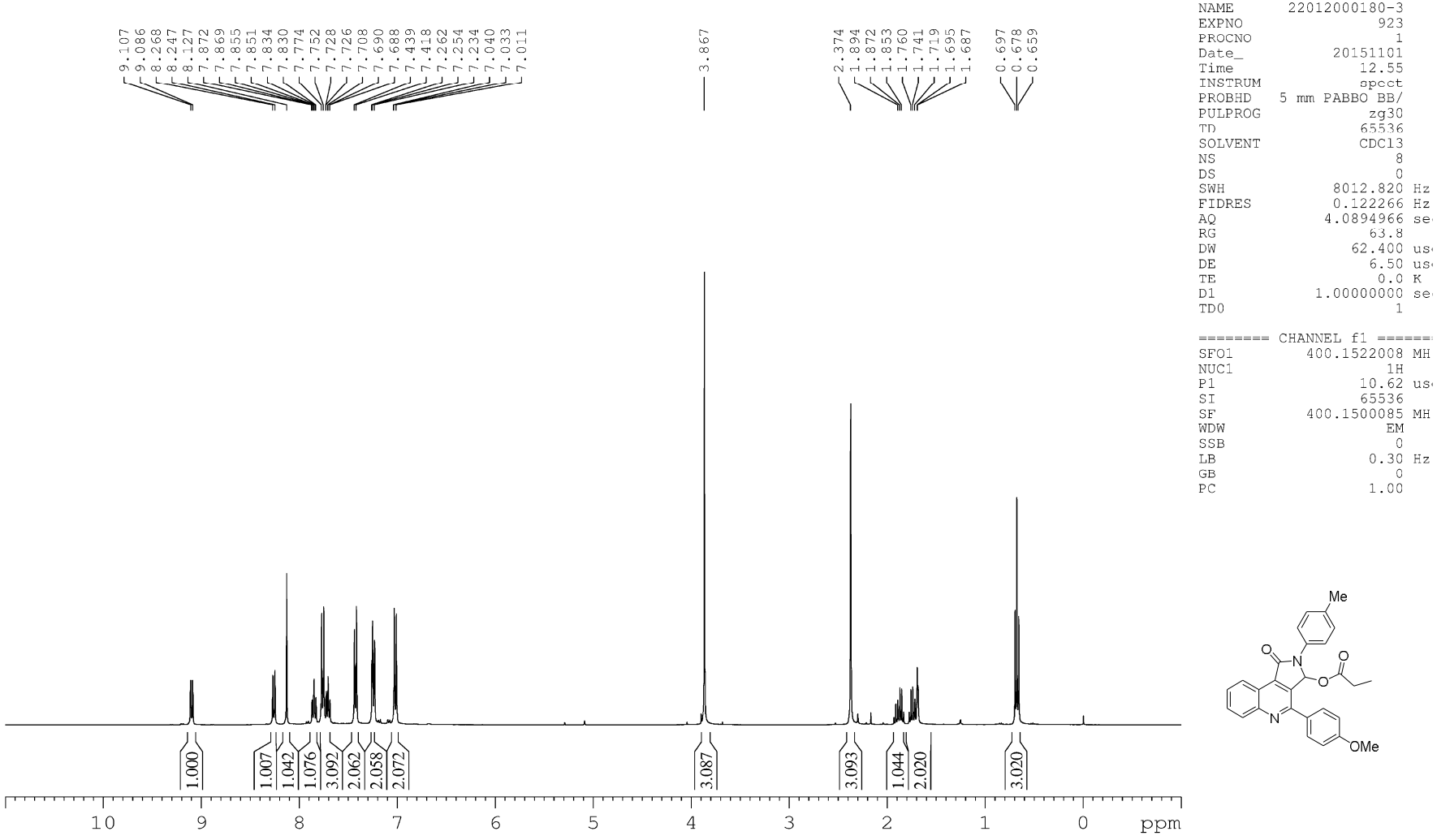


Figure 27. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ba**

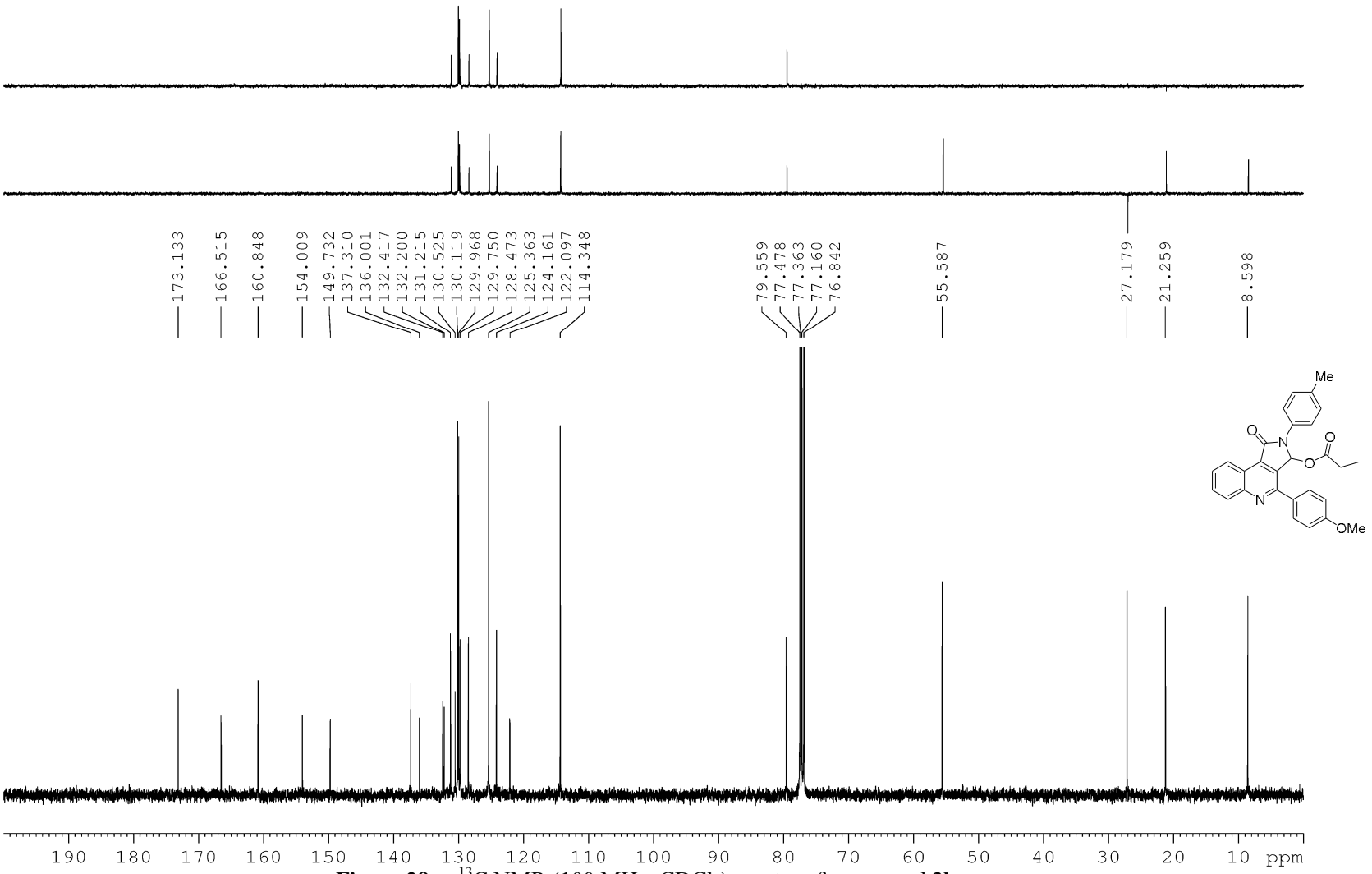


Figure 28. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ba**

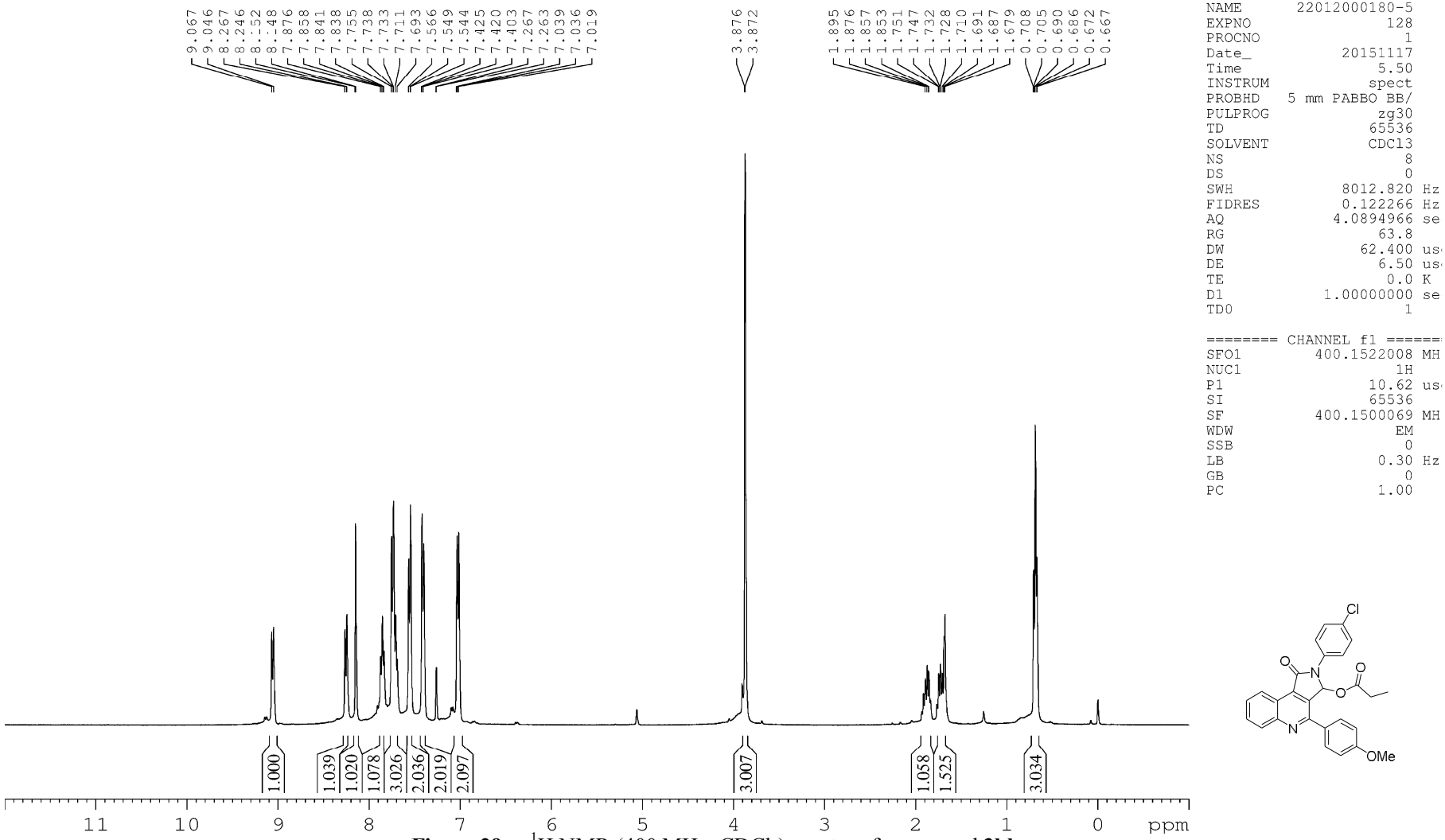



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Figure 29. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3bb**

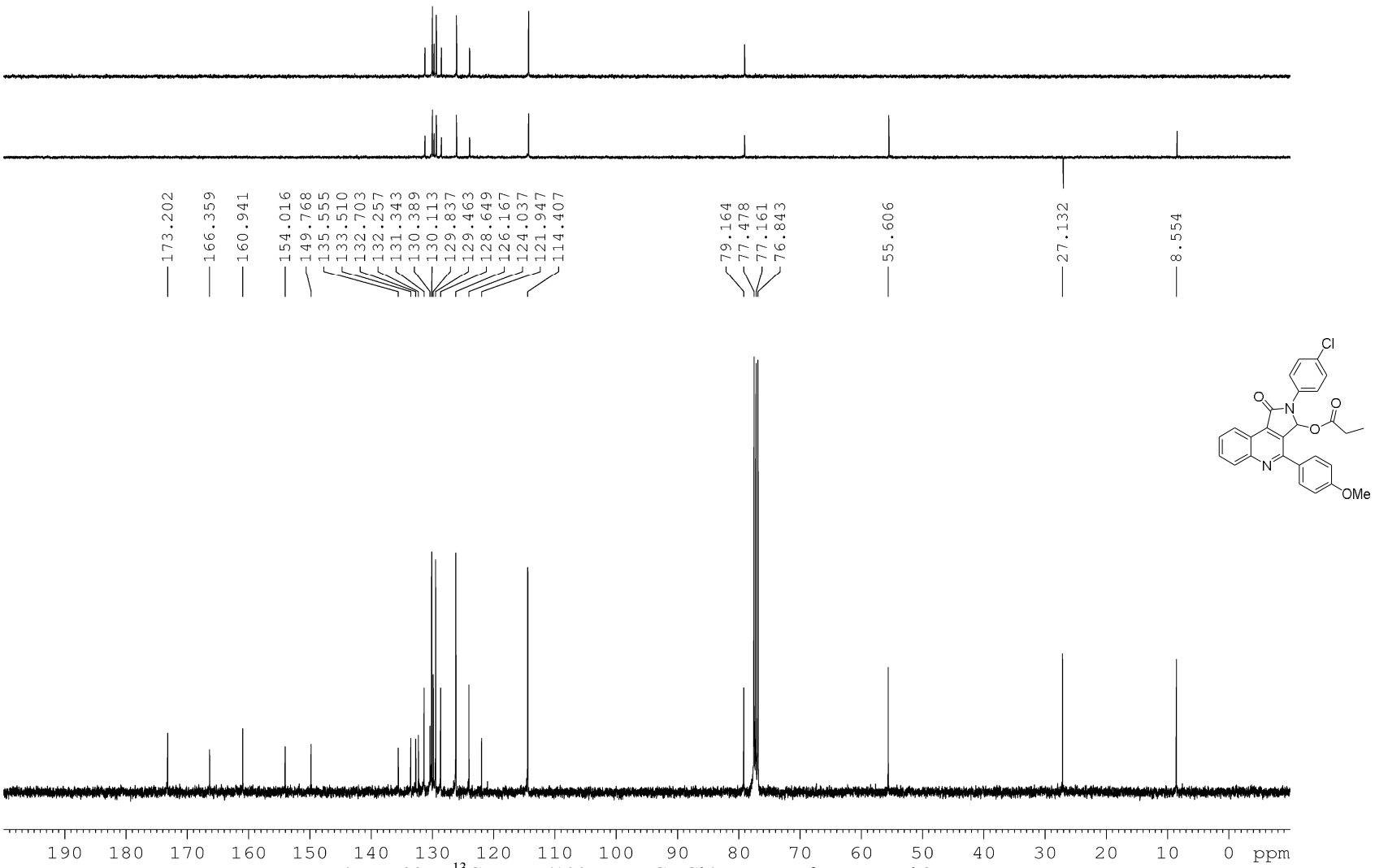

Figure 30. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3bb**

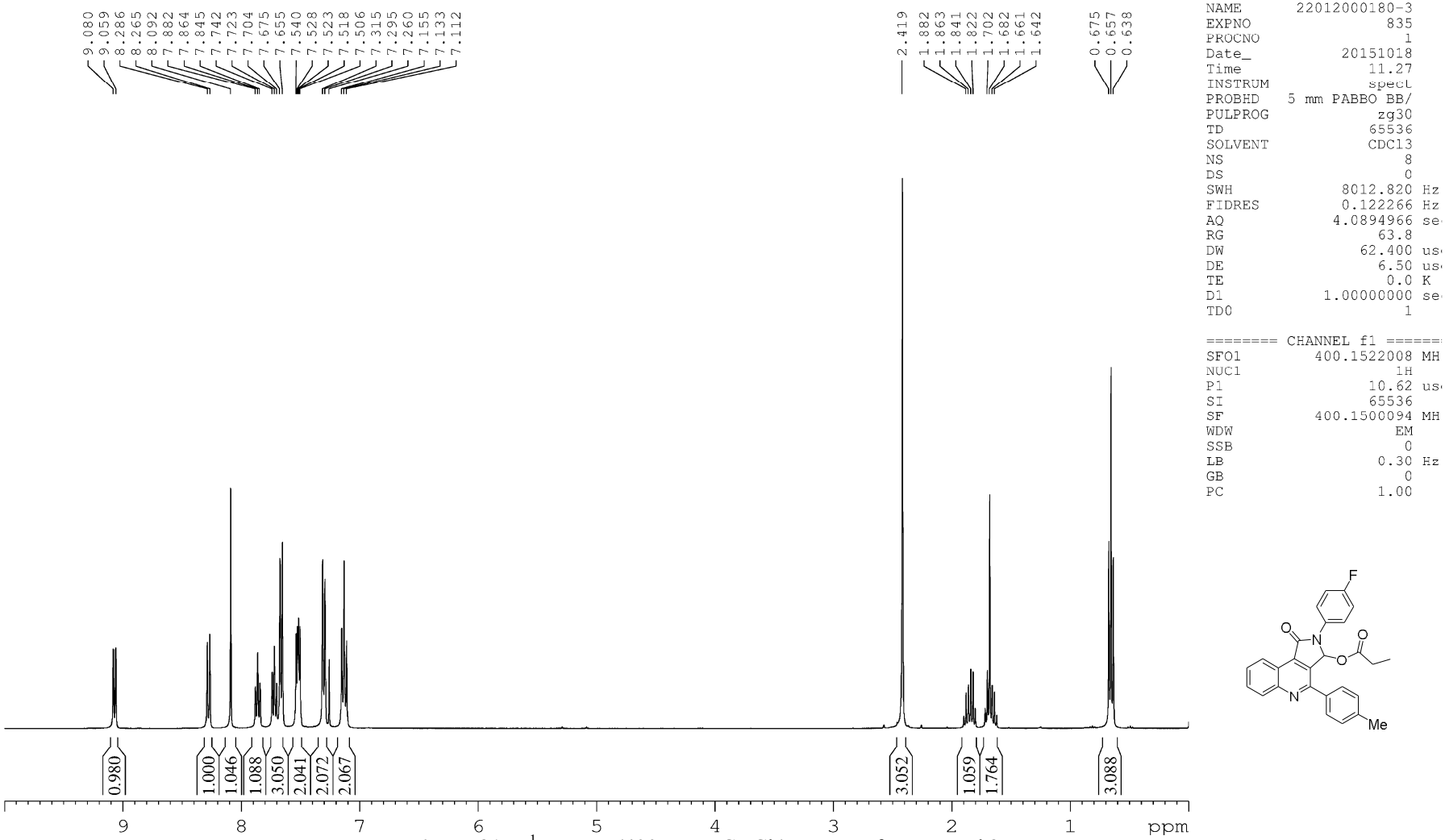

Figure 31. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3bc**

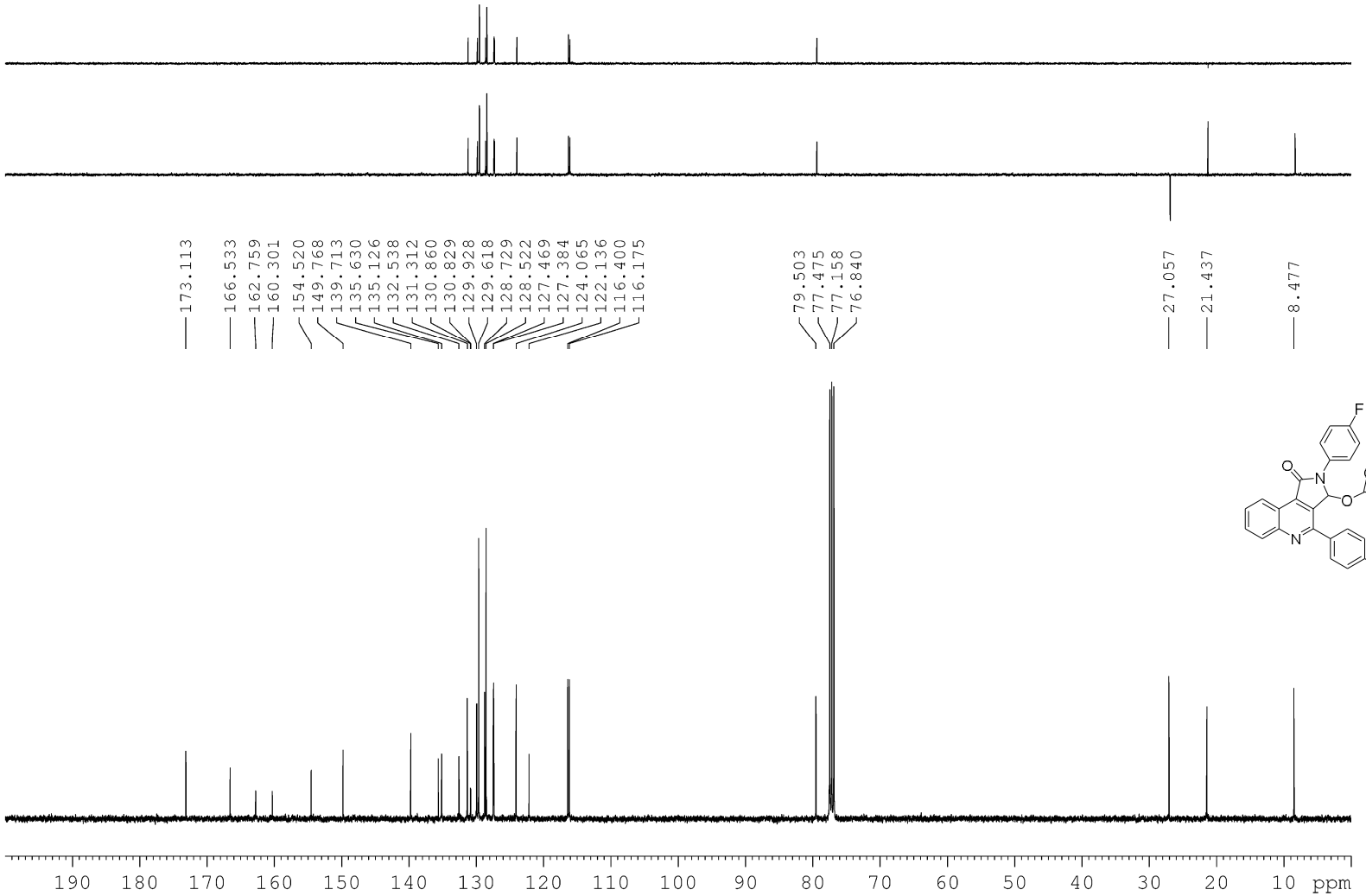

Figure 32. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3bc**

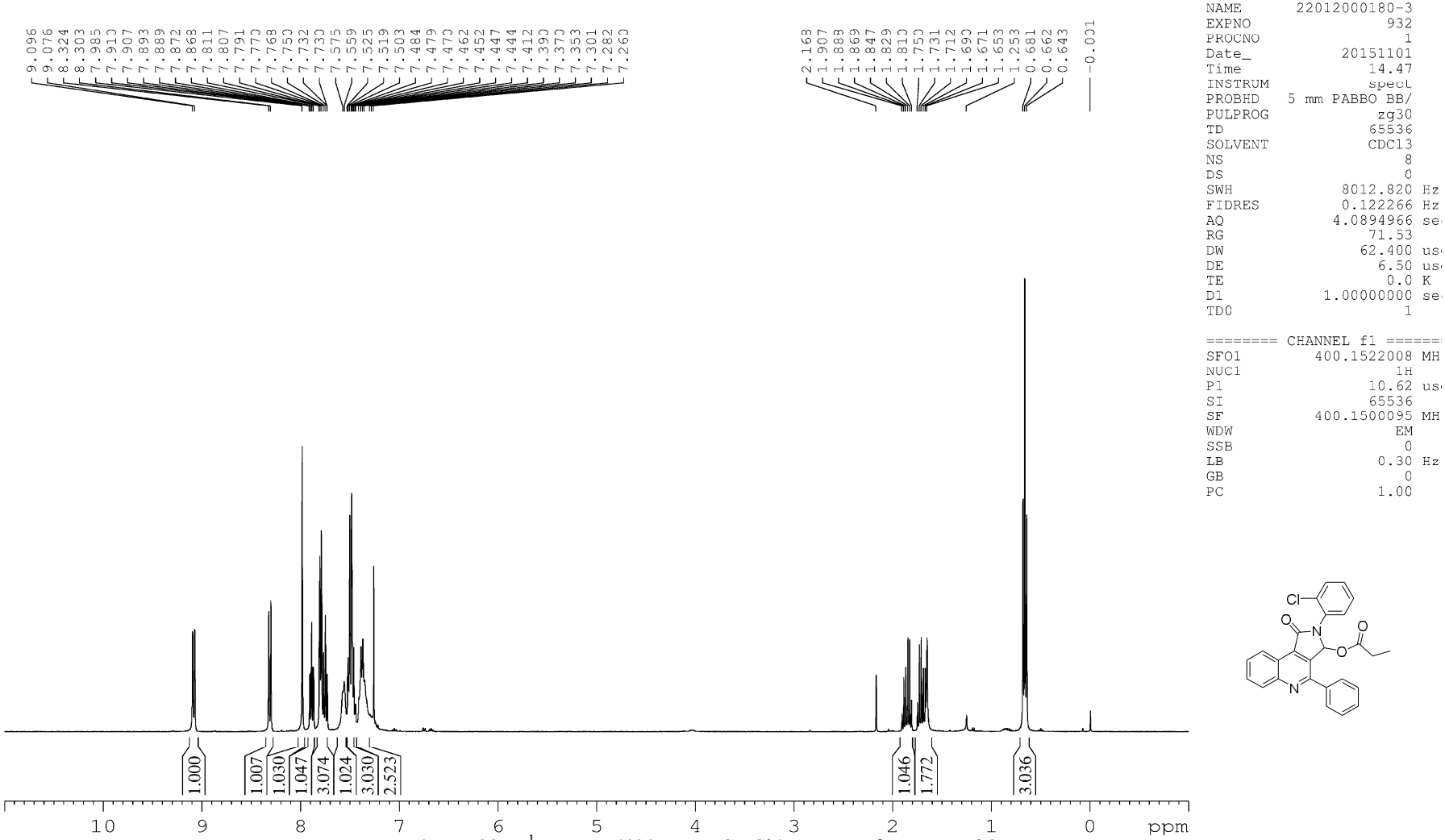

Figure 33. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3bd**

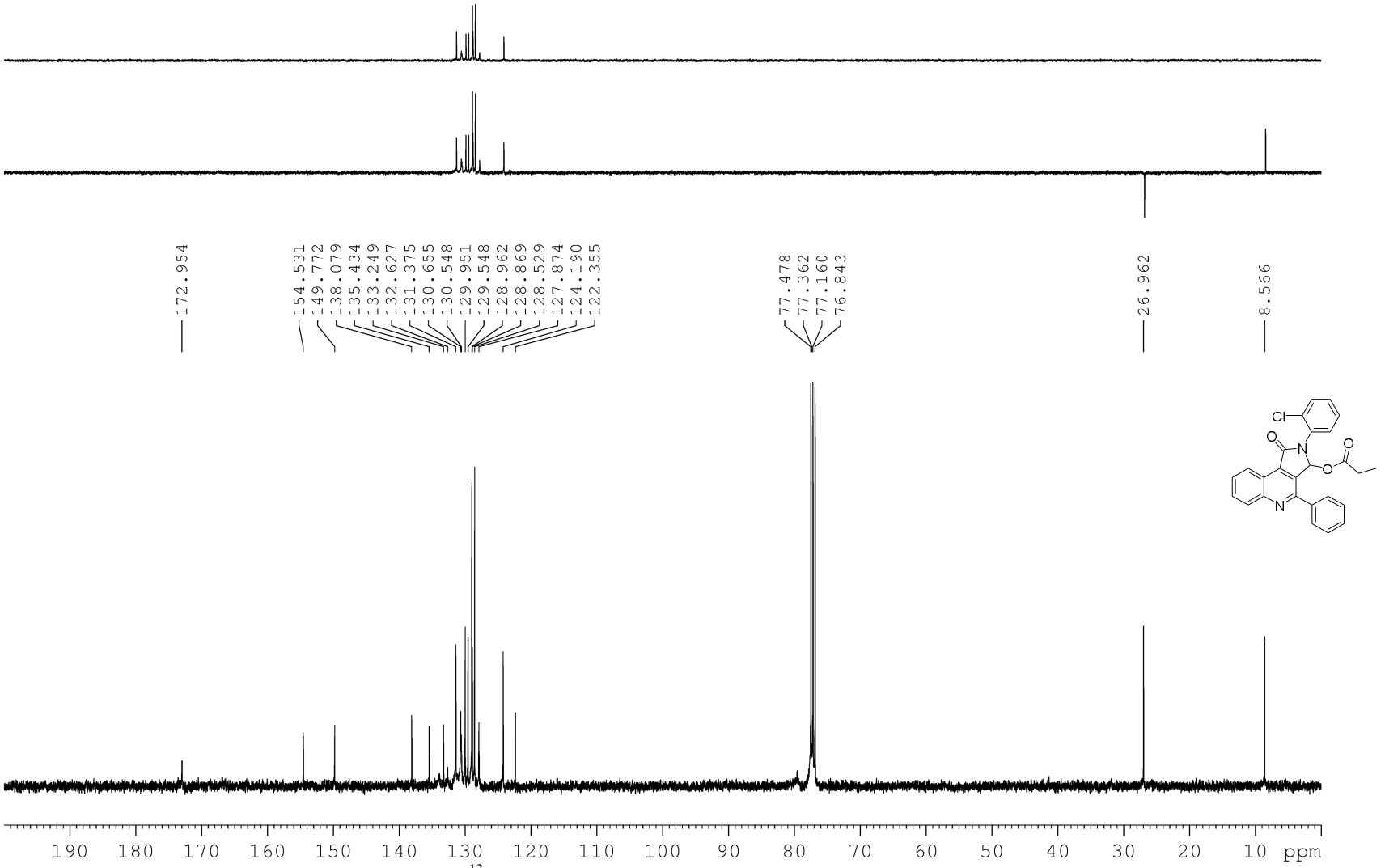

Figure 34. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3bd**

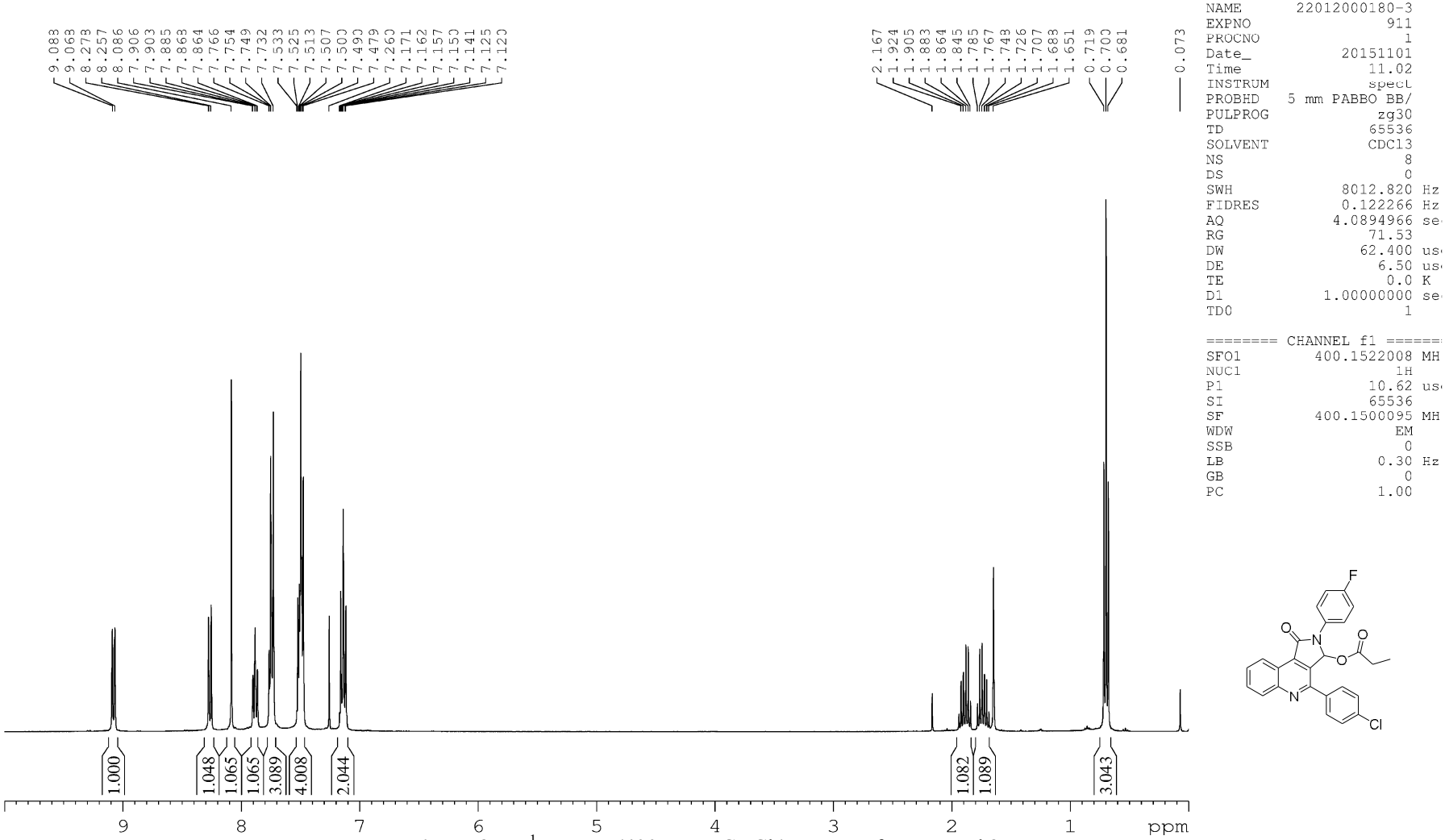

Figure 35. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3be**

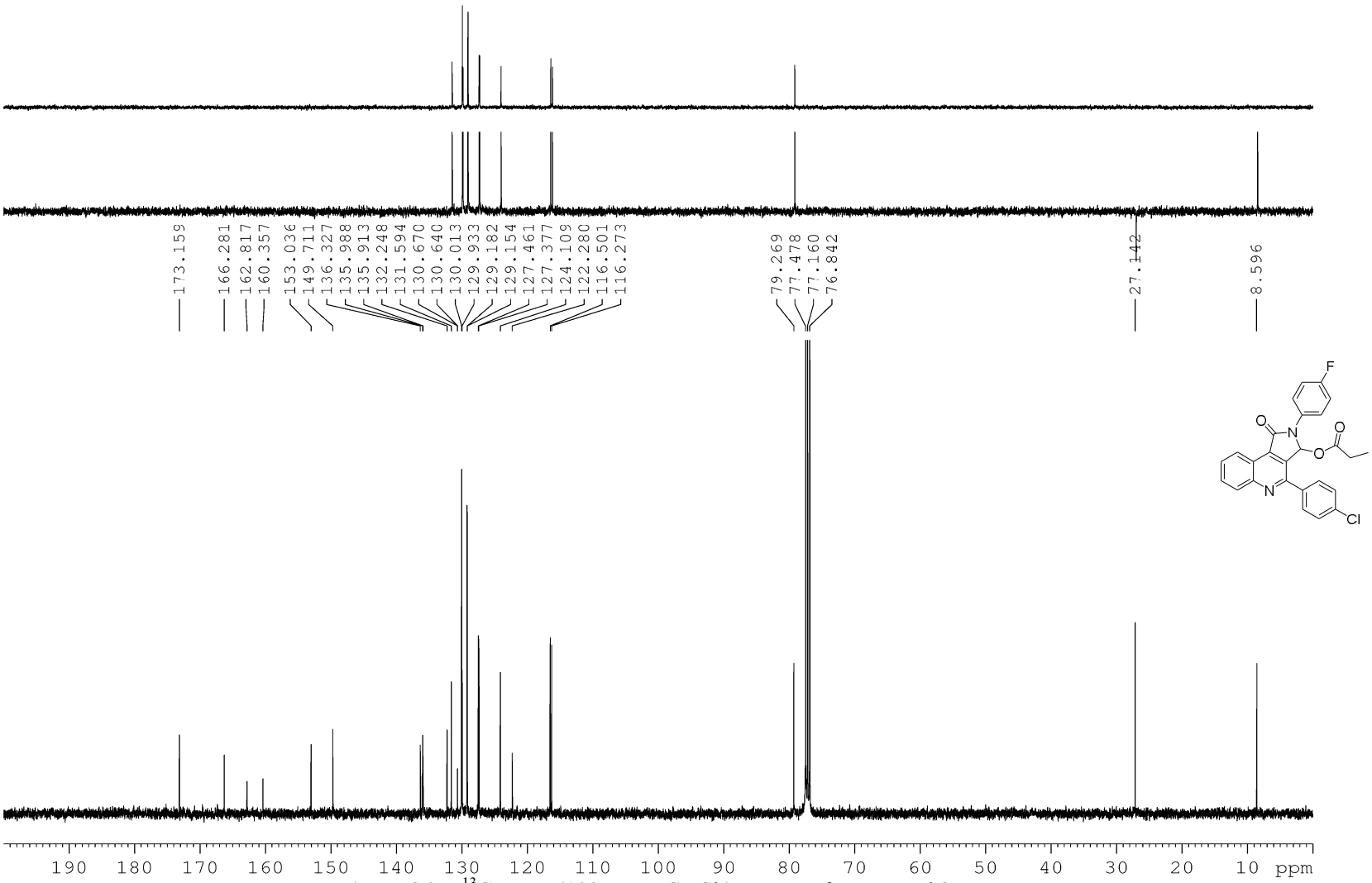

Figure 36. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3be**

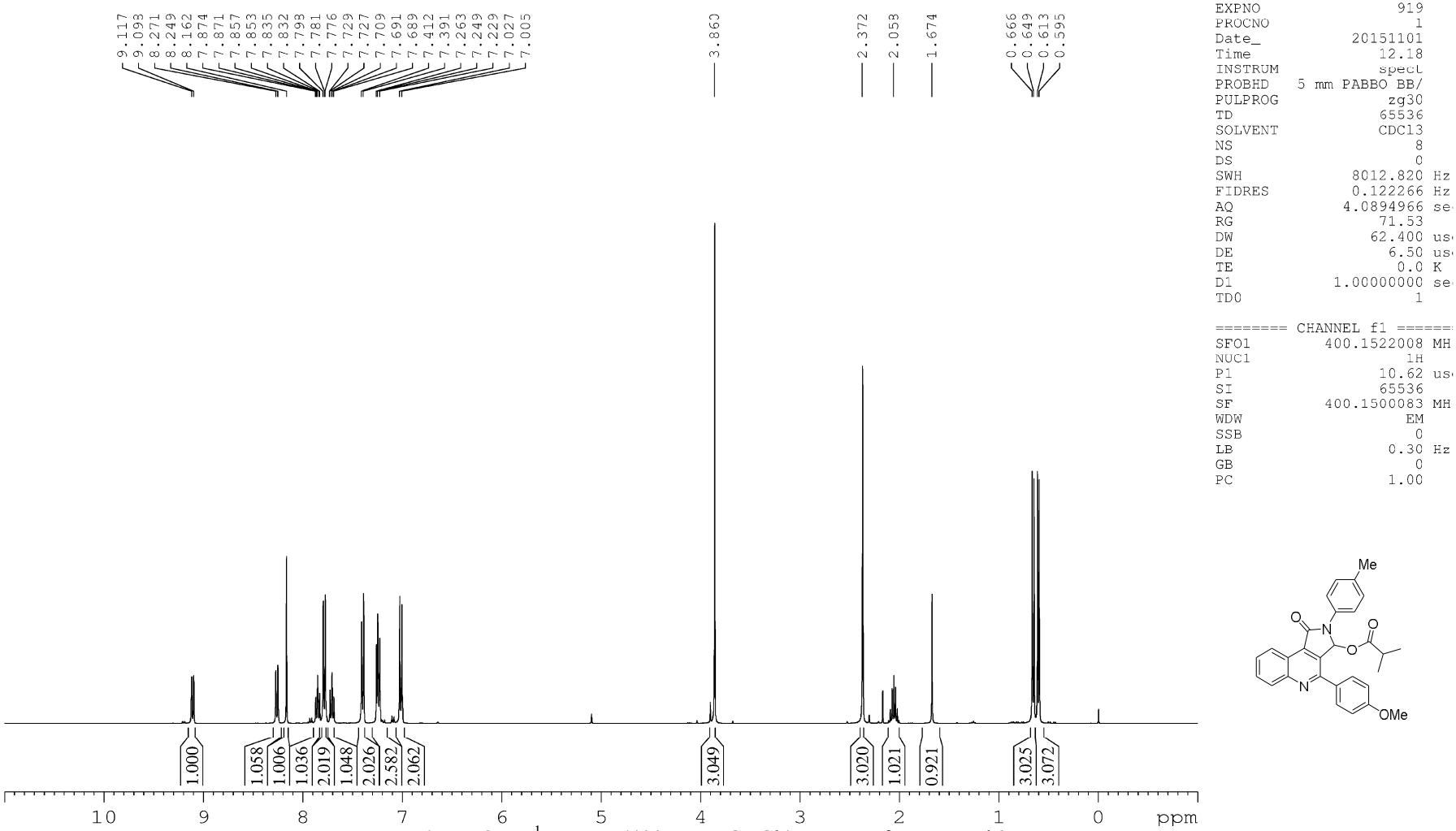

Figure 37. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ca**

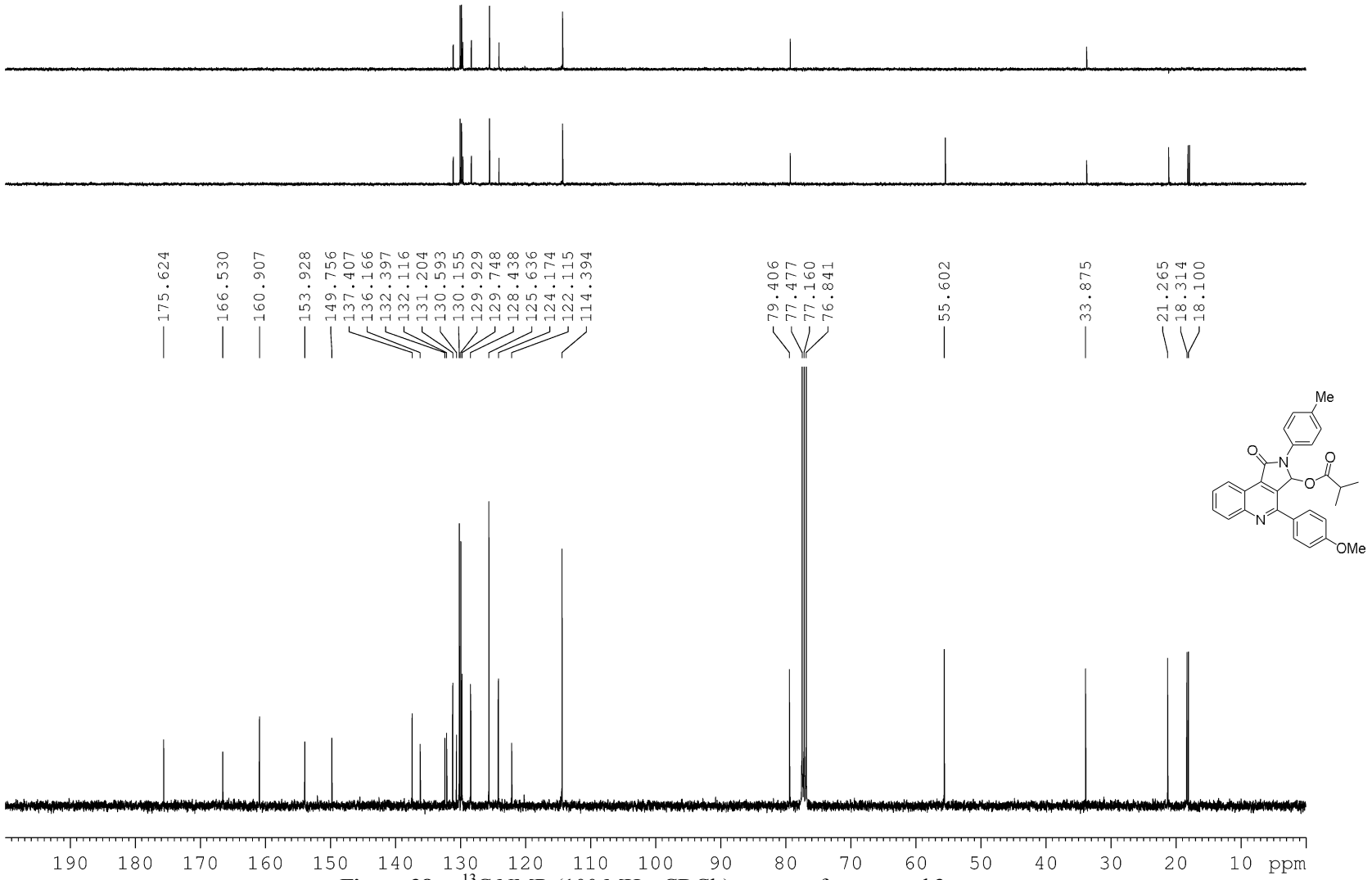

Figure 38. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ca**

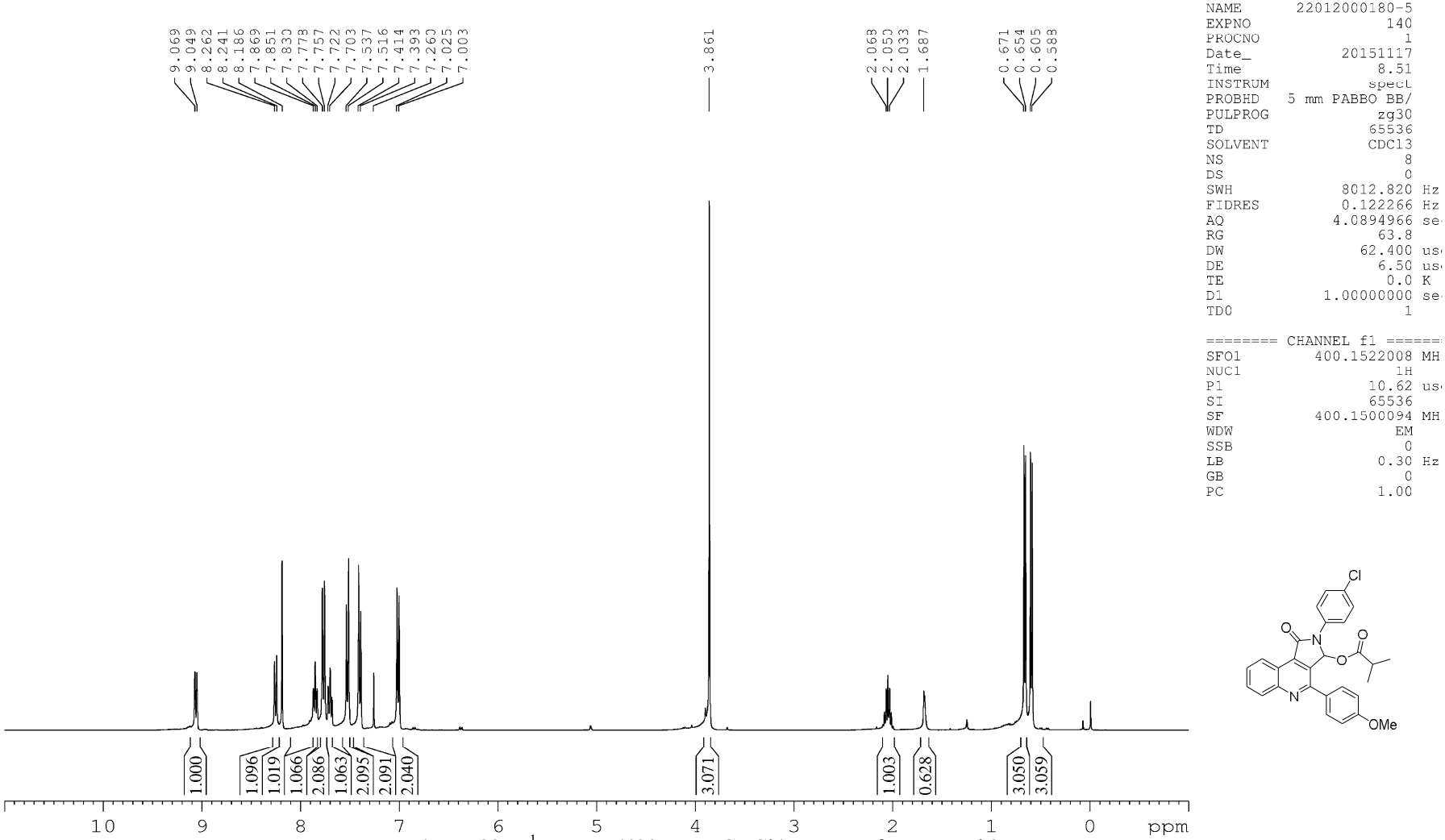

Figure 39. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3cb**

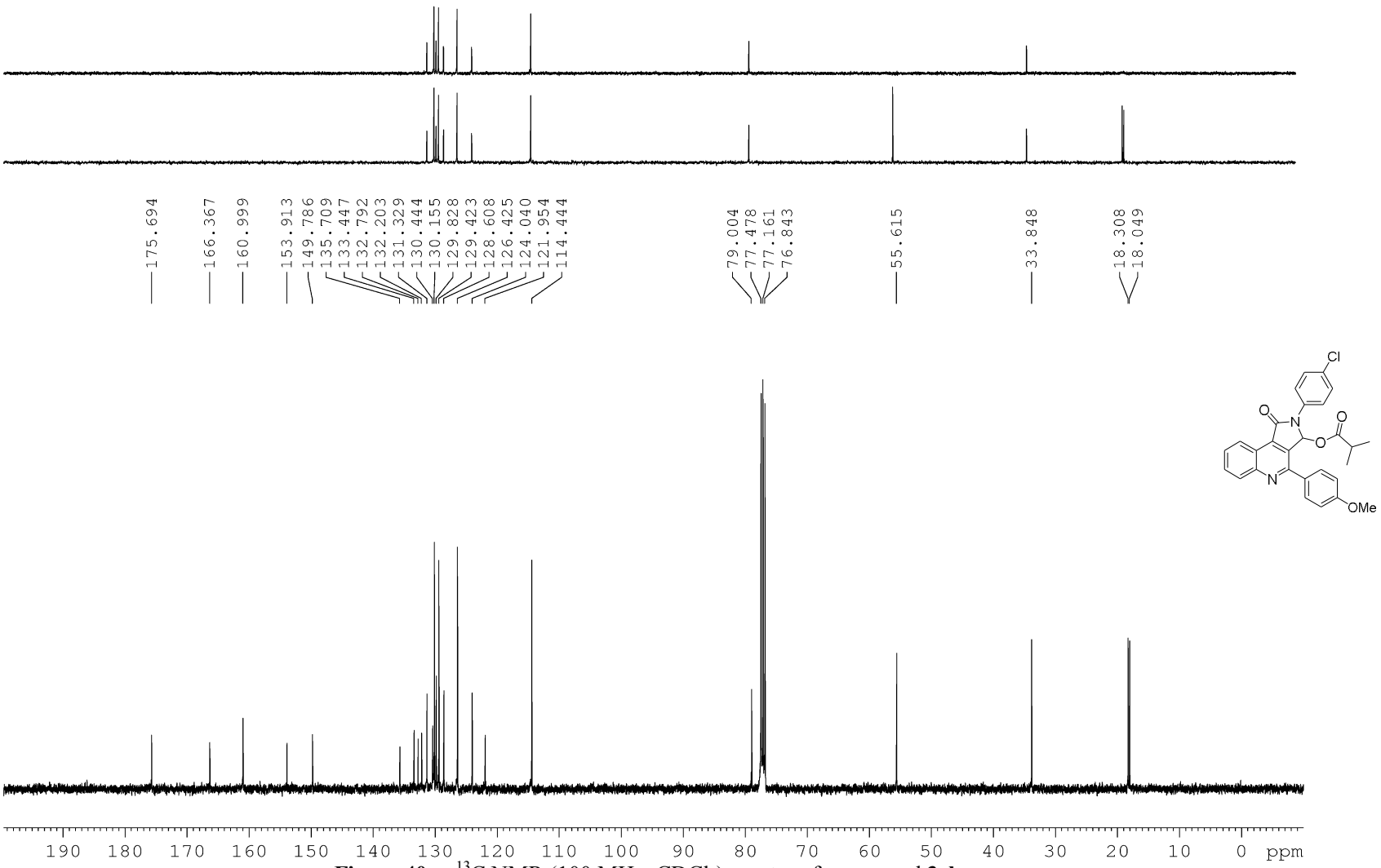

Figure 40. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3cb**

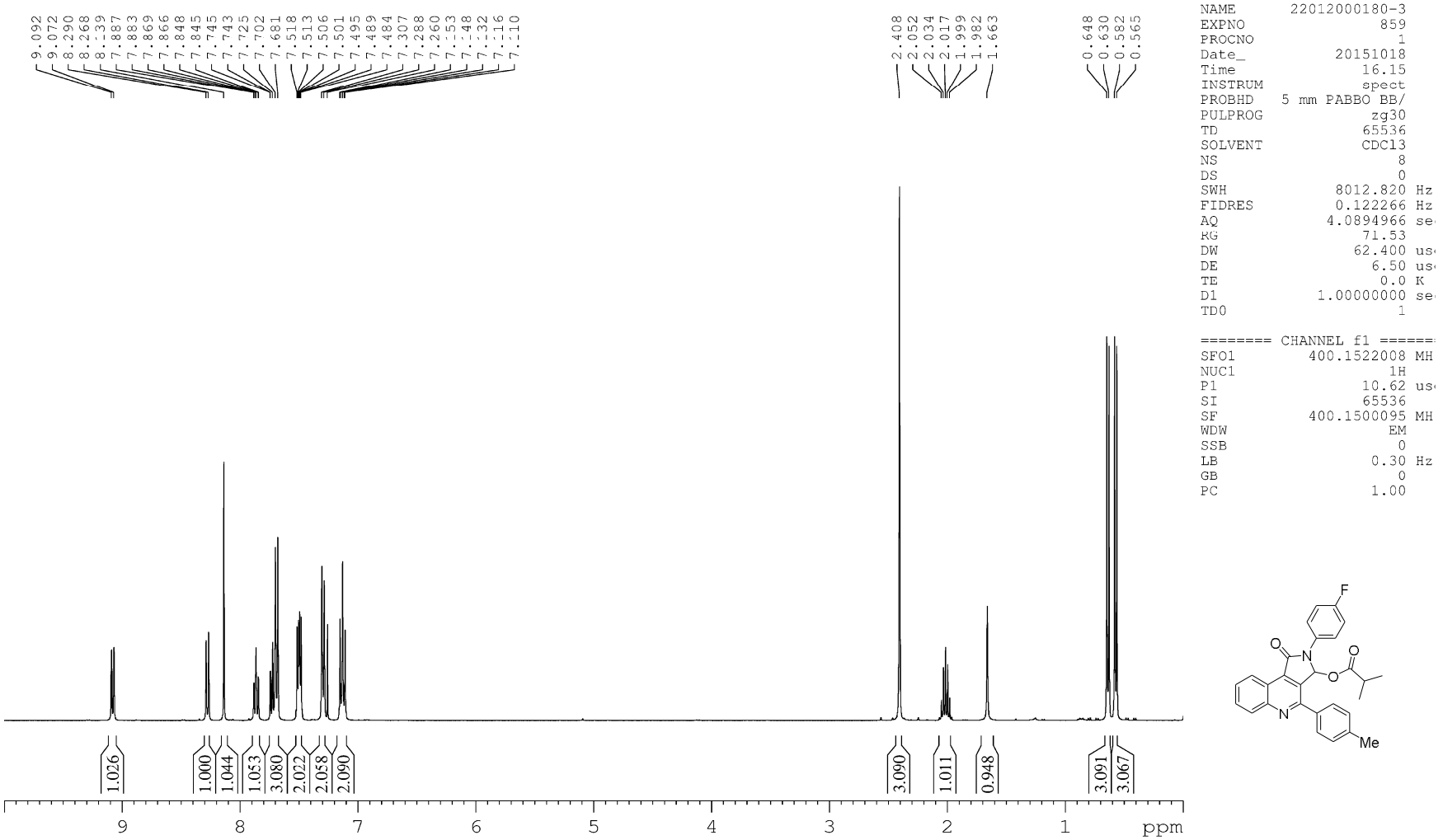

Figure 41. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3cc**

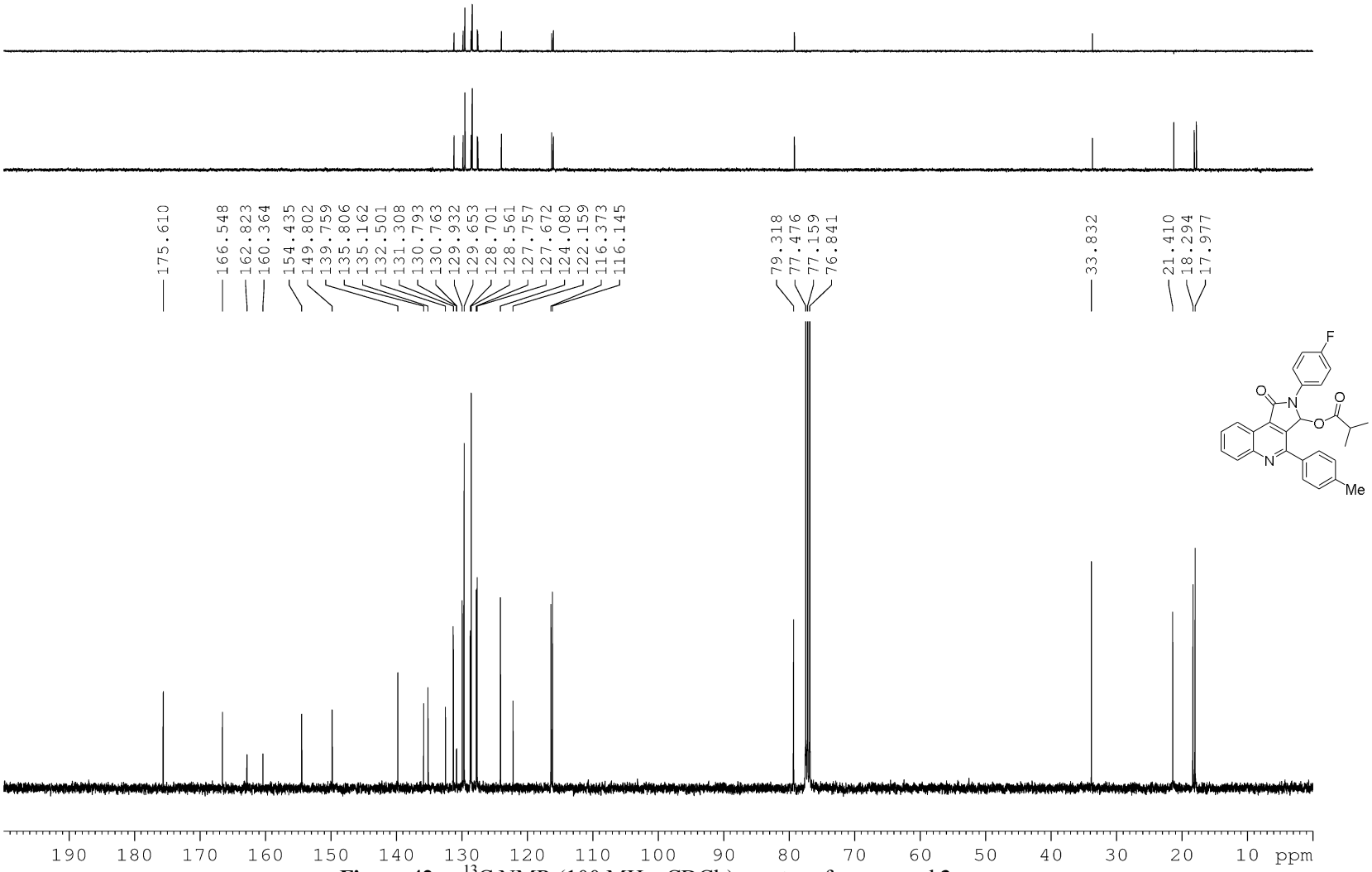

Figure 42. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3cc**

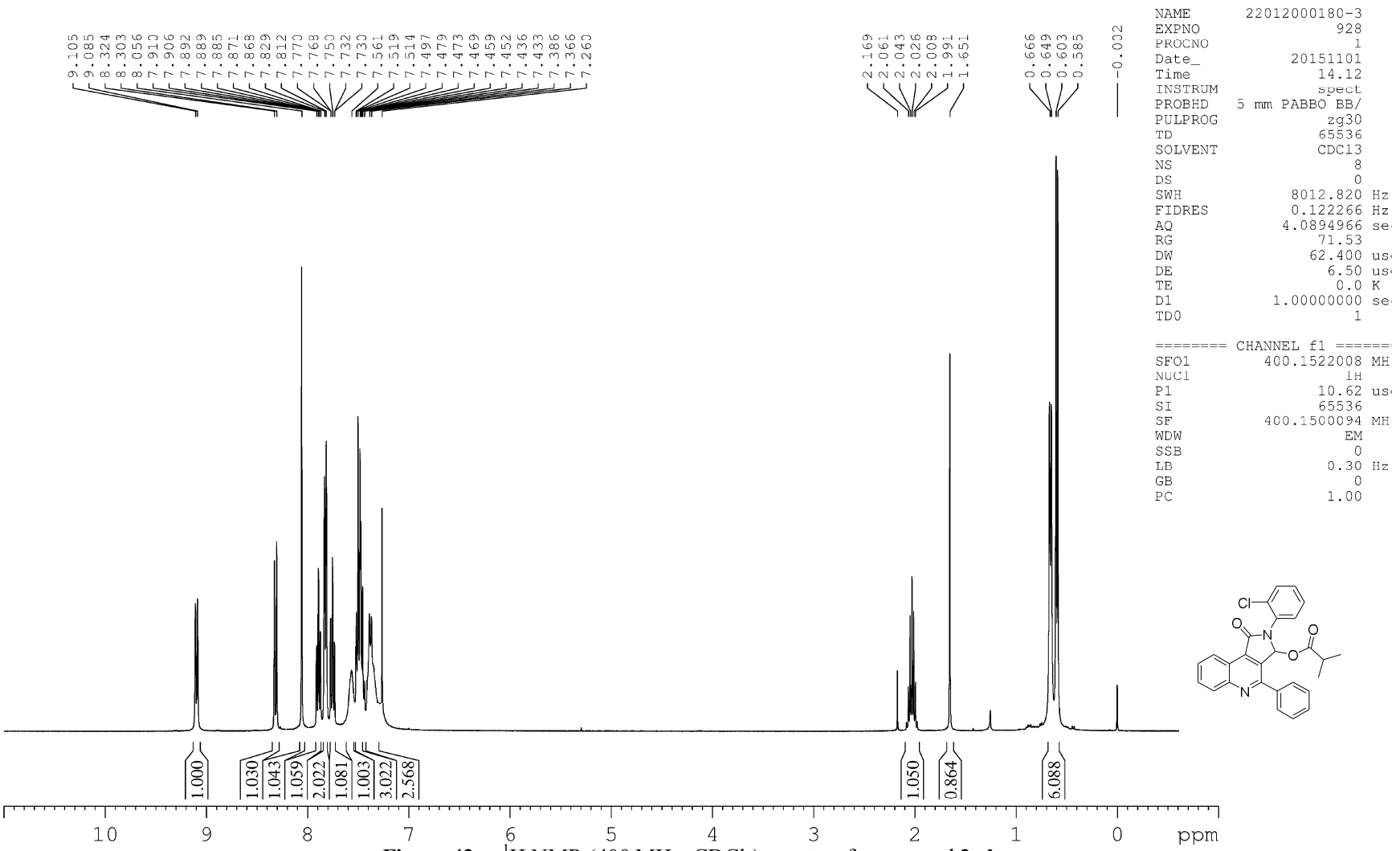

Figure 43. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3cd**

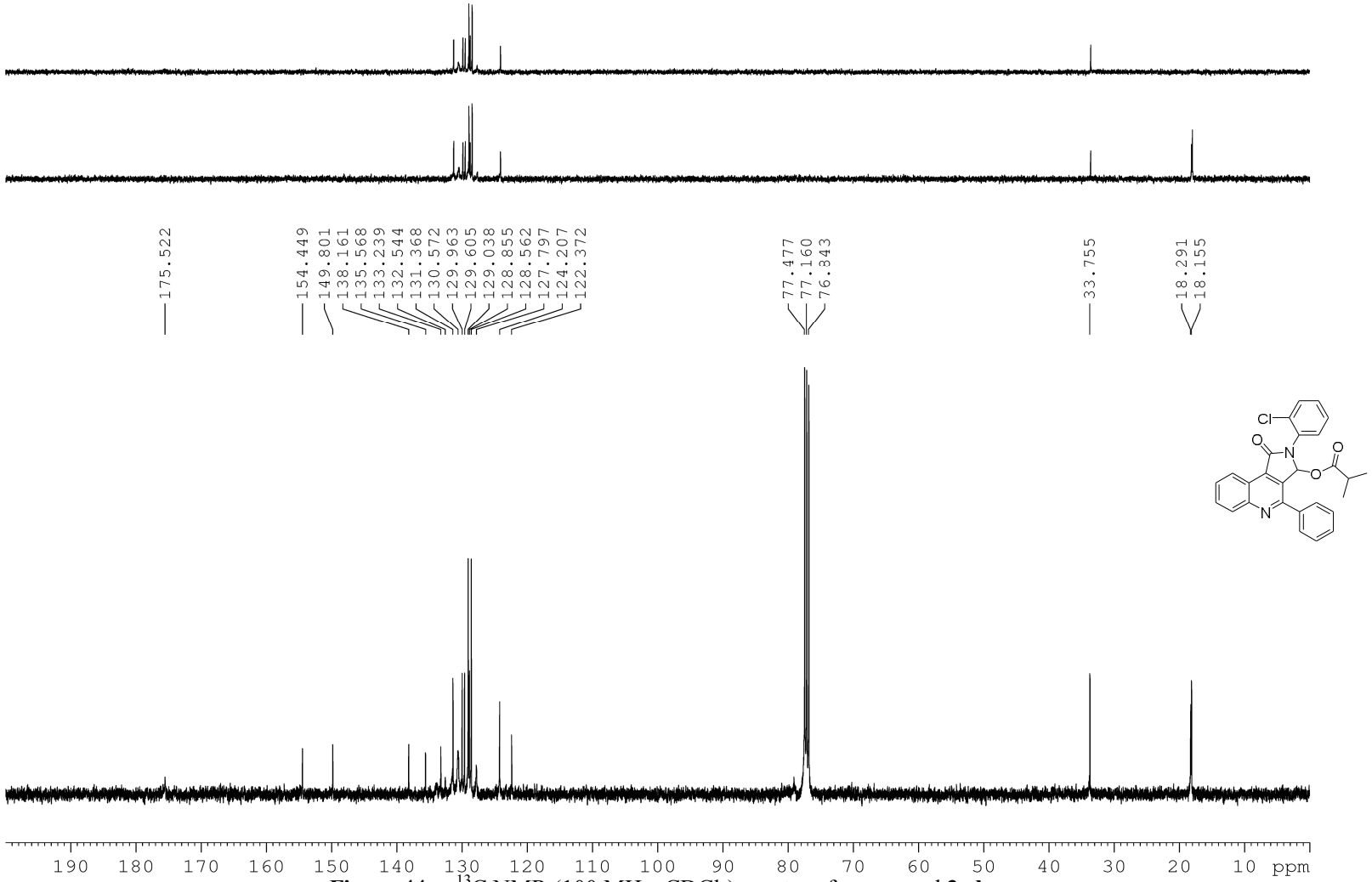

Figure 44. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3cd**

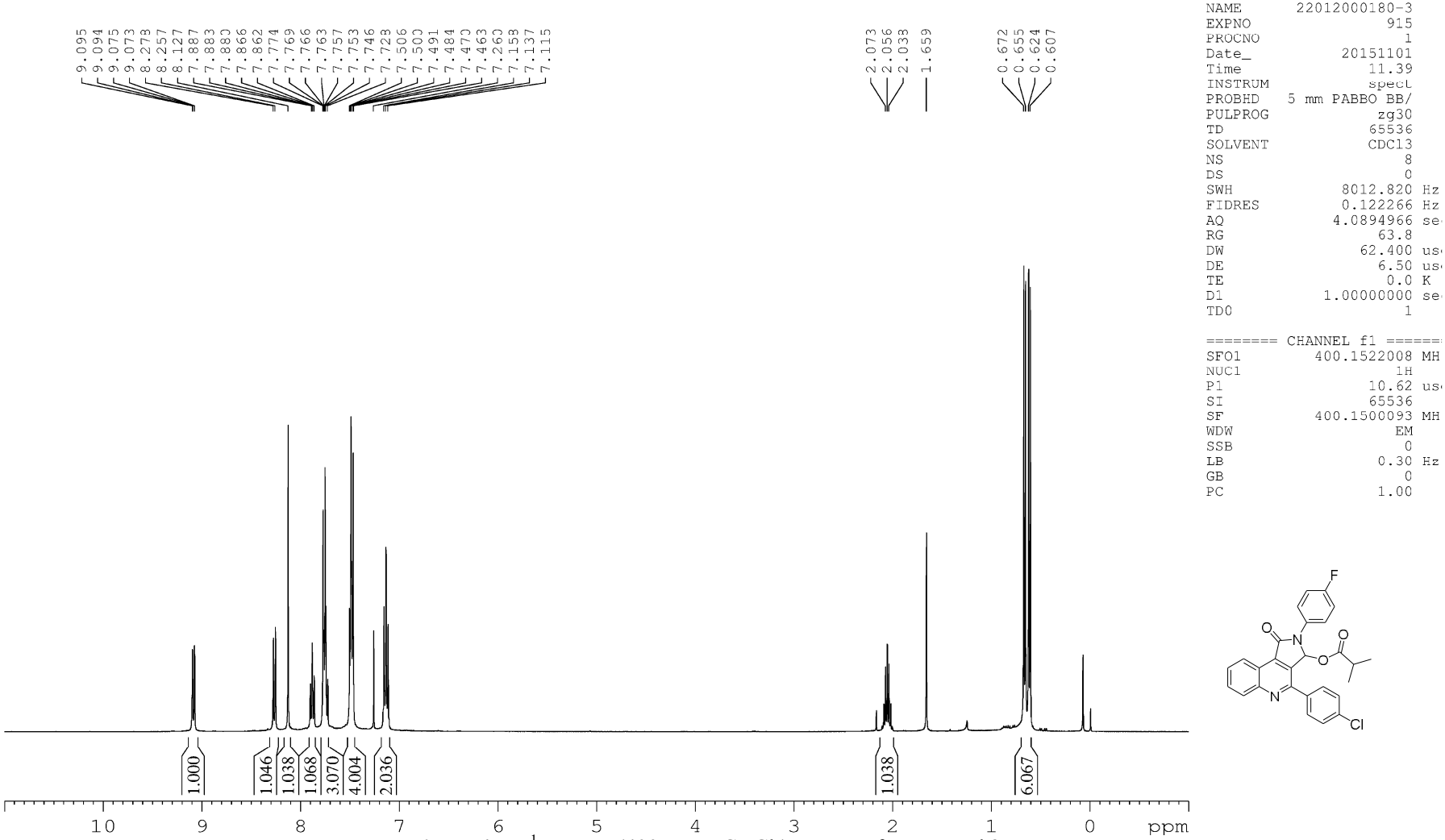

Figure 45. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3ce**

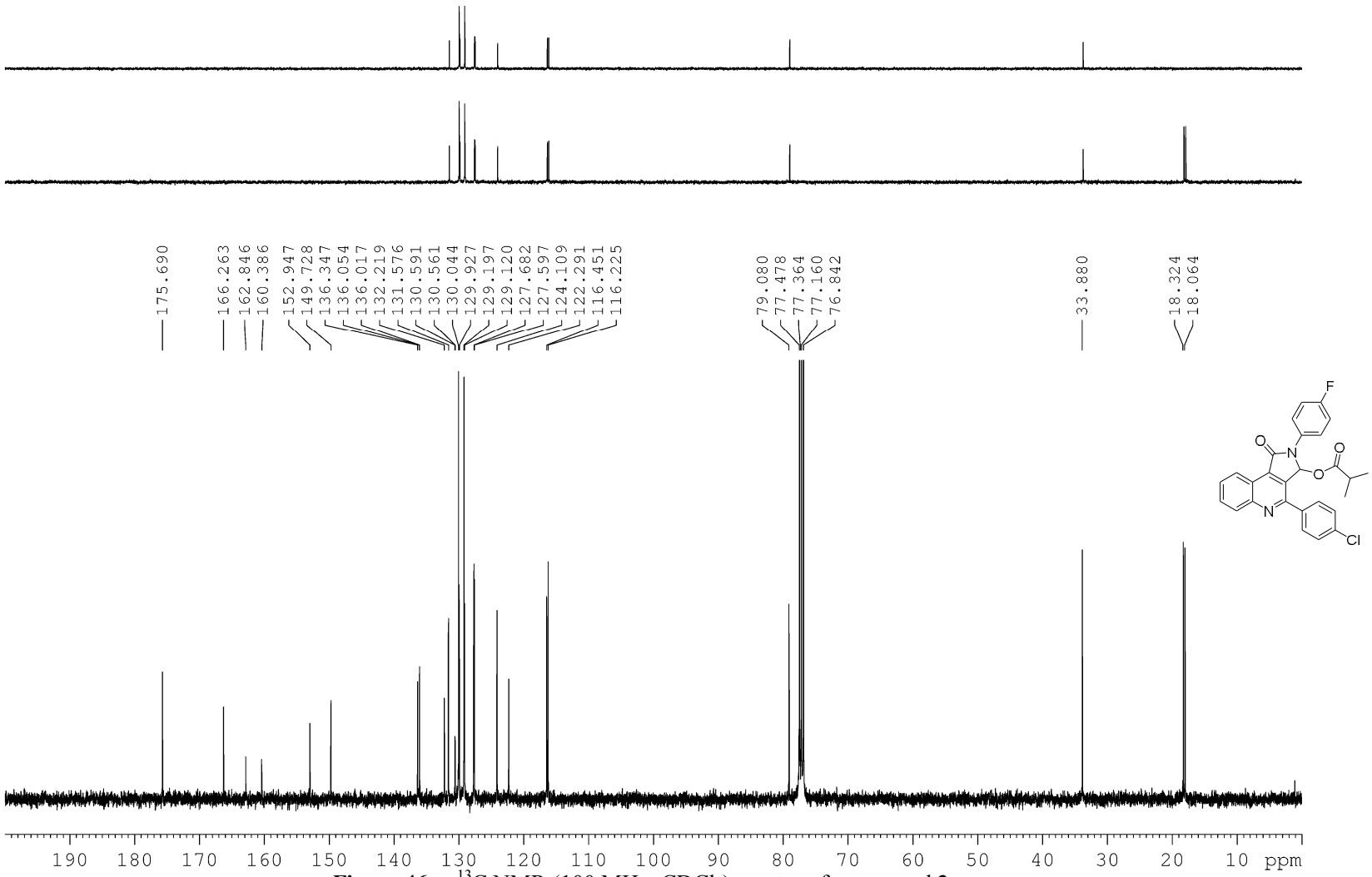

Figure 46. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3ce**

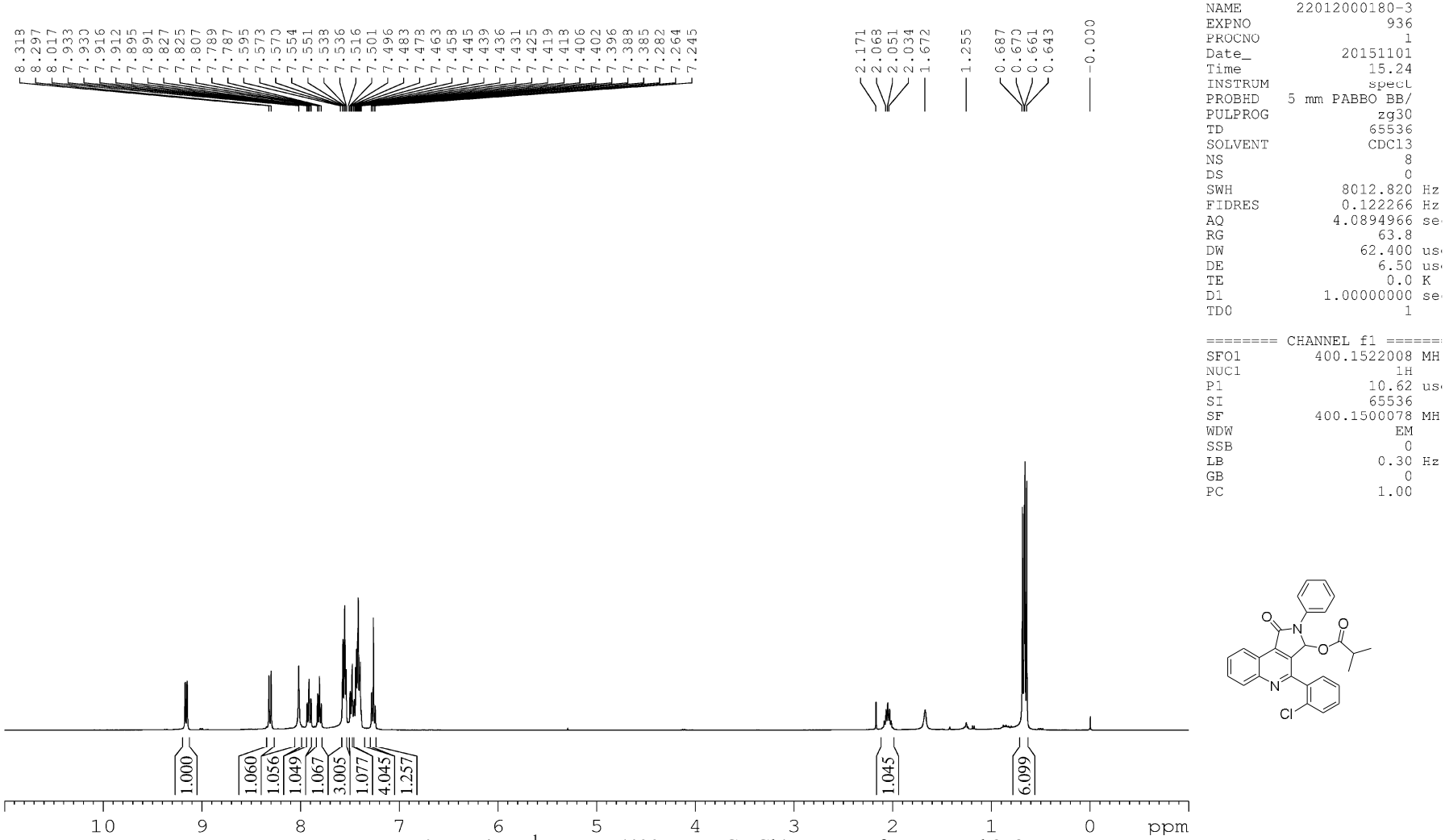

Figure 47. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3cf**

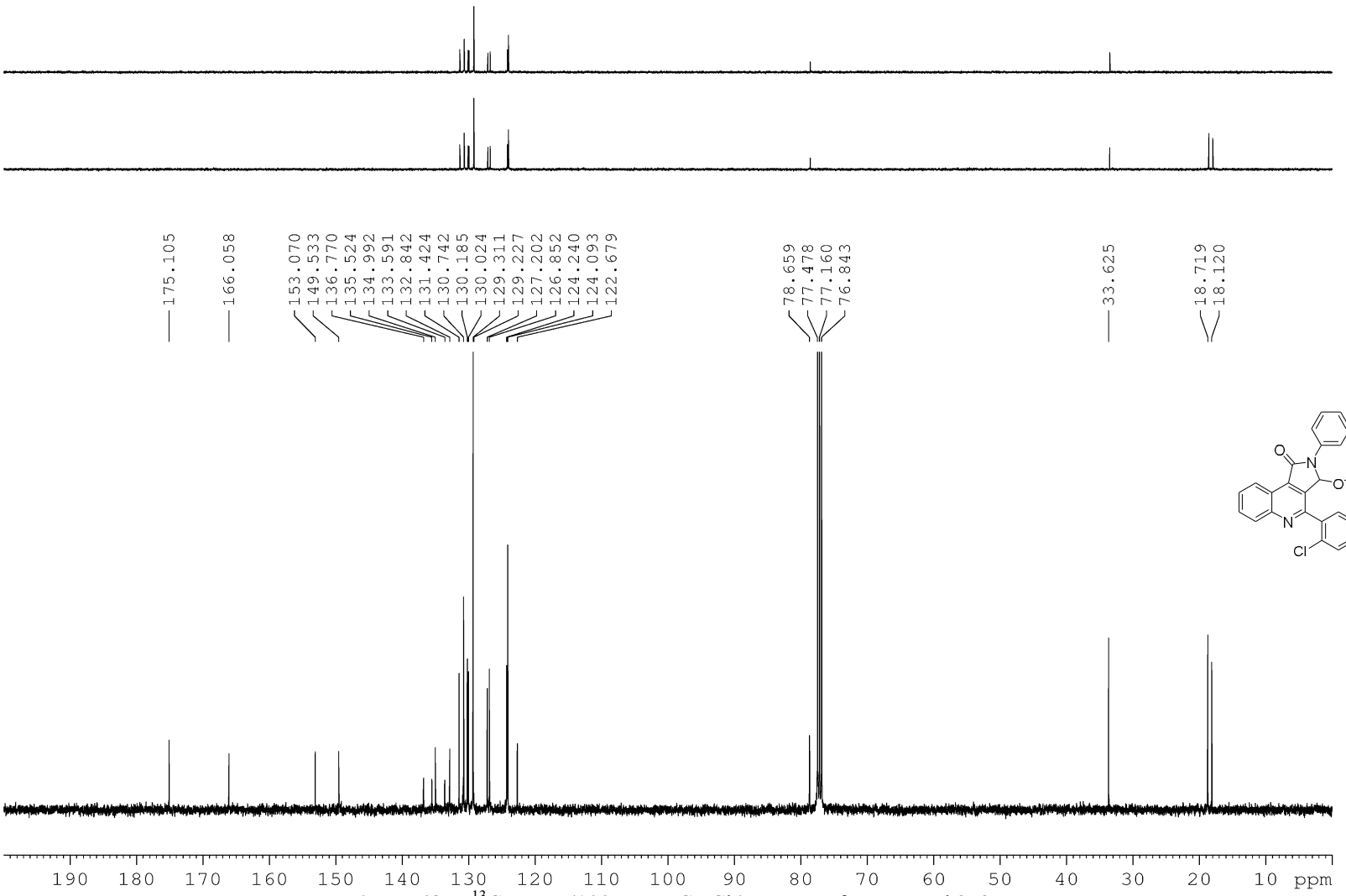

Figure 48. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3cf**

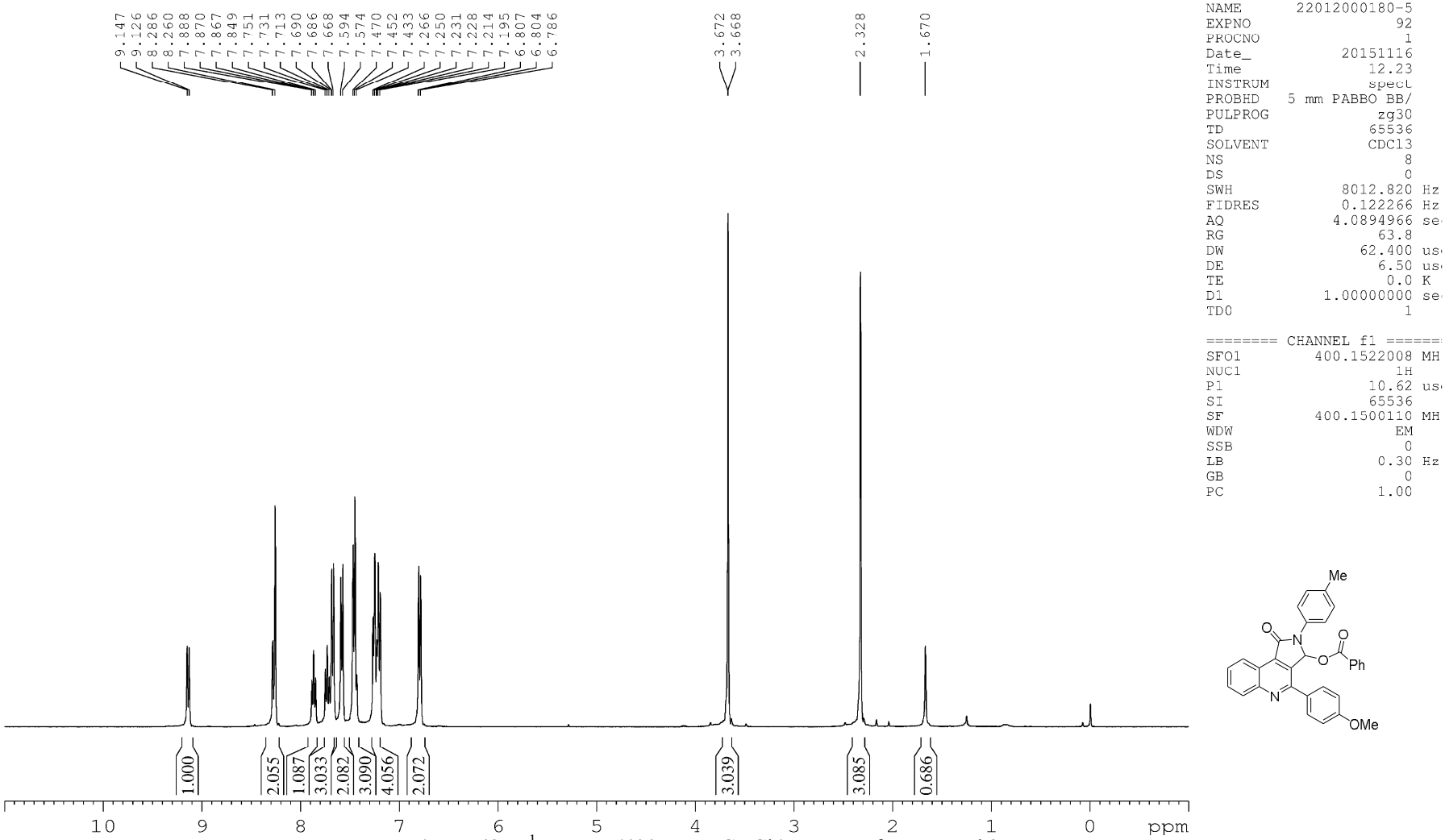

Figure 49. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3da**

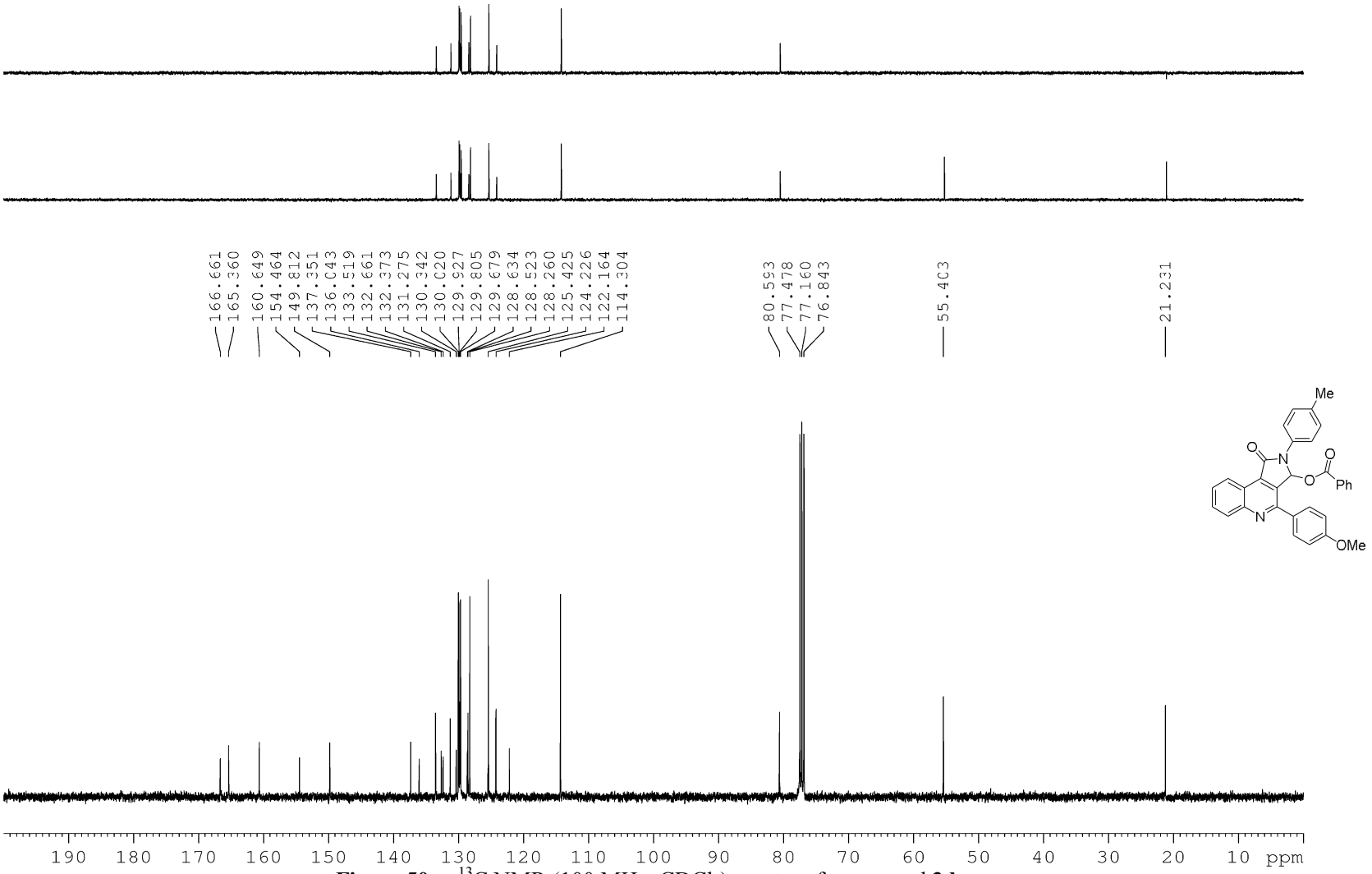

Figure 50. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3da**

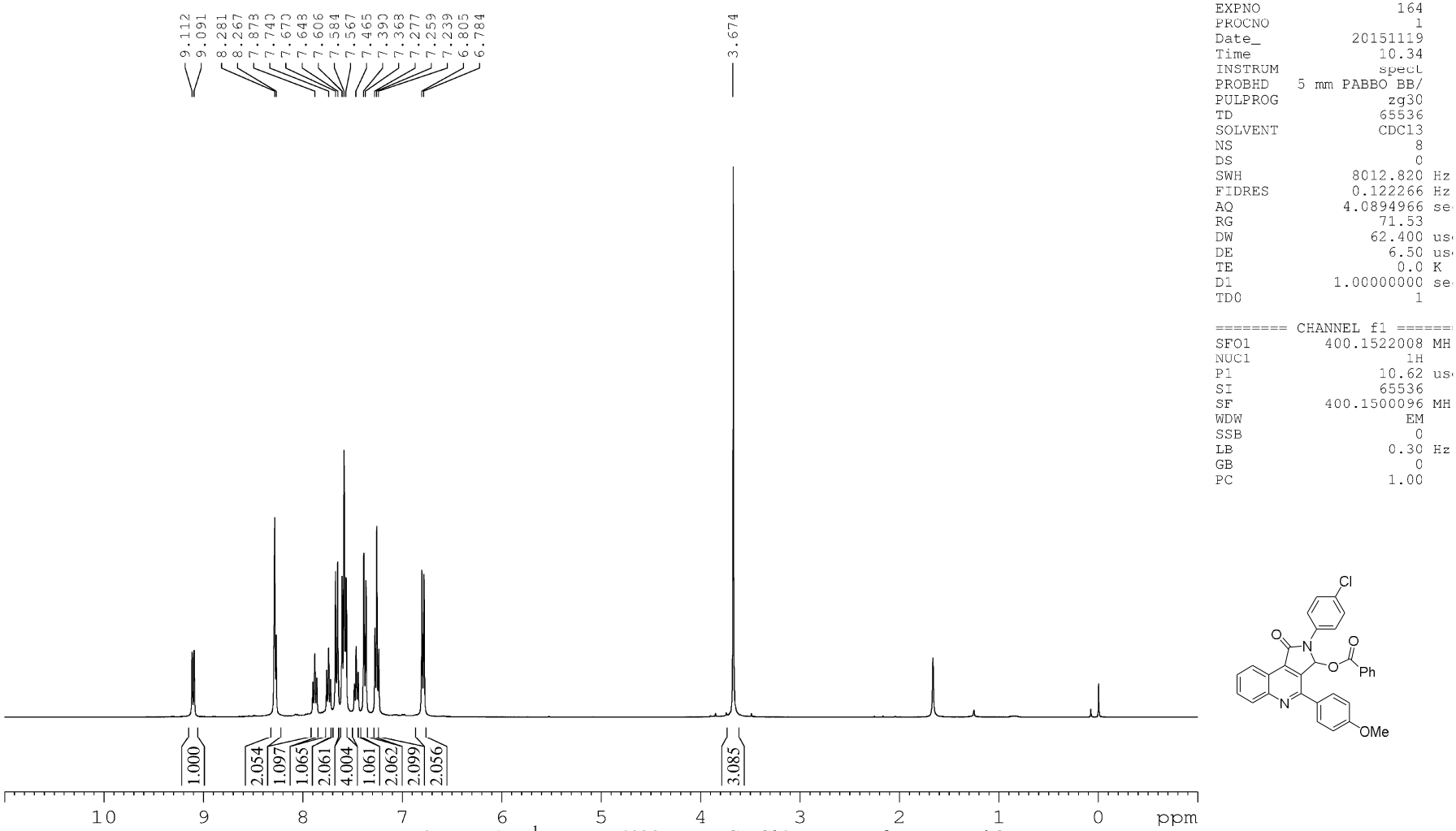

Figure 51. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3db**

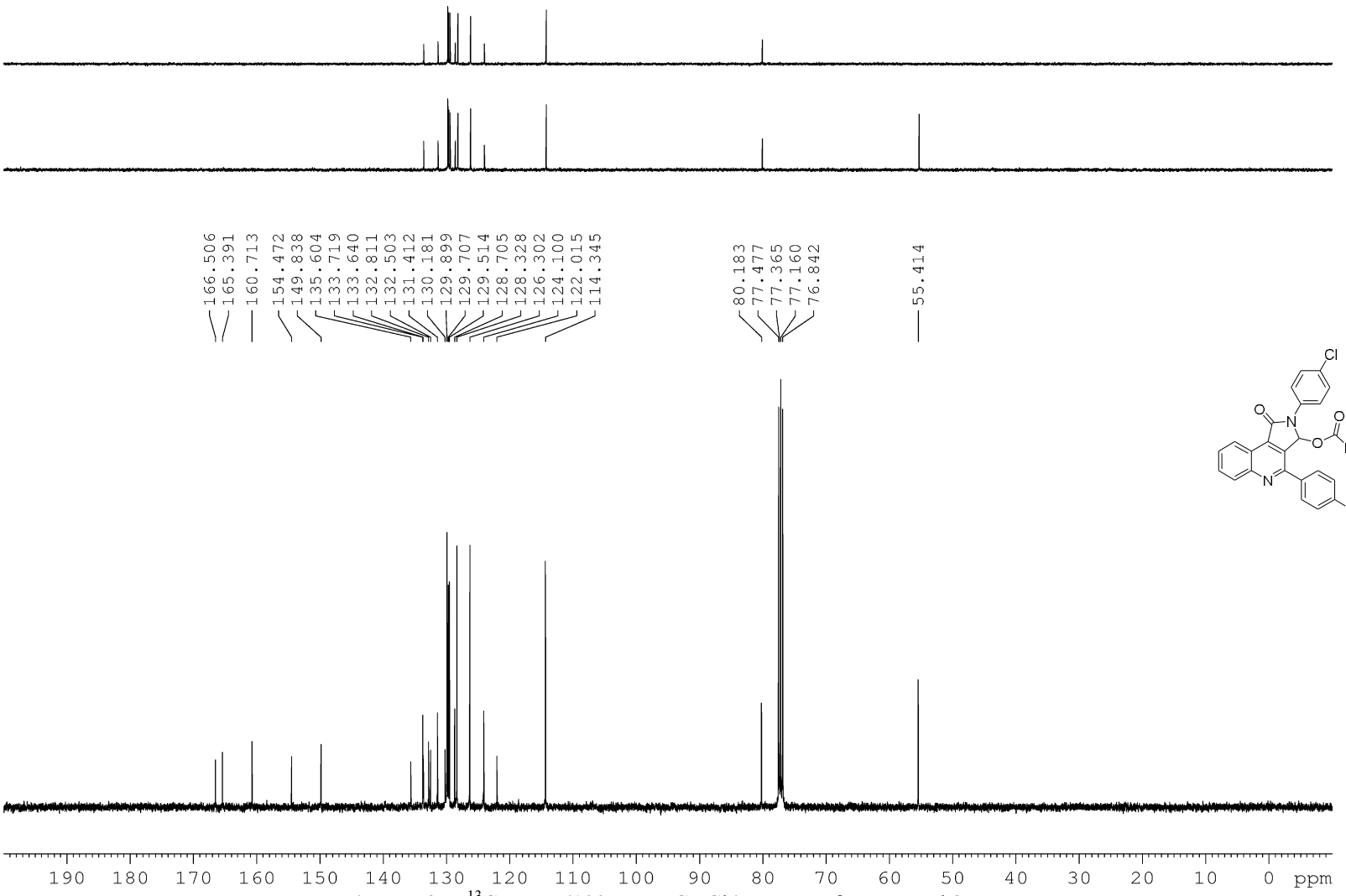

Figure 52. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3db**

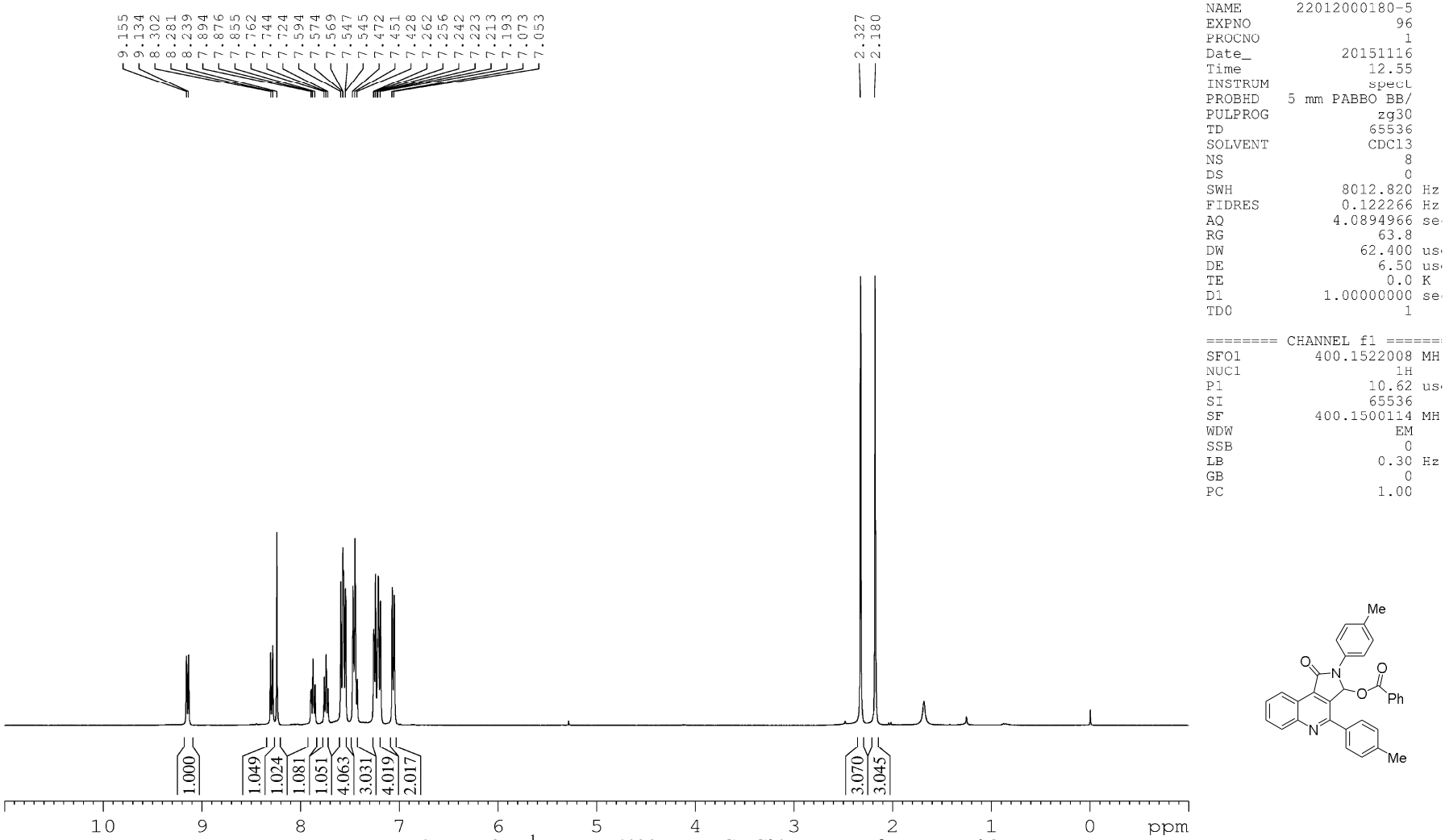

Figure 53. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3dc**

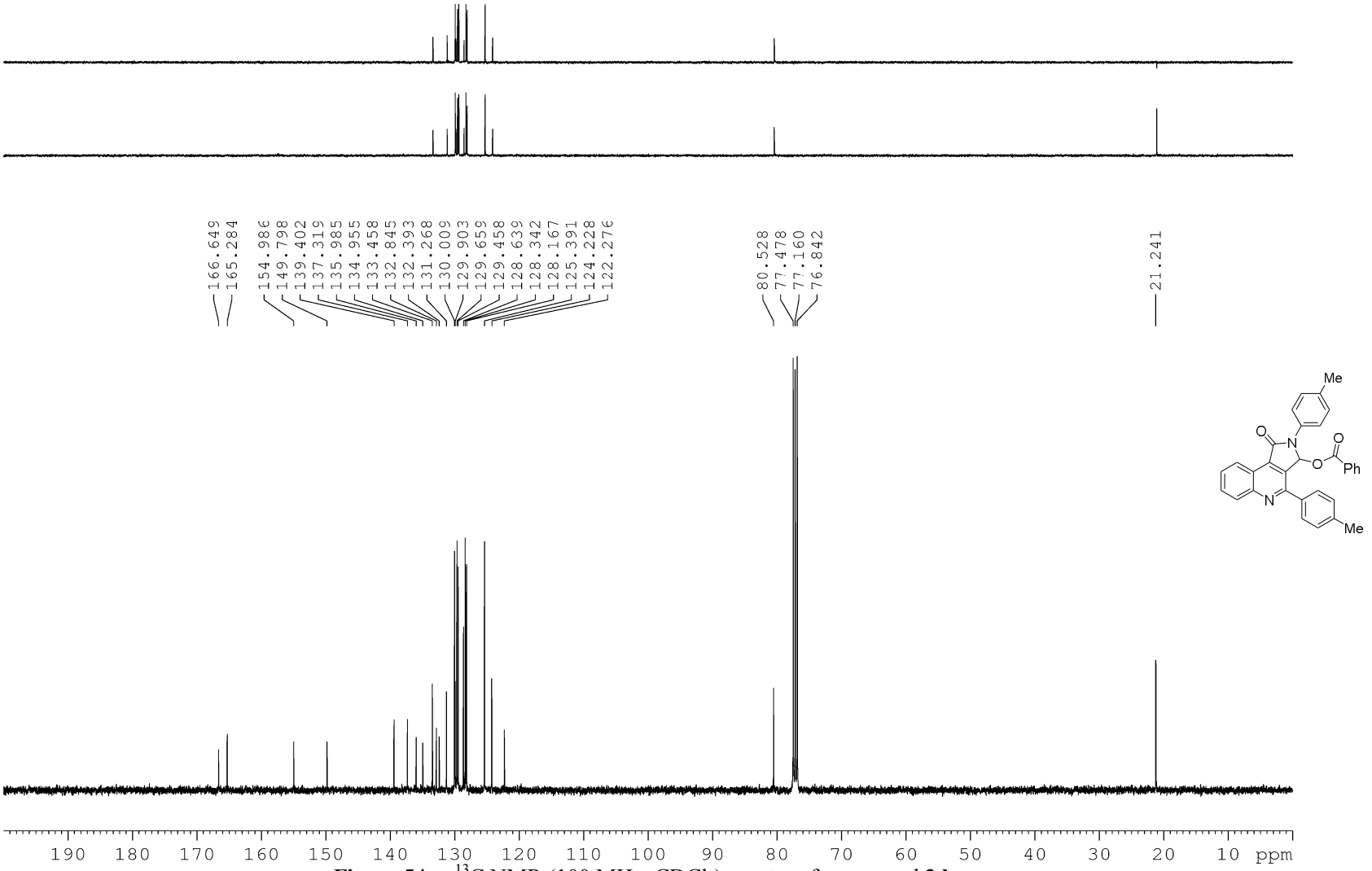

Figure 54. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3dc**

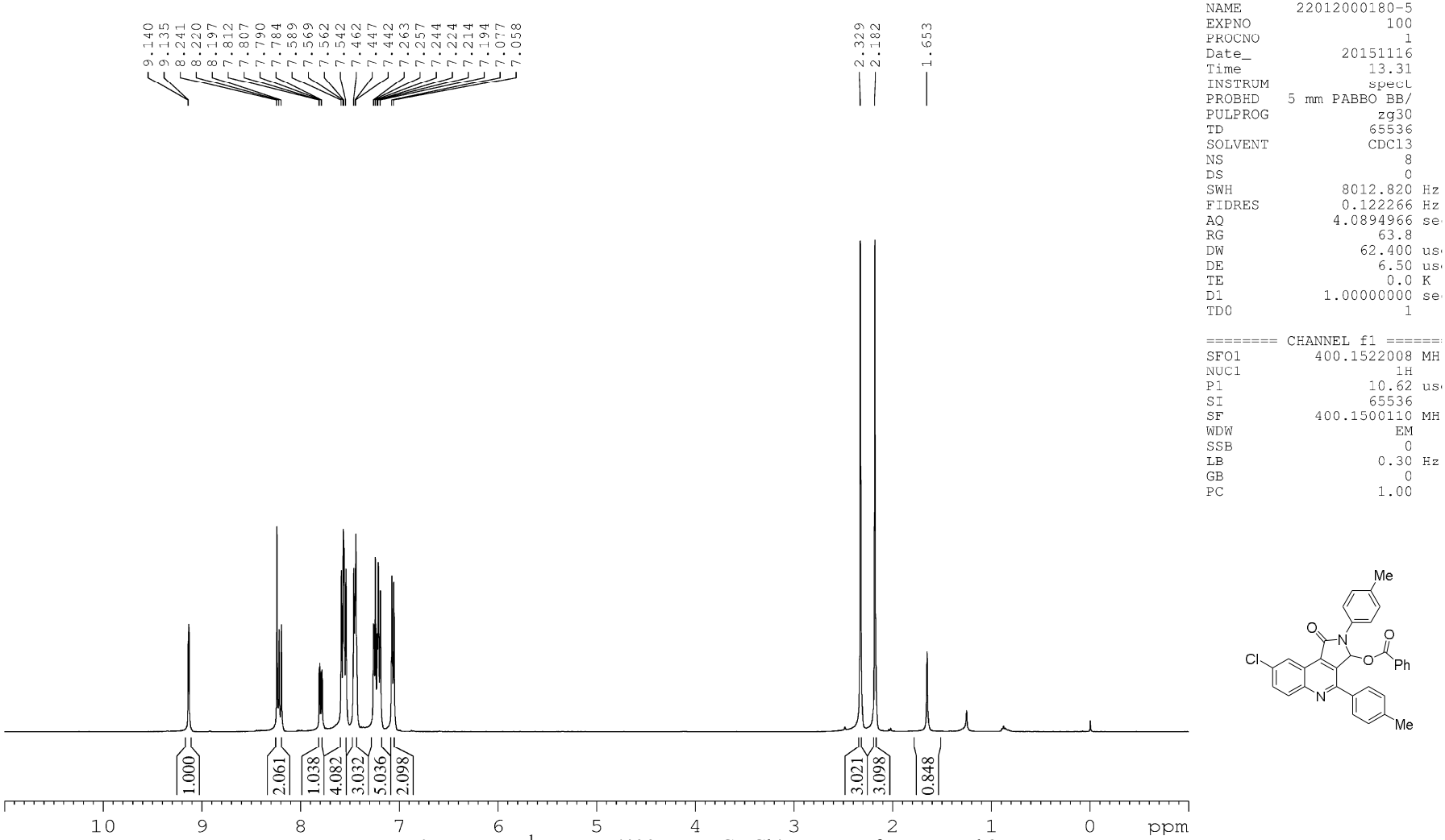


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Figure 55. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3dd**

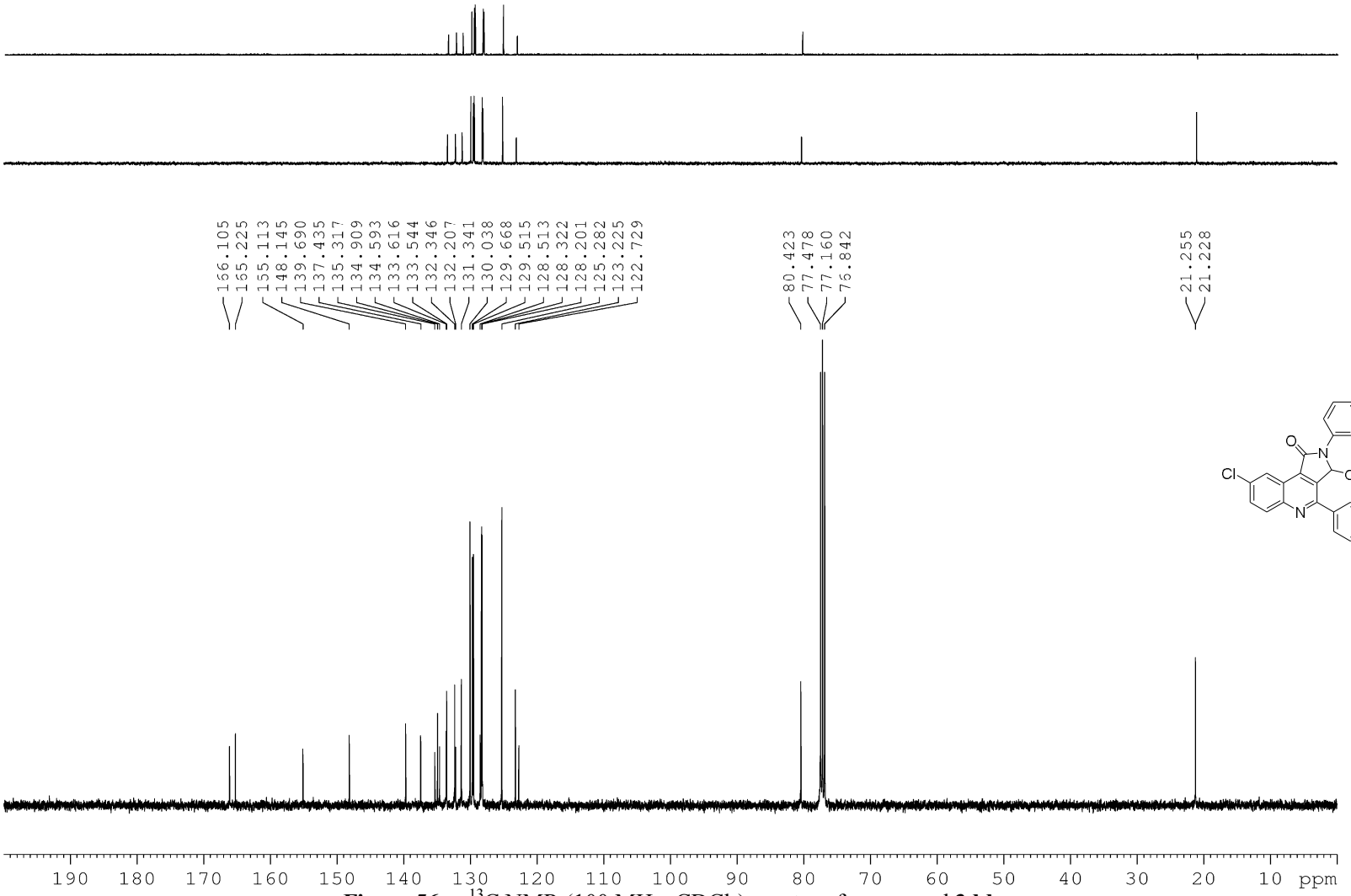

Figure 56. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3dd**

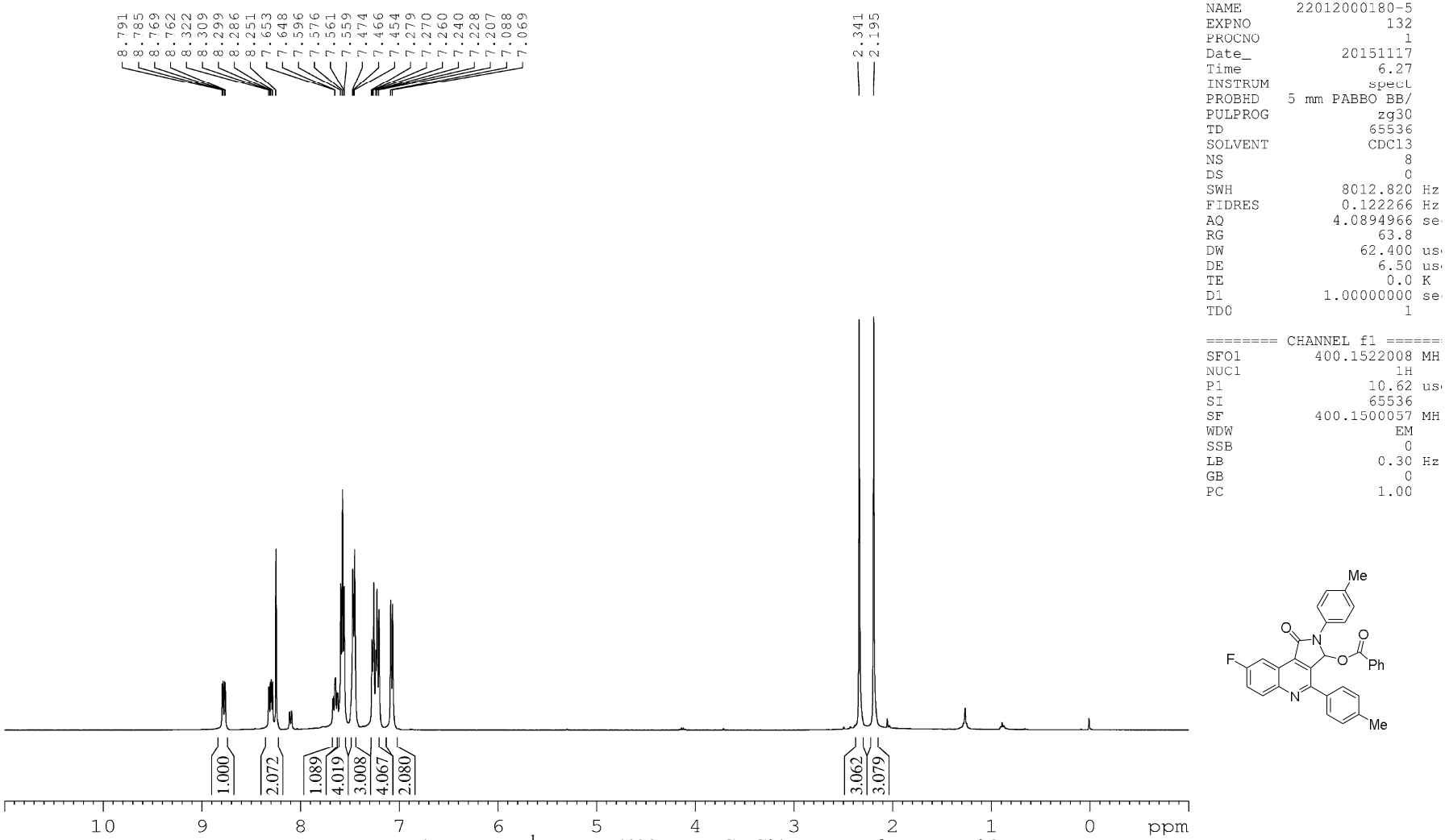


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Figure 57. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3de**

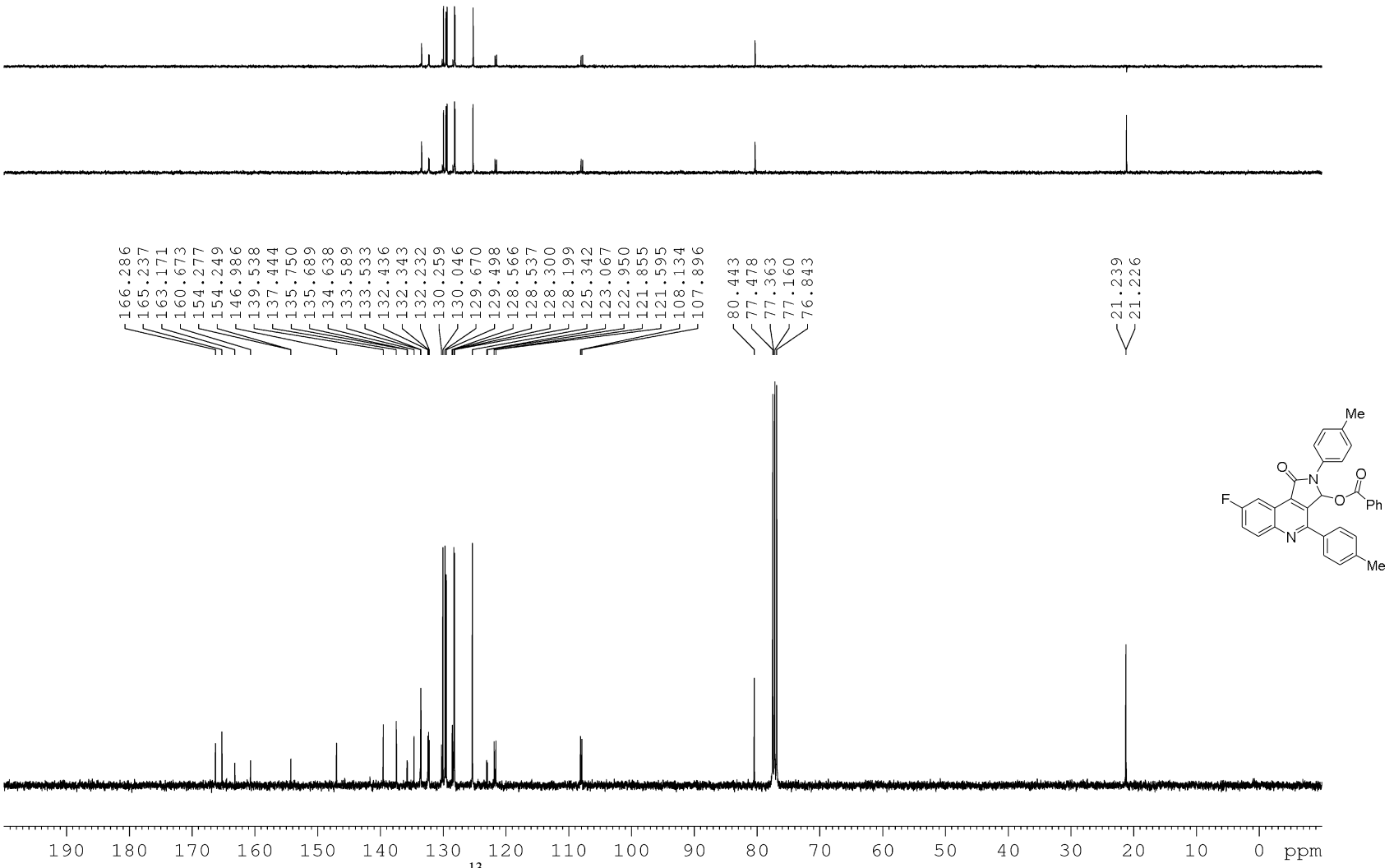


Figure 58. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3de**

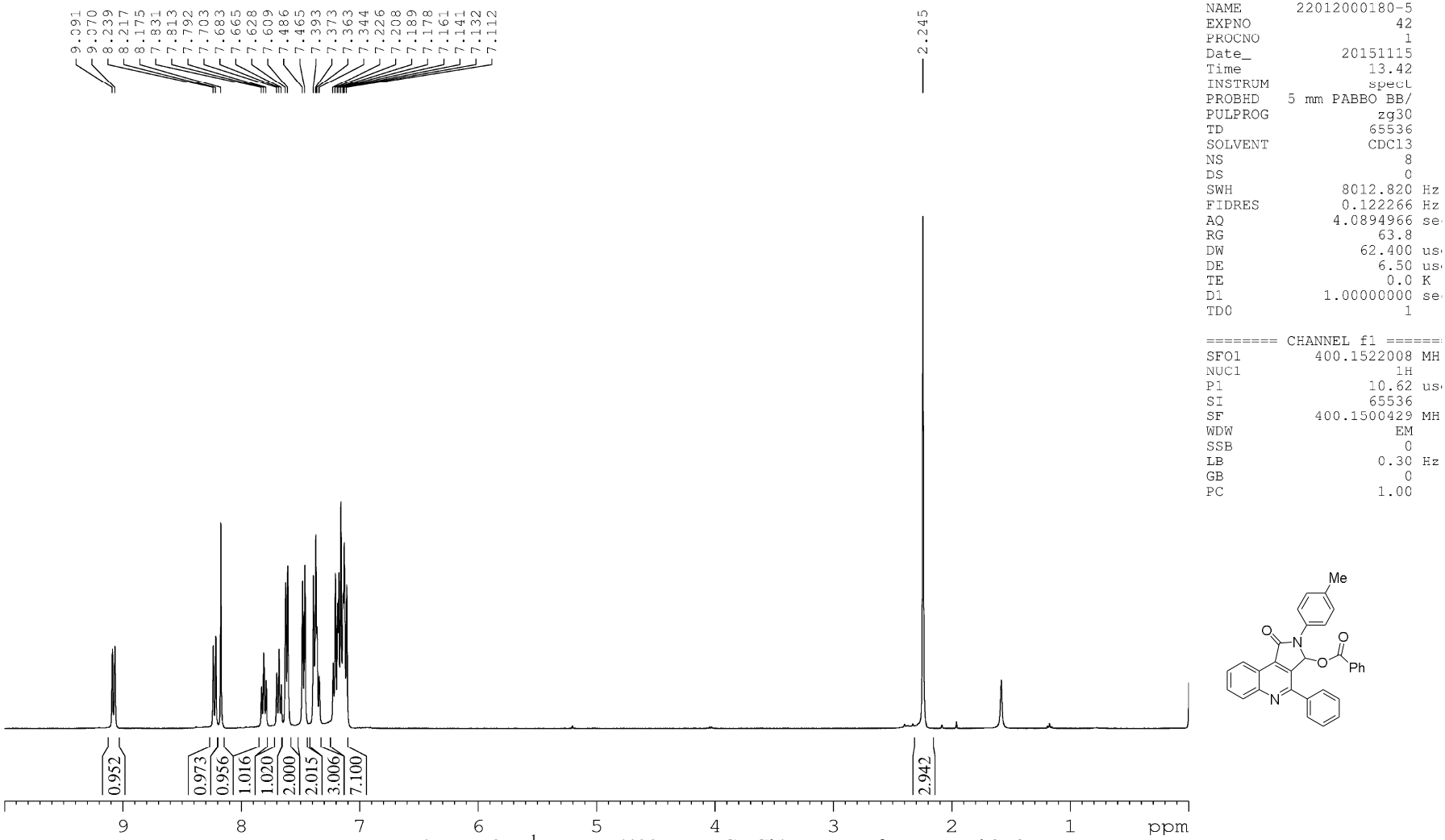


Figure 59. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3df**

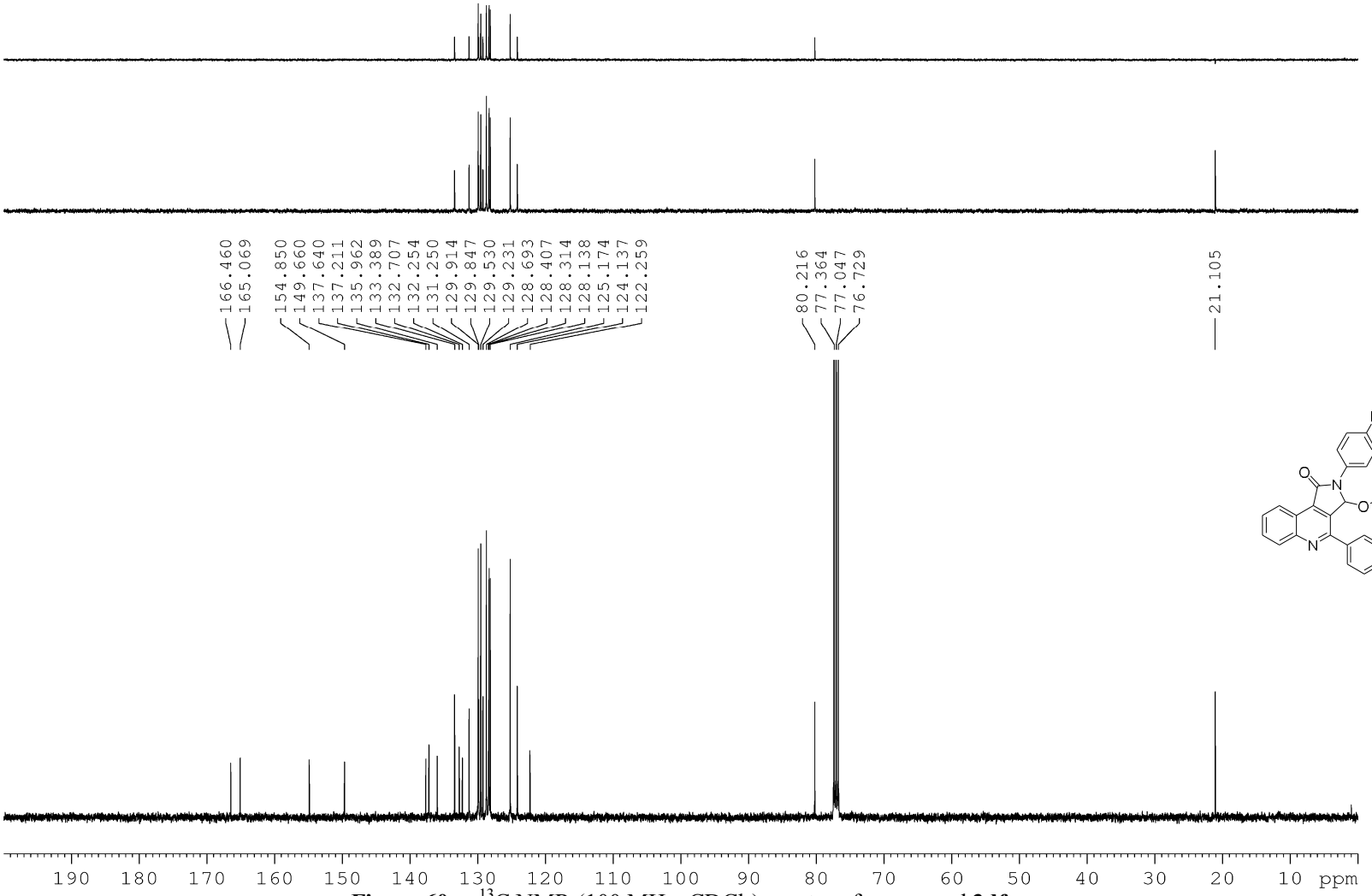


Figure 60. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3df**

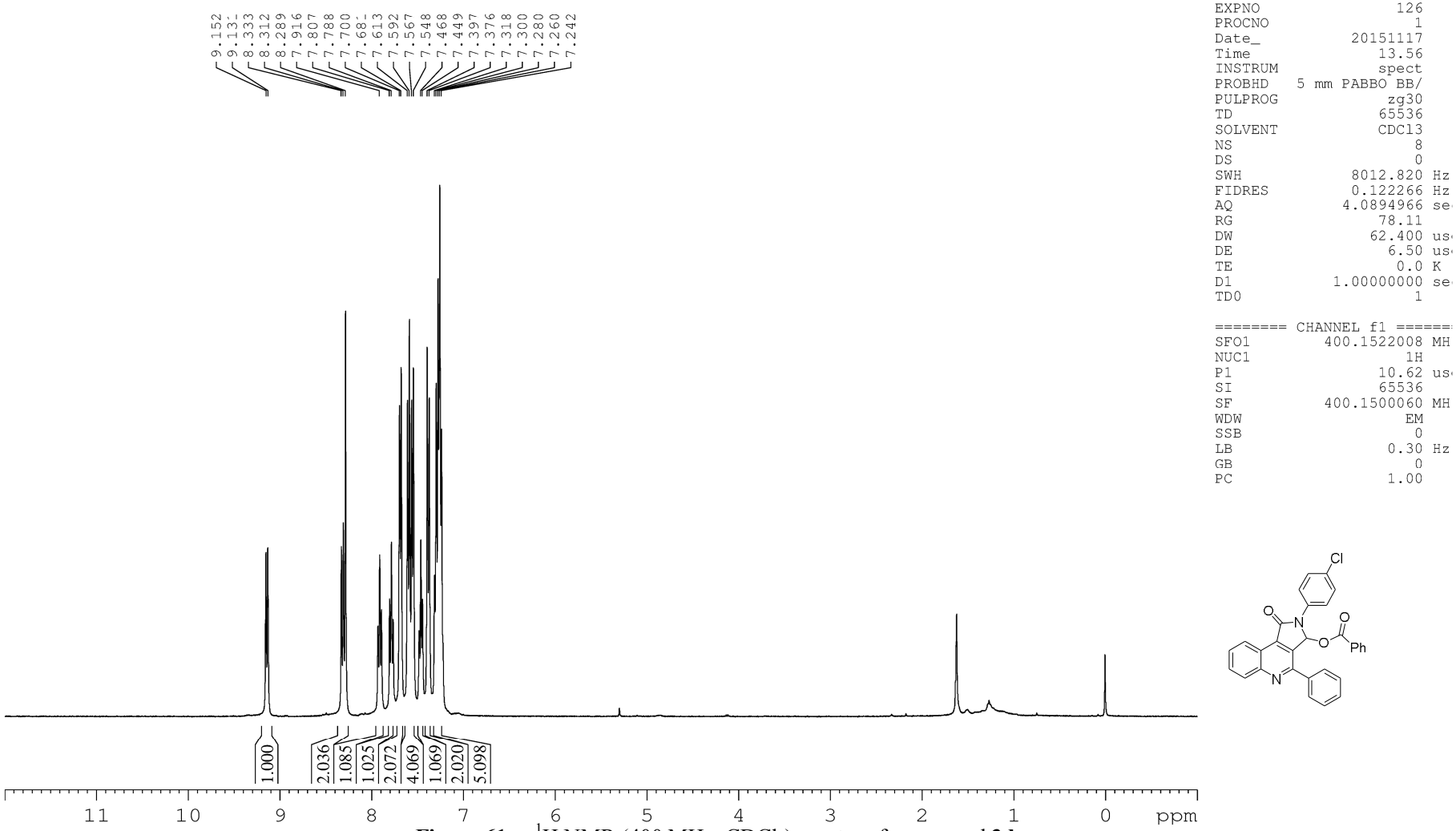


Figure 61. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3dg**

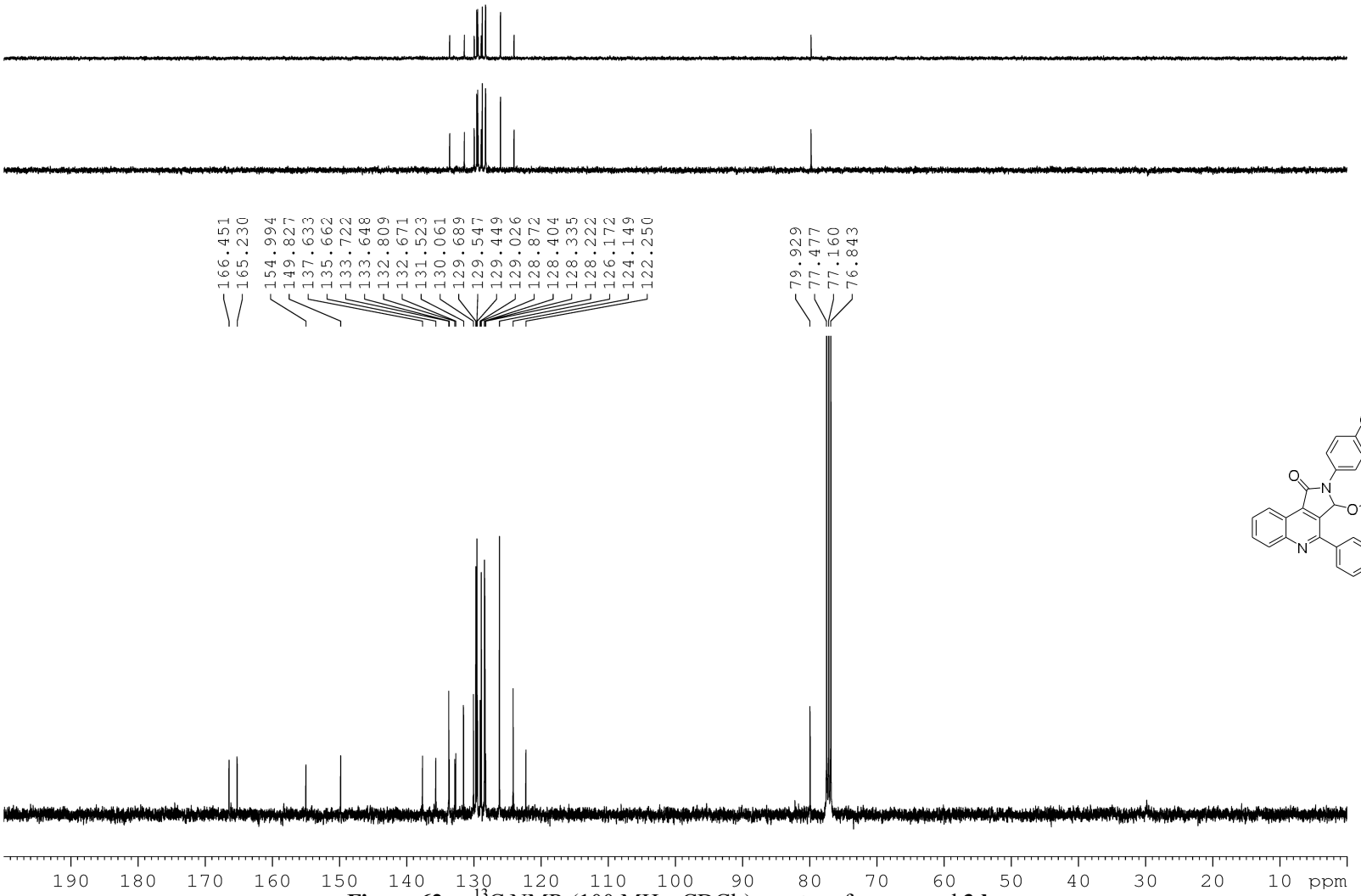


Figure 62. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3dg**

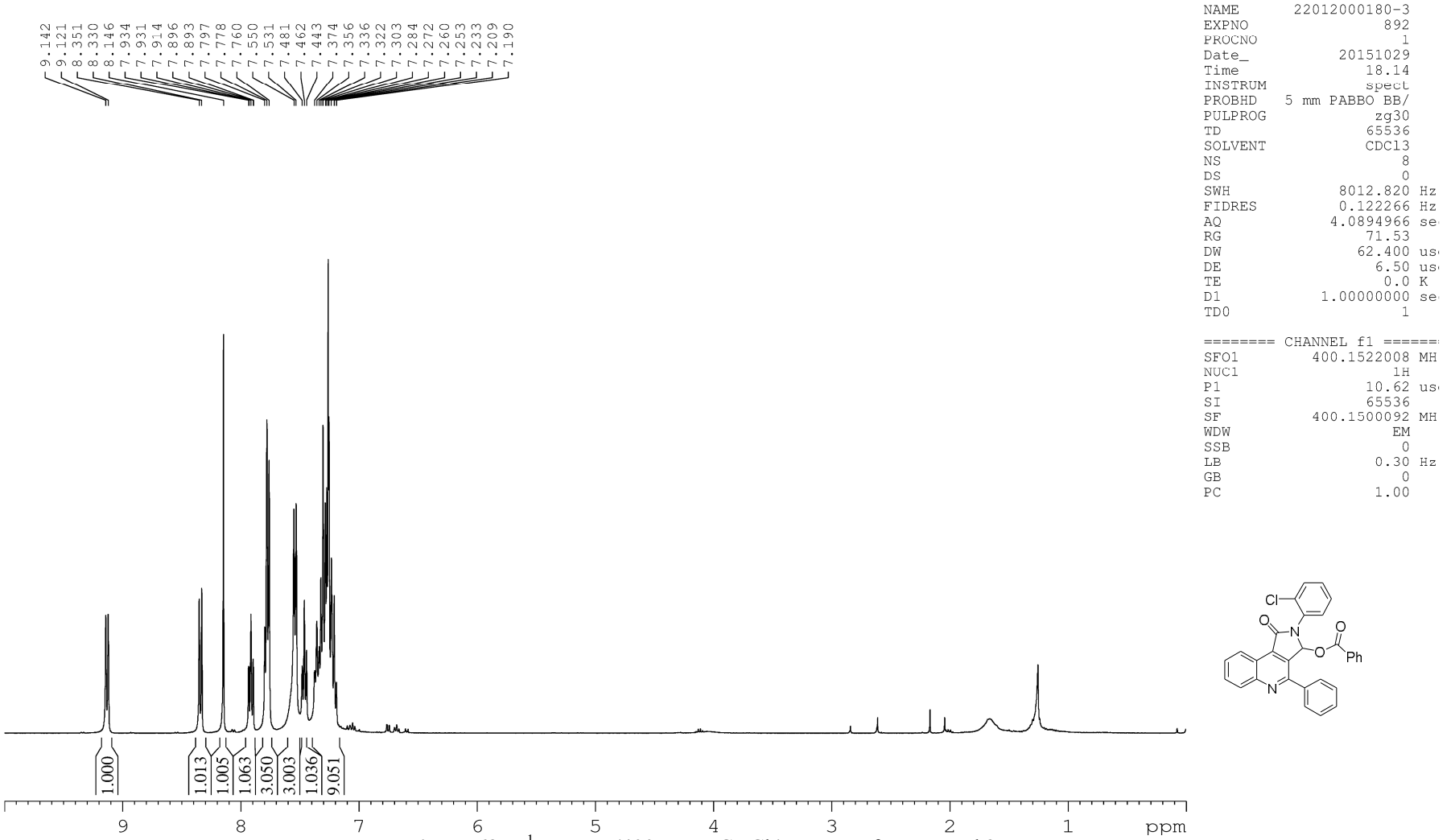


Figure 63. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3dh**

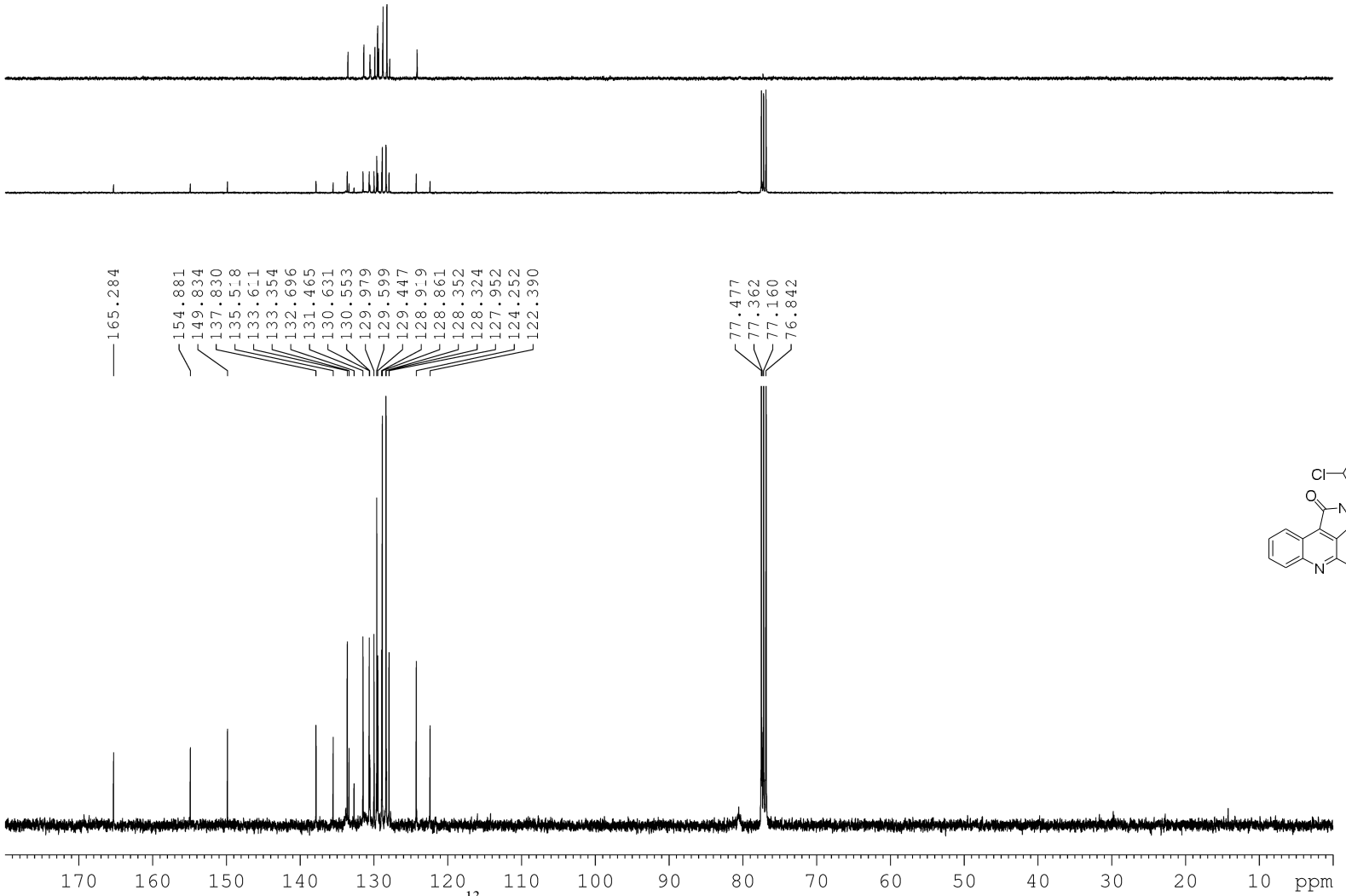


Figure 64. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3dh**

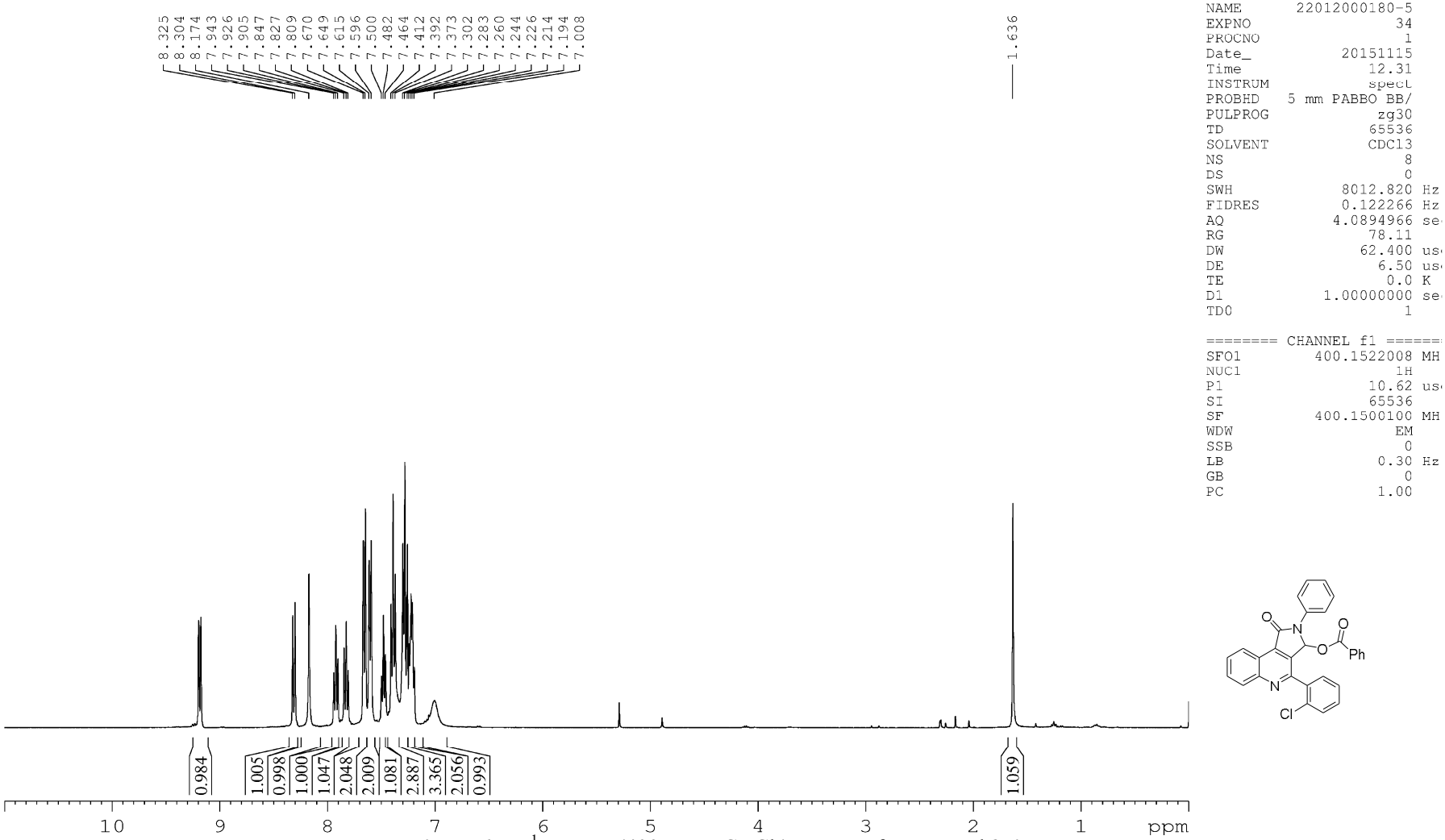


Figure 65. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **3di**

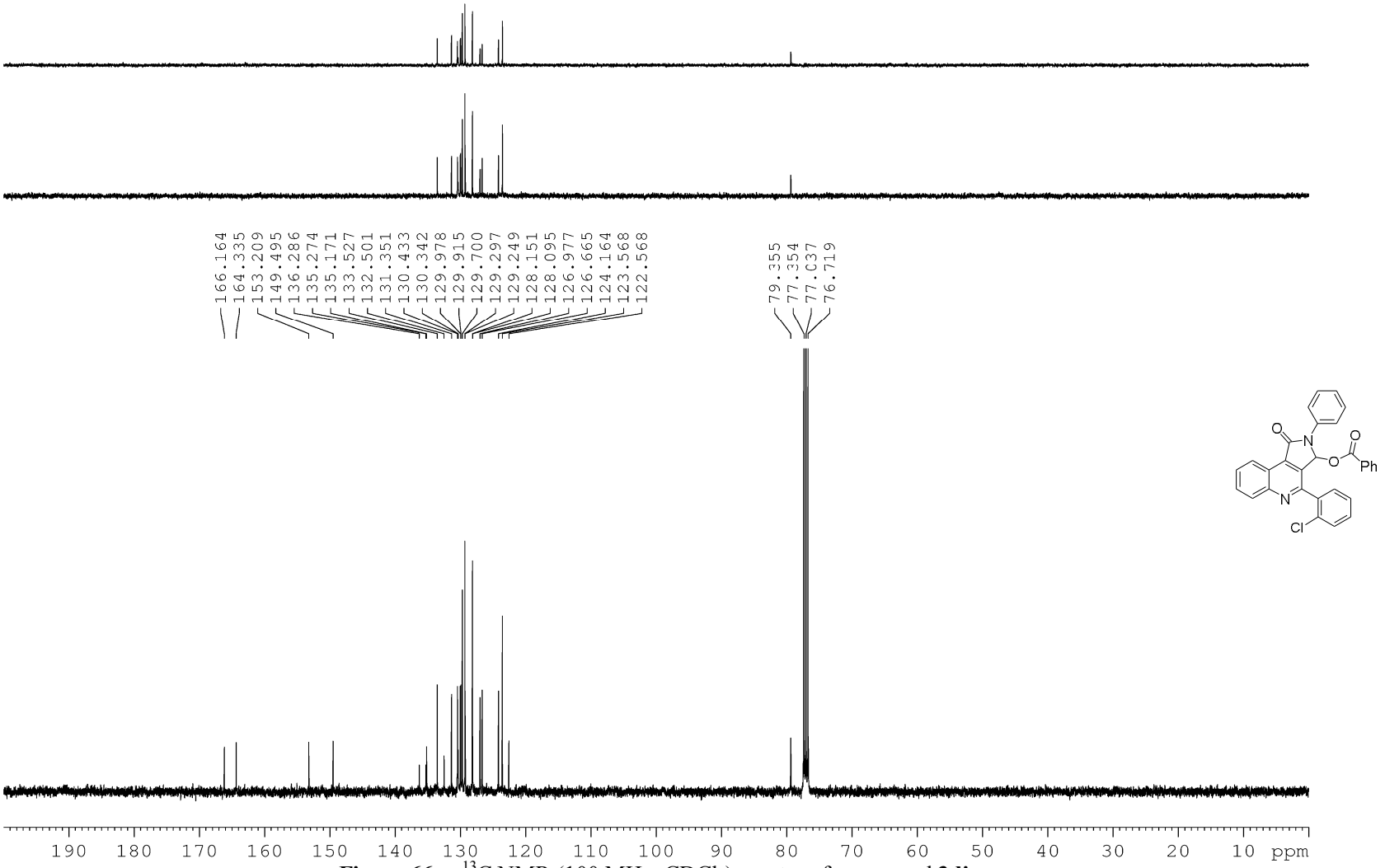


Figure 66. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **3di**

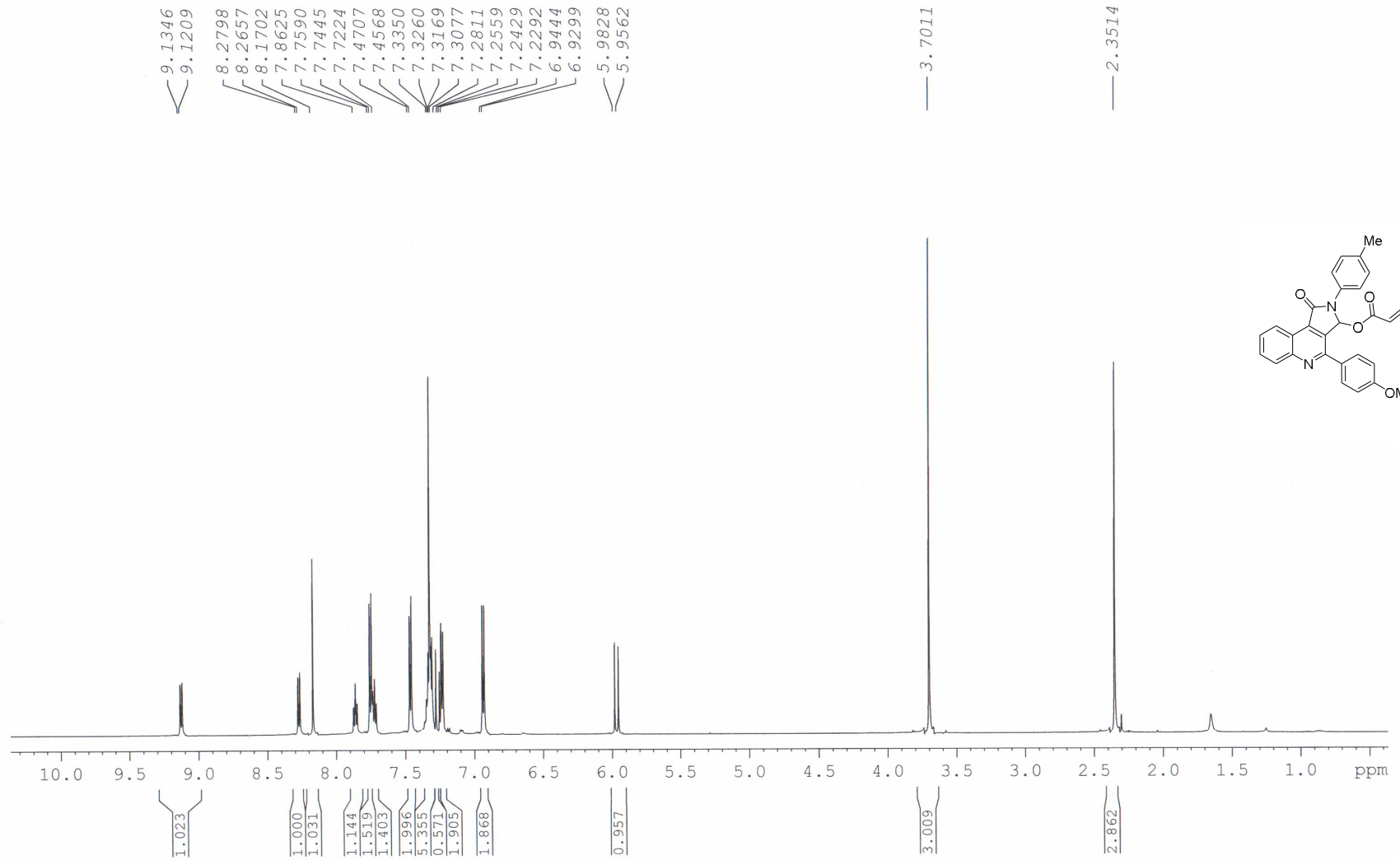


Figure 67. ^{1}H NMR (600 MHz, $CDCl_3$) spectra of compound **3dj**

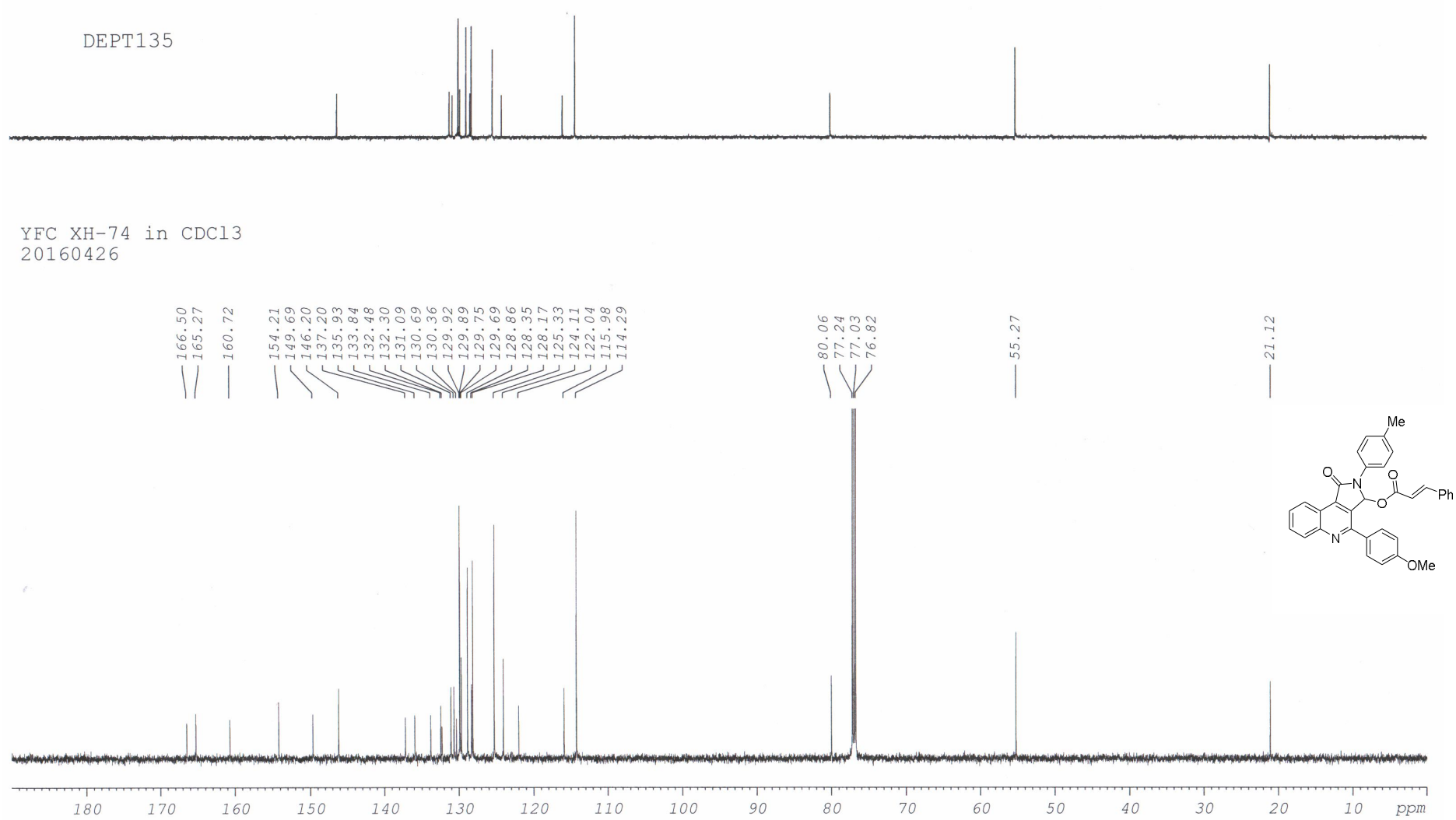


Figure 68. ^{13}C NMR (150 MHz, $CDCl_3$) spectra of compound **3dj**

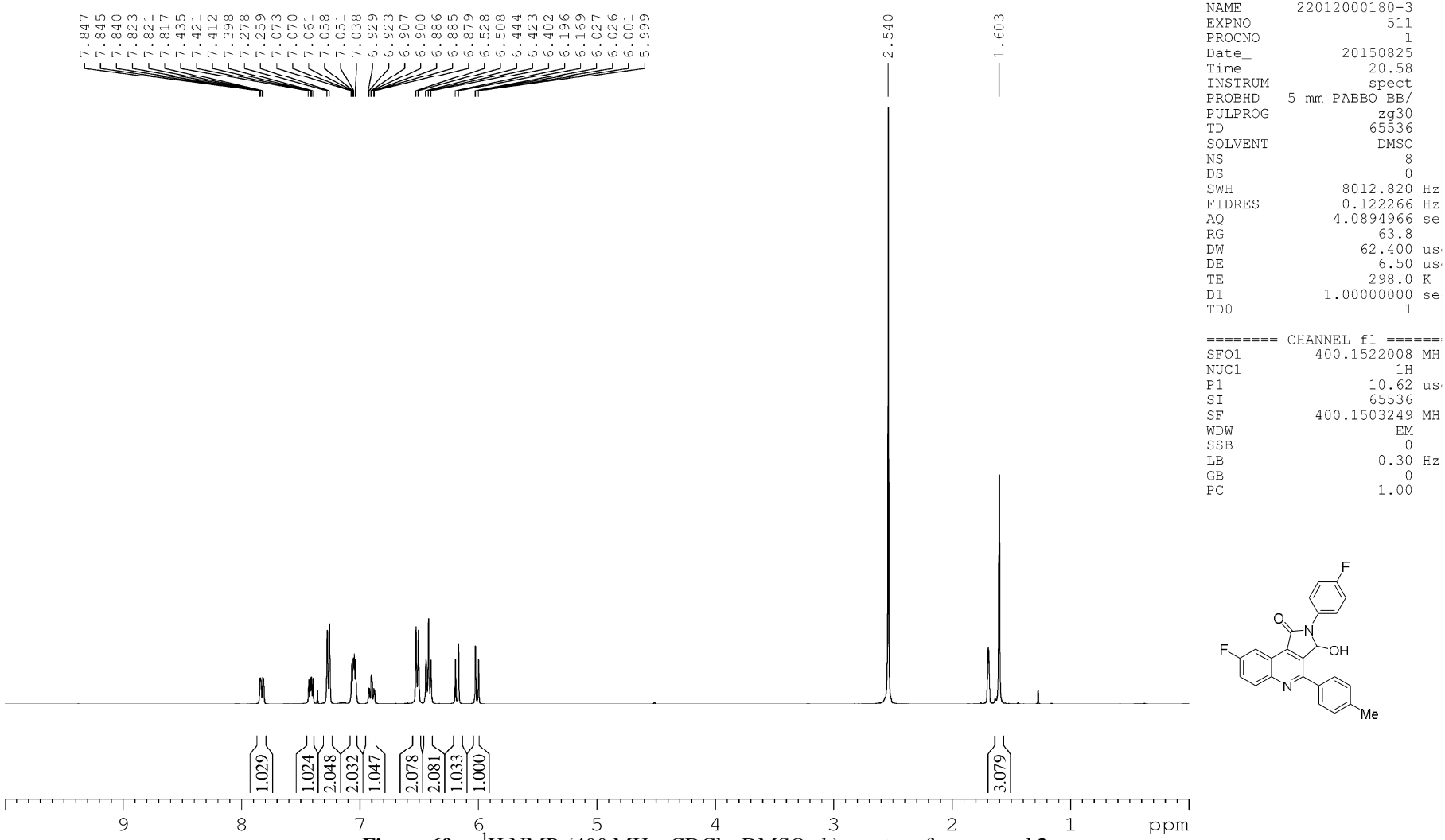


Figure 69. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ea**

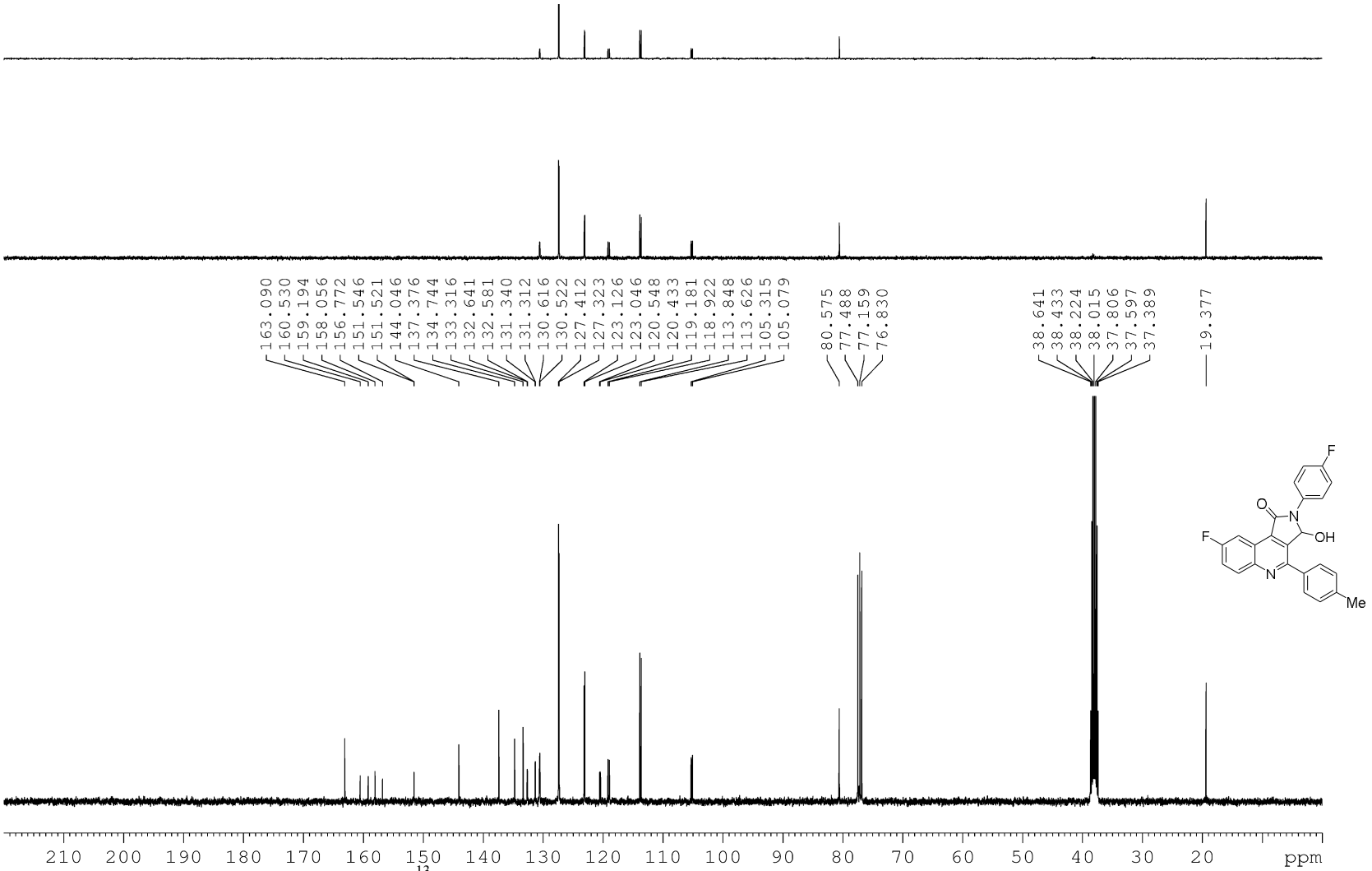


Figure 70. ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ea**

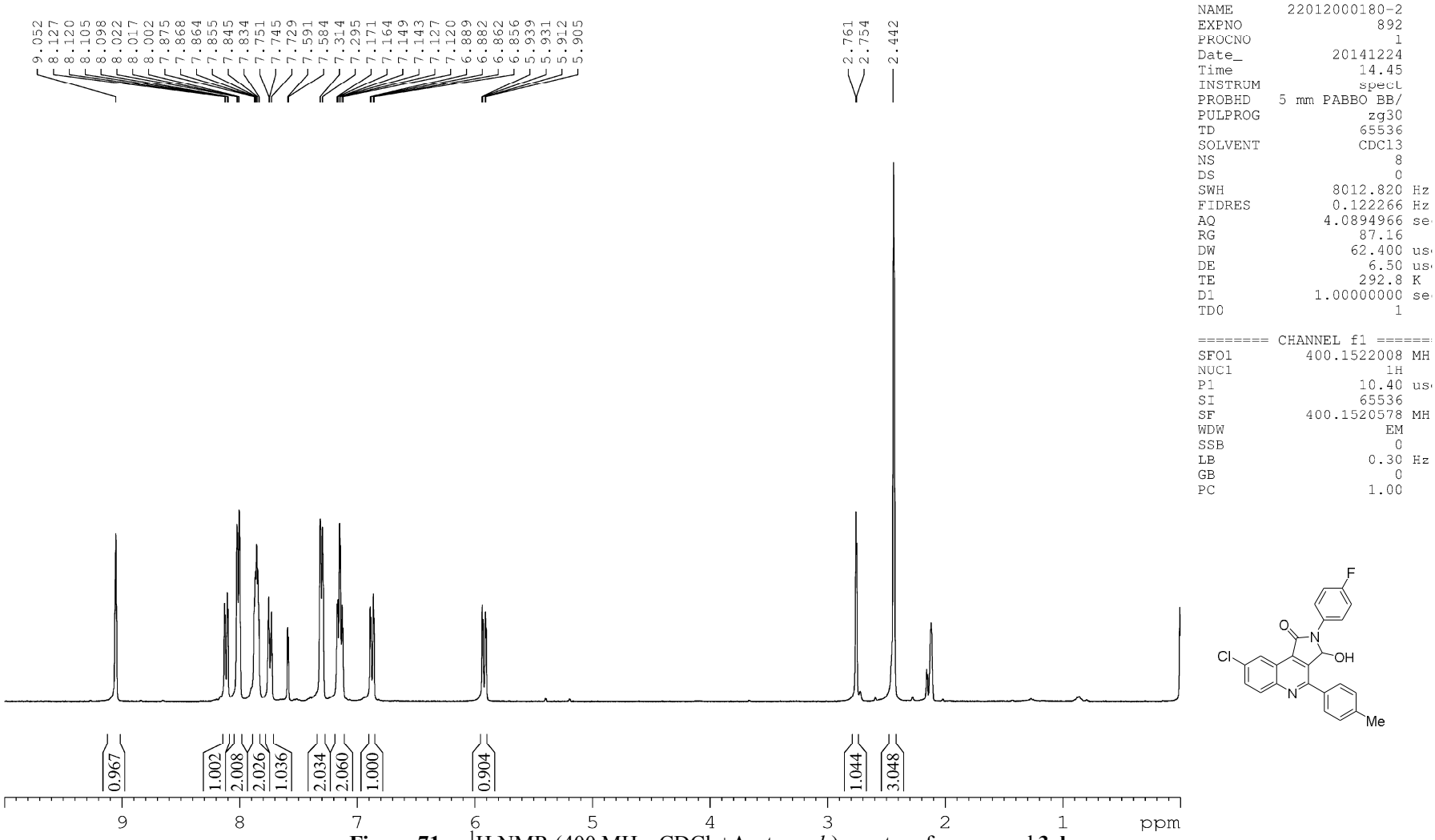


Figure 71. ^{1}H NMR (400 MHz, $CDCl_3$+Acetone-d_6) spectra of compound **3eb**

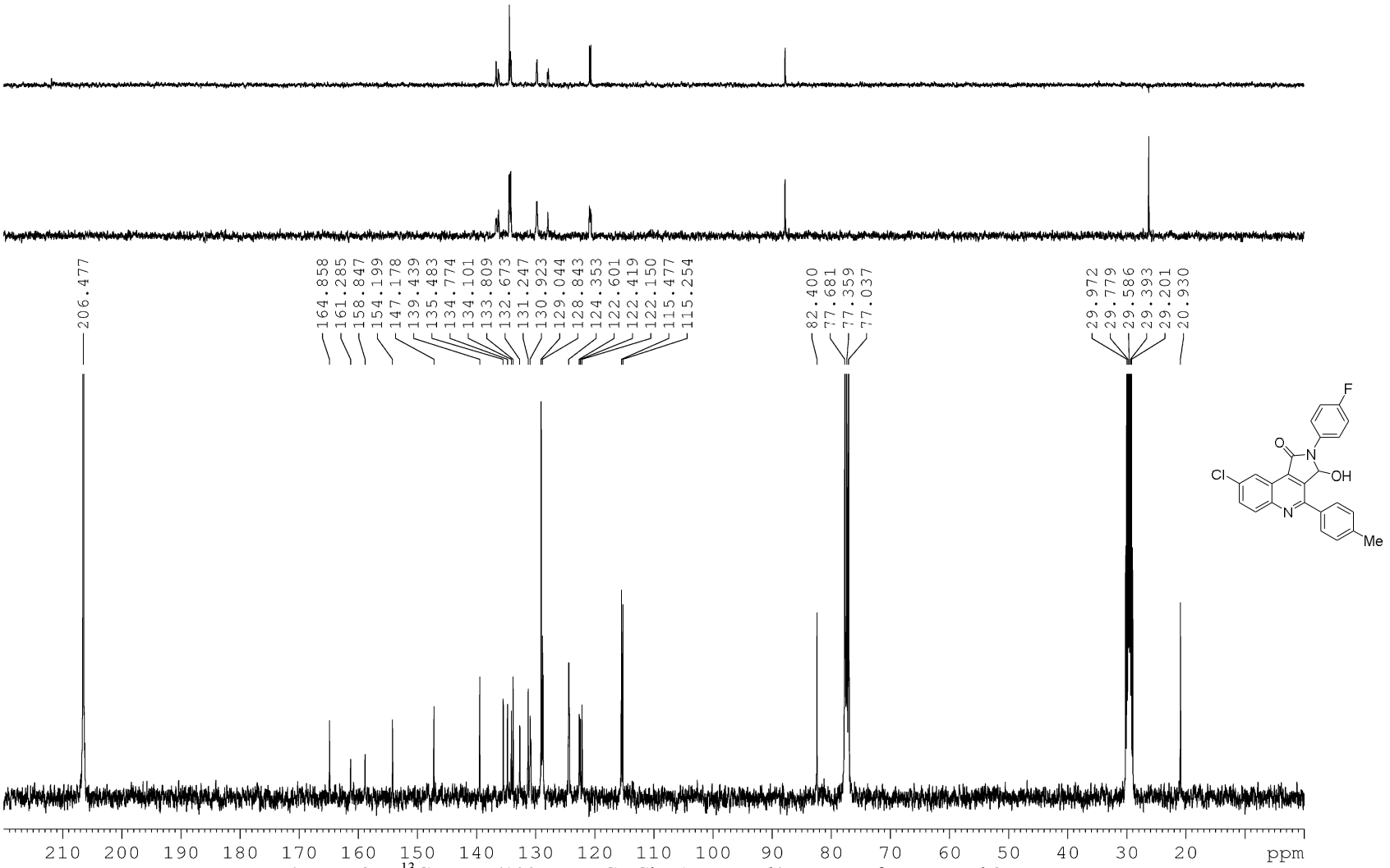


Figure 72. ^{13}C NMR (100 MHz, $CDCl_3$+Acetone-d_6) spectra of compound **3eb**

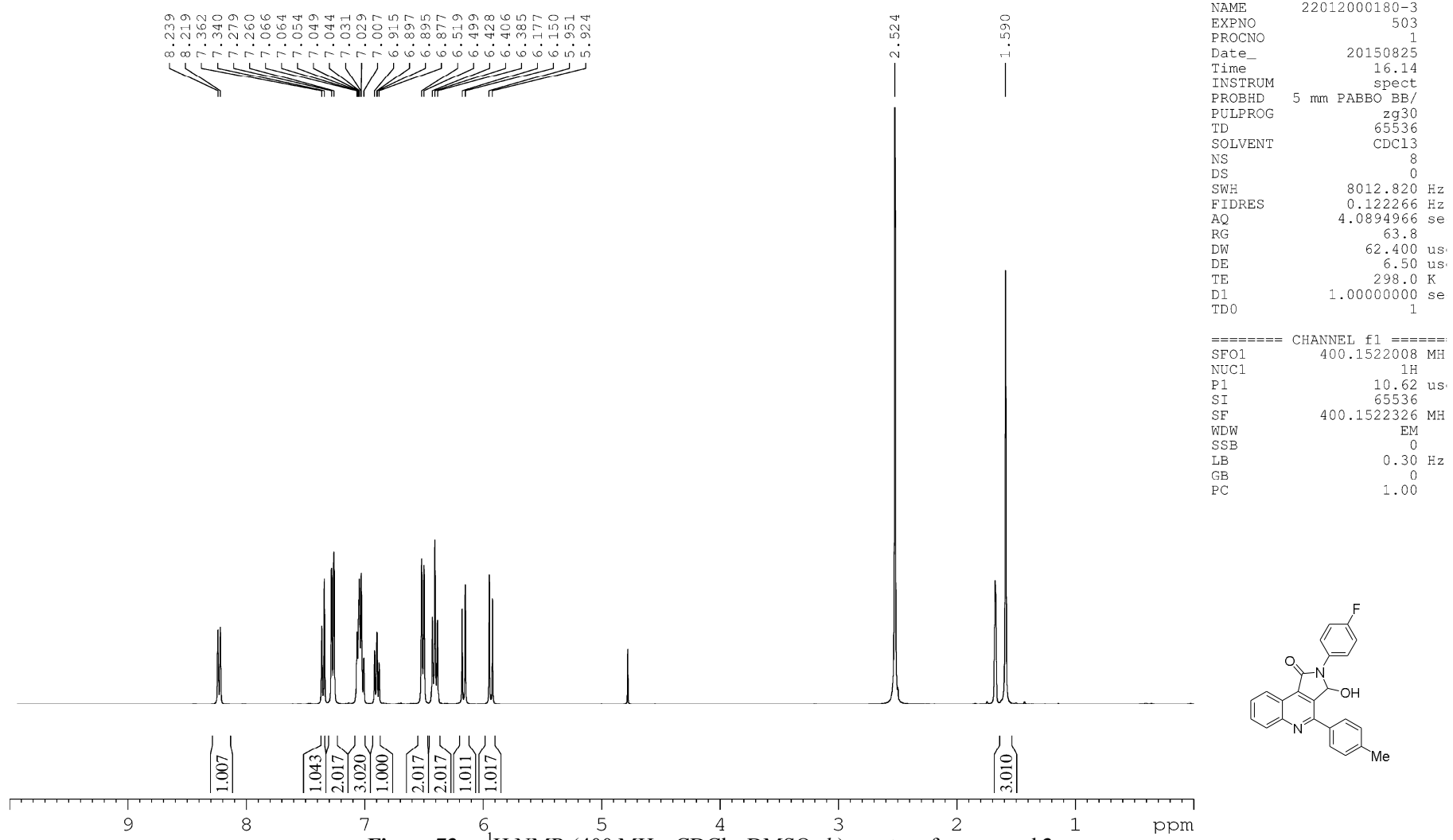


Figure 73. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ec**

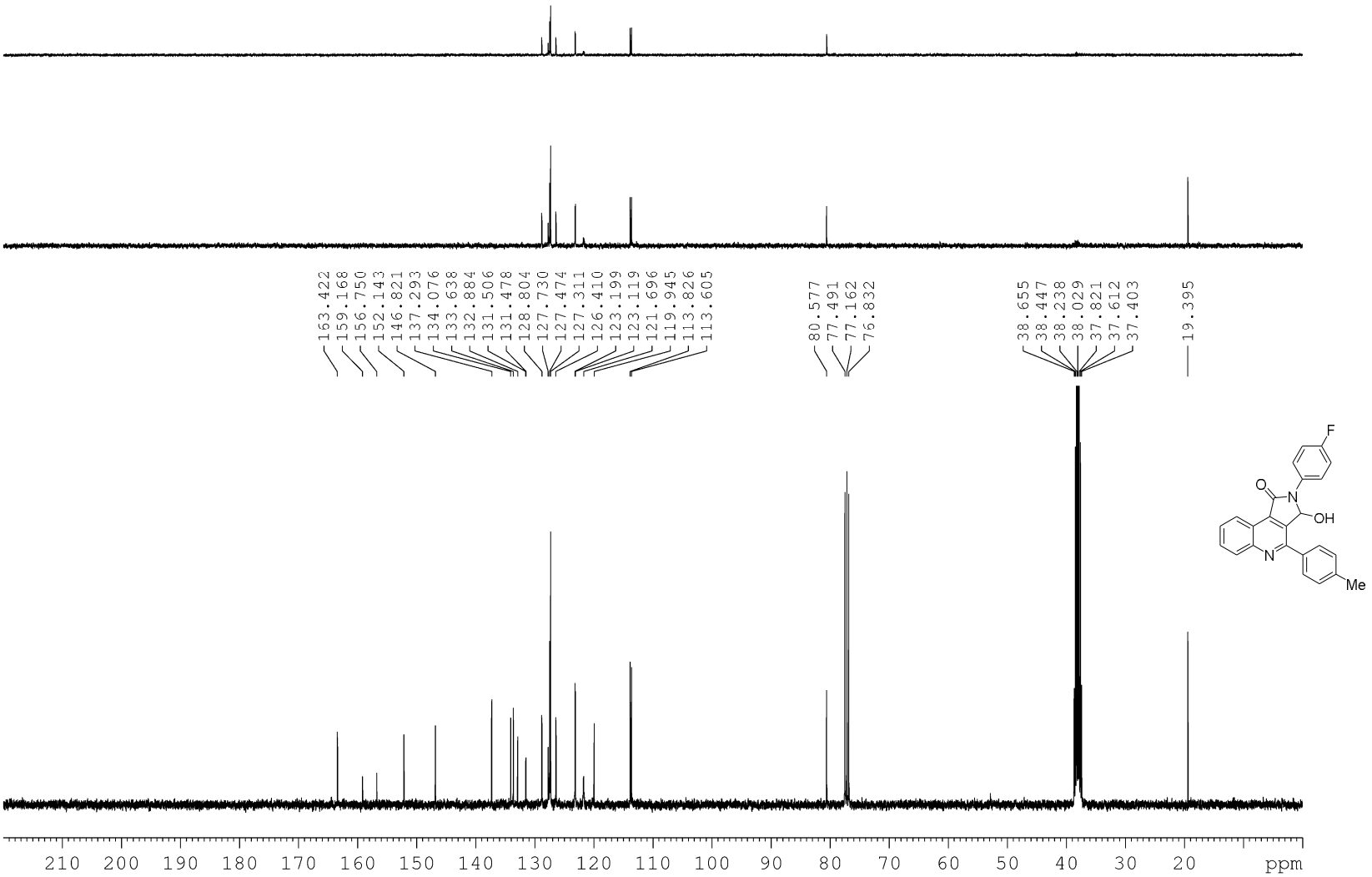


Figure 74. ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ec**

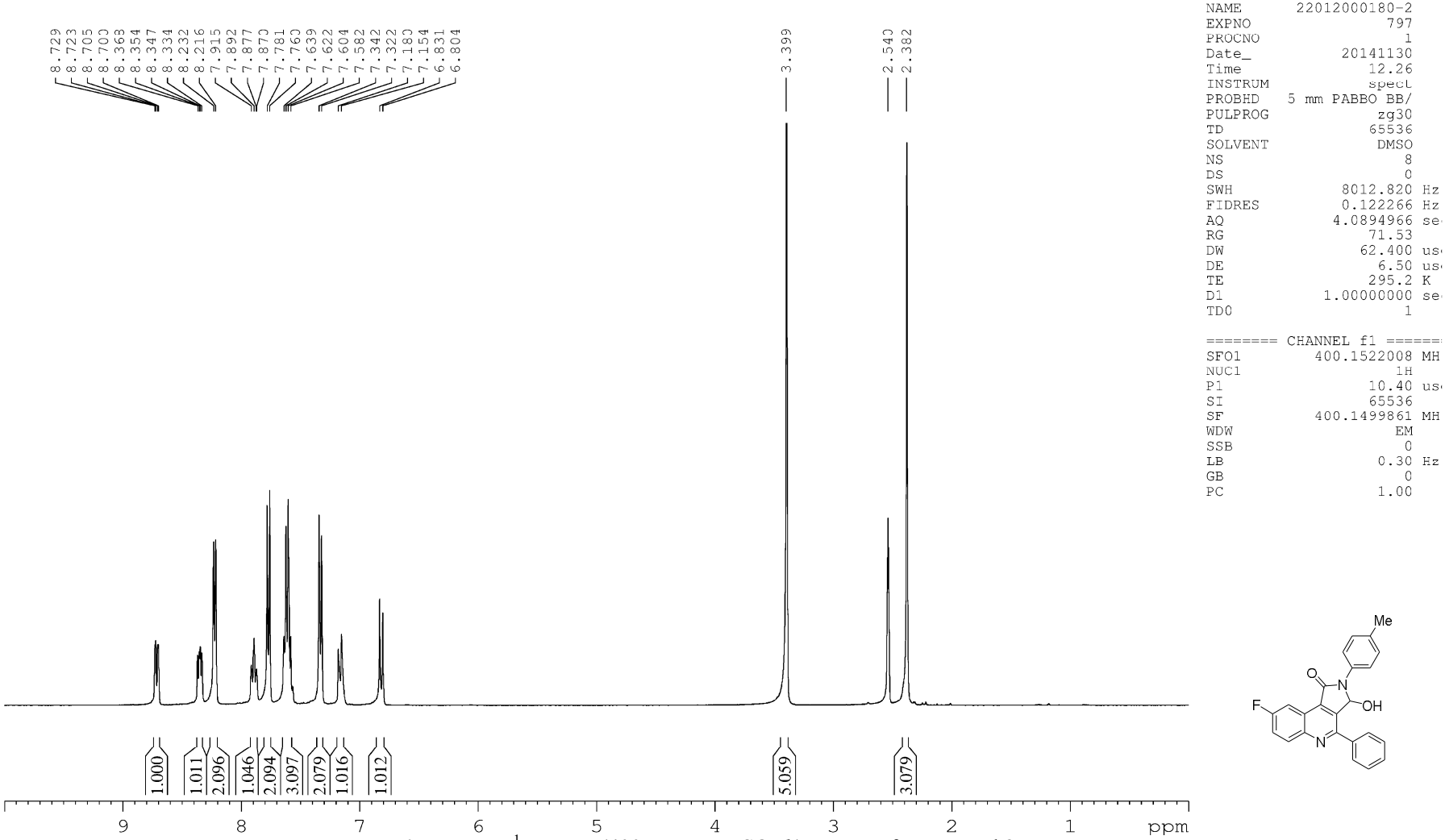


Figure 75. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3ed**

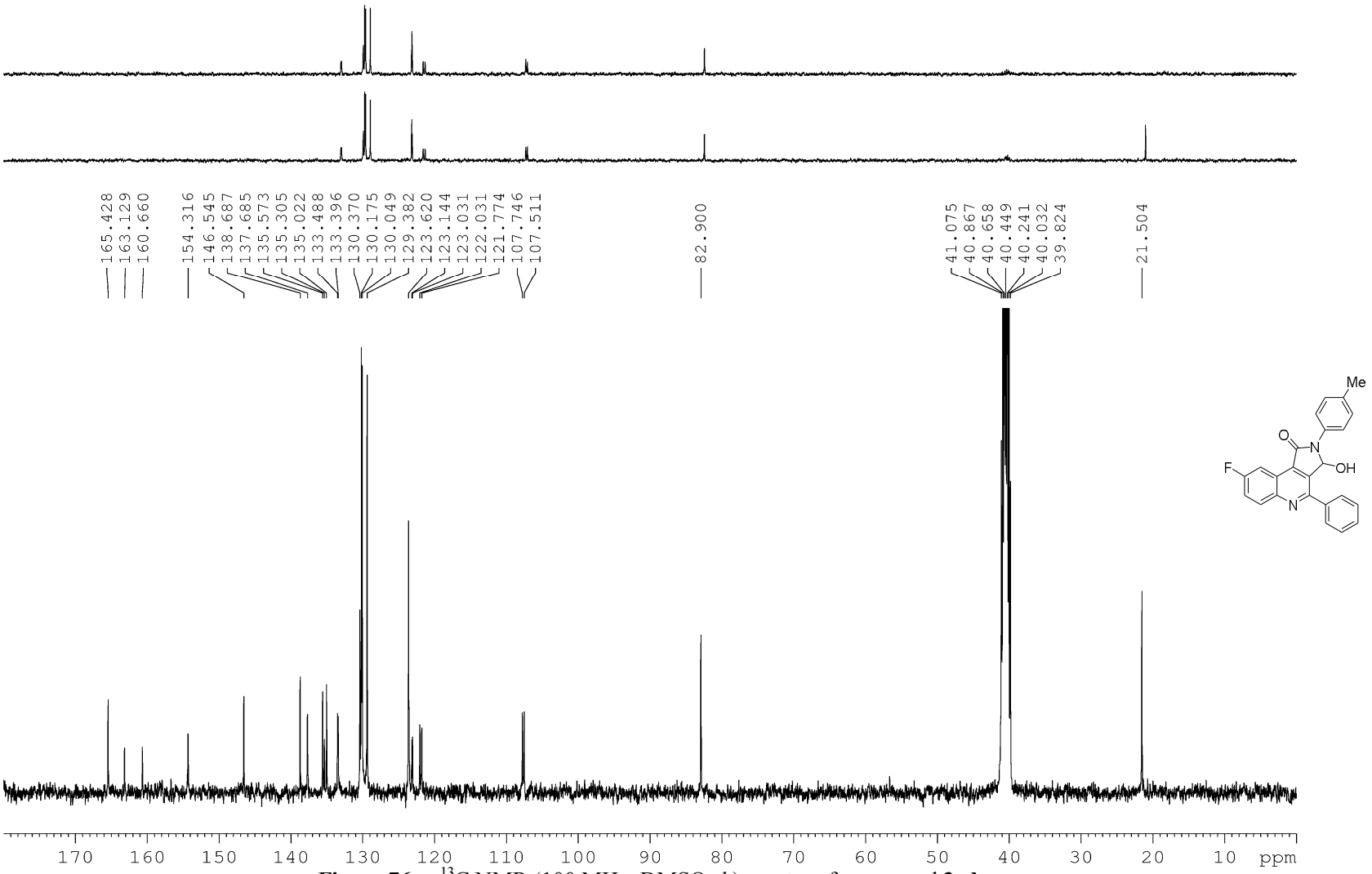
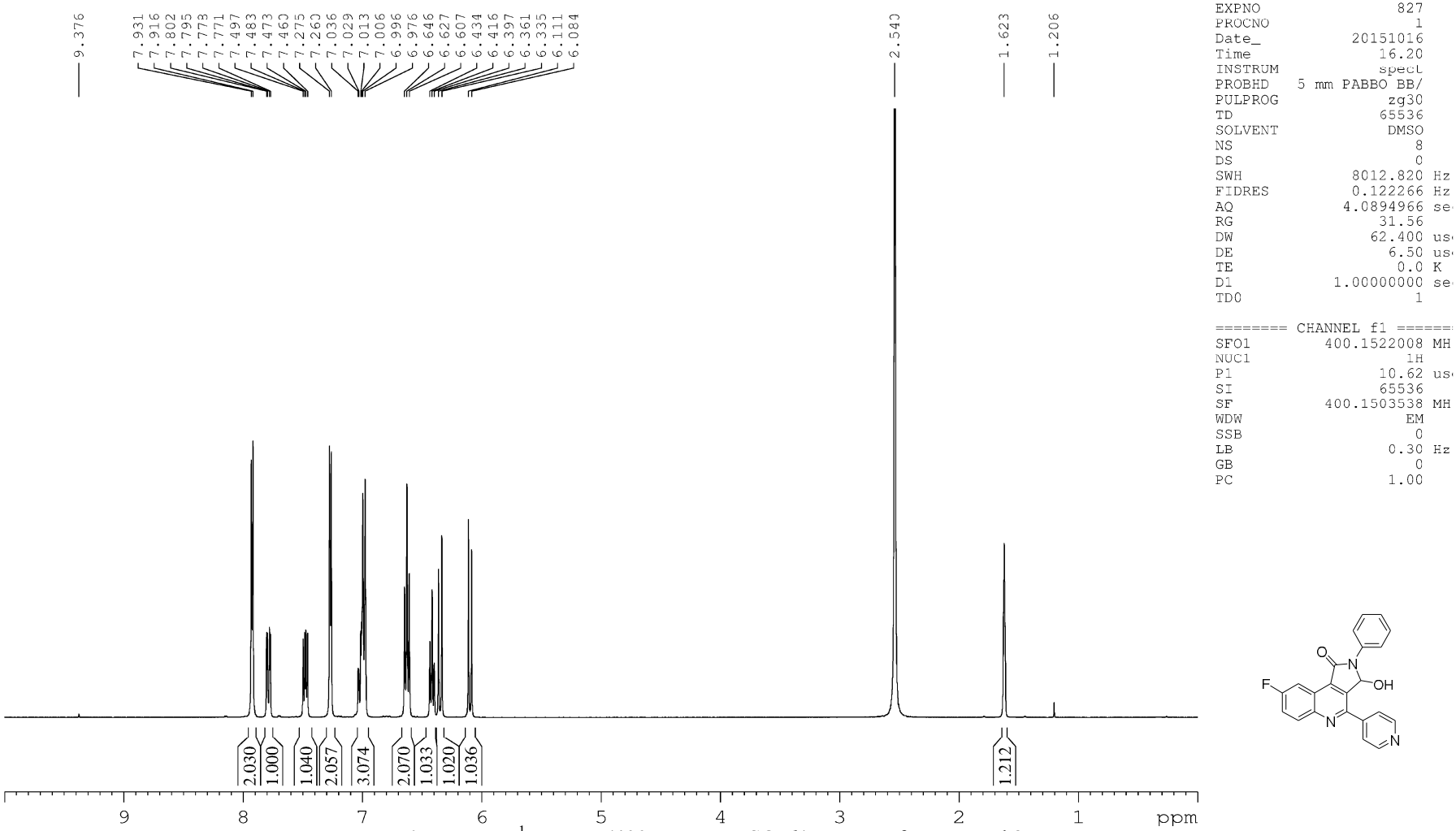


Figure 76. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **3ed**

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PC                  1.00
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Figure 77. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3ee**

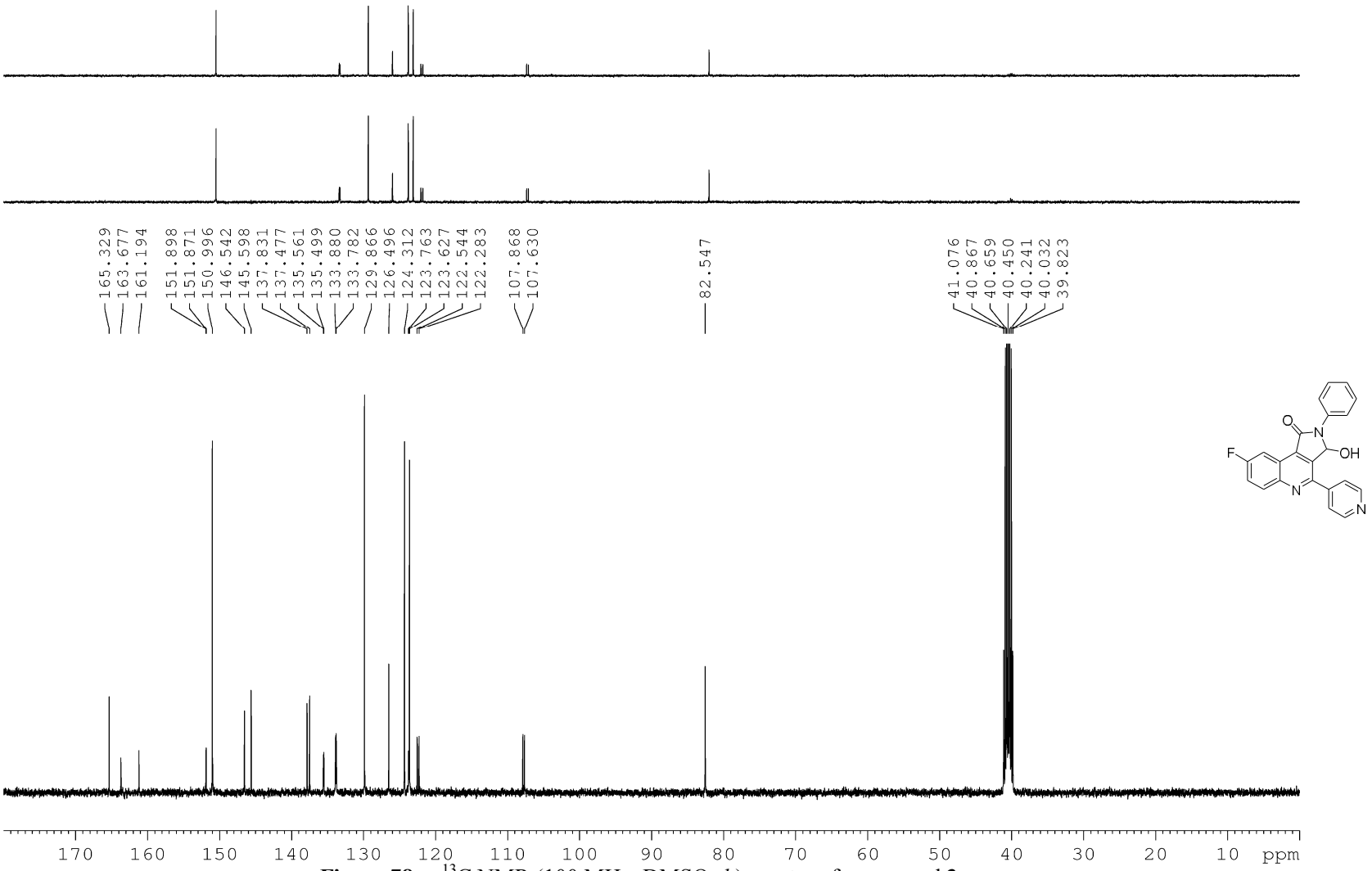

Figure 78. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **3ee**

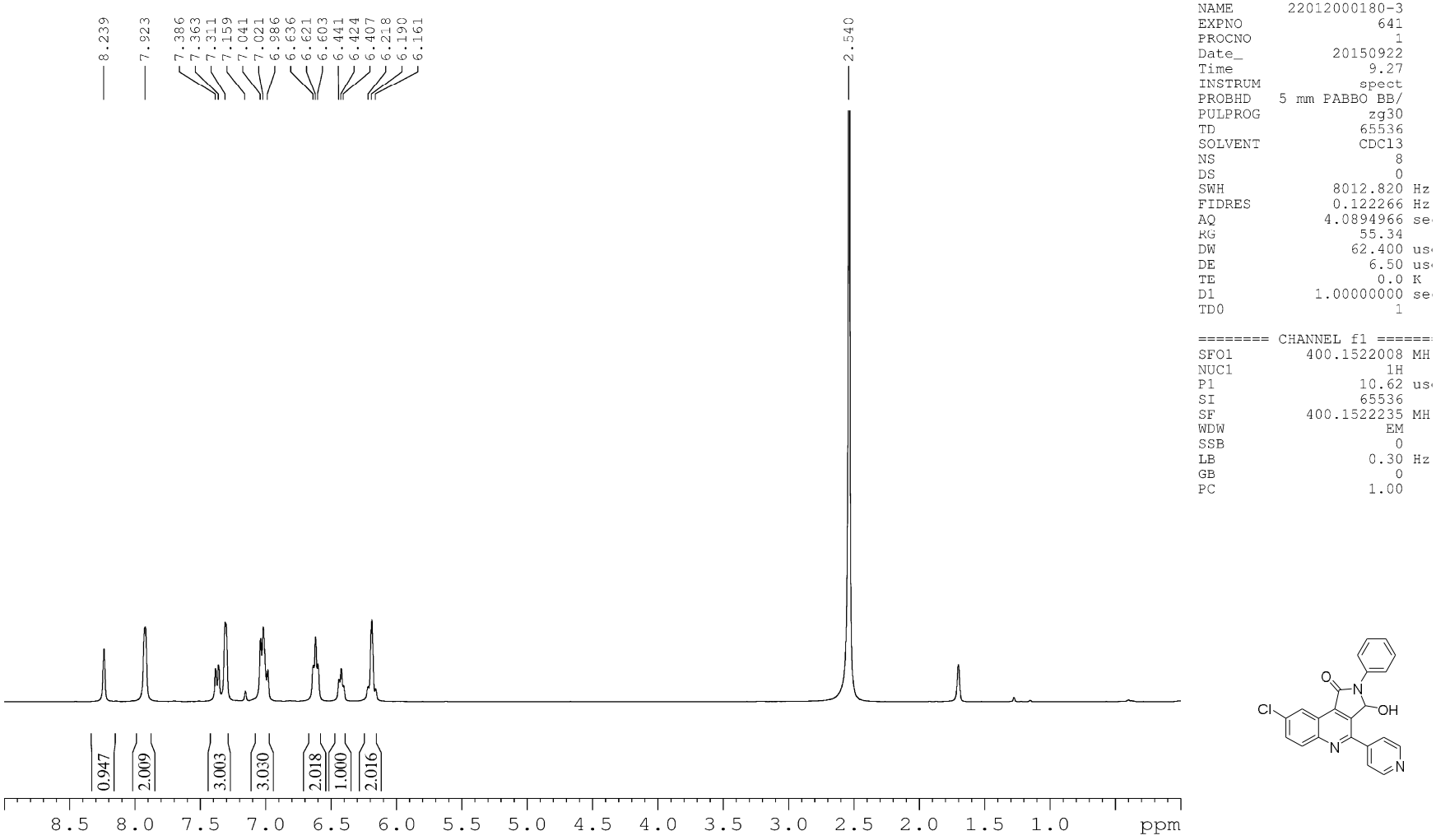

Figure 79. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ef**

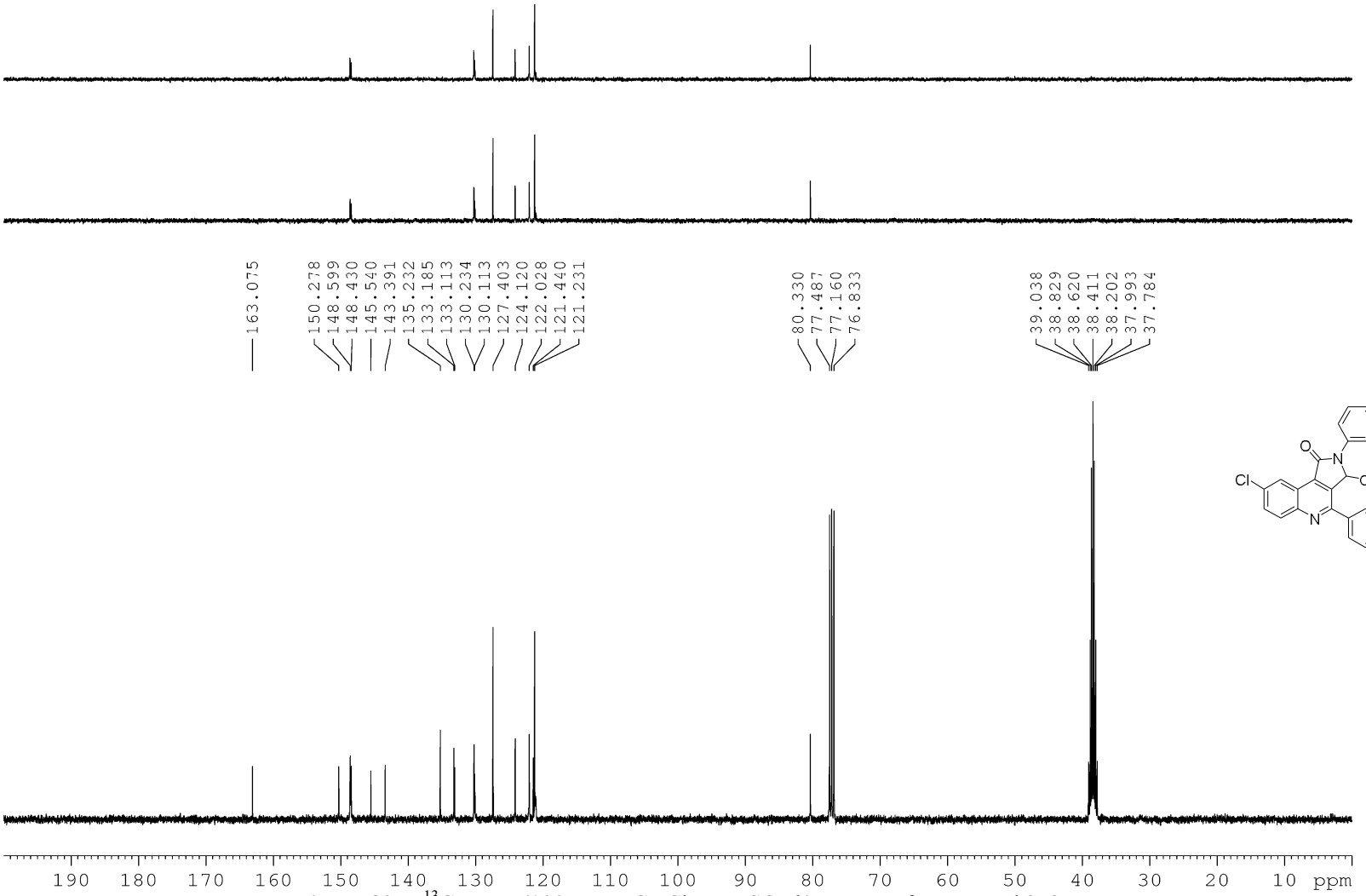

Figure 80. ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **3ef**

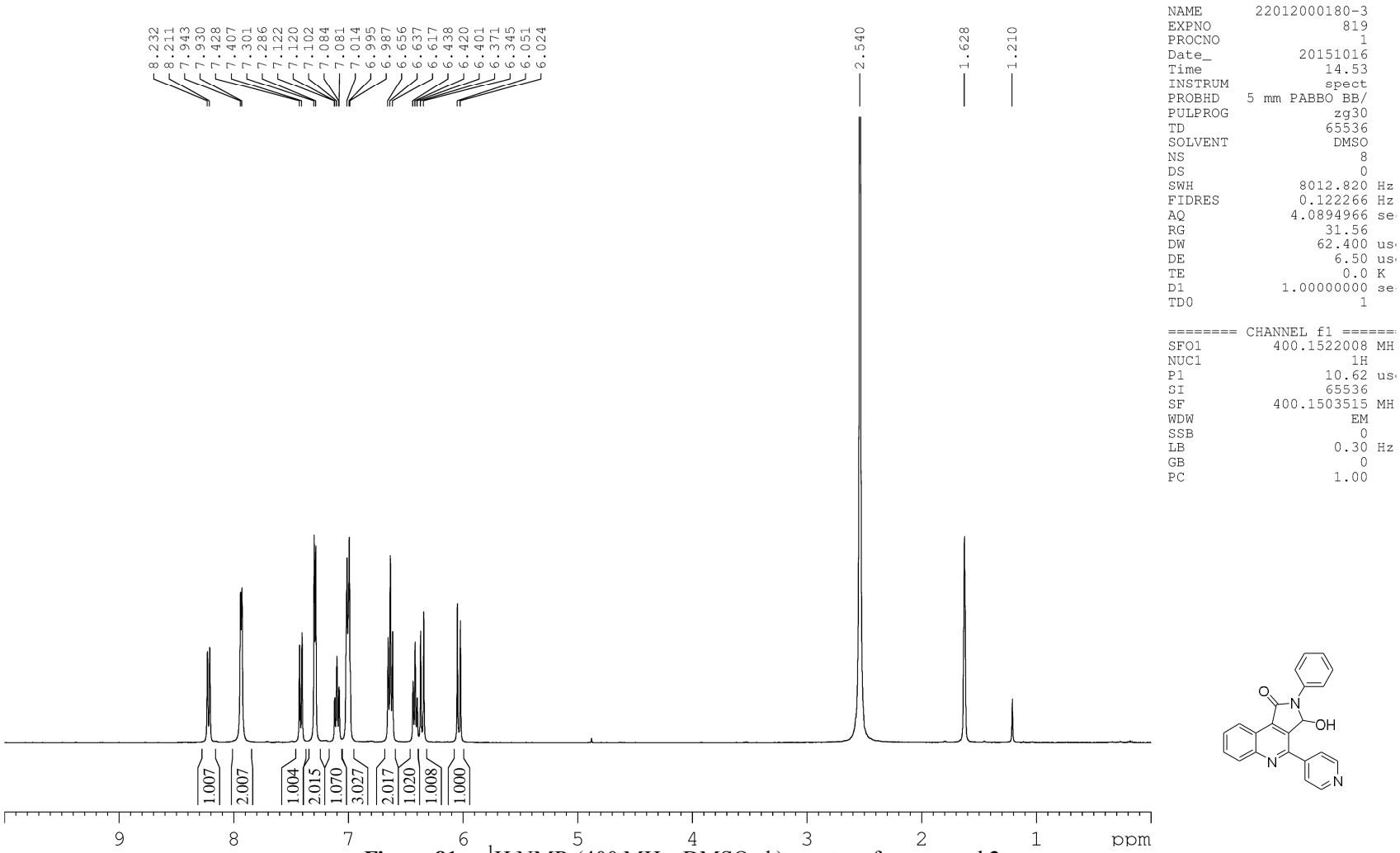

Figure 81. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **3eg**

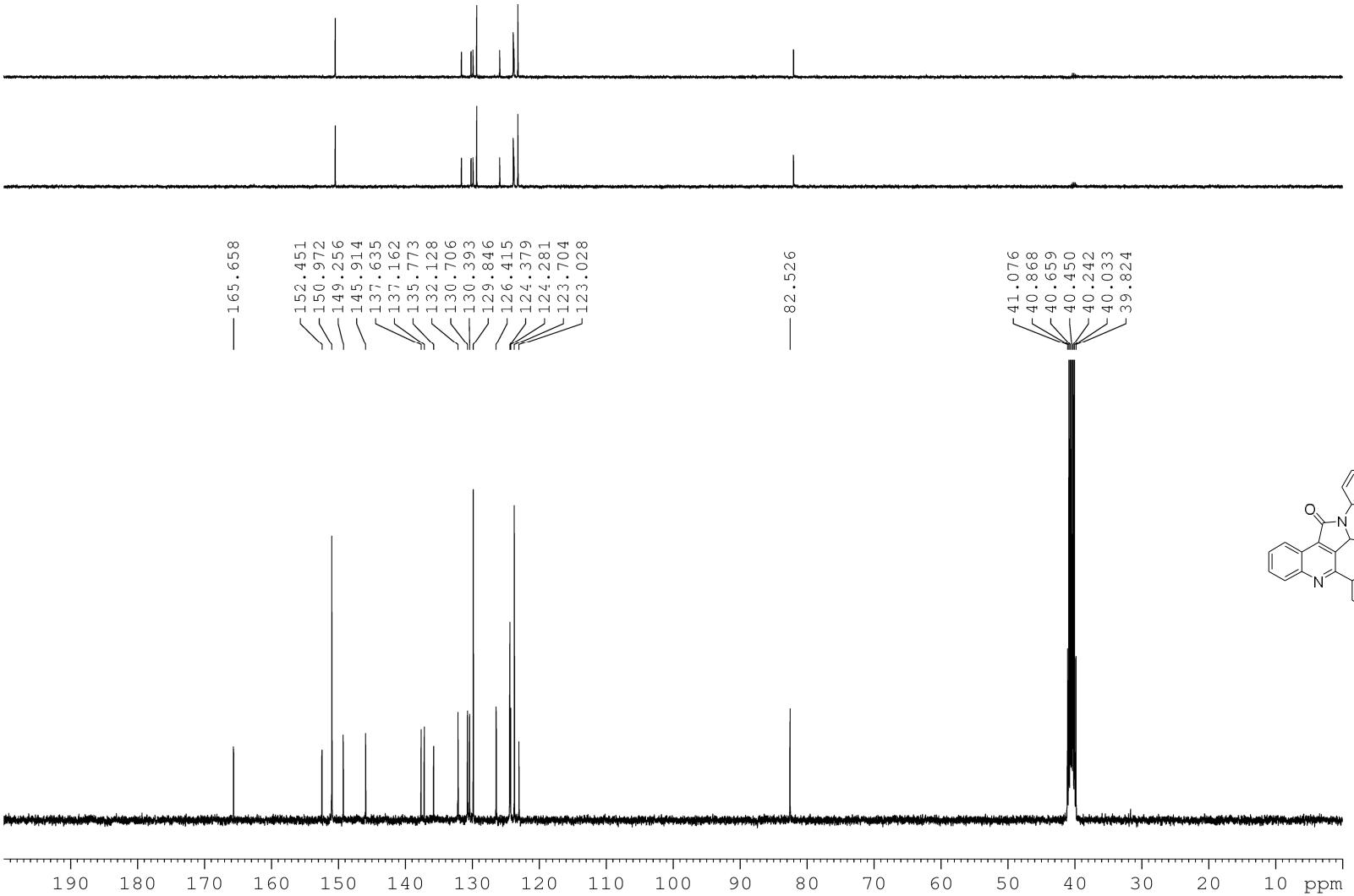

Figure 82. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **3eg**

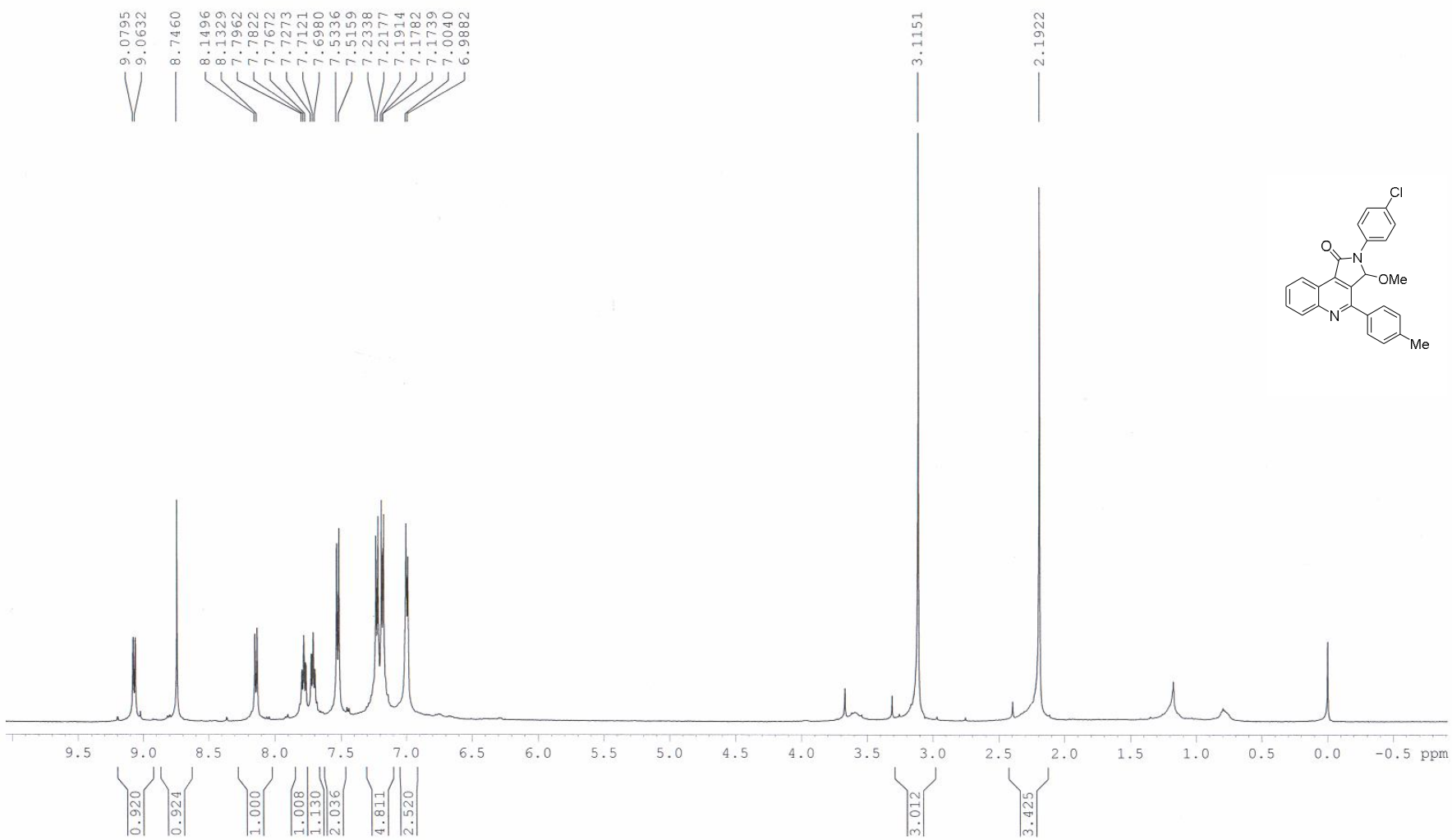

Figure 83. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **3eh**

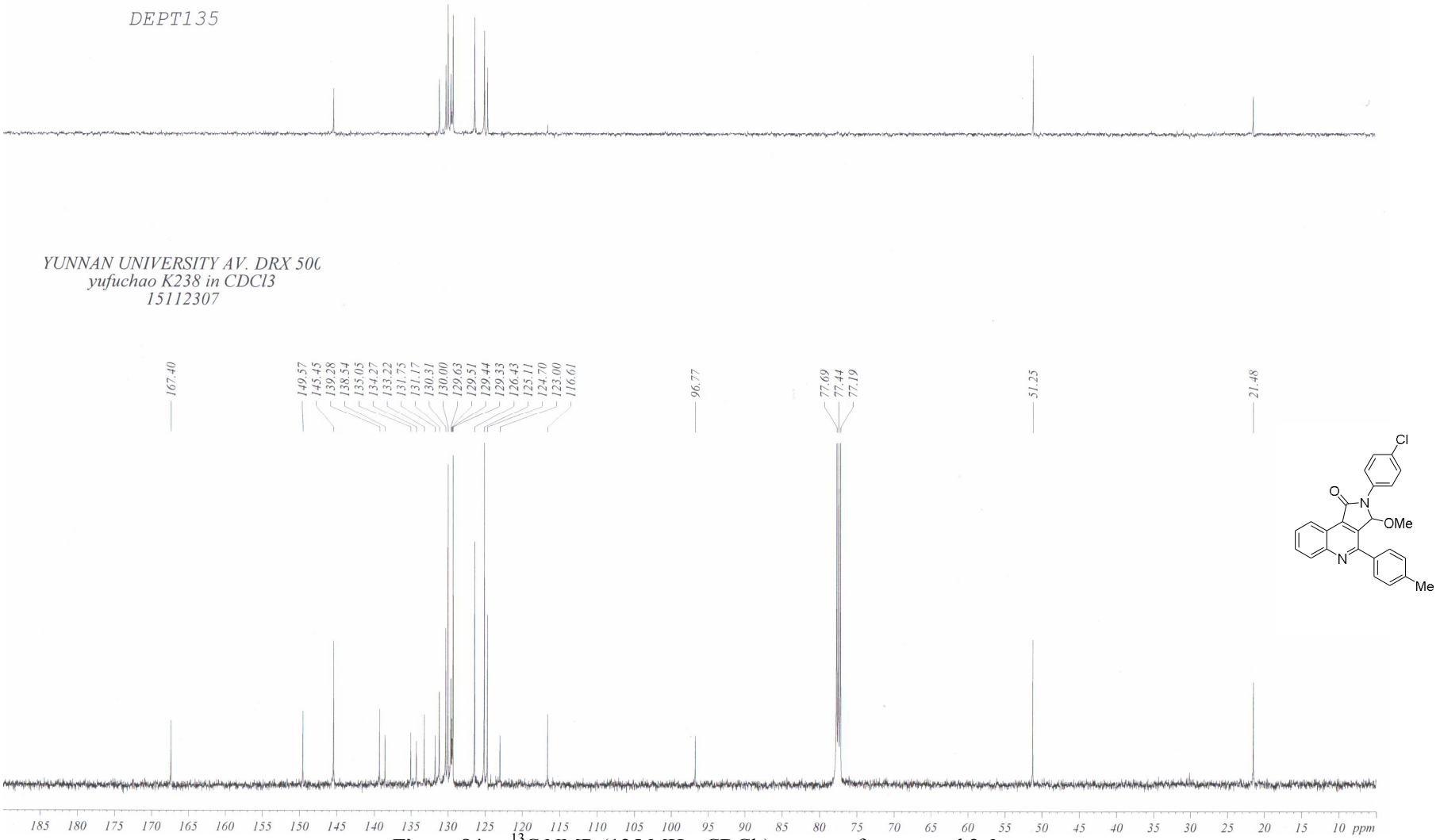

Figure 84. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **3eh**

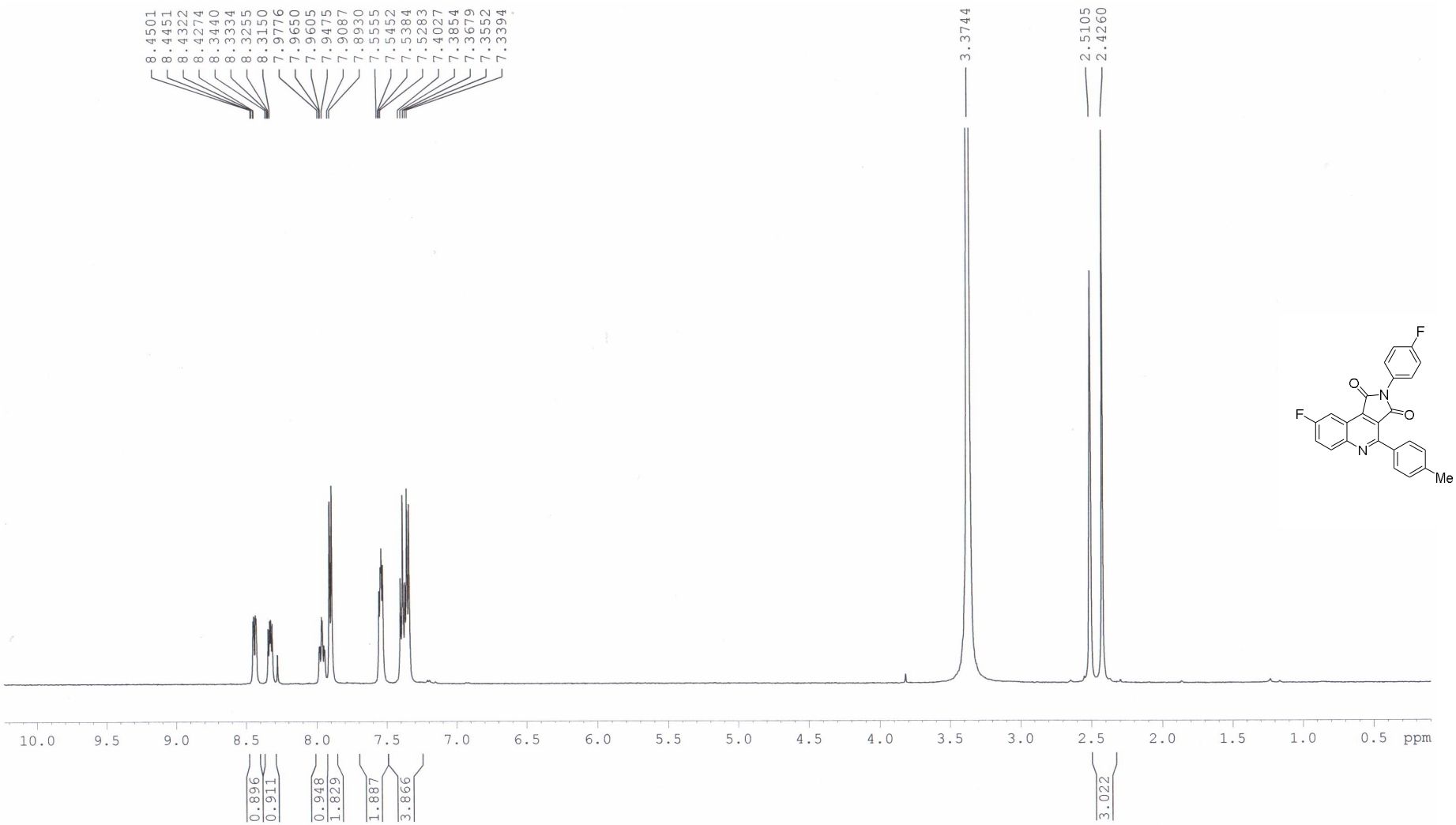

Figure 85. ^{1}H NMR (500 MHz, $CDCl_3$+ DMSO-d_6) spectra of compound **3ei**

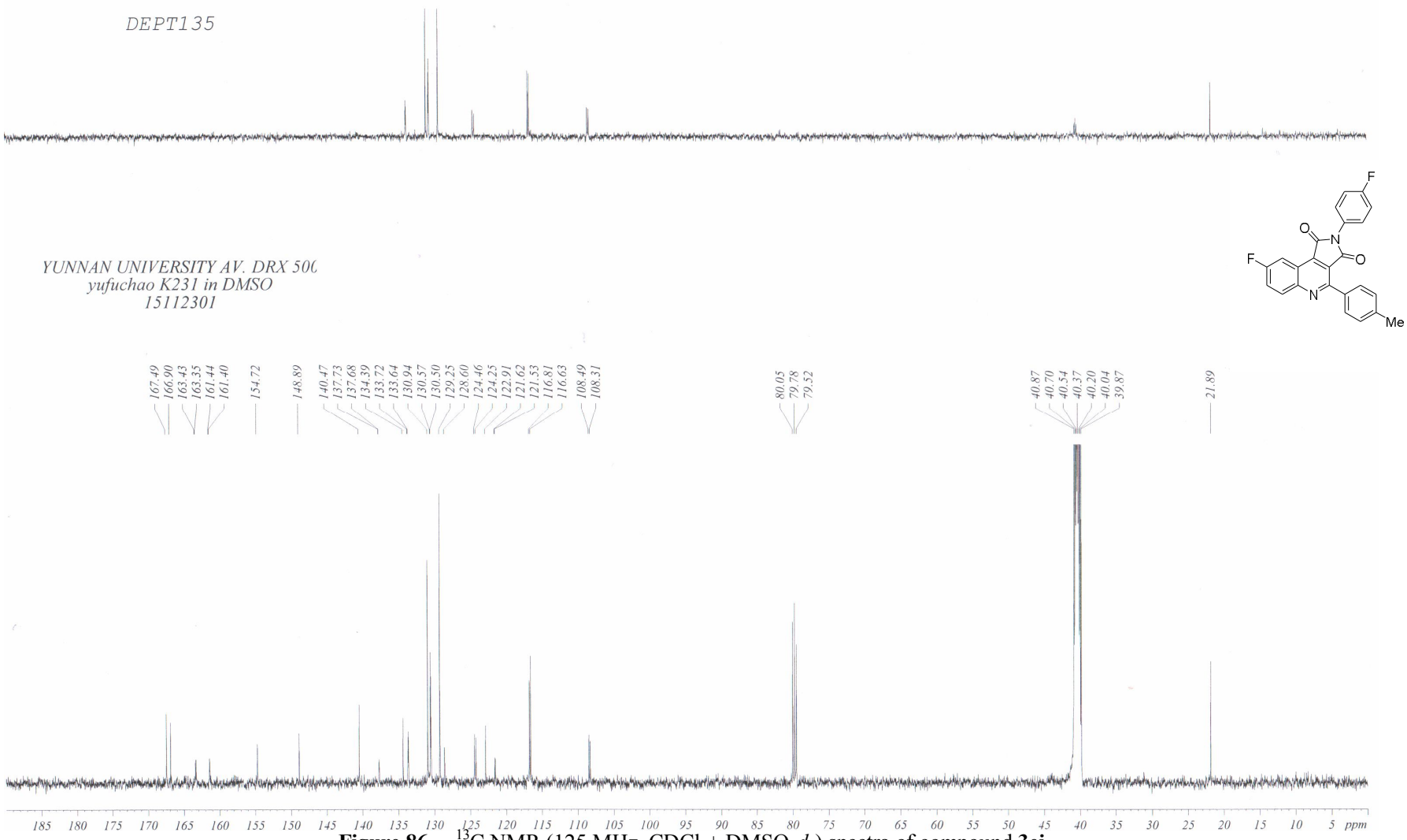

Figure 86. ^{13}C NMR (125 MHz, $CDCl_3$+ DMSO-d_6) spectra of compound **3ei**

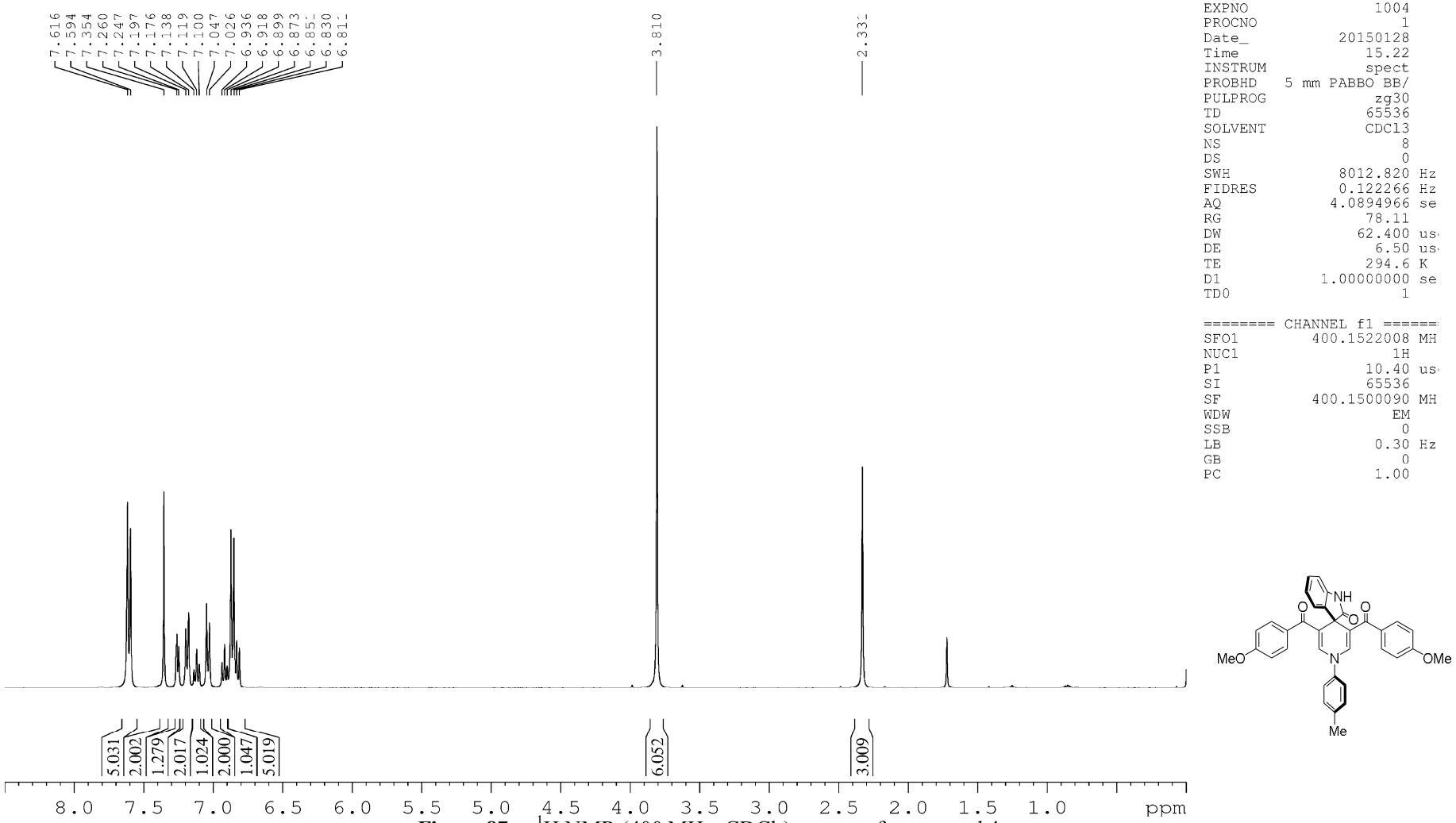

Figure 87. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4a**

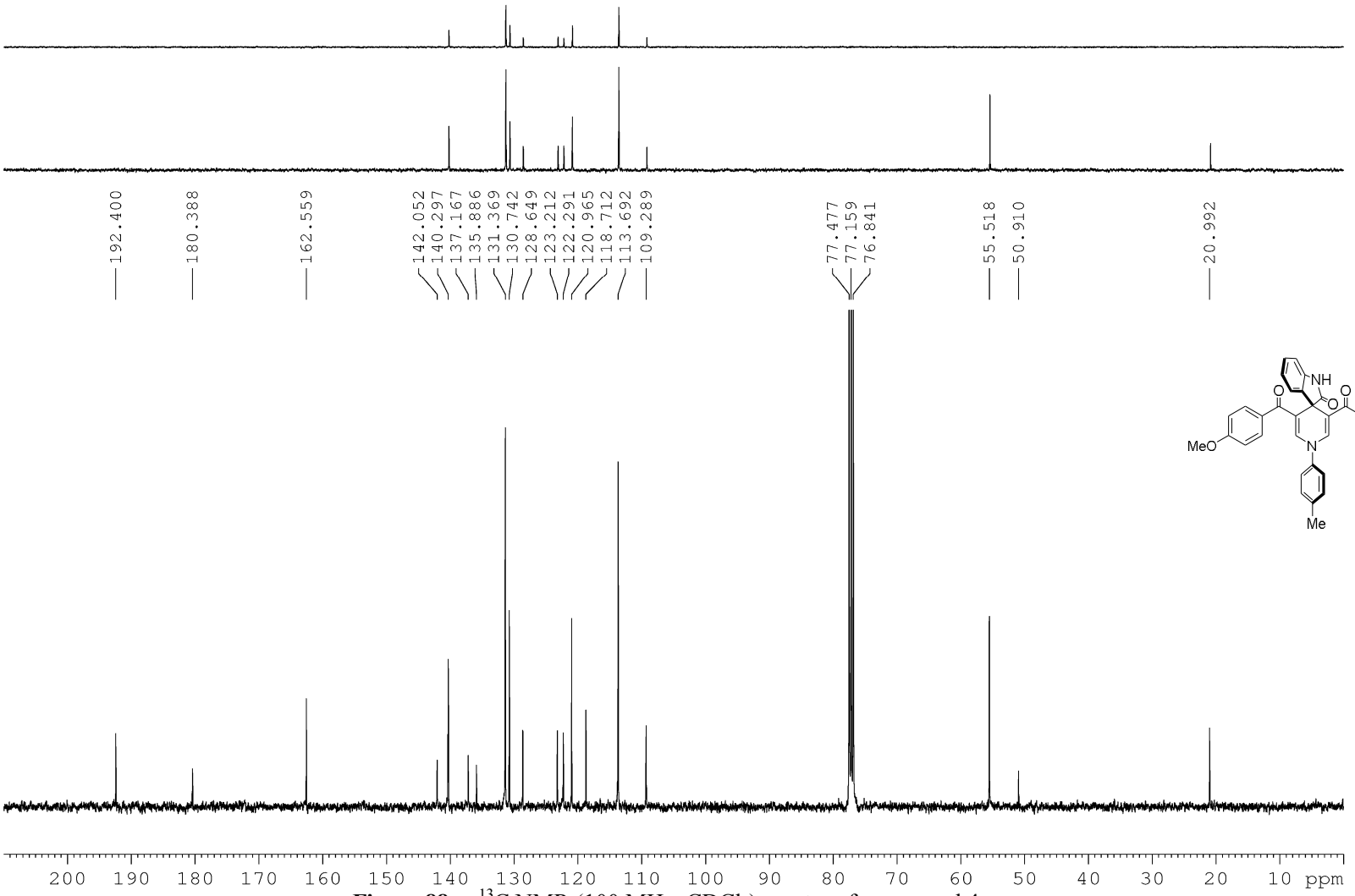

Figure 88. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **4a**

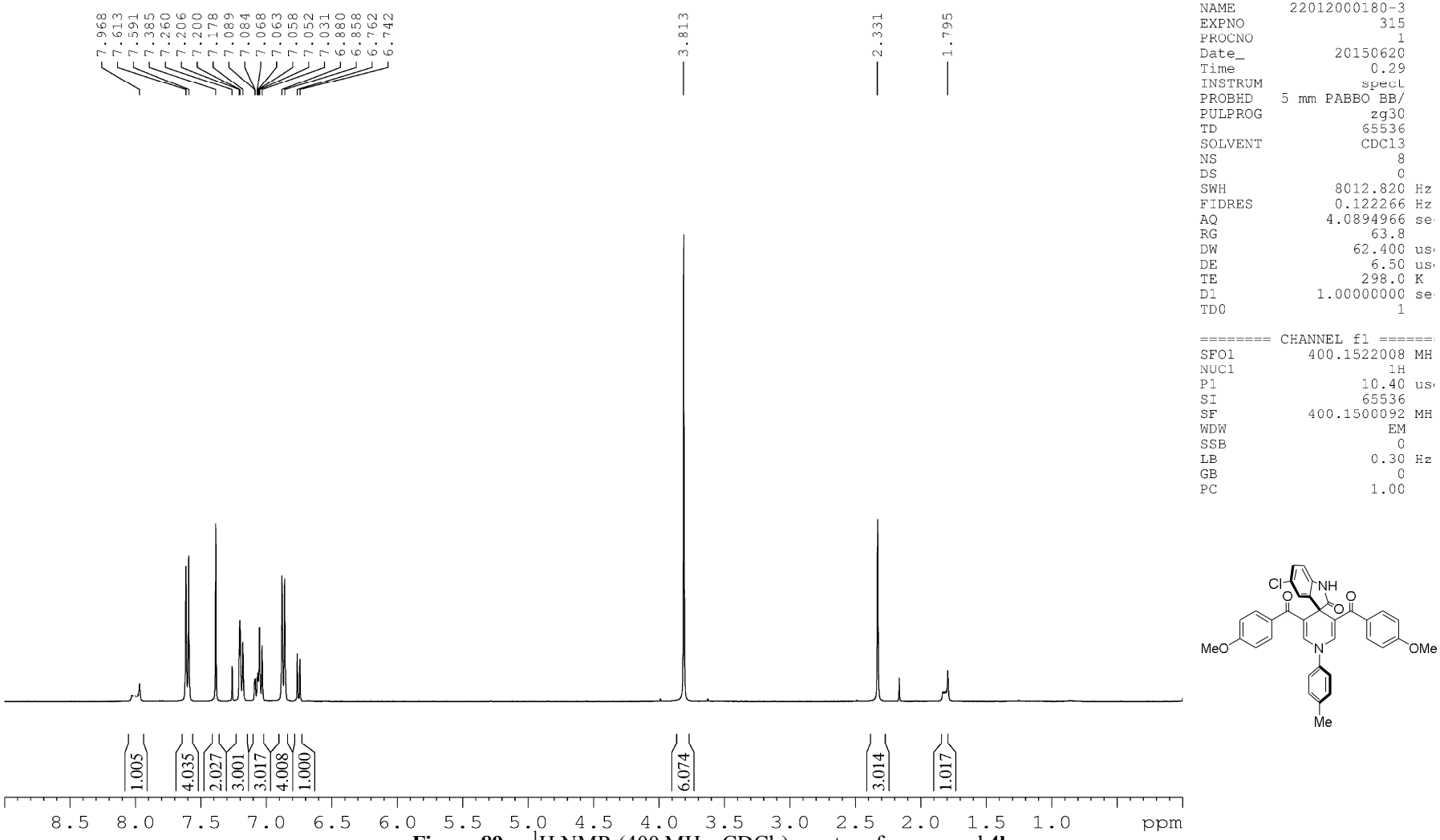

Figure 89. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4b**

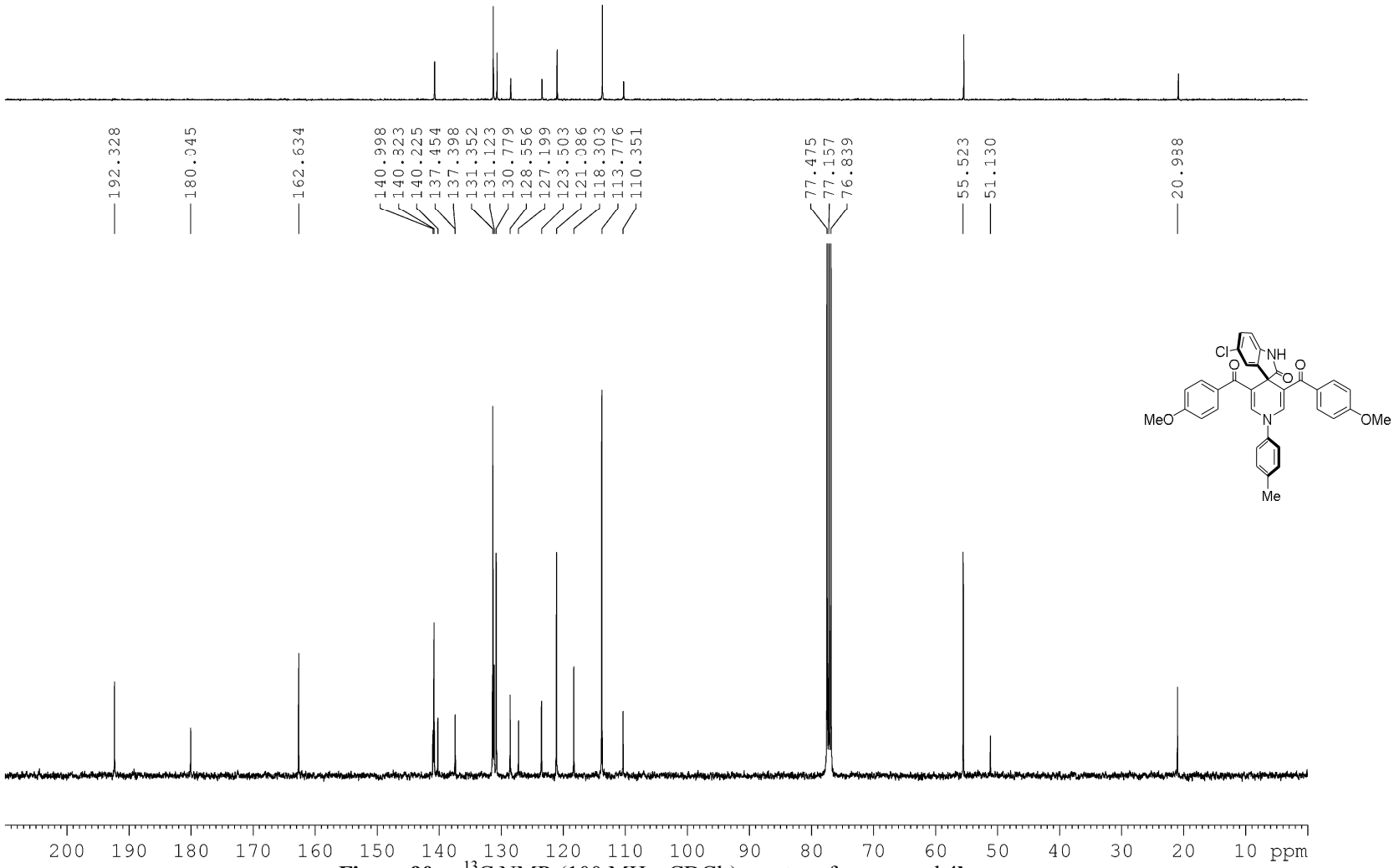

Figure 90. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **4b**

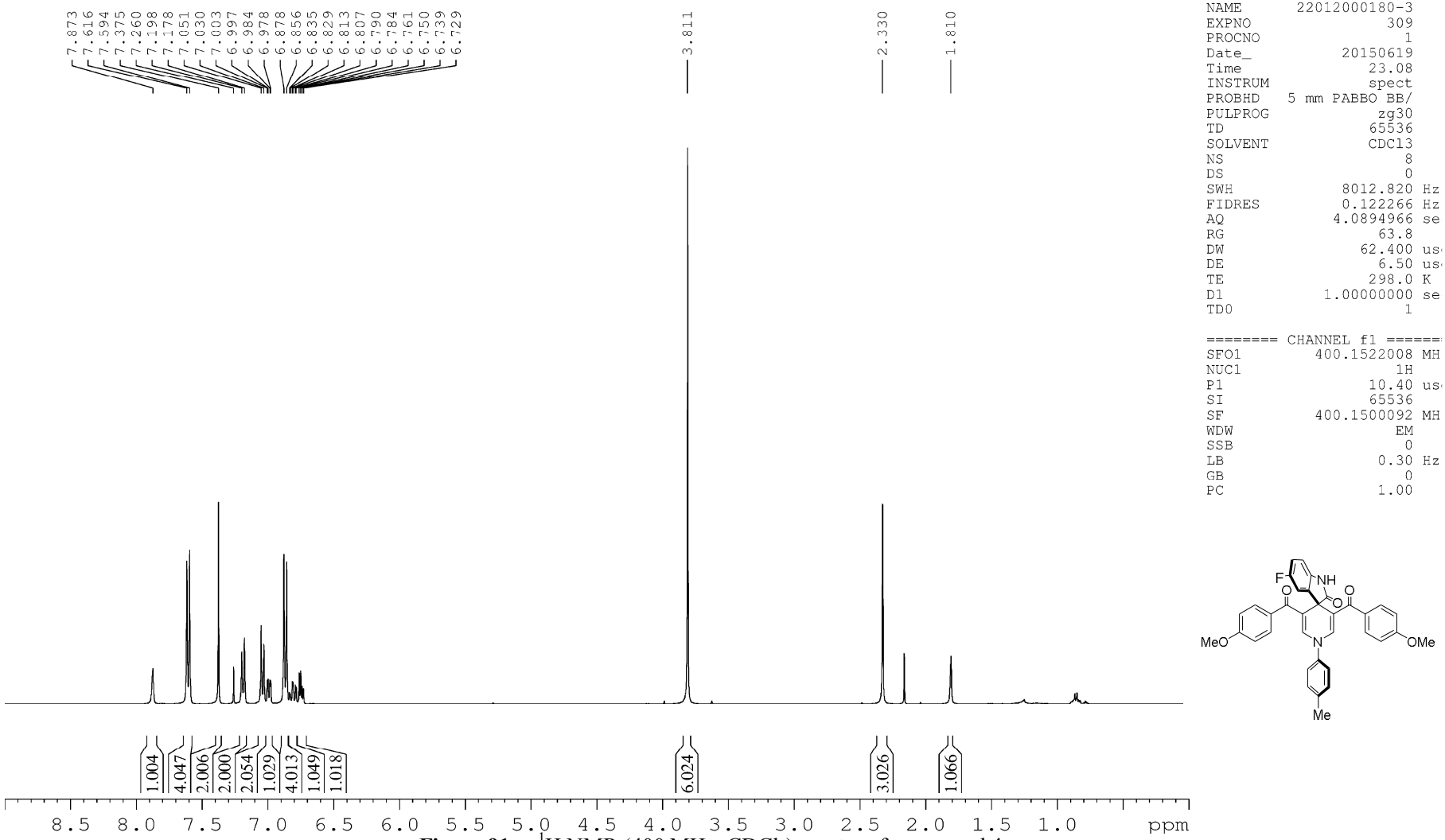

Figure 91. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4c**

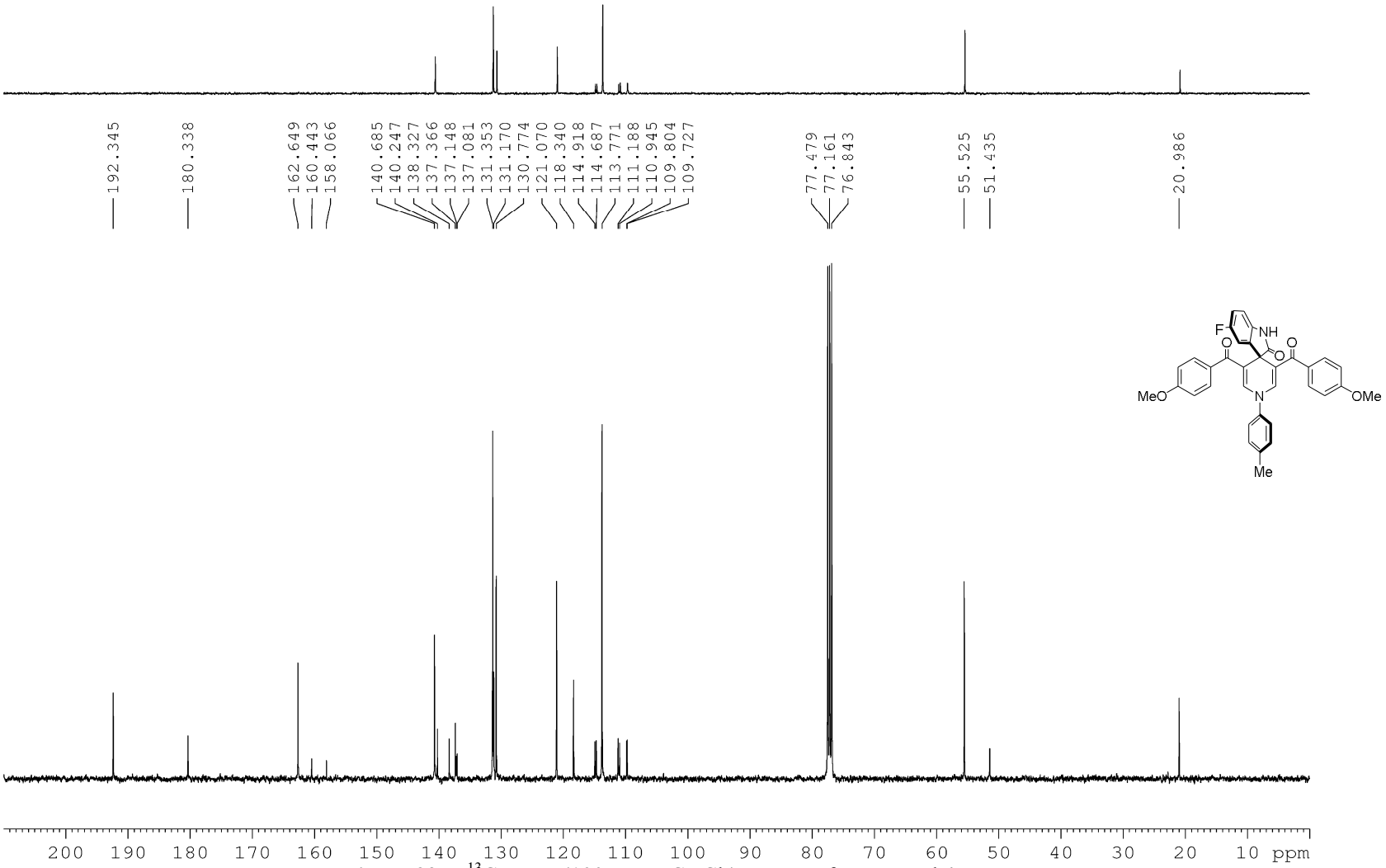

Figure 92. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **4c**

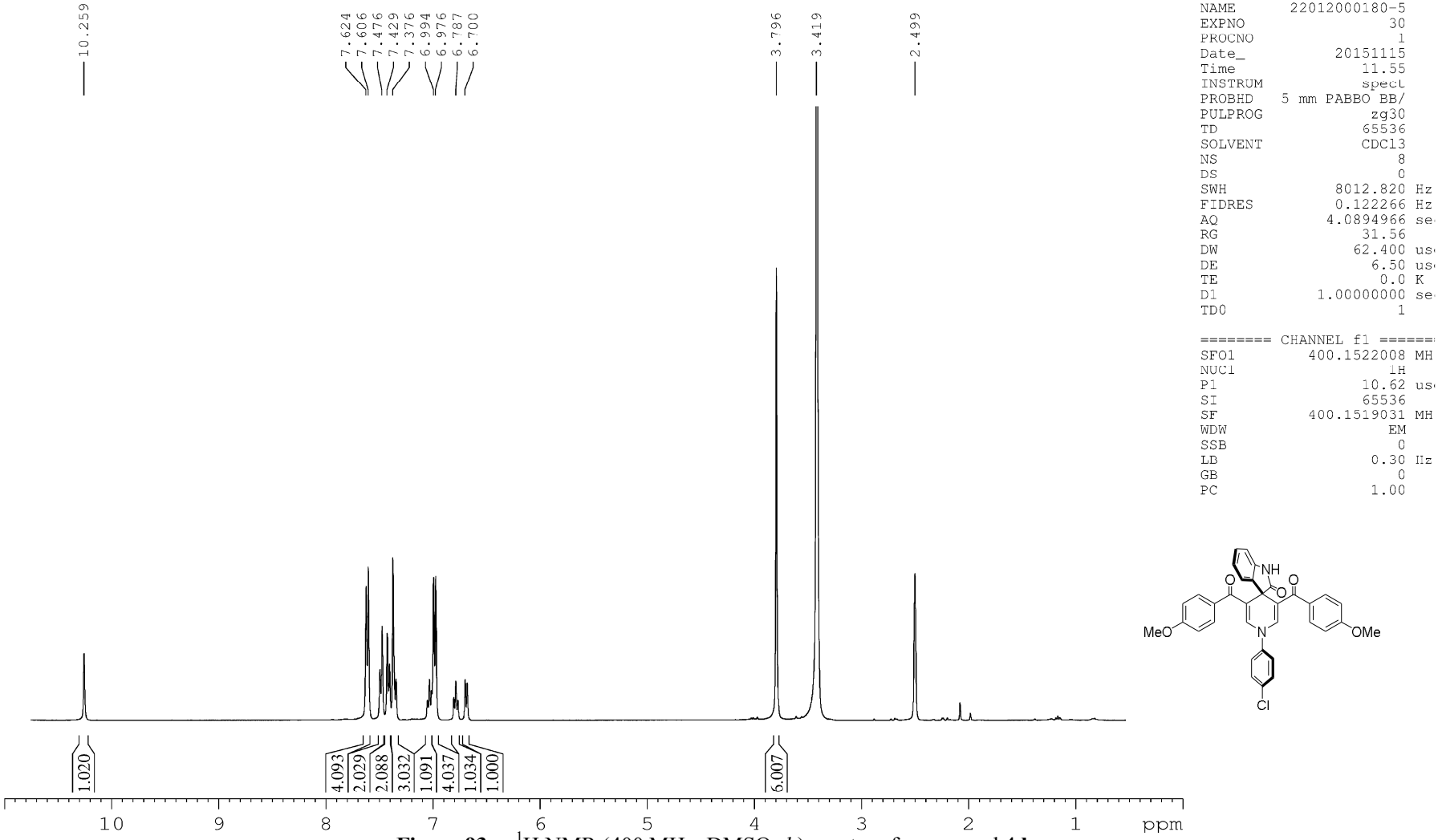

Figure 93. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4d**

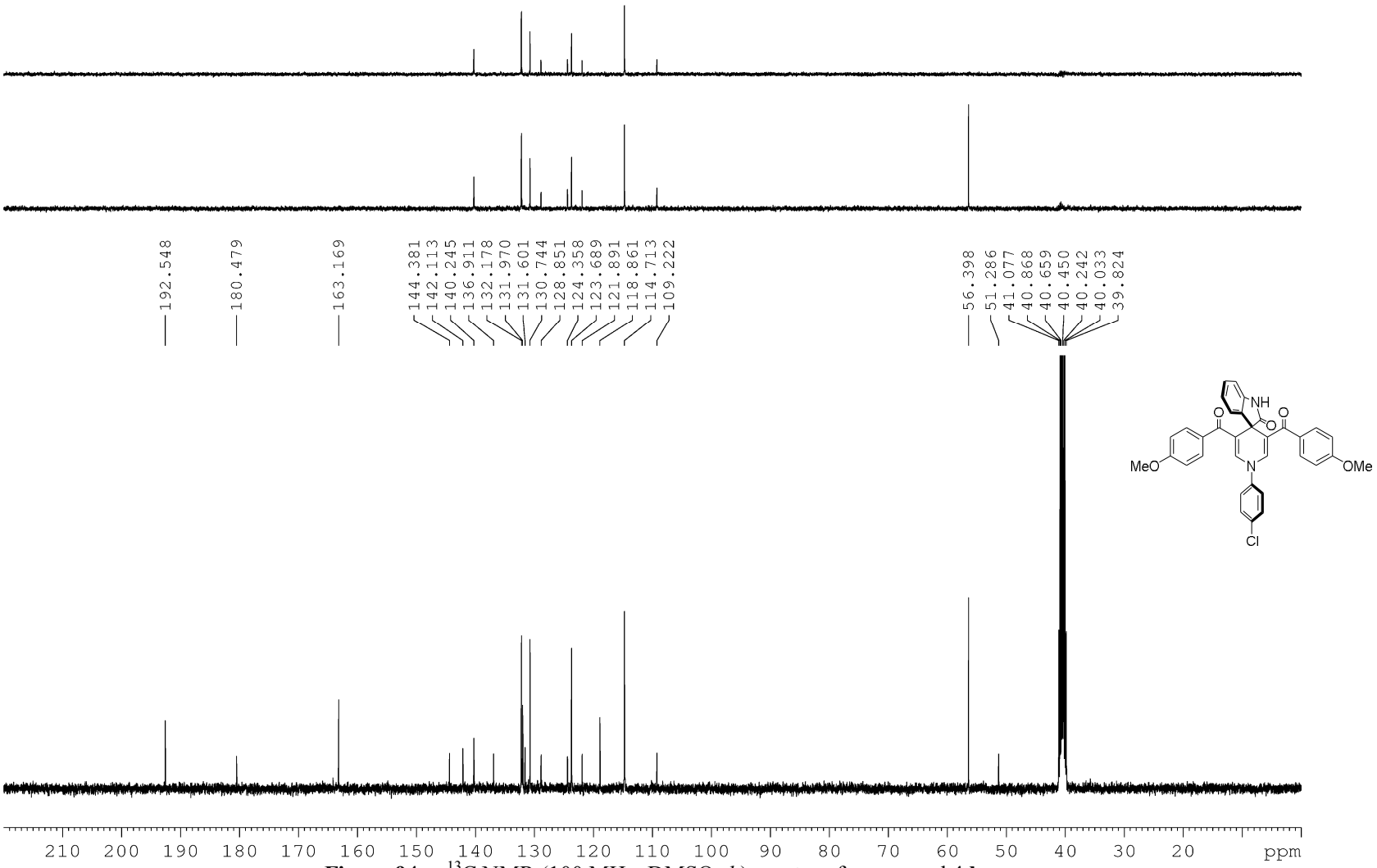

Figure 94. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4d**

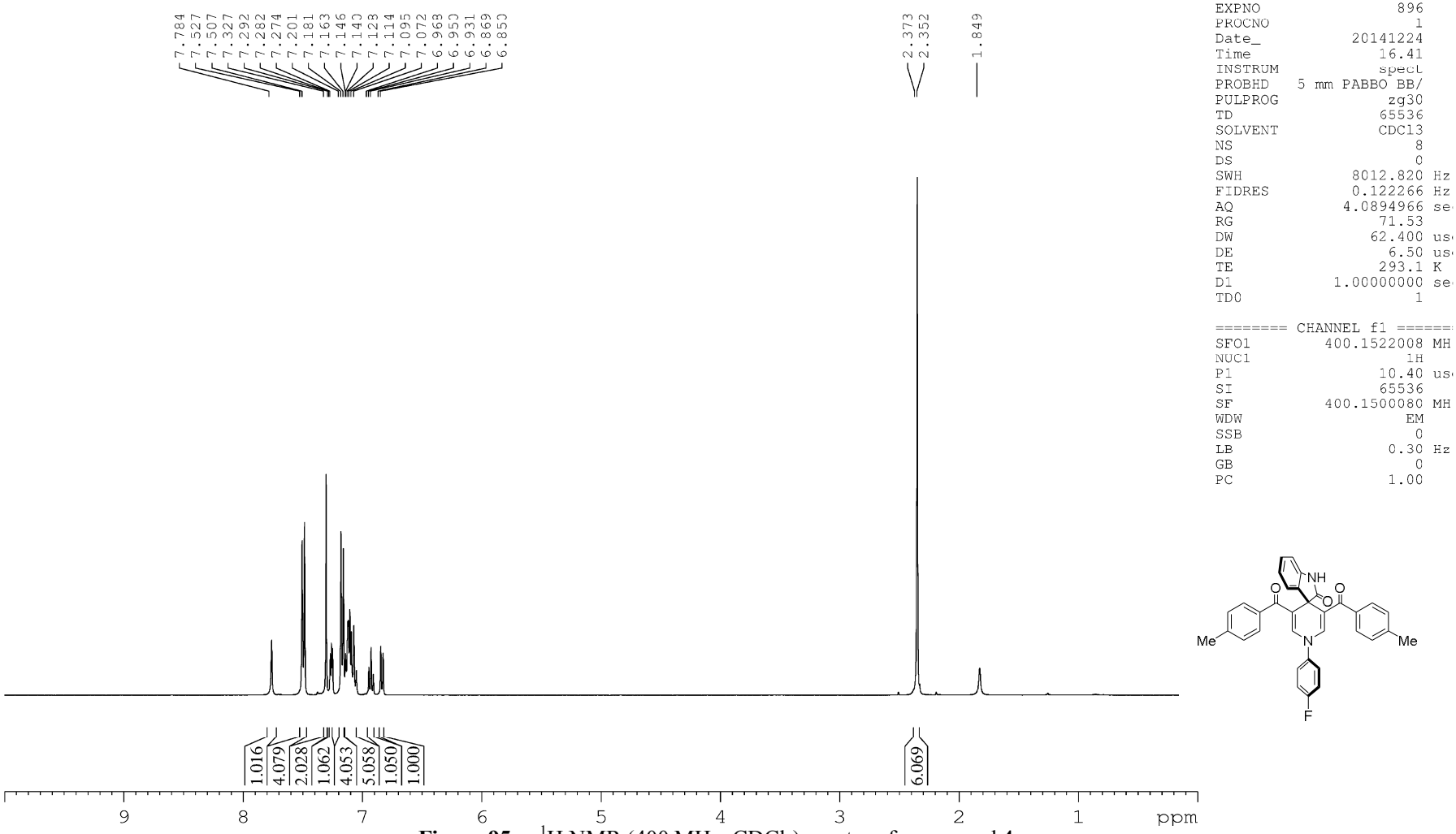

Figure 95. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4e**

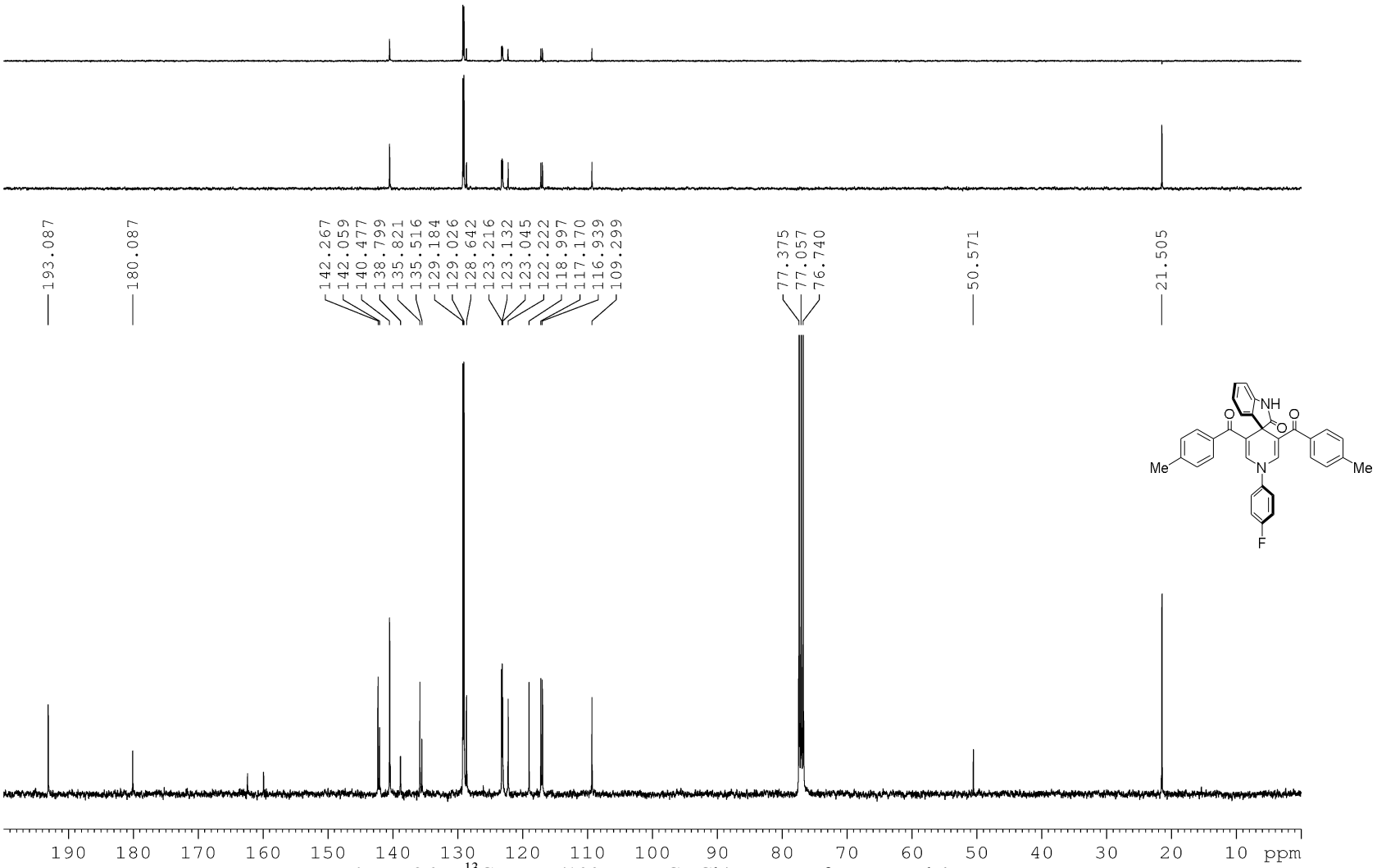

Figure 96. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **4e**

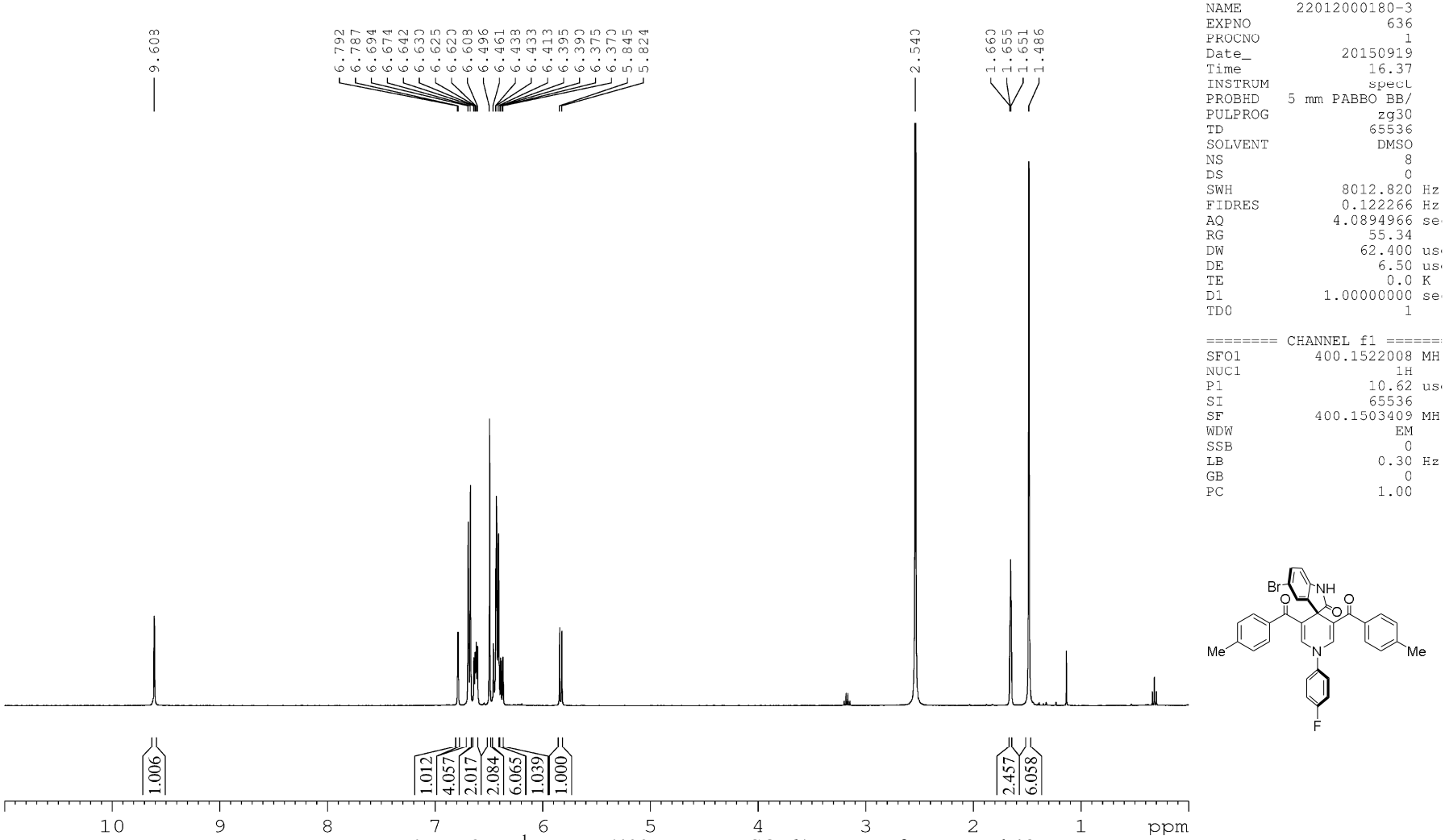

Figure 97. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4f**

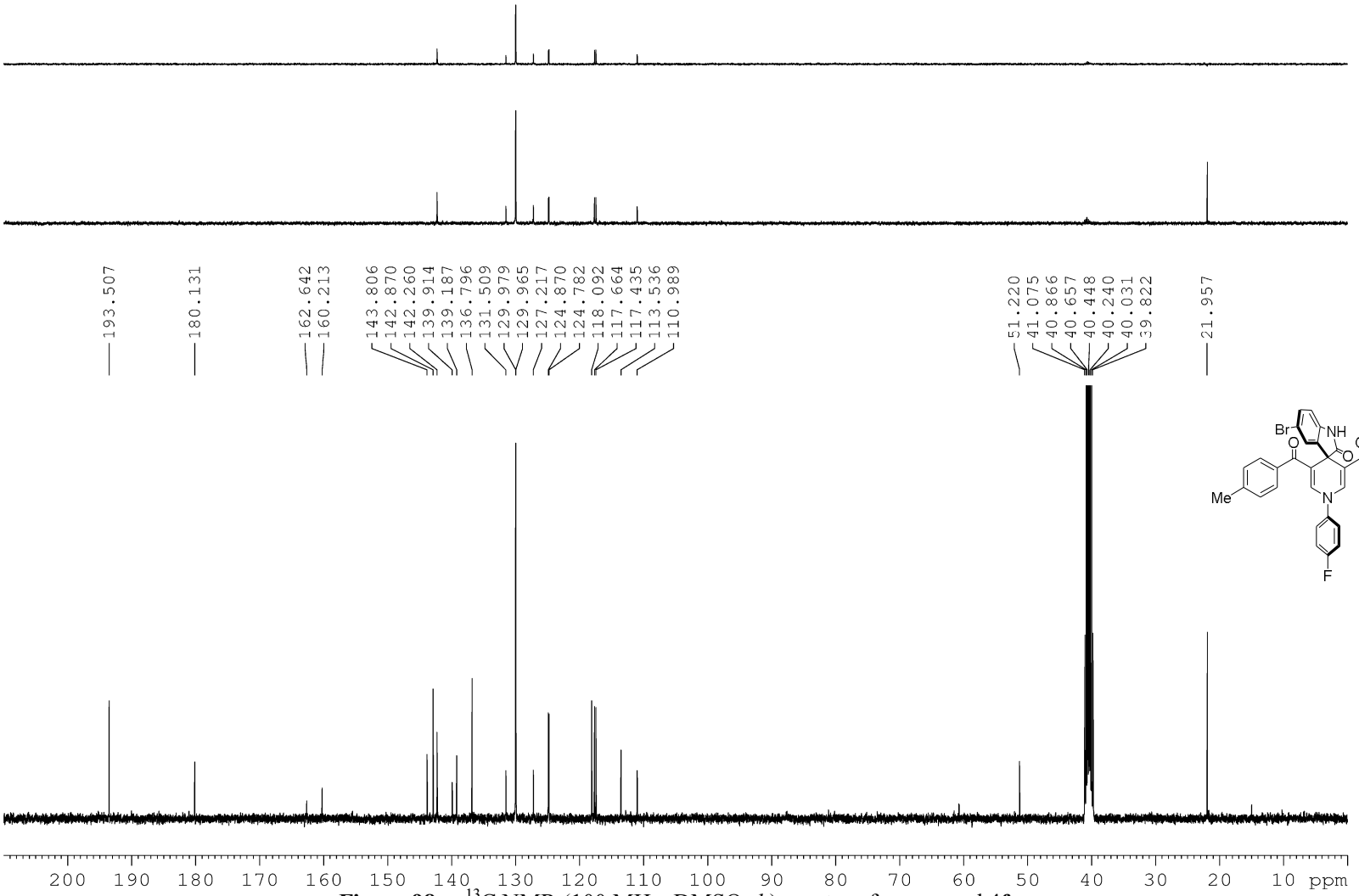

Figure 98. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4f**

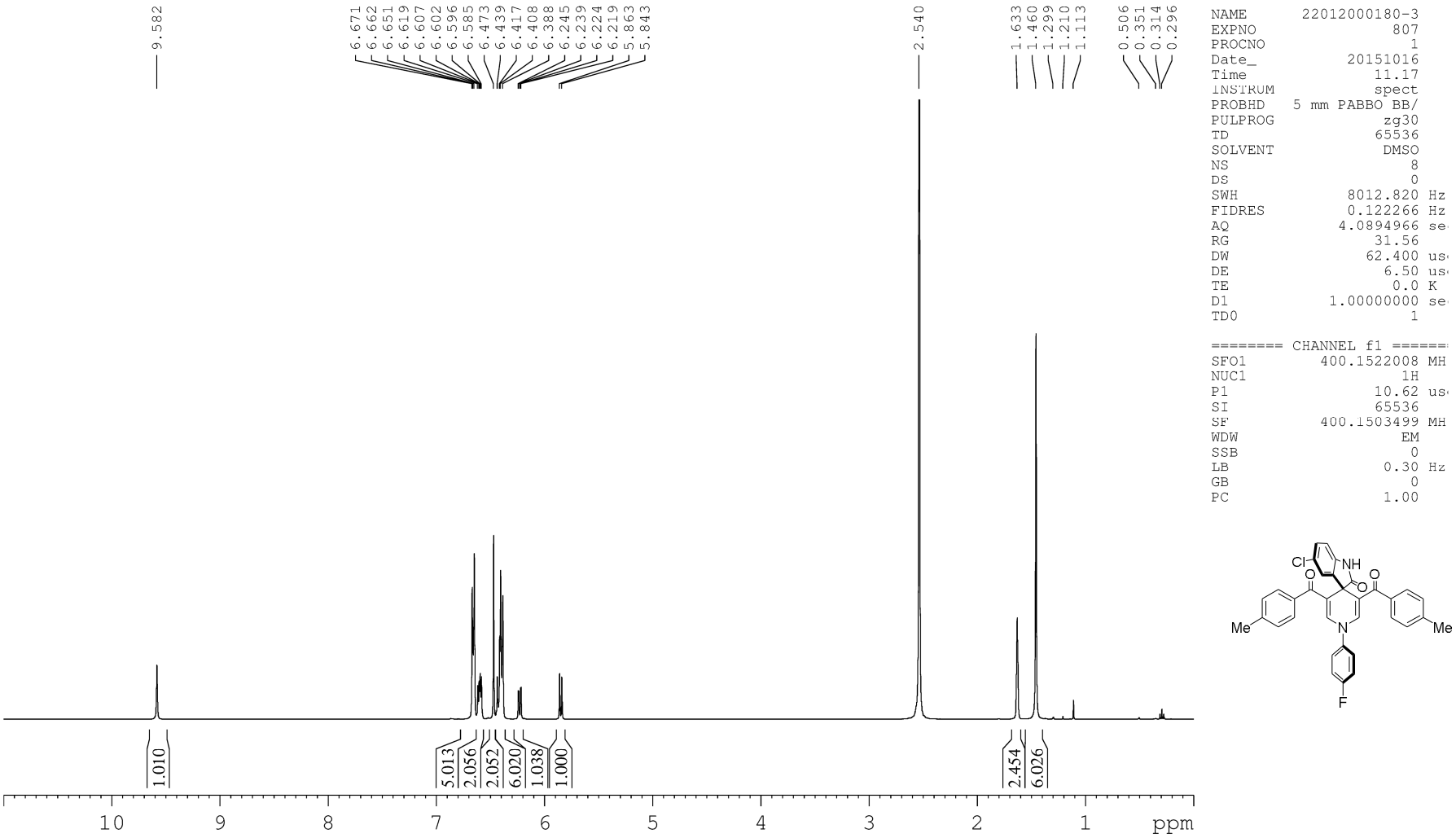

Figure 99. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4g**

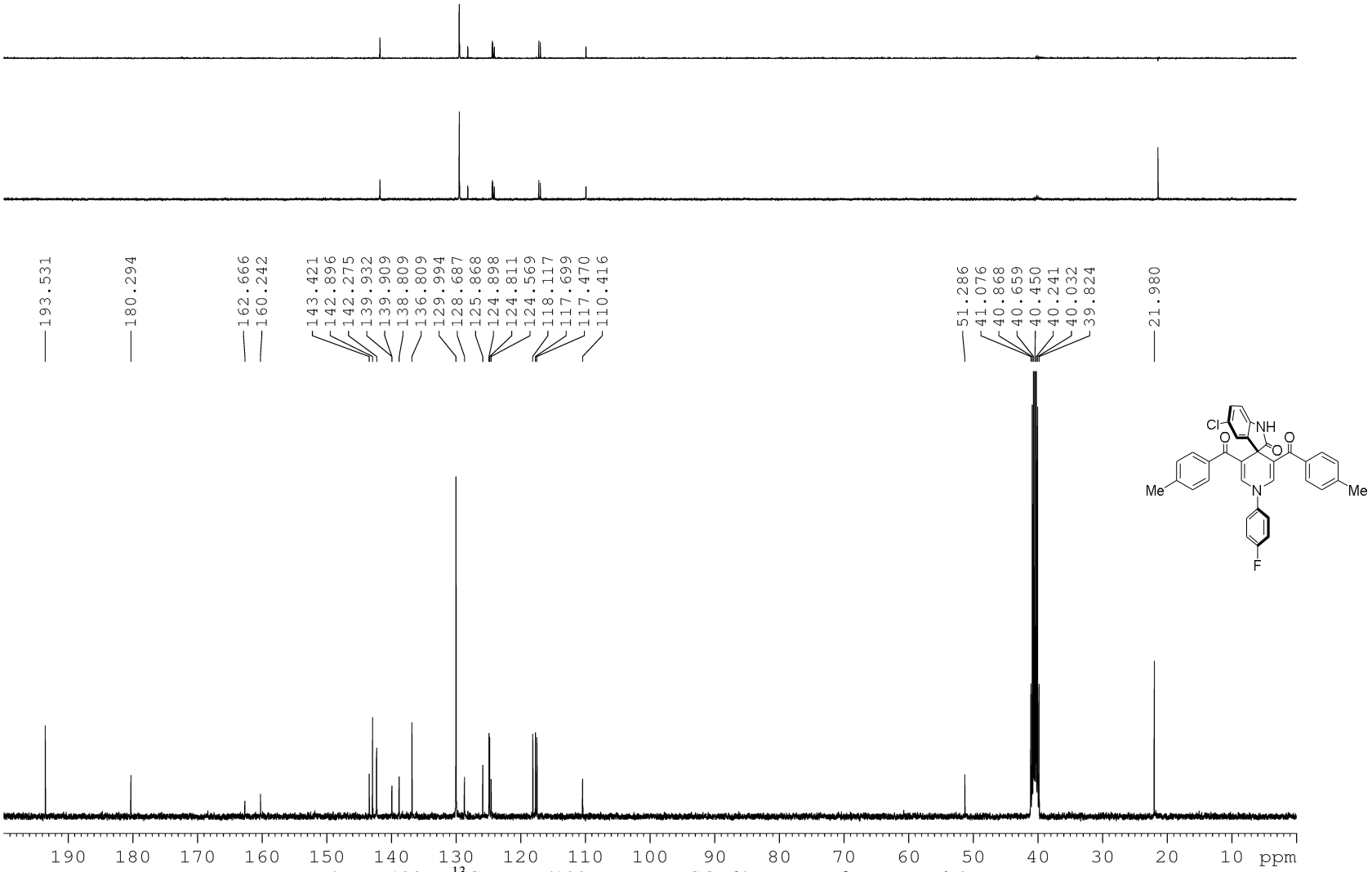

Figure 100. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4g**

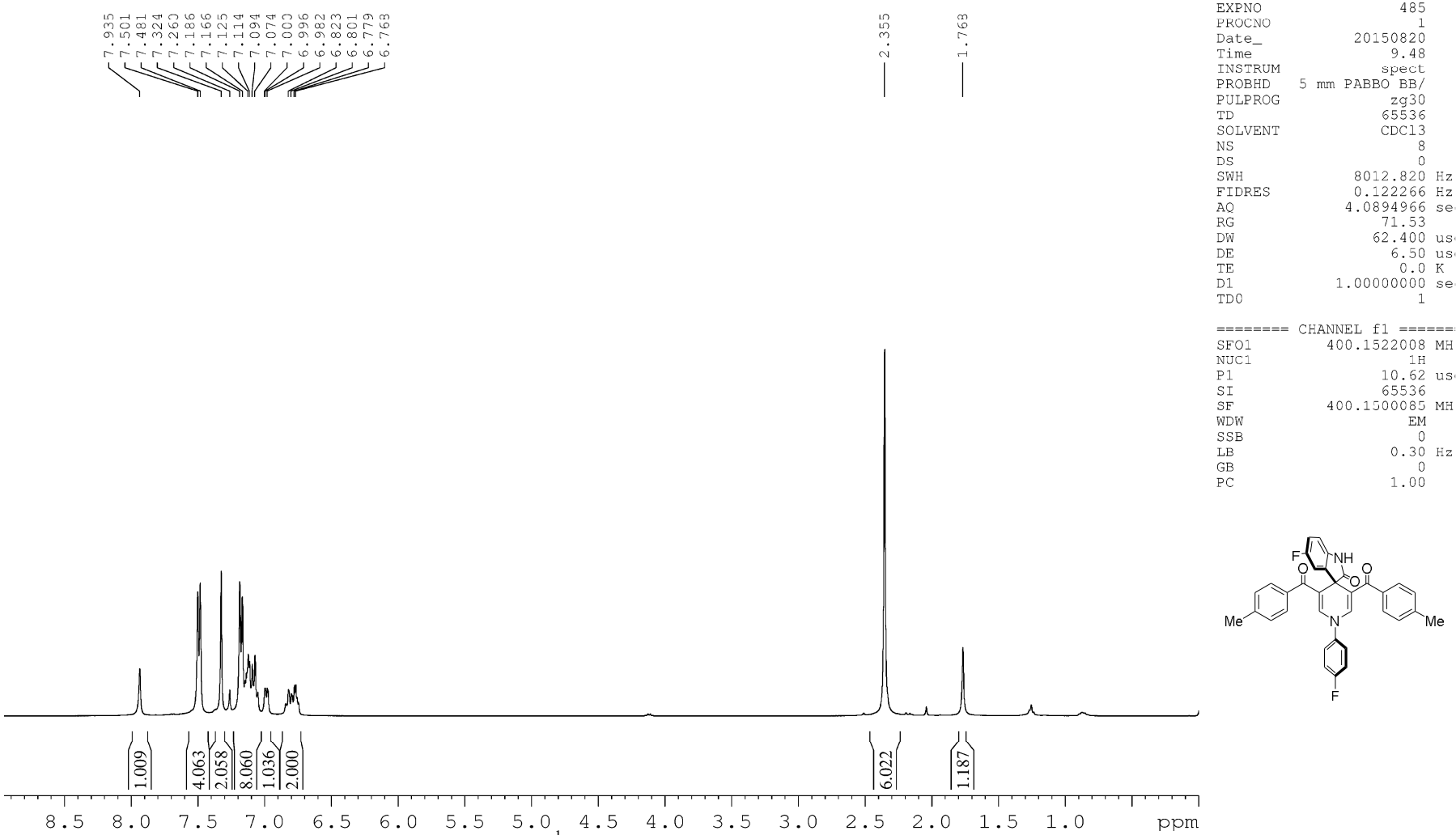


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Figure 101. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4h**

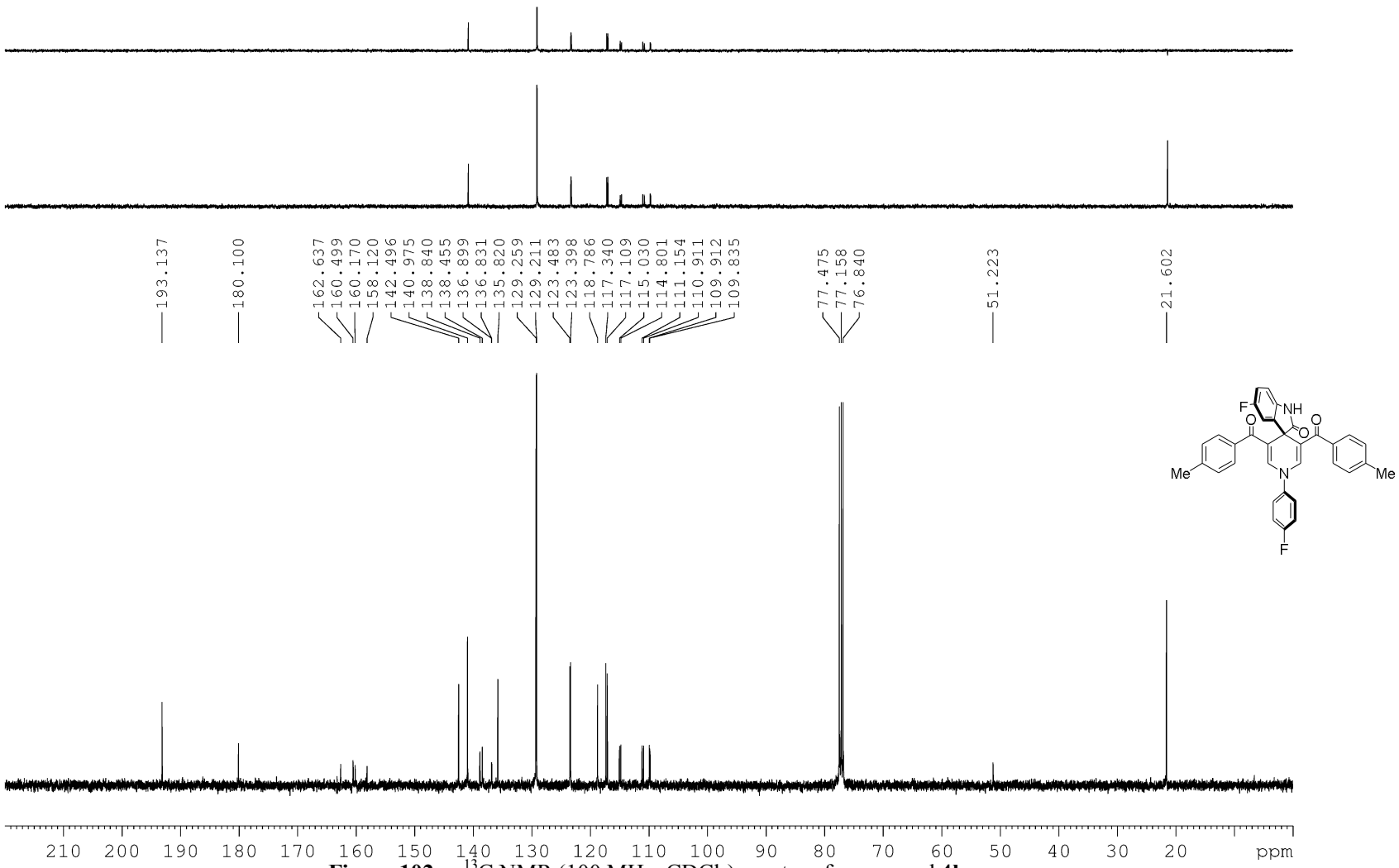

Figure 102. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **4h**

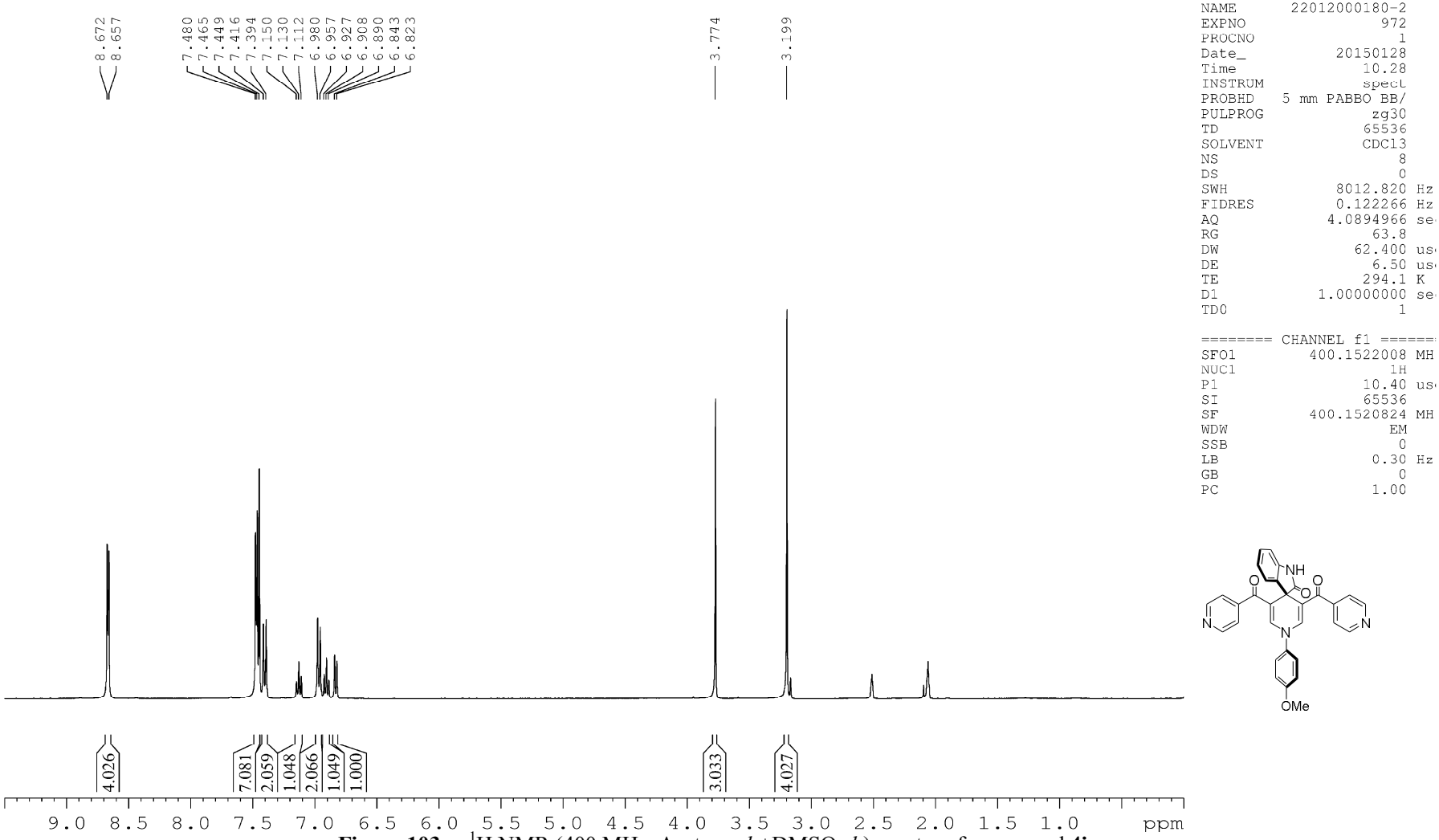

Figure 103. ^{1}H NMR (400 MHz, Acetone-d_6+DMSO-d_6) spectra of compound **4i**

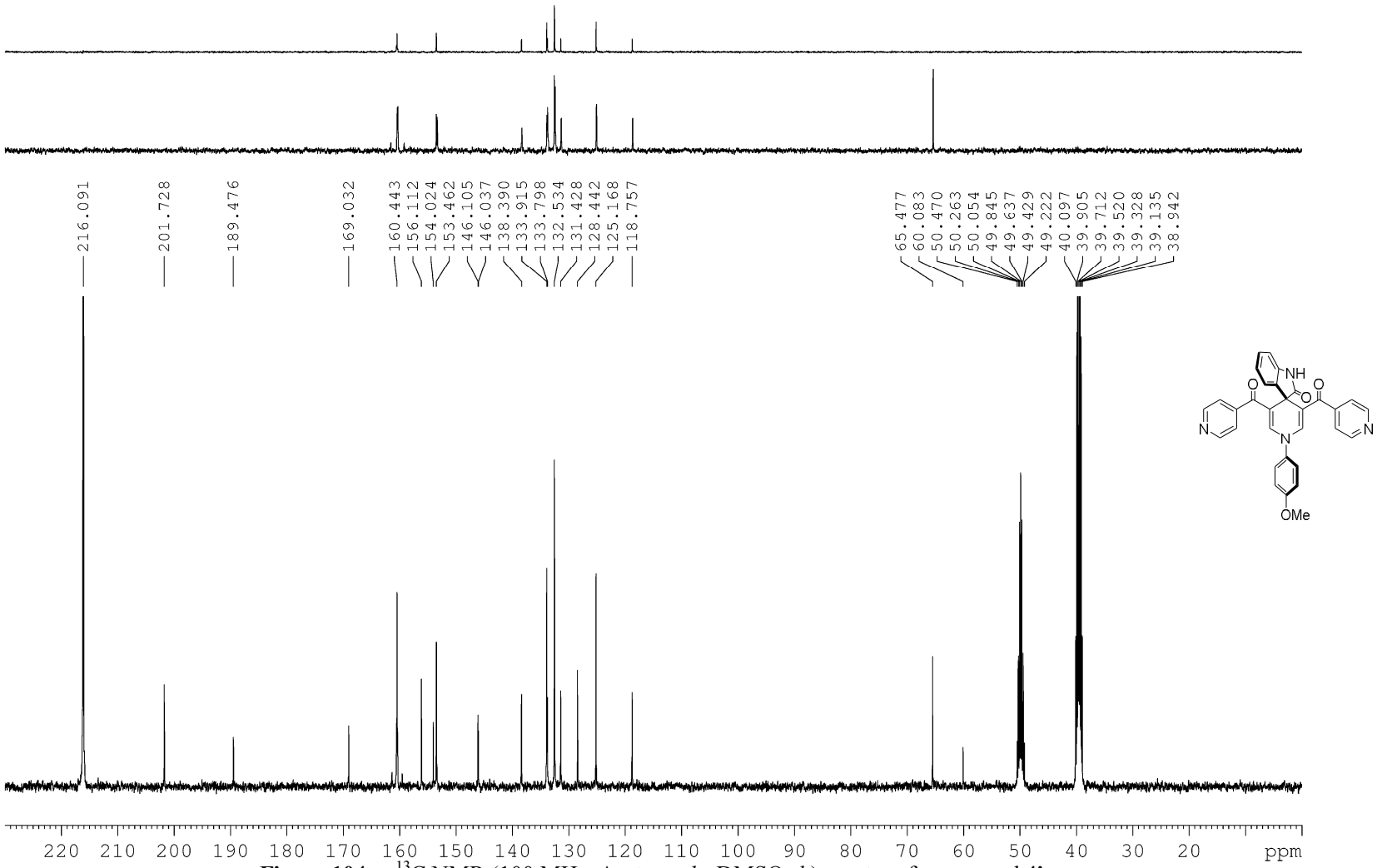

Figure 104. ^{13}C NMR (100 MHz, Acetone-d_6+DMSO-d_6) spectra of compound **4i**

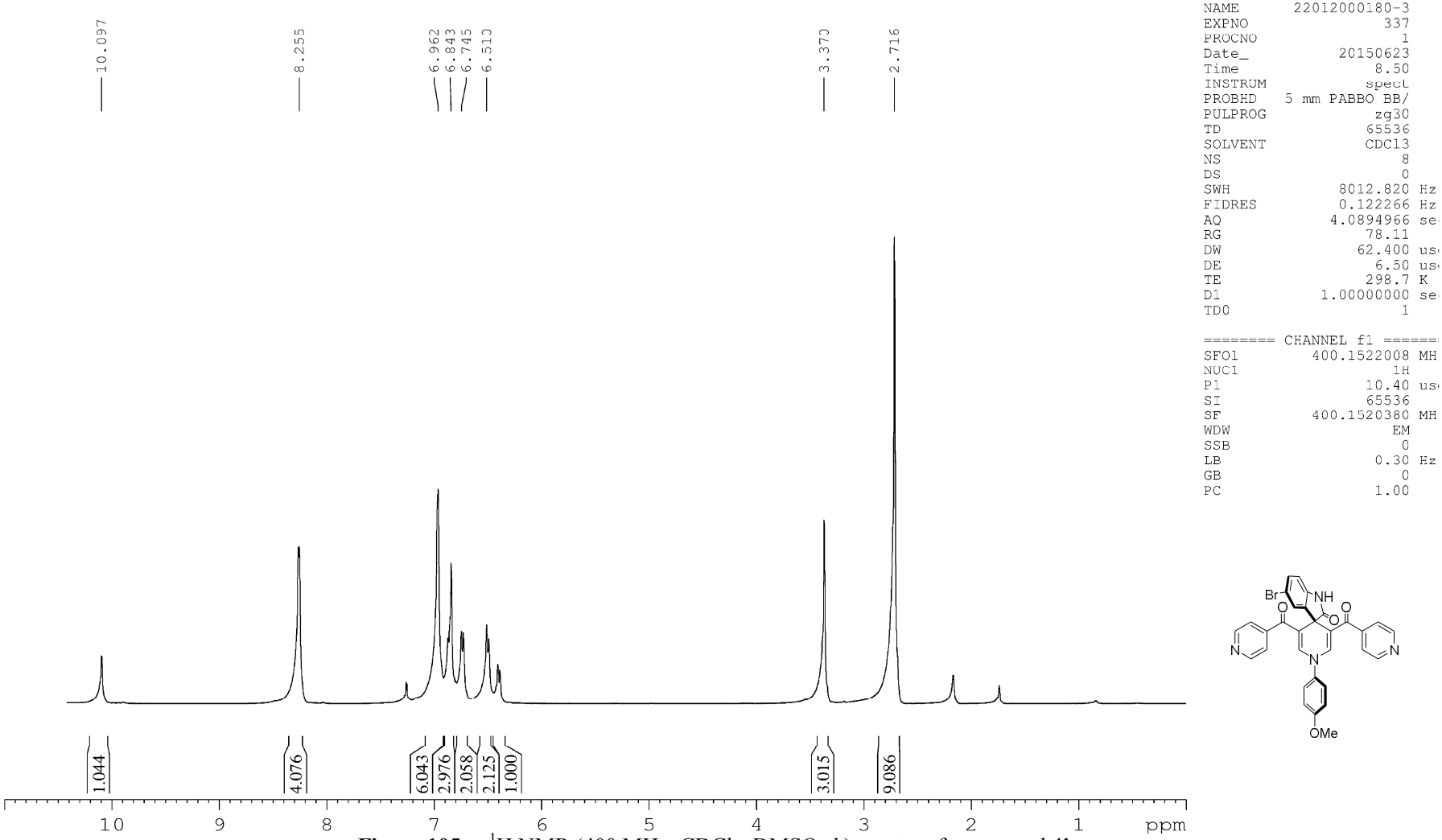

Figure 105. ^{1}H NMR (400 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **4j**

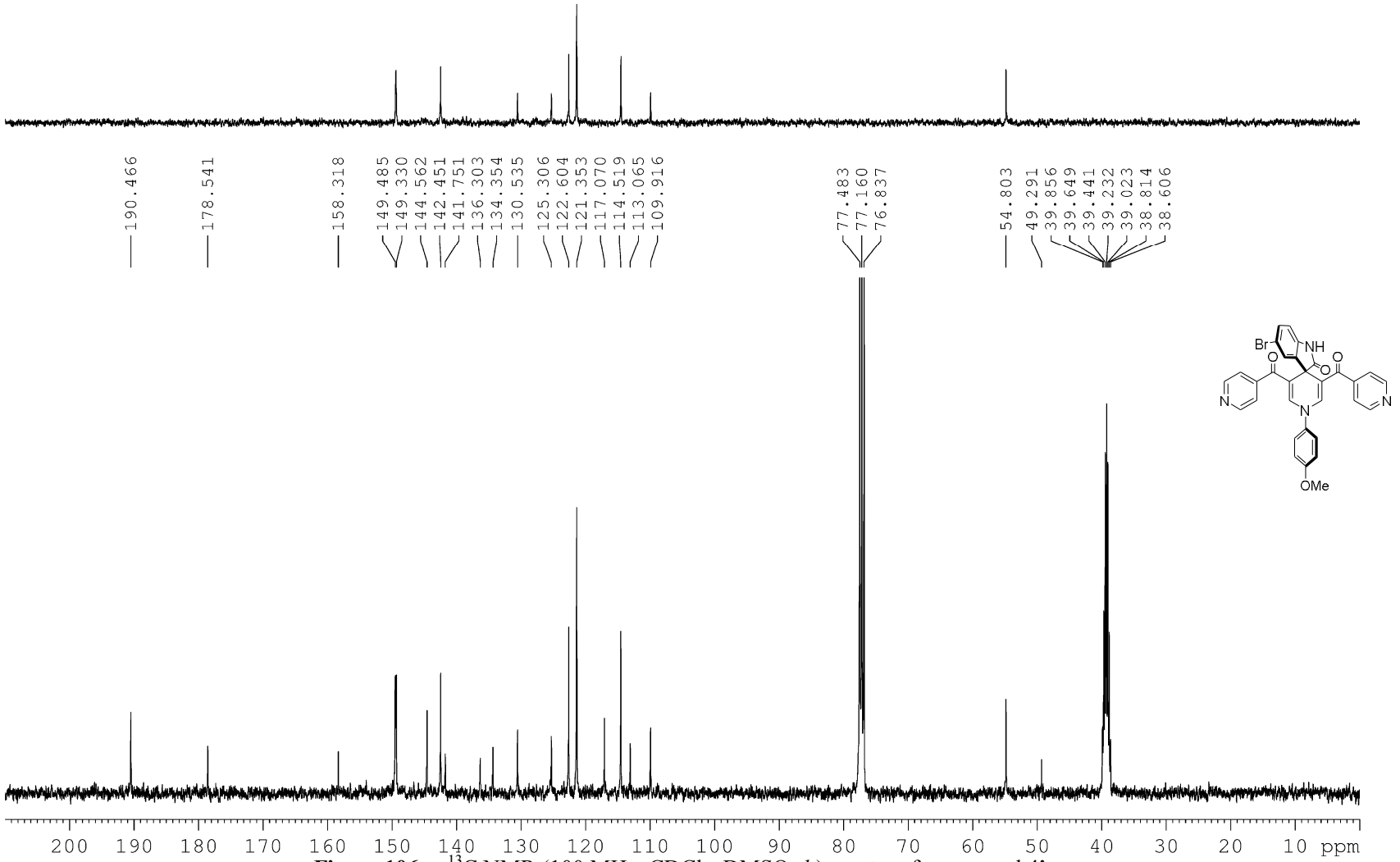

Figure 106. ^{13}C NMR (100 MHz, $CDCl_3$+DMSO-d_6) spectra of compound **4j**

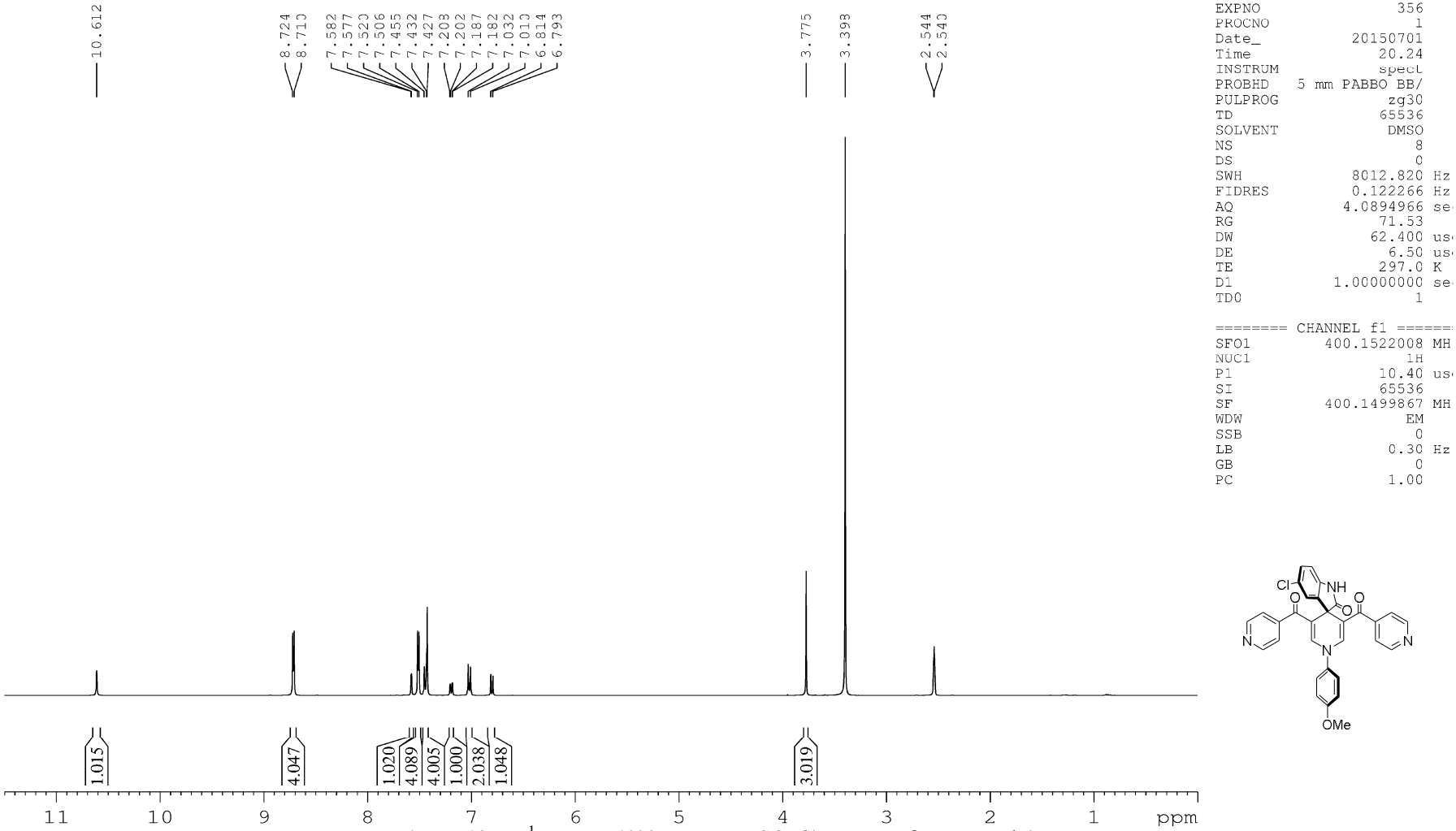


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Figure 107. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4k**

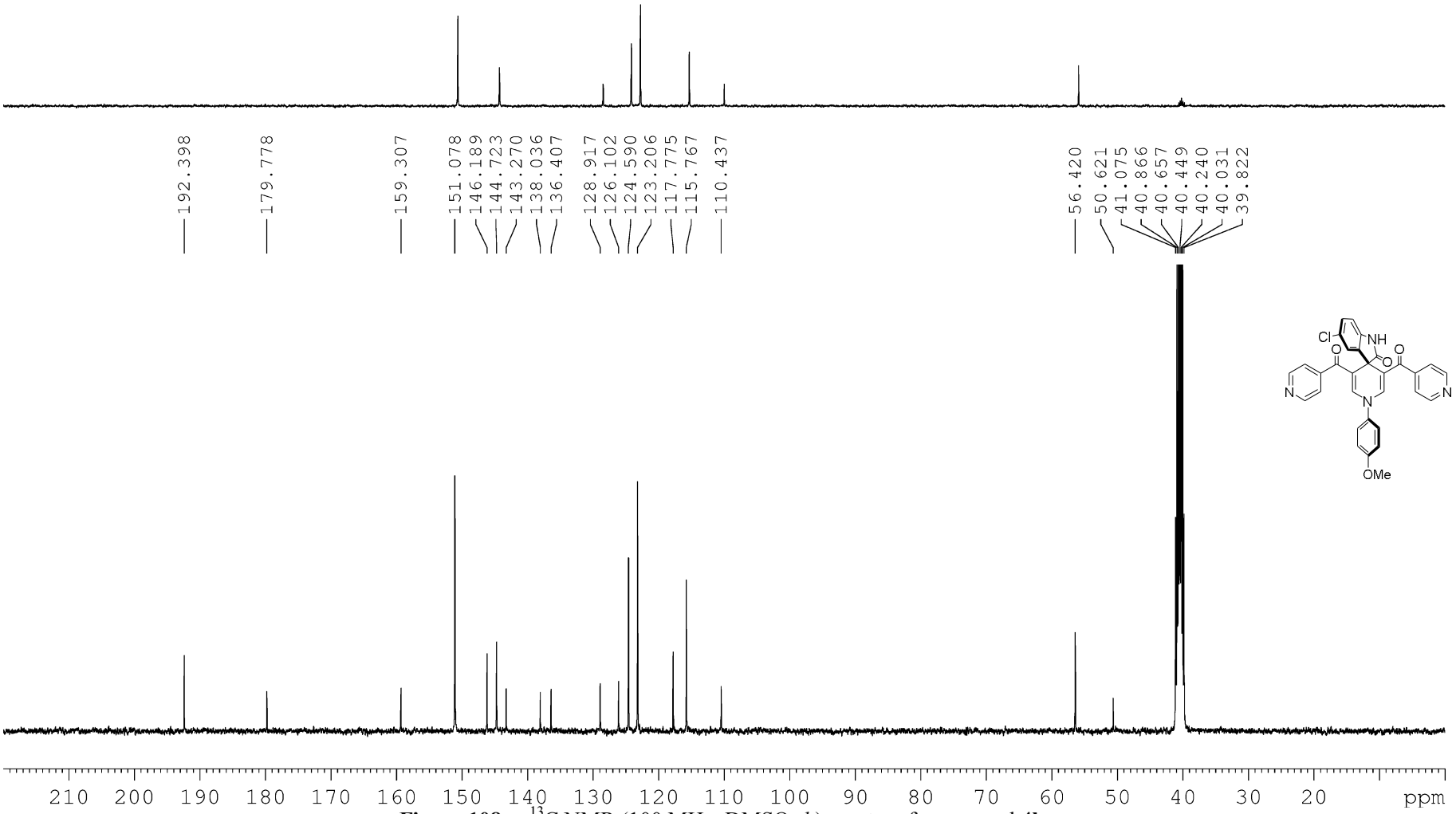

Figure 108. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4k**

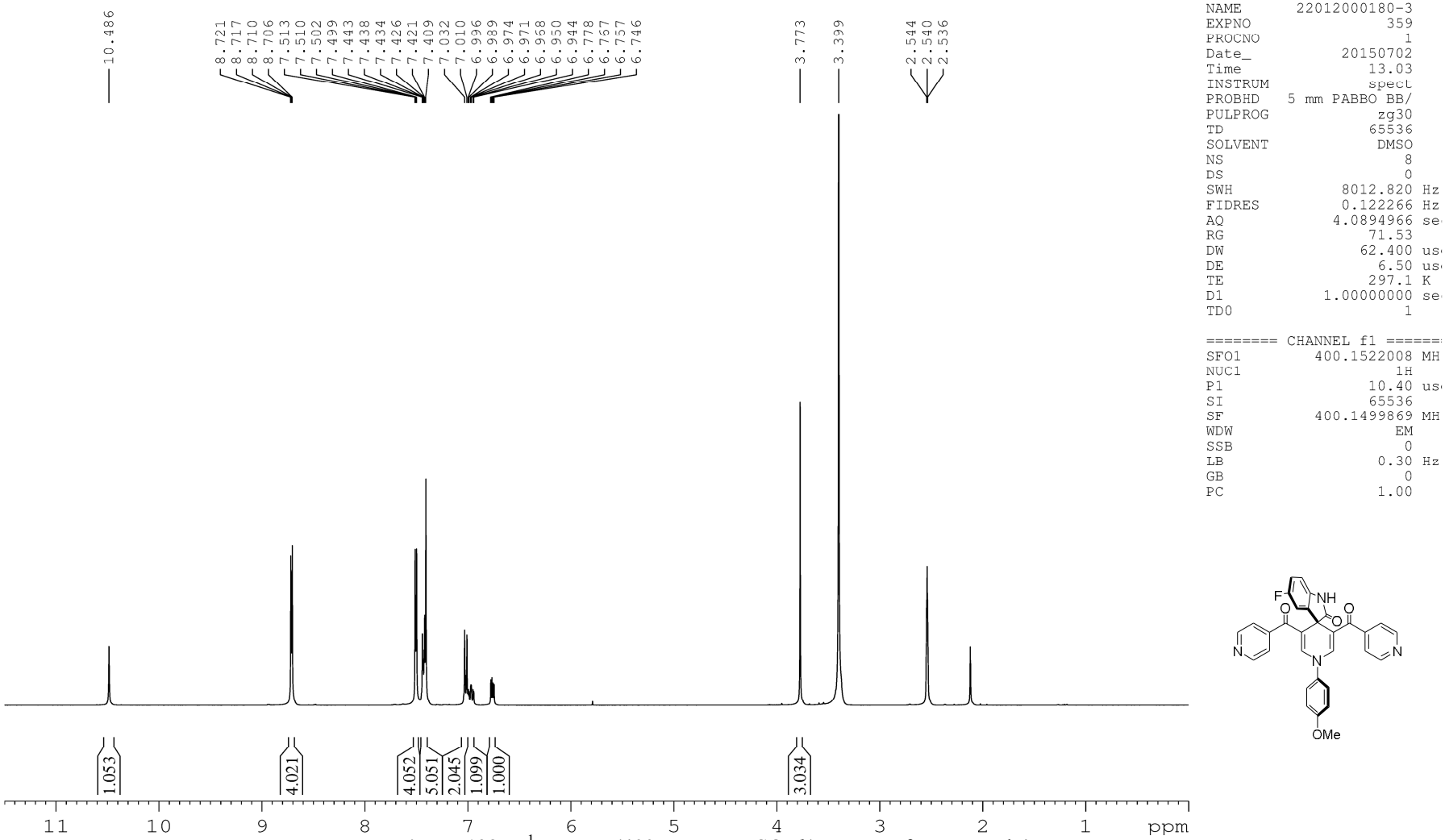

Figure 109. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4l**

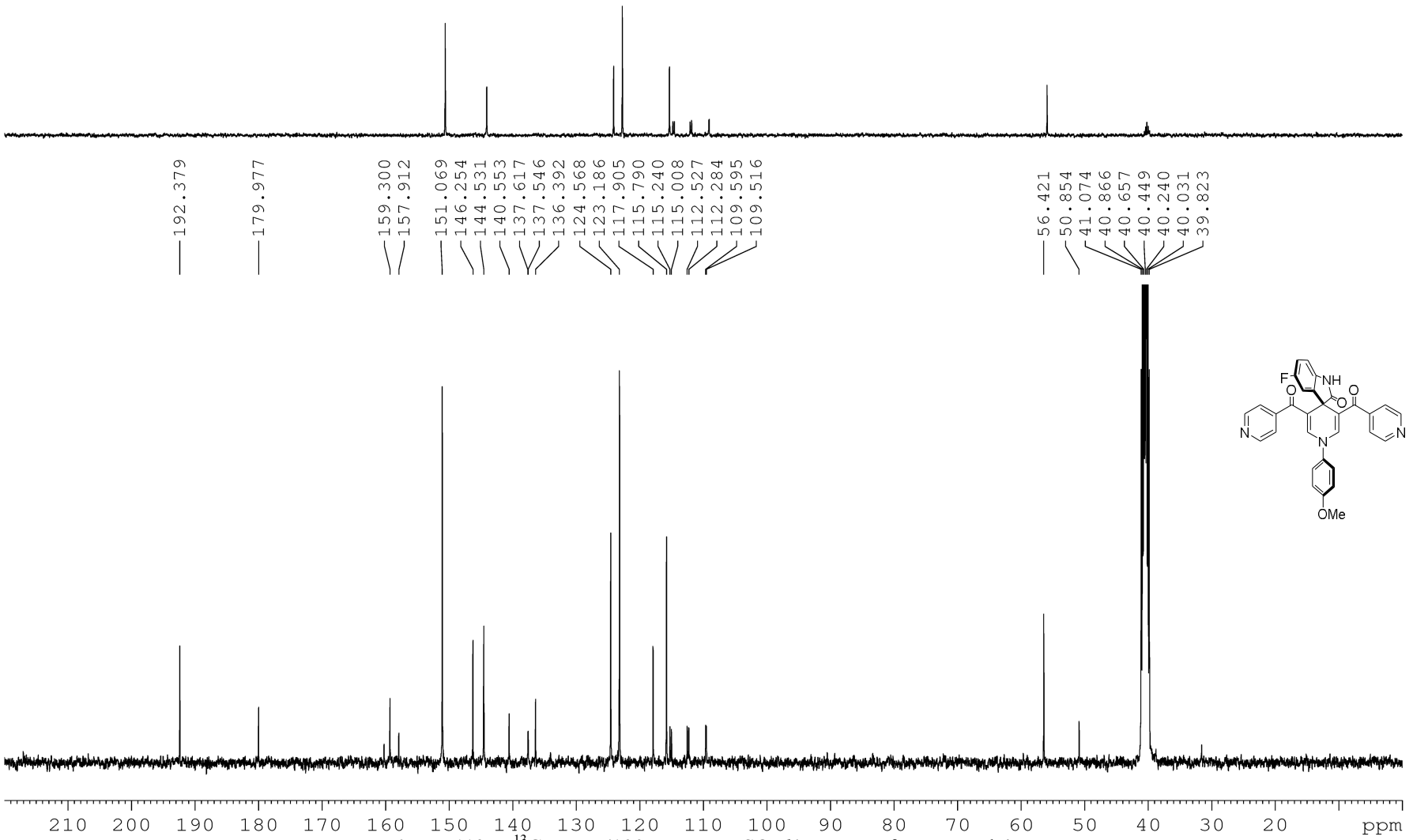

Figure 110. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4l**

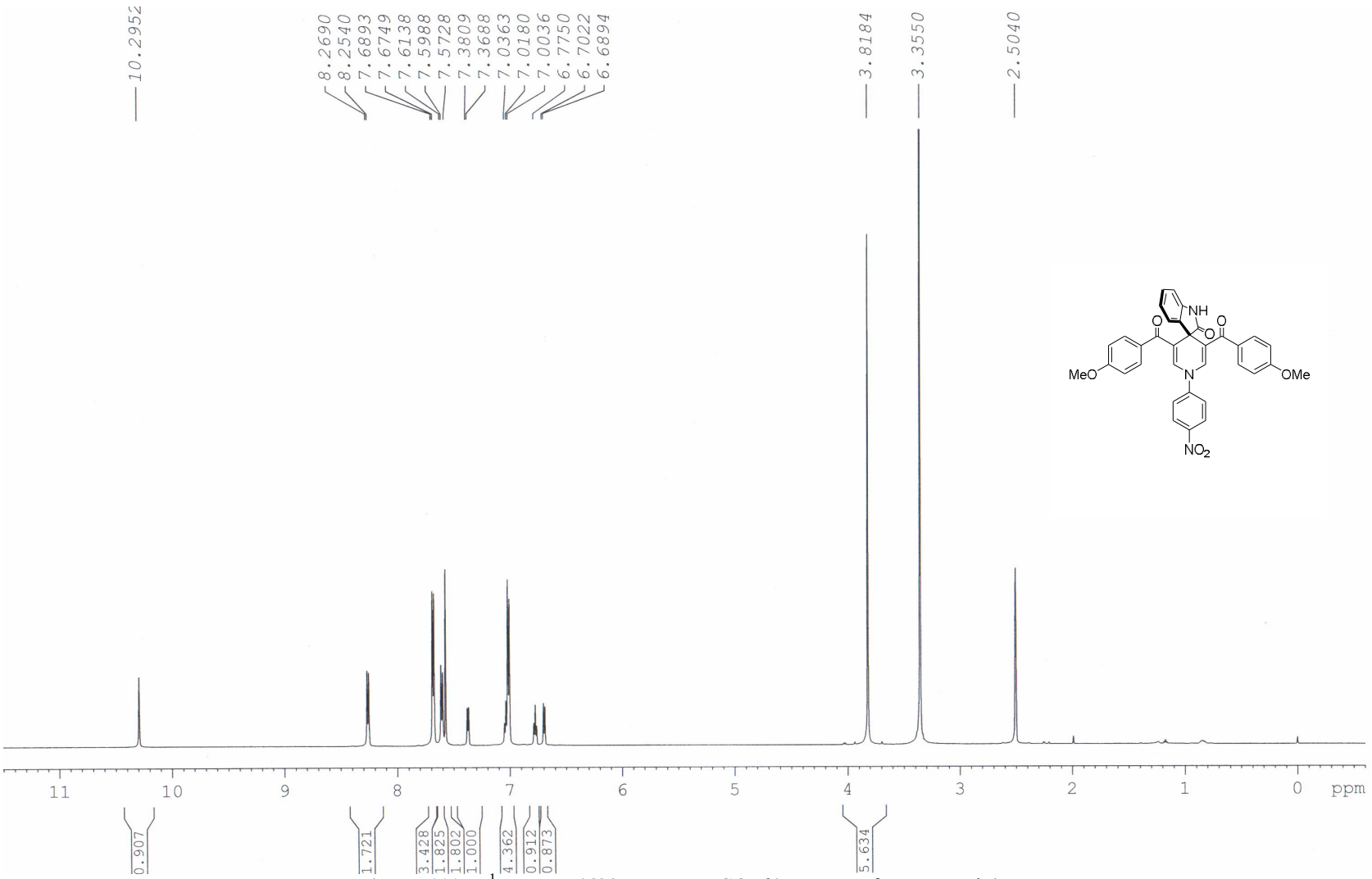

Figure 111. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4m**

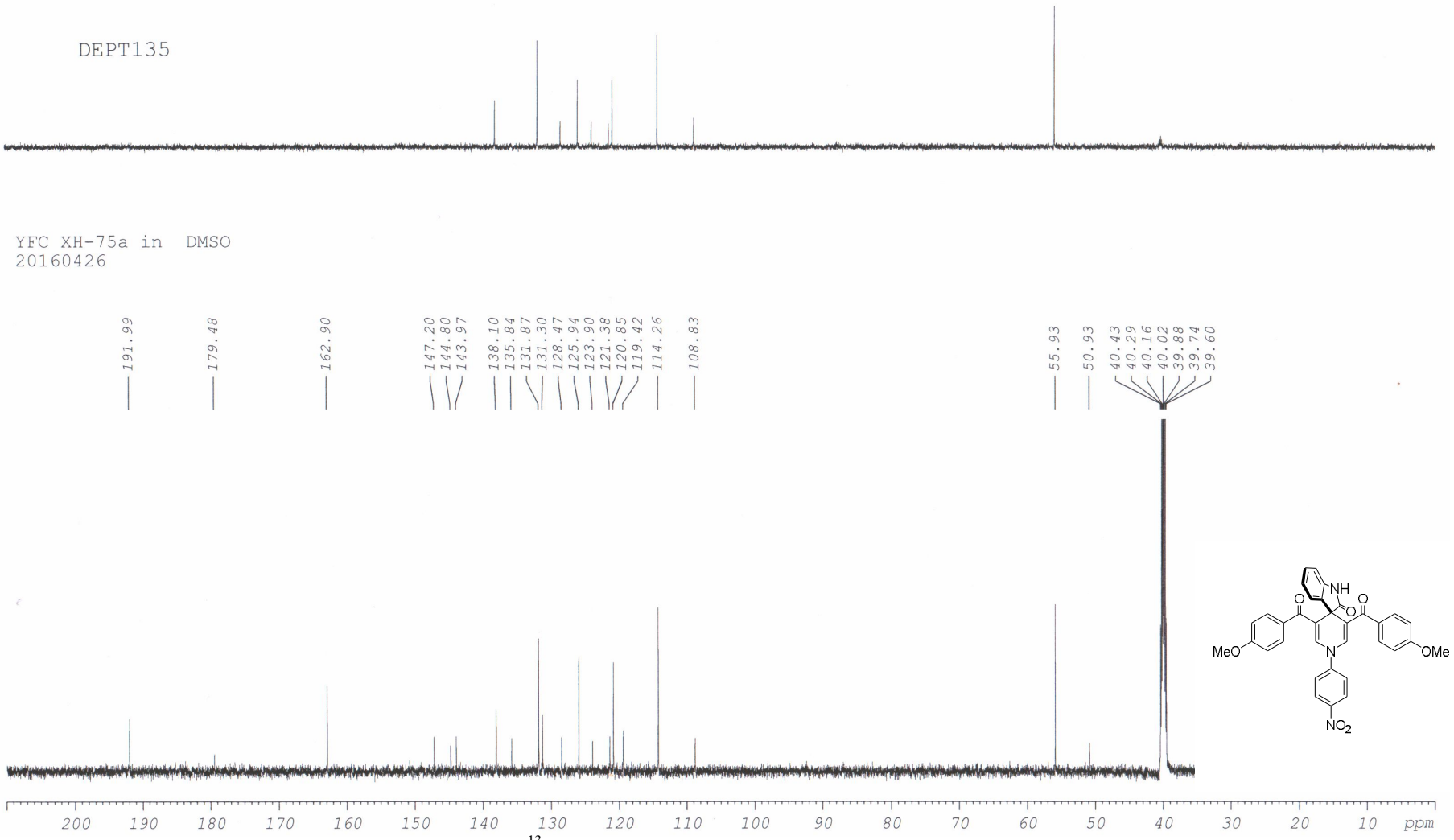

Figure 112. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4n**

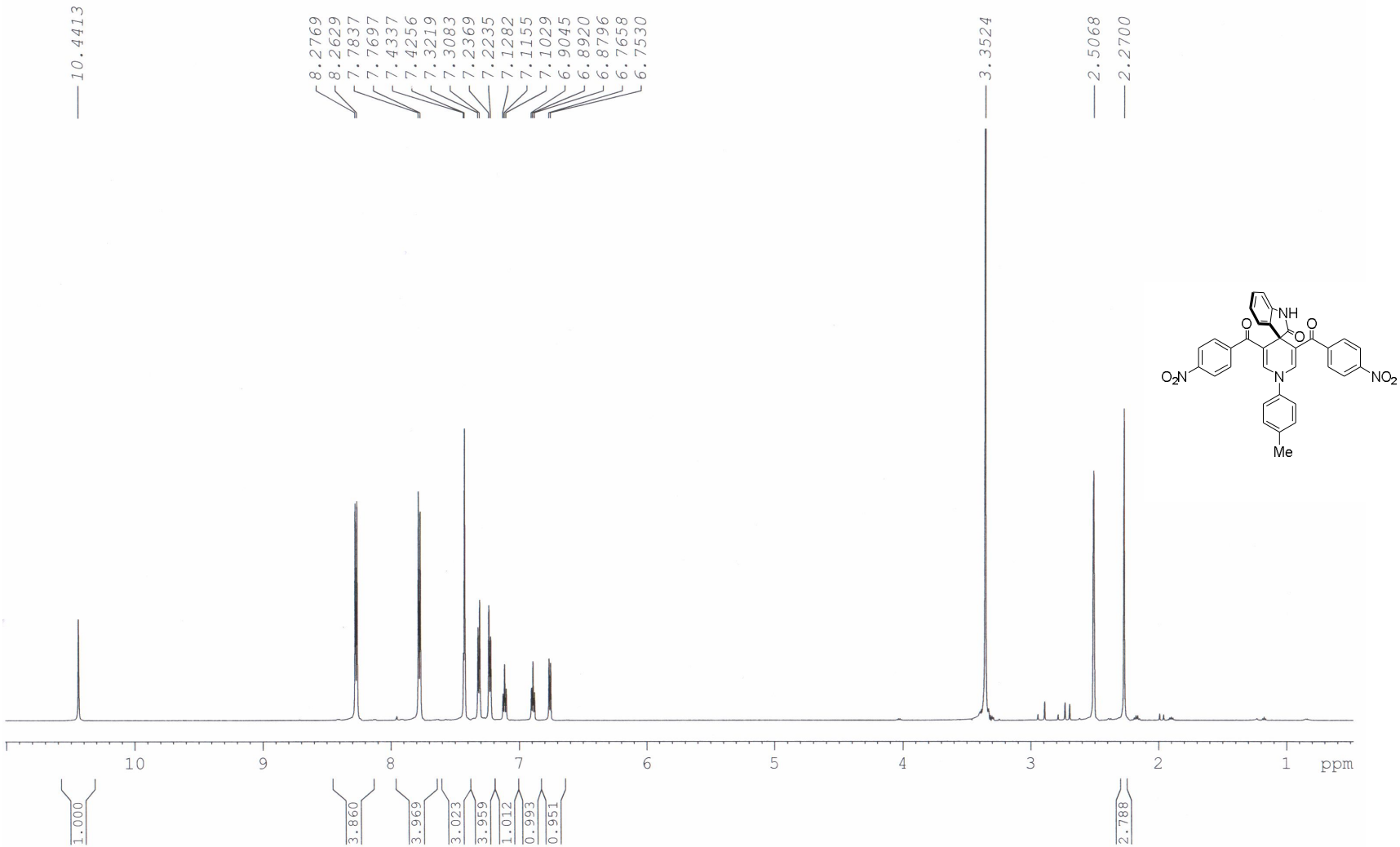

Figure 113. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4n**

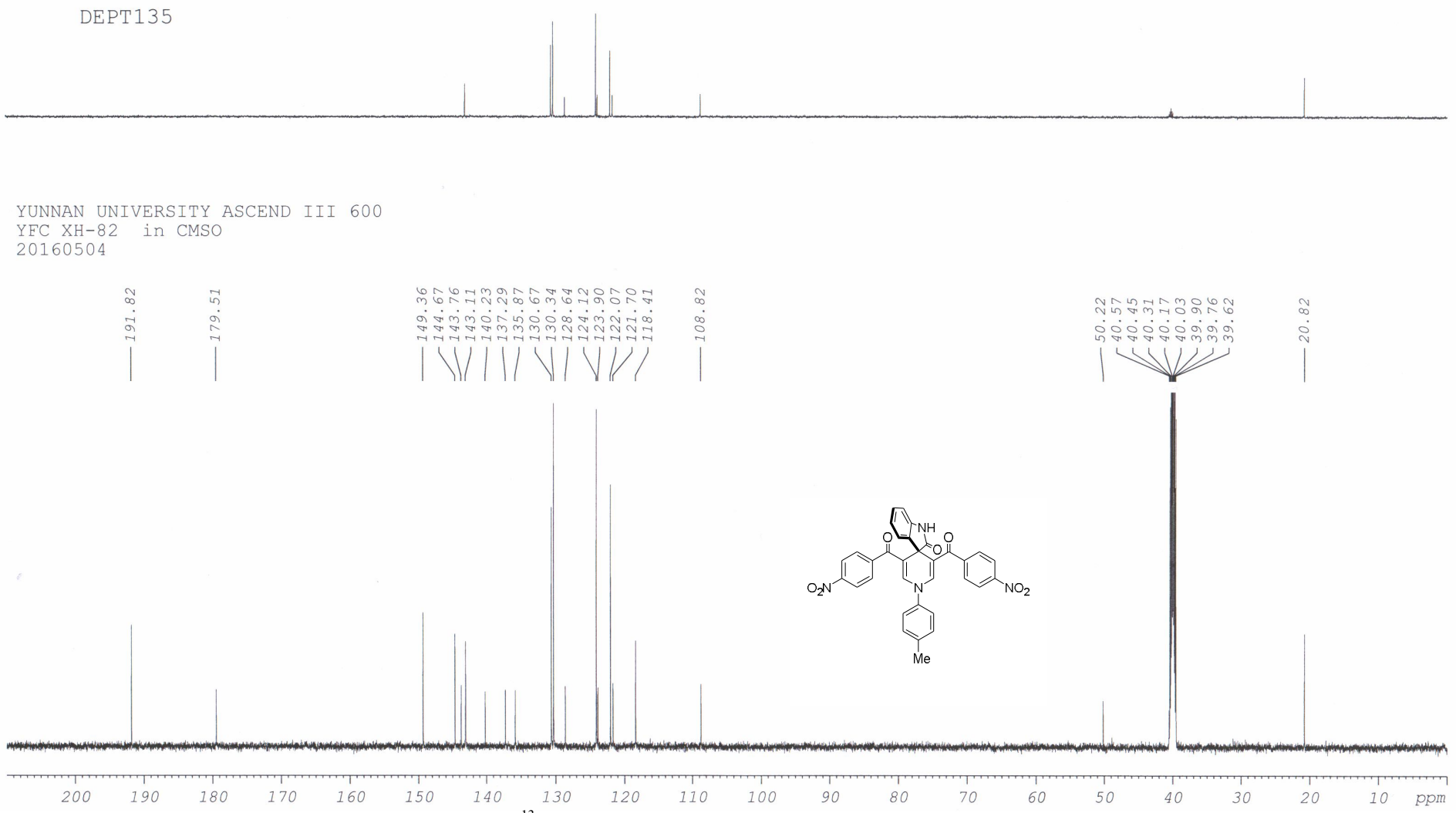

Figure 114. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4n**

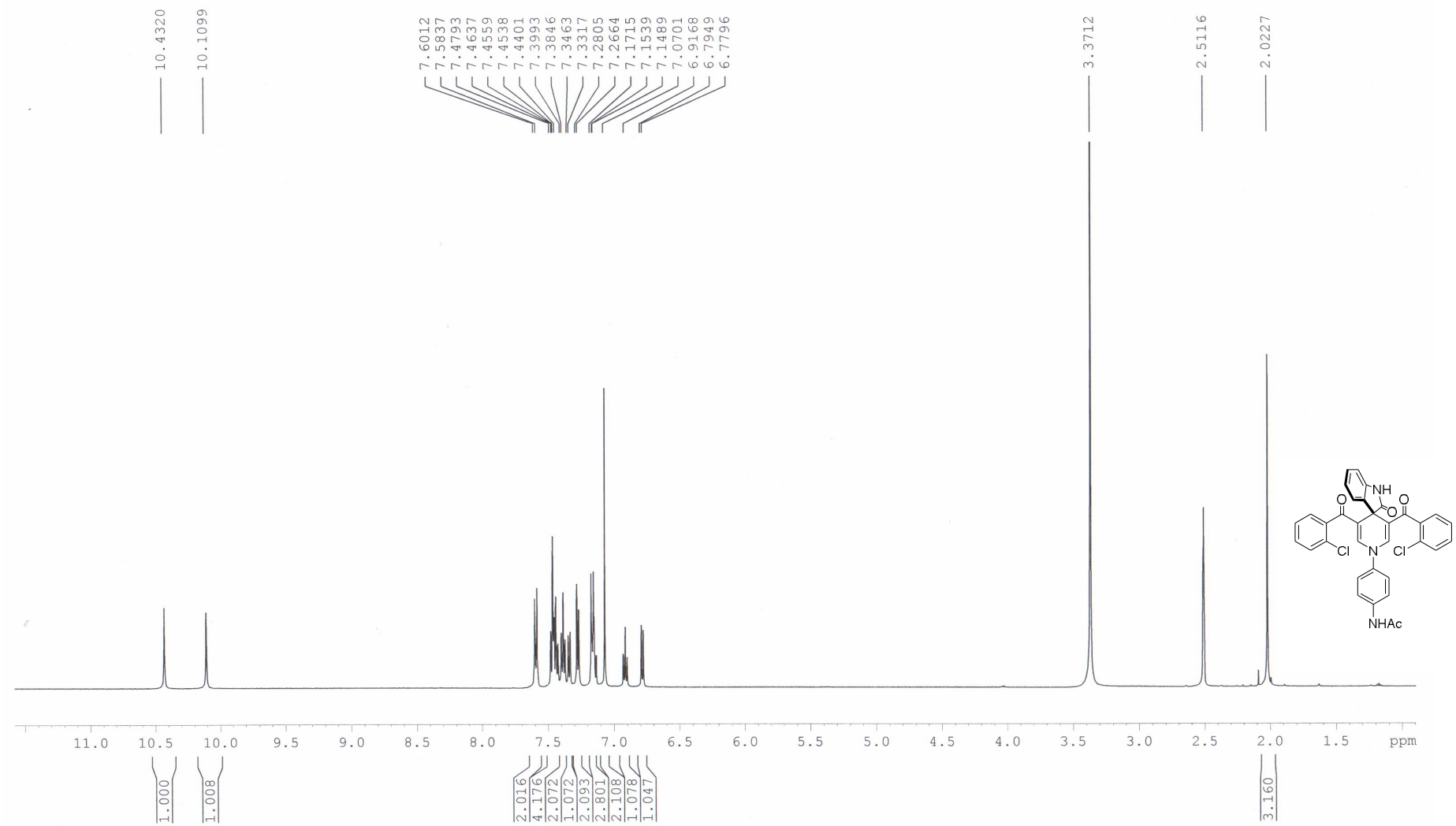

Figure 115. ^{1}H NMR (600 MHz, DMSO-d_6) spectra of compound **4o**

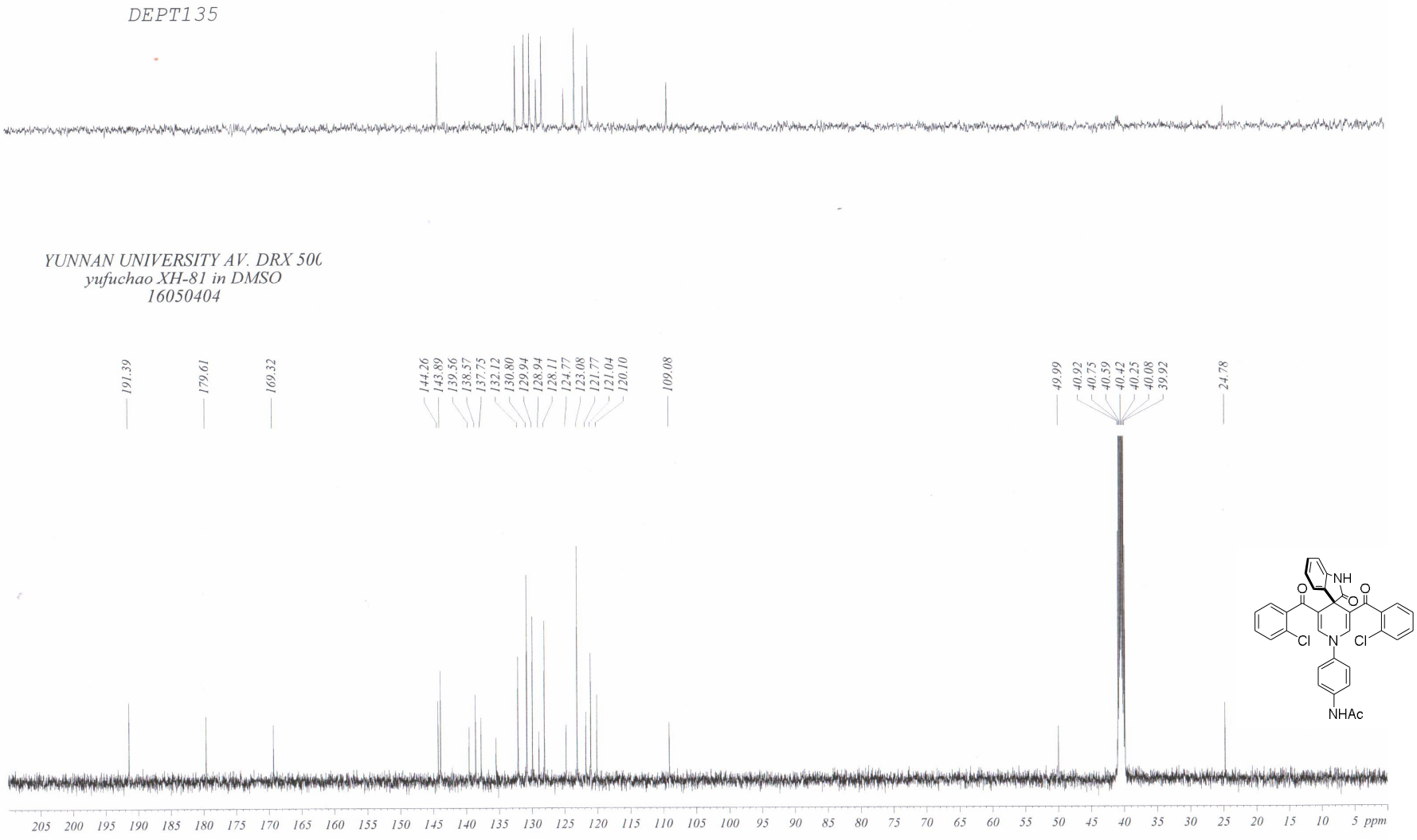

Figure 116. ^{13}C NMR (150 MHz, DMSO-d_6) spectra of compound **4o**

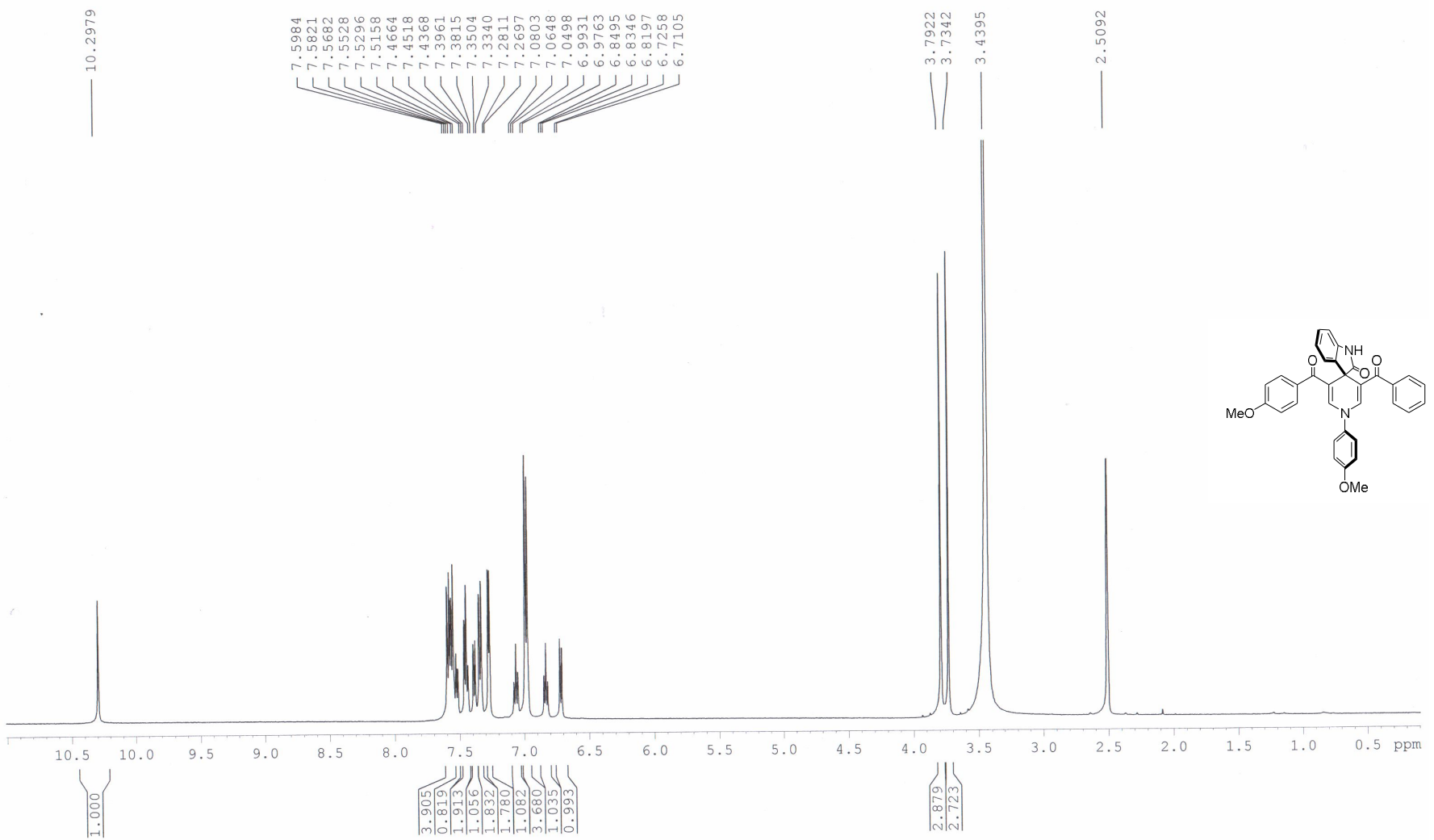

Figure 117. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4p**

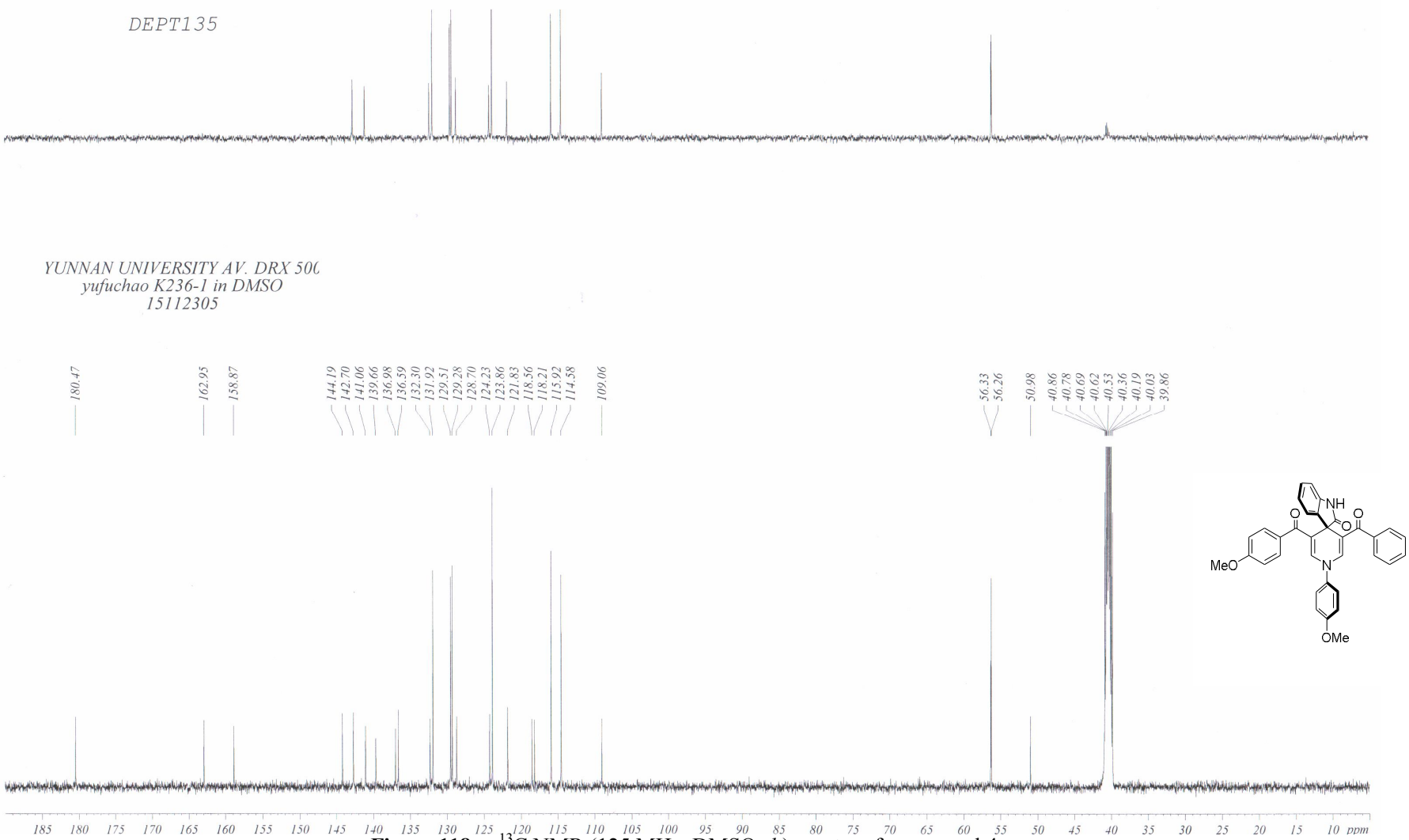

Figure 118. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4p**

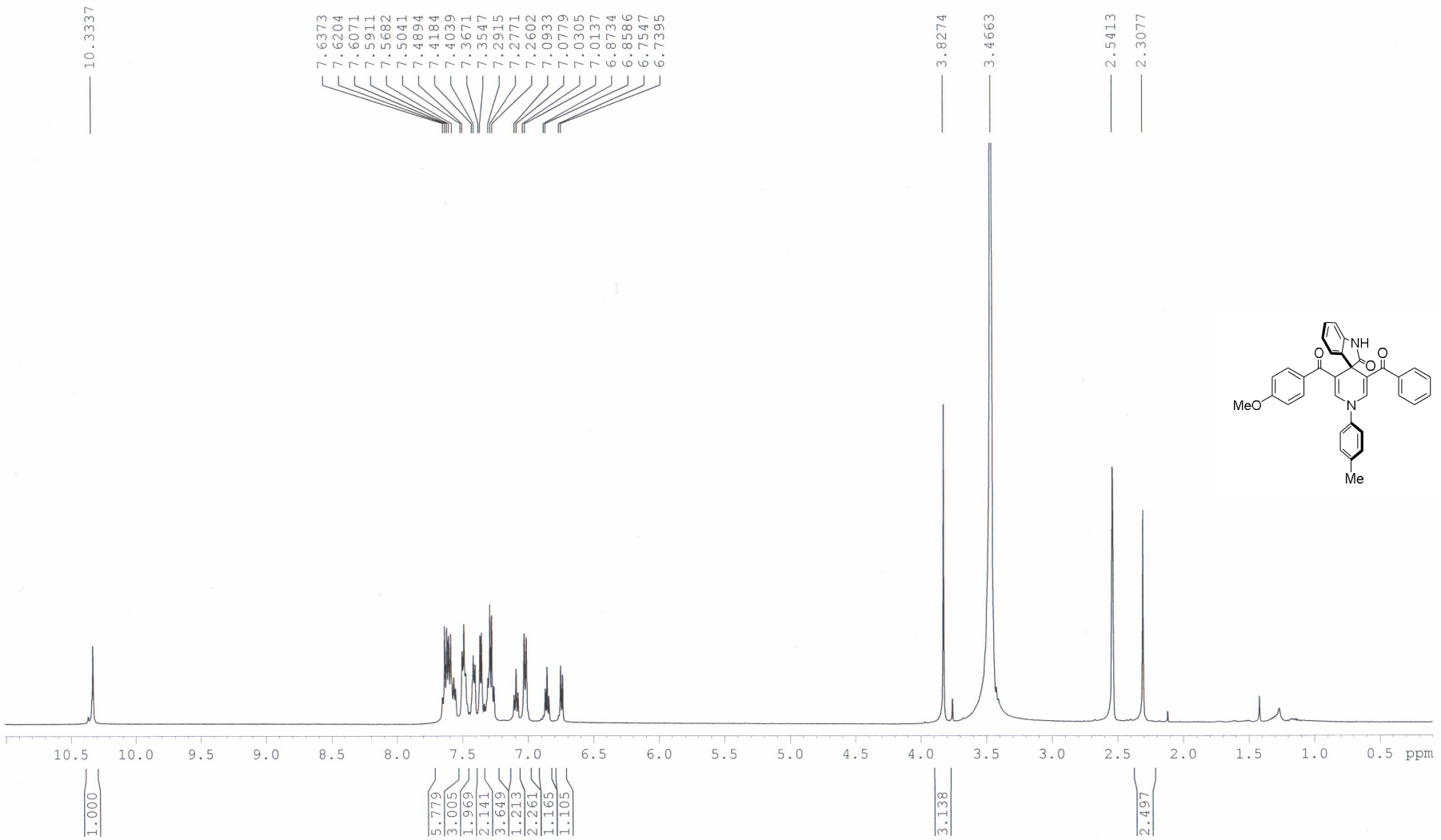

Figure 119. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4q**

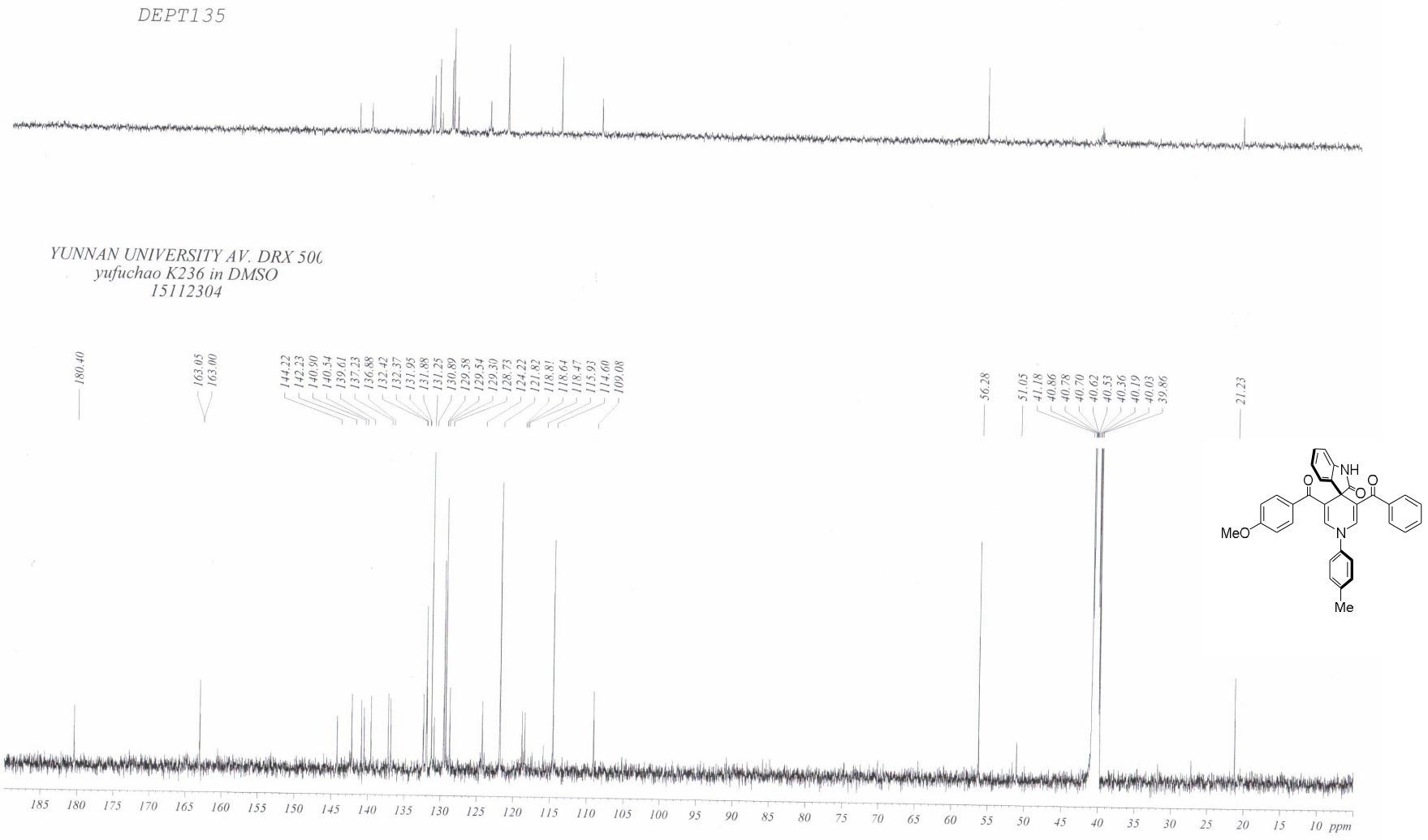

Figure 120. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4q**

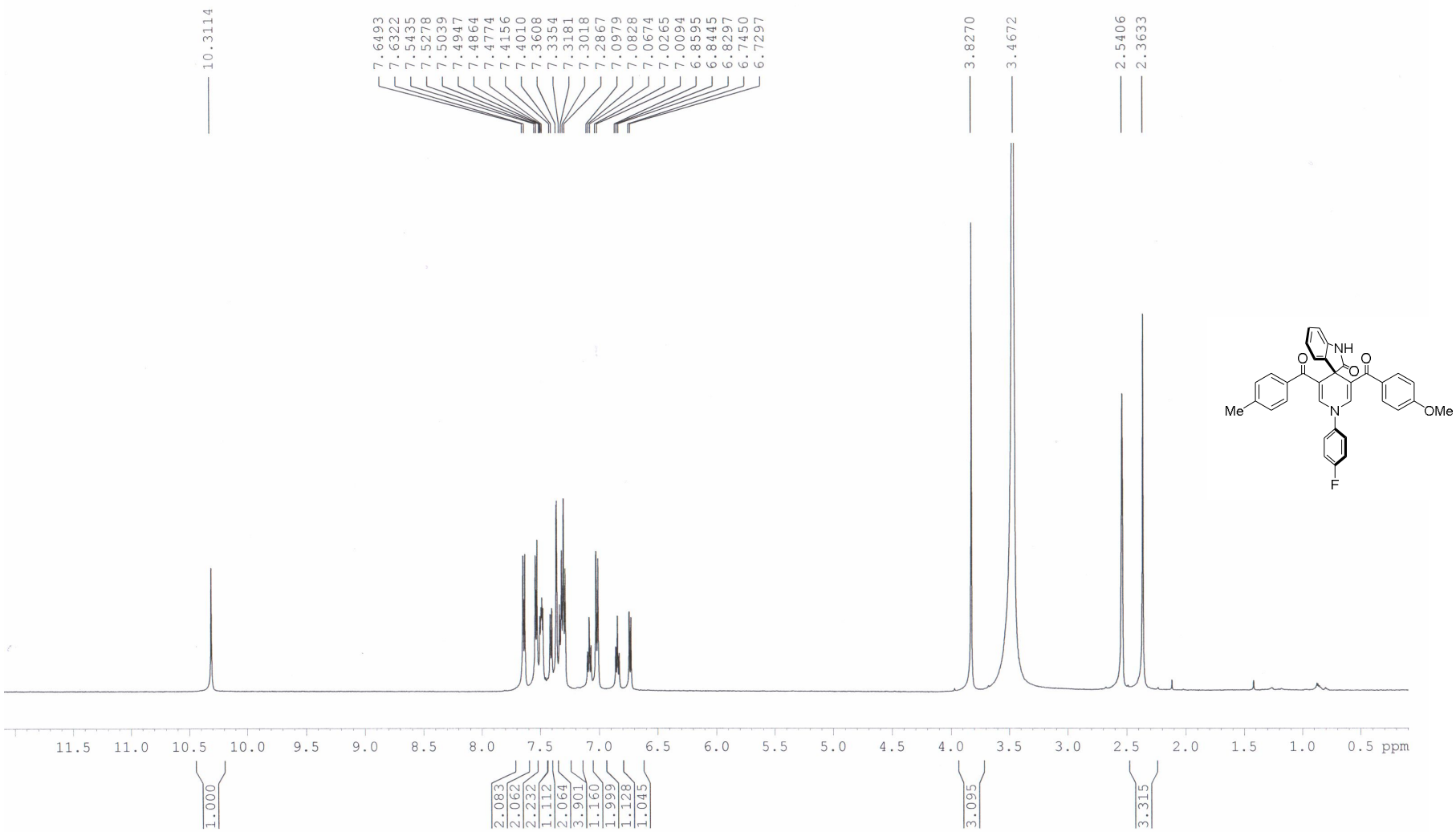

Figure 121. ^{1}H NMR (500 MHz, DMSO-d_6) spectra of compound **4r**

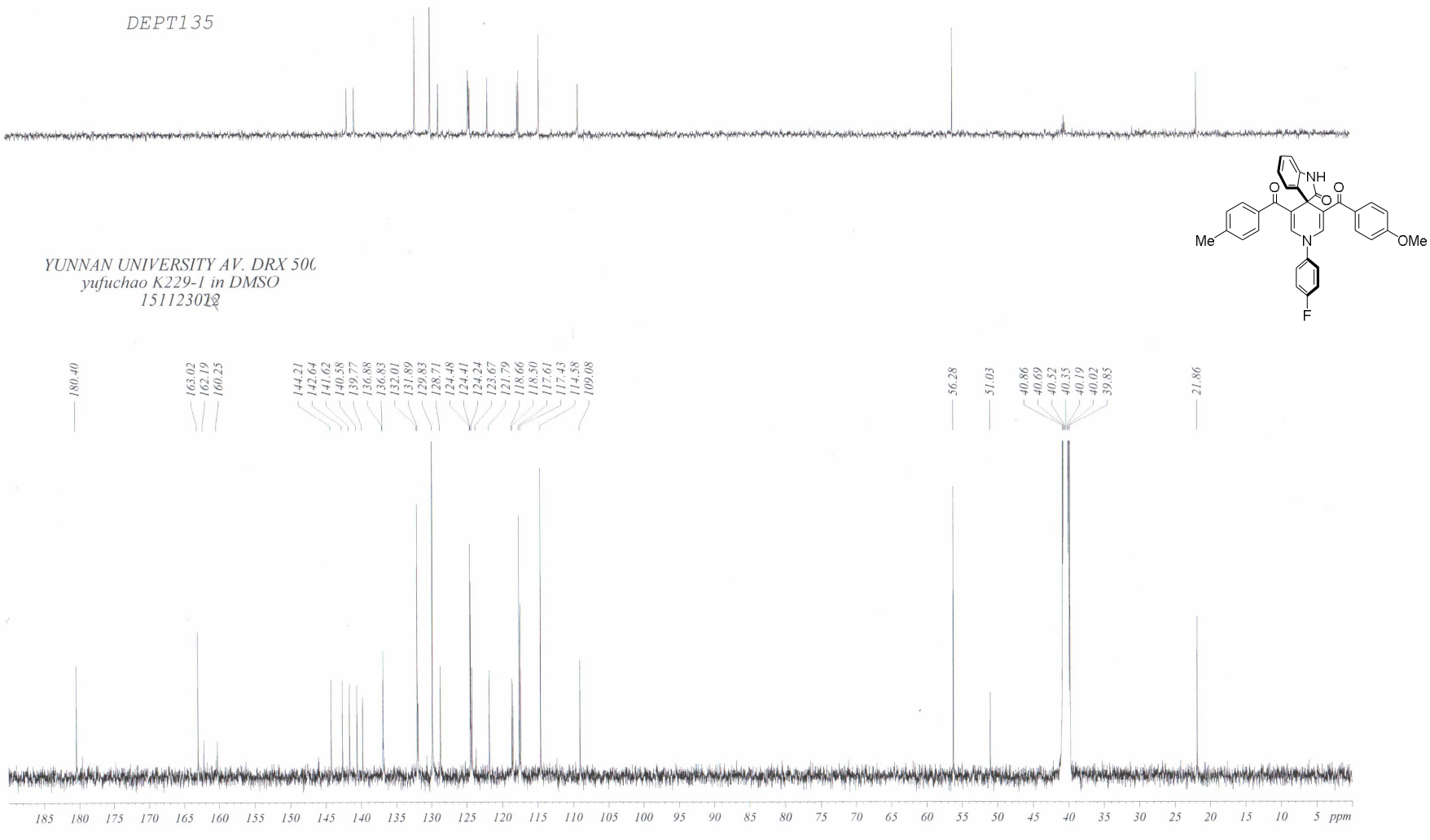

Figure 122. ^{13}C NMR (125 MHz, DMSO-d_6) spectra of compound **4r**

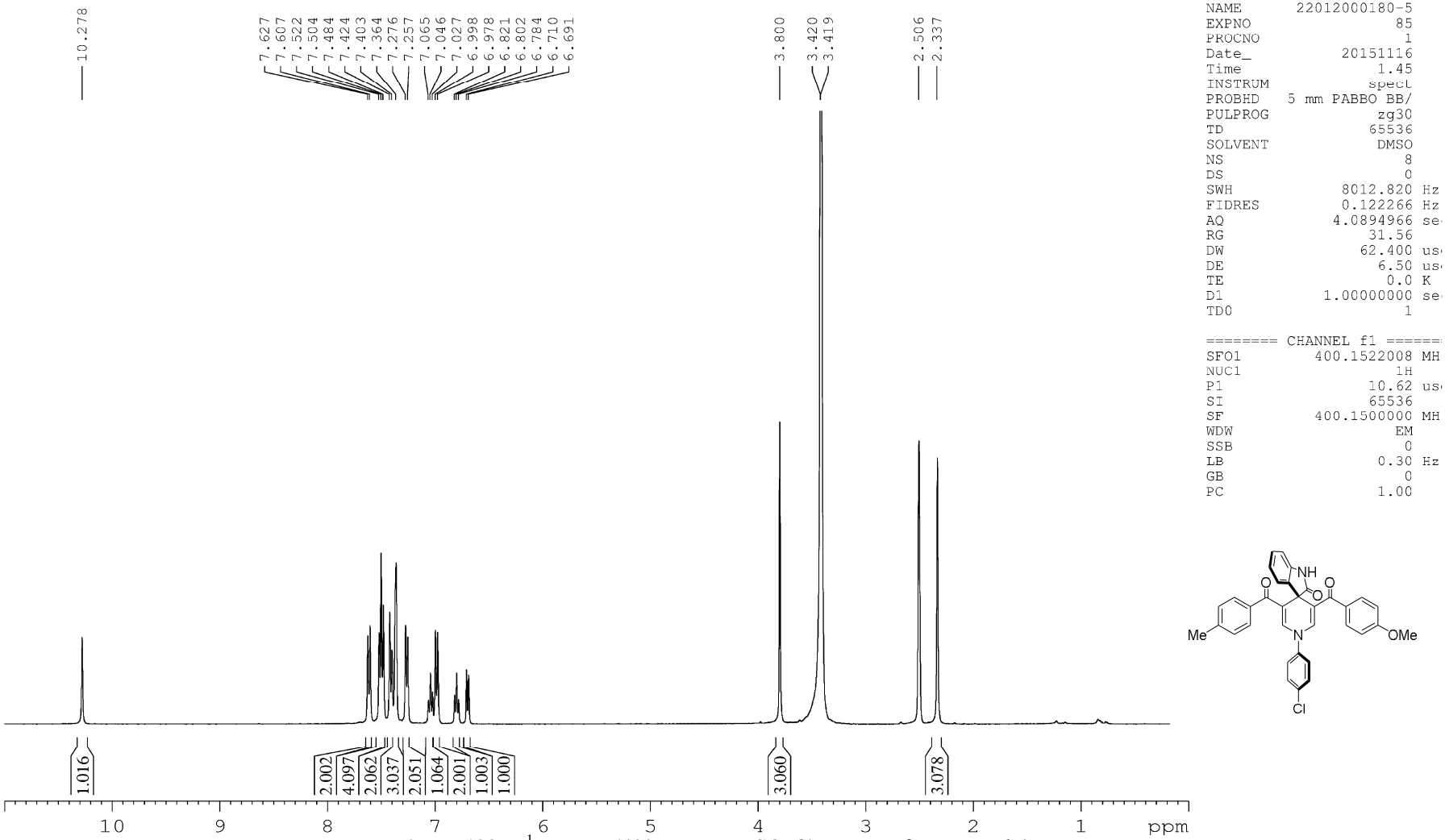

Figure 123. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4s**

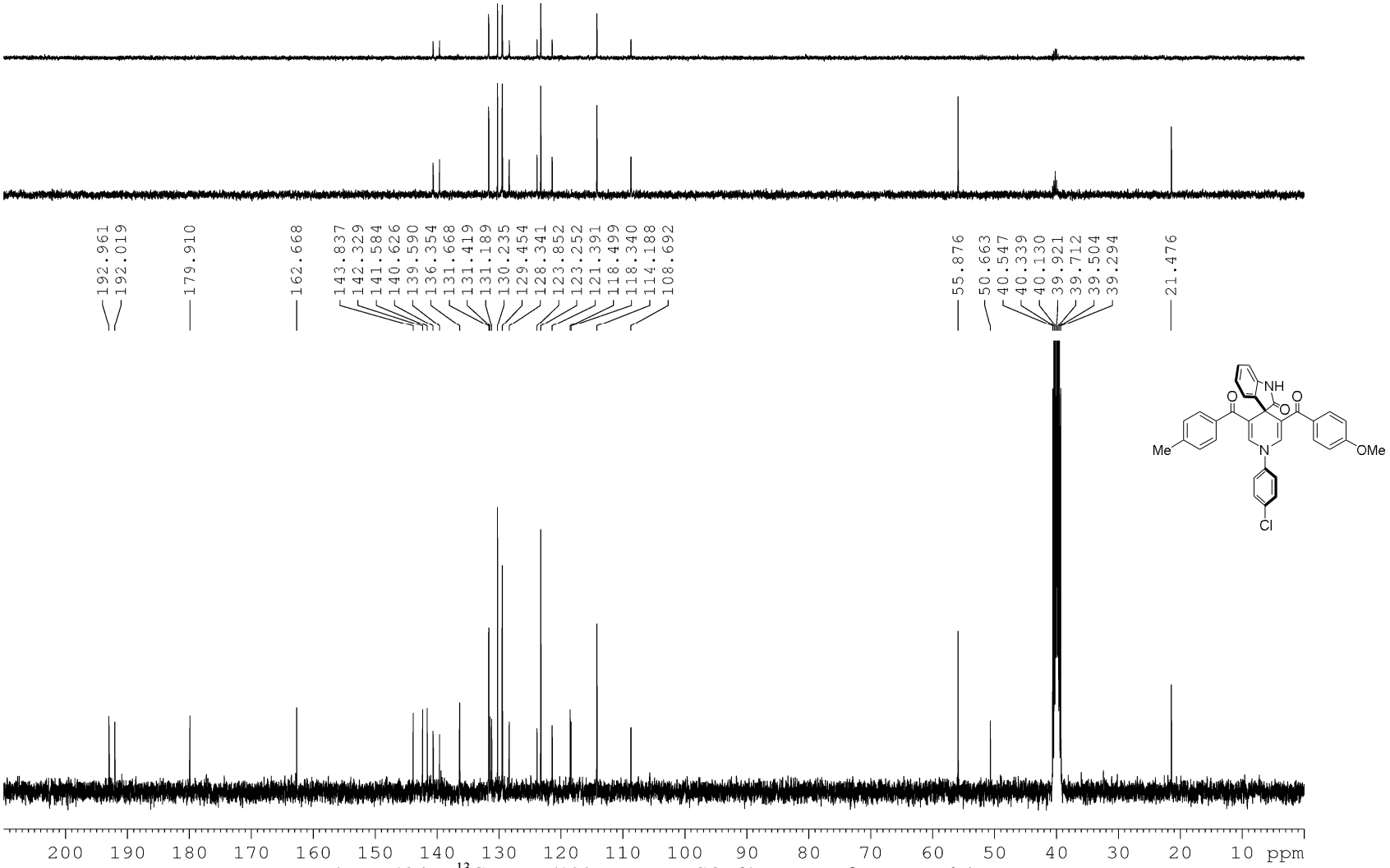

Figure 124. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4s**

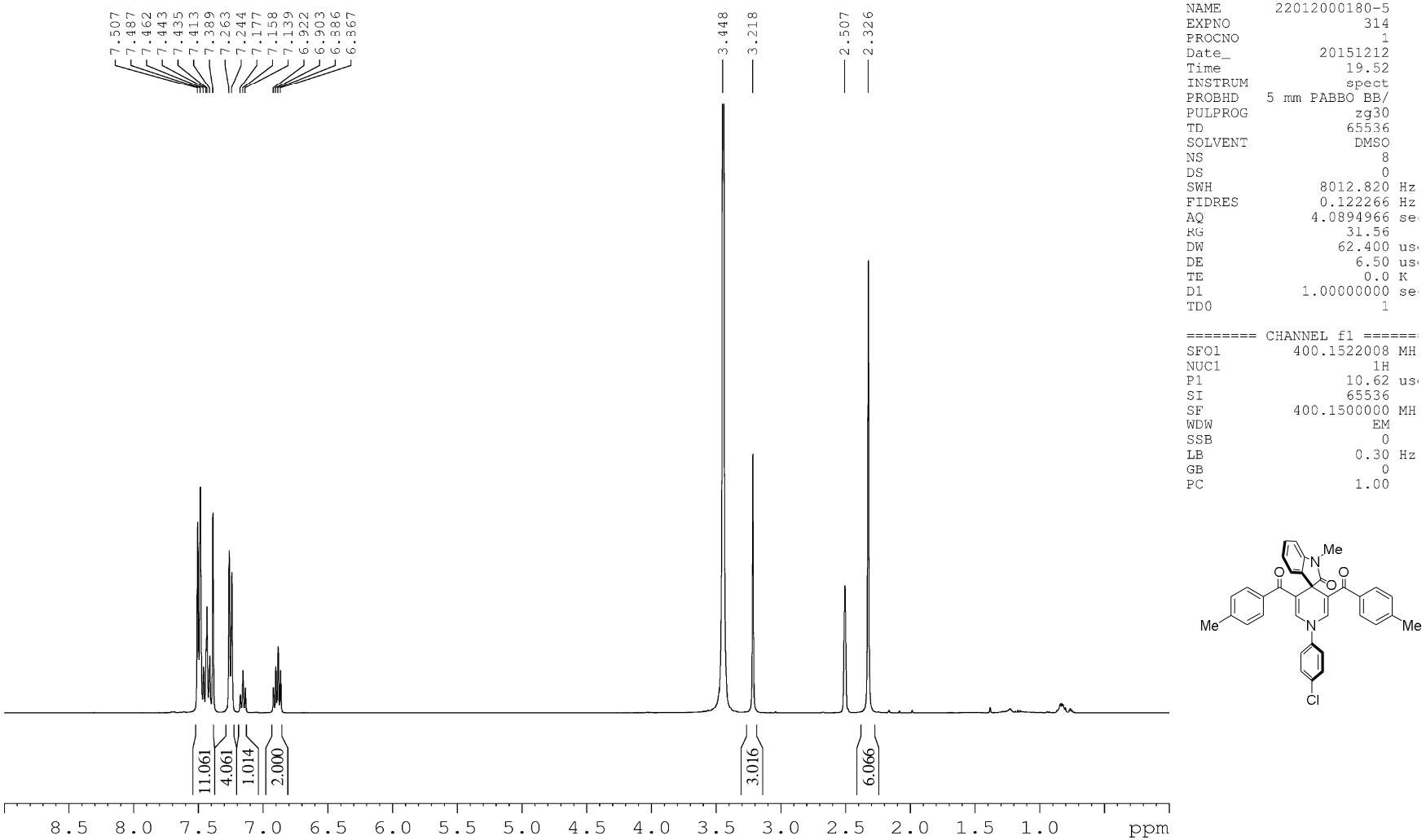

Figure 125. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4t**

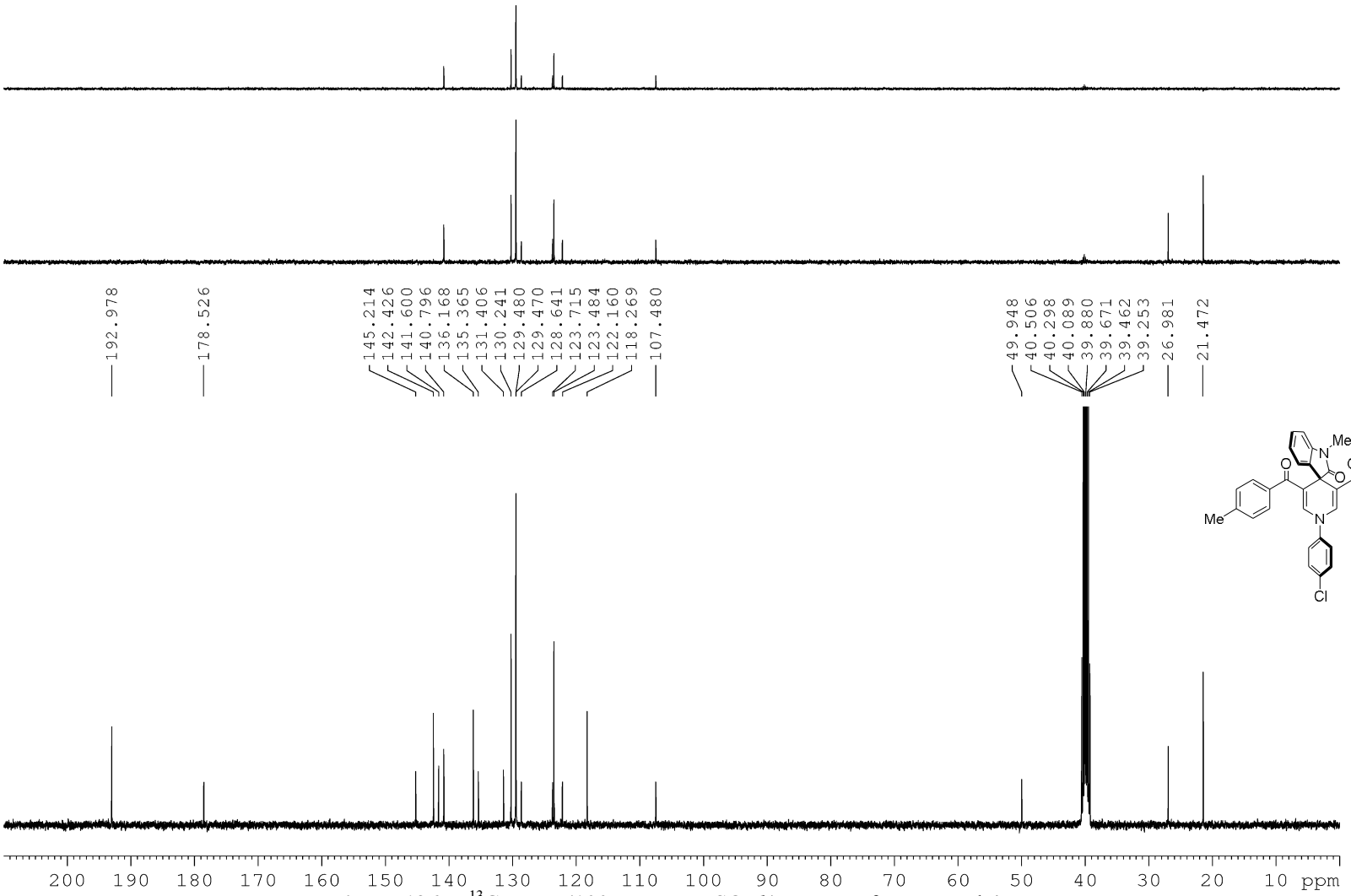

Figure 126. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **4t**

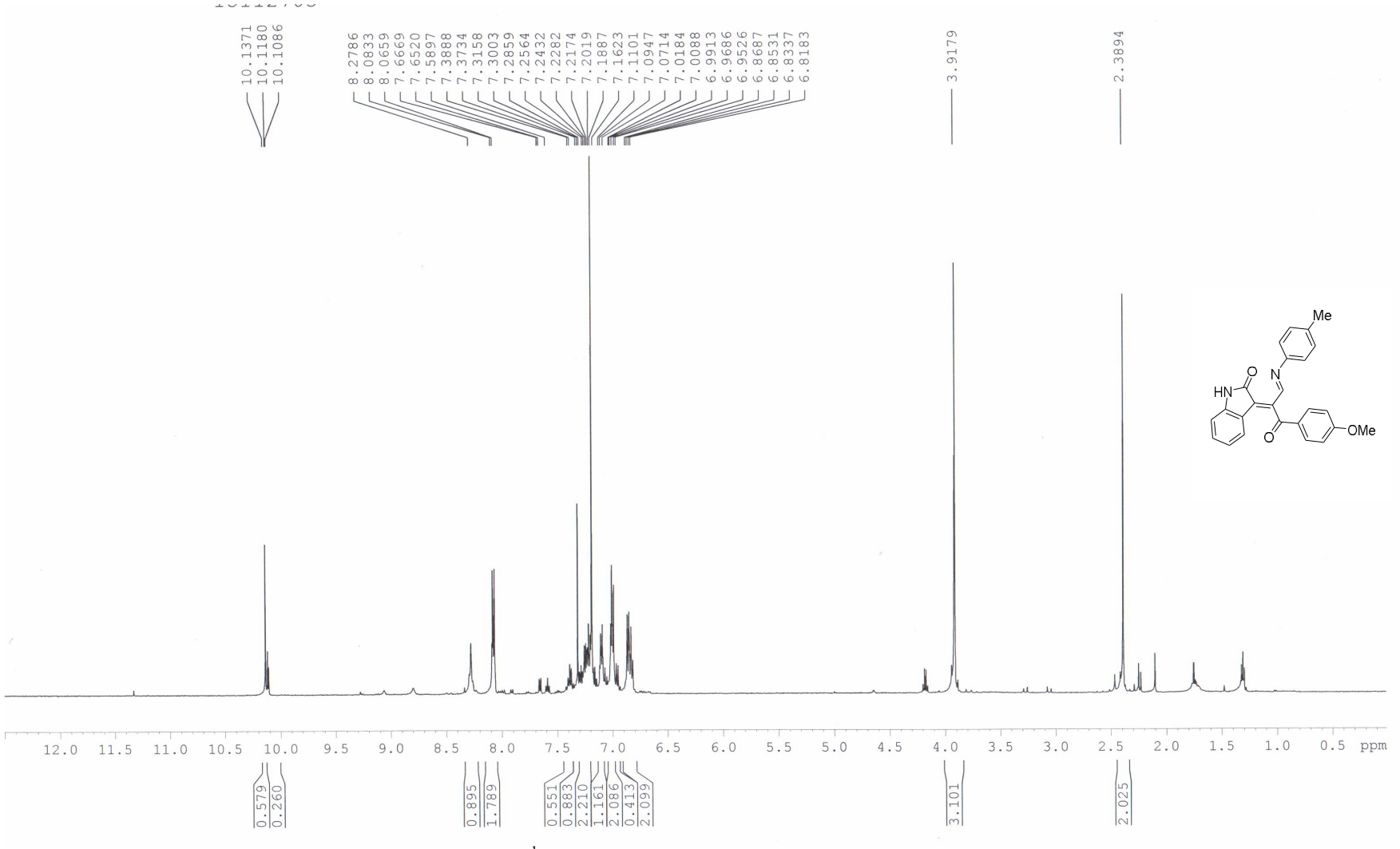

Figure 127. ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **5a**

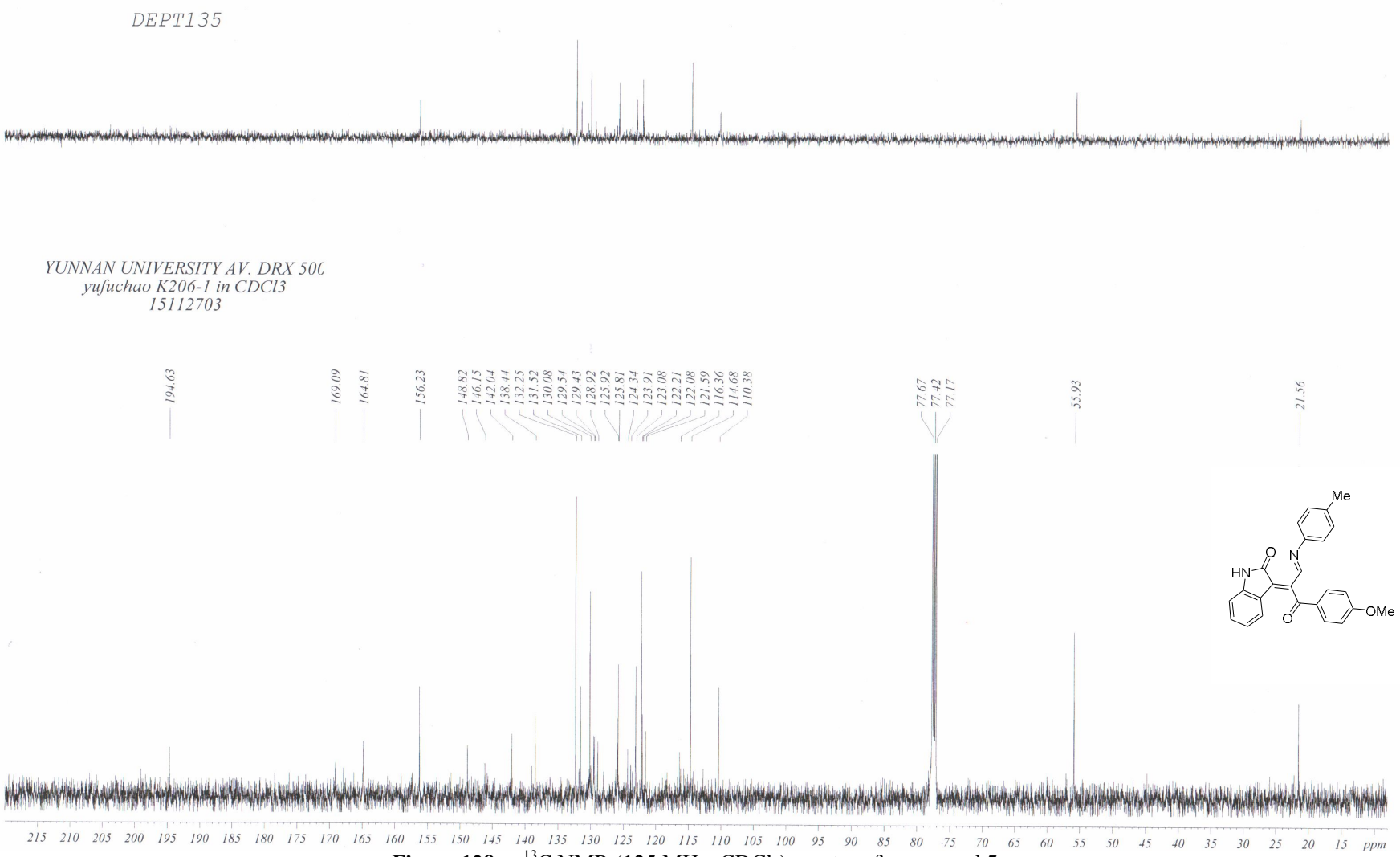

Figure 128. ^{13}C NMR (125 MHz, $CDCl_3$) spectra of compound **5a**

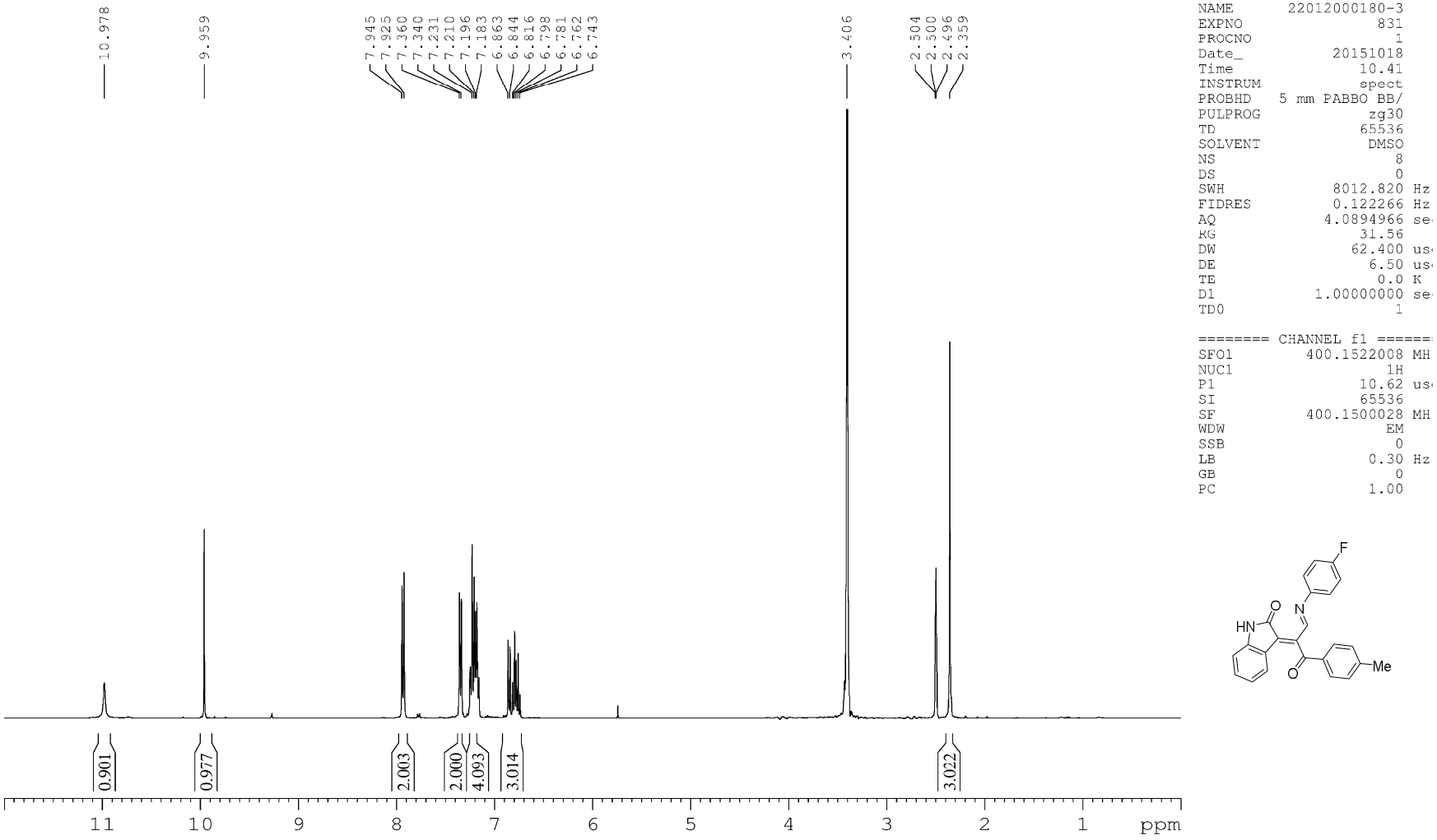

Figure 129. ^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **5b**

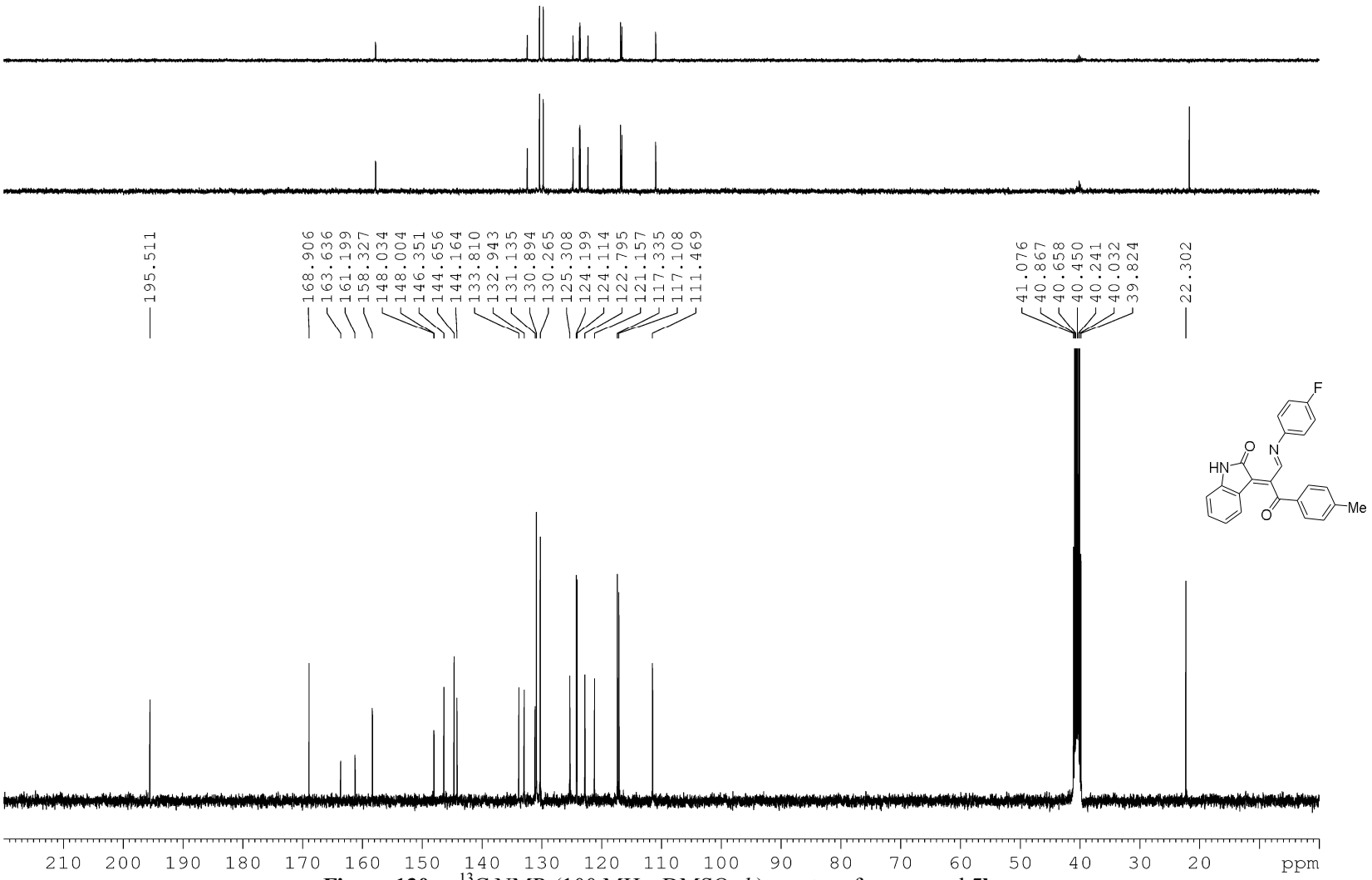

Figure 130. ^{13}C NMR (100 MHz, DMSO-d_6) spectra of compound **5b**

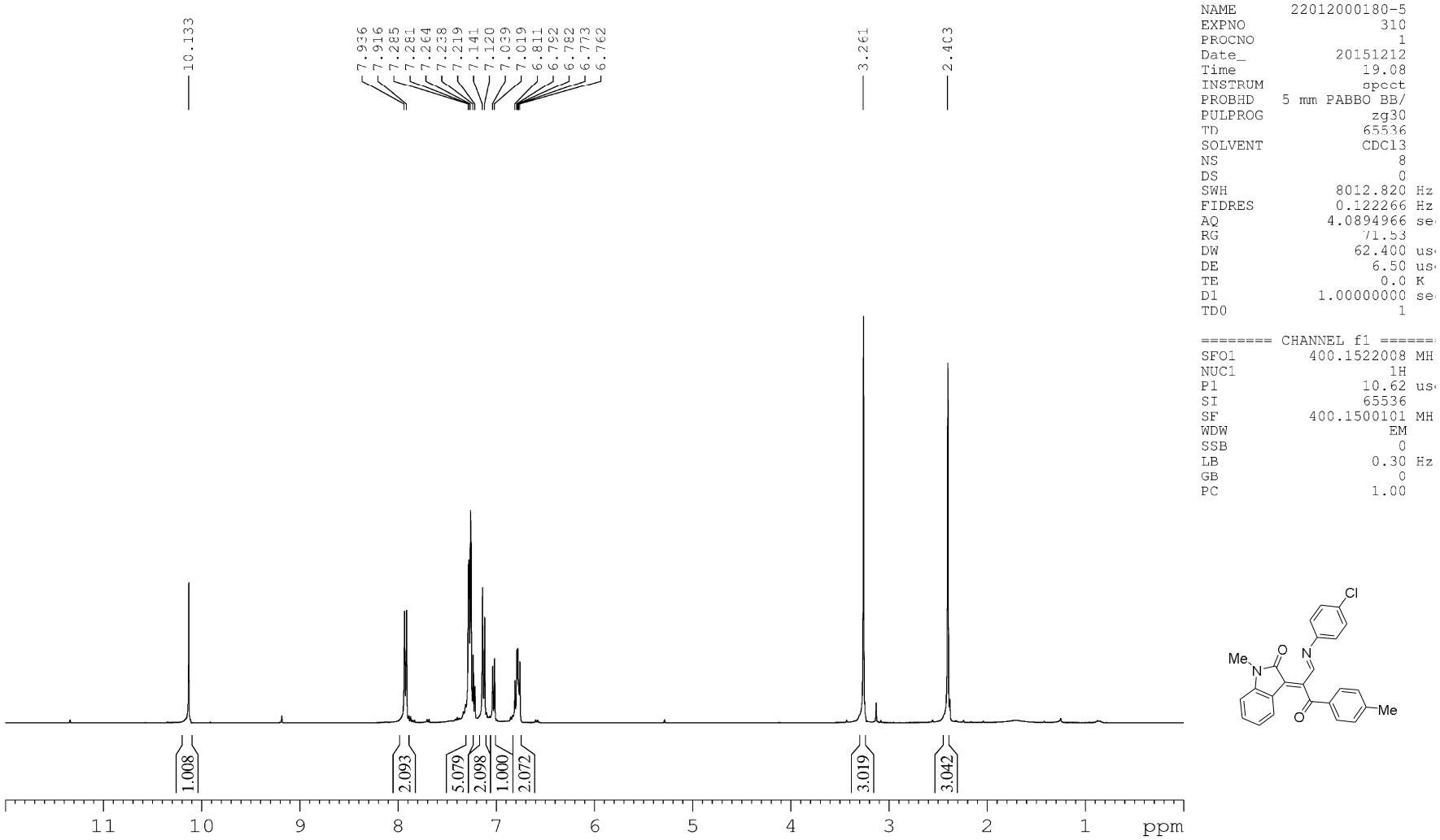

Figure 131. ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **5c**

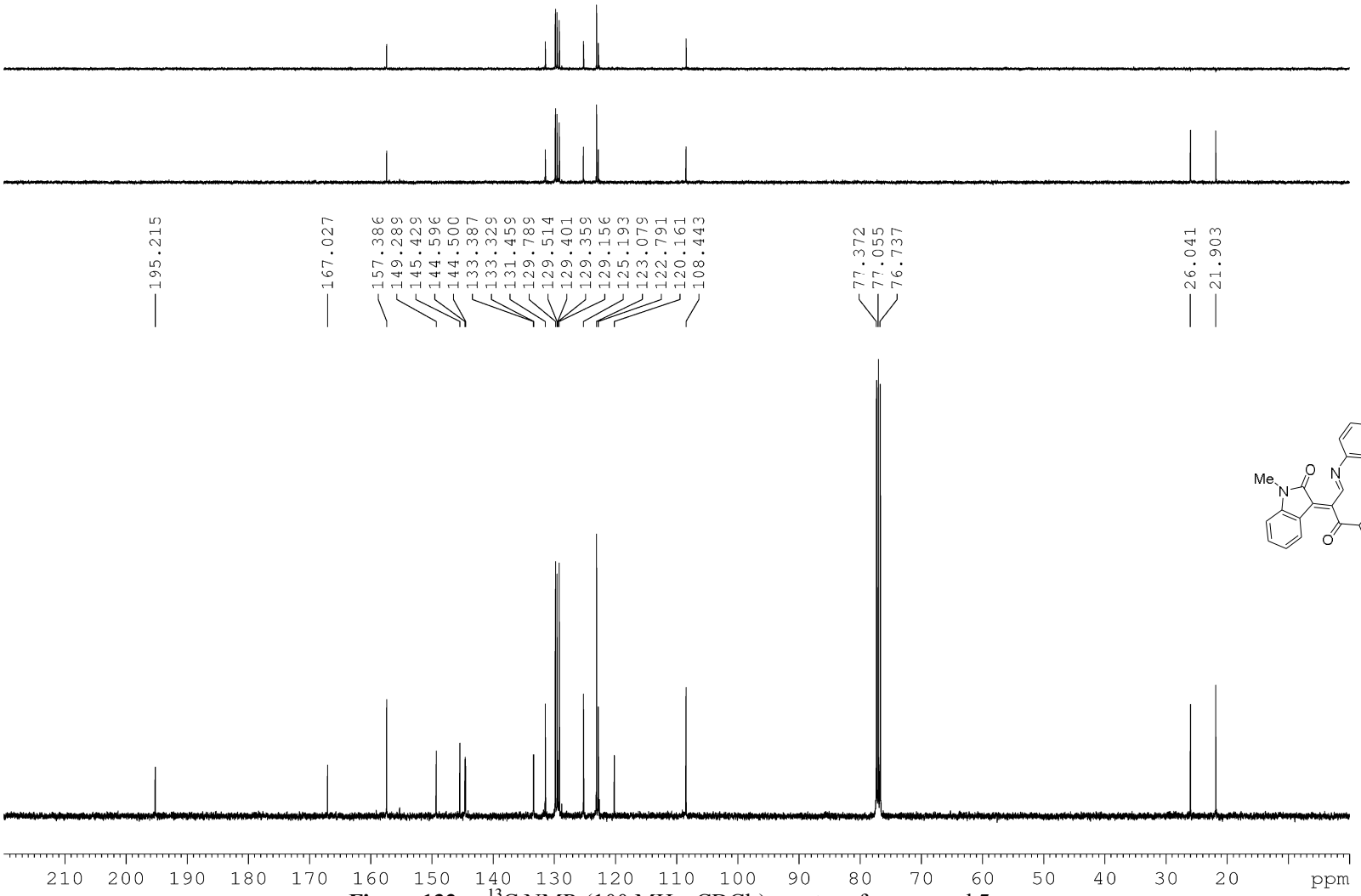

Figure 132. ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound **5c**

9. References and Notes

1. M. S. Shmidt, A. M. Reverdito, L. Kremenchuzky, I. A. Perillo, M. M. Blanco. *Molecules* **2008***, 13,* 831.
2. (*a*) Y. Liu, R. Zhou, J.-P. Wan. *Synth. Commun.* **2013**, *43*, 2475; (*b*) Z.-Z. Zhou, F.-S. Liu, D.-S. Shen, C. Tan, L.-Y. Luo. *Inorg. Chem. Commun.* **2011**, *14*, 659; (*c*) N. A. Larina, V. Lokshin, J. Berthet, S. Delbaere, G. Vermeersch, V. Khodorkovsky, *Tetrahedron* **2010**, *66*, 8291.
3. CCDC 1409628 contain the supplementary crystallographic data for compound **3ak**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.
4. CCDC 1431049 contain the supplementary crystallographic data for compound **4l**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.