Electronic supplementary information

Blue-Light Assisted Transformation of C=S and P=S Bonds of Thioamides and Thiophosophonyl Diamides into C=N and P=N= bonds of *N*-Sulfonyl Amidines via Interaction with Iminoiodinanes

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Table of content

General Information

All chemicals were obtained from commercial sources and were used without further purification. Dry solvents were obtained according to the literature protocols and stored over molecular sieves. Analytical thin-layer chromatography was performed on aluminum foil plates coated with 0.2 mm of silica gel. Column chromatography was performed by using 230−400 mesh silica gel or neutral alumina. Melting points were determined on a Stuart SMP10 melting point apparatus and were uncorrected. All NMR spectra were recorded at 400 or 600 (^{1}H NMR), 100 or 150 MHz (^{13}C NMR), 565 MHz (^{19}F) and 162 MHz (^{19}P) in $CDCl_3$ or DMSO-d_6. The chemical shifts are given in parts per million (ppm) relative to the resonance of the solvents [^{1}H: δ ($CDCl_3$) = 7.26, δ (DMSO-d_6) = 2.50, ^{13}C: δ ($CDCl_3$) = 77.2, δ (DMSO-d_6) = 39.5 ppm]. Multiplicities were given as s (singlet), d (doublet), t (triplet) and m (multiplet). Coupling constants are reported as the J value in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded using a Nexera HPLC system (Shimadzu, Japan) equipped with a DGU-20A degasser, two LC-30AD chromatographic pumps, and a CTO-20A column thermostat, coupled with a high-resolution Orbitrap QExactive Plus mass spectrometer (Thermo Scientific, USA) with an orbital ion trap mass analyzer. The analysis time was 2 minutes. The mobile phase flow rate was set at 250 µL/min. The injection volume was 0.2 µL. The high-resolution mass spectrometer operated in positive ion detection mode under electrospray ionization conditions. Optimal ion source parameters were applied to achieve maximum analyte mass spectrum intensity: desolvation gas pressure – 30, sheath and auxiliary gas flows – 15 and 3 arbitrary units, desolvation line temperature – 320 °C, evaporator temperature – 200 °C, spray needle voltage – 3.8 kV, and S-lens RF voltage – 55 a.u. The mass spectrometer was operated in full scan mode over the m/z range 100–1500 Da with a resolving power of 70,000. Control of the mass spectrometer, data acquisition, and preliminary processing were performed using Xcalibur software (Thermo Scientific, USA). The XRD analysis was carried out using equipment of the Center for Joint Use “Spectroscopy and Analysis of Organic Compounds” at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch). The experiments were accomplished on the automated X-ray diffractometer “Xcalibur 3” with CCD detector on the standard procedure (MoKα-irradiation, graphite monochromator, ω-scans with a 1o step at T = 295(2) K). Empirical absorption correction was applied. The solution and refinement of the structures were accomplished using the Olex program package. The structures were solved by the method of the intrinsic phases in the ShelXT program and refined by ShelXL by the full-matrixleast-squared method for non-hydrogen atoms. The H atoms were placed in the calculated positions and were refined in isotropic approximation. The XRD data were deposited in the Cambridge Structural Database with CCDC numbers 2486258. This data can be requested free of charge via www.ccdc.cam.ac.uk.

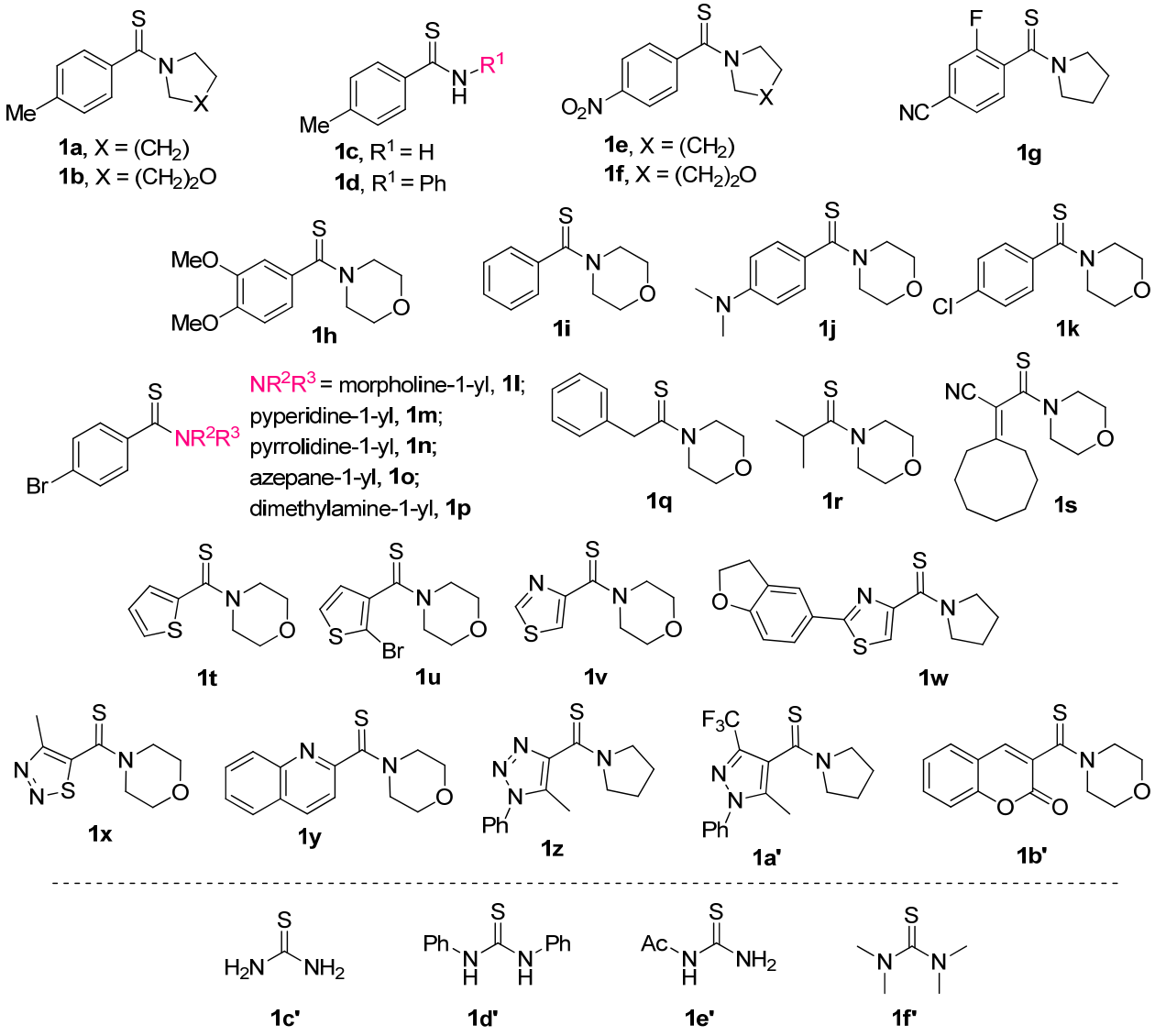
Preparation of Starting Reagents and Products

Thioamides **1a**, **b**, **i, k, m**,[1] **e**, **n**,[2] **f**, **h**,[3] **g**, **t**, **u**, **v**, **w**, **z**, **a′**,[4] **j**,[5] **b′**,[6] **l**,[7] **p**,[8] **q**,[9] **r**,[10] **s**,[11] **y**,[12] and iminoiodinanes **2a**,[13] **b**,[14] **c**,[15] **d**,[15] **e**,[16] **f**[17] were synthesized according to the previously reported procedures. Synthesis of thioamides **4a**,**b**[18] **c**,[19] **k**,[19] **l**,[20] **m**[20] also was previously reported.[14]

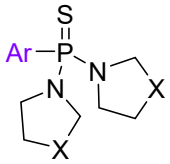
N-Sulfonyl amidines **3aa**,[21]**ba**,**da**,**fa**,**ga**,**ha**,**ia**,**ja**,**wa**[22],**na**[23],**oa**[24],**pa**[25],**ra**[26],**5aa**[27] were previously synthesized by different approaches and characterized.

Primary thioamide **1c** was synthesized by known procedure.[28]

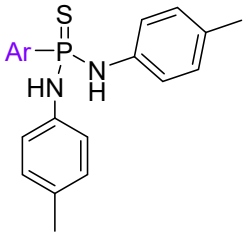
Thiocarbonyl Compounds were Used in the Research



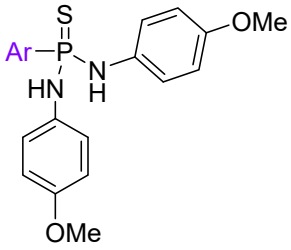
Thiophosphonyl Diamides were Used in the Research



4a, X = CH_2;
4b, X = CH_2O



4c



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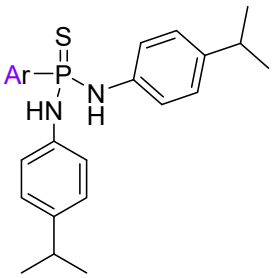

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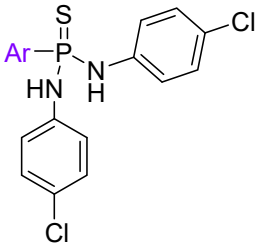

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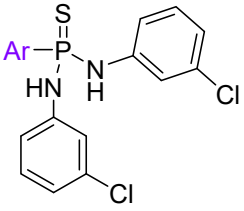

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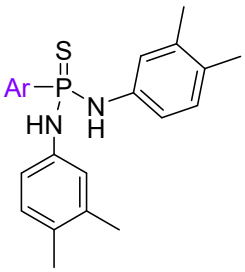
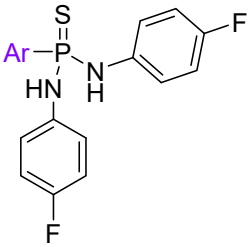


4h



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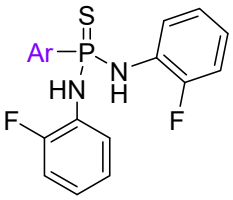
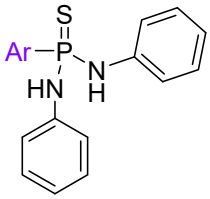
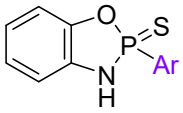


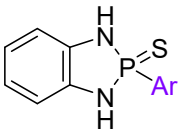
4j



4k



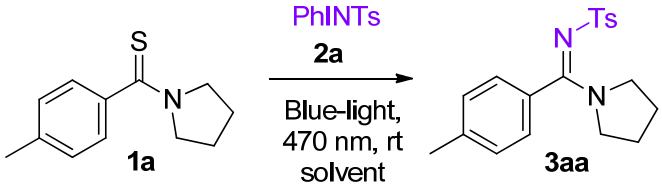
4l



4m

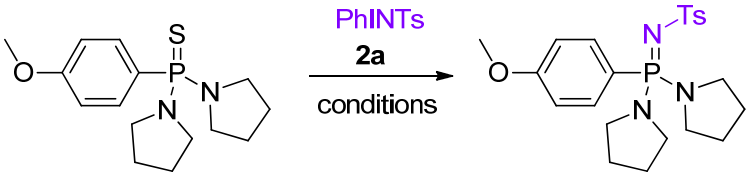
Ar = C_6H_4OMe-*p*

Evaluation of the Reaction of Thioamide 1a with Iminoiodinane 2a



Entry	Equiv of **2a**	Cat. (mol %)	Solv. (*T*, ºC)	Time, h	Yield of **3aa**, %
"Dark" conditions (Ar) **2a** was added in one portion to the solution of **1a** (2.5 mL) at rt					
1	1.5	CuI (5)	1,2-DCE (80)	24	49
2	1.5	$[CuCF_3SO_3]_2 \cdot C_6H_6$ (5)	1,2-DCE (80)	24	41
3	1.5	$Cu(OAc)_2$ (5)	1,2-DCE (80)	24	70
4	1.5	$Cu(OAc)_2$ (5)	EtOH (80)	24	60
5	1.5	$Cu(OAc)_2$ (5)	1,4-Dioxane (80)	24	64
6	1.5	$Cu(OAc)_2$ (10)	1,2-DCE (80)	24	80
1a (1.5 mL) was added dropwise to the suspension of **2a** (1.0 mL) at T					
7	1.5	$Cu(OAc)_2$ (10)	DCM (0 ºC to rt)	24	76
8	1.5	–	DCM (0 ºC to rt)	24	58
9	1.5	–	DCM (rt)	24	34
Under blue-light irradiation (Ar) (470 nm)					
10	1.5	–	DCM (rt)	2	69
11	1.7	–	DCM (rt)	2	54
2a was added in three portions after 10 min (1/3×3)					
12	**1.5**	–	**DCM (rt)**	**2**	**82**
13	1.5	–	Acetone (rt)	2	30
14	1.5	–	Ethanol (rt)	2	trace
15	1.5	–	MeCN (rt)	2	45
16	1.5	–	TFE (rt)	2	43
17	1.5	–	DCM (rt)[b)]	2	61
18	1.7	–	DCM (rt)	2	73
19	2.0	–	DCM (rt)	2	66
20	1.5	Eosin Y (1.0)	DCM (rt)	2	79
Under ambient light (Ar)					
21	1.5	–	DCM (rt)	2	40

Evaluation of the Reaction of Thiophosphonyldiamide 4a with Iminoiodinane 2a

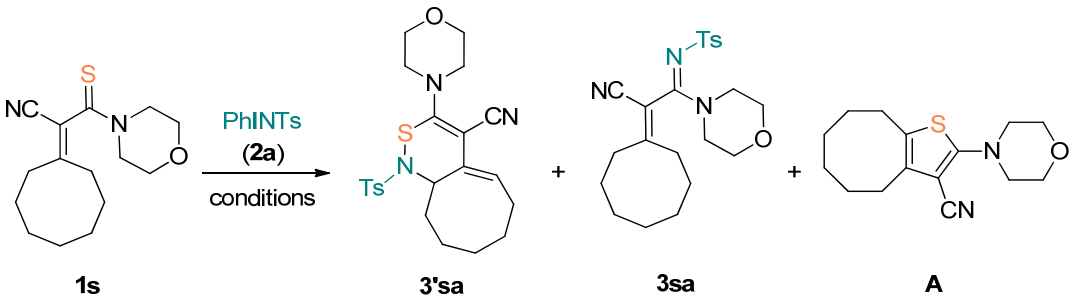


4a **5aa**

Entry	Equiv of **2a**	Cat. (mol %)	Solv. (T, ºC)	Time, h	Yield of **5aa**, %[a]
"Dark" conditions (Ar) **4a** was added dropwise (1.5 mL) to the suspension of **2a** (1 mL) at T, ºC					
1	2.95	$Cu(OAc)_2$ (10)	DCM (0 ºC to rt)	24	21
2	2.95	–	DCM (0 ºC to rt)	24	trace
470 nm (Ar) **2a** was added in several portions (see SI for details)					
3	2.95	–	DCM (rt)	3	37[b]
4	2.95	Eosin Y (2.0)	DCM (rt)	3	34[b]
5	2.95	4-CzIPN (2.0)	DCM (rt)	3	34[b]
6	2.95	$Ru(phen)_3(PF_6)_2$ (1.0)	DCM (rt)	3	46[b]
7	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	DCM (rt)	3	47[b]
8	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	MeCN (rt)	3	22[b]
9	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	1,4-Dioxane (rt)	3	NR[b]
10	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	1,2-DCE (rt)	3	43[b]
11	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFE (rt)	3	15[b]
12	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT (rt)	3	51[b]
13	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT (rt)	3	42[b,c]
14	3.45	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT (rt)	3	45[b]
15	2.5	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT (rt)	3	41[b]
16	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT (rt)	3	55[d]
17	**2.95**	**$Ru(bpy)_3Cl_2·6H_2O$ (1.0)**	**TFT (rt)**	**3**	**67[e]**
18	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT, 3 mL (rt)	3	66[e]
19	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT, 2 mL (rt)	3	66[e]
20	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (0.5)	TFT (rt)	3	64[e]
21	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (0.5)	TFT (rt)	4	58[e]
22	2.95	–	TFT (rt)	3	10[e]
23	2.95	$Ru(bpy)_3Cl_2·6H_2O$ (1.0)	TFT/DCM 1:1 (rt)	3	35[e]

Evaluation of the Reaction of Thioamide 1q with Iminoiodinane 2a

Table S1. Evaluation of the Reaction of Thioamide **1q** with Iminoiodinane **2a**

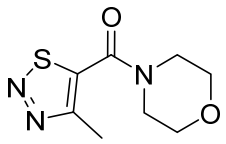


1s **3'sa** **3sa** **A**

Entry	Equiv of **2a**	Cat. (mol %)	Solv. (T, °C)	Yield of **3′sa**/**3sa**/**A** (%)
"Dark" conditions (Ar)				
	Salt (**2a**) was added in one portion			
1	2.0	–	DCM (rt)	NR
2	**3.0**	**$[Cu(MeCN)_4]PF_6$ (5)**	**DCM (0)**	**18/41/trace**
3	2.0	$[Cu(MeCN)_4]PF_6$ (5)	DCM (0)	20/21/29
4	1.5	$[Cu(MeCN)_4]PF_6$ (5)	DCM (0)	26/16/50
5	1.05	$[Cu(MeCN)_4]PF_6$ (5)	DCM (0)	4/13/50
6	3.0	$[Cu(MeCN)_4]PF_6$ (5)	DCE-1,2 (70)	10/15/trace
Under blue-light irradiation (Ar)				
7	3.0	-	DCM (rt)	Decomp.
8	3.0	$Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2)	DCM (rt)	19/16/15
9	3.0	Eosin Y (2)	DCM (rt)	34/trace/20
10	3.0	Eosin Y (10)	DCM (0)	52/trace/8

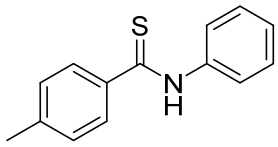
Preparation of Amides and Thioamides

(4-Methyl-1,2,3-thiadiazol-5-yl)(morpholino)methanone (Am-1)



A mixture of 4-methyl-1,2,3-thiadiazole-5-carboxylic acid (500 mg, 1 equiv, 3.47 mmol), thionyl chloride (3 mL) and five drops of DMF in benzene (2 mL) was stirred at 80 °C for 2.0 h in a round-bottom flask (25 mL). The flask was cooled to room temperature, and the solution was concentrated under reduced pressure. Dry 1,4-dioxane (3 mL) was added to the residue, and the solution was cooled down to 15 °C. Then, the solution of morpholine (604 mg, 2 equiv, 6.93 mmol) and Et_3N (422 mg, 1 equiv, 4.17 mmol) in dry 1,4-dioxane (3 mL) was added dropwise. The formed yellow solution was stirred at rt for 3 h and concentrated under reduced pressure. The purification of the crude product by column chromatography on SiO_2 (eluent PE/EtOAc, gradient 3:2 to 1:4) afforded the desired product **Am-1** as a colorless powder (91%, 676 mg), mp 106–108 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 3.66 (br. s, 4H), 3.55 (br. s, 2H), 3.23 (br. s, 2H), 2.64 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-*d*$_6$): δ 159.5, 156.5, 143.1, 65.9, 65.7, 47.1, 42.3, 12.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_8H_{12}N_3O_2S^+$ 214.0645; found 214.0648.

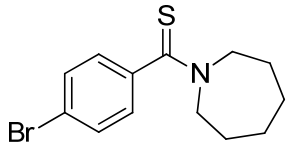
4-Methyl-*N*-phenylbenzothioamide (1d)



P_4S_{10} (3787 mg, 1.2 equiv, 8.52 mmol) was added to dry pyridine (20 mL), and the resulting suspension was stirred at room temperature (rt) for 30 min. 4-Methyl-*N*-phenylbenzamide (1500 mg, 1.0 equiv, 7.10 mmol) was then added to the suspension, and the flask was transferred to an oil bath preheated to 115 °C. After 3.5 h, the solution was cooled to rt, and 20 mL of 2 M HCl was added. The crude product was extracted with DCM (2 × 25 mL), and the organic layer was washed with 20 mL of 2 M HCl, then with a saturated solution of $NaHCO_3$ (2 × 25 mL), and finally with distilled water (20 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was kept in the hood overnight to crystallize. Diethyl ether (25 mL) was then added, and the suspension was stirred at rt for 30 min. After filtration and washing with hexane and diethyl ether, the product **1d** was obtained as a yellow powder (79%, 1271 mg). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 11.65 (s, 1H), 7.82 – 7.77 (m, 4H), 7.43 (t, J = 7.7 Hz, 2H), 7.28

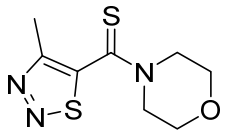
(d, J = 7.5 Hz, 3H), 2.37 (s, 3H). $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6): δ 197.3, 140.8, 140.1, 139.8, 128.5, 128.4, 127.5, 126.1, 124.3, 20.9.

Azepan-1-yl(4-bromophenyl)methanethione (1m)



A mixture of 4-bromobenzaldehyde (370 mg, 1 equiv, 2 mmol), azepane (198 mg, 1 equiv, 2 mmol) and sulfur (128 mg, 2 equiv, 4 mmol) was heated at 100 °C for 2.5 h in an oven-dried 10 mL standard microwave vial. The vial was cooled to room temperature, then DCM (2 mL) was added, and the solution was transferred on the column filled with SiO_2. The purification of the crude product by column chromatography (eluent PE/DCM, gradient 4:1 to 3:1) afforded the desired product **1m** as a colorless powder (78%, 465 mg), mp 98–99 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.22 – 4.19 (m, 2H), 3.57 – 3.54 (m, 2H), 2.02 – 1.96 (m, 2H), 1.71 – 1.65 (m, 2H), 1.62 – 1.59 (m, 4H). $^{13}C\{1H\}$ NMR (100 MHz, $CDCl_3$-*d*): δ 199.3, 143.0, 131.6, 127.1, 122.1, 54.6, 53.9, 29.2, 27.5, 26.3, 25.5. HRMS (ESI) m/z: $[M+H]^+$ calcd. for $C_{13}H_{17}BrNS$ 298.0260; found: 298.0269.

(4-Methyl-1,2,3-thiadiazol-5-yl)(morpholino)methanethione (1v)



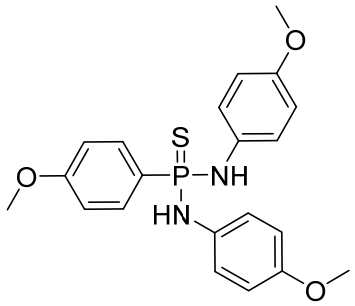
A mixture of (4-methyl-1,2,3-thiadiazol-5-yl)(morpholino)methanone (618 mg, 1 equiv, 2.90 mmol) and Lawesson's reagent (1172 mg, 1 equiv, 2.90 mmol) in dry 1,4-dioxane (10 mL) was stirred at 101 °C for 1 h in a round-bottom flask (25 mL). The flask was cooled to room temperature, and the solution was concentrated under reduced pressure. The residue was treated with ethanol (5 mL) and kept in a fridge for 2 h. The formed precipitate was filtered off and washed with cold ethanol (3 mL) to afford the desired product **1v** as a yellow powder (83%, 552 mg), mp 153–155 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 4.31 – 4.28 (m, 2H), 3.81 – 3.78 (m, 2H), 3.61 – 3.58 (m, 2H), 3.52 – 3.50 (m, 2H), 2.56 (s, 3H). $^{13}C\{1H\}$ NMR (100 MHz, DMSO-d_6): δ 183.7, 153.6, 149.8, 65.8, 65.4, 52.2, 48.8, 12.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_8H_{12}N_3OS_2^+$ 230.0416; found 214.0421.

Preparation of Thiophosphonyl Diamides 4

General procedure

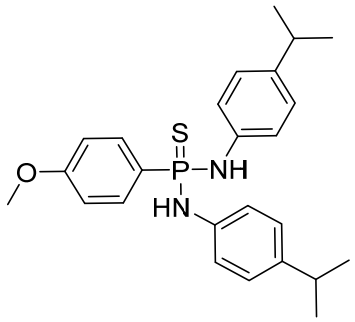
A mixture of Lawesson's reagent (1.0 equiv) and appropriate aniline derivative (4.0 equiv) in xylene was stirred for 6-8 h at 140 °C in a 25 mL round-bottom flask with the attached reflux condenser. The reaction solution was cooled to room temperature, washed with 1 M HCl (3x10 mL) and then with water (3x10 mL) (in the case of product **4g** xylene was evaporated under reduced pressure, and the residue was dissolved in DCM and washed). The organic layer was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The residue was dissolved in DCM and mixed with SiO_2 (or neutral alumina for product **4f**), and the solvent was evaporated under reduced pressure. The purification of the crude product by column chromatography on SiO_2 (or neutral alumina for product **4f**) afforded the desired products **4**.

***N*,*N'*-Bis(4-methoxyphenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4d)**



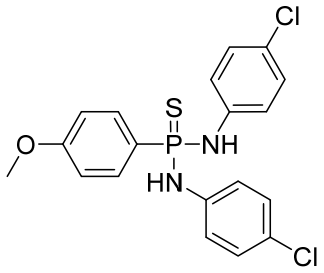
Compound **4d** was obtained according to the general procedure from Lawesson's reagent (2000 mg, 1.0 equiv, 4.94 mmol), 4-methoxyaniline (2430 mg, 4.0 equiv, 19.78 mmol), xylene (20 mL), reaction time is 7 h. The purification of the crude product by column chromatography on SiO_2 (eluent DCM) with subsequent centrifugation in a mixture Et_2O/EtOAc (1:0.25) afforded product **4d** as a colorless powder (85%, 1740 mg), mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.89 – 7.83 (m, 2H), 7.00 (d, J = 8.8 Hz, 4H), 6.92 – 6.89 (m, 2H), 6.75 (d, J = 8.9 Hz, 4H), 4.92 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 53.65. ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 162.8 (d, J = 3.2 Hz), 155.8, 133.2 (d, J = 13.0 Hz), 132.9 (d, J = 3.2 Hz), 125.7 (d, J = 130.9 Hz), 122.3 (d, J = 5.7 Hz), 114.6, 114.17 (d, J = 15.2 Hz), 55.6, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{24}N_2O_3PS^+$ 415.1240; found 415.1255.

***N*,*N'*-Bis(4-(propan-2-yl)phenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4e)**



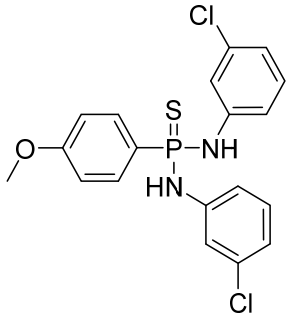
Compound **4e** was obtained according to the general procedure from Lawesson's reagent (404 mg, 1.0 equiv, 1 mmol), 4-(propan-2-yl)aniline (540 mg, 4.0 equiv, 4 mmol), xylene (6 mL), reaction time is 6 h. The purification of the crude product by column chromatography on SiO_2 (eluent DCM) afforded product **4e** as a colorless powder (52%, 230 mg), mp 113–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.95 – 7.90 (m, 2H), 7.07 (d, J = 8.4 Hz, 4H), 6.99 (d, J = 8.3 Hz, 4H), 6.95 – 6.92 (m, 2H), 5.08 (d, J = 8.1 Hz, 2H), 3.84 (s, 3H), 2.87 – 2.77 (m, 2H), 1.20 (s, 3H), 1.19 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 52.16. ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 162.8 (d, J = 3.3 Hz), 143.2, 137.6 (d, J = 2.6 Hz), 133.2 (d, J = 13.3 Hz), 127.3, 125.9 (d, J = 132.1 Hz), 119.7 (d, J = 6.2 Hz),114.3 (d, J = 15.4 Hz), 55.5, 33.5, 24.1. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{25}H_{32}N_2OPS^+$ 439.1967; found 439.1984.

***N*,*N*'-Bis(4-chlorophenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4f)**



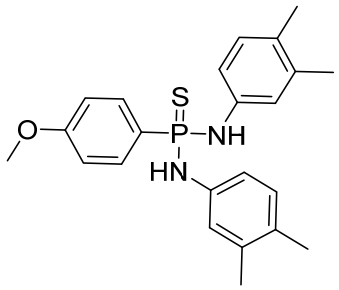
Compound **4f** was obtained according to the general procedure from Lawesson's reagent (809 mg, 1.0 equiv, 2 mmol), 4-chloroaniline (1021 mg, 4.0 equiv, 8 mmol), xylene (6 mL), reaction time is 7 h. The purification of the crude product by column chromatography on SiO_2 (eluent DCM) with subsequent centrifugation in Et_2O (3 mL) afforded product **4f** as a colorless powder (60%, 507 mg), mp 170–172 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.21 (d, J = 9.9 Hz, 2H), 7.88 – 7.82 (m, 2H), 7.22 – 7.17 (m, 8H), 7.11 – 7.09 (m, 2H), 3.81 (s, 3H). ^{31}P NMR (162 MHz, DMSO-d_6): δ 49.05. ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 162.2 (d, J = 2.9 Hz), 140.5, 133.0 (d, J = 13.5 Hz), 128.4, 125.6 (d, J = 130.7 Hz), 126.4, 120.2 (d, J = 7.4 Hz), 114.1 (d, J = 15.2 Hz), 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}Cl_2N_2OPS^+$ 423.0249; found 423.0265.

***N*,*N*'-Bis(3-chlorophenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4g)**



Compound **4g** was obtained according to the general procedure from Lawesson's reagent (1500 mg, 1.0 equiv, 3.71 mmol), 3-chloroaniline (1892 mg, 4.0 equiv, 14.83 mmol), xylene (10 mL), reaction time is 8 h. The purification of the crude product by column chromatography on neutral Al_2O_3 (eluent PE/EtOAc, gradient is up to 4:1) with subsequent trituration in a mixture Et_2O/hexane (1:1) and centrifugation (centrifugation was repeated in Et_2O (2 mL)) afforded product **4g** as a colorless powder (42%, 655 mg), mp 133–134 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.37 (d, J = 10.1 Hz, 2H), 7.89 – 7.83 (m, 2H), 7.26 (s, 2H), 7.21 – 7.11 (m, 6H), 6.89 (d, J = 7.9 Hz, 2H), 3.83 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-d): δ 48.7. ^{13}C{1H} NMR (100 MHz, $CDCl_3$-d): δ 162.3 (d, J = 3.1 Hz), 143.1, 133.1, 132.9, 130.2, 125.3 (d, J = 131.2 Hz), 120.4, 118.1 (d, J = 7.7 Hz), 117.2 (d, J = 7.5 Hz), 114.14 (d, J = 15.2 Hz), 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}Cl_2N_2OPS^+$ 423.0249; found 423.0264.

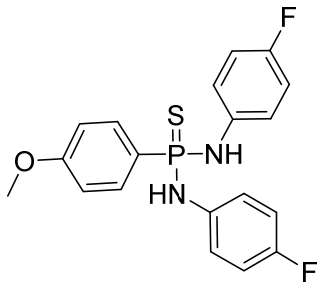
***N*,*N'*-Bis(3,4-dimethylphenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4h)**



Compound **4h** was obtained according to the general procedure from Lawesson's reagent (600 mg, 1.0 equiv, 1.48 mmol), 3,4-dimethylaniline (719 mg, 4.0 equiv, 5.93 mmol), xylene (5 mL), reaction time is 7 h. The purification of the crude product by column chromatography on SiO_2 (eluent PE/DCM, gradient 4:1 to 0:5) with subsequent trituration in hexane and centrifugation in a mixture Et_2O/EtOAc (3:1) afforded product **4h** as a colorless powder (63%, 385 mg), mp 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 7.95 – 7.89 (m, 2H), 6.96 – 6.91 (m, 4H), 6.85 – 6.82 (m, 4H), 5.03 (d, J = 8.3 Hz, 1H), 3.83 (s, 3H), 2.16 (s, 12H). ^{31}P NMR (162 MHz, $CDCl_3$-d): δ 52.32. ^{13}C{1H} NMR (100 MHz, $CDCl_3$-d): δ 162.7 (d, J = 3.2 Hz), 137.7 (d, J = 2.7 Hz), 137.5, 133.2 (d, J = 13.3 Hz), 130.8, 130.3, 126.1 (d, J = 132.0 Hz), 121.3 (d, J = 6.5 Hz), 117.2 (d, J =

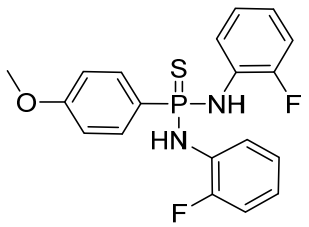
5.8 Hz), 114.2 (d, J = 15.4 Hz), 55.5, 20.0, 19.0. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{23}H_{28}N_2OPS^+$ 411.1654; found 411.1669.

***N*,*N*'-Bis(4-fluorophenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4i)**



Compound **4i** was obtained according to the general procedure from Lawesson's reagent (809 mg, 1.0 equiv, 2 mmol), 4-fluoroaniline (889 mg, 4.0 equiv, 8 mmol), xylene (7 mL), reaction time is 7 h. The purification of the crude product by column chromatography on SiO_2 (eluent DCM) with subsequent centrifugation in Et_2O (3 mL) afforded product **4i** as a colorless powder (52%, 409 mg), mp 149–150 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (d, J = 9.7 Hz, 2H), 7.89 – 7.83 (m, 2H), 7.20 – 7.16 (m, 4H), 7.11 – 7.08 (m, 2H), 7.01 (t, J = 8.9 Hz, 4H), 3.82 (s, 3H). ^{31}P NMR (162 MHz, DMSO-d_6): δ 49.76. ^{19}F NMR (565 MHz, DMSO-d_6): δ -123.17. ^{13}C{1H} NMR (151 MHz, DMSO-d_6): δ 162.1 (d, J = 2.8 Hz), 157.0 (d, J = 237.1 Hz), 137.9, 133.0 (d, J = 13.2 Hz), 126.1 (d, J = 130.1 Hz), 120.3 (t, J = 7.4 Hz), 115.1 (d, J = 22.2 Hz), 114.0 (d, J = 14.8 Hz), 55.4. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}F_2N_2OPS^+$ 391.0840; found 391.0854.

***N*,*N*'-Bis(2-fluorophenyl)-*P*-(4-methoxyphenyl)phosphonothioic diamide (4j)**



Compound **4j** was obtained according to the general procedure from Lawesson's reagent (600 mg, 1.0 equiv, 1.48mmol), 2-fluoroaniline (659 mg, 4.0 equiv, 5.93 mmol), xylene (5 mL), reaction time is 8 h. The purification of the crude product by column chromatography on SiO_2 (eluent PE/EtOAc, gradient 5:0 to 4:1) with subsequent trituration in hexane (3 mL) and centrifugation in a mixture Et_2O/hexane (0.5:3) afforded product **4j** as a colorless powder (49%, 285 mg), mp 122–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.97 – 7.91 (m, 2H), 7.47 – 7.43 (m, 2H), 7.07 – 6.97 (m, 6H), 6.95 – 6.89 (m, 2H), 5.41 (dd, J = 8.2, 3.2 Hz, 2H), 3.85 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 53.04. ^{19}F NMR (565 MHz, $CDCl_3$-*d*): δ -131.87. ^{13}C{1H} NMR (100 MHz, $CDCl_3$-*d*): δ 163.2 (d, J = 3.2 Hz), 154.6 (d, J = 8.2 Hz), 152.2 (d, J = 8.2 Hz), 133.0 (d, J = 13.7 Hz),

128.1 (d, J = 12.0 Hz), 125.1 (d, J = 133.2 Hz), 124.6 (d, J = 3.8 Hz), 122.9 (d, J = 7.4 Hz), 120.3 (d, J = 5.1 Hz), 115.3 (d, J = 19.4 Hz), 114.6 (d, J = 15.7 Hz), 55.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{18}F_2N_2OPS^+$ 391.0840; found 391.0853.

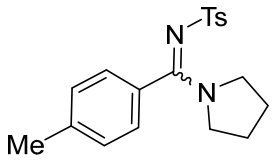
Preparation of *N*-Sulfonyl Amidines 3

General procedure

Method A. The Schlenk tube (10 mL) equipped with a magnetic stirring bar was purged with argon three times, then thioamide **1** (1.0 equiv) and dry degassed DCM (2.5 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 5 min and irradiated with blue LEDs (470 nm, 30 W, 25 cm from the light source, cooling with fun). Then iminoiodinane PhINTs (**2a**) (1.5 – 2.45 equiv) was added in several portions (1/3 every 10 min (1/3×3)), and the reaction mixture was additionally stirred under irradiation upon consumption of starting thioamides. The reaction solution was transferred on SiO_2 and purified to afford *N*-sulfonyl amidine **3**. In the case of *N*-sulfonyl amidines **3wa**,**za** the solution of thioamide **1w** or **1z** in DCM (2.0 mL) was added dropwise to the stirred suspension of iminoiodinane **2a** in DCM (1.5 mL) under irradiation.

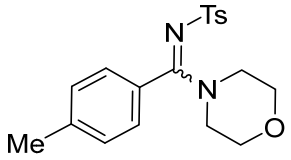
Method B. The Schlenk tube (10 mL) equipped with a magnetic stirring bar was purged with argon for three times, then iminoiodinane PhINTs (**2a**) (1.5 – 2.0 equiv), $Cu(OAc)_2$ (10.0 mol %) and dry degassed DCM (1.0 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 5 min, and the tube was transferred into an ice bath. After 10 min, thioamide **1** (1.0 equiv) in 1.5 mL of DCM was added via syringe, and the reaction mixture was additionally stirred at 0 °C for 30 min and then 24 h at room temperature. The reaction solution was transferred on SiO_2 and purified to afford *N*-sulfonyl amidine **3**.

4-Methyl-*N*-(pyrrolidin-1-yl(*p*-tolyl)methylene)benzenesulfonamide (3aa)



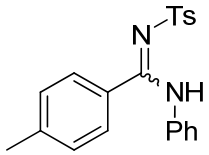
Method A. Thioamide **1a** (40 mg, 1.0 equiv, 0.19 mmol), PhINTs (**2a**) (109 mg, 1.5 equiv, 0.29 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 24:3) afforded product **3aa** (82%, 55 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.53 (d, J = 7.4 Hz, 2H), 7.14 – 7.04 (m, 6H), 3.69 – 3.66 (m, 2H), 3.09 – 3.06 (m, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 1.99 – 1.89 (m, 2H), 1.87 – 1.77 (m, 2H).

4-Methyl-*N*-(morpholino(phenyl)methylene)benzenesulfonamide (3ba)



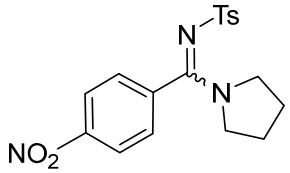
Method A. Thioamide **1b** (40 mg, 1.0 equiv, 0.18 mmol), PhINTs (**2a**) (101 mg, 1.5 equiv, 0.27 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/acetone, gradient 20:0 to 20:0.5) afforded product **3ba** (85%, 55 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.55 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 8.1 Hz, 2H), 3.90 (br. s, 2H), 3.75 (br. s, 2H), 3.54 (br. s, 2H), 3.14 (br. s, 2H), 2.38 (s, 3H), 2.36 (s, 3H).

4-Methyl-*N*-phenyl-*N*'-tosylbenzimidamide (3ca)



Method A. Thioamide **1c** (50 mg, 1.0 equiv, 0.22 mmol), PhINTs (**2a**) (123 mg, 1.5 equiv, 0.33 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 20:5) afforded product **3ca** (47%, 35 mg) as a colorless powder, mp 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 9.86 (br s, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.32 – 7.27 (m, 4H), 7.20 (t, J = 7.6 Hz, 2H), 7.13 (t, J = 7.3 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.94 (br s, 2H), 2.41 (s, 3H), 2.30 (s, 3H). ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 163.3, 143.1, 142.1, 139.5, 138.1, 130.2, 129.7, 129.5, 129.2, 129.0, 126.7, 126.2, 124.3, 21.6, 21.6. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{21}H_{21}N_2O_2S^+$ 365.1318; found 365.1328.

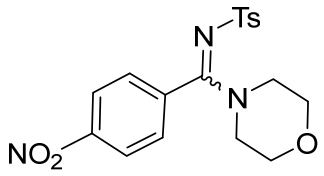
4-Methyl-*N*-((4-nitrophenyl)(pyrrolidin-1-yl)methylene)benzenesulfonamide (3ea)



Method A. Thioamide **1e** (60 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (142 mg, 1.5 equiv, 0.38 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:1.5) afforded product **3ea** (79%, 75 mg) as a colorless powder, mp 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.23 (d, J = 8.8 Hz, 2H), 7.49 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 3.57 – 3.53 (m, 2H), 3.02 – 2.99 (m, 2H), 2.34 (s, 3H), 1.93 – 1.86 (m, 2H), 1.82 – 1.76 (m, 2H). ^{13}C{1H} NMR (100 MHz, $CDCl_3$-

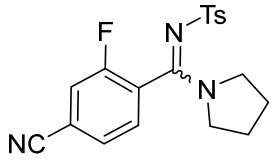
d): δ 161.3, 147.8, 141.5, 141.1, 139.8, 129.0, 128.8, 125.8, 123.1, 49.6, 48.3, 25.0, 23.8, 20.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{18}H_{20}N_3O_4S^+$ 374.1169; found 374.1183.

4-Methyl-*N*-(morpholino(4-nitrophenyl)methylene)benzenesulfonamide (3fa)



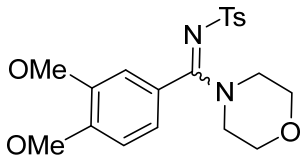
Method A. Thioamide **1f** (63 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (140 mg, 1.5 equiv, 0.37 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 40:10) afforded product **3fa** (75%, 73 mg) as a colorless powder, mp 195–196 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.96 – 3.86 (m, 2H), 3.82 – 3.74 (m, 2H), 3.61 – 3.53 (m, 2H), 3.14 – 3.06 (m, 2H), 2.39 (s, 3H).

***N*-((4-Cyano-2-fluorophenyl)(pyrrolidin-1-yl)methylene)-4-methylbenzenesulfonamide (3ga)**



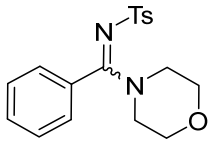
Method A. Thioamide **1g** (60 mg, 1.0 equiv, 0.26 mmol), PhINTs (**2a**) (143 mg, 1.5 equiv, 0.38 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:2) with subsequent centrifugation in Et_2O (1 mL) and hexane (2 mL) afforded product **3ga** (60%, 57 mg) as a colorless powder, mp 163–164 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94 (d, *J* = 10.6 Hz, 1H), 7.78 (d, *J* = 9.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.57 – 3.53 (m, 2H), 3.11 – 3.05 (m, 1H), 3.03 – 2.96 (m, 1H), 2.35 (s, 3H), 1.93 – 1.87 (m, 2H), 1.85 – 1.78 (m, 2H). ^{19}F NMR (565 MHz, DMSO-d_6): δ -111.46 – -111.43. ^{13}C{1H} NMR (100 MHz, DMSO-d_6): δ 156.8 (d, *J* = 249.4 Hz), 156.4, 141.2 (d, *J* = 124.7 Hz), 130.4 (d, *J* = 3.5 Hz), 129.1, 128.6 (d, *J* = 3.6 Hz), 126.5 (d, *J* = 18.2 Hz), 125.9, 119.6 (d, *J* = 25.1 Hz), 117.1 (d, *J* = 3.0 Hz), 114.3 (d, *J* = 9.9 Hz), 49.1, 48.4, 24.9, 23.8, 20.9. HRMS (ESI) m/z: $[M + H]^+$ calcd. for $C_{19}H_{19}FN_3O_2S^+$ 372.1176; found 372.1192.

***N*-((3,4-Dimethoxyphenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3ha)**



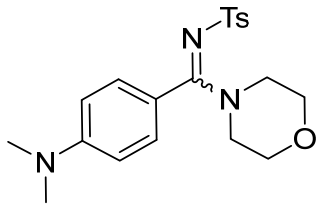
Method A. Thioamide **1h** (60 mg, 1.0 equiv, 0.22 mmol), PhINTs (**2a**) (126 mg, 1.5 equiv, 0.34 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on neutral Al_2O_3 (PE/EtOAc, gradient 25:0 to 5:20) afforded product **3ha** (65%, 55 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.47 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.81 (d, J = 8.3 Hz, 1H), 6.75 (dd, J = 8.2, 1.9 Hz, 1H), 6.54 (d, J = 1.9 Hz, 1H), 3.93 – 3.85 (m, 5H), 3.73 (br. s, 5H), 3.54 – 3.53 (m, 2H), 3.16 (br. s, 2H), 2.33 (s, 3H).

4-Methyl-*N*-(morpholino(phenyl)methylene)benzenesulfonamide (3ia)



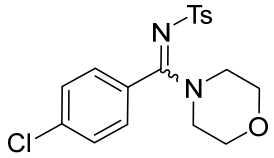
Method A. Thioamide **1i** (52 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (140 mg, 1.5 equiv, 0.38 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/acetone, gradient 20:0 to 20:1) afforded product **3ia** (87%, 75 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.51 (d, J = 8.3 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.38 – 7.34 (m, 2H), 7.16 – 7.14 (m, 2H), 7.12 (d, J = 8.0 Hz, 2H), 3.93 – 3.91 (m, 2H), 3.77 – 3.75 (m, 2H), 3.55 – 3.53 (m, 2H), 3.13 – 3.10 (m, 2H), 2.36 (s, 3H).

***N*-((4-(Dimethylamino)phenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3ja)**



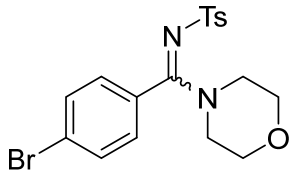
Method A. Thioamide **1j** (63 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (141 mg, 1.5 equiv, 0.38 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 40:10) afforded product **3ja** (77%, 75 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.58 (d, J = 8.2 Hz, 2H), 7.11 (t, J = 8.5 Hz, 4H), 6.62 (d, J = 8.8 Hz, 2H), 3.64 (br. s, 6H), 3.28 (br. s, 2H), 2.99 (s, 3H), 2.35 (s, 3H).

***N*-((4-Chlorophenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3ka)**



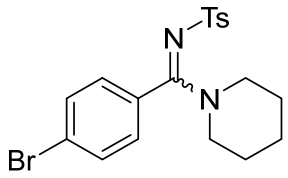
Method A. Thioamide **1k** (60 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (139 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 35:15) with subsequent centrifugation in Et_2O (1 mL) afforded product **3ka** (74%, 70 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.55 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.20 – 7.11 (m, 4H), 3.97 – 3.84 (m, 2H), 3.81 – 3.71 (m, 2H), 3.61 – 3.51 (m, 2H), 3.19 – 3.07 (m, 2H), 2.38 (s, 3H).

***N*-((4-Bromophenyl)(morpholino)methylene)-4-methylbenzenesulfonamide (3la)**



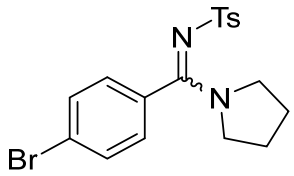
Method A. Thioamide **1l** (71 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (139 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/acetone, gradient 40:10 to 30:10) with subsequent centrifugation with Et_2O (2 mL) afforded product **3la** (71%, 75 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): 7.55 – 7.50 (m, 4H), 7.15 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 3.90 – 3.88 (m, 2H), 3.76 – 3.74 (m, 2H), 3.55 – 3.53 (m, 2H), 3.13 – 3.11 (m, 2H), 2.38 (s, 3H).

***N*-((4-Bromophenyl)(piperidin-1-yl)methylene)-4-methylbenzenesulfonamide (3ma)**



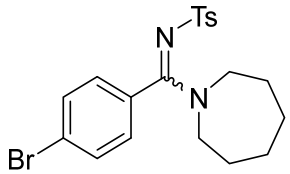
Method A. Thioamide **1m** (71 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (140 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/acetone, gradient 40:10 to 30:10) with subsequent centrifugation with Et_2O (2 mL) afforded product **3ma** (70%, 74 mg) as a colorless powder, mp 177–178 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.52 (d, J = 8.2 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.3 Hz, 2H), 3.84 (br. s, 2H), 3.07 – 3.05 (m, 2H), 2.37 (s, 3H), 1.67 (br. s, 2H), 1.43 (br. s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 164.3, 141.8, 141.2, 131.7, 131.2, 129.0, 129.0, 126.6, 124.4, 49.2, 46.1, 26.7, 25.6, 24.3, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}N_2O_2BrS^+$ 421.0585; found 421.0585.

***N*-((4-Bromophenyl)(pyrrolidin-1-yl)methylene)-4-methylbenzenesulfonamide (3na)**



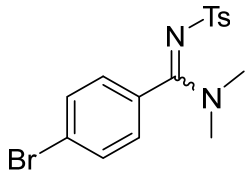
Method A. Thioamide **1n** (67 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (139 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/acetone, gradient 40:10 to 30:10) with subsequent centrifugation with Et_2O (2 mL) afforded product **3na** (74%, 75 mg) as a colorless powder, mp 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.54 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.69 – 3.66 (m, 2H), 3.08 – 3.04 (m, 2H), 2.37 (s, 3H), 1.99 – 1.92 (m, 2H), 1.88 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.5, 141.8, 141.3, 132.6, 131.7, 129.0, 128.8, 126.7, 124.3, 50.0, 48.5, 25.7, 24.5, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{20}N_2O_2BrS^+$ 407.0429; found 407.0429.

***N*-(Azepan-1-yl(4-bromophenyl)methylene)-4-methylbenzenesulfonamide (3oa)**



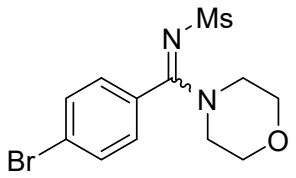
Method A. Thioamide **1o** (74 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (139 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:0.5) with subsequent centrifugation with Et_2O (2 mL) afforded product **3oa** (74%, 80 mg) as a colorless powder, mp 140–141 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.52 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 3.80 – 3.77 (m, 2H), 3.17 – 3.14 (m, 2H), 2.37 (s, 3H), 1.89 – 1.86 (m, 2H), 1.63 – 1.48 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 165.2, 141.7, 141.4, 131.6, 131.4, 129.1, 129.0, 126.6, 124.2, 50.5, 49.6, 29.3, 27.4, 26.2, 26.0, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}N_2O_2BrS^+$ 435.0742; found 435.0742.

4-Bromo-*N*,*N*-dimethyl-*N*'-tosylbenzimidamide (3pa)



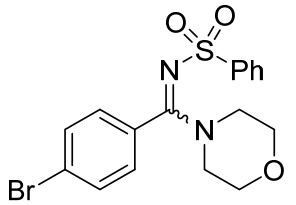
Method A. Thioamide **1p** (61 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (140 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:3) with subsequent centrifugation with Et_2O (2 mL) afforded product **3pa** (84%, 80 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.53 (d, J = 8.3 Hz, 2H), 7.49 (d, J =8.5 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 7.03 (d, J = 8.5 Hz, 2H), 3.20 (s, 3H), 2.77 (s, 3H), 2.37 (s, 3H).

***N*-((4-Bromophenyl)(morpholino)methylene)methanesulfonamide (3lb)**



Method B. Thioamide **1l** (71 mg, 1.0 equiv, 0.25 mmol), PhINMs (**2b**) (110 mg, 1.5 equiv, 0.37 mmol), $Cu(OAc)_2$ (6.7 mg). Reaction time is 24 h. Organic layer (DCM) was washed with water (2×5 mL) and dried with anhydrous Na_2SO_4. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 30:10 to 20:20) with subsequent centrifugation with Et_2O (2 mL) afforded product **3lb** (77%, 66 mg) as a colorless powder, mp 157–158 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.60 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 3.87 (br. s, 2H), 3.79 (br. s, 2H), 3.57 (br. s, 2H), 3.15 (br. s, 2H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 164.7, 132.2, 130.7, 129.2, 125.2, 66.8, 66.4, 48.3, 45.2, 43.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{16}N_2O_3BrS^+$ 347.0065; found 347.0064.

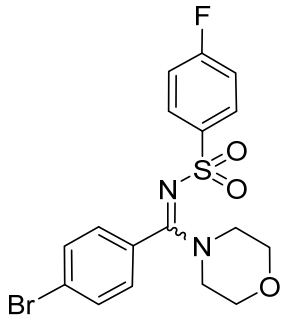
***N*-((4-Bromophenyl)(morpholino)methylene)benzenesulfonamide (3lc)**



Method B. Thioamide **1l** (72 mg, 1.0 equiv, 0.25 mmol), $PhINSO_2Ph$ (**2c**) (135 mg, 1.5 equiv, 0.38 mmol), $Cu(OAc)_2$ (6.8 mg). Reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 35:15 to 25:25) with subsequent centrifugation with Et_2O (2 mL) afforded product **3lc** (80%, 82 mg) as a colorless powder, mp 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.66 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.48 – 7.41 (m, 1H), 7.40 – 7.32 (m, 2H), 7.06 (d, J = 8.4 Hz, 2H), 3.97 – 3.86 (m, 2H), 3.82 – 3.70 (m, 2H), 3.62 – 3.51 (m, 2H), 3.20 – 3.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 164.9,

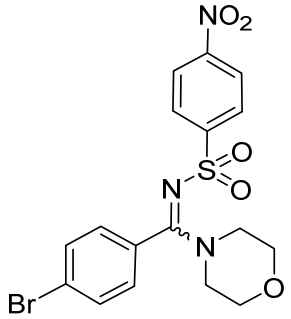
143.6, 132.0, 131.6, 130.4, 129.2, 128.5, 126.6, 124.9, 66.8, 66.5, 48.4, 45.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}BrN_2O_3S^+$ 409.0216; found 409.0233.

***N*-((4-Bromophenyl)(morpholino)methylene)-4-fluorobenzenesulfonamide (3ld)**



Method B. Thioamide **1l** (60 mg, 1.0 equiv, 0.21 mmol), $PhINSO_2C_6H_4F$-4 (**2d**) (119 mg, 1.5 equiv, 0.31 mmol), $Cu(OAc)_2$ (5.7 mg). Reaction time is 24 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:1.5) with subsequent centrifugation with Et_2O (2 mL) afforded product **3ld** (77%, 69 mg) as a colorless powder, mp 149–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.67 – 7.63 (m, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.07 – 7.01 (m, 4H), 3.90 – 3.88 (m, 2H), 3.77 – 3.75 (m, 2H), 3.56 – 3.54 (m, 2H), 3.15 – 3.12 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$-*d*): δ -107.23. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 164.8, 164.5 (d, J = 252.9 Hz), 139.5 (d, J = 3.2 Hz), 132.0, 130.2, 129.2 (d, J = 9.1 Hz), 129.1, 125.0, 115.6 (d, J = 22.4 Hz), 66.7, 66.4, 48.4, 45.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}BrFN_2O_3S$ 427.0122; found 427.0138.

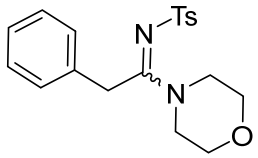
***N*-((4-Bromophenyl)(morpholino)methylene)-4-nitrobenzenesulfonamide (3le)**



Method B. Thioamide **1l** (60 mg, 1.0 equiv, 0.21 mmol), $PhINSO_2C_6H_4NO_2$-4 (**2e**) (169 mg, 2.0 equiv, 0.42 mmol), $Cu(OAc)_2$ (7.6 mg). Reaction time is 1.5 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 25:25) with subsequent centrifugation with Et_2O (2 mL) afforded product **3le** (65%, 62 mg) as a colorless powder, mp 194–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.24 (d, J = 8.8 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 3.90 – 3.87 (m, 2H), 3.79 – 3.76 (m, 2H), 3.60

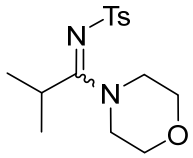
– 3.57 (m, 2H), 3.21 – 3.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 165.2, 149.5, 149.1, 132.3, 130.1, 129.0, 127.9, 125.5, 123.9, 66.7, 66.3, 48.6, 45.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}BrN_3O_5S$ 454.0067; found 454.0085.

4-Methyl-*N*-(1-morpholino-2-phenylethylidene)benzenesulfonamide (3qa)



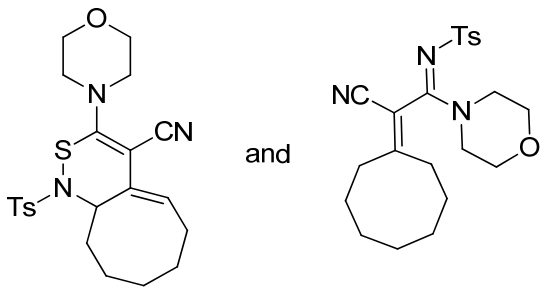
Method A. Thioamide **1q** (55 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (139 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 35:15 to 25:25) with subsequent centrifugation with Et_2O (2 mL) afforded product **3qa** (82%, 73 mg) as a colorless powder, mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.80 (d, J = 8.1 Hz, 2H), 7.30 – 7.15 (m, 7H), 4.43 (s, 2H), 3.78 (br. s, 2H), 3.61 (br. s, 2H), 3.32 (br. s, 4H), 2.38 (s, 3H).

4-Methyl-*N*-(2-methyl-1-morpholinopropylidene)benzenesulfonamide (3ra)



Method A. Thioamide **1r** (60 mg, 1.0 equiv, 0.35 mmol), PhINTs (**2a**) (194 mg, 1.5 equiv, 0.52 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 40:10 to 35:15) with subsequent centrifugation with Et_2O (2 mL) afforded product **3ra** (65%, 70 mg) as a colorless powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.79 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.12 (m, 1H), 3.73 – 3.62 (m, 8H), 2.39 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H).

3-Morpholino-1-tosyl-6,7,8,9,10,10a-hexahydro-1*H*-cycloocta[c][1,2]thiazine-4-carbonitrile (3′sa) and (*E*)-*N*-(2-Cyano-2-cyclooctylidene-1-morpholinoethylidene)-4-methylbenzenesulfonamide (3sa)

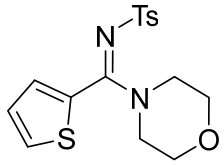


3'sa **3sa**

The Schlenk tube (10 mL) equipped with a magnetic stirring bar was purged with argon for three times, then thioamide **1s** (80 mg, 1.0 equiv, 0.29 mmol), $[Cu(MeCN)_4]PF_6$ (5.0 mol %, 16 mg) and dry degassed DCM (3.5 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 5 min, and the tube was transferred into an ice bath. After 10 min, iminoiodinane PhINTs (**2a**) (322 mg, 3.0 equiv, 0.86 mmol) was added in a one portion, and the reaction mixture was additionally stirred at 0 °C for 30 min. The reaction solution was transferred on SiO_2 and purified with eluents PE/EtOAc (gradient 25:0 to 30:20) to afford 1,2-thiazine **3′sa** (18%, 23 mg) as a colorless powder, mp 123–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.65 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 7.4 Hz, 2H), 5.74 (t, J = 8.5 Hz, 1H), 5.30 (dd, J = 11.7, 4.7 Hz, 1H), 3.70 – 3.65 (m, 2H), 3.61 – 3.56 (m, 2H), 3.48 – 3.42 (m, 2H), 3.18 – 3.12 (m, 2H), 2.43 (s, 3H), 2.40 – 2.35 (m, 1H), 2.30 – 2.21 (m, 1H), 2.01 – 1.94 (m, 1H), 1.89 – 1.64 (m, 4H), 1.46 – 1.39 (m, 1H), 1.35 – 1.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 156.8, 145.6, 132.8, 129.2, 128.5, 127.1, 125.9, 116.0, 87.8, 67.0, 55.8, 51.2, 34.4, 29.4, 27.2, 27.0, 24.0, 21.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{28}N_3O_3S_2$ 446.1566; found 446.1571.

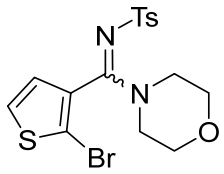
The fraction, containing *N*-sulfonyl amidine **3sa**, was additionally purified on neutral Al_2O_3 with eluents PE/EtOAc (gradient 25:0 to 15:35) to afford *N*-sulfonyl amidine **3sa** (41%, 31 mg) as a colorless powder, mp 134–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.79 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.82 – 3.64 (m, 6H), 3.59 – 3.53 (m, 1H), 3.49 – 3.43 (m, 1H), 2.84 – 2.78 (m, 1H), 2.70 – 2.56 (m, 2H), 2.40 (s, 3H), 2.37 – 2.30 (m, 1H), 2.06 – 1.89 (m, 2H), 1.82 – 1.42 (m, 8H), 1.16 – 1.07 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 173.6, 156.1, 142.7, 140.2, 129.4, 126.7, 114.2, 102.0, 66.6, 66.2, 47.7, 45.2, 33.9, 33.7, 28.2, 27.9, 26.0, 25.6, 23.9, 21.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{30}N_3O_3S$ 416.2002; found 416.2004.

4-Methyl-*N*-(4-morpholinyl-2-thienylmethylene)benzenesulfonamide (3ta)



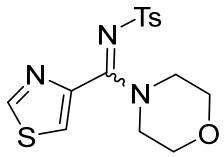
Method A. Thioamide **1t** (60 mg, 1.0 equiv, 0.28 mmol), PhINTs (**2a**) (210 mg, 2.0 equiv, 0.56 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 20:0 to 20:30) with subsequent centrifugation with Et_2O (2 mL) afforded product **3ta** (78%, 76 mg) as a colorless powder, mp 174–175 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.81 (d, J = 6.1 Hz, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.16 (dd, J = 3.5, 1.2 Hz, 1H), 7.12 (dd, J = 4.9, 3.7 Hz, 1H), 3.60 (br. s, 8H), 2.34 (s, 3H).

***N*-((2-Bromothiophen-3-yl)(morpholino)methylene)-4-methylbenzenesulfonamide (3ua)**



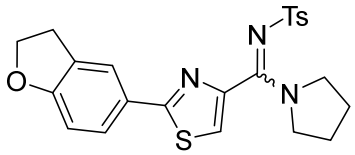
Method A. Thioamide **1u** (66 mg, 1.0 equiv, 0.22 mmol), PhINTs (**2a**) (168 mg, 2.0 equiv, 0.45 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:3) afforded product **3ua** (76%, 74 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.52 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 5.7 Hz, 1H), 7.14 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 5.7 Hz, 1H), 3.96 – 3.93 (m, 2H), 3.78 – 3.75 (m, 2H), 3.73 – 3.67 (m, 1H), 3.59 – 3.54 (m, 1H), 3.24 – 3.18 (m, 1H), 3.13 – 3.07 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 159.9, 142.2, 139.9, 131.9, 129.1, 128.6, 127.4, 126.8, 112.7, 66.8, 66.3, 47.7, 45.2, 21.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{18}BrN_2O_3S_2^+$ 428.9937; found 428.9954.

4-Methyl-*N*-(morpholino(thiazol-4-yl)methylene)benzenesulfonamide (3va)



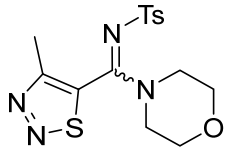
Method A. Thioamide **1v** (60 mg, 1.0 equiv, 0.28 mmol), PhINTs (**2a**) (157 mg, 1.5 equiv, 0.42 mmol). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:25 to 0:50) with subsequent centrifugation with Et_2O/hexane (1:1) afforded product **3va** (72%, 71 mg) as a colorless powder, mp 139–140 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.13 (d, J = 1.8 Hz, 1H), 8.00 (d, J = 1.8 Hz, 1H), 7.48 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 3.78 (br. s, 2H), 3.68 (br. s, 2H), 3.53 (br. s, 2H), 3.05 (br. s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.2, 154.6, 144.1, 141.5, 140.9, 129.1, 125.8, 123.6, 65.9, 65.4, 47.9, 45.0, 20.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}N_3O_3S_2^+$ 352.0784; found 352.0798.

***N*-((2-(2,3-Dihydrobenzofuran-5-yl)thiazol-4-yl)(pyrrolidin-1-yl)methylene)-4-methylbenzenesulfonamide (3wa)**



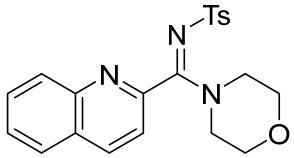
Method A. Thioamide **1w** (40 mg, 1.0 equiv, 0.13 mmol), PhINTs (**2a**) (71 mg, 1.5 equiv, 0.19 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 20:0 to 35:15) with subsequent centrifugation with Et_2O/hexane (0.5:3 mL) afforded product **3wa** (72%, 41 mg) as a colorless powder, mp 197–200 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.80 (s, 1H), 7.63 (s, 1H), 7.54 (d, J = 9.7 Hz, 1H), 7.43 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.85 (d, J = 8.3 Hz, 1H), 4.61 (t, J = 8.7 Hz, 2H), 3.56 (t, J = 7.0 Hz, 1H), 3.26 – 3.18 (m, 4H), 2.19 (s, 3H), 1.94 – 1.87 (m, 2H), 1.84 – 1.78 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.0, 161.8, 158.0, 145.2, 141.1, 141.0, 128.8, 128.6, 127.0, 125.9, 125.1, 123.4, 121.4, 109.3, 71.7, 49.2, 48.4, 39.9, 28.6, 25.0, 23.8, 20.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}N_3O_3S_2^+$ 454.1253; found 454.1269.

4-Methyl-*N*-((4-methyl-1,2,3-thiadiazol-5-yl)(morpholino)methylene)benzenesulfonamide (3xa)



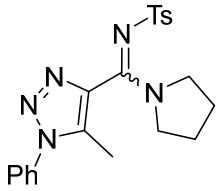
Method A. Thioamide **1x** (40 mg, 1.0 equiv, 0.17 mmol), PhINTs (**2a**) (159 mg, 2.45 equiv, 0.43 mmol). Reaction time is 1.5 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 40:10 to 35:15) with subsequent centrifugation with Et_2O (1 mL) afforded product **3xa** (63%, 41 mg) as a colorless powder, mp 160–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 7.51 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 3.96 – 3.94 (m, 2H), 3.78 – 3.76 (m, 2H), 3.58 – 3.56 (m, 2H), 3.05 – 3.03 (m, 2H), 2.49, 2.39. ^{13}C NMR (100 MHz, $CDCl_3$-d): δ 158.2, 155.5, 143.1, 139.3, 137.3, 129.4, 126.7, 66.6, 66.3, 47.9, 45.7, 21.6, 12.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{19}N_4O_3S_2^+$ 367.0893; found 367.0908.

4-Methyl-*N*-(morpholino(quinolin-2-yl)methylene)benzenesulfonamide (3ya)



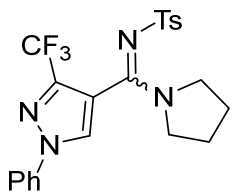
Method A. Thioamide **1y** (50 mg, 1.0 equiv, 0.19 mmol), PhINTs (**2a**) (177 mg, 2.45 equiv, 0.47 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on neutral Al_2O_3 (PE/EtOAc, gradient 20:0 to 15:35) with subsequent centrifugation with Et_2O (2 mL) afforded product **3ya** (70%, 53 mg) as a colorless powder, mp 111–114 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (d, J = 8.2 Hz, 1H), 8.07 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.6 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.73 – 7.69 (m, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.45 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 3.87 – 3.85 (m, 2H), 3.75 – 3.72 (m, 2H), 3.52 – 3.49 (m, 2H), 3.03 – 3.00 (m, 2H), 2.31 (s, 3H).

4-Methyl-*N*-((5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)(pyrrolidin-1-yl)methylene)benzenesulfonamide (3za)



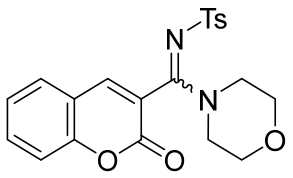
Method A. Thioamide **1z** (50 mg, 1.0 equiv, 0.18 mmol), PhINTs (**2a**) (168 mg, 2.45 equiv, 0.45 mmol). Reaction time is 1 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:5.5) with subsequent centrifugation with hexane (2 mL) afforded product **3za** (73%, 55 mg) as a colorless powder, mp 138–140 °C. ^{1}H NMR (400 MHz, $CDCl_3$-d): δ 7.62 – 7.50 (m, 7H), 7.17 (d, J = 7.6 Hz, 2H), 3.71 – 3.68 (m, 2H), 3.36 – 3.33 (m, 2H), 2.45 (s, 3H), 2.35 (s, 3H), 1.98 – 1.91 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$-d): δ 155.4, 142.0, 141.0, 137.8, 135.8, 134.9, 130.0, 129.7, 129.1, 126.5, 125.2, 49.8, 48.9, 25.6, 24.5, 21.6, 10.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{24}N_5O_2S^+$ 410.1645; found 410.1660.

4-Methyl-*N*-((1-phenyl-3-(trifluoromethyl)-1*H*-pyrazol-4-yl)(pyrrolidin-1-yl)methylene)benzenesulfonamide (3a′a)



Method A. Thioamide **1a′** (60 mg, 1.0 equiv, 0.18 mmol), PhINTs (**2a**) (169 mg, 2.45 equiv, 0.45 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:1.5) with subsequent centrifugation with Et_2O (2 mL) afforded product **3a′a** (55%, 47 mg) as a colorless powder, mp 189–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 8.08 (s, 1H), 7.70 – 7.67 (m, 2H), 7.53 – 7.40 (m, 5H), 7.09 (d, J = 8.3 Hz, 2H), 3.73 – 3.70 (m, 2H), 3.25 – 3.22 (m, 2H), 2.32 (s, 3H), 2.02 – 1.96 (m, 2H), 1.93 – 1.87 (m, 2H). ^{19}F NMR (565 MHz, $CDCl_3$-*d*): δ -61.71. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 155.6, 142.2, 140.0, 139.69 (q, J = 38.1 Hz), 138.7, 129.9, 129.1, 129.1, 128.6, 126.7, 120.40 (q, J = 270.5 Hz), 120.1, 112.9 (d, J = 1.2 Hz), 49.7, 48.8, 25.6, 24.5, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}F_3N_4O_2S^+$ 463.1410; found 463.1430.

4-Methyl-*N*-(morpholino(2-oxo-2*H*-chromen-3-yl)methylene)benzenesulfonamide (3b′a)



Method A. Thioamide **1b′** (69 mg, 1.0 equiv, 0.25 mmol), PhINTs (**2a**) (140 mg, 1.5 equiv, 0.37 mmol). Reaction time is 2 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 25:25) afforded product **3b′a** (80%, 80 mg) as a colorless powder, mp 238–239 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.87 (s, 1H), 7.65 – 7.60 (m, 2H), 7.59 – 7.55 (m, 2H), 7.37 – 7.32 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.03 – 3.95 (m, 1H), 3.83 – 3.72 (m, 4H), 3.66 – 3.59 (m, 1H), 3.44 – 3.31 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 158.5, 157.1, 154.4, 143.9, 142.5, 140.3, 133.4, 129.2, 126.8, 125.2, 120.9, 117.9, 117.0, 66.6, 66.2, 48.0, 45.3, 21.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}N_2O_5S^+$ 413.1171; found 413.1170.

Reaction of Tetramethylthiourea 1f′ with Salt 2a

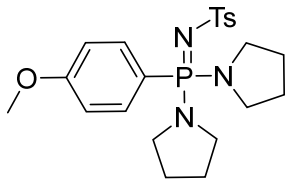
The Schlenk tube (10 mL) equipped with a magnetic stirring bar was purged with argon three times, then tetramethylthiourea **1f′** (50 mg, 1.0 equiv, 0.38 mmol) and dry degassed DCM (2.5 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 5 min and irradiated with blue LEDs (470 nm, 30 W, 25 cm from the light source, cooling with fun). Then iminoiodinane PhINTs (**2a**) (282 mg, 2.0 equiv, 0.76 mmol) was added in several portions (1/3 every 15 min (1/3×3)), and the reaction mixture was additionally stirred under irradiation for 3 h. The reaction solution was transferred on SiO_2 and purified by column chromatography on SiO_2 (PE/EtOAc, gradient 50:0 to 5:45) afforded product **3f′a** (23%, 24 mg) as a pale-yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.79 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.91 (s, 12H), 2.36 (s, 3H).

Preparation of *N*-Sulfonyl Amidines 5

General procedure

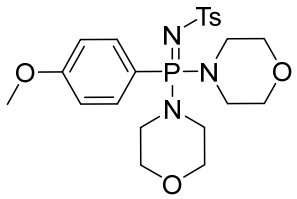
The Schlenk tube (10 mL) equipped with a magnetic stirring bar was purged with argon three times, then thioamide **4** (1.0 equiv), catalyst $Ru(bpy)_3Cl_2·6H_2O$ (1.0 mol %) and dry degassed solvent (2.5 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 5 min and irradiated with blue LEDs (470 nm, 15 W, 25 cm from the light source, cooling with fun). Then iminoiodinane PhINTs (**2a**) was added in several portions: 0.5 equiv every 10 min (0.5×3), 0.95 equiv after 30 min and, finally, 0.5 equiv after 1 h, and the reaction mixture was additionally stirred under irradiation upon consumption of starting thioamides. The solvent was evaporated, and the residue was purified by column chromatography on SiO_2 to afford *N*-sulfonyl amidine **5**.

N-((4-Methoxyphenyl)di(pyrrolidin-1-yl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5aa)



Thioamide **4a** (60 mg, 1.0 equiv, 0.19 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (4.3 mg), PhINTs (**2a**) (213 mg, 2.95 equiv, 0.57 mmol) and TFT (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (DCM/EtOAc, gradient 25:0 to 25:5) afforded product **5aa** (67%, 58 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.87 (d, J = 8.2 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.96 – 6.93 (m, 2H), 3.83 (s, 3H), 3.24 – 3.13 (m, 8H), 2.36 (s, 3H), 1.80 – 1.76 (m, 8H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 17.08.

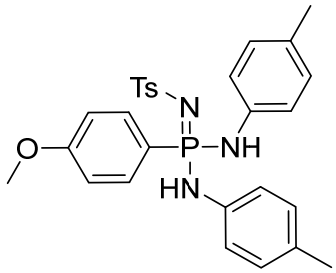
N-((4-Methoxyphenyl)dimorpholino-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ba)



Thioamide **4b** (60 mg, 1.0 equiv, 0.17 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (3.9 mg), PhINTs (**2a**) (193 mg, 2.95 equiv, 0.52 mmol) and DCM (2.5 mL). Reaction time is 4 h. The crude product was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 10:40). The residue was

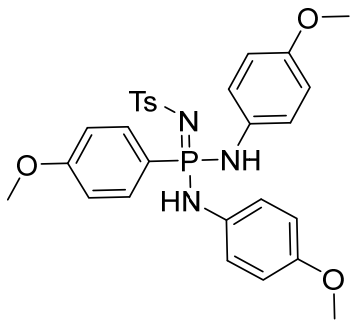
triturated in Et_2O/hexane (1:1), then $CHCl_3$ was added (1 mL). The resulting solution was partially evaporated in the fume hood. The formed suspension was centrifugated, and the mother liquor was evaporated under reduced pressure to afford product **5ba** (50%, 42 mg) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.84 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.98 (dd, J = 8.8, 3.1 Hz, 2H), 3.86 (s, 3H), 3.67 – 3.58 (m, 8H), 3.21 – 3.10 (m, 8H), 2.38 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 20.65. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.3 (d, J = 3.2 Hz), 143.7 (d, J = 6.0 Hz), 141.1, 134.4 (d, J = 11.1 Hz), 129.1, 125.8, 117.1 (d, J = 167.6 Hz), 114.8 (d, J = 15.0 Hz), 66.8, 66.7, 55.6, 45.3, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{31}N_3O_5PS^+$ 480.1716; found 480.1720.

***N*-((4-Methoxyphenyl)bis(p-tolylamino)- λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ca)**



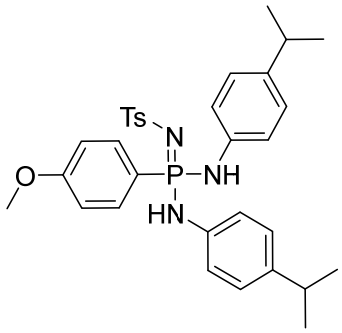
Thioamide **4c** (60 mg, 1.0 equiv, 0.16 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.5 mg), PhINTs (**2a**) (173 mg, 2.95 equiv, 0.46 mmol) and TFT (2.5 mL). Reaction time is 4 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent centrifugation in Et_2O afforded product **5ca** (52%, 42 mg) as a colorless powder, mp 196–197 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.81 – 7.75 (m, 2H), 7.62 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.84 – 6.78 (m, 10H), 6.34 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.31 (s, 3H), 2.20 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 5.28. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.4 (d, J = 3.3 Hz), 142.5 (d, J = 3.4 Hz), 141.0, 136.2, 134.6 (d, J = 12.7 Hz), 132.2, 129.7, 128.8, 126.0, 119.9 (d, J = 6.5 Hz), 118.5 (d, J = 169.7 Hz), 114.4 (d, J = 16.2 Hz), 55.4, 21.4, 20.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{32}N_3O_3PS^+$ 520.1818; found 520.1819.

***N*-((4-Methoxyphenyl)bis((4-methoxyphenyl)amino)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5da)**



Thioamide **4d** (60 mg, 1.0 equiv, 0.14 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.2 mg), PhINTs (**2a**) (159 mg, 2.95 equiv, 0.43 mmol) and DCM (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent trituration and centrifugation in a mixture Et_2O/hexane (1:1) and Et_2O (3×2 mL) afforded product **5da** (55%, 44 mg) as a colorless powder, mp 203 – 204 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.75 – 7.70 (m, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 8.8 Hz, 4H), 6.81 – 6.78 (m, 2H), 6.59 (d, J = 8.8 Hz, 4H), 6.18 (d, J = 8.9 Hz, 2H), 3.77 (s, 3H), 3.69 (s, 6H), 2.32 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 6.62. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.4 (d, J = 3.2 Hz), 155.9, 142.6 (d, J = 3.6 Hz), 141.1, 134.6 (d, J = 12.4 Hz), 131.4, 128.8, 126.0, 122.4 (d, J = 6.0 Hz), 118.6 (d, J = 168.8 Hz), 114.5, 114.4 (d, J = 16.2 Hz), 55.5, 55.4, 21.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{28}H_{31}N_3O_5PS^+$ 552.1716; found 552.1716.

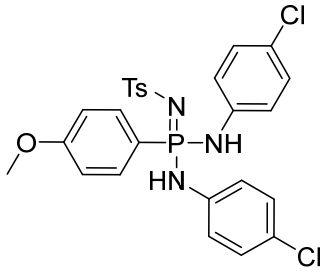
***N*-(Bis((4-isopropylphenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ea)**



Thioamide **4e** (60 mg, 1.0 equiv, 0.14 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.0 mg), PhINTs (**2a**) (151 mg, 2.95 equiv, 0.40 mmol) and TFT (2.5 mL). Reaction time is 6 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 25:25) with subsequent centrifugation in a mixture Et_2O/hexane (0.25:1) afforded product **5ea** (56%, 44 mg) as a colorless powder, mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.83 – 7.77 (m, 2H), 7.60 (d, J = 8.2 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.89 (d, J = 8.5 Hz, 4H), 6.84 – 6.80 (m, 6H), 6.33 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H), 2.79 – 2.73 (m, 2H), 2.29 (s, 3H), 1.17 (s, 6H), 1.15 (s, 6H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 5.25. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.4 (d, J = 3.2 Hz), 143.3, 142.4 (d,

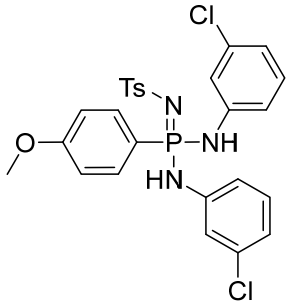
J = 3.2 Hz), 141.0, 136.3, 134.6 (d, *J* = 12.8 Hz), 128.7, 127.1, 126.1, 119.8 (d, *J* = 6.4 Hz), 118.6 (d, *J* = 169.9 Hz), 114.5 (d, *J* = 16.2 Hz), 55.5, 33.4, 24.1, 24.1, 21.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{32}H_{39}N_3O_3PS^+$ 576.2444; found 576.2457.

***N*-(Bis((4-chlorophenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5fa)**



Thioamide **4f** (60 mg, 1.0 equiv, 0.14 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (3.1 mg), PhINTs (**2a**) (156 mg, 2.95 equiv, 0.42 mmol) and TFT (2.5 mL). Reaction time is 5 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent centrifugation in a mixture Et_2O/hexane (1:1) afforded product **5fa** (59%, 47 mg) as a colorless powder, mp 211–213 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.60 (d, *J* = 11.4 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 4H), 7.10 – 7.00 (m, 8H), 3.82 (s, 3H), 2.26 (s, 3H). ^{31}P NMR (162 MHz, DMSO-d_6): δ 4.78. ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.9 (d, *J* = 3.2 Hz), 143.0 (d, *J* = 2.8 Hz), 140.2, 139.1, 134.1 (d, *J* = 13.2 Hz), 128.6, 128.4, 125.5, 125.2, 120.2 (d, *J* = 7.3 Hz), 118.3 (d, *J* = 155.6 Hz), 114.3 (d, *J* = 15.6 Hz), 55.5, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}Cl_2N_3O_3PS^+$ 560.0726; found 560.0745.

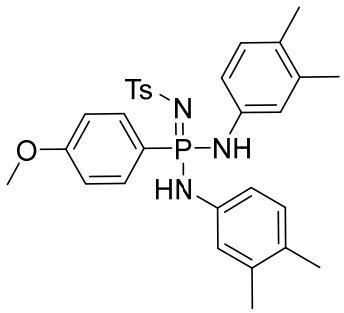
***N*-(Bis((3-chlorophenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ga)**



Thioamide **4g** (60 mg, 1.0 equiv, 0.14 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (3.1 mg), PhINTs (**2a**) (156 mg, 2.95 equiv, 0.42 mmol) and DCM (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 25:25) with subsequent centrifugation in a mixture Et_2O/hexane (0.5:1) afforded product **5ga** (61%, 48 mg) as a colorless

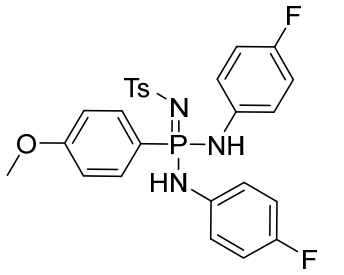
powder, mp 165–167 °C. ^{1}H NMR (400 MHz, $CDCl_3$-*d*): δ 7.87 – 7.81 (m, 2H), 7.72 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.87 – 6.77 (m, 10H), 3.76 (s, 3H), 2.37 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 3.60. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 163.8 (d, J = 3.2 Hz), 141.9, 141.7 (d, J = 4.9 Hz), 140.1 (d, J = 1.3 Hz), 135.0 (d, J = 12.9 Hz), 134.6, 130.1, 129.2, 125.9, 122.5, 119.1 (d, J = 7.7 Hz), 117.2 (d, J = 6.8 Hz), 116.9 (d, J = 174.8 Hz), 114.8 (d, J = 16.5 Hz), 55.5, 21.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}Cl_2N_3O_3PS^+$ 560.0726; found 560.0746.

***N*-(Bis((3,4-dimethylphenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ha)**



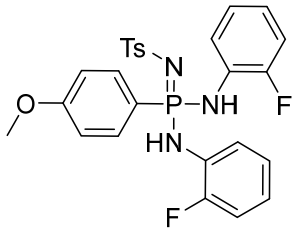
Thioamide **4h** (60 mg, 1.0 equiv, 0.15 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.2 mg), PhINTs (**2a**) (161 mg, 2.95 equiv, 0.43 mmol) and TFT (2.5 mL). Reaction time is 4.5 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) afforded product **5ha** (54%, 43 mg) as a colorless powder, mp 202–203 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08 (d, J = 11.8 Hz, 2H), 7.81 – 7.75 (m, 2H), 7.37 (d, J = 7.9 Hz, 2H), 7.02 (t, J = 8.5 Hz, 4H), 6.86 – 6.78 (m, 6H), 3.80 (s, 3H), 2.25 (s, 3H), 2.05 (s, 6H), 2.02 (s, 6H). ^{31}P NMR (162 MHz, DMSO-d_6): δ 4.49. ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.6 (d, J = 3.2 Hz), 143.4 (d, J = 3.0 Hz), 139.8, 137.7, 136.2, 134.0 (d, J = 12.9 Hz), 129.5, 129.0, 128.3, 125.2, 120.2 (d, J = 4.8 Hz), 119.4 (d, J = 152.6 Hz), 116.2 (d, J = 7.0 Hz), 113.9 (d, J = 15.4 Hz), 55.4, 20.8, 19.6, 18.5. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{30}H_{35}N_3O_3PS^+$ 548.2131; found 548.2147.

***N*-(Bis((4-fluorophenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ia)**



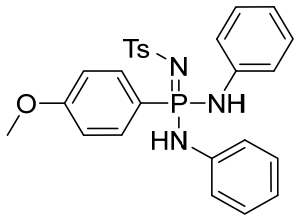
Thioamide **4i** (60 mg, 1.0 equiv, 0.15 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.4 mg), PhINTs (**2a**) (161 mg, 2.95 equiv, 0.45 mmol) and TFT (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent centrifugation in a mixture Et_2O/hexane (0.12:1) afforded product **5ia** (53%, 43 mg) as a colorless powder, mp 210–213 °C. ^1H NMR (400 MHz, DMSO-d_6): δ 8.38 (d, J = 11.3 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.37 (d, J = 8.2 Hz, 2H), 7.08 – 7.01 (m, 8H), 6.97 – 6.92 (m, 4H), 3.81 (s, 3H), 2.25 (s, 3H). ^{31}P NMR (162 MHz, DMSO-d_6): δ 5.31. ^{19}F NMR (565 MHz, DMSO-d_6): δ -122.09. ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.8 (d, J = 3.2 Hz), 157.5 (d, J = 237.9 Hz), 143.2 (d, J = 2.9 Hz), 140.1, 136.3 (d, J = 2.3 Hz), 134.1 (d, J = 13.0 Hz), 128.4, 125.3, 120.5 (t, J = 7.4 Hz), 118.7 (d, J = 155.1 Hz), 115.3 (d, J = 22.4 Hz), 114.2 (d, J = 15.5 Hz), 55.5, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}F_2N_3O_3PS^+$ 528.1317; found 528.1330.

***N*-(Bis((2-fluorophenyl)amino)(4-methoxyphenyl)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ja)**



Thioamide **4j** (60 mg, 1.0 equiv, 0.15 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.4 mg), PhINTs (**2a**) (161 mg, 2.95 equiv, 0.45 mmol) and TFT (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) afforded product **5ja** (49%, 40 mg) as a colorless powder, mp 181–183 °C. ^1H NMR (400 MHz, $CDCl_3$-*d*): δ 7.75 – 7.65 (m, 4H), 7.12 (t, J = 7.5 Hz, 2H), 6.97 (t, J = 8.5 Hz, 4H), 6.93 – 6.83 (m, 6H), 6.27 (d, J = 11.1 Hz, 2H), 3.80 (s, 3H), 2.27 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 5.92. ^{19}F NMR (565 MHz, $CDCl_3$-*d*): δ -129.74. ^{13}C NMR (100 MHz, $CDCl_3$-*d*): δ 164.0 (d, J = 3.3 Hz), 154.8 (d, J = 8.4 Hz), 152.4 (d, J = 8.5 Hz), 142.0 (d, J = 2.2 Hz), 141.3, 134.3 (d, J = 13.1 Hz), 128.8, 126.7 (d, J = 12.2 Hz), 126.0, 124.7 (d, J = 3.8 Hz), 123.9 (d, J = 7.4 Hz), 120.0 (d, J = 3.0 Hz), 117.2 (d, J = 170.0 Hz), 115.5 (d, J = 19.3 Hz), 114.7 (d, J = 16.4 Hz), 55.6, 21.4. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{25}F_2N_3O_3PS^+$ 528.1317; found 528.1329.

***N*-((4-Methoxyphenyl)bis(phenylamino)-λ^5-phosphanylidene)-4-methylbenzenesulfonamide (5ka)**



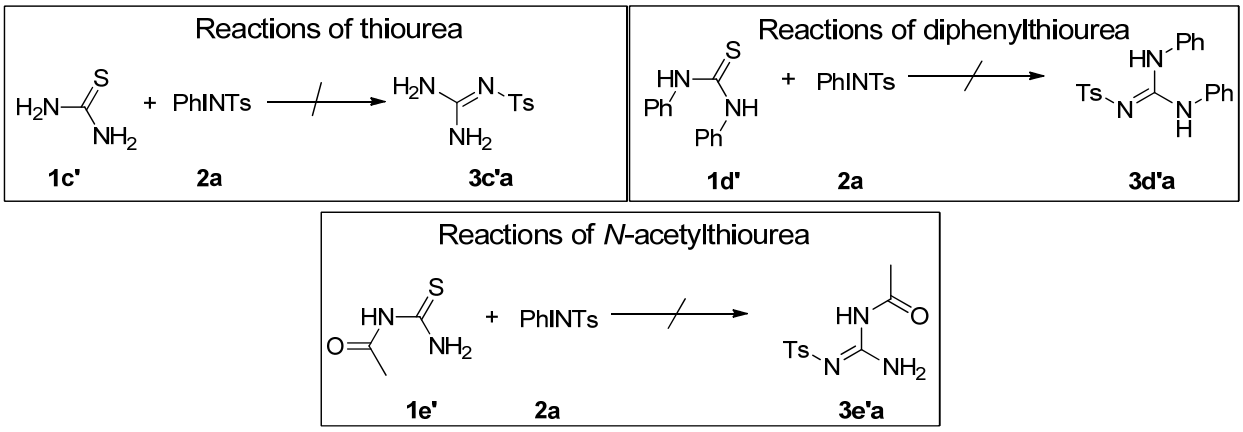
Thioamide **4k** (60 mg, 1.0 equiv, 0.17 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (3.7 mg), PhINTs (**2a**) (186 mg, 2.95 equiv, 0.50 mmol) and DCM (2.5 mL). Reaction time is 3 h. The purification of the crude product by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent centrifugation in a mixture Et_2O/hexane (0.15:1) afforded product **5ka** (57%, 47 mg) as a colorless powder, mp 168–171 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.36 (d, J = 11.7 Hz, 2H), 7.84 – 7.78 (m, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.12 – 7.04 (m, 10H), 7.01 (d, J = 7.9 Hz, 2H), 6.86 – 6.82 (m, 2H), 3.81 (s, 3H), 2.25 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$-*d*): δ 9.79. ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 162.8 (d, J = 3.2 Hz), 143.2 (d, J = 3.1 Hz), 140.1, 140.0, 134.1 (d, J = 13.0 Hz), 128.7, 128.4, 125.3, 121.4, 118.9 (d, J = 155.3 Hz), 118.7 (d, J = 7.3 Hz), 114.1 (d, J = 15.5 Hz), 55.5, 20.8. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{26}H_{27}N_3O_3PS^+$ 492.1505; found 492.1523.

Scaled-Up Synthesis

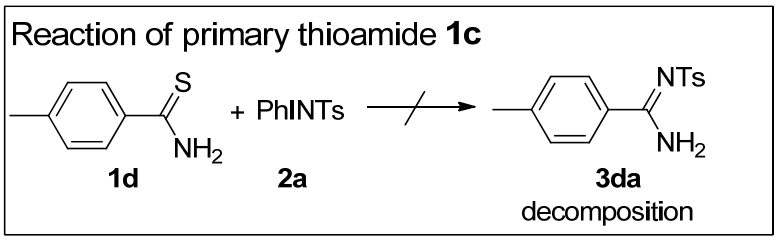
The Schlenk tube (20 mL) equipped with a magnetic stirring bar was purged with argon for three times, then thioamide **4b** (250 mg, 1.0 equiv, 0.65 mmol), catalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (14.0 mg, 1.0 mol %) and dry degassed TFT (12.5 mL) were added under argon atmosphere. The reaction solution was stirred at room temperature for 15 min and irradiated with blue LEDs (470 nm, 15 W, 25 cm from the light source). Then iminoiodinane PhINTs (**2a**) was added in several portions: 0.5 equiv every 20 min (3×0.5), 0.95 equiv after 1 h and, finally, 0.5 equiv after 1 h, and the reaction mixture was additionally stirred under irradiation upon consumption of starting thioamide. Reaction time is 5.7 h. The solvent was evaporated, and the residue was purified by column chromatography on SiO_2 (PE/EtOAc, gradient 25:0 to 30:20) with subsequent centrifugation in Et_2O afforded *N*-sulfonyl amidine **5ba** (55%, 186 mg) as a colorless powder.

Reactions of Thiocarbonyl Compounds with PhINTs (2a) were Unsuccessful

All reactions were performed according to the general procedures (method A) for the synthesis of *N*-sulfonyl amidines **3**.



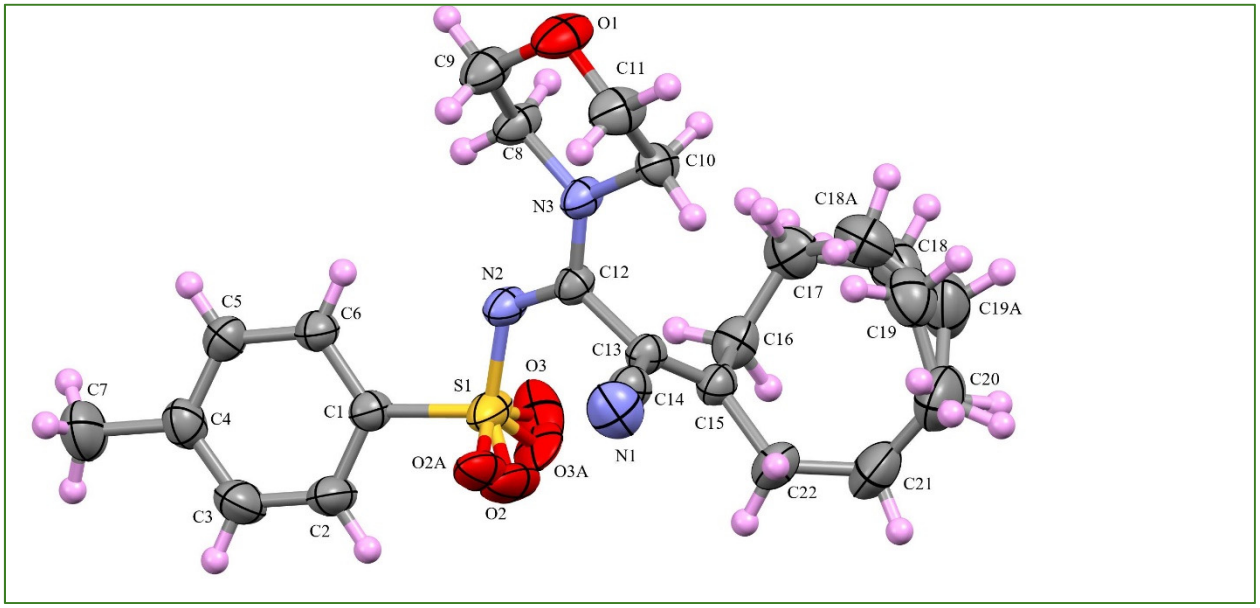
Conditions: 2.0 equiv of PhINTs **2a** (**2a** was added in three portions at 15-min intervals), 470 nm, 30 W, 2.5 mL DCM, 3 h



X-Ray Crystallographic Data

A single crystal of **3qa** was obtained by crystallization via evaporation at room temperature from its ethyl acetate–chloroform solution. The deposition number for **3qa** at the Cambridge Crystallographic Data Centre is CCDC 2486258.

Crystal Data for **3qa**. $C_{22}H_{29}N_3O_3S$ (M = 415.54 g/mol): monoclinic, space group P21/n, a = 9.1024(3) Å, b = 19.3688(6)Å, c = 12.6664(4) Å, β = 107.710(3)°, V = 2127.29(12) Å3, Z = 4, T = 295(2) K, μ(MoKα) = 0.180 mm^{-1}, Dcalc = 1.297 g/cm^3, 9274 reflections measured (4.88° ≤ 2Θ ≤ 62.16°), 5691 [R_{int} = 0.0254, R_{sigma} = 0.0555] which were used in all calculations. The final R_1 = 0.0597, wR_2 = 0.1558 (I > 2σ(I)) and R_1 = 0.1069, wR_2 = 0.1954 (all data). GooF = 1.021. Largest diff. peak/hole 0.41/-0.28.



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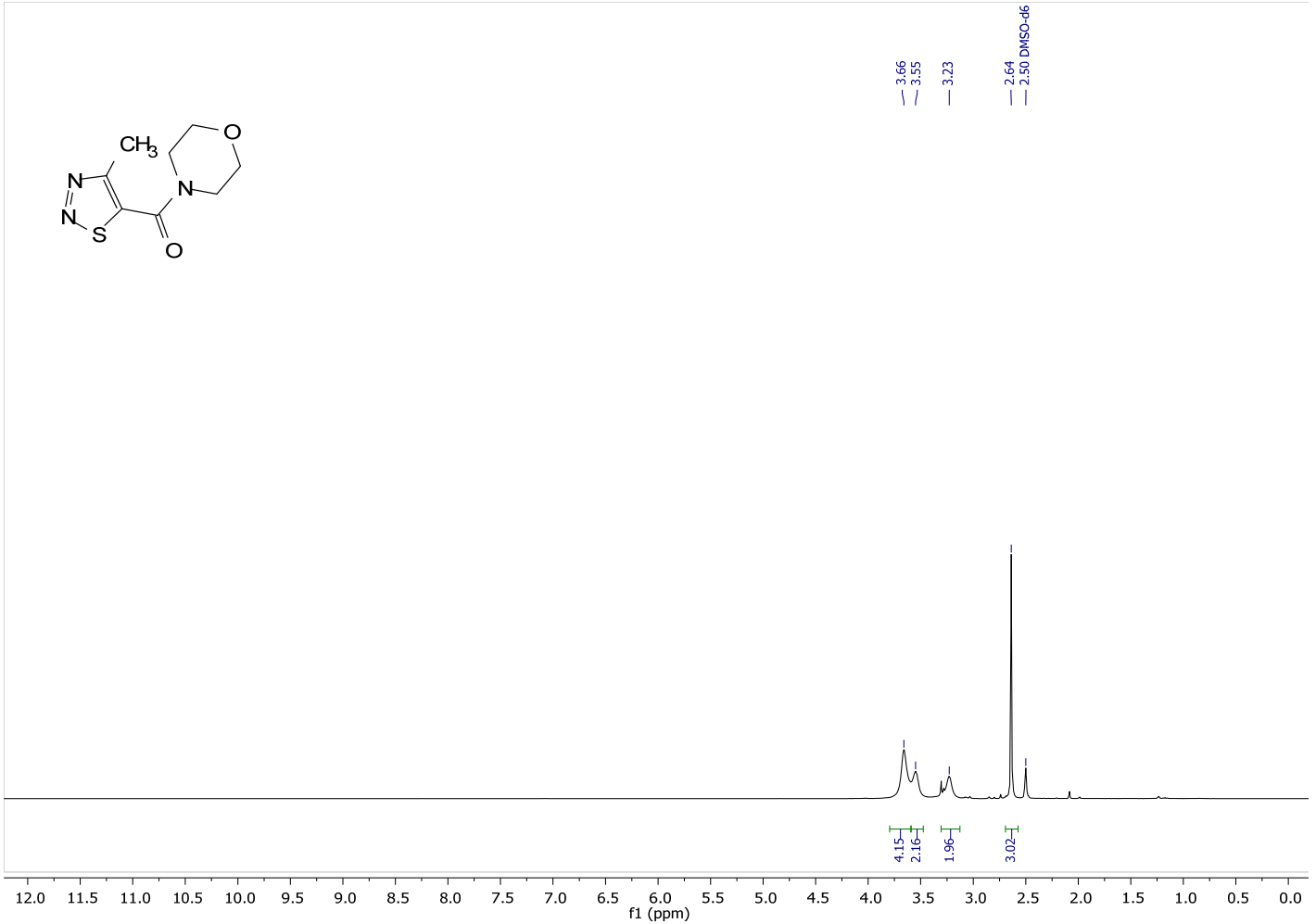
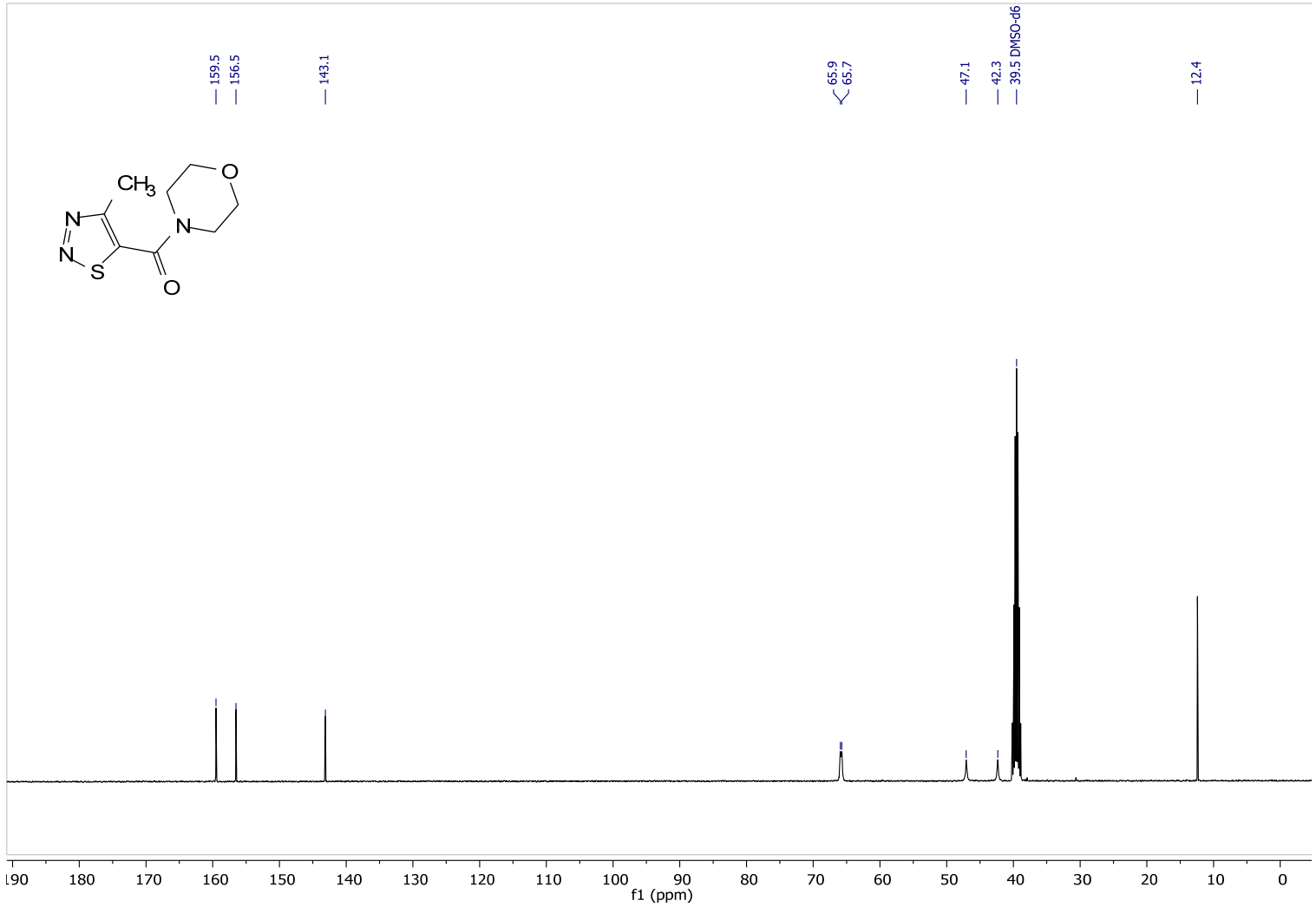
NMR spectra



^{1}H NMR (400 MHz, DMSO–d_6) of **Am-1**



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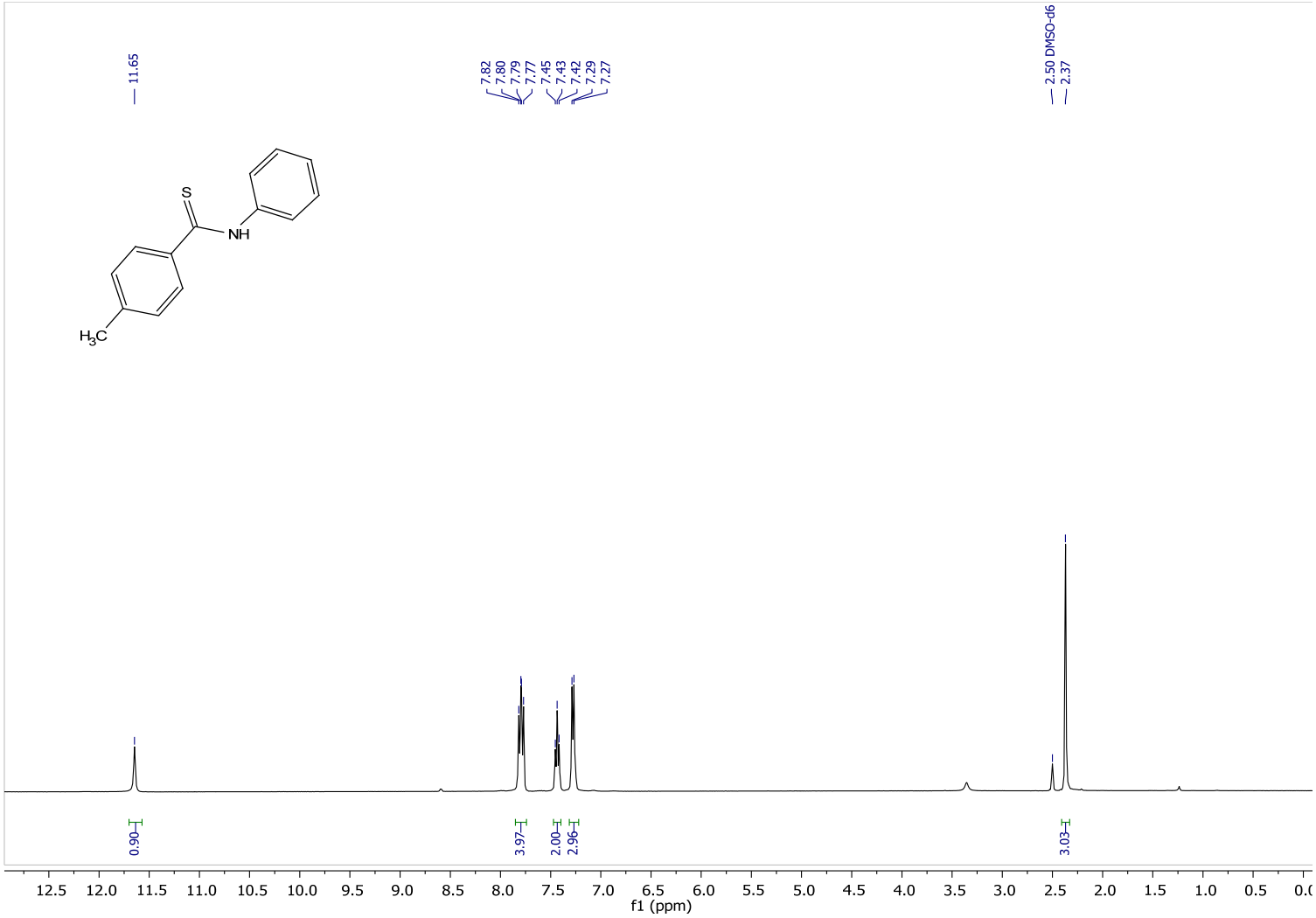

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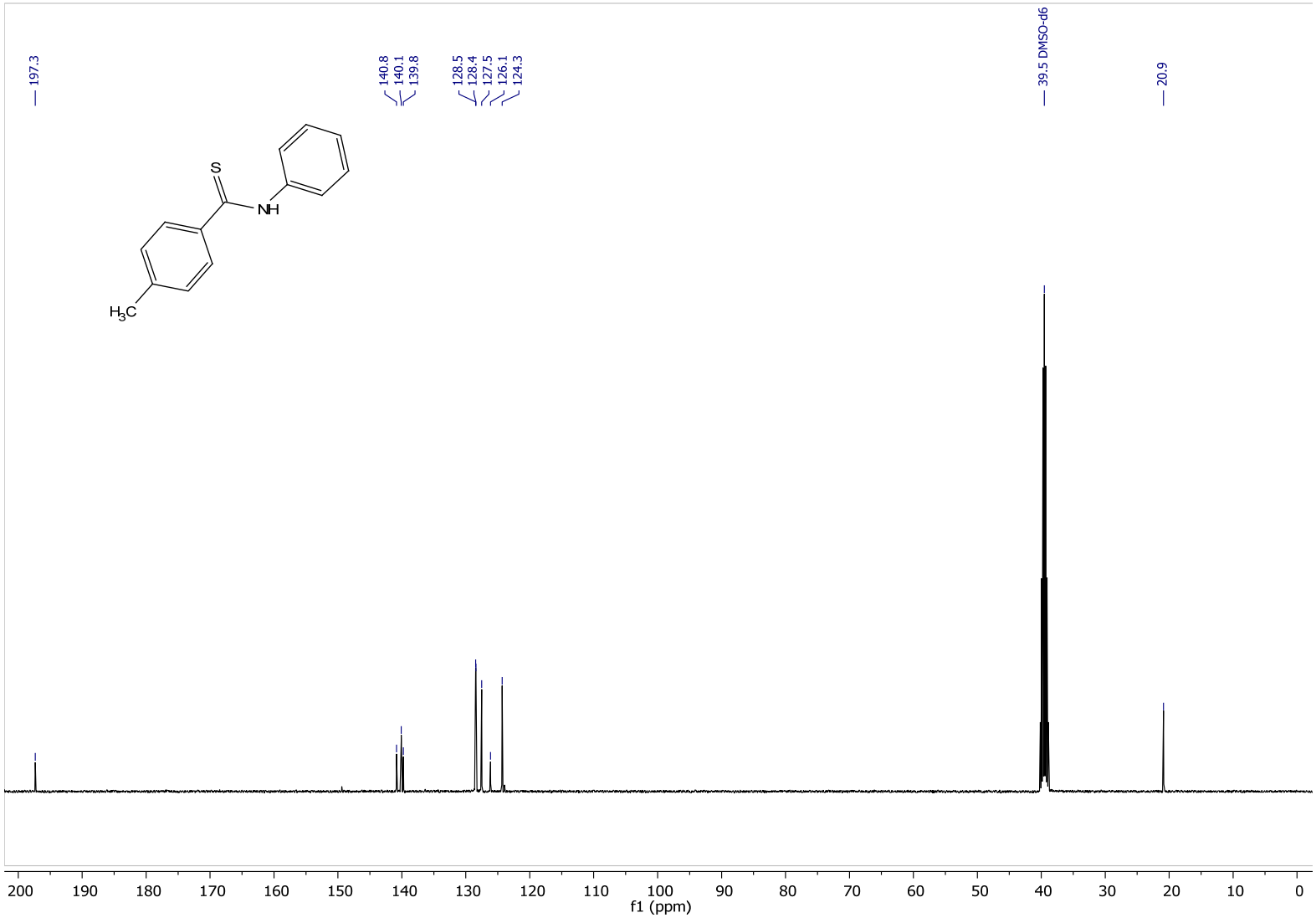

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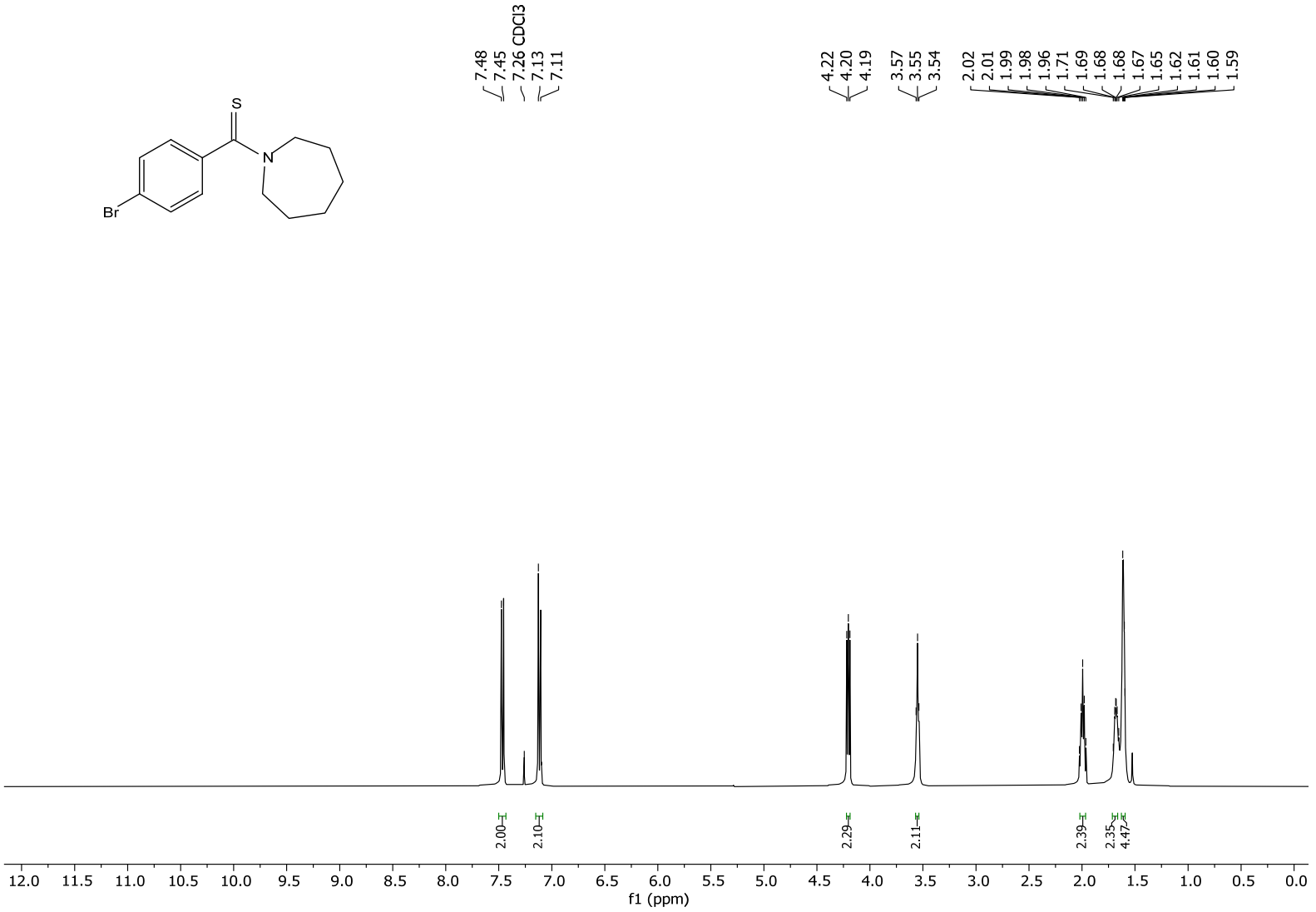

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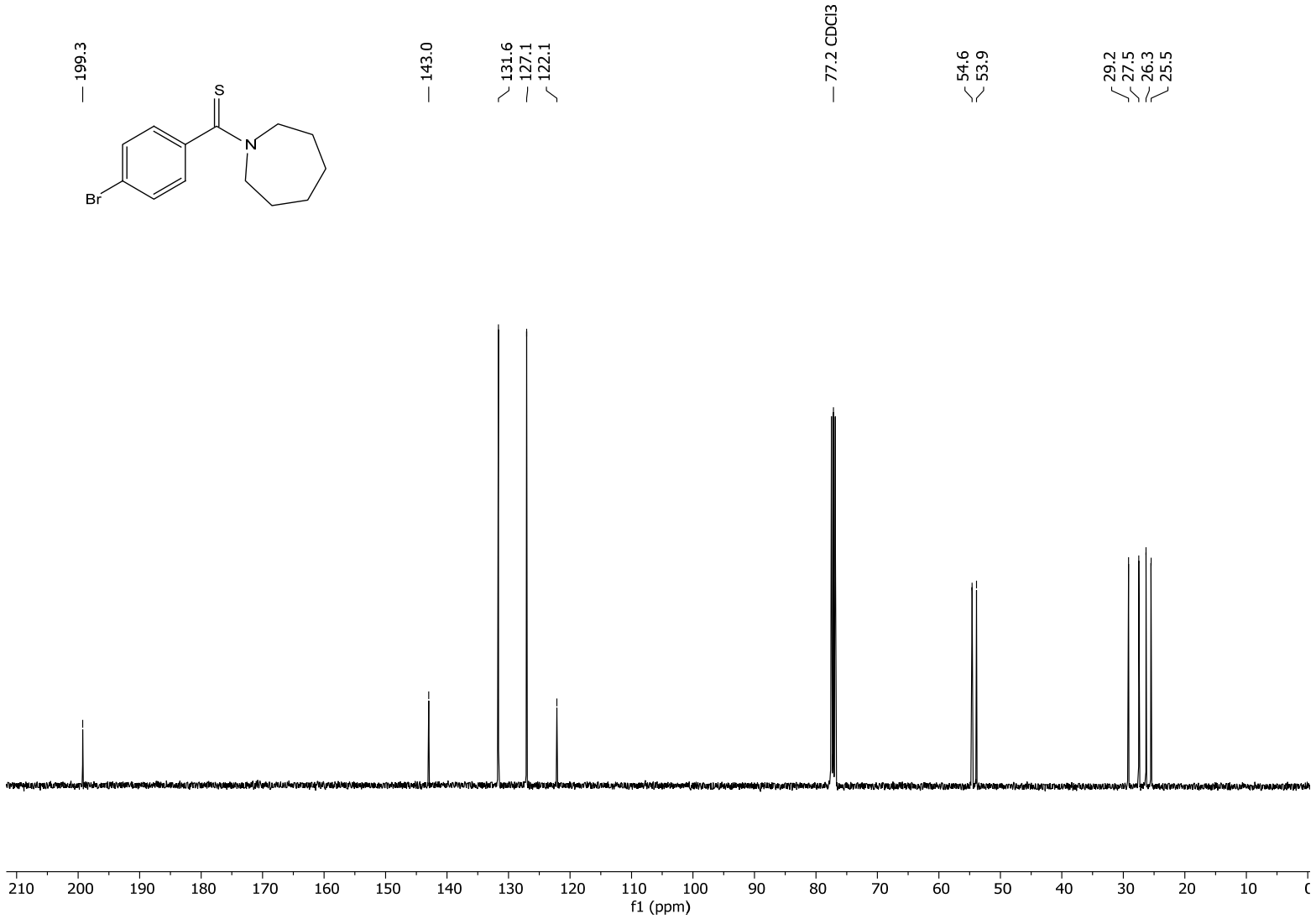

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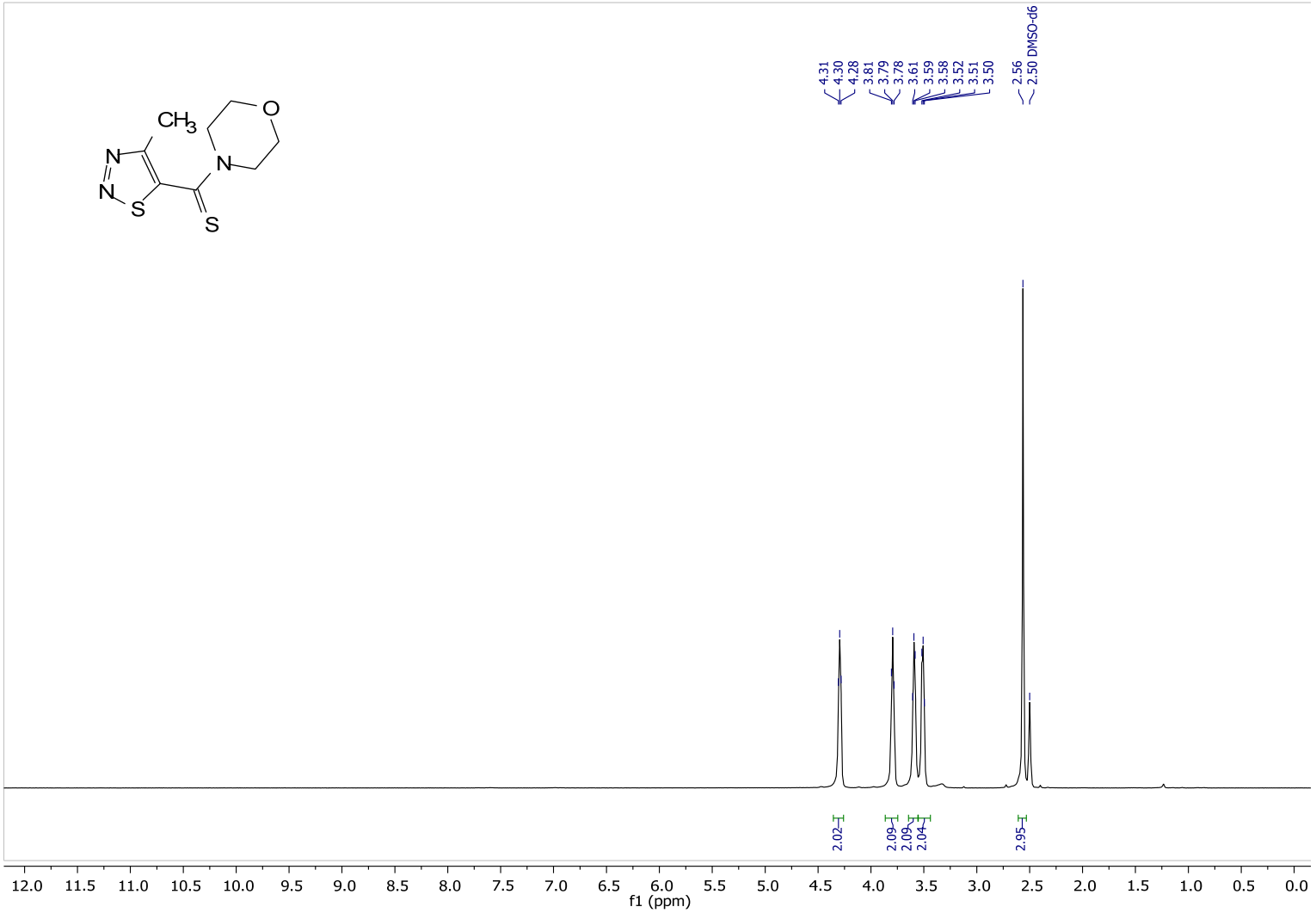

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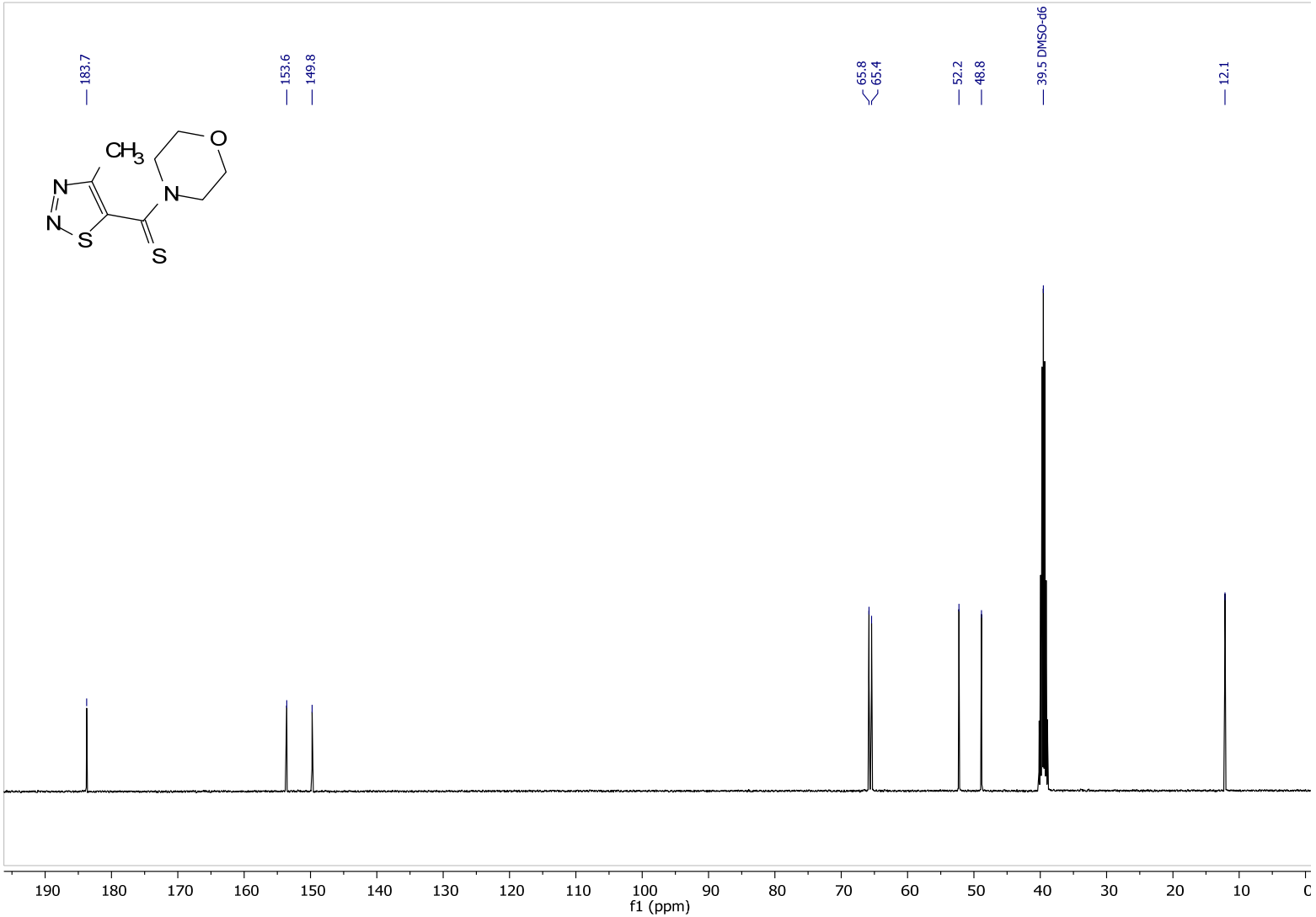

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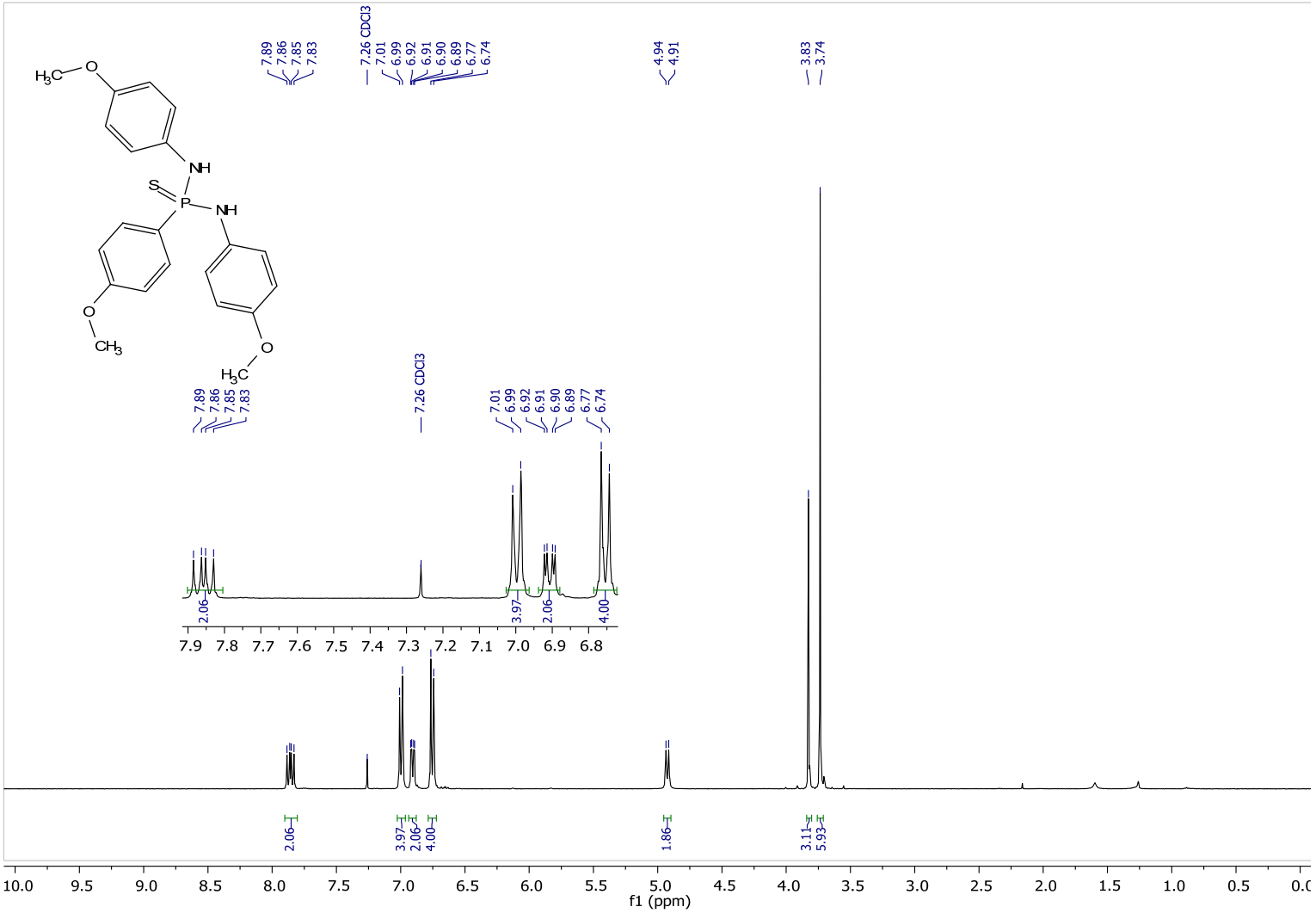

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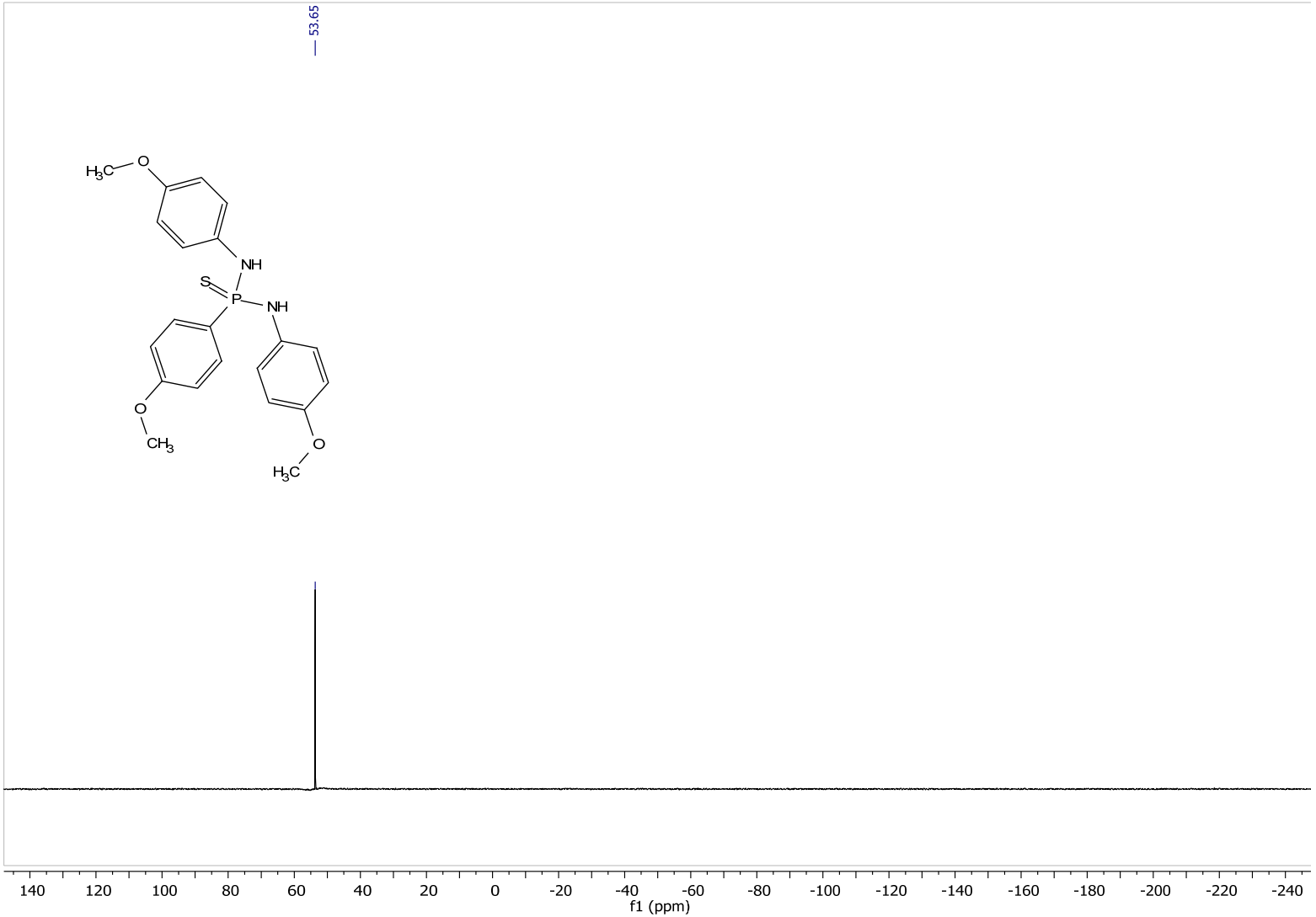

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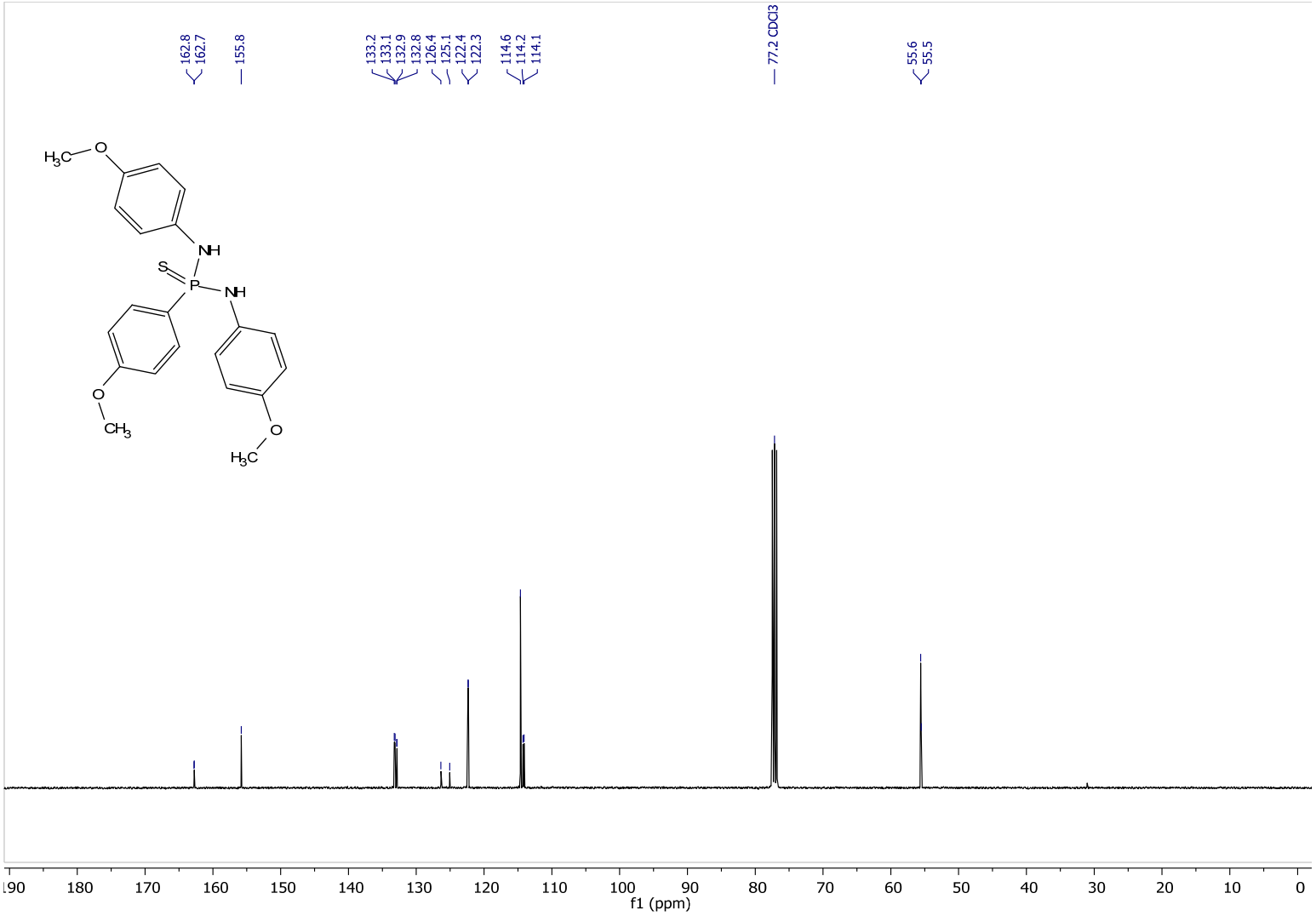

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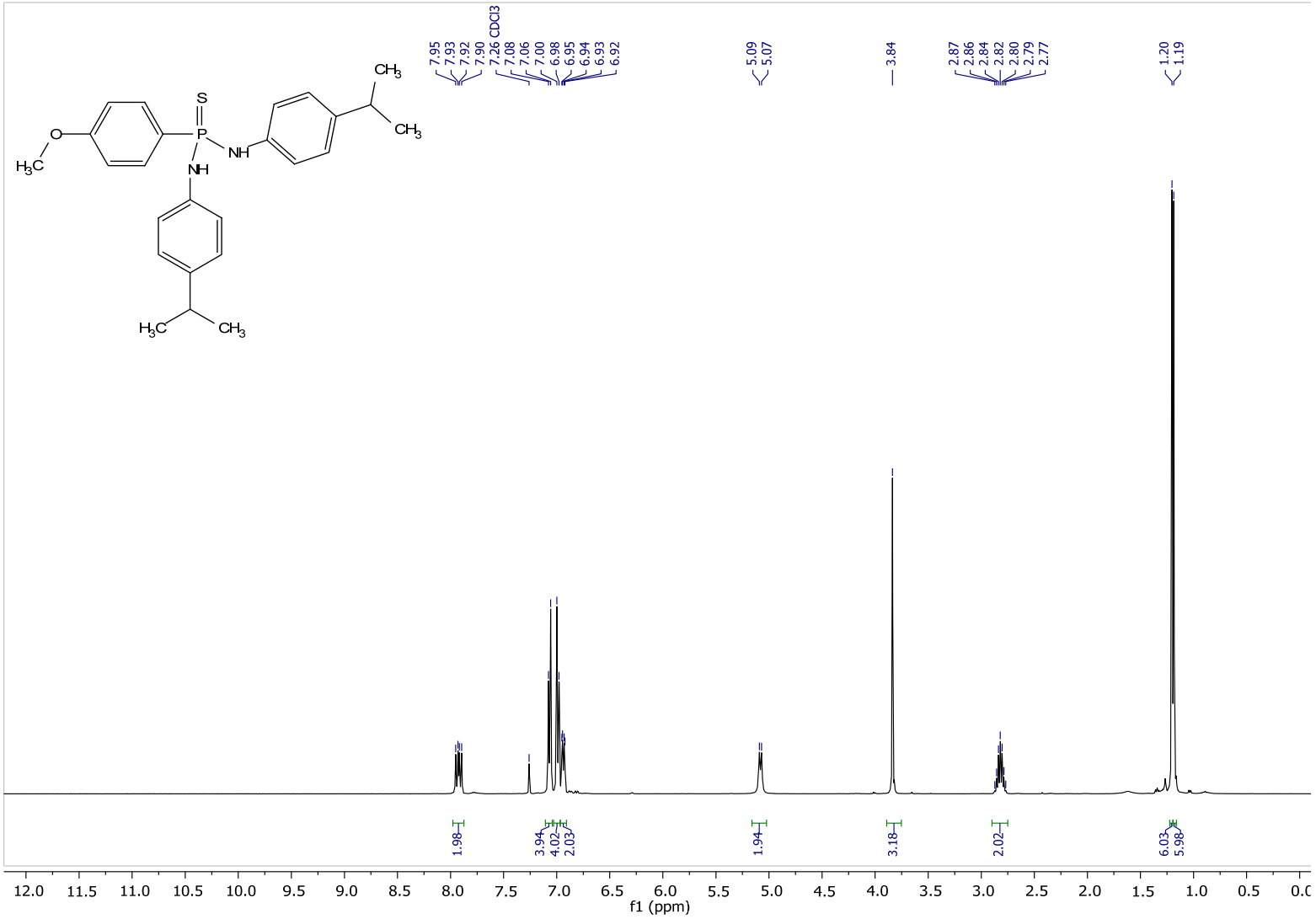

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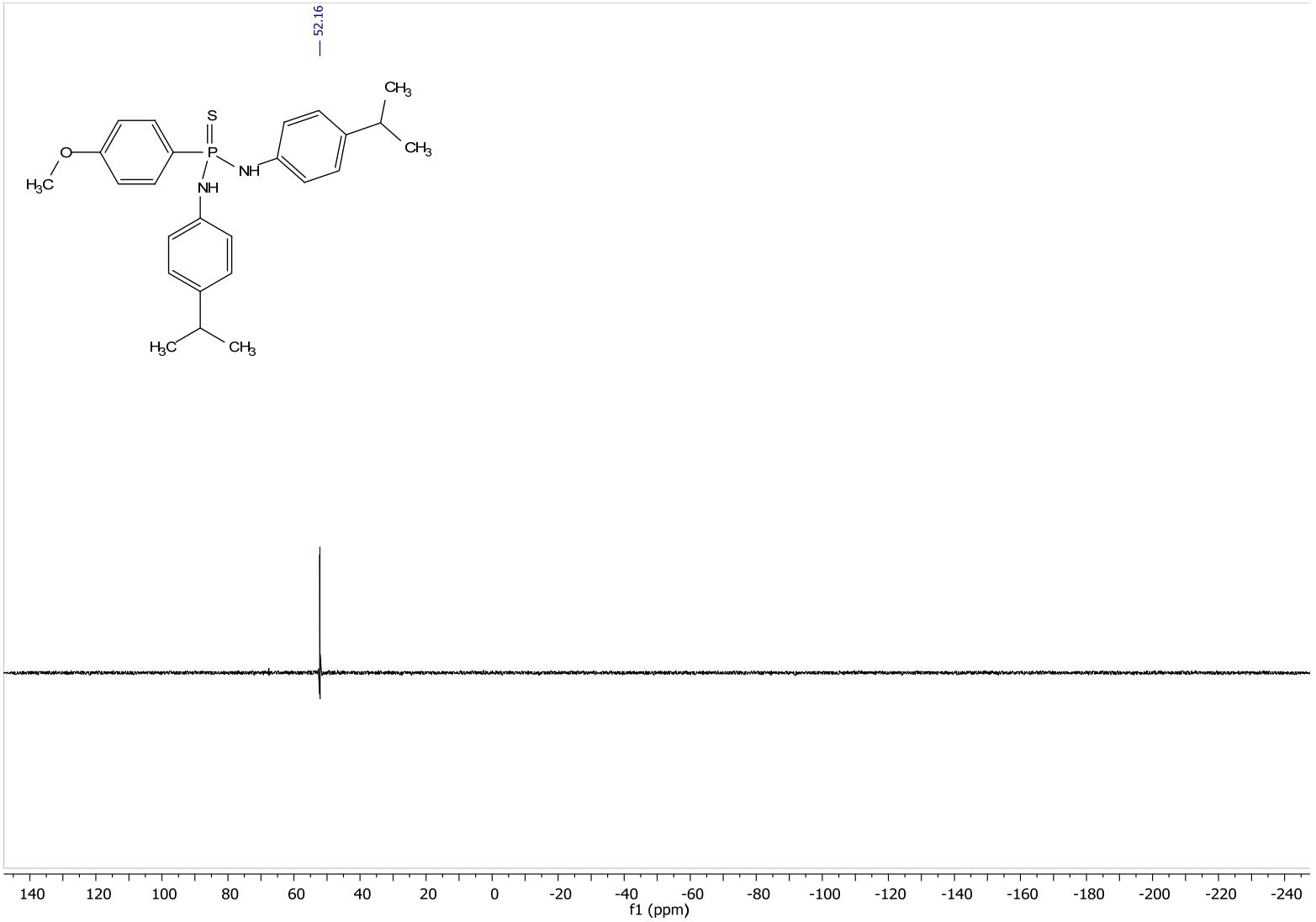

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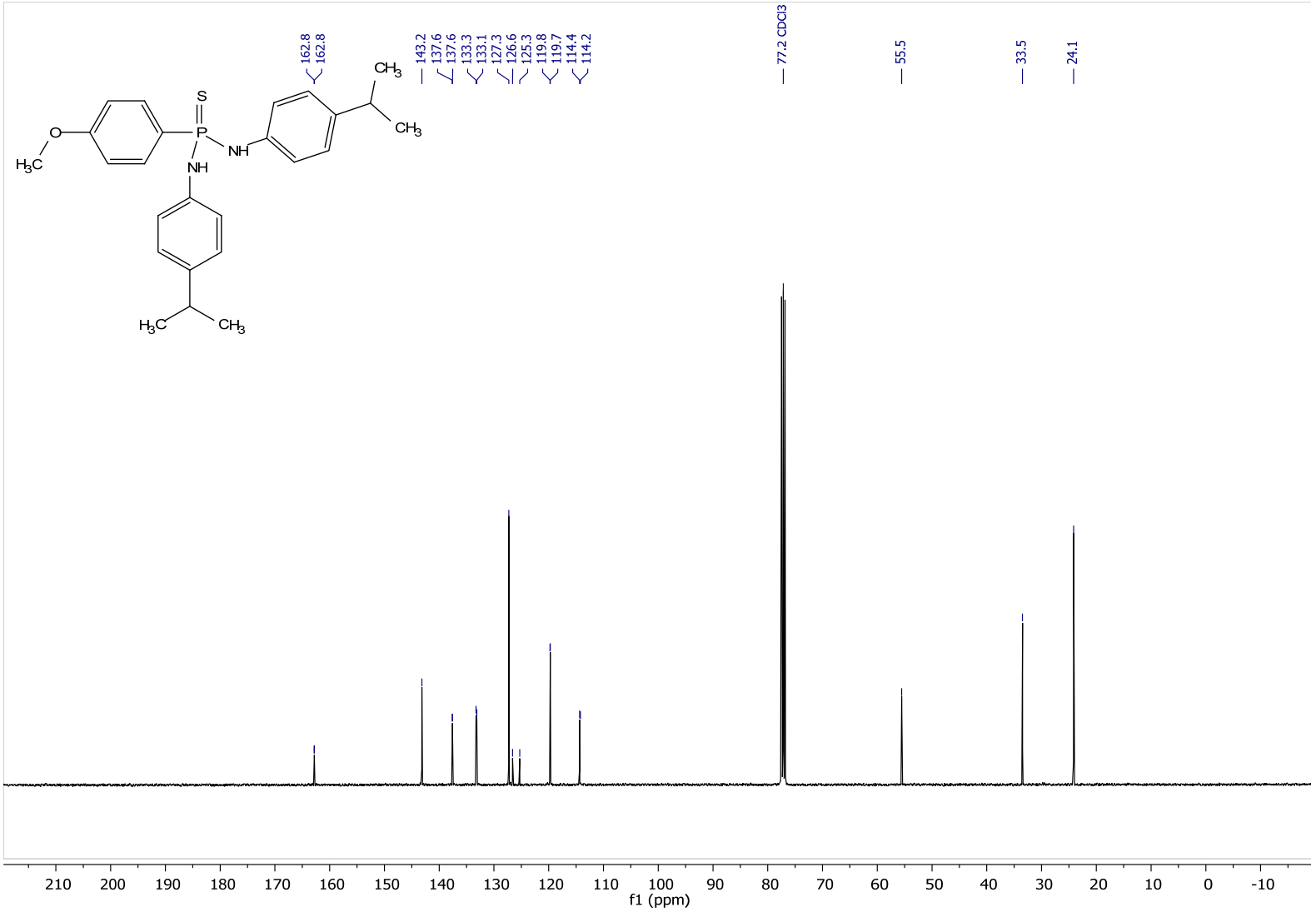

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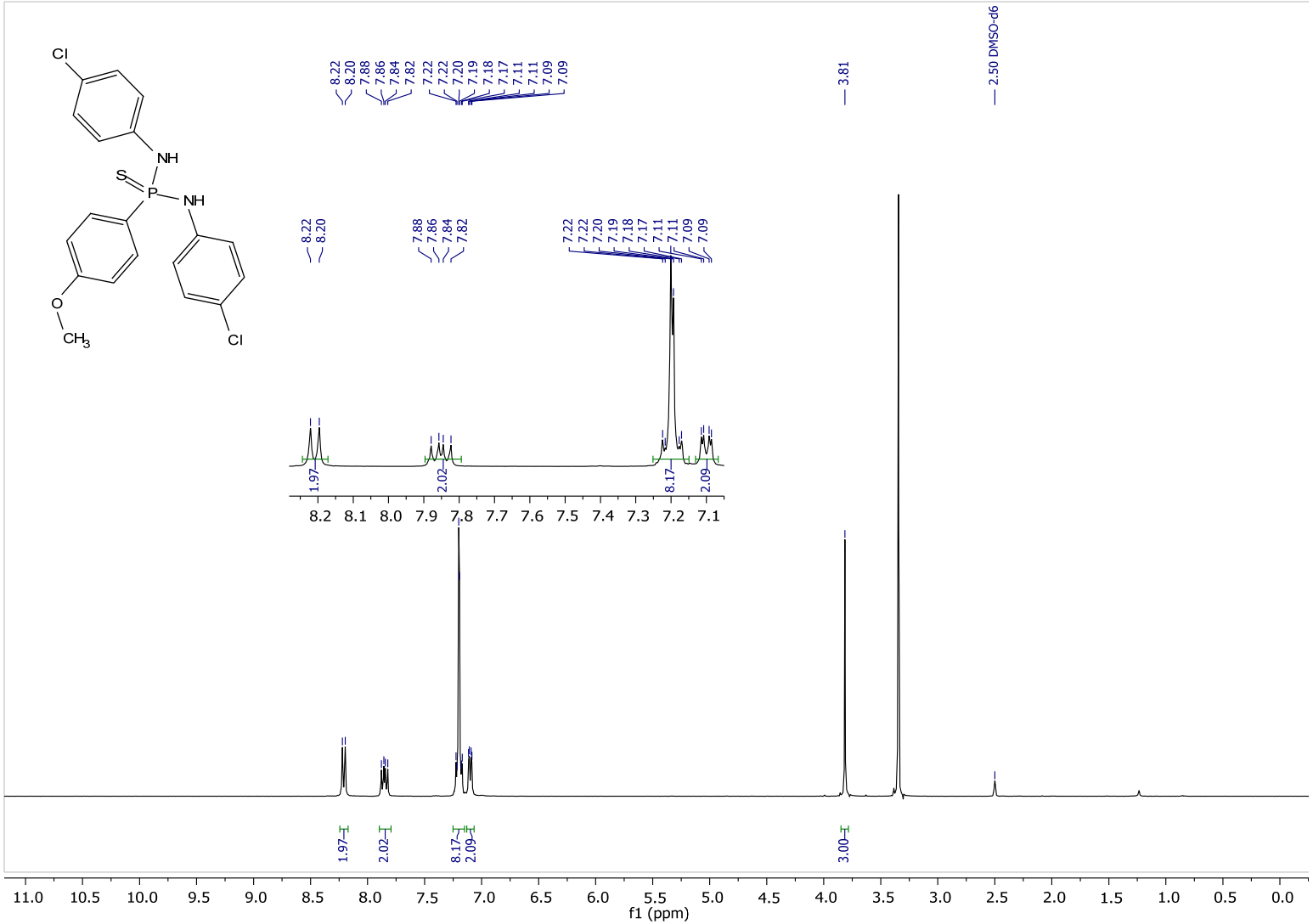

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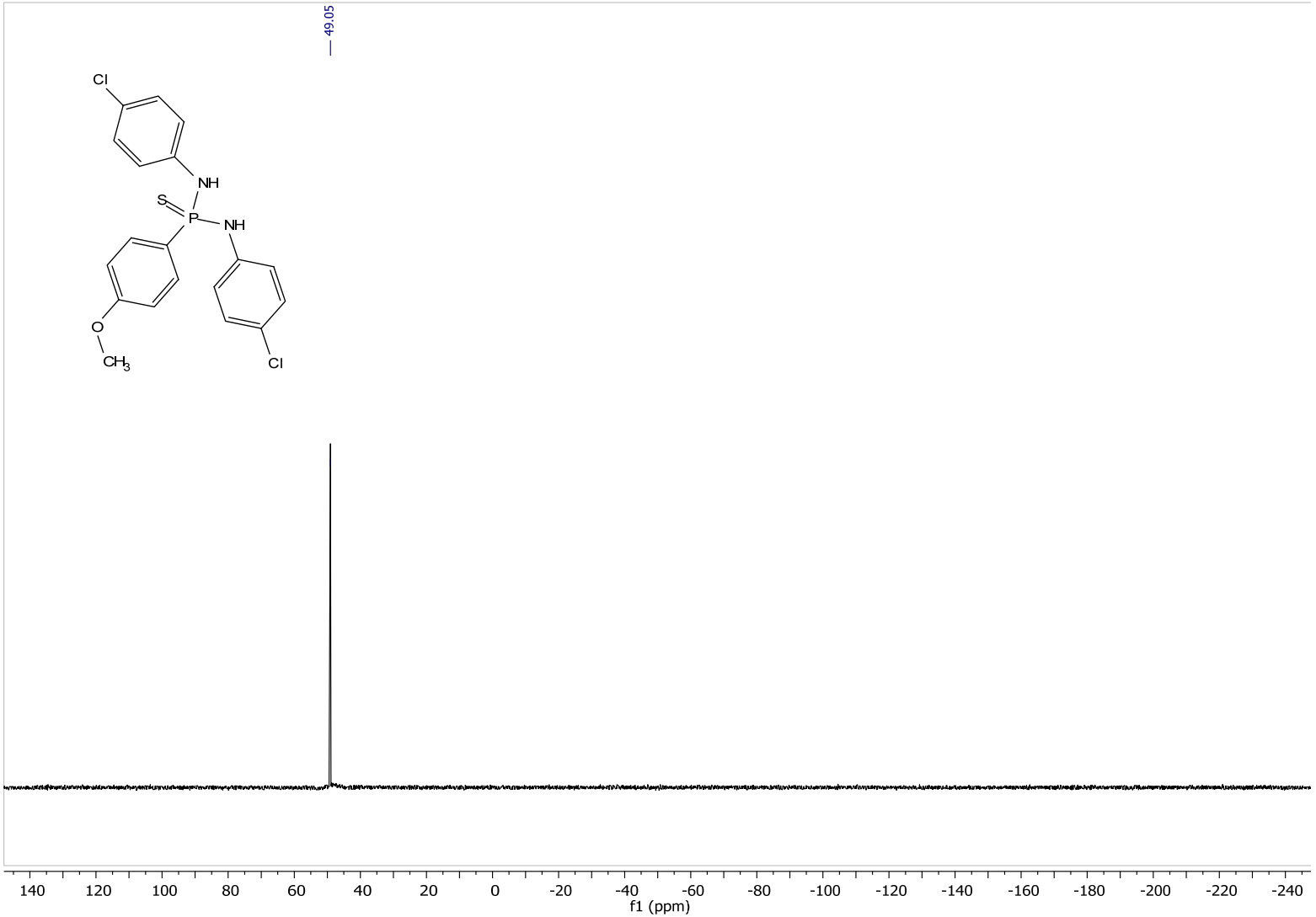

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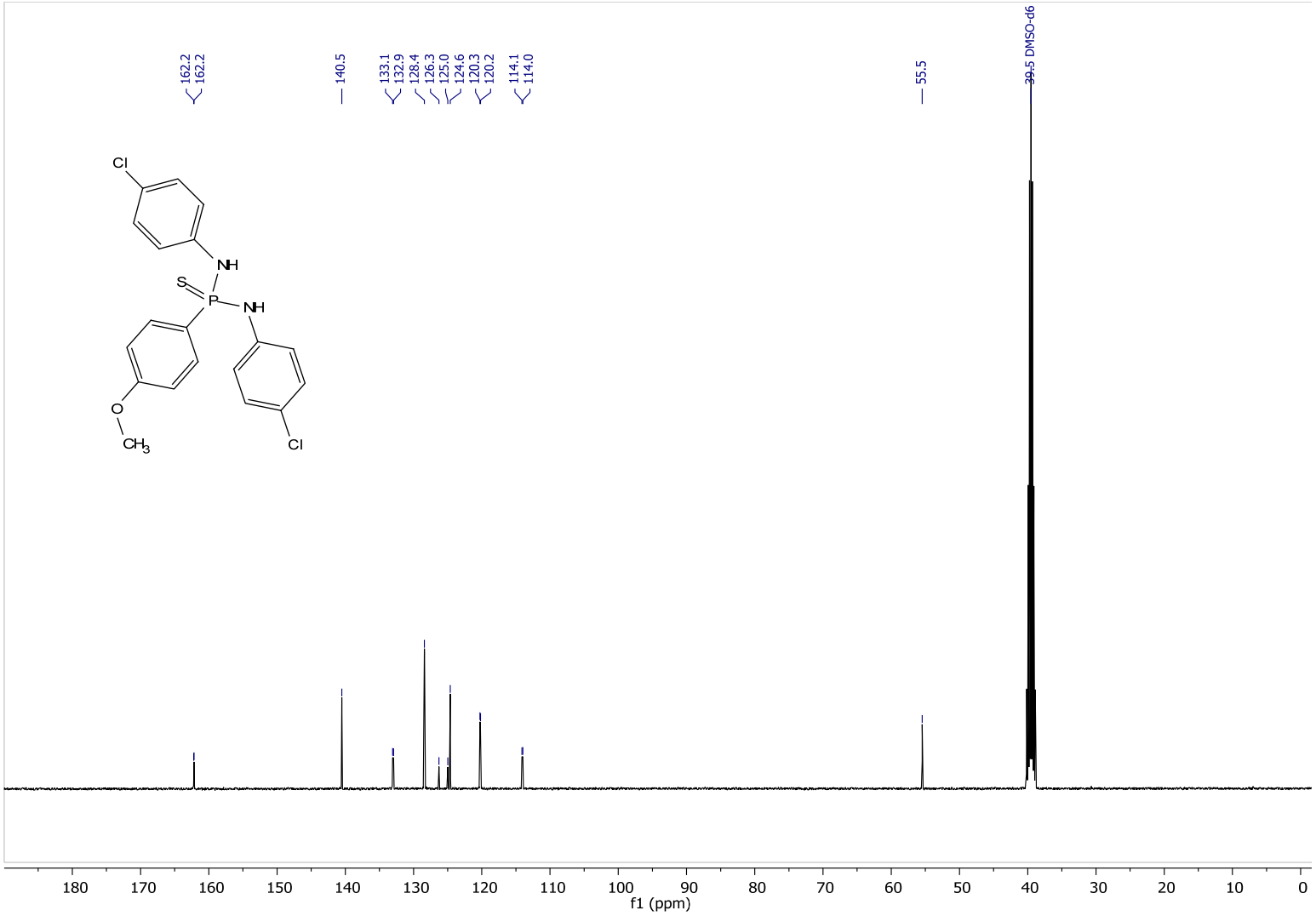

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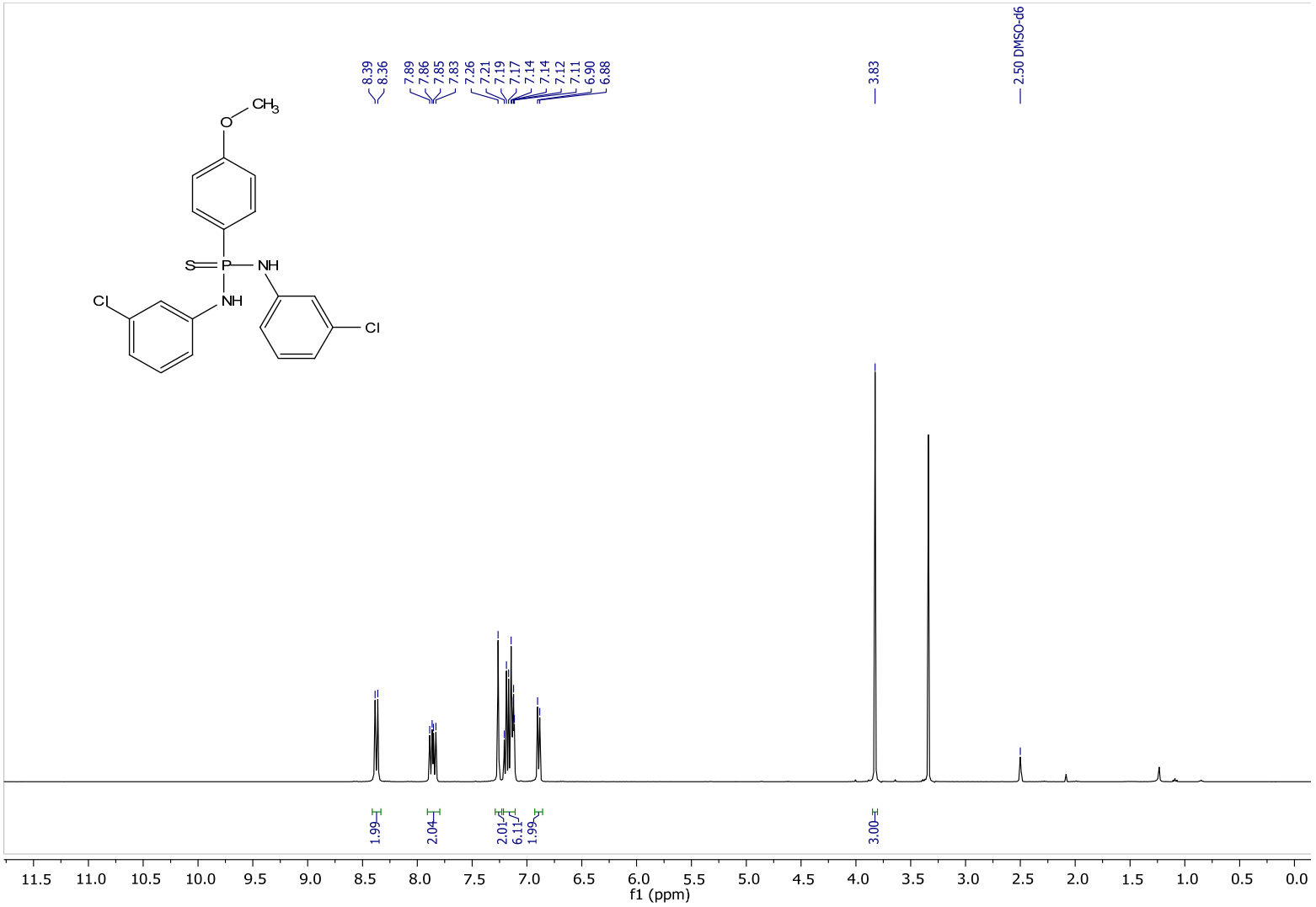

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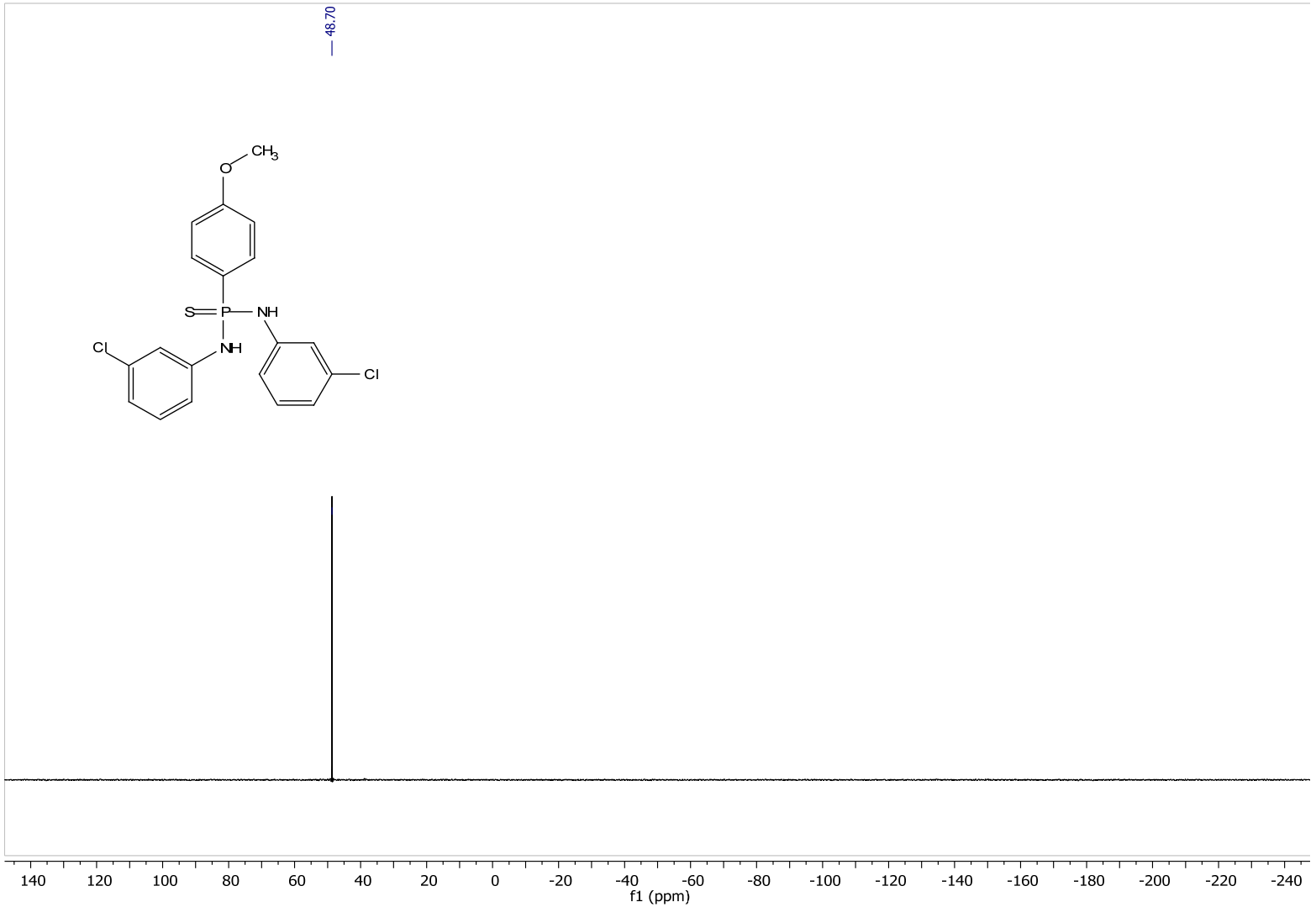

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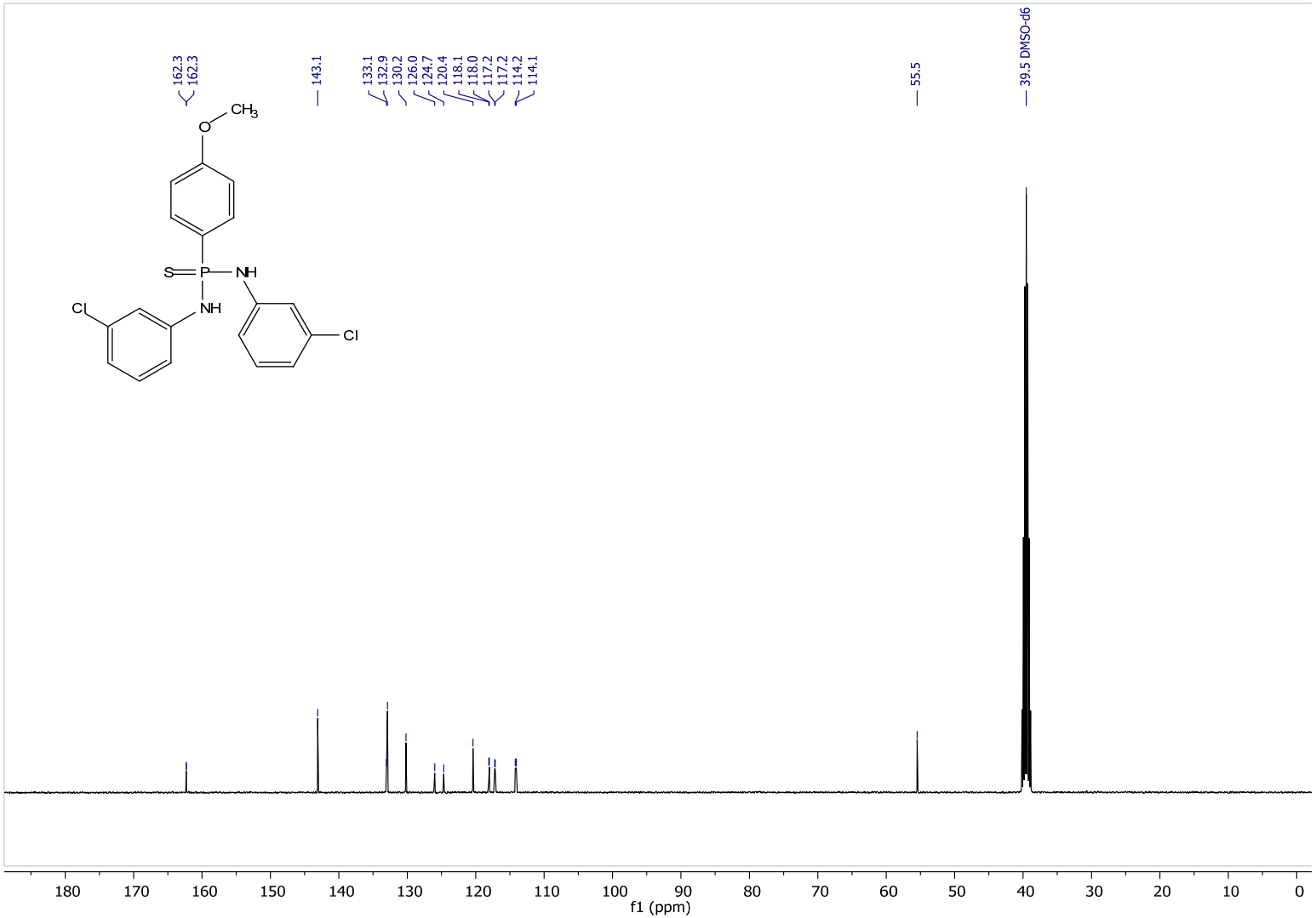

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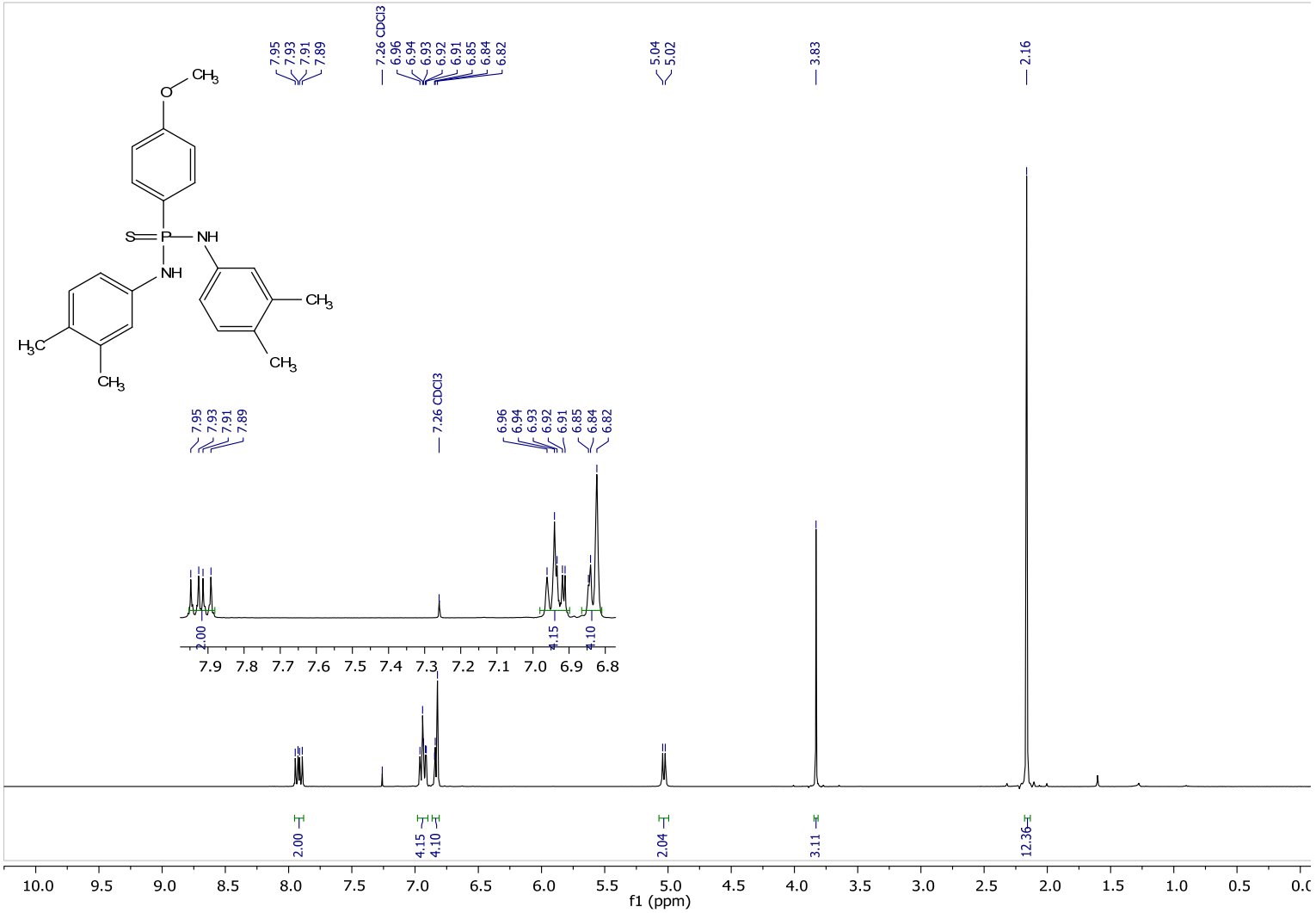

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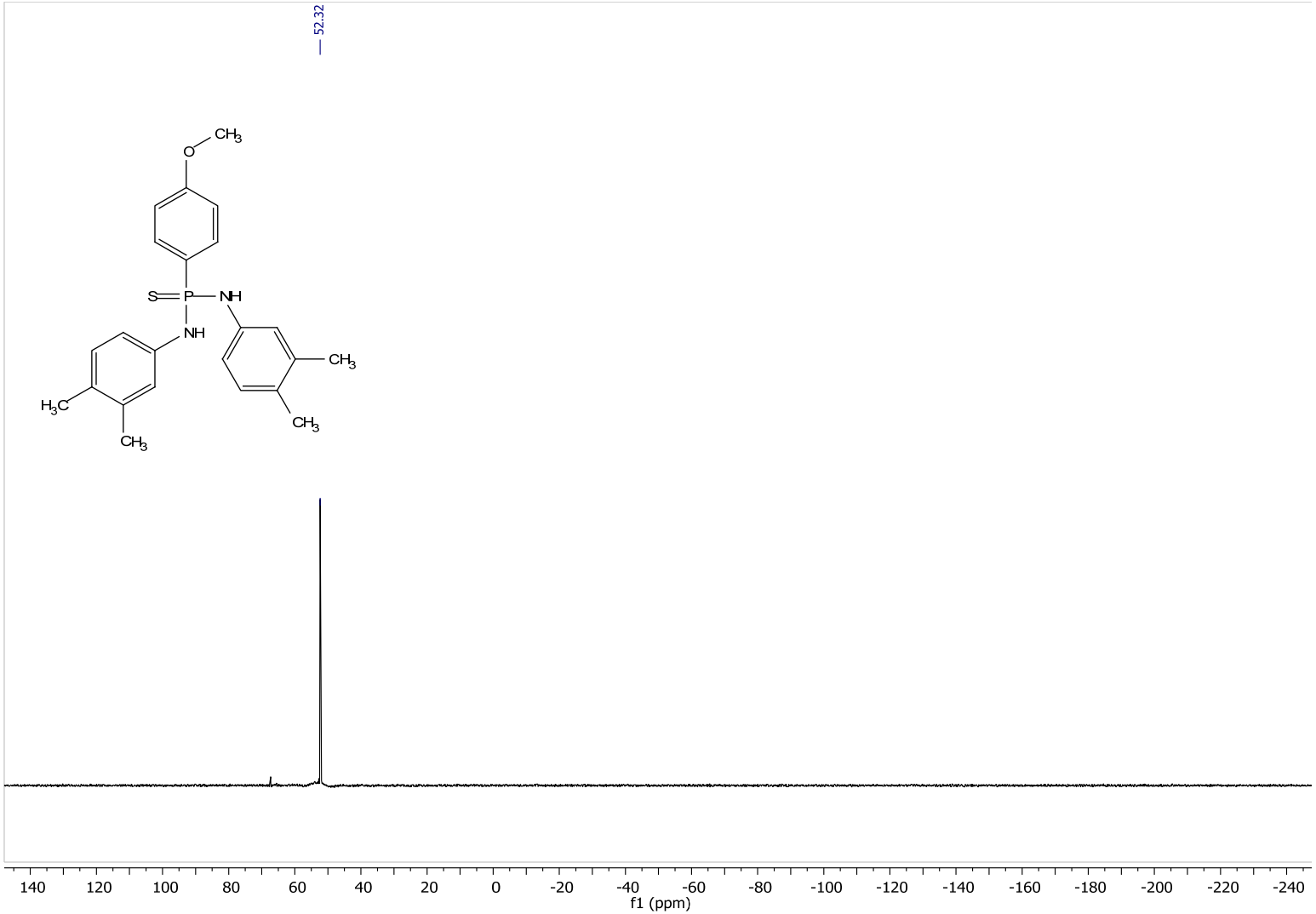

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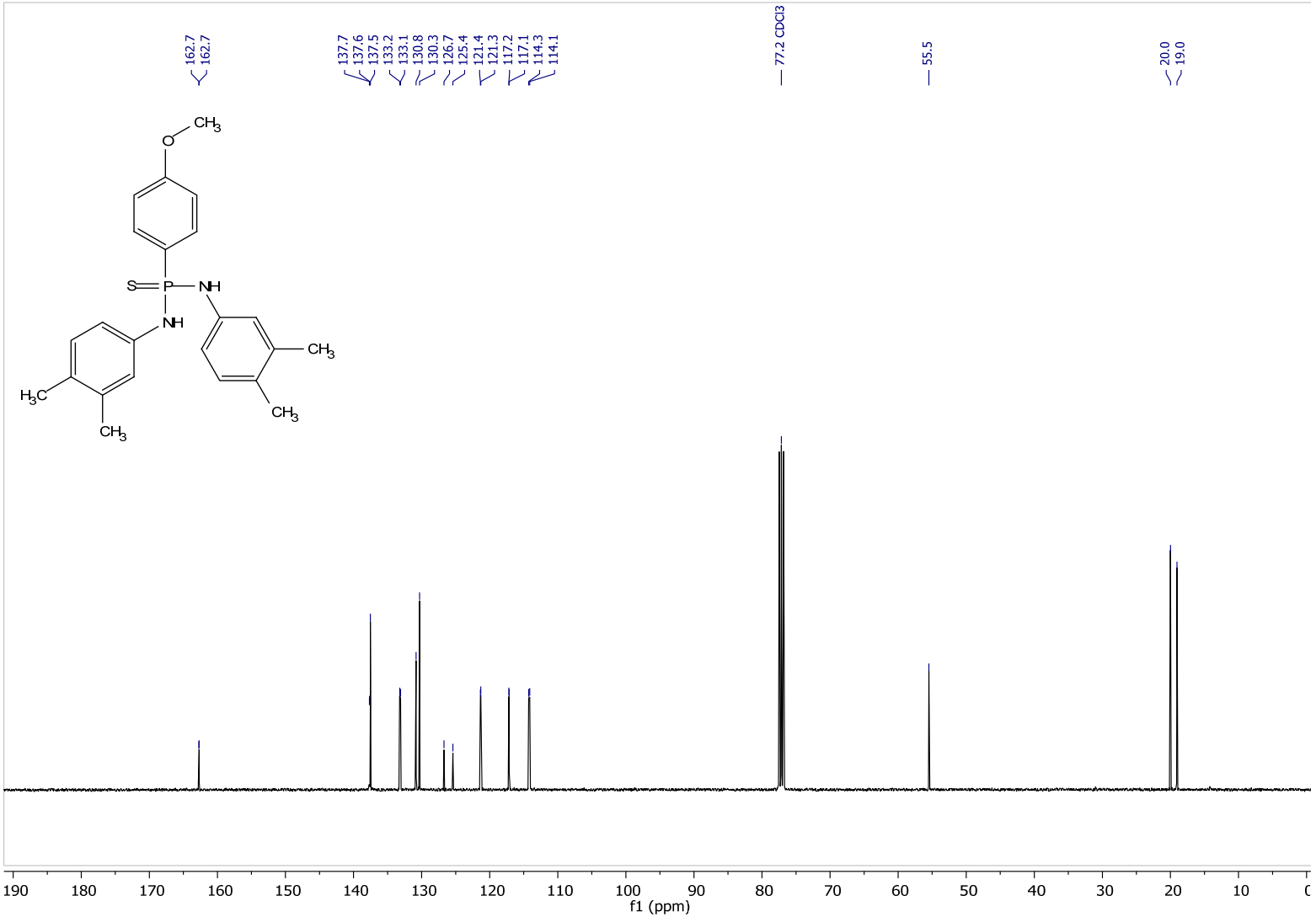

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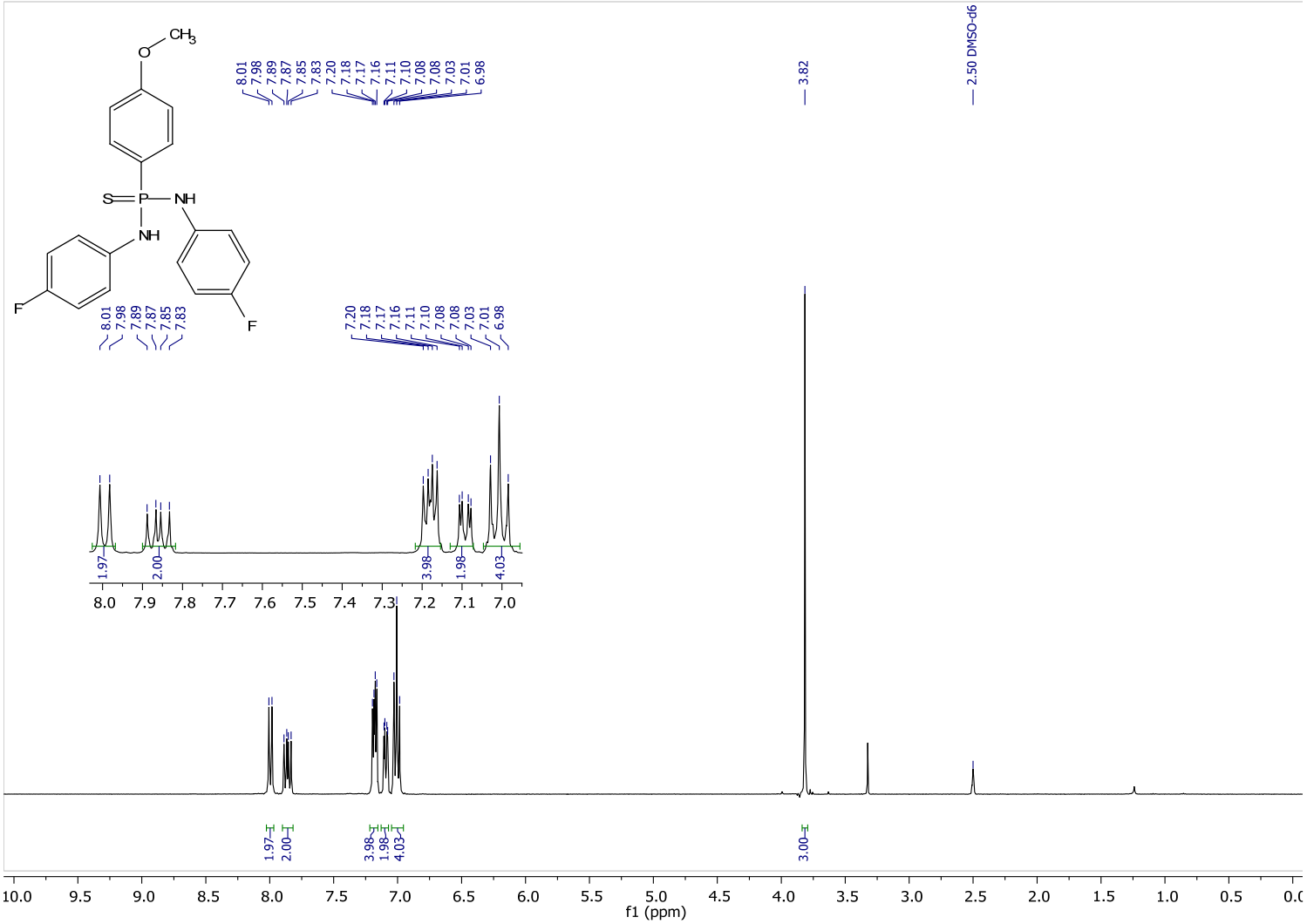

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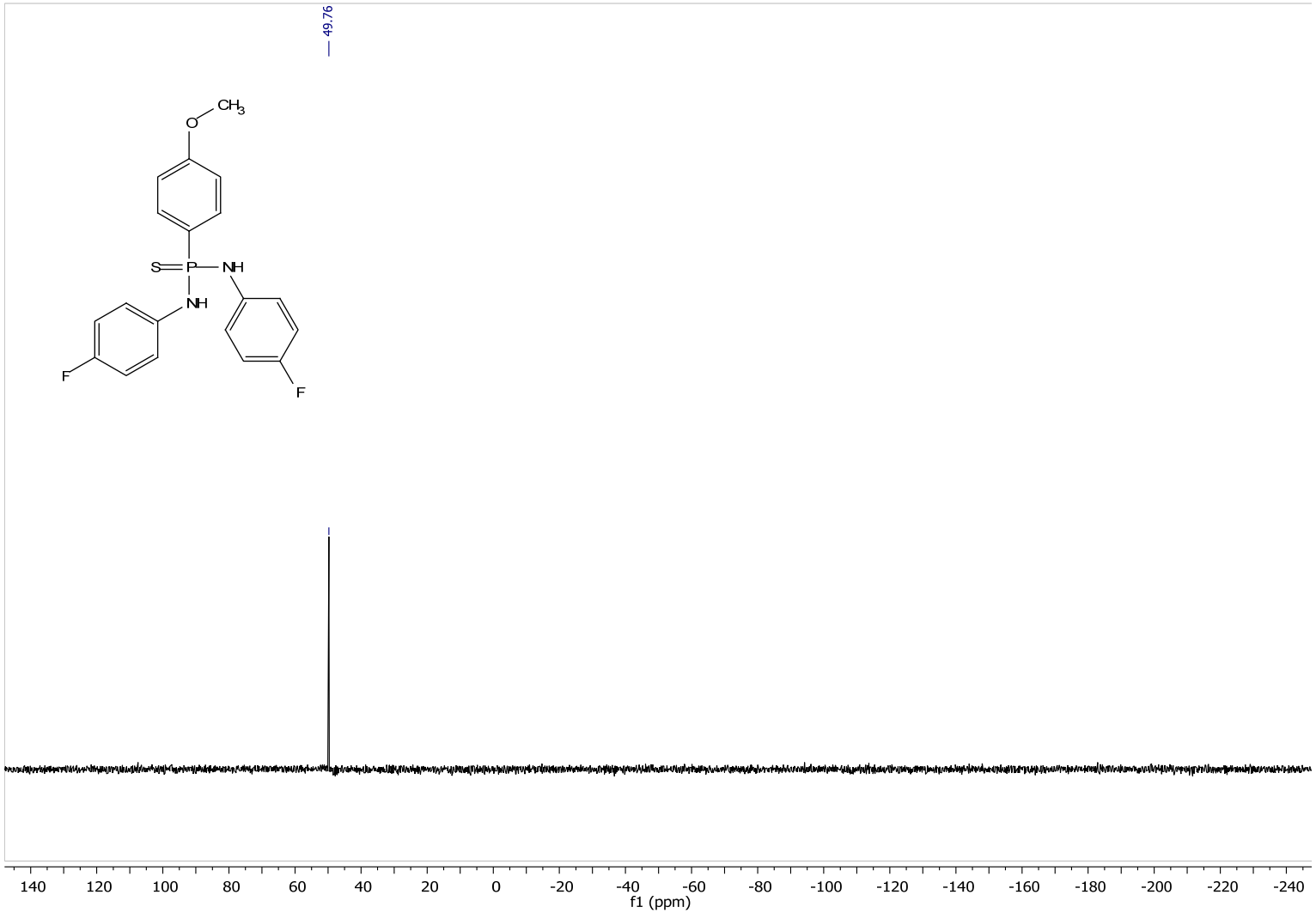

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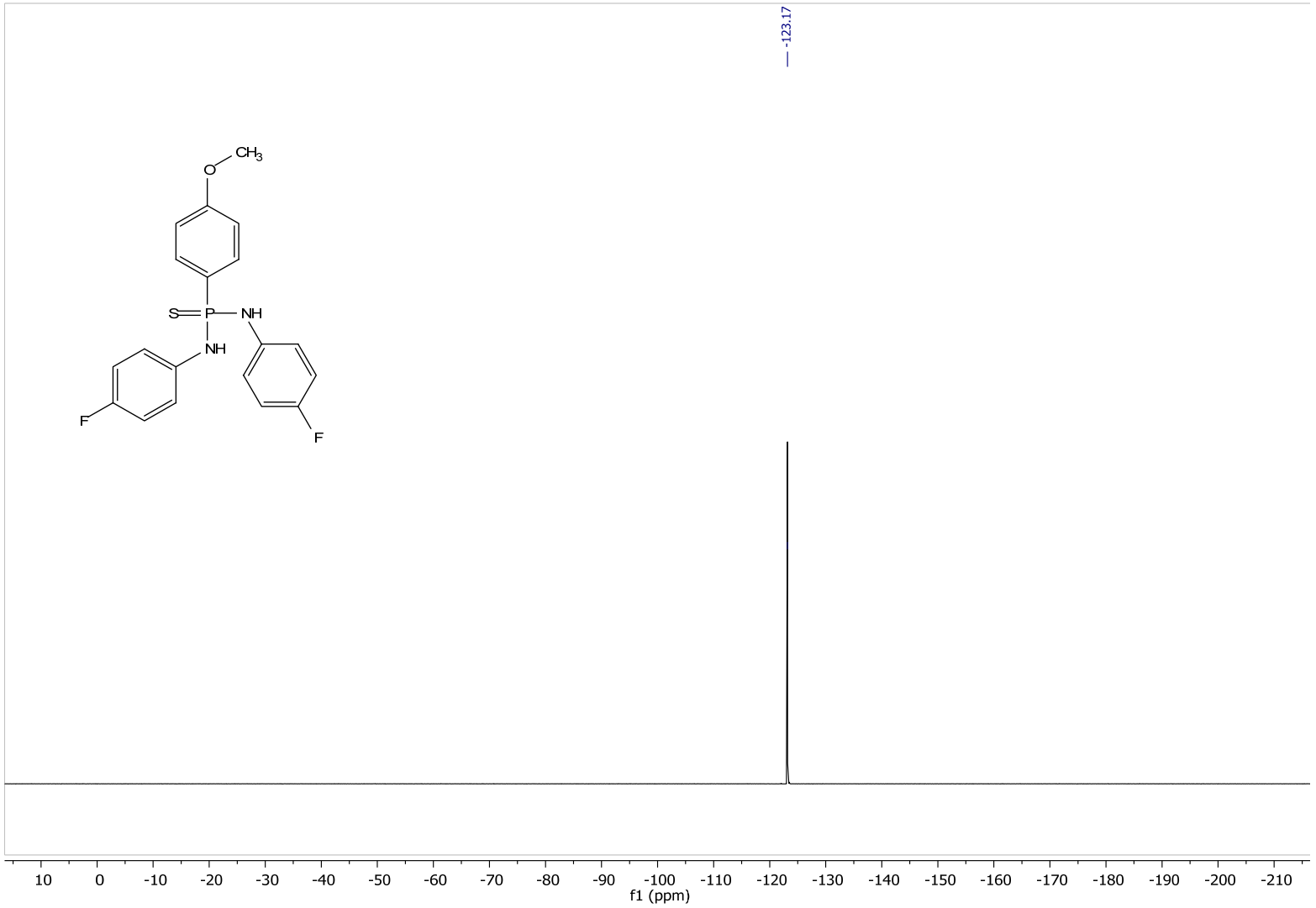

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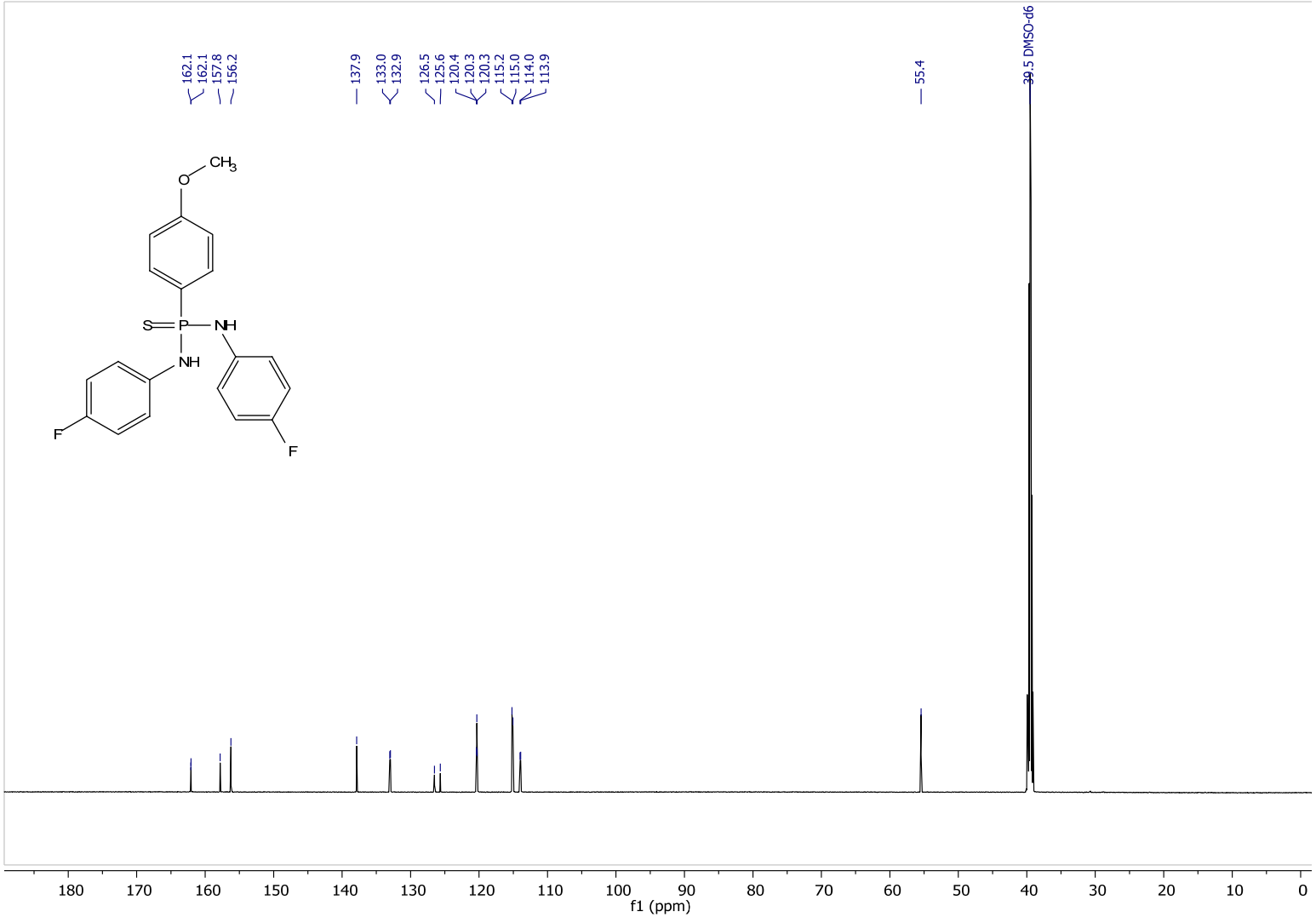

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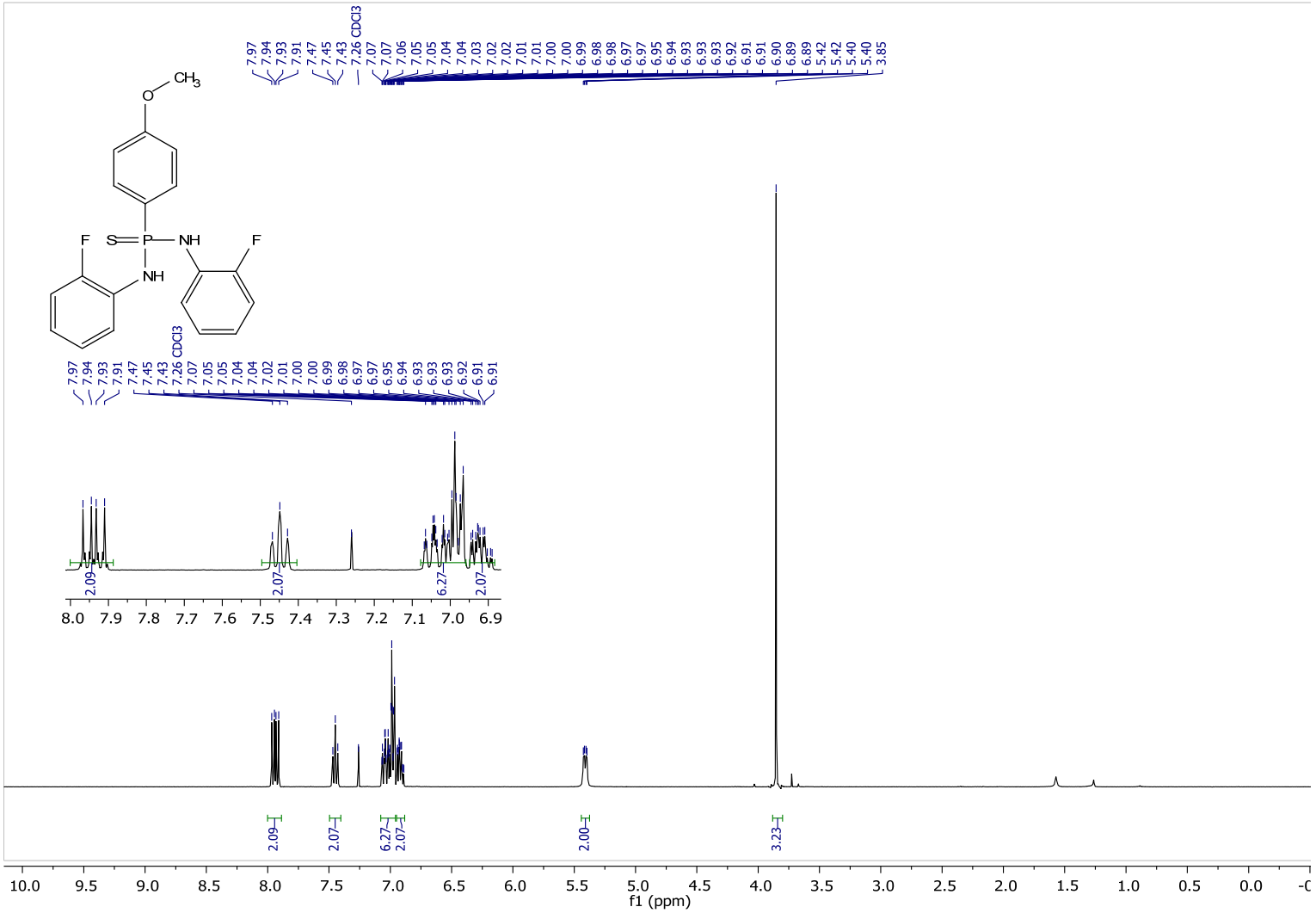

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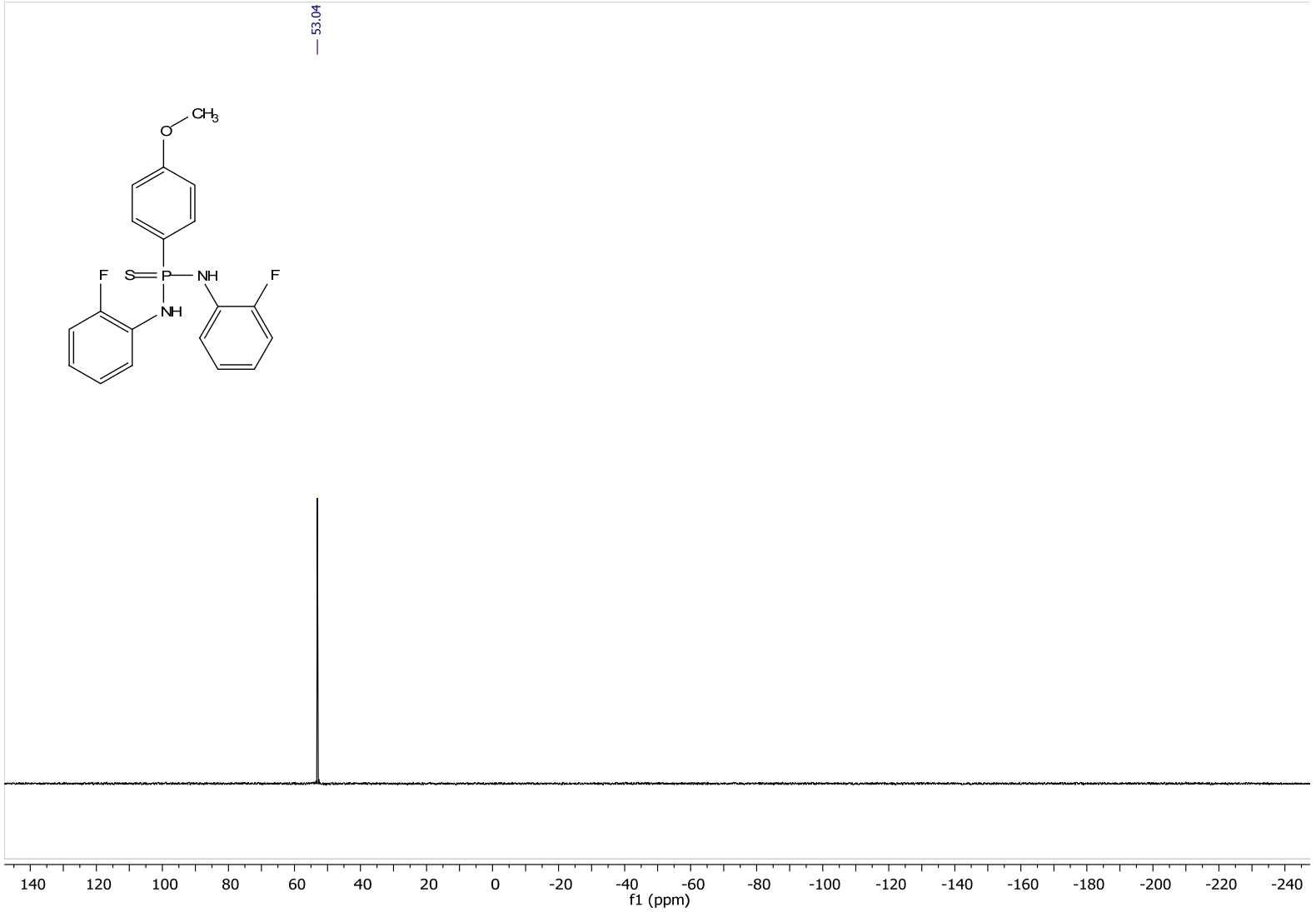

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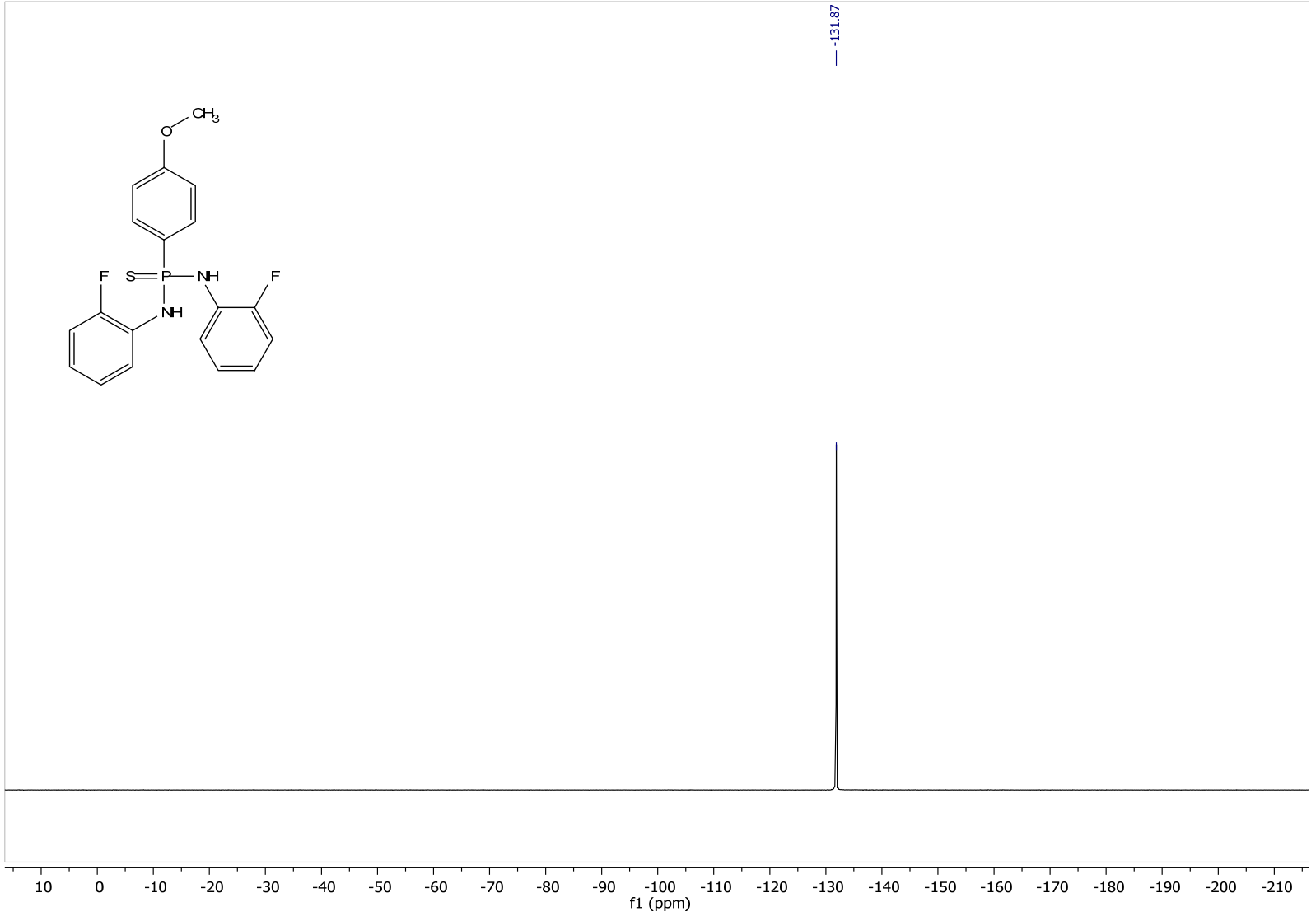

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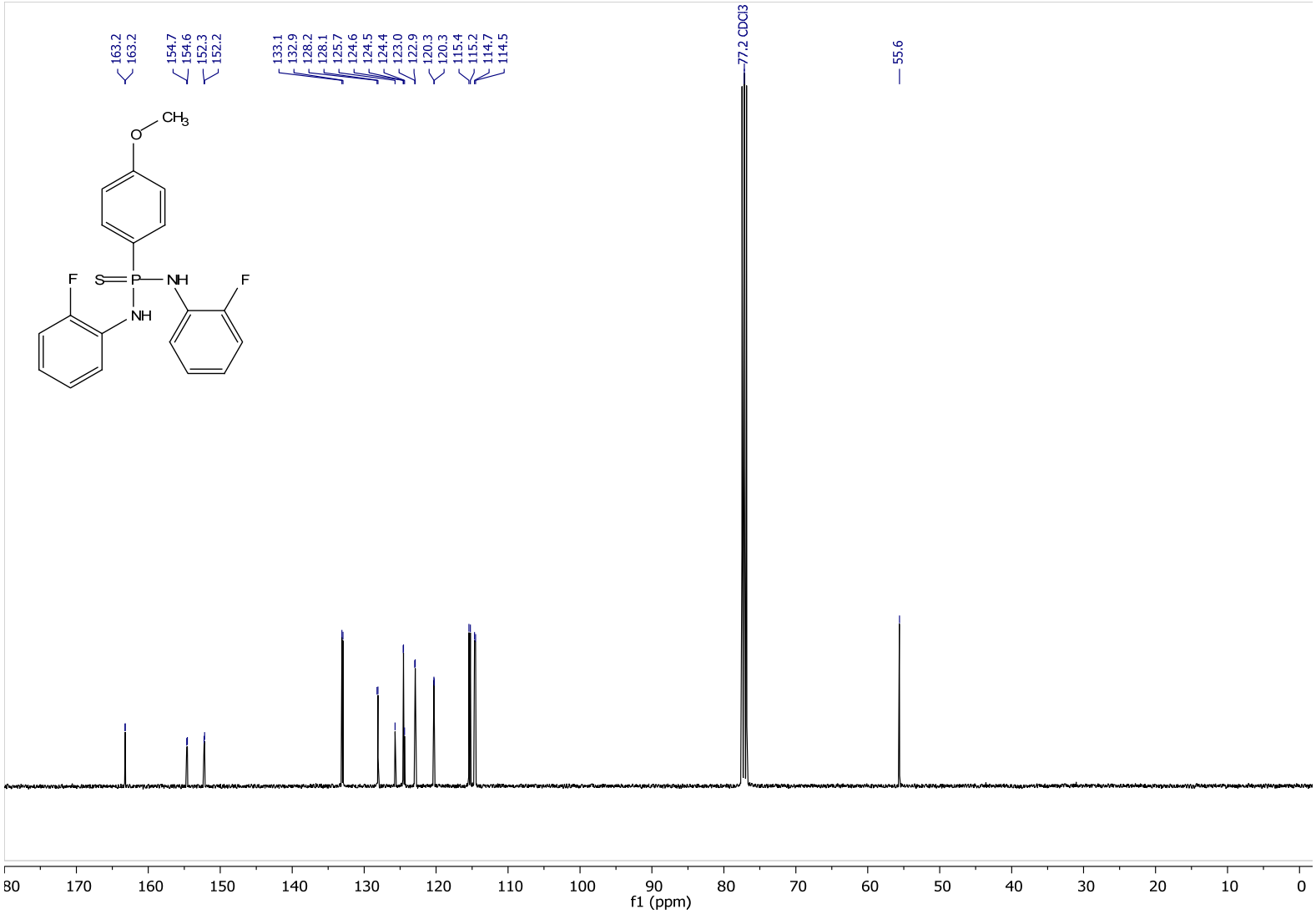

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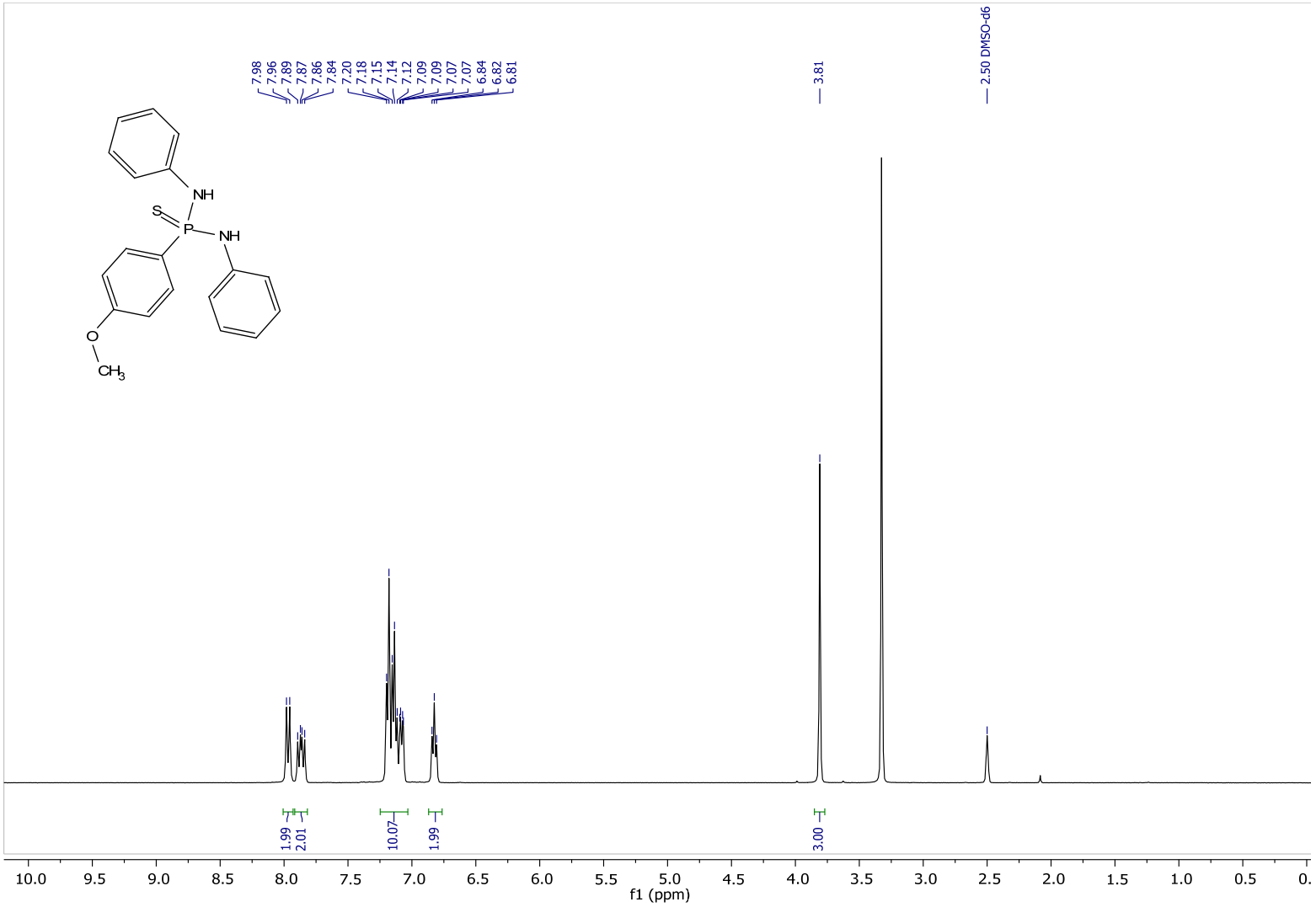

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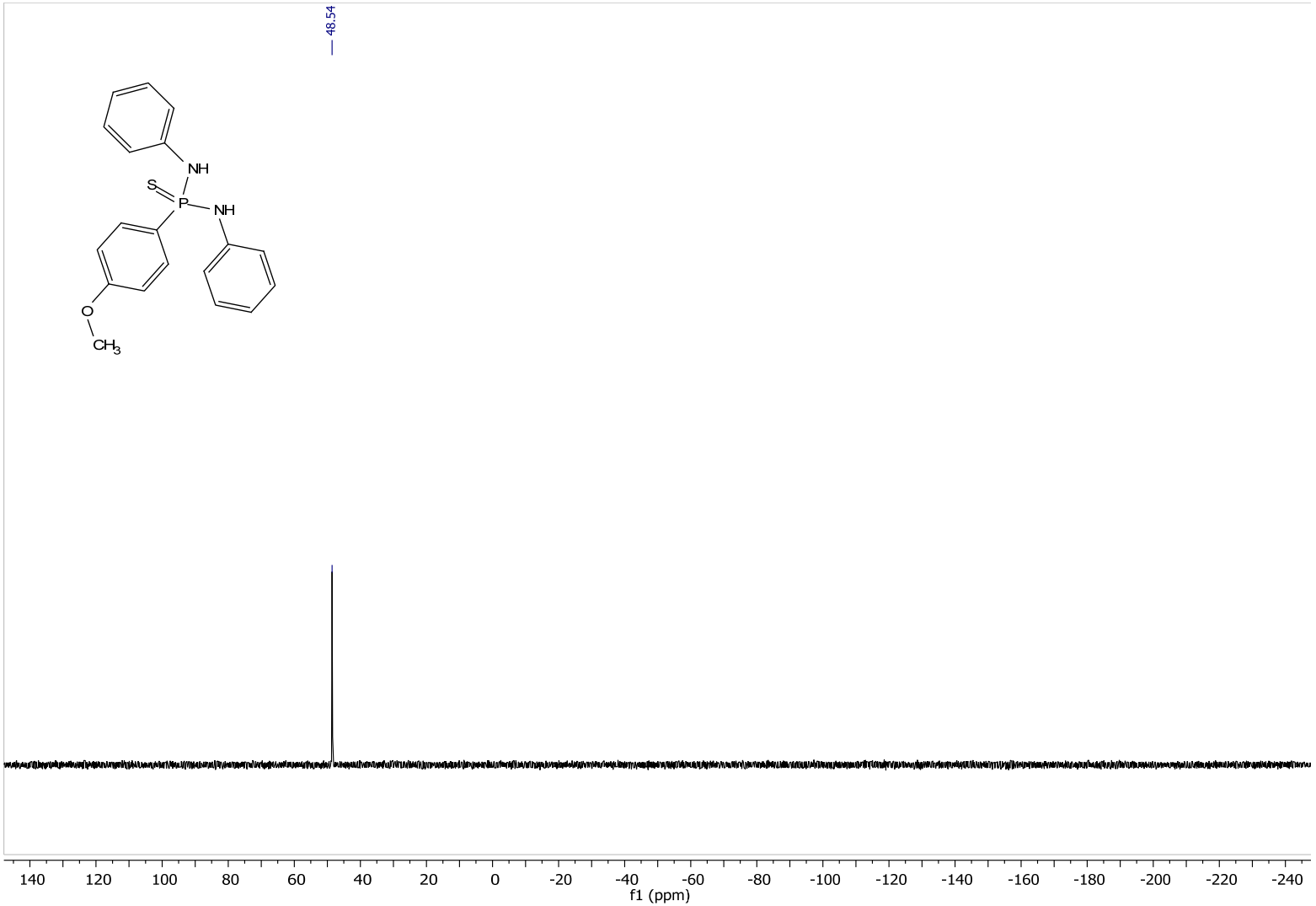

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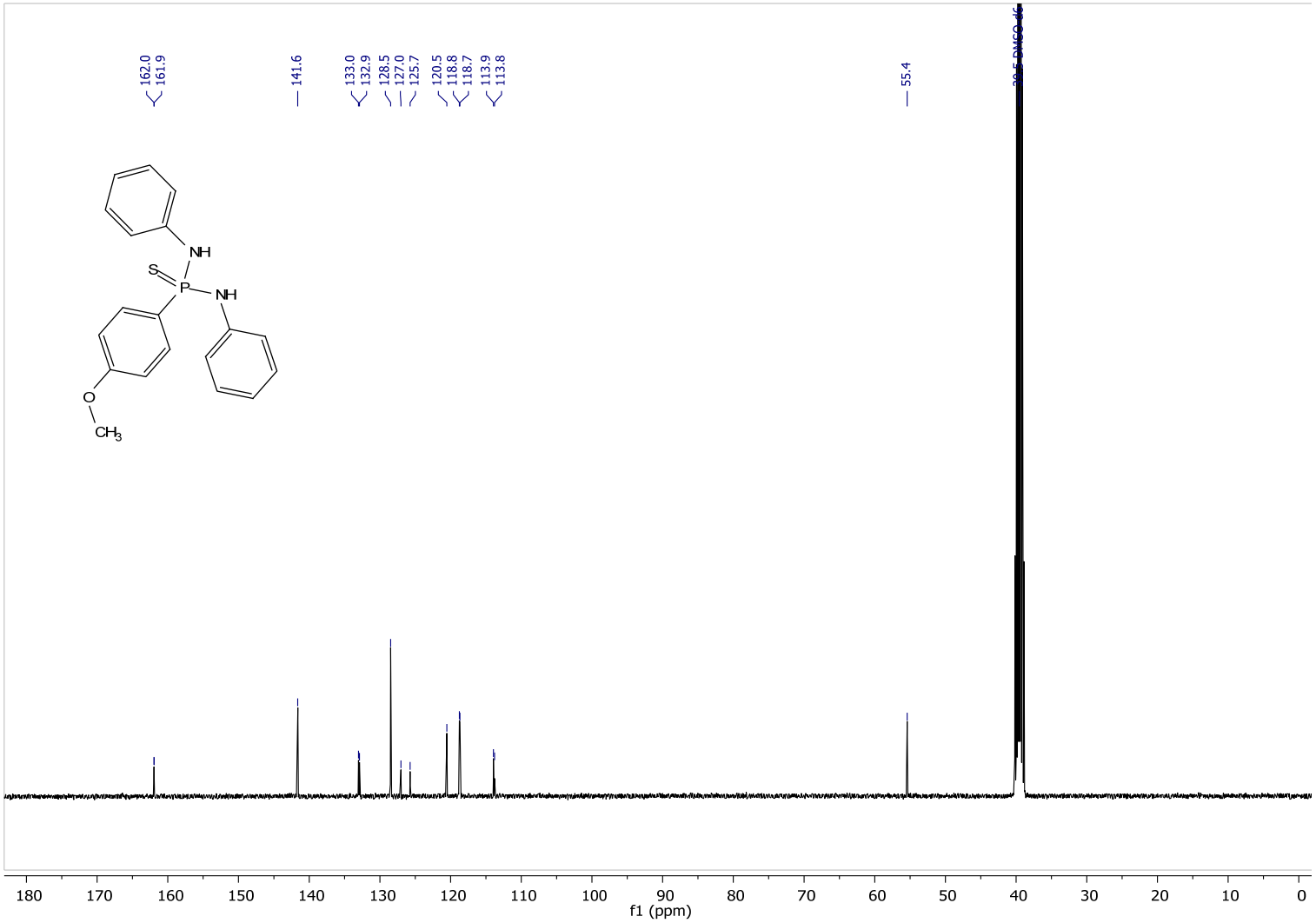

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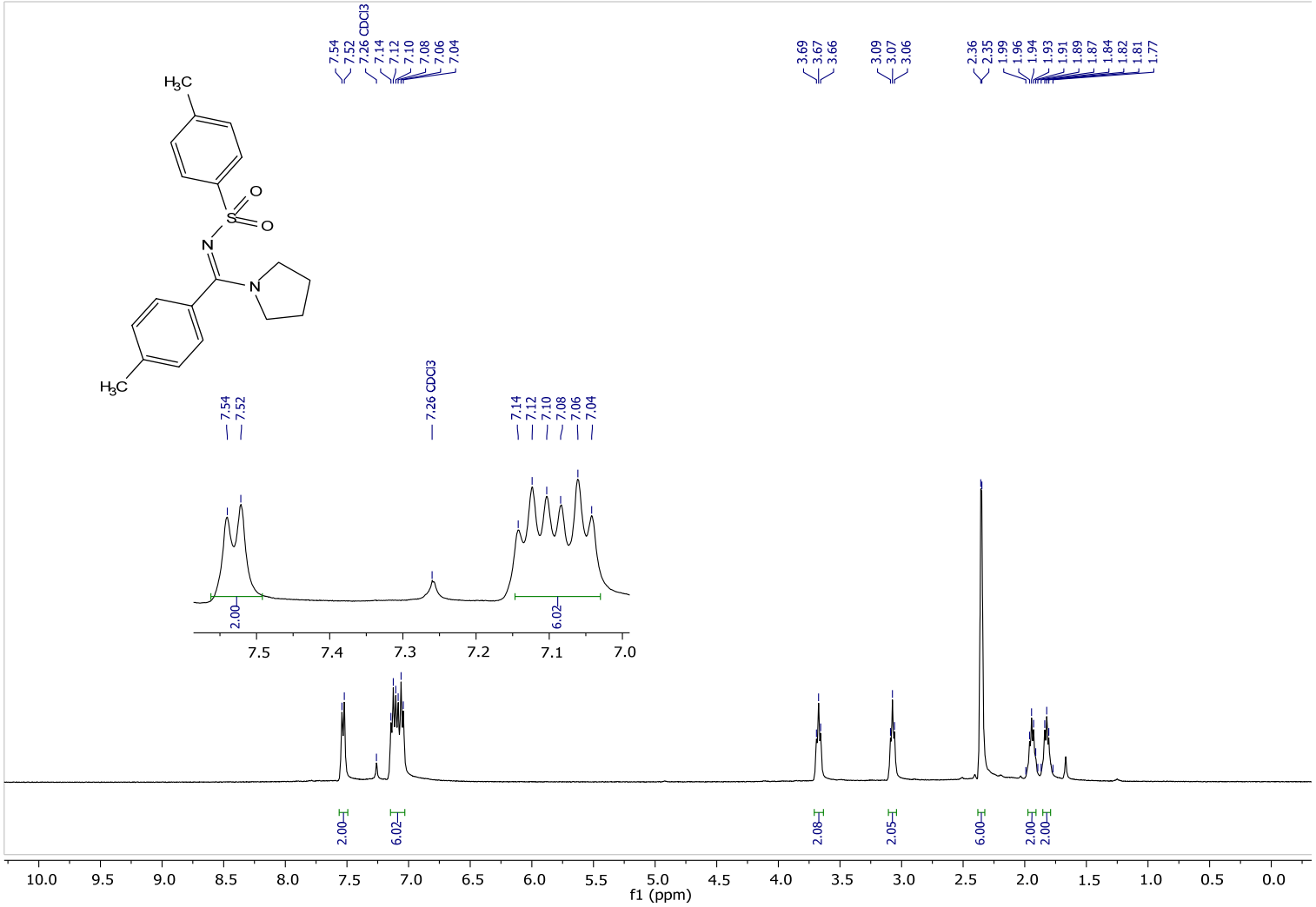

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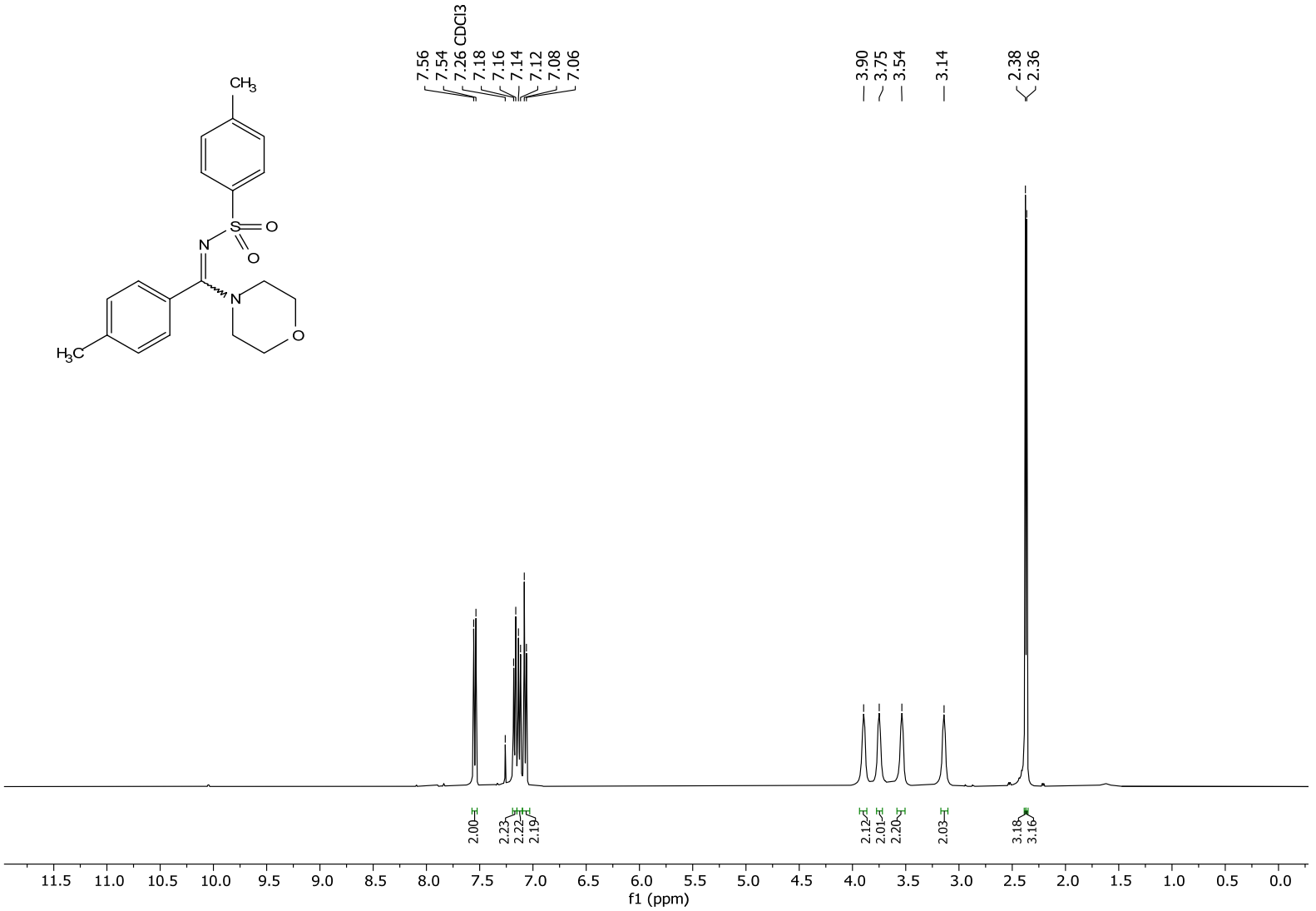

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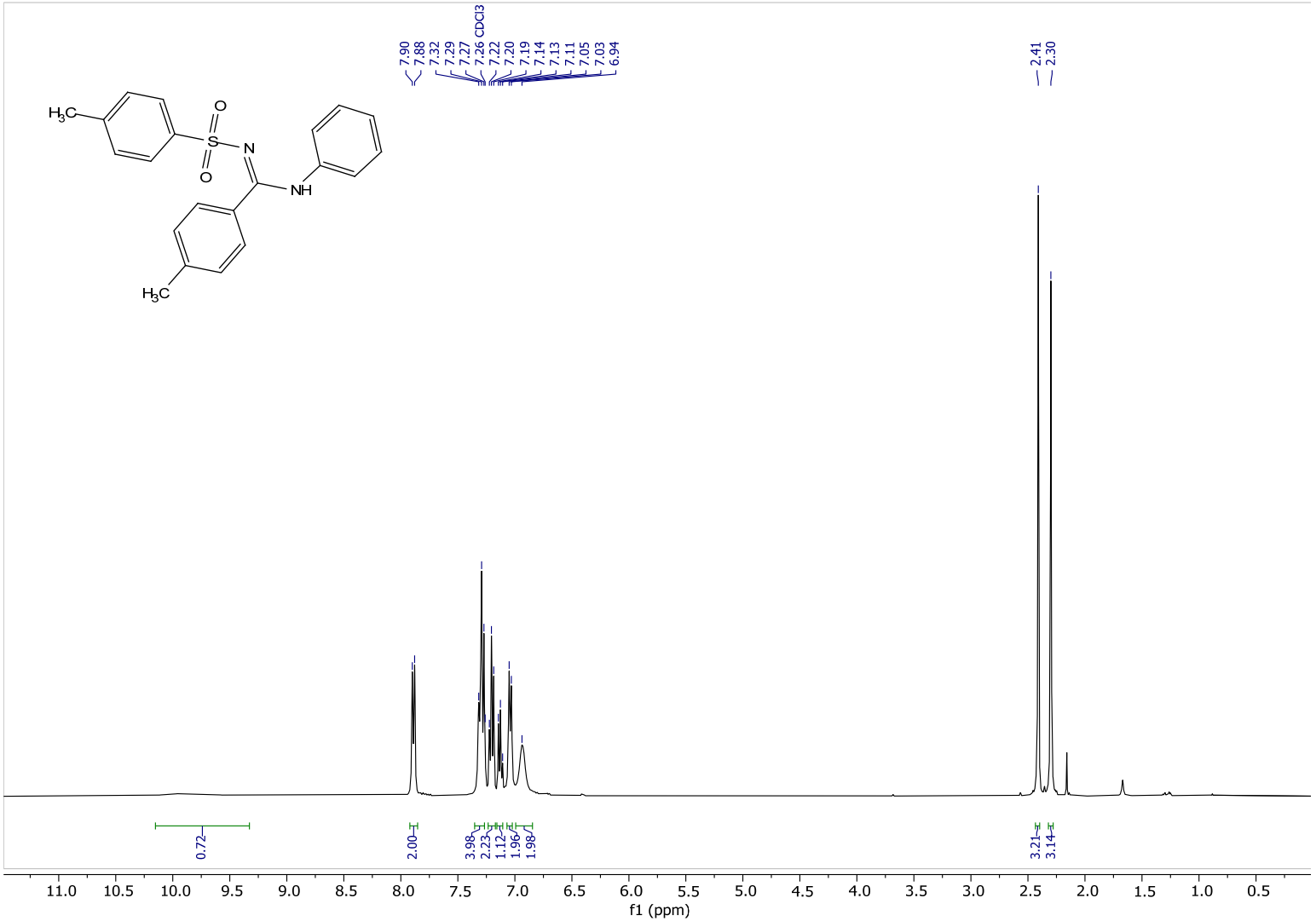

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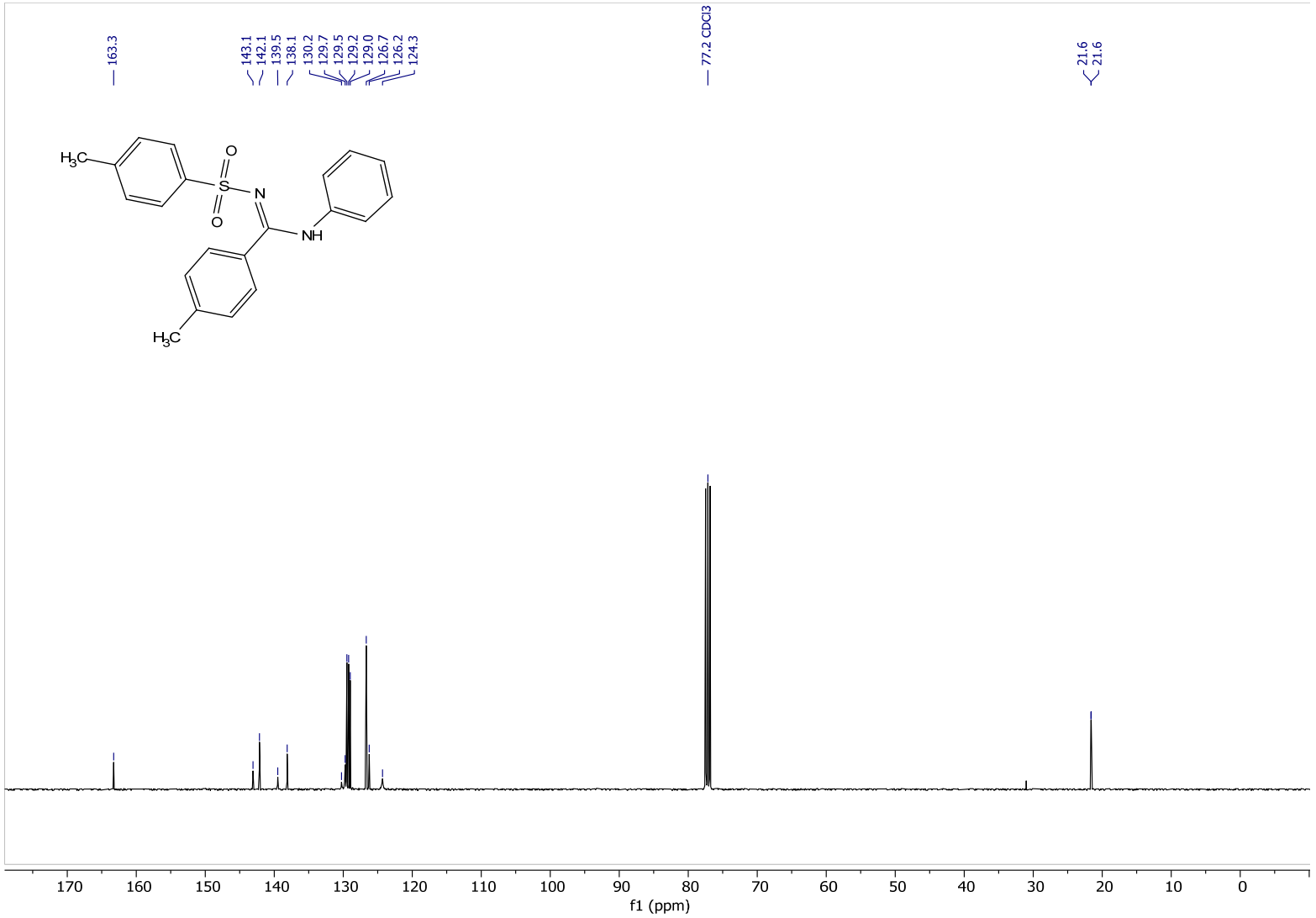

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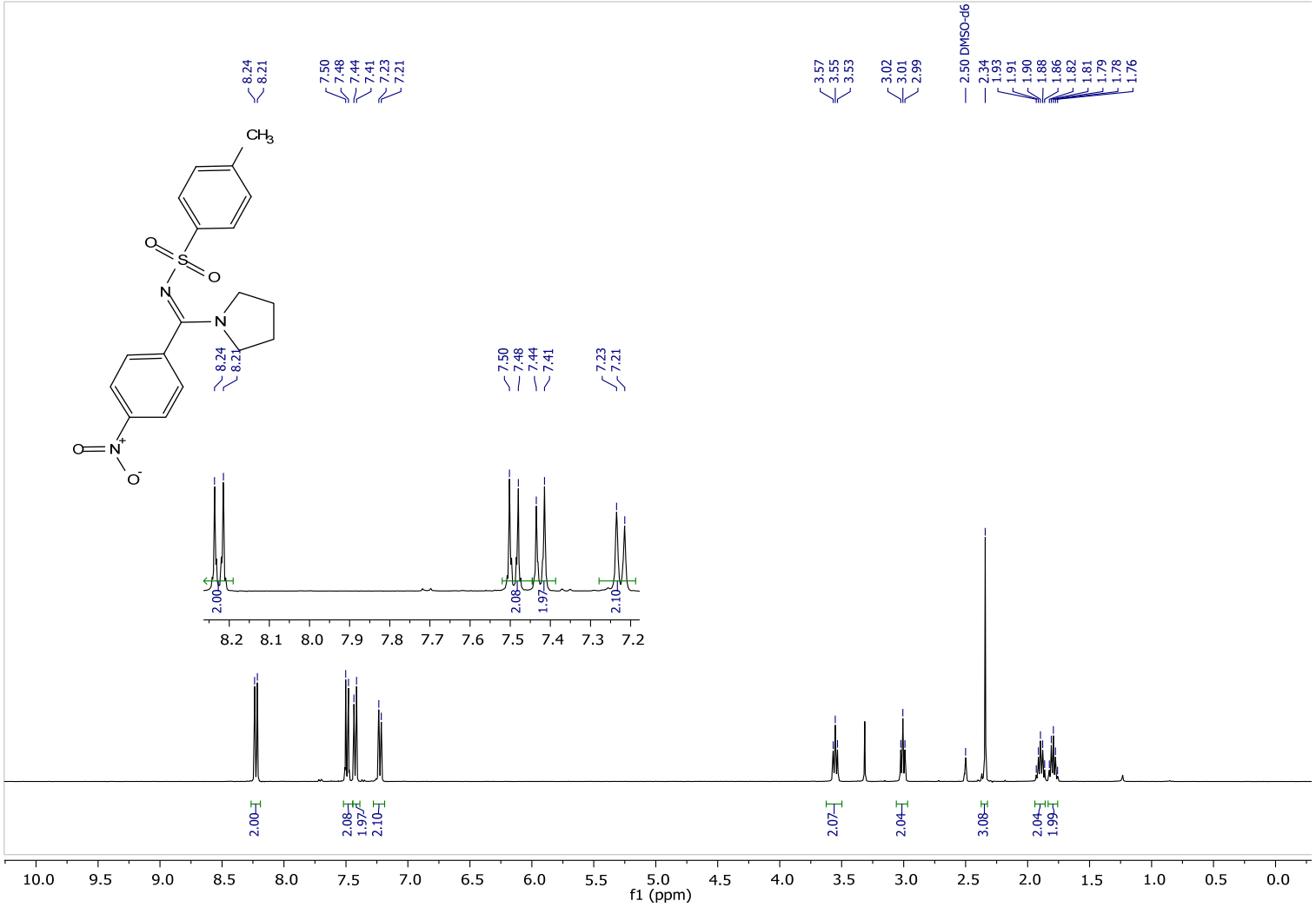
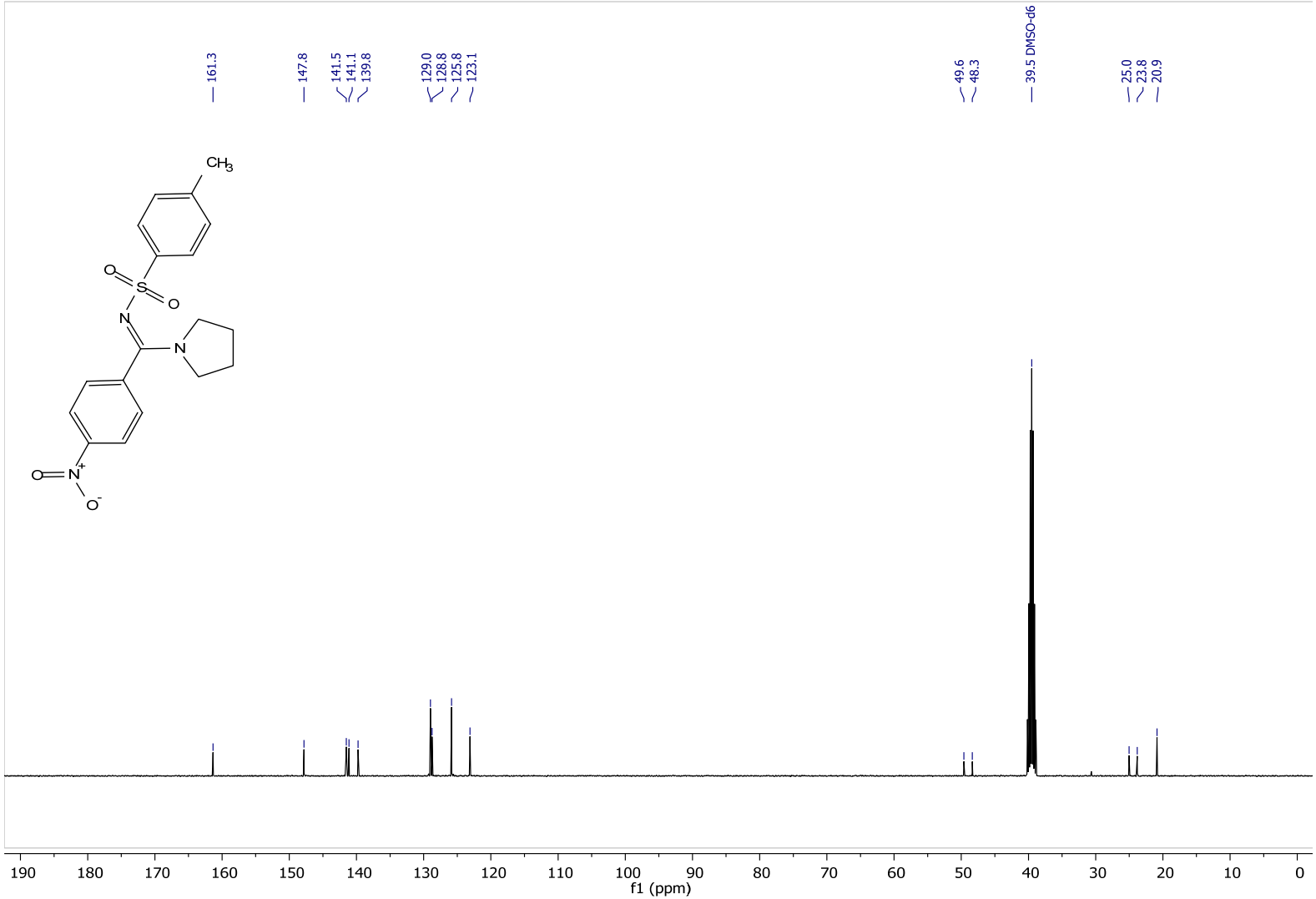
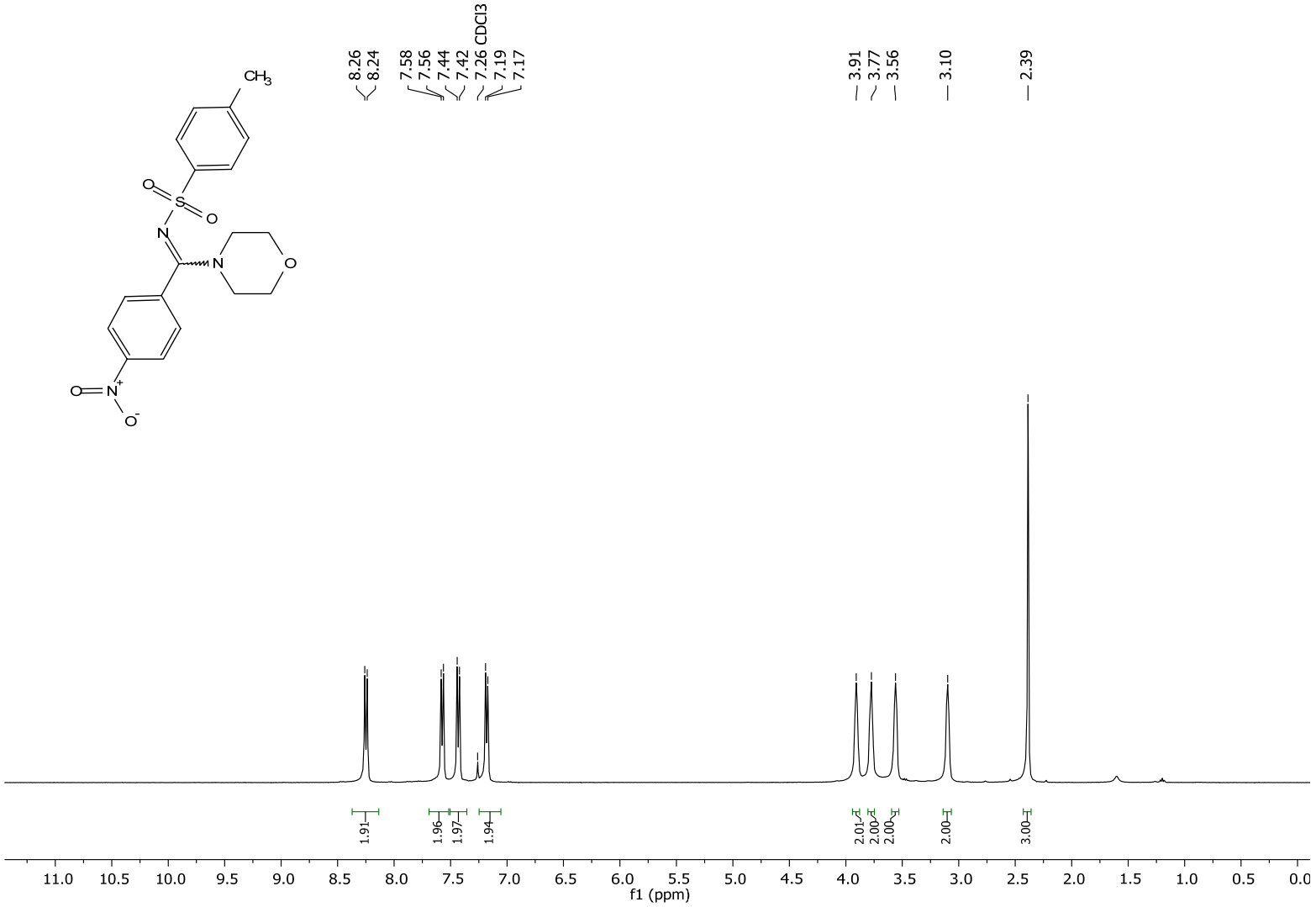


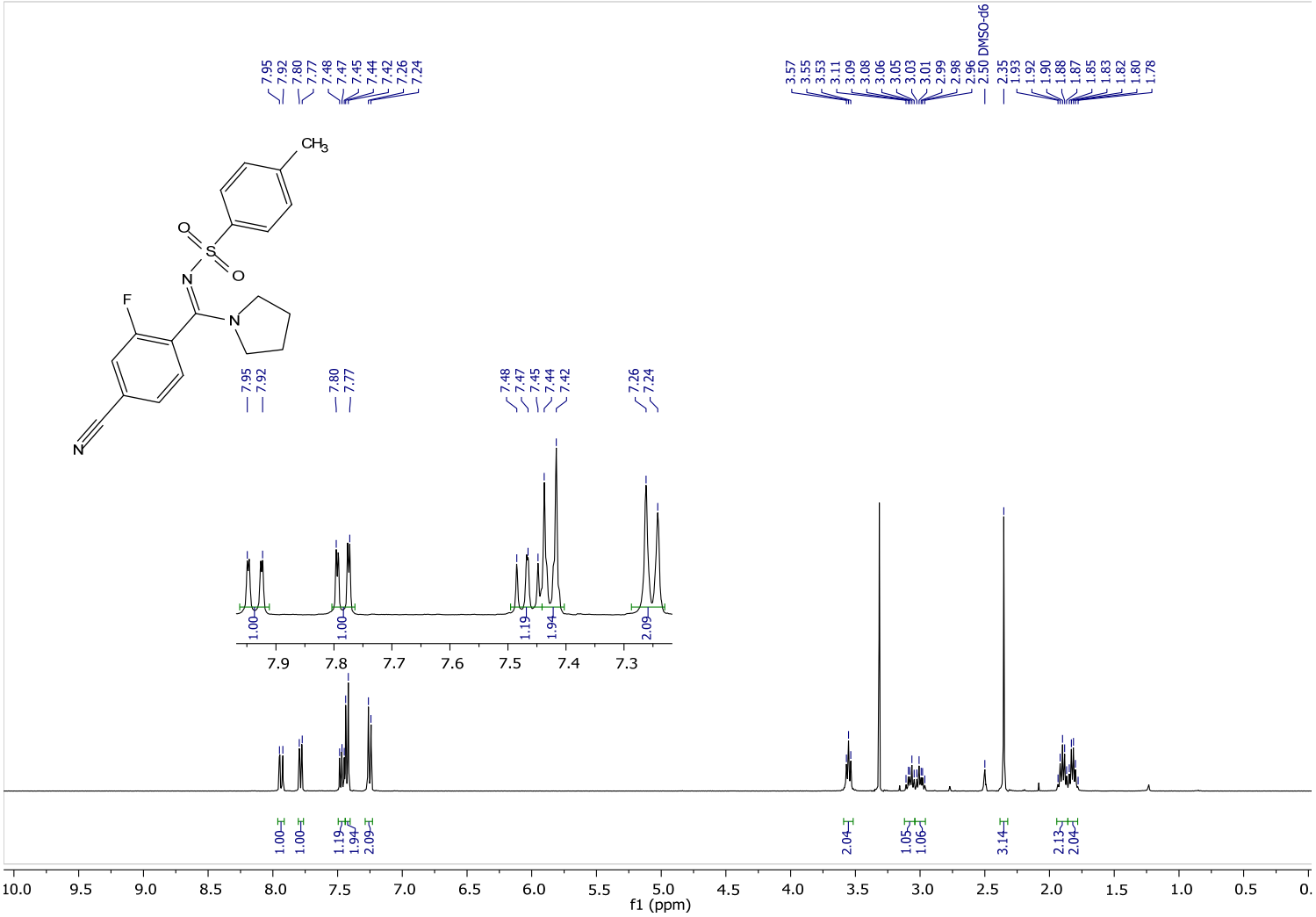
^{1}H NMR (400 MHz, DMSO–d_6) of **3ea**



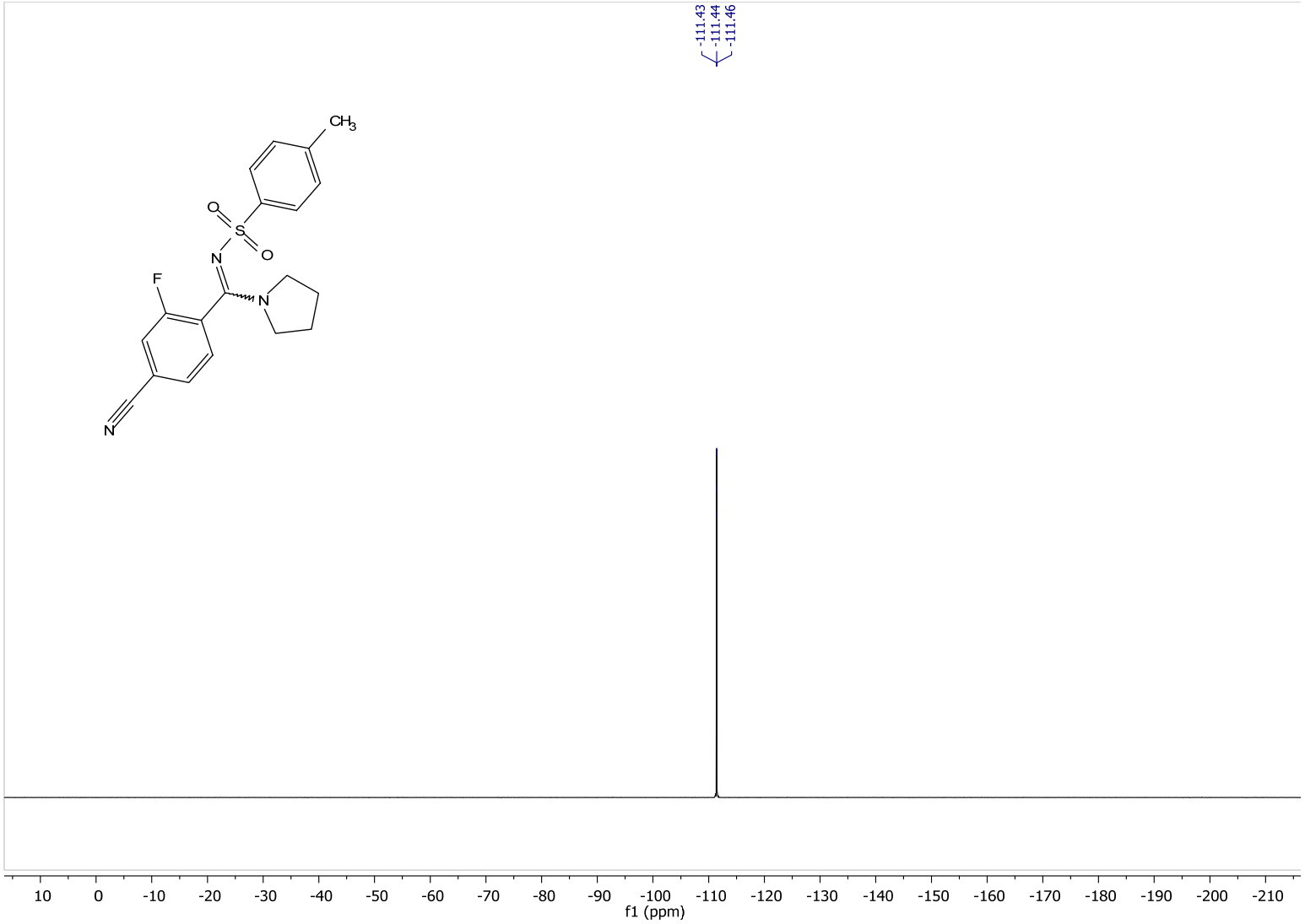
^{13}C NMR (100 MHz, DMSO–*d*$_6$) of **3ea**



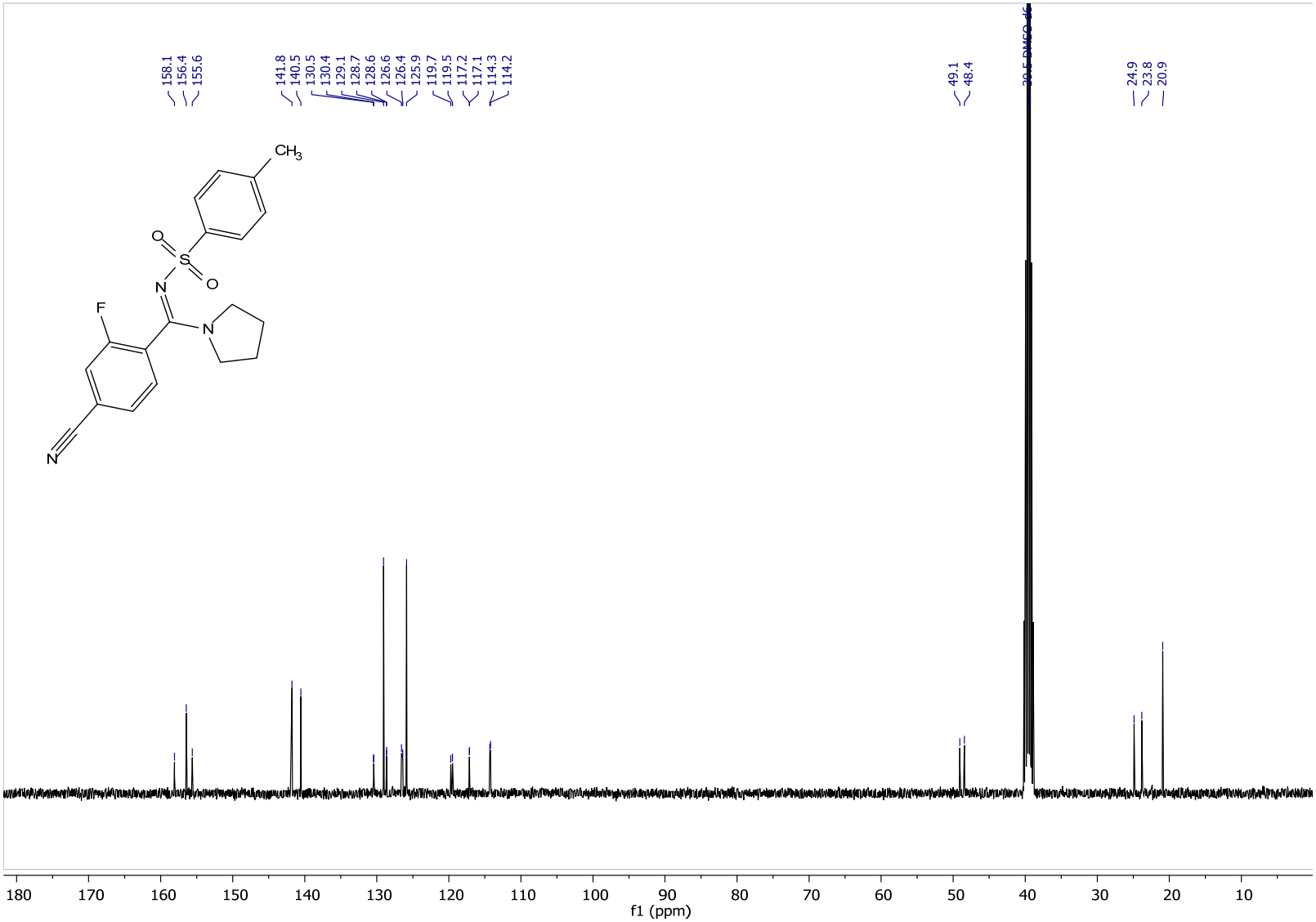
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3fa**



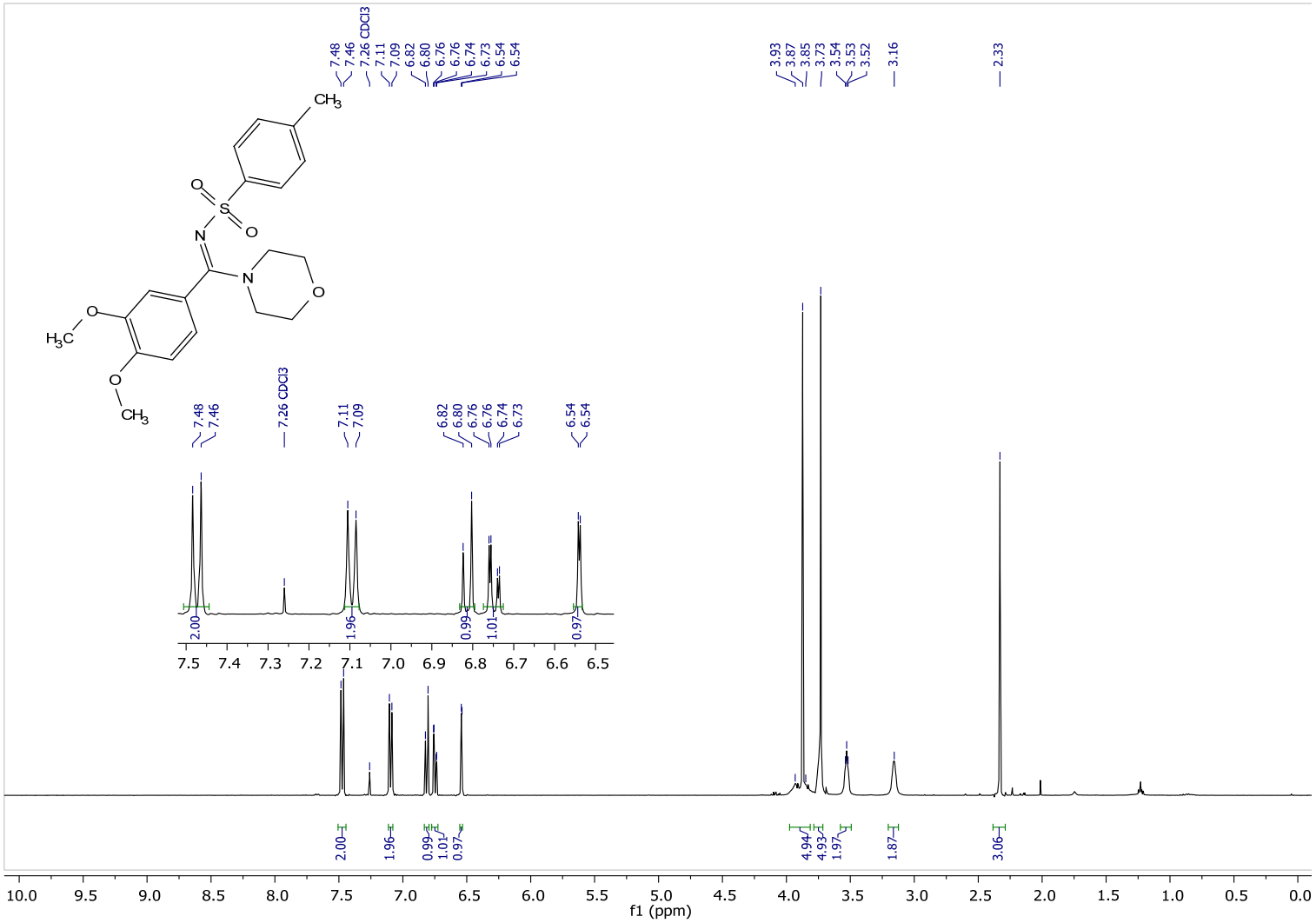
^{1}H NMR (400 MHz, DMSO–d_6) of **3ga**



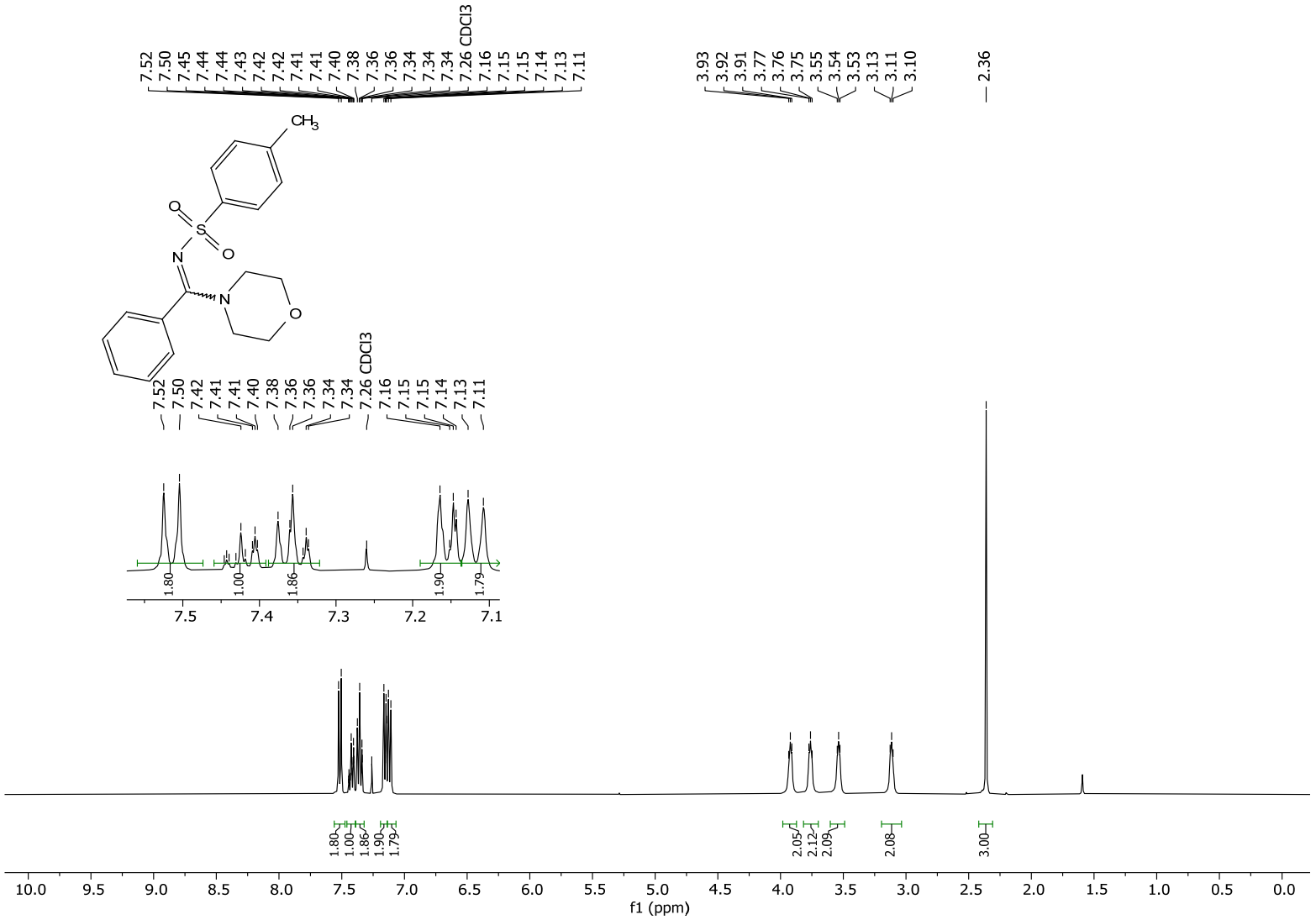
^{19}F NMR (565 MHz, DMSO-d_6) of **3ga**



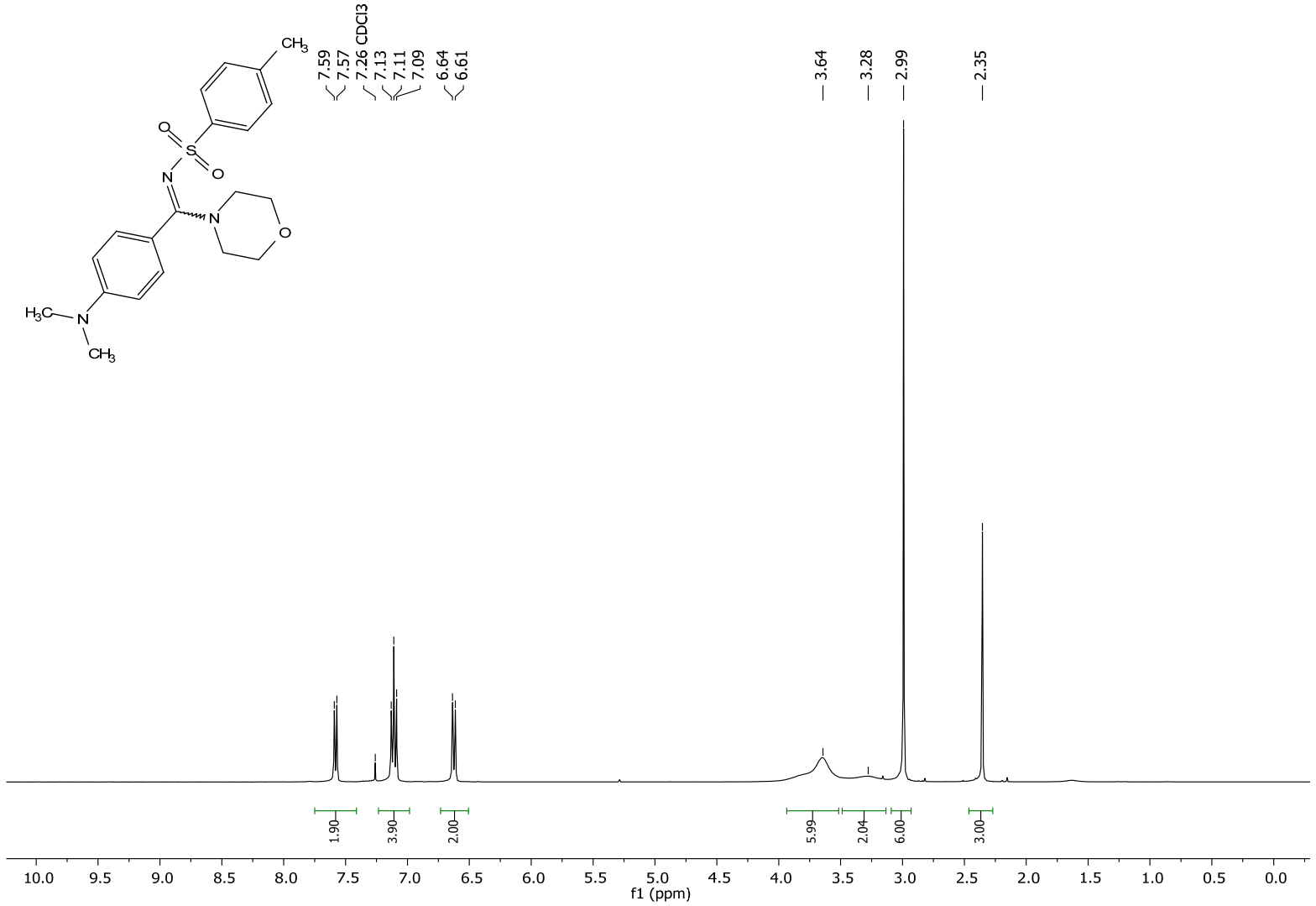
^{13}C NMR (100 MHz, DMSO–d_6) of **3ga**



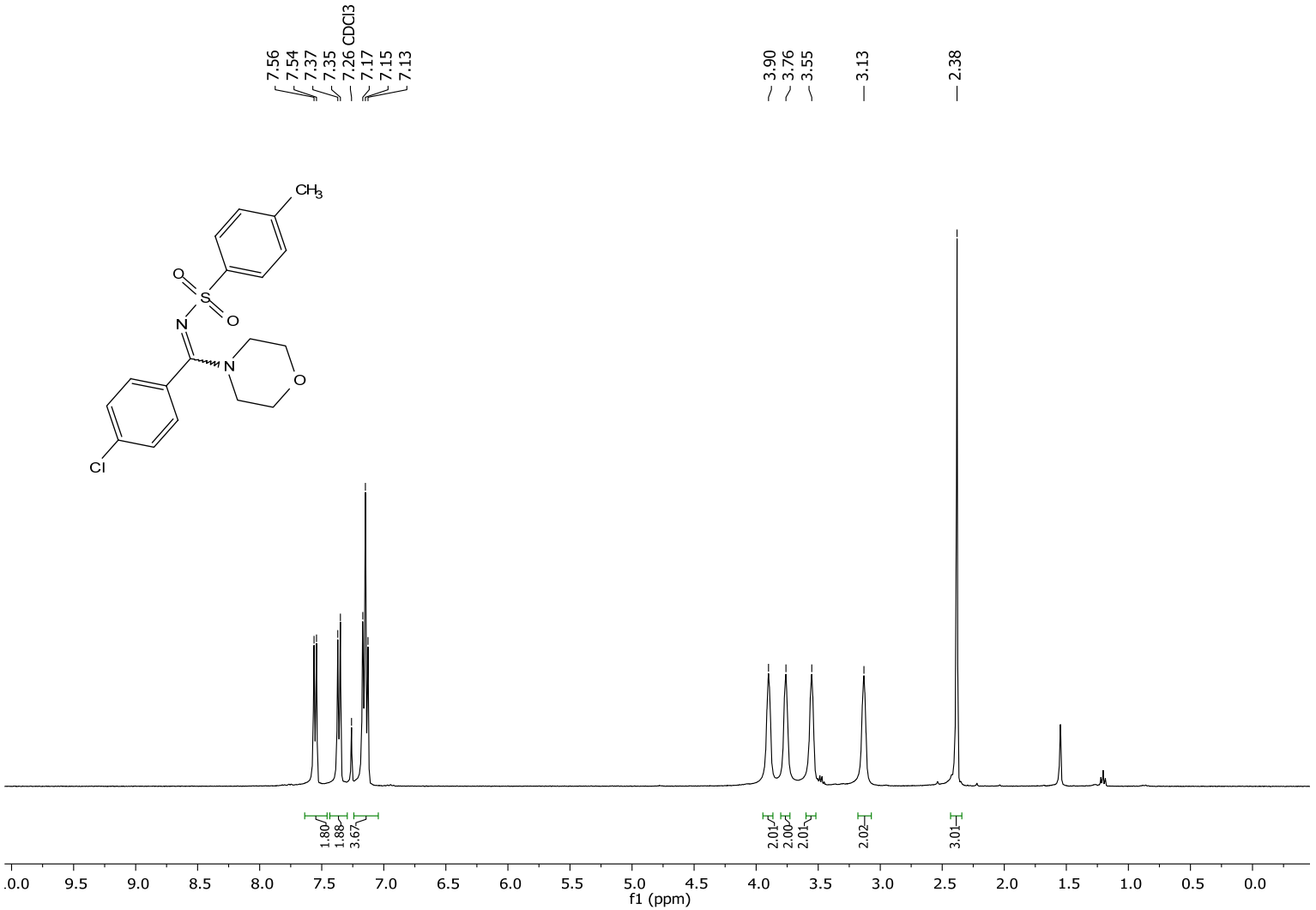
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ha**



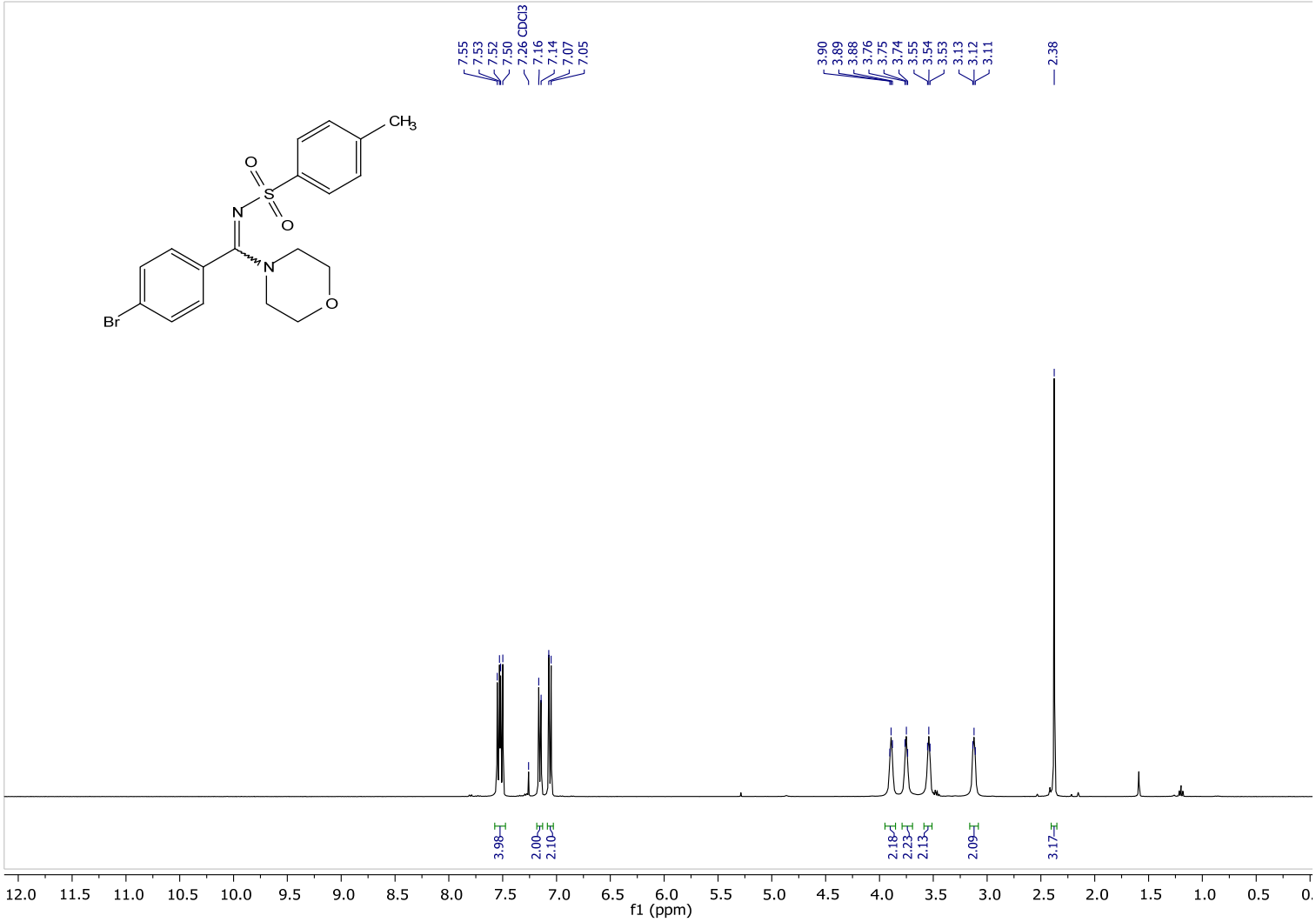
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ia**



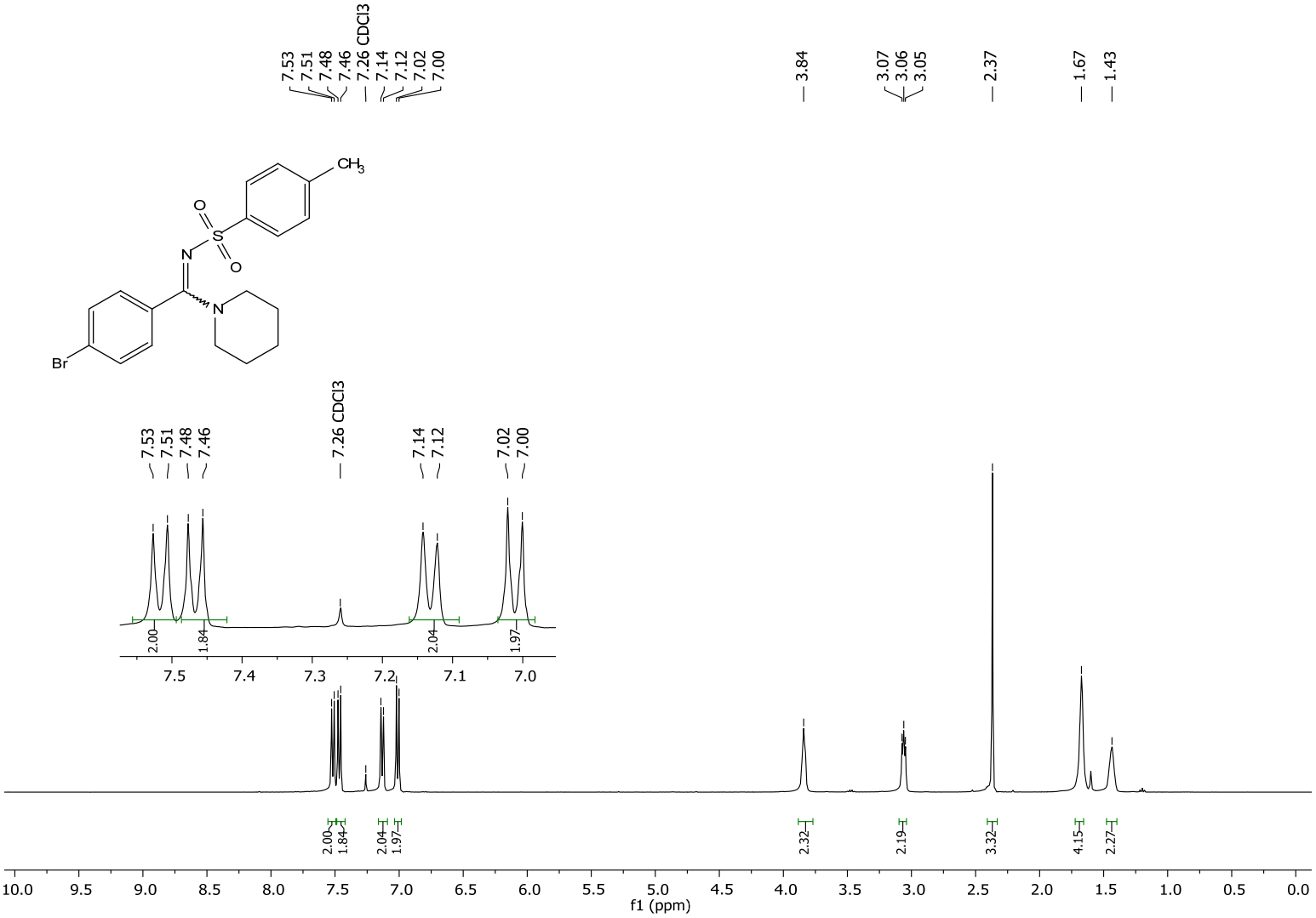
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ja**



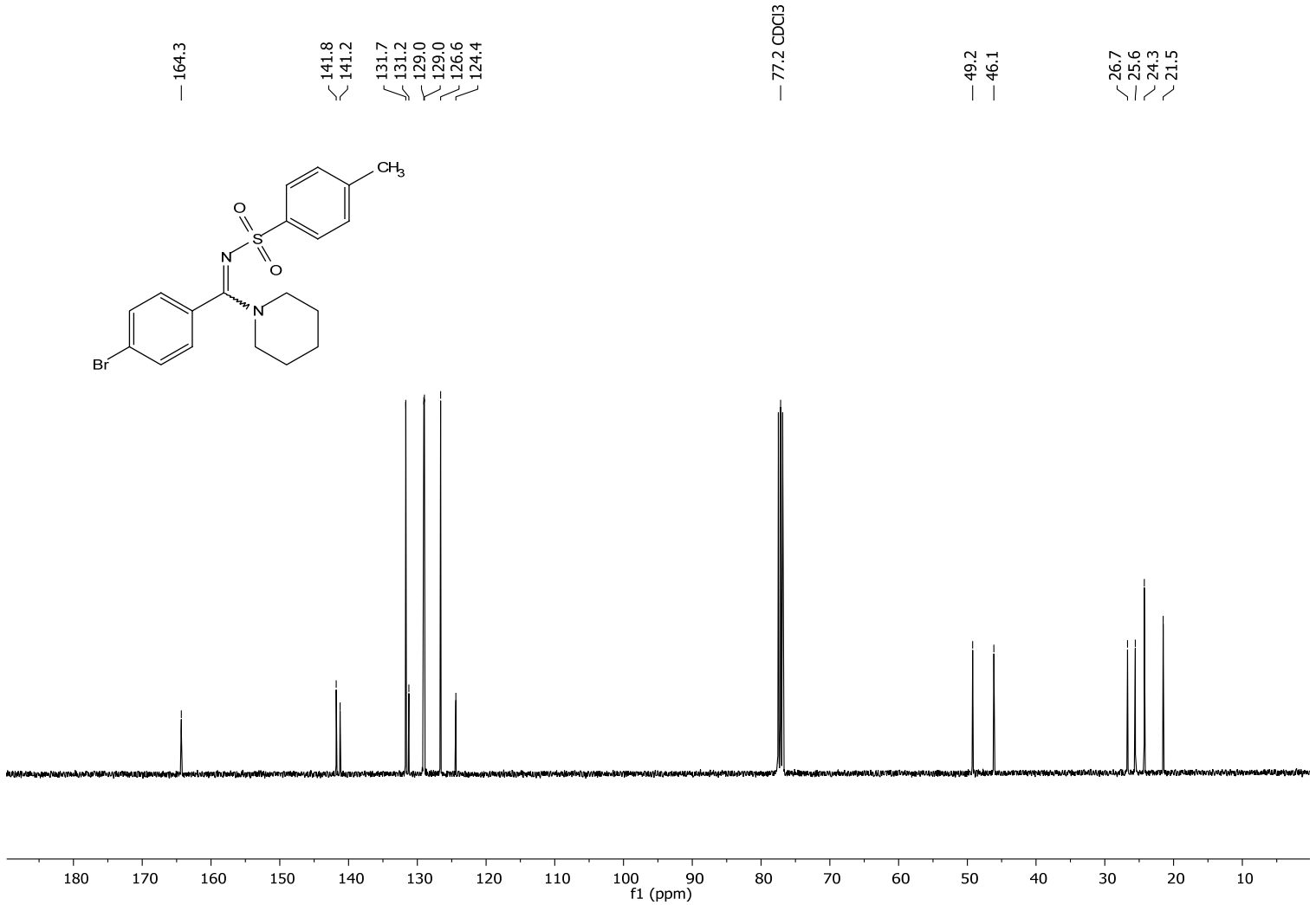
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ka**



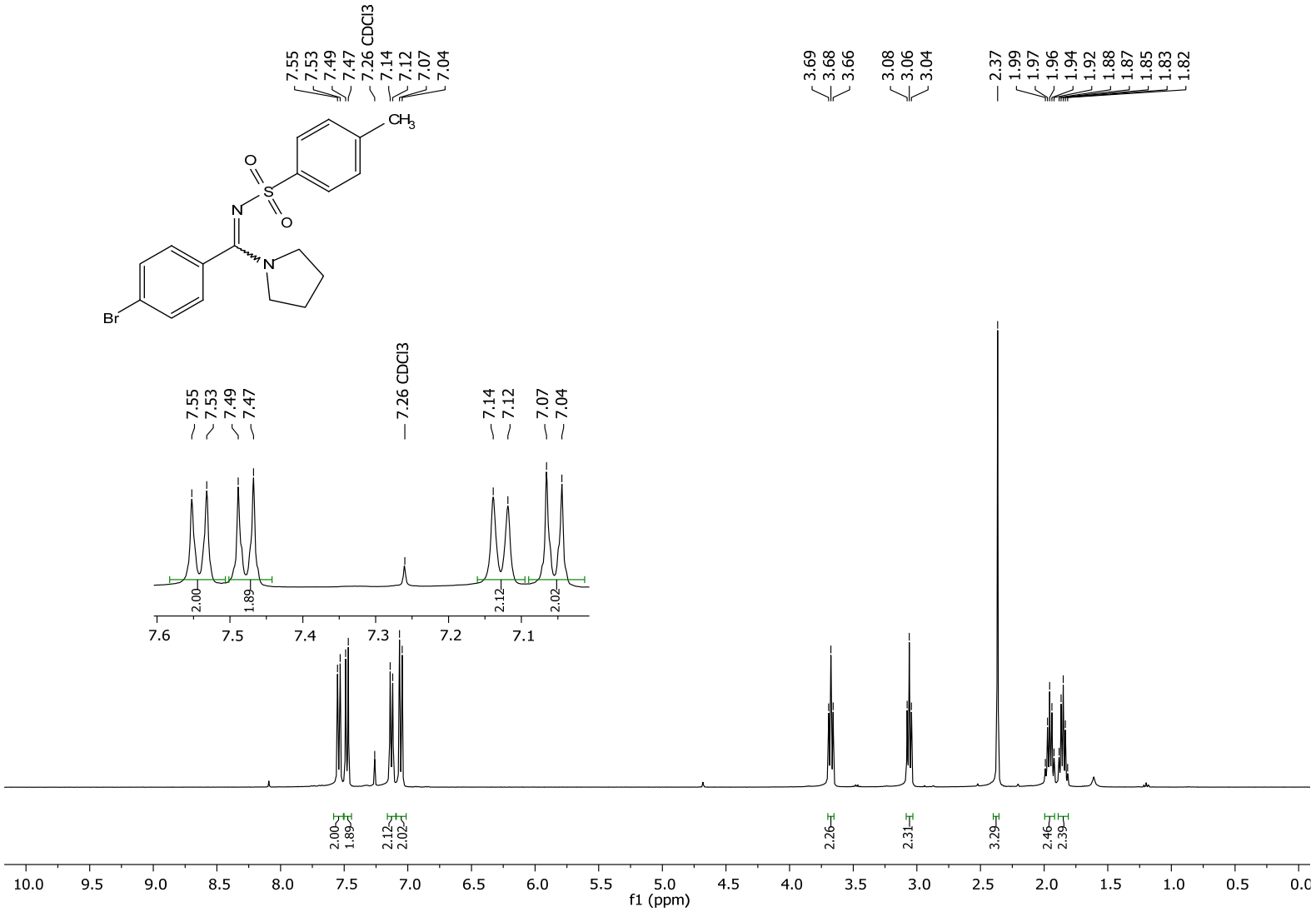
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3la**



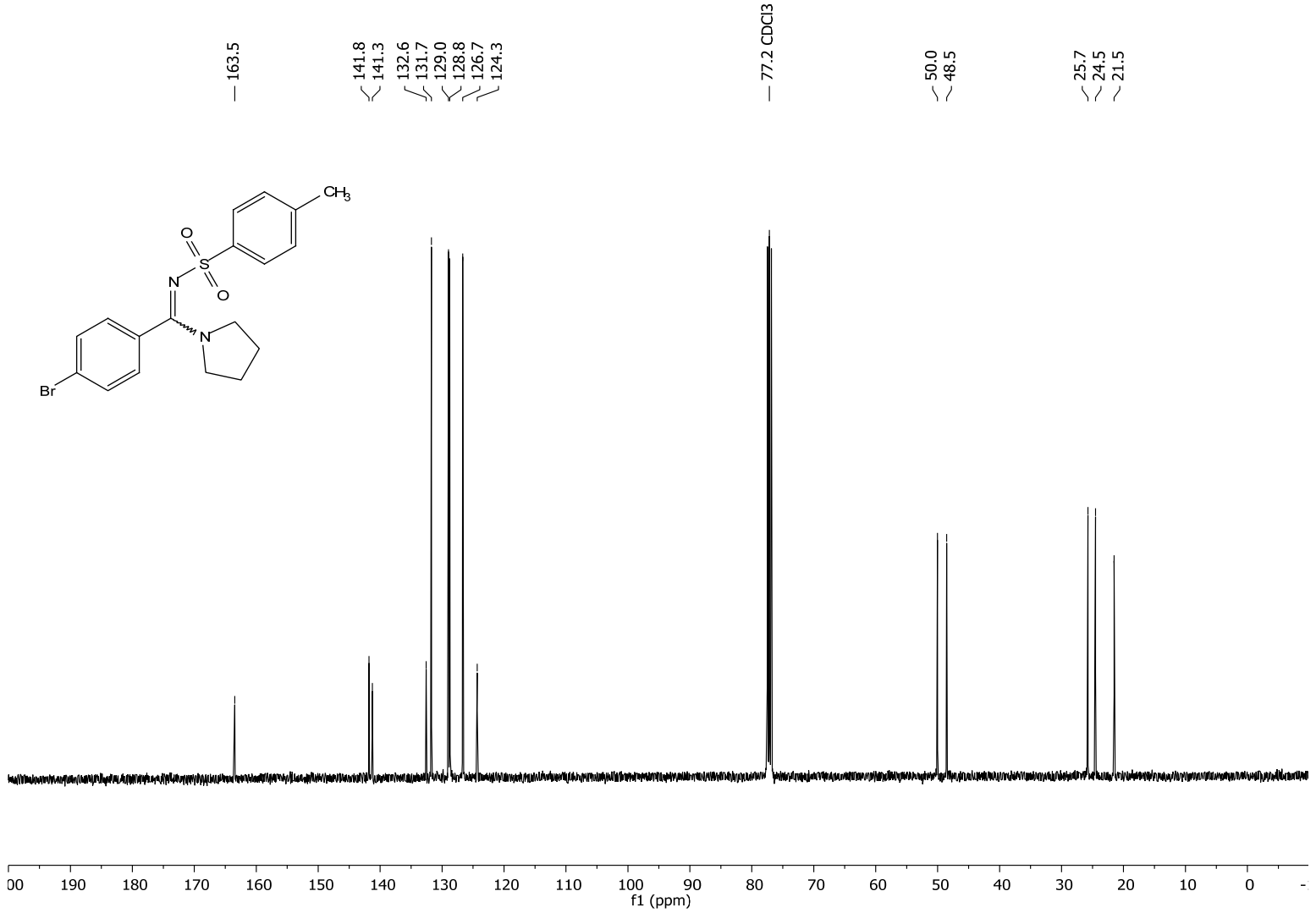
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ma**



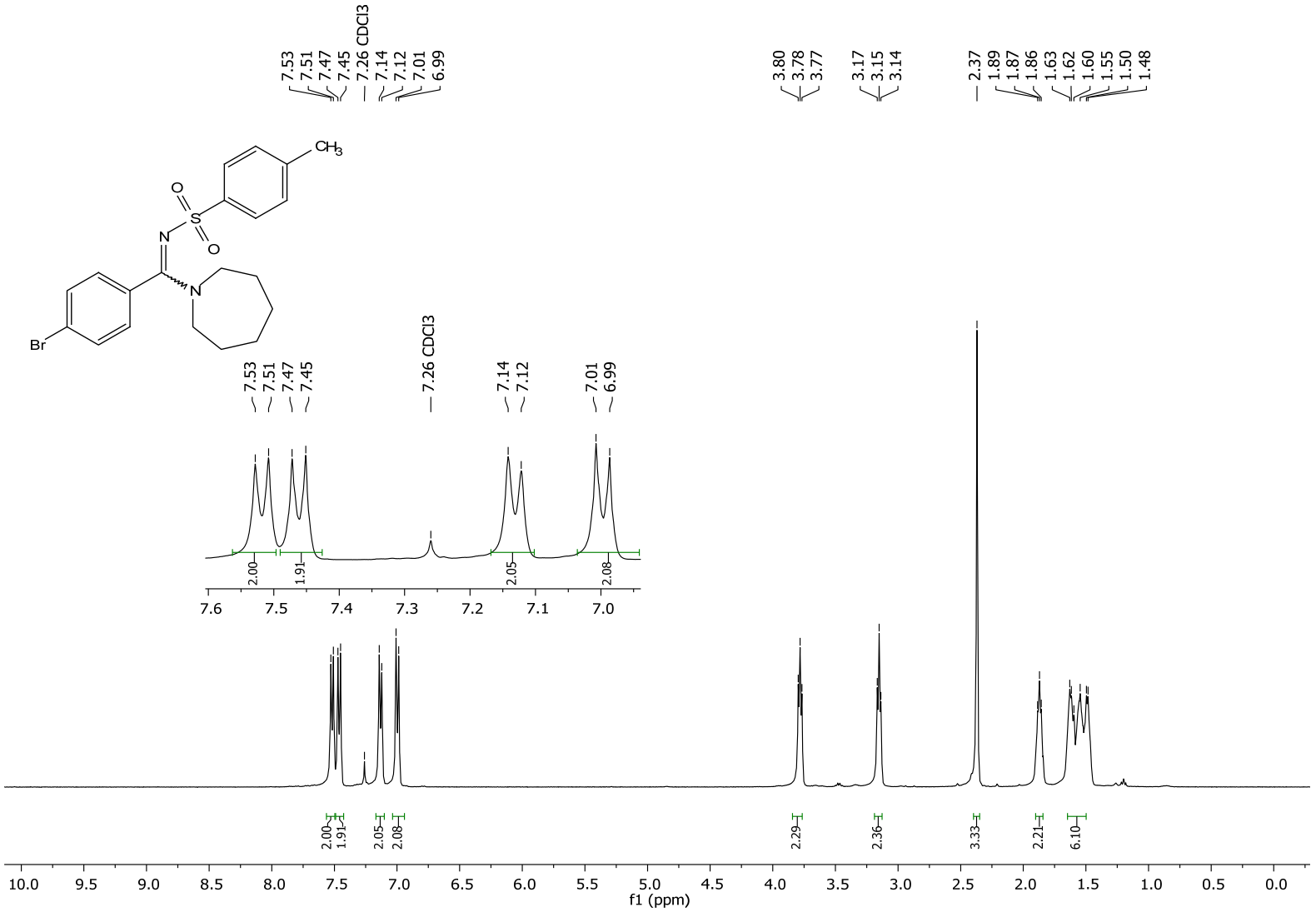
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3ma**



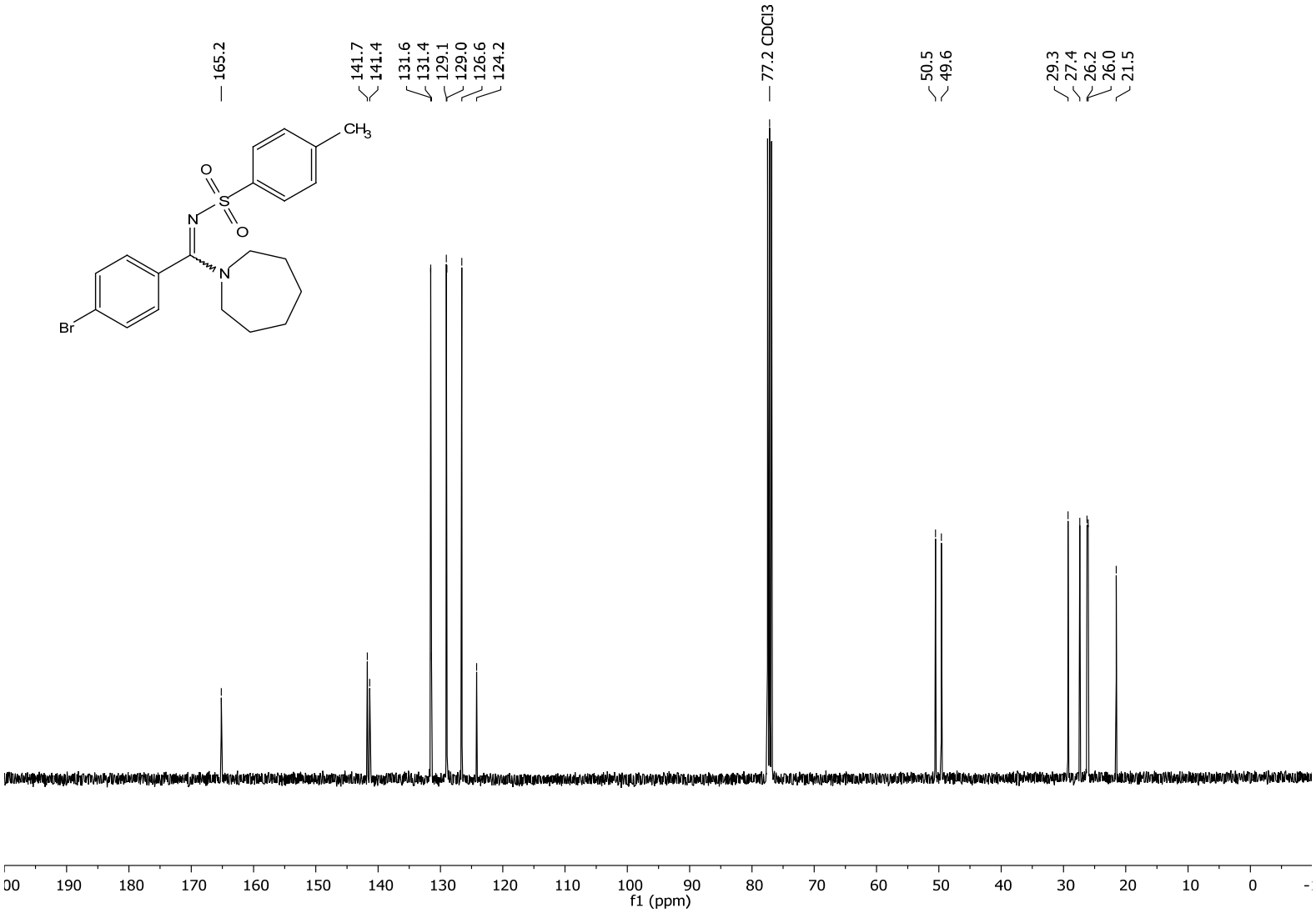
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3na**



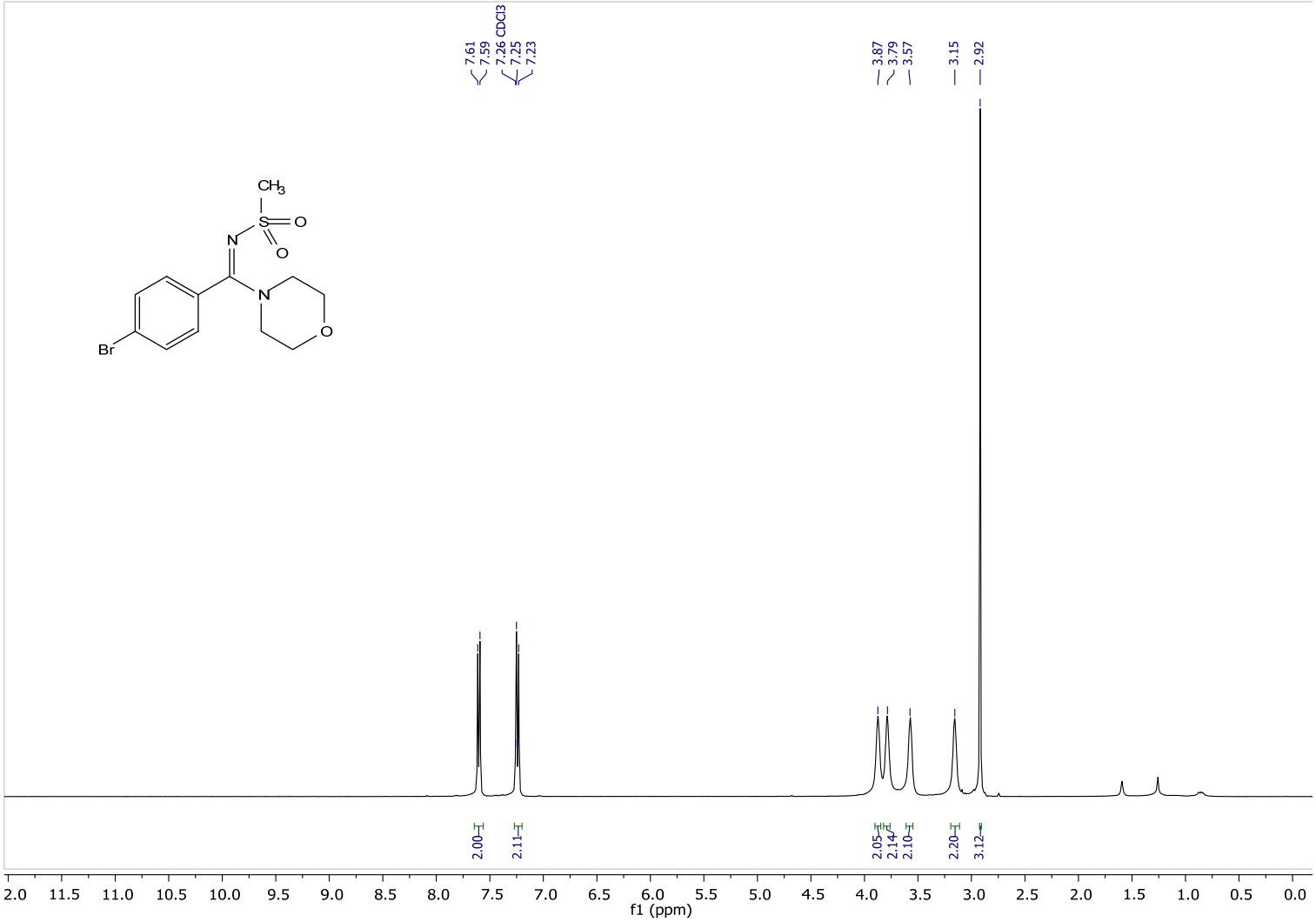
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3na**



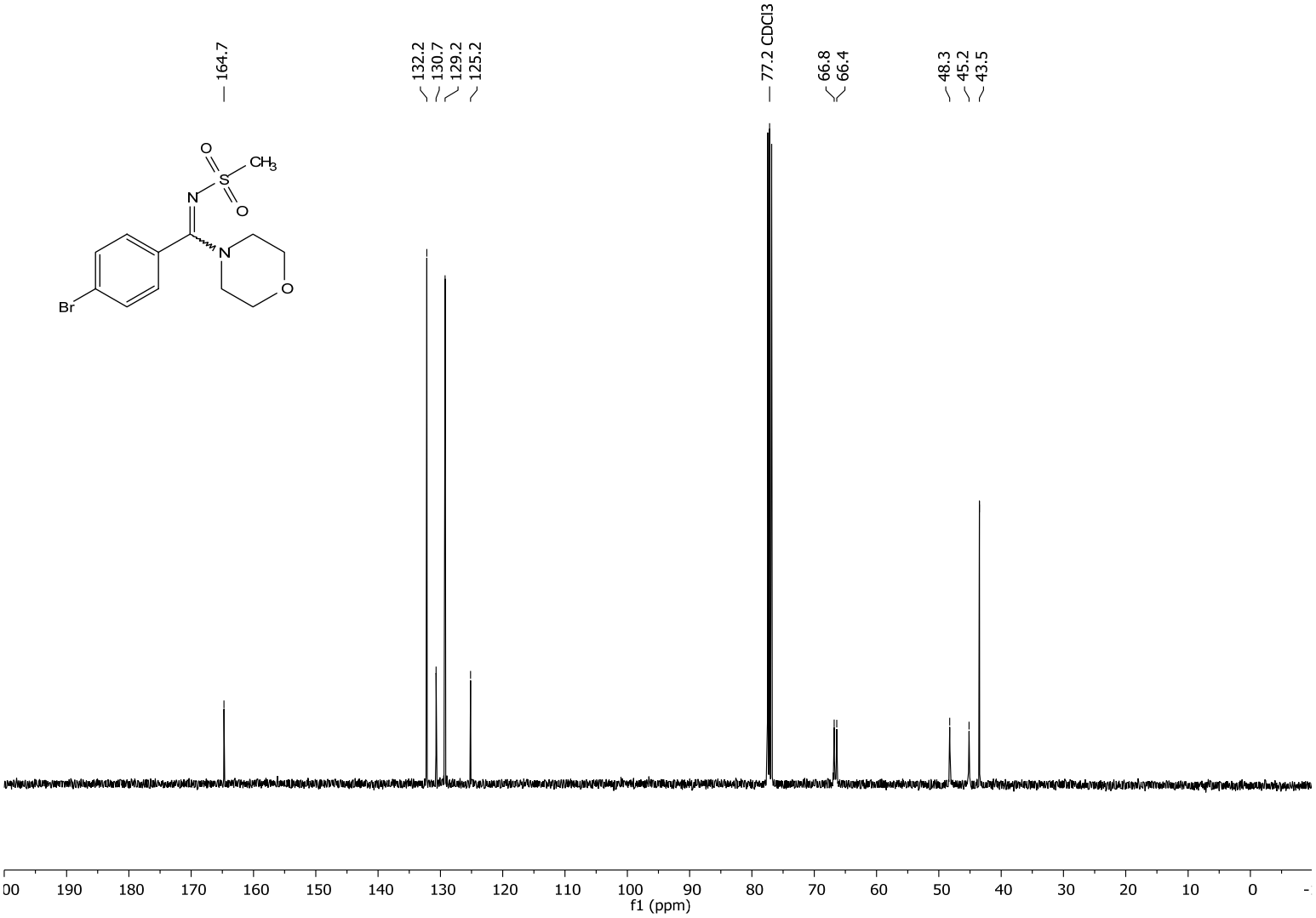
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3oa**



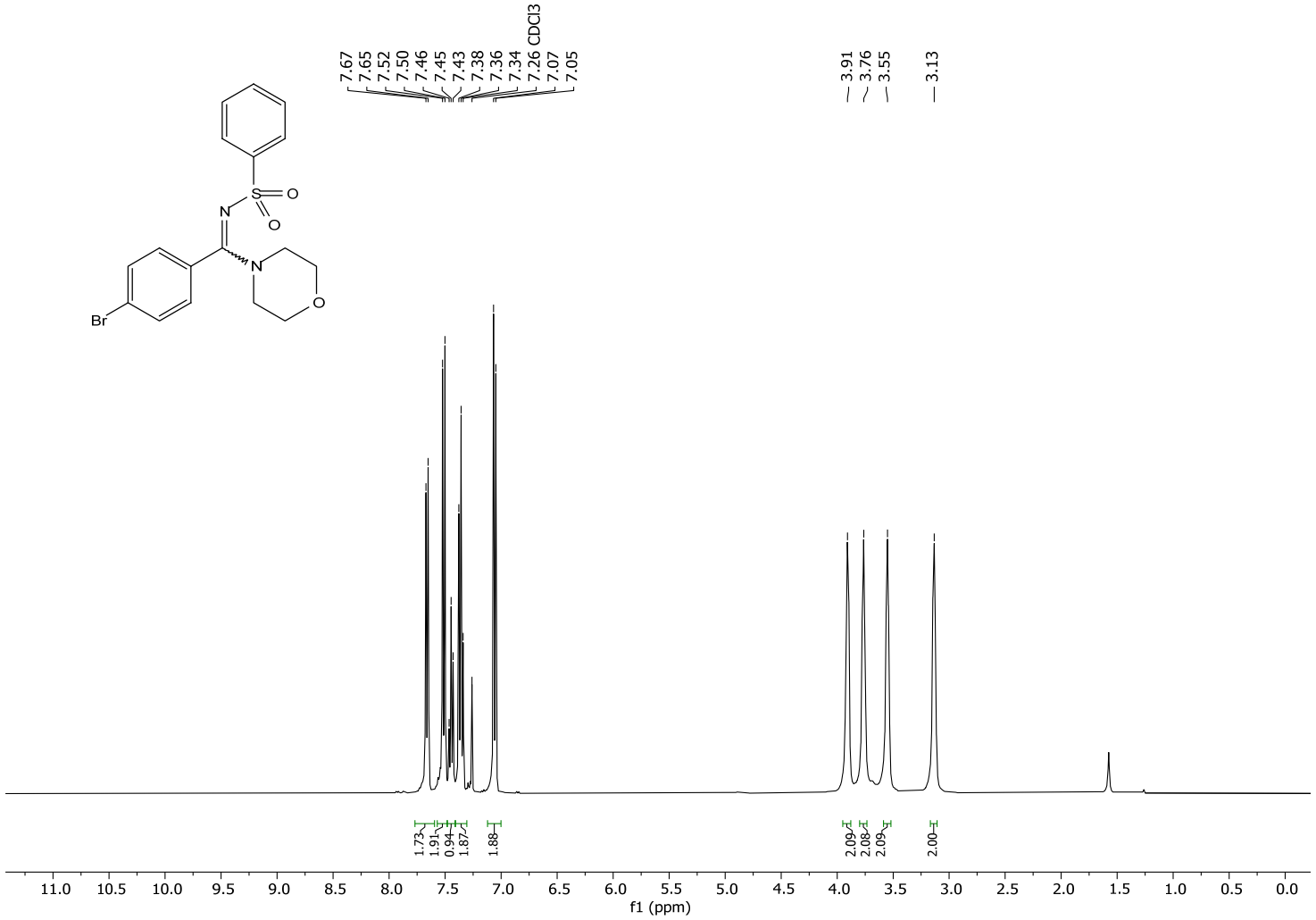
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3oa**



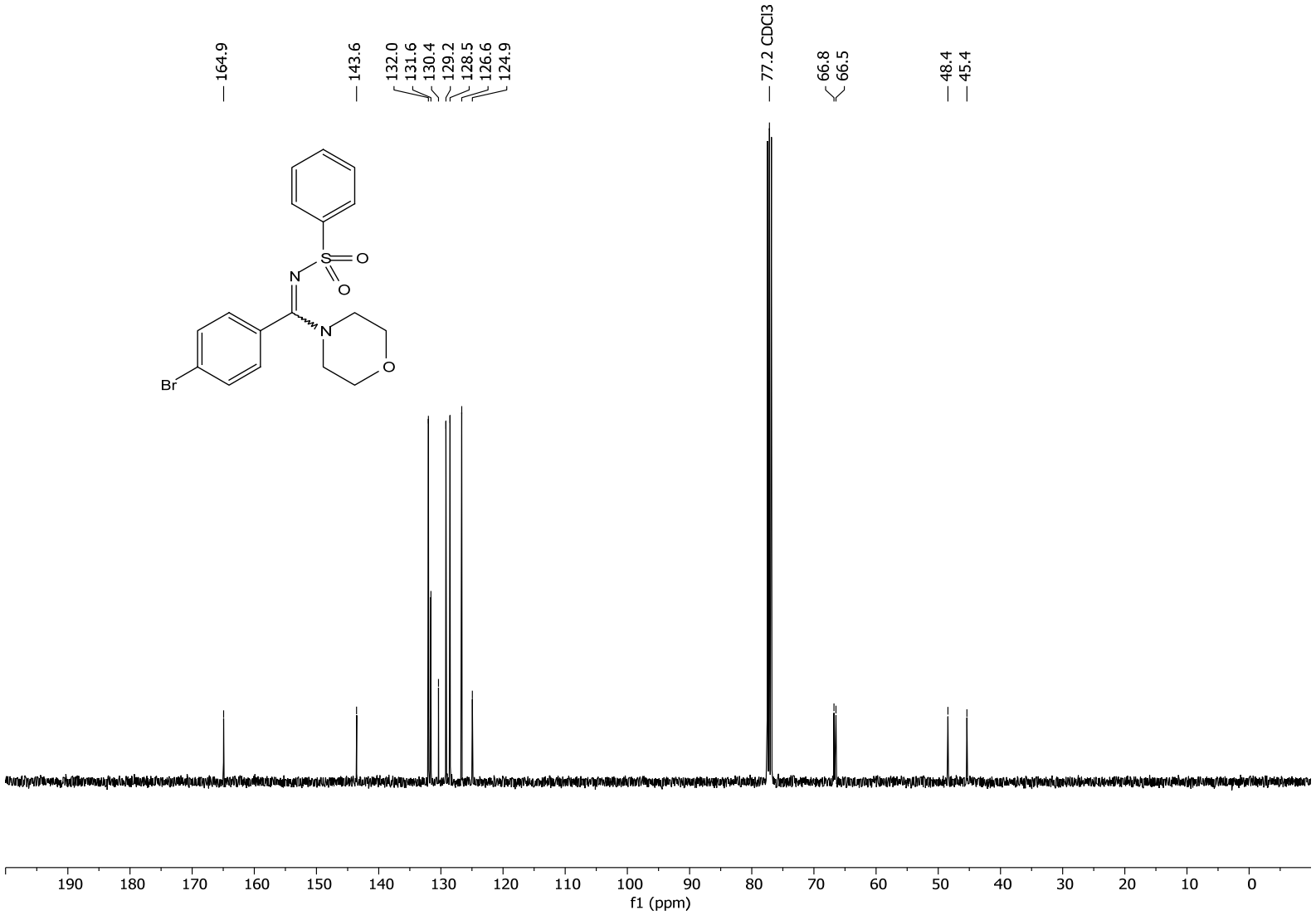
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3lb**



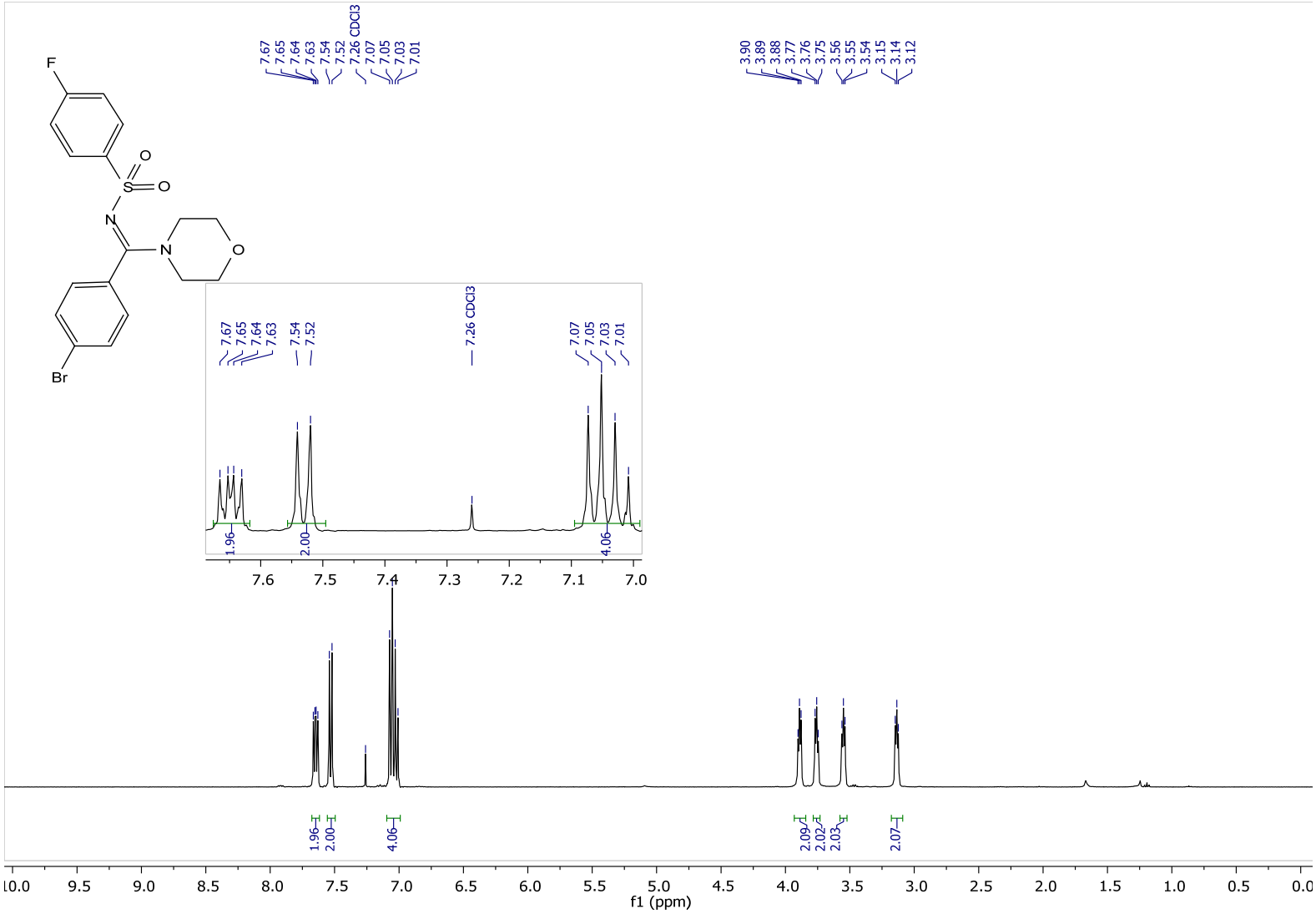
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3lb**



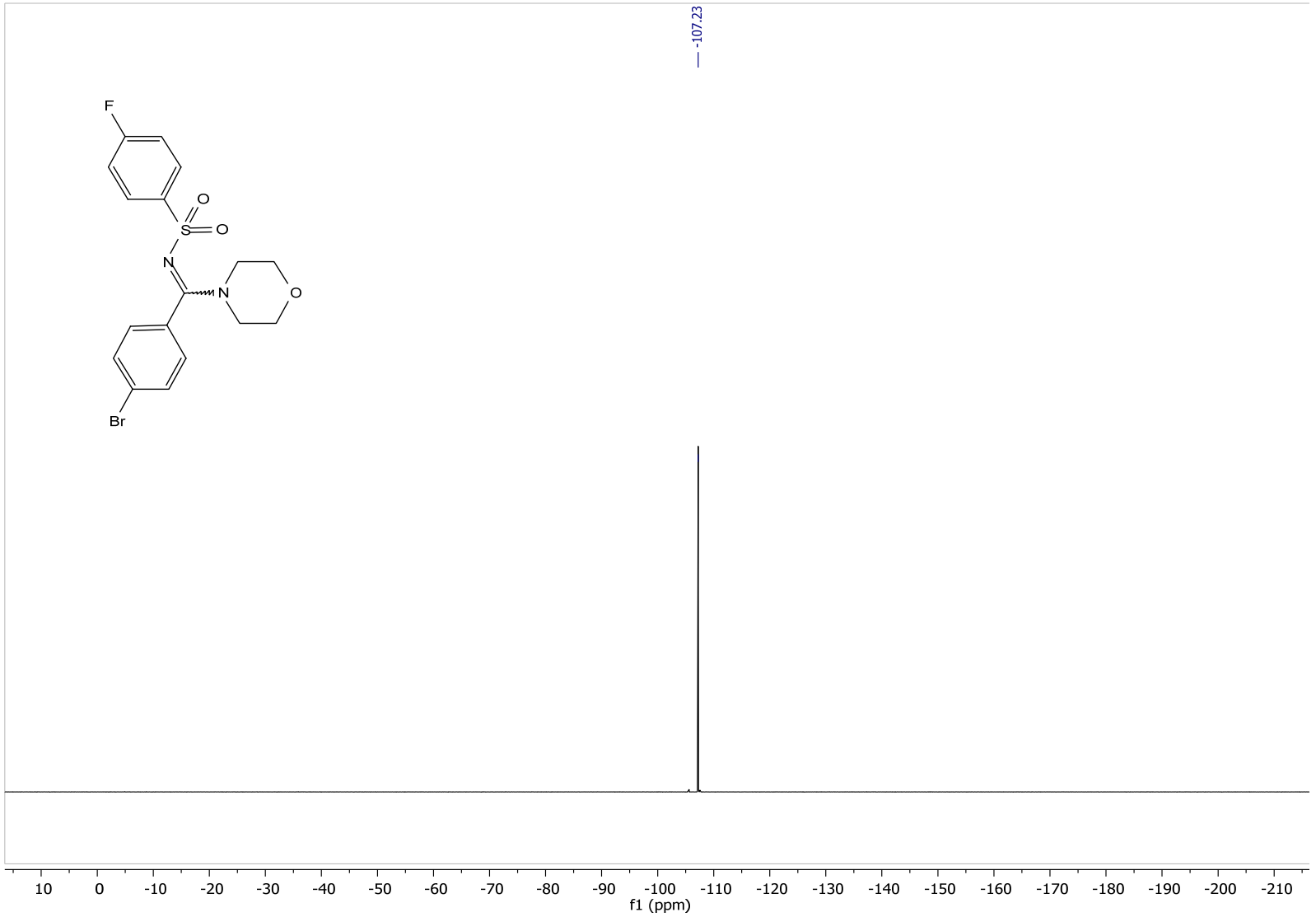
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3lc**



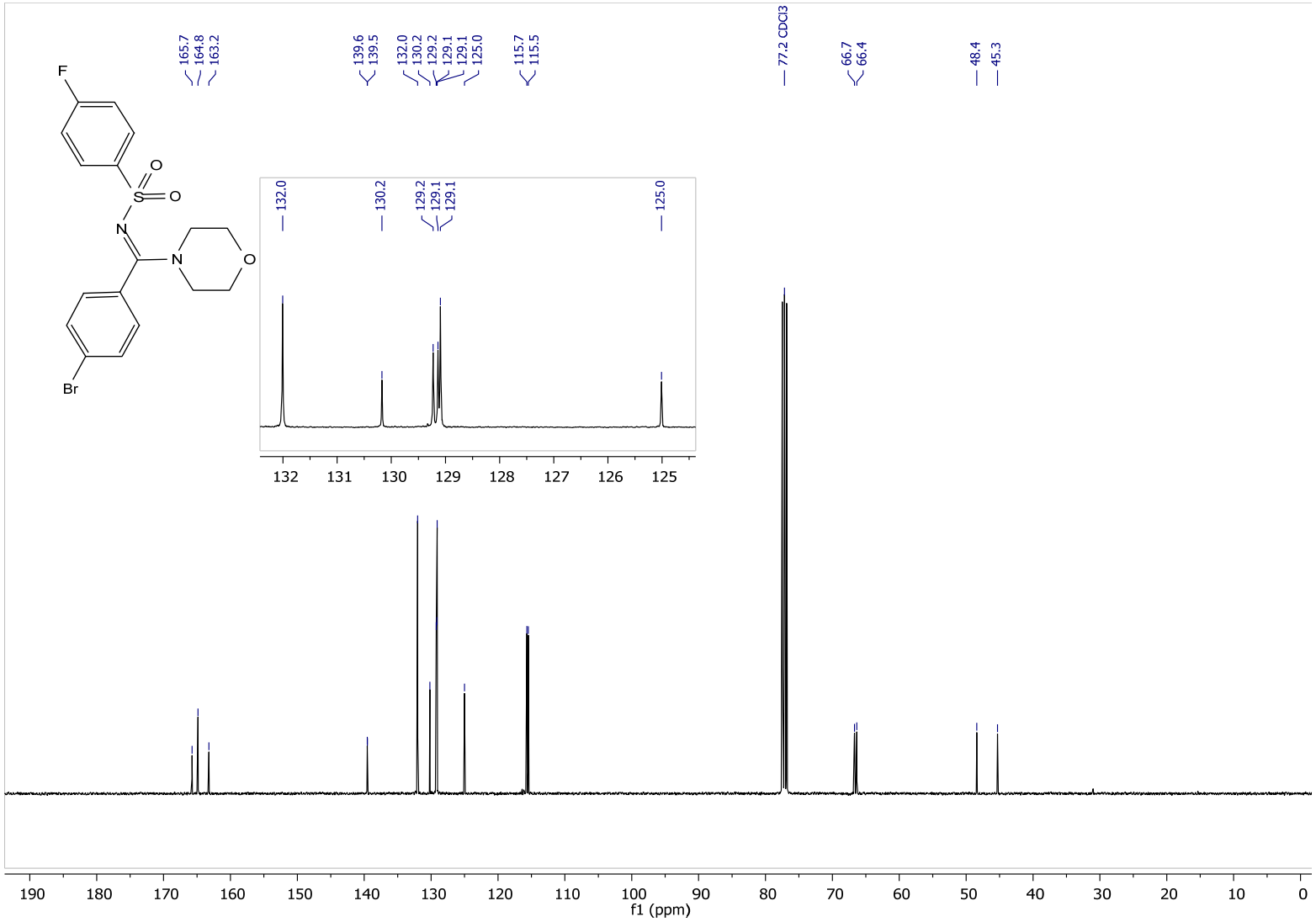
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3lc**



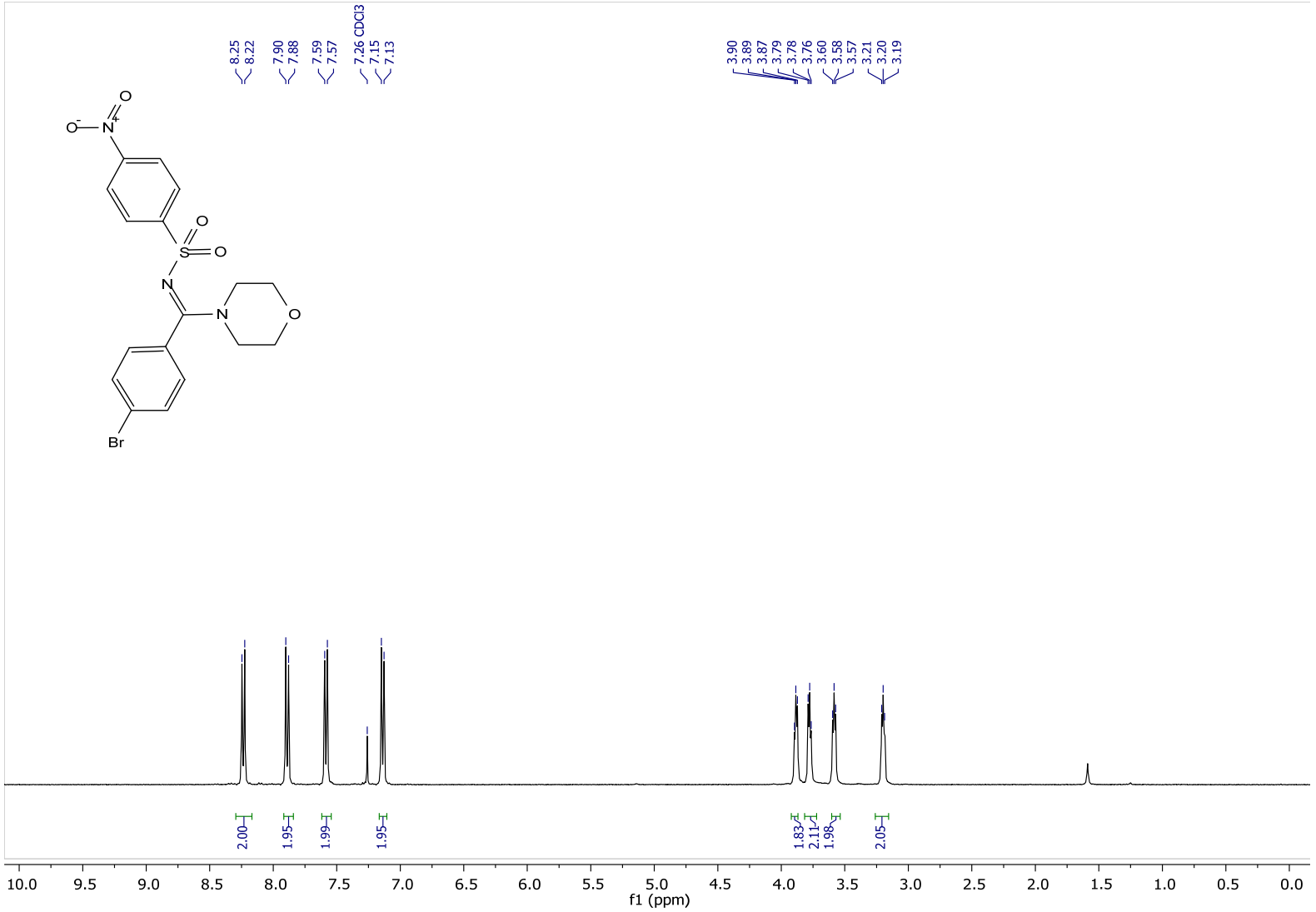
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ld**



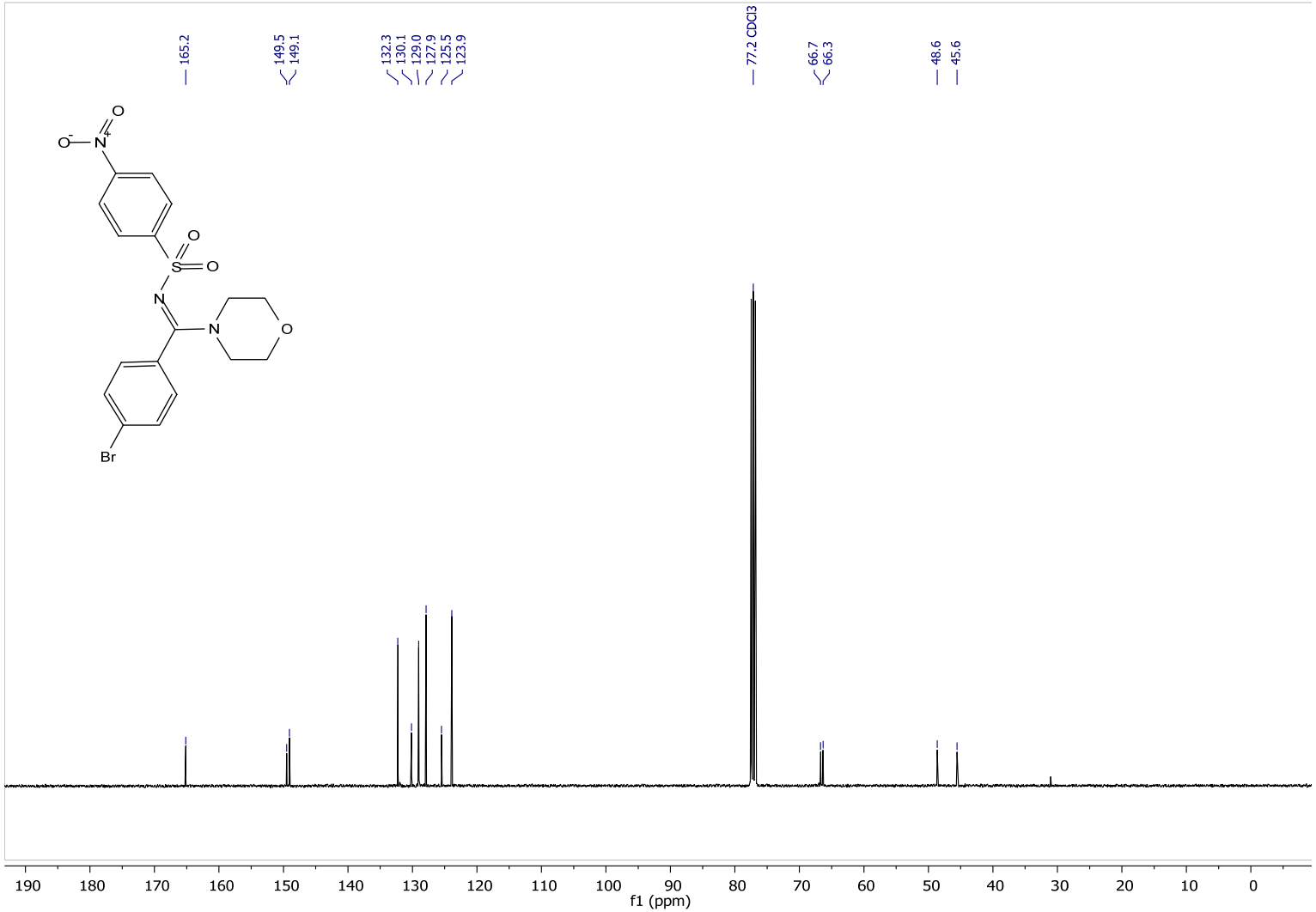
^{19}F NMR (565 MHz, $CDCl_3$-*d*) of **3ld**



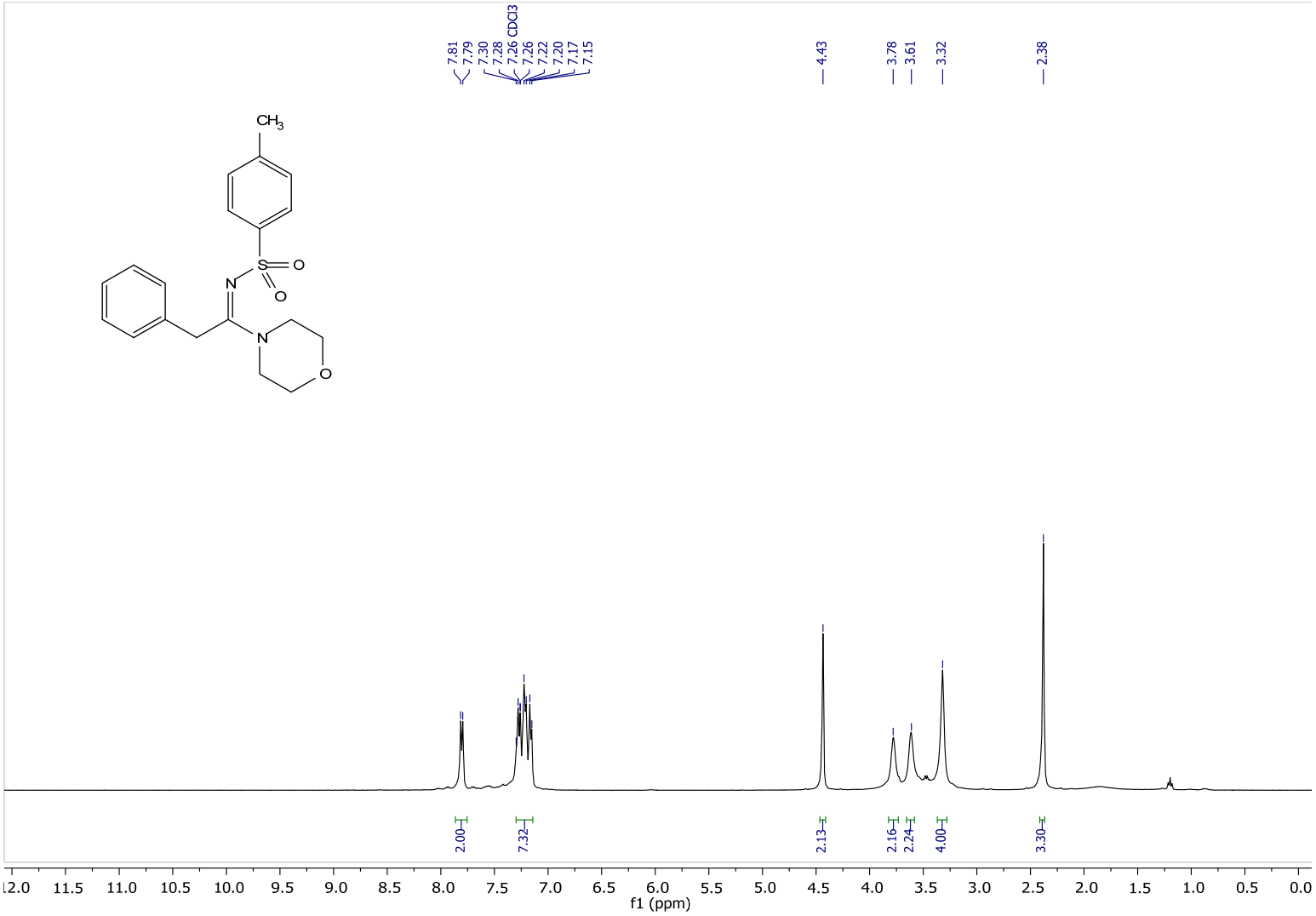
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3ld**



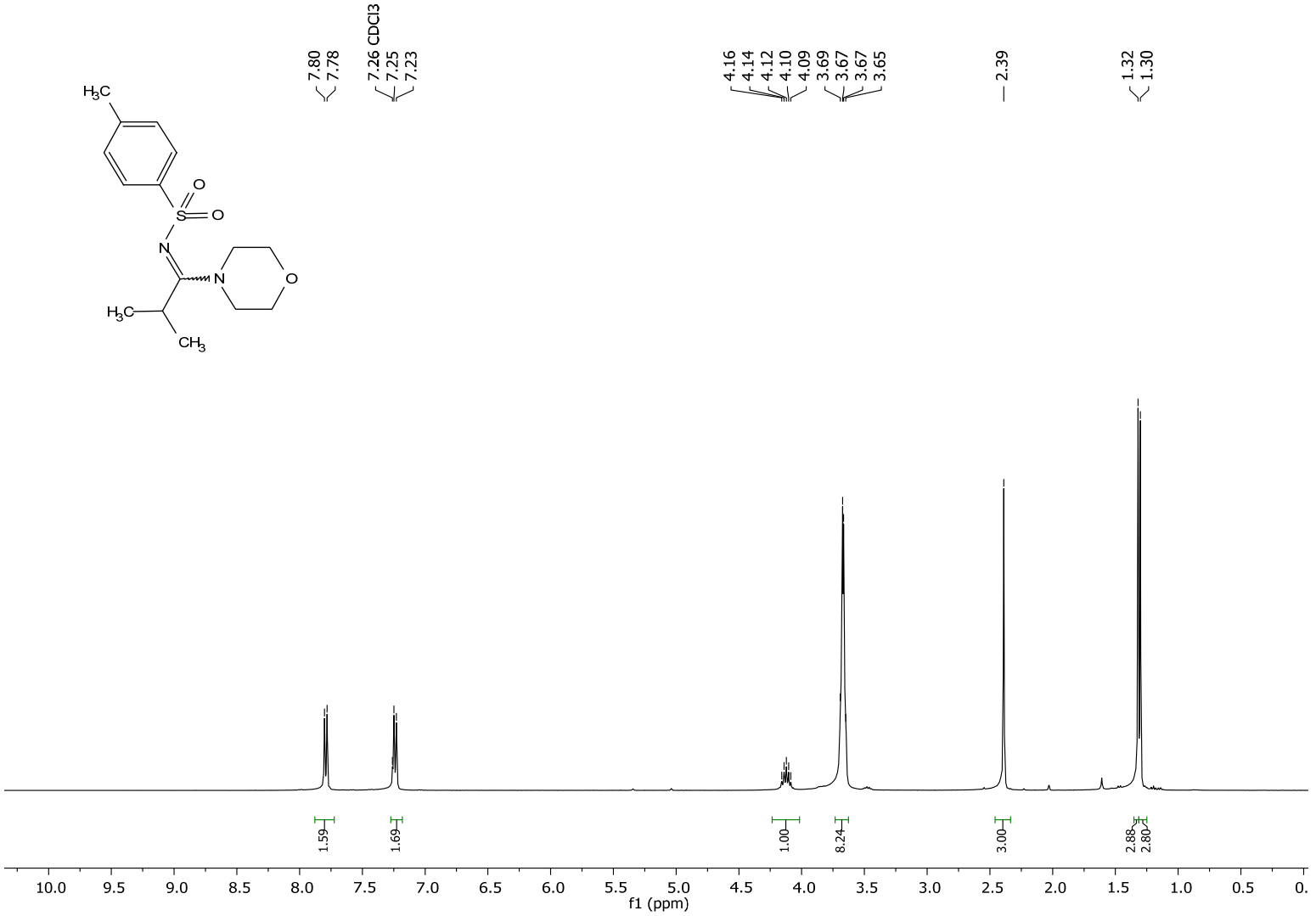
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3le**



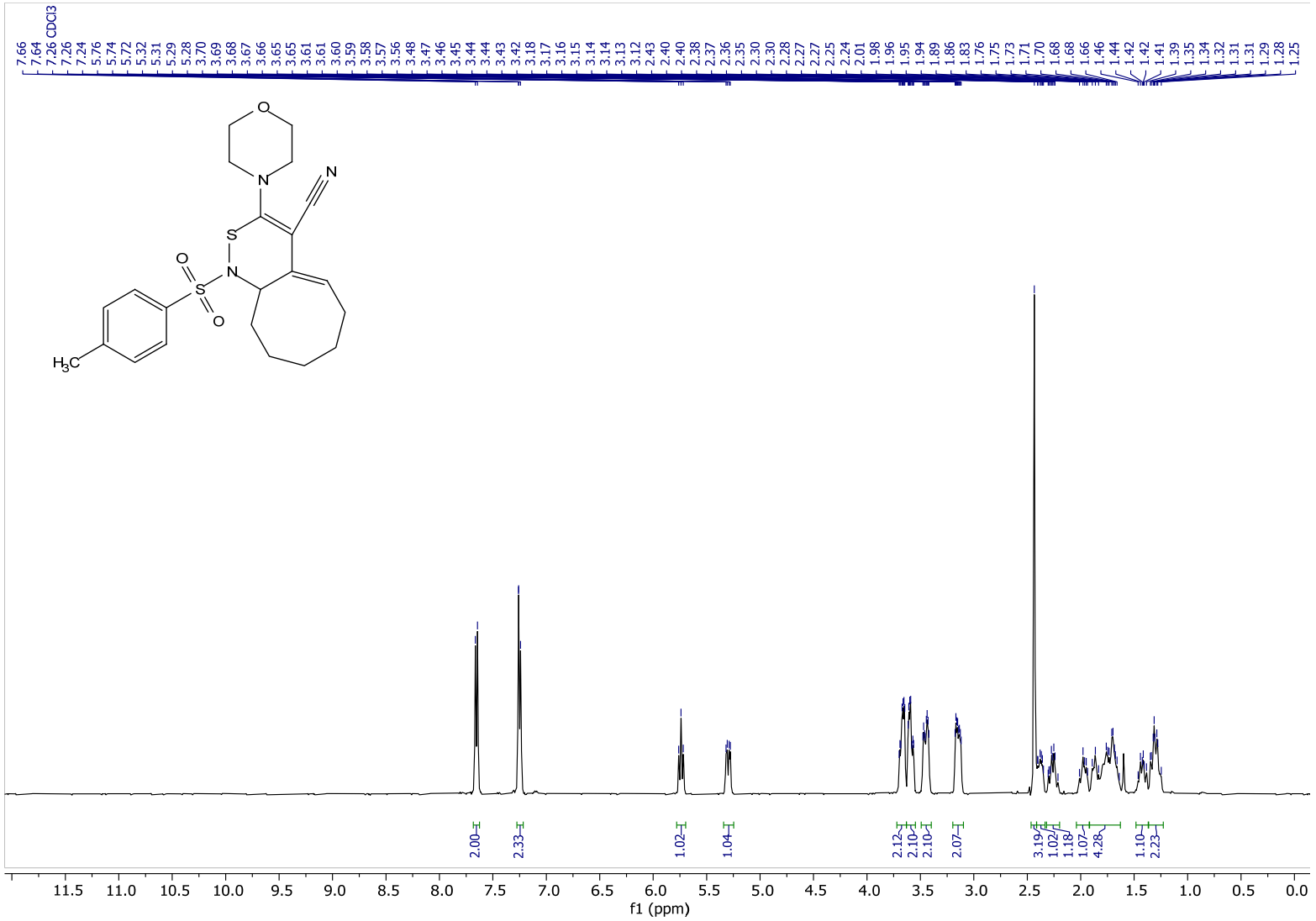
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3le**



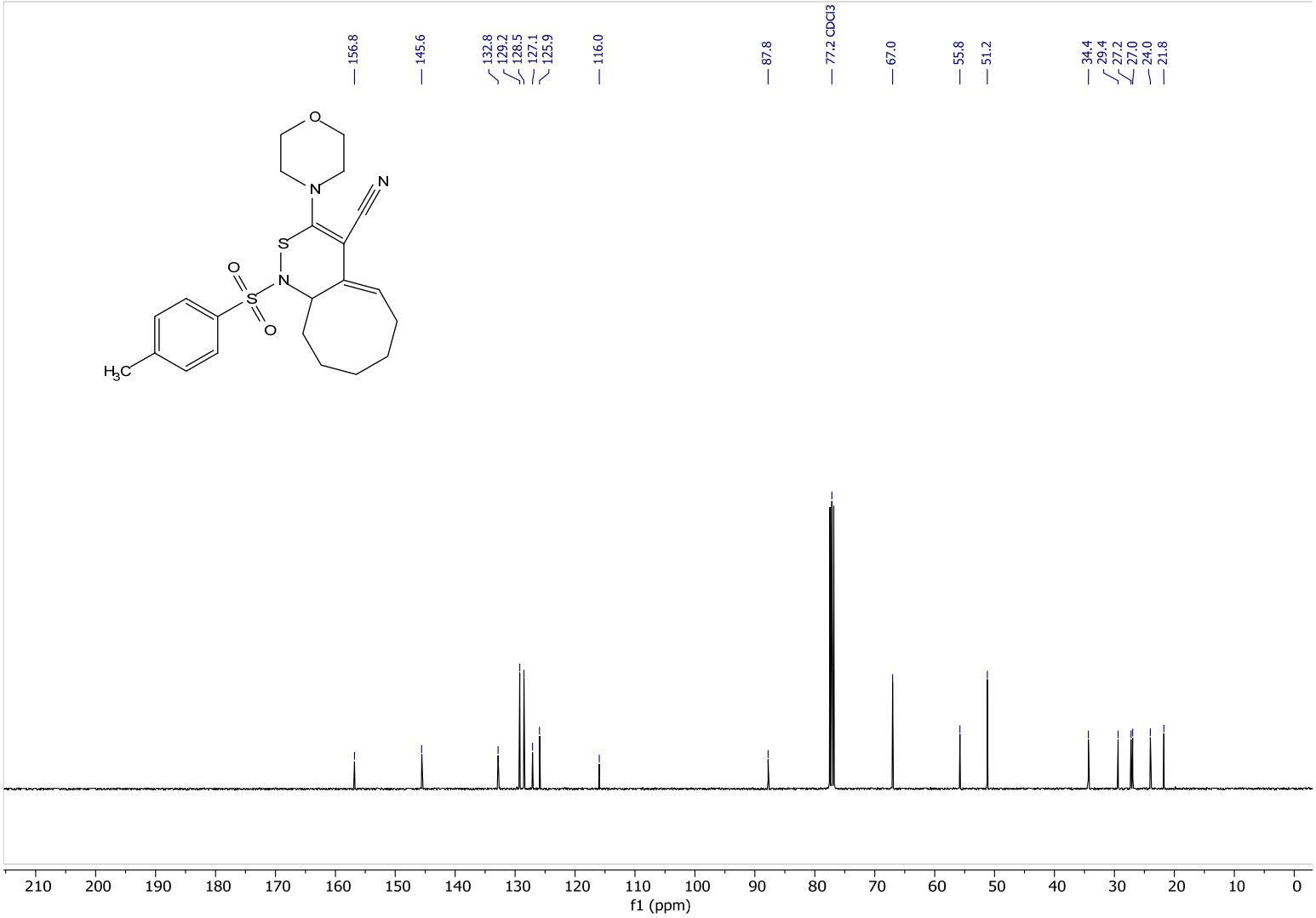
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3qa**



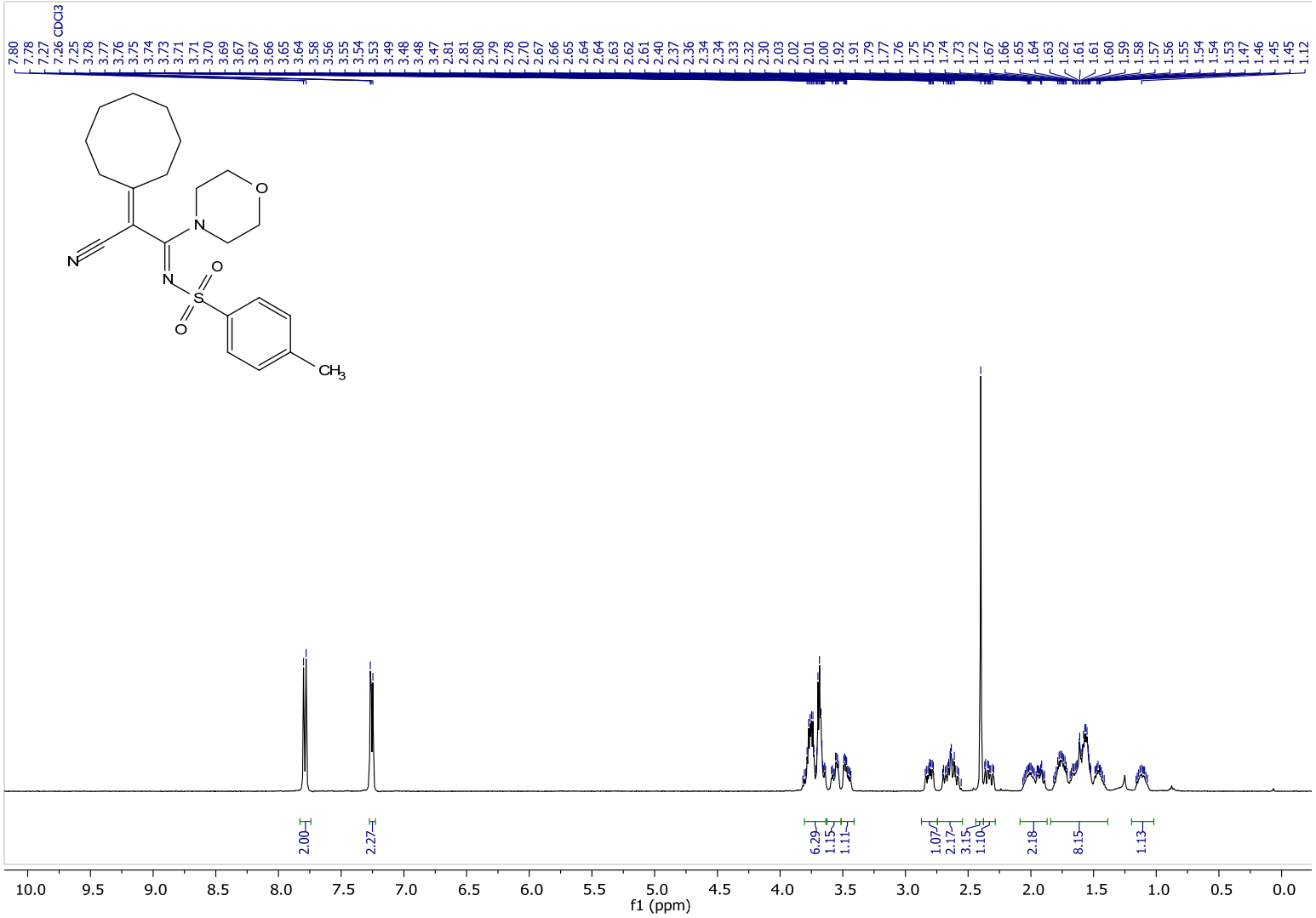
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ra**



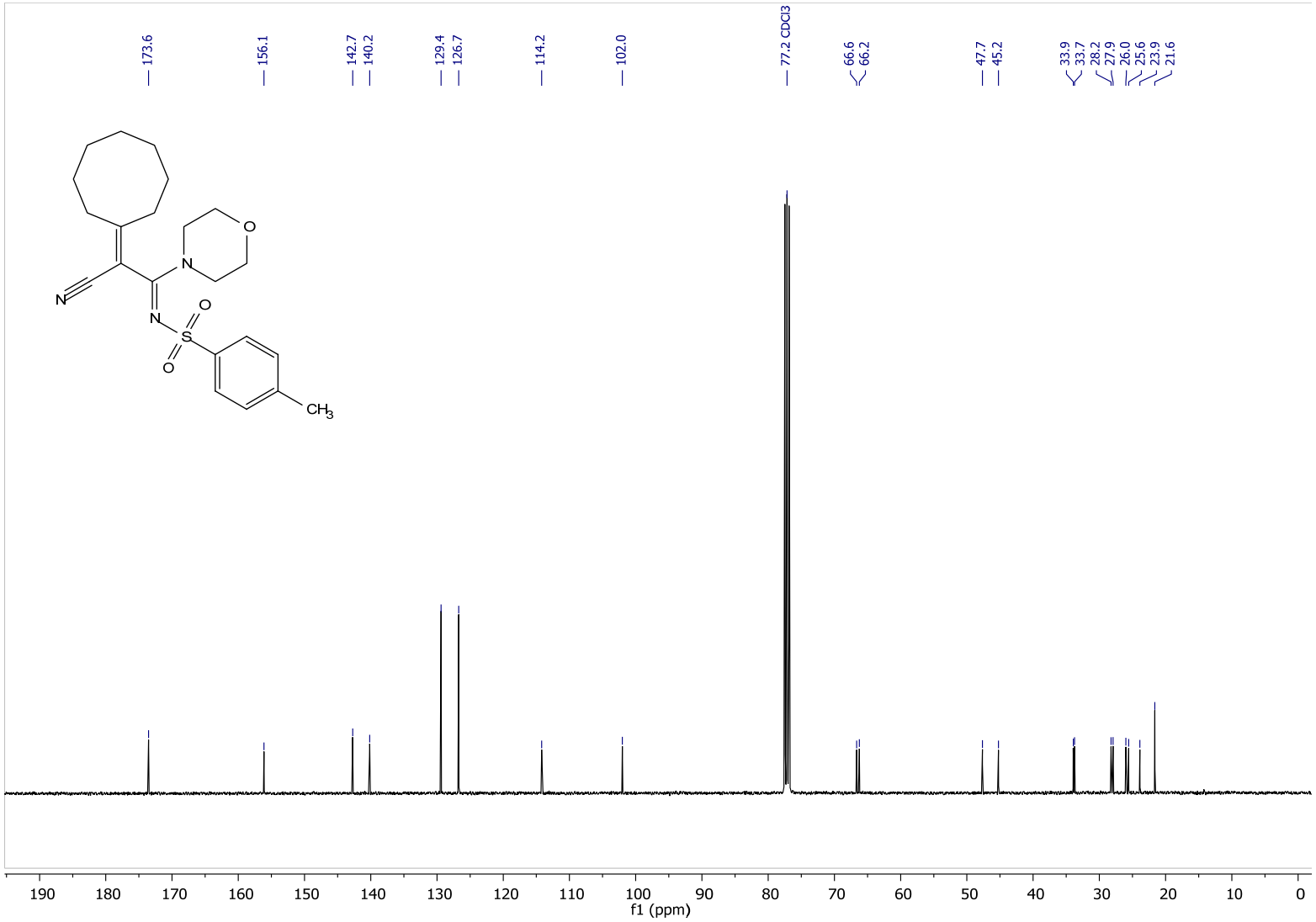
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3´sa**



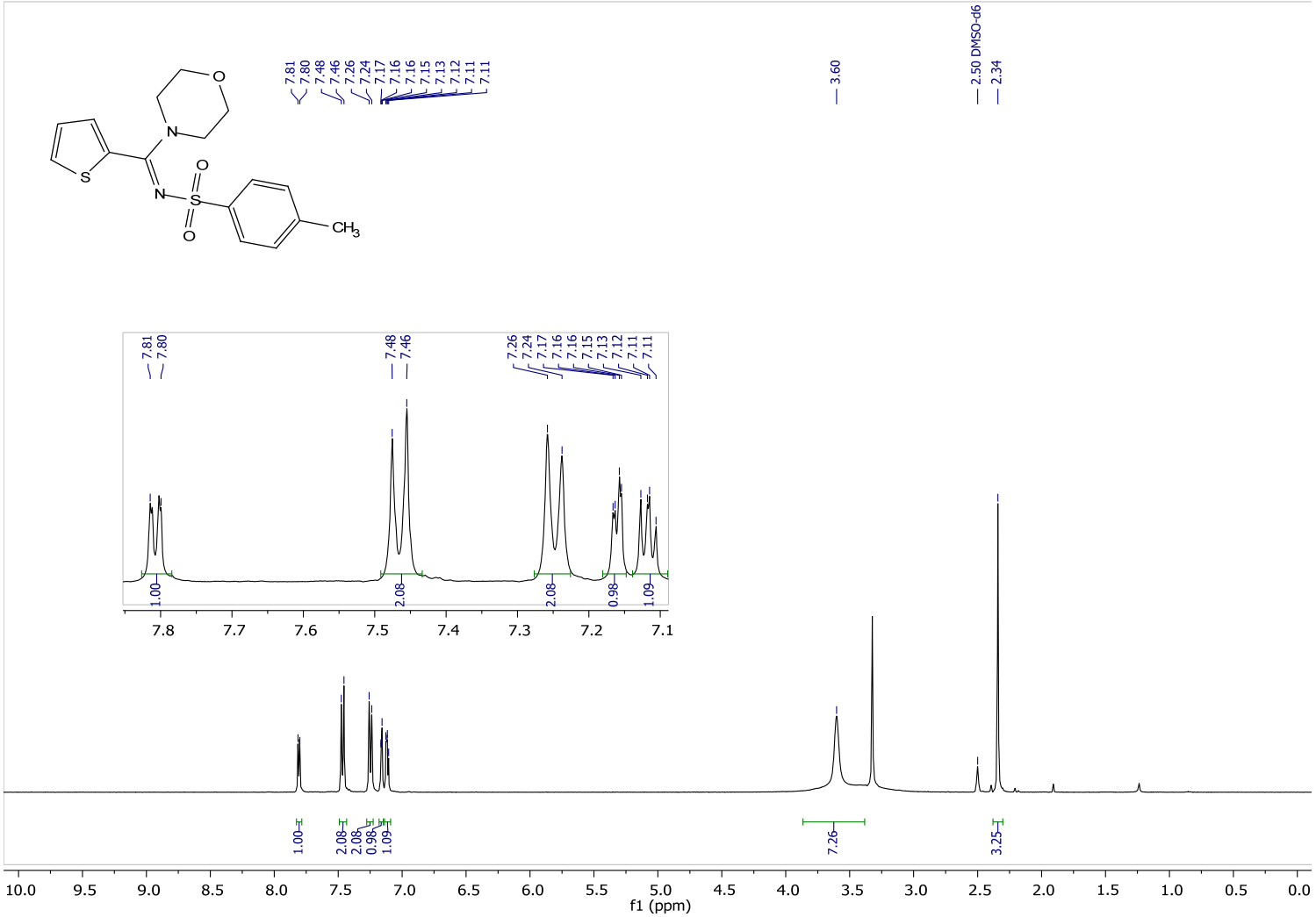
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3´sa**



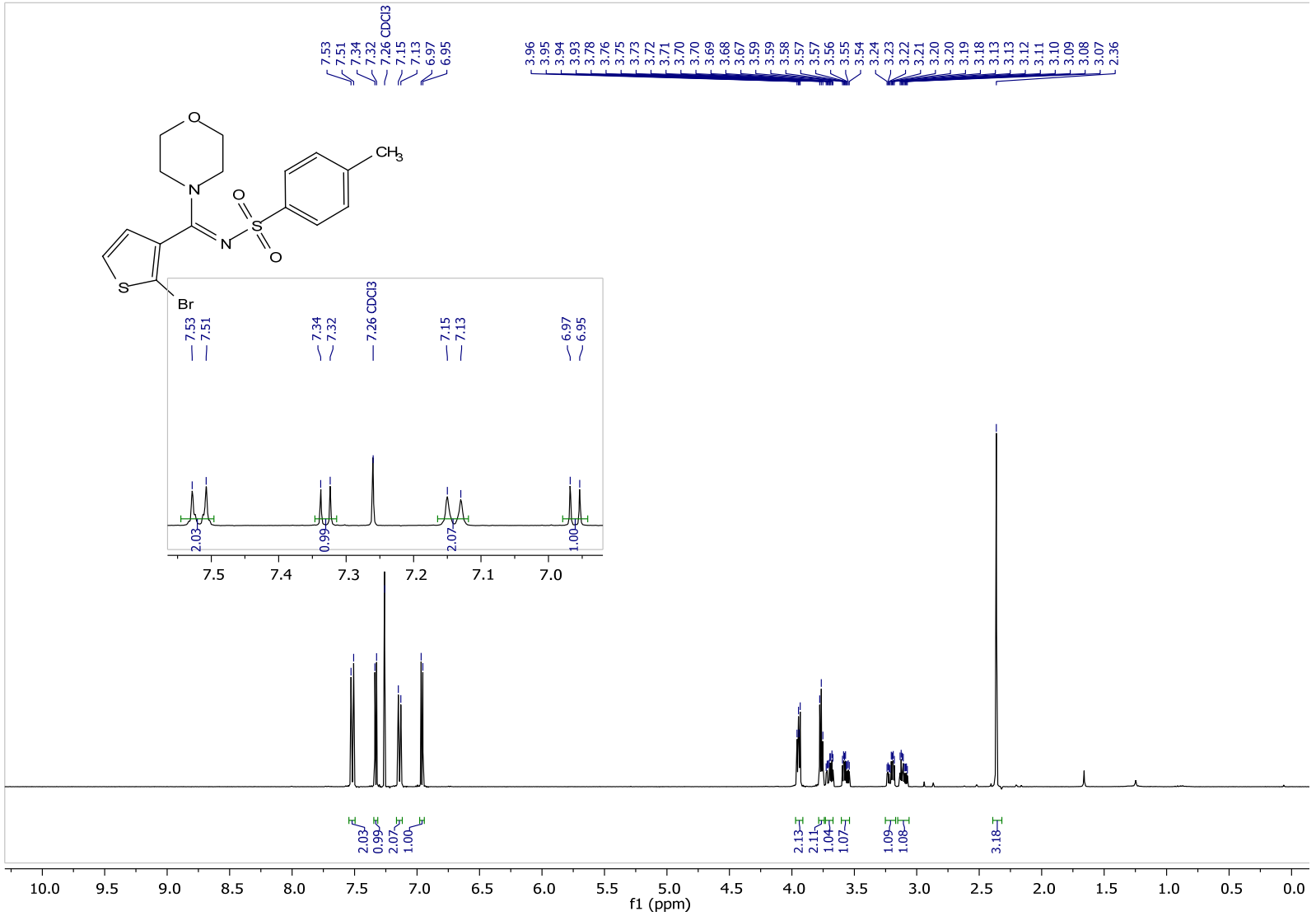
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3sa**



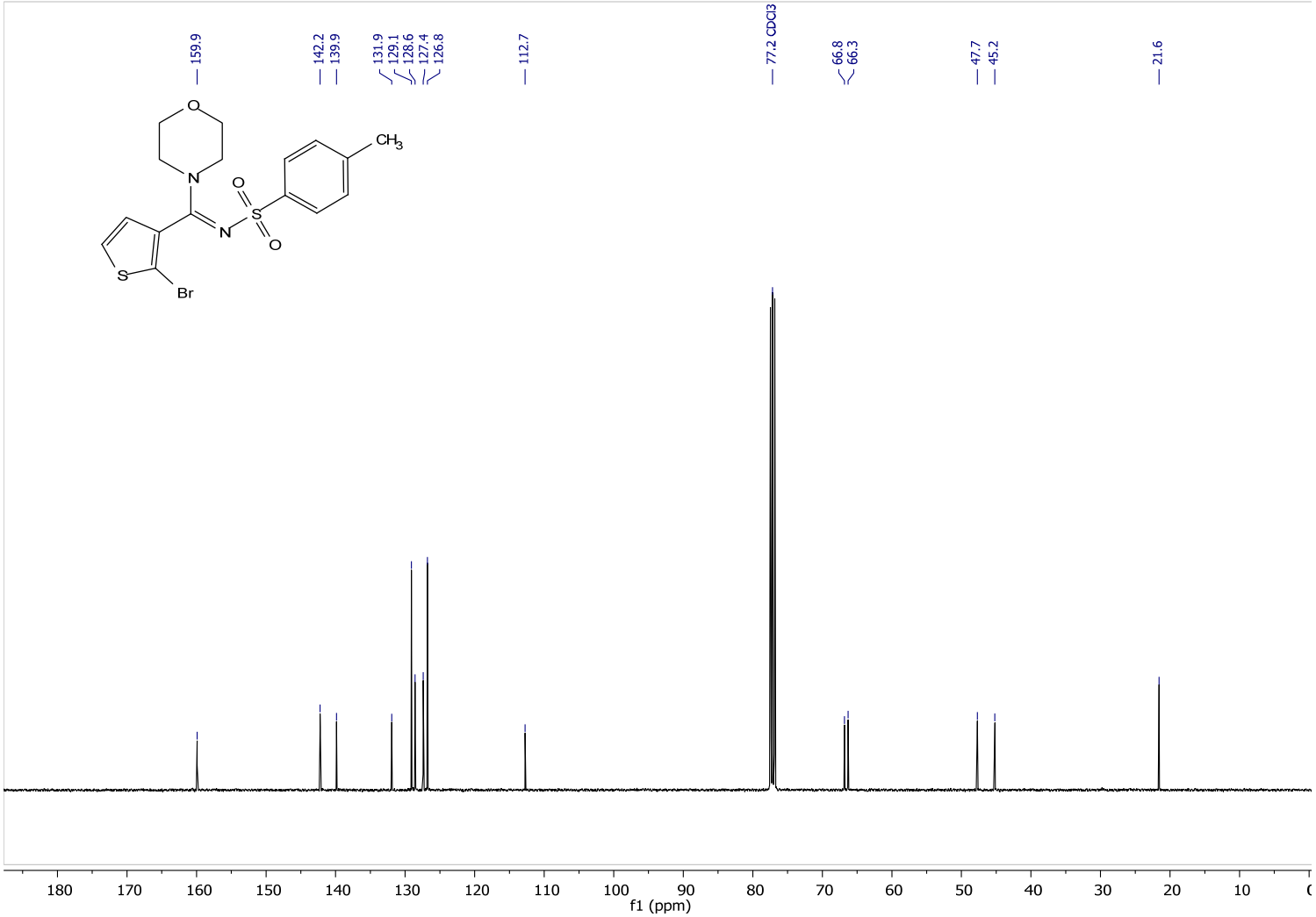
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3sa**



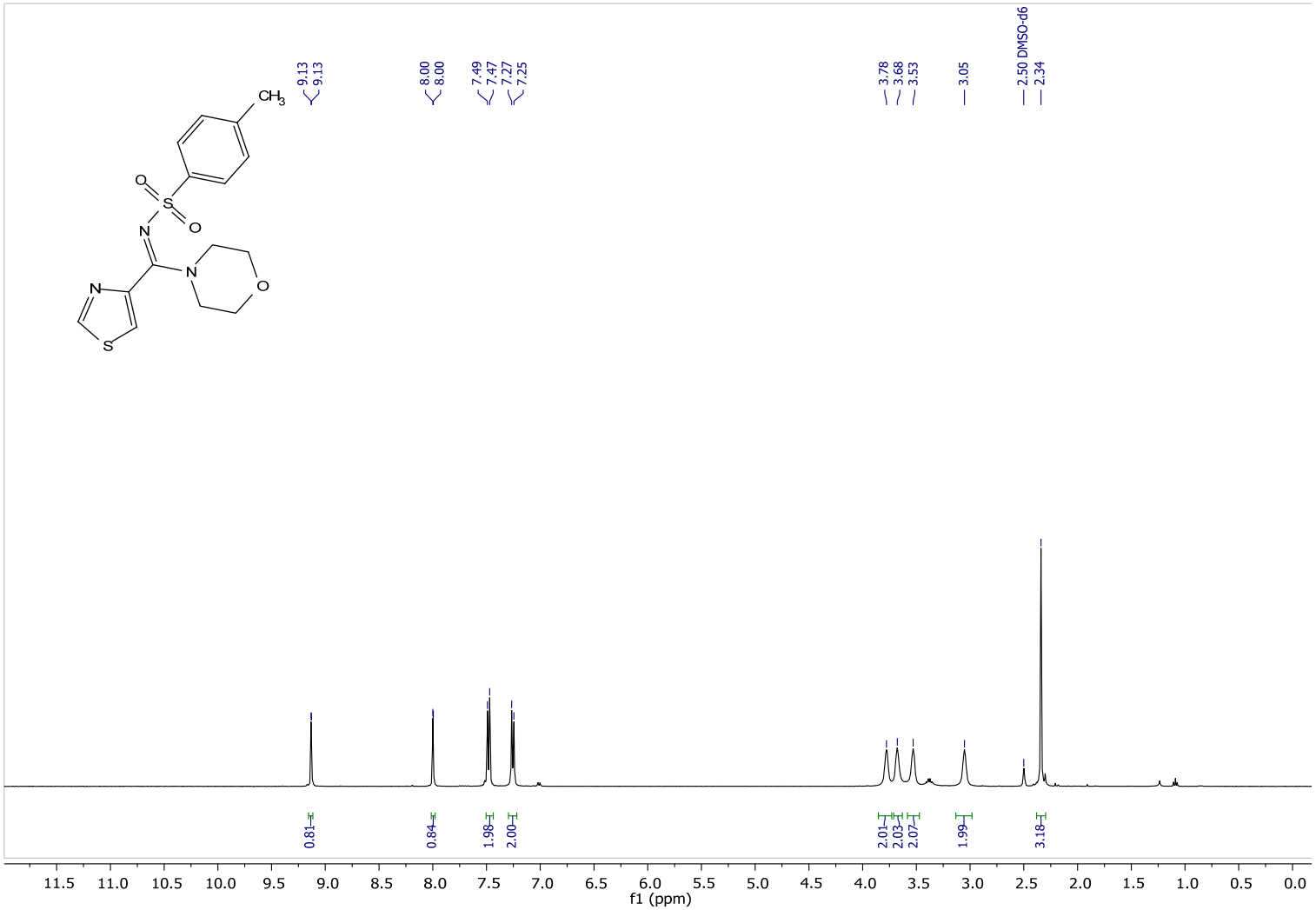
^{1}H NMR (400 MHz, DMSO–d_6) of **3ta**



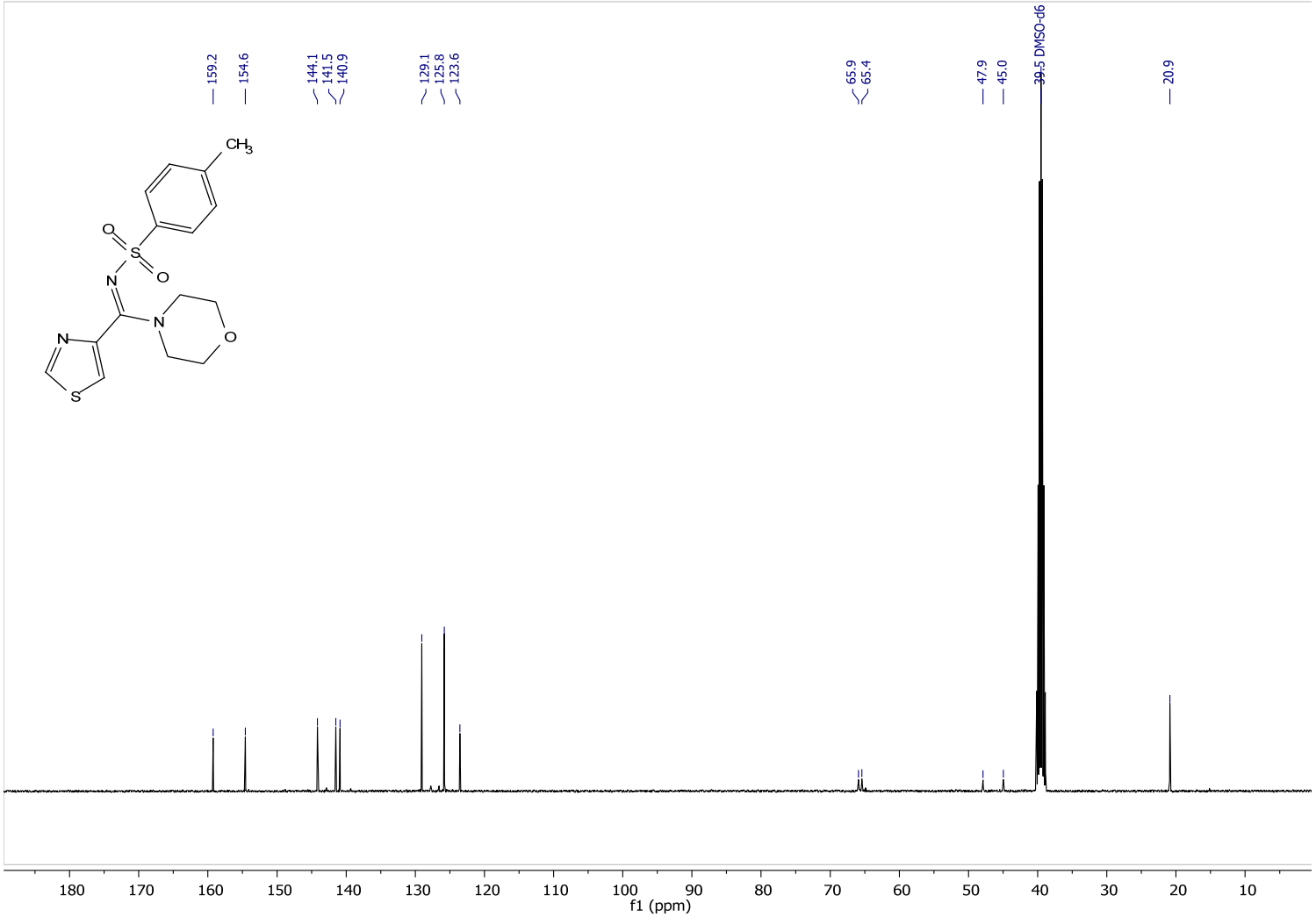
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3ua**



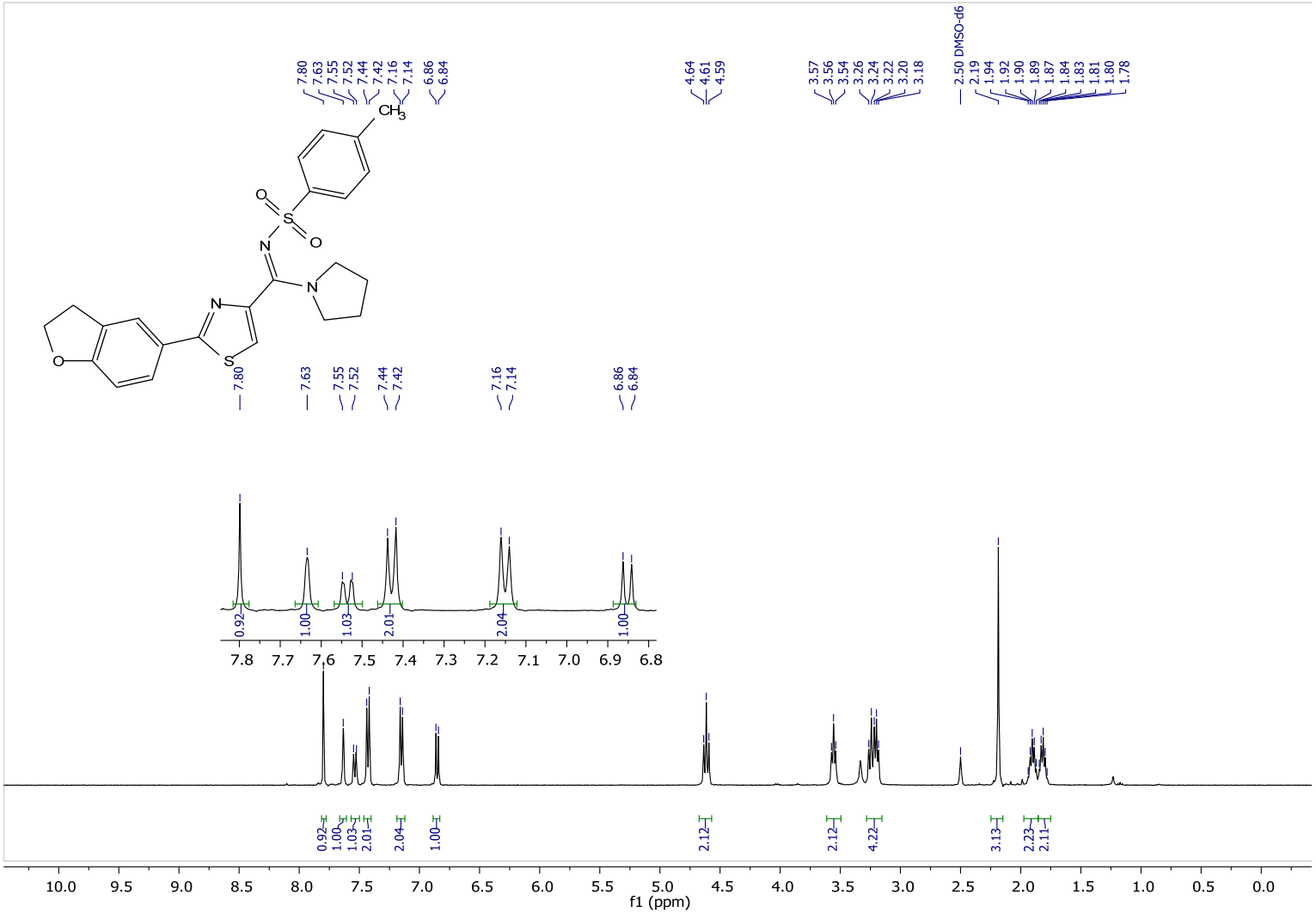
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3ua**



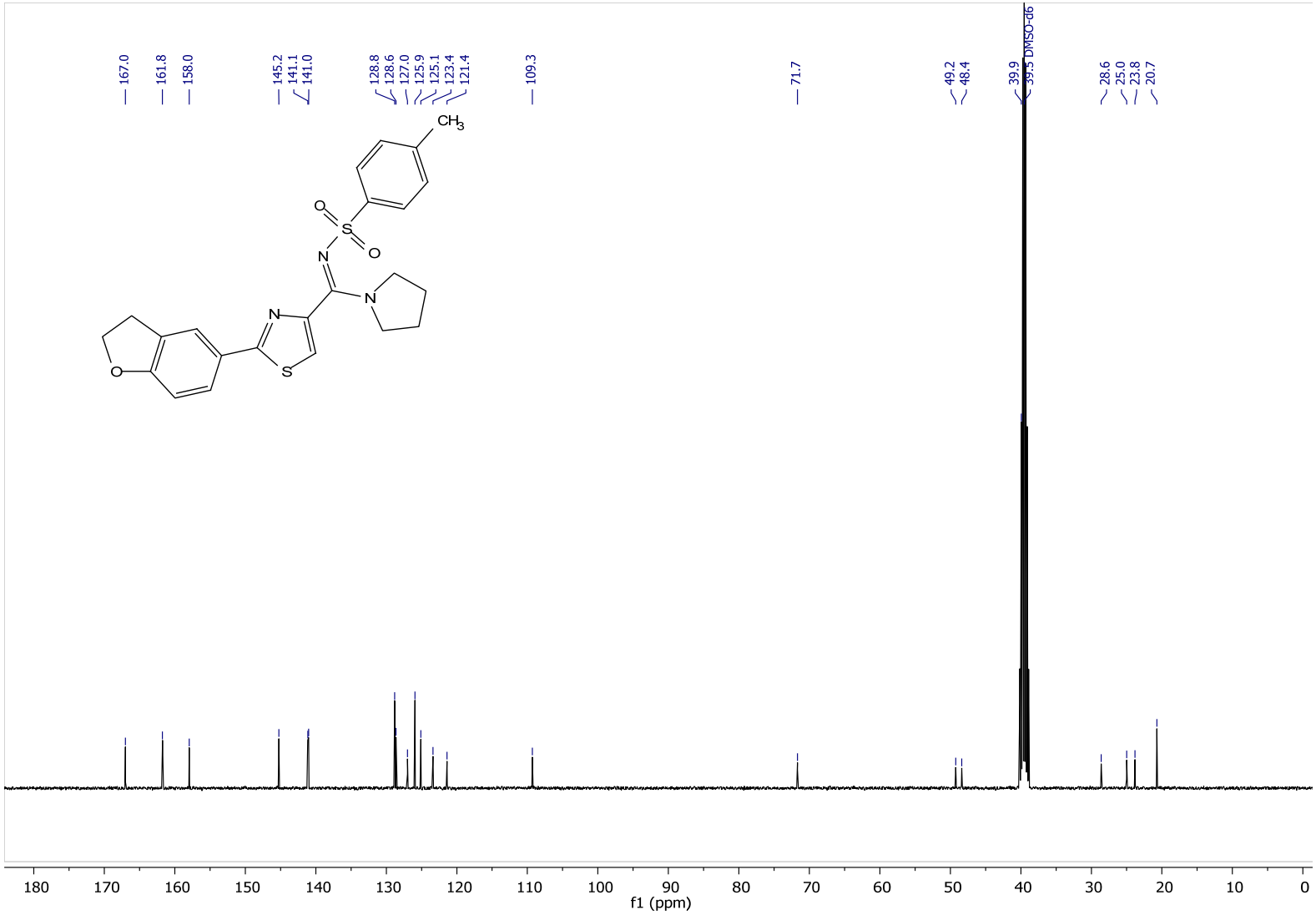
^{1}H NMR (400 MHz, DMSO–d_6) of **3va**



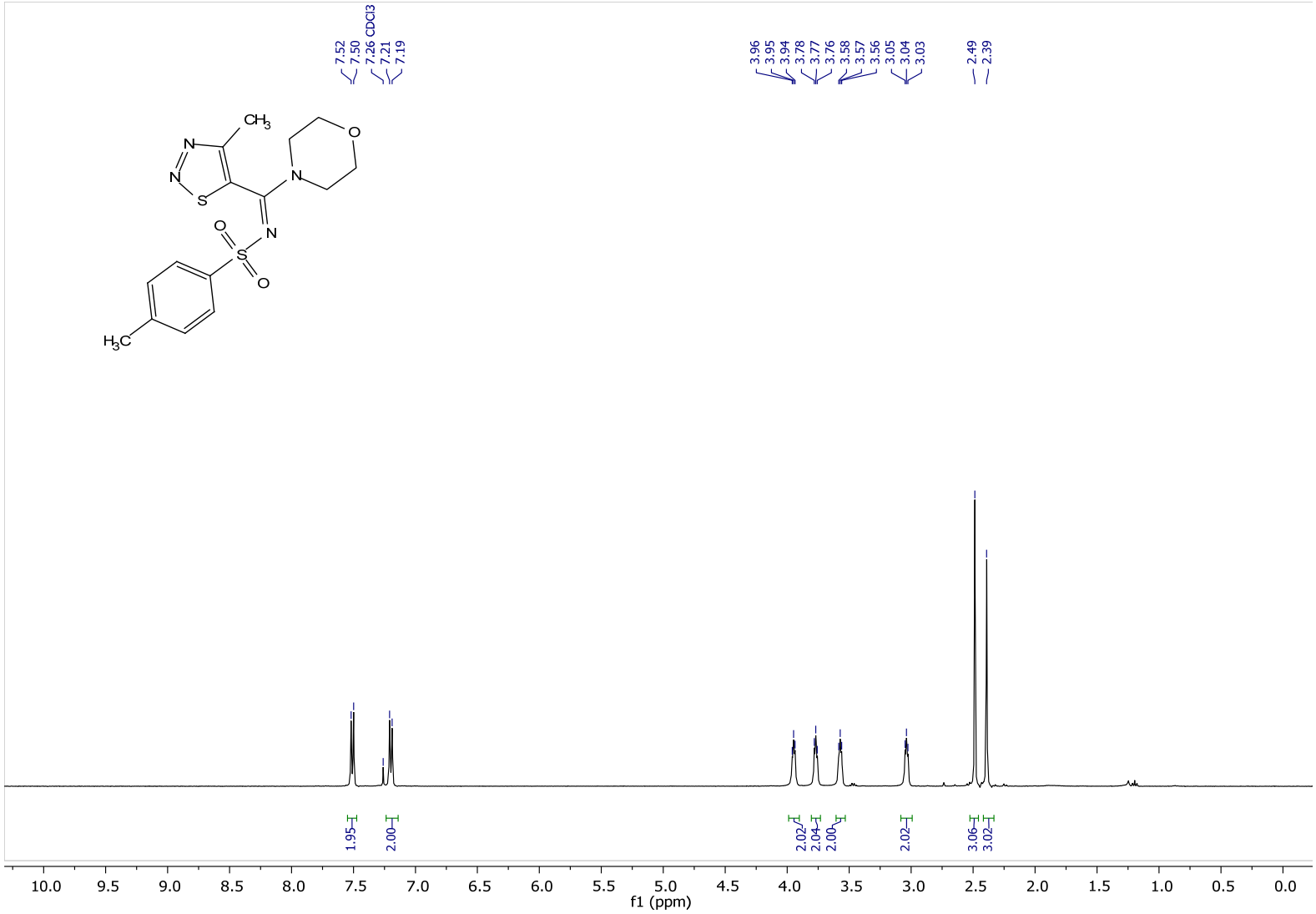
^{13}C NMR (100 MHz, DMSO–d_6) of **3va**



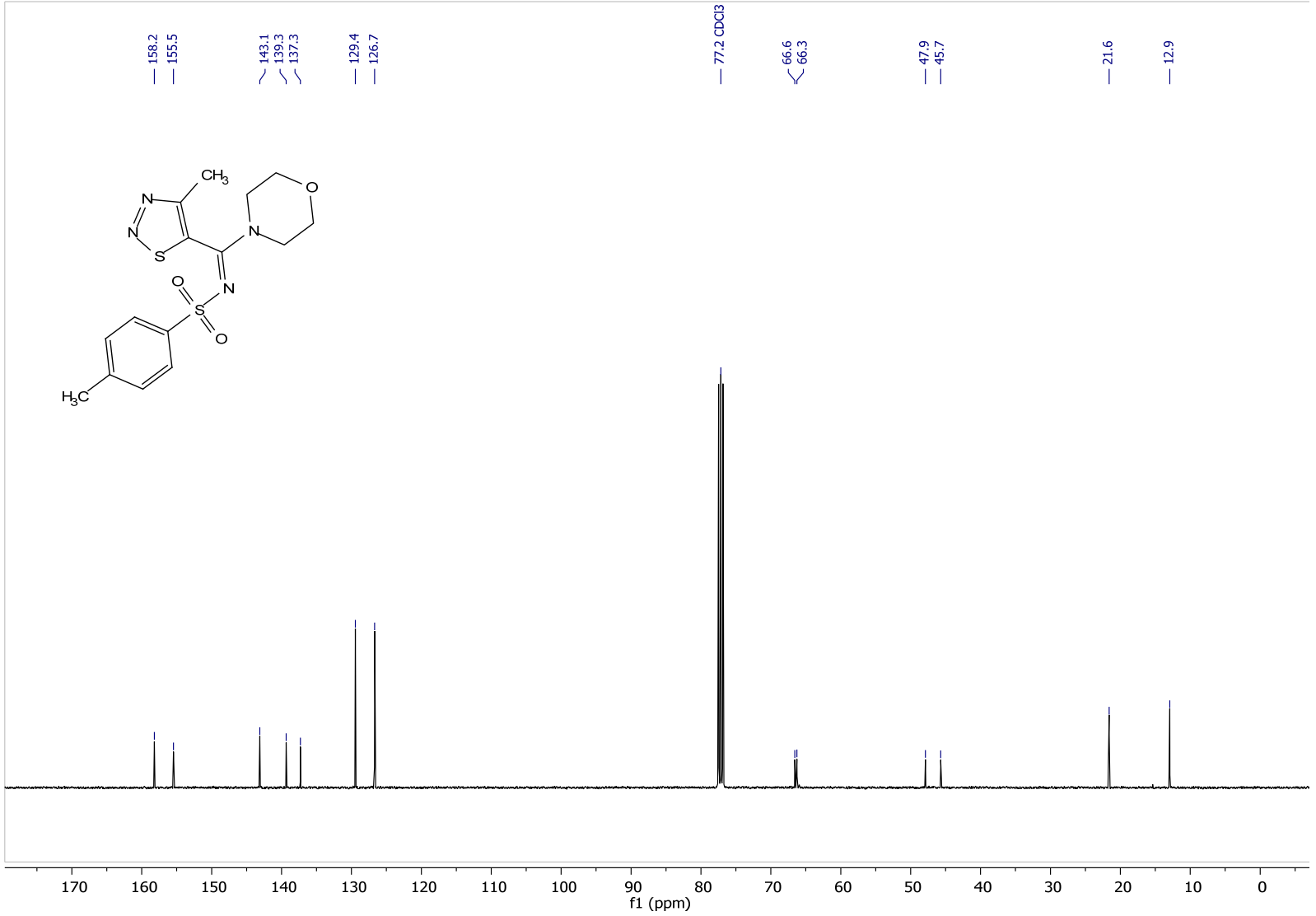
^{1}H NMR (400 MHz, DMSO–d_6) of **3wa**



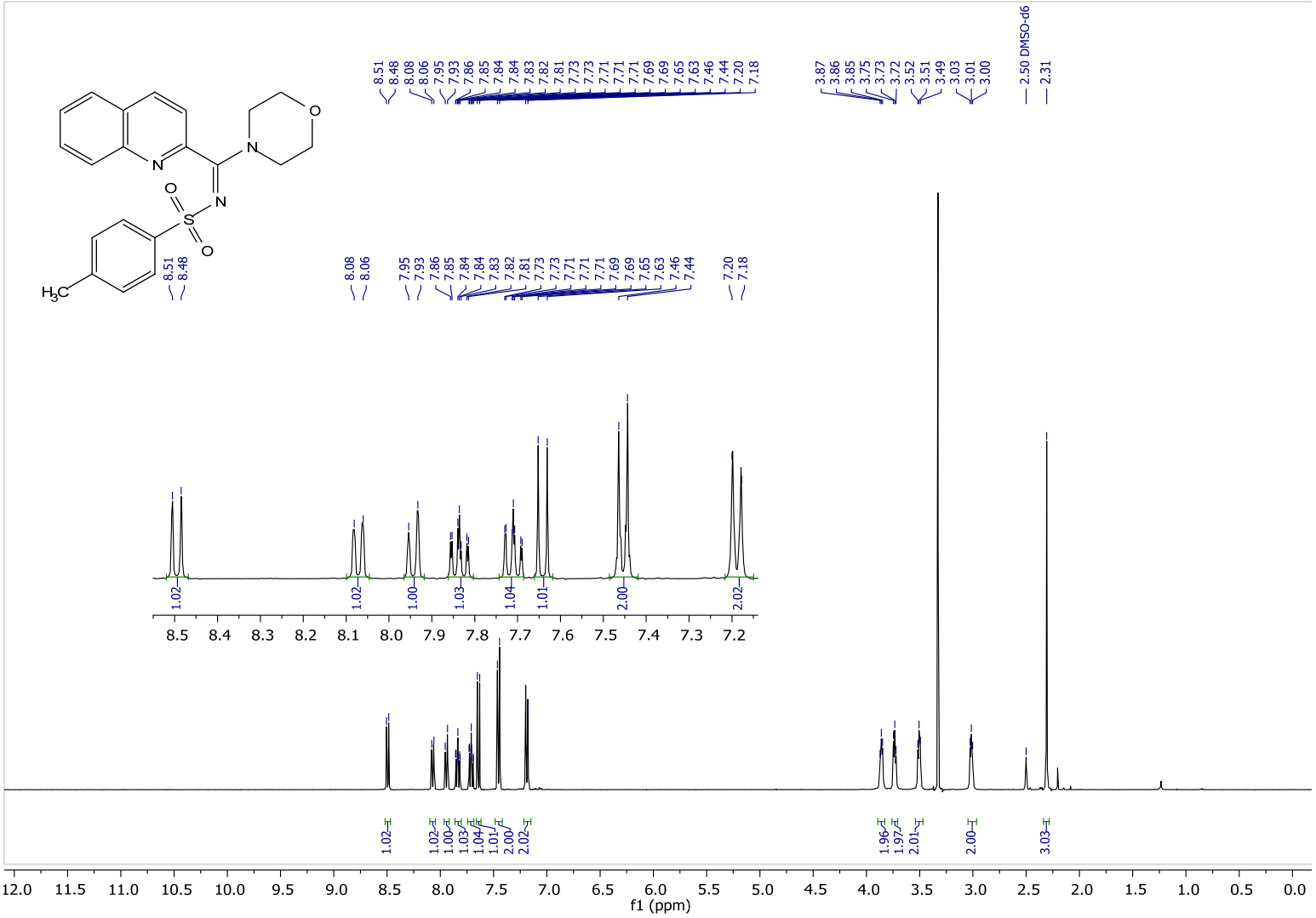
^{13}C NMR (400 MHz, DMSO–d_6) of **3wa**



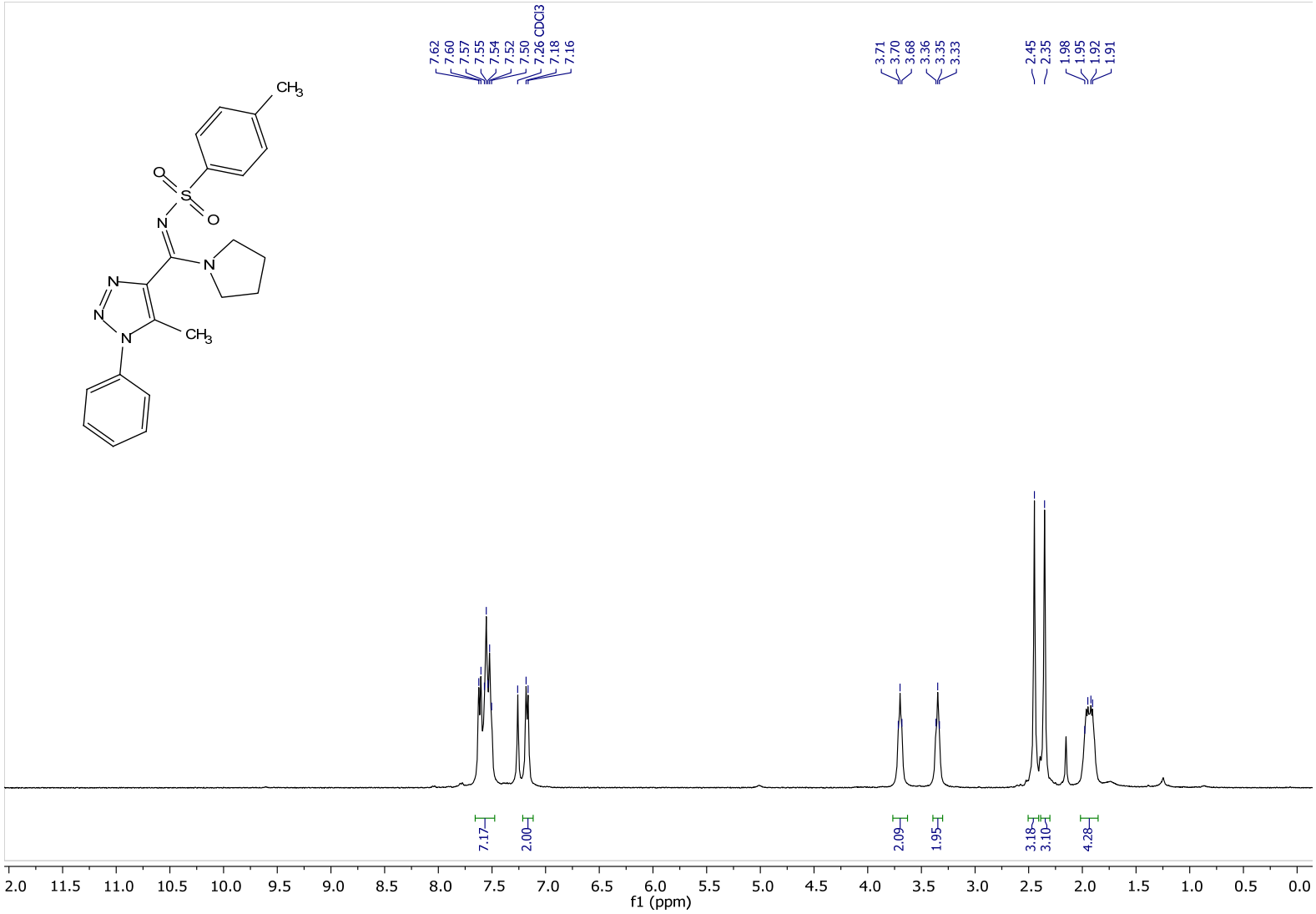
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3xa**



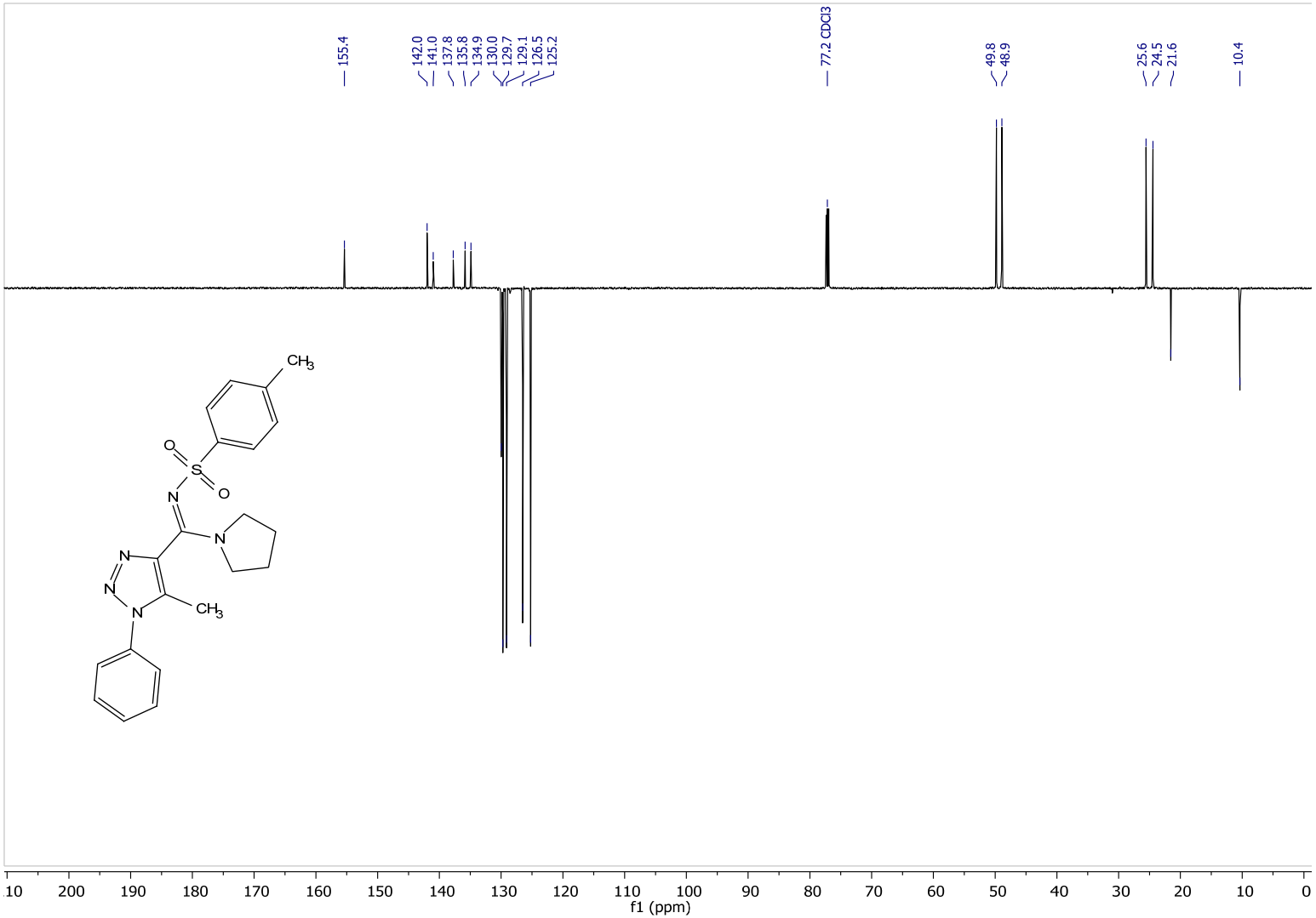
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3xa**



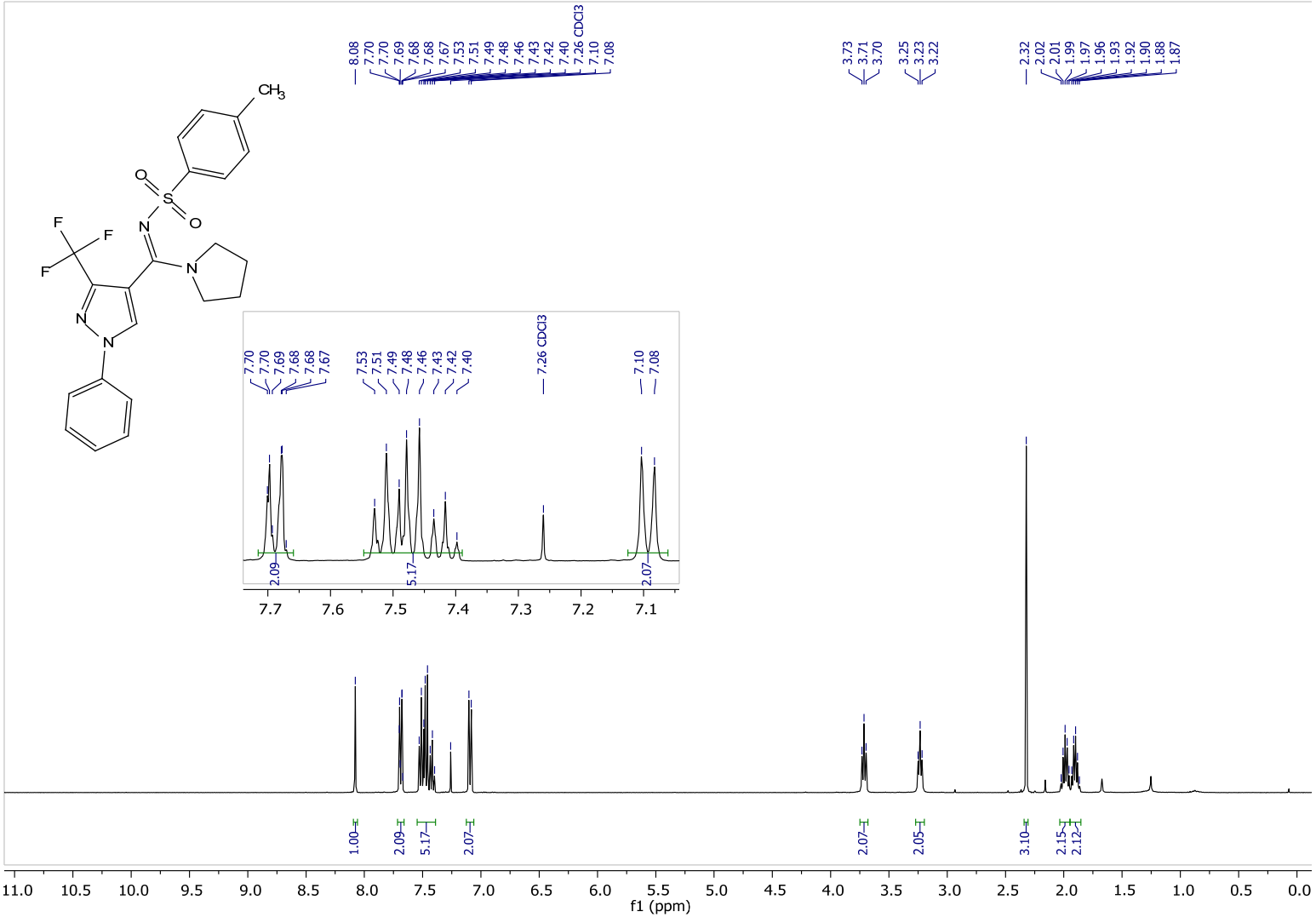
^{1}H NMR (400 MHz, DMSO–d_6) of **3ya**



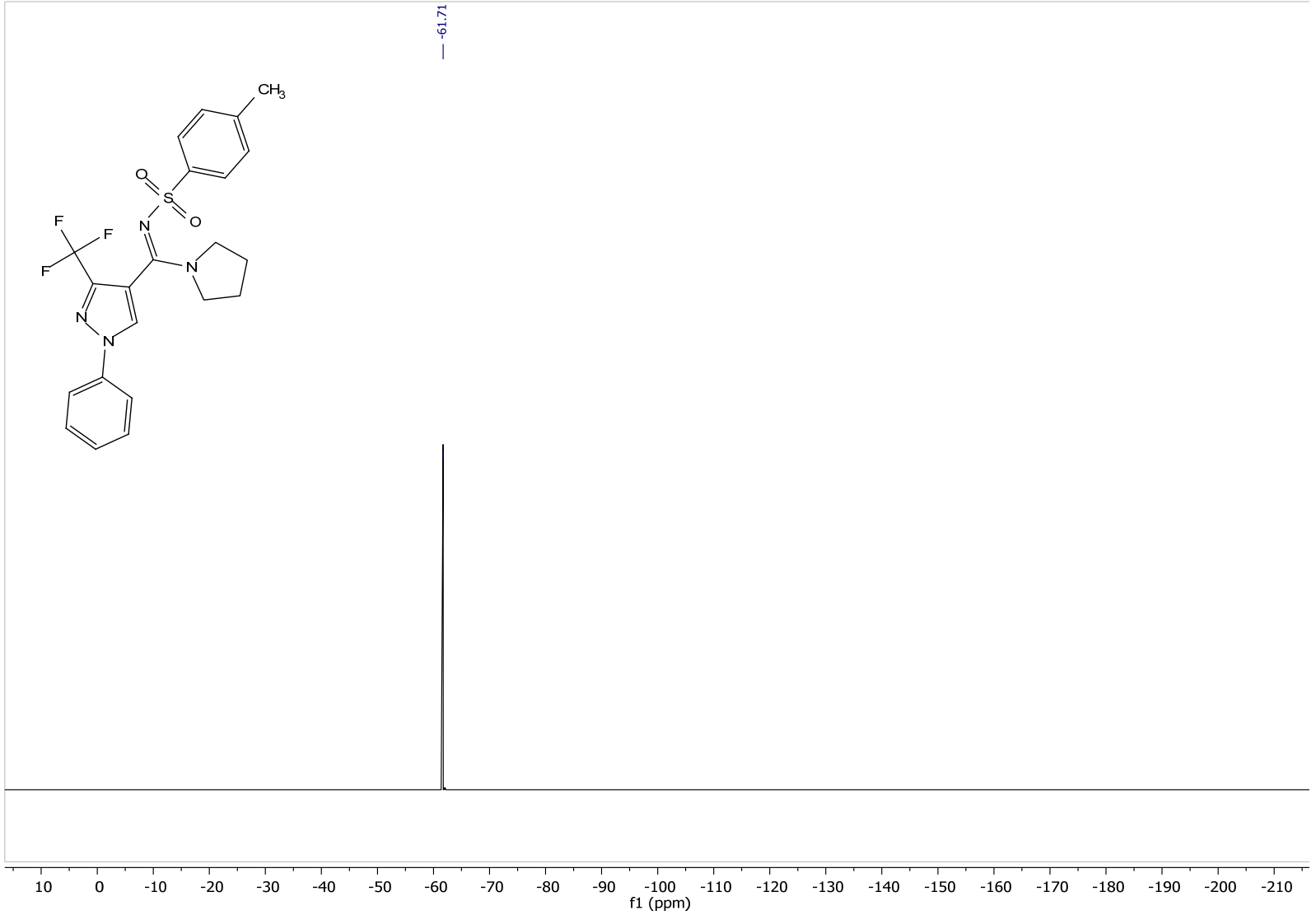
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3za**



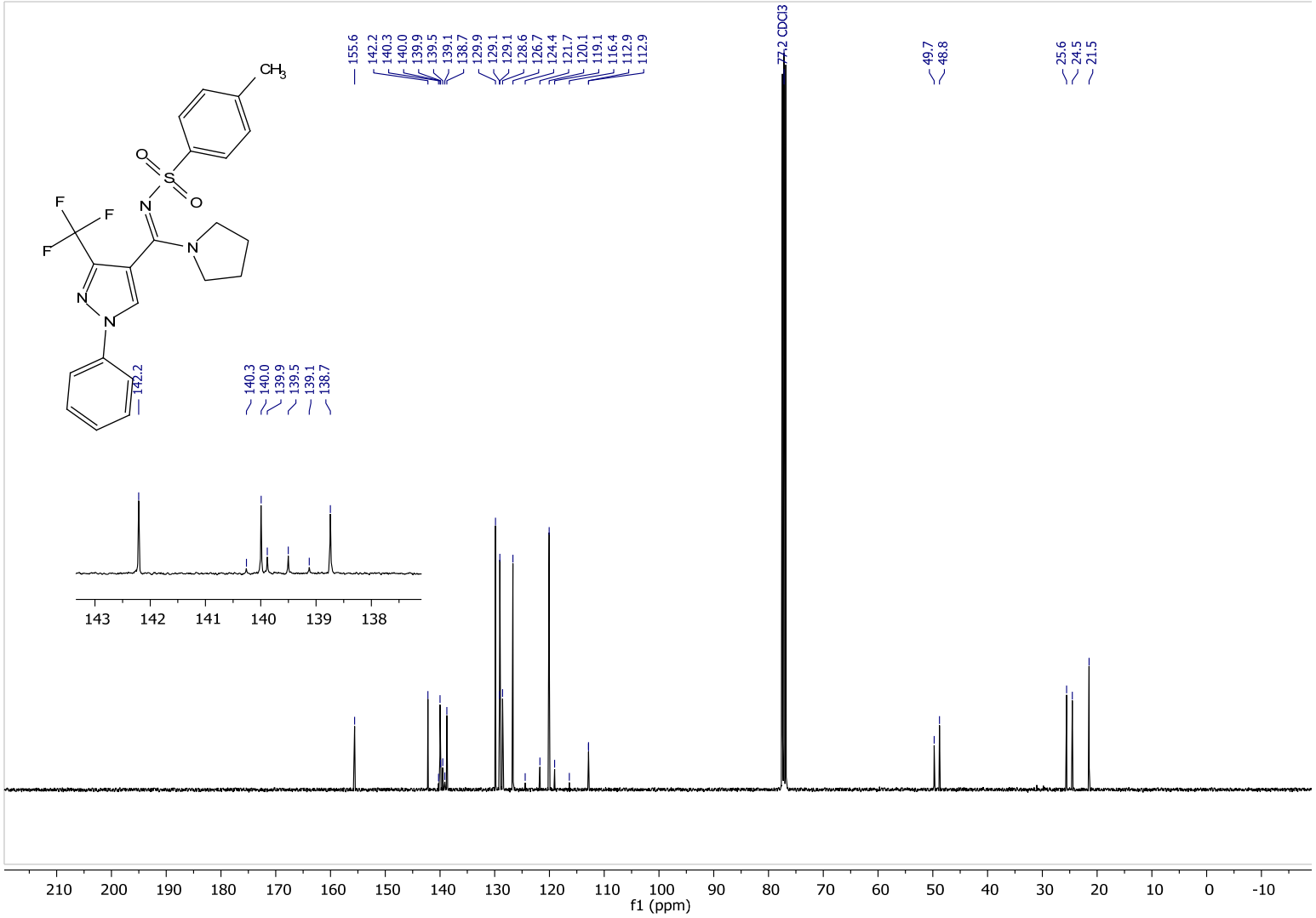
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3za**



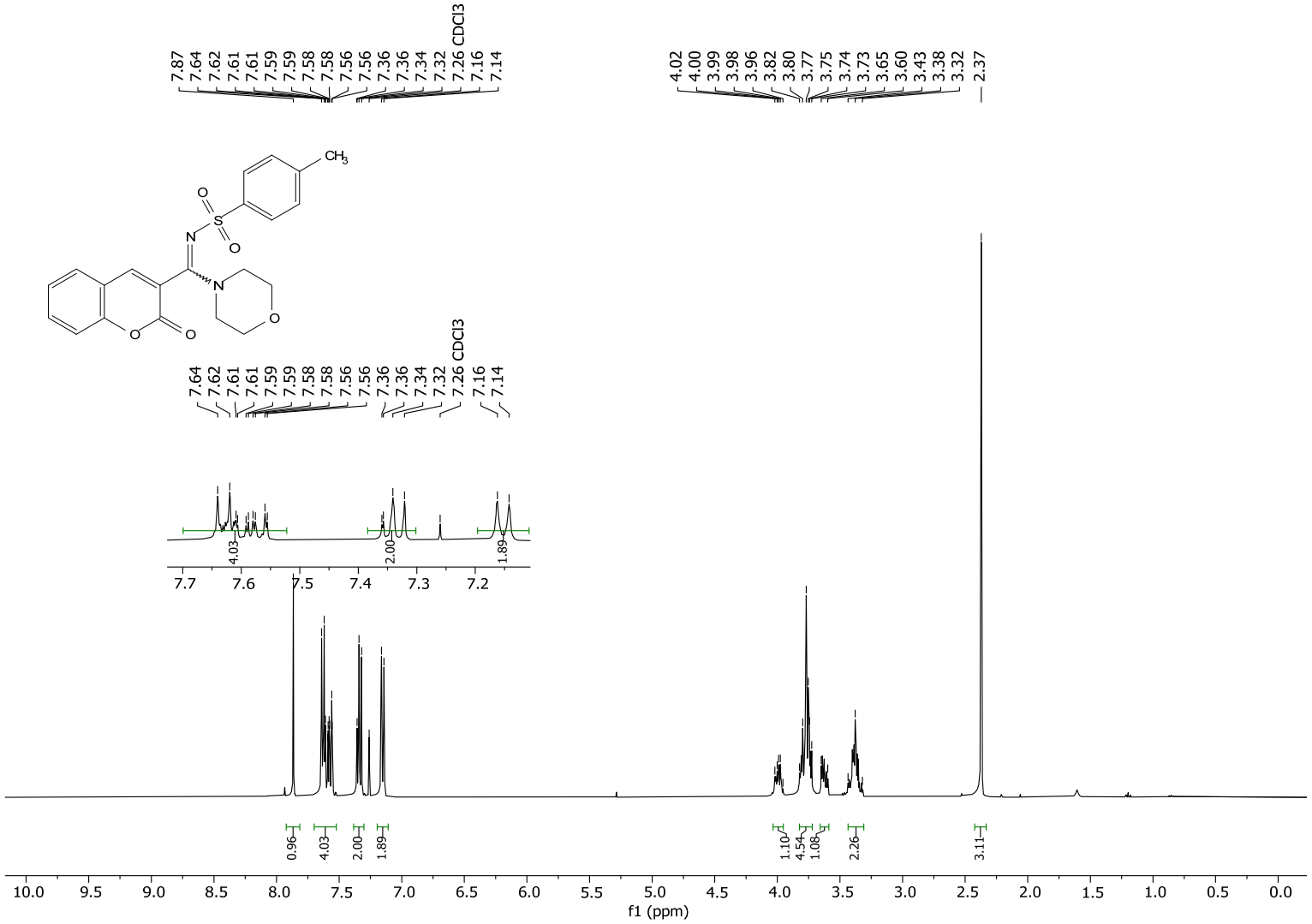
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3a´a**



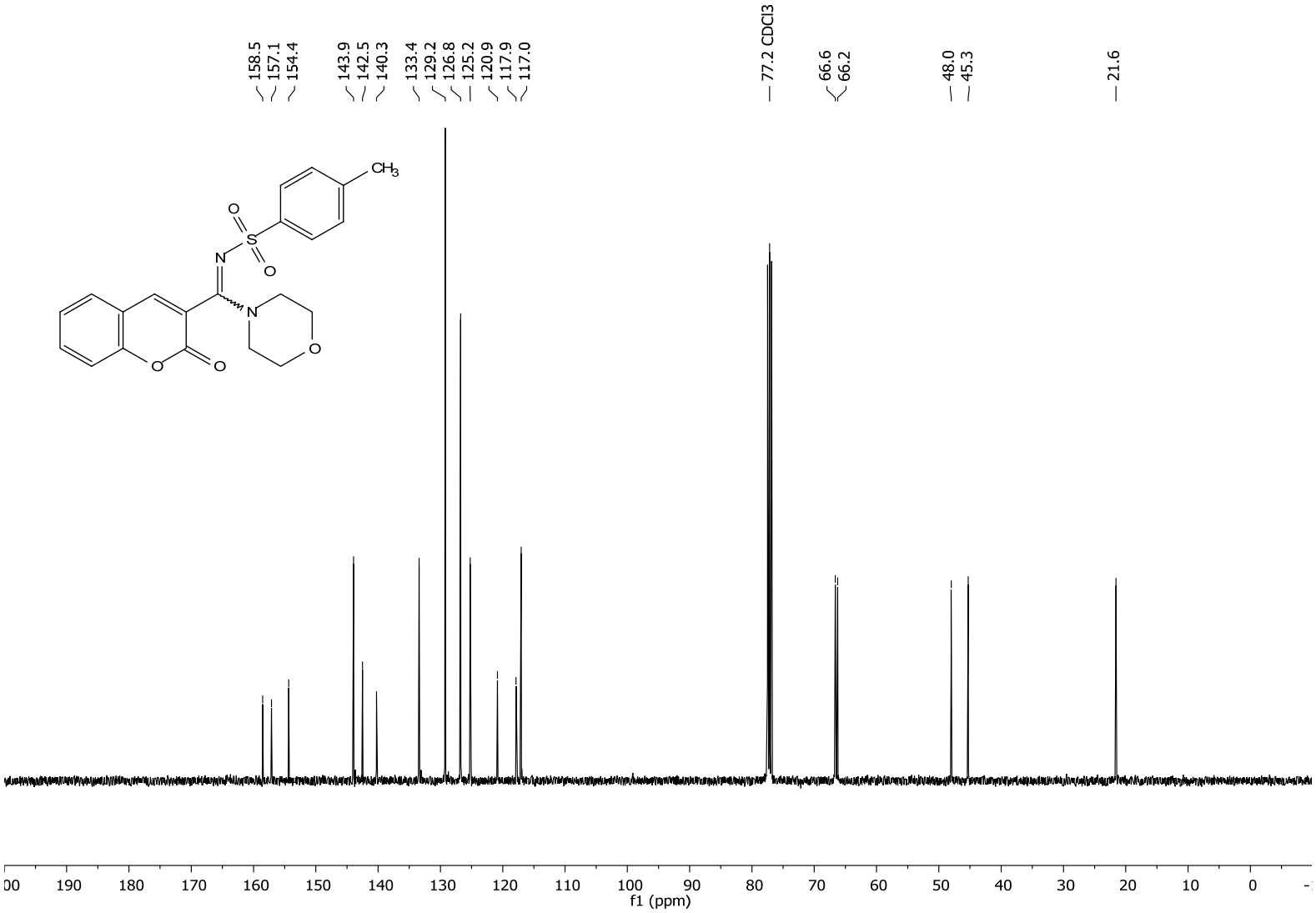
^{19}F NMR (565 MHz, $CDCl_3$-*d*) of **3a´a**



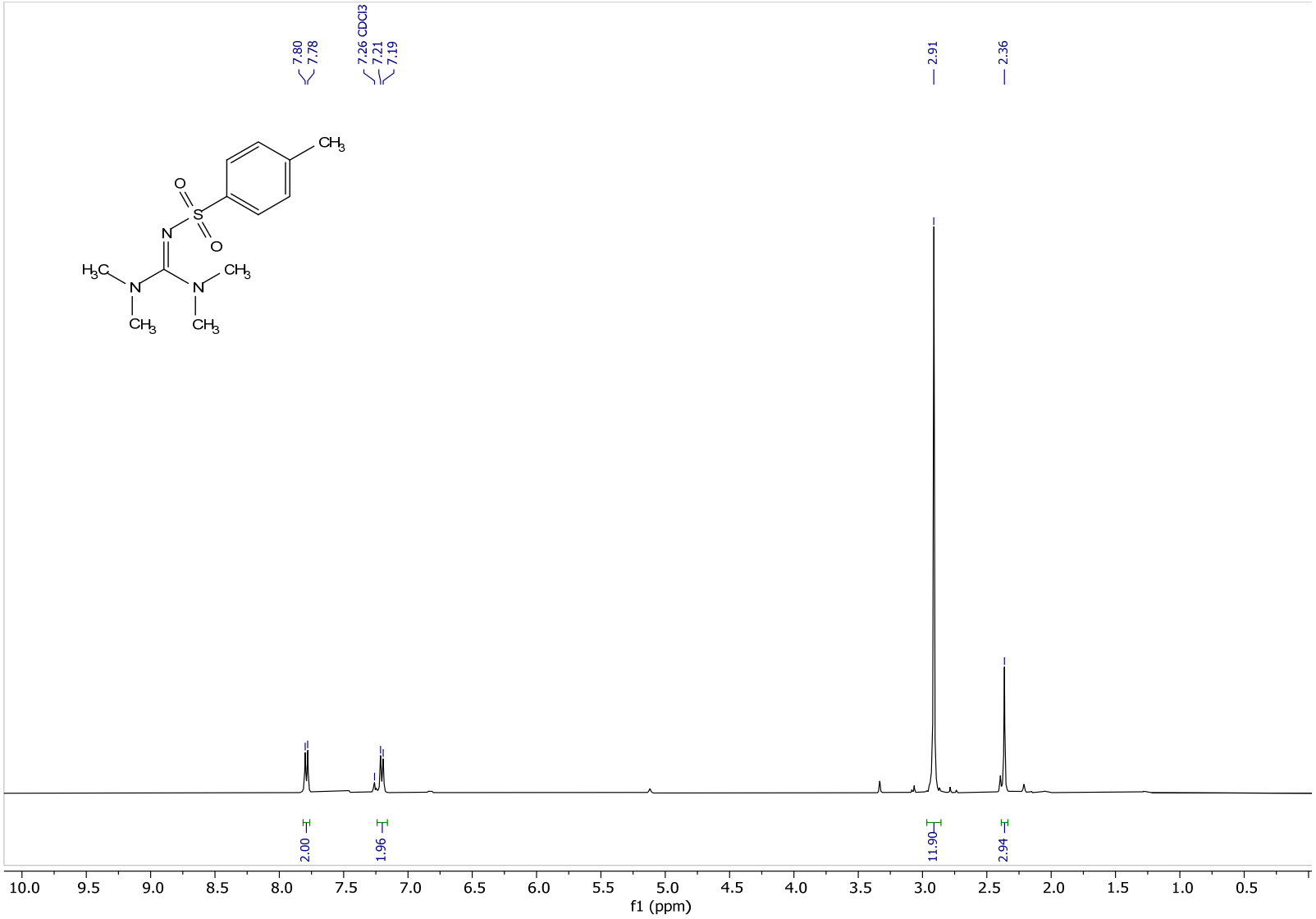
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3a´a**



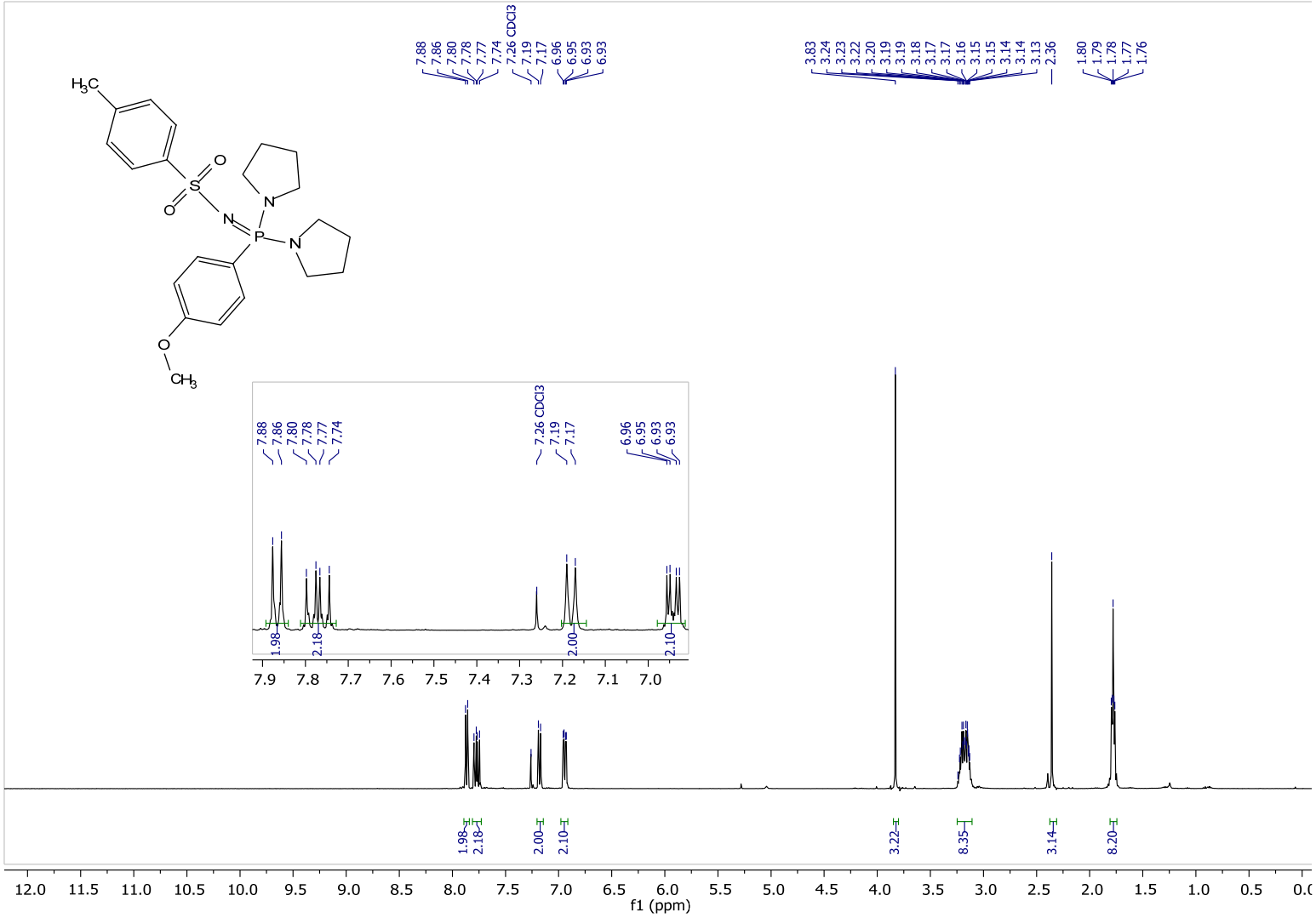
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3b´a**



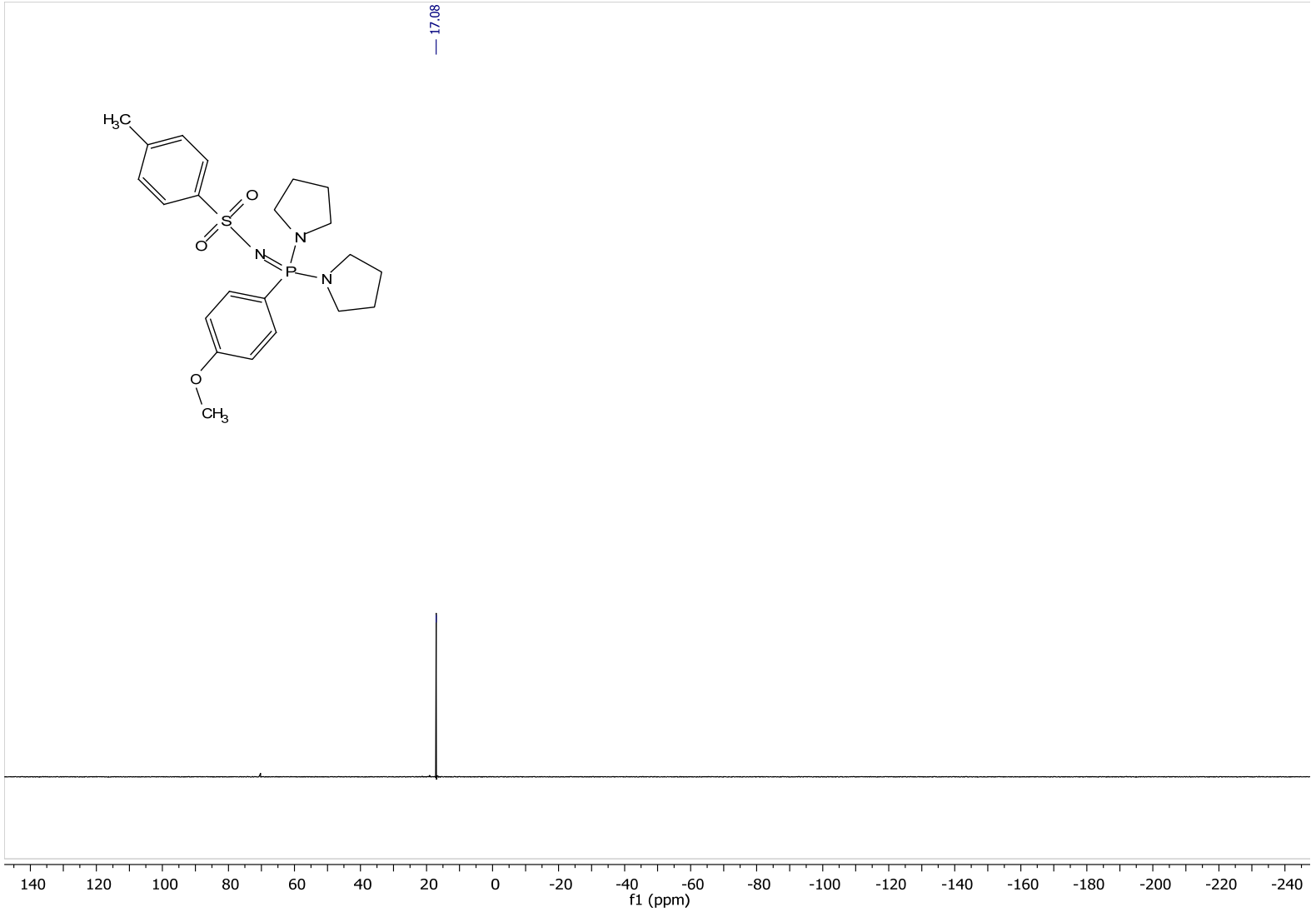
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **3b´a**



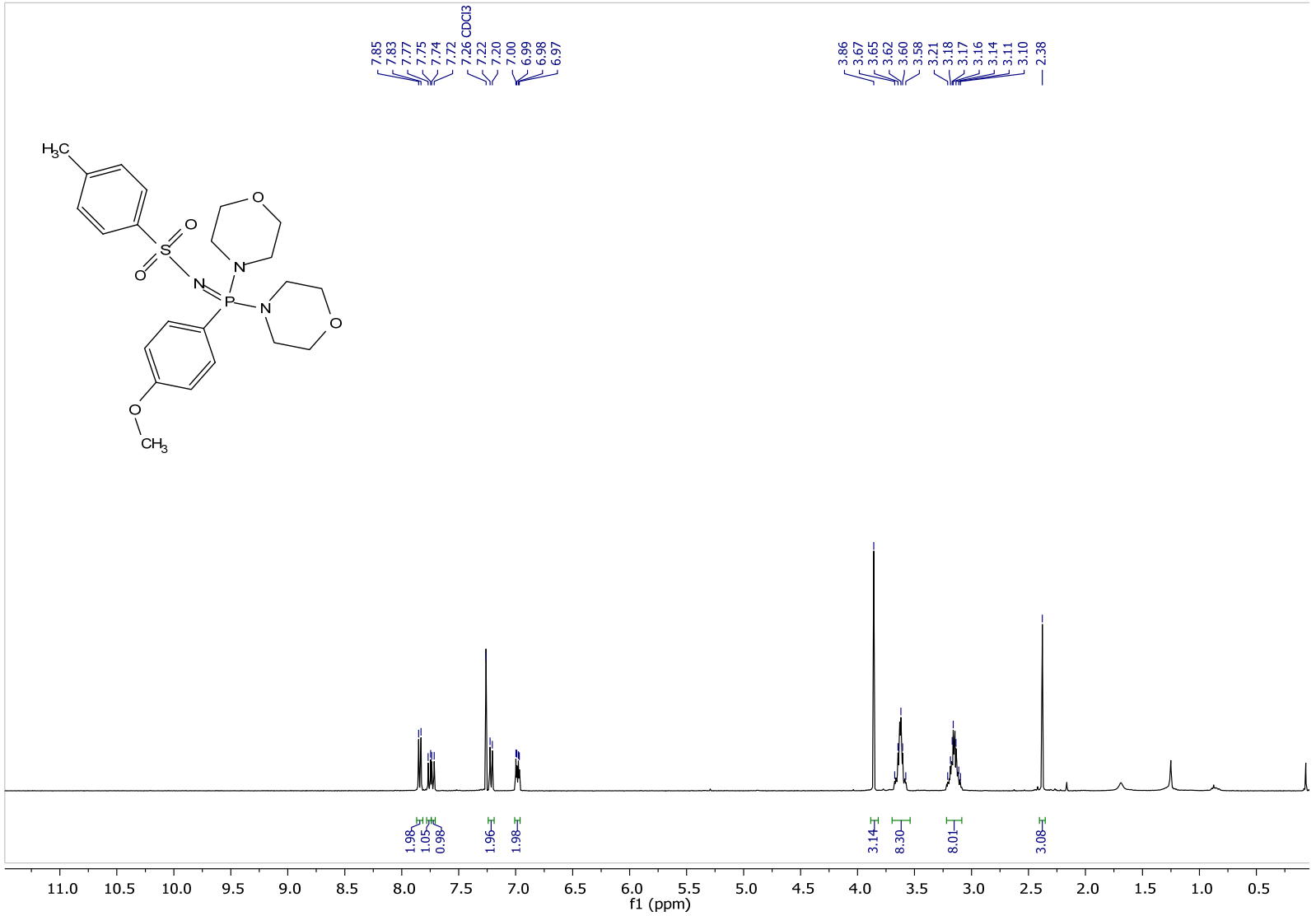
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **3f′a**



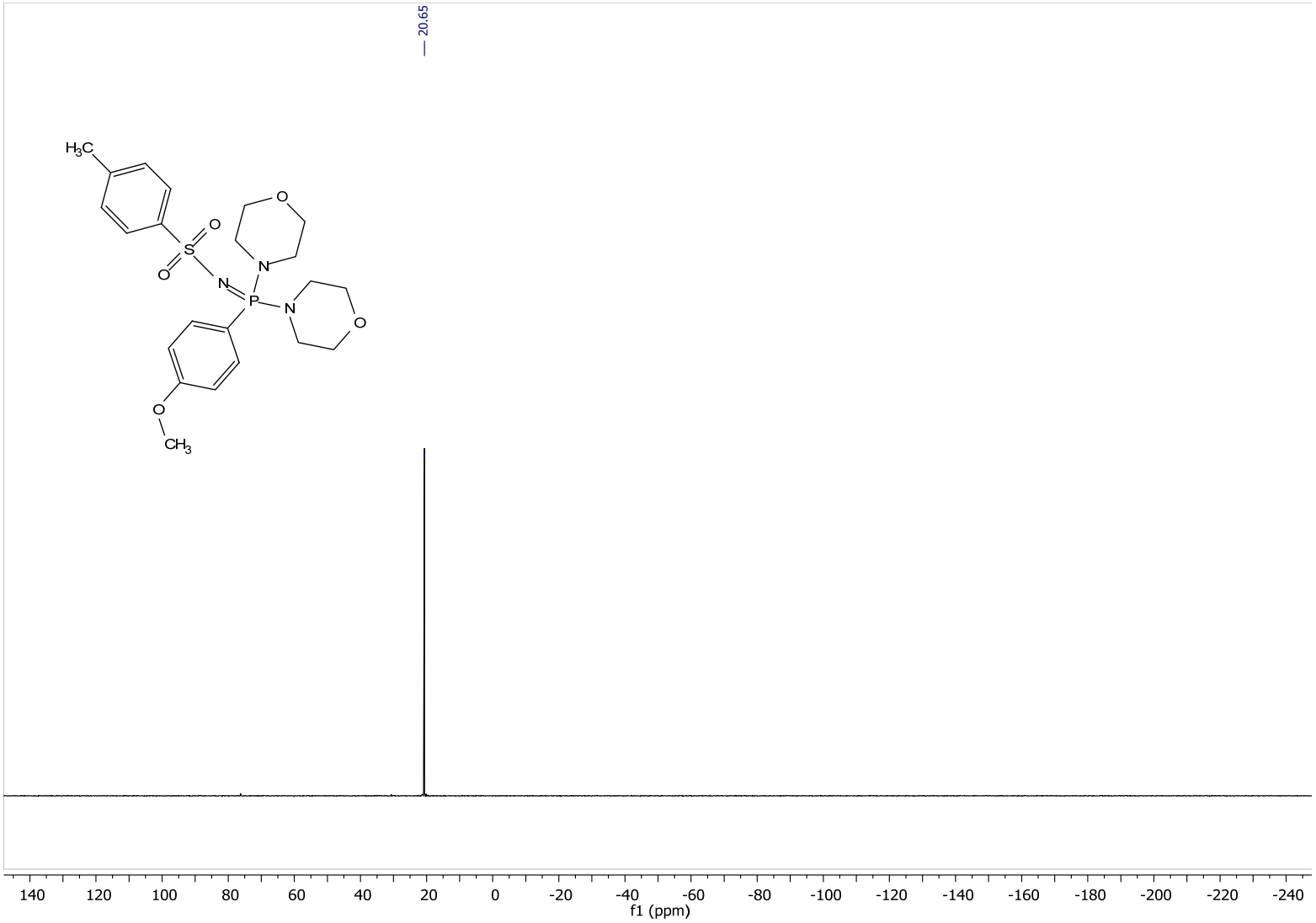
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5aa**



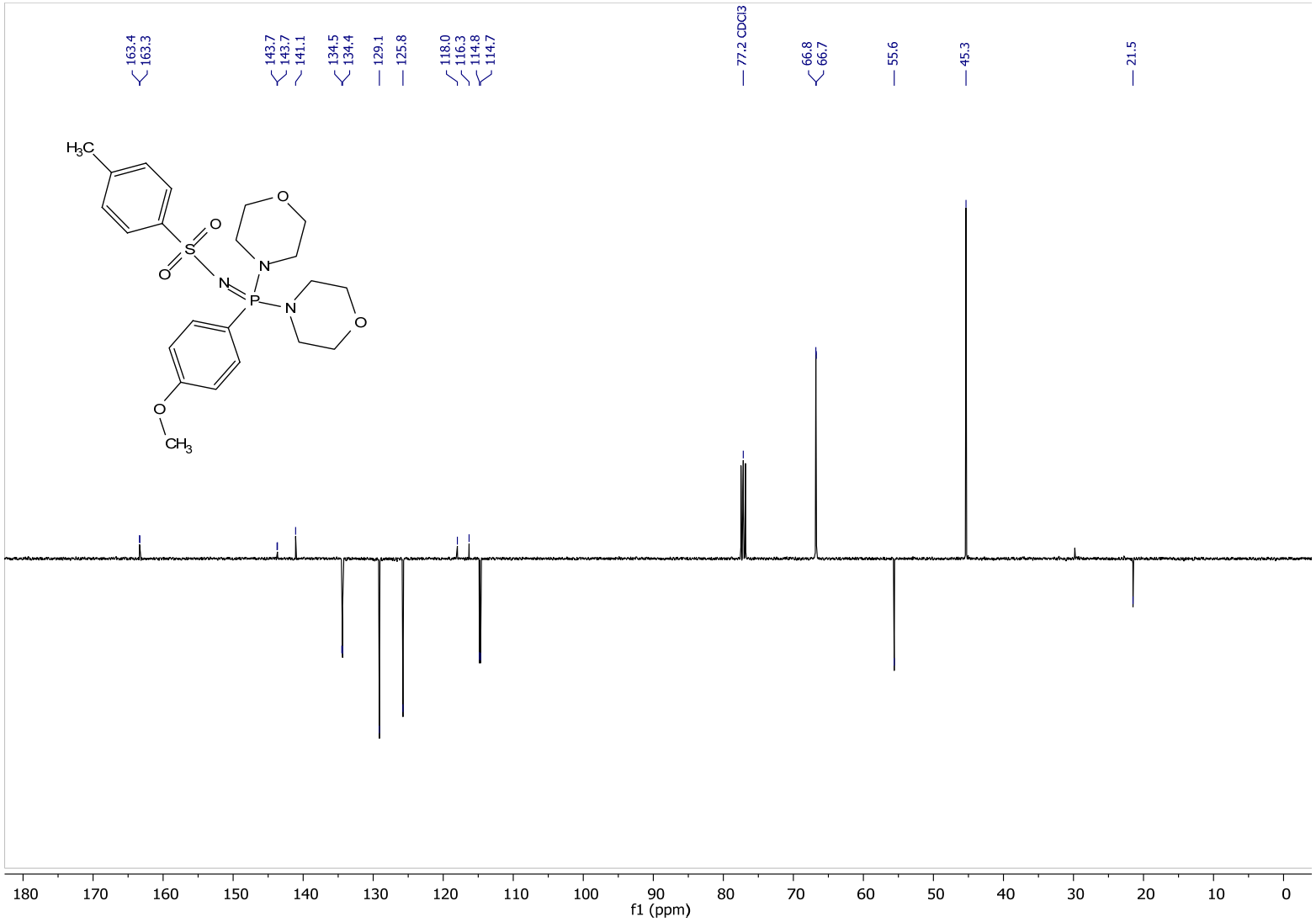
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5aa**



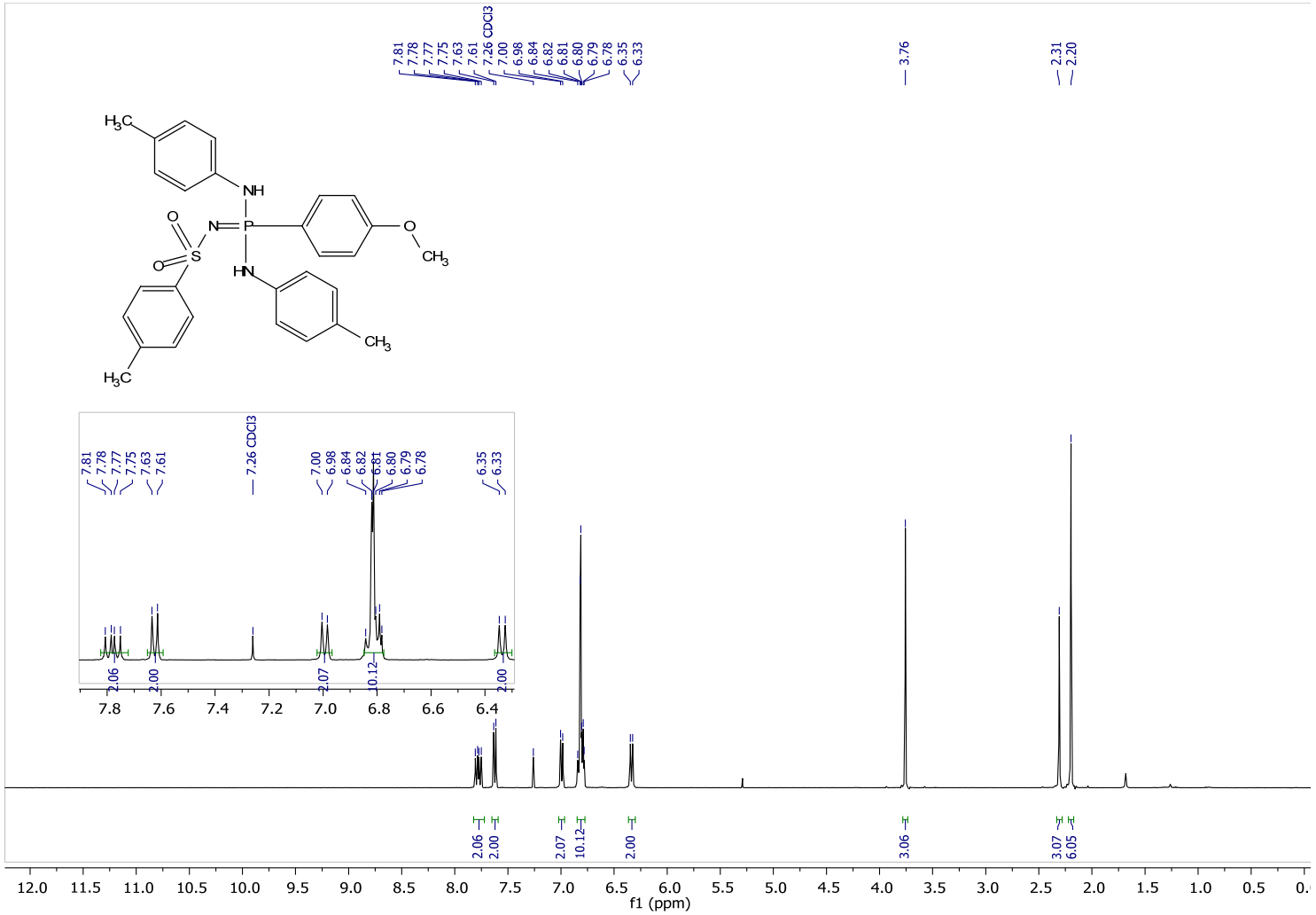
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ba**



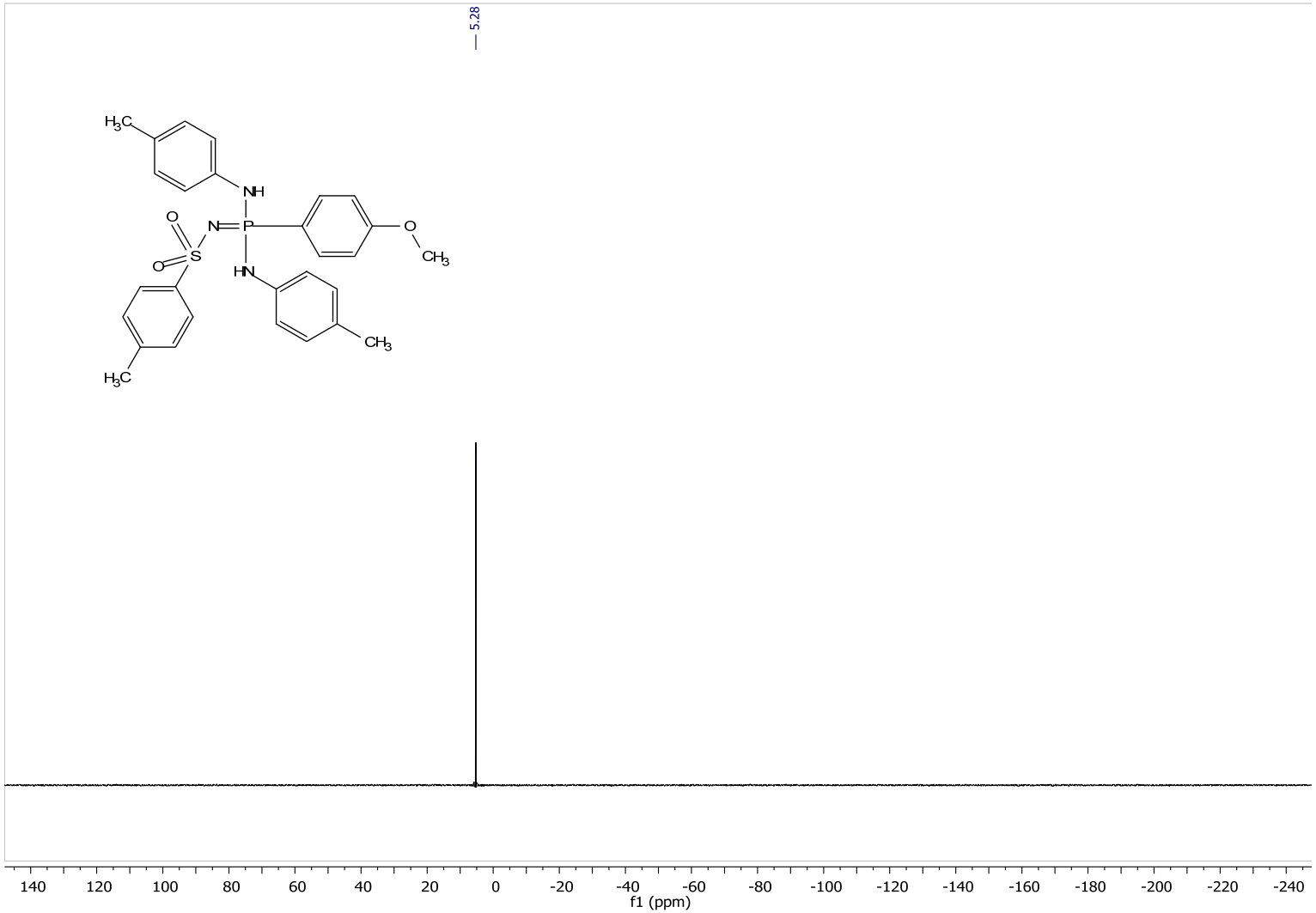
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5ba**



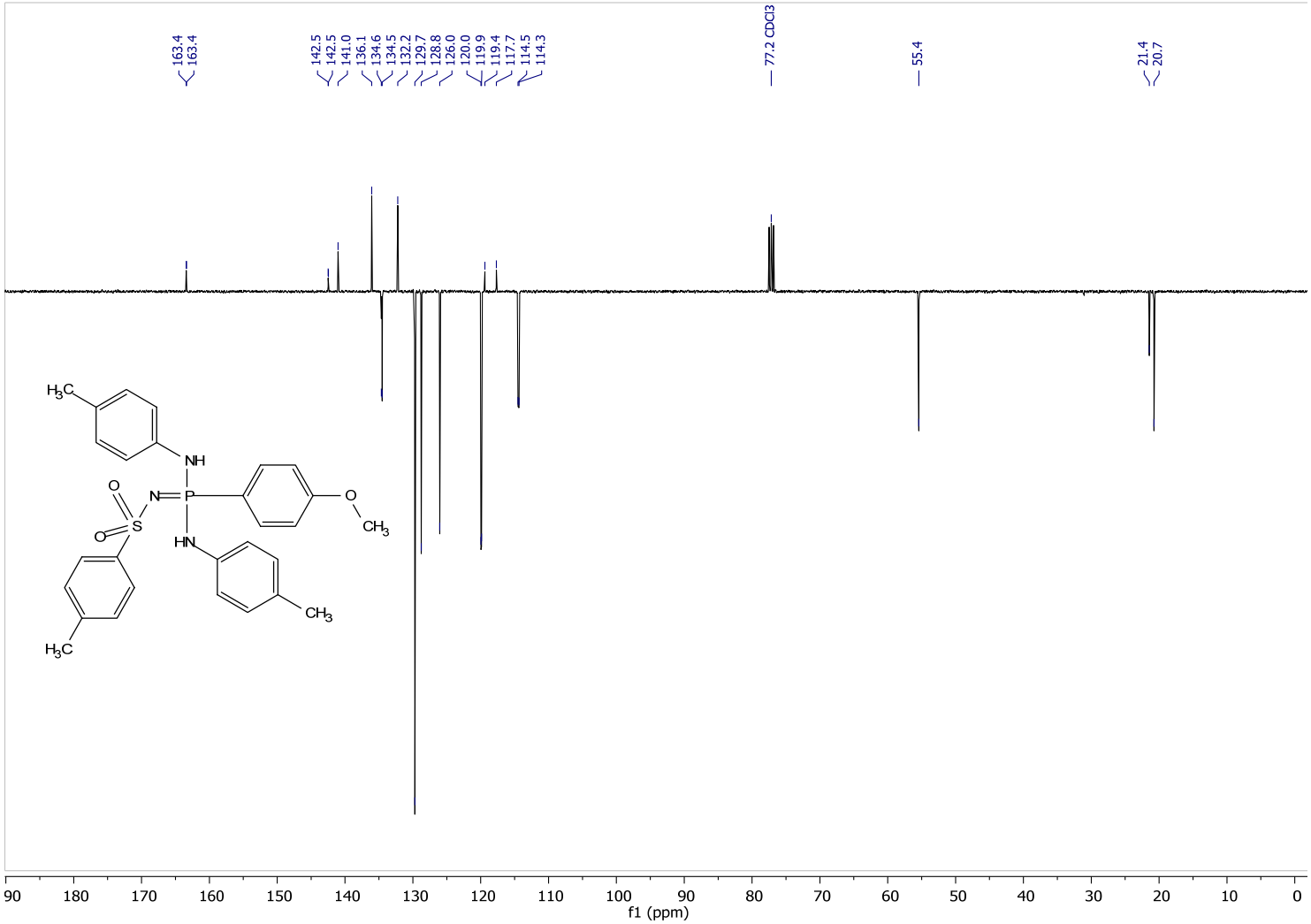
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5ba**



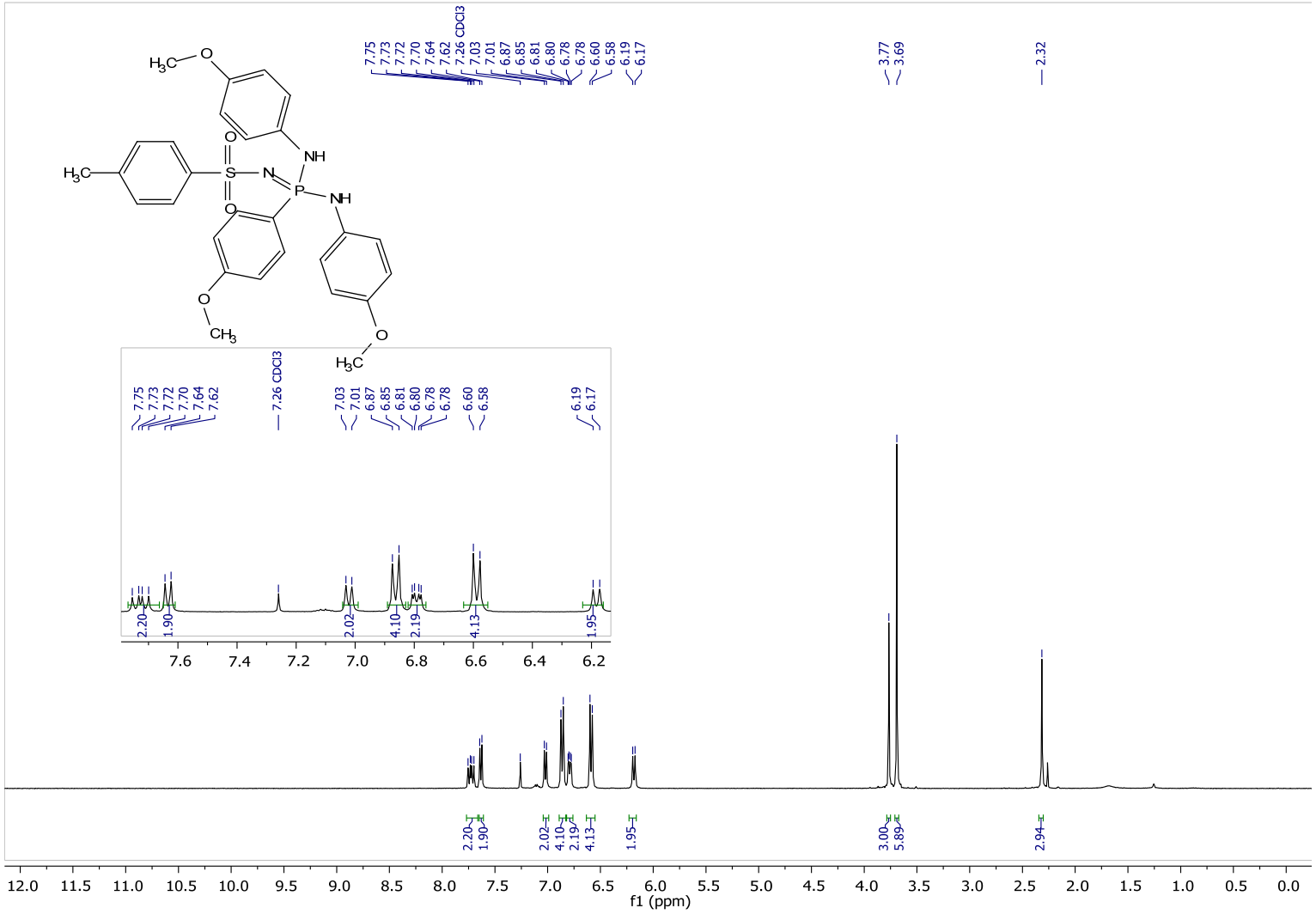
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ca**



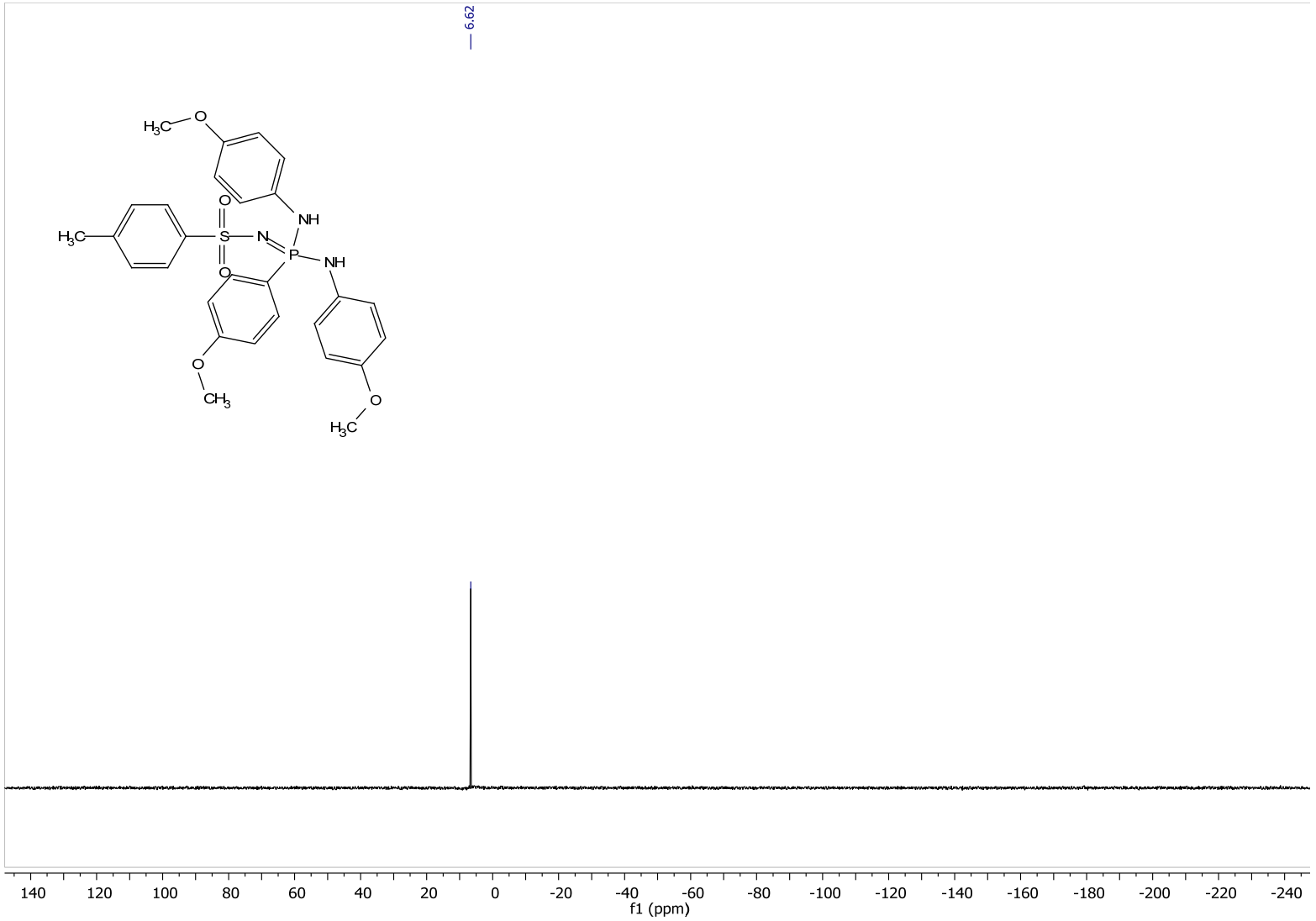
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5ca**



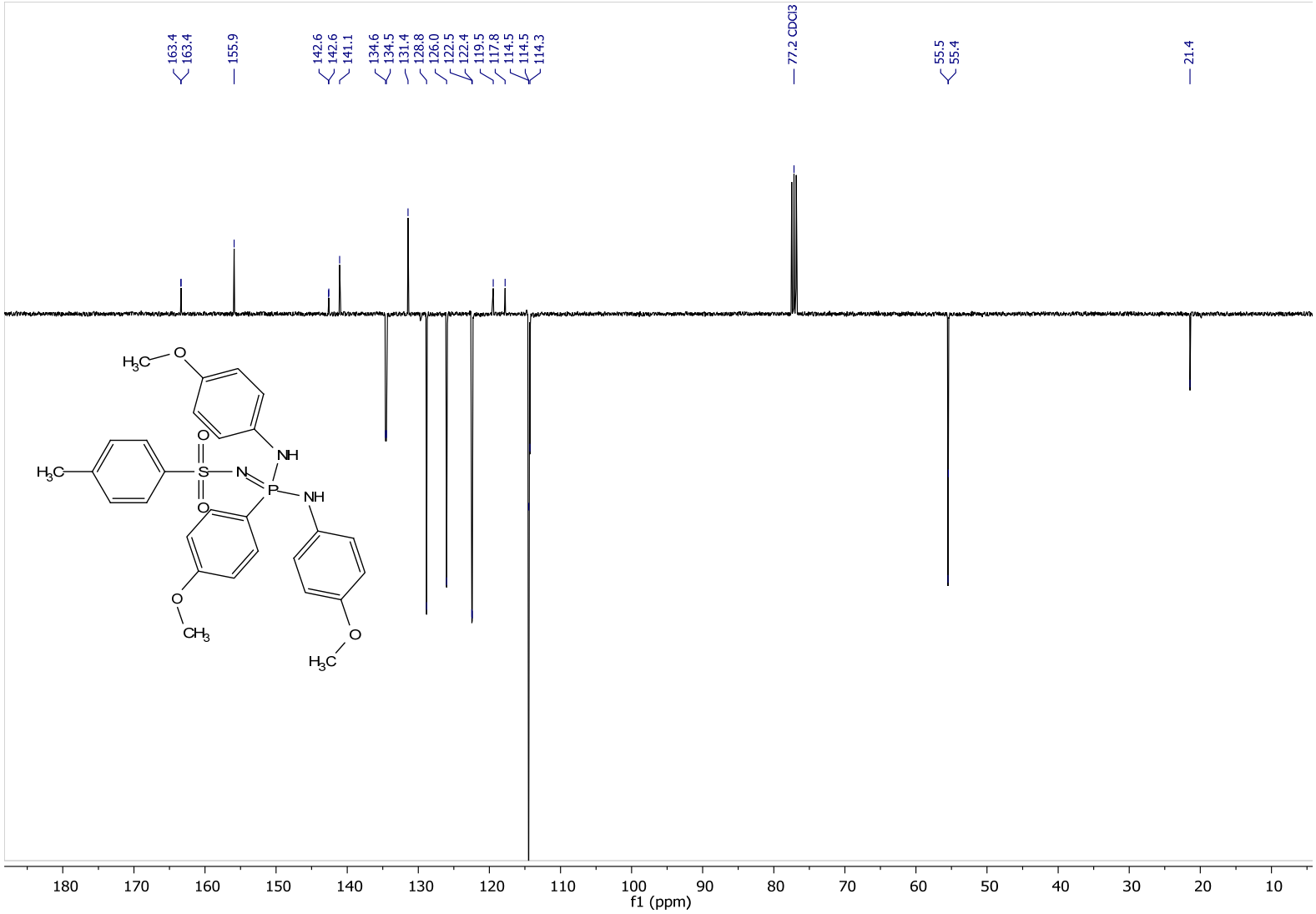
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5ca**



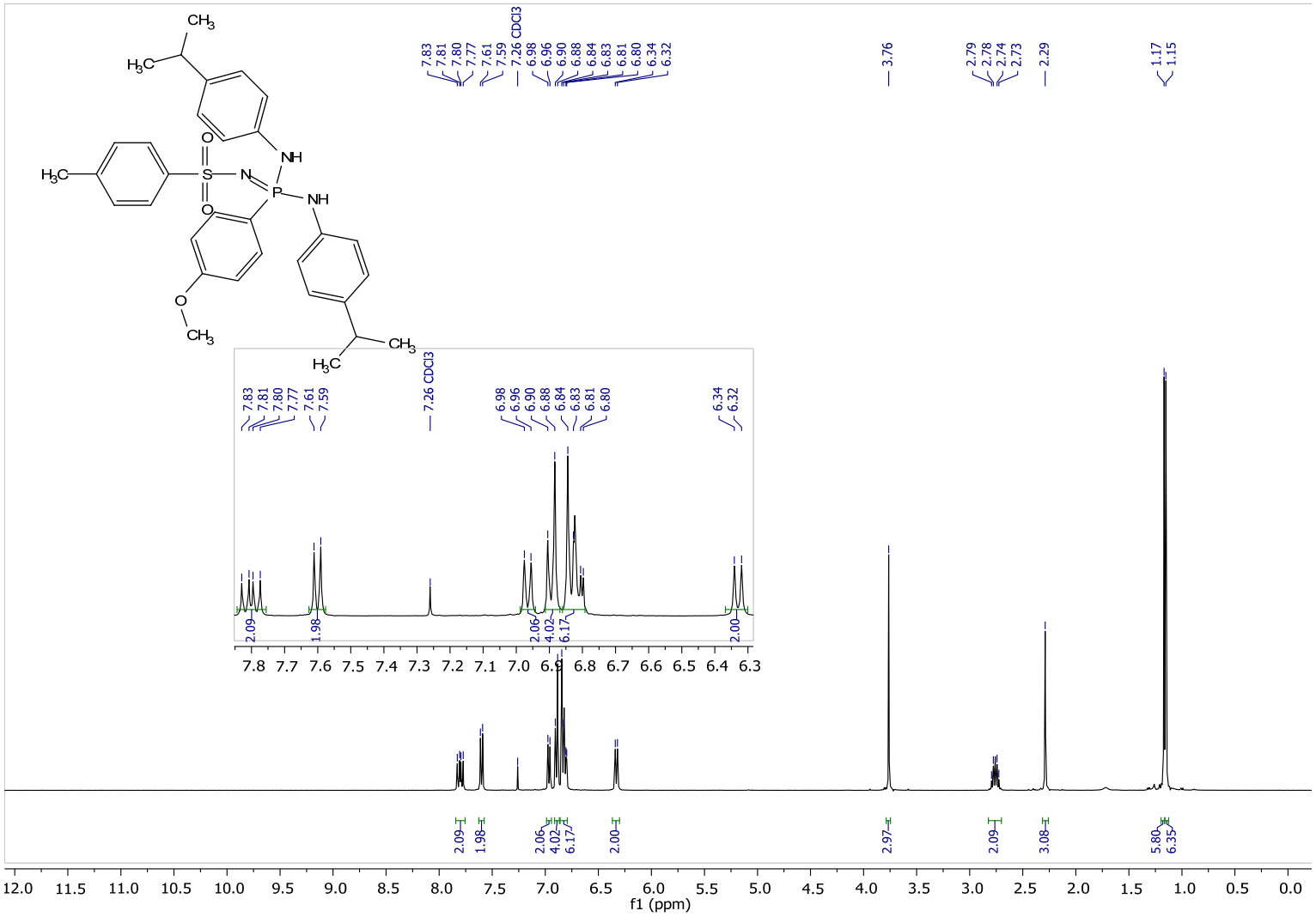
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5da**



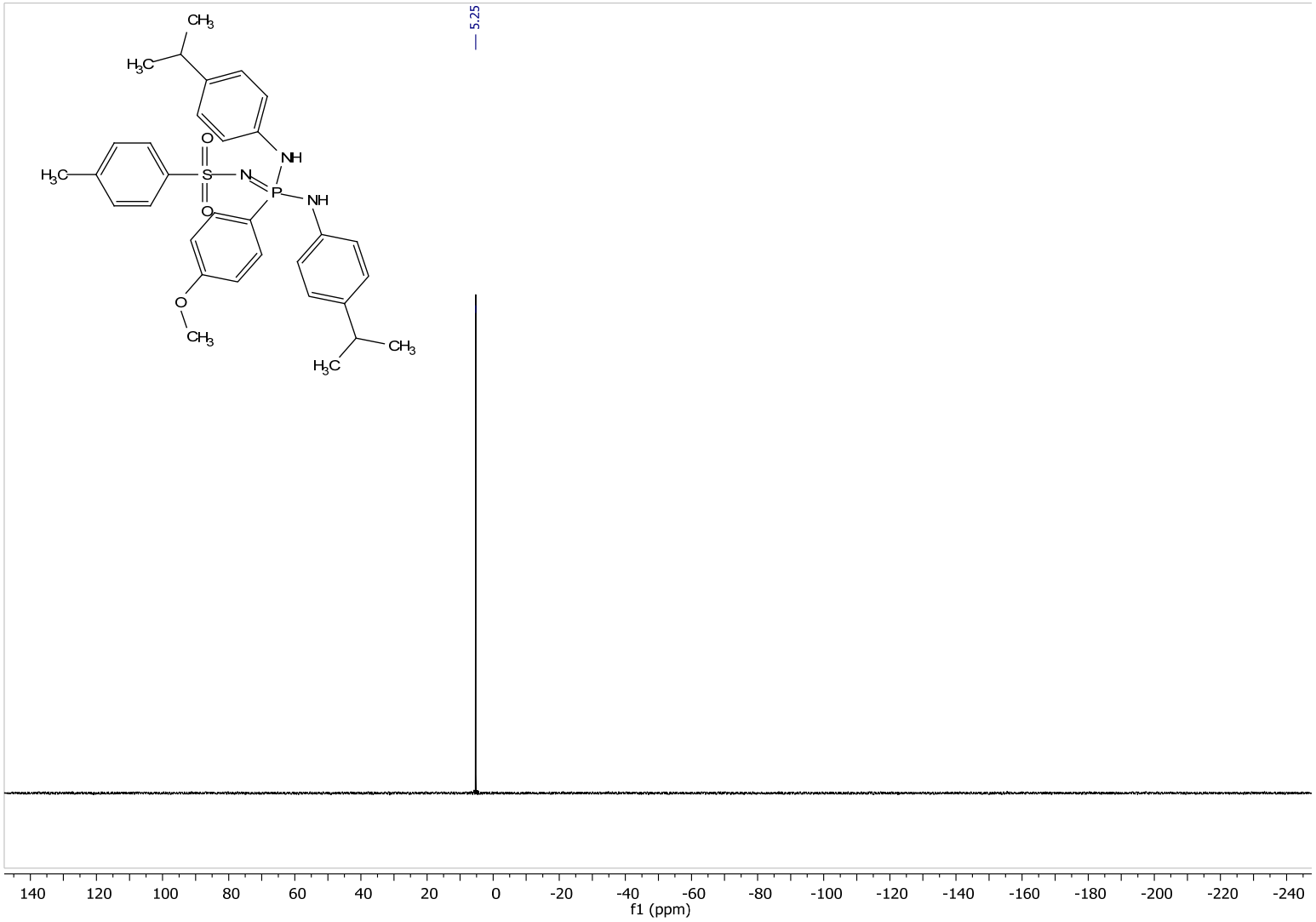
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5da**



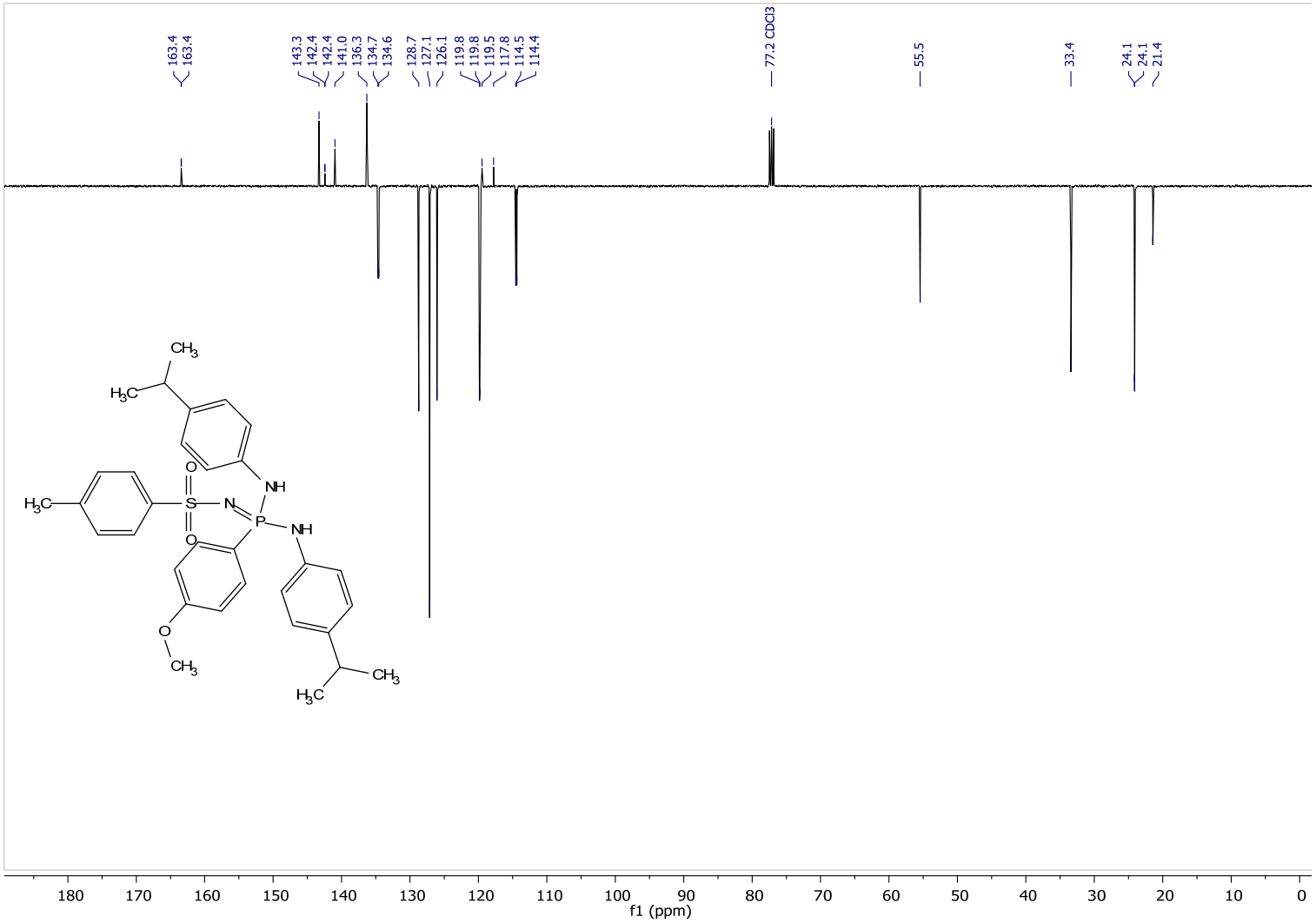
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5da**



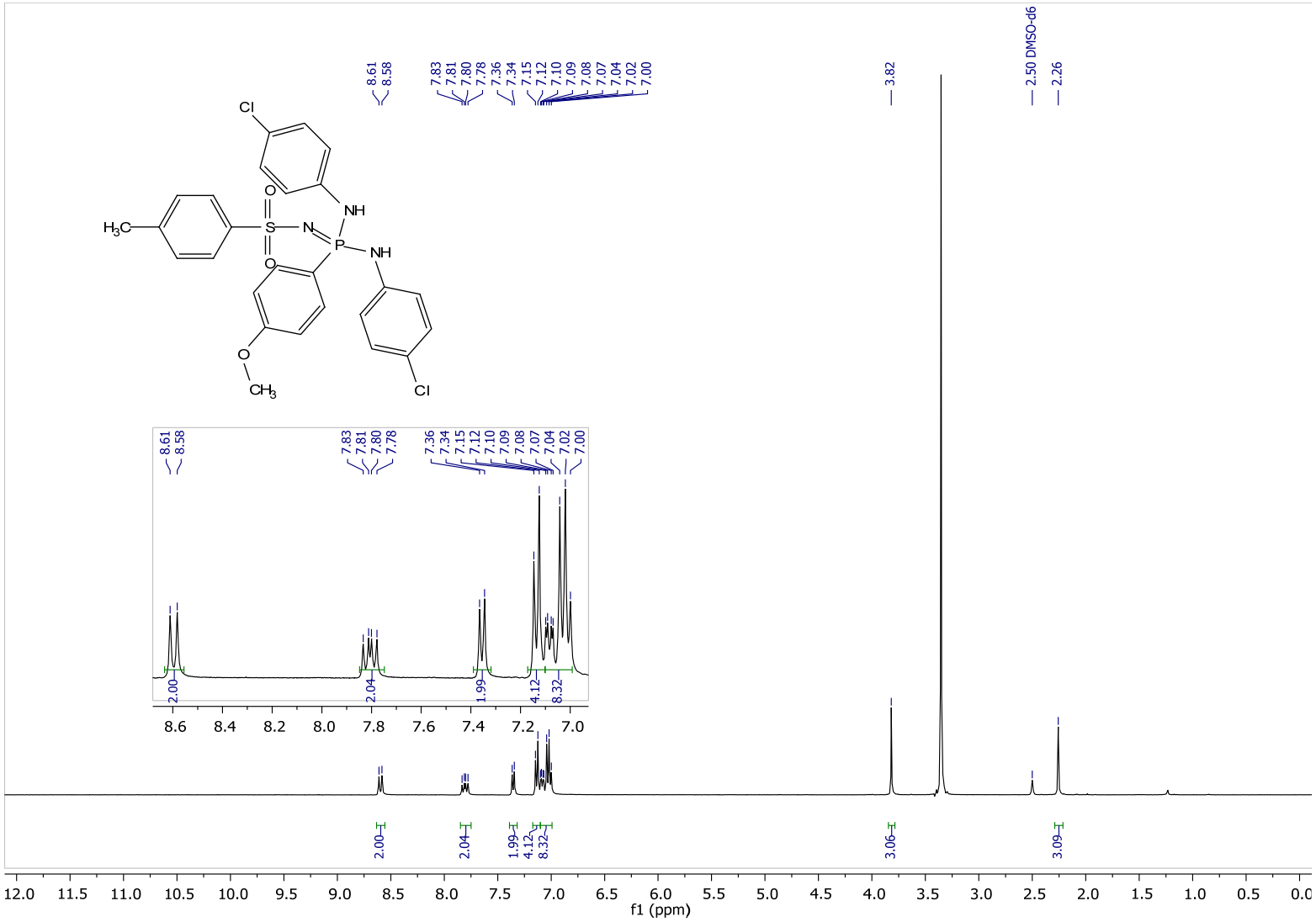
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ea**



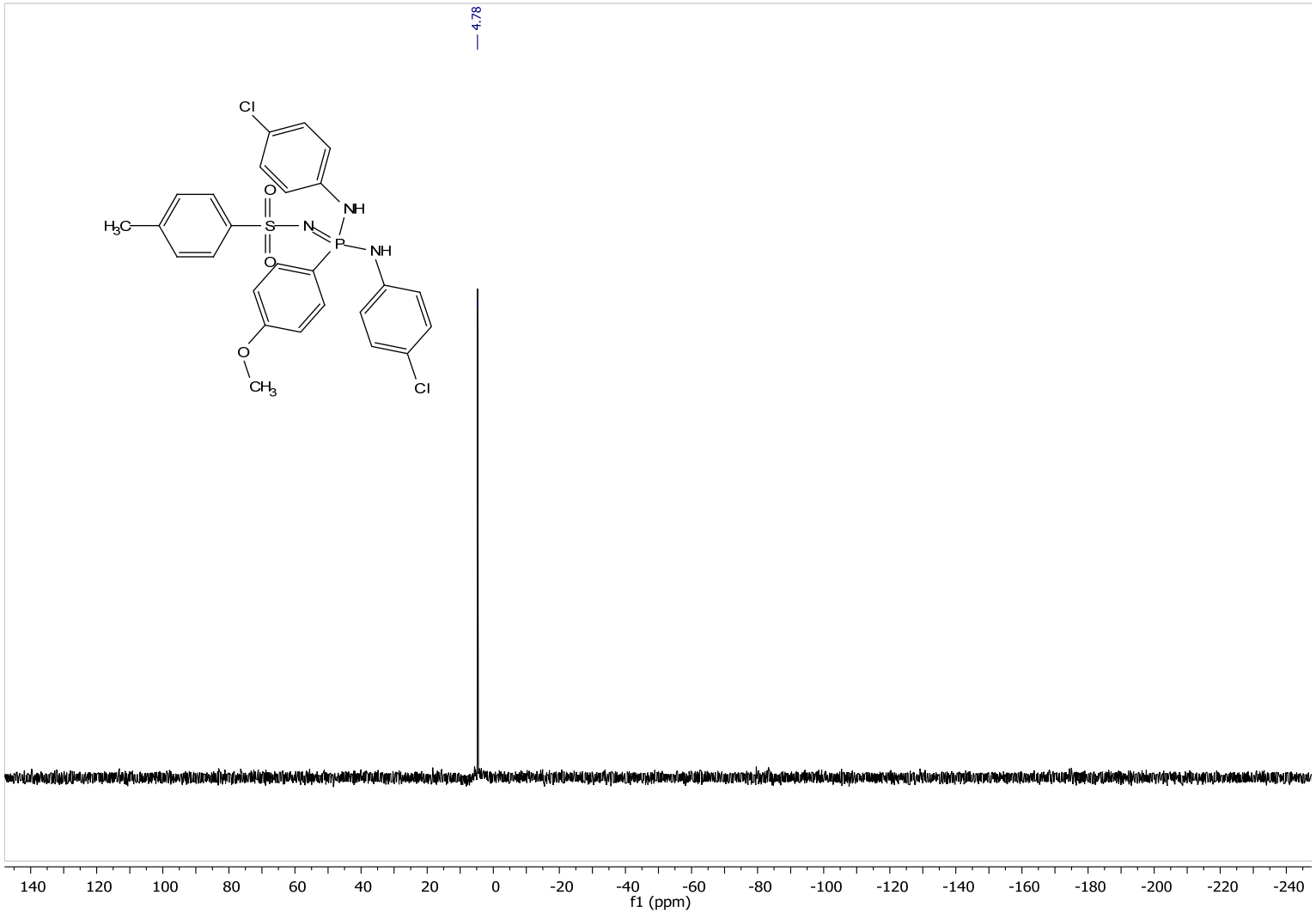
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5ea**



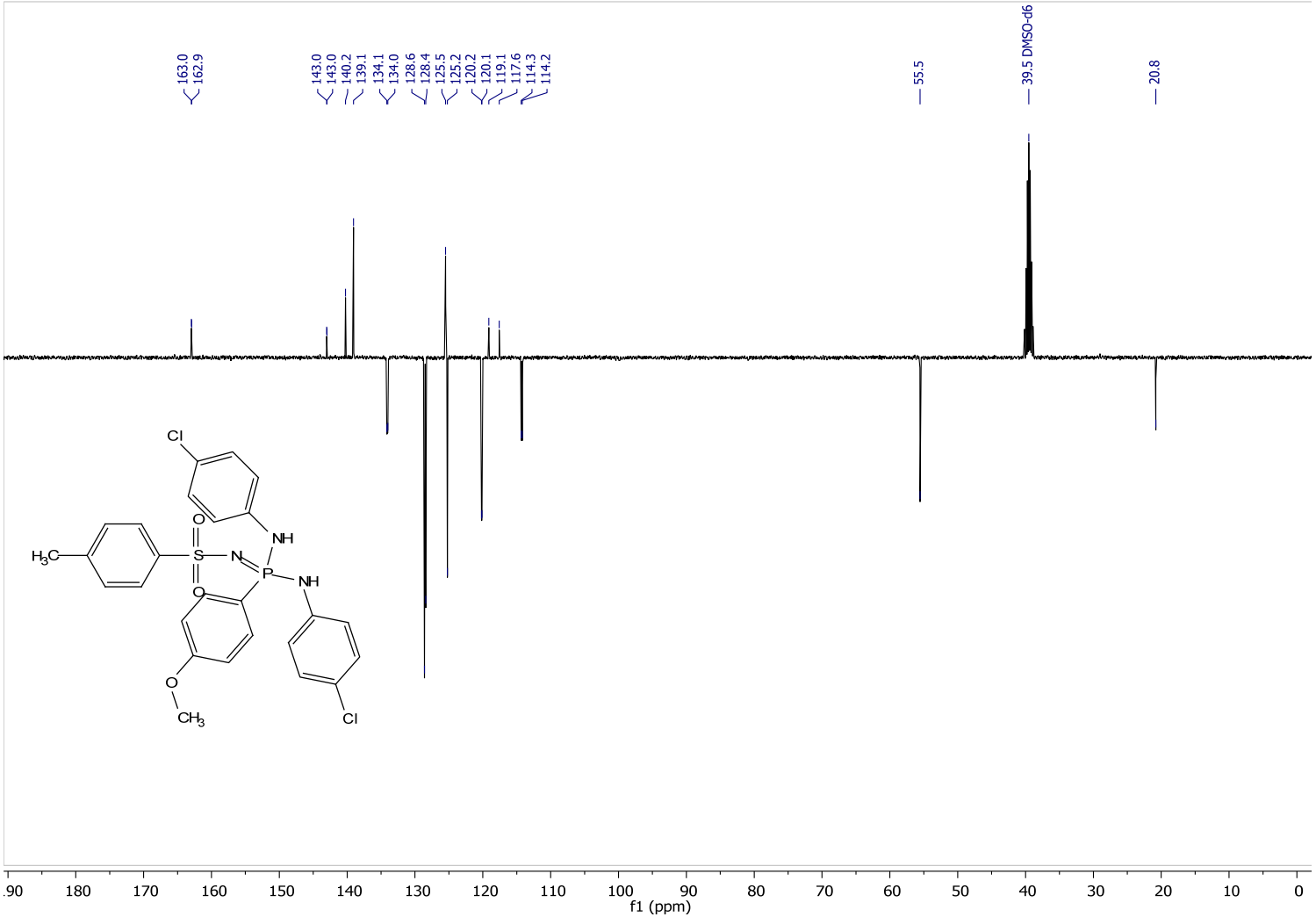
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5ea**



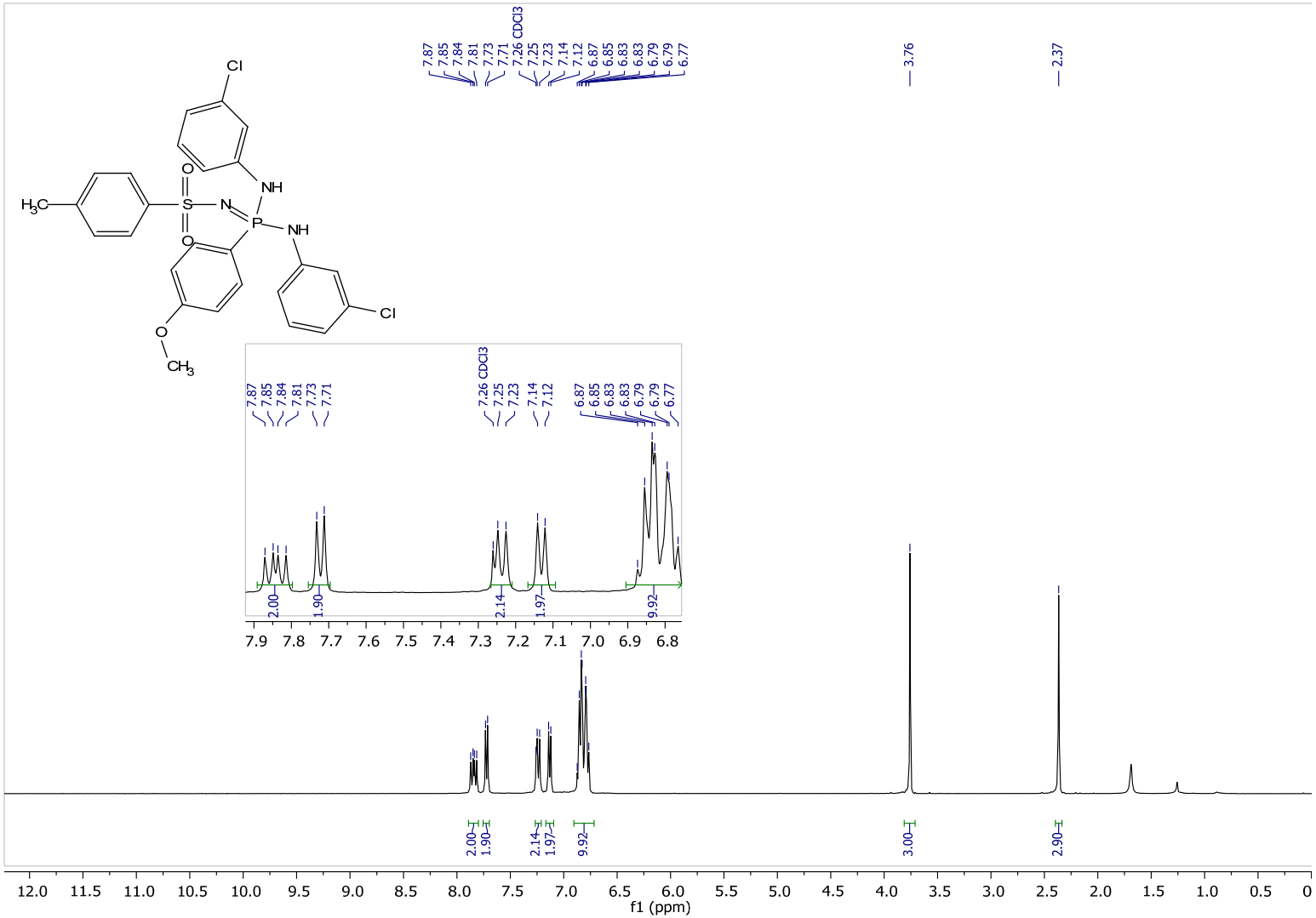
^{1}H NMR (400 MHz, DMSO–d_6) of **5fa**



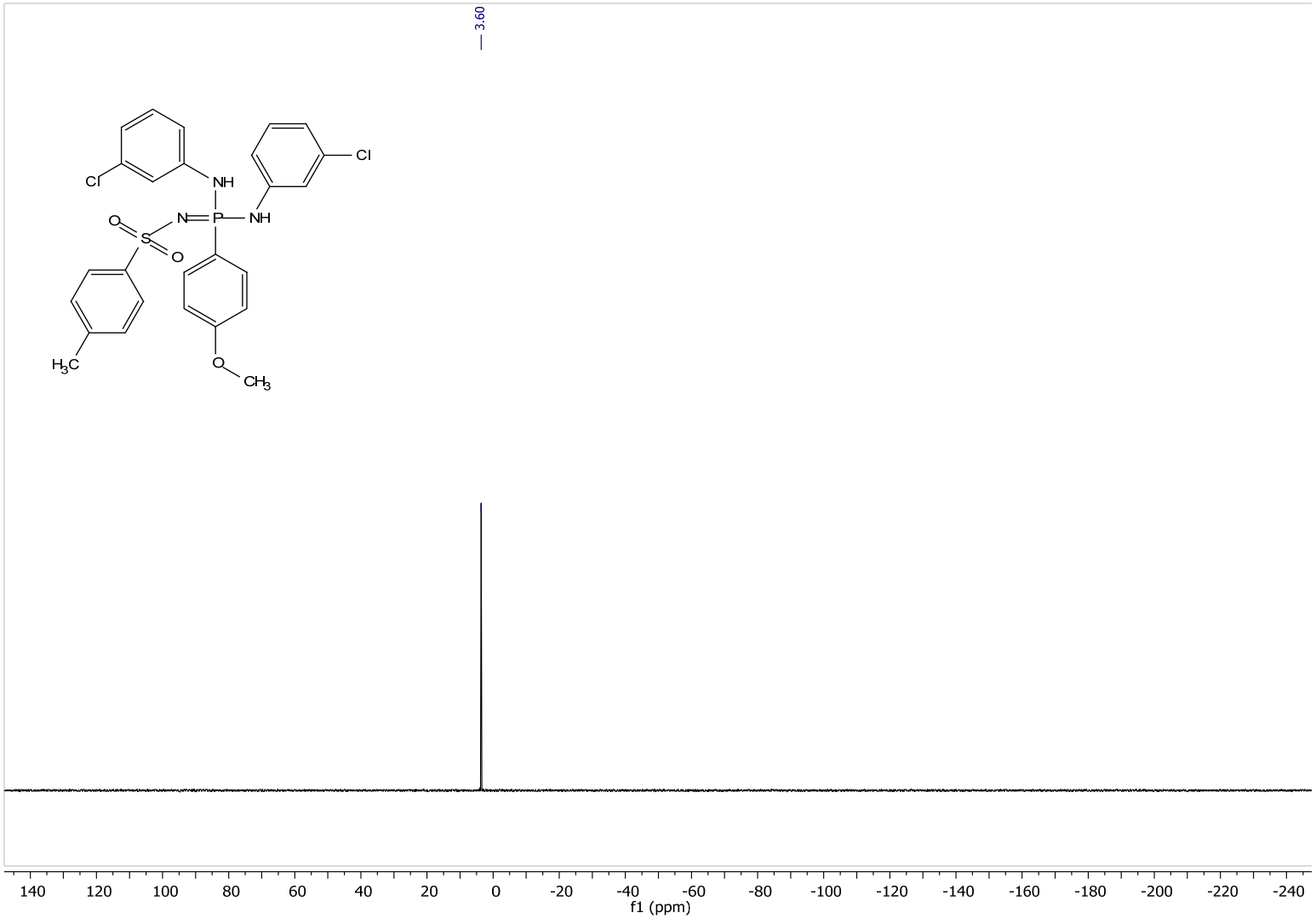
^{31}P NMR (162 MHz, DMSO–*d*$_6$) of **5fa**



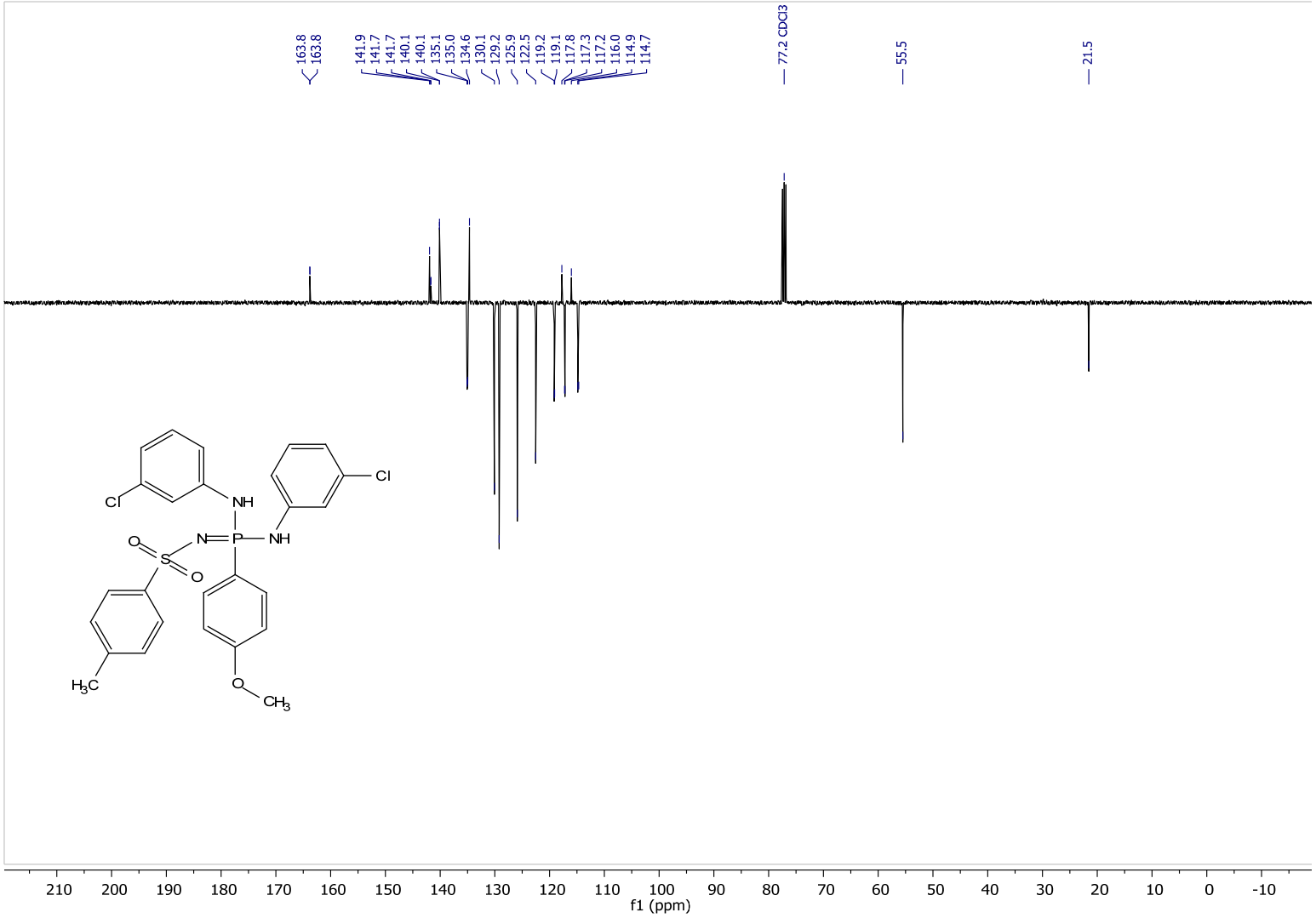
^{13}C NMR (100 MHz, DMSO–*d*$_6$) of **5fa**



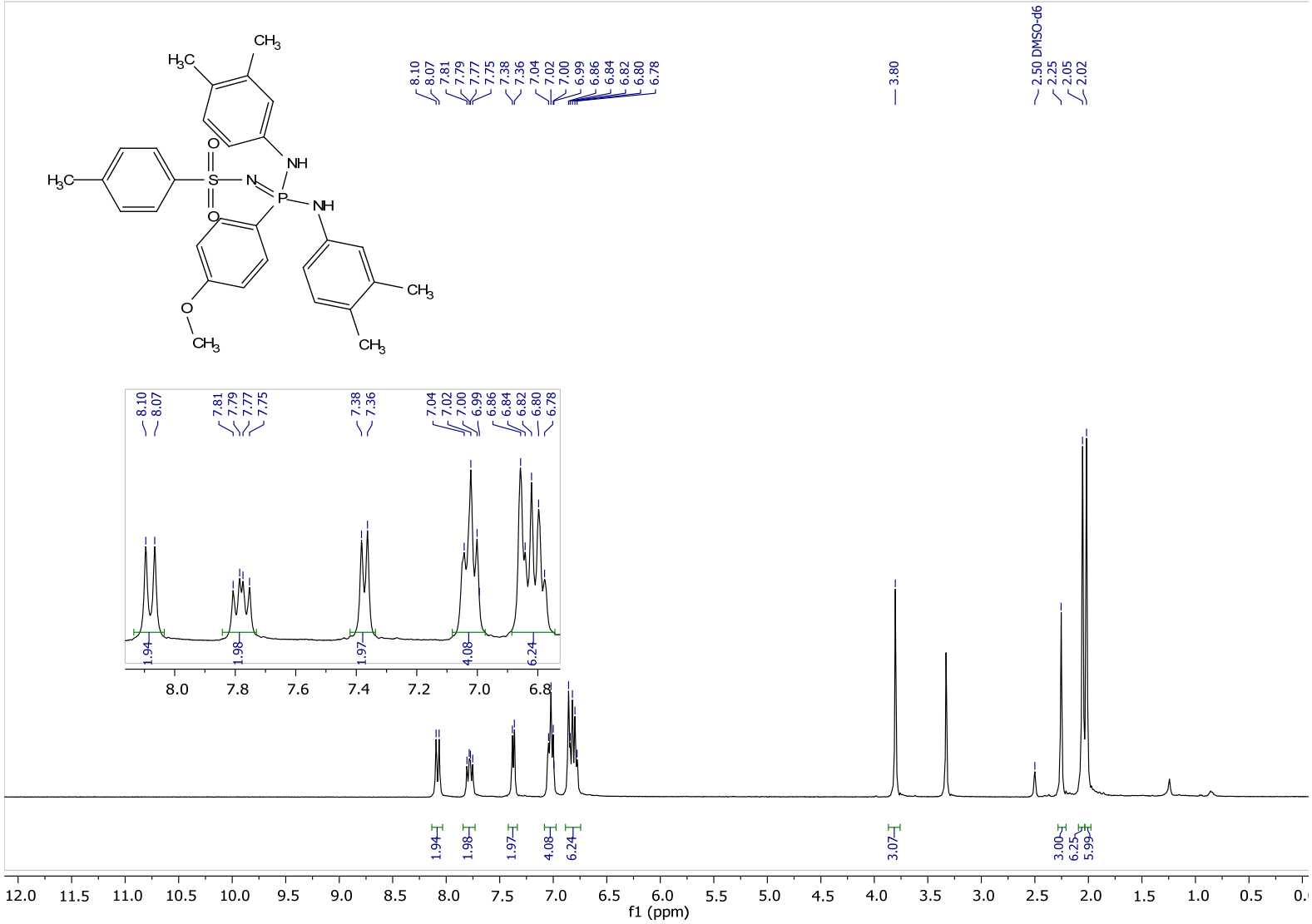
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ga**



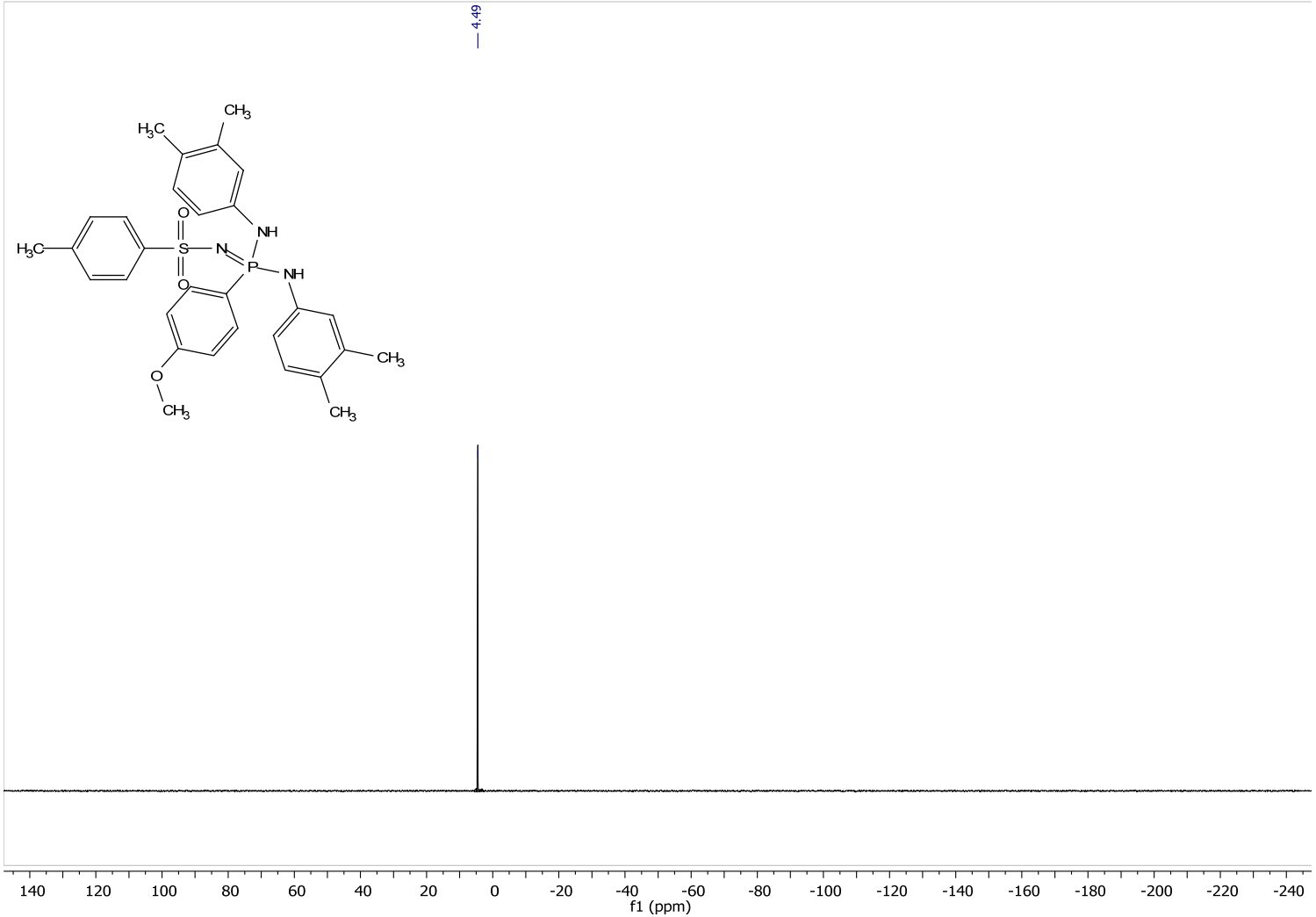
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5ga**



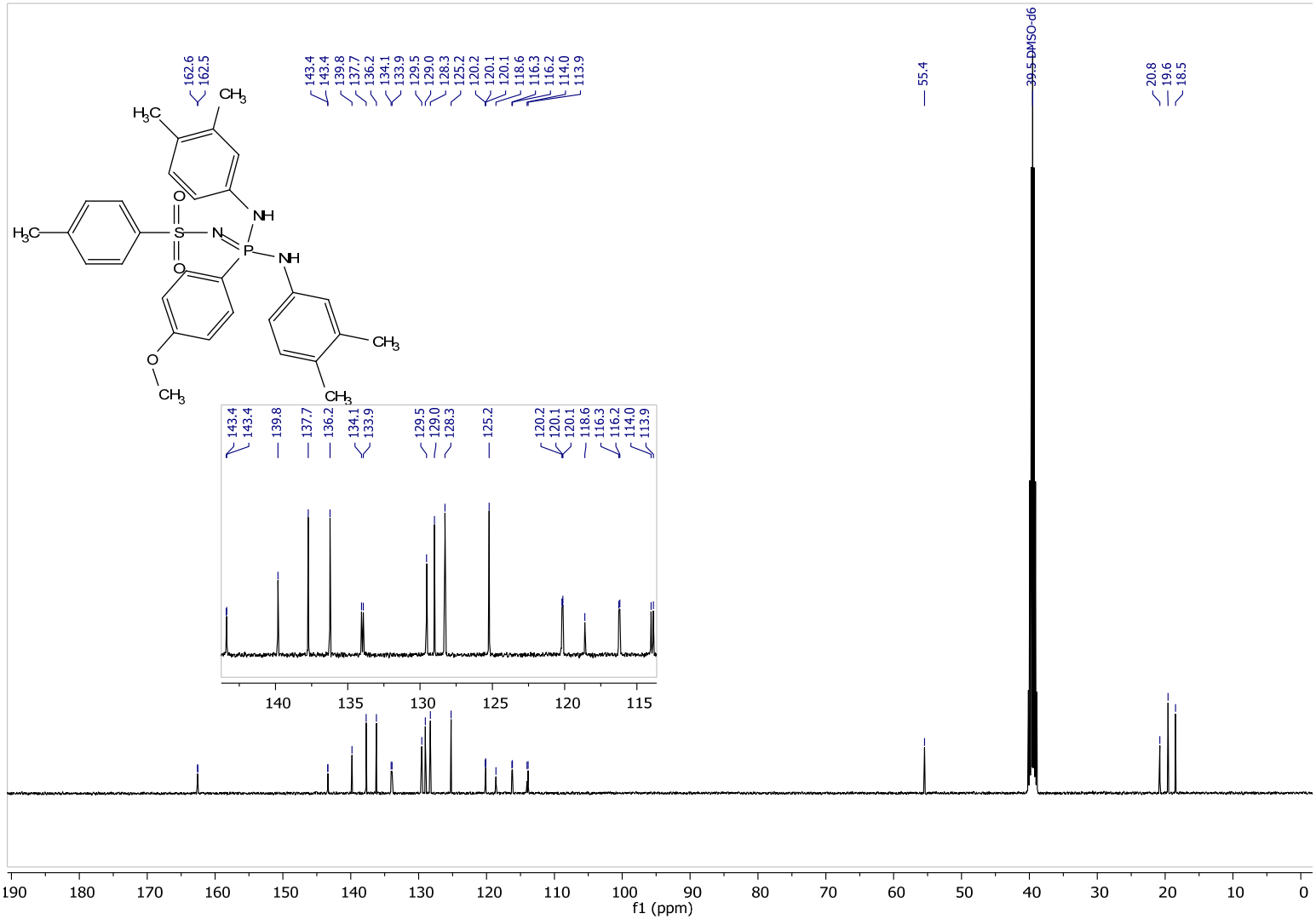
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5ga**



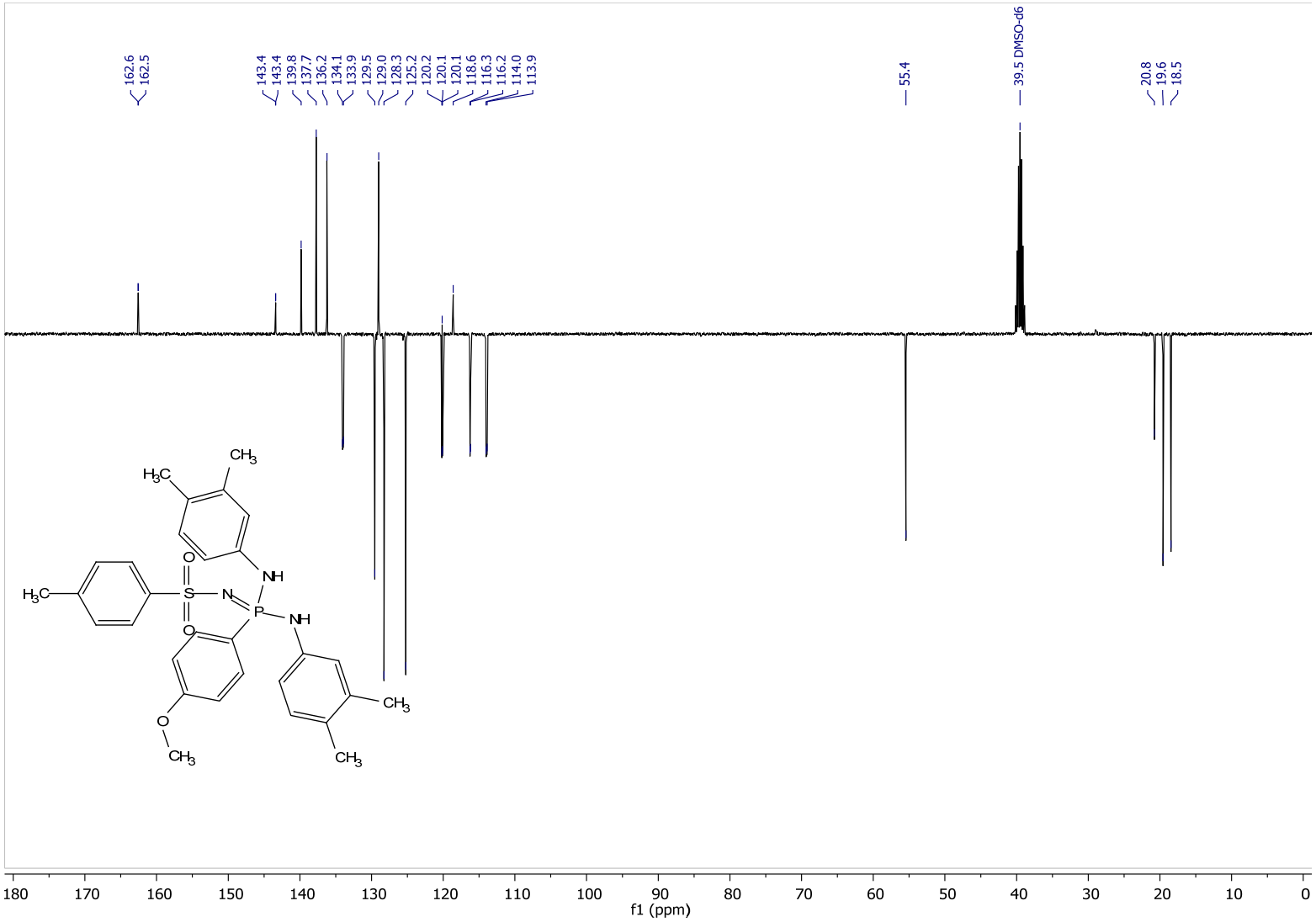
^{1}H NMR (400 MHz, DMSO–d_6) of **5ha**



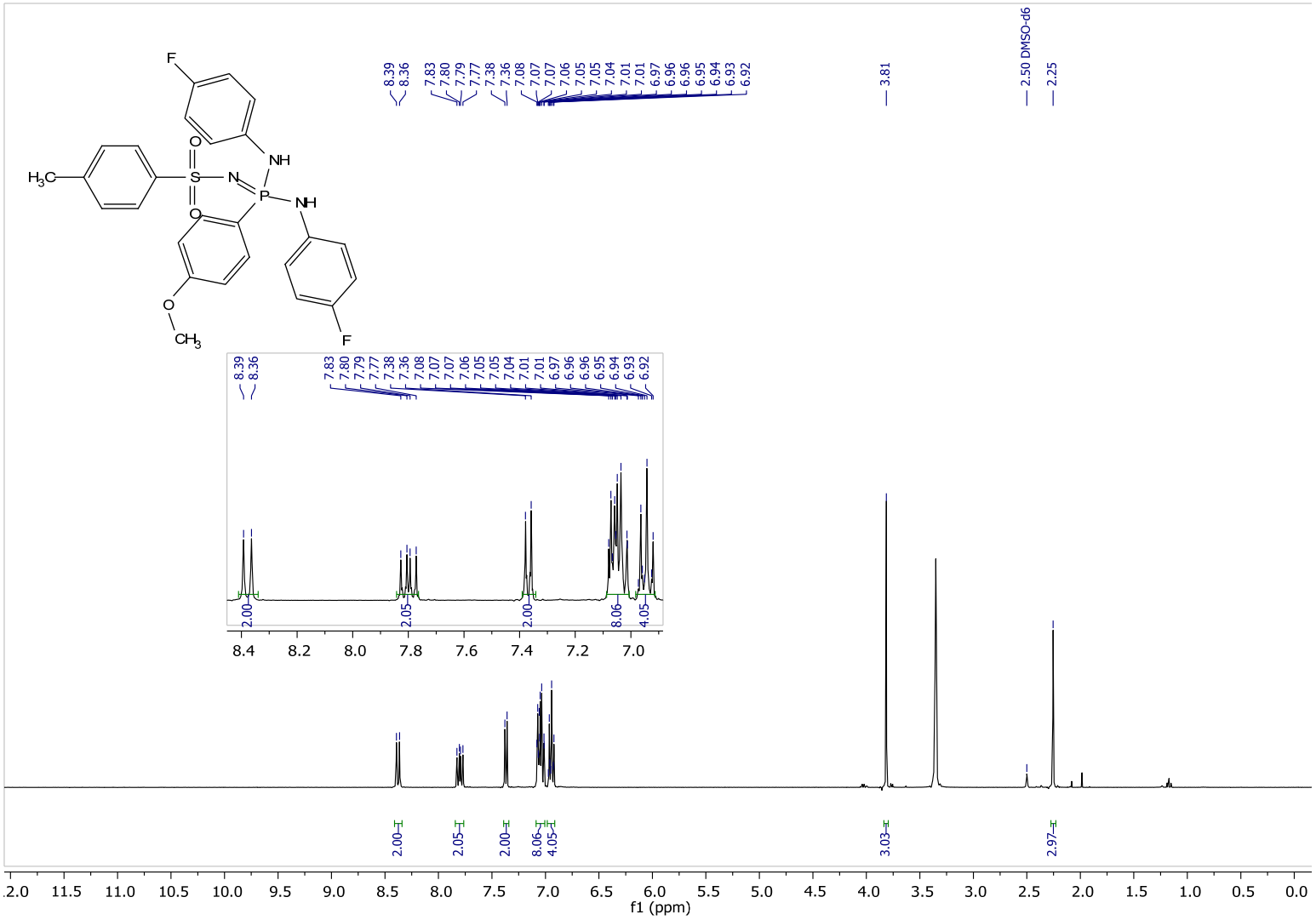
^{31}P NMR (162 MHz, DMSO–d_6) of **5ha**



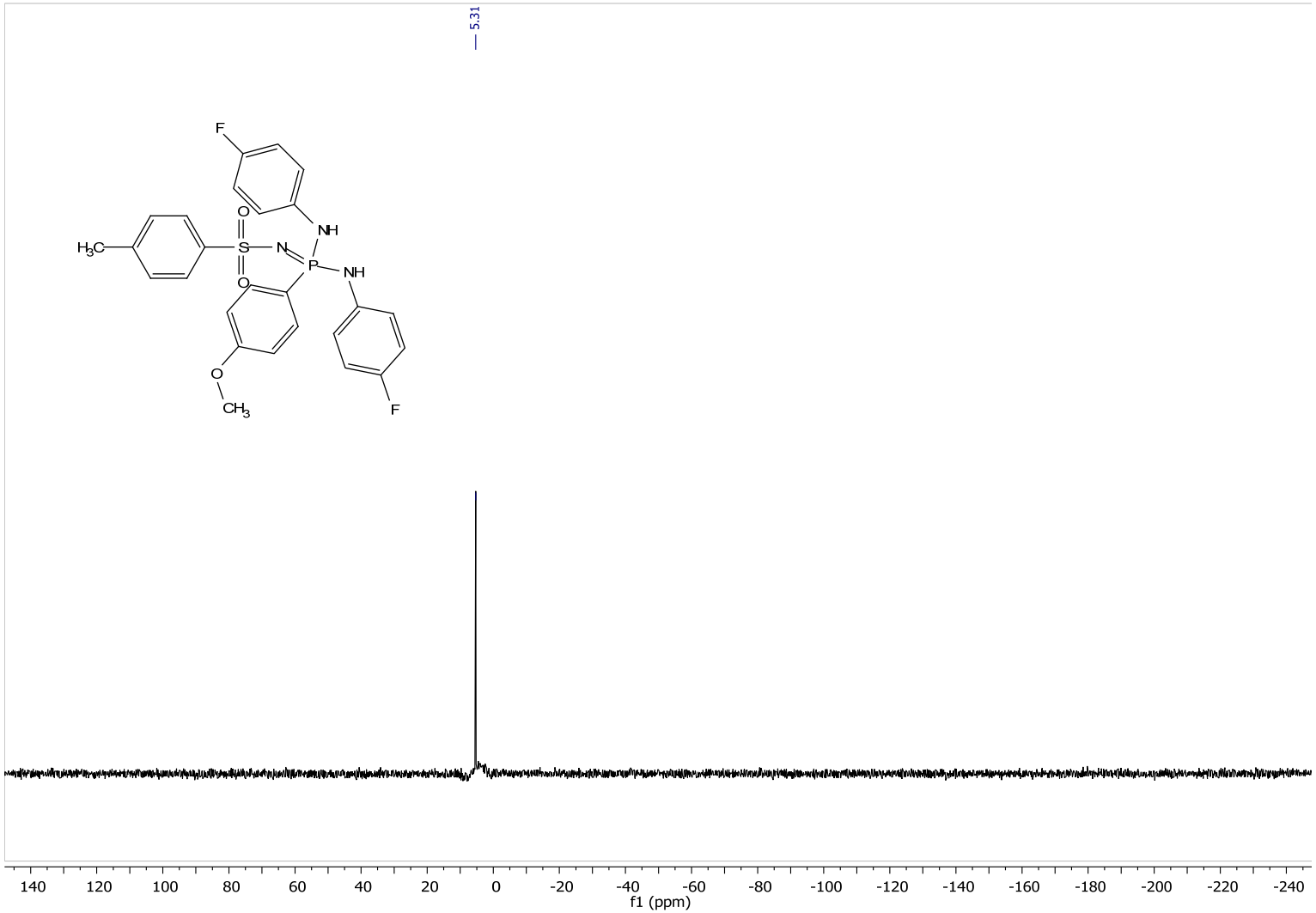
^{13}C NMR (100 MHz, DMSO–*d*$_6$) of **5ha**



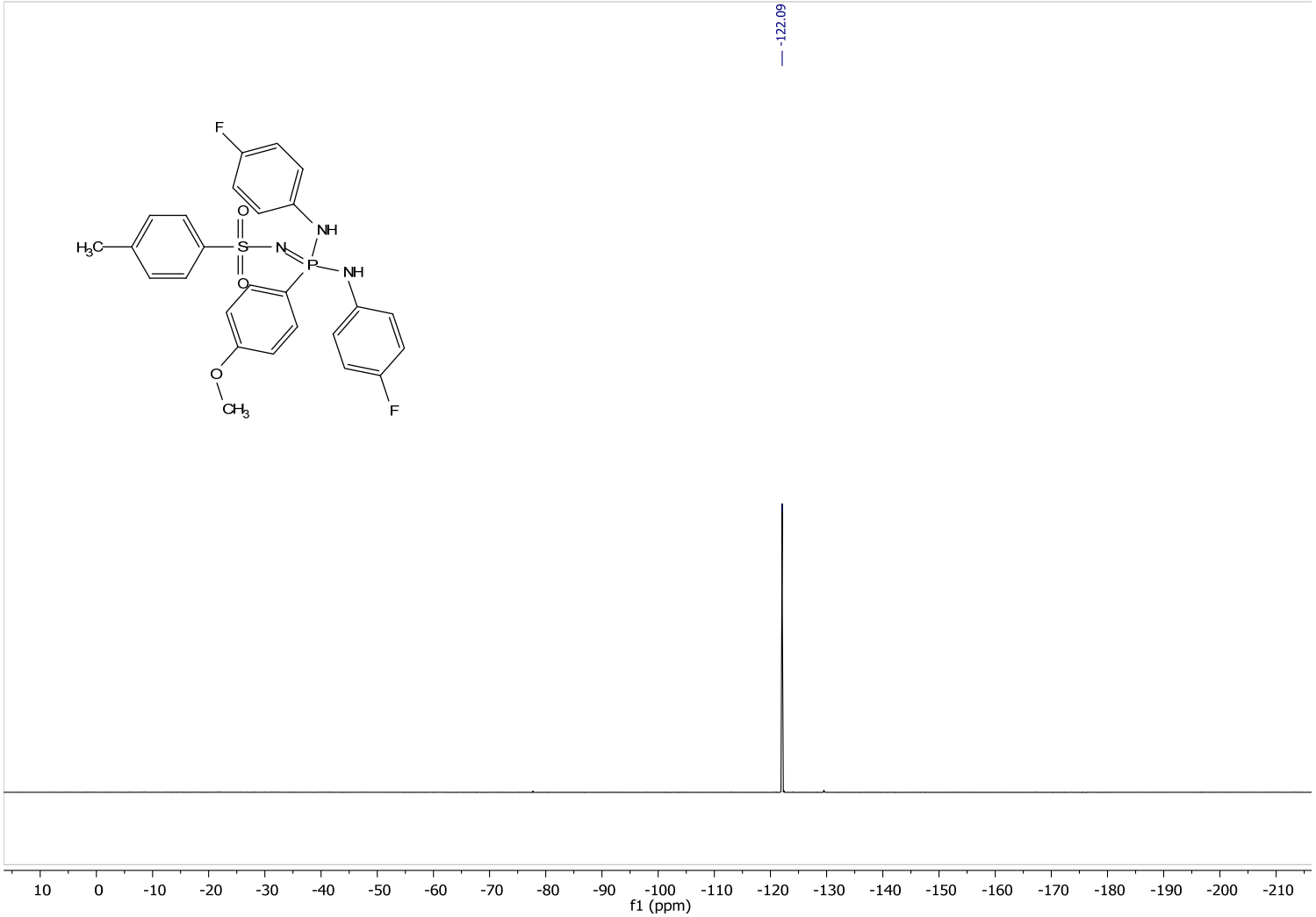
^{13}C NMR (100 MHz, DMSO–d_6) of **5ha**



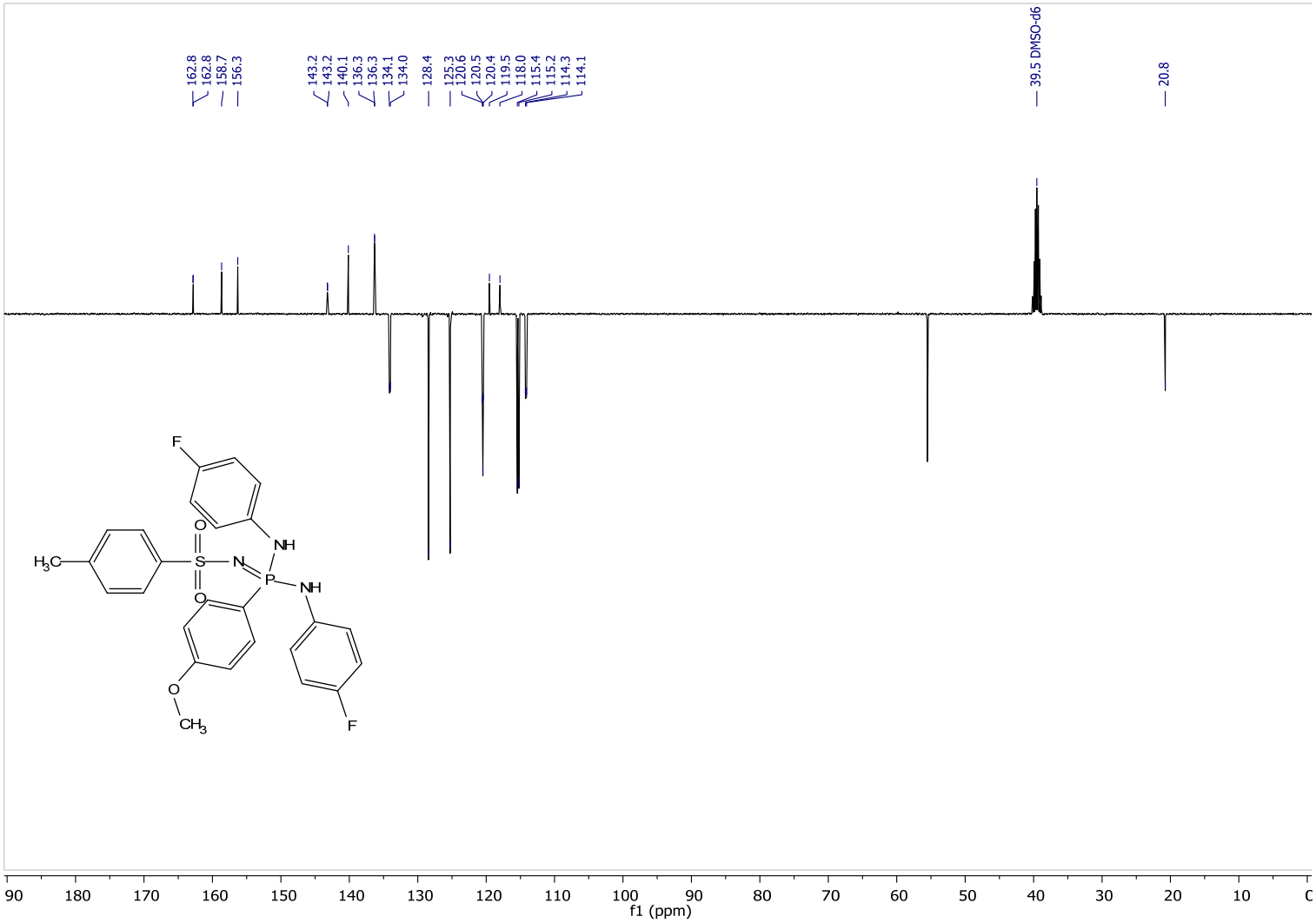
^{1}H NMR (400 MHz, DMSO–*d*$_6$) of **5ia**



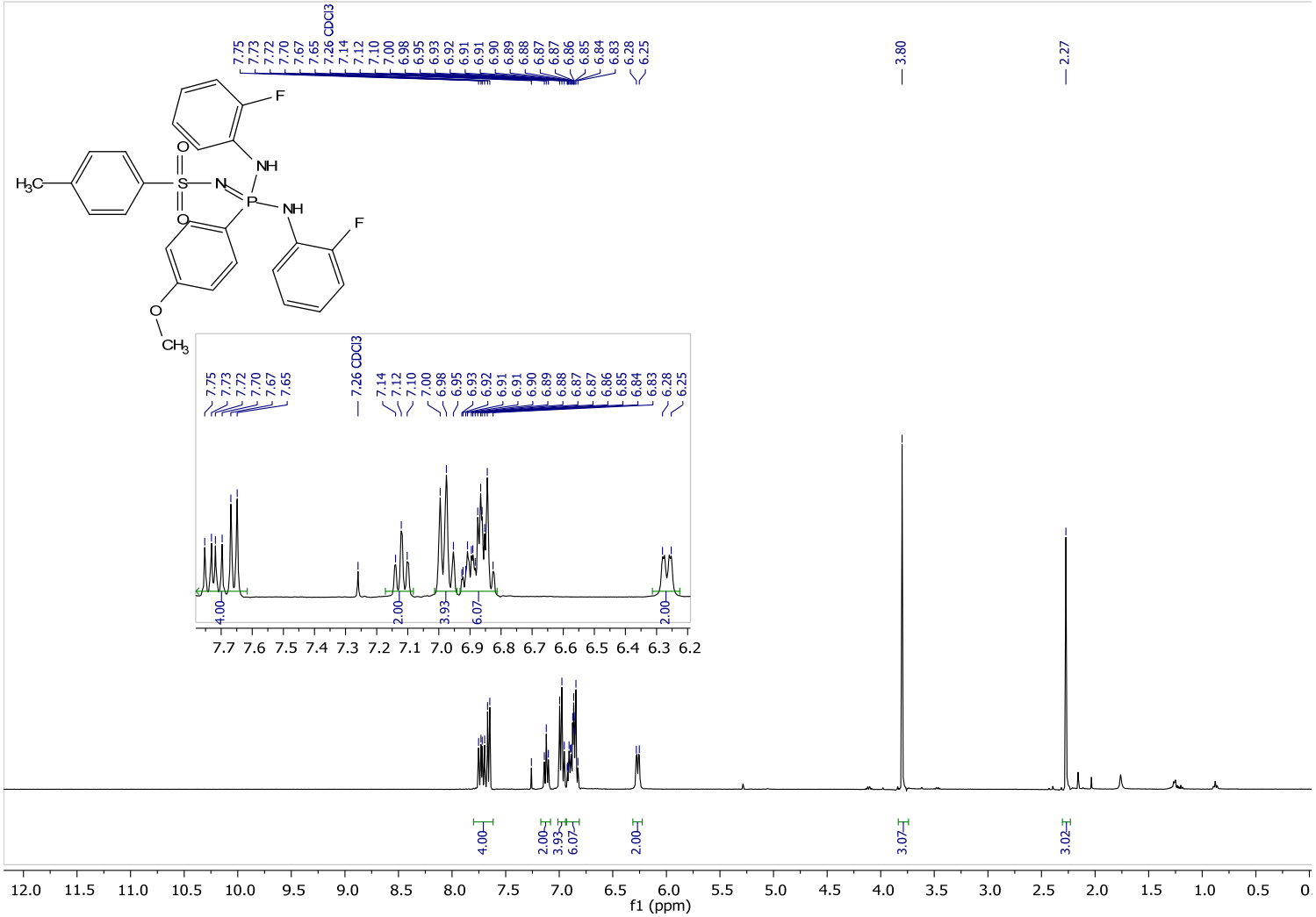
^{31}P NMR (162 MHz, DMSO–*d*$_6$) of **5ia**



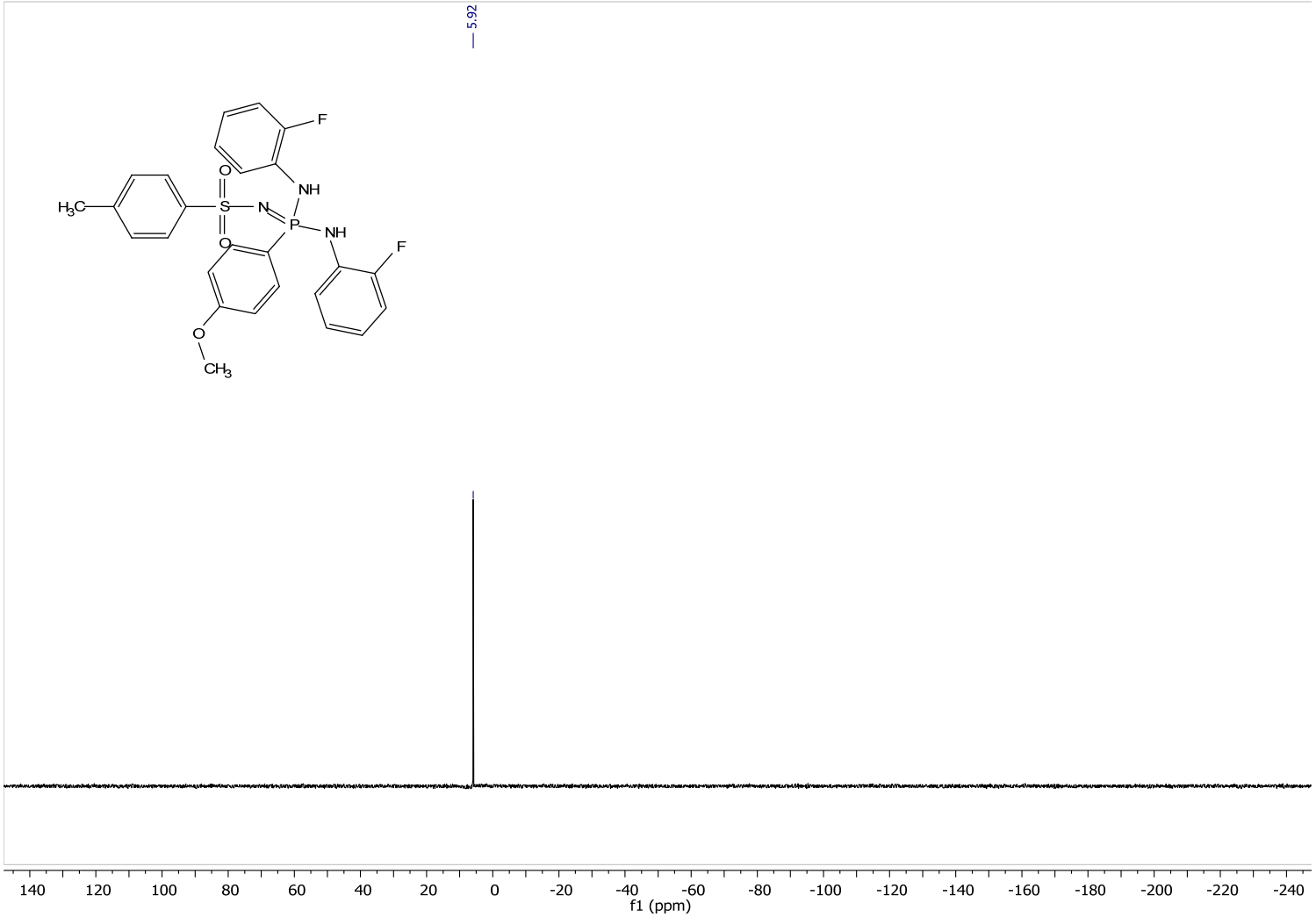
^{19}F NMR (565 MHz, DMSO-d_6) of **5ia**



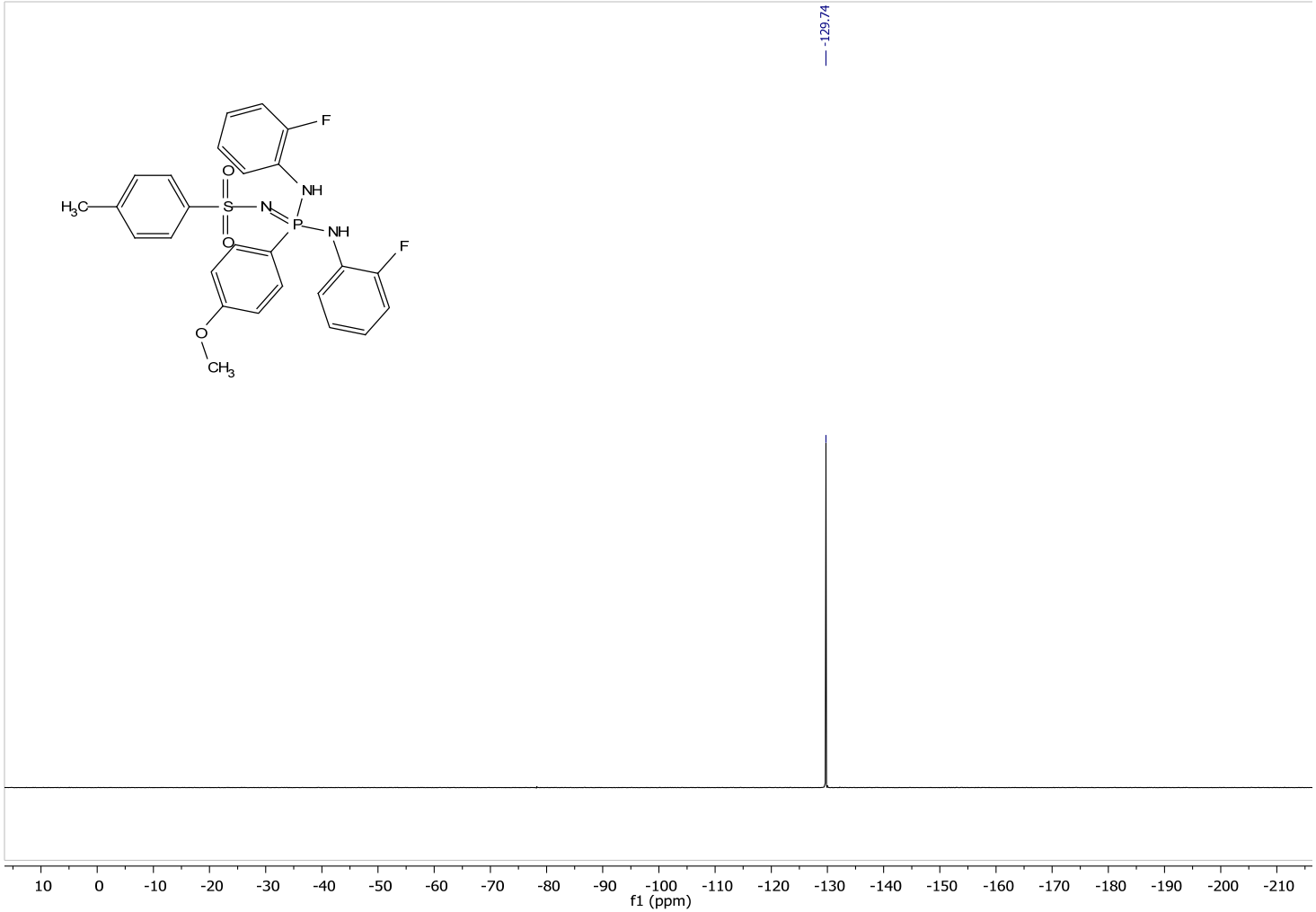
^{13}C NMR (100 MHz, DMSO–*d*$_6$) of **5ia**



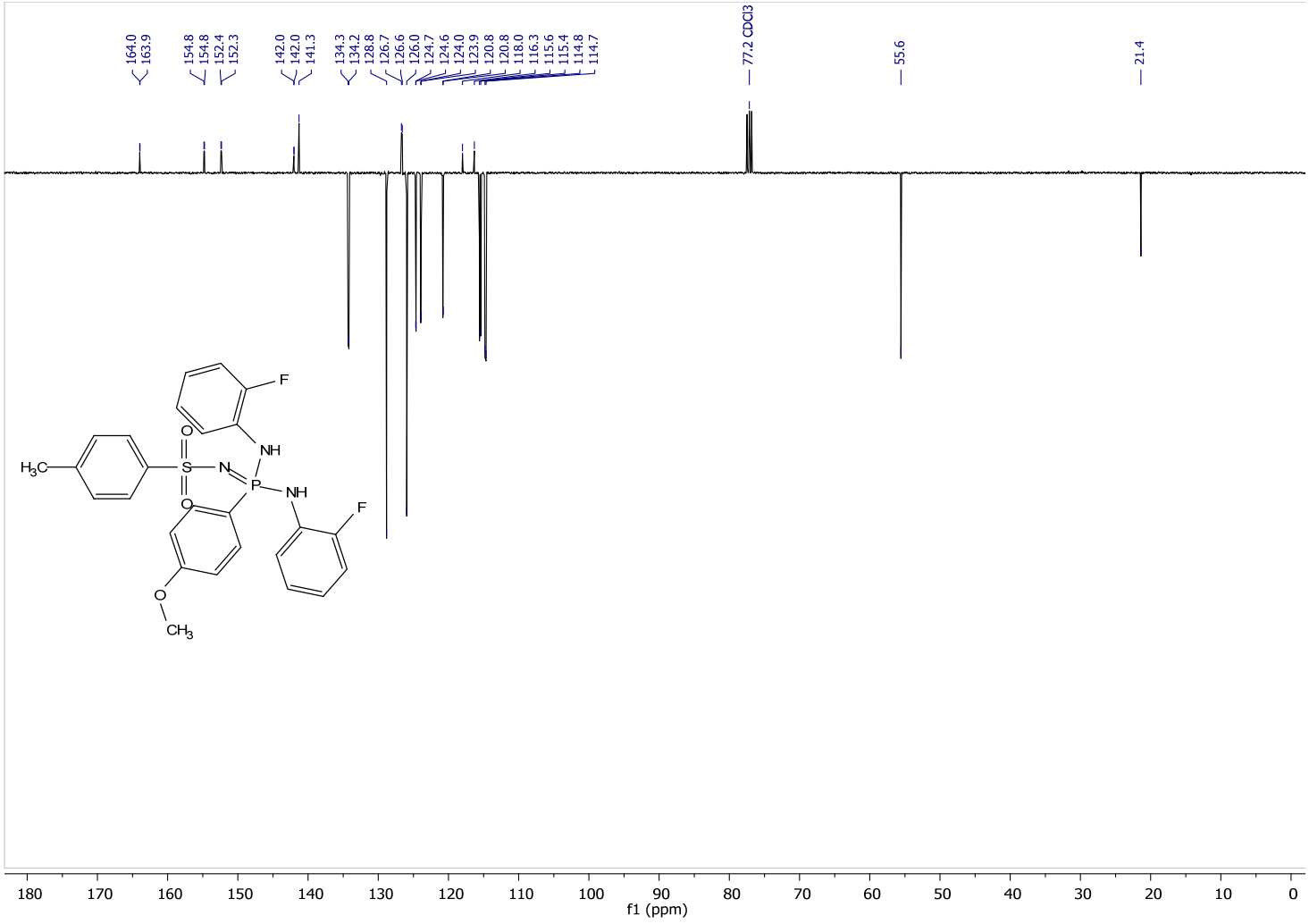
^{1}H NMR (400 MHz, $CDCl_3$–*d*) of **5ja**



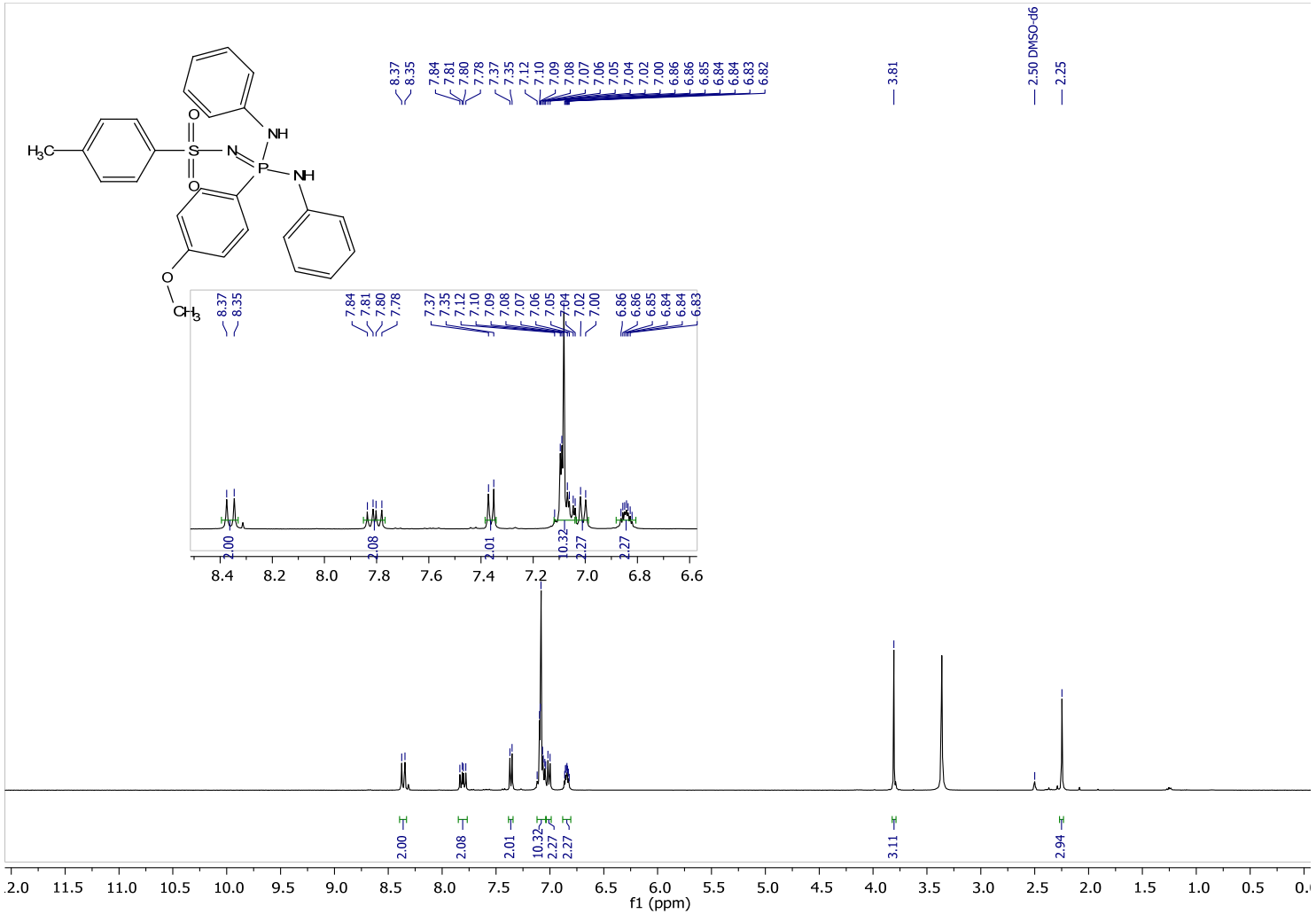
^{31}P NMR (162 MHz, $CDCl_3$–*d*) of **5ja**



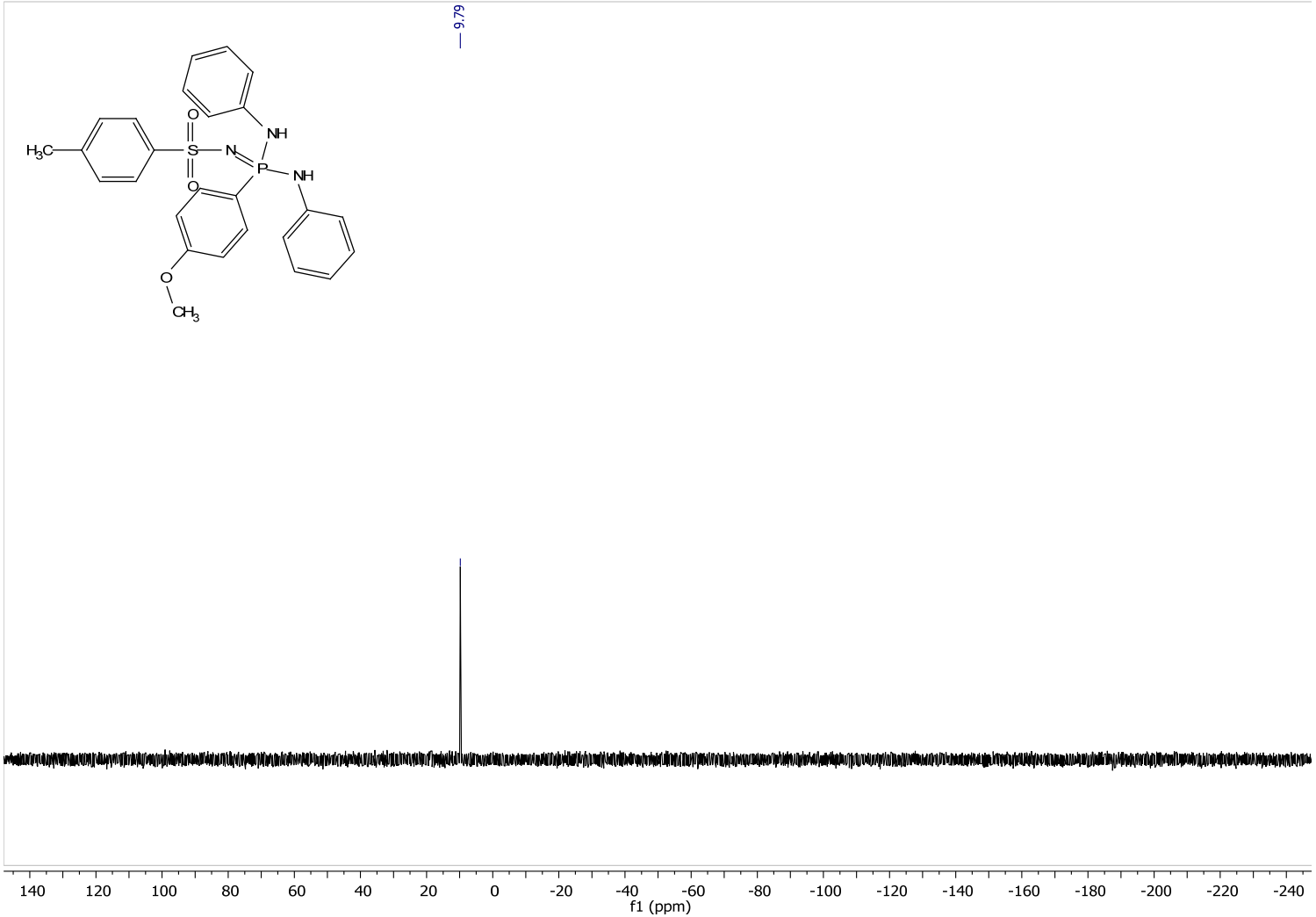
^{19}F NMR (565 MHz, $CDCl_3$-*d*) of **5ja**



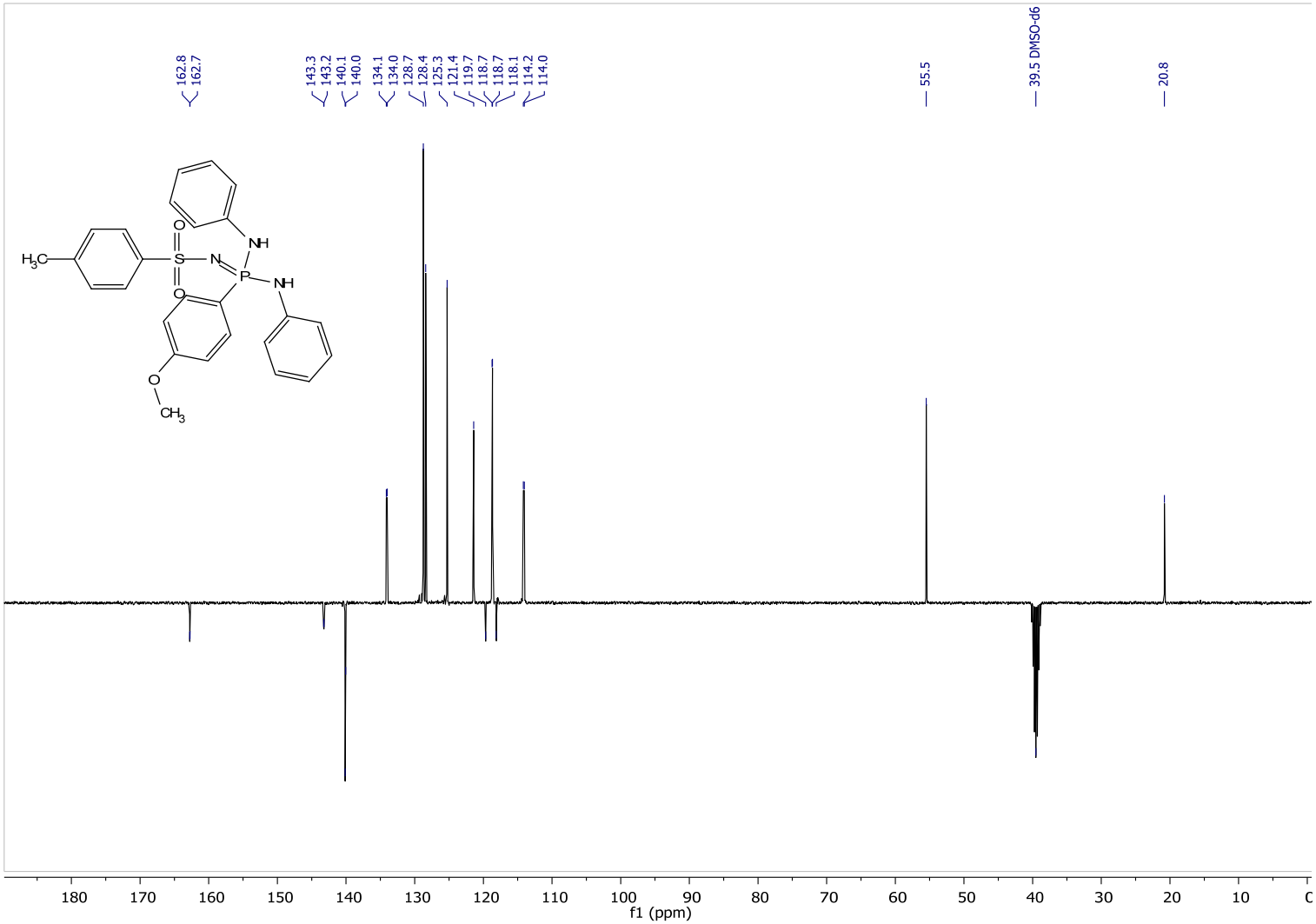
^{13}C NMR (100 MHz, $CDCl_3$–*d*) of **5ja**



^{1}H NMR (400 MHz, DMSO–d_6) of **5ka**



^{31}P NMR (162 MHz, DMSO–*d*$_6$) of **5ka**



^{13}C NMR (100 MHz, DMSO–*d*$_6$) of **5ka**