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Supporting information

Ni/NHC catalysis in C-H functionalization using air-tolerant nickelocene and sodium formate for *in situ* catalyst generation

Oleg V. Khazipov,[a] Konstantin E. Shepelenko,[a] Dmitry V. Pasyukov,[a] Vasilii V. Chesnokov,[a] Safarmurod B. Soliev,[a] Victor M. Chernyshev,[a]* Valentine P. Ananikov[a]*

[a] Platov South-Russian State University (NPI), Prosveschenya 132, Novocherkassk, 346428, Russia

[b] Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 119991, Russia

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S1. General information and materials

General Procedures. Solvents were purified and dried according to standard methods and stored over activated 3Å molecular sieves prior to use. All the reactions were conducted under Ar atmosphere using standard Schlenk techniques. Column chromatography was conducted on silica gel 60 (230−400 mesh, Merck). Glassware was dried at 120 °C in an oven for at least 3 h before the use.

Instrumentation. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C, a Bruker Avance III 400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C, a Bruker Avance II 600 spectrometer at 600 MHz for ^{1}H and 150 MHz for ^{13}C and Bruker Avance NEO 300 spectrometer at 300 MHz for ^{1}H and 75 MHz for ^{13}C in DMSO-d_6 or $CDCl_3$. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to the solvent signals as internal standards: δ 2.50 (DMSO-d_6), 7.26 ($CDCl_3$) or 5.35 (CD_2Cl_2) for ^{1}H, δ 39.5 (DMSO-d_6), 77.2 ($CDCl_3$) or 54.0 (CD_2Cl_2) for ^{13}C.

High-resolution mass spectra (HRMS) were obtained on a Bruker maXis Q-TOF instrument (Bruker Daltonik GmbH, Bremen, Germany) equipped with an electrospray ionization (ESI) ion source. The HRMS measurements were performed in positive (+) MS ion mode (HV Capillary: 4500 V; Spray Shield: –500 V) with a scan range of *m/z* 50 – 1500. External calibration of the mass spectrometer was performed using a low-concentration tuning mix solution (Agilent). Direct syringe injection was applied for the analyzed solutions at a 3 μL min^{-1} flow rate. Nitrogen was applied as the nebulizer gas (0.4 bar) and dry gas (4.0 L min^{-1}) in HRMS measurements. The dry temperature was 250 °C. All the spectra were recorded with 1 Hz frequency and processed using the Bruker Data Analysis 4.0 software.

GC-MS experiments were performed using an Agilent 7890A GC instrument, equipped with an Agilent 5975C mass-selective detector (electron ionization, 70 eV) and a HP-5MS column (30 m × 0.25 mm × 0.25 μm film) using He as carrier gas at a flow rate of 1.0 mL min^{-1}.

Preparative HPLC separations were performed using an Agilent 1260 Infinity LC system equipped with a reversed-phase Zorbax SB-C18 semi-preparative column (100 × 9.4 mm) thermostated at 30 °C, detection wavelength was 260 nm. The mobile phase contained 80% MeCN in water, elution with a flow rate of 5 mL·min^{-1} was applied.

The search for known structures among the synthesized compounds **4** and **6** was performed using Reaxys and SciFinder databases (totally, 45 compounds were identified as new; their structures were absent in the databases, searched on 08 Jan 2021).

Materials. 1,3-Dimethyl-1*H*-benzimidazol-3-ium iodide (**7a**),[1] 1,3-dibutyl-1*H*-benzmidazol-3-ium bromide (**7b**),[2] 1,3-bis(4-methylphenyl)-1*H*-benzimidazol-3-ium chloride (**7c**),[3] 1,3-bis(2,4,6-trimethylphenyl)-1*H*-benzimidazol-3-ium chloride (**7d**);[4] 1,3-bis(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium chloride (IMes·HCl),[5] 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (SIMes·HCl),[6] 1,3-bis[2,6-bis(propan-2-yl)phenyl]-1*H*-imidazol-3-ium chloride (IPr·HCl),[5] 1,3-bis[2,6-bis(propane-2-yl)phenyl]-4,5-dihydro-1*H*-imidazol-3-ium chloride (SIPr·HCl),[6] 1,3-bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]-1*H*-imidazol-3-ium chloride (IPr^{*OMe}·HCl),[7] {1,3-dimethyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene}(cyclopentadienyl)(iodo)nickel (**3a**),[8] {1,3-dibutyl-1,3-dihydro-2*H*-benzimidazol-2-ylidene}(bromo)(cyclopentadienyl)nickel (**3b**),[2] {1,3-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(cyclopentadienyl)nickel (**3e**),[9] {1,3-bis[2,4,6-trimethylphenyl]-imidazolidin-2-ylidene}(chloro)(cyclopentadienyl)nickel (**3f**),[10] {1,3-bis[2,6-diisopropylphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(cyclopentadienyl)nickel (**3g**),[10] {1,3-bis[2,6-diisopropylphenyl]-imidazolidin-2-ylidene}(chloro)(cyclopentadienyl)nickel (**3h**),[10] {1,3-bis[2,6-bis(diphenylmethyl)-4-methoxyphenyl]-1,3-dihydro-2*H*-imidazol-2-ylidene}(chloro)(cyclopentadienyl)nickel (**3i**),[11] 5-(pyridin-3-yl)-1*H*-1,2,4-triazol-3-amine,[12] and 5-(thiophen-2-yl)-1*H*-1,2,4-triazol-3-amine[12], $[NiPy_4](HCOO)_2$,[13] $NiCl_2Py_2$[14] were synthesized as described in the literature. All other chemicals were purchased from commercial sources.

Structures of heterocyclic substrates, alkenes, alkynes and azolium salts-proligands used in the study are presented on Figure S1.

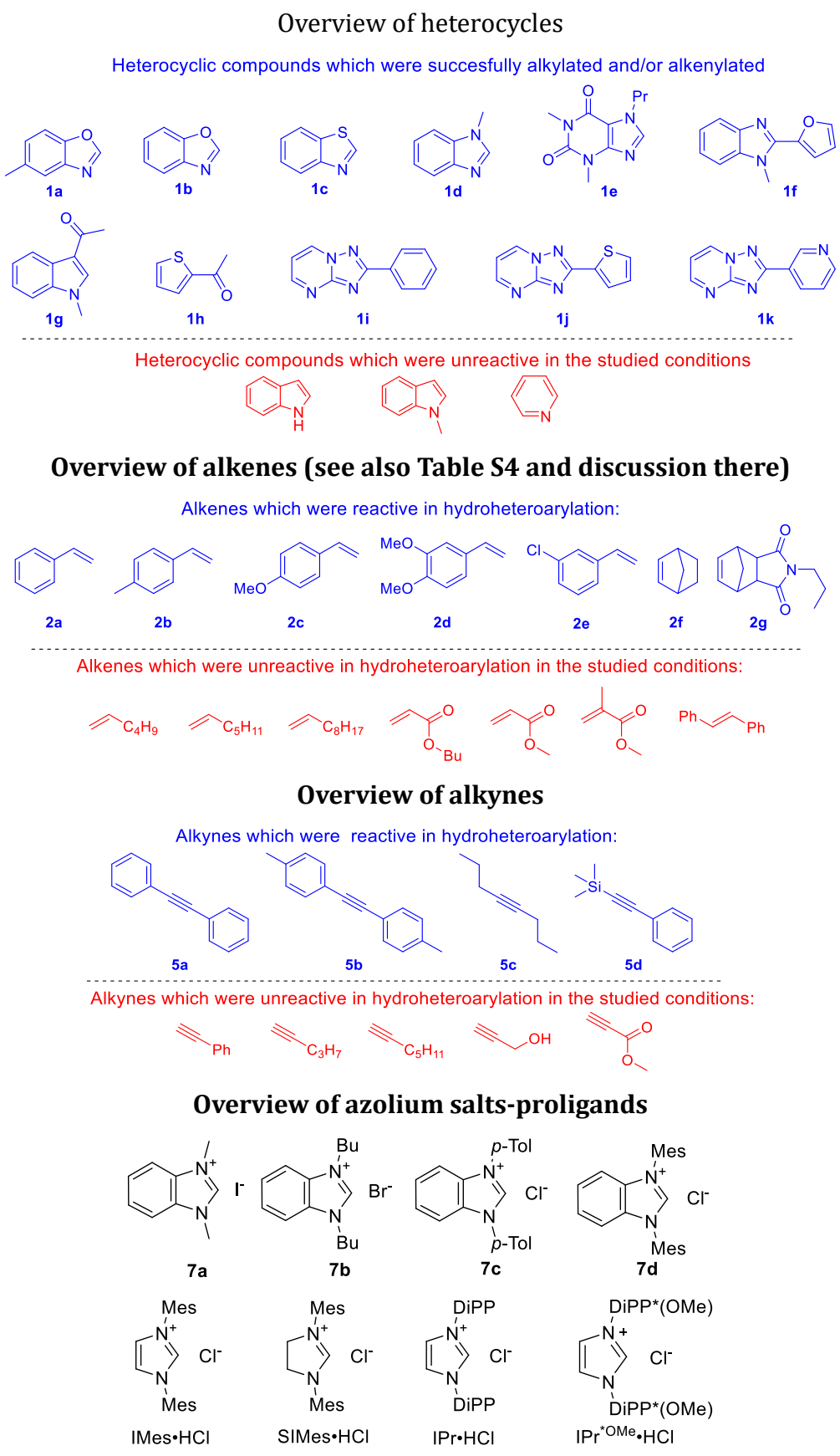


Figure S1. Heterocycles **1**, alkenes **2**, alkynes **5** and azolium salts (NHC·HX) used in the study.

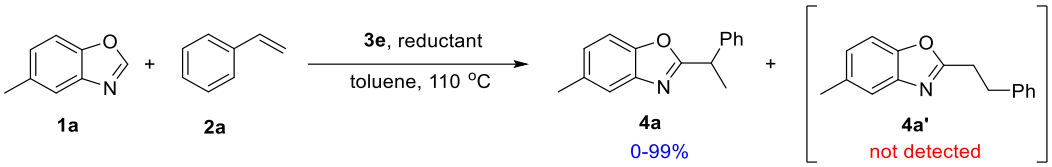
Heterocyclic substrates of low CH-acidity such as indole, 1-methylindole and pyridine were inactive in the reactions with alkenes and alkynes in the conditions under study. Such substrates usually require to use nickel/Lewis acid cooperative catalysis with organoaluminium compounds ($AlMe_3$, MAD)[15-18] or bulkier NHC ligands and harsher reaction conditions.[19,20]

Alkenes with aliphatic substituents such as 1-hexene, 1-heptene and 1-decene afforded very low, usually trace yields of alkylated products. These alkenes are usually reluctantly undergo to Ni-catalyzed CH-hyproheteroarylation[21] and typically require to use bulkier NHC-ligands and harsh reaction conditions[19] or cooperative Ni/Al catalysis.[15,16,22] Electronwithdrawing alkenes such as acrylates were completely inactive. Such alkenes usually not undergo to Ni-catalyzed hydroheteroarylation reactions.[21] Moreover, we revealed that even small amounts of acrylates can inhibit hydroarylation reactions with styrenes (Table S4). Apparently, electronwithdrawing alkenes can form too stable complexes $(NHC)Ni^0(alkene)_2$[23] which may be low active in hydroheteroarylation. Stilbene was also unreactive, probably due to formation too stable complexes with Ni(0) active species.[24] We have not found examples of stilbenes use in Ni/NHC catalyzed hydroheteroarylation reactions.

Terminal alkynes afforded only oligomerization products, apparently due to higher CH-acidity than heterocyclic substrates.

S2. Extended experimental data

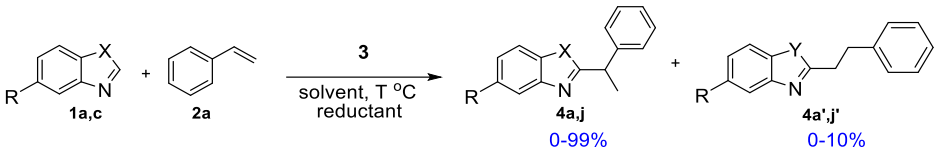
Table S1. Effect of reductant and preactivation time on the yield of compound **4a** in the reaction between **1a** and **2a** catalyzed with precatalyst **3e**[a]

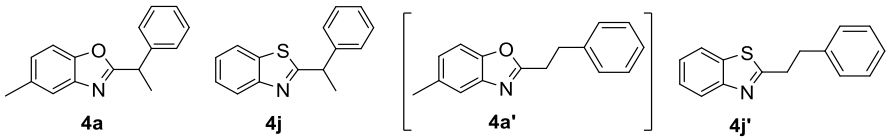


Entry	Reductant (mol%)	Preactivation time	Reaction time, h	GC-MS yield of **4a**, %
1	NaH (100)	1 h	3	95
2	NaH (100)	3 h	3	80
3	NaH (100)	3 h[b]	3[b]	2
4	$NaBH_4$ (100)	1 h	3	3
5	$NaBH_4$ (100)	20 h	3	44
6	$LiAlH_4$ (100)	1 h	1	10
7	Bu^tOK (100)	3 h	3	12
8	MeOK (100)	3 h	3	trace
9	Bu^tONa (100)	3 h	3	5
10	HCOONa (100)	3 h	3	98
11	HCOONa (100)	1 h	3	98
12	HCOONa (50)	1 h	3	92
13	HCOONa (100)	1 h	1	78
14	Na (100)	5 min	3	20
15	Na (100)	10 min	3	40
16	Na (100)	1 h	3	trace
17	Mg (100)	3 h	3	0
18	Mn (100)	3 h	3	0
19	Zn (100)	3 h	3	0

[a] Reaction conditions: Complex **3e** (10 mol%, 12 mg, 0.025 mmol), reductant (0.125 - 0.25 mmol, 50-100 mol%) and toluene (2 mL) were heated at 110 °C within corresponding preactivation time, then the solution formed was filtered and added to the mixture of **1a** (33 mg, 0.25 mmol) and **2a** (31 mg, 0.3 mmol) and the resulted mixture was heated at 110 °C within appropriate reaction time. [b]At 100 °C.

Table S2. Effect of reaction conditions on the yield of products **4** in the reaction between **1a,c** and **2a** catalyzed by precatalysts **3** without initial preactivation.[a]



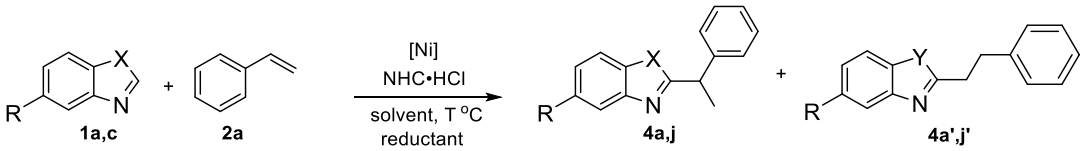


Entry	**3**, (mol%)	Reductant (mol%)	Solvent	T, °C	Reaction time, h	GC-MS yield of **4**, %	GC-MS yield of **4'**, %
1.	No catalyst	HCOONa (100)	toluene	110	5	0 (**4a**)	0 (**4a'**)
2.	**3a** (10)	HCOONa (100)	toluene	110	5	0 (**4a**)	0 (**4a'**)
3.	**3b** (10)	HCOONa (100)	toluene	110	5	10 (**4a**)	0 (**4a'**)
4.	**3c** (10)	HCOONa (100)	toluene	110	5	3 (**4a**)	0 (**4a'**)
5.	**3c** (10)	HCOONa (100)	toluene	110	20	45 (**4a**)	0 (**4a'**)
6.	**3d** (10)	HCOONa (100)	toluene	110	5	95 (**4a**)	0 (**4a'**)
7.	**3e** (10)	HCOONa (100)	toluene	110	5	99 (**4a**)	0 (**4a'**)
8.	**3e** (10)	HCOONa (100)	toluene	120	5	98 (**4a**)	0 (**4a'**)
9.	**3e** (10)	HCOONa (100)	toluene	100	5	85 (**4a**)	0 (**4a'**)
10.	**3e** (10)	HCOONa (100)	toluene	80	20	23 (**4a**)	0 (**4a'**)
11.	**3e** (10)	HCOONa (100)	1,4-dioxane	110	5	95 (**4a**)	0 (**4a'**)
12.	**3e** (10)	HCOONa (100)	o-xylene	140	5	93 (**4a**)	0 (**4a'**)
13.	**3e** (10)	HCOONa (100)	DMA	140	5	48 (**4a**)	0 (**4a'**)
14.	**3e** (10)	HCOONa (100)	acetonitrile	65	5	0 (**4a**)	0 (**4a'**)
15.	**3e** (10)	HCOONa (100)	toluene	110	2	80 (**4a**)	0 (**4a'**)
16.	**3e** (10)	HCOONa (10)	toluene	110	3	44 (**4a**)	0 (**4a'**)
17.	**3e** (10)	HCOONa (20)	toluene	110	3	67 (**4a**)	0 (**4a'**)
18.	**3e** (10)	HCOONa (50)	toluene	110	3	88 (**4a**)	0 (**4a'**)
19.	**3e** (10)	HCOONa (100)	toluene	110	3	95 (**4a**)	0 (**4a'**)
20.	**3e** (10)	HCOONa (150)	toluene	110	3	99 (**4a**)	0 (**4a'**)
21.	**3e** (10)	HCOONa (200)	toluene	110	3	99 (**4a**)	0 (**4a'**)
22.	**3e** (10)	HCOONa (100)	toluene	110	20	99 (**4a**)	0 (**4a'**)
23.	**3e** (5)	HCOONa (100)	toluene	110	20	99 (**4a**)	0 (**4a'**)
24.	**3e** (2.5)	HCOONa (100)	toluene	110	20	82 (**4a**)	0 (**4a'**)
25.	**3e** (1.25)	HCOONa (100)	toluene	110	20	33 (**4a**)	0 (**4a'**)
26.	**3e** (10)	HCOONa (100) + Bu^{t}OK (20)	toluene	110	20	0 (**4a**)	0 (**4a'**)
27.	**3e** (10)	NaH (100)	toluene	110	3	trace (**4a**)	0 (**4a'**)
28.	**3e** (10)	CaH_2 (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
29.	**3e** (10)	Mg (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
30.	**3e** (10)	TPED[b] (1000)	toluene	110	20	35 (**4a**)	0 (**4a'**)
31.	**3e** (10)	TPED[b] (100)	toluene	110	20	5 (**4a**)	0 (**4a'**)
32.	**3e** (10)	Hydroquinone (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
33.	**3e** (10)	Pyrogallol (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
34.	**3e** (10)	without reductant	toluene	110	20	0 (**4a**)	0 (**4a'**)
35.	**3f** (10)	HCOONa (100)	toluene	110	5	34 (**4a**)	0 (**4a'**)
36.	**3f** (10)	HCOONa (100)	toluene	110	20	98 (**4a**)	0 (**4a'**)

37.	**3g** (10)	HCOONa (100)	toluene	110	5	4 (**4a**)	0 (**4a'**)
38.	**3g** (10)	HCOONa (100)	1,4-dioxane	110	20	6 (**4a**)	0 (**4a'**)
39.	**3h** (10)	HCOONa (100)	toluene	110	5	1 (**4a**)	0 (**4a'**)
40.	**3i** (10)	HCOONa (100)	toluene	110	5	0 (**4a**)	0 (**4a'**)
41.	**3i** (10)	HCOONa (100)	1,4-dioxane	110	20	trace (**4a**)	0 (**4a'**)
42.	**3a** (10)	HCOONa (100)	toluene	110	5	0 (**4j**)	0 (**4j'**)
43.	**3b** (10)	HCOONa (100)	toluene	110	20	2 (**4j**)	0 (**4j'**)
44.	**3c** (10)	HCOONa (100)	toluene	110	20	1 (**4j**)	0 (**4j'**)
45.	**3d** (10)	HCOONa (100)	toluene	110	20	96 (**4j**)	trace (**4j'**)
46.	**3e** (10)	HCOONa (100)	toluene	110	20	98 (**4j**)	trace (**4j'**)
47.	**3f** (10)	HCOONa (100)	toluene	110	20	86 (**4j**)	trace (**4j'**)
48.	**3g** (10)	HCOONa (100)	o-xylene	140	20	8 (**4j**)	6 (**4j'**)
49.	**3g** (10)	HCOONa (100)	1,4-dioxane	110	20	13 (**4j**)	10 (**4j'**)
50.	**3h** (10)	HCOONa (100)	1,4-dioxane	110	20	8 (**4j**)	10 (**4j'**)
51.	**3i** (10)	HCOONa (100)	toluene	110	20	trace (**4j**)	trace (**4j'**)
52.	**3i** (10)	HCOONa (100)	1,4-dioxane	110	20	trace (**4j**)	trace (**4j'**)
53.	**3i** (10)	HCOONa (100)	o-xylene	140	20	trace (**4j**)	trace (**4j'**)

[a] Reaction conditions: Precatalyst **3** (0.003125-0.025 mmol, 1.25-10 mol%), reductant (0.025 – 2.5 mmol, 10-1000 mol%), **1a,c** (0.25 mmol), **2a** (31 mg, 0.3 mmol) and solvent (2 mL) were heated at 110 °C for 1 - 20 h. [b]TPED = 1,1,2,2-tetraphenyl-1,2-ethanediol.

Table S3. Optimization of reaction conditions.[a]



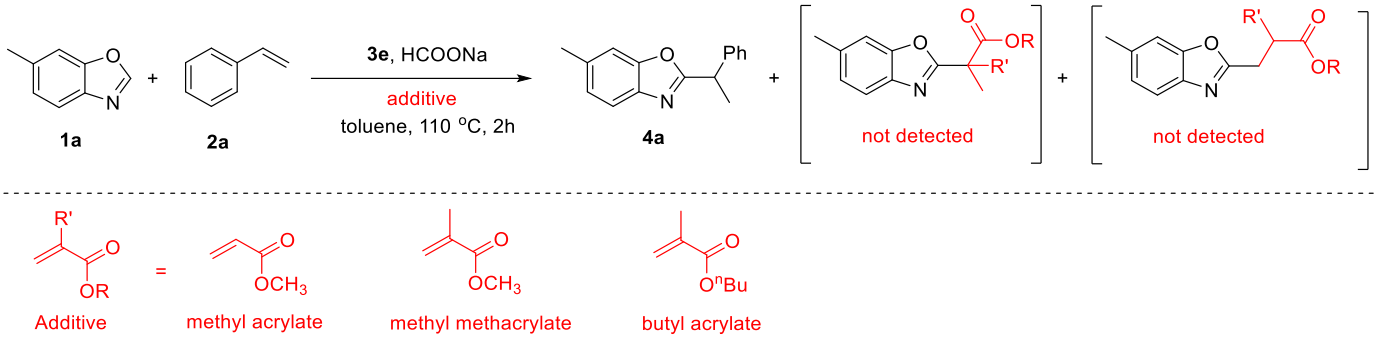
1a, 4a, 4a': X = O; R = CH_3
1c, 4j, 4j': X = S; R = H

Entry	[Ni] (mol%)	NHC·HX (mol%)	Reductant (mol%)	solvent	T, °C	Reaction time, h	Yield of **4**, %	Yield of **4'**, %
1.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	without reductant	toluene	110	20	0 (**4a**)	0 (**4a'**)
2.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	2	64 (**4a**)	0 (**4a'**)
3.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	99 (**4a**)	0 (**4a'**)
4.	$Ni(Cp)_2$ (5)	IMes·HCl (5)	HCOONa (100)	toluene	110	5	98 (**4a**)	0 (**4a'**)
5.	$Ni(Cp)_2$ (5)	IMes·HCl (10)	HCOONa (100)	toluene	110	5	97 (**4a**)	0 (**4a'**)
6.	$Ni(Cp)_2$ (2.5)	IMes·HCl (2.5)	HCOONa (100)	toluene	110	5	81 (**4a**)	0 (**4a'**)
7.	$NiSO_4$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
8.	$NiCl_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
9.	$NiCO_3$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
10.	$Ni(OAc)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
11.	$Ni(acac)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
12.	$NiCl_2(PPh_3)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
13.	$Ni(HCOO)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
14.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
15.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	HCOONa (100) + Bu^tOK (20)	toluene	110	20	1 (**4a**)[b]	0 (**4a'**)
16.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	Bu^tOK (20)	toluene	110	20	0 (**4a**)[b]	0 (**4a'**)
17.	$Ni(Cp)_2$ (10)	SIMes·HCl (10)	HCOONa (100)	toluene	110	5	31 (**4a**)[b]	0 (**4a'**)
18.	$Ni(Cp)_2$ (10)	SIMes·HCl (10)	HCOONa (100)	toluene	110	20	97 (**4a**)[b]	0 (**4a'**)
19.	$Ni(Cp)_2$ (10)	**7d** (10)	HCOONa (100)	toluene	110	5	98 (**4a**)[b]	0 (**4a'**)
20.	$Ni(HCOO)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
21.	$Ni(HCOO)_2$ (10)	IMes·HCl (10)	without reductant	toluene	110	20	0 (**4a**)	0 (**4a'**)
22.	$[NiPy_4](HCOO)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	0 (**4a**)	0 (**4a'**)
23.	$[NiPy_4](HCOO)_2$ (10)	IMes·HCl (10)	without reductant	toluene	110	20	0 (**4a**)	0 (**4a'**)
24.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	96 (**4j**)[b]	1 (**4j'**)
25.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	toluene	110	20	20 (**4j**)[b]	trace (**4j'**)
26.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	dioxane	110	20	95 (**4j**)[b]	trace (**4j'**)
27.	$Ni(Cp)_2$ (10)	IMes·HCl (10)	HCOONa (100)	o-xylene[c]	140	20	95 (**4j**)[b]	1 (**4j'**)

28.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	HCOONa (100) + Bu^tOK (20)	toluene	110	20	90 (**4j**)[b]	1 (**4j'**)
29.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	Bu^tOK (20)	toluene	110	20	40 (**4j**)[b]	trace (**4j'**)
30.	$NiCl_2Py_2$ (10)	IMes·HCl (10)	HCOONa (100) + Bu^tOK (100)	toluene	110	20	trace (**4j**)[b]	trace (**4j'**)
31.	$Ni(Cp)_2$ (10)	IPr·HCl (10)	HCOONa (100)	dioxane	110	20	6 (**4j**)[b]	5 (**4j'**)
32.	$Ni(Cp)_2$ (10)	IPr·HCl (10)	HCOONa (100)	o-xylene	140	20	7 (**4j**)[b]	5 (**4j'**)
33.	$NiCl_2Py_2$ (10)	IPr·HCl (10)	HCOONa (100) + Bu^tOK (20)	dioxane	110	20	2 (**4j**)[b]	1 (**4j'**)
34.	$NiCl_2Py_2$ (10)	IPr·HCl (10)	HCOONa (100) + Bu^tOK (20)	o-xylene	140	20	3 (**4j**)[b]	2 (**4j'**)
35.	$Ni(Cp)_2$ (10)	IPr^{*OMe}·HCl (10)	HCOONa (100)	toluene	110	20	trace (**4j**)[b]	trace (**4j'**)
36.	$Ni(Cp)_2$ (10)	IPr^{*OMe}·HCl (10)	HCOONa (100)	dioxane	110	20	trace (**4j**)[b]	trace (**4j'**)
37.	$Ni(Cp)_2$ (10)	IPr^{*OMe}·HCl (10)	HCOONa (100)	o-xylene	140	20	trace (**4j**)[b]	trace (**4j'**)
38.	$Ni(Cp)_2$ (10)	**7a** (10)	HCOONa (100)	toluene	110	5	0 (**4j**)[b]	0 (**4j'**)
39.	$Ni(Cp)_2$ (10)	**7b** (10)	HCOONa (100)	toluene	110	5	4 (**4j**)[b]	trace (**4j'**)
40.	$Ni(Cp)_2$ (10)	**7c** (10)	HCOONa (100)	toluene	110	5	2 (**4j**)[b]	trace (**4j'**)

[a]Reaction conditions: Ni compound (0.00625-0.025 mmol, 2.5-10 mol%), NHC·HX (0.00625-0.025 mmol, 2.5-10 mol%), reductant (0.05-0.25 mmol, 20-100 mol%), **1a,c** (0.25 mmol), **2a** (0.3 mmol) and solvent (2 mL).

Table S4. Inhibiting effect of acrylates on the reaction between **1a** and **2a**[a]



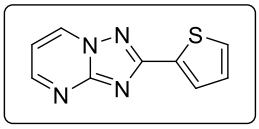
Entry	Additive (mol%)	GC-MS yield of **4a**, %
1	-	79
2	methyl methacrylate (10)	47
3	methyl methacrylate (20)	34
4	methyl methacrylate (50)	23
5	methyl methacrylate (100)	12
6	methyl acrylate (10)	8
7	methyl acrylate (20)	2
8	methyl acrylate (50)	0
9	methyl acrylate (100)	0
10	*n*-butyl acrylate (10)	15
11	*n*-butyl acrylate (20)	3
12	*n*-butyl acrylate (50)	0
13	*n*-butyl acrylate (100)	0

[a] Reaction conditions: Complex **3e** (10 mol%, 12 mg, 0.025 mmol), HCOONa (17mg, 0.25 mmol), **1a** (33 mg, 0.25 mmol), **2a** (31 mg, 0.3 mmol), additive and toluene (2 mL) were heated at 110 °C within 2h.

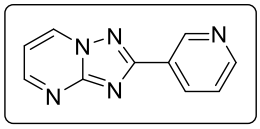
S3. Experimental procedures and characterization of synthesized compounds

Synthesis of heterocycles 1j and 1k.

A solution of corresponding 2-hetaryl-1,2,4-triazole-5-amine (1 mmol) and malonaldehyde tetramethyl acetal (1,5 mmol) in acetic acid (1 mL) was refluxed for 1 h and then evaporated to dryness in vacuo. A residue obtained was recrystallized from DMF-ethanol (1:5) mixture and dried at 100 °C in vacuum.



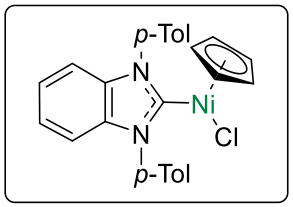
2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (**1j**). Yield 172 mg (85%), white powder, mp 198-200 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.08-7.10 (m, 1H, Ar), 7.17-7.19 (m, 1H, Ar), 7.49-7.50 (m, 1H, Ar), 7.98-7.99 (m, 1H, Ar), 8.78-8.82 (m, 2H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 110.2, 128.3, 129.0, 129.2, 133.1, 135.5, 154.7, 156.1, 162.7. Anal. calcd for $C_9H_6N_4S$ (%): C, 53.45; H, 2.99; N, 27.70. Found (%): C, 53.50; H, 3.05; N, 27.77.



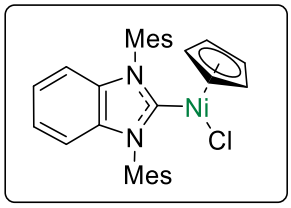
2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (**1k**). Yield 162 mg (82%), white powder, mp 205-206 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.14-7.16 (m, 1H, Ar), 7.44-7.46 (m, 1H, Ar), 8.60-8.61 (m, 1H, Ar), 8.73-8.74 (m, 1H, Ar), 8.84-8.90 (m, 2H, Ar), 9.56 (broad signal, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 110.5, 123.8, 126.5, 135.0, 135.8, 149.0, 151.7, 155.0, 156.3, 164.3. Anal. calcd for $C_{10}H_7N_5$ (%): C, 60.91; H, 3.58; N, 35.51. Found C, 61.00; H, 3.64; N, 35.60.

Synthesis of complexes 3c and 3d.

A solution of azolium salt **7c,d** (0.5 mmol) and $Ni(Cp)_2$ (104 mg, 0.55 mmol) in THF (15 mL) was stirred under reflux for 20 h. Then the reaction mixture was cooled to room temperature, filtered through celite and evaporated to dryness in vacuo. The crude solid residue was dissolved in CH_2Cl_2 (2 mL) and purified by column chromatography using silica gel and CH_2Cl_2 as eluent.



{1,3-bis[4-methylphenyl]-1,3-dihydro-2*H*-benzimidazol-2-ylidene}(chloro)(cyclopentadienyl)nickel (3c). Yield 164 mg (72%), crimson powder. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.57 (s, 6H), 4.60 (s, 5H), 7.19-7.26 (m, 4H), 7.50-7.53 (m, 4H), 7.94-7.97 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 92.3, 110.9, 123.4, 127.9, 130.2, 136.1, 136.4, 139.3, 180.4. Anal. calcd for $C_{26}H_{23}ClN_2Ni$ (%): C, 68.24; H, 5.07; N, 6.12. Found (%): C, 68.11 0; H, 5.04; N, 6.17.



{1,3-bis[2,4,6-trimethylphenyl]-1,3-dihydro-2*H*-benzimidazol-2-ylidene}(chloro)(cyclopentadienyl)nickel (3d). Yield 218 mg (85%), crimson powder. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 2.07 (s, 12H), 2.51 (s, 6H), 4.65 (s, 5H), 6.90-6.92 (m, 2H), 7.19-7.22 (m, 6H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 18.5, 21.5, 93.0, 110.7, 123.7, 129.9, 134.3, 136.0, 137.2, 139.9, 181.4. Anal. calcd for $C_{30}H_{31}ClN_2Ni$ (%): C, 70.14; H, 6.08; N, 5.45. Found (%): C, 70.04; H, 5.99; N, 5.38.

Study of complex 3e decomposition during catalysis of the reaction between 1a and 2a.

A 5 mL screw-capped glass tube equipped with a magnetic stir bar was charged with complex **3e** (116 mg, 0.25 mmol), HCOONa (170 mg, 2.5 mmol), **1a** (271 mg, 2.5 mmol), **2a** (312 mg, 3 mmol) and toluene (10 mL). Then the tube was purged with argon and sealed with a screw cap fitted with a septum, additionally purged with argon via septum, and heated at 110 °C and vigorous stirring within 20 h. After cooling to room temperature, the mixture was evaporated to dryness in vacuo, the residue was dissolved in acetonitrile (10 mL) and passed through a short pad of Celite®. Acetonitrile solution was analyzed by ESI-MS to determine IMes·HCl, compound **8a** and compound **9**, then evaporated to dryness in vacuo. The residue obtained was extracted with hot water (3 ×6 mL). The aqueous extract was then evaporated to a small volume (~ 0.5 mL) and cooled to 5 °C. A precipitate formed was collected by centrifugation and recrystallized from acetonitrile to give IMes·HCl, 51 mg (60% yield). The spectral characteristics of the product were identical with the authentic sample of IMes·HCl.[5]

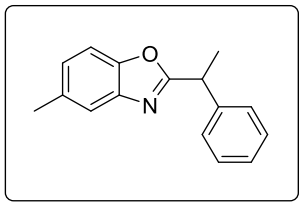
General procedure for Ni-catalyzed CH-alkylation and alkenylation

Method A. An oven-dried vial equipped with a magnetic stir bar and a septum was charged in air with **3e** (12 mg, 0.025 mmol, 5 mol %), freshly dried HCOONa (17 mg, 0.25 mmol), corresponding compound **1** (0.5 mmol), alkene **2** or alkyne **5** (0.6 mmol), and toluene (2 mL). Then the resulted mixture was degassed and purged with argon three times using standard Schlenk techniques and heated at 110 °C and vigorous stirring within 5-20 h (see Schemes 2 and 3). After cooling to room temperature, the mixture was diluted with toluene (5 mL) and filtered through a short pad of Celite. Then toluene was removed in vacuo and the residue obtained was chromatographed on silica gel (eluent hexane/EtOAc).

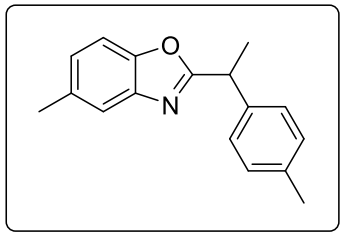
Method B. An oven-dried vial equipped with a magnetic stir bar and a septum was charged in air with $Ni(Cp)_2$ (4.7 mg, 0.025 mmol, 5 mol%), IMes·HCl (8.5 mg, 0.025 mmol, 5 mol%), HCOONa (17 mg, 0.25 mmol), corresponding compound **1** (0.5 mmol), alkene **2** or alkyne **5** (0.6 mmol), and toluene (2 mL). Then the resulted mixture was degassed and purged by argon three times using standard Schlenk techniques and heated at 110 °C and vigorous stirring within 5-20 h (see Schemes 2 and 3). Purification manipulations were performed as described in the Method A.

Procedure for the separation of *E* and *Z* isomers of compounds 6i, 6l and 6p

Separation of *E* and *Z* stereoizomers was performed by preparative HPLC using Agilent 1260 Infinity HPLC system equipped with a semi-preparative reversed-phase Zorbax SB-C18 column (9.4 × 100 mm) thermostated at 30 °C, detection wavelength 260 nm, elution mobile phase contained MeCN (80%) and water (20%), flow rate was 5 mL min^{-1}.

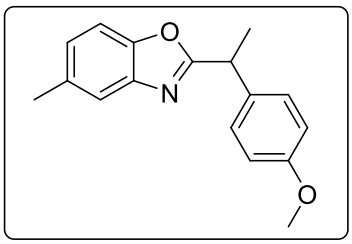


2-(1-phenylethyl)-5-methyl-1,3-benzoxazole (4a). Yield 117 mg (99%) method A (5 h), and 117 mg (99%) method B (5 h), orange oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.81 (d, *J*=7.2 Hz, 3H, CH_3), 2.45 (s, 3H, CH_3), 4.40 (q, *J*=7.2 Hz, 1H, CH), 7.07-7.09 (m, 1H, Ar), 7.23-7.26 (m, 1H, Ar), 7.29-7.36 (m, 5H, Ar), 7.49 (s, 1H, Ar). Anal. calcd for $C_{16}H_{15}NO$ C, 80.98; H, 6.37; N, 5.90. Found C, 80.87; H, 6.27; N, 5.81. The spectral characteristics of the product obtained are similar to those described in the literature.[25]

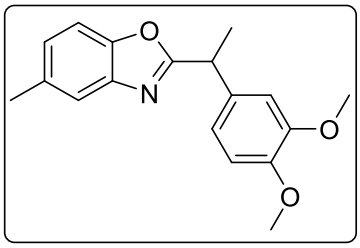


2-[1-(4-methylphenyl)ethyl]-5-methyl-1,3-benzoxazole (4b). Yield 116 mg (92%) method A (5 h), and 108 mg (86%) method B (5 h), yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.82 (d, *J*=7.2 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.41 (q, *J*=7.2 Hz, 1H, CH), 7.10-7.12 (m, 1H, Ar), 7.15-7.17 (m, 2H, Ar), 7.27-7.28 (m, 2H, Ar), 7.32-7.33 (m, 1H, Ar), 7.52 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 20.0, 21.2, 21.6, 39.9, 110.0, 119.9, 125.8, 127.4, 129.6,

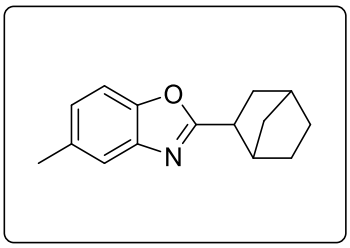
134.0, 137.0, 138.5, 141.5, 149.3, 169.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO$ 252.1383, Found 252.1398.



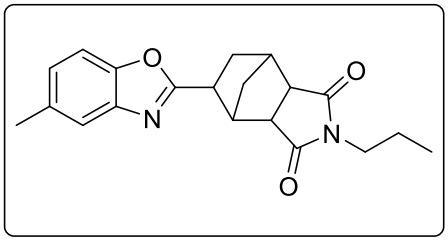
2-[1-(4-methoxyphenyl)ethyl]-5-methyl-1,3-benzoxazole (4c). Yield 132 mg (99%) method A (5 h), and 128 mg (96%) method B (5 h), white powder, mp 75–76 °C. ^{1}H NMR($CDCl_3$, 400 MHz): δ 1.80 (d, *J*=6.9 Hz, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 4.34 (q, *J*=7.2 Hz, 1H, CH), 6.84-6.88 (m, 2H), 7.07-7.09 (m, 1H, Ar), 7.27-7.29 (m, 3H), 7.50 (broad signal, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.0, 21.6, 39.5, 55.4, 110.0, 114.3, 119.9, 125.8, 128.6, 133.6, 134.0, 141.5, 149.2, 158.9, 169.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_2$ 268.1332 Found 268.1345.



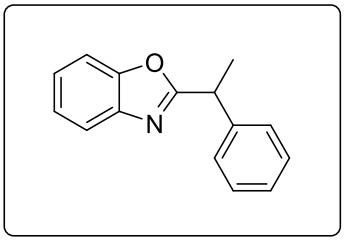
2-[1-(3,4-dimethoxyphenyl)ethyl]-5-methyl-1,3-benzoxazole (4d). Yield 147 mg (99%) method A (5 h), and 147 mg (99%) method B (5 h), pale yellow powder, mp 91-92°C. ^{1}H NMR($CDCl_3$, 400 MHz): δ 1.80 (d, 3H, *J*=7.2 Hz, CH_3), 2.45 (s, 3H, CH_3), 3.848 (s, 3H, CH_3), 3.853 (s, 3H, CH_3), 4.33 (q, *J*=7.2 Hz, 1H, CH), 6.81-6.83 (m, 1H, Ar), 6.87-6.88 (m, 1H, Ar), 6.90-6.92 (m, 1H, Ar), 7.07-7.10 (m, 1H, Ar), 7.30-7.32 (m, 1H, Ar), 7.49 (broad signal, 1H, Ar), ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.0, 21.6, 39.9, 56.0, 110.0, 110.1, 110.8, 111.5, 119.6, 119.9, 125.8, 133.95, 134.04, 141.5, 148.4, 149.2, 169.2 (signals of two carbons are overlapped). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NO_3$ 298.1438. Found 298.1445.



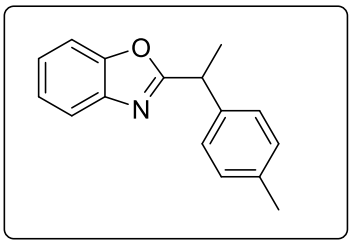
2-(2-norbornyl)-5-methyl-1,3-benzoxazole (4e). Yield 112 mg (99%) method A (20 h), and 109 mg (96%) method B (20 h), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.23-1.35 (m, 2H, CH_{norb}), 1.38-1.46 (m, 1H, CH_{norb}), 1.56-1.71 (m, 3H, CH_{norb}), 1.72-1.80 (m, 1H, CH_{norb}), 2.12-2.21 (m, 1H, CH_{norb}), 2.41-2.45 (m, 1H, CH_{norb}), 2.45 (s, 3H, CH_3), 2.66-2.67 (m, 1H, CH_{norb}), 2.94-2.99 (m, 1H, CH_{norb}), 7.06-7.09 (m, 1H, Ar), 7.31-7.34 (m, 1H, Ar), 7.44 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 28.9, 29.7, 35.6, 36.4, 36.6, 41.8, 42.2, 109.7, 119.7, 125.4, 133.8, 141.6, 149.2, 170.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}NO$ 228.1383 Found 228.1409.



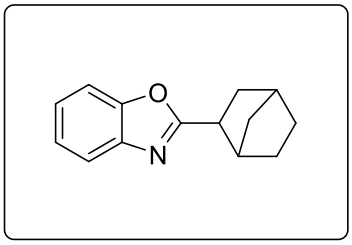
2-[N-propyl-hexahydro-1H-4,7-mehtanoisoindol-1,3(2H)-dione-5-yl]-5-methyl-1,3-benzoazole (4f). Yield 144 mg (85%) method A (20 h), and 147 mg (87%) method B (20 h), yellow oil solidifying on standing. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.95 (t, *J*=7.4 Hz, 3H, CH_3), 1.61-1.69 (m, 3H, CH), 1.79-1.82 (m, 1H, CH), 2.02-2.05 (m, 1H, CH), 2.28-2.33 (m, 1H, CH), 2.44 (s, 3H, CH_3), 2.94-2.99 (m, 2H, CH), 3.15-3.18 (m, 1H, CH), 3.20-3.28 (m, 2H, CH), 3.43-3.53 (m, 2H, CH), 7.09-7.11 (m, 1H, Ar), 7.32-7.34 (m, 1H, Ar), 7.43 (broad signal, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 11.6, 21.5, 21.6, 30.4, 36.9, 39.2, 40.3, 40.5, 44.1, 48.3, 109.9, 119.8, 126.0, 134.2, 141.2, 149.3, 168.4, 177.5, 177.8 (signals of two carbons are overlapped). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2O_3$ 339.1703. Found 339.1712.



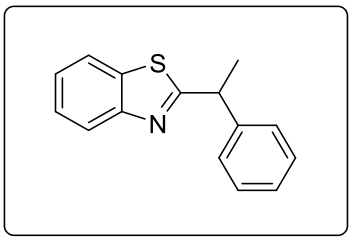
2-(1-phenylethyl)-1,3-benzoxazole (4g). Yield 106 mg (95%) method A (5 h), and 103 mg (92%) method B (5 h), white powder, mp 54-55 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.84 (d, *J*=7.2 Hz, 3H, CH_3), 4.45 (q, *J*=7.2 Hz, 1H, CH), 7.26-7.39 (m, 7H, Ar), 7.45-7.47 (m, 1H, Ar), 7.73-7.74 (m, 1H, Ar). Anal. calcd for $C_{15}H_{13}NO$ C, 80.69; H, 5.87; N, 6.27. Found C, 80.72; H, 5.91; N, 6.32. The spectral characteristics of the product obtained are similar to those described in the literature.[25]



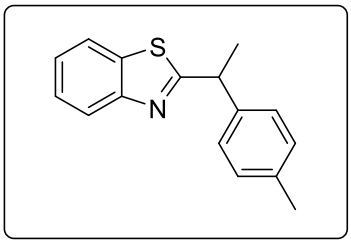
2-[1-(4-methylphenyl)ethyl]-1,3-benzoxazole (4h). Yield 117 mg (99%) method A (5 h), and 114 mg (96%) method B (5 h), yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.82 (d, *J*=7.2 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 4.40 (q, *J*=7.2Hz, 1H, CH), 7.15-7.16 (m, 2H, Ar), 7.26-7.31 (m, 4H, Ar), 7.44-7.45 (m, 1H, Ar), 7.71-7.73 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 20.0, 21.2, 39.9, 110.6, 120.0, 124.2, 124.8, 127.5, 129.6, 137.1, 138.4, 141.3, 151.0, 169.1. Anal. calcd for $C_{16}H_{15}NO$ C, 80.98; H, 6.37; N, 5.90. Found C, 81.01; H, 6.42; N, 5.95. The spectral characteristics of the product obtained are similar to those described in the literature.[26]



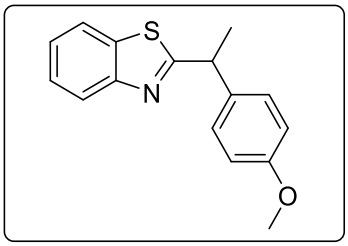
2-(2-norbornyl)-1,3-benzoxazole (4i). Yield 80 mg (75%) method A (20 h), and 77 mg (72%) method B (20 h), yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.25-1.36 (m, 2H), 1.37–1.47 (m, 1H) 1.55–1.72 (m, 3H), 1.74-1.79 (m, 1H), 2.16-2.19 (m, 1H), 2.42-2.44 (m, 1H), 2.68-2.69 (m, 1H), 2.92–3.02 (m, 1H), 7.26-7.32 (m, 2H), 7.41–7.50 (m, 1H), 7.62-7.72 (m, 1H). Anal. calcd for $C_{14}H_{15}NO$ C, 78.84; H, 7.09; N, 6.57. Found C, 78.88; H, 7.13; N, 6.63. The spectral characteristics of the product obtained are similar to those described in the literature.[27]



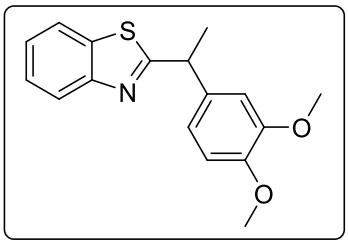
2-(1-phenylethyl)-1,3-benzothiazole (4j). Yield 118 mg (99%) method A (5 h), and 112 mg (94%) method B (5 h), pale yellow powder, mp 33-35 °C (lit[25] mp 32-34 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.87 (d, *J*=7.2 Hz, 3H, CH_3), 4.62 (q, *J*=7.2 Hz, 1H, CH), 7.28-7.29 (m, 1H, Ar), 7.32-7.36 (m, 3H, Ar), 7.39-7.40 (m, 2H, Ar), 7.44-7.45 (m, 1H, Ar), 7.78-7.79 (m, 1H, Ar), 8.02-8.03 (m, 1H, Ar). Anal. calcd for $C_{15}H_{13}NS$ C, 75.28; H, 5.48; N, 5.85. Found C, 75.38; H, 5.57; N, 5.96. The spectral characteristics of the product obtained are similar to those described in the literature.[25]



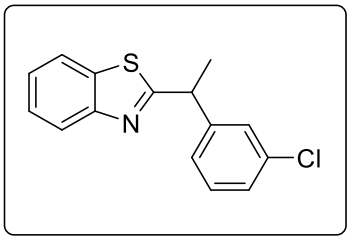
2-(1-(4-methylphenyl)ethyl)-1,3-benzothiazole (4k). Yield 125 mg (99%) method A (5 h), and 119 mg (94%) method B (5 h), yellow powder, mp 32-35 °C (lit[25] mp 33-35 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.86 (d, *J*=7.2 Hz, 3H, CH_3), 2.34 (s, 3H, CH_3), 4.57 (q, *J*=7.2 Hz, 1H, CH), 7.16-7.17 (m, 2H, Ar) 7.28-7.34 (m, 3H, Ar), 7.43-7.46 (m, 1H, Ar), 7.77-7.79 (m, 1H, Ar), 8.01-8.02 (m, 1H, Ar). Anal. calcd for $C_{16}H_{15}NS$ C, 75.85; H, 5.97; N, 5.53 Found C, 75.88; H, 5.92; N, 5.50. The spectral characteristics of the product obtained are similar to those described in the literature.[25]



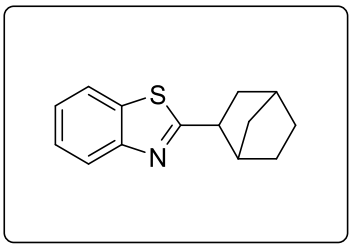
2-[1-(4-methoxyphenyl)ethyl]-1,3-benzothiazole (4l). Yield 134 mg (99%) method A (5 h), and 128 mg (95%) method B (5 h), white powder, mp 60-62 °C. ^{1}H NMR($CDCl_3$, 400 MHz): δ 1.85 (d, *J*=7.2 Hz, 3H, CH_3), 3.80 (s, 3H, OCH_3), 4.52-4.57 (q, *J*=7.2 Hz, 1H, CH), 6.88-6.90 (m, 2H, Ar) 7.31-7.34 (m, 3H, Ar), 7.42-7.45 (m, 1H, Ar), 7.77-7.79 (m, 1H, Ar), 8.00-8.02 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 44.2, 55.4, 114.3, 121.6, 123.0, 124.8, 126.0, 128.9, 135.4, 135.5, 153.3, 158.9, 177.1. Anal. calcd for $C_{16}H_{15}NOS$ C, 71.34; H, 5.61; N, 5.20. Found C, 71.41; H, 5.69; N, 5.25. The spectral characteristics of the product obtained are similar to those described in the literature.[28]



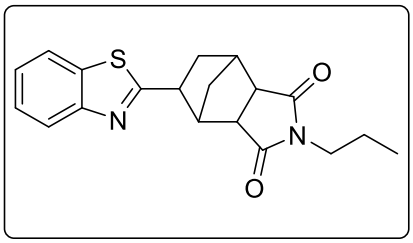
2-[1-(3,4-dimethoxyphenyl)ethyl]-1,3-benzothiazole (4m). Yield 144 mg (96%) method A (5 h), and 134 mg (90%) method B (5 h), white powder mp 75-77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.86 (d, *J*=7.2 Hz, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 4.53 (q, *J*=7.2 Hz, 1H, CH), 6.84-6.86 (m, 1H, Ar), 6.90-6.91 (m, 1H, Ar), 6.94-6.96 (m, 1H, Ar), 7.31-7.35 (m, 1H, Ar), 7.43-7.47 (m, 1H, Ar), 7.78-7.80 (m, 1H, Ar), 8.00-8.01 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.5, 44.6, 56.0, 56.1, 111.2, 111.4, 119.7, 121.7, 122.9, 124.9, 126.0, 135.5, 135.8, 148.4, 149.2, 153.3, 177.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}NO_2S$ 300.1053 Found 300.1065.



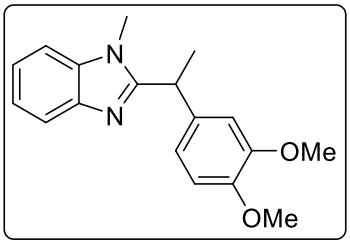
2-[1-(3-chlorophenyl)ethyl]-1,3-benzothiazole (4n). Yield 123 mg (90%) method A (5 h), and 115 mg (84%) method B (5 h), yellow oil. ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.85 (d, *J*=7.2 Hz, 3H, CH_3), 4.56 (q, *J*=7.2 Hz, 1H, CH), 7.23-7.29 (m, 3H, Ar), 7.34-7.39 (m, 2H, Ar), 7.43-7.49 (m, 1H, Ar), 7.79-7.82 (m, 1H, Ar), 8.00-8.03 (m, 1H, Ar) ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.4, 44.6, 121.7, 123.1, 125.1, 126.05, 126.14, 127.6, 128.0, 130.2, 134.7, 135.4, 145.2, 153.43, 175.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}ClNS$ 274.0452 Found 274.0472.



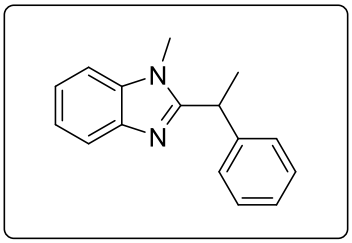
2-(2-norbornyl)-1,3-benzothiazole (4o). Yield 86 mg (75%) method A (20 h), and 78 mg (68%) method B (20 h), orange oil. ^{1}H NMR($CDCl_3$, 500 MHz): δ 1.26-1.35 (m, 2H, CH_{norb}), 1.43-1.49 (m, 1H, CH_{norb}), 1.58-1.71 (m, 3H, CH_{norb}), 1.88-1.92 (m, 1H, CH_{norb}), 2.10-2.15 (m, 1H, CH_{norb}), 2.44-2.46 (m, 1H, CH_{norb}), 2.64-2.65 (m, 1H, CH_{norb}), 3.21-3.24 (m, 1H, CH_{norb}), 7.32-7.35 (m, 1H, Ar), 7.43-7.46 (m, 1H, Ar), 7.82-7.84 (m, 1H, Ar), 7.97-7.98 (m, 1H, Ar). Anal. calcd for $C_{14}H_{15}NS$ C, 73.32; H, 6.59; N, 6.11. Found C, 73.41; H, 6.64; N, 6.18. The spectral characteristics of the product obtained are similar to those described in the literature.[29]



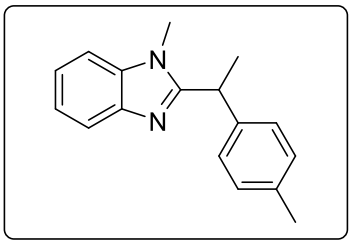
2-[N-propyl-hexahydro-1H-4,7-mehtanoisoindol-1,3(2H)-dione-5-yl]-1,3-benzothiazole (4p). Yield 148 mg (87%) method A (20 h), and 142 mg (84%) method B (20 h), white solid, mp 99-100 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.95 (t, *J*=7.4 Hz, 3H, CH_3), 1.58-1.70 (m, 4H), 1.83-1.89 (m, 1H), 2.06-2.11 (m, 1H), 2.39-2.46 (m, 1H), 2.94-2.97 (m, 1H), 3.13-3.18 (m, 3H), 3.23-3.27 (m, 1H), 3.47-3.52 (m, 2H), 7.32-7.37 (m, 1H, Ar), 7.42-7.47 (m, 1H, Ar), 7.81-7.84 (m, 1H, Ar), 7.94-7.96 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.6, 21.5, 32.2, 39.4, 40.1, 40.5, 41.9, 46.4, 48.4, 48.5, 121.7, 123.0, 125.1, 126.2, 135.2, 153.1, 174.4, 177.6, 177.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2S$ 341.1318 Found 341.1340.



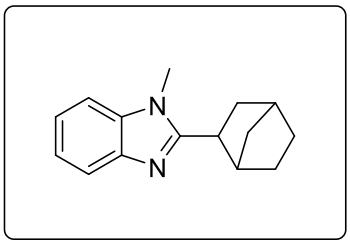
2-[1-(3,4-dimethoxyphenyl)ethyl]-1-methyl-1*H*-benzimidazole (4q). Yield 130 mg (88%) method A (5 h), and 120 mg (81%) method B (5 h), white powder 100-101 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (d, *J*=7.0 Hz, 3H, CH_3), 3.51 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 4.29 (q, *J*=7.0 Hz, 1H, CH), 6.73-6.77 (m, 3H, Ar), 7.23-7.25 (m, 3H, Ar), 7.82-7.85 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.9, 29.9, 38.8, 56.0, 56.1, 109.0, 110.5, 111.5, 119.6, 119.7, 121.9, 122.4, 135.6, 136.3, 142.5, 148.1, 149.5, 157.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}N_2O_2$ 297.1598 Found 297.1611.



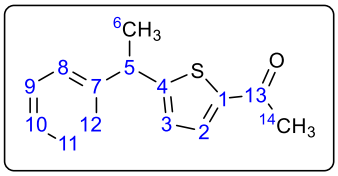
2-(1-phenylethyl)-1-methyl-1*H*-benzimidazole (4r). Yield 99 mg (84%) method A (5 h), and 90 mg (76%) method B (5 h), white powder, mp 89-90 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.94 (d, *J*=7.1 Hz, 3H, CH_3), 3.55 (s, 3H, NCH_3), 4.44 (q, *J*=7.1 Hz, 1H, CH), 7.22-7.27 (m, 3H, Ar), 7.29-7.33 (m, 5H, Ar), 7.95-7.96 (m, 1H, Ar). Anal. calcd for $C_{16}H_{16}N_2$ C, 81.32; H, 6.82; N, 11.85. Found C, 81.33; H, 6.85; N, 11.87. The spectral characteristics of the product obtained are similar to those described in the literature.[30]



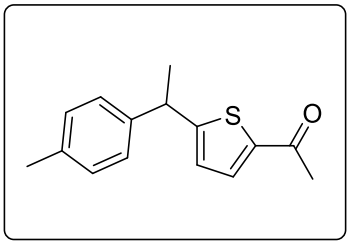
2-[1-(4-methylphenyl)ethyl]-1-methyl-1*H*-benzimidazole (4s). Yield 110 mg (88%) method A (5 h), and 101 mg (81%) method B (5 h), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.86 (d, *J*=7.1 Hz, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.50 (s, 3H, NCH_3), 4.32 (q, *J*=7.1 Hz, 1H, CH), 7.114-7.117 (m, 4H, Ar), 7.26-7.29 (m, 3H, Ar), 7.84-7.87 (m, 1H, Ar). Anal. calcd for $C_{17}H_{18}N_2$ C, 81.56; H, 7.25; N, 11.19. Found C, 81.63; H, 7.30; N, 11.28. The spectral characteristics of the product obtained are similar to those described in the literature.[31]



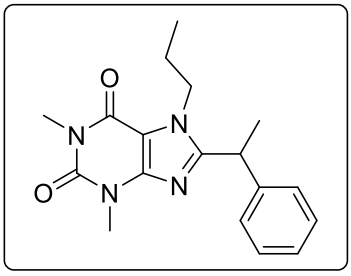
2-(2-norbornyl)-1-methyl-1*H*-benzimidazole (4t). Yield 93 mg (82%) method A (20 h), and 88 mg (78%) method B (20 h), white powder, mp 89-90 °C. ^{1}H NMR($CDCl_3$, 500 MHz): δ 1.23-1.25 (m, 1H, CH_{norb}), 1.33-1.41 (m, 1H, CH_{norb}), 1.41-1.45 (m, 1H, CH_{norb}), 1.60-1.79 (m, 4H, CH_{norb}), 2.30-2.35 (m, 1H, CH_{norb}), 2.44-2.46 (m, CH_{norb}), 2.54-2.55 (m, 1H, CH_{norb}), 2.89-2.92 (m, 1H, CH_{norb}), 3.73 (s, 3H, CH_3), 7.20-7.25 (m, 2H, Ar), 7.27-7.29 (m, 1H, Ar), 7.74-7.76 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 29.2, 29.8, 30.0, 35.8, 36.3, 36.5, 40.1, 42.0, 108.8, 119.5, 121.7, 122.0, 136.4, 142.4, 158.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2$ 297.1543 Found 297.1550.



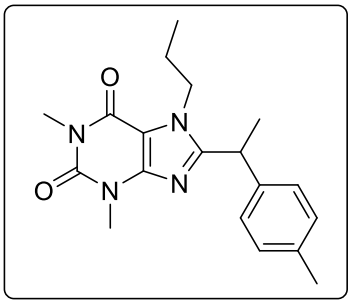
1-acetyl-5-(1-phenylethyl)thiophen (4u). Yield 104 mg (90%) method A (20 h), and 102 mg (89%) method B (20 h), brown oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.72 (d, *J*=7.2 Hz, 3H, $^6CH_3$), 2.49 (s, 3H, $^{14}CH_3$), 4.34 (q, *J*=7.2 Hz, 1H, ^5CH), 6.81-6.82 (m, 1H, ^3CH), 7.25-7.27 (m, 3H, Ph), 7.31-7.35 (m, 2H, Ph), 7.52-7.53 (m, 1H, ^2CH). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 23.0(C6), 26.6(C14), 41.6(C5), 125.2 (C3), 127.1 (C10), 127.4 (C9, C11), 128.9 (C8, C12), 132.7 (C2), 142.5 (C1), 144.8 (C7), 160.7 (C4), 190.7 (C13). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{15}OS$ 231.0838 Found 231.0846 The spectral characteristics of the product obtained are similar to those described in the literature.[32]



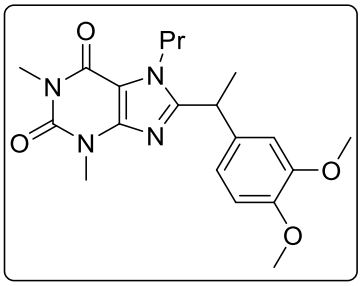
1-acetyl-5-(1-(4-methylphenyl)ethyl)thiophen (4v). Yield 110 mg (90%) method A (20 h), and 109 mg (89%) method B (20 h), yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.70 (d, *J*=7.2 Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.49 (s, 3H, CH_3), 4.31 (q, *J*=7.2 Hz, 1H, CH), 6.81-6.82 (m, 1H, Ar), 7.09-7.18 (m, 4H), 7.52 (d, *J*=3.9 Hz, 1H, Ar) ^{13}C NMR ($CDCl_3$, 125 MHz): δ 21.2, 23.1, 26.6, 41.2, 125.1, 127.2, 129.5, 132.7, 136.7, 141.9, 142.4, 161.1, 190.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}OS$ 245.0995. Found 245.0990.



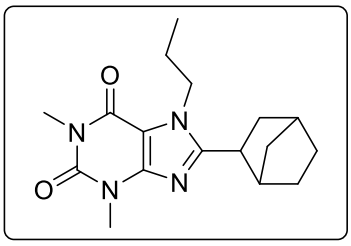
8-(1-phenylethyl)-7-propyl-1,3-dimethylxanthine (4w). Yield 145 mg (89%) method A (20 h), and 135 mg (83%) method B (20 h), colorless crystals mp 95-96 °C. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.72 (t, *J*=7.4 Hz, 3H, CH_3), 1.17-1.24 (m, 1H, CH_2), 1.52-1.59 (m, 1H, CH_2), 1.63 (d, *J*=7.0 Hz, 3H, CH_3), 3.21 (s, 3H, CH_3), 3.47 (s, 3H, CH_3), 4.01-4.06 (m, 1H, CH_2), 4.12-4.18 (m, 1H, CH_2), 4.48 (q, *J*=7.0 Hz, 1H, CH), 7.20-7.25 (m, 1H, Ar), 7.30-7.34 (m, 4H, Ar). ^{13}C NMR (DMSO-d_6, 100 MHz) δ 10.5, 21.8, 23.3, 27.5, 29.5, 36.3, 45.9, 106.1, 126.8, 127.1, 128.7, 142.9, 147.6, 150.9, 154.2, 155.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{23}N_4O_2$ 327.1816 Found 327.1814.



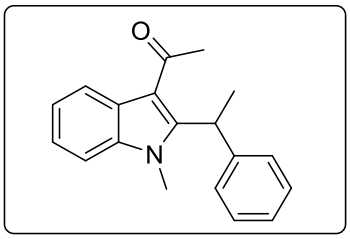
8-[1-(4-methylphenyl)ethyl)-7-propyl-1,3-dimethylxanthine (4x). Yield 150 mg (88%) method A (20 h), and 145 mg (85%) method B (20 h), yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.85 (t, *J*=7.4, 3H, CH_3), 1.39-1.47 (m, 1H, CH_2), 1.64-1.70 (m, 1H, CH_2), 1.72 (d, *J*=7.1 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 3.39 (s, 3H, CH_3), 3.64 (s, 3H, CH_3), 3.94-4.00 (m, 1H, CH_2), 4.10-4.19 (m, 2H), 7.11 (s, 4H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 11.1, 21.2, 22.0, 24.1, 28.0, 30.0, 37.9, 46.8, 107.2, 127.1, 129.7, 137.0, 139.6, 148.2, 152.0, 155.2, 155.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{25}N_4O_2$ 341.1972 Found 341.1994.



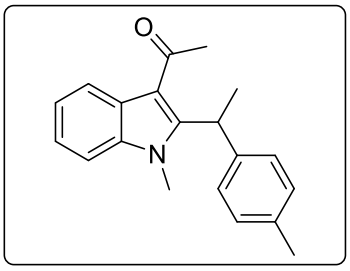
2-[1-(3,4-dimethoxyphenyl)ethyl]-7-propyl-1,3-dimethylxanthine (4y). Yield 156 mg (81%) method A (20 h), and 151 mg (78%) method B (20 h), white solid, mp 88-89 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.85 (t, *J*=7.4 Hz, 3H, CH_3), 1.38-1.50 (m, 1H), 1.65-1.68 (m, 1H), 1.72 (d, *J*=7.0 Hz, 3H, CH_3), 3.39 (s, 3H, CH_3), 3.62 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 3.855 (s, 3H, CH_3), 3.98-4.16 (m, 3H), 6.73-6.81 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): 11.1, 22.1, 24.2, 28.0, 30.0, 37.8, 46.8, 56.05, 56.08, 107.2, 110.5, 111.5, 119.4, 135.1, 148.2, 148.3, 149.5, 151.9, 155.2, 155.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}N_4O_4$ 387.2027 Found 387.2034.



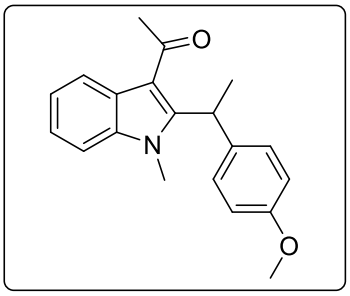
8-(2-norbornyl)-7-propyl-1,3-dimethylxanthine (4z). Yield 131 mg (83%) method A (20 h), and 128 mg (81%) method B (20 h), white powder, mp 115-116 °C. ^{1}H NMR($CDCl_3$, 500 MHz): δ 0.97 (t, *J*=7.4 Hz, 3H), 1.20-1.31 (m, 1H), 1.31-1.37 (m, 2H), 1.61-1.72 (m, 3H), 1.78-1.91 (m, 3H), 2.05-2.15 (m, 1H), 2.34-2.35 (m, 1H), 2.40-2.42 (m, 1H), 2.68-2.71 (m, 1H), 3.39 (s, 3H), 3.56 (s, 3H), 4.15-4.29 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 11.2, 24.5, 28.0, 28.9, 29.8, 30.2, 36.3, 36.8, 39.1, 43.1, 46.5, 106.9, 129.4, 148.1, 152.0, 155.2, 157.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{25}N_4O_2$ 317.1972 Found 317.1976.



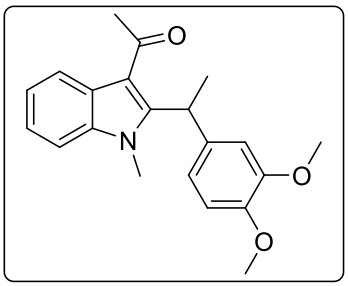
1-methyl-2-(1-phenylethyl)-3-acetyl-1*H*-indole (4aa) Yield 113 mg (99%) method A (20 h), and 111 mg (98%) method B (20 h), white powder, mp 79-80°C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.76 (d, *J*=7.3 Hz, 3H, CH_3), 2.77 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 6.10 (q, *J*=7.5 Hz, 1H, $\underline{CH}CH_3$), 7.17-7.33 (m, 8H, Ar), 7.95-7.96 (m, 1H, Ar). Anal. calcd for $C_{19}H_{19}NO$ C, 82.28; H, 6.90; N, 5.50. Found C, 82.33; H, 6.96; N, 5.58. The spectral characteristics of the product obtained are similar to those described in the literature.[15]



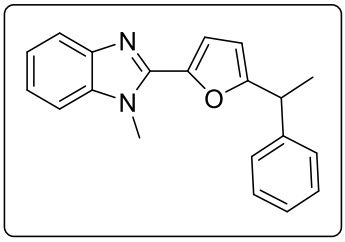
1-methyl-2-[1-(4-methylphenyl)ethyl]-3-acetyl-1*H*-indole (4ab). Yield 140 mg (96%) method A (20 h), and 137 mg (94%) method B (20 h), yellow oil. ^{1}H NMR($CDCl_3$, 500 MHz): δ 1.75 (d, *J*=7.4 Hz, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.77 (s, 3H, CH_3), 3.32 (s, 3H, CH_3), 6.04 (q, *J*=7.4 Hz, 1H, CH), 7.08 (s, 4H, Ar), 7.25 – 7.26 (m, 1H, Ar), 7.27 – 7.29 (m, 2H, Ar), 7.95-7.99 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 16.9, 21.1, 31.5, 32.4, 33.5, 109.7, 114.5, 121.0, 122.1, 122.3, 126.3, 126.9, 129.4, 135.8, 137.4, 139.1, 151.4, 195.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO$ 292.1696 Found 292.1706.



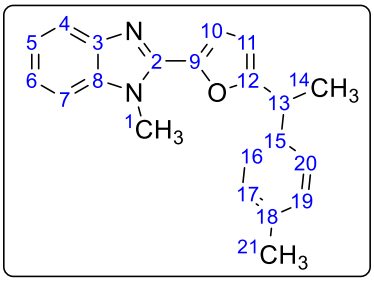
1-methyl-2-[1-(4-methoxyphenyl)ethyl]-3-acetyl-1*H*-indole (4ac). Yield 134 mg (87%) method A (20 h), and 129 mg (84%) method B (20 h), yellow oil. ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.74 (d, *J*=7.4 Hz, 3H, CH_3), 2.77 (s, 3H), 3.33 (s, 3H), 3.77 (s, 3H), 5.98-6.08 (q, *J*=7.4 Hz, 1H, CH), 6.79-6.83 (m, 2H), 7.10-7.13 (m, 2H), 7.22-7.32 (m, 3H), 7.94-7.97 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.0, 31.4, 32.4, 33.1, 55.4, 109.7, 114.0, 114.4, 121.0, 122.0, 122.3, 126.2, 128.0, 134.1, 137.4, 151.4, 158.0, 195.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_2$ 308.1645 Found 308.1651.



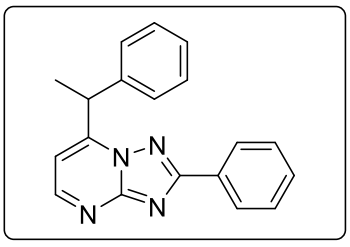
1-methyl-2-[1-(3,4-dimethoxyphenyl)ethyl]-3-acetyl-1*H*-indole (4ad). Yield 152 mg (90%) method A (20 h), and 140 mg (83%) method B (20 h), yellow oil. ^{1}H NMR($CDCl_3$, 400 MHz): δ 1.74 (d, *J*=7.4 Hz, 3H, CH_3), 2.79 (s, 3H, CH_3), 3.37 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 6.02 (q, *J*=7.4 Hz, 1H, CH), 6.72-6.77 (m, 1H, Ar), 6.79-6.83 (m, 2H, Ar), 7.28 – 7.33 (m, 3H, Ar), 7.95 – 7.98 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 31.4, 32.4, 33.5, 56.0, 56.1, 109.8, 110.8, 111.2, 114.4, 118.8, 121.0, 122.1, 122.4, 126.3, 134.8, 137.4, 147.6, 149.3, 151.2, 195.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}NO_3$ 348.1751 Found 348.1757.



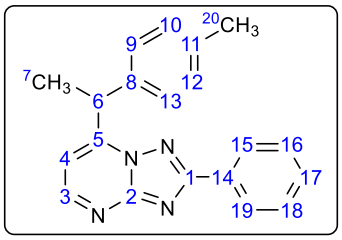
1-methyl-2-[5-(1-phenylethyl)furan-2-yl]-1*H*-benzimidazole (4ae). Yield 287 mg (95%) method A (20 h), and 278 mg (92%) method B (20 h), white powder, mp 80-81°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.70 (d, *J*=7.2 Hz, 3H, CH_3), 3.90 (s, 3H, CH_3), 4.27 (q, *J*=7.2 Hz, 1H, CH), 6.27-6.28 (m, 1H, Ar), 7.23-7.35 (m, 9H, Ar), 7.77-7.79 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.4, 31.6, 39.6, 107.7, 109.3, 113.4, 119.7, 122.6, 122.8, 126.9, 127.5, 128.7, 136.2, 143.2, 143.4, 144.6, 144.8, 161.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}N_2O$ 303.1492 Found 303.1514



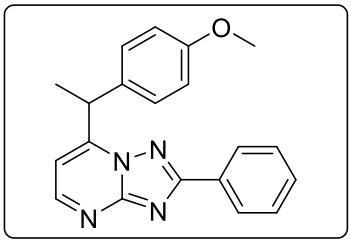
1-methyl-2-{5-[1-(4-methylphenyl)ethyl]furan-2-yl}-1*H*-benzimidazole (4af). Yield 120 mg (76%) method A (20 h), and 117 mg (74%) method B (20 h), white powder, mp 82-83°C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.67 (d, *J*=7.2 Hz, 3H, $^{14}CH_3$), 2.33 (s, 3H, $^{21}CH_3$), 3.93 (s, 3H, $^{1}CH_3$), 4.23 (q, *J*=7.2Hz, 1H, ^{13}CH), 6.26 (d, *J*=3.4 Hz, 1H, ^{11}CH), 7.13–7.17 (m, 4H, Tol), 7.27–7.34 (m, 4H, ^{10}CH + Ar), 7.77-7.79 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.5(C14), 21.2(C21), 31.6(C1), 39.2(C13), 107.6(C11), 109.3(C18), 113.4(C10), 119.7(C7), 122.6(C6), 122.8(C5), 127.4(C16 and C20), 129.4(C19 and C17), 136.2(C8), 136.5(C2), 140.4(C15), 143.2(C4), 144.5(C9), 144.9(C3), 161.4(C12). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}N_2O$ 317.1648 Found 317.1664.



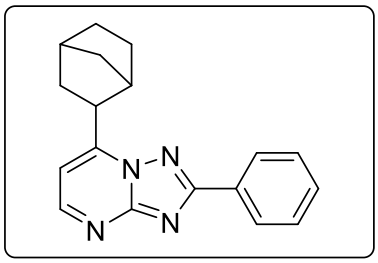
7-(1-phenylethyl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (4ag). Yield 143 mg (95%) method A (20 h), and 135 mg (90%) method B (20 h), colorless crystals mp 102-103 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.78 (d, *J*=7.2 Hz, 3H, CH_3), 5.04 (q, *J*=7.2Hz, 1H, CH), 7.23-7.26 (m, 1H, Ar), 7.32–7.35 (m, 3H, Ar), 7.47–7.49 (m, 2H, Ar), 7.54-7.57 (m, 3H, Ar), 8.21-8.23 (m, 2H, Ar), 8.85–8.86 (m, 1H, Ar). ^{13}C NMR (DMSO-d_6, 125 MHz) δ 18.6, 39.5, 108.0, 126.9, 127.2, 127.9, 128.6, 129.0, 130.3, 130.7, 140.7, 153.9, 155.0, 155.8, 163.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}N_4$ 301.1448. Found 301.1451.



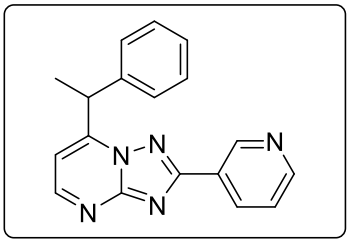
7-[1-(4-methylphenyl)ethyl]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (4ah). Yield 149 mg (95%) method A (20 h), and 143 (91%) method B (20 h), white crystals mp 120-121°C. ^{1}H NMR (DMSO-d_6, 300 MHz): δ 1.76 (d, *J*=7.2 Hz, 3H, ^{7}CH$_3$), 2.23 (s, 3H, ^{20}CH$_3$), 5.00 (q, *J*=7.2 Hz, 1H, ^{6}CH), 7.12 (d, *J*=7.9 Hz, 2H, ^{10}CH and ^{12}CH), 7.32 (d, *J*=4.8, 1H, ^{4}CH) 7.36 (d, *J*=8.0 Hz, 2H, ^{9}CH and ^{13}CH), 7.54 – 7.57 (m, 3H, Ph), 8.21–8.24 (m, 2H, Ph), 8.83 (d, *J*=4.8 Hz, 1H, ^{3}CH). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 18.6(C7), 20.6(C20), 39.1(C6), 107.9 (C4), 126.9(C15 and C19), 127.8(C9 and C13), 129.0(C10 and C12), 129.2(C16 and C18), 130.3(C14), 130.7(C17), 136.4(C11), 137.7(C8), 154.1(C5), 155.0(C3), 155.8(C2), 163.8(C1). HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{20}H_{19}N_4$ 315.1604 Found 315.1621.



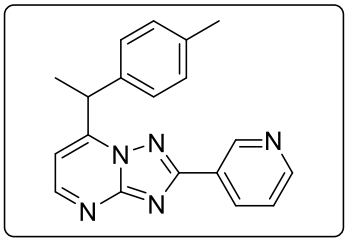
7-[1-(4-methoxyphenyl)ethyl]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (4ai). Yield 164 mg (99%) method A (5 h), and 155 mg (94%) method B (5 h), white powder, mp 101-102°C. ^{1}H NMR(DMSO-d_6, 500 MHz): δ 1.76 (d, *J* = 7.2 Hz, 3H, CH$_3$), 3.70 (s, 3H, CH$_3$), 5.00 (q, *J* = 7.2 Hz, 1H, CH), 6.87-6.91 (m, 2H, Ar), 7.30 (d, *J* = 4.7 Hz, 1H, Ar), 7.40-7.42 (m, 2H, Ar), 7.54-7.59 (m, 3H, Ar), 8.22-8.26 (m, 2H, Ar), 8.83 (d, *J* = 4.7 Hz, 1H, Ar). ^{13}C NMR (125 MHz, DMSO) δ 18.6, 38.6, 55.0, 107.8, 114.0, 126.9, 128.98, 129.04, 130.3, 130.7, 132.5, 154.3, 155.0, 155.8, 158.4, 163.8. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{20}H_{19}N_4O$ 331.1553 Found 331.1563.



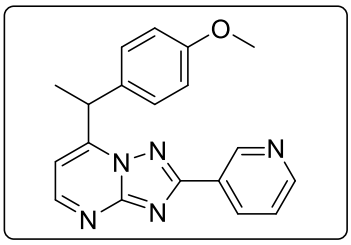
7-(2-norbornyl)-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (4aj). Yield 138 mg (95%) method A (20 h), and 128 mg (88%) method B (20 h), colorless crystals mp 124-126 °C. ^{1}H NMR(CDCl$_3$, 300 MHz): δ 1.37-1.81 (m, 7H, CH$_{norb}$), 2.11-2.19 (m, 1H, CH$_{norb}$), 2.46-2.48 (m, 1H, CH$_{norb}$), 2.64-2.66 (m, 1H, CH$_{norb}$), 3.56-3.61 (m, 1H, CH$_{norb}$), 6.89-6.90 (m, 1H, Ar), 7.48-7.51 (m, 3H, Ar), 8.37-8.40 (m, 2H, Ar), 8.68-8.70 (m, 1H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ 28.7, 30.0, 36.7, 36.9, 37.0, 40.3, 42.3, 105.8, 127.7, 128.8, 130.6, 130.9, 153.9, 155.4, 156.6, 165.3. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{18}H_{19}N_4$ 291.1604 Found 291.1614.



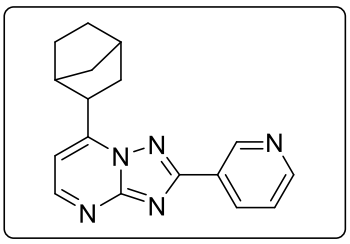
7-(1-phenylethyl)-2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4ak). Yield 137 mg (91%) method A (20 h), and 133 mg (88%) method B (20 h), white crystals, mp 119-120 °C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.86 (d, *J* = 7.2 Hz, 3H, CH$_3$), 5.11 (q, *J* = 7.2 Hz, 1H, CH), 6.89 (d, *J* = 4.6 Hz, 1H, Ar), 7.27 – 7.31 (m, 1H, Ar), 7.34 – 7.47 (m, 3H, Ar), 8.60-8.61 (m, 1H, Ar), 8.71-8.73 (m, 2H, Ar), 9.56 (broad signal, 1H, Ar).^{13}C NMR (CDCl$_3$, 125 MHz): δ 18.6, 40.1, 107.7, 123.7, 127.9, 128.1, 128.9, 129.1, 135.0, 139.9, 149.1, 151.5, 154.5, 154.9, 156.5, 163.3. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{18}H_{16}N_5$ 302.1400 Found 302.1418.



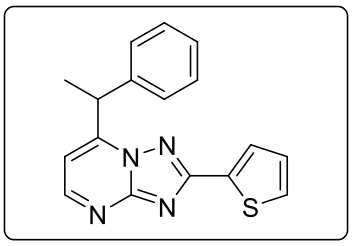
7-[1-(4-methylphenyl)ethyl]-2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4al). Yield 142 mg (90%) method A (20 h), and 137 mg (87%) method B (20 h), white powder, mp 110-111°C. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 1.84 (d, *J*=7.2 Hz, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$), 5.08 (q, *J*=7.2 Hz, 1H, CH), 6.89 (d, *J*=4.6 Hz, 1H, Ar), 7.16-7.18 (m, 2H, Ar), 7.29-7.31 (m, 2H, Ar), 7.44 (broad signal, 1H, Ar), 8.60-8.61 (m, 1H, Ar), 8.72-8.73 (m, 2H, Ar), 9.57 (broad signal, 1H, Ar). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 18.7, 21.2, 39.7, 107.6, 123.7, 126.9, 128.0, 129.7, 135.0, 136.9, 137.7, 149.1, 151.4, 154.5, 155.2, 156.5, 163.3. HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{19}H_{18}N_5$ 316.1557 Found 316.1563.



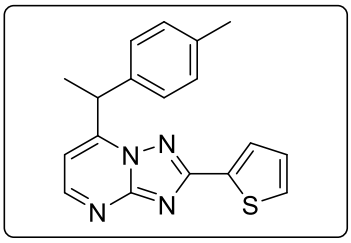
7-[1-(4-methoxyphenyl)ethyl]-2-(pyridin-3-yl)[1,2,4]triazolo-[1,5-*a*]pyrimidine (4am). Yield 146 mg (88%) method A (20 h), and 139 mg (84%) method B (20 h), yellow solid, mp 91-92 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ 1.76 (d, J = 7.2 Hz, 3H, CH_3), 3.70 (s, 3H, OCH_3), 5.00 (q, J = 7.2 Hz, 1H, CH), 6.87-6.91 (m, 2H, Ar), 7.35 (d, J = 4.9 Hz, 1H, Ar), 7.41-7.44 (m, 2H, Ar), 7.58-7.63 (m, 1H, Ar), 8.52-8.56 (m, 1H, Ar), 8.73-8.75 (m, 1H, Ar), 8.87-8.89 (m, 1H, Ar), 9.38-9.39 (m, 1H, Ar). ^{13}C NMR (DMSO-d_6, 125 MHz): δ 18.6, 38.7, 55.0, 108.1, 114.0, 124.2, 126.3, 128.6, 129.1, 132.4, 134.3, 147.8, 151.5, 154.5, 155.4, 155.8, 158.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}N_5O$ 332.1506 Found 332.1516.



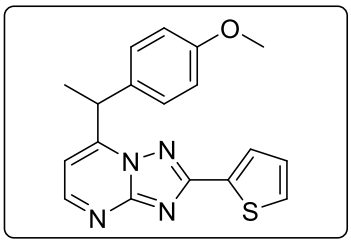
7-(1-norbornyl)-2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4an). Yield 138 mg (95%) method A (20 h), and 124 mg (85%) method B (20 h), pale yellow crystals, mp 125-127 °C. ^{1}H NMR($CDCl_3$, 500 MHz): δ 1.38-1.52 (m, 3H, CH_{norb}), 1.60-1.79 (m, 4H, CH_{norb}), 2.12-2.17 (m, 1H, CH_{norb}), 2.47-2.50 (m, 1H, CH_{norb}), 2.65-2.66 (m, 1H, CH_{norb}), 3.56-3.59 (m, 1H, CH_{norb}), 6.94-6.94 (m, 1H, Ar), 7.42-7.45 (m, 1H, Ar), 8.61-8.64 (m, 1H, Ar), 8.71-8.75 (m, 2H, Ar), 9.58 (broad signal, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 24.1, 28.7, 29.8, 30.0, 33.1, 36.7, 36.8, 37.0, 37.3, 40.0, 40.3, 40.9, 42.1, 42.4, 106.2, 107.8, 123.7, 126.9, 135.0, 149.1, 151.4, 154.0, 154.3, 155.6, 156.6, 163.1 (mixture of diastereomers). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}N_5$ 292.1557 Found 292.1570.



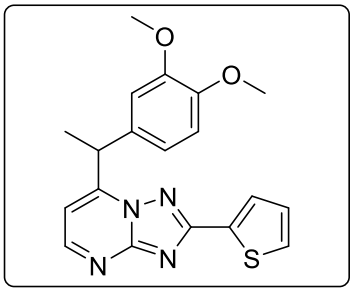
7-(1-phenylethyl)-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4ao). Yield 146 mg (95%) method A (20 h), and 141 mg (92%) method B (20 h), pale yellow crystals, mp 162-163 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.85 (d, J=7.2 Hz, 3H, CH_3), 5.10 (q, J = 7.2 Hz, 1H, CH), 6.81 (broad signal, 1H, Ar), 7.16-7.18 (m, 1H, Ar), 7.28-7.32 (m, 1H, Ar), 7.35-7.38 (m, 2H, Ar), 7.40-7.43 (m, 2H, Ar), 7.47-7.49 (m, 1H, Ar), 7.98-7,99 (m, 1H, Ar), 8.68 (broad signal, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.4, 40.0, 107.5, 127.9, 128.1, 128.2, 128.8, 128.96, 129.01, 133.6, 139.9, 154.2, 154.6, 156.3, 161.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_4S$ 307.1012 Found 307.1016.



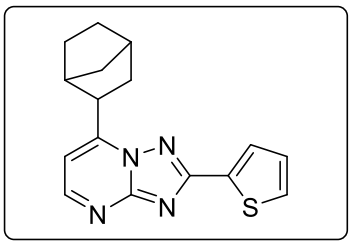
7-[1-(4-methylphenyl)ethyl]-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4ap). Yield 152 mg (95%) method A (20 h), and 146 mg (91%) method B (20 h), pale yellow crystals, mp 159-160 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.82 (d, J=7.2 Hz, 3H, CH_3), 2.34 (s, CH_3), 5.06 (q, J = 7.2 Hz, 1H, CH), 6.78-6.79 (m, 1H, Ar), 7.16-7.18 (m, 3H, Ar), 7.29-7.31 (m, 2H, Ar), 7.47-7.48 (m, 1H, Ar) 7.98-7.99 (m, 1H, Ar), 8.65-8.66 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 18.5, 21.2, 39.6, 107.3, 128.06, 128.01, 128.7, 128.8, 129.7, 133.7, 136.9, 137.6, 154.2, 155.0, 156.3, 161.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_4S$ 321.1168 Found 321.1178.



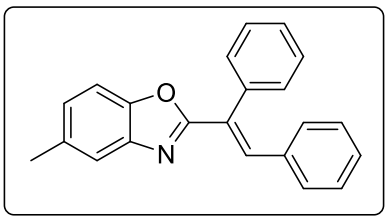
7-[1-(4-methoxyphenyl)ethyl]-2-(thiophen-2-yl)[1,2,4]triazolo-[1,5-*a*]pyrimidine (4aq). Yield 167 mg (99%) method A (5 h), and 160 mg (95%) method B (5 h), white powder, mp 132-133 °C. ^{1}H NMR(DMSO-d_6, 300 MHz): δ 1.74 (d, J = 7.2 Hz, 3H, CH_3), 3.70 (s, 3H, OCH_3), 4.94 (q, J = 7.2 Hz, 1H, CH), 6.88-6.91 (m, 2H, Ar), 7.24 – 7.27 (m, 2H, Ar), 7.37 – 7.44 (m, 2H, Ar), 7.78-7.89 (m, 1H, Ar), 7.87-7.89 (m, 1H, Ar), 8.81 (d, J = 4.7 Hz, 1H, Ar). ^{13}C NMR (75 MHz, DMSO-d_6): δ 18.5, 38.6, 55.0, 107.9, 114.0, 128.3, 128.4, 129.0, 129.6, 132.3, 133.1, 154.3, 155.1, 155.6, 158.4, 160.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_4OS$ 337.1118 Found 337.1127.



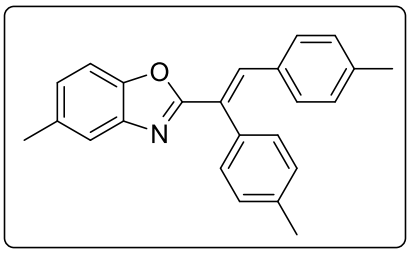
7-[1-(3,4-dimethoxyphenyl)ethyl]-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4ar). Yield 147 mg (80%) method A (20 h), and 139 mg (76%) method B (20 h), white powder, mp 155-156 °C. ^{1}H NMR($CDCl_3$, 300 MHz): δ 1.83 (d, *J* = 7.2 Hz, 3H, CH_3), 3.86 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3), 5.02 (q, *J* = 7.2 Hz, 1H, CH), 6.77-6.87 (m, 2H), 6.93-6.95 (m, 1H, Ar), 6.99 (d, *J*=2.1 Hz, 1H, Ar), 7.16-7.18 (m, 1H, Ar), 7.47-7.48 (m, 1H, Ar), 7.97-7.99 (m, 1H, Ar), 8.68 (broad signal, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.3, 39.6, 56.1, 56.1, 107.2, 111.5, 112.0, 119.9, 128.2, 128.7, 128.9, 132.3, 133.7, 148.7, 149.2, 154.3, 155.0, 156.4, 161.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}N_4O_2S$ 367.1223 Found 367.1229.



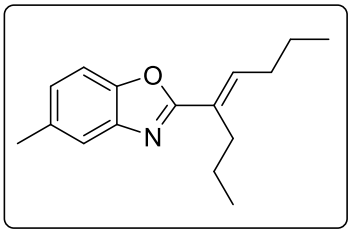
7-(1-norbornyl)-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (4as). Yield 141 mg (95%) method A (20 h), and 136 mg (92%) method B (20 h), white crystals, mp 139-140 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.38 – 1.52 (m, 3H, CH_{norb}), 1.57-1.79 (m, 4H, CH_{norb}), 2.11-2.16 (m, 1H, CH_{norb}), 2.45-2.47 (m, 1H, CH_{norb}), 2.63-2.64 (m, 1H, CH_{norb}), 3.53-3.56 (m, 1H, CH_{norb}), 6.88-6.89 (m, 1H, Ar), 7.16-7.17 (m, 1H, Ar), 7.46-7.48 (m, 1H, Ar), 7.97-7.98 (m, 1H, Ar), 8.68 (d, *J*=4.7 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 28.7, 29.9, 36.7, 36.9, 37.1, 40.3, 42.3, 105.9, 128.1, 128.6, 128.7, 133.8, 154.0, 155.3, 156.4, 161.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}N_4S$ 297.1168 Found 297.1178.



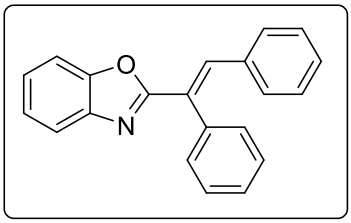
2-[(*E*)-1,2-diphenylethenyl]-5-methyl-1,3-benzoxazole (6a). Yield 154 mg (99%) method A (20 h), and 152 mg (98%) method B (20 h), white powder, mp 109-110 °C. ^{1}H NMR (DMSO-d_6, 600 MHz): δ 2.41 (s, 3H, CH_3), 7.12-7.14 (m, 2H, Ar), 7.20-7.26 (m, 4H, Ar), 7.34-7.36 (m, 2H, Ar), 7.46-7.50 (m, 4H, Ar), 7.58-7.59 (m, 1H, Ar), 7.93 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 150 MHz): 21.7, 109.9, 120.3, 126.4, 128.4, 128.5, 128.7, 129.1, 129.4, 130.2, 130.5, 134.3, 135.4, 135.8, 136.1, 142.6, 149.0, 164.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{18}NO$ 312.1383 Found 312.1376.



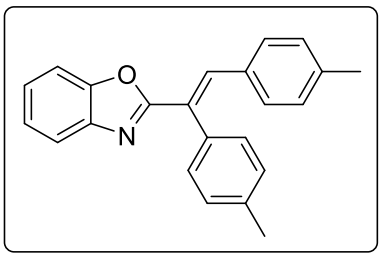
2-[(*E*)-1,2-di(4-mehylphenyl)ethenyl]-5-methyl-1,3-benzoxazole (6b). Yield 168 mg (99%) method A (20 h), and 166 mg (98%) method B (20 h), white powder, mp 150-151 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H, CH_3), 2.42 (s, 1H, CH_3), 2.43 (s, 1H, CH_3), 6.97-7.04 (m, 4H, Ar), 7.09-7.11 (m, 1H, Ar), 7.23-7.29 (m, 4H, Ar), 7.35-7.38 (m, 1H, Ar), 7.48 (broad signal, 1H, Ar), 7.88 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 21.6, 21.7, 109.8, 120.2, 126.2, 128.4, 129.1, 129.9, 130.0, 130.4, 132.7, 133.0, 134.1, 135.9, 138.2, 138.8, 142.7, 149.0, 165.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}NO$ 340.1696 Found 340.1697.



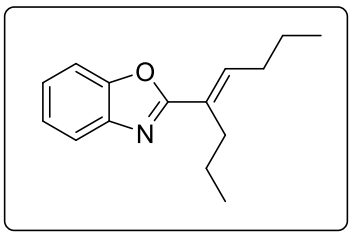
5-methyl-2-[(4*E*)-oct-4-en-4-yl]-1,3-benzoxazole (6c). Yield 117 mg (96%) method A (20 h), and 113 mg (93%) method B (20 h), yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.96-1.02 (m, 6H, $2CH_3$), 1.49-1.66 (m, 4H, $2CH_2$), 2.28 (q, *J* = 7.3 Hz, 2H, CH_2), 2.45 (s, 3H, CH_3), 2.59-2.64 (m, 2H), 6.84 (t, *J* = 7.3 Hz, 1H, CH), 7.06-7.10 (m, 1H, Ar), 7.32-7.35 (m, 1H, Ar), 7.47-7.48 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.11, 14.13, 21.6, 22.57, 22.60, 29.6, 30.8, 109.6, 119.8, 125.8, 128.7, 133.9, 138.6, 142.4, 148.7, 165.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}NO$ 244.1696 Found 244.1689. The spectral characteristics of the product obtained are similar to those described in the literature.[33]



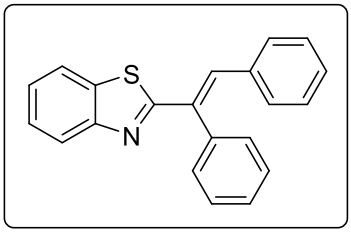
2-[(*E*)-1,2-diphenylethenyl]-1,3-benzoxazole (6d). Yield 135 mg (91%) method A (20 h), and 131 mg (88%) method B (20 h), white powder, mp 154-155 °C (lit[34] mp 157-159°C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.10-7.14 (m, 2H, Ar), 7.17-7.22 (m, 3H, Ar), 7.30-7.34 (m, 2H, Ar), 7.39-7.55 (m, 6H, Ar), 7.72-7.75 (m, 1H, Ar), 7.98 (s, 1H, CH). Anal. calcd for $C_{21}H_{15}NO$ C, 84.82; H, 5.08; N, 4.71. Found C, 84.87; H, 5.17; N, 4.81. The spectral characteristics of the product obtained are similar to those described in the literature. [33,35]



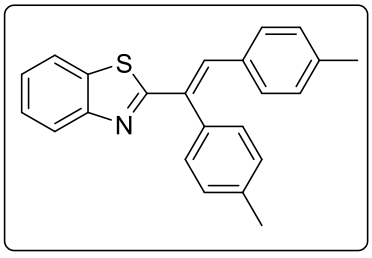
2-[(*E*)-1,2-bis(4-methylphenyl)ethenyl]-1,3-benzoxazole (6e). Yield 153 mg (94%) method A (20 h), and 148 mg (91%) method B (20 h), white needles, mp 108-109 °C. ^{1}H NMR($CDCl_3$, 300 MHz): δ 2.28 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 6.97-7.04 (m, 4H, Ar), 7.23-7.32 (m, 6H, Ar), 7.48-7.51 (m, 1H, Ar), 7.68-7.71 (m, 1H, Ar), 7.90 (s, 1H, CH). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.5, 21.6, 110.4, 120.3, 124.4, 125.1, 128.3, 129.2, 130.0, 130.5, 132.6, 133.0, 136.2, 138.2, 139.0, 142.5, 150.8, 165.3 (some carbon signals are overlapped). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}NO$ 326.1539 Found 326.1554.



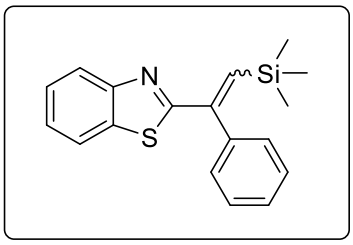
2-[(4*E*)-oct-4-en-4-yl]-1,3-benzoxazole (6f). Yield 96 mg (84%) method A (20 h), and 92 mg (80%) method B (20 h), yellow oil. ^{1}H NMR($CDCl_3$, 300 MHz): δ 0.97-1.03 (m, 6H, $2CH_3$), 1.50-1.66 (m, 4H, $2CH_2$), 2.28-2.35 (m, 2H, CH_2), 2.61-2.66 (m, 2H, CH_2), 6.88 (t, *J*=7.7 Hz, 1H, CH), 7.27-7.32 (m, 2H, Ar), 7.46-7.48 (m, 1H, Ar), 7.69-7.72 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.56, 22.60, 29.6, 30.8, 110.3, 119.9, 124.2, 124.7, 128.6, 139.0, 142.3, 150.5, 164.9 (signals of two carbons are overlapped). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO$ 230.1539 Found 230.1542. The spectral characteristics of the product obtained are similar to those described in the literature.[33]



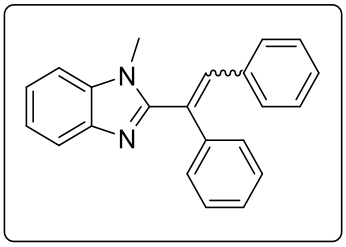
2-[(*E*)-1,2-diphenylethenyl]-1,3-benzothiazole (6g). Yield 122 mg (78%) method A (20 h), and 113 mg (72%) method B (20 h), yellow powder mp 109-110 °C. (lit [24] =108°C) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.12-7.13 (m, 2H, Ar), 7.16-7.19 (m, 3H, Ar), 7.32-7.35 (m, 1H, Ar), 7.40-7.42 (m, 2H, Ar), 7.47-7.49 (m, 4H, Ar), 7.78 (d, *J*=8.0 Hz, 1H, Ar), 8.01 (s, 1H, CH), 8.06 (d, *J*=8.2 Hz, 1H, Ar). Anal. calcd for $C_{21}H_{15}NS$ C, 80.48; H, 4.82; N, 4.47. Found C, 80.47; H, 5.87; N, 4.51. The spectral characteristics of the product obtained are similar to those described in the literature.[33,36]



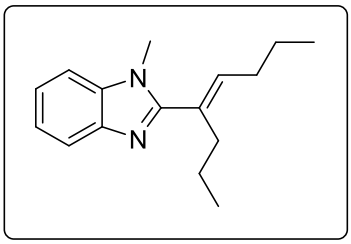
2-[(*E*)-1,2-bis(4-methylphenyl)ethenyl]-1,3-benzothiazole (6h). Yield 135 mg (79%) method A (20 h), and 128 mg (75%) method B (20 h), orange crystals, mp 95-96 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 6.97-7.05 (m, 4H, Ar), 7.25-7.34 (m, 5H, Ar), 7.43-7.49 (m, 1H, Ar), 7.75-7.79 (m, 1H, Ar), 7.92 (s, 1H, CH), 8.02-8.05 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 21.7, 121.5, 123.1, 124.8, 126.4, 129.1, 130.0, 130.2, 130.5, 132.8, 132.9, 134.0, 135.5, 135.9, 138.59, 138.61, 154.2, 172.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{20}NS$ 342.1311 Found 342.1319.



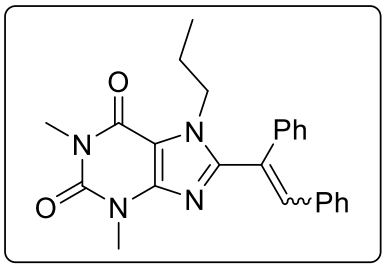
2-[1-phenyl-2-(trimethylsilyl)ethenyl]-1,3-benzothiazole (6i), a mixture of *E*/*Z* isomers in 76:24 molar ratio. Yield 128 mg (83%) method A (20 h), and 119 mg (77%) method B (20 h), both methods produced mixtures of *E/Z* isomers in molar ratio 76/24. The product samples from the methods A and B were combined and separated by preparative HPLC to give 180 mg of pure *E*-isomer and 38 mg of pure *Z*-isomer. **2-[(*E*)-1-phenyl-2-(trimethylsilyl)ethenyl]-1,3-benzothiazole,** yellowish oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ -0.07 (s, 9H, $SiMe_3$), 7.26 (s 1H, CH, overlapped with $CDCl_3$ residue signal), 7.30-7.47 (m, 7H, Ar), 7.76-7.79 (m, 1H, Ar), 8.01-8.04 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ -0.2, 121.6, 123.6, 125.2, 126.3, 128.3, 128.6, 130.0, 136.2, 137.5, 140.2, 149.4, 154.1, 171.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NSSi$ 310.1080 Found 310.1099. **2-[(*Z*)-1-phenyl-2-(trimethylsilyl)ethenyl]-1,3-benzothiazole**, yellowish oil, ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.10 (s, 9H, $SiMe_3$), 6.45 (s, 1H, CH), 7.33-7.45 (m, 6H, Ar), 7.48-7.54 (m, 1H, Ar), 7.85-7.87 (m, 1H, Ar), 8.06-8.09 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.1, 121.7, 123.5, 125.4, 126.3, 127.9, 128.4, 128.6, 136.4, 137.0, 139.1, 141.9, 149.1 (some carbon signals are overlapped). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{20}NSSi$ 310.1080 Found 310.1099.



2-[1,2-diphenylethenyl]-1-methyl-1*H*-benzimidazole (6j), a mixture of *E*/*Z* isomers in 5:1 molar ratio. Yield 120 mg (77%) method A (20 h), and 115 mg (74%) method B (20 h), both methods produced mixtures with the same 5:1 molar ratio of *E*/*Z* isomers. Yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.28 and 3.30 (s, 3H, CH_3), 6.78 (s, CH), 6.86-6.90 (m, 2H, Ar), 7.05-7.13 (m, 3H, Ar), 7.20-7.33 (m, 8H, Ar), 7.39 (broad signal, 1H, Ar), 7.78-7.81 (m, 1H, Ar). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 30.2, 31.3, 109.5, 109.8, 120.0, 120.4, 122.4, 122.9, 122.9, 126.8, 128.0, 128.3, 128.3, 128.4, 128.76, 128.83, 129.1, 129.9, 130.0, 130.7, 131.7, 134.1, 135.4, 136.0, 137.4, 139.9, 143.5, 152.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2$ 311.1543 Found 311.1553.

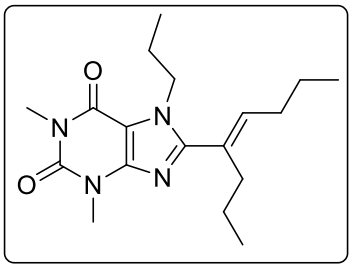


1-methyl-2-[(4*E*)-oct-4-en-4-yl]-1*H*-benzimidazole (6k). Yield 103 mg (85%) method A (20 h), and 101 mg (83%) method B (20 h), yellow oil. ^{1}H NMR($CDCl_3$, 300 MHz): δ 0.89 (t, *J* = 7.3 Hz, 3H, CH_3), 1.00 (t, *J* = 7.4 Hz, 3H, CH_3), 1.40 (sext, *J*=7.5 Hz, 2H, CH_2), 1.51 (sext, *J*=7.4 Hz, 1H, CH_2), 2.29 (q, *J*=7.4 Hz, 2H, CH_2), 2.63 (t, *J*=7.7 Hz, 2H, CH_2), 3.76 (s, 3H, NCH_3), 5.77 (t, *J*=7.2 Hz, 1H, CH), 7.26-7.34 (m, 3H, Ar), 7.74-7.77 (m, 1H, Ar). HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{23}N_2$ 243.1856 Found 243.1862. The spectral characteristics of the product obtained are similar to those described in the literature. [37]

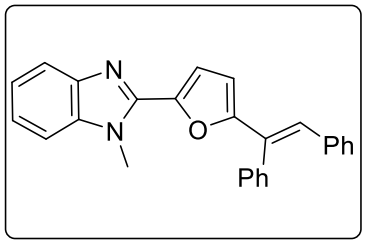


8-[1,2-diphenylethenyl]-1,3-dimethyl-7-propyl-3,7-dihydro-1*H*-purine-2,6-dione (*E*/*Z* mixture 77:23) (6l). Yield 160 mg (80 %) method A (20 h), and 144 mg (72%) method B (20 h), both methods produced mixtures of *E/Z* isomers in the same molar ratio 77:23, yellow oil solidifying on standing. The product samples from the methods A and B were combined and separated by preparative HPLC to give 192 mg of pure *E*-isomer and 45 mg of pure *Z*-isomer. **8-[(*E*)-1,2-diphenylethenyl]-1,3-dimethyl-7-propyl-3,7-dihydro-1*H*-purine-2,6-dione** ^{1}H NMR($CDCl_3$, 300 MHz): δ 0.72 (t, *J* = 7.2 Hz, 3H, CH_3), 1.44-1.54 (m, 2H, CH_2), 3.44 (s, 3H, CH_3), 3.61 (s, 3H, CH_3), 3.80-3.85 (m, 2H, CH_2), 7.11-7.25 (m, 7H, Ar), 7.22-7.26 (m 3H, Ar), 7.28 (s, 1H, CH), 7.33-7.35 (m, 5H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.1, 24.0, 28.2, 30.2, 47.8, 107.4, 126.6, 128.8, 128.89, 128.94, 129.0, 135.0, 135.4, 139.0, 148.9, 150.1, 151.9, 155.2 (some carbon signals are overlapped). HRMS (ESI)

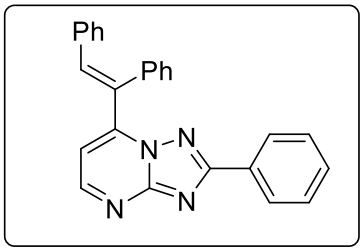
m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_4O_2$ 401.1972 Found 401.1983. **8-[(*Z*)-1,2-diphenylethenyl]-1,3-dimethyl-7-propyl-3,7-dihydro-1*H*-purine-2,6-dione**: ^1H NMR($CDCl_3$, 300 MHz): δ 0.72 (t, *J* = 7.4 Hz, 3H, CH_3), 1.42-1.54 (m, 2H, CH_2), 3.44 (s, 3H, NCH_3), 3.61 (s, 3H, NCH_3), 3.80-3.85 (m, 2H, CH_2), 6.95-7.00 (m, 2H, Ar), 7.22-7.26 (m 3H, Ar), 7.32-7.39 (m, 5H, Ar), 7.42 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.9, 24.3, 28.2, 30.0, 47.7, 128.3, 128.4, 128.8, 129.0, 129.3, 129.7, 130.1, 130.5, 135.4, 136.5, 137.1, 148.3, 151.9, 153.5, 155.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{25}N_4O_2$ 401.1972 Found 401.1983.



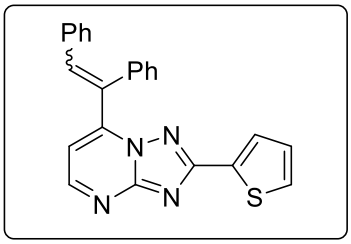
1,3-dimethyl-8-[(4*E*)-oct-4-en-4-yl]-7-propyl-3,7-dihydro-1*H*-purine-2,6-dione (**6m**). Yield 130 mg (78%) method A (20 h), and 125 mg (75%) method B (20 h), white solid, mp 59-60 °C. ^1H NMR($CDCl_3$, 300 MHz): δ 0.86-1.01 (m, 9H $3CH_3$), 1.32-1.40 (m, 2H, CH_2), 1.47-1.54 (m, 2H, CH_2), 1.80-1.88 (m, 2H, CH_2), 2.22-2.29 (m, 2H, CH_2), 2.46-2.51 (m, 2H, CH_2), 3.41 (s, 3H, NCH_3), 3.57 (s, 3H, NCH_3), 4.15-4.21 (m, 2H, CH_2), 5.72-5.77 (m, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.2, 14.1, 14.2, 22.0, 22.7, 25.0, 28.1, 29.9, 30.5, 32.7, 48.0, 107.2, 130.0, 137.3, 148.4, 152.0, 154.5, 155.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{29}N_4O_2$ 333.2285 Found 333.2289.



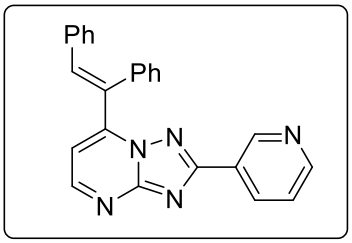
2-{5-[(*E*)-1,2-diphenylethenyl]furan-2-yl}-1-methyl-1*H*-benzimidazole (6n). Yield 171 mg (91%) method A (20 h), and 168 mg (84%) method B (20 h), yellow crystals, mp 170-171 °C. ^1H NMR($CDCl_3$, 300 MHz): δ 4.12 (s, 3H, NCH_3), 6.15 (d, *J*=3.6 Hz, 1H, Ar), 7.02-7.05 (m, 2H, Ar), 7.12-7.19 (m, 3H, Ar), 7.20 (d, *J*=3.6 Hz, 1H, Ar), 7.31-7.43 (m, 9H, Ar), 7.78-7.81 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 31.9, 109.4, 111.7, 114.7, 119.9, 122.9, 123.1, 126.1, 127.4, 128.2, 128.3, 129.1, 129.8, 130.1, 131.3, 136.3, 136.4, 137.3, 143.3, 144.5, 145.4, 157.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}N_2O$ 377.1648 Found 377.1652.



7-[(*E*)-1,2-diphenylethenyl]-2-phenyl[1,2,4]triazolo[1,5-*a*]pyrimidine (6o). Yield 150 mg (80%) method A (20 h), and 138 mg (74%) method B (20 h), pale yellow crystals, mp 155-156 °C. ^1H NMR($CDCl_3$, 500 MHz): δ 6.64 (broad signal, 1H, Ar), 7.12-7.14 (m, 2H, Ar), 7.21-7.27 (m, 3H, Ar), 7.31-7.33 (m, 2H, Ar), 7.45-7.49 (m, 3H, Ar), 7.50-7.52 (m, 3H, Ar), 8.38-8.40 (m, 2H, Ar), 8.64 (broad signal, 1H, Ar), 8.96 (s, 1H, CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 110.5, 127.7, 128.5, 128.80, 128.83, 129.1, 129.6, 130.6, 130.7, 130.7, 130.8, 131.8, 135.6, 137.1, 141.2, 148.3, 153.6, 157.6, 165.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{19}N_4$ 375.1604 Found 375.1607.



7-[1,2-diphenylethenyl]-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (6p). **(*E*/*Z* mixture 71:29)** Yield 156 mg (82%) method A (20 h), and 141 mg (74%) method B (20 h), both methods produced mixtures of *E/Z* isomers in the same molar ratio 71:29, white powder. The product samples from the methods A and B were combined and *E*-isomer was separated by preparative HPLC to give 140 mg of pure **7-[(*E*)-1,2-diphenylethenyl]-2-(thiophen-2-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine,** mp 126-127 °C (from acetonitrile). ^1H NMR($CDCl_3$, 300 MHz): δ 6.61 (d, *J*=4.8 Hz, 1H, Ar), 7.09-7.25 (m, 6H, Ar), 7.29-7.32 (m, 2H, Ar), 7.45-7.49 (m, 4H, Ar), 7.98-8.00 (m, 1H, Ar), 8.59 (d, *J*=4.8 Hz, 1H, Ar), 8.94 (s, 1H, CH). ^{13}C NMR (75 MHz, $CDCl_3$) δ 110.5, 128.2, 128.4, 128.8, 128.8, 128.9, 129.2, 129.6, 130.5, 130.9, 131.6, 133.7, 135.6, 137.0, 141.4, 148.1, 153.7, 157.4, 161.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}N_4S$ 381.1168 Found 381.1178.



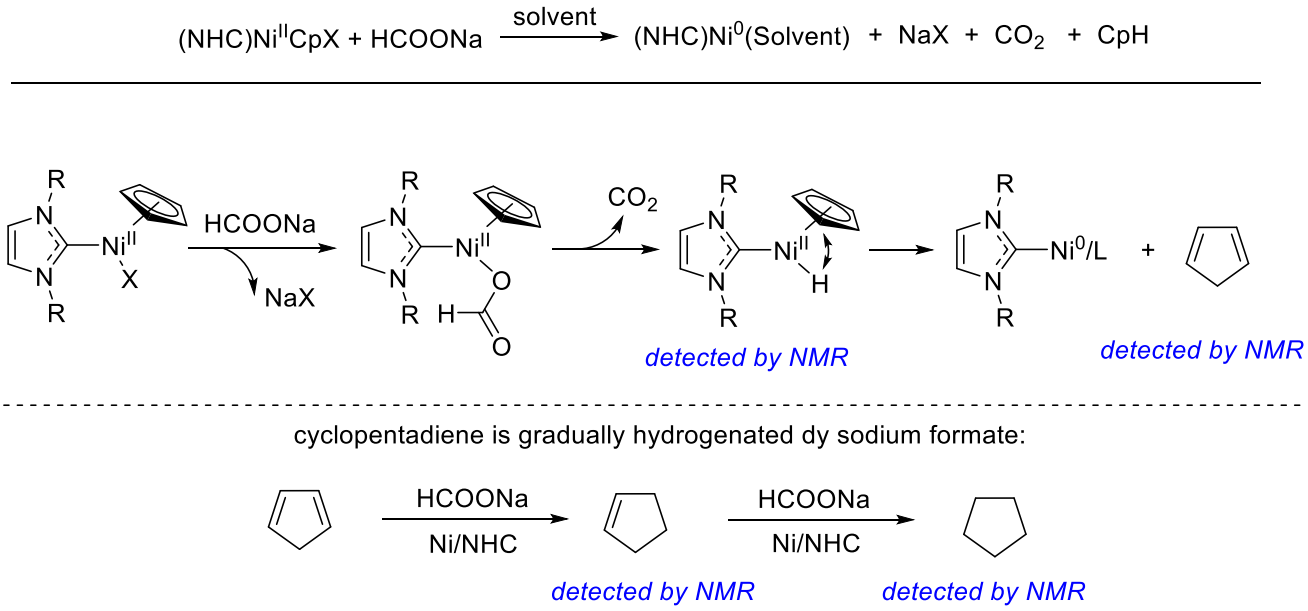
7-[(*E*)-1,2-diphenylethenyl]-2-(pyridin-3-yl)[1,2,4]triazolo[1,5-*a*]pyrimidine (6q). Yield 160 mg (85%) method A (20 h), and 135 mg (72%) method B (20 h), yellow crystals, mp 190-191 °C. ^{1}H NMR($CDCl_3$, 300 MHz): δ 6.70 (d, *J* = 4.8 Hz, 1H, Ar), 7.11-7.14 (m, 2H, Ar), 7.20-7.26 (m, 3H, Ar), 7.30-7.33 (m, 2H, Ar), 7.42-7.48 (m, 4H, Ar), 8.60-8.64 (m, 1H, Ar), 8.67-8.68 (m, 1H, Ar), 8.71-8.74 (m, 1H, Ar), 8.88 (s, 1H, CH), 9.57-9.58 (m, 1H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.7, 123.8, 126.8, 128.5, 128.9, 129.3, 129.6, 130.5, 130.9, 131.6, 135.0, 135.4, 136.9, 141.3, 148.7, 149.1, 151.5, 154.1, 157.6, 163.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for 375.1478 $C_{24}H_{17}N_5$ Found 375.1487

Procedure for scaled-up preparation of 7-(1-phenylethyl)-2-phenyl[1,2,4]triazolo[1,5-a]pyrimidine (4ag).

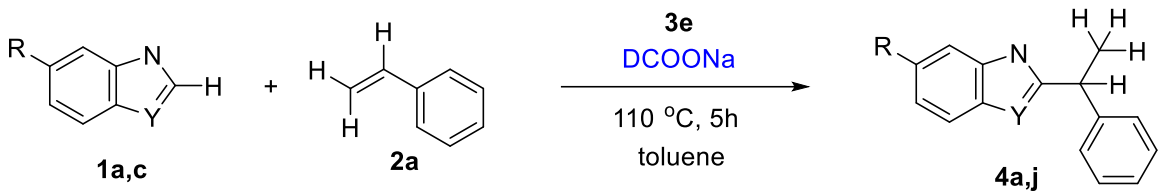
A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged in air with $Ni(Cp)_2$ (19 mg, 0.1 mmol, 5 mol%), IMes·HCl (34 mg, 0.1 mmol, 5 mol%), HCOONa (136 mg, 2 mmol), compound 1i (392 mg, 2 mmol), styrene 2a (229 mg, 2.2 mmol) and toluene (10 mL). Then the tube was purged with argon, sealed with a septum and heated at 110 °C and vigorous stirring within 20 h. After cooling to room temperature, the mixture was diluted with toluene (10 mL) and filtered through a short pad of Celite. Then toluene was removed in vacuo and the residue obtained was chromatographed on silica gel using hexane/ethyl acetate 1:1 mixture as eluent to give 552 mg (92% yield) of compound 4ag.

S4. Reaction mechanism studies

Scheme S1. Proposed stoichiometry and mechanism for the reduction of (NHC)Ni(Cp)X complexes by sodium formate.



Scheme S2. Experiments with deuterium-labelled sodium formate (DCOONa).



No deuterium label was detected by NMR in the isolated products

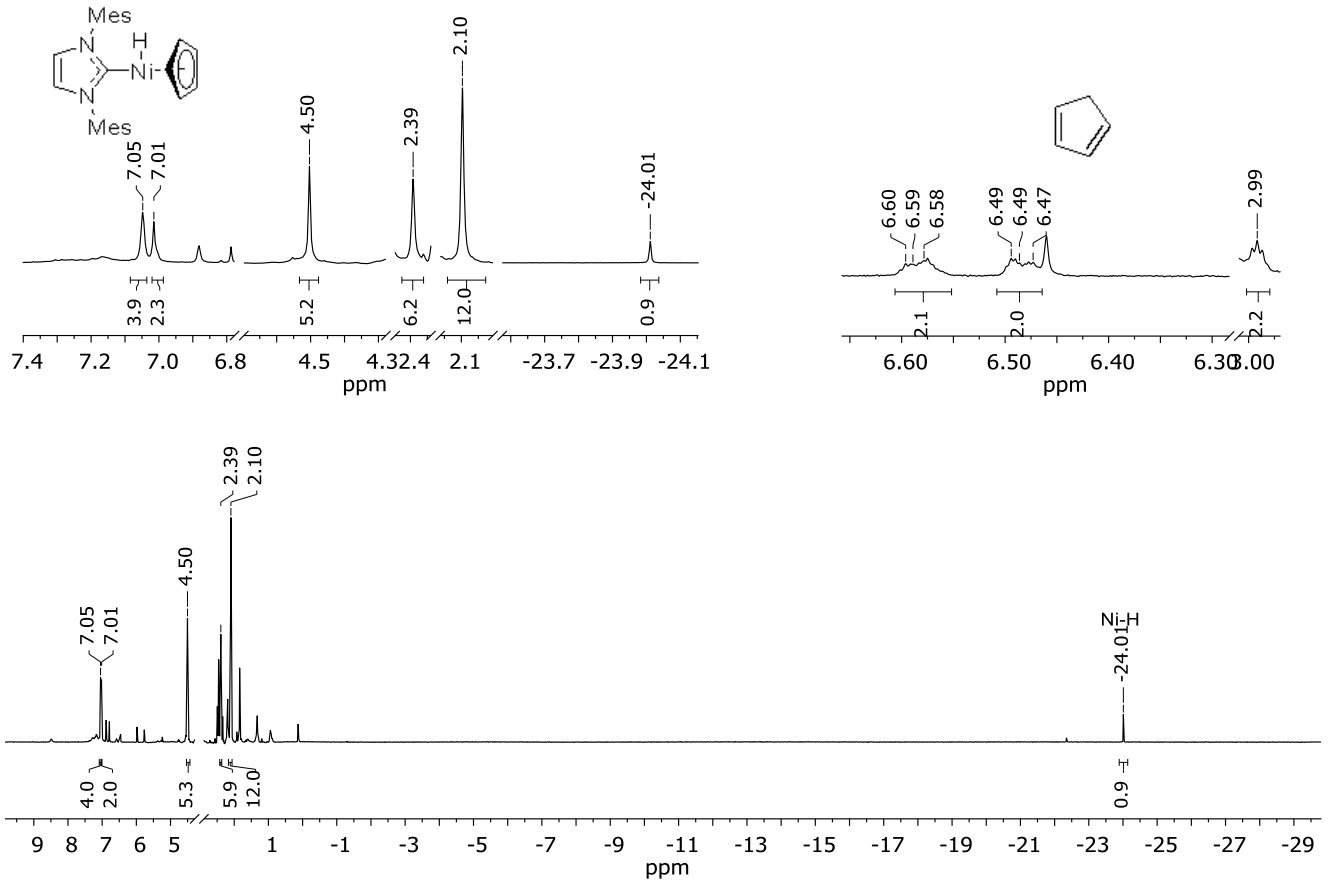


Figure S2. ^{1}H NMR spectrum of a reaction mixture after heating complex **3e** with HCOONa in 1,4-dioxane-H_8(90%) + 1,4-dioxane-D_8(10%) at 110 °C within 1 h.

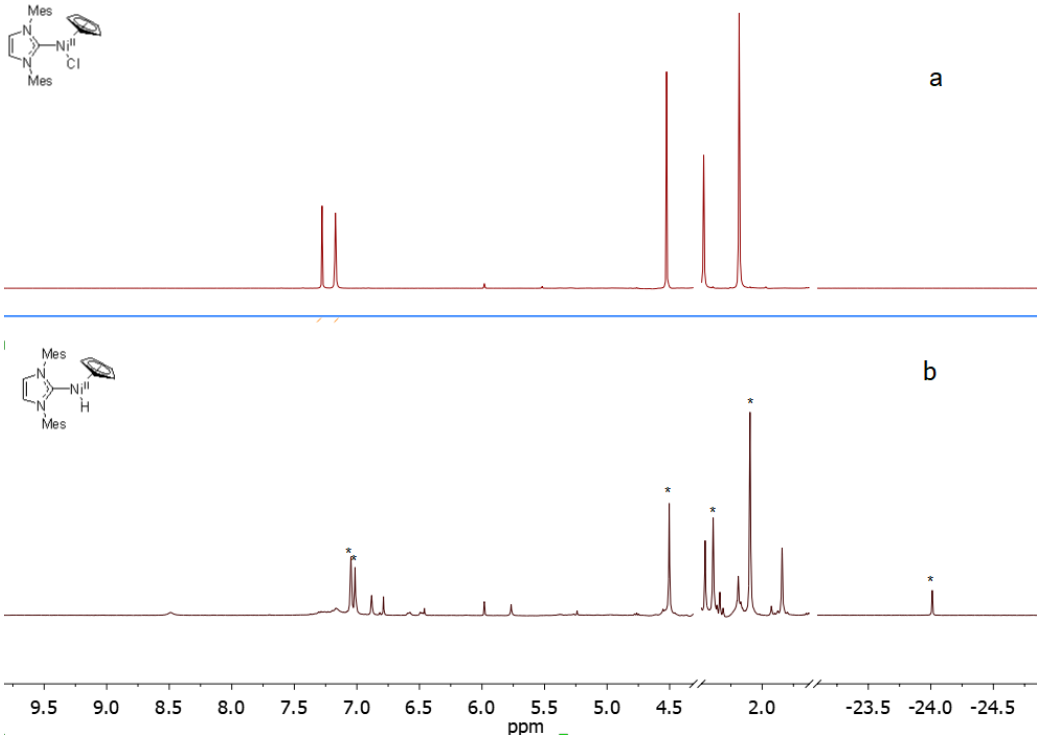


Figure S3. Stacked ^{1}H NMR spectra of initial complex **3e** (a) and reaction mixture after heating complex **3e** with HCOONa in 1,4-dioxane-H_8(90%) + 1,4-dioxane-D_8(10%) at 110 °C within 1 h.

Observed spectrum of the (IMes)Ni(Cp)H in dioxane is very close to the literature[38] reported spectrum of this compound in THF-d_8: δ -24.04 (s, 1H, Ni-H), 2.07 (s, 12H, CH_3), 2.34 (s, 6H, CH_3), 4.46 (s, 5H, CH), 6.98 (s, 4H, Ar), 7.00 (s, 2H, NCH).

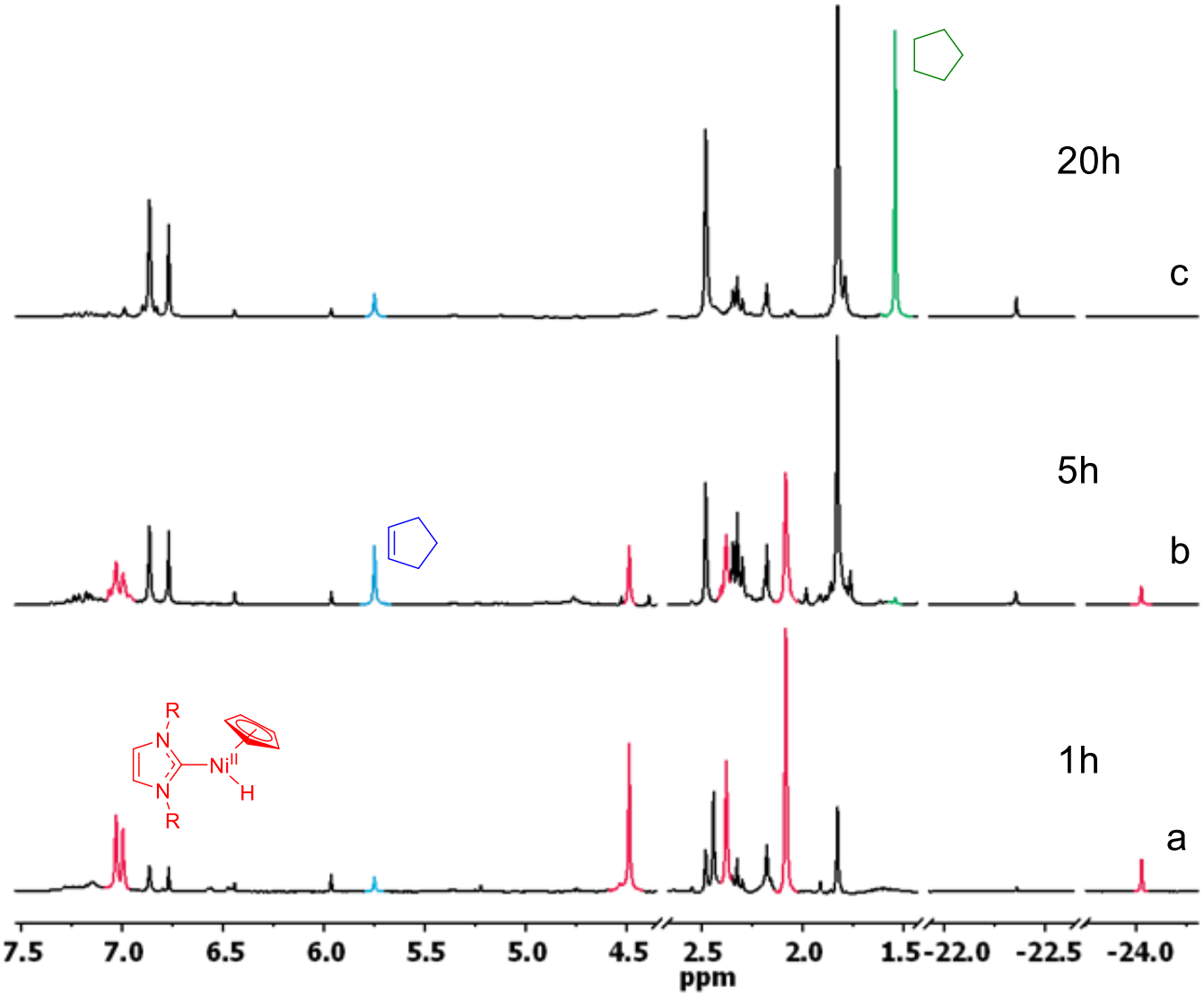


Figure S4. Stacked ^{1}H NMR spectra of reaction mixtures after heating complex **3e** with HCOONa in 1,4-dioxane-H_8(90%) + 1,4-dioxane-D_8(10%) at 110 °C within 1 h (a), 5 h (b) and 20 h (c).

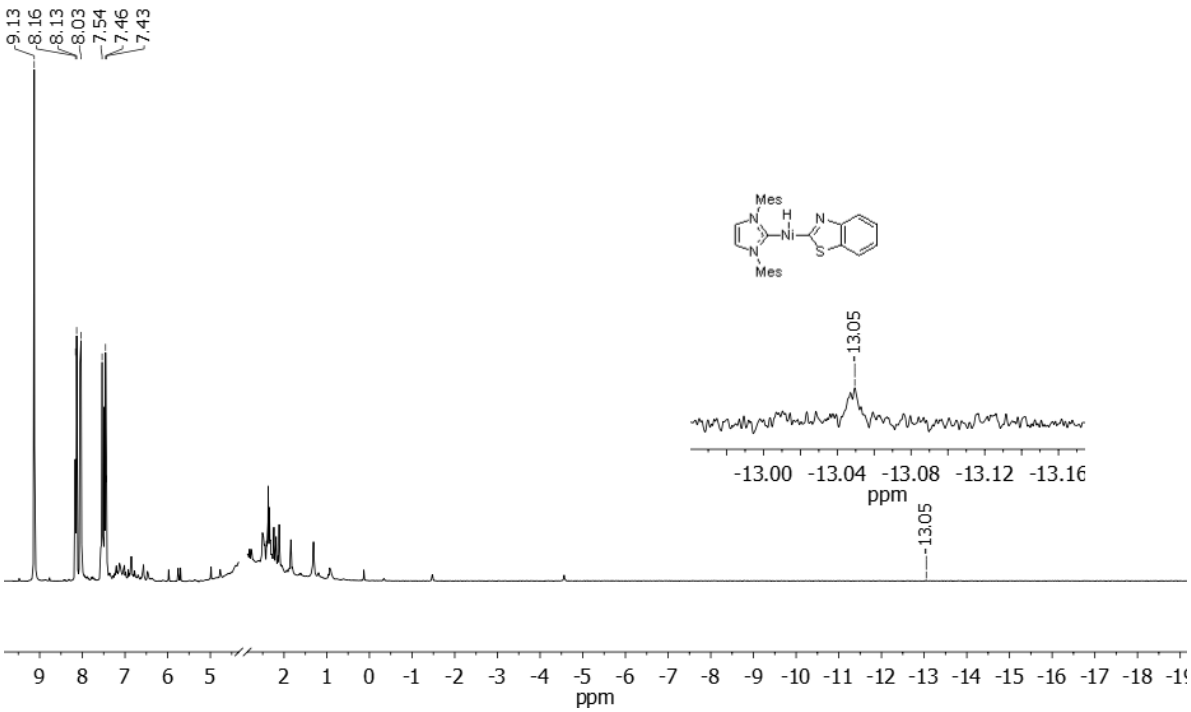
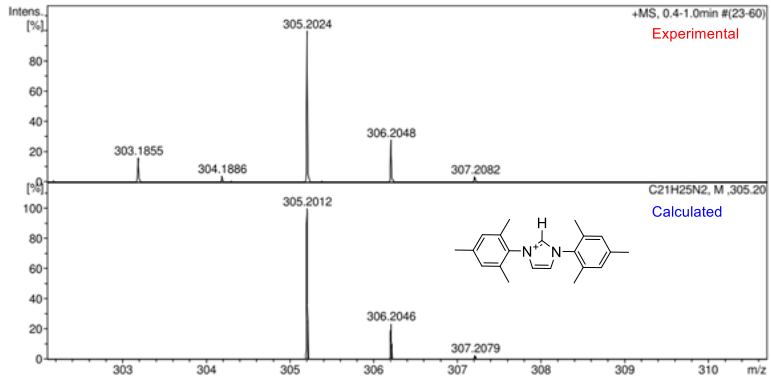
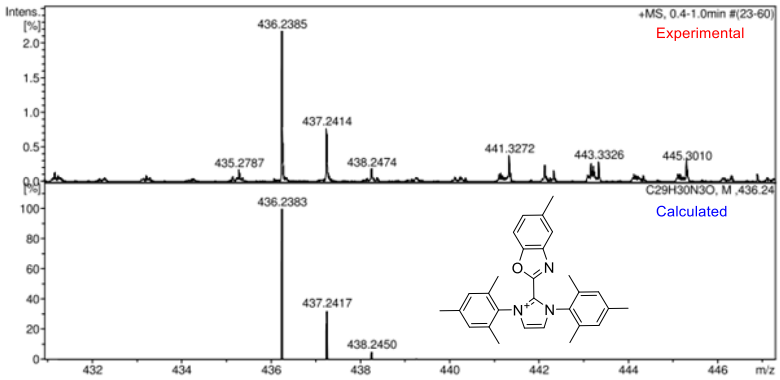


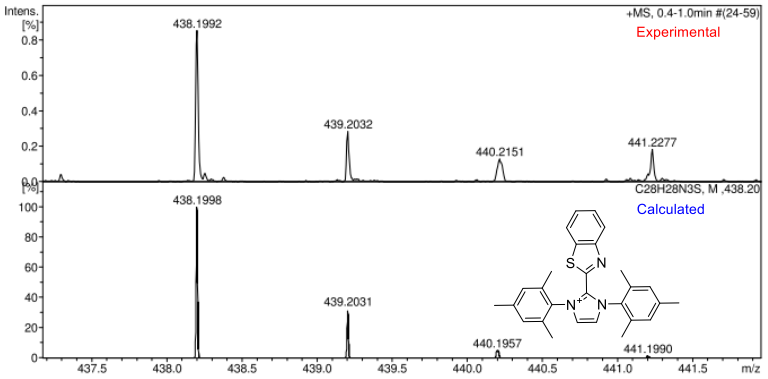
Figure S5. ^{1}H NMR spectrum of a reaction mixture after heating complex **3e**, benzothiazole **1a** and HCOONa in 1,4-dioxane-H_8(90%) + 1,4-dioxane-D_8(10%) at 110 °C within 20 h; the insert shows high field region, which possibly corresponds to the hydride species.



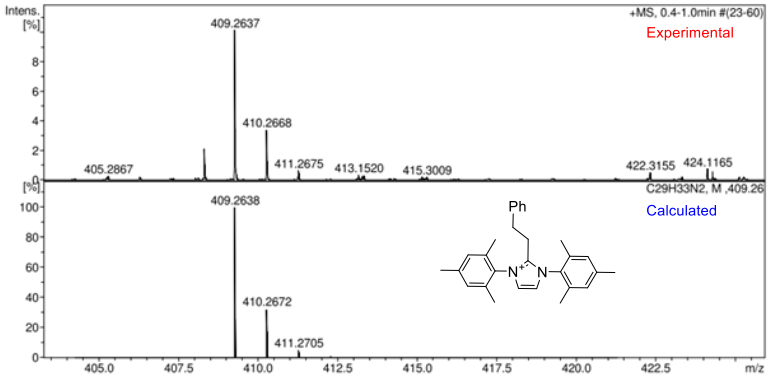
a)



b)



c)



d)

Figure S6. HRMS spectra of complex **3e** decomposition products formed in the reaction between **1a** or **1c** and **2a**: IMes·HCl (*a*), compound **12a** (*b*), compound **12b** (*c*) and compound **9** (*d*).

S5. Single Crystal X-Ray Diffraction Data

Experimental

X-ray diffraction data for compound **3d** were collected at 295 K on a STOE STADIVARI Pilatus 100K diffractometer using Mo K\a-radiation. Data collection, determination and refinement of the unit cell parameters were preformed using STOE X-Area software package (STOE & Cie GmbH, Germany). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences in intensities of the symmetry-equivalent reflections (multi-scan method). X-ray diffraction data for compounds **4ak** and **4ap** were collected at 100K on a Bruker AXS D8 QUEST diffractometer equipped with a Photon-III area-detector (graphite monochromator, shutterless φ- and ω-scan technique), using Mo K\a-radiation. The intensity data were integrated by the SAINT program[39] and corrected for absorption and decay using SADABS.[40] The structure was solved by direct methods using SHELXT[41] and refined on F^2 using SHELXL program.[42] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. The SHELXTL program suite[1] was used for molecular graphics. Crystallographic data for **3d**, **4ak** and **4ap** have been deposited in the Cambridge Crystallographic Data Center. CCDC 2041133 (**3d**), CCDC 2041290 (**4ak**) and CCDC 2041286 (**4ap**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Compound 3d

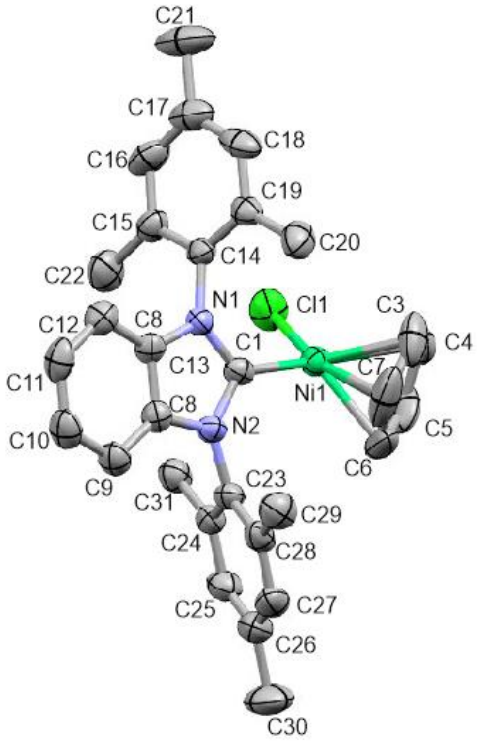


Figure S7. The molecular structure of compound **3d** according to single-crystal X-ray diffraction data.

Crystal data

$C_{30}H_{31}ClN_2Ni$	D_x = 1.332 Mg m^{-3}
M_r = 513.73	Mo *K*a radiation, l = 0.71073 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 1653 reflections
a = 13.6888 (4) Å	q = 2.2–24.2°
b = 10.4380 (3) Å	m = 0.88 mm^{-1}
c = 17.9355 (6) Å	*T* = 295 K
V = 2562.69 (14) Å^3	Block, green
Z = 4	0.24 × 0.21 × 0.18 mm
F(000) = 1080	

Data collection

STOE diffractometer	6211 independent reflections
Radiation source: Mo LFF Sealed Tube	3585 reflections with $I > 2s(I)$
Plane graphite monochromator	$R_{int} = 0.131$
Detector resolution: 5.81 pixels mm^{-1}	$q_{max} = 28.3°$, $q_{min} = 1.9°$
rotation method scans	$h = -17 \rightarrow 17$
Absorption correction: multi-scan [c.f. r.h. blessing, acta cryst. (1995), a51, 33-38]	$k = -13 \rightarrow 13$
$T_{min} = 0.371$, $T_{max} = 0.707$	$l = -23 \rightarrow 23$
39154 measured reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[s^2(F_o^2) + (0.0546P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2s(F^2)] = 0.051$	$(D/s)_{max} = 0.012$
$wR(F^2) = 0.116$	$D\rho_{max} = 0.38$ e $Å^{-3}$
$S = 0.88$	$D\rho_{min} = -0.59$ e $Å^{-3}$
6211 reflections	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^* = kFc[1+0.001xFc^2l^3/\sin(2q)]^{-1/4}$
314 parameters	Extinction coefficient: 0.0164 (16)
0 restraints	Absolute structure: Flack x determined using 1127 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: -0.030 (11)

Compound 4ak

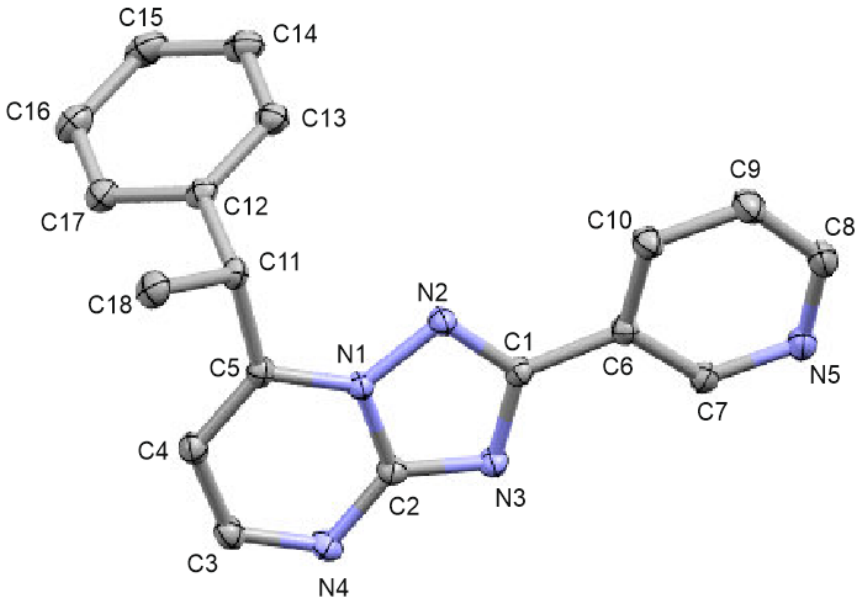


Figure S8. The molecular structure of compound **4ak** according to single-crystal X-ray diffraction data.

Crystal data

$C_{18}H_{15}N_5$	$F(000)$ = 632
M_r = 301.35	D_x = 1.344 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 10.0740 (3) Å	Cell parameters from 9895 reflections
b = 11.5334 (3) Å	θ = 2.4–37.8°
c = 12.8541 (4) Å	μ = 0.08 mm^{-1}
β = 94.0366 (6)°	T = 100 K
V = 1489.78 (7) Å^3	Block, colourless
Z = 4	0.59 × 0.56 × 0.45 mm

Data collection

Bruker AXS D8 QUEST, Photon III detector diffractometer	7589 independent reflections
Radiation source: fine-focus sealed X-Ray tube	6270 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.036
Detector resolution: 7.31 pixels mm^{-1}	θ_{max} = 37.0°, θ_{min} = 2.7°
φ and ω shutterless scans	h = −17→17
Absorption correction: multi-scan *SADABS* 2016/2 (Krause et al., J. Appl. Cryst. 2015, 48, 3-10)	k = −19→19
T_{min} = 0.816, T_{max} = 0.863	l = −21→21
50812 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.123$	$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.3537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.001$
7589 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
248 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
9 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

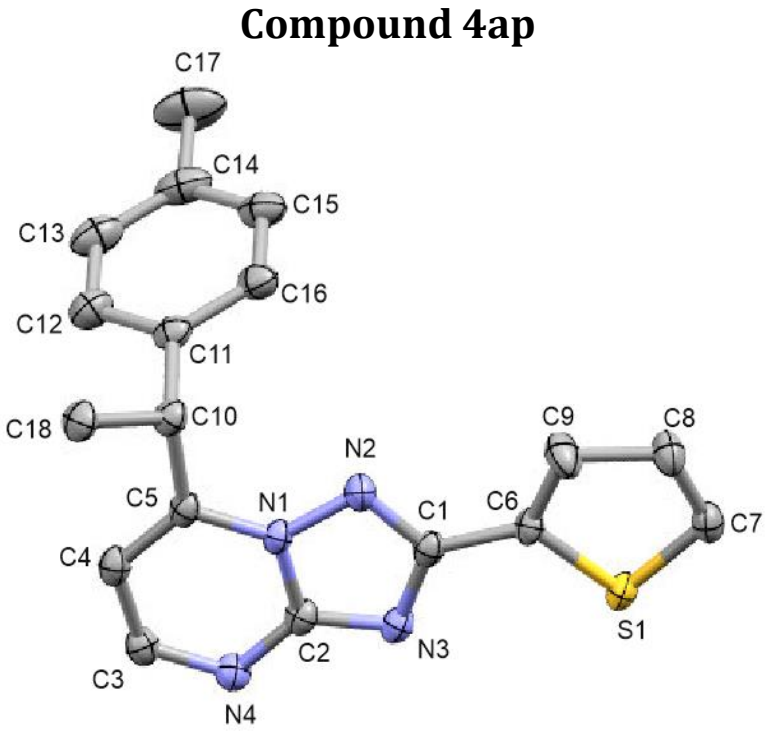


Figure S9. The molecular structure of compound **4ap** according to single-crystal X-ray diffraction data.

Crystal data

$C_{18}H_{16}N_4S$	$F(000) = 672$
$M_r = 320.41$	$D_x = 1.330$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

a = 11.7847 (2) Å	Cell parameters from 9962 reflections
b = 11.4013 (2) Å	θ = 2.5–33.3°
c = 11.9092 (2) Å	μ = 0.21 mm^{-1}
β = 90.6061 (6)°	T = 100 K
V = 1600.04 (5) Å^3	Block, colourless
Z = 4	0.42 × 0.30 × 0.22 mm

Data collection

Bruker AXS D8 QUEST, Photon III detector diffractometer	8158 independent reflections
Radiation source: fine-focus sealed X-Ray tube	4963 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.087
Detector resolution: 7.31 pixels mm^{-1}	θ_{max} = 37.0°, θ_{min} = 2.5°
φ and ω shutterless scans	h = −19→19
Absorption correction: multi-scan SADABS 2016/2 (Krause et al., J. Appl. Cryst. 2015, 48, 3-10)	k = −19→19
T_{min} = 0.698, T_{max} = 0.748	l = −20→20
83334 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.061	H-atom parameters constrained
$wR(F^2)$ = 0.161	$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 0.8249P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.02	$(\Delta/\sigma)_{max}$ = 0.001
8158 reflections	$\Delta\rho_{max}$ = 0.46 e Å^{-3}
227 parameters	$\Delta\rho_{min}$ = −0.36 e Å^{-3}
5 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

S6. NMR spectra of synthesized compounds

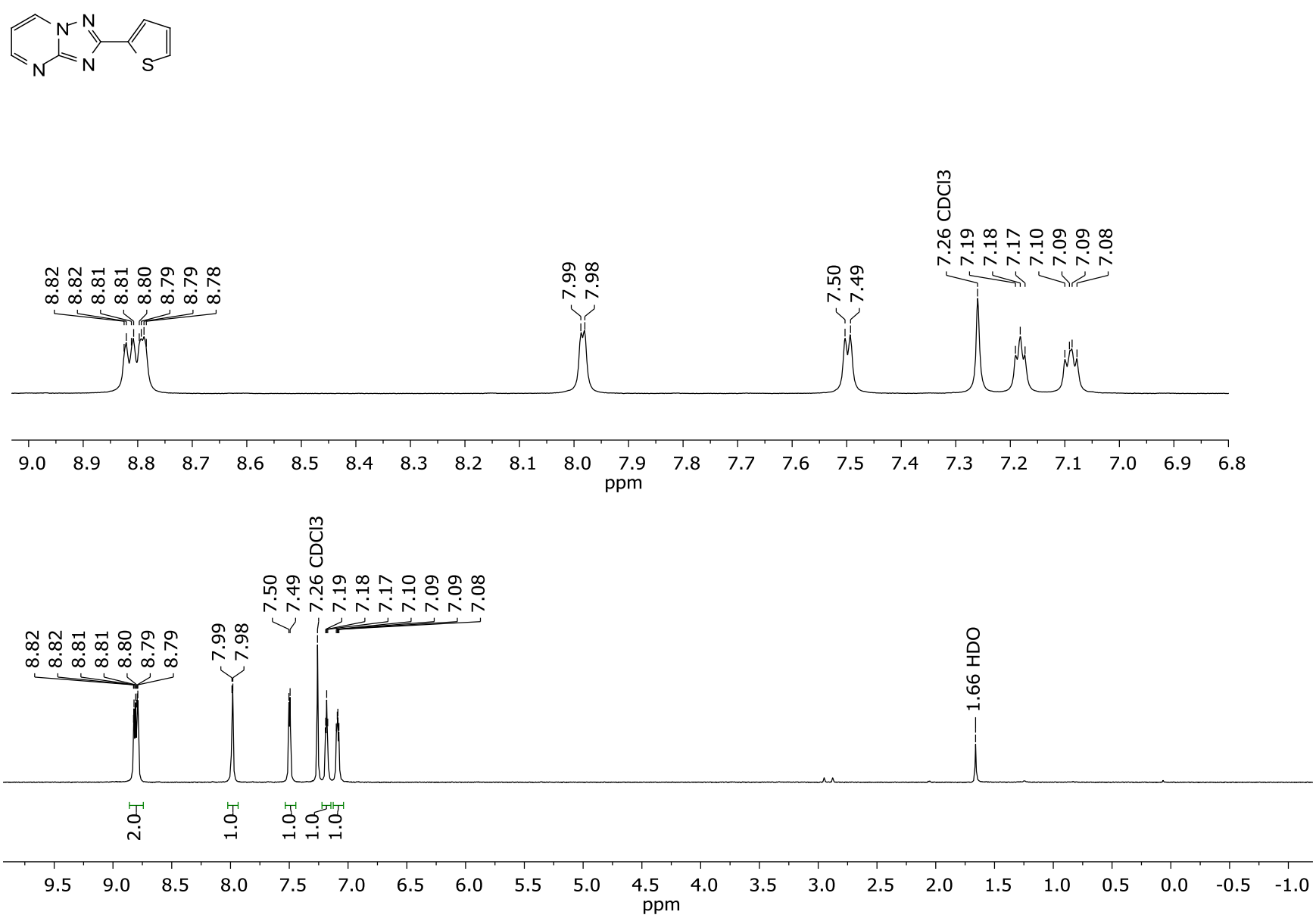


Figure S10. ^{1}H NMR spectrum of compound **1j** ($CDCl_3$, 500 MHz)

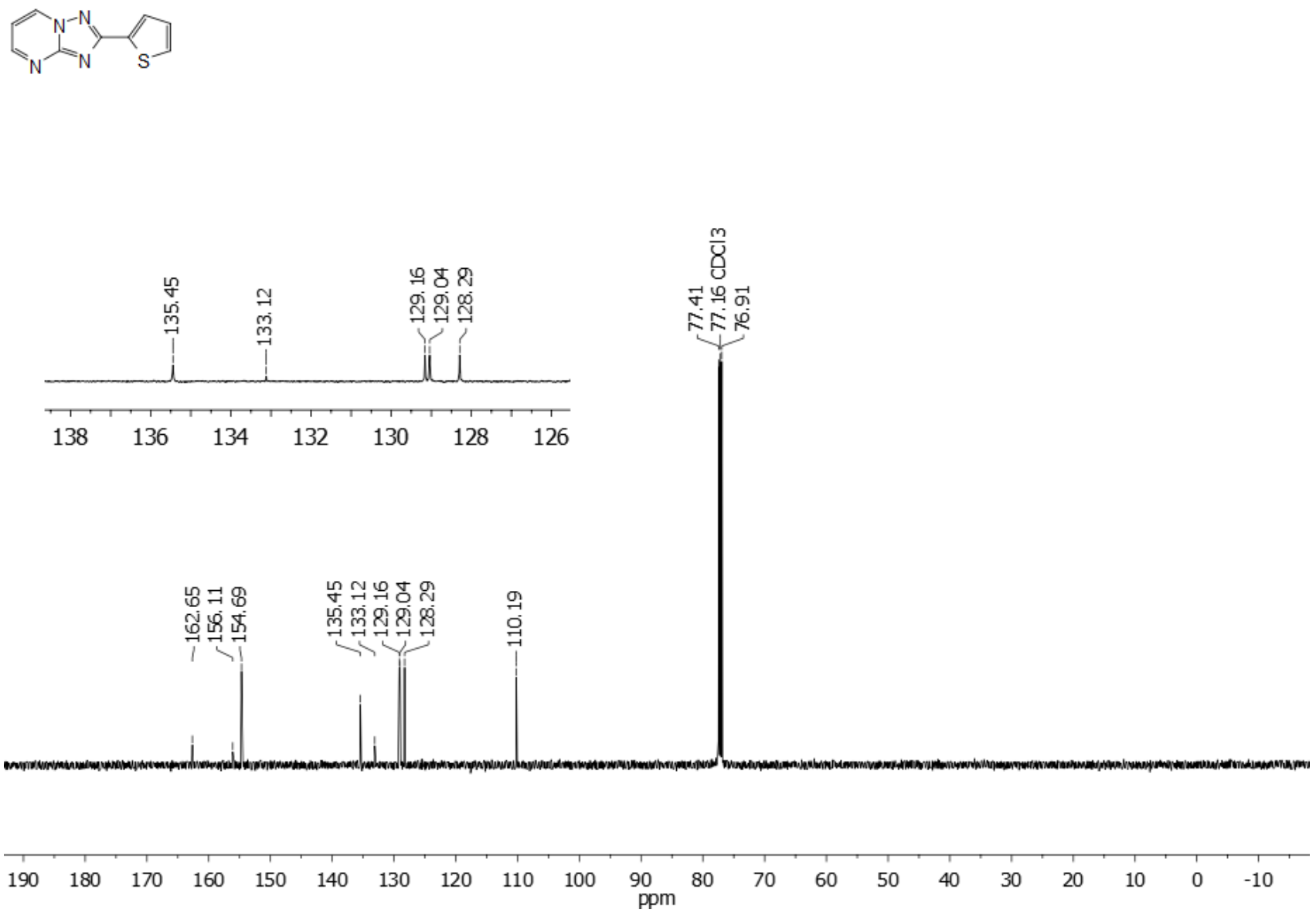


Figure S11. ^{13}C NMR spectrum of compound **1j** ($CDCl_3$, 126 MHz)

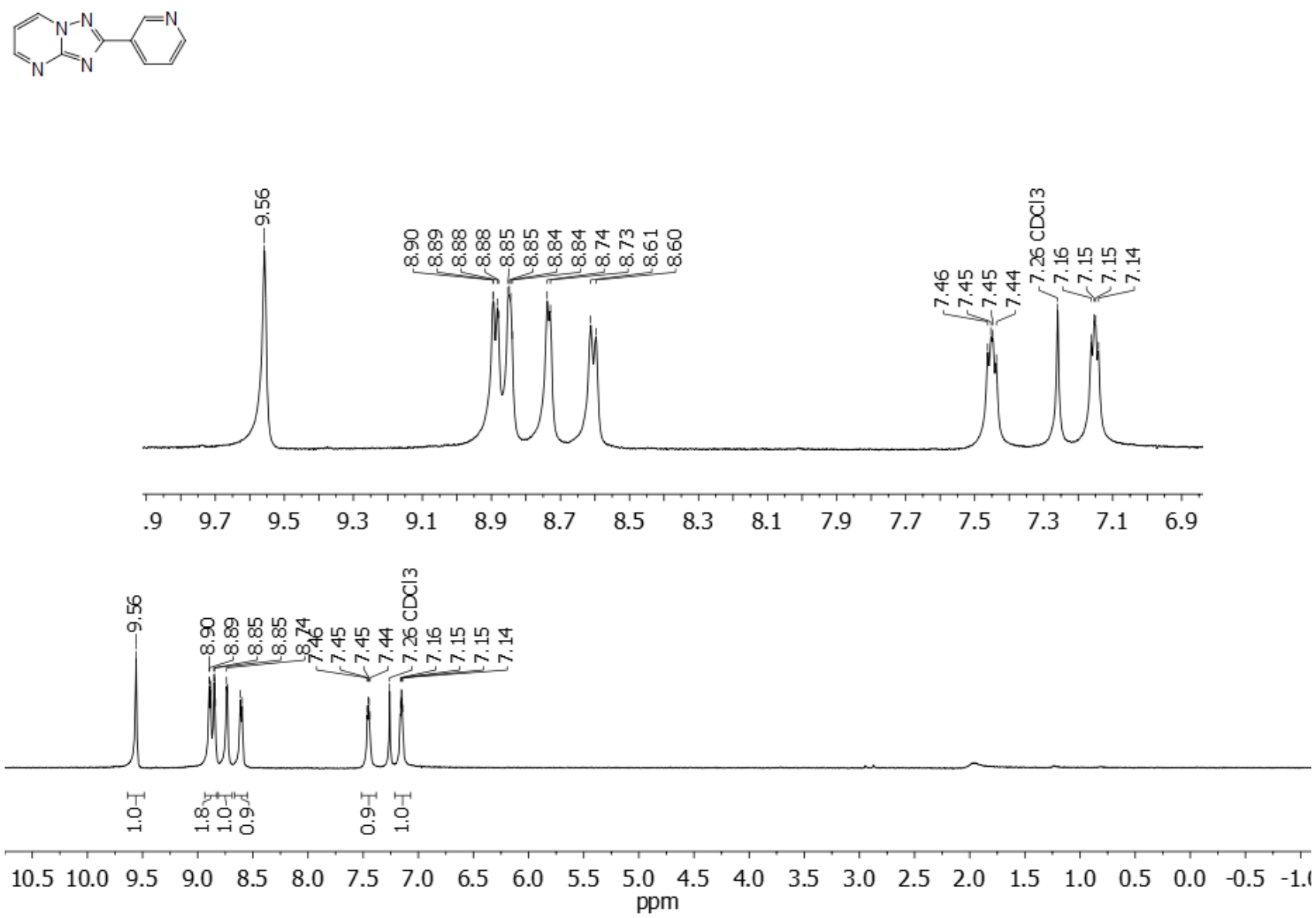


Figure S12. ^{1}H NMR spectrum of compound **1k** ($CDCl_3$, 300 MHz)

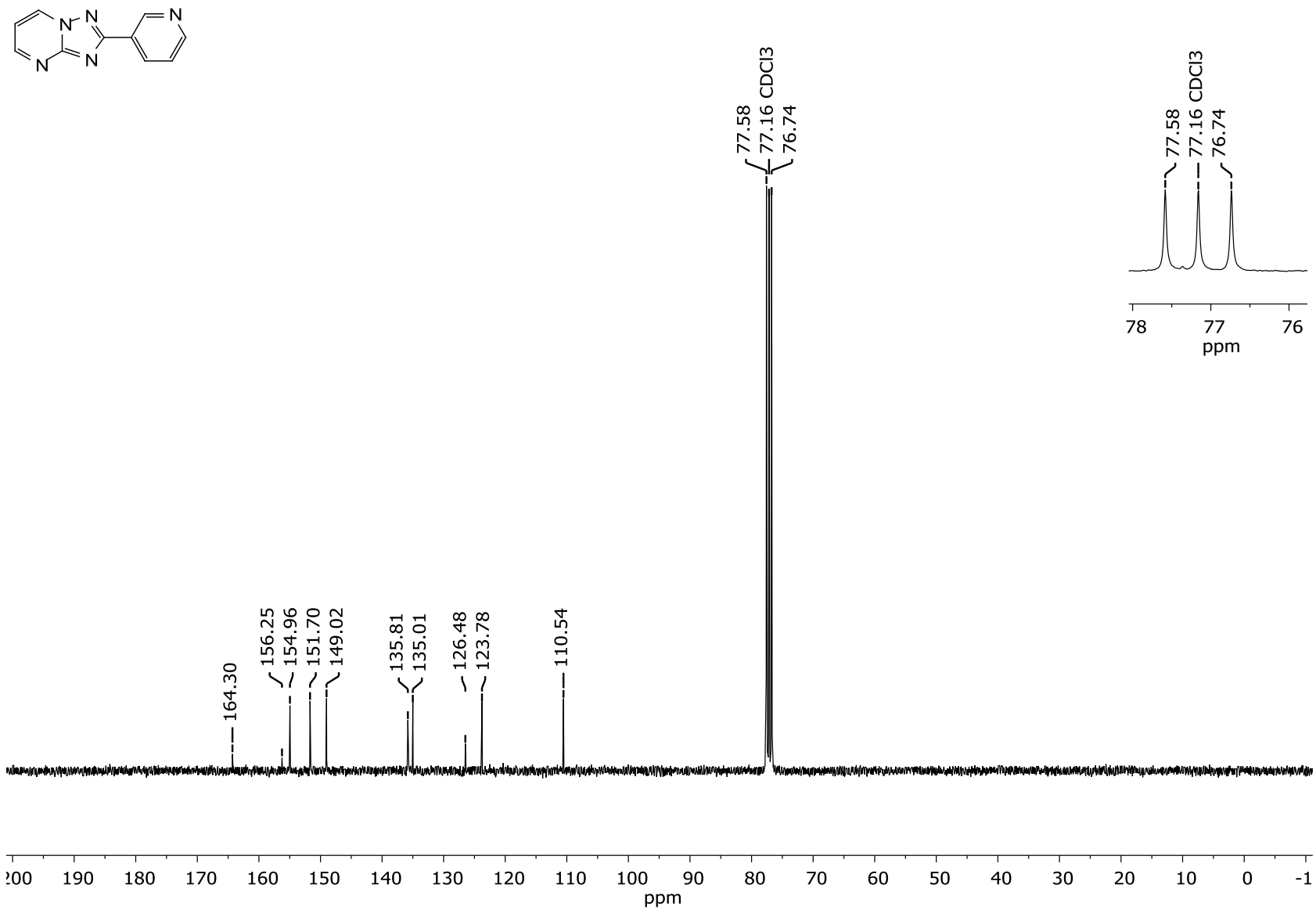


Figure S13. ^{13}C NMR spectrum of compound **1k** ($CDCl_3$, 125 MHz)

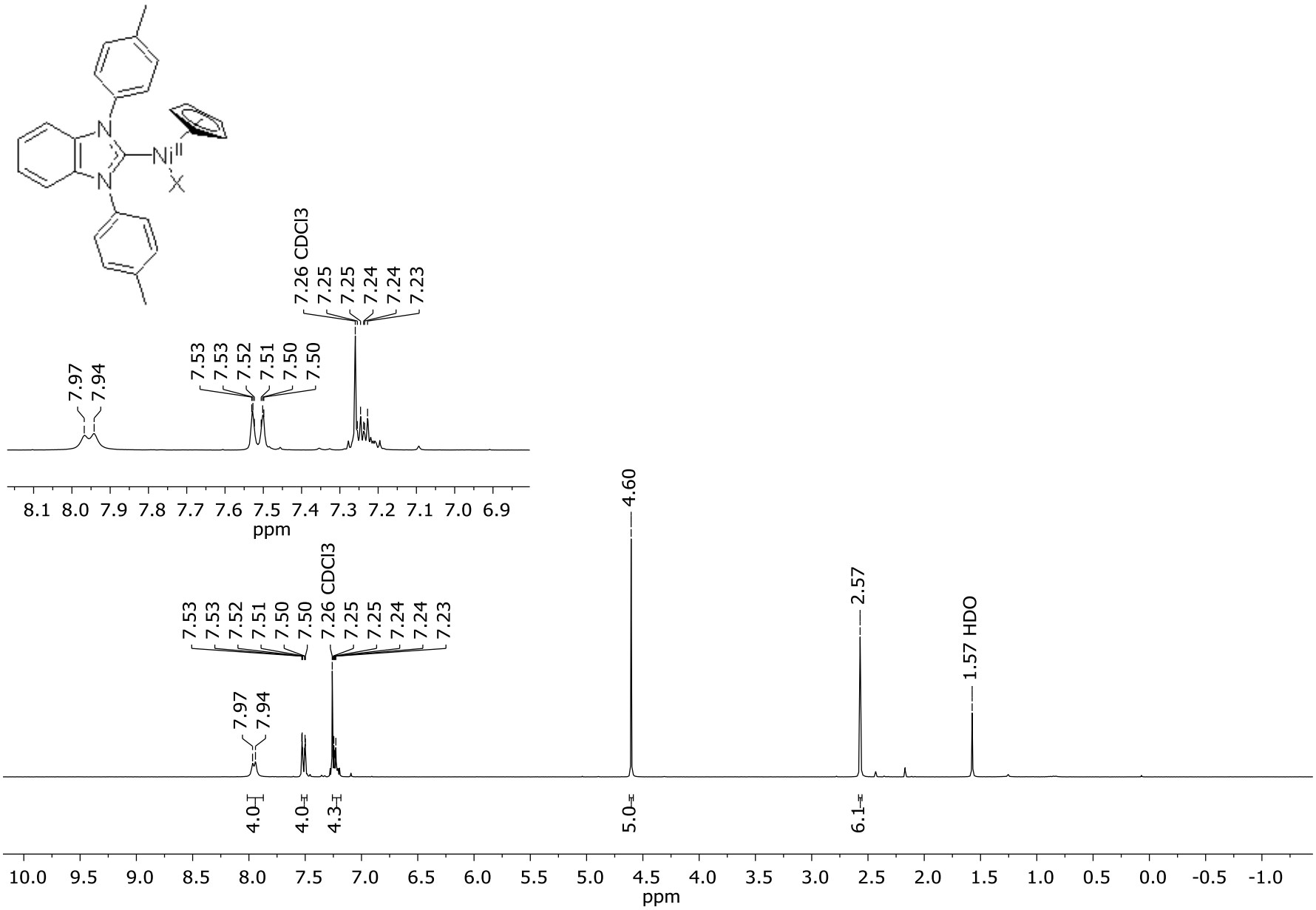


Figure S14. ^{1}H NMR spectrum of compound **3c** ($CDCl_3$, 300 MHz)

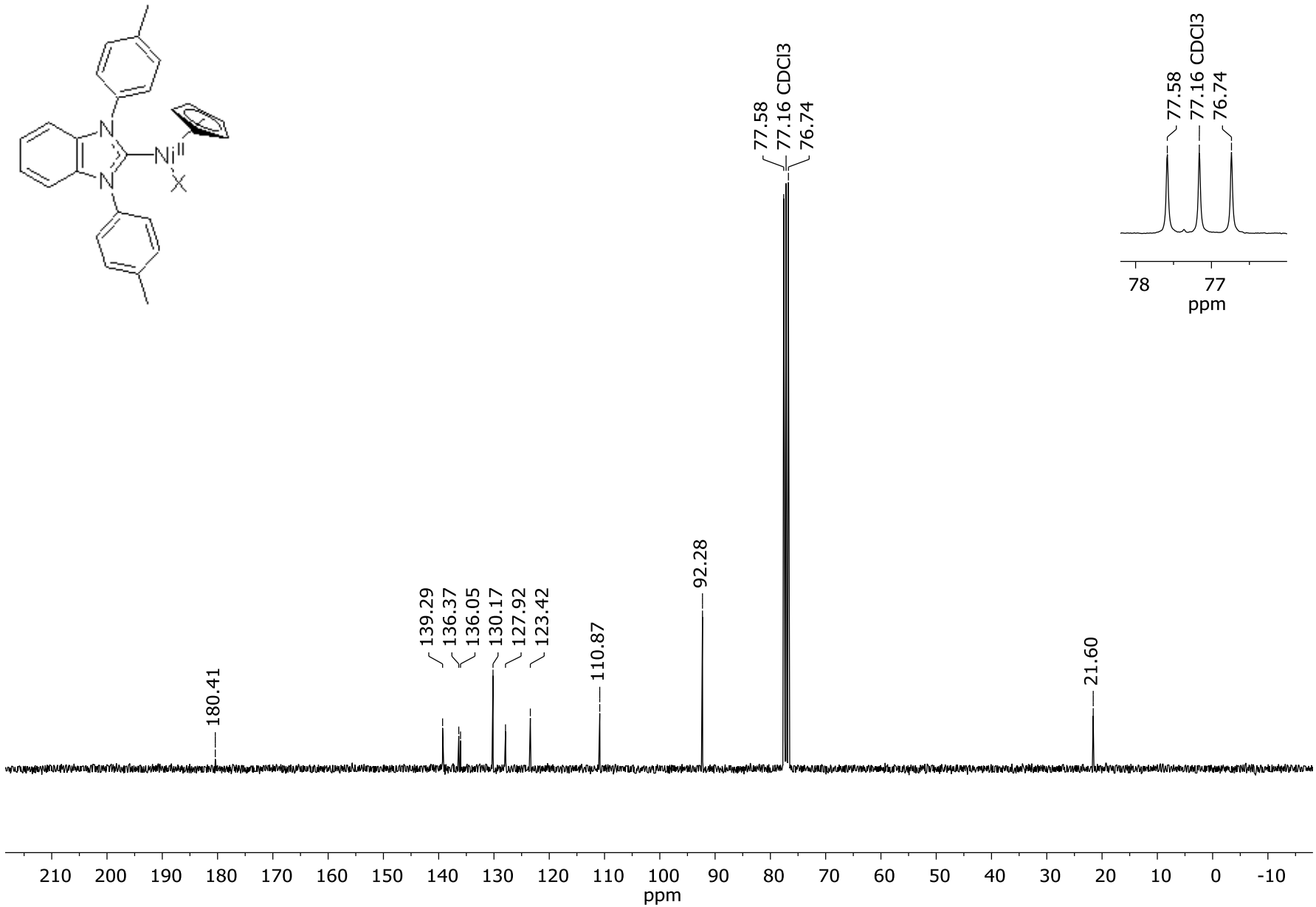


Figure S15. ^{13}C NMR spectrum of compound **3c** ($CDCl_3$, 75 MHz)

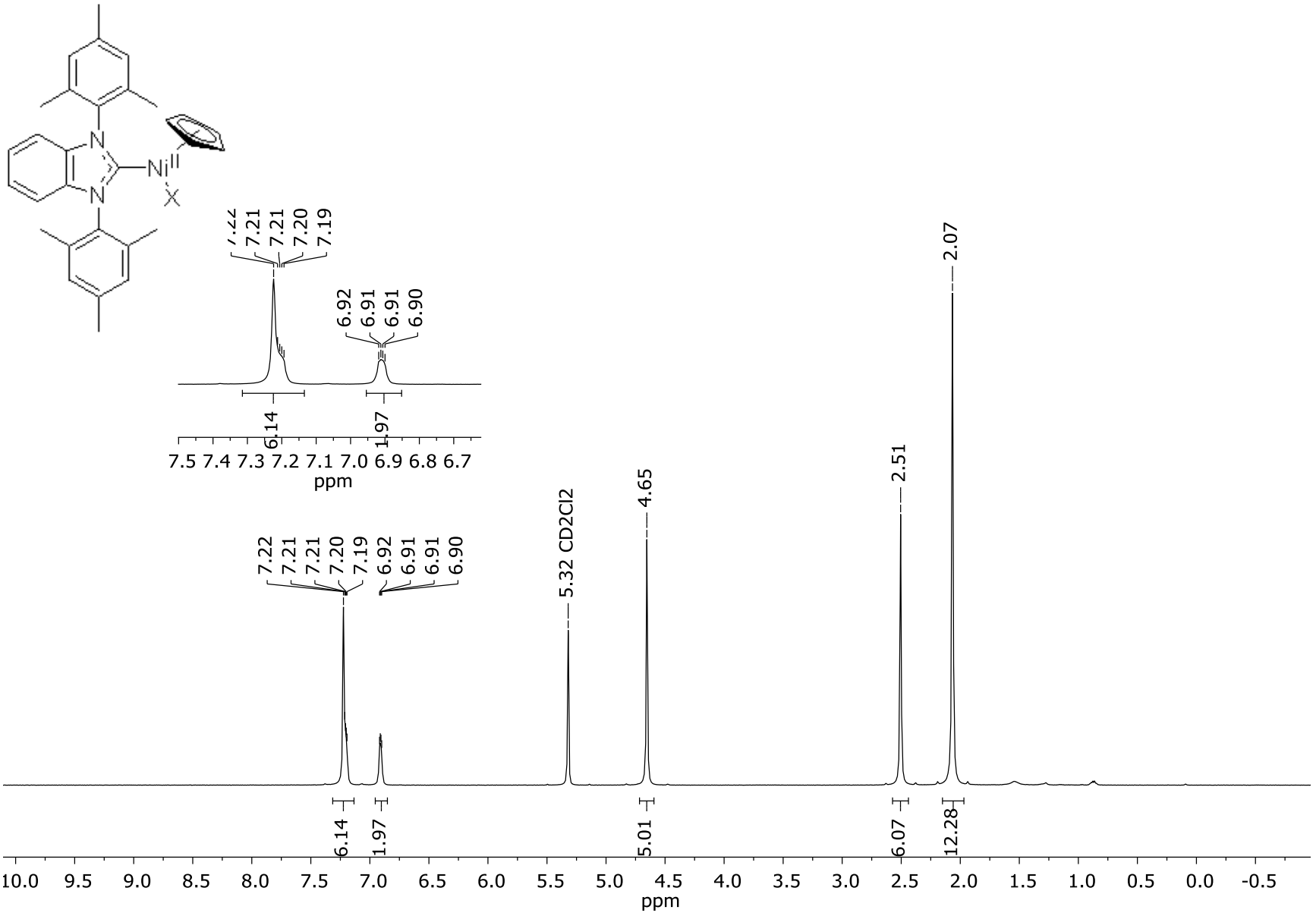


Figure S16. ^{1}H NMR spectrum of compound **3d** (CD_2Cl_2, 400 MHz)

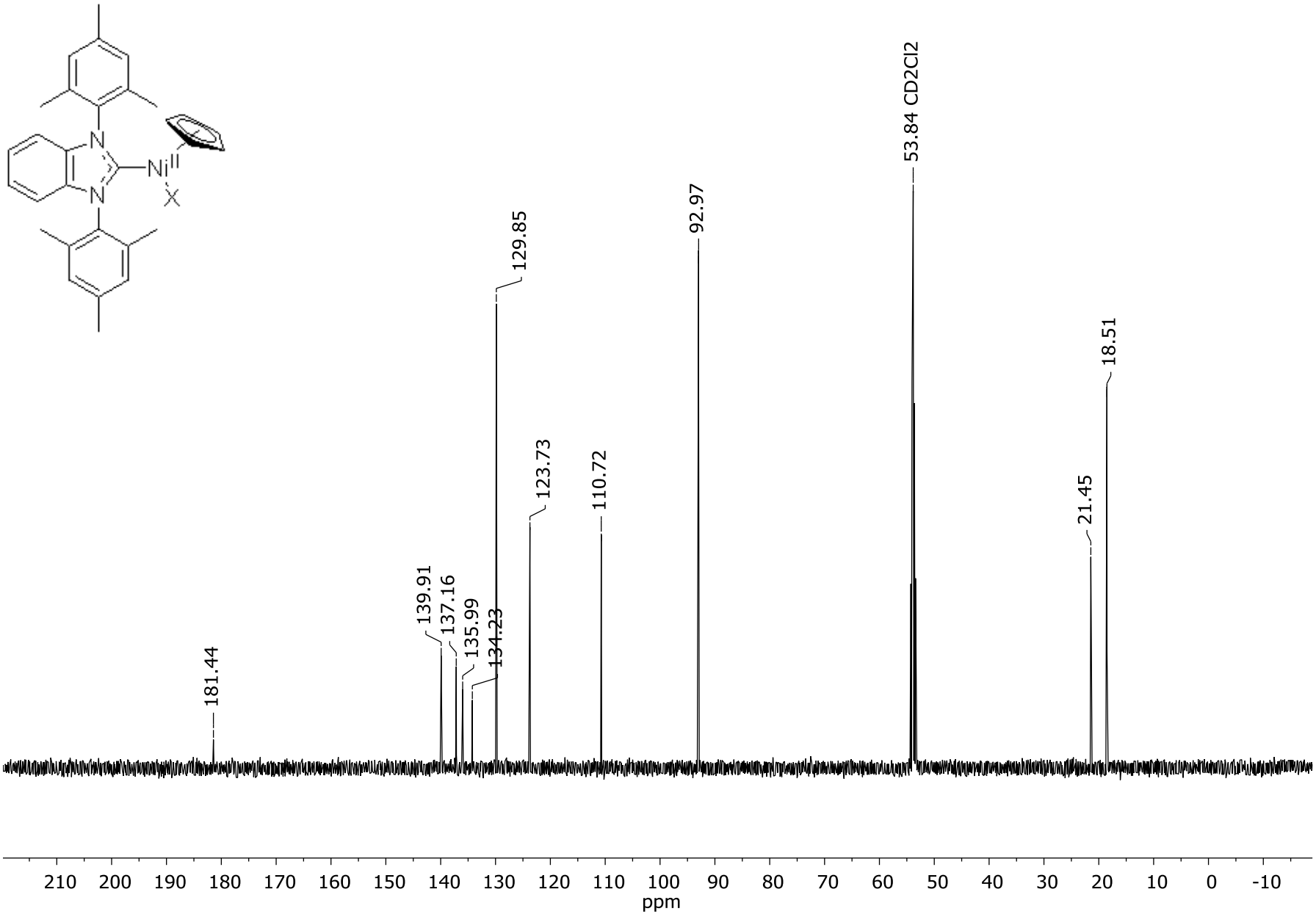


Figure S17. ^{13}C NMR spectrum of compound **3d** (CD_2Cl_2, 100 MHz)

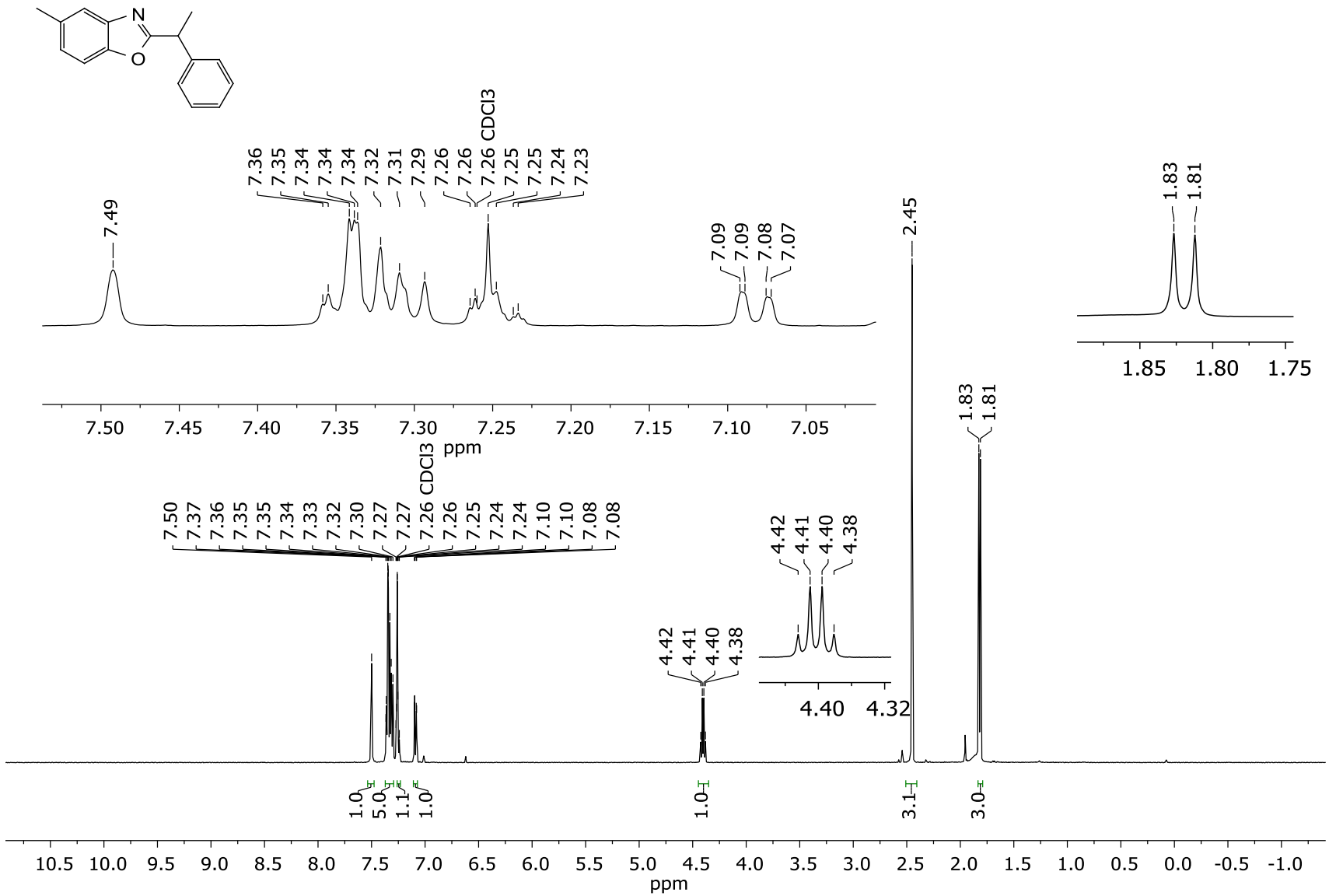


Figure S18. ^{1}H NMR spectrum of compound **4a** ($CDCl_3$, 300 MHz)

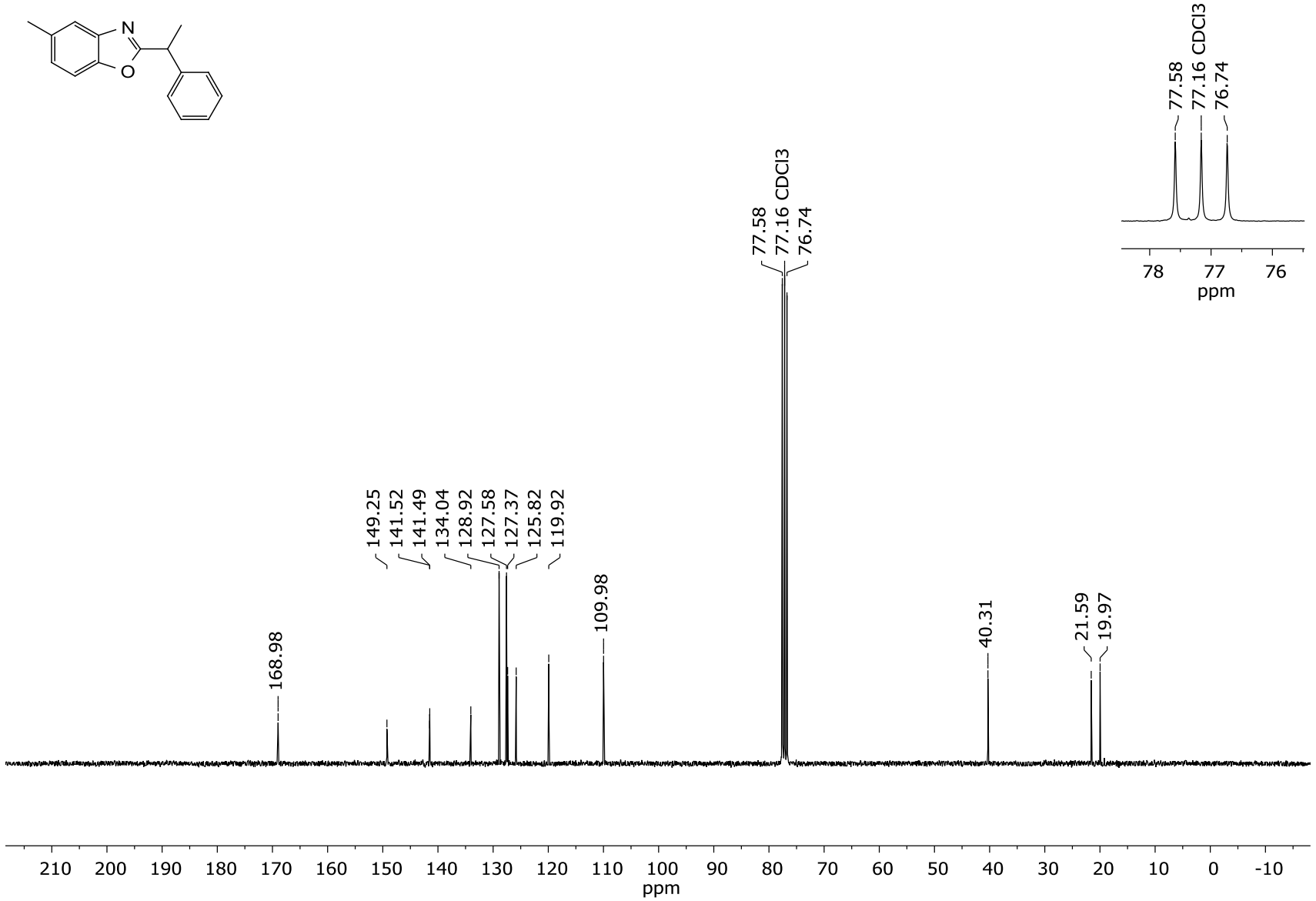


Figure S19. ^{13}C NMR spectrum of compound **4a** ($CDCl_3$, 75 MHz)

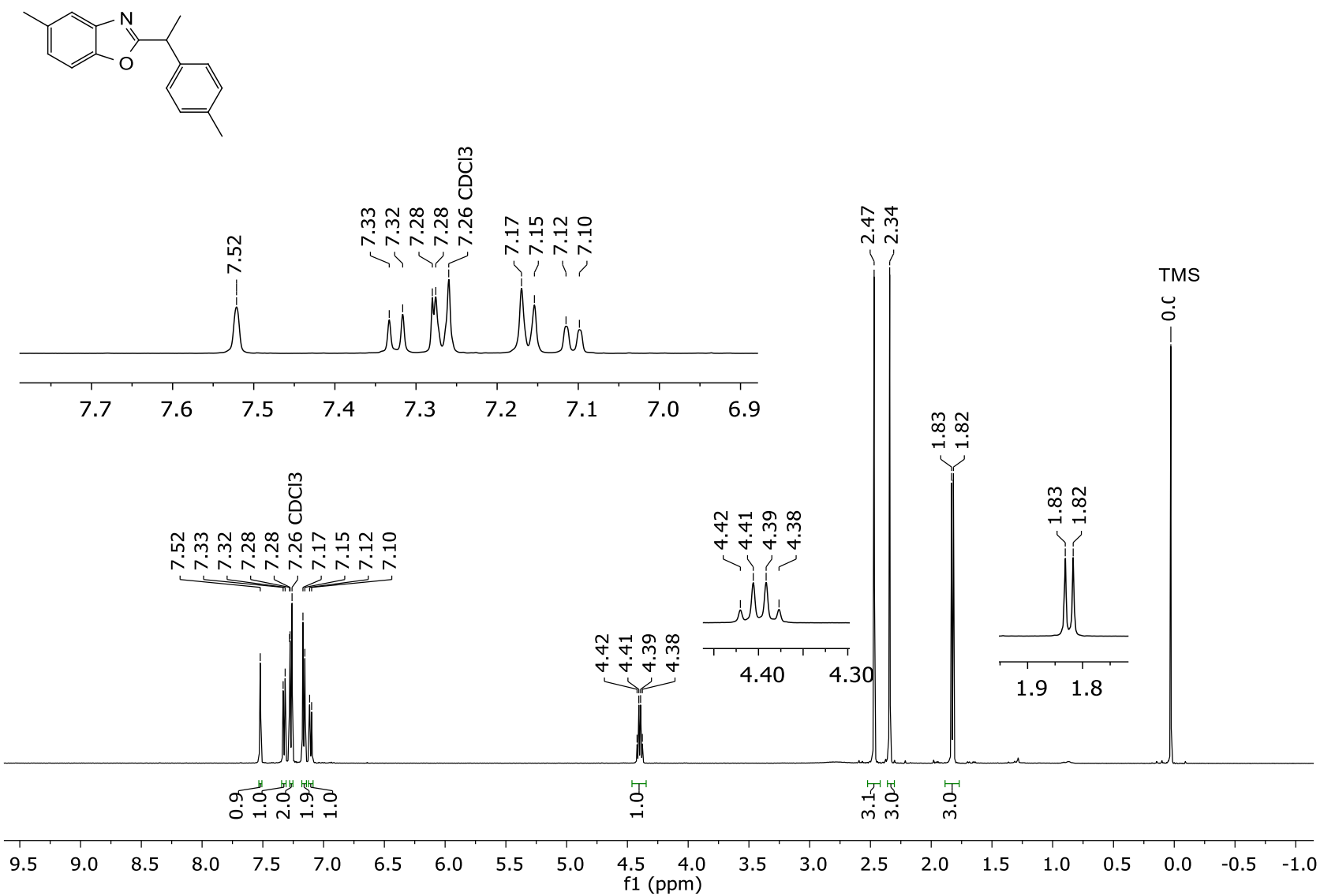


Figure S20. ^{1}H NMR spectrum of compound **4b** ($CDCl_3$, 600 MHz)

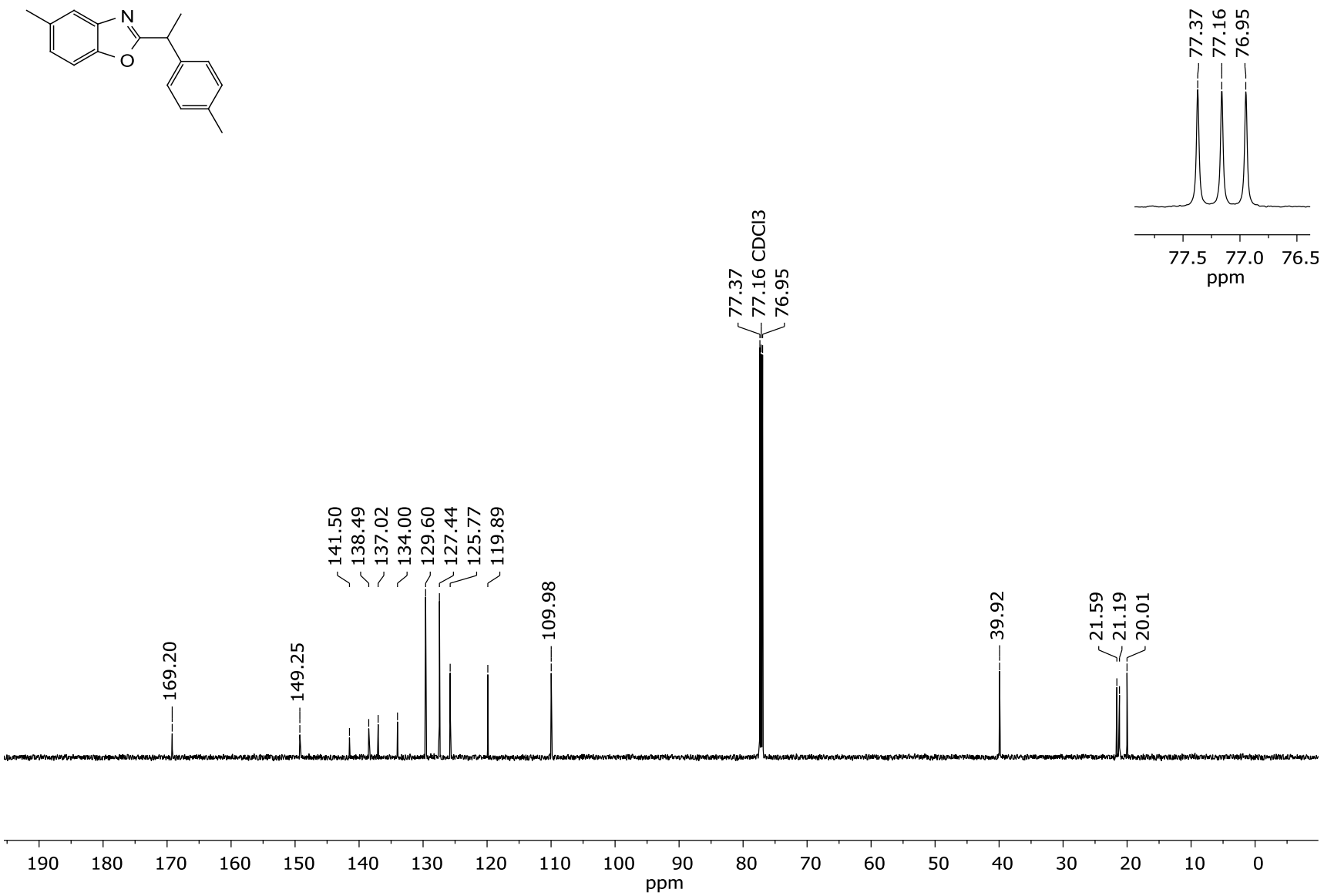


Figure S21. ^{13}C NMR spectrum of compound **4b** ($CDCl_3$, 150 MHz)

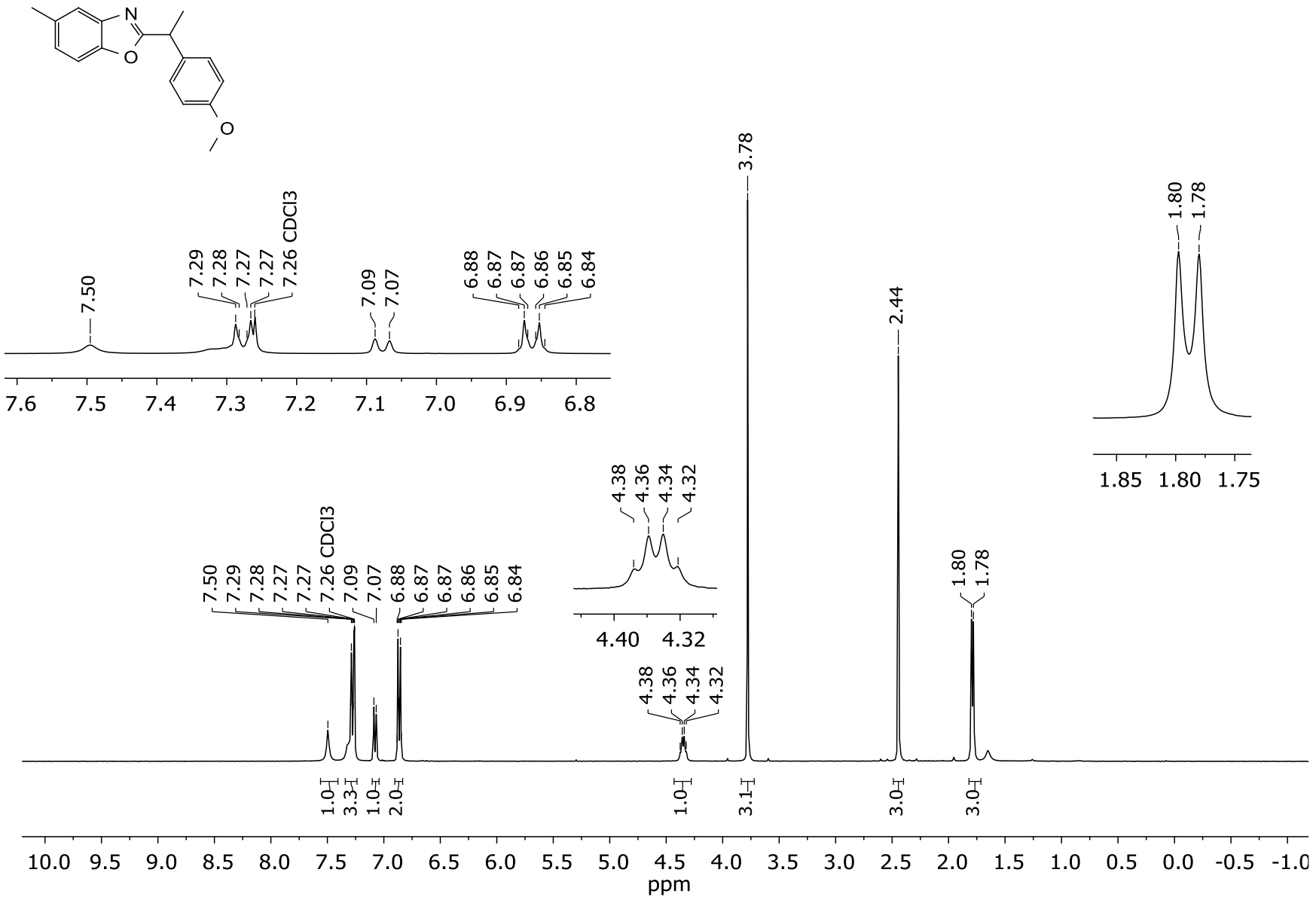


Figure S22. ^{1}H NMR spectrum of compound **4c** ($CDCl_3$, 400 MHz)

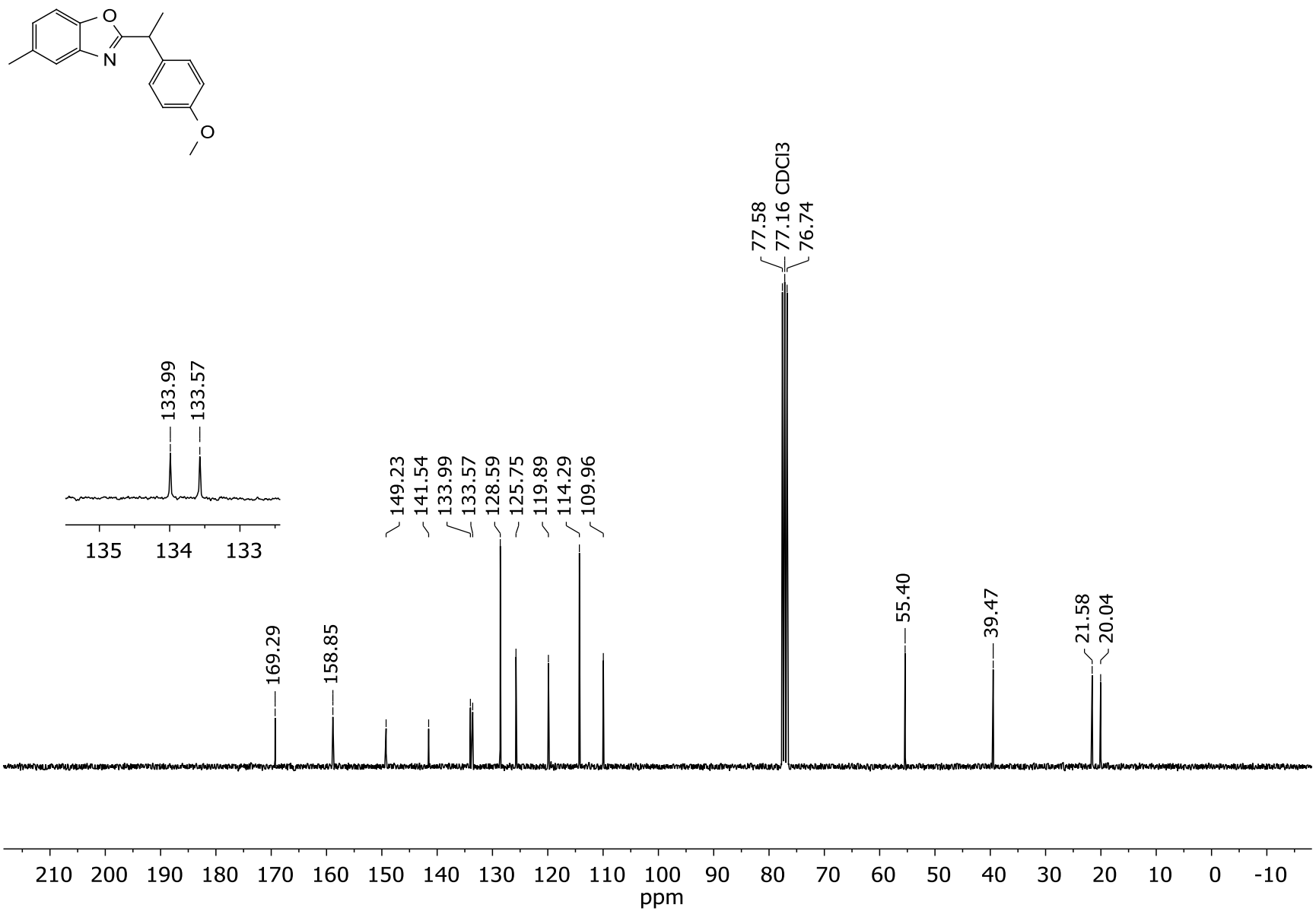


Figure S23. ^{13}C NMR spectrum of compound **4c** ($CDCl_3$, 100 MHz)

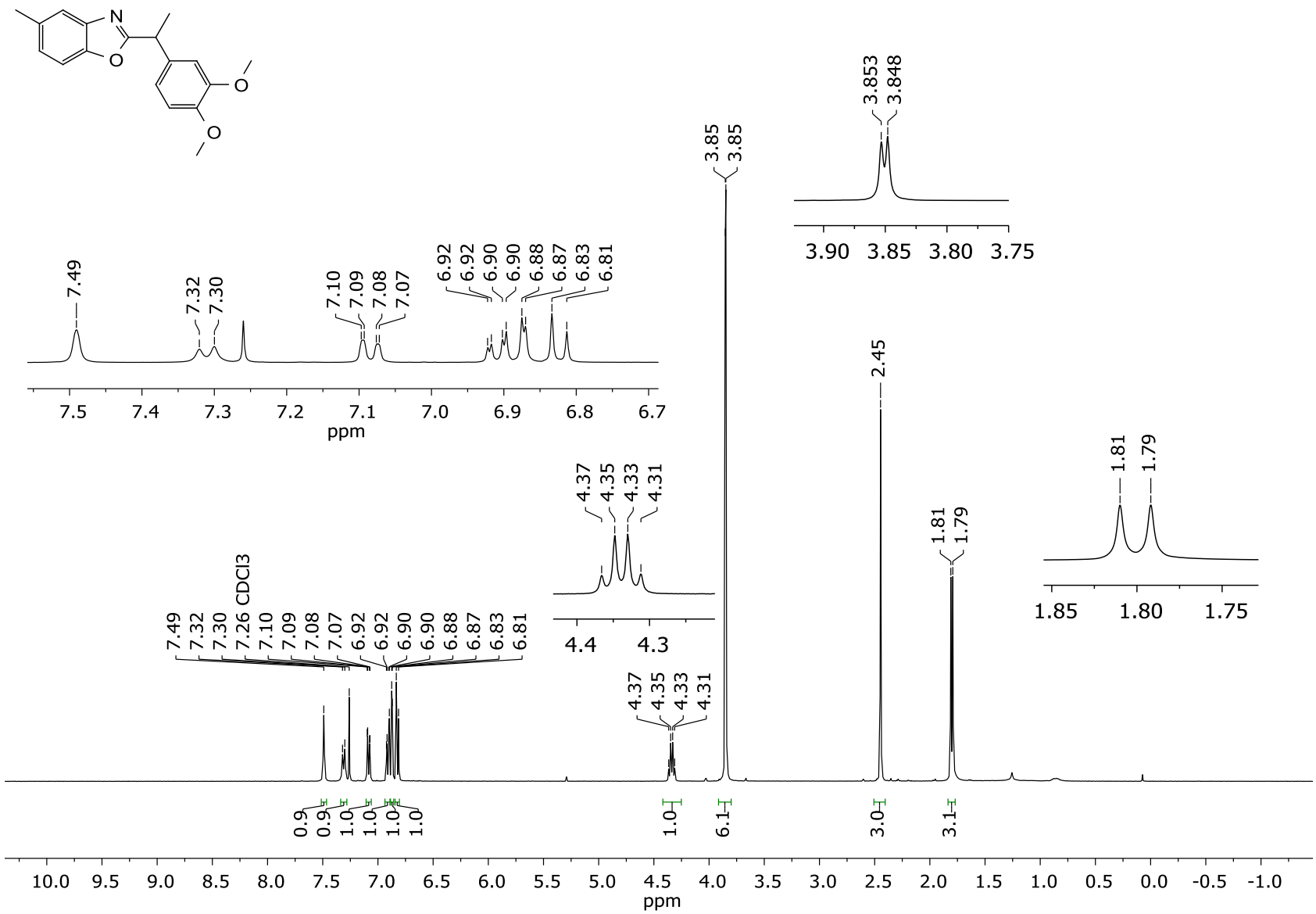


Figure S24. ^{1}H NMR spectrum of compound **4d** ($CDCl_3$, 400 MHz)

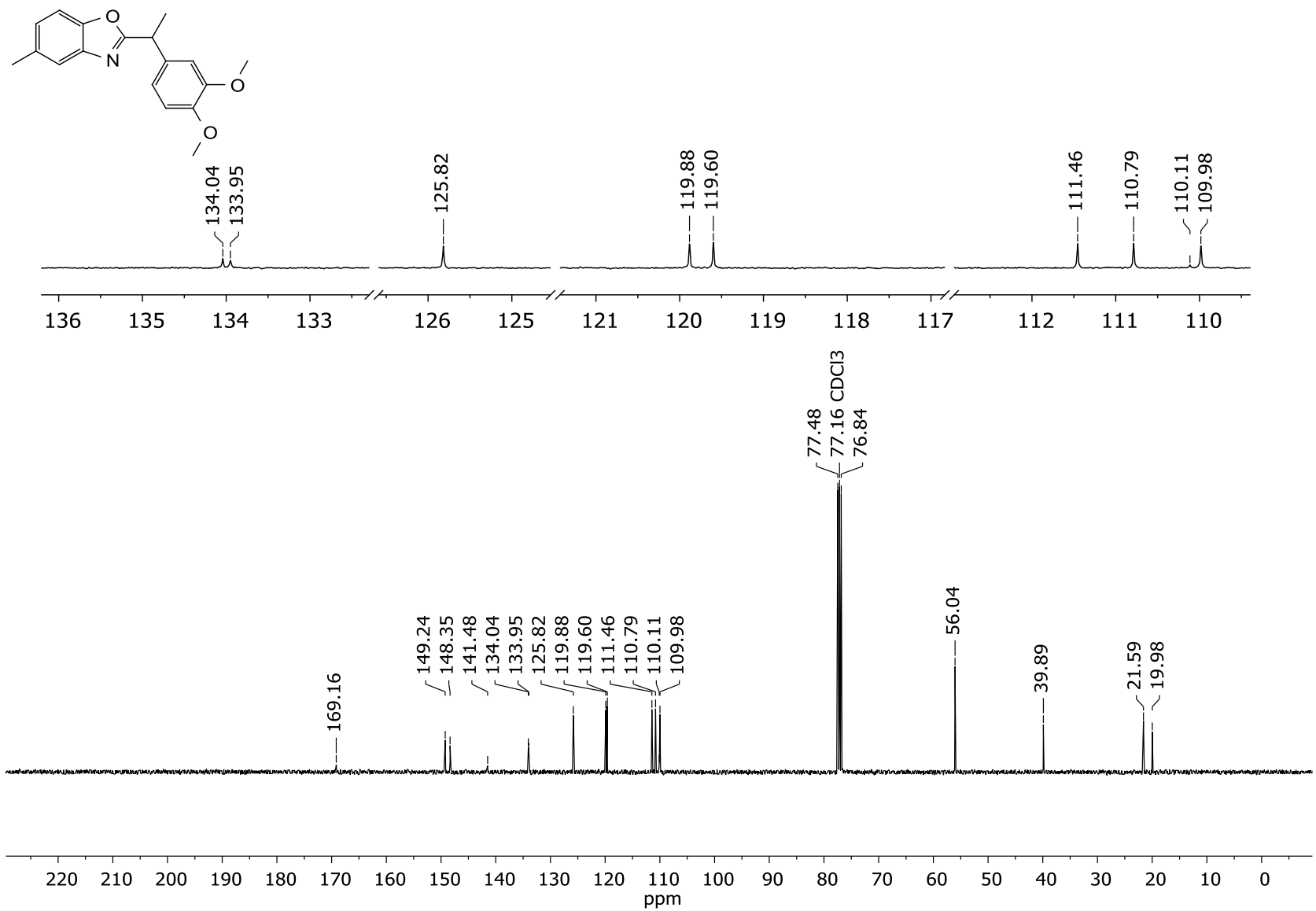


Figure S25. ^{13}C NMR spectrum of compound **4d** ($CDCl_3$, 100 MHz)

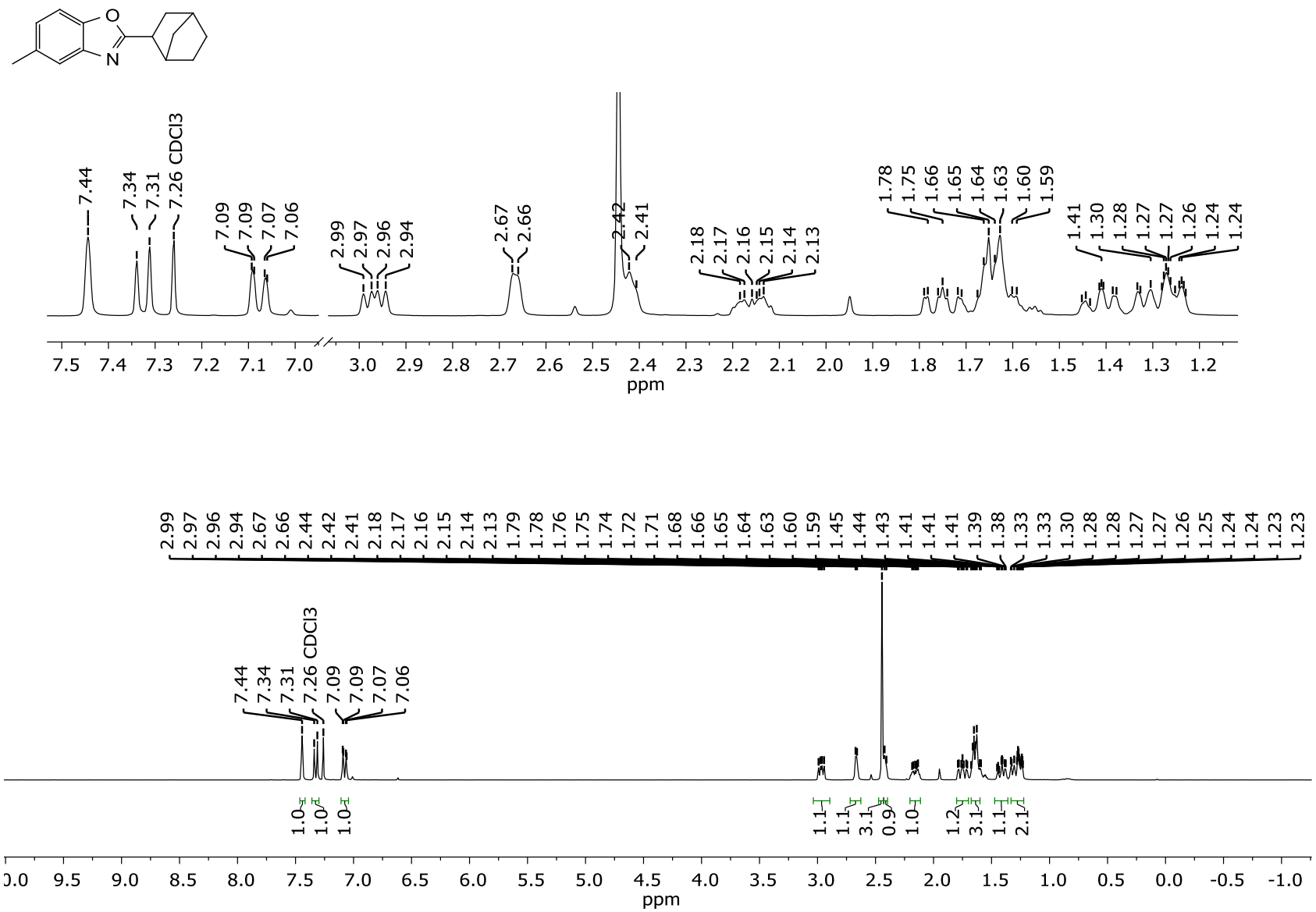


Figure S26. ^{1}H NMR spectrum of compound **4e** ($CDCl_3$, 300 MHz)

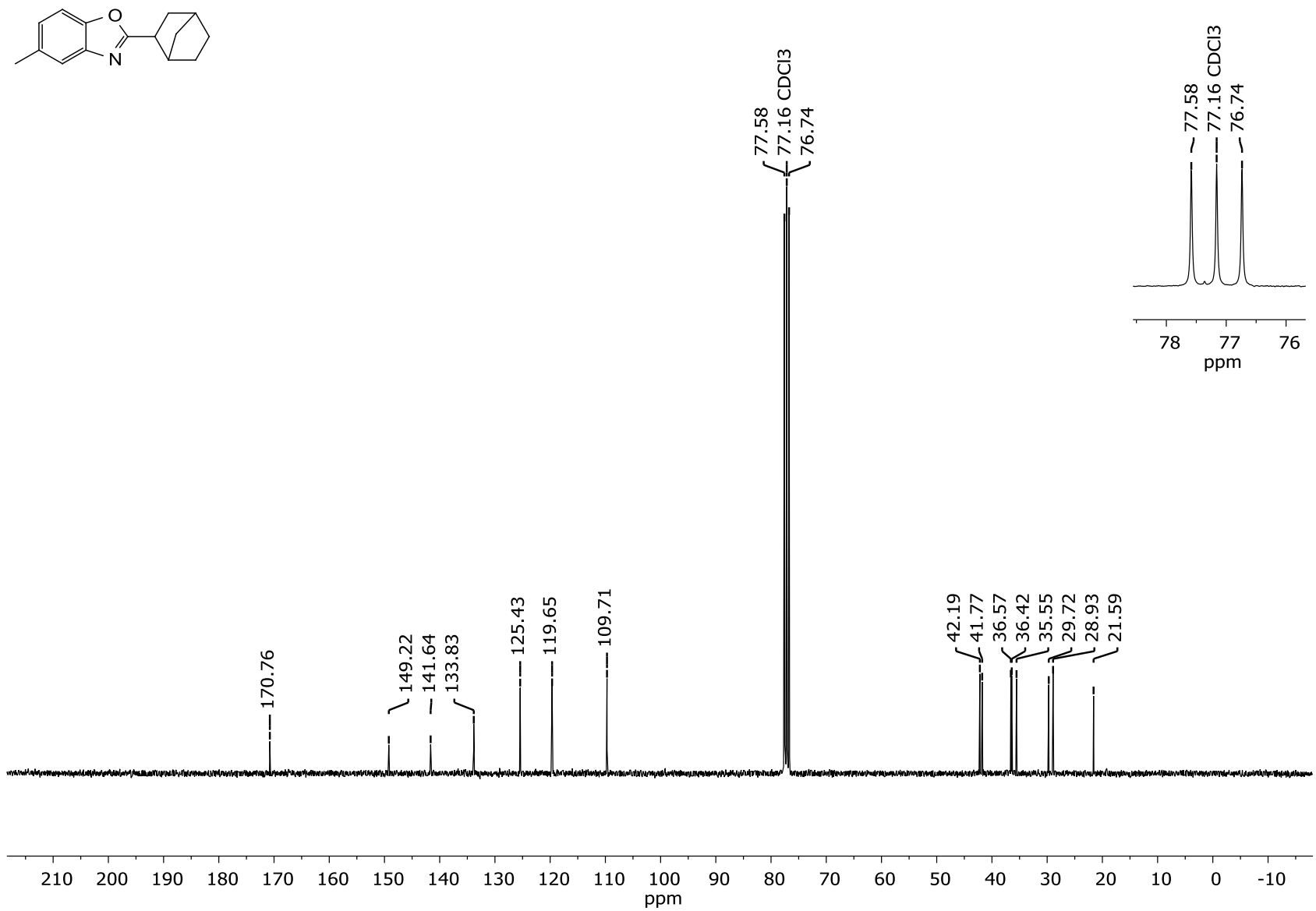


Figure S27. ^{13}C NMR spectrum of compound **4e** ($CDCl_3$, 75 MHz)

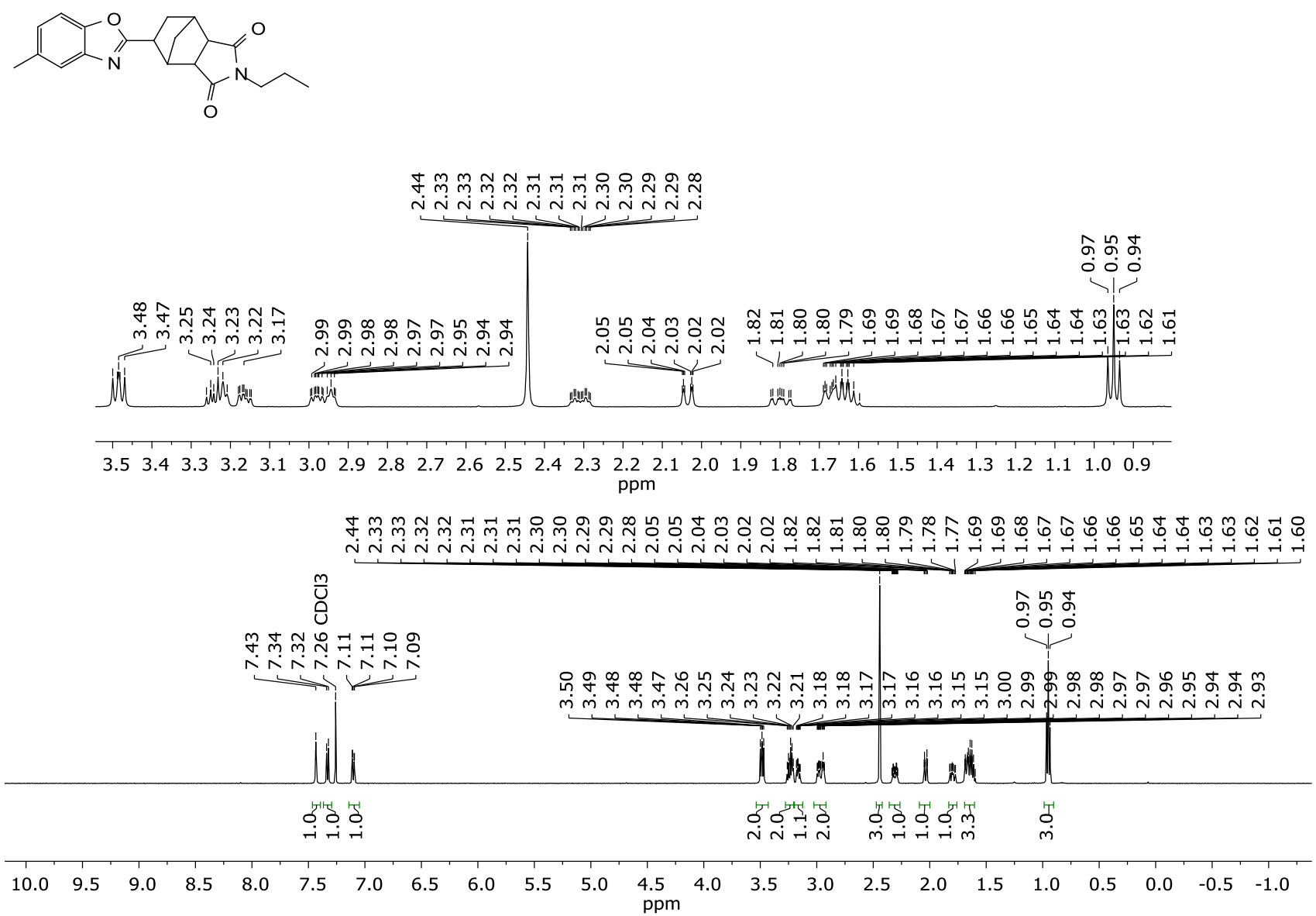


Figure S28. ^{1}H NMR spectrum of compound **4f** ($CDCl_3$, 500 MHz)

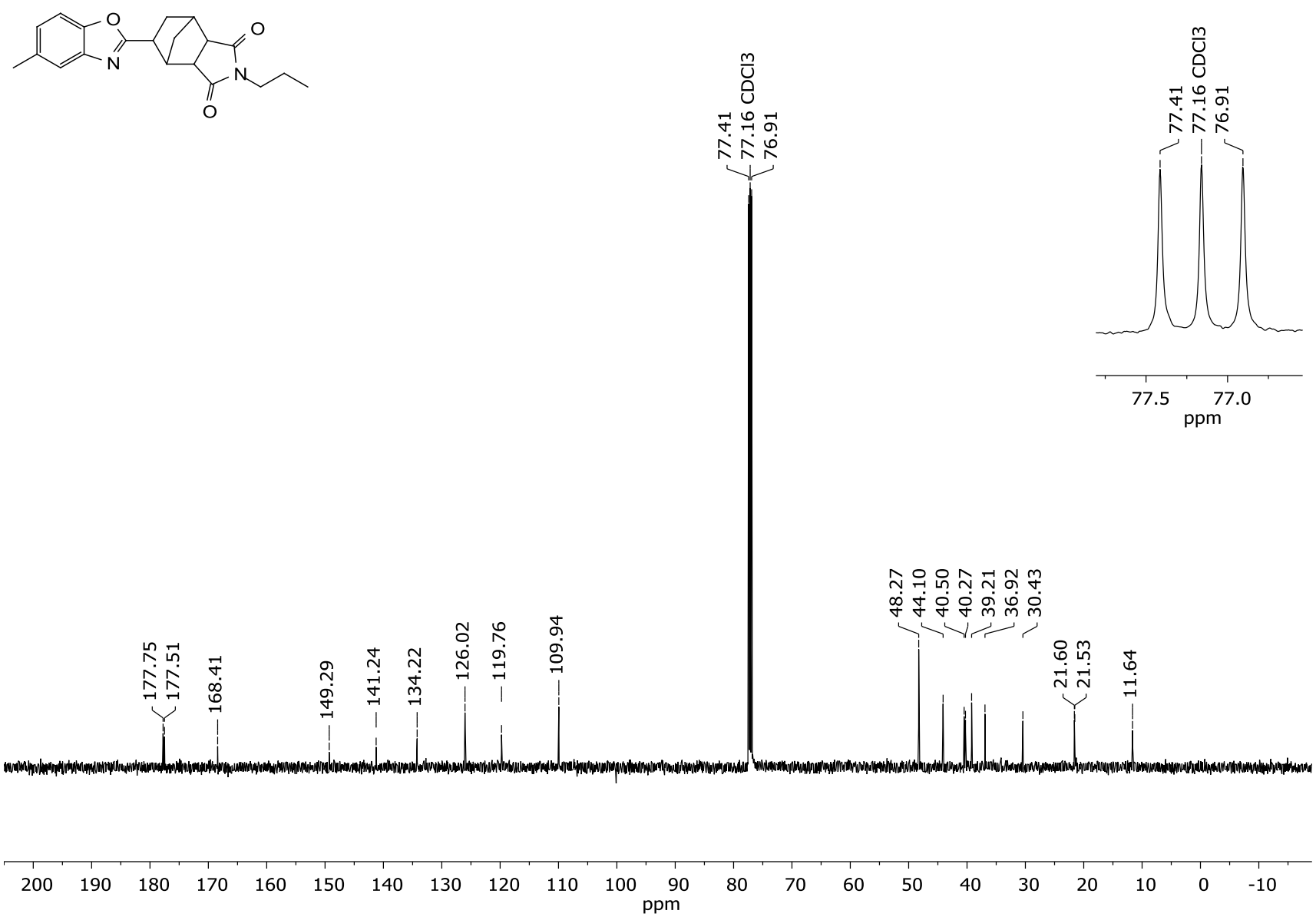


Figure S29. ^{13}C NMR spectrum of compound **4f** ($CDCl_3$, 125 MHz)

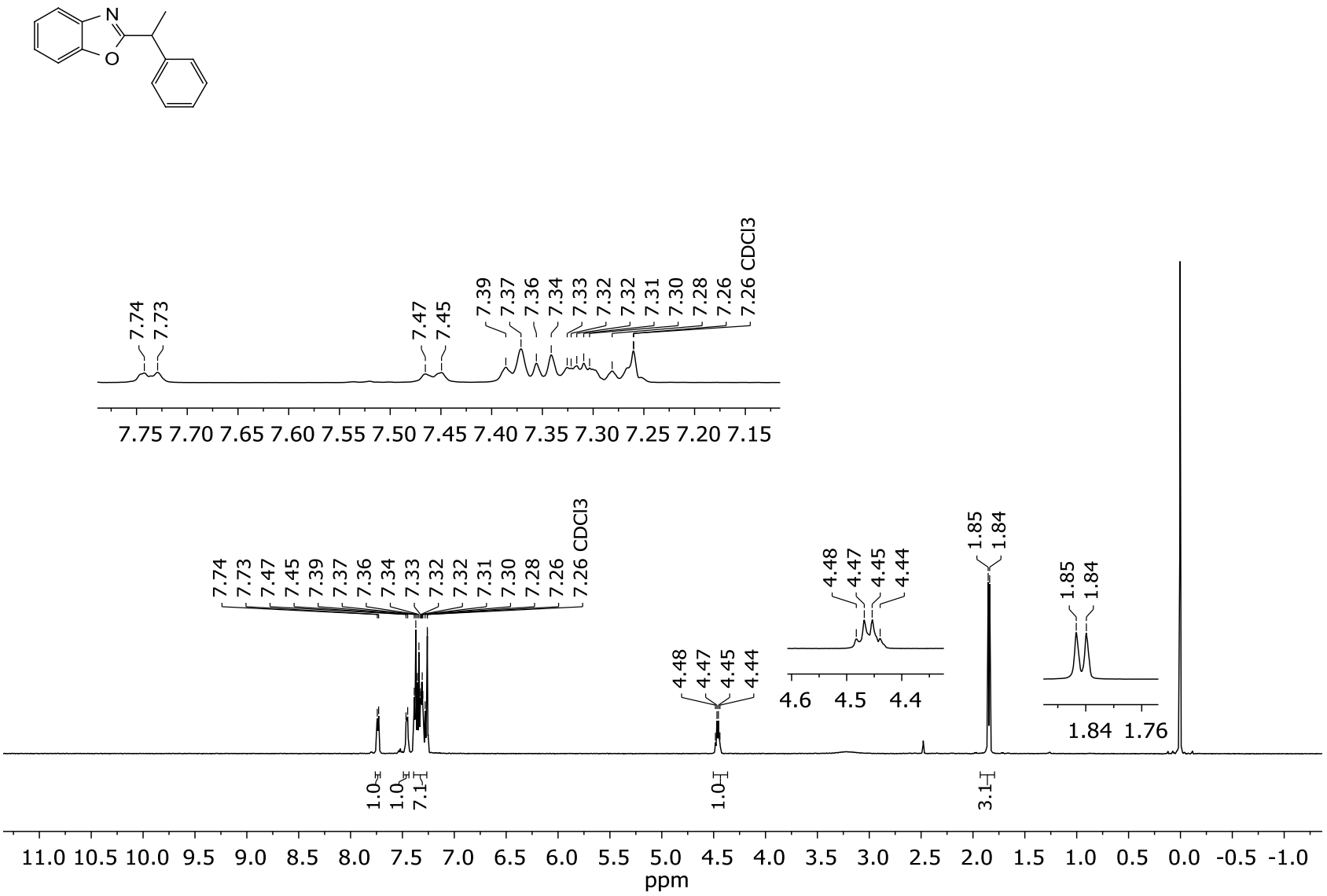


Figure S30. ^{1}H NMR spectrum of compound **4g** ($CDCl_3$, 500 MHz)

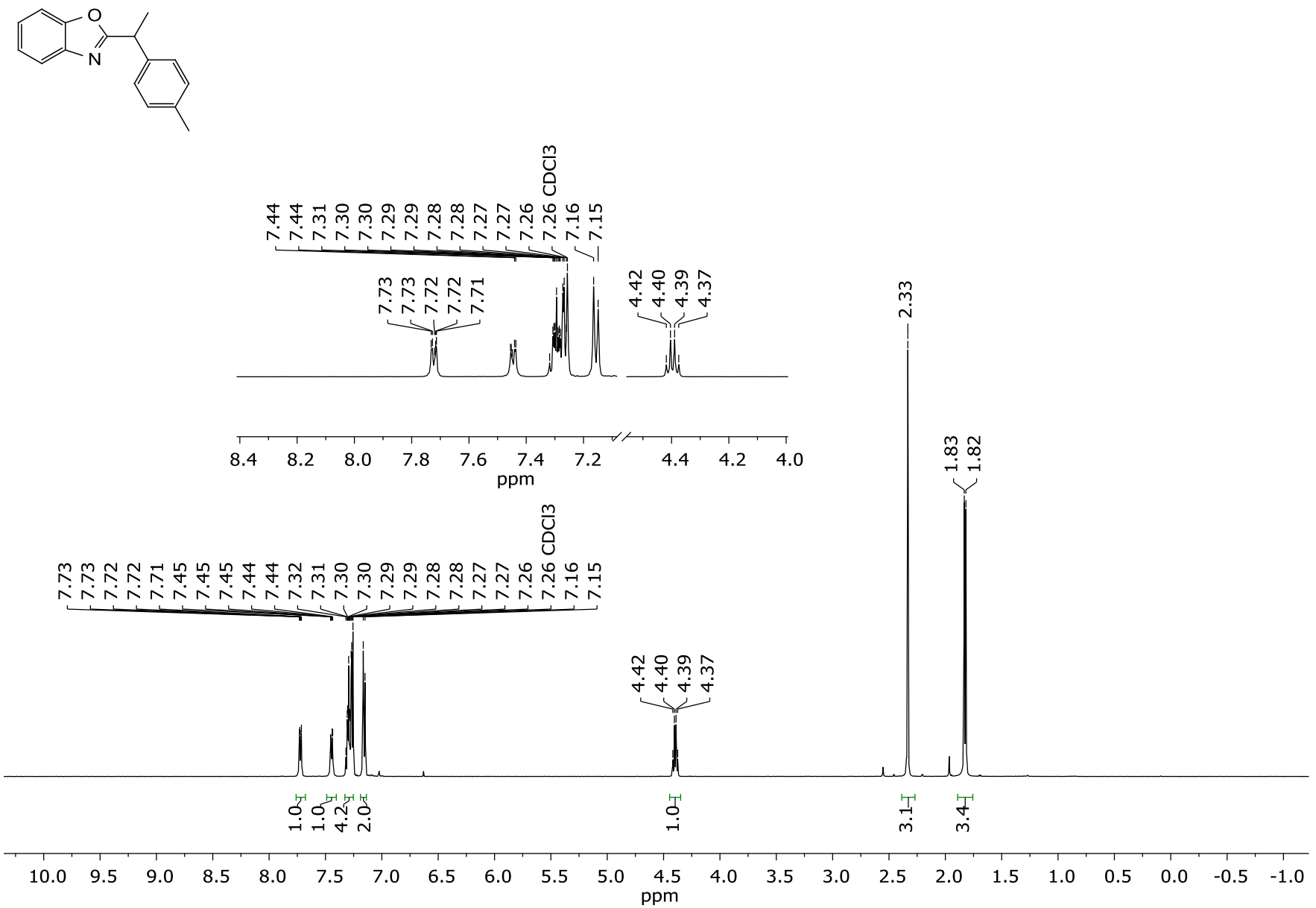


Figure S31. ^{1}H NMR spectrum of compound **4h** ($CDCl_3$, 500 MHz)

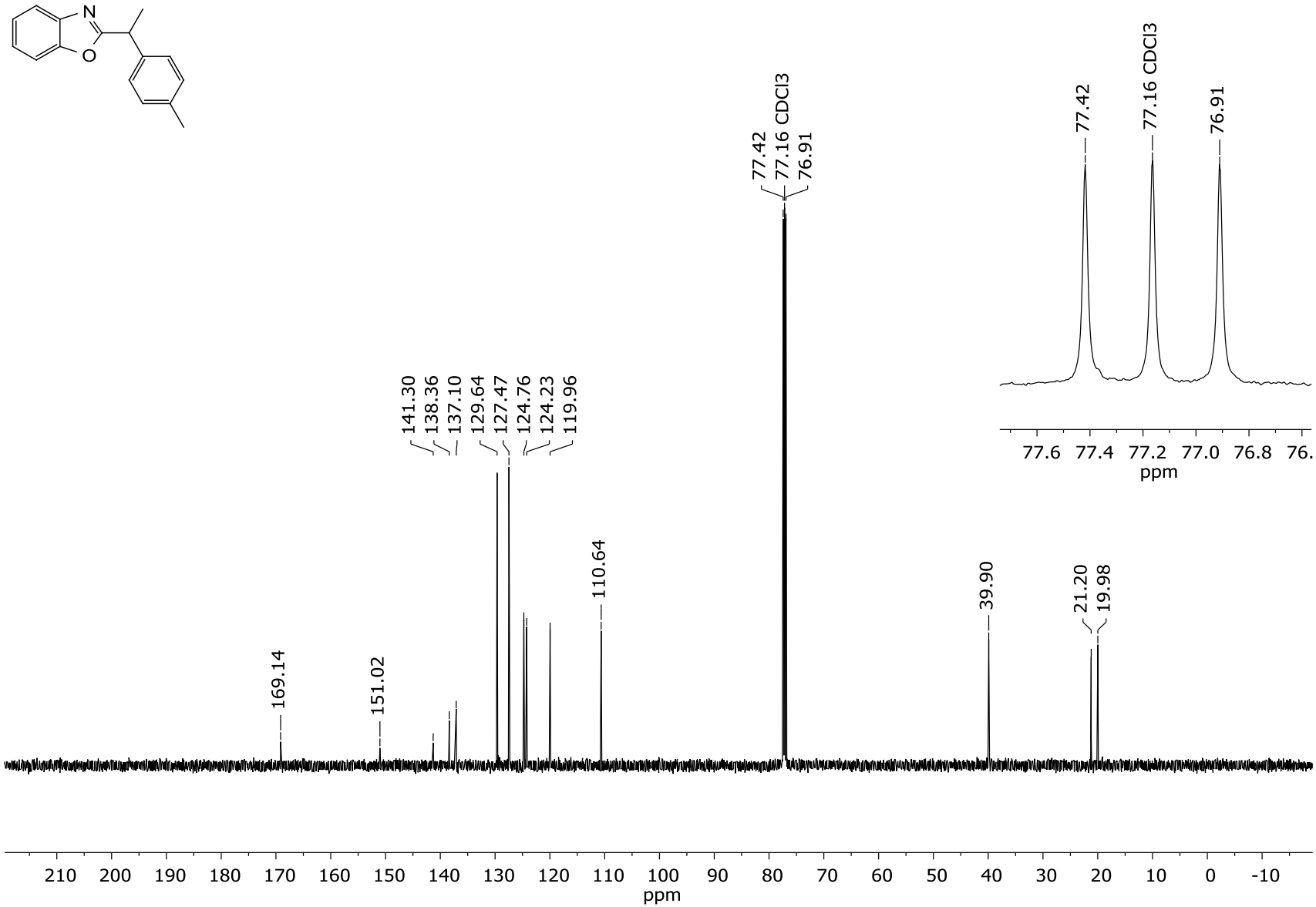


Figure S32. ^{13}C NMR spectrum of compound **4h** ($CDCl_3$, 125 MHz)

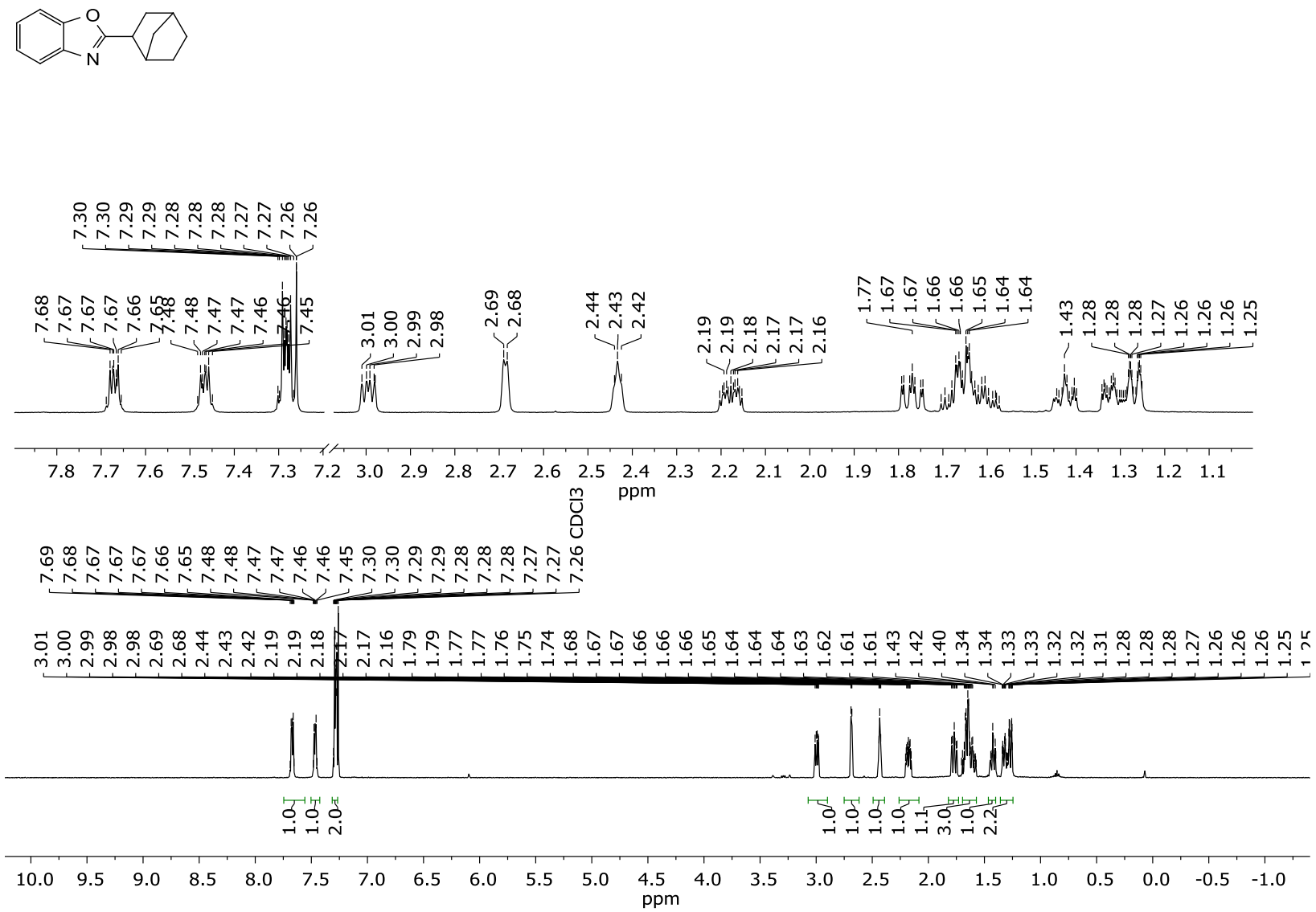


Figure S33. ^{1}H NMR spectrum of compound **4i** ($CDCl_3$, 500 MHz)

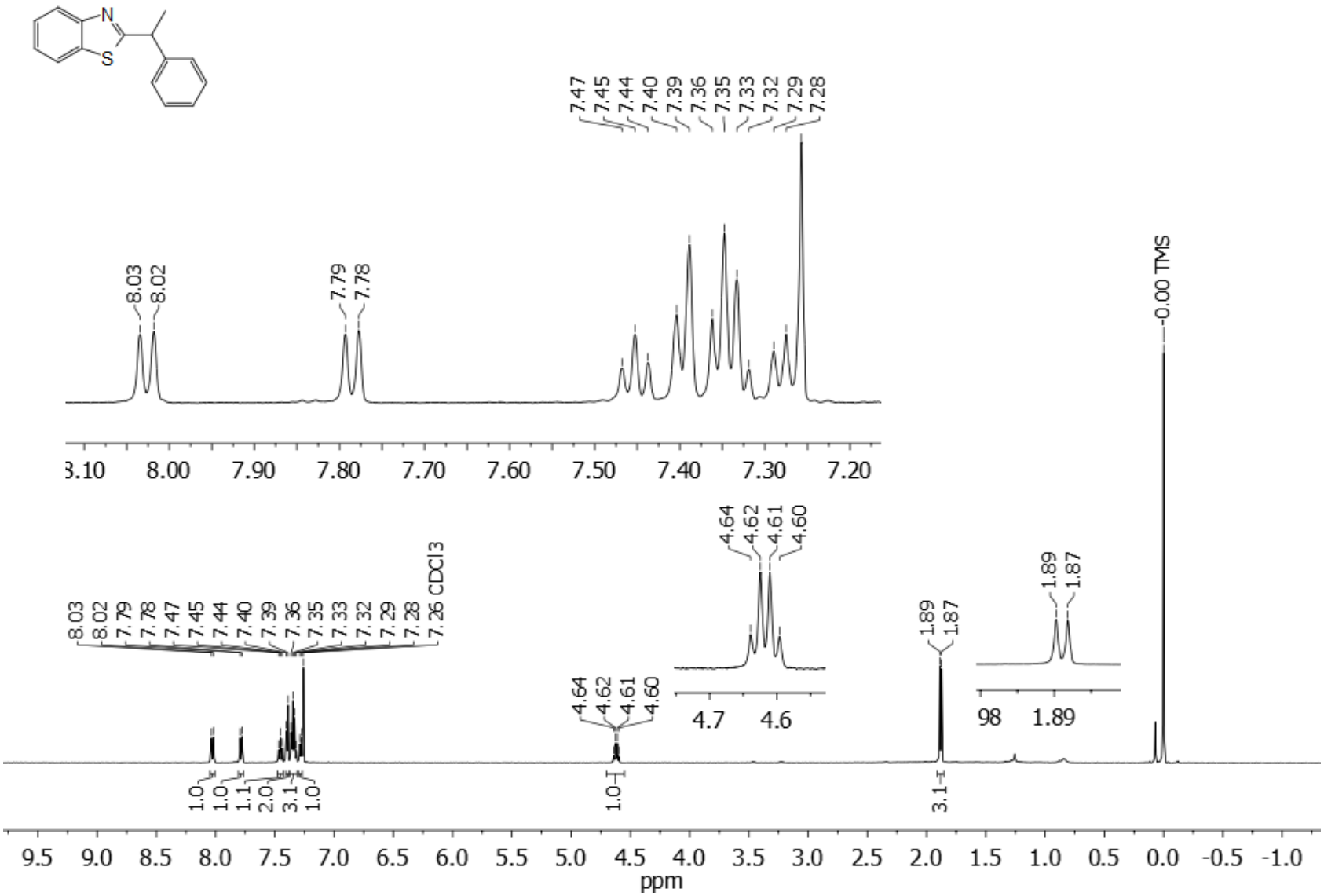


Figure S34. ^{1}H NMR spectrum of compound **4j** ($CDCl_3$, 125 MHz)

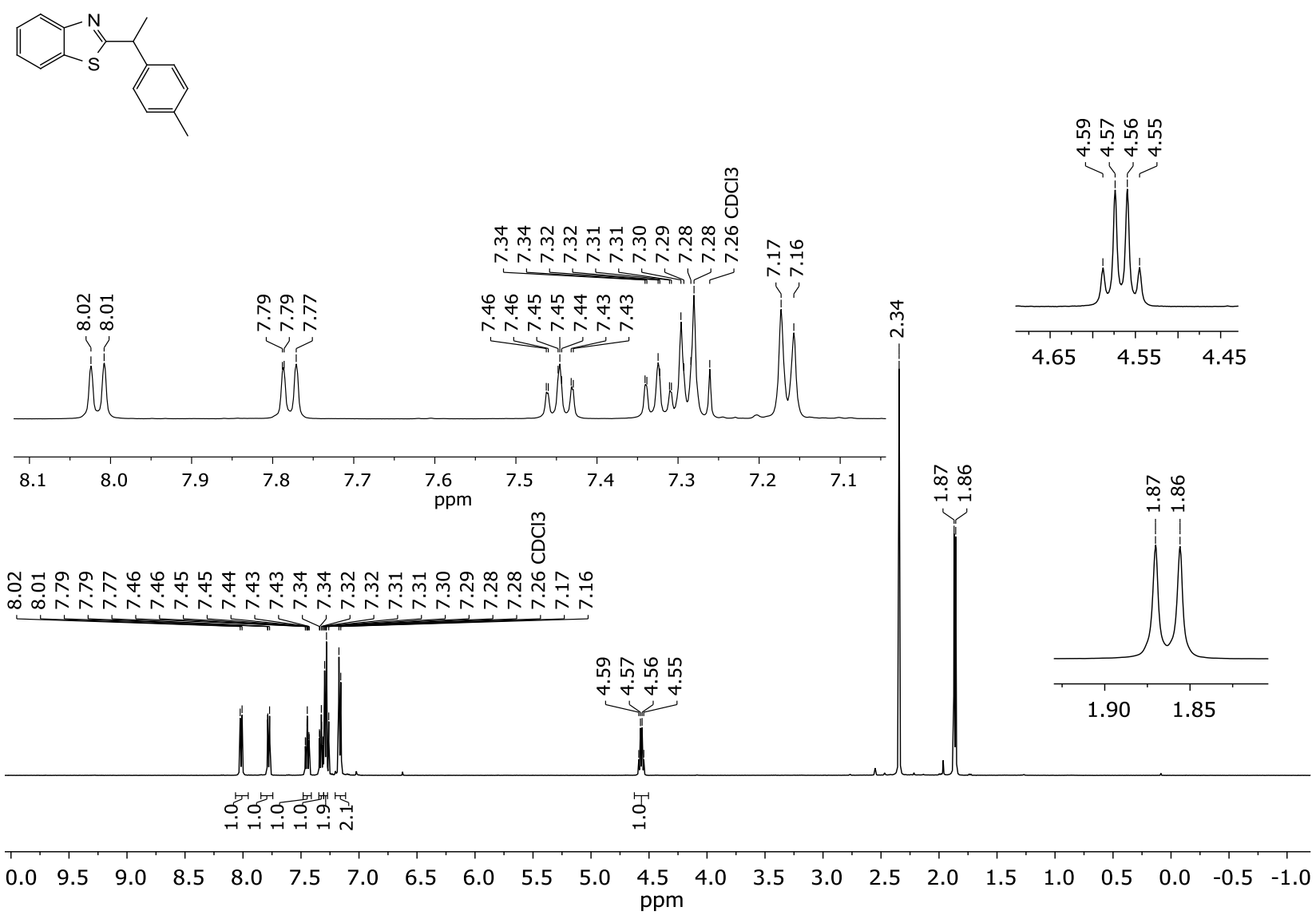


Figure S35. ^{1}H NMR spectrum of compound **4k** ($CDCl_3$, 500 MHz)

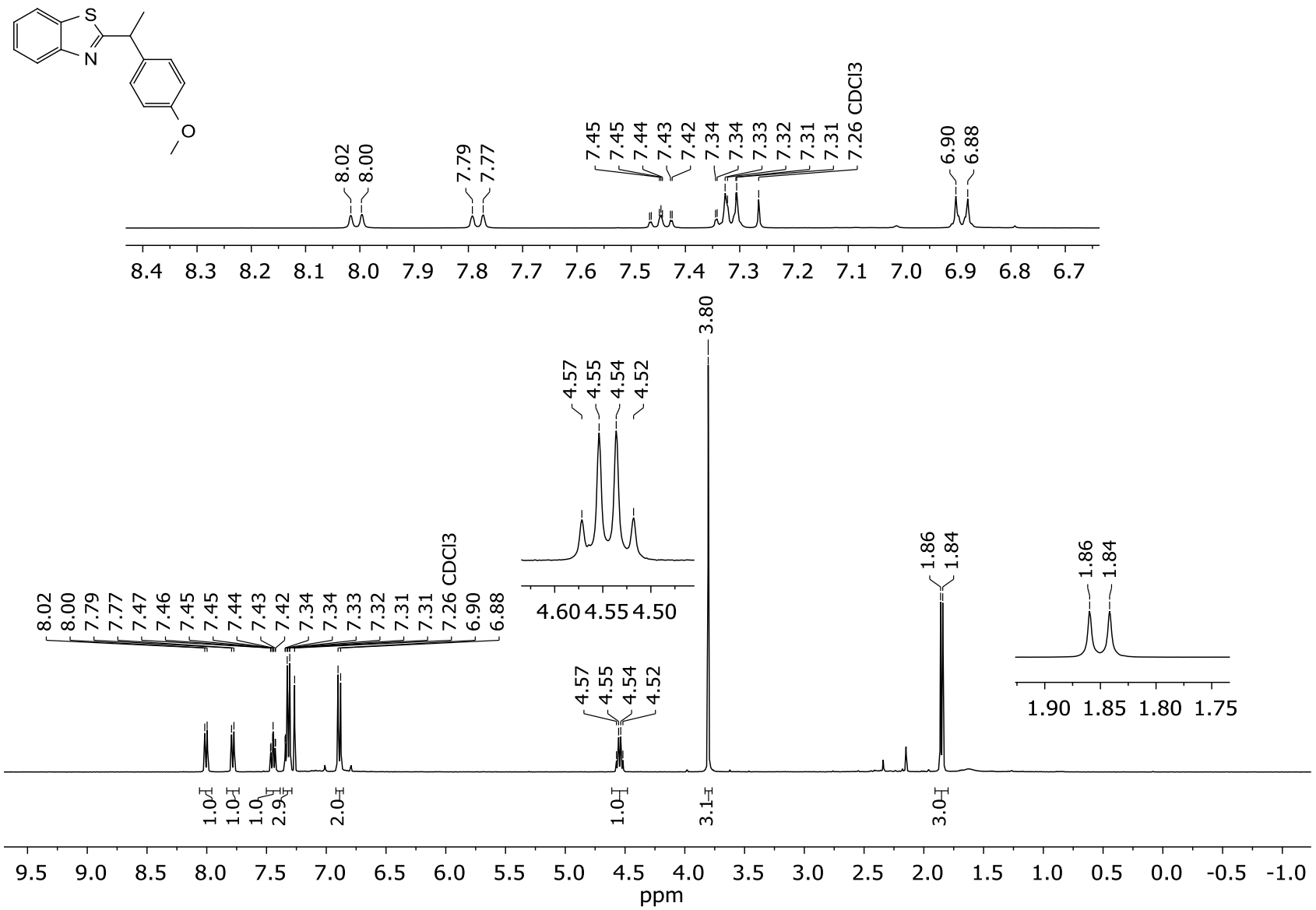


Figure S36. ^{1}H NMR spectrum of compound **4l** ($CDCl_3$, 400 MHz)

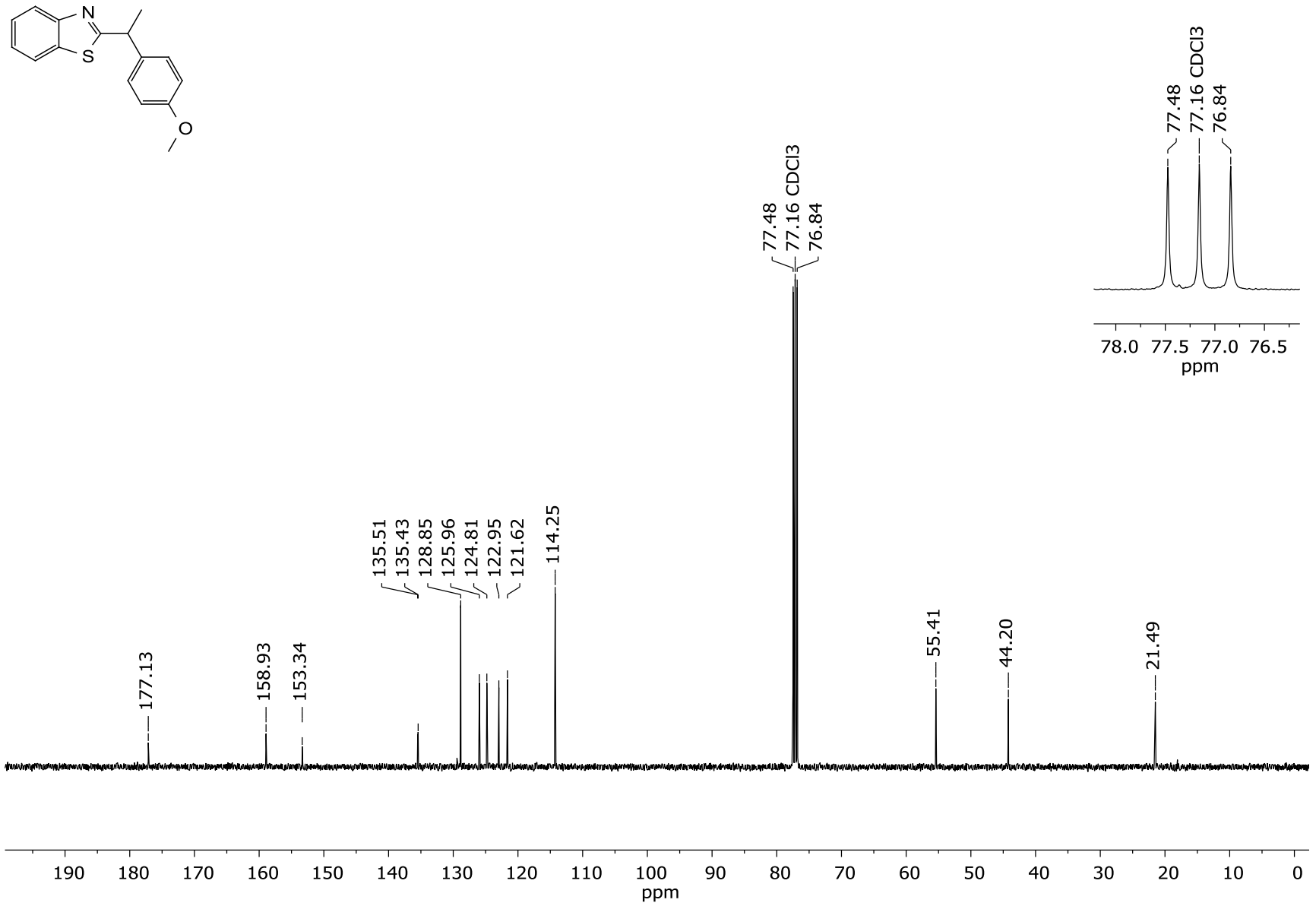


Figure S37. ^{13}C NMR spectrum of compound **4l** ($CDCl_3$, 100 MHz)

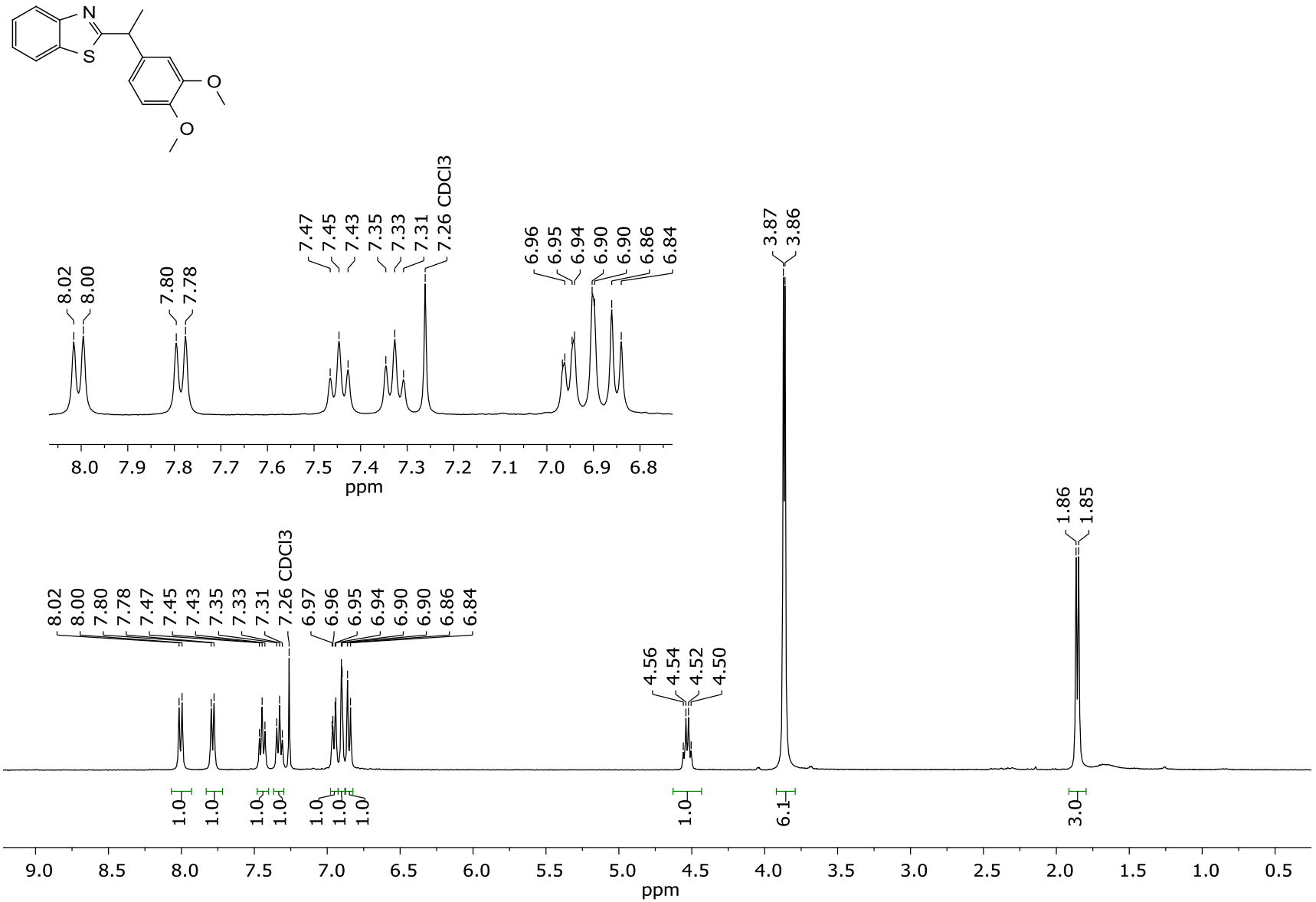


Figure S38. ^{1}H NMR spectrum of compound **4m** ($CDCl_3$, 400 MHz)

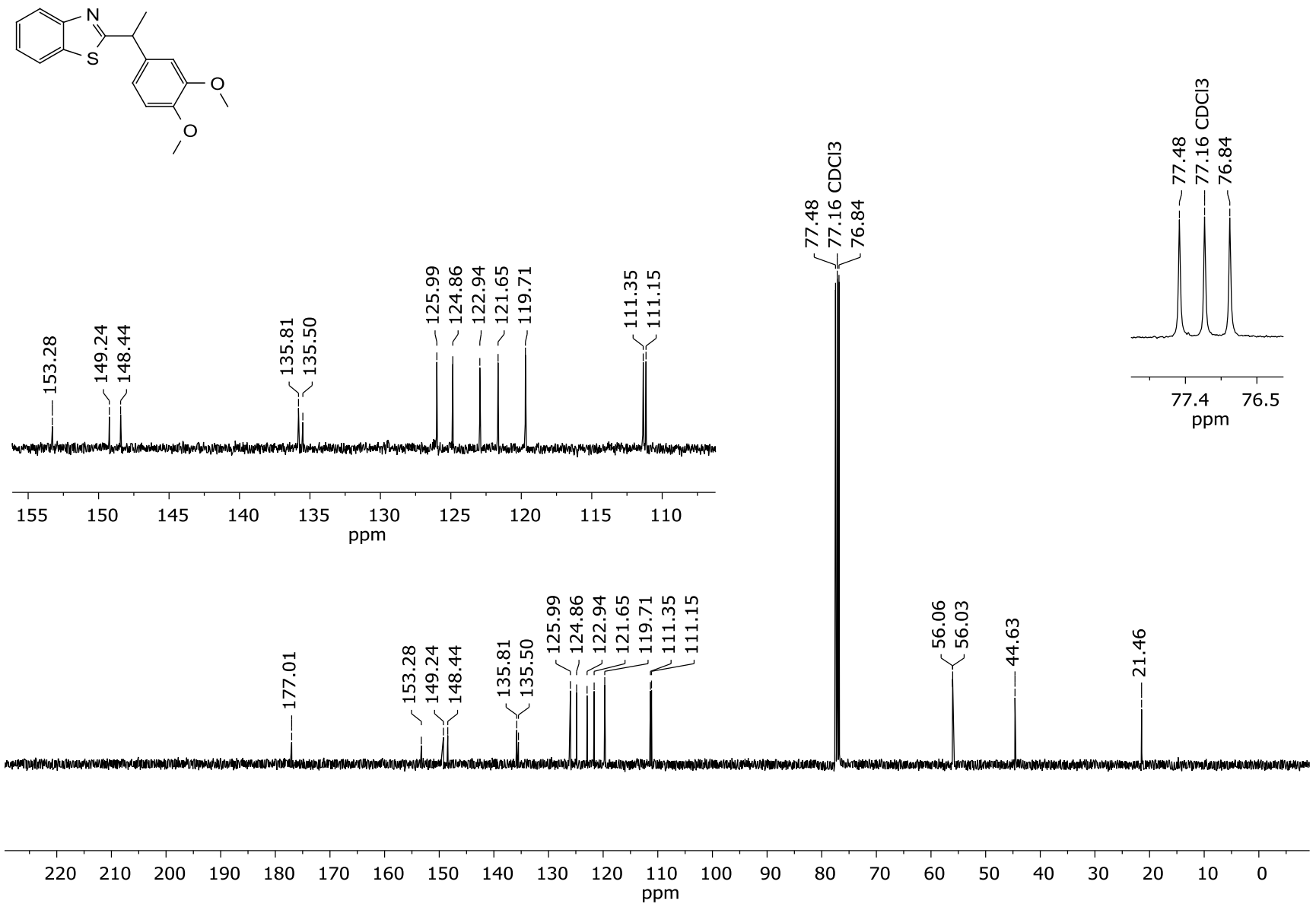


Figure S39. ^{13}C NMR spectrum of compound **4m** ($CDCl_3$, 100 MHz)

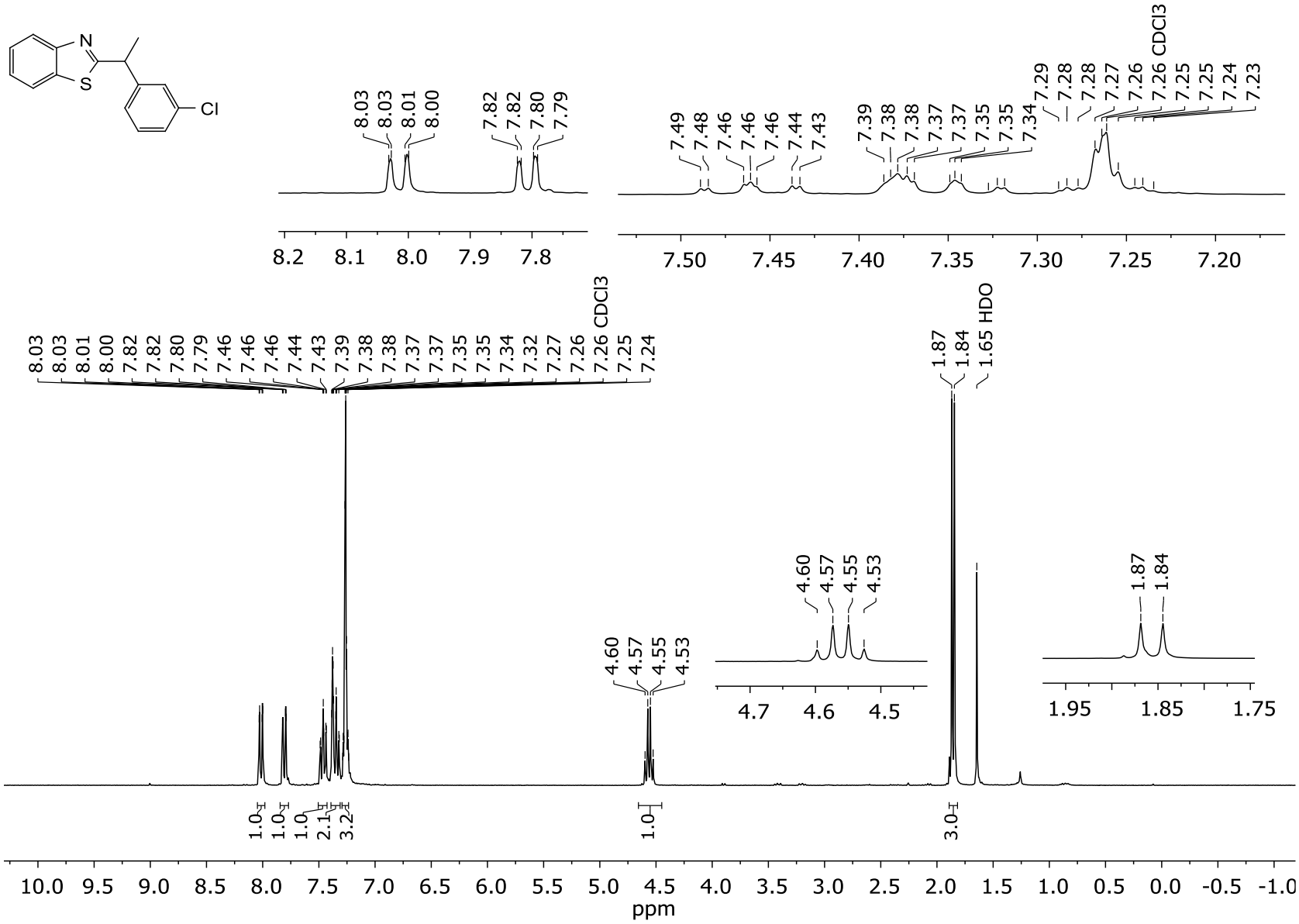


Figure S40. ^{1}H NMR spectrum of compound **4n** ($CDCl_3$, 300 MHz)

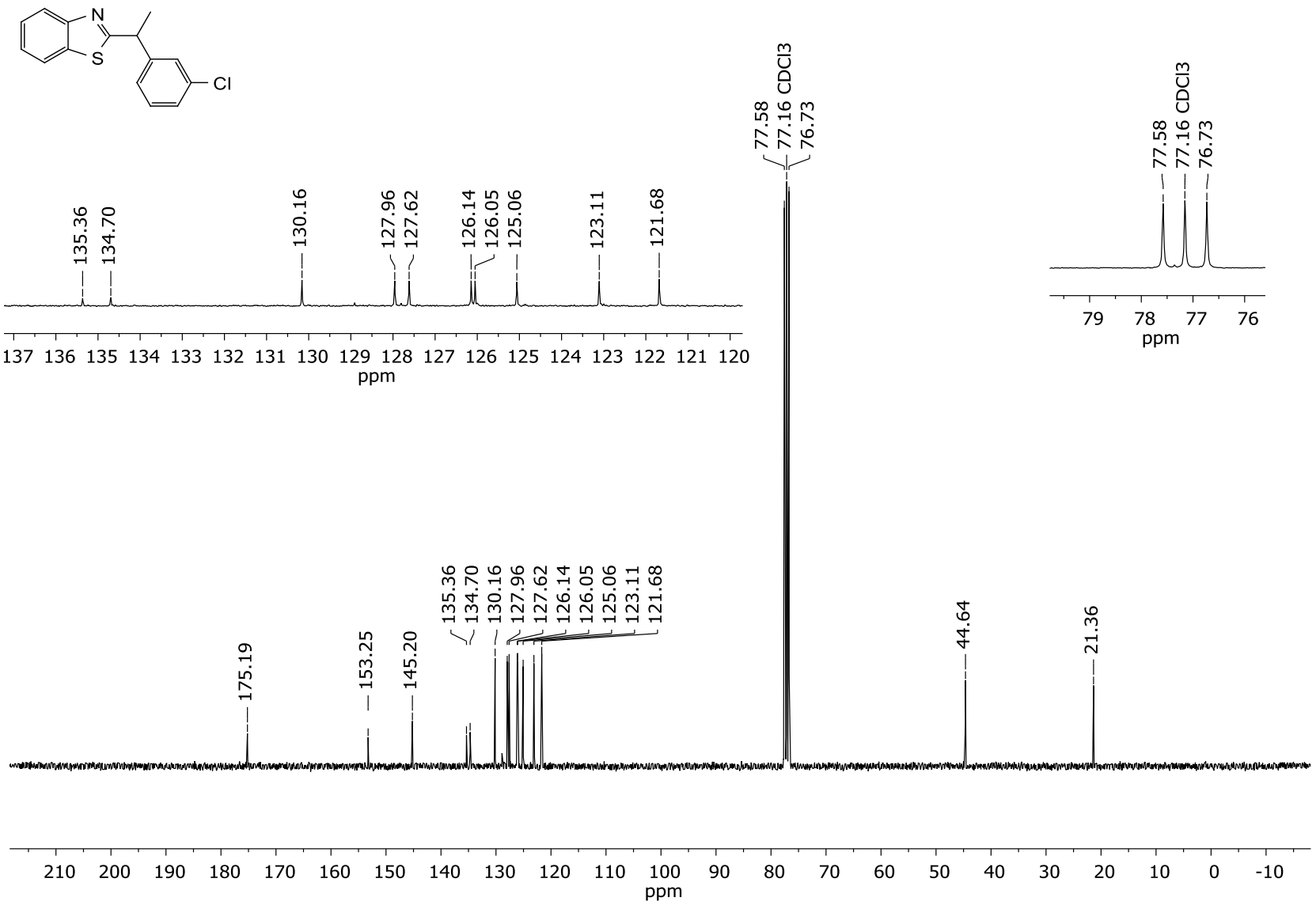


Figure S41. ^{13}C NMR spectrum of compound **4n** ($CDCl_3$, 75 MHz)

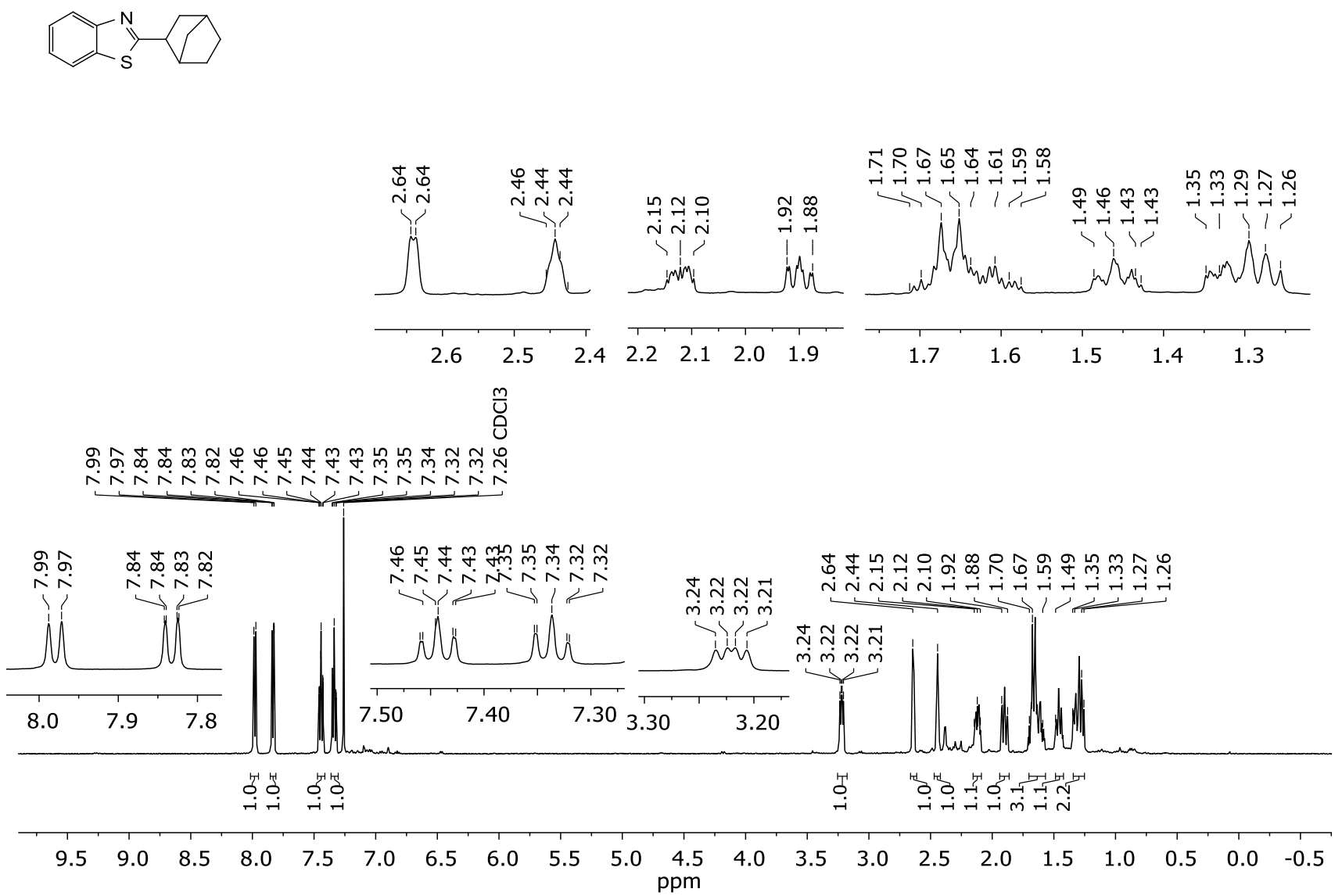


Figure S42. ^{1}H NMR spectrum of compound **4o** ($CDCl_3$, 500 MHz)

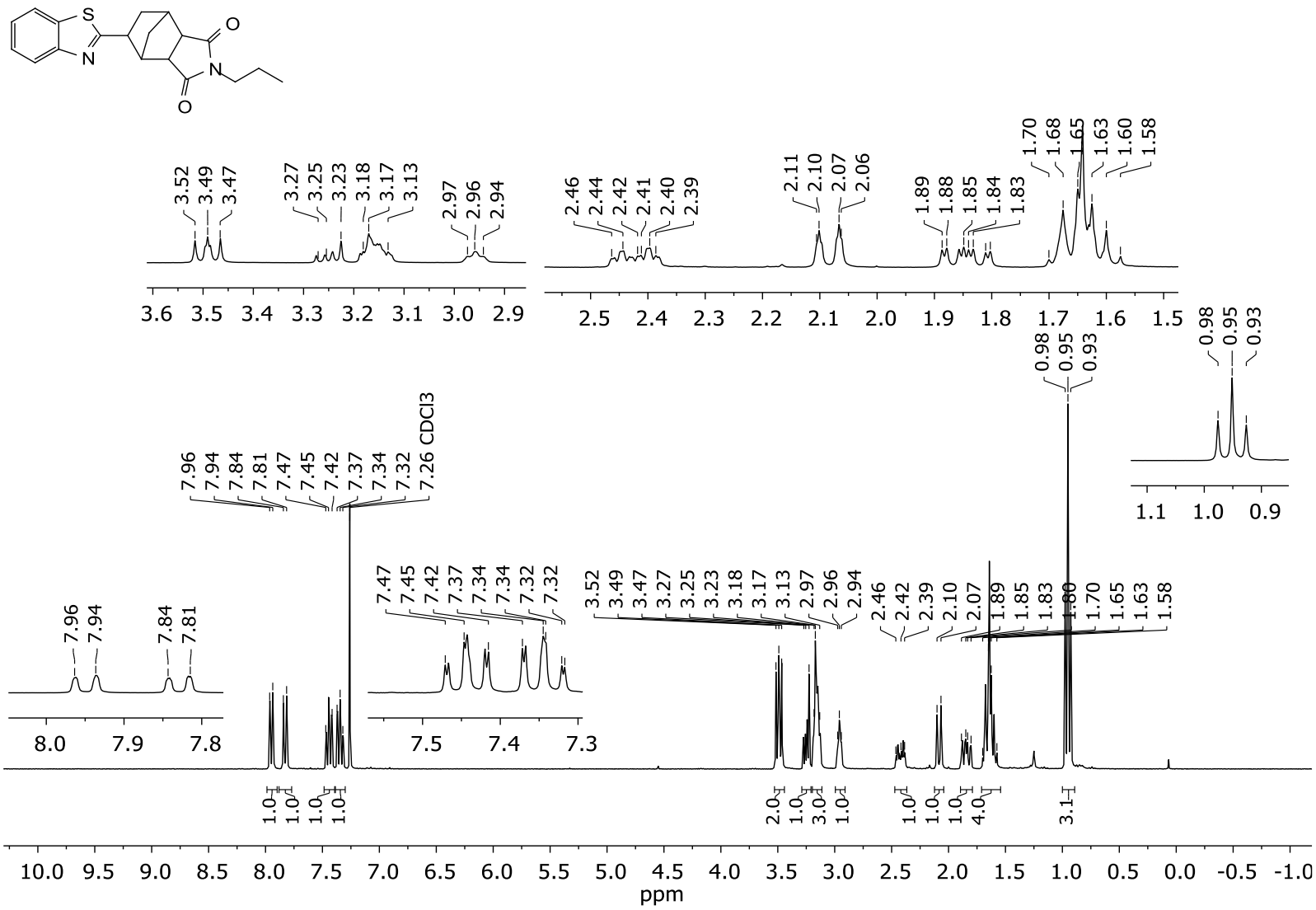


Figure S43. ^{1}H NMR spectrum of compound **4p** ($CDCl_3$, 300 MHz)

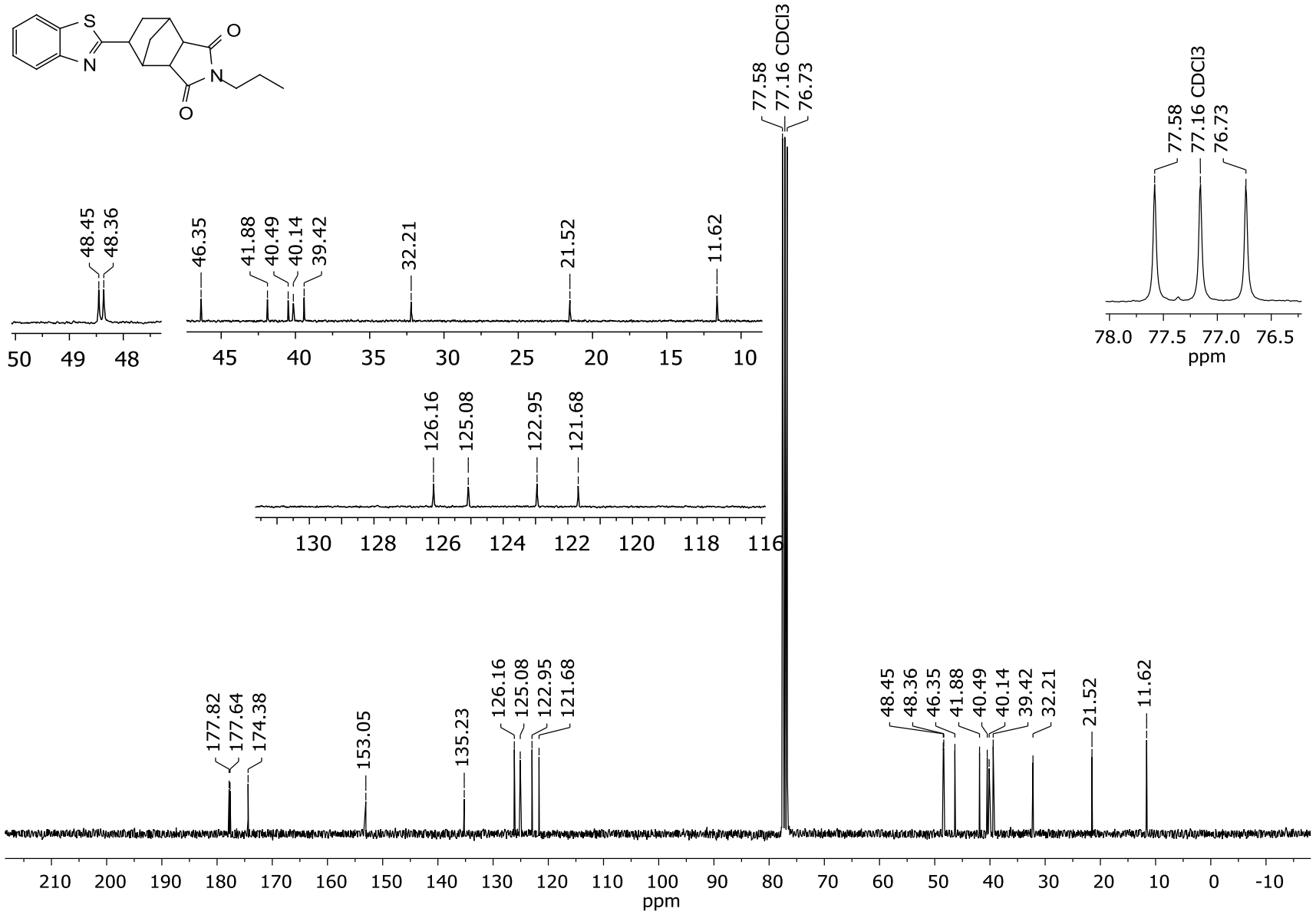


Figure S44. ^{13}C NMR spectrum of compound **4p** ($CDCl_3$, 75 MHz)

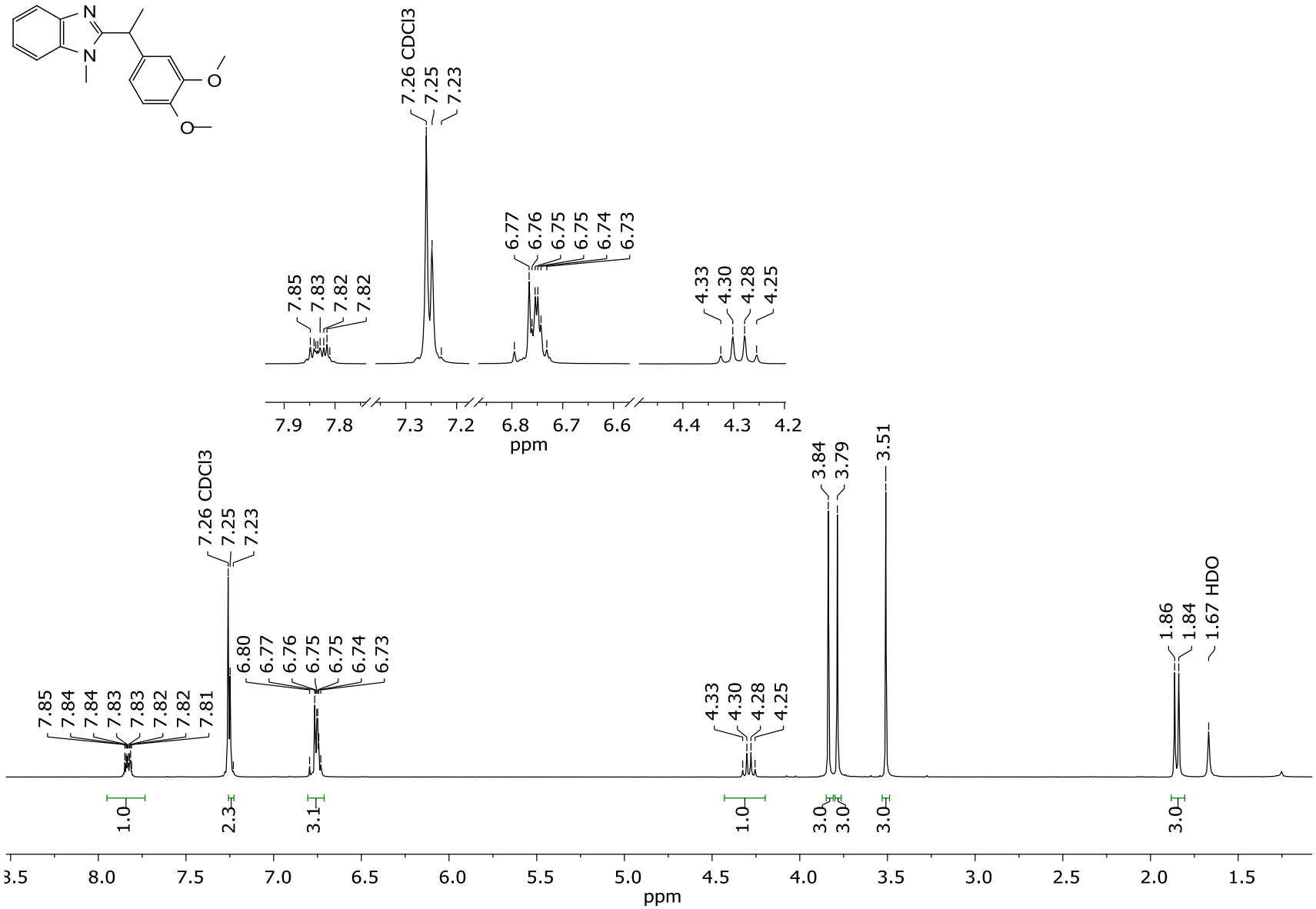


Figure S45. ^{1}H NMR spectrum of compound **4q** ($CDCl_3$, 300 MHz)

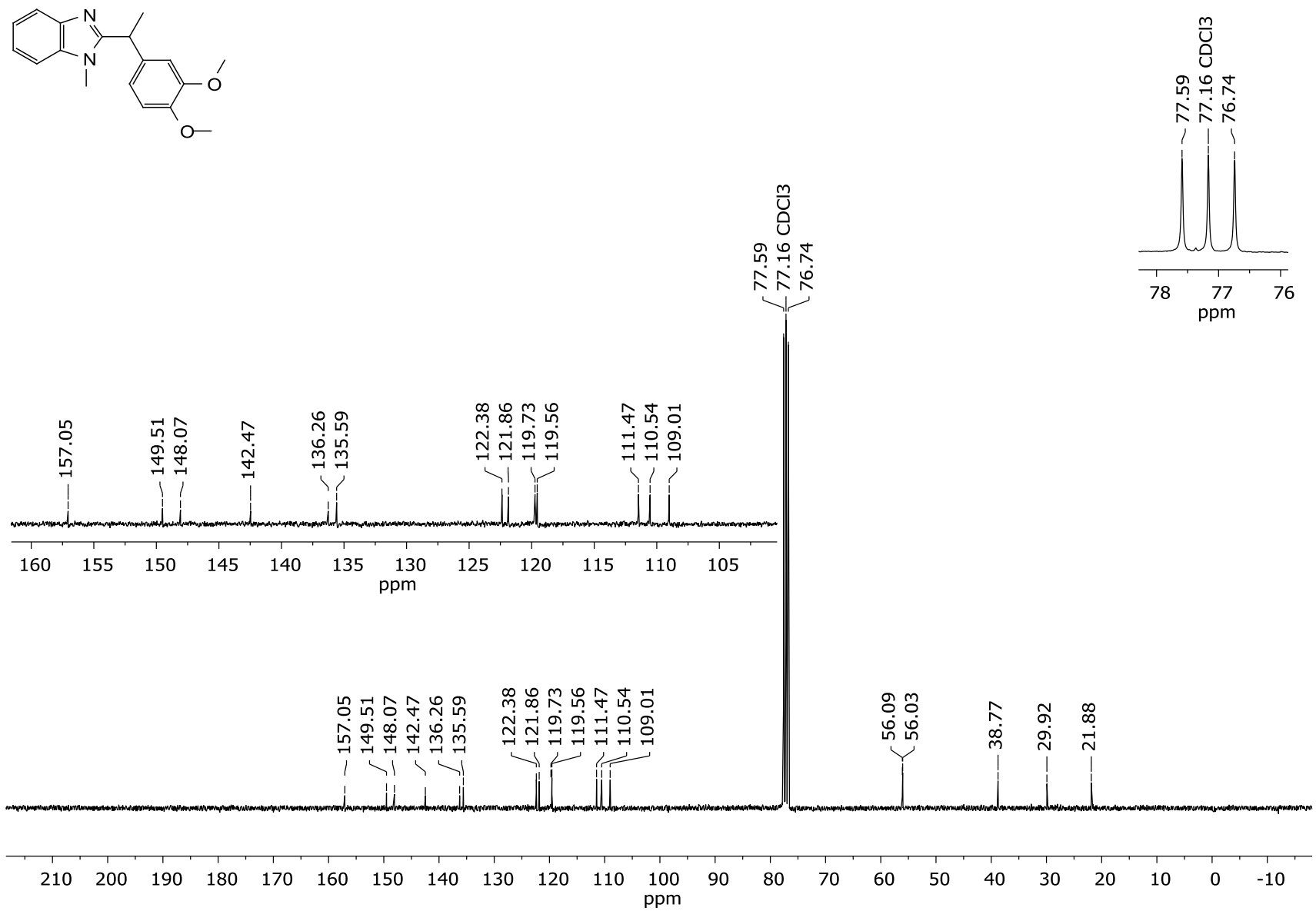


Figure S46. ^{13}C NMR spectrum of compound **4q** ($CDCl_3$, 75 MHz)

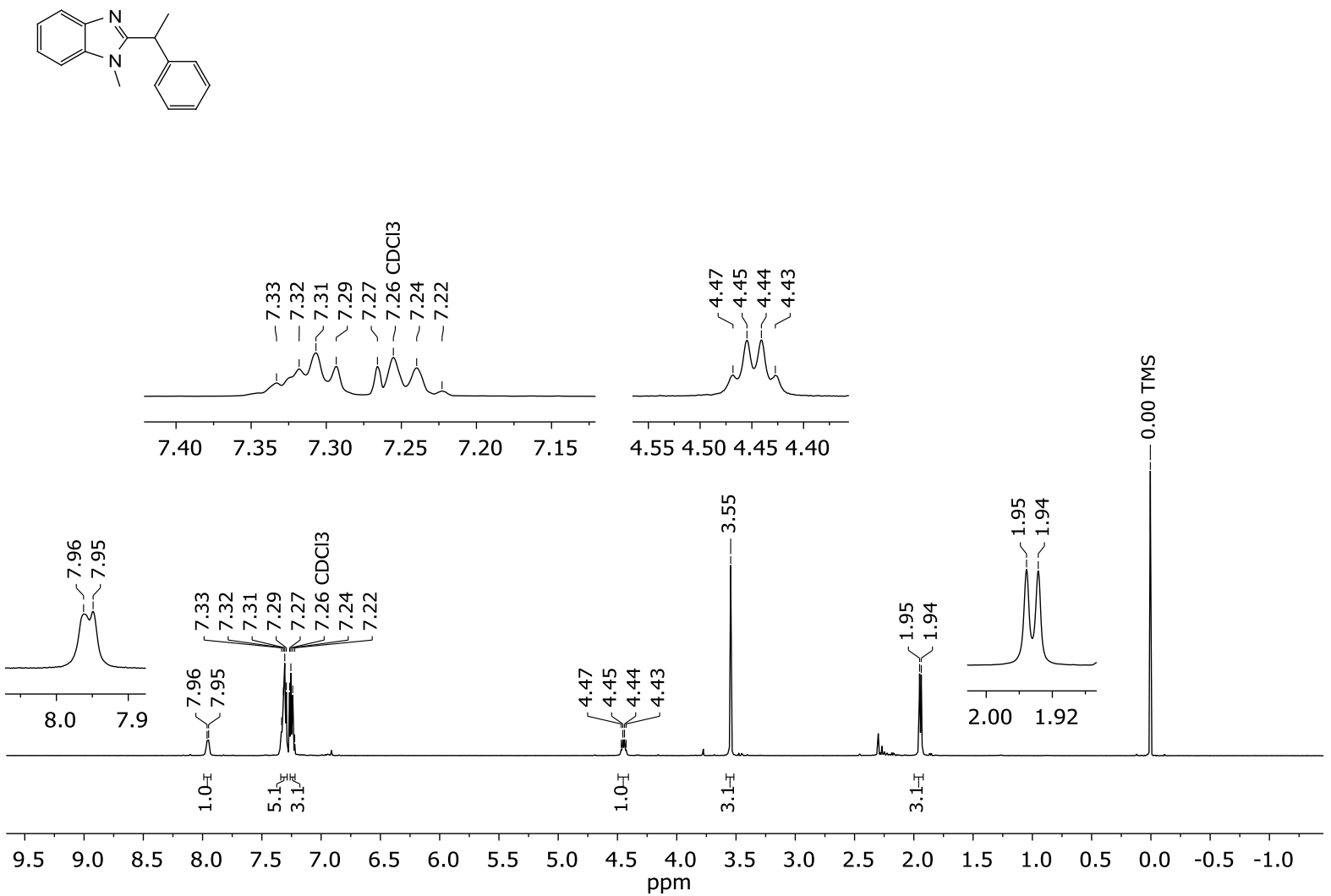


Figure S47. ^{1}H NMR spectrum of compound **4r** ($CDCl_3$, 500 MHz)

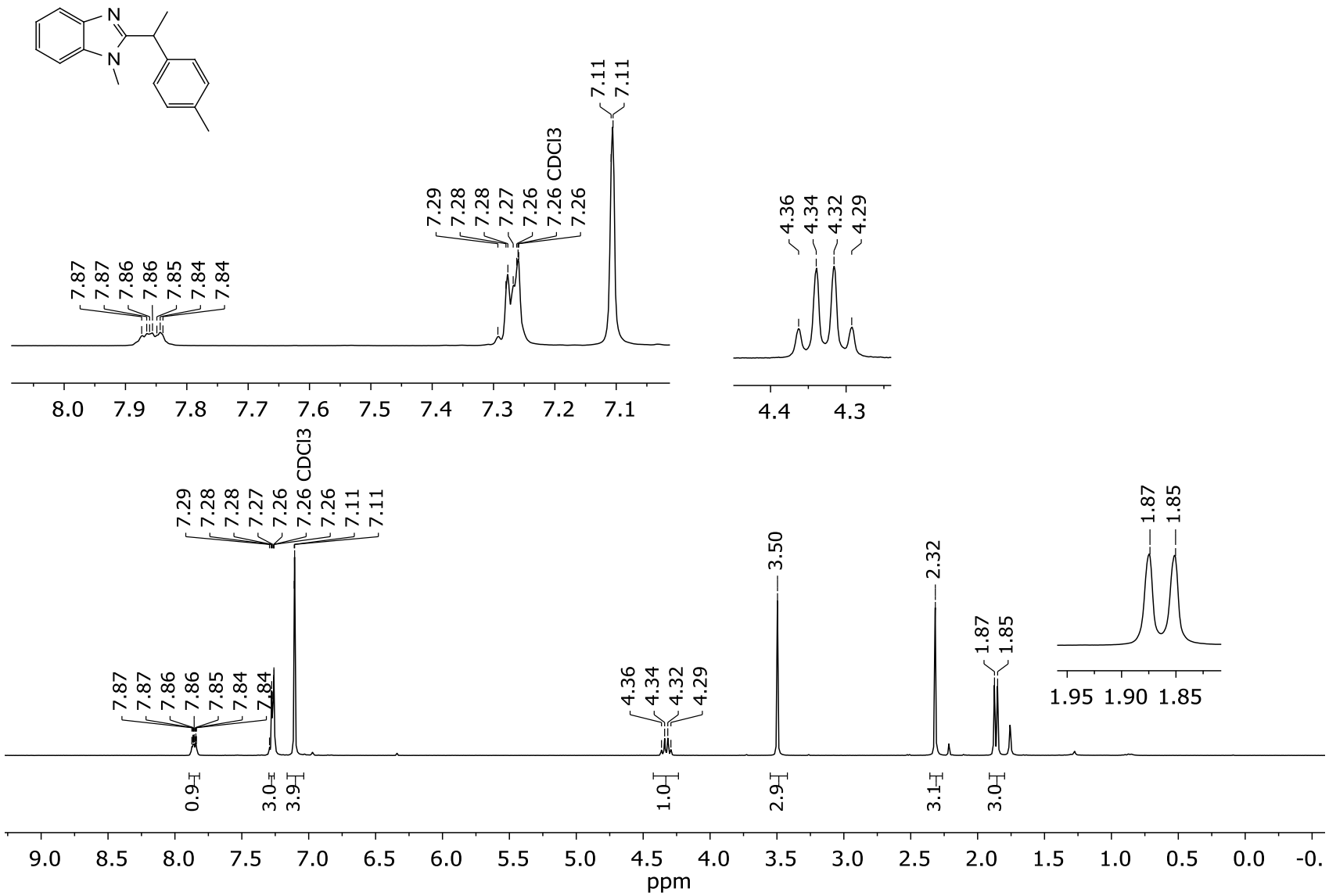


Figure S48. ^{1}H NMR spectrum of compound **4s** ($CDCl_3$, 300 MHz)

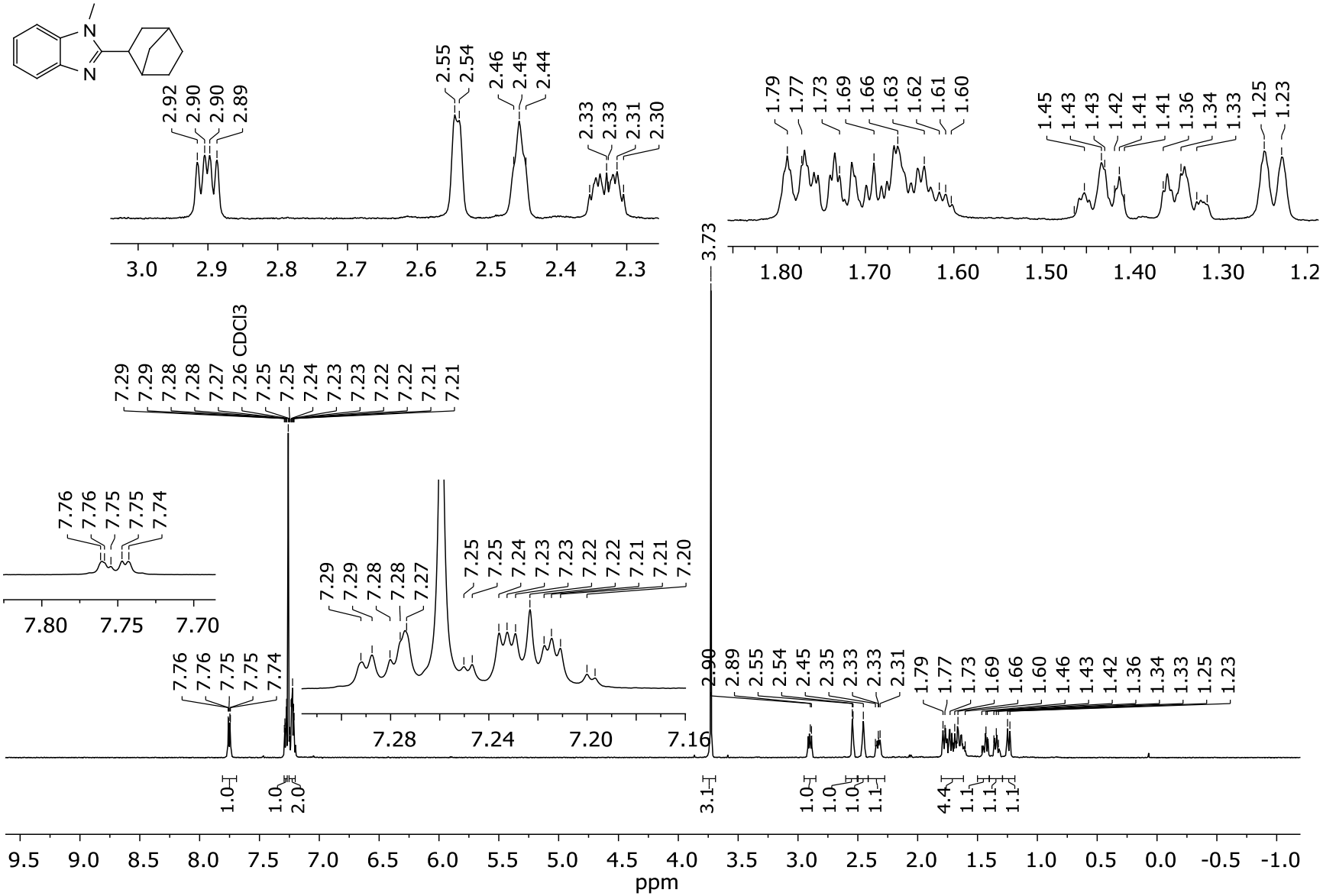


Figure S49. ^{1}H NMR spectrum of compound **4t** ($CDCl_3$, 500 MHz)

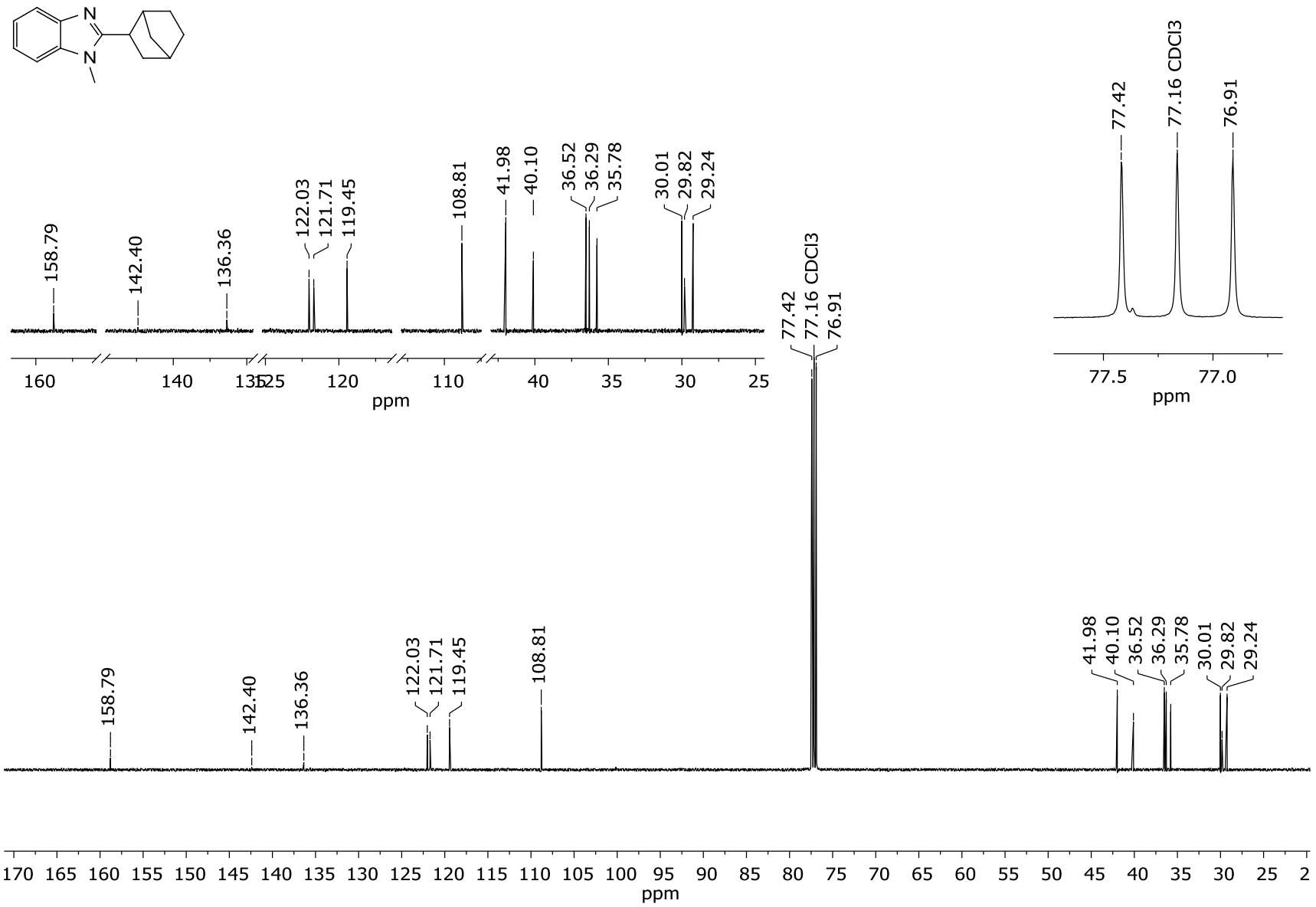


Figure S50. ^{13}C NMR spectrum of compound **4t** ($CDCl_3$, 125 MHz)

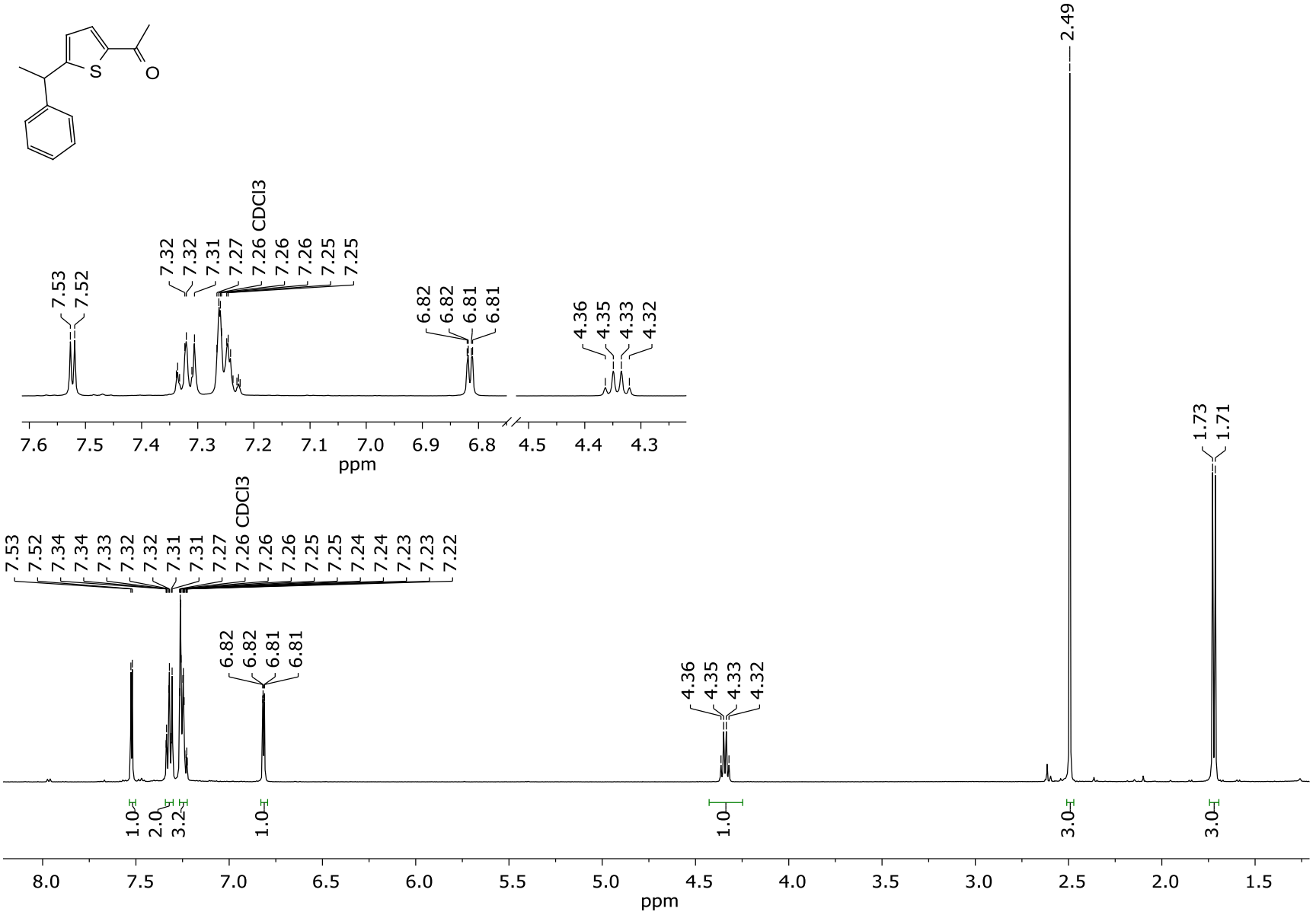


Figure S51. ^{1}H NMR spectrum of compound **4u** ($CDCl_3$, 500 MHz)

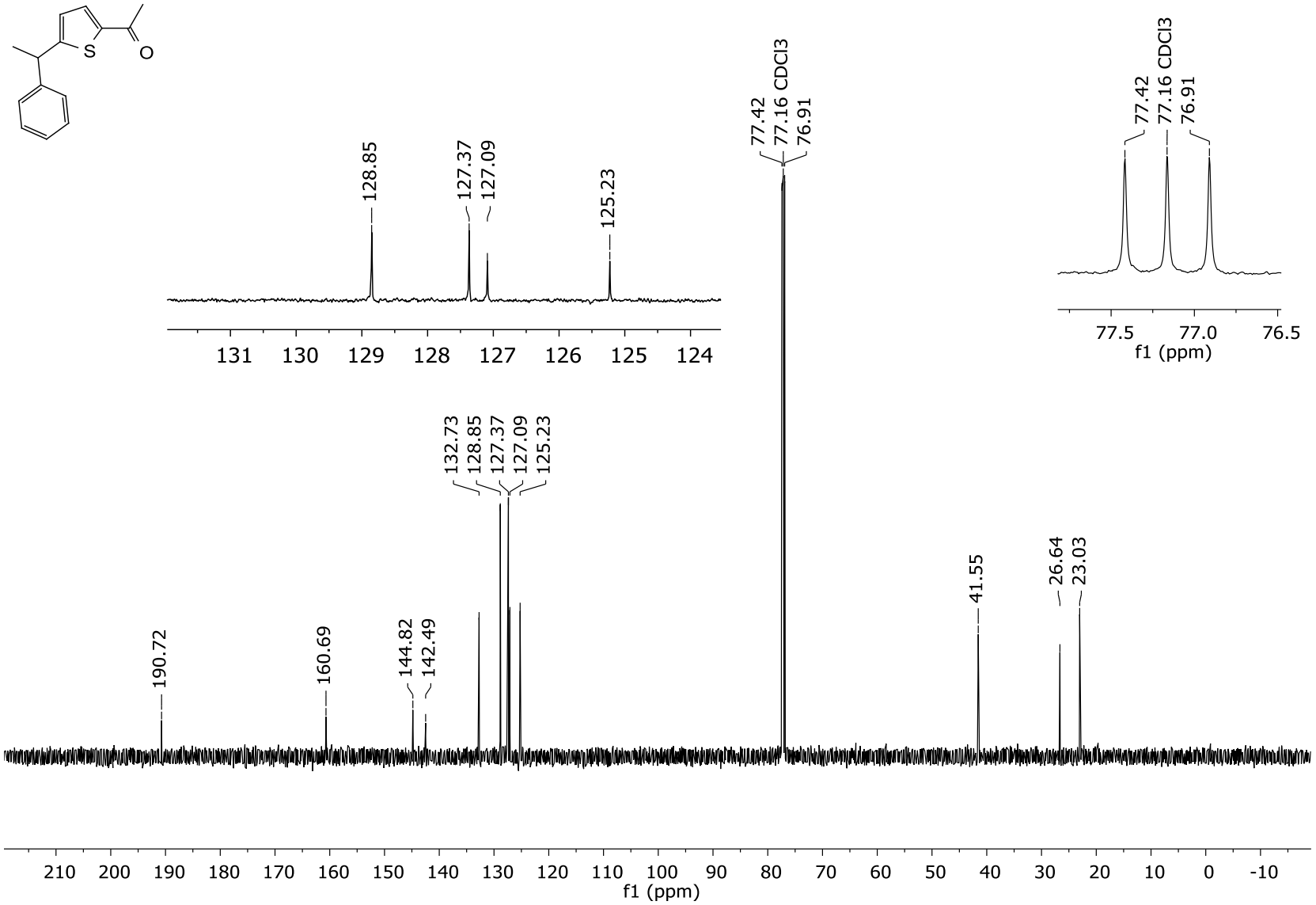


Figure S52. ^{13}C NMR spectrum of compound **4u** ($CDCl_3$, 125 MHz)

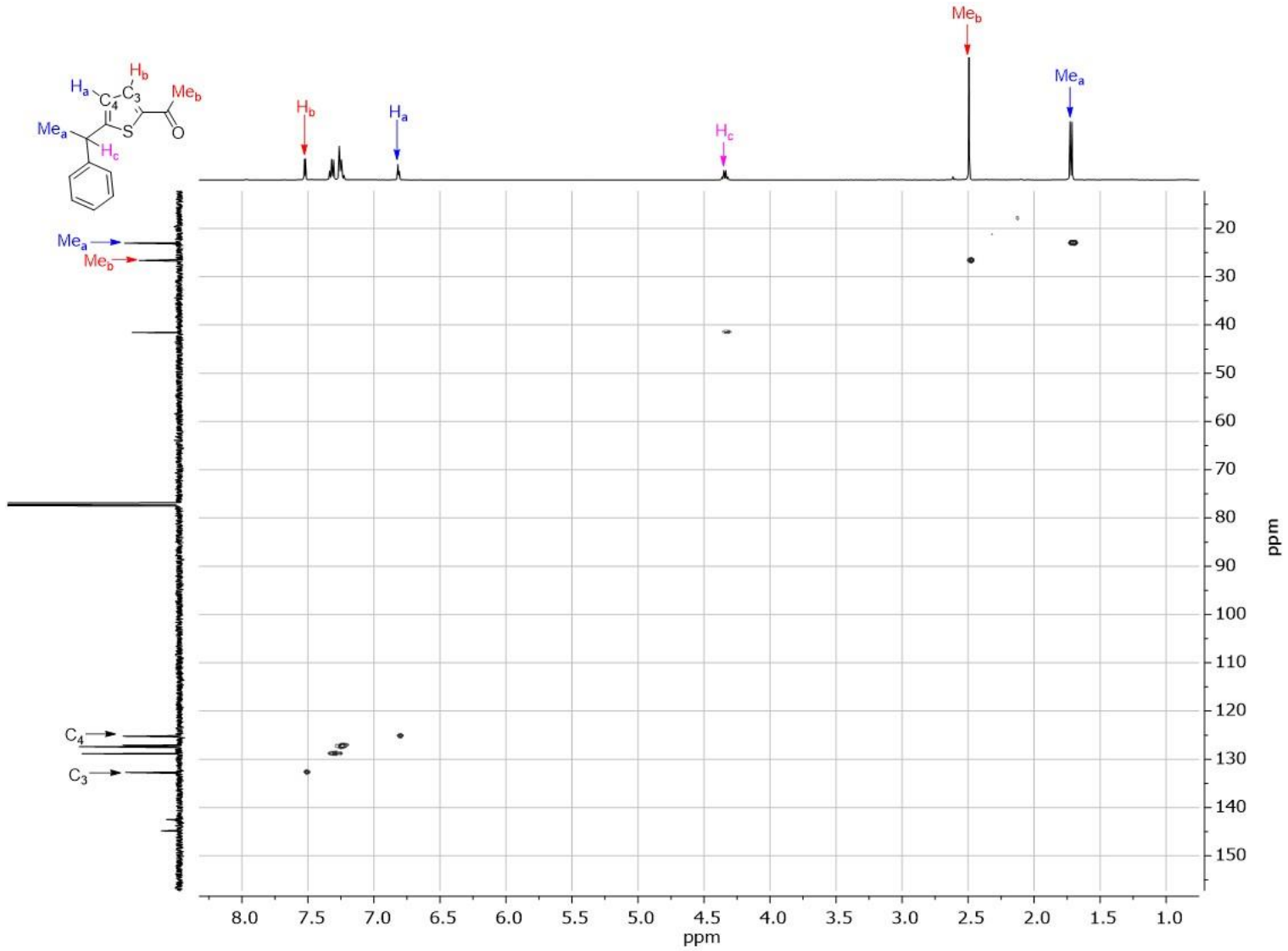


Figure S53. ^{1}H-^{13}C HSQC spectrum of compound **4u** ($CDCl_3$)

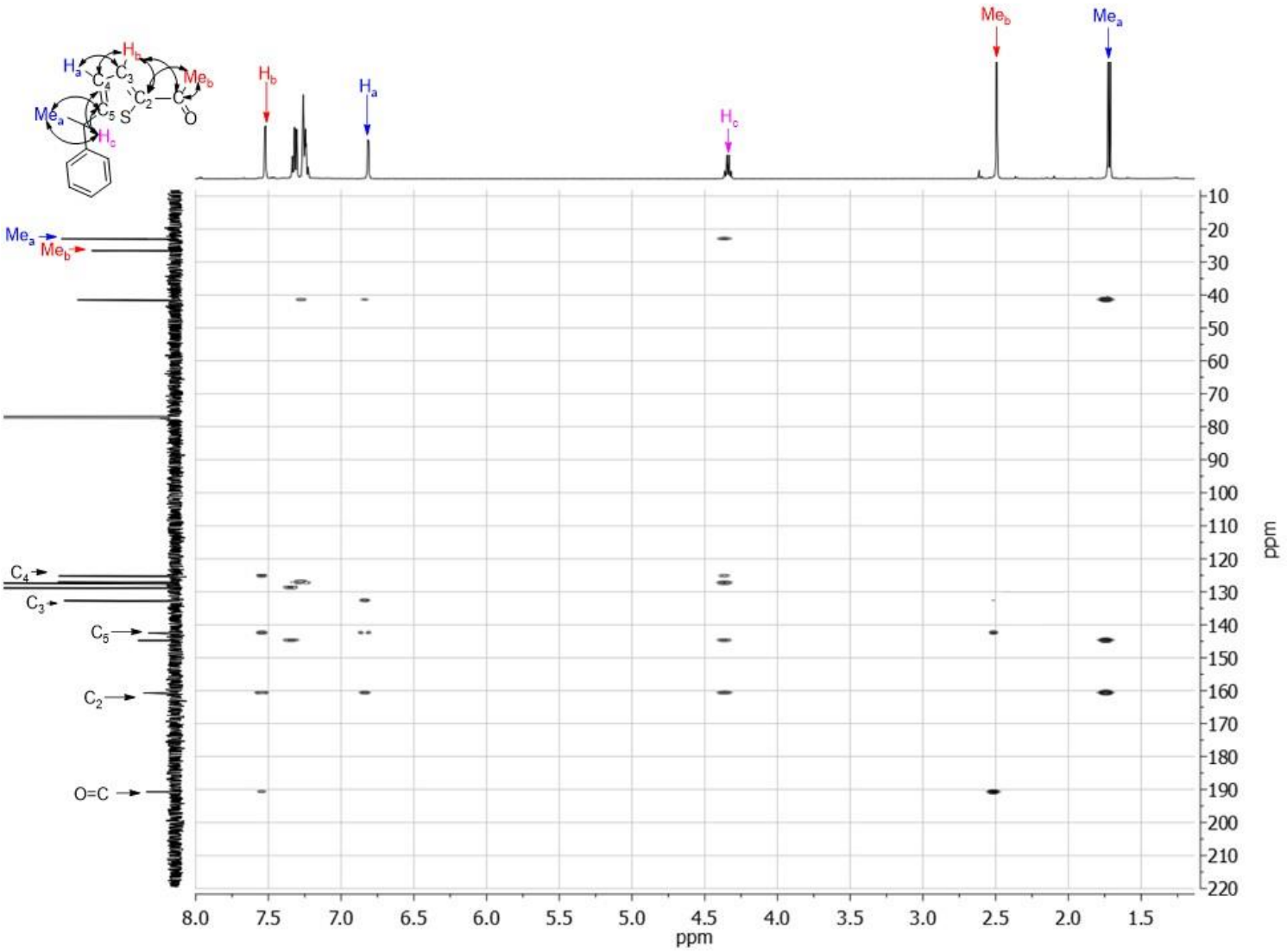


Figure S54. ^{1}H-^{13}C HMBC spectrum of compound **4u** ($CDCl_3$)

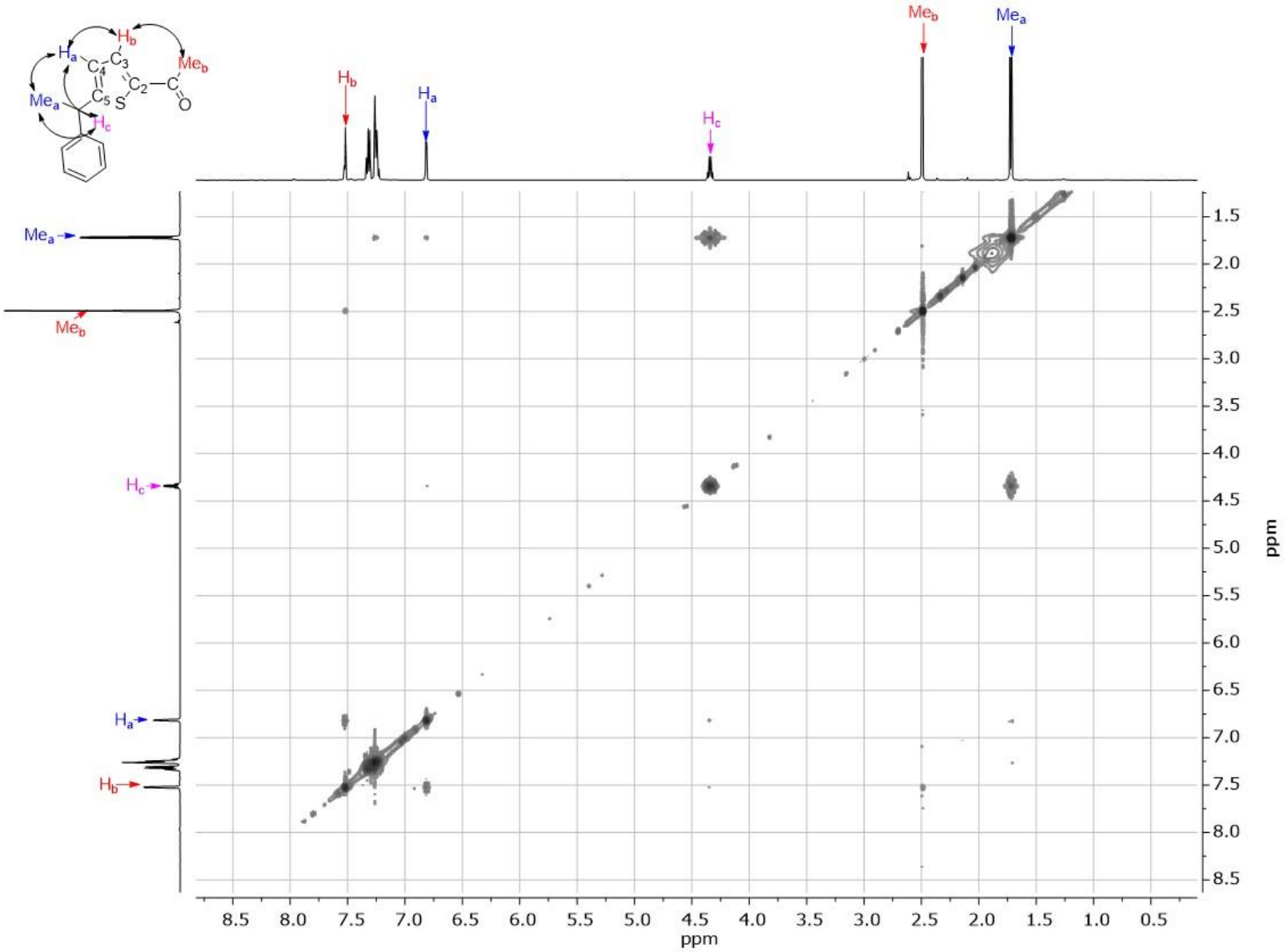


Figure S55. ^{1}H-^{1}H NOESY spectrum of compound **4u** ($CDCl_3$)

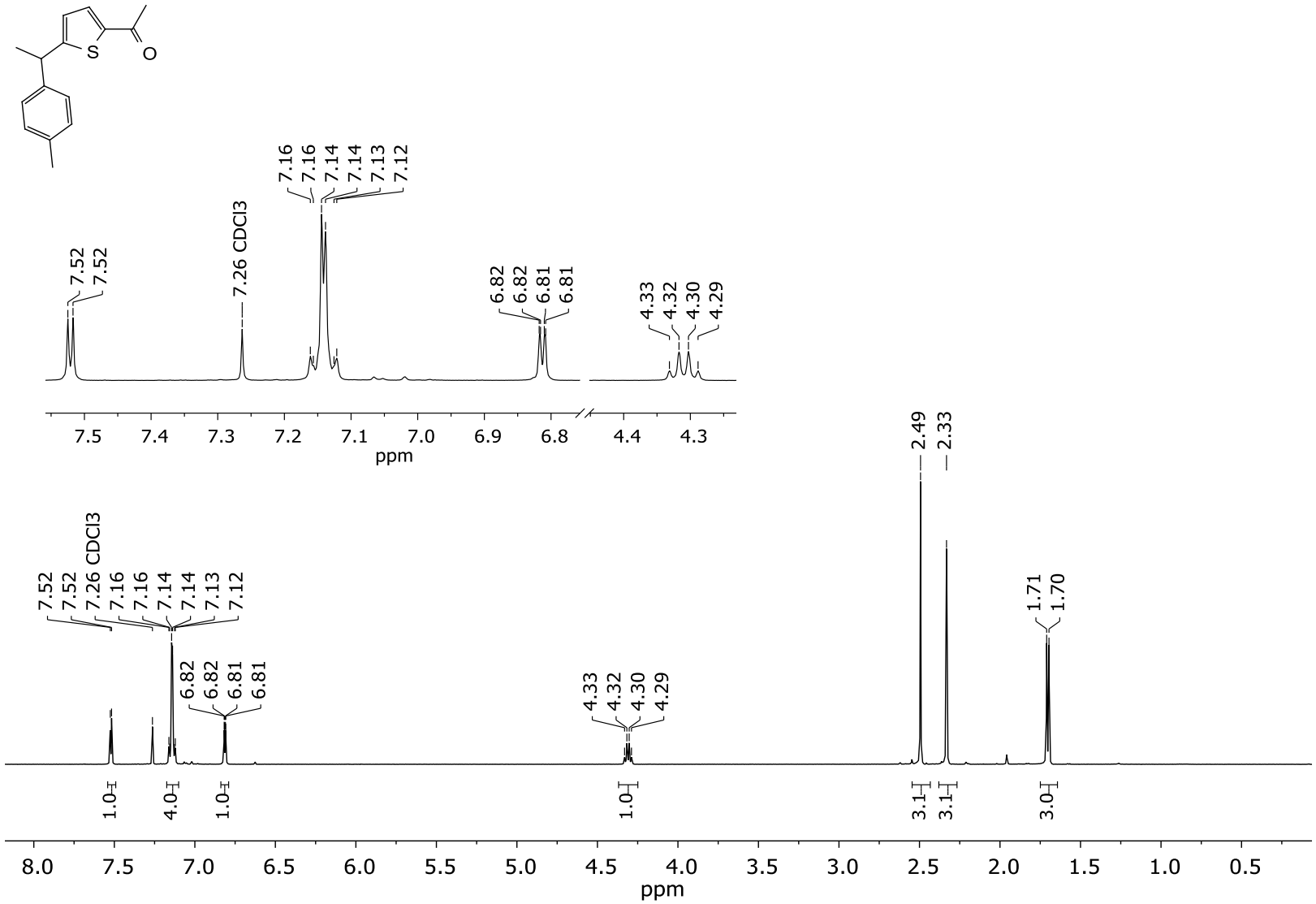


Figure S56. ^{1}H NMR spectrum of compound **4v** ($CDCl_3$, 500 MHz)

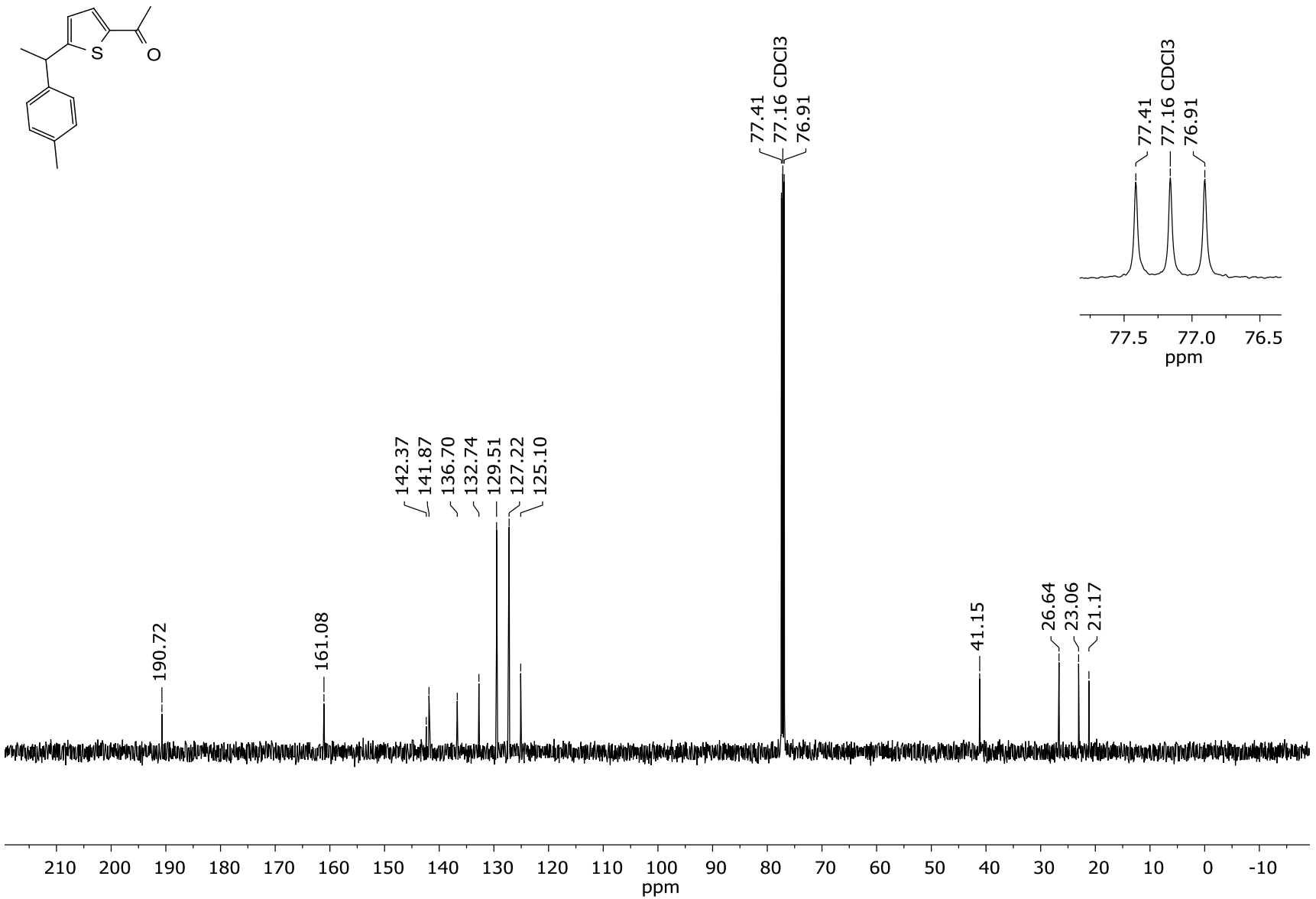


Figure S57. ^{13}C NMR spectrum of compound **4v** ($CDCl_3$, 125 MHz)

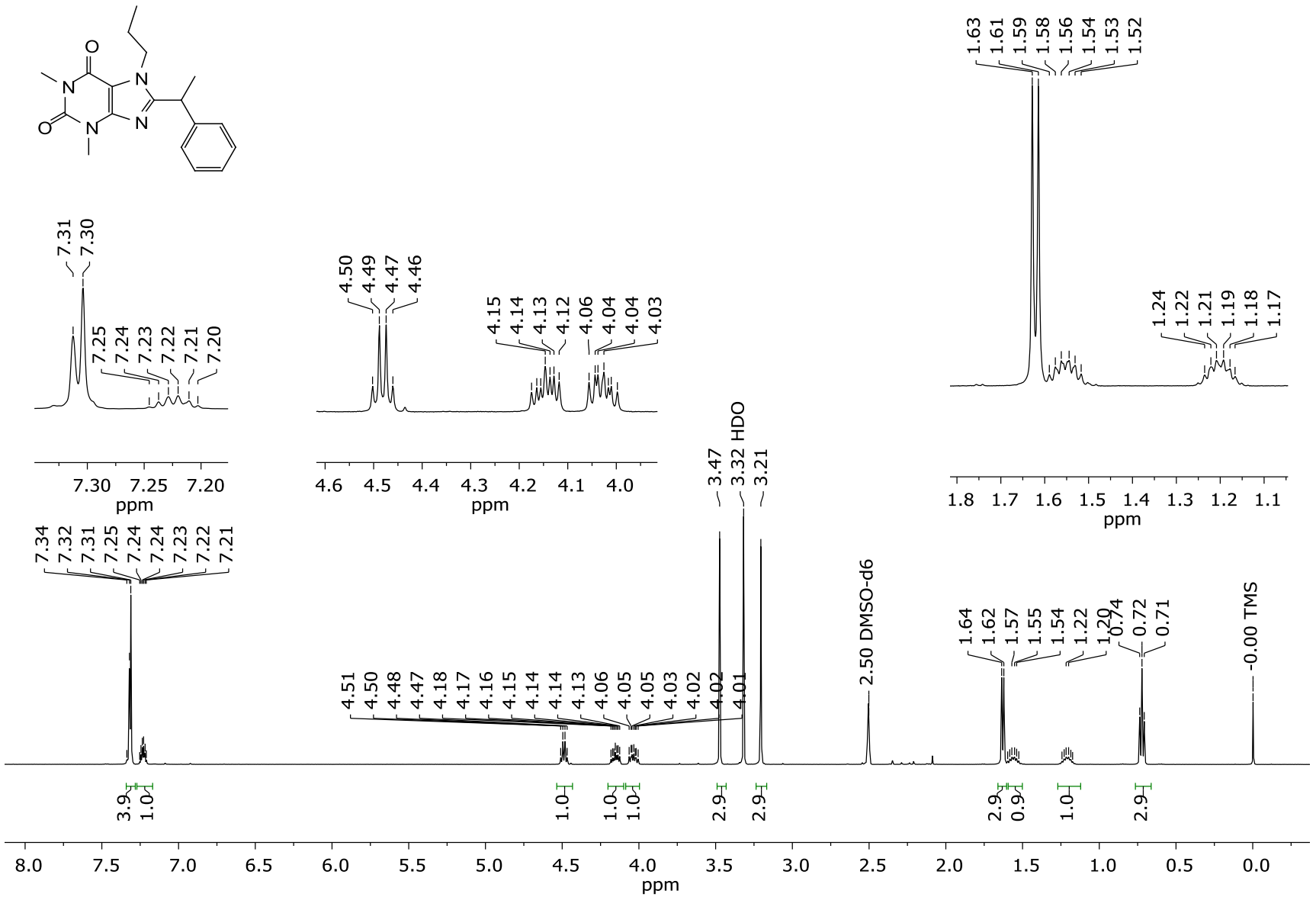


Figure S58. ^{1}H NMR spectrum of compound **4w** (DMSO-d_6, 400 MHz)

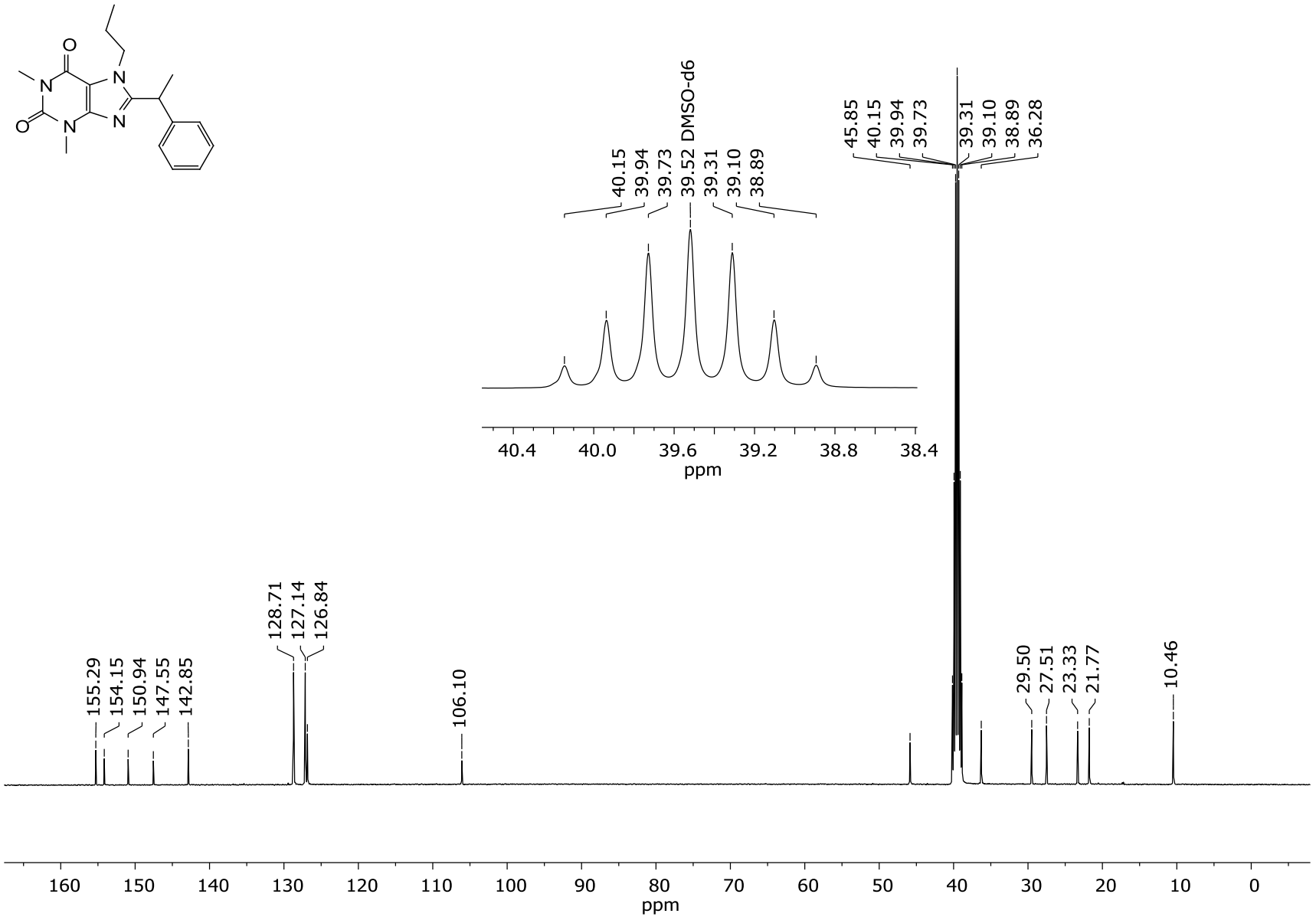


Figure S59. ^{13}C NMR spectrum of compound **4w** (DMSO-d_6, 100 MHz)

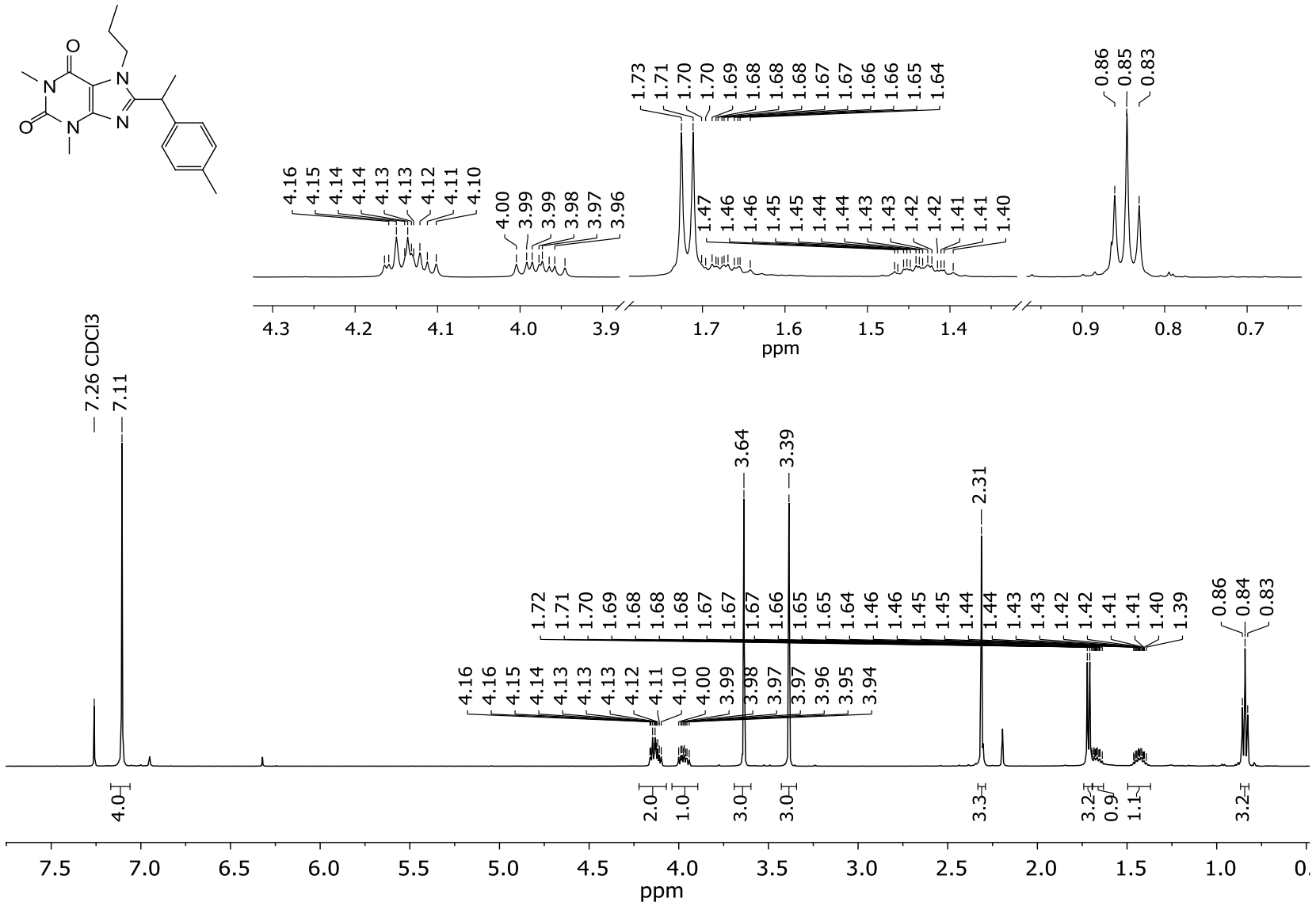


Figure S60. ^{1}H NMR spectrum of compound **4x** ($CDCl_3$, 500 MHz)

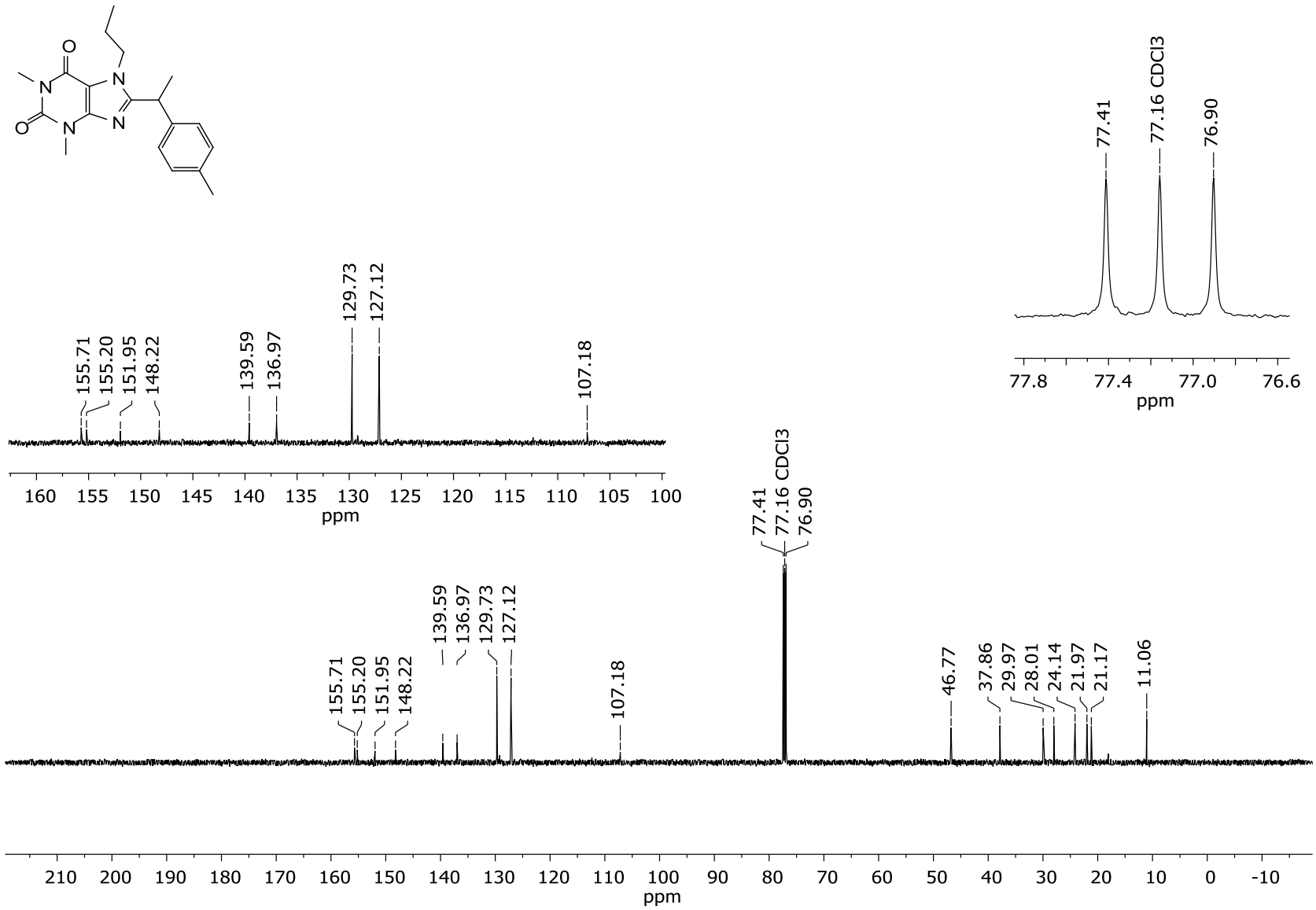


Figure S61. ^{13}C NMR spectrum of compound **4x** ($CDCl_3$, 125 MHz)

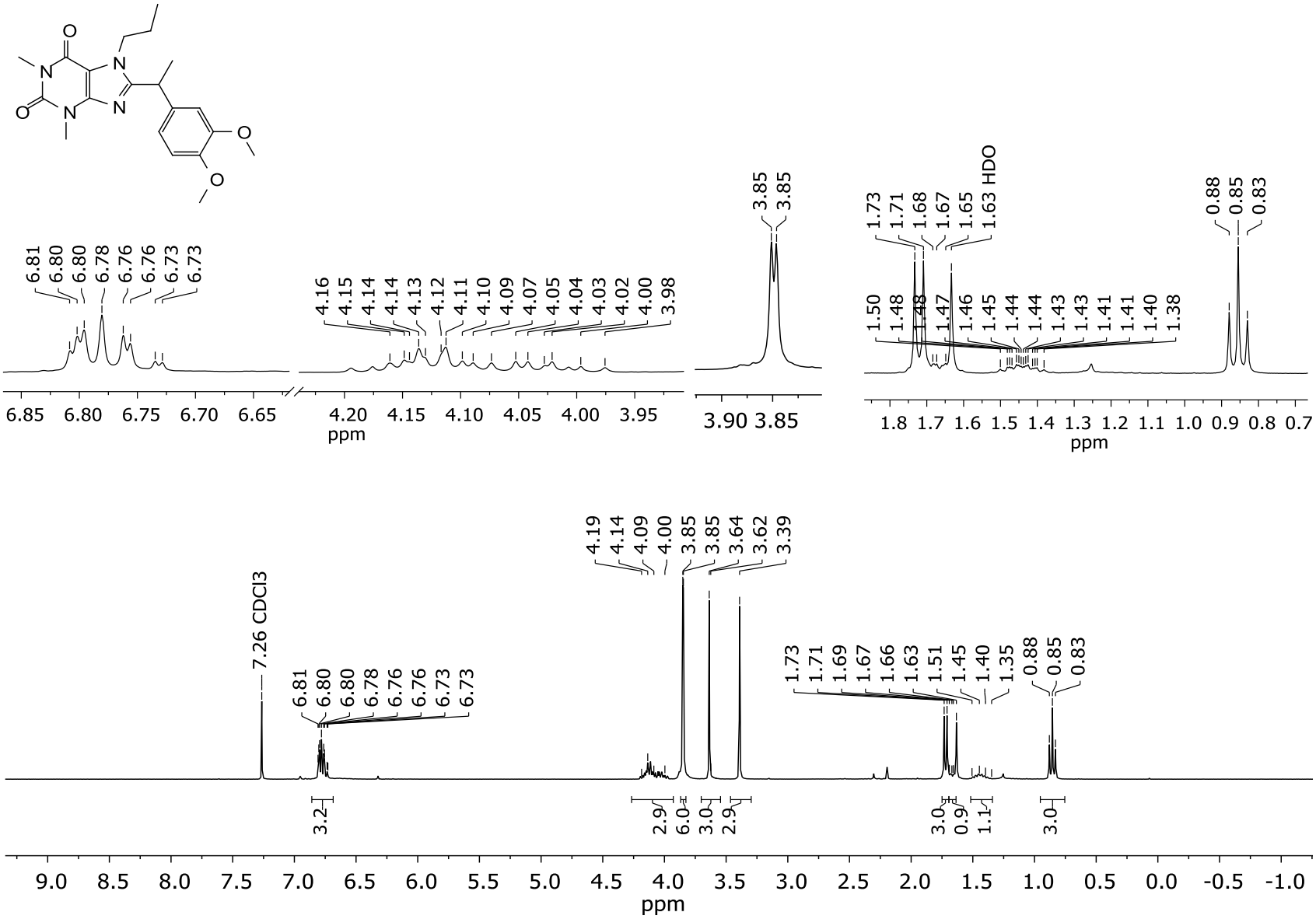


Figure S62. ^{1}H NMR spectrum of compound **4y** ($CDCl_3$, 300 MHz)

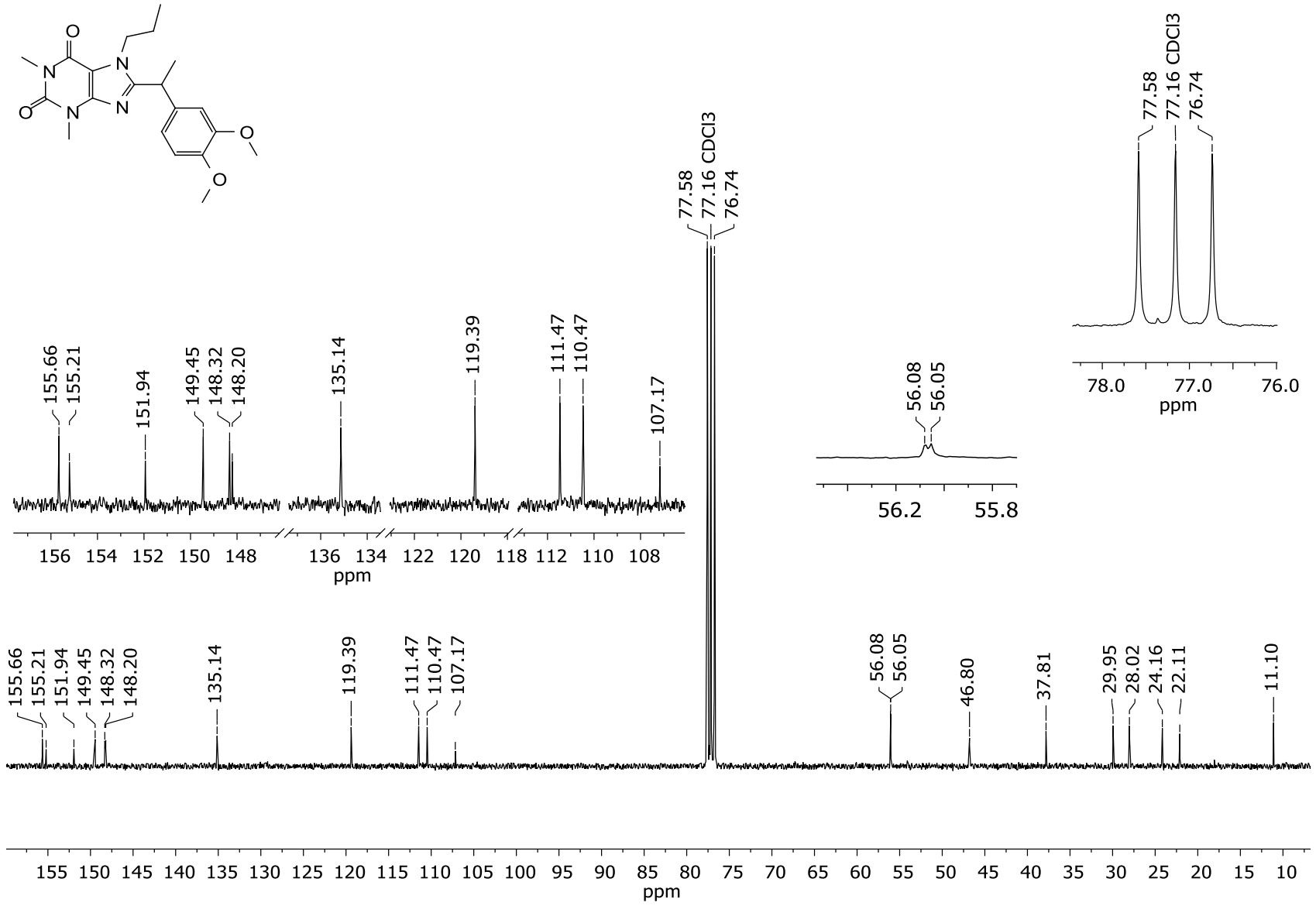


Figure S63. ^{13}C NMR spectrum of compound **4y** ($CDCl_3$, 75 MHz)

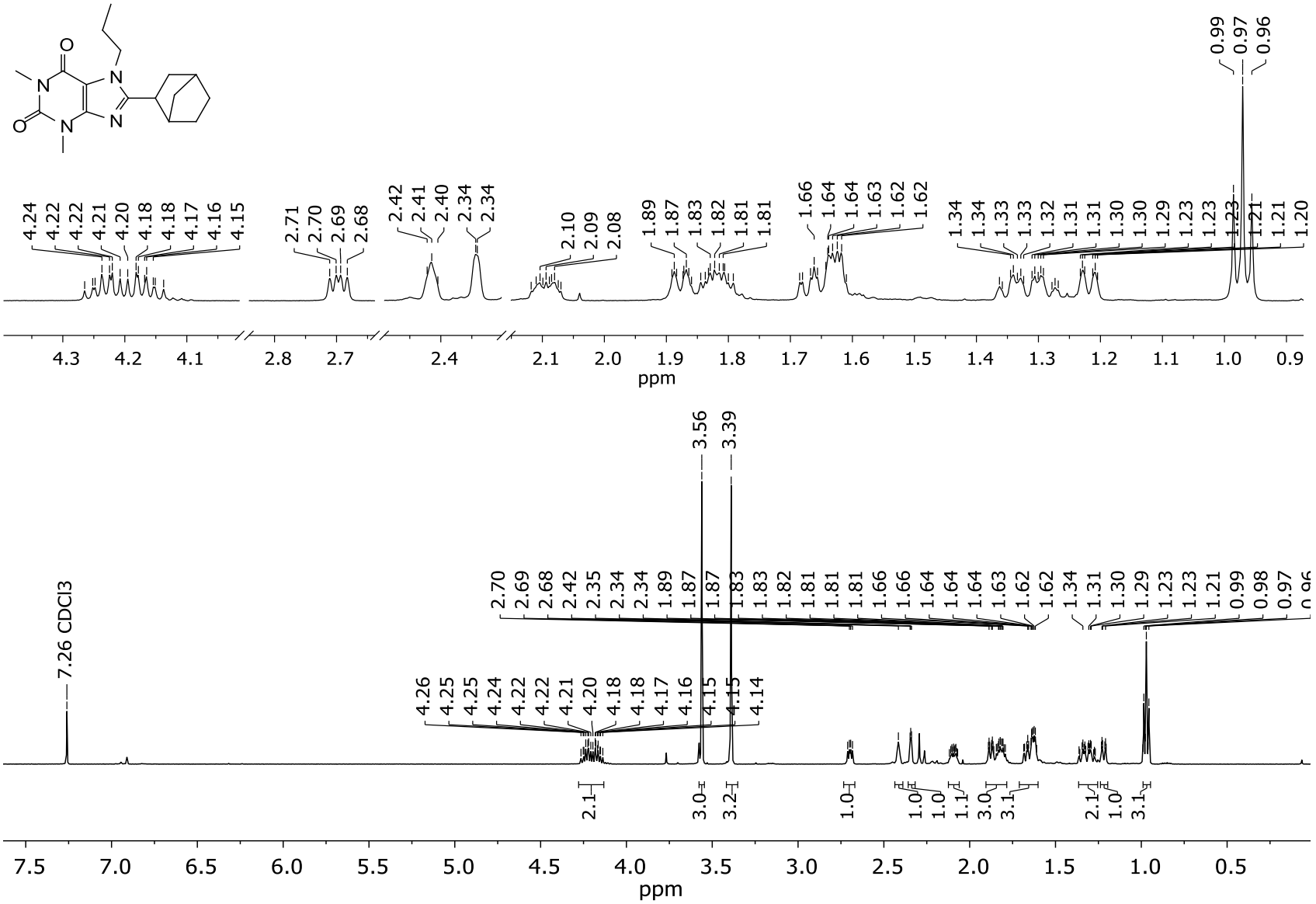


Figure S64. ^{1}H NMR spectrum of compound **4z** ($CDCl_3$, 500 MHz)

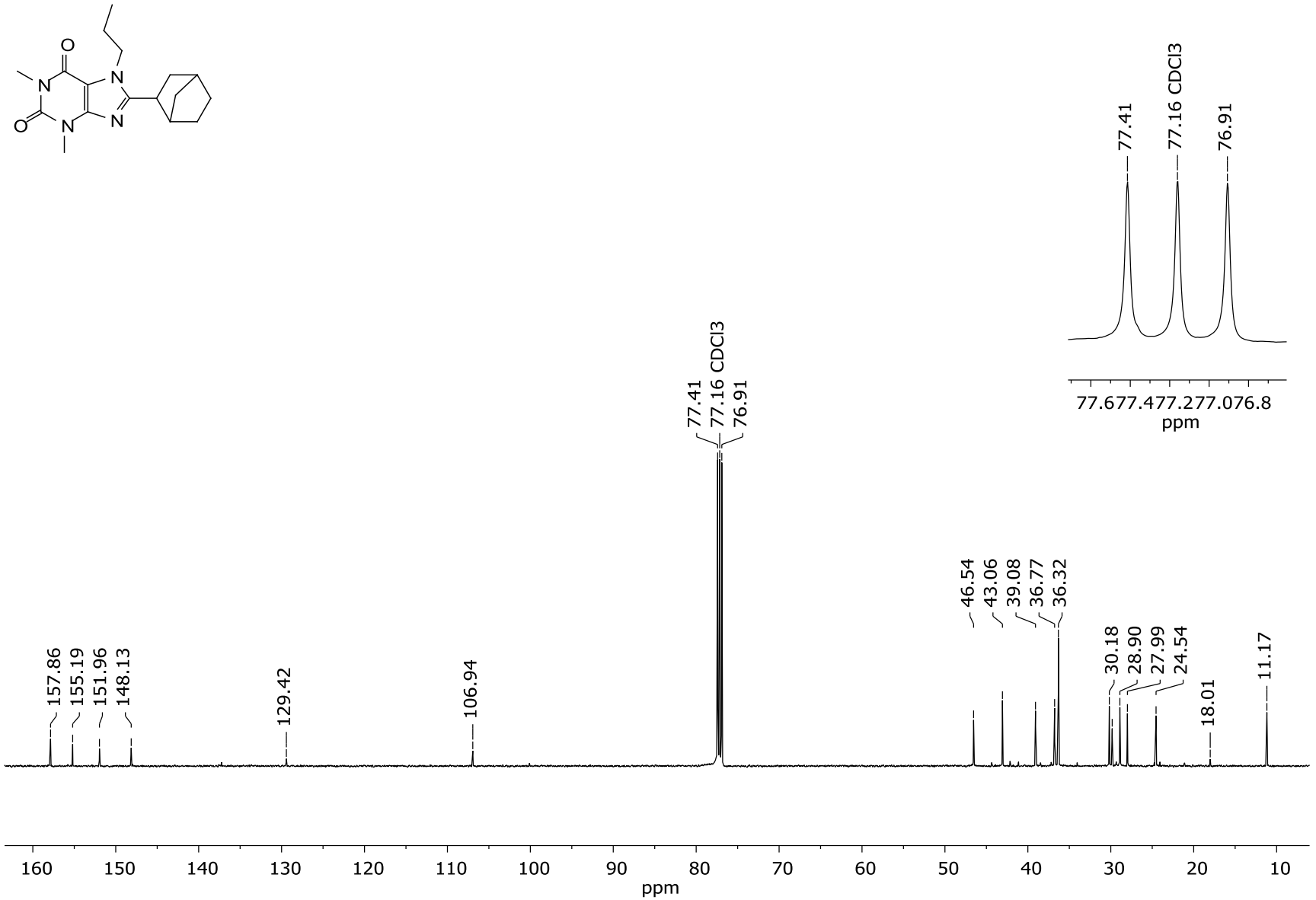


Figure S65. ^{13}C NMR spectrum of compound **4z** ($CDCl_3$, 125 MHz)

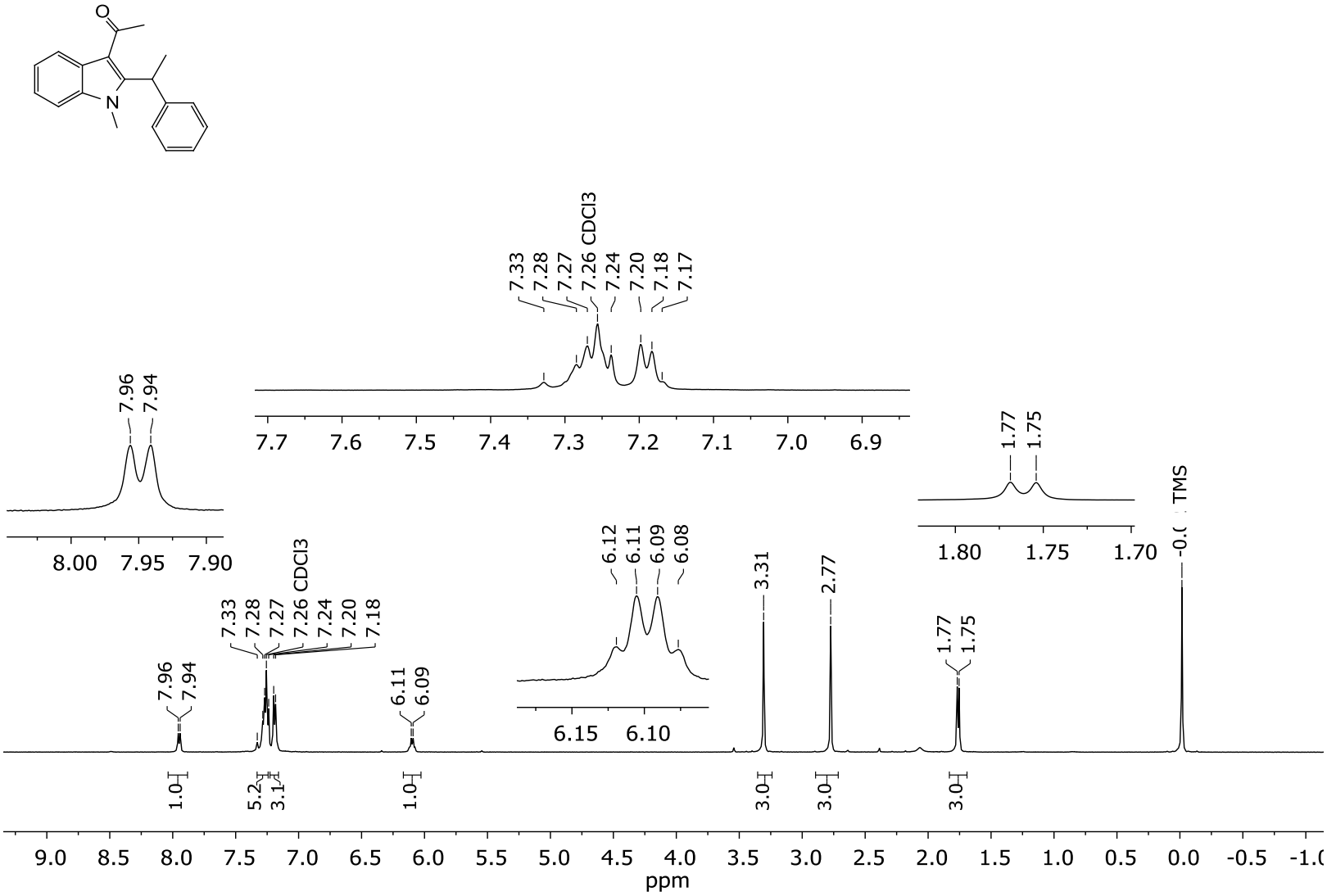


Figure S66. ^{1}H NMR spectrum of compound **4aa** ($CDCl_3$, 500 MHz)

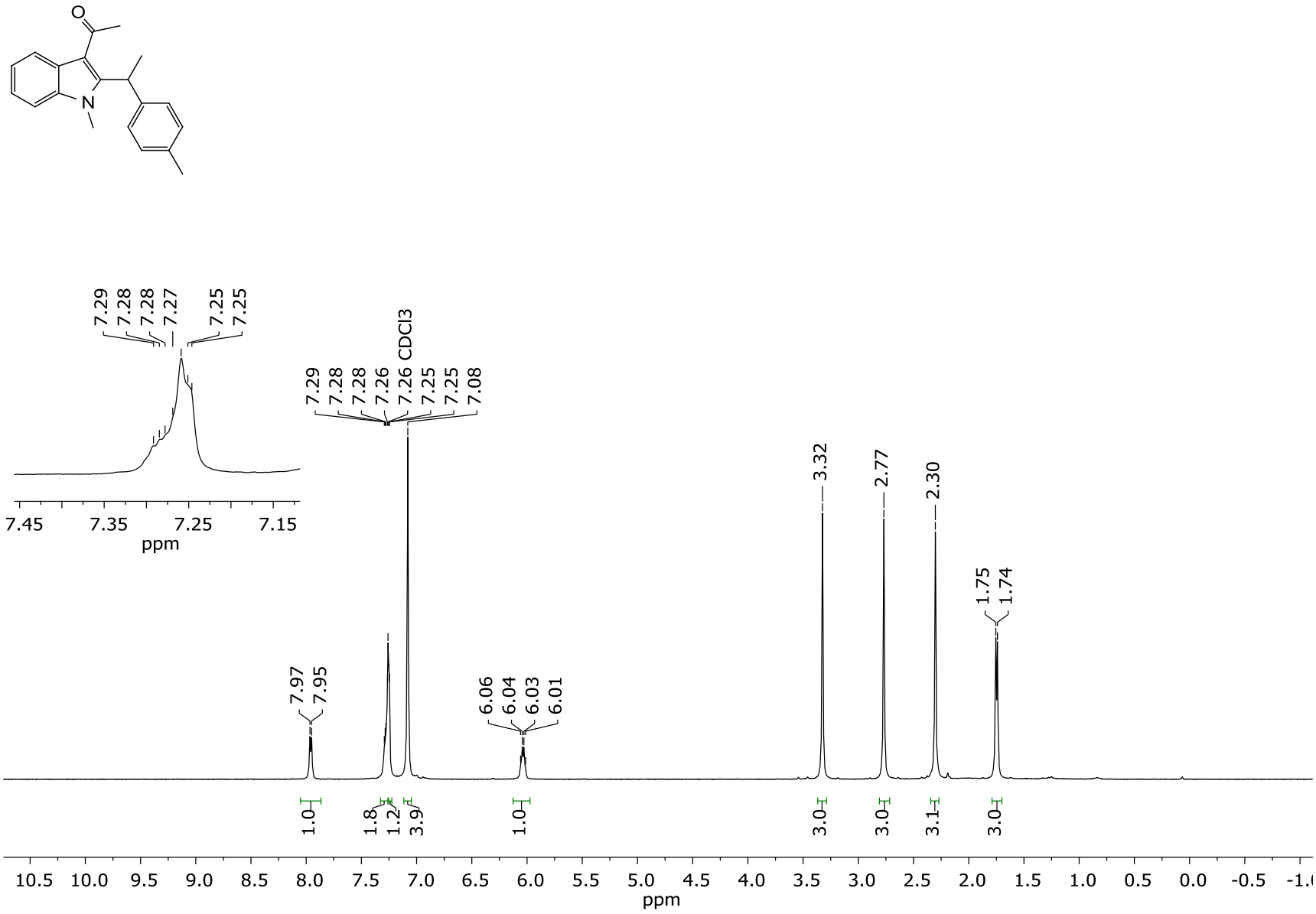


Figure S67. ^{1}H NMR spectrum of compound **4ab** ($CDCl_3$, 500 MHz)

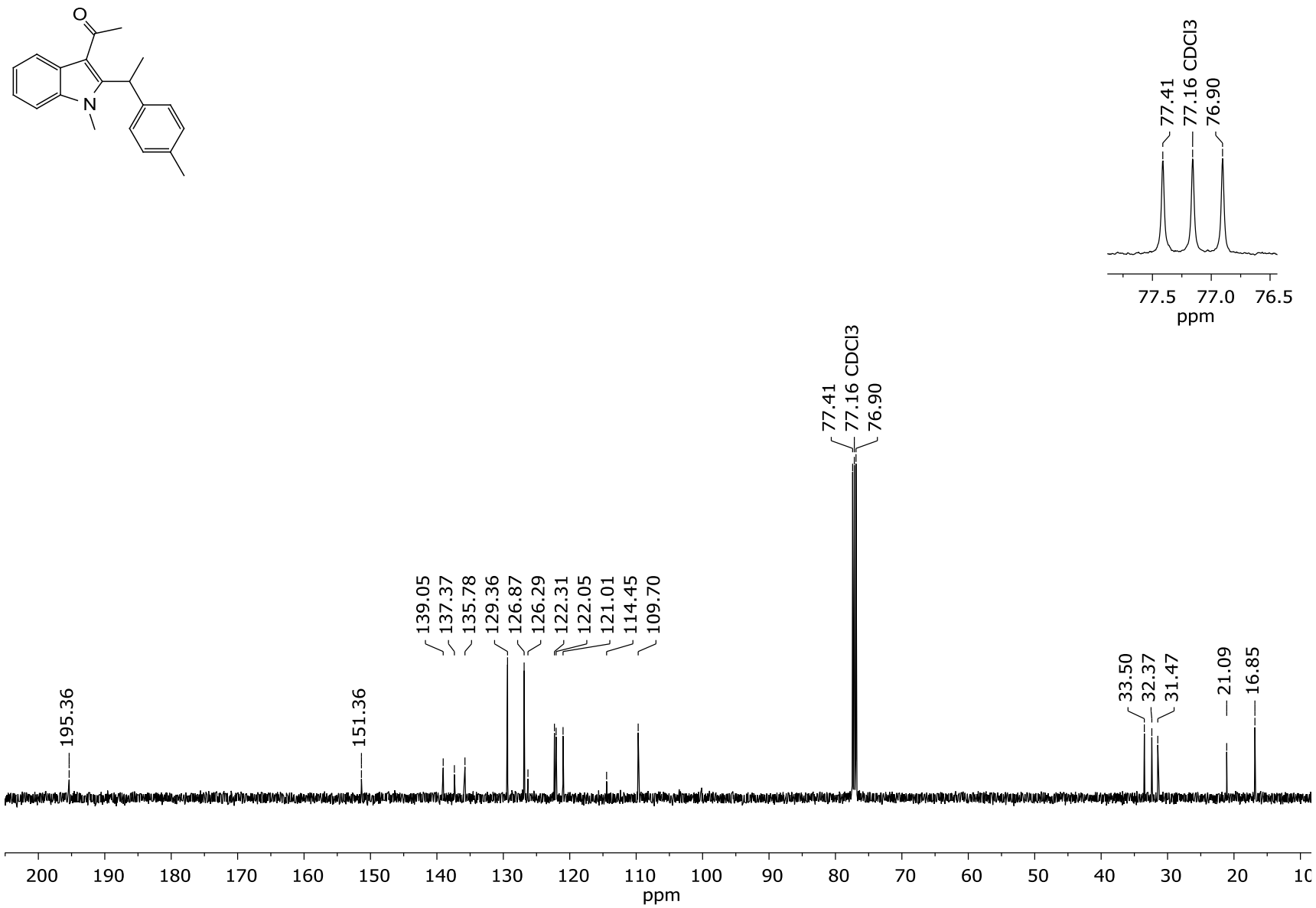


Figure S68. ^{13}C NMR spectrum of compound **4ab** ($CDCl_3$, 125 MHz)

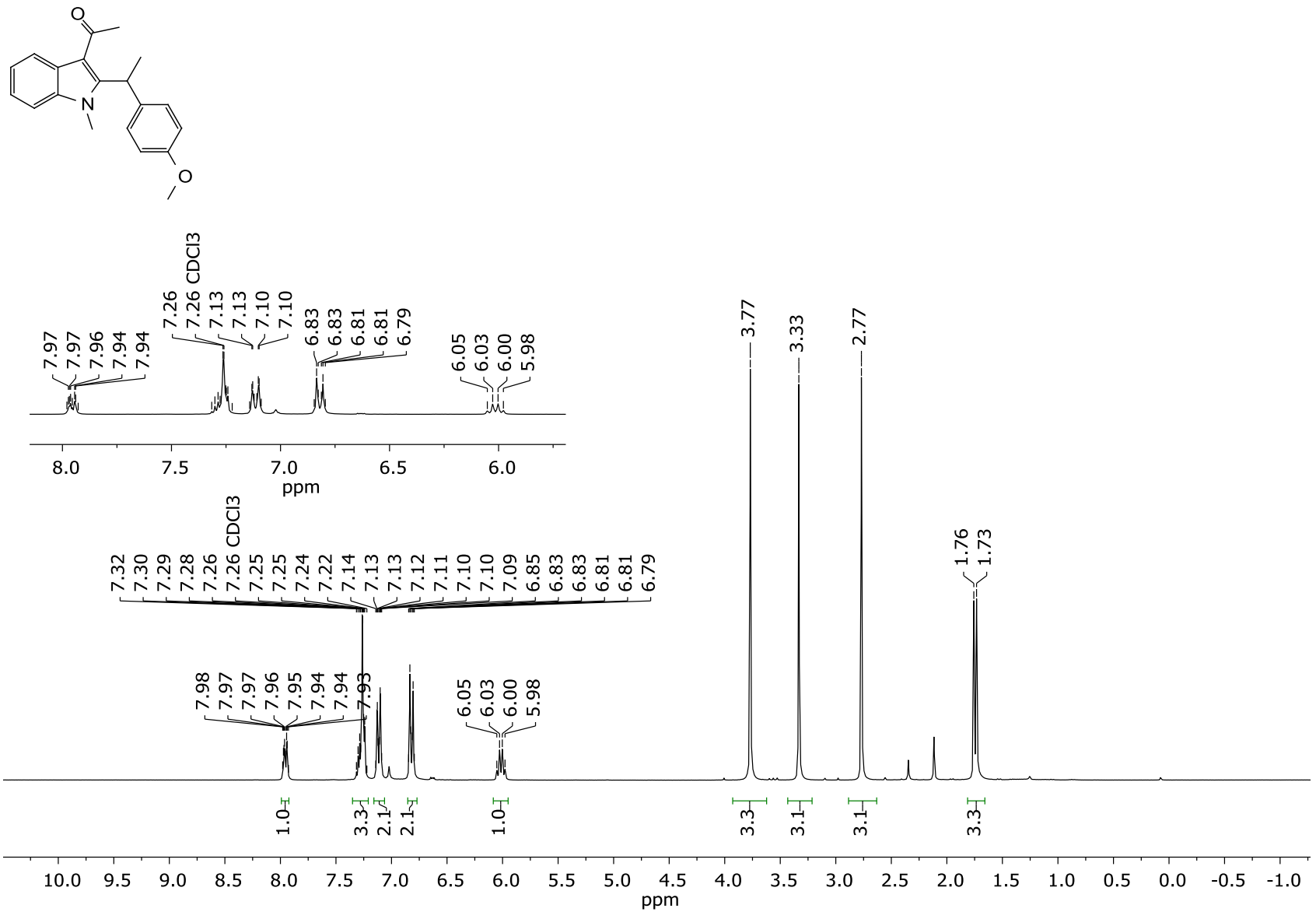


Figure S69. ^{1}H NMR spectrum of compound **4ac** ($CDCl_3$, 300 MHz)

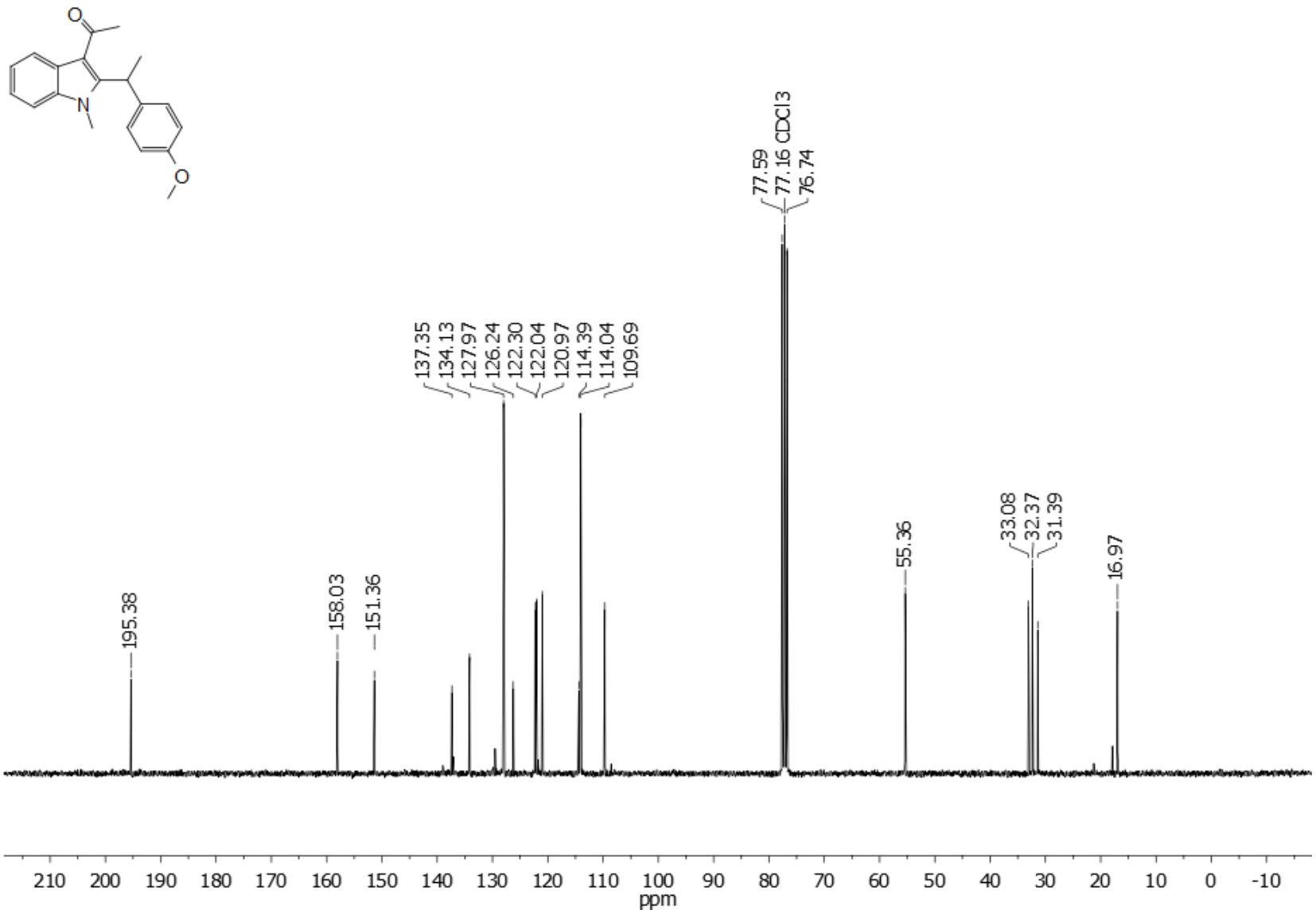


Figure S70. ^{13}C NMR spectrum of compound **4ac** ($CDCl_3$, 75 MHz)

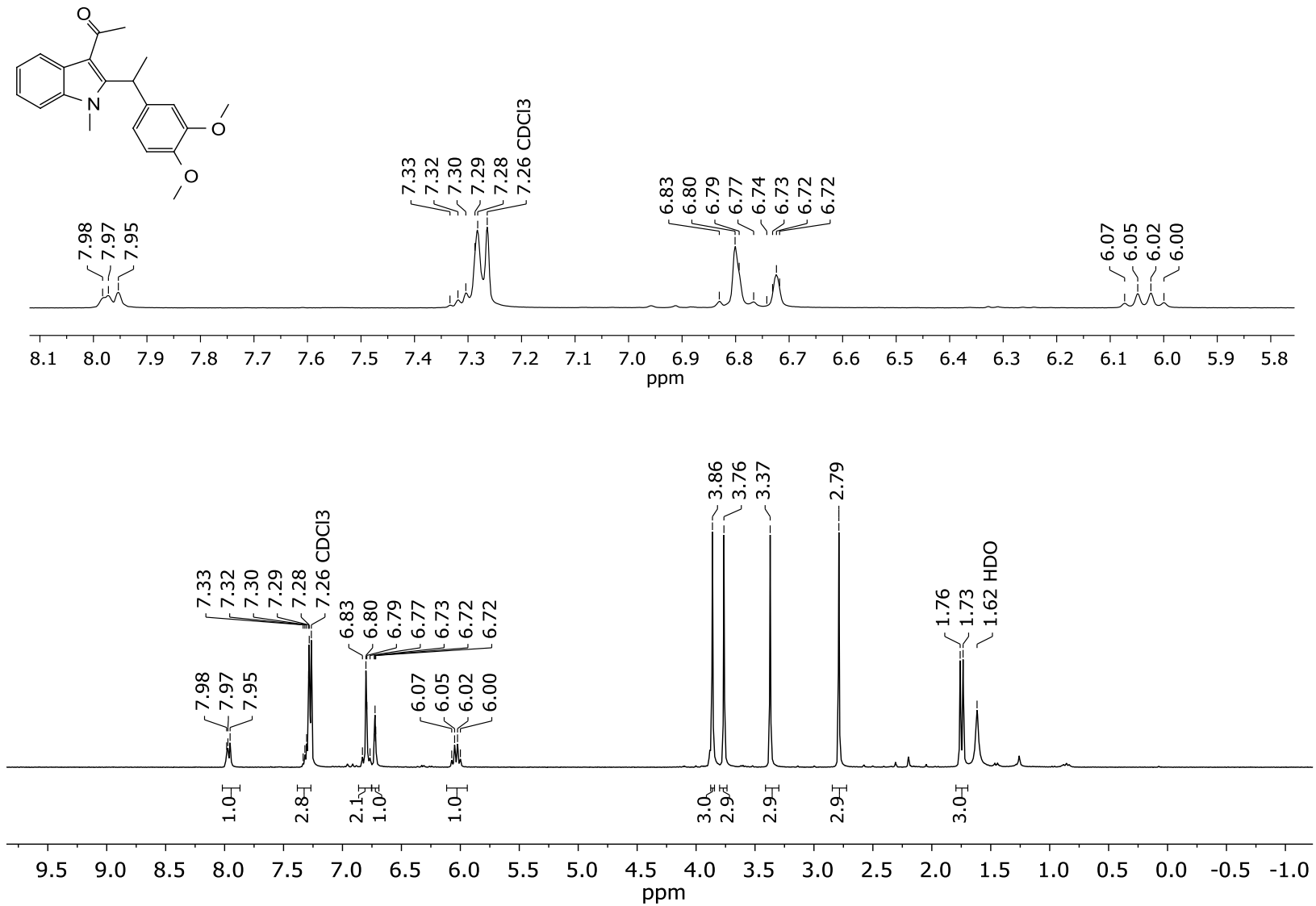


Figure S71. ^{1}H NMR spectrum of compound **4ad** ($CDCl_3$, 400 MHz)

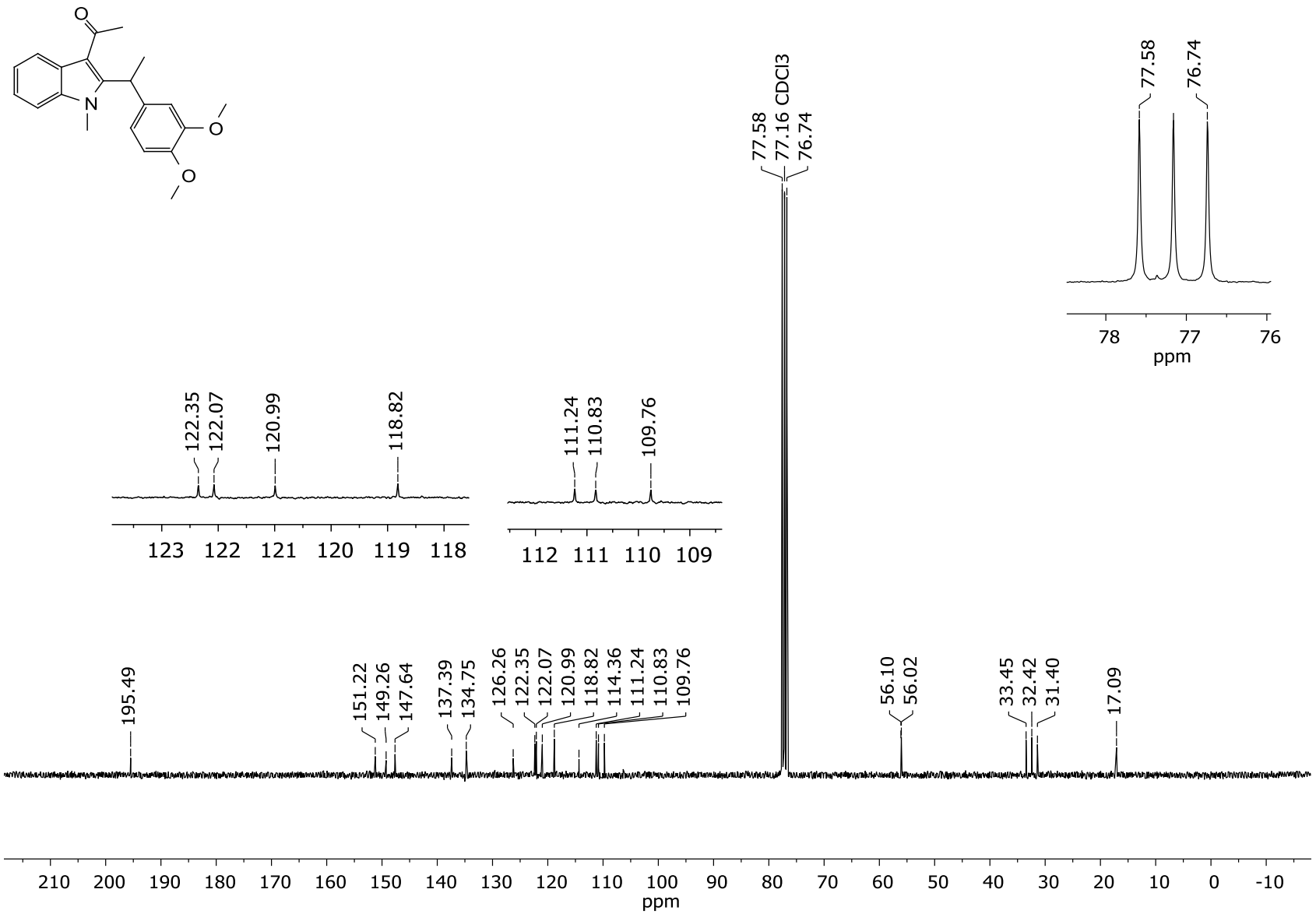


Figure S72. ^{13}C NMR spectrum of compound **4ad** ($CDCl_3$, 100 MHz)

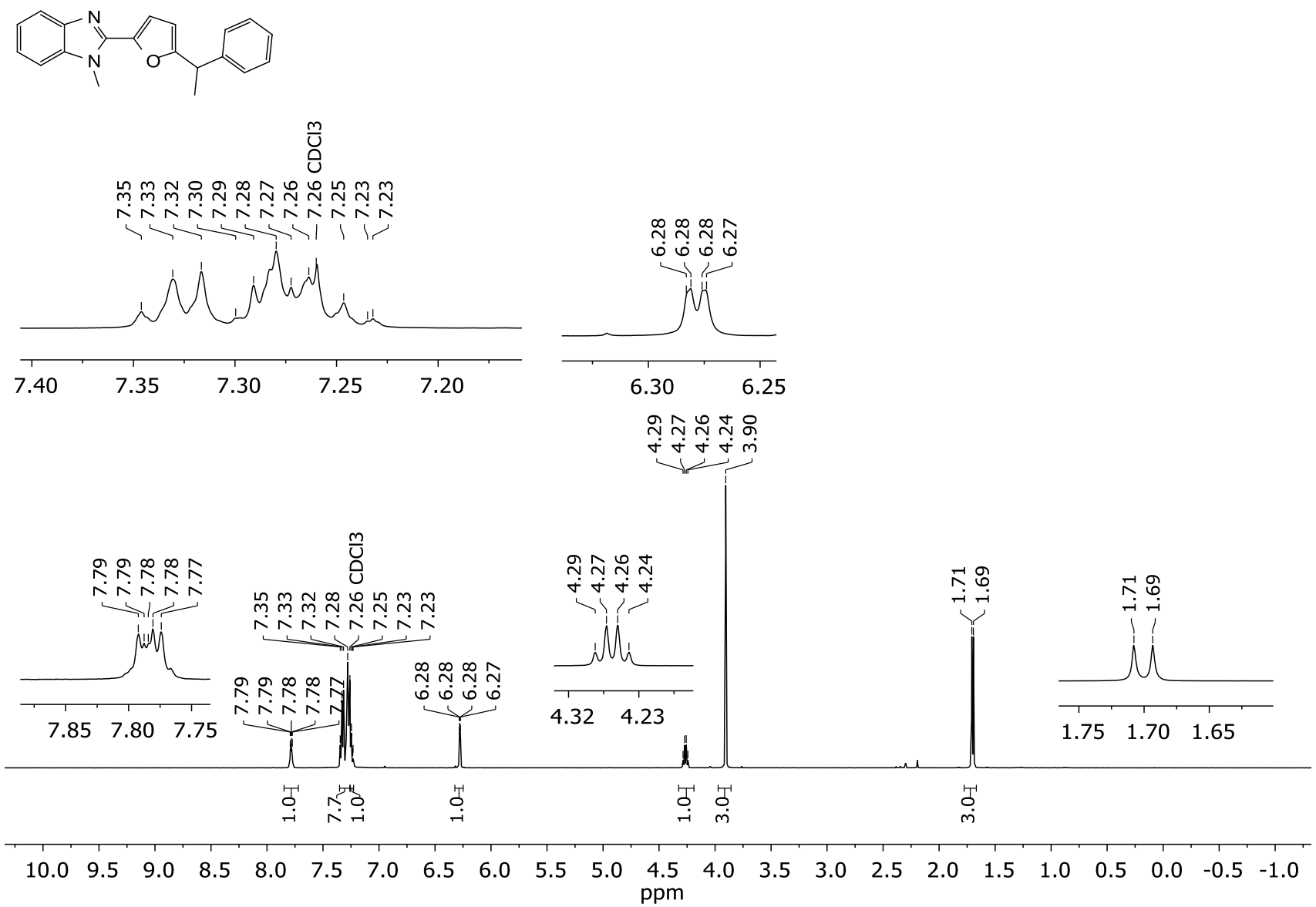


Figure S73. ^{1}H NMR spectrum of compound **4ae** ($CDCl_3$, 300 MHz)

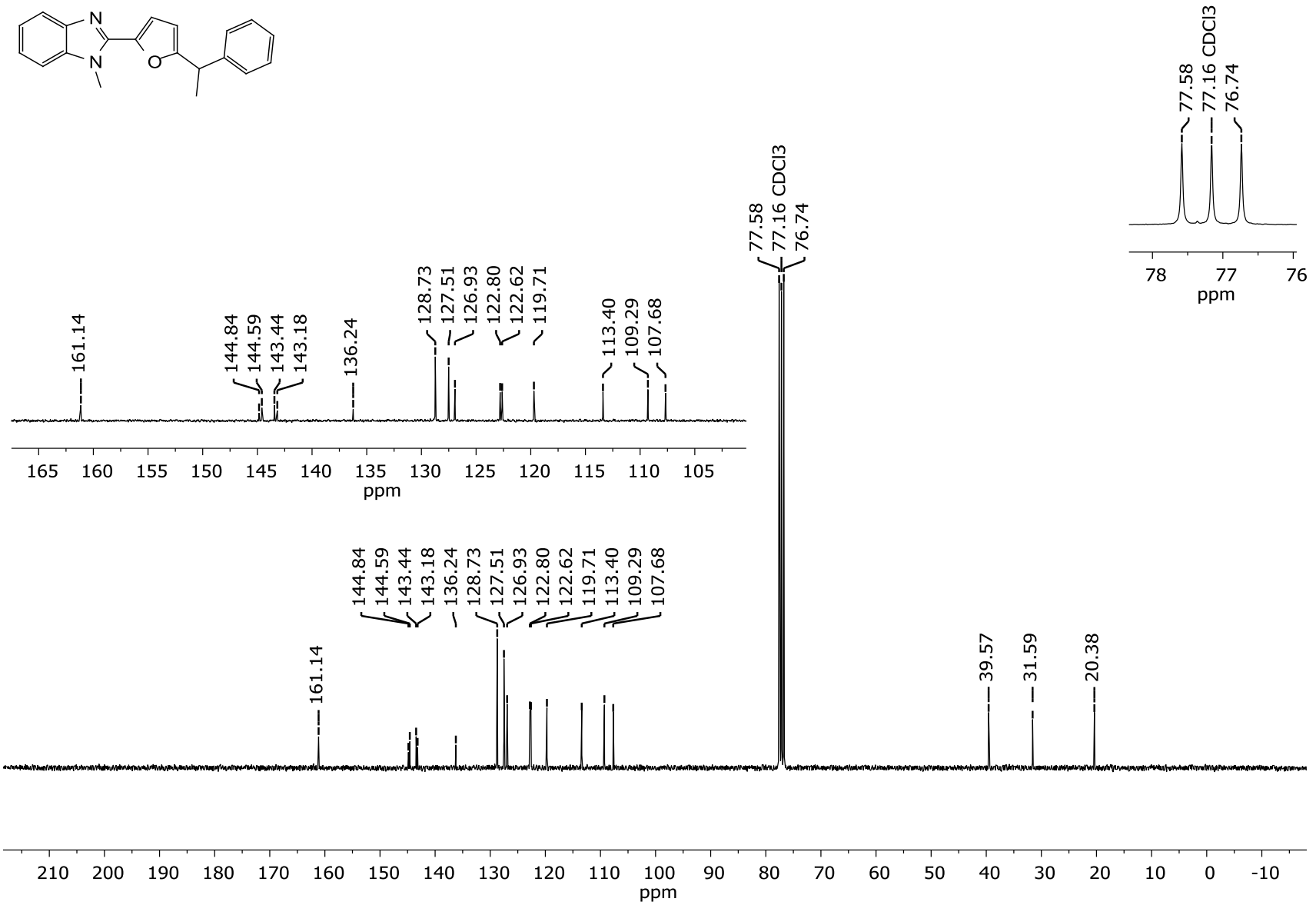


Figure S74. ^{13}C NMR spectrum of compound **4ae** ($CDCl_3$, 75 MHz)

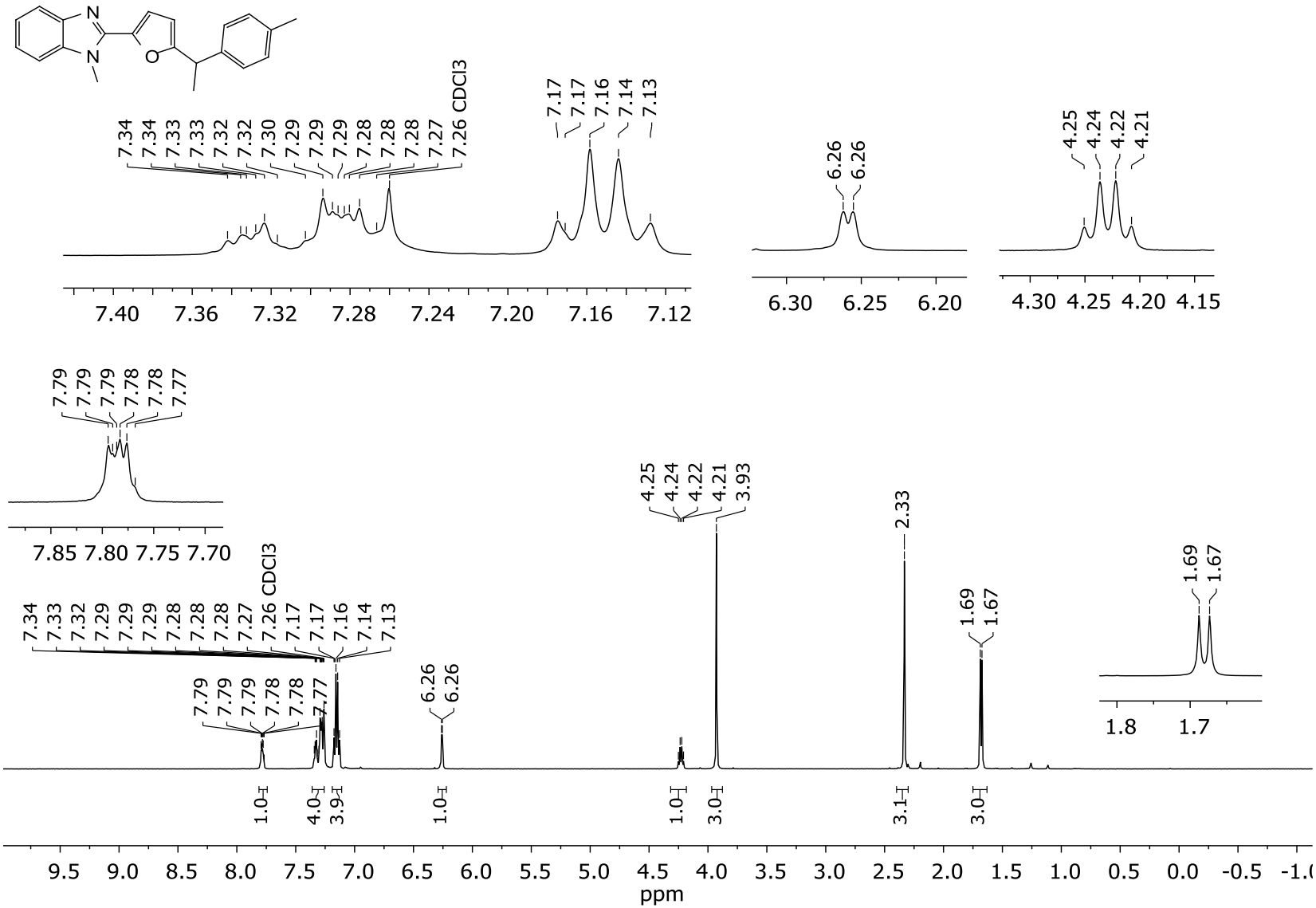


Figure S75. ^{1}H NMR spectrum of compound **4af** ($CDCl_3$, 300 MHz)

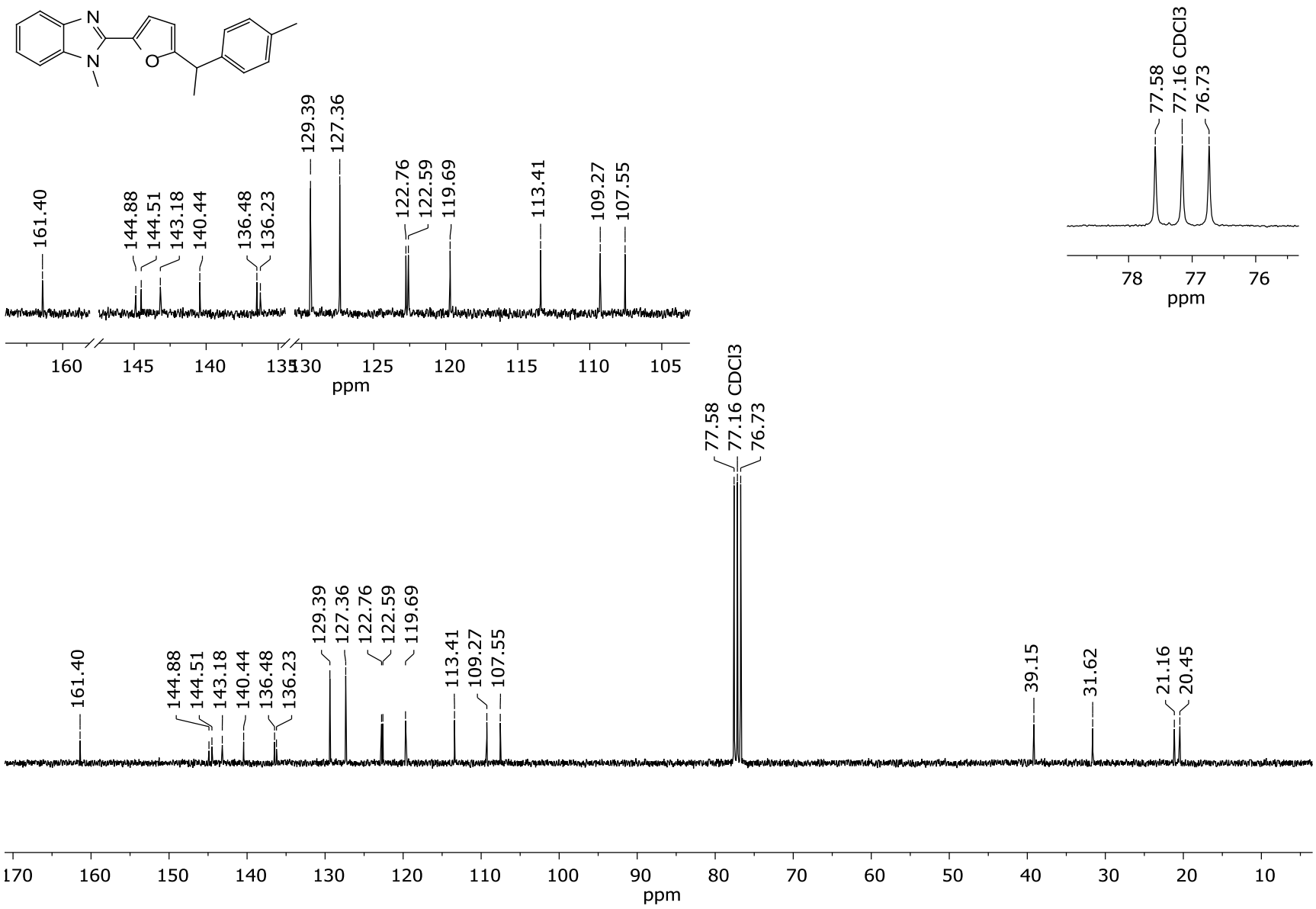


Figure S76. ^{13}C NMR spectrum of compound **4af** ($CDCl_3$, 75 MHz)

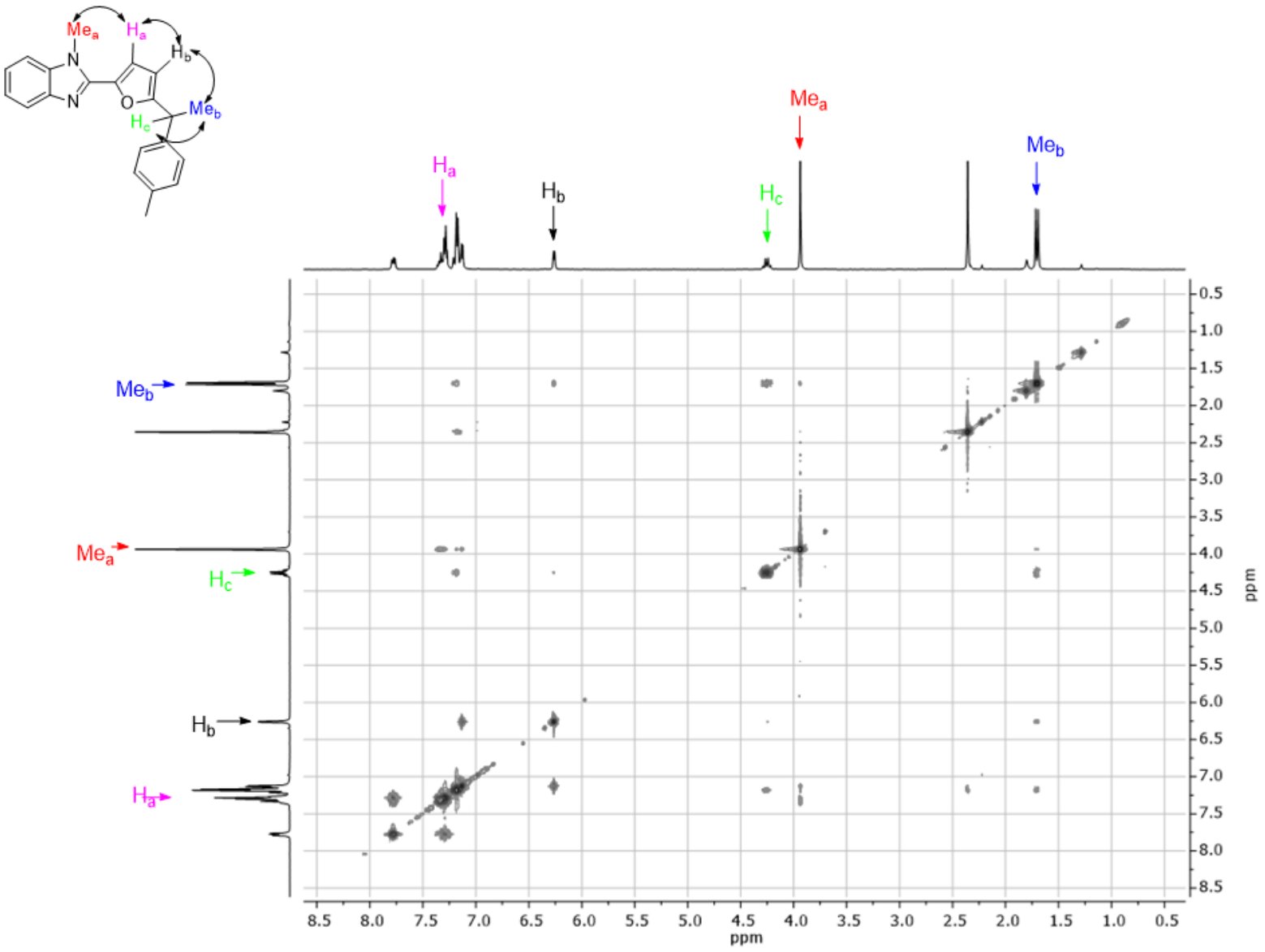


Figure S77. ^{1}H-^{1}H NOESY spectrum of compound **4af** ($CDCl_3$)

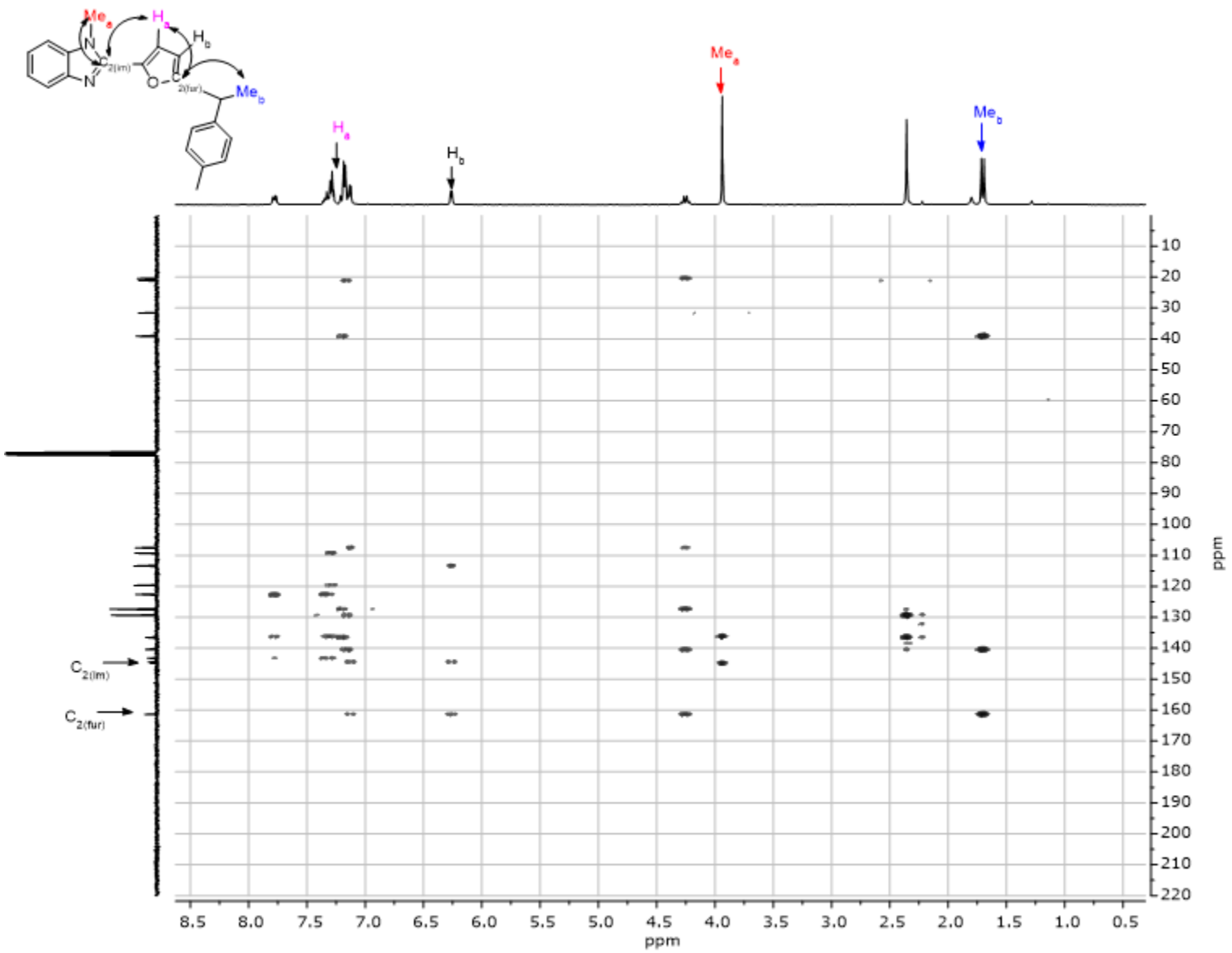


Figure S78. ^{1}H-^{13}C HMBC spectrum of compound **4af** ($CDCl_3$)

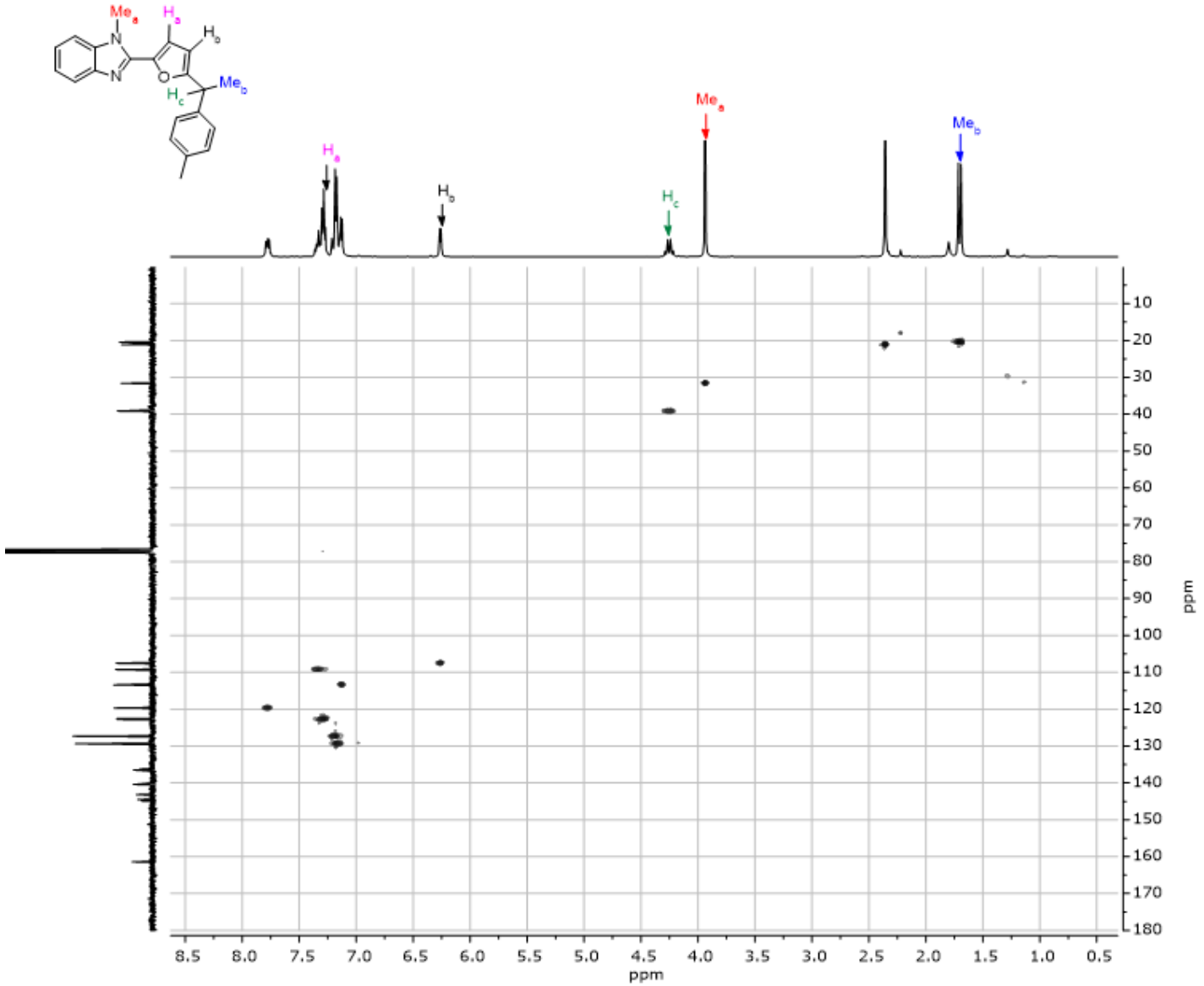


Figure S79. ^{1}H-^{13}C HSQC spectrum of compound **4af** ($CDCl_3$)

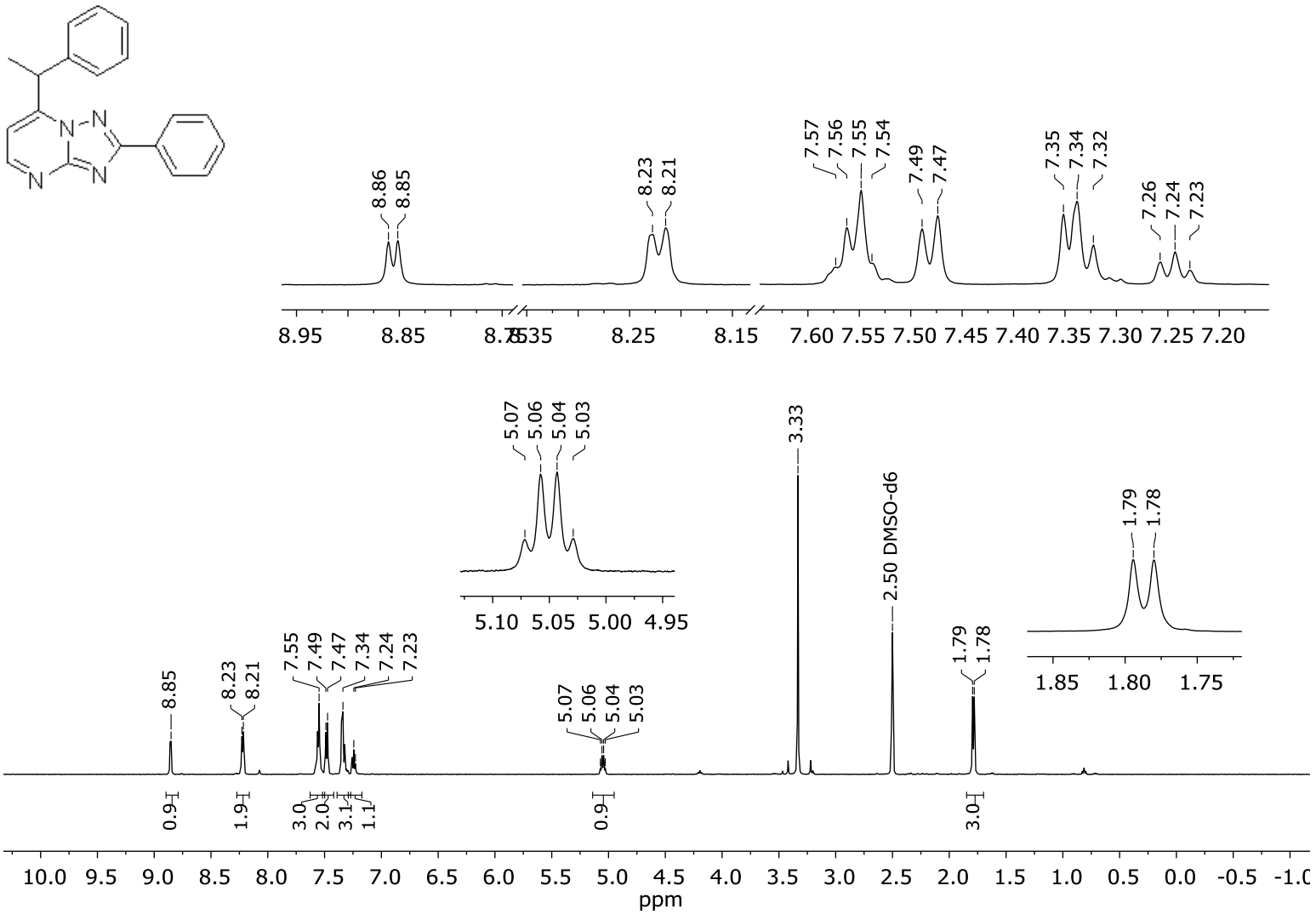


Figure S80. ^{1}H NMR spectrum of compound **4ag** (DMSO-d_6, 500 MHz)

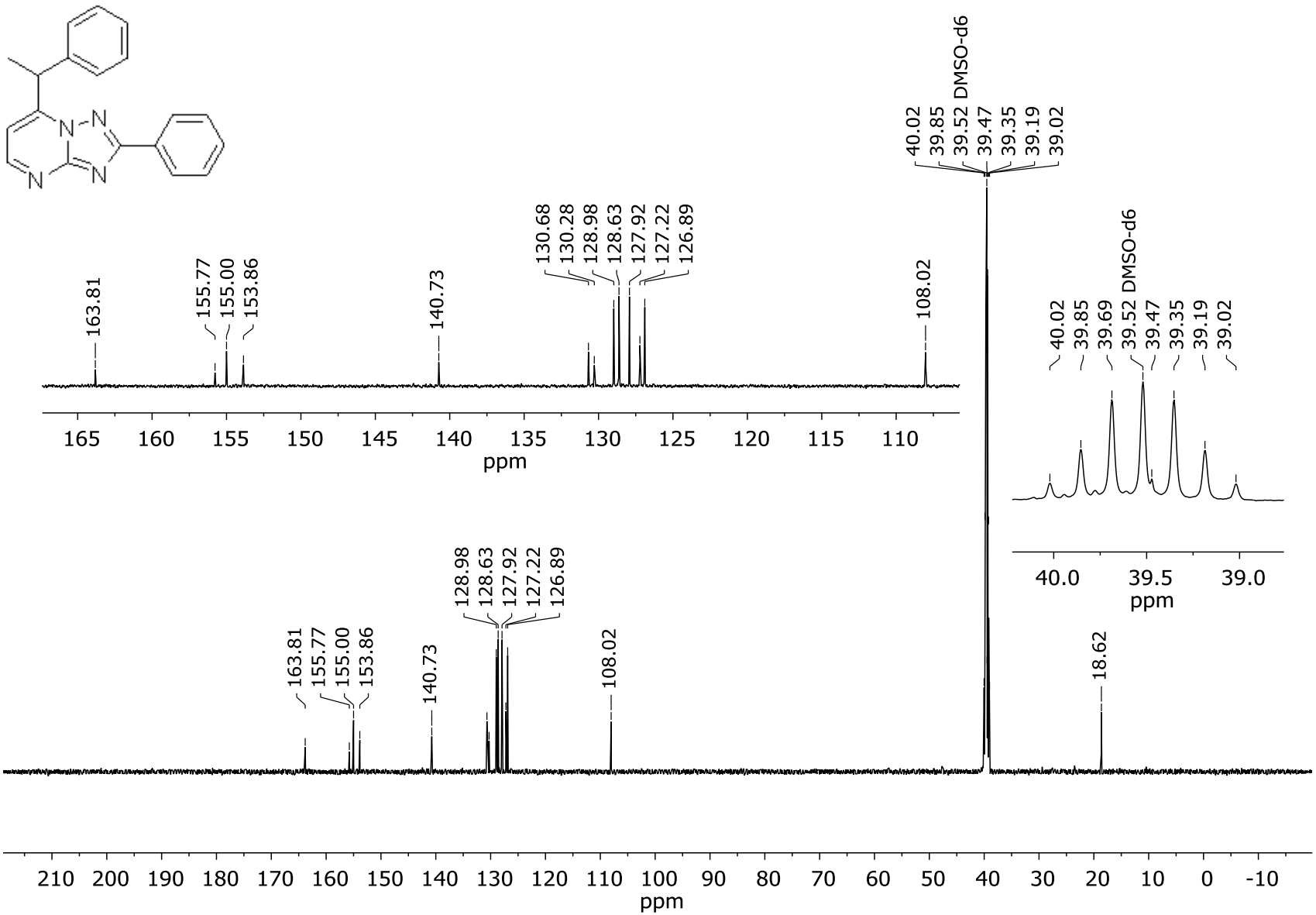


Figure S81. ^{13}C NMR spectrum of compound **4ag** (DMSO-d_6, 125 MHz)

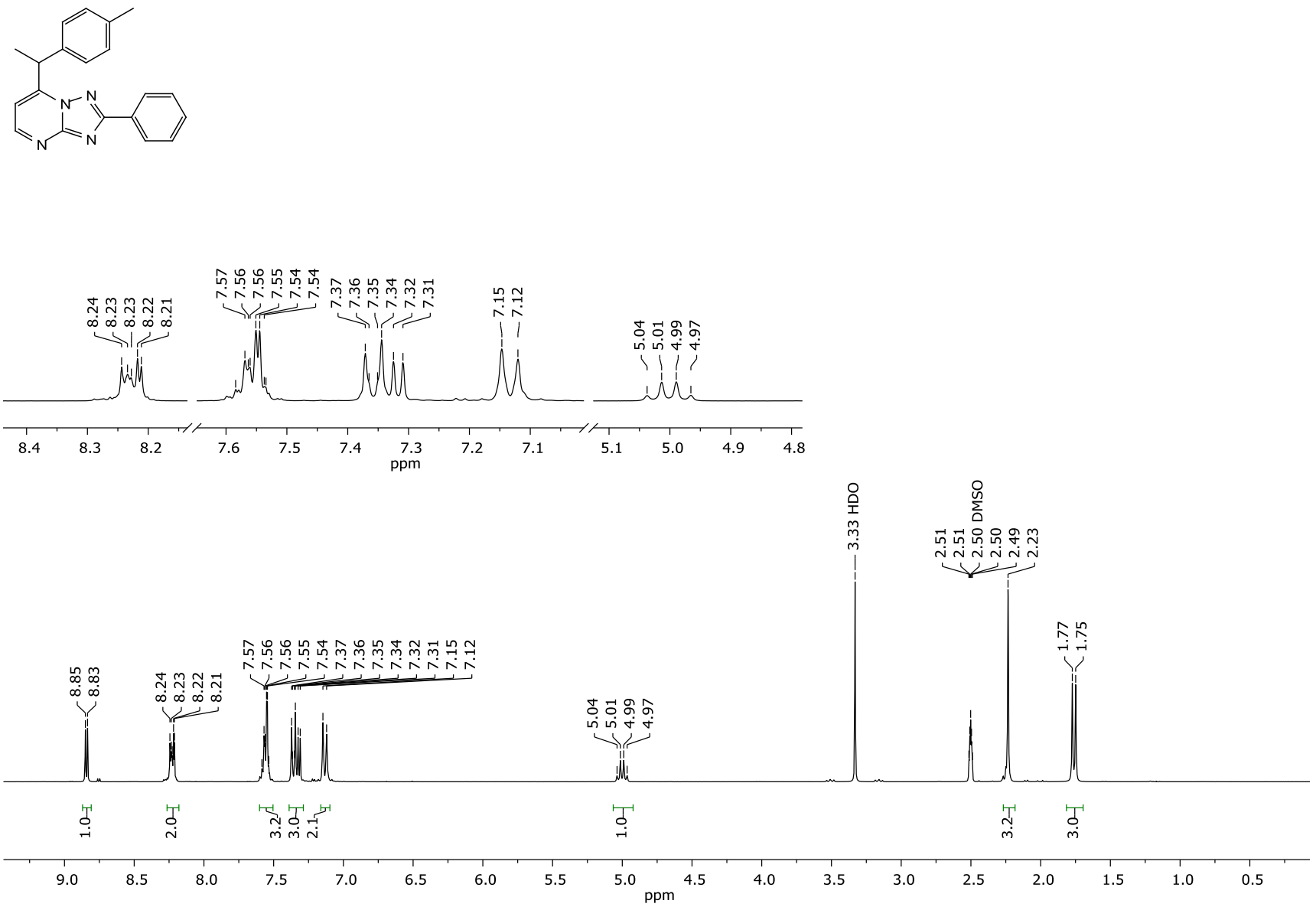


Figure S82. ^{1}H NMR spectrum of compound **4ah** (DMSO-d_6, 300 MHz)

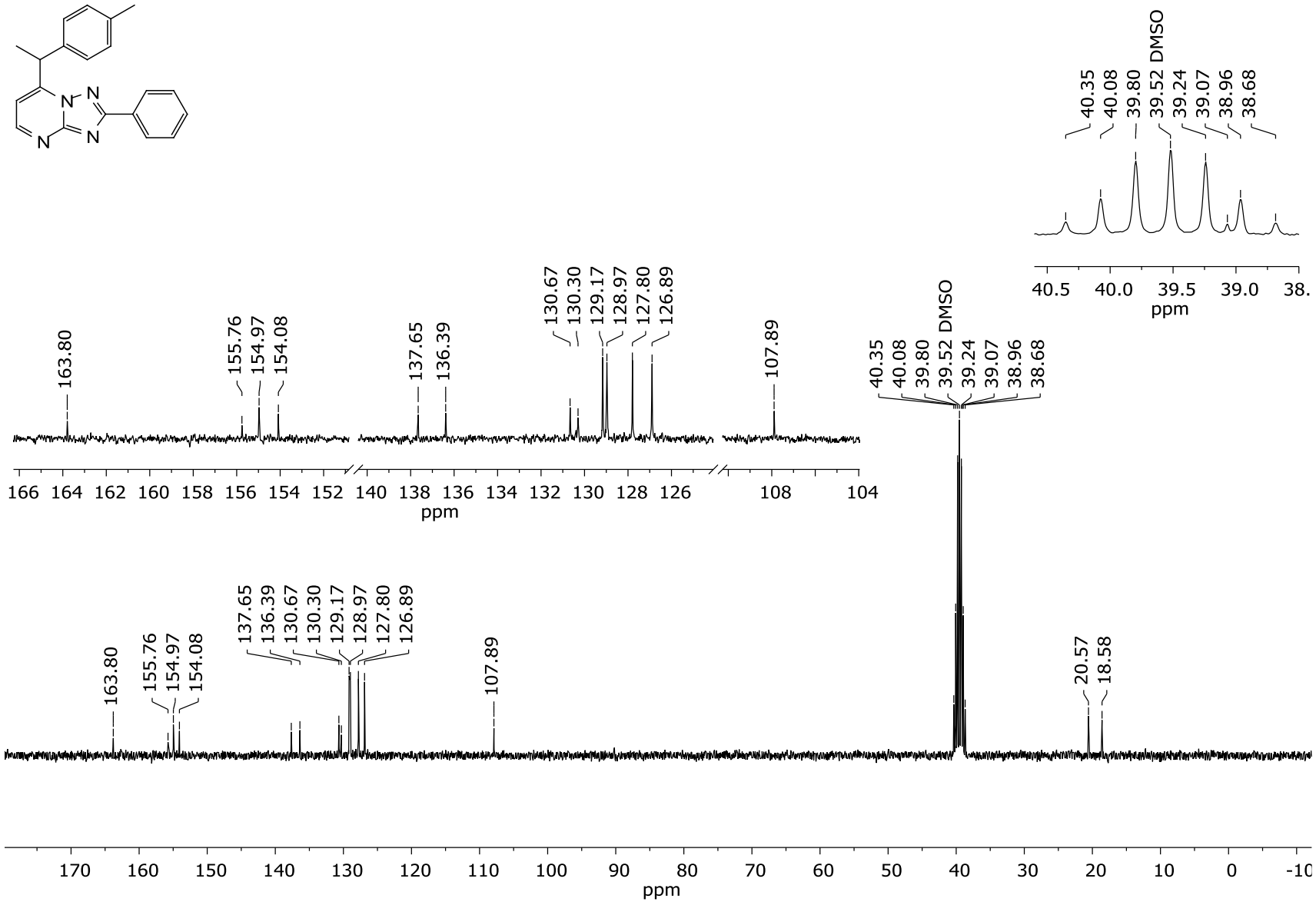


Figure S83. ^{13}C NMR spectrum of compound **4ah** (DMSO-d_6, 75 MHz)

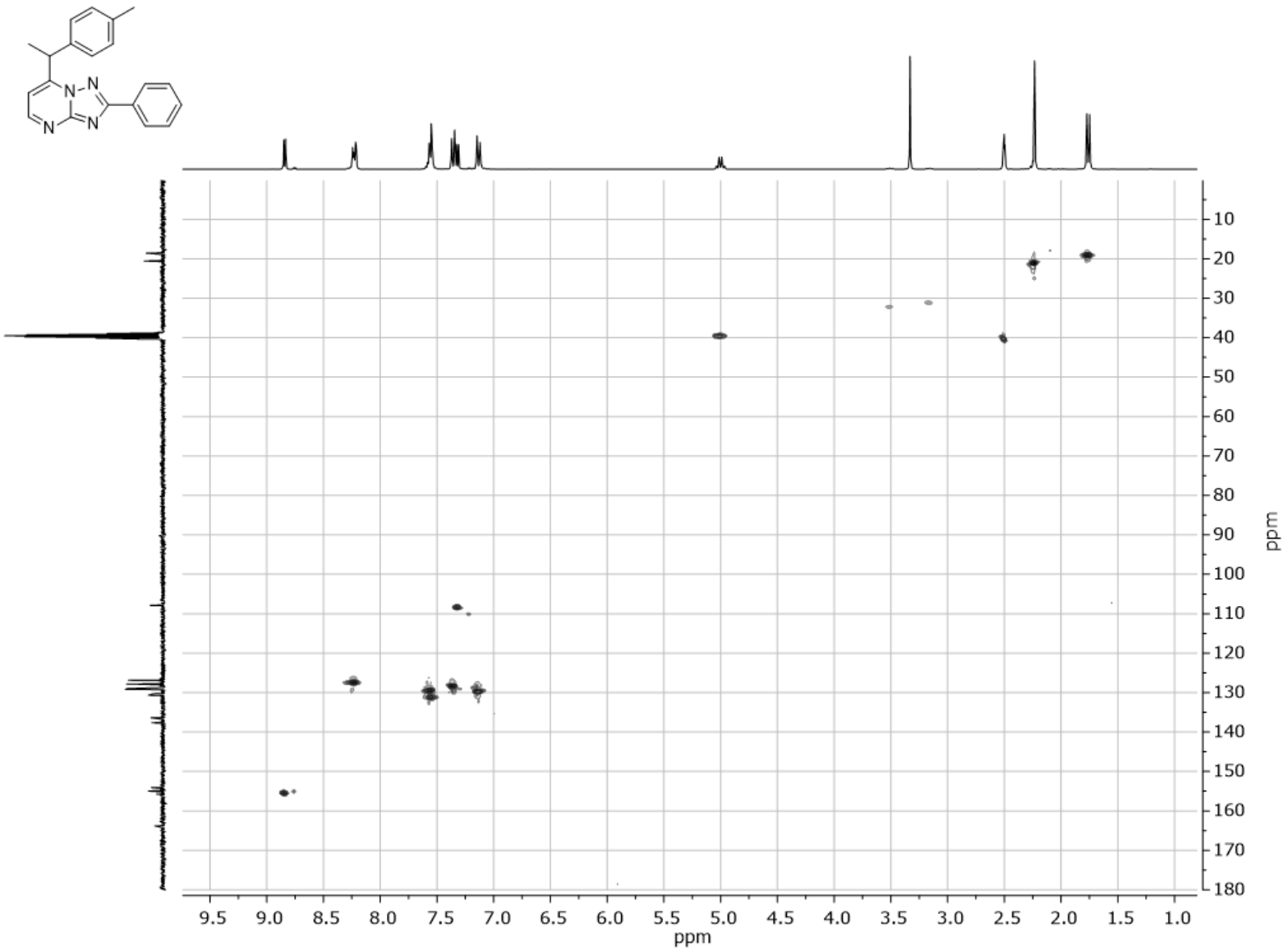


Figure S84. ^{1}H-^{13}C HSQC spectrum of compound **4ah** (DMSO-d_6)

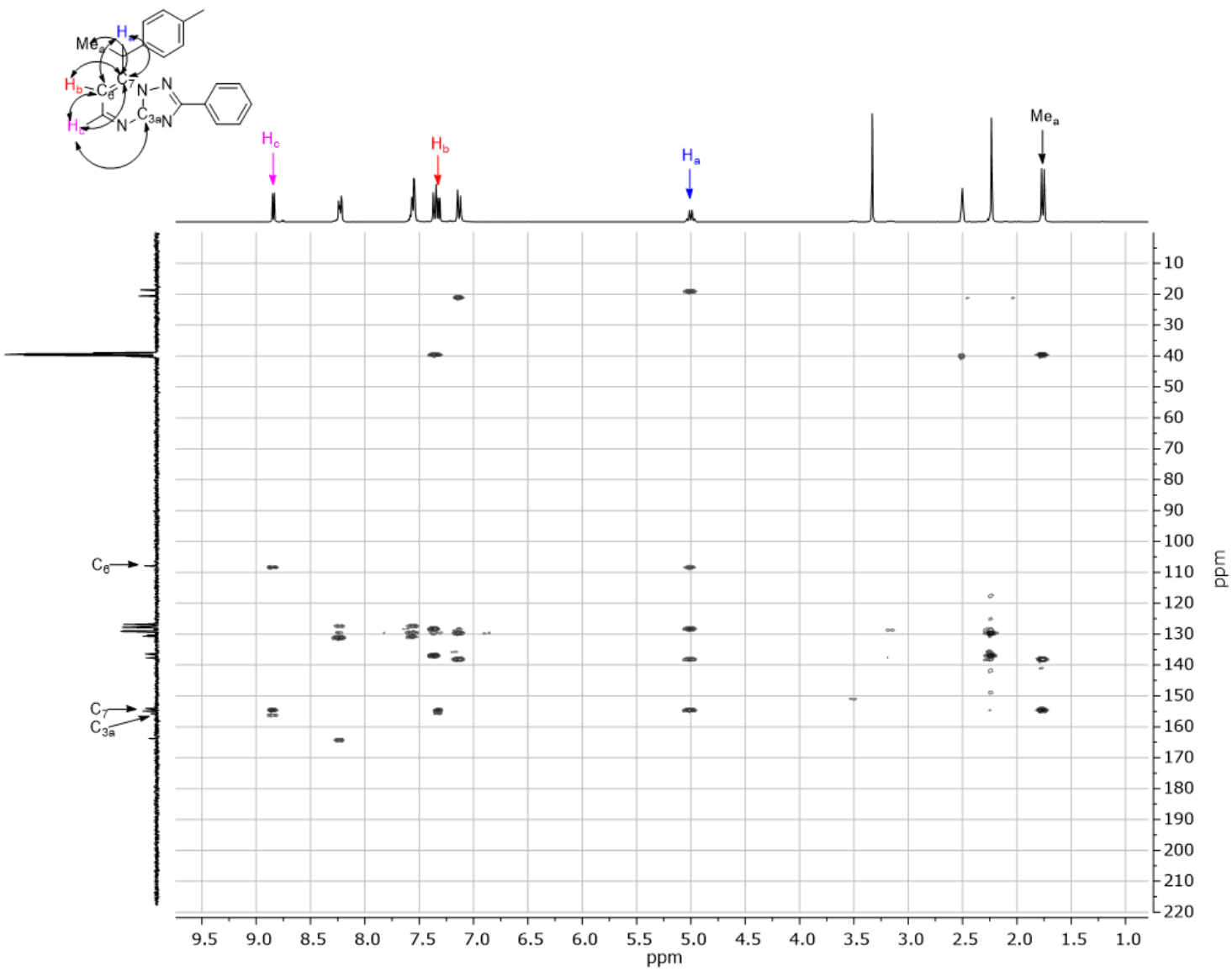


Figure S85. ^{1}H-^{13}C HMBC spectrum of compound **4ah** (DMSO-d_6)

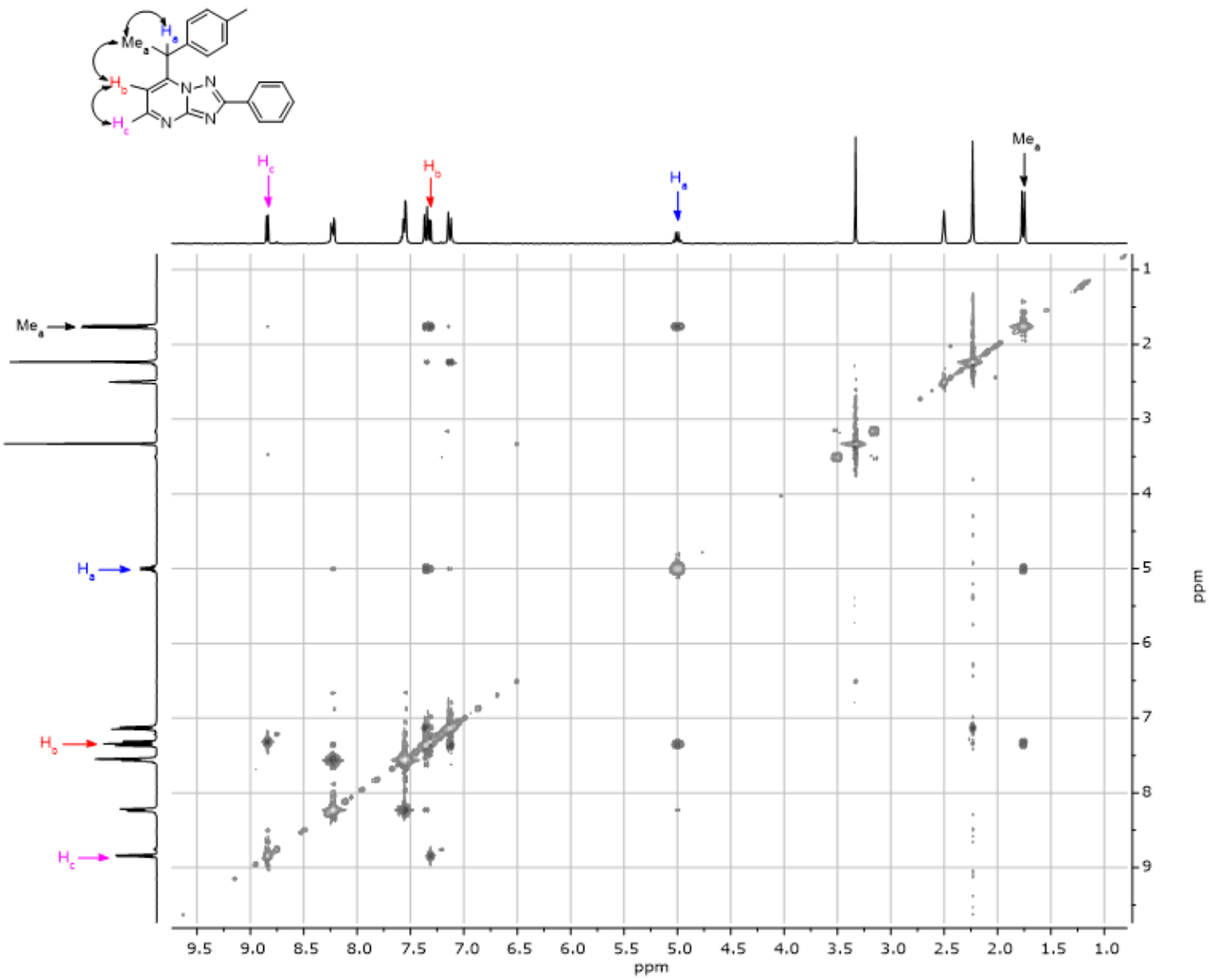


Figure S86. ^{1}H-^{1}H NOESY spectrum of compound **4ah** (DMSO-d_6)

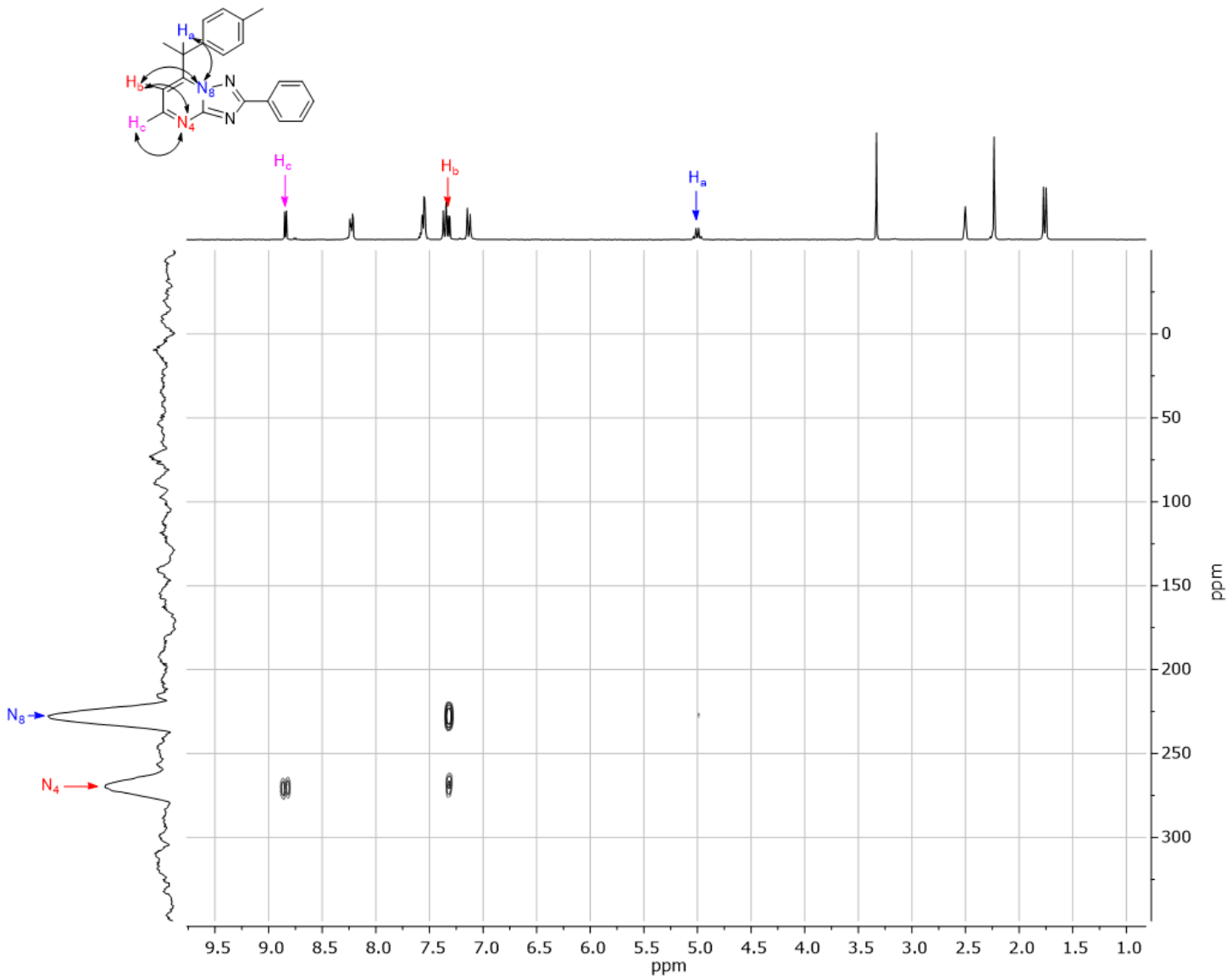


Figure S87. ^{1}H-^{15}N HMBC spectrum of compound **4ah** (DMSO-d_6)

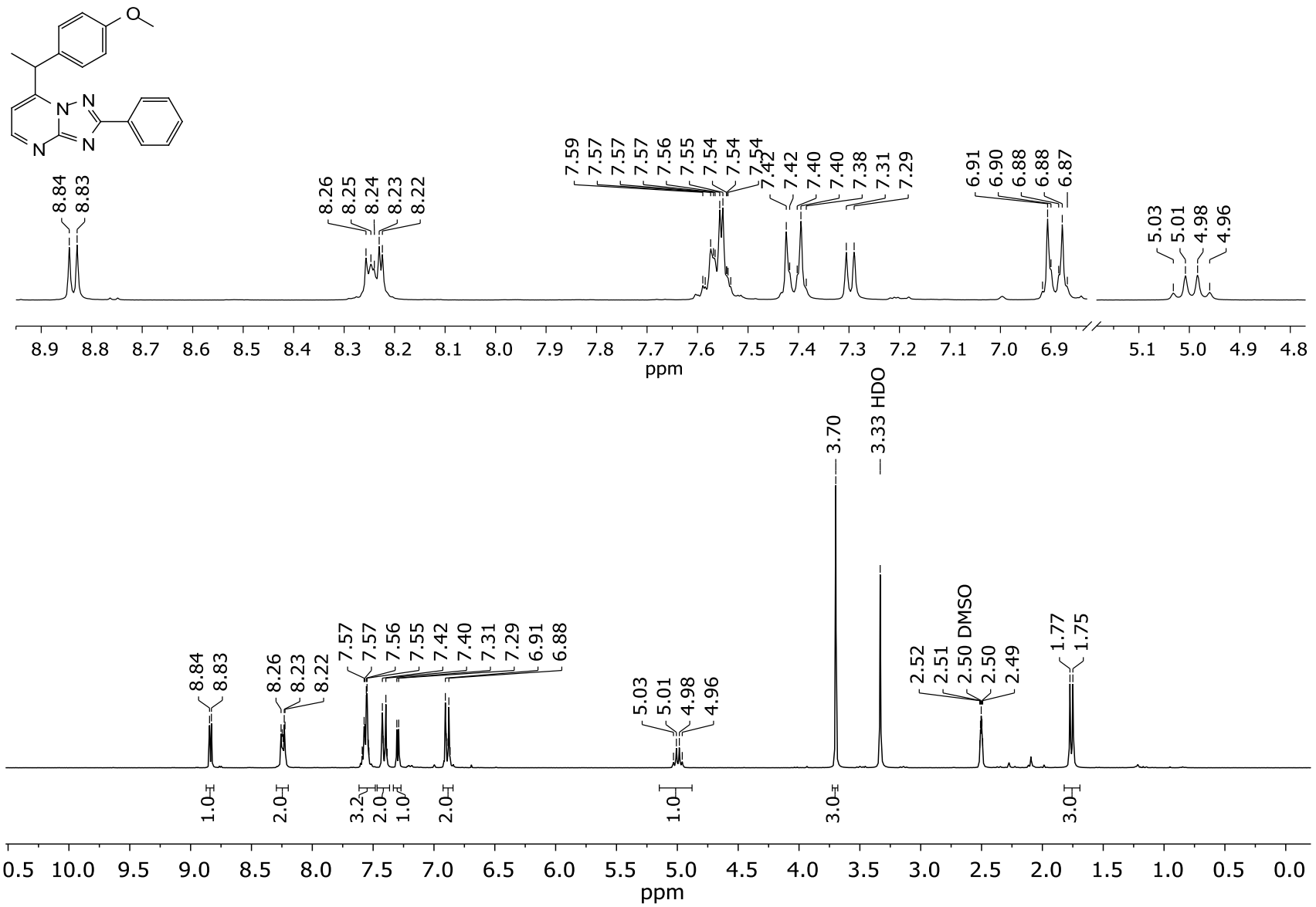


Figure S88. ^{1}H NMR spectrum of compound **4ai** (DMSO-d_6, 500 MHz)

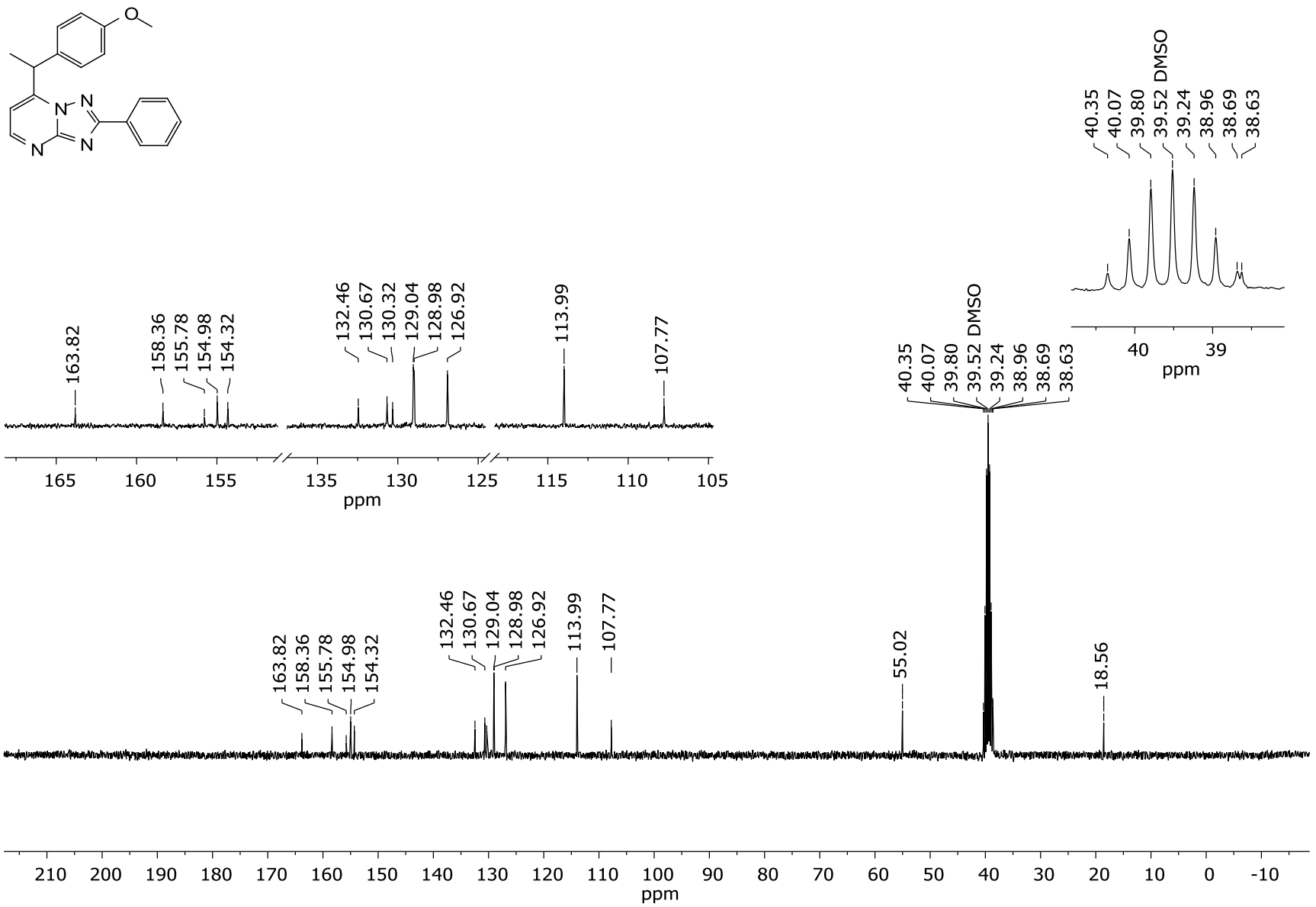


Figure S89. ^{13}C NMR spectrum of compound **4ai** (DMSO-d_6, 125 MHz)

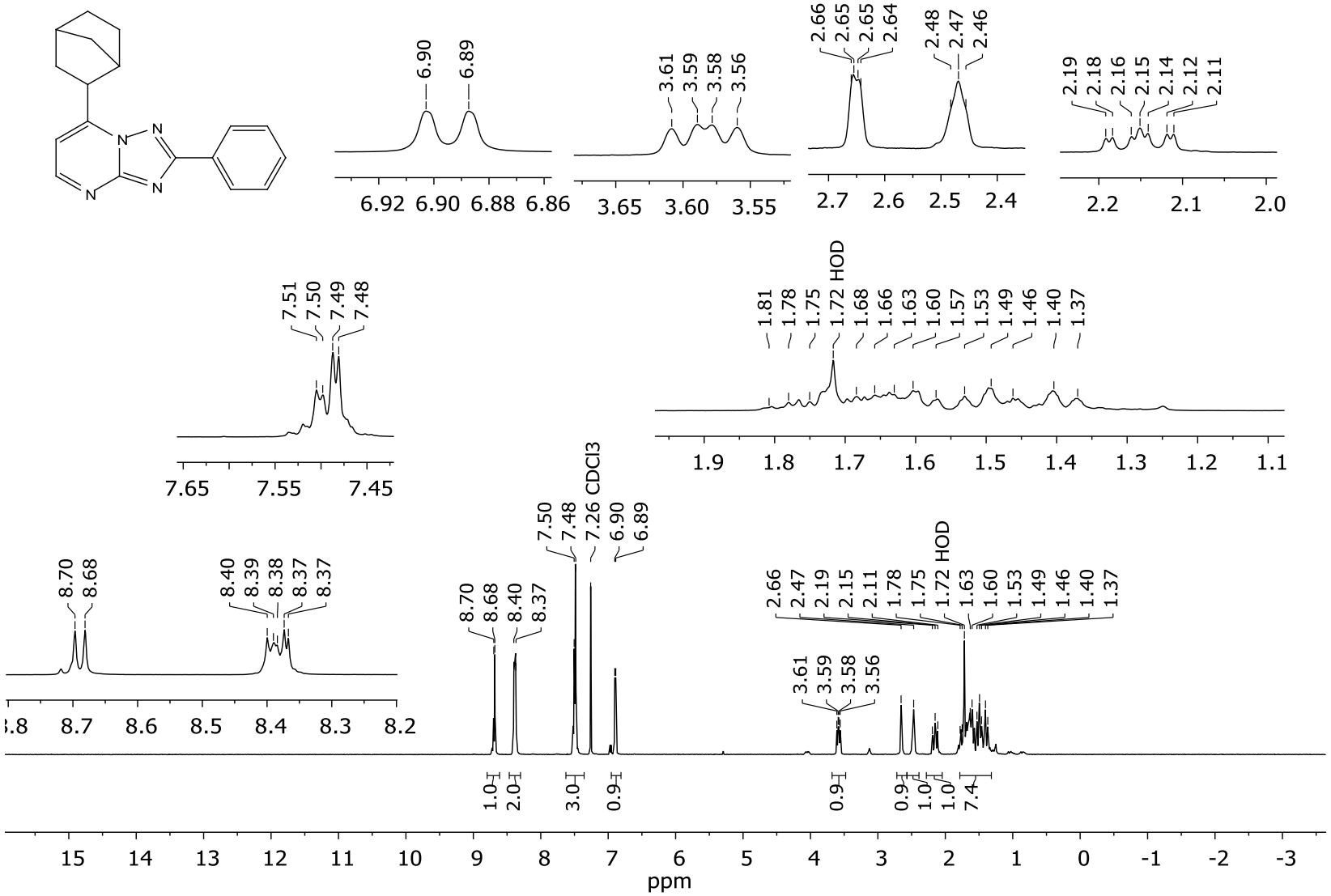


Figure S90. ^{1}H NMR spectrum of compound **4aj** ($CDCl_3$, 300 MHz)

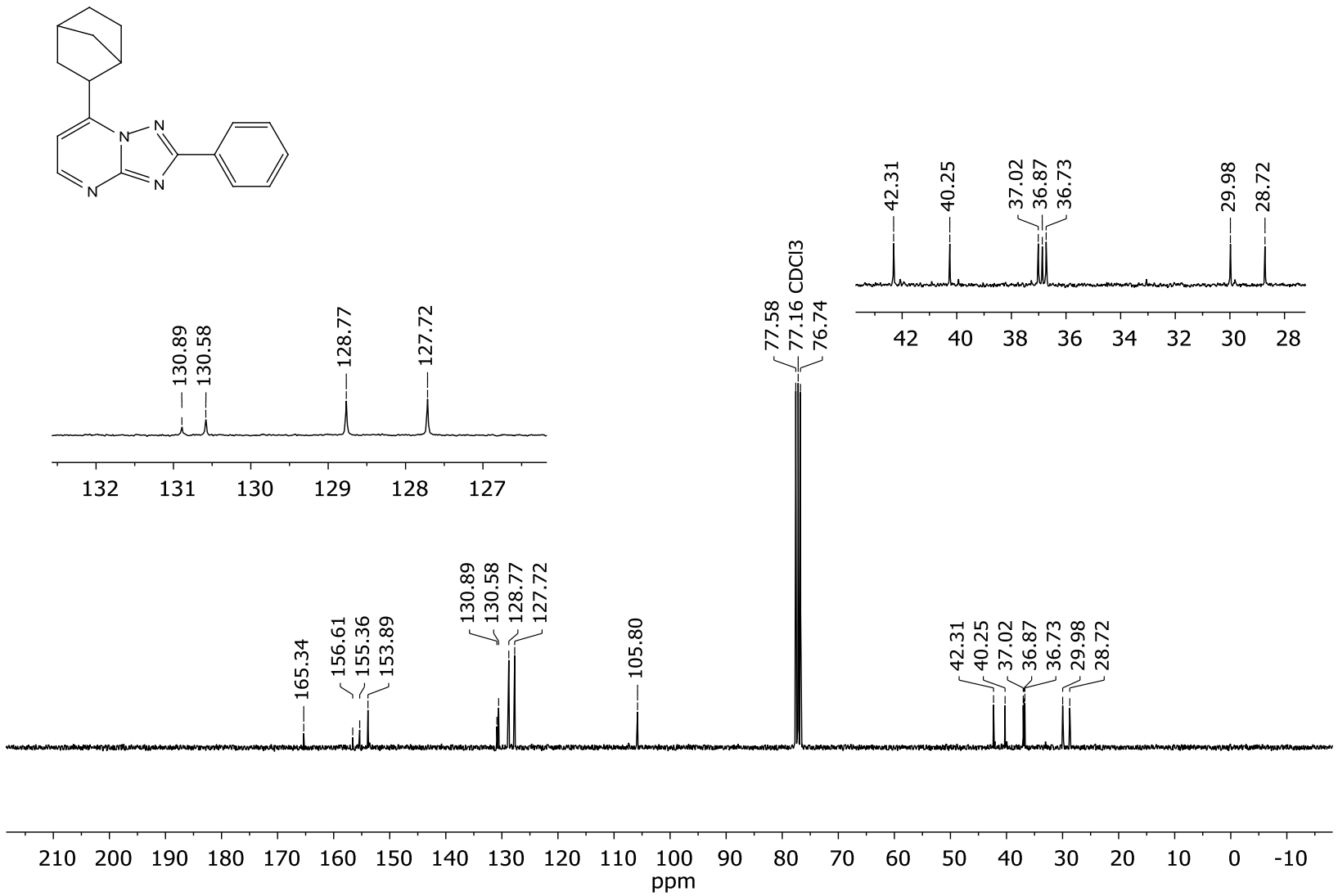


Figure S91. ^{13}C NMR spectrum of compound **4aj** ($CDCl_3$, 75 MHz)

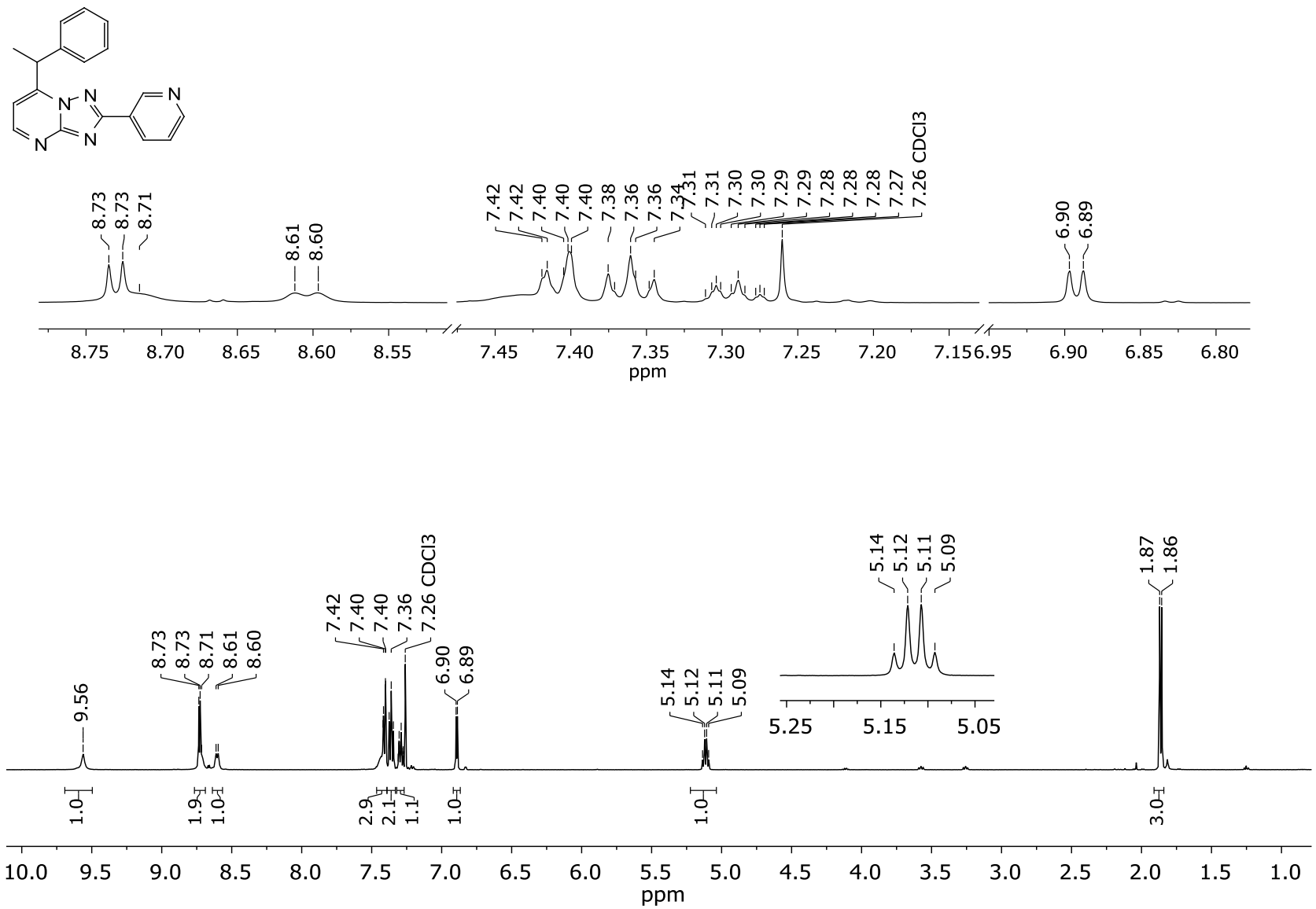


Figure S92. ^{1}H NMR spectrum of compound **4ak** ($CDCl_3$, 500 MHz)

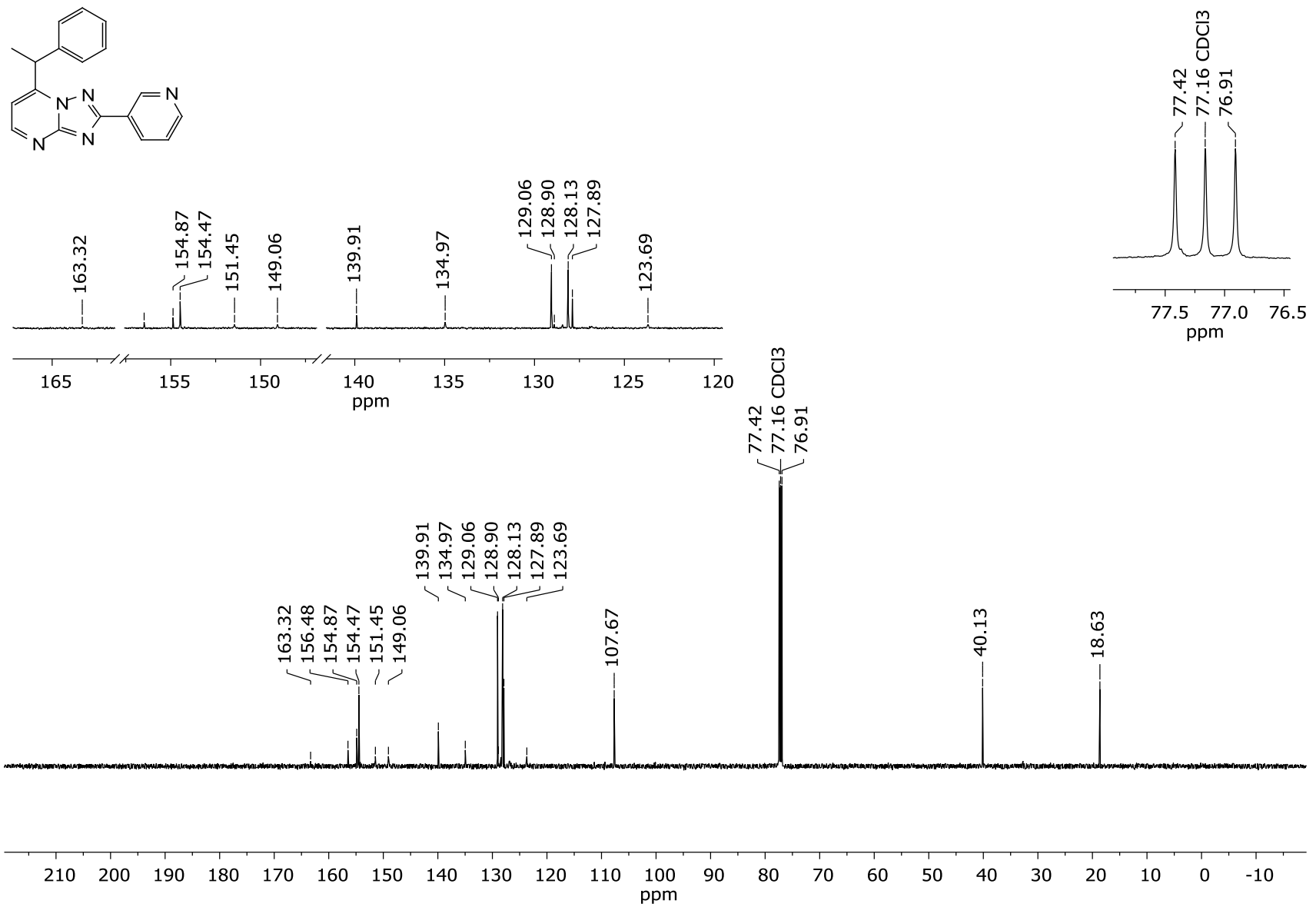


Figure S93. ^{13}C NMR spectrum of compound **4ak** ($CDCl_3$, 125 MHz)

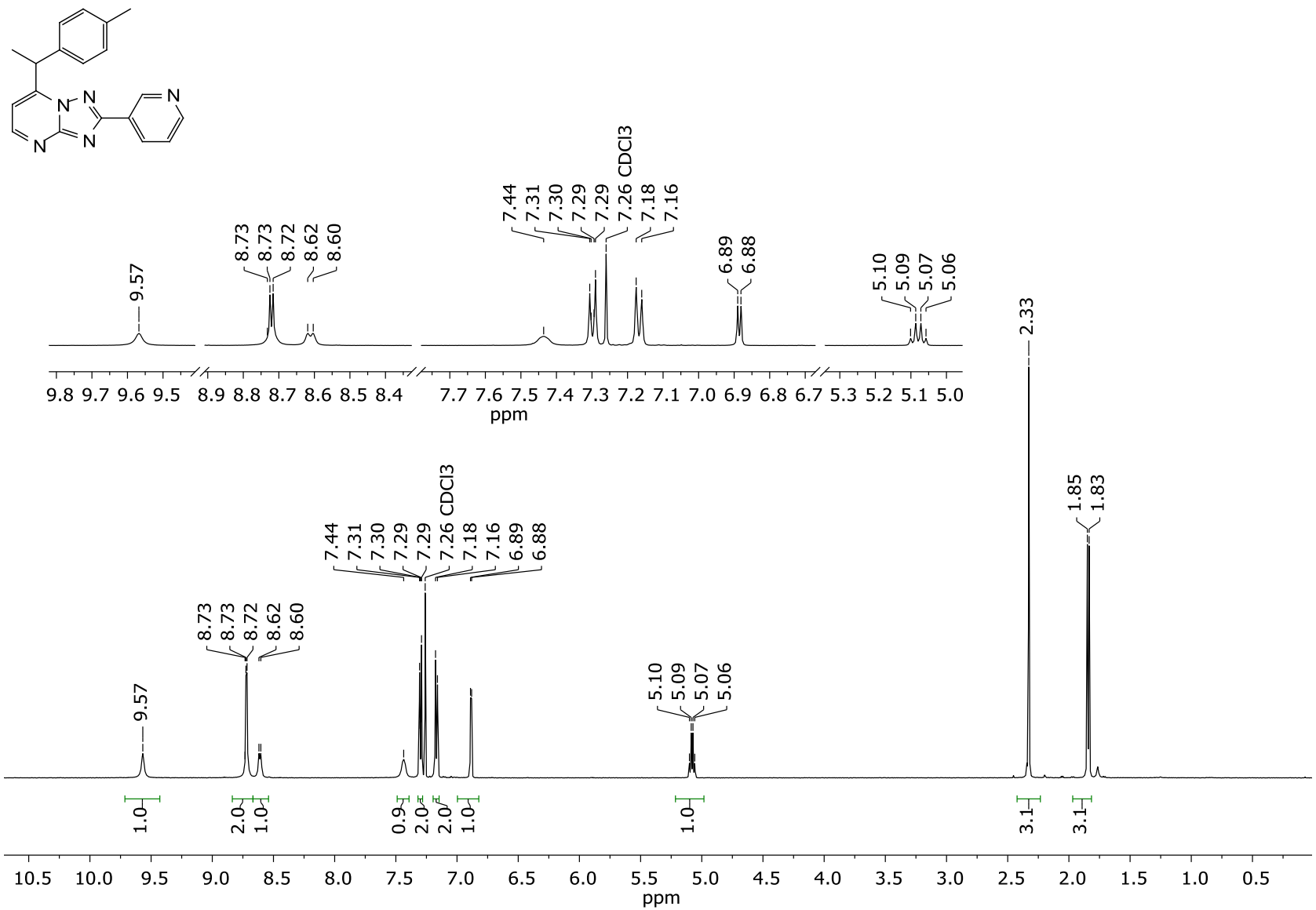


Figure S94. ^{1}H NMR spectrum of compound **4al** ($CDCl_3$, 500 MHz)

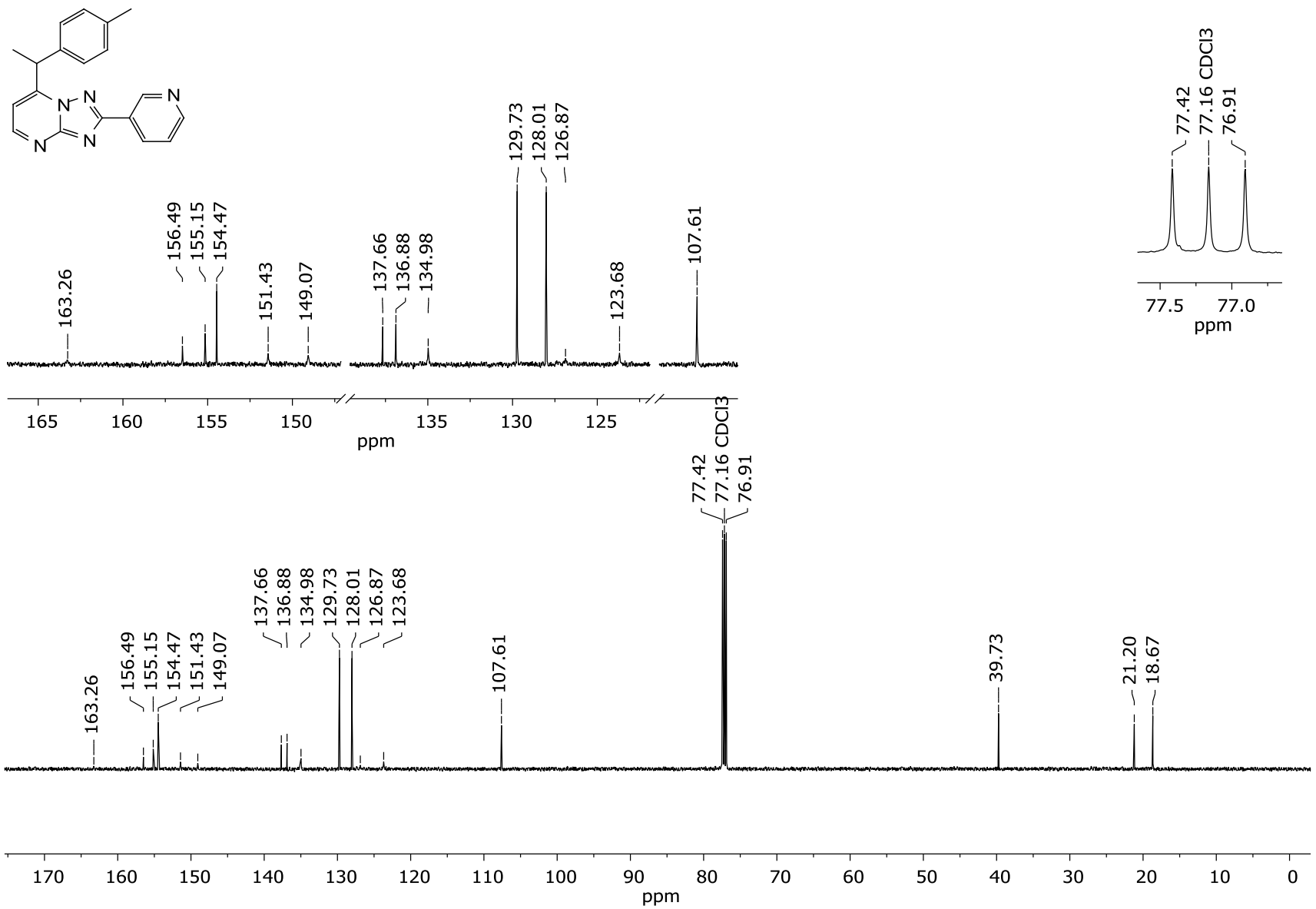


Figure S95. ^{13}C NMR spectrum of compound **4al** ($CDCl_3$, 125 MHz)

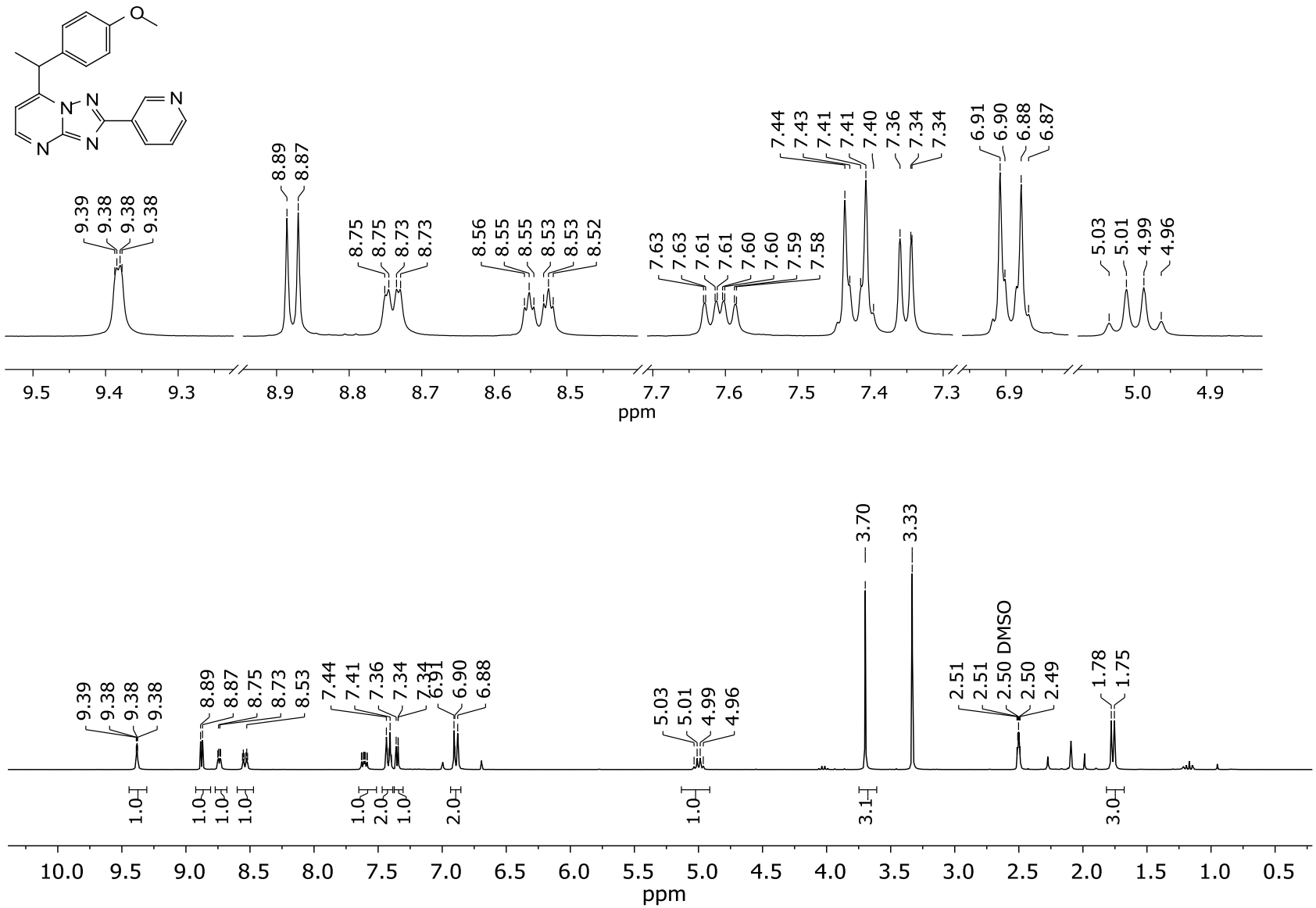


Figure S96. ^{1}H NMR spectrum of compound **4am** (DMSO-d_6, 500 MHz)

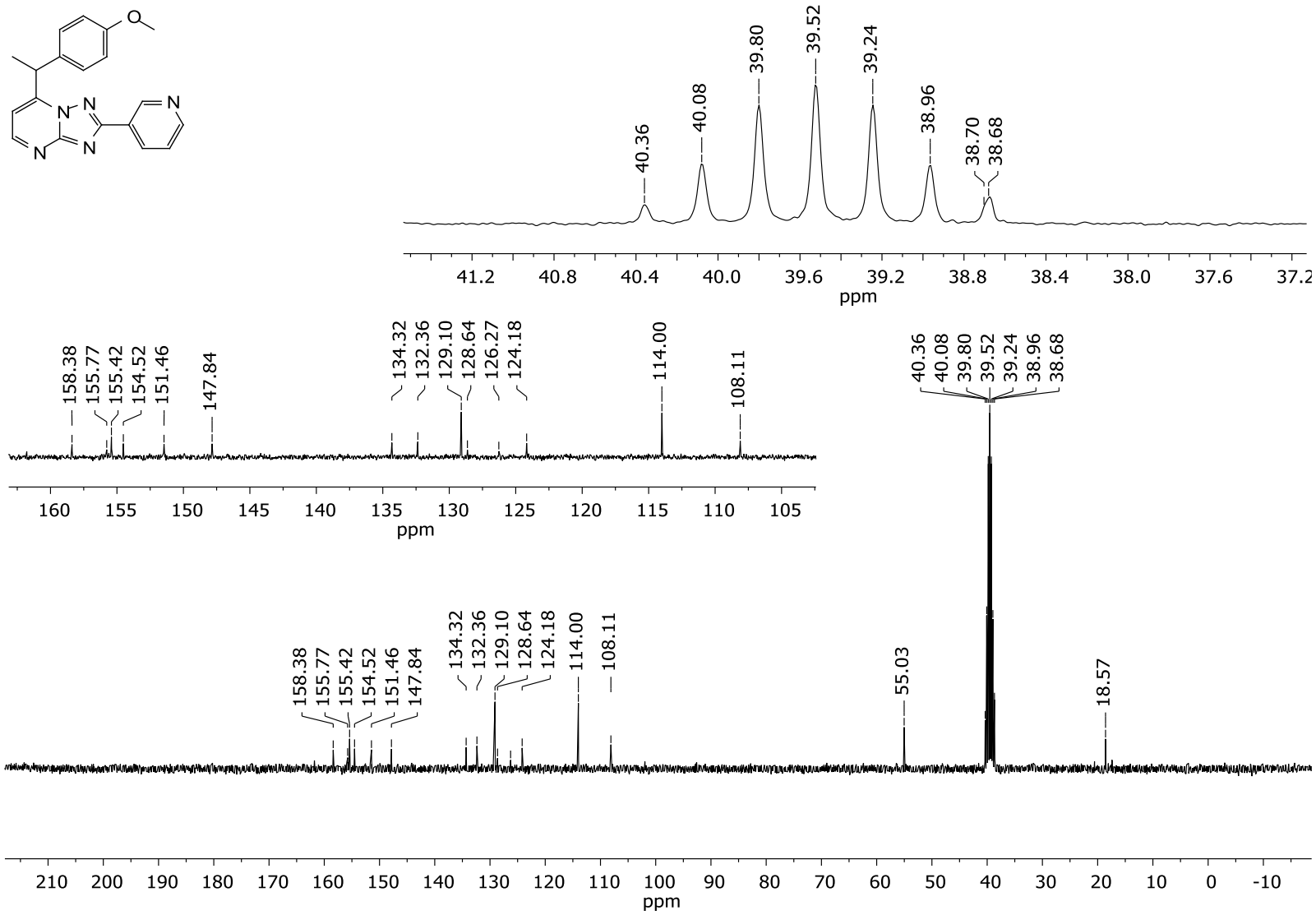


Figure S97. ^{13}C NMR spectrum of compound **4am** (DMSO-d_6, 125 MHz)

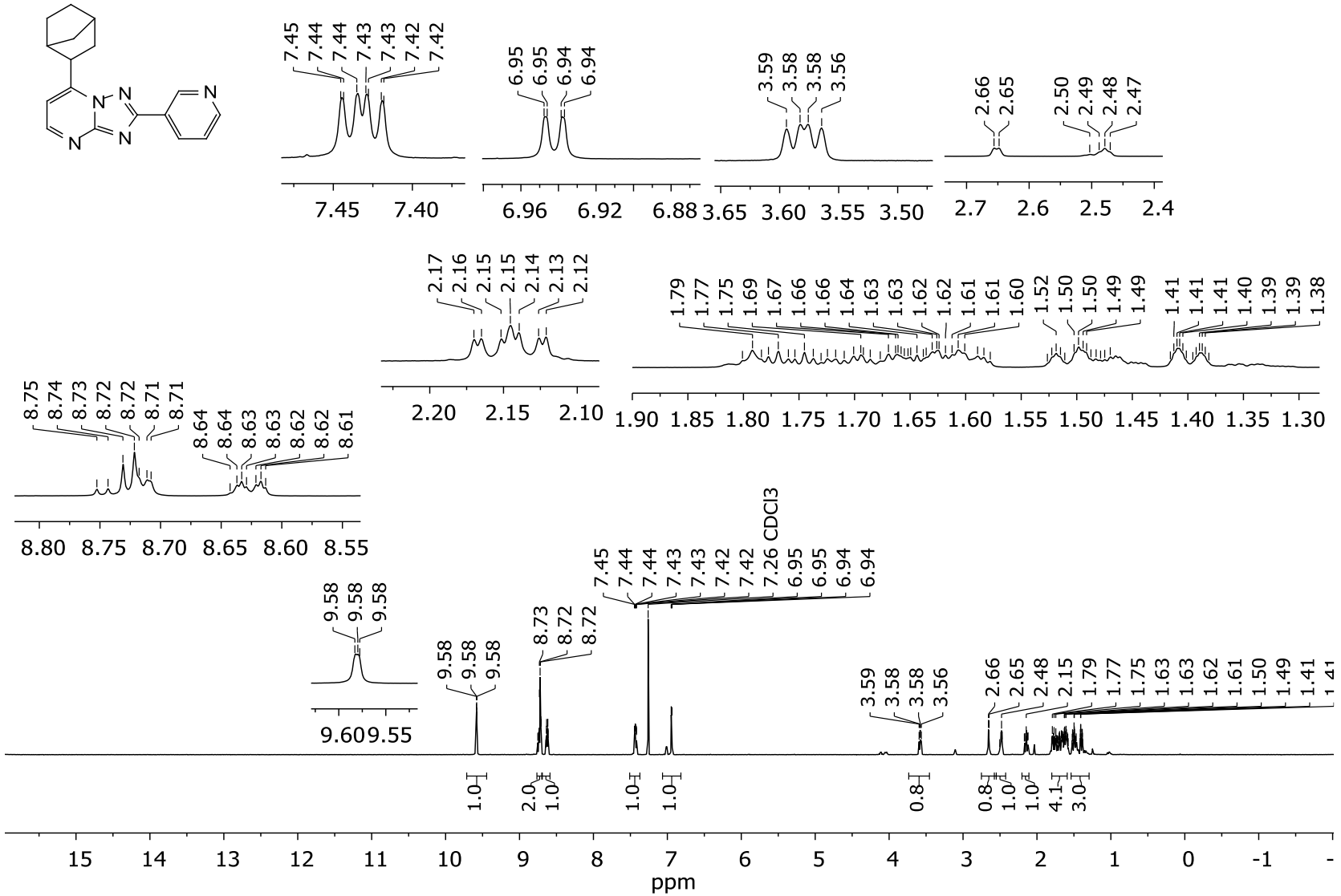


Figure S98. ^{1}H NMR spectrum of compound **4an** ($CDCl_3$, 500 MHz)

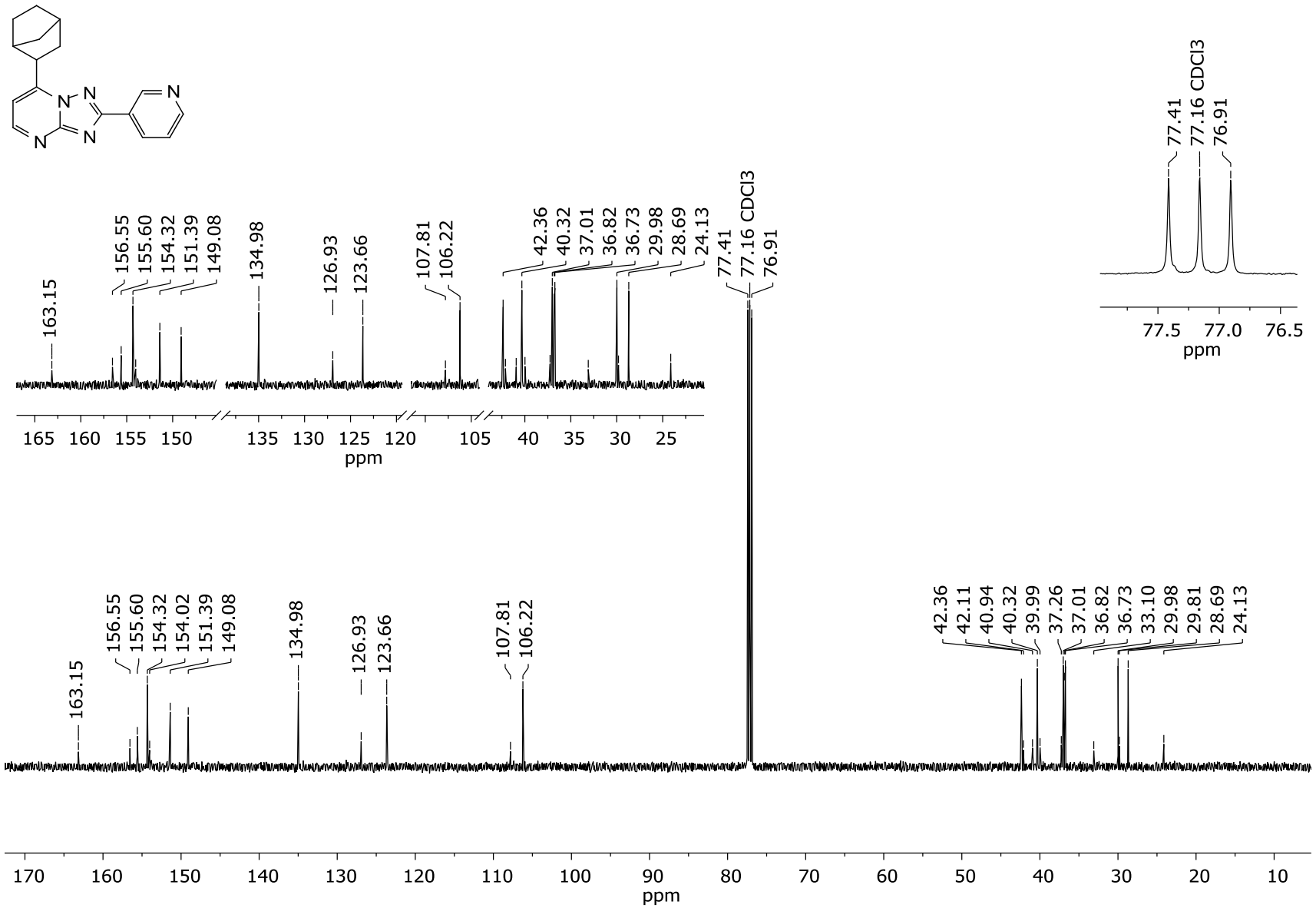


Figure S99. ^{13}C NMR spectrum of compound **4an** ($CDCl_3$, 125 MHz)

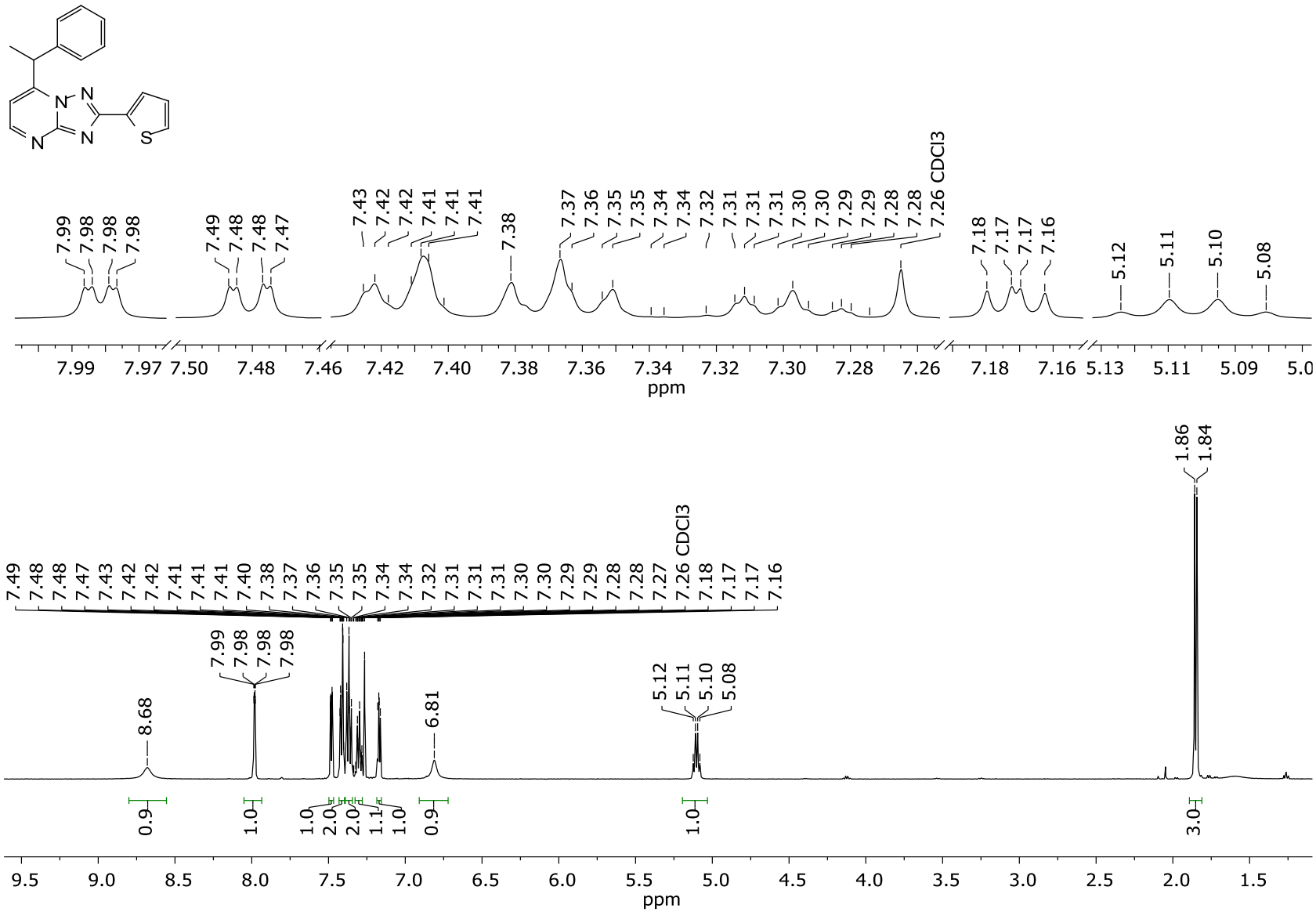


Figure S100. ^{1}H NMR spectrum of compound **4ao** ($CDCl_3$, 500 MHz)

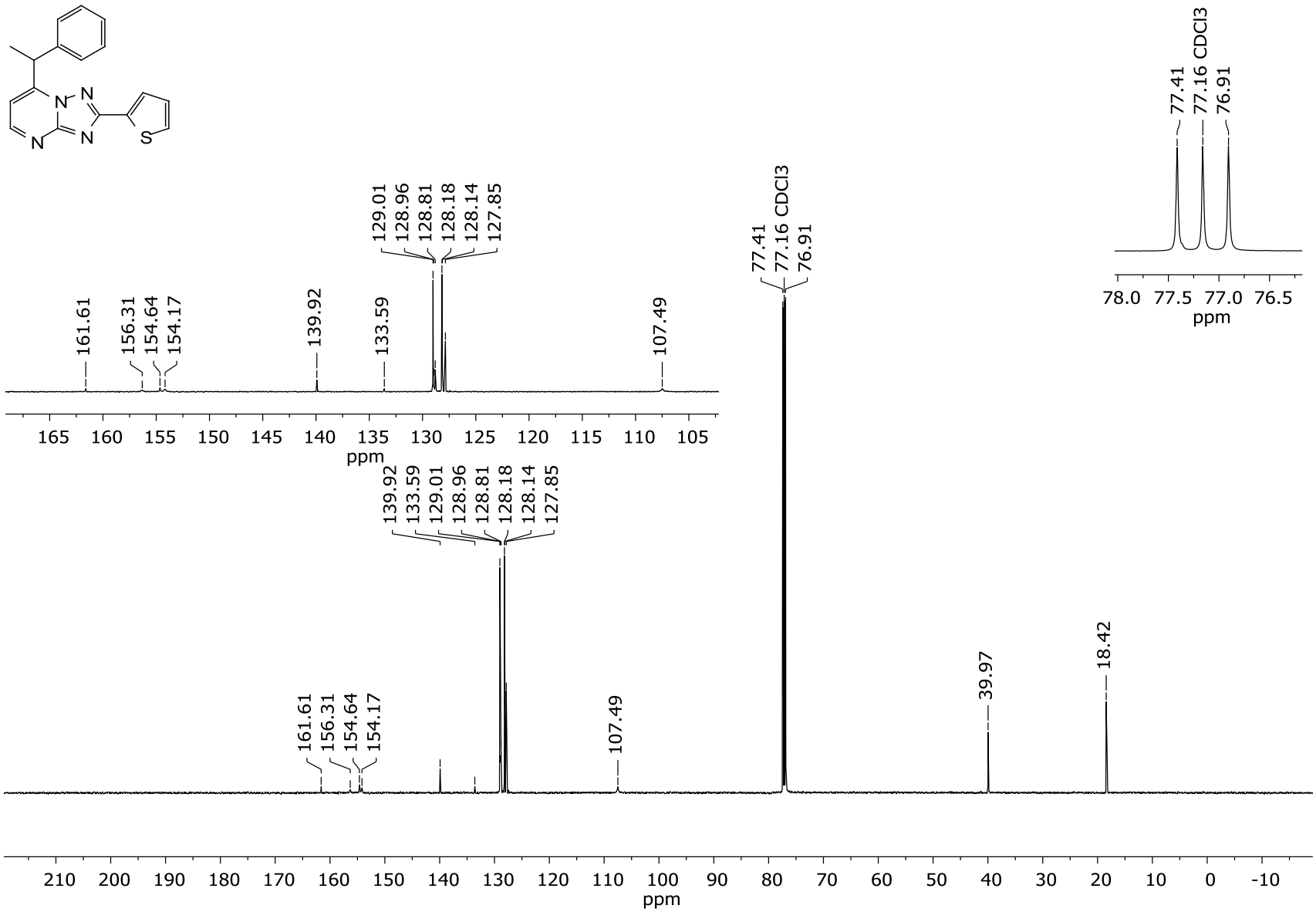


Figure S101. ^{13}C NMR spectrum of compound **4ao** ($CDCl_3$, 125 MHz)

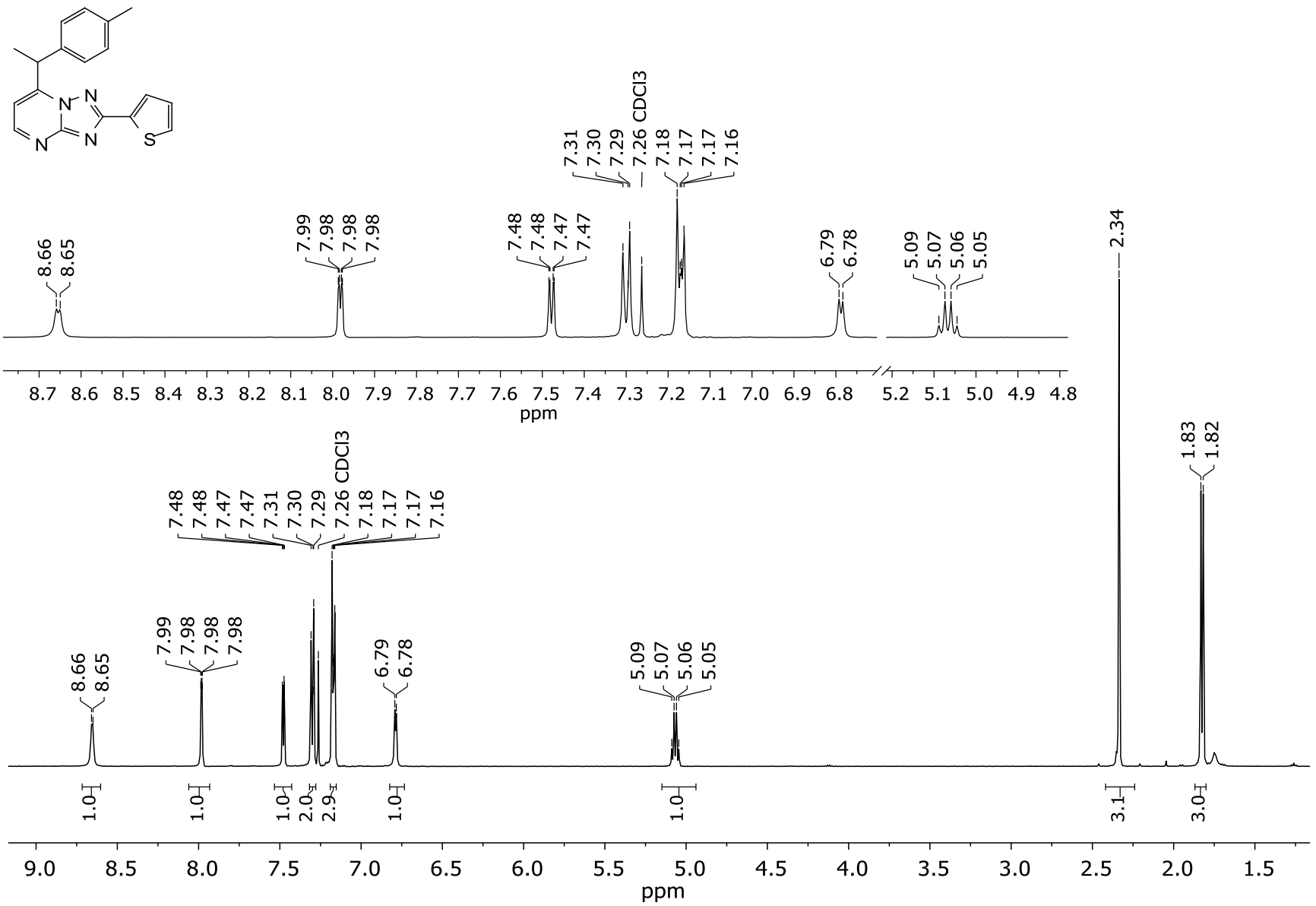


Figure S102. ^{1}H NMR spectrum of compound **4ap** ($CDCl_3$, 500 MHz)

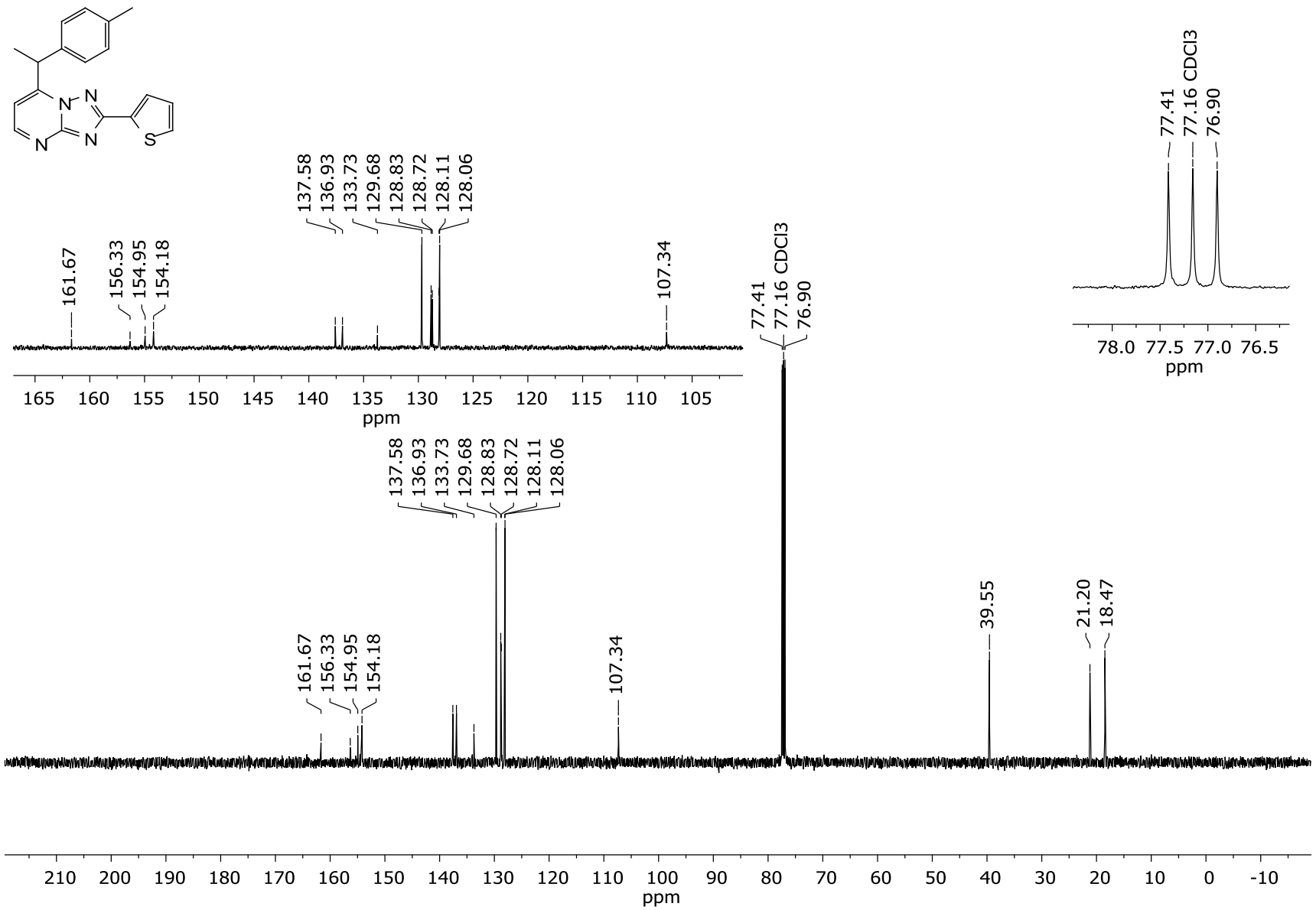


Figure S103. ^{13}C NMR spectrum of compound **4ap** ($CDCl_3$, 125 MHz)

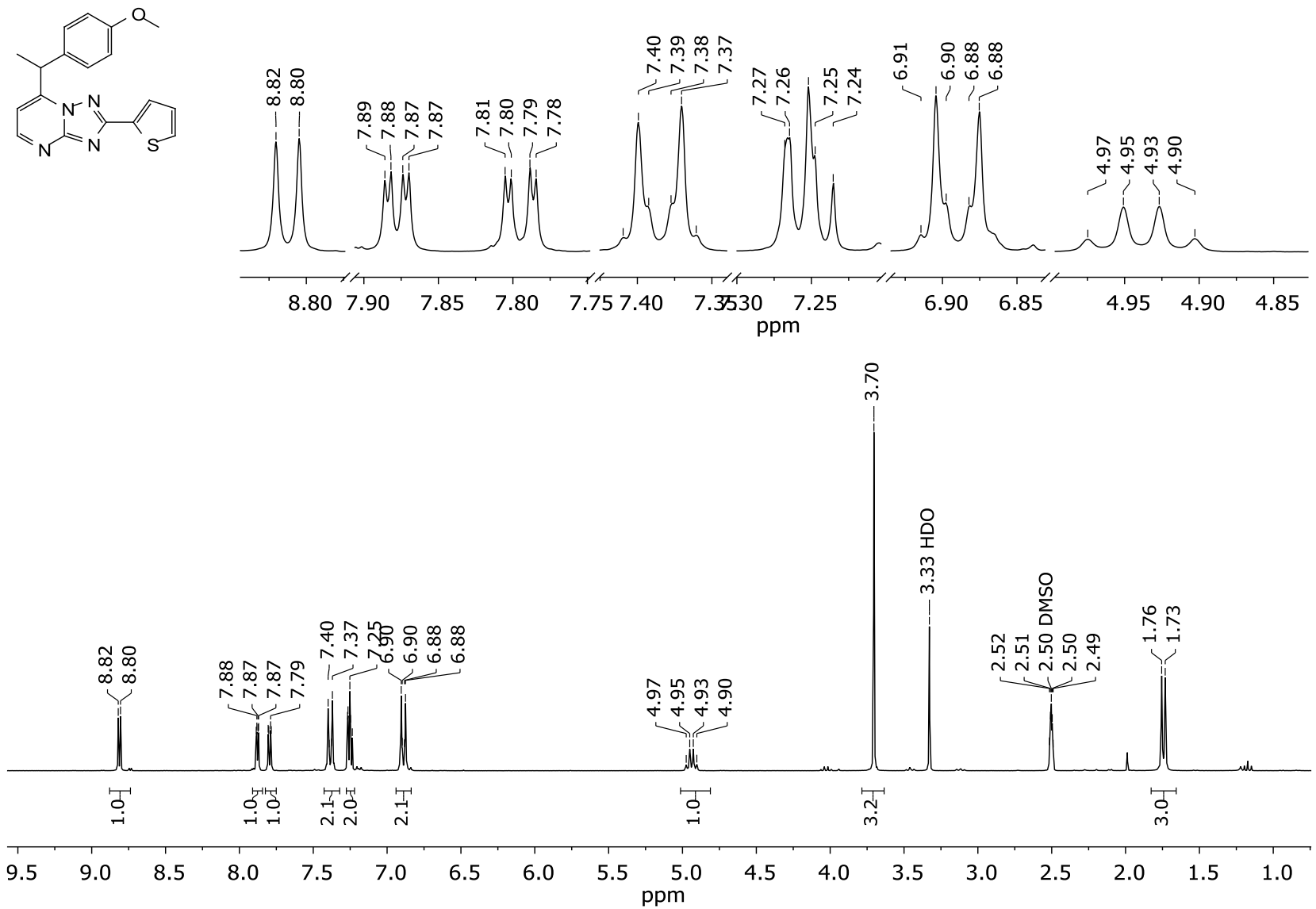


Figure S104. ^{1}H NMR spectrum of compound **4aq** (DMSO-d_6, 300 MHz)

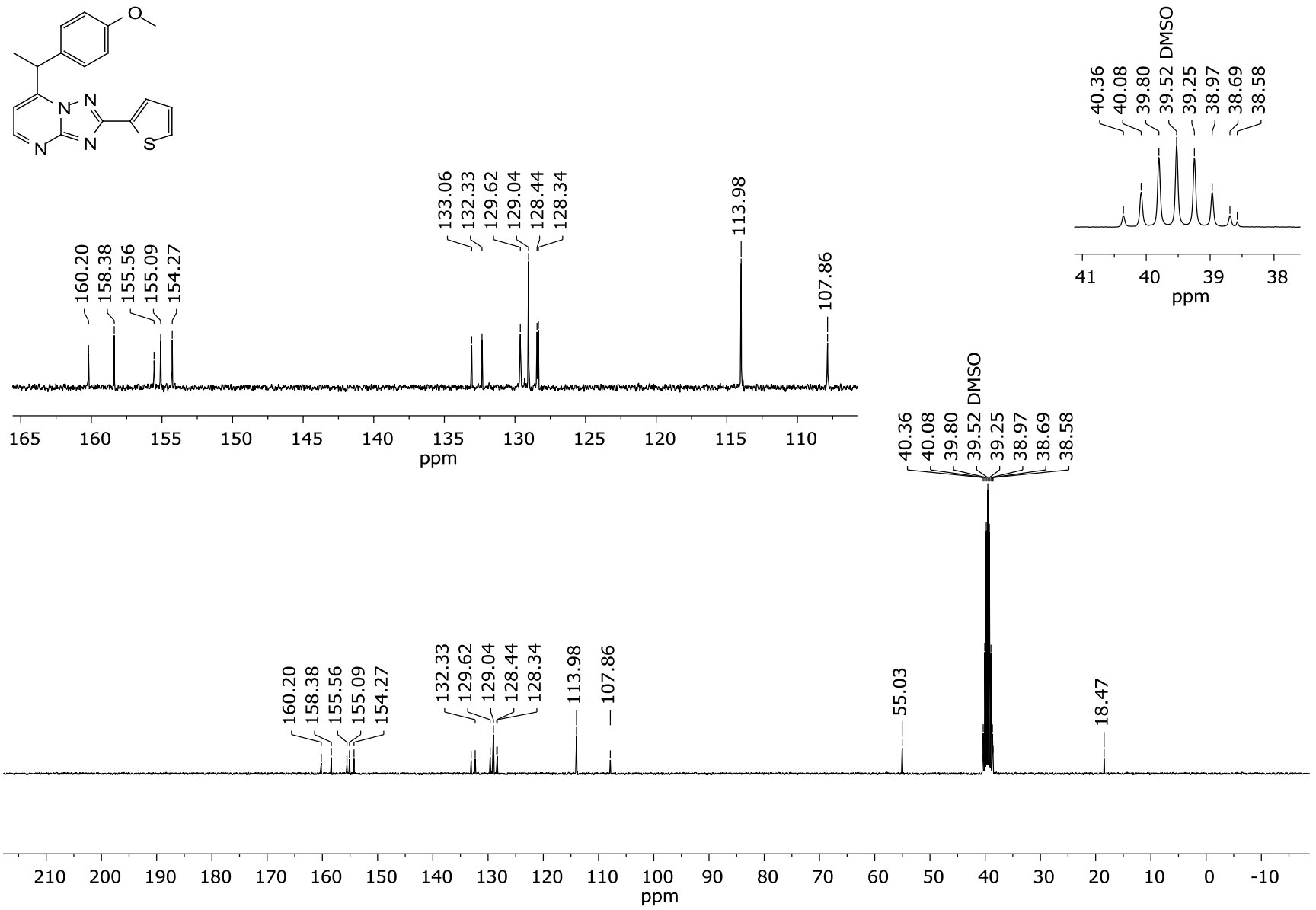


Figure S105. ^{13}C NMR spectrum of compound **4aq** (DMSO-d_6, 75 MHz)

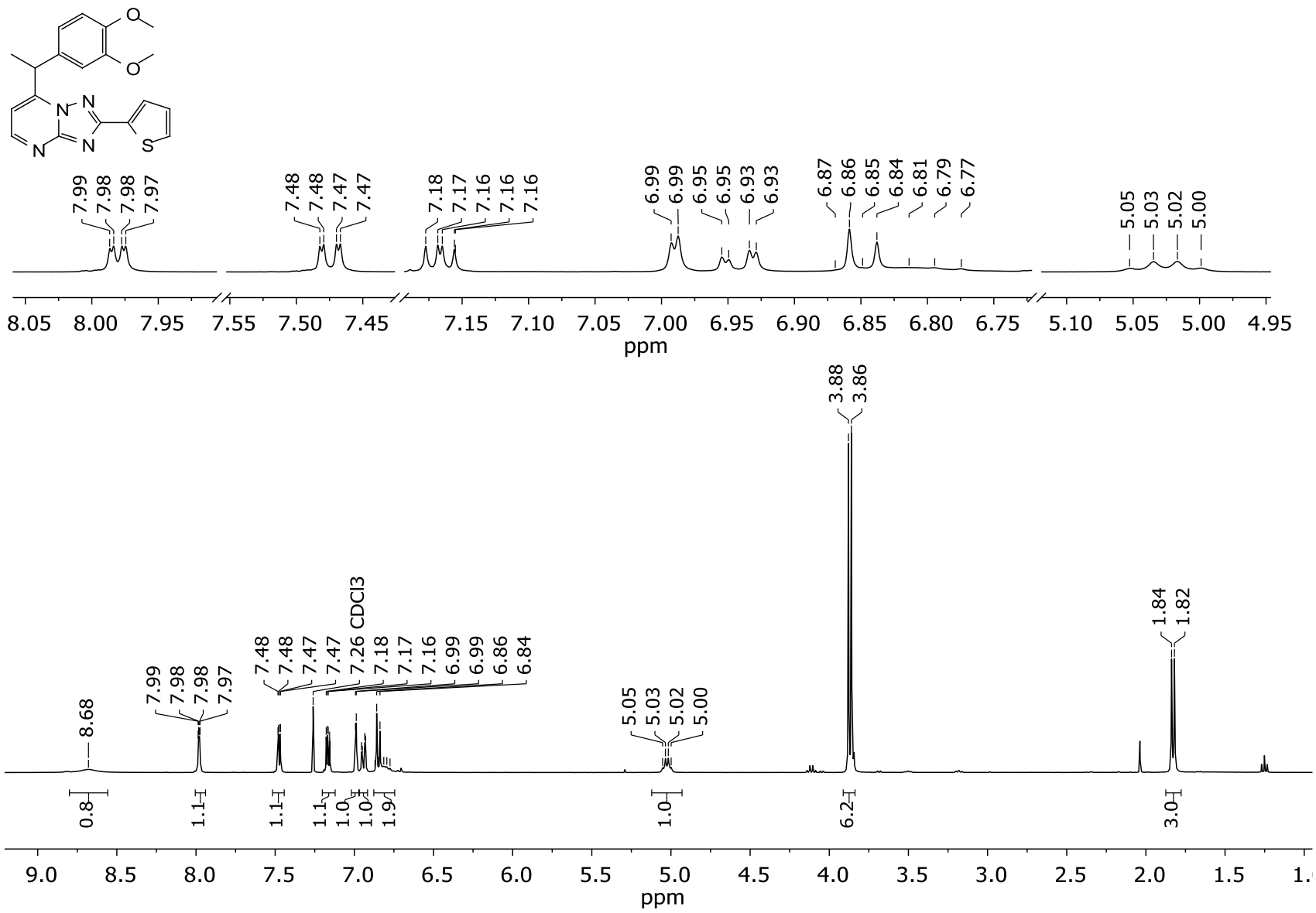


Figure S106. ^{1}H NMR spectrum of compound **4ar** ($CDCl_3$, 300 MHz)

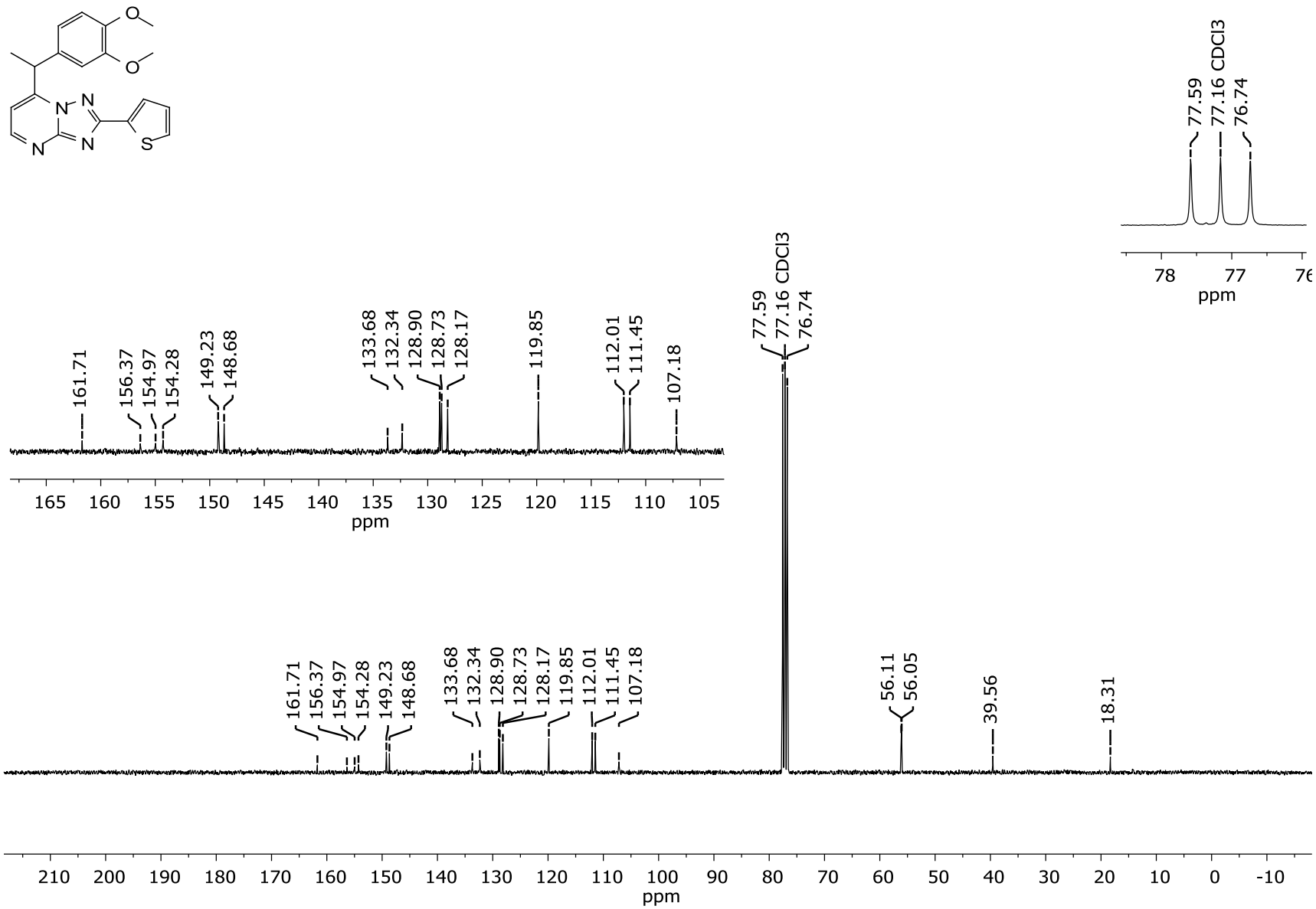


Figure S107. ^{13}C NMR spectrum of compound **4ar** ($CDCl_3$, 75 MHz)

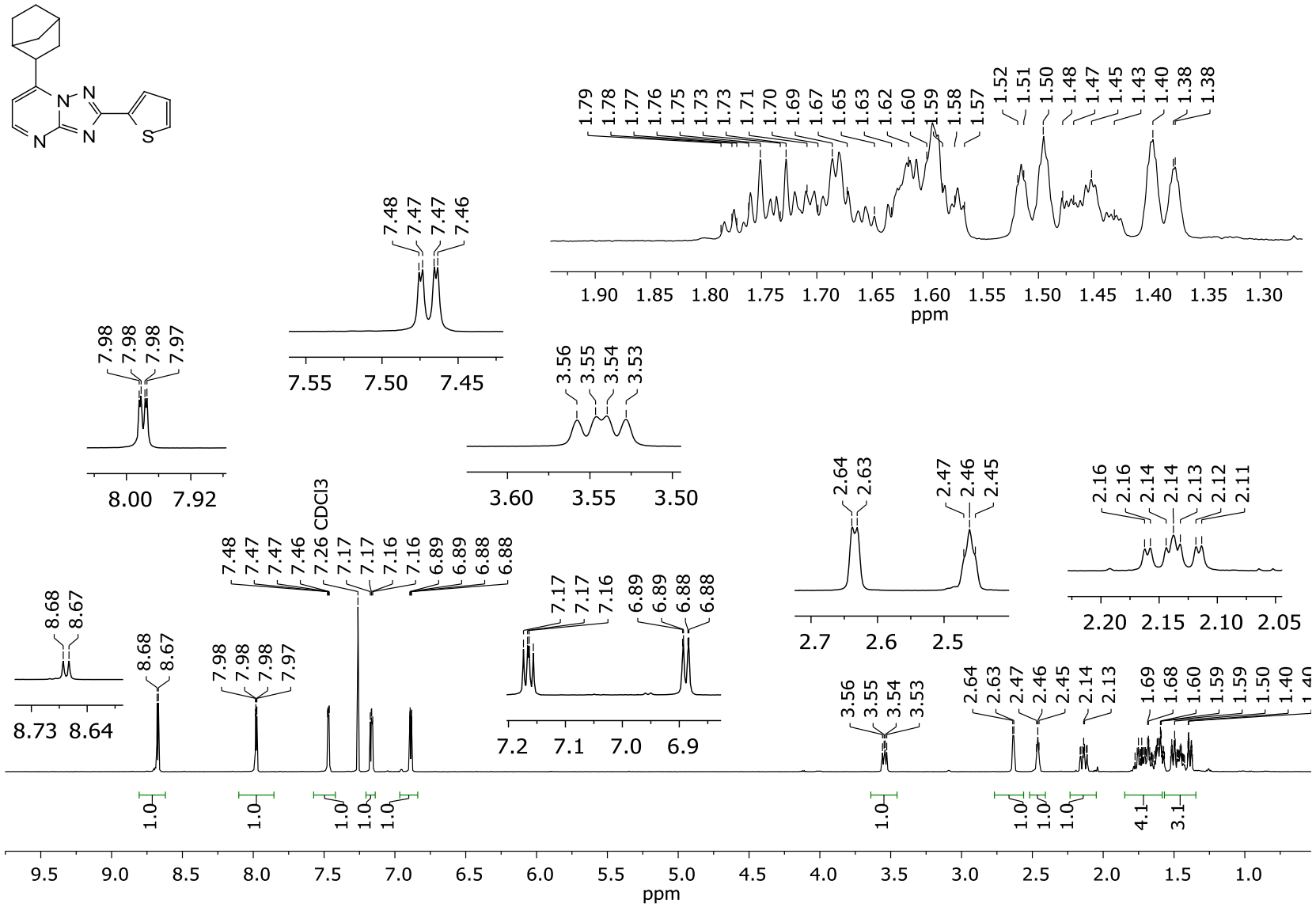


Figure S108. ^{1}H NMR spectrum of compound **4as** ($CDCl_3$, 500 MHz)

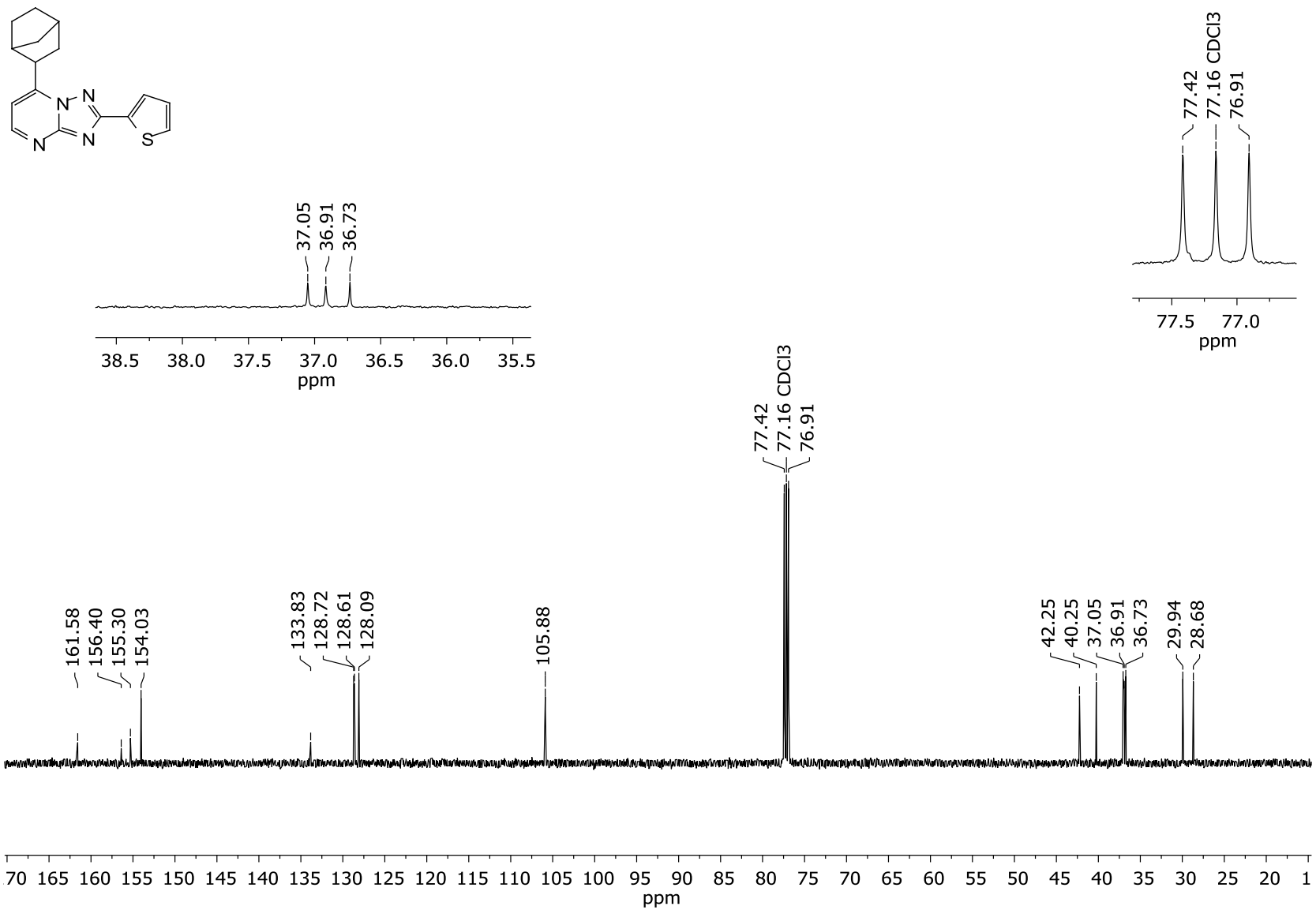


Figure S109. ^{13}C NMR spectrum of compound **4as** ($CDCl_3$, 125 MHz)

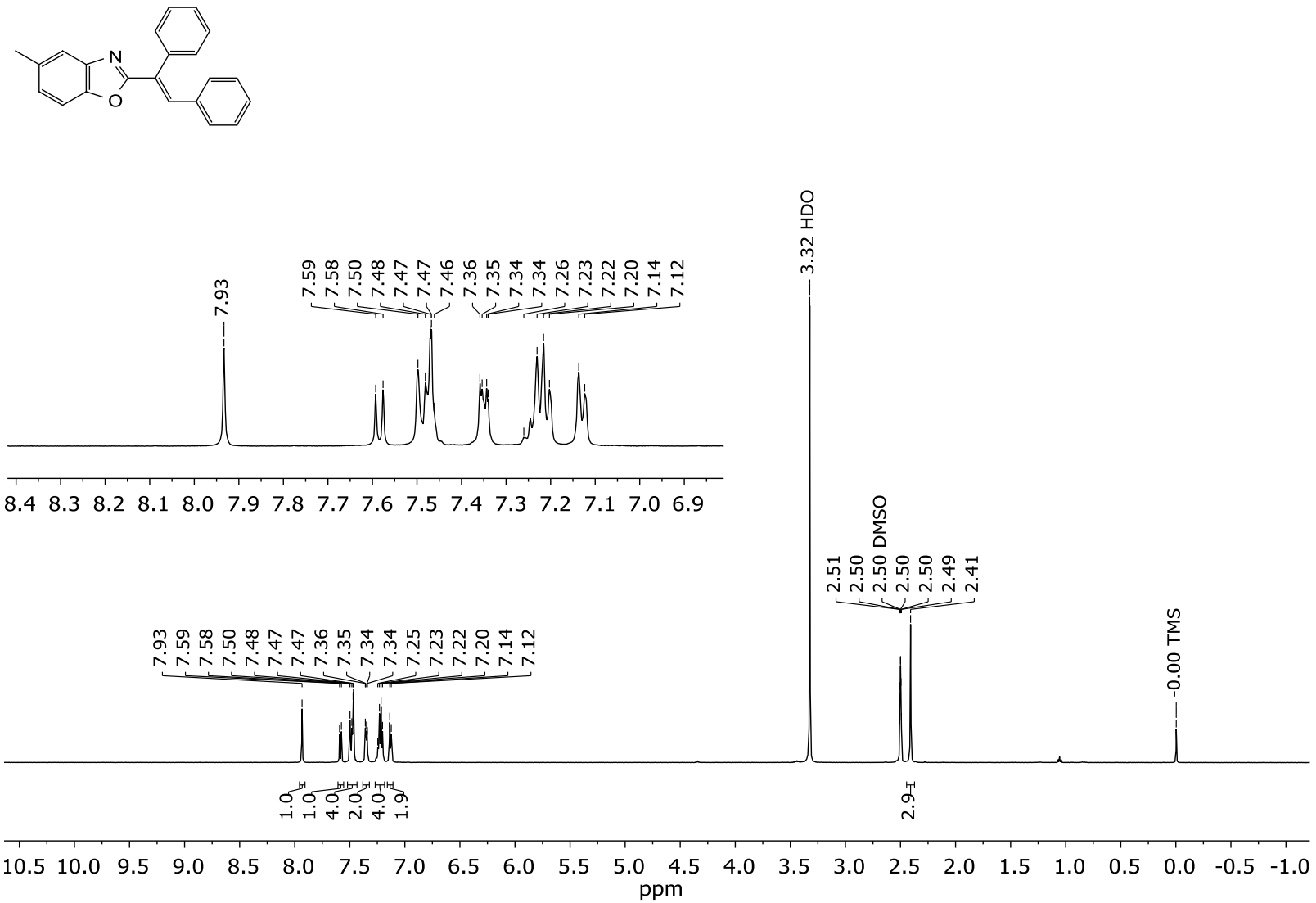


Figure S110. ^{1}H NMR spectrum of compound **6a** (DMSO-d_6, 600 MHz)

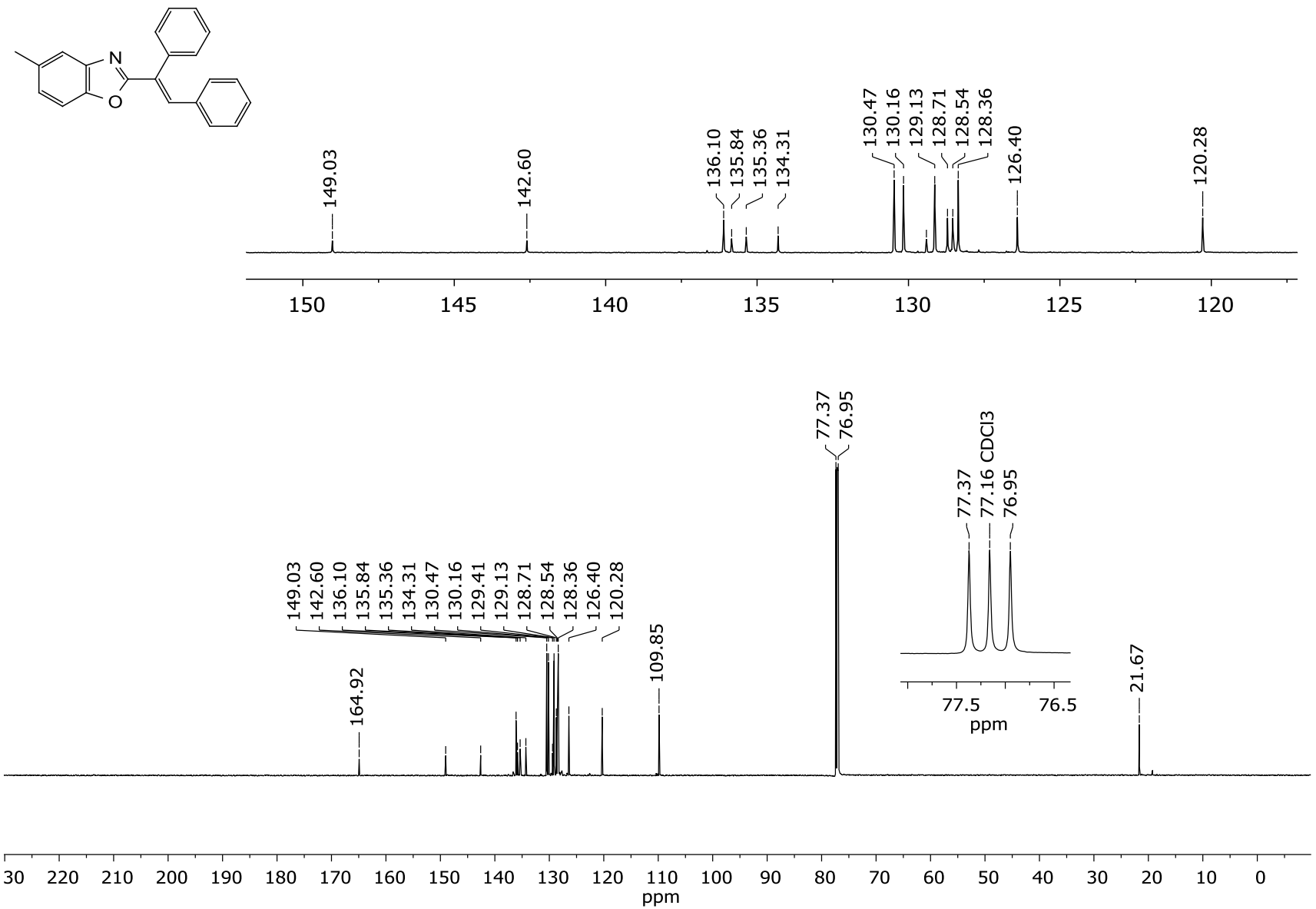


Figure S111. ^{13}C NMR spectrum of compound **6a** ($CDCl_3$, 150 MHz)

Figure S112. ^{1}H-^{13}C HSQC spectrum of compound **6a** ($CDCl_3$)

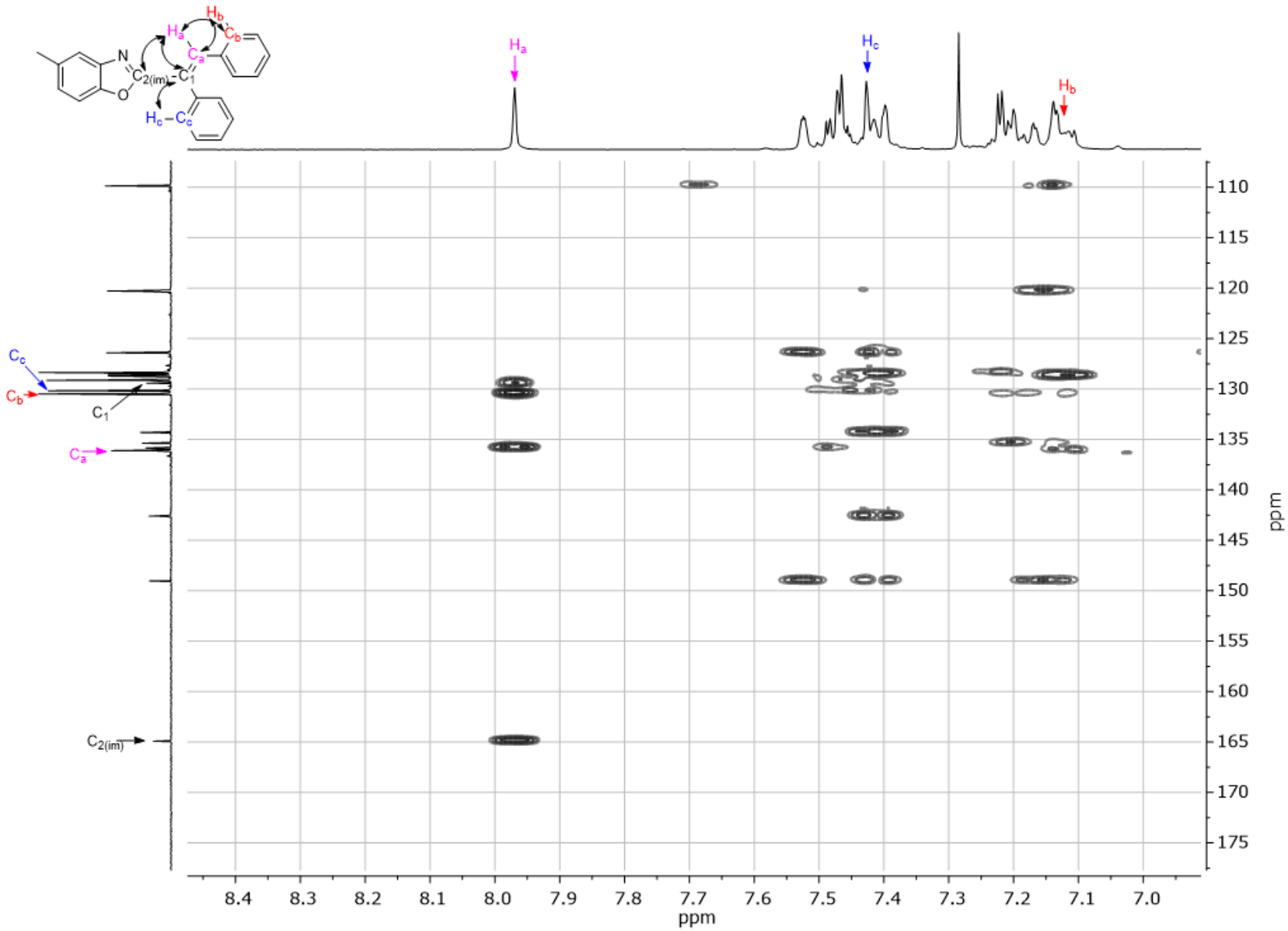


Figure S113. ^{1}H-^{13}C HMBC spectrum of compound **6a** ($CDCl_3$)

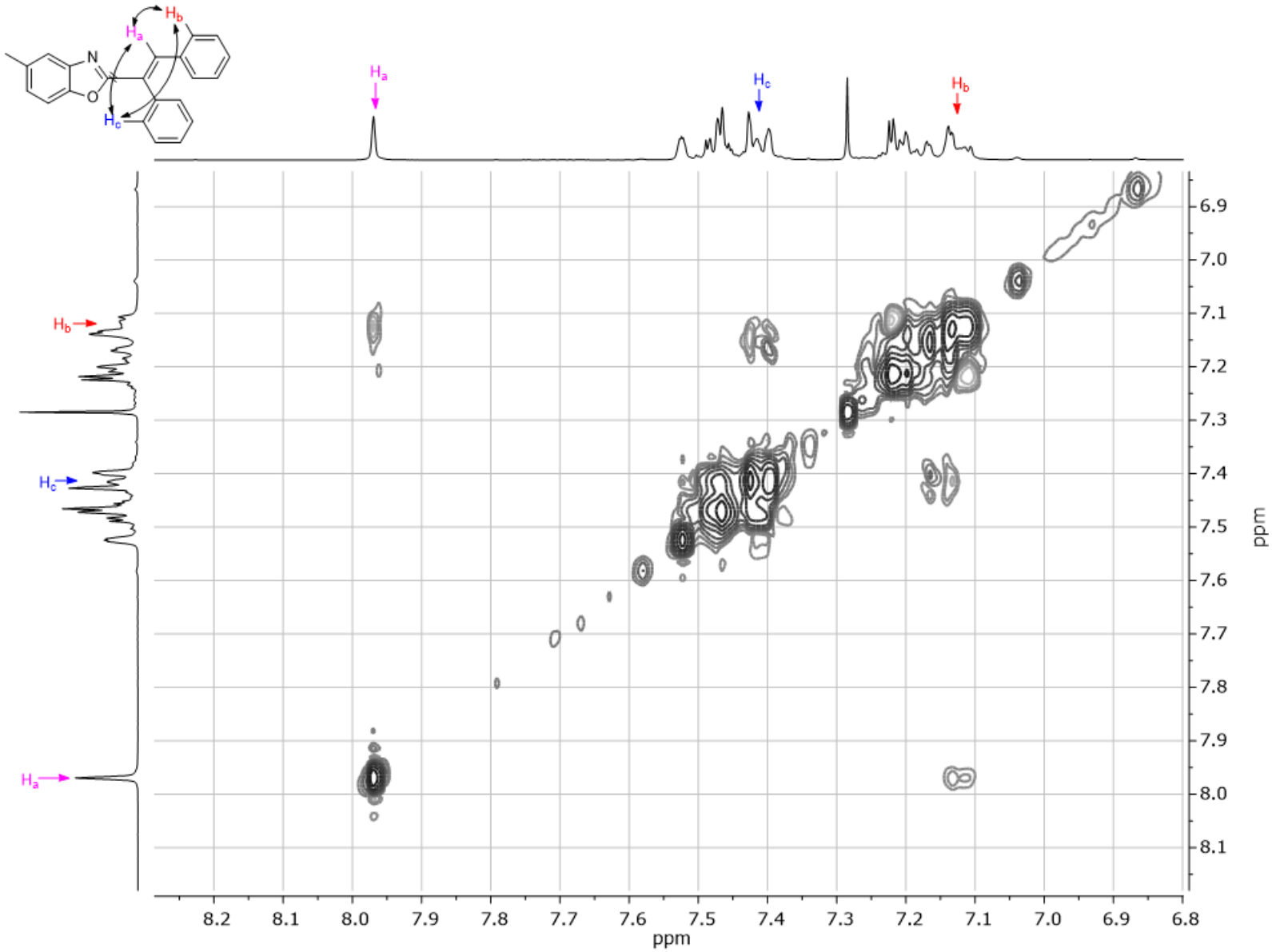


Figure S114. ^{1}H-^{1}H NOESY spectrum of compound **6a** ($CDCl_3$)

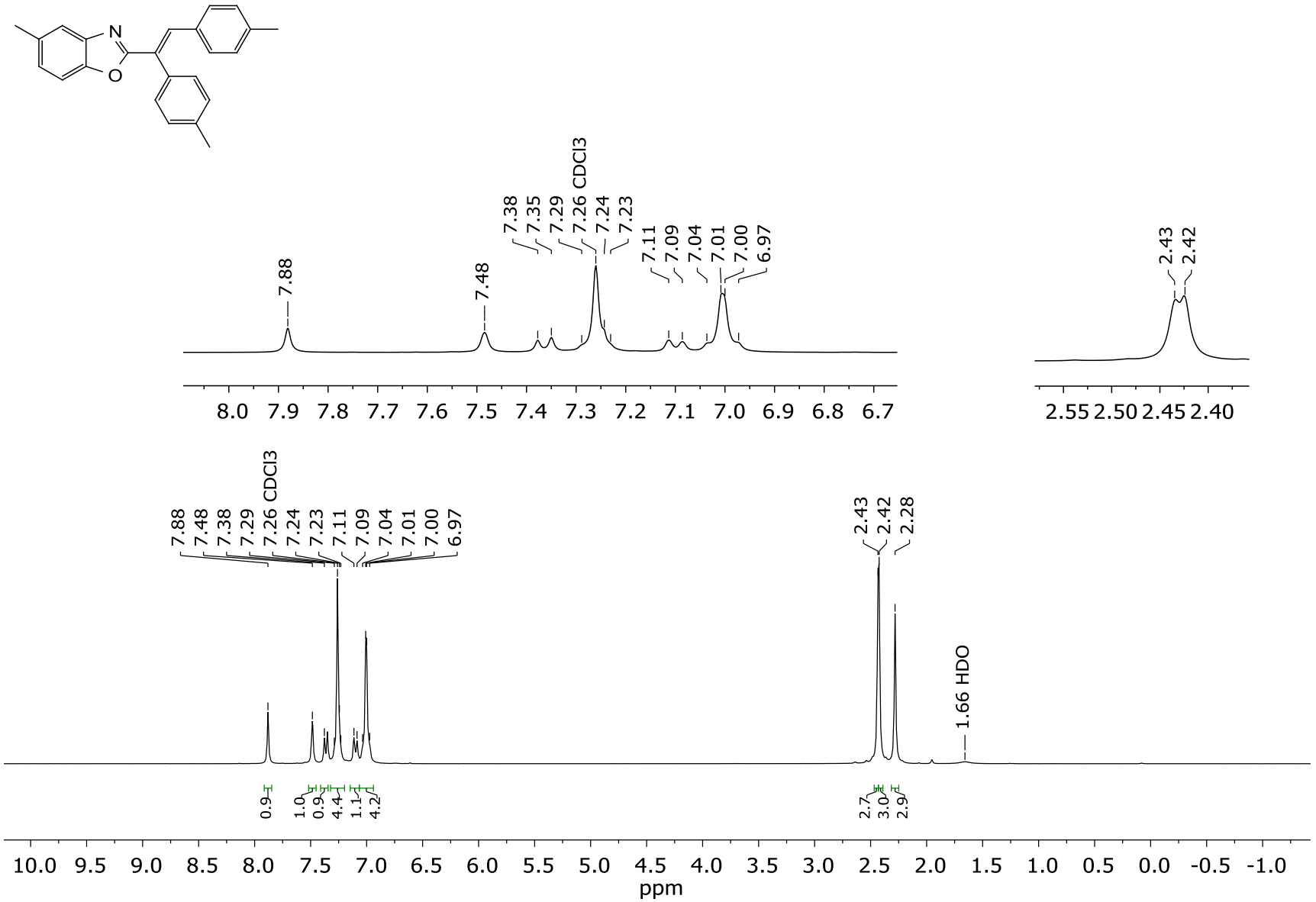


Figure S115. ^{1}H NMR spectrum of compound **6b** ($CDCl_3$, 300 MHz)

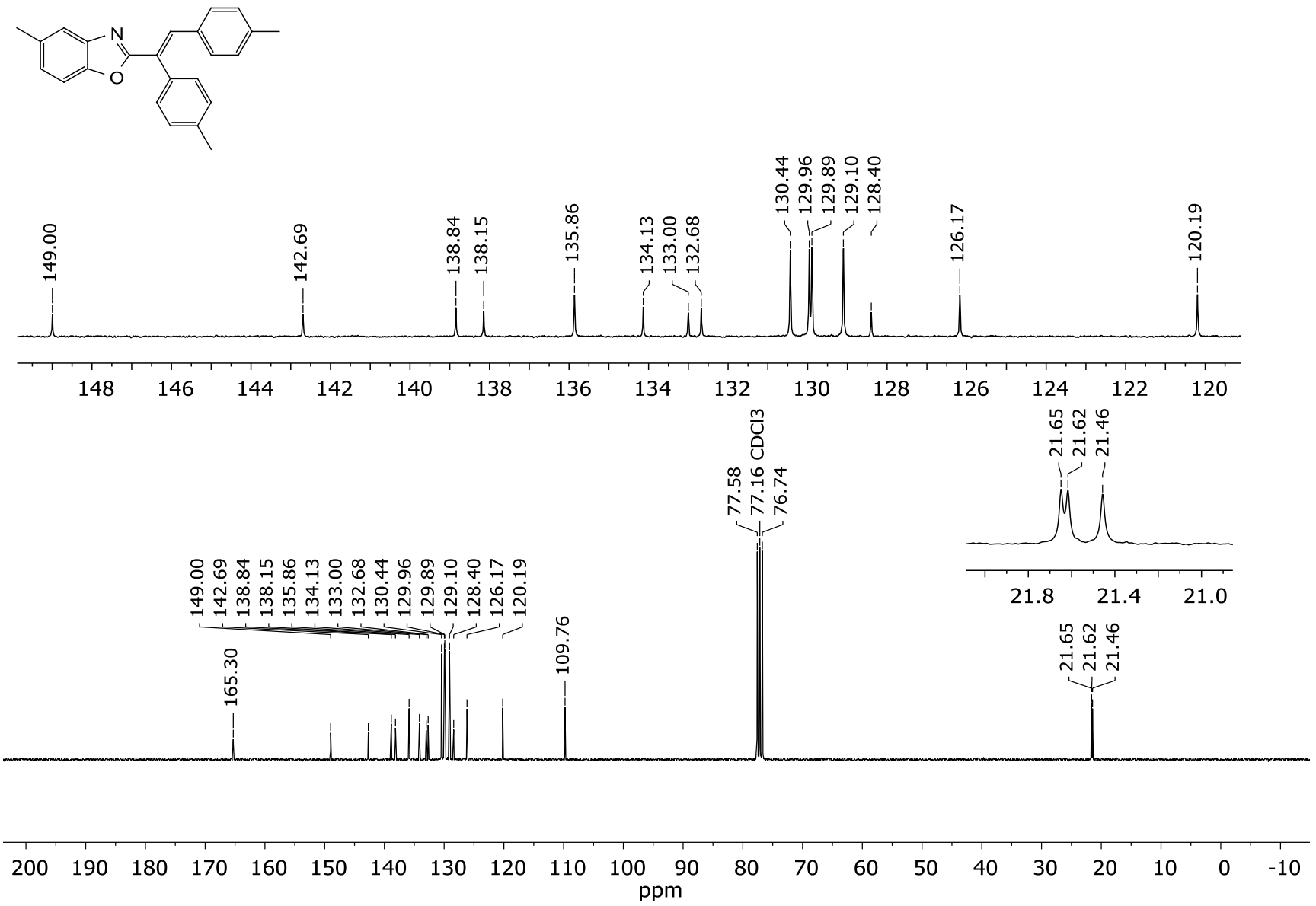


Figure S116. ^{13}C NMR spectrum of compound **6b** ($CDCl_3$, 75 MHz)

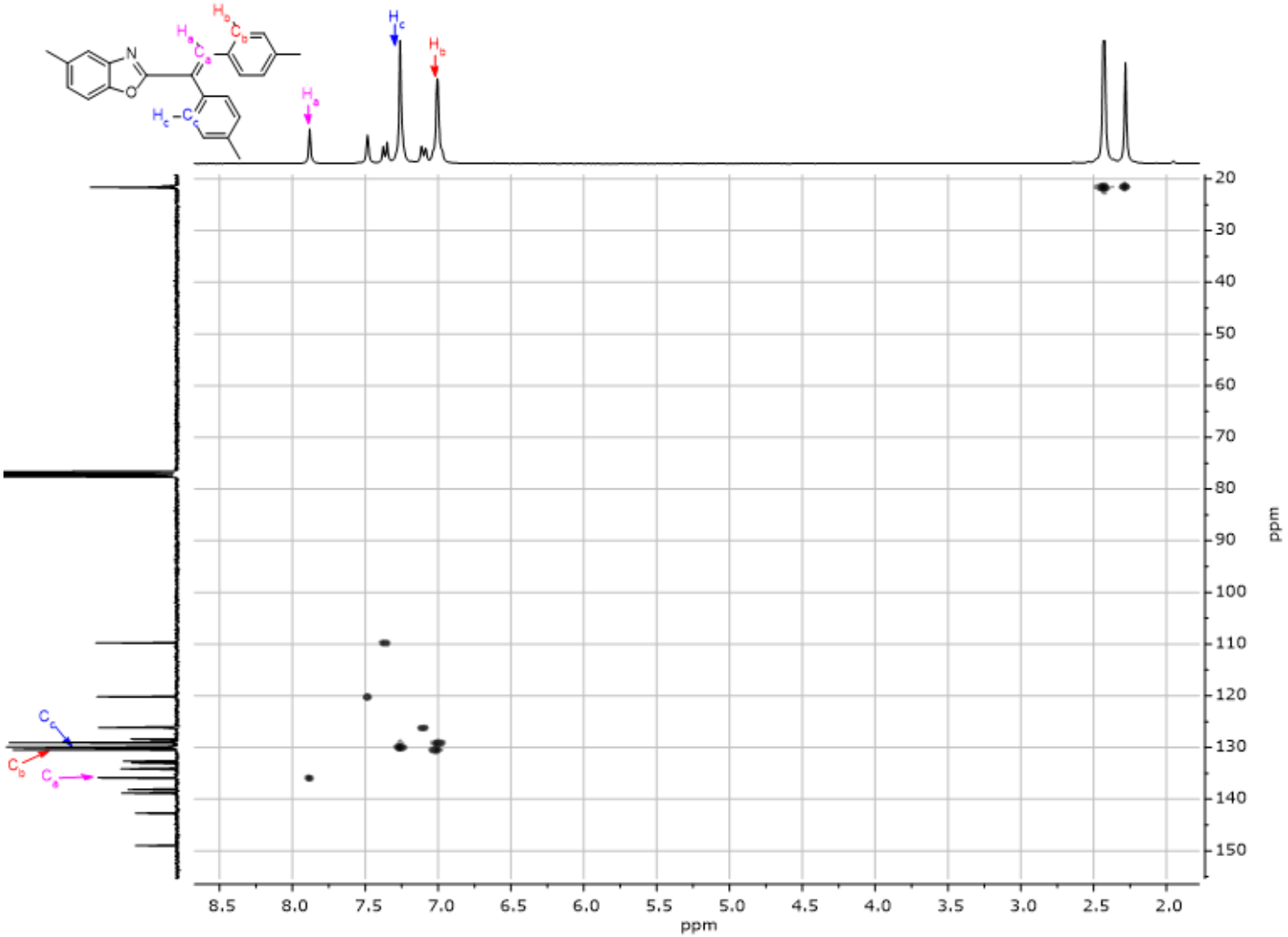


Figure S117. ^{1}H-^{13}C HSQC spectrum of compound **6b** ($CDCl_3$)

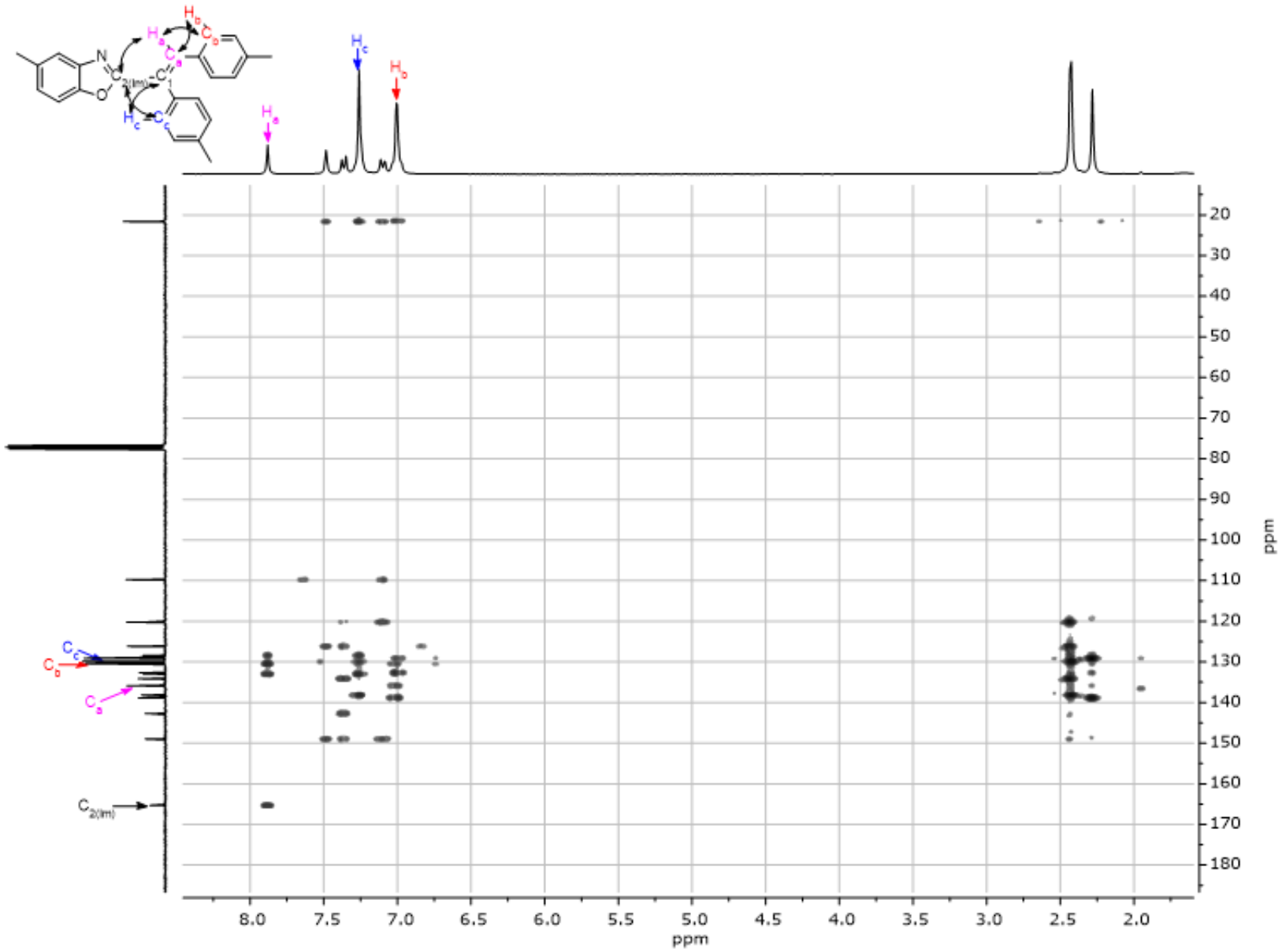


Figure S118. ^{1}H-^{13}C HMBC spectrum of compound **6b** ($CDCl_3$)

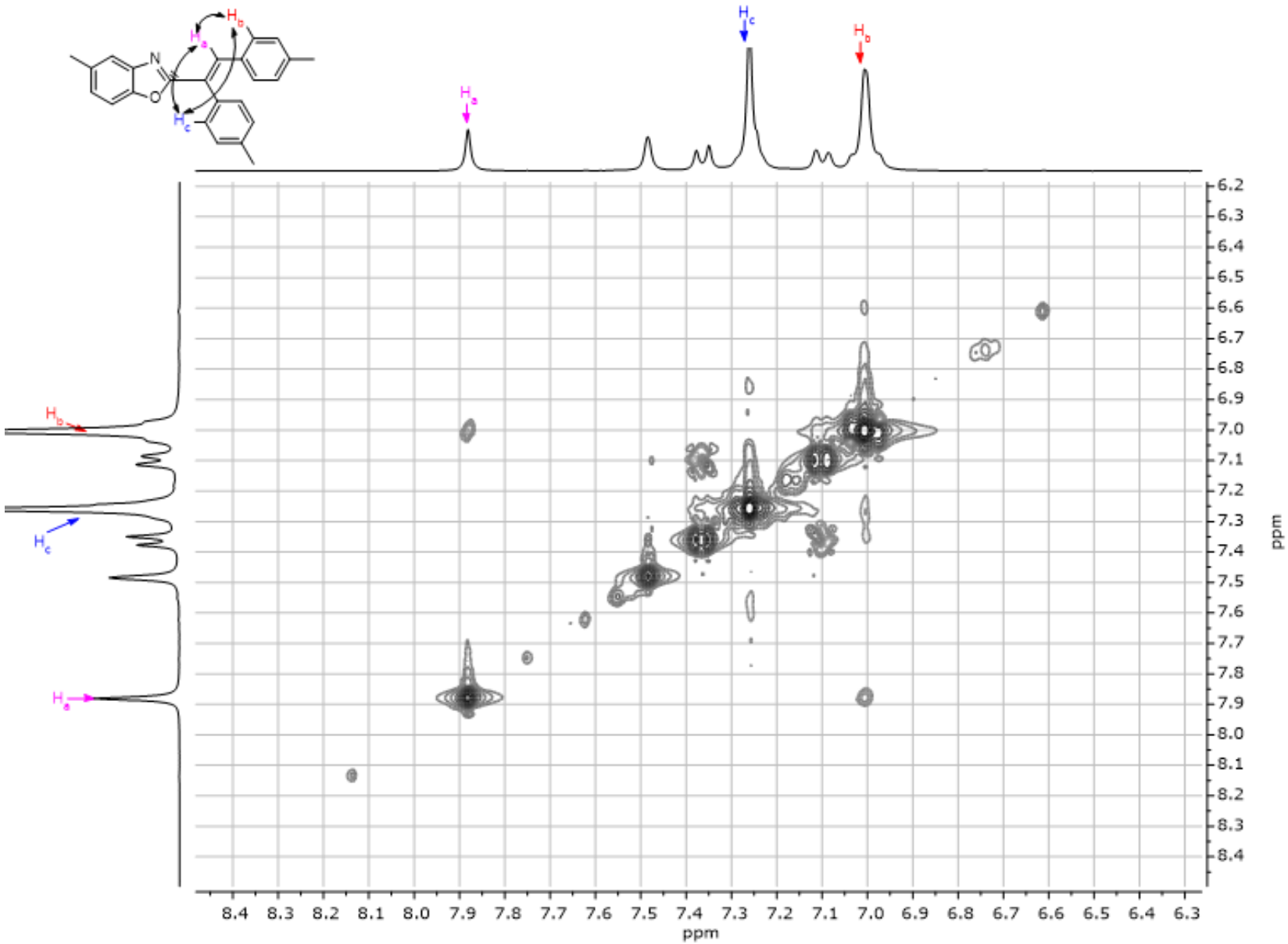


Figure S119. ^{1}H-^{1}H NOESY spectrum of compound **6b** ($CDCl_3$)

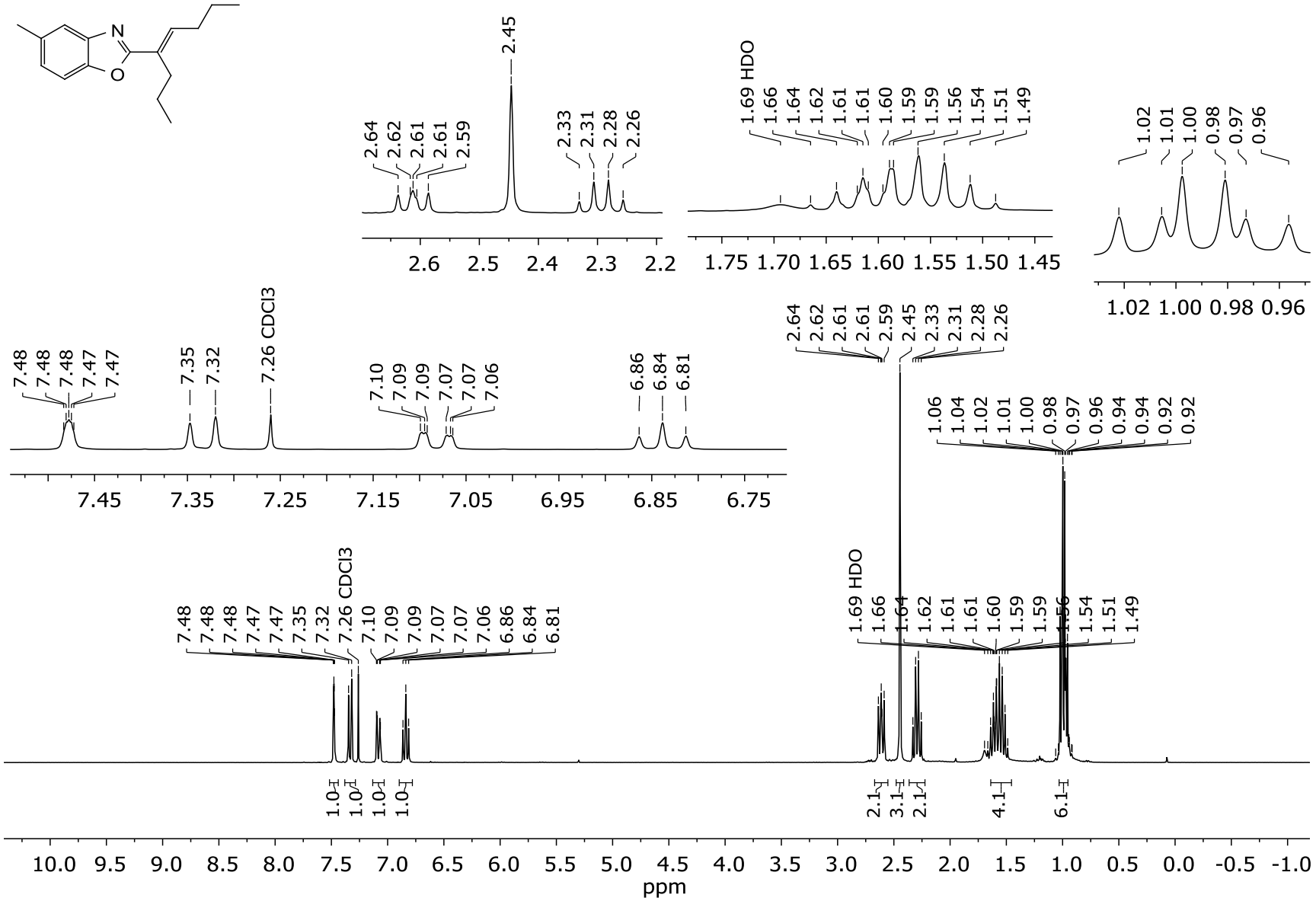


Figure S120. ^{1}H NMR spectrum of compound **6c** ($CDCl_3$, 300 MHz)

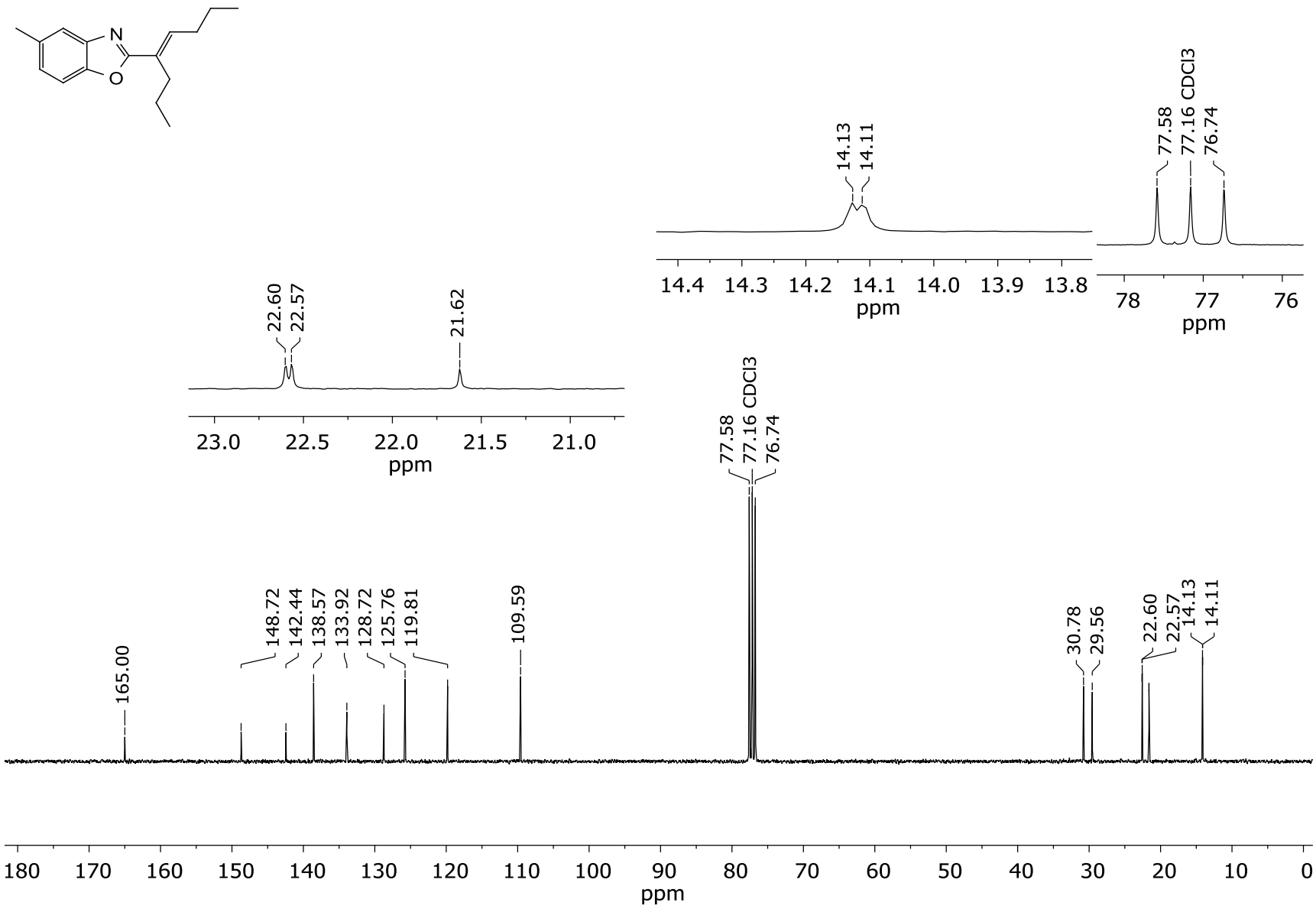


Figure S121. ^{13}C NMR spectrum of compound **6c** ($CDCl_3$, 75 MHz)

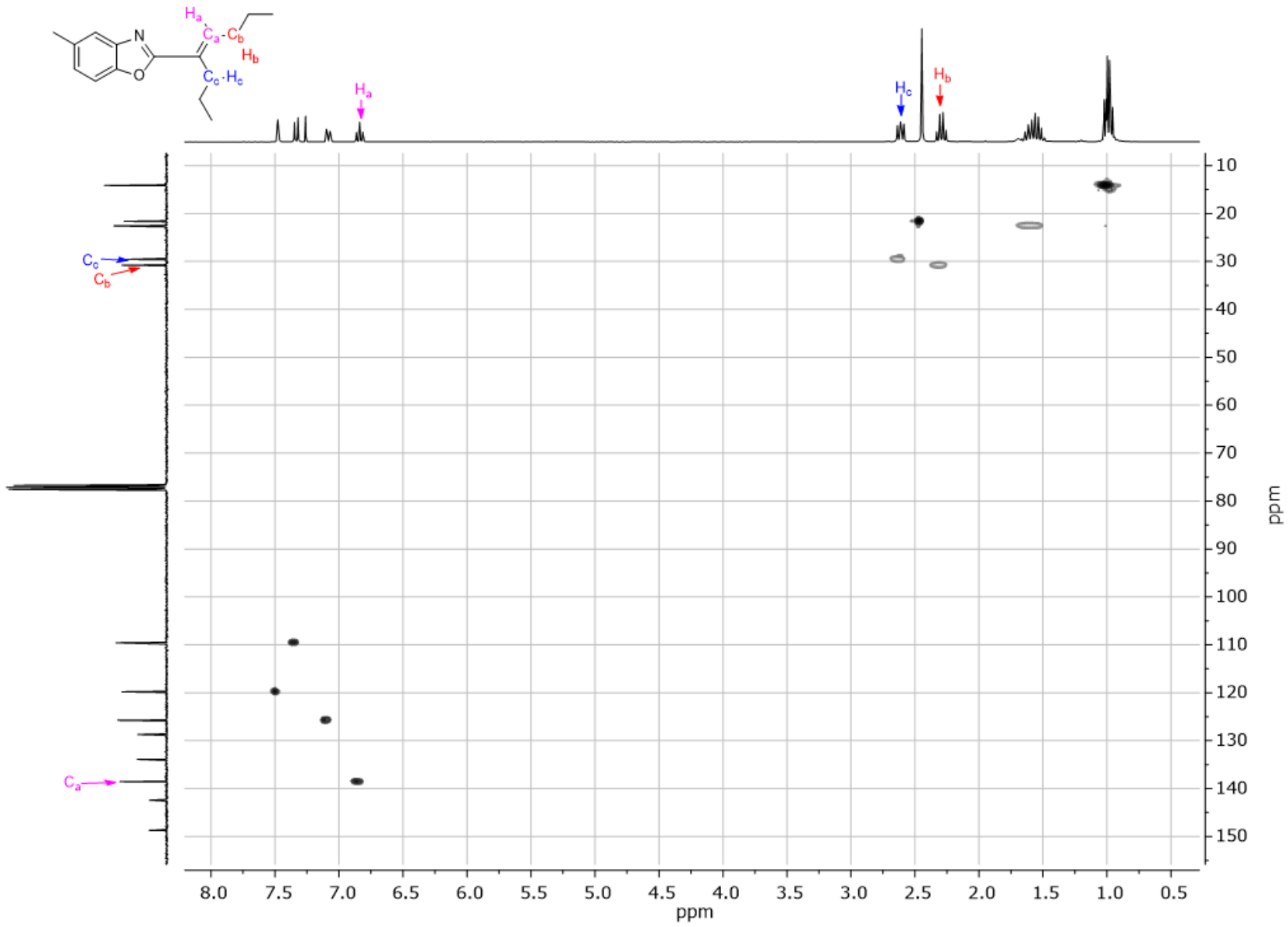


Figure S122. ^{1}H-^{13}C HSQC spectrum of compound **6c** ($CDCl_3$)

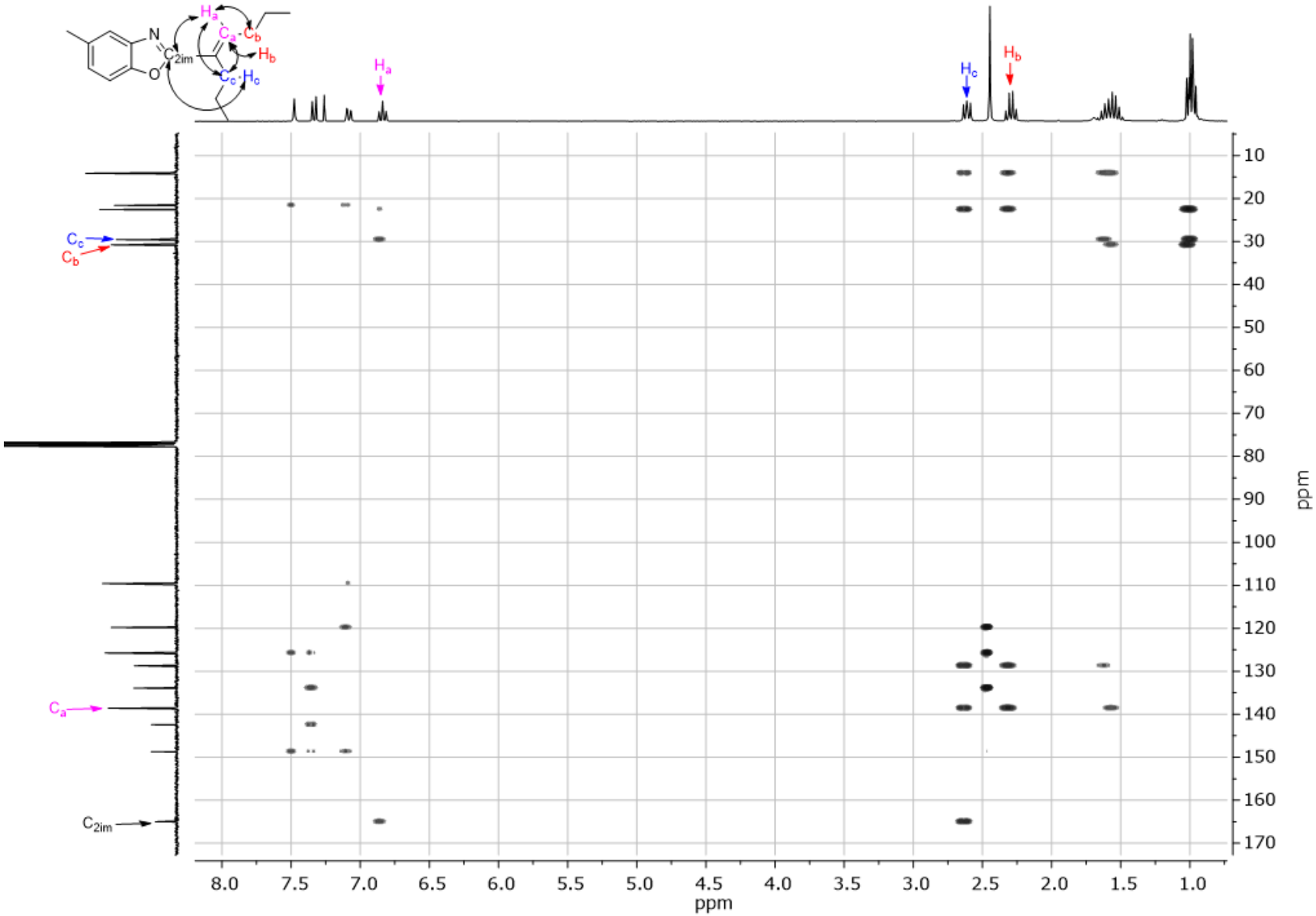


Figure S123. ^{1}H-^{13}C HMBC spectrum of compound **6c** ($CDCl_3$)

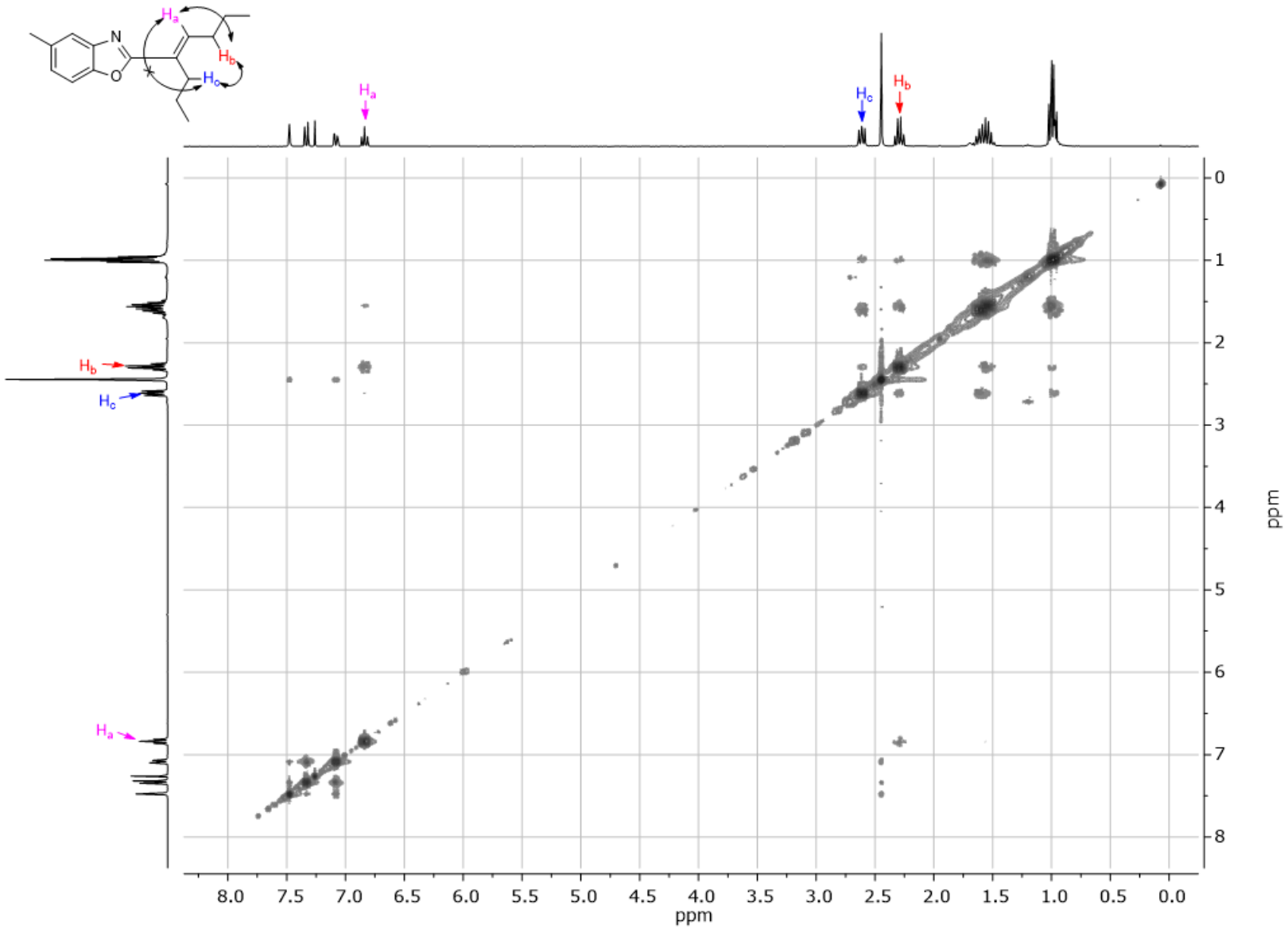


Figure S124. ^{1}H-^{1}H NOESY spectrum of compound **6c** ($CDCl_3$)

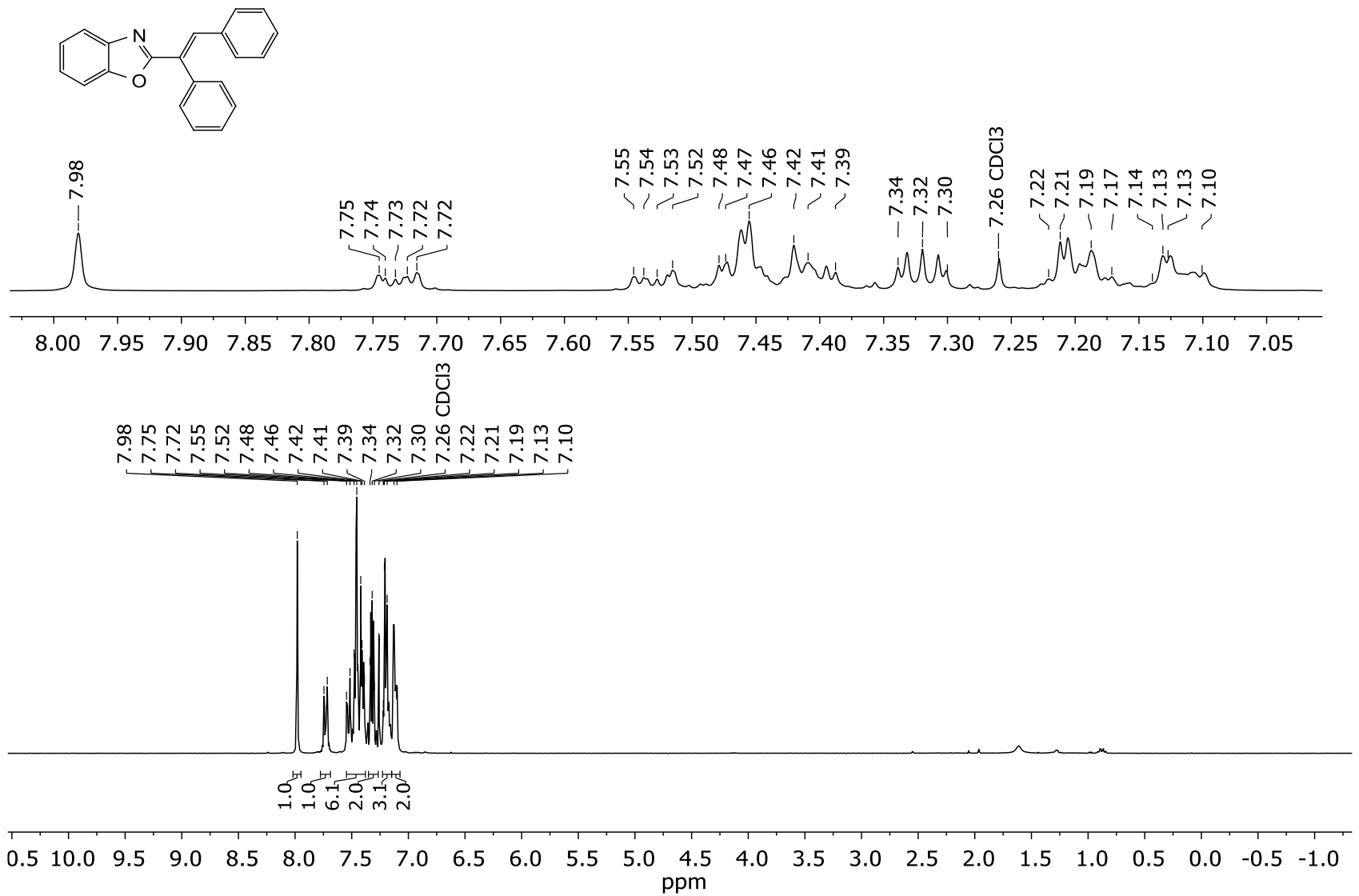


Figure S125. ^{1}H NMR spectrum of compound **6d** ($CDCl_3$, 500 MHz)

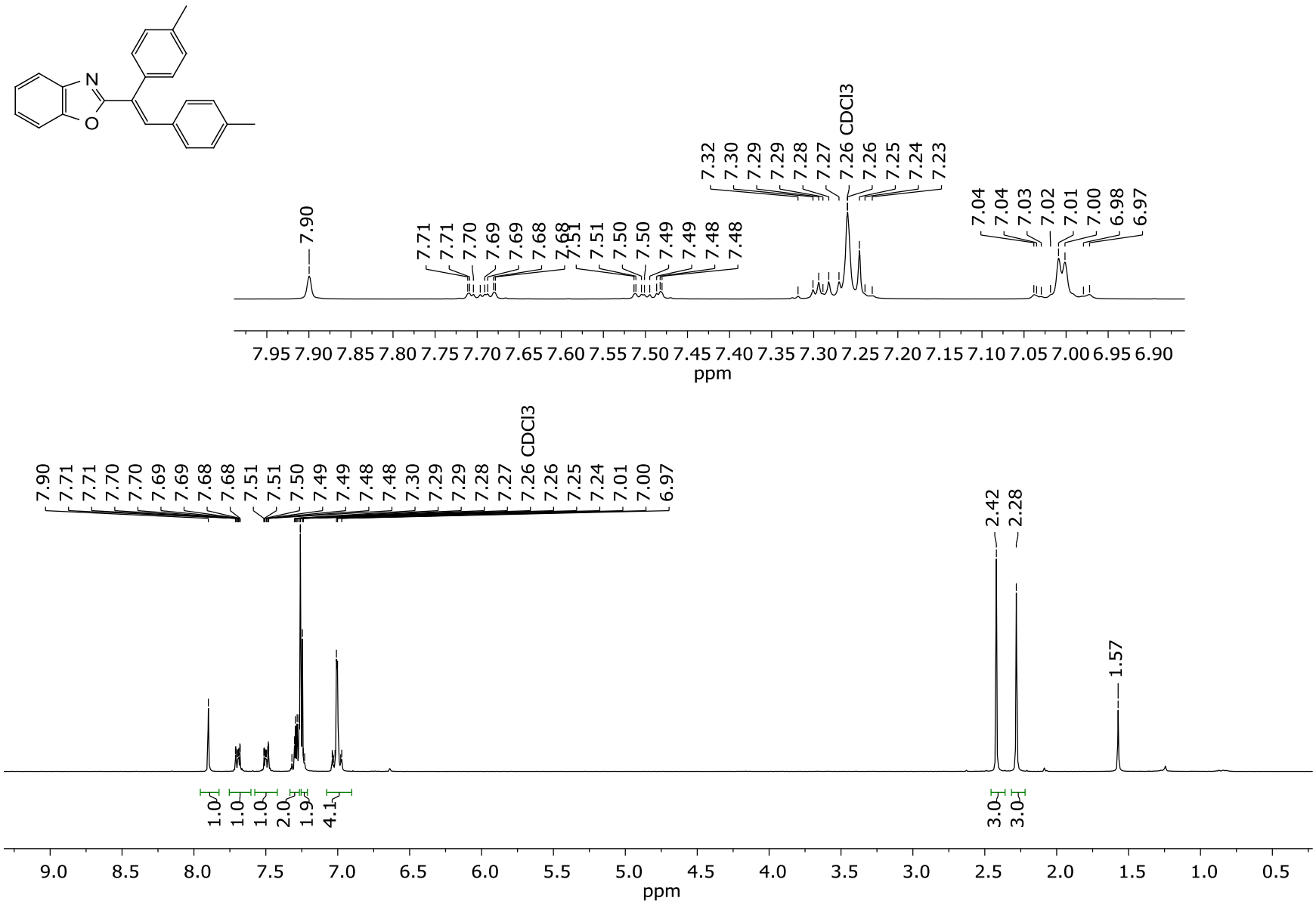


Figure S126. ^{1}H NMR spectrum of compound **6e** ($CDCl_3$, 300 MHz)

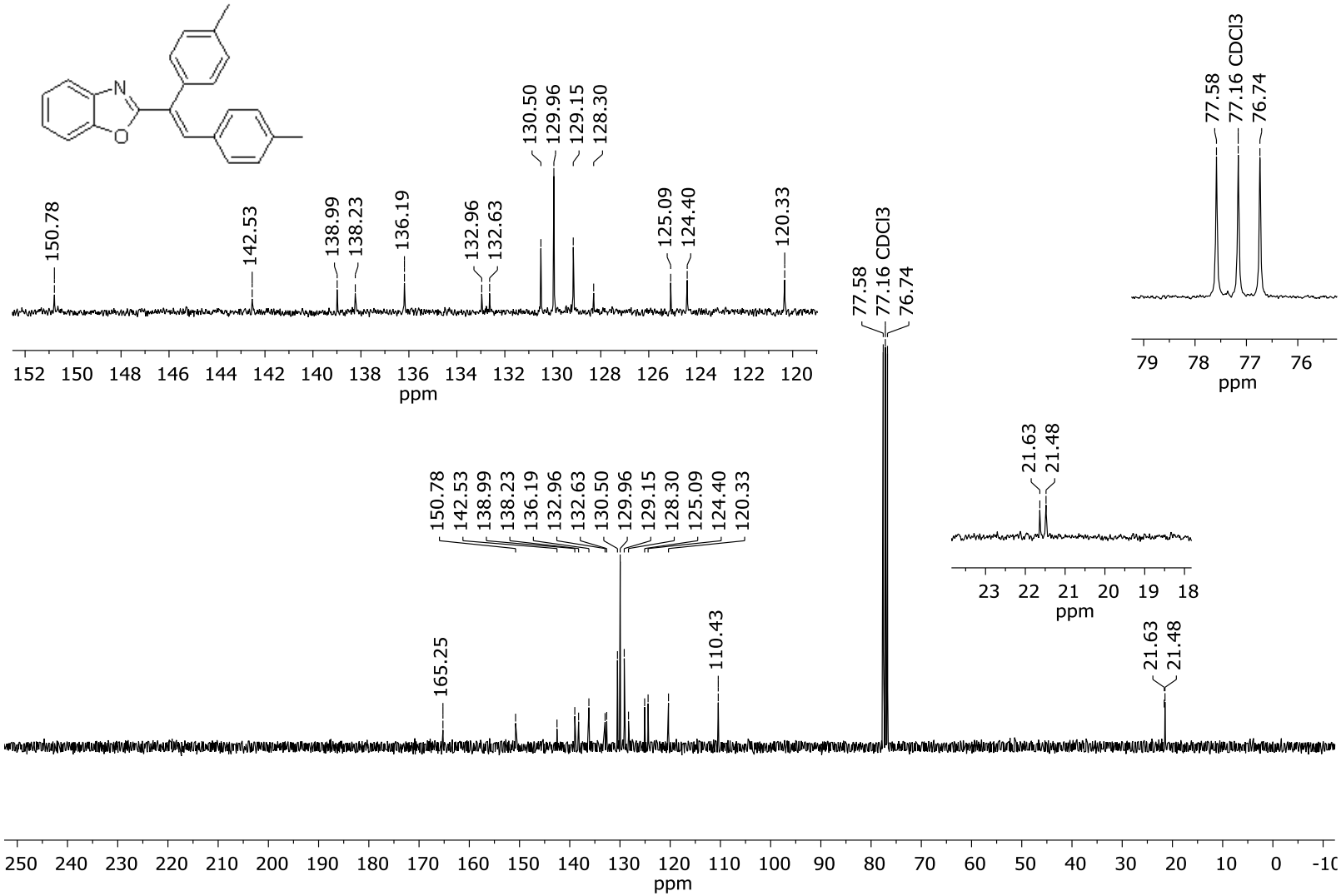


Figure S127. ^{13}C NMR spectrum of compound **6e** ($CDCl_3$, 75 MHz)

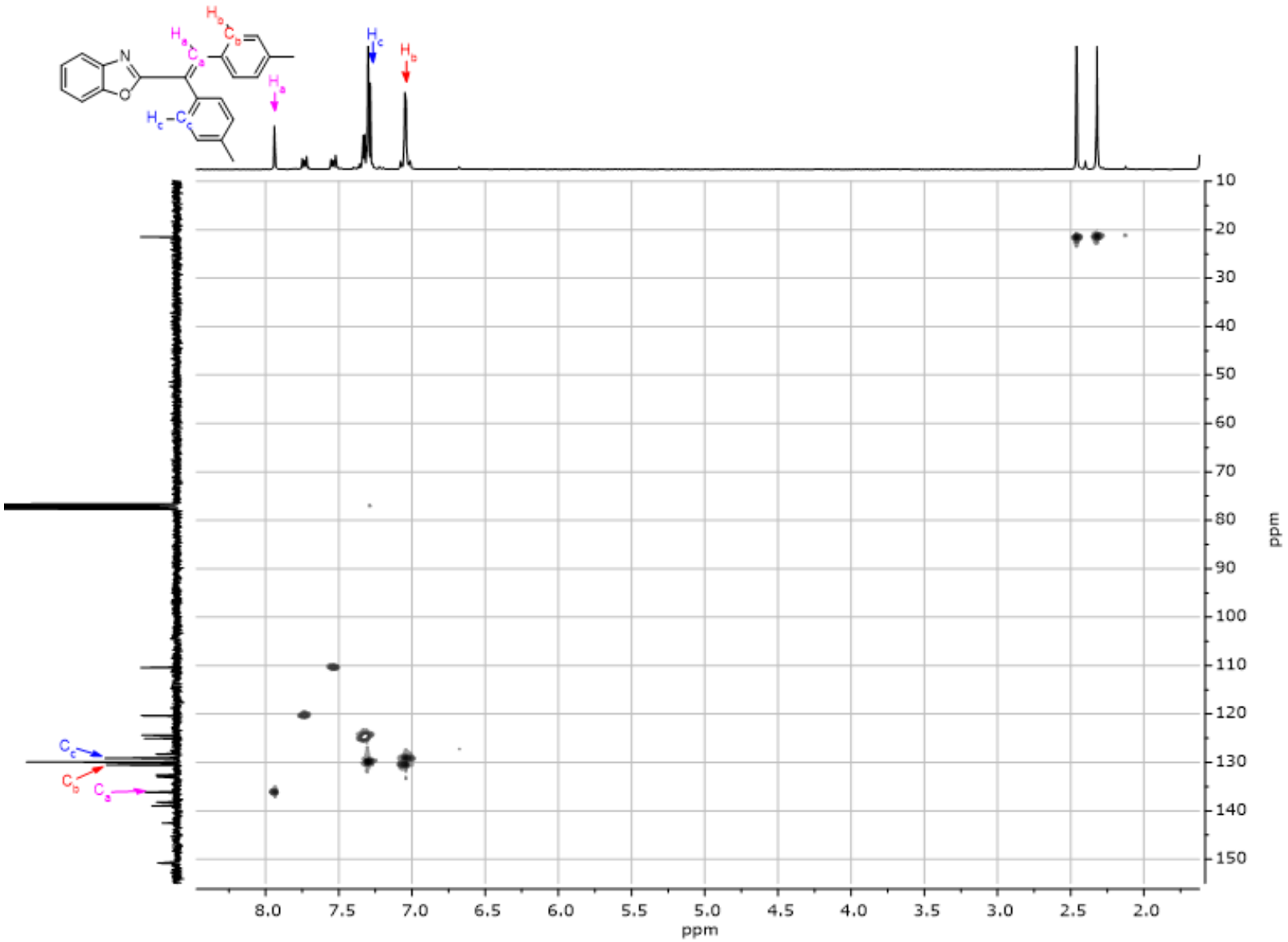


Figure S128. ^{1}H-^{13}C HSQC spectrum of compound **6e** ($CDCl_3$)

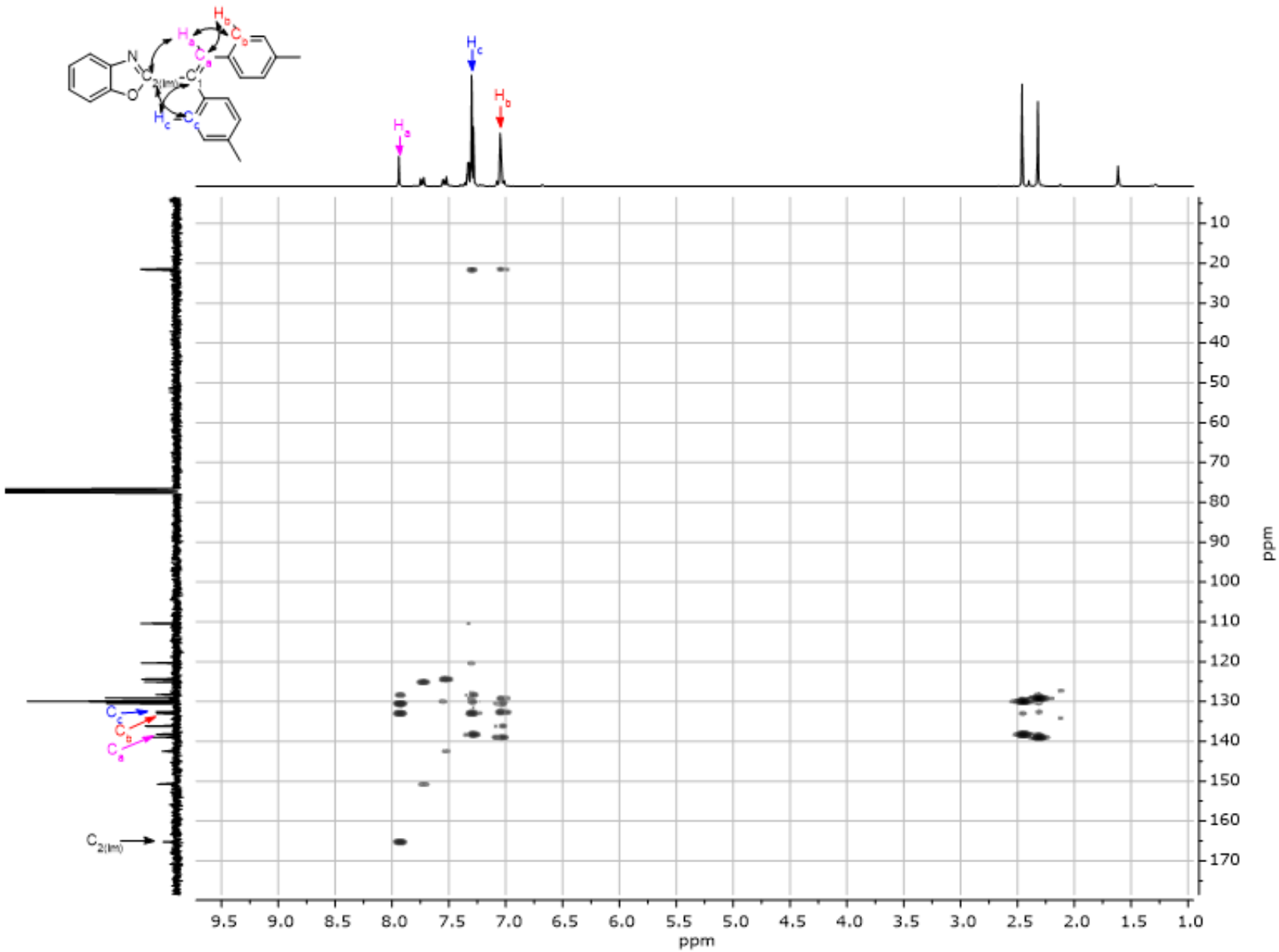


Figure S129. ^{1}H-^{13}C HMBC spectrum of compound **6e** ($CDCl_3$)

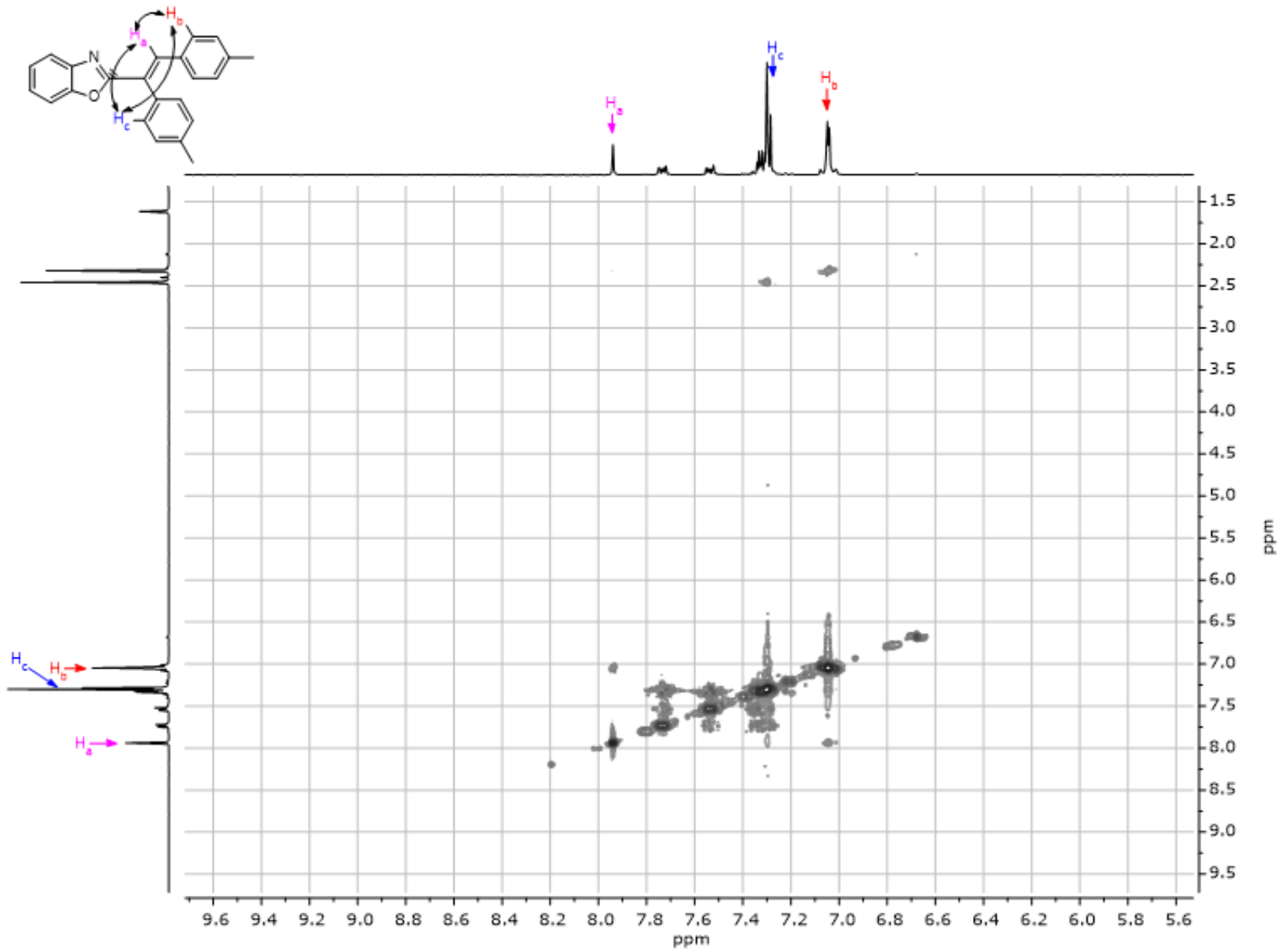


Figure S130. ^{1}H-^{1}H NOESY spectrum of compound **6e** ($CDCl_3$)

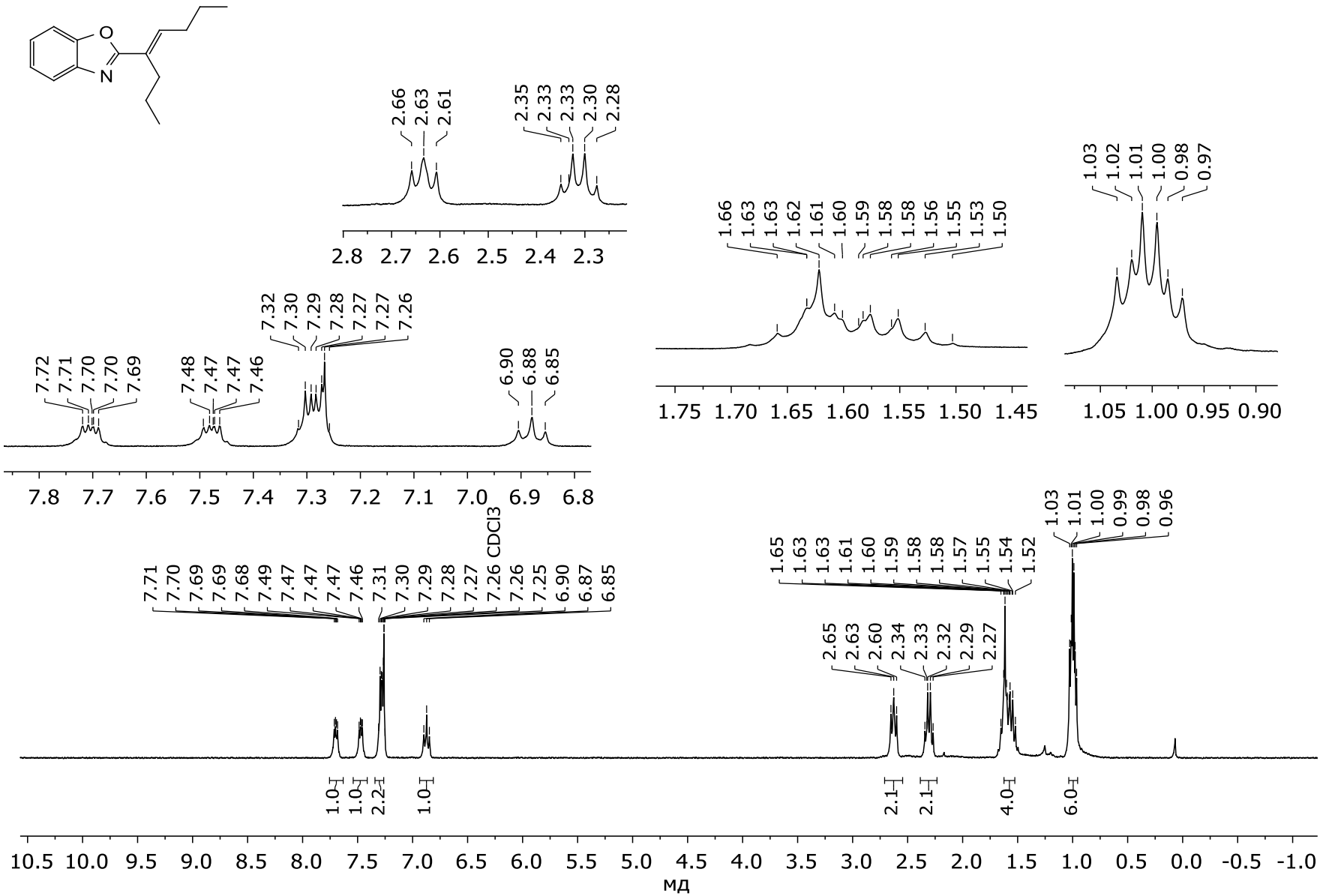


Figure S131. ^{1}H NMR spectrum of compound **6f** ($CDCl_3$, 300 MHz)

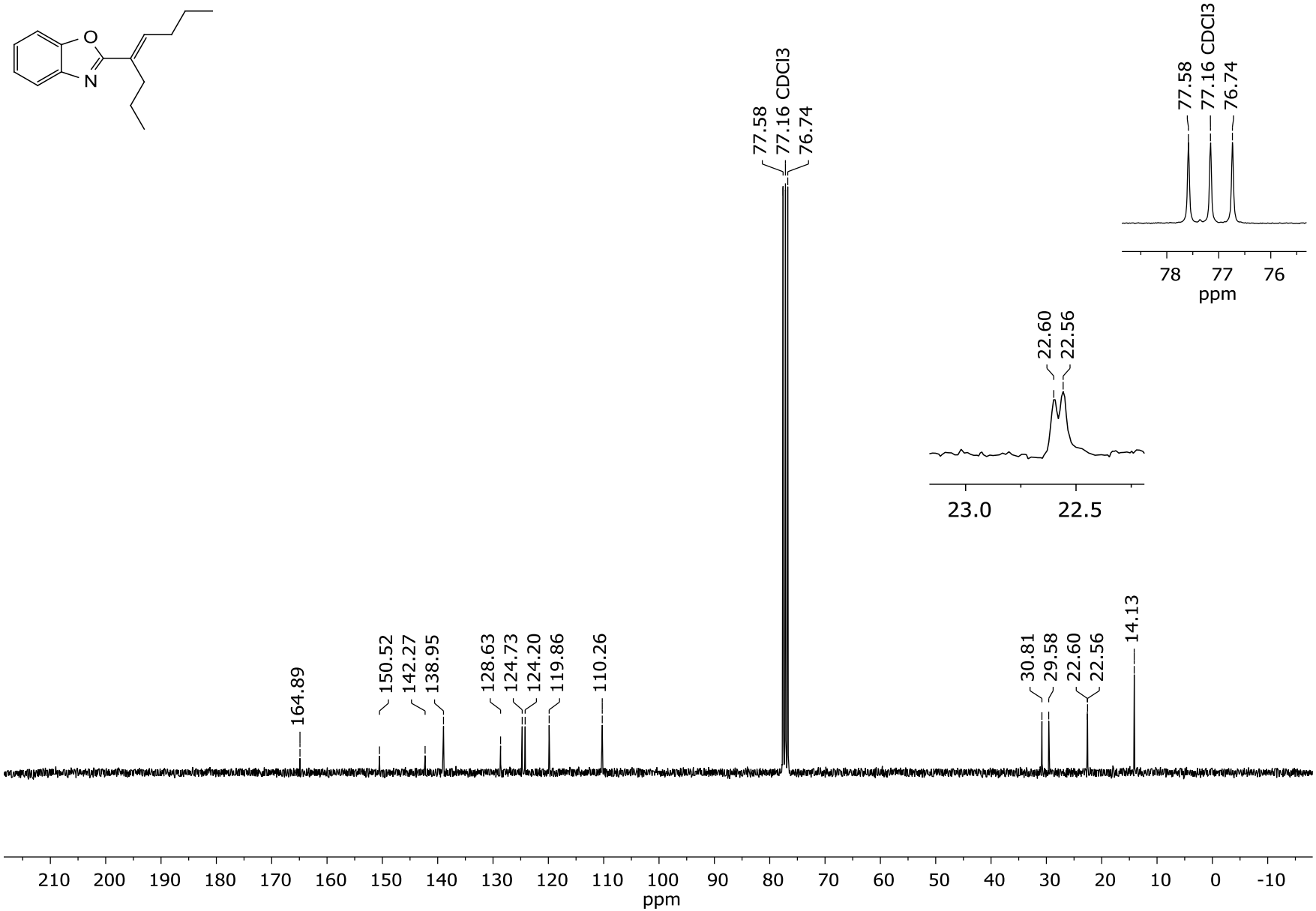


Figure S132. ^{13}C NMR spectrum of compound **6f** ($CDCl_3$, 75 MHz)

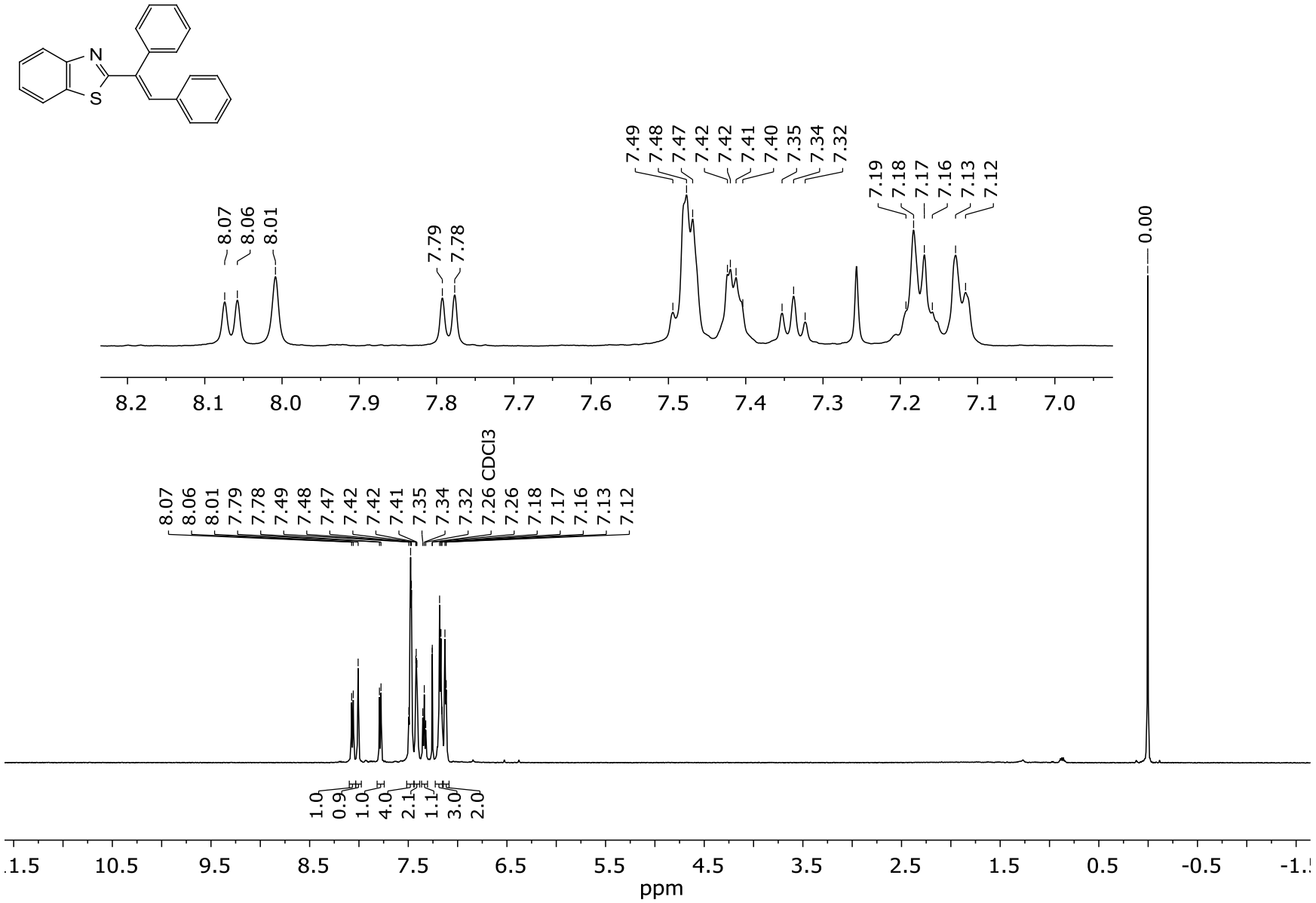


Figure S133. ^{1}H NMR spectrum of compound **6g** ($CDCl_3$, 500 MHz)

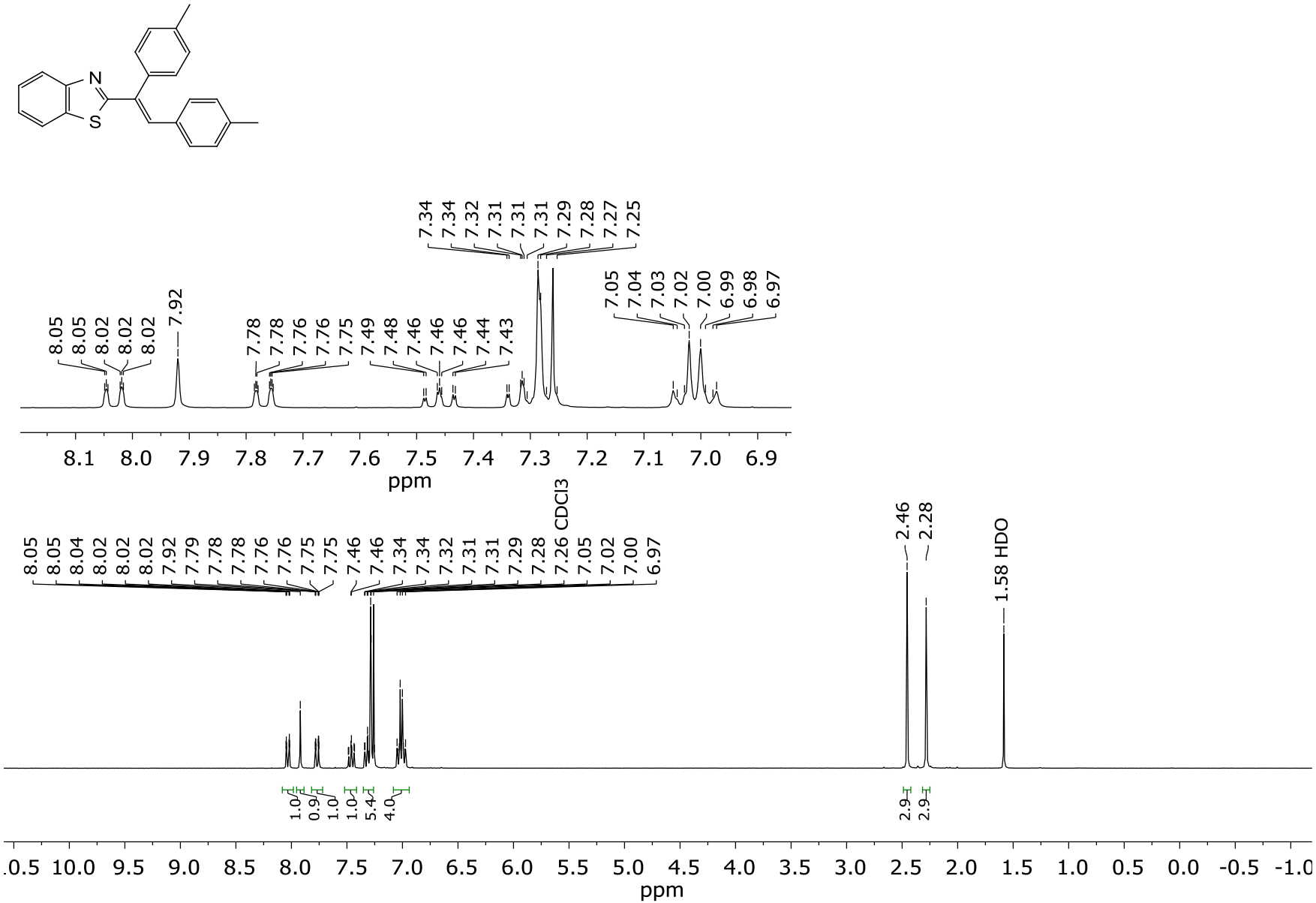


Figure S134. ^{1}H NMR spectrum of compound **6h** ($CDCl_3$, 300 MHz)

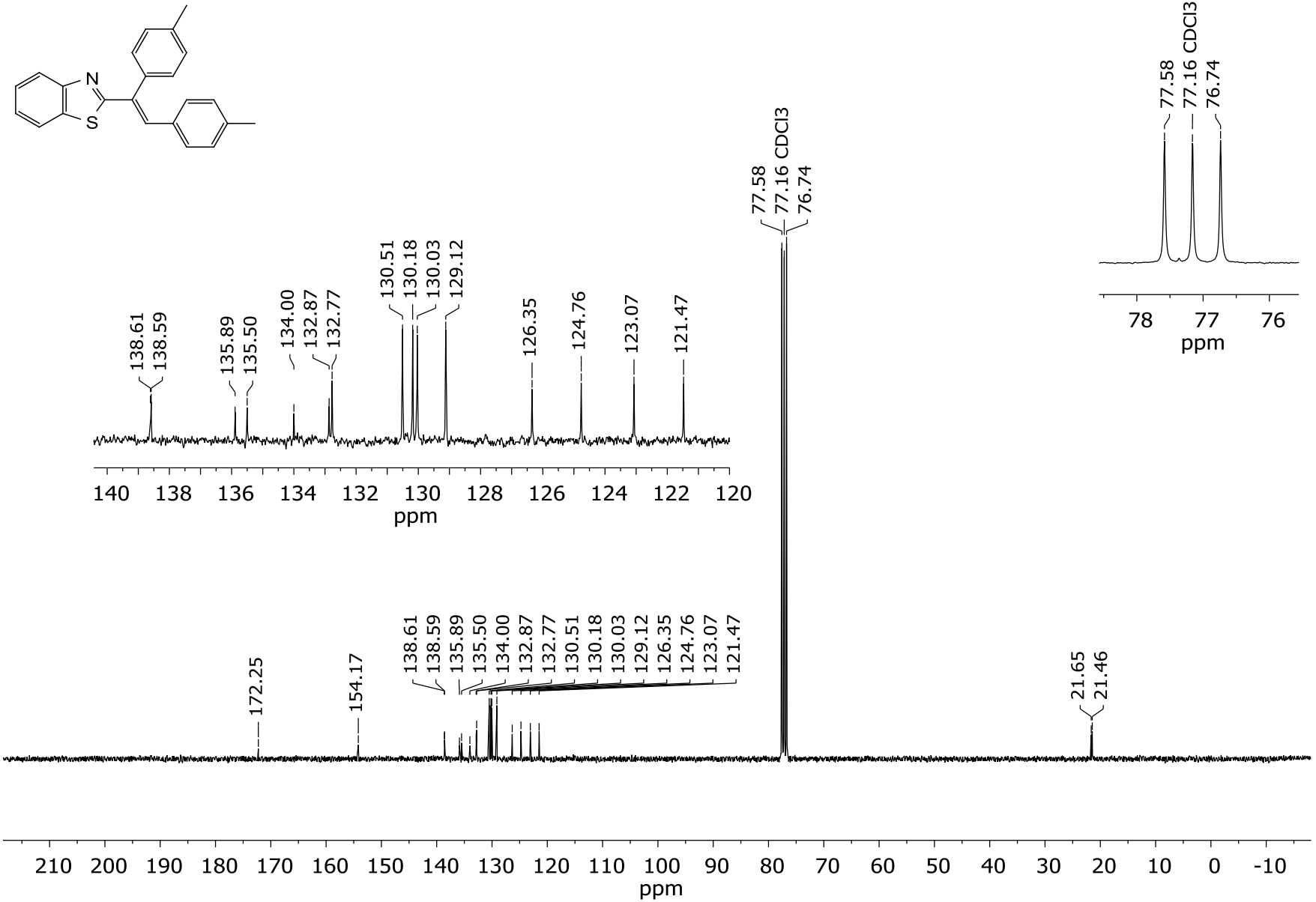


Figure S135. ^{13}C NMR spectrum of compound **6h** ($CDCl_3$, 75 MHz)

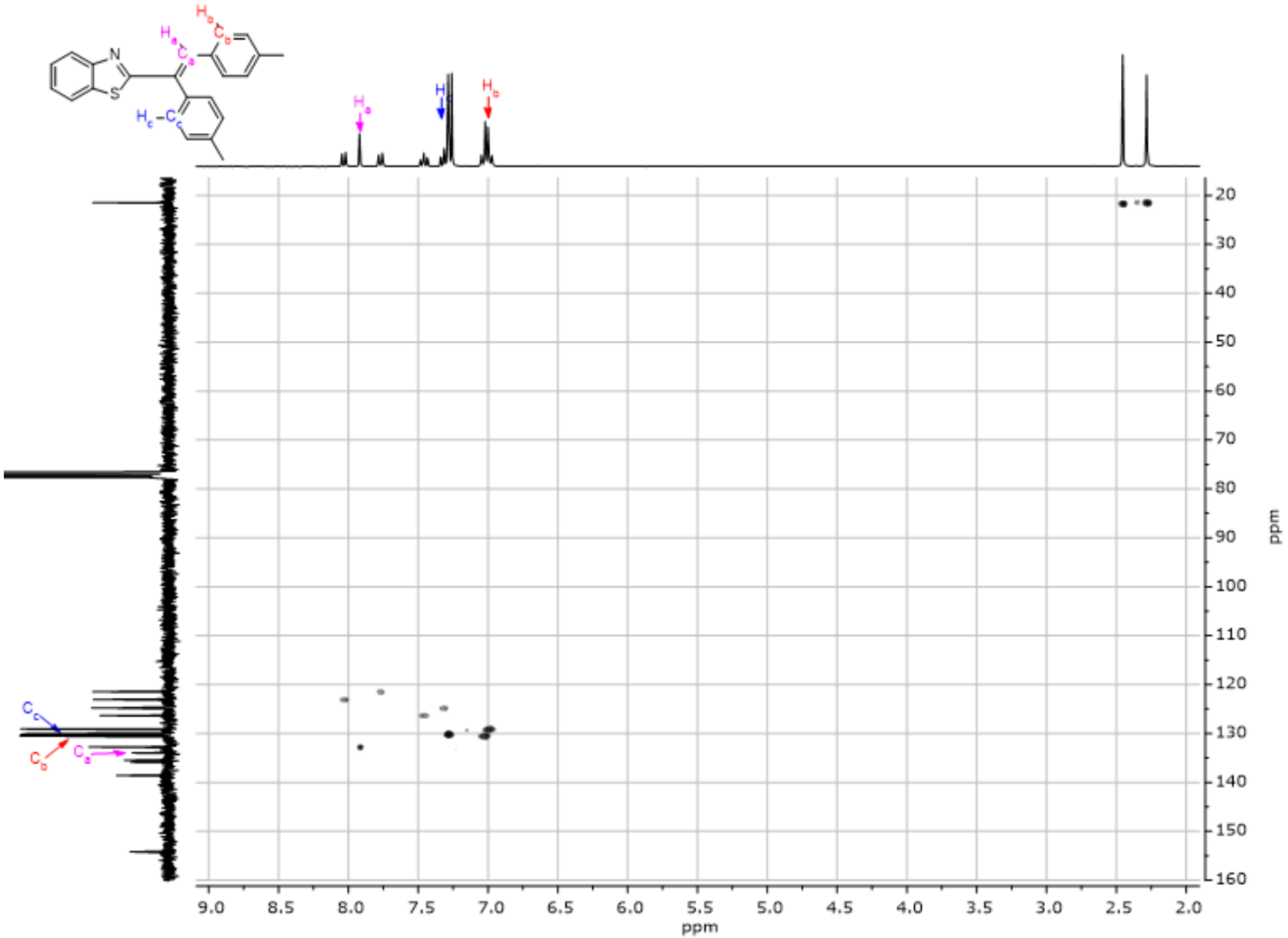


Figure S136. ^{1}H-^{13}C HSQC spectrum of compound **6h** ($CDCl_3$)

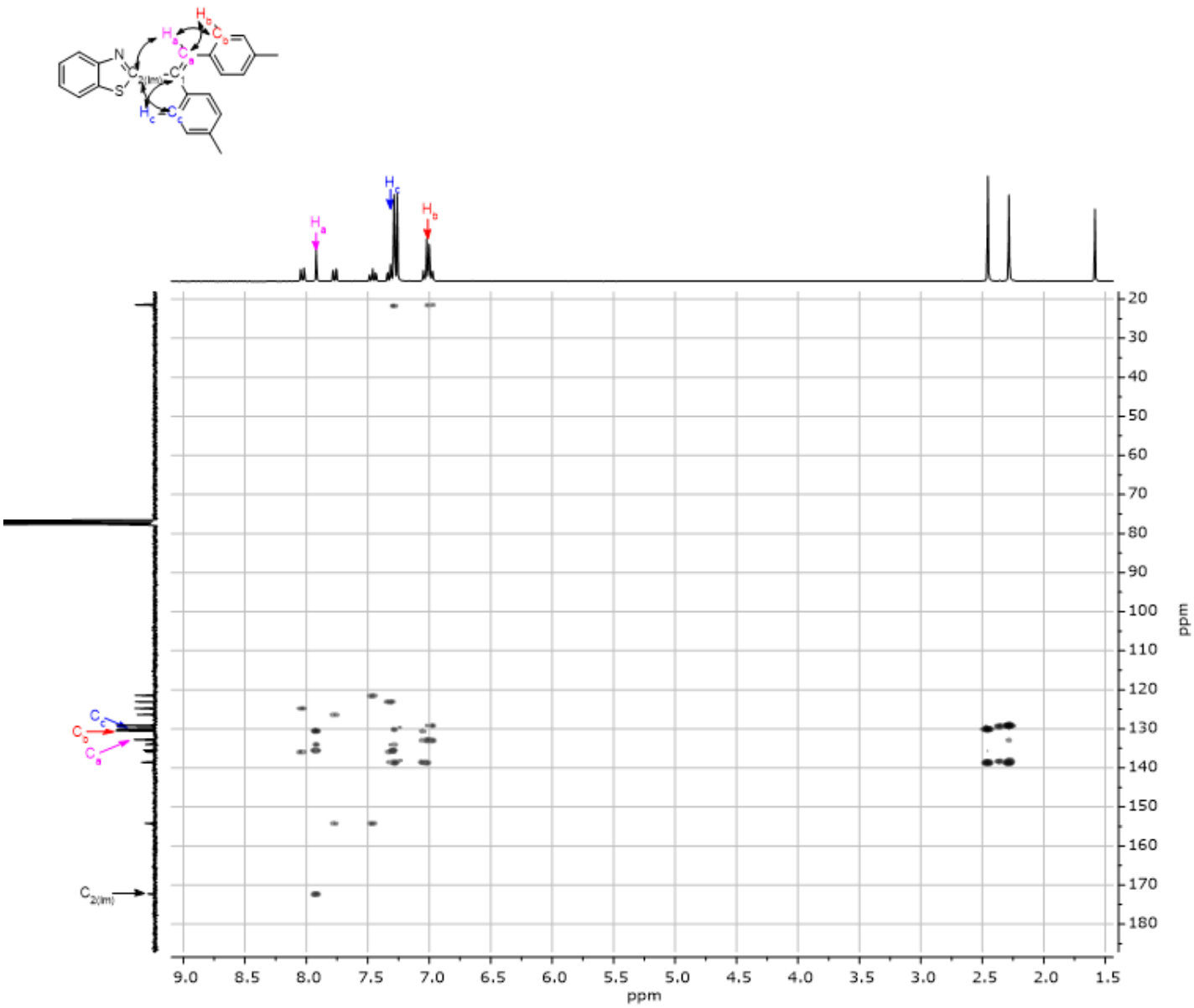


Figure S137. ^{1}H-^{13}C HMBC spectrum of compound **6h** ($CDCl_3$)

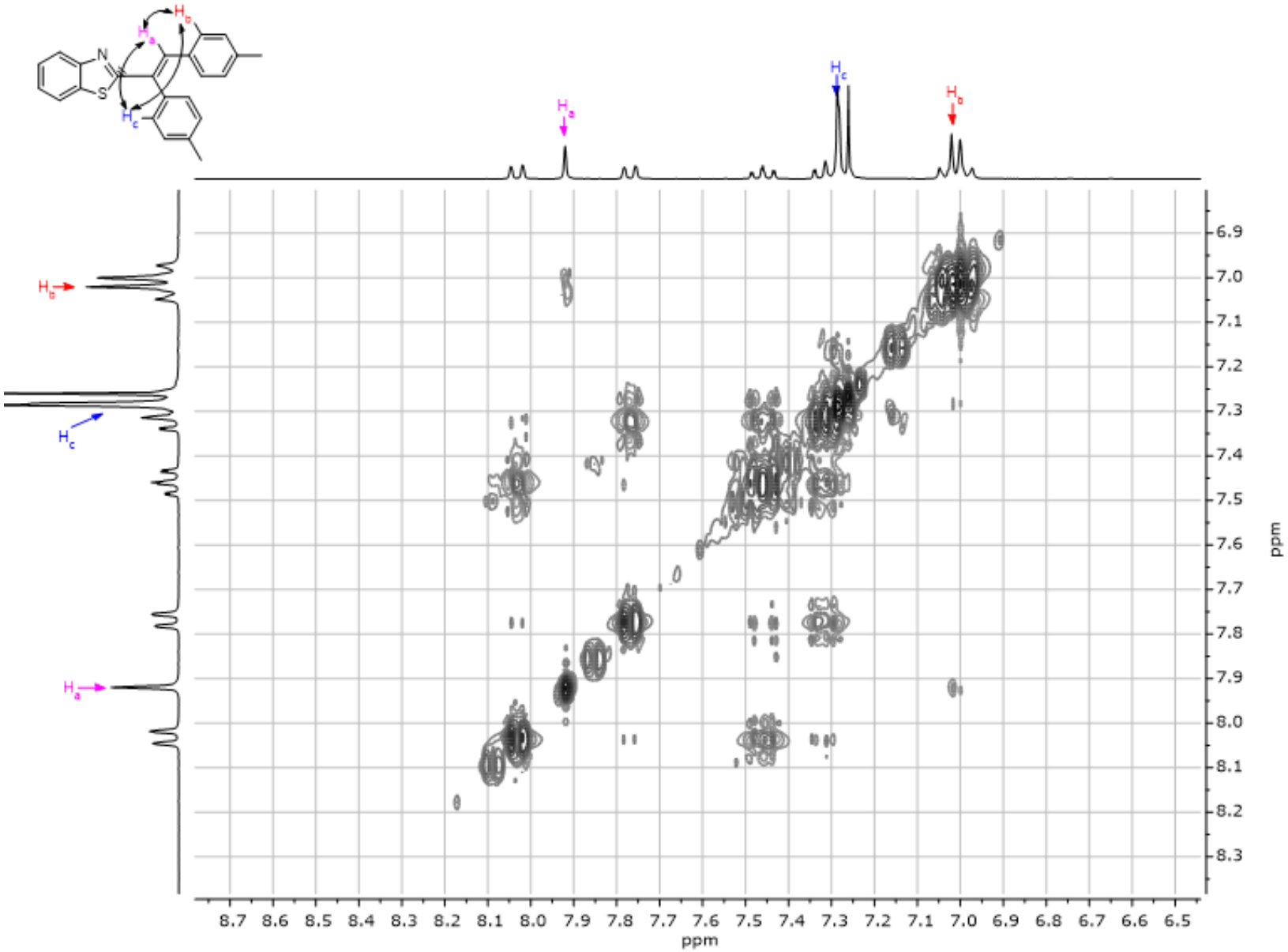


Figure S138. ^{1}H-^{1}H NOESY spectrum of compound **6h** ($CDCl_3$)

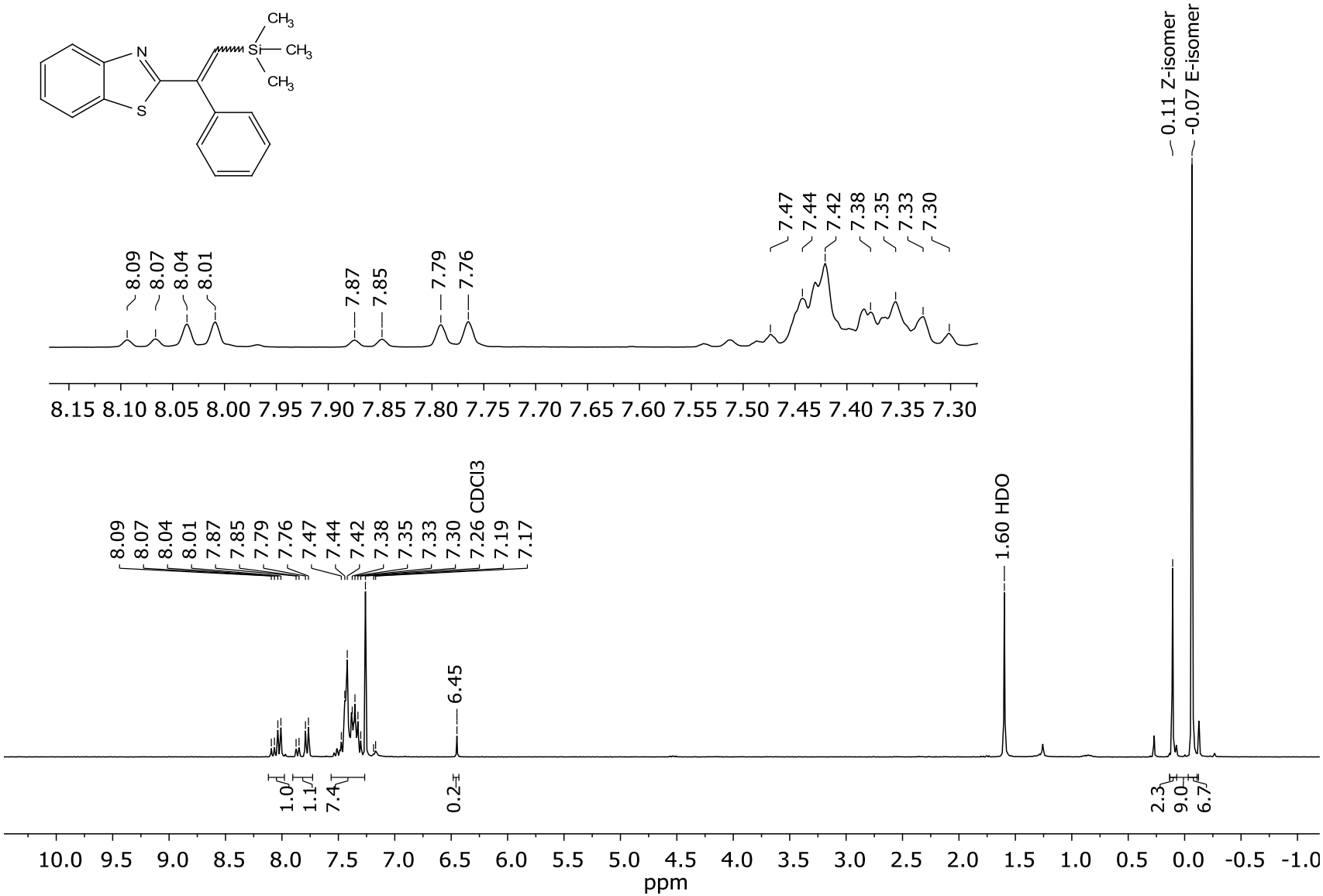


Figure S139. ^{1}H NMR spectrum of compound **6i (*E+Z* isomers)**($CDCl_3$, 300 MHz)

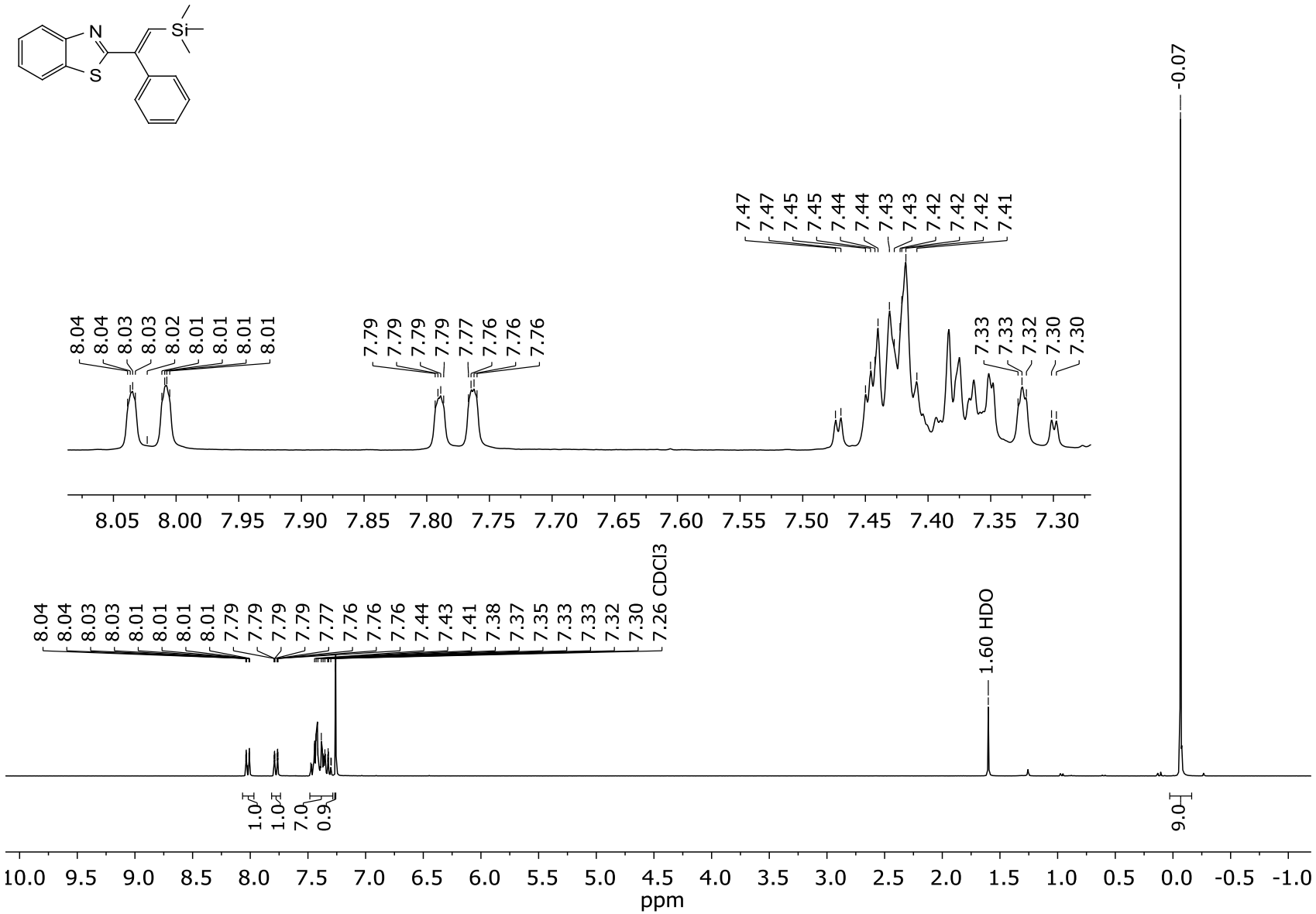


Figure S140. ^{1}H NMR spectrum of compound **6i *E*-isomer** ($CDCl_3$, 300 MHz)

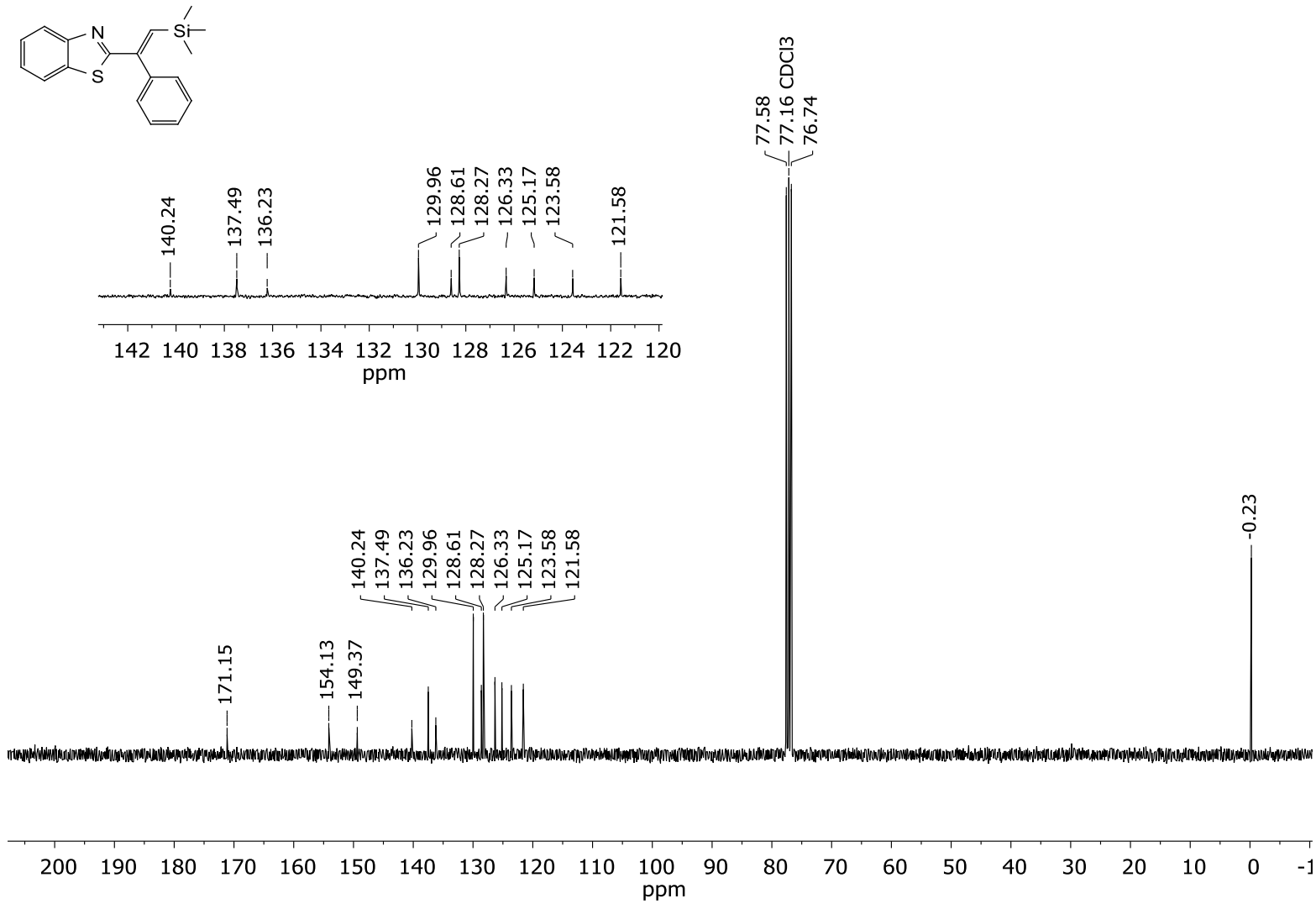


Figure S141. ^{13}C NMR spectrum of compound **6i *E*-isomer** ($CDCl_3$, 75 MHz)

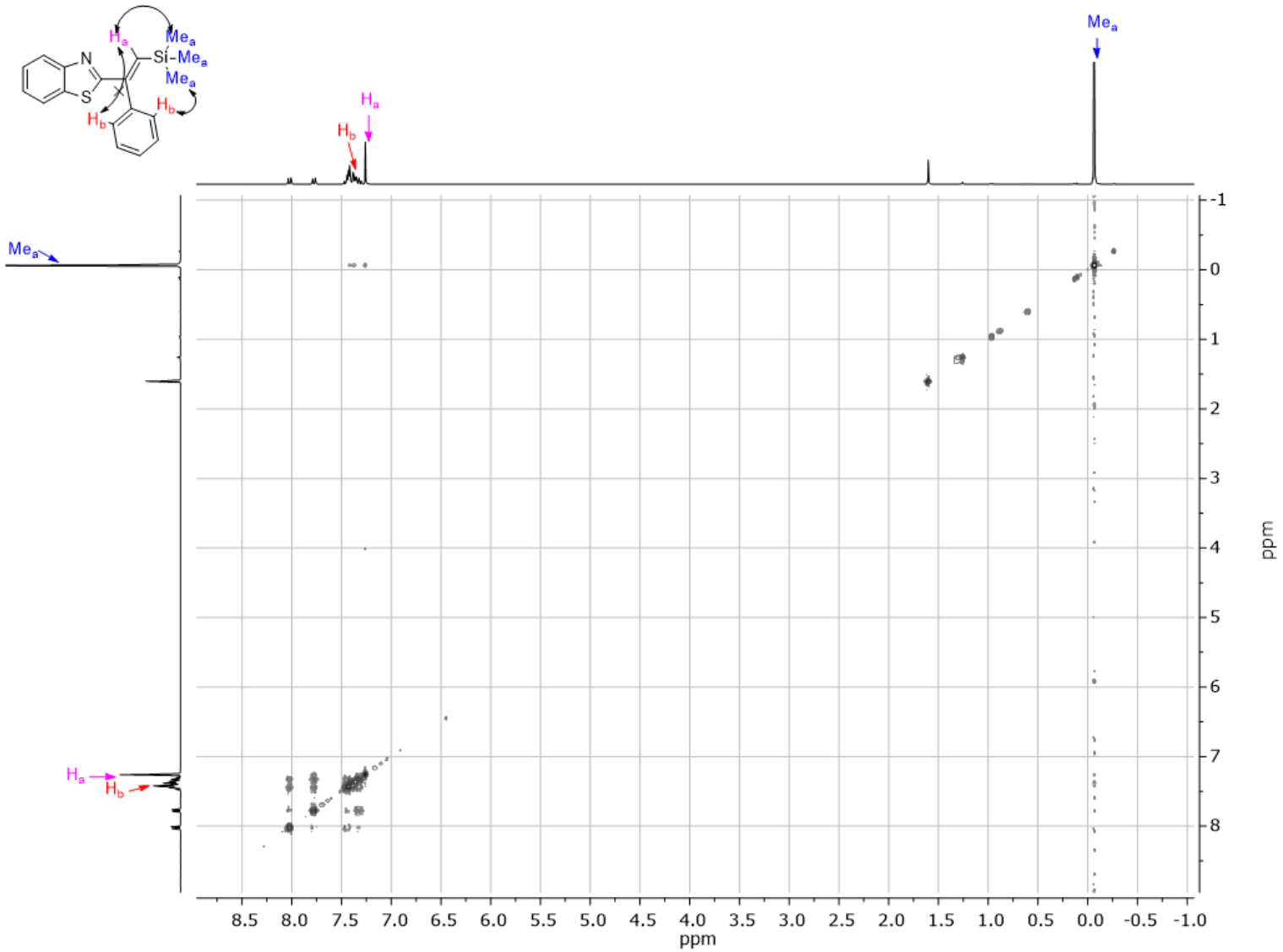


Figure S142. ^{1}H-^{1}H NOESY spectrum of compound **6i *E*-isomer** ($CDCl_3$)

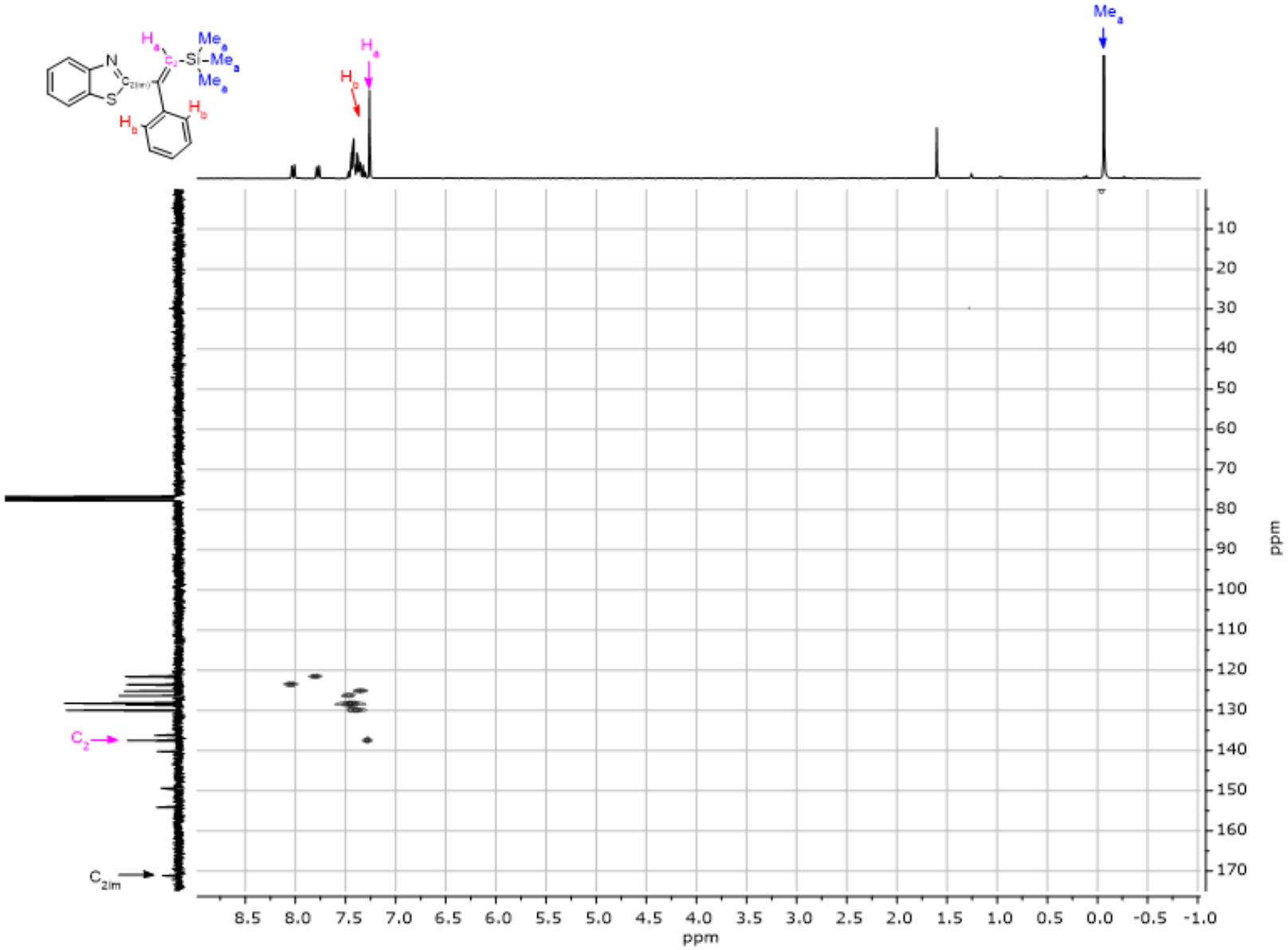


Figure S143. ^{1}H-^{13}C HSQC spectrum of compound **6i *E*-isomer** ($CDCl_3$)

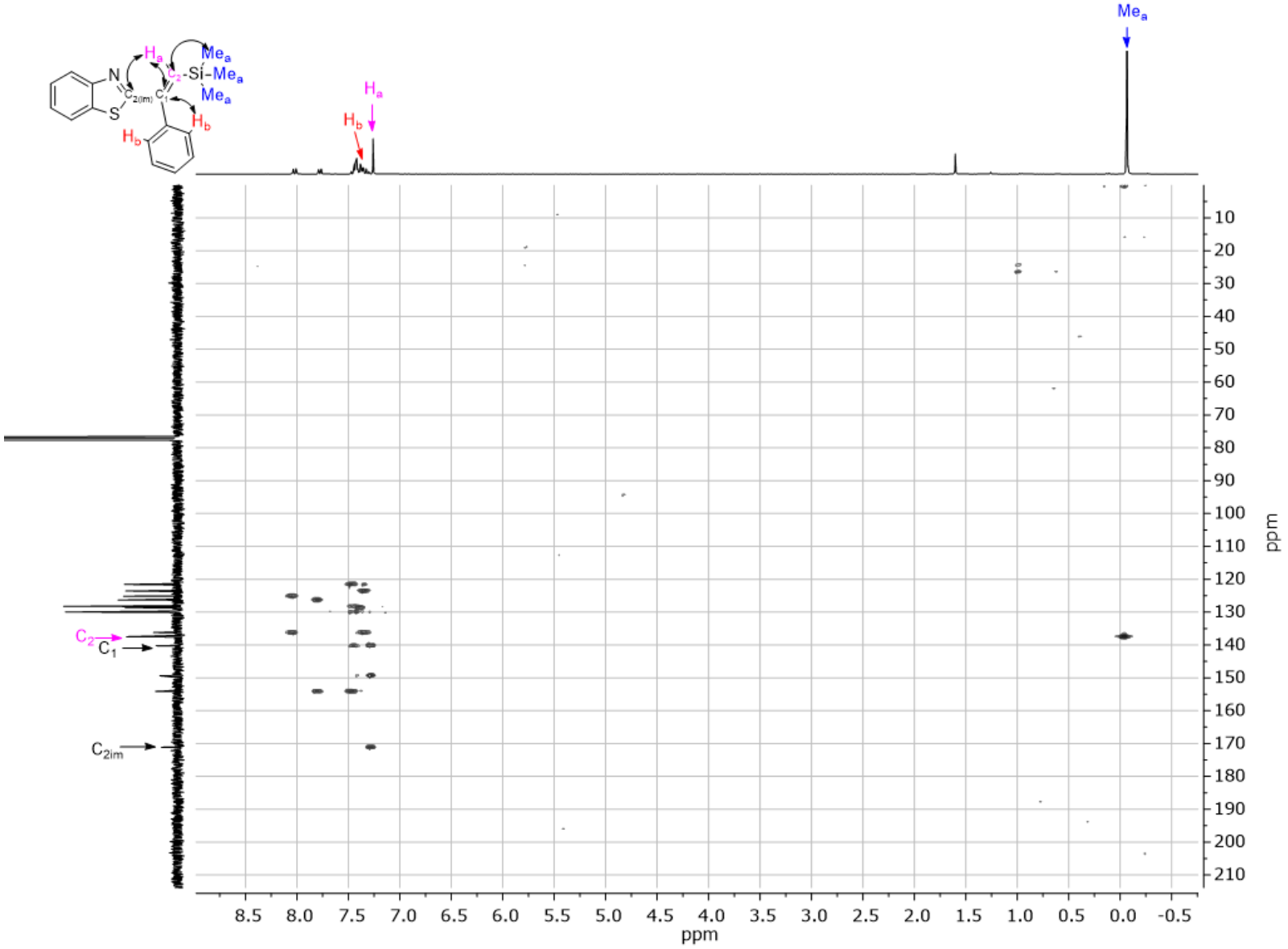


Figure S144. ^{1}H-^{13}C HMBC spectrum of compound **6i *E*-isomer** ($CDCl_3$)

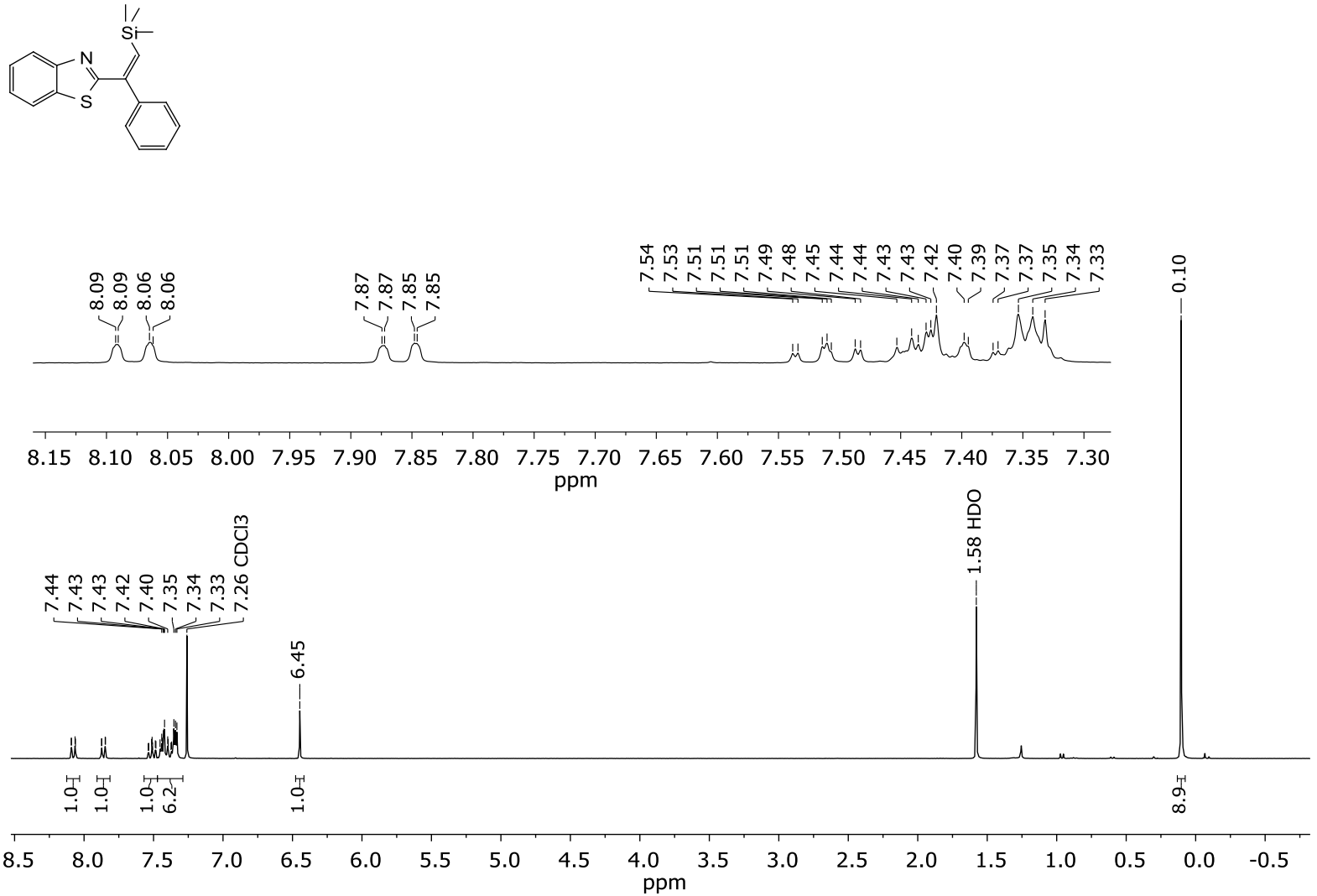


Figure S145. ^{1}H NMR spectrum of compound **6i *Z*-isomer** ($CDCl_3$, 300 MHz)

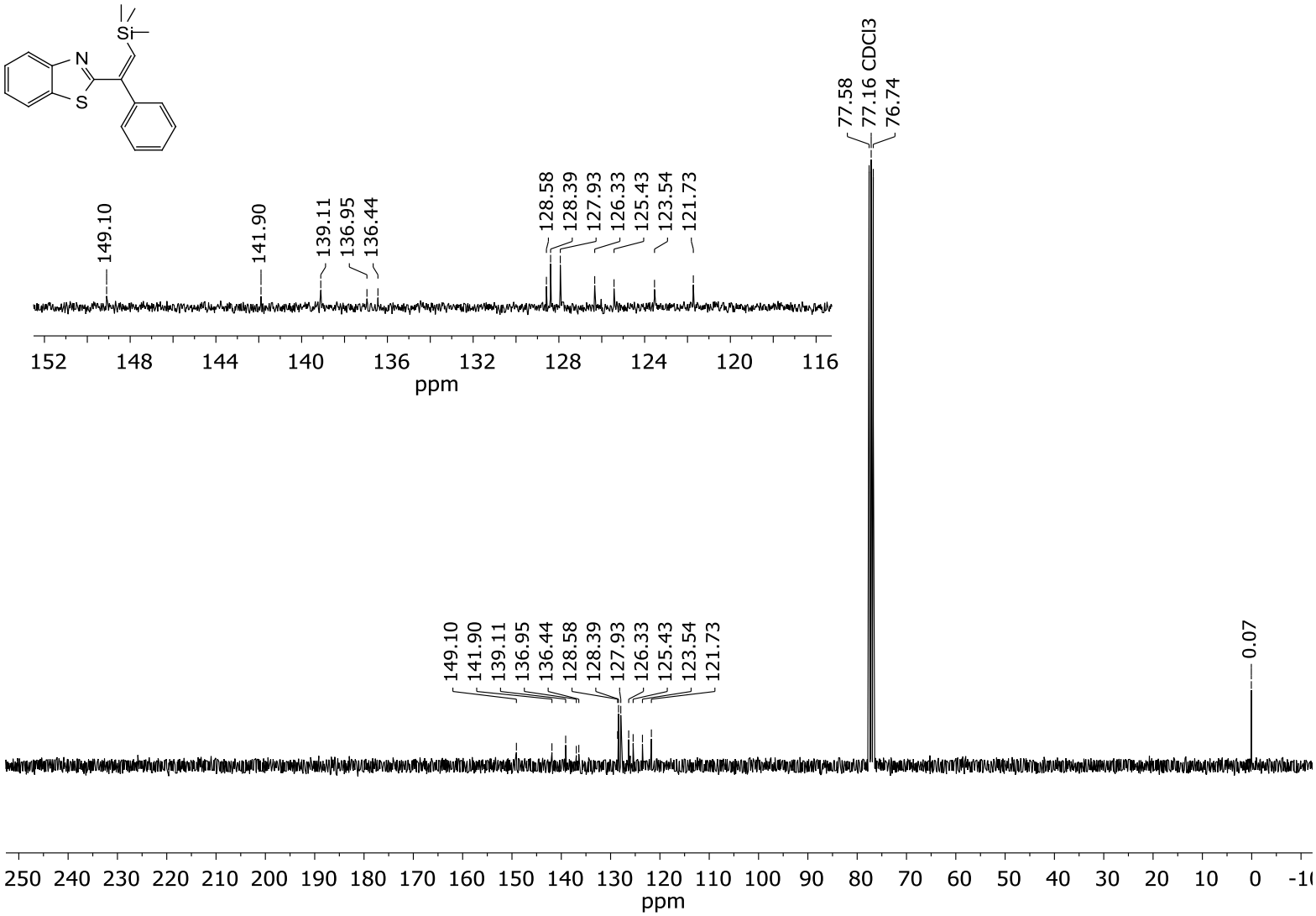


Figure S146. ^{13}C NMR spectrum of compound **6i *Z*-isomer** ($CDCl_3$, 75 MHz)

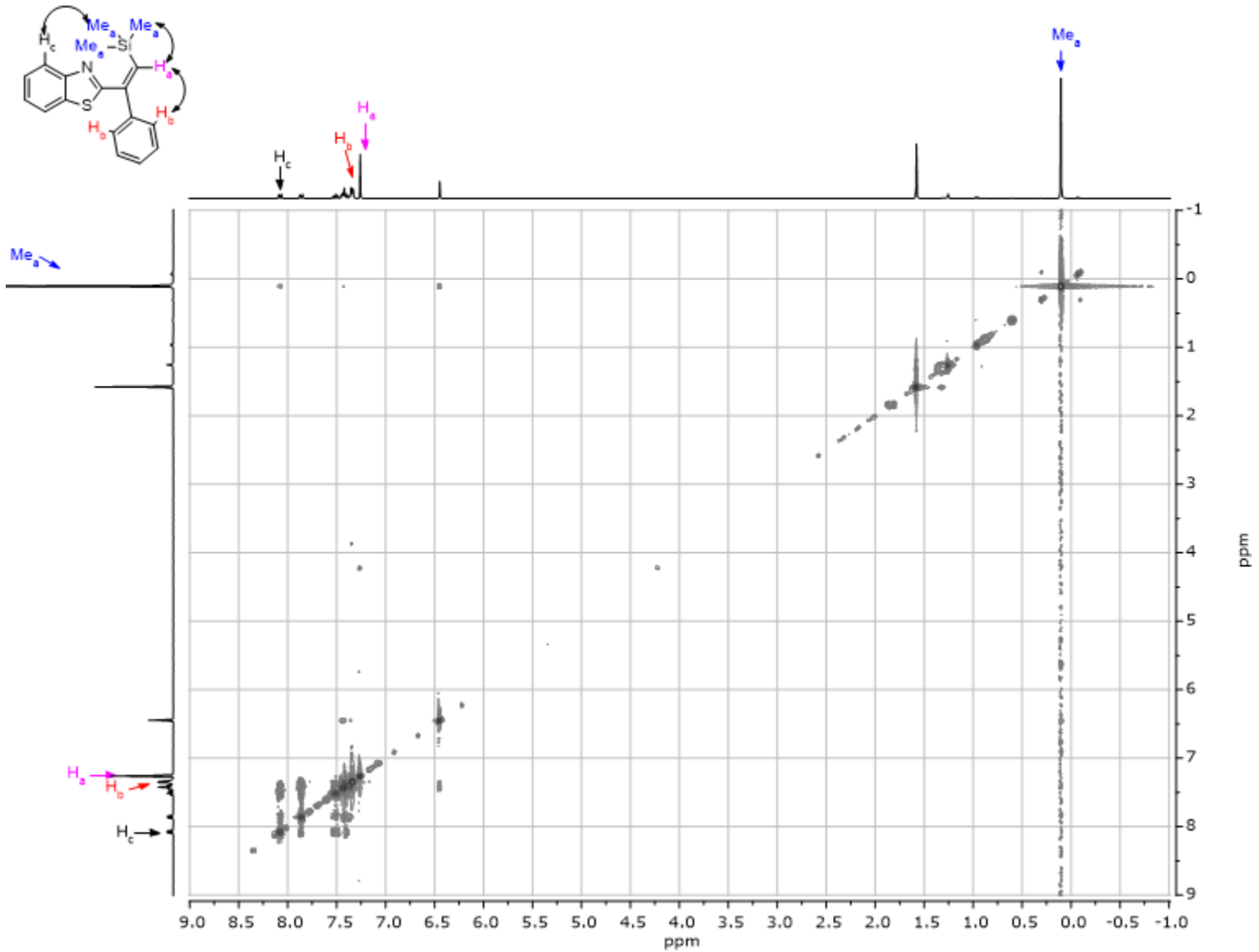


Figure S147. ^{1}H-^{1}H NOESY spectrum of compound **6i *Z*-isomer** ($CDCl_3$)

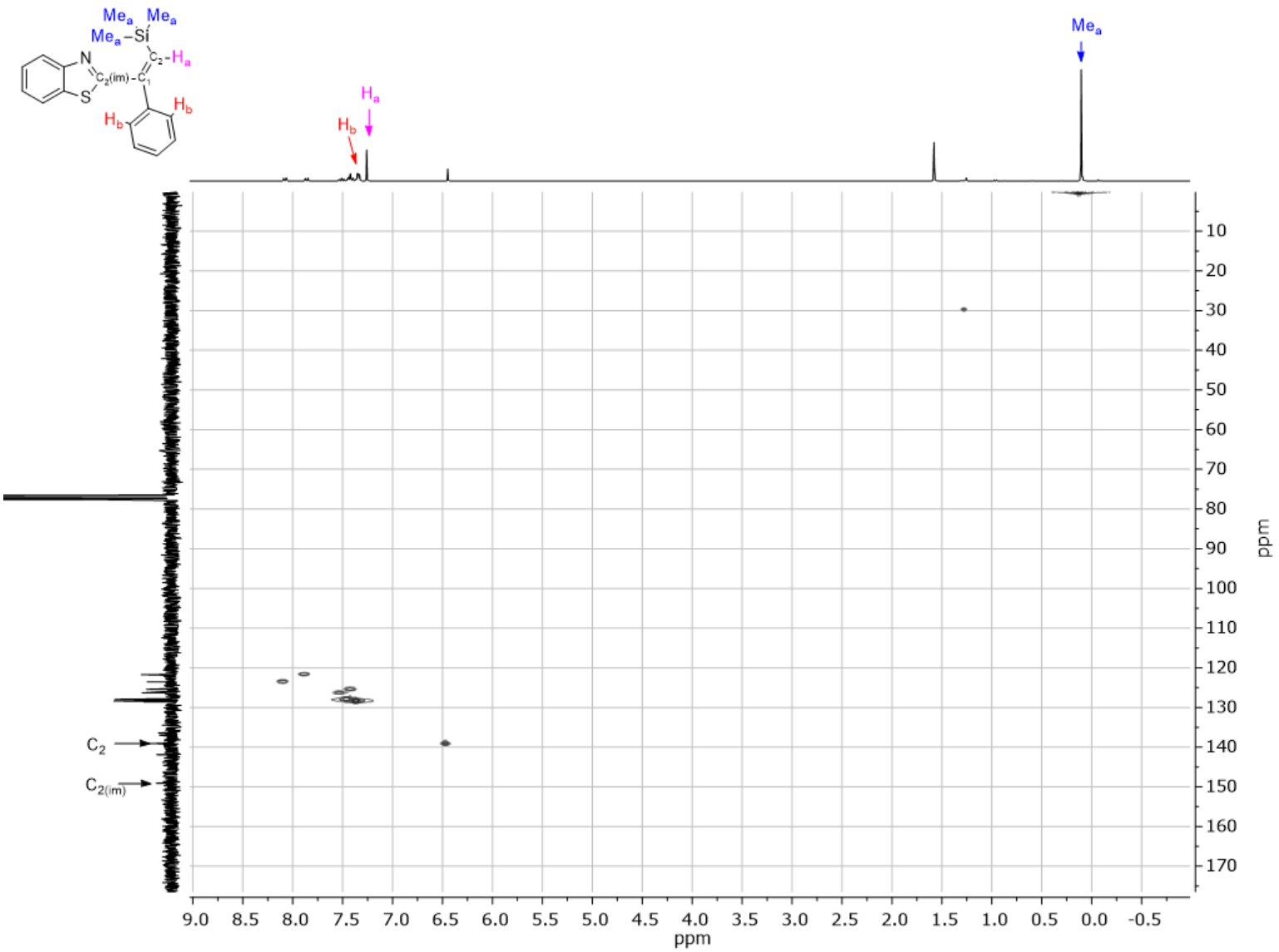


Figure S148. ^{1}H-^{13}C HSQC spectrum of compound **6i *Z*-isomer** ($CDCl_3$)

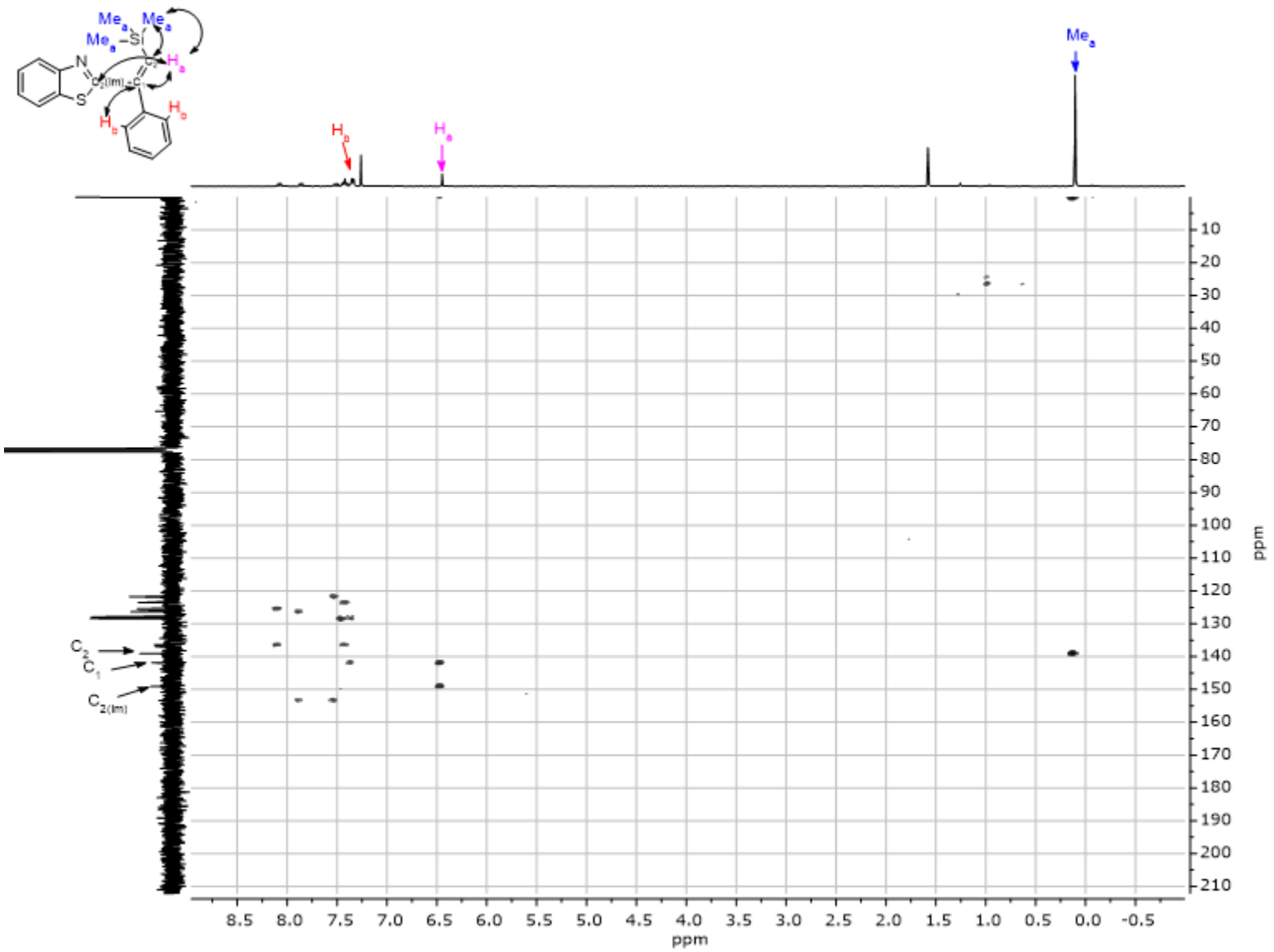


Figure S149. ^{1}H-^{13}C HMBC spectrum of compound **6i *Z*-isomer** ($CDCl_3$)

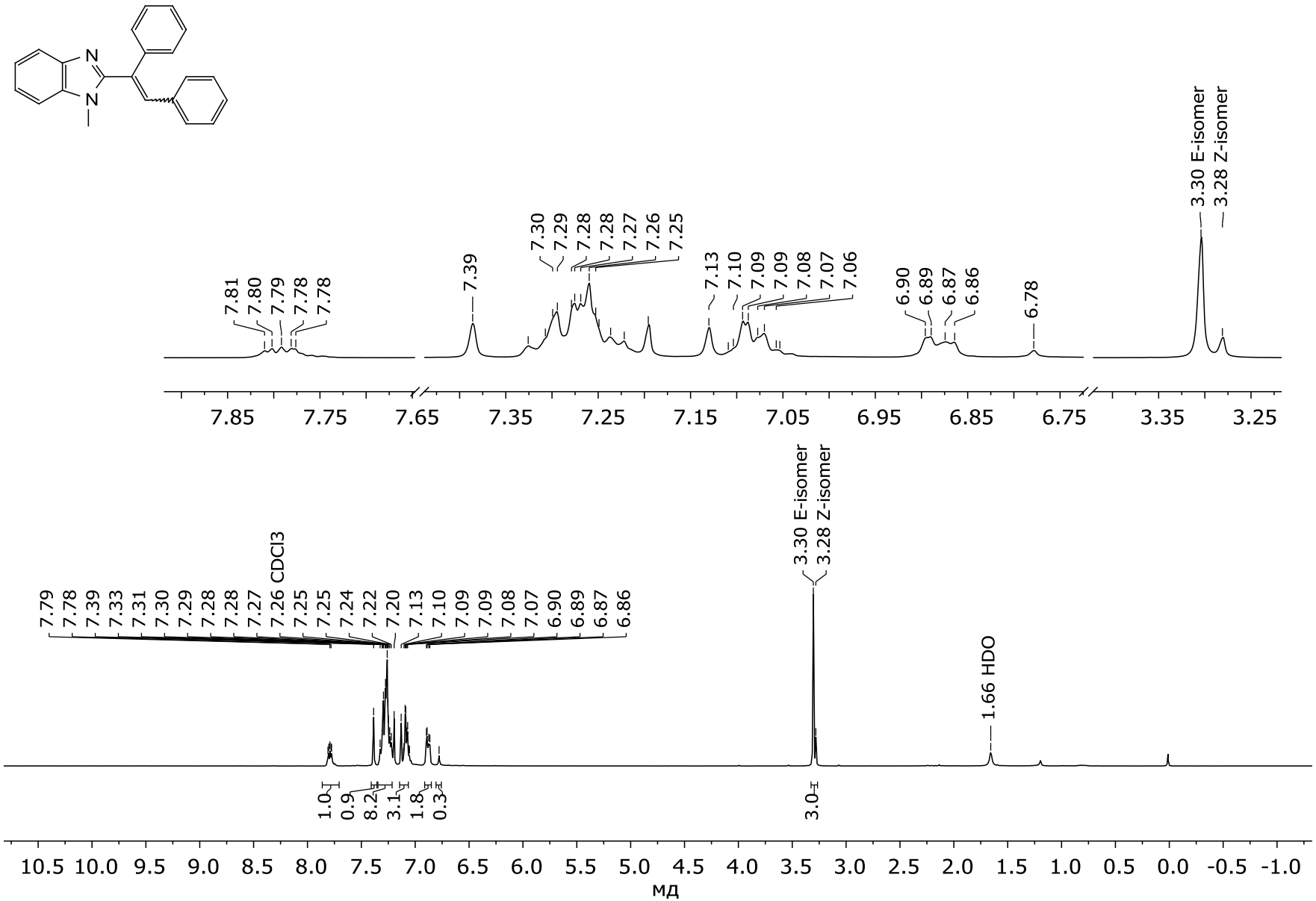


Figure S150. ^{1}H NMR spectrum of compound **6j (*E+Z* isomers)** ($CDCl_3$, 300 MHz)

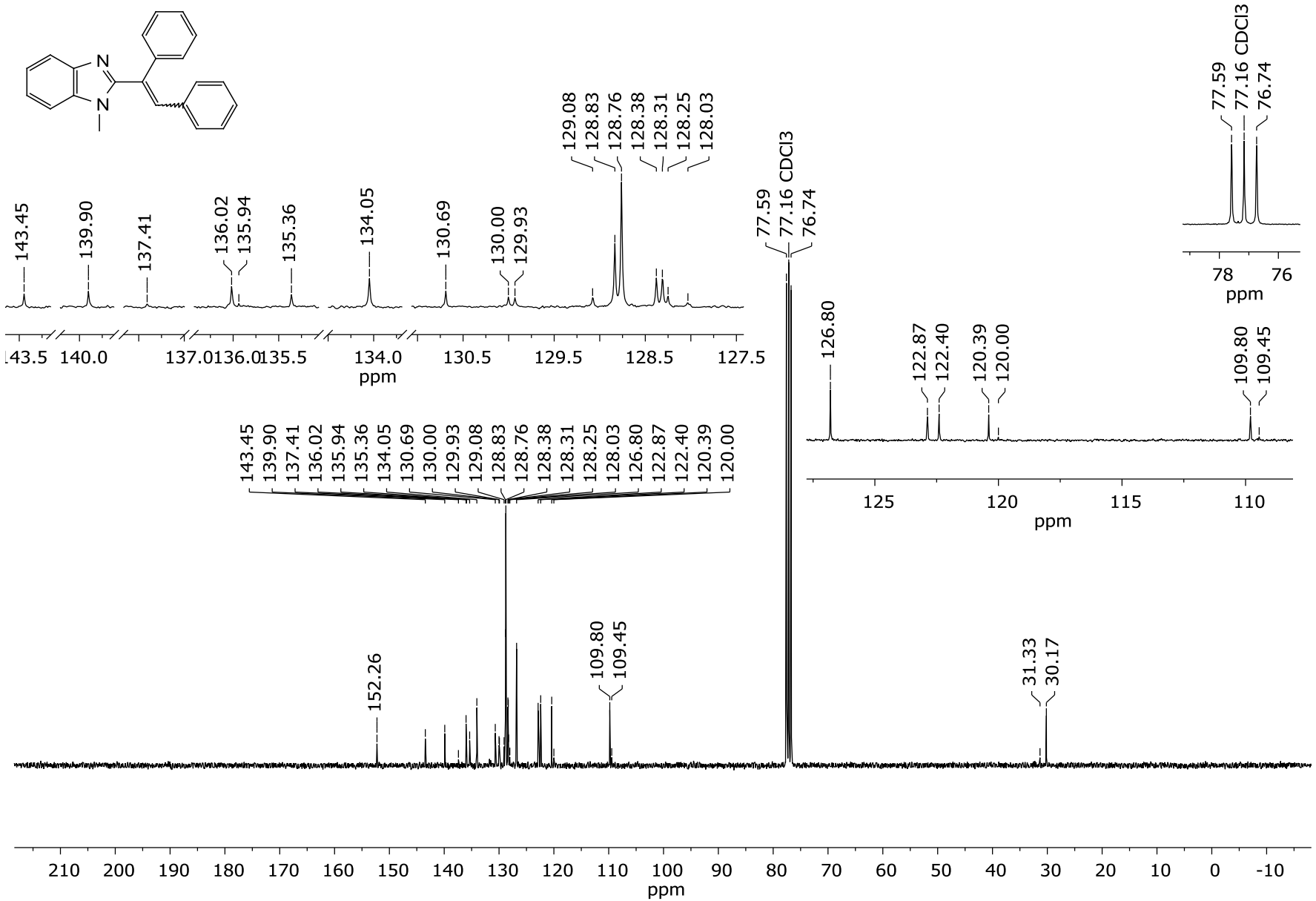


Figure S151. ^{13}C NMR spectrum of compound **6j (*E+Z* isomers)** ($CDCl_3$, 75 MHz)

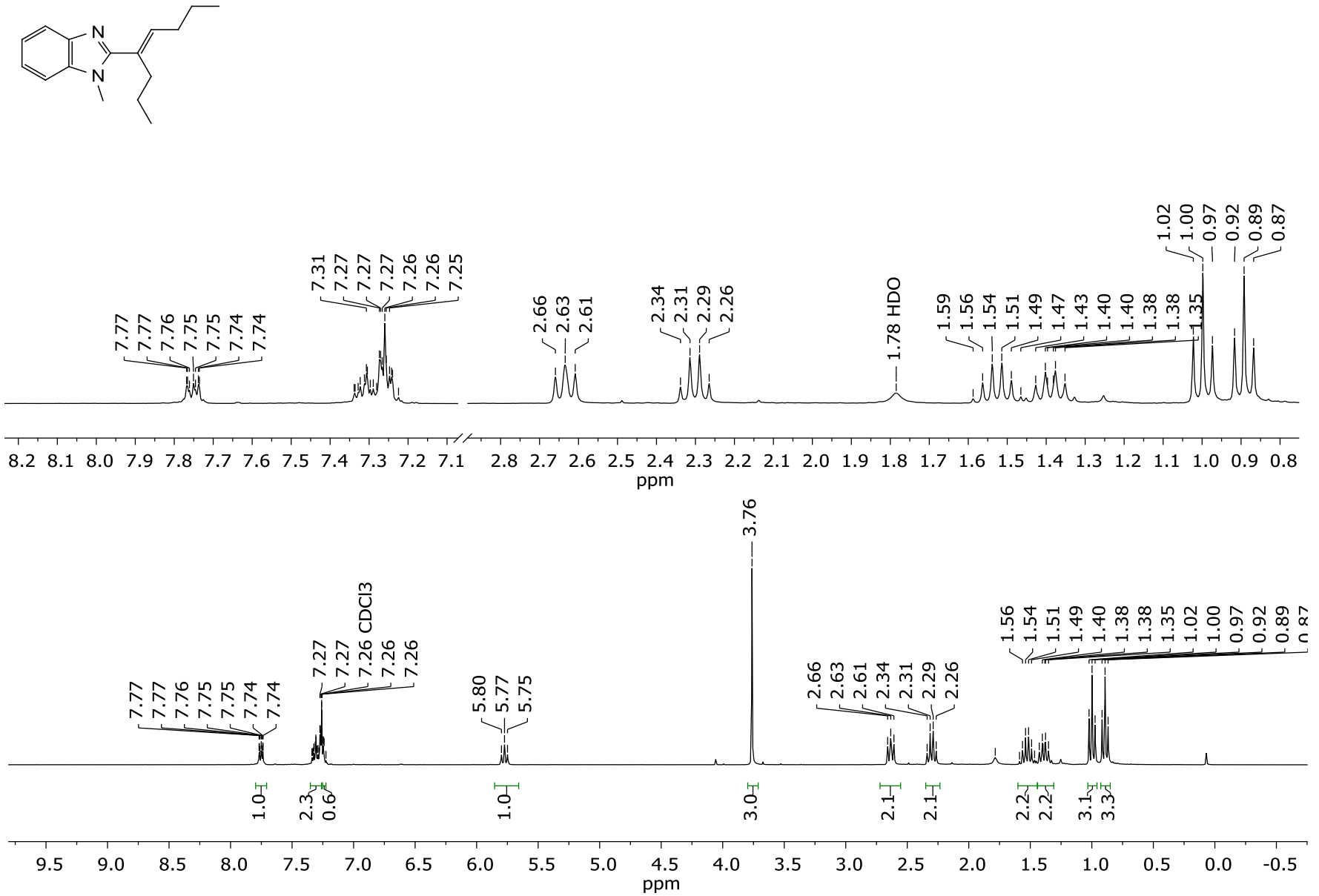


Figure S152. ^{1}H NMR spectrum of compound **6k** ($CDCl_3$, 300 MHz)

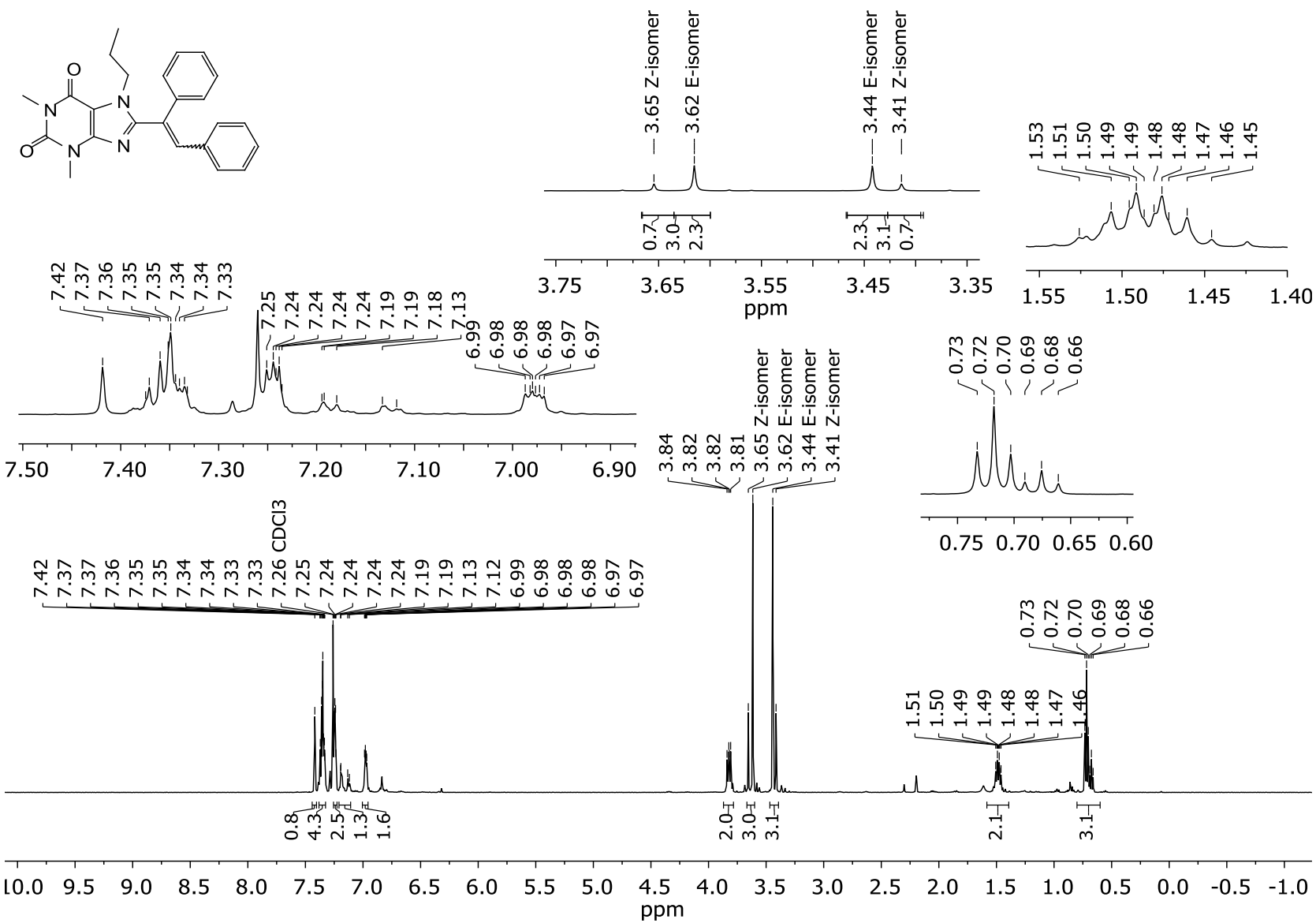


Figure S153. ^{1}H NMR spectrum of compound **6l (*E+Z* isomers)** ($CDCl_3$, 500 MHz)

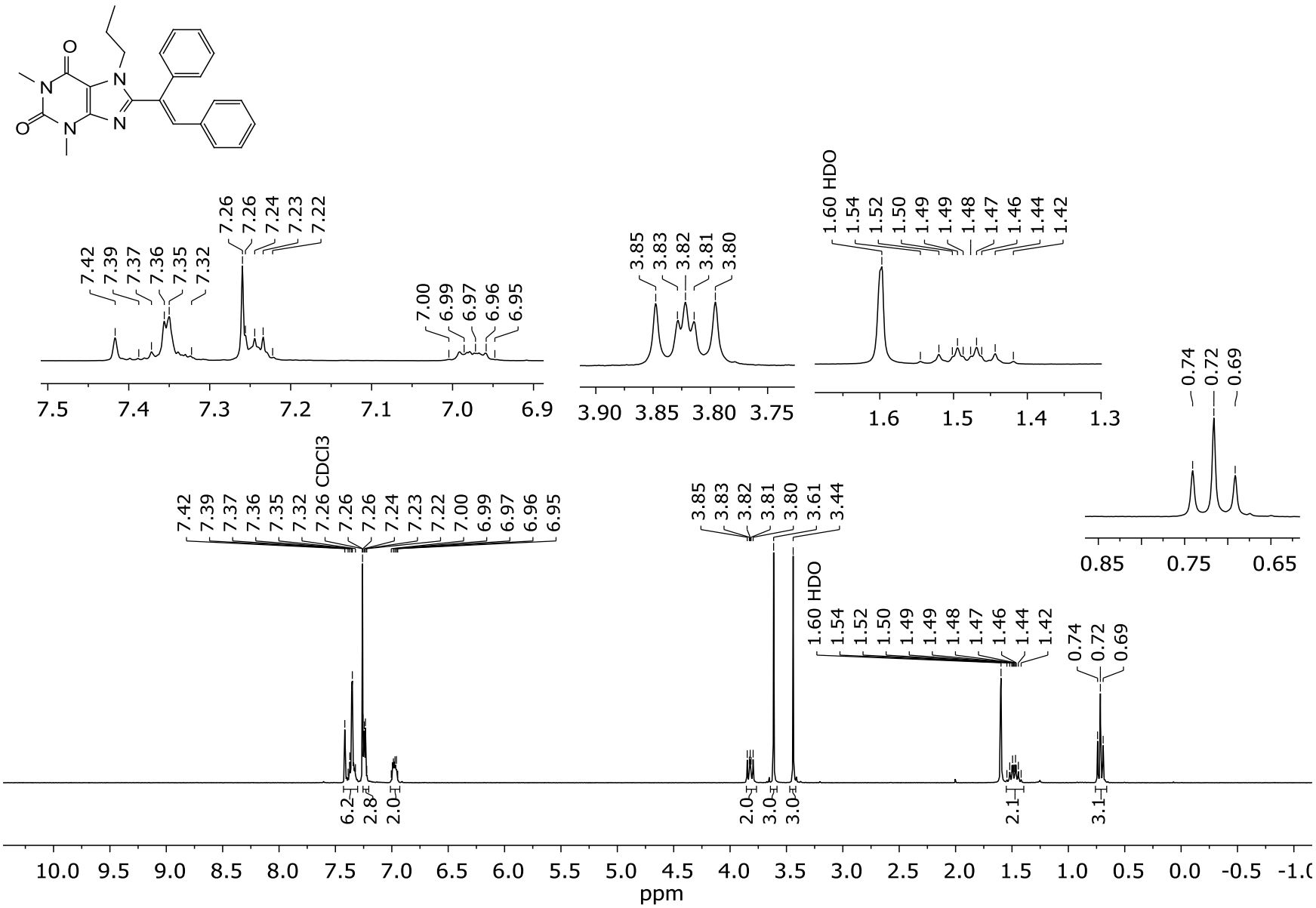


Figure S154. ^{1}H NMR spectrum of compound **6l *E*-isomer** ($CDCl_3$, 300 MHz)

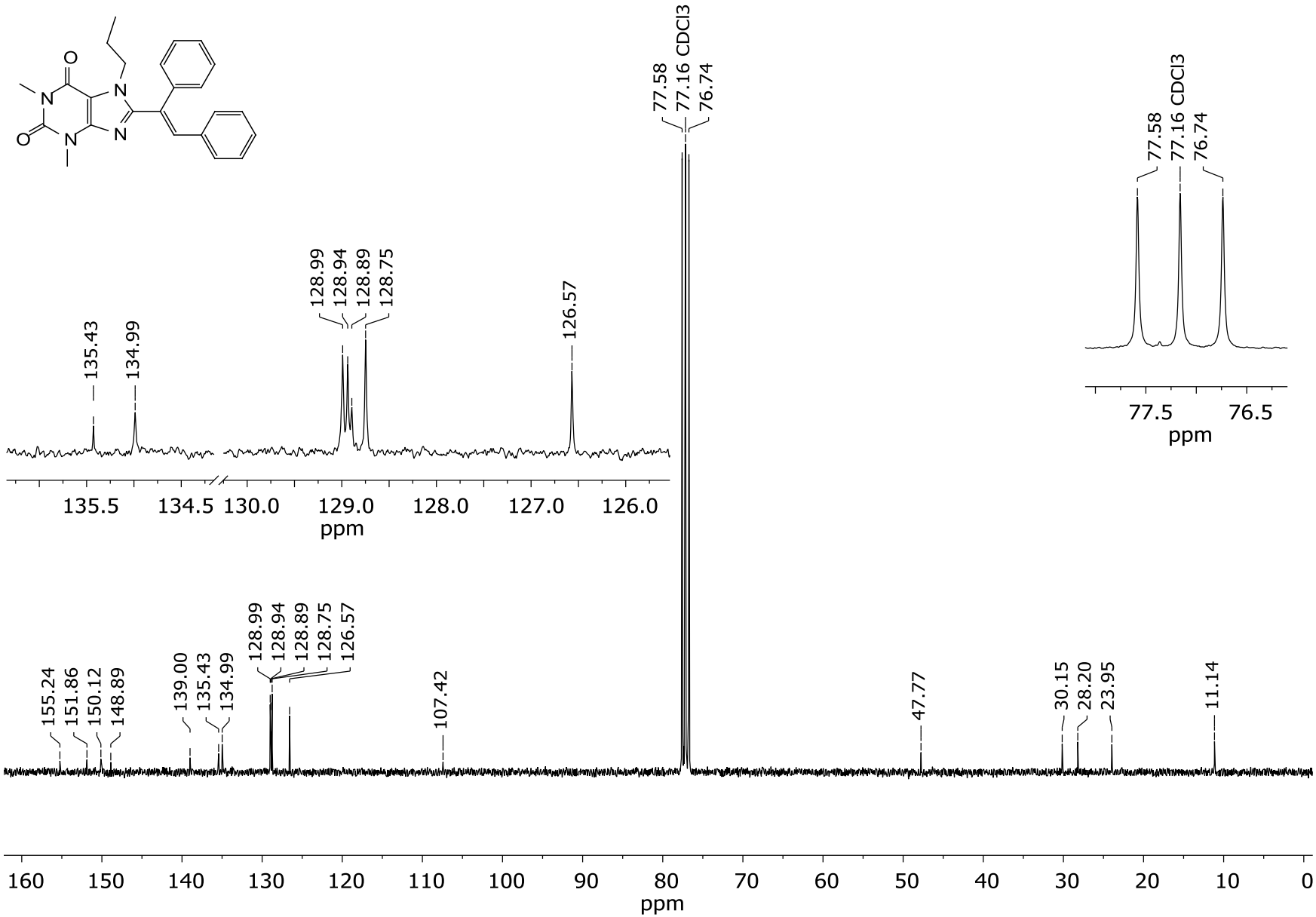


Figure S155. ^{13}C NMR spectrum of compound **6l *E*-isomer** ($CDCl_3$, 75 MHz)

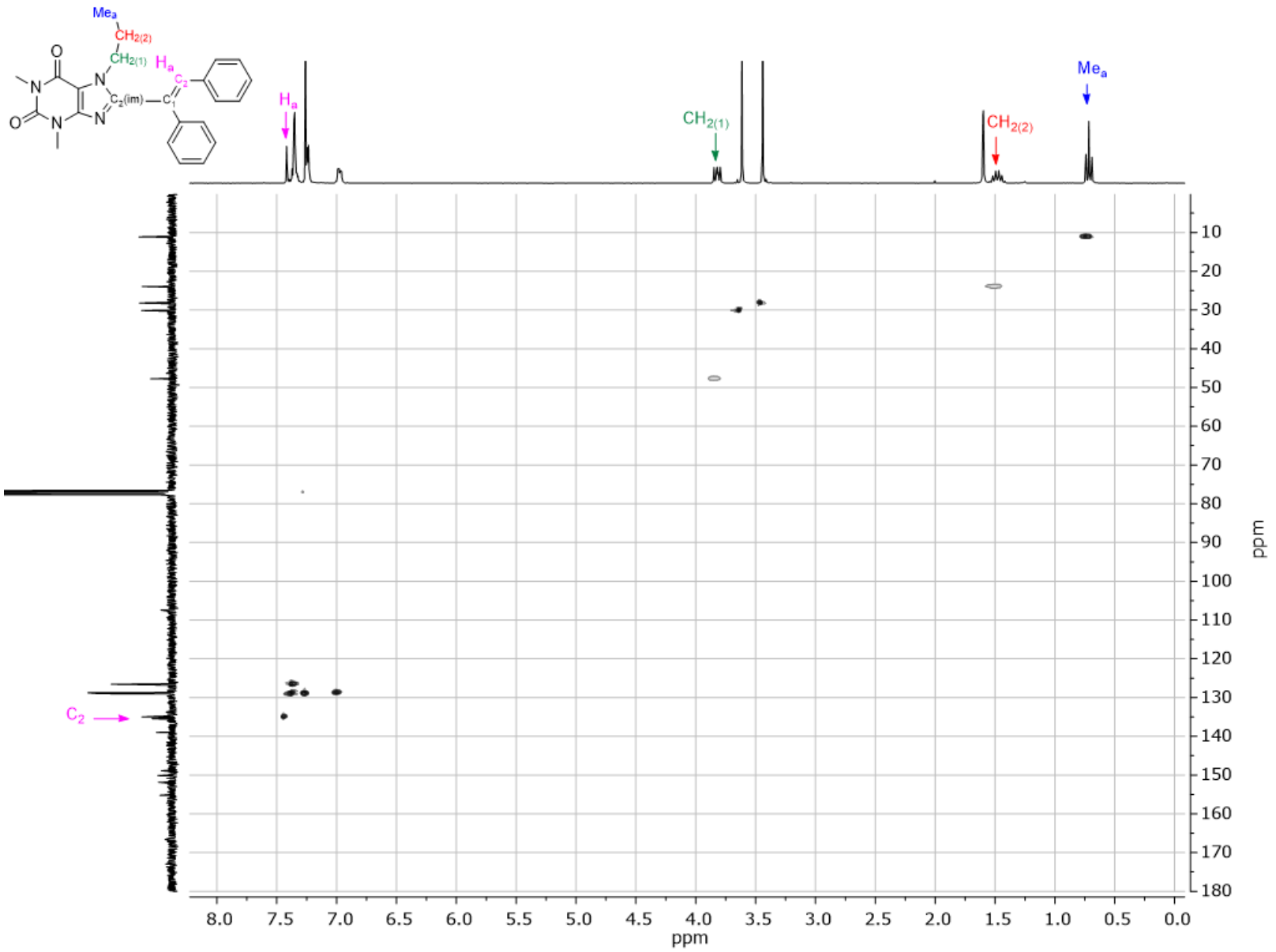


Figure S156. ^{1}H-^{13}C HSQC spectrum of compound **6l *E*-isomer** ($CDCl_3$)

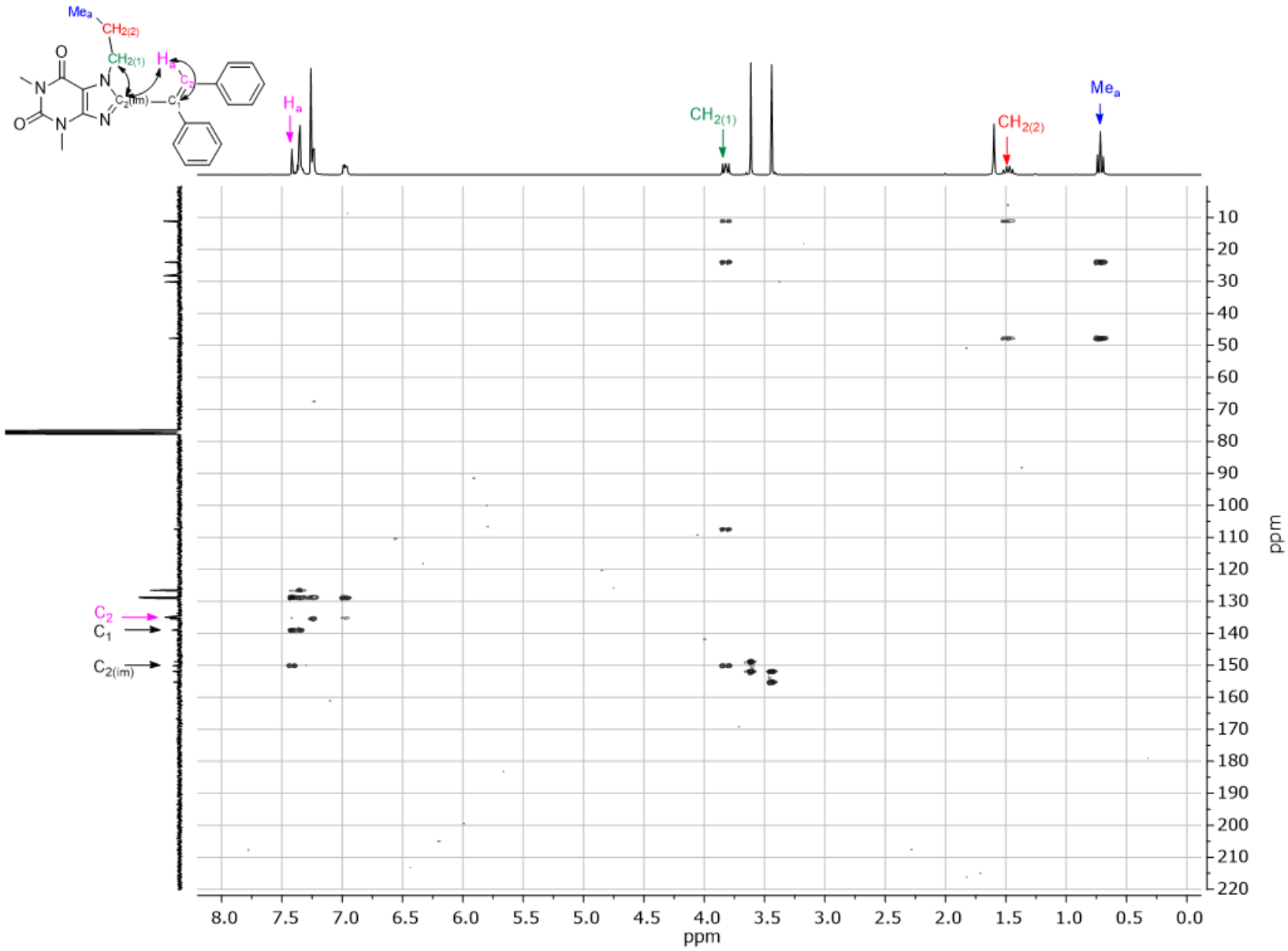


Figure S157. ^{1}H-^{13}C HMBC spectrum of compound **6l *E*-isomer** ($CDCl_3$)

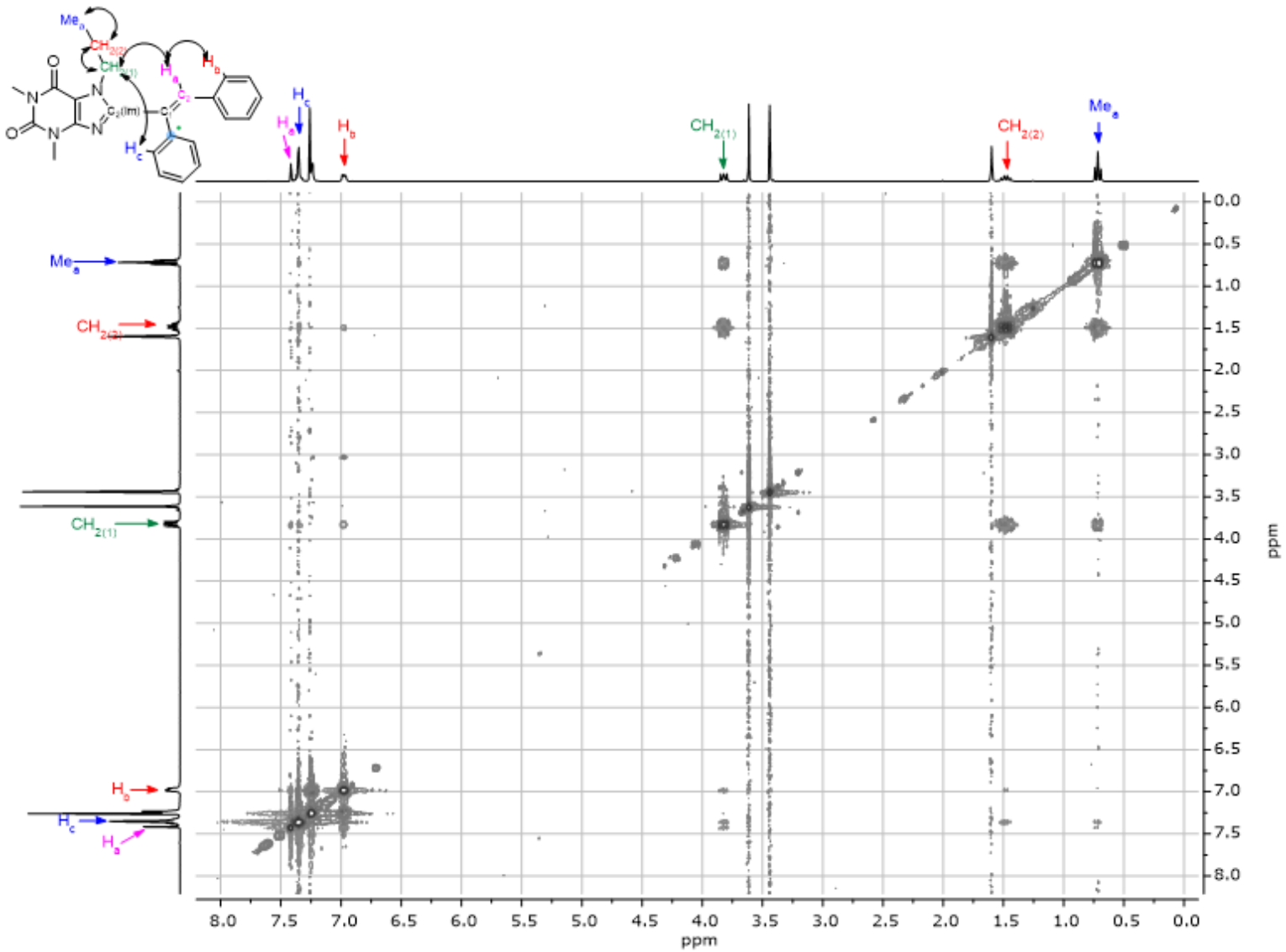


Figure S158. ^{1}H-^{1}H NOESY spectrum of compound **6l *E*-isomer** ($CDCl_3$)

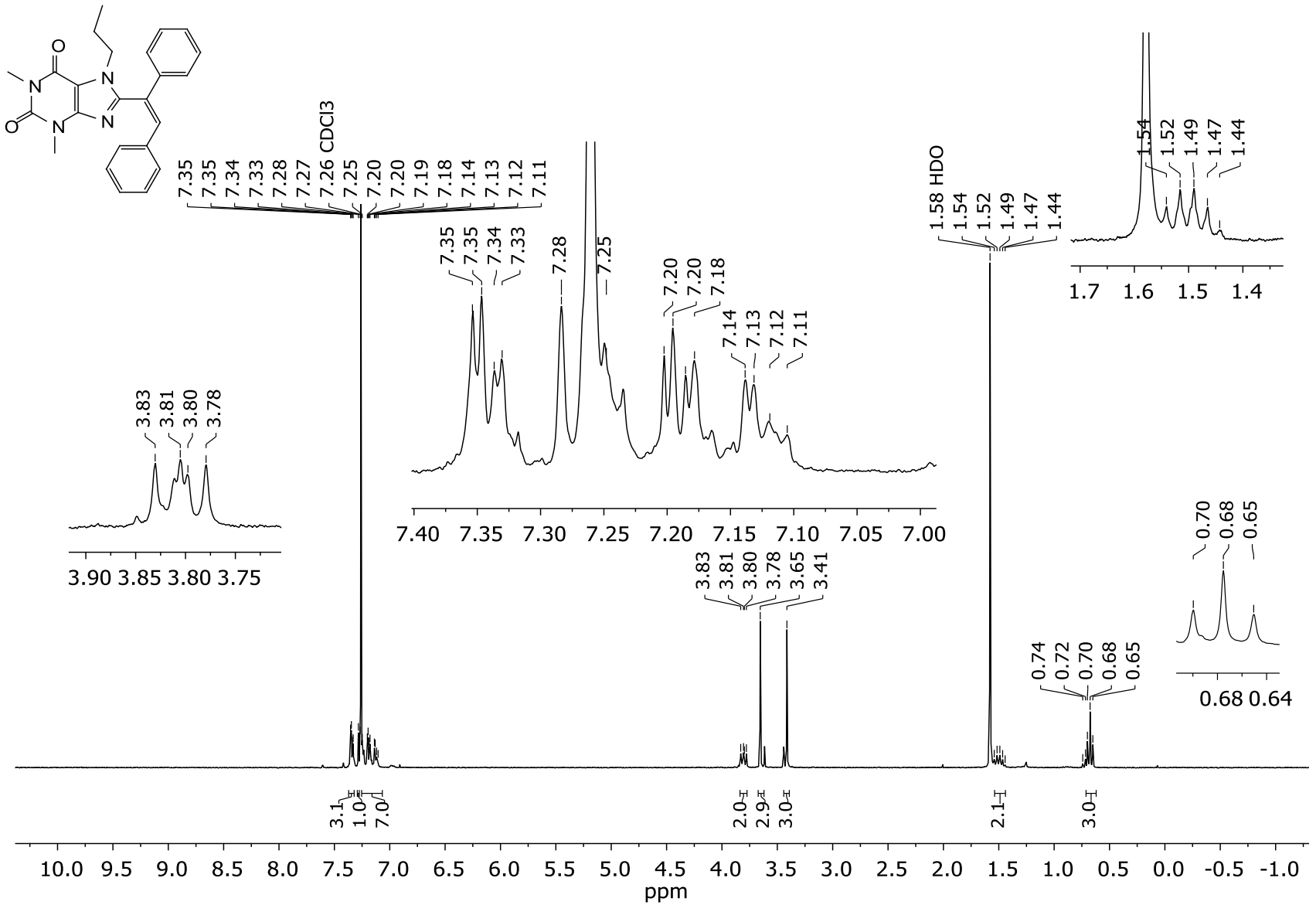


Figure S159. ^{1}H NMR spectrum of compound **6l *Z*-isomer** ($CDCl_3$, 300 MHz)

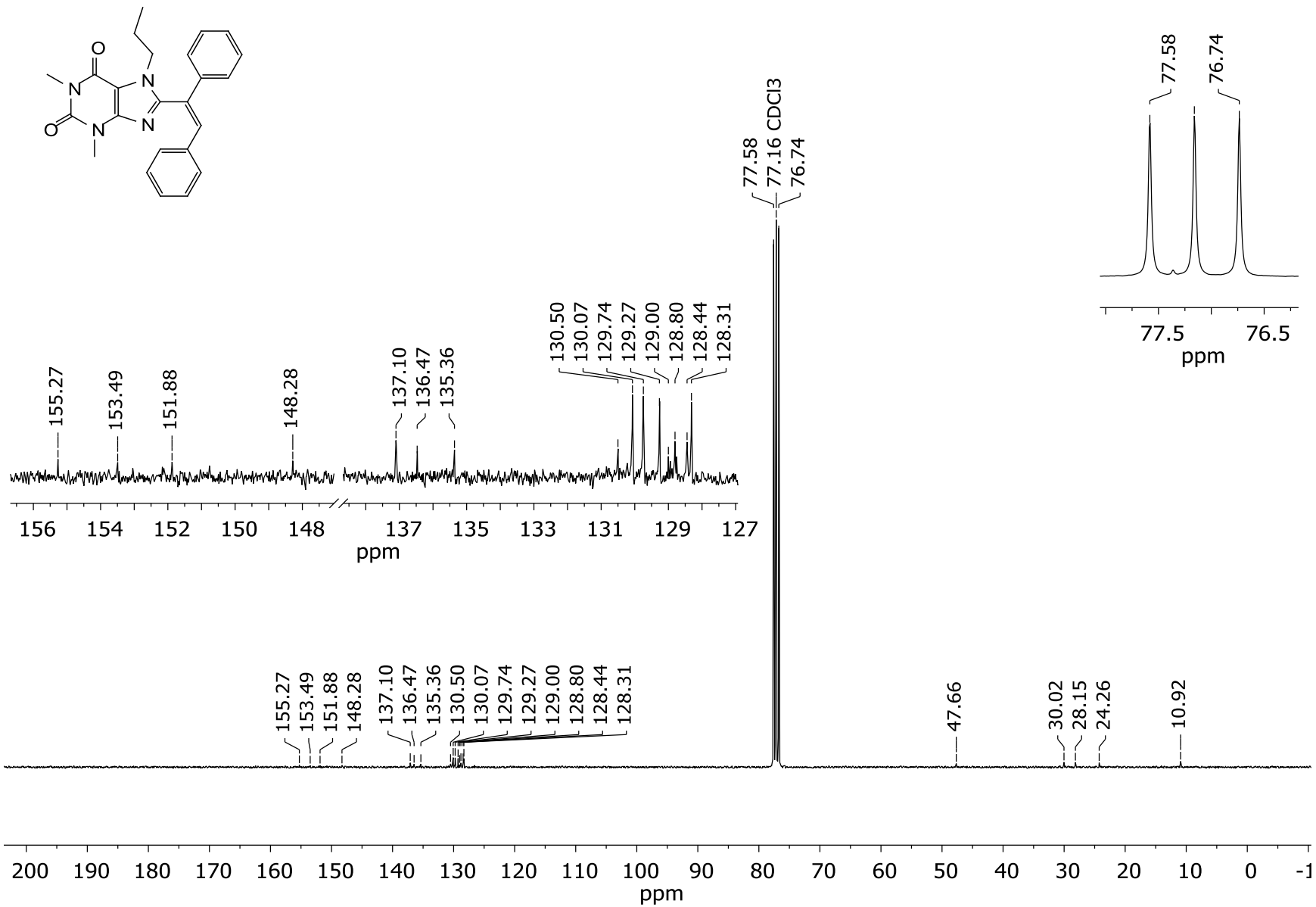


Figure S160. ^{13}C NMR spectrum of compound **6l *Z*-isomer** ($CDCl_3$, 75 MHz)

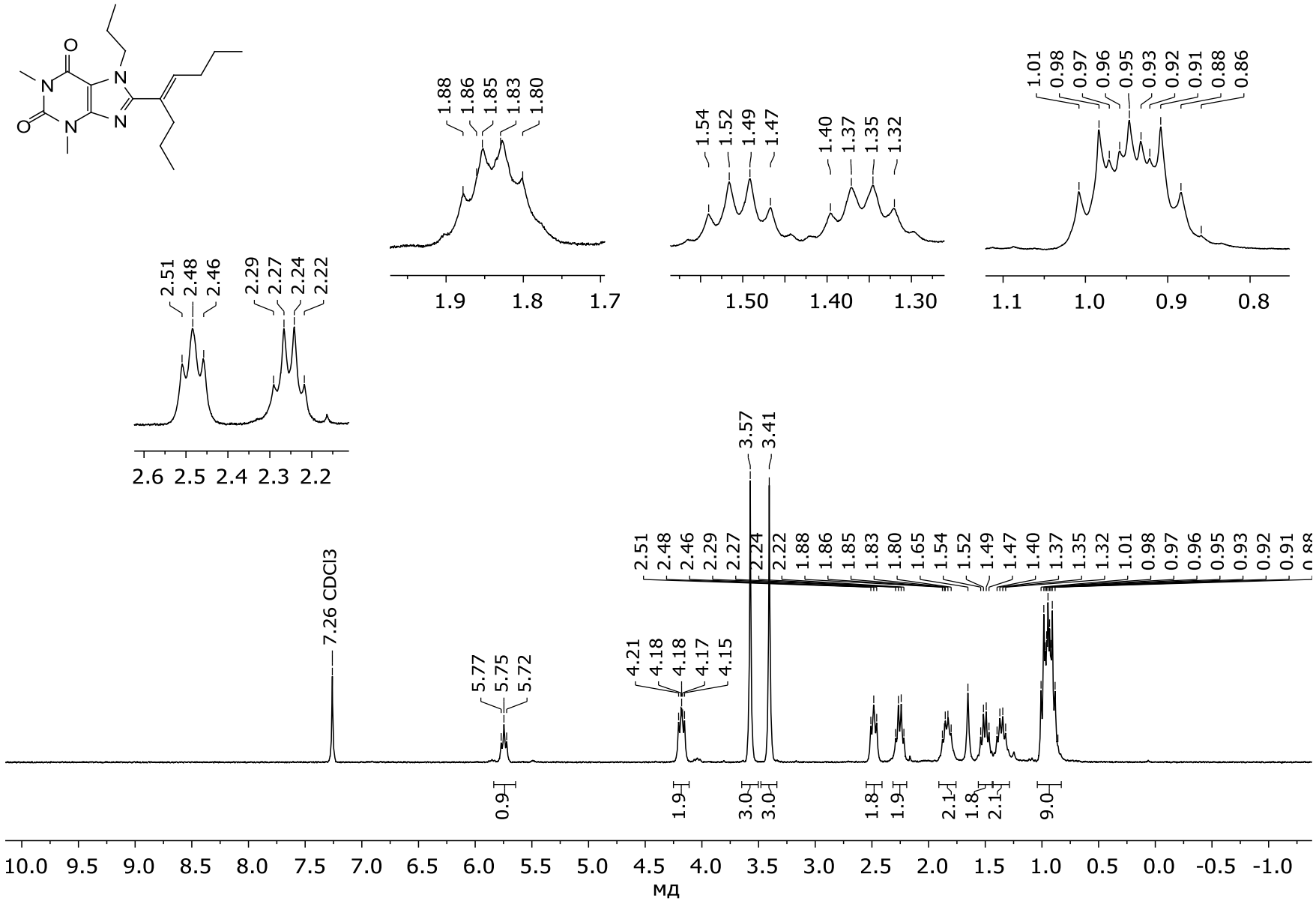


Figure S161. ^{1}H NMR spectrum of compound **6m** ($CDCl_3$, 300 MHz)

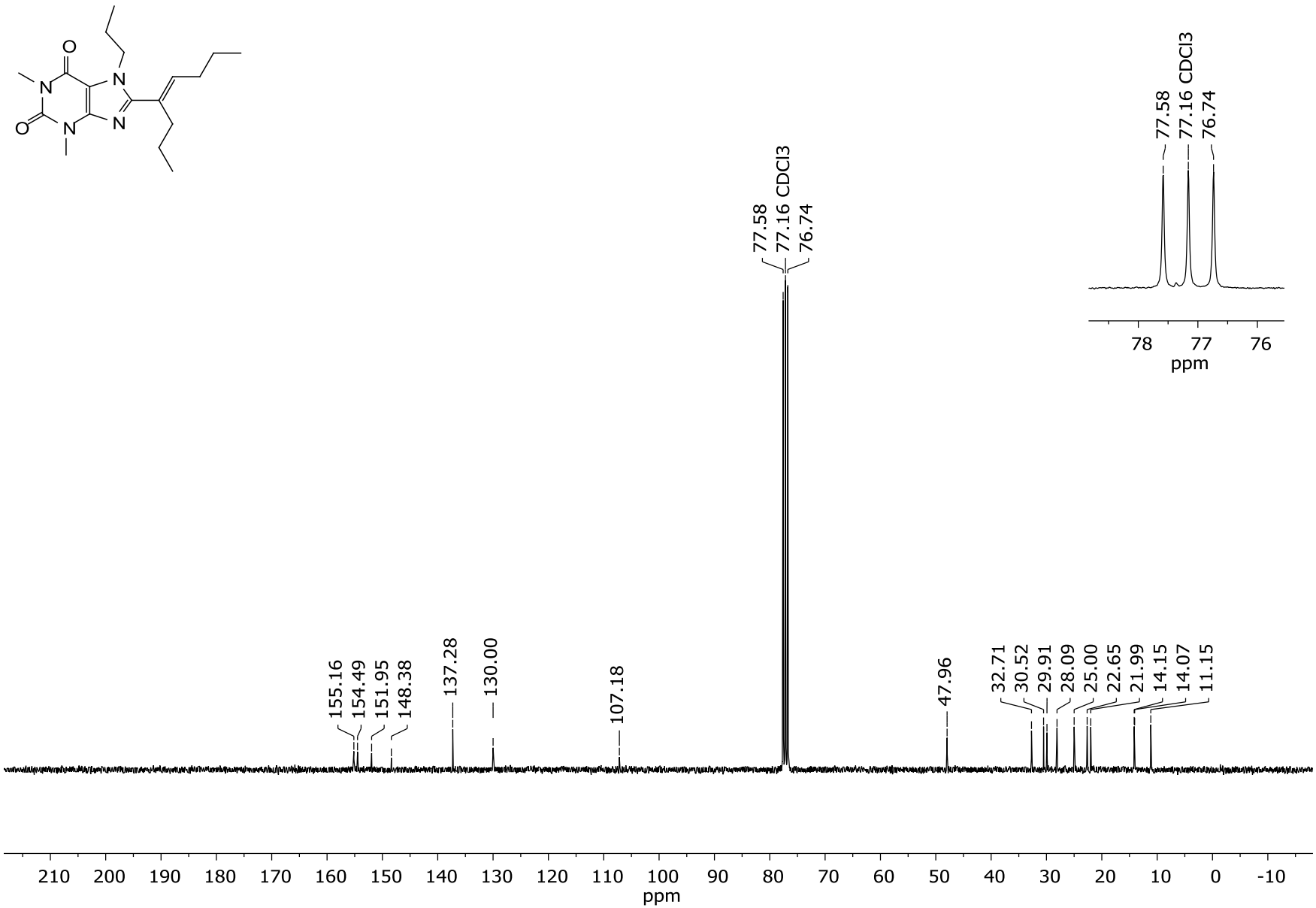


Figure S162. ^{13}C NMR spectrum of compound **6m** ($CDCl_3$, 75 MHz)

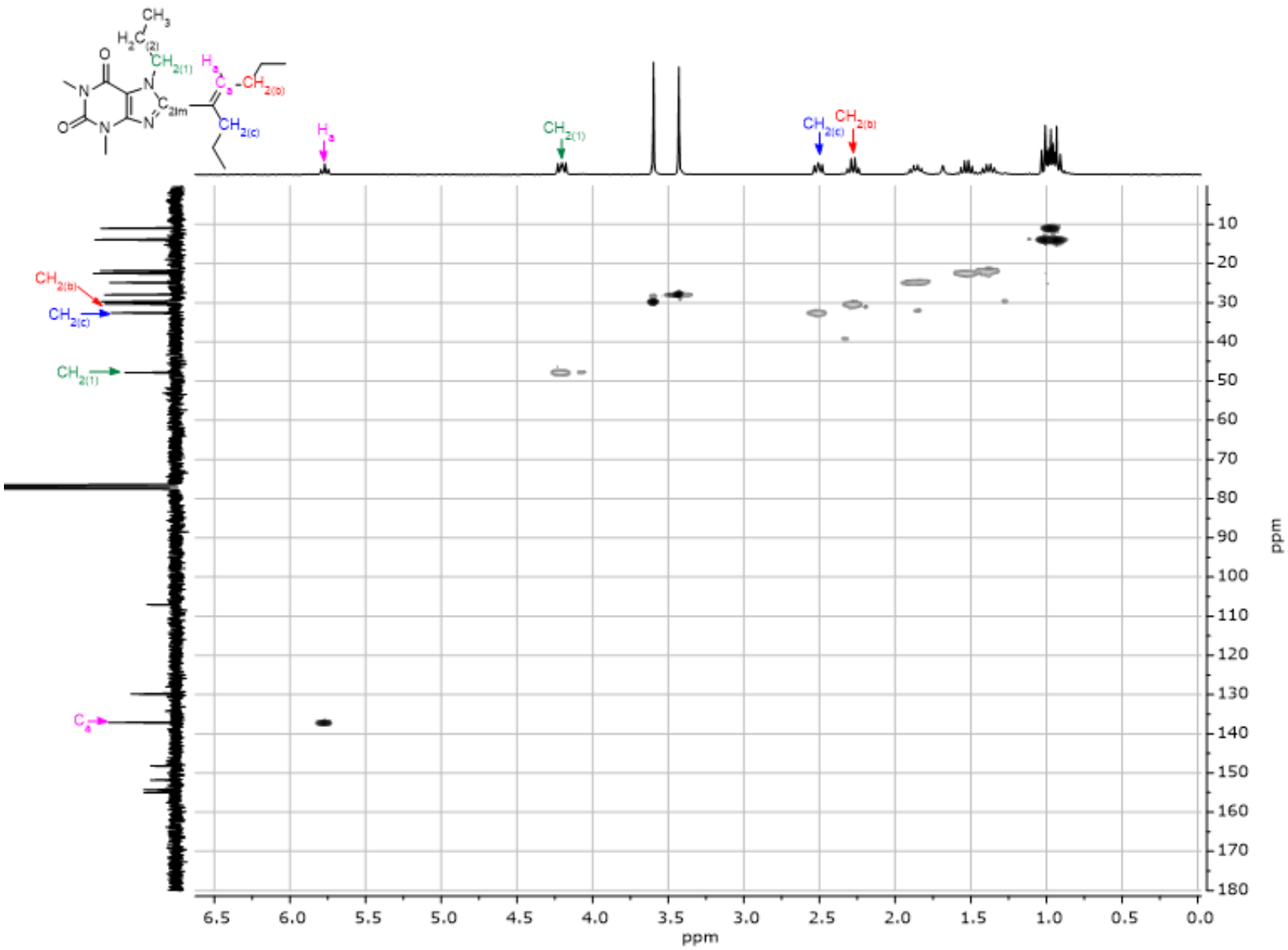


Figure S163. ^{1}H-^{13}C HSQC spectrum of compound **6m** ($CDCl_3$)

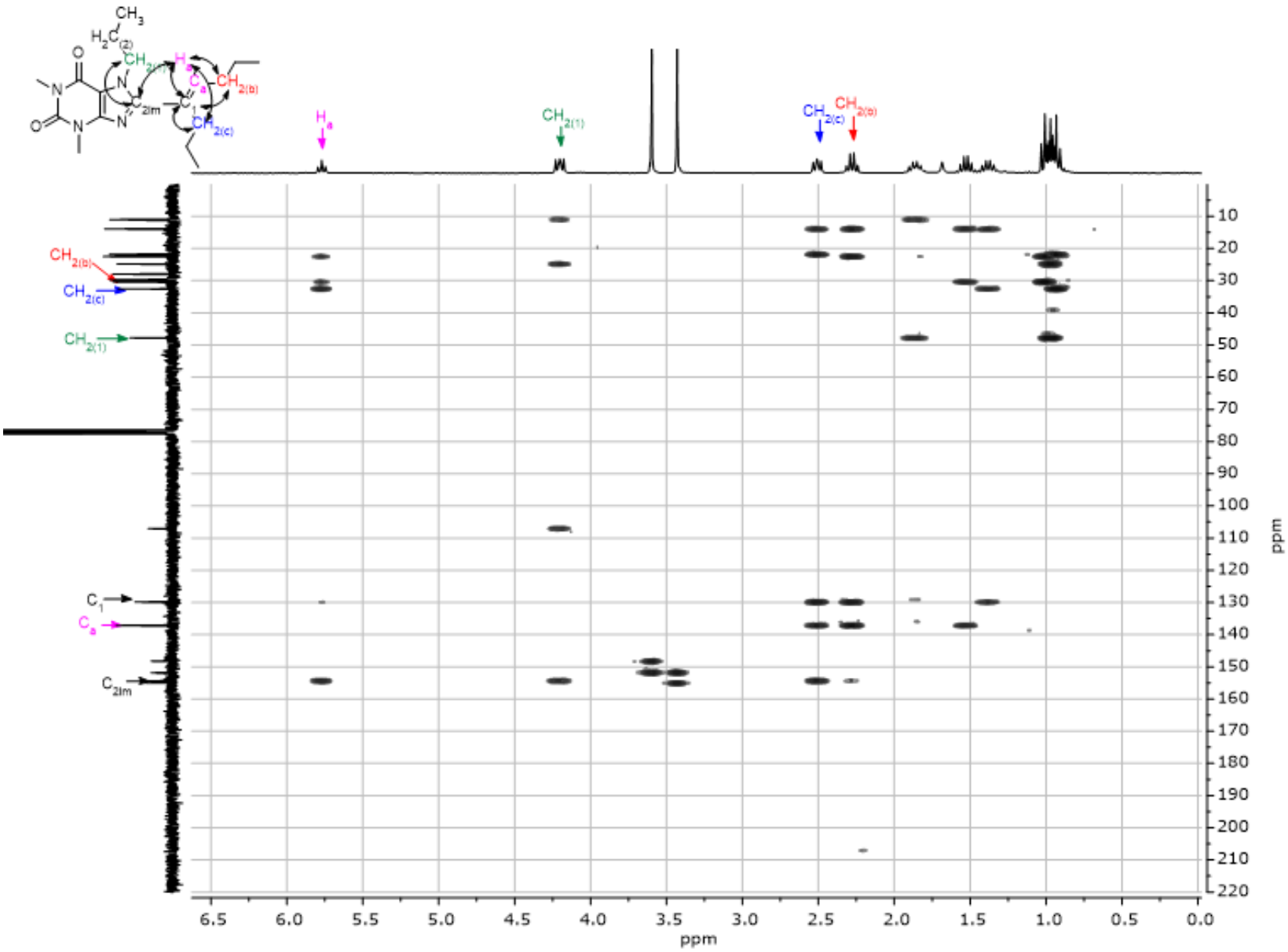


Figure S164. ^{1}H-^{13}C HMBC spectrum of compound **6m** ($CDCl_3$)

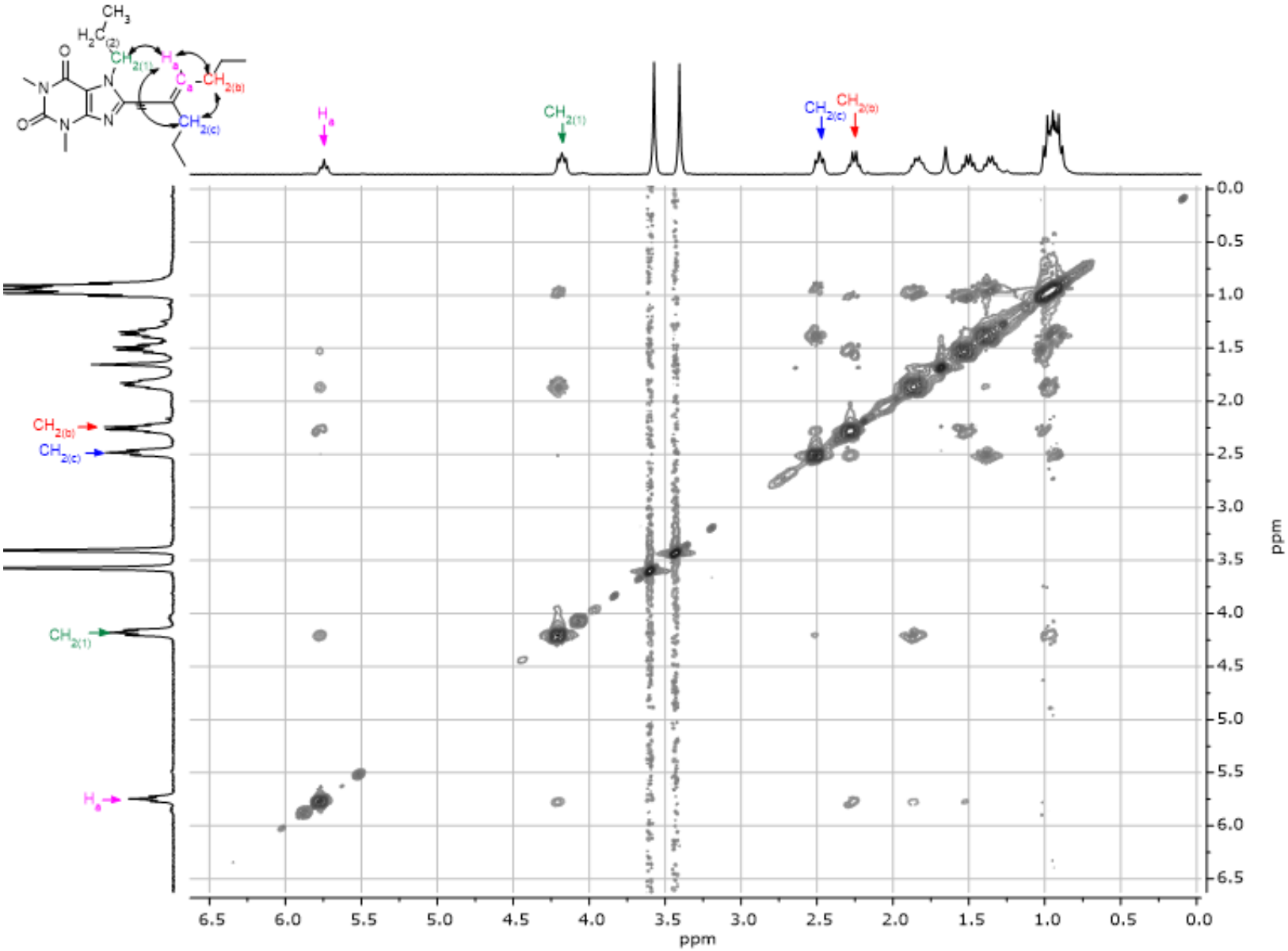


Figure S165. ^{1}H-^{1}H NOESY spectrum of compound **6m** ($CDCl_3$)

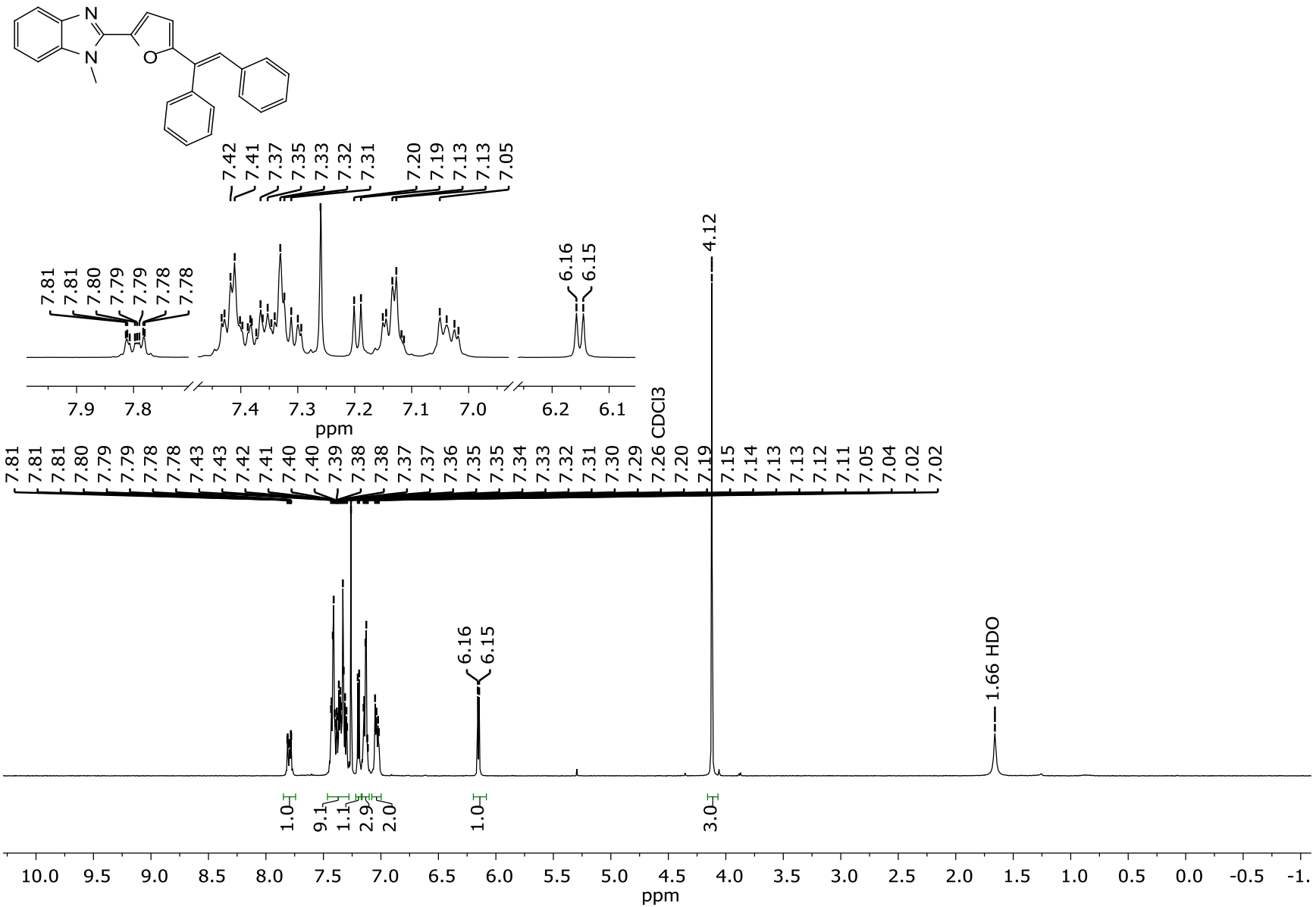


Figure S166. ^{1}H NMR spectrum of compound **6n** ($CDCl_3$, 300 MHz)

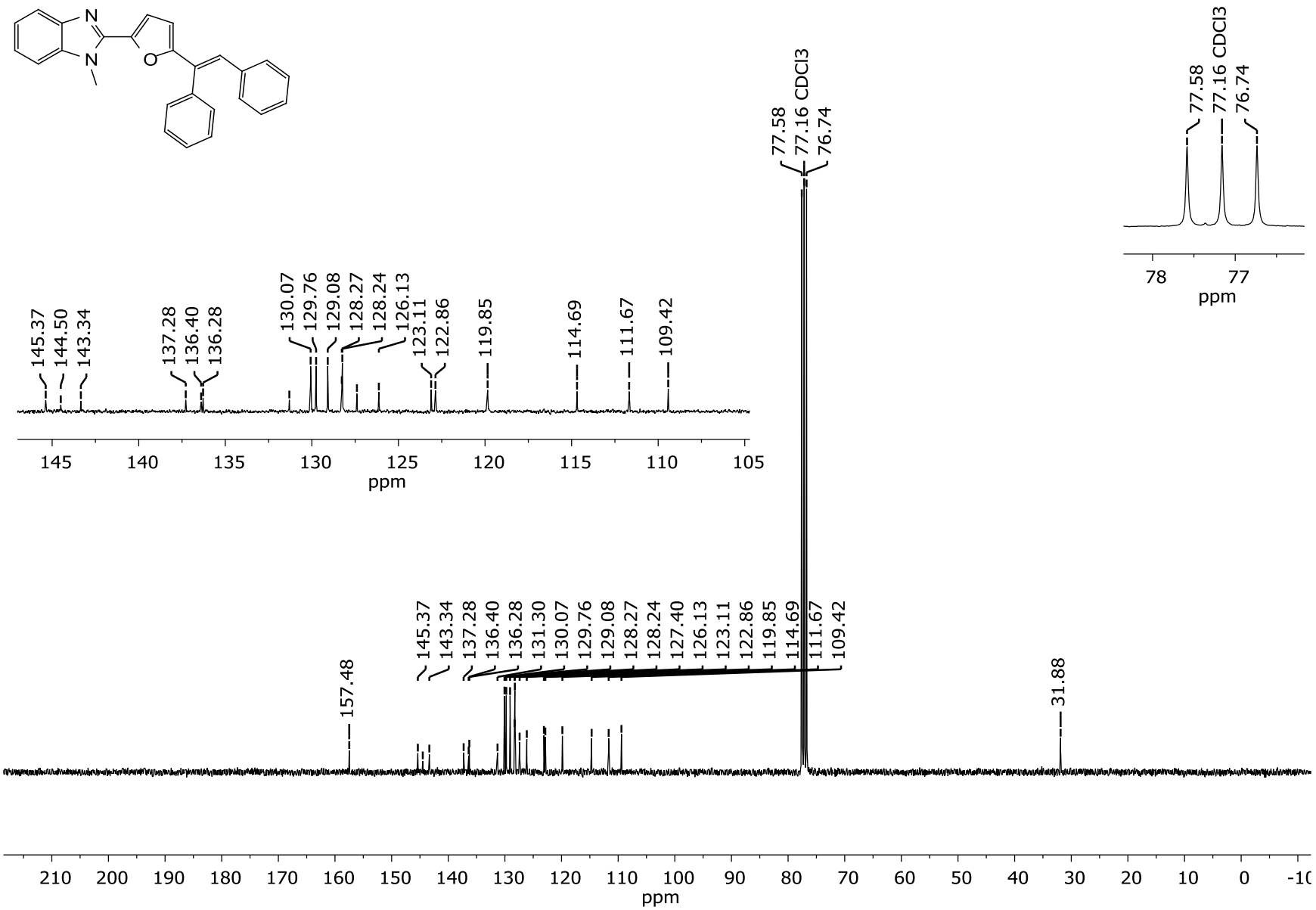


Figure S167. ^{13}C NMR spectrum of compound **6n** ($CDCl_3$, 75 MHz)

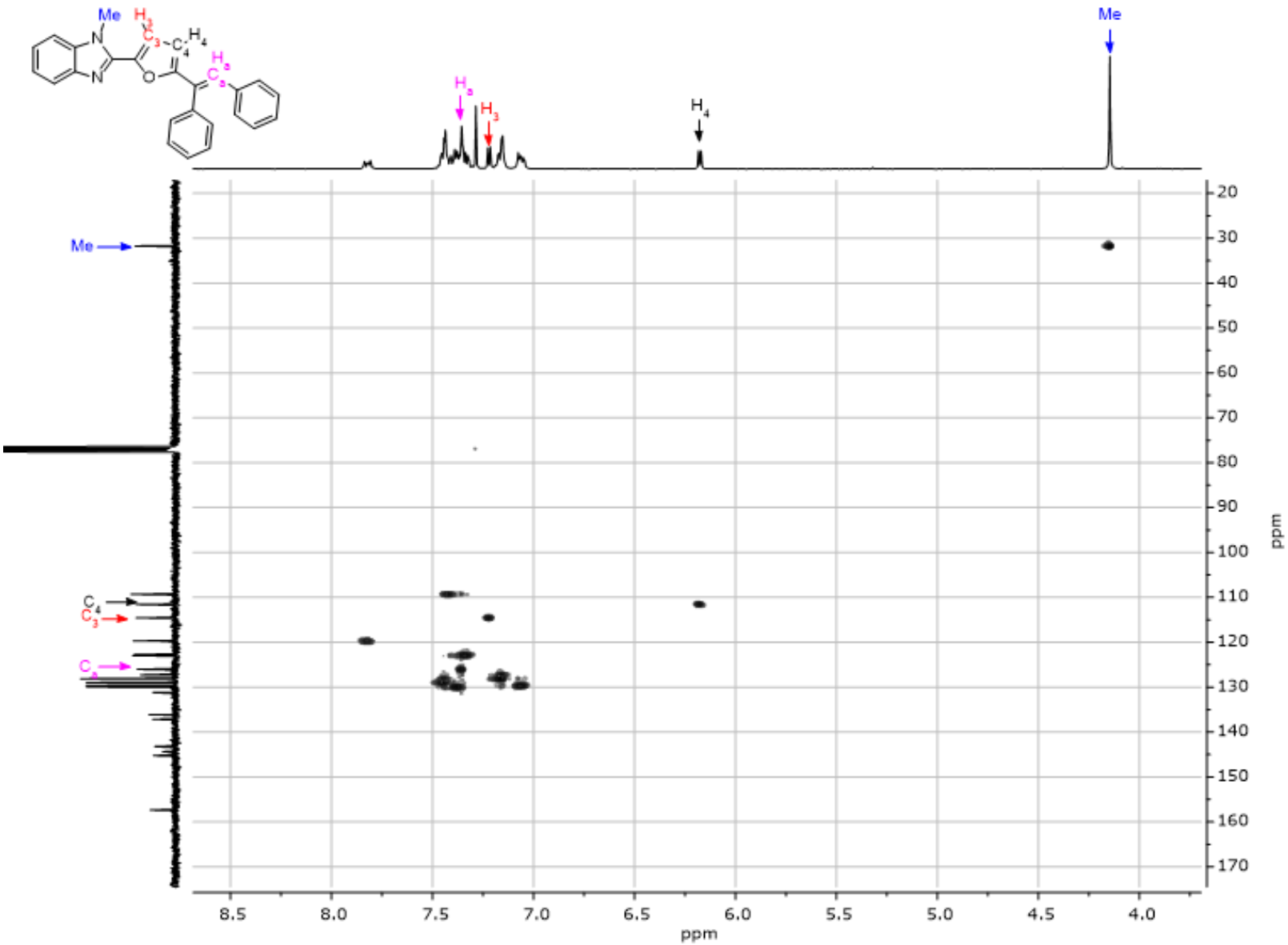


Figure S168. ^{1}H-^{13}C HSQC spectrum of compound **6n** ($CDCl_3$)

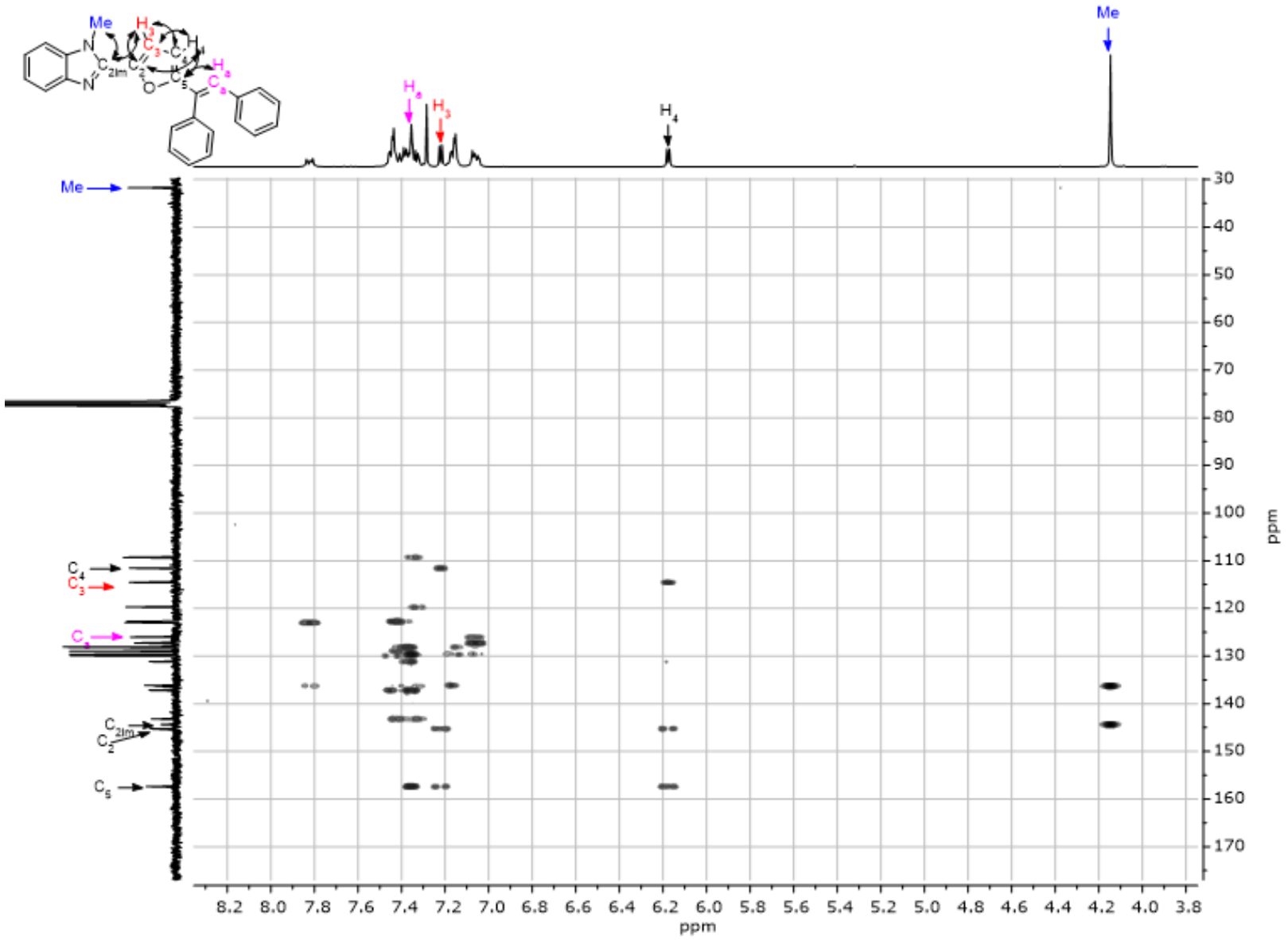


Figure S169. ^{1}H-^{13}C HMBC spectrum of compound **6n** ($CDCl_3$)

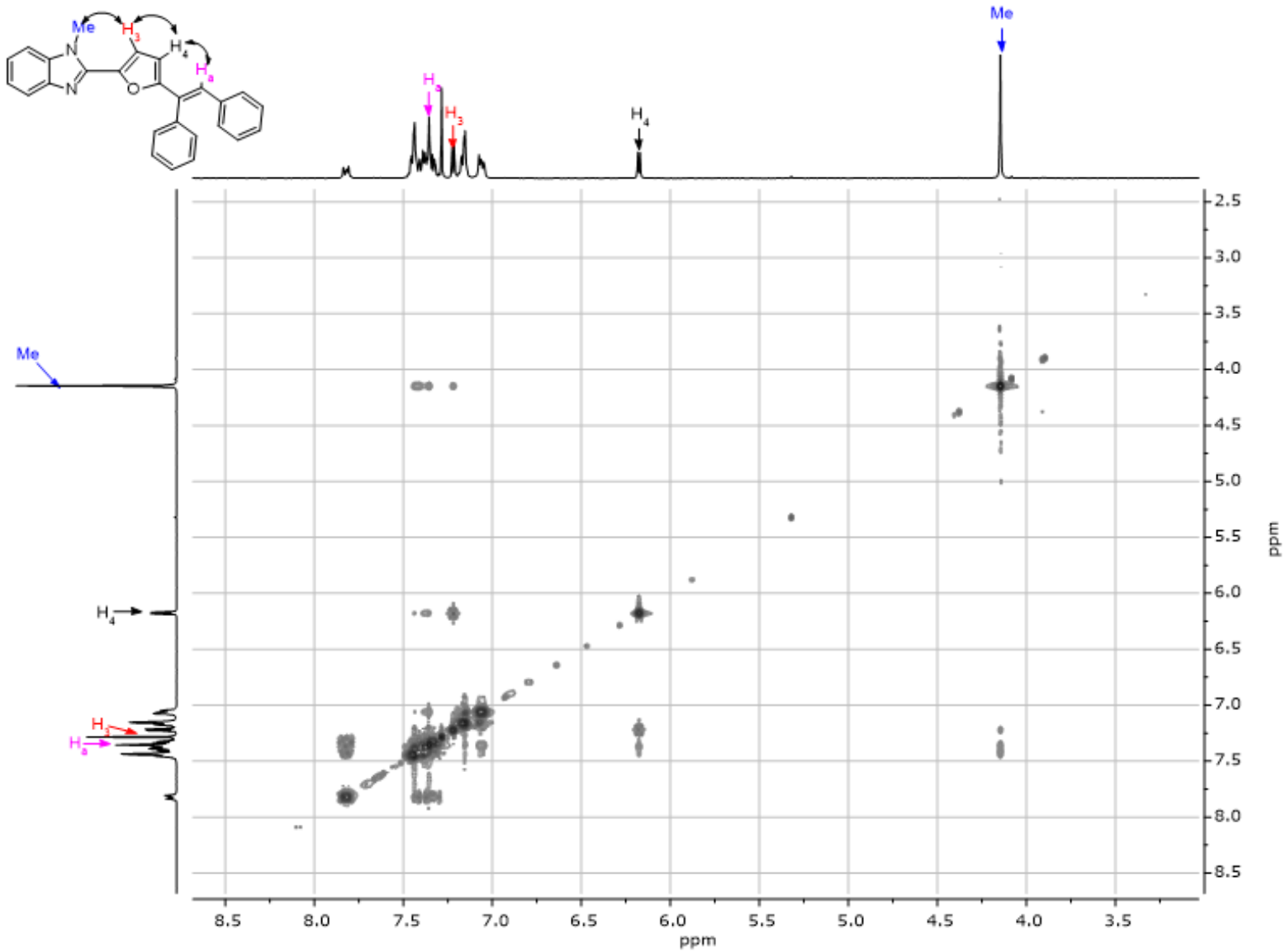


Figure S170. ^{1}H-^{1}H NOESY spectrum of compound **6n** ($CDCl_3$)

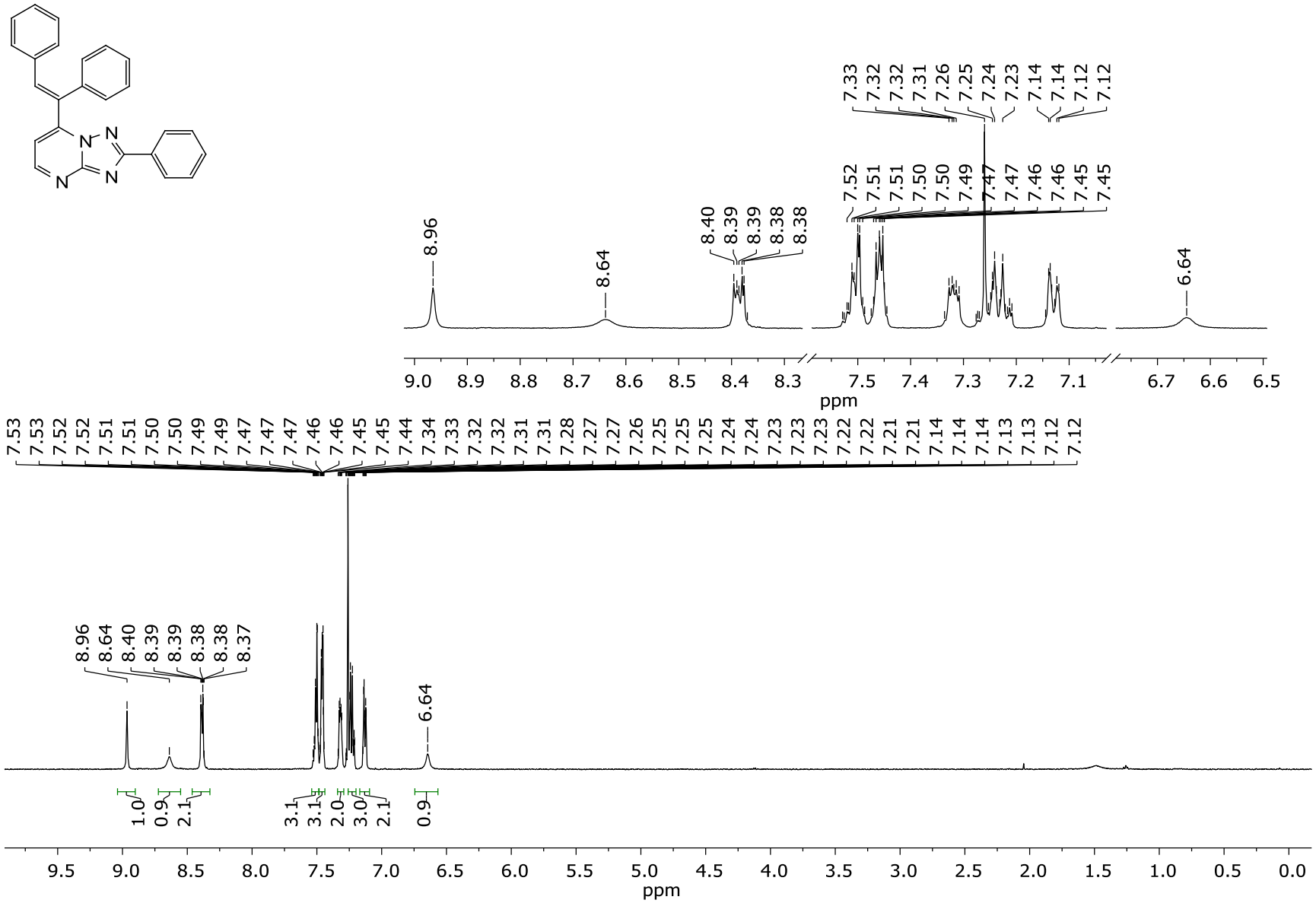


Figure S171. ^{1}H NMR spectrum of compound **6o** ($CDCl_3$, 500 MHz)

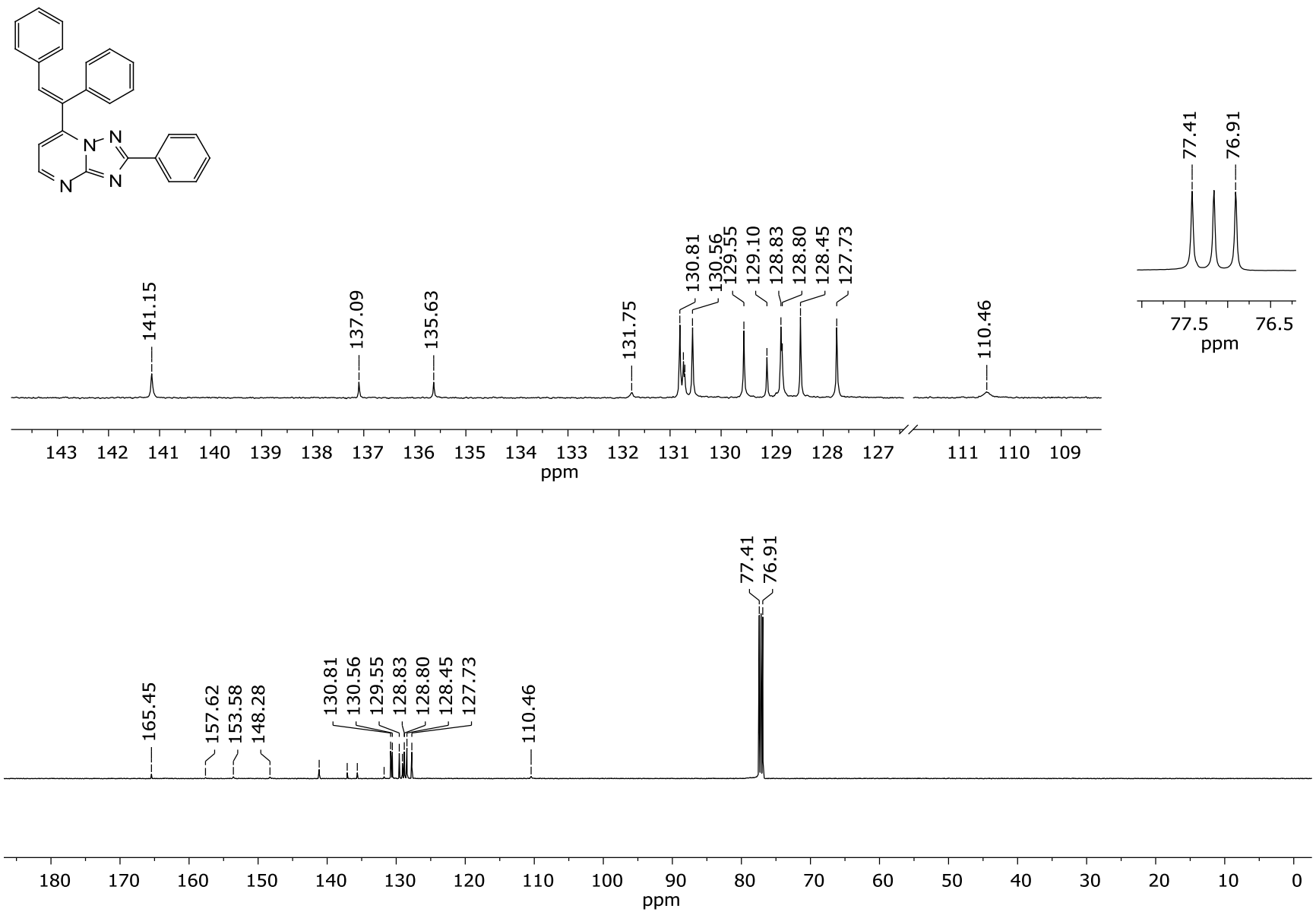


Figure S172. ^{13}C NMR spectrum of compound **6o** ($CDCl_3$, 125 MHz)

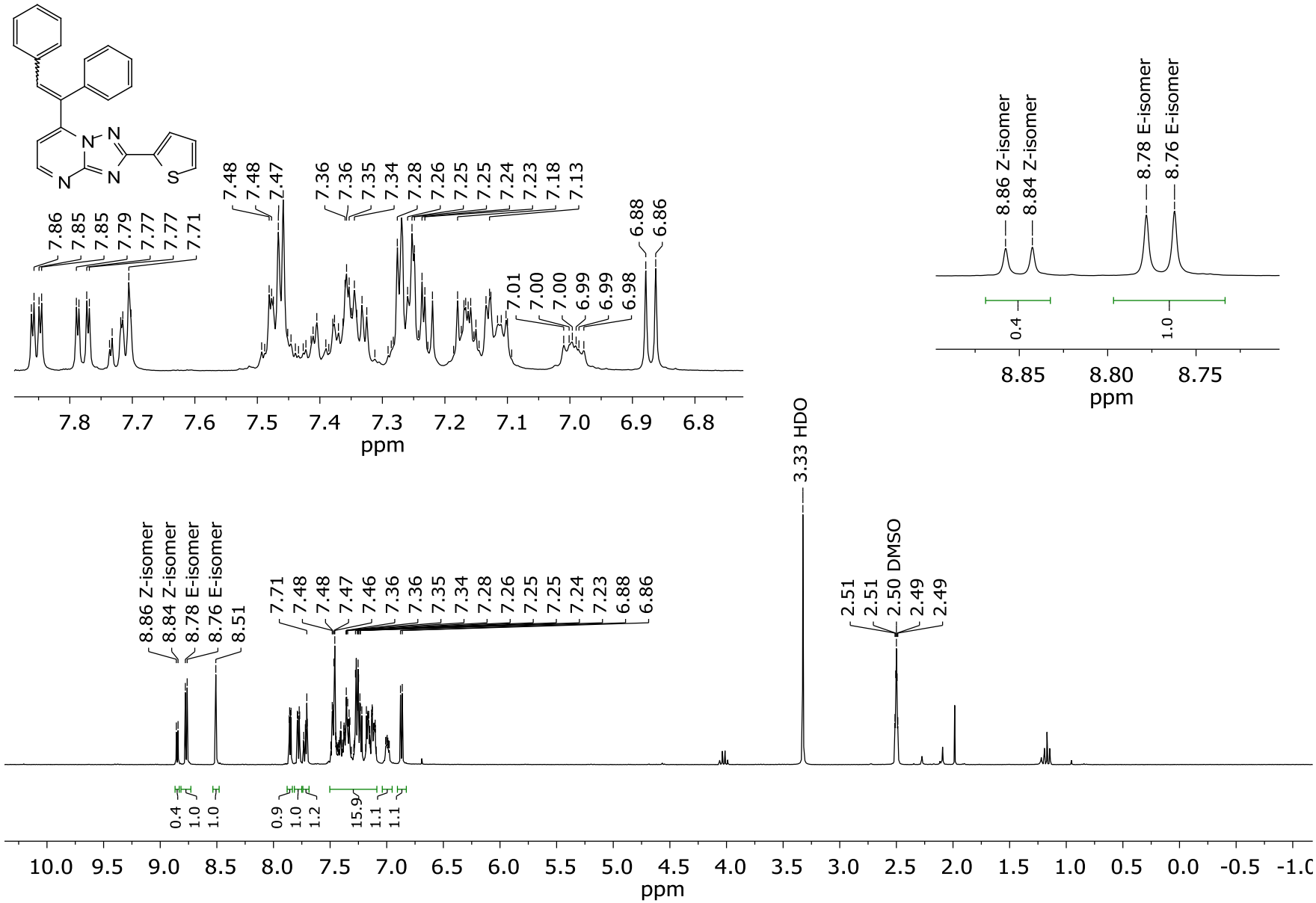


Figure S173. ^{1}H NMR spectrum of compound **6p *E+Z*** isomers (DMSO-d_6, 500 MHz)

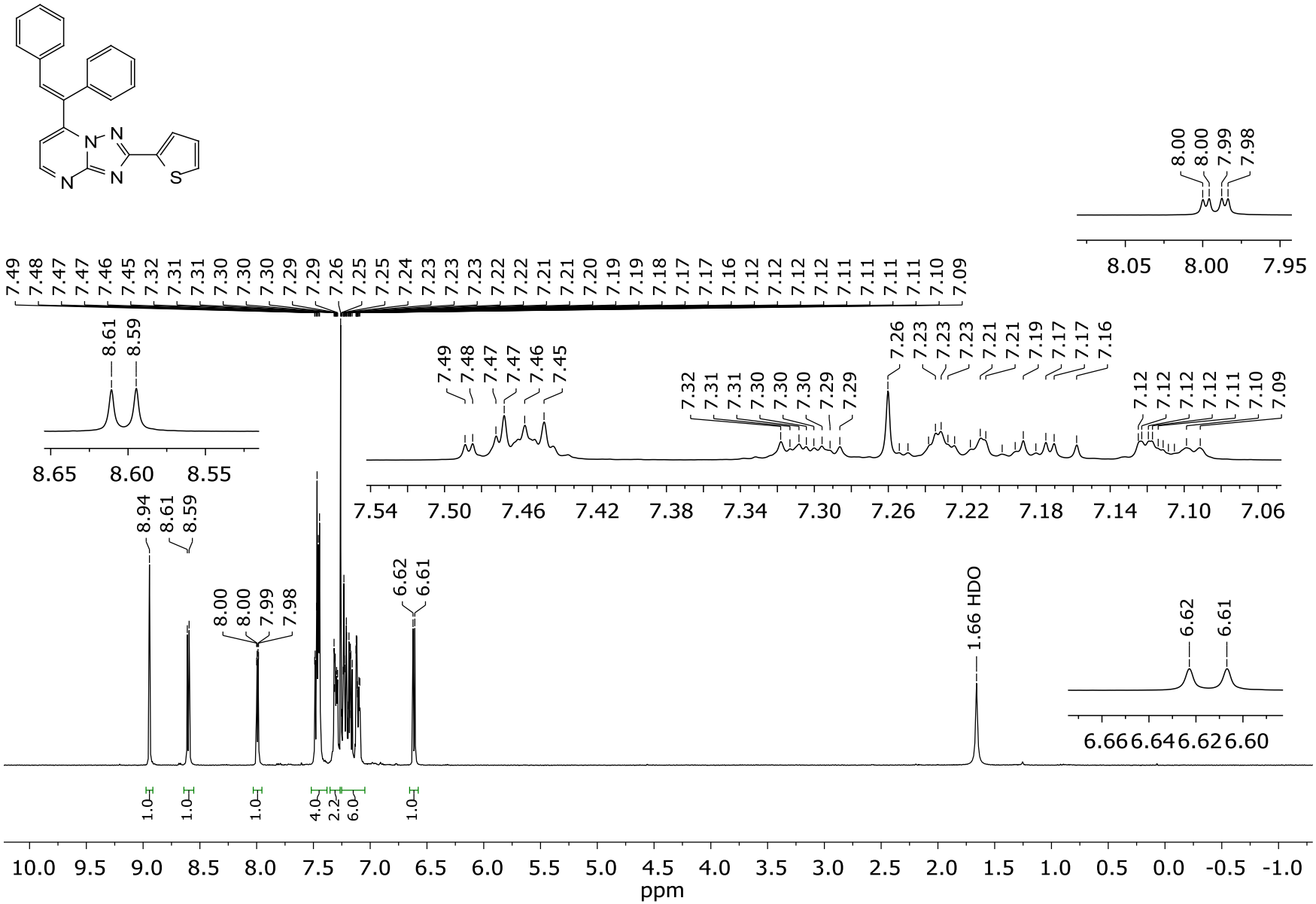


Figure S174. ^{1}H NMR spectrum of compound **6p *E*-isomer** ($CDCl_3$, 300 MHz)

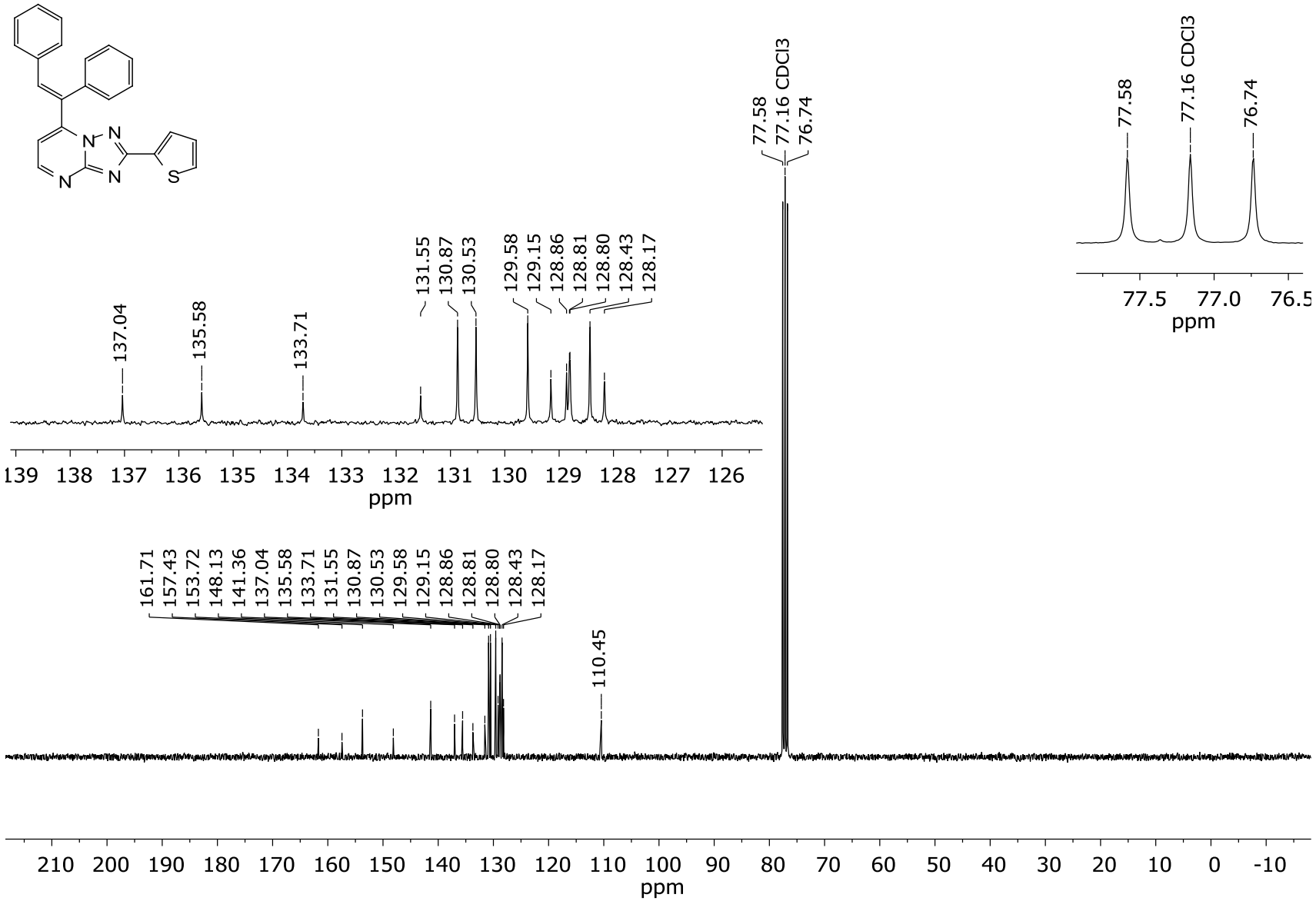


Figure S175. ^{13}C NMR spectrum of compound **6p *Z*-isomer** ($CDCl_3$, 75 MHz)

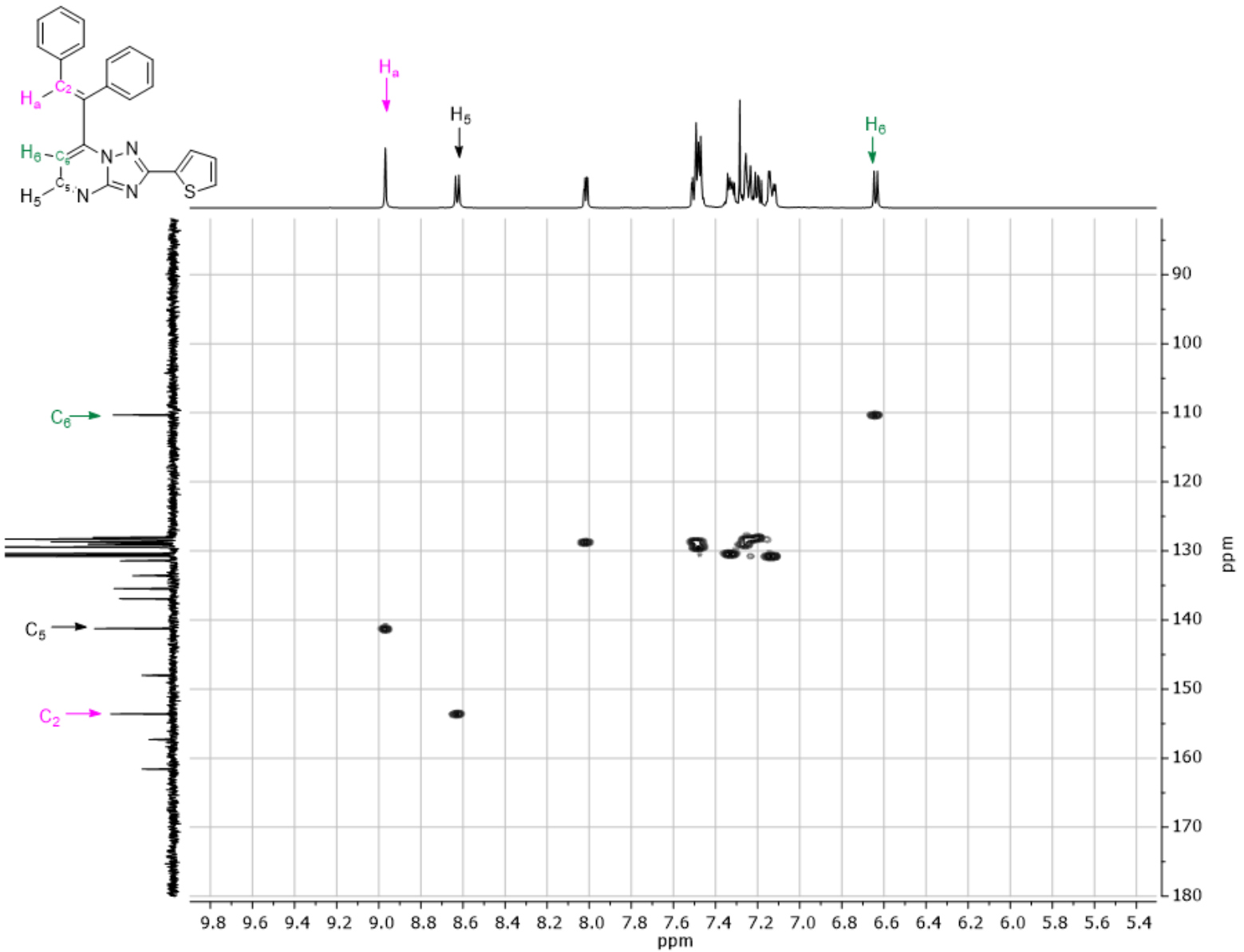


Figure S176. ^{1}H-^{13}C HSQC spectrum of compound **6p *Z*-isomer** ($CDCl_3$)

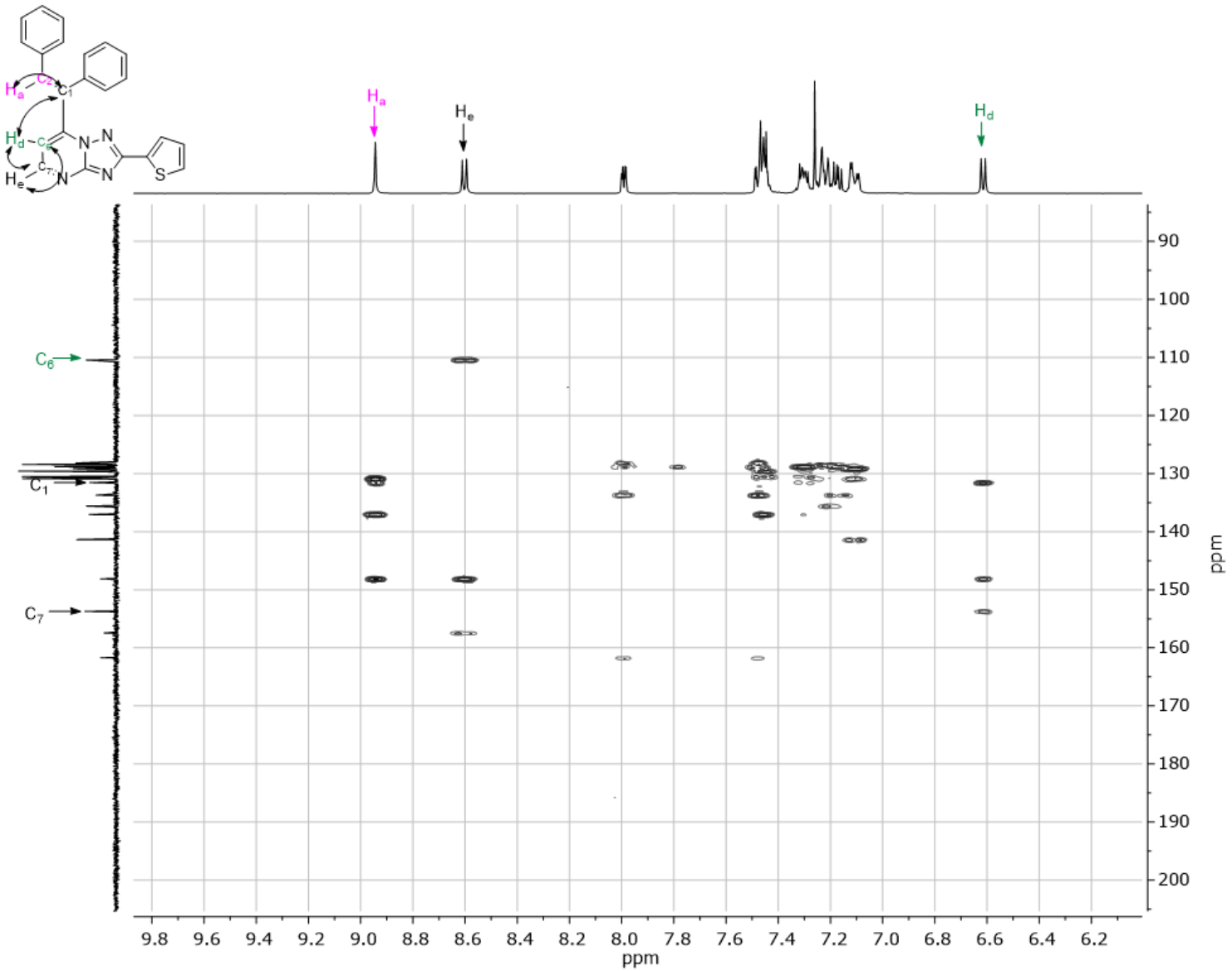


Figure S177. ^{1}H-^{13}C HMBC spectrum of compound **6p *Z*-isomer** ($CDCl_3$)

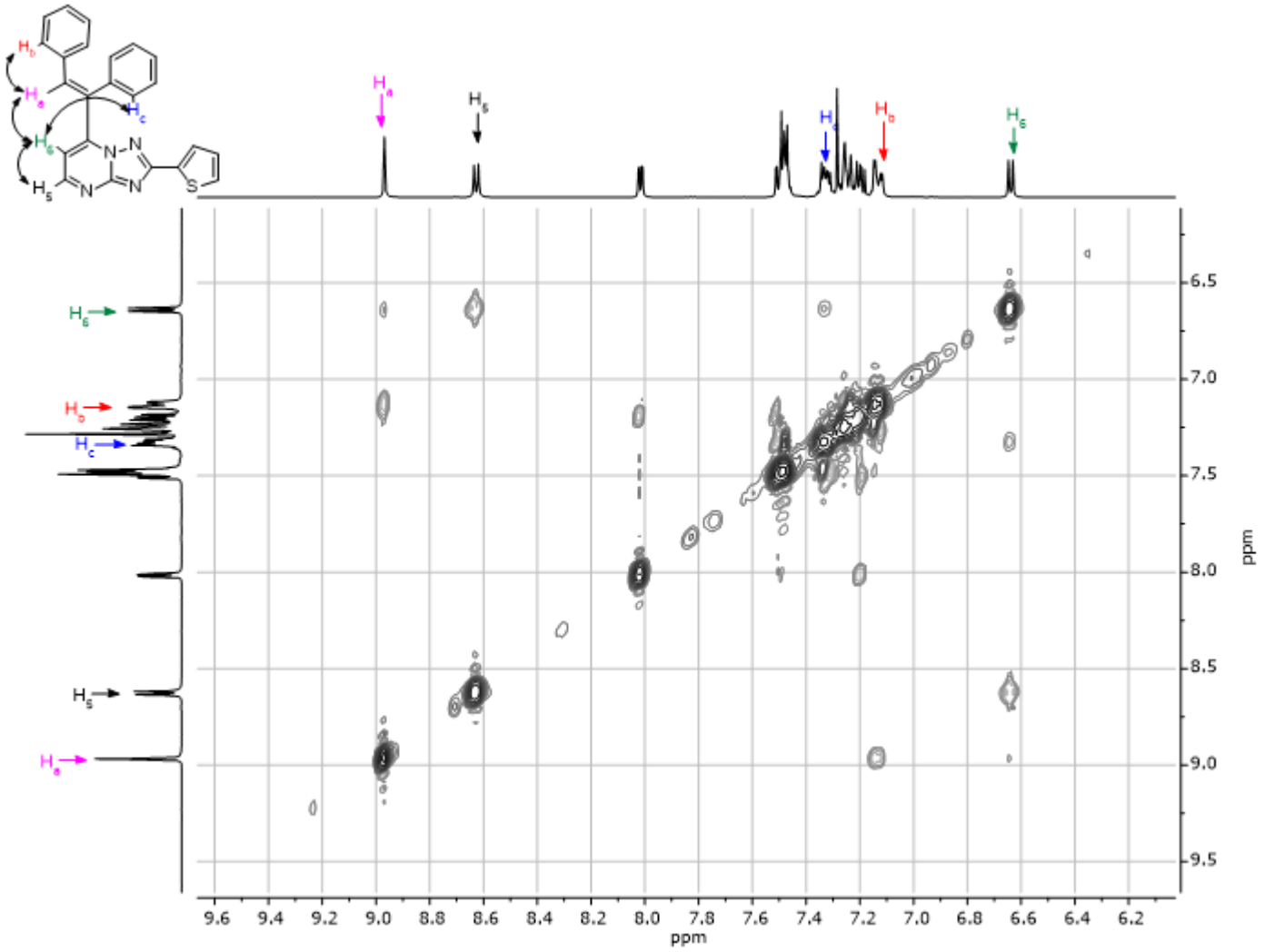


Figure S178. ^{1}H-^{1}H NOESY spectrum of compound **6p *Z*-isomer** ($CDCl_3$)

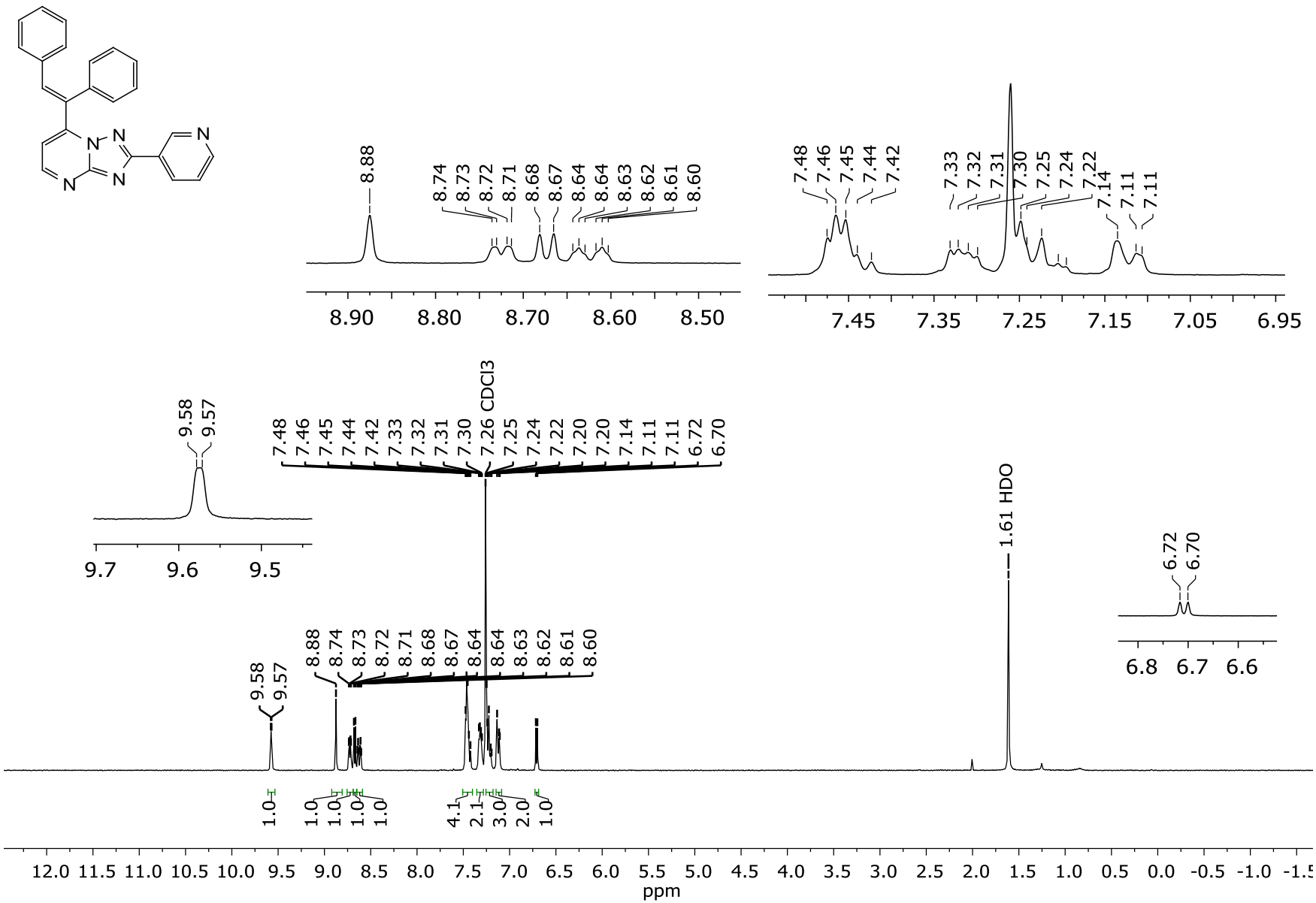


Figure S179. ^{1}H NMR spectrum of compound **6q** ($CDCl_3$, 300 MHz)

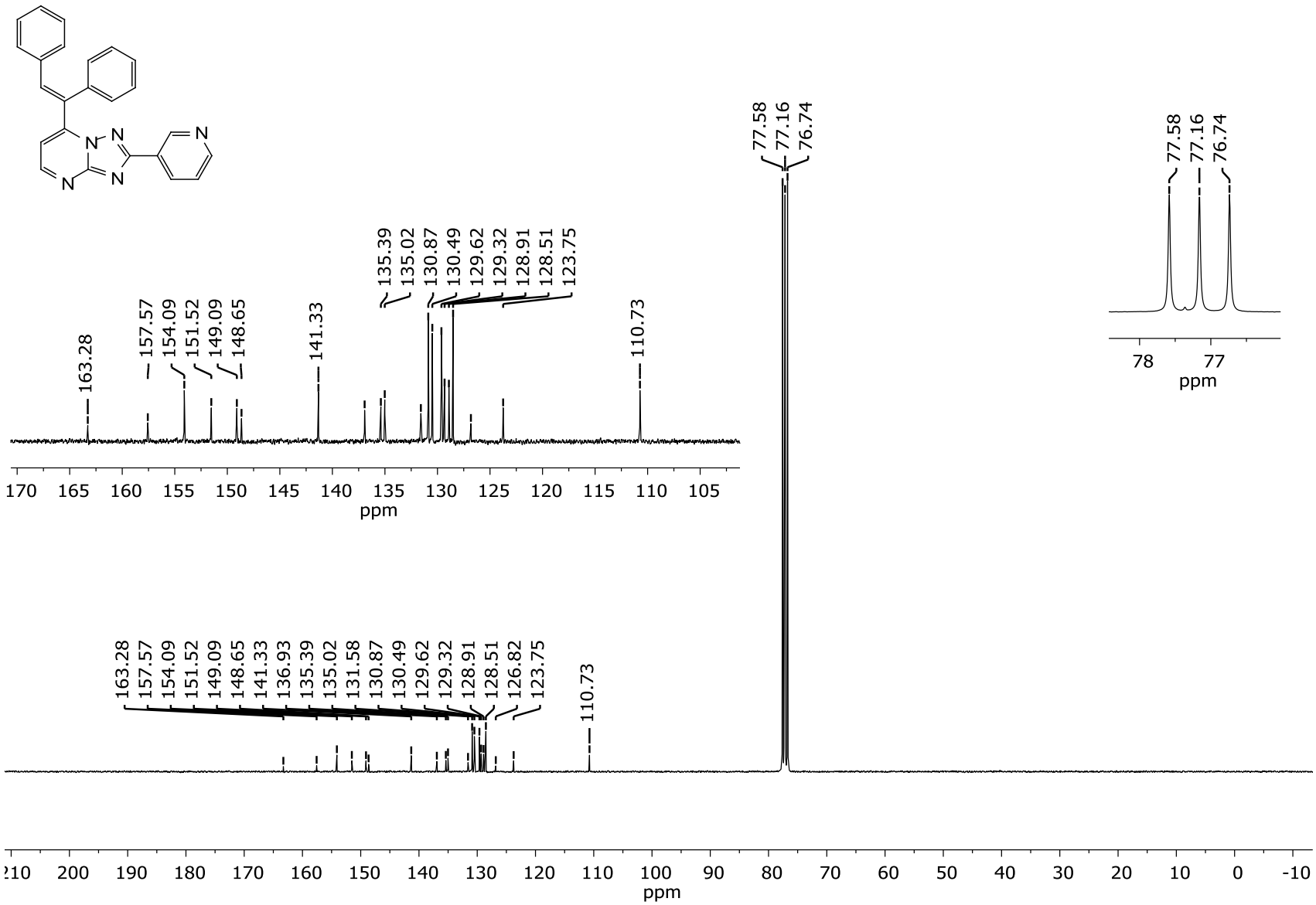


Figure S180. ^{1}H NMR spectrum of compound **6q** ($CDCl_3$, 75 MHz)

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