Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic supporting information for the paper titled:

Engineering organic semiconducting solids. Multicomponent access to crystalline 3-(4-aryl-1,2,3-triazolyl)coumarins.

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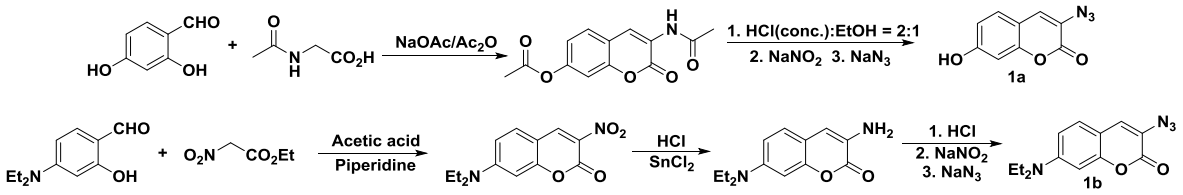
Reaction optimization experiments

Entry	CuI (mol %)	Piperidine (mol %)	Time (h)	Yield[b] (%)
1	0.1	----	24	No reaction
2	----	1.25	24	No reaction
3	0.05	0.6	4	32
4	0.1	1.25	4	89
5	0.1	2.5	4	84
6	0.2	1.25	4	80

Table S1. Catalyst screening for the synthesis of **5a**.

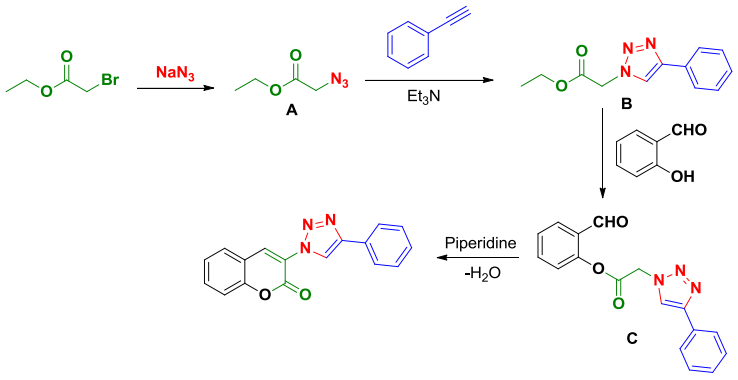
[a] Reaction conditions: Salicylaldehyde (1 equiv), ethyl bromoacetate (1.5 equiv), NaN_3 (3.0 equiv), phenylacetylene (1.0 equiv) and piperidine (1.25 equiv) in *i*PrOH:DMF (3:1) at 80 °C.

[b] Products purified by crystallization.



Scheme S1. Synthesis of 3-azidocoumarins **1a-b**

A proposal of the plausible reaction sequence is shown in Scheme S2. The reaction may be rationalized by the initial Huisgen 1,3-dipolar cycloaddition between the acetylene group with ethyl 2-azidoacetate (**A**) to produce the corresponding 1,2,3-triazole intermediate (**B**). Then, a nucleophilic attack of the phenolic group (influenced by the presence of electron donating groups in relative 1,4-position) onto the carbonyl moiety of the 1,2,3-triazole intermediate leads to the formation of the 2-fomylaryl precursor (**C**). Finally, condensation of salicylaldehyde or its derivatives with acetate derivatives in the presence of piperidine, leads the formation of the title ATCs.



Scheme S2. Probable sequence leading to ATCs in the studied multicomponent reaction.

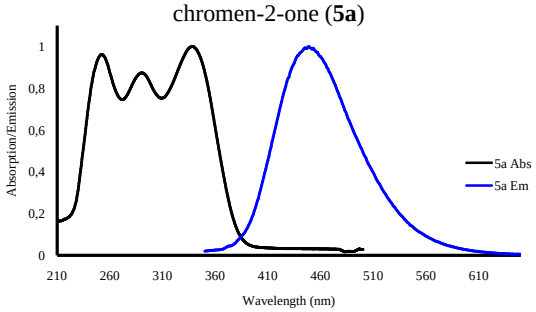
Crystallographic Data and X-Ray Diffraction studies of compounds 5a-c, 5f, 5h, 5j-l

Table S2. Selected dihedral angles (°) for 3-[1,2,3-triazo-yl]coumarins **5a**, **5b**, **5c**, **5f**, **5h**, **5j**, **5k** and **5l**

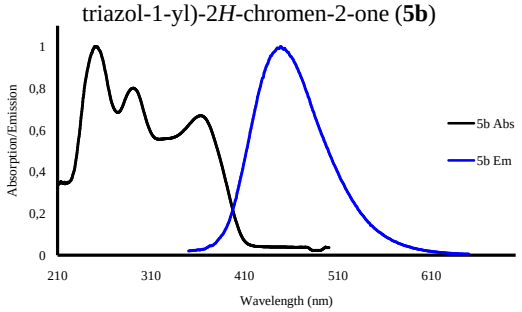
Compound	Mean Planes	Dihedral angle (°)
5a	1-2	5.8
	1-3	2.4
	2-3	7.7
5b	1-2	11.4
	1-3	27.6
	2-3	18.1
5c	1-2	21.5
	1-3	12.3
	2-3	13.0
5f	1-2	18.6
	1-3	19.7
	2-3	1.6
5h	1-2	5.9
	1-3	1.6
	2-3	7.1
5j	1-2	5.9
	1-3	1.0
	2-3	6.9
5k	1-2	11.3
	1-3	6.4
	2-3	5.3
5l	1-2	1.2
	1-3	1.0
	2-3	1.2

Absorption and emission profiles of coumarins 5a-l

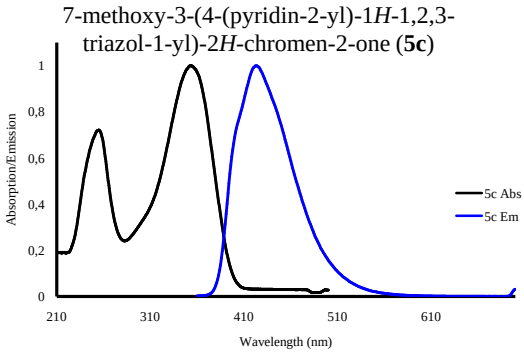
3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5a**)



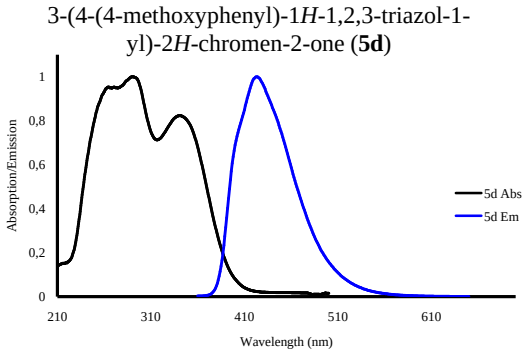
6-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5b**)



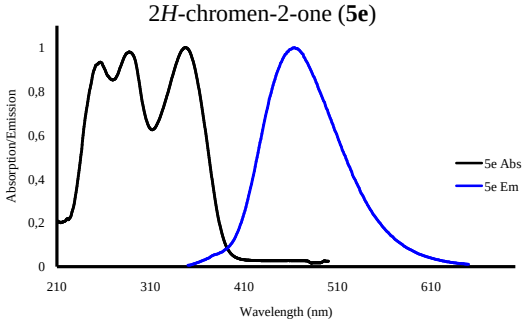
7-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5c**)



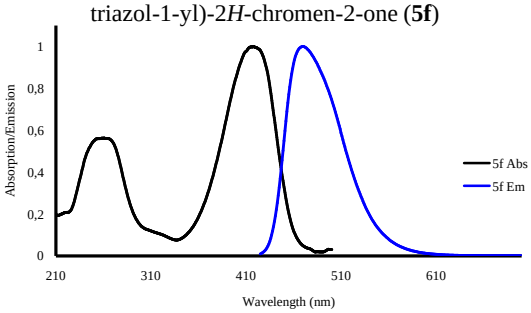
3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5d**)



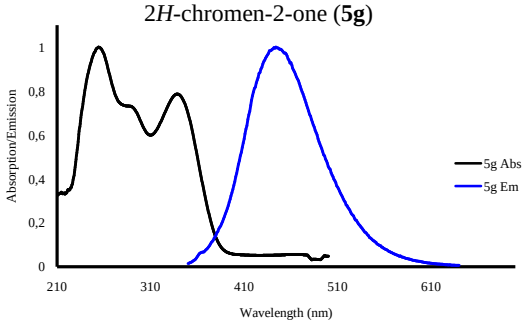
6-chloro-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5e**)



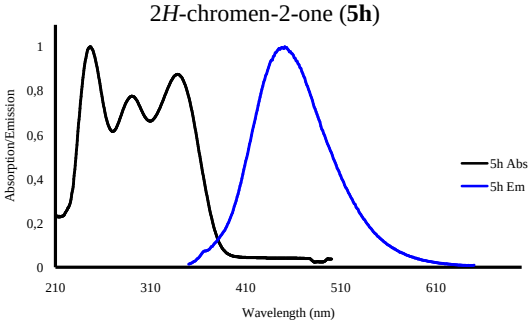
7-(diethylamino)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5f**)



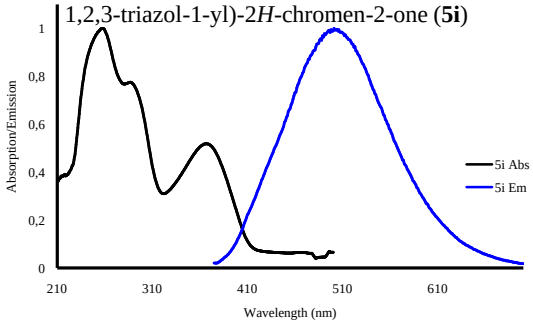
3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5g**)



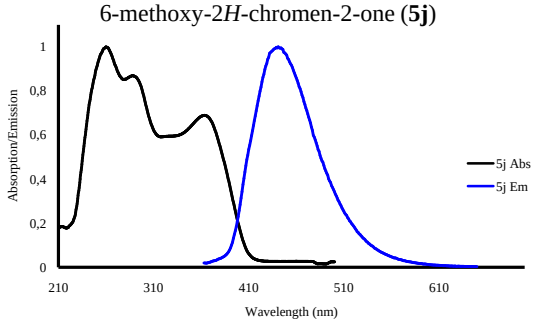
3-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5h**)



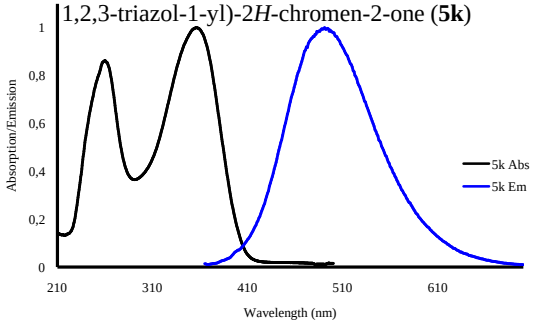
6-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5i**)



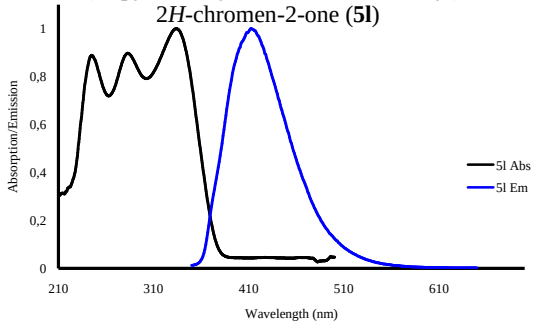
3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-6-methoxy-2*H*-chromen-2-one (**5j**)



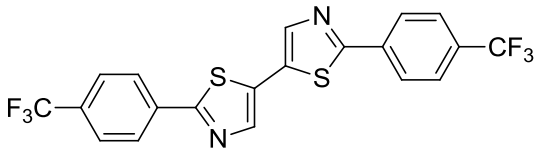
7-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5k**)



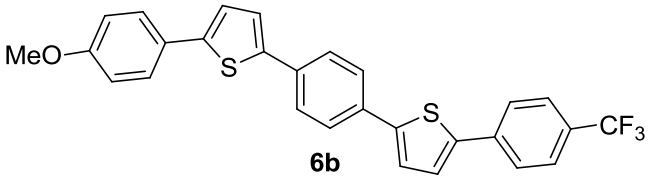
3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5l**)



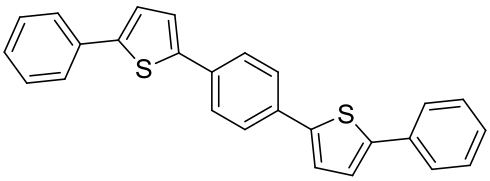
Reference molecules, selected for theoretical benchmarking.



6a



6b



6c

Benchmarking study for selection of theoretical methods (Mean squared errors included)

Reference 6a

	HOMO	LUMO	GAP	MSE GAP	MSE HOMO	MSE LUMO
HF 3-21	-8.35	1.18	9.53	43.98	7.41	15.28
HF 6-31+G(d)	-8.10	0.90	8.99	37.14	6.09	13.15
MP2	-8.10	0.90	8.99	37.14	6.09	13.15
b3lyp	-6.27	-2.41	3.86	0.92	0.41	0.10
pbepbe	-5.63	-3.00	2.63	0.07	0.00	0.07
wb97xd	-8.08	-0.65	7.44	20.58	6.01	4.34
m062x	-7.46	-1.57	5.89	8.93	3.34	1.35
Reported	-5.63	-2.73	2.90	0.00	0.00	0.00

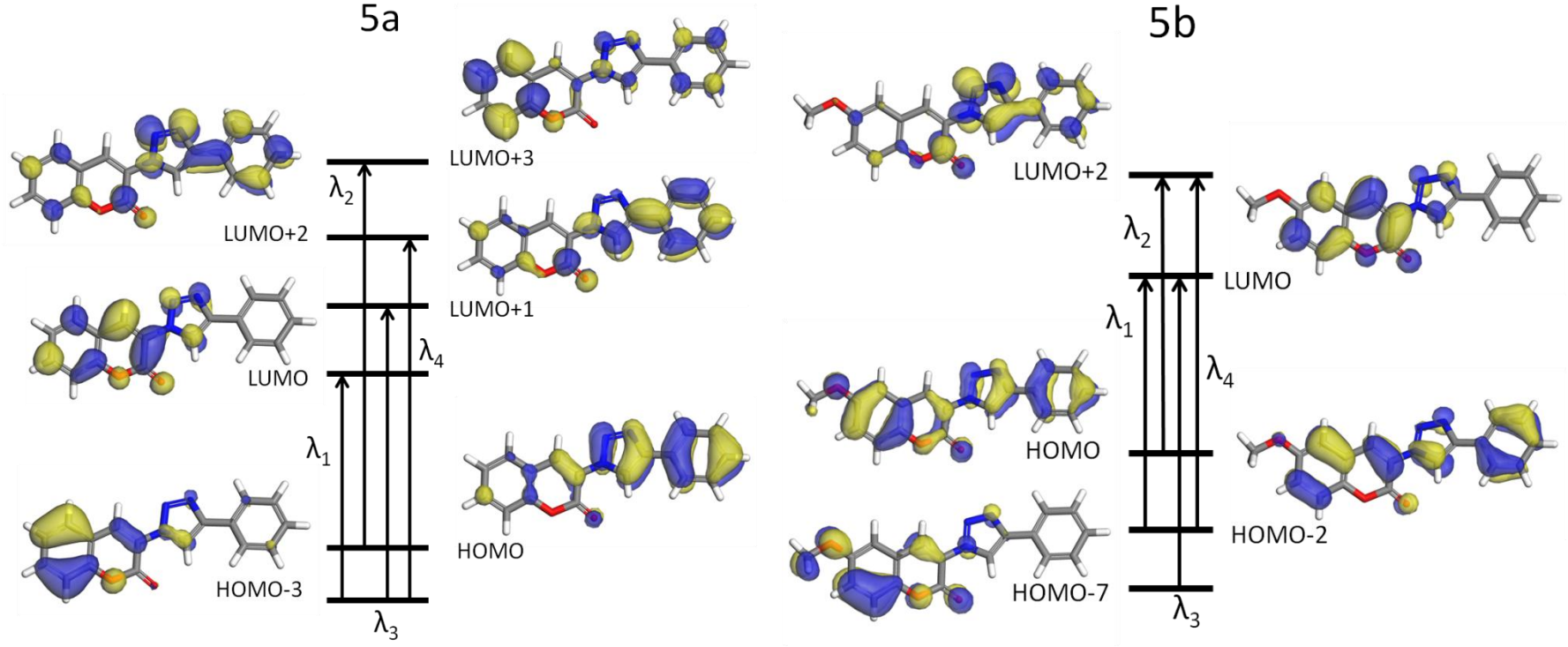
Reference 6b

	HOMO	LUMO	GAP	MSE GAP	MSE HOMO	MSE LUMO
HF 3-21	-6.97	0.97	7.94	21.58	3.28	8.03
HF 6-31+G(d)	-6.86	0.74	7.60	18.53	2.90	6.77
MP2	-6.86	0.74	7.60	18.53	2.90	6.77
b3lyp	-5.29	-2.29	3.00	0.09	0.02	0.19
pbepbe	-4.73	-2.79	1.94	1.86	0.19	0.87
wb97xd	-7.00	-0.68	6.32	9.12	3.39	1.39
m062x	-6.43	-1.60	4.83	2.34	1.60	0.07
Reported	-5.16	-1.86	3.30	0.00	0.00	0.00

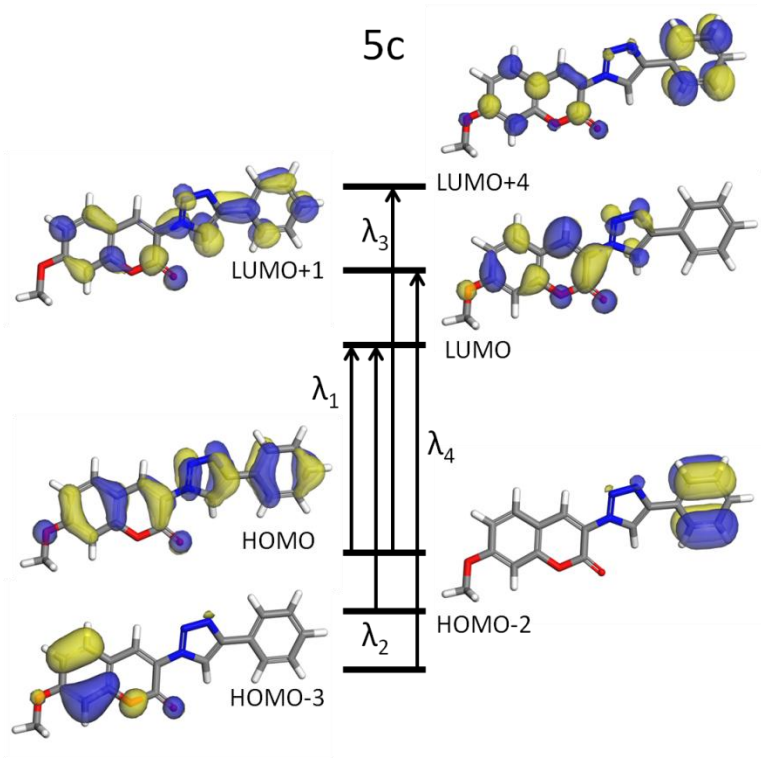
Reference 6c

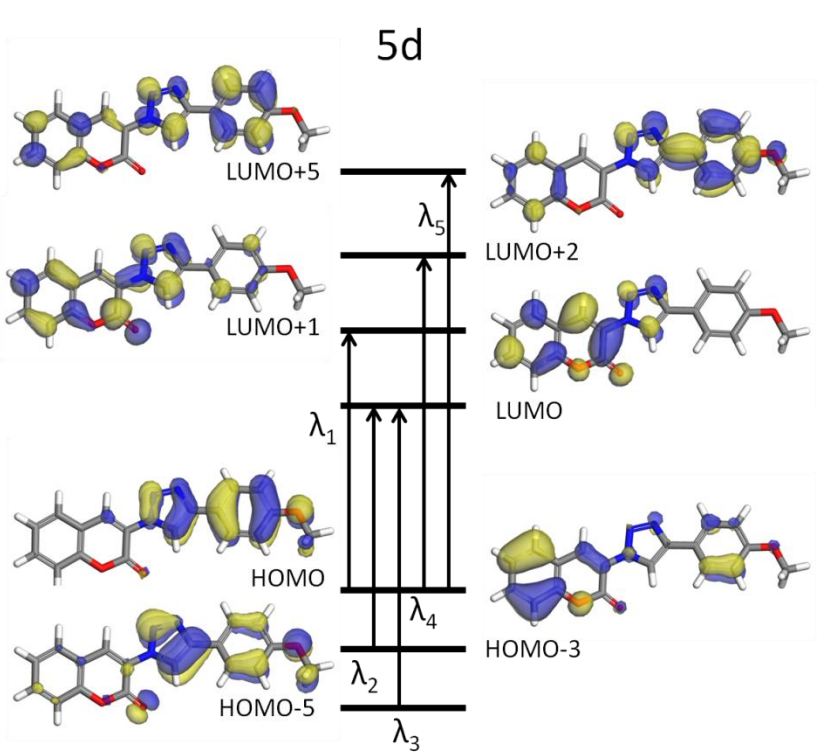
	HOMO	LUMO	GAP	MSE GAP	MSE HOMO	MSE LUMO
HF 3-21	-7.45	0.74	8.19	22.98	3.76	8.15
HF 6-31+G(d)	-7.31	0.54	7.85	19.79	3.24	7.01
MP2	-7.31	0.54	7.85	19.79	3.24	7.01
b3lyp	-5.72	-2.53	3.19	0.04	0.04	0.17
pbepbe	-5.16	-3.04	2.12	1.64	0.12	0.87
wb97xd	-7.44	-0.89	6.55	9.90	3.71	1.49
m062x	-6.86	-1.81	5.05	2.72	1.82	0.09
Reported	-5.51	-2.11	3.40	0.00	0.00	0.00

UV-Vis excitations for compounds **5a** and **5b**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane

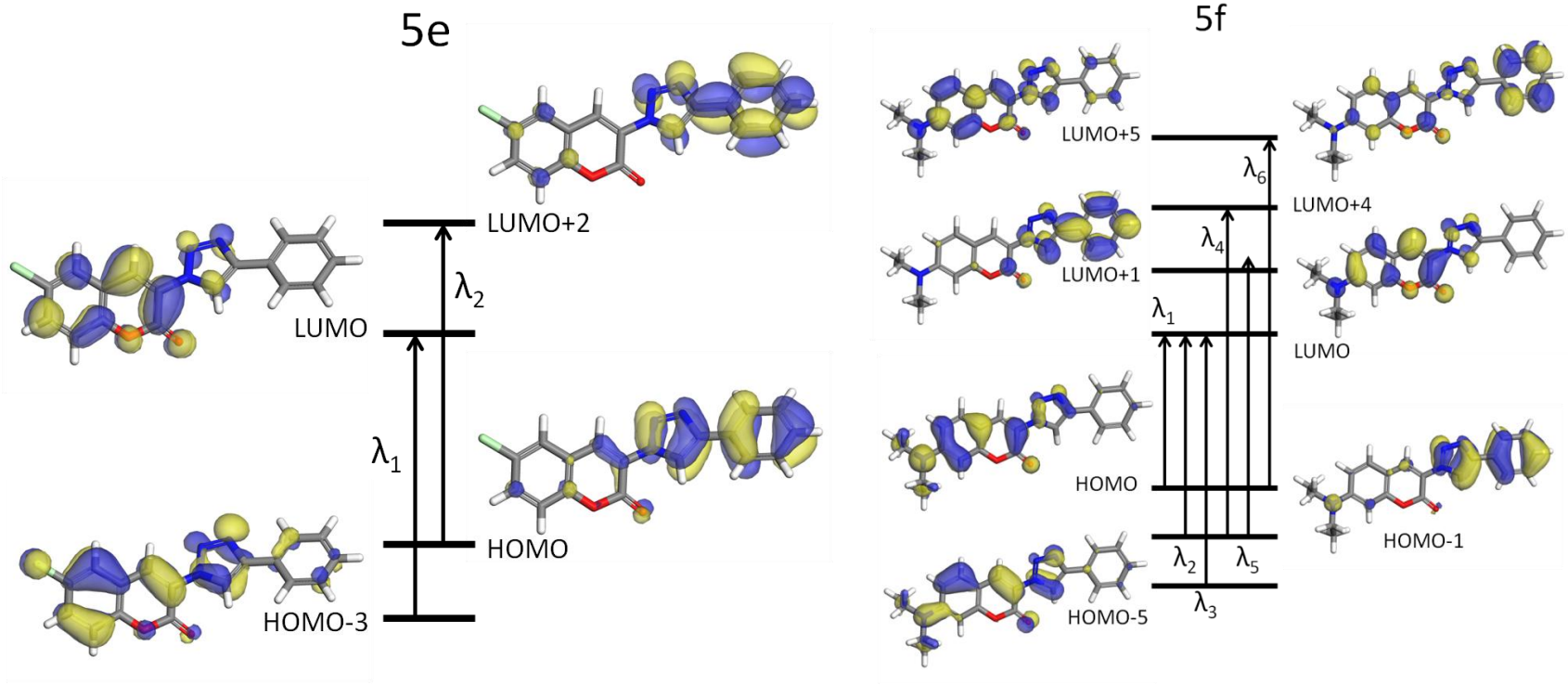


UV-Vis excitations for compounds **5c** and **5d**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane

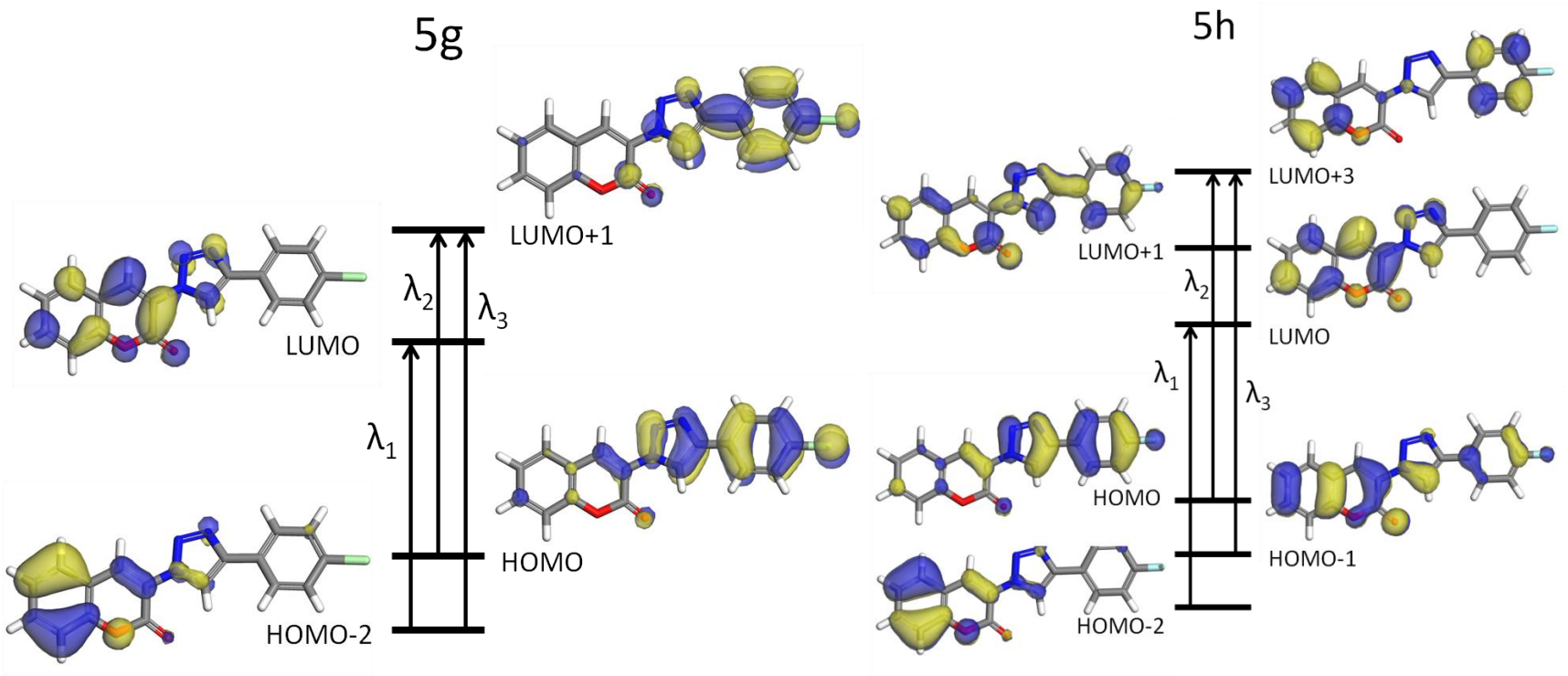




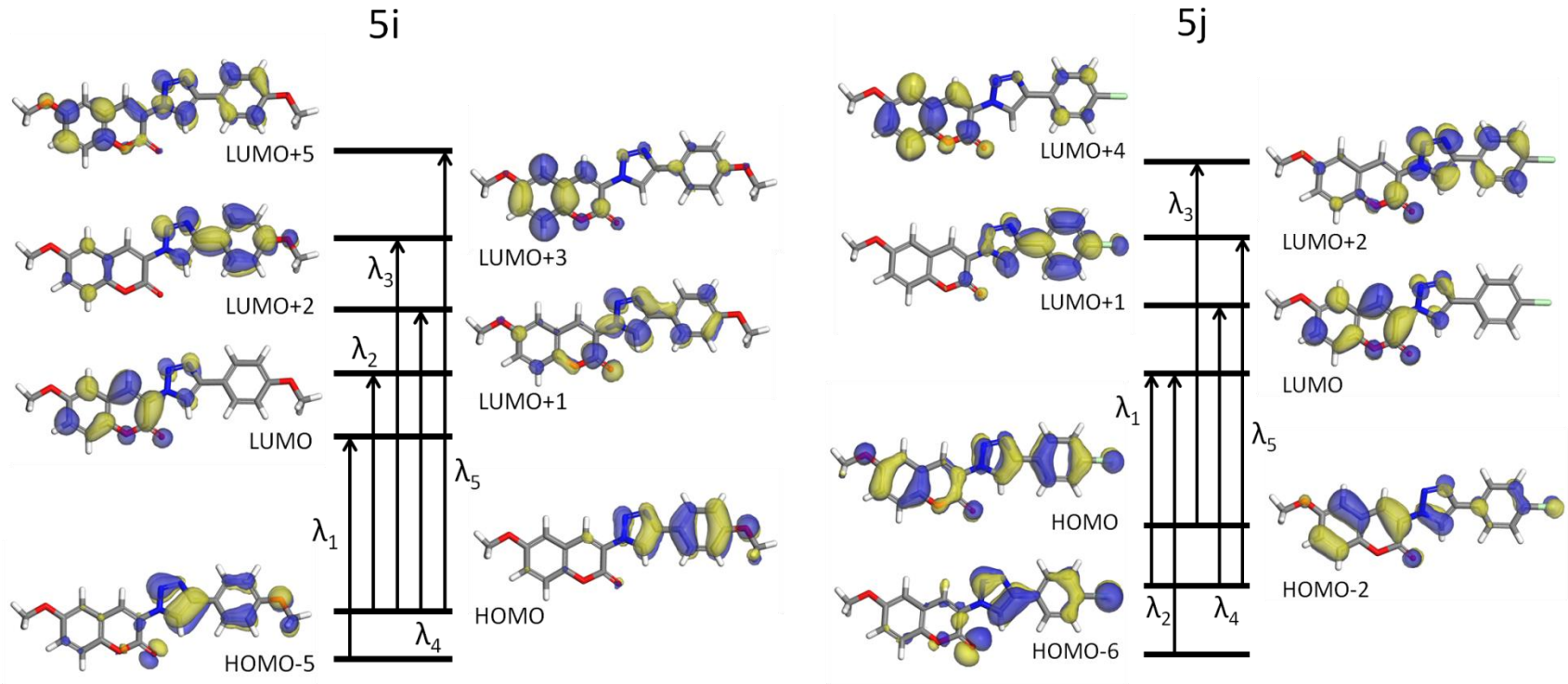
UV-Vis excitations for compounds **5e** and **5f**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane



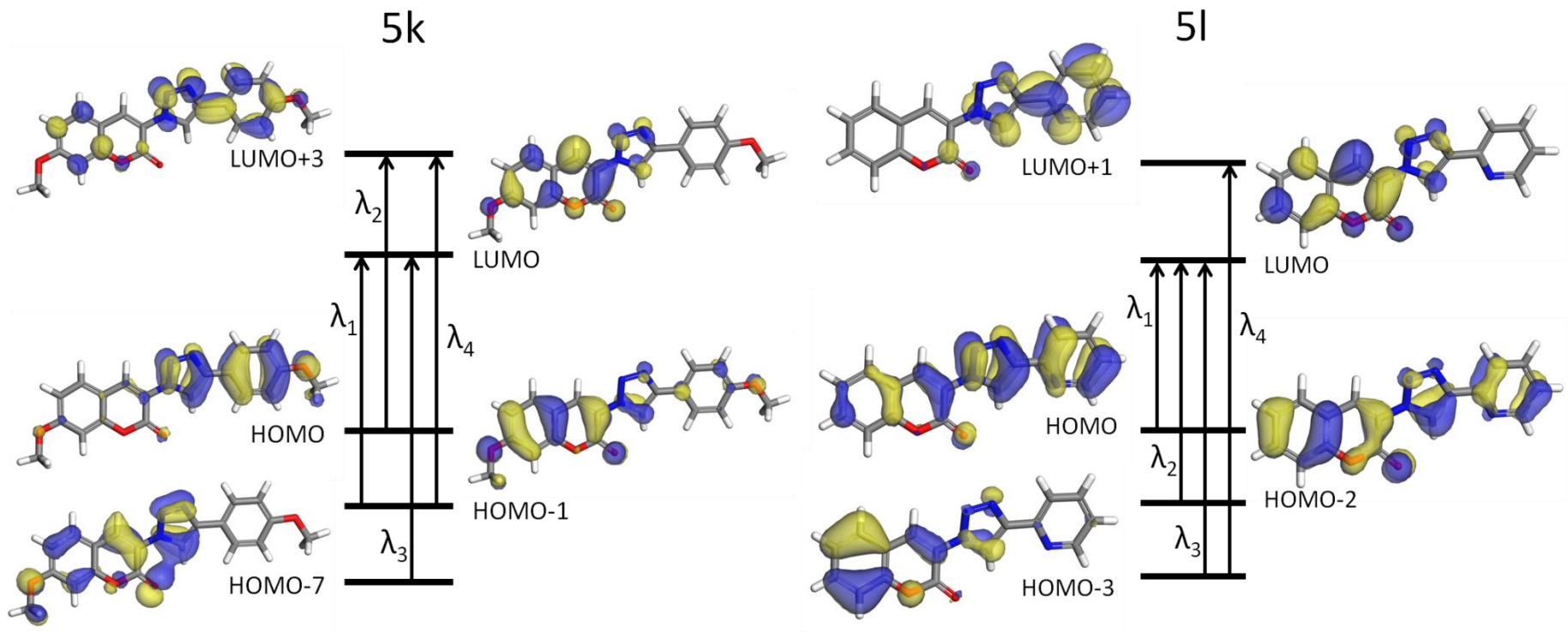
UV-Vis excitations for compounds **5g** and **5h**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane



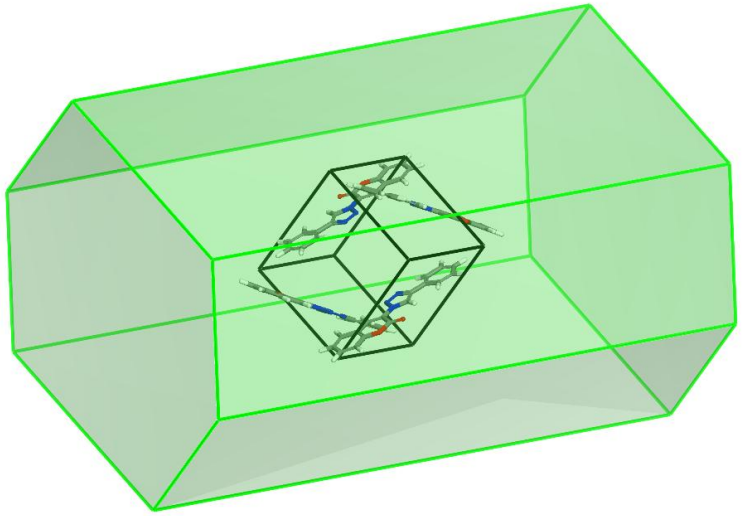
UV-Vis excitations for compounds **5i** and **5j**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane

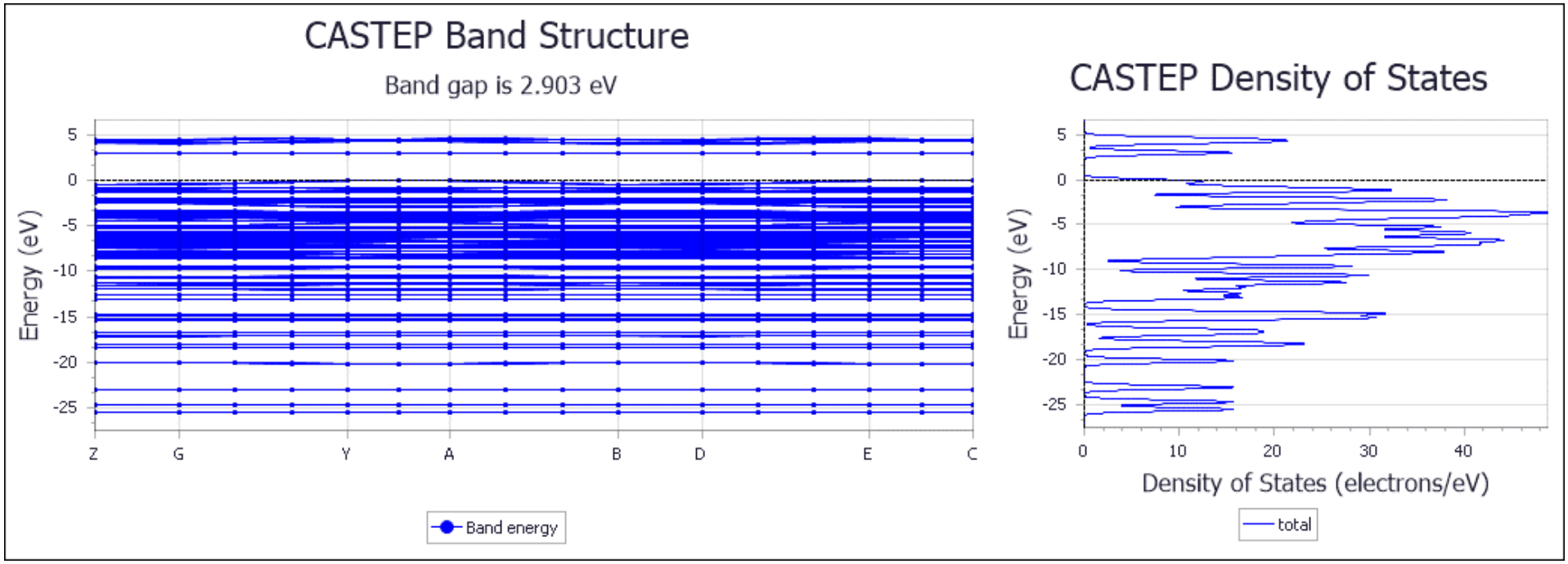


UV-Vis excitations for compounds **5k** and **5l**, derived through TDDFT, at the B3LYP/6-31+G(d) level in dichloromethane

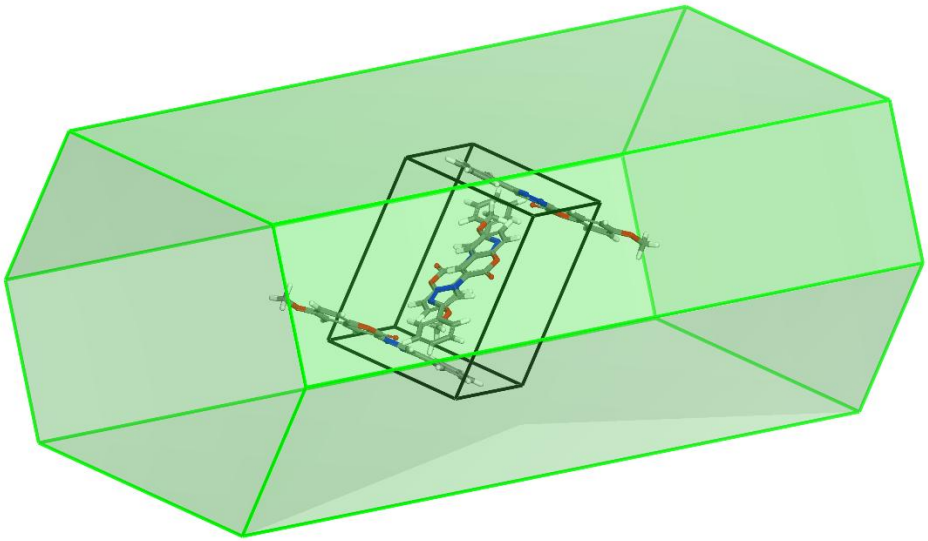


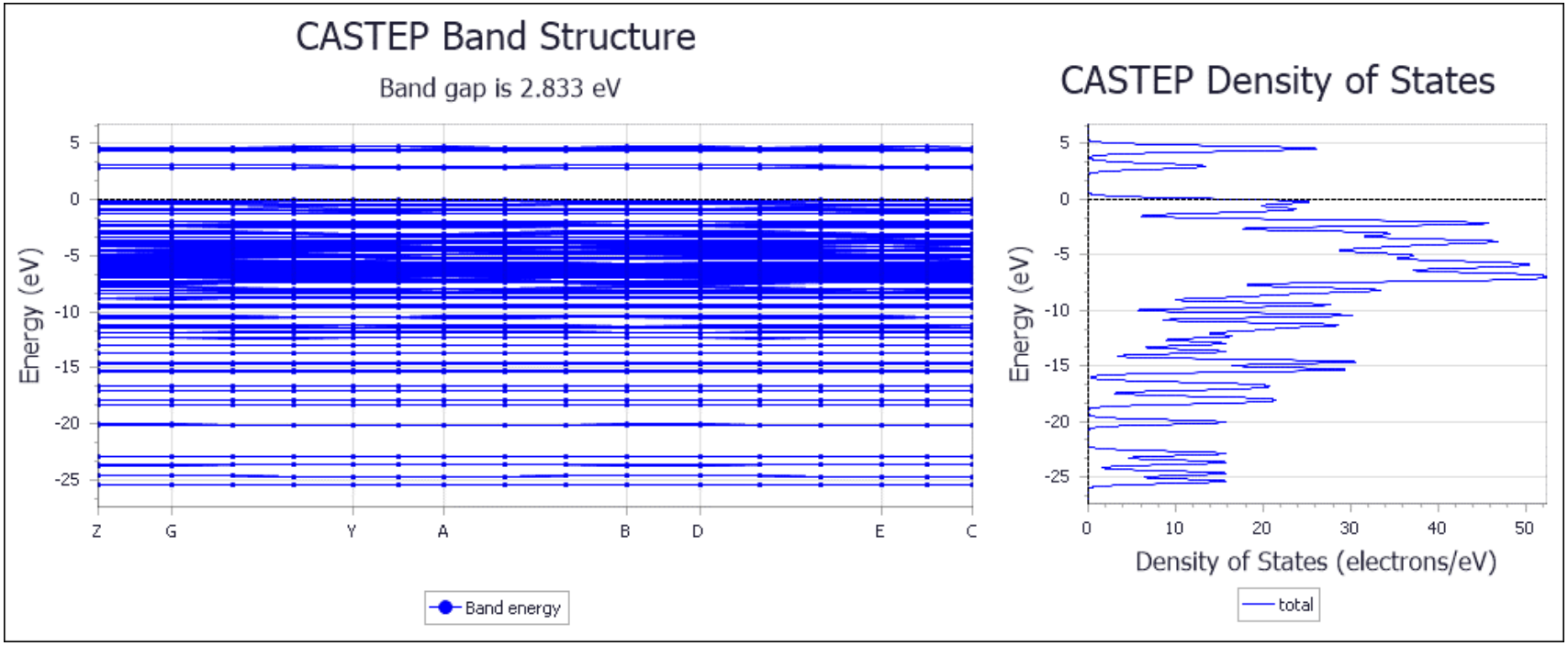
Unit cell of single crystal of **5a**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff



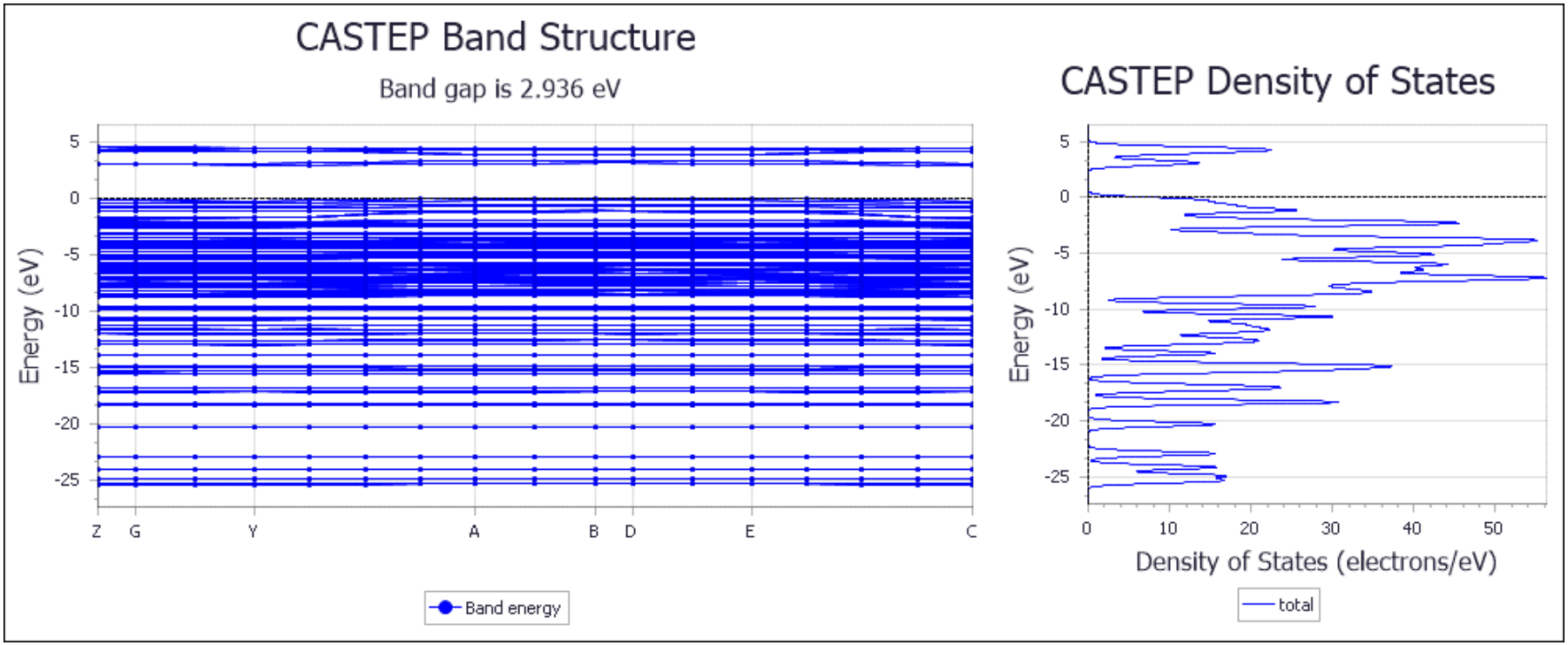


Unit cell of single crystal of **5b**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff

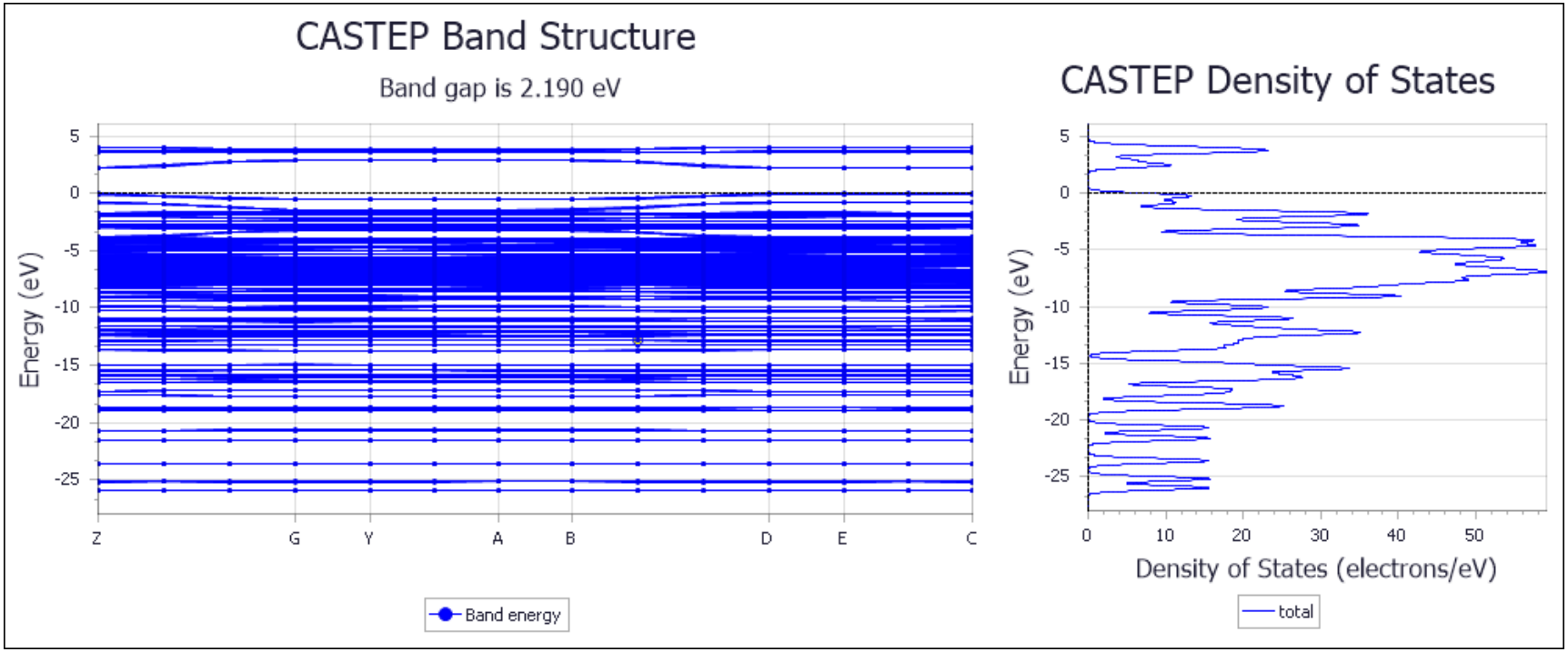




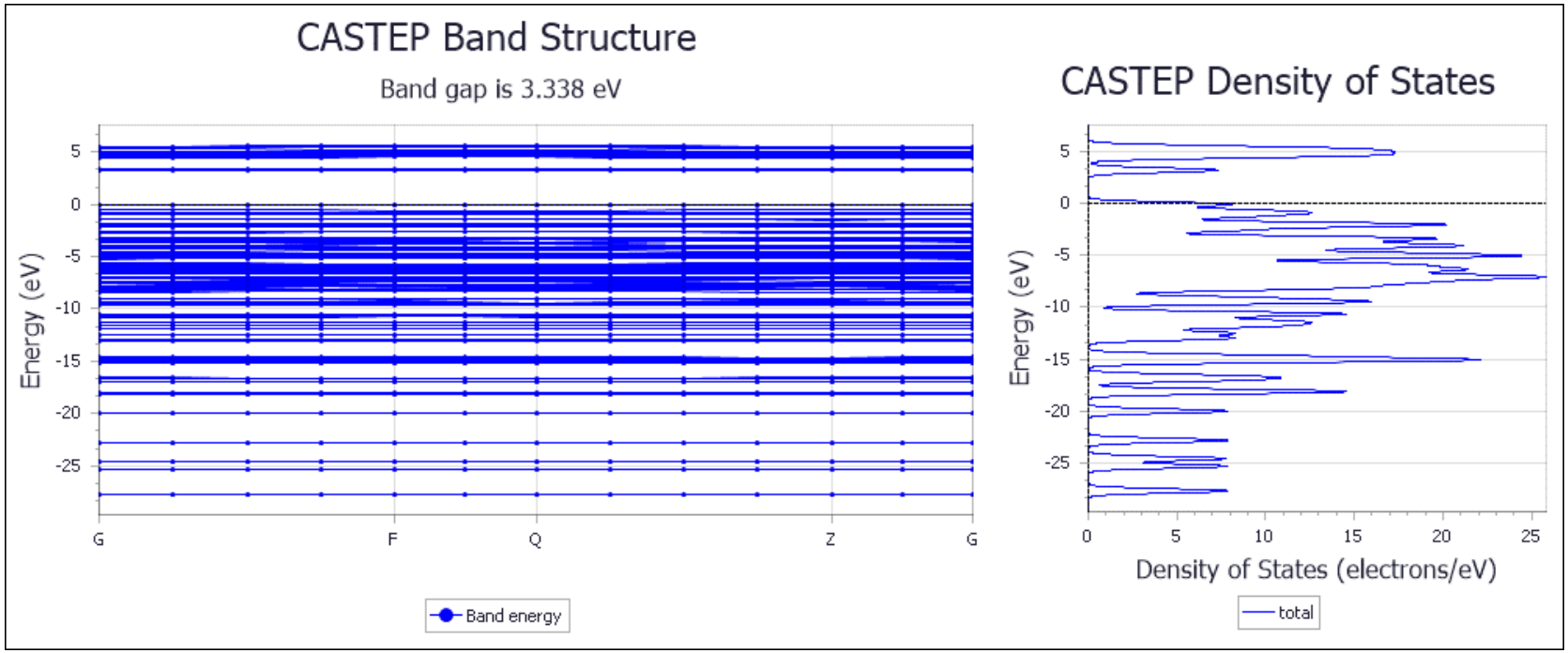
Unit cell of single crystal of **5c**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff



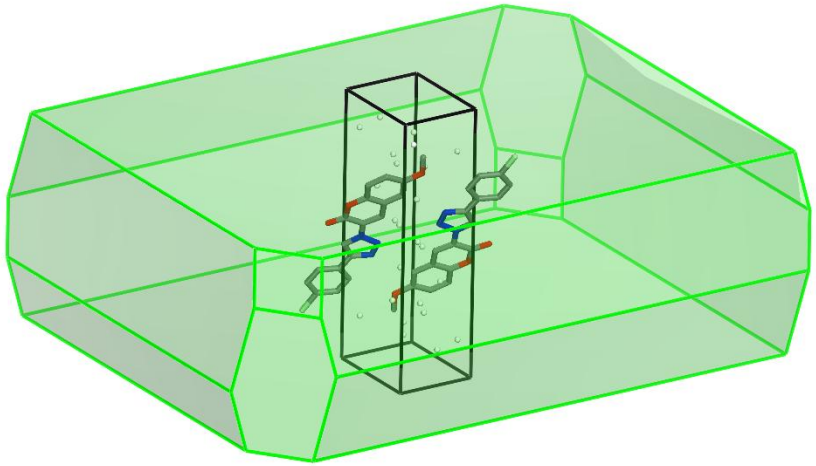
Unit cell of single crystal of **5f**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff

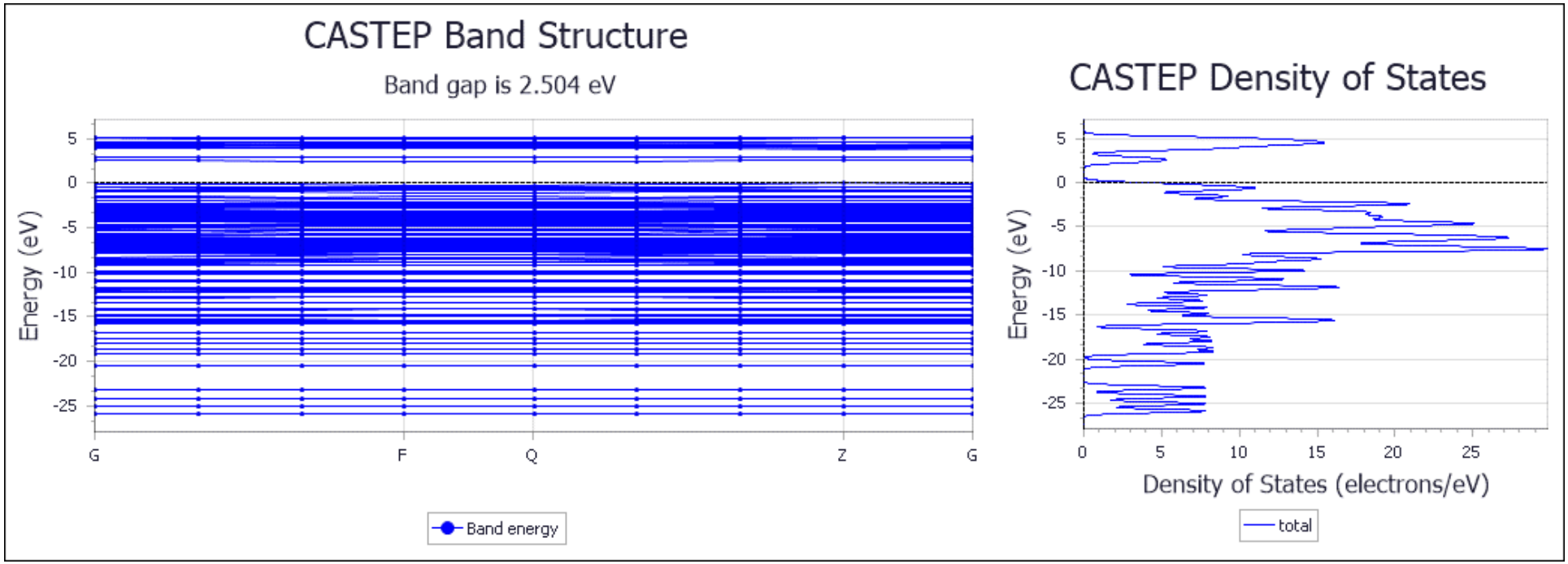


Unit cell of single crystal of **5h**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff

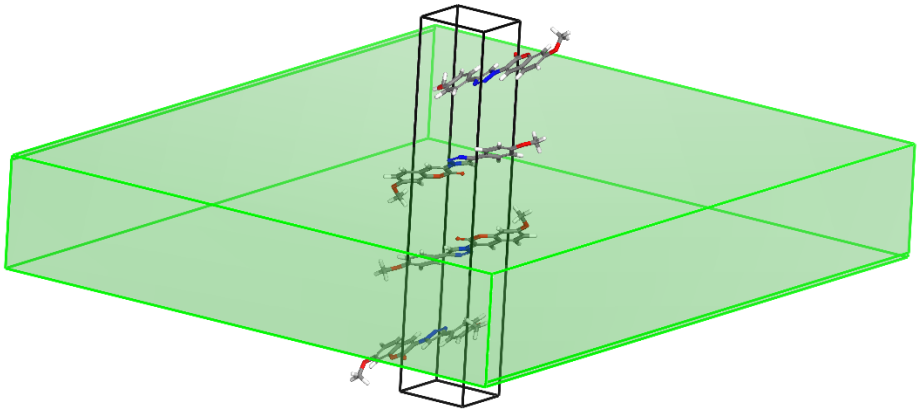


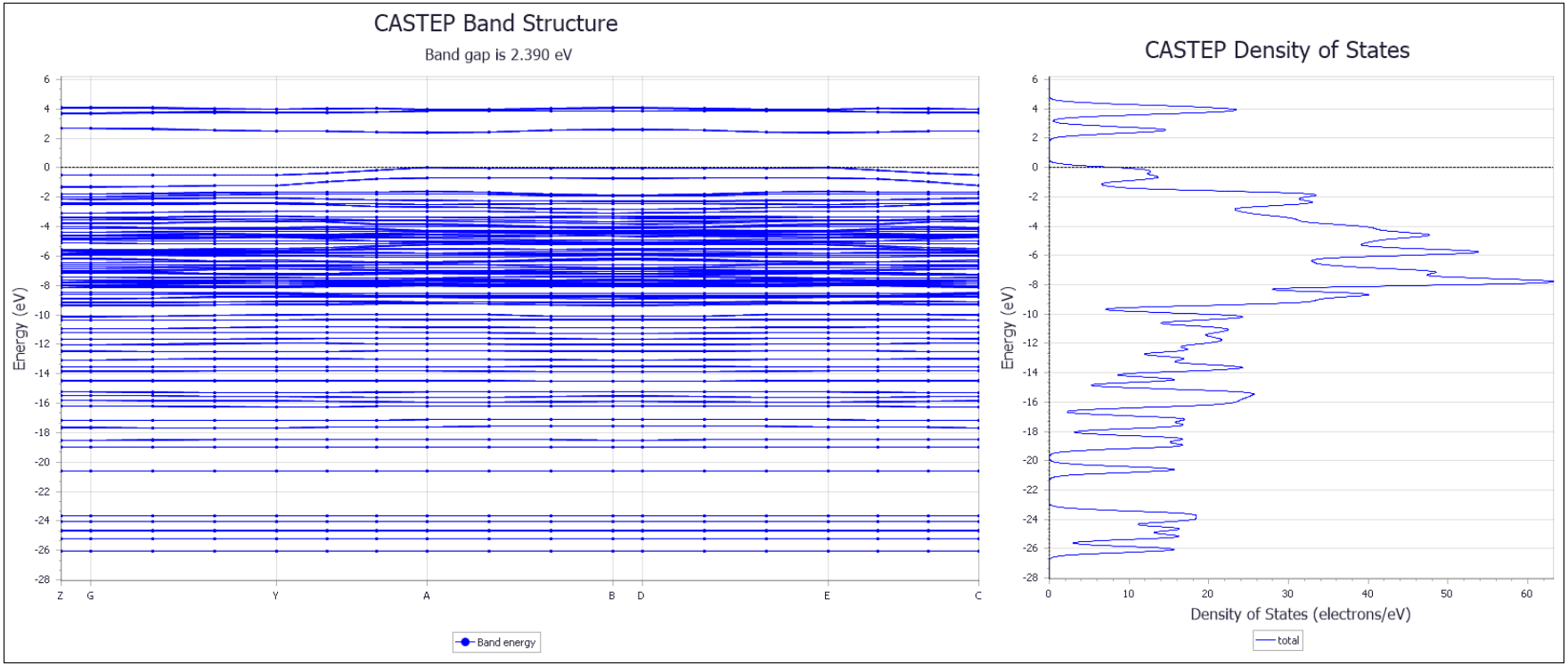
Unit cell of single crystal of **5j**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff



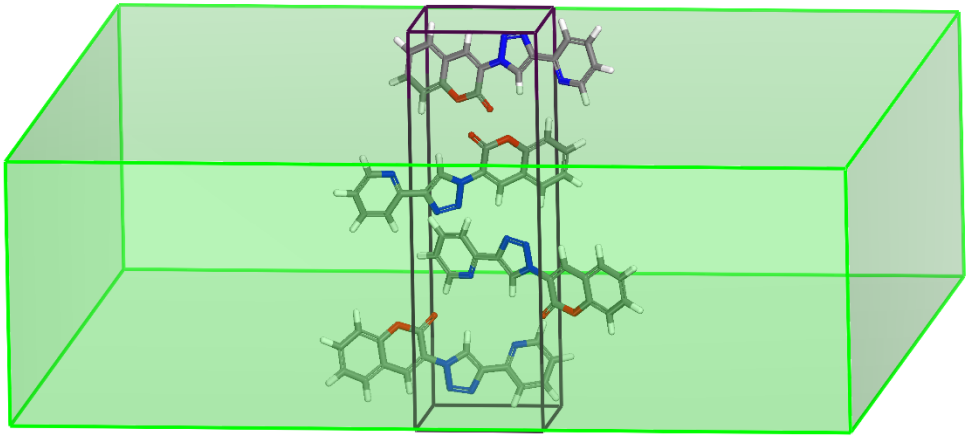


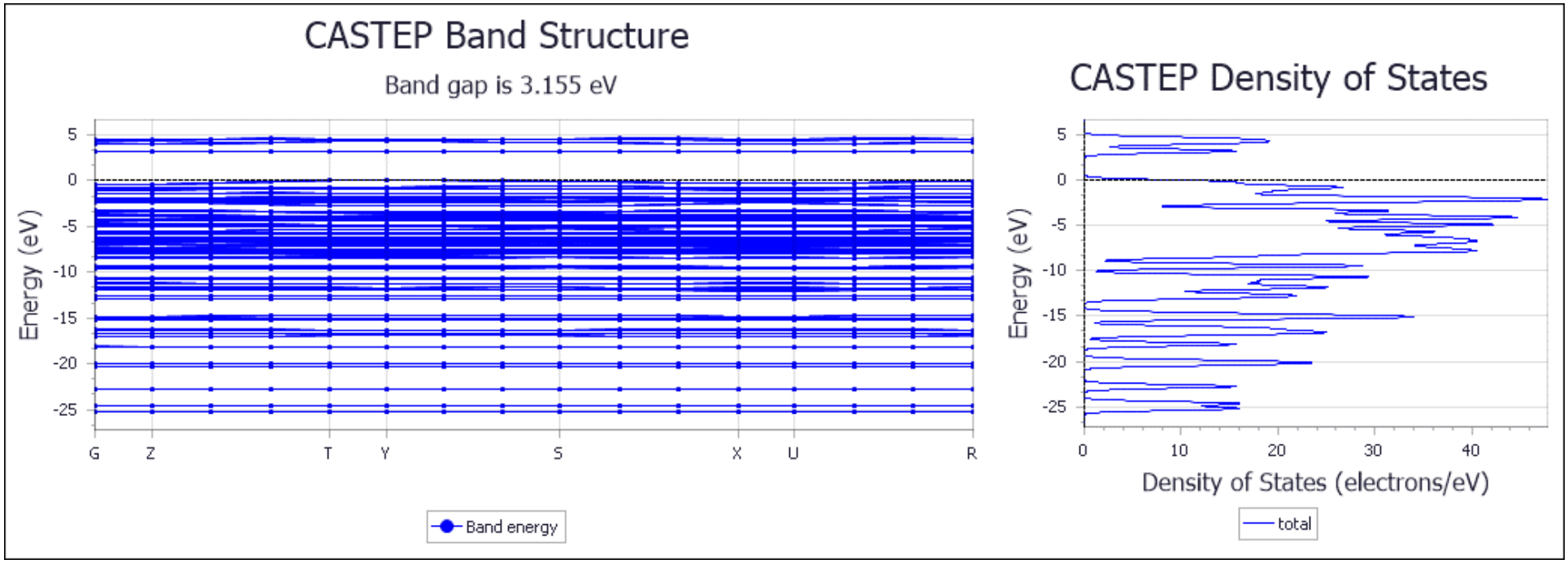
Unit cell of single crystal of **5k**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff



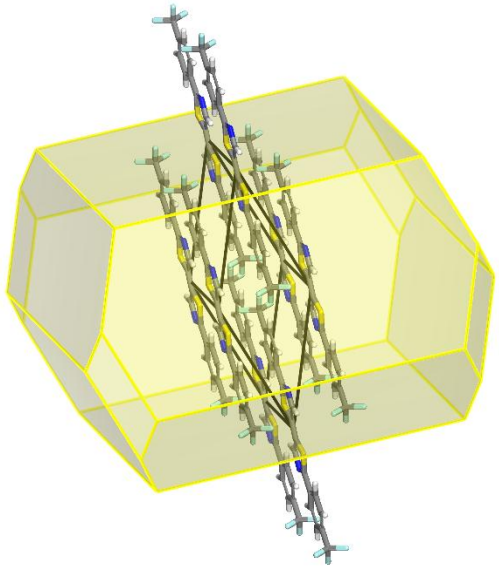


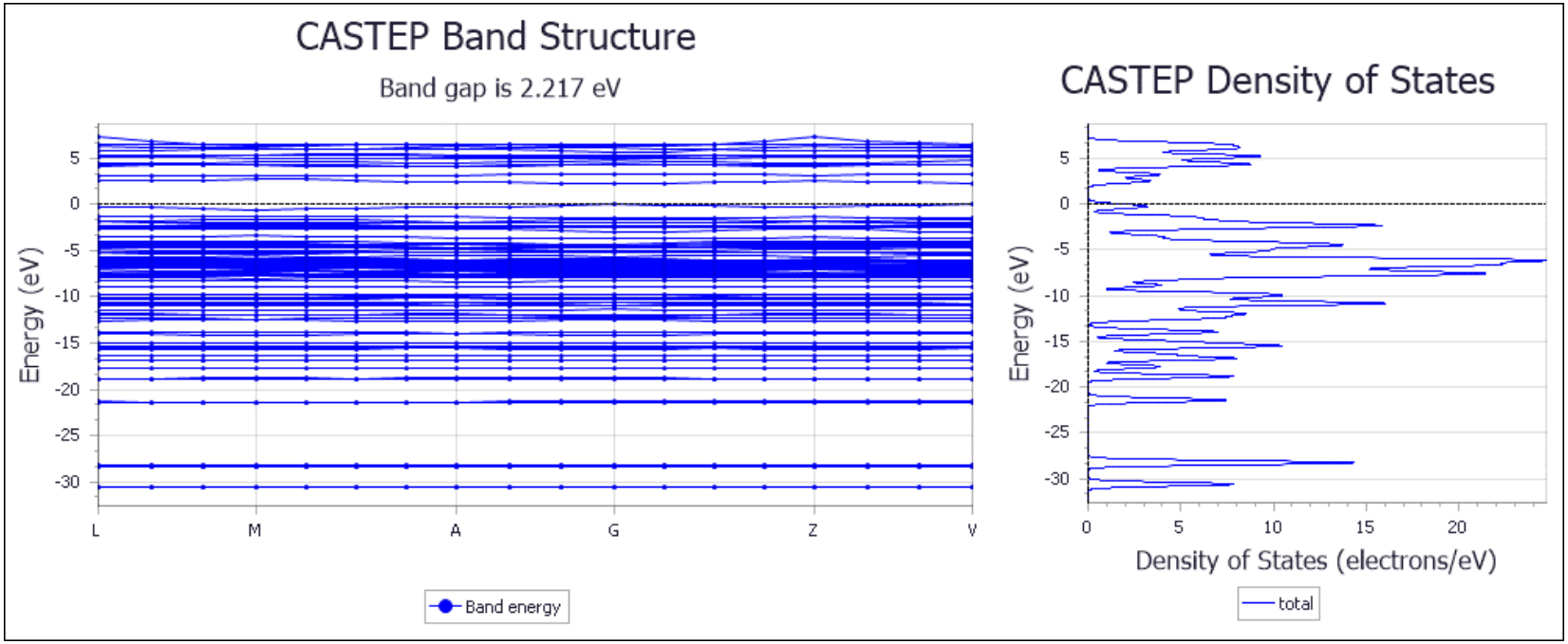
Unit cell of single crystal of **5l**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff



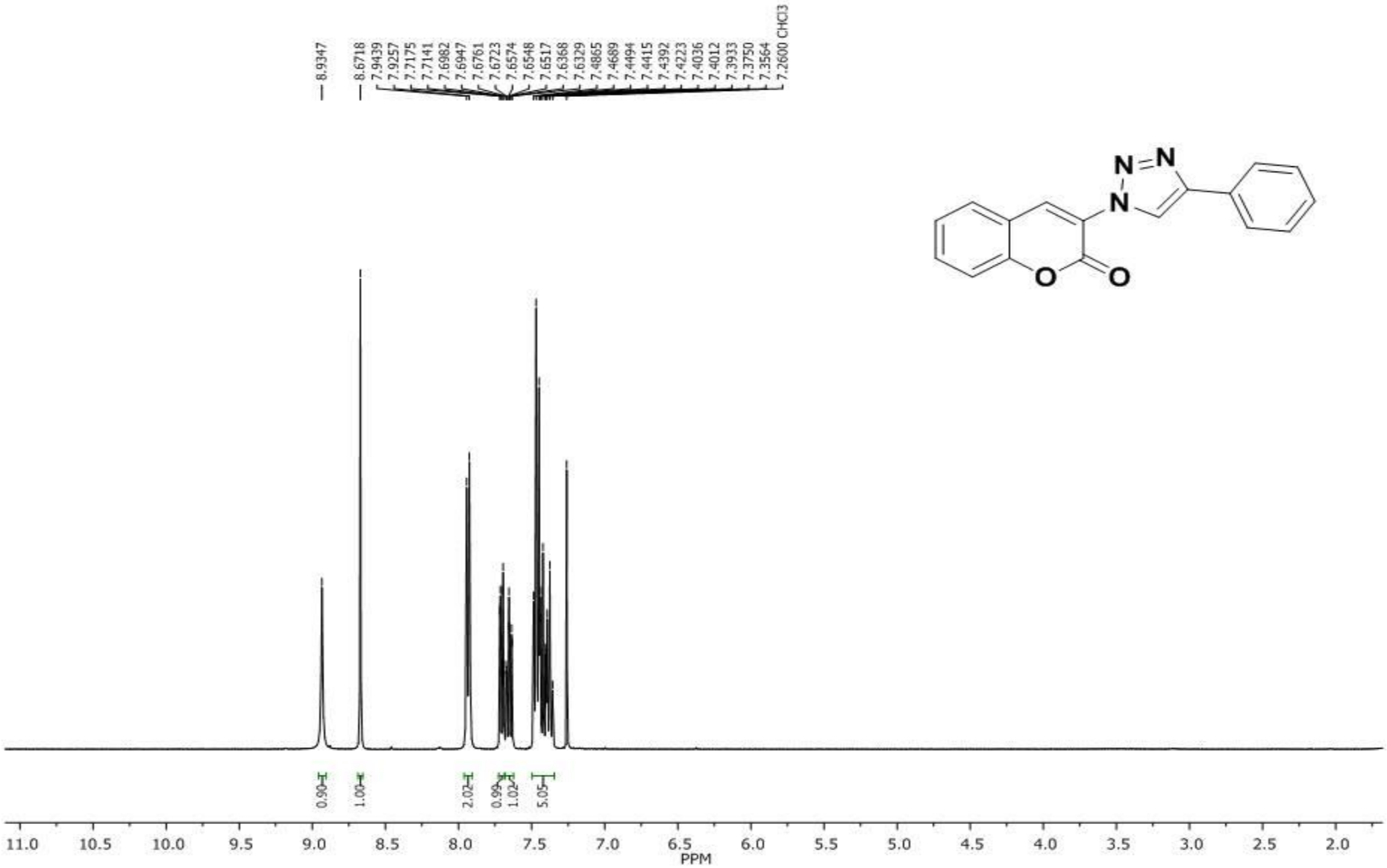


Unit cell of single crystal of **6a**, and band structure derived through plane-wave DFT, at the HSE06 level, with 850 eV cutoff

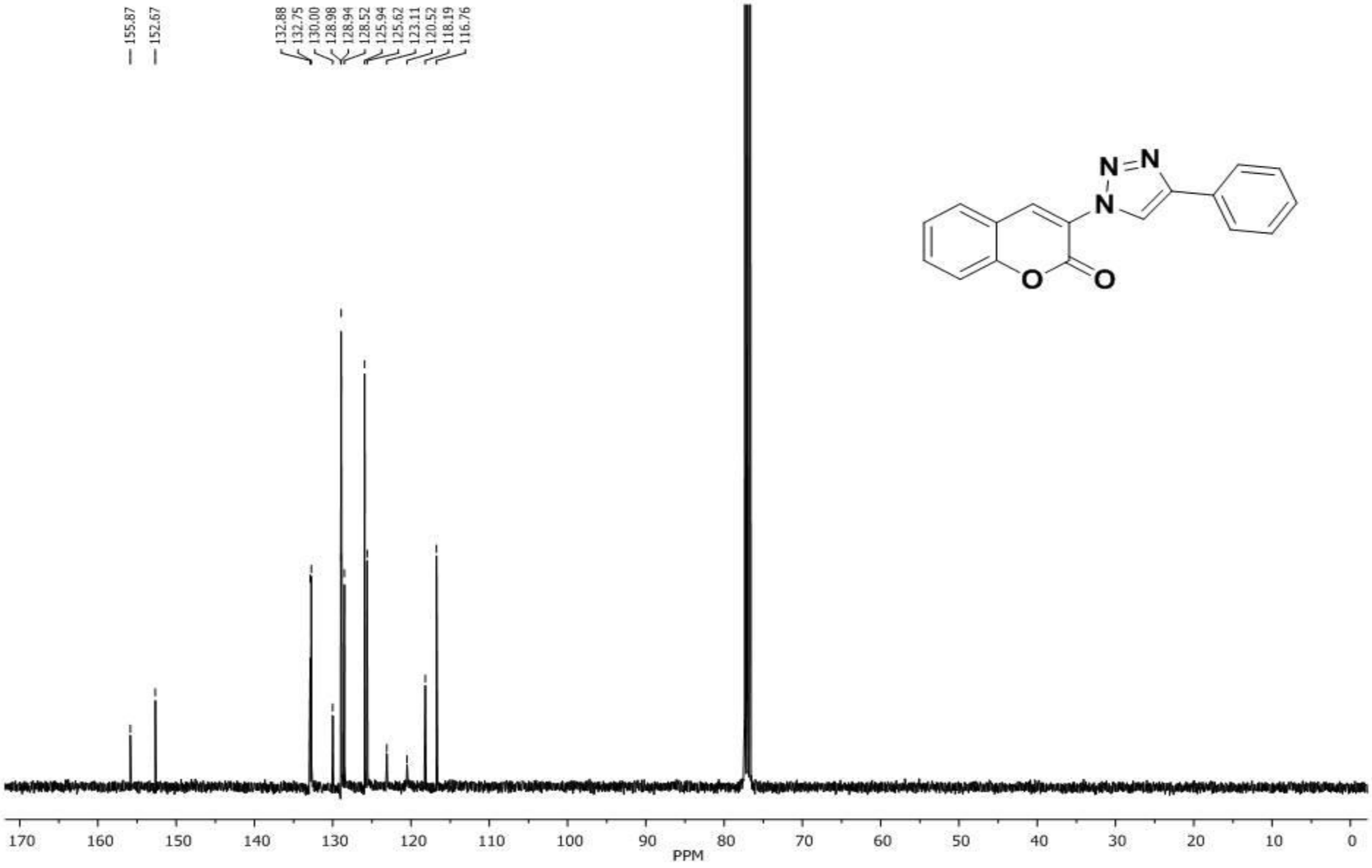



CASTEP Band Structure
Band gap is 2.217 eV
Energy (eV)
5
0
-5
-10
-15
-20
-25
-30
L
M
A
G
Z
V
Band energy
CASTEP Density of States
Energy (eV)
0
5
10
15
20
Density of States (electrons/eV)
total

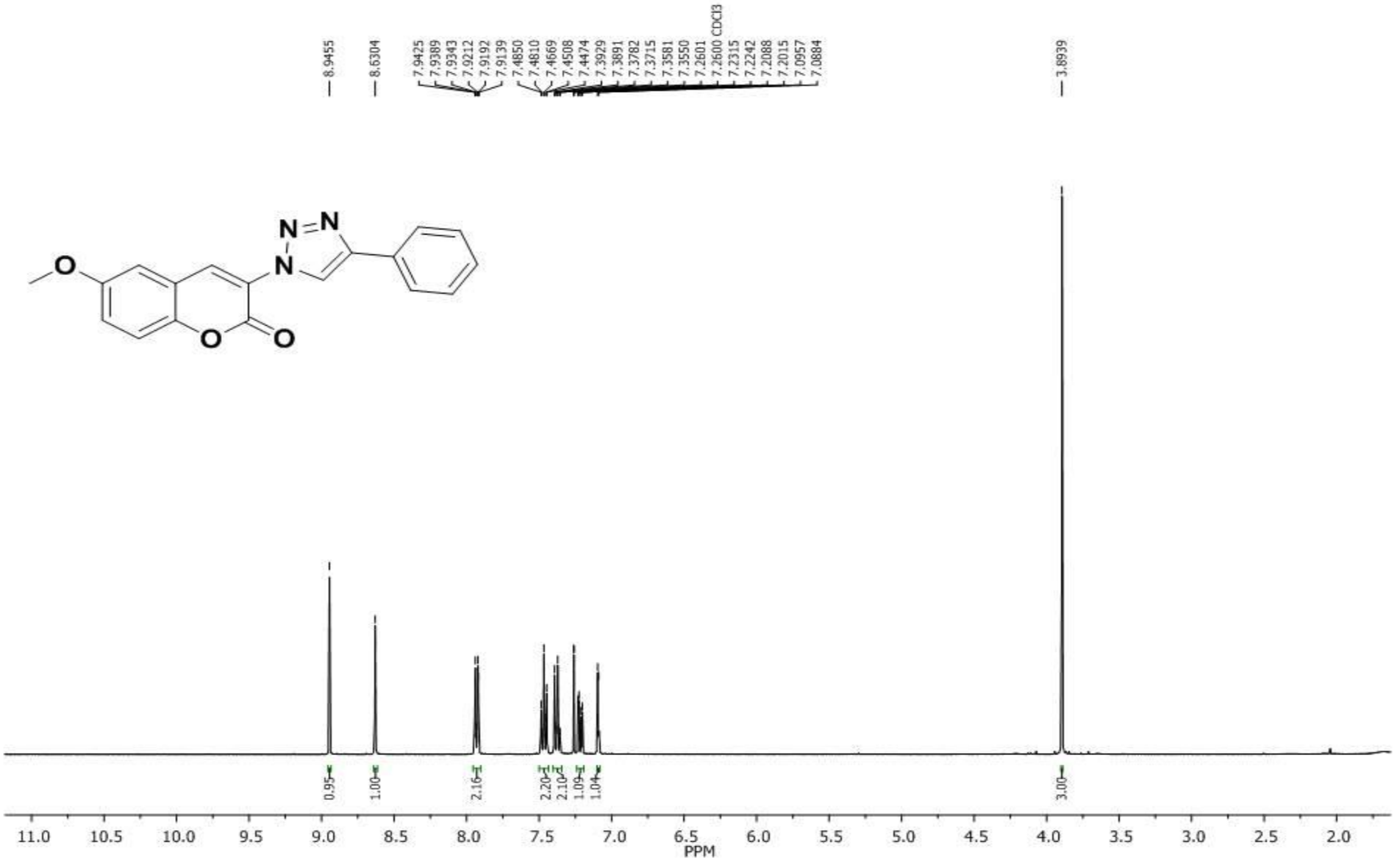
[1]H-NMR spectrum for compound 3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5a**)



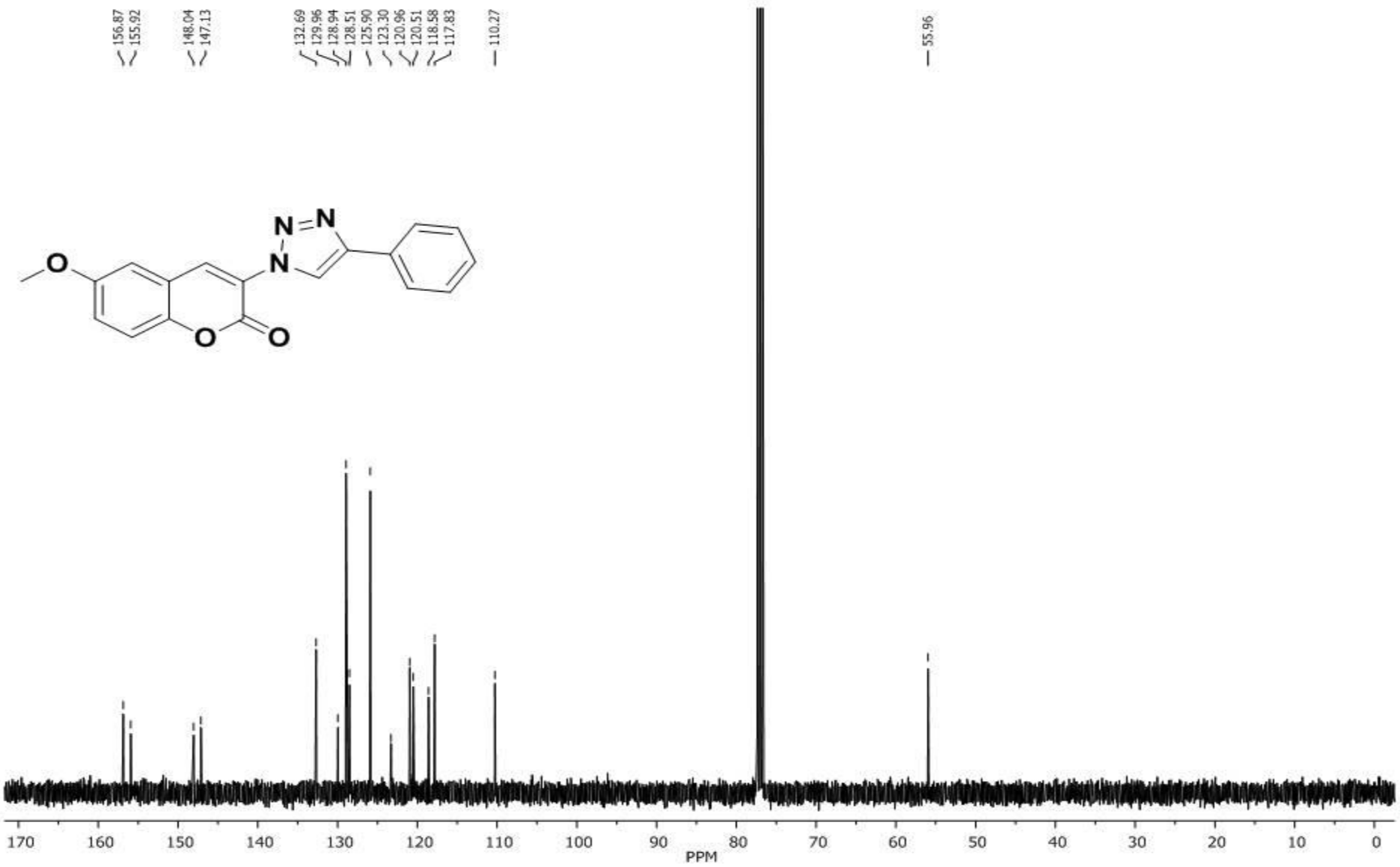
^{13}C-NMR spectrum for compound 3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5a**)



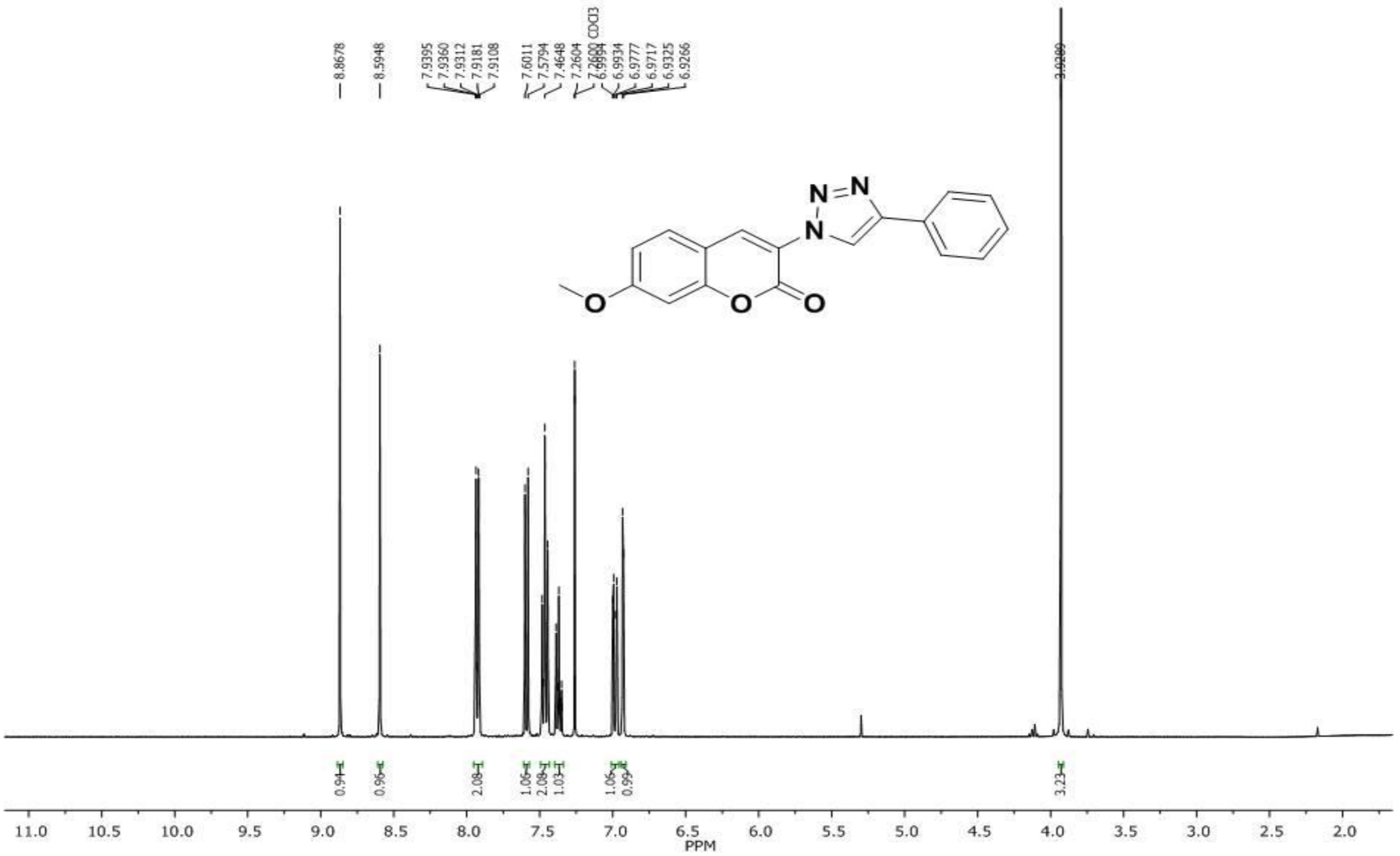
[1]H-NMR spectrum for compound 6-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5b**)



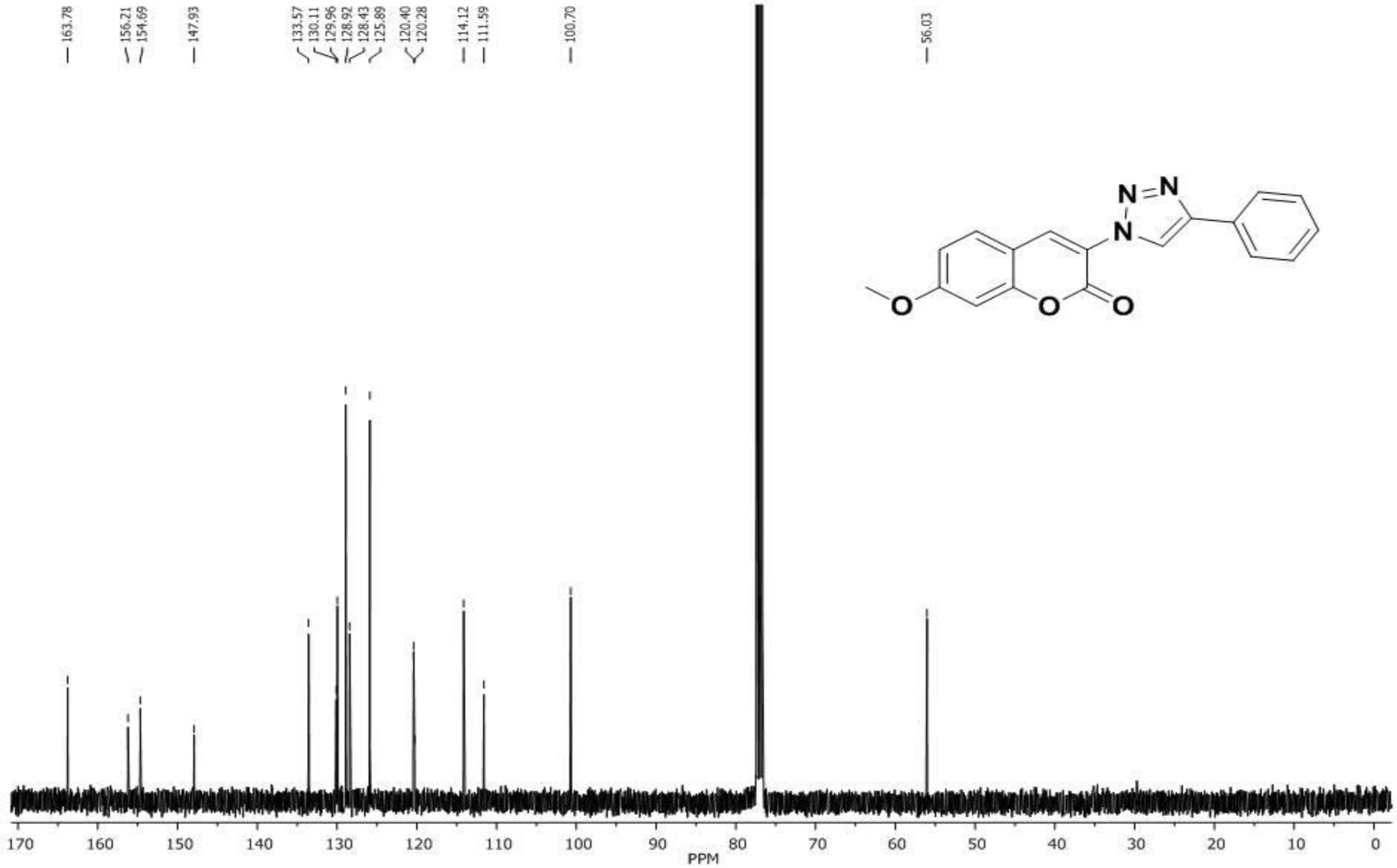
^{13}C-NMR spectrum for compound 6-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5b**)



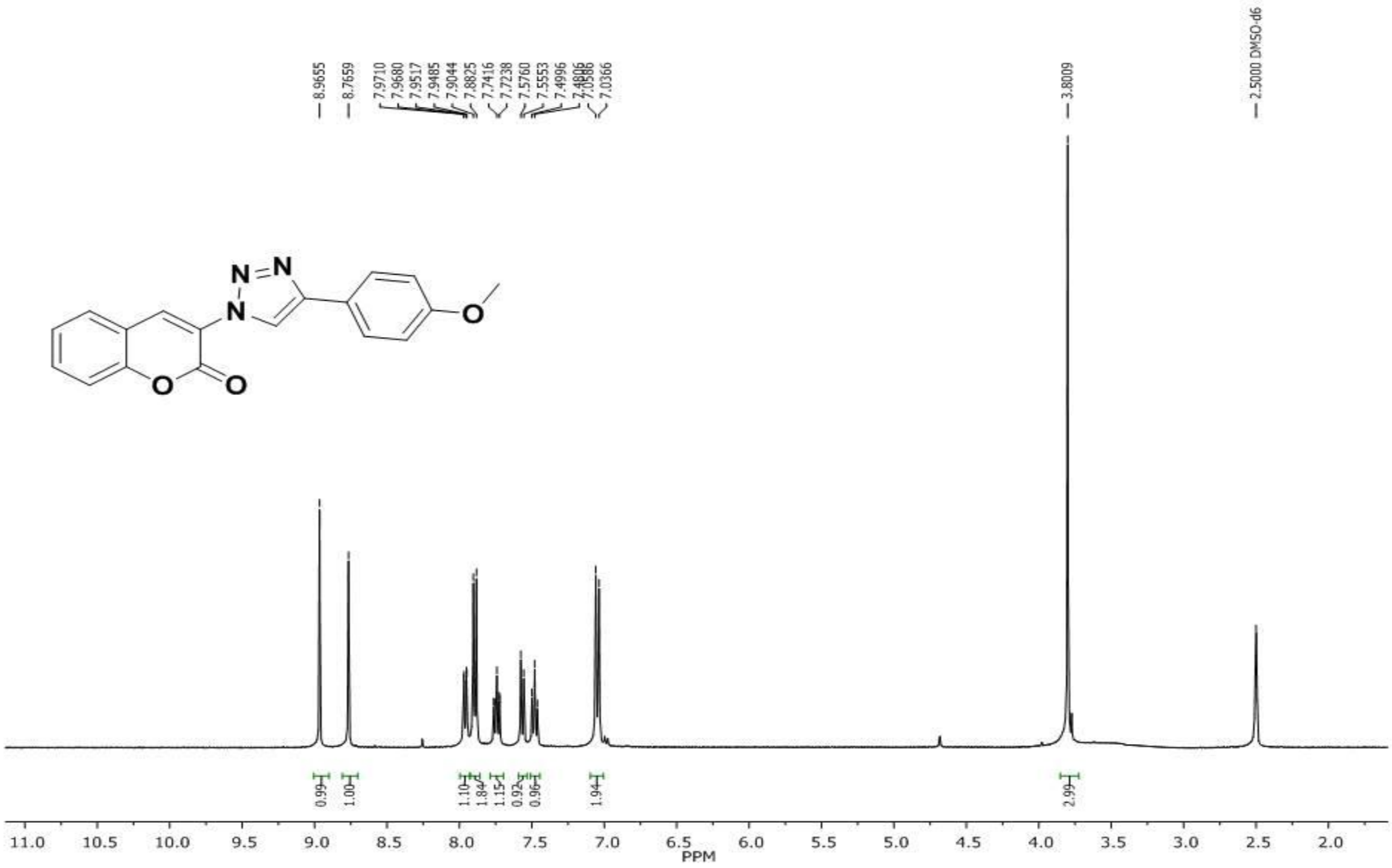
[1]H-NMR spectrum for compound 7-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5c**)



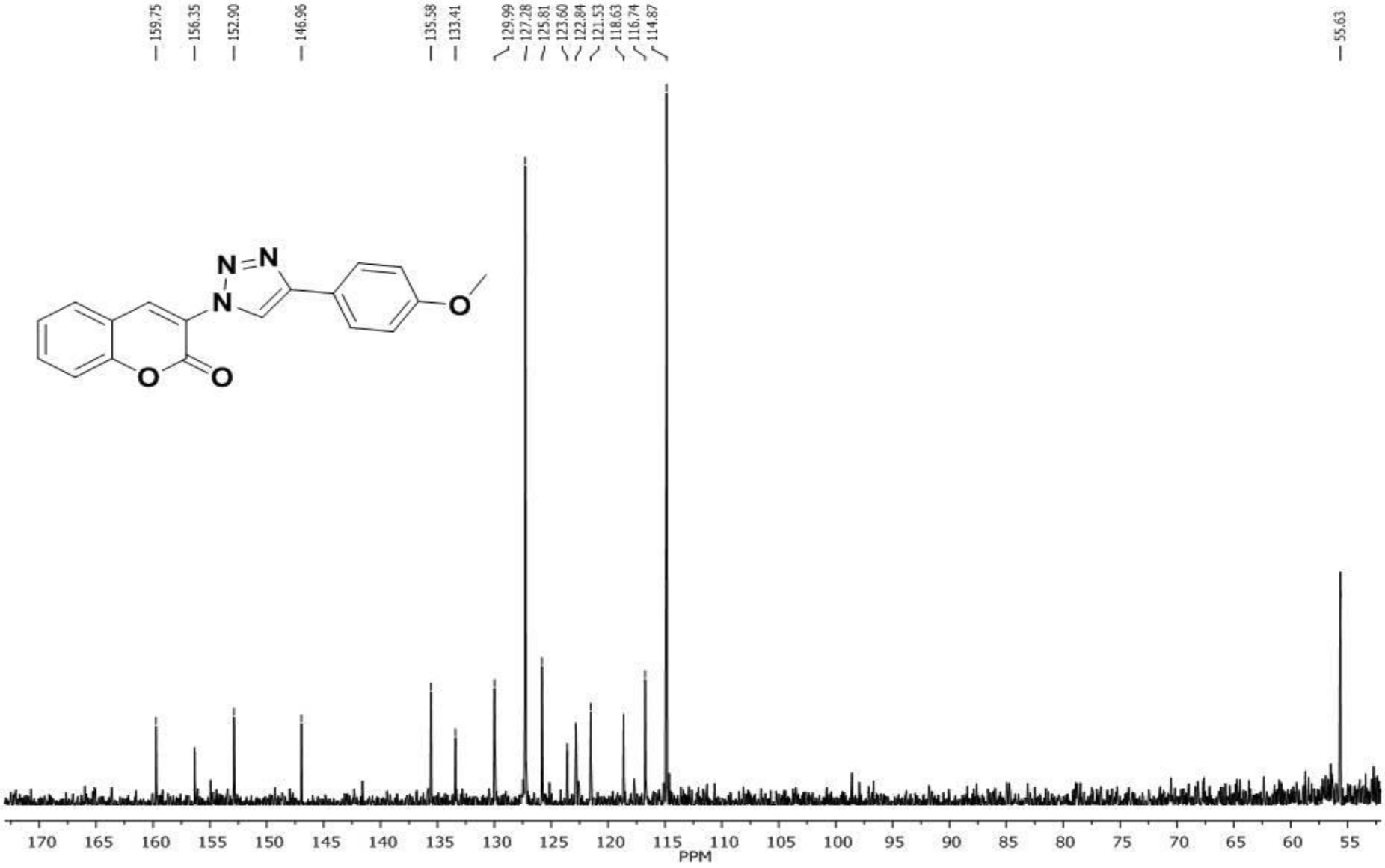
^{13}C-NMR spectrum for compound 7-methoxy-3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5c**)



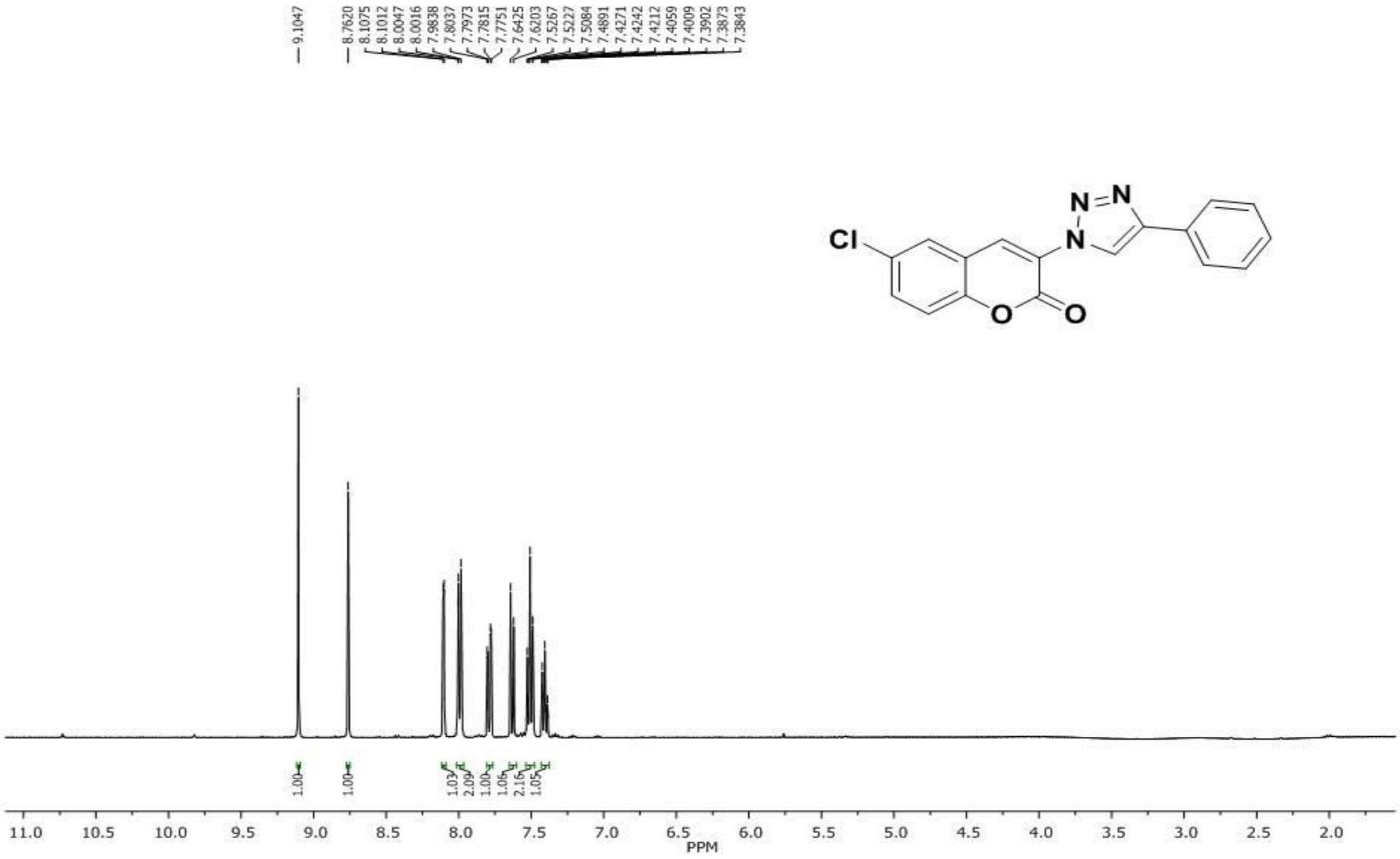
[1]H-NMR spectrum for compound 3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5d**)



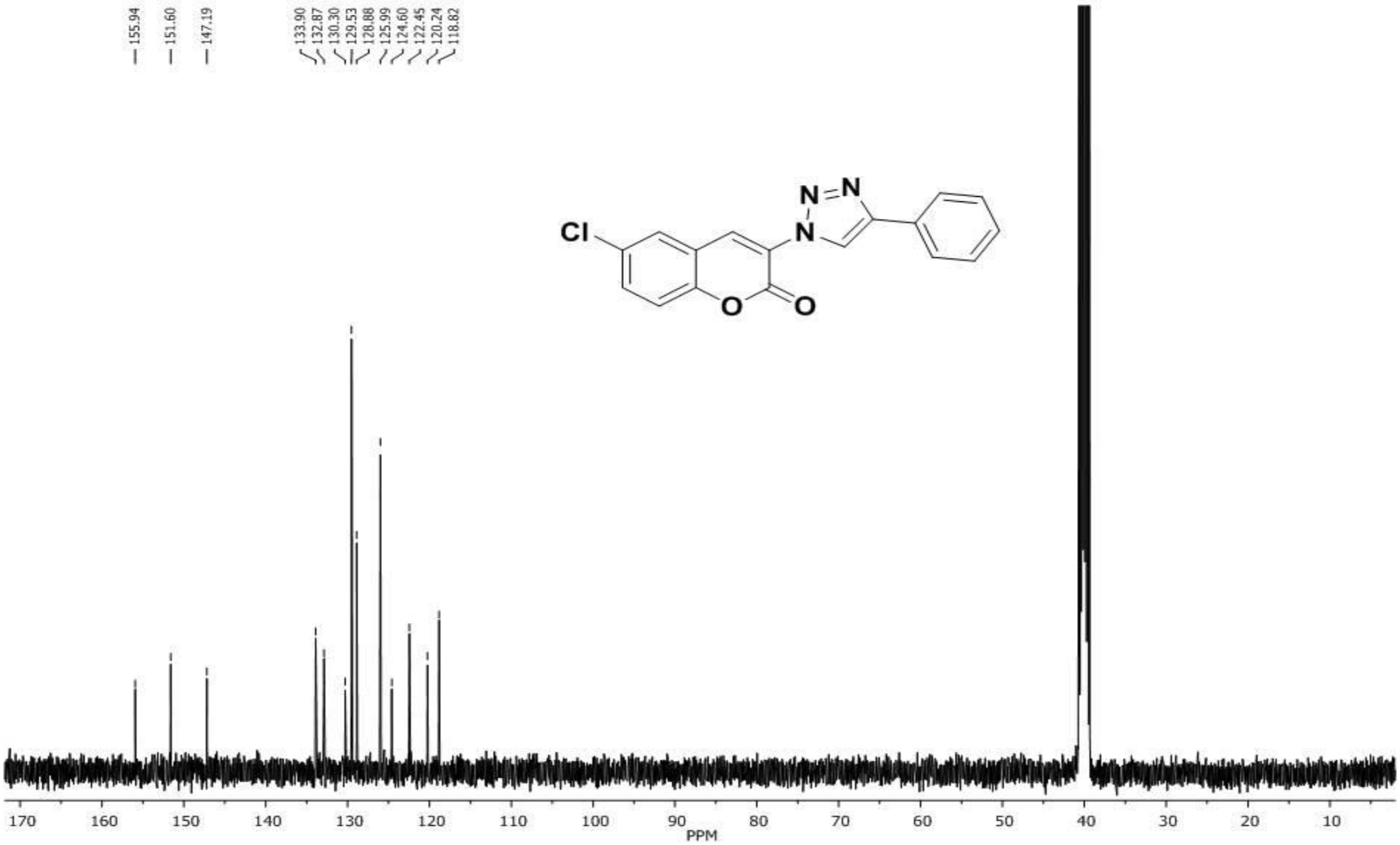
^{13}C-NMR spectrum for compound 3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5d**)



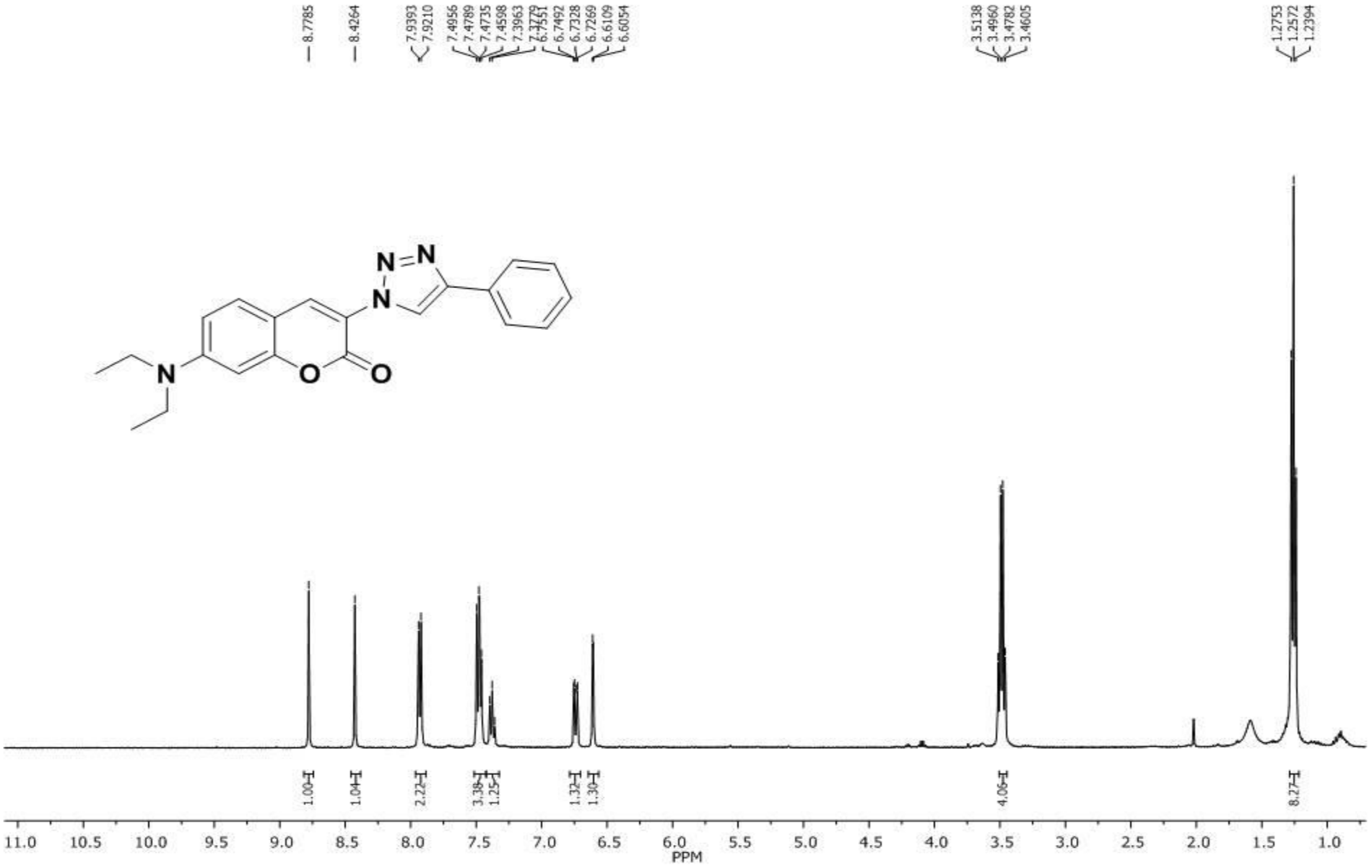
^{1}H-NMR spectrum for compound 6-chloro-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5e**)



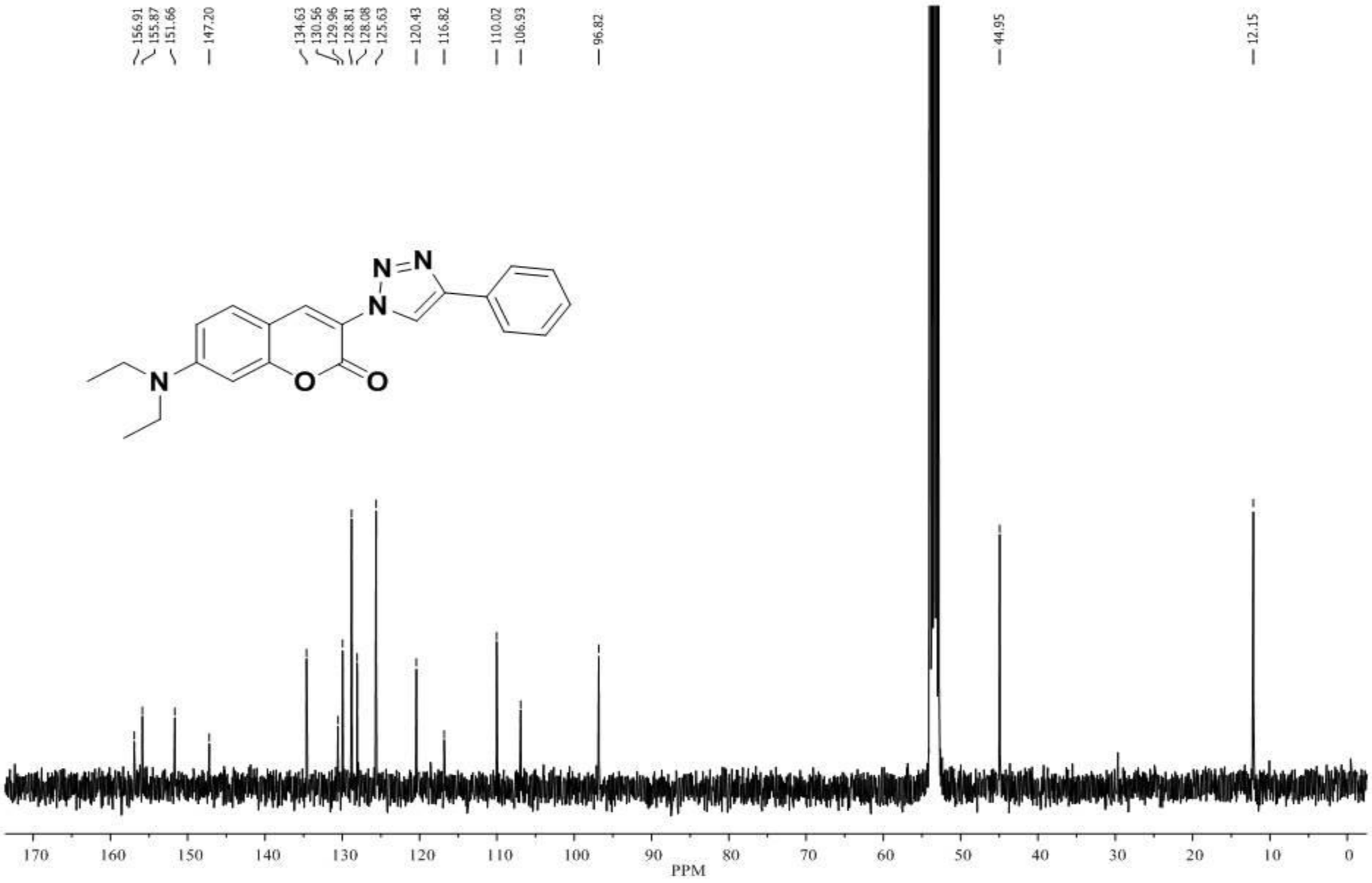
^{13}C-NMR spectrum for compound 6-chloro-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5e**)



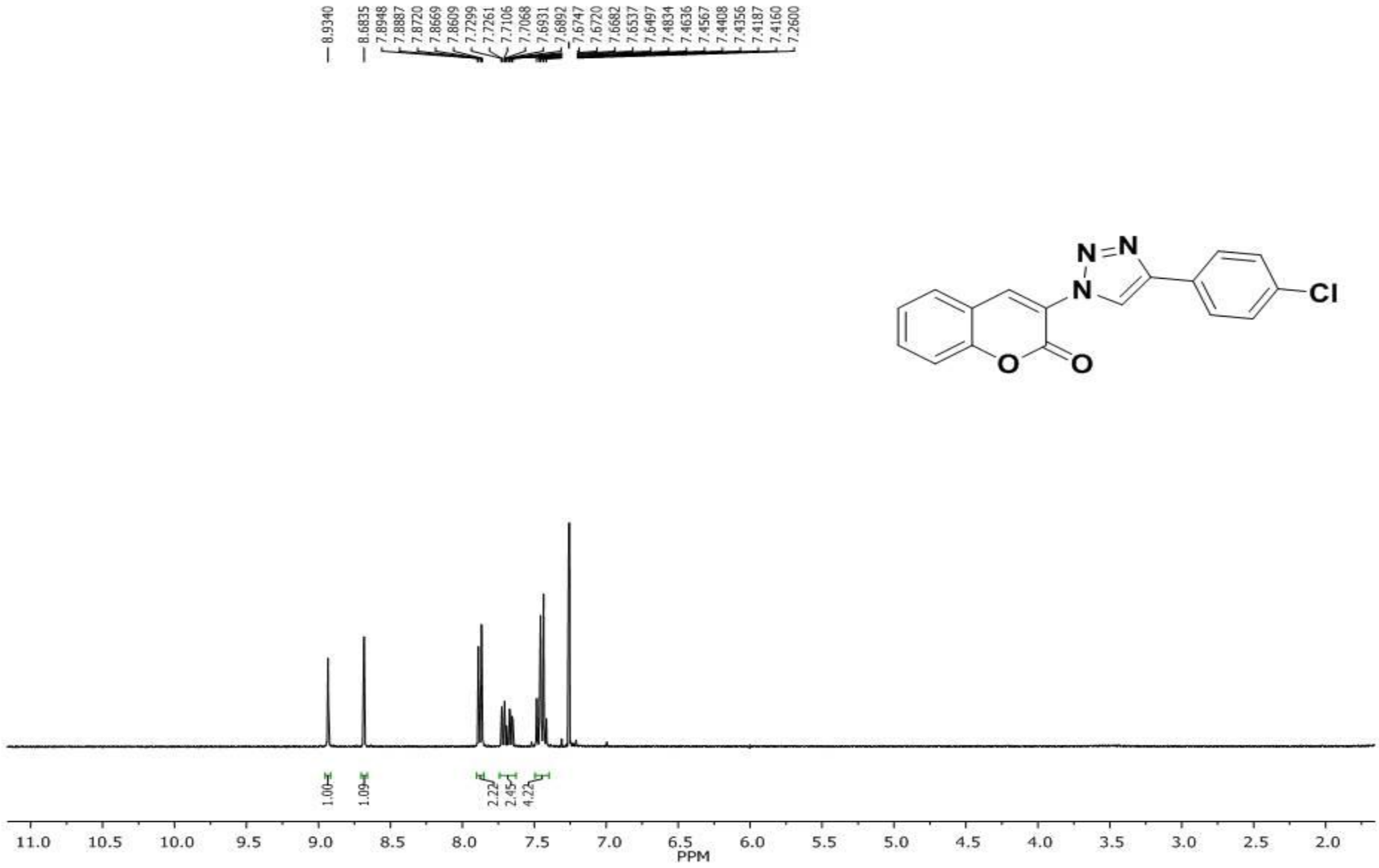
[1]H-NMR spectrum for compound 7-(diethylamino)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one **(5f)**



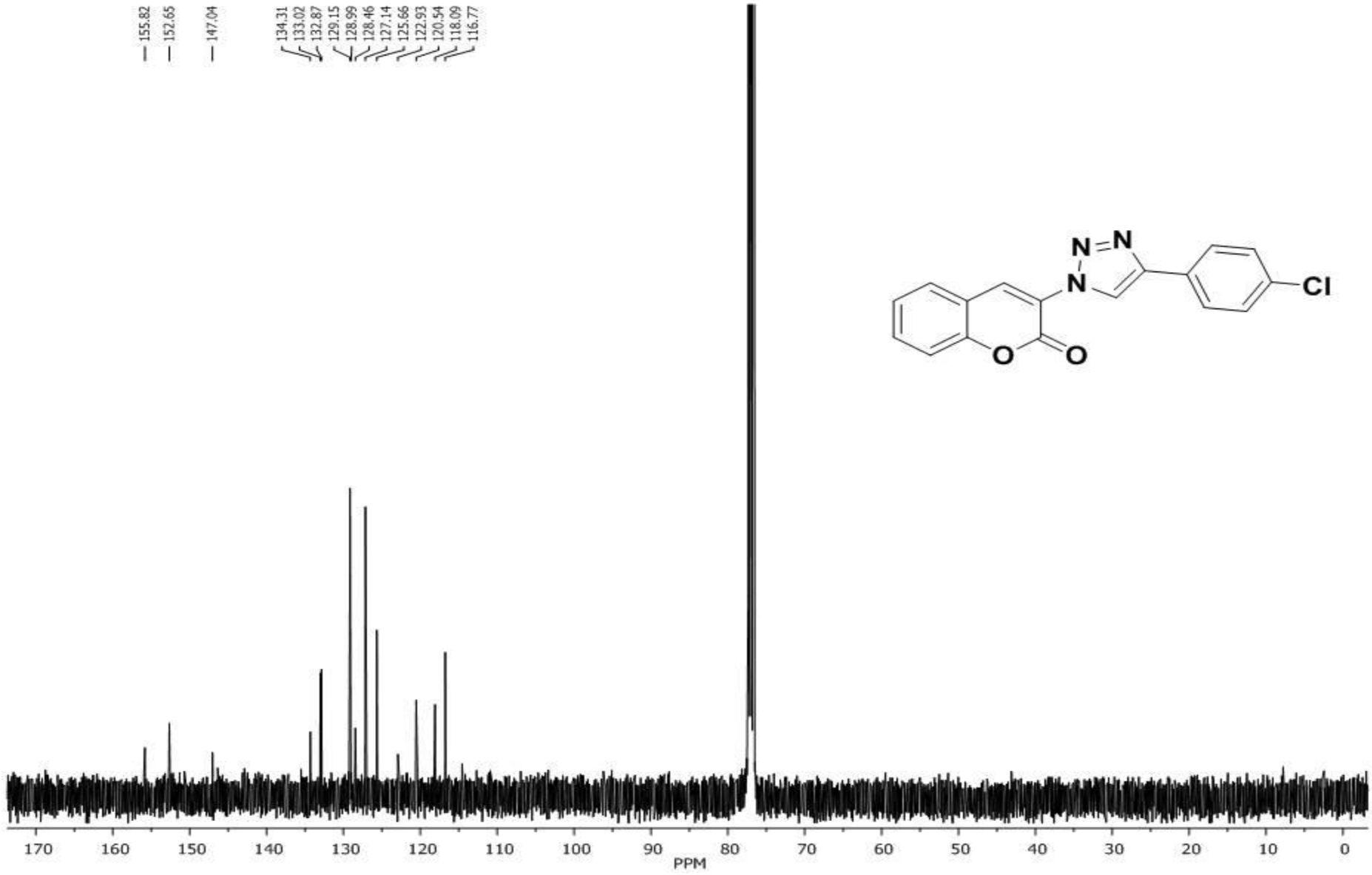
^{13}C-NMR spectrum for compound 7-(diethylamino)-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one **(5f)**



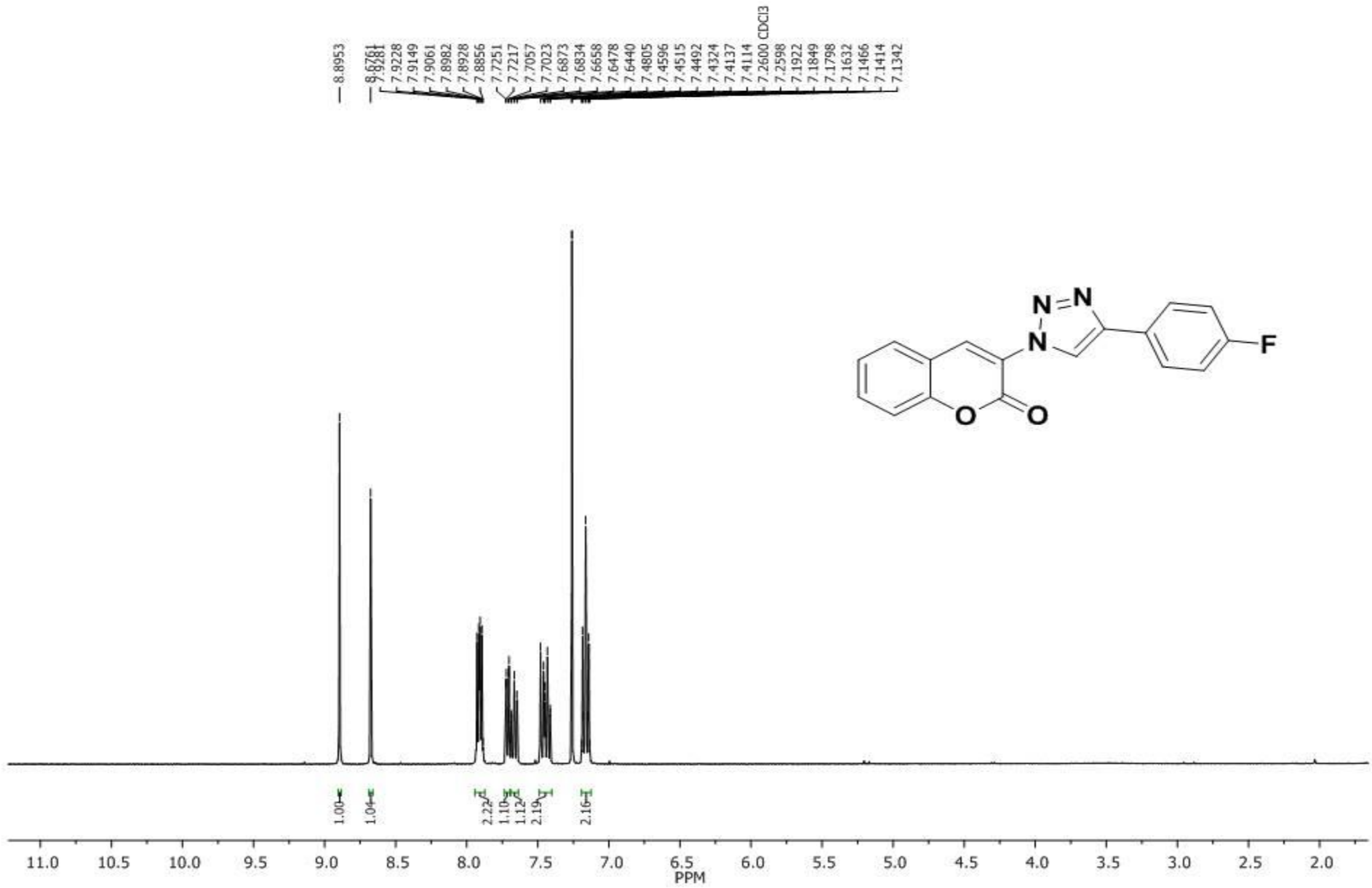
^{1}H-NMR spectrum for compound 3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5g**)



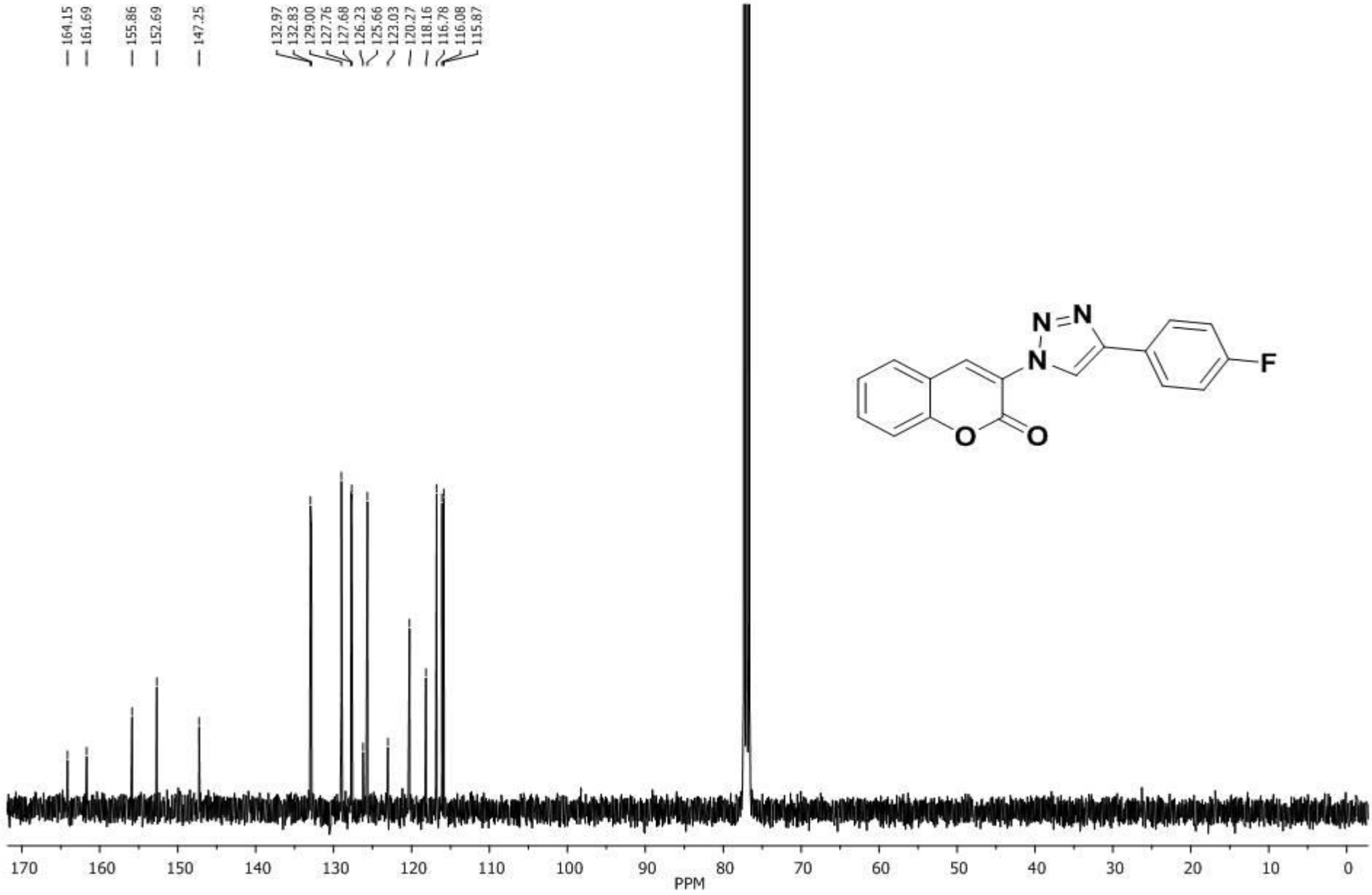
^{13}C-NMR spectrum for compound 3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5g**)



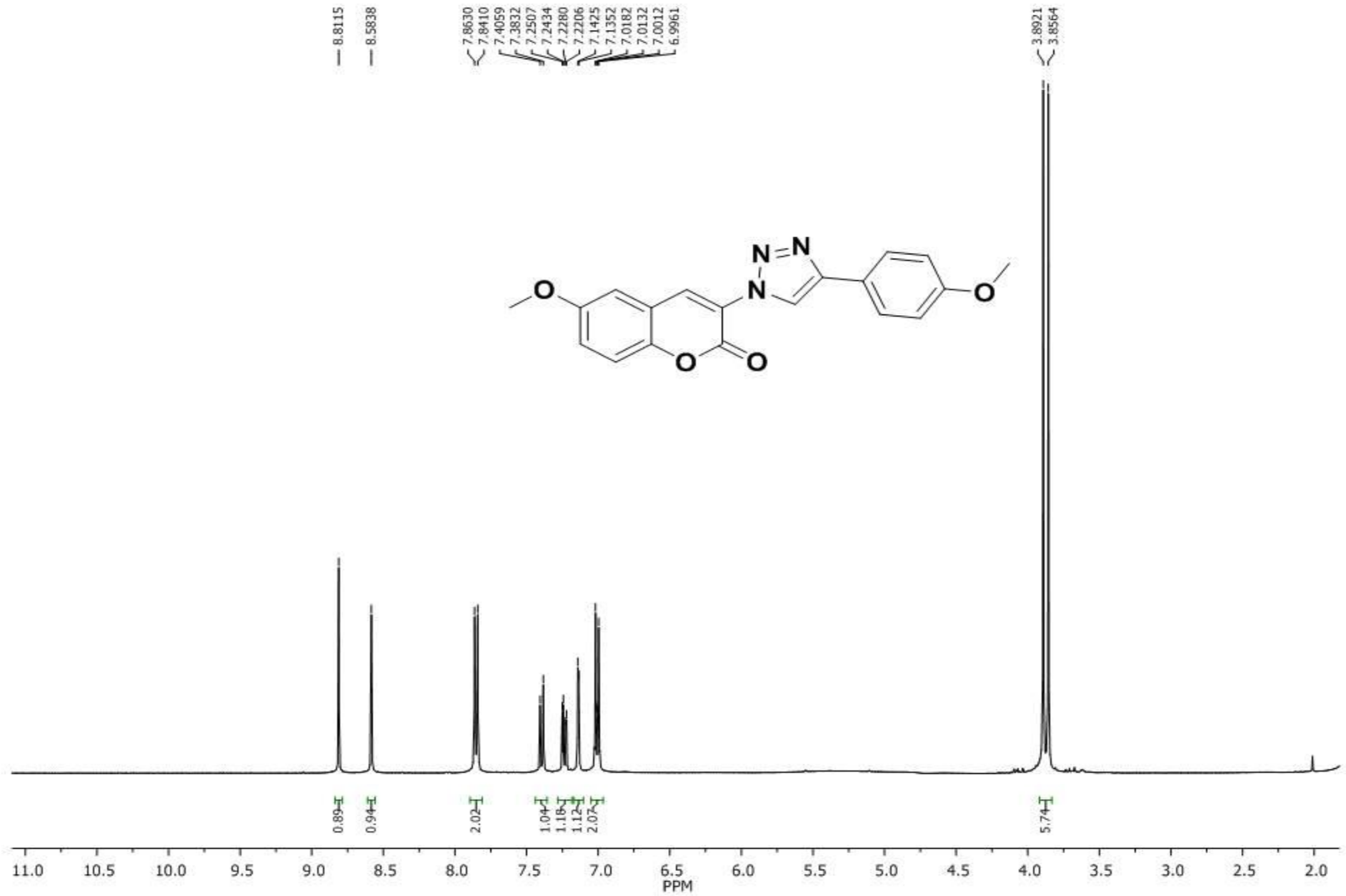
^{1}H-NMR spectrum for compound 3-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5h**)



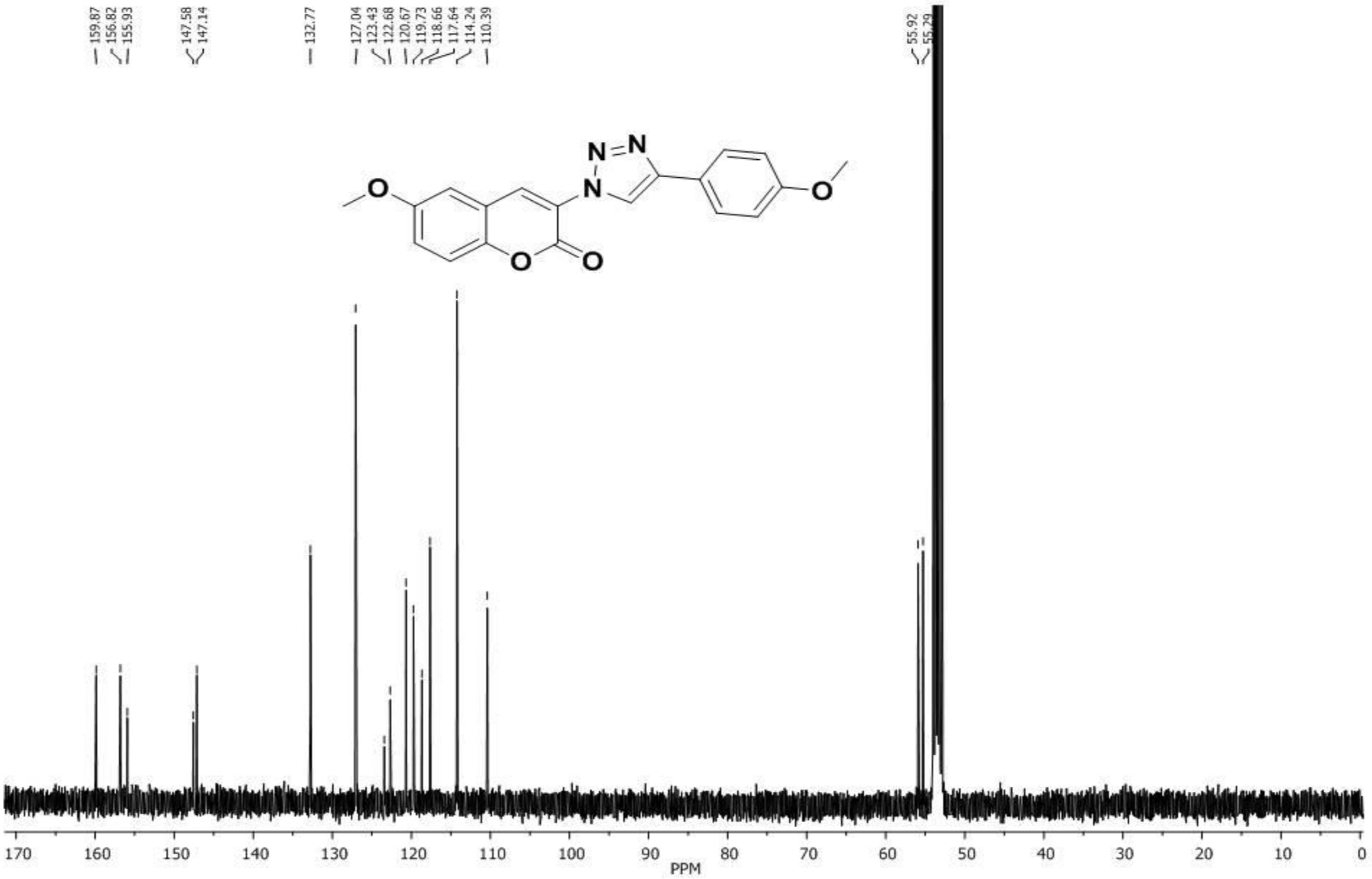
^{13}C-NMR spectrum for compound 3-(4-(4-fluorophenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5h**)



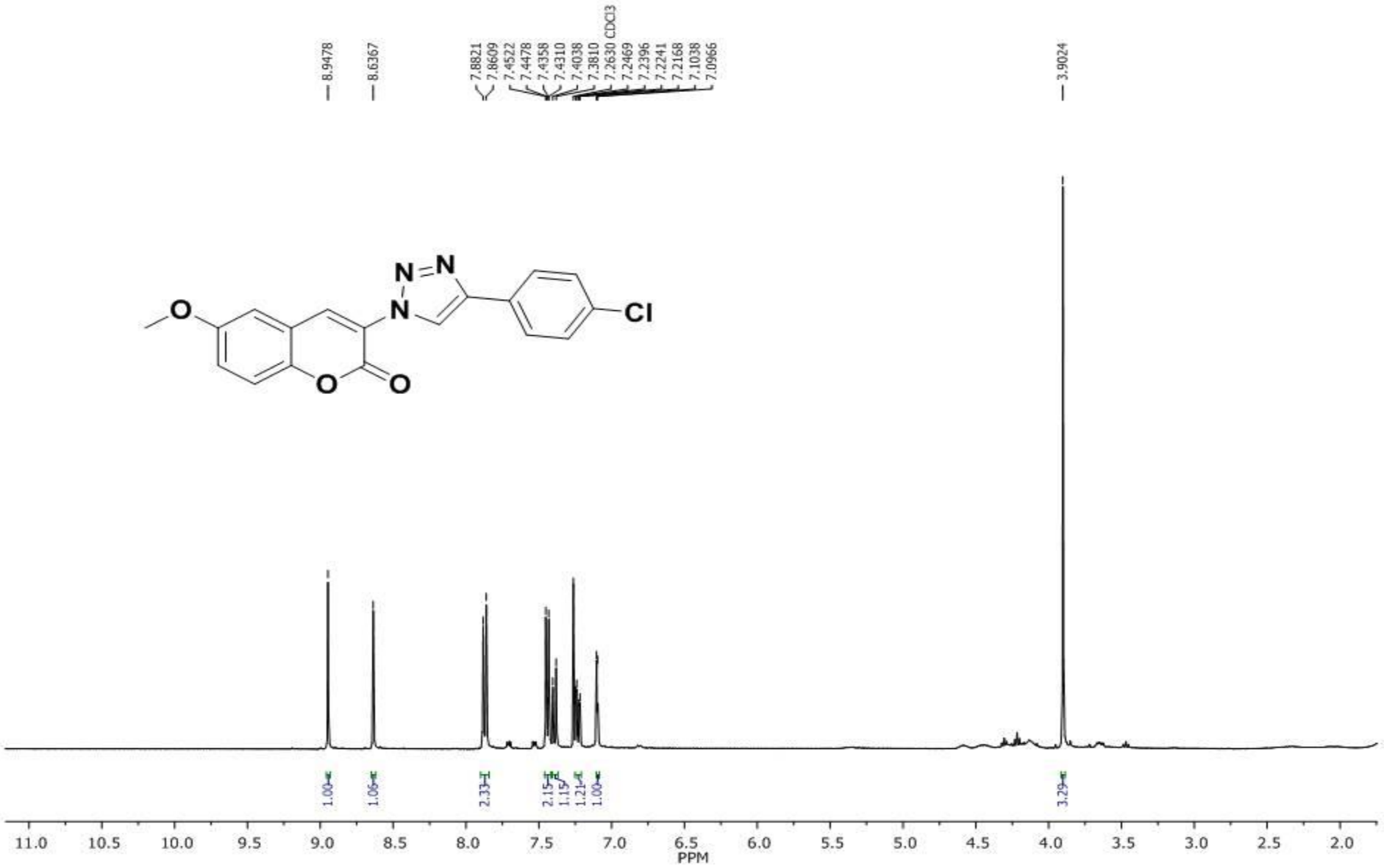
[1]H-NMR spectrum for compound 6-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5i**)



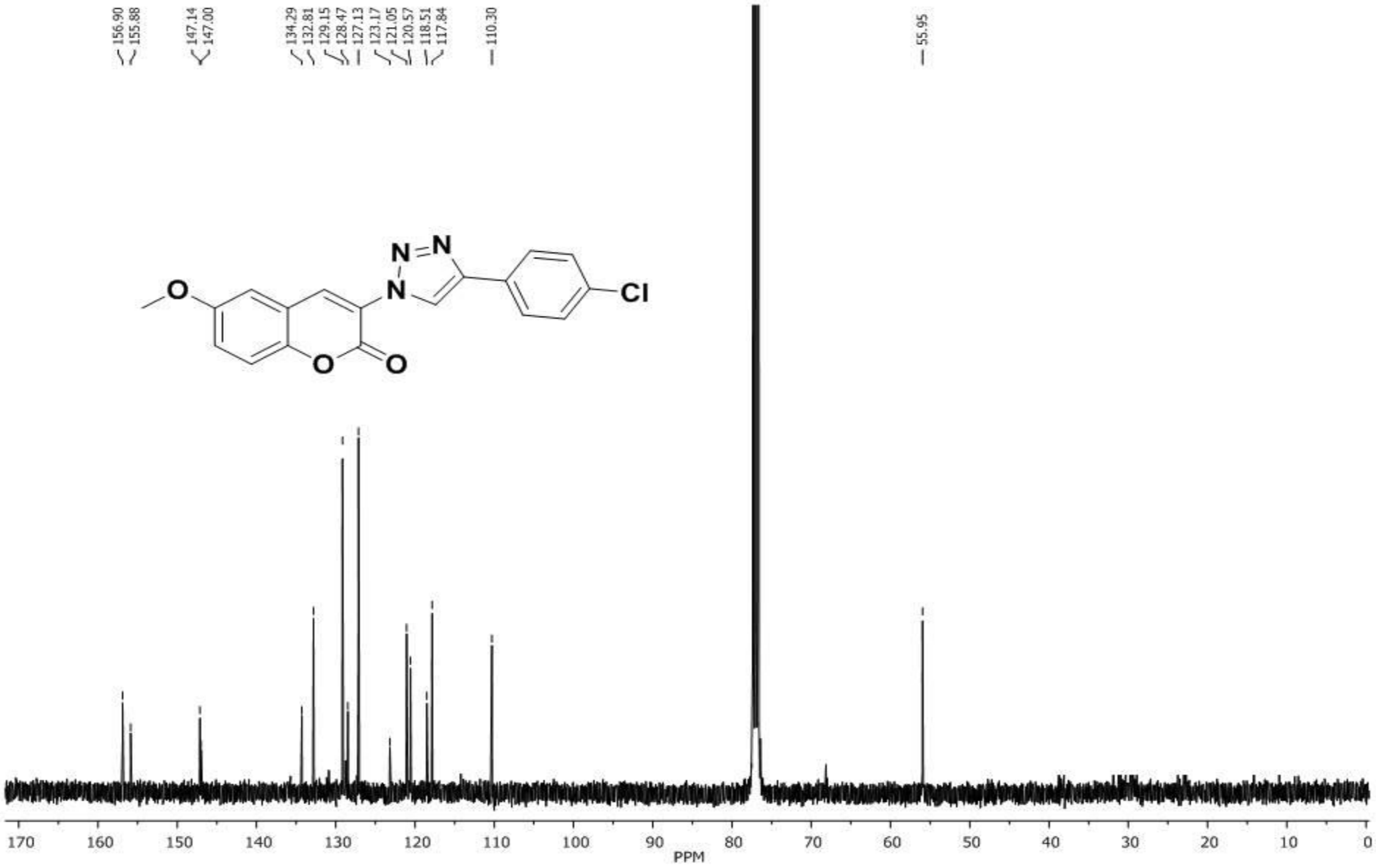
^{13}C-NMR spectrum for compound 6-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5i**)



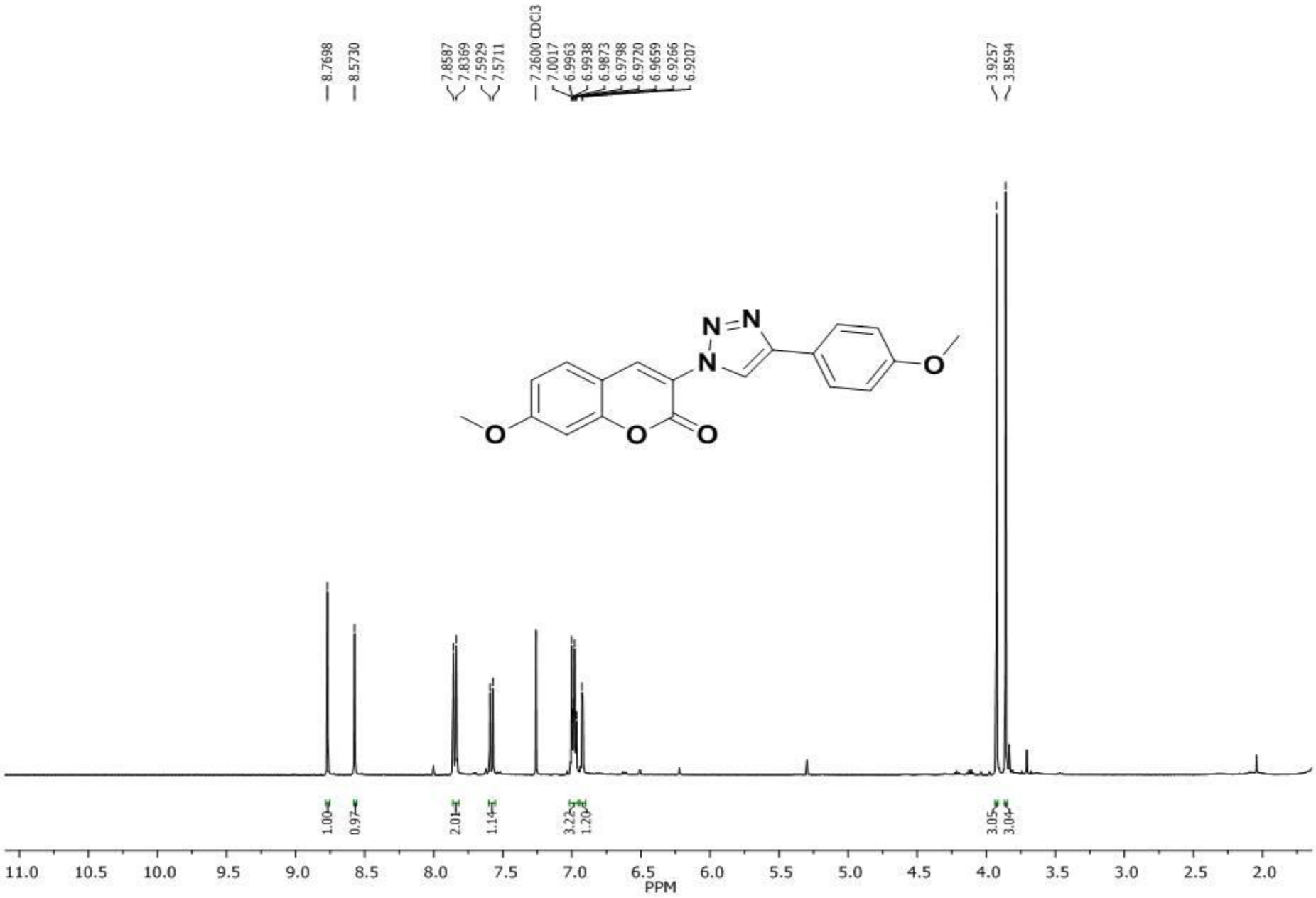
[1]H-NMR spectrum for compound 3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-6-methoxy-2*H*-chromen-2-one (**5j**



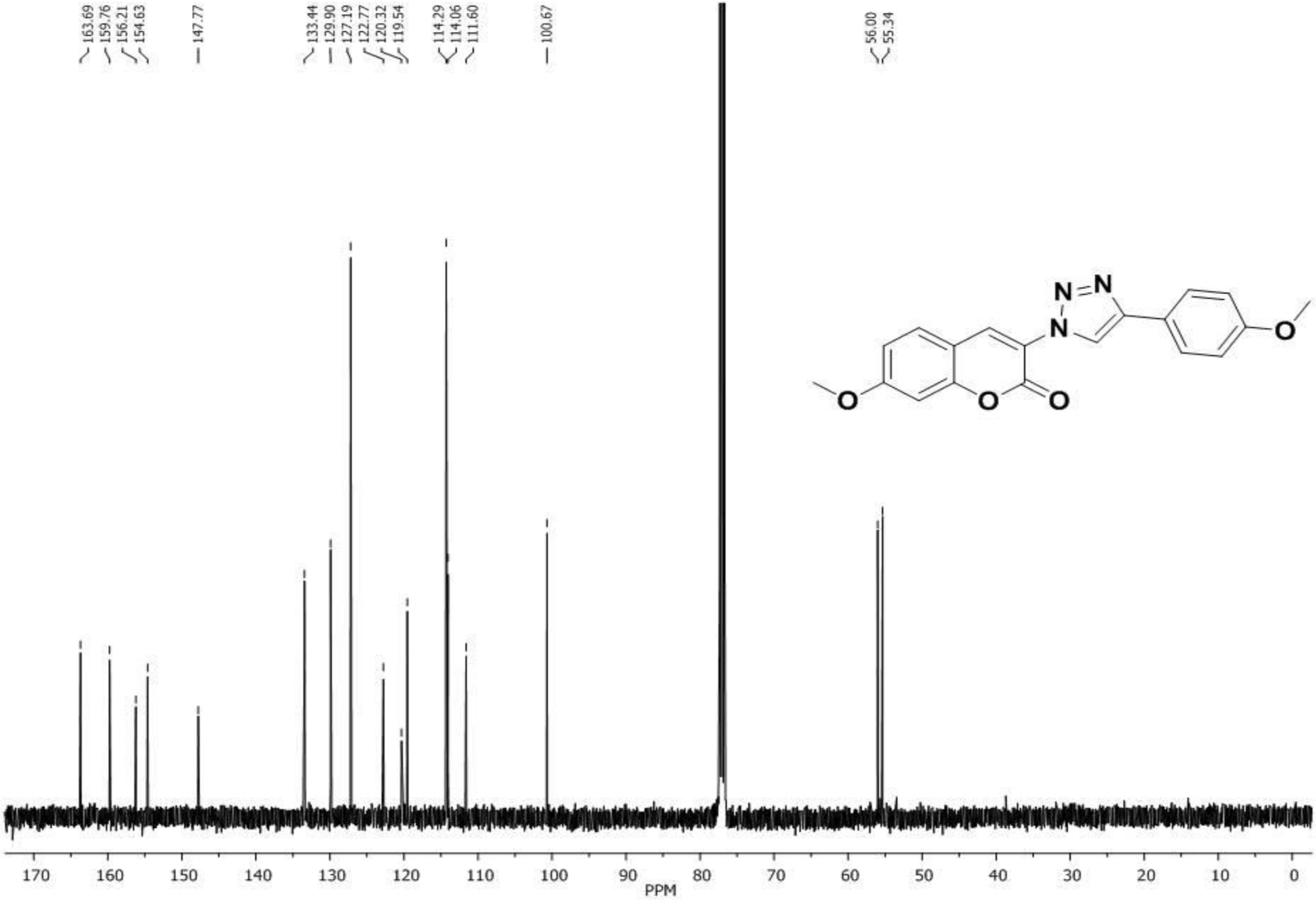
^{13}C-NMR spectrum for compound 3-(4-(4-chlorophenyl)-1*H*-1,2,3-triazol-1-yl)-6-methoxy-2*H*-chromen-2-one (**5j**)



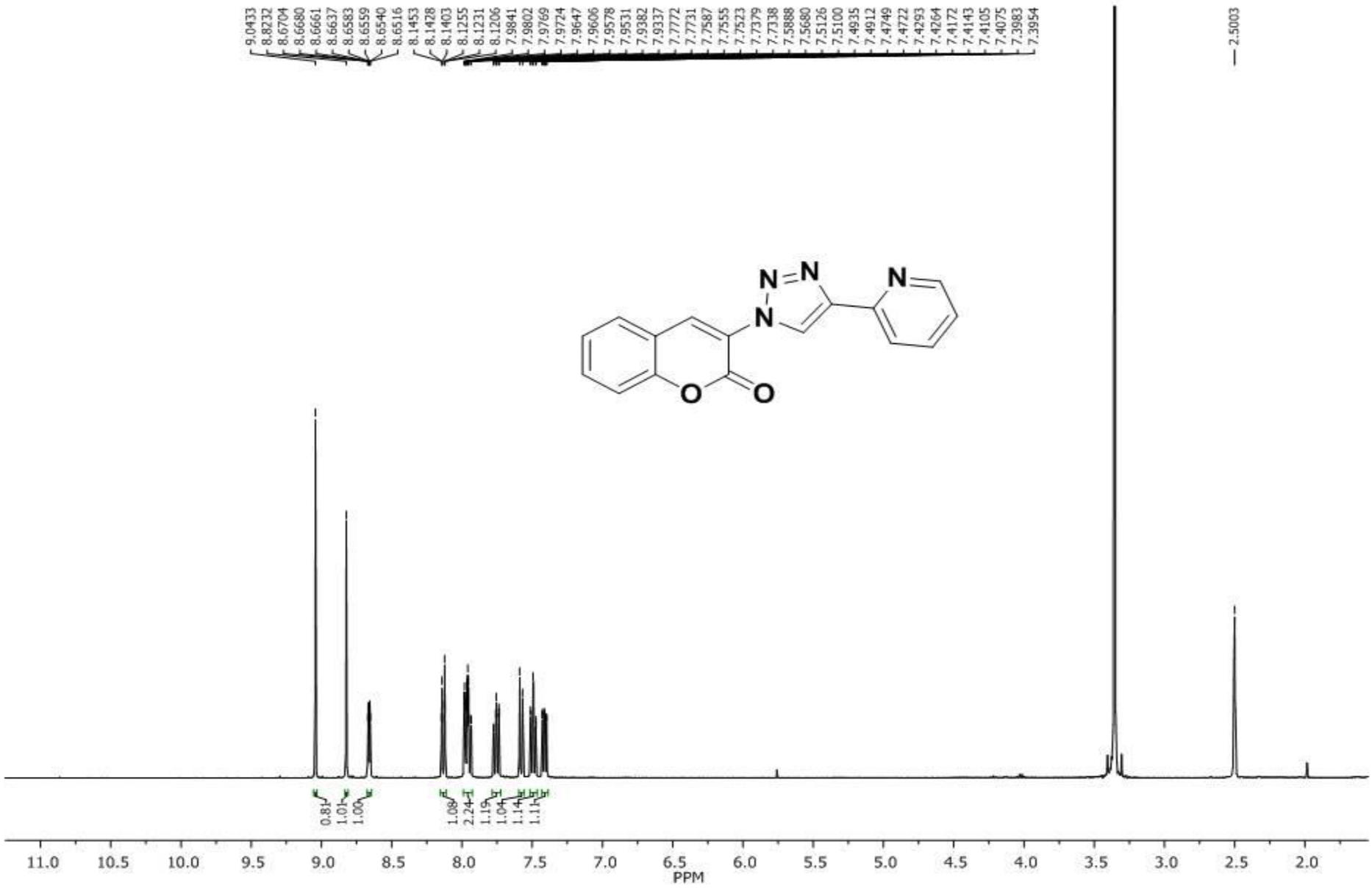
[1]H-NMR spectrum for compound 7-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5k**)



^{13}C-NMR spectrum for compound 7-methoxy-3-(4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5k**)



^{13}H-NMR spectrum for compound 3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5**l)



^{13}C-NMR spectrum for compound 3-(4-(pyridin-2-yl)-1*H*-1,2,3-triazol-1-yl)-2*H*-chromen-2-one (**5l**)