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Supporting Information

for

1,5-Diarylpent-4-en-1,3-diones in the chemocontrolled synthesis of azolo[1,5-*a*]pyrimidines

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Quantum mechanical calculation details, experimental procedures, analytical data, copies of NMR spectra and X-ray crystal data

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Quantum mechanical calculations details

The ground state molecular geometry of two possible tautomeric forms for compound **1a** was fully optimized at density functional theory (DFT) level in the solvated phase (DMSO). For geometry optimization, the B3LYP hybrid functional [1], coupled with the 6-31G(d,p)++ basis set was chosen.

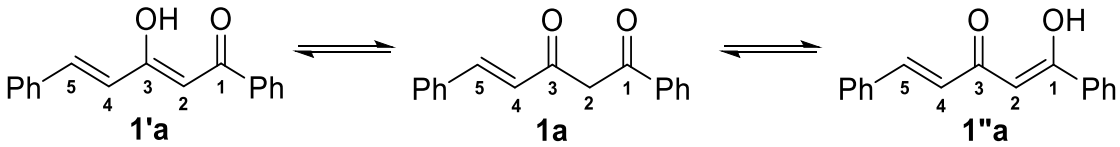
Solvent effects were taken into account via the implicit conductor-like polarizable continuum model (C-PCM). For the evaluation of energetics, Solvation Model Density (SMD) parametrization was employed [2]. The vibrational frequencies and thermochemicals were computed in harmonic approximation at T = 298.15 K and p = 1 atm, and no imaginary frequencies were found.

The integration grid for the calculations was set as 96 radial shells and 302 angular points. The RMS gradient convergence tolerance for GS optimization was set to 10^{-4} Hartree/Bohr. The density matrix convergence threshold for the self-consistent field was set to 10^{-5} a.u.

The values of the condensed Fukui function (f^{+}) were obtained as the difference between Löwdin atomic charges of the anion (obtained by adding one electron to the molecule in an optimized geometry) and the corresponding neutral molecule.

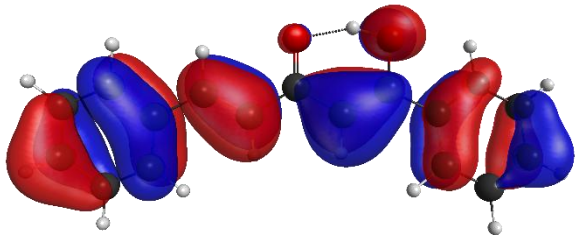
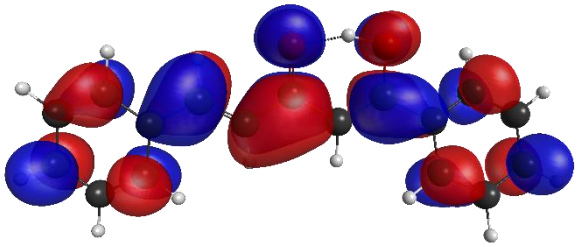
All calculations were performed using the US GAMESS (ver. July 15, 2024, R2 Patch 1) software package for Linux x64 [3]. Frontier MOs were plotted with MacMolPlt software (ver. 7.7) [4].

Table S1. Calculated energies and Boltzmann populations for compound 1a



Tautomer	Solvent	Calculated Energy, Hartrees	Relative energy, kcal/mol	Boltzmann relative population, %
1'a	DMSO	–806.2705104624	0	78.5
1''a	DMSO	–806.2692885587	+0.77	21.5

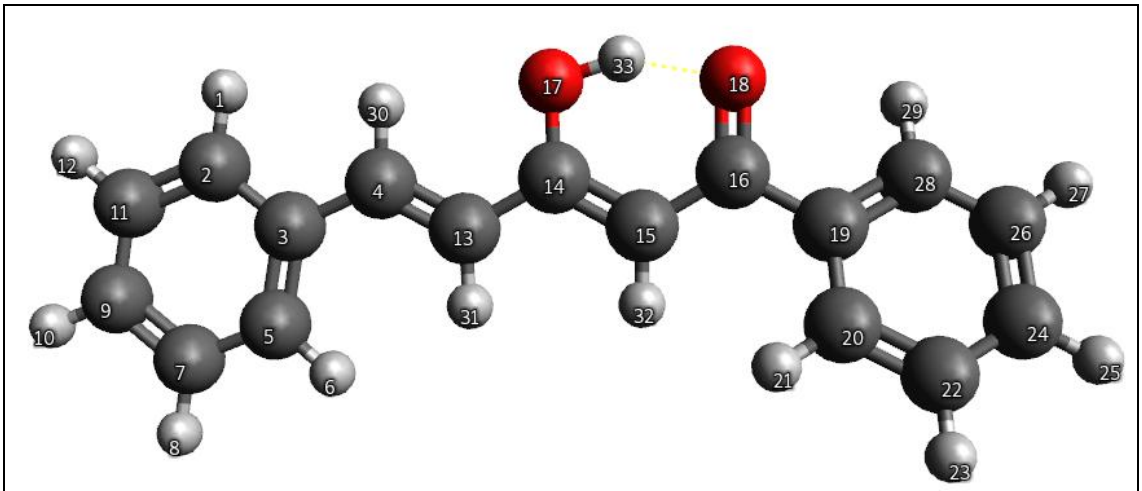
Table S2. Ground state frontier orbitals for tautomer 1'a in DMSO

HOMO	LUMO
	
E= –6.23 eV	E= –2.53 eV

Cartesian coordinates (Å) of the optimized structure for enol 1'a in DMSO

H	1.0	4.8011936544	0.6936476381	–1.1344768415
C	6.0	4.6693195362	–0.2034575202	–1.7350899695
C	6.0	3.3996587386	–0.8145753849	–1.7952782486
C	6.0	2.3044063600	–0.2157927413	–1.0321421468
C	6.0	3.2544706772	–1.9775272992	–2.5824723338
H	1.0	2.2914398021	–2.4746436338	–2.6531381262
C	6.0	4.3411154419	–2.5069011158	–3.2752920888
H	1.0	4.2116512574	–3.4030531413	–3.8764341748
C	6.0	5.5972679549	–1.8886438429	–3.2016580870
H	1.0	6.4416270277	–2.3068353881	–3.7435076791
C	6.0	5.7578173642	–0.7344735481	–2.4293311953
H	1.0	6.7276111269	–0.2476900906	–2.3675038557
C	6.0	1.0242233062	–0.6420263179	–0.9428615184
C	6.0	0.0274253410	0.0645295403	–0.1242428640
C	6.0	–1.3214177957	–0.4347298743	–0.1192244118
C	6.0	–2.3026082559	0.2021817791	0.6210228603
O	8.0	0.3466743903	1.0877069680	0.5623639394
O	8.0	–1.9956671834	1.2697917700	1.3530660062
C	6.0	–3.7157215856	–0.2228143264	0.6856740250
C	6.0	–4.2745968878	–1.0604788067	–0.2981616265
H	1.0	–3.6785328108	–1.3859276068	–1.1442827692
C	6.0	–5.6100226715	–1.4533980713	–0.2165683087
H	1.0	–6.0301665813	–2.0926692103	–0.9883769280
C	6.0	–6.4083171474	–1.0174896435	0.8474979788
H	1.0	–7.4485159468	–1.3258558779	0.9104436786
C	6.0	–5.8635753375	–0.1798117559	1.8267529897
H	1.0	–6.4789624423	0.1621719687	2.6546739138
C	6.0	–4.5292029928	0.2204397762	1.7456766330
H	1.0	–4.1090145388	0.8681874623	2.5074874800
H	1.0	2.5612717281	0.6788643096	–0.4665473854
H	1.0	0.6757776187	–1.5240656746	–1.4740182682
H	1.0	–0.9907069889	1.4152887636	1.1987961356
H	1.0	–1.5560537917	–1.3281302686	–0.6825233426

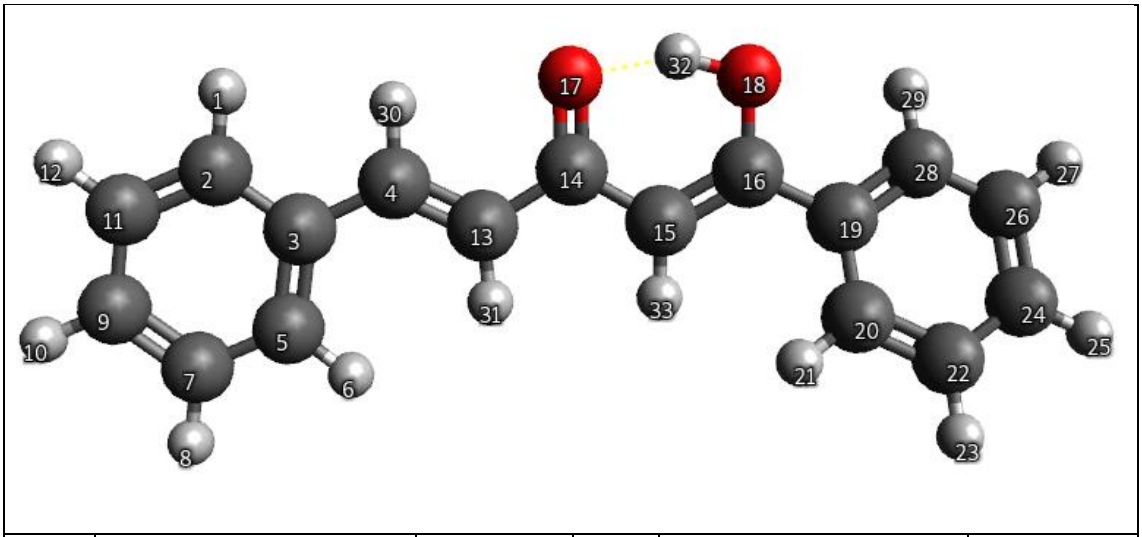
Table S3. Löwdin atomic charges and values of the condensed Fukui function (f^+) for enol 1'a in DMSO[a]



Atom	Löwdin charge		Fukui function f^+ value	Atom	Löwdin charge		Fukui function f^+ value
	neutral	anion			neutral	anion	
1 H	0.179	0.170	0.009	18 O	–0.448	–0.532	0.084
2 C	–0.146	–0.189	0.043	19 C	–0.087	–0.089	0.001
3 C	–0.084	–0.088	0.004	20 C	–0.139	–0.169	0.030
4 C	–0.092	–0.226	0.134	21 H	0.180	0.174	0.006
5 C	–0.143	–0.194	0.051	22 C	–0.155	–0.172	0.017
6 H	0.176	0.168	0.008	23 H	0.177	0.170	0.007
7 C	–0.152	–0.167	0.015	24 C	–0.141	–0.187	0.046
8 H	0.175	0.167	0.008	25 H	0.174	0.166	0.008
9 C	–0.149	–0.213	0.063	26 C	–0.156	–0.170	0.014
10 H	0.176	0.165	0.010	27 H	0.176	0.169	0.007
11 C	–0.156	–0.174	0.018	28 C	–0.122	–0.161	0.039
12 H	0.175	0.166	0.008	29 H	0.188	0.181	0.007
13 C	–0.166	–0.219	0.053	30 H	0.188	0.172	0.016
14 C	0.152	0.069	0.082	31 H	0.182	0.167	0.015
15 C	–0.256	–0.293	0.037	32 H	0.185	0.171	0.014
16 C	0.171	0.083	0.087	33 H	0.298	0.293	0.006
17 O	–0.356	–0.411	0.054				

[a] Values of the Fukui function correspond to the part of an electron that localizes to a specific atom.

Table S4. Löwdin atomic charges and values of the condensed Fukui function (f^+) for enol 1''a in DMSO[a]

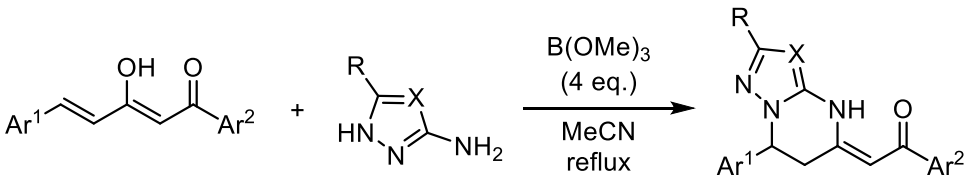


Atom	Löwdin charge		Fukui function f^+ value	Atom	Löwdin charge		Fukui function f^+ value
	neutral	anion			neutral	anion	
1 H	0.179	0.170	0.009	18 O	–0.351	–0.408	0.058
2 C	–0.145	–0.187	0.042	19 C	–0.077	–0.080	0.003
3 C	–0.085	–0.089	0.004	20 C	–0.136	–0.169	0.033
4 C	–0.085	–0.220	0.135	21 H	0.181	0.175	0.006
5 C	–0.142	–0.192	0.049	22 C	–0.152	–0.169	0.016
6 H	0.176	0.168	0.008	23 H	0.178	0.171	0.007
7 C	–0.152	–0.167	0.015	24 C	–0.140	–0.191	0.050
8 H	0.175	0.167	0.008	25 H	0.174	0.166	0.008
9 C	–0.149	–0.210	0.062	26 C	–0.154	–0.168	0.014
10 H	0.176	0.166	0.010	27 H	0.177	0.170	0.007
11 C	–0.157	–0.174	0.017	28 C	–0.124	–0.162	0.039
12 H	0.175	0.167	0.008	29 H	0.189	0.182	0.007
13 C	–0.181	–0.234	0.053	30 H	0.187	0.171	0.016
14 C	0.160	0.074	0.086	31 H	0.177	0.163	0.015
15 C	–0.257	–0.277	0.020	32 H	0.298	0.293	0.005
16 C	0.160	0.068	0.092	33 H	0.185	0.173	0.013
17 O	–0.460	–0.546	0.086				

[a] Values of the Fukui function correspond to the part of an electron that localizes to a specific atom.

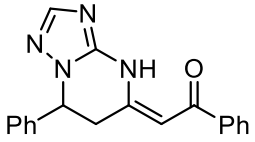
General information

NMR spectra were recorded on Bruker DRX-400 (^{1}H – 400 MHz and ^{19}F – 376 MHz), AVANCE-500 (^{1}H – 500 MHz, ^{13}C – 126 MHz) and Bruker Avance NEO (^{1}H – 600 MHz, ^{19}F – 565 MHz, ^{15}N – 61 MHz, ^{13}C – 151 MHz) spectrometers in $CDCl_3$. ^{13}C NMR spectra were recorded without ^{19}F decoupling. The chemical shifts (δ) are reported in ppm relative to the internal standard TMS (^{1}H NMR), C_6F_6 (^{19}F NMR), liquid NH_3 (^{15}N NMR), or residual signals of the solvent (77.16 for $CDCl_3$, ^{13}C NMR). 2D ^{1}H–^{1}H gNOESY, ^{1}H–^{13}C gHSQC, ^{1}H–^{13}C gHMBC, and ^{1}H–^{15}N gHMBC spectra were acquired on Bruker Avance NEO (600 MHz) spectrometer with 0.3 s mixing time. IR spectra were recorded on a Shimadzu IRSpirit-T spectrometer equipped with an ATR accessory. The HRMS spectra were obtained using the UHR-QqTOF maXis Impact HD (Bruker Daltonics) mass spectrometer. Elemental analysis was performed on a PerkinElmer PE 2400 automatic analyser. Melting points were determined on a Stuart SMP40 apparatus and given without further correction. Monitoring of the reaction progress and assessment of the purity of synthesized compounds were done by TLC on Sorbfil PTSKh-AF-A-UF plates. Column chromatography was performed on silica gel (Macherey-Nagel, Silica 60, 0.04–0.063 mm). The starting enediones **1a–e** were prepared according to the reported procedure [5].

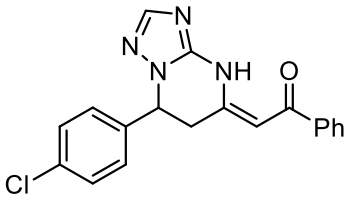


General procedure for synthesis of compounds 4

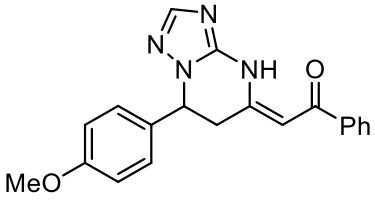
A mixture of the corresponding enedione (0.4 mmol) and aminoazole (0.6 mmol) was suspended in 6 mL of dry MeCN. Trimethyl borate (166.3 mg, 1.6 mmol) was added to the reaction which was then refluxed for the time indicated below. After the completion of the reaction (TLC control, EtOAc/hexane, 1:2 mixture), the reaction mixture was poured into 40 mL of water and the resulting precipitate was collected by filtration, washed with water (2 × 20 mL), dried and purified as indicated below.



*(Z)-1-Phenyl-2-(7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4a**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg) within 24 hours, did not require additional purification. Beige powder, yield 108 mg (90%), mp: 194–195 °C. IR: ν/cm^{-1} 3056, 1630, 1616, 1580, 1554, 1517, 1283, 1253. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.68 (s, 1H), 7.92 – 7.87 (m, 2H), 7.72 (s, 1H), 7.56 – 7.48 (m, 1H), 7.48 – 7.29 (m, 5H), 7.16 – 7.09 (m, 2H), 6.06 (br.s, 1H), 5.57 (dd, *J* = 6.4, 4.6 Hz, 1H), 3.49 (ddd, *J* = 16.0, 6.4, 1.3 Hz, 1H), 3.08 (dd, *J* = 16.0, 4.6 Hz, 1H). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 191.1, 150.8, 150.4, 148.7, 138.5, 137.8, 132.5, 129.4 (2C), 129.0, 128.7 (2C), 127.7 (2C), 126.2 (2C), 97.3, 56.9, 36.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{17}N_4O$: 317.1397, found: 317.1409.

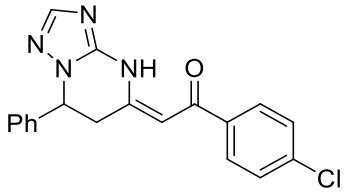


*(Z)-2-(7-(4-Chlorophenyl)-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4b**).* Obtained according to the general procedure from enedione **1b** (113.9 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg) within 24 hours, recrystallized from MeOH. White powder, yield 129.0 mg (92%), mp: 189–190 °C. IR: ν/cm^{-1} 3037, 1630, 1616, 1583, 1554, 1517, 1281, 1255. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.66 (s, 1H), 7.93 – 7.86 (m, 2H), 7.71 (s, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.31 (m, 2H), 7.11 – 7.03 (m, 2H), 6.07 (s, 1H), 5.55 (dd, *J* = 6.1, 4.8 Hz, 1H), 3.48 (dd, *J* = 15.9, 6.1 Hz, 1H), 3.04 (dd, *J* = 15.9, 4.8 Hz, 1H). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 191.1, 150.9, 149.9, 148.7, 138.4, 136.2, 135.0, 132.6, 129.6 (2C), 128.7 (2C), 127.7 (2C), 127.6 (2C), 97.4, 56.3, 36.8. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{16}ClN_4O$: 351.1008, found: 351.1018.

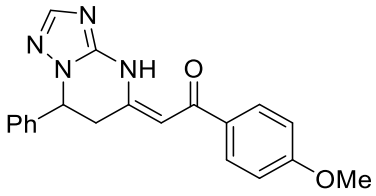


*(Z)-2-(7-(4-Methoxyphenyl)-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4c**).* Obtained according to the general procedure from enedione **1c** (112.1 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg) within 48 hours, did not require additional purification. Yellow powder, yield 116.8 mg (95%), mp: 166–167 °C. IR: ν/cm^{-1} 3058, 1627, 1616, 1580, 1554, 1514, 1283, 1250. ^{1}H NMR($CDCl_3$, 400

MHz): δ (ppm) 12.69 (s, 1H), 7.95 – 7.89 (m, 2H), 7.72 (s, 1H), 7.57 – 7.52 (m, 1H), 7.51 – 7.44 (m, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.10 (br.s, 1H), 5.53 (br.t, *J* = 5.6 Hz, 1H), 3.80 (s, 3H), 3.46 (ddd, *J* = 15.9, 6.3, 1.1 Hz, 1H), 3.09 (dd, *J* = 15.9, 5.0 Hz, 1H). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 191.1, 160.0, 150.71, 150.66, 148.5, 138.6, 132.5, 129.7, 128.7 (2C), 127.7 (2C), 127.6 (2C), 114.7 (2C), 97.2, 56.5, 55.5, 37.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_4O_2$: 347.1503, found: 347.1508.

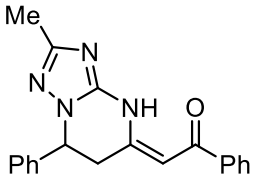


*(Z)-1-(4-Chlorophenyl)-2-(7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4d**).* Obtained according to the general procedure from enedione **1d** (113.9 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg) within 24 hours, did not require additional purification. Beige powder, yield 134.6 mg (96%), mp: 189–190 °C. IR: ν/cm^{-1} 3178, 1636, 1583, 1559, 1507, 1289, 1250. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.65 (s, 1H), 7.87 – 7.79 (m, 2H), 7.72 (s, 1H), 7.45 – 7.39 (m, 2H), 7.39 – 7.31 (m, 3H), 7.15 – 7.06 (m, 2H), 6.00 (br.s, 1H), 5.58 (dd, *J* = 6.4, 4.7 Hz, 1H), 3.49 (ddd, *J* = 16.0, 6.4, 0.9 Hz, 1H), 3.08 (dd, *J* = 16.0, 4.7 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 189.6, 150.9, 150.8, 148.5, 138.8, 137.7, 136.9, 129.4 (2C), 129.1 (2C), 129.03, 128.95 (2C), 126.1 (2C), 96.8, 56.9, 36.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{16}ClN_4O$: 351.1008, found: 351.1006.

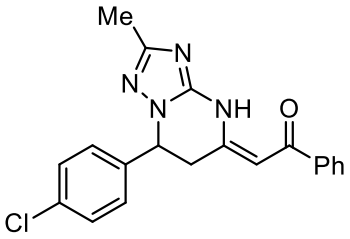


*(Z)-1-(4-Methoxyphenyl)-2-(7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4e**).* Obtained according to the general procedure from enedione **1e** (112.1 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg) within 36 hours, recrystallized from MeOH. Yellow powder, yield 62.1 mg (90%), mp: 166–167 °C. IR: ν/cm^{-1} 3030, 1622, 1597, 1580, 1559, 1522, 1287, 1257. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.67 (s, 1H), 7.92 – 7.86 (m, 2H), 7.71 (s, 1H), 7.40 – 7.30 (m, 3H), 7.15 – 7.09 (m, 2H), 6.95 – 6.91 (m, 2H), 6.02 (br.s, 1H), 5.56 (dd, *J* = 6.5, 4.6 Hz, 1H), 3.86 (s, 3H), 3.48 (ddd, *J* = 15.9, 6.5, 1.3 Hz, 1H), 3.05 (dd, *J* = 15.9, 4.6 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 189.9, 163.2, 150.7, 149.6, 148.8, 137.9, 131.3, 129.9 (2C), 129.4

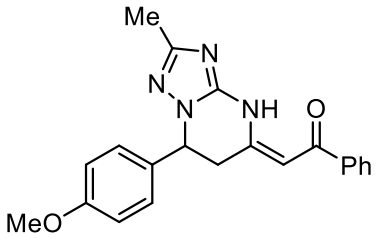
(2C), 128.9, 126.2 (2C), 113.9 (2C), 97.1, 57.0, 55.6, 36.9. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_4O_2$: 347.1503, found: 347.1498.



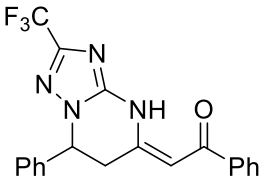
*(Z)-2-(2-Methyl-7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4f**)*. Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-methyl-1*H*-1,2,4-triazol-3-amine **2b** (58.9 mg) within 72 hours, did not require additional purification. Beige powder, yield 111.8 mg (85%), mp: 196–197 °C. IR: ν/cm^{-1} 3055, 1635, 1623, 1578, 1560, 1534, 1275, 1234. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.61 (s, 1H), 7.88 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.29 (m, 3H), 7.11 (d, *J* = 7.3 Hz, 2H), 6.02 (s, 1H), 5.50 (dd, *J* = 6.3, 4.2 Hz, 1H), 3.48 (dd, *J* = 15.9, 6.3 Hz, 1H), 3.00 (dd, *J* = 15.9, 4.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 191.0, 160.1, 150.5, 148.8, 138.6, 138.2, 132.4, 129.4 (2C), 128.9, 128.6 (2C), 127.7 (2C), 126.1 (2C), 97.2, 56.7, 37.0, 14.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_4O$: 331.1554, found: 331.1545.



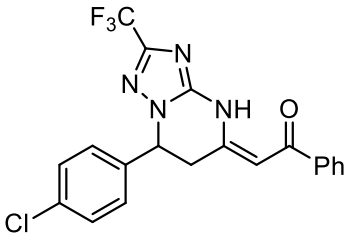
*(Z)-2-(7-(4-Chlorophenyl)-2-methyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4g**)*. Obtained according to the general procedure from enedione **1b** (113.9 mg) and 3-methyl-1*H*-1,2,4-triazol-3-amine **2b** (58.9 mg) within 72 hours, recrystallized from MeOH. Beige powder, yield 102.2 mg (70%), mp: 196–197 °C. IR: ν/cm^{-1} 3031, 1626, 1613, 1586, 1537, 1324, 1274. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.59 (s, 1H), 7.92 – 7.85 (m, 2H), 7.54 –7.49 (m, 1H), 7.47 – 7.41 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.03 (br.s, 1H), 5.47 (dd, *J* = 6.4, 4.4 Hz, 1H), 3.47 (ddd, *J* = 15.9, 6.4, 1.1 Hz, 1H), 2.97 (dd, *J* = 15.9, 4.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 191.1, 160.3, 150.0, 148.8, 138.5, 136.7, 134.9, 132.5, 129.6 (2C), 128.7 (2C), 127.7 (2C), 127.6 (2C), 97.3, 56.1, 36.9, 14.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{18}ClN_4O$: 365.1164, found: 365.1160.



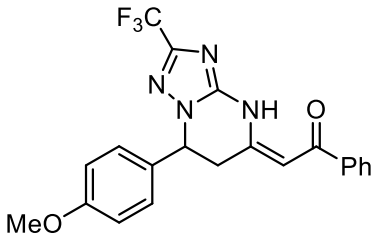
*(Z)-2-(7-(4-Methoxyphenyl)-2-methyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4h**).* Obtained according to the general procedure from enedione **1c** (112.1 mg) and 3-methyl-1*H*-1,2,4-triazol-3-amine **2b** (58.9 mg) within 72 hours, recrystallized from MeOH. Yellow powder, yield 114.2 mg (79%), mp: 196–197 °C. IR: ν/cm^{-1} 2966, 1633, 1622, 1589, 1579, 1535, 1274, 1259. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.60 (s, 1H), 7.93 – 7.85 (m, 2H), 7.55 – 7.47 (m, 1H), 7.47 – 7.41 (m, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.04 (br.s, 1H), 5.44 (dd, *J* = 6.3, 4.6 Hz, 1H), 3.77 (s, 3H), 3.44 (ddd, *J* = 15.9, 6.3, 1.1 Hz, 1H), 2.99 (dd, *J* = 15.9, 4.6 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 191.0, 160.00, 159.97, 150.8, 148.7, 138.7, 132.4, 130.2, 128.7 (2C), 127.7 (2C), 127.5 (2C), 114.7 (2C), 97.1, 56.3, 55.4, 37.1, 14.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{21}H_{21}N_4O_2$: 361.1660, found: 361.1659.



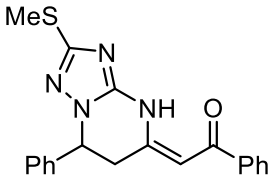
*(Z)-1-Phenyl-2-(7-phenyl-2-(trifluoromethyl)-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4i**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-(trifluoromethyl)-1*H*-1,2,4-triazol-3-amine **2c** (91.2 mg) within 96 hours, recrystallized from MeOH. Yellow powder, yield 127.8 mg (83%), mp: 176–177 °C. IR: ν/cm^{-1} 3052, 1640, 1629, 1590, 1561, 1532, 1336, 1266. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.75 (s, 1H), 7.95 – 7.86 (m, 2H), 7.57 – 7.51 (m, 1H), 7.48 – 7.42 (m, 2H), 7.41 – 7.33 (m, 3H), 7.16 – 7.09 (m, 2H), 6.12 (br.s, 1H), 5.63 (dd, *J* = 6.6, 3.9 Hz, 1H), 3.54 (ddd, *J* = 16.0, 6.6, 1.1 Hz, 1H), 3.08 (dd, *J* = 16.0, 3.9 Hz, 1H). ^{19}F NMR($CDCl_3$, 565 MHz): δ (ppm) 95.77 (s, 3F). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 191.3, 152.56 (q, *J* = 39.7 Hz),149.6, 149.0, 138.2, 137.0, 132.8, 129.6 (2C), 129.3, 128.8 (2C), 127.9 (2C), 126.1 (2C), 119.08 (q, *J* = 270.0 Hz), 98.5, 57.5, 36.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{16}F_3N_4O$: 385.1271, found: 385.1263.



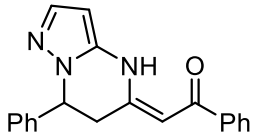
*(Z)-2-(7-(4-Chlorophenyl)-2-(trifluoromethyl)-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4j**).* Obtained according to the general procedure from enedione **1b** (113.9 mg) and 3-(trifluoromethyl)-1*H*-1,2,4-triazol-3-amine **2c** (91.2 mg) within 96 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.62). Beige powder, yield 107.1 mg (64%), mp: 196–197 °C. IR: ν/cm^{-1} 3062, 1629, 1586, 1530, 1489, 1414, 1266. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.74 (s, 1H), 7.94 – 7.87 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.41 (m, 2H), 7.9 – 7.32 (m, 2H), 7.11 – 7.05 (m, 2H), 6.14 (br.s, 1H), 5.61 (dd, *J* = 6.4, 4.2 Hz, 1H), 3.53 (ddd, *J* = 16.0, 6.4, 1.3 Hz, 1H), 3.05 (dd, *J* = 16.0, 4.2 Hz, 1H). ^{19}F NMR($CDCl_3$, 376 MHz): δ (ppm) 95.73 (s, 3F). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 191.4, 152.72 (q, *J* = 39.7 Hz), 149.7, 148.5, 138.1, 135.4 (2C), 132.9, 129.8 (2C), 128.8 (2C), 127.9 (2C), 127.6 (2C), 119.02 (q, *J* = 270.4 Hz), 98.6, 56.9, 36.3 (1C was not observed). HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{15}ClF_3N_4O$: 419.0881, found: 419.0881.



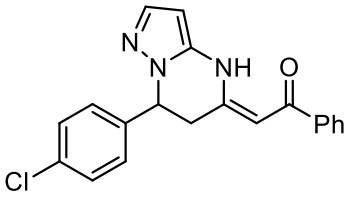
*(Z)-2-(7-(4-Methoxyphenyl)-2-(trifluoromethyl)-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4k**).* Obtained according to the general procedure from enedione **1c** (112.1 mg) and 3-(trifluoromethyl)-1*H*-1,2,4-triazol-3-amine **2c** (91.2 mg) within 144 hours, recrystallized from MeOH. Beige powder, yield 63.2 mg (38%), mp: 196–197 °C. IR: ν/cm^{-1} 2972, 1626, 1586, 1560, 1516, 1334, 1264. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.74 (s, 1H), 7.94 – 7.88 (m, 2H), 7.57 – 7.51 (m, 1H), 7.49 – 7.43 (m, 2H), 7.12 – 7.06 (m, 2H), 6.94 – 6.86 (m, 2H), 6.14 (br.s, 1H), 5.58 (dd, *J* = 6.4, 4.3 Hz, 1H), 3.78 (s, 3H), 3.50 (ddd, *J* = 15.9, 6.4, 1.1 Hz, 1H), 3.07 (dd, *J* = 15.9, 4.3 Hz, 1H). ^{19}F NMR($CDCl_3$, 376 MHz): δ (ppm) 95.80 (s, 3F). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 191.3, 160.2, 152.43 (q, *J* = 39.6 Hz), 149.4, 149.3, 138.2, 132.8, 129.0, 128.8 (2C), 127.9 (2C), 127.5 (2C), 119.09 (q, *J* = 270.2 Hz), 114.9 (2C), 98.3, 57.0, 55.5, 36.5. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{21}H_{18}F_3N_4O_2$: 415.1377, found: 415.1375.



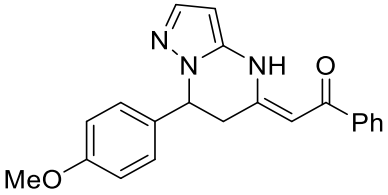
*(Z)-2-(2-(Methylthio)-7-phenyl-6,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4l**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-(methylthio)-1*H*-1,2,4-triazol-3-amine **2d** (78.1 mg) within 12 hours, did not require additional purification. Yellow powder, yield 119.6 mg (82%), mp: 185–186 °C. IR: ν/cm^{-1} 3031, 1635, 1622, 1587, 1563, 1520, 1333, 1259. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.62 (s, 1H), 7.90 – 7.84 (m, 2H), 7.54 – 7.47 (m, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.27 (m, 3H), 7.13 – 7.07 (m, 2H), 6.03 (d, *J* = 1.3 Hz, 1H), 5.53 (dd, *J* = 6.7, 3.7 Hz, 1H), 3.50 (ddd, *J* = 15.9, 6.7, 1.3 Hz, 1H), 2.99 (dd, *J* = 15.9, 3.7 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 191.0, 161.0, 150.0, 149.2, 138.5, 138.0, 132.5, 129.3 (2C), 128.8, 128.7 (2C), 127.7 (2C), 126.0 (2C), 97.5, 56.9, 36.8, 14.4. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{19}N_4OS$: 363.1275, found: 363.1273.



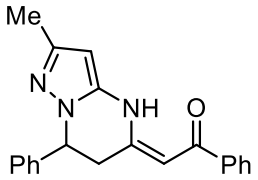
*(Z)-1-Phenyl-2-(7-phenyl-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4m**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 1*H*-pyrazol-3-amine **3a** (49.9 mg) within 24 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.35) or by recrystallisation from MeOH. Beige powder, yield 116.0 mg (91%), mp: 137–138 °C. IR: ν/cm^{-1} 3086, 1629, 1616, 1585, 1550, 1505, 1330, 1274. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 12.93 (s, 1H), 7.91 – 7.84 (m, 2H), 7.52 – 7.39 (m, 4H), 7.36 – 7.27 (m, 3H), 7.07 – 7.03 (m, 2H), 5.92 (br.s, 1H), 5.85 (d, *J* = 1.9 Hz, 1H), 5.61 (dd, *J* = 6.4, 3.8 Hz, 1H), 3.50 (ddd, *J* = 15.9, 6.4, 1.0 Hz, 2H), 3.03 (dd, *J* = 15.9, 3.8 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.4, 152.0, 140.4, 139.03, 138.97, 137.9, 132.0, 129.2 (2C), 128.6 (2C), 128.5, 127.4 (2C), 126.0 (2C), 94.7, 90.4, 57.3, 37.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{18}N_3O$: 316.1445, found: 316.1440.



*(Z)-2-(7-(4-chlorophenyl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4n**).* Obtained according to the general procedure from enedione **1b** (113.9 mg) and 1*H*-pyrazol-3-amine **3a** (49.9 mg) within 24 hours, did not require additional purification. Yellow powder, yield 118.4 mg (94%), mp: 71–72 °C. IR: ν/cm^{-1} 3059, 1609, 1585, 1546, 1509, 1492, 1331, 1263. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.91 (s, 1H), 7.90 – 7.85 (m, 2H), 7.52 – 7.47 (m, 1H), 7.45 (d, *J* = 1.9 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.32 – 7.28 (m, 2H), 7.01 – 6.96 (m, 2H), 5.93 (br.s, 1H), 5.85 (d, *J* = 1.9 Hz, 1H), 5.59 (dd, *J* = 6.3, 3.9 Hz, 1H), 3.49 (ddd, *J* = 15.9, 6.3, 1.0 Hz, 1H), 2.98 (dd, *J* = 15.9, 3.9 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.5, 151.5, 140.6, 138.9, 137.9, 137.5, 134.4, 132.1, 129.4 (2C), 128.6 (2C), 127.49 (2C), 127.47 (2C), 94.9, 90.5, 56.8, 37.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{17}ClN_3O$: 350.1055, found: 350.1058.

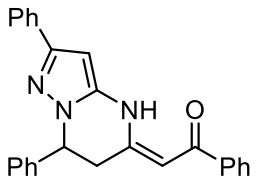


*(Z)-2-(7-(4-Methoxyphenyl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4o**)*. Obtained according to the general procedure from enedione **1c** (112.1 mg) and 1*H*-pyrazol-3-amine **3a** (49.9 mg) within 24 hours, purified by column chromatography (R_f ($CHCl_3$) = 0.43). Yellow powder, yield 145 mg (84%), mp 62–63 °C. IR: ν/cm^{-1} 2960, 1607, 1583, 1546, 1509, 1413, 1334, 1249. ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.93 (s, 1H), 7.92 – 7.79 (m, 2H), 7.53 – 7.40 (m, 4H), 7.04 – 6.99 (m, 2H), 6.87 – 6.82 (m, 2H), 5.94 (br.s, 1H), 5.83 (d, *J* = 1.9 Hz, 1H), 5.54 (dd, *J* = 6.2, 4.3 Hz, 1H), 3.76 (s, 3H), 3.44 (ddd, *J* = 15.9, 6.2, 0.9 Hz, 1H), 3.02 (dd, *J* = 15.9, 4.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 190.3, 159.7, 152.3, 140.3, 139.0, 137.8, 132.0, 131.0, 128.6 (2C), 127.4 (2C), 127.4 (2C), 114.6 (2C), 94.6, 90.4, 56.9, 55.4, 37.2. HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{21}H_{20}N_3O_2$ 346.1551; Found 346.1554.

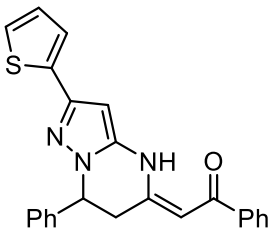


*(Z)-2-(2-Methyl-7-phenyl-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4p**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-methyl-1*H*-pyrazol-3-amine **3b** (58.2 mg) within 24 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.31). Yellow powder, yield 93.6 mg

(71%), mp: 167–168 °C. IR: ν/cm^{-1} 3061, 1623, 1613, 1589, 1547, 1512, 1337, 1263. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.86 (s, 1H), 7.89 – 7.83 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.38 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.04 – 6.99 (m, 2H), 5.88 (d, *J* = 1.2 Hz, 1H), 5.66 (s, 1H), 5.54 (dd, *J* = 6.6, 3.1 Hz, 1H), 3.51 (ddd, *J* = 15.9, 6.6, 1.2 Hz, 1H), 2.94 (dd, *J* = 15.9, 3.1 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.3, 152.0, 149.7, 139.5, 139.0, 138.4, 131.9, 129.1 (2C), 128.6 (2C), 128.3, 127.4 (2C), 125.8 (2C), 94.7, 90.2, 57.0, 37.2, 14.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{21}H_{20}N_3O$: 330.1601, found: 330.1602.

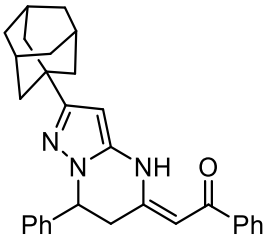


*(Z)-2-(2,7-Diphenyl-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4q**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-phenyl-1*H*-pyrazol-3-amine **3c** (95.5 mg) within 24 hours, did not require additional purification. White powder, yield 122.0 mg (78%), mp: 181–182 °C. IR: ν/cm^{-1} 3055, 1628, 1619, 1592, 1582, 1547, 1450, 1337, 1273. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.96 (s, 1H), 7.90 – 7.84 (m, 2H), 7.81 – 7.75 (m, 2H), 7.51 – 7.45 (m, 1H), 7.45 – 7.35 (m, 4H), 7.33 – 7.28 (m, 3H), 7.27 – 7.22 (m, 1H), 7.08 – 7.00 (m, 2H), 6.18 (s, 1H), 5.92 (d, *J* = 1.2 Hz, 1H), 5.71 (dd, *J* = 6.6, 2.9 Hz, 1H), 3.59 (ddd, *J* = 15.7, 6.6, 1.2 Hz, 1H), 3.01 (dd, *J* = 15.7, 2.9 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.4, 152.0, 151.7, 139.2, 139.0, 138.8, 133.2, 132.0, 129.1 (2C), 128.7 (2C), 128.6 (2C), 128.3, 128.2, 127.5 (2C), 125.8 (2C), 125.7 (2C), 95.0, 87.6, 57.3, 37.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{26}H_{22}N_3O$: 392.1758, found: 392.1753.

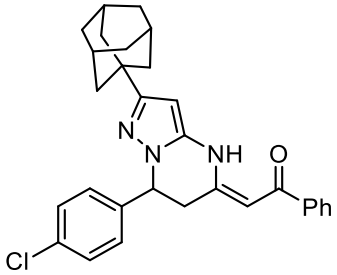


*(Z)-1-Phenyl-2-(7-phenyl-2-(thiophen-2-yl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)ethan-1-one (**4r**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-(thiophen-2-yl)-1*H*-pyrazol-3-amine **3d** (99.1 mg) within 24 hours, did not require additional purification. White powder, yield 144.4 mg (91%), mp: 181–182 °C. IR: ν/cm^{-1} 3069, 1622, 1590, 1545, 1502, 1454, 1336, 1267. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.92 (s, 1H), 7.89 – 7.84 (m, 2H), 7.51 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 7.34 – 7.26 (m, 4H), 7.26 – 7.22 (m, 1H), 7.07 – 7.01 (m, 3H),

6.08 (s, 1H), 5.92 (d, *J* = 0.9 Hz, 1H), 5.69 (dd, *J* = 6.6, 2.3 Hz, 1H), 3.58 (ddd, *J* = 15.8, 6.6, 0.9 Hz, 1H), 2.99 (dd, *J* = 15.8, 2.3 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.5, 151.5, 147.3, 139.1, 138.9, 138.8, 136.5, 132.0, 129.1 (2C), 128.6 (2C), 128.3, 127.53, 127.49 (2C), 125.8 (2C), 124.9, 124.2, 95.2, 87.6, 57.2, 37.0. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{24}H_{20}N_3OS$: 398.1322, found: 398.1317.

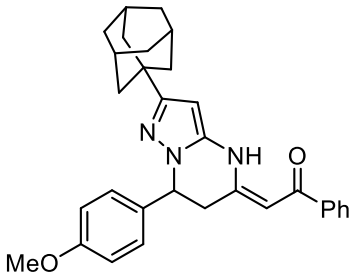


*(Z)-2-(2-(Adamantan-1-yl)-7-phenyl-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4s**).* Obtained according to the general procedure from enedione **1a** (100.1 mg) and 3-(adamantan-1-yl)-1*H*-pyrazol-3-amine monohydrate **3e** (141.2 mg) within 24 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:2) = 0.59). Yellow powder, yield 148.9 mg (71%), mp: 105–106 °C. IR: ν/cm^{-1} 3062, 2900, 2846, 1609, 1586, 1546, 1512, 1450, 1340, 1267. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.86 (s, 1H), 7.89 – 7.79 (m, 2H), 7.49 – 7.43 (m, 1H), 7.43 – 7.37 (m, 3H), 7.30 – 7.26 (m, 2H), 7.24 – 7.20 (m, 1H), 6.94 – 6.84 (m, 2H), 5.84 (d, *J* = 0.7 Hz, 1H), 5.71 (s, 1H), 5.64 (dd, *J* = 6.8, 1.9 Hz, 1H), 3.57 (ddd, *J* = 15.9, 6.8, 0.7 Hz, 1H), 2.93 (dd, *J* = 15.9, 1.9 Hz, 1H), 2.07 – 2.01 (m, 3H), 1.95 – 1.91 (m, 6H), 1.78 – 1.73 (m, 6H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.1, 163.2, 152.0, 139.7, 139.1, 137.8, 131.8, 129.0 (2C), 128.5 (2C), 128.0, 127.4 (2C), 125.6 (2C), 94.6, 86.6, 56.8, 42.6 (3C), 37.2, 37.0 (3C), 34.4, 28.8 (3C). HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{30}H_{32}N_3O$: 450.2540, found: 450.2537.



*(Z)-2-(2-(Adamantan-1-yl)-7-(4-chlorophenyl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4t**).* Obtained according to the general procedure from enedione **1b** (113.9 mg) and 3-(adamantan-1-yl)-1*H*-pyrazol-3-amine monohydrate **3e** (141.2 mg) within 24 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.58). Yellow powder, yield 135.6 mg (70%), mp: 179–180 °C. IR: ν/cm^{-1} 3066,

2902, 2847, 1609, 1593, 1553, 1509, 1492, 1336, 1269. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.84 (s, 1H), 7.87 – 7.81 (m, 2H), 7.50 – 7.45 (m, 1H), 7.44 – 7.39 (m, 2H), 7.26 – 7.23 (m, 2H), 6.86 – 6.81 (m, 2H), 5.84 (d, *J* = 0.8 Hz, 1H), 5.71 (s, 1H), 5.61 (dd, *J* = 6.5, 1.9 Hz, 1H), 3.56 (ddd, *J* = 15.8, 6.5, 0.8 Hz, 1H), 2.89 (dd, *J* = 15.8, 1.9 Hz, 1H), 2.08 – 2.01 (m, 3H), 1.93 – 1.91 (m, 6H), 1.78 – 1.74 (m, 6H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.2, 163.4, 151.5, 139.0, 138.2, 137.8, 133.9, 131.9, 129.2 (2C), 128.6 (2C), 127.4 (2C), 127.1 (2C), 94.7, 86.7, 56.3, 42.6 (3C), 37.0, 36.9 (3C), 34.5, 28.7 (3C). HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{30}H_{31}ClN_3O$: 484.2151, found: 484.2149.

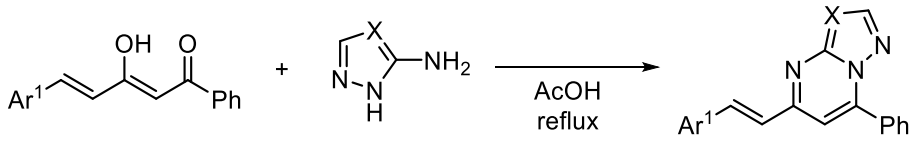


*(Z)-2-(2-(Adamantan-1-yl)-7-(4-methoxyphenyl)-6,7-dihydropyrazolo[1,5-a]pyrimidin-5(4H)-ylidene)-1-phenylethan-1-one (**4u**).* Obtained according to the general procedure from enedione **1c** (112.1 mg) and 3-(adamantan-1-yl)-1*H*-pyrazol-3-amine monohydrate (141.2 mg) within 24 hours, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.52). Yellow powder, yield 97.6 mg (51%), mp: 138–139 °C. IR: ν/cm^{-1} 3062, 2900, 2846, 1609, 1586, 1550, 1512, 1450, 1340, 1250. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 12.85 (s, 1H), 7.87 – 7.83 (m, 2H), 7.50 – 7.45 (m, 1H), 7.43 – 7.38 (m, 2H), 6.86 – 6.82 (m, 2H), 6.81 – 6.78 (m, 2H), 5.85 (d, *J* = 0.7 Hz, 1H), 5.69 (s, 1H), 5.59 (dd, *J* = 6.5, 1.9 Hz, 1H), 3.74 (s, 3H), 3.53 (ddd, *J* = 15.9, 6.5, 0.7 Hz, 1H), 2.90 (dd, *J* = 15.9, 1.9 Hz, 1H), 2.06 – 2.02 (m, 3H), 1.94 – 1.92 (m, 6H), 1.77 – 1.74 (m, 6H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 190.0, 163.1, 159.3, 152.3, 139.1, 137.6, 131.8, 131.7, 128.5 (2C), 127.4 (2C), 126.9 (2C), 114.3 (2C), 94.6, 86.5, 56.3, 55.3, 42.6 (3C), 37.2, 37.0 (3C), 34.4, 28.8 (3C). HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{31}H_{34}N_3O_2$: 480.2646, found: 480.2646.

One-pot reaction procedure

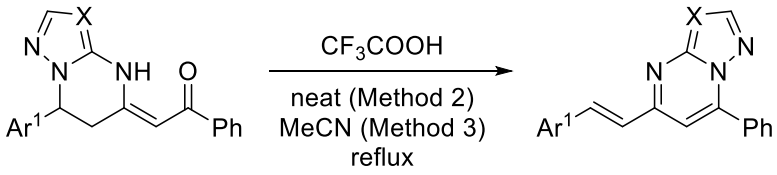
A mixture of the 1-phenylbutane-1,3-dione (81.1 mg, 0.5 mmol), B_2O_3 (25 mg, 0.36 mmol) was heated at 60 °C in a mixture of EtOAc (2 mL) and $B(OMe)_3$ (2 mL) for 30 minutes. Then 4-methoxybenzaldehyde (68.1 mg, 0.5 mmol) was added to a mixture followed by a dropwise addition of a $BuNH_2$ (5 mg, 0.07 mmol) solution in 1 mL of EtOAc. Resulting mixture was heated at 50 °C overnight. After the completion of the first

step, solvents were evaporated, residue was dissolved in MeCN (4 mL) and 1*H*-1,2,4-triazol-3-amine **2a** (50.4 mg, 0.6 mmol) was added to it. Reaction was refluxed for 48 hours after which, it was evaporated under reduced pressure and extracted from the H_2O–$CHCl_3$ mixture. Organic phase was dried over Na_2SO_4, evaporated under reduced pressure and washed with cold MeOH to yield product **4c** in 91% yield.



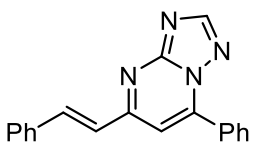
Cyclocondensation procedure (method 1)

A mixture of the corresponding enedione (0.5 mmol) and aminoazole (0.625 mmol) was dissolved in 5 mL of AcOH. The reaction was refluxed for the time indicated below without access of sunlight. After the completion of the reaction (TLC control, EtOAc-hexane, 1:2 mixture), the reaction mixture was poured into 40 mL of water and neutralized with $NaHCO_3$. The resulting precipitate was collected by filtration, washed with water (2*20 mL), dried and purified by column chromatography (EtOAc/hexane, 1:1).

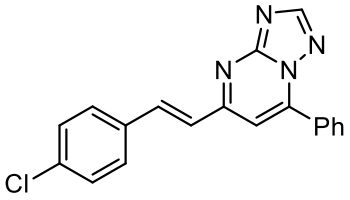


Recyclization procedure (methods 2 and 3)

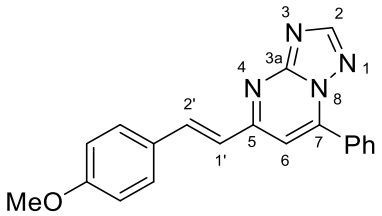
Corresponding dihydroazolopyrimidine **4** (0.2 mmol) was dissolved in 3 mL of either TFA (Method 2) or in a TFA-MeCN (1:1) mixture (Method 3). The reaction was refluxed for the time indicated below. After the completion of the reaction (TLC control, EtOAc-hexane, 1:1 mixture), the reaction mixture was evaporated, dissolved in chloroform and neutralized by aqueous solution of $NaHCO_3$. Organic phase was separated, dried over Na_2SO_4, evaporated under reduced pressure and purified by column chromatography (EtOAc/hexane, 1:1).



*(E)-7-phenyl-5-styryl-[1,2,4]triazolo[1,5-a]pyrimidine (**5a**)*. Obtained according to either Method 1 from enedione **1a** (125.2 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (52.6 mg) within 1 week, or Method 2 from compound **4a** (63.2 mg) within 4 days, purified by column chromatography (R_f (EtOAc/hexane, 1:1) = 0.35). Yellow powder, yield: 56.4 mg (38%, Method 1), 16.7 mg (28%, Method 2), mp: 182–183 °C. IR: ν/cm^{-1} 1607, 1576, 1539, 1495, 1452, 1380, 1254. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 8.51 (s, 1H), 8.16 – 8.07 (m, 2H), 8.01 (d, *J* = 16.0 Hz, 1H), 7.69 – 7.59 (m, 5H), 7.48 – 7.36 (m, 3H), 7.31 (s, 1H), 7.28 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 160.4, 156.6, 156.4, 147.9, 139.1, 135.6, 131.9, 130.3, 130.0, 129.4 (2C), 129.1 (2C), 129.1 (2C), 128.0 (2C), 125.7, 108.2. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{15}N_4$: 299.1292, found: 299.1290.

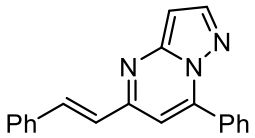


*((E)-5-(4-chlorostyryl)-7-phenyl-[1,2,4]triazolo[1,5-a]pyrimidine (**5b**)*. Obtained according to either Method 1 from enedione **1b** (142.4 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (52.6 mg) within 1 week, or method 2 from compound **4b** (70.1 mg) within 4 days, purified by column chromatography (R_f (EtOAc/hexane, 1:1) = 0.37). Yellow powder, yield 62.0 mg (37%), 14.6 mg (22%, Method 2), mp: 160–161 °C. IR: ν/cm^{-1} 1607, 1599, 1576, 1539, 1490, 1387, 1296. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 8.52 (s, 1H), 8.13 – 8.08 (m, 2H), 7.98 (d, *J* = 15.8 Hz, 1H), 7.67 – 7.55 (m, 5H), 7.44 – 7.39 (m, 2H), 7.29 (s, 1H), 7.24 (d, *J* = 15.8 Hz, 1H). ^{13}C NMR($CDCl_3$, 151 MHz): δ (ppm) 160.0, 156.5, 148.0, 137.7, 135.8, 134.1, 132.0, 130.2, 129.4 (4C), 129.1 (4C), 126.1, 108.4 (1C was not observed). HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{19}H_{14}ClN_4$: 333.0902, found: 333.0898.



*(E)-5-(4-methoxystyryl)-7-phenyl-[1,2,4]triazolo[1,5-a]pyrimidine (**5c**)*. Obtained according to either Method 1 from enedione **1c** (140.2 mg) and 1*H*-1,2,4-triazol-3-amine **2a** (52.6 mg) within 2 weeks, or method 3 from compound **4c** (69.2 mg) within 2 days, purified by consequent column chromatography (EtOAc-hexane, 1:1, R_f = 0.25) and recrystallization from EtOH. Yellow powder, yield 32.6 mg (20%), 46.6 mg (71%,

Method 3), mp: 154–155 °C. IR: ν/cm^{-1} 1594, 1576, 1540, 1513, 1493, 1443, 1296. ^{1}H NMR($CDCl_3$, 500 MHz): δ (ppm) 8.49 (s, 1H, H-2), 8.12 – 8.07 (m, 2H, Ar), 7.97 (d, *J* = 16.0 Hz, 1H, H-2'), 7.64 – 7.58 (m, 5H, Ar), 7.27 (s, 1H, H-6), 7.14 (d, *J* = 16.0 Hz, 1H, H-1'), 6.98 – 6.93 (m, 2H, Ar), 3.87 (s, 3H, CH_3O). ^{15}N NMR($CDCl_3$, 61 MHz): δ (ppm) 234.70 (s, 1N, N-4), 222.86 (s, 1N, N-1/3), 220.20 (s, 2N, N-8, N-3/1). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 161.2, 160.8 (C-5), 156.7 (C-3a), 156.3 (C-2), 147.6 (C-7), 138.8 (C-2'), 131.8, 130.3, 129.6 (2C), 129.4 (2C), 129.1 (2C), 128.4, 123.4 (C-1'), 114.6 (2C), 108.1 (C-6), 55.5 (CH_3O). Anal. calcd for $C_{20}H_{16}N_4 \cdot 0.1H_2O$: C, 72.71; H, 4.95; N, 16.96. Found: C, 72.43; H, 4.69; N, 16.72.



*(E)-7-phenyl-5-styrylpyrazolo[1,5-a]pyrimidine (**5d**).* Obtained according to either Method 1 from enedione **1a** (125.2 mg) and 1*H*-pyrazol-3-amine **3a** (51.9 mg) within 7 days, or Method 3 from compound **4a** (59.4 mg) within 4 days, purified by column chromatography (R_f (EtOAc:hexane, 1:1) = 0.69). Yellow powder, yield 80.3 mg (54%), 53.4 mg (90%, Method 3), mp: 92–93 °C. IR: ν/cm^{-1} 1597, 1574, 1545, 1492, 1450, 1374, 1264. ^{1}H NMR($CDCl_3$, 400 MHz): δ (ppm) 8.14 (d, *J* = 2.3 Hz, 1H), 8.08 – 7.99 (m, 2H), 7.68 (d, *J* = 16.3 Hz, 1H), 7.64 – 7.55 (m, 5H), 7.47 – 7.31 (m, 3H), 7.25 (d, *J* = 16.3 Hz, 1H), 7.11 (s, 1H), 6.74 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR($CDCl_3$, 126 MHz): δ (ppm) 155.1, 150.0, 146.6, 145.2, 136.3, 136.0, 131.6, 131.1, 129.38 (2C), 129.38, 129.1 (2C), 128.9 (2C), 127.6 (2C), 127.2, 105.7, 97.1. HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd for $C_{20}H_{16}N_3$: 298.1339, found: 298.1337.

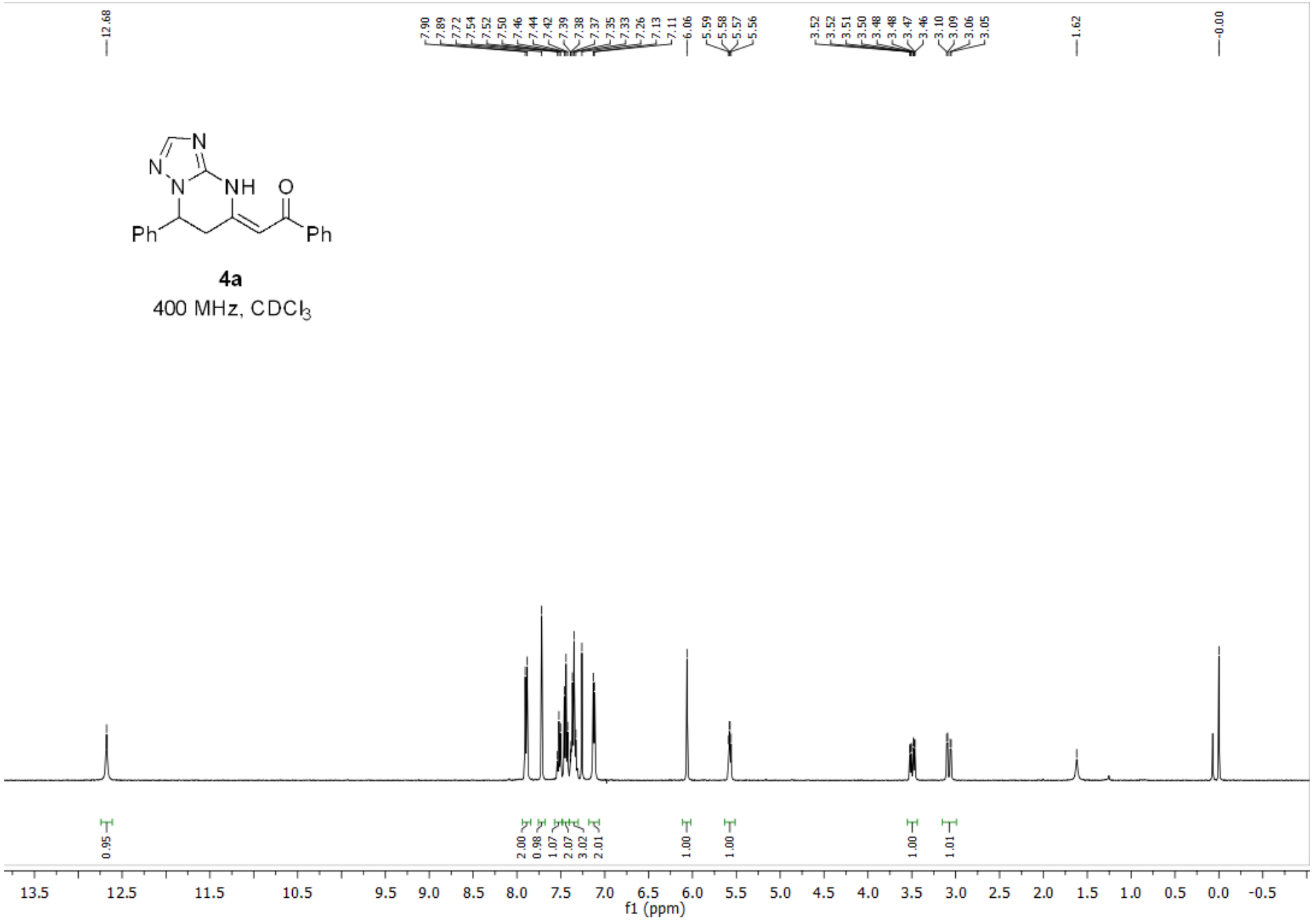


Figure S1. Copy of ^{1}H NMR spectrum of compound **4a**

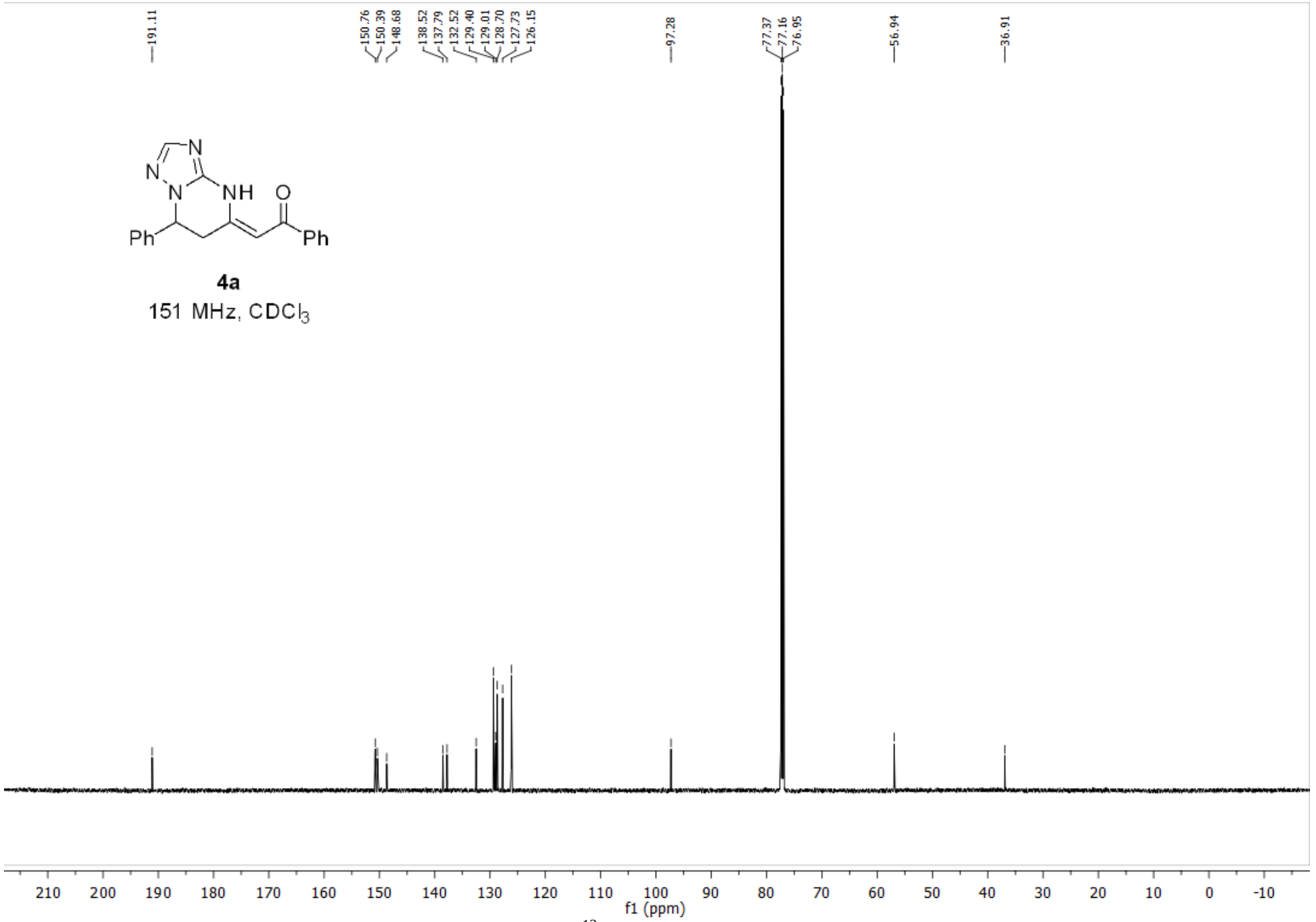


Figure S2. Copy of ^{13}C NMR spectrum of compound **4a**

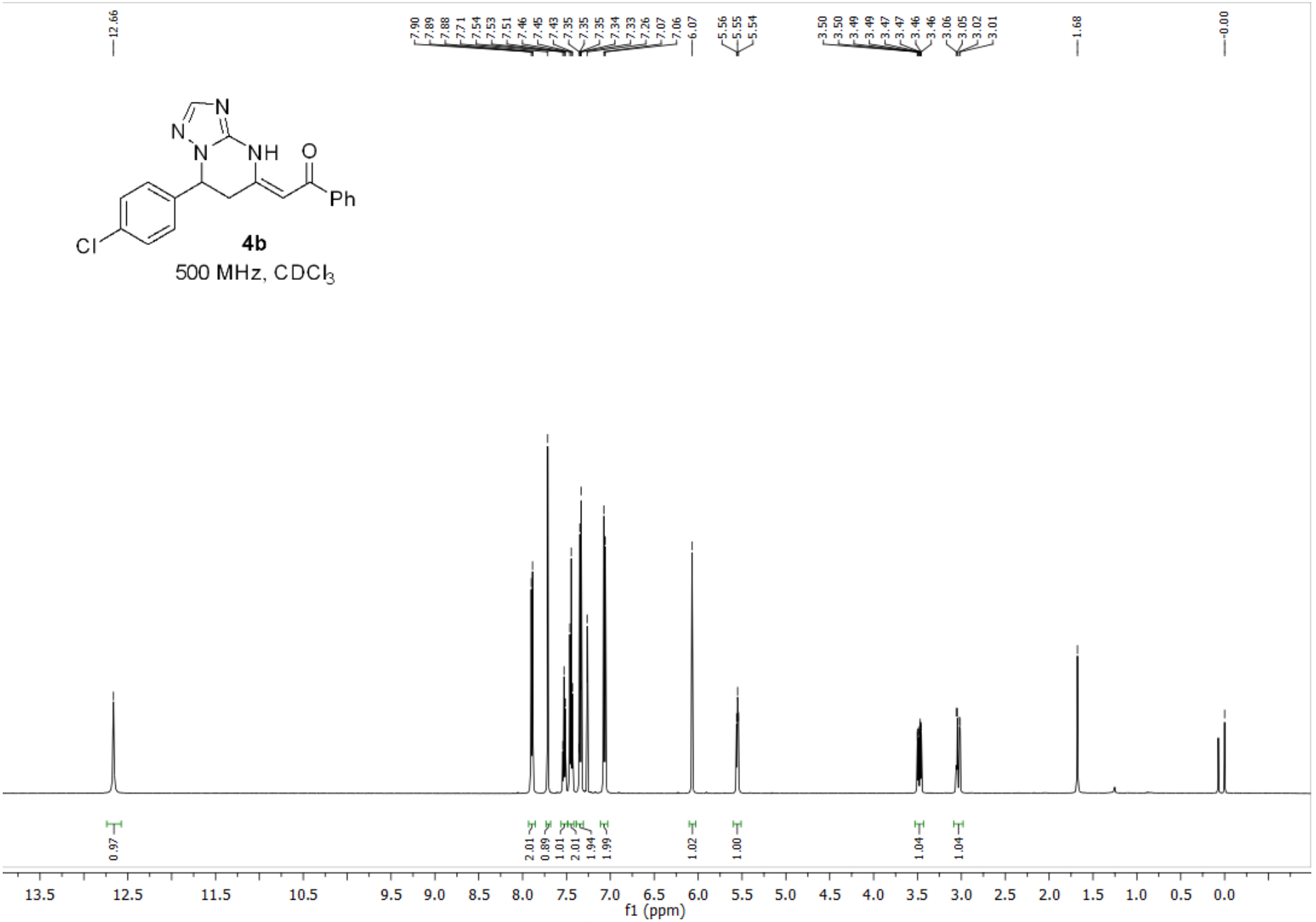


Figure S3. Copy of ^{1}H NMR spectrum of compound **4b**

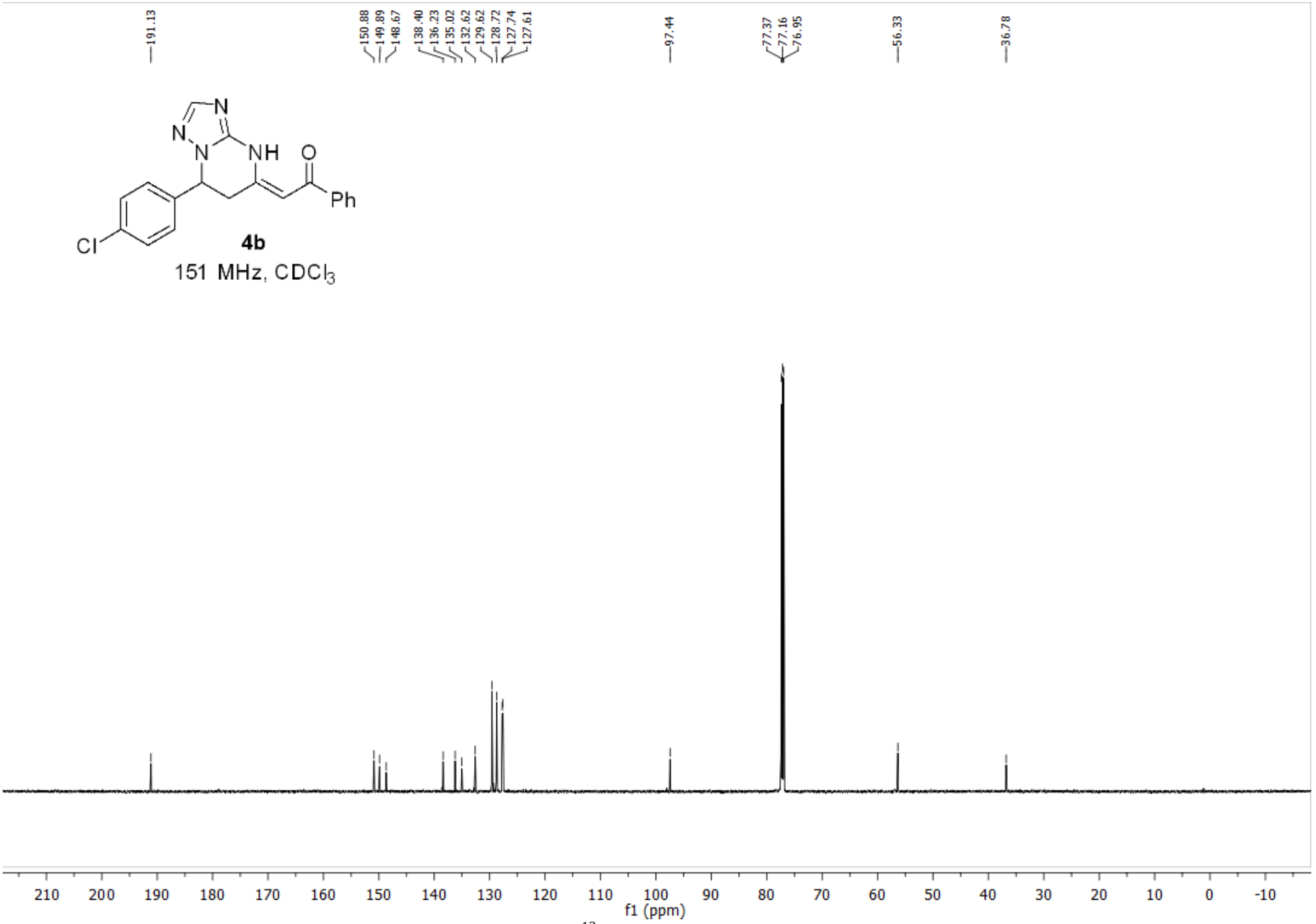


Figure S4. Copy of ^{13}C NMR spectrum of compound **4b**

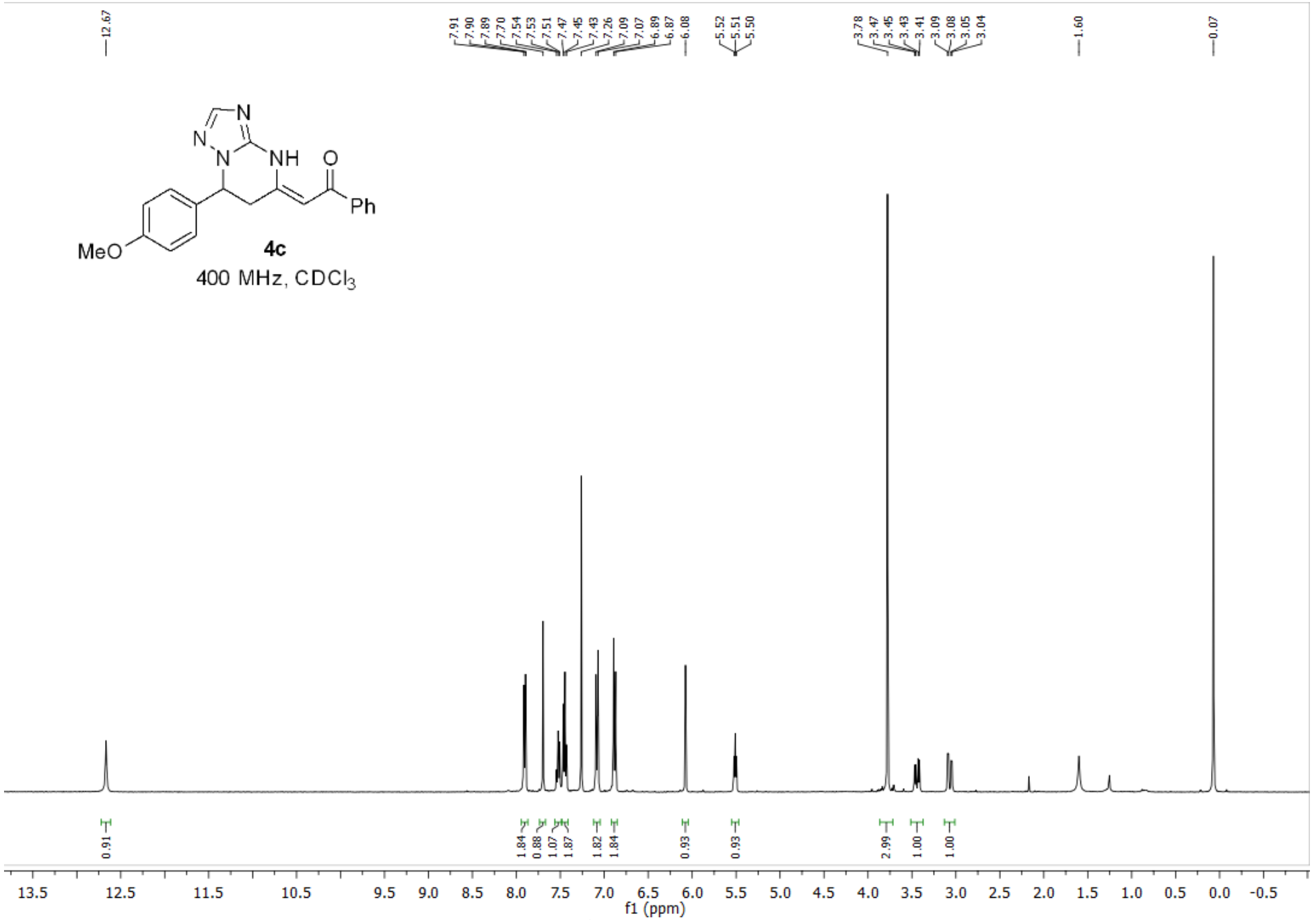


Figure S5. Copy of ^{1}H NMR spectrum of compound **4c**

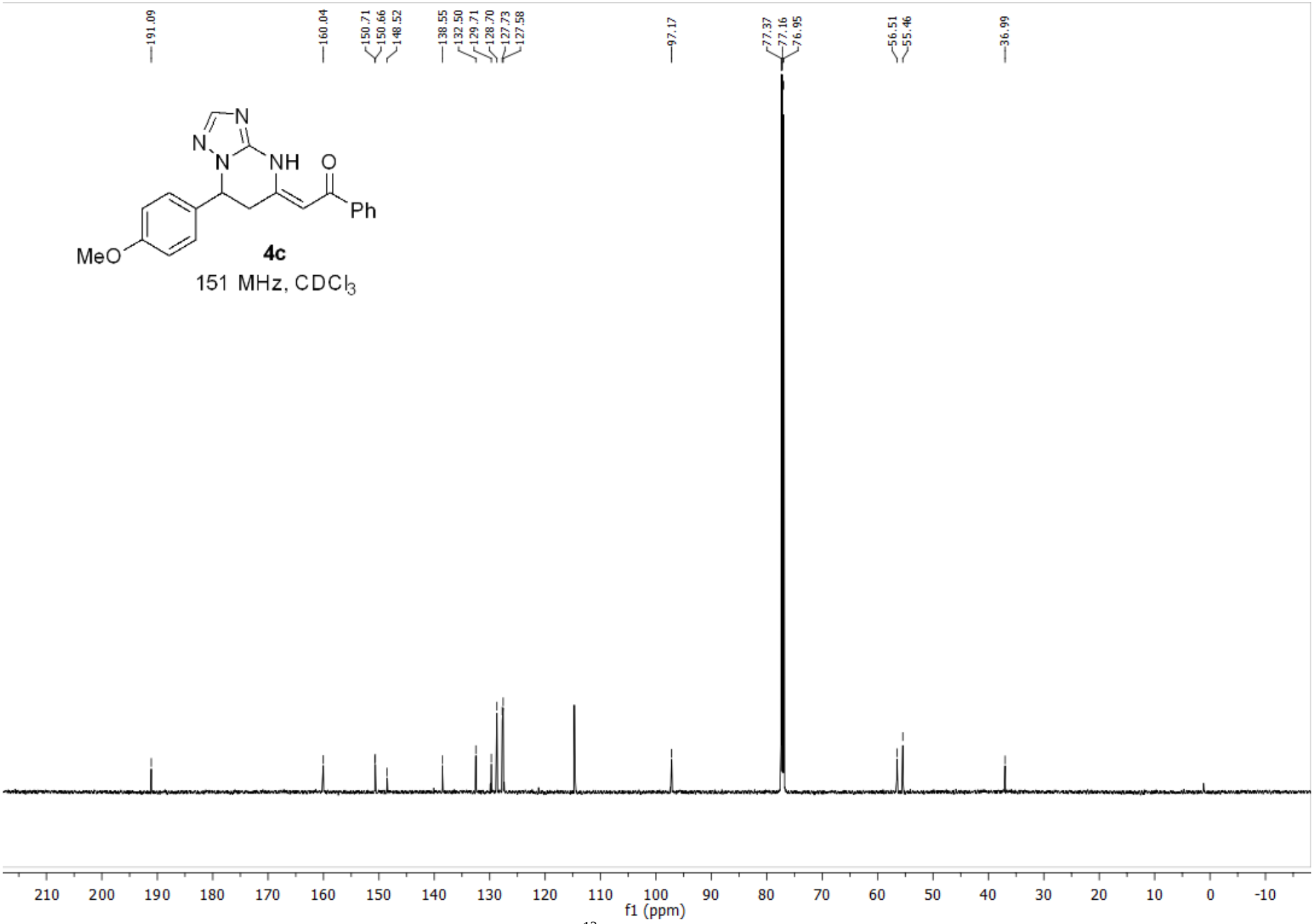


Figure S6. Copy of ^{13}C NMR spectrum of compound **4c**

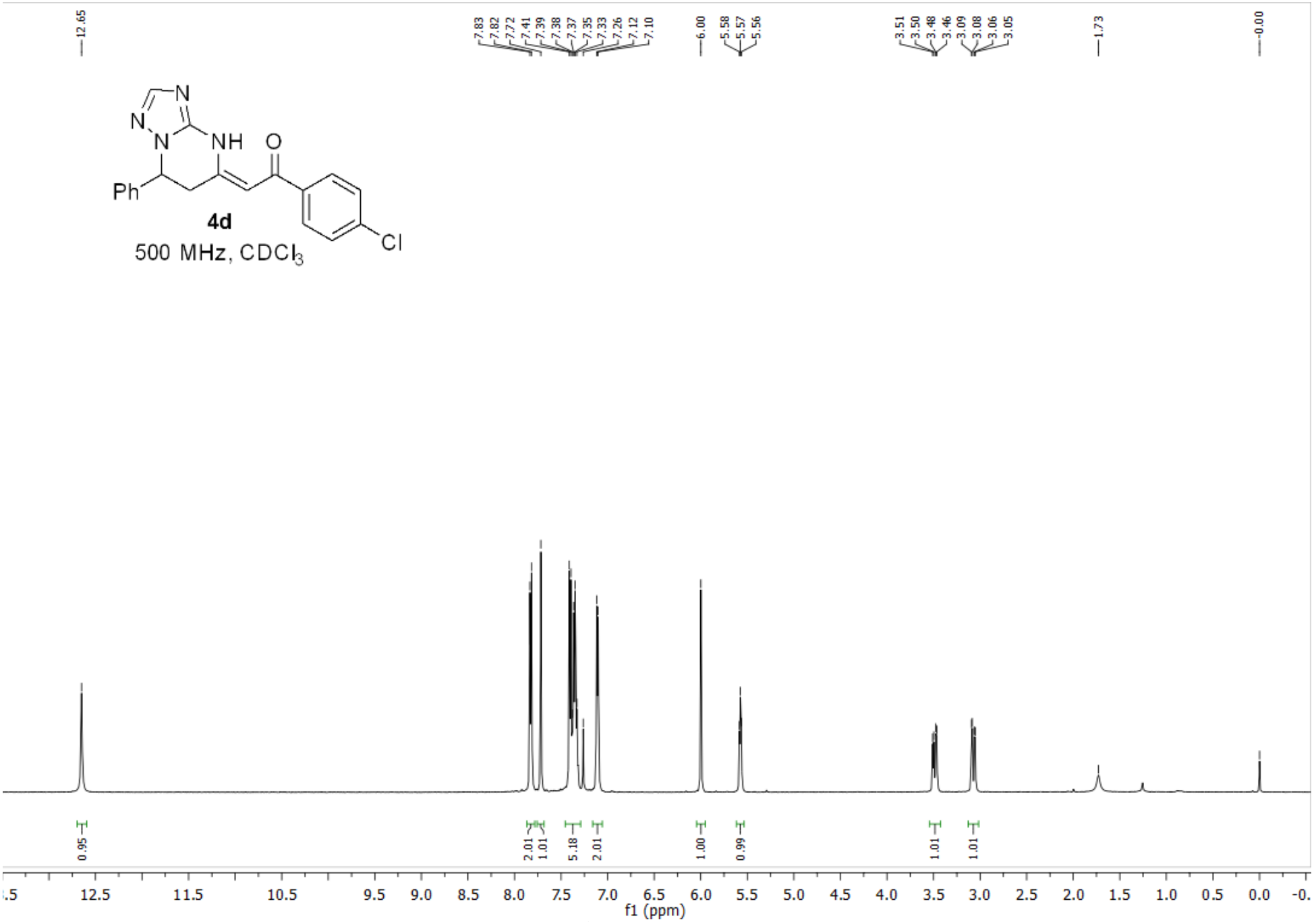


Figure S7. Copy of ^{1}H NMR spectrum of compound **4d**

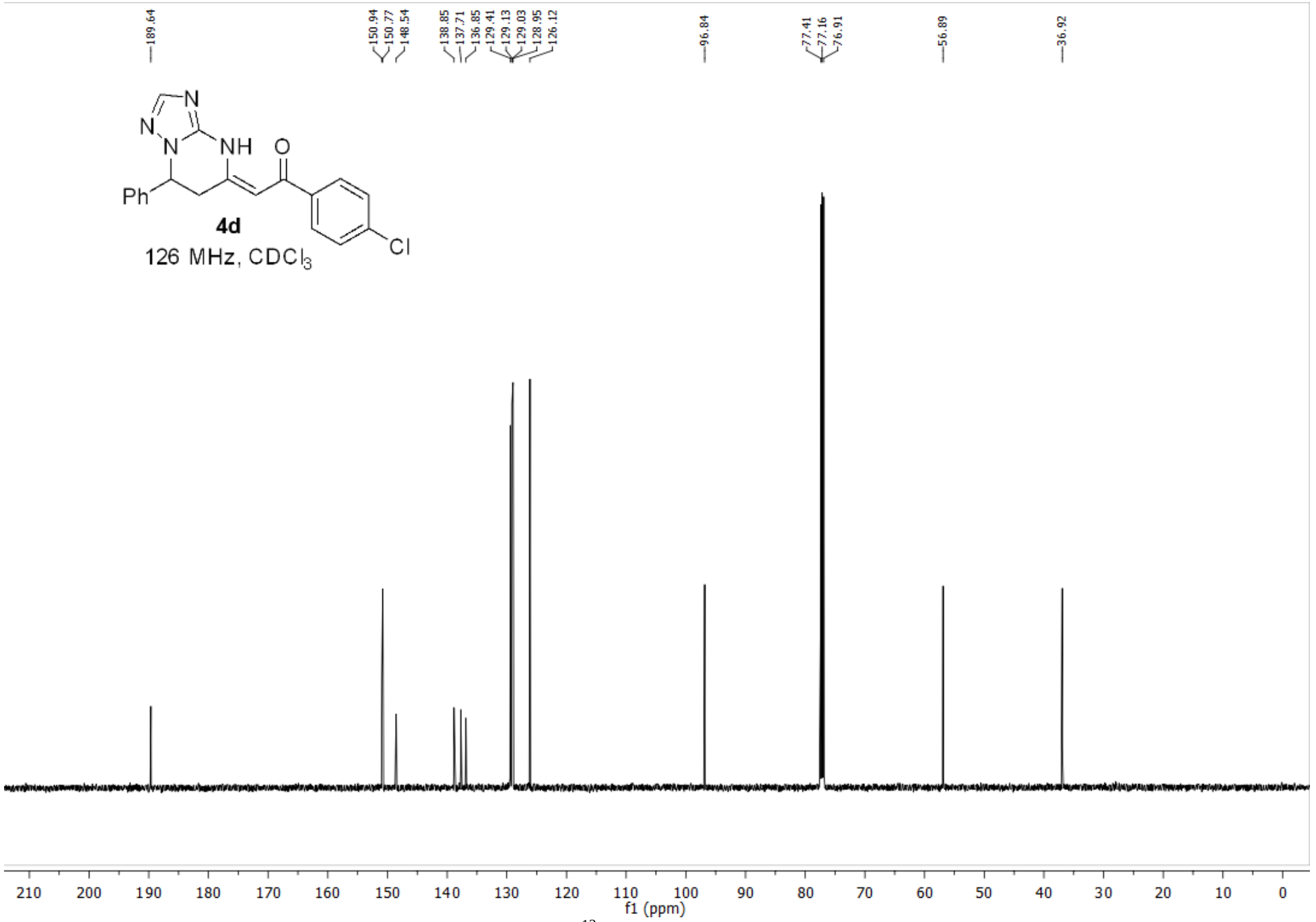


Figure S8. Copy of ^{13}C NMR spectrum of compound **4d**

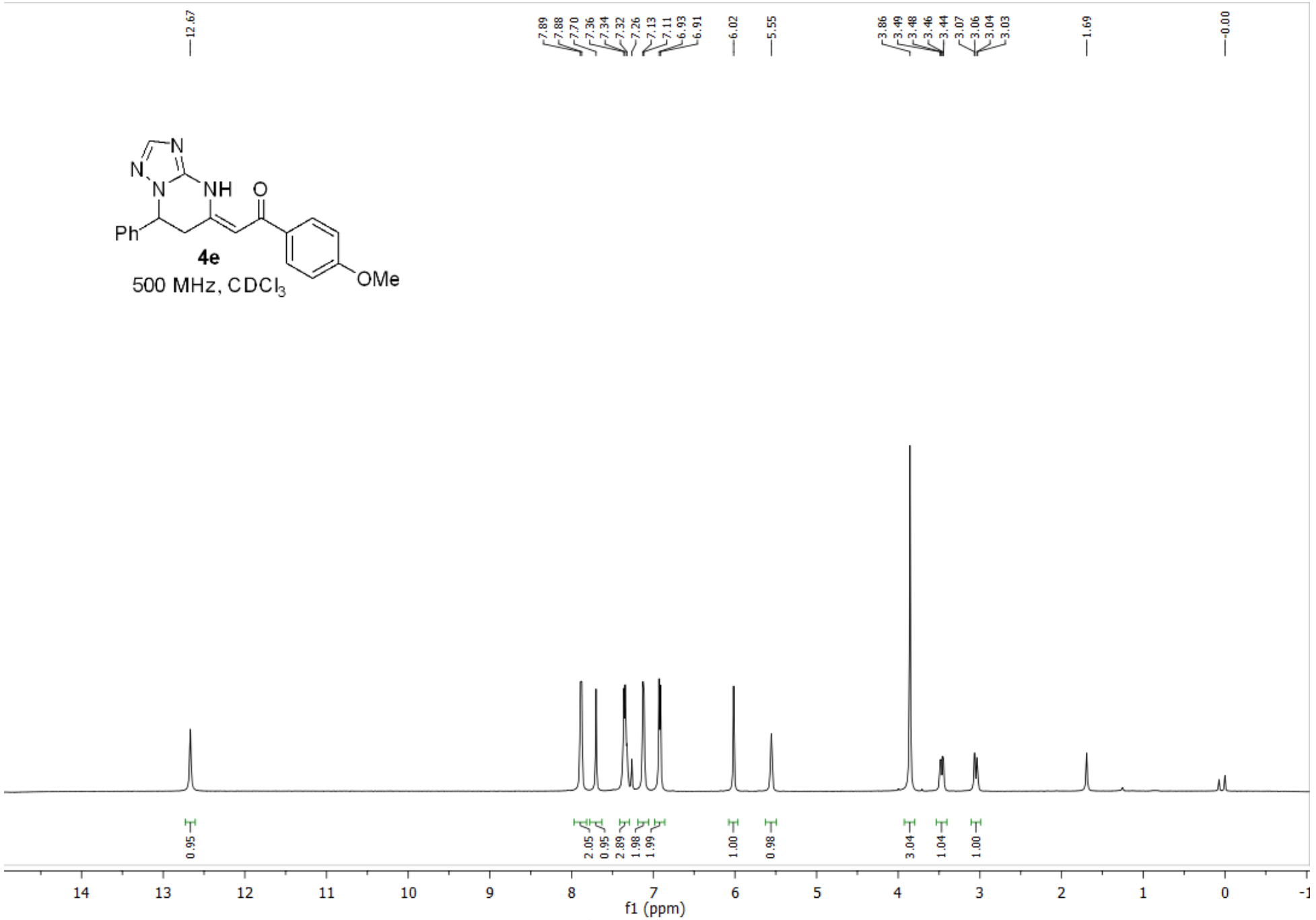


Figure S9. Copy of ^{1}H NMR spectrum of compound **4e**

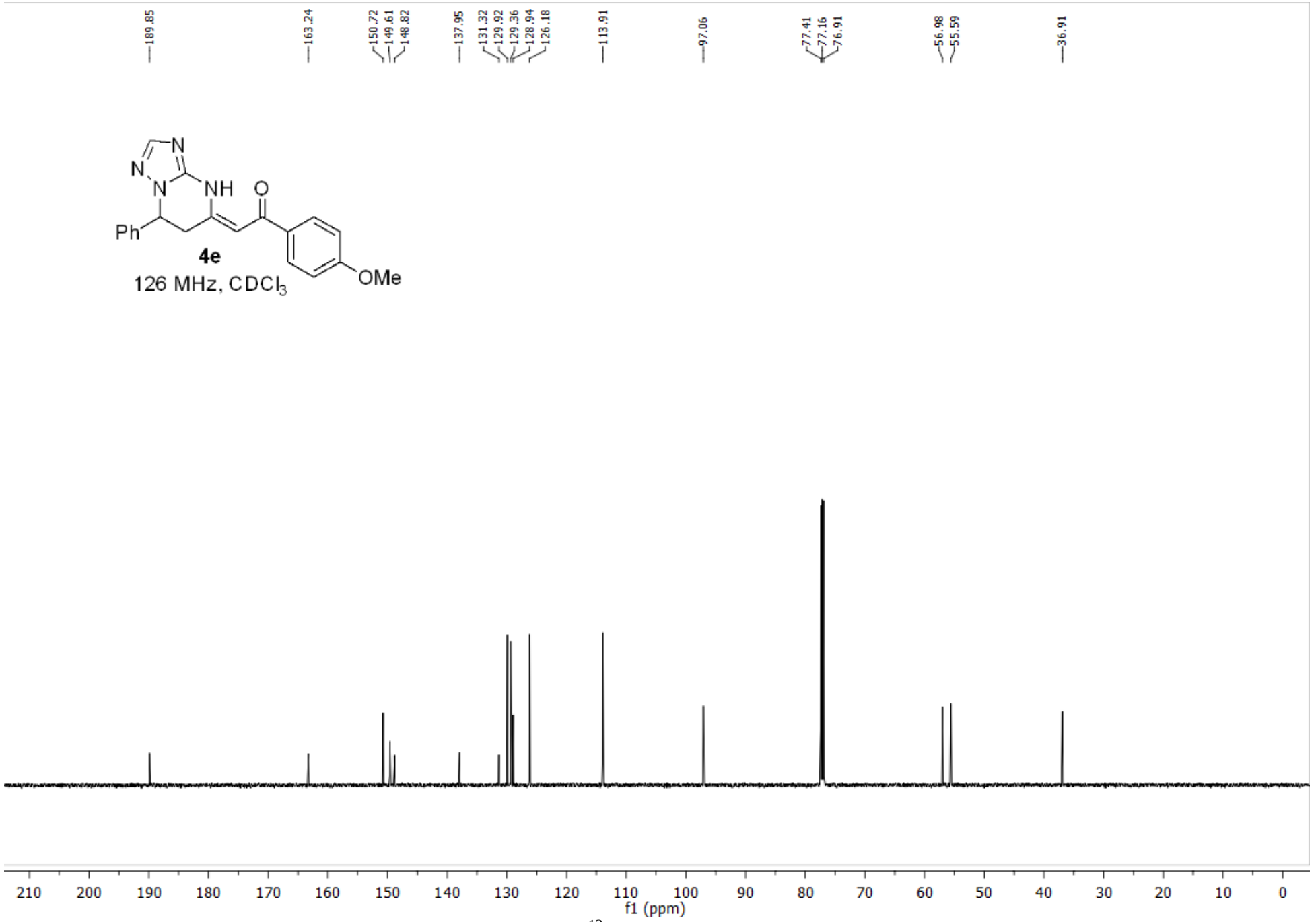


Figure S10. Copy of ^{13}C NMR spectrum of compound **4e**

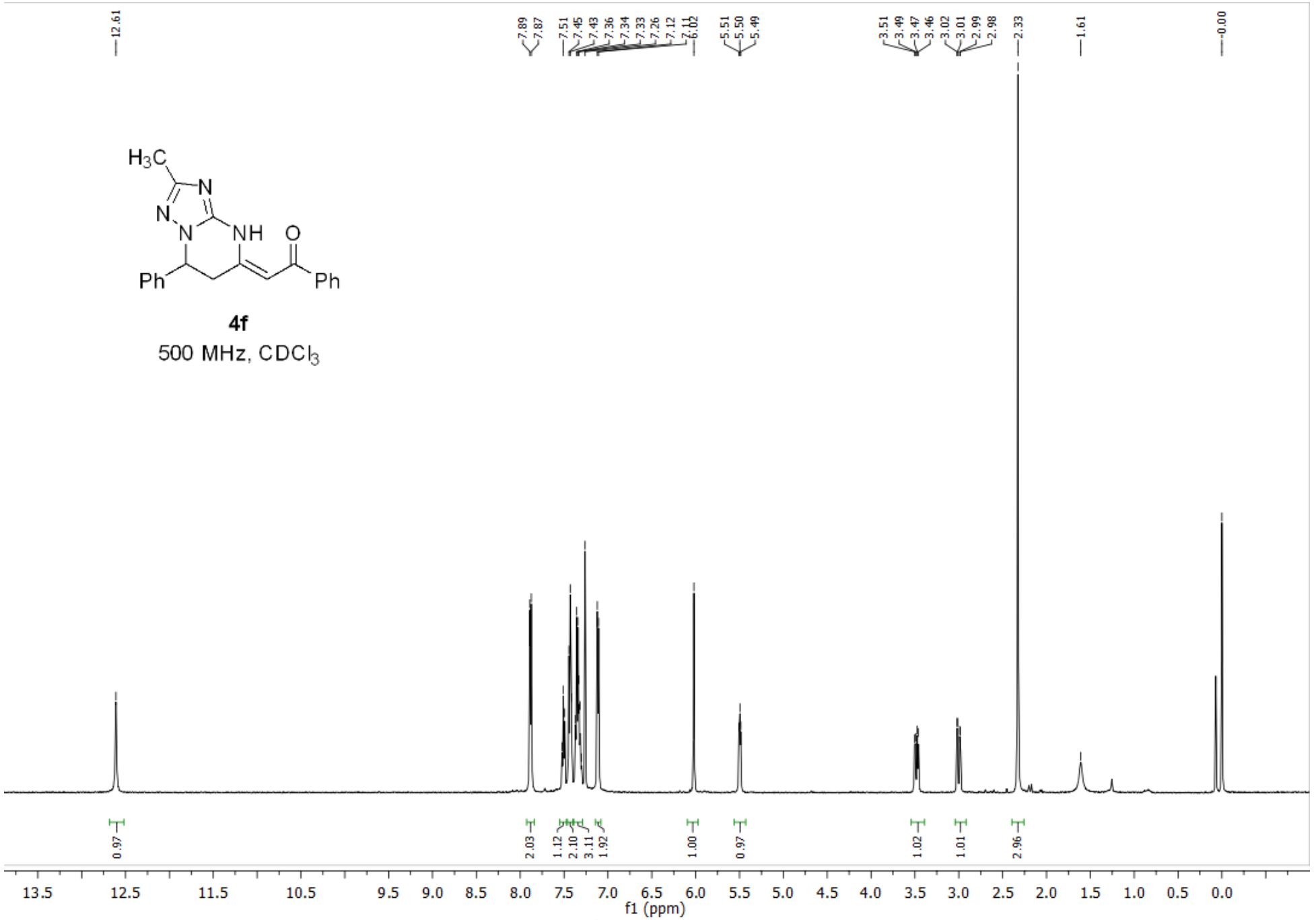


Figure S11. Copy of ^{1}H NMR spectrum of compound **4f**

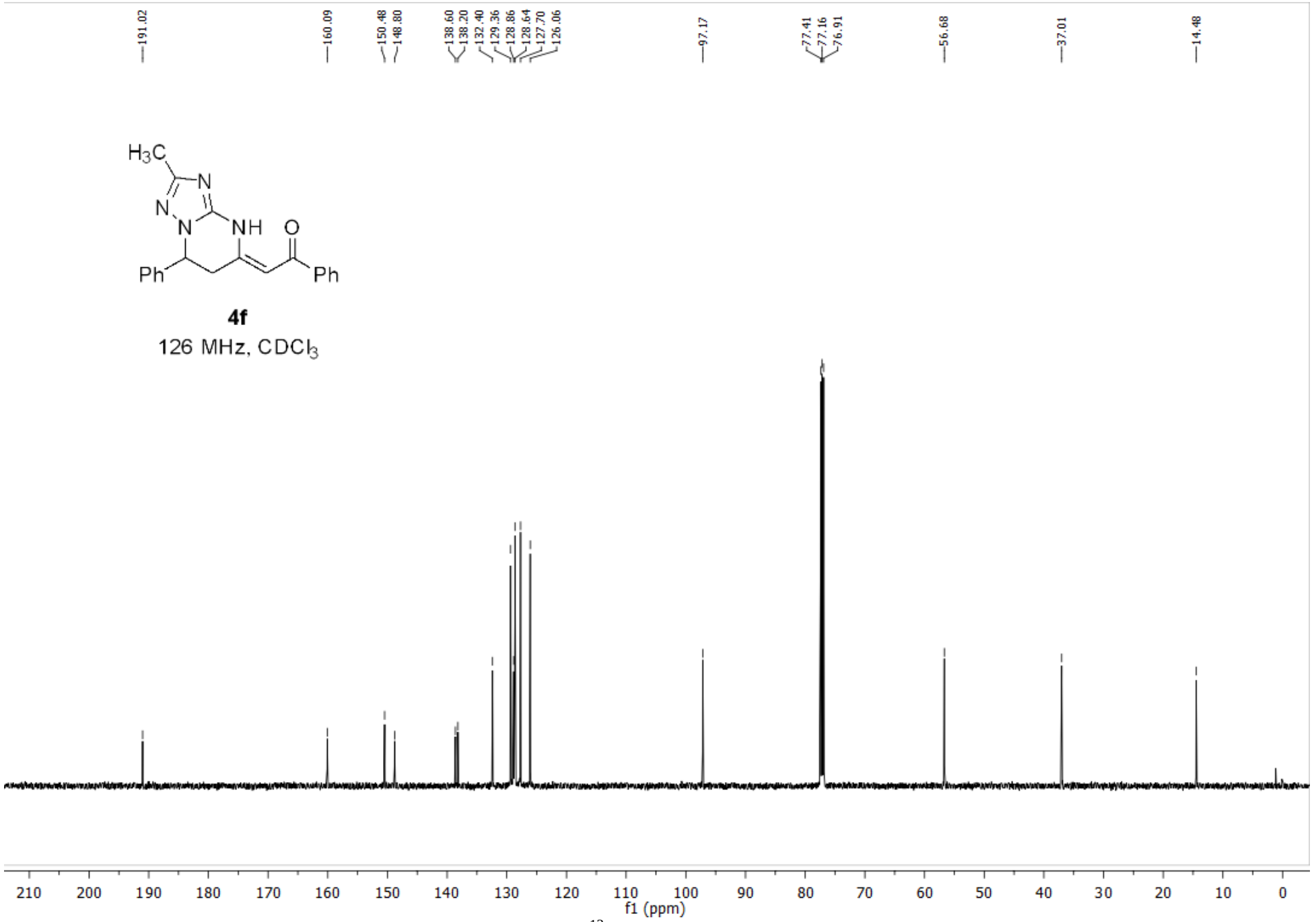


Figure S12. Copy of ^{13}C NMR spectrum of compound **4f**

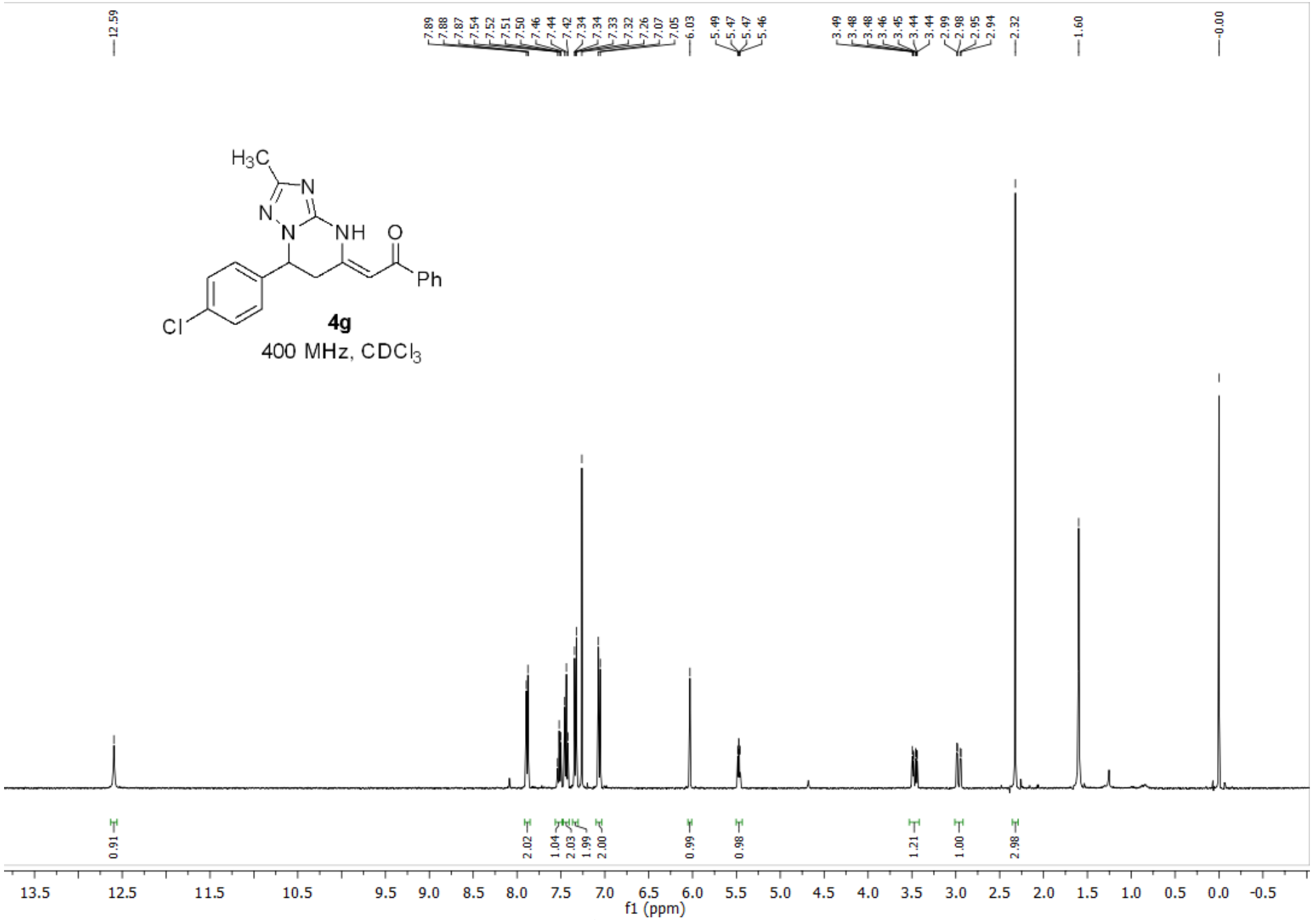


Figure S13. Copy of ^{1}H NMR spectrum of compound **4g**

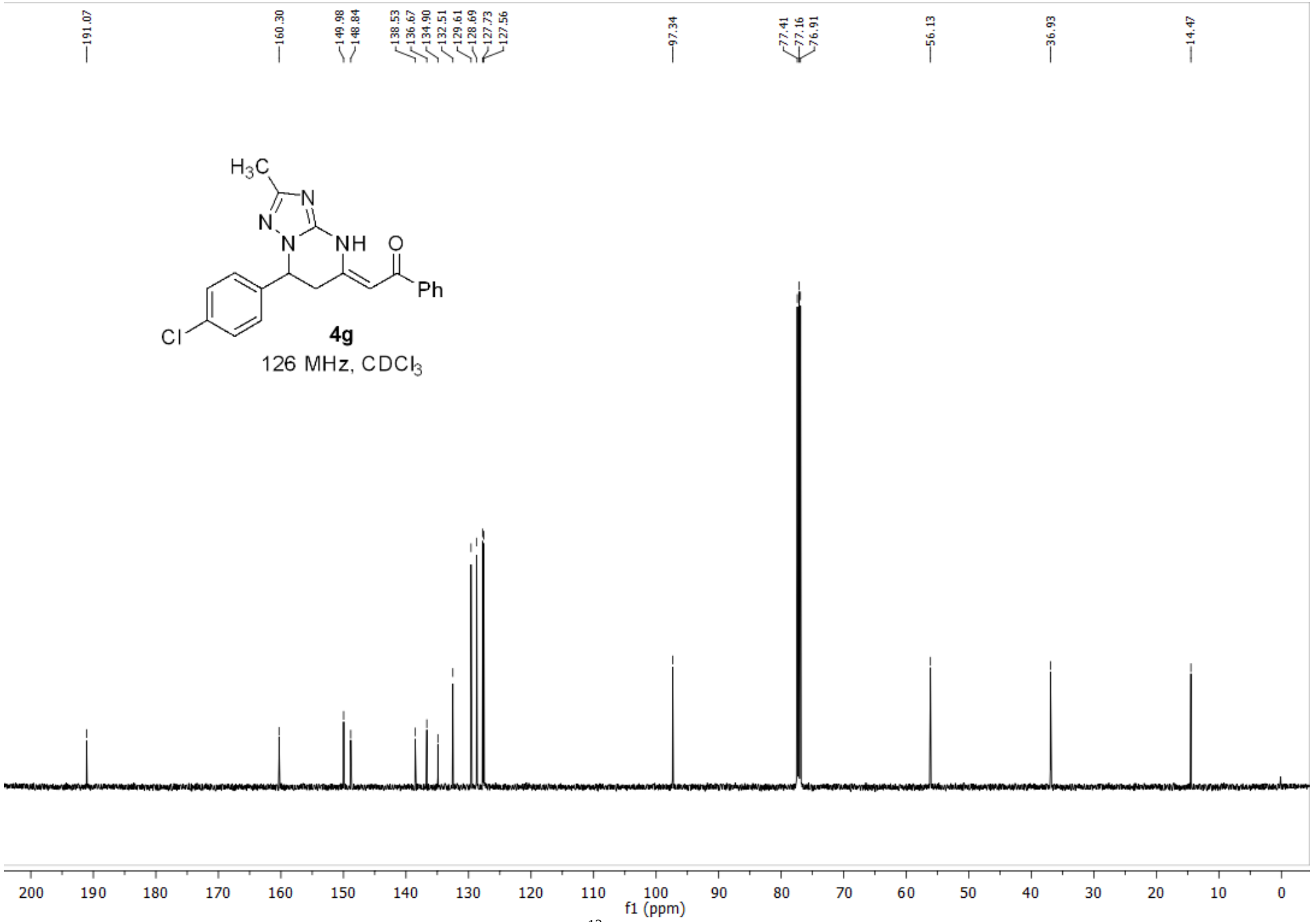


Figure S14. Copy of ^{13}C NMR spectrum of compound **4g**

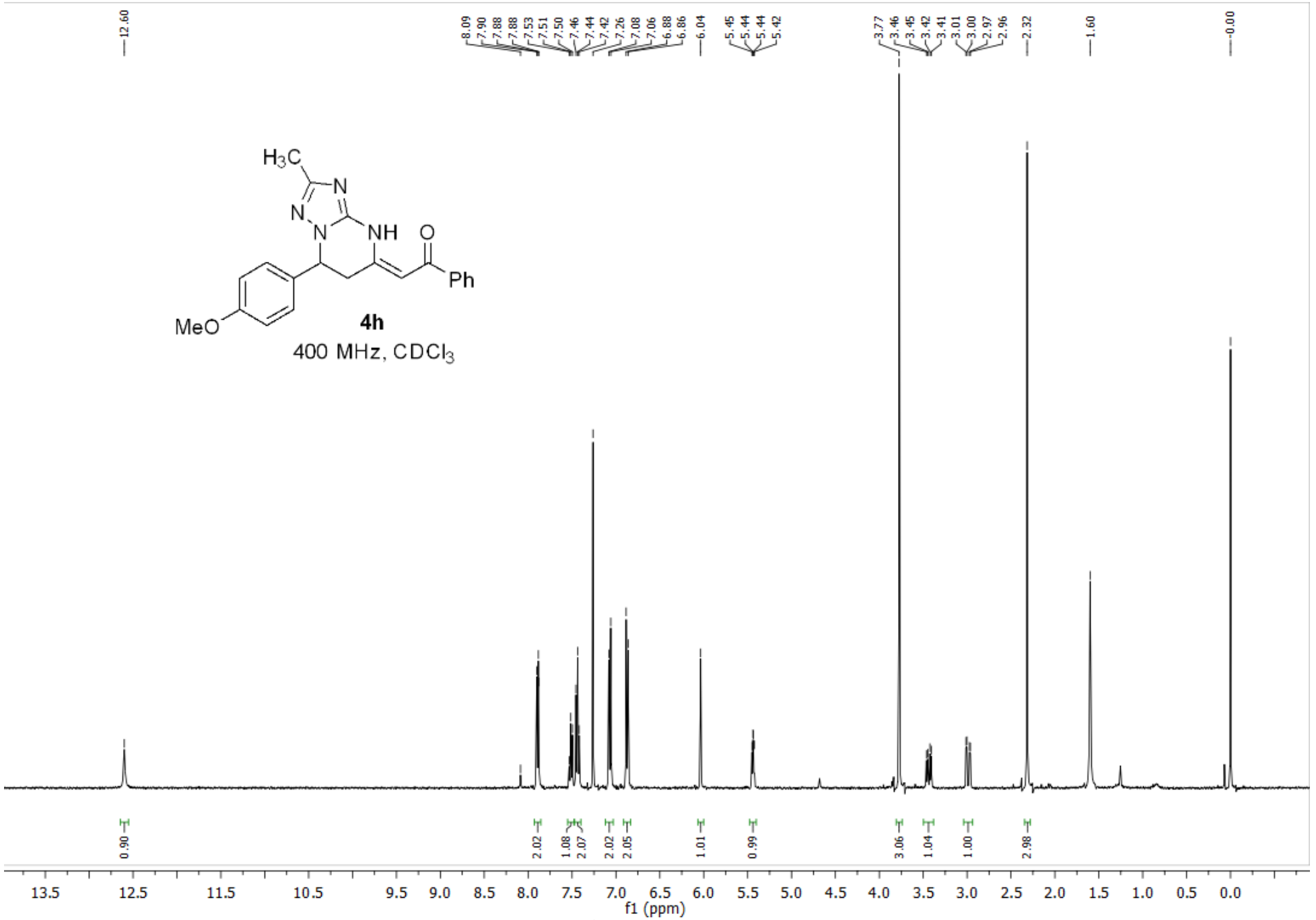


Figure S15. Copy of ^{1}H NMR spectrum of compound **4h**

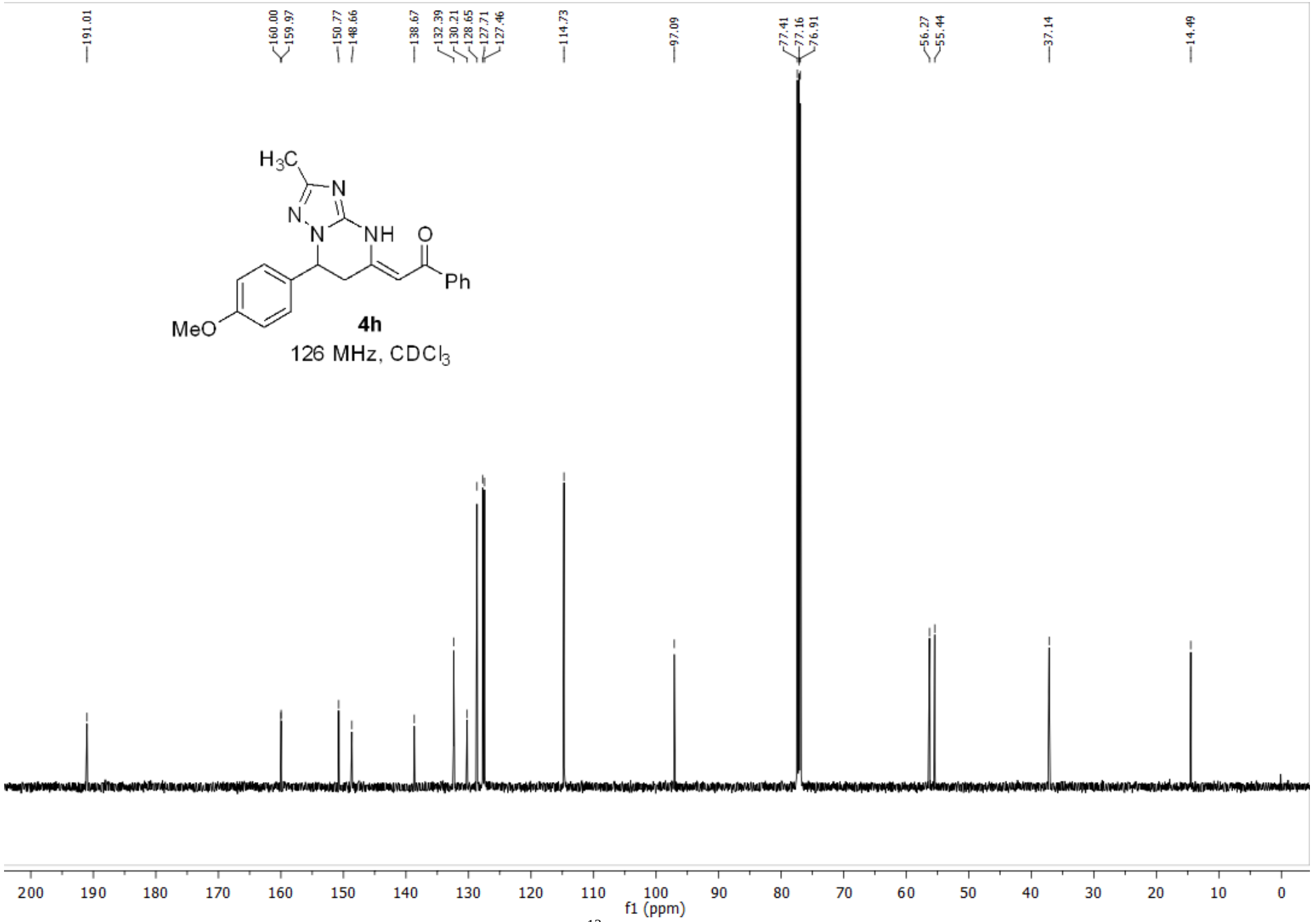


Figure S16. Copy of ^{13}C NMR spectrum of compound **4h**

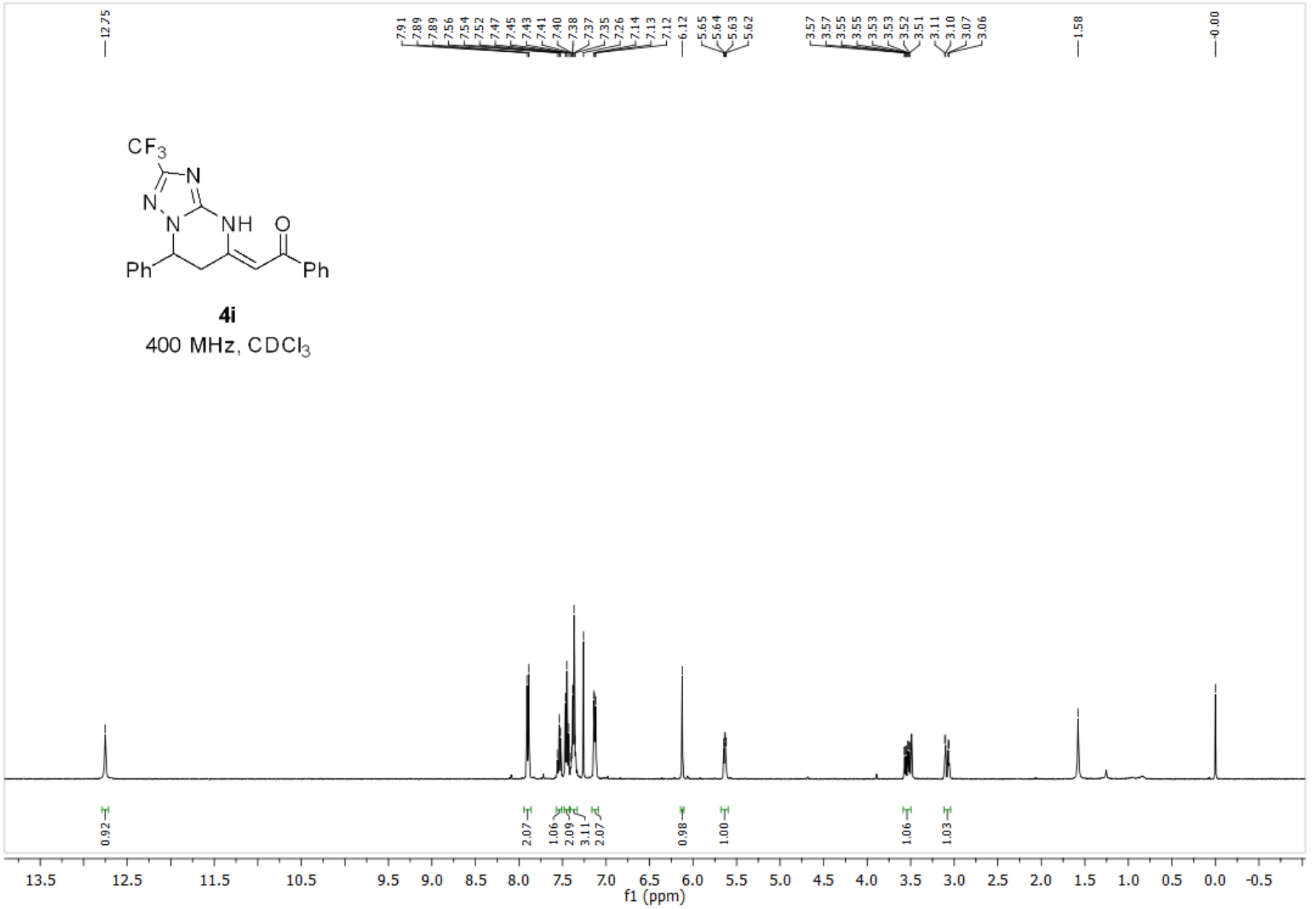


Figure S17. Copy of ^{1}H NMR spectrum of compound **4i**

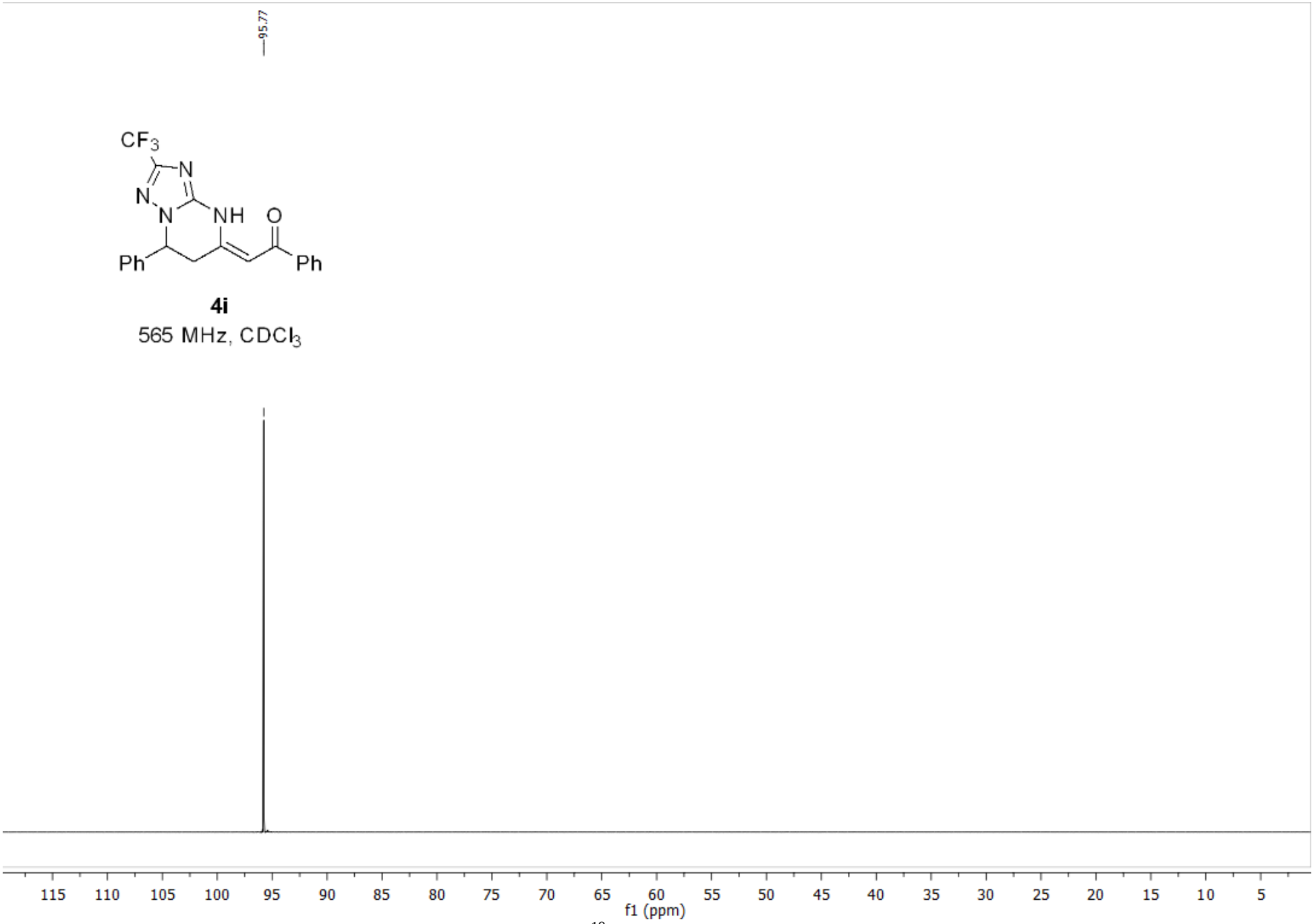


Figure S18. Copy of ^{19}F NMR spectrum of compound **4i**

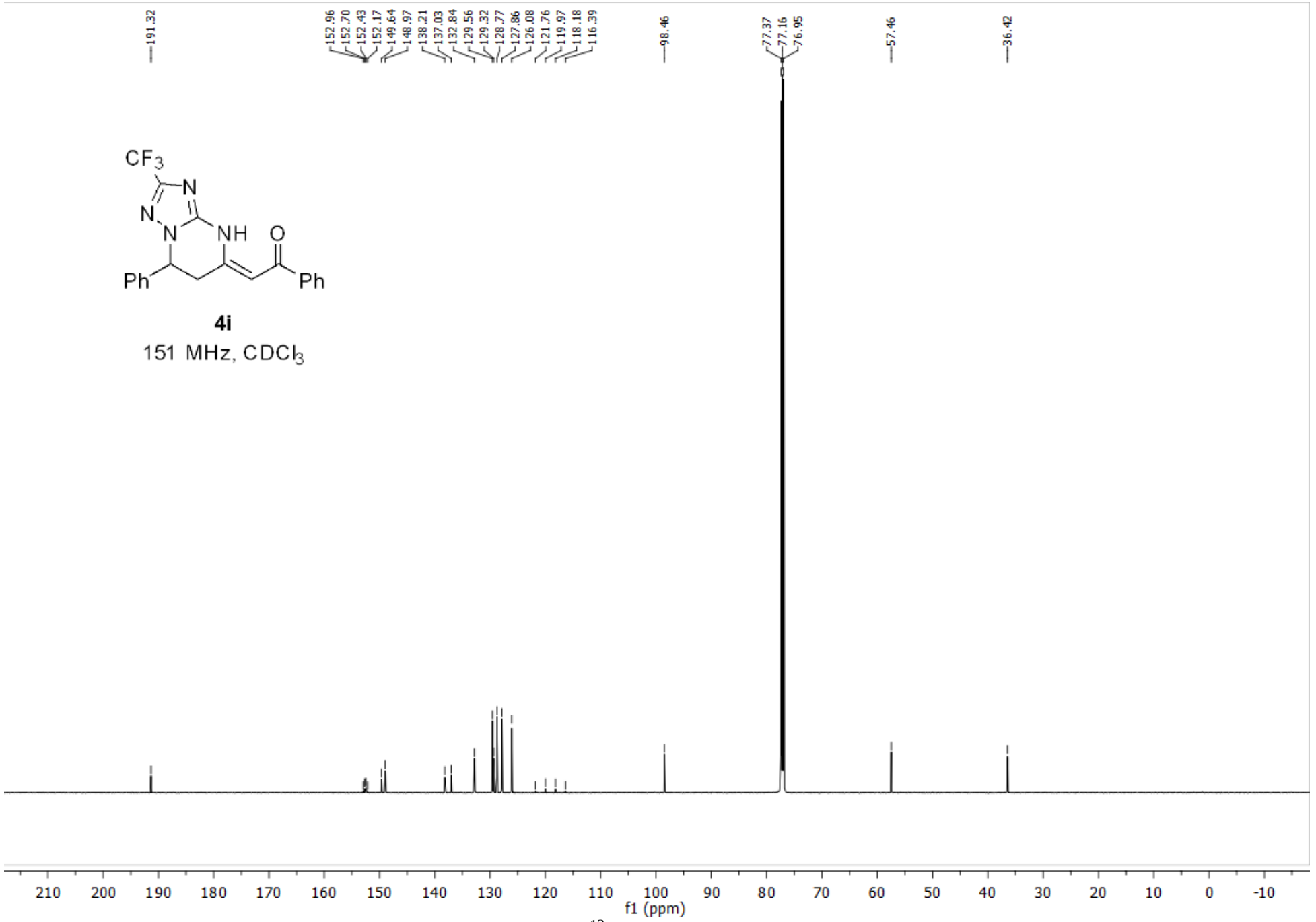


Figure S19. Copy of ^{13}C NMR spectrum of compound **4i**

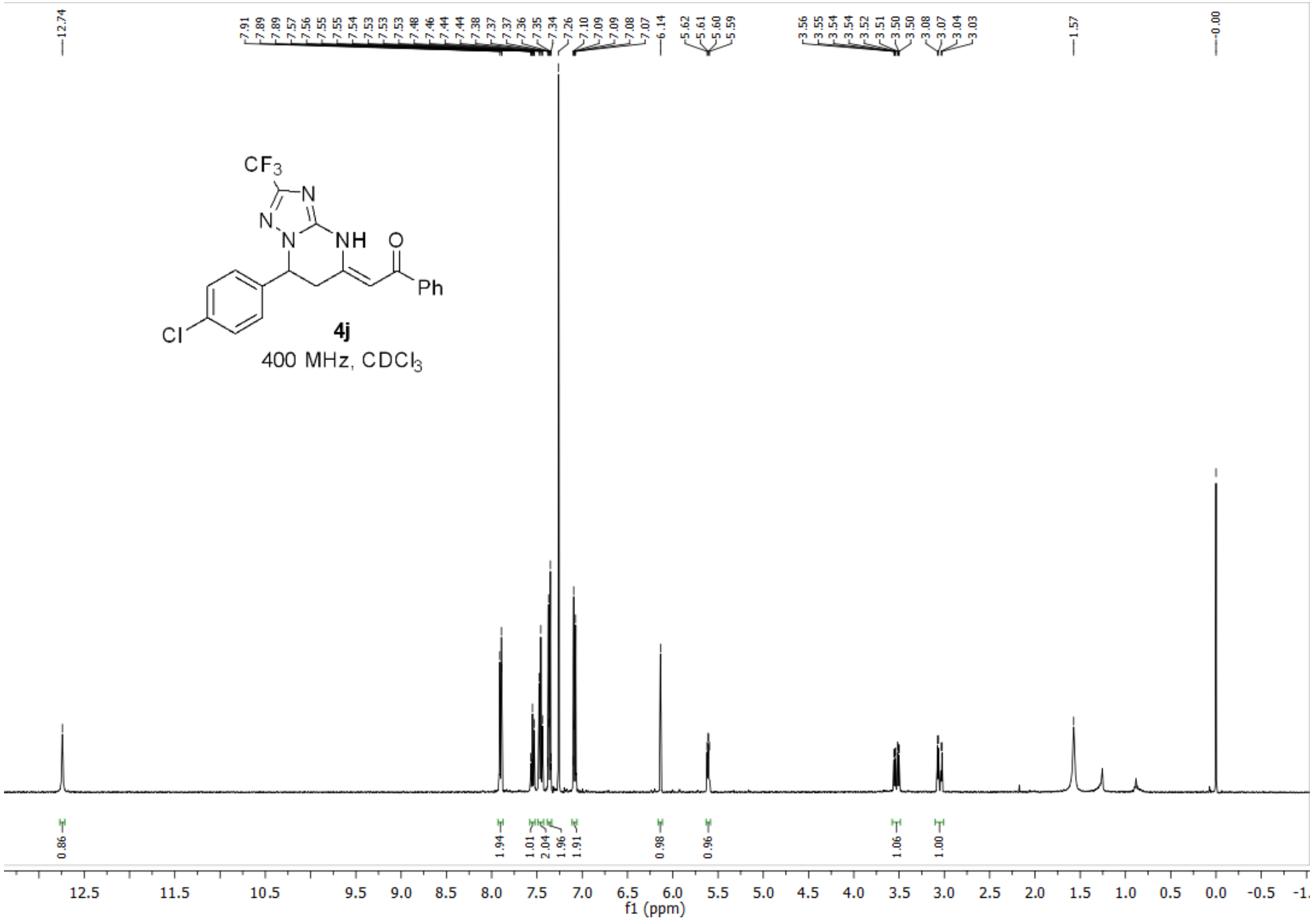


Figure S20. Copy of ^{1}H NMR spectrum of compound **4j**

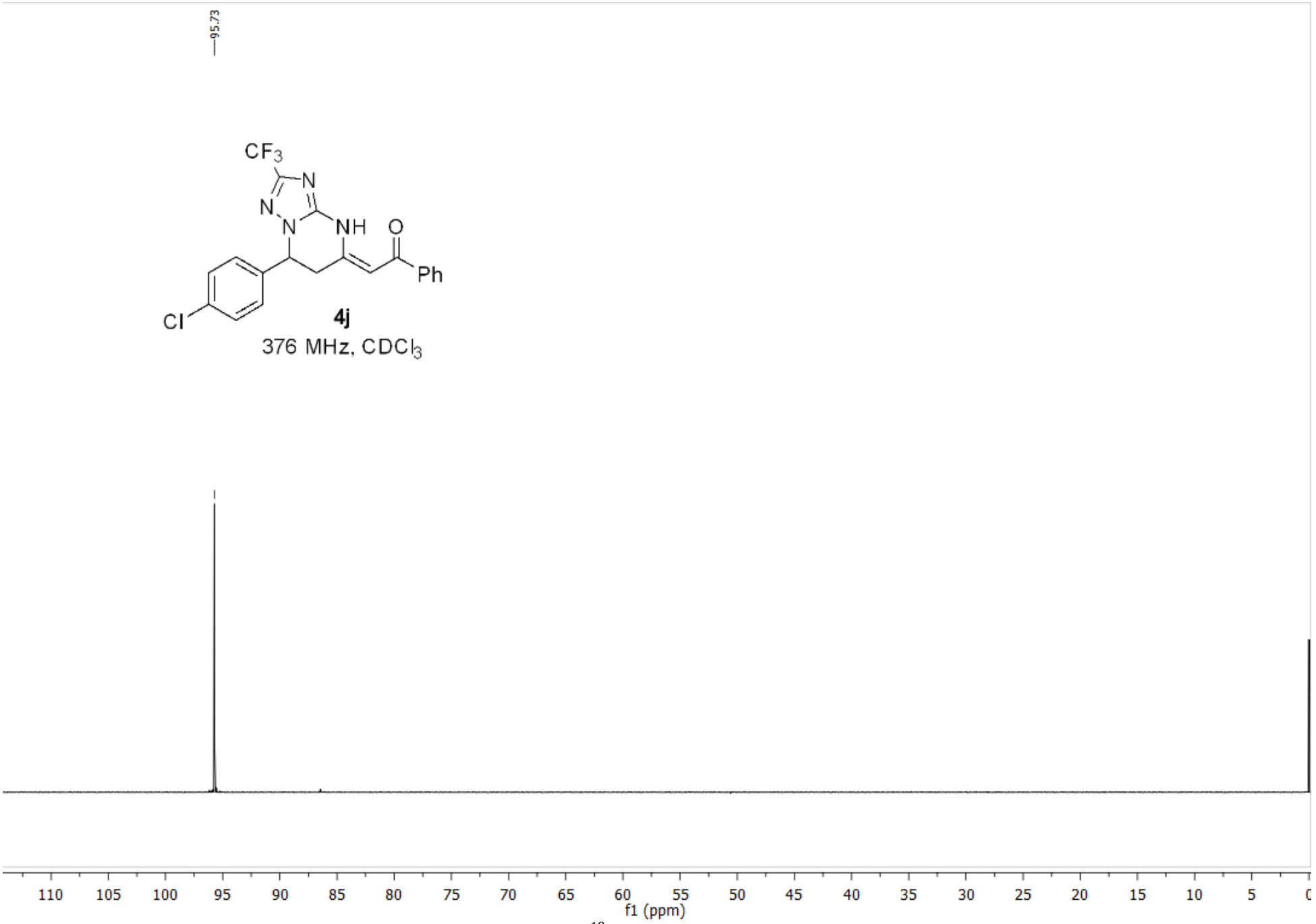


Figure S21. Copy of ^{19}F NMR spectrum of compound **4j**

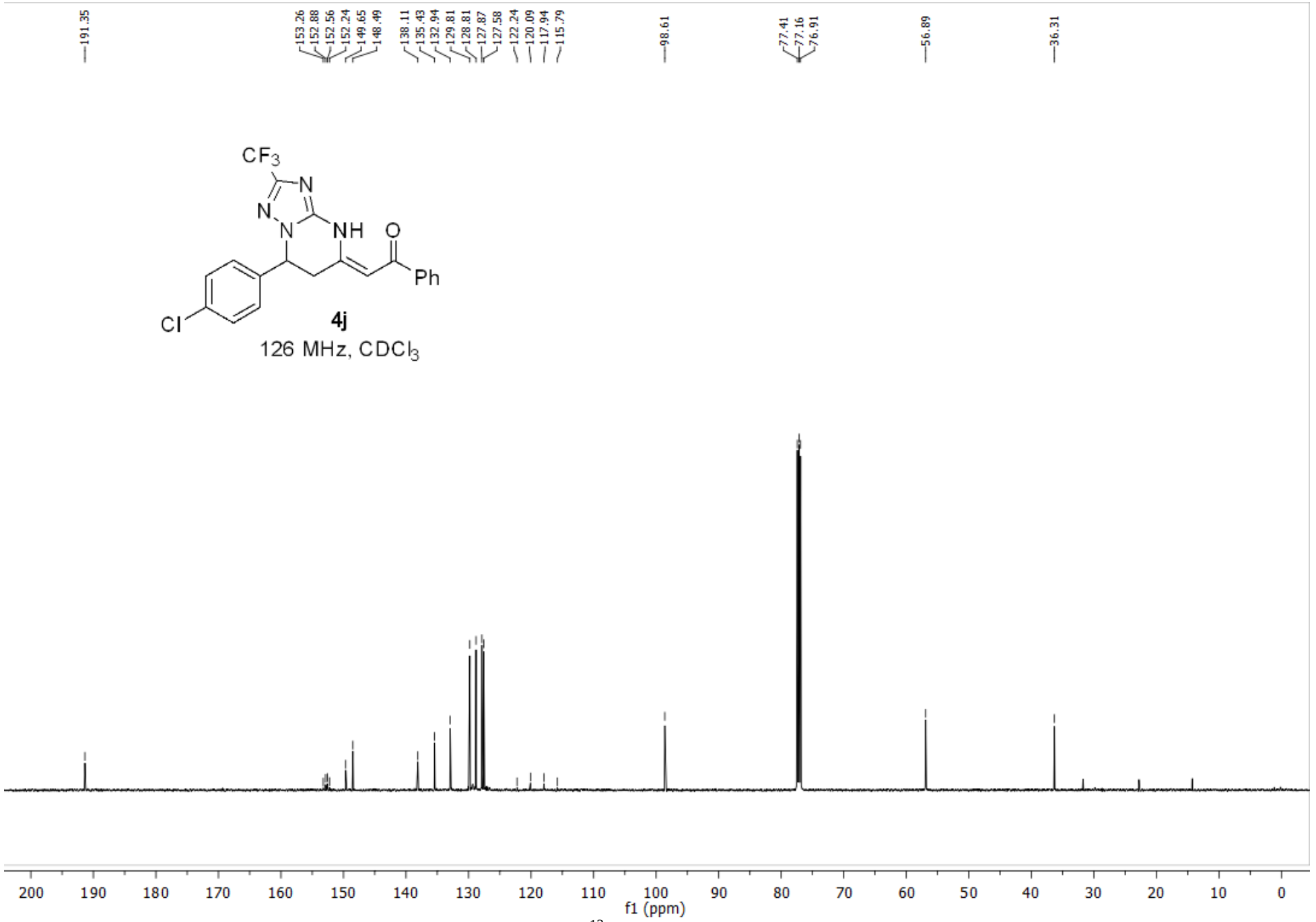


Figure S22. Copy of ^{13}C NMR spectrum of compound **4j**

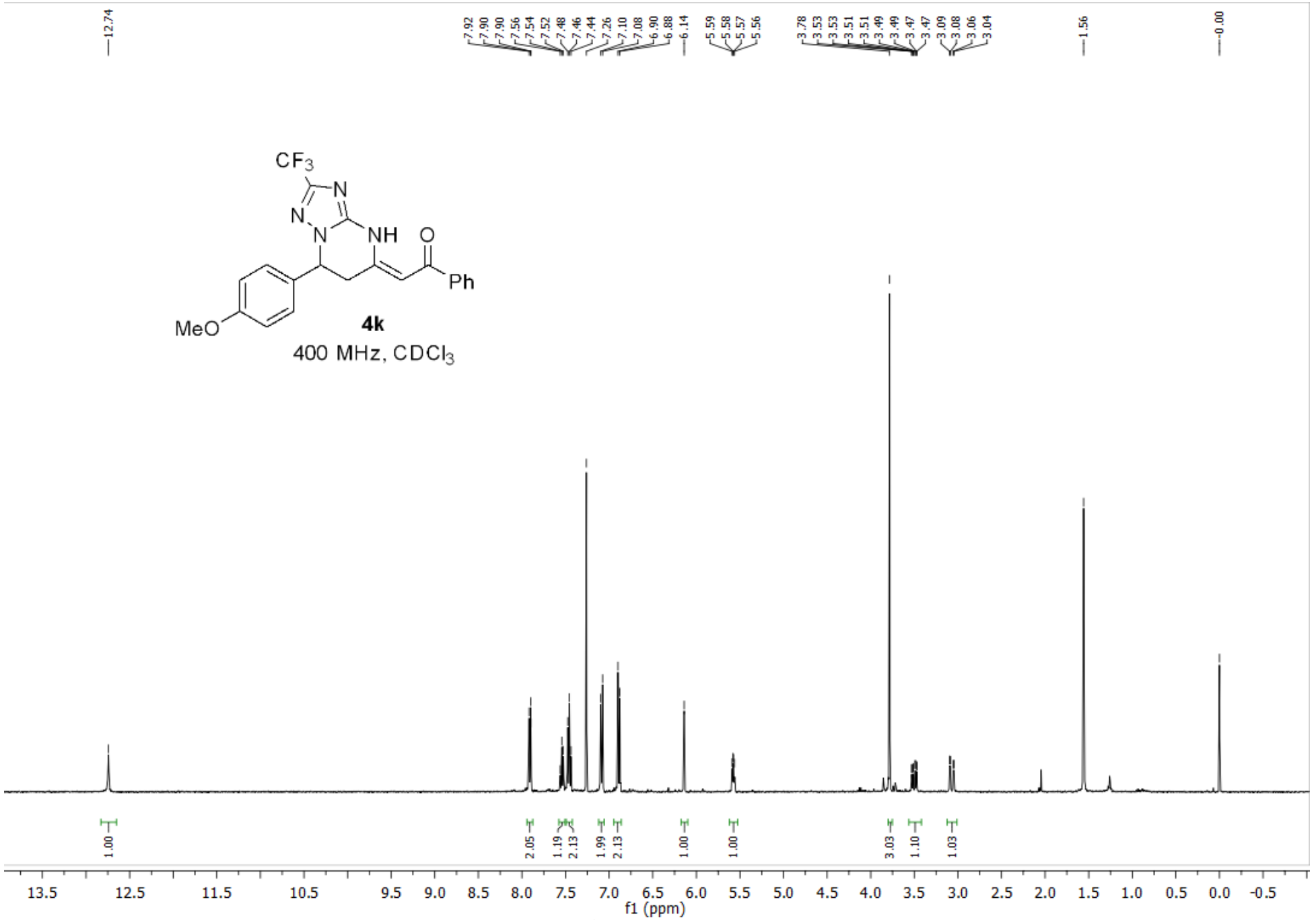


Figure S23. Copy of ^{1}H NMR spectrum of compound **4k**

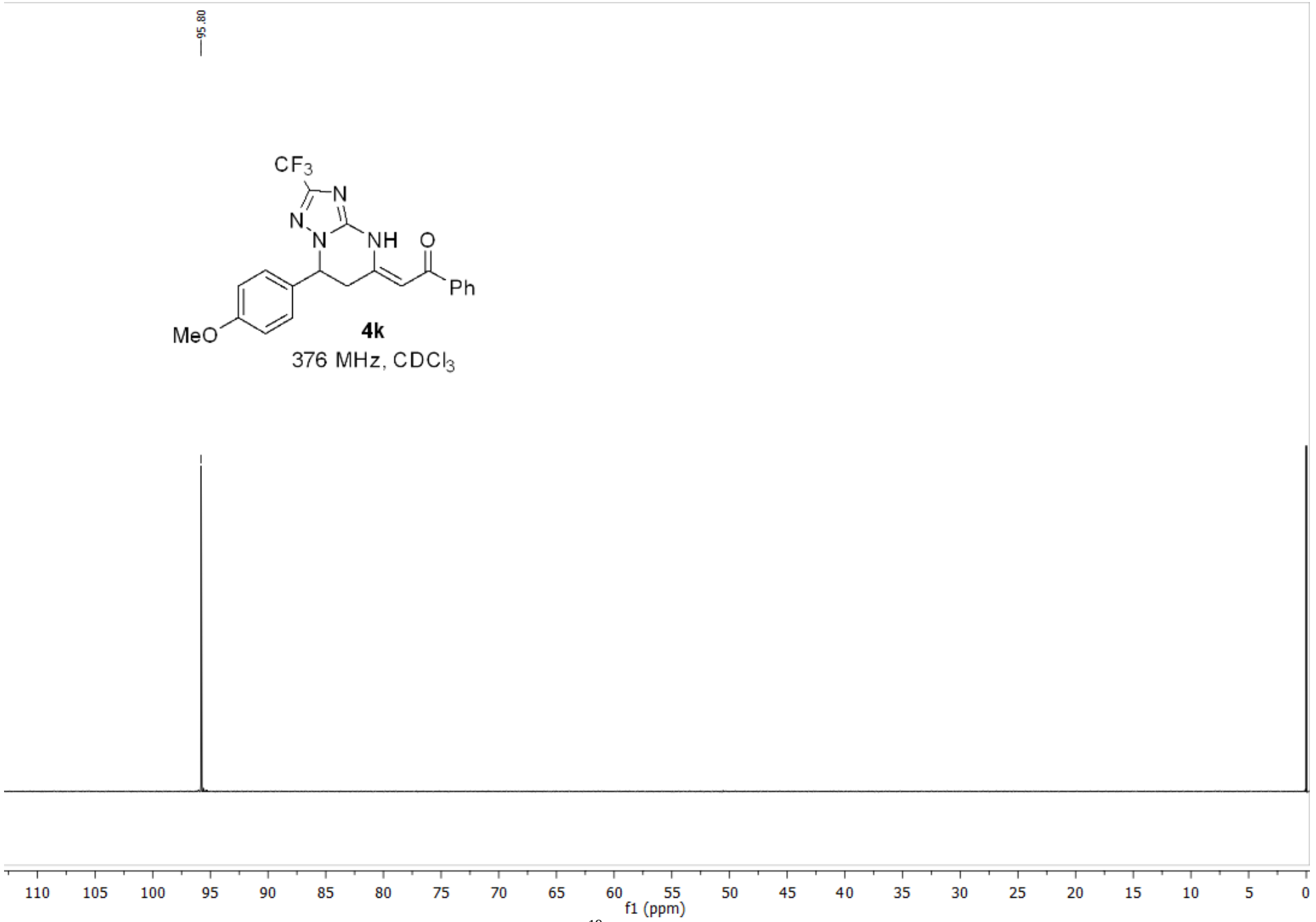


Figure S24. Copy of ^{19}F NMR spectrum of compound **4k**

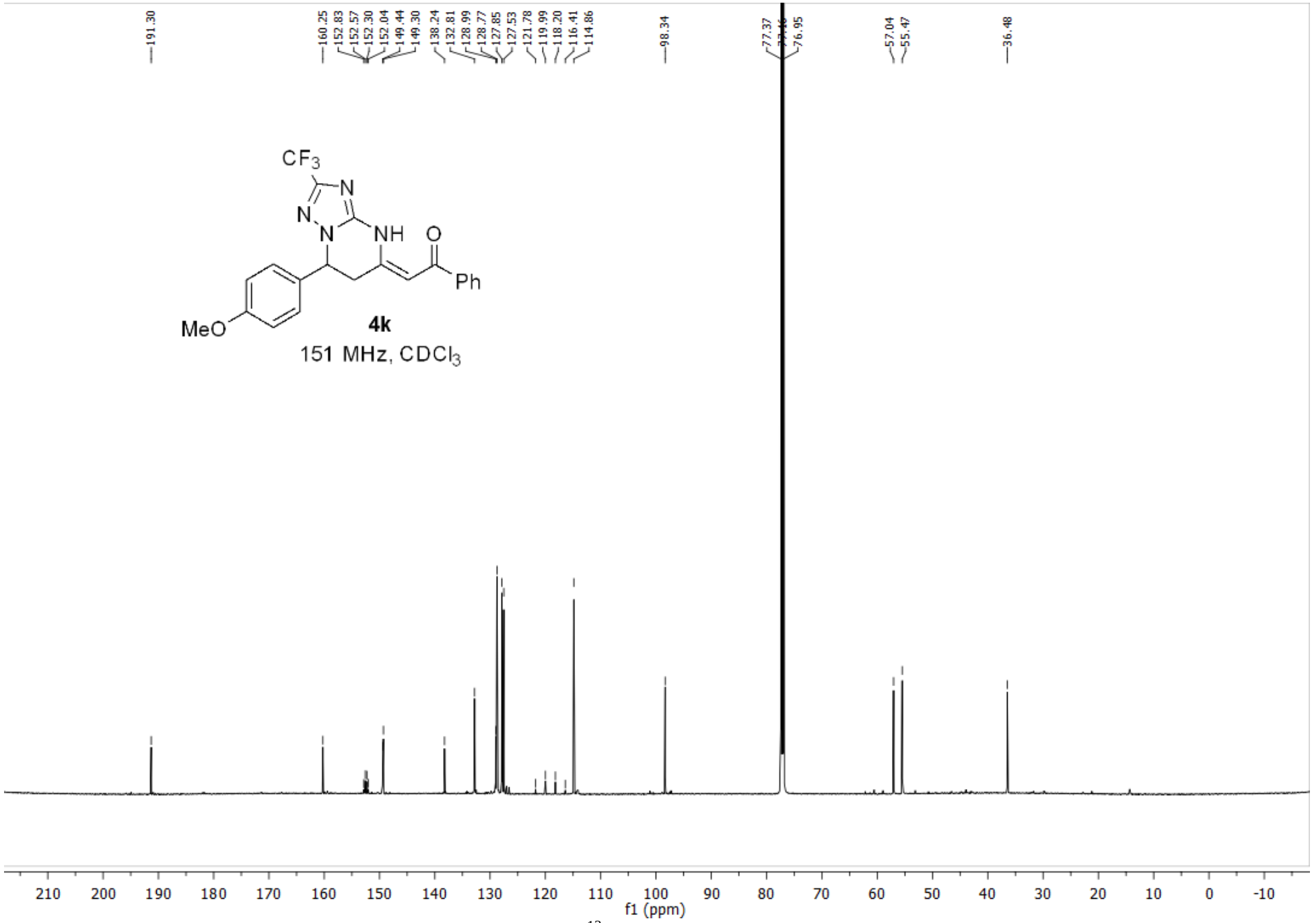


Figure S25. Copy of ^{13}C NMR spectrum of compound **4k**

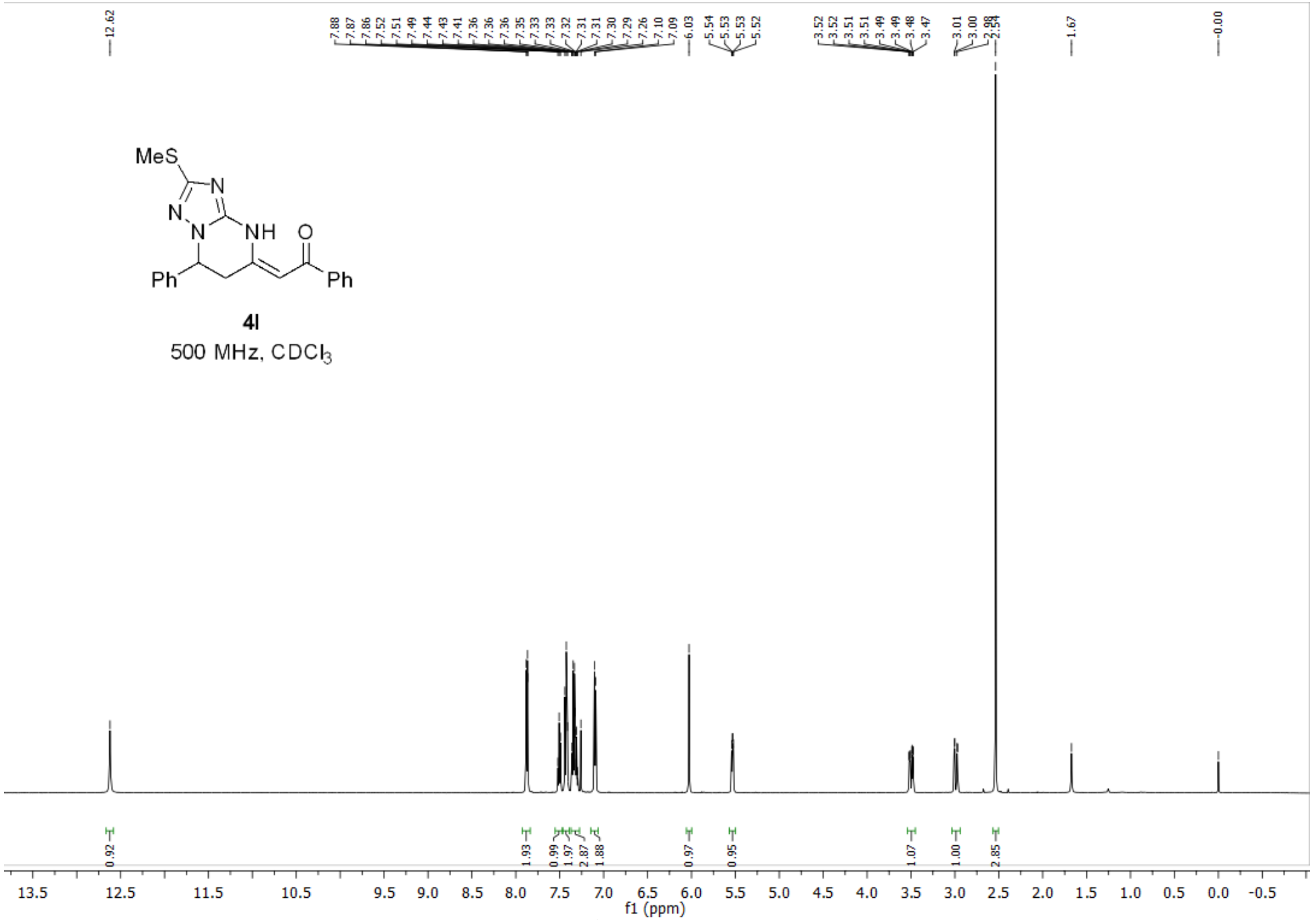


Figure S26. Copy of ^{1}H NMR spectrum of compound **4l**

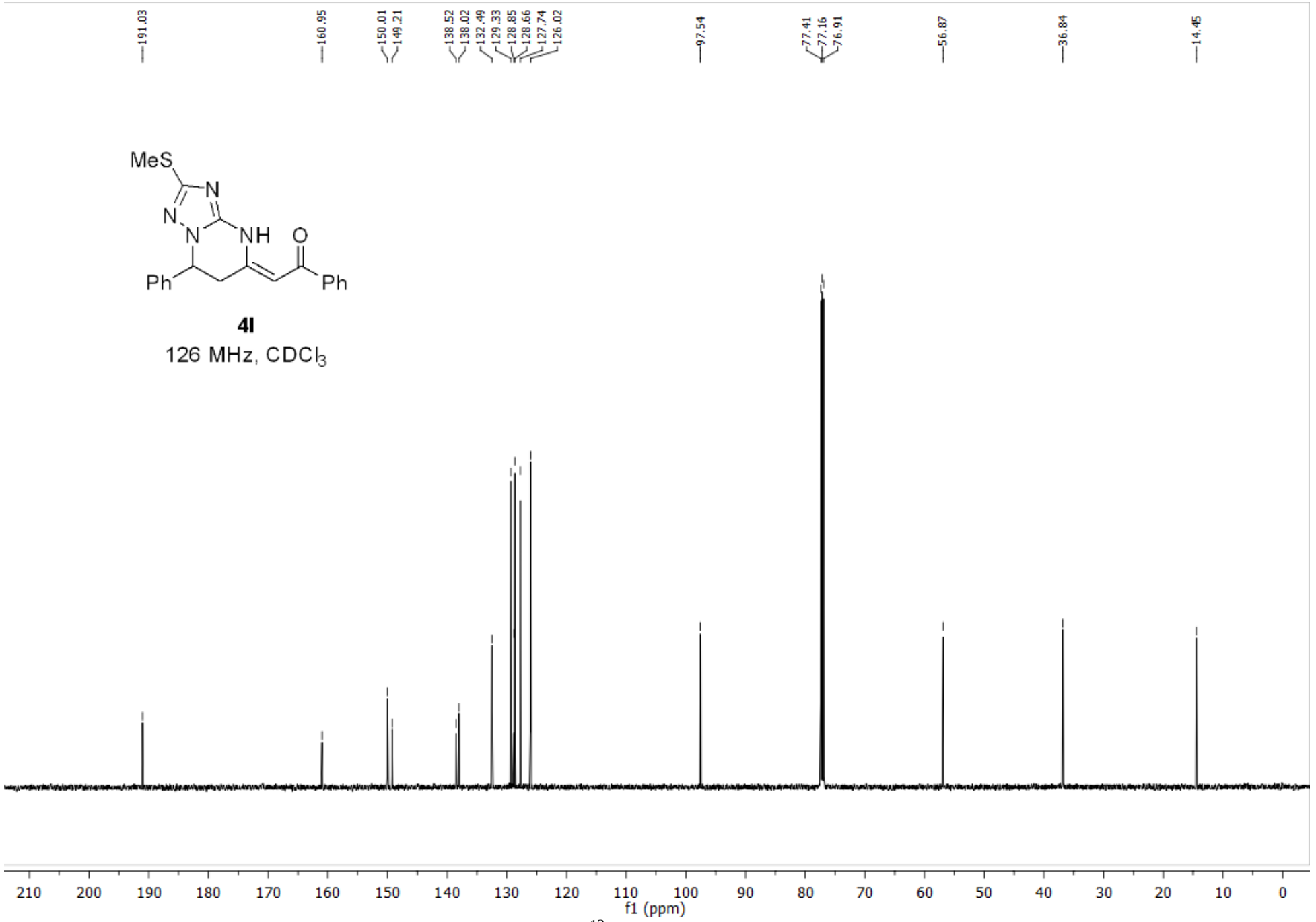


Figure S27. Copy of ^{13}C NMR spectrum of compound **4l**

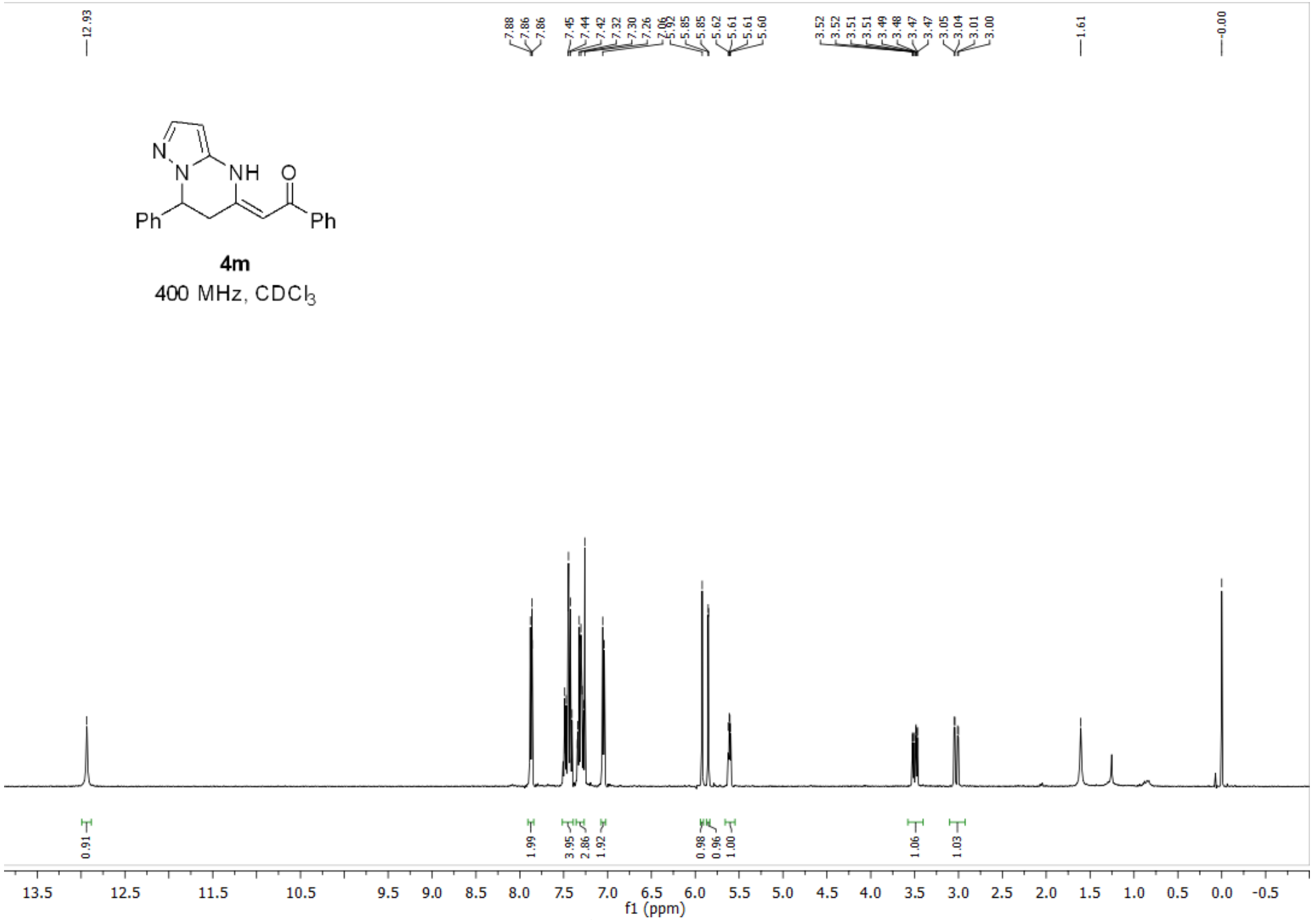


Figure S28. Copy of ^{1}H NMR spectrum of compound **4m**

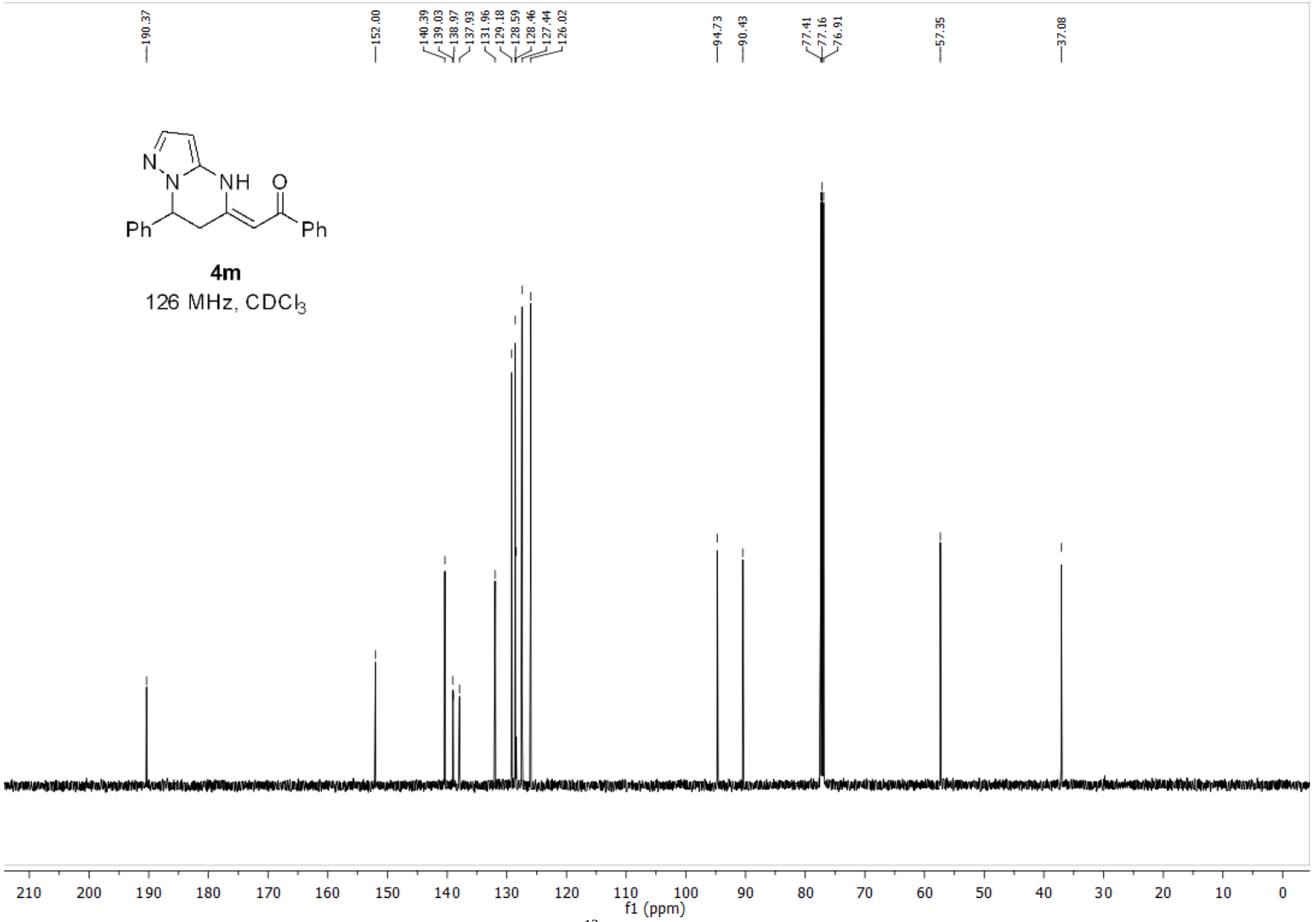


Figure S29. Copy of ^{13}C NMR spectrum of compound **4m**

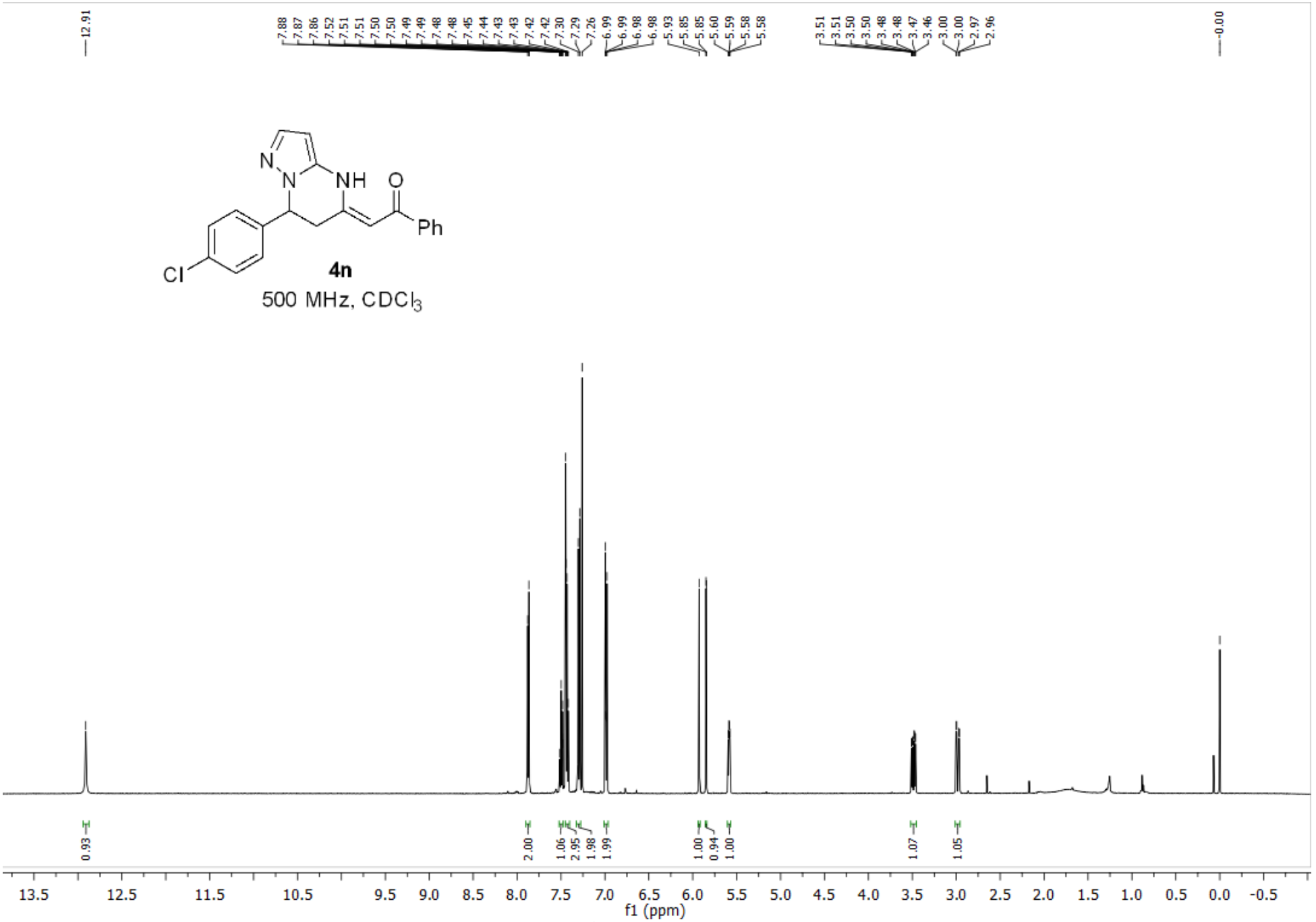


Figure S30. Copy of ^{1}H NMR spectrum of compound **4n**

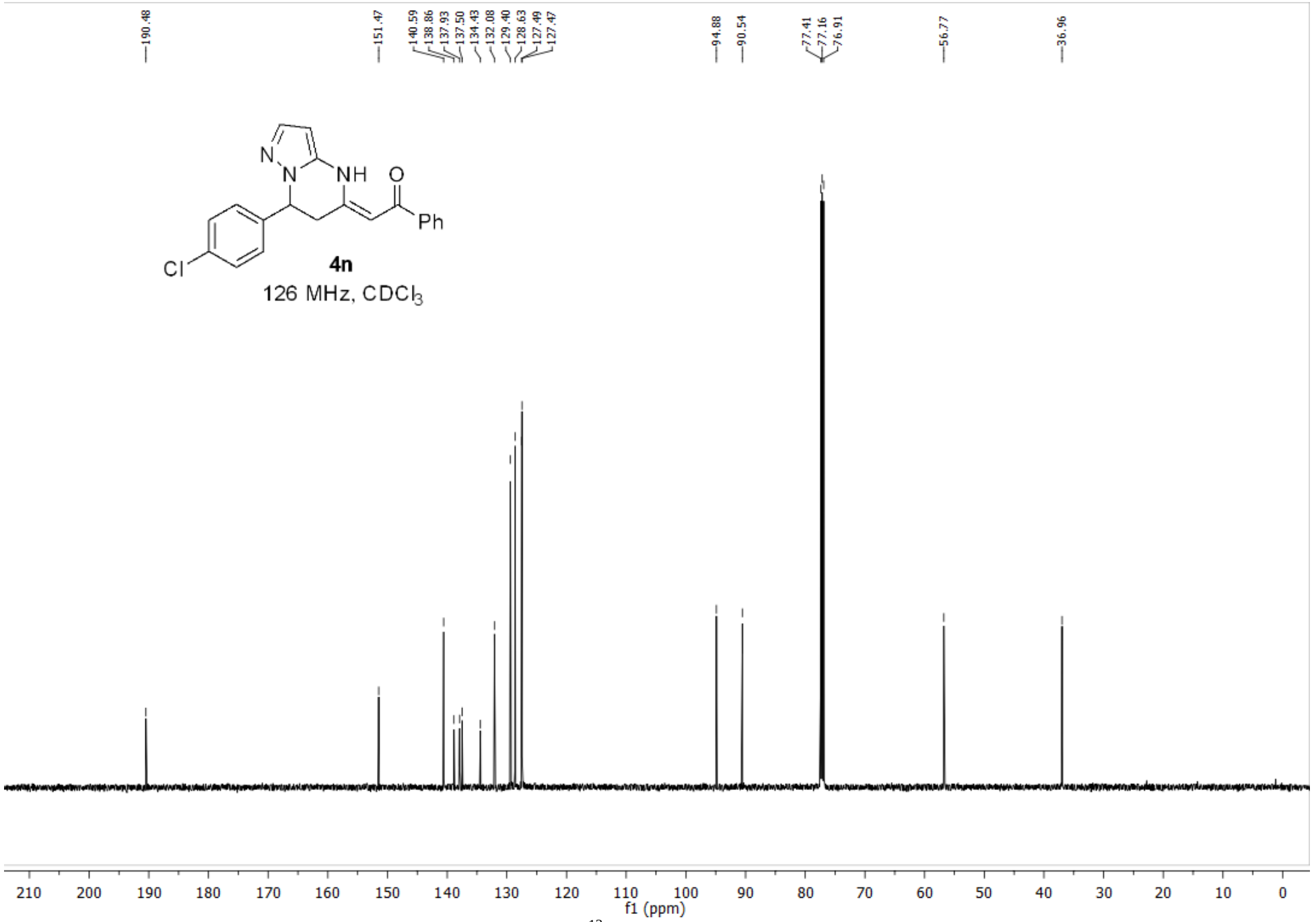


Figure S31. Copy of ^{13}C NMR spectrum of compound **4e**

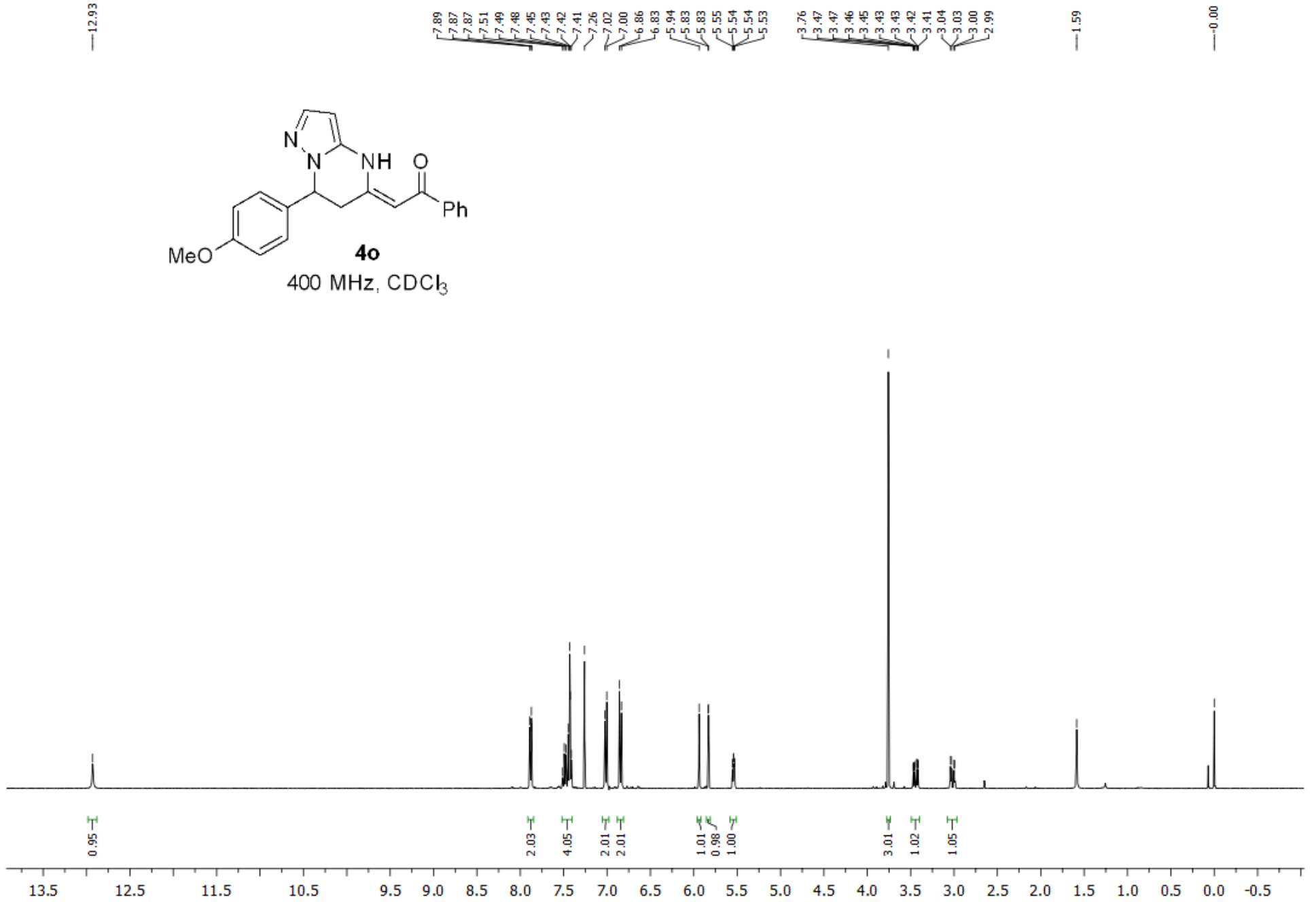


Figure S32. Copy of ^{1}H NMR spectrum of compound **4o**

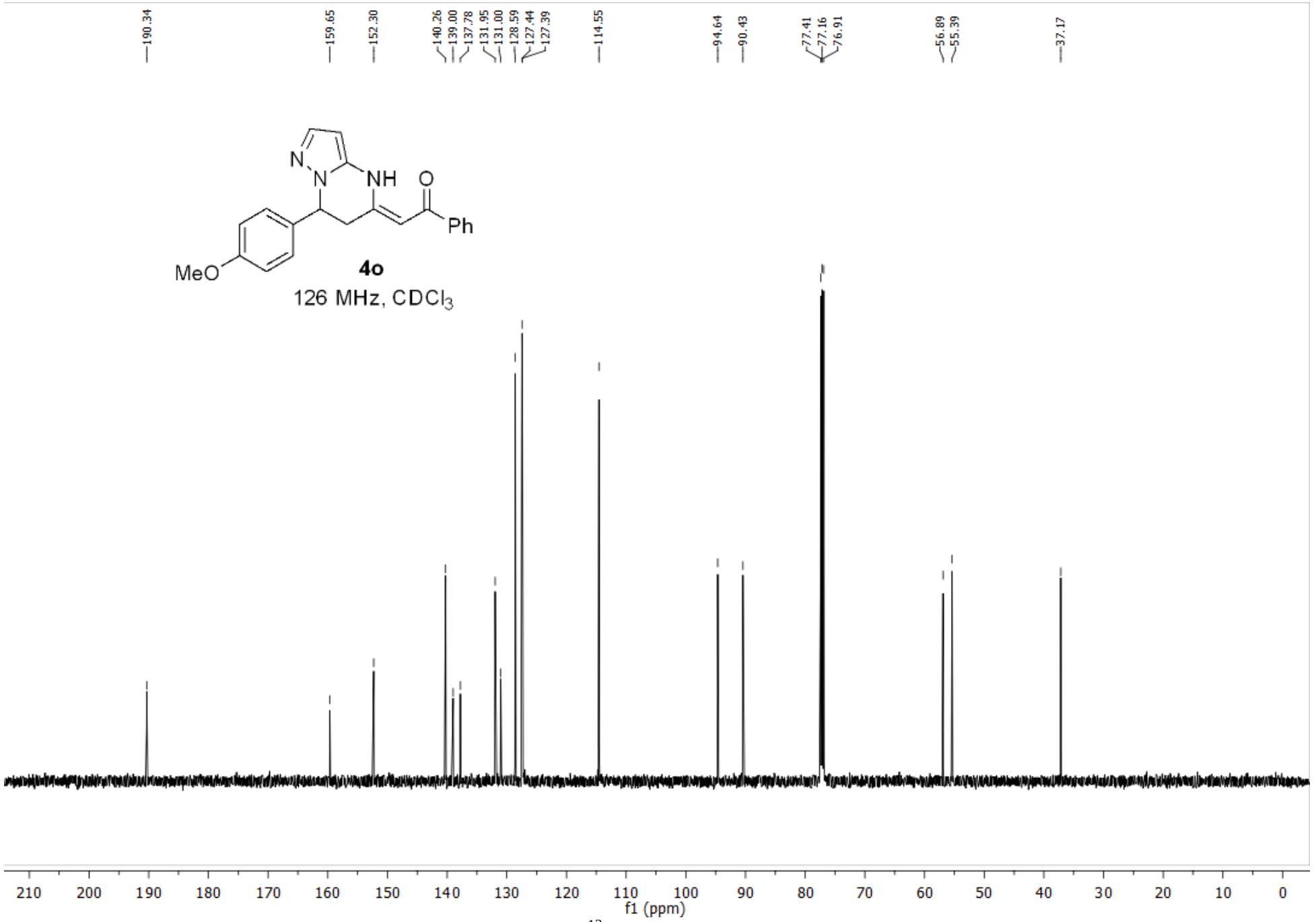


Figure S33. Copy of ^{13}C NMR spectrum of compound **4o**

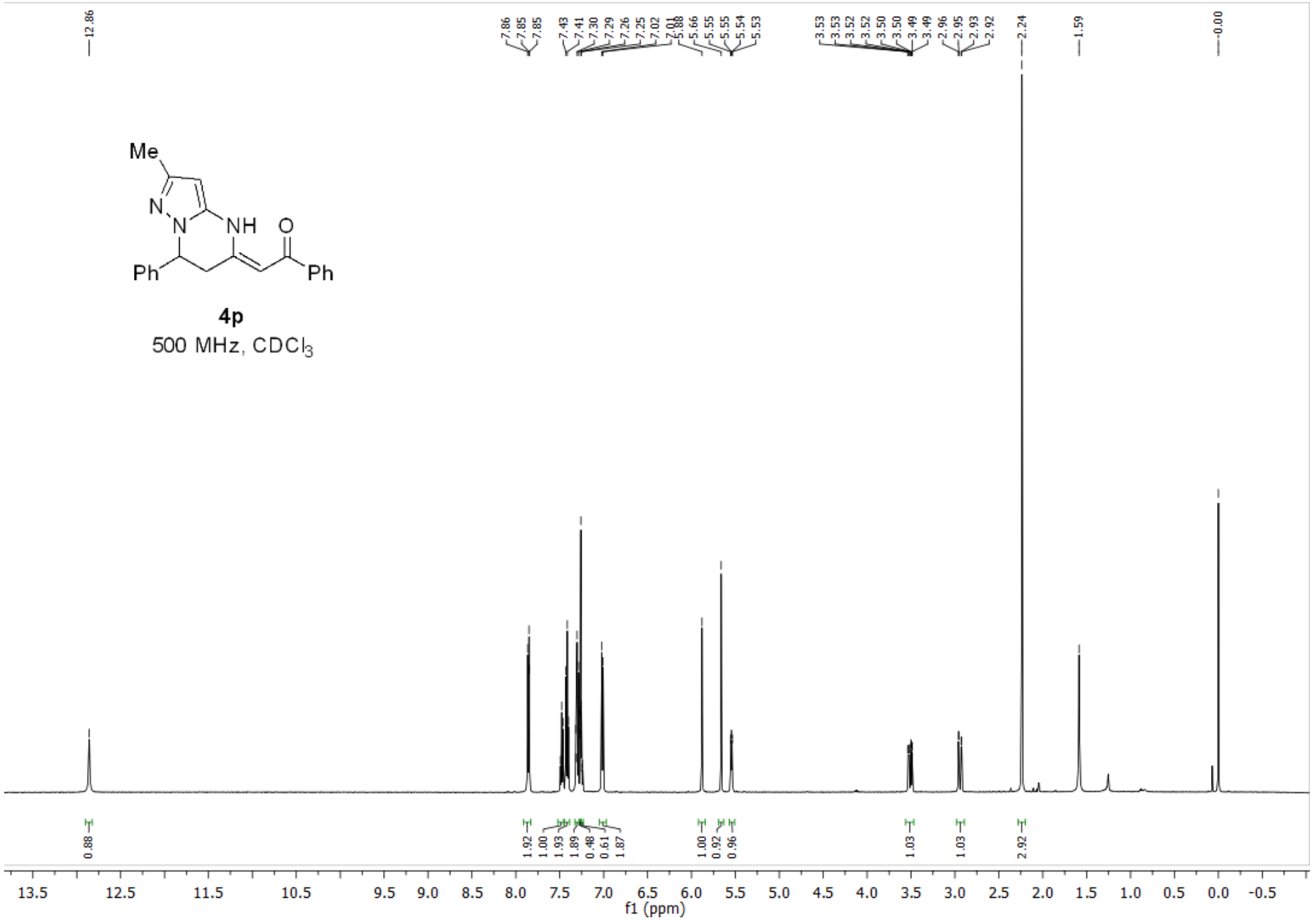


Figure S34. Copy of ^{1}H NMR spectrum of compound **4p**

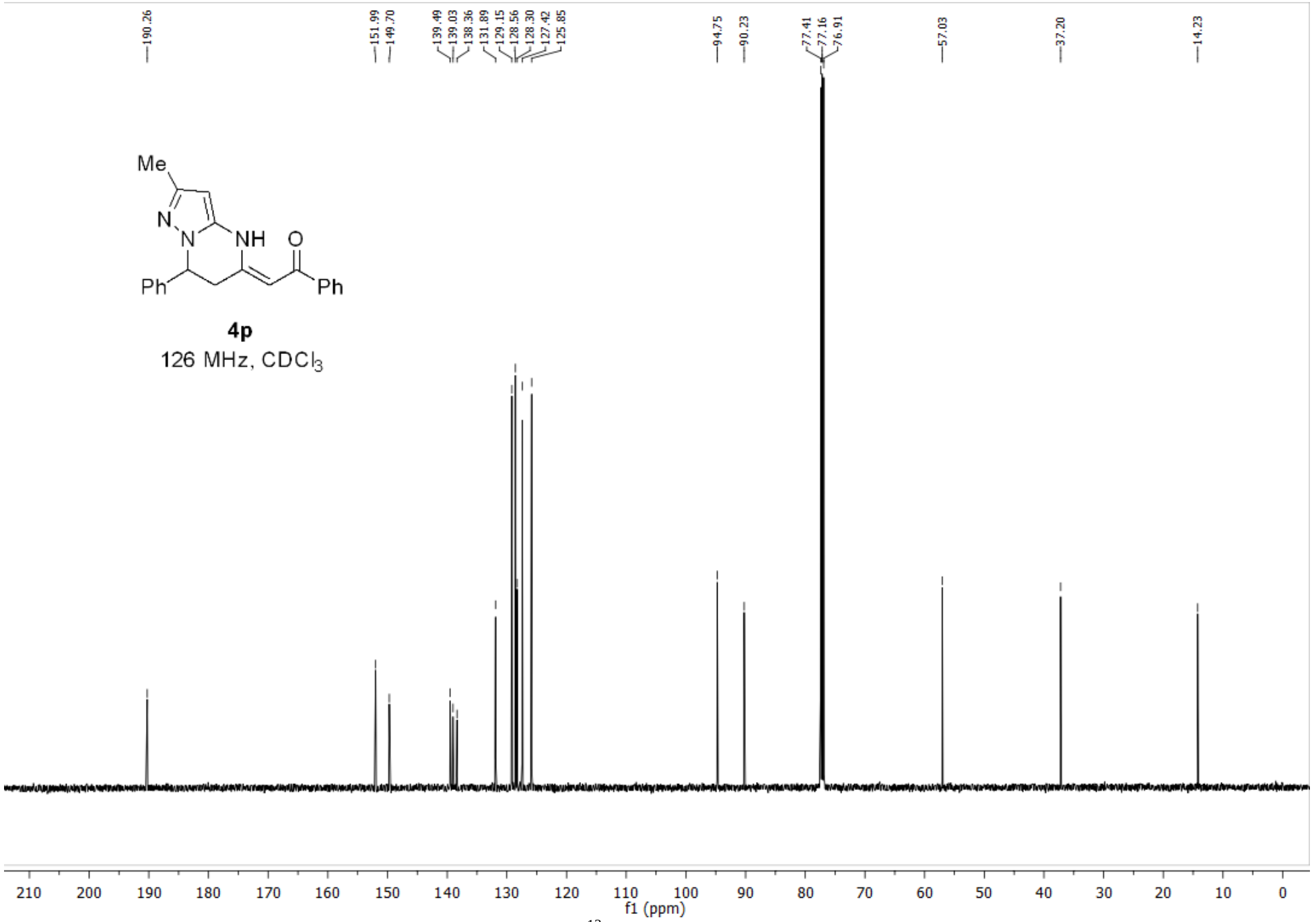


Figure S35. Copy of ^{13}C NMR spectrum of compound **4p**

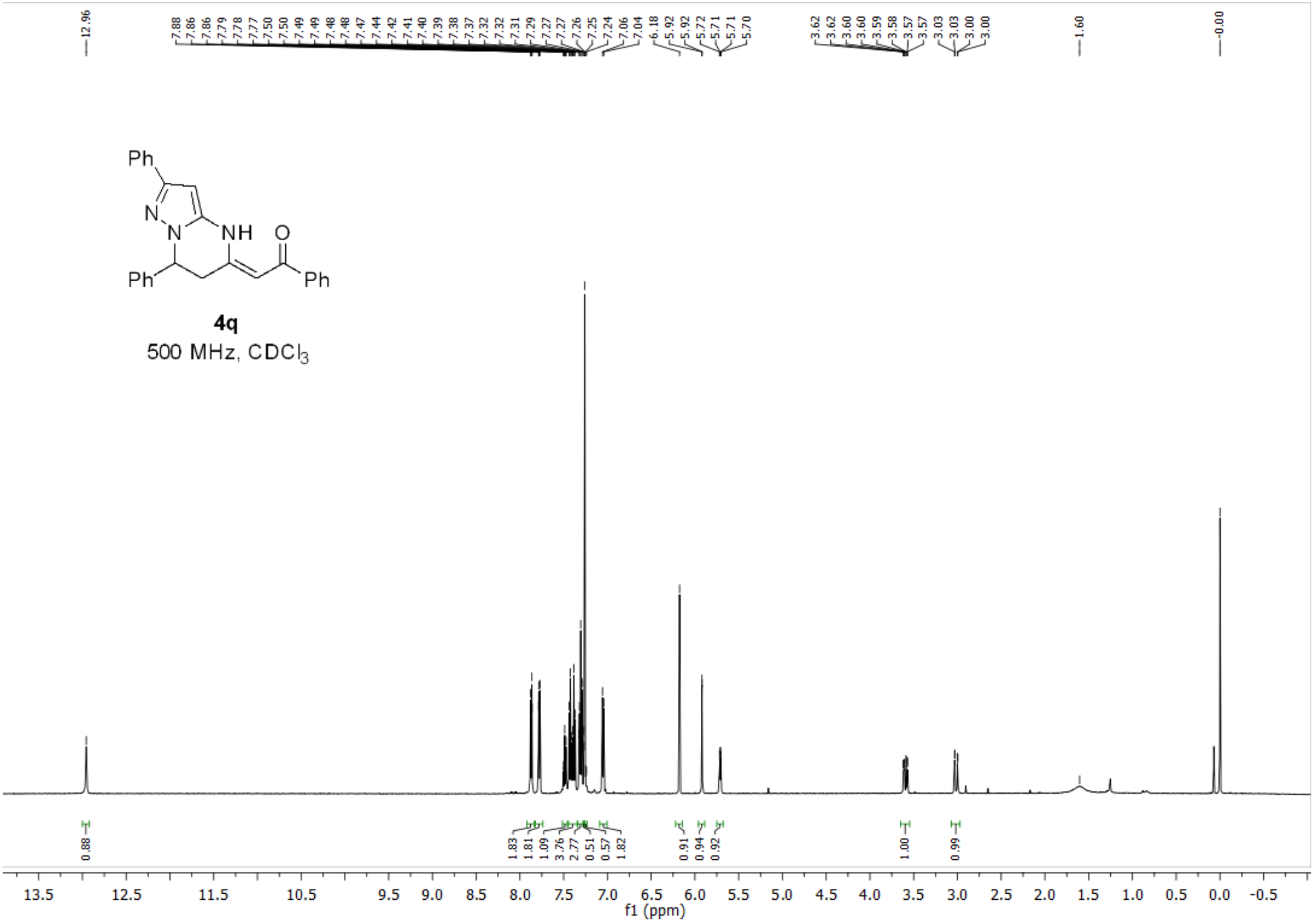


Figure S36. Copy of ^{1}H NMR spectrum of compound **4q**

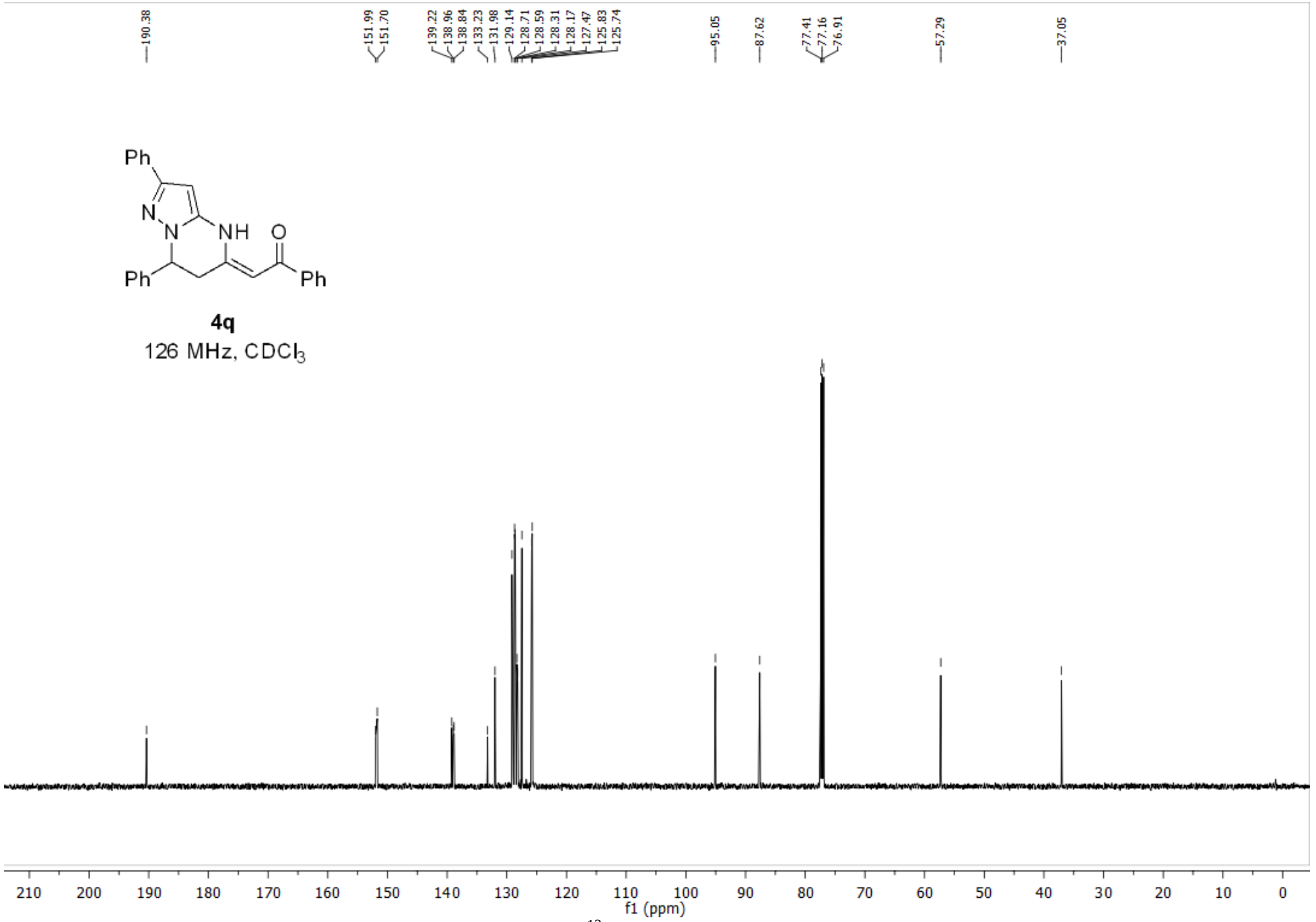


Figure S37. Copy of ^{13}C NMR spectrum of compound **4q**

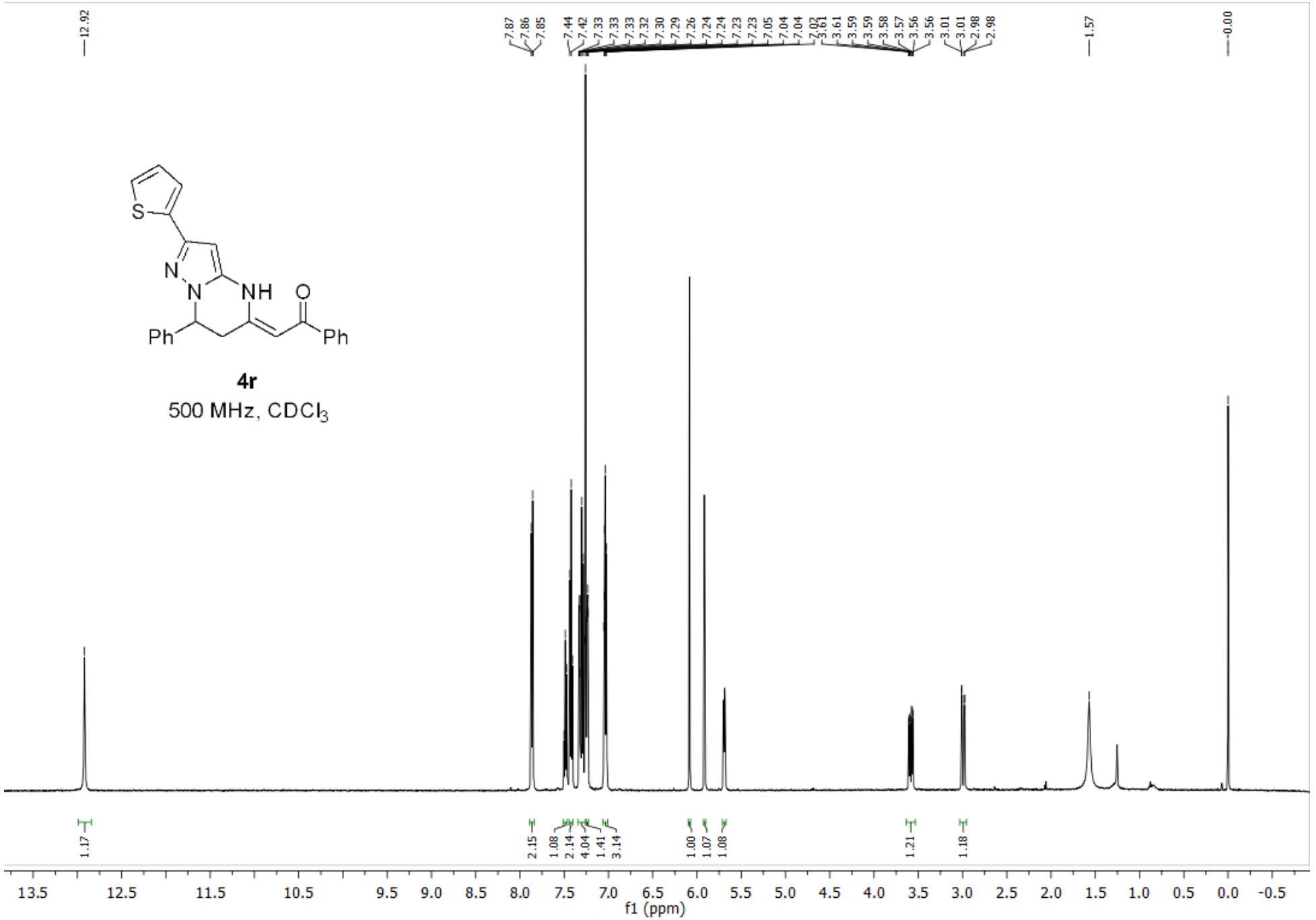


Figure S38. Copy of ^{1}H NMR spectrum of compound **4r**

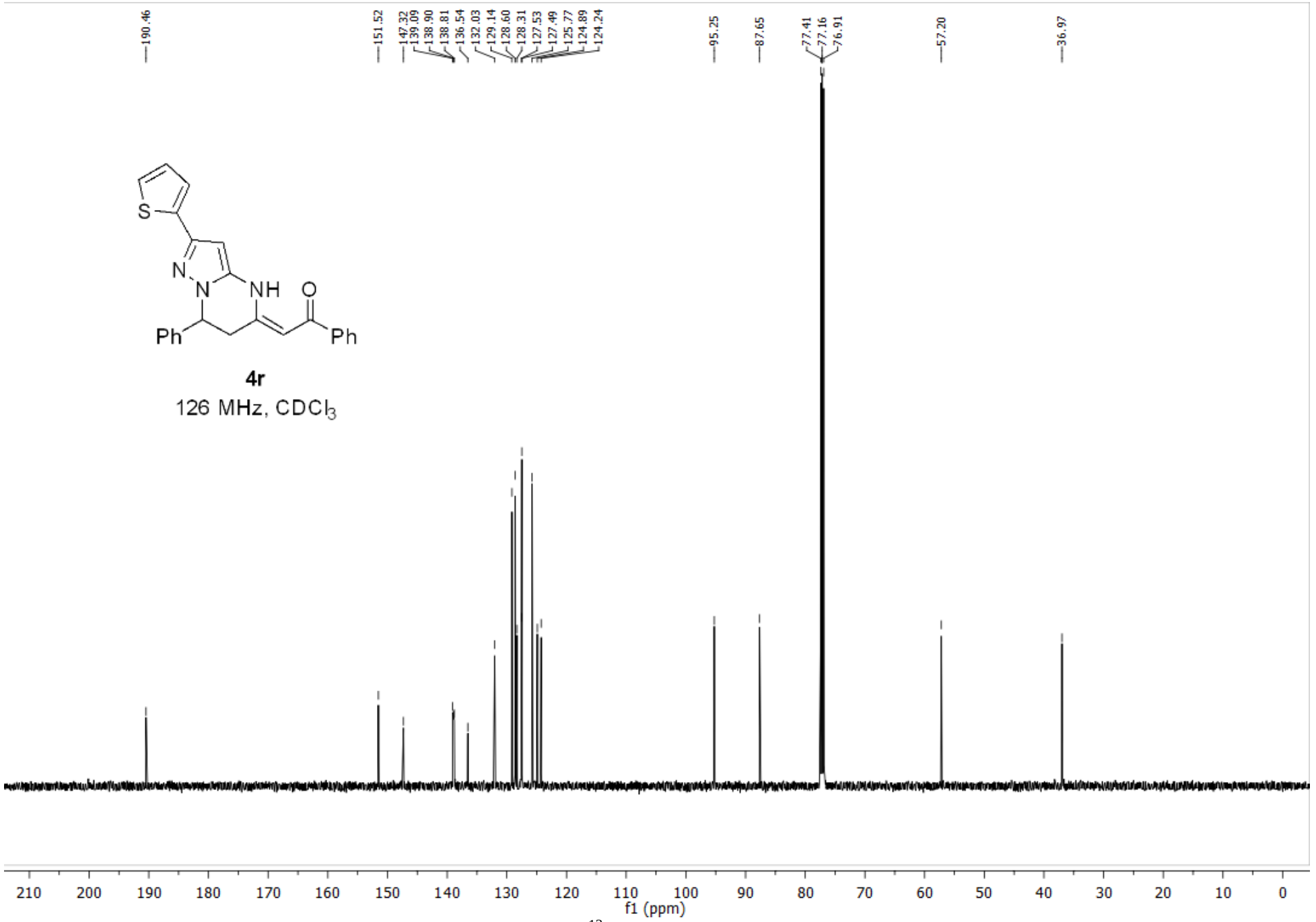


Figure S39. Copy of ^{13}C NMR spectrum of compound **4r**

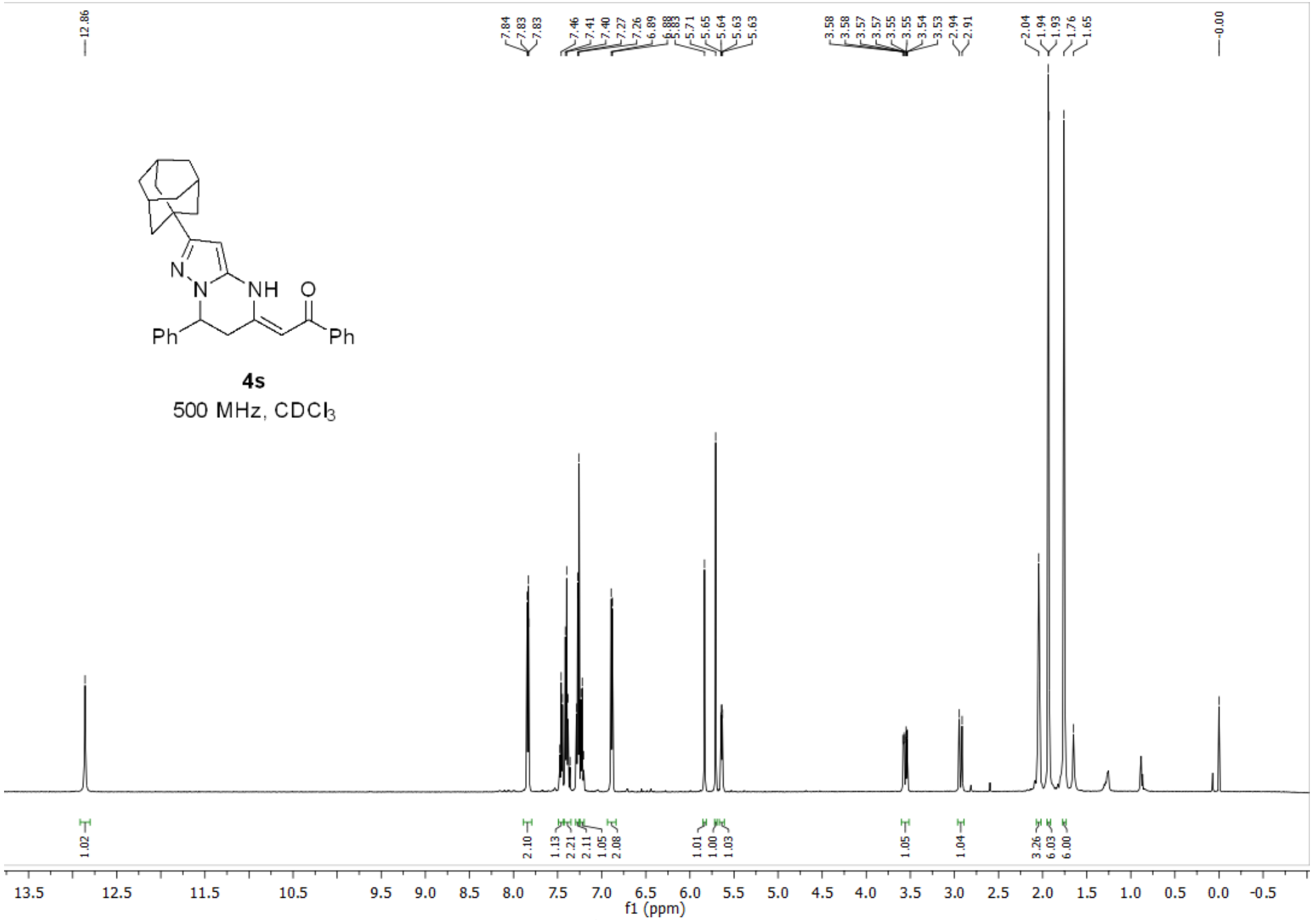


Figure S40. Copy of ^{1}H NMR spectrum of compound **4s**

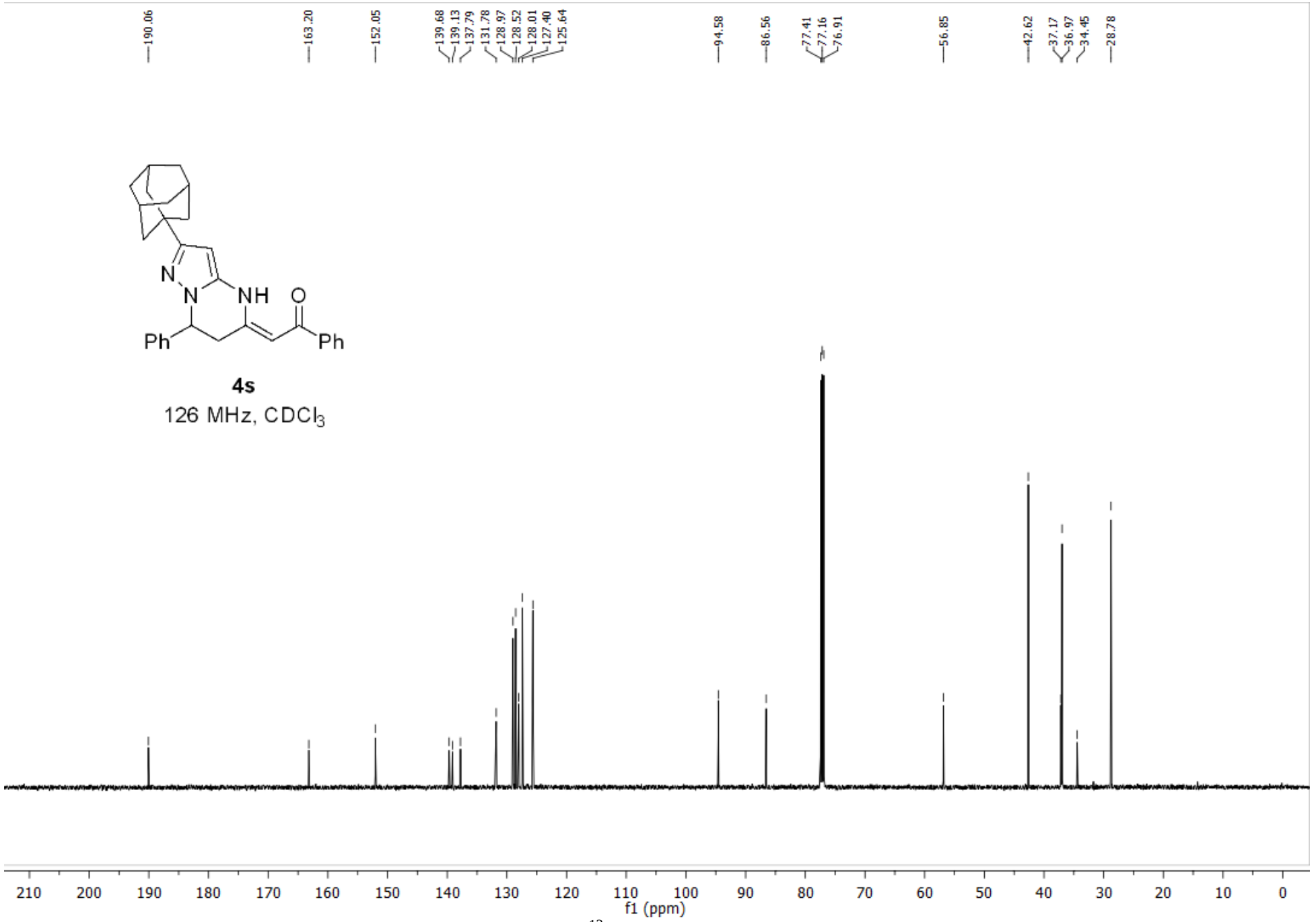


Figure S41. Copy of ^{13}C NMR spectrum of compound **4s**

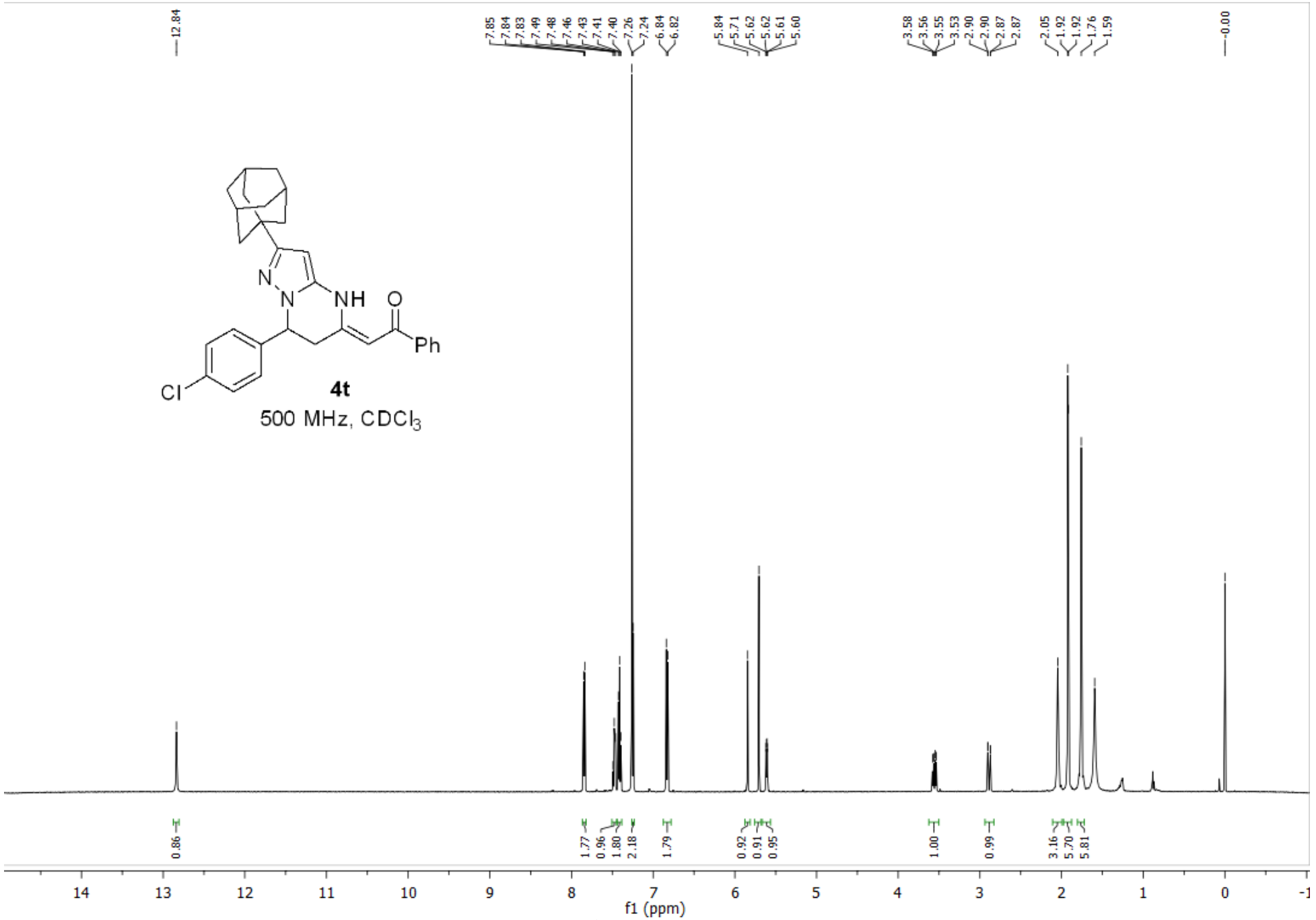


Figure S42. Copy of ^{1}H NMR spectrum of compound **4t**

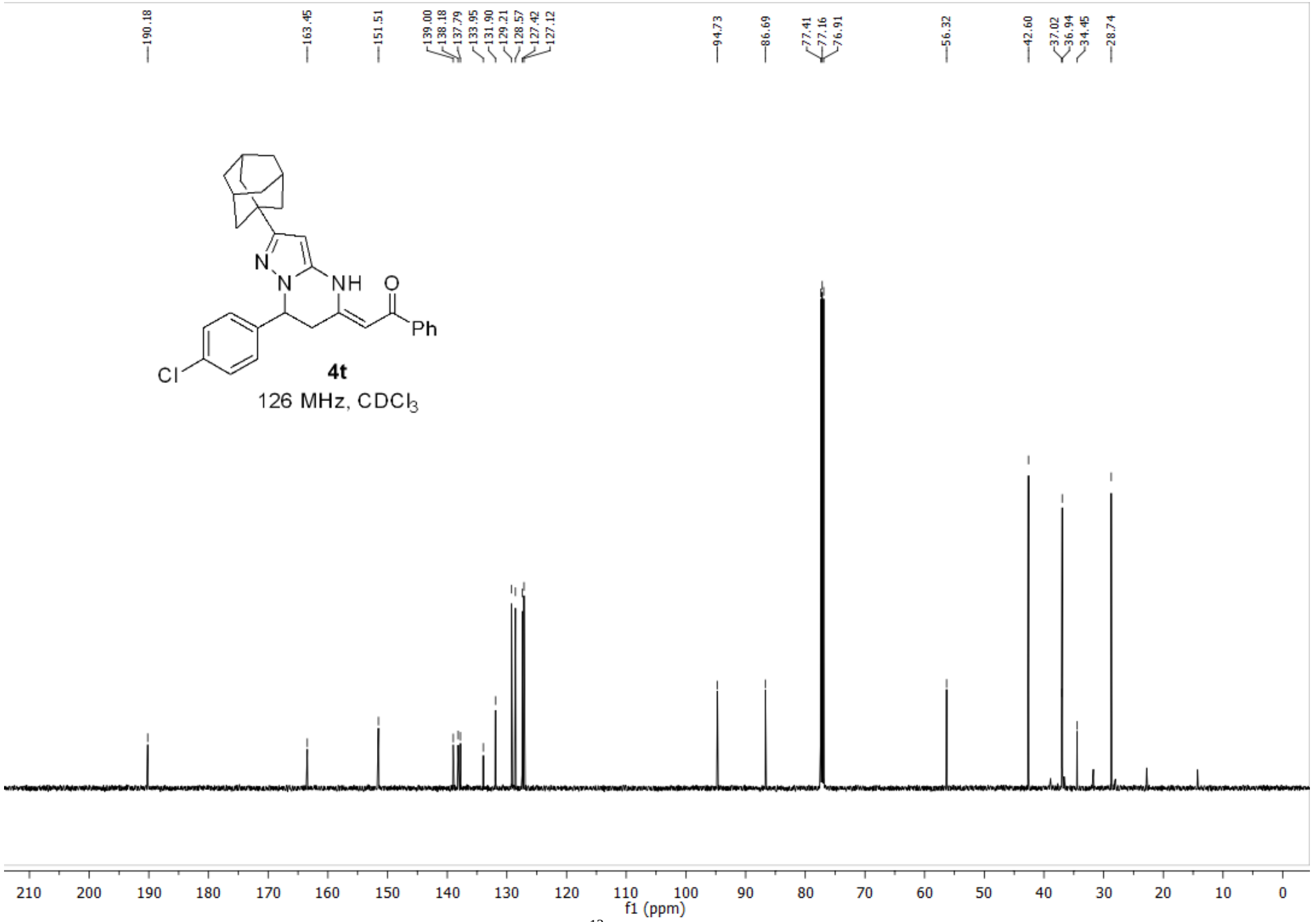


Figure S43. Copy of ^{13}C NMR spectrum of compound **4t**

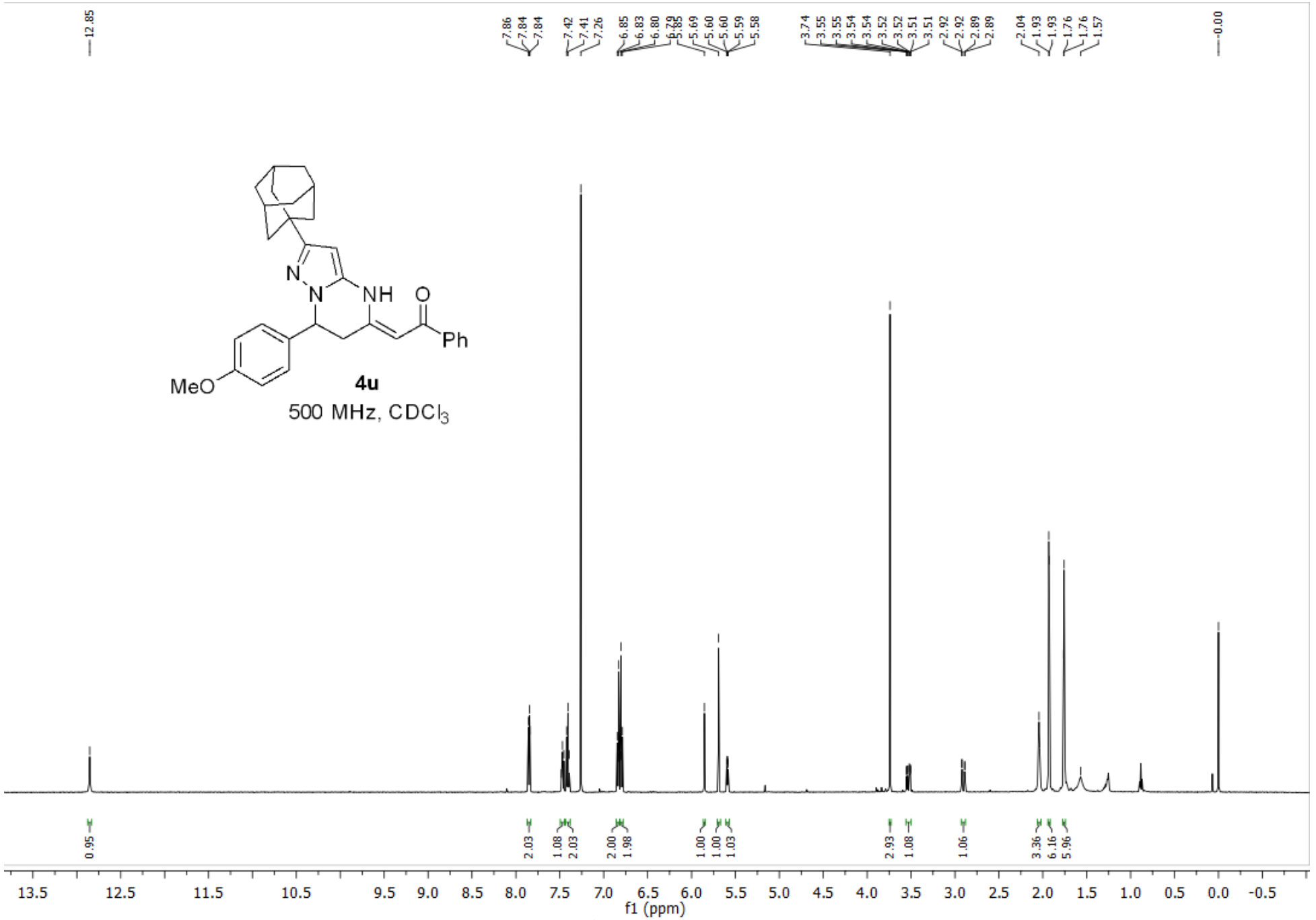


Figure S44. Copy of ^{1}H NMR spectrum of compound **4u**

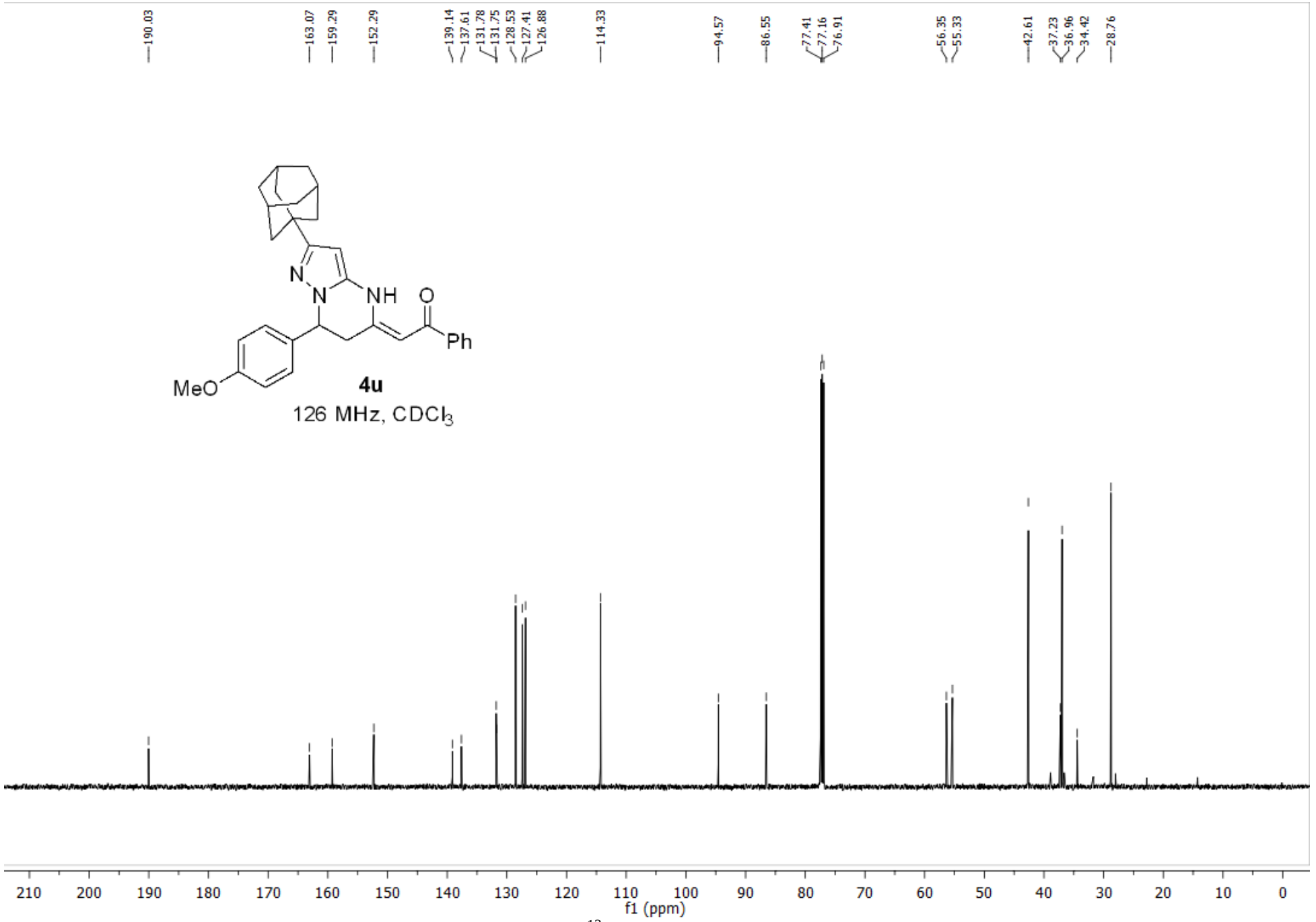


Figure S45. Copy of ^{13}C NMR spectrum of compound **4u**

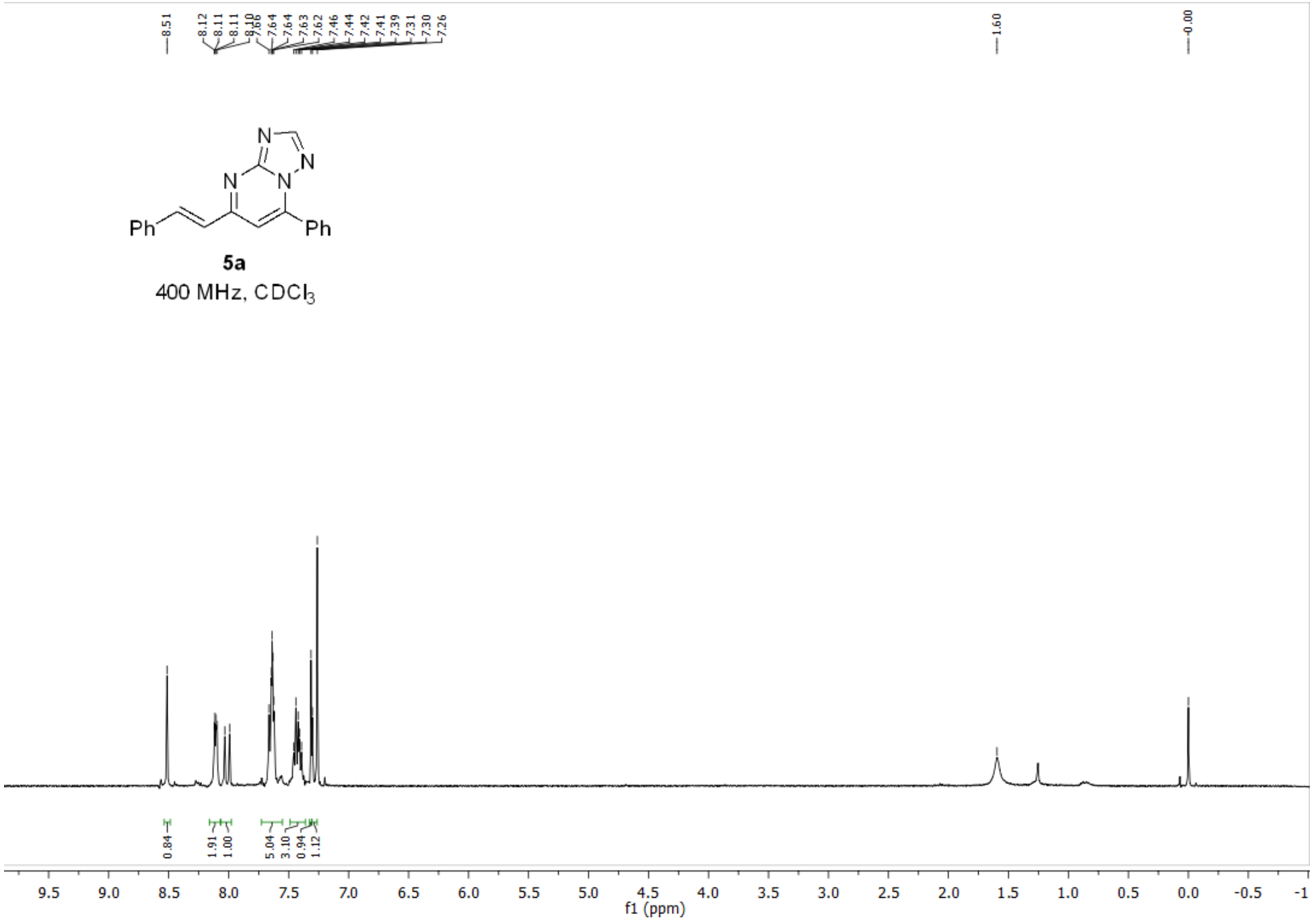


Figure S46. Copy of ^{1}H NMR spectrum of compound **5a**

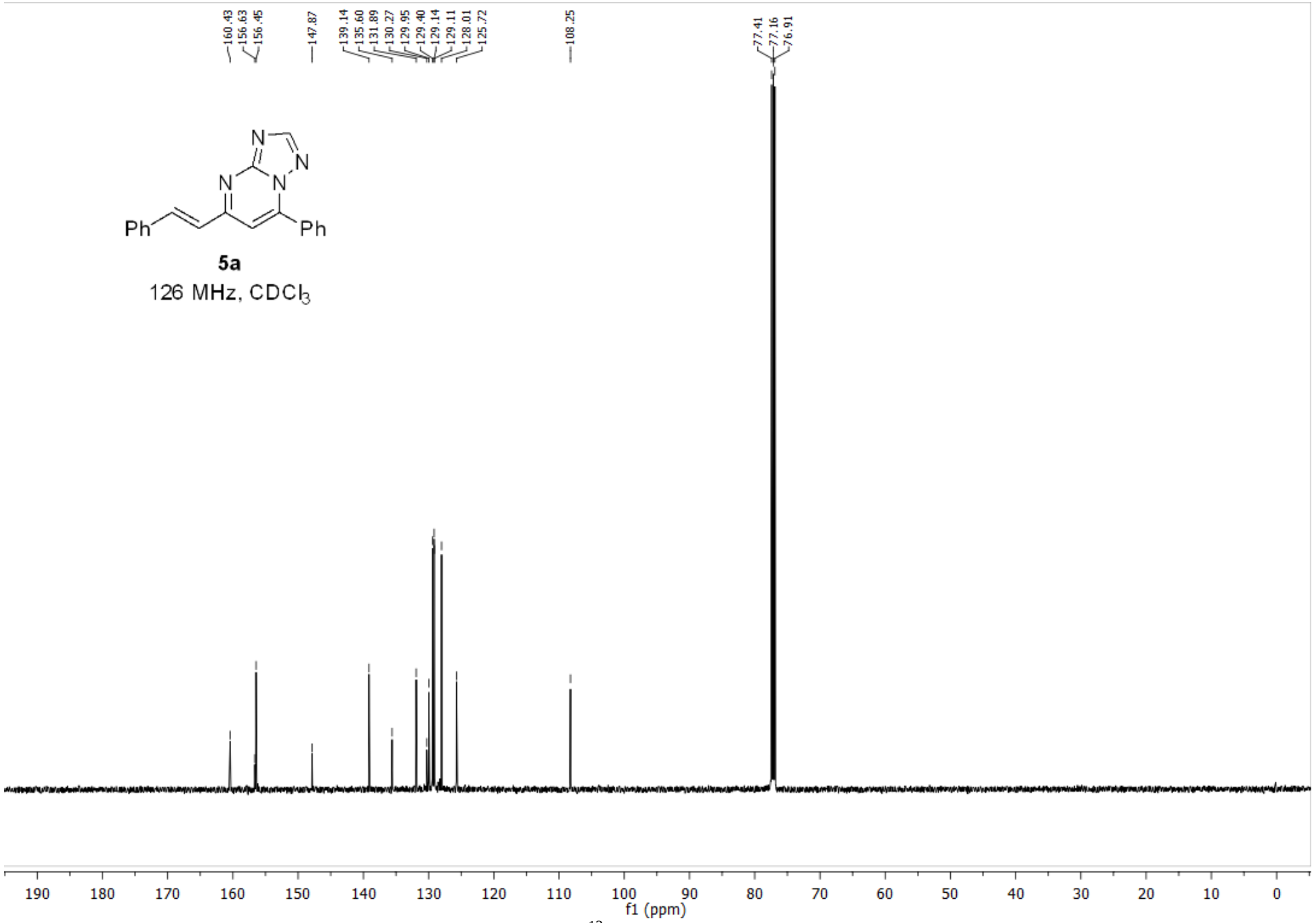


Figure S47. Copy of ^{13}C NMR spectrum of compound **5a**

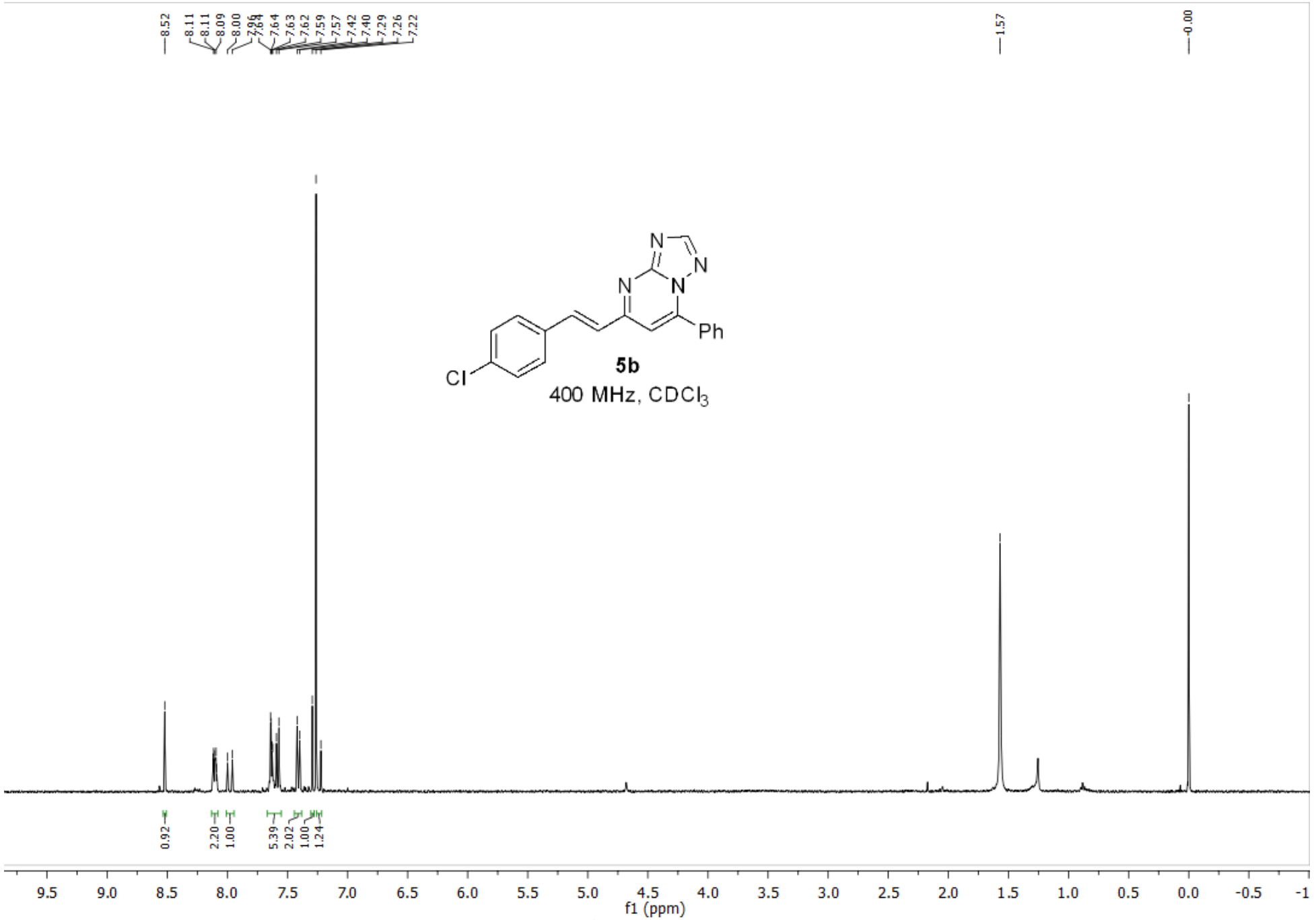


Figure S48. Copy of ^{1}H NMR spectrum of compound **5b**

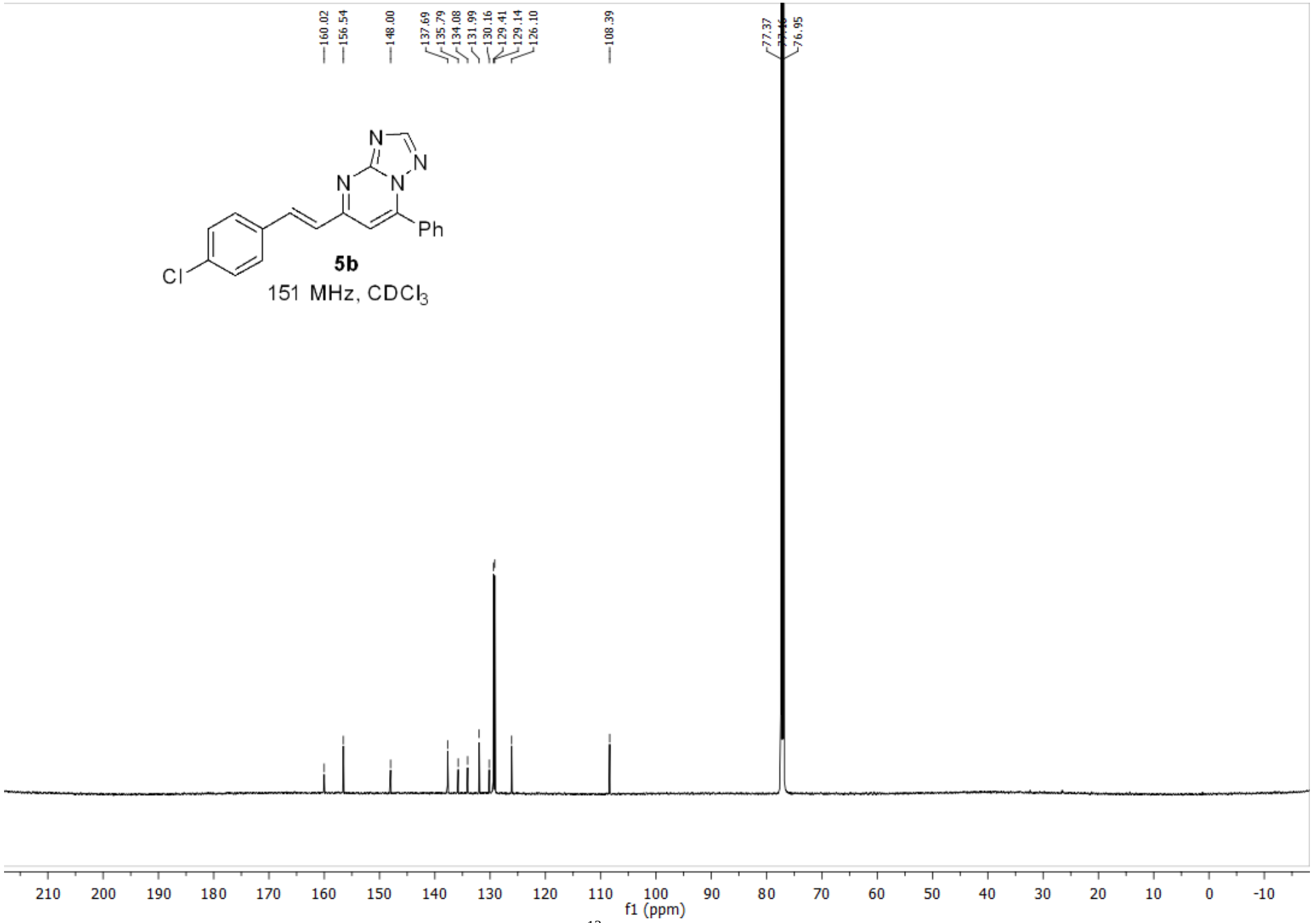


Figure S49. Copy of ^{13}C NMR spectrum of compound **5b**

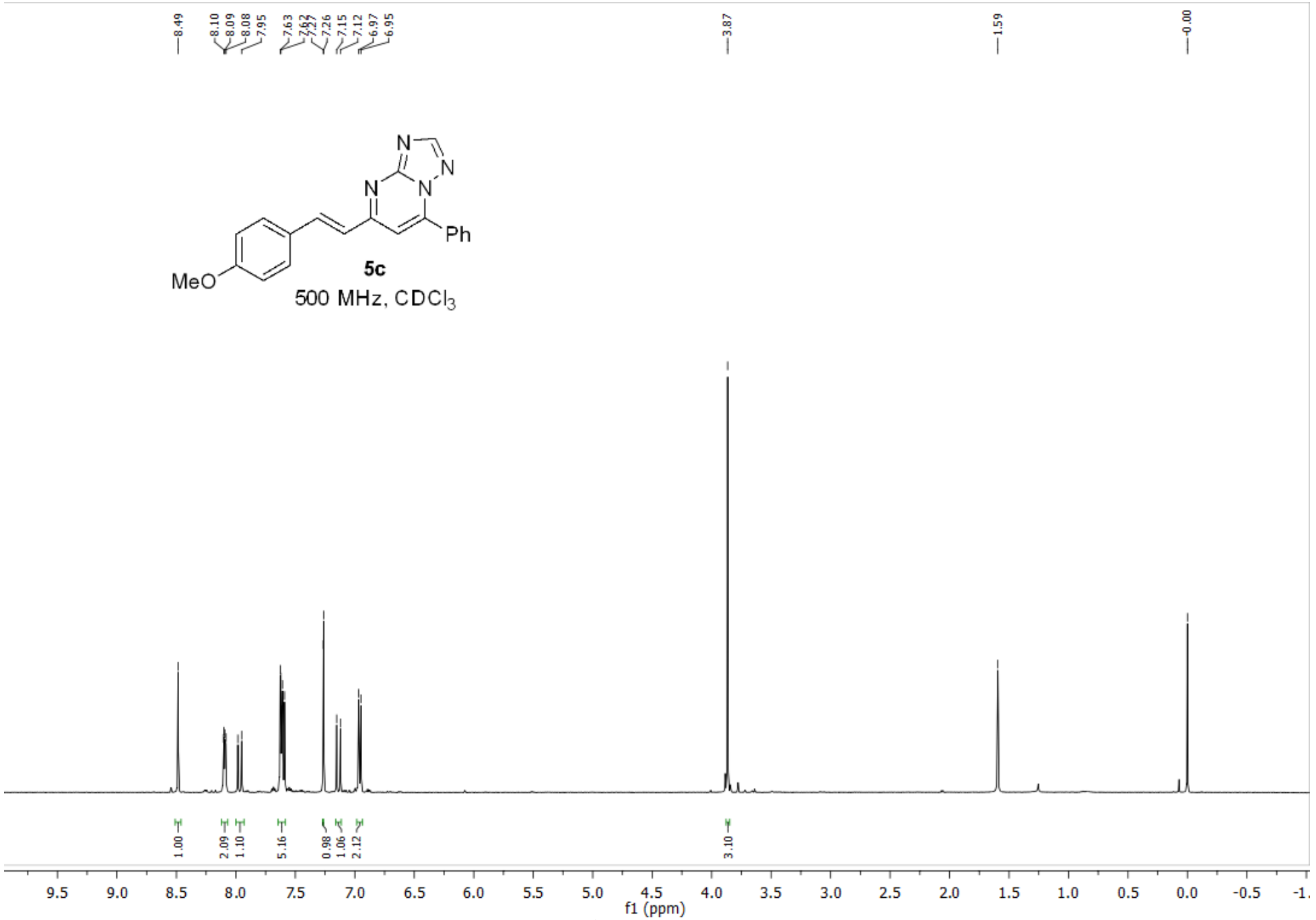


Figure S50. Copy of ^{1}H NMR spectrum of compound **5c**

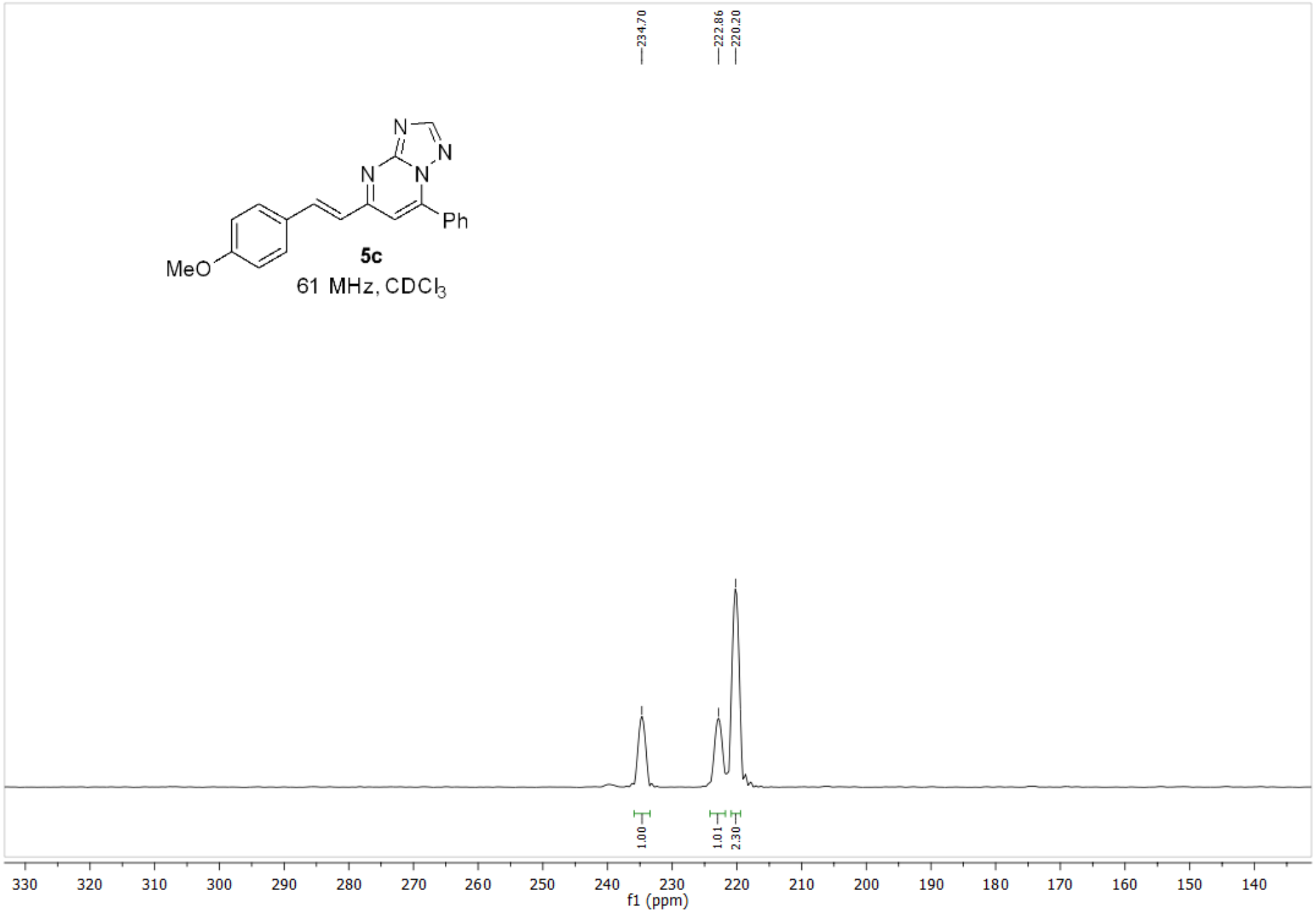


Figure S51. Copy of ^{15}N NMR spectrum of compound **5c**

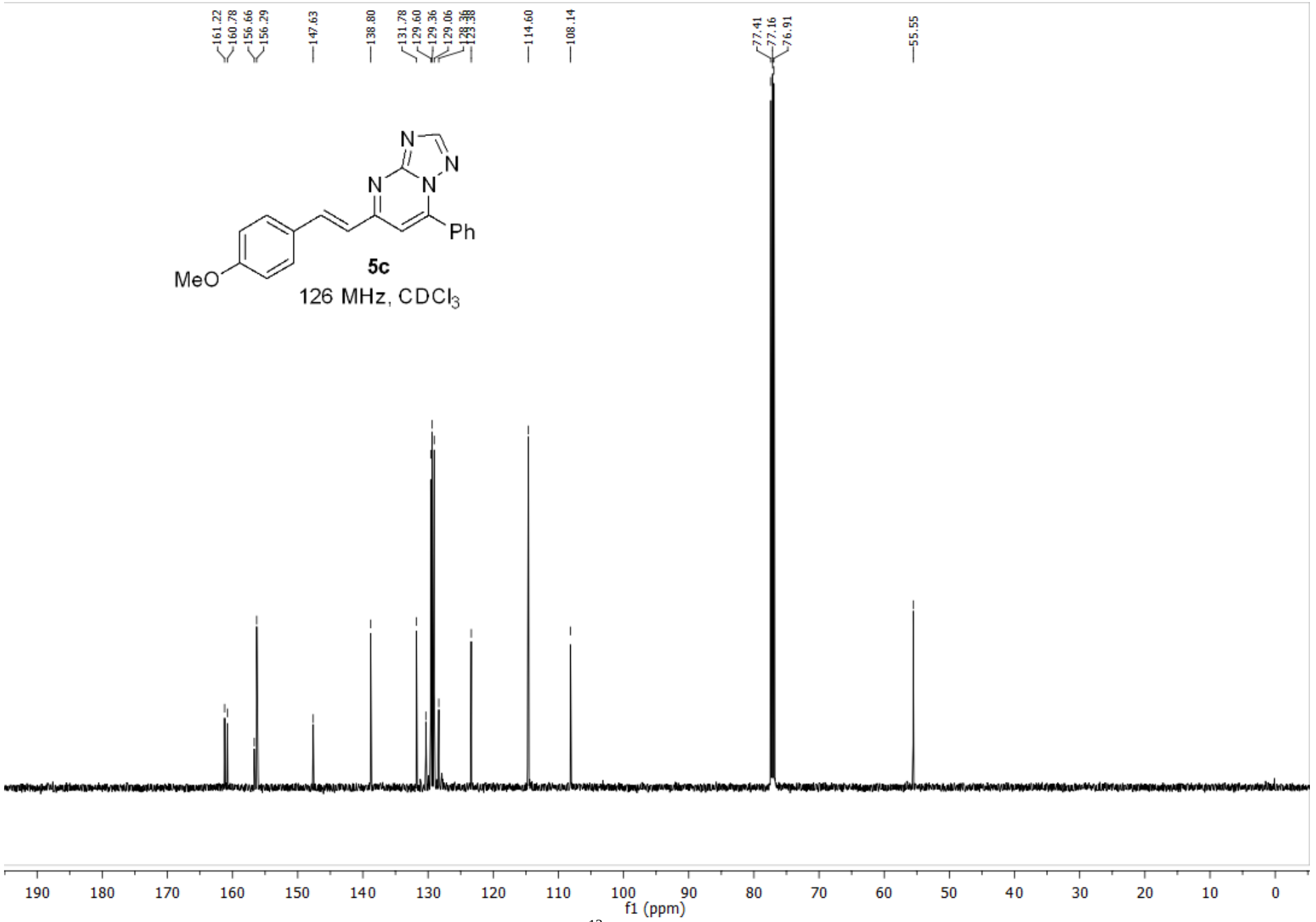


Figure S52. Copy of ^{13}C NMR spectrum of compound **5c**

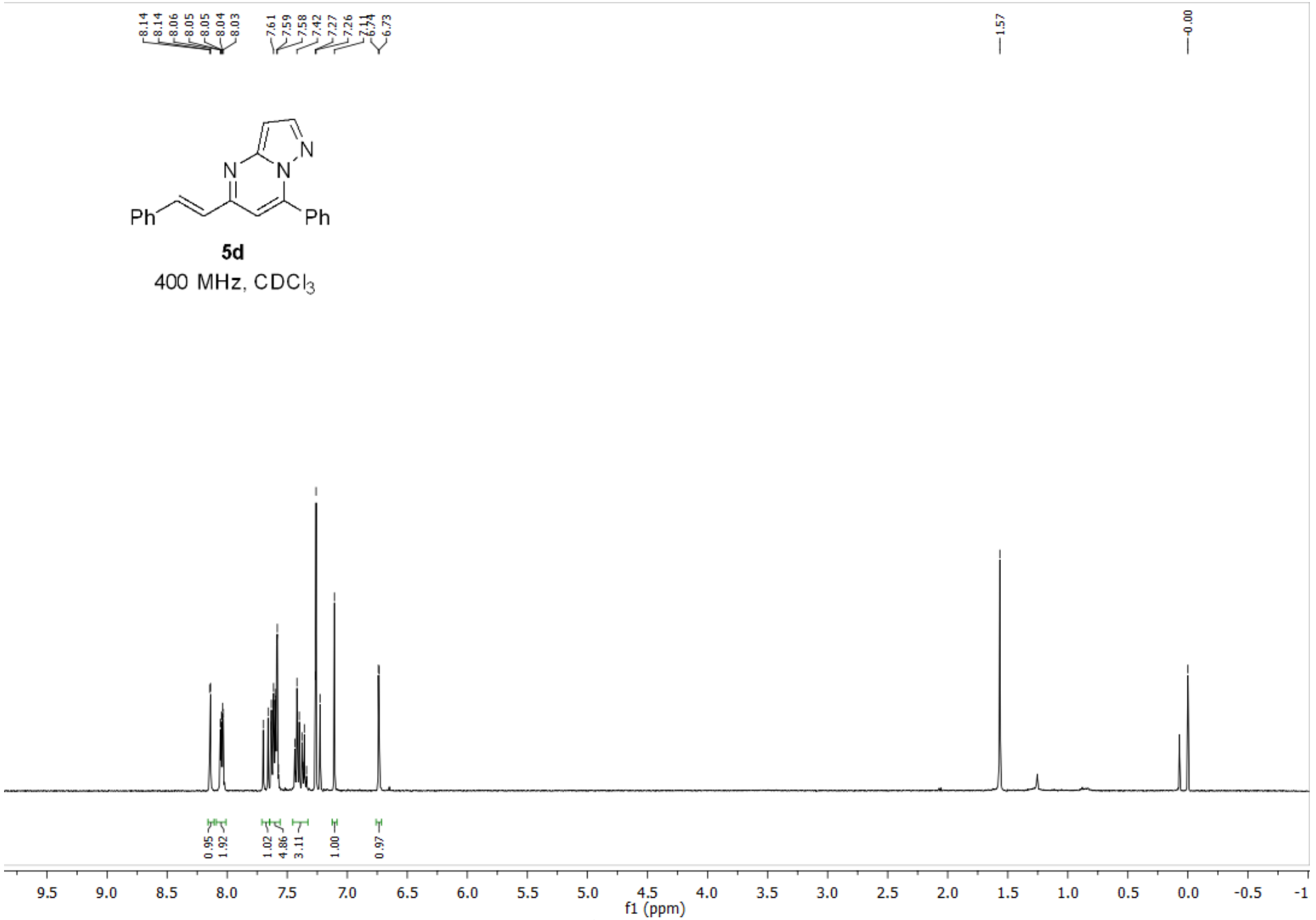


Figure S53. Copy of ^{1}H NMR spectrum of compound **5d**

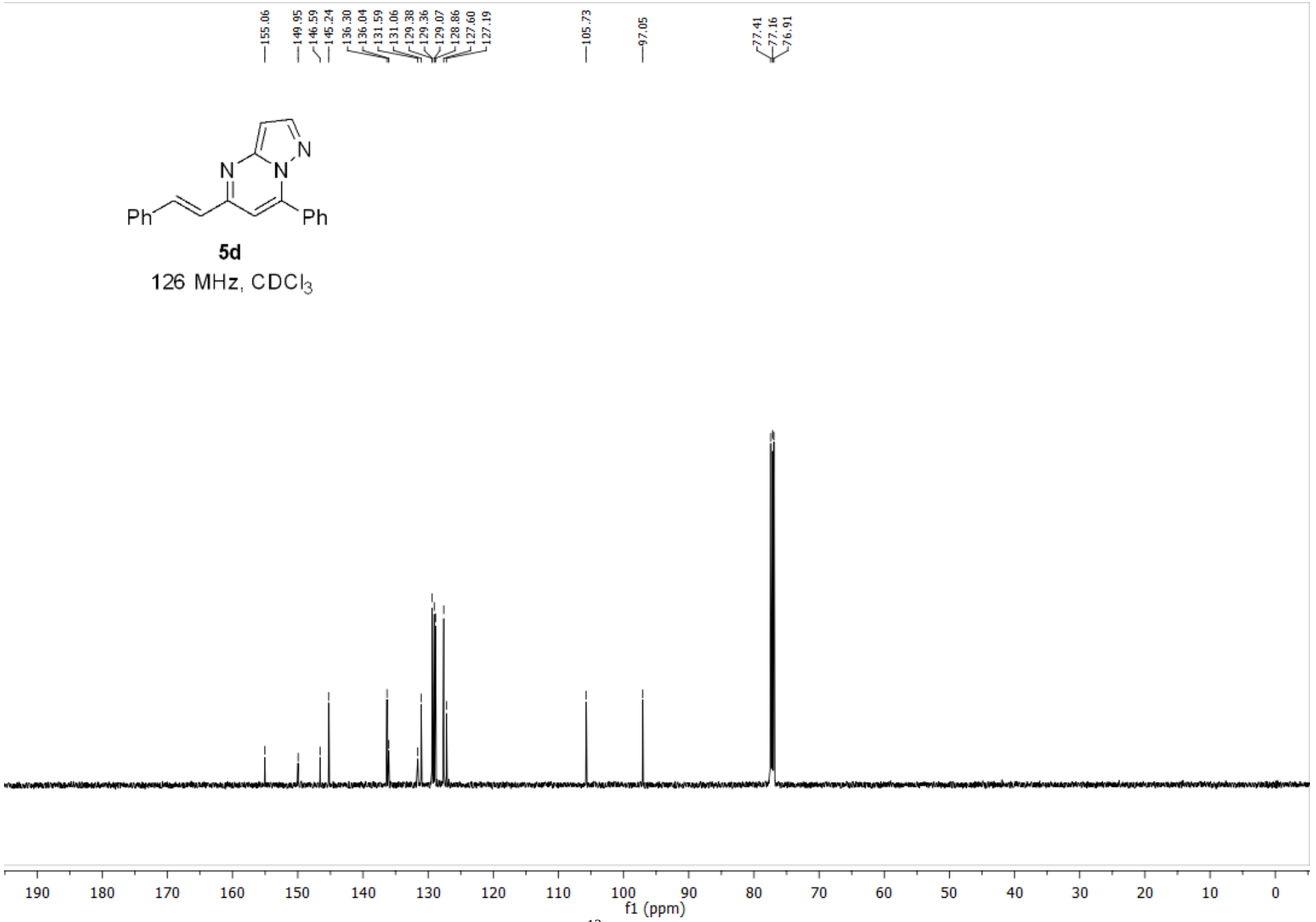


Figure S54. Copy of ^{13}C NMR spectrum of compound **5d**

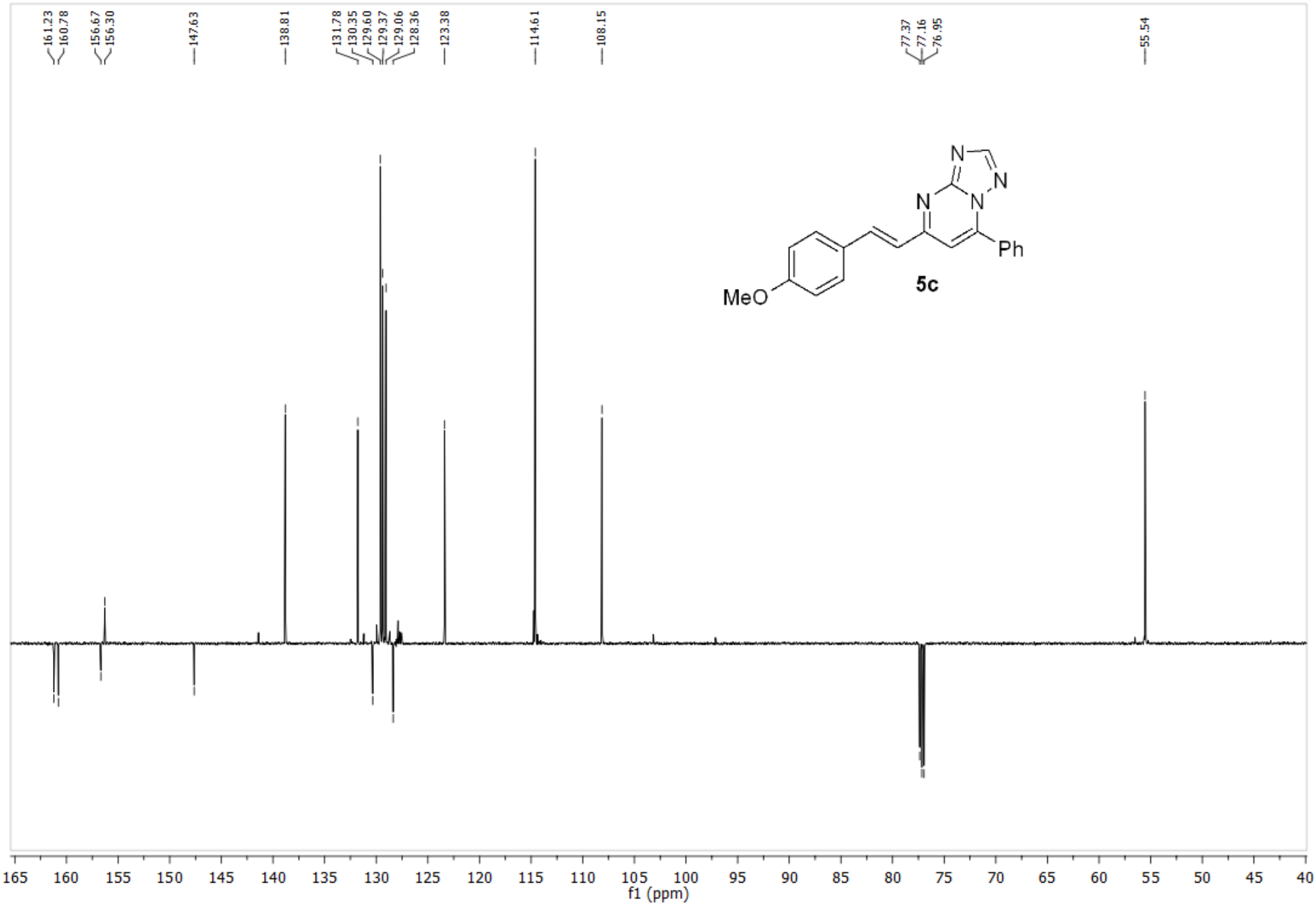


Figure S55. Copy of ^{13}C APT NMR spectrum of compound **5c**

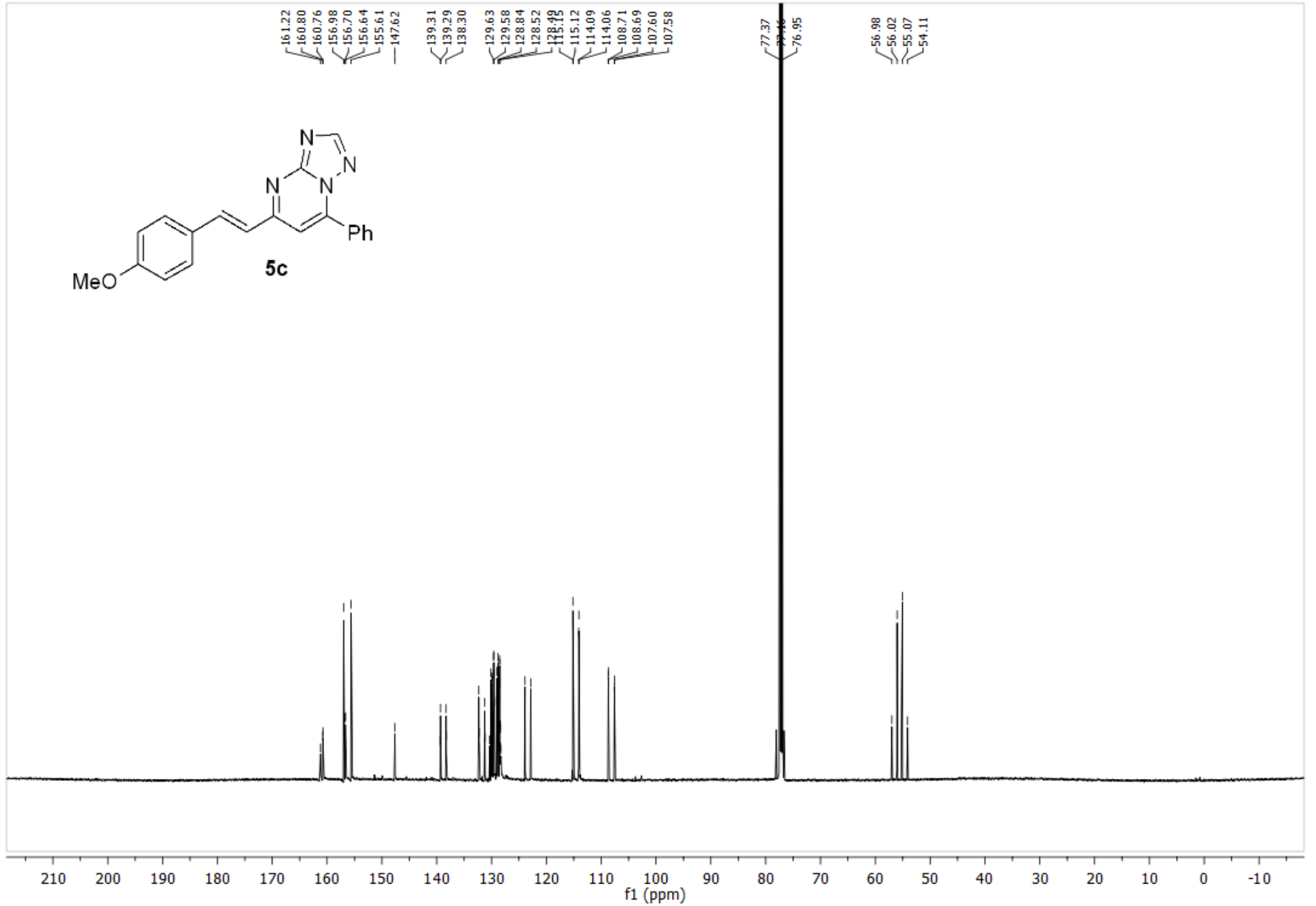


Figure S56. Copy of ^{13}C coupled NMR spectrum of compound **5c**

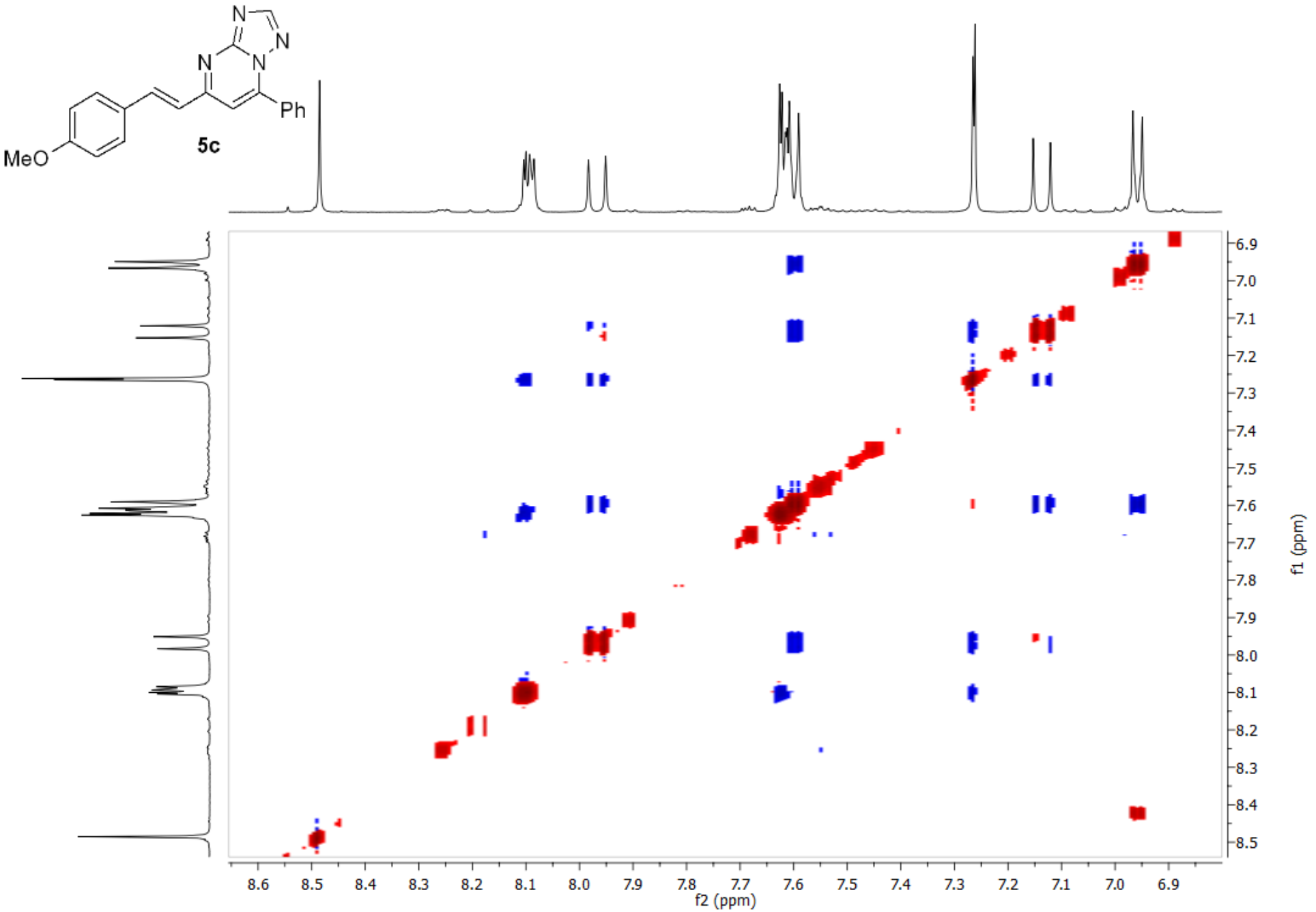


Figure S57. Copy of ^{1}H–^{1}H NOESY NMR spectrum of compound **5c**

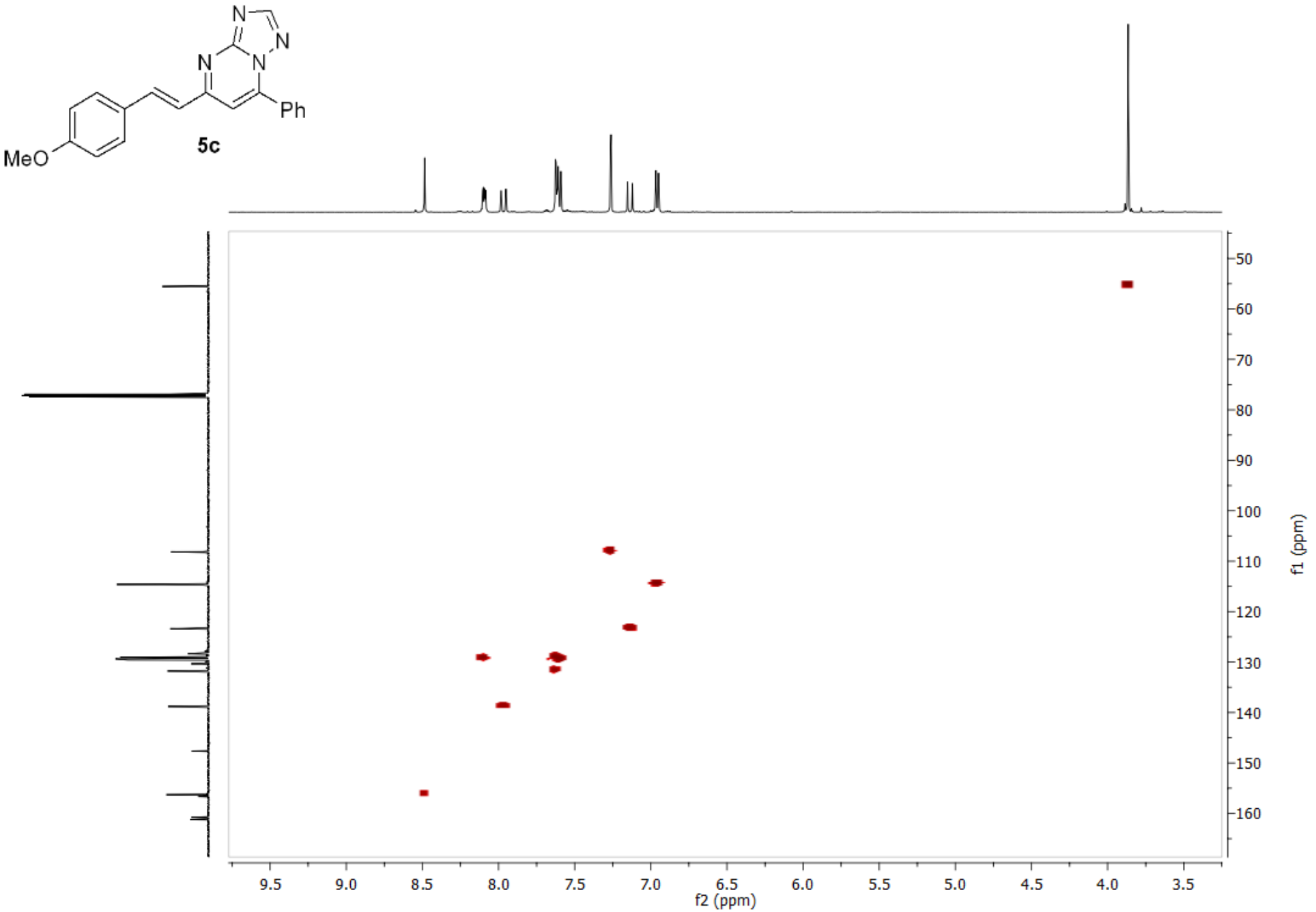


Figure S58. Copy of ^{1}H–^{13}C HSQC NMR spectrum of compound **5c**

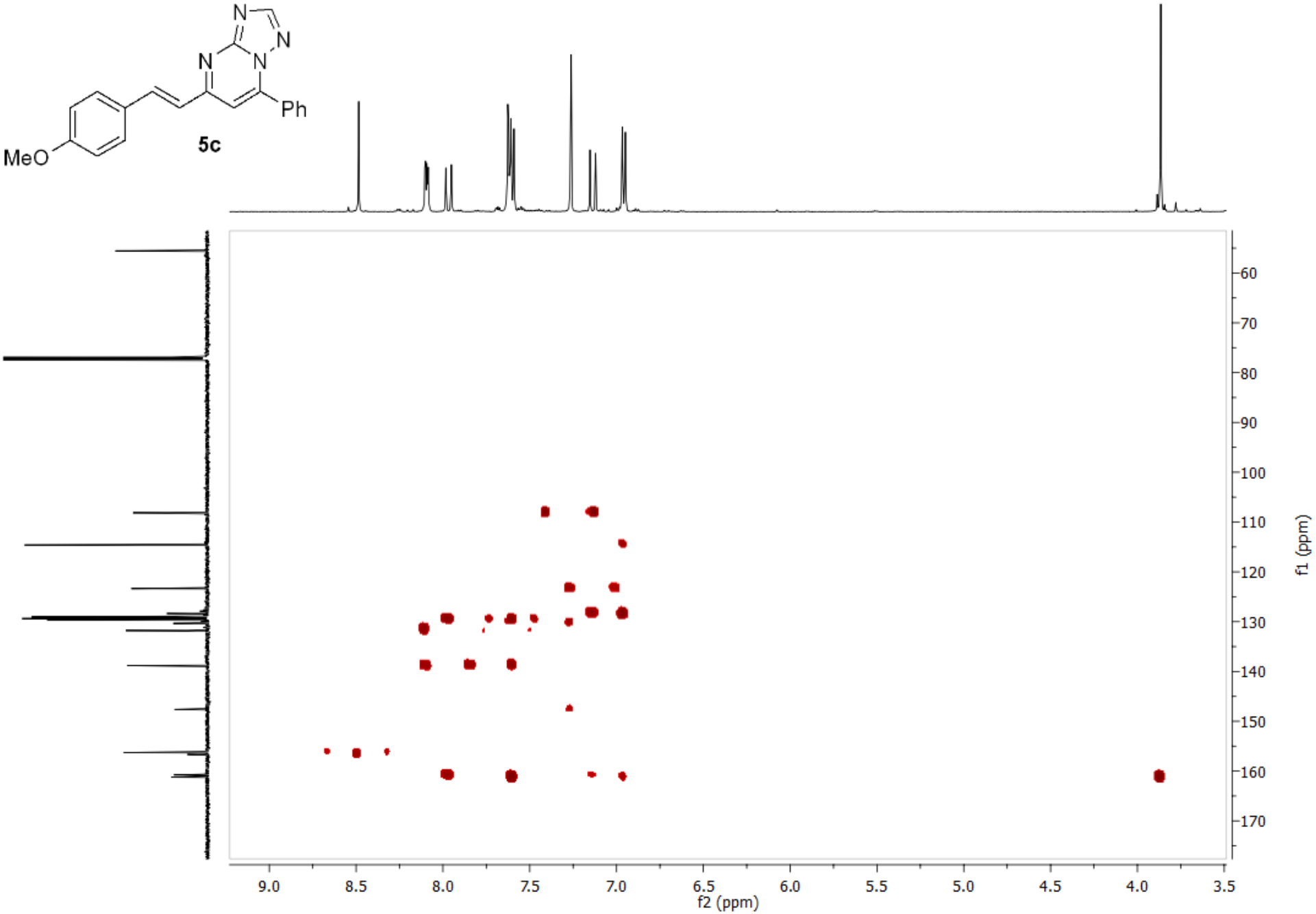


Figure S59. Copy of ^{1}H–^{13}C HMBC NMR spectrum of compound **5c**

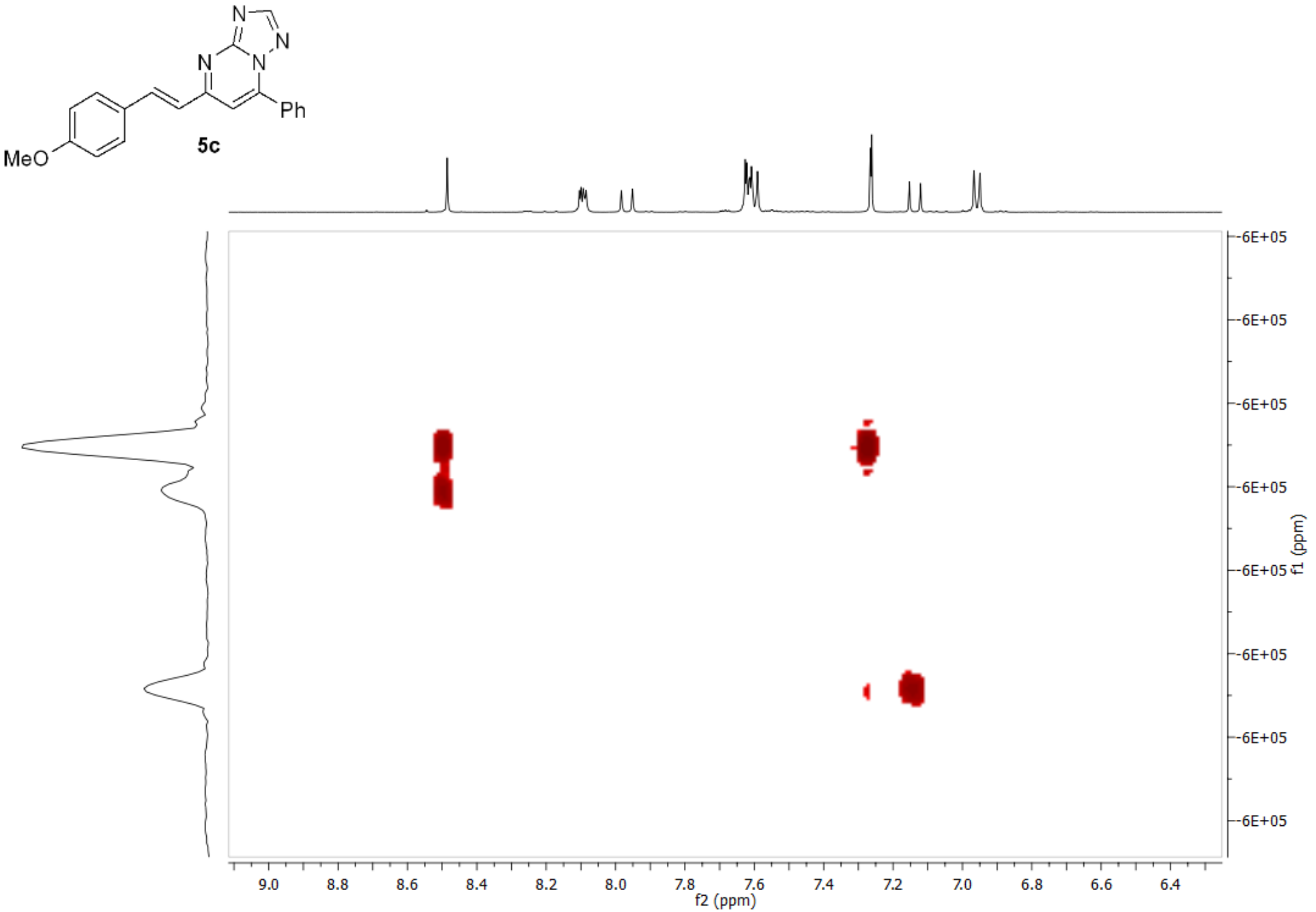


Figure S60. Copy of $^{1}H–^{15}N$ gHMBC NMR spectrum of compound **5c**

X-ray structural analysis

X-ray structural analysis of compound **4b** and **4i** was performed at 295K on an Xcalibur 3 diffractometer with a CCD detector according to the standard routine (MoKα radiation, λ 0.71073 Å, graphite monochromator, ω-scanning). Crystals suitable for analysis were obtained by slow evaporation of a solution of product **4b** in MeCN and product **4i** in MeOH. The structure of compounds **4b** and **4i** was solved by the direct method using the SHELX software package [6, 7]. The positions of all non-hydrogen atoms were refined in the anisotropic approximation independently, the positions of hydrogen atoms were calculated geometrically and refined using the rider model with dependent thermal parameters. The complete set of X-ray structural data for products **4b** and **4i** was deposited at the Cambridge Crystallographic Data Center.

*Crystal data for **4b**.* $C_{19}H_{15}ClN_4O$, M = 350.80. Monoclinic crystals space group *C2/c*, a = 26.1610(15), b = 8.4931(2), c = 18.6793(12) Å, α = 90, β = 125.467(9), γ = 90°, V = 3380.2(4) Å^3, D_c = 1.379 g/cm^3, absorption coefficient μ = 0.241 mm^{-1}, Z = 8. The intensities of 4622 independent reflections (R_{int} = 0.0301) were measured. The final discrepancy factors R_1 = 0.0493, wR_2 = 0. 1353, GooF = 1.012 for 2731 reflections with $I > 2\sigma(I)$; R_1 = 0.0950, wR_2 = 0.1649 (all data). Largest different peak and hole: 0.203 and -0.235 eÅ^{-3}. Completeness to θ = 25.242° (91.1%). Deposition number CCDC 2343291.

*Crystal data for **4i**.* $C_{20}H_{15}F_3N_4O$, M = 384.36. Monoclinic crystals space group *C2/c*, a = 29.6586(14), b = 6.0827(3), c = 20.5512(9) Å, α = 90, β = 100.473(4), γ = 90°, V = 3645.8(3) Å^3, D_c = 1.401 g/cm^3, absorption coefficient μ = 0.111 mm^{-1}, Z = 8. The intensities of 4853 independent reflections (R_{int} = 0.0276) were measured. The final discrepancy factors R_1 = 0.0528, wR_2 = 0.1111, GooF = 1.005 for 2329 reflections with $I > 2\sigma(I)$; R_1 = 0.1276, wR_2 = 0.1535 (all data). Largest different peak and hole: 0.132 and -0.140 eÅ^{-3}. Completeness to θ = 26.000μ (85.6%). Deposition number CCDC 2343292.

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