Transition metal-free reductive coupling of allylic sulfonylhydrazones with aryl boronic acids for C(sp^3)-C(sp^2) bond formation

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SUPPORTING INFORMATION

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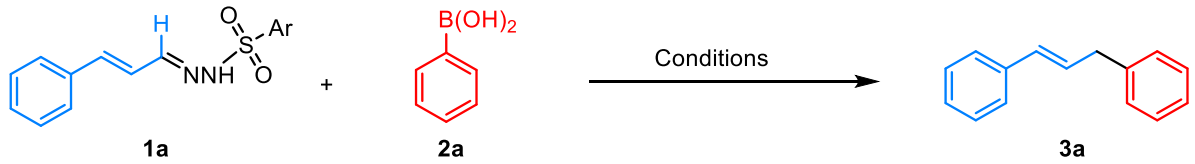
Optimization Table



1a 2a 3a

Ar	Base	Solvent	Time (h)	Yield (%)[a]
4-MeC$_6$H$_4$	Cs_2CO_3	Toluene	10	45
4-MeOC$_6$H$_4$	**Cs_2CO_3**	**Toluene**	**10**	86
4-NO$_2$C$_6$H$_4$	Cs_2CO_3	Toluene	10	15
2,4,6-Me C$_6$H$_4$	Cs_2CO_3	Toluene	10	51
4-MeOC$_6$H$_4$	Cs_2CO_3	1,4-dioxane	10	70
4-MeOC$_6$H$_4$	Cs_2CO_3	Toluene	8	75
4-MeOC$_6$H$_4$	K_2CO_3	Toluene	10	53
4-MeOC$_6$H$_4$	Cs_2CO_3	THF	10	48[b]
4-MeOC$_6$H$_4$	K_2CO_3	1,4-dioxane	10	50
4-MeOC$_6$H$_4$	NaOH	Toluene	10	NR
4-MeOC$_6$H$_4$	Na_2CO_3	Toluene	10	30
4-MeOC$_6$H$_4$	KOH	Toluene	10	26
4-MeOC$_6$H$_4$	CsF	Toluene	10	18
4-MeOC$_6$H$_4$	Ag_2CO_3	Toluene	10	ND

Reaction conditions: allylic sulfonylhydrazones **1a**, (1.0 equiv.); aryl boronic acid **2a**, (1.5 equiv.); Cs_2CO_3, (2.5 equiv.); Toluene (1.6 M), 110 ^oC, 10 h. Performed in a sealed screw-capped vial under N_2 [a] Yields of isolated products after column chromatography. [b] Reaction performed at 70 °C, NR: No Reaction, ND: Not Determined.

NMR Study

NMR data were acquired on Bruker Avance-III HD 400 and 500 MHz NMR spectrometer at 300K and 303K in suitable solvents, respectively. Resonance assignments were carried out using various one-dimensional, two-dimensional ^{1}H-^{1}H COSY, NOESY and indirect detection experiments like ^{1}H-^{13}C HSQC and HMBC. All NMR data were analysed and processed using TopSpin3.1 software. Proton spectra were acquired with 16 to 32 transients with 16K points zero-filled to 32k data points. 2D ^{1}H–^{13}C HSQC NMR data were acquired, with ^{13}C decoupling during the acquisition period, over an F2 frequency width of 12 ppm into 2k complex data points. 16 to 32 transients were accumulated for each of 128 t1 increments over an F1 frequency width of 200 ppm centred at 100 ppm. Phase-sensitive data were acquired in a sensitivity-improved manner using an echo-anti-echo acquisition mode. 2D ^{1}H–^{13}C HMBC NMR data were acquired over an F2 frequency width of 12 ppm into 2k complex data points. 32 to 64 transients were accumulated for each of 128 t1 increments over an F1 frequency width of 200 ppm centred at 100 ppm. Integration of ^{1}H NMR spectra (20H protons) supports the suggested molecular formula $C_{20}H_{20}O$ of compound **3ad**. The characteristics of HMBC correlation in the compound **3ad** in which double bonds exist between C_2 and C_3 positions, are C_3H (δ 6.23 ppm) with C_1/C_{11}, C_2, C_4 and C_5 (δ 142.34, 139.42, 35.03 and 132.4 ppm respectively) and C_4H (δ 3.40 ppm) with C_2, C_3, C_5 and C_{10} (δ 139.42, 128.11, 133.04 and 129.30 ppm respectively) confirms the double bond position.

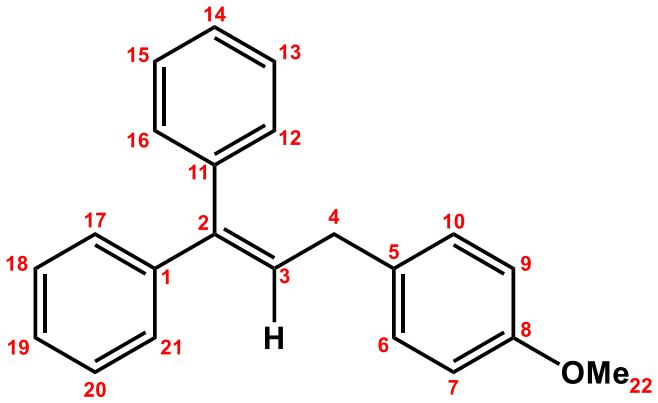


Fig. SI-5: Structure for the compound **3ad**

Table 1: Chemical shift assignment for **3ad**

Proton	**^{1}H Chemical shift and coupling constant**	**^{13}C Chemical shift**
C_3H	6.23 (t, $^{3}J_{C4H-C3H}$ = 7.57, 15.10)	128.11
C_4H	3.40 (d, $^{3}J_{C4H-C3H}$ = 7.57)	35.03
C_6H/$C_{10}H$	7.10 (d, $^{3}J_{C6H-C7H}$ = 8.63)	129.30
C_7H/C_9H	6.84 (d, $^{3}J_{C7H-C6H}$ = 8.63)	113.97
OMe	3.78 (s)	55.30

Others: Aromatic (Ph) 7.41-7.08 (m, 10H) & 131-113 (10C), Quaternary: C_1/C_{11} = 142.34 C_2 = 139.42 C_5 = 133.04, C_8 = 157.7

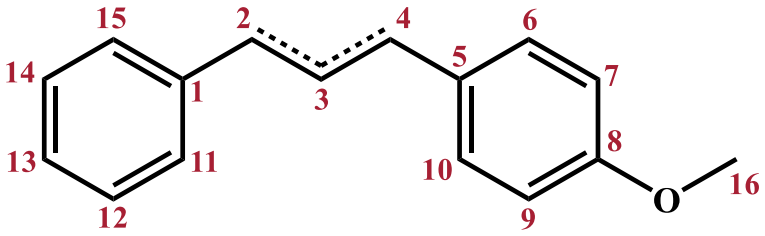


Fig. SI-6: Structure for the compound **3j**

Table 2: Chemical shift assignment for **3j**

Proton	**Major regioisomer**		**Minor regioisomer**	
	^{1}H Chemical shift and coupling constant	**^{13}C Chemical shift**	**^{1}H Chemical shift and coupling constant**	**^{13}C Chemical shift**
C_2H	6.40(bd, $^3J_{C2H-C3H}$ = 13.94)	130.46	6.42(bd, $^3J_{C2H-C3H}$ = 13.40)	130.764
C_3H	6.20 (dt, $^3J_{C3H-C2H}$ = 6.92, 13.94)	127.08	6.33 (dt, $^3J_{C3H-C2H}$ = 6.41, 13.40)	129.70
C_4H	3.52 (bd, $^3J_{C4H-C3H}$ = 6.84)	39.35	3.48 (bd, $^3J_{C4H-C3H}$ = 6.63)	38.42
C_6H/C_{10}H	7.28 (m)	127.24	7.15 (m)	129.61
C_7H/C_9H	6.82 (m)	113.94	6.85 (m)	113.70
C_{11}H/C_{15}H	7.30 (m)	128.36	7.31 (m)	128.72
C_{12}H/C_{14}H	7.28 (m)	127.24	7.26 (m)	127.52
C_{13}H	7.24 (m)	128.67	7.23 (m)	128.52
OMe	3.78 (s)	55.30	3.76 (s)	55.30
Others: Quaternary: C_1 =140.50, C_5 = 158.87, C_8 = 132.15			**Others:** Quaternary: C_1 =137.58, C_5 = 158.10, C_8 = 132.23	

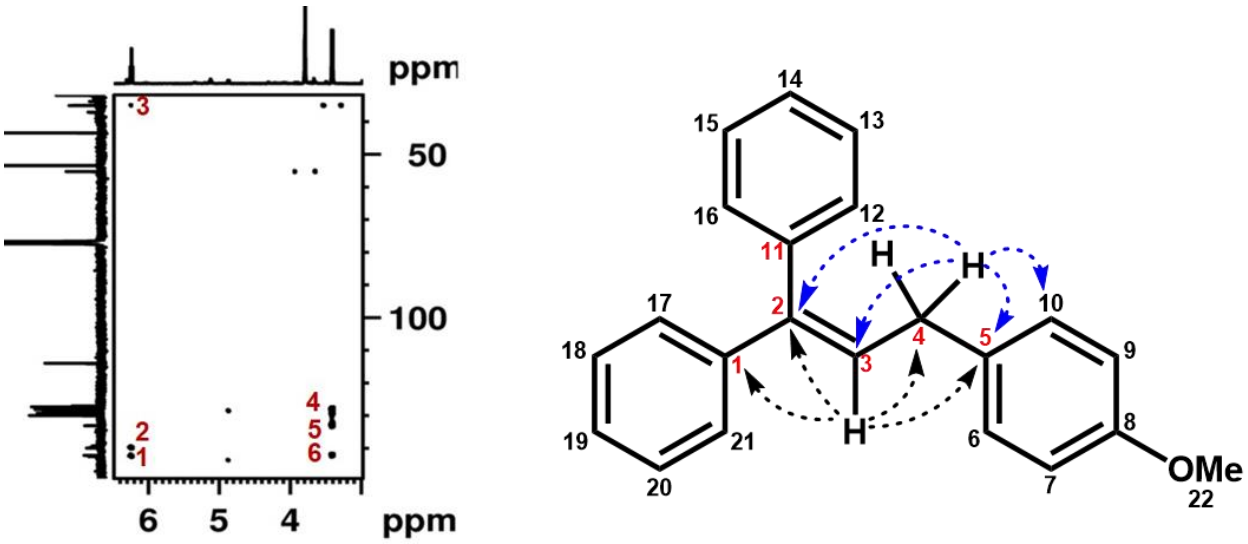


Fig. SI-1: (A) Characteristics HMBC correlation of C_3H (δ 6.23 ppm) with C_1/C_{11}, C_2 and C_4 (δ 142.34, 139.42, and 35.03 ppm respectively) and C_4H (δ 3.40 ppm) with C_3, C_{10}, C_5 and C_2 (δ 128.11, 129.30, 133.04 and 139.42 ppm respectively) as mentioned by 1-6 respectively.

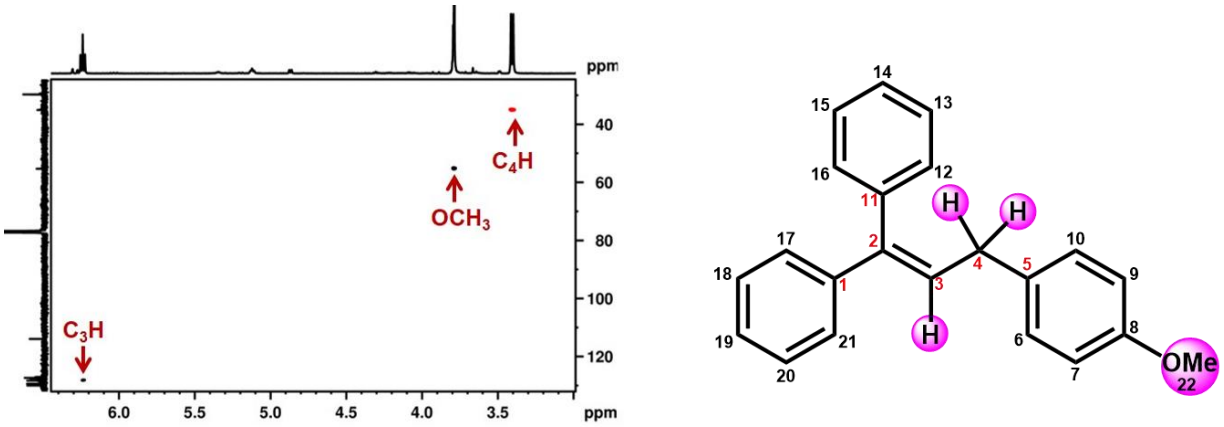


Fig. SI-2: Characteristics HSQC peak showing the presence of three CH and one OMe as highlighted in the structure

Computational Study

For validating and understanding the experimental results towards the formation of regioselective 1,3-diarylpropenes derivative Gaussian G09 program[1] were used for all the computational calculation by using hybrid B3LYP[2,3] functional with a 6-31G++(d,p) basic set,[4] in gaseous phase. The frequency calculations were performed to confirm that these optimized structures are real minima on the potential energy surface with all positive frequencies and one imaginary frequency. Intrinsic reaction coordinates (IRC) were also calculated to validate the transition states that linked the related reactant and products. Minima were used to describe stationary points (ground state), Transition state (TS-1, TS-1a and TS-2a) via frequency calculation and Intermediate of the reaction (Int-1 and Int-2). The reaction intermediate proceeds via two regioisomeric products. There were some questions to address: First, does both the regioisomeric products takes place equally, if not then which regioisomer is majorally obtained, second, does the substituting group play a role in the regio-selectivity, if yes then what will be the energy differences. In order to validate the possible major regioisomeric products, Density Function Calculation (DFT) were performed for the compound **3j**, which were taken as a reactant with one transition state. The transition state proceeds with two different intermediates (Int-1 and Int-2). The reaction proceeds through Int-1 are thermodynamically stable (-1.36 kcal) and forming more stable intermediate (-18.91 kcal), whereas the reaction proceeds through Int-2 form less stable intermediate (-17.55). Nucleophilic addition of water at boronic acid (Int-1) passes through low activation energy (-2.64 kcal) and forming more stable intermediate (-7.83 kcal), whereas Int-2 passes through high activation energy (-5.19 kcal). We have notice that the formation of regioselective 1,3-diarylpropenes derivative proceeds through Int-1 is preferred, as it proceed with a low activation barrier and forms a stable product.

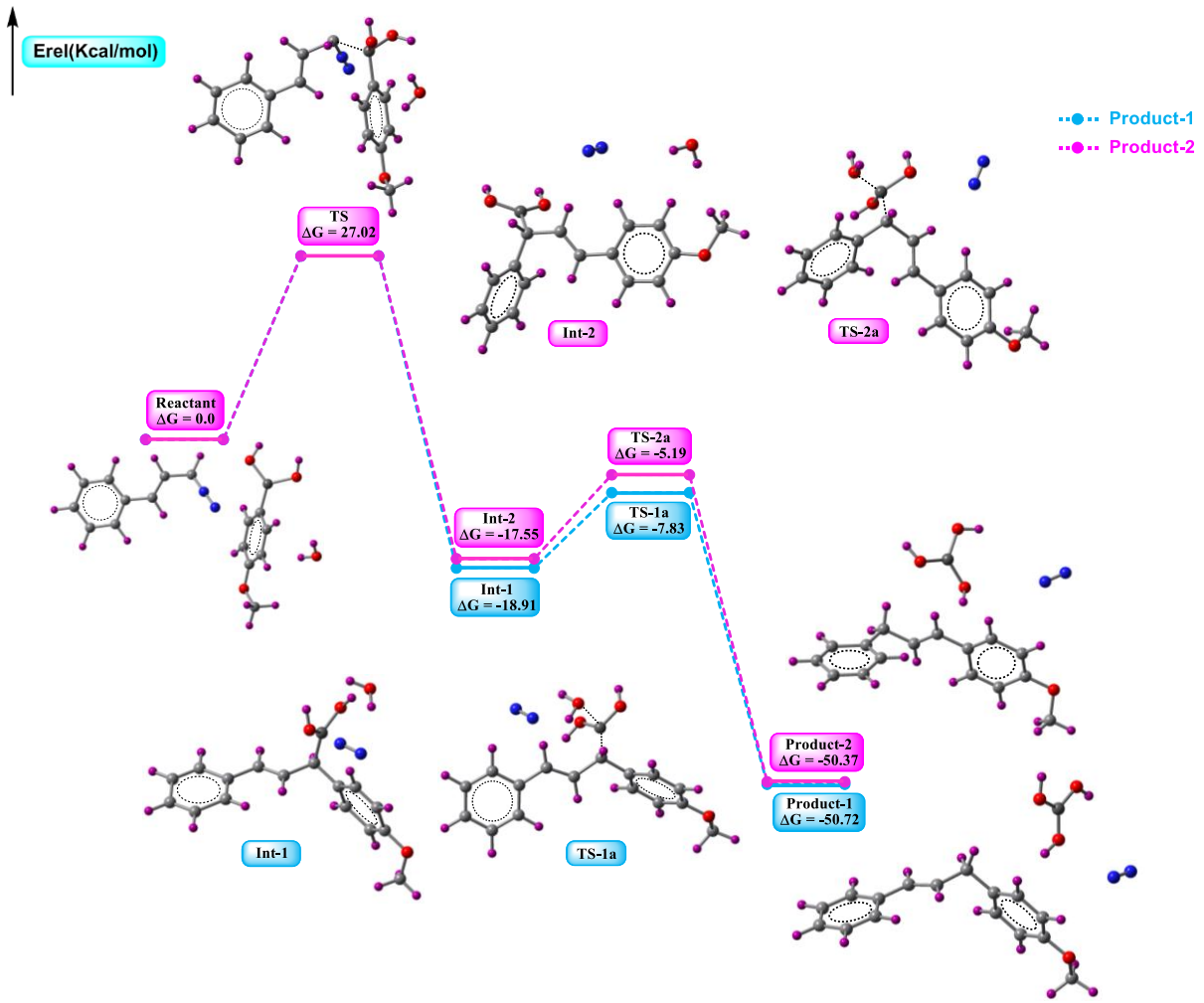
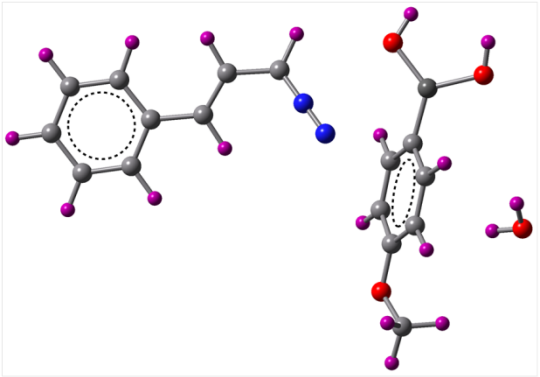


Fig. SI-3: Comparative energy profile diagram for the regioselective intermolecular nucleophilic addition reaction for 3e at the B3LYP//6-31 G++G(d,p) level of theory in the gas phase.

The absolute energy value E in Hartree, Cartesian coordinates xyz and name of the compound used in computational study



Reactant, E = -1056.57364

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C	-7.13054	-2.12609	0.72737
C	-6.98622	-0.67877	0.22136
C	-8.07458	-0.00466	-0.22318
C	-5.60516	0.00257	0.22048
C	-5.47826	1.27612	-0.22511
C	-4.09733	1.95771	-0.22585
H	-3.99714	2.96316	-0.57781
N	-3.05844	1.31474	0.19903
N	-1.95374	1.86015	0.19858
H	-10.31503	-0.15366	-0.57312
H	-10.54234	-2.43281	0.22379
H	-8.44621	-3.73119	1.07963
H	-6.27121	-2.65837	1.07834
H	-7.97433	1.00093	-0.57484
H	-4.74582	-0.52953	0.57166
H	-6.33759	1.80809	-0.57642

C	0.50656	0.73591	-1.23288
C	0.60325	-0.61465	-1.28963
C	1.24486	-1.39034	-0.12422
C	1.71284	-0.72239	0.95812
C	1.60297	0.81234	1.02261
C	1.03833	1.49494	-0.00295
B	0.92061	3.13929	0.06617
O	-0.32823	3.79663	0.68255
O	2.05959	4.01667	-0.48568
O	1.34683	-2.81545	-0.18406
C	2.49786	-3.24226	0.54933
H	0.06075	1.27486	-2.04262
H	0.23378	-1.14203	-2.14419
H	2.15865	-1.26134	1.76786
H	1.97246	1.33973	1.87717
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H	2.09602	4.84034	0.00608
H	2.57409	-4.30826	0.50456
H	2.40512	-2.93384	1.56971
H	3.37557	-2.80372	0.12248
O	4.08345	0.18789	-0.67592
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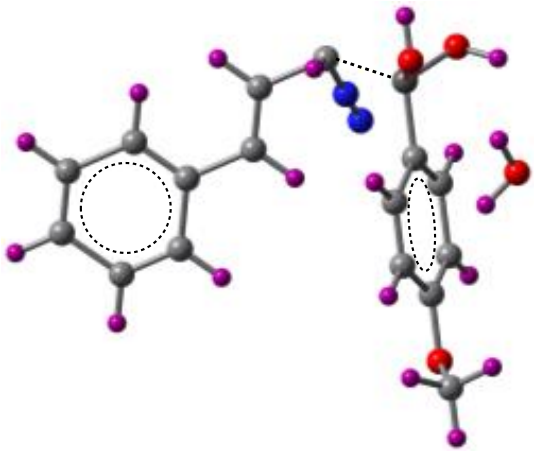
TS-1



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C	-7.84271	-2.42896	0.15345
C	-8.21063	-0.95659	0.41511
C	-9.42142	-0.64311	0.93751
C	-7.20321	0.16011	0.08358
C	-7.52649	1.45466	0.32041
C	-6.52289	2.57433	-0.01293
N	-6.24659	1.84385	-1.25798
N	-6.03794	1.30372	-2.18399
B	-4.89735	2.85703	-0.02155
O	-4.48708	3.53217	1.30024
C	-4.09009	1.42702	-0.18326
O	-4.54371	3.78127	-1.20155
C	-3.78556	0.95777	-1.41782
C	-3.03104	-0.37593	-1.57047
C	-2.67141	-1.08049	-0.47009
C	-3.01813	-0.54789	0.93313
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H	-10.80676	-3.82987	1.26569
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H	-6.24883	-0.08608	-0.33307
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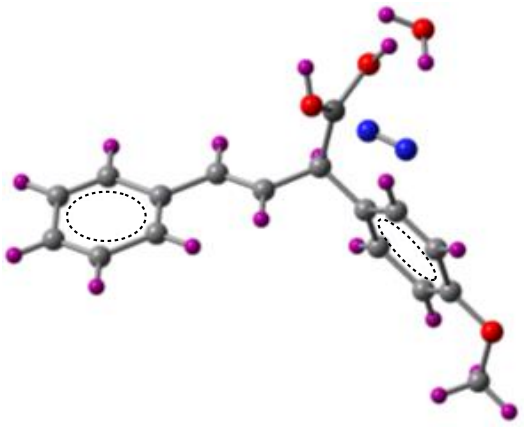
Int-1



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O	-3.82241	-0.86128	-2.84563
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C	-5.78661	5.67597	1.56605
H	-9.90248	-2.91296	-0.65736
H	-9.97784	-5.17483	0.21433
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H	-4.17329	1.18657	2.09161
H	-4.69272	3.73469	2.31375
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C	-1.86995	-0.23942	2.04744
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O	-2.67247	0.10135	-2.21346
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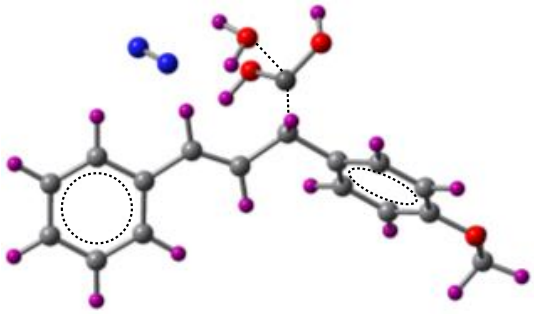
TS-1a



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C	-5.10402	0.76776	-0.50582
C	-3.91645	1.74191	-0.61684
C	-2.90541	1.44899	0.50725
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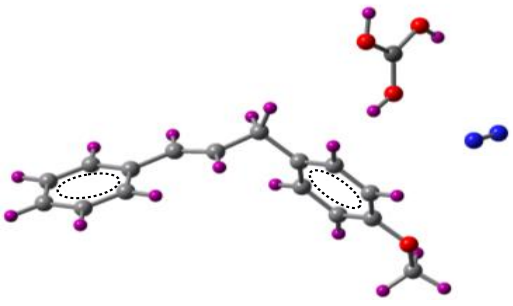
C	-1.13295	2.15731	2.13571

Product-1



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H	-5.13284	0.80018	0.90726
H	-5.83424	6.52302	0.48311
H	-6.11535	5.12711	-0.52956
H	-5.93751	4.93186	1.19767
B	0.96263	0.56581	0.35555
O	2.45315	0.93038	0.48784
O	0.54733	-0.72256	-0.37877
O	-0.11243	1.48961	0.95758
H	2.54737	1.88525	0.51831
H	1.23635	-1.38364	-0.27968
H	-0.91726	1.42486	0.43829
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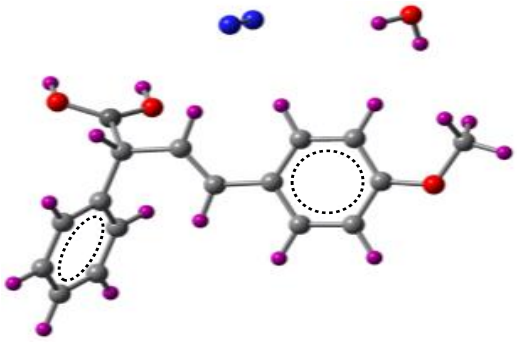
N	5.39239	-0.79344	-0.04545

Int-2



Int-2, E = -1056.60162

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C	-4.42387	-1.22464	-2.38639
C	-4.26613	0.26845	-2.04374

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C	-2.89332	0.77364	0.37539
C	-2.18067	0.65106	1.73502
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C	-2.19314	0.48901	4.23877
C	-0.84068	0.42061	4.29113
C	-0.01652	0.46547	2.99123
C	-0.64371	0.57334	1.79452
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O	-2.02682	0.69266	-4.74545
O	-1.09264	-1.01569	-2.92191
O	-0.17887	0.30688	5.55365
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H	-2.76577	0.45784	5.14211
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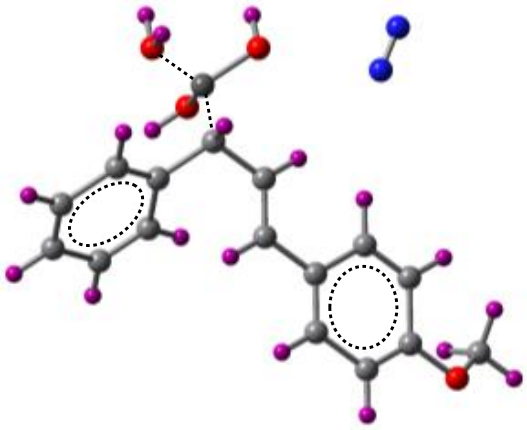
TS-2a



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O	-1.87678	0.15243	-3.36663
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H	-3.91536	1.21668	-4.76572
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O	-1.21736	-0.50947	5.54014
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H	-7.73262	-1.19856	-0.05308
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H	-2.25558	0.21917	-0.69652
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N	0.63801	-0.29824	-1.11741
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C	-7.78498	-3.40443	-1.21834
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H	-4.72485	4.20366	-2.37575
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O	0.69484	0.49003	0.25571
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O	-1.78618	1.32065	0.77474
H	0.85776	1.42702	0.12491
H	-0.73138	-1.81087	-0.05383
H	-2.62775	1.23958	0.32457
N	3.18621	-1.78957	-0.00948
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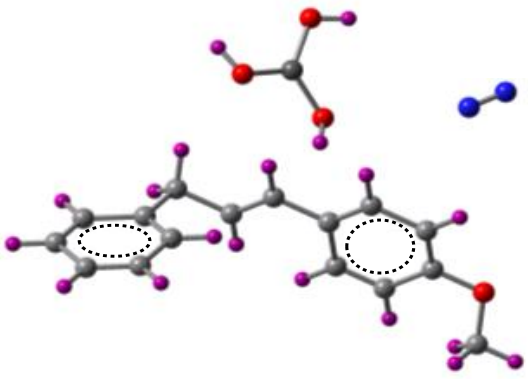
Product-2



Product-2, E = -1056.65391

Molecular Dynamics Study

Energy minimization and molecular dynamics (MD) calculations were performed on Discovery Studio 3.0 version[5], using CHARMm4 force field with default parameters throughout the simulation. Distance restraints used in the simulated molecular dynamics were calculated from the volume integrals of the cross-peaks in the NOESY spectra using a two-spin approximation with a reference distance of 1.80 Å for the geminal protons. Force constant of 10 K cal/Å and 5 K cal/Å were used for distance and torsional restraints respectively. Minimization was done with steepest descent algorithm followed by conjugate gradient methods for maximum 1000 iterations each. The molecules were initially equilibrated for 1 nS and then subjected to 5 nS production run. Starting from 50 K, they were heated to 300 K in five steps increasing the temperature 50 K at each step. 10 structures were stored from the production run and are again energy minimized with the above-mentioned protocol.

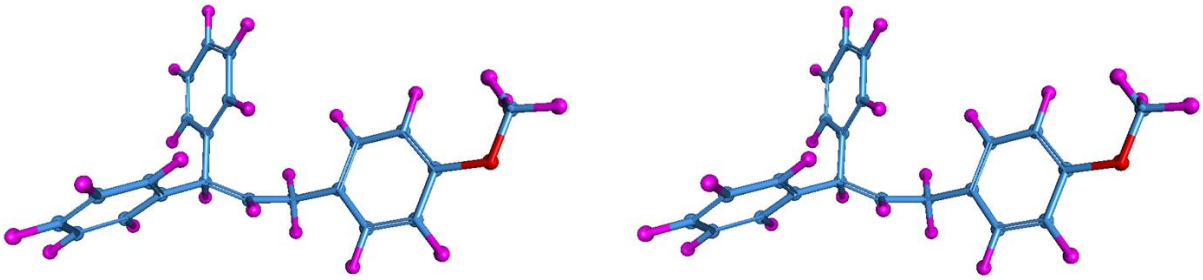


Fig. SI-4: Single structure of least energy conformations of compound **3ad**

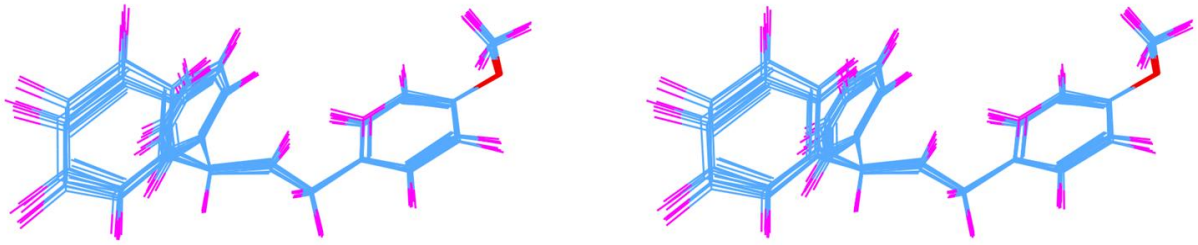


Fig. SI-5: Stereo-view of the 10 superimposed least energy conformations of compound **3ad**

References

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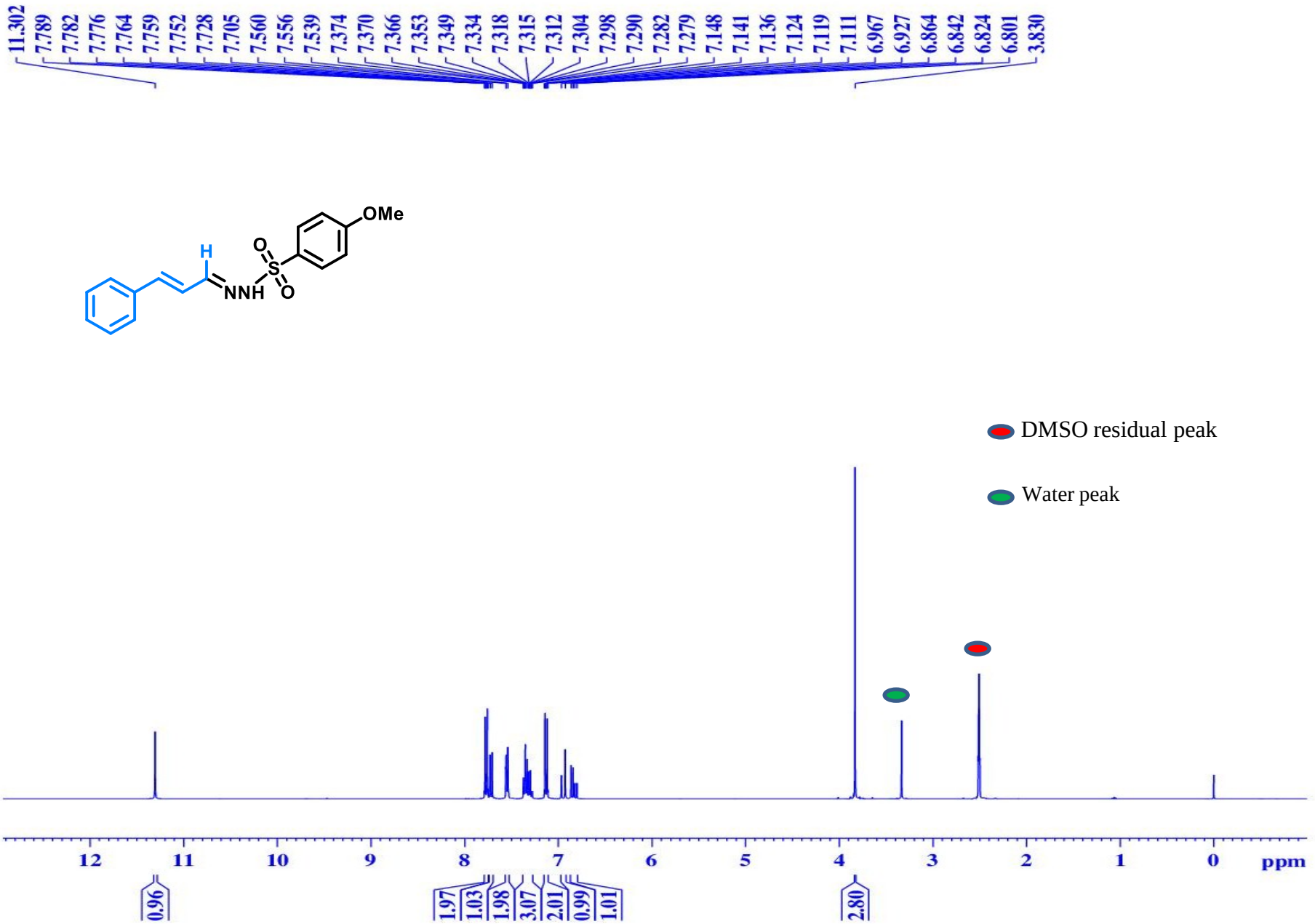
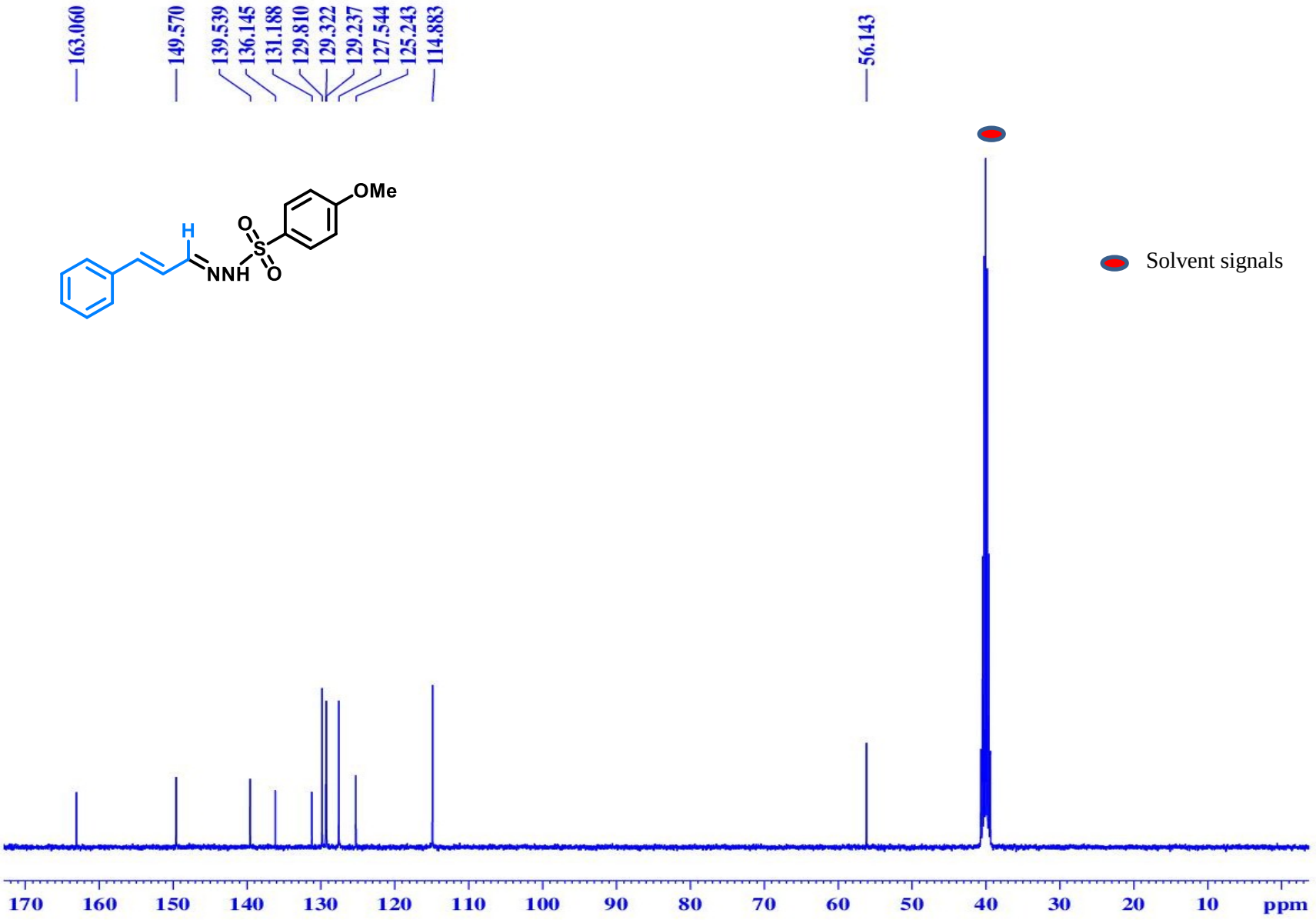
(5) 16. (a) B. R. Brooks, R. E. Bruccoleri, B. D. Olafson, D. J. States, S. Swaminathan, M. Karplus, *J. Com-put. Chem.* 1983, **4,** 187-217. (b) A. Siriwardena, K. K. Pulukuri, P. S. Kandiyal, S. Roy, O. Ghosh, S. Bande, J. M. G. Fernndez, F. A. Martin, J. M. Ghigo, C. Beloin, K. Ito, R. J. Woods, R. S. Ampapathi, T. K. Chakraborty, *Angew. Chem. Int. Ed.* 2013, **52,** 10221-10226.

Transition metal-free reductive coupling of allylic sulfonylhydrazones with aryl boronic acids for C(sp^3)-C(sp^2) bond formation

NMR Spectra for allylic sulfonylhydrazones



Compound 1a ^{1}H NMR (400 MHz, DMSO-d_6)



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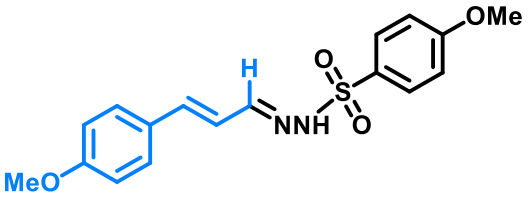

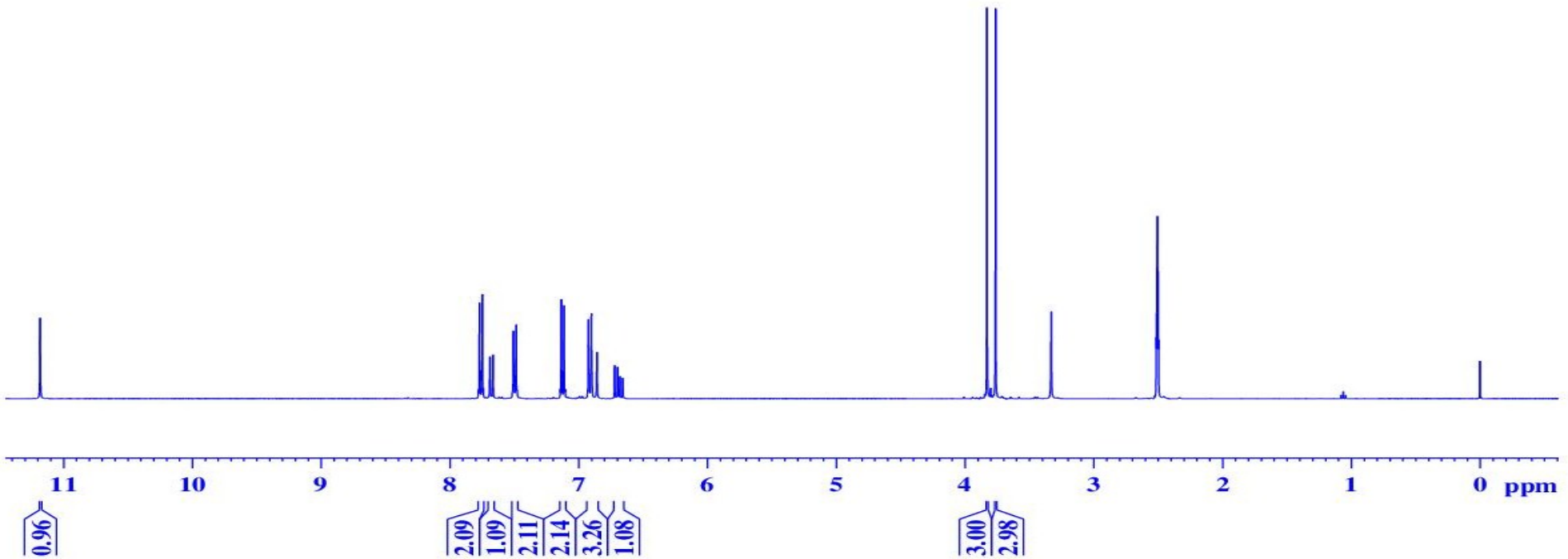

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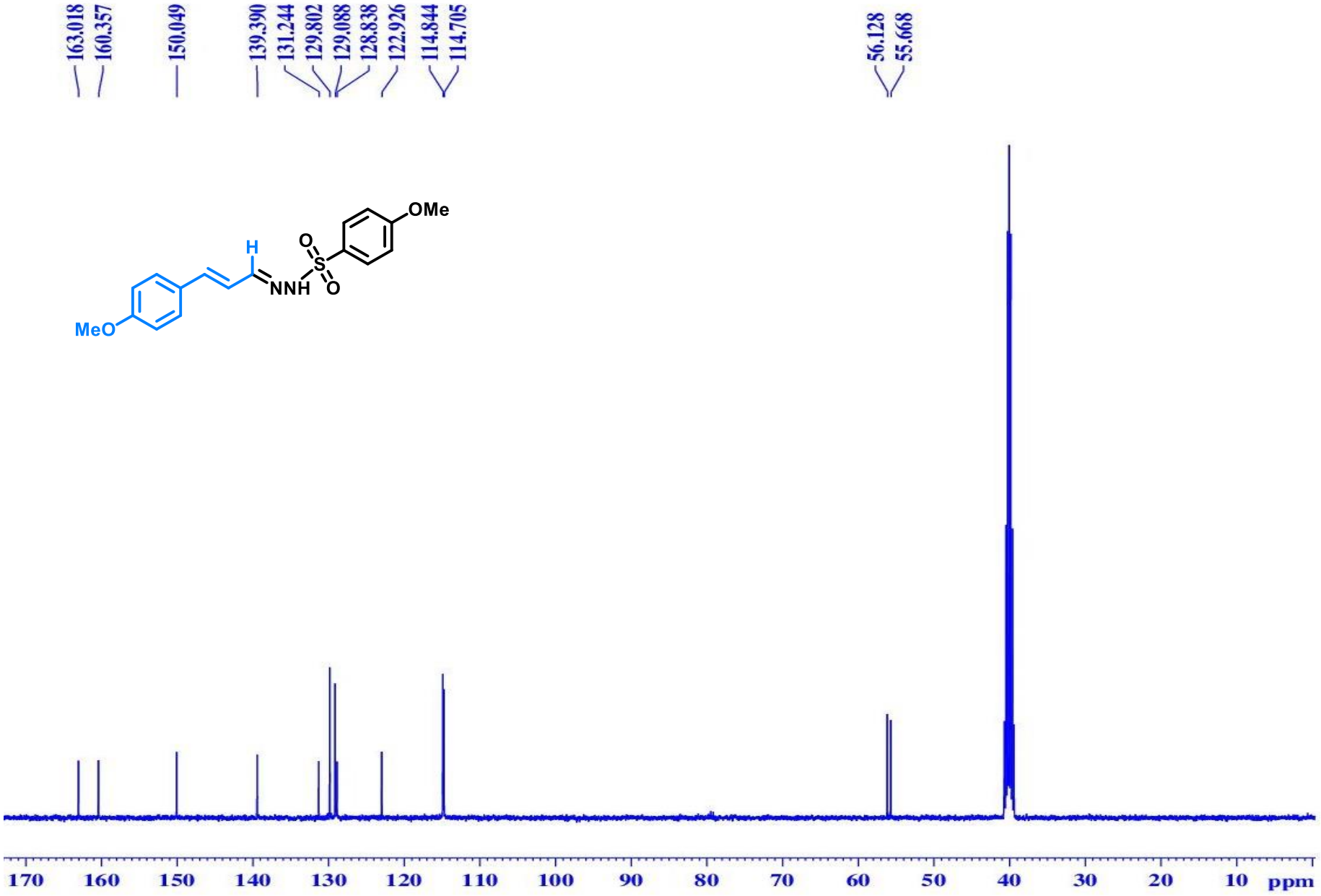

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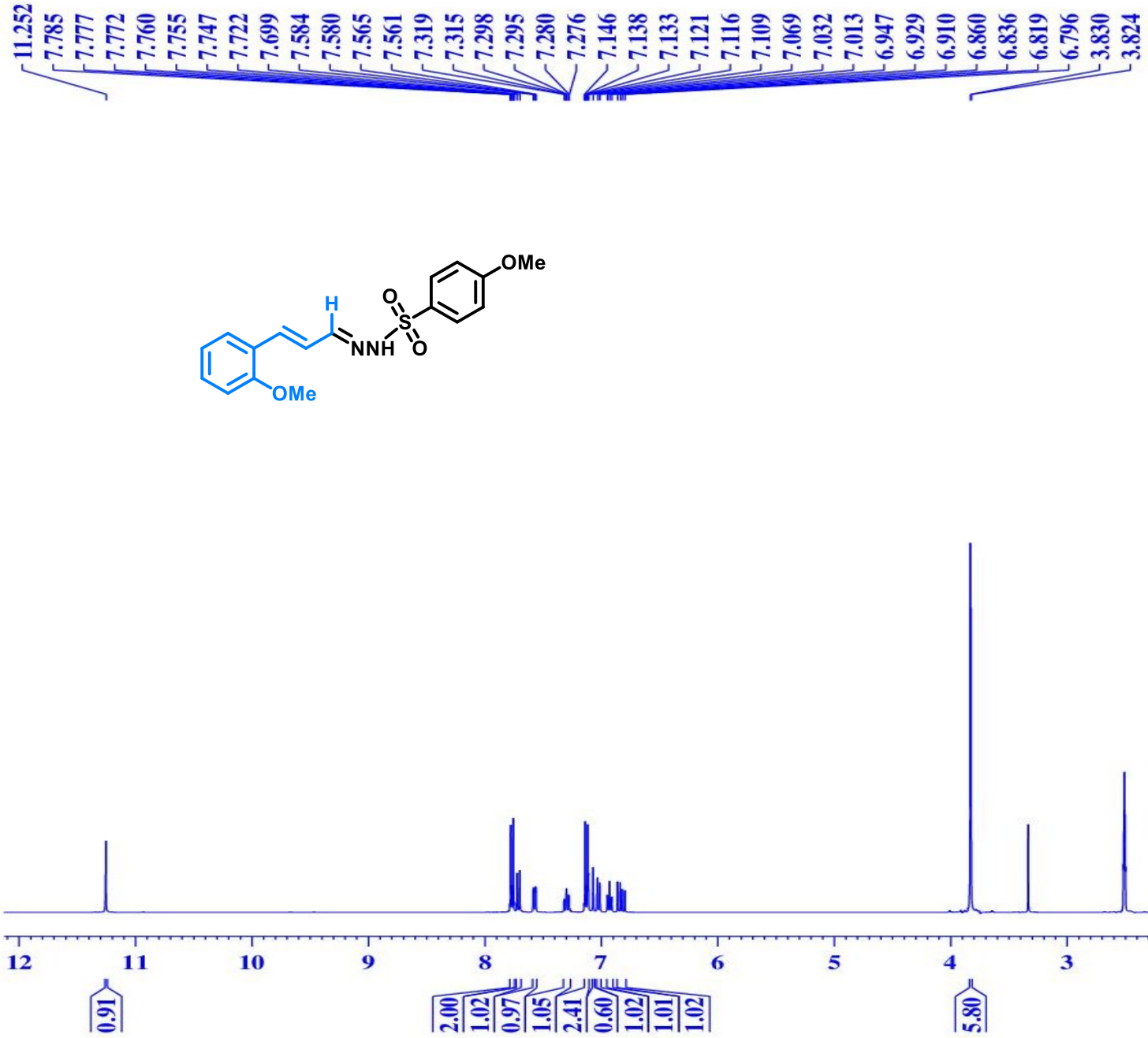

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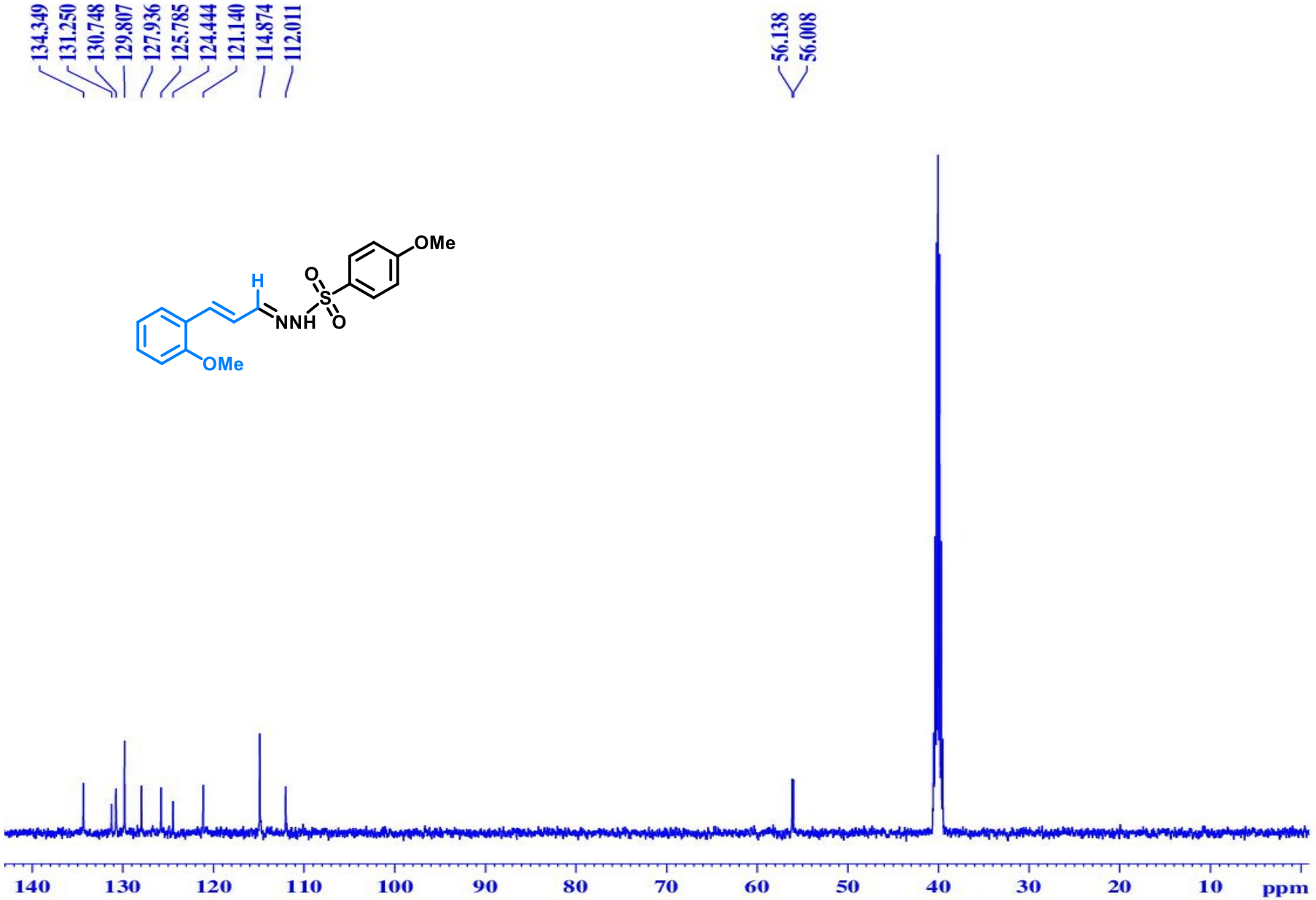

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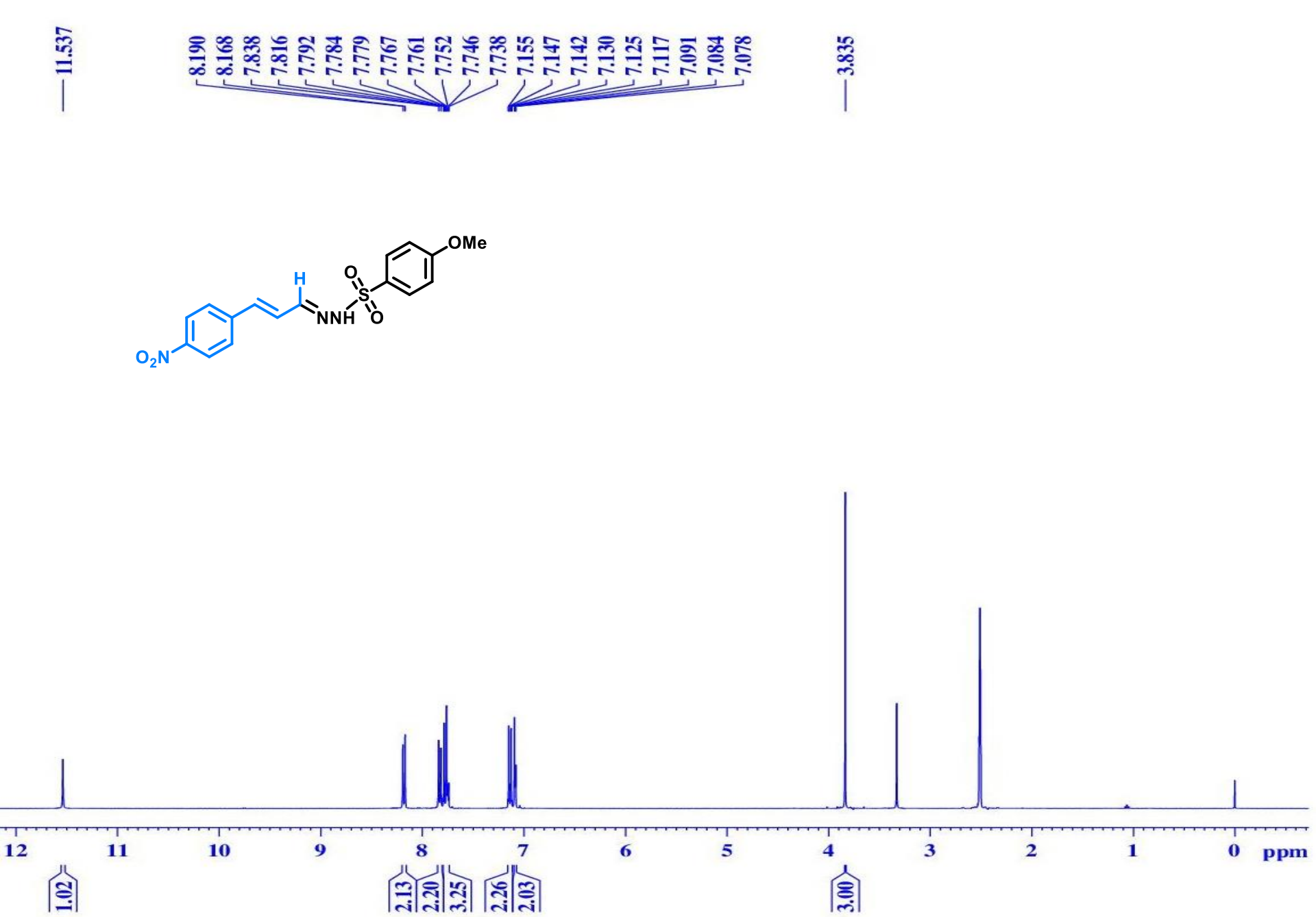

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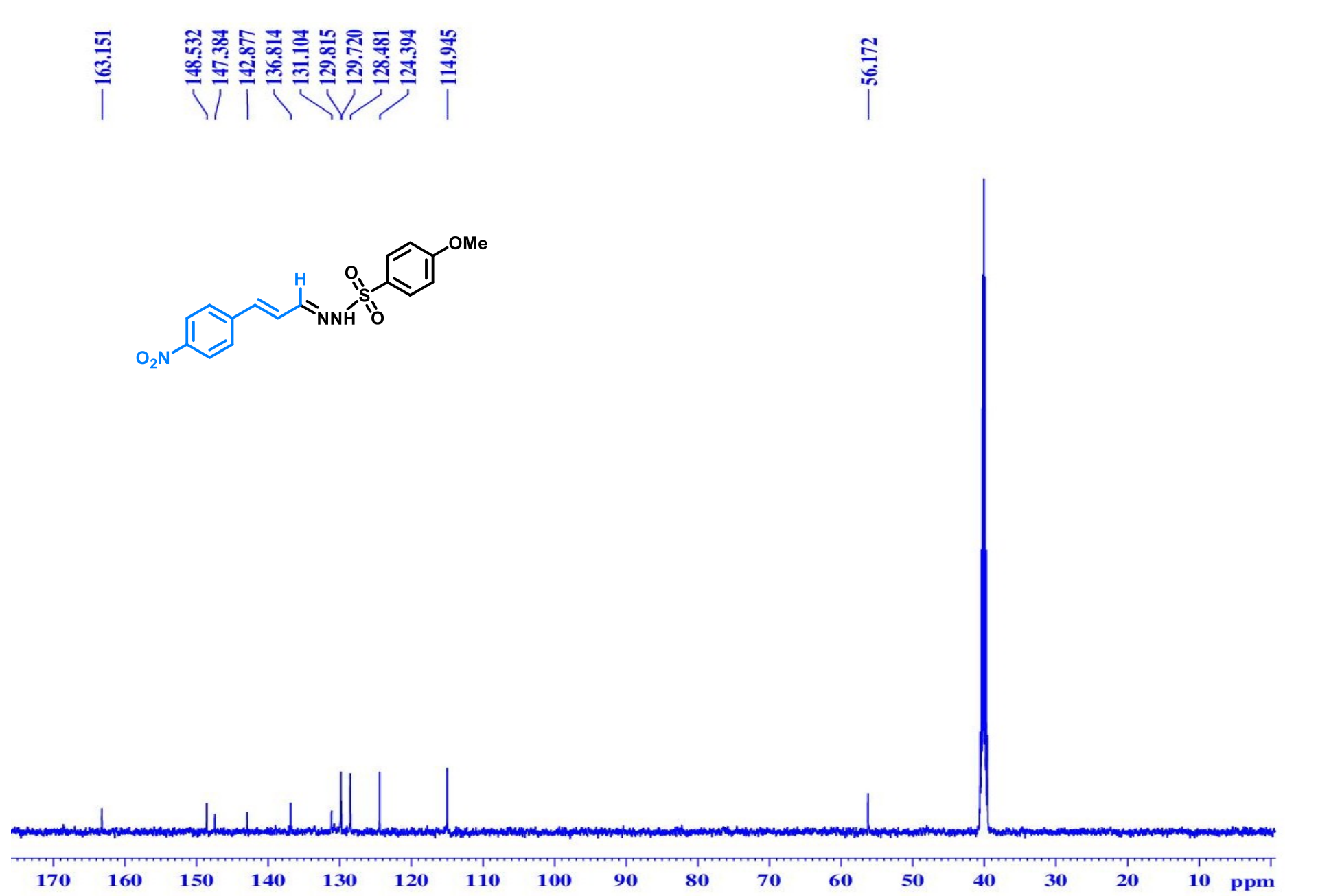

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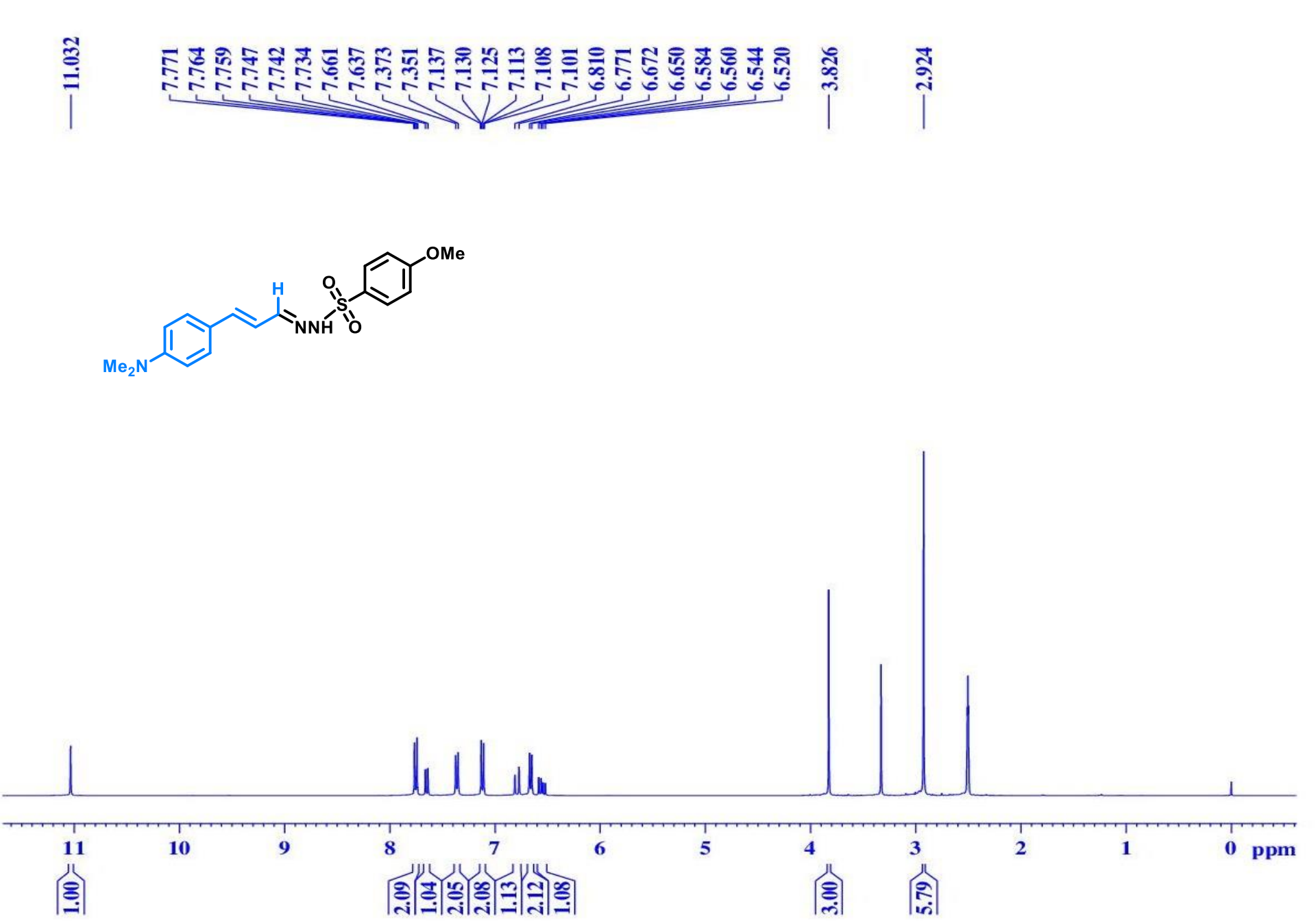

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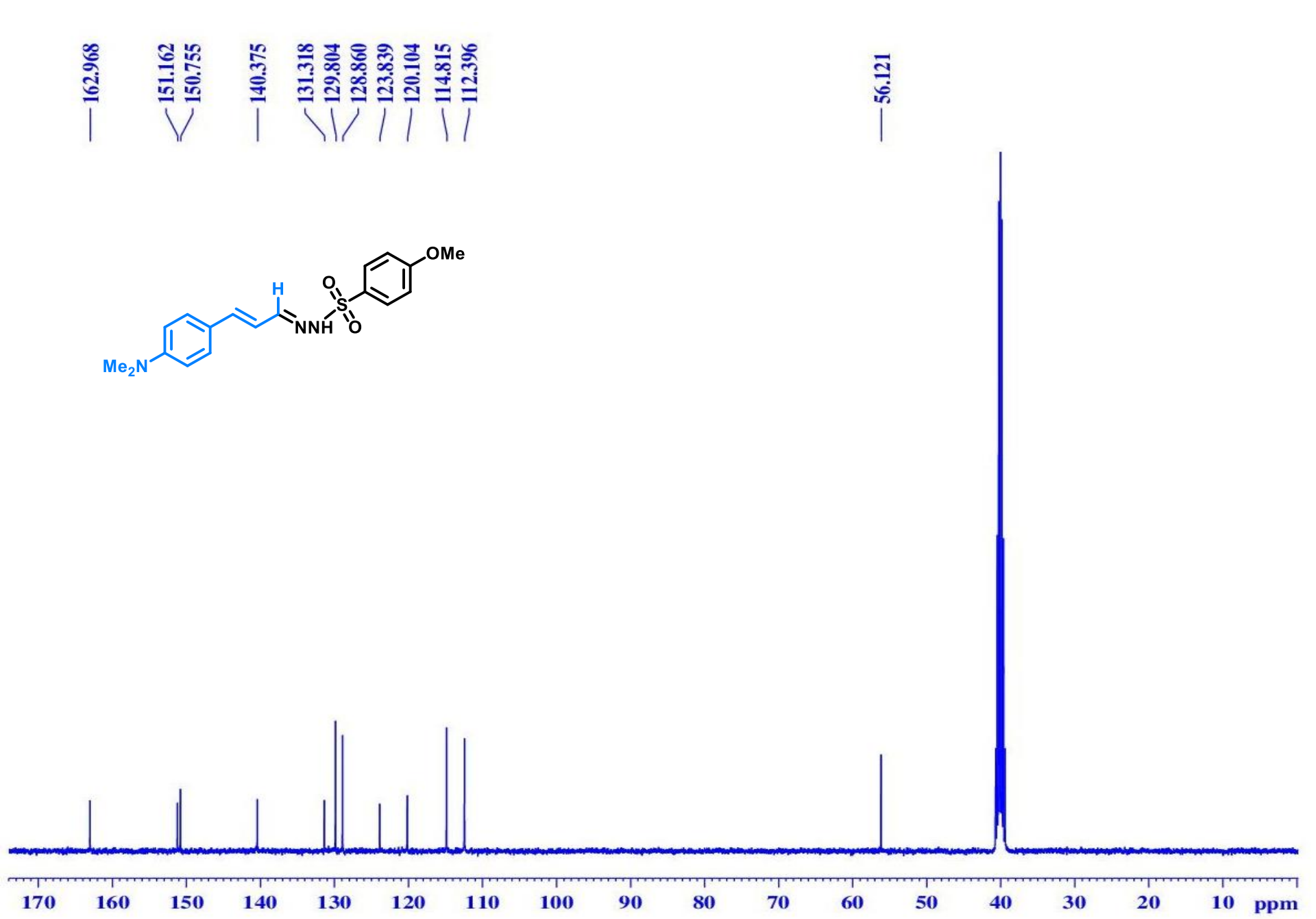

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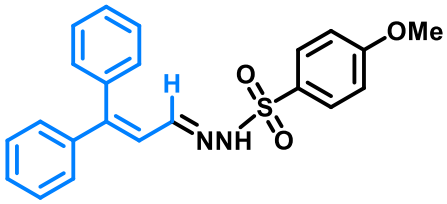

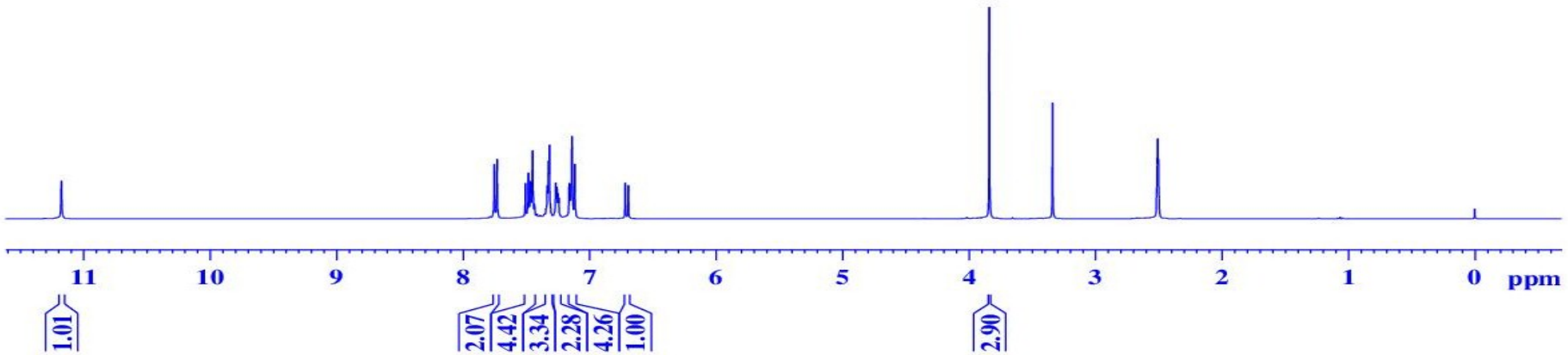

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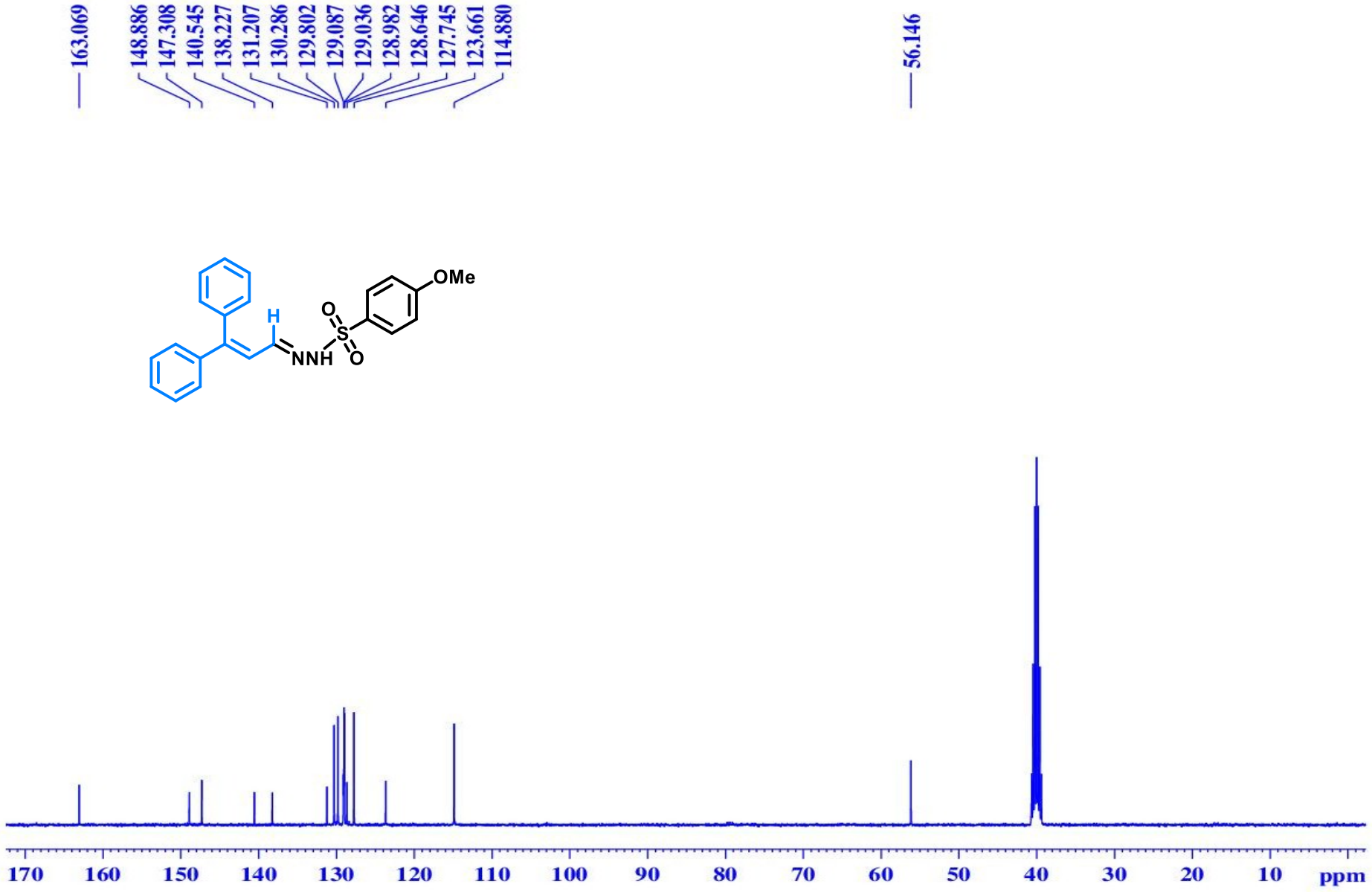
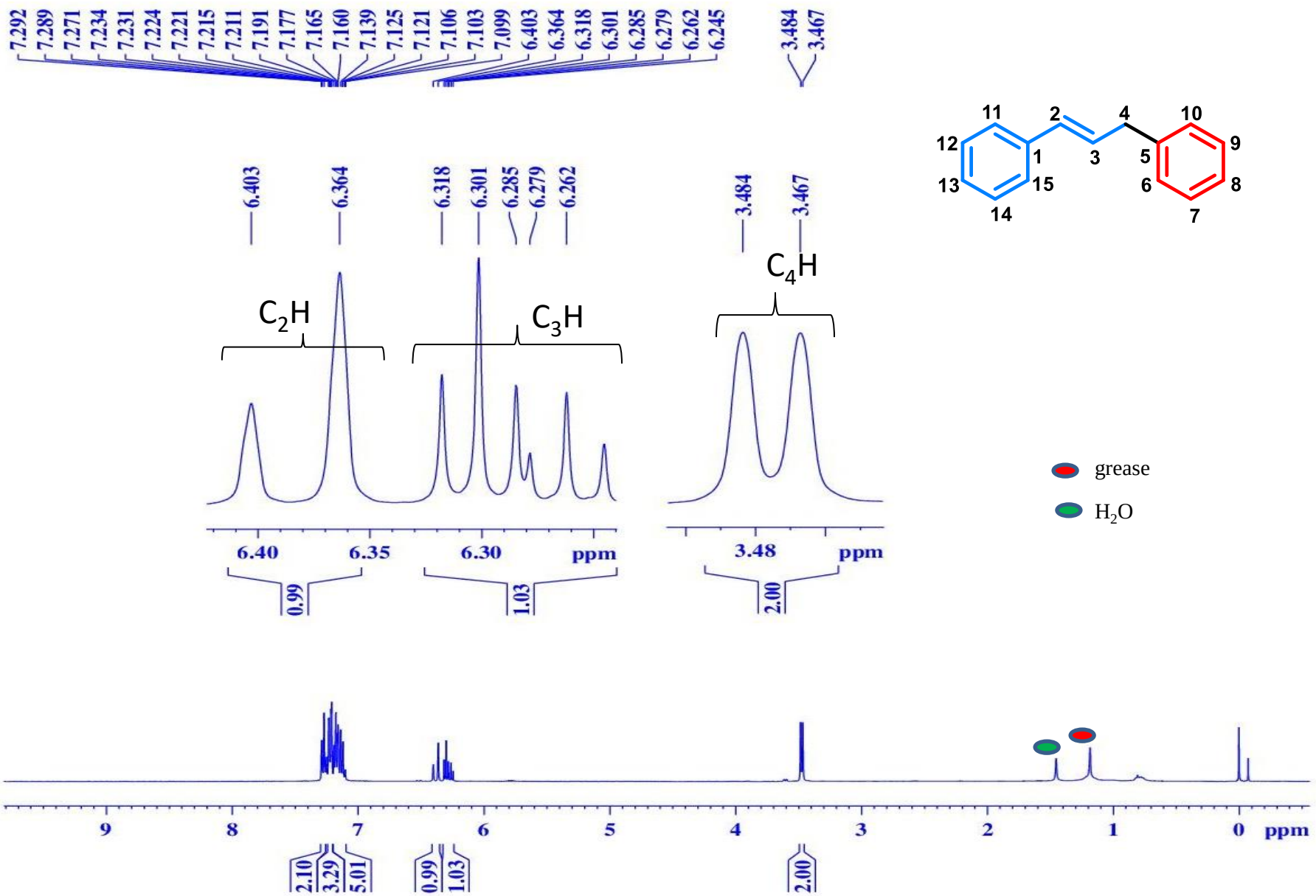
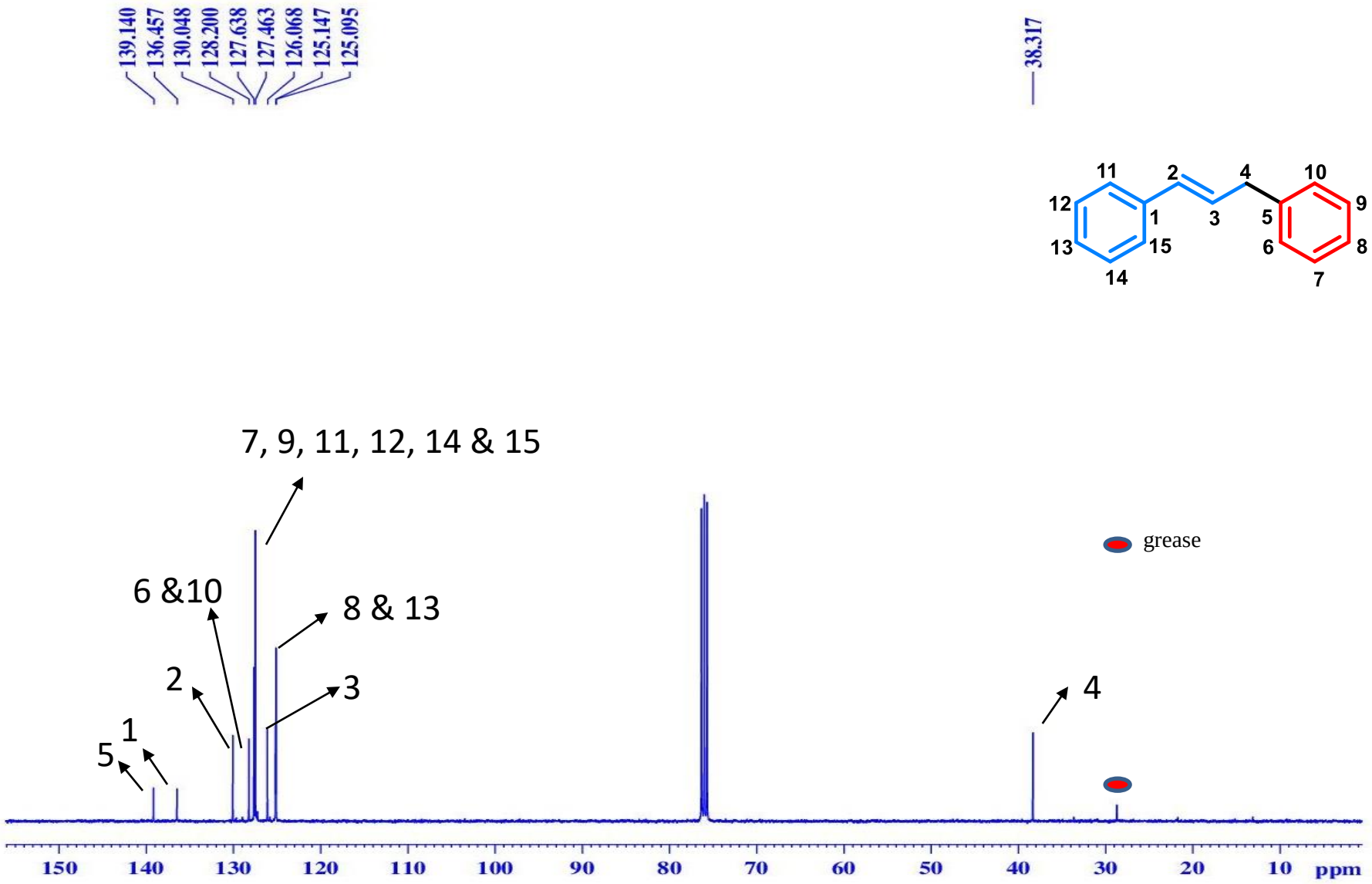


Compound 1f ^{13}C NMR (100 MHz, DMSO-d_6)

NMR Spectra for Cross–Coupling Products



Compound 3a ^{1}H NMR (400 MHz, $CDCl_3$)



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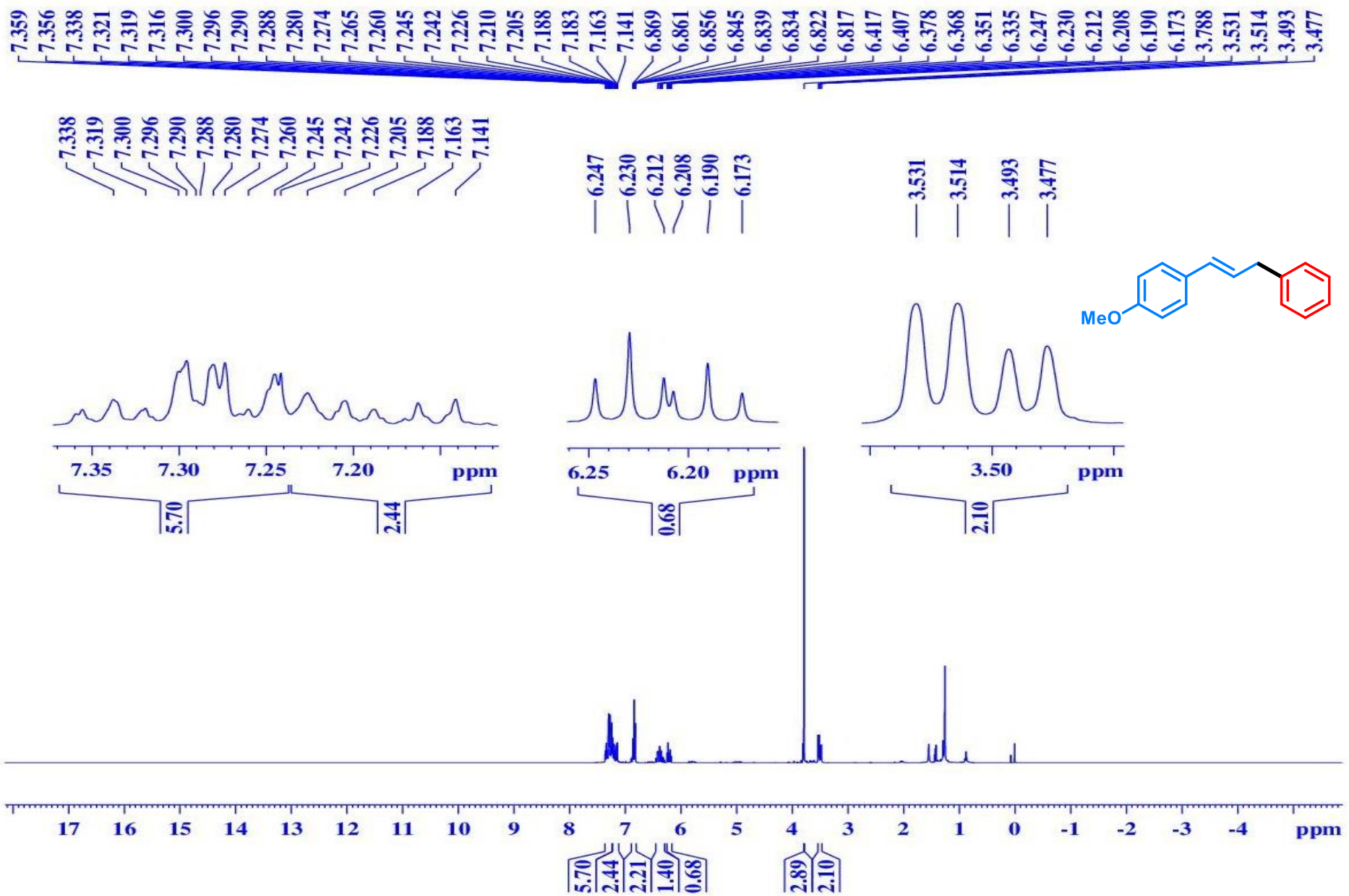

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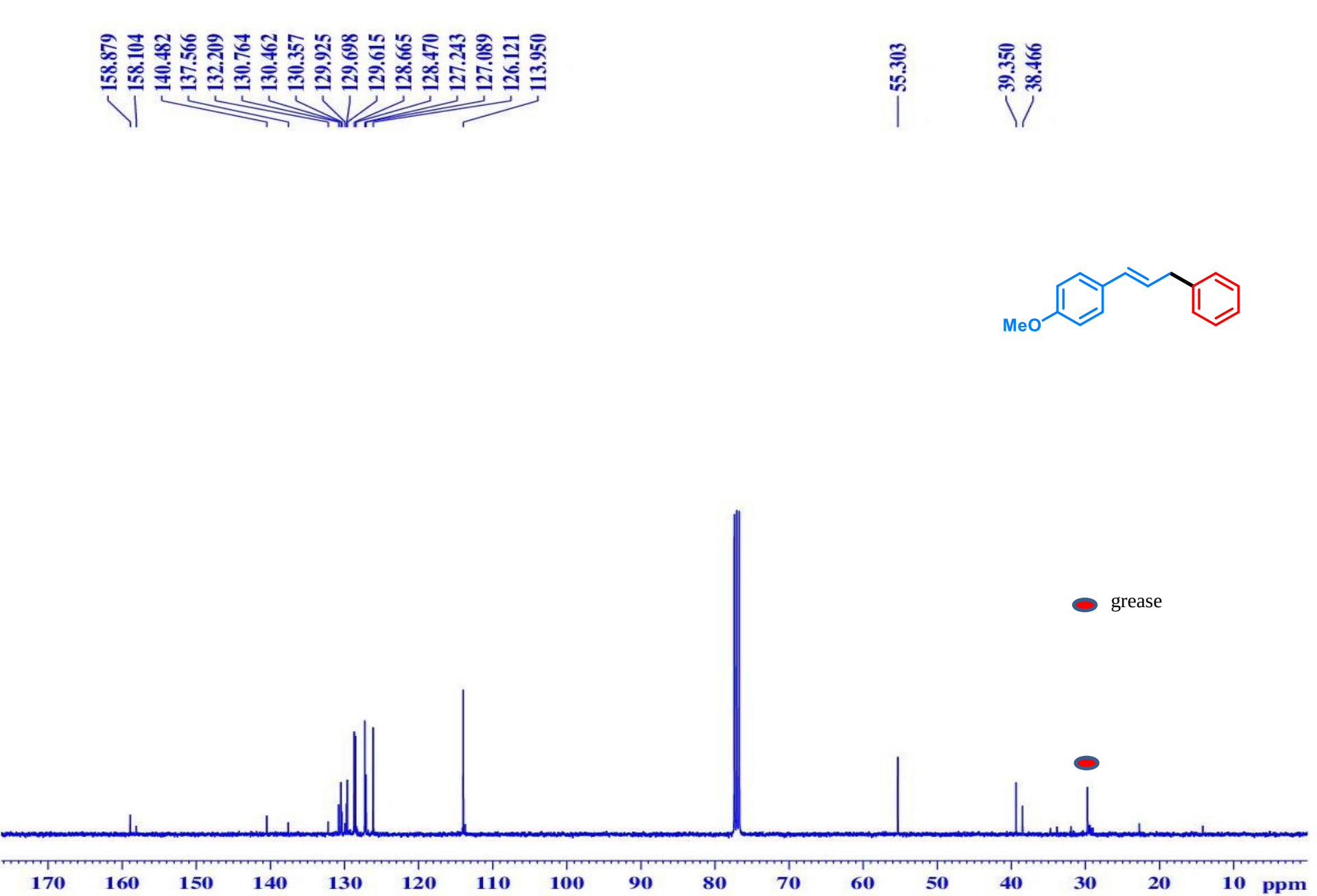

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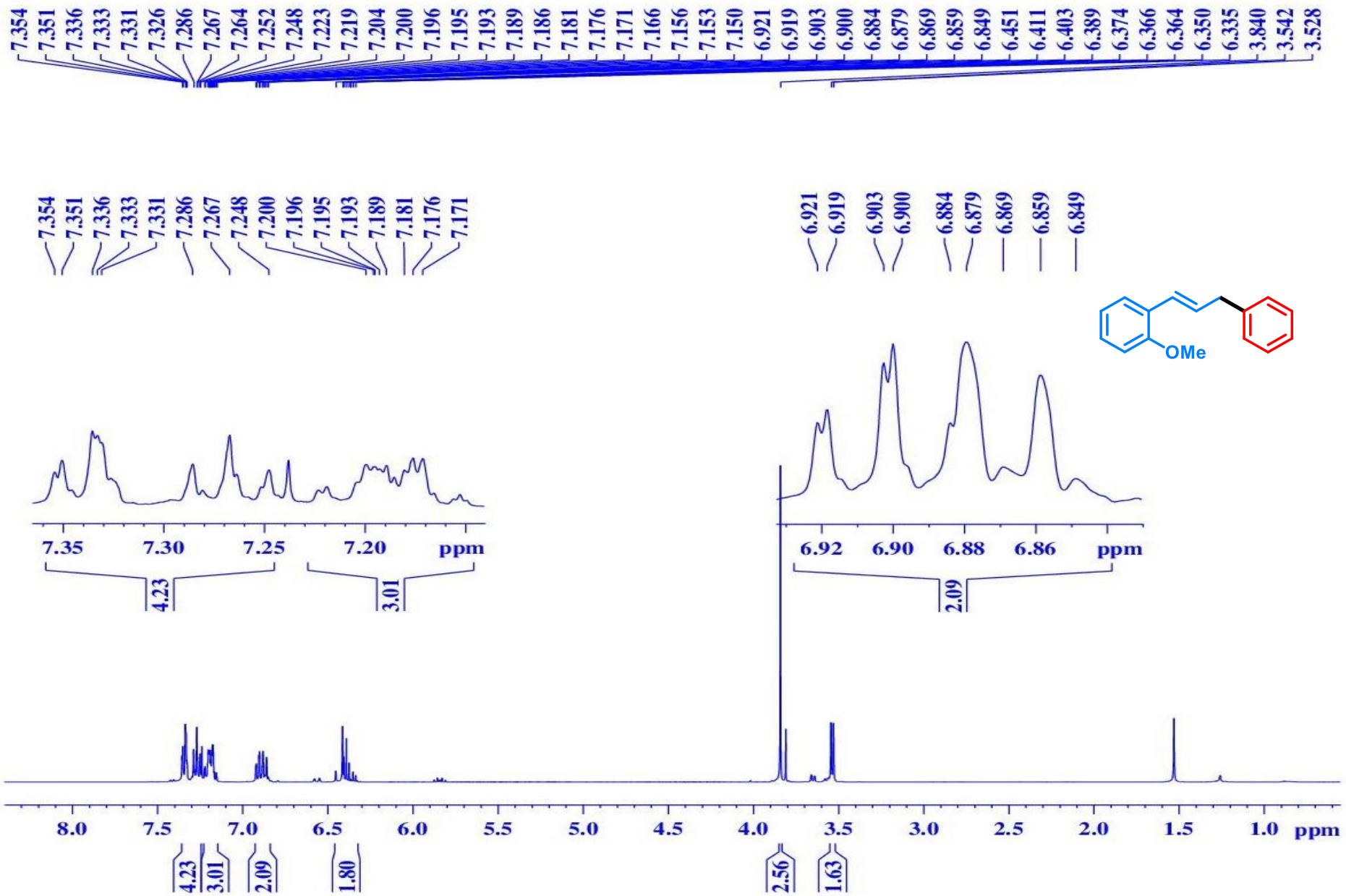

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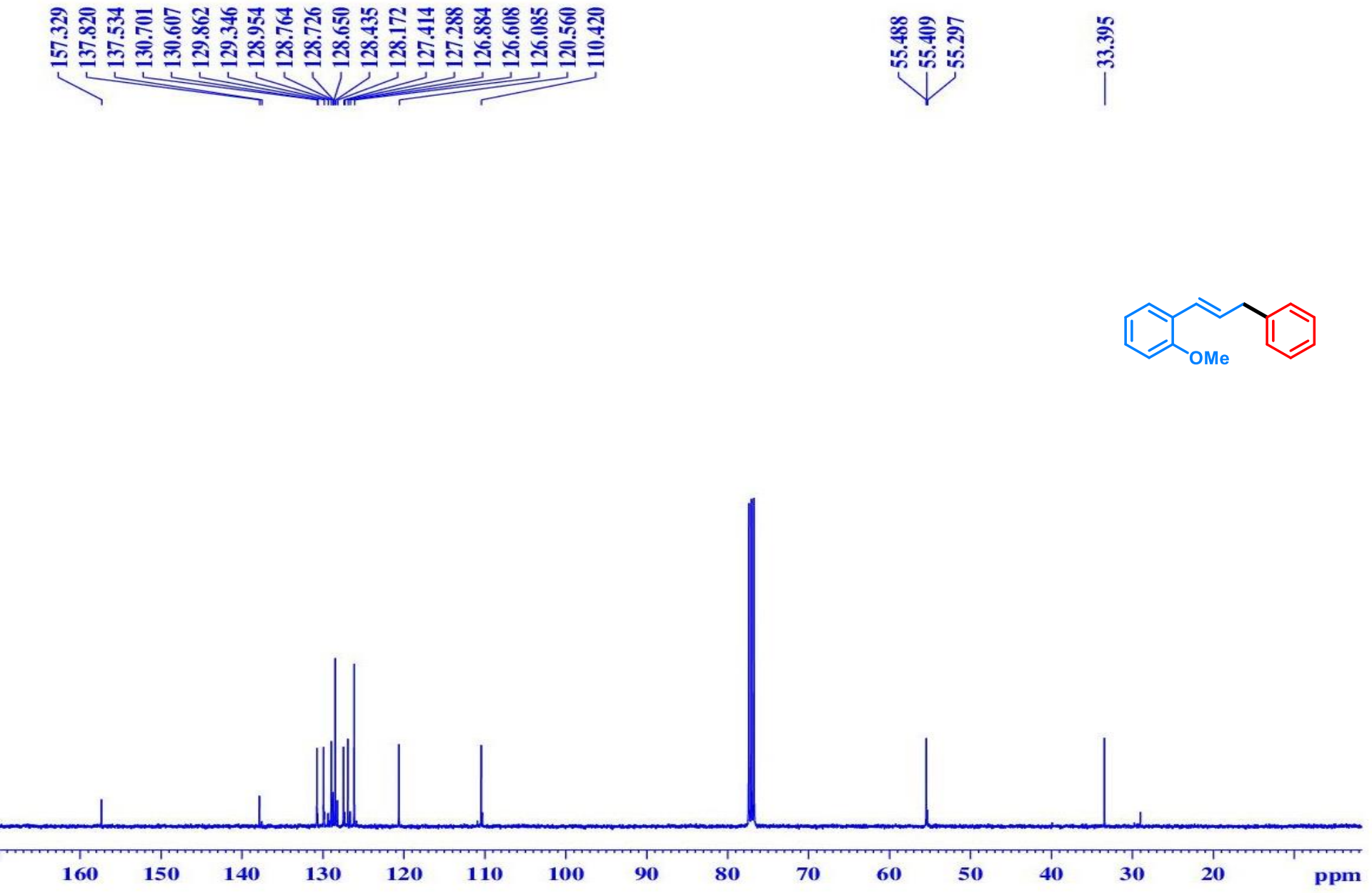

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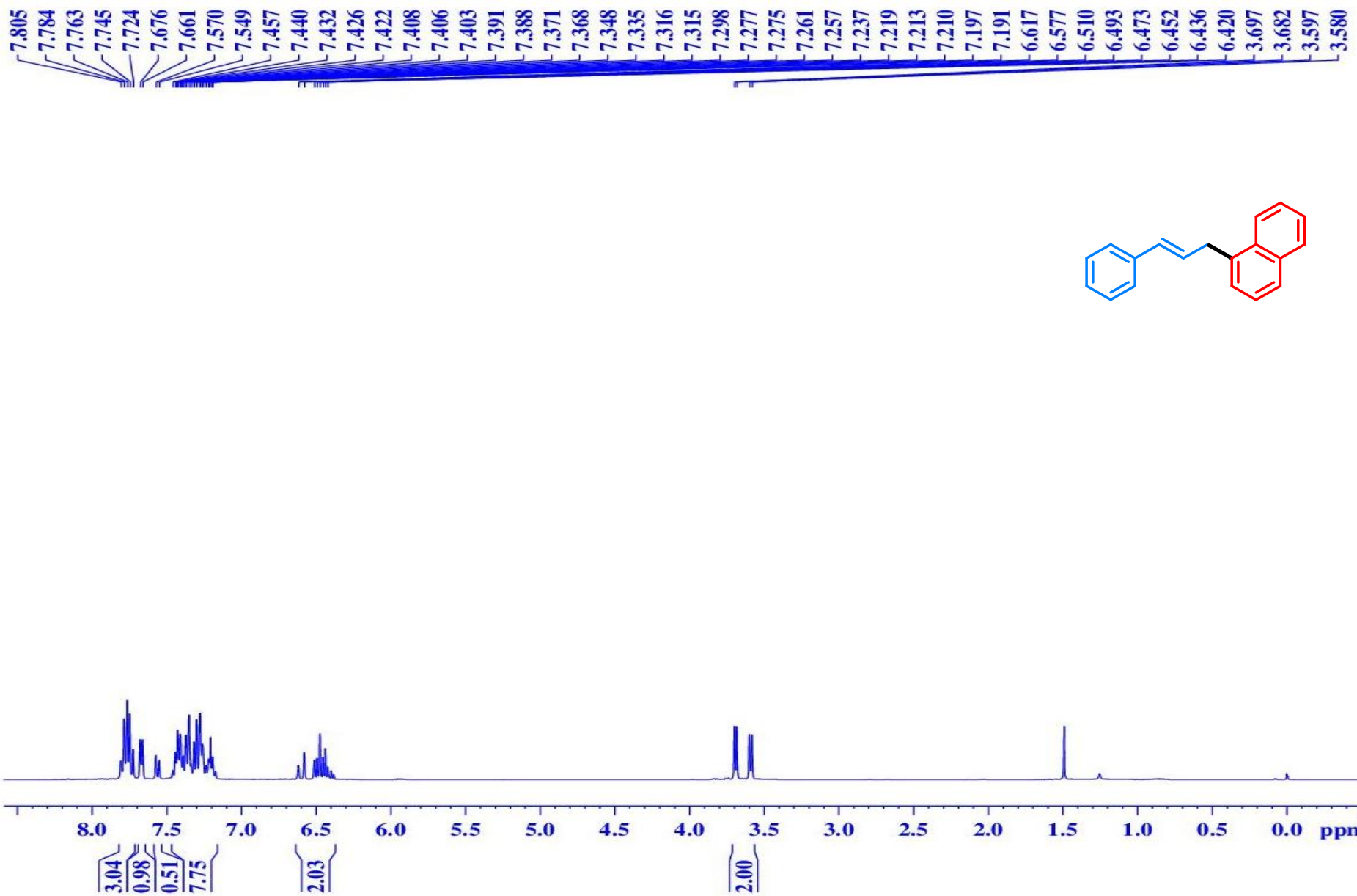

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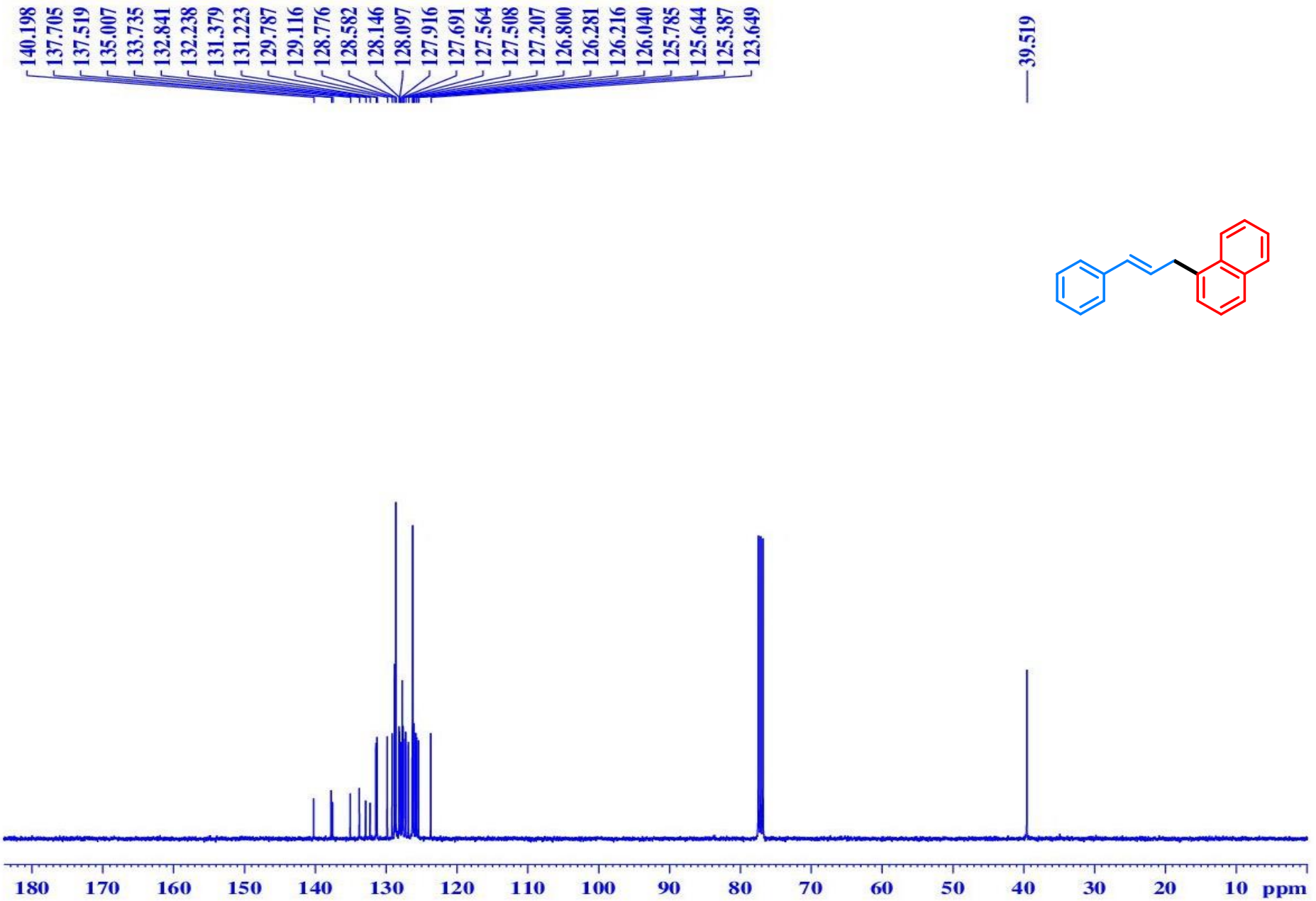

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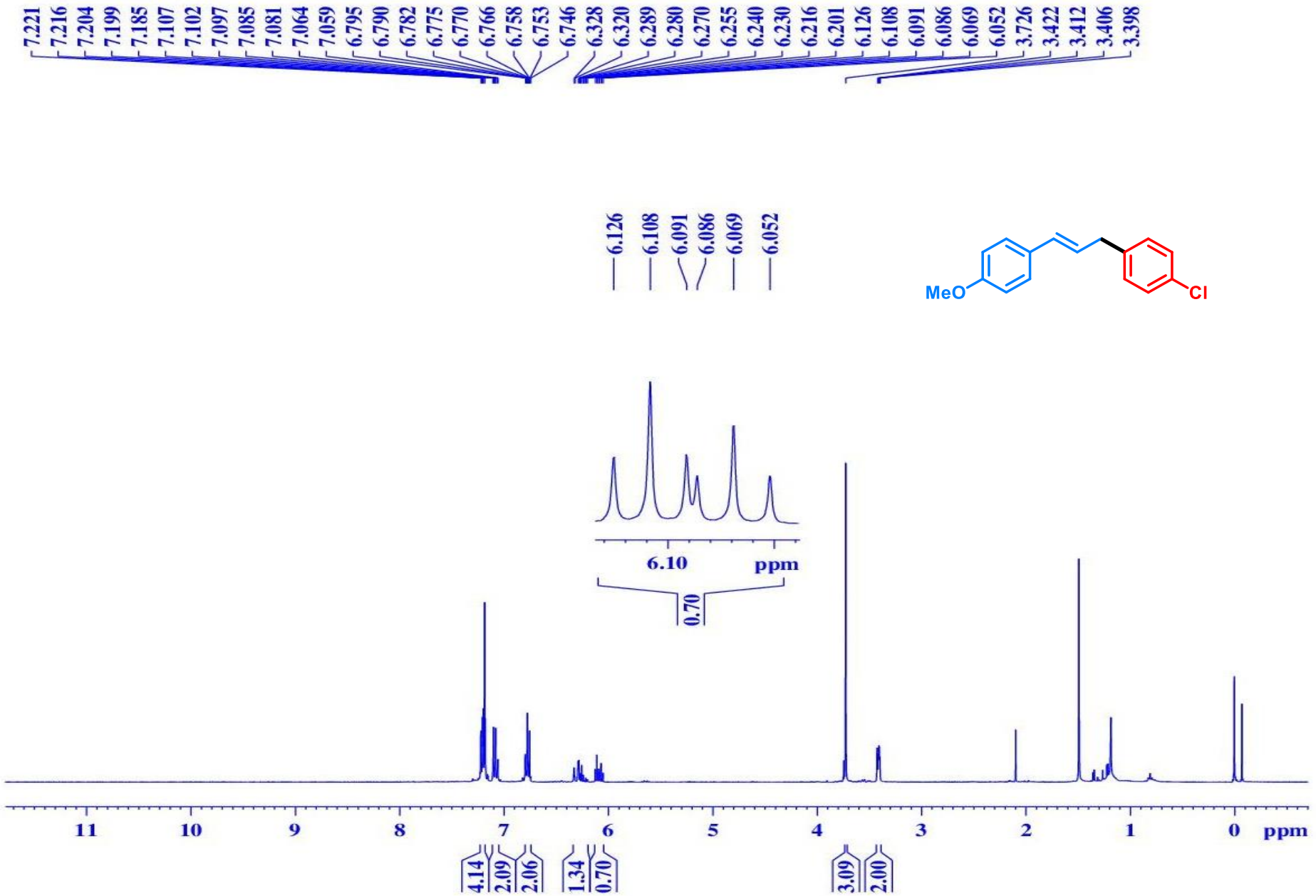
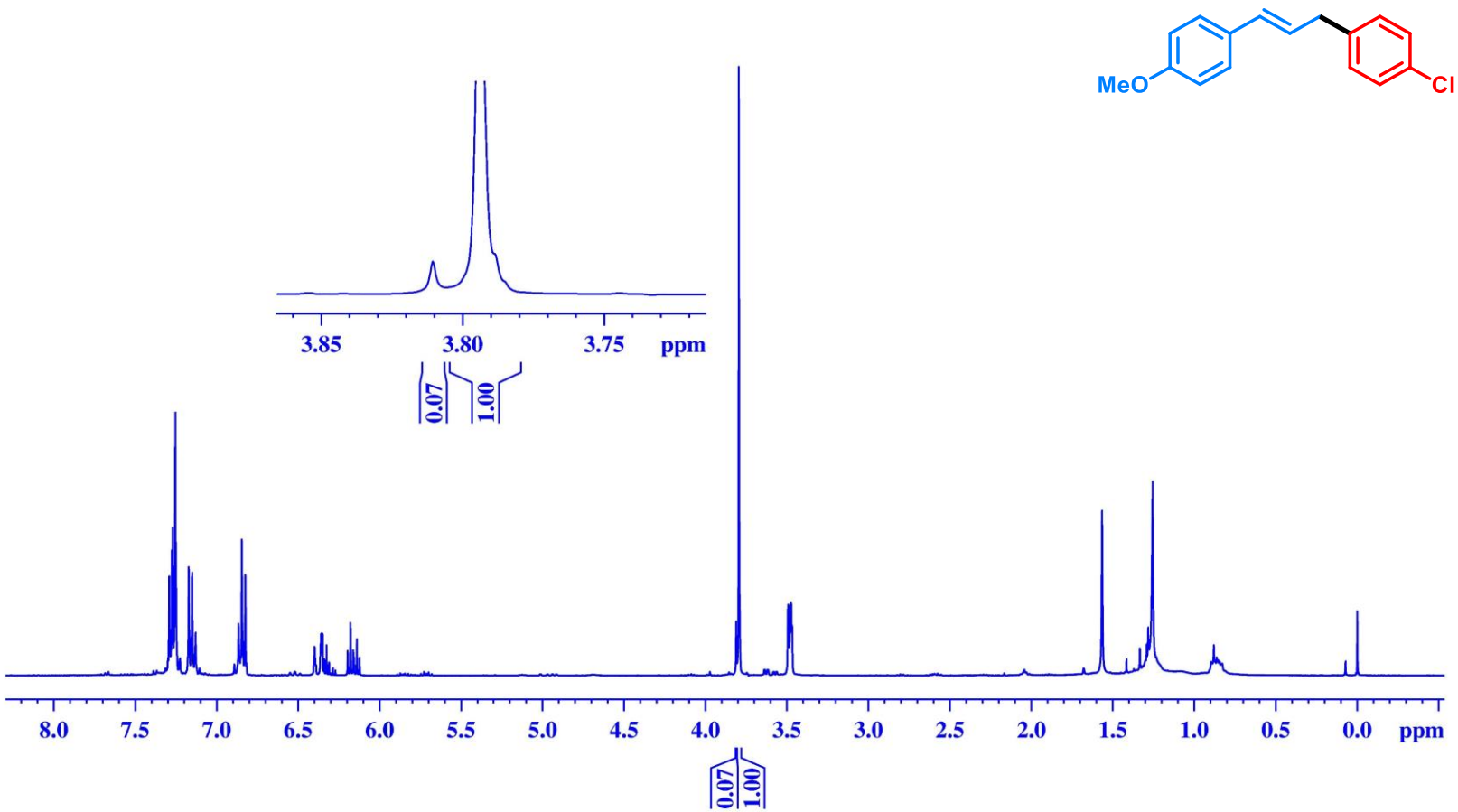
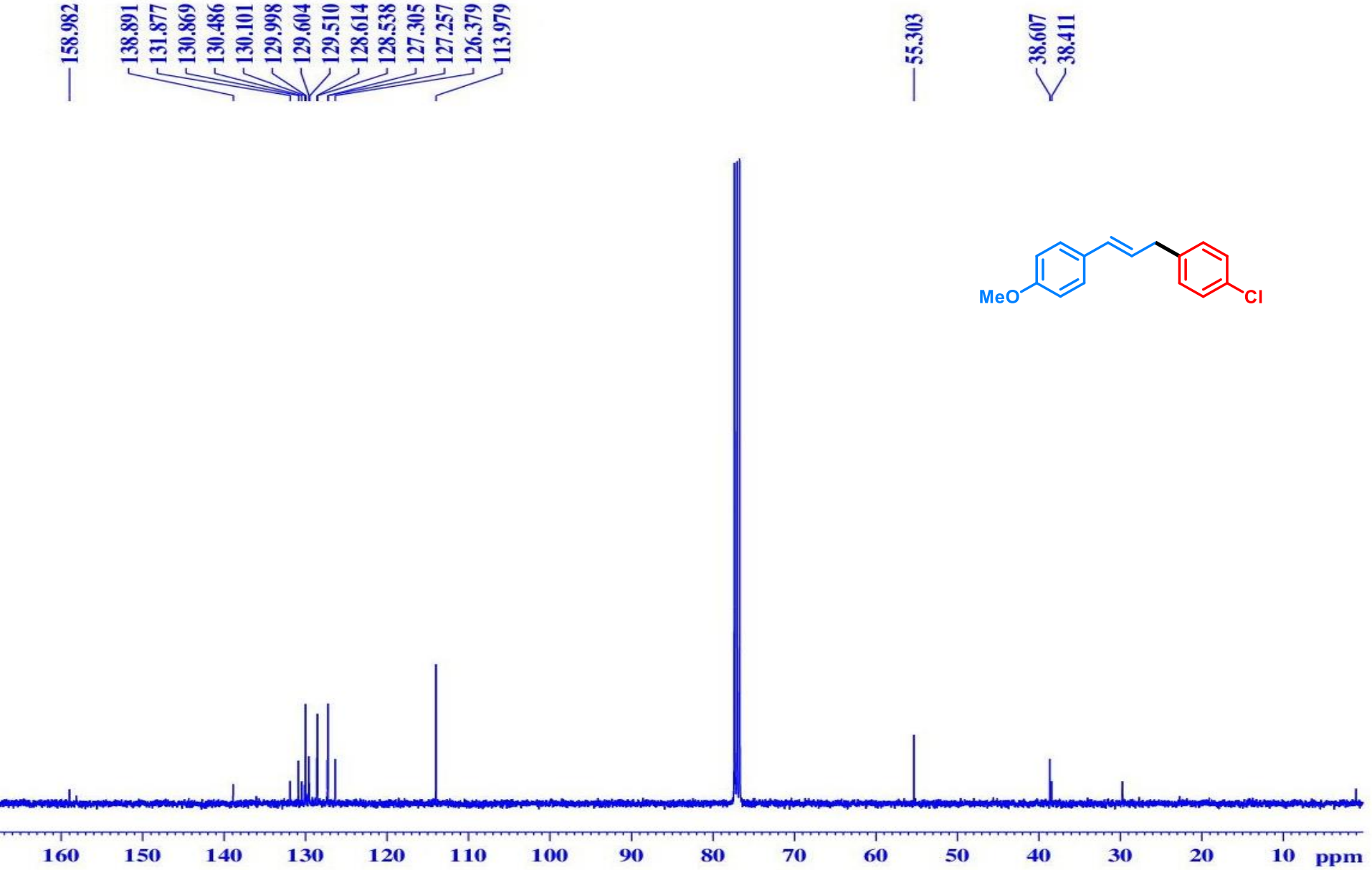


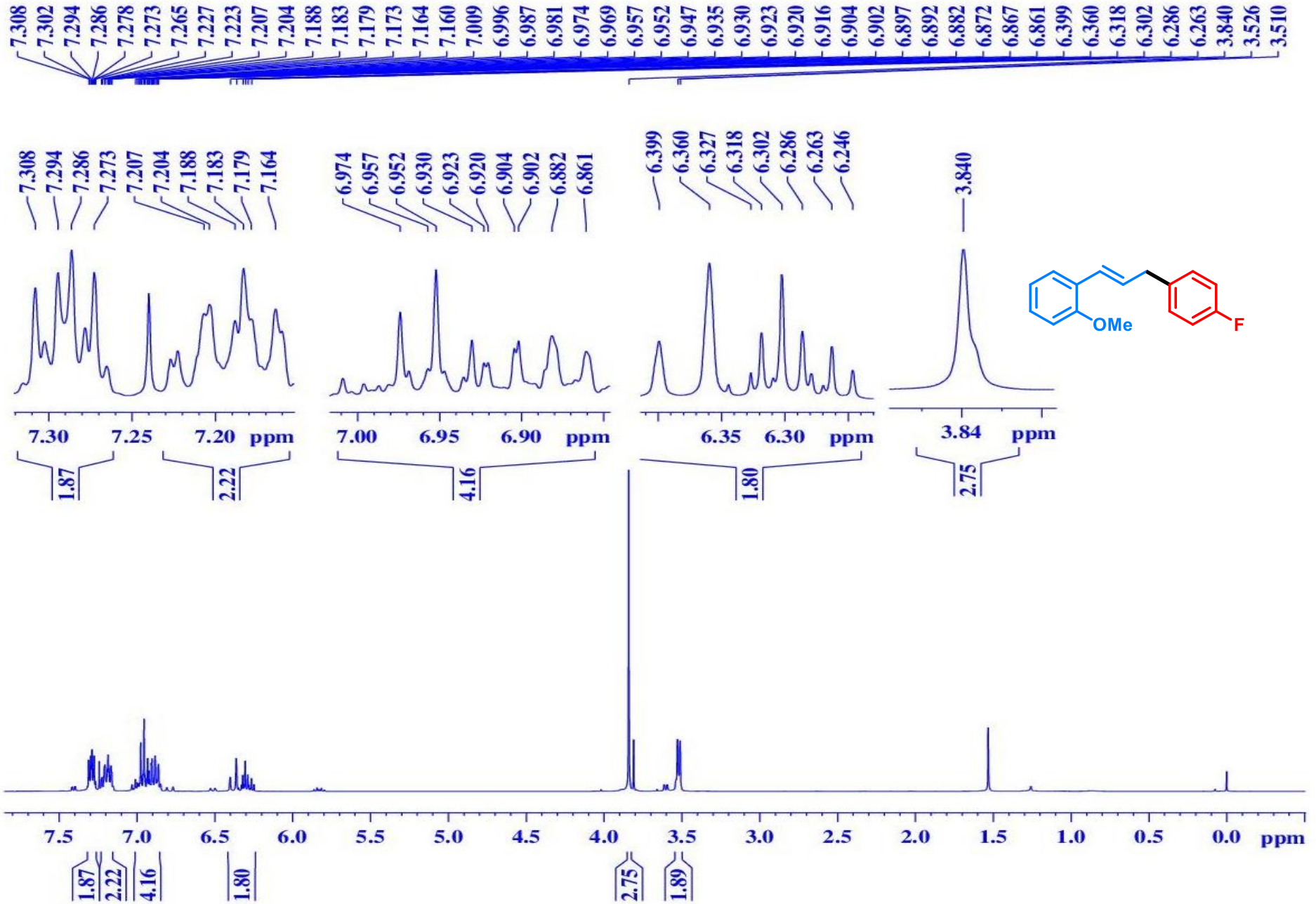
Compound 3e ^{1}H NMR (400 MHz, $CDCl_3$)



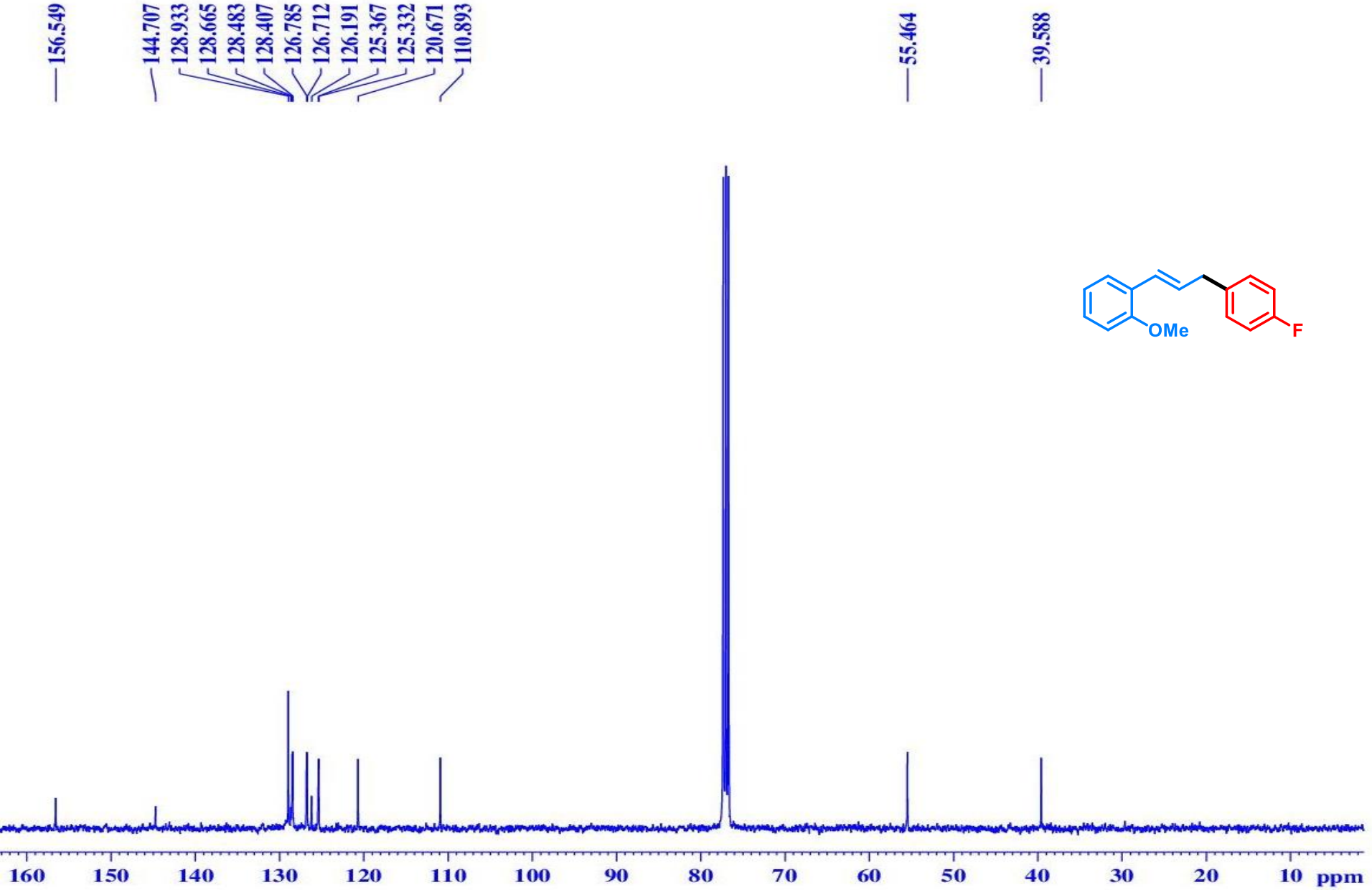
Compound 3e (crude) ^{1}H NMR (400 MHz, $CDCl_3$)



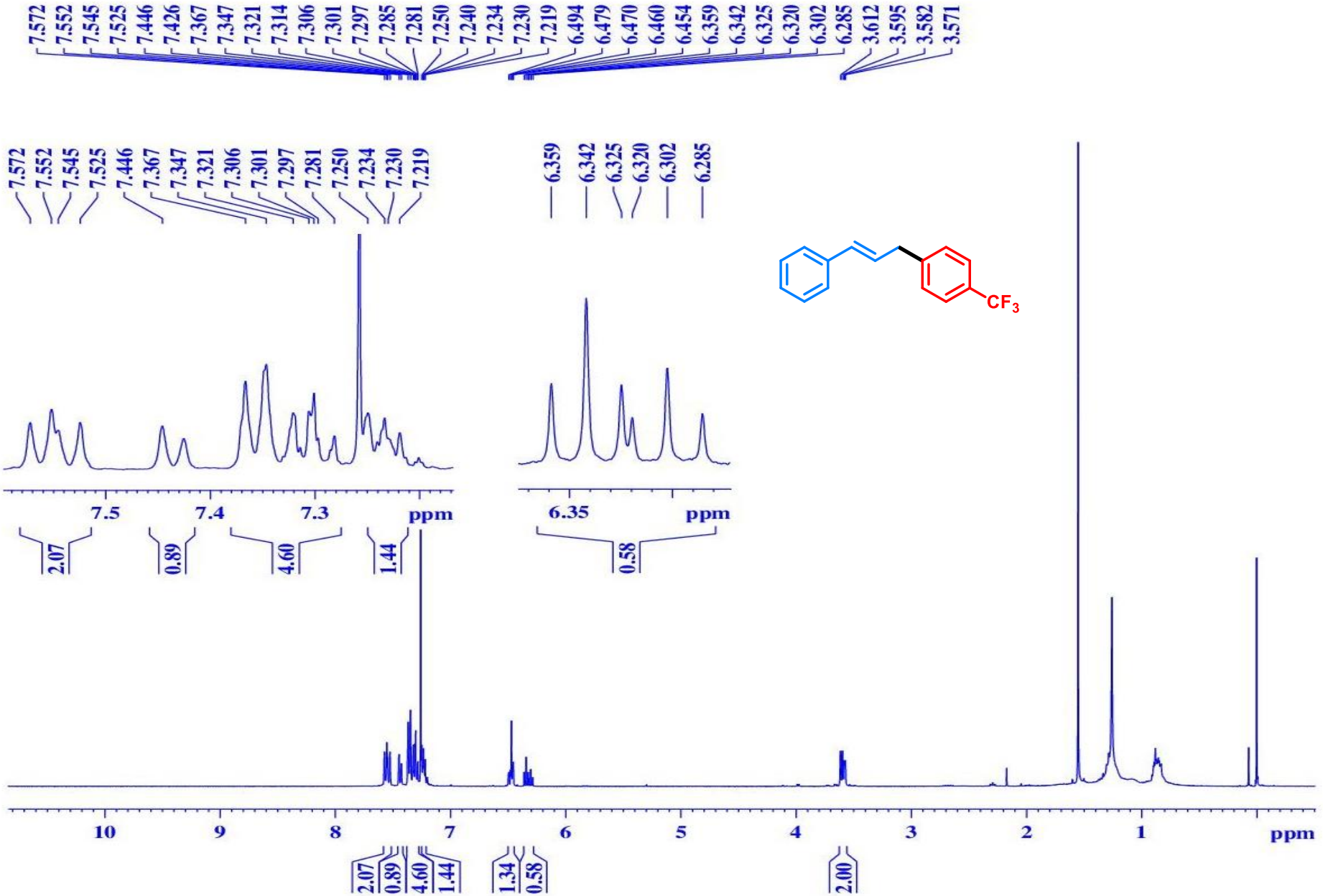
Compound 3e ^{13}C NMR (100 MHz, $CDCl_3$)



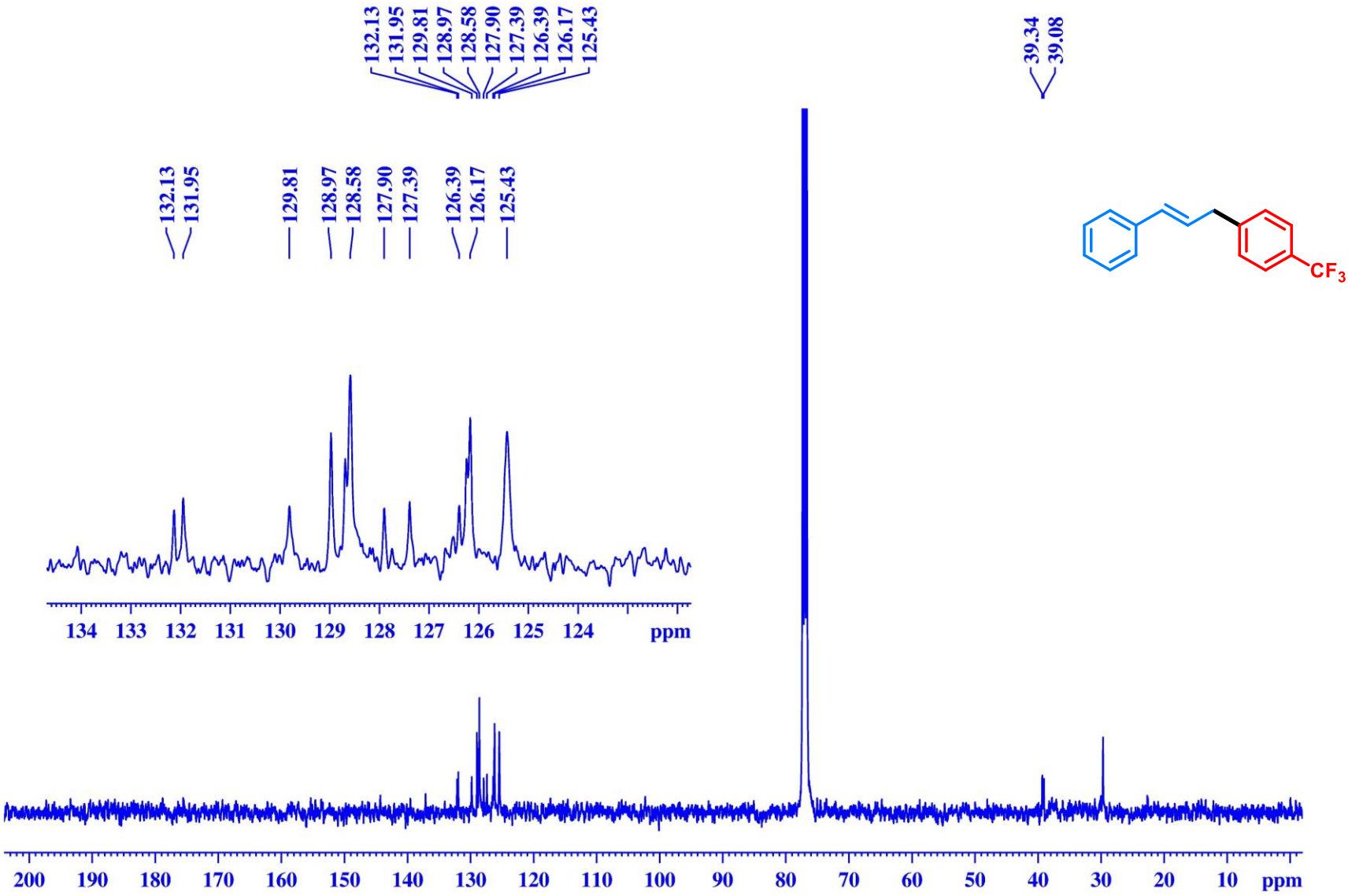
Compound 3f ^{1}H NMR (400 MHz, $CDCl_3$)



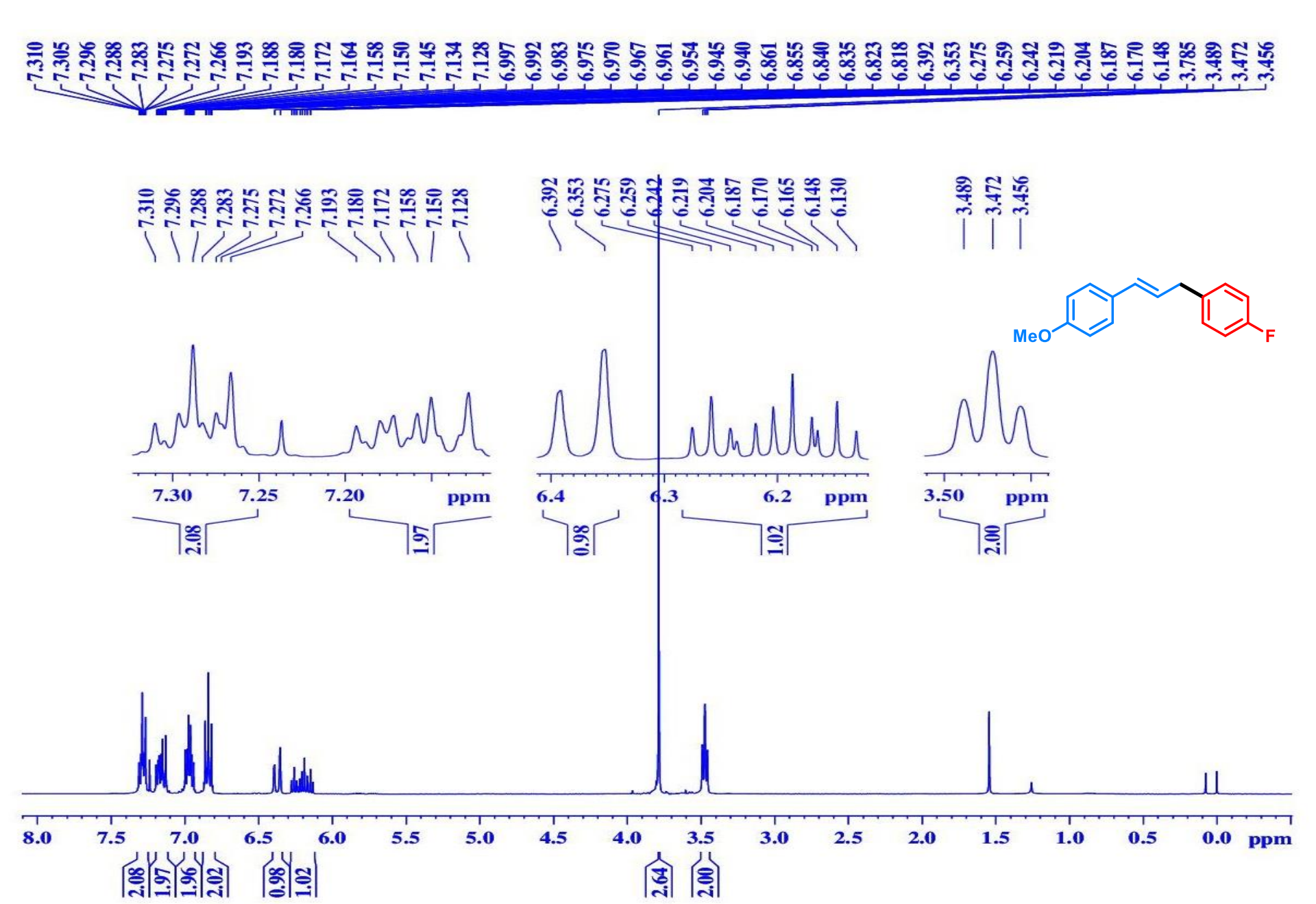
Compound 3f ^{13}C NMR (100 MHz, $CDCl_3$)



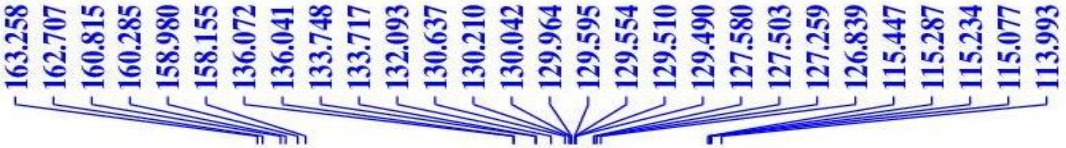
Compound 3g ^{1}H NMR (400 MHz, $CDCl_3$)

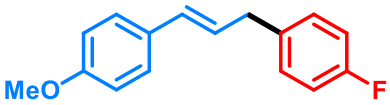


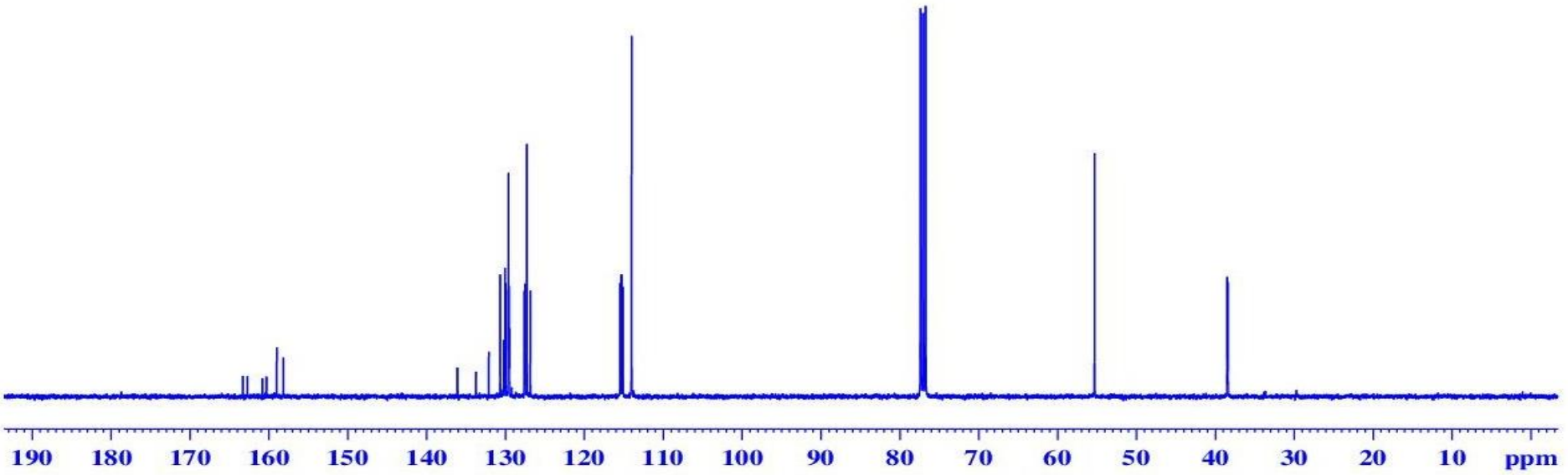
Compound 3g ^{13}C NMR (100 MHz, $CDCl_3$)



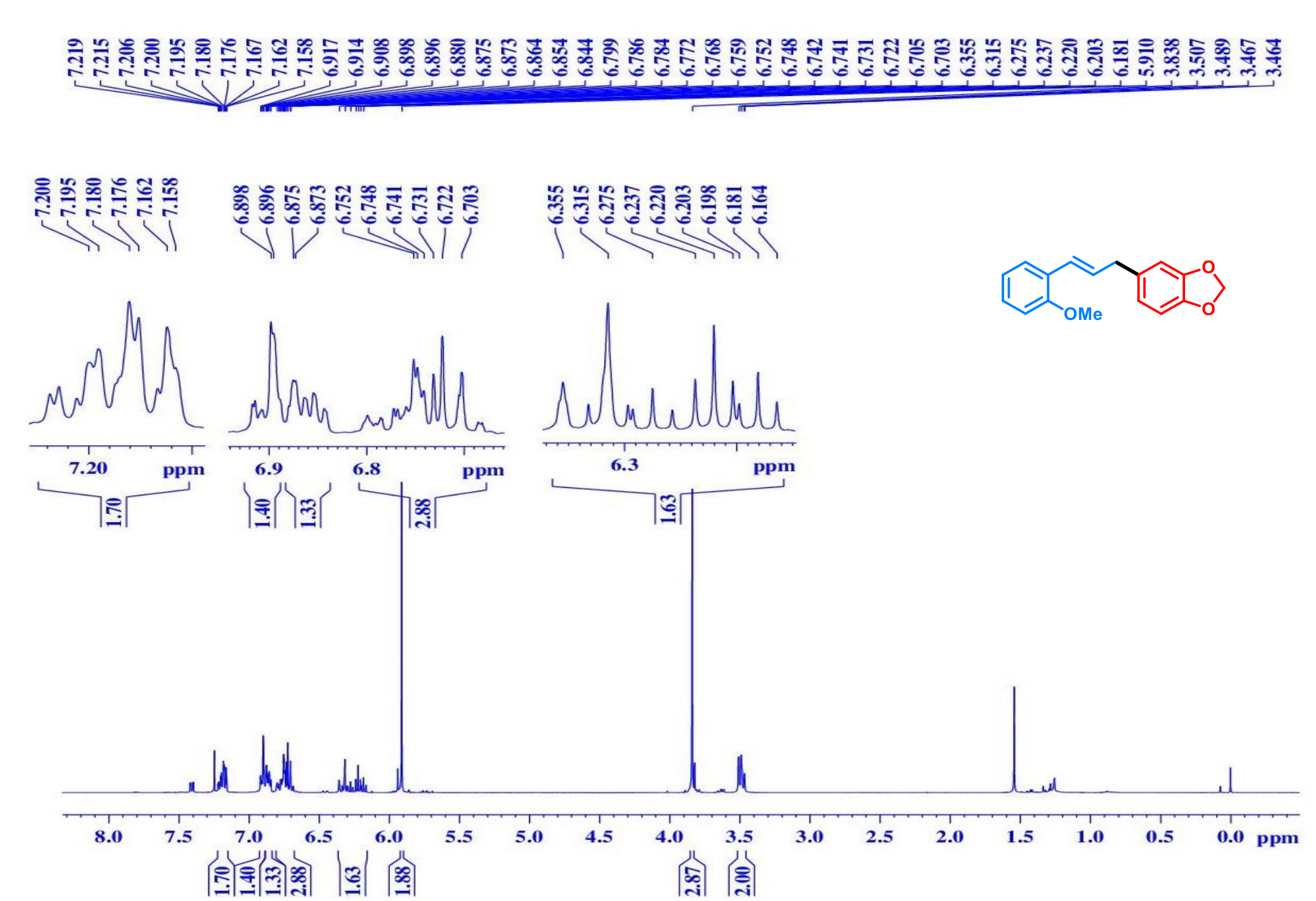
Compound 3h ^{1}H NMR (400 MHz, $CDCl_3$)



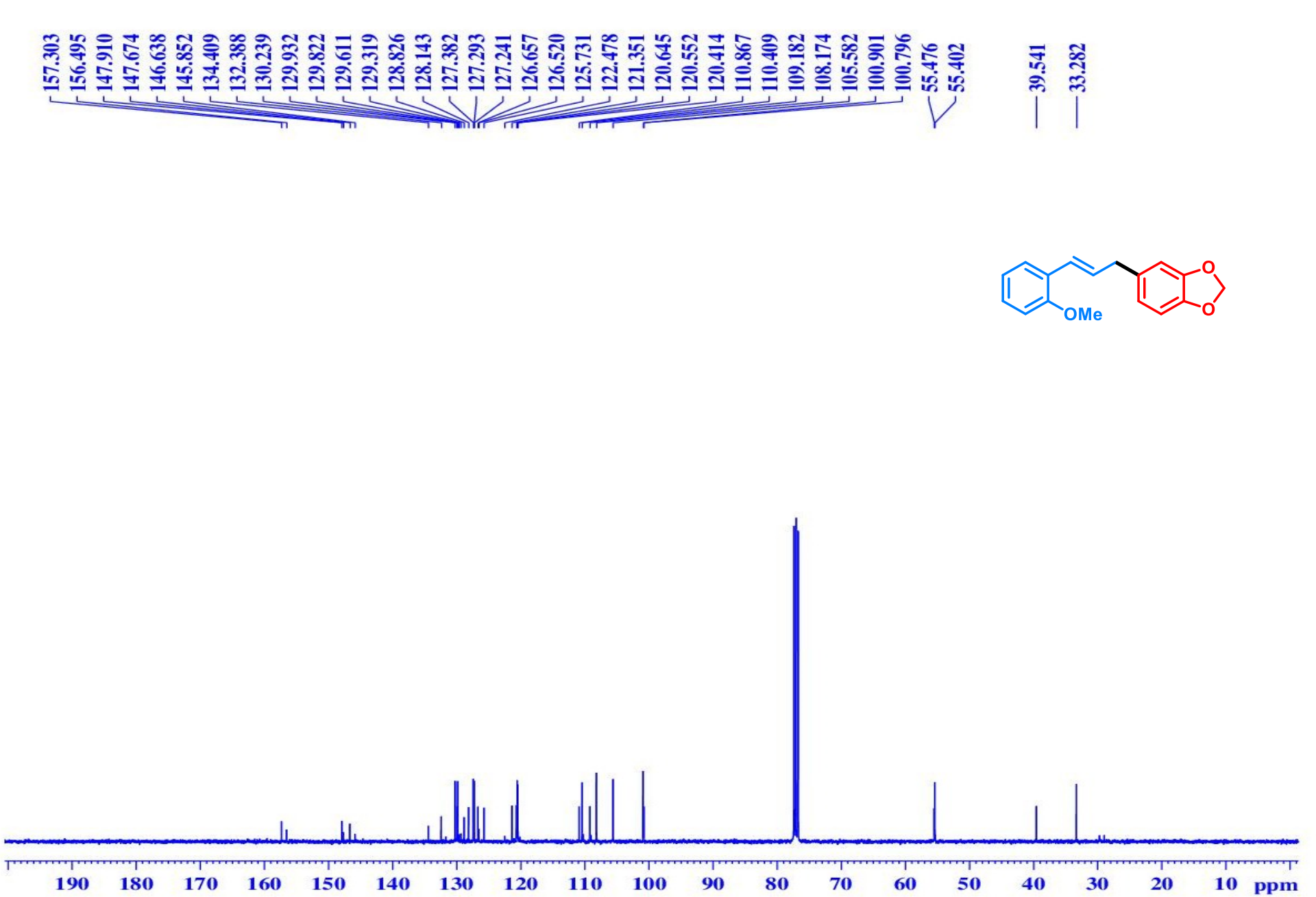




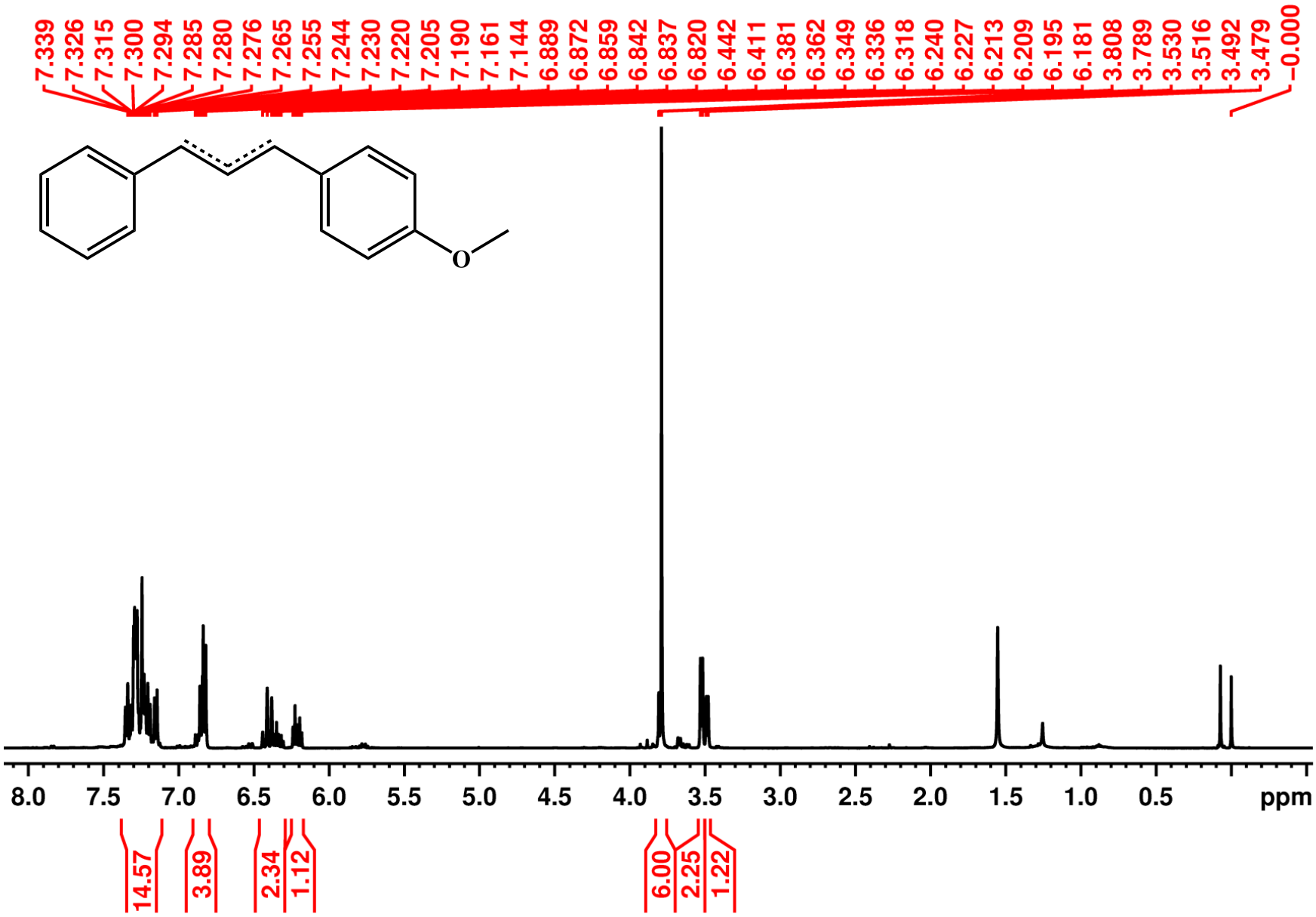
Compound 3h ^{13}C NMR (100 MHz, $CDCl_3$)



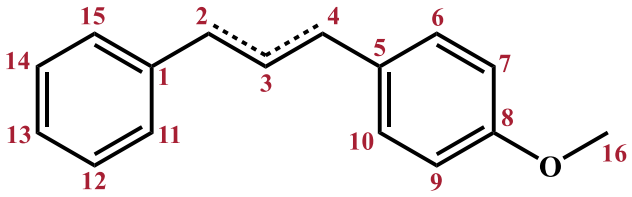
Compound 3i ^{1}H NMR (400 MHz, $CDCl_3$)

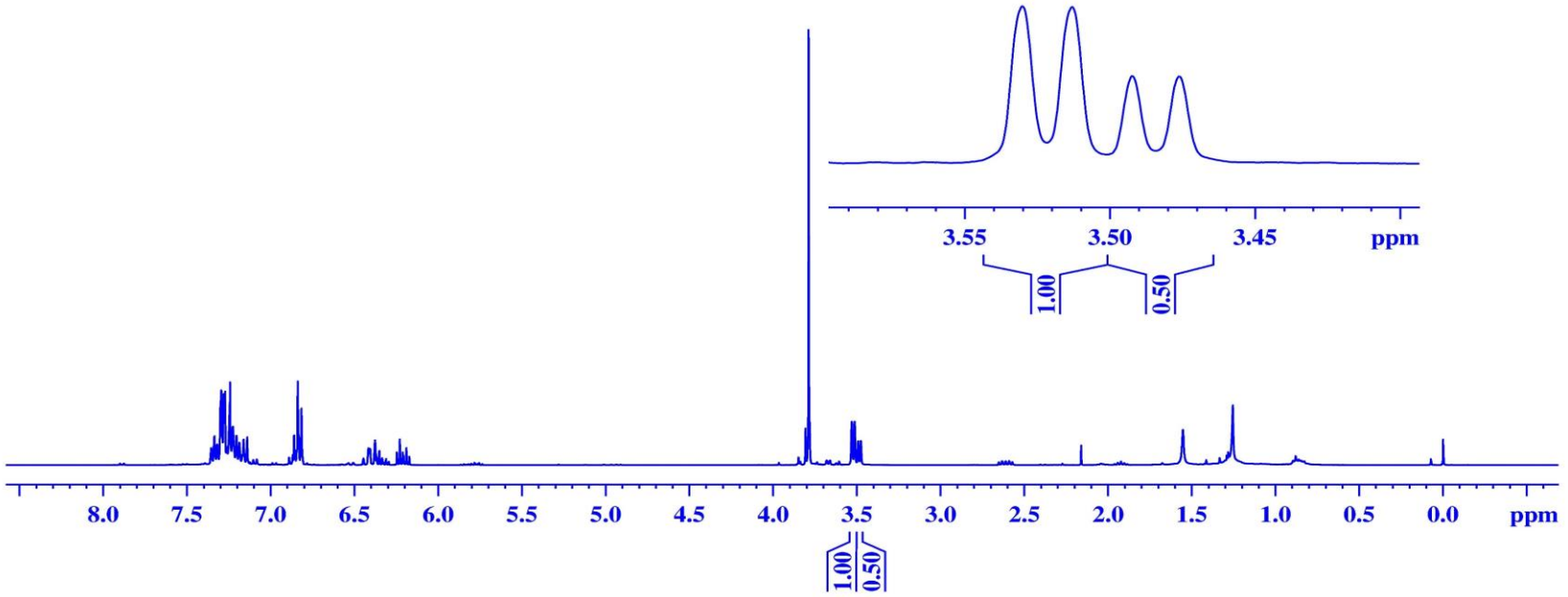


Compound 3i ^{13}C NMR (100 MHz, $CDCl_3$)

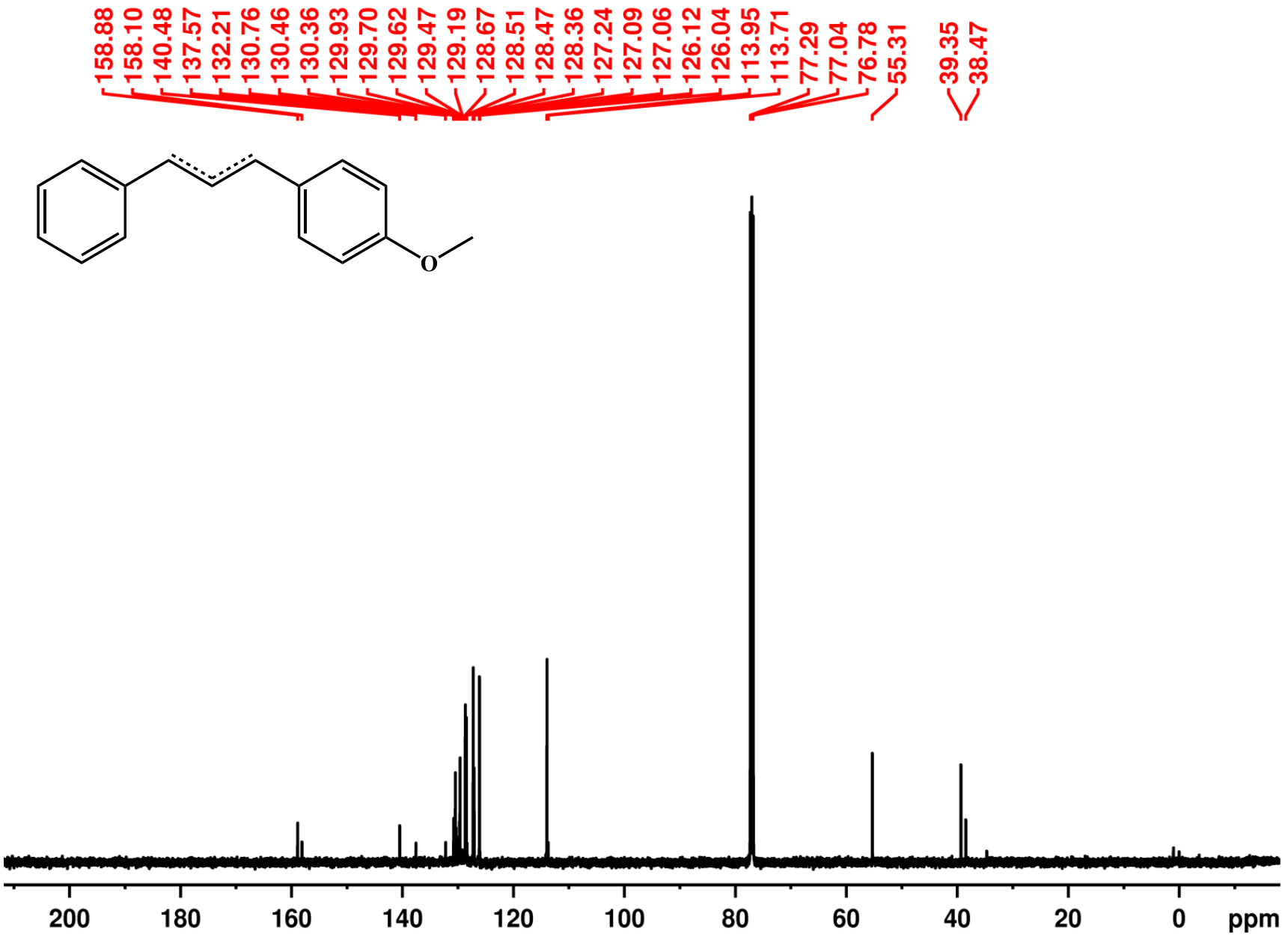


Compound 3j ^{1}H NMR (500 MHz, $CDCl_3$)

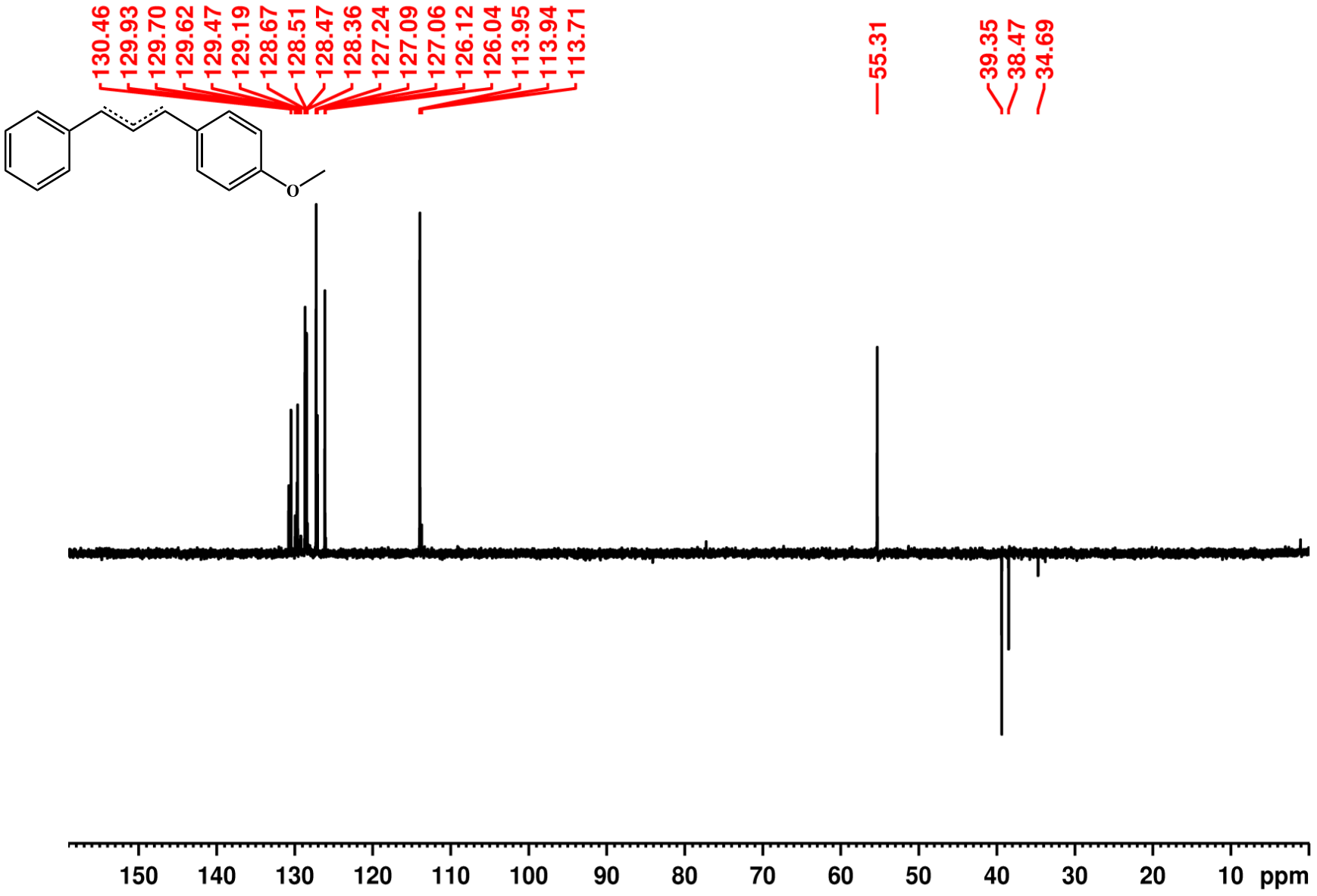




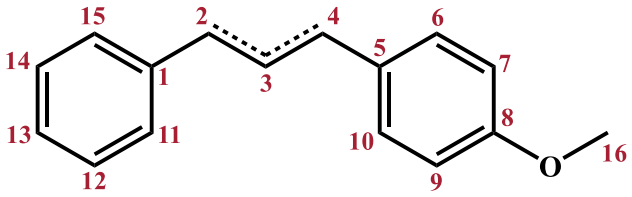
Compound 3j (crude) ^{1}H NMR (500 MHz, $CDCl_3$)

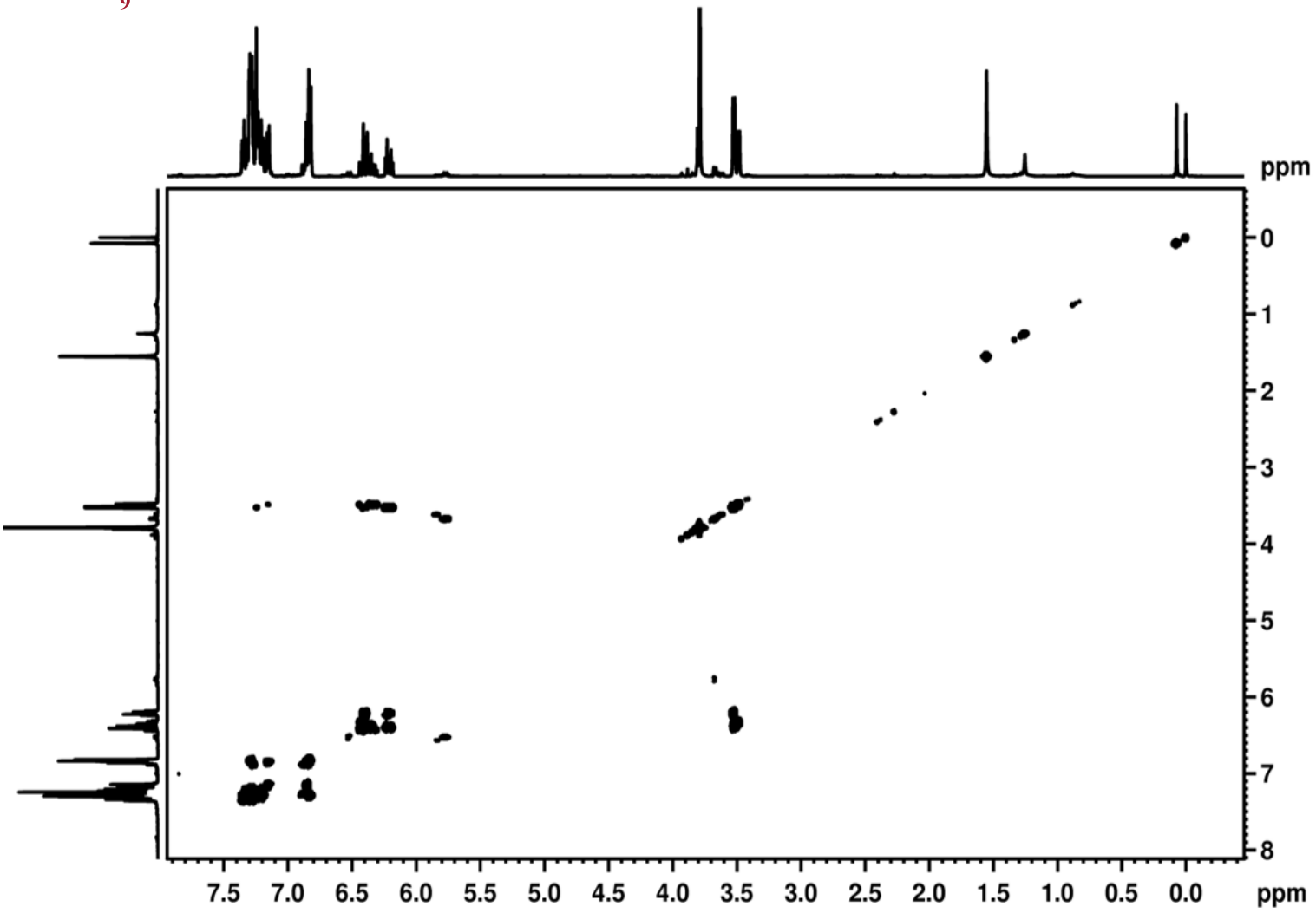


Compound 3j ^{13}C NMR (125 MHz, $CDCl_3$)

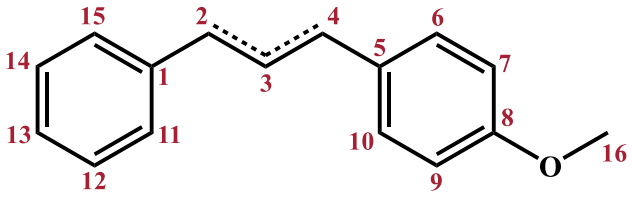


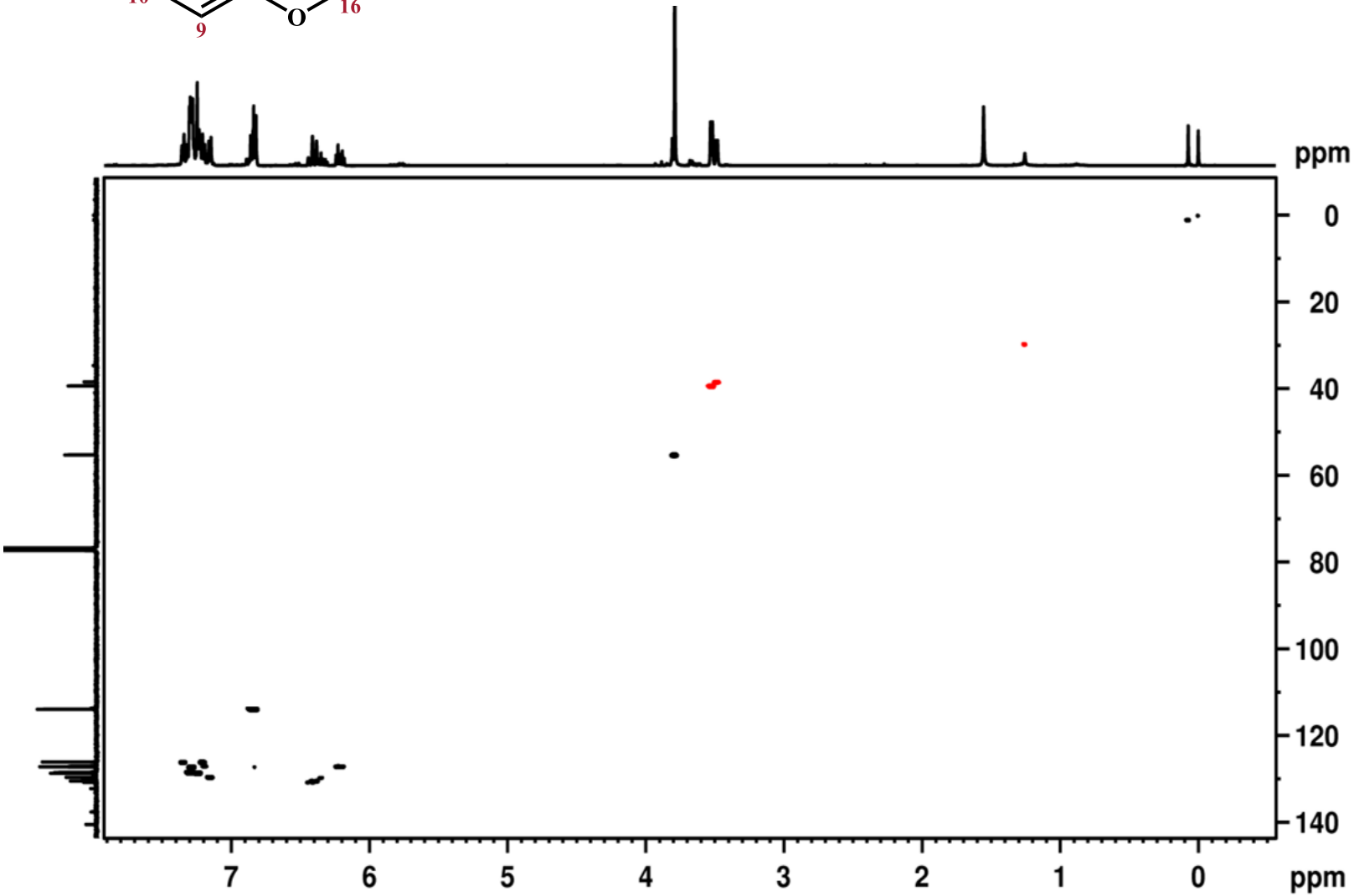
Compound 3j ^{13}C Dept-135^{0} (125 MHz, $CDCl_3$)



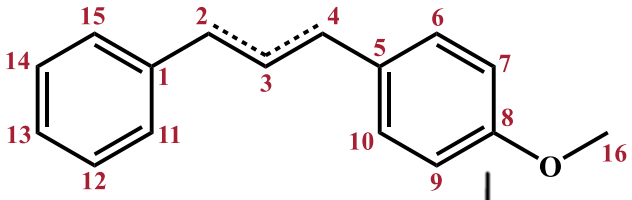


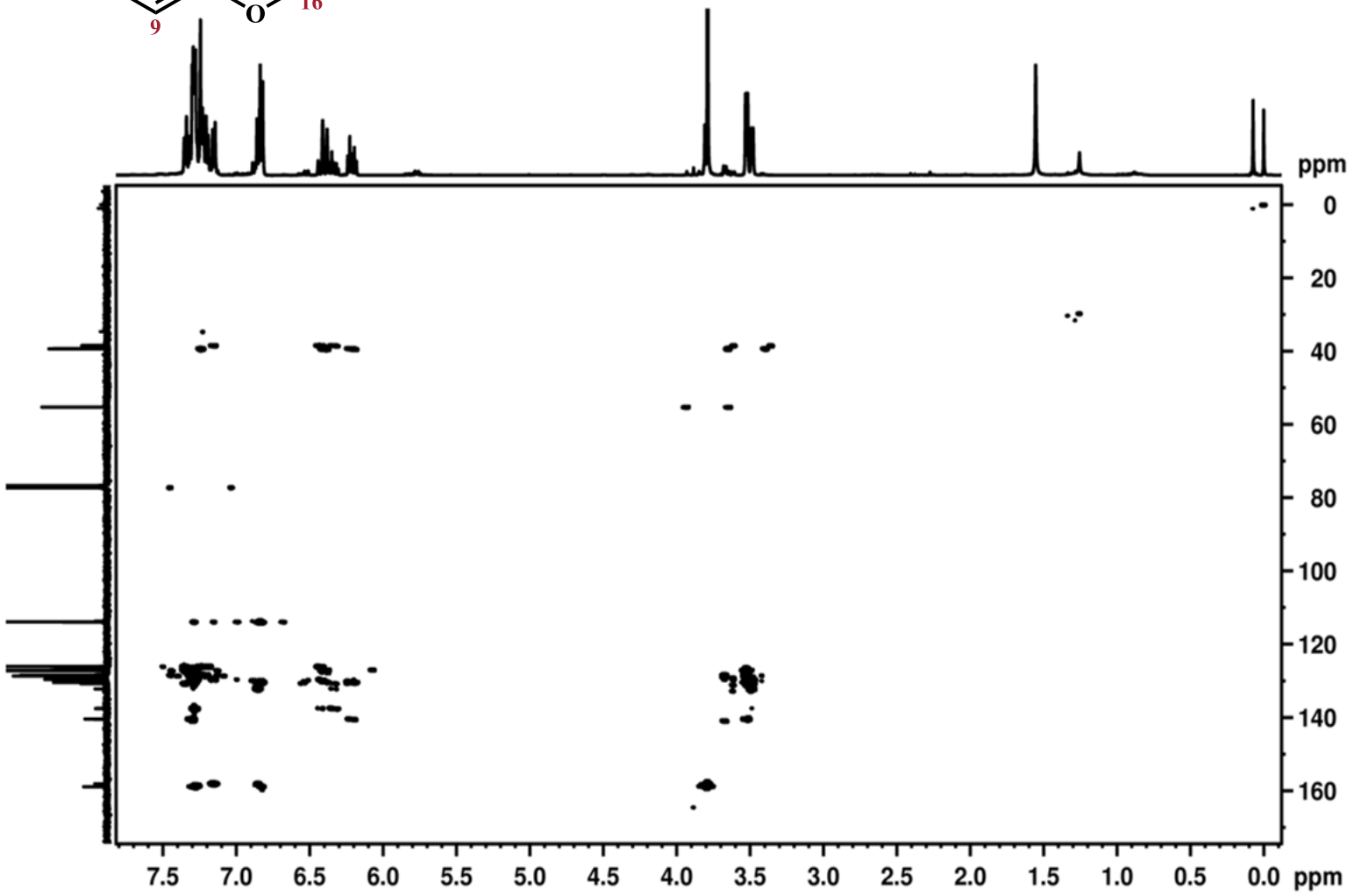
Compound 3j 2D-COSY (500 MHz, $CDCl_3$)



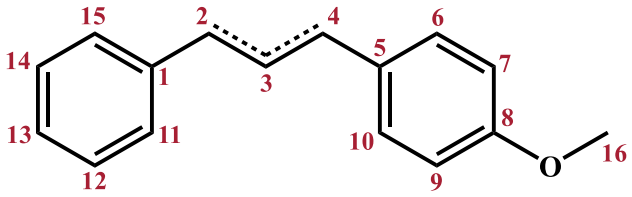


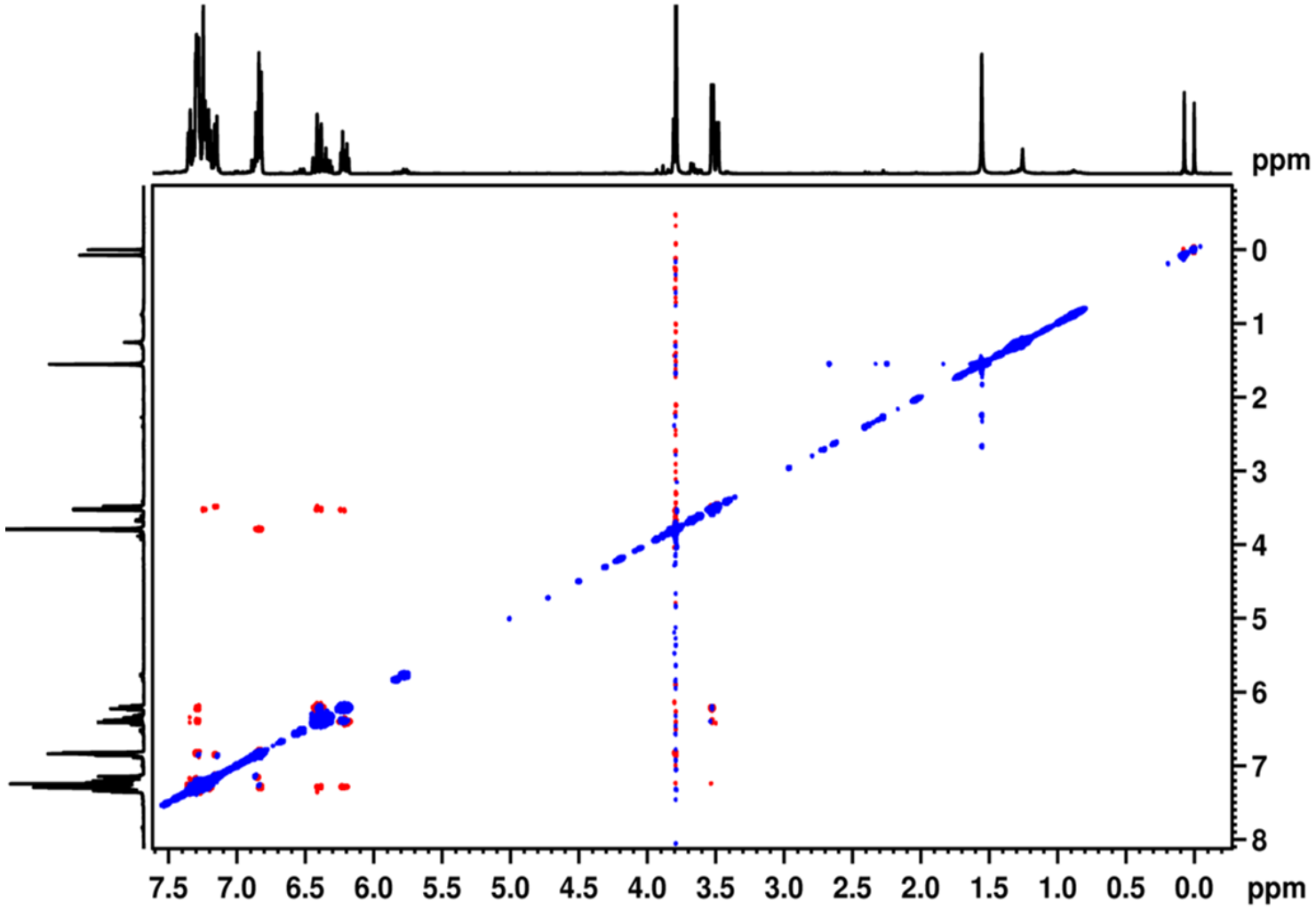
Compound 3j 2D-HSQC (500 MHz, $CDCl_3$)



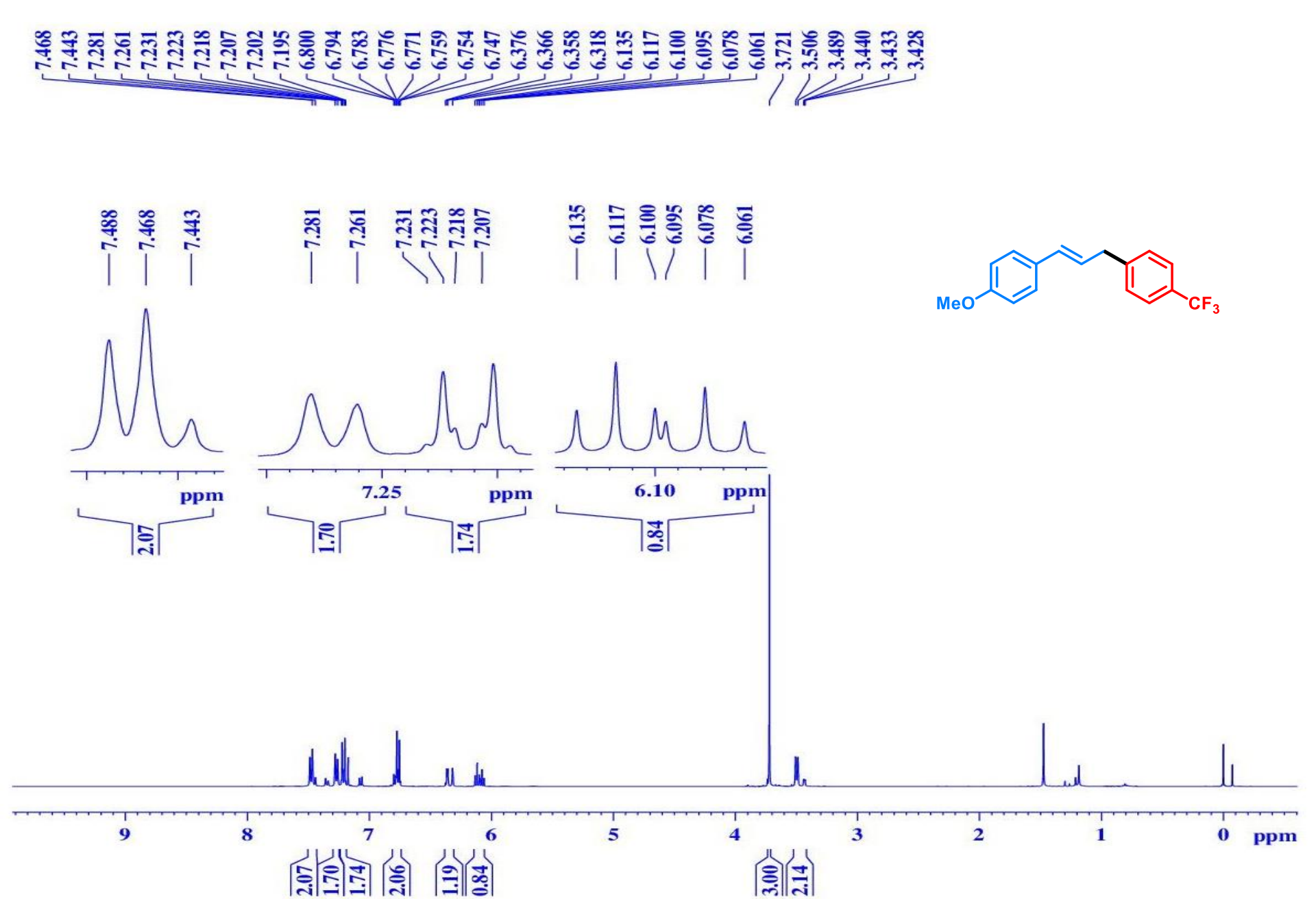


Compound 3j 2D-HMBC (500 MHz, $CDCl_3$)

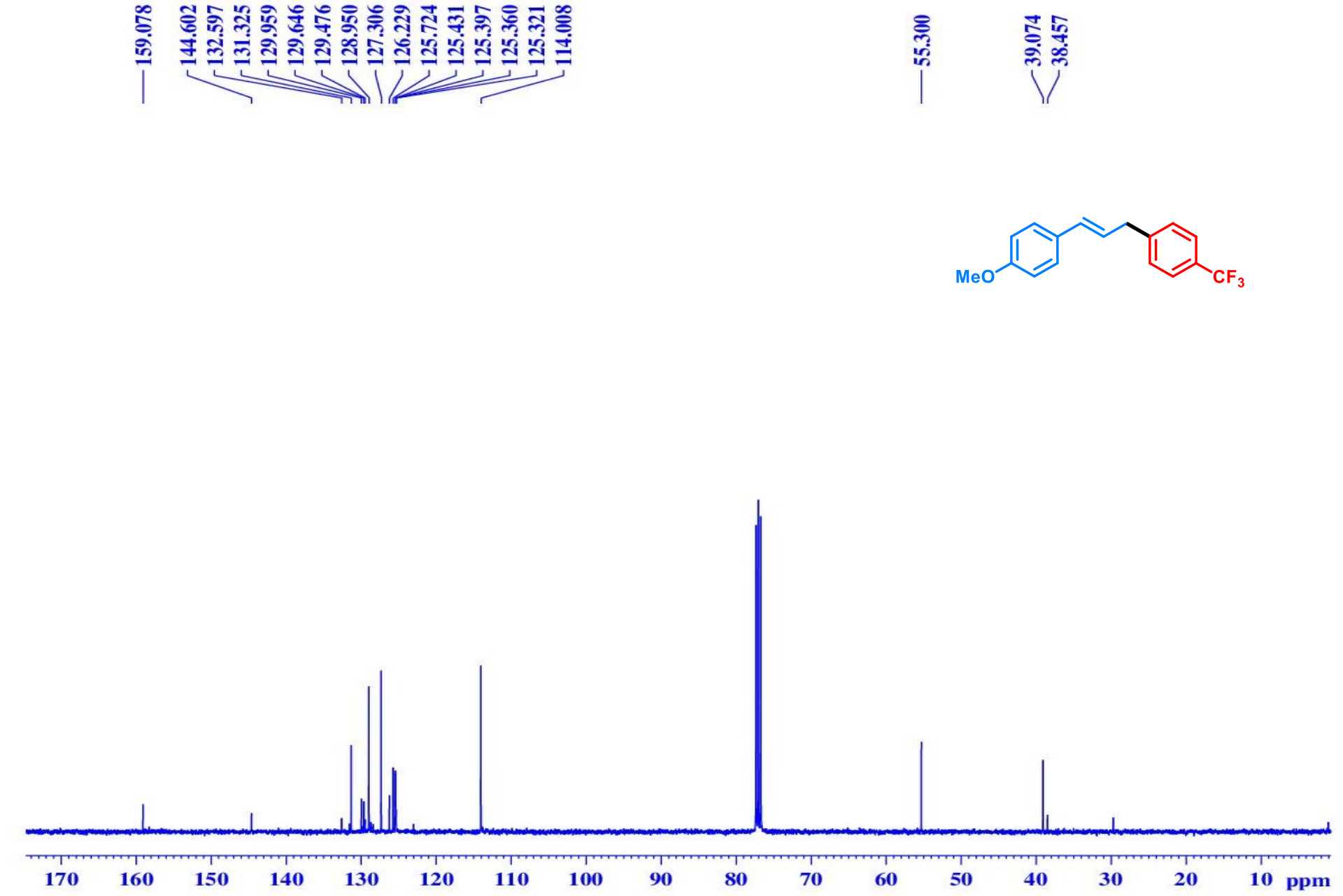




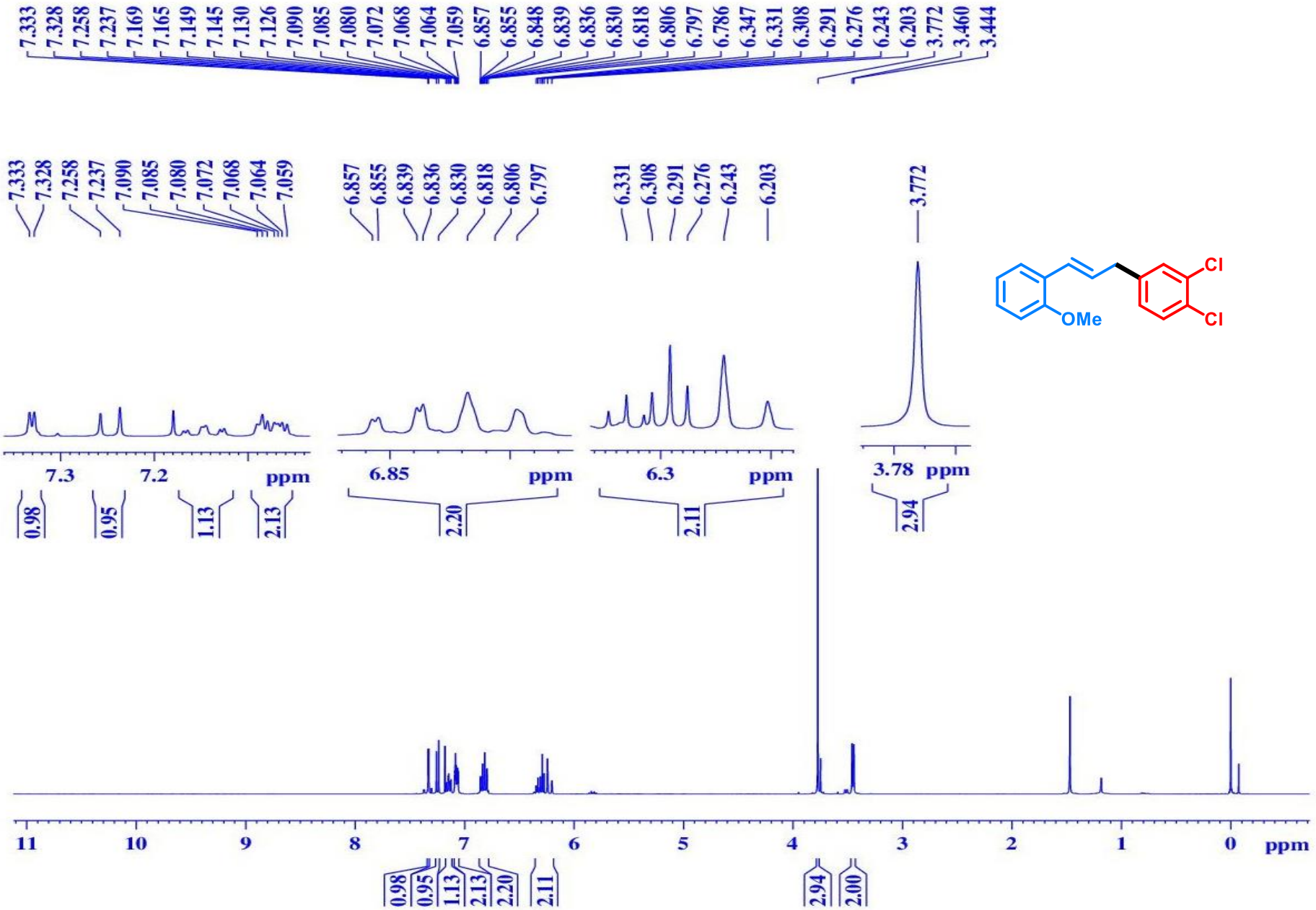
Compound 3j 2D-NOESY (500 MHz, $CDCl_3$)



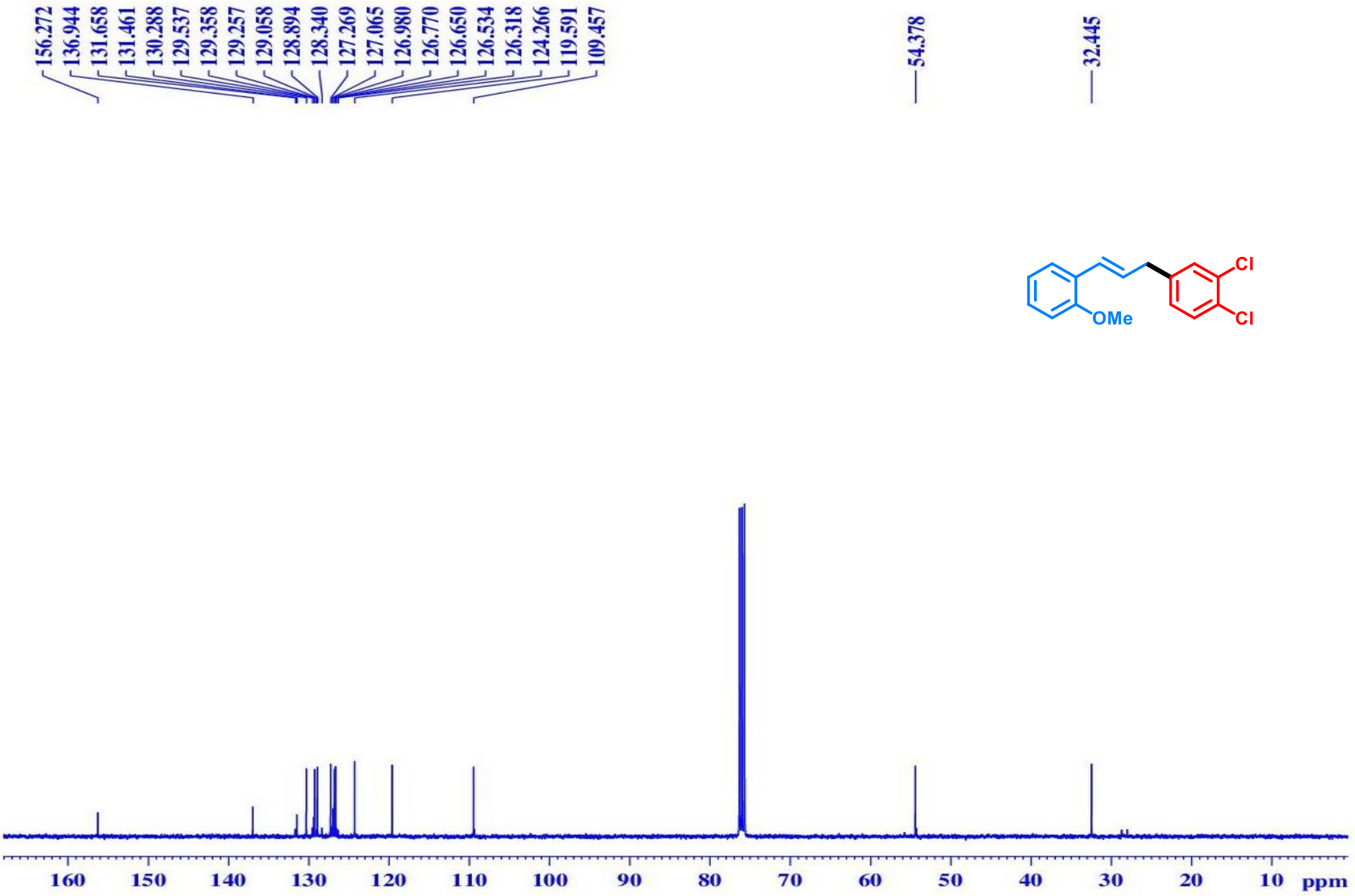
Compound 3k ^{1}H NMR (400 MHz, $CDCl_3$)



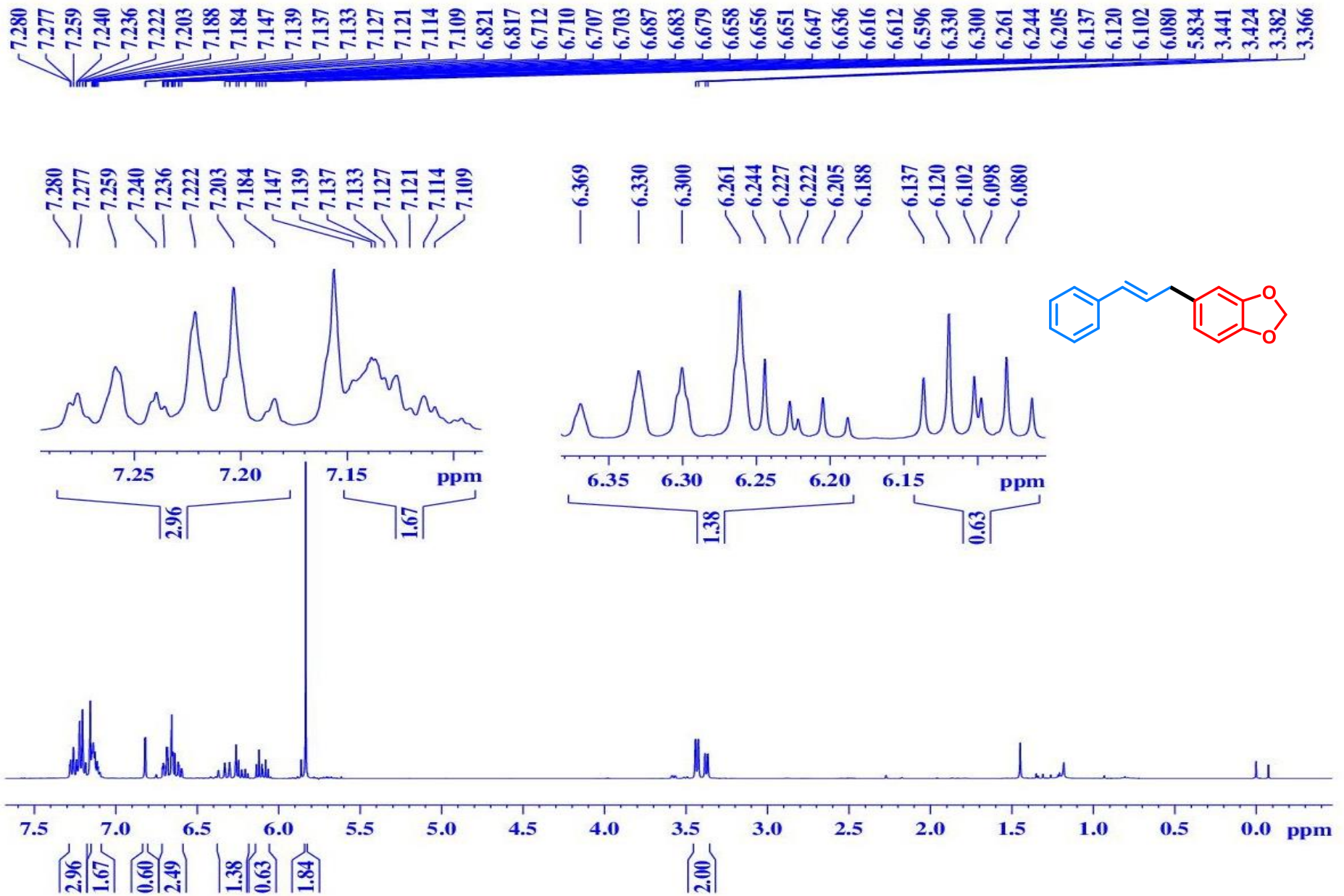
Compound 3k ^{13}C NMR (100 MHz, $CDCl_3$)



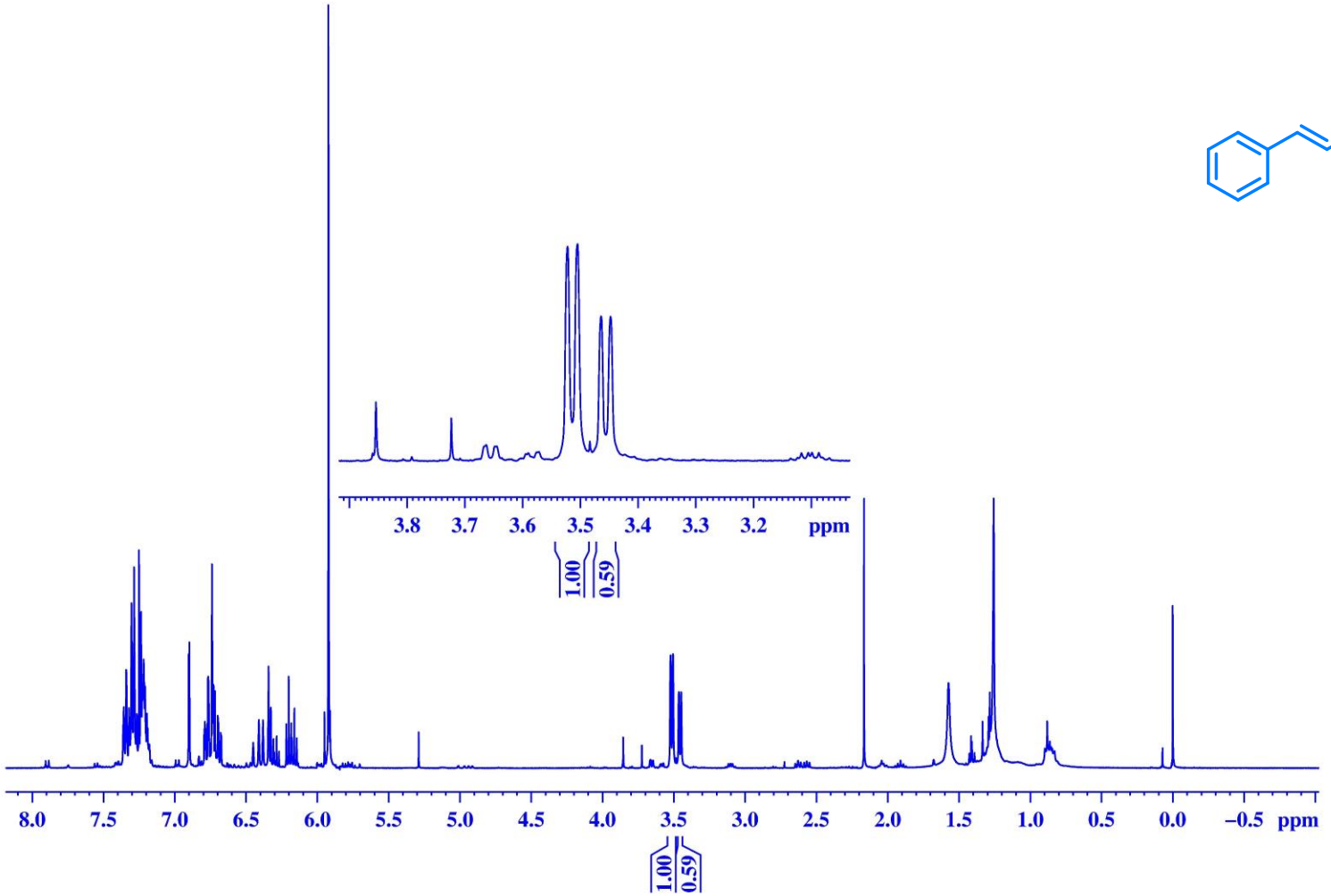
Compound 3l ^{1}H NMR (400 MHz, $CDCl_3$)



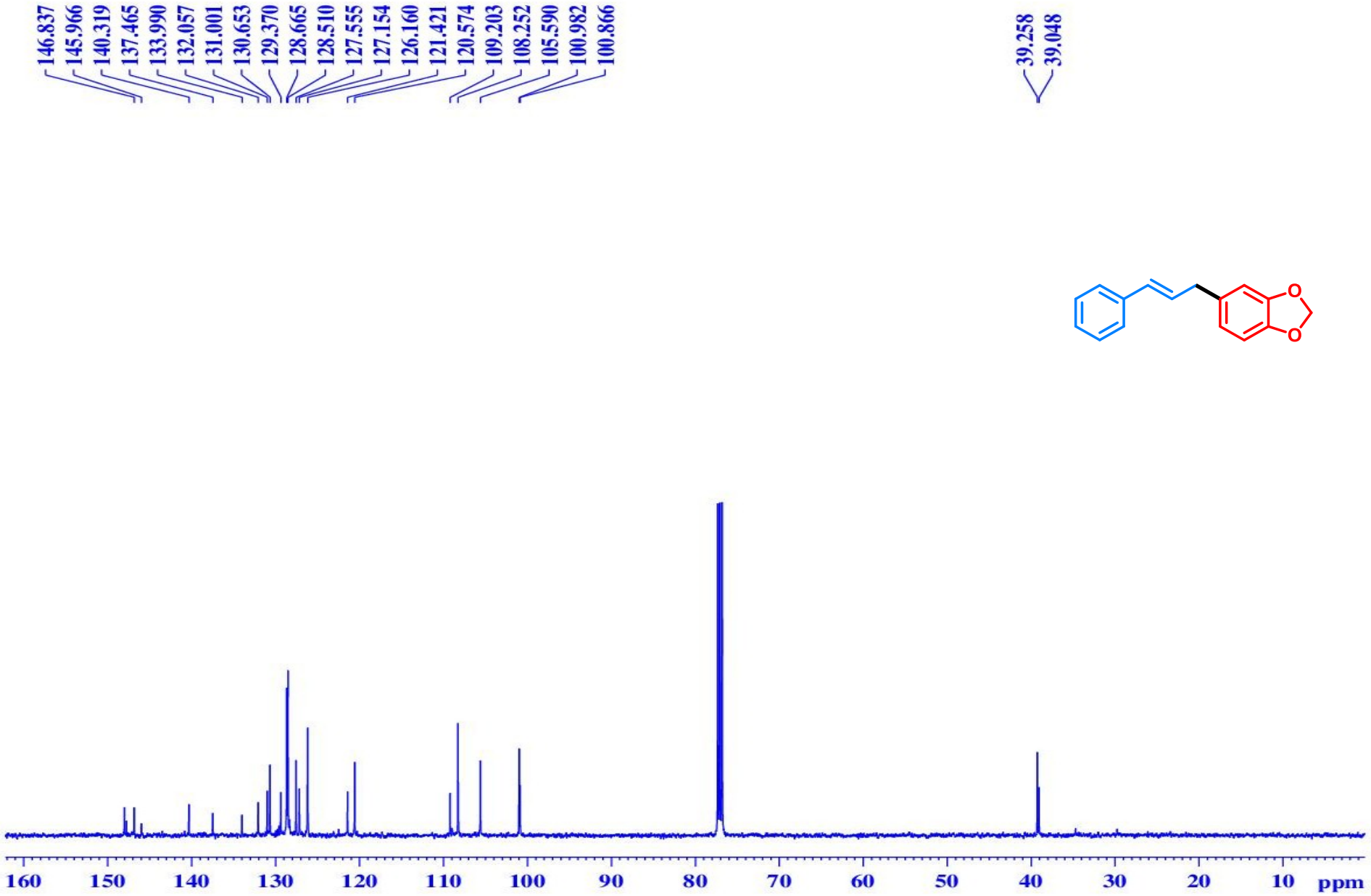
Compound 3l ^{13}C NMR (100 MHz, $CDCl_3$)



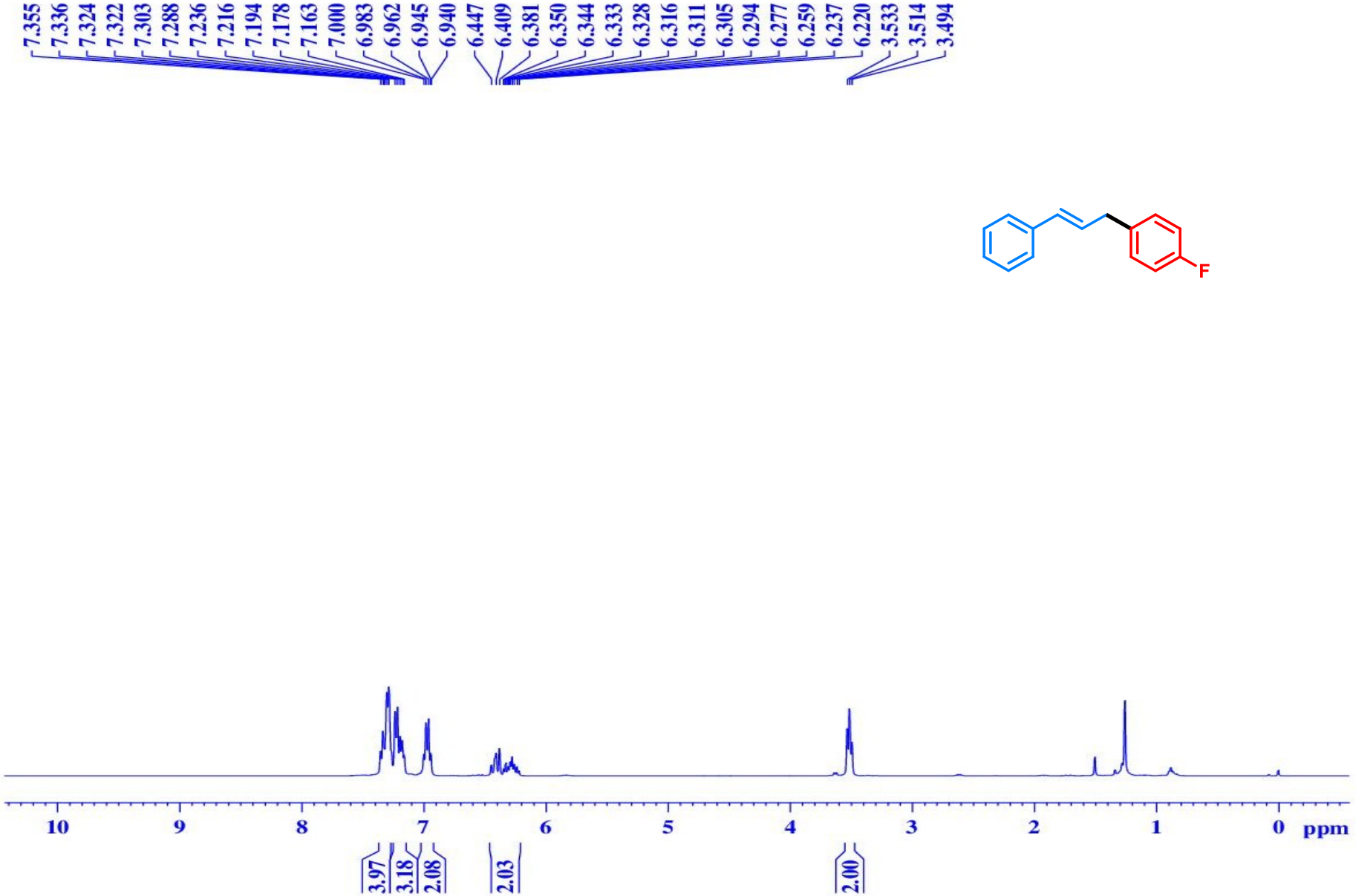
Compound 3m ^{1}H NMR (400 MHz, $CDCl_3$)



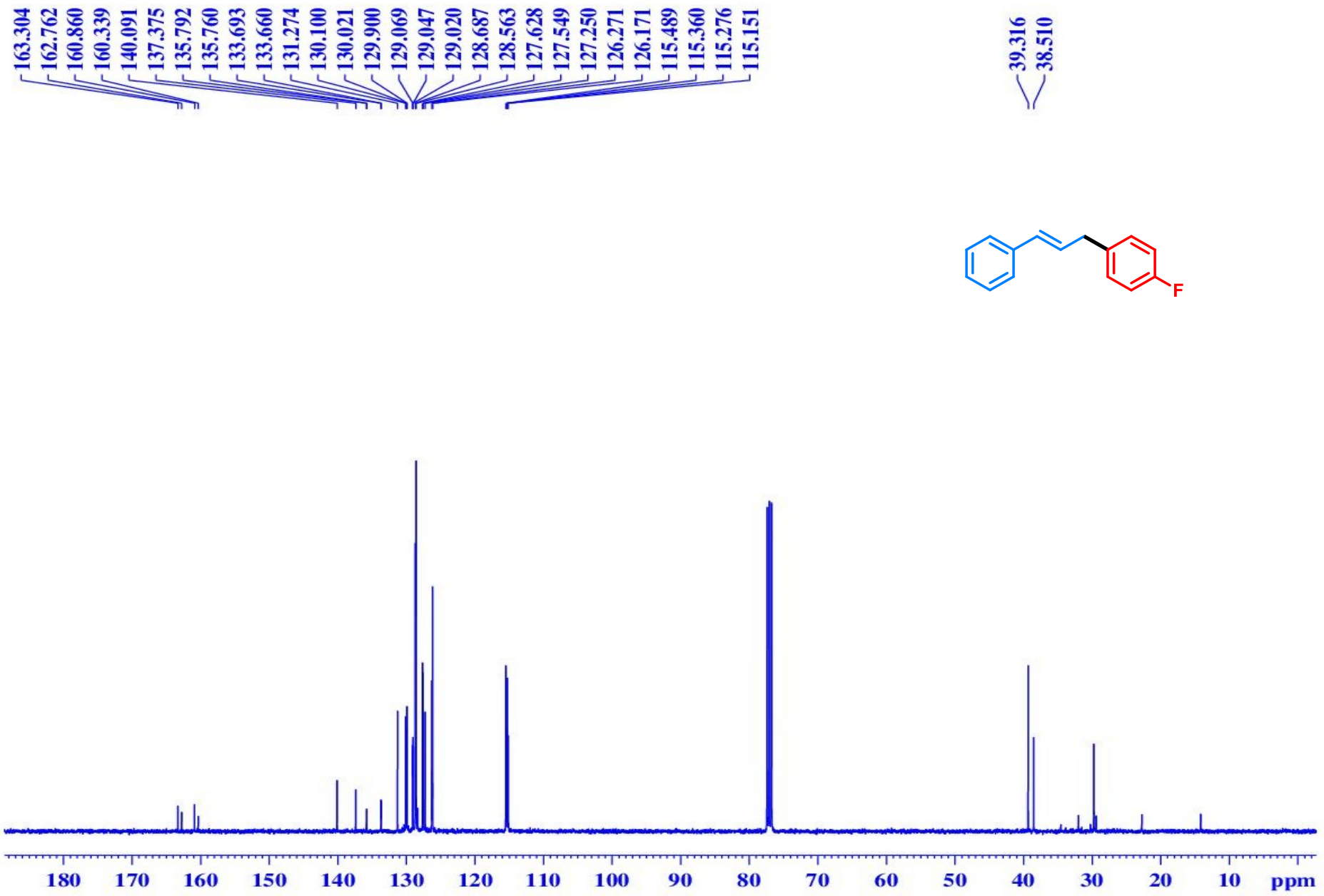
Compound 3m (crude) ^{1}H NMR (400 MHz, $CDCl_3$)



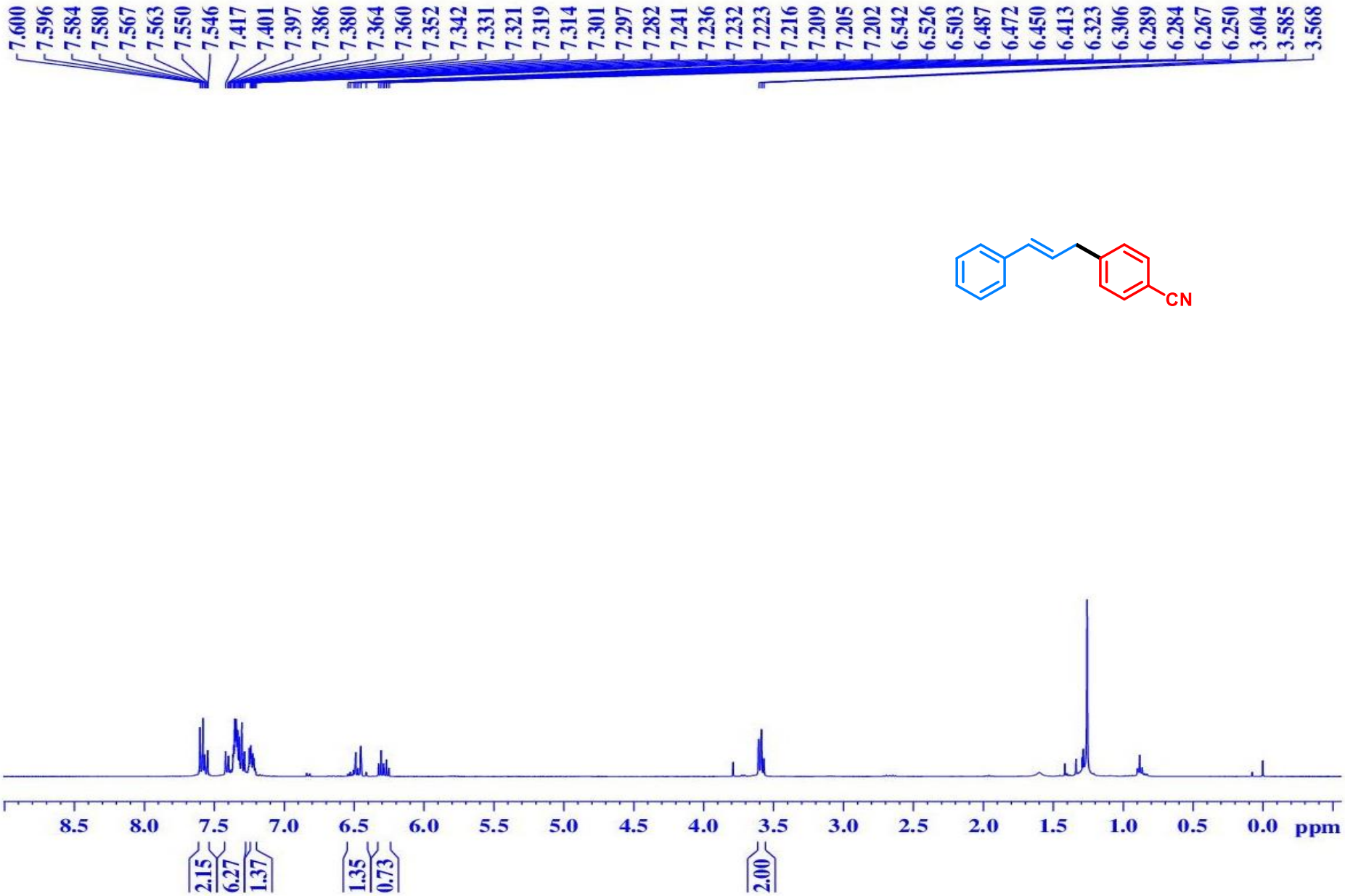
Compound 3m ^{13}C NMR (100 MHz, $CDCl_3$)



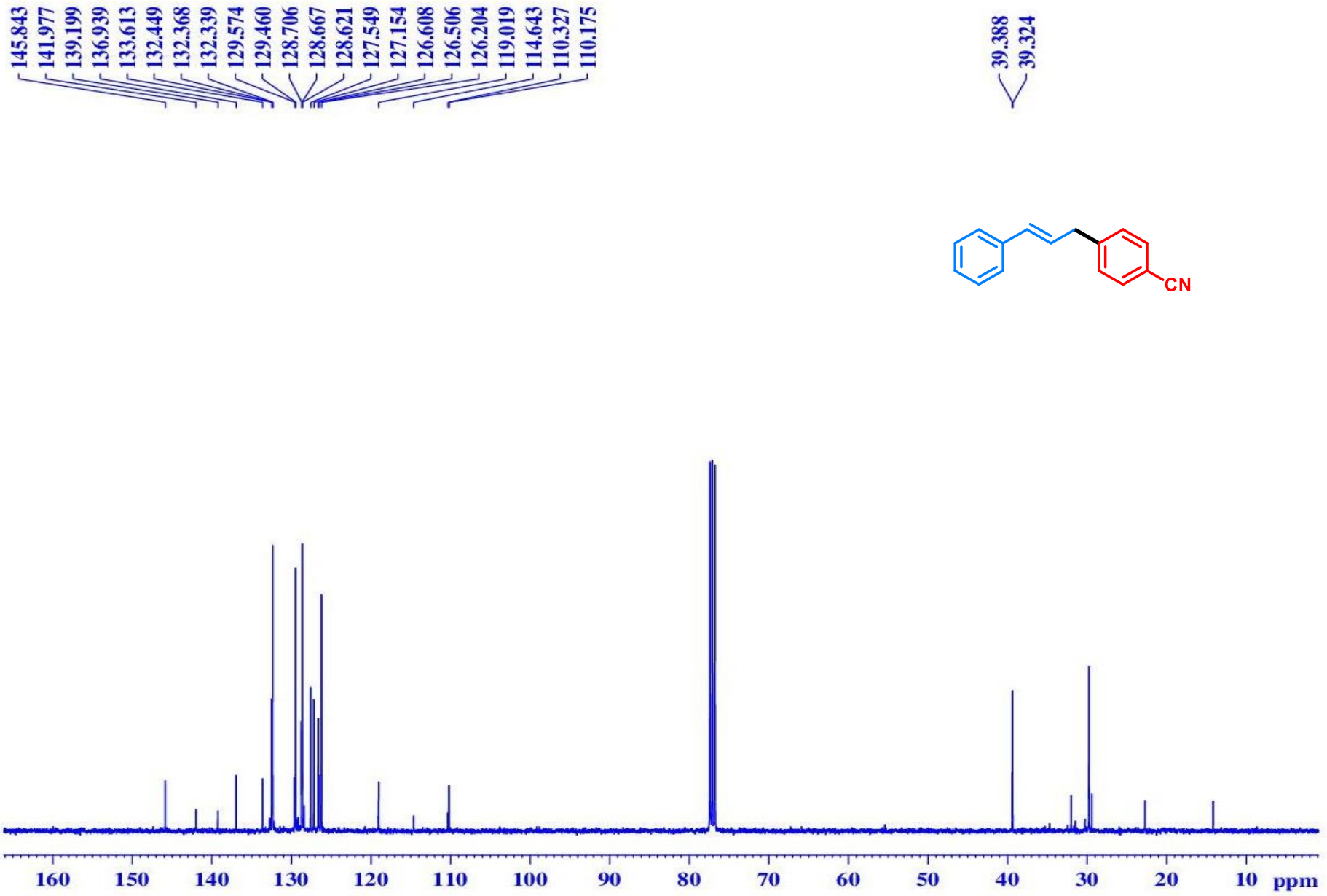
Compound 3n ^{1}H NMR (400 MHz, $CDCl_3$)



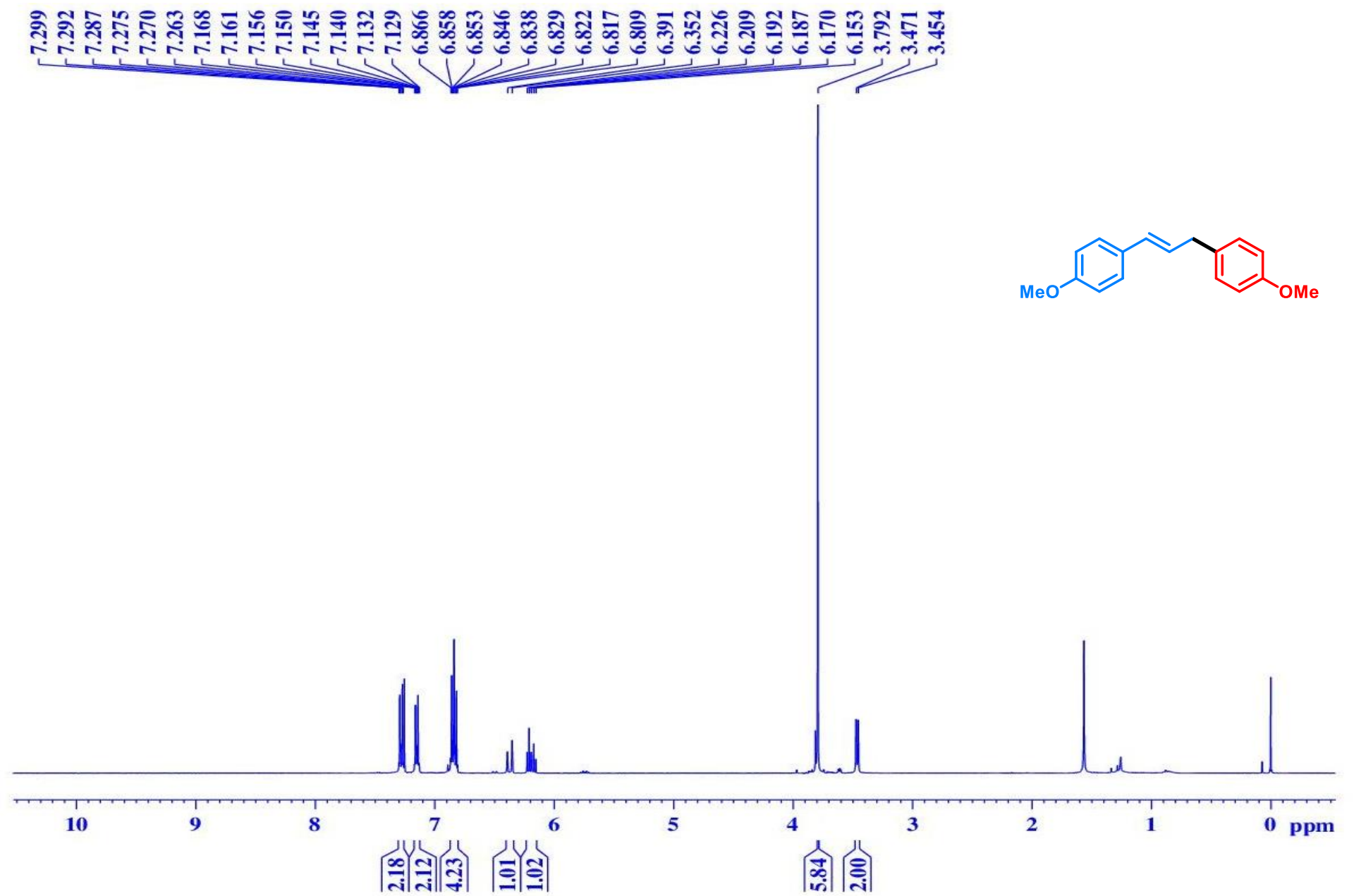
Compound 3n ^{13}C NMR (100 MHz, $CDCl_3$)



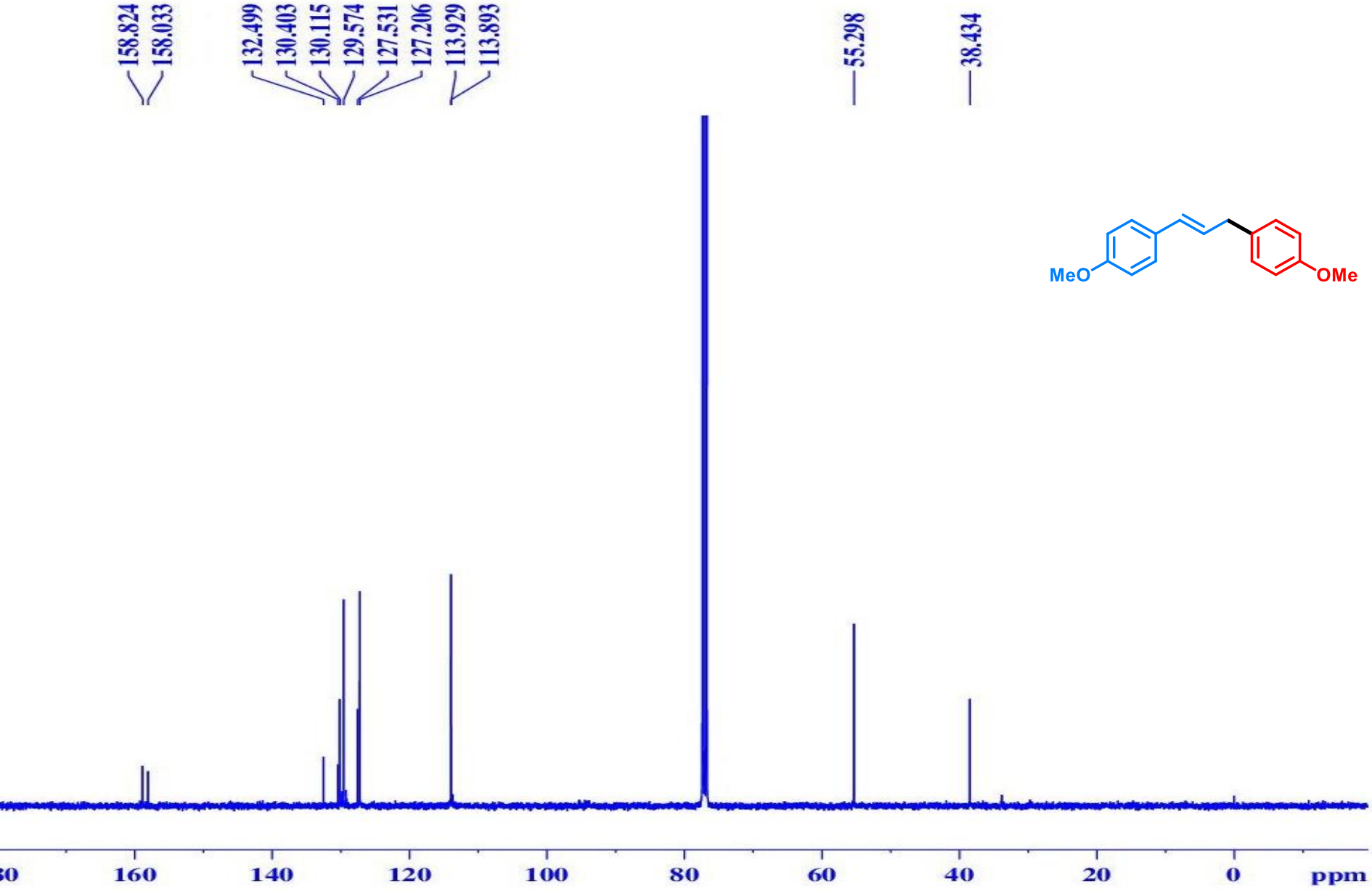
Compound 3o ^{1}H NMR (400 MHz, $CDCl_3$)



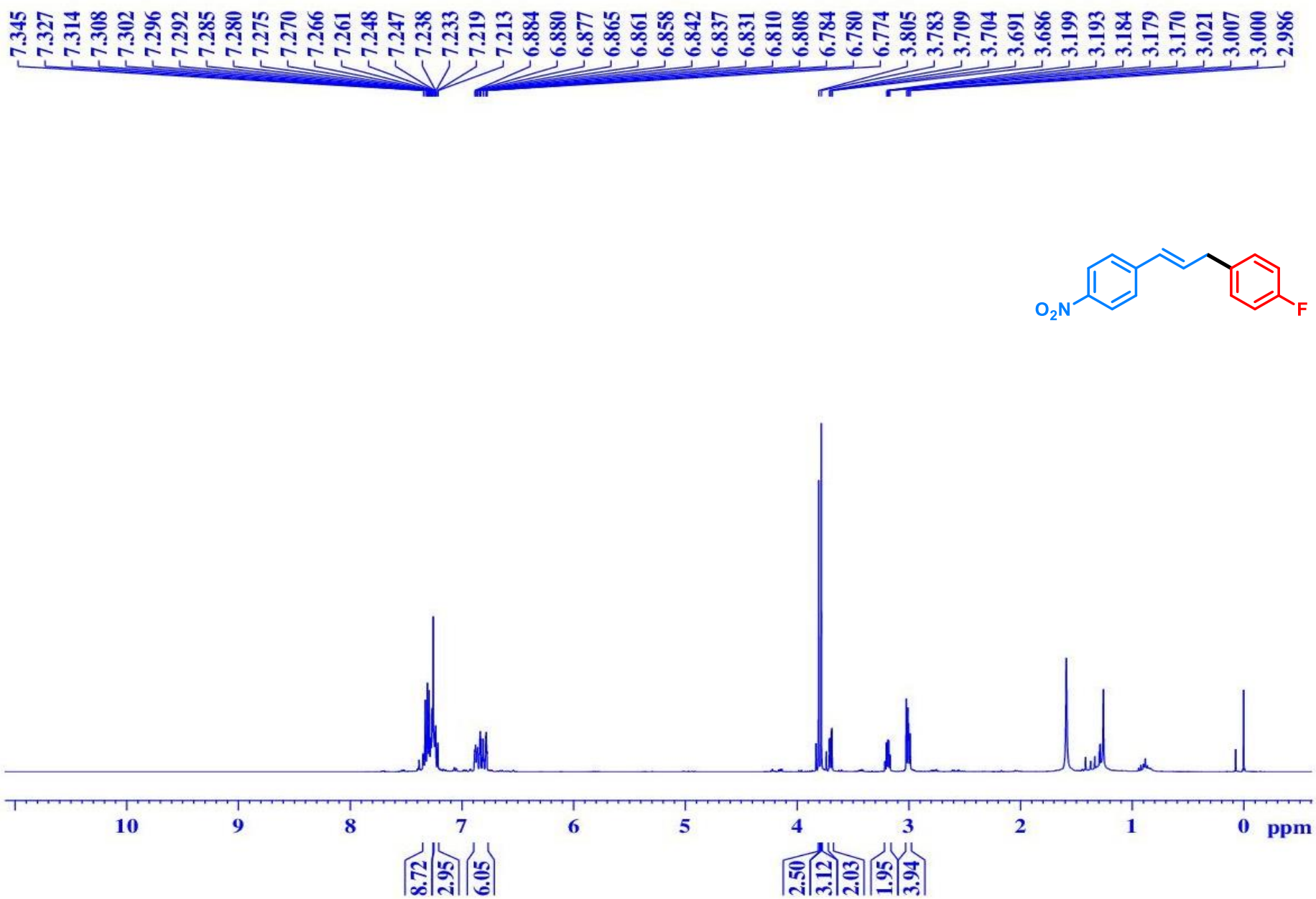
Compound 3o ^{13}C NMR (100 MHz, $CDCl_3$)



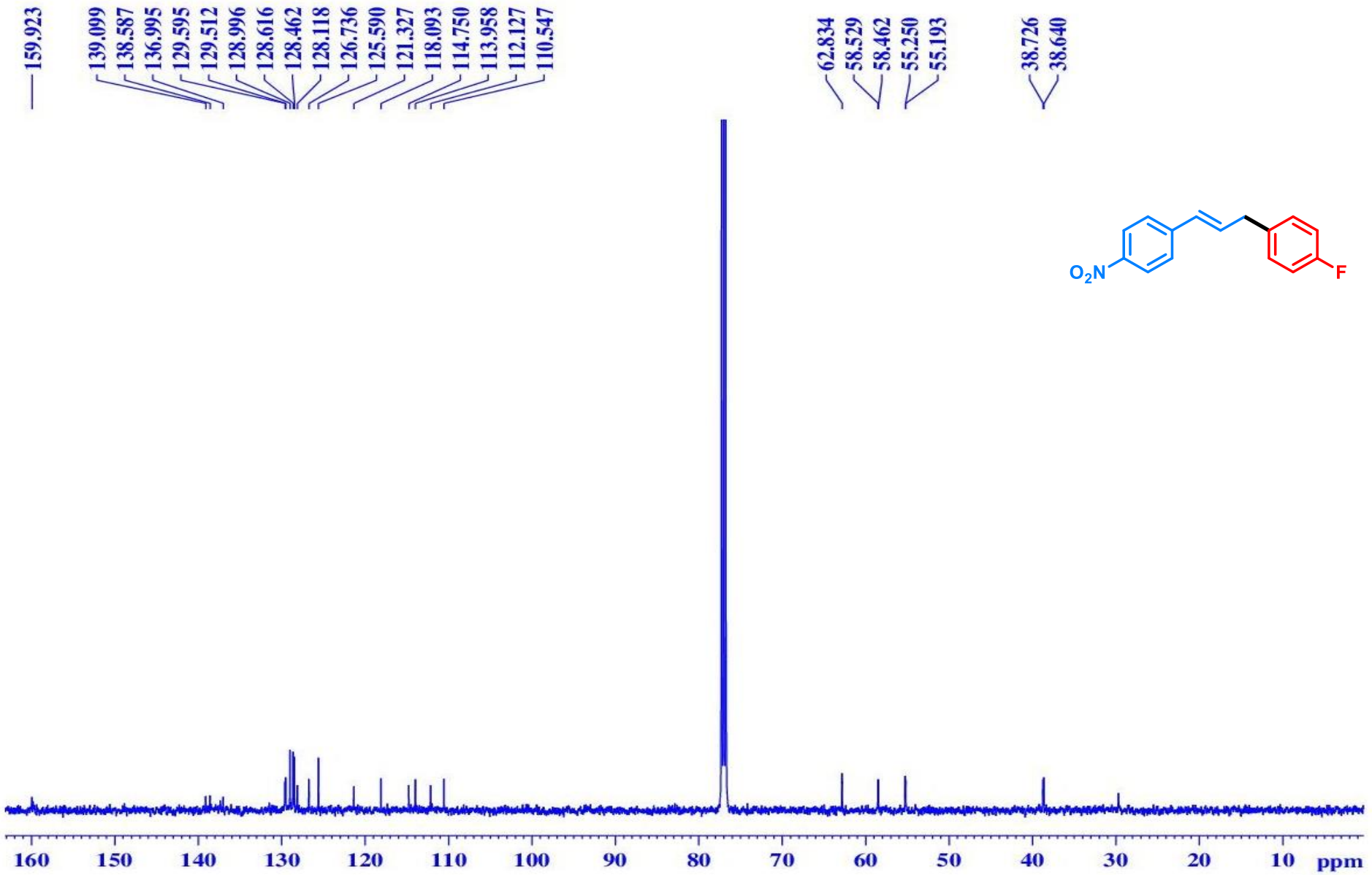
Compound 3p ^{1}H NMR (400 MHz, $CDCl_3$)



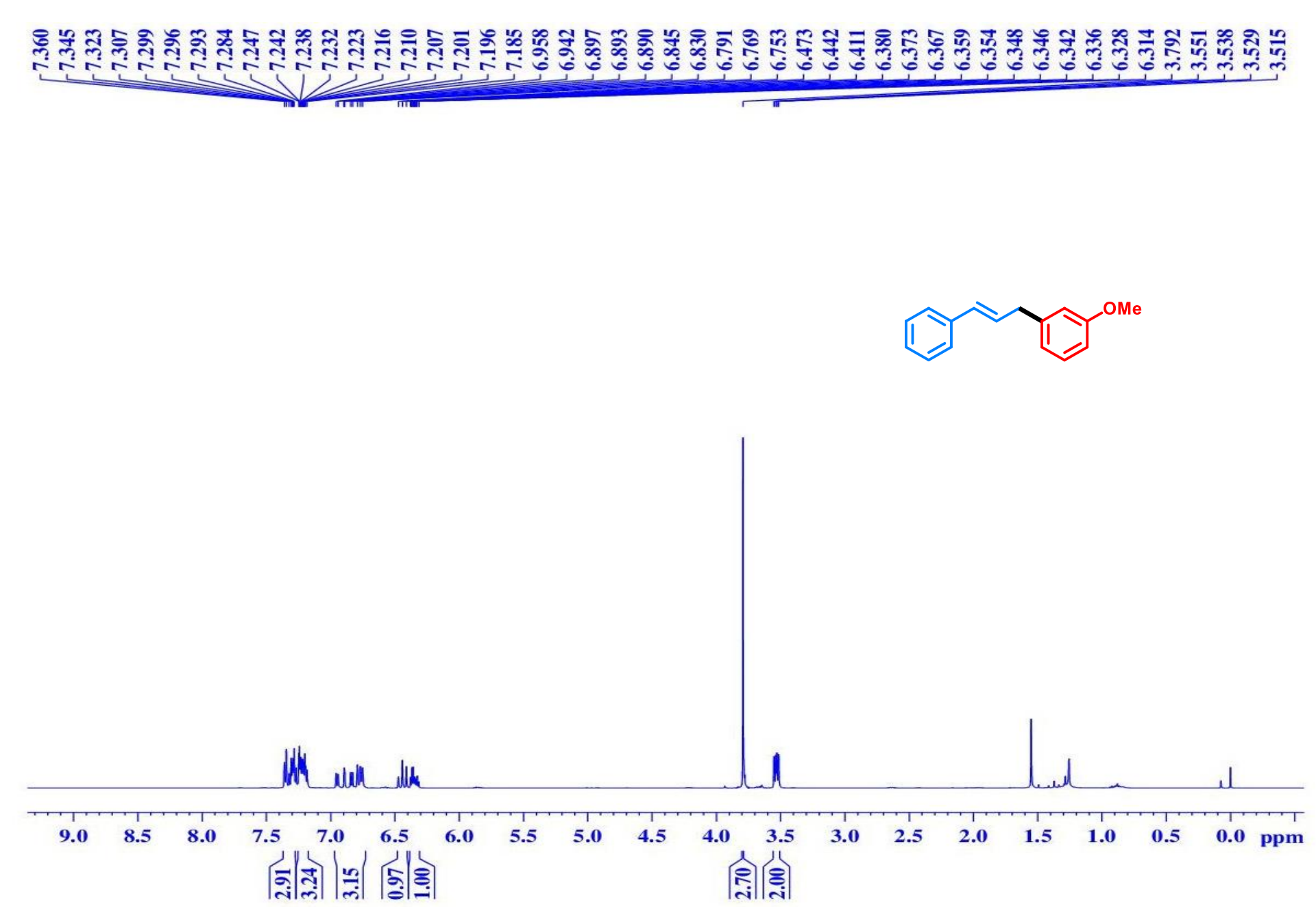
Compound 3p ^{13}C NMR (100 MHz, $CDCl_3$)



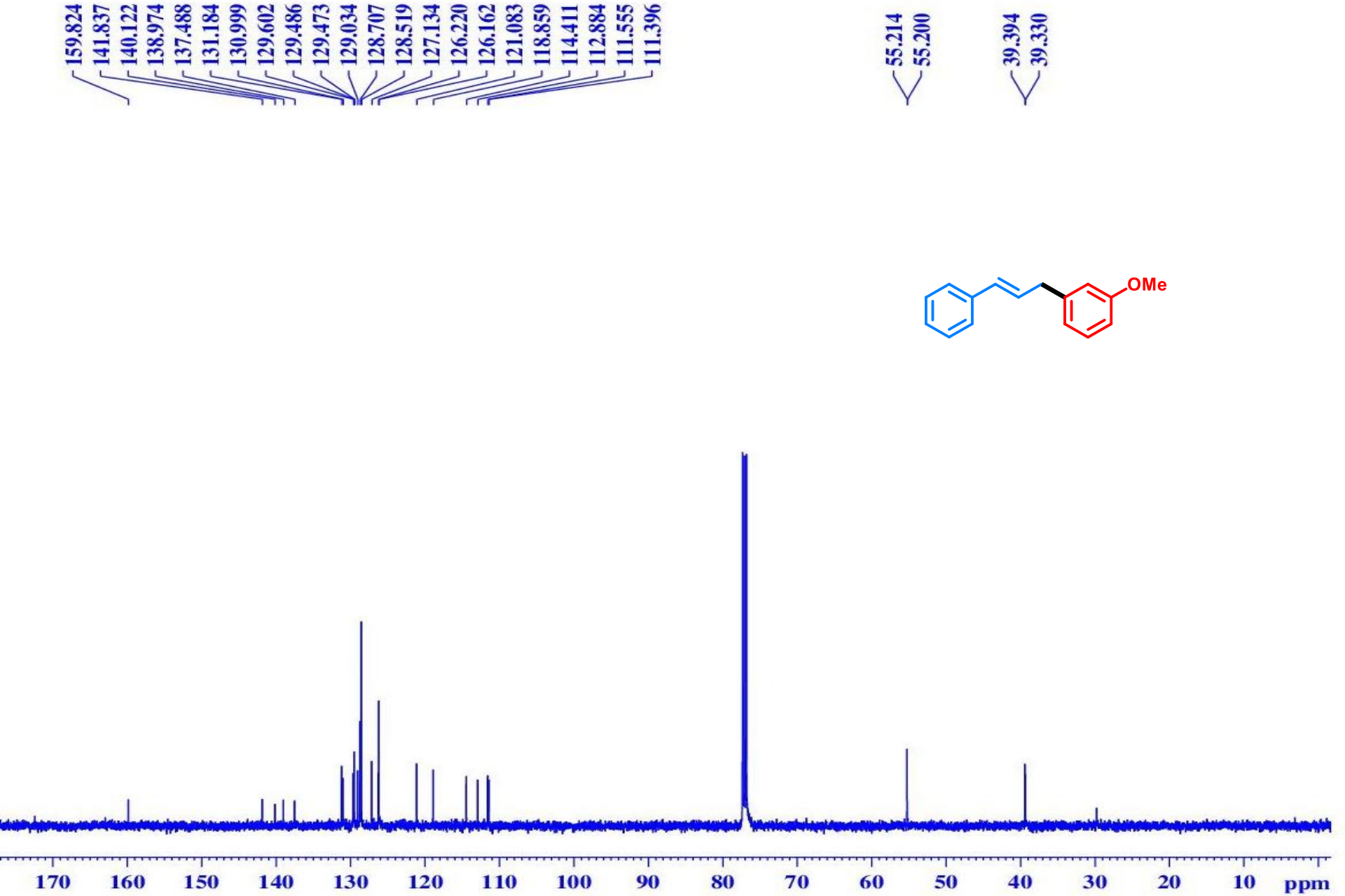
Compound 3q ^{1}H NMR (400 MHz, $CDCl_3$)



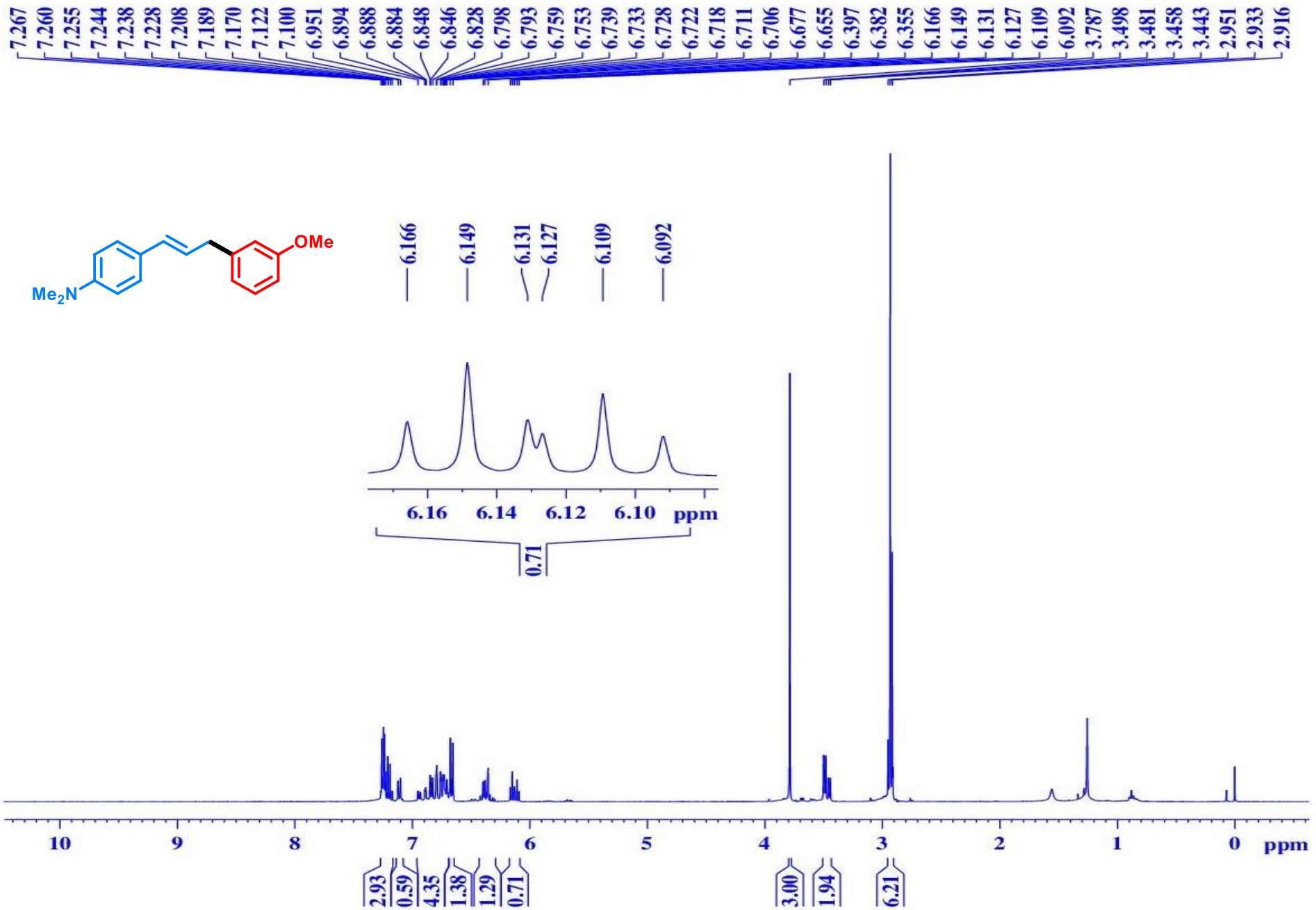
Compound 3q ^{13}C NMR (100 MHz, $CDCl_3$)



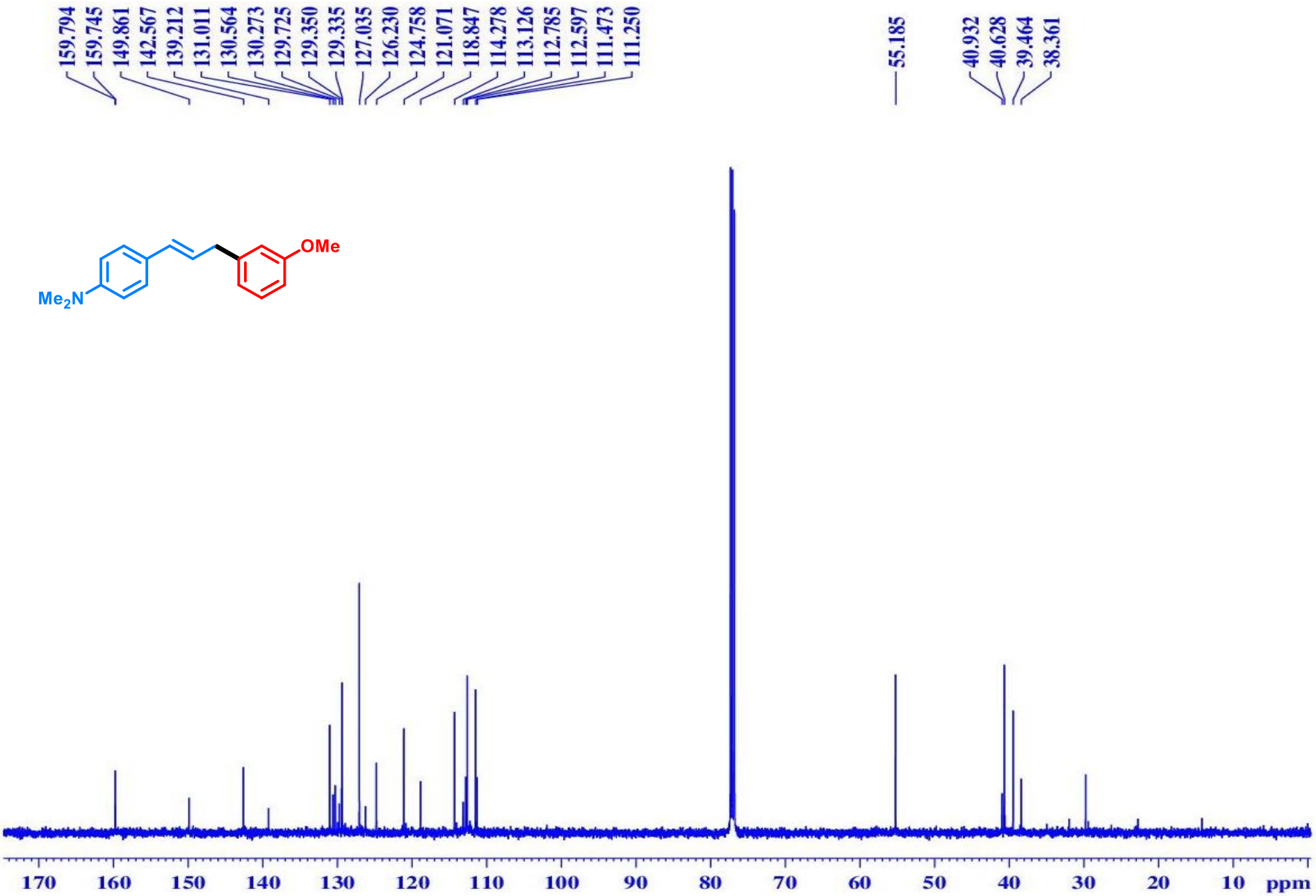
Compound 3r ^{1}H NMR (400 MHz, $CDCl_3$)



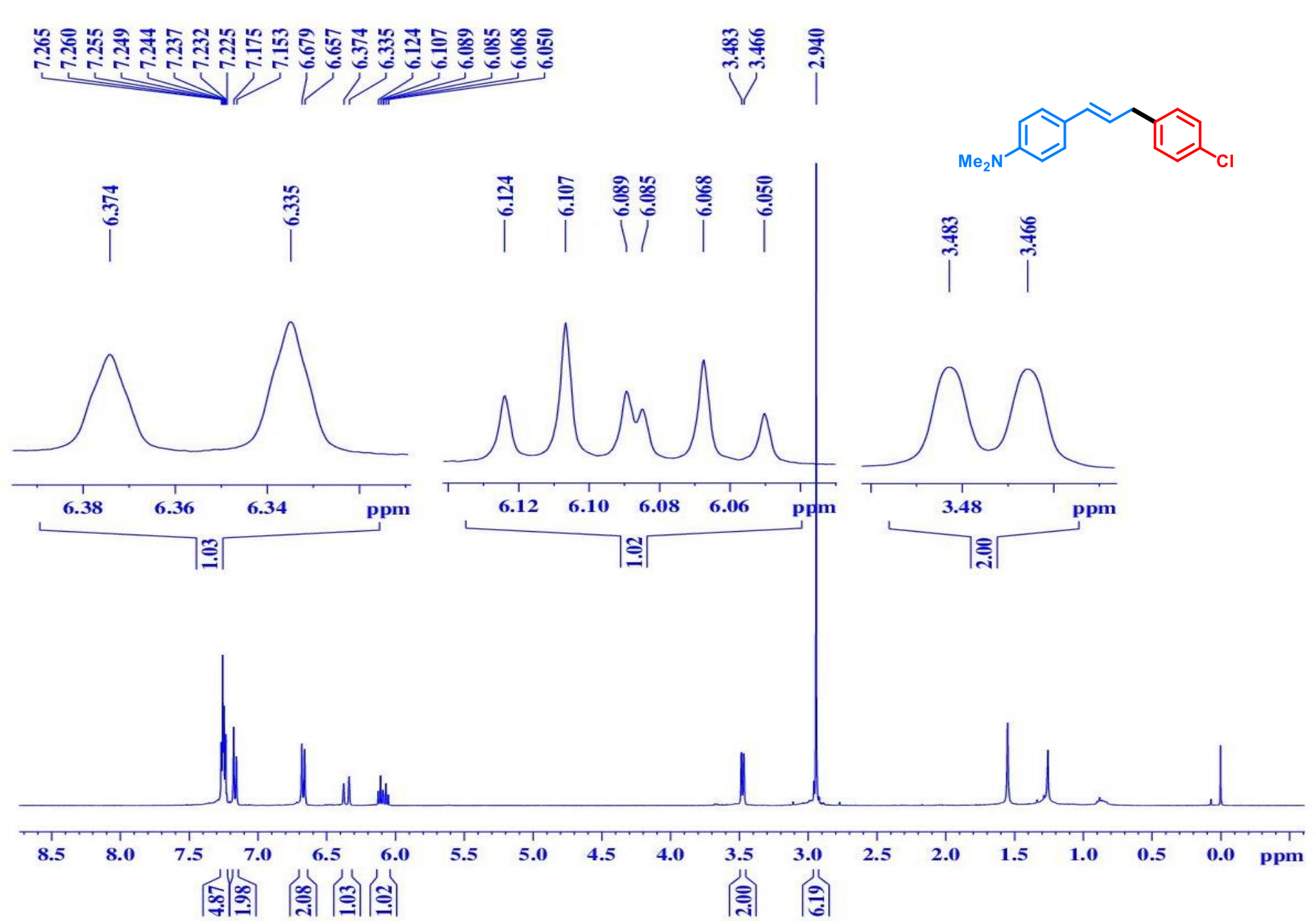
Compound 3r ^{13}C NMR (100 MHz, $CDCl_3$)



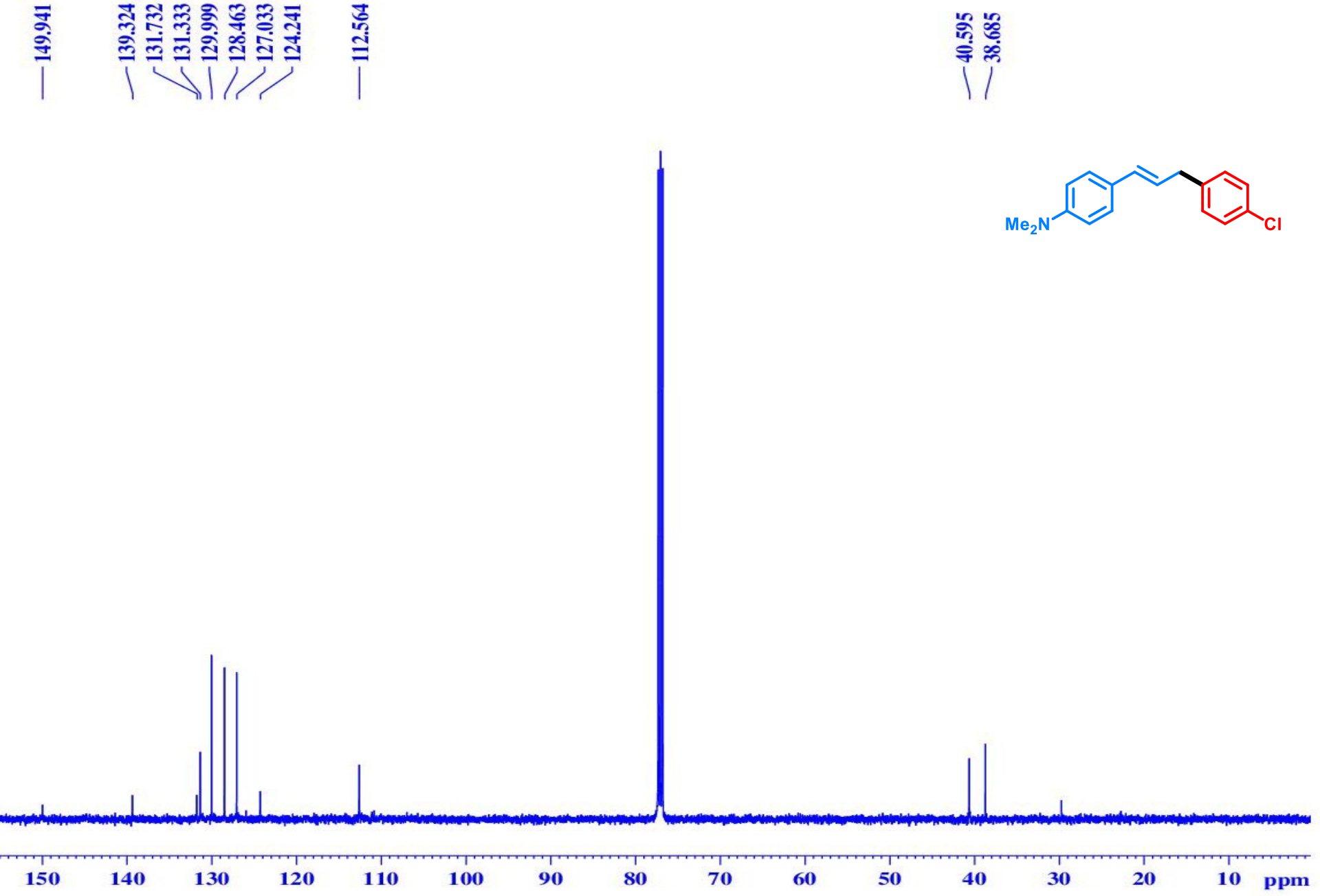
Compound 3s ^{1}H NMR (400 MHz, $CDCl_3$)



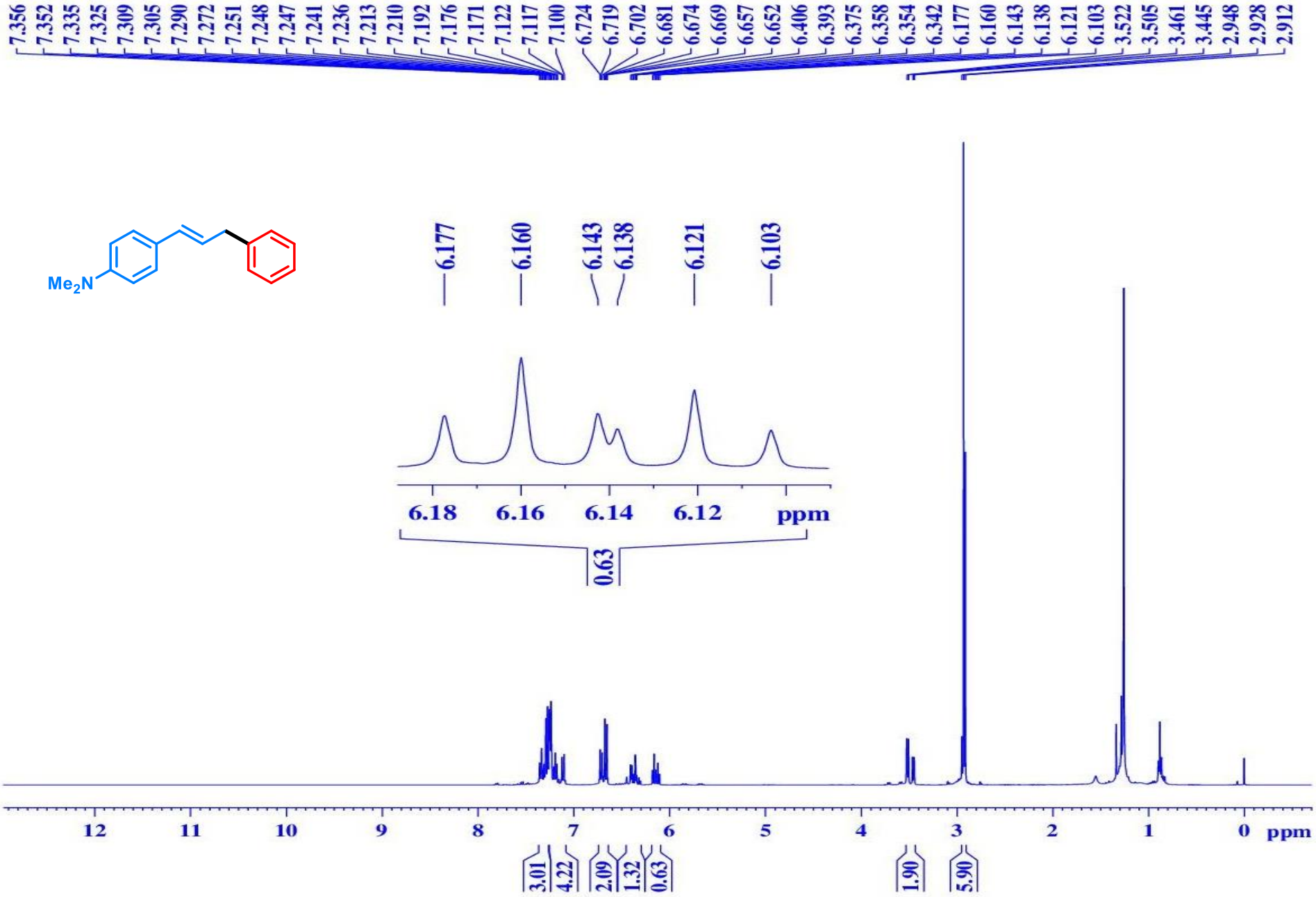
Compound 3s ^{13}C NMR (100 MHz, $CDCl_3$)



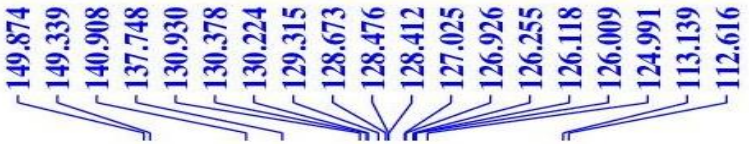
Compound 3t ^{1}H NMR (400 MHz, $CDCl_3$)

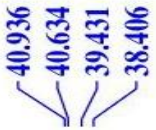


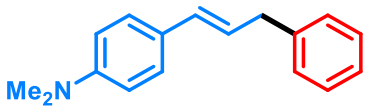
Compound 3t ^{13}C NMR (100 MHz, $CDCl_3$)

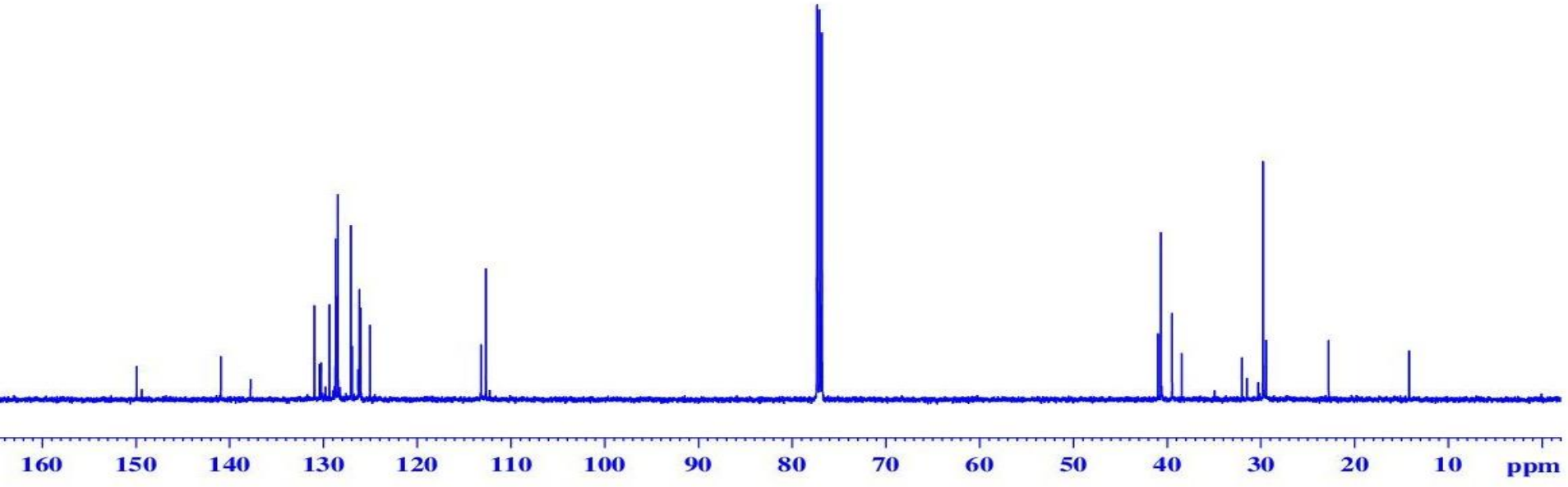


Compound 3u ^{1}H NMR (400 MHz, $CDCl_3$)

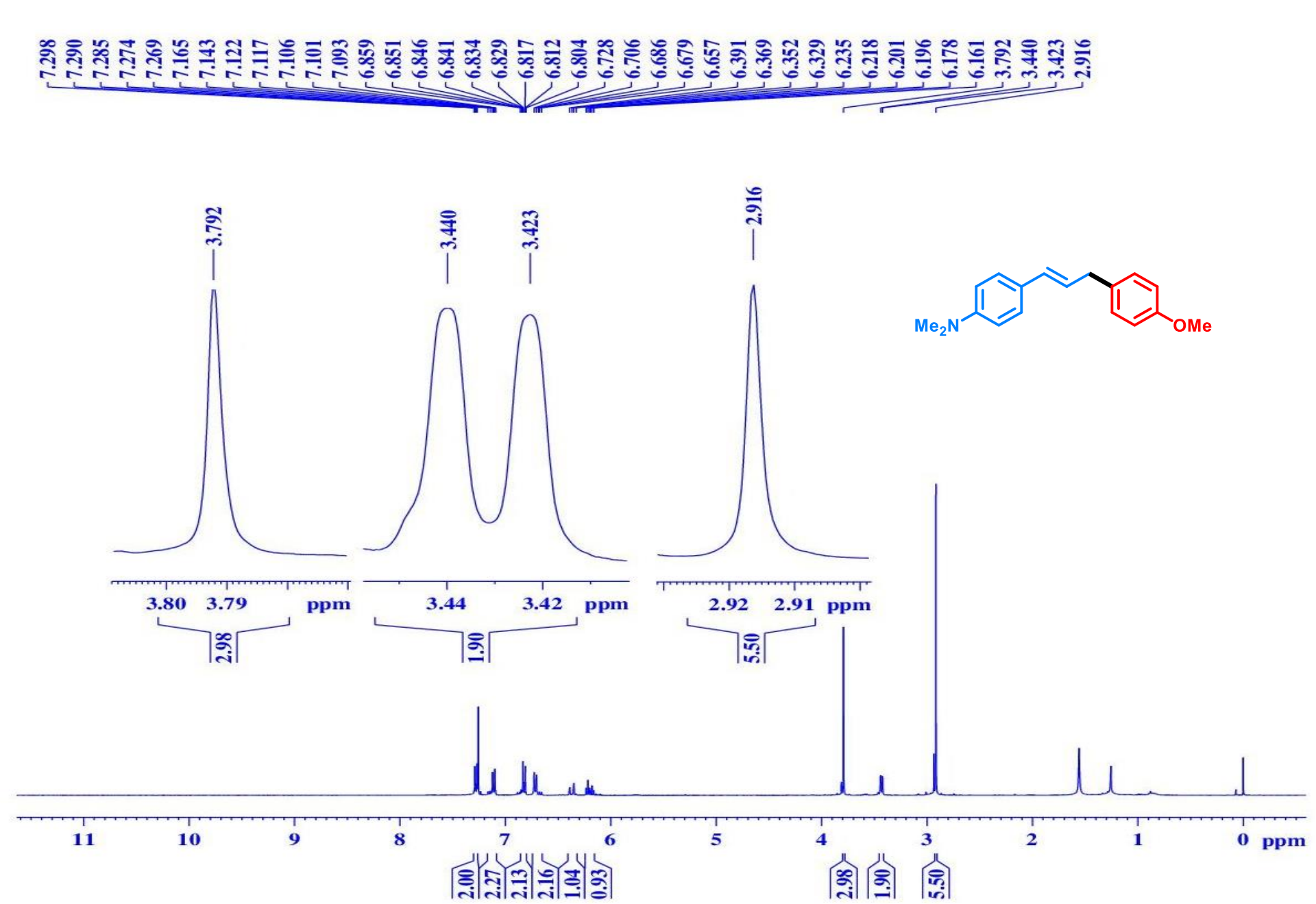




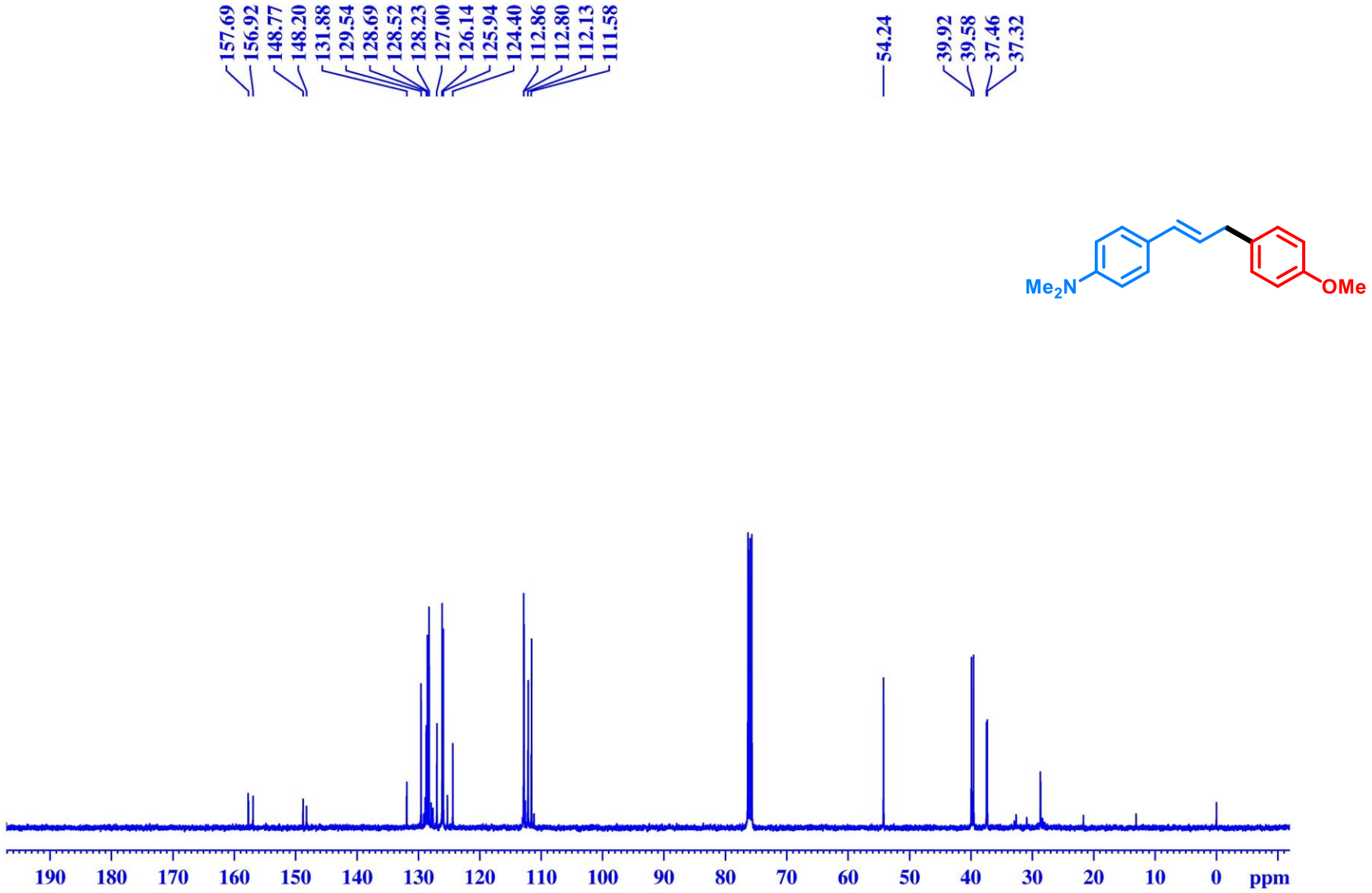




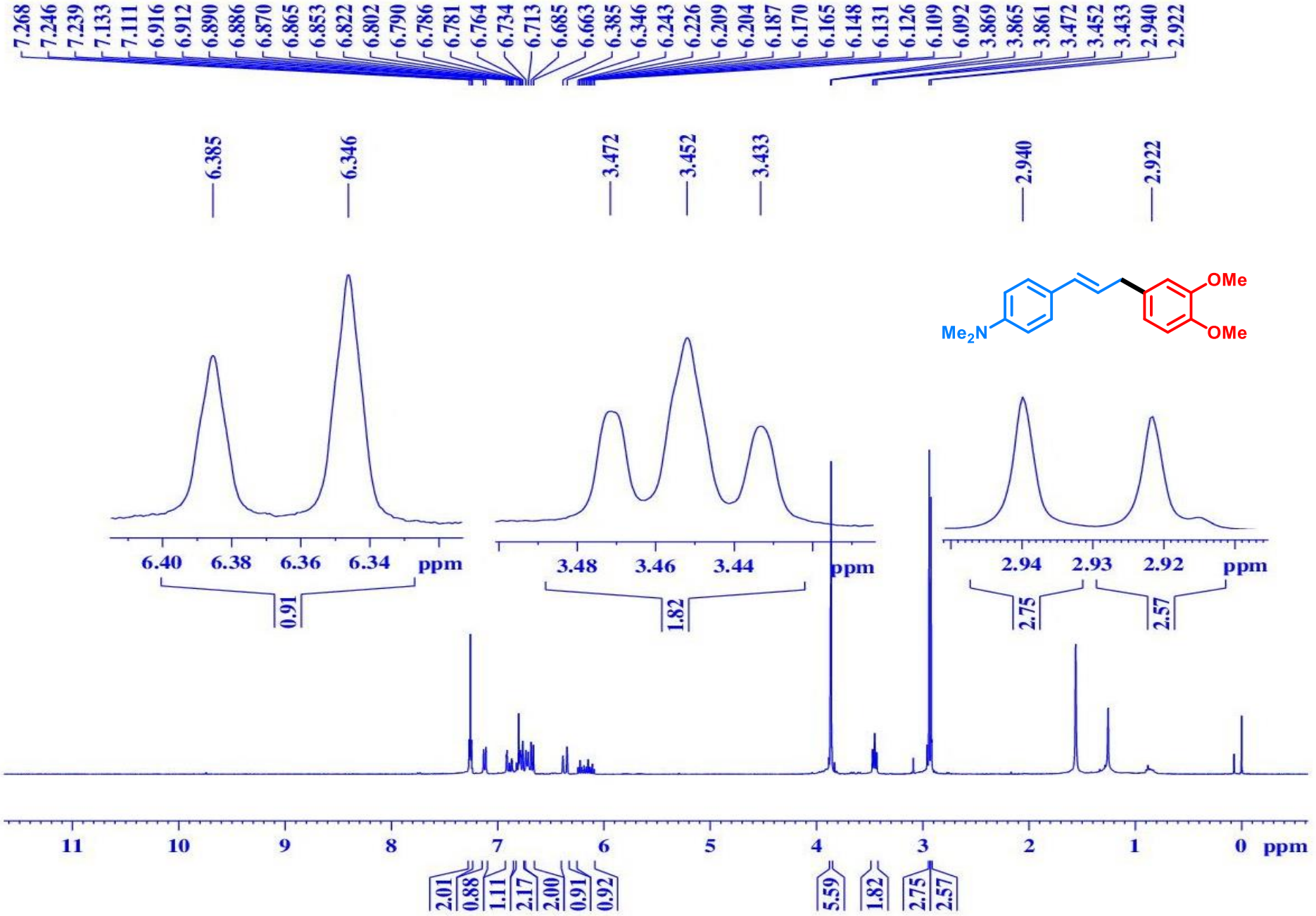
Compound 3u ^{13}C NMR (100 MHz, $CDCl_3$)



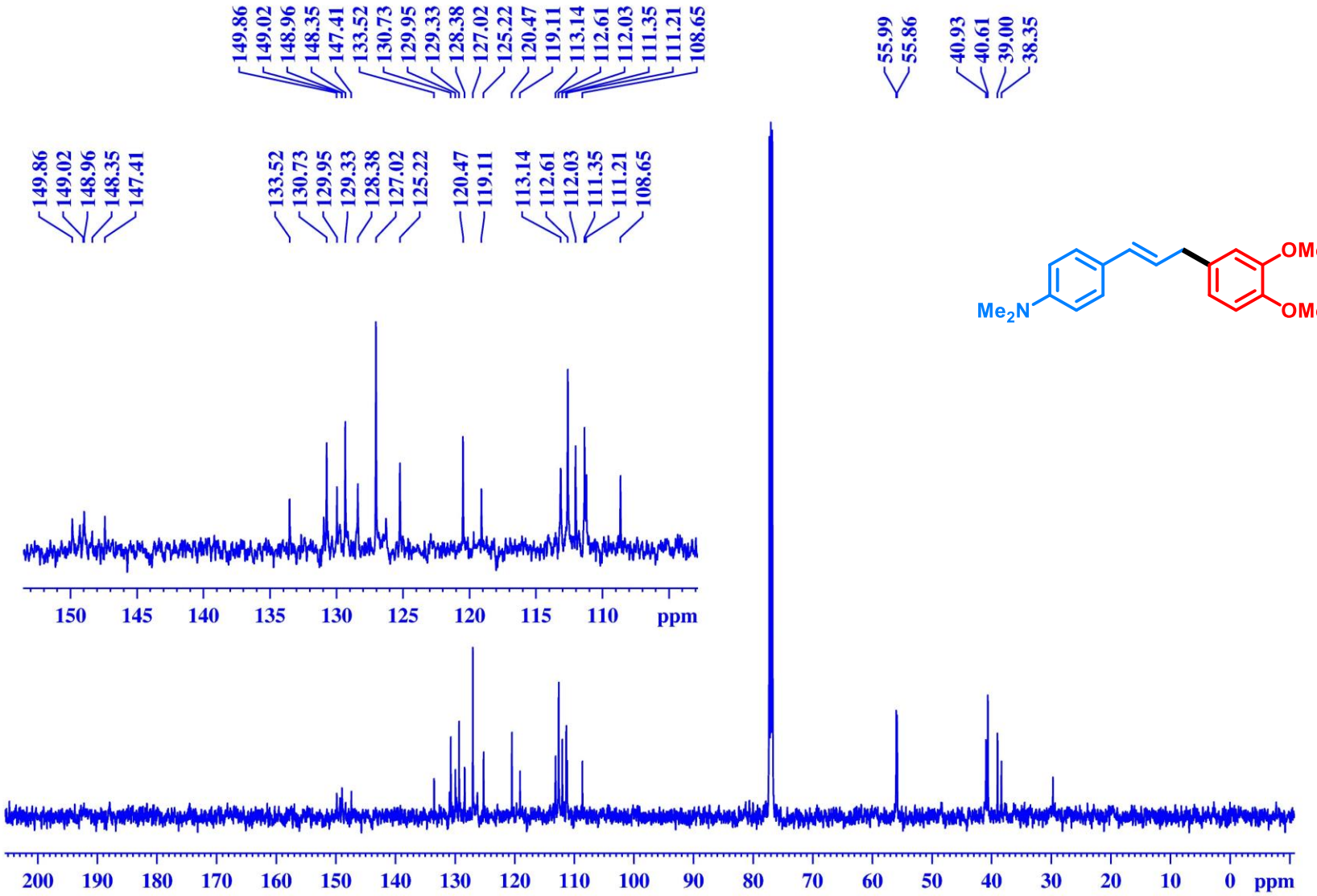
Compound 3v ^{1}H NMR (400 MHz, $CDCl_3$)



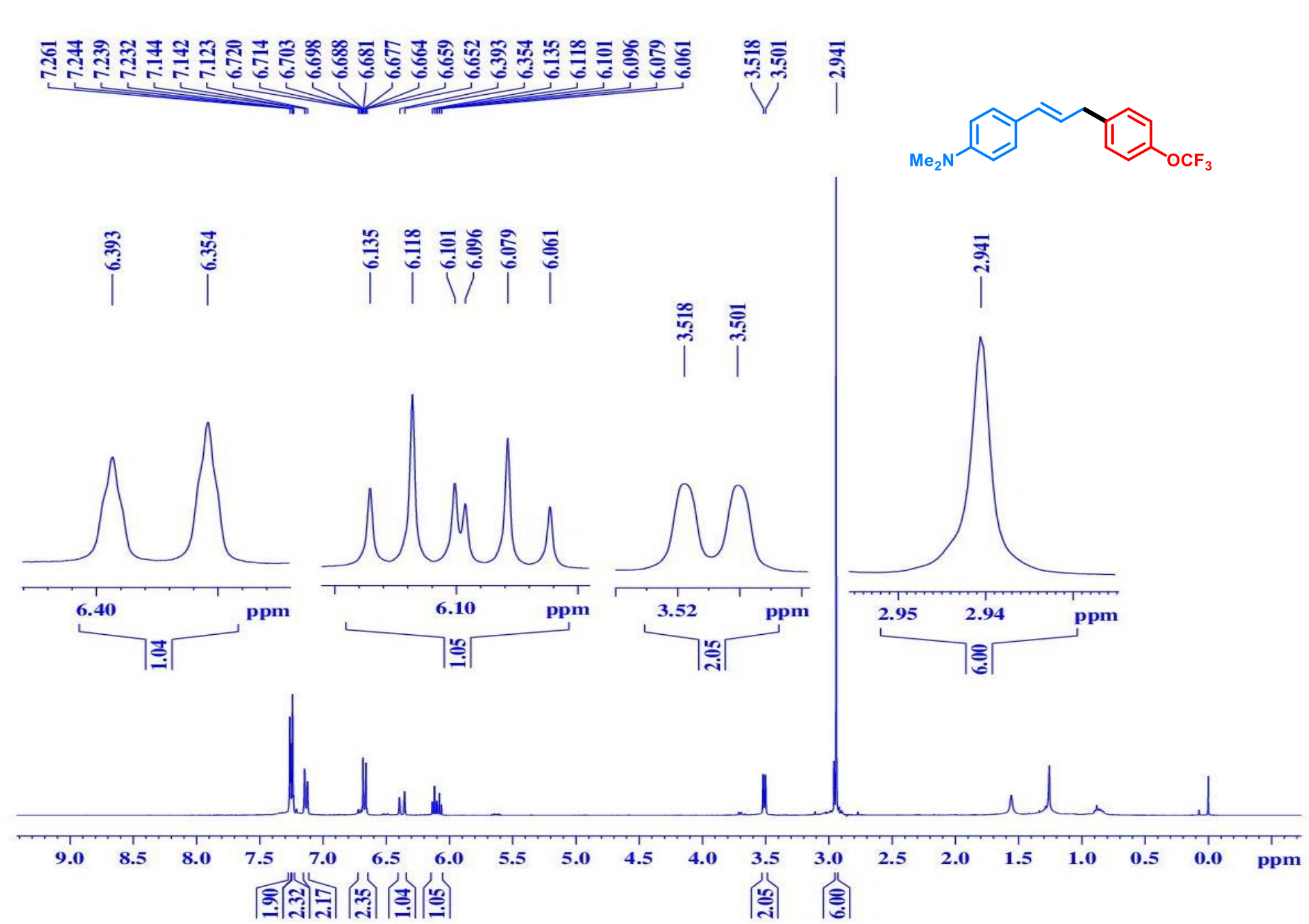
Compound 3v ^{13}C NMR (100 MHz, $CDCl_3$)



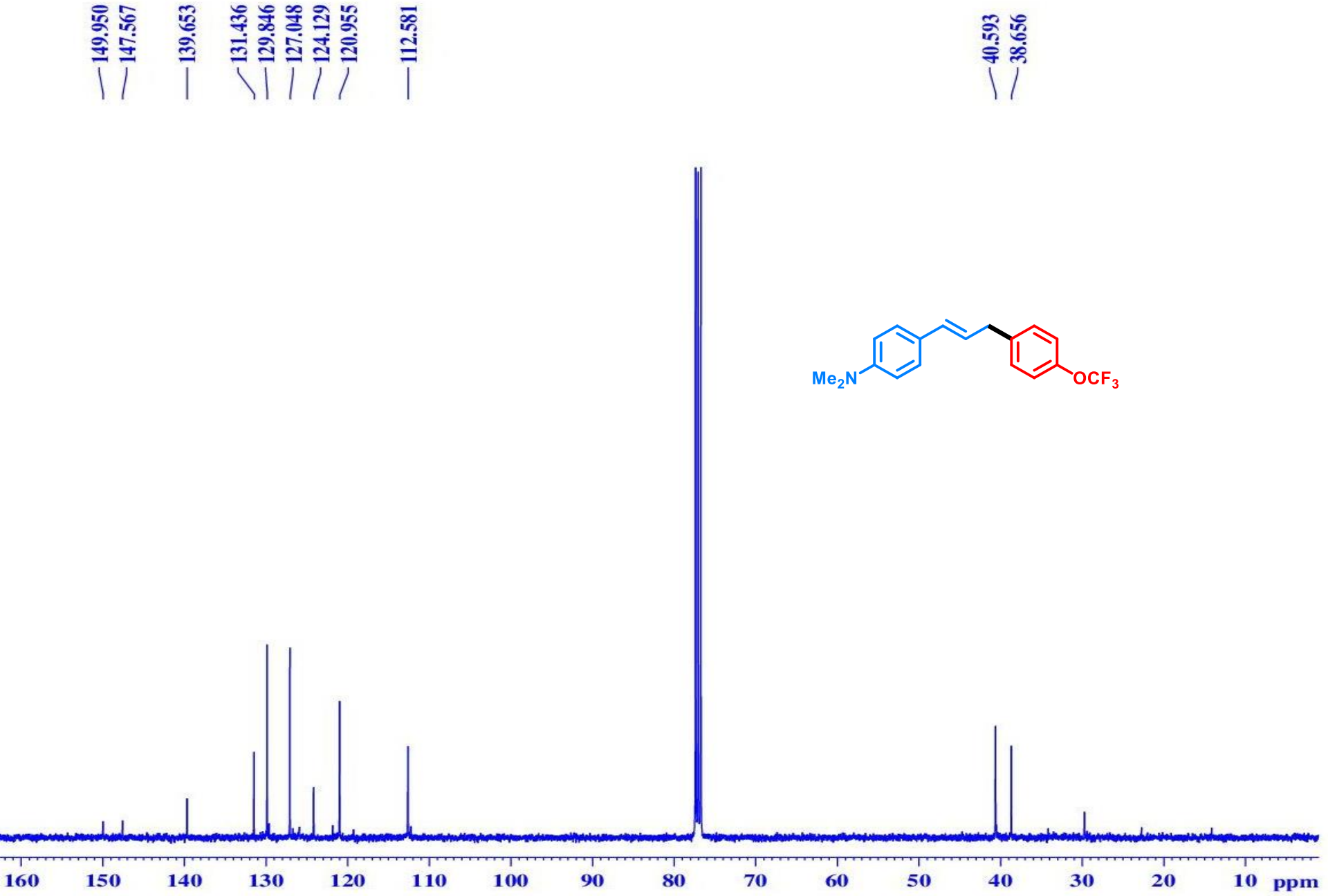
Compound 3w ^{1}H NMR (400 MHz, $CDCl_3$)



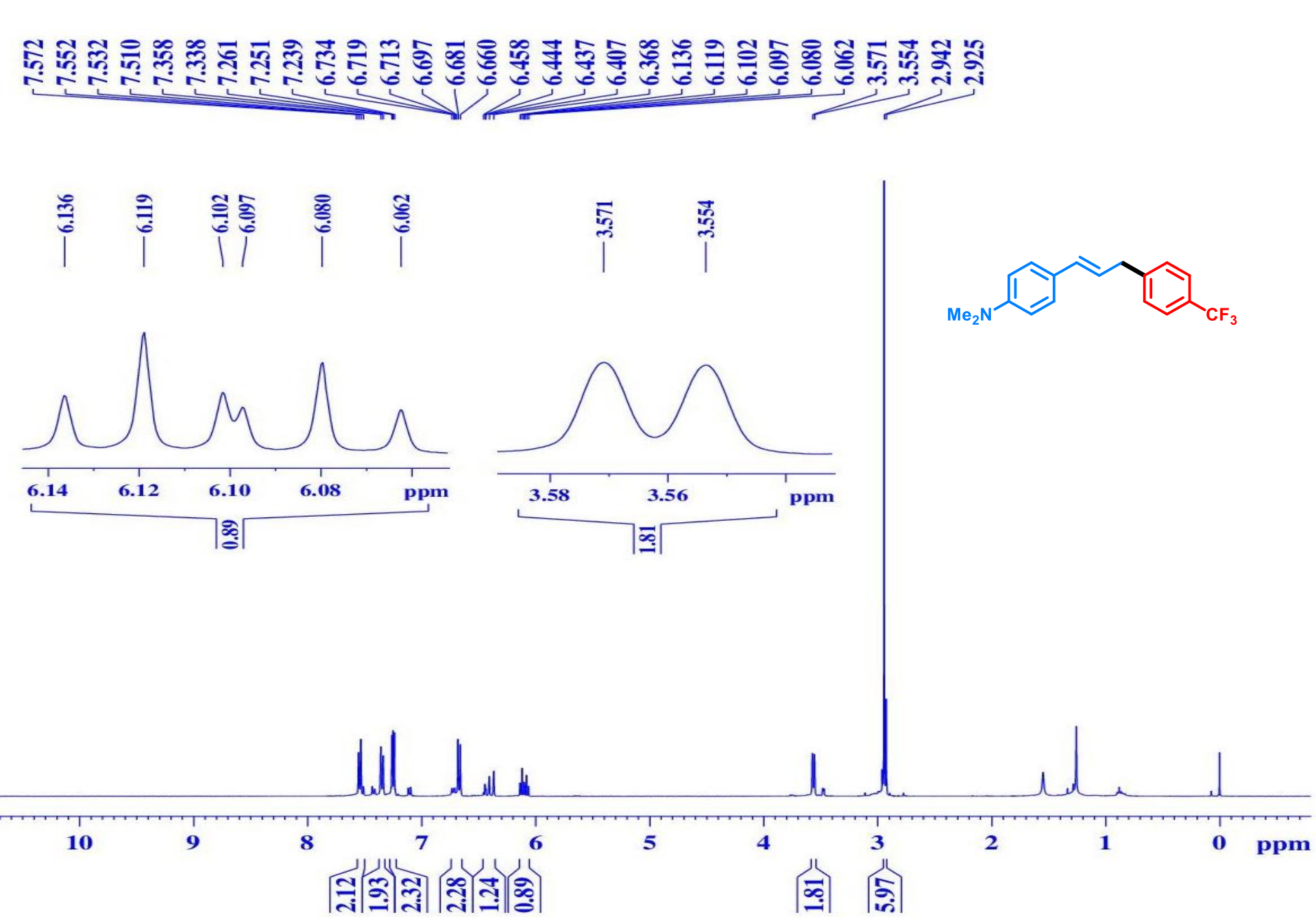
Compound 3w ^{13}C NMR (100 MHz, $CDCl_3$)



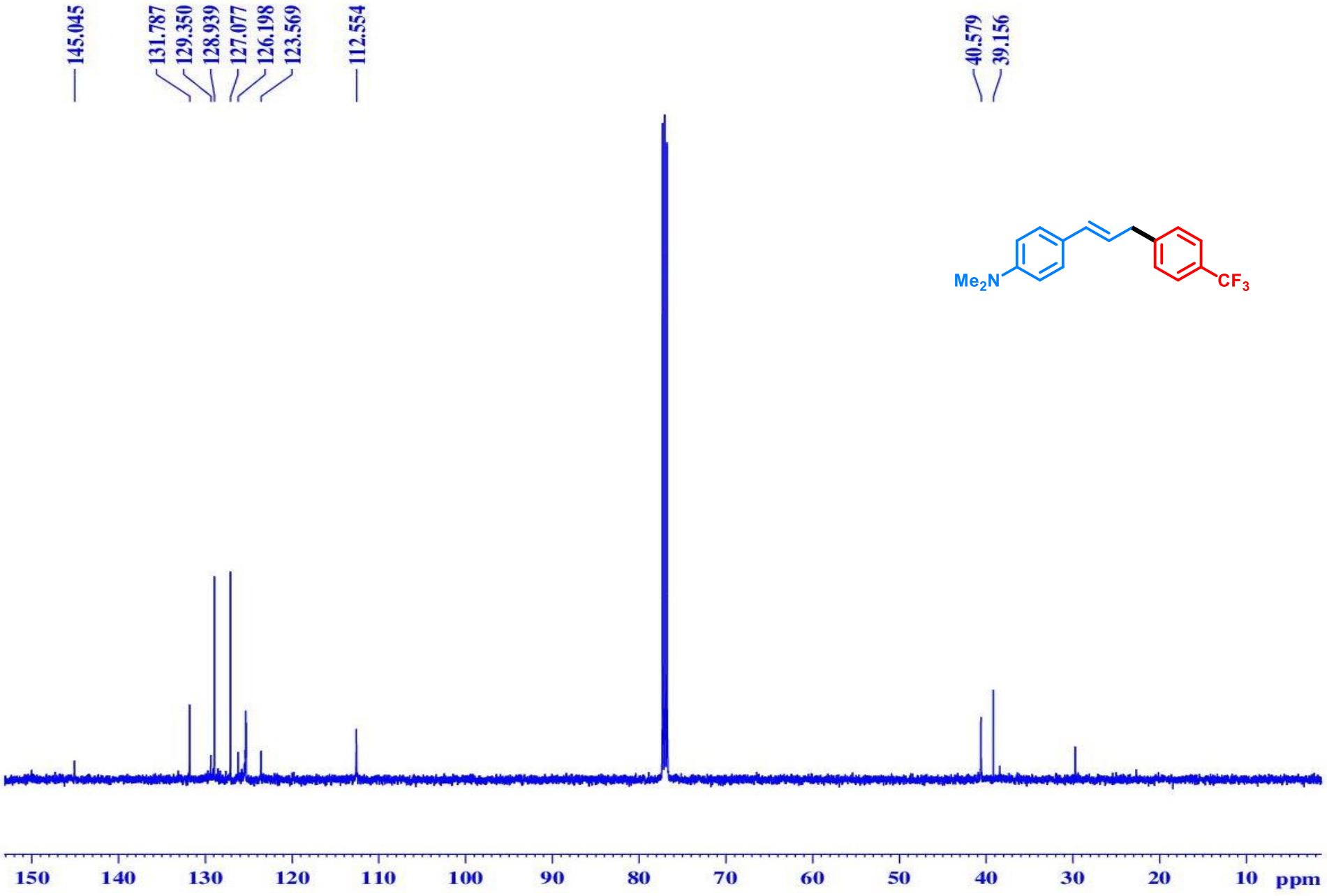
Compound 3x ^{1}H NMR (400 MHz, $CDCl_3$)



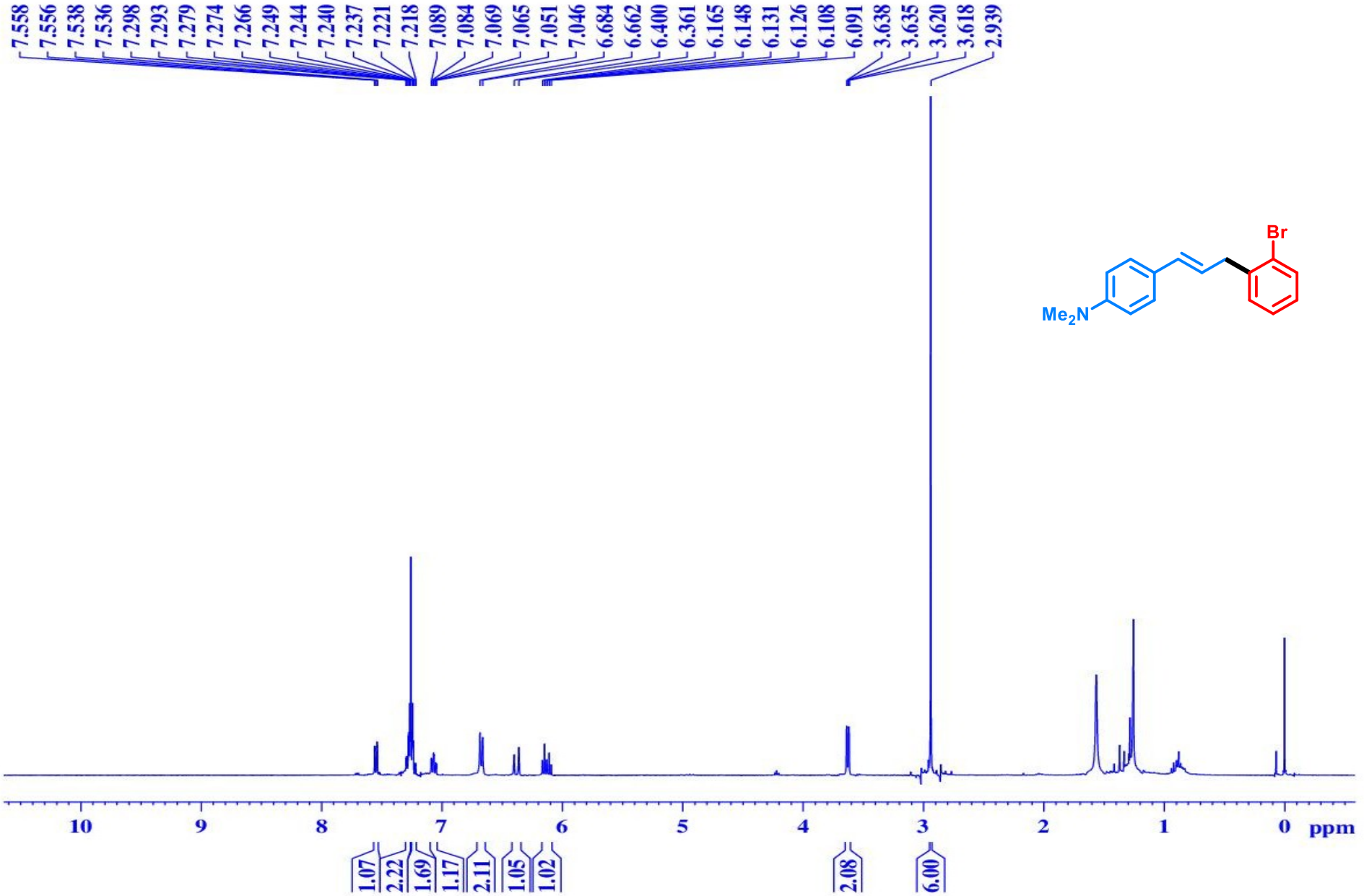
Compound 3x ^{13}C NMR (100 MHz, $CDCl_3$)



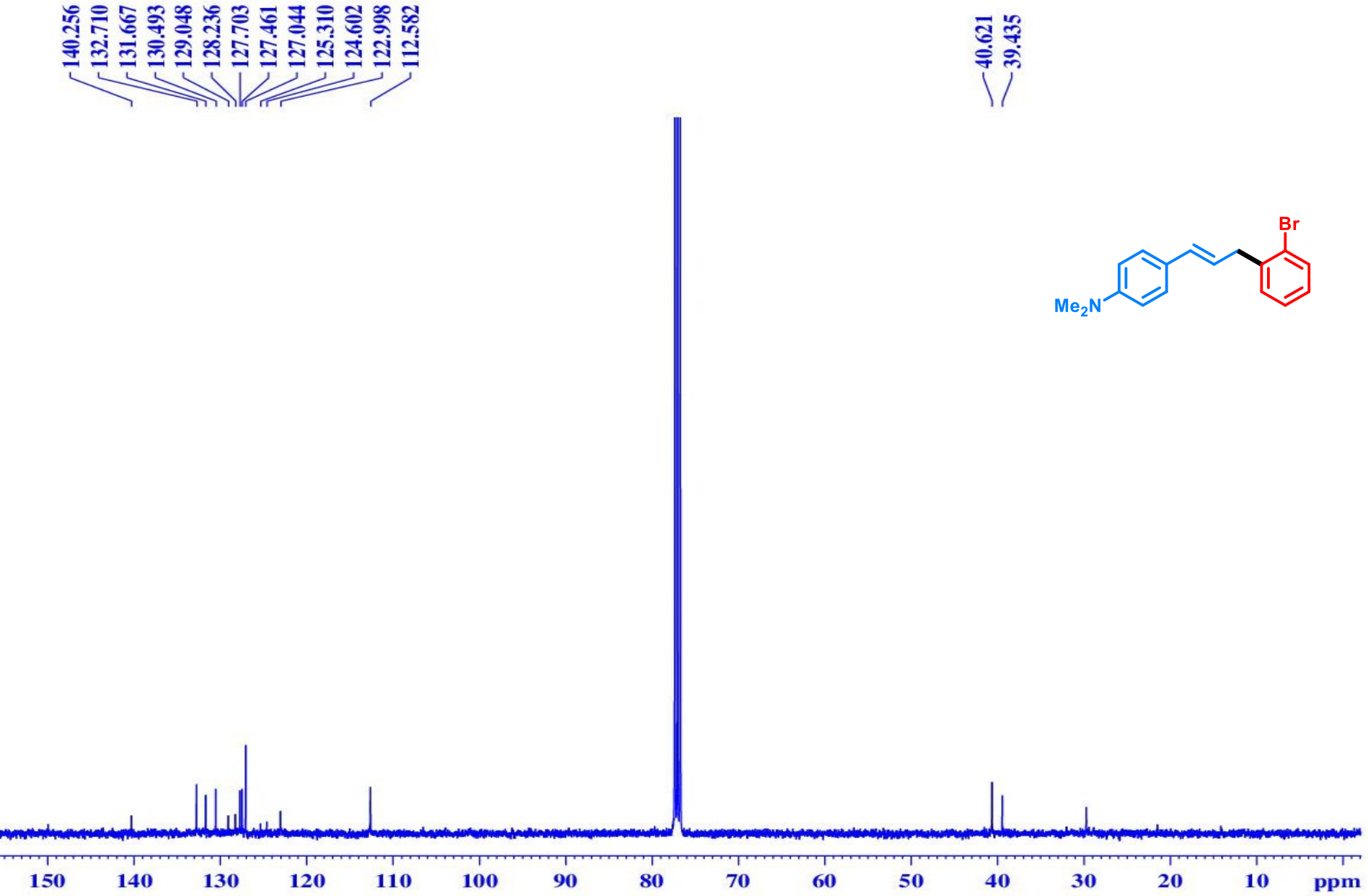
Compound 3y ^{1}H NMR (400 MHz, $CDCl_3$)



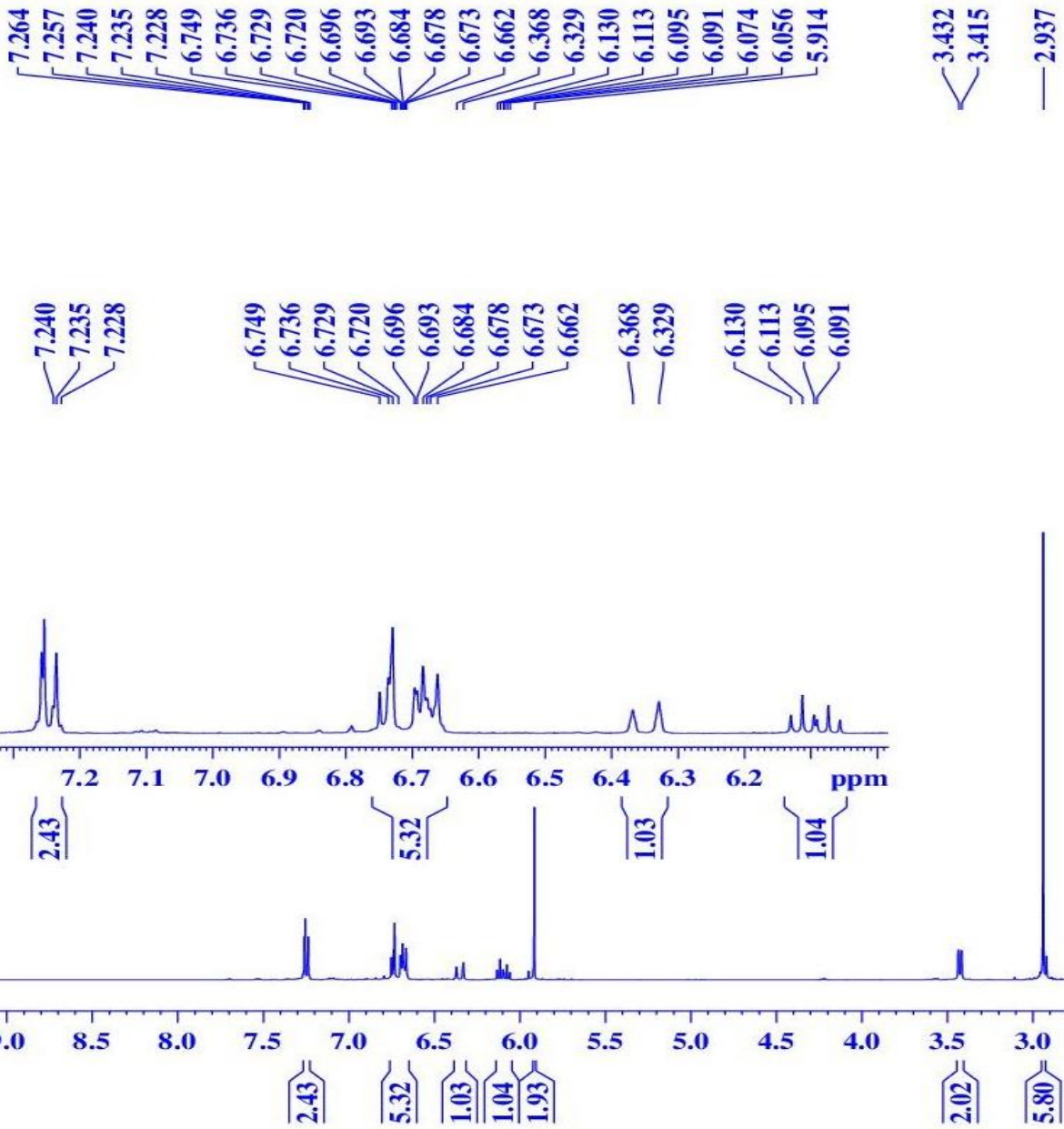
Compound 3y ^{13}C NMR (100 MHz, $CDCl_3$)



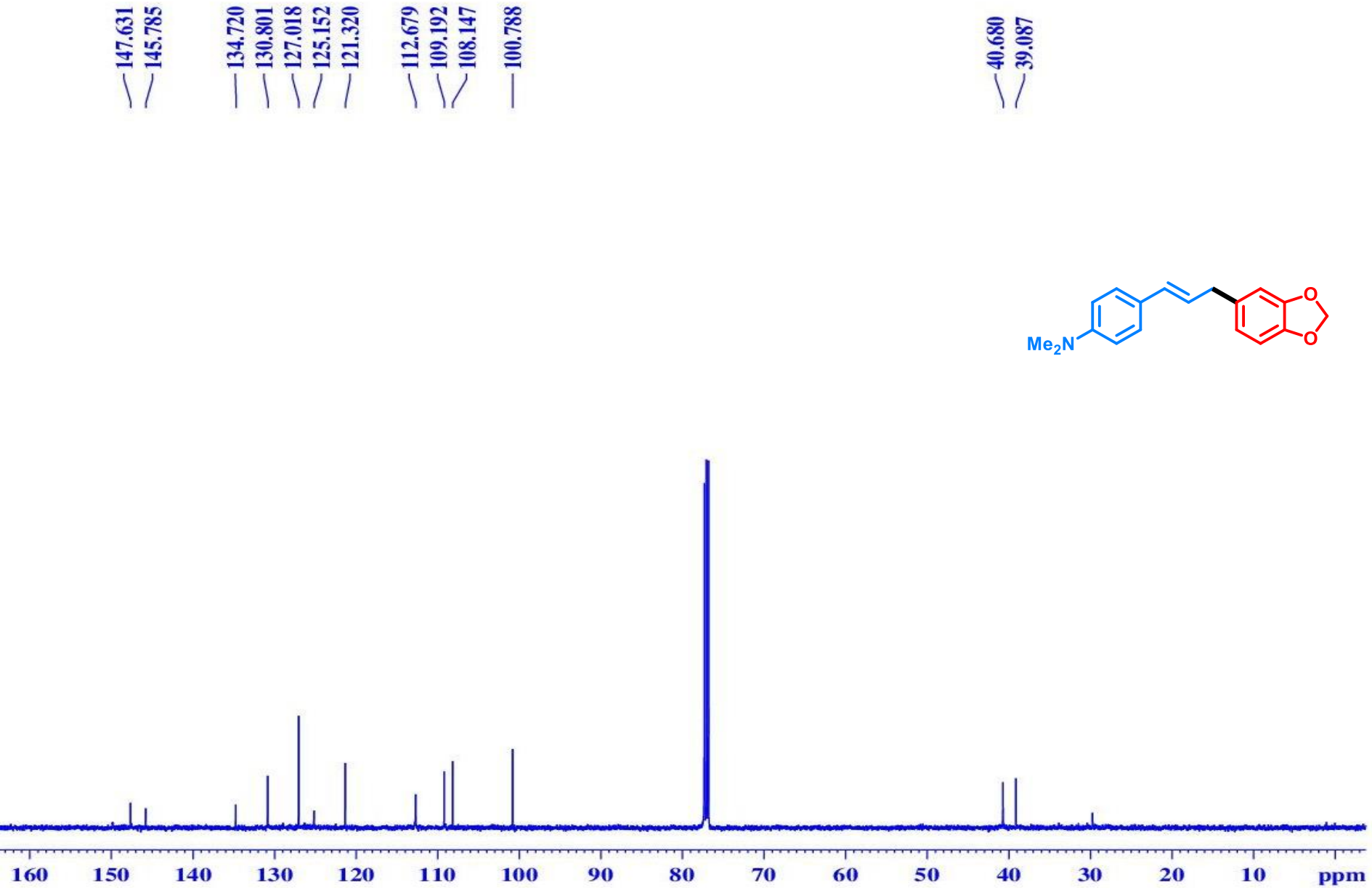
Compound 3z ^{1}H NMR (400 MHz, $CDCl_3$)



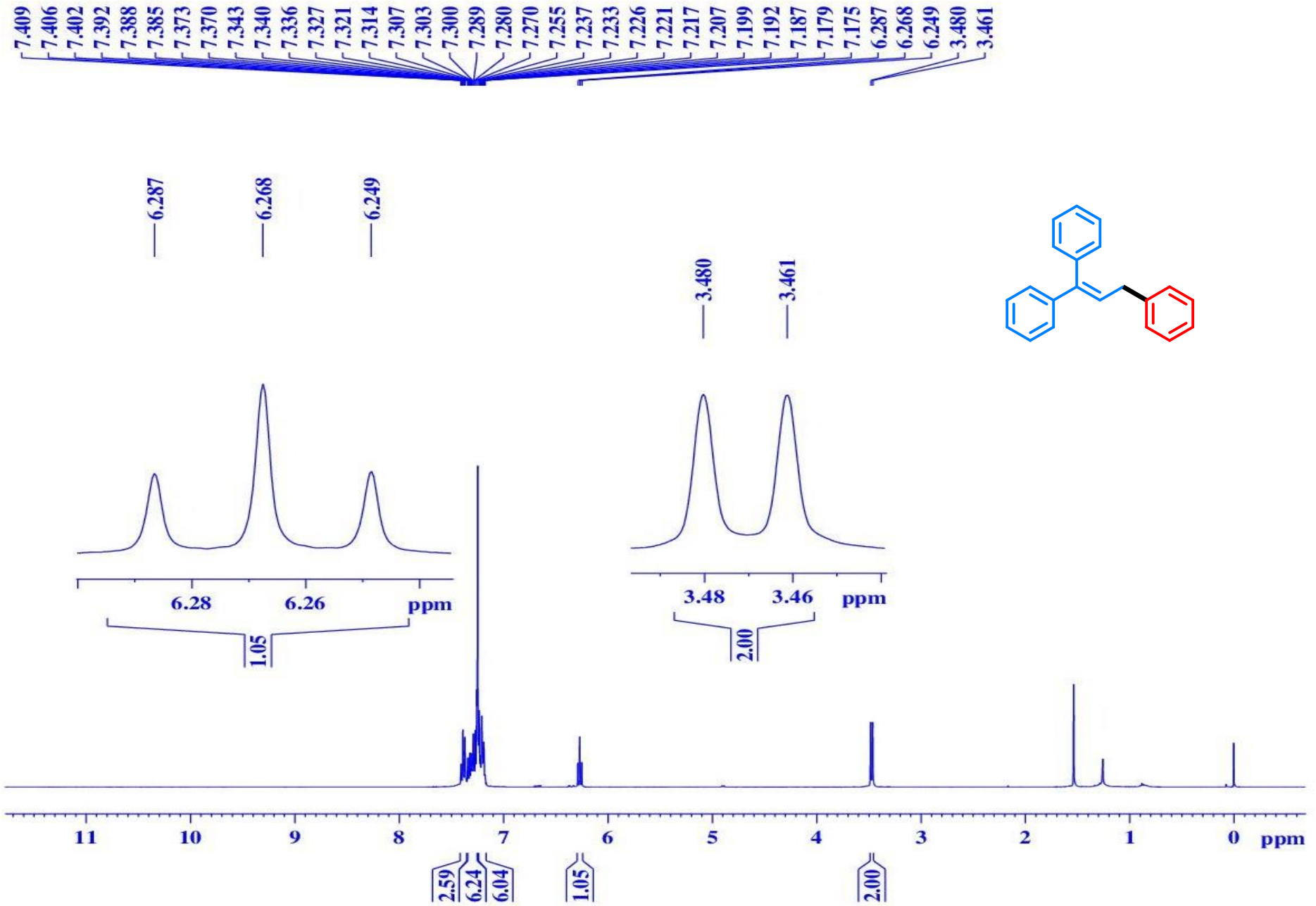
Compound 3z ^{13}C NMR (100 MHz, $CDCl_3$)



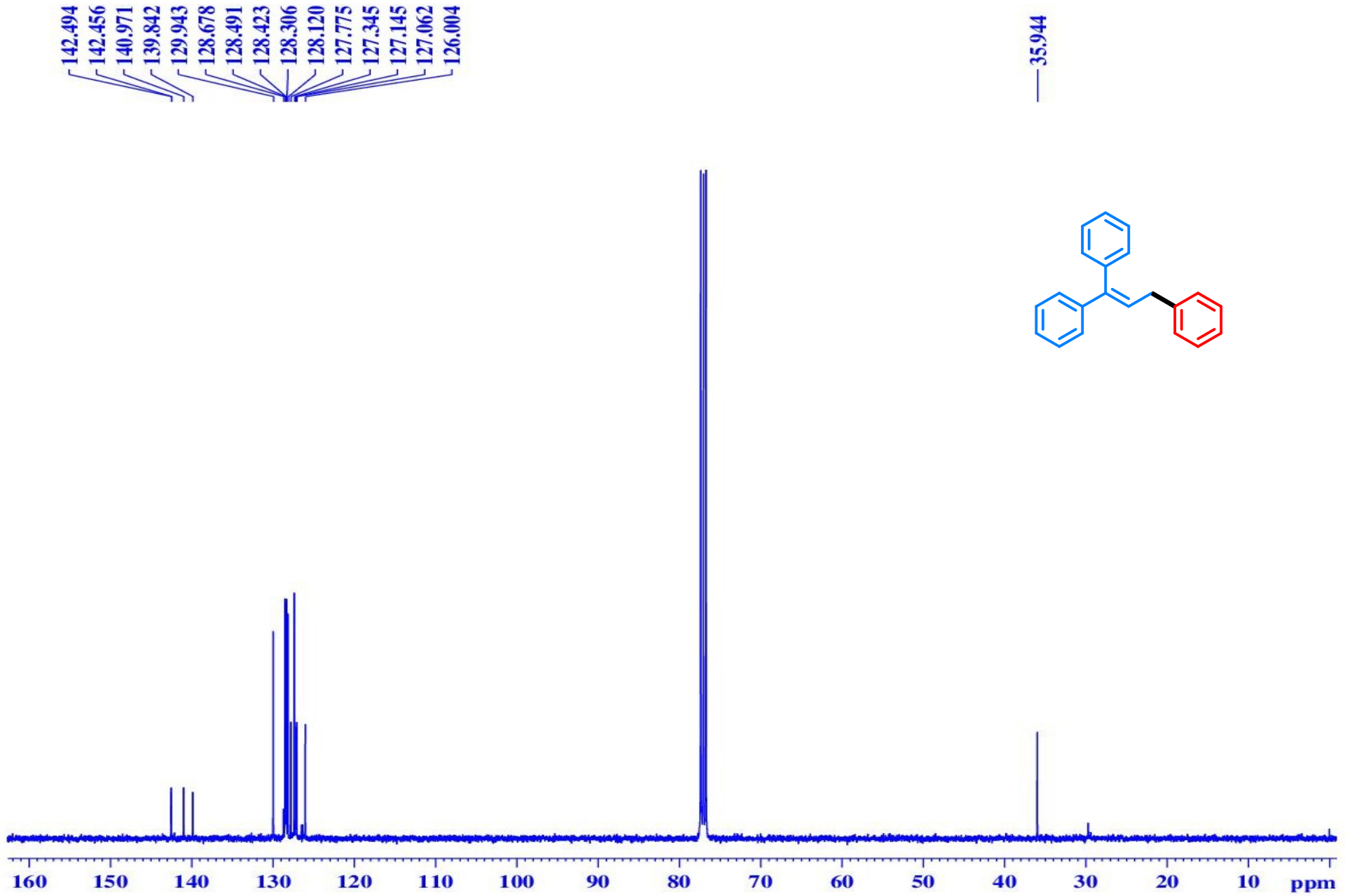
Compound 3aa ^{1}H NMR (400 MHz, $CDCl_3$)



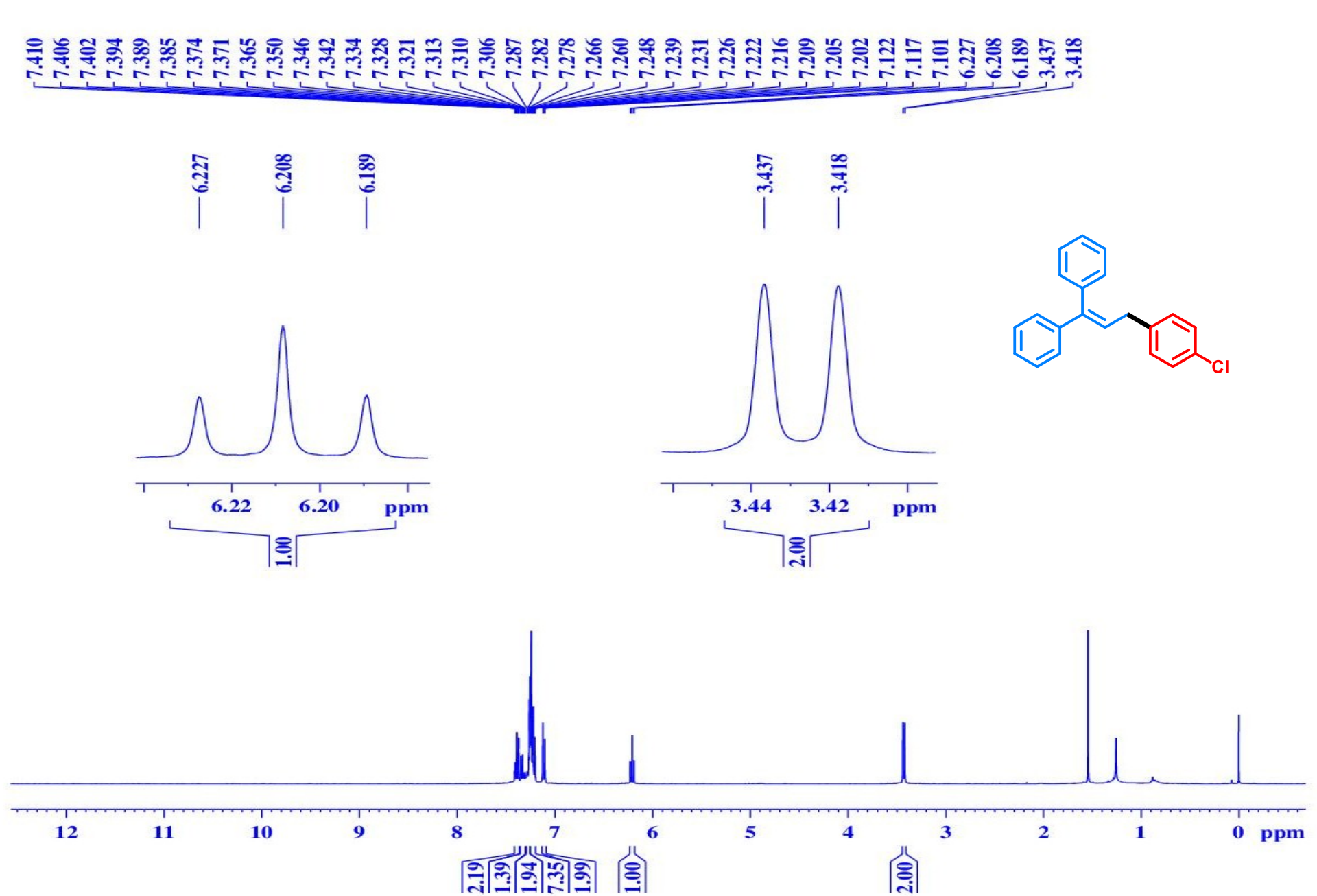
Compound 3aa ^{13}C NMR (100 MHz, $CDCl_3$)



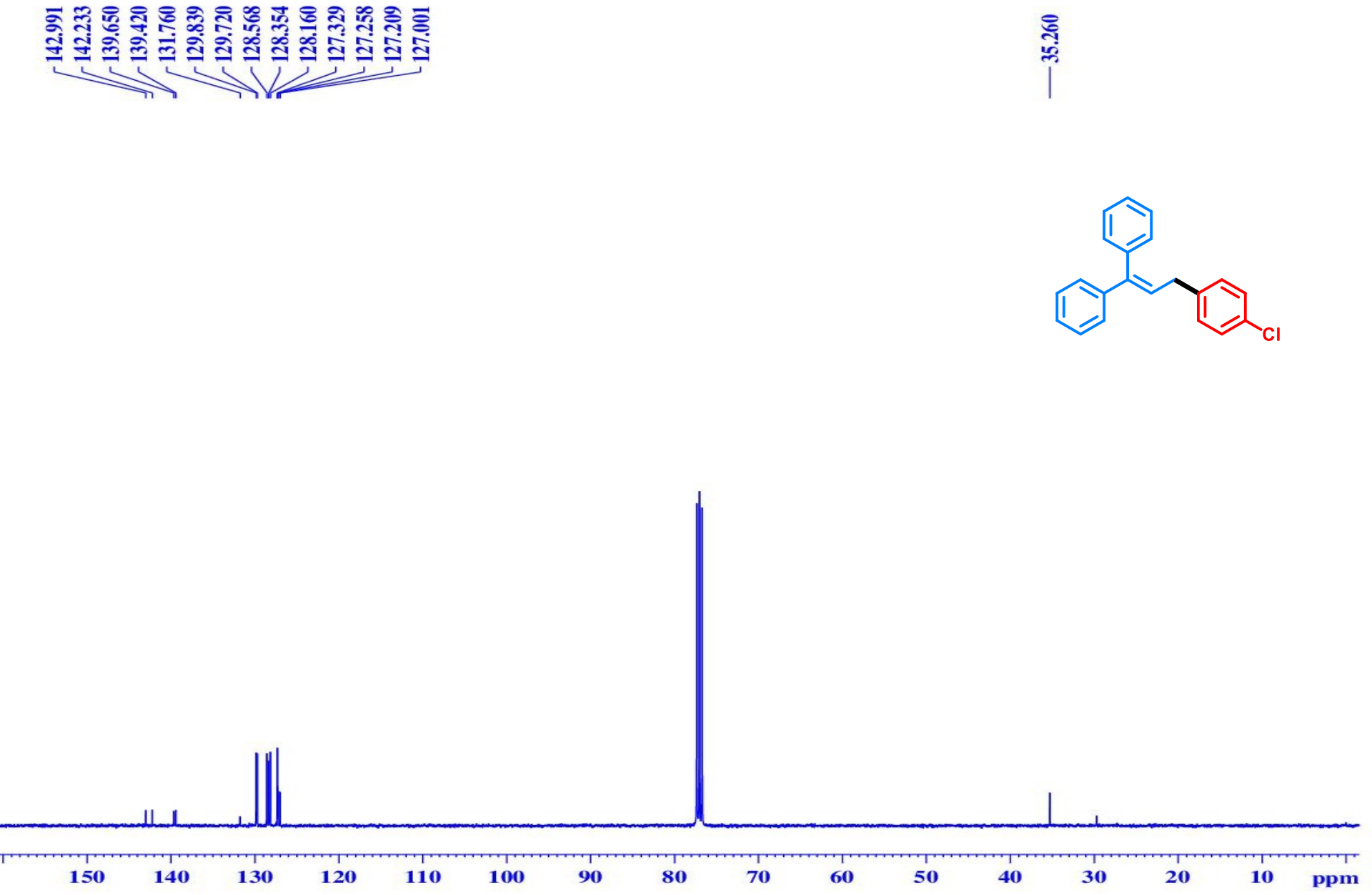
Compound 3ab ^{1}H NMR (400 MHz, $CDCl_3$)



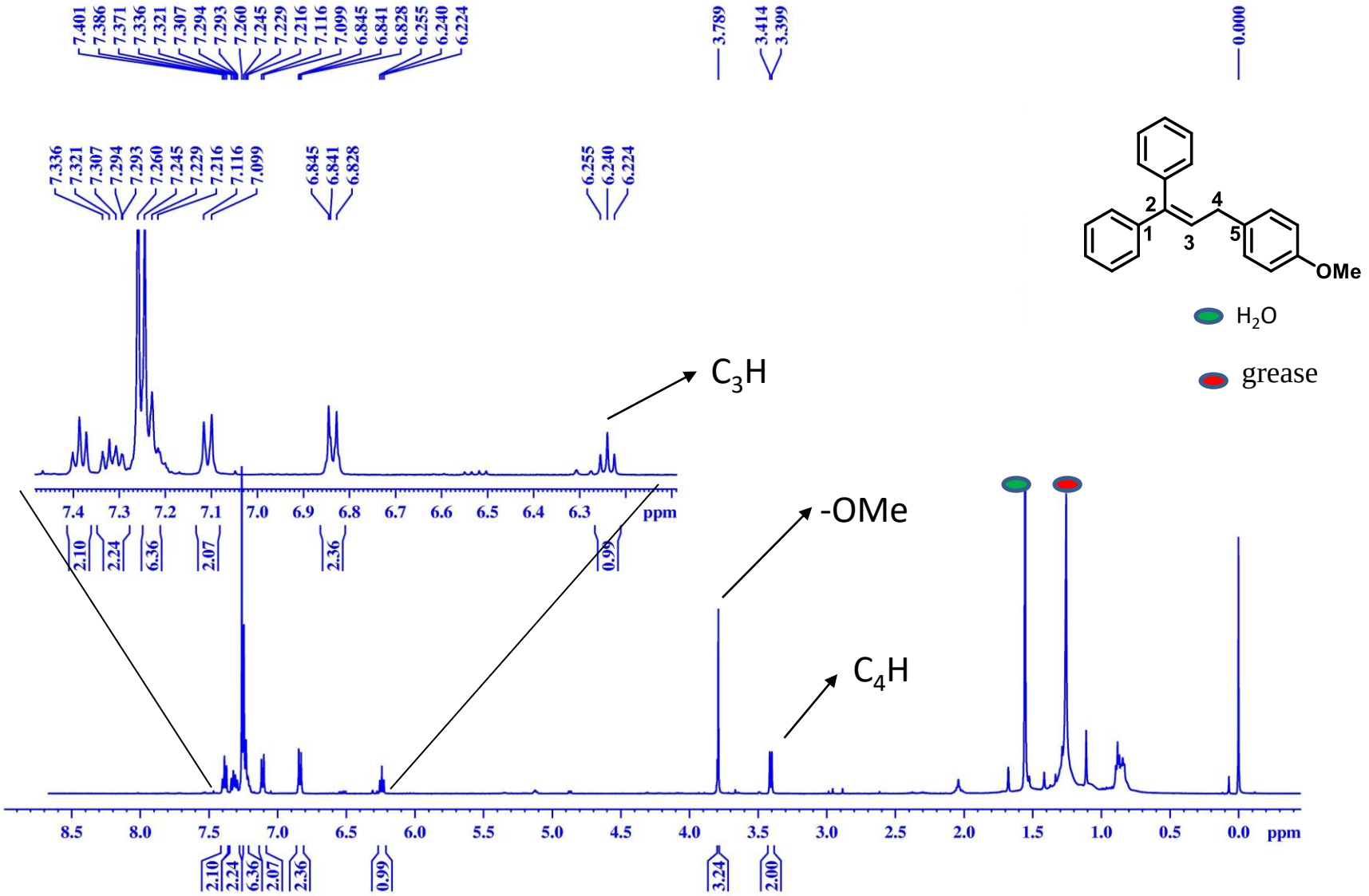
Compound 3ab ^{13}C NMR (100 MHz, $CDCl_3$)



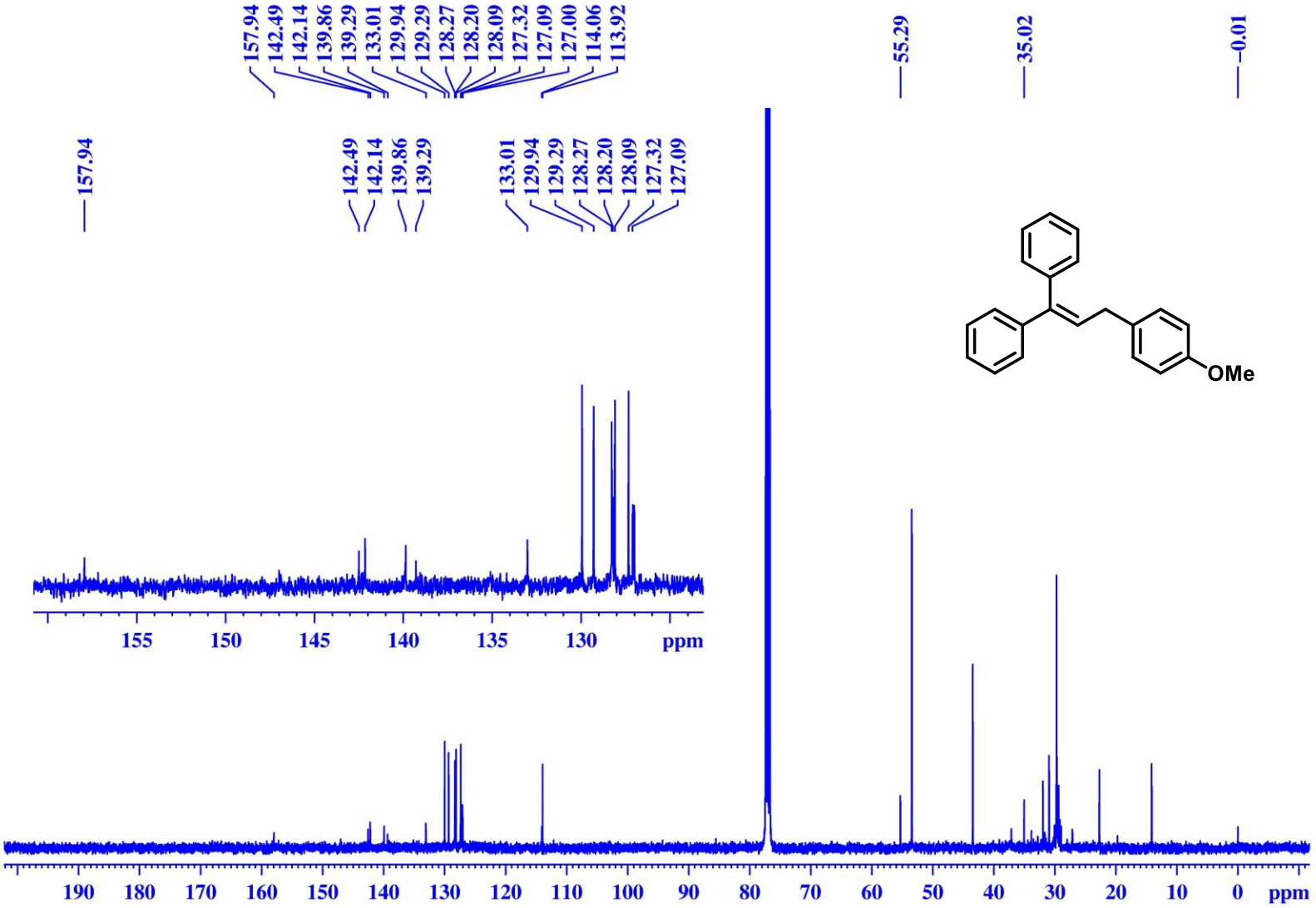
Compound 3ac ^{1}H NMR (400 MHz, $CDCl_3$)



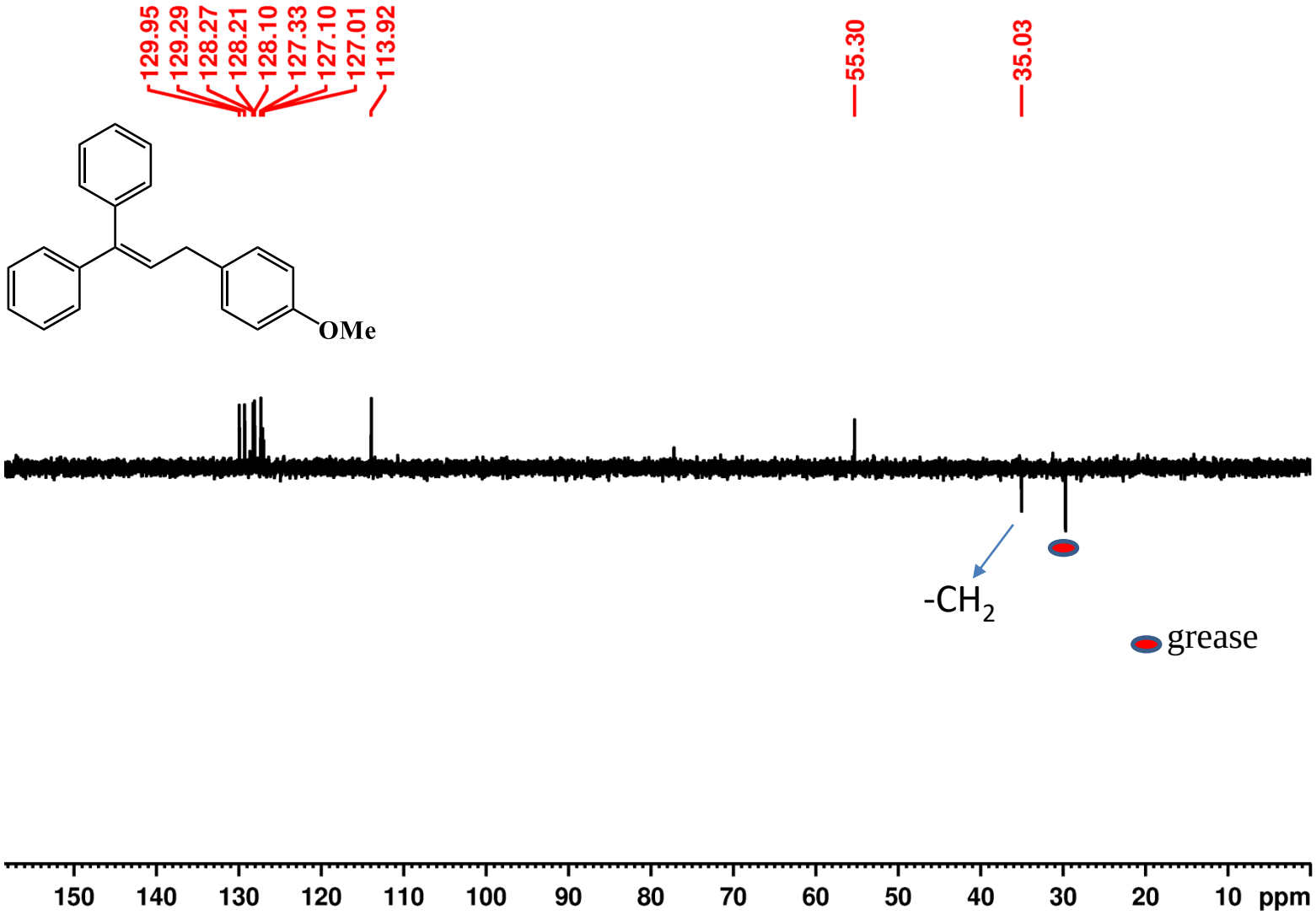
Compound 3ac ^{13}C NMR (100 MHz, $CDCl_3$)



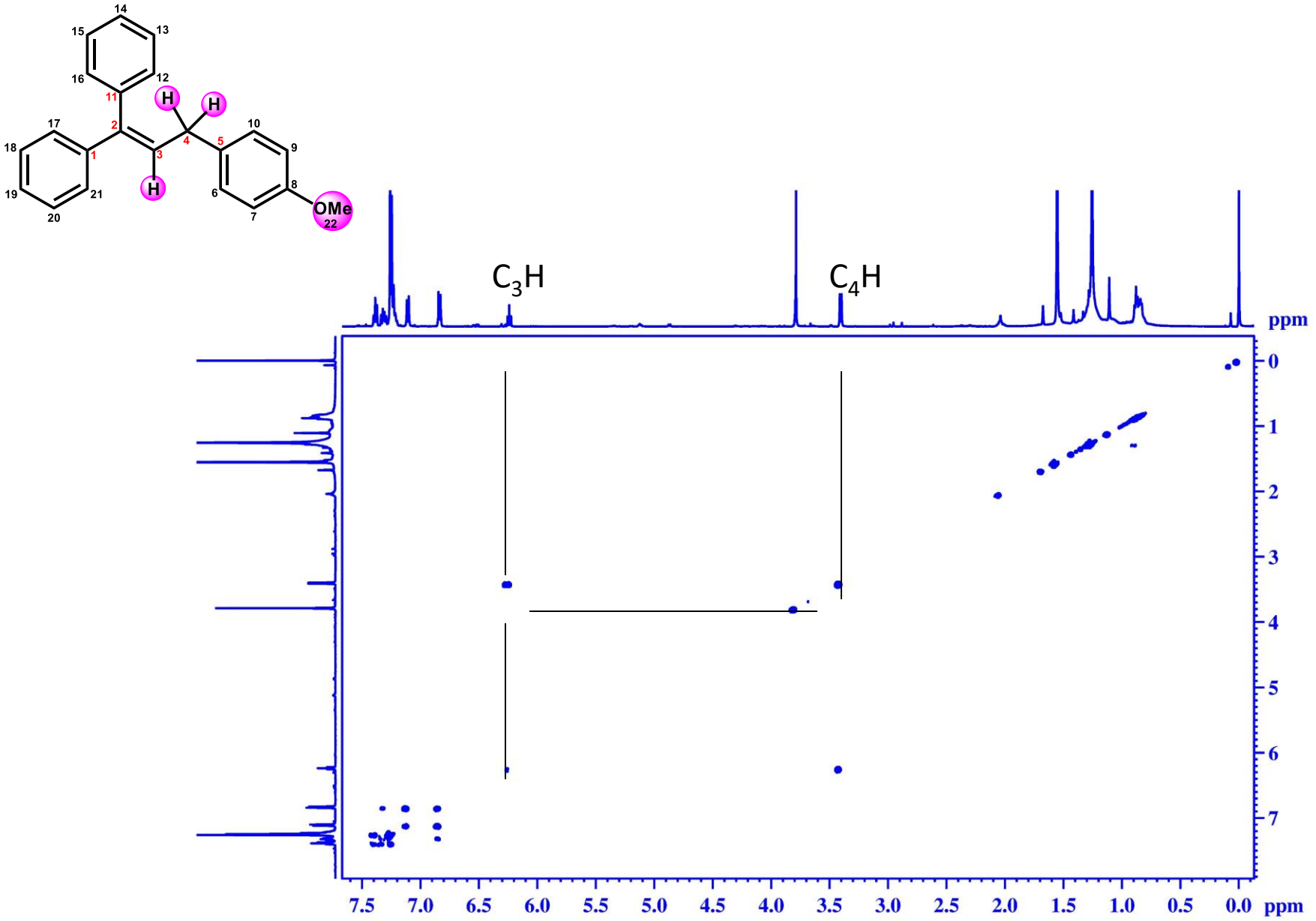
Compound 3ad ^{1}H NMR (500 MHz, $CDCl_3$)



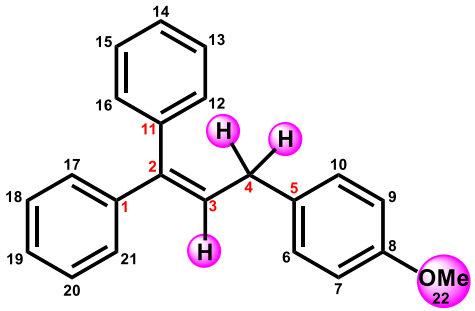
Compound 3ad ^{13}C NMR (125 MHz, $CDCl_3$)

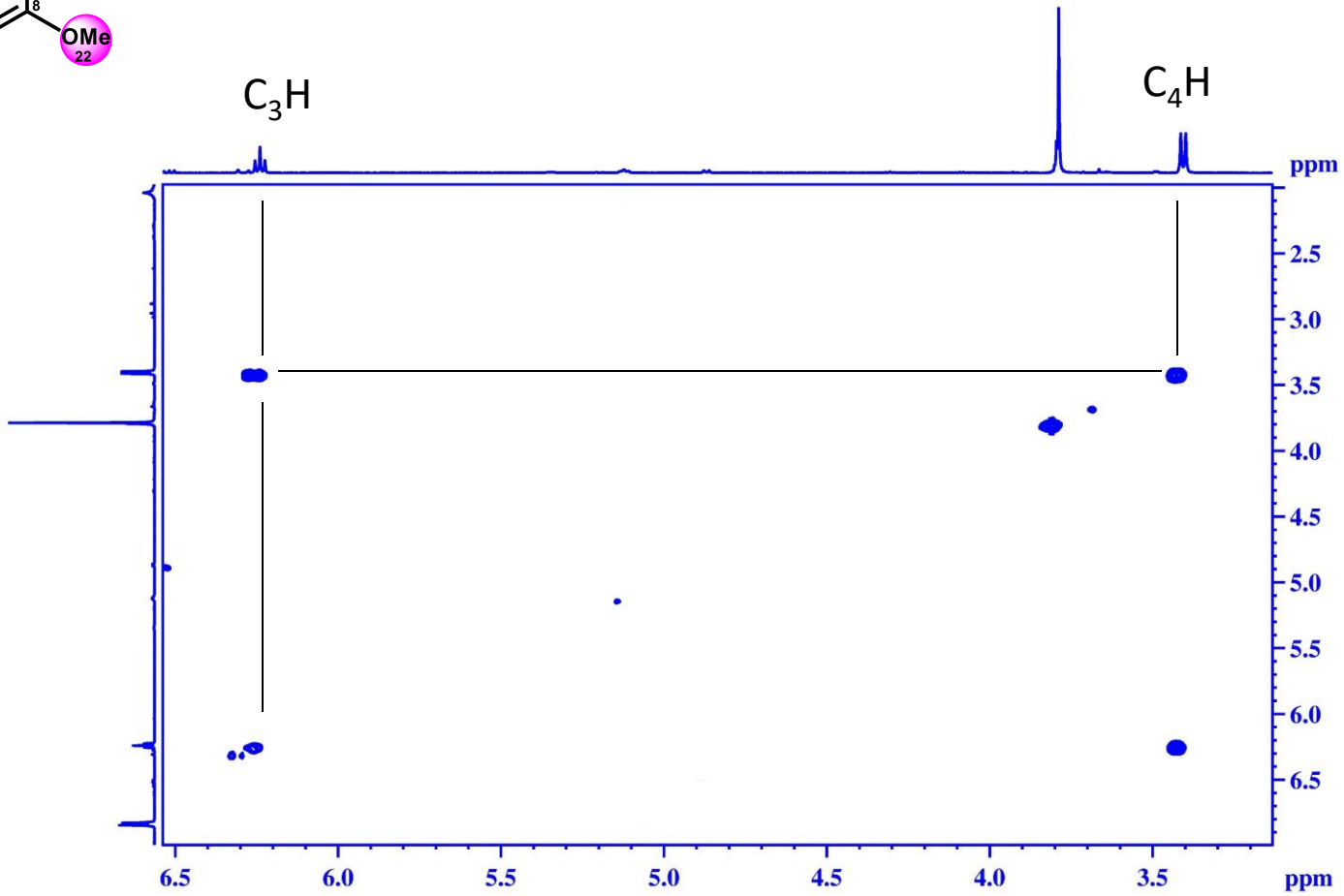


Compound 3ad ^{13}C Dept-135^{0} (125 MHz, $CDCl_3$)

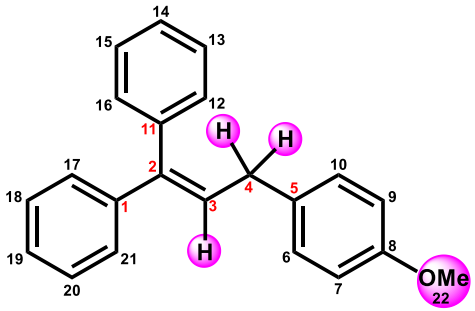


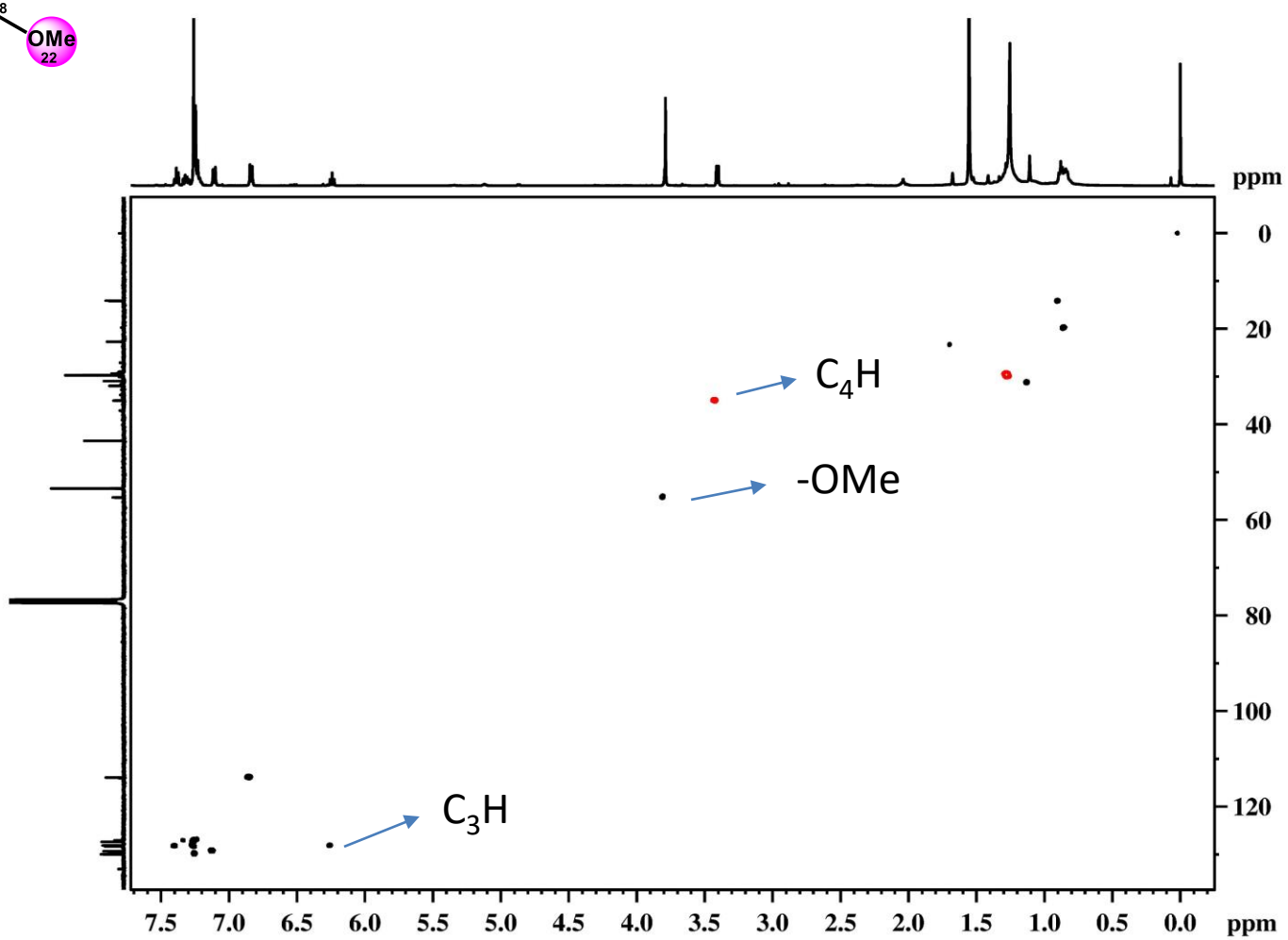
Compound 3ad 2D-COSY (500 MHz, $CDCl_3$)



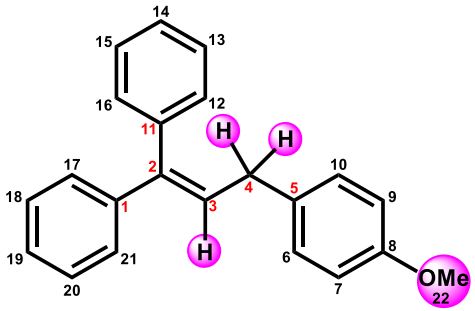


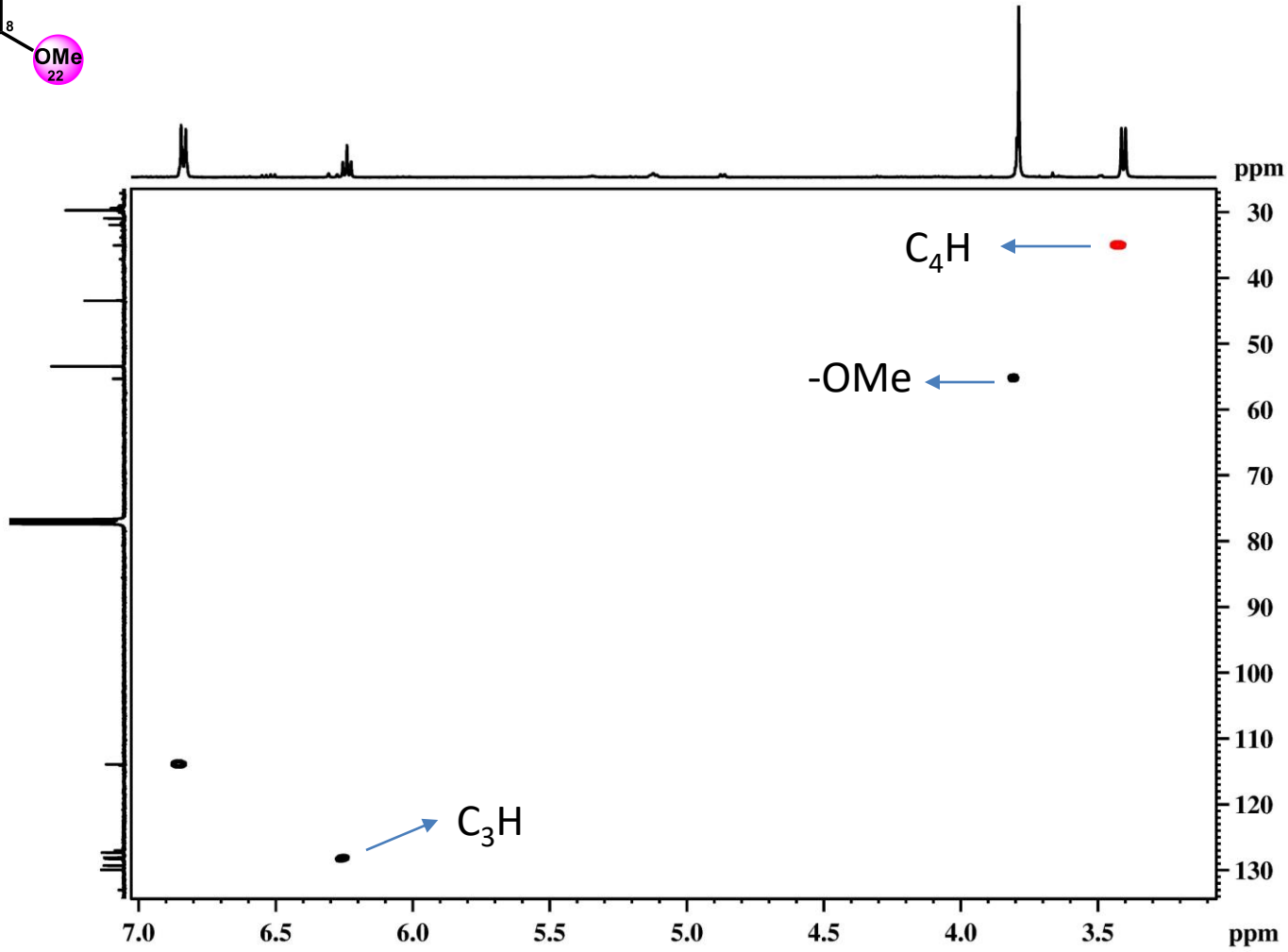
Compound 3ad 2D-COSY (500 MHz, $CDCl_3$)



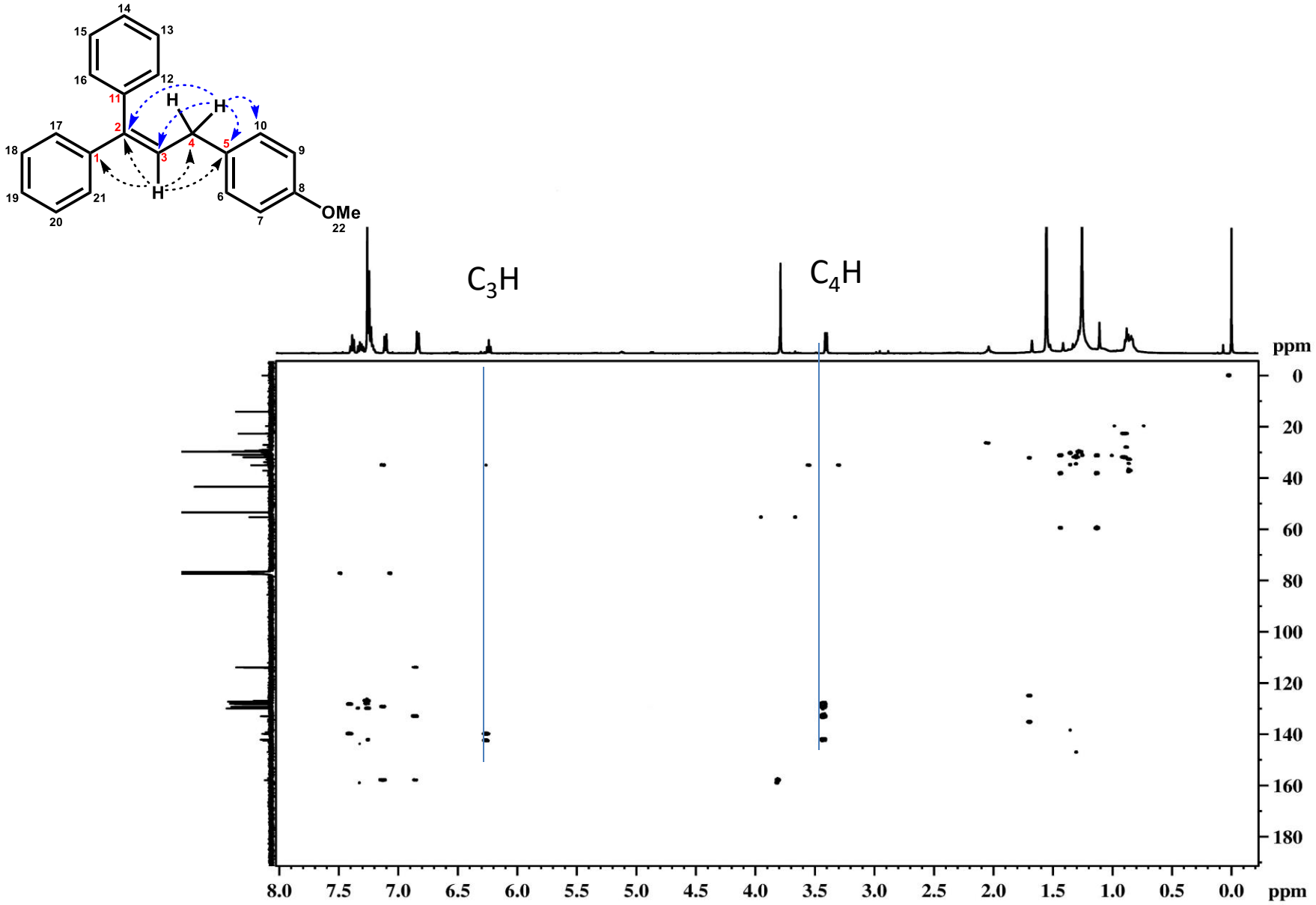


Compound 3ad 2D-HSQC (500 MHz, $CDCl_3$)

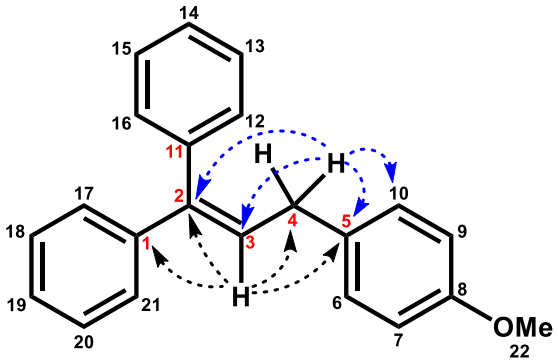


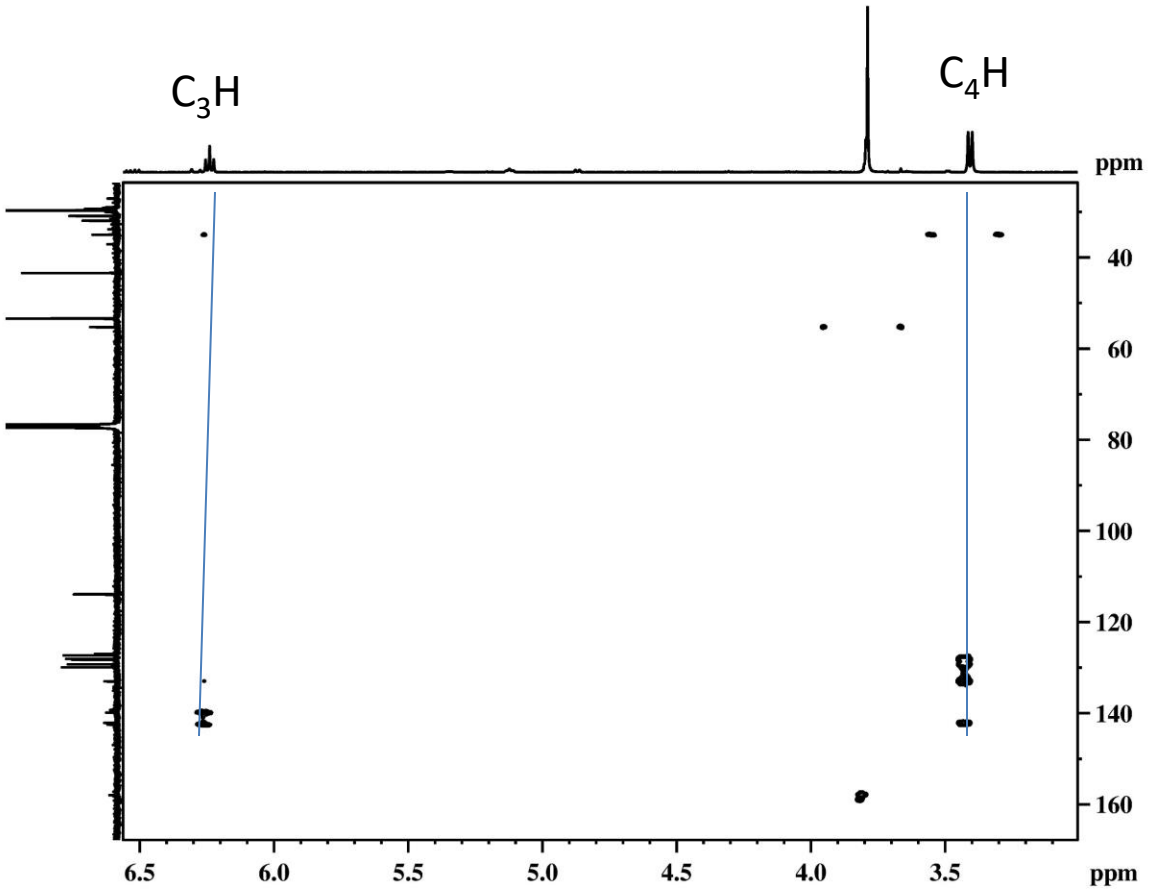


Compound 3ad 2D-HSQC (500 MHz, $CDCl_3$)

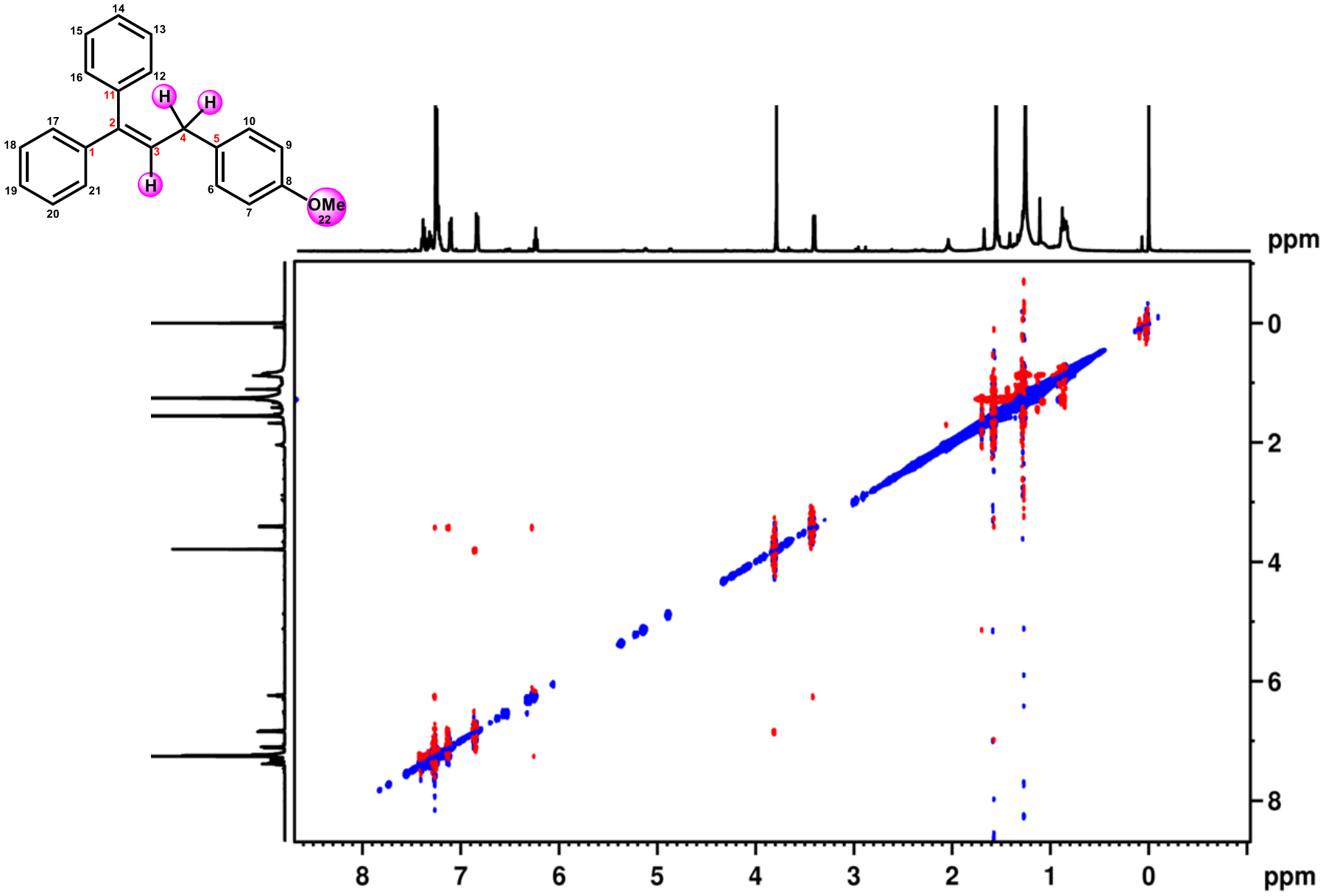


Compound 3ad 2D-HMBC (500 MHz, $CDCl_3$)

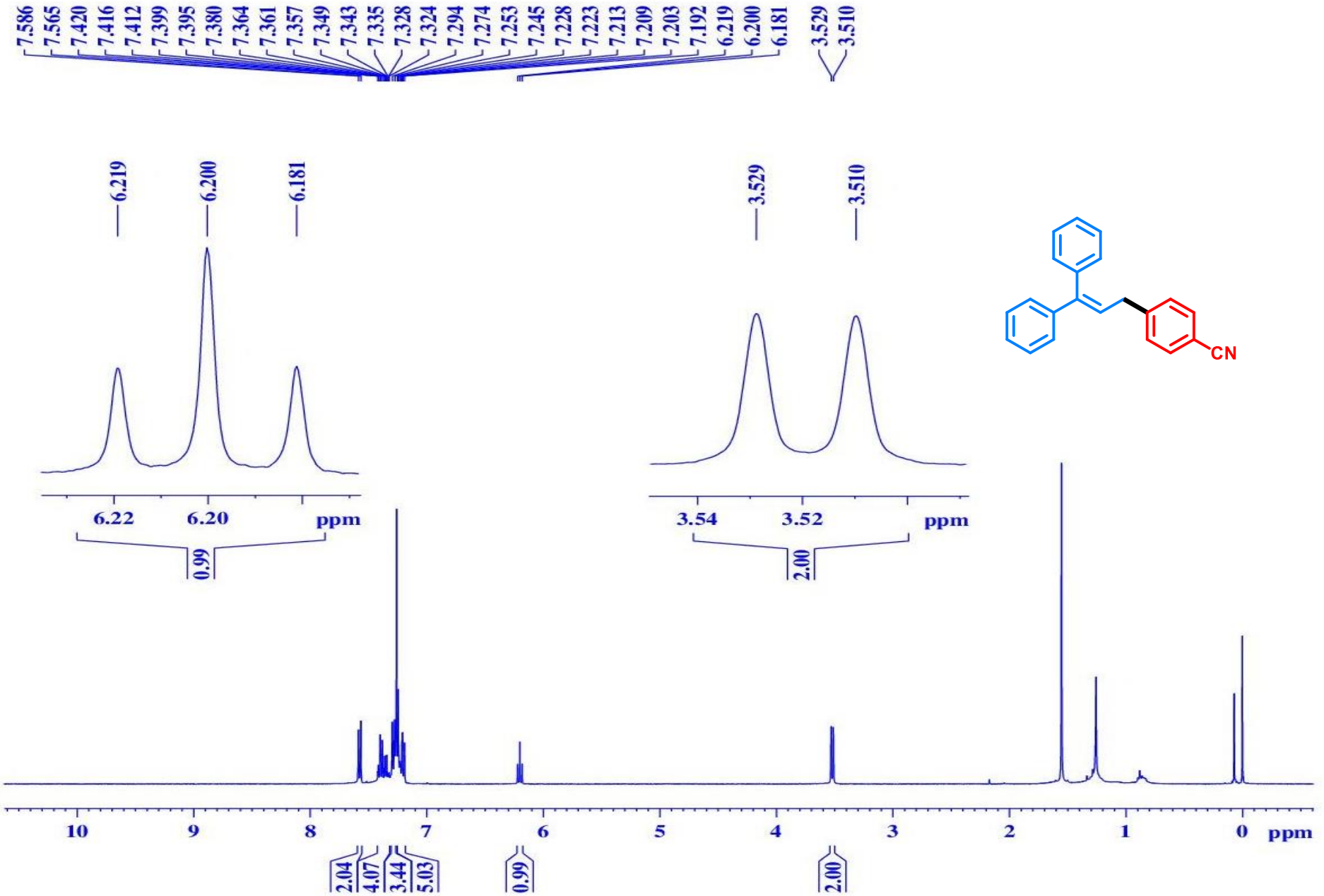




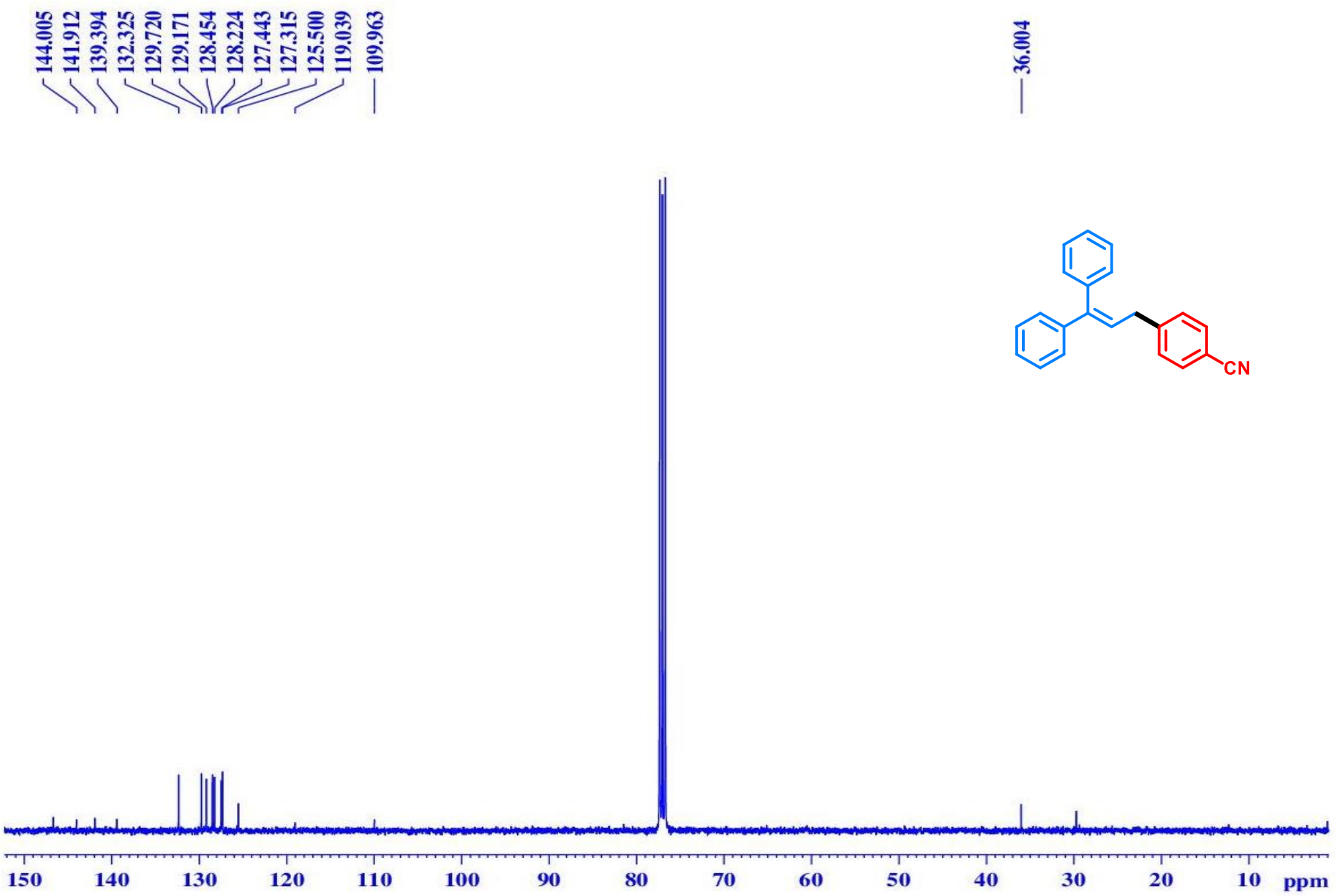
Compound 3ad 2D-HMBC (500 MHz, $CDCl_3$)



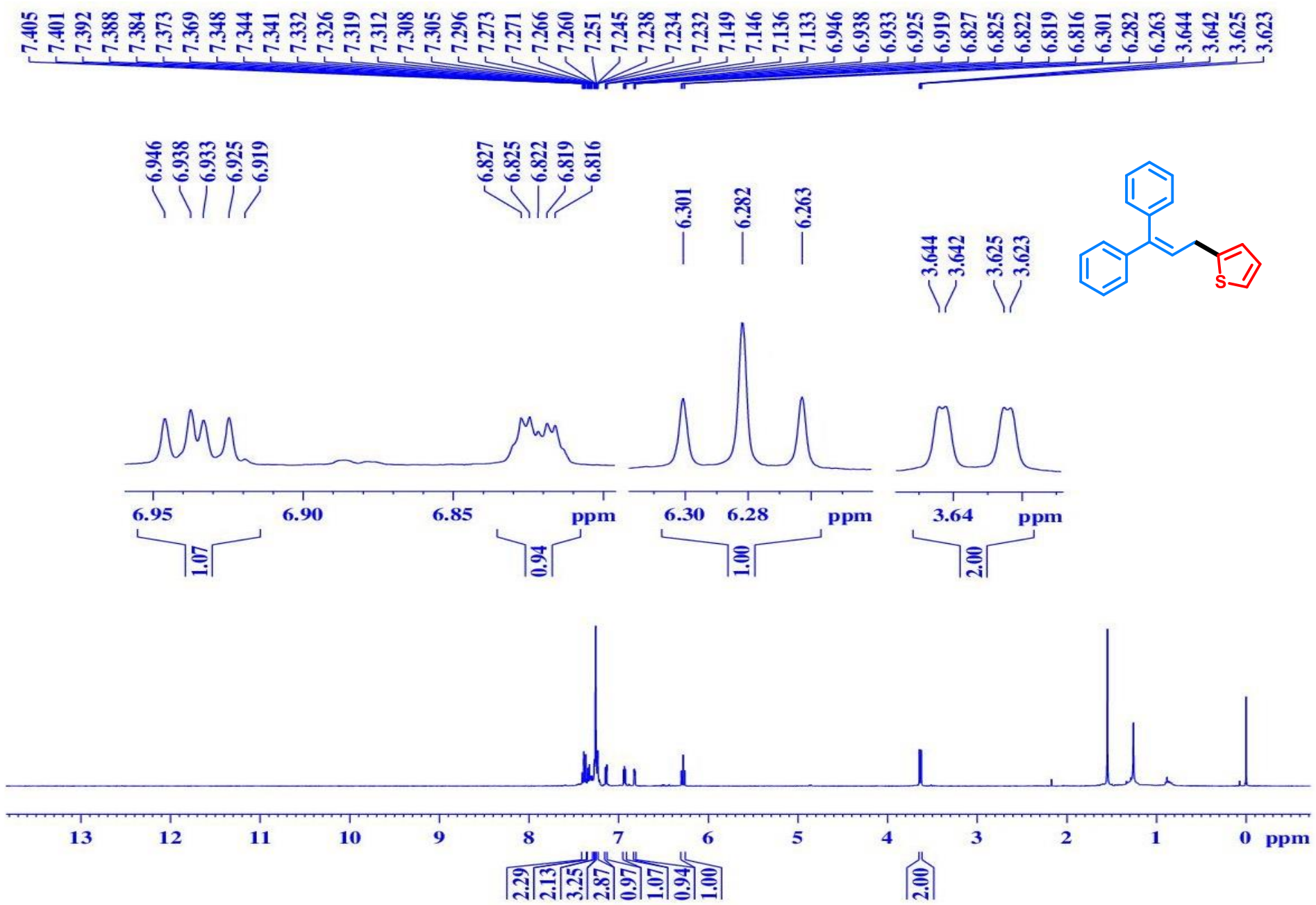
Compound 3ad 2D-NOESY (500 MHz, $CDCl_3$)



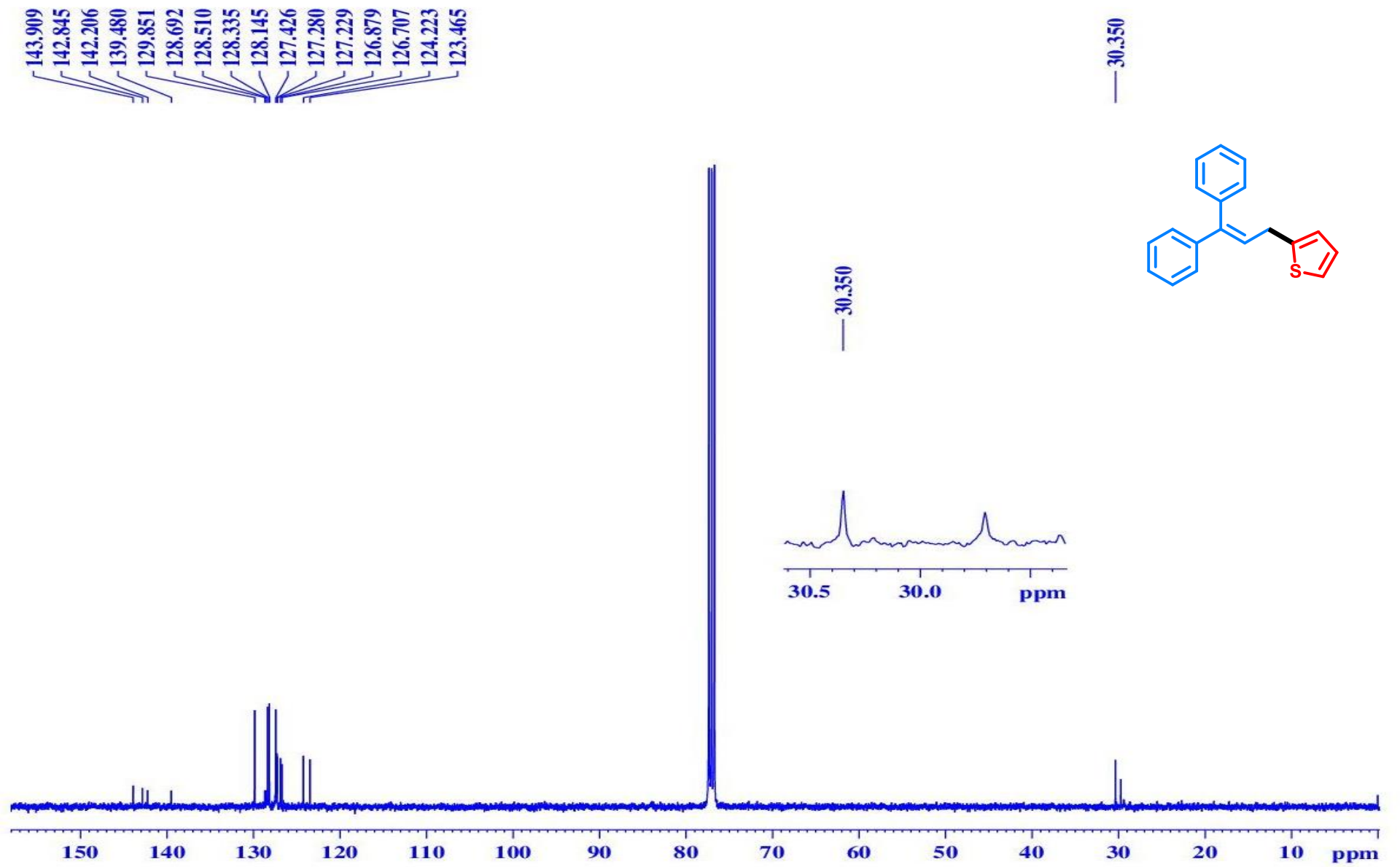
Compound 3ae ^{1}H NMR (400 MHz, $CDCl_3$)



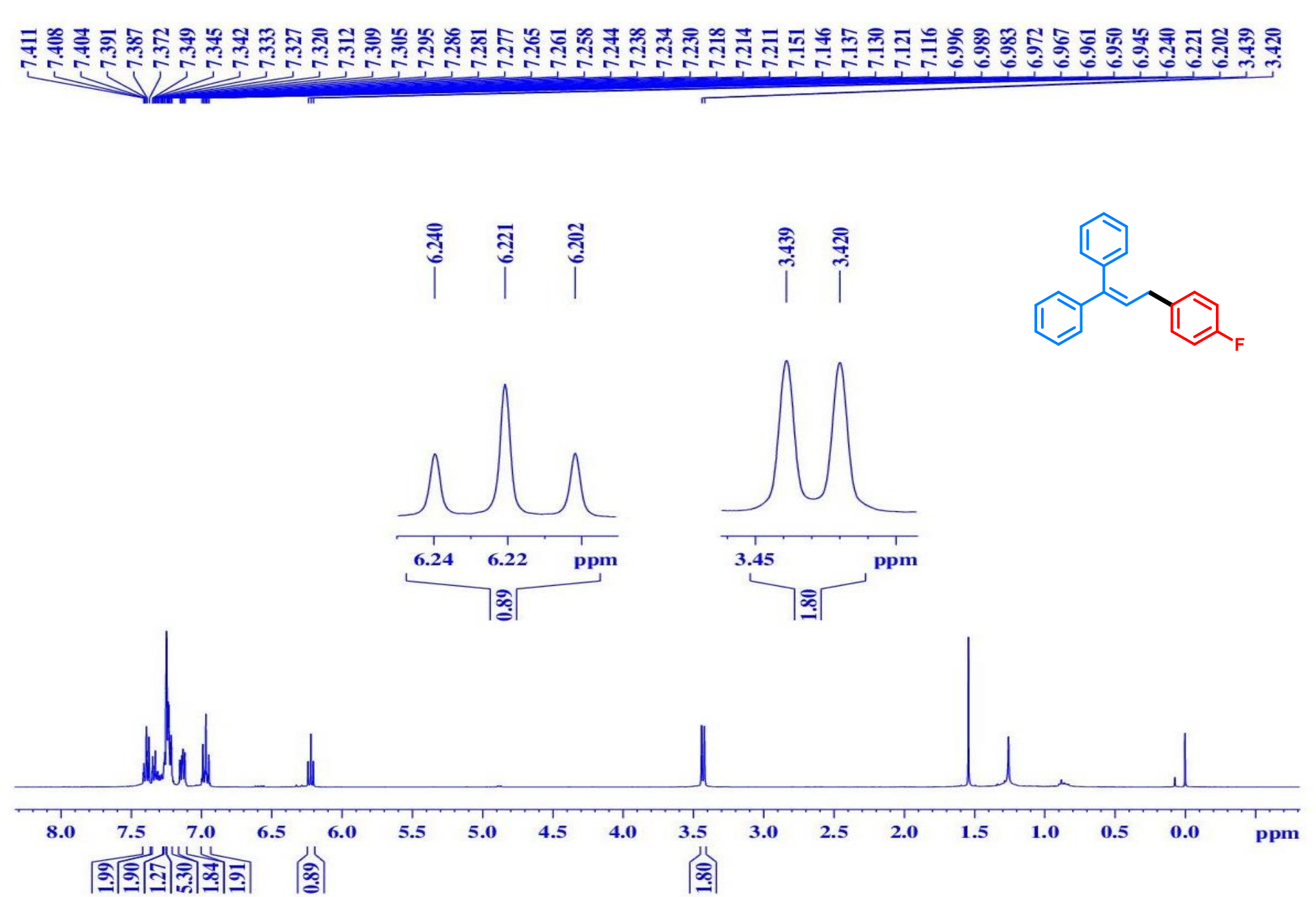
Compound 3ae ^{13}C NMR (100 MHz, $CDCl_3$)



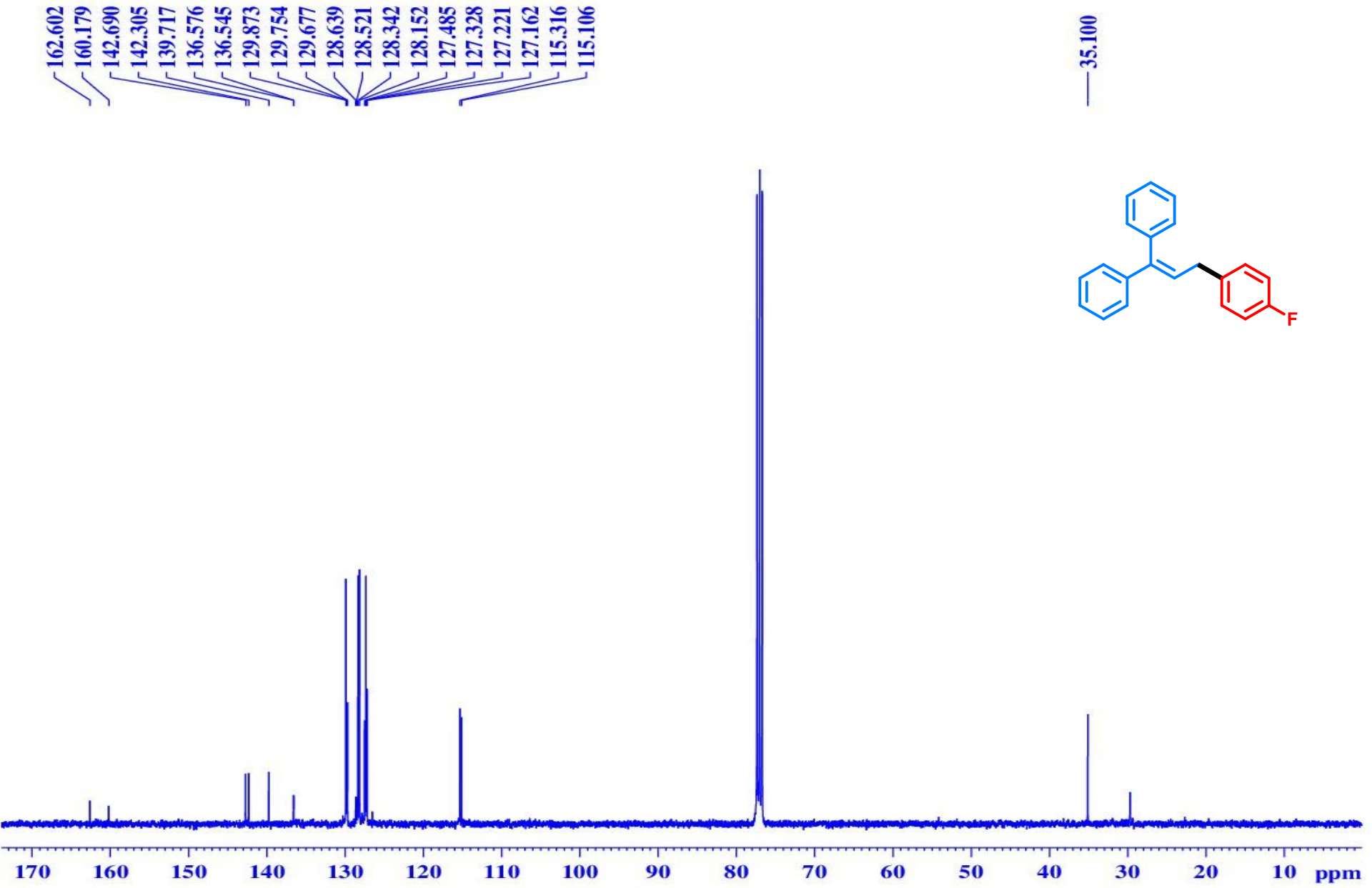
Compound 3af ^{1}H NMR (400 MHz, $CDCl_3$)



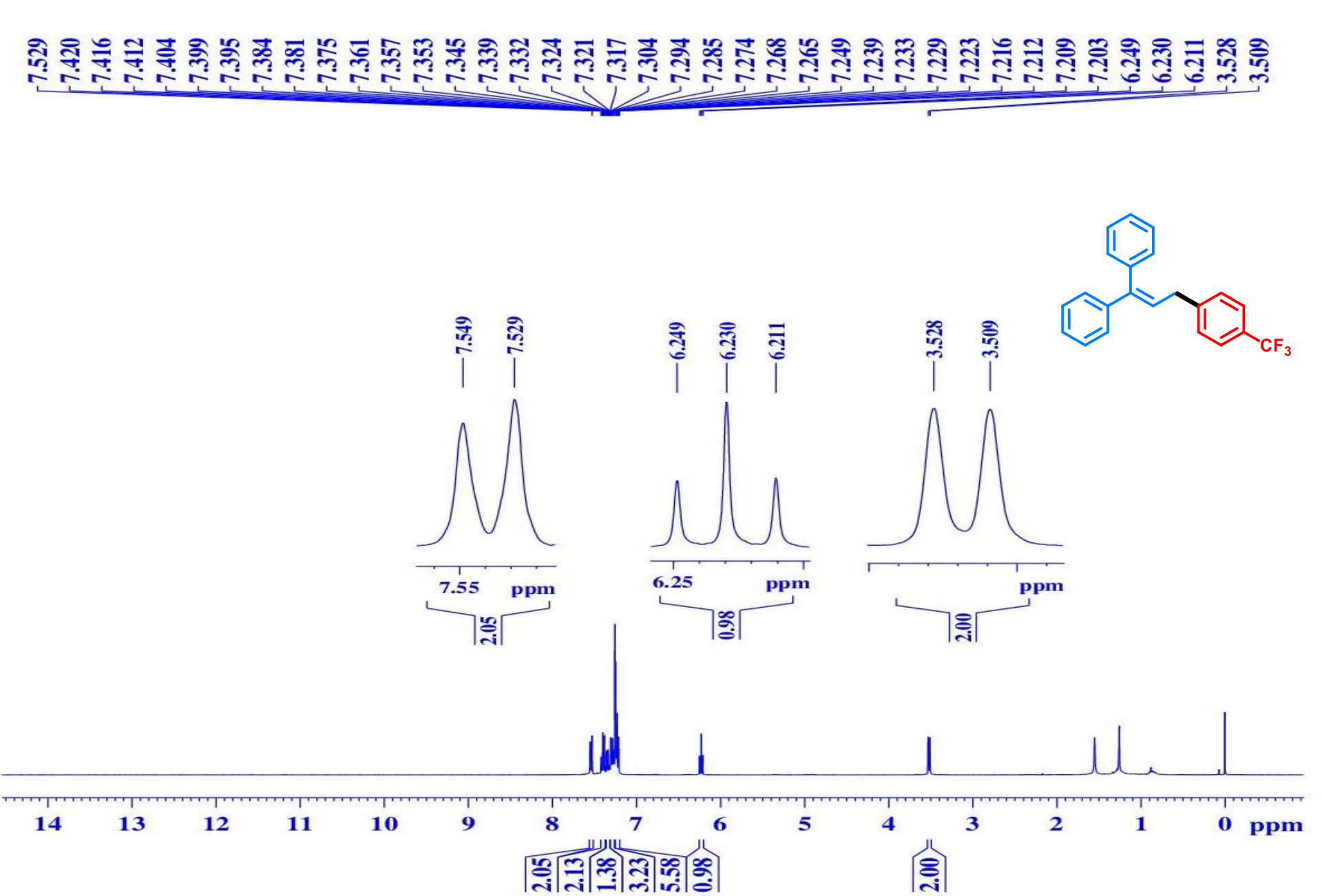
Compound 3af ^{13}C NMR (100 MHz, $CDCl_3$)



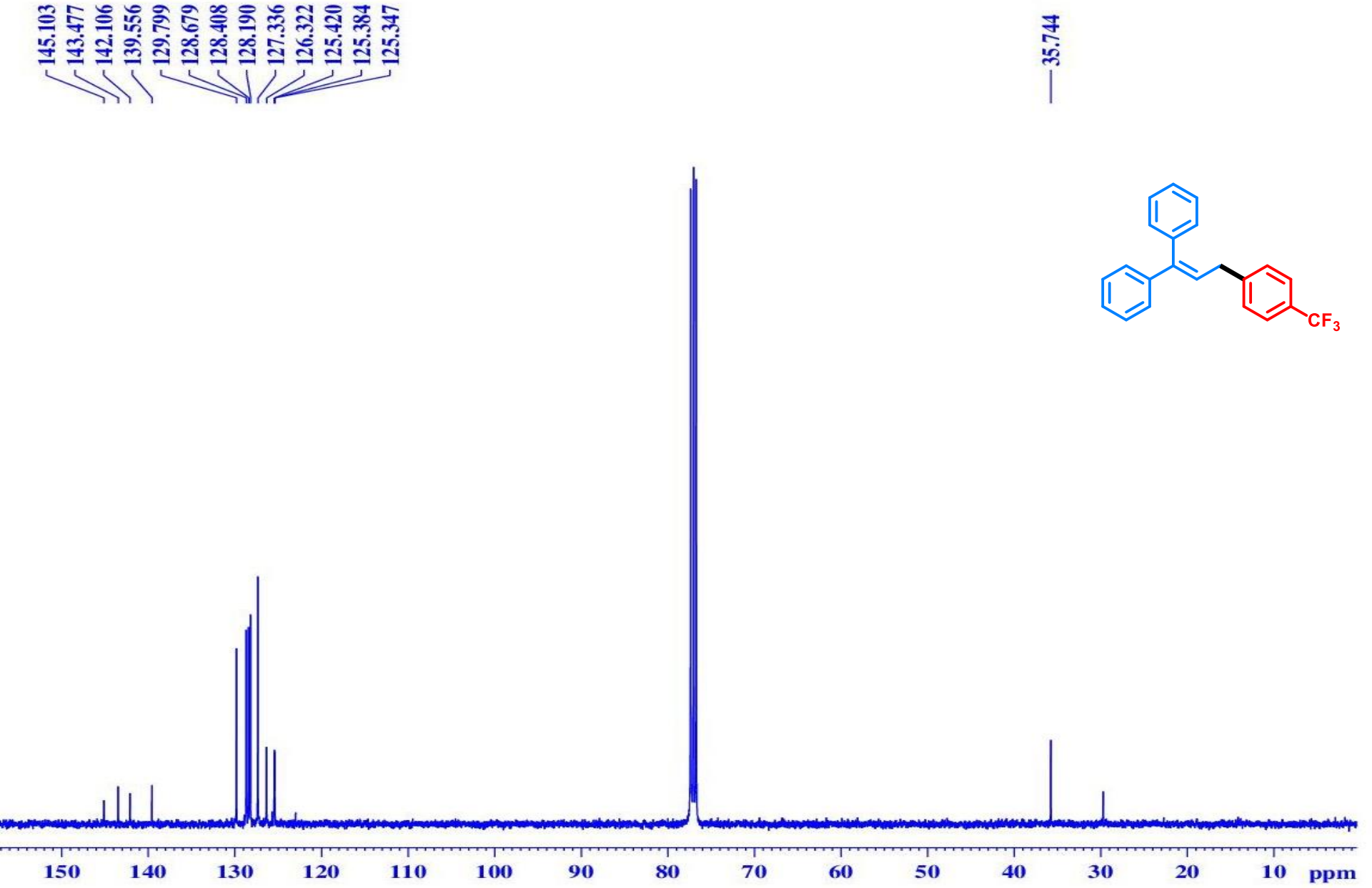
Compound 3ag ^{1}H NMR (400 MHz, $CDCl_3$)



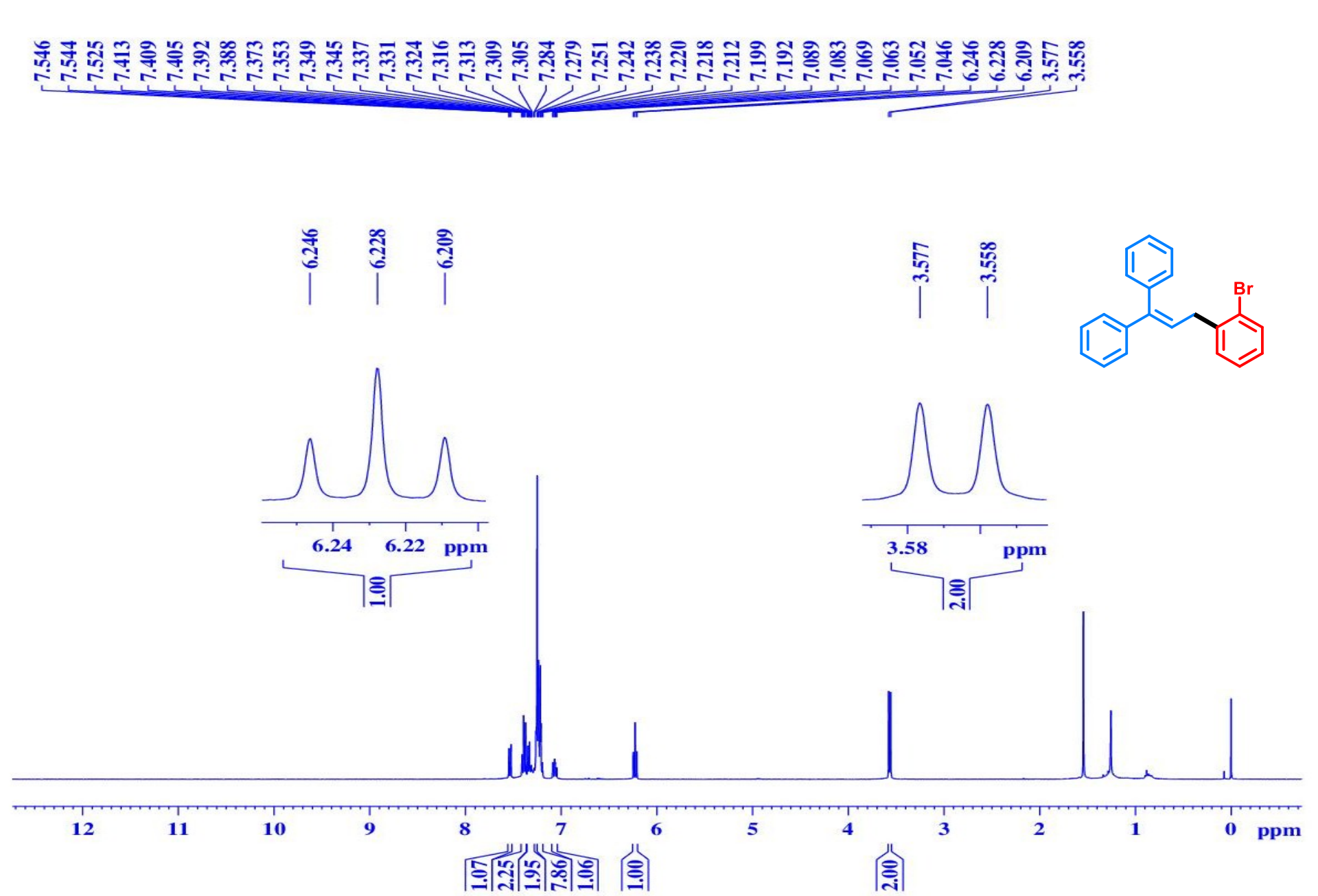
Compound 3ag ^{13}C NMR (100 MHz, $CDCl_3$)



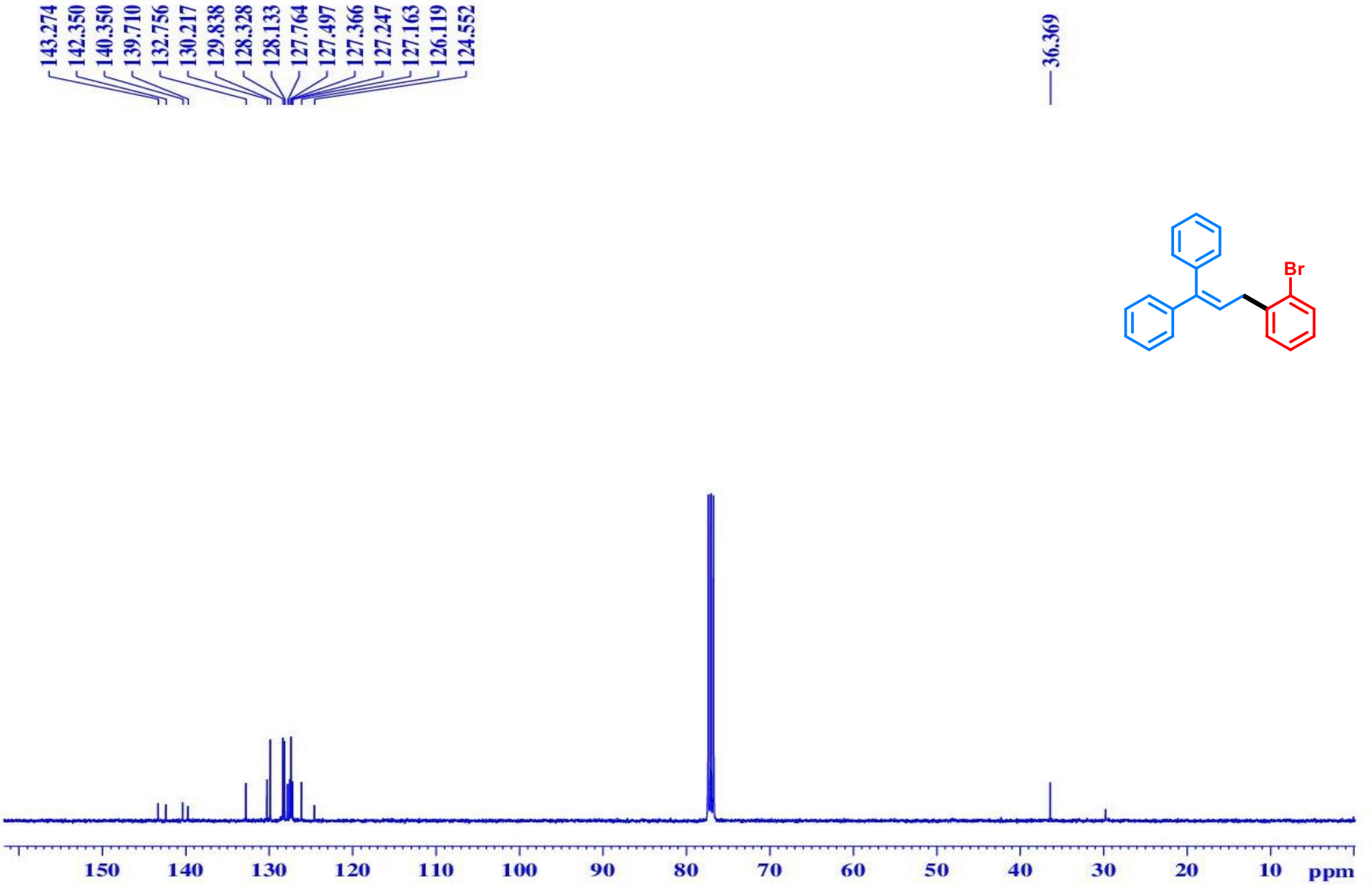
Compound 3ah ^{1}H NMR (400 MHz, $CDCl_3$)



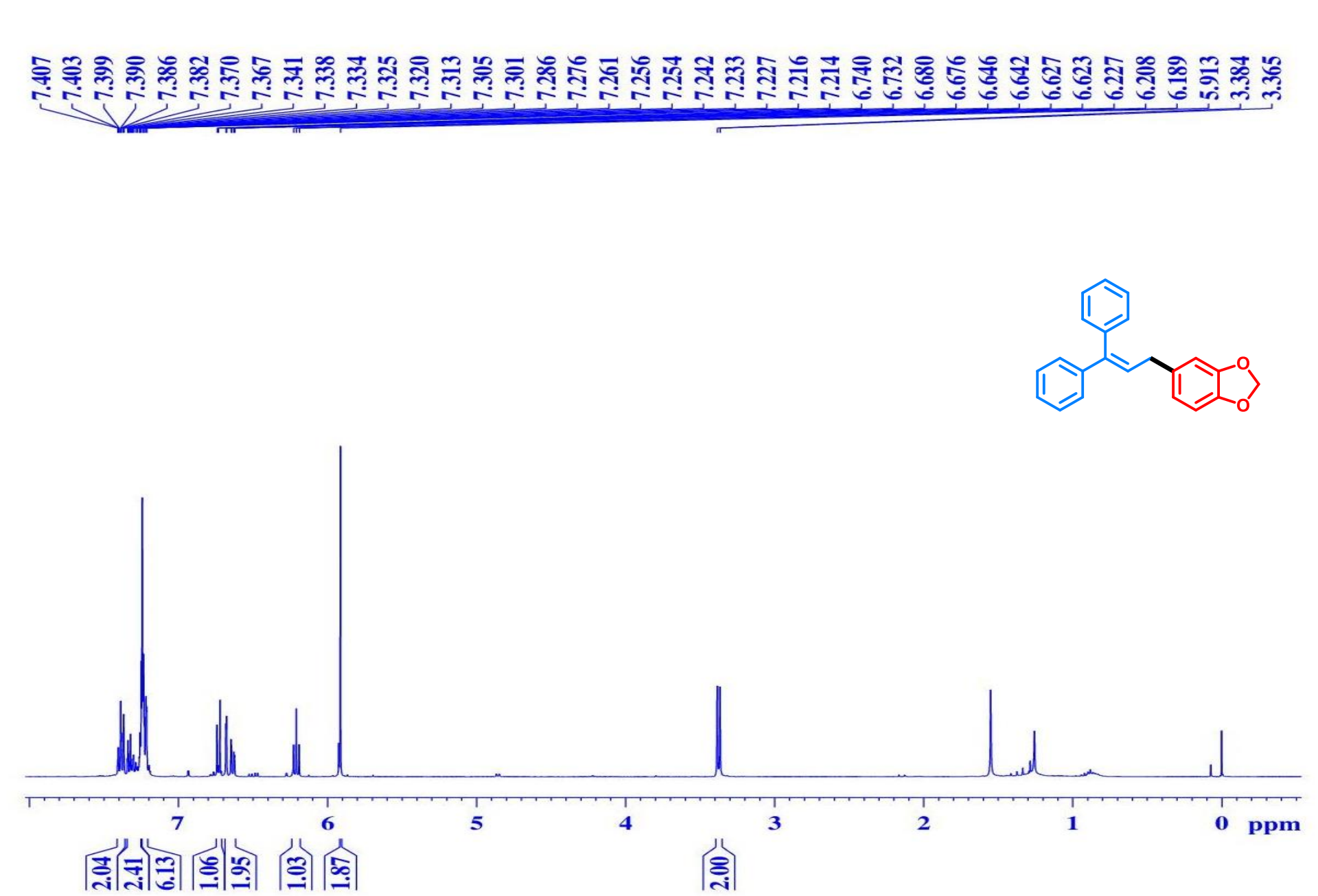
Compound 3ah ^{13}C NMR (100 MHz, $CDCl_3$)



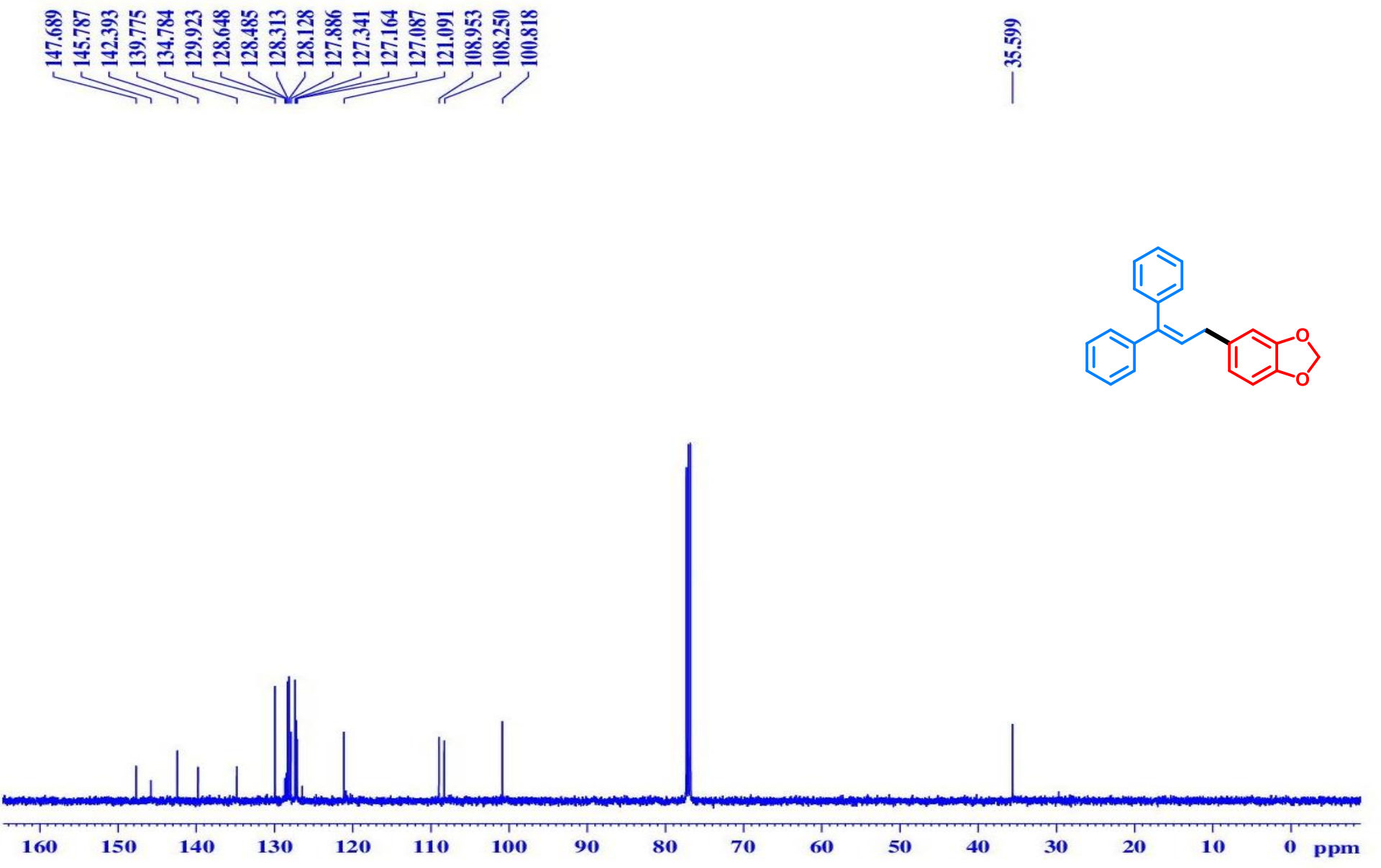
Compound 3ai ^{1}H NMR (400 MHz, $CDCl_3$)



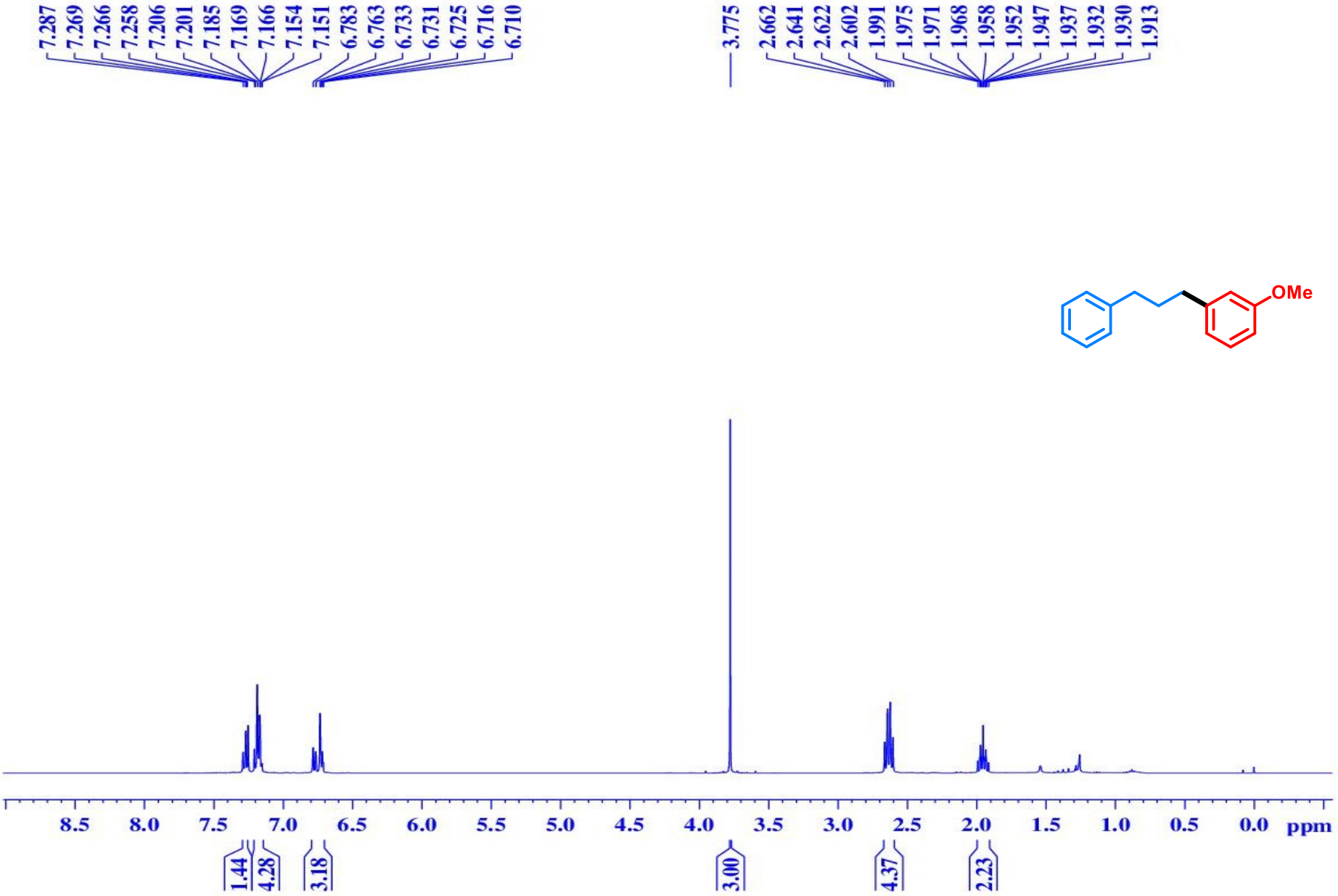
Compound 3ai ^{13}C NMR (100 MHz, $CDCl_3$)



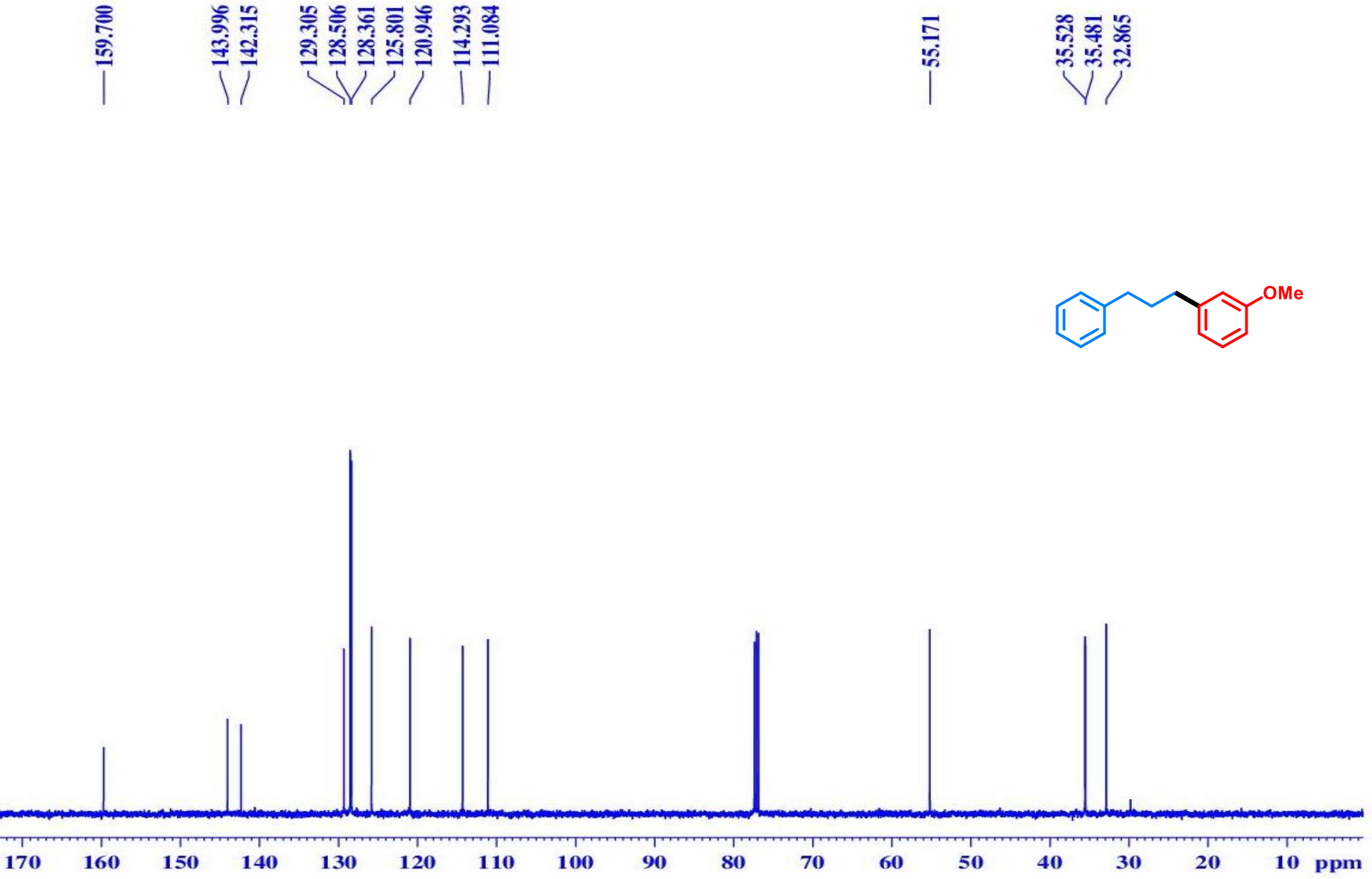
Compound 3aj ^{1}H NMR (400 MHz, $CDCl_3$)



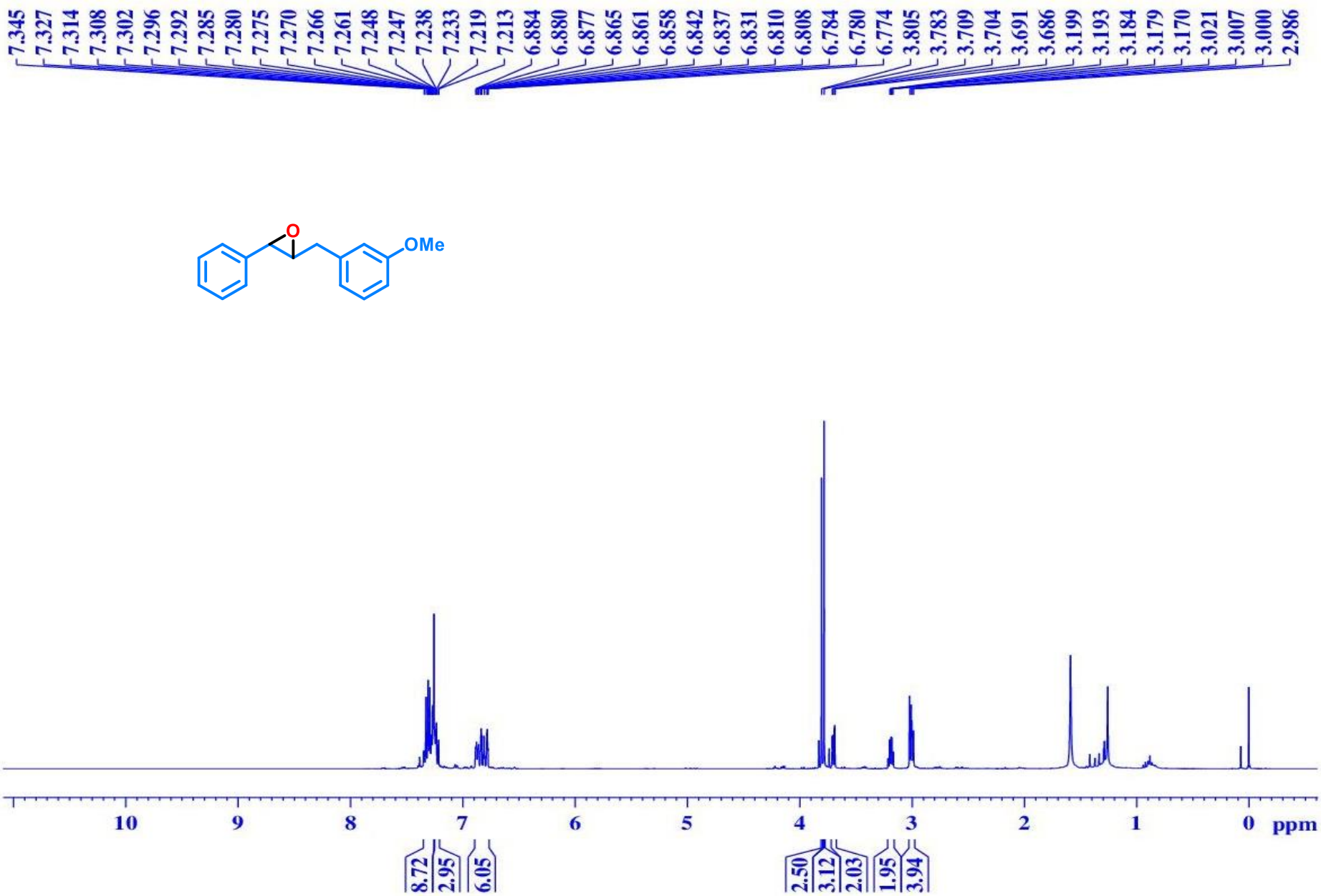
Compound 3aj ^{13}C NMR (100 MHz, $CDCl_3$)



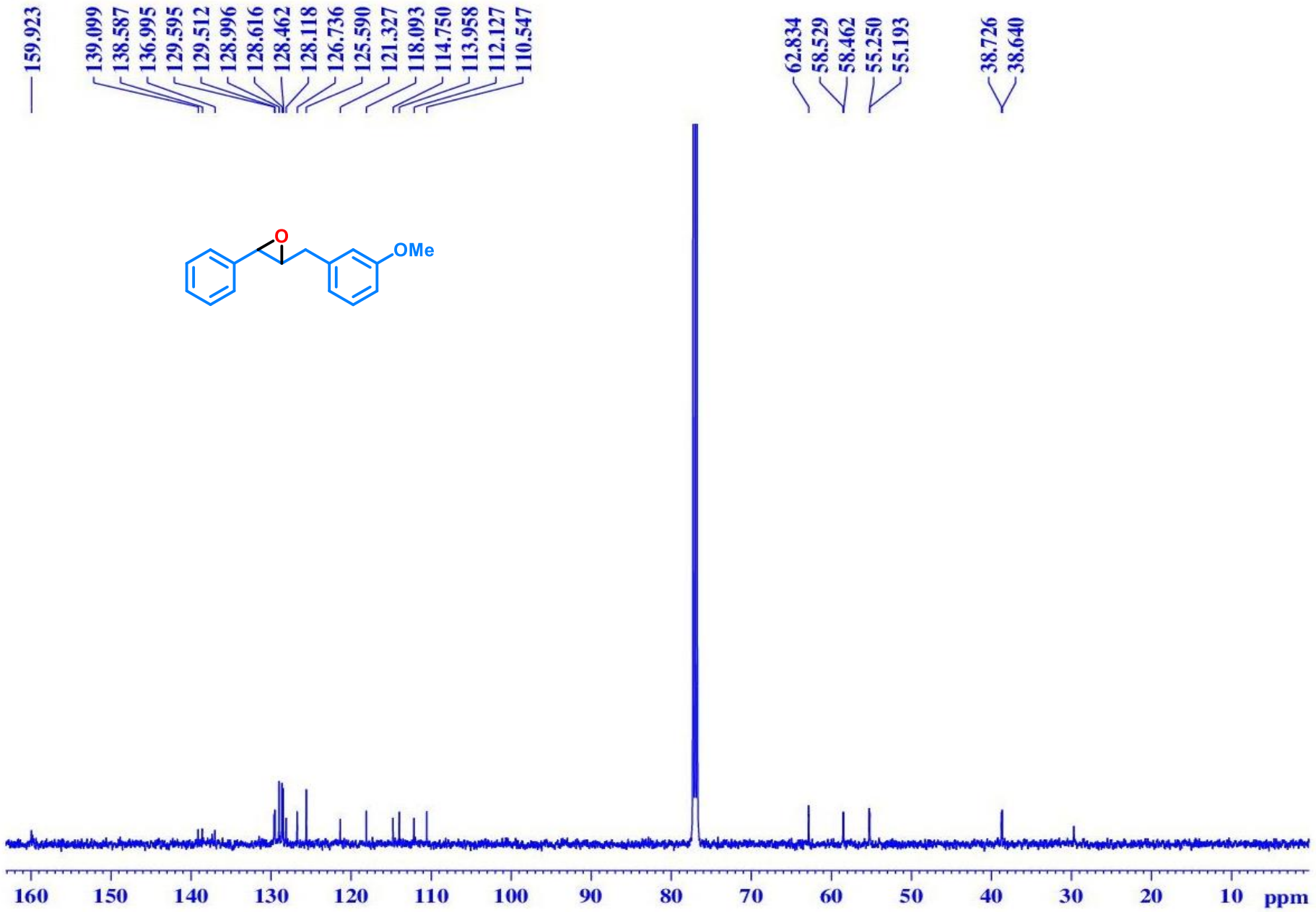
Compound 4 ^{1}H NMR (400 MHz, $CDCl_3$)



Compound 4 ^{13}C NMR (100 MHz, $CDCl_3$)



Compound 5 ^{13}C NMR (100 MHz, $CDCl_3$)



Compound 5 ^{13}C NMR (100 MHz, $CDCl_3$)