Supporting Information

A MULTIFIELD STUDY ON DIMETHYL ACETYLENEDICARBOXYLATE: A REAGENT ABLE TO BUILD A NEW CYCLE ON DIAMINOIMIDAZOLES

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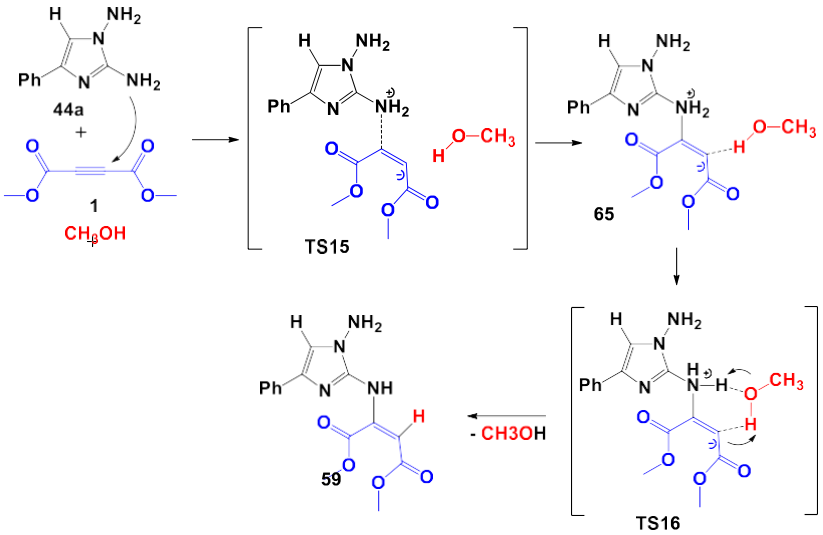
Content

Discussion of the results of quantum chemical calculations when alcohol molecules were included in the processes shown in Schemes S1 and S2

When alcohol molecules were included in the formation of covalent adduct **59** in **Scheme 11**, a similar picture was observed (**Scheme S1**). The alcohol molecule is coordinated in zwitterionic associate **65** with a negatively charged double bond carbon atom. Structure **65** was 38.5 kcal/mol higher in energy than the initial reagents (**Figure S1**). As in the previous cases, we observe the destabilization of the zwitterionic complex in comparison with a similar bimolecular processes. Associate **65** is 5.1 kcal/mol higher in energy than structure **58**.

Scheme S1.



The inclusion of an alcohol molecule at the molecular level did not affect the possibility of further cyclization, and the covalent product is still the final stage of the studied process.

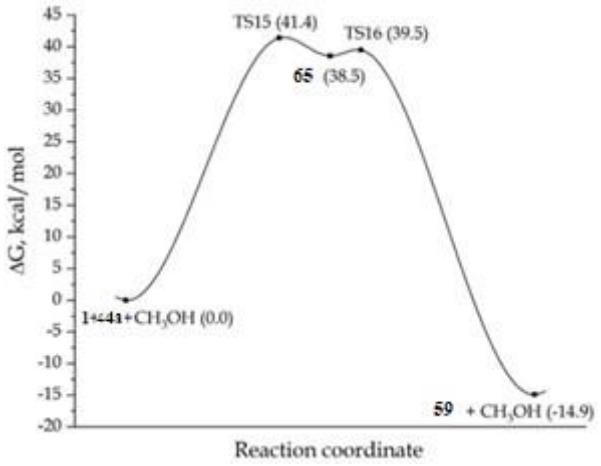
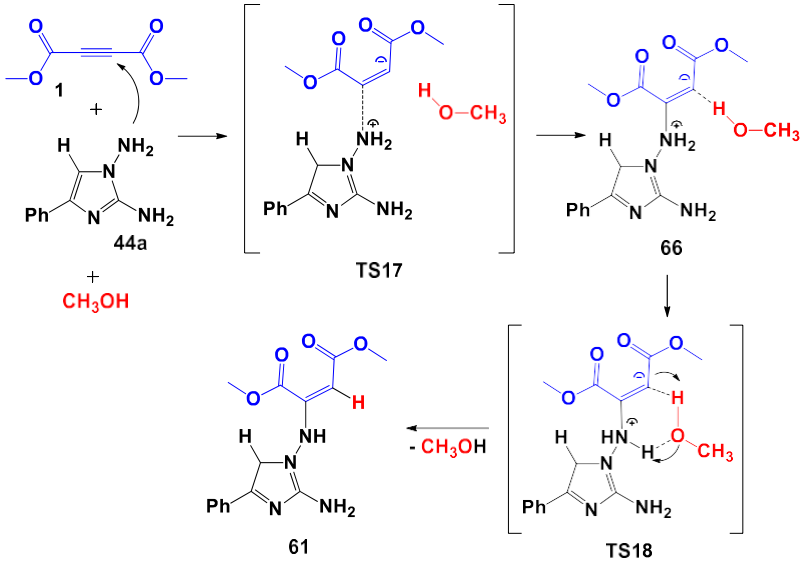


Figure S1. The MEP for the trimolecular reaction of the formation of adduct **59**. The total energy of the starting reagents is taken as the reference point.

The transition from a bimolecular process in **Scheme 12** to a trimolecular process involving an alcohol molecule in **Scheme S2** has a tendency similar to the three previously described cases. In particular, the formation of zwitterionic complex **66** becomes less advantageous in comparison with the bimolecular process (**Figure S2, Figure 6**.), and the proton transfer during the formation of covalent adduct **61** from structure **66** becomes barrier-free with the involvement of alcohol molecules.

Scheme S2.



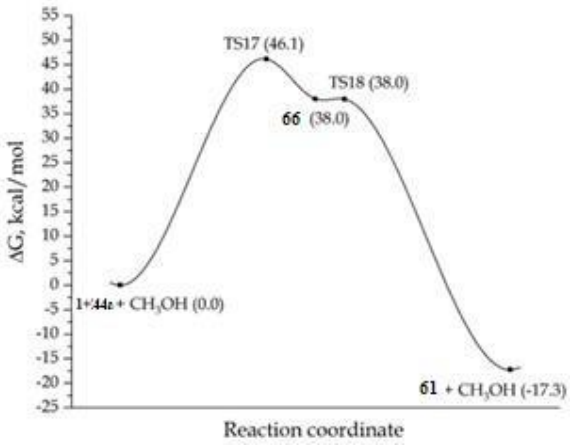
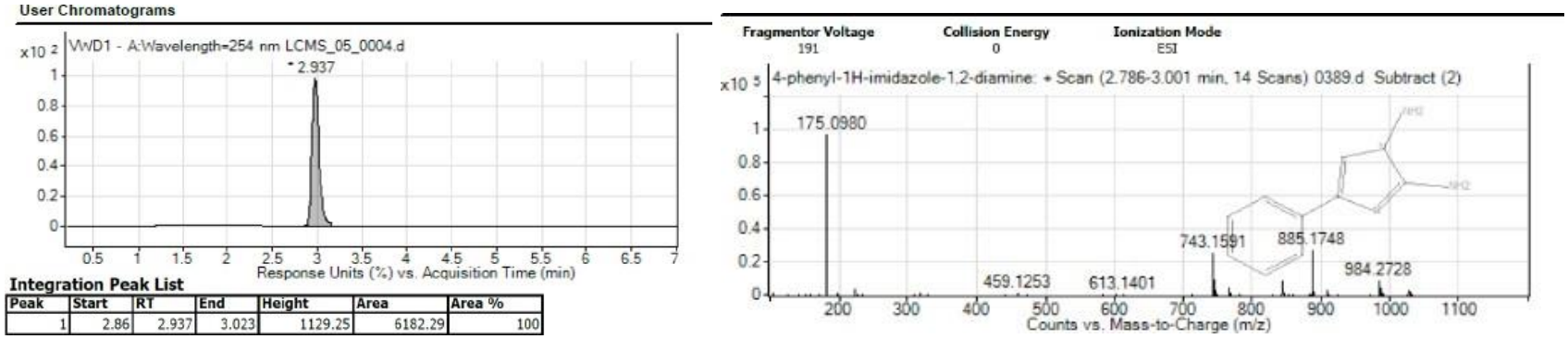


Figure S2. MEP for the trimolecular reaction of the formation of product **61**.The total energy of the starting reagents was taken as the reference point.

Results of HPLC-MS analysis in assessing the conversion of the studied process

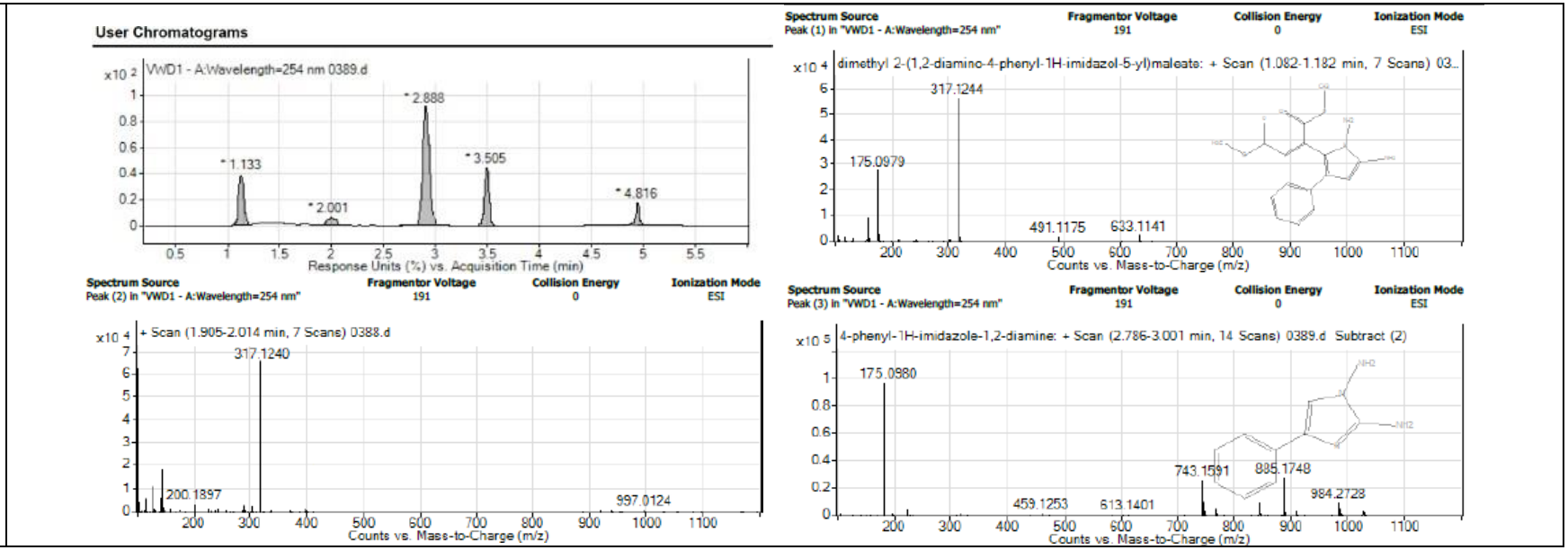
Table S1. Start of the reaction 0 minutes (independent of the solvent).



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	2.86	2.937	3.023	1129.25	6182.29	100

Table S2. Conducting the reaction in benzene.

60 minutes	

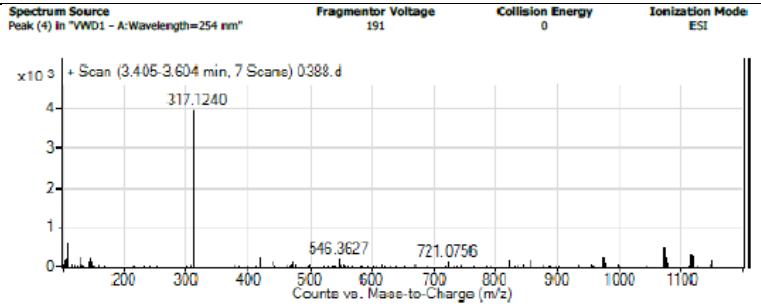
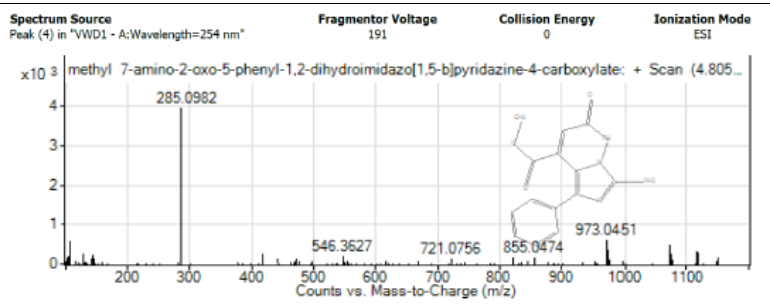
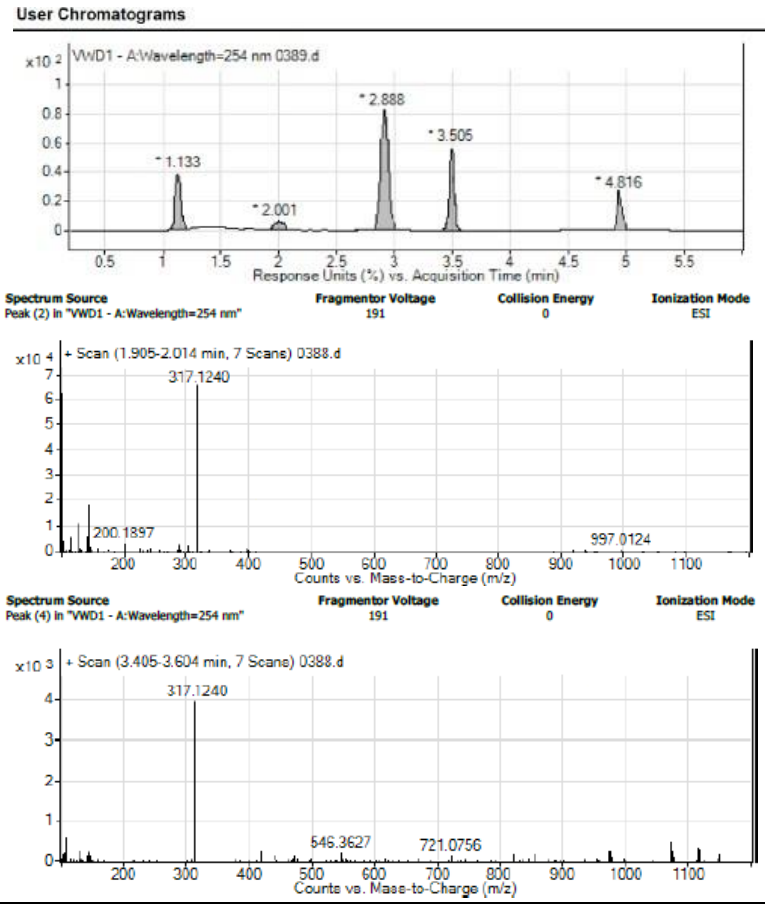
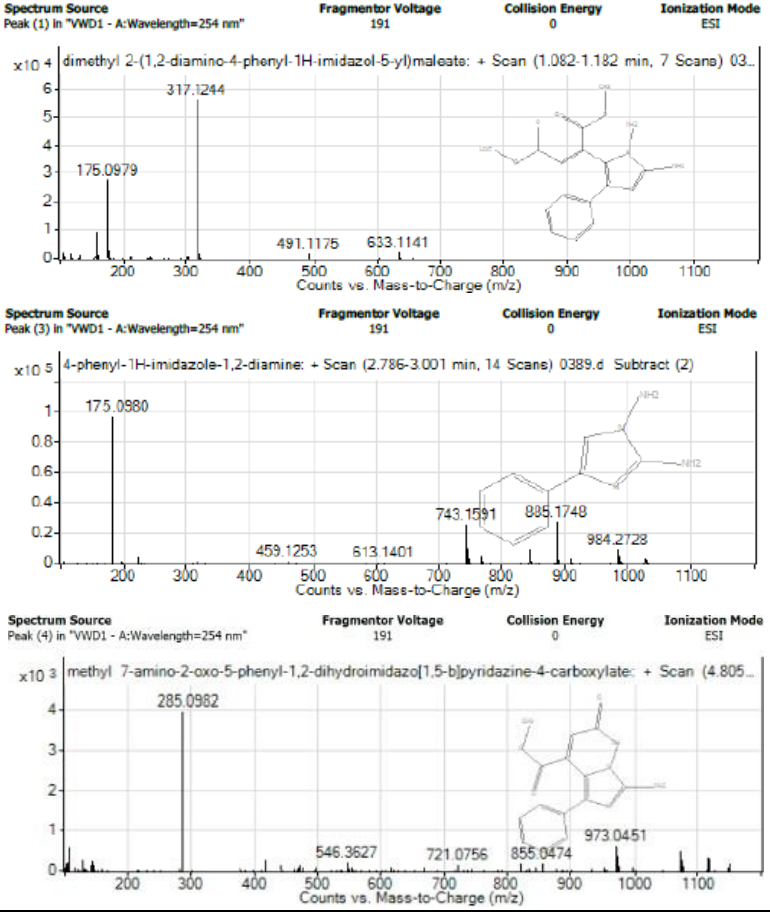
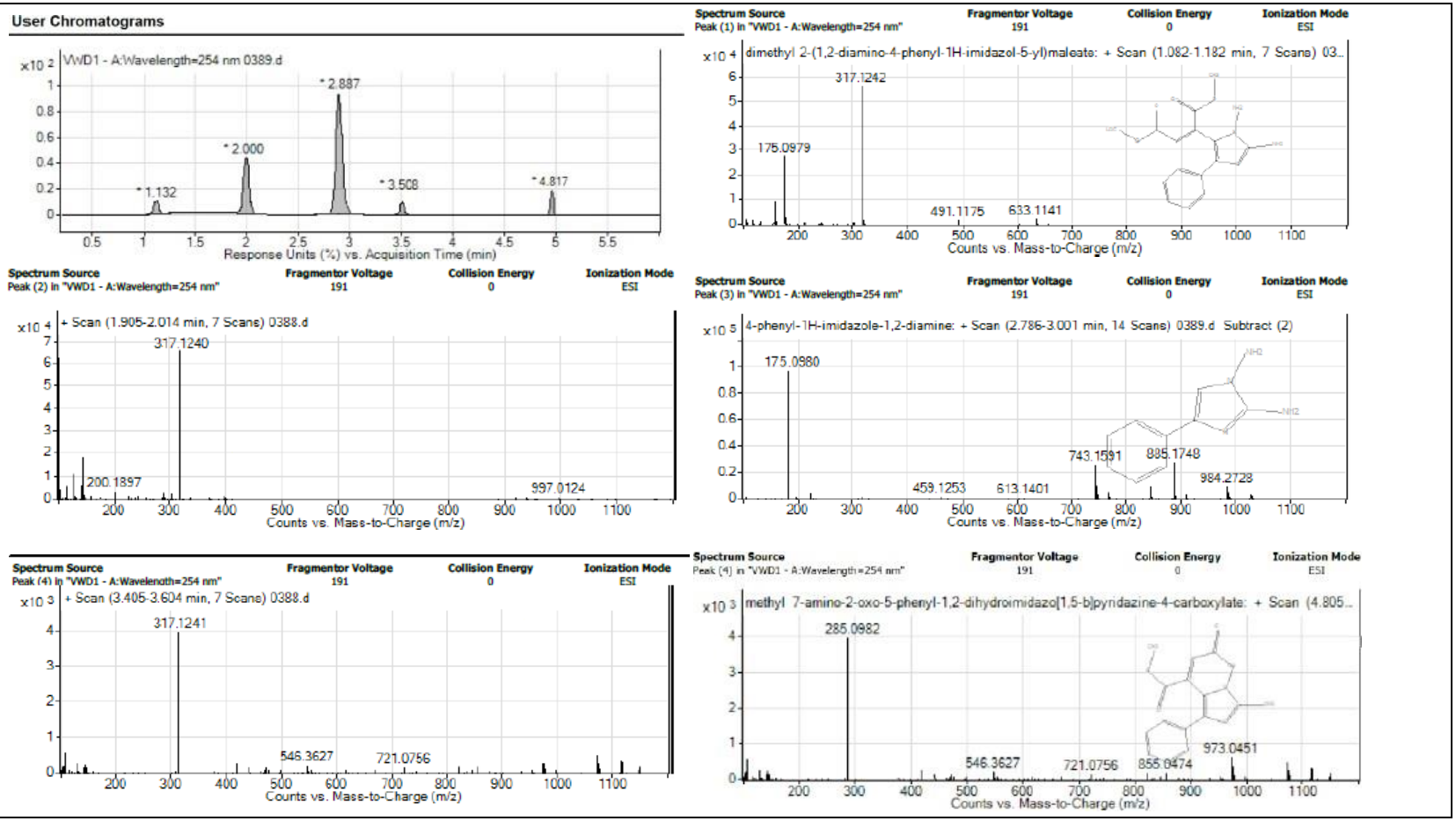
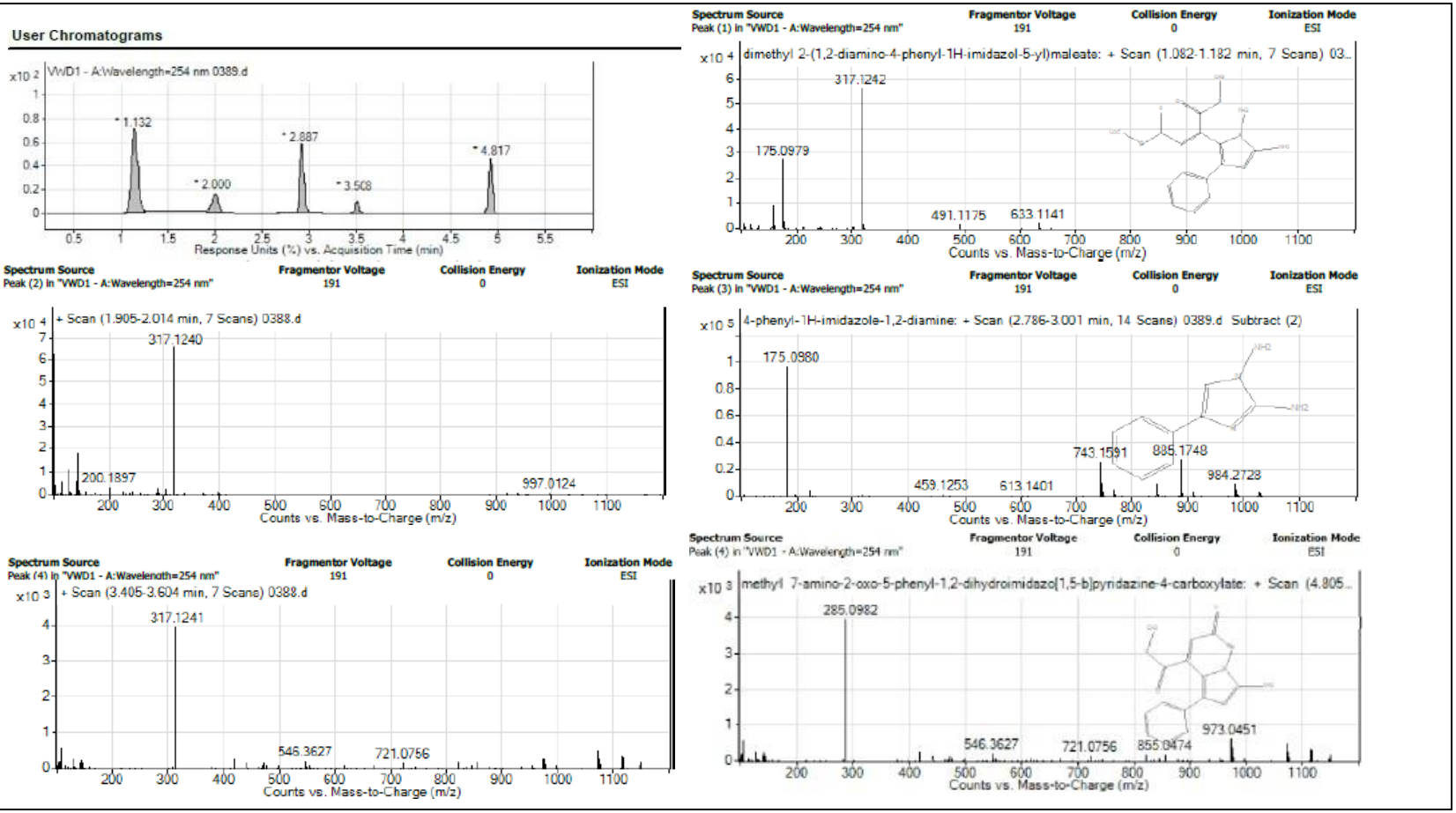
	 Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI + Scan (3.405-3.604 min, 7 Scans) 0388.d 317.1240 546.3627 721.0756 Counts vs. Mass-to-Charge (m/z)	 Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI methyl 7-amino-2-oxo-5-phenyl-1,2-dihydroimidazo[1,5-b]pyridazine-4-carboxylate: + Scan (4.805... 285.0982 546.3627 721.0756 855.0474 973.0451 Counts vs. Mass-to-Charge (m/z)
120 minutes	 User Chromatograms VWD1 - A:Wavelength=254 nm 0389.d * 1.133 * 2.001 * 2.888 * 3.505 * 4.816 Response Units (%) vs. Acquisition Time (min) Spectrum Source Peak (2) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI + Scan (1.905-2.014 min, 7 Scans) 0388.d 317.1240 200.1897 997.0124 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI + Scan (3.405-3.604 min, 7 Scans) 0388.d 317.1240 546.3627 721.0756 Counts vs. Mass-to-Charge (m/z)	 Spectrum Source Peak (1) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI dimethyl 2-(1,2-diamino-4-phenyl-1H-imidazol-5-yl)maleate: + Scan (1.082-1.182 min, 7 Scans) 03... 317.1244 175.0979 491.1175 633.1141 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (3) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI 4-phenyl-1H-imidazole-1,2-diamine: + Scan (2.786-3.001 min, 14 Scans) 0389.d Subtract (2) 175.0980 459.1253 613.1401 743.1591 885.1748 984.2728 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI methyl 7-amino-2-oxo-5-phenyl-1,2-dihydroimidazo[1,5-b]pyridazine-4-carboxylate: + Scan (4.805... 285.0982 546.3627 721.0756 855.0474 973.0451 Counts vs. Mass-to-Charge (m/z)

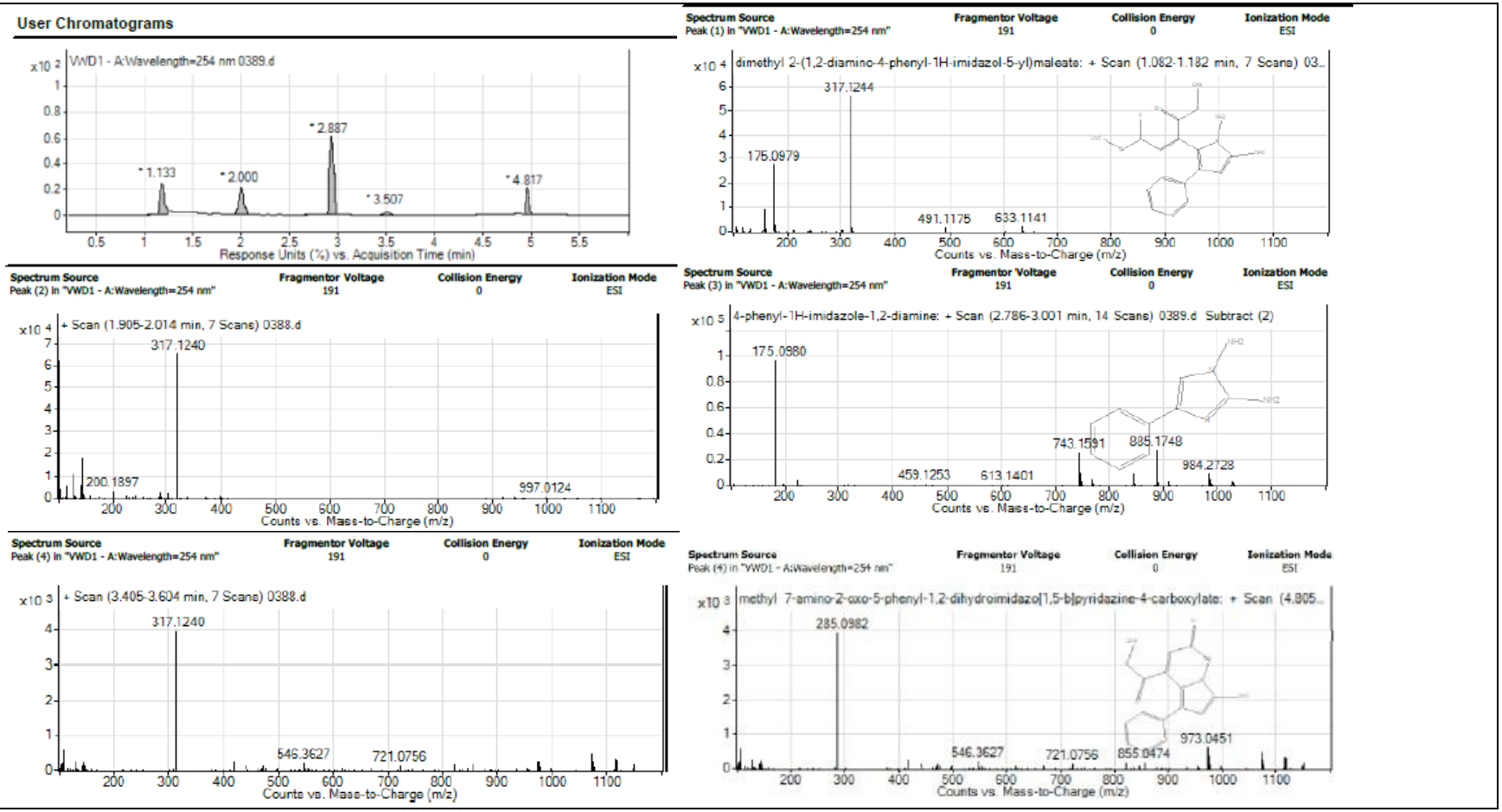
Table S3. Conducting the reaction in 1,4-dioxane.

60 minutes	

120 minutes	

User Chromatograms
VWD1 - A:Wavelength=254 nm 0389.d
1.132
2.000
2.887
3.508
4.817
Response Units (%) vs. Acquisition Time (min)
Spectrum Source
Peak (1) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
dimethyl 2-(1,2-diamino-4-phenyl-1H-imidazol-5-yl)maleate: + Scan (1.082-1.182 min, 7 Scans) 03...
317.1242
175.0979
491.1175
633.1141
Counts vs. Mass-to-Charge (m/z)
Spectrum Source
Peak (2) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
+ Scan (1.905-2.014 min, 7 Scans) 0388.d
317.1240
200.1897
997.0124
Counts vs. Mass-to-Charge (m/z)
Spectrum Source
Peak (3) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
4-phenyl-1H-imidazole-1,2-diamine: + Scan (2.786-3.001 min, 14 Scans) 0389.d Subtract (2)
175.0980
459.1253
613.1401
743.1591
885.1748
984.2728
Counts vs. Mass-to-Charge (m/z)
Spectrum Source
Peak (4) in "VWD1 - A:Wavelenoth=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
+ Scan (3.405-3.604 min, 7 Scans) 0388.d
317.1241
546.3627
721.0756
Counts vs. Mass-to-Charge (m/z)
Spectrum Source
Peak (4) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
methyl 7-amino-2-oxo-5-phenyl-1,2-dihydroimidazo[1,5-b]pyridazine-4-carboxylate: + Scan (4.805...
285.0982
546.3627
721.0756
855.0474
973.0451
Counts vs. Mass-to-Charge (m/z)

Table S4. Conducting the reaction in methylene chloride.

60 minutes	

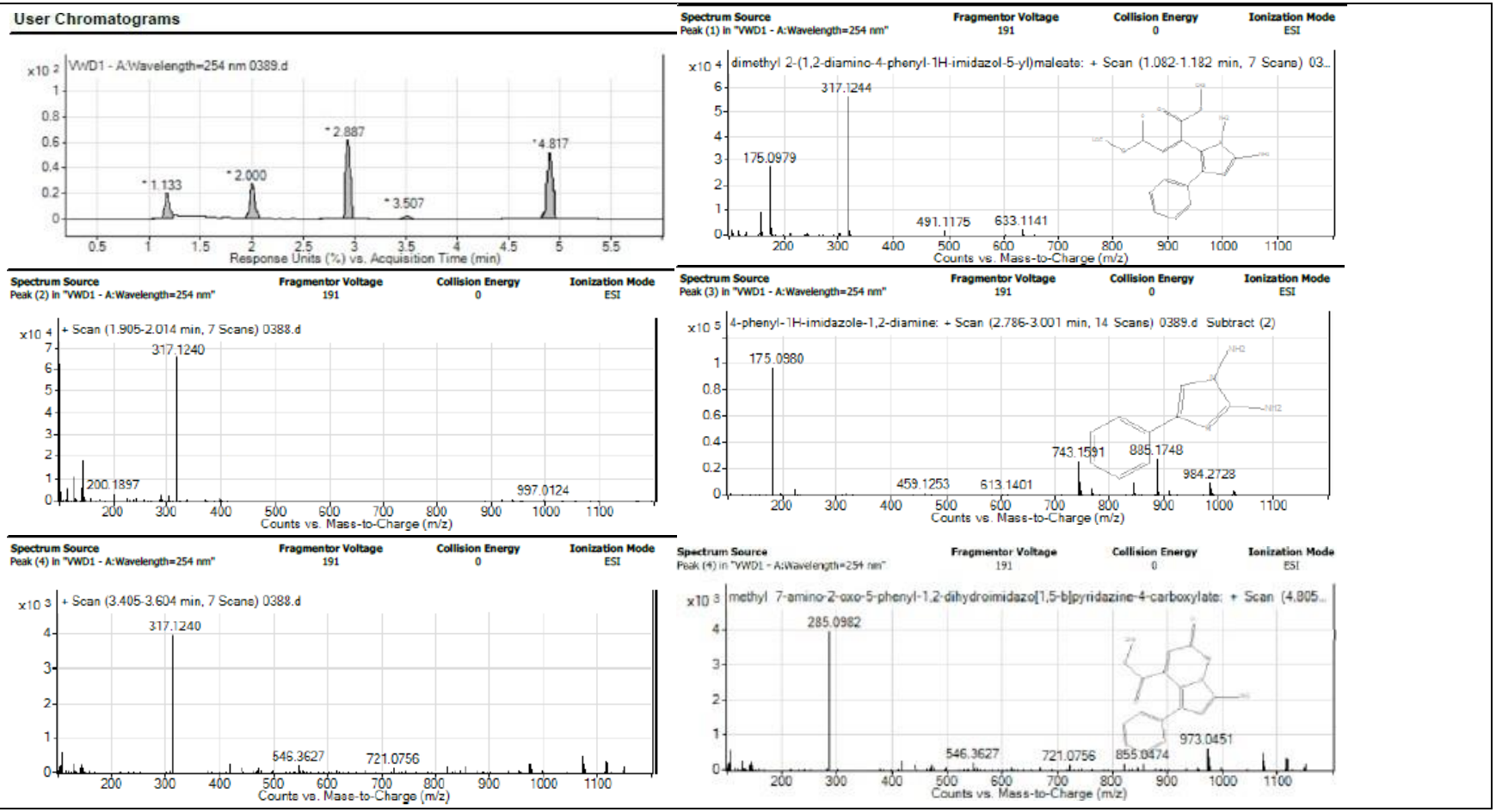
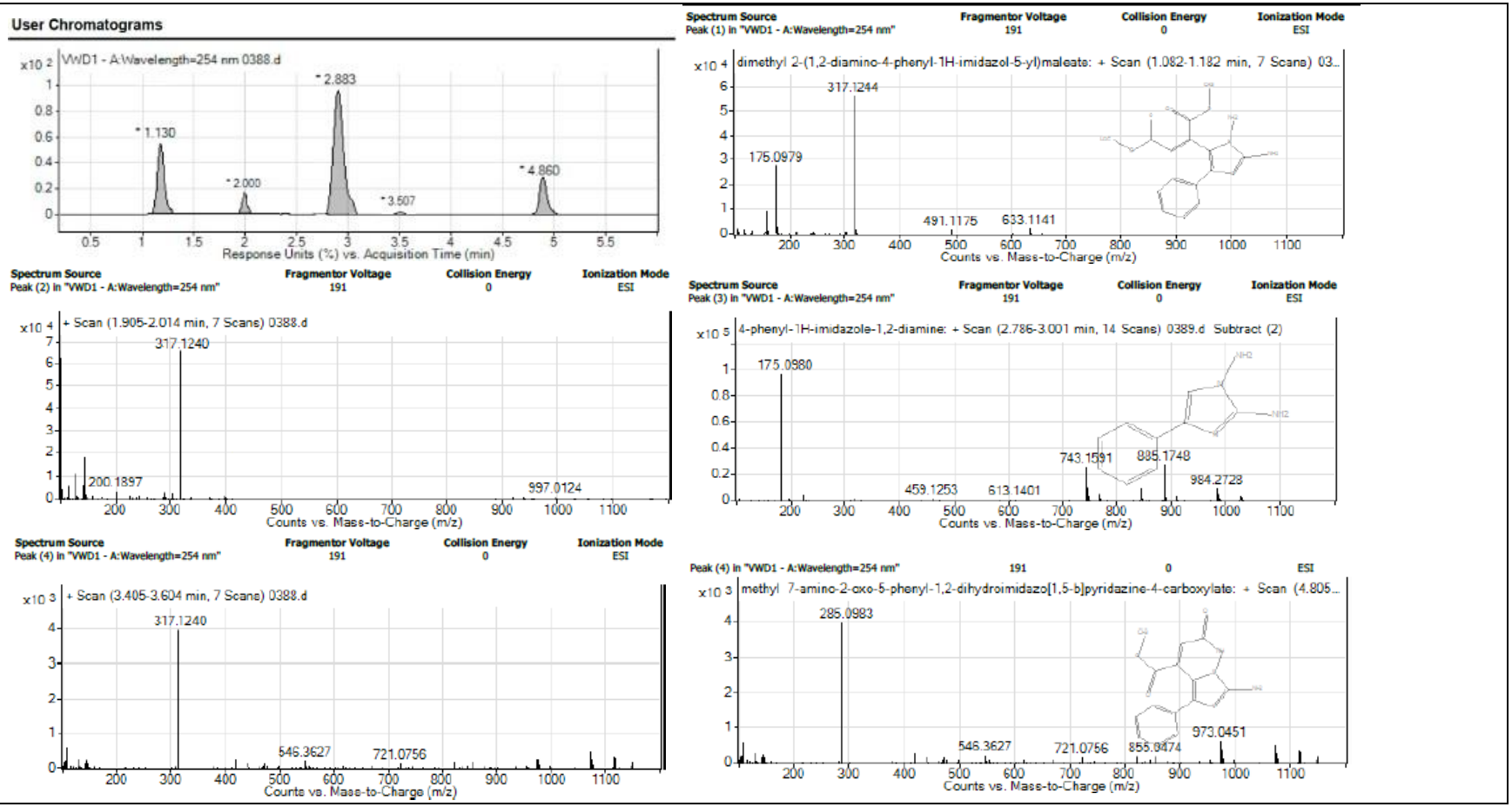
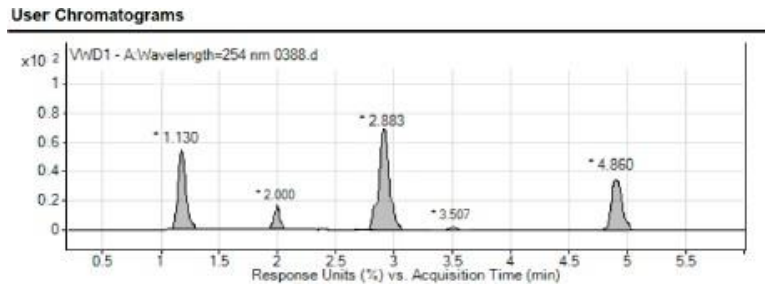
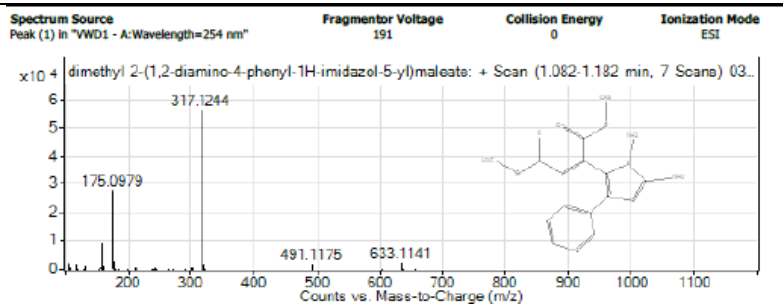
120 minutes	 User Chromatograms VWD1 - A:Wavelength=254 nm 0389.d * 1.133 * 2.000 * 2.887 * 3.507 * 4.817 Response Units (%) vs. Acquisition Time (min) Spectrum Source Peak (1) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI dimethyl 2-(1,2-diamino-4-phenyl-1H-imidazol-5-yl)maleate: + Scan (1.082-1.182 min, 7 Scans) 03... 317.1244 175.0979 491.1175 633.1141 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (2) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI + Scan (1.905-2.014 min, 7 Scans) 0388.d 317.1240 200.1897 997.0124 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (3) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI 4-phenyl-1H-imidazole-1,2-diamine: + Scan (2.786-3.001 min, 14 Scans) 0389.d Subtract (2) 175.0980 743.1591 885.1748 984.2728 459.1253 613.1401 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI + Scan (3.405-3.604 min, 7 Scans) 0388.d 317.1240 546.3627 721.0756 Counts vs. Mass-to-Charge (m/z) Spectrum Source Peak (4) in "VWD1 - A:Wavelength=254 nm" Fragmentor Voltage 191 Collision Energy 0 Ionization Mode ESI methyl 7-amino-2-oxo-5-phenyl-1,2-dihydroimidazo[1,5-b]pyridazine-4-carboxylate: + Scan (4.805... 285.0982 546.3627 721.0756 855.0474 973.0451 Counts vs. Mass-to-Charge (m/z)

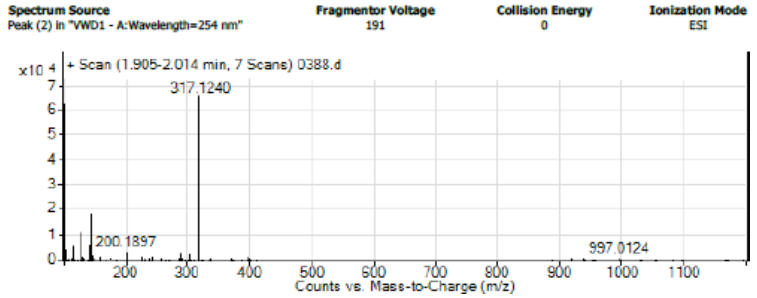
Table S5. Conducting the reaction in chloroform.

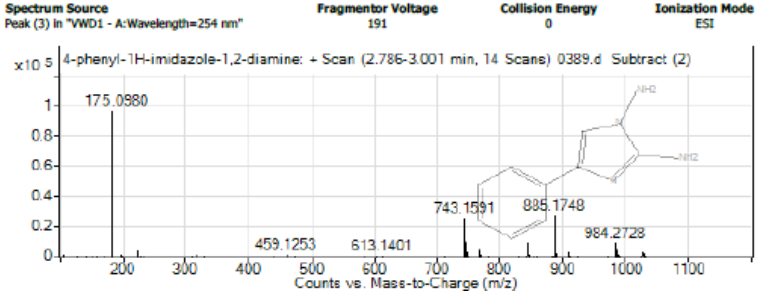
60 minutes	

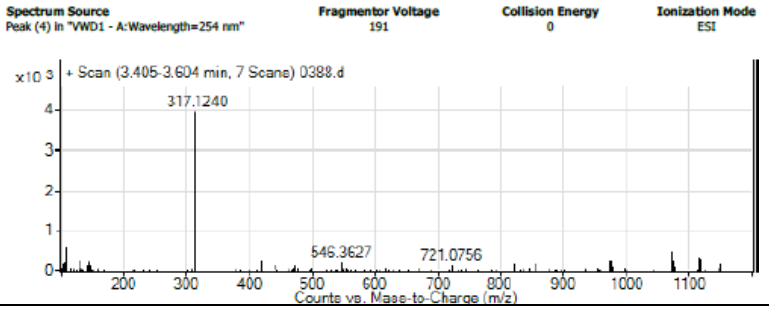
120 minutes


User Chromatograms
VWD1 - A:Wavelength=254 nm 0388.d
1.130
2.000
2.883
3.507
4.860
Response Units (%) vs. Acquisition Time (min)


Spectrum Source
Peak (1) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
dimethyl 2-(1,2-diamino-4-phenyl-1H-imidazol-5-yl)maleate: + Scan (1.082-1.182 min, 7 Scans) 03...
317.1244
175.0979
491.1175
633.1141
Counts vs. Mass-to-Charge (m/z)


Spectrum Source
Peak (2) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
+ Scan (1.905-2.014 min, 7 Scans) 0388.d
317.1240
200.1897
997.0124
Counts vs. Mass-to-Charge (m/z)


Spectrum Source
Peak (3) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
4-phenyl-1H-imidazole-1,2-diamine: + Scan (2.786-3.001 min, 14 Scans) 0389.d Subtract (2)
175.0980
743.1591
885.1748
984.2728
459.1253
613.1401
Counts vs. Mass-to-Charge (m/z)


Spectrum Source
Peak (4) in "VWD1 - A:Wavelength=254 nm"
Fragmentor Voltage
191
Collision Energy
0
Ionization Mode
ESI
+ Scan (3.405-3.604 min, 7 Scans) 0388.d
317.1240
546.3627
721.0756
Counts vs. Mass-to-Charge (m/z)

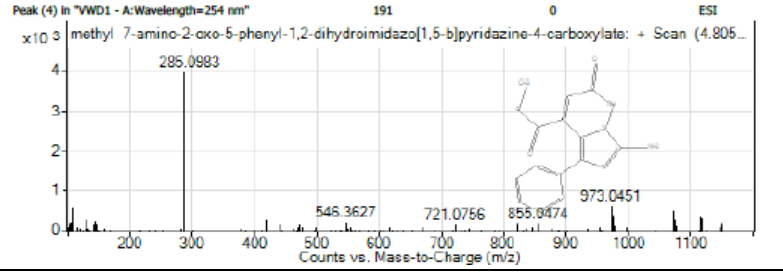

Peak (4) in "VWD1 - A:Wavelength=254 nm"
191
0
ESI
methyl 7-amino-2-oxo-5-phenyl-1,2-dihydroimidazo[1,5-b]pyridazine-4-carboxylate: + Scan (4.805...
285.0983
546.3627
721.0756
855.9474
973.0451
Counts vs. Mass-to-Charge (m/z)

Table S6. Conducting the reaction in methanol.

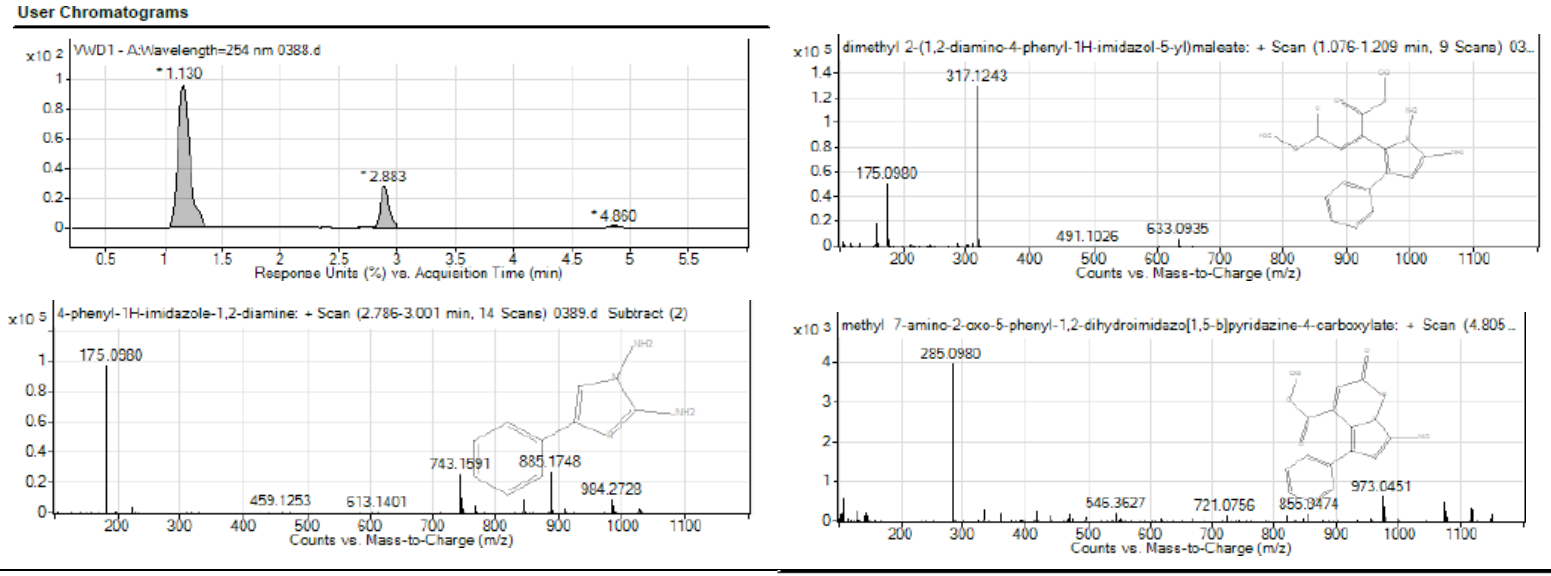
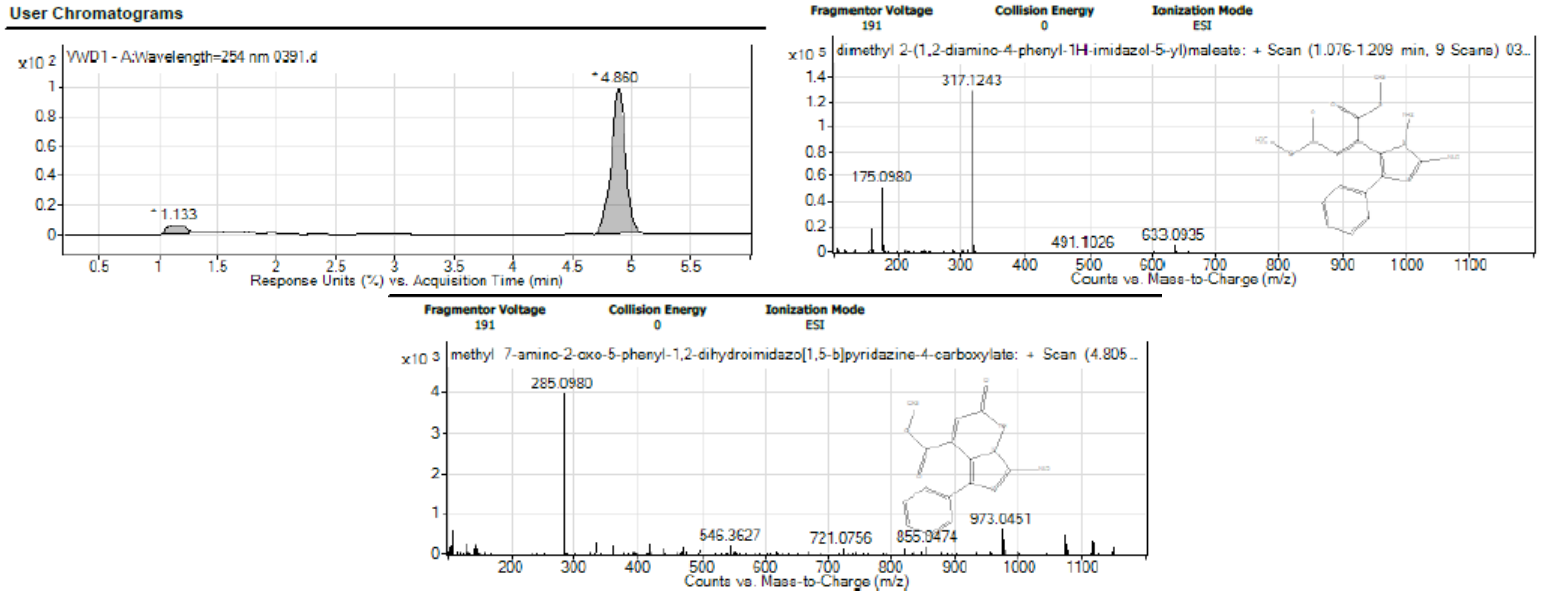
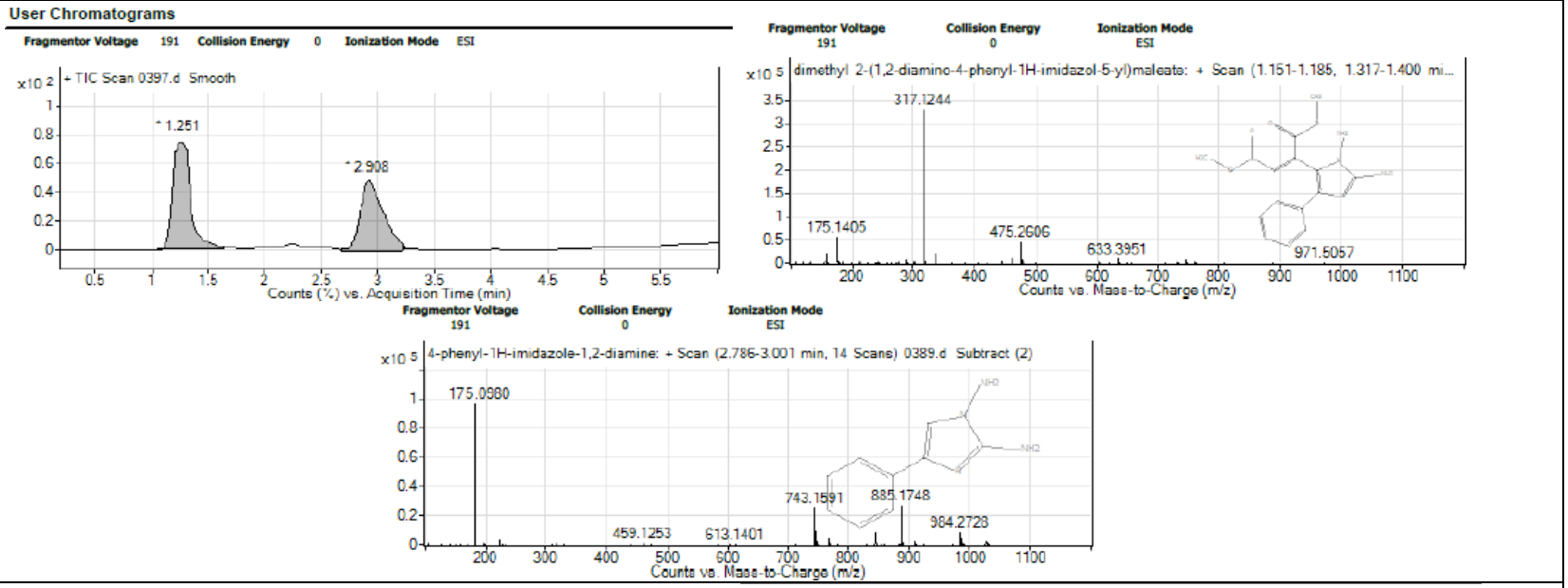
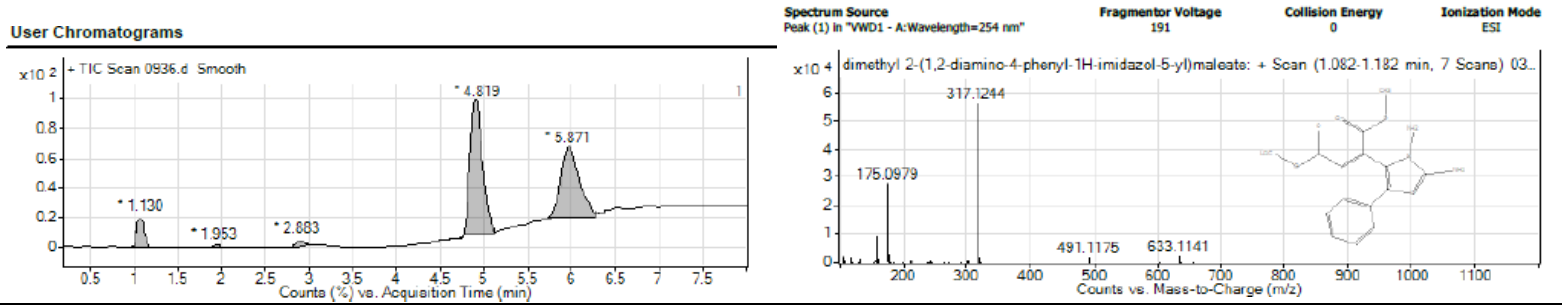
60 minutes	
120 minutes	

Table S7. Conducting the reaction in ethanol.

60 minutes	
120 minutes	

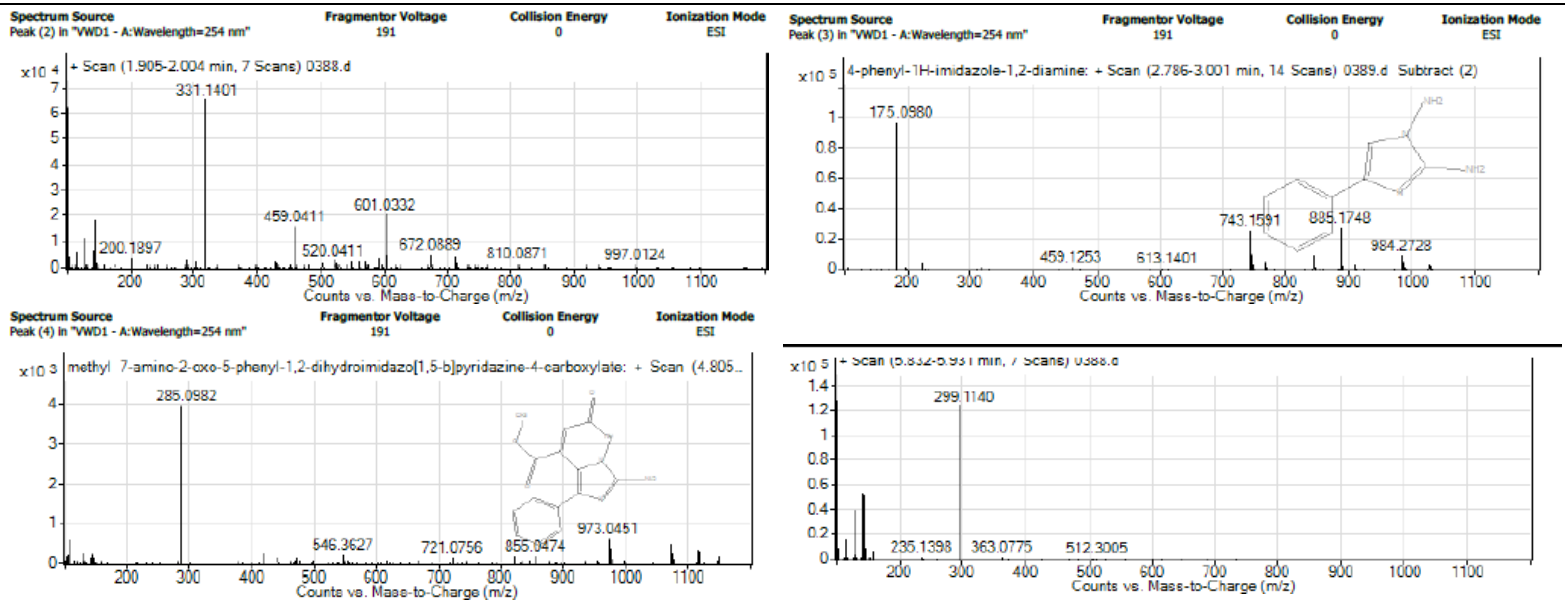
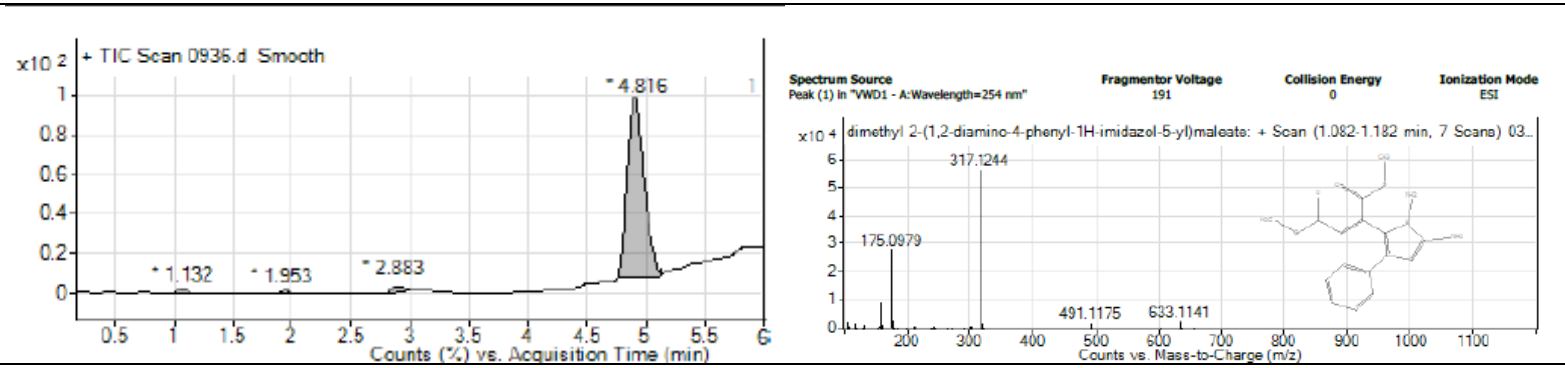
	

Table S8. Reaction in methanol with the addition of acetic acid as a catalyst.

60 minutes	

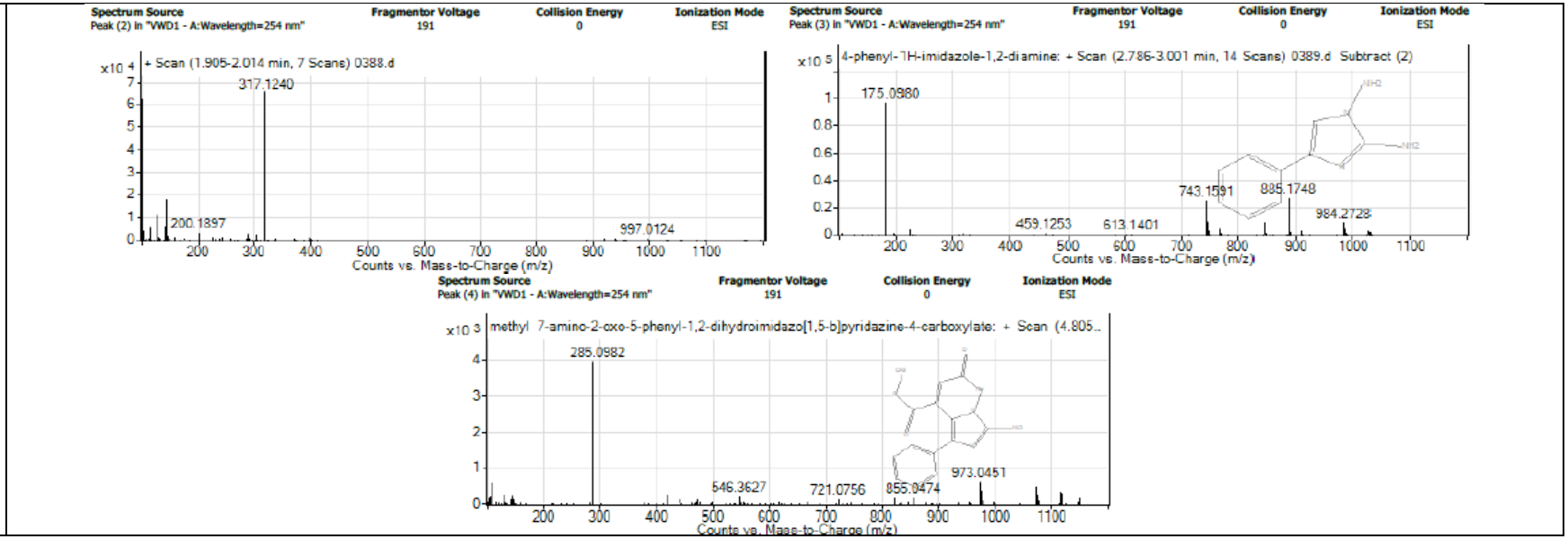
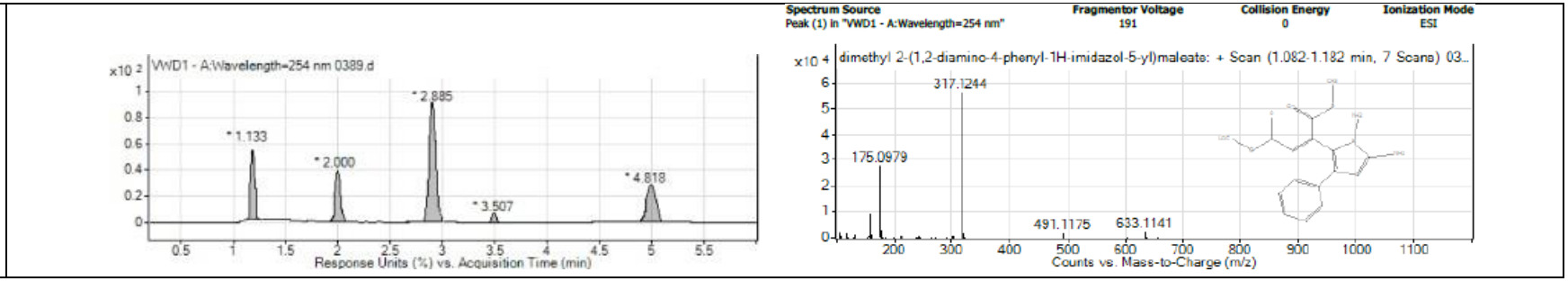
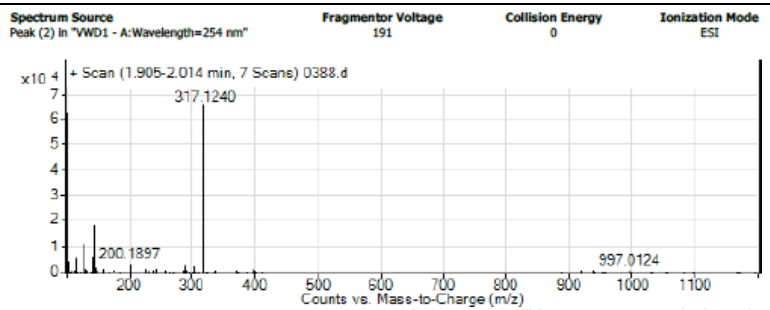
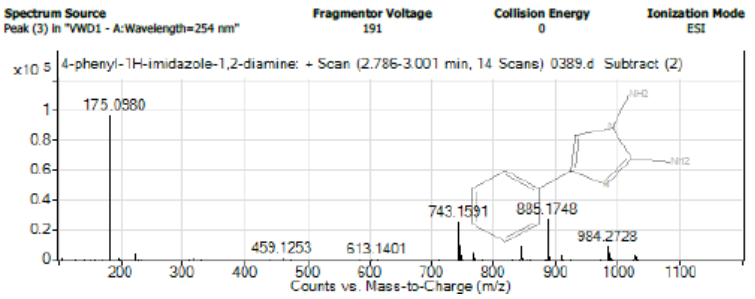
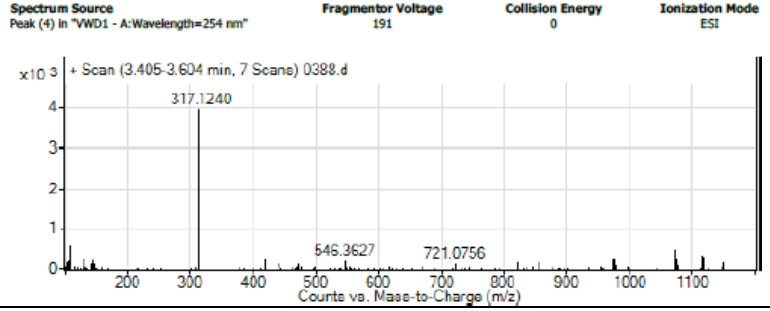
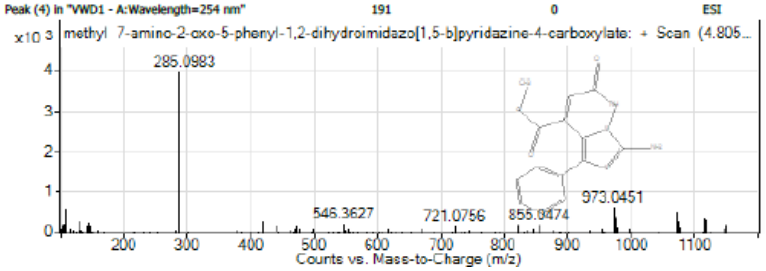
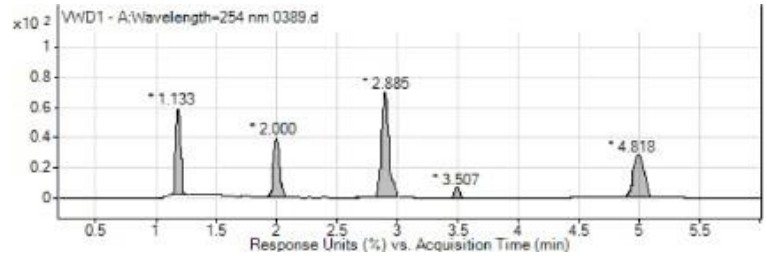
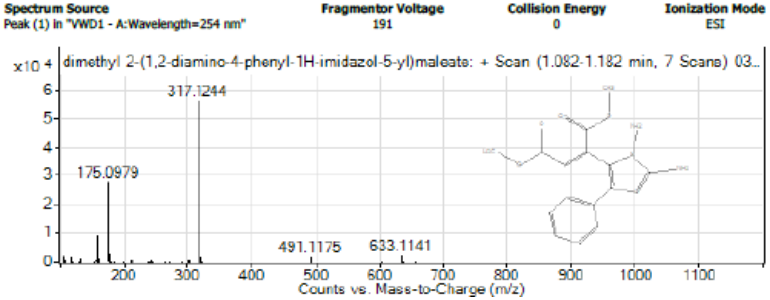
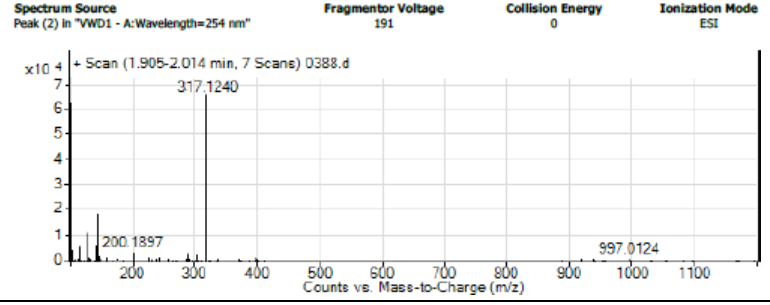
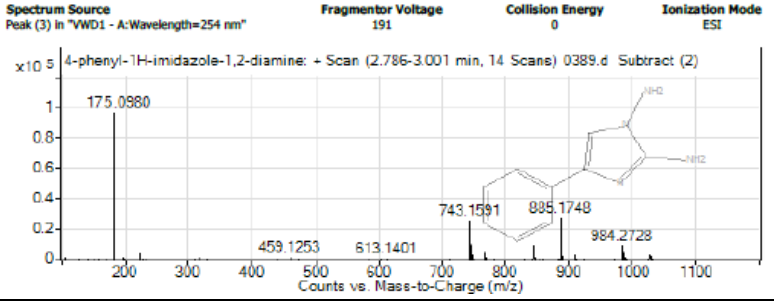
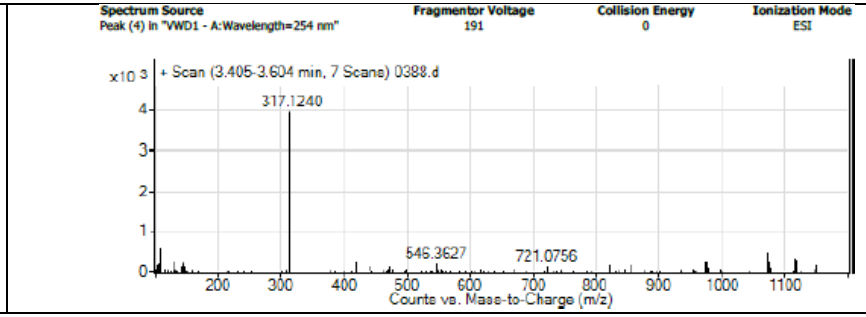
	

Table S9. Conducting the reaction in a 1:1 mixture of methanol and acetic acid.

60 minutes	

	   
120 minutes	   



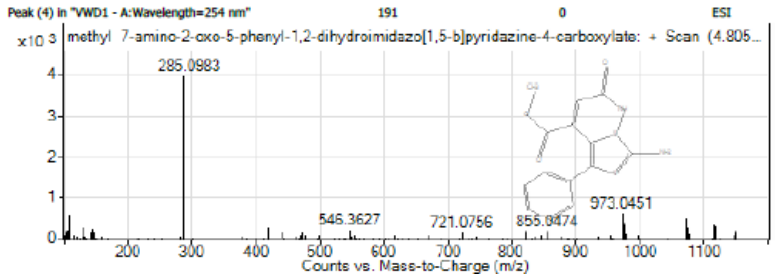
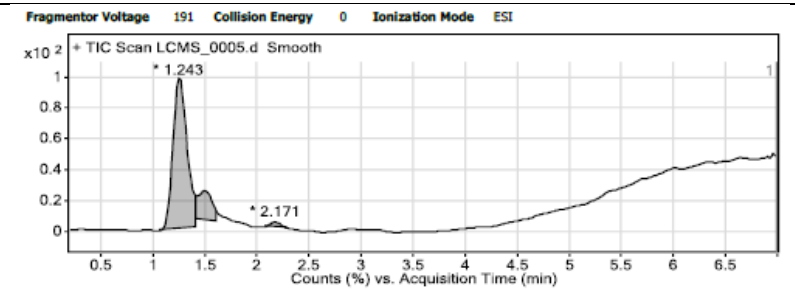
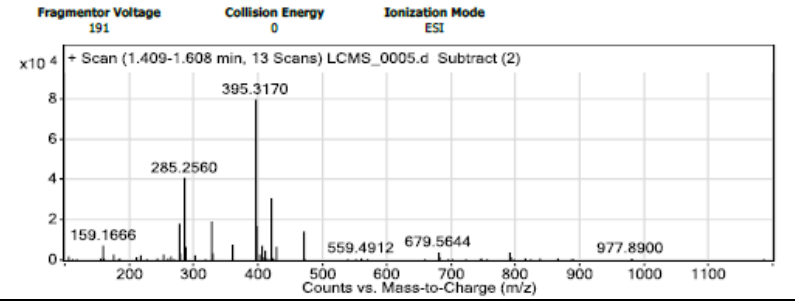
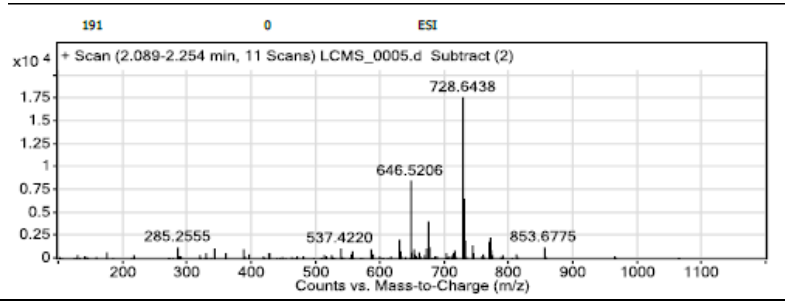
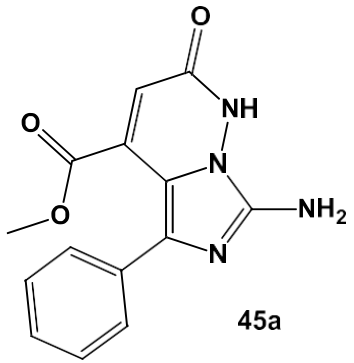


Table S10. Conducting the reaction in acetic acid.

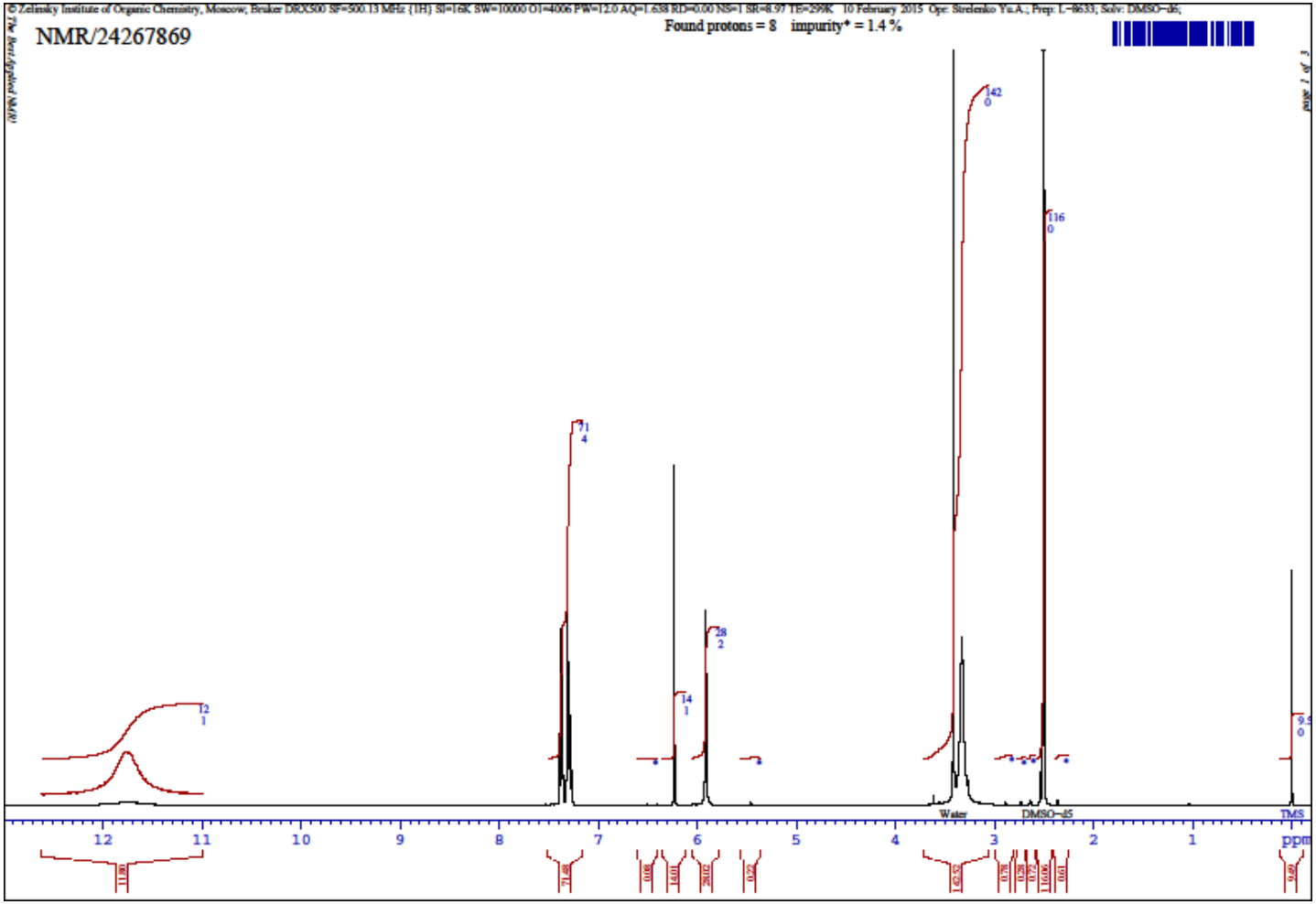
60 minutes	  

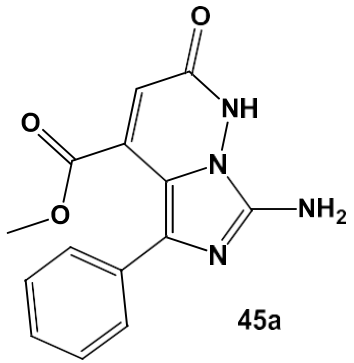
Spectral data of the obtained compounds

Table S11.



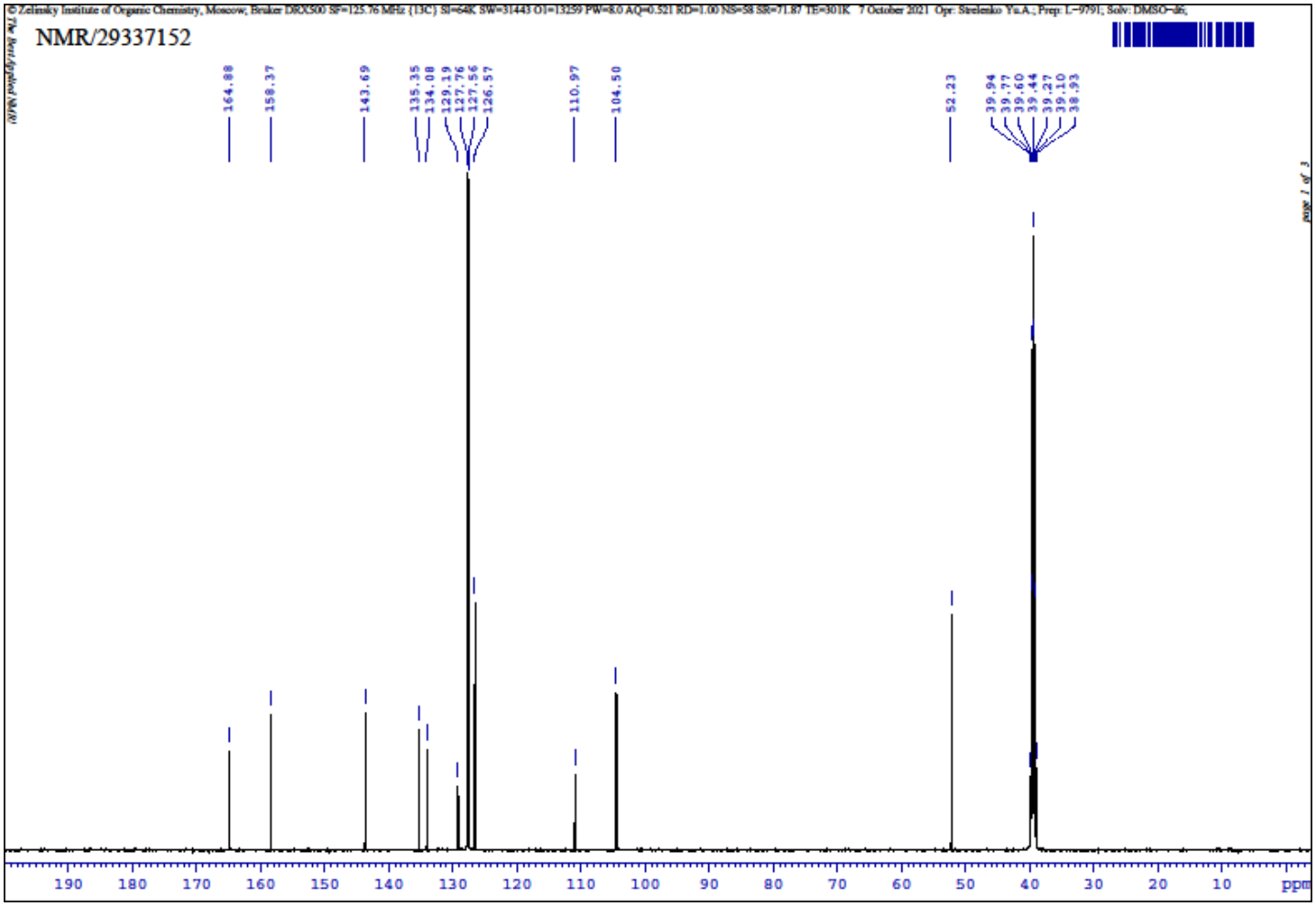
7-amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

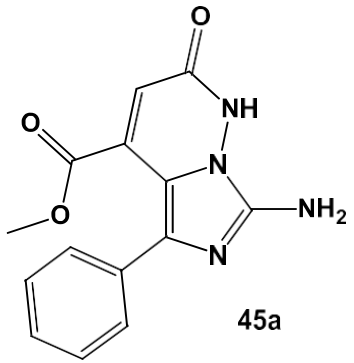




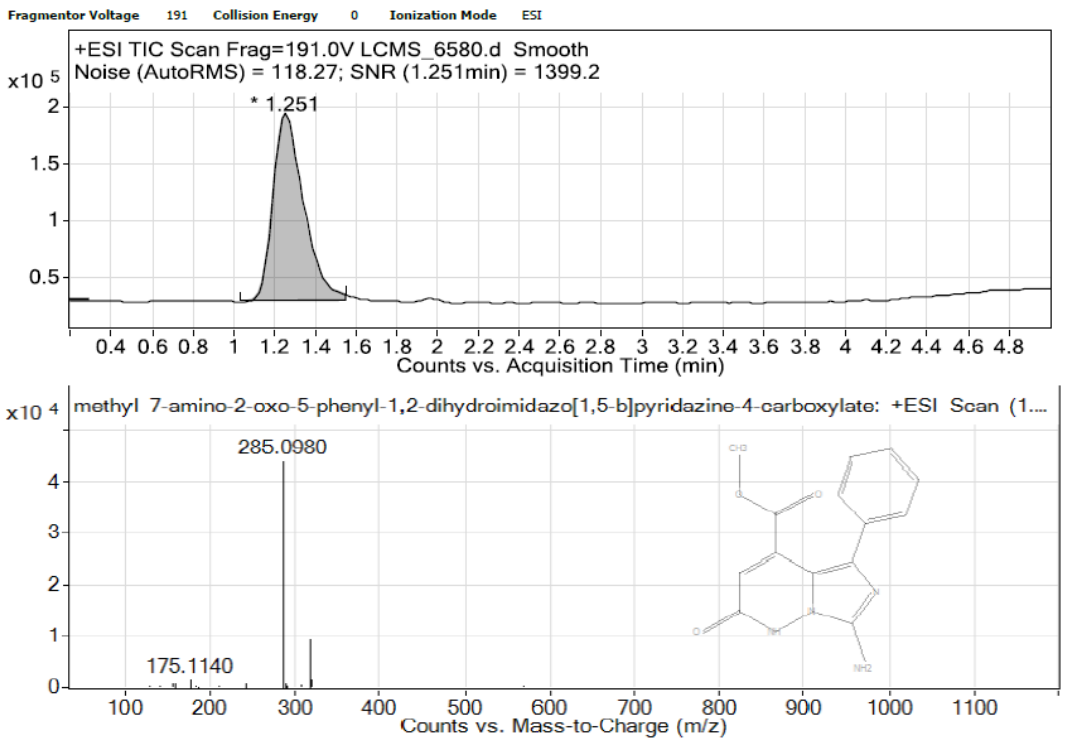
45a

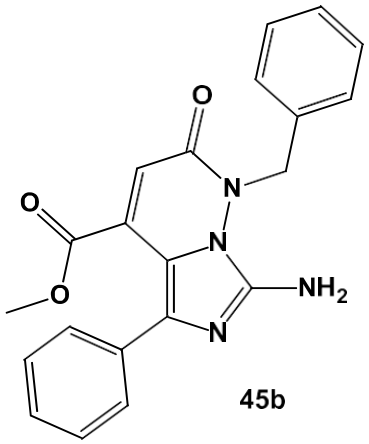
7-amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate





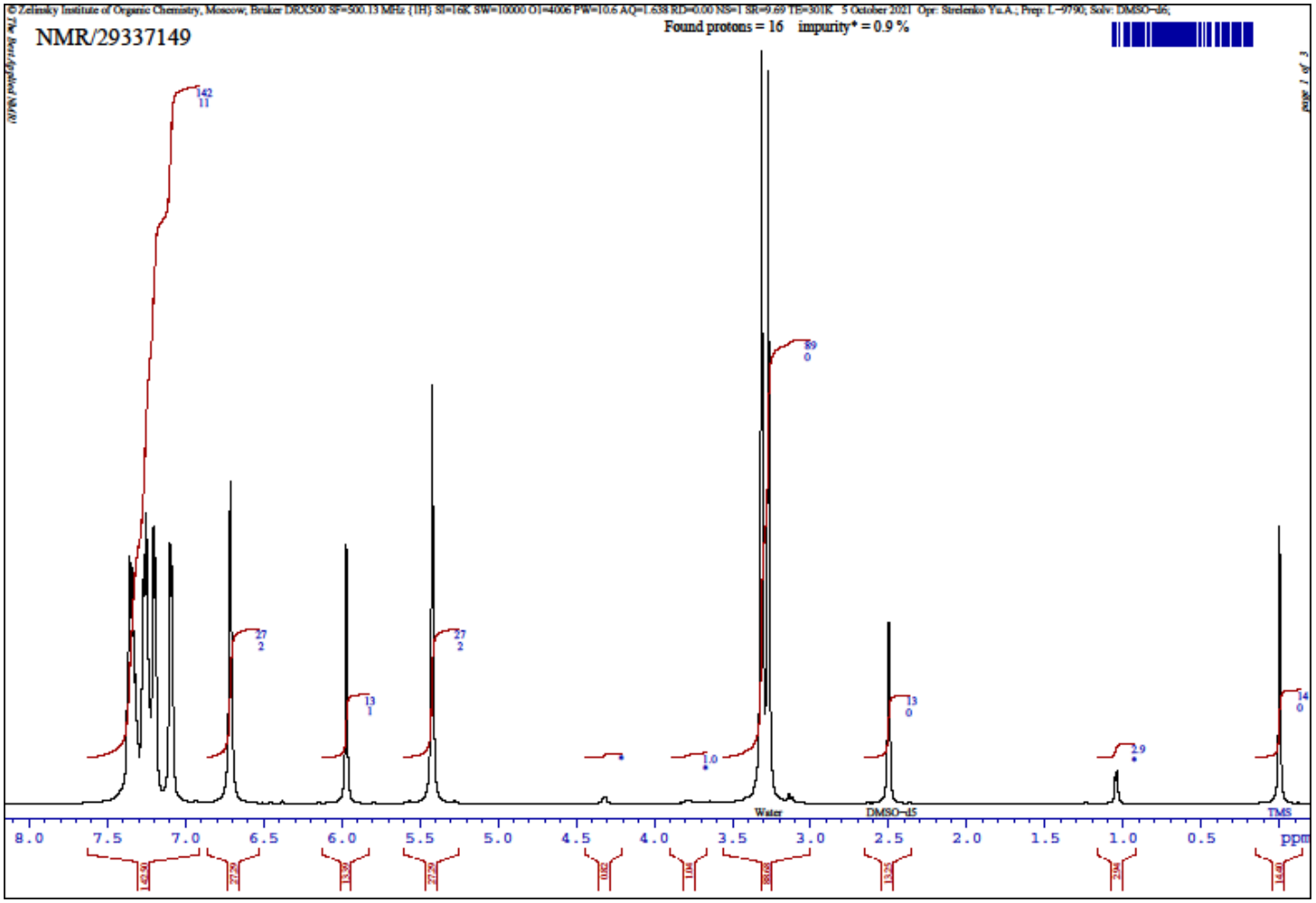
7-amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

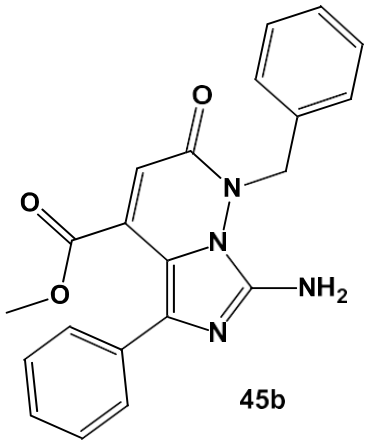




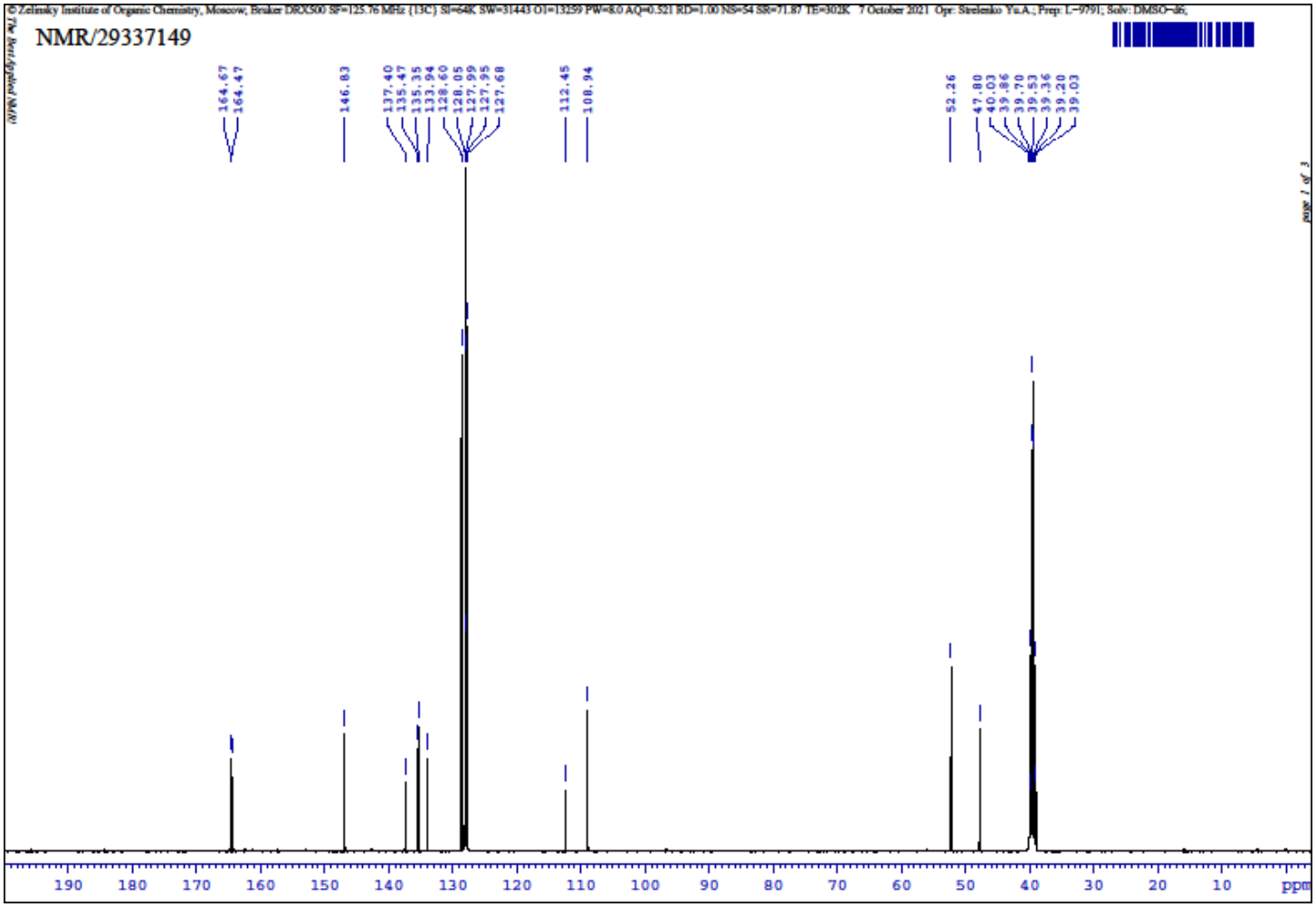
45b

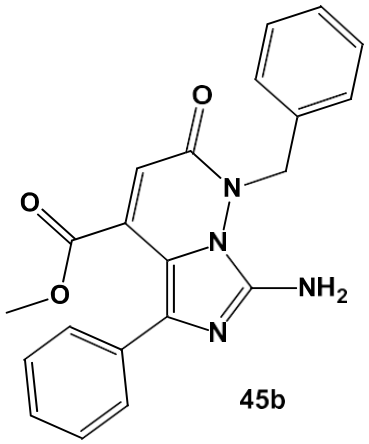
7-amino-1-benzyl-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate





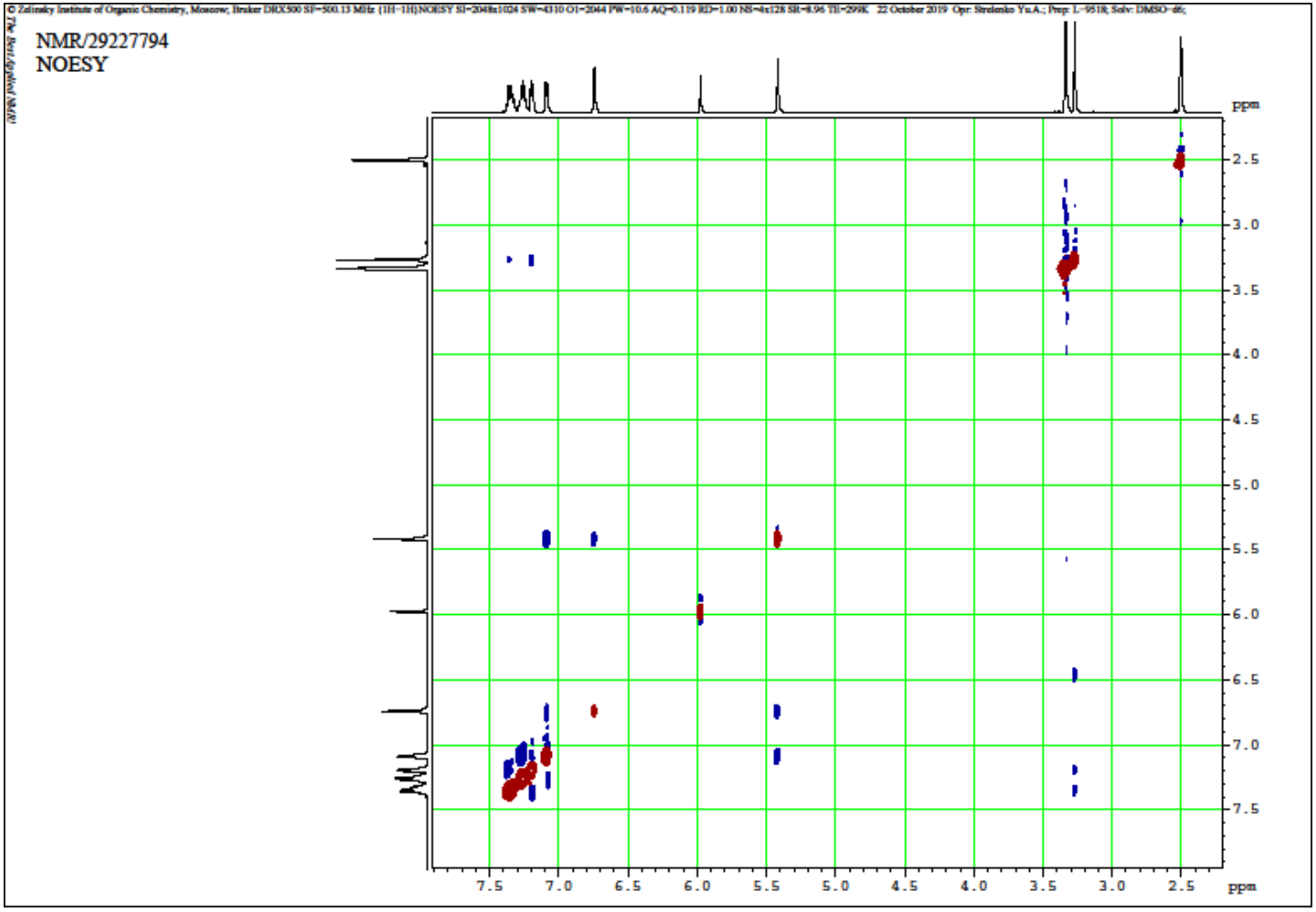
7-amino-1-benzyl-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

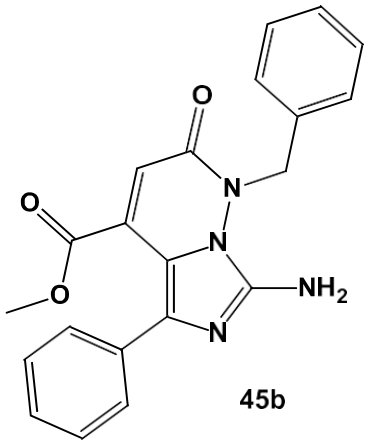




45b

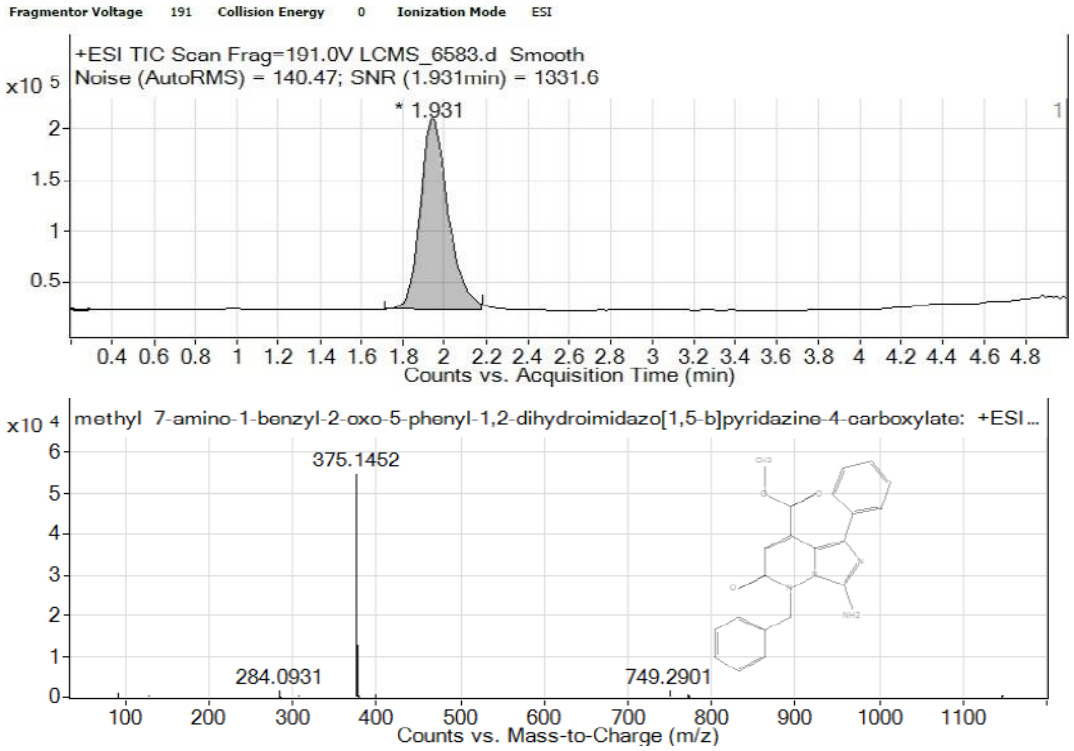
7-amino-1-benzyl-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

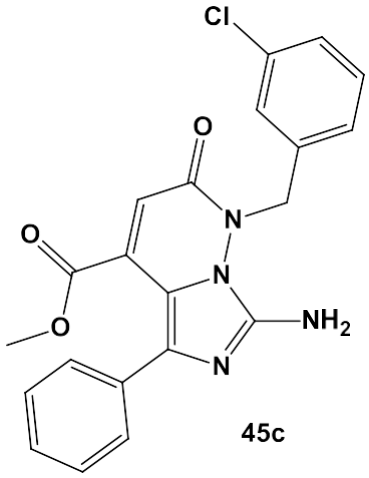




45b

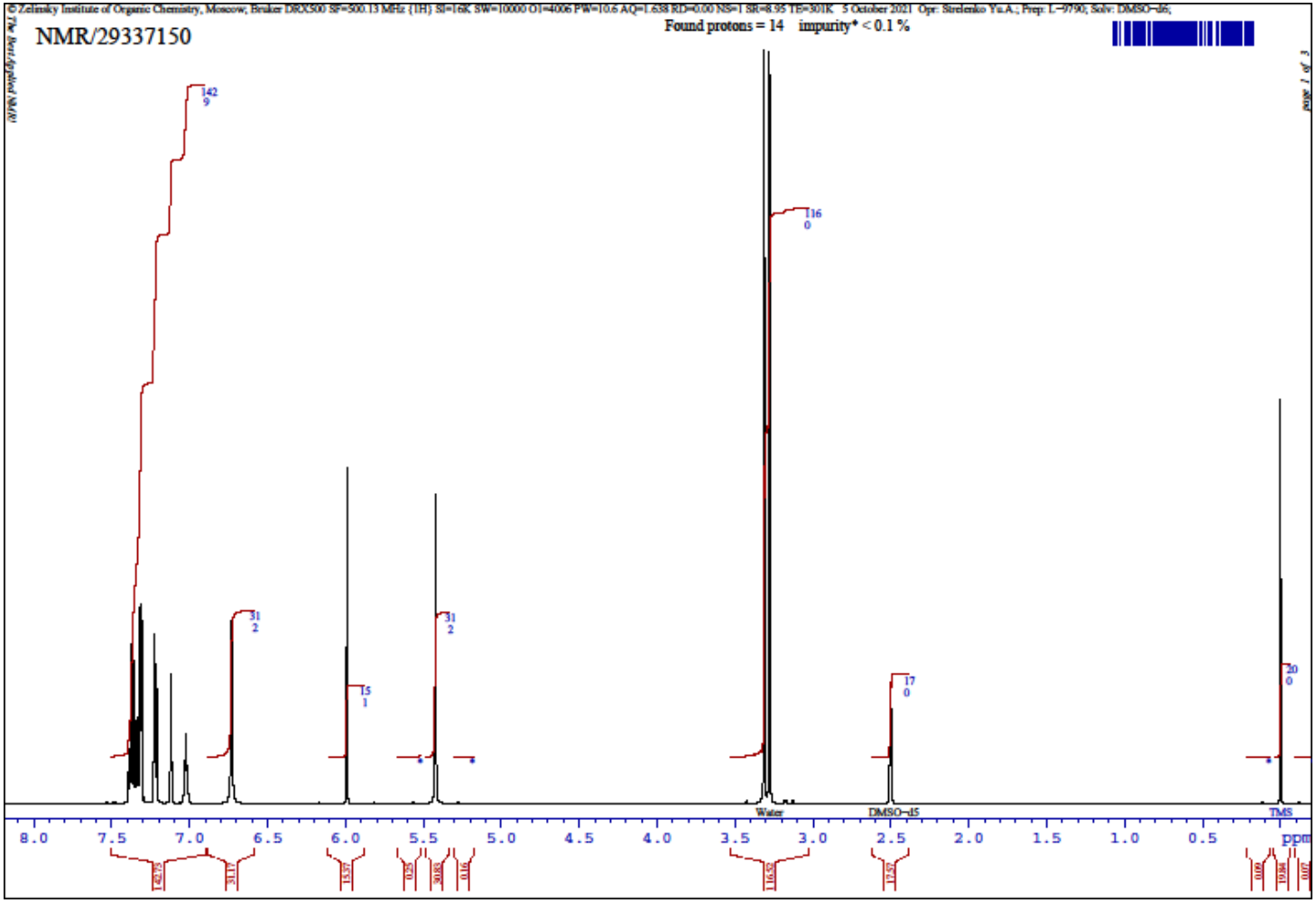
7-amino-1-benzyl-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

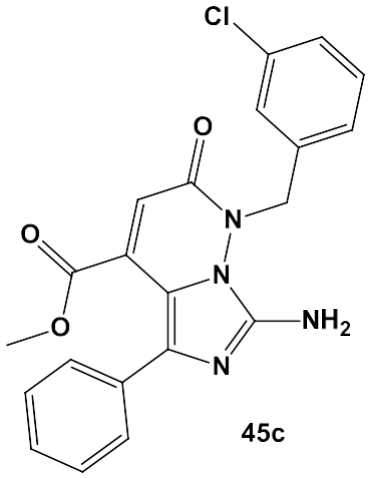




45c

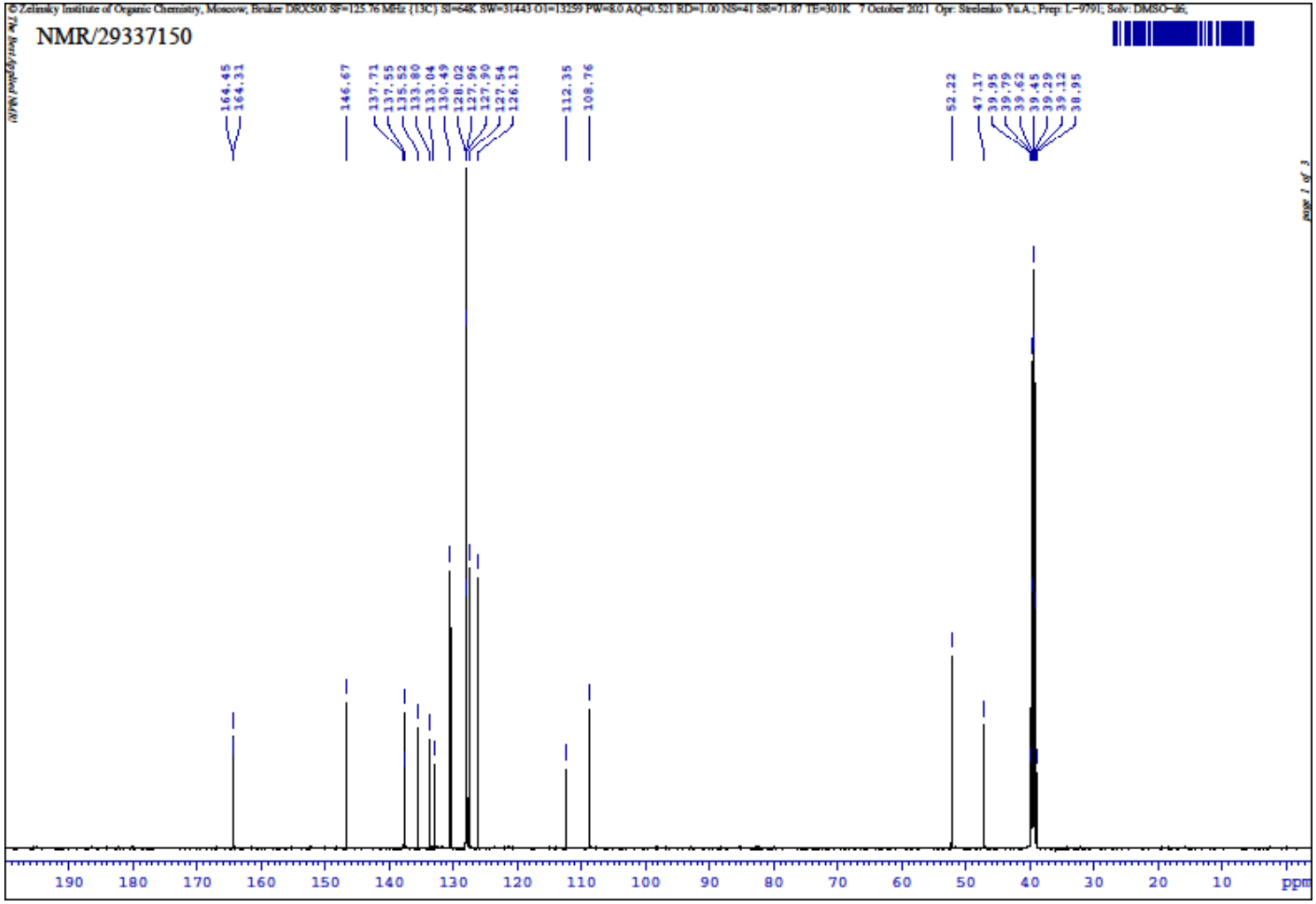
7-amino-1-(3-chlorobenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

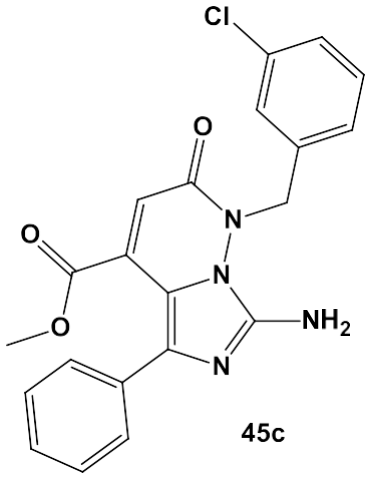




45c

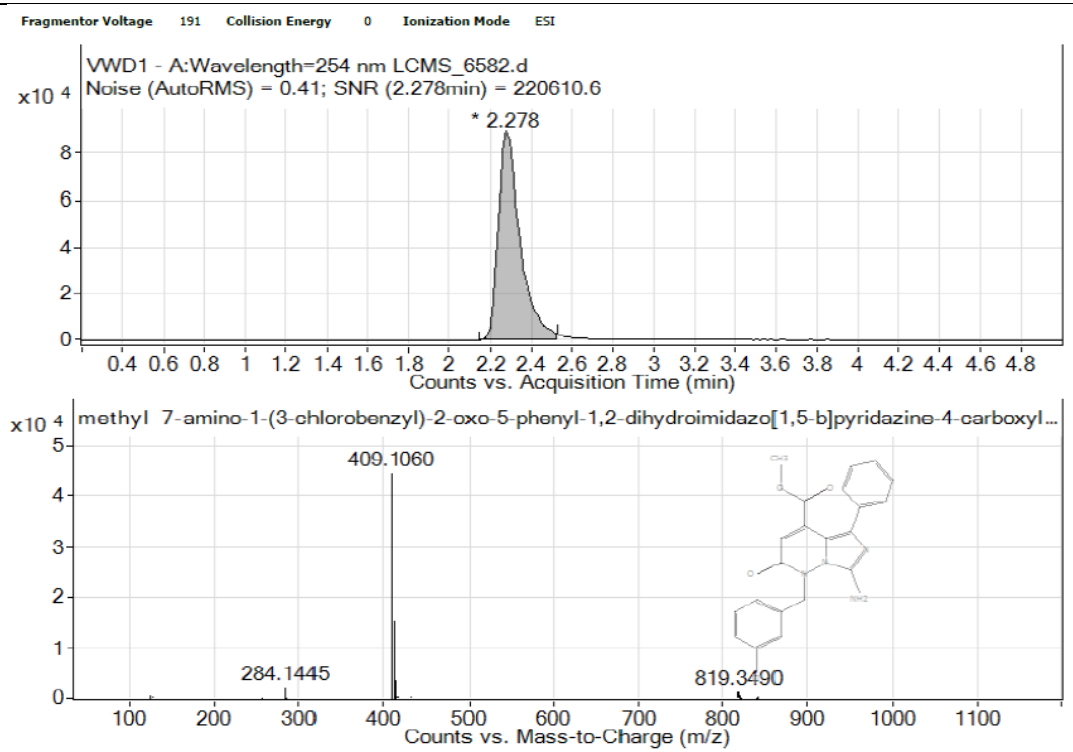
7-amino-1-(3-chlorobenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

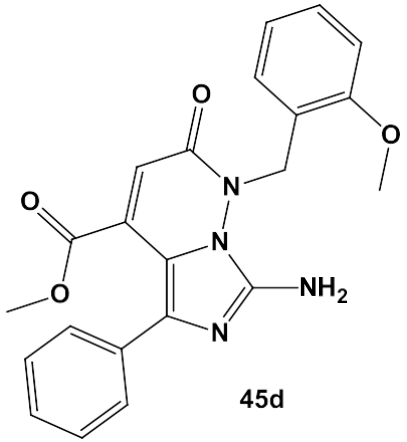




45c

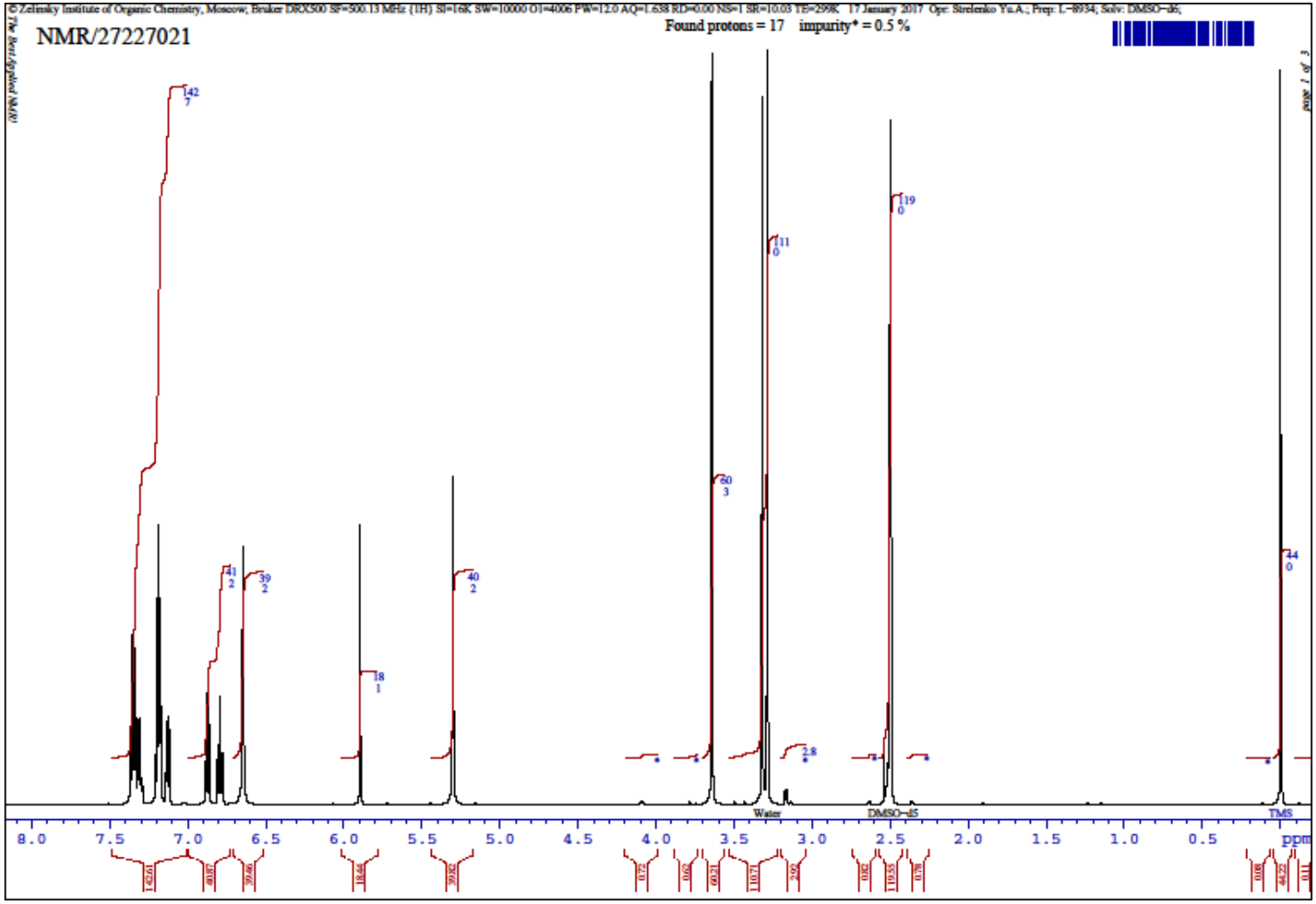
7-amino-1-(3-chlorobenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

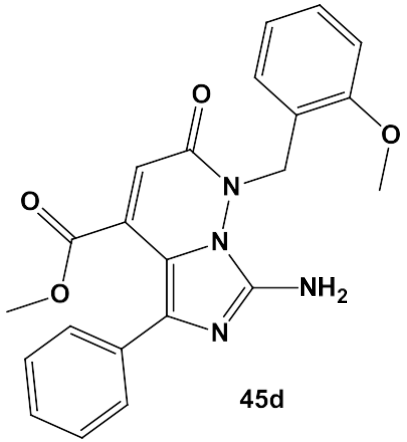




45d

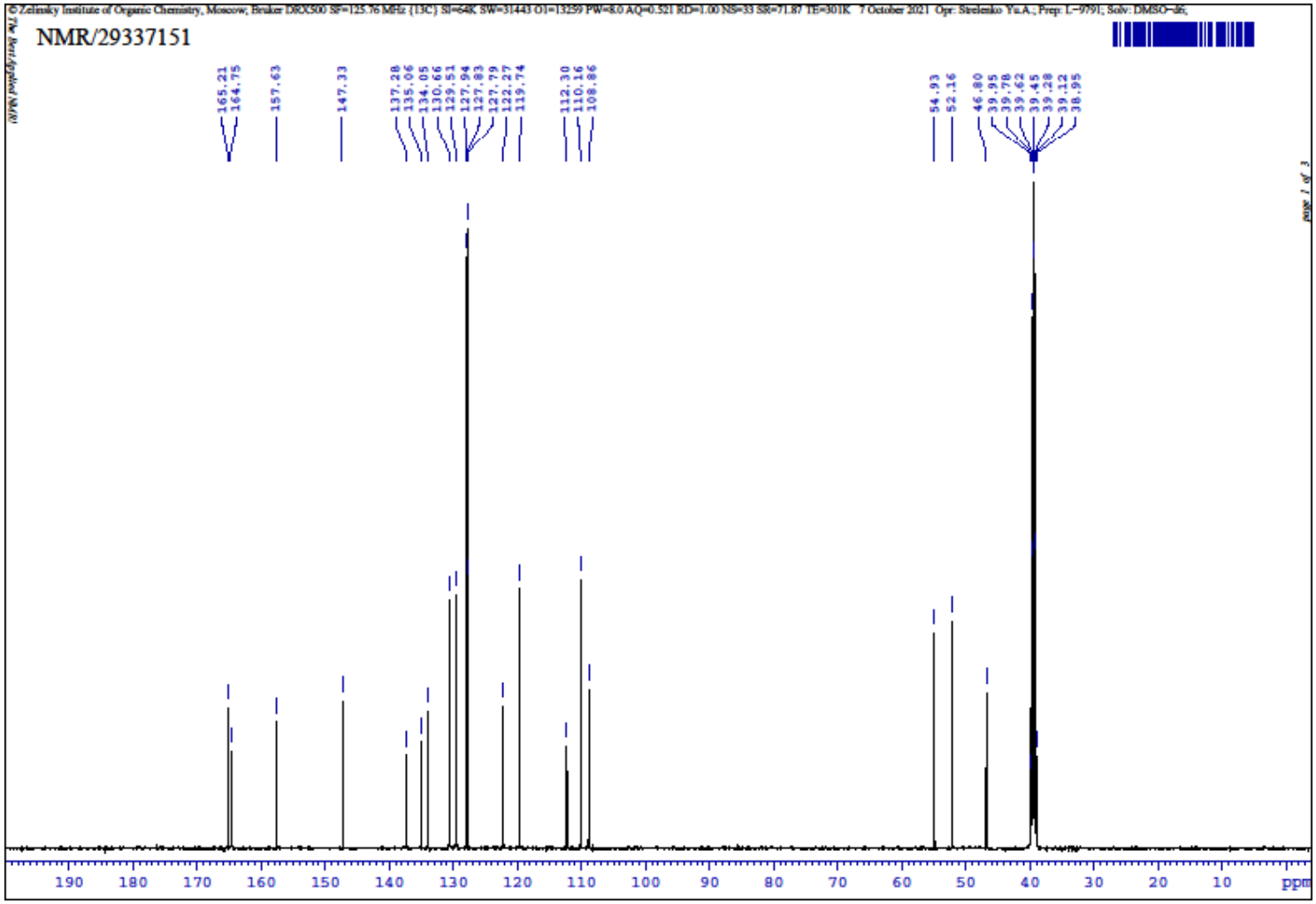
7-amino-1-(2-methoxybenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

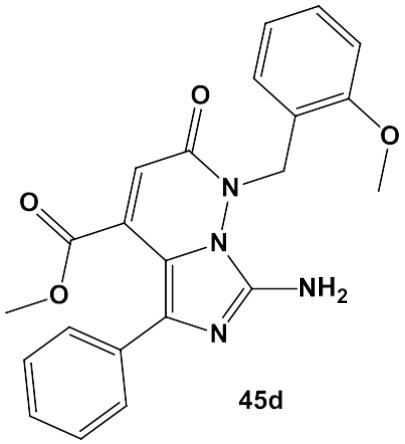




45d

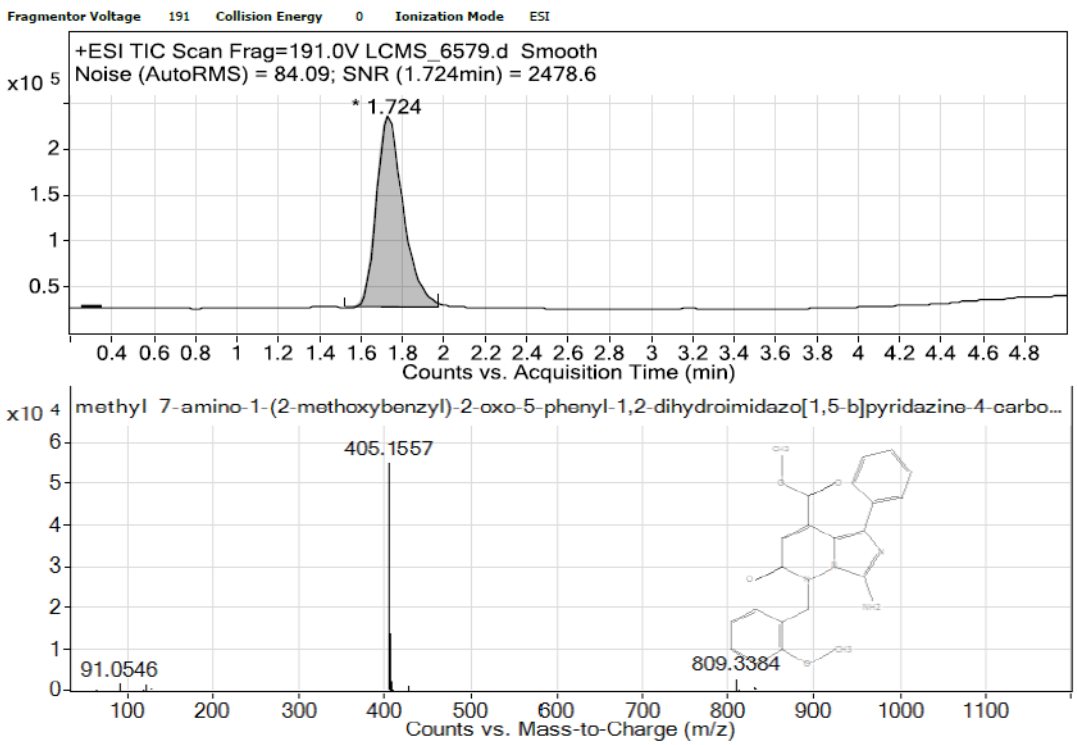
7-amino-1-(2-methoxybenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

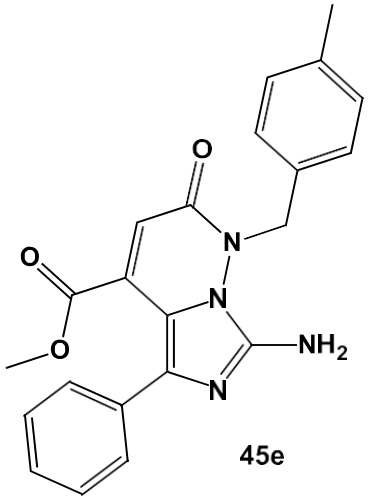




45d

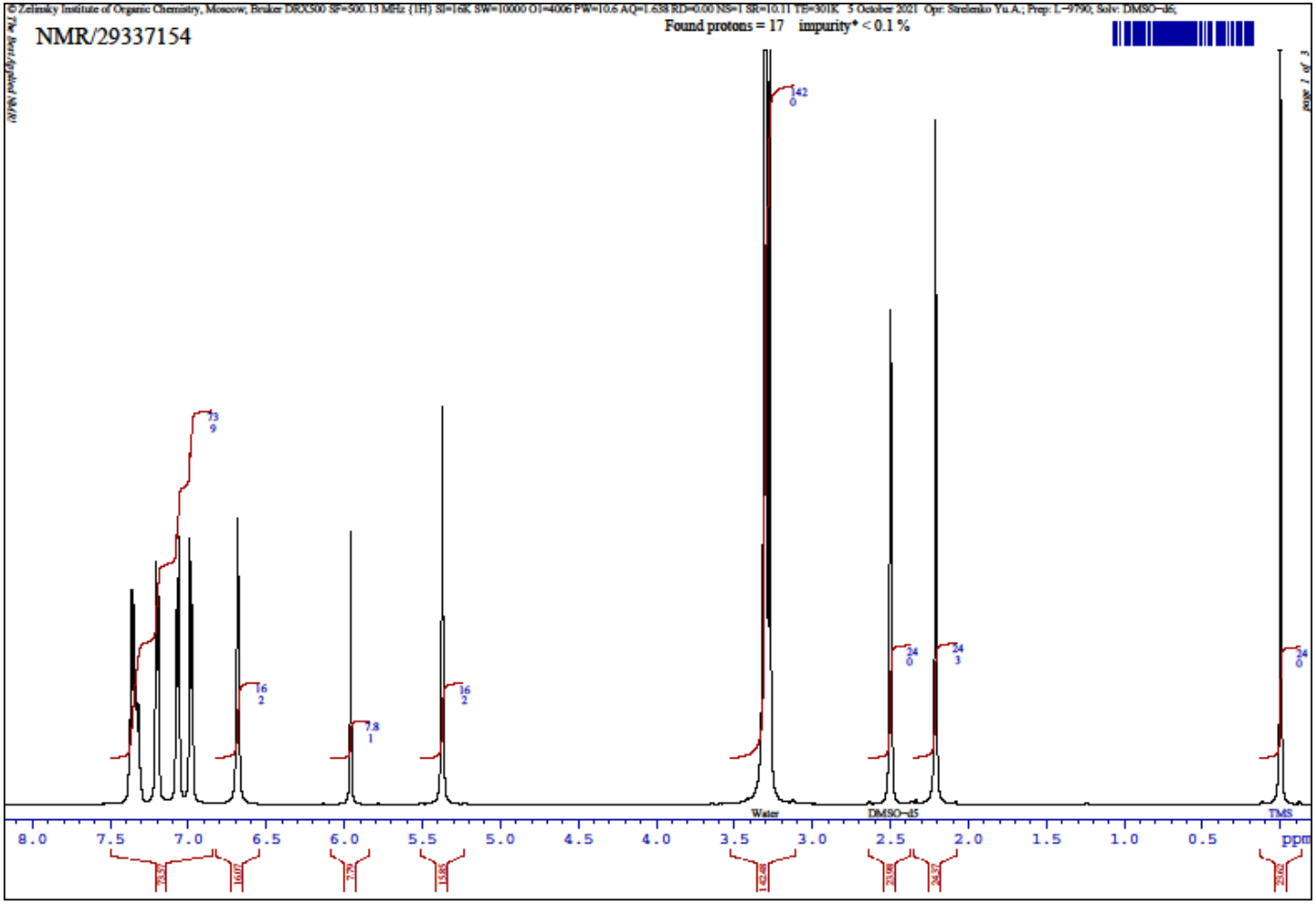
7-amino-1-(2-methoxybenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

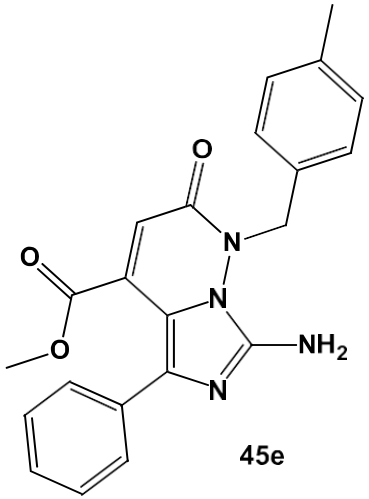




45e

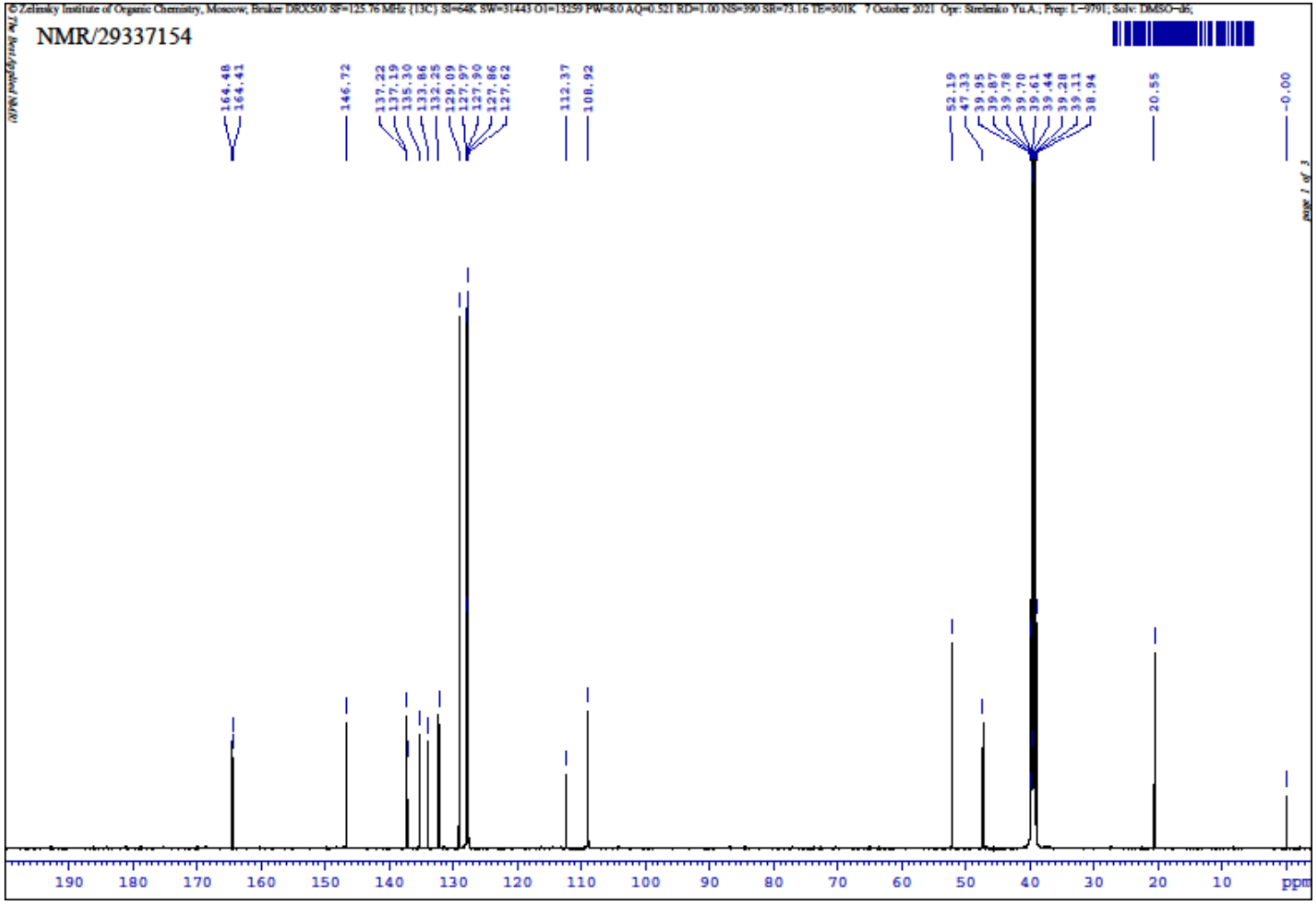
7-amino-1-(4-methylbenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

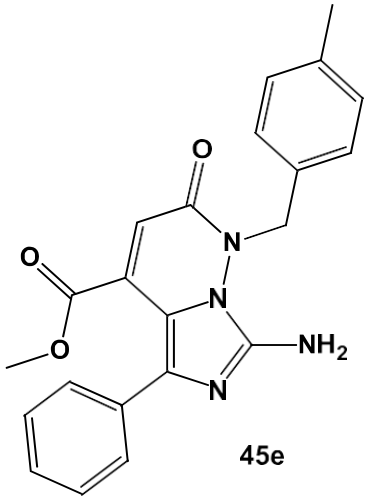




45e

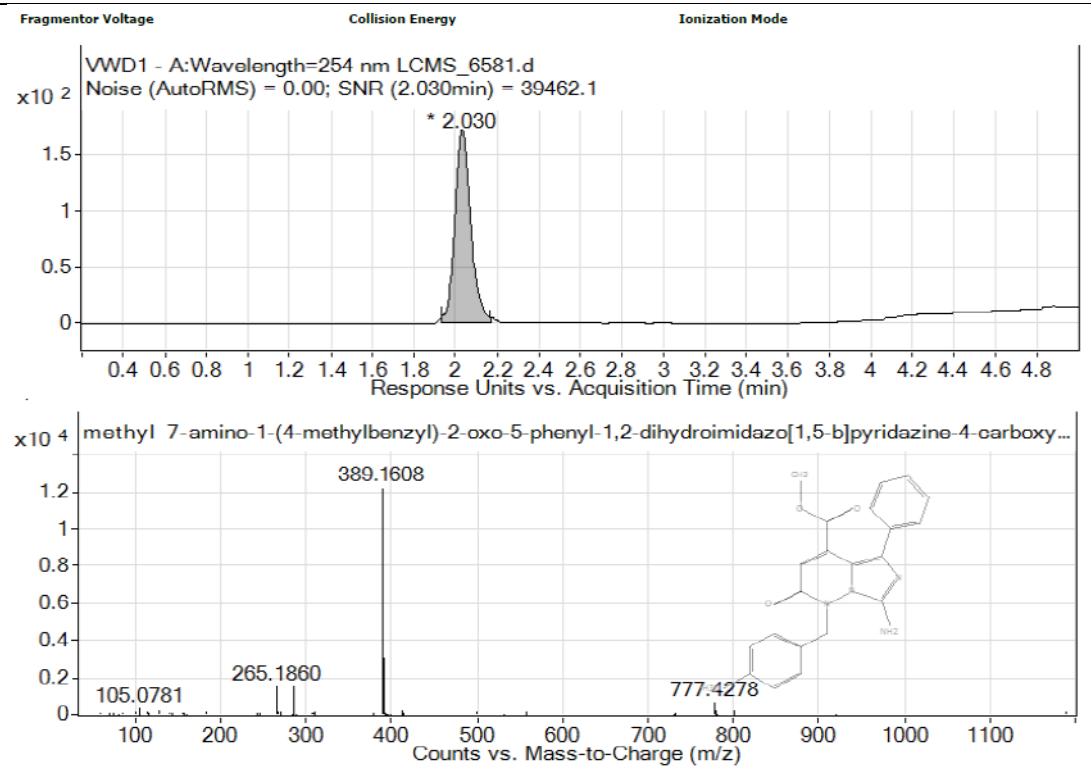
7-amino-1-(4-methylbenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate

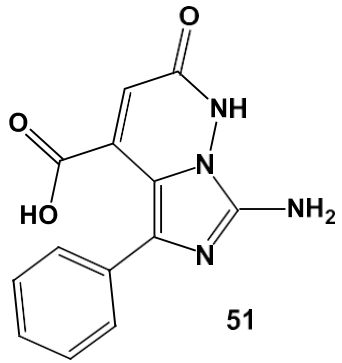




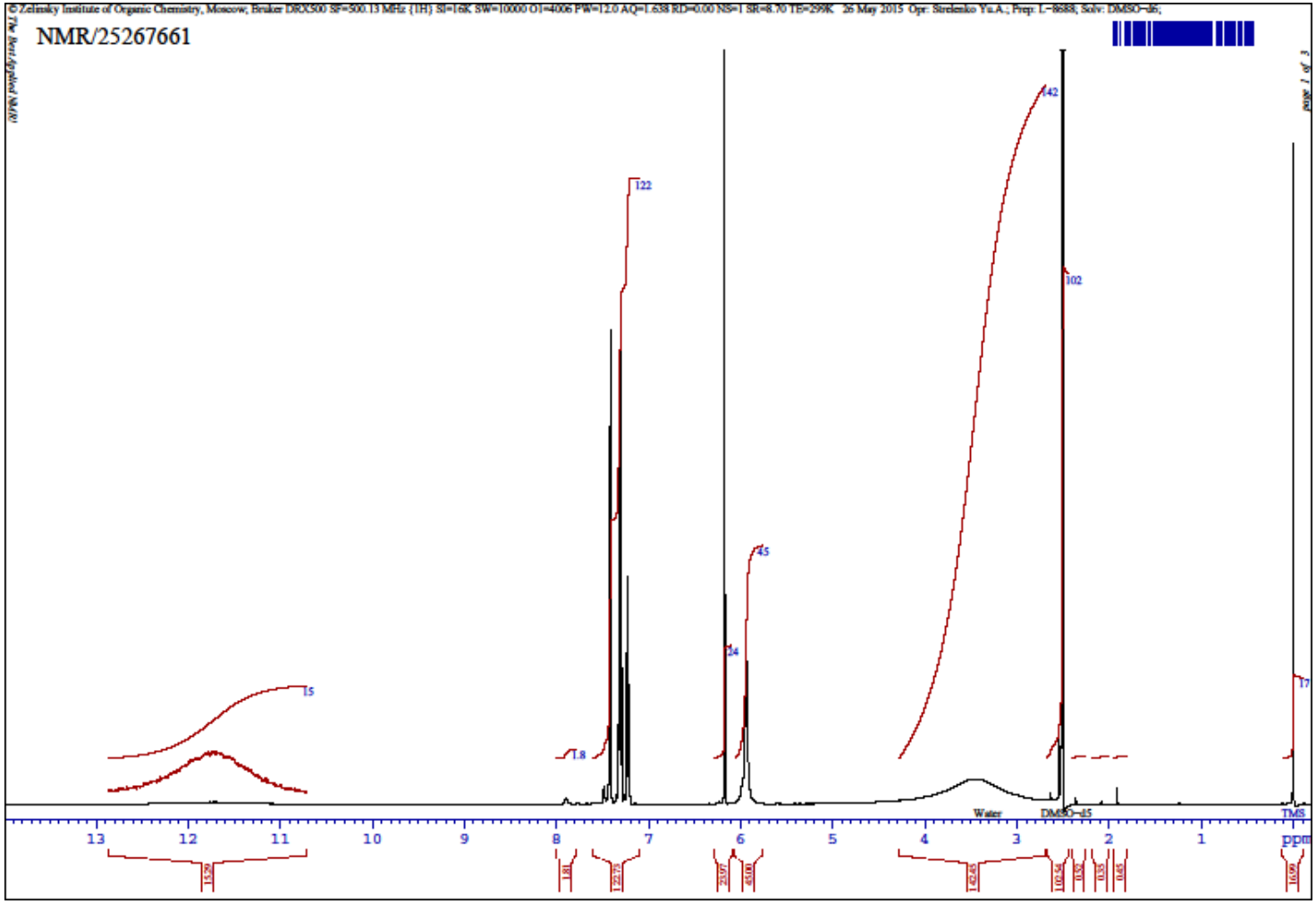
45e

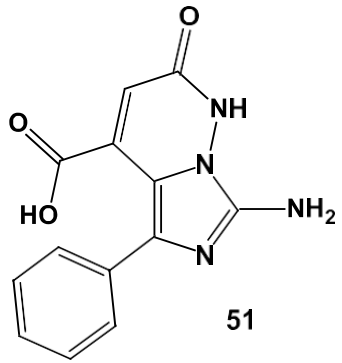
7-amino-1-(4-methylbenzyl)-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylate





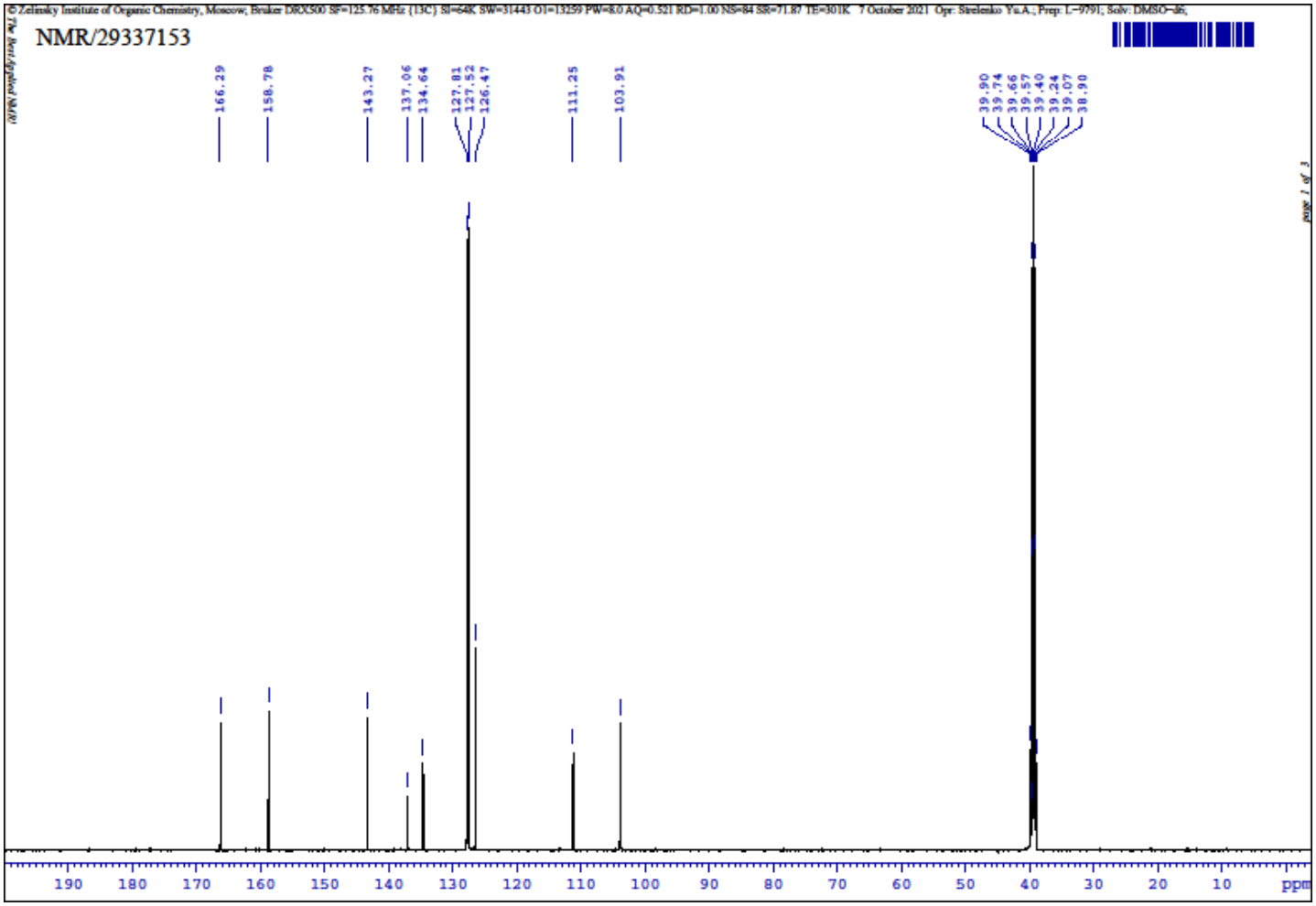
7-Amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylic acid

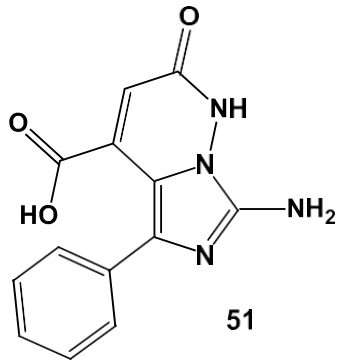




51

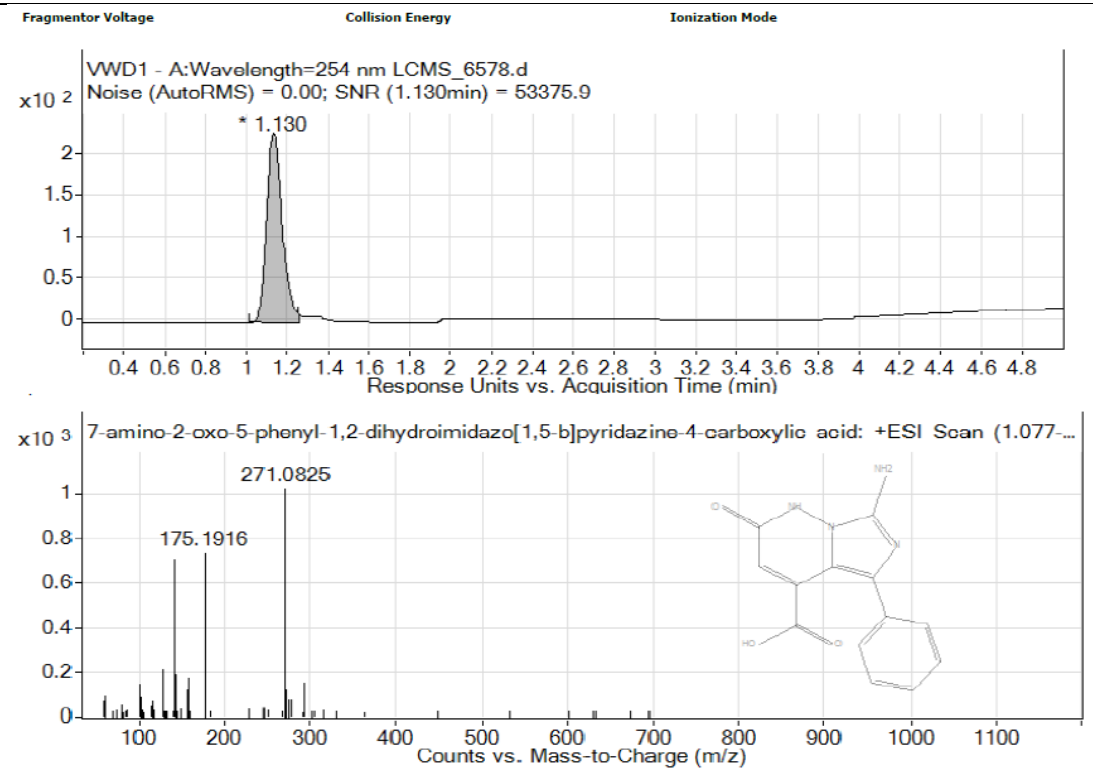
7-Amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylic acid

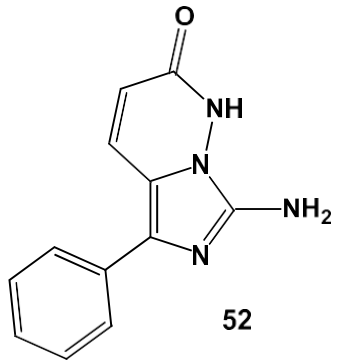




51

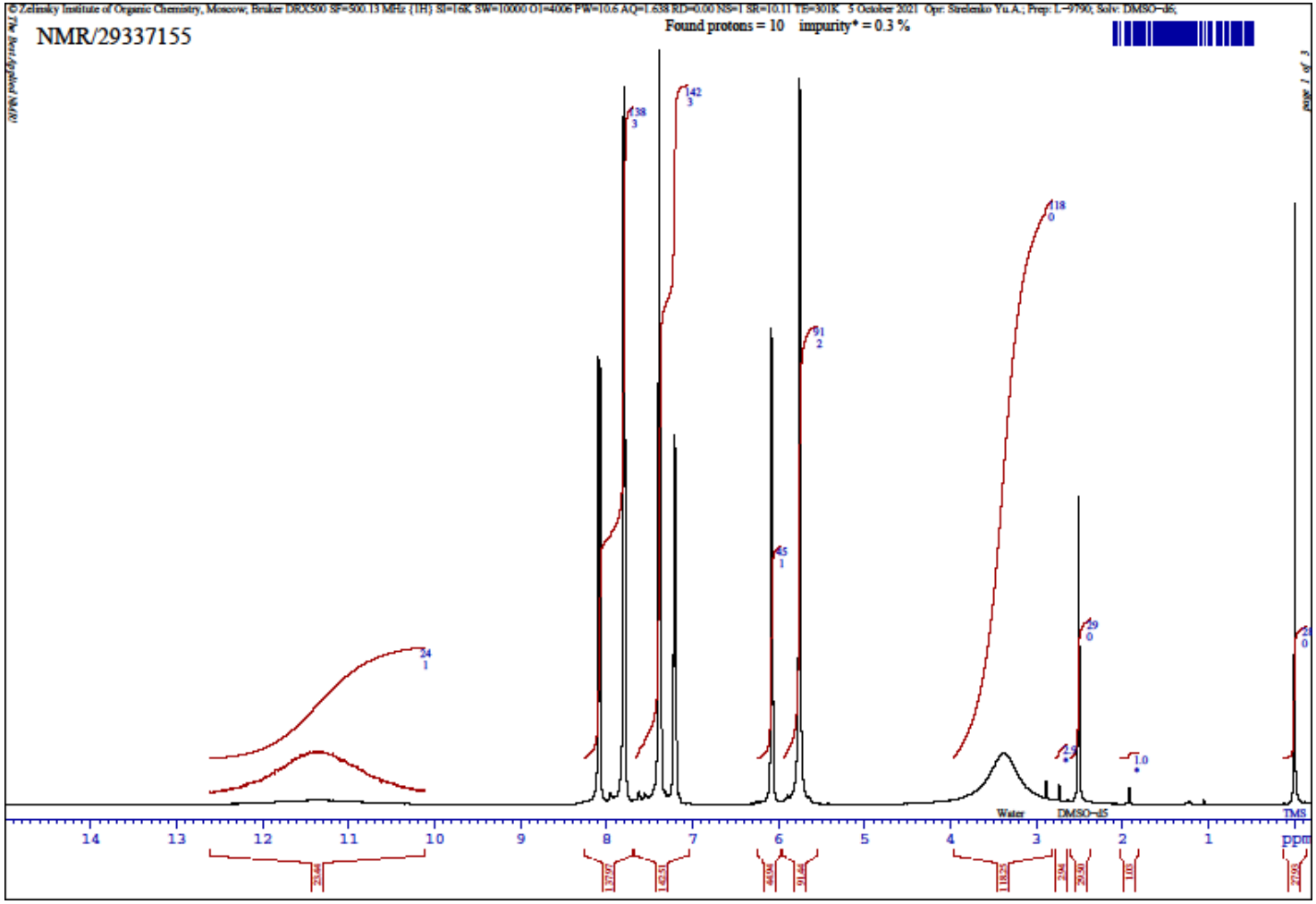
7-Amino-1,2-dihydro-2-oxo-5-phenylimidazo[1,5-b]pyridazine-4-carboxylic acid

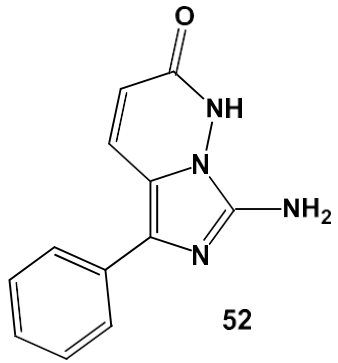




52

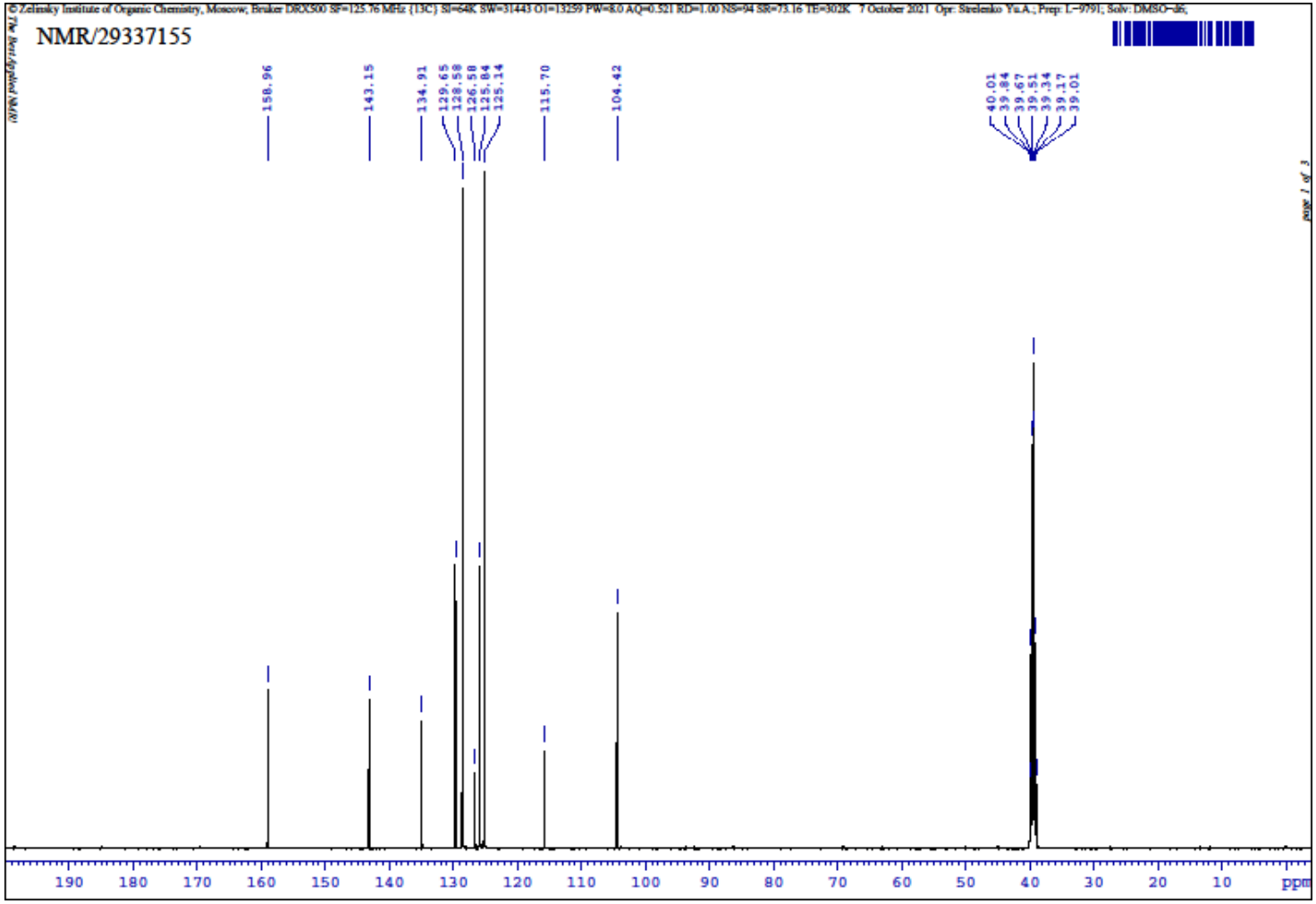
7-Amino-5-phenylimidazo[1,5-b]pyridazin-2(1H)-one

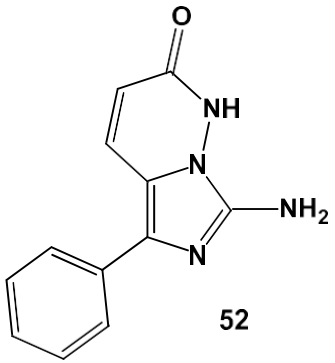




52

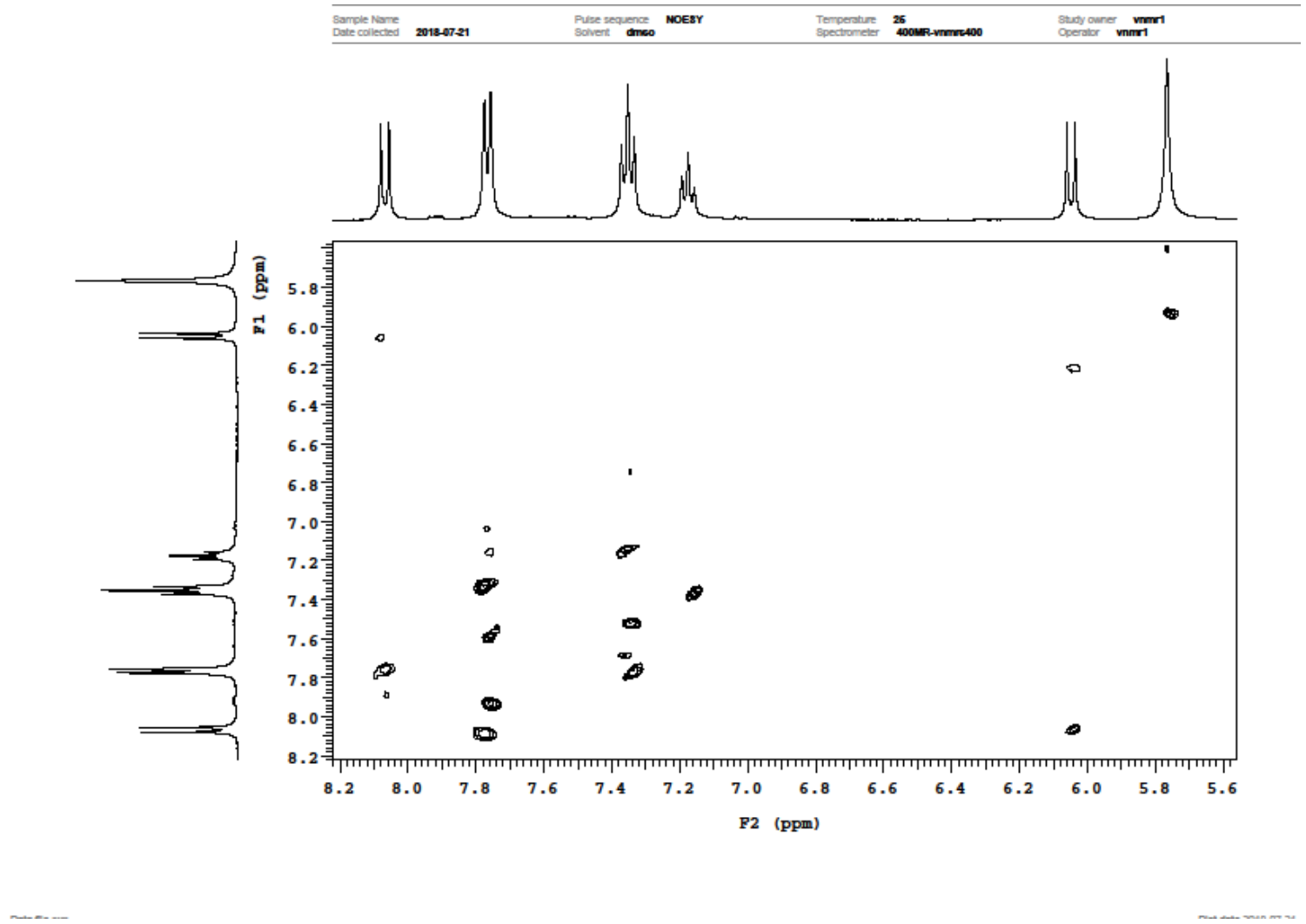
7-Amino-5-phenylimidazo[1,5-b]pyridazin-2(1H)-one

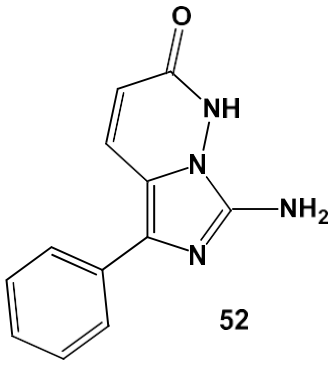




52

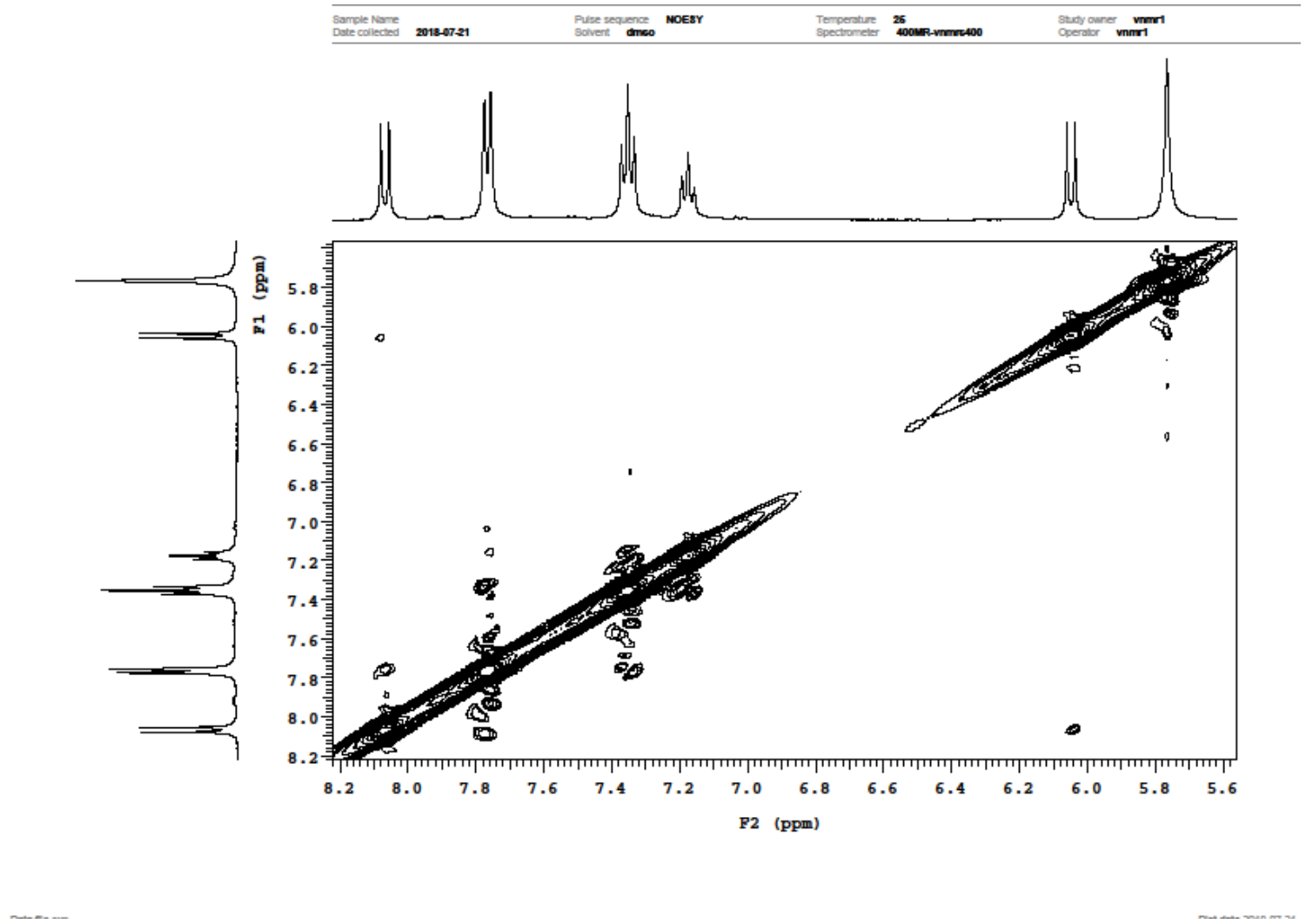
7-Amino-5-phenylimidazo[1,5-b]pyridazin-2(1H)-one

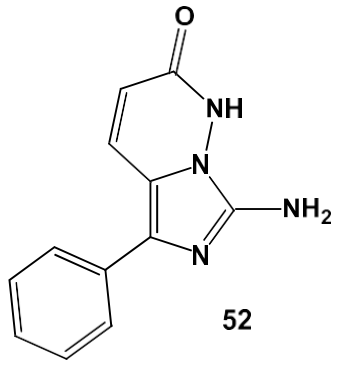




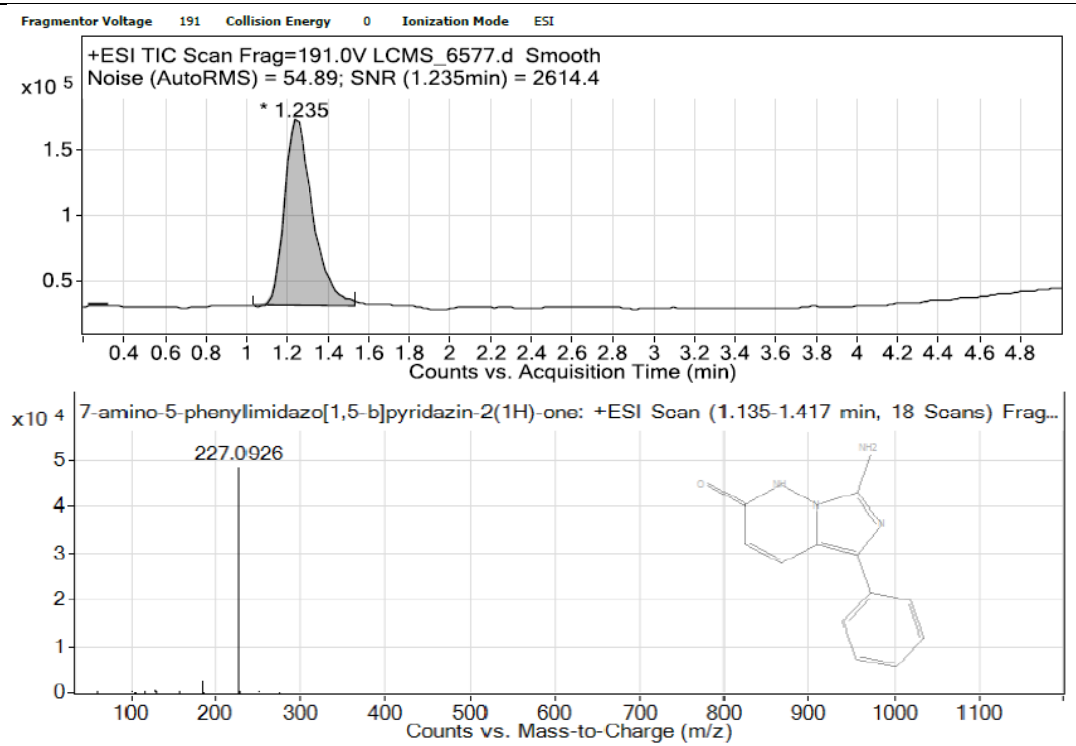
52

7-Amino-5-phenylimidazo[1,5-b]pyridazin-2(1H)-one





7-Amino-5-phenylimidazo[1,5-b]pyridazin-2(1H)-one



DFT calculation

Table S12. Optimized geometries of stationary points of the Scheme 9. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

1

$\nu_{im.}$ = 0 cm^{-1}(-533,18109)

6	-0.599208000	-0.188711000	-0.061238000
6	0.599187000	-0.188585000	0.061348000
6	-2.030004000	-0.248251000	-0.280073000
8	-2.540787000	-0.987031000	-1.091905000
8	-2.677402000	0.599821000	0.516534000
6	-4.123637000	0.629453000	0.391561000
1	-4.402662000	0.918512000	-0.620988000
1	-4.536455000	-0.349844000	0.630939000
1	-4.452831000	1.373742000	1.110535000
6	2.030000000	-0.248238000	0.280069000
8	2.540789000	-0.987001000	1.091906000
8	2.677410000	0.599781000	-0.516584000
6	4.123644000	0.629439000	-0.391590000
1	4.402662000	0.918436000	0.620979000
1	4.536490000	-0.349828000	-0.631026000
1	4.452832000	1.373782000	-1.110511000

44a

$\nu_{im.}$ = 0 (-567.98908)

7	-1.013234000	1.096078000	0.049545000
6	-2.270924000	0.714569000	0.036552000
6	-0.255253000	-0.074629000	0.002893000
6	-1.088173000	-1.163345000	-0.037888000
7	-2.377762000	-0.651835000	-0.016397000
1	-0.922994000	-2.225825000	-0.075669000
7	-3.534082000	-1.437705000	-0.086237000
1	-4.106209000	-1.133793000	-0.869455000
1	-4.068750000	-1.350885000	0.773630000
7	-3.377135000	1.540228000	-0.022346000
1	-3.152173000	2.501040000	0.199922000
1	-4.188434000	1.222280000	0.493142000
6	1.212397000	-0.039241000	0.004304000
6	1.895083000	1.186255000	-0.057576000
6	1.974219000	-1.219710000	0.064971000
6	3.288186000	1.229659000	-0.063239000
6	3.364854000	-1.174309000	0.057634000
6	4.032238000	0.051332000	-0.006622000
1	1.321130000	2.103202000	-0.103187000
1	1.477526000	-2.181873000	0.122100000
1	3.793351000	2.188275000	-0.112967000
1	3.930516000	-2.098445000	0.105374000
1	5.115773000	0.085162000	-0.011015000

TS1

$\nu_{im.}$ = -403.2cm^{-1}(-1101.11573)

7	1.965759000	1.484722000	-0.680306000
6	2.624938000	0.411457000	-1.147239000
6	0.654164000	1.154570000	-0.689395000
6	0.477263000	-0.215263000	-1.063511000
7	1.776963000	-0.595932000	-1.476265000
1	-0.344111000	-0.591593000	-1.651994000
7	2.101951000	-1.900251000	-1.849239000
1	2.679907000	-2.334851000	-1.133790000
1	2.572342000	-1.904710000	-2.748668000
7	3.961986000	0.324417000	-1.230047000
1	4.495324000	1.169521000	-1.096390000
1	4.397776000	-0.418767000	-1.753129000
6	-0.383864000	2.114060000	-0.322894000
6	-0.026547000	3.415123000	0.074102000
6	-1.746595000	1.770858000	-0.366693000
6	-1.003565000	4.342298000	0.418370000
6	-2.720196000	2.701758000	-0.020405000
6	-2.353935000	3.990186000	0.372790000
1	1.020878000	3.685799000	0.107156000
1	-2.050947000	0.775065000	-0.663302000
1	-0.713079000	5.341456000	0.722438000
1	-3.766682000	2.422000000	-0.057515000
1	-3.115025000	4.714223000	0.640268000
6	-1.106463000	-1.887446000	0.601921000
6	-0.039997000	-1.219709000	0.613061000
6	-2.238909000	-2.439178000	-0.039029000
8	-2.250631000	-3.490712000	-0.672846000
8	-3.359416000	-1.692090000	0.163292000
6	-4.582859000	-2.214160000	-0.391951000
1	-4.509105000	-2.300077000	-1.476728000
1	-4.812704000	-3.190511000	0.036788000
1	-5.351400000	-1.493426000	-0.122268000
6	0.998281000	-0.964282000	1.634387000
8	0.783029000	-0.448828000	2.709462000
8	2.211322000	-1.382632000	1.239250000
6	3.295873000	-1.202268000	2.183356000
1	3.412285000	-0.146134000	2.424327000
1	3.097762000	-1.771803000	3.090953000

54

$\nu_{im.}$ = 0 cm^{-1}(-1101.13298)

7	2.691232000	-0.800820000	-0.237211000
6	2.273625000	-2.080739000	-0.523370000
6	1.681346000	-0.007778000	-0.487790000
6	0.469587000	-0.753313000	-1.015950000
7	1.024250000	-2.123092000	-0.982066000
1	0.312661000	-0.472582000	-2.061764000
7	0.311257000	-3.232326000	-1.422261000
1	0.141429000	-3.885436000	-0.663410000
1	0.783540000	-3.686514000	-2.198353000
7	3.071663000	-3.120818000	-0.357345000
1	4.007235000	-2.969158000	-0.011840000
1	2.776897000	-4.063214000	-0.564171000
6	1.765915000	1.435909000	-0.314006000
6	2.874113000	1.992772000	0.352063000
6	0.766091000	2.286464000	-0.817112000
6	2.974282000	3.367454000	0.512638000
6	0.877018000	3.663883000	-0.658863000
6	1.976724000	4.205750000	0.006539000
1	3.641583000	1.336607000	0.741850000
1	-0.091853000	1.872589000	-1.331327000
1	3.826693000	3.789829000	1.031310000
1	0.105827000	4.314164000	-1.054037000
1	2.058239000	5.279425000	0.131408000
6	-1.946322000	-0.217311000	-1.071606000
6	-0.889468000	-0.584837000	-0.330153000
6	-3.288009000	-0.052213000	-0.619815000
8	-4.180257000	-0.901650000	-0.689169000
8	-3.566370000	1.240618000	-0.246693000
6	-4.938904000	1.538272000	0.054191000
1	-5.580146000	1.342872000	-0.807406000
1	-5.290736000	0.951323000	0.904521000
1	-4.960451000	2.598392000	0.301079000
6	-0.968702000	-0.838196000	1.135289000
8	-1.977165000	-0.791182000	1.812872000
8	0.242140000	-1.132640000	1.670723000
6	0.287856000	-1.371680000	3.091845000
1	-0.057395000	-0.492511000	3.636458000
1	-0.331709000	-2.230371000	3.352340000

1	4.180214000	-1.580818000	1.678371000

1	1.331671000	-1.573812000	3.320252000

TS2

$v_{im.}$ = -1724.2cm^{-1}(-1101.09963)

7	2.744405000	-0.887713000	-0.723411000
6	2.283504000	-2.146844000	-0.850981000
6	1.675448000	-0.106980000	-0.487021000
6	0.448778000	-0.864663000	-0.564539000
7	0.946735000	-2.212649000	-0.698204000
1	-0.327009000	-0.473402000	-1.613176000
7	0.121908000	-3.317290000	-0.898121000
1	0.247919000	-3.996711000	-0.154529000
1	0.298702000	-3.742067000	-1.804238000
7	3.060441000	-3.193334000	-1.172055000
1	4.059031000	-3.053731000	-1.155730000
1	2.724684000	-4.137323000	-1.057571000
6	1.849718000	1.328668000	-0.245187000
6	3.141155000	1.822143000	0.018703000
6	0.776063000	2.235414000	-0.275782000
6	3.349329000	3.176700000	0.249122000
6	0.991800000	3.592548000	-0.052085000
6	2.275389000	4.068494000	0.213928000
1	3.972326000	1.129853000	0.046192000
1	-0.225122000	1.886951000	-0.485103000
1	4.349689000	3.538757000	0.457150000
1	0.153852000	4.279222000	-0.086291000
1	2.438404000	5.125122000	0.393055000
6	-1.709643000	-0.255395000	-0.938096000
6	-0.886135000	-0.617222000	0.066385000
6	-3.125099000	0.080248000	-0.928440000
8	-4.027712000	-0.721232000	-1.121269000
8	-3.334631000	1.413095000	-0.816684000
6	-4.701215000	1.864550000	-0.928232000
1	-5.117360000	1.587162000	-1.897377000
1	-5.311385000	1.437954000	-0.131467000
1	-4.656329000	2.946691000	-0.831086000
6	-1.210903000	-0.749042000	1.504999000
8	-2.301312000	-0.524389000	1.993827000
8	-0.145066000	-1.152819000	2.222965000
6	-0.344618000	-1.312480000	3.644622000
1	-0.639333000	-0.363836000	4.093782000
1	-1.109956000	-2.064662000	3.837101000
1	0.615801000	-1.637161000	4.036732000

55

$v_{im.}$ = 0 cm^{-1}(-1101.19909)

7	2.125459000	-2.208112000	-0.111096000
6	1.146361000	-3.081825000	0.038982000
6	1.524104000	-0.970686000	-0.185246000
6	0.143468000	-1.084201000	-0.070217000
7	-0.078162000	-2.479383000	0.041089000
1	-2.385019000	-1.267218000	-1.002472000
7	-1.286817000	-3.083845000	0.393698000
1	-1.171025000	-3.608540000	1.256290000
1	-1.603211000	-3.702296000	-0.347180000
7	1.304457000	-4.421915000	0.270347000
1	2.236398000	-4.760947000	0.075598000
1	0.578429000	-5.038307000	-0.069233000
6	2.355472000	0.220300000	-0.433616000
6	3.563874000	0.379313000	0.264904000
6	2.005131000	1.175326000	-1.397817000
6	4.386041000	1.474751000	0.019275000
6	2.831474000	2.270421000	-1.644883000
6	4.022166000	2.425679000	-0.936824000
1	3.849143000	-0.360372000	1.003406000
1	1.093093000	1.052560000	-1.968850000
1	5.311584000	1.587515000	0.572818000
1	2.547772000	2.996773000	-2.398164000
1	4.664975000	3.276896000	-1.130889000
6	-2.174019000	-0.349882000	-0.474134000
6	-0.919105000	-0.105245000	-0.024803000
6	-3.330071000	0.528603000	-0.253963000
8	-3.414394000	1.435395000	0.553864000
8	-4.350135000	0.174221000	-1.067933000
6	-5.569239000	0.933755000	-0.940300000
1	-5.966401000	0.846741000	0.071588000
1	-5.390249000	1.983588000	-1.174476000
1	-6.258953000	0.497041000	-1.658263000
6	-0.590926000	1.236763000	0.601806000
8	-0.594943000	2.290653000	0.012086000
8	-0.273391000	1.093473000	1.893834000
6	0.054697000	2.304345000	2.615839000
1	0.924759000	2.783745000	2.167780000
1	-0.793754000	2.988363000	2.604556000
1	0.274249000	1.982804000	3.630394000

TS3

$v_{im.}$ = -677.4cm^{-1}(-1101.12660)

7	0.394072000	2.503318000	-0.217839000
6	-0.908305000	2.505474000	-0.427636000
6	0.778347000	1.185479000	-0.078929000
6	-0.311880000	0.341817000	-0.251632000
7	-1.383526000	1.225350000	-0.477085000
1	-2.003346000	-2.635679000	-0.325496000
7	-2.731389000	0.831726000	-0.535448000
1	-3.197280000	1.200183000	-1.366903000
1	-3.246558000	0.913159000	0.451480000
7	-1.690818000	3.600858000	-0.662574000
1	-1.228700000	4.476369000	-0.456582000
1	-2.644399000	3.575028000	-0.324754000
6	2.170346000	0.868543000	0.277815000
6	3.224451000	1.542429000	-0.356773000
6	2.471022000	-0.058410000	1.286175000
6	4.545776000	1.275051000	-0.009029000
6	3.794188000	-0.324349000	1.633029000
6	4.835958000	0.338614000	0.984783000
1	3.001126000	2.269537000	-1.128226000
1	1.668560000	-0.551596000	1.822772000
1	5.350310000	1.797555000	-0.514270000
1	4.009186000	-1.039217000	2.419167000
1	5.865121000	0.133594000	1.256740000
6	-1.834124000	-1.567381000	-0.298051000
6	-0.574752000	-1.068612000	-0.252398000
6	-3.039316000	-0.760700000	-0.448859000
8	-4.076345000	-1.080110000	-0.983052000

45a

$v_{im.}$ = 0 cm^{-1}(-1101.19909)

7	-0.304793000	-2.427925000	0.072134000
6	-1.626974000	-2.302706000	0.067182000
6	0.222553000	-1.166607000	-0.016633000
6	-0.807746000	-0.222255000	-0.040252000
7	-1.977014000	-0.997448000	0.018524000
1	-2.391271000	2.789080000	-0.280071000
7	-3.255617000	-0.468005000	-0.055863000
1	-3.971200000	-1.013583000	0.412729000
7	-2.552562000	-3.313380000	0.187958000
1	-2.123442000	-4.229704000	0.167936000
1	-3.339935000	-3.264568000	-0.449546000
6	1.677385000	-0.980409000	-0.137763000
6	2.545112000	-1.713830000	0.685459000
6	2.226743000	-0.121828000	-1.100859000
6	3.924865000	-1.573229000	0.562888000
6	3.607985000	0.018073000	-1.221650000
6	4.461896000	-0.704368000	-0.388621000
1	2.130304000	-2.387744000	1.425511000
1	1.574739000	0.415729000	-1.780010000
1	4.582143000	-2.141209000	1.211749000
1	4.015736000	0.681204000	-1.976212000
1	5.536364000	-0.597441000	-0.484592000
6	-2.240083000	1.720510000	-0.219736000
6	-0.988551000	1.188798000	-0.120934000
6	-3.445156000	0.908977000	-0.110284000
8	-4.585456000	1.361116000	-0.043492000
6	0.158881000	2.160401000	-0.041519000

8	-3.443826000	-0.176455000	1.414347000
6	-4.671938000	-0.658896000	1.890381000
1	-5.271227000	-1.088396000	1.070807000
1	-4.527509000	-1.435698000	2.653950000
1	-5.265913000	0.150271000	2.337094000
6	0.531319000	-2.087653000	-0.309276000
8	0.555635000	-3.092625000	0.365649000
8	1.432647000	-1.781614000	-1.243628000
6	2.529108000	-2.711340000	-1.416989000
1	3.106564000	-2.780227000	-0.495511000
1	2.146714000	-3.693377000	-1.693841000
1	3.132912000	-2.294252000	-2.218009000
8	0.325337000	3.065745000	-0.826504000
8	0.913108000	1.931141000	1.031817000
6	2.031783000	2.827927000	1.245089000
1	2.726661000	2.758164000	0.408864000
1	1.673871000	3.851343000	1.352186000
1	2.499858000	2.485287000	2.163415000

CH_3OH

$\nu_{im.}$ = 0cm^{-1}(-115.74626)

1	1.146969000	-0.755172000	0.000004000
8	0.752515000	0.122872000	0.000001000
6	-0.671353000	-0.019805000	0.000000000
1	-1.090218000	0.986428000	-0.000251000
1	-1.024356000	-0.547914000	-0.891719000
1	-1.024395000	-0.547487000	0.891959000

Table S13. Optimized geometries of stationary points of the Scheme 10. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS4

$\nu_{im.}$ = -249.5cm^{-1}(-1101.11891)

7	0.224306000	0.742692000	-0.205663000
6	0.846818000	1.915531000	-0.238670000
6	-1.045676000	0.925784000	-0.764555000
6	-1.168321000	2.230428000	-1.142945000
7	0.030491000	2.851759000	-0.808362000
1	-1.943451000	2.774018000	-1.654015000
7	0.301635000	4.198813000	-1.059986000
1	1.074726000	4.289985000	-1.712881000
1	0.515903000	4.684226000	-0.193914000
7	2.073921000	2.210621000	0.277096000
1	2.743080000	1.443276000	0.316335000
1	2.485020000	3.078799000	-0.037257000
6	-2.008371000	-0.168462000	-0.933246000
6	-1.576968000	-1.495884000	-1.082000000
6	-3.387807000	0.095867000	-0.974149000
6	-2.497434000	-2.525804000	-1.267140000
6	-4.303868000	-0.933619000	-1.169254000
6	-3.863833000	-2.250770000	-1.314153000
1	-0.517455000	-1.718031000	-1.065209000
1	-3.744124000	1.110787000	-0.838117000
1	-2.144197000	-3.544577000	-1.381898000
1	-5.364335000	-0.709002000	-1.196387000
1	-4.578632000	-3.052728000	-1.459064000
6	0.892196000	-0.648378000	1.116621000
6	2.002600000	-1.165499000	0.864844000
6	-0.146862000	-0.680216000	2.160813000
8	-0.315194000	-1.660215000	2.857749000
8	-0.828236000	0.457293000	2.295523000
6	-1.830152000	0.480744000	3.338533000
1	-2.576037000	-0.293493000	3.160298000
1	-1.363709000	0.329348000	4.311904000
1	-2.280369000	1.467873000	3.278984000
6	3.143199000	-1.101996000	0.021129000
8	3.950960000	-0.175076000	0.041043000
8	3.266686000	-2.170161000	-0.787940000
6	4.394872000	-2.169145000	-1.691610000
1	4.348726000	-1.308057000	-2.358501000
1	5.329292000	-2.152875000	-1.130586000
1	4.307004000	-3.092958000	-2.257605000

56

$\nu_{im.}$ = 0 cm^{-1}(-1101.13791)

7	-0.415246000	1.099756000	-0.224734000
6	-0.546113000	2.439113000	-0.252653000
6	-1.684410000	0.514714000	-0.442853000
6	-2.563915000	1.536967000	-0.582798000
7	-1.850558000	2.727929000	-0.462793000
1	-3.617242000	1.548183000	-0.797022000
7	-2.433186000	3.989628000	-0.586623000
1	-2.048316000	4.482542000	-1.387041000
1	-2.298194000	4.527645000	0.264110000
7	0.439208000	3.330115000	-0.042810000
1	1.370643000	2.984772000	-0.250660000
1	0.261168000	4.294349000	-0.285368000
6	-1.934643000	-0.929714000	-0.532784000
6	-1.073529000	-1.783243000	-1.239262000
6	-3.091126000	-1.465844000	0.054472000
6	-1.363970000	-3.141324000	-1.348968000
6	-3.382272000	-2.821780000	-0.067855000
6	-2.517839000	-3.665153000	-0.766431000
1	-0.185302000	-1.384635000	-1.712366000
1	-3.754014000	-0.819818000	0.618244000
1	-0.690674000	-3.788650000	-1.899130000
1	-4.278771000	-3.221141000	0.392481000
1	-2.741124000	-4.722159000	-0.854774000
6	0.853872000	0.430527000	0.076980000
6	1.910460000	0.671795000	-0.695668000
6	0.854096000	-0.359110000	1.343789000
8	1.729287000	-1.140208000	1.658483000
8	-0.203995000	-0.084717000	2.132104000
6	-0.267081000	-0.784382000	3.393362000
1	-0.290853000	-1.861607000	3.228255000
1	0.592447000	-0.526032000	4.012374000
1	-1.188398000	-0.450194000	3.863797000
6	3.236036000	0.195225000	-0.447689000
8	4.095682000	0.788896000	0.203024000
8	3.525676000	-0.940636000	-1.150319000
6	4.882278000	-1.412708000	-1.076681000
1	5.577306000	-0.660625000	-1.453880000
1	5.150263000	-1.671352000	-0.051027000
1	4.915269000	-2.300459000	-1.705366000

TS5

$\nu_{im.}$ = -1307.1cm^{-1}(-1101.13233)

57

$\nu_{im.}$ = 0 cm^{-1}(-1101.16720)

7	-0.139164000	1.152850000	-0.041770000
6	0.139502000	2.496280000	-0.016541000
6	-1.546027000	0.984234000	-0.145958000
6	-2.090332000	2.222853000	-0.094012000
7	-1.054433000	3.151026000	0.005733000
1	-3.111867000	2.546447000	-0.181293000
7	-1.245840000	4.532276000	-0.024985000
1	-0.808721000	4.927363000	-0.853930000
1	-0.847370000	4.956344000	0.807861000
7	1.365248000	2.967899000	-0.057748000
1	2.081921000	2.018323000	-0.258582000
1	1.515570000	3.965452000	0.009259000
6	-2.235165000	-0.285726000	-0.412811000
6	-1.754017000	-1.183431000	-1.378204000
6	-3.438866000	-0.579435000	0.244762000
6	-2.458371000	-2.349160000	-1.670713000
6	-4.146510000	-1.739248000	-0.060528000
6	-3.657180000	-2.630891000	-1.015644000
1	-0.839075000	-0.962975000	-1.915743000
1	-3.811251000	0.097724000	1.004618000
1	-2.074428000	-3.031933000	-2.420094000
1	-5.075136000	-1.952037000	0.456887000
1	-4.204791000	-3.537250000	-1.246980000
6	0.916051000	0.173153000	0.059939000
6	2.165099000	0.546524000	-0.247850000
6	0.612418000	-1.113760000	0.760885000
8	1.176527000	-2.161218000	0.523057000
8	-0.275315000	-0.954739000	1.754035000
6	-0.597956000	-2.131271000	2.529022000
1	-1.020275000	-2.901625000	1.883981000
1	0.294765000	-2.511411000	3.025493000
1	-1.330797000	-1.801875000	3.260821000
6	3.349862000	-0.265403000	-0.051453000
8	3.996310000	-0.331371000	0.985483000
8	3.762901000	-0.856411000	-1.200486000
6	5.001301000	-1.591925000	-1.137552000
1	5.823079000	-0.937011000	-0.845084000
1	4.922885000	-2.417543000	-0.429187000
1	5.162564000	-1.973199000	-2.143398000

7	-0.176435000	1.133340000	-0.236194000
6	0.026256000	2.529664000	-0.147817000
6	-1.576515000	0.856886000	-0.270773000
6	-2.211250000	2.043751000	-0.177905000
7	-1.258892000	3.051084000	-0.078582000
1	-3.259166000	2.278351000	-0.243995000
7	-1.579904000	4.405433000	-0.051401000
1	-1.193070000	4.874752000	-0.867109000
1	-1.207257000	4.835579000	0.790992000
7	1.162865000	3.125528000	-0.125612000
1	2.199905000	1.102251000	-1.303430000
1	1.039176000	4.124546000	0.022189000
6	-2.156191000	-0.466777000	-0.527322000
6	-1.629068000	-1.315287000	-1.514949000
6	-3.302782000	-0.875914000	0.172252000
6	-2.235077000	-2.537039000	-1.793244000
6	-3.913271000	-2.093357000	-0.118903000
6	-3.380283000	-2.930376000	-1.099526000
1	-0.753073000	-1.012509000	-2.076632000
1	-3.707036000	-0.239734000	0.951104000
1	-1.817135000	-3.178965000	-2.560404000
1	-4.798718000	-2.393461000	0.430007000
1	-3.851116000	-3.881609000	-1.319530000
6	0.841222000	0.198853000	0.006396000
6	2.053825000	0.334566000	-0.557675000
6	0.527040000	-0.910794000	0.989694000
8	0.722594000	-2.083754000	0.784309000
8	0.004393000	-0.406910000	2.111395000
6	-0.352746000	-1.358825000	3.142859000
1	-1.106546000	-2.049805000	2.766189000
1	0.530903000	-1.909181000	3.464747000
1	-0.751564000	-0.761582000	3.958073000
6	3.255558000	-0.437635000	-0.182572000
8	3.478891000	-0.953114000	0.893533000
8	4.127249000	-0.457448000	-1.209797000
6	5.375504000	-1.147265000	-0.983231000
1	5.915085000	-0.688096000	-0.154577000
1	5.192324000	-2.199652000	-0.765603000
1	5.935503000	-1.041468000	-1.908712000

Table S14. Optimized geometries of stationary points of the Scheme 11. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS6			
$\nu_{im.}$ = -223.0cm^{-1}(-1101.11271)			
7	-1.213953000	1.111637000	0.096488000
6	-0.201891000	1.098583000	-0.731139000
6	-2.234644000	0.427575000	-0.547975000
6	-1.788306000	-0.004803000	-1.777446000
7	-0.483352000	0.423996000	-1.883021000
1	-2.240597000	-0.569365000	-2.573981000
7	0.335164000	0.168280000	-2.991300000
1	1.190174000	-0.280015000	-2.673439000
1	0.551503000	1.035888000	-3.474293000
7	1.068881000	1.644864000	-0.449946000
1	0.995133000	2.304813000	0.322576000
1	1.482845000	2.137934000	-1.240109000
6	-3.553617000	0.244347000	0.073647000
6	-3.783293000	0.670982000	1.390653000
6	-4.611314000	-0.358783000	-0.626891000
6	-5.029967000	0.497709000	1.988145000
6	-5.855052000	-0.533053000	-0.026977000
6	-6.072265000	-0.105497000	1.284318000
1	-2.976484000	1.137606000	1.941766000
1	-4.466727000	-0.691857000	-1.648342000
1	-5.186327000	0.833955000	3.007243000
1	-6.657804000	-1.001090000	-0.585820000
1	-7.041865000	-0.240590000	1.749815000
6	2.315628000	0.344370000	0.055933000
6	1.967984000	-0.849290000	-0.160294000

58			
$\nu_{im.}$ = 0 cm^{-1}(-1101.11690)			
7	-1.343920000	0.504050000	-0.702693000
6	-0.328914000	-0.097066000	-1.254666000
6	-2.280991000	-0.493622000	-0.480061000
6	-1.770391000	-1.700316000	-0.912752000
7	-0.516263000	-1.434333000	-1.412585000
1	-2.157921000	-2.704139000	-0.925837000
7	0.356670000	-2.405457000	-1.932281000
1	1.291628000	-2.197182000	-1.553357000
1	0.363858000	-2.336440000	-2.947679000
7	0.896867000	0.579088000	-1.617834000
1	0.683600000	1.583077000	-1.683953000
1	1.222070000	0.277867000	-2.540847000
6	-3.587452000	-0.203488000	0.127377000
6	-3.966899000	1.120421000	0.395434000
6	-4.483292000	-1.235311000	0.451112000
6	-5.205095000	1.403229000	0.967824000
6	-5.720451000	-0.949851000	1.021499000
6	-6.088847000	0.371108000	1.282946000
1	-3.284788000	1.925117000	0.151310000
1	-4.214217000	-2.268433000	0.262876000
1	-5.479976000	2.433166000	1.166793000
1	-6.397314000	-1.761119000	1.265029000
1	-7.052153000	0.591776000	1.728326000
6	2.072667000	0.403688000	-0.618455000
6	2.556098000	-0.812234000	-0.457700000

6	3.462995000	1.096440000	0.591782000
8	4.439624000	0.542167000	1.047355000
8	3.318822000	2.428385000	0.521052000
6	4.413637000	3.228999000	1.028746000
1	4.569625000	3.018327000	2.086188000
1	5.322304000	3.015913000	0.466799000
1	4.104783000	4.260407000	0.883712000
6	2.398278000	-2.198028000	-0.103949000
8	2.992266000	-2.781027000	-1.003508000
8	2.028257000	-2.806153000	1.052172000
6	2.375166000	-4.200684000	1.180071000
1	1.905747000	-4.787083000	0.389440000
1	3.456814000	-4.333807000	1.142641000
1	1.991900000	-4.502659000	2.151973000

6	2.480654000	1.690862000	-0.006028000
8	3.354968000	1.800310000	0.823733000
8	1.769005000	2.735445000	-0.485548000
6	2.081279000	4.047703000	0.040356000
1	1.909176000	4.066548000	1.115863000
1	3.119105000	4.297042000	-0.177637000
1	1.406288000	4.729652000	-0.469104000
6	3.681184000	-1.143796000	0.372567000
8	4.841789000	-1.206374000	-0.017338000
8	3.310770000	-1.517455000	1.625609000
6	4.361329000	-1.987673000	2.493261000
1	4.844241000	-2.869912000	2.070817000
1	5.105475000	-1.207291000	2.657027000
1	3.869916000	-2.240504000	3.430202000

TS7

$\nu_{im.}$ = -1760.2cm^{-1}(-1101.09278)

7	1.532893000	0.048422000	0.867942000
6	0.354908000	-0.461169000	0.624021000
6	2.419958000	-0.634950000	0.049344000
6	1.727517000	-1.568185000	-0.688885000
7	0.406451000	-1.455626000	-0.312945000
1	2.020496000	-2.297499000	-1.423918000
7	-0.602144000	-2.299906000	-0.803515000
1	-1.342197000	-1.741244000	-1.217517000
1	-0.990372000	-2.843801000	-0.037988000
7	-0.839187000	-0.065305000	1.293659000
1	-0.572285000	0.585039000	2.035474000
1	-1.745360000	-0.877699000	1.678304000
6	3.858211000	-0.333360000	0.045577000
6	4.396997000	0.568047000	0.976259000
6	4.725341000	-0.935429000	-0.881007000
6	5.760278000	0.855560000	0.981654000
6	6.087194000	-0.648203000	-0.872155000
6	6.613039000	0.249251000	0.059262000
1	3.738848000	1.039770000	1.695157000
1	4.336415000	-1.628797000	-1.618120000
1	6.156946000	1.554655000	1.709638000
1	6.739066000	-1.123403000	-1.596717000
1	7.673604000	0.473402000	0.063878000
6	-2.065033000	0.384271000	0.544612000
6	-3.017053000	-0.456281000	0.955307000
6	-2.082806000	1.569943000	-0.336232000
8	-3.064324000	1.925732000	-0.954128000
8	-0.900973000	2.199417000	-0.357419000
6	-0.810249000	3.386033000	-1.181731000
1	-1.015550000	3.135159000	-2.222128000
1	-1.517787000	4.137946000	-0.833155000
1	0.211280000	3.737293000	-1.066003000
6	-4.442171000	-0.427999000	0.656229000
8	-5.273289000	0.124570000	1.356399000
8	-4.752202000	-1.168972000	-0.425482000
6	-6.156176000	-1.284593000	-0.750688000
1	-6.700593000	-1.742229000	0.075557000
1	-6.577059000	-0.303721000	-0.972115000
1	-6.194955000	-1.921561000	-1.630710000

59

$\nu_{im.}$ = 0 cm^{-1}(-1101.19391)

7	1.387294000	0.024973000	0.908534000
6	0.402784000	-0.830579000	0.758722000
6	2.486070000	-0.536681000	0.284218000
6	2.132099000	-1.759283000	-0.250869000
7	0.811425000	-1.943610000	0.064162000
1	2.669363000	-2.501402000	-0.815691000
7	0.069705000	-3.077605000	-0.303290000
1	-0.720730000	-2.766421000	-0.866643000
1	-0.287061000	-3.518406000	0.540485000
7	-0.893192000	-0.709642000	1.279534000
1	-0.989002000	-0.793767000	2.283983000
1	-3.289815000	-0.157215000	2.252191000
6	3.788121000	0.145149000	0.244621000
6	3.950275000	1.402089000	0.847473000
6	4.896896000	-0.437305000	-0.391506000
6	5.180849000	2.054521000	0.815182000
6	6.125298000	0.216670000	-0.423016000
6	6.275100000	1.466833000	0.180217000
1	3.103246000	1.862018000	1.340870000
1	4.803912000	-1.407794000	-0.865725000
1	5.284400000	3.025352000	1.287336000
1	6.967974000	-0.251300000	-0.919758000
1	7.232281000	1.975057000	0.155064000
6	-1.986866000	-0.245525000	0.592457000
6	-3.182993000	-0.013189000	1.184078000
6	-1.771691000	-0.075060000	-0.901145000
8	-1.729647000	-1.013650000	-1.666733000
8	-1.566904000	1.191963000	-1.223172000
6	-1.357956000	1.481925000	-2.630008000
1	-0.490260000	0.936266000	-2.998409000
1	-2.246923000	1.204776000	-3.195464000
1	-1.189203000	2.553748000	-2.676493000
6	-4.362768000	0.396763000	0.438470000
8	-4.449841000	0.518906000	-0.773766000
8	-5.404445000	0.628659000	1.270958000
6	-6.643680000	1.031006000	0.654388000
1	-6.515345000	1.971801000	0.118043000
1	-6.994891000	0.261966000	-0.034425000
1	-7.347104000	1.155486000	1.474065000

Table S15. Optimized geometries of stationary points of the Scheme 12. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS8

$\nu_{im.}$ = -201.9cm^{-1}(-1101.10937)

7	2.410478000	-1.484710000	-0.685771000
6	1.206983000	-1.879664000	-1.022181000
6	2.329682000	-0.112533000	-0.463202000
6	1.039821000	0.318708000	-0.657581000
7	0.339876000	-0.816272000	-1.036158000
1	0.555077000	1.274948000	-0.565941000
7	-1.018501000	-0.868594000	-1.379402000
1	-1.202722000	-1.797277000	-1.767728000

60

$\nu_{im.}$ = 0 cm^{-1}(-1101.11532)

7	2.264143000	-1.698926000	-0.310565000
6	1.046501000	-2.056407000	-0.616379000
6	2.286044000	-0.302693000	-0.313145000
6	1.043086000	0.190027000	-0.615372000
7	0.254604000	-0.942945000	-0.791742000
1	0.629022000	1.180666000	-0.680136000
7	-1.040128000	-0.967986000	-1.380256000
1	-1.242277000	-1.961782000	-1.564383000

1	-1.219625000	-0.176419000	-2.105120000
7	0.785711000	-3.139297000	-1.420729000
1	1.568881000	-3.767959000	-1.550982000
1	0.101623000	-3.561311000	-0.800972000
6	3.506981000	0.670264000	-0.064332000
6	4.749663000	0.041223000	0.108326000
6	3.424703000	2.056085000	0.153116000
6	5.872775000	0.774043000	0.486903000
6	4.547319000	2.785388000	0.532514000
6	5.778850000	2.148837000	0.701794000
1	4.825599000	-1.026131000	-0.056330000
1	2.479406000	2.571388000	0.025993000
1	6.823574000	0.268369000	0.614921000
1	4.461224000	3.853917000	0.695690000
1	6.652543000	2.718526000	0.997105000
6	-3.117564000	0.490569000	-0.589082000
6	-2.357666000	-0.410756000	-0.151106000
6	-4.276129000	1.286961000	-0.445484000
8	-5.400985000	0.956637000	-0.802054000
8	-3.996985000	2.499814000	0.097498000
6	-5.110761000	3.404686000	0.246977000
1	-5.559725000	3.624234000	-0.722273000
1	-5.863481000	2.982086000	0.913220000
1	-4.688537000	4.308062000	0.680807000
6	-2.197855000	-1.282391000	1.022833000
8	-2.813034000	-1.086190000	2.048209000
8	-1.348385000	-2.305757000	0.845255000
6	-1.179258000	-3.191150000	1.982251000
1	-0.823133000	-2.626898000	2.842930000
1	-2.125106000	-3.677295000	2.217932000
1	-0.438693000	-3.923793000	1.673423000

1	-1.017179000	-0.472829000	-2.282062000
7	0.526237000	-3.318560000	-0.844618000
1	1.252390000	-4.021806000	-0.904707000
1	-0.185527000	-3.598727000	-0.177425000
6	3.513871000	0.441078000	0.001953000
6	4.706571000	-0.246873000	0.270872000
6	3.528023000	1.845298000	0.035927000
6	5.878346000	0.448709000	0.562368000
6	4.699171000	2.537240000	0.328051000
6	5.881599000	1.842810000	0.592704000
1	4.706827000	-1.329217000	0.249217000
1	2.621257000	2.404298000	-0.165215000
1	6.790329000	-0.101109000	0.766966000
1	4.689187000	3.621203000	0.349697000
1	6.793042000	2.383559000	0.820542000
6	-2.579252000	0.859358000	-1.116287000
6	-2.146697000	-0.275095000	-0.593442000
6	-3.661928000	1.640298000	-0.588271000
8	-4.834708000	1.527229000	-0.928923000
8	-3.234011000	2.626788000	0.243712000
6	-4.237980000	3.542244000	0.724636000
1	-4.715926000	4.061937000	-0.106882000
1	-4.993608000	3.015449000	1.308701000
1	-3.704164000	4.251039000	1.353865000
6	-2.589300000	-1.020971000	0.606457000
8	-3.393618000	-0.599115000	1.405840000
8	-2.016067000	-2.242923000	0.699177000
6	-2.419627000	-3.054315000	1.832071000
1	-2.157361000	-2.550128000	2.761195000
1	-3.492687000	-3.236571000	1.794410000
1	-1.870639000	-3.987157000	1.735174000

TS9

$\nu_{im.}$ = -1702.5cm^{-1}(-1101.09939)

7	-2.283631000	1.599393000	-0.479420000
6	-1.047448000	1.894414000	-0.793327000
6	-2.339347000	0.210571000	-0.354787000
6	-1.104378000	-0.333682000	-0.595604000
7	-0.282056000	0.754472000	-0.870070000
1	-0.720817000	-1.338615000	-0.579102000
7	1.032087000	0.681414000	-1.367530000
1	1.197999000	1.519489000	-1.933621000
1	1.478121000	-0.387788000	-1.876558000
7	-0.511950000	3.124872000	-1.122909000
1	-1.210224000	3.857500000	-1.111463000
1	0.298984000	3.383088000	-0.570085000
6	-3.589122000	-0.475228000	0.001226000
6	-4.776746000	0.255426000	0.159436000
6	-3.632421000	-1.867399000	0.187362000
6	-5.969159000	-0.385508000	0.490269000
6	-4.824196000	-2.505055000	0.517517000
6	-6.000527000	-1.767904000	0.671086000
1	-4.755870000	1.328749000	0.019743000
1	-2.730951000	-2.459310000	0.076336000
1	-6.875779000	0.197992000	0.607274000
1	-4.835000000	-3.580348000	0.656841000
1	-6.928007000	-2.266139000	0.929251000
6	2.633928000	-0.804671000	-0.968760000
6	2.148942000	0.320250000	-0.438153000
6	3.820548000	-1.552761000	-0.575738000
8	4.925912000	-1.371776000	-1.056590000
8	3.538462000	-2.532507000	0.302815000
6	4.634601000	-3.394717000	0.685348000
1	5.038717000	-3.904627000	-0.189353000
1	5.420127000	-2.816816000	1.172312000
1	4.205283000	-4.112466000	1.379638000
6	2.553695000	1.151913000	0.710695000
8	3.433398000	0.839405000	1.482350000
8	1.843819000	2.291611000	0.796307000
6	2.172450000	3.168852000	1.904983000
1	2.023058000	2.645397000	2.848325000
1	3.205967000	3.502338000	1.820451000
1	1.489597000	4.009627000	1.821132000

61

$\nu_{im.}$ = 0 cm^{-1}(-1101.19769)

7	2.239846000	-1.502352000	-0.655825000
6	0.984499000	-1.674342000	-0.988698000
6	2.415721000	-0.126292000	-0.478946000
6	1.239533000	0.532382000	-0.705314000
7	0.310864000	-0.471869000	-1.010745000
1	0.942144000	1.565535000	-0.663034000
7	-0.980522000	-0.305663000	-1.471345000
1	-1.046156000	0.034080000	-2.424907000
1	-3.225927000	0.957355000	-2.042692000
7	0.380286000	-2.850484000	-1.355899000
1	0.886177000	-3.673048000	-1.057127000
1	-0.612053000	-2.907952000	-1.167584000
6	3.720361000	0.429734000	-0.094273000
6	4.828533000	-0.414970000	0.073117000
6	3.896938000	1.808869000	0.111728000
6	6.072239000	0.102201000	0.431547000
6	5.139256000	2.322916000	0.469384000
6	6.235630000	1.472512000	0.631518000
1	4.704459000	-1.479258000	-0.081307000
1	3.059464000	2.487163000	-0.006607000
1	6.915446000	-0.568629000	0.555074000
1	5.252643000	3.390349000	0.623183000
1	7.202864000	1.874633000	0.910690000
6	-3.135190000	0.626245000	-1.015413000
6	-1.999191000	0.027749000	-0.599546000
6	-4.290002000	0.817337000	-0.142793000
8	-4.404273000	0.415212000	1.002732000
8	-5.258404000	1.514245000	-0.776035000
6	-6.462995000	1.771262000	-0.025409000
1	-6.932858000	0.833603000	0.272753000
1	-6.239608000	2.367628000	0.859664000
1	-7.111626000	2.323195000	-0.701024000
6	-1.746239000	-0.375139000	0.842958000
8	-1.372639000	0.395073000	1.691965000
8	-1.926954000	-1.684510000	1.002883000
6	-1.699134000	-2.213463000	2.335847000
1	-0.669647000	-2.026712000	2.638966000
1	-2.389141000	-1.748099000	3.038652000
1	-1.891093000	-3.279443000	2.255395000

Table S16. Optimized geometries of stationary points of the Scheme 13. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS10			
$\nu_{im.}$ = -362.1 cm^{-1}(-1216.84814)			
7	1.856643000	1.947339000	-0.718550000
6	2.799056000	1.027703000	-0.961235000
6	0.676487000	1.283048000	-0.720651000
6	0.874375000	-0.123692000	-0.867653000
7	2.265834000	-0.213447000	-1.111559000
1	0.238792000	-0.804603000	-1.421025000
7	2.922245000	-1.412341000	-1.399825000
1	3.663099000	-1.590788000	-0.727907000
1	3.304383000	-1.388522000	-2.340755000
7	4.121412000	1.282673000	-1.003138000
1	4.394134000	2.253166000	-1.043696000
1	4.743694000	0.626514000	-1.450687000
6	-0.600529000	1.972143000	-0.580684000
6	-0.646118000	3.281120000	-0.067603000
6	-1.800916000	1.353019000	-0.969419000
6	-1.859659000	3.944647000	0.062706000
6	-3.013956000	2.024564000	-0.840535000
6	-3.048602000	3.318636000	-0.322513000
1	0.276668000	3.761966000	0.231553000
1	-1.784029000	0.359952000	-1.401322000
1	-1.882642000	4.950828000	0.465605000
1	-3.931655000	1.539211000	-1.151965000
1	-3.993907000	3.840075000	-0.224098000
6	-0.798784000	-1.284734000	1.133569000
6	0.385348000	-0.934009000	0.907629000
6	-2.159377000	-1.576259000	0.964369000
8	-2.598033000	-2.468916000	0.225539000
8	-2.972858000	-0.816907000	1.736035000
6	-4.388268000	-1.065706000	1.616638000
1	-4.722812000	-0.904112000	0.591410000
1	-4.625513000	-2.085010000	1.923248000
1	-4.860912000	-0.350396000	2.285526000
6	1.636945000	-1.060610000	1.688437000
8	2.091374000	-2.113499000	2.081520000
8	2.195926000	0.131940000	1.928670000
6	3.406338000	0.131826000	2.723355000
1	3.201101000	-0.266330000	3.716863000
1	4.177117000	-0.465123000	2.236397000
1	3.709033000	1.173570000	2.783881000
1	-1.731423000	-2.498097000	-1.413290000
8	-1.263172000	-2.298020000	-2.245161000
6	-0.792722000	-3.517987000	-2.815715000
1	-1.618841000	-4.195621000	-3.059983000
1	-0.266410000	-3.268266000	-3.738203000
1	-0.096430000	-4.037022000	-2.147038000

62			
$\nu_{im.}$ = 0 (-1216.87323)			
7	-2.747769000	-1.074427000	0.311310000
6	-2.159747000	-2.318307000	0.310984000
6	-1.786257000	-0.199542000	0.459494000
6	-0.424048000	-0.850250000	0.611713000
7	-0.839509000	-2.262729000	0.477665000
1	-0.077371000	-0.694121000	1.639231000
7	0.052589000	-3.322576000	0.594225000
1	0.093880000	-3.863741000	-0.263954000
1	-0.180504000	-3.911278000	1.388385000
7	-2.874051000	-3.420938000	0.170609000
1	-3.873982000	-3.345538000	0.060183000
1	-2.452602000	-4.337458000	0.169584000
6	-2.044715000	1.232773000	0.518013000
6	-3.319592000	1.721806000	0.174992000
6	-1.048340000	2.136054000	0.927037000
6	-3.586014000	3.082143000	0.236133000
6	-1.324984000	3.497580000	0.993374000
6	-2.589708000	3.972635000	0.646437000
1	-4.084956000	1.025622000	-0.142813000
1	-0.063945000	1.776635000	1.196757000
1	-4.567361000	3.452824000	-0.035202000
1	-0.554259000	4.187443000	1.315479000
1	-2.800776000	5.034735000	0.695389000
6	1.894009000	-0.059312000	0.259397000
6	0.729465000	-0.428557000	-0.300160000
6	3.083226000	0.313857000	-0.456807000
8	4.018770000	-0.439820000	-0.717886000
8	3.165534000	1.660839000	-0.671914000
6	4.397406000	2.148077000	-1.232444000
1	5.241430000	1.910714000	-0.582655000
1	4.570961000	1.721075000	-2.221516000
1	4.276032000	3.226966000	-1.308120000
6	0.508570000	-0.454431000	-1.773263000
8	1.340420000	-0.188333000	-2.618530000
8	-0.757627000	-0.809930000	-2.094854000
6	-1.090372000	-0.843466000	-3.498006000
1	-0.951434000	0.141509000	-3.944239000
1	-0.467744000	-1.572509000	-4.017325000
1	-2.136442000	-1.136806000	-3.542367000
1	2.016107000	-0.078078000	2.152285000
8	1.959685000	-0.115590000	3.151111000
6	2.774856000	-1.185757000	3.610718000
1	3.833586000	-1.031653000	3.365083000
1	2.681991000	-1.239706000	4.697744000
1	2.461787000	-2.151084000	3.192319000

TS11			
$\nu_{im.}$ = -1083.8cm^{-1}(-1216.86763)			
7	-2.806607000	-0.839402000	0.248461000
6	-2.333618000	-2.120519000	0.412989000
6	-1.781522000	-0.036765000	0.390034000
6	-0.503524000	-0.776670000	0.703567000
7	-1.027378000	-2.154135000	0.677801000
1	-0.181845000	-0.528231000	1.731646000
7	-0.234767000	-3.263000000	0.951868000
1	-0.203177000	-3.896922000	0.159204000
1	-0.549538000	-3.740589000	1.791190000
7	-3.131210000	-3.170953000	0.325817000
1	-4.110240000	-3.025695000	0.130800000
1	-2.794518000	-4.114848000	0.441263000
6	-1.904945000	1.411176000	0.295254000
6	-3.033534000	1.973507000	-0.329375000
6	-0.920229000	2.256595000	0.835656000
6	-3.166267000	3.352193000	-0.419764000

63			
$\nu_{im.}$ = 0 cm^{-1}(-1101.19909)			
7	2.125459000	-2.208112000	-0.111096000
6	1.146361000	-3.081825000	0.038982000
6	1.524104000	-0.970686000	-0.185246000
6	0.143468000	-1.084201000	-0.070217000
7	-0.078162000	-2.479383000	0.041089000
1	-2.385019000	-1.267218000	-1.002472000
7	-1.286817000	-3.083845000	0.393698000
1	-1.171025000	-3.608540000	1.256290000
1	-1.603211000	-3.702296000	-0.347180000
7	1.304457000	-4.421915000	0.270347000
1	2.236398000	-4.760947000	0.075598000
1	0.578429000	-5.038307000	-0.069233000
6	2.355472000	0.220300000	-0.433616000
6	3.563874000	0.379313000	0.264904000
6	2.005131000	1.175326000	-1.397817000
6	4.386041000	1.474751000	0.019275000

6	-1.067028000	3.637364000	0.751257000
6	-2.183806000	4.186404000	0.120842000
1	-3.788119000	1.319721000	-0.747710000
1	-0.060202000	1.838979000	1.343596000
1	-4.032162000	3.780237000	-0.910774000
1	-0.311109000	4.285013000	1.178993000
1	-2.291021000	5.262845000	0.051573000
6	1.857103000	-0.152581000	0.421556000
6	0.723570000	-0.549131000	-0.177536000
6	3.138425000	0.070376000	-0.248713000
8	4.035639000	-0.754431000	-0.309141000
8	3.284951000	1.349565000	-0.658141000
6	4.565936000	1.705167000	-1.220331000
1	5.362206000	1.537578000	-0.494397000
1	4.761817000	1.122477000	-2.121083000
1	4.491255000	2.762496000	-1.463217000
6	0.628231000	-0.770389000	-1.647942000
8	1.556516000	-0.688671000	-2.426791000
8	-0.627227000	-1.069874000	-2.035101000
6	-0.841975000	-1.282651000	-3.447468000
1	-0.582956000	-0.384108000	-4.007473000
1	-0.240524000	-2.121738000	-3.797390000
1	-1.901403000	-1.503471000	-3.549162000
1	1.741335000	0.072887000	1.710788000
8	1.381545000	0.259462000	2.933689000
6	2.042197000	-0.670195000	3.747334000
1	2.679044000	-0.183215000	4.505515000
1	1.341944000	-1.324488000	4.295224000
1	2.703474000	-1.338198000	3.163505000
6	2.831474000	2.270421000	-1.644883000
6	4.022166000	2.425679000	-0.936824000
1	3.849143000	-0.360372000	1.003406000
1	1.093093000	1.052560000	-1.968850000
1	5.311584000	1.587515000	0.572818000
1	2.547772000	2.996773000	-2.398164000
1	4.664975000	3.276896000	-1.130889000
6	-2.174019000	-0.349882000	-0.474134000
6	-0.919105000	-0.105245000	-0.024803000
6	-3.330071000	0.528603000	-0.253963000
8	-3.414394000	1.435395000	0.553864000
8	-4.350135000	0.174221000	-1.067933000
6	-5.569239000	0.933755000	-0.940300000
1	-5.966401000	0.846741000	0.071588000
1	-5.390249000	1.983588000	-1.174476000
1	-6.258953000	0.497041000	-1.658263000
6	-0.590926000	1.236763000	0.601806000
8	-0.594943000	2.290653000	0.012086000
8	-0.273391000	1.093473000	1.893834000
6	0.054697000	2.304345000	2.615839000
1	0.924759000	2.783745000	2.167780000
1	-0.793754000	2.988363000	2.604556000
1	0.274249000	1.982804000	3.630394000

TS12

$\nu_{im.}$ = -418.5cm^{-1}(-1216.86865)

7	-0.493685000	-2.418416000	-0.320114000
6	0.774726000	-2.207797000	-0.613796000
6	-1.070681000	-1.172530000	-0.133218000
6	-0.134754000	-0.176880000	-0.354875000
7	1.050585000	-0.872154000	-0.638857000
1	1.206265000	2.959548000	-0.206056000
7	2.281272000	-0.249420000	-0.920556000
1	2.331992000	-0.039370000	-1.918588000
1	3.466314000	-0.942908000	-0.356732000
7	1.689440000	-3.177279000	-0.952719000
1	2.644268000	-3.011424000	-0.661732000
1	1.376922000	-4.106220000	-0.702060000
6	-2.468249000	-1.072280000	0.312604000
6	-3.426485000	-1.969840000	-0.184227000
6	-2.870962000	-0.121650000	1.262821000
6	-4.751309000	-1.901568000	0.238712000
6	-4.197488000	-0.052838000	1.683718000
6	-5.144120000	-0.940359000	1.171806000
1	-3.124572000	-2.716029000	-0.909223000
1	-2.138963000	0.549342000	1.697715000
1	-5.479218000	-2.598587000	-0.161703000
1	-4.487867000	0.685613000	2.422678000
1	-6.175426000	-0.888999000	1.502034000
6	1.139805000	1.879026000	-0.197762000
6	-0.058621000	1.266737000	-0.303224000
6	2.463253000	1.151378000	-0.206184000
8	3.469346000	1.750646000	-0.668889000
8	2.690929000	0.582834000	1.270355000
6	2.914421000	1.609735000	2.241058000
1	3.705445000	2.290150000	1.914087000
1	1.994448000	2.173261000	2.418343000
1	3.214899000	1.121431000	3.168717000
6	-1.260185000	2.144325000	-0.487621000
8	-1.407619000	3.218677000	0.056209000
8	-2.125539000	1.631154000	-1.369375000
6	-3.313982000	2.409076000	-1.638123000
1	-3.888395000	2.544212000	-0.721726000
1	-3.043060000	3.379857000	-2.053001000
1	-3.879472000	1.828225000	-2.361797000
8	4.150941000	-1.188162000	0.450581000
6	5.562930000	-0.989490000	0.137990000
1	5.833863000	-1.729547000	-0.610711000

1	5.715784000	0.020937000	-0.237911000
1	6.123576000	-1.156925000	1.054294000
1	3.735657000	-0.433144000	1.059965000

Table S17. Optimized geometries of stationary points of the Scheme 14. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS13

$\nu_{im.}$ = -227.0 cm^{-1}(-1216.85586)

7	0.098176000	-0.749067000	-0.433120000
6	-0.548220000	-1.845688000	-0.814302000
6	1.410824000	-0.851409000	-0.911641000
6	1.531618000	-2.019776000	-1.604669000
7	0.290350000	-2.644020000	-1.542753000
1	2.336435000	-2.451164000	-2.173628000
7	0.006642000	-3.870062000	-2.149483000
1	-0.712693000	-3.758045000	-2.858463000
1	-0.292805000	-4.547020000	-1.453565000
7	-1.811798000	-2.218783000	-0.480264000
1	-2.494624000	-1.491634000	-0.248715000
1	-2.207148000	-2.970703000	-1.027171000
6	2.435586000	0.180039000	-0.705953000
6	2.099700000	1.539612000	-0.612698000
6	3.791775000	-0.180224000	-0.627185000
6	3.090007000	2.506273000	-0.448368000
6	4.779512000	0.788693000	-0.473293000
6	4.433580000	2.137828000	-0.380147000
1	1.063316000	1.842240000	-0.680763000
1	4.070693000	-1.226980000	-0.672298000
1	2.809897000	3.551739000	-0.380330000
1	5.819829000	0.488670000	-0.413247000
1	5.202039000	2.891746000	-0.252496000
6	-0.550641000	0.319725000	1.192663000
6	-1.230385000	1.339180000	0.965944000
6	-0.010073000	-0.422911000	2.346839000
8	-0.139837000	0.007613000	3.475569000
8	0.600919000	-1.569932000	2.056882000
6	1.125283000	-2.312277000	3.182036000
1	1.867370000	-1.716396000	3.712968000
1	0.317872000	-2.588822000	3.859873000
1	1.583079000	-3.197907000	2.749765000
6	-1.927017000	2.250276000	0.145562000
8	-3.095224000	2.107671000	-0.222151000
8	-1.192953000	3.332919000	-0.175176000
6	-1.842193000	4.339340000	-0.985323000
1	-2.136083000	3.921939000	-1.948351000
1	-2.717625000	4.734413000	-0.469980000
1	-1.096261000	5.118333000	-1.120471000
8	-4.080273000	-0.469969000	0.055836000
6	-5.226958000	-0.704546000	-0.763896000
1	-5.022728000	-0.484129000	-1.817525000
1	-5.487788000	-1.759658000	-0.671787000
1	-6.081287000	-0.104047000	-0.434369000
1	-3.820528000	0.469731000	-0.021202000

64

$\nu_{im.}$ = 0 (-1216.87167)

7	-0.182655000	1.032520000	0.066818000
6	0.184586000	2.302102000	0.342482000
6	-1.529630000	1.032611000	-0.367090000
6	-1.953573000	2.318635000	-0.326128000
7	-0.888423000	3.097785000	0.114275000
1	-2.888483000	2.771458000	-0.602882000
7	-0.945765000	4.489560000	0.196662000
1	-0.260664000	4.911357000	-0.423955000
1	-0.800841000	4.796378000	1.153482000
7	1.382790000	2.711526000	0.805079000
1	2.207877000	2.314905000	0.335528000
1	1.461925000	3.707858000	0.961145000
6	-2.268835000	-0.163341000	-0.792457000
6	-1.686733000	-1.132854000	-1.623540000
6	-3.608926000	-0.316562000	-0.404818000
6	-2.431231000	-2.228942000	-2.052746000
6	-4.351449000	-1.409182000	-0.844890000
6	-3.764293000	-2.370979000	-1.667159000
1	-0.658066000	-1.024117000	-1.941934000
1	-4.062941000	0.415964000	0.252312000
1	-1.969805000	-2.969059000	-2.696442000
1	-5.385194000	-1.514228000	-0.536051000
1	-4.340517000	-3.225260000	-2.003515000
6	0.594579000	-0.157828000	0.418716000
6	1.726060000	-0.448083000	-0.222208000
6	0.043683000	-0.919008000	1.581152000
8	0.406535000	-2.033298000	1.898873000
8	-0.875494000	-0.220205000	2.274918000
6	-1.437499000	-0.869922000	3.435593000
1	-1.931731000	-1.797757000	3.147315000
1	-0.655986000	-1.080512000	4.165947000
1	-2.157684000	-0.164081000	3.841583000
6	2.574199000	-1.563523000	0.119424000
8	3.514022000	-1.522496000	0.907153000
8	2.333495000	-2.651993000	-0.663384000
6	3.227009000	-3.769314000	-0.503233000
1	4.254369000	-3.478959000	-0.728581000
1	3.175507000	-4.164724000	0.512261000
1	2.884663000	-4.518597000	-1.214060000
8	3.426261000	1.689624000	-0.981328000
6	3.374683000	2.268617000	-2.284813000
1	2.350211000	2.532819000	-2.573206000
1	3.976368000	3.178751000	-2.269860000
1	3.787945000	1.590753000	-3.039627000
1	2.857101000	0.869687000	-0.958858000

TS14

$\nu_{im.}$ = -1149.9cm^{-1}(-1216.86918)

7	-0.256724000	1.040493000	0.088638000
6	-0.025687000	2.347733000	0.383425000
6	-1.622903000	0.886111000	-0.261974000
6	-2.198707000	2.103553000	-0.132775000
7	-1.211935000	2.997571000	0.272070000
1	-3.199339000	2.442704000	-0.331587000
7	-1.434279000	4.369322000	0.395671000
1	-0.847131000	4.882288000	-0.256189000
1	-1.257104000	4.672801000	1.348253000
7	1.154477000	2.887274000	0.713661000
1	1.965269000	2.612598000	0.072845000
1	1.118861000	3.872610000	0.941665000
6	-2.224147000	-0.372145000	-0.721024000

6	-1.558726000	-1.213920000	-1.625727000
6	-3.515594000	-0.718283000	-0.294700000
6	-2.173640000	-2.374473000	-2.089306000
6	-4.129959000	-1.873629000	-0.770054000
6	-3.460056000	-2.707705000	-1.665668000
1	-0.568506000	-0.954853000	-1.978679000
1	-4.030745000	-0.086319000	0.419208000
1	-1.648937000	-3.013851000	-2.789896000
1	-5.127865000	-2.127960000	-0.431632000
1	-3.936342000	-3.610862000	-2.029416000
6	0.644568000	-0.058957000	0.386635000
6	1.862447000	-0.126934000	-0.154805000
6	0.154429000	-1.018783000	1.427407000
8	0.621606000	-2.125448000	1.595157000
8	-0.817377000	-0.498312000	2.191025000
6	-1.327020000	-1.339834000	3.250301000
1	-1.742435000	-2.257396000	2.834140000
1	-0.530996000	-1.579669000	3.955052000
1	-2.102995000	-0.753550000	3.735197000
6	2.837142000	-1.165974000	0.192709000
8	3.646049000	-1.076533000	1.100397000
8	2.848077000	-2.167026000	-0.711320000
6	3.855582000	-3.185682000	-0.533542000
1	4.853273000	-2.747907000	-0.577241000
1	3.718714000	-3.693861000	0.421441000
1	3.710340000	-3.881516000	-1.356347000
8	2.926021000	2.032687000	-1.071669000
6	2.581857000	2.390637000	-2.392372000
1	1.896206000	3.251831000	-2.421436000
1	3.473316000	2.660750000	-2.974212000
1	2.084997000	1.560351000	-2.920150000
1	2.418116000	0.935949000	-0.771209000

Table S18. Optimized geometries of stationary points of the Scheme 15. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS15			
$\nu_{im.}$ = -219.9 cm^{-1}(-1216.85047)			
7	1.262607000	-0.737020000	0.643969000
6	0.192017000	-0.892098000	-0.094273000
6	2.300251000	-0.495040000	-0.244737000
6	1.810935000	-0.509926000	-1.532692000
7	0.459902000	-0.753101000	-1.425345000
1	2.265792000	-0.379120000	-2.499017000
7	-0.413071000	-0.833787000	-2.524466000
1	-1.052079000	-0.043286000	-2.479030000
1	-0.955866000	-1.694403000	-2.448057000
7	-1.105720000	-1.124708000	0.398499000
1	-1.057343000	-1.448108000	1.361910000
1	-1.624180000	-1.822268000	-0.158617000
6	3.678045000	-0.277720000	0.217119000
6	4.006142000	-0.436947000	1.572421000
6	4.697143000	0.092016000	-0.676597000
6	5.310557000	-0.235116000	2.018575000
6	6.000082000	0.290265000	-0.229035000
6	6.315206000	0.127893000	1.121555000
1	3.229572000	-0.720903000	2.271517000
1	4.473000000	0.232141000	-1.728059000
1	5.542429000	-0.363589000	3.070210000
1	6.771036000	0.575878000	-0.936096000
1	7.330042000	0.284482000	1.469007000
6	-2.146811000	0.450987000	0.412542000
6	-1.663734000	1.430913000	-0.210273000
6	-3.345854000	0.112347000	1.198329000
8	-4.234330000	0.913230000	1.397132000
8	-3.353964000	-1.144863000	1.666687000
6	-4.504865000	-1.536532000	2.452295000
1	-4.582757000	-0.908350000	3.339115000
1	-5.411657000	-1.451257000	1.854312000
1	-4.323476000	-2.571252000	2.729597000

65			
$\nu_{im.}$ = 0 (-1216.85502)			
7	-1.641198000	-0.069440000	-0.679723000
6	-0.486023000	-0.613004000	-0.420785000
6	-2.517147000	-0.591736000	0.259617000
6	-1.835531000	-1.470384000	1.073751000
7	-0.532053000	-1.479410000	0.632187000
1	-2.127847000	-2.088531000	1.904695000
7	0.467010000	-2.298181000	1.186537000
1	1.180660000	-1.703693000	1.601196000
1	0.903988000	-2.833215000	0.435182000
7	0.713981000	-0.361819000	-1.193809000
1	0.410463000	0.164081000	-2.019738000
1	1.136100000	-1.273075000	-1.507772000
6	-3.935857000	-0.209041000	0.289299000
6	-4.464684000	0.633107000	-0.700486000
6	-4.792908000	-0.675372000	1.299339000
6	-5.809603000	0.996054000	-0.681085000
6	-6.136577000	-0.312646000	1.315378000
6	-6.652950000	0.525323000	0.325285000
1	-3.814067000	0.999491000	-1.484635000
1	-4.411193000	-1.322573000	2.080746000
1	-6.199342000	1.647728000	-1.455262000
1	-6.781447000	-0.683208000	2.104327000
1	-7.699320000	0.808014000	0.339755000
6	1.840571000	0.405687000	-0.486304000
6	2.903702000	-0.283549000	-0.100273000
6	1.613382000	1.872889000	-0.436389000
8	2.281267000	2.641217000	0.220553000
8	0.607986000	2.254069000	-1.245496000
6	0.308716000	3.668244000	-1.302792000
1	0.025132000	4.028939000	-0.314490000
1	1.175823000	4.219132000	-1.666032000
1	-0.522265000	3.758577000	-1.996875000

6	-1.763709000	2.742907000	-0.714345000	6	4.070979000	0.308324000	0.507531000
8	-2.257592000	3.043057000	-1.797323000	8	5.055990000	0.696554000	-0.107468000
8	-1.201587000	3.659508000	0.118485000	8	4.025751000	0.264521000	1.863307000
6	-1.214358000	5.027651000	-0.336821000	6	5.200958000	0.723669000	2.561218000
1	-0.668780000	5.125915000	-1.276068000	1	6.071876000	0.130201000	2.280294000
1	-2.237561000	5.381180000	-0.468913000	1	5.390322000	1.775784000	2.345051000
1	-0.718889000	5.594823000	0.447851000	1	4.979305000	0.591029000	3.617784000
8	-2.225361000	-3.066110000	-1.451685000	8	2.124698000	-2.703590000	-1.302768000
6	-1.931319000	-4.469672000	-1.308597000	6	2.820421000	-3.462955000	-2.300848000
1	-0.892392000	-4.541217000	-0.990318000	1	2.083351000	-4.075941000	-2.818864000
1	-2.573455000	-4.927972000	-0.552844000	1	3.311863000	-2.806842000	-3.025070000
1	-2.052814000	-4.988919000	-2.261875000	1	3.565974000	-4.115970000	-1.839346000
1	-3.142346000	-2.963611000	-1.732394000	1	2.736212000	-2.067795000	-0.837056000
TS16							
$v_{im.}$ = -1218.4cm^{-1}(-1216.85351)							
7	-1.665145000	-0.049044000	-0.683757000				
6	-0.504550000	-0.572982000	-0.403902000				
6	-2.548439000	-0.582908000	0.241692000				
6	-1.868946000	-1.453940000	1.065567000				
7	-0.557992000	-1.444161000	0.646046000				
1	-2.167248000	-2.077084000	1.890672000				
7	0.440920000	-2.256509000	1.210673000				
1	1.070866000	-1.670599000	1.752925000				
1	0.974260000	-2.691056000	0.452606000				
7	0.694199000	-0.339528000	-1.177841000				
1	0.398383000	0.169955000	-2.014850000				
1	1.140052000	-1.308353000	-1.463528000				
6	-3.972132000	-0.218384000	0.250757000				
6	-4.499614000	0.609544000	-0.751780000				
6	-4.835960000	-0.687873000	1.253687000				
6	-5.849284000	0.955072000	-0.751958000				
6	-6.184370000	-0.342811000	1.250111000				
6	-6.699212000	0.480863000	0.247256000				
1	-3.843835000	0.978592000	-1.530380000				
1	-4.455404000	-1.323351000	2.045244000				
1	-6.237626000	1.595895000	-1.535871000				
1	-6.834184000	-0.715687000	2.033938000				
1	-7.749263000	0.749995000	0.246535000				
6	1.829669000	0.397346000	-0.495965000				
6	2.919455000	-0.318407000	-0.235324000				
6	1.631454000	1.856632000	-0.298105000				
8	2.367732000	2.550768000	0.368343000				
8	0.570258000	2.311781000	-0.978036000				
6	0.290026000	3.728904000	-0.886566000				
1	0.108410000	4.005675000	0.151448000				
1	1.127869000	4.300758000	-1.284437000				
1	-0.601562000	3.884226000	-1.487463000				
6	4.146952000	0.221525000	0.341742000				
8	5.080794000	0.646089000	-0.316294000				
8	4.183916000	0.076319000	1.680572000				
6	5.403755000	0.480673000	2.341789000				
1	6.249804000	-0.093850000	1.964096000				
1	5.583049000	1.545216000	2.189844000				
1	5.241991000	0.270253000	3.396013000				
8	2.061413000	-2.500119000	-1.231817000				
6	2.743905000	-3.198250000	-2.266807000				
1	2.018721000	-3.685758000	-2.924705000				
1	3.354119000	-2.517281000	-2.873613000				
1	3.400034000	-3.968373000	-1.846385000				
1	2.708518000	-1.633217000	-0.723235000				

Table S19. Optimized geometries of stationary points of the Scheme 16. PCM/B3LYP/6-311++G(d,p) calculations (Methanol, 64.7 °C). Coordinates in Angstroms. Sum of electronic and thermal Free Energies in a.u. are in parentheses.

TS17				**66**			
$v_{im.}$ = -161.3 cm^{-1}(-1216.84290)				$v_{im.}$ = 0 (-1216.85589)			
7	2.533873000	-1.255072000	-1.140898000	7	2.360133000	1.721061000	0.434603000
6	1.263013000	-1.360246000	-1.449212000	6	1.138601000	2.022666000	0.789215000
6	2.669619000	-0.061718000	-0.437089000	6	2.363400000	0.360942000	0.125659000

6	1.447482000	0.555811000	-0.320452000
7	0.563871000	-0.271957000	-0.995246000
1	1.122980000	1.471638000	0.142266000
7	-0.813818000	-0.074416000	-1.151956000
1	-1.095017000	-0.512232000	-2.031906000
1	-1.008140000	0.941528000	-1.222589000
7	0.630542000	-2.336691000	-2.201658000
1	1.295262000	-2.994497000	-2.590062000
1	-0.094791000	-2.830200000	-1.689308000
6	3.972411000	0.387540000	0.070283000
6	5.149932000	-0.268949000	-0.320782000
6	4.077825000	1.476990000	0.951715000
6	6.391385000	0.152413000	0.151227000
6	5.319141000	1.897794000	1.419257000
6	6.484132000	1.237725000	1.022403000
1	5.082156000	-1.110292000	-0.998839000
1	3.185112000	1.995956000	1.282308000
1	7.288790000	-0.368459000	-0.164302000
1	5.377281000	2.740078000	2.099751000
1	7.450112000	1.565021000	1.389661000
6	-3.292356000	-0.000350000	-0.329991000
6	-2.224617000	-0.551119000	0.038144000
6	-4.688809000	0.098007000	-0.089082000
8	-5.529555000	-0.698235000	-0.481882000
8	-4.994410000	1.228296000	0.598559000
6	-6.385527000	1.421990000	0.931341000
1	-7.005211000	1.379788000	0.035771000
1	-6.715738000	0.664725000	1.643679000
1	-6.437742000	2.410184000	1.382164000
6	-1.705872000	-1.476515000	1.056417000
8	-2.175961000	-1.537666000	2.171823000
8	-0.724991000	-2.269346000	0.608372000
6	-0.191730000	-3.230954000	1.554868000
1	0.217681000	-2.711534000	2.420373000
1	-0.976345000	-3.919036000	1.867073000
1	0.591522000	-3.758626000	1.017965000
8	-1.832989000	2.601785000	-1.315220000
6	-1.546446000	3.697636000	-0.431822000
1	-0.592028000	4.116818000	-0.748091000
1	-2.316927000	4.469597000	-0.504936000
1	-1.464940000	3.361975000	0.606105000
1	-2.679547000	2.199528000	-1.065340000

6	1.106236000	-0.162757000	0.287906000
7	0.330344000	0.913305000	0.702866000
1	0.677380000	-1.133933000	0.115108000
7	-0.988908000	0.828885000	1.232724000
1	-1.201078000	1.767336000	1.594896000
1	-0.992608000	0.146645000	2.052429000
7	0.637655000	3.216742000	1.281614000
1	1.378364000	3.873031000	1.496230000
1	-0.055223000	3.650957000	0.680423000
6	3.585669000	-0.316402000	-0.329557000
6	4.768840000	0.413343000	-0.519477000
6	3.603973000	-1.698193000	-0.582170000
6	5.933721000	-0.219135000	-0.949430000
6	4.767800000	-2.326906000	-1.013623000
6	5.940002000	-1.590940000	-1.199851000
1	4.766207000	1.478912000	-0.328430000
1	2.706773000	-2.289707000	-0.439335000
1	6.837836000	0.362735000	-1.090624000
1	4.760772000	-3.394454000	-1.203053000
1	6.846058000	-2.082449000	-1.535284000
6	-2.552086000	-0.857659000	0.473123000
6	-2.041255000	0.347694000	0.254209000
6	-3.608022000	-1.441242000	-0.317151000
8	-4.801585000	-1.344976000	-0.060990000
8	-3.132300000	-2.236059000	-1.308439000
6	-4.112045000	-2.965016000	-2.075335000
1	-4.688524000	-3.629567000	-1.430636000
1	-4.786105000	-2.279373000	-2.590051000
1	-3.540456000	-3.543382000	-2.797653000
6	-2.394360000	1.332889000	-0.797413000
8	-3.126474000	1.092072000	-1.730381000
8	-1.835160000	2.545099000	-0.583856000
6	-2.164842000	3.579079000	-1.546417000
1	-1.812684000	3.290431000	-2.535932000
1	-3.241798000	3.739827000	-1.564295000
1	-1.651452000	4.473367000	-1.203767000
8	-1.393651000	-1.122261000	3.038015000
6	-0.537774000	-2.146224000	3.564641000
1	0.065841000	-1.694173000	4.351135000
1	-1.131013000	-2.958166000	3.993381000
1	0.124549000	-2.549590000	2.793156000
1	-1.911195000	-1.452232000	2.258887000

TS18

$\nu_{im.}$ = -1184.1cm^{-1}(-1216.85595)

7	2.388849000	1.684526000	0.454315000
6	1.164014000	1.976981000	0.814916000
6	2.398345000	0.324164000	0.152852000
6	1.146397000	-0.206352000	0.336363000
7	0.362594000	0.864110000	0.748208000
1	0.731147000	-1.186701000	0.183801000
7	-0.947759000	0.768107000	1.289165000
1	-1.139486000	1.677803000	1.719741000
1	-1.003924000	-0.093287000	2.148341000
7	0.669291000	3.174122000	1.304814000
1	1.406032000	3.854184000	1.444917000
1	-0.079674000	3.567541000	0.744499000
6	3.620090000	-0.351908000	-0.304448000
6	4.848082000	0.327261000	-0.300764000
6	3.595521000	-1.684789000	-0.748302000
6	6.014659000	-0.308068000	-0.721752000
6	4.762006000	-2.317430000	-1.167018000
6	5.979275000	-1.632945000	-1.155971000
1	4.879075000	1.355641000	0.036405000
1	2.659996000	-2.232166000	-0.773316000
1	6.953692000	0.234311000	-0.709861000
1	4.720507000	-3.346452000	-1.506397000
1	6.886864000	-2.126608000	-1.484116000
6	-2.644507000	-0.767248000	0.560032000
6	-2.007828000	0.376605000	0.305875000
6	-3.755948000	-1.284375000	-0.223321000
8	-4.929788000	-1.047838000	0.012844000
8	-3.352099000	-2.168767000	-1.159687000
6	-4.391187000	-2.828120000	-1.915340000

1	-5.046632000	-3.392433000	-1.251336000
1	-4.975772000	-2.098778000	-2.476701000
1	-3.871045000	-3.499203000	-2.594532000
6	-2.288472000	1.327101000	-0.801912000
8	-3.011891000	1.073177000	-1.739121000
8	-1.678449000	2.517779000	-0.634644000
6	-1.929673000	3.513496000	-1.659286000
1	-1.582003000	3.148479000	-2.624820000
1	-2.994279000	3.738712000	-1.705142000
1	-1.365804000	4.391737000	-1.356630000
8	-1.464382000	-1.119229000	2.804196000
6	-0.622503000	-2.235653000	3.128006000
1	0.223553000	-1.880948000	3.718090000
1	-1.191221000	-2.957909000	3.717220000
1	-0.248518000	-2.726619000	2.224384000
1	-2.110086000	-1.276653000	1.901655000