Supporting Information

Aerobic Oxidation of Primary Amines to Amides Catalyzed by an Annulated Mesoionic Carbene (MIC) Stabilized Ru Complex

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(61 pages including the cover page)

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1. Experimental Section

1.1 General procedures

The metal complexes were synthesized under an atmosphere of purified nitrogen using standard Schlenk-vessel and vacuum-line techniques. Unless otherwise stated, all catalytic reactions were carried out in air in reaction tubes. NMR spectra were obtained on JEOL JNM–LA 400 MHz and 500 MHz spectrometers. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. The chemical shifts are given as dimensionless δ values and is frequency referenced relative to TMS for ^{1}H and ^{13}C NMR. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Vertex 70 Bruker spectrophotometer on KBr pellets. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC-MS experiments were performed using an Agilent 7890 A GC and 5975C MS system.

1.2 Materials

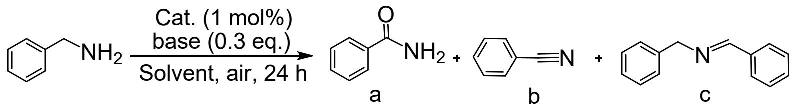
All solvents for catalysis reaction were purchased from Merck, India and were used as received without using any drying agents. $RuCl_3.xH_2O$ was purchased from Arora Matthey, India. Lithium bis(trimethylsilyl)amide (LiHMDS), $PhCD_2NH_2$, and organic substrates were purchased from Sigma-Aldrich. Ligand [L^1H]Br,[1] [Ru(COD)Cl_2]$_n$,[2] catalyst **1**,[1] [Ru^{II}(IMeNHC)(η^6-*p*-cymene)$(Cl)_2$],[3] and [Ru^{II}(py-NHC)$(CO)_2(Br)_2$][4] were prepared according to the literature procedures.

2. Catalysis reaction

2.1 General procedure for the oxidation of primary amine to amide

Amine (0.5 mmol) and KO^{t}Bu 30 mol% were sequentially added to a solution of catalyst **1** (1 mol%) in 2 mL ^{t}BuOH. The mixture was stirred at 70 ºC for 24 h in air. After completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography using silica (hexane/EtOAc) to afford the amide. The isolated products were characterized by NMR spectroscopy. Yields were calculated by GCMS using mesitylene as an internal standard.

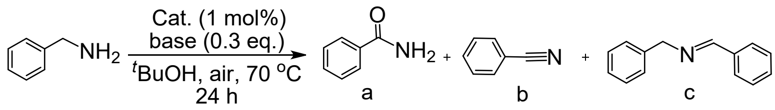
Table S1. Reaction optimization.[a]

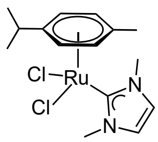
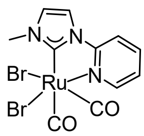


Entry	Solvent	Temp	Base	Conversion (%)[a]	(a)	(b)	(c)
1[b]	^{t}BuOH	80 ºC	KO^{t}Bu(0.5 eq)	100	98	2	0
2	**^{t}BuOH**	**70 ºC**	**KO^{t}Bu(0.3 eq)**	**100**	**98**	**2**	**0**
3[c]	^{t}BuOH	70 ºC	KO^{t}Bu	60	98	2	0
4	^{t}BuOH	70 ºC	KO^{t}Bu (0.2 eq)	90	86	13	1
5	^{t}BuOH	60 ºC	KO^{t}Bu	75	85	15	0
6[d]	^{t}BuOH	70 ºC	KO^{t}Bu	<1	0	0	100
7	^{t}BuOH	70 ºC	NaO^{t}Bu	100	48	0	52
8	^{t}BuOH	70 ºC	Na_2CO_3	44	0	20	80
9	^{t}BuOH	70 ºC	K_2CO_3	8	0	21	79
10	^{t}BuOH	70 ºC	Cs_2CO_3	78	72	0	28
11	^{t}BuOH	70 ºC	Et_3N	45	0	18	82
12	^{t}BuOH	70 ºC	KOH	80	90	2	8
13	^{t}BuOH	70 ºC	NaOH	73	57	3	40
14	EtOH	70 ºC	KO^{t}Bu	63	53	35	12
15	^{i}PrOH	70 ºC	KO^{t}Bu	48	84	4	12
16	MeOH	70 ºC	KO^{t}Bu	50	24	6	70
17	Toluene	70 ºC	KO^{t}Bu	65	0	85	15
18	*p*-Xylene	70 ºC	KO^{t}Bu	55	0	72	28
19	DMF	70 ºC	KO^{t}Bu	55	0	45	55
20	DMSO	70 ºC	KO^{t}Bu	39	100	0	0
21	Dioxane	70 ºC	KO^{t}Bu	30	0	44	56
22	THF	70 ºC	KO^{t}Bu	35	0	44	56
23	CH_3CN	70 ºC	KO^{t}Bu	5	0	39	61
24	EtOAc	70 ºC	KO^{t}Bu	28	2	38	60
25	DCE	70 ºC	KO^{t}Bu	2	0	100	0

[a]Reaction conditions: Catalyst (1 mol%), benzylamine (0.5 mmol) and KO^{t}Bu (0.15 mmol) unless otherwise mentioned. Conversions are determined by GC–MS using mesitylene as an internal standard. [b]Catalyst (2 mol%). [c]Catalyst (0.5 mol%). [d]Reaction performed under nitrogen atmosphere.

Table S2. Catalyst Screening.[a]



Entry	Catalyst	Conversion (%)	(a)	(b)	(c)
1	$RuH(CO)Cl(PPh_3)_3$	68	40	2	58
2	$[Ru(COD)Cl_2]n$	70	34	2	64
3	$Ru(PPh_3)_3Cl_2$	80	40	3	57
4	$RuCl_3.xH_2O$	72	58	0	42
5		75	40	2	58
6		79	55	2	43

[a]Reaction conditions: [a]Reaction conditions: Catalyst (1 mol%), benzylamine (0.5 mmol) and KO^{t}Bu (0.15 mmol). Conversions are determined by GC–MS using mesitylene as an internal standard.

3. Kinetic studies

3.1 General procedure for reaction profile

An oven dried Schlenk tube was charged with benzylamine (0.5 mmol), ^{t}BuOK (0.15 mmol), catalyst (0.005 mmol), mesitylene (0.25 mmol) and 2 mL ^{t}BuOH. The tube was placed in a pre-heated oil bath at 70 ^{o}C with stirring under air. Small aliquots (200 µL) were taken out after stipulated time intervals and passed through a bed of silica with MeOH as eluent. These samples were then analyzed by GC–MS and the decay of benzylamine was measured relative to mesitylene as an internal standard. Data were averaged from three reactions.

3.2. General procedures for the kinetic studies

[Benzylamine]

A set of five different oven dried Schlenk tubes containing variable benzylamine amounts were prepared using the following procedure. 0.1066 mmol, 0.2132 mmol, 0.4265 mmol, 0.6397 mmol and 0.8531 mmol of amine were added along with halfmolar mesitylene in different reaction vessels. To each tube, measured amount of **1** (0.0043 mmol), KO^{t}Bu (0.1278 mmol) and 2 mL ^{t}BuOH were added. All tubes were placed on preheated (70 ºC) oil–baths with stirring UNDER air. After stipulated time intervals, aliquots of 200 µL were taken out and passed through a bed of silica with MeOH as eluent. These samples were then analyzed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene).

mmol of benzylamine	slope
0.1066	8.1428 X 10^{-4}
0.2132	0.00154
0.4265	0.00269
0.6397	0.00415
0.8531	0.00585

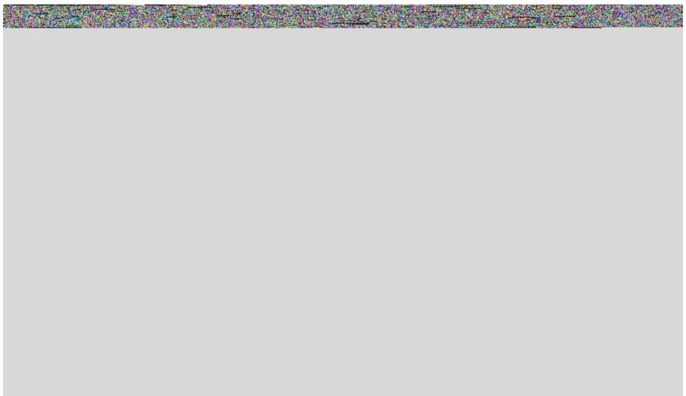


Figure S1. Concentration [Product] vs time plot at different [benzylamine] concentration.

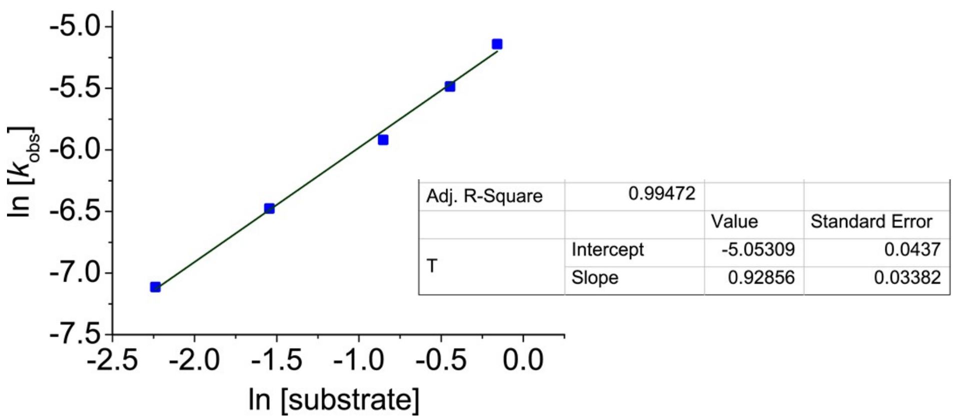


Figure S2. ln[k_{obs}] vs ln[substrate].

[Catalyst]

A set of five different oven dried Schlenk tubes containing variable catalyst amounts were prepared using the following procedure. 1.07 X 10^{-3} mmol, 2.13 X 10^{-3} mmol, 4.26 X 10^{-3} mmol, 8.53 X 10^{-3} mmol and 1.28 X 10^{-2} mmol of catalyst were added and to each tube, measured amount of benzylamine (0.4265 mmol), mesitylene (0.2132 mmol), KO^{t}Bu (0.1278 mmol) and 2 mL ^{t}BuOH were added. All tubes were placed on preheated (70 ºC) oil–baths with stirring in air. After stipulated time intervals, aliquots of 200 µL were taken out and passed through a bed of silica with MeOH as eluent. These samples were then analyzed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene).

mmol of catalyst	slope
1.07 X 10^{-3}	5.1190 X 10^{-4}
2.13 X 10^{-3}	9.5476 X 10^{-4}
4.26 X 10^{-3}	0.00269
8.53 X 10^{-3}	0.00367
1.28 X 10^{-2}	0.00566

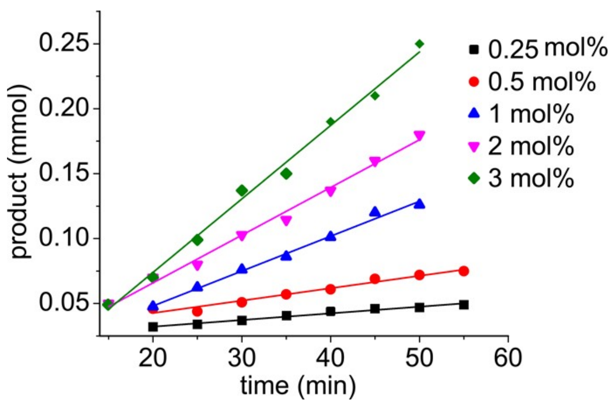


Figure S3. Concentration [Product] vs time plot at different [catalyst] concentration.

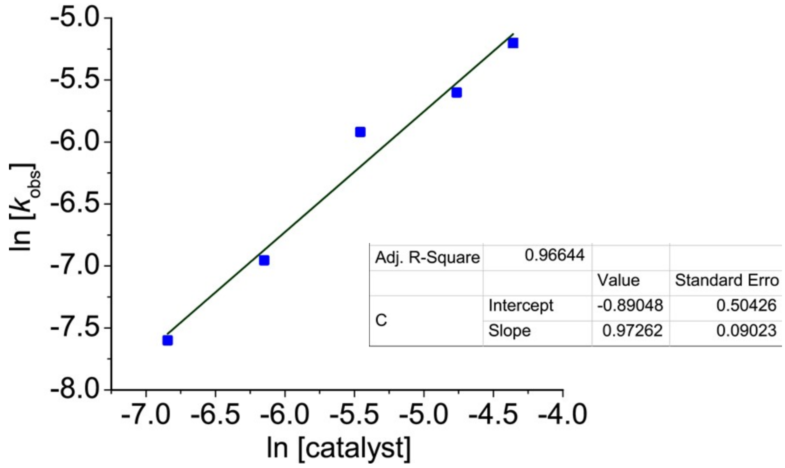


Figure S4. ln[k_{obs}] vs ln[catalyst].

[KO^{t}Bu]

A set of three different oven dried Schlenk tubes containing variable KO^{t}Bu concentrations were prepared using the following procedure. 0.1280 mmol, 0.1706 mmol and 0.2133 mmol of KO^{t}Bu were added and to each tube, measured amount of benzylamine (0.4265 mmol), mesitylene (0.2132 mmol), **1** (0.0043 mmol) and 2 mL ^{t}BuOH were added. All tubes were placed on preheated (70 ºC) oil–baths with stirring in air. After stipulated time intervals, aliquots of 200 μL were taken out and passed through a bed of silica with MeOH as eluent. These samples were then analyzed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene).

mmol of KO^{t}Bu	slope
0.1280	0.00244
0.1706	0.00255
0.2133	0.00262

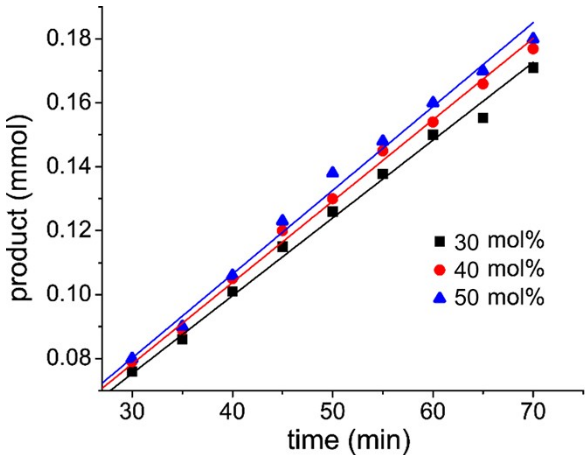


Figure S5. Concentration [Product] vs time plot at different [KO^{t}Bu] concentration.

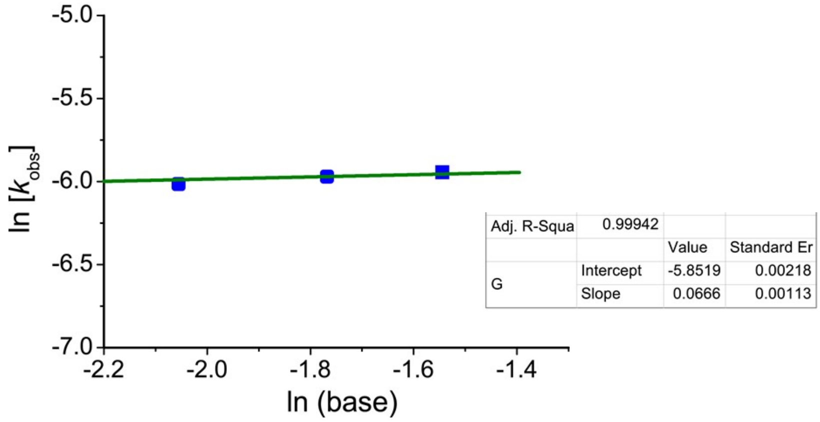


Figure S6. ln[k_{obs}] vs ln[base].

Temperature–Dependent Kinetic Study

An oven dried Schlenk tube was charged with benzylamine (0.4265 mmol), **1** (0.0043 mmol), KO^{t}Bu (0.1278 mmol) and mesitylene (0.25 mmol) in 2 mL ^{t}BuOH. The tube was placed in a pre-heated oil bath at desired temperature (50ºC, 55 ºC, 60 ºC, 65 ºC, 70 ºC, 75ºC) with stirring under air. Small aliquots of 200 μL were taken out after stipulated time intervals and passed through a bed of silica with MeOH as an eluent. These samples were then analyzed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene). The activation parameters were determined from the ln(k/T) versus 1/T plot which is linear over the temperature range studied (323–348K).

Temperature dependent kinetic study data			
Temp. (K)	Slope	ln(k/T)	1/T x 10^{-3}
323	9.888 X 10^{-4}	-12.697	3.09
328	0.00132	-12.423	3.04
333	0.00194	-12.053	3
338	0.00269	-11.741	2.95
343	0.00369	-11.439	2.91
348	0.0063	-10.919	2.87

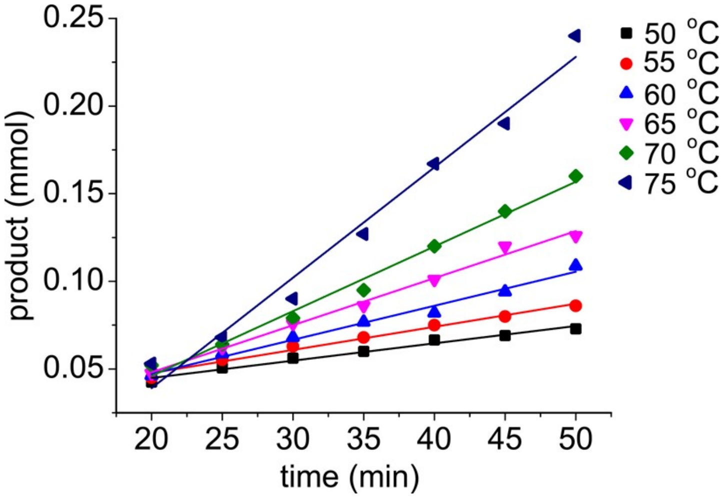


Figure S7. Concentration [Product] vs time plot at different temperature with catalyst **1**.

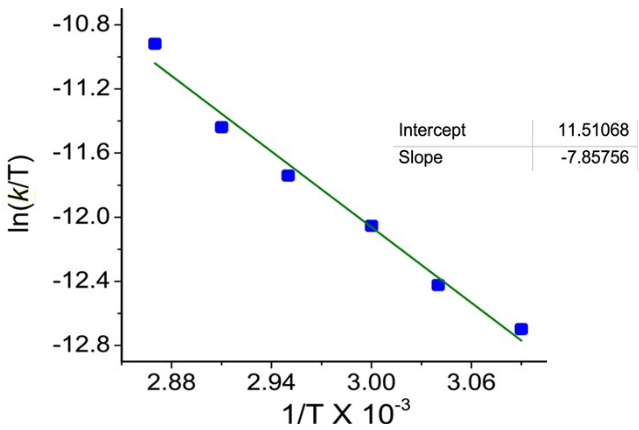


Figure S8. Plot of ln(k/T) vs 1/T for benzylamine oxygenation with catalyst **1**.

Activation enthalpy (∆H‡) and activation entropy (∆S‡) values were obtained from the slope and intercept of plots of ln(*k2/T*) *vs* 1/*T* using the following equation:

$$\ln(k/T) = \ln(R/Nh) + \Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT$$

where *N* = Avogadro's number, *R* = universal gas constant, and *h* = Planck's constant.

Hammett Studies

An oven dried Schlenk tube was charged with appropriate benzylamine derivatives (0.4265 mmol), **1** (0.0043 mmol), KO^{t}Bu (0.1278 mmol) and mesitylene (0.2132 mmol) in 2 mL ^{t}BuOH. All tubes were placed on preheated (70 ºC) oil–baths with stirring under air. Aliquots of 200 µL were taken out after stipulated time intervals and passed through a bed of silica with MeOH as an eluent. These samples were then analyzed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene). Reactivity towards oxygenation reaction follows the sequence *p*–Cl >*p*–F >*p*–H >*p*–Me >*p*–OMe.

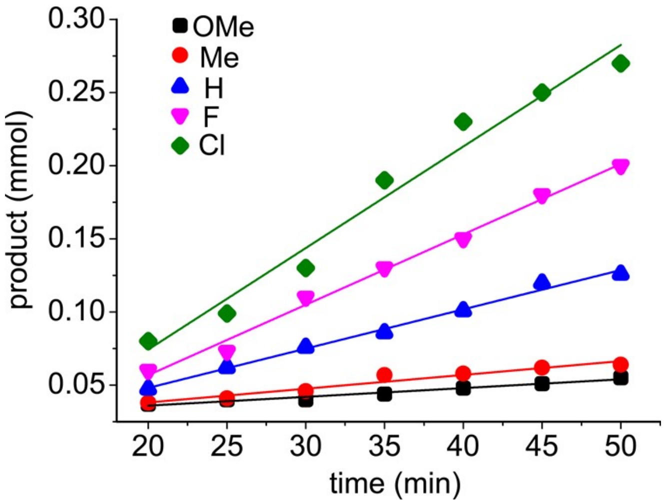


Figure S9. Kinetic data for the oxygenation of benzylamine and its *para*-substituted derivatives.

Hammett plot kinetic study data			
Substrate	Slope	[log(k_x/k_H)]	σ_p
p–Cl	0.00694	0.409	0.227
p–F	0.00481	0.252	0.062
p–H	0.00269	0	0
p–Me	0.00094	-0.455	-0.17
p–OMe	0.0006	-0.651	-0.268
ρ = 2.28			

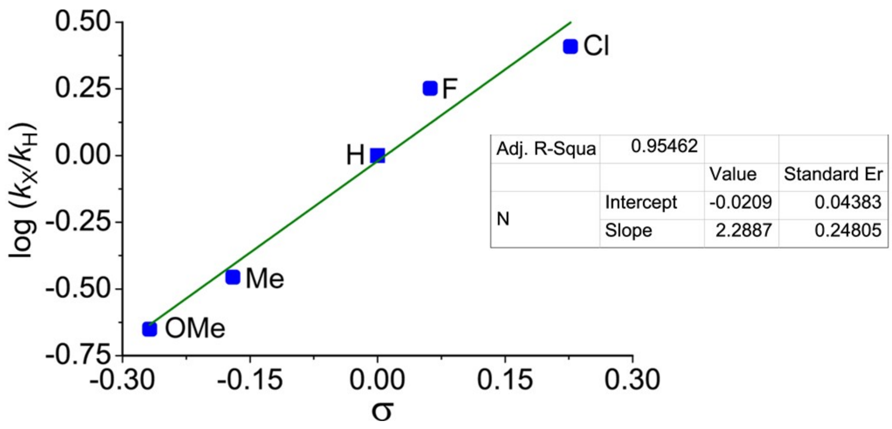


Figure S10. Hammett plot for the oxygenation of amines.

Experimental Procedure for determining KIE

Parallel reactions were carried out for the oxygenation of benzylamine with deuterated and non-deuterated substrates under similar conditions. Oven dried Schlenk tube was charged with $PhCH_2NH_2$ (0.4265 mmol), **1** (0.0043 mmol), KO^{t}Bu (0.1278 mmol) and mesitylene (0.2132 mmol) in 2 mL ^{t}BuOH. Similarly, other Schlenk tube was charged with $PhCD_2NH_2$ (0.4265 mmol), **1** (0.0043 mmol), KO^{t}Bu (0.1278 mmol) and mesitylene (0.2132 mmol) in 2 mL ^{t}BuOH. Both tubes were placed on pre-heated (70 ºC) oil–baths with stirring in air. After stipulated time intervals, aliquots of 200 µL were taken out and passed through a bed of silica with MeOH as an eluent. These samples were then analysed by GC–MS and the decay of amine was measured relative to the internal standard (mesitylene). The following plot was used to analysis the KIE value for deuterated and non-deuterated benzylamines. For $PhCH_2NH_2/PhCD_2NH_2$, the KIE value is found to be 2.9.

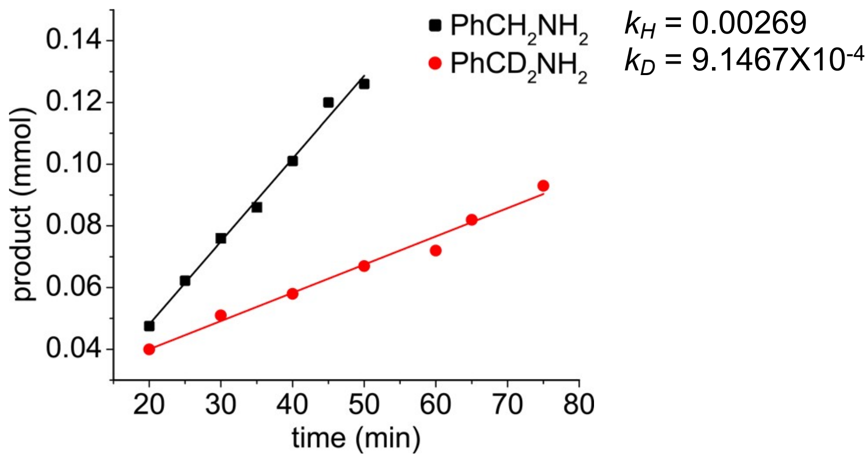


Figure S11. Concentration [Product] vs time plot for $PhCH_2NH_2$ and $PhCD_2NH_2$ with catalyst **1**.

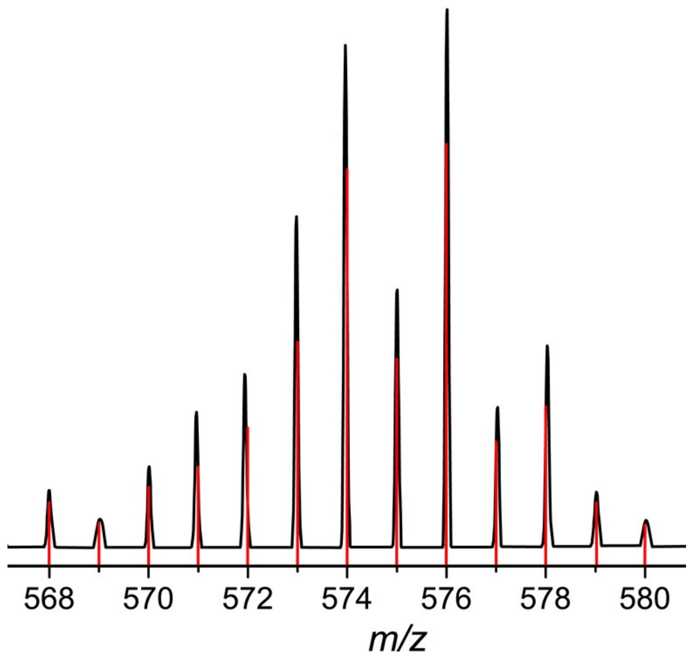


Figure S12. ESI-MS, m/z: 573.9969 (z = 1) of $[Ru(\mathbf{L^1})Br(O)(CH_3CN)]^+$. Oxygen was passed using a balloon in CH_3CN solution of catalyst **1** at room temperature. ESI-MS spectrum was recorded after 30 min.

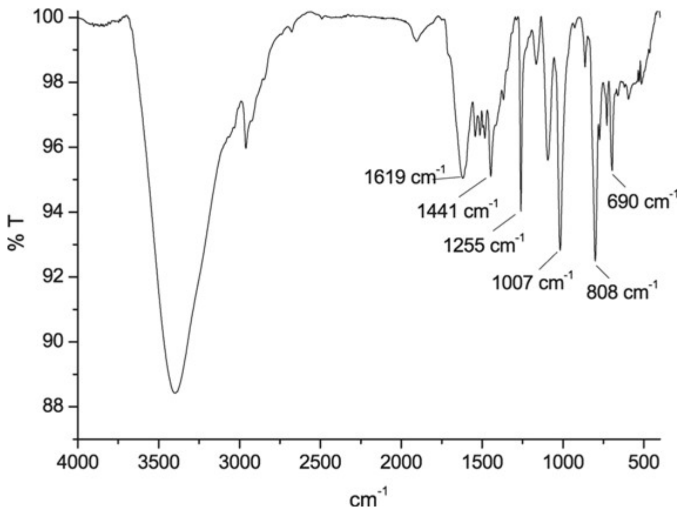


Figure S13. IR spectrum of $[Ru(\mathbf{L^1})Br(O)(CH_3CN)]^+$. Oxygen was passed through a solution of catalyst **1** in CH_3CN at room temperature. IR spectrum was recorded after 30 min. Stretching frequency at 808 cm^{-1} is generated because of the Ru oxo species.

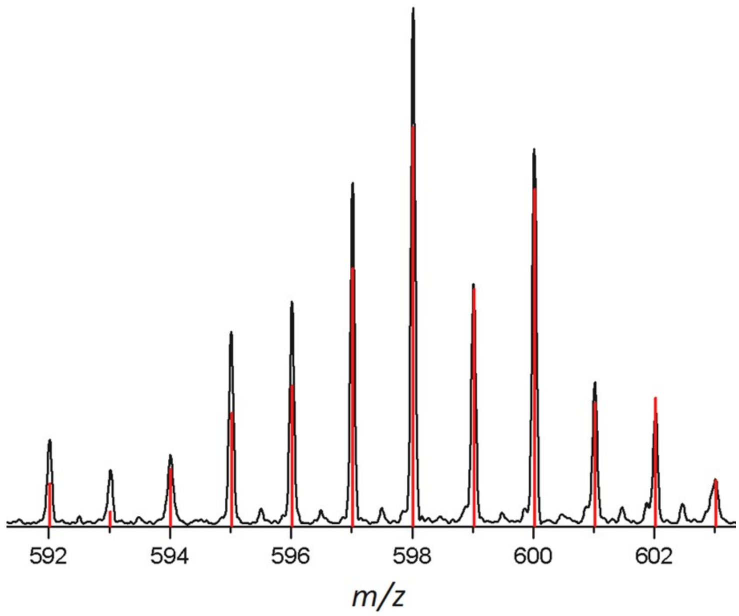
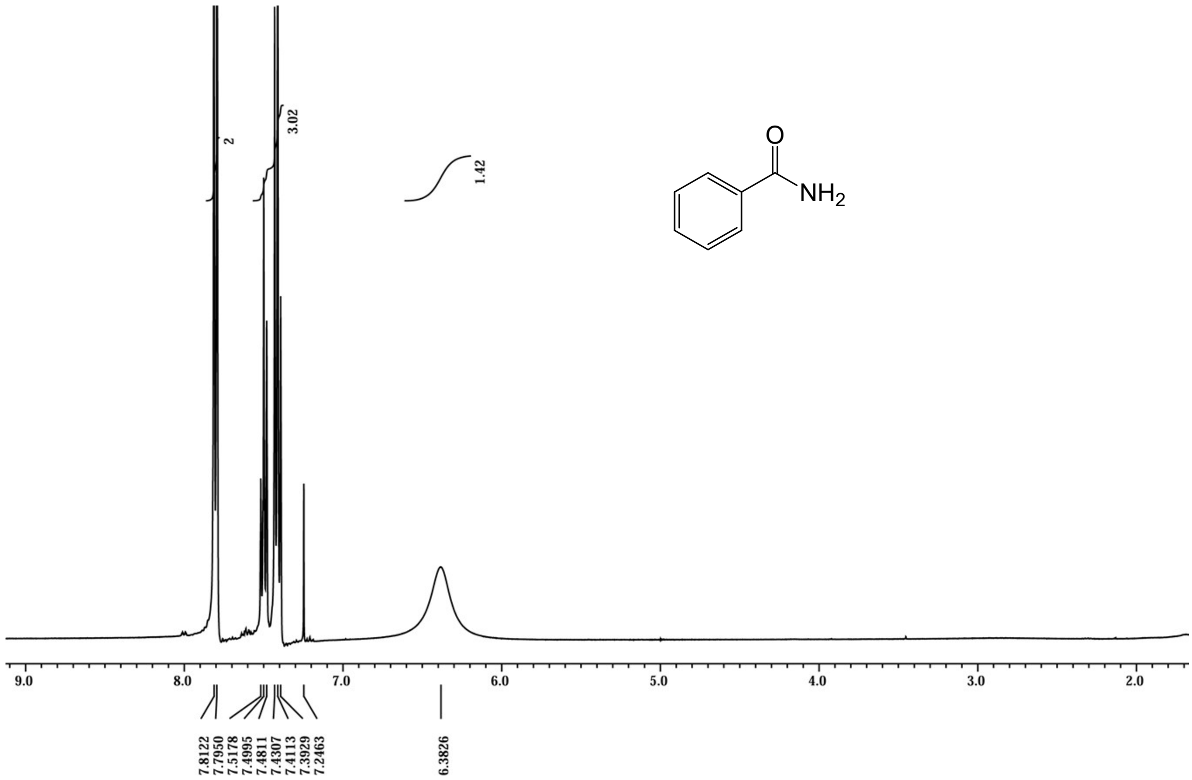
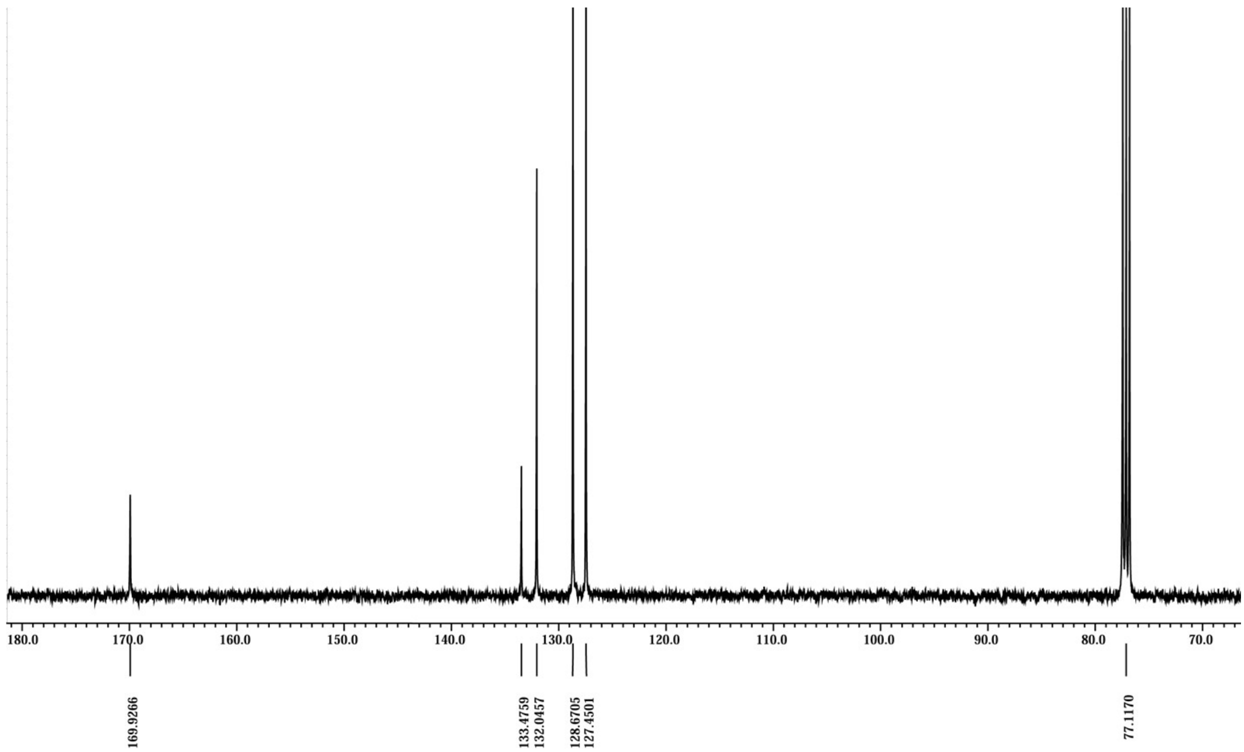
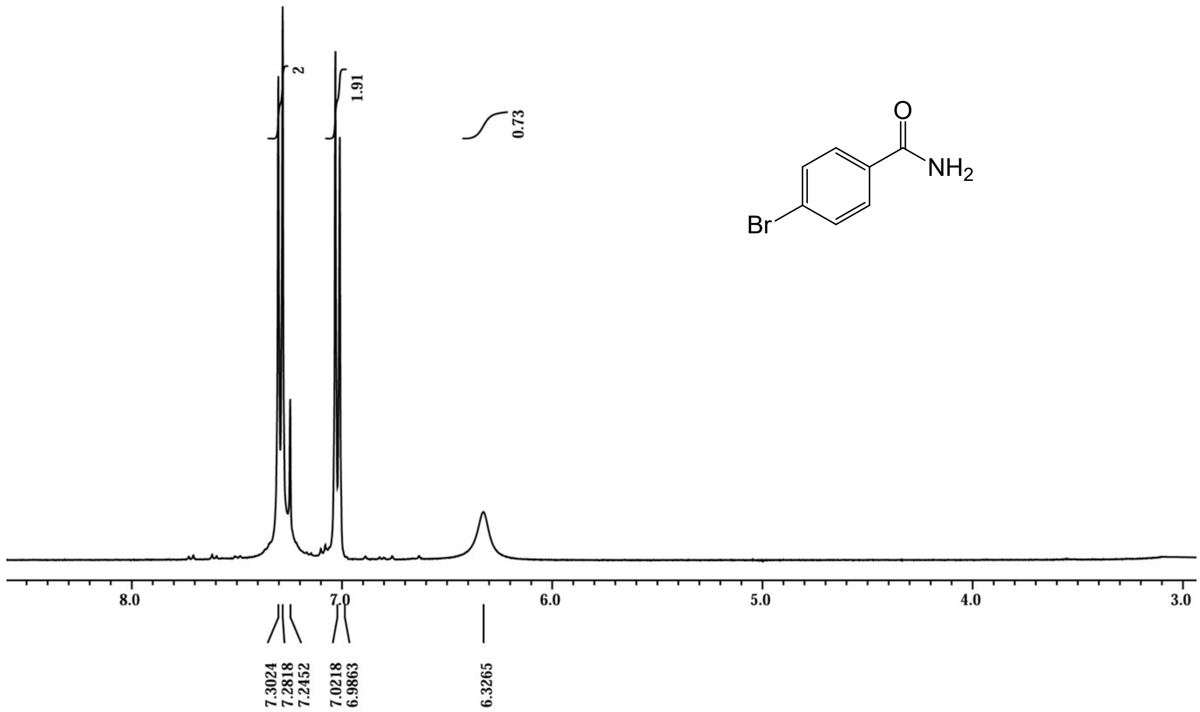


Figure S14. ESI-MS of $[Ru(\mathbf{L^1})Br(CH_3CN)_2]^+$.

4. NMR Spectra



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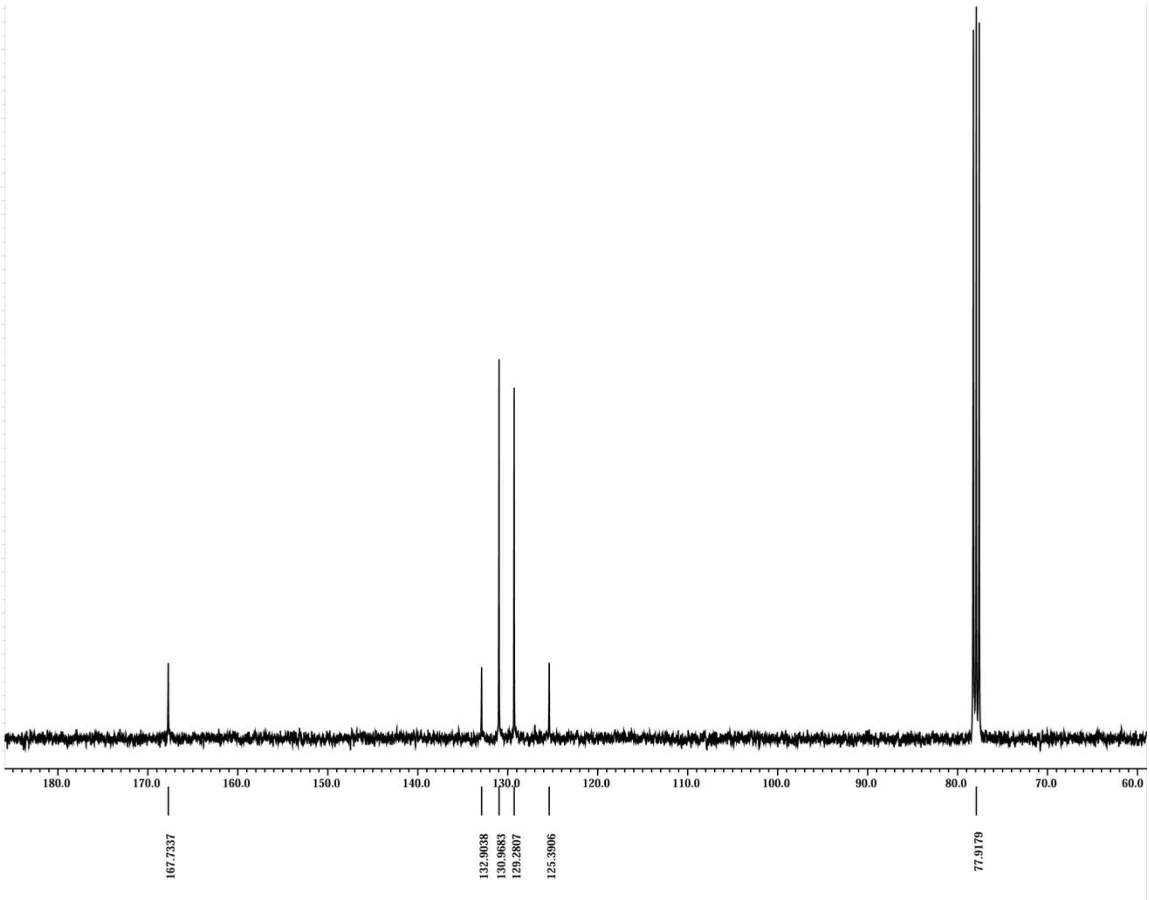
6.3265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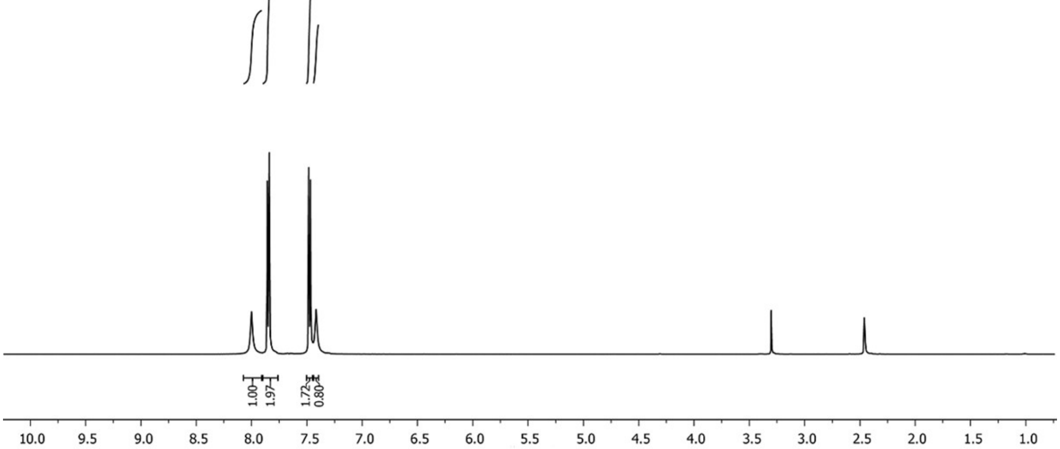
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7.84
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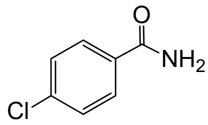
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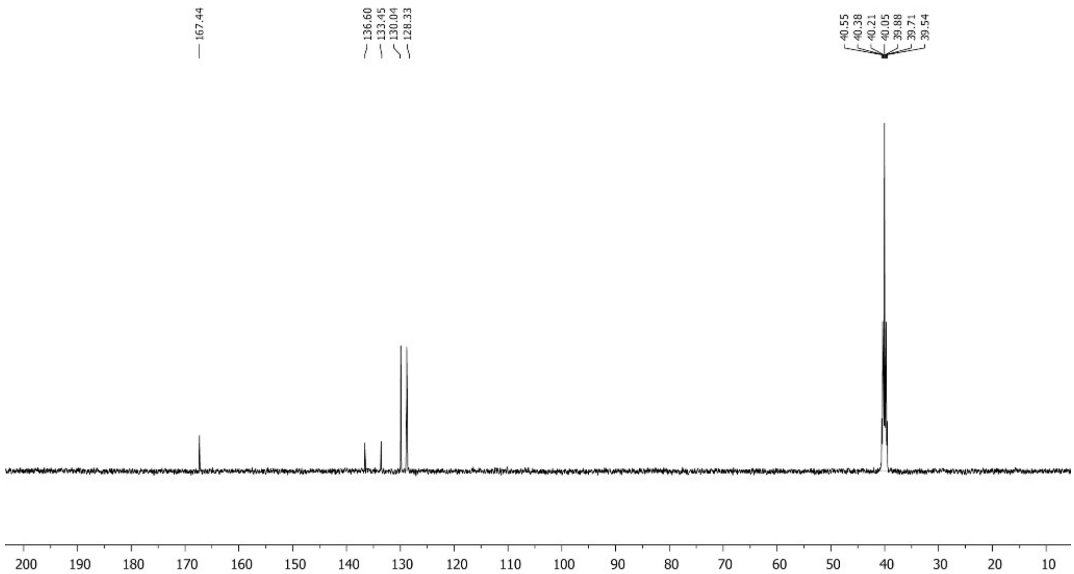
NH2
Cl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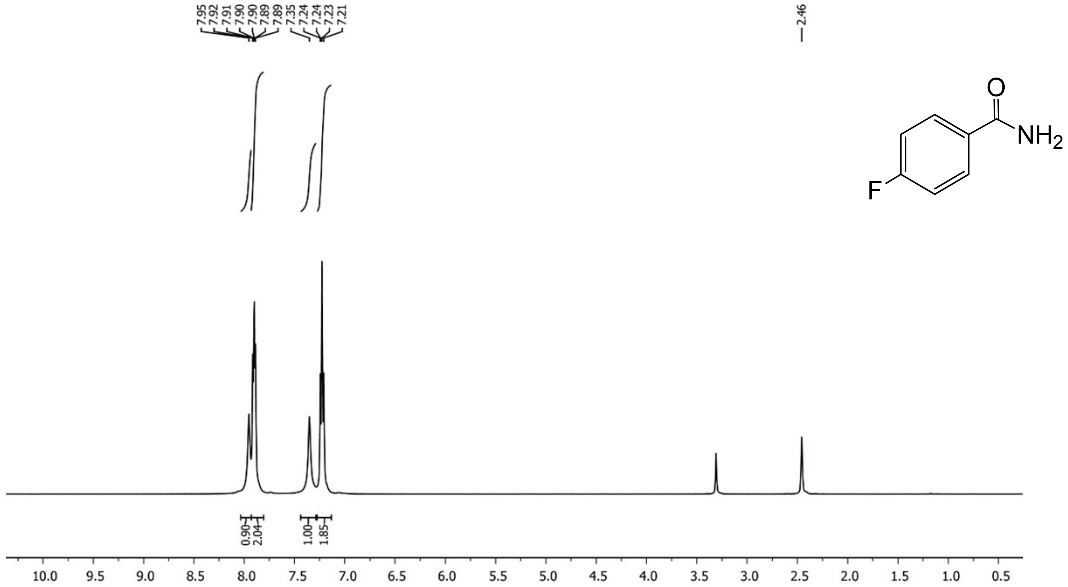

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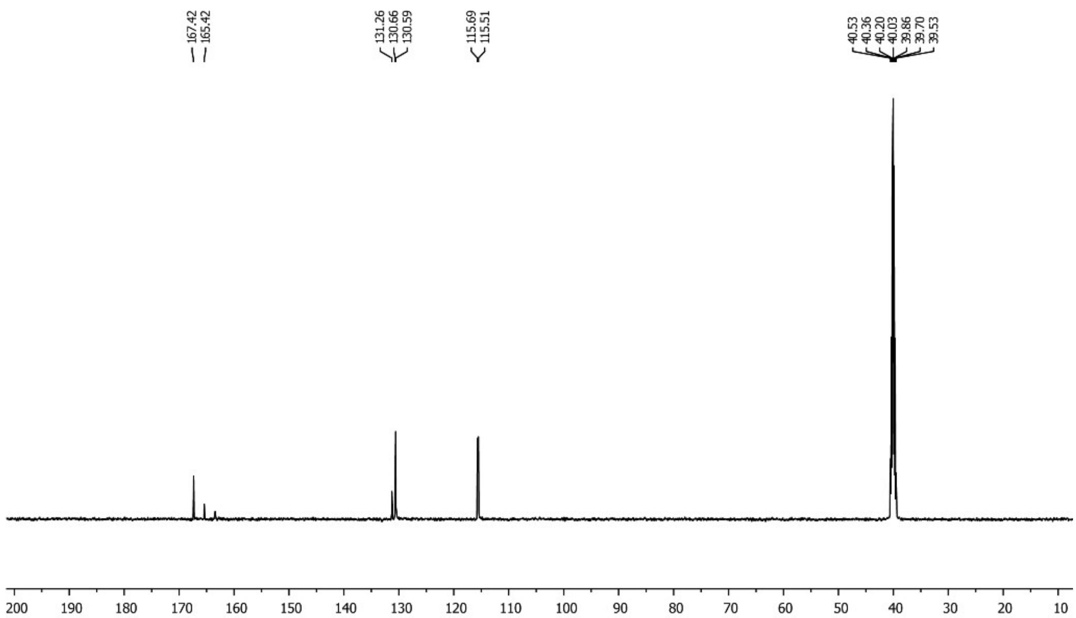
2.46
O
NH2
F
0.90 2.04 1.00 1.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5



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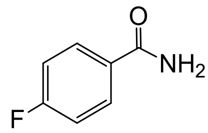
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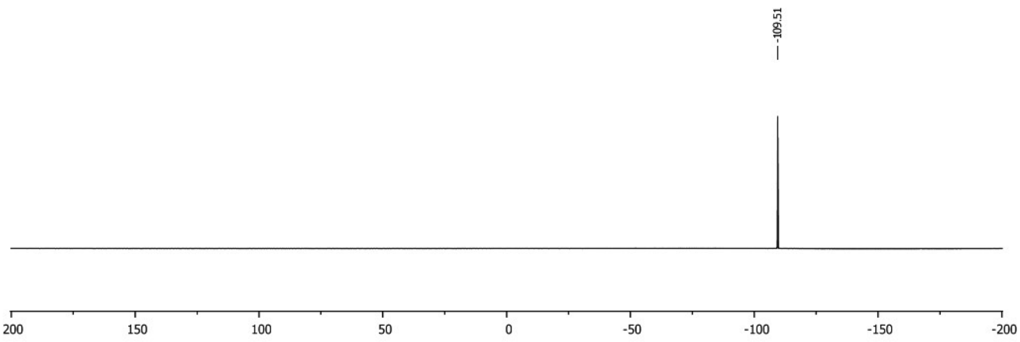
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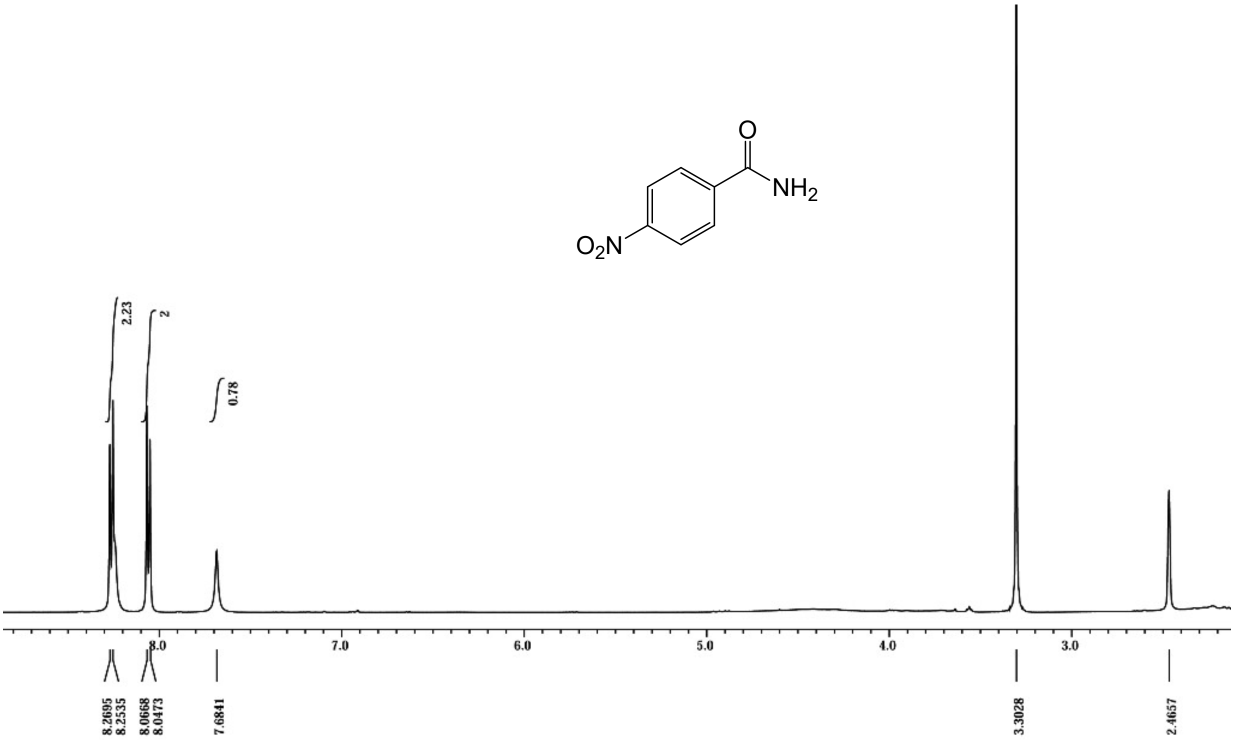
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7.6841
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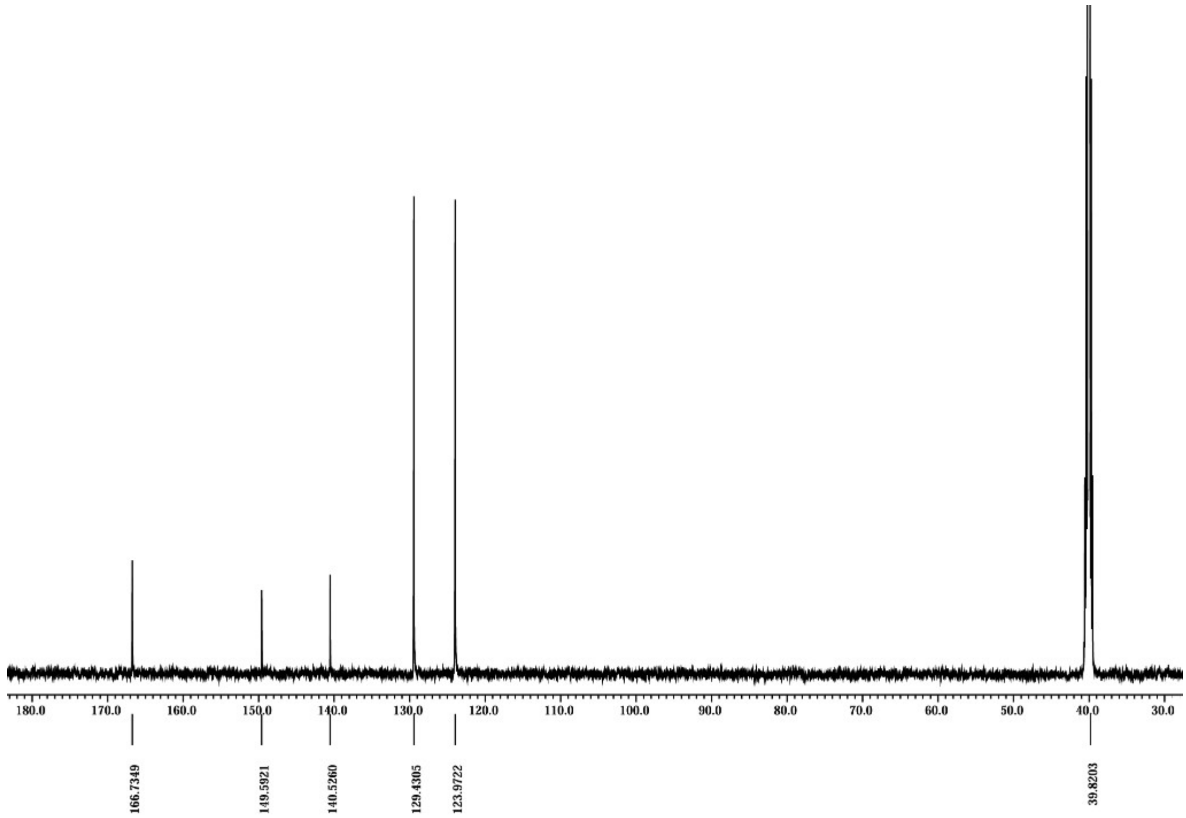
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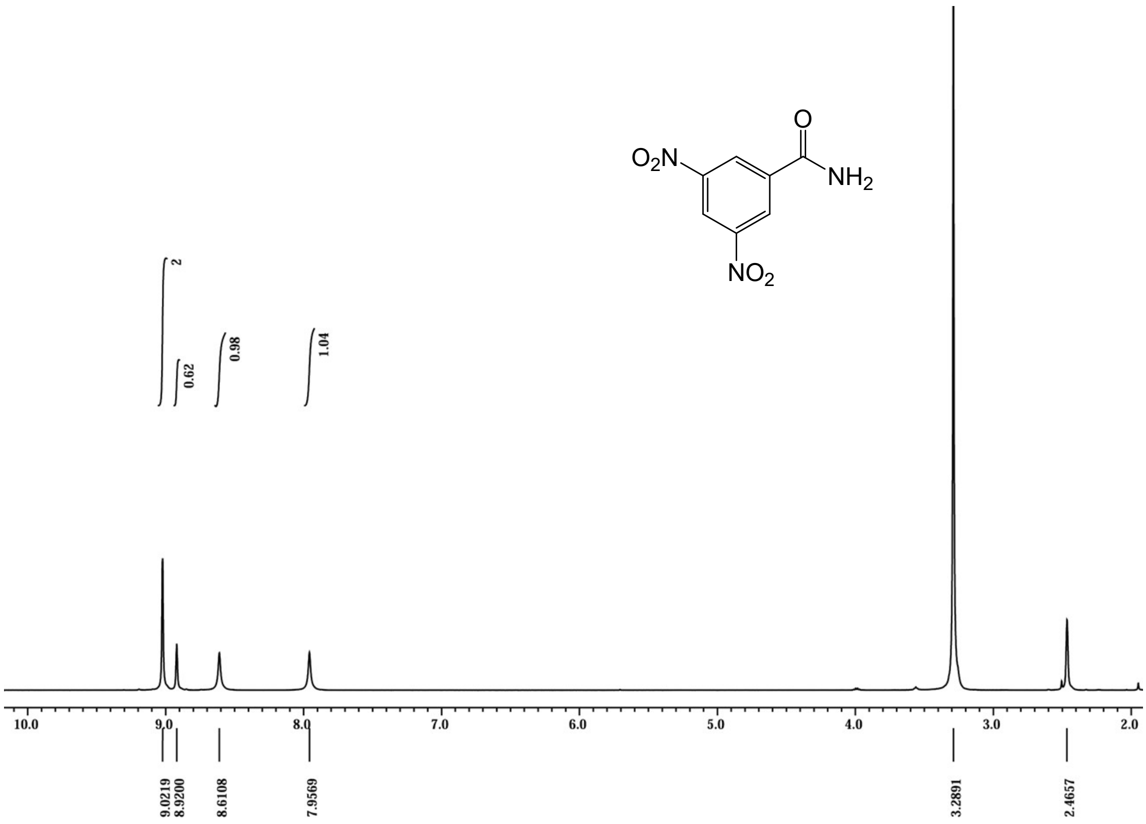
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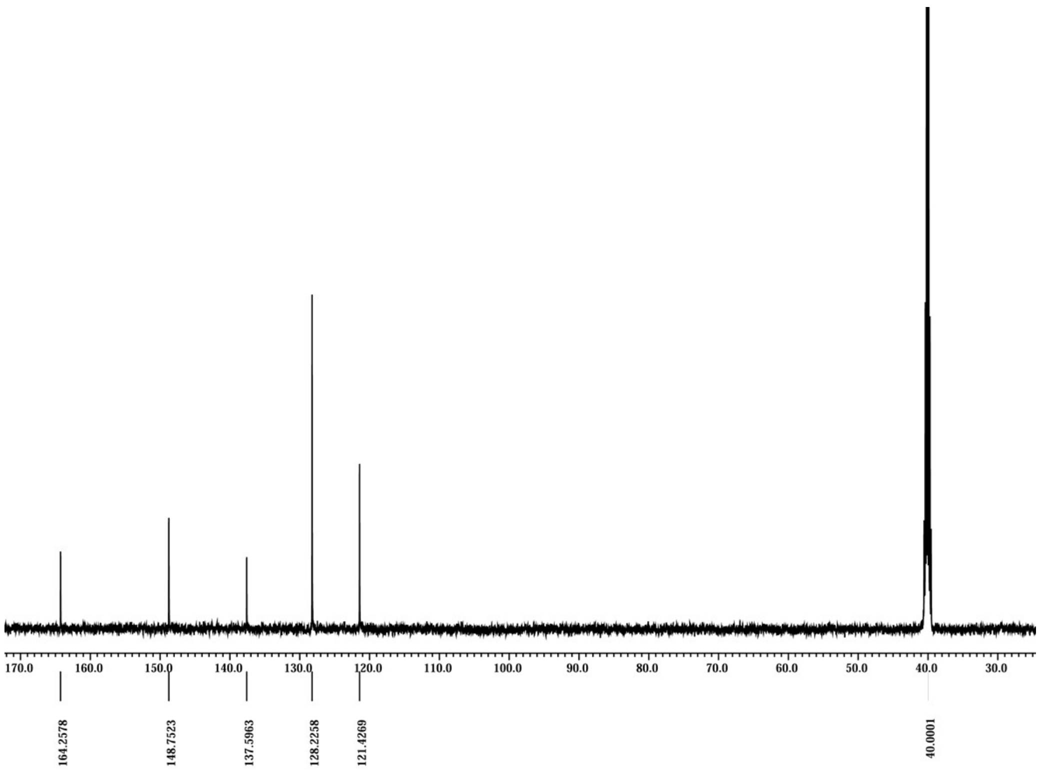
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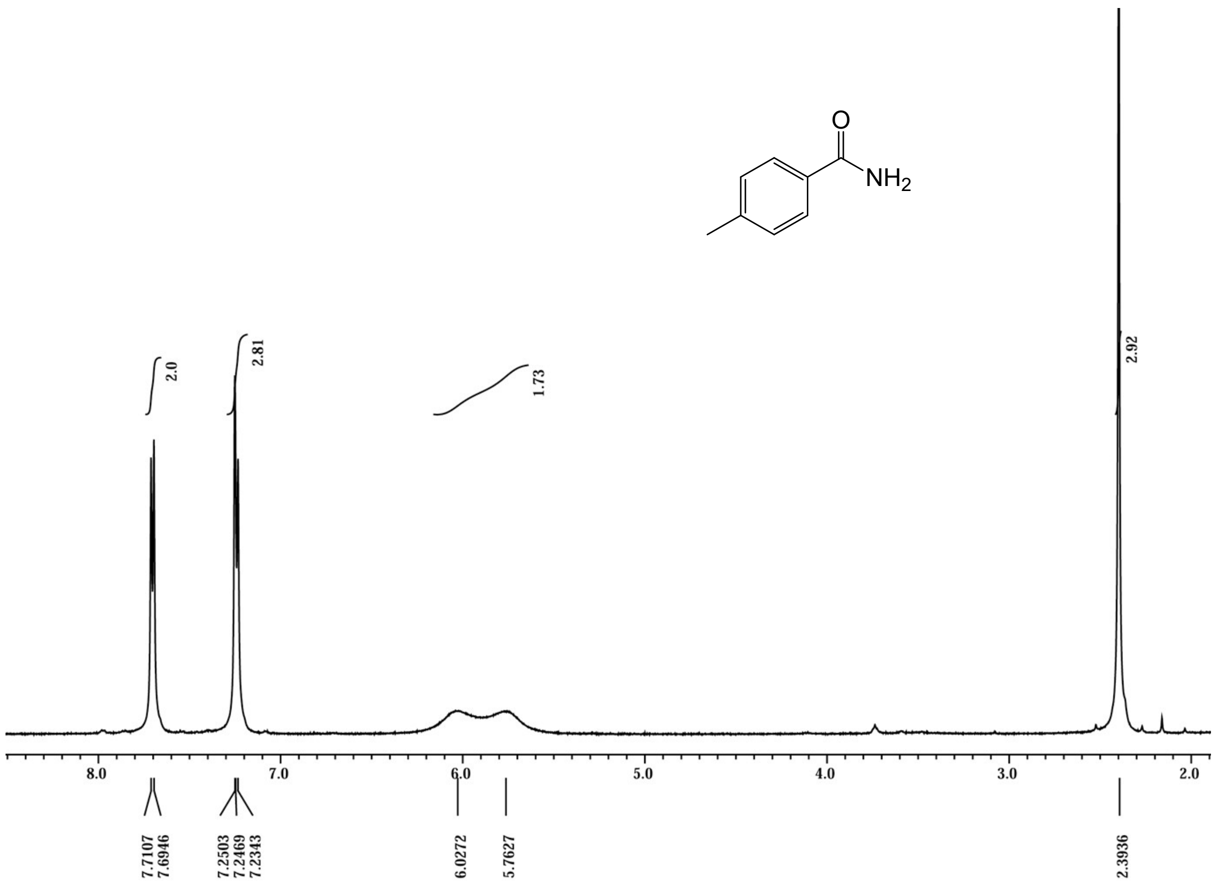
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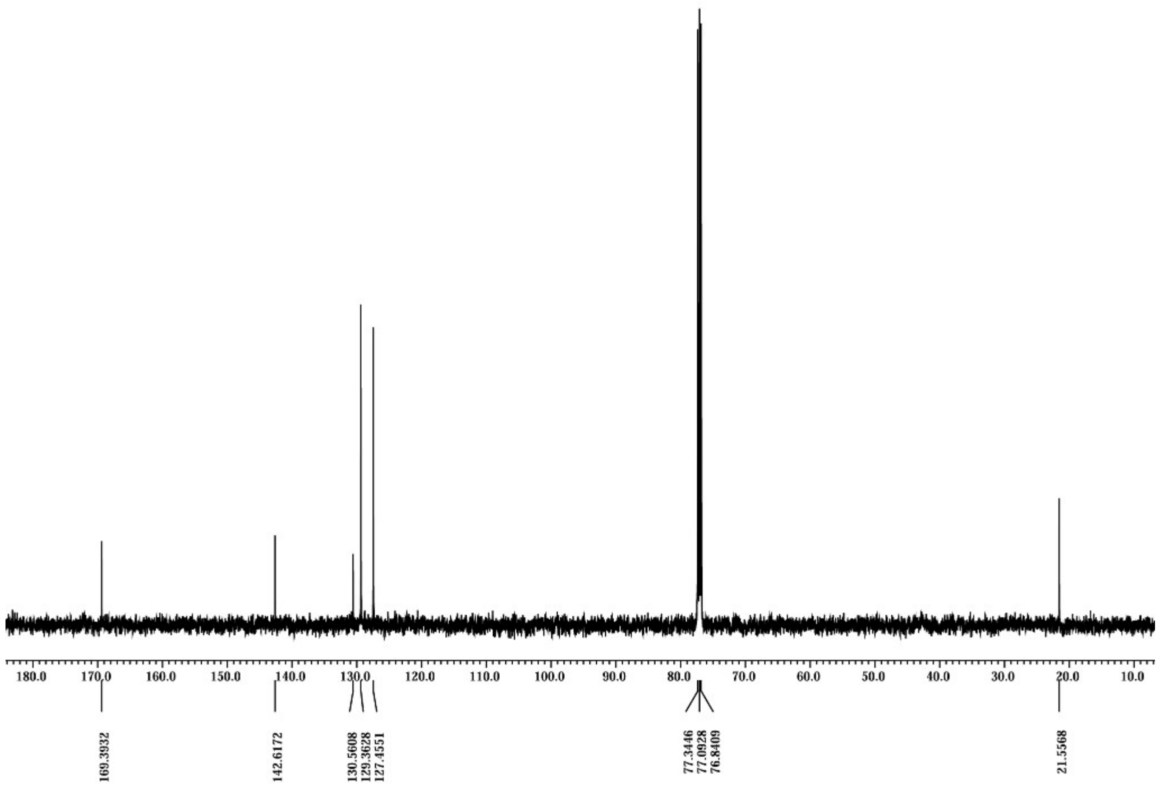
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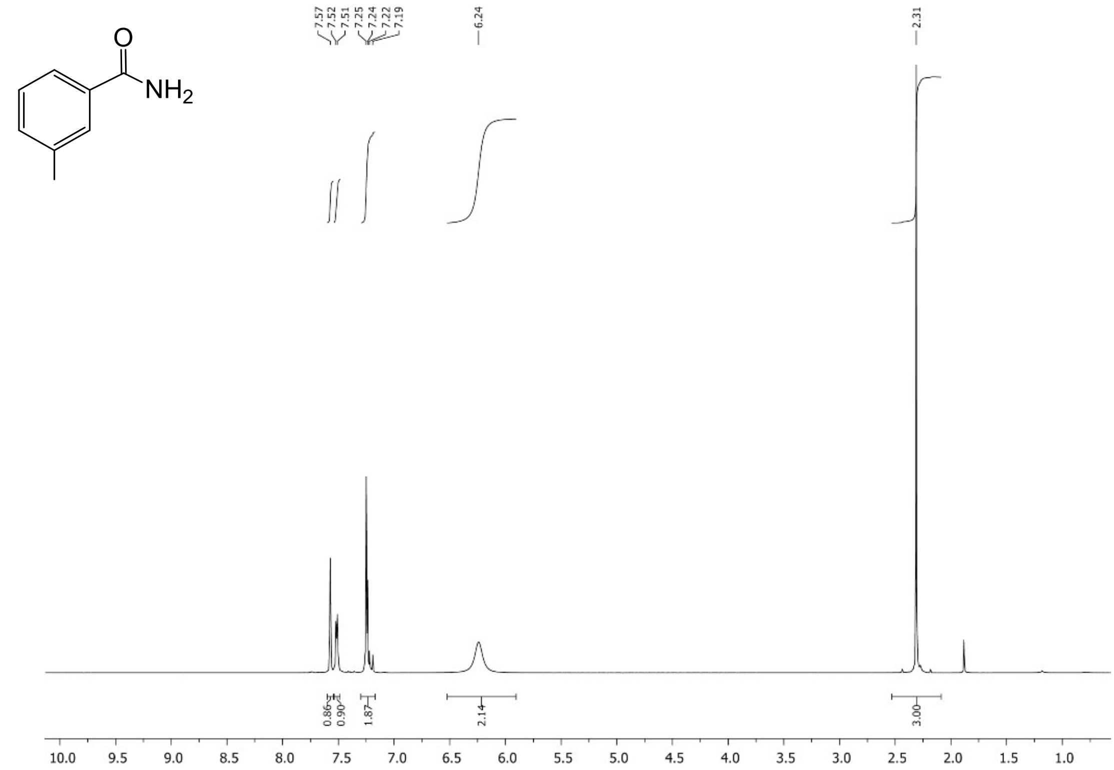
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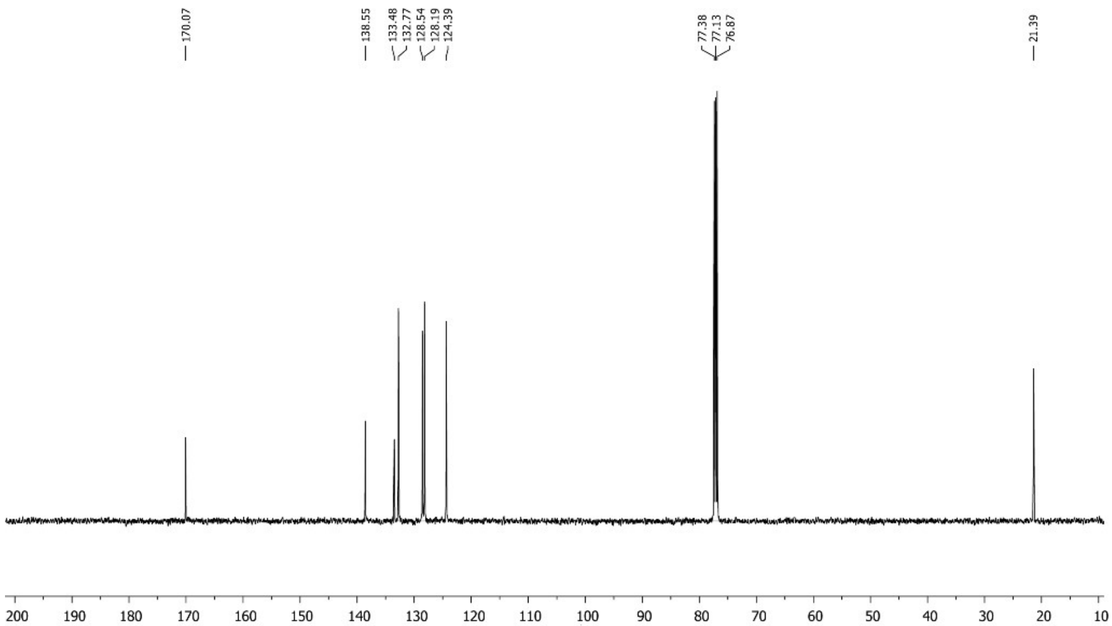
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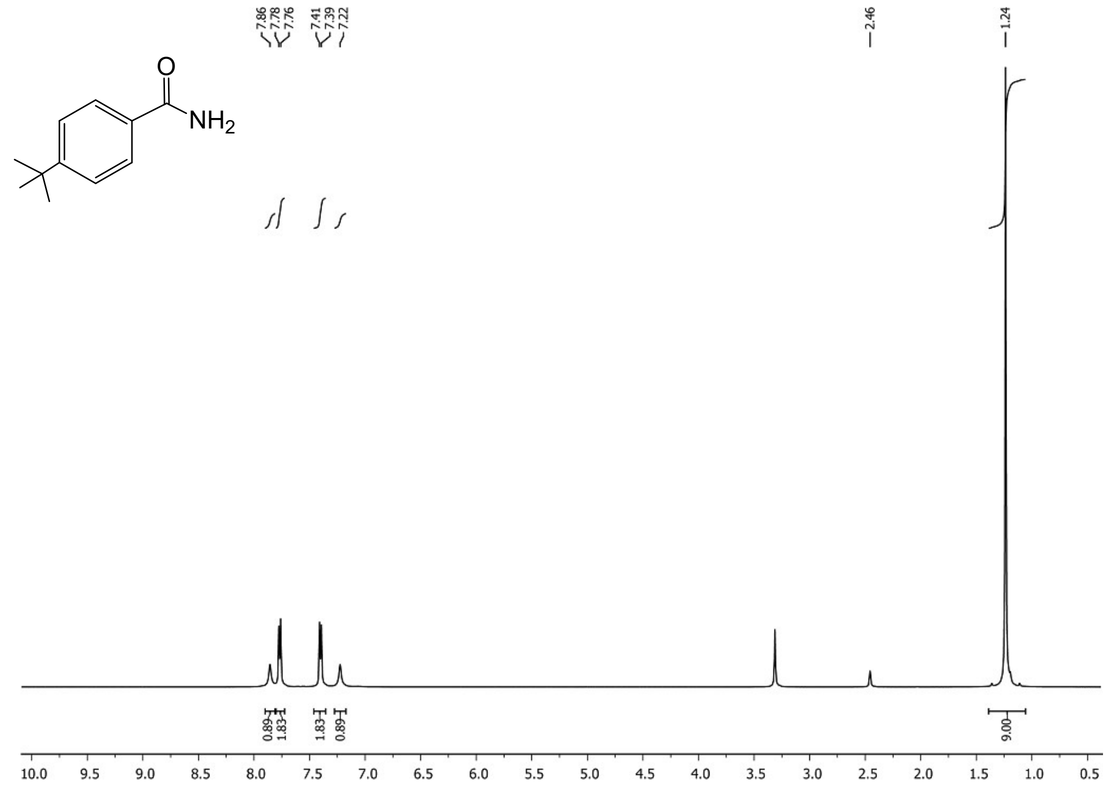
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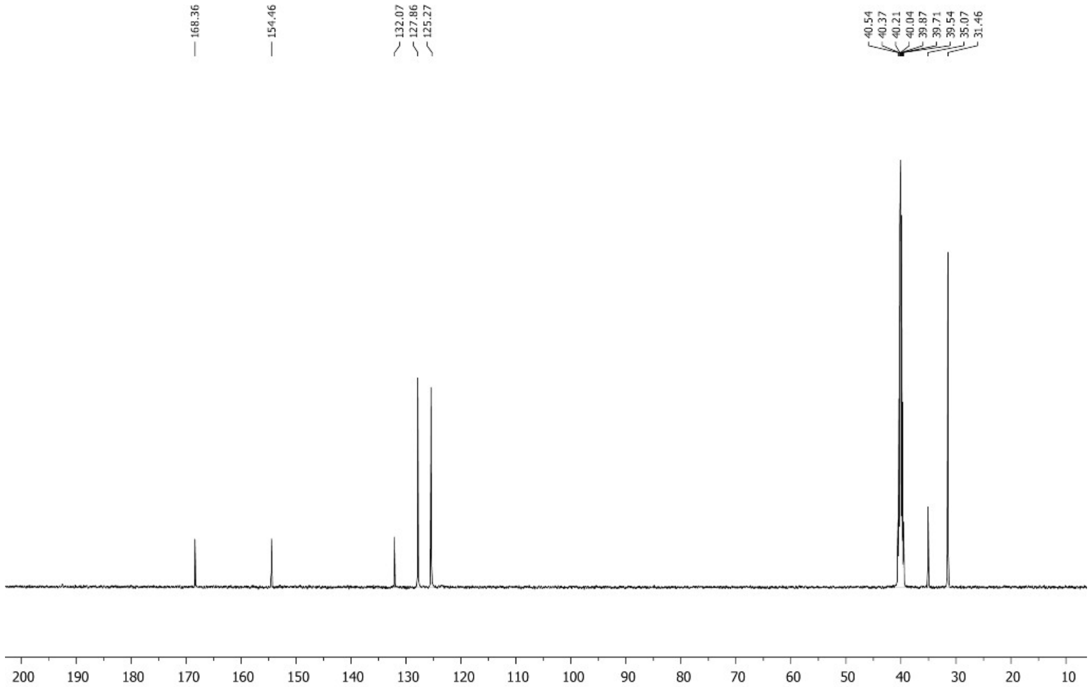
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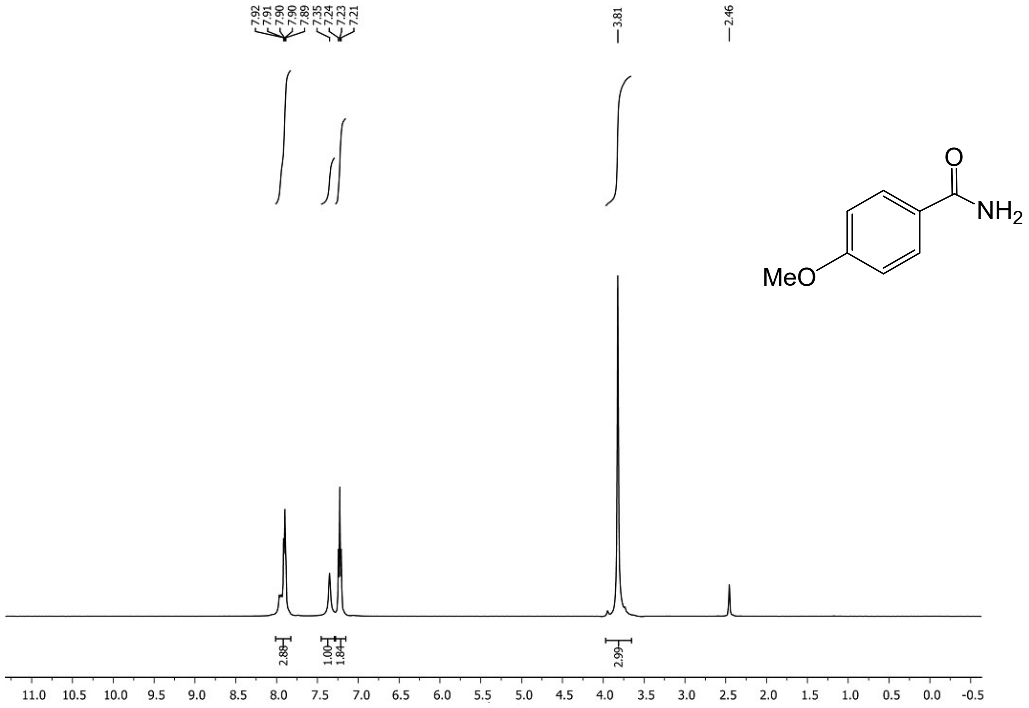
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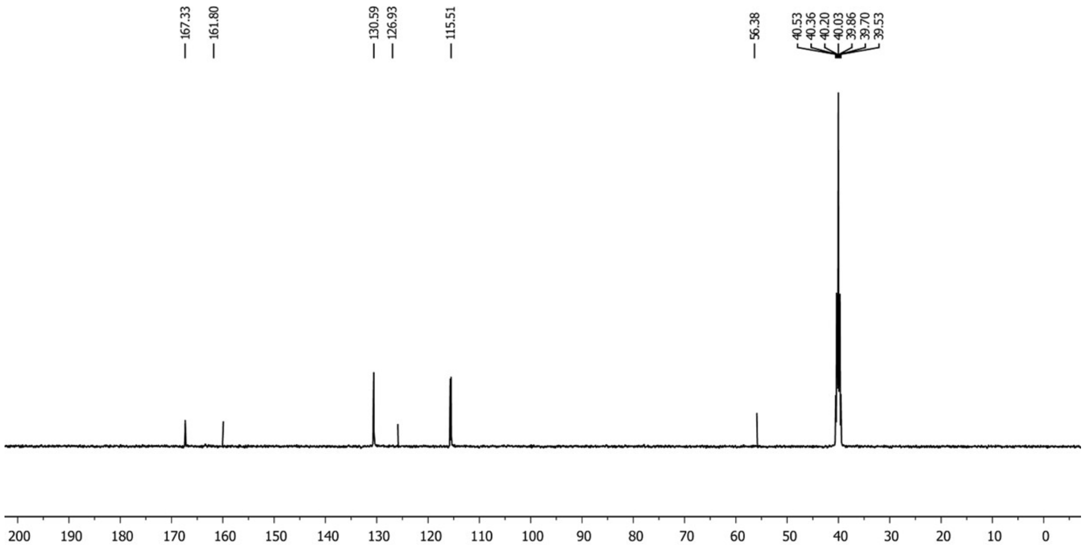
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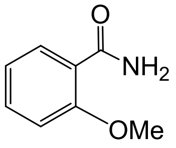
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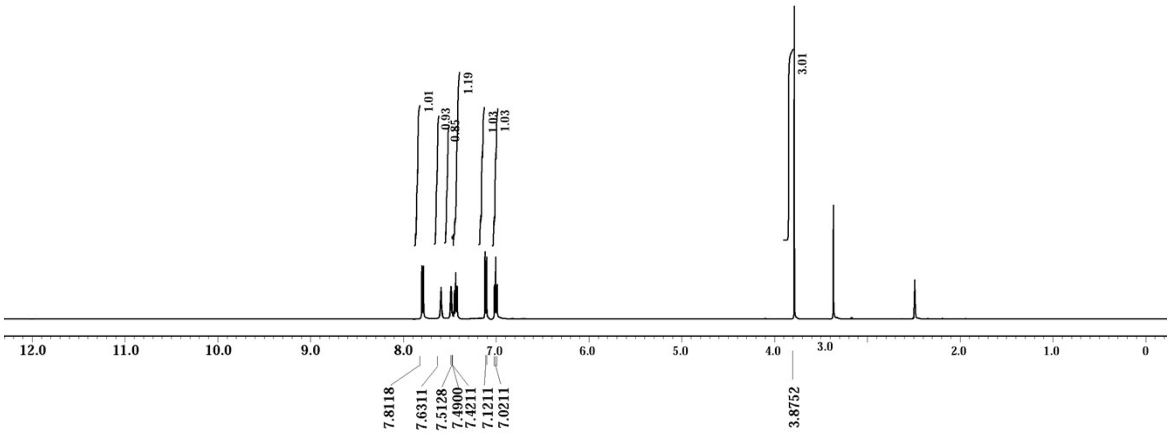
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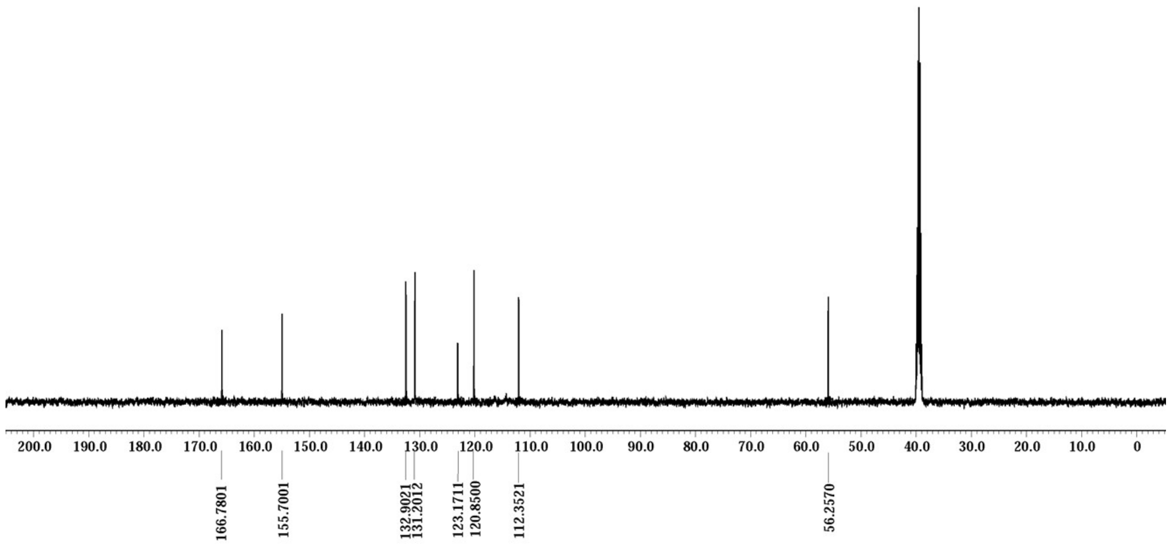
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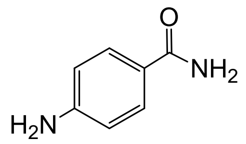
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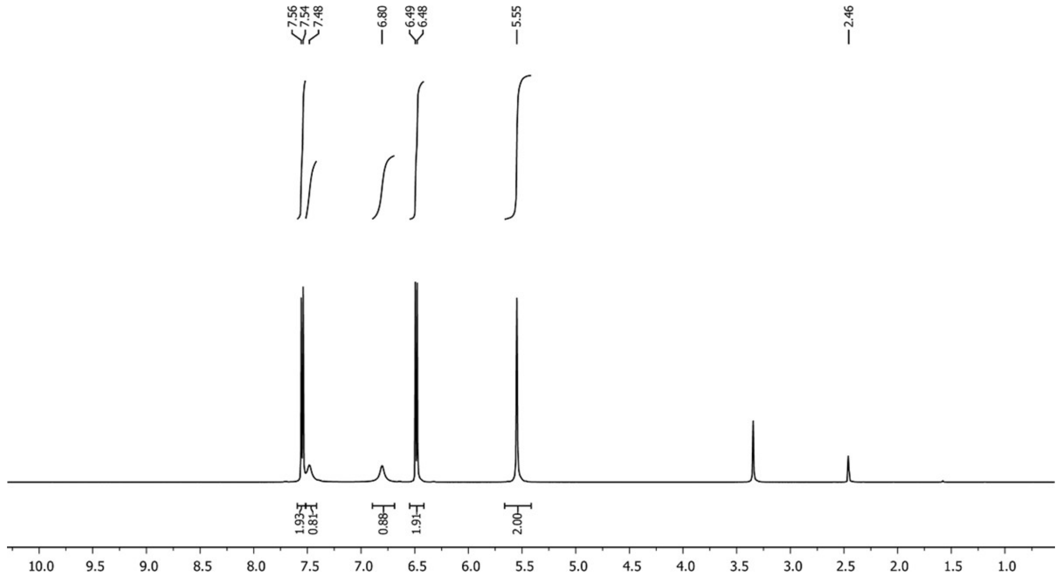
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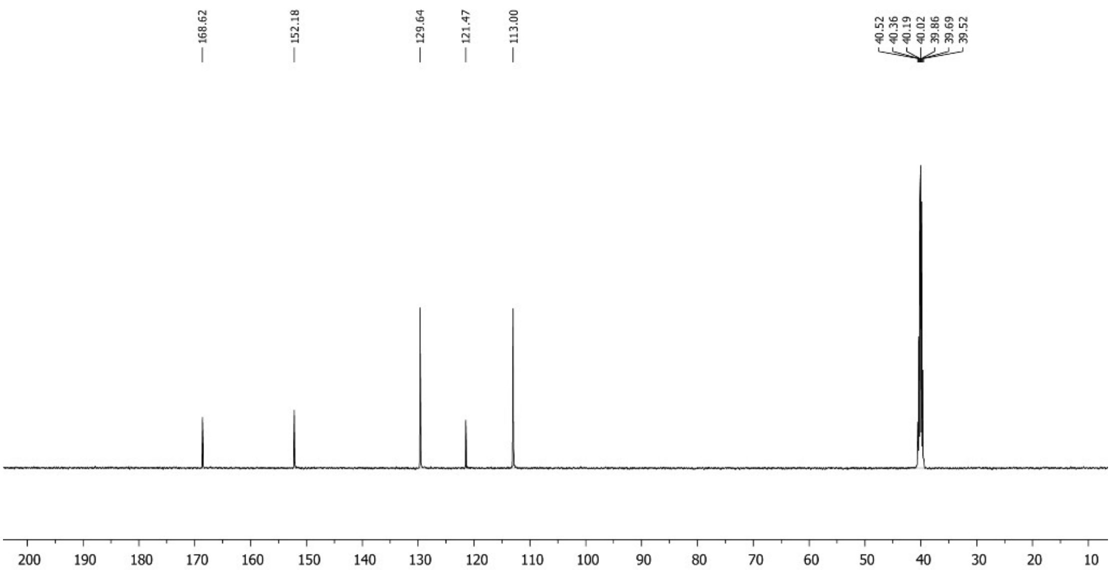
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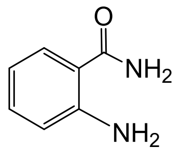
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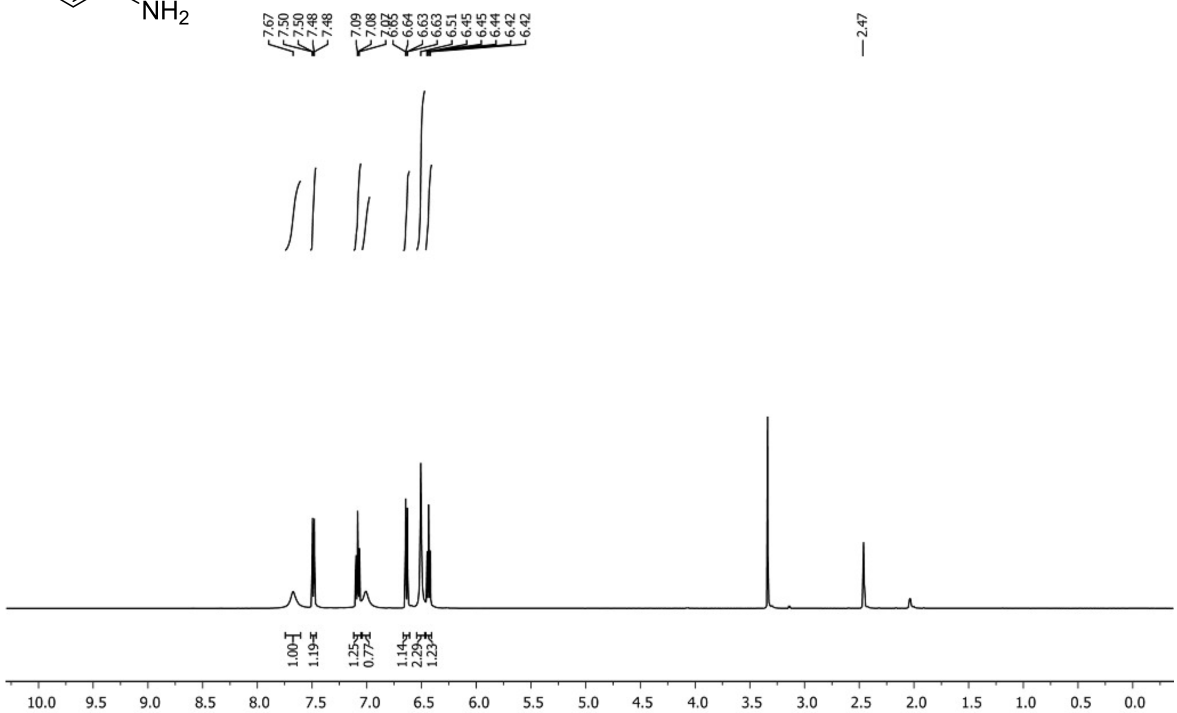
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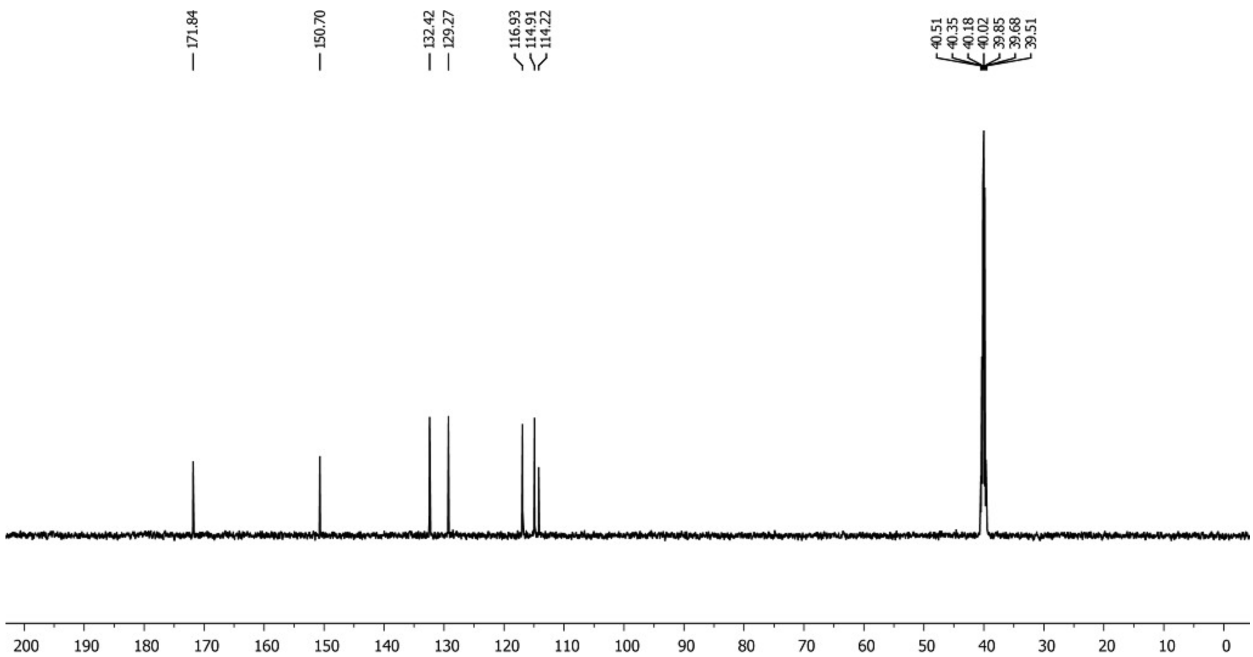
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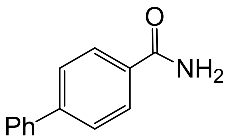
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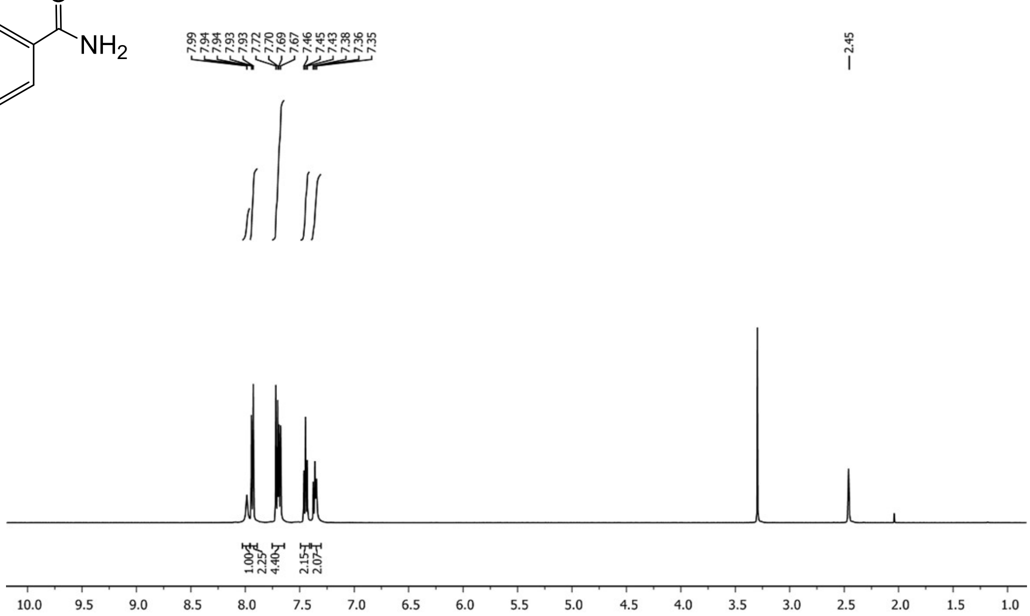
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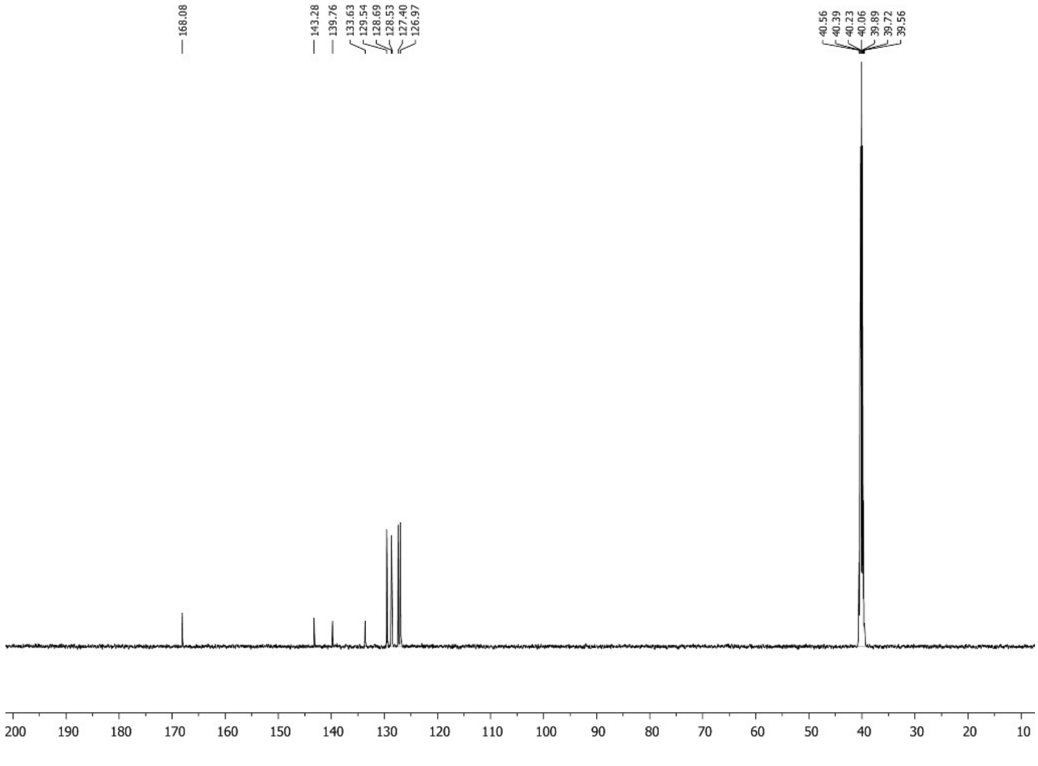
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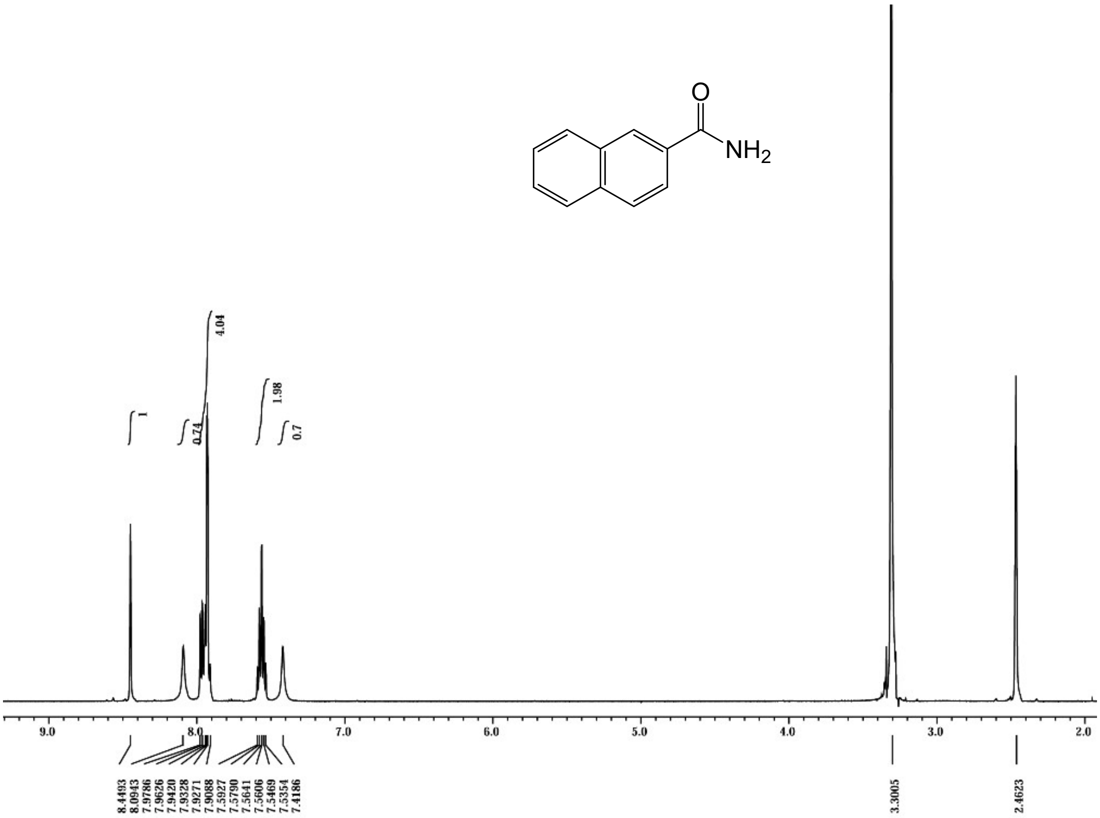
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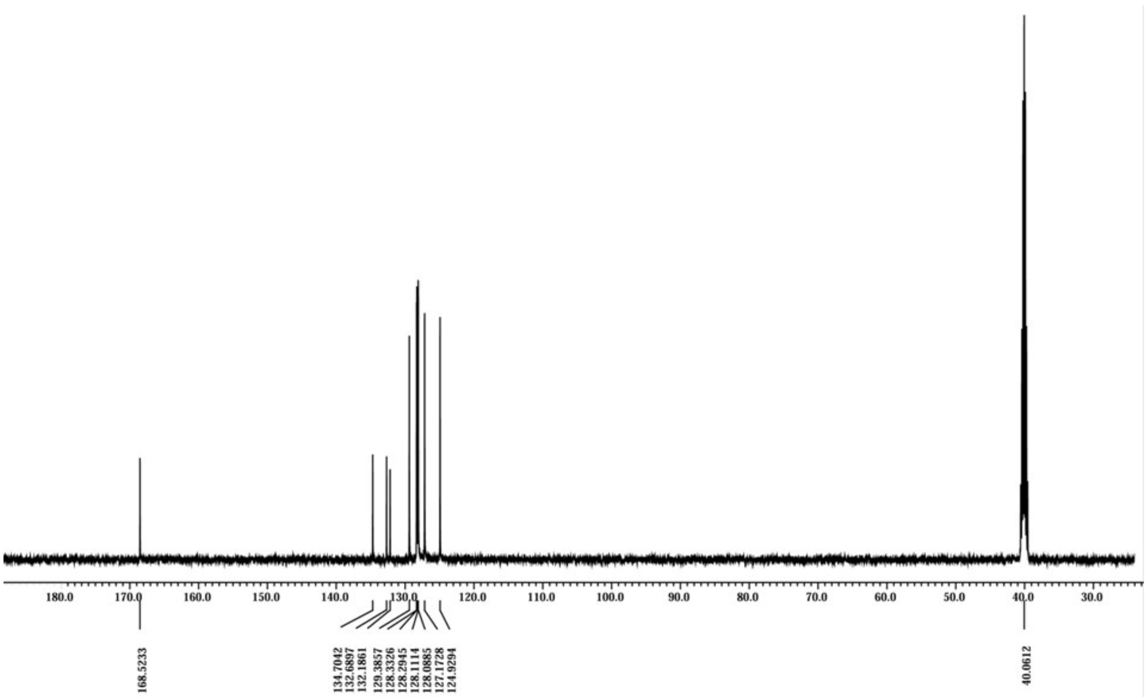
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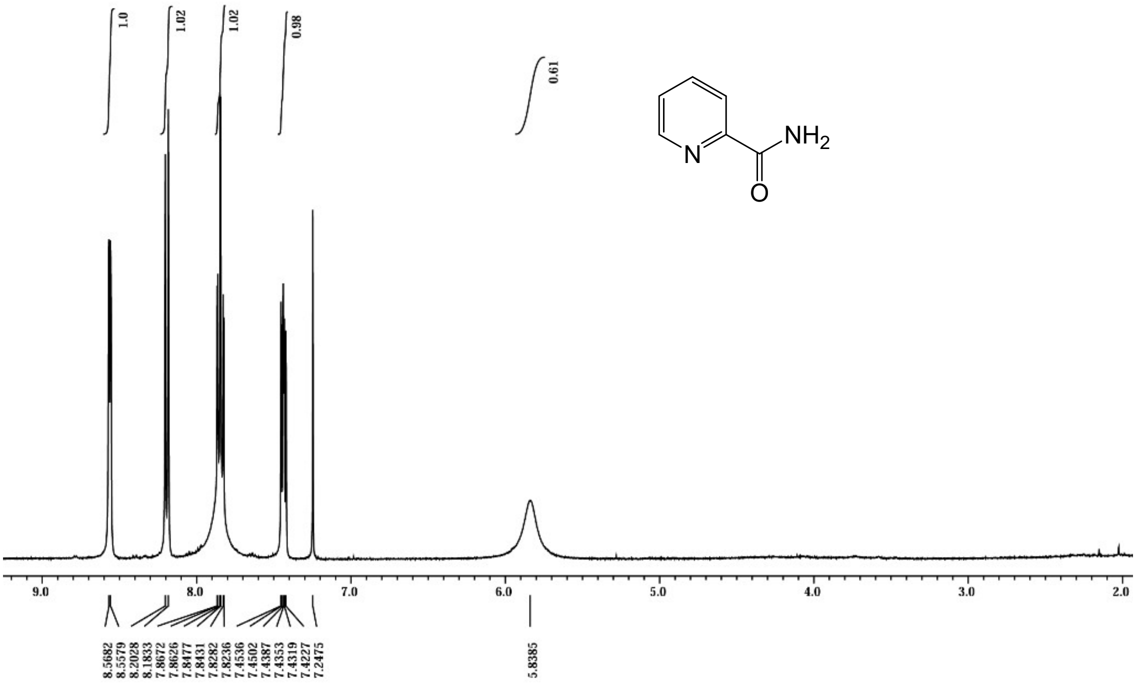
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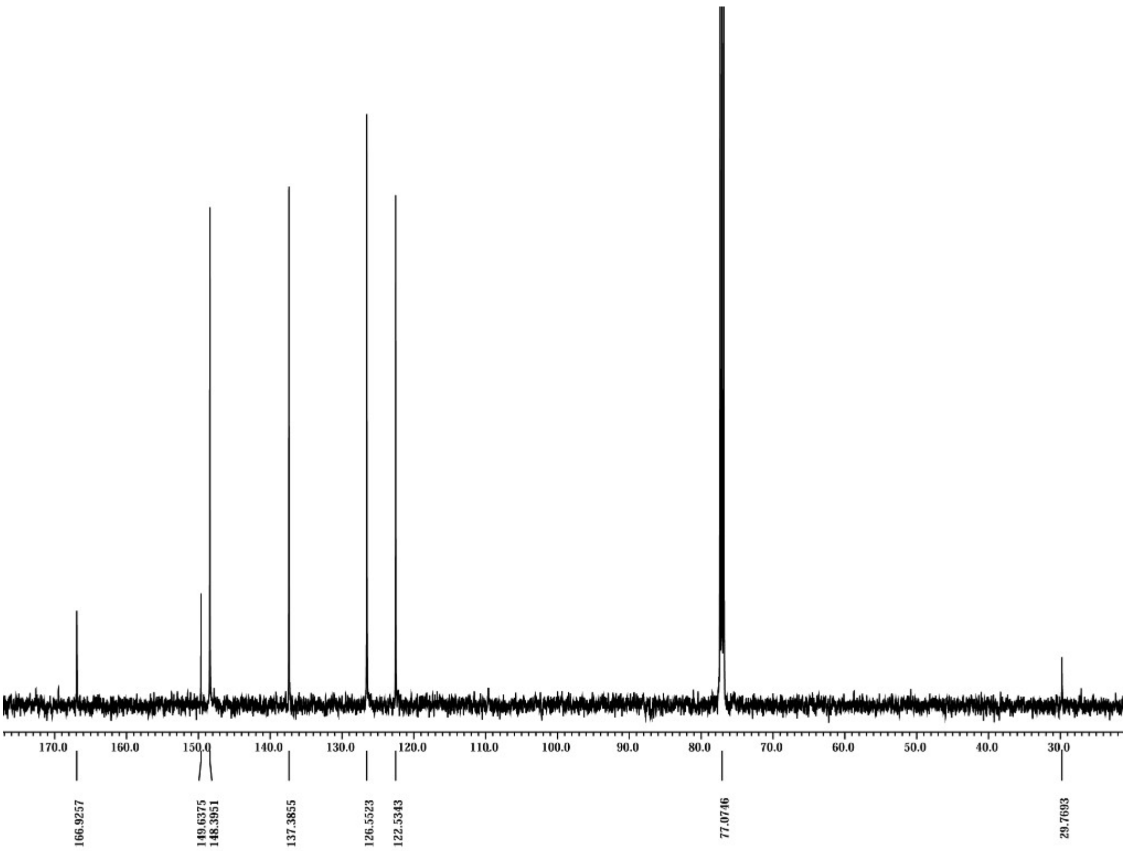
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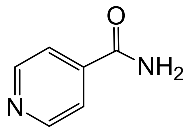
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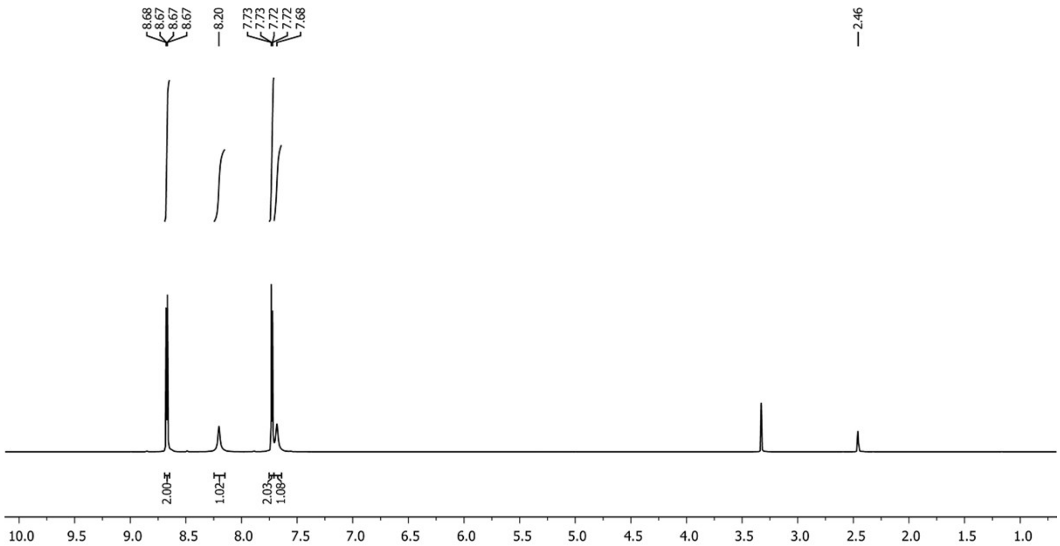

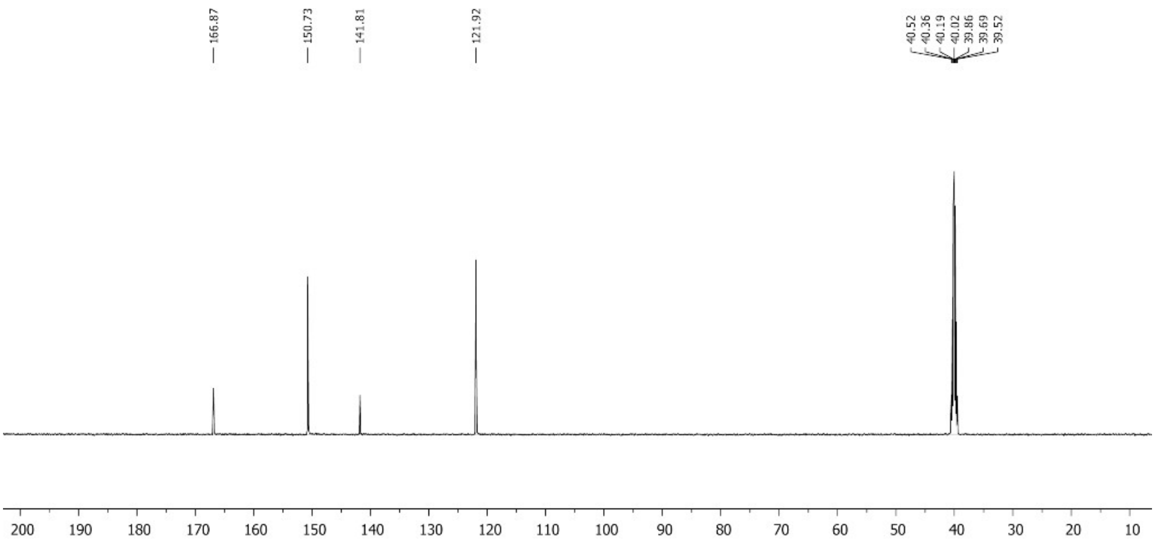

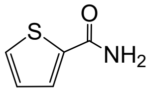
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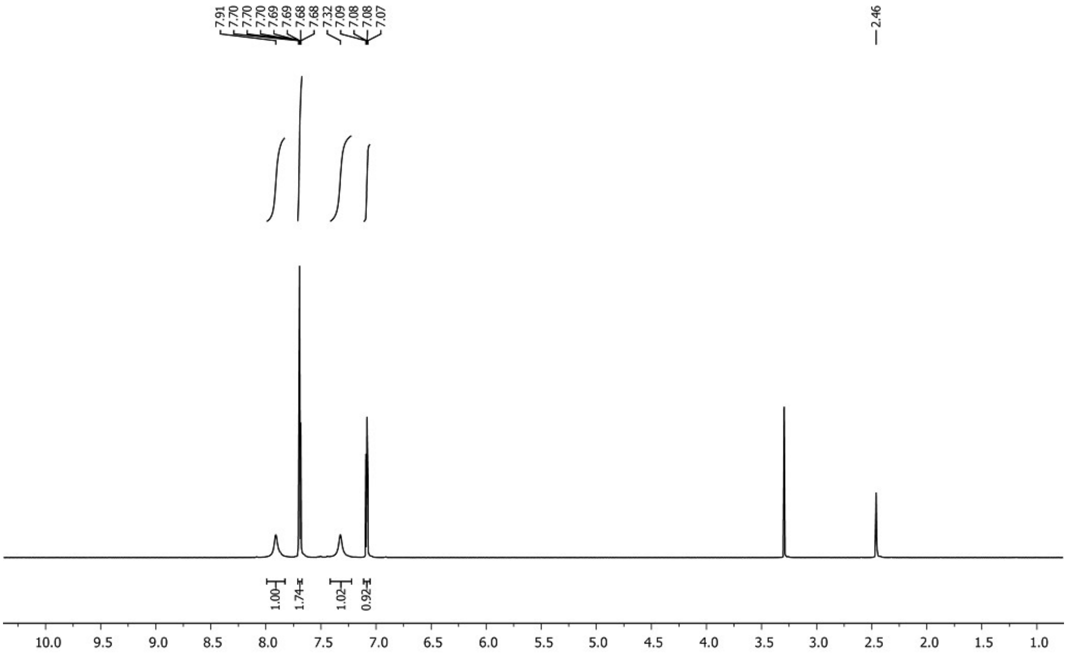
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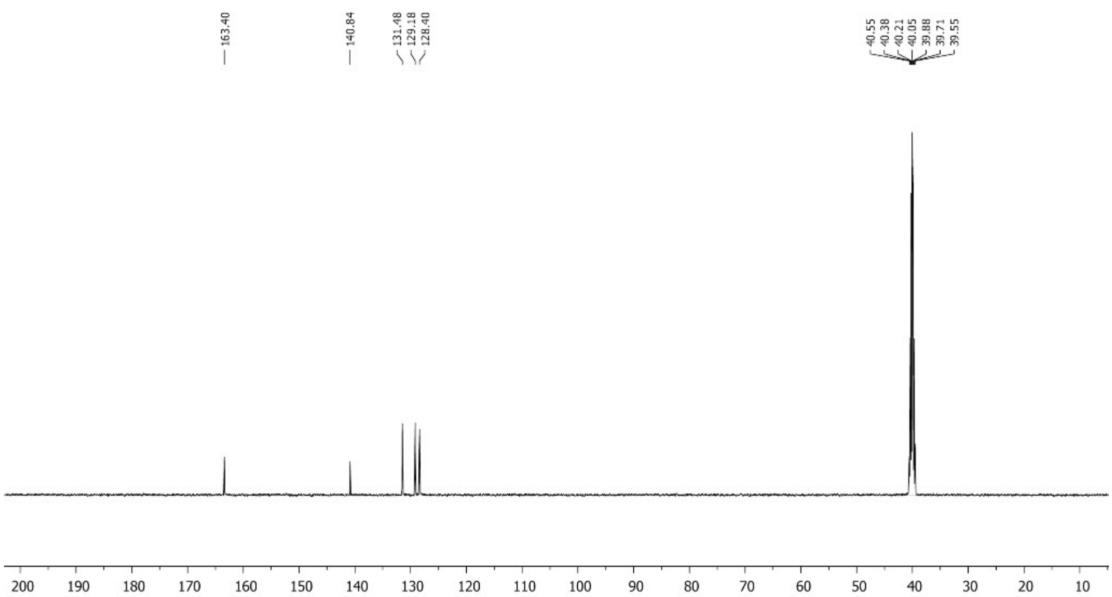
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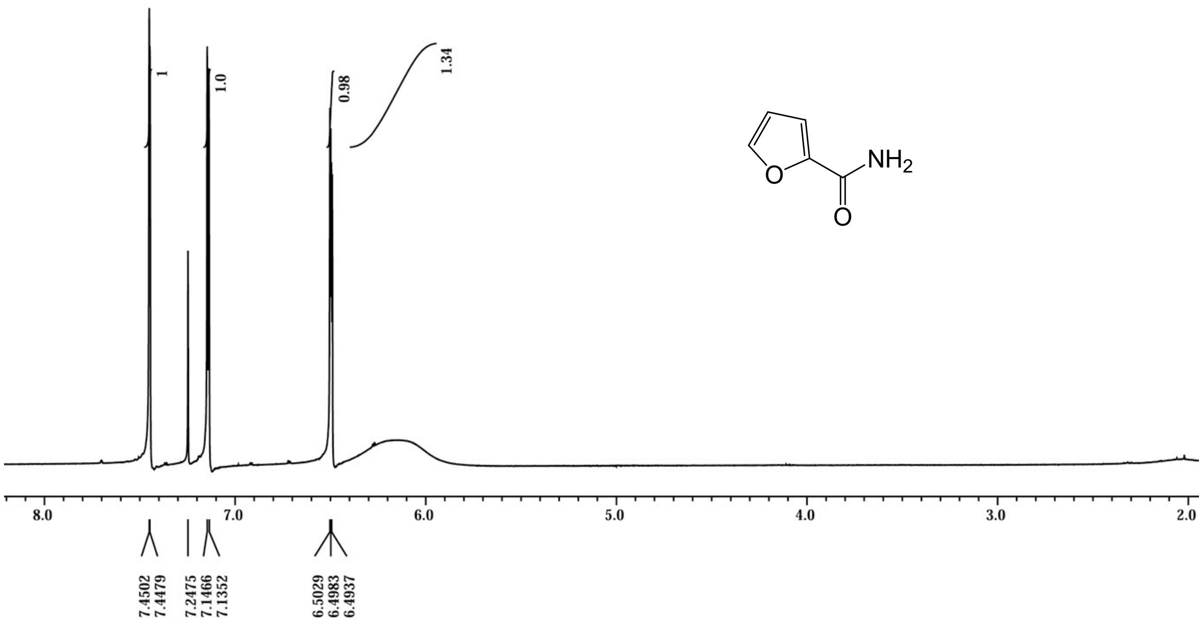
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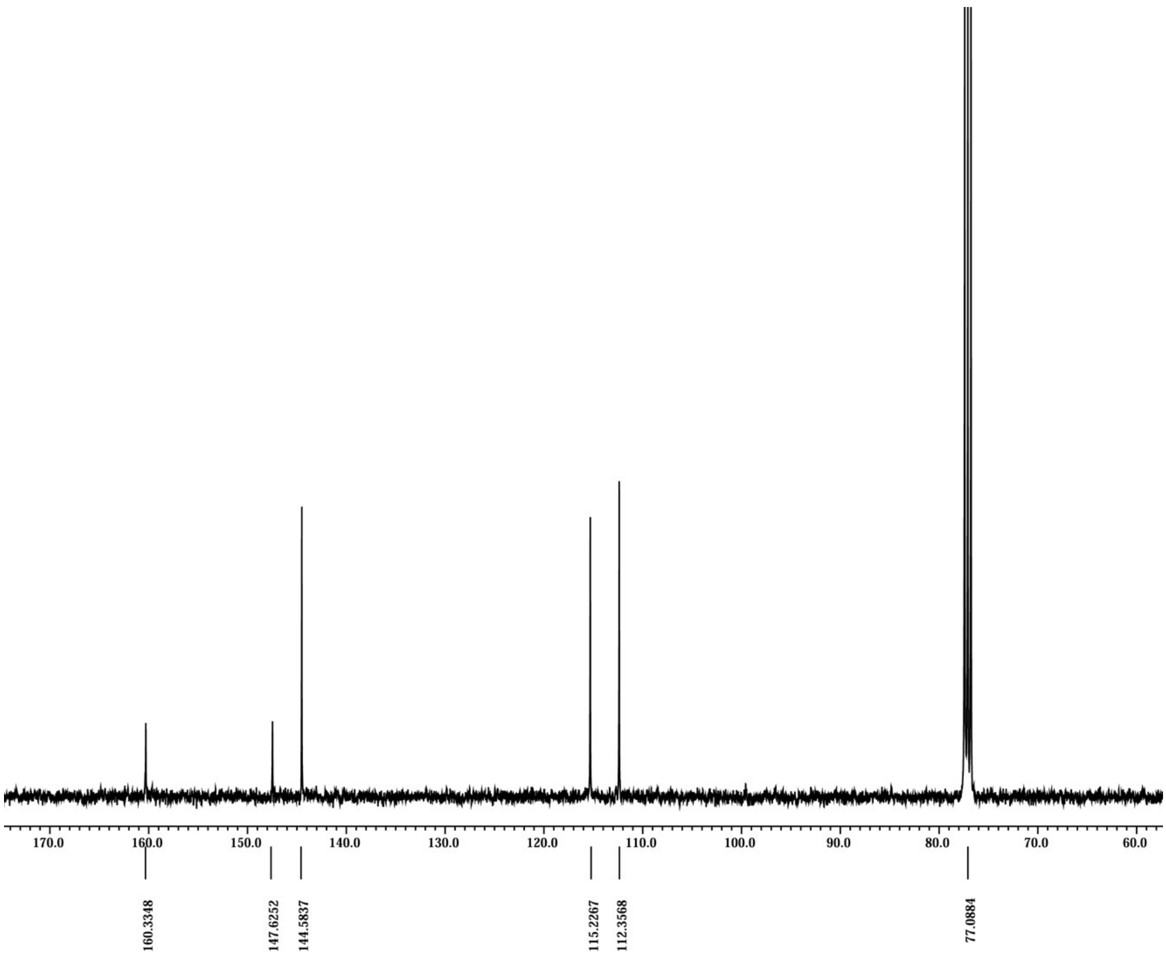
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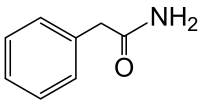

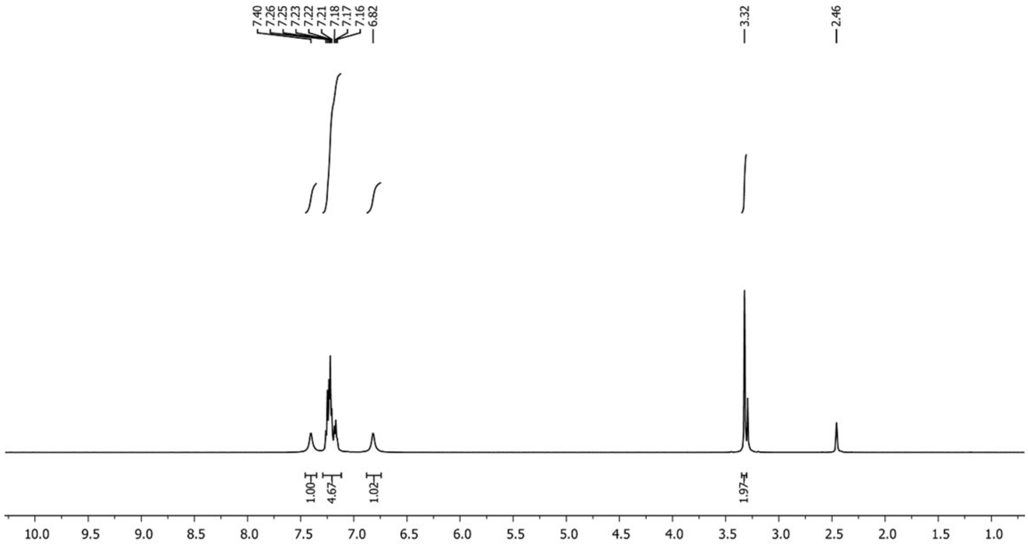
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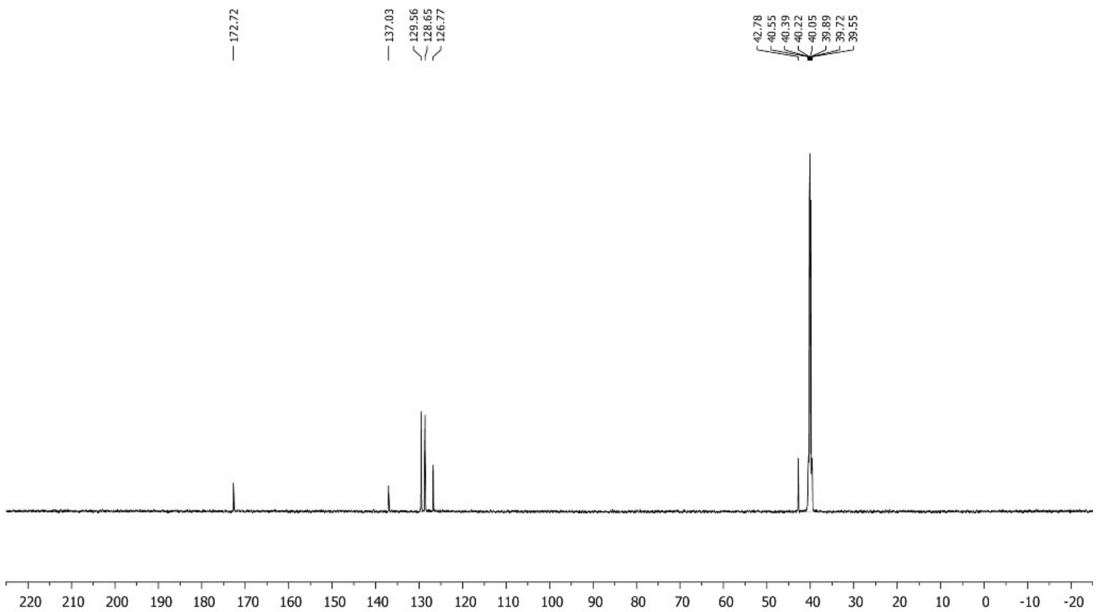
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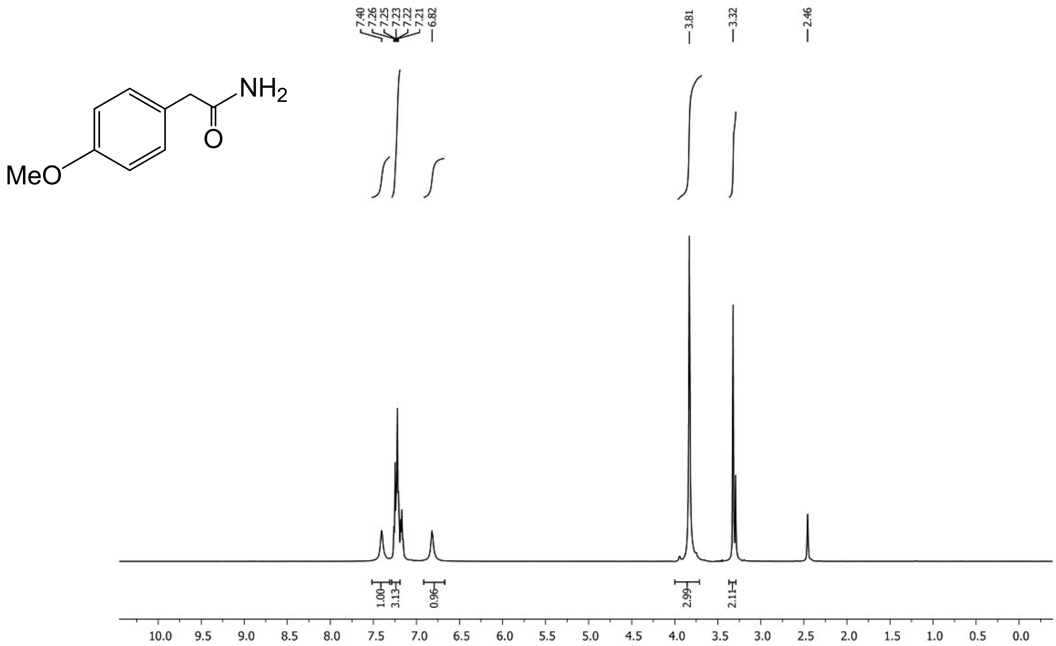
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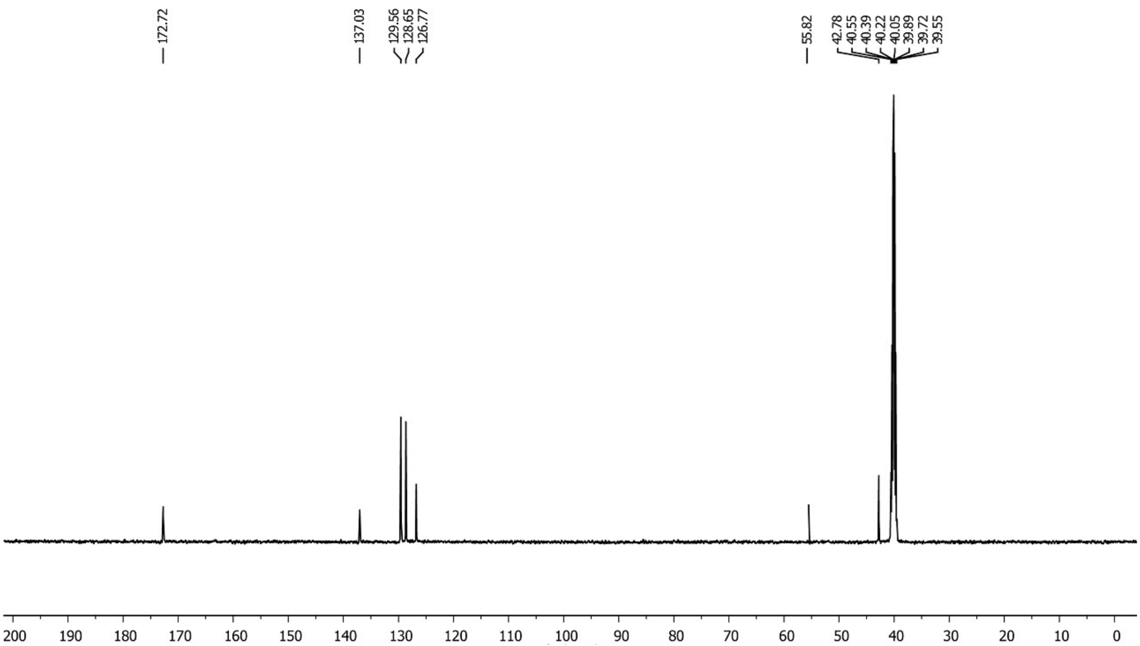
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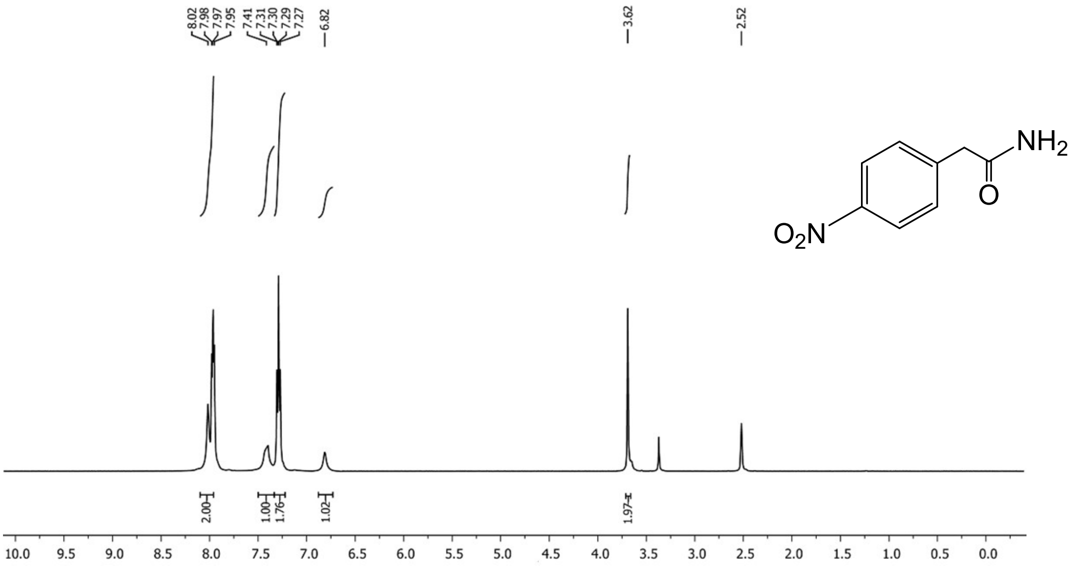
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O
O2N
2.00
1.00
1.76
1.02
1.97
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
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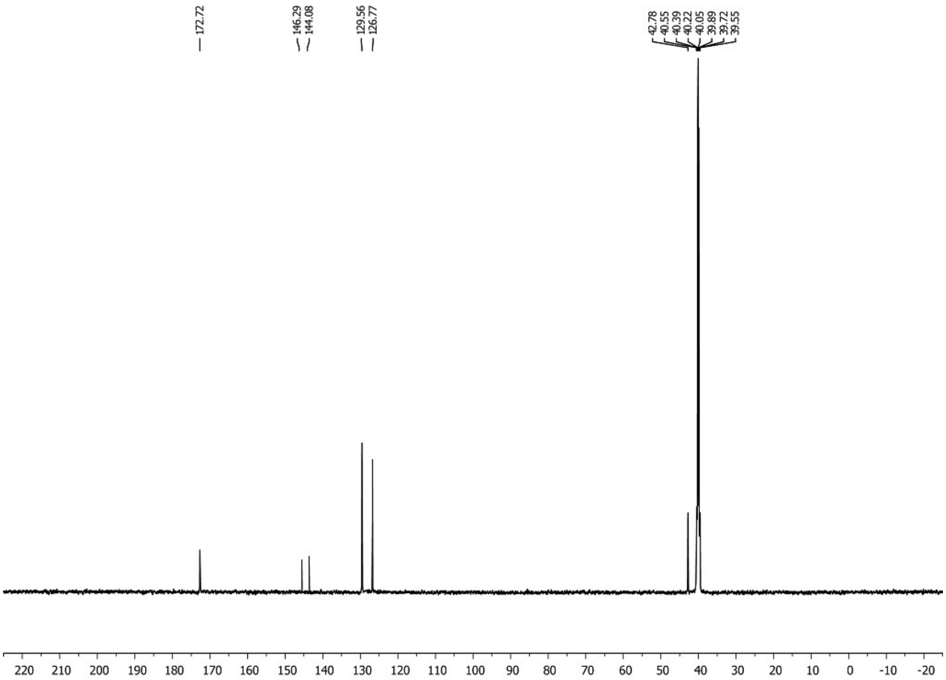
0.0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39.55
220
210
200
190
180
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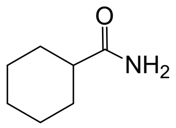
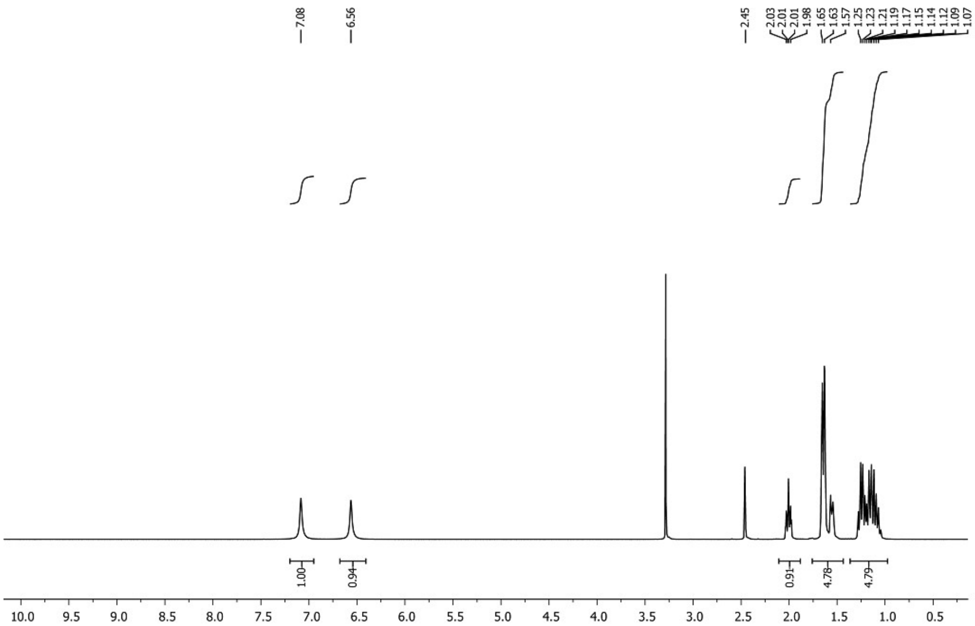
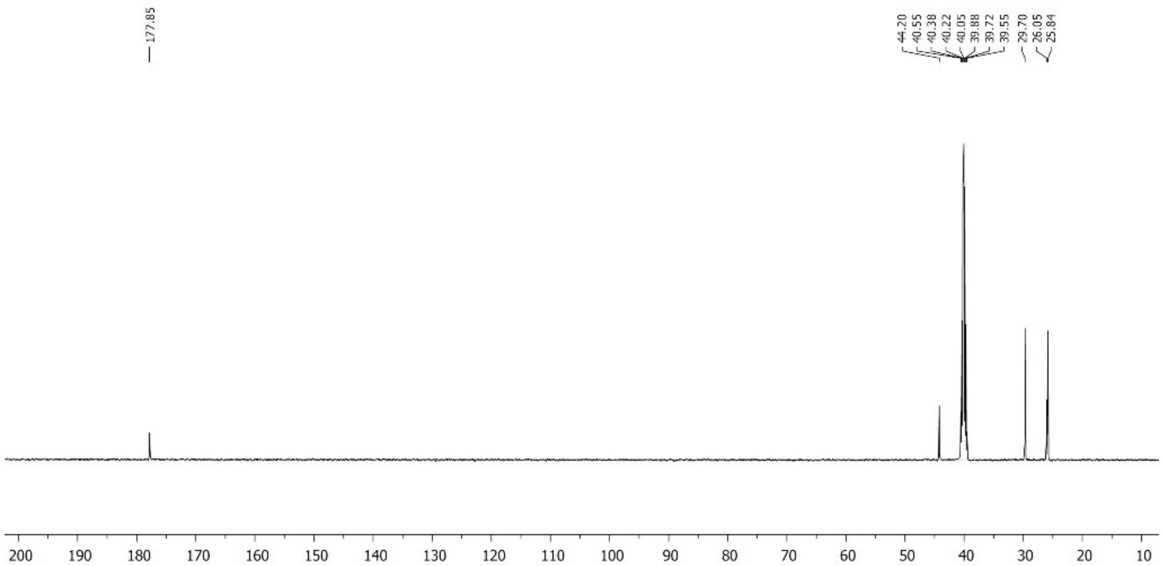
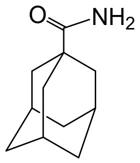
-10
-20





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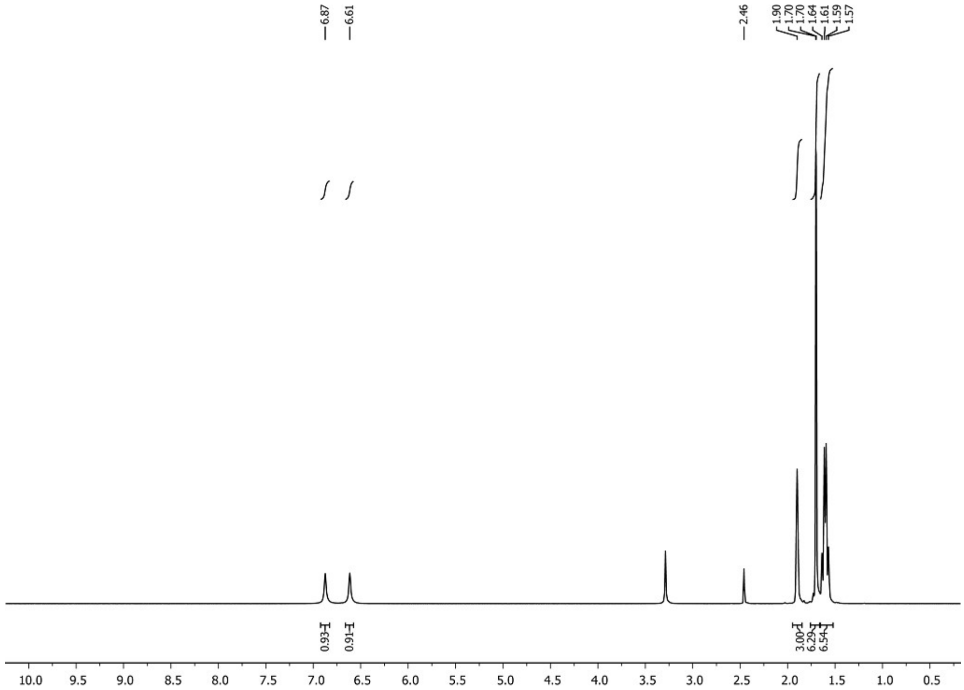
NH2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6.29
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9.0
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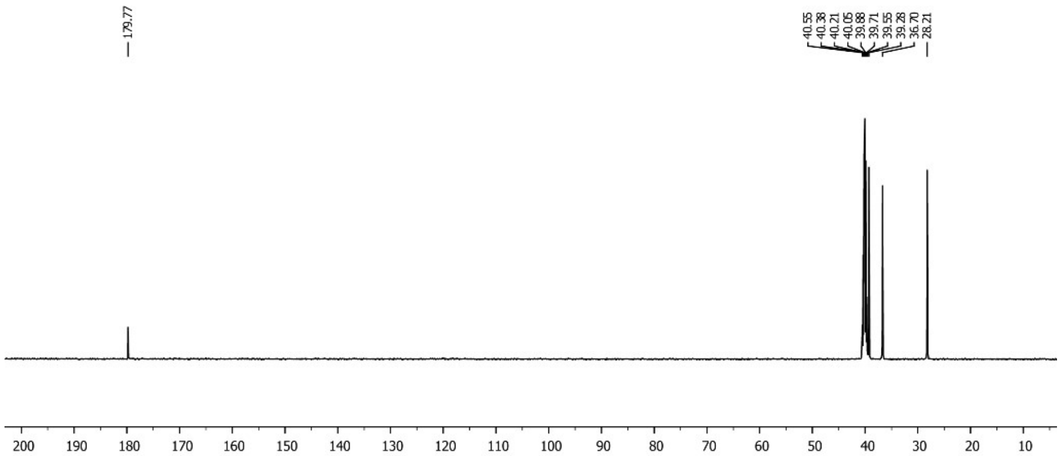
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20
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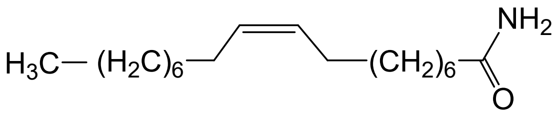
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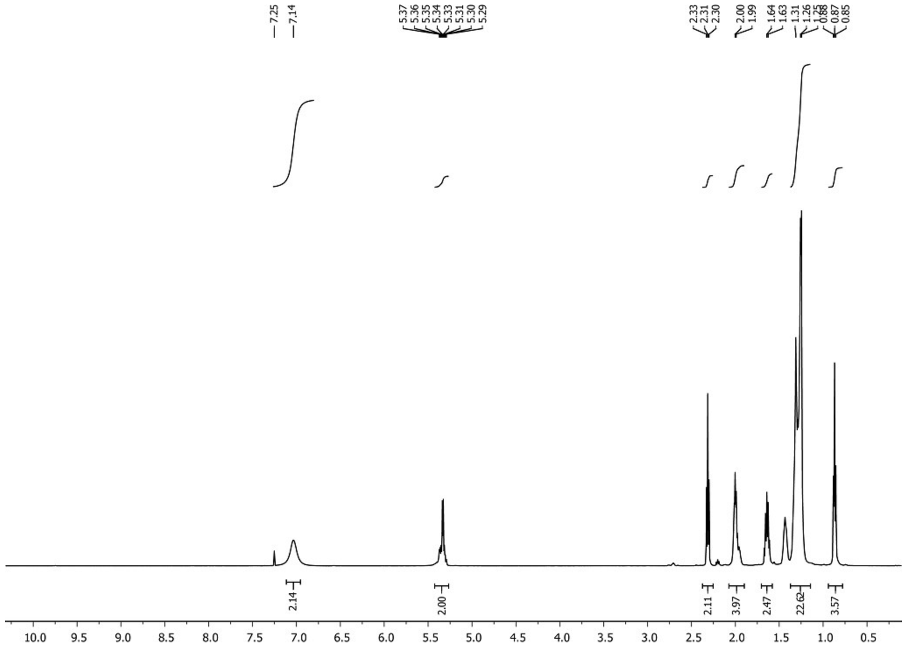
H3C— (H2C)6
(CH2)6
O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2.30
2.00
1.99
1.64
1.63
1.31
1.26
0.87
0.85
2.14
2.00
2.11
3.97
2.47
22.62
3.57
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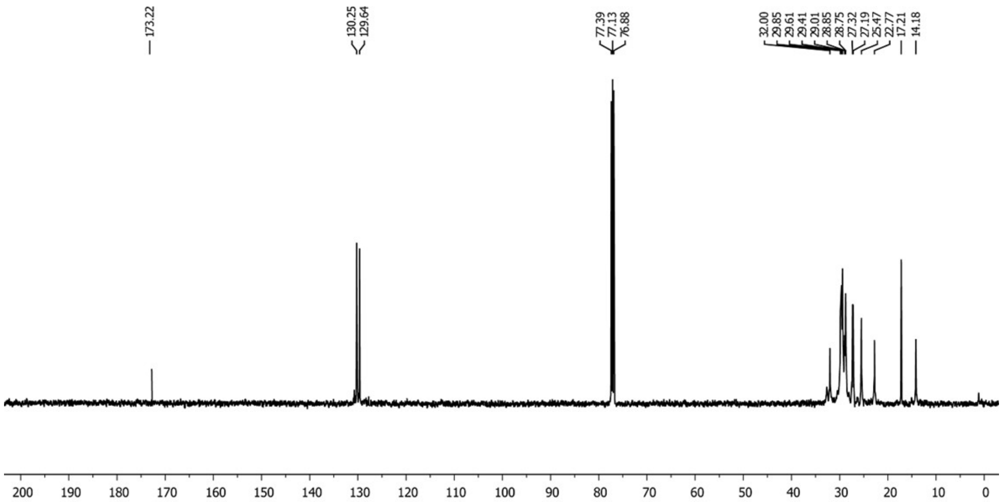
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29.41
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27.19
25.47
22.77
17.21
14.18
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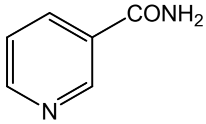
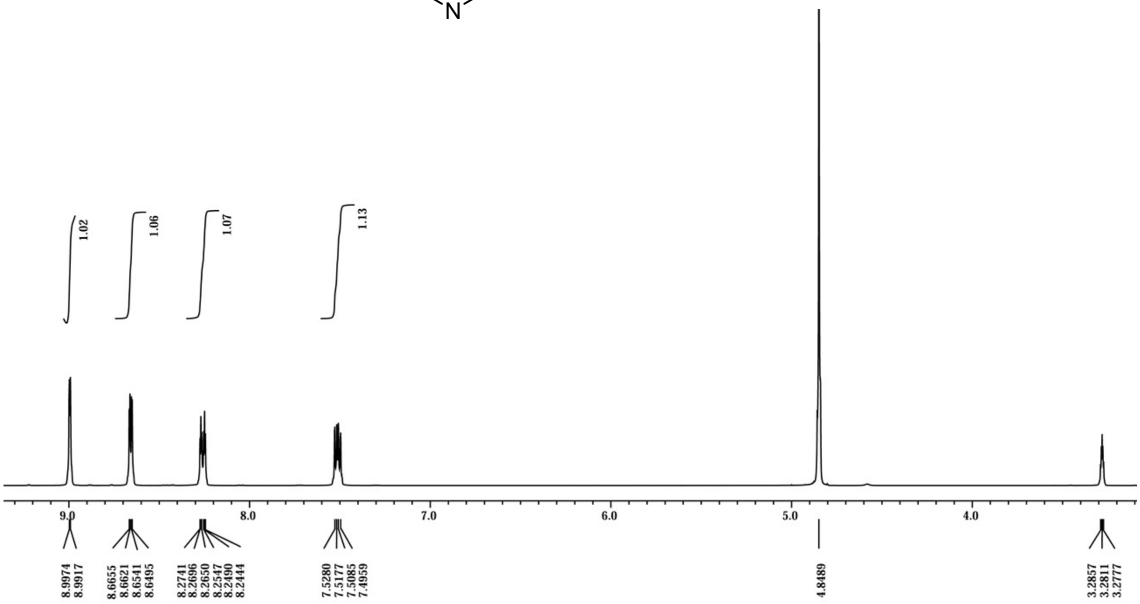

CONH2
N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8.6541
8.6495
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8.2696
8.2650
8.2547
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7.5085
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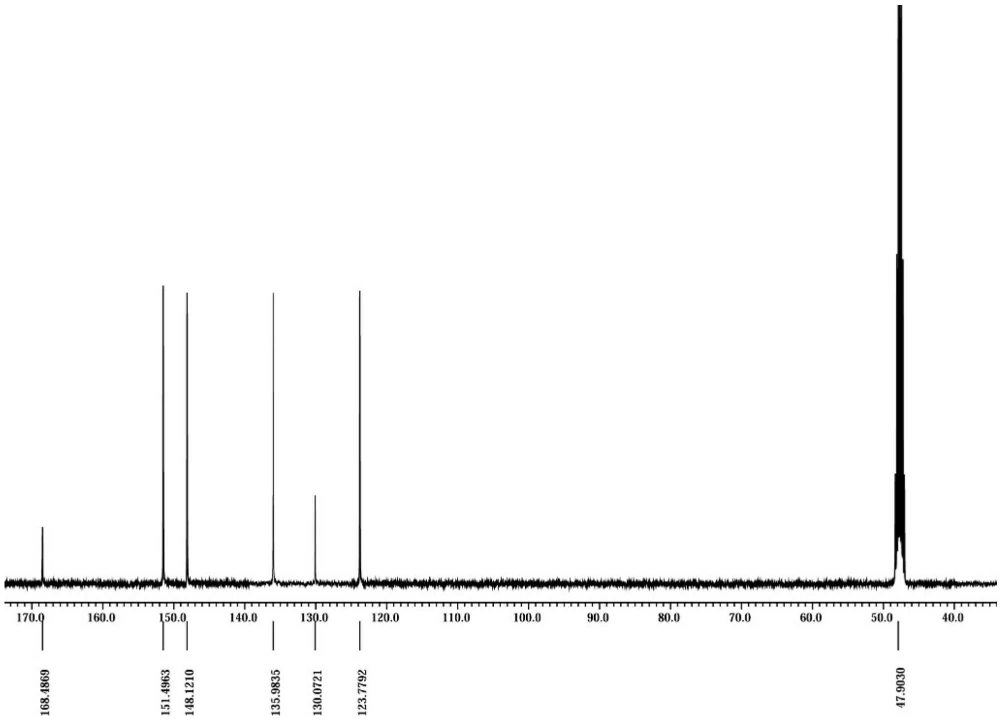
3.2811
3.2777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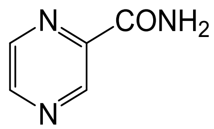
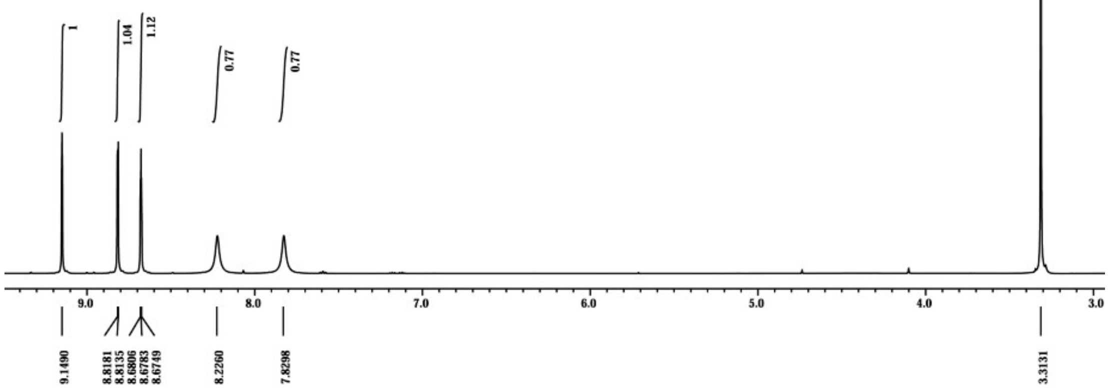
130.0721
123.7792
47.9030

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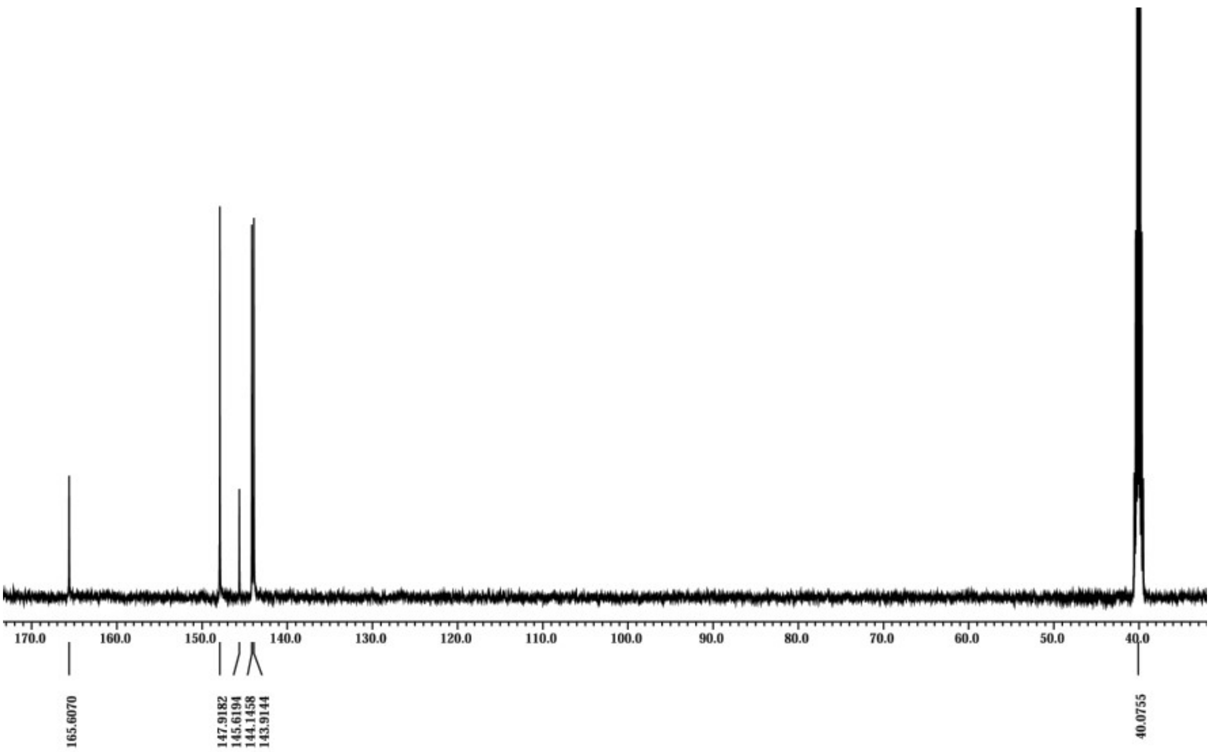
8.6749
8.2260
7.8298
3.3131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50.0
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165.6070
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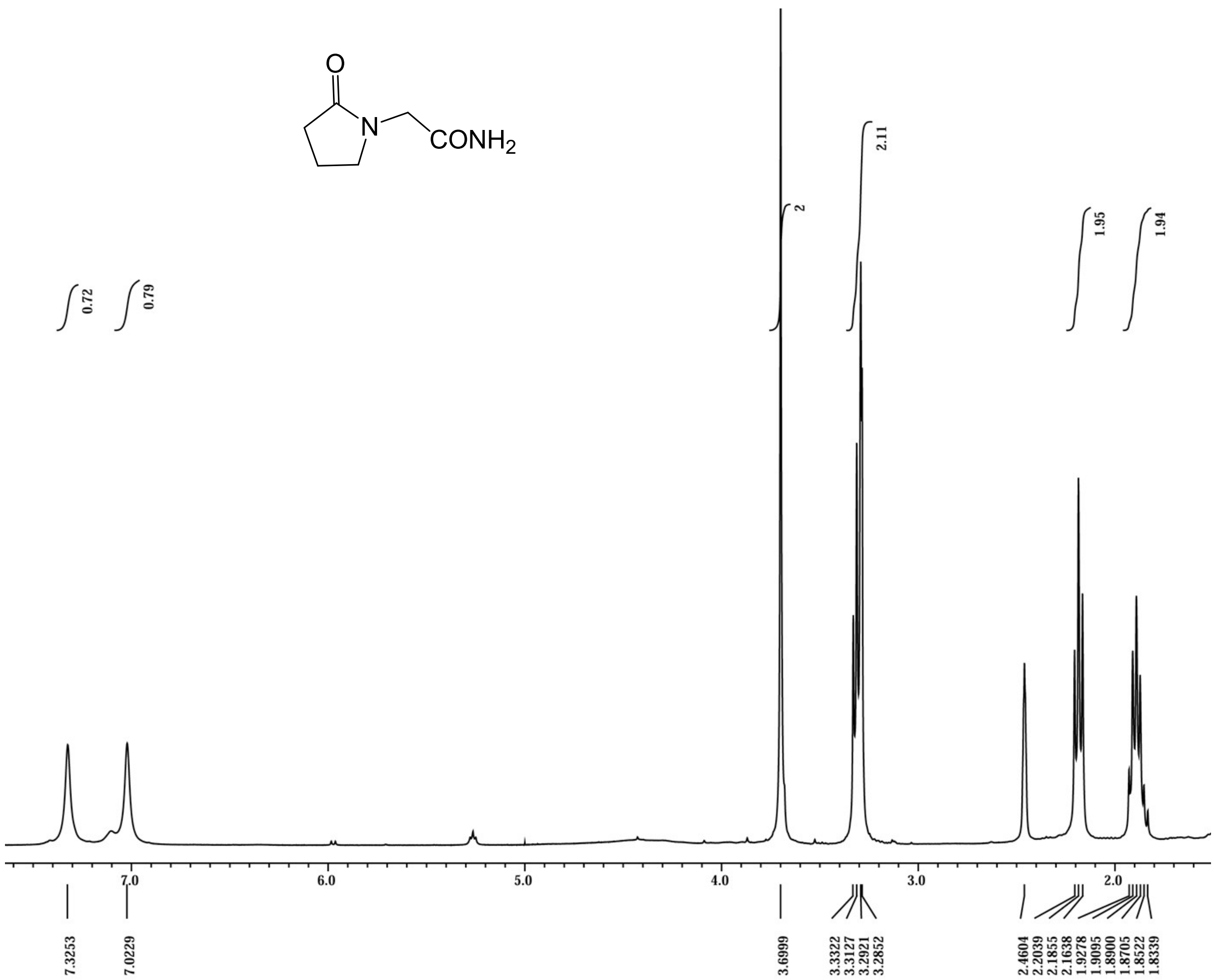
145.6194
144.1458
143.9144
40.0755



O
N
CONH$_2$
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2
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1.94
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6.0
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3.0
2.0
7.3253
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3.6999
3.3322
3.3127
3.2921
3.2852
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1.9278
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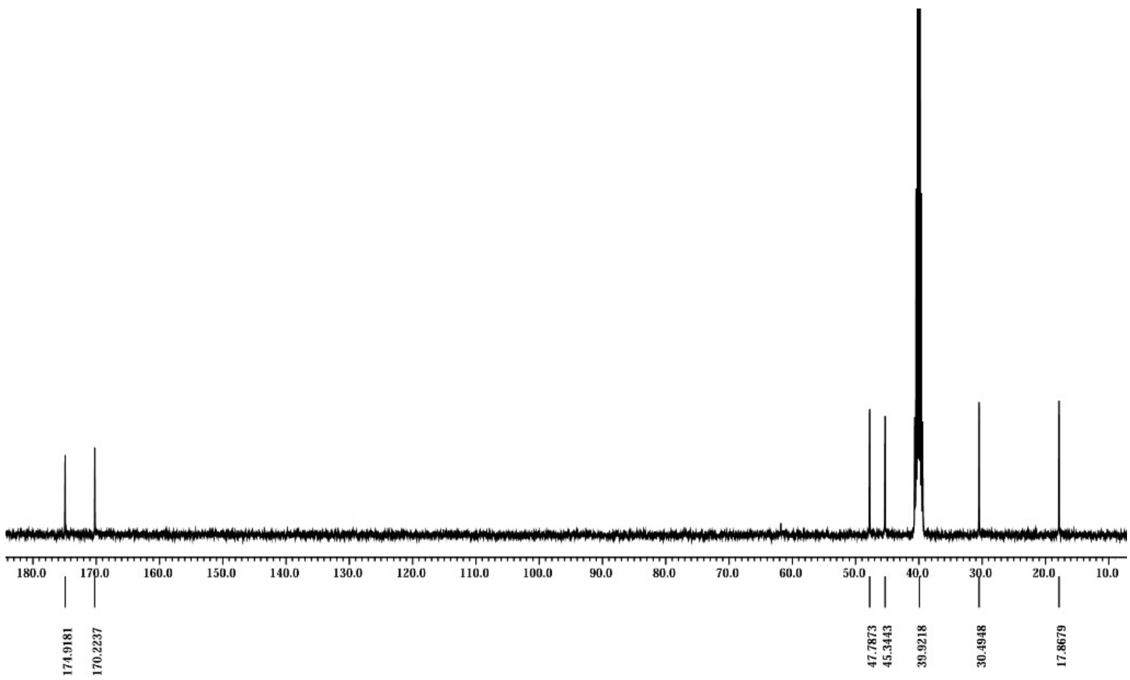
1.8522
1.8339



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60.0
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10.0
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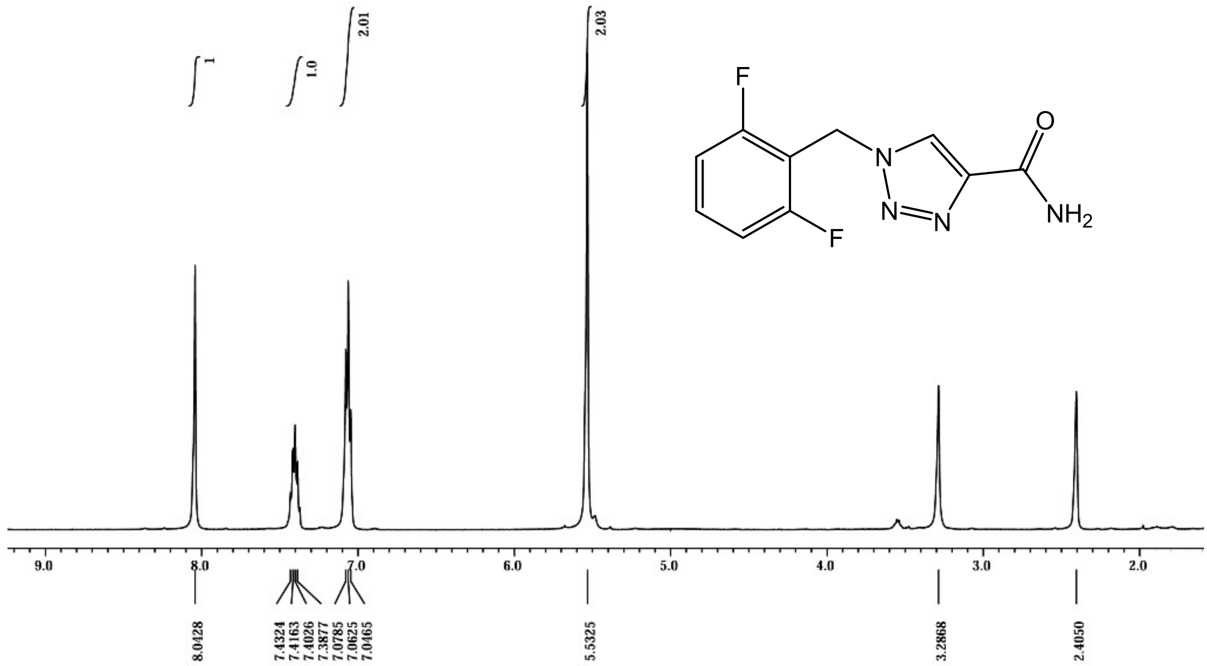
47.7873
45.3443
39.9218
30.4948
17.8679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F
N
N
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O
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4.0
3.0
2.0
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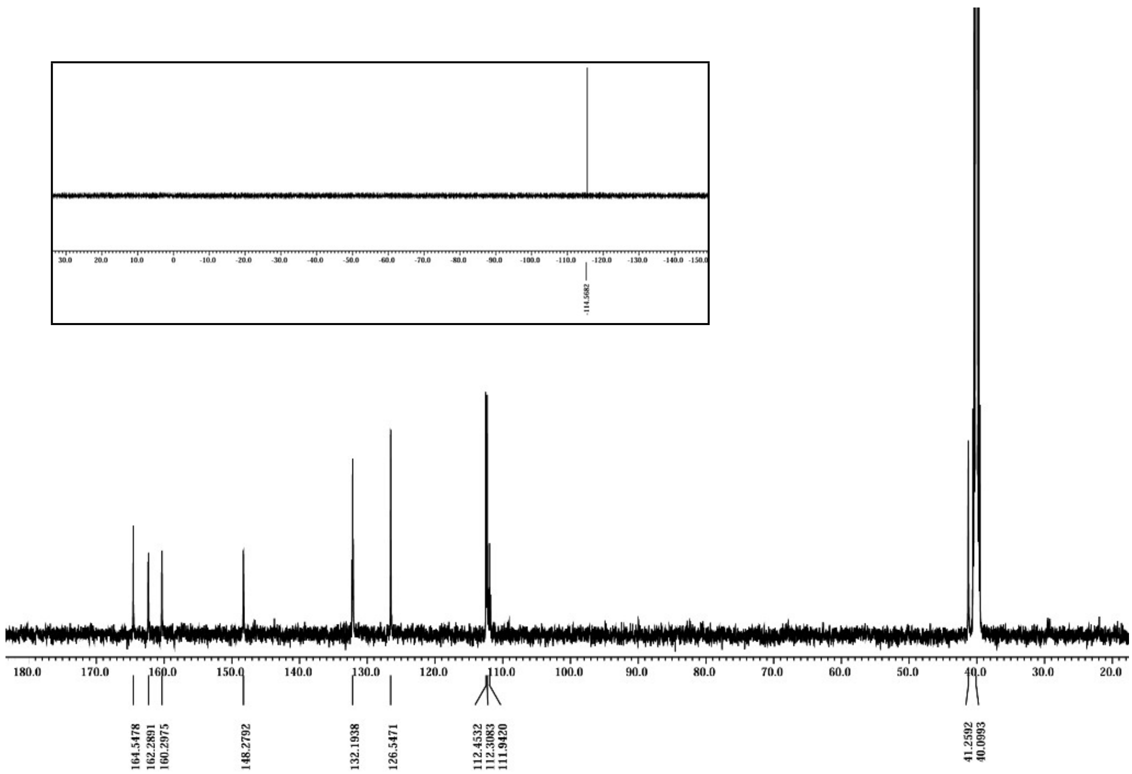
3.2868
2.4050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50.0
40.0
30.0
20.0
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162.2891
160.2975
148.2792
132.1938
126.5471
112.4532
112.3083
111.9420
41.2592
40.0993

5. Computational Details

Density functional theory (DFT) calculations were performed using Gaussian 09 program suite.[5] The oxidation of bezyl amine at 70 °C in ^{t}BuOH was used as a model reaction. The density functional used here is M06 hybrid meta-GGA functional.[6] LanL2DZ basis set with effective core potentials[7] was employed for ruthenium and 6-31+G(d,p) basis set was used for other elements.[8,9] Normal mode analysis was performed to ascertain the nature of the stationary state points on the potential energy surface. All stationary points on the potential energy surface were characterized to be either local minima with no imaginary vibrational frequency or transition states with a single imaginary frequency. Solvent effects were introduced by performing single point calculation for the gas phase optimized geometries using SMD implicit solvent model with ^{t}BuOH as the solvent. The Gibbs free energies were then computed at 343.15 K and the computed free energy values include both zero-point correction and thermal correction to enthalpy and entropy to the total electronic energy.

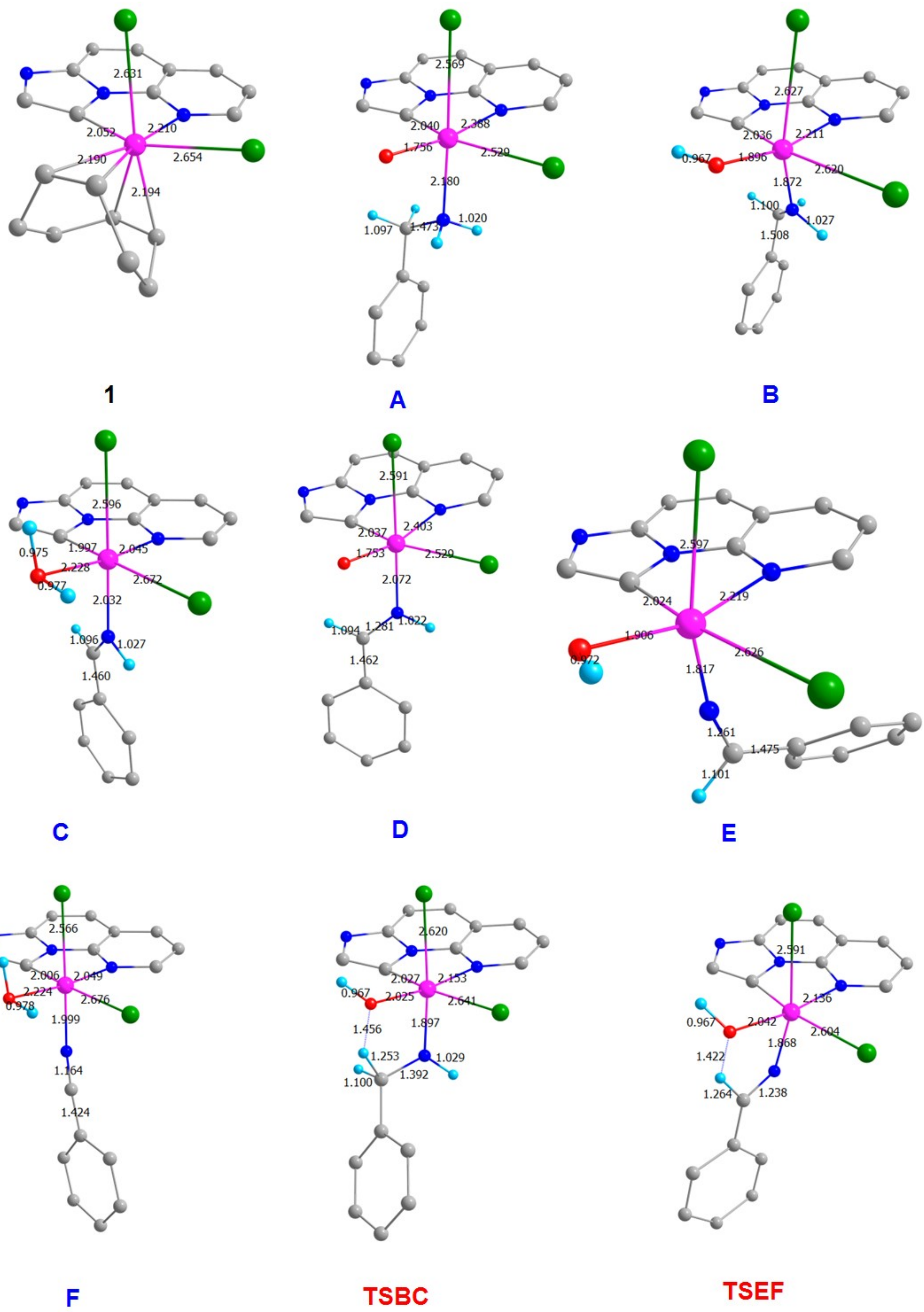

Figure S15. Optimized structures with important distances (in Å.) labeled. For clarity, the phenyl and benzyl groups are not shown in the picture. Hydrogen atoms except for those involved in the reaction are also omitted. Atom color codes: Ru (pink), C (grey), N (blue), O (red), H (sky blue) and Br (green).

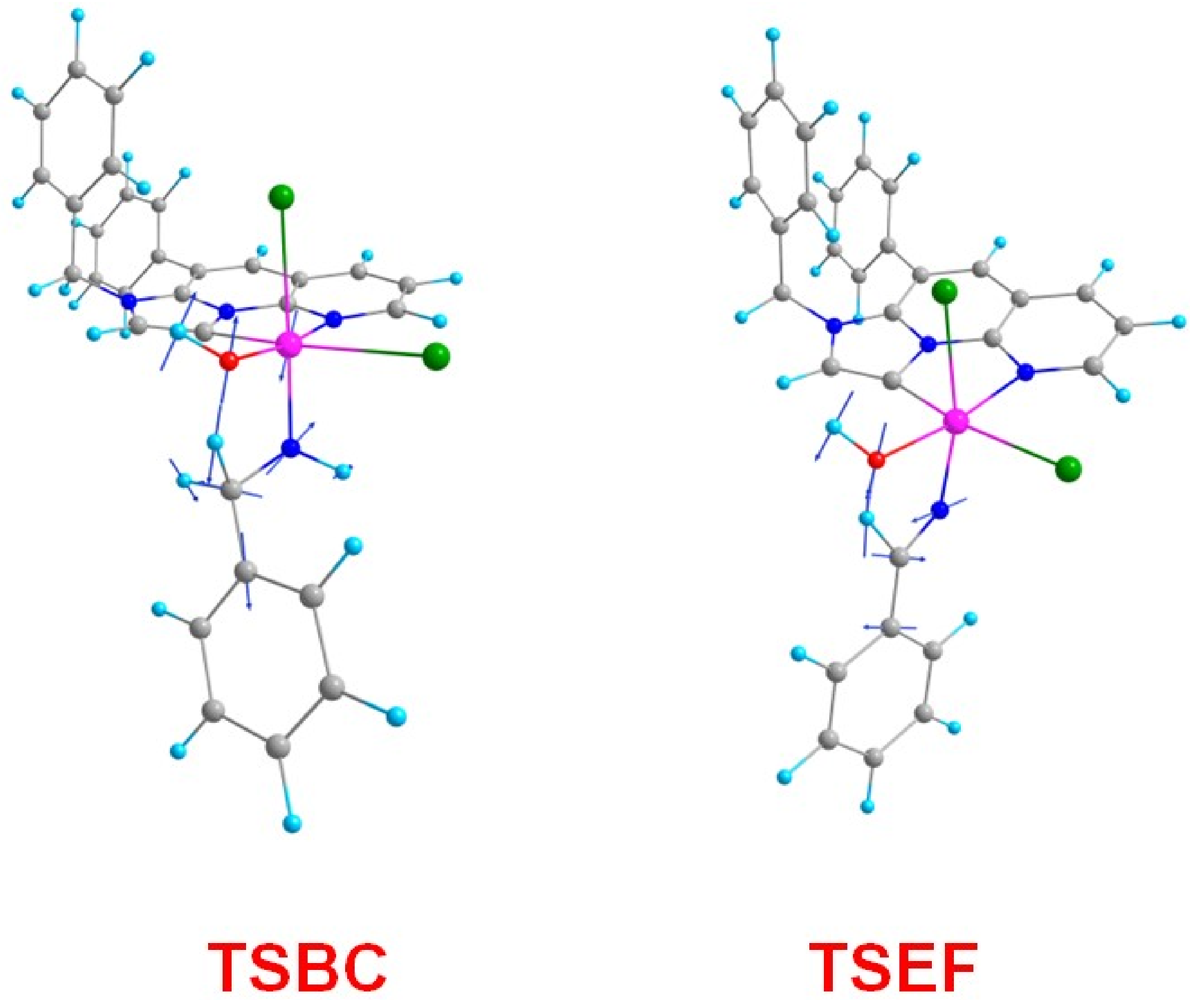

Figure S16. The unique imaginary mode for the transition states.

Table S3. Values of the unique imaginary frequencies (in cm^{-1}) in ^{t}BuOH for the transition states.

	Frequency (cm^{-1})
TSBC	-1250.0
TSEF	-1565.5

Table S4. Free energies (au) in ^{t}BuOH for all the chemical species.

	G(au)
1	-6598.110435
A	-6688.141807
B	-6688.15782
TSBC	-6688.144599
C	-6688.215018
D	-6686.949709
E	-6686.979191
TSEF	-6686.948235
F	-6687.02053
H_2O	-76.410056
$PhCH_2NH_2$	-326.58478
COD	-311.665014
O_2	-150.277613
PhCN	-324.210365

Table S5. Optimized cartesian coordinates of the computed structures

1				**A**			
Ru	-2.20379	-0.15984	0.195803	Ru	1.834138	-0.93913	-0.48383
Br	-1.00776	-0.9397	-2.01442	Br	0.052315	-2.69071	-1.08309
Br	-4.14641	0.775049	-1.35251	Br	3.529824	-2.57057	0.443753
N	0.521102	0.638583	0.65333	N	-0.60968	0.258436	0.63608
C	1.850297	0.392349	0.844148	C	-1.80841	0.877587	0.427347
N	1.924473	-0.9029	1.213551	N	-1.74294	1.377347	-0.82664

C	0.632058	-1.43397	1.219934	C	-0.50418	1.034593	-1.37358
H	0.497523	-2.48652	1.431974	H	-0.27898	1.263764	-2.4069
C	-0.28569	-0.48748	0.846736	C	0.225009	0.314276	-0.46813
C	2.810623	1.413476	0.579852	C	-2.82365	0.806818	1.426853
C	3.113137	-1.75355	1.175243	C	-2.87852	1.763363	-1.66509
H	2.790189	-2.72807	1.562683	H	-2.44279	2.111254	-2.60999
H	3.873792	-1.37144	1.864923	H	-3.40308	2.615817	-1.2199
C	5.032463	-2.12335	-0.39477	N	0.847982	-1.15148	1.68011
H	5.684439	-2.19135	0.476793	C	-2.55503	0.031254	2.529368
C	3.670168	-1.87689	-0.22172	H	-3.31462	-0.04756	3.306293
C	2.842015	-1.75674	-1.3404	C	-1.3229	-0.67375	2.704227
H	1.770163	-1.56986	-1.23755	C	1.109234	-1.9845	2.689556
C	5.565989	-2.24555	-1.67452	H	2.057437	-2.51626	2.62265
H	6.63101	-2.42905	-1.80044	C	-0.33631	-0.53447	1.720404
N	-1.27873	1.824022	-0.1121	C	0.220186	-2.18204	3.755104
C	2.331792	2.604299	0.09047	H	0.496673	-2.86734	4.55068
H	3.041452	3.403961	-0.11801	C	-0.99948	-1.53233	3.770741
C	0.942539	2.839089	-0.1539	H	-1.71375	-1.68828	4.576611
C	5.15025	1.331842	-0.26787	H	4.090561	0.209319	-0.79898
H	4.756098	1.489042	-1.27134	C	3.091069	1.947059	-0.35233
C	4.260843	1.222224	0.804783	H	2.355988	2.2607	0.399999
C	-3.6629	0.455403	1.714647	H	2.603608	1.995116	-1.33403
H	-3.90703	1.493748	1.485374	O	2.243729	-0.61774	-2.1611
C	-1.77944	2.946918	-0.63027	C	-3.82663	0.610367	-1.88572
H	-2.84534	2.919366	-0.85755	C	-3.3722	-0.71075	-1.88135
C	-2.44439	-2.33073	2.439658	C	-5.17985	0.874621	-2.09813
H	-1.74541	-3.10801	2.776861	C	-4.27185	-1.75486	-2.07685

H	-3.44086	-2.69738	2.724549	H	-2.31764	-0.95011	-1.72458
C	-4.8487	-0.48649	1.819296	C	-6.07571	-0.17056	-2.30344
H	-5.76679	0.104276	1.72355	H	-5.53842	1.904267	-2.07227
H	-4.86535	-0.91521	2.8333	C	-5.6233	-1.48851	-2.28799
C	-2.437	0.213123	2.353325	H	-3.90293	-2.77818	-2.06483
H	-1.82776	1.0872	2.603375	H	-7.13029	0.044551	-2.46276
C	-3.51608	-1.90084	0.15784	H	-6.32381	-2.30651	-2.44034
H	-3.52231	-2.21888	-0.88631	C	-4.11385	1.517933	1.297559
C	4.761391	0.976418	2.087893	C	-4.15224	2.911078	1.173394
H	4.071315	0.913112	2.929615	C	-5.31285	0.800955	1.338301
C	-2.38425	-2.21744	0.923129	C	-5.37197	3.575493	1.088102
H	-1.60476	-2.78754	0.413719	H	-3.21928	3.475079	1.162204
C	0.039431	1.807119	0.127195	C	-6.53183	1.4666	1.2554
C	-2.1379	-1.0178	3.175389	H	-5.27981	-0.28669	1.391436
H	-2.69359	-0.97194	4.12683	C	-6.56381	2.853262	1.129129
H	-1.07487	-0.99329	3.447544	H	-5.39295	4.659229	1.000058
C	-0.97947	4.065026	-0.90712	H	-7.45848	0.897614	1.273518
H	-1.44545	4.952629	-1.32421	H	-7.51703	3.372504	1.062303
C	0.382055	4.015844	-0.6836	C	4.308218	2.82691	-0.31365
H	1.024454	4.861645	-0.92042	C	5.154225	2.897699	-1.4245
C	4.74037	-2.11645	-2.79009	C	4.63792	3.548276	0.835137
H	5.158507	-2.2062	-3.79022	C	6.307897	3.673848	-1.38594
C	3.379199	-1.87288	-2.61925	H	4.89803	2.337728	-2.32508
H	2.720372	-1.77325	-3.4791	C	5.791112	4.32851	0.87667
C	-4.86721	-1.60605	0.761763	H	3.980337	3.500927	1.70364
H	-5.28157	-2.53327	1.193092	C	6.628349	4.39127	-0.23419
H	-5.53592	-1.31358	-0.05267	H	6.957499	3.722399	-2.25697

C	6.519318	1.193877	-0.06132	H	6.035878	4.889078	1.776255
H	7.201533	1.267204	-0.905	H	7.528761	5.000647	-0.20495
C	6.130475	0.836028	2.29268	N	3.403122	0.527778	-0.11189
H	6.512147	0.654187	3.294757	H	3.820941	0.384605	0.807717
C	7.011471	0.944804	1.217423				
H	8.081548	0.836325	1.378075				
B				**C**			
Ru	1.900065	-0.91423	-0.49764	Ru	1.750272	-1.0042	-0.32116
Br	0.184312	-2.88652	-0.24022	Br	0.1226	-3.02205	-0.1911
Br	3.916592	-2.34531	0.368247	Br	3.92344	-2.3532	0.451995
N	-0.50793	0.38882	0.30718	N	-0.57579	0.456887	0.257022
C	-1.75867	0.889264	0.090723	C	-1.82203	0.938441	-0.00157
N	-1.85862	1.042767	-1.24602	N	-1.95135	0.863194	-1.34495
C	-0.66307	0.609897	-1.83125	C	-0.77811	0.310377	-1.878
H	-0.57574	0.619607	-2.90987	H	-0.72178	0.12092	-2.9417
C	0.218103	0.168441	-0.87906	C	0.125422	0.012918	-0.88012
C	-2.66394	1.057004	1.183328	C	-2.66796	1.297355	1.089824
C	-3.09442	1.177555	-2.01566	C	-3.20258	0.910481	-2.09521
H	-2.78178	1.277021	-3.06254	H	-2.91966	0.832012	-3.15243
H	-3.60765	2.107173	-1.74459	H	-3.68396	1.886694	-1.96409
N	1.105147	-0.66515	1.550272	N	1.110381	-0.38906	1.520776
C	-2.23695	0.627808	2.416501	C	-2.17141	1.09661	2.359321
H	-2.90865	0.738138	3.266798	H	-2.79921	1.364919	3.20811
C	-0.95108	0.040866	2.628091	C	-0.87313	0.547312	2.615539
C	1.539224	-1.18078	2.695499	C	1.622162	-0.67471	2.727339
H	2.49975	-1.69761	2.634407	H	2.577013	-1.1977	2.715887
C	-0.08917	-0.06635	1.531941	C	-0.09096	0.220619	1.505726

C	0.77834	-1.09048	3.870301	C	0.945786	-0.34668	3.90789
H	1.166726	-1.52081	4.788116	H	1.407774	-0.59888	4.857735
C	-0.46532	-0.48835	3.838865	C	-0.3013	0.256106	3.868466
H	-1.08371	-0.43635	4.732957	H	-0.84485	0.485362	4.782404
N	3.000657	0.540015	-0.07545	N	3.099259	0.504743	-0.5039
H	3.911993	0.264594	0.309948	H	4.050405	0.131681	-0.40389
O	2.264749	-1.39444	-2.29554	C	3.013375	1.779721	-0.6472
H	1.606088	-1.01937	-2.8966	H	2.007181	2.196076	-0.7678
C	-4.0106	-0.00624	-1.82543	H	1.628494	-2.61612	-2.27823
C	-3.51327	-1.27185	-1.5046	C	-4.14635	-0.19799	-1.69845
C	-5.38563	0.176893	-1.97245	C	-3.67399	-1.41111	-1.19162
C	-4.39024	-2.33815	-1.32322	C	-5.51931	-0.00355	-1.85197
H	-2.44196	-1.44652	-1.38532	C	-4.57293	-2.41315	-0.83625
C	-6.25955	-0.89231	-1.80132	H	-2.60401	-1.59344	-1.06893
H	-5.77605	1.171556	-2.19048	C	-6.41569	-1.00916	-1.5031
C	-5.76319	-2.15198	-1.47139	H	-5.891	0.951159	-2.22579
H	-3.98774	-3.31526	-1.06561	C	-5.94385	-2.21554	-0.98973
H	-7.33087	-0.73821	-1.91125	H	-4.18964	-3.35125	-0.44077
H	-6.44579	-2.98645	-1.32826	H	-7.48486	-0.84447	-1.61933
C	-4.01043	1.648271	1.021101	H	-6.64304	-3.00043	-0.71019
C	-4.16834	2.955252	0.547219	C	-4.02845	1.845305	0.894476
C	-5.13972	0.914077	1.39527	C	-4.22916	3.045501	0.204854
C	-5.43799	3.51475	0.442079	C	-5.12962	1.179003	1.440846
H	-3.28776	3.539216	0.278014	C	-5.51172	3.564993	0.05561
C	-6.40806	1.47586	1.292233	H	-3.36985	3.581903	-0.19825
H	-5.01758	-0.11573	1.729632	C	-6.41095	1.699989	1.292448
C	-6.55968	2.775245	0.814262	H	-4.97644	0.229228	1.951727

H	-5.55157	4.533706	0.079282	C	-6.60511	2.891379	0.598005
H	-7.28096	0.891281	1.573309	H	-5.65667	4.503805	-0.4742
H	-7.55139	3.213785	0.731825	H	-7.26124	1.165944	1.710262
C	3.821623	2.838302	-0.24788	H	-7.60692	3.298154	0.481172
C	4.571469	2.583379	-1.40007	C	4.124551	2.726459	-0.67476
C	4.128481	3.956355	0.529049	C	5.444903	2.358906	-0.37246
C	5.607051	3.437932	-1.76625	C	3.855881	4.058579	-1.01764
H	4.344022	1.702949	-2.00009	C	6.462978	3.300469	-0.42561
C	5.159164	4.816363	0.158684	H	5.680455	1.336006	-0.08094
H	3.557029	4.152447	1.436462	C	4.877211	4.999761	-1.0724
C	5.902069	4.557468	-0.99042	H	2.831494	4.348409	-1.24954
H	6.189432	3.225134	-2.65999	C	6.184966	4.622372	-0.77722
H	5.389723	5.683488	0.773873	H	7.481626	3.004703	-0.1861
H	6.714052	5.22188	-1.2773	H	4.653008	6.028516	-1.34473
C	2.679665	1.931627	0.136963	H	6.987	5.355635	-0.81691
H	2.423788	2.111007	1.198592	O	2.306931	-1.91641	-2.27609
H	1.784001	2.176892	-0.45239	H	3.116449	-2.36383	-1.96018
D				**E**			
Ru	1.850264	-0.87435	-0.54103	Ru	1.860702	-1.15817	-0.6899
Br	0.095459	-2.66688	-1.19151	Br	0.696553	-2.55298	1.165273
Br	3.59728	-2.47469	0.344232	Br	4.222272	-1.85453	0.223961
N	-0.60878	0.23497	0.641724	N	-0.51593	0.382654	-0.33282
C	-1.80994	0.857756	0.46663	C	-1.83817	0.65101	-0.53866
N	-1.75644	1.408583	-0.76664	N	-2.19988	-0.12602	-1.58318
C	-0.51977	1.092513	-1.33578	C	-1.0934	-0.88235	-1.98395
H	-0.30294	1.356008	-2.36268	H	-1.19073	-1.61525	-2.77352
C	0.215552	0.338787	-0.46558	C	-0.01211	-0.58762	-1.20292

C	-2.81949	0.743431	1.468685	C	-2.53274	1.524923	0.353553
C	-2.90208	1.808795	-1.58501	C	-3.56159	-0.44537	-2.00487
H	-2.47626	2.180852	-2.52523	H	-3.45432	-1.0715	-2.89914
H	-3.42737	2.647869	-1.11586	H	-4.0833	0.468396	-2.3123
N	0.859716	-1.21048	1.622359	N	1.421556	0.339525	0.888056
C	-2.54351	-0.07945	2.533947	C	-1.83505	1.982856	1.445464
H	-3.29774	-0.19312	3.311822	H	-2.34459	2.639558	2.149326
C	-1.30867	-0.78749	2.670881	C	-0.47354	1.62758	1.701141
C	1.127446	-2.08605	2.590568	C	2.094604	0.629779	1.996437
H	2.078579	-2.60798	2.498074	H	3.069441	0.1503	2.09197
C	-0.32619	-0.60174	1.691154	C	0.181117	0.821493	0.763618
C	0.242401	-2.33576	3.64958	C	1.555648	1.459817	2.988242
H	0.52409	-3.05475	4.412869	H	2.145835	1.681421	3.872028
C	-0.97844	-1.69134	3.697554	C	0.27847	1.966843	2.8412
H	-1.68932	-1.88429	4.49848	H	-0.16415	2.598845	3.608614
N	3.239441	0.580923	-0.04703	N	2.701656	0.150936	-1.6291
H	3.954161	0.285777	0.621335	O	1.779879	-2.6443	-1.88042
C	3.409623	1.718326	-0.61164	H	2.535501	-3.21482	-1.66207
H	2.663426	2.007052	-1.35791	C	-4.34553	-1.15733	-0.93099
C	-3.84573	0.65632	-1.82527	C	-3.71721	-1.92914	0.049036
C	-3.3822	-0.66094	-1.87215	C	-5.73606	-1.04388	-0.93261
C	-5.2043	0.91754	-2.00367	C	-4.47948	-2.57094	1.021938
C	-4.27859	-1.70466	-2.08441	H	-2.63151	-2.03904	0.066333
H	-2.32309	-0.89739	-1.74364	C	-6.49618	-1.69264	0.034914
C	-6.097	-0.12667	-2.22691	H	-6.2237	-0.41994	-1.68226
H	-5.56891	1.943195	-1.93632	C	-5.86773	-2.45457	1.018188
C	-5.63563	-1.441	-2.26208	H	-3.97956	-3.16623	1.782253

H	-3.90264	-2.72507	-2.11216	H	-7.57937	-1.5926	0.028651
H	-7.15579	0.085841	-2.35961	H	-6.4588	-2.95762	1.779993
H	-6.33336	-2.2588	-2.42772	C	-3.94482	1.913917	0.148671
C	-4.10857	1.461952	1.379135	C	-4.88997	1.644894	1.143233
C	-4.14276	2.858433	1.298791	C	-4.34232	2.593256	-1.00801
C	-5.31032	0.749167	1.416573	C	-6.21321	2.041267	0.980297
C	-5.3605	3.530291	1.253625	H	-4.58791	1.087407	2.029134
H	-3.20754	3.418686	1.29057	C	-5.66666	2.988984	-1.16954
C	-6.52734	1.422224	1.374659	H	-3.60231	2.830009	-1.77285
H	-5.2818	-0.33976	1.434361	C	-6.60439	2.712211	-0.17573
C	-6.55494	2.812279	1.29202	H	-6.94327	1.813778	1.753508
H	-5.37772	4.616288	1.199176	H	-5.96454	3.525752	-2.06734
H	-7.45626	0.856879	1.390615	H	-7.63903	3.021799	-0.30303
H	-7.50655	3.337574	1.257293	C	3.778141	2.287679	-1.14489
C	4.498601	2.661944	-0.3641	C	3.731861	3.609963	-1.59735
C	5.593971	2.35596	0.455872	C	4.32228	2.002575	0.111762
C	4.440418	3.91992	-0.97667	C	4.180208	4.644721	-0.78208
C	6.596124	3.29299	0.664145	H	3.333717	3.824706	-2.5887
H	5.677128	1.375132	0.921494	C	4.776106	3.039574	0.919341
C	5.443531	4.859285	-0.76598	H	4.423154	0.958899	0.41296
H	3.596087	4.154428	-1.62358	C	4.696493	4.361311	0.481219
C	6.522155	4.547998	0.057815	H	4.133071	5.672638	-1.13471
H	7.444914	3.043503	1.296306	H	5.211916	2.813623	1.890933
H	5.38515	5.833127	-1.24621	H	5.054591	5.16893	1.115913
H	7.310338	5.278884	0.222751	C	3.28452	1.201688	-2.01234
O	2.159405	-0.45961	-2.21642	H	3.443451	1.312493	-3.09648
F				**TSBC**			

Ru	1.642494	-0.80294	-0.28815	Ru	1.763937	-0.51753	-0.24542
Br	0.18938	-2.90386	-0.0459	Br	0.18539	-2.09278	-1.61977
Br	3.861015	-2.01569	0.58981	Br	3.729814	-2.26694	-0.0177
N	-0.77613	0.531932	0.226305	N	-0.78121	0.18051	0.768583
C	-2.03498	0.967138	-0.053	C	-2.01878	0.745657	0.692885
N	-2.15688	0.836779	-1.39228	N	-1.94082	1.650769	-0.3067
C	-0.9653	0.300978	-1.90102	C	-0.64906	1.60001	-0.84708
H	-0.896	0.084201	-2.95854	H	-0.41324	2.220698	-1.70231
C	-0.05587	0.078394	-0.89202	C	0.113366	0.658747	-0.20686
C	-2.89457	1.34812	1.020686	C	-3.07251	0.270365	1.532292
C	-3.3974	0.866391	-2.1589	C	-3.06484	2.236409	-1.03721
H	-3.10132	0.754299	-3.20944	H	-2.61773	2.926294	-1.76394
H	-3.87309	1.849633	-2.06315	H	-3.68223	2.839456	-0.36185
N	0.948672	-0.16363	1.530568	N	0.736167	-1.41437	1.420425
C	-2.39919	1.210034	2.298455	C	-2.78255	-0.79465	2.350881
H	-3.03696	1.495231	3.134217	H	-3.56841	-1.18094	2.998637
C	-1.08425	0.714523	2.578568	C	-1.49705	-1.41929	2.385186
C	1.46698	-0.37876	2.747054	C	1.043167	-2.50242	2.122436
H	2.449596	-0.84788	2.758122	H	2.037737	-2.91026	1.928533
C	-0.28432	0.37572	1.485616	C	-0.49361	-0.89922	1.564495
C	0.766972	-0.04155	3.912318	C	0.128131	-3.08246	3.013918
H	1.235176	-0.23347	4.873163	H	0.422766	-3.96565	3.572084
C	-0.50502	0.501421	3.844064	C	-1.13957	-2.55081	3.144399
H	-1.06226	0.745335	4.745992	H	-1.87167	-3.00448	3.809754
N	2.891691	0.732846	-0.56792	N	3.048909	0.659108	0.504801
H	1.695366	-2.51629	-2.16725	H	3.870281	0.189332	0.909254
C	-4.35759	-0.22141	-1.74631	C	3.337466	1.867057	-0.12303

C	-3.90712	-1.42318	-1.19516	H	2.509944	2.590097	-0.07552
C	-5.72533	-0.02036	-1.93462	H	3.152697	1.395107	-1.26878
C	-4.82251	-2.40749	-0.83118	O	2.520937	0.273369	-1.94914
H	-2.84118	-1.60462	-1.04413	H	1.801877	0.598158	-2.50833
C	-6.63797	-1.00797	-1.57716	C	-3.90322	1.184904	-1.72197
H	-6.0806	0.926325	-2.34301	C	-3.35209	-0.03417	-2.12392
C	-6.18787	-2.20321	-1.02038	C	-5.25386	1.442843	-1.95772
H	-4.45935	-3.33818	-0.40145	C	-4.15208	-0.98722	-2.74849
H	-7.70286	-0.8376	-1.72101	H	-2.29742	-0.26295	-1.95617
H	-6.8996	-2.97423	-0.73408	C	-6.04982	0.492265	-2.59002
C	-4.26205	1.867545	0.797206	H	-5.69115	2.382551	-1.61834
C	-5.35913	1.203176	1.353335	C	-5.5005	-0.72676	-2.9833
C	-4.47198	3.045744	0.072739	H	-3.70841	-1.93337	-3.05051
C	-6.64577	1.703111	1.179318	H	-7.10363	0.699062	-2.76433
H	-5.19788	0.271804	1.894562	H	-6.1232	-1.47292	-3.47155
C	-5.75951	3.544825	-0.10099	C	-4.43044	0.856696	1.523976
H	-3.61614	3.582078	-0.33783	C	-4.6417	2.197203	1.86398
C	-6.84899	2.872173	0.450248	C	-5.52775	0.045274	1.220983
H	-7.49285	1.170403	1.605317	C	-5.93228	2.717042	1.895687
H	-5.9116	4.466771	-0.65775	H	-3.79008	2.825759	2.125689
H	-7.8548	3.262857	0.314364	C	-6.81716	0.565742	1.255241
O	2.301955	-1.75491	-2.18672	H	-5.3575	-0.98771	0.919726
H	3.142741	-2.1048	-1.82898	C	-7.02151	1.901943	1.591228
C	3.805951	1.445221	-0.6797	H	-6.08954	3.757644	2.169969
C	5.026895	2.173387	-0.75415	H	-7.66251	-0.07069	1.004462
C	5.068871	3.503562	-1.19252	H	-8.02933	2.309525	1.618012
C	6.203621	1.512969	-0.36611	C	4.696245	2.43509	0.048777

C	6.287096	4.168962	-1.24296	C	5.812987	1.60679	-0.12859
H	4.149139	4.00101	-1.49057	C	4.892335	3.787513	0.34276
C	7.414115	2.19062	-0.42657	C	7.097115	2.119311	0.015776
H	6.141024	0.48027	-0.02617	H	5.666609	0.560359	-0.40344
C	7.45796	3.515007	-0.86142	C	6.178743	4.300978	0.479888
H	6.324217	5.201244	-1.5821	H	4.027606	4.437862	0.473145
H	8.328553	1.682828	-0.13013	C	7.283745	3.466779	0.321763
H	8.409534	4.039814	-0.90416	H	7.95605	1.467304	-0.12492
				H	6.319942	5.353933	0.714539
				H	8.288887	3.868459	0.429072
TSEF							
Ru	1.816308	-0.66753	-0.24184				
Br	0.254779	-2.26341	-1.5559				
Br	3.708236	-2.4349	0.039737				
N	-0.7147	0.14906	0.729068				
C	-1.93516	0.751594	0.643268				
N	-1.84553	1.584462	-0.41473				
C	-0.56749	1.455319	-0.97462				
H	-0.32515	2.018237	-1.86671				
C	0.17571	0.533928	-0.28403				
C	-2.98006	0.367012	1.537311				
C	-2.96142	2.183951	-1.14354				
H	-2.50696	2.826172	-1.90817				
H	-3.53838	2.835338	-0.47695				
N	0.78415	-1.41294	1.473726				
C	-2.70062	-0.64403	2.425476				
H	-3.48166	-0.95917	3.116077				

C	-1.42914	-1.2974	2.481746				
C	1.09172	-2.44311	2.262373				
H	2.078219	-2.87763	2.086763				
C	-0.43576	-0.86891	1.596834				
C	0.185577	-2.92839	3.215274				
H	0.478726	-3.76492	3.841872				
C	-1.07246	-2.36638	3.32504				
H	-1.7958	-2.74989	4.042191				
N	2.953248	0.726547	0.26269				
O	2.589034	-0.07894	-2.03819				
H	1.867253	0.158491	-2.63666				
C	-3.8595	1.140653	-1.76264				
C	-3.37899	-0.12626	-2.10239				
C	-5.19893	1.454755	-1.99589				
C	-4.23753	-1.06967	-2.66071				
H	-2.33505	-0.39867	-1.93512				
C	-6.05287	0.513727	-2.56273				
H	-5.58282	2.432183	-1.70143				
C	-5.57427	-0.7531	-2.89251				
H	-3.84975	-2.05379	-2.914				
H	-7.09729	0.765416	-2.73436				
H	-6.24301	-1.492	-3.32805				
C	-4.31879	0.996852	1.514498				
C	-5.44762	0.213929	1.255989				
C	-4.47753	2.359148	1.790716				
C	-6.7161	0.785261	1.267153				
H	-5.3198	-0.83984	1.010966				

C	-5.74716	2.928969	1.801672				
H	-3.60148	2.967085	2.018209				
C	-6.86806	2.142814	1.538229				
H	-7.58598	0.170091	1.049302				
H	-5.86299	3.986717	2.026617				
H	-7.85943	2.589681	1.547166				
C	4.718964	2.438105	-0.11687				
C	5.37143	3.094264	-1.16563				
C	5.086137	2.714614	1.208376				
C	6.376504	4.016619	-0.89624				
H	5.088681	2.866391	-2.19167				
C	6.086294	3.639785	1.471502				
H	4.580251	2.191793	2.017314				
C	6.734058	4.292512	0.421444				
H	6.88403	4.51909	-1.71633				
H	6.369287	3.850862	2.500346				
H	7.520046	5.014142	0.632077				
C	3.671271	1.476545	-0.41225				
H	3.314358	1.039162	-1.54353				

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