Electronic Supplementary Information (ESI)

Phosphine-free ruthenium-arene complex for low temperature one-pot catalytic conversion of aldehydes to primary amides in water

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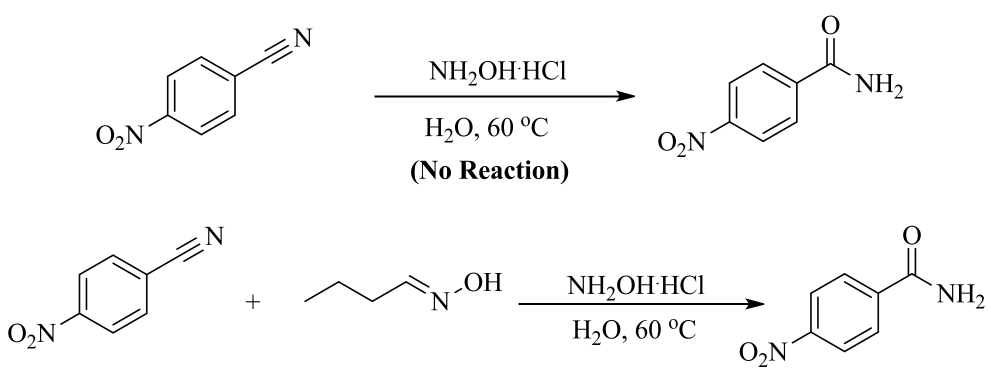
Catalytic hydration of 4-Nitrobenzonitrile in water in the presence of [Ru]-2a: 4-Nitrobenzonitrile (0.148g, 1 mmol), [Ru]-2a (0.017 g, 5 mol%) and water (8 ml) were taken into a 25 ml round bottom flask. The reaction mixture was heated at 60 °C for 5 h. But no conversion to amide was observed from the ^{1}H NMR spectrum of the reaction mixture.

Catalytic hydration of 4-Nitrobenzonitrile with the aid of butylaldoxime in water in the presence of [Ru]-2a: To a 25 ml round bottom flask added butyraldehyde (2 mmol), $NH_2OH{\cdot}HCl$ (0.090 g, 1.3 mmol), $NaHCO_3$ (0.109 g, 1.3 mmol) with 3 ml of water, and stirred the solution for 1 hour to get the butyraldoxime. Then to this butylaldoxime added 4-Nitrobenzonitrile (0.148 g, 1 mmol), with [Ru]-2a (5 mol%) and water (5 ml). The reaction mixture was heated at 60 °C for 24 h. After this time the reaction mixture was extracted with dichloromethane. The organic layer was dried with sodium sulfate, evaporated the solvent under reduced pressure which led to give the 37% conversion to 4-nitrobenzamide.



Scheme S1

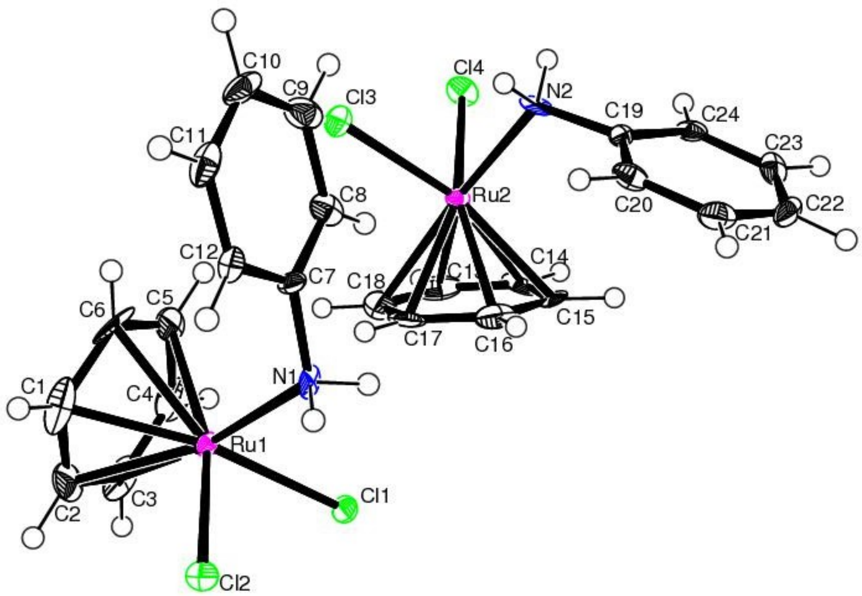


Figure S1. ORPET diagram of complex [Ru]-2a

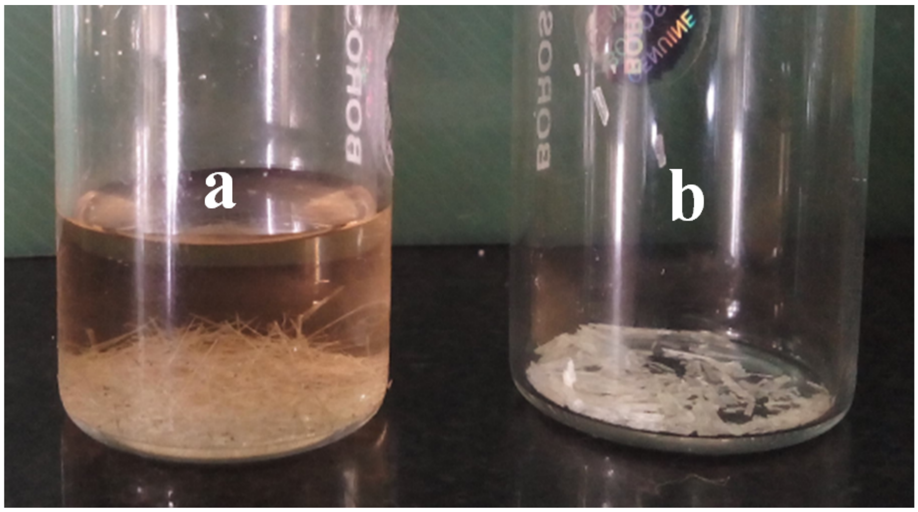


Figure S2. Catalytic conversion of 3-chlorobenzaldehyde to 3-chlorobenzamide. a) 3-chlorobenzamide crystal appears after cooling of the reaction mixture at 0 °C. b) After isolation of the 3-chlorobenzamide crystal from the reaction mixture.

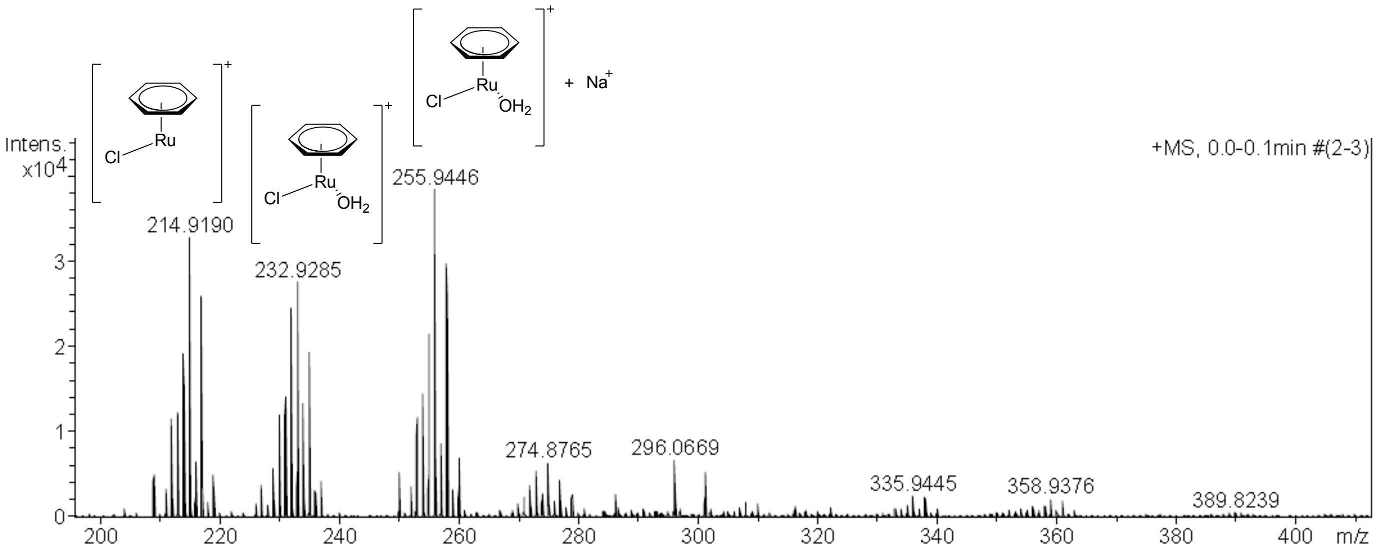


Figure S3. Mass spectra for the recovered **[Ru]-2a** catalyst.

Table S1: Selected bond lengths of complex [Ru]-2a.

Bond lengths [Å]	
Ru(1)-C(6)	2.159(8)
Ru(1)-N(1)	2.162(7)
Ru(1)-C(4)	2.169(9)
Ru(1)-C(2)	2.172(8)
Ru(1)-C(1)	2.173(7)
Ru(1)-C(5)	2.183(9)
Ru(1)-C(3)	2.199(8)
Ru(1)-Cl(1)	2.4242(15)
Ru(1)-Cl(2)	2.4329(18)
Ru(2)-N(2)	2.154(7)
Ru(2)-C(17)	2.173(8)
Ru(2)-C(16)	2.177(9)
Ru(2)-C(14)	2.178(7)
Ru(2)-C(18)	2.178(8)
Ru(2)-C(13)	2.180(8)
Ru(2)-C(15)	2.183(8)
Ru(2)-Cl(4)	2.4323(18)
Ru(2)-Cl(3)	2.4337(17)
N(1)-C(7)	1.448(9)
N(1)-H(1A)	0.9200
N(1)-H(1B)	0.9200
N(2)-C(19)	1.418(10)
N(2)-H(2A)	0.9200
N(2)-H(2B)	0.9200
C(1)-C(2)	1.386(14)
C(1)-C(6)	1.451(15)
C(2)-C(3)	1.400(14)
C(3)-C(4)	1.415(14)
C(4)-C(5)	1.377(15)
C(5)-C(6)	1.413(15)
C(7)-C(12)	1.381(11)
C(7)-C(8)	1.392(12)
C(8)-C(9)	1.394(12)
C(9)-C(10)	1.402(14)
C(10)-C(11)	1.372(14)
C(11)-C(12)	1.356(11)
C(13)-C(14)	1.384(16)
C(13)-C(18)	1.409(15)

Table S2: Selected bond angles of complex [Ru]-2a.

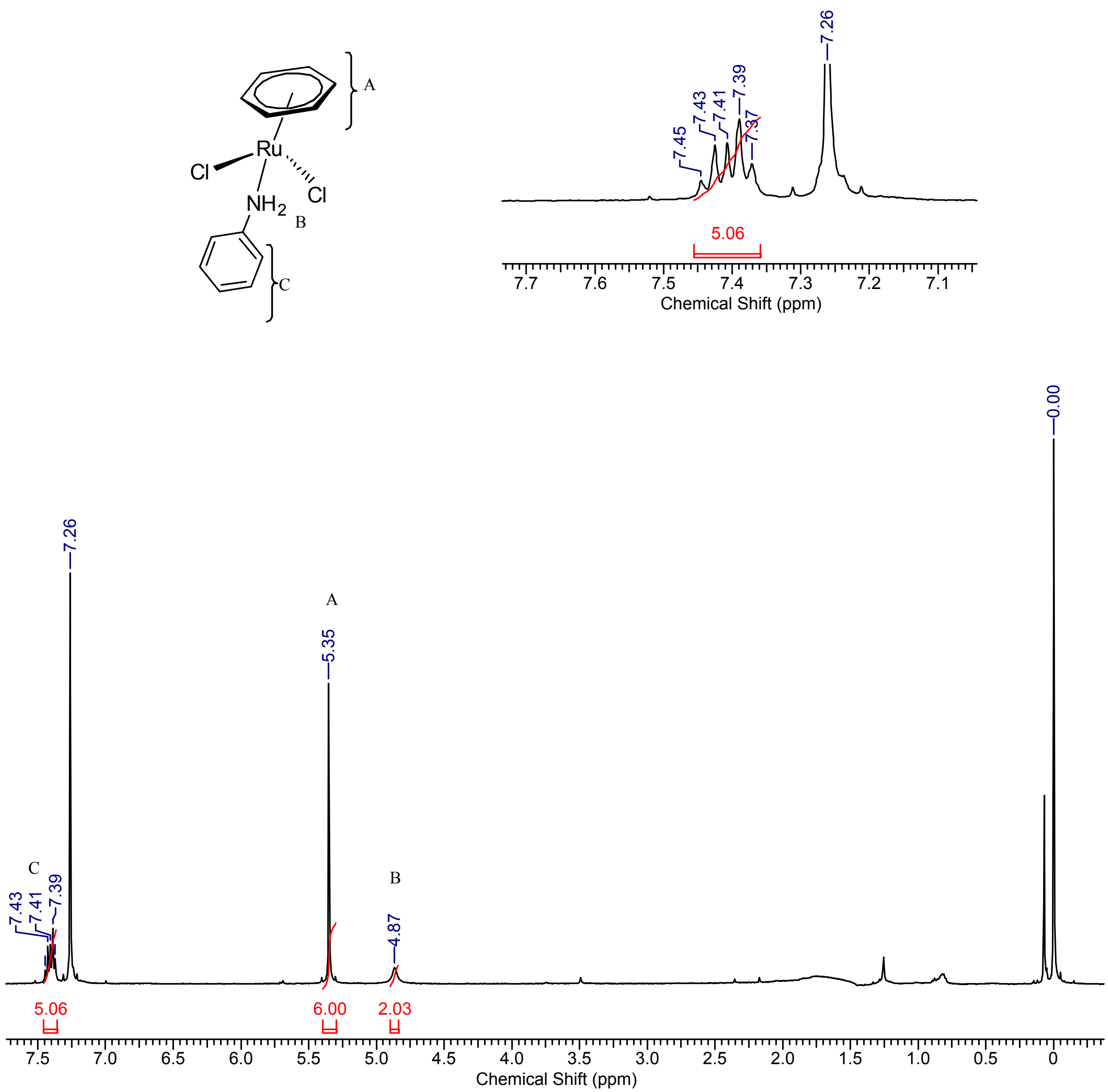
Bond angles [°]

C(6)-Ru(1)-N(1)	94.1(3)	C(5)-C(4)-C(3)	122.8(9)
C(6)-Ru(1)-C(4)	67.4(4)	C(5)-C(4)-Ru(1)	72.1(5)
N(1)-Ru(1)-C(4)	129.1(3)	C(3)-C(4)-Ru(1)	72.2(5)
C(6)-Ru(1)-C(2)	68.7(4)	C(4)-C(5)-C(6)	118.9(9)
N(1)-Ru(1)-C(2)	150.6(3)	C(4)-C(5)-Ru(1)	71.0(5)
C(4)-Ru(1)-C(2)	67.6(4)	C(6)-C(5)-Ru(1)	70.1(5)
C(6)-Ru(1)-C(1)	39.1(4)	C(5)-C(6)-C(1)	119.6(8)
N(1)-Ru(1)-C(1)	115.5(3)	C(5)-C(6)-Ru(1)	71.9(5)
C(4)-Ru(1)-C(1)	80.2(3)	C(1)-C(6)-Ru(1)	71.0(5)
C(2)-Ru(1)-C(1)	37.2(4)	C(12)-C(7)-C(8)	121.0(7)
C(6)-Ru(1)-C(5)	38.0(4)	C(12)-C(7)-N(1)	119.1(7)
N(1)-Ru(1)-C(5)	100.6(3)	C(8)-C(7)-N(1)	119.9(7)
C(4)-Ru(1)-C(5)	36.9(4)	C(7)-C(8)-C(9)	117.9(8)
C(2)-Ru(1)-C(5)	80.7(4)	C(8)-C(9)-C(10)	120.3(9)
C(1)-Ru(1)-C(5)	69.3(4)	C(11)-C(10)-C(9)	119.8(8)
C(6)-Ru(1)-C(3)	80.8(3)	C(12)-C(11)-C(10)	120.4(8)
N(1)-Ru(1)-C(3)	166.9(3)	C(11)-C(12)-C(7)	120.5(8)
C(4)-Ru(1)-C(3)	37.8(4)	C(14)-C(13)-C(18)	119.9(9)
C(2)-Ru(1)-C(3)	37.4(4)	C(14)-C(13)-Ru(2)	71.4(5)
C(1)-Ru(1)-C(3)	67.7(3)	C(18)-C(13)-Ru(2)	71.1(5)
C(5)-Ru(1)-C(3)	68.0(4)	C(13)-C(14)-C(15)	120.8(8)
C(6)-Ru(1)-Cl(1)	146.1(3)	C(13)-C(14)-Ru(2)	71.6(5)
N(1)-Ru(1)-Cl(1)	82.26(15)	C(15)-C(14)-Ru(2)	71.2(4)
C(4)-Ru(1)-Cl(1)	88.8(2)	C(16)-C(15)-C(14)	119.6(8)
C(2)-Ru(1)-Cl(1)	125.4(3)	C(16)-C(15)-Ru(2)	70.9(5)
C(1)-Ru(1)-Cl(1)	162.3(3)	C(14)-C(15)-Ru(2)	70.9(5)
C(5)-Ru(1)-Cl(1)	109.3(3)	C(17)-C(16)-C(15	119.2(9)
C(3)-Ru(1)-Cl(1)	95.1(2)	C(17)-C(16)-Ru(2)	71.1(5)

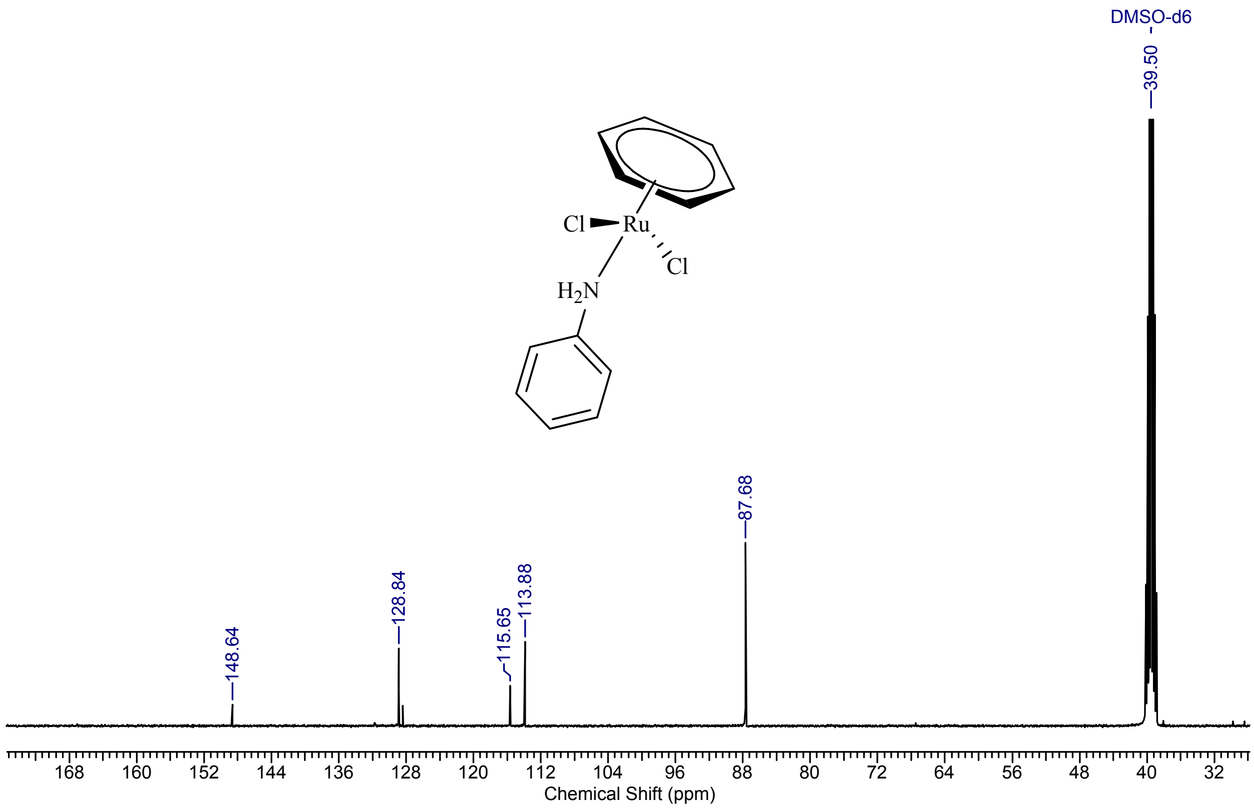
C(6)-Ru(1)-Cl(2)	124.9(3)	C(15)-C(16)-Ru(2)	71.3(5)
N(1)-Ru(1)-Cl(2)	82.99(18)	C(16)-C(17)-C(18)	120.8(8)
C(4)-Ru(1)-Cl(2)	147.0(3)	C(16)-C(17)-Ru(2)	71.3(5)
C(2)-Ru(1)-Cl(2)	87.7(3)	C(18)-C(17)-Ru(2)	71.3(5)
C(1)-Ru(1)-Cl(2)	93.4(2)	C(18)-C(17)- 17)	119.6
C(5)-Ru(1)-Cl(2)	162.3(3)	C(17)-C(18)-C(1)	119.6(8)
C(3)-Ru(1)-Cl(2)	109.9(3)	C(17)-C(18)-Ru(2)	70.9(5)
Cl(1)-Ru(1)-Cl(2)	88.35(6)	C(13)-C(18)-Ru(2)	71.2(5)
N(2)-Ru(2)-C(17)	124.9(3)	C(20)-C(19)-C(24)	120.4(7)
N(2)-Ru(2)-C(16)	97.4(3)	C(20)-C(19)-N(2)	120.5(7)
C(17)-Ru(2)-C(16)	37.6(4)	C(24)-C(19)-N(2)	118.9(7)
N(2)-Ru(2)-C(14)	117.6(3)	C(19)-C(20)-C(21)	119.4(8)
C(17)-Ru(2)-C(14)	80.0(3)	C(20)-C(21)-C(22)	119.9(8)
C(16)-Ru(2)-C(14)	68.3(4)	C(23)-C(22)-C(21)	119.5(8)
N(2)-Ru(2)-C(18)	162.6(3)	C(22)-C(23)-C(24)	120.4(8)
C(17)-Ru(2)-C(18)	37.8(4)	C(23)-C(24)-C(19)	120.2(8)
C(16)-Ru(2)-C(18)	68.3(4)	C(3)-C(2)-Ru(1)	72.4(5)
C(14)-Ru(2)-C(18)	67.4(3)	C(2)-C(3)-C(4)	118.0(8)
N(2)-Ru(2)-C(13)	153.4(3)	C(2)-C(3)-Ru(1)	70.3(5)
C(17)-Ru(2)-C(13)	68.0(4)	C(16)-Ru(2)-Cl(4)	158.6(3)
C(16)-Ru(2)-C(13)	80.8(4)	C(14)-Ru(2)-Cl(4)	92.3(3)
C(14)-Ru(2)-C(13)	37.0(4)	C(18)-Ru(2)-Cl(4)	113.4(3)
C(18)-Ru(2)-C(13)	37.7(4)	C(13)-Ru(2)-Cl(4)	88.8(3)
N(2)-Ru(2)-C(15)	94.4(3)	C(15)-Ru(2)-Cl(4)	120.9(3)
C(17)-Ru(2)-C(15)	67.7(3)	N(2)-Ru(2)-Cl(3)	82.64(17)
C(16)-Ru(2)-C(15)	37.8(4)	C(17)-Ru(2)-Cl(3)	89.5(2)
C(14)-Ru(2)-C(15)	37.9(4)	C(16)-Ru(2)-Cl(3)	112.7(3)
C(18)-Ru(2)-C(15)	80.3(3)	C(14)-Ru(2)-Cl(3)	159.7(3)
C(13)-Ru(2)-C(15)	67.8(4)	C(18)-Ru(2)-Cl(3)	93.6(2)
N(2)-Ru(2)-Cl(4)	83.6(2)	C(13)-Ru(2)-Cl(3)	122.8(3)
C(17)-Ru(2)-Cl(4)	150.9(3)	C(15)-Ru(2)-Cl(3)	150.0(3)

Cl(4)-Ru(2)-Cl(3)	88.61(6)	C(19)-N(2)-H(2B)	107.9
C(7)-N(1)-Ru(1)	117.7(4)	Ru(2)-N(2)-H(2B)	107.9
C(7)-N(1)-H(1A)	107.9	H(2A)-N(2)-H(2B)	107.2
Ru(1)-N(1)-H(1A)	107.9	C(2)-C(1)-C(6)	118.9(8)
C(7)-N(1)-H(1B)	107.9	C(2)-C(1)-Ru(1)	71.3(5)
Ru(1)-N(1)-H(1B)	107.9	C(6)-C(1)-Ru(1)	69.9(4)
H(1A)-N(1)-H(1B)	107.2	C(1)-C(2)-C(3)	121.8(9)
C(19)-N(2)-Ru(2)	117.8(5)	C(1)-C(2)-Ru(1)	71.5(5)
C(19)-N(2)-H(2A)	107.9	C(4)-C(3)-Ru(1)	70.0(5
Ru(2)-N(2)-H(2A)	107.9		

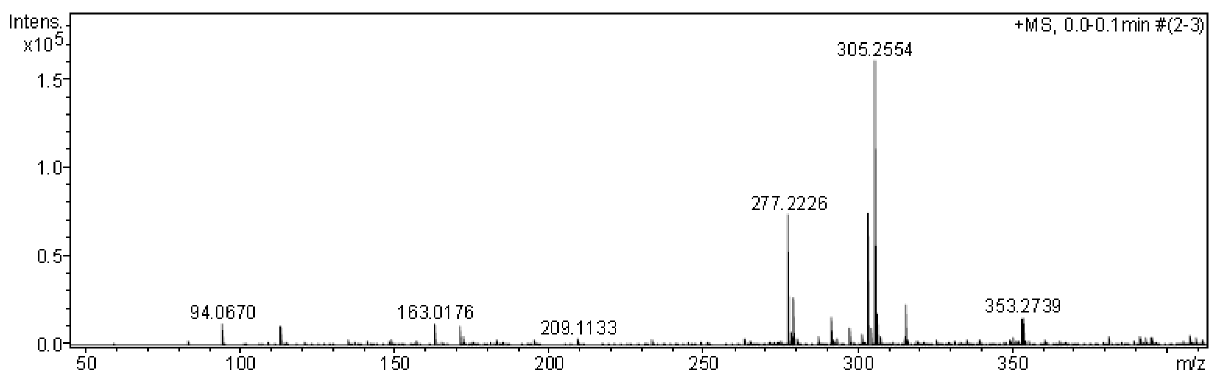
Spectra of ruthenium-arene complexes [(η^6-arene)$RuCl_2(C_6H_5NH_2)$] (η^6-arene = C_6H_6 ([Ru]-2a) and $C_{10}H_{14}$ ([Ru]-2b)):



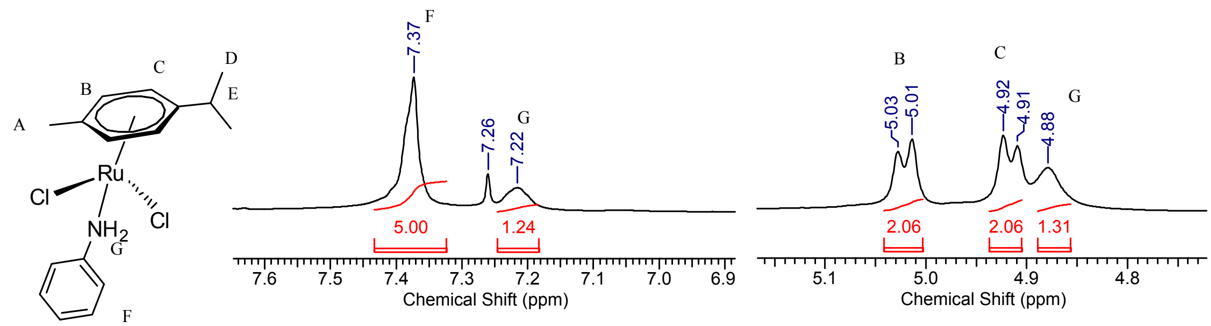
^{1}H NMR of complex [Ru]-2a

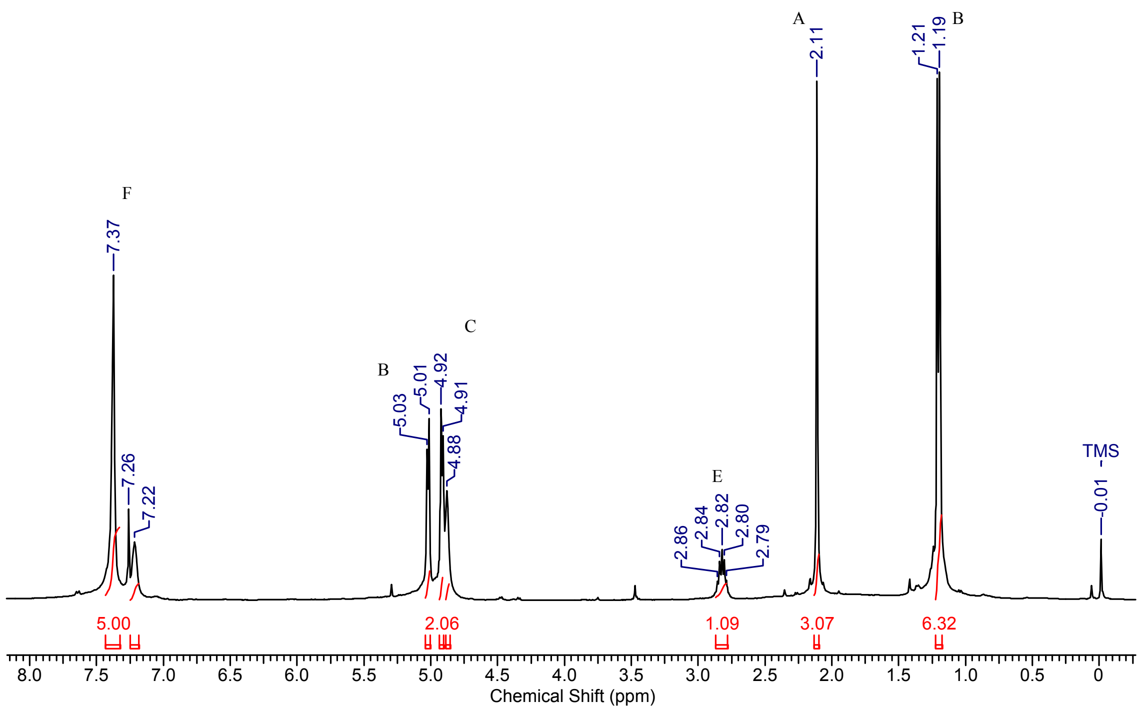


^{13}C NMR of complex [Ru]-2a

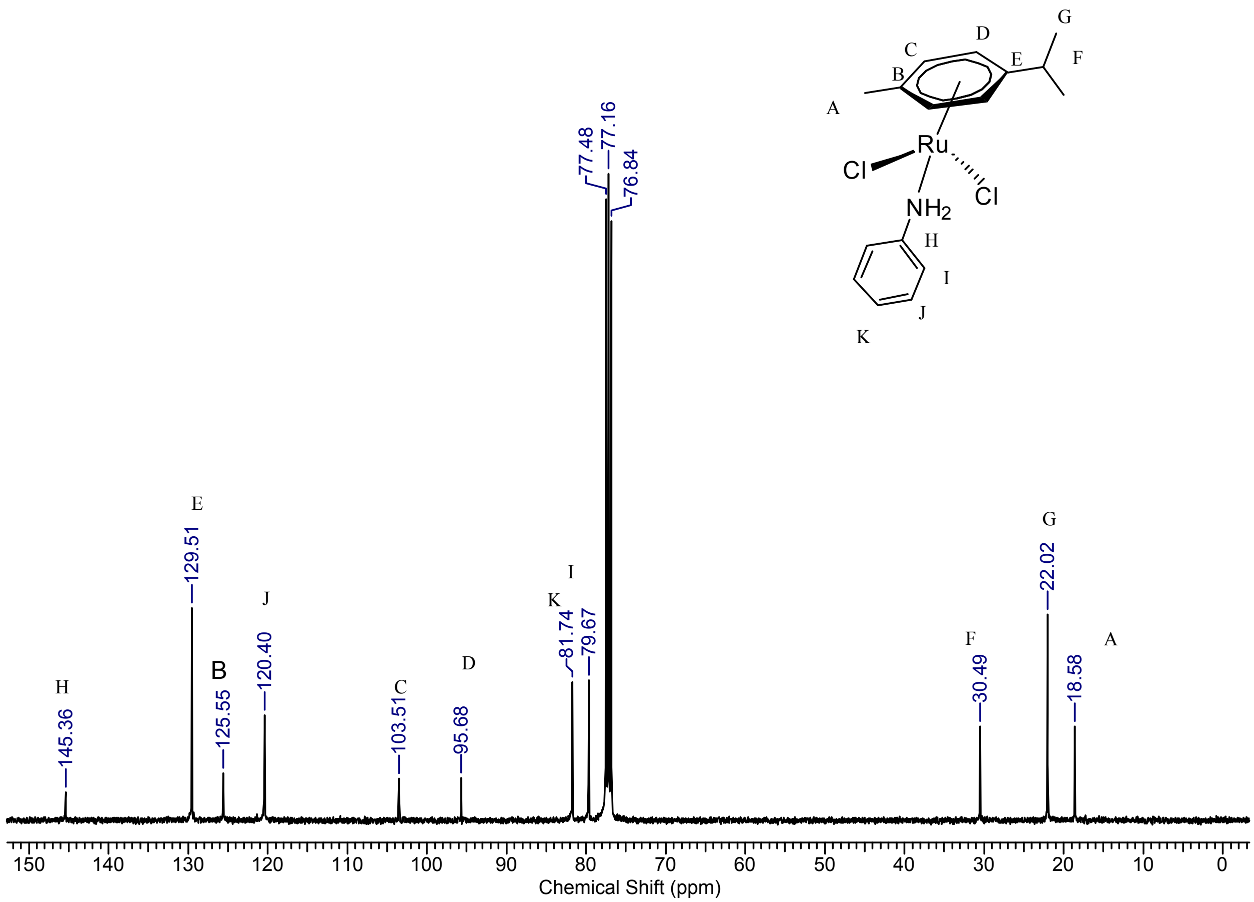


Mass spectra of complex [Ru]-2a

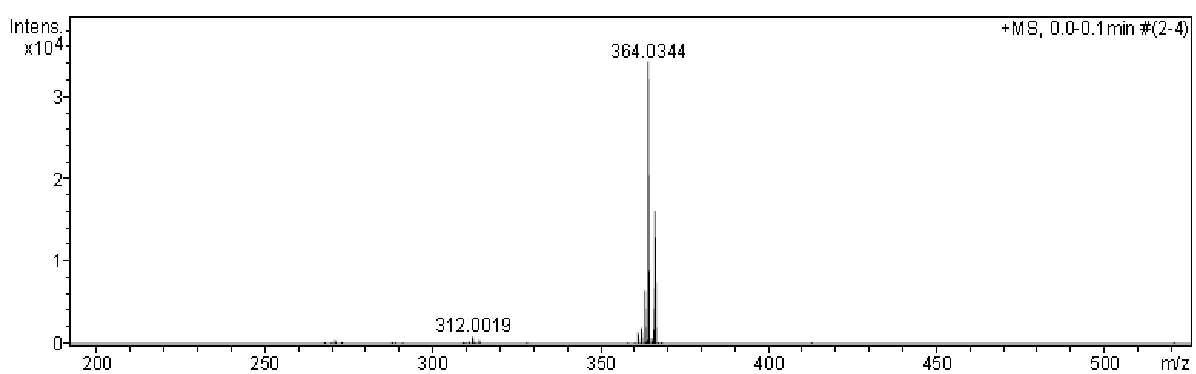




^{1}H NMR spectra of complex [Ru]-2b

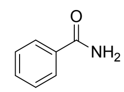


^{13}C NMR spectra of complex [Ru]-2b

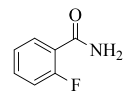


Mass spectra of complex [Ru]-2b

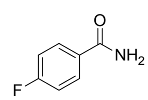
Spectral data of amide products obtained from catalytic conversion of various aldehydes in the presence of ruthenium catalyst [Ru]-2a in water:



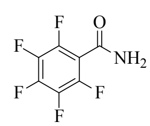
Benzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.83 (d, 2H, J = 8Hz), 7.54 (t, 1H, J = 8Hz) 7.47 (t, 2H, J = 8Hz), 6.21 (br, 2H), **^{13}C NMR (100 MHz, CDCl$_3$)**: δ (ppm) = 169.81, 133.31, 131.95, 128.56, 127.31.



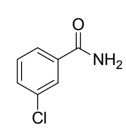
2-Flurorobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 8.16-8.12 (m, 1H), 7.53-7.49 (m, 1H), 7.30-7.26(m, 1H), 7.17-7.14(m, 1H), 6.70(br, 1H), 6.05(br, 1H).



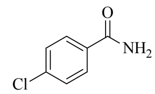
4-Flurorobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.85-7.81 (m, 2H), 7.15-7.10 (m, 2H), 5.89-5.71 (br., 2H).



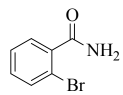
Pentafluorobenzamide: ^{19}F NMR (376.5 MHz, CDCl$_3$): δ (ppm) = -140.33 (2F), -151.27 (1F), -161.20 (2F).



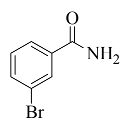
3-Chlorobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.81 (s, 1H), 7.68 (d, 1H, J = 8Hz) 7.51 (d, 1H, J = 4Hz), 7.40 (t, 1H, J = 8Hz), 5.98 (br, 1H), 5.59 (br, 1H), **^{13}C NMR (100 MHz, CDCl$_3$)** : δ (ppm) = 167.98, 135.03, 134.84, 132.07, 129.96, 127.72, 125.38.



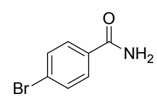
4-Chlorobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.75-7.69 (m, 2H), 7.42-7.37 (m, 2H), 5.96-5.69 (br, 2H).



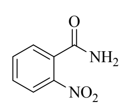
2-Bromobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.68-7.66 (m, 1H), 7.63-7.61 (m, 1H), 7.41-7.37 (m, 2H), 6.12 (br, 1H).



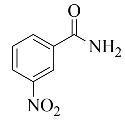
3-Bromobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.9 (s, 1H), 7.66-7.59 (m, 2H), 7.27-7.20 (m, 1H), 6.03-5.77 (br, 2H).



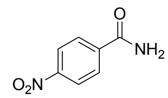
4-Bromobenzamide: ^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.82 (d, 1H, J = 8Hz), 7.69 (d, 1H, J = 8Hz), 7.60(d, 1H, J = 8Hz), 7.48-7.44(m, 1H), 6.02 (br, 1H), 5.62 (br, 1H).



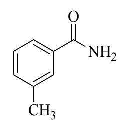
2-Nitrobenzamide: ^{1}NMR (400 MHz, CDCl$_3$): δ (ppm) = 7.71-7.52 (m, 4H), 6.04-5.93 (br, 2H).



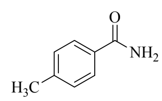
3-Nitrobenzamide: ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 8.68 (s, 1H), 8.36-8.34 (m, 1H), 8.29 (m, 1H), 7.78-7.73 (m, 1H), **^{13}C NMR (100 MHz, DMSO-d$_6$)**: δ (ppm) = 165.80, 147.82, 133.79, 132.34, 130.40, 125.89, 122.28.



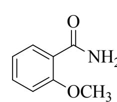
4-Nitrobenzamide: [1]H NMR (400 MHz, DMSO-d_6): δ (ppm) = 8.29 (m, 2H) 8.09 (d, 2H, J = 8Hz), **[13]C NMR (100 MHz, DMSO-d_6)**: δ (ppm) = 166.21, 149.05, 139.98, 128.92, 123.45.



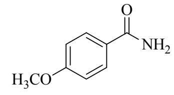
3-Methylbenzamide: [1]H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.57 (s, 1H), 7.52-7.51 (m, 1H), 7.26-7.24 (m, 2H), 6.18 (br, 2H), 2.32 (s, 3H)



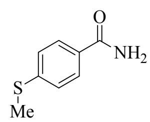
4-Methylbenzamide: [1]H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (d, 2H, J = 8Hz), 7.25 (d, 2H, J = 8Hz), 6.02-5.63 (br, 2H), 2.41 (s, 3H), **[13]C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 169.43, 142.57, 130.38, 129.28, 127.37, 21.48.



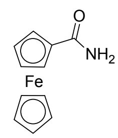
2-Methoxybenzamide: [1]NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.22 (dd, 1H, J_1 = 8Hz, J_2 = 4Hz), 7.73 (br, 1H), 7.51-7.46 (m, 1H), 7.11-7.07 (m, 1H), 7.01-6.99 (m, 1H), 5.89 (br, 1H), **[13]C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 167.23, 157.77, 133.30, 132.39, 121.10, 120.71, 111.28, 55.83.



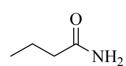
4-Methoxybenzamide: [1]H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.78 (d, 2H, J = 8Hz), 6.94 (d, 2H, J = 8Hz), 5.84 (br, 2H).



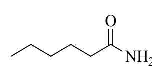
4-(Methylthio)benzamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.66 (d, 2H, J = 8Hz), 7.20 (d, 2H, J = 8Hz), 5.94-5.68(br, 2H), 2.45 (s, 3H), **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 168.71, 144.26, 129.76, 127.27, 125.33, 14.93.



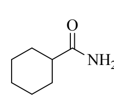
Ferrocenylcarbamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.49 (br, 2H), 4.68-4.67 (m, 2H), 4.39-4.38 (m, 2H), 4.23 (s, 5H), **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 172.80, 74.41, 70.89, 69.94, 68.59.



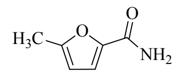
Butyramide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.48-5.42 (br, 2H), 2.16-2.13 (m, 2H), 1.65-1.57 (m, 2H), 0.91 (t, 3H, J = 4Hz).



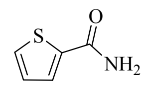
Hexamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 5.76-5.52 (br., 2H), 2.20 (t, 2H, J = 8Hz), 1.66-1.59 (m, 2H), 1.33-1.29 (m, 4H), 0.89 (s, 3H), **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 176.37, 35.82, 31.25, 25.12, 22.25, 13.78.



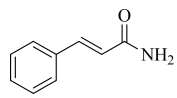
Cyclohexanecarboxamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =5.42 (br, 2H), 2.18-2.14 (m, 1H), 1.92-1.89 (m, 2H), 1.81-1.78 (m, 4H), 1.30-1.19 (m, 4H), **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 179.08, 44.77, 36.53, 29.61, 25.65.



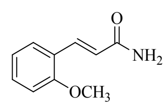
5-Methylfuran-2-carboxamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) =7.06 (s, 1H), 6.12 (s, 1H), 5.56 (br, 2H), 2.34 (s, 3H).



Thiophene-2-carboxamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.27 (m, 1H), 7.05 (m, 1H), 6.96 (m, 1H), 6.32 (br, 1H).

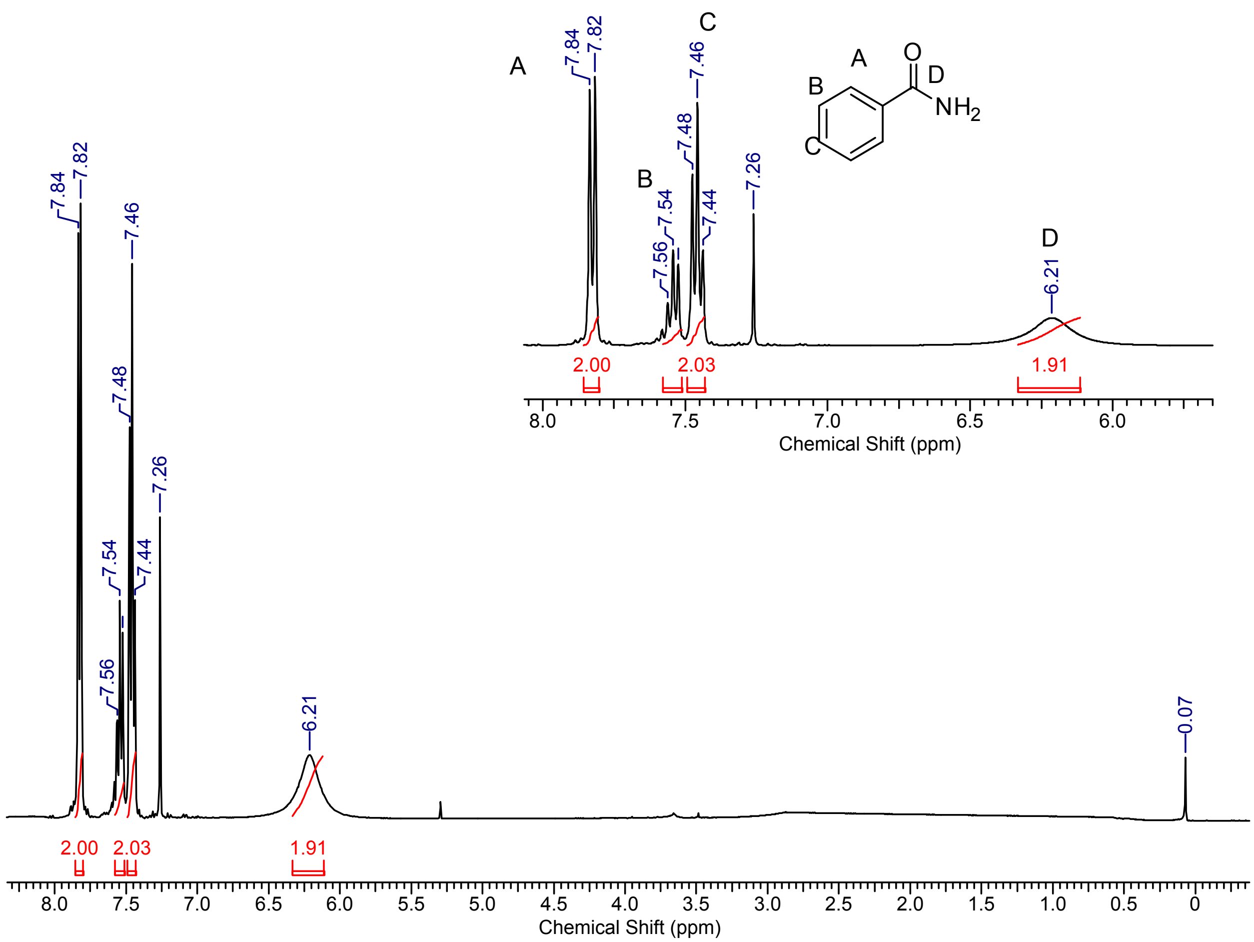


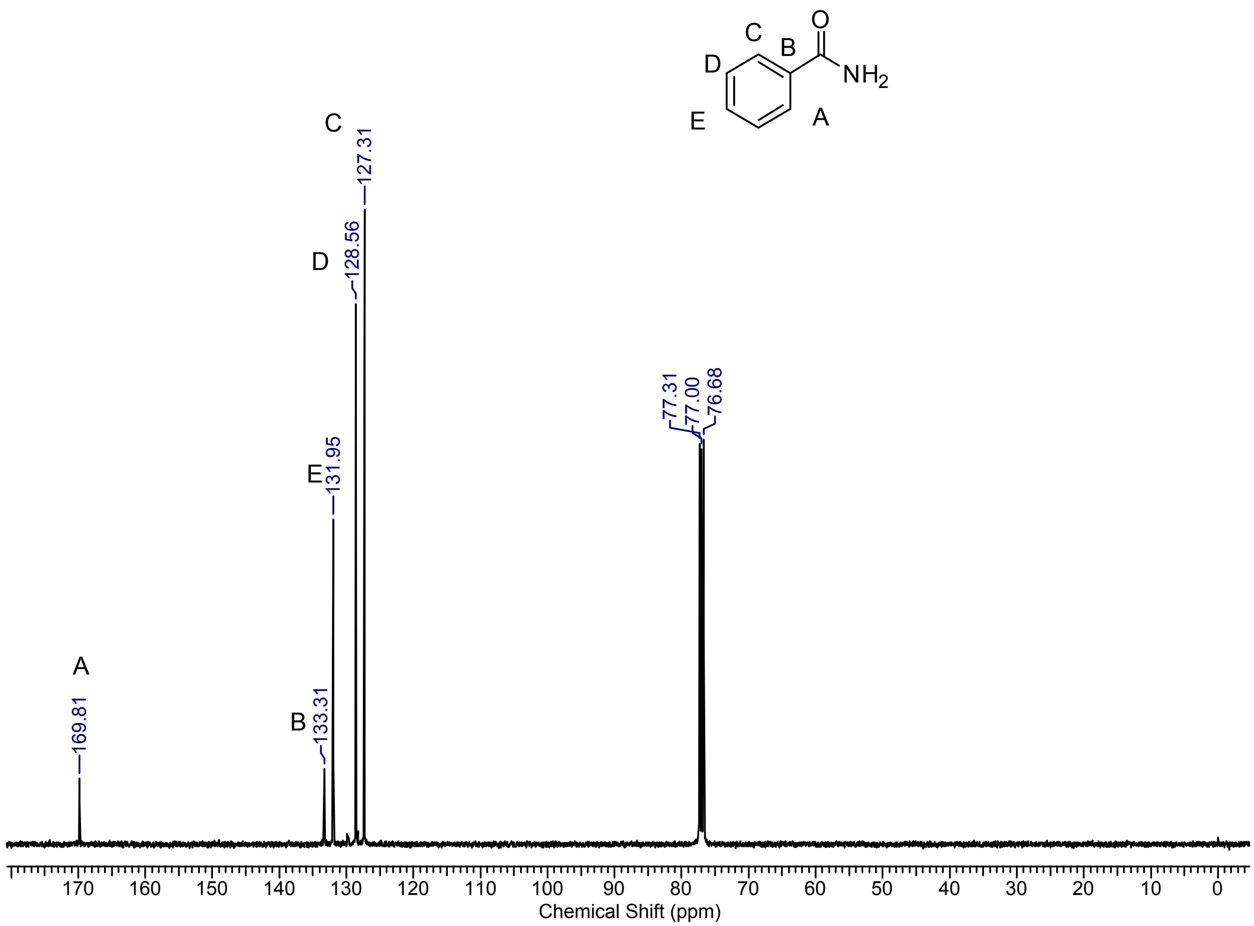
Cinnamamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.65 (d, 1H, J = 16Hz), 7.53-7.51 (m, 2H), 7.39-7.37 (m, 3H), 6.46 (d, 1H, J = 16Hz), 5.59 (br, 2H), **^{13}C NMR (100 MHz, $CDCl_3$)**: δ (ppm) = 168.24, 142.40, 134.47, 129.91, 128.80, 127.89, 119.58.



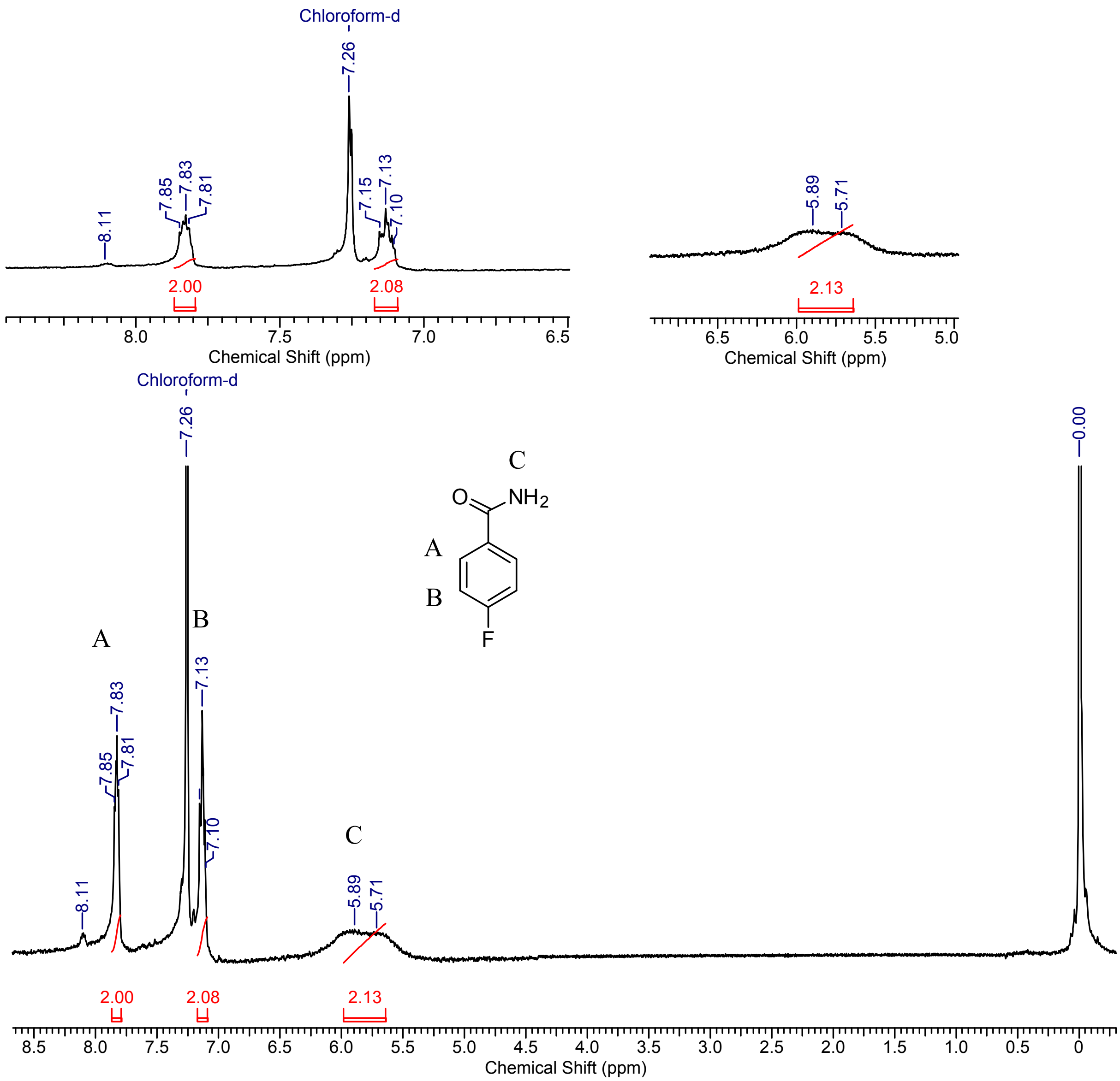
2-Methoxycinnamamide: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.89 (d, 1H, J = 16Hz), 7.49 (d, 1H, J = 8Hz), 7.34 (t, 1H, J = 8Hz), 6.98-6.41 (m, 2H), 6.57 (d, 1H, J = 16Hz), 5.51 (br, 2H), 3.89 (s, 3H).

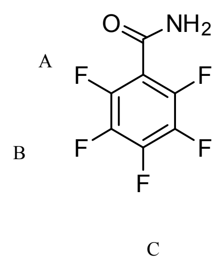
Spectra of amide products obtained from catalytic conversion of various aldehydes in the presence of ruthenium catalyst [Ru]-2a in water:

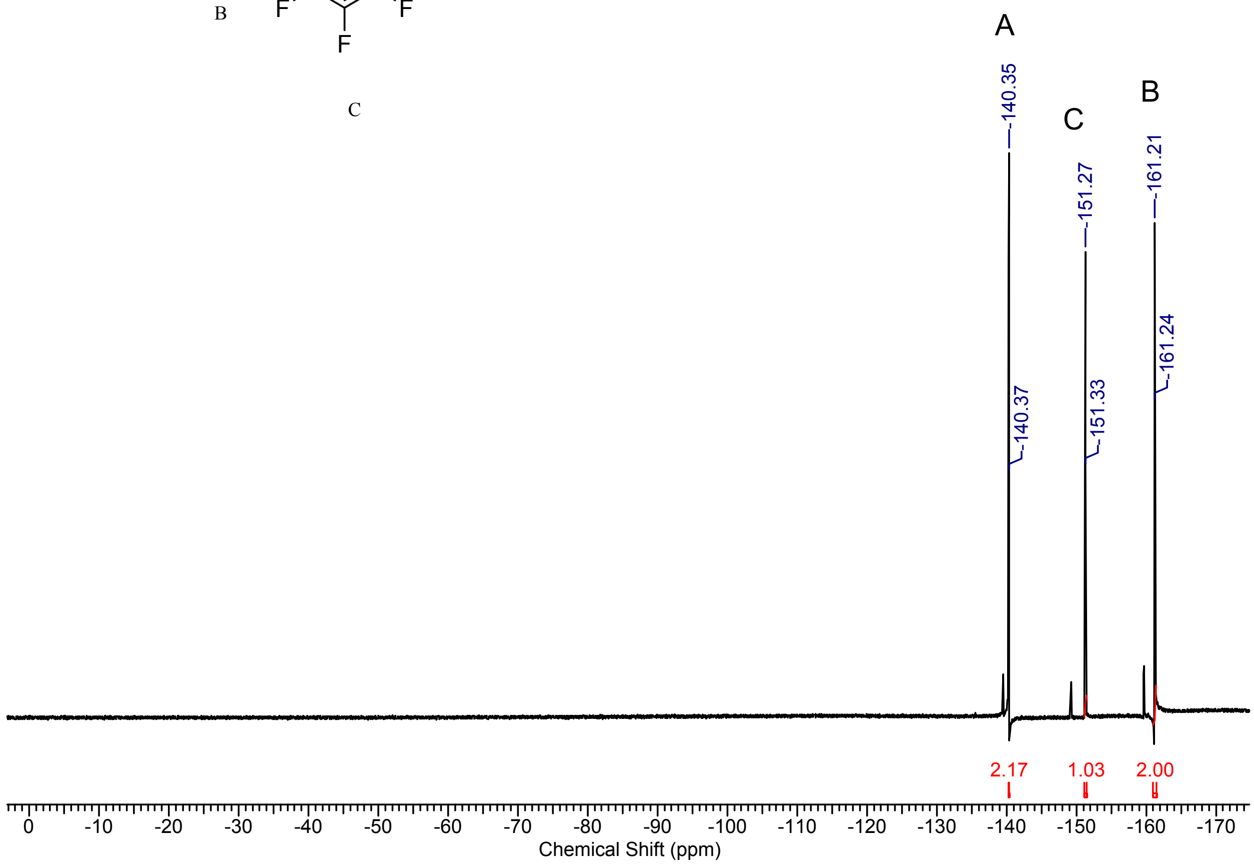


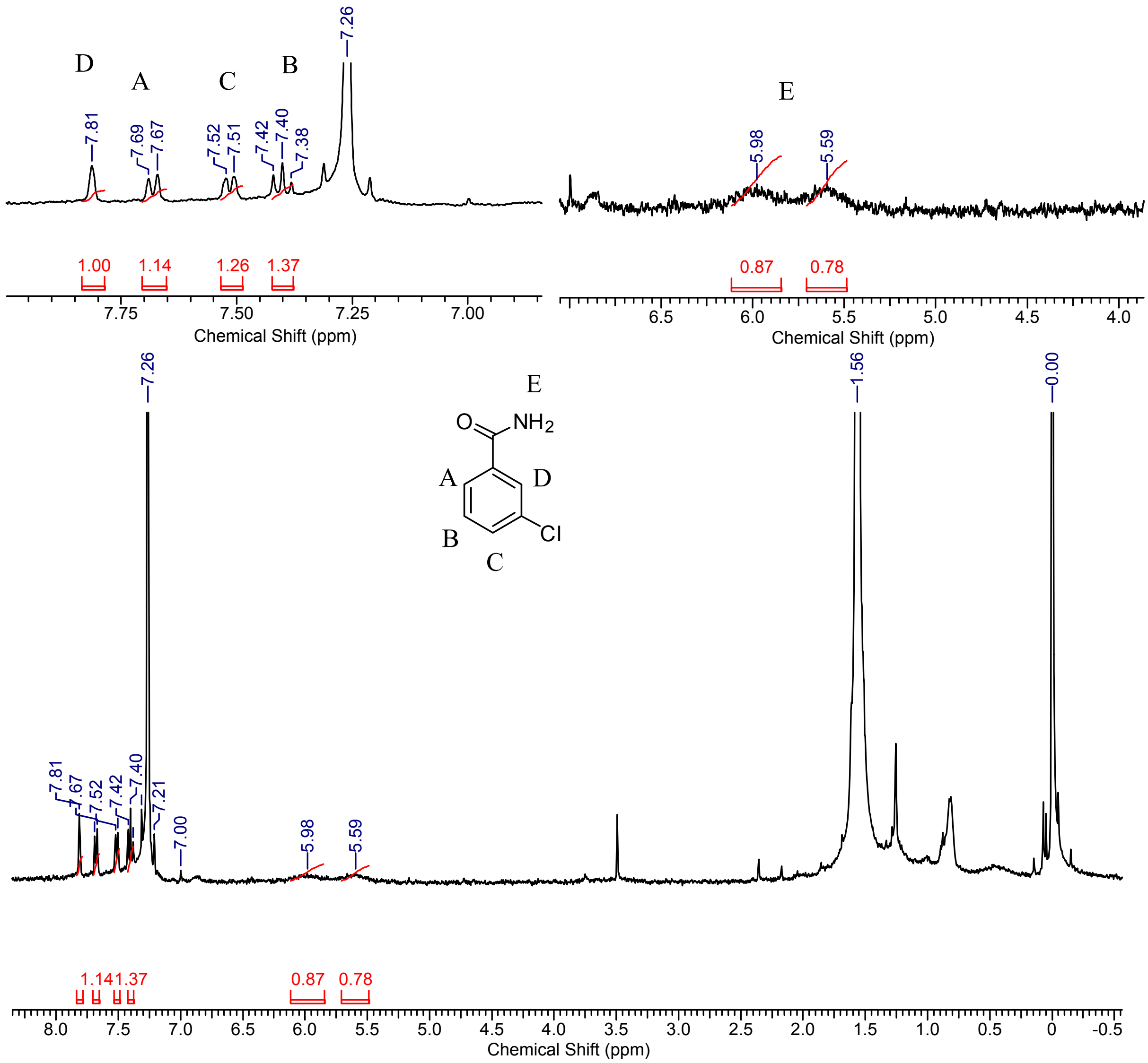


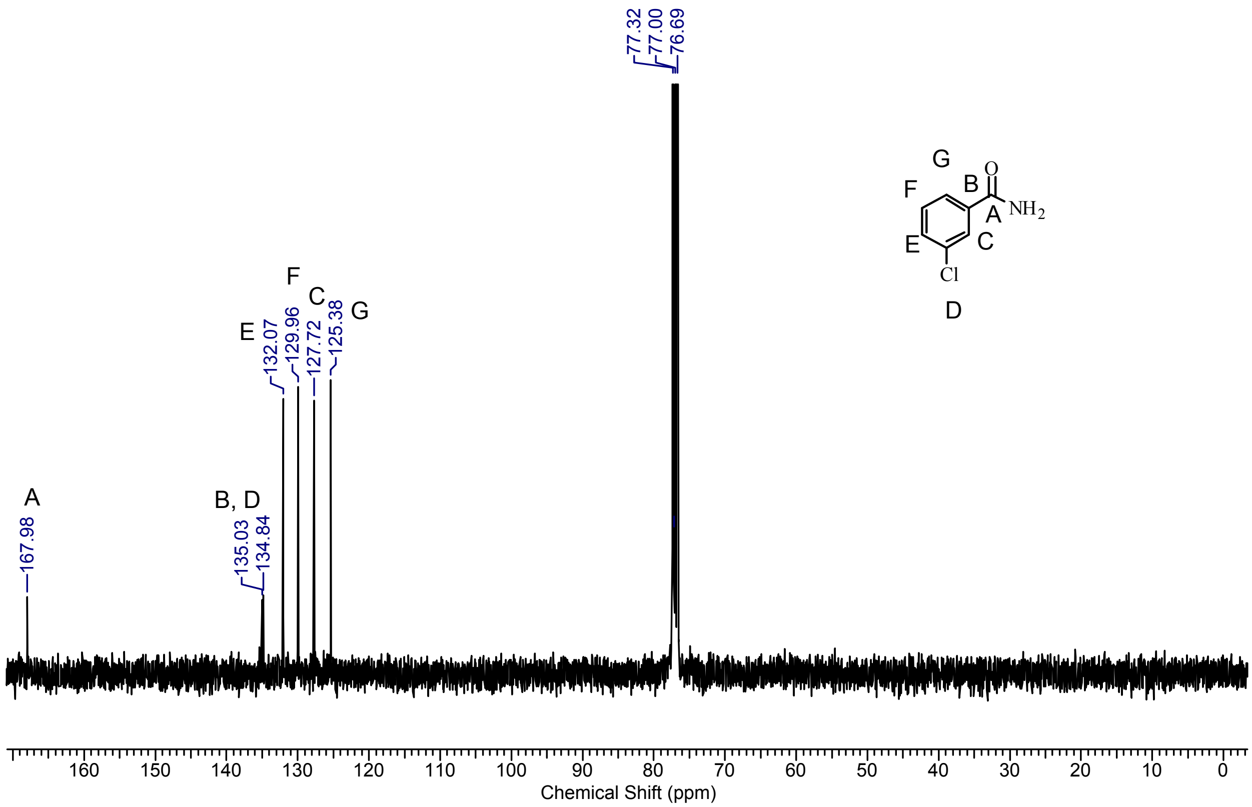
O
NH2
A
B
C
D
E
169.81
133.31
131.95
128.56
127.31
77.31
77.00
76.68
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

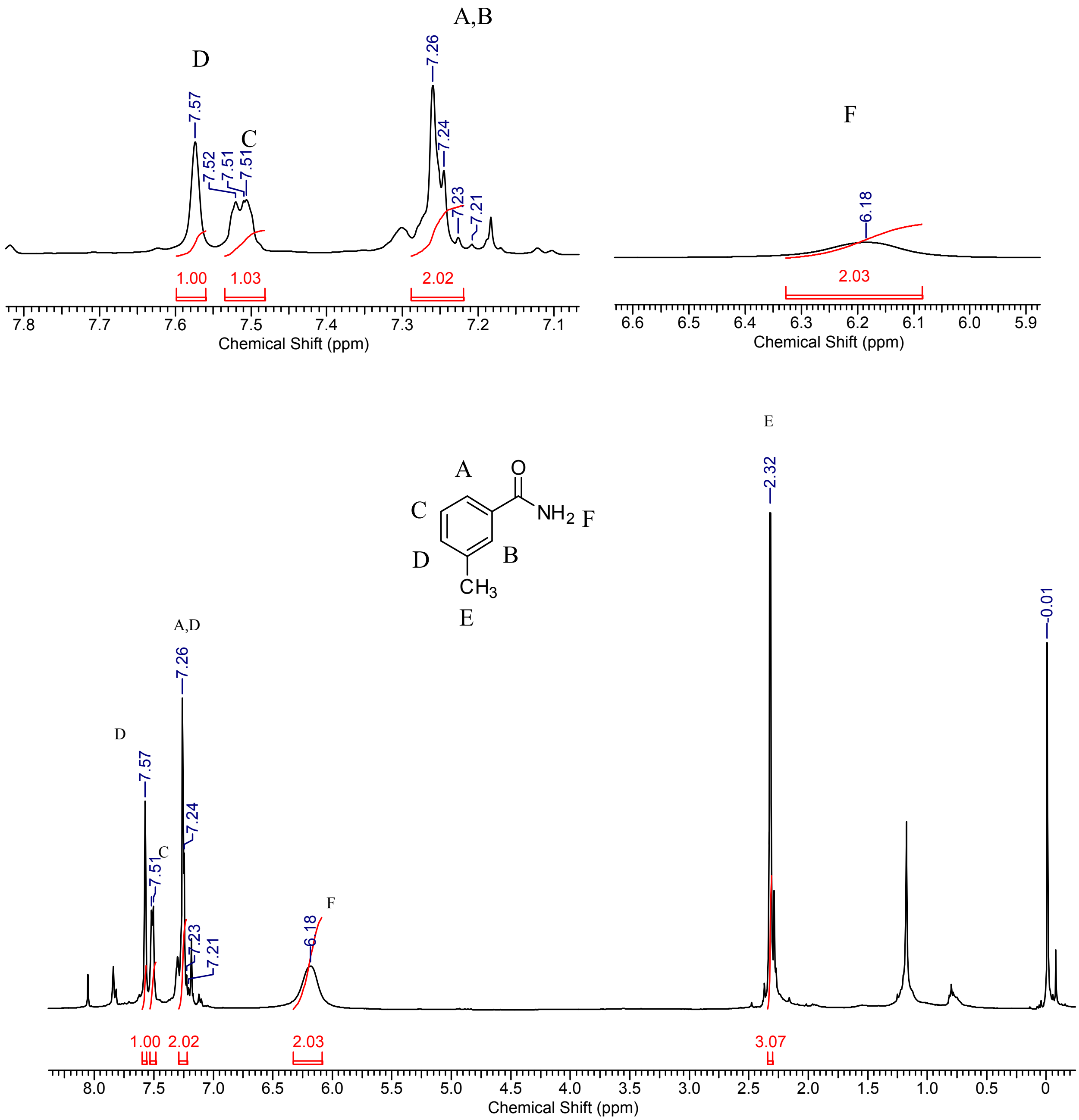

Chloroform-d
7.26
8.11
7.85
7.83
7.81
7.15
7.13
7.10
2.00
2.08
8.0
7.5
7.0
6.5
Chemical Shift (ppm)
5.89
5.71
2.13
6.5
6.0
5.5
5.0
Chemical Shift (ppm)
Chloroform-d
7.26
0.00
C
O
NH2
A
B
F
A
B
C
2.00
2.08
2.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

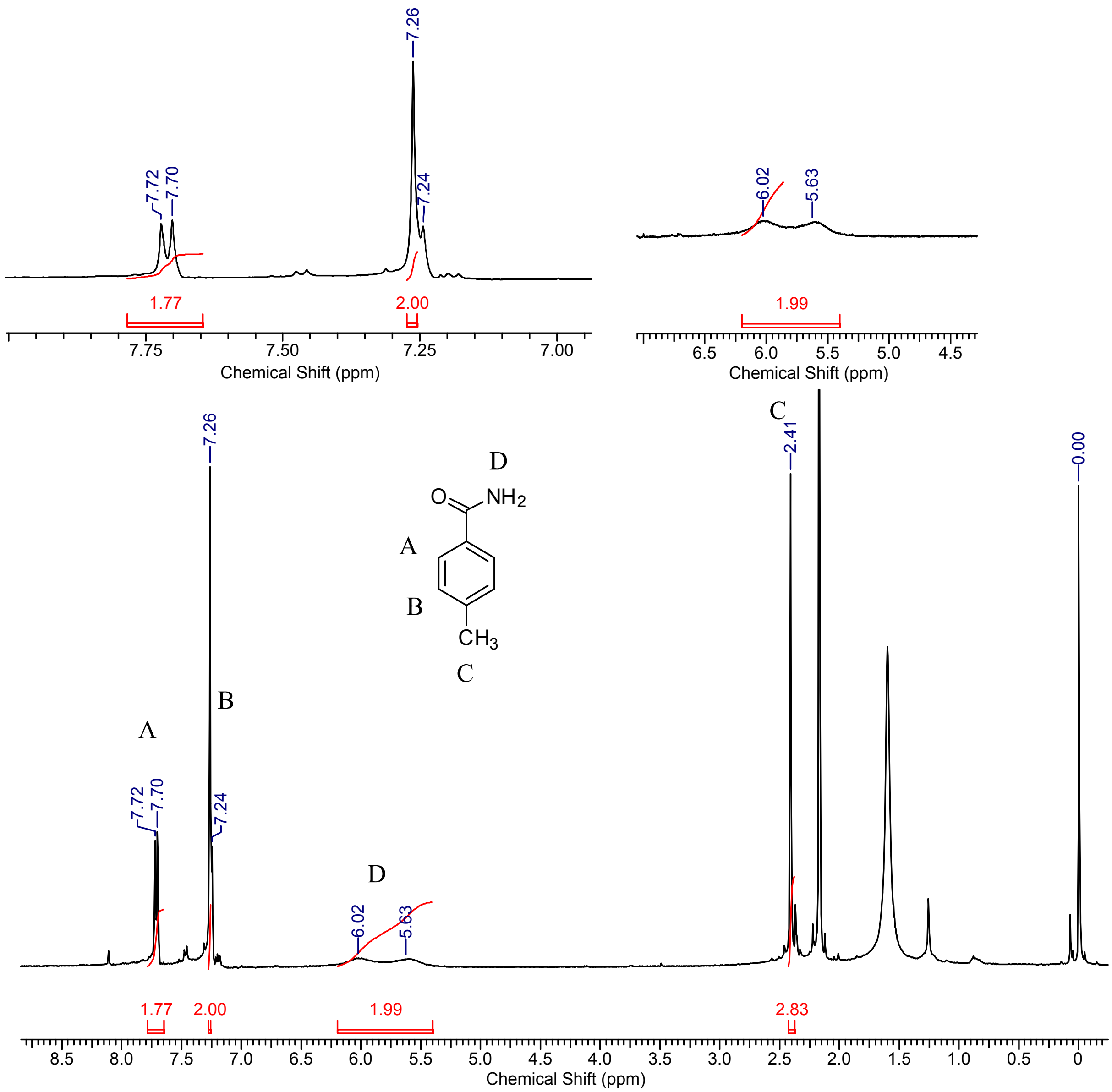

O
NH2
F
F
F
F
F
A
B
C

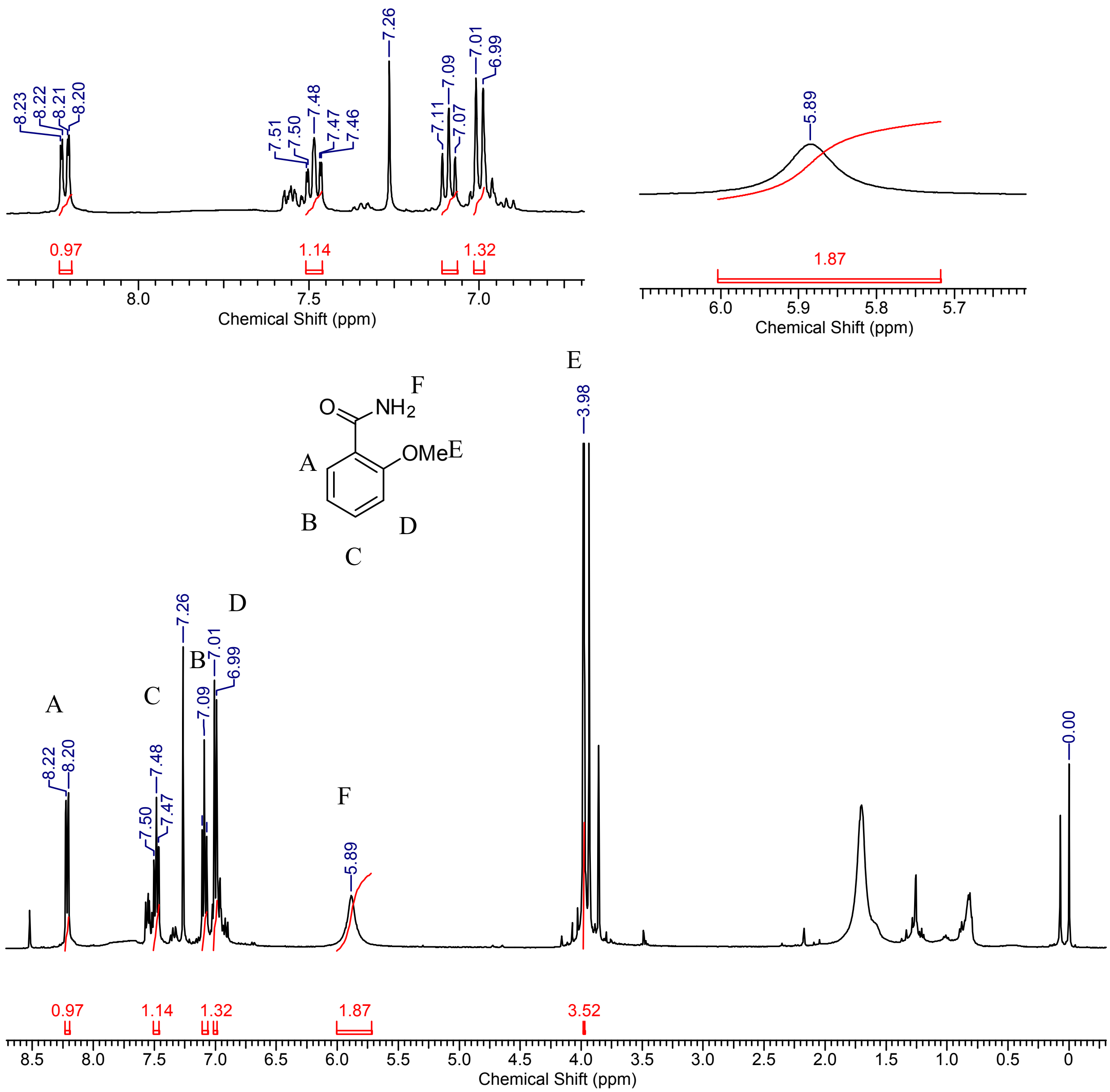

A
C
B
-140.35
-140.37
-151.27
-151.33
-161.21
-161.24
2.17
1.03
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
Chemical Shift (ppm)

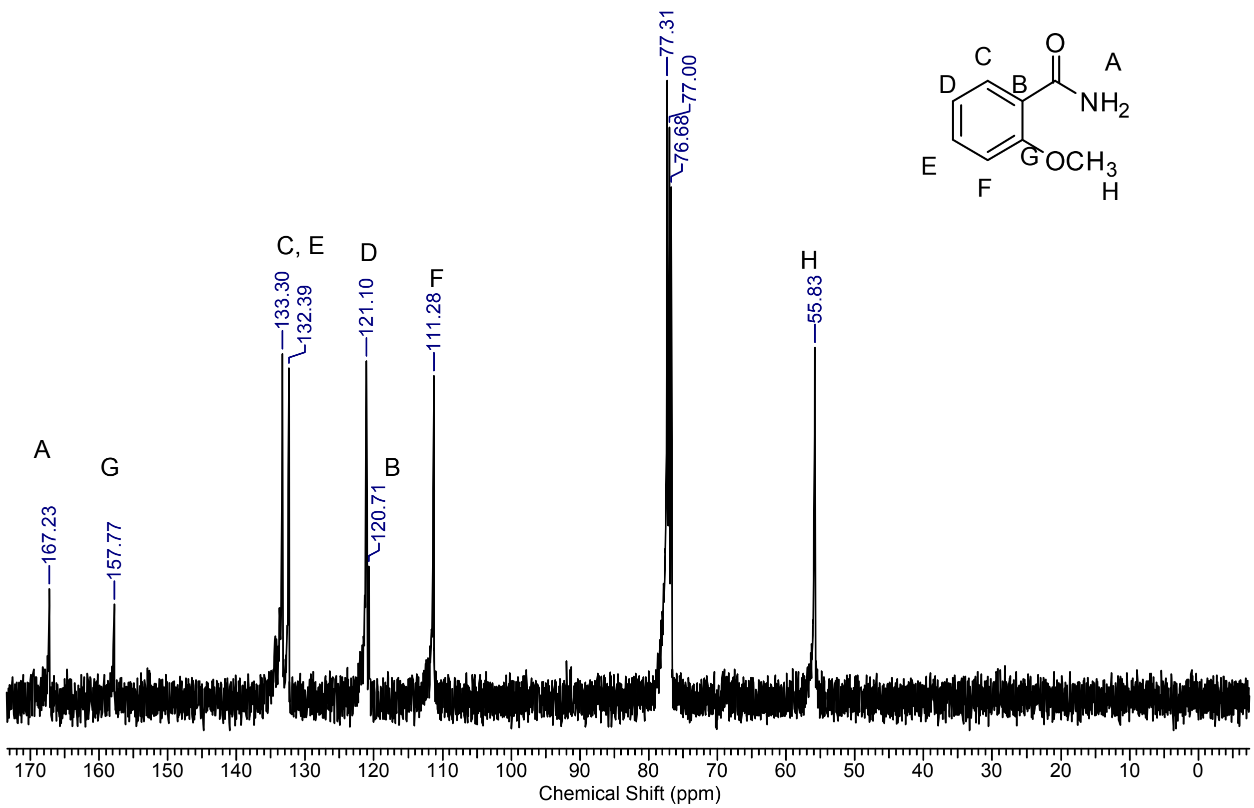

D
A
C
B
7.81
7.69
7.67
7.52
7.51
7.42
7.40
7.38
7.26
1.00
1.14
1.26
1.37
7.75
7.50
7.25
7.00
Chemical Shift (ppm)
E
5.98
5.59
0.87
0.78
6.5
6.0
5.5
5.0
4.5
4.0
Chemical Shift (ppm)
7.26
1.56
0.00
O
NH2
A
D
B
C
Cl
7.81
7.67
7.52
7.42
7.40
7.21
7.00
5.98
5.59
1.14
1.37
0.87
0.78
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


77.32
77.00
76.69
G
F
B
O
NH2
A
E
C
Cl
D
F
C
E
132.07
129.96
127.72
125.38
G
A
167.98
B, D
135.03
134.84
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

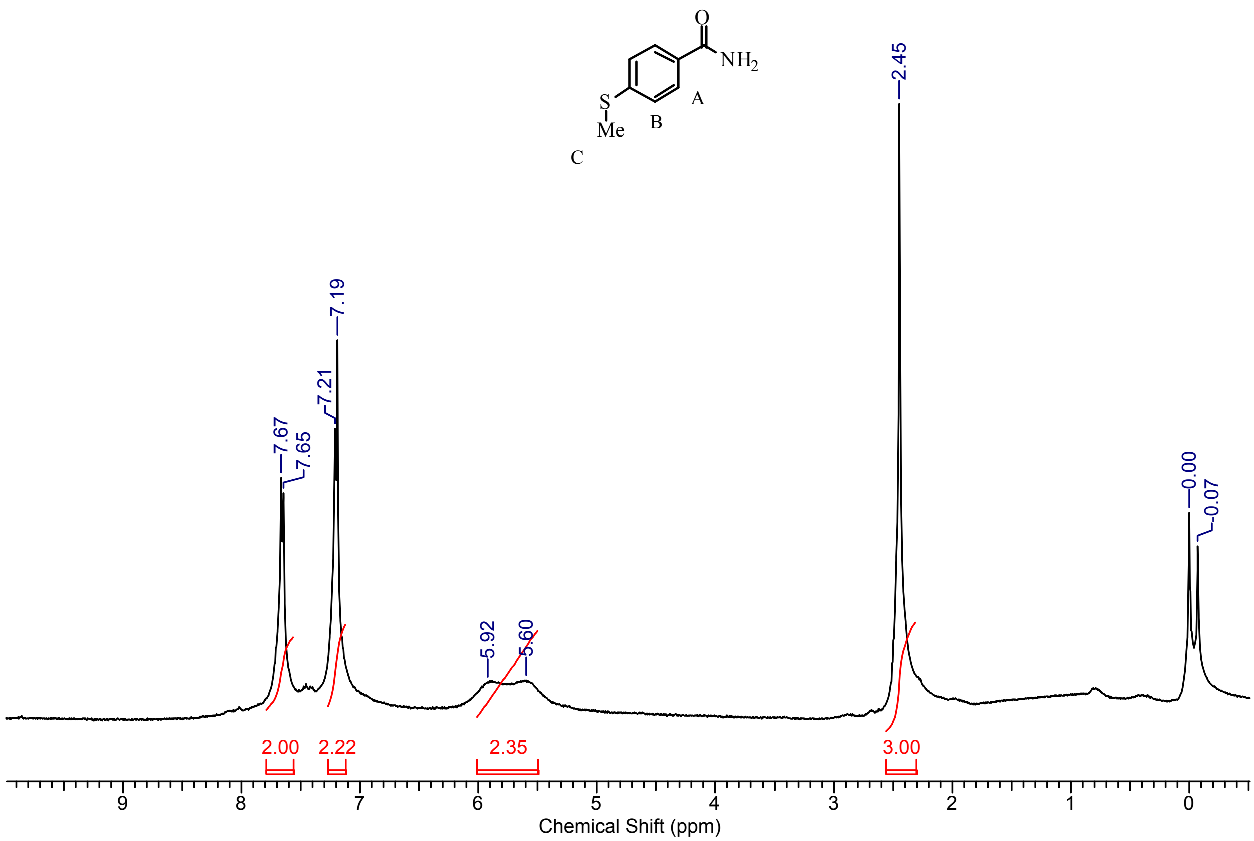

A,B
D
C
F
7.57
7.52
7.51
7.51
7.26
7.24
7.23
7.21
6.18
1.00
1.03
2.02
2.03
Chemical Shift (ppm)
Chemical Shift (ppm)
E
2.32
A
C
D
B
E
F
O
NH2
CH3
A,D
D
C
F
-0.01
1.00
2.02
2.03
3.07
Chemical Shift (ppm)


7.72
7.70
7.26
7.24
1.77
2.00
7.75
7.50
7.25
7.00
Chemical Shift (ppm)
6.02
5.63
1.99
6.5
6.0
5.5
5.0
4.5
Chemical Shift (ppm)
D
NH_2
O
A
B
CH_3
C
2.41
0.00
1.77
2.00
1.99
2.83
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
0
Chemical Shift (ppm)

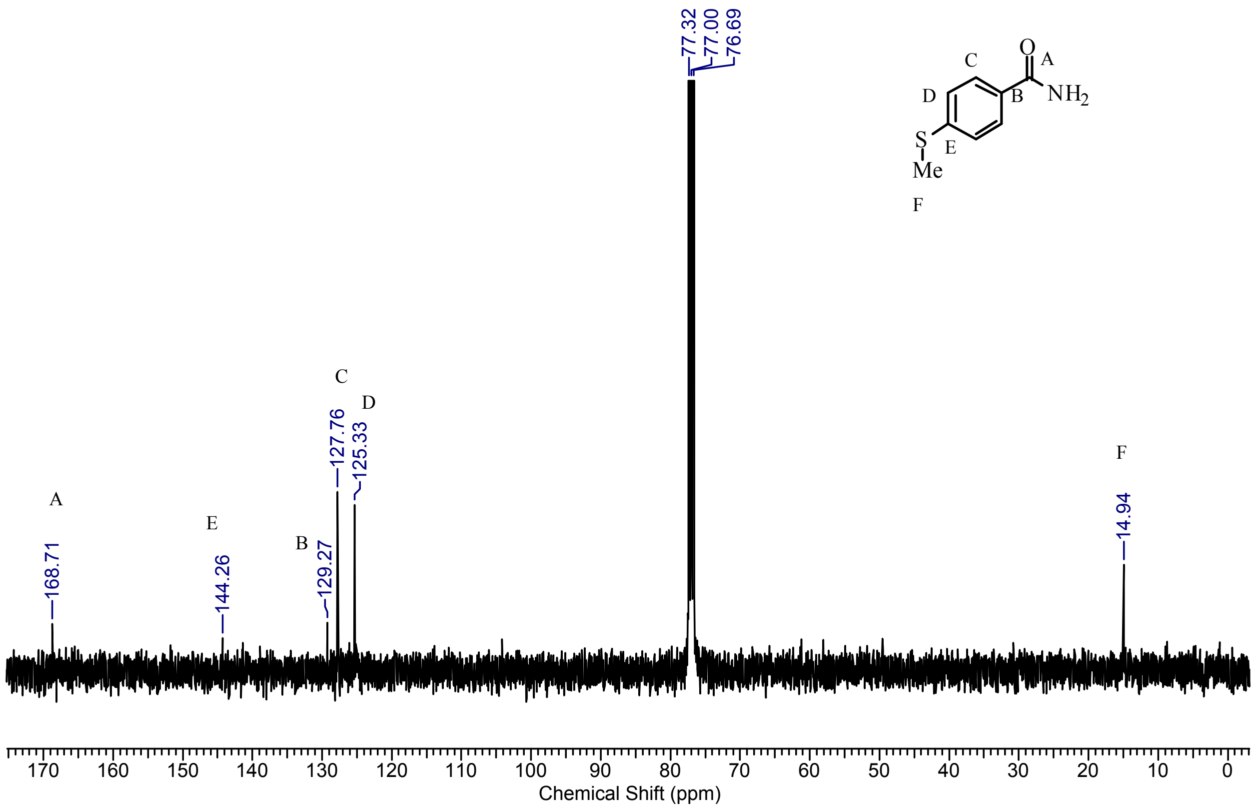

Chemical Shift (ppm)
0.97
1.14
1.32
1.87
3.52
O
NH2
OMe
A
B
C
D
E
F

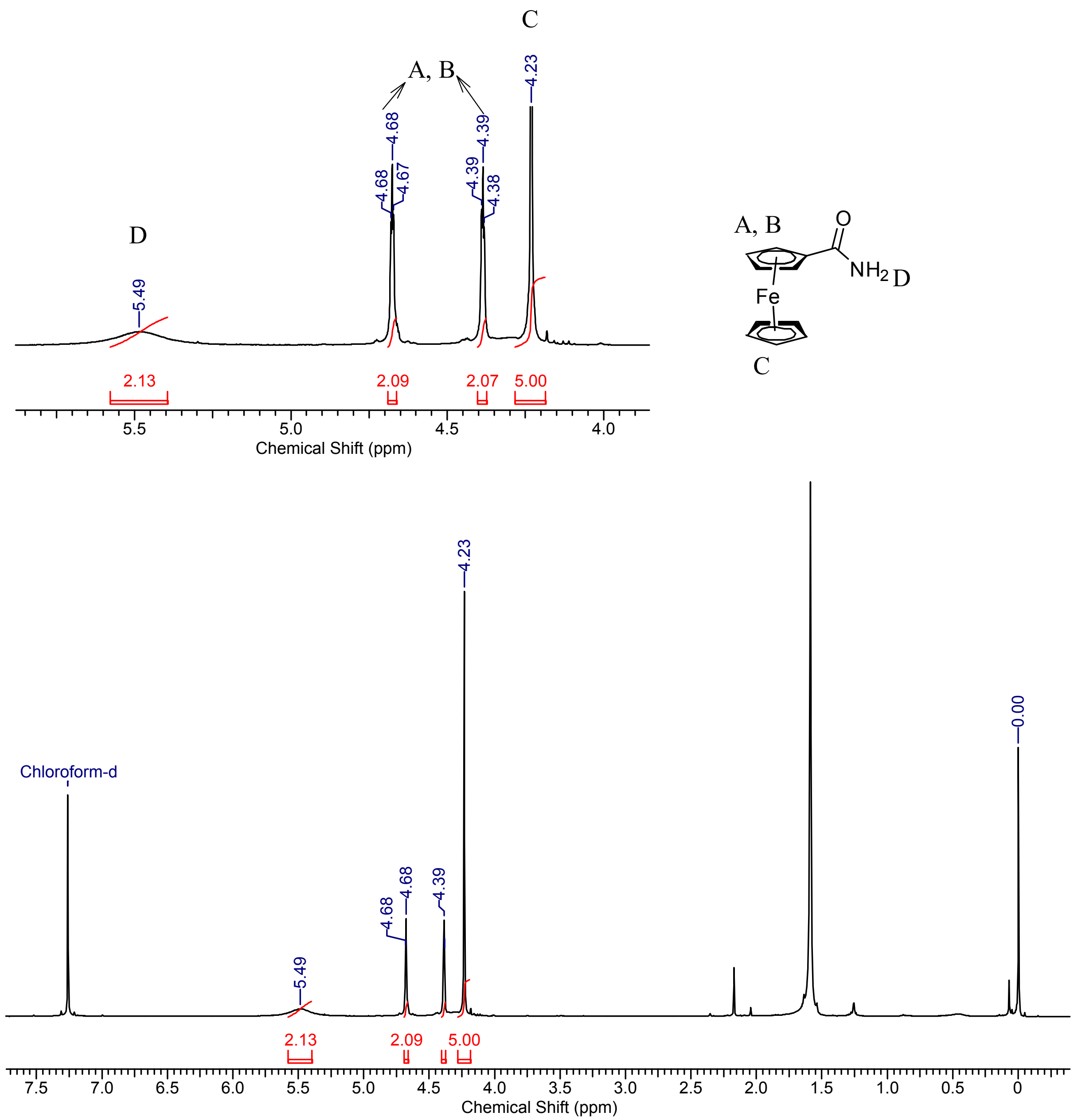


A
G
C, E
D
B
F
H
167.23
157.77
133.30
132.39
121.10
120.71
111.28
77.31
77.00
76.68
55.83
O
NH2
OCH3
Chemical Shift (ppm)

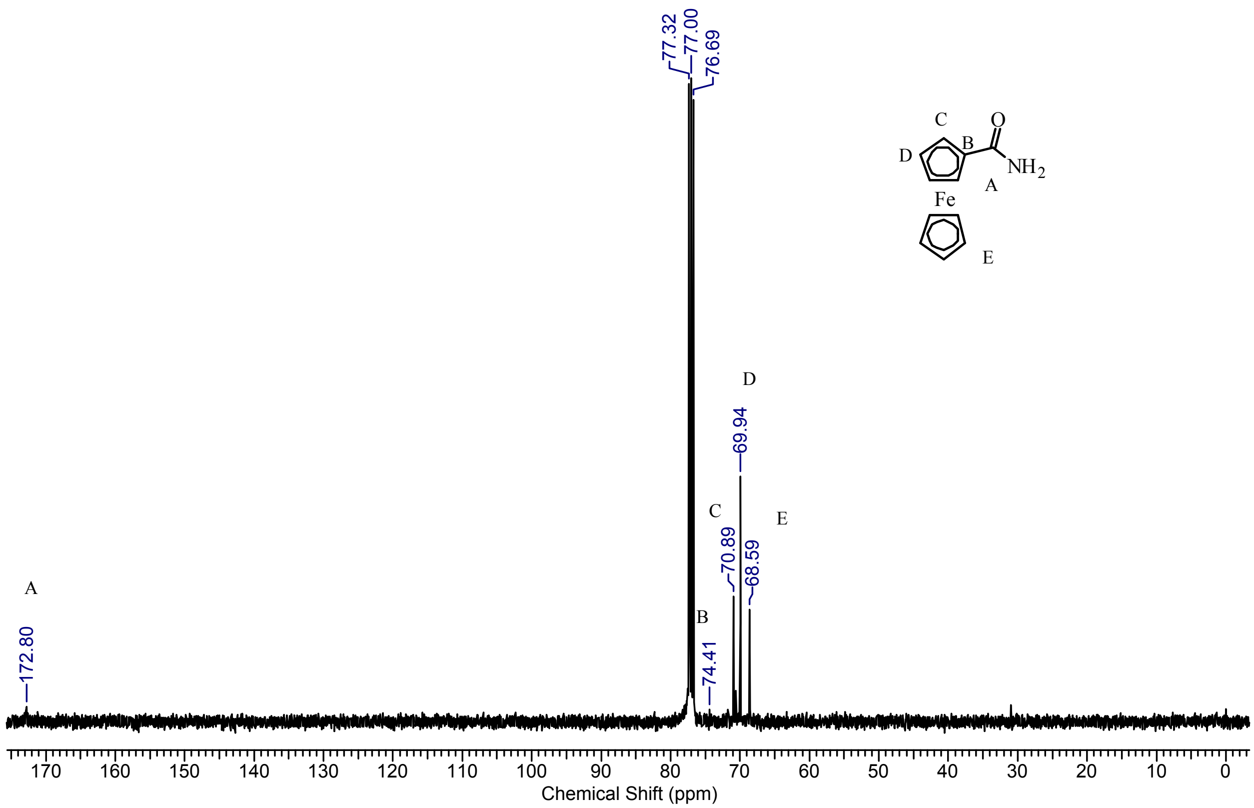


O
NH2
A
B
S
Me
C
2.45
7.19
7.21
7.67
7.65
5.92
5.60
0.00
-0.07
2.00
2.22
2.35
3.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

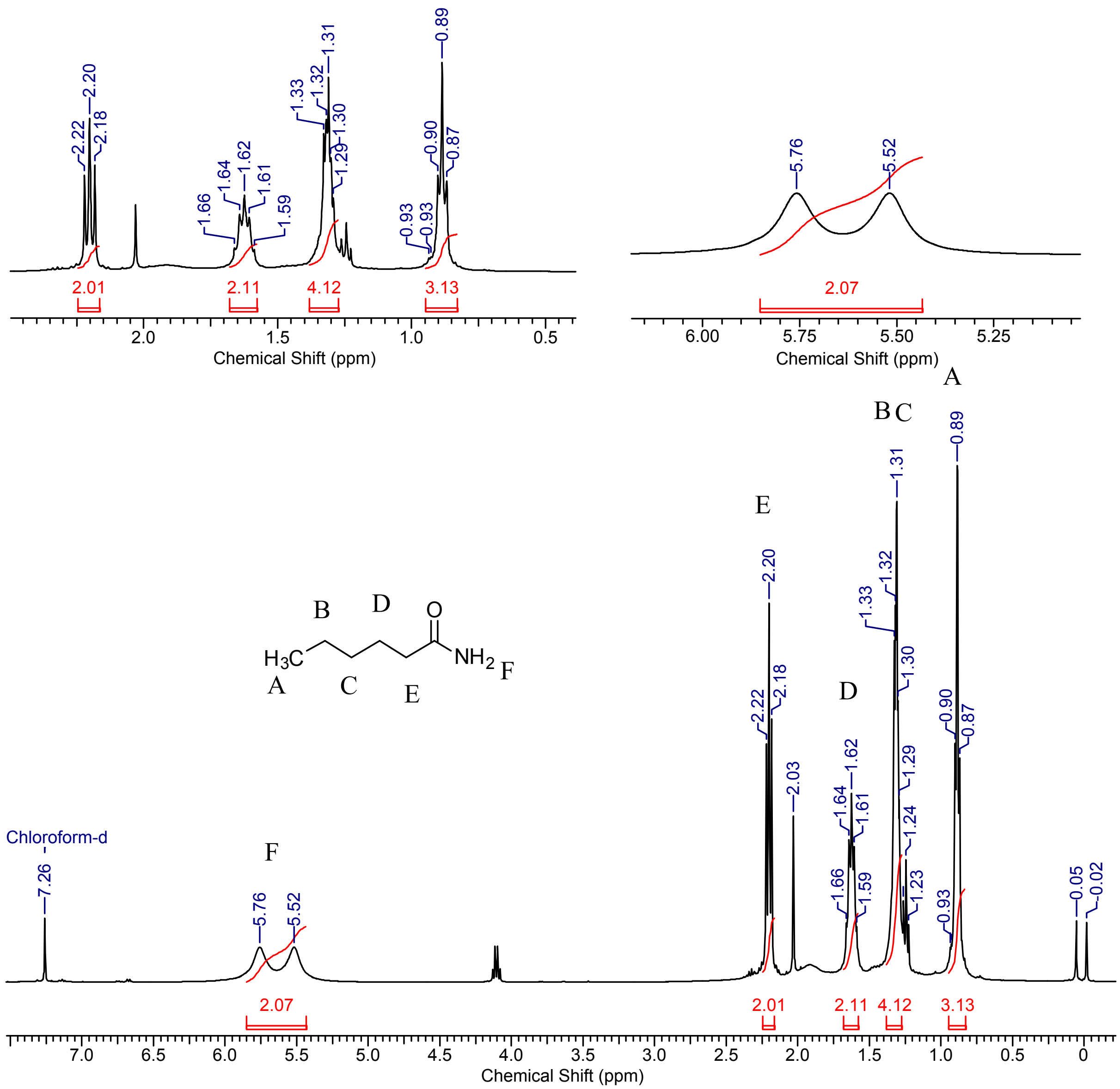

77.32
77.00
76.69
C
D
B
A
NH2
O
S
Me
E
F
A
168.71
E
144.26
B
129.27
C
127.76
D
125.33
F
14.94
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)



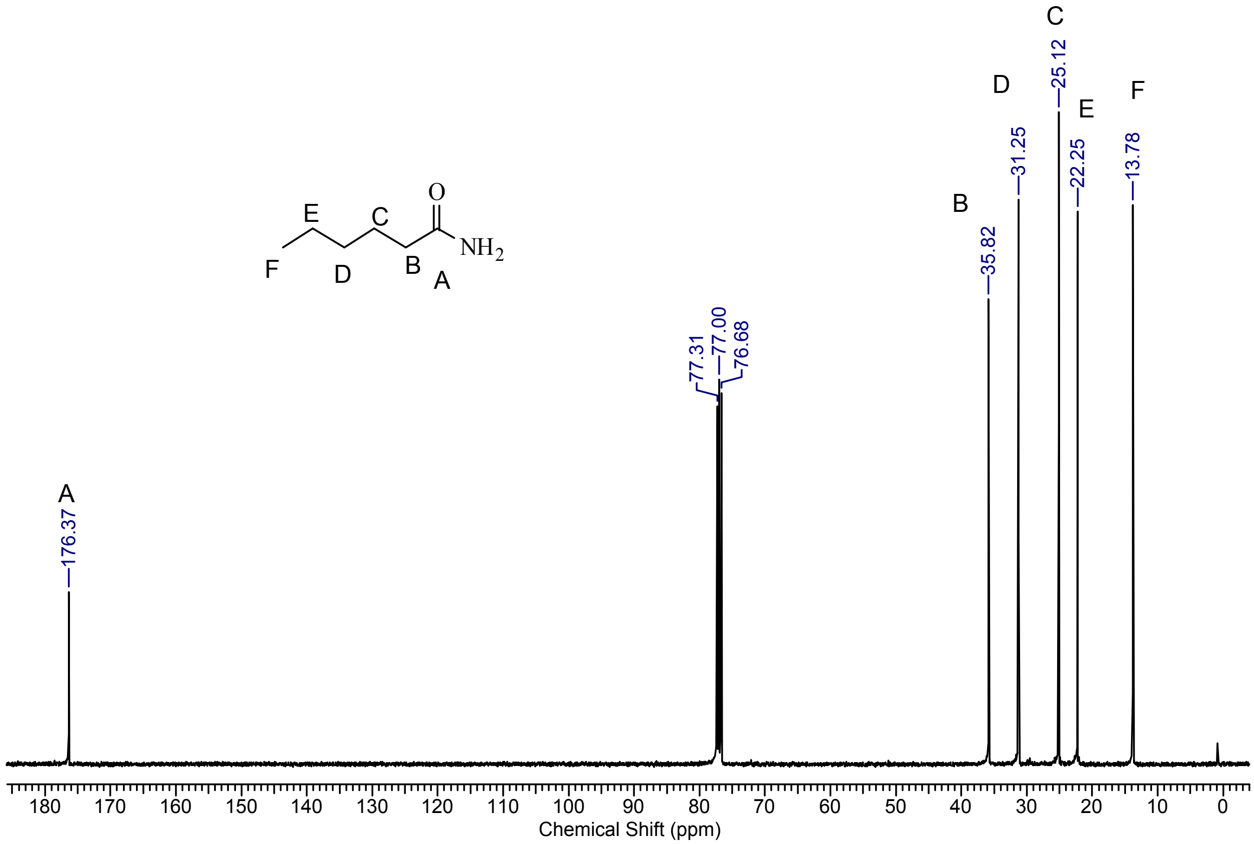
C
A, B
4.23
4.68
4.68
4.67
4.39
4.39
4.38
D
5.49
2.13
2.09
2.07
5.00
5.5
5.0
4.5
4.0
Chemical Shift (ppm)
A, B
O
NH2
D
Fe
C
Chloroform-d
0.00
7.5
7.0
6.5
6.0
5.5
4.5
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0

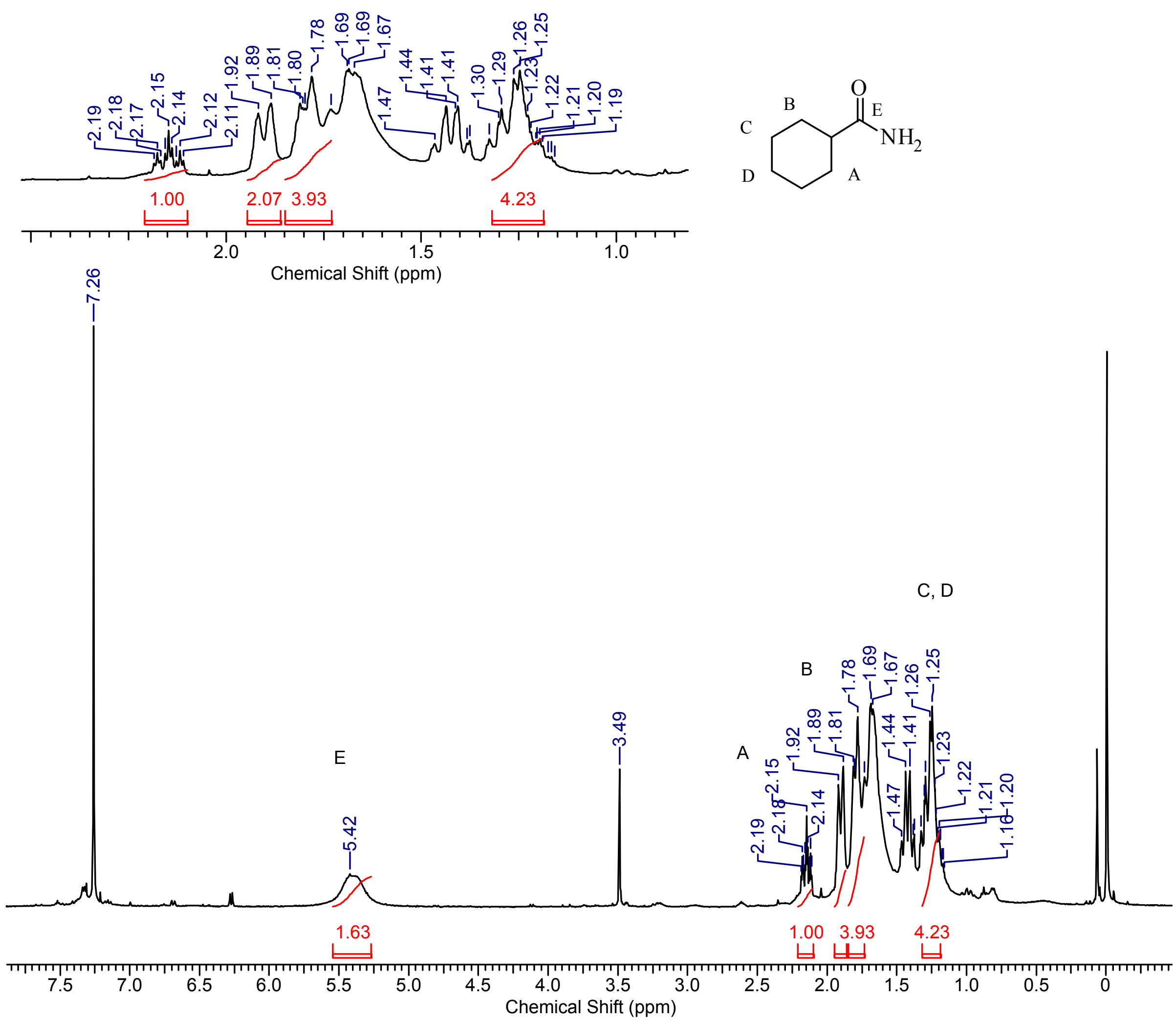


77.32
77.00
76.69
C
O
B
D
NH2
A
Fe
E
D
69.94
C
E
70.89
68.59
A
B
172.80
74.41
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

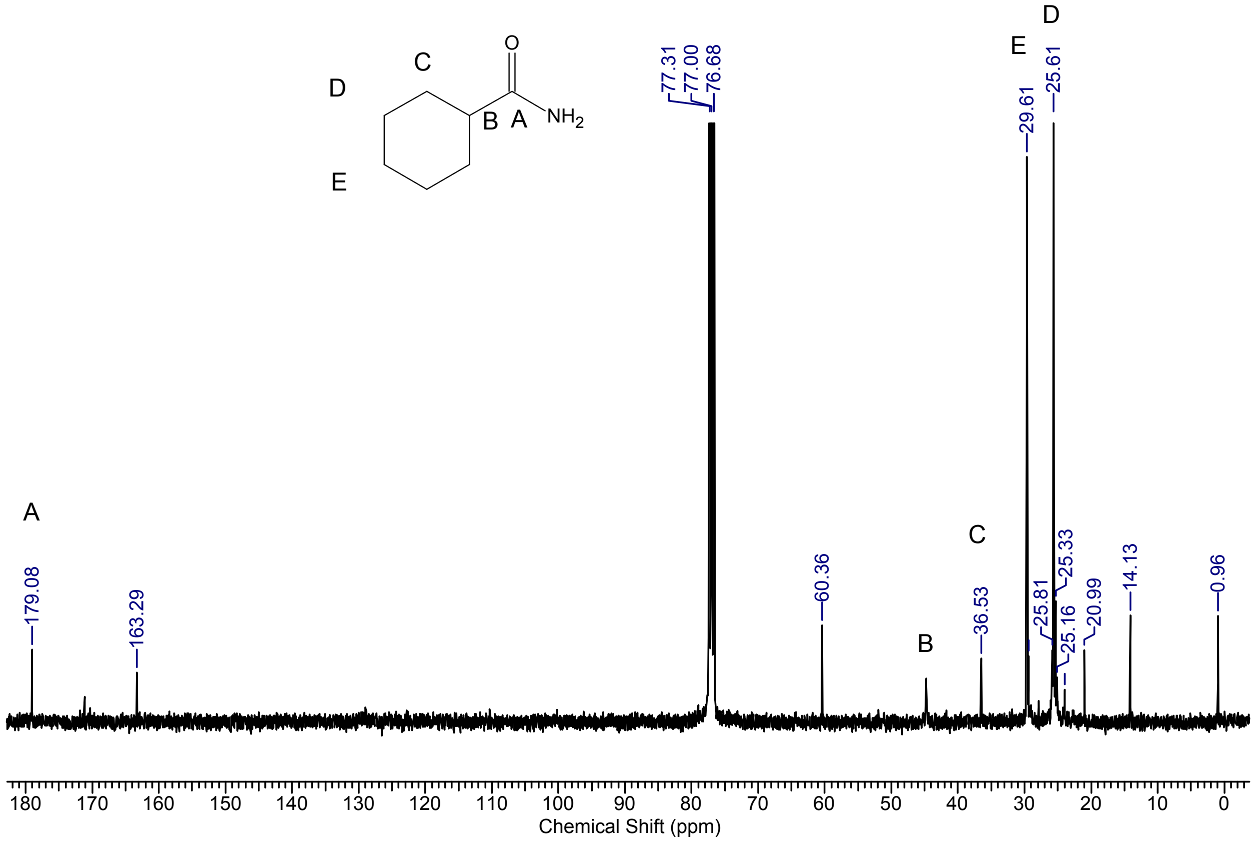


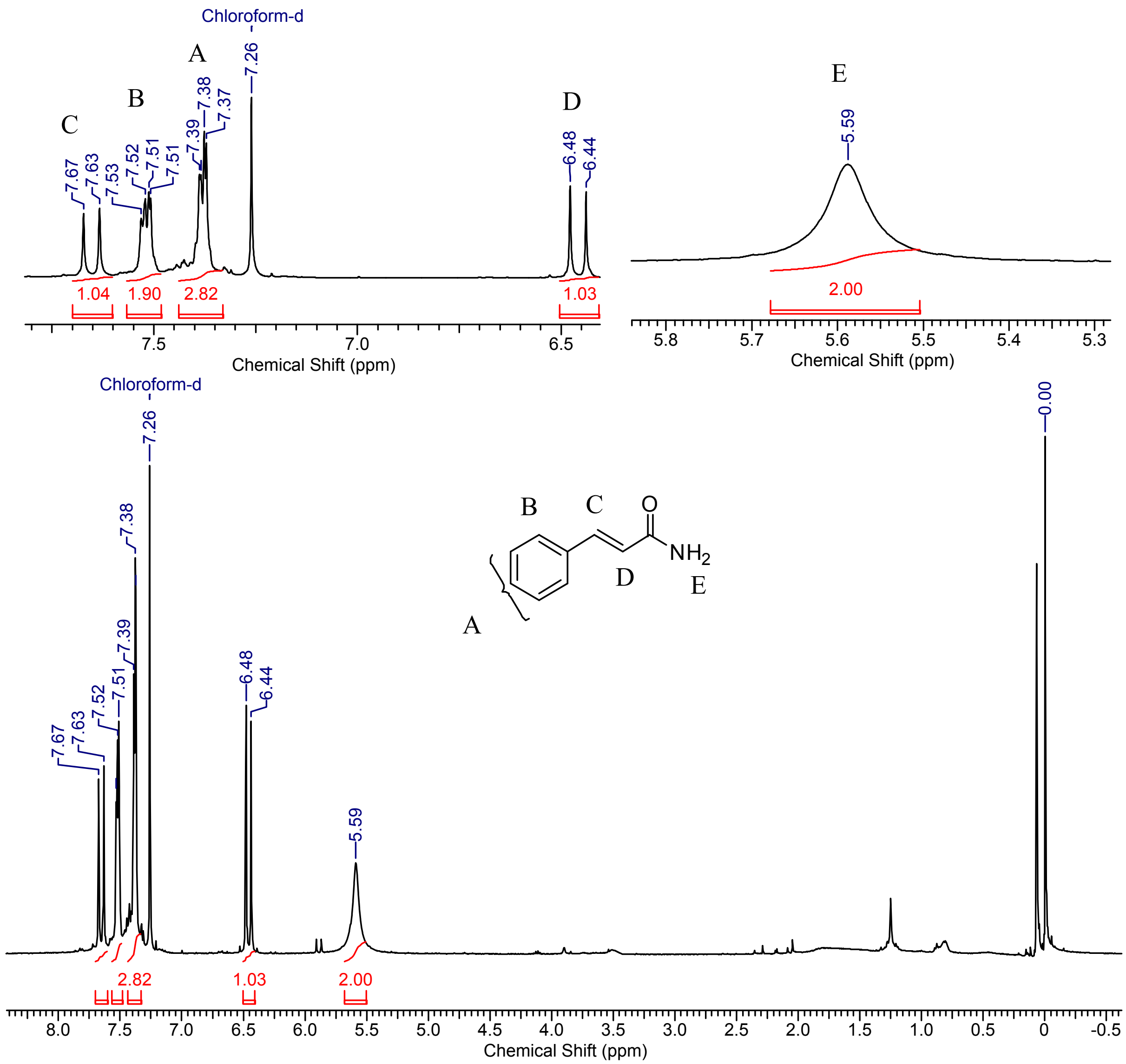
Chemical Shift (ppm)
2.01
2.11
4.12
3.13
2.07
Chloroform-d
7.26
5.76
5.52
2.22
2.20
2.18
2.03
1.66
1.64
1.62
1.61
1.59
1.33
1.32
1.31
1.30
1.29
1.24
1.23
0.93
0.90
0.89
0.87
0.05
-0.02
A
B
C
D
E
F
O
H_3C
NH_2

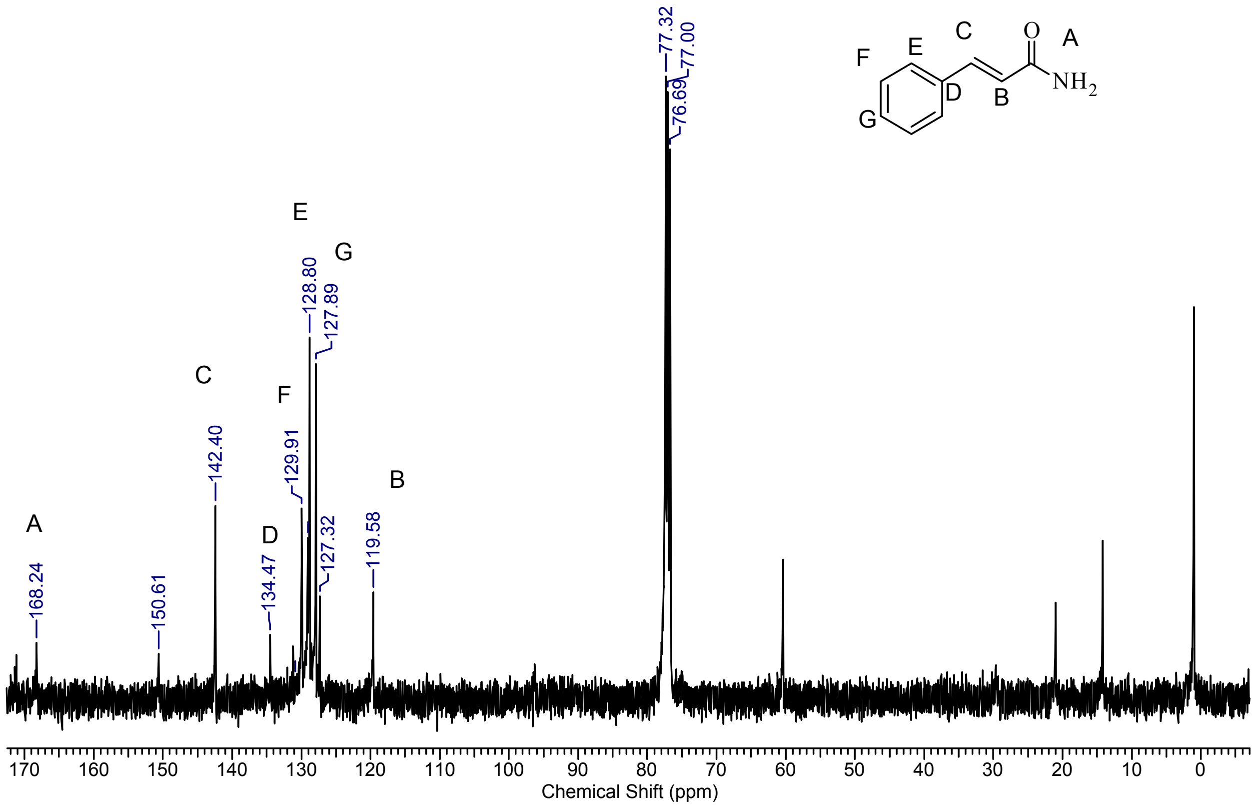

O
NH2
A
B
C
D
E
F
176.37
77.31
77.00
76.68
35.82
31.25
25.12
22.25
13.78
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)



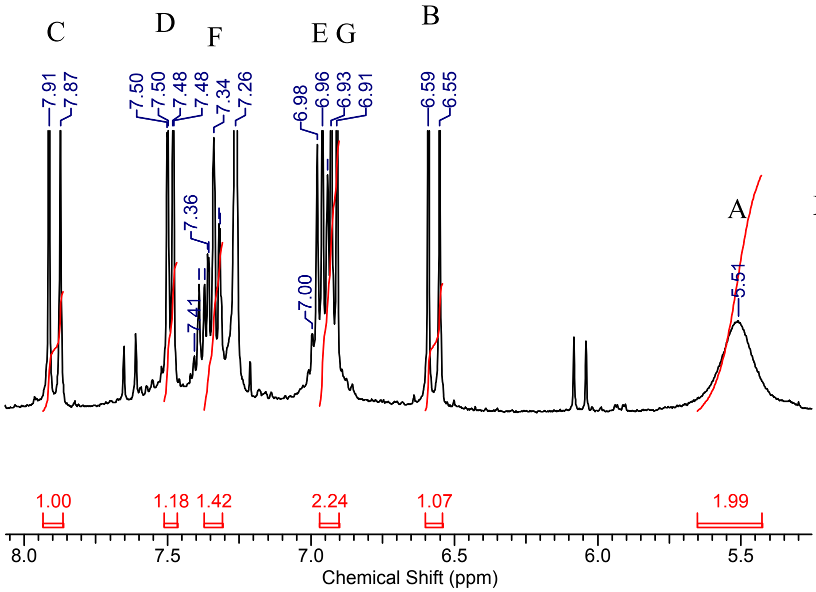
B
C
E
D
A
O
NH_2
1.00
2.07
3.93
4.23
Chemical Shift (ppm)
7.26
E
5.42
3.49
A
B
C, D
1.63
1.00
3.93
4.23
Chemical Shift (ppm)

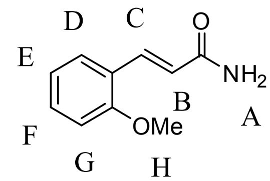

O
NH2
A
B
C
D
E
77.31
77.00
76.68
179.08
163.29
60.36
36.53
29.61
25.81
25.61
25.33
25.16
20.99
14.13
0.96
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical Shift (ppm)

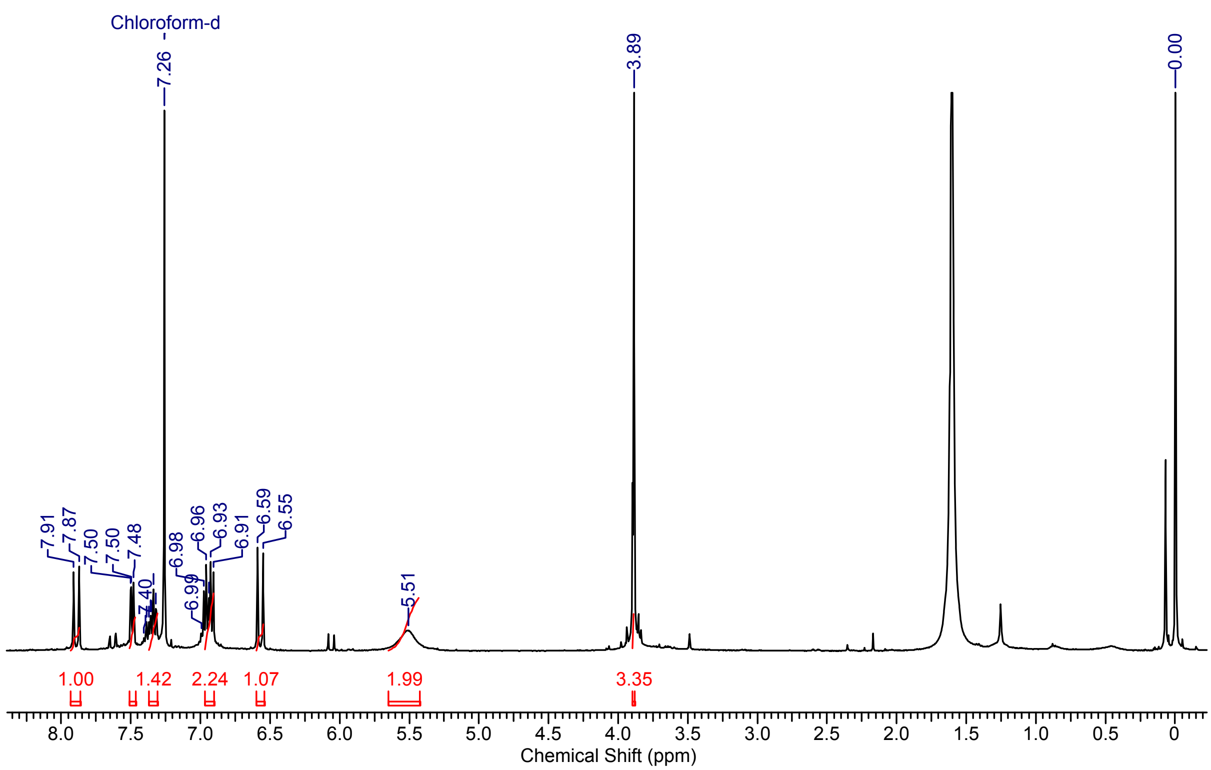

Chloroform-d
7.26
A
B
C
D
E
7.67
7.63
7.53
7.52
7.51
7.51
7.39
7.38
7.37
6.48
6.44
5.59
1.04
1.90
2.82
1.03
2.00
0.00
O
NH2
Chemical Shift (ppm)



F
E
C
O
A
NH2
D
B
G
A
168.24
150.61
C
142.40
D
134.47
F
129.91
E
128.80
G
127.89
127.32
B
119.58
77.32
77.00
76.69
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)


C D F E G B
7.91 7.87 7.50 7.50 7.48 7.48 7.34 7.26 7.36 7.41
7.00 6.98 6.96 6.93 6.91 6.59 6.55
A
5.51
1.00 1.18 1.42 2.24 1.07 1.99
8.0 7.5 7.0 6.5 6.0 5.5
Chemical Shift (ppm)


D
C
O
E
NH2
B
A
F
OMe
G
H


Chloroform-d
7.26
3.89
0.00
7.91 7.87 7.50 7.50 7.48 6.98 6.96 6.93 6.91 6.59 6.55
7.40 6.99
5.51
1.00 1.42 2.24 1.07 1.99 3.35
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 0
Chemical Shift (ppm)