Electronic Supplementary Information

Cu(0) nanoparticle catalyzed efficient reductive cleavage of isoxazoline, carbonyl azide and domino cyclization in water medium

Krishnanka S. Gayen,[a] Tista Sengupta,[a] Yasmin Saima,[a] Adita Das,[a] Dilip K. Maiti[a]* and Atanu Mitra[b]*

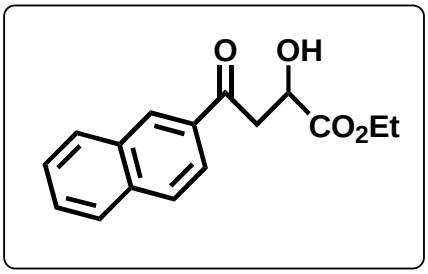
[a]Department of Chemistry, University of Calcutta, University College of Science, 92, A. P. C. Road, Kolkata-700009 and [b]Sree Chaitanya College, Habra-743268, India

*Corresponding author. Fax: 91-33-2351-9755, Tel: 91-33-2350-1014
maitidk@yahoo.com; mitatanu@gmail.com

1. General procedure for Cu-NPs catalyzed reductive hydrolysis of Δ^2-isoxazolines (2): In a 50 ml RB, Δ^2-isoxazoline (1 mmol) was taken, to it 1.5 mL 0.04 (M) $CuSO_4$ (0.006 mmol) solution was added followed by the addition of 23.5 mL distilled water. It was degassed with Argon for 20 mins. SDS (43 mg) and ascorbic acid (175 mg, 1 mmol) were added and sonicated under argon atmosphere for 5 mins. The content of the reaction mixture was heated at 60 °C until completion of the reaction. Progress of the reaction was monitored by TLC. The reaction mixture became transparent after completion of the reaction without deposition of any precipitate. The organic compound was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was concentrated in a rotary evaporator under reduced pressure at room temperature. The crude product was chromatographed on silica gel (60-120 mesh) and eluted with ethyl acetate-petroleum ether. Thus, reaction with 3-naphthyl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (1a, 1 mmol) afforded 2-hydroxy-4-naphthyl-4-oxobutyric acid ethyl ester (2a) after processing in an isolated yield of 84 % (228 mg, 0.84 mmol).

2. Characterization data of β-hydroxy-ketones (2a-h)

4-(2-Naphthyl)-2-hydroxy-4-oxobutyric acid ethyl ester (2a)



(2a)

Yield: 84% (228 mg, 0.84 mmol).

Characteristic**:** Yellow liquid.

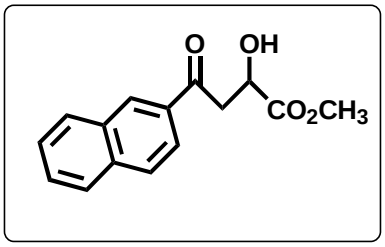
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.34 (3H, t, *J* = 6.9 Hz), 3.66-3.71 (2H, m), 4.33 (2H, q, *J* = 6.9 Hz), 4.76 (1H, m), 7.58-7.69 (2H, m), 7.69-8.17 (4H, m), 8.74 (1H, s).

^{13}CNMR(75MHz,$CDCl_3$):δ 14.1, 42.3, 61.9, 67.3, 123.6, 126.9, 127.8, 128.6, 128.8, 129.6, 130.2, 132.4, 133.8, 135.8, 173.9, 197.5.

FT-IR (neat, cm^{-1}): 1085, 1365, 1590, 1688, 1735, 2985, 3478.

HR-MS (*m*/*z*) for $C_{16}H_{16}O_4$ (M^+): Calculated 272.1049, found 272.1047.

4-(2-Naphthyl)-2-hydroxy-4-oxobutyric acid methyl ester (2b)



(2b)

Yield: 89% (230 mg, 0.89 mmol).

Characteristic**:** Yellow liquid.

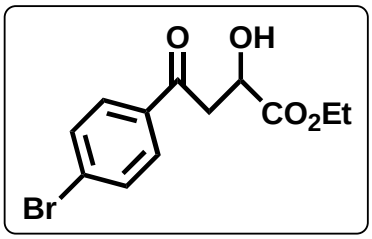
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.49-3.67 (2H, m), 3.77 (3H, s), 4.66-4.69 (1H, m), 7.50-7.58 (2H, m), 7.80-7.96 (4H, m), 8.40 (1H, s).

^{13}C NMR (75MHz, $CDCl_3$):
δ 42.2, 52.7, 67.3, 123.5, 126.9, 127.8, 128.6, 128.7, 129.6, 130.1, 132.4, 133.7, 135.8, 174.1, 197.5.

FT-IR (neat, cm^{-1}): 1627, 1679, 1741, 2851, 2922, 3445.

HR-MS (*m*/*z*) for $C_{15}H_{14}O_4$ (M^+): Calculated 258.2692, found 258.2690.

4-(4-Bromophenyl)-2-hydroxy-4-oxobutyric acid ethyl ester (2c)



(2c)

Yield: 88% (265 mg, 0.88 mmol).

Characteristic**:** Yellow liquid.

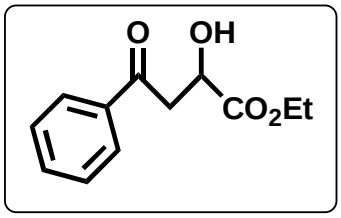
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, t, *J* = 7.2 Hz), 3.29 (1H, d, *J* = 5.4 Hz), 3.37-3.54 (2H, m), 4.28 (2H, q, *J* = 7.2 Hz), 4.65 (1H, d, *J* = 3.9 Hz), 7.63 (2H, d, *J* = 8.7 Hz), 7.82 (2H, d, *J* = 8.7 Hz).

^{13}CNMR(75MHz,$CDCl_3$):δ 14.1, 42.1, 61.9, 67.1, 128.9, 129.6, 132.0, 135.2, 173.6,196.4.

FT-IR (neat, cm^{-1}): 1110, 1361, 1450, 1671, 1725, 2963, 3450.

HR-MS (*m*/*z*) for $C_{12}H_{13}O_4Br$ (M^+): Calculated 299.9997, found 299.9990 (one of the peaks).

4-Phenyl-2-hydroxy-4-oxobutyric acid ethyl ester (2d)



(2d)

Yield: 79% (175 mg, 0.79 mmol).

Characteristic**:** Yellow liquid.

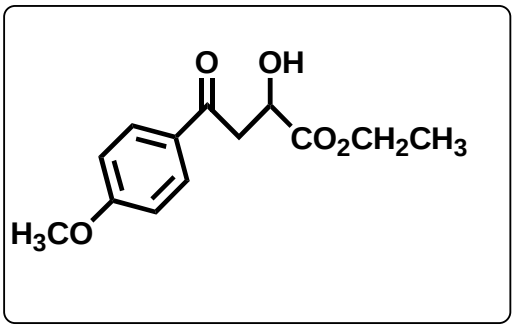
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, t, *J* = 7.2 Hz), 3.48-3.58 (2H, m), 4.28 (2H, q, *J* = 6.9 Hz), 4.66 (1H, dd, *J* = 4.2, 5.7 Hz), 7.46 -7.51 (2H, m), 7.58-7.63 (1H, m), 7.87 (2H, d, *J* = 7.2 Hz).

^{13}C NMR(75MHz,$CDCl_3$):δ 14.1, 42.2, 61.9, 67.3, 128.1, 128.7, 133.5, 136.5, 173.7 , 197.5.

FT-IR (neat, cm^{-1}): 1039, 1096, 1205, 1367, 1449, 1597, 1683, 1733, 2982, 3481.

HR-MS (*m*/*z*) for $C_{12}H_{14}O_4$ (M^+): Calculated 222.0892, found 222.0891.

4-(4-Methoxyphenyl)-2-hydroxy-4-oxobutyric acid ethyl ester (2e)



(2e)

Yield: 83% (209 mg, 0.83 mmol).

Characteristic**:** Yellow liquid.

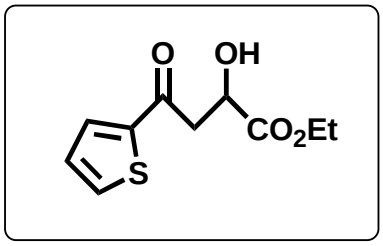
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.2 Hz), 3.30-3.47 (2H, m), 3.81 (3H, s), 4.20 (2H, q, *J* = 7.2 Hz) 4.56-4.59 (1H, m), 6.88 (2H, dd, *J* = 2.1, 6.9 Hz), 7.87 (2H, dd, *J* = 2.1, 6.9 Hz).

^{13}C NMR (75MHz, $CDCl_3$):
δ 14.1, 41.7, 55.5, 61.7, 67.4, 108.5, 113.8, 129.6, 130.5, 163.9, 173.7, 196.1.

FT-IR (neat, cm^{-1}): 1027, 1175, 1258, 1602, 1732, 2932, 3446.

HR-MS (*m*/*z*) for $C_{13}H_{16}O_5$ (M^+): Calculated 252.0998, found 252.0996.

2-Hydroxy-4-oxo-4-thiophen-2-yl-butyric acid ethyl ester (2f)



(2f)

Yield: 82% (187 mg, 0.82 mmol).

Characteristic**:** Yellow liquid.

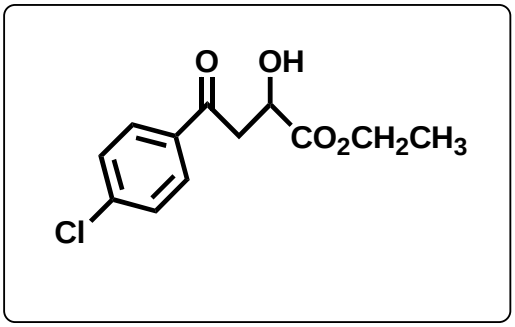
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21 (3H, t, *J* = 7.2 Hz), 3.27-3.44 (2H, m), 4.2 (2H, q, *J* = 7.2 Hz), 4.55-4.59 (1H, m), 7.06-7.09 (2H, m), 7.61 (1H, d, *J* = 4.8 Hz), 7.67 (1H, d, *J* = 3.6 Hz).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.0, 42.8, 61.9, 67.3, 128.1, 132.6, 134.4, 143.7, 173.5, 190.0.

FT-IR (neat, cm^{-1}): 1416, 1659, 1736, 2926, 2982, 3446.

HR-MS (*m*/*z*) for $C_{10}H_{12}O_4S$ (M^+): Calculated 228.2649, found 228.2647.

4-(4-Chlorophenyl)-2-hydroxy-4-oxobutyric acid ethyl ester (2g)



(2g)

Yield: 81% (207 mg, 0.81 mmol).

Characteristic**:** Yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (3H, t, *J* = 7.2 Hz), 3.31-3.48 (2H, m), 4.21 (2H, q, *J* = 7.2 Hz), 4.58 (1H, dd, *J* = 3.9, 6.0 Hz), 7.39 (2H, d, *J* = 8.4 Hz), 7.83 (2H, d, *J* = 8.4 Hz).

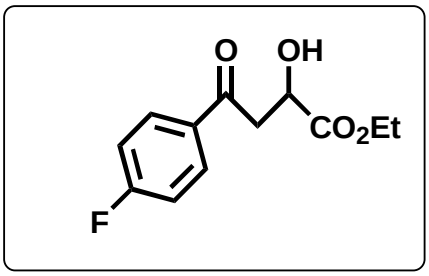
^{13}C NMR (75MHz, $CDCl_3$): δ 14.1, 42.1, 61.9, 67.1, 129.0, 129.5, 134.8, 140.1, 173.6,

196.2.

FT-IR (neat, cm^{-1}): 1214, 1401, 1590, 1684, 1738, 2926, 2982, 3435.

HR-MS (*m*/*z*) for $C_{12}H_{13}ClO_4$ (M^+): Calculated 256.0502, found 256.0501 (one of the peaks).

4-(4-Fluorophenyl)-2-hydroxy-4-oxobutyric acid ethyl ester (2h)



(2h)

Yield: 83% (199 mg, 0.83 mmol).

Characteristic**:** Yellow liquid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (3H, t, *J* = 7.2 Hz), 3.37-3.42 (2H, m), 4.21 (2H, q, *J* = 7.2 Hz), 4.56-4.59 (1H, m), 7.08 (2H, t, *J* = 8.7 Hz), 7.89-7.94 (2H, m).

^{13}C NMR (75MHz, $CDCl_3$): δ 14.1, 42.0, 61.9, 67.2, 115.7, 116.0, 130.8, 130.9, 132.9,

173.6, 195.8.

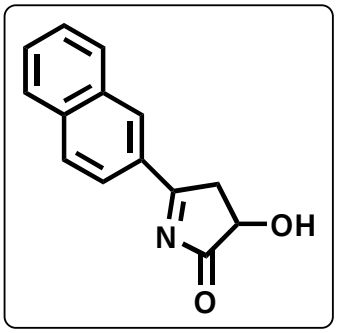
FT-IR (neat, cm^{-1}): 1598, 1684, 1737, 2853, 2924, 3432.

HR-MS (*m*/*z*) for $C_{12}H_{13}O_4F$ (M^+): Calculated 240.2276, found 240.2275.

3. General procedure for the synthesis of 3-hydroxy-5-substituted-3,4-dihydropyrrol-2-one (3): In a 50 ml RB, Δ^2-isoxazolines (1 mmol) was taken, to it 1.5 mL 0.04 (M) $CuSO_4$ (0.006 mmol) solution was added followed by the addition of 23.5 mL distilled water. It was degassed with Argon for 20 mins. SDS (43 mg) and ascorbic acid (175 mg, 1 mmol) were added and sonicated under argon atmosphere for 5 mins. The content of the reaction mixture was heated at 80 °C until completion of the reaction. Progress of the reaction was monitored by TLC. The reaction mixture became transparent after completion of the reaction without deposition of any precipitate. The organic compound was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was concentrated in a rotary evaporator under reduced pressure at room temperature. The crude product was chromatographed on silica gel (60-120 mesh) and eluted with ethyl acetate-petroleum ether. Thus, reaction with 3-naphthyl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (**1a**, 1mmol) afforded 3-Hydroxy-5-naphthalen-2-yl-3,4-dihydropyrrol-2-one (**3a**) after processing in an isolated yield of 89 % (200 mg, 0.89 mmol).

4. Characterization data of γ-Hydroxy pyrrolinones (3a-g)

3-Hydroxy-5-naphthalen-2-yl-3,4-dihydropyrrol-2-one (3a)



(3a)

Yield: 89%[a] (200 mg, 0.89 mmol); 88% (198 mg, 0.88 mmol).[b]

Characteristic**:** Yellow liquid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.76-2.98 (2H, m), 4.31 (1H, dd, *J* = 6.9, 11.4 Hz), 6.66-6.69 (2H, m), 6.96-7.10 (4H, m), 7.26 (1H, s).

^{13}C NMR (75 MHz, DMSO-d_6) :
δ 38.8, 78.4, 123.6, 126.6, 127.3, 127.8, 128.0, 128.1, 128.8, 128.9, 133.1, 134.0, 156.7,

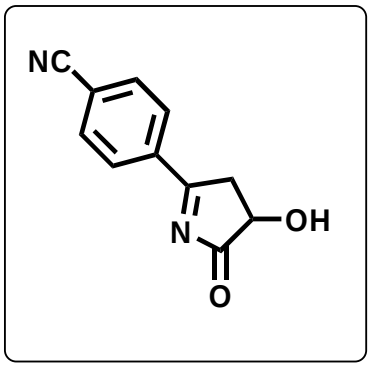
172.0.

FT-IR (neat, cm^{-1}): 1230, 1727, 2928, 3427.

HR-MS (*m*/*z*) for $C_{14}H_{11}NO_2$ (M^+): Calculated 225.0790, found 225.0788 (one of the peaks).

a: when 1a is the starting material, and **b**: when 1b is the starting material.

5-(4-Cyanophenyl)-3-hydroxy-3,4-dihydropyrrol-2-one (3b)



(3b)

Yield: 88% (176 mg, 0.88 mmol).

Characteristic**:** Yellow viscous liquid.

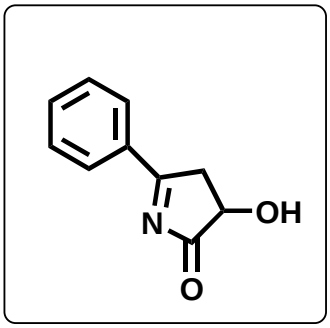
^{1}H NMR (300 MHz, DMSO-d_6): δ 3.57-3.81 (2H, m), 5.25 (1H, dd, *J* = 6.9 Hz, 11.7 Hz), 7.86 (1H, d, *J* = 8.4 Hz), 7.92 (1H, d, *J* = 8.7 Hz).

^{13}C NMR (75 MHz, DMSO-d_6): δ 38.3, 78.9, 113.0, 127.1, 127.9, 129.1, 133.2, 155.9, 171.6.

FT-IR (neat, cm^{-1}): 1406, 1727, 2925, 3433.

HR-MS (*m*/*z*) for $C_{11}H_8N_2O_2$ (M^+): Calculated 200.0586, found 200.0585.

3-Hydroxy-5-phenyl-3,4-dihydropyrrol-2-one (3c)



(3c)

Yield: 85% (149 mg, 0.85 mmol).

Characteristic**:** Pale yellow liquid.

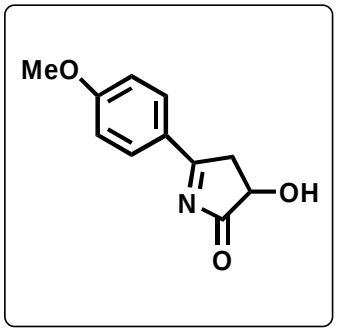
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65-3.73 (2H, m), 5.22 (1H, dd, *J* = 7.8, 9.9 Hz), 7.38-7.47 (3H, m), 7.67 (2H, dd, *J* = 2.1, 7.8 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 39.3, 77.2, 127.0, 128.0, 128.9, 130.9, 156.6, 162.3.

FT-IR (neat, cm^{-1}): 1228, 1717, 2924, 3440.

HR-MS (*m*/*z*) for $C_{10}H_9NO_2$ (M^+): Calculated 175.0633, found 175.0631.

5-(4-Methoxyphenyl)-3-hydroxy-3,4-dihydropyrrol-2-one (3d)



(3d)

Yield: 83% (170 mg, 0.83 mmol).

Characteristic**:** Pale yellow liquid.

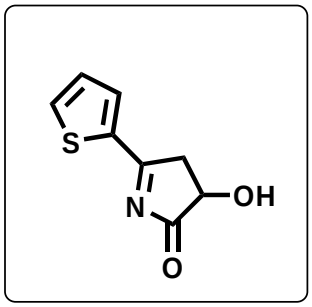
^{1}H NMR (300 MHz, DMSO-d_6): δ 3.45-3.70 (2H, m), 3.76 (3H, s), 5.07 (1H, dd, *J* = 6.9 Hz, 11.7 Hz), 6.97 (2H, d, *J* = 8.7 Hz), 7.59 (2H, d, *J* = 9.0 Hz).

^{13}C NMR (75 MHz, DMSO-d_6) : δ 42.5, 55.8, 77.9, 114.7, 121.5, 128.8, 155.9, 161.3, 172.1.

FT-IR (neat, cm^{-1}): 1423, 1639, 1735, 2926, 3433.

HR-MS (*m*/*z*) for $C_{11}H_{11}NO_3$ (M^+): Calculated 205.0739, found 205.0737.

3-Hydroxy-5-thiophen-2yl-3,4-dihydropyrrol-2-one (3e)



(3e)

Yield: 85% (154 mg, 0.85 mmol).

Characteristic**:** Pale yellow liquid.

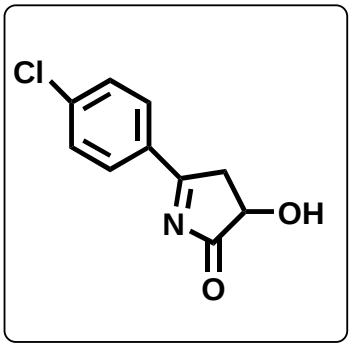
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.71-3.74 (2H, m), 5.21 (1H, dd, *J* = 8.1 Hz, 9.6 Hz), 7.07-7.09 (1H, m), 7.27 (1H, s), 7.44 (1H, dd, *J* = 1.2 Hz, 5.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 30.8, 40.0, 127.4, 129.3, 129.5, 130.1, 152.3, 206.9.

FT-IR (neat, cm^{-1}): 1231, 1436, 1732, 2852, 2925, 3422.

HR-MS (*m*/*z*) for $C_8H_7NO_2S$ (M^+): Calculated 181.0197, found 181.0196.

5-(4-Chlorophenyl)-3-hydroxy-3,4-dihydropyrrol-2-one (3f)



(3f)

Yield: 81% (169 mg, 0.81 mmol).

Characteristic**:** Pale yellow liquid.

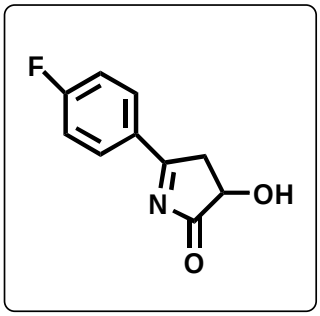
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.61-2.85 (2H, m), 4.29 (1H, dd, *J* = 6.9, 11.7 Hz), 6.64 (2H, d, *J* = 8.4 Hz), 6.82 (2H, d, *J* = 8.4 Hz).

^{13}C NMR (75 MHz, DMSO-d_6) : δ 38.7, 78.5, 127.9, 129.0, 129.4, 135.4, 155.8, 171.9.

FT-IR (neat, cm^{-1}): 1108, 1235, 1419, 1626, 2923, 3426.

HR-MS (*m*/*z*) for $C_{10}H_8NO_2Cl$ (M^+): Calculated 209.0244, found 209.0242 (one of the peaks).

5-(4-Fluorophenyl)-3-hydroxy-3,4-dihydropyrrol-2-one (3g)



(3g)

Yield: 80% (155 mg, 0.80 mmol).

Characteristic**:** Pale yellow liquid.

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.45-3.74 (2H, m), 5.13 (1H, dd, *J* = 6.9, 11.7 Hz), 7.23-7.29 (2H, m), 7.68-7.73 (2H, m).

^{13}C NMR (75 MHz, DMSO-d_6) : δ 78.3, 116.2, 116.5, 125.7, 129.5, 129.6, 155.7, 161.9, 165.2, 172.0.

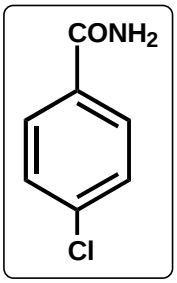
FT-IR (neat, cm^{-1}): 1158, 1352, 1414, 1513, 1603, 1725, 2372.

HR-MS (*m*/*z*) for $C_{10}H_8NO_2F$ (M^+): Calculated 193.0539, found 193.0537 (one of the peaks).

5. General procedure for synthesis of primary amide: In a 50 ml RB, carbonyl azide (1 mmol) was taken, to it 50 µL 0.04 (M) $CuSO_4$ (0.002 mmol) solution was added followed by the addition of 23.5 mL distilled water. It was degassed with Argon for 20 mins. SDS (43 mg) and ascorbic acid (175 mg, 1 mmol) were added and sonicated under argon atmosphere for 5 mins. The content of the reaction mixture was heated at 60 °C until completion of the reaction. Progress of the reaction was monitored by TLC. The reaction mixture became transparent after completion of the reaction without deposition of any precipitate. The organic compound was extracted with ethyl acetate (3 x 10 mL). The combined organic layer was concentrated in a rotary evaporator under reduced pressure at room temperature. The crude product was chromatographed on silica gel (60-120 mesh) and eluted with ethyl acetate-petroleum ether. Thus, reaction with 4-chlorobenzoylazide (**4a**, 181 mg, 1mmol) afforded 4-chlorobenzamide (**5a**) after processing in an isolated yield of 95 % (147 mg, 0.95 mmol).

6. Characterization data of primary amides (5a-j)

4-Chlorobenzamide (5a)



(**5a**)

Yield: 95 % (148 mg, 0.95 mmol).

Characteristic: Pale yellow solid

Melting point: 180 °C

^{1}H NMR (300 MHz, DMSO-d_6): δ 7.51 (2H, d, *J* = 9.0 Hz), 7.87 (2H, d, *J* = 8.4 Hz), 8.04 (2H, s)

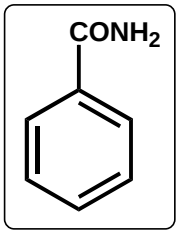
^{13}C NMR (75 MHz, DMSO-d_6): δ 128.7, 129.8, 133.5, 136.5, 167.2

FT-IR (KBr, cm^{-1}): 1085, 1403, 1655, 2367, 3180, 3370

EI-MS (m/z): 157 (M+2), 155 (M^+), 141, 139, 113, 111

HR-MS (*m*/*z*) for C_7H_6NOCl (M^+): Calculated 155.0138, found 155.0160 (one of the peaks).

Benzamide (5b)



(5b)

Yield: 85 % (103 mg, 0.85 mmol).

Characteristic: White solid.

Melting point: 126 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.09 (2H, bs), 7.25-7.55 (3H, m), 7.79-7.83 (2H, m).

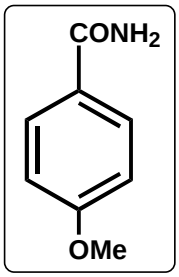
^{13}C NMR (75 MHz, $CDCl_3$): δ 127.2, 128.5, 131.9, 133.3, 169.3.

FT-IR (KBr, cm^{-1}): 1121, 1400, 1657, 3173, 3369.

EI-MS (m/z): 121 (M^+), 105, 77.

HR-MS (*m*/*z*) for C_7H_7NO (M^+): Calculated 121.0528, found 121.0506.

4-Methoxybenzamide (5c)



(5c)

Yield: 91% (138 mg, 0.91 mmol).

Characteristic: White solid.

Melting point: 167 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.85 (3H, s), 5.87 (2H, bs), 6.93 (2H, d, *J* = 8.7 Hz), 7.78 (2H, d, *J* = 8.7 Hz).

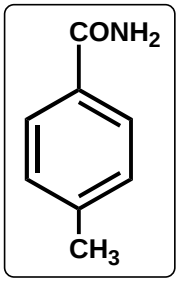
^{13}C NMR (75 MHz, $CDCl_3$): δ 55.2, 113.4, 125.9, 129.4, 162.2, 168.9.

FT-IR (KBr, cm^{-1}): 1021, 1180, 1250, 1392, 1648, 2922, 3169, 3390.

EI-MS (m/z): 151 (M^+), 135, 107.

HR-MS (*m*/*z*) for $C_8H_9NO_2$ (M^+): Calculated 151.0633, found 151.0650.

4-Methylbenzamide (5d)



(5d)

Yield: 90% (121 mg, 0.90 mmol).

Characteristic: White solid.

Melting point: 160 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.25 (3H, s), 7.15 (2H, d, *J* = 7.8 Hz), 7.69 (2H, d, *J* = 8.1 Hz), 7.79 (2H, bs).

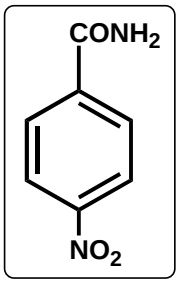
^{13}C NMR (75 MHz, DMSO-d_6): δ 21.3, 127.9, 129.1, 131.9, 141.4, 168.2.

FT-IR (KBr, cm^{-1}): 1350, 1580, 1650, 3300.

EI-MS (m/z): 135 (M^+), 120, 119.

HR-MS (*m*/*z*) for C_8H_9NO (M^+): Calculated 135.0684, found 135.0666.

4-Nitrobenzamide (5e)



(5e)

Yield: 79% (131 mg, 0.79 mmol).

Characteristic: Yellow solid.

Melting point: 200 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82 (1H, bs), 6.07 (1H, bs), 7.92 (2H, d, *J* = 8.7 Hz), 8.25 (2H, d, *J* = 8.7 Hz).

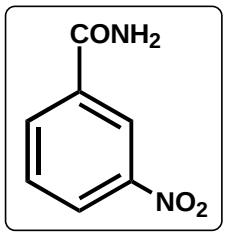
^{13}C NMR (75 MHz, $CDCl_3$): δ 118.1, 128.0, 133.8, 144.5, 172.0.

FT-IR (KBr, cm^{-1}):1010, 1123, 1345, 1527, 1661, 3175, 3371.

EI-MS (m/z): 166 (M^+), 150, 120, 104, 76.

HR-MS (*m*/*z*) for $C_7H_6N_2O_3$ (M^+): Calculated 166.0378, found 166.0390.

3-Nitrobenzamide (5f)



(5f)

Yield: 88% (146 mg, 0.88 mmol).

Characteristic: Pale yellow solid.

Melting point: 140 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.21 (1H, bs), 6.28 (1H, bs), 7.70 (1H, t, *J* = 7.8 Hz), 8.20 (1H, d, *J* = 7.8 Hz), 8.39 (1H, dd, *J* = 5.7, 6.6 Hz), 8.66 (1H, s).

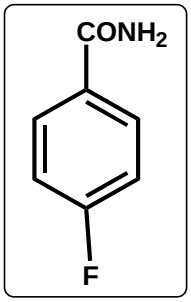
^{13}C NMR (75 MHz, DMSO-d_6): δ 122.6, 126.3, 130.5, 134.2, 136.2, 148.2, 166.1.

FT-IR (KBr, cm^{-1}): 1155, 1326, 1397, 1528, 1596, 1659, 3295.

EI-MS (m/z): 166 (M^+), 150, 120, 104.

HR-MS (*m*/*z*) for $C_7H_6N_2O_3$ (M^+): Calculated 166.0378, found 166.0362.

4-Fluorobenzamide (5g)[1]



(5g)

Yield: 88% (123 mg, 0.88 mmol).

Characteristic**:** White solid.

Melting point: 153 °C.

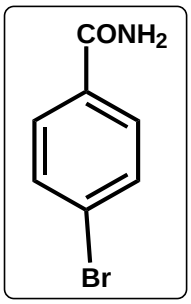
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (2H, bs), 7.16 (2H, d, *J* = 8.7, 6.0 Hz), 7.84 (2H, dd, *J* = 8.7, 6.0 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 116.1, 116.3, 130.1, 130.3, 163.8, 167.2.

FT-IR (KBr, cm^{-1}): 837, 1011, 1071, 1129, 1147, 1389, 1410, 1590, 1623, 1662, 3179, 3360.

HR-MS (*m*/*z*) for C_7H_6FNO (M^+): Calculated 139.0433, found 139.0436 (one of the peaks).

4-Bromobenzamide (5h)[2]



(**5h**)

Yield: 89% (177 mg, 0.89 mmol).

Characteristic**:** White solid.

Melting point: 190-192 °C

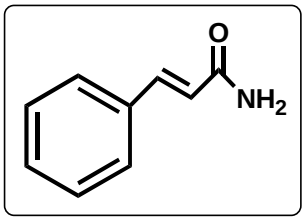
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.82 (2H, br. s, NH), 7.60 (2H, d, *J* = 8.4 Hz), 7.69 (2H, d, *J* = 8.4 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): δ 126.1, 129.0, 131.9, 132.1, 168.2.

FT-IR (KBr, cm^{-1}): 1125, 1162, 1225, 1402, 1416, 1513, 1588, 1623, 1674, 3155, 3327.

HR-MS (*m*/*z*) for C_7H_6BrNO (M^+): Calculated 198.9633, found 198.9639 (One of the peaks).

Cinnamamide (5i)



(5i)

Yield: 85% (125 mg, 0.85 mmol).

Characteristic**:** Yellow solid.

Melting point: 140 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 5.67 (2H, bs), 6.47 (1H, d, *J* = 15.9 Hz), 7.37-7.39 (3H, m), 7.51-7.54 (2H, m), 7.65 (1H, d, *J* = 15.9 Hz).

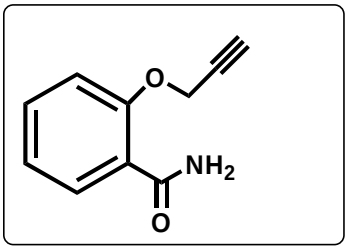
^{13}C NMR (75 MHz, $CDCl_3$): δ 119.4, 127.9, 128.8, 129.9, 134.5, 142.5, 167.6.

FT-IR (KBr, cm^{-1}): 1111, 1242, 1605, 1662, 3171.

EI-MS (m/z): 147 (M^+), 146, 103, 77.

HR-MS (*m*/*z*) for C_9H_9NO (M^+): Calculated 147.0684, found 147.0688.

2-Prop-2-ynyloxybenzamide (5j)



(5j)

Yield: 90% (158 mg, 0.90 mmol).

Characteristic**:** White solid.

Melting point: 138 °C.

^{1}H NMR (300 MHz, DMSO-d_6): δ 3.57 (1H, t, *J* = 2.1 Hz), 4.86 (2H, d, *J* = 2.1 Hz), 6.85-6.94 (2H, m), 7.04-7.07 (1H, m), 8.04 (1H, dd, *J* = 2.7, 7.5 Hz), 8.8 (2H, s).

^{13}CNMR(75MHz, DMSO-d_6):

δ 61.2, 83.7, 84.5, 117.8, 125.0, 126.4, 127.0, 134.4, 151.3, 157.8.

FT-IR (KBr, cm^{-1}): 1016, 1208, 1449, 1544, 1601, 1664, 3288.

HR-MS (*m*/*z*) for $C_{10}H_9NO_2$ (M^+): Calculated 175.0633, found 175.0631.

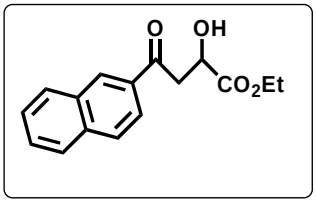
References:

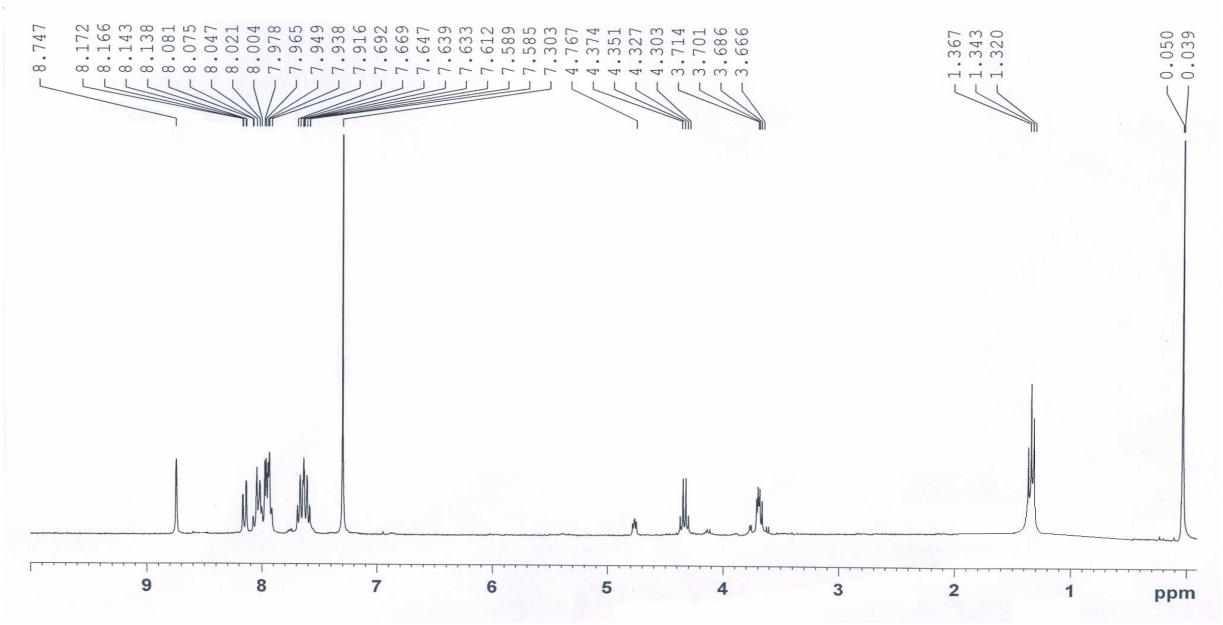
1) L. Cao, J. Ding, M. Gao, Z. Wang, J. Li and A. Wu, *Org. Lett.*, 2009, **11**, 3810.

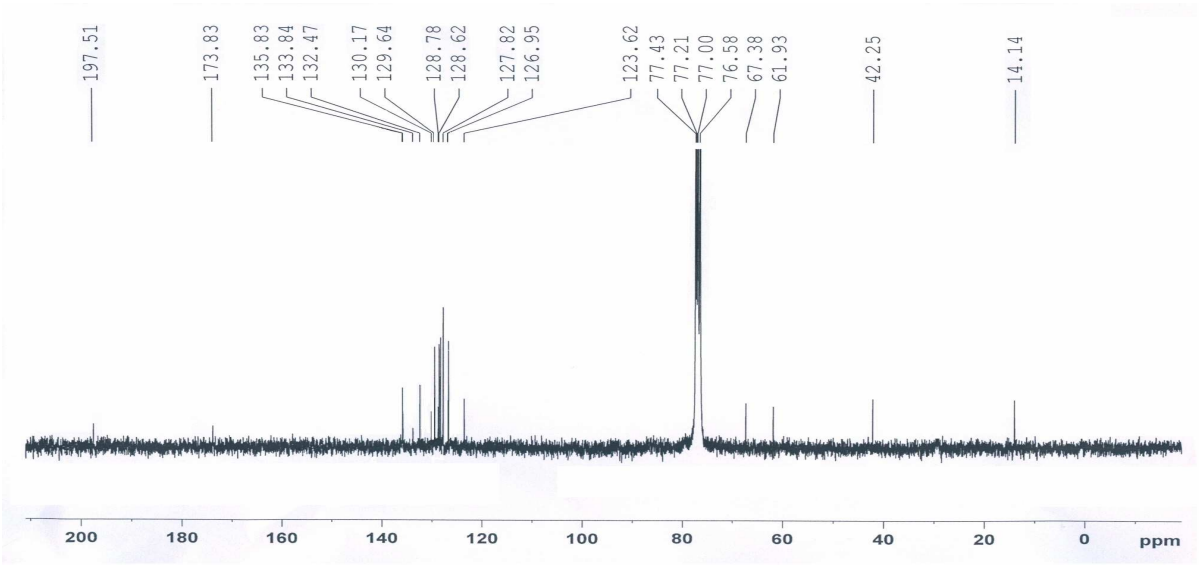
2) L. Zhang, S. Wang, S. Zhou, G. Yang, and E. Sheng, *J. Org. Chem.*, 2006, **71**, 3149.

7. ^{1}H and ^{13}C NMR spectra of compounds (2a-h, 3a-g and 5a-j)

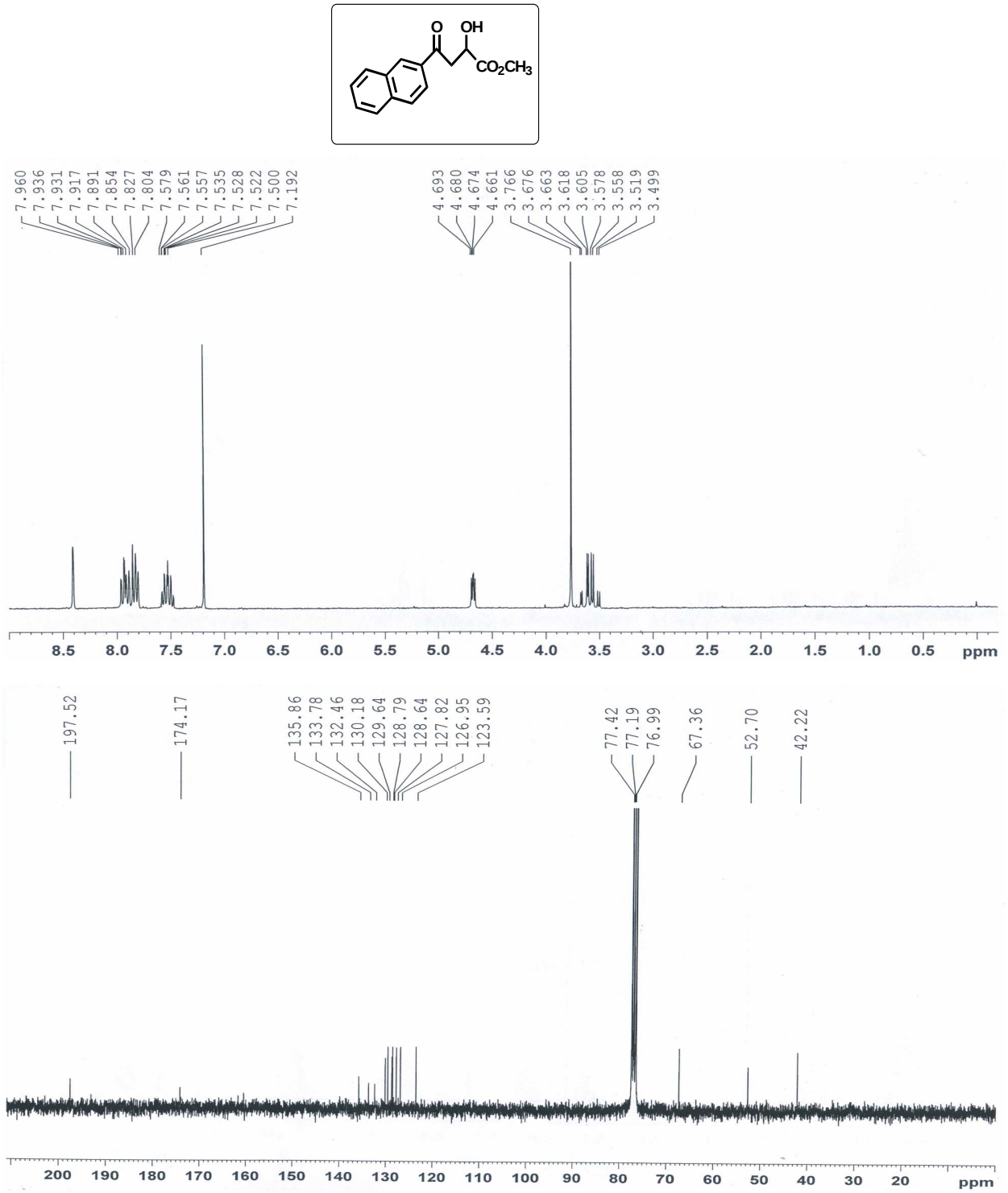
SI Figure 1. ^{1}H & ^{13}C spectrum **2a**



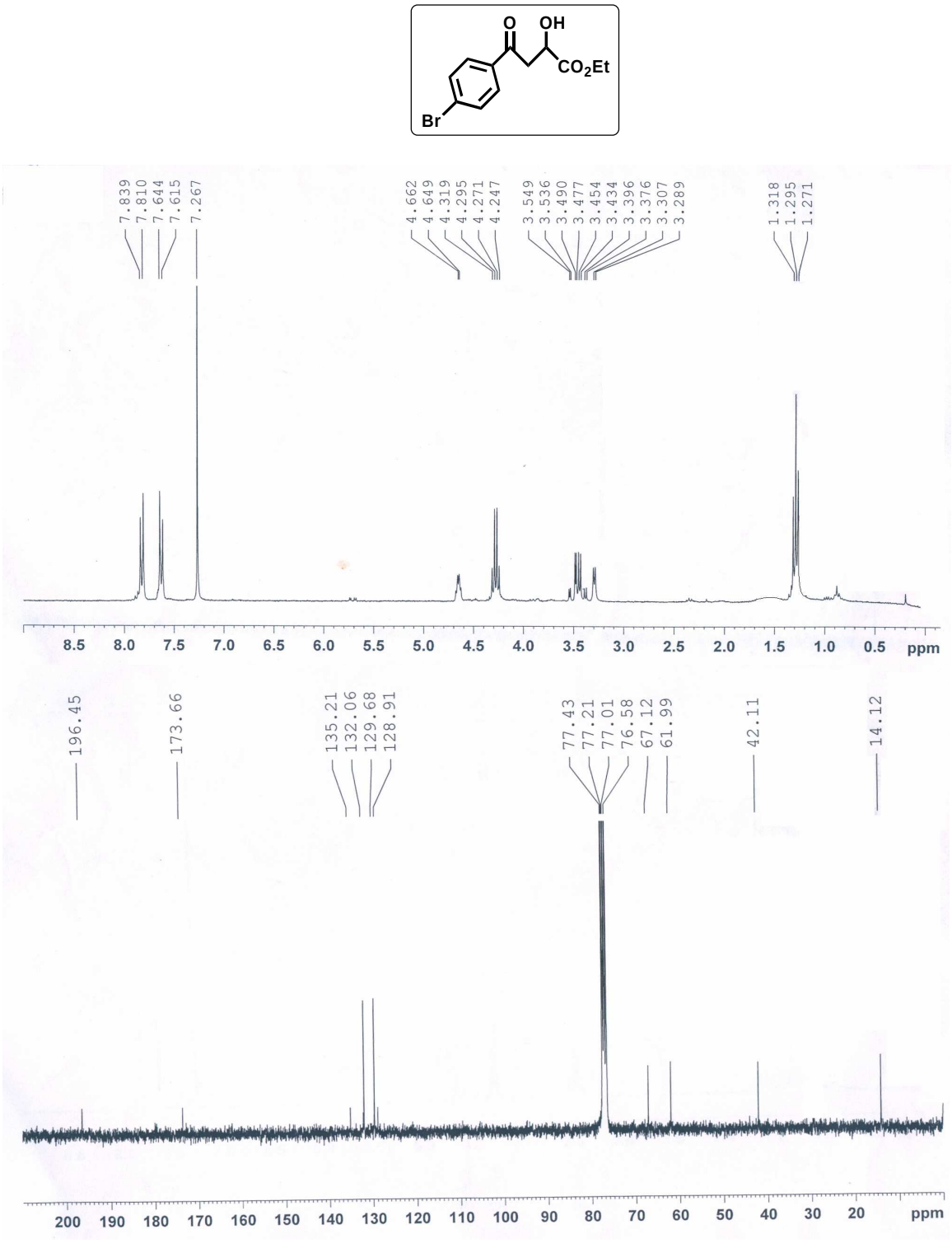




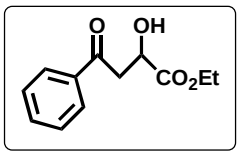
SI Figure 2. ^{1}H & ^{13}C spectrum **2b**

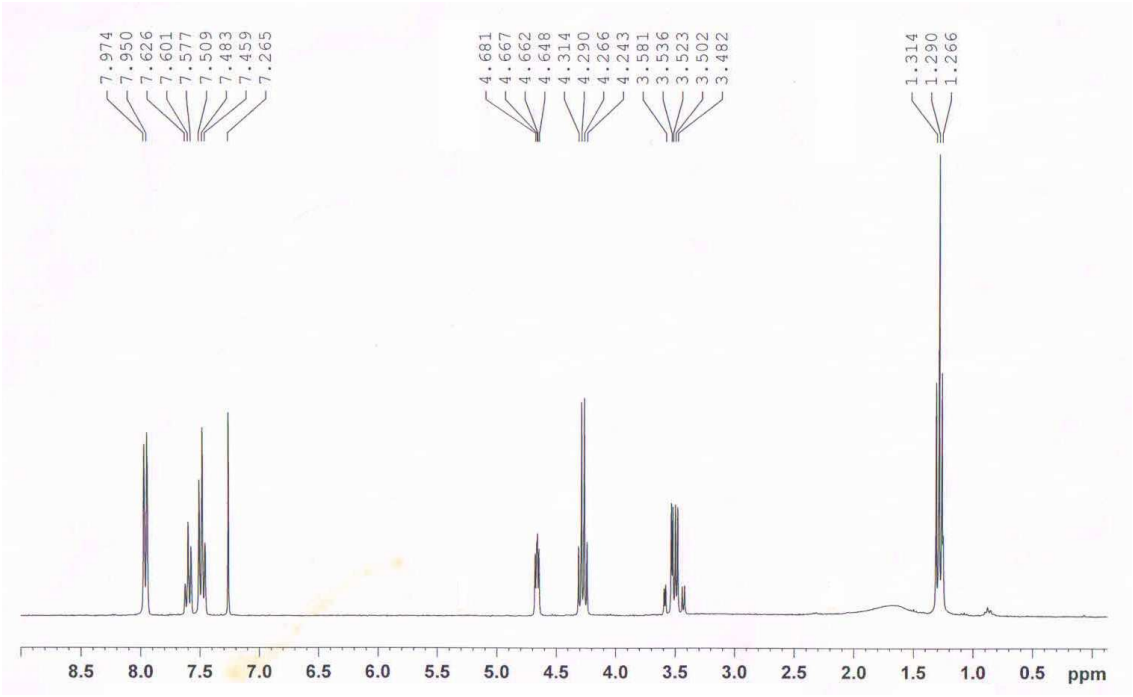


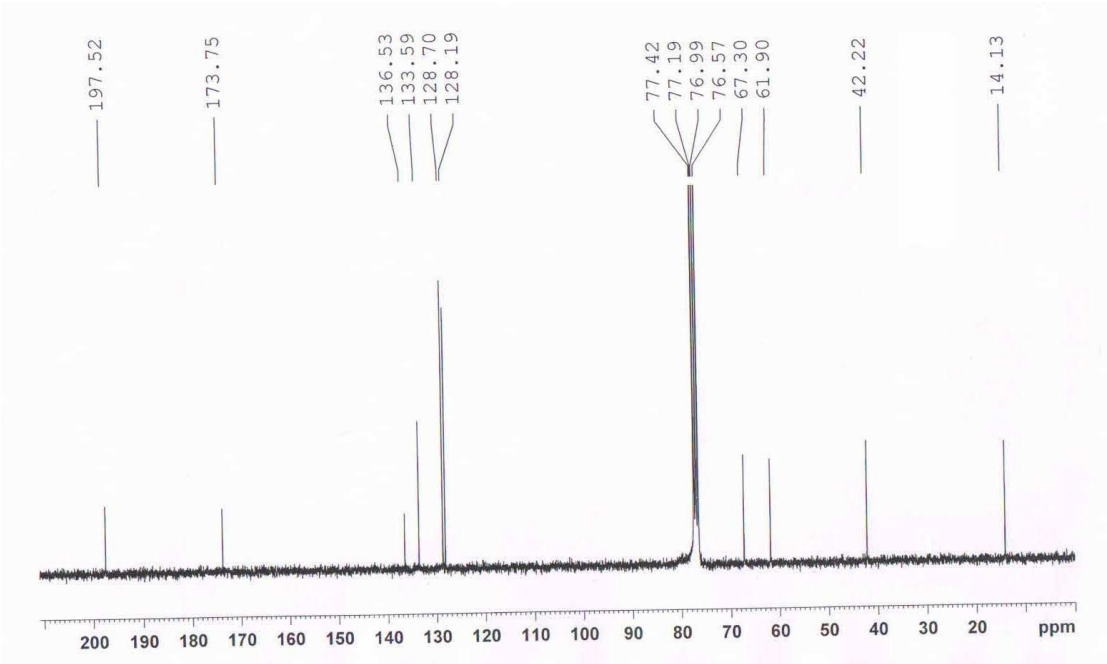
SI Figure 3. ^{1}H & ^{13}C spectrum **2c**



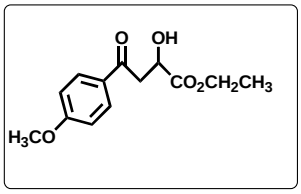
SI Figure 4. ^{1}H spectrum **2d**

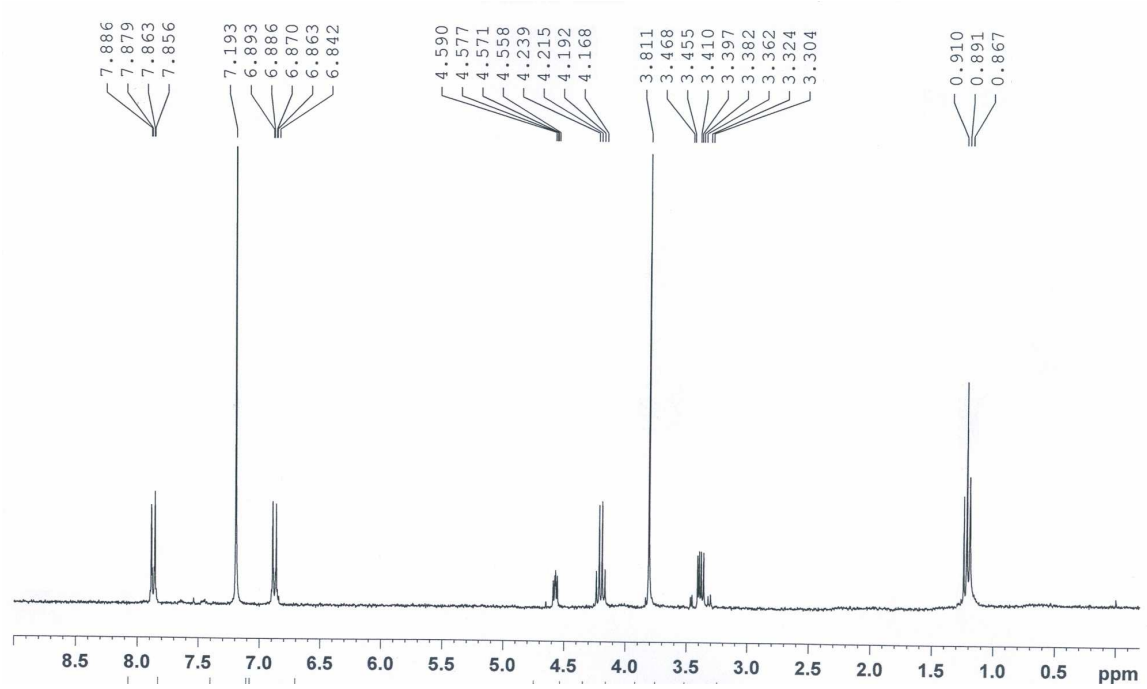


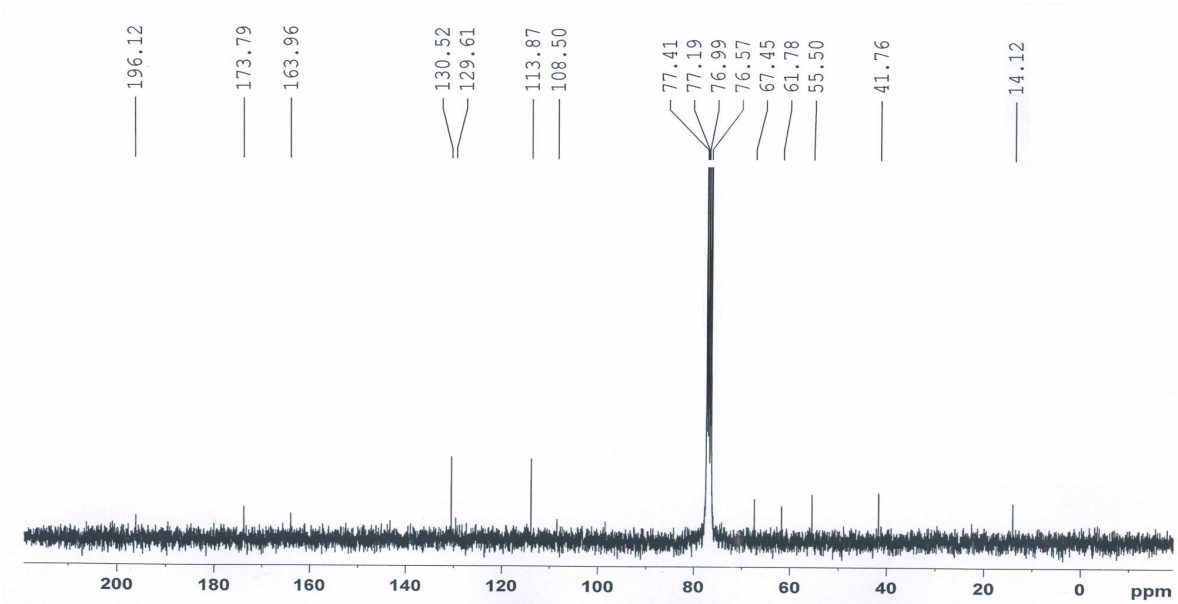




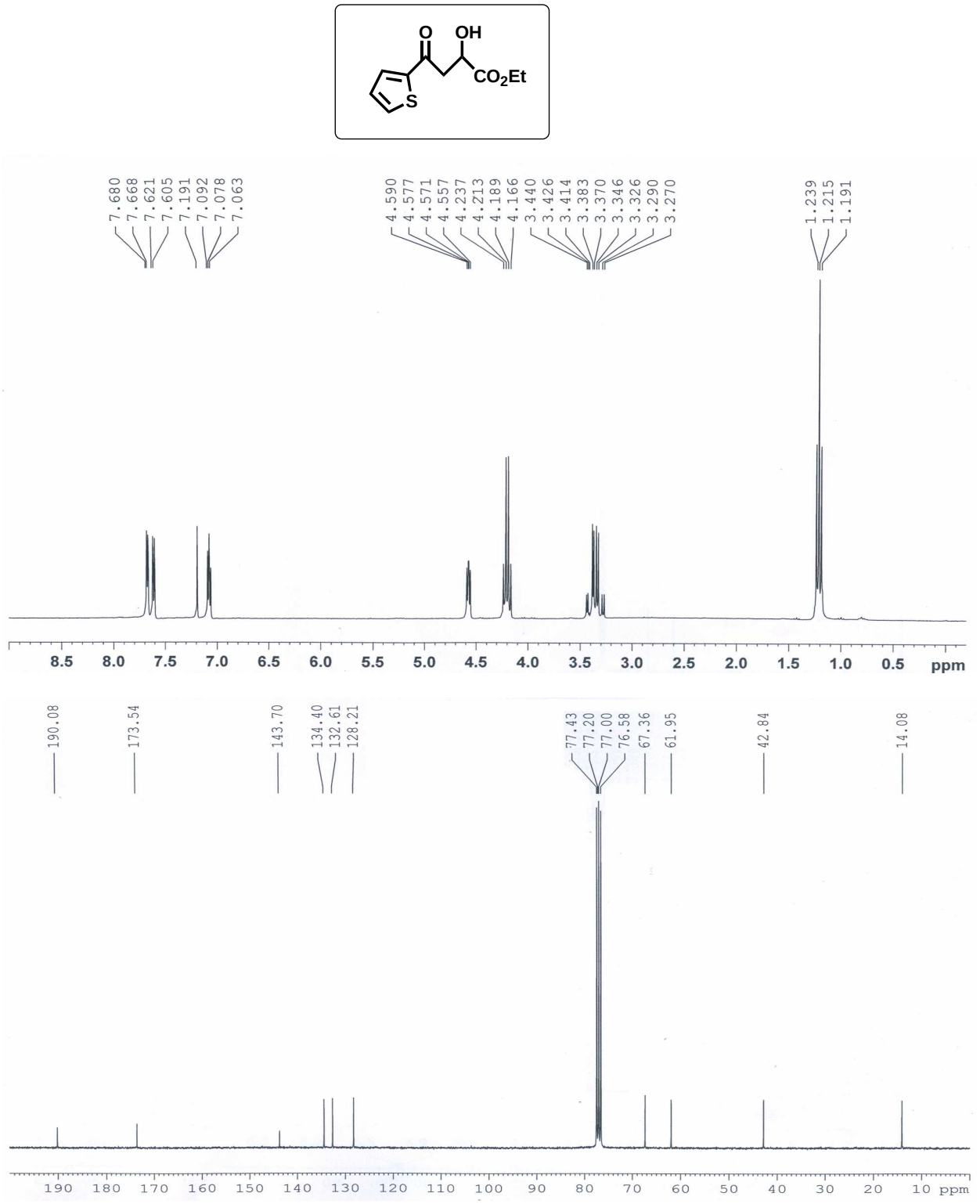
SI Figure 5. ^{1}H & ^{13}C spectrum **2e**



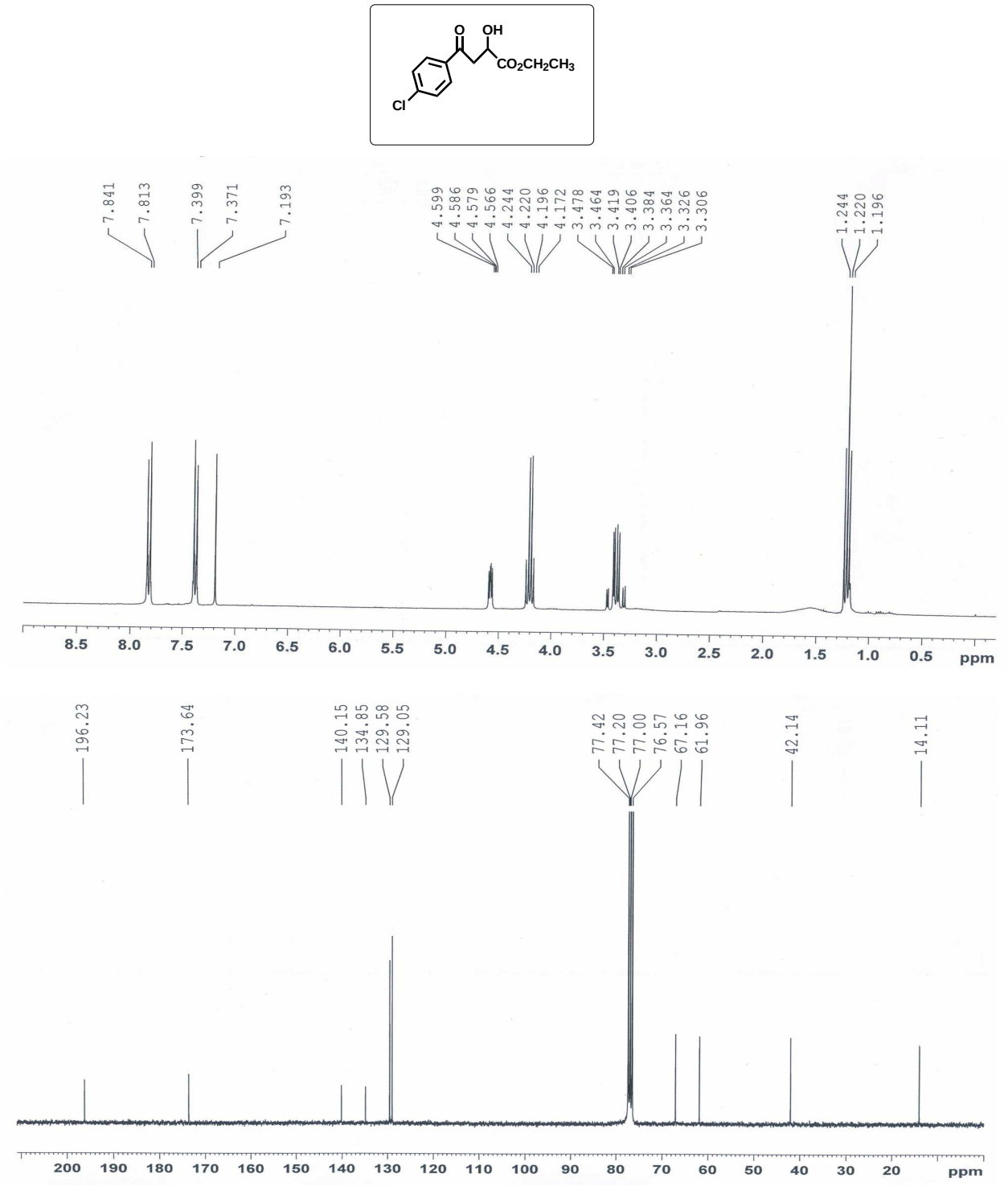




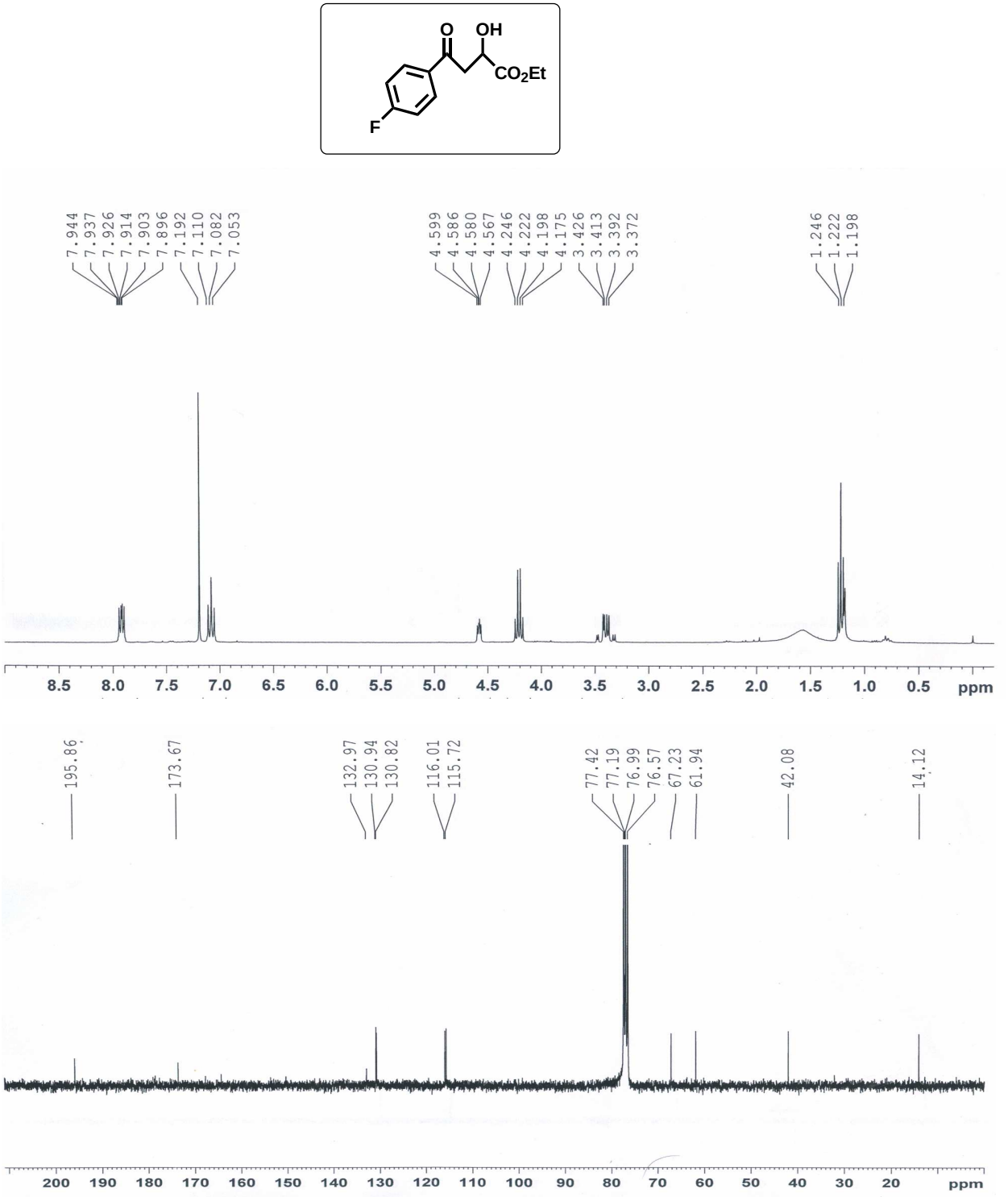
SI Figure 6. ^{1}H & ^{13}C spectrum **2f**



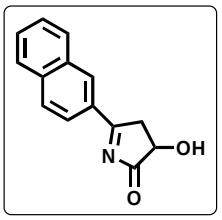
SI Figure 7. ^{1}H & ^{13}C spectrum **2g**

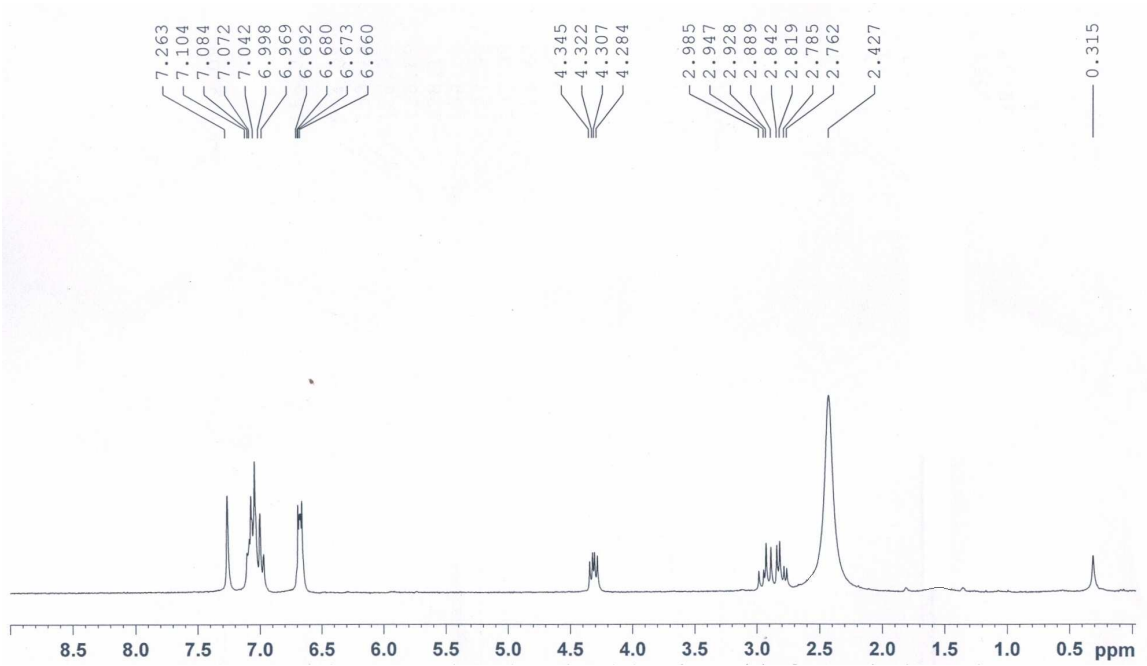


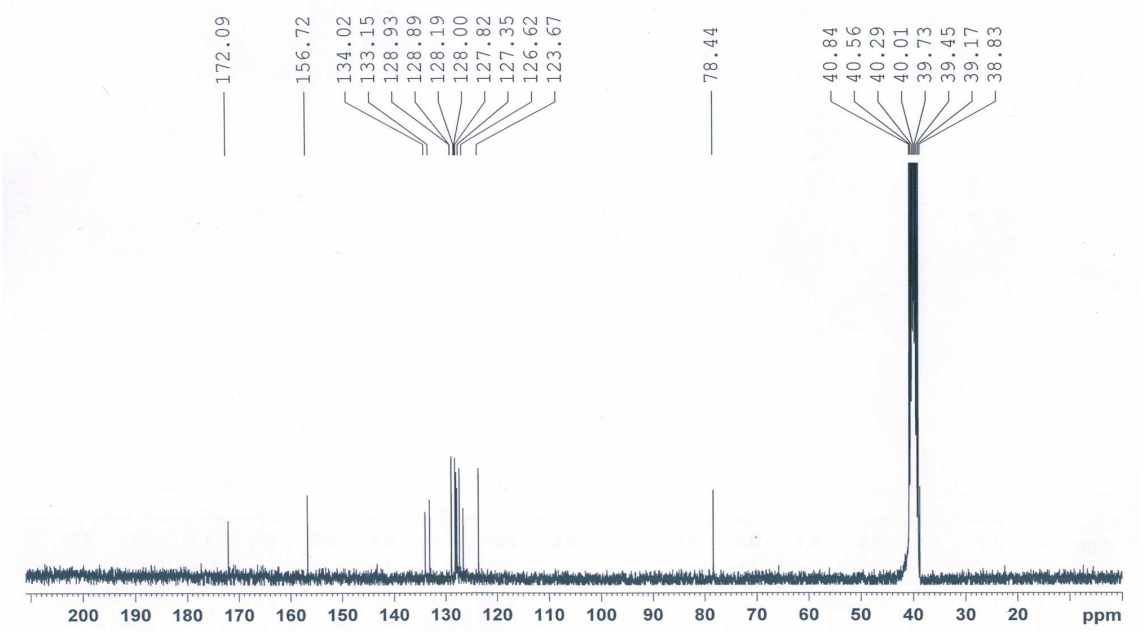
SI Figure 8. ^{1}H & ^{13}C spectrum **2h**



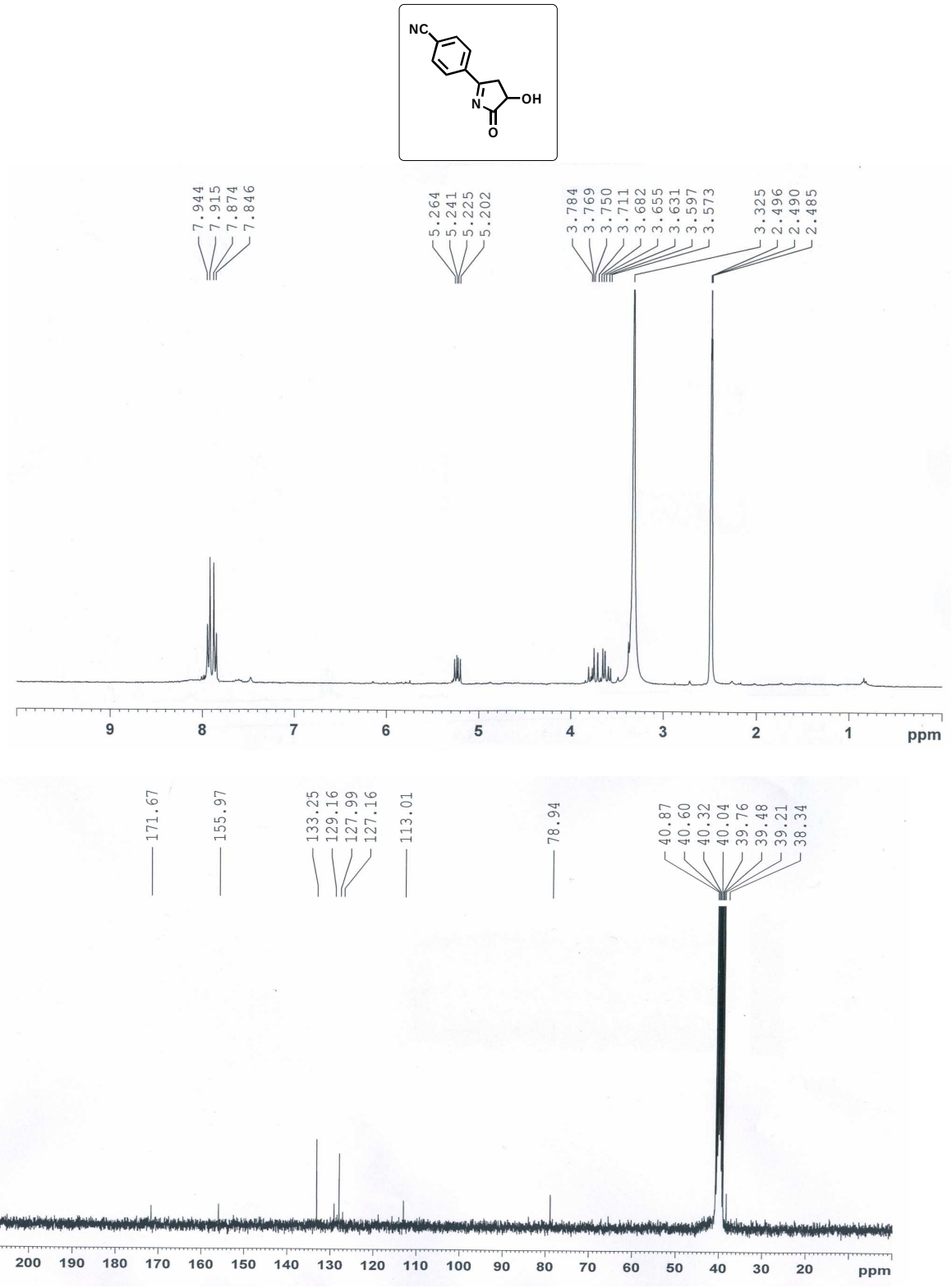
SI Figure 9. ^{1}H & ^{13}C spectrum **3a**



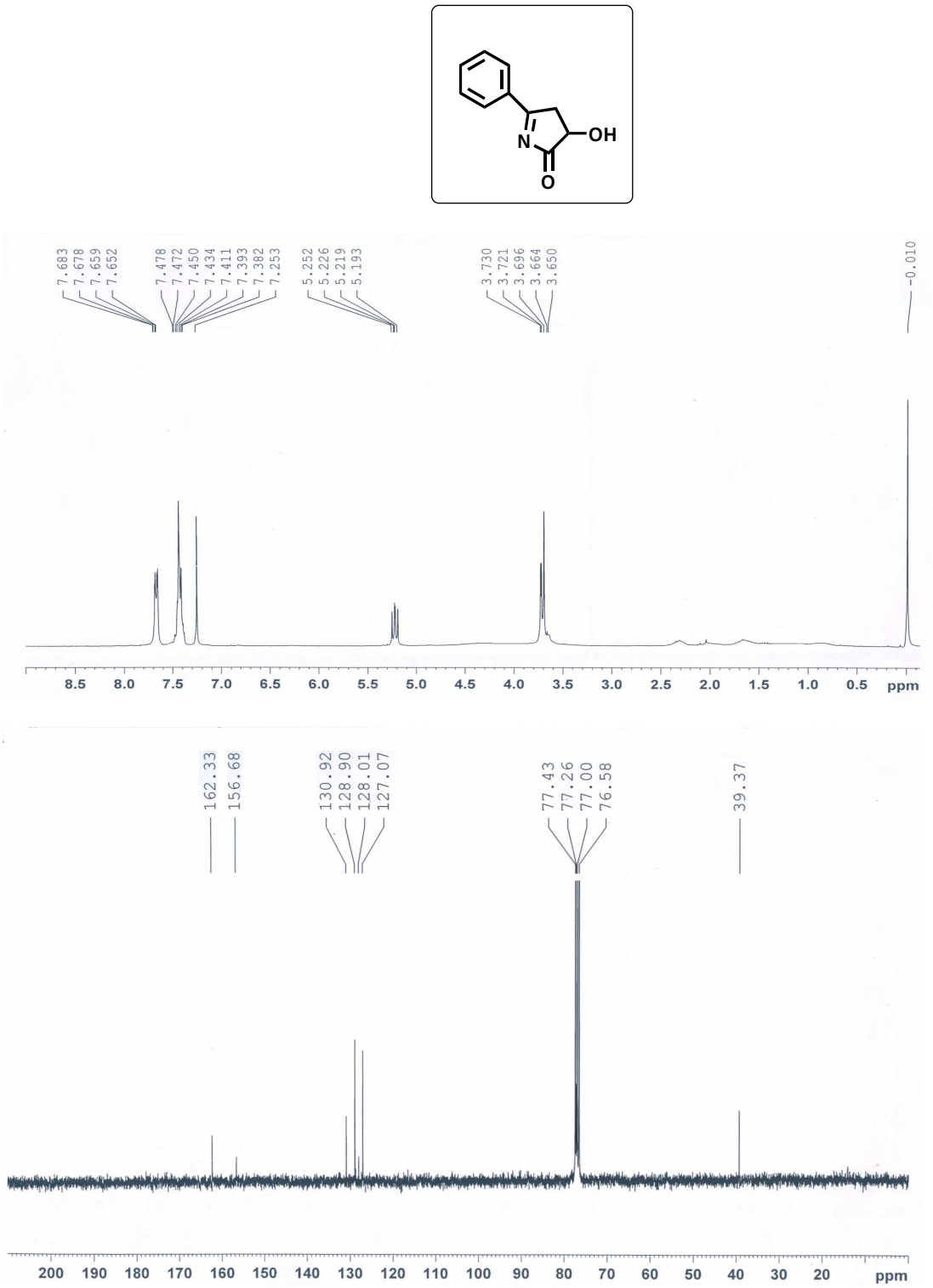




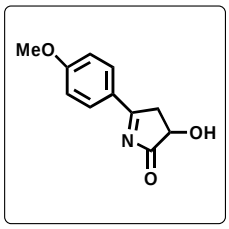
SI Figure 10. ^{1}H & ^{13}C spectrum **3b**

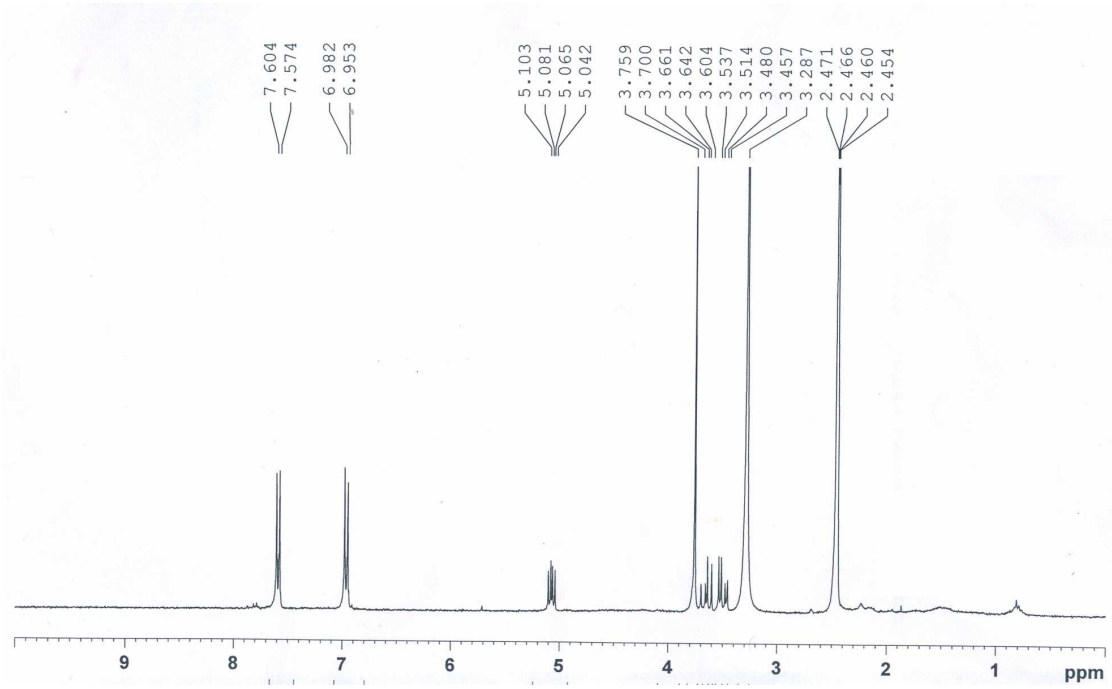


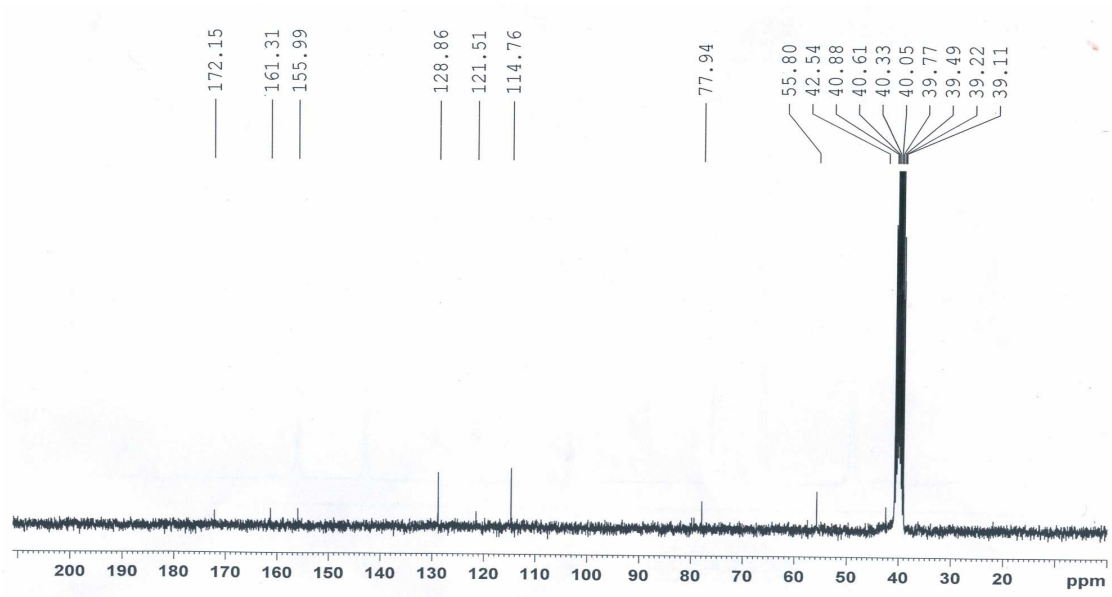
SI Figure 11. ^{1}H & ^{13}C spectrum **3c**



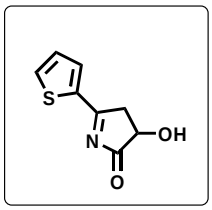
SI Figure 12. ^{1}H & ^{13}C spectrum **3d**

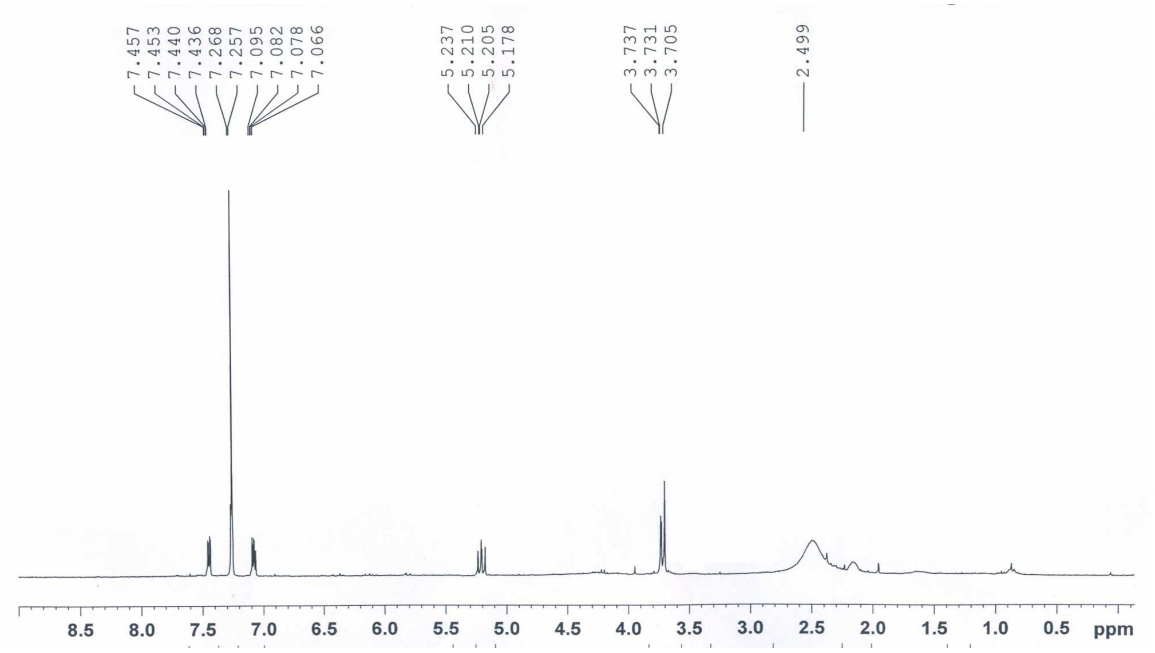


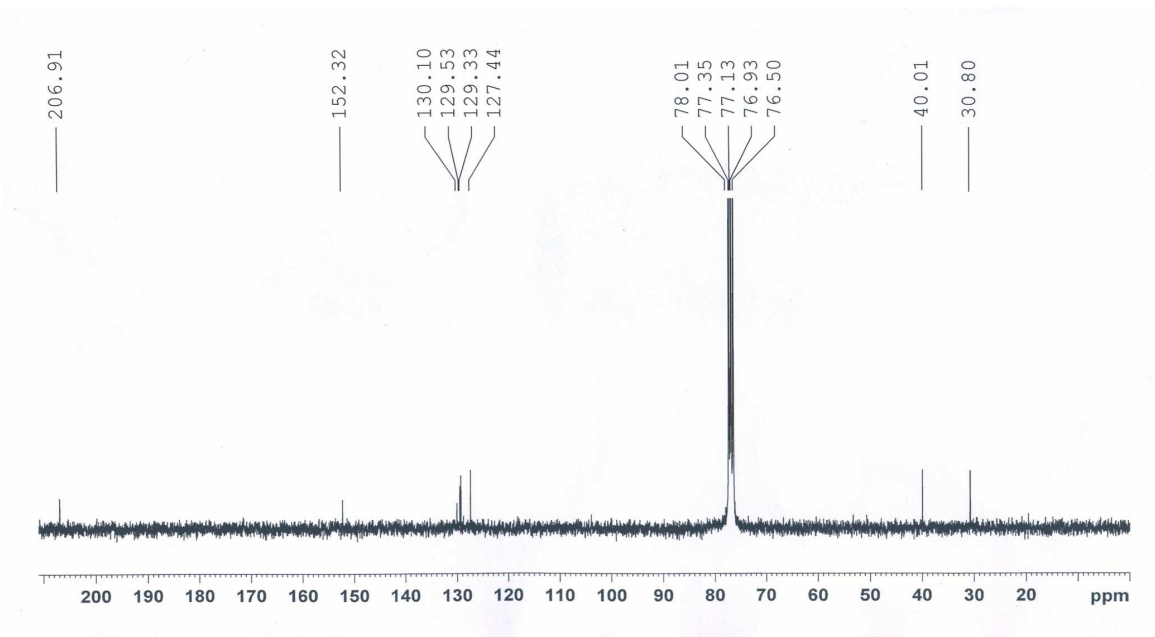




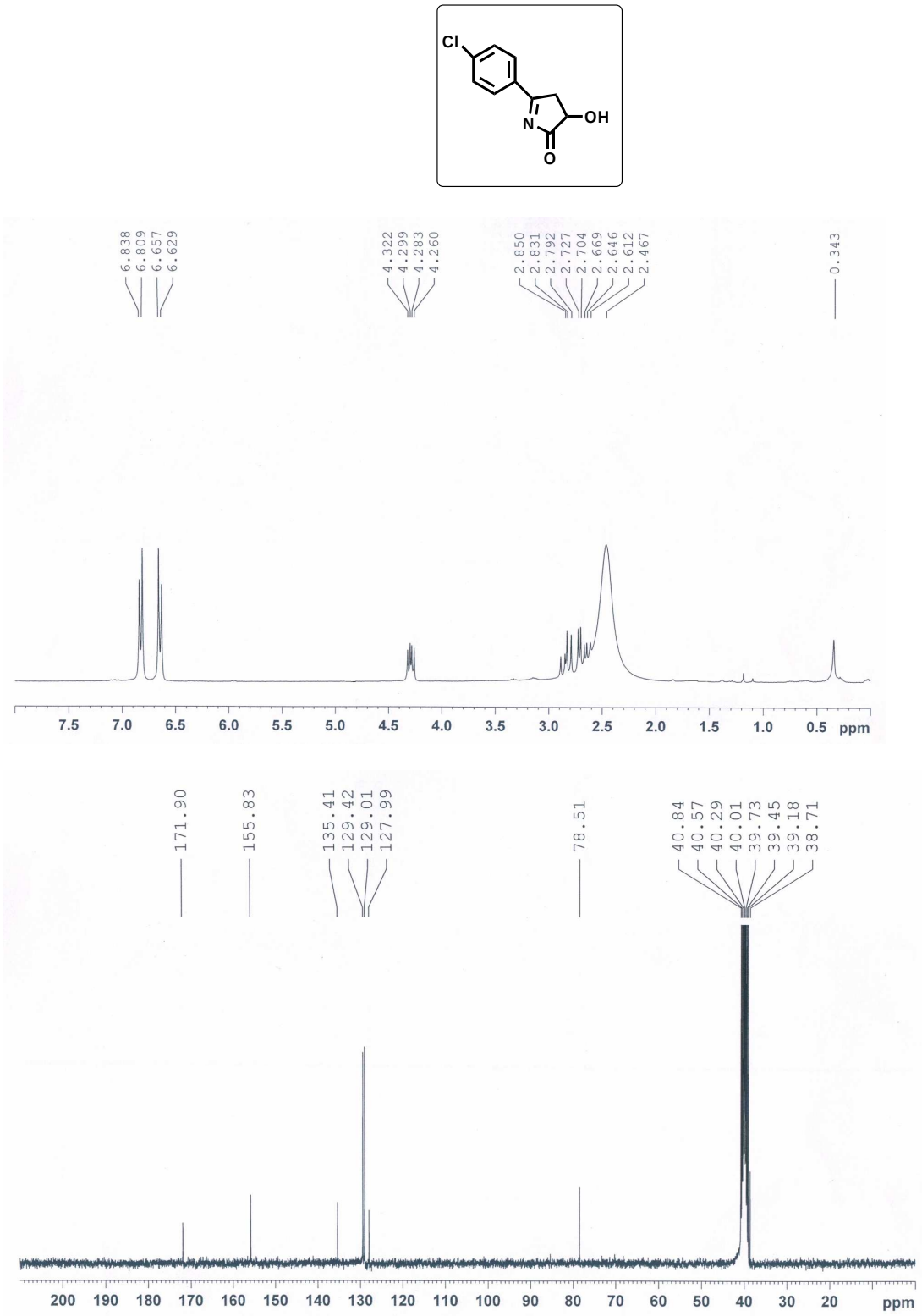
SI Figure 13. ^{1}H & ^{13}C spectrum **3e**



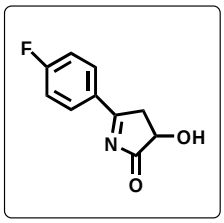


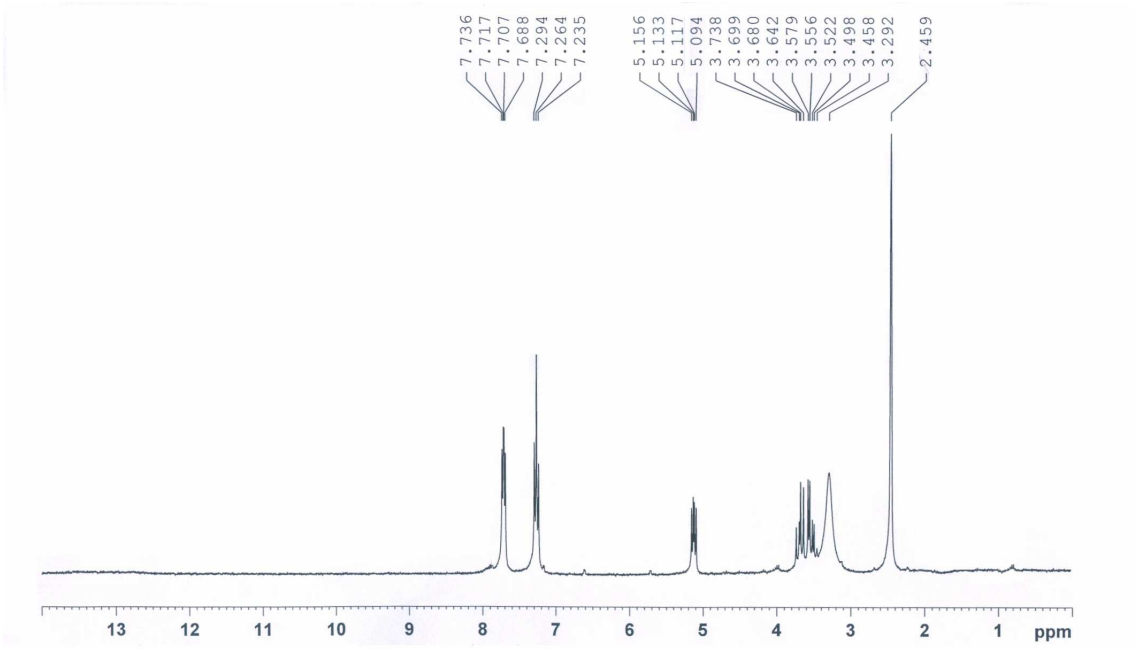


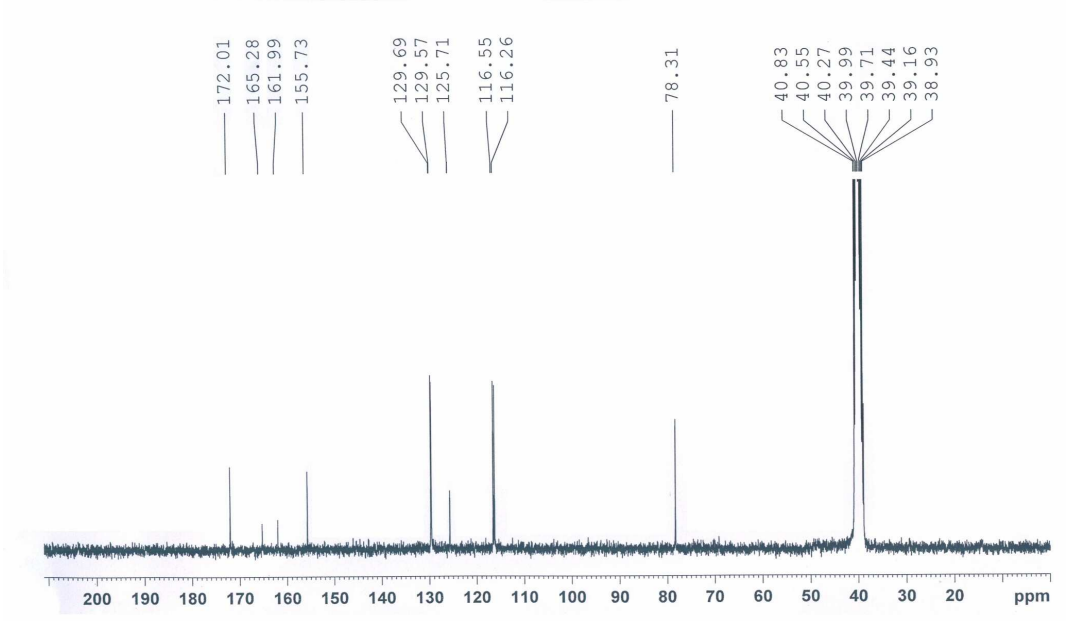
SI Figure 14. ^{1}H & ^{13}C spectrum **3f**



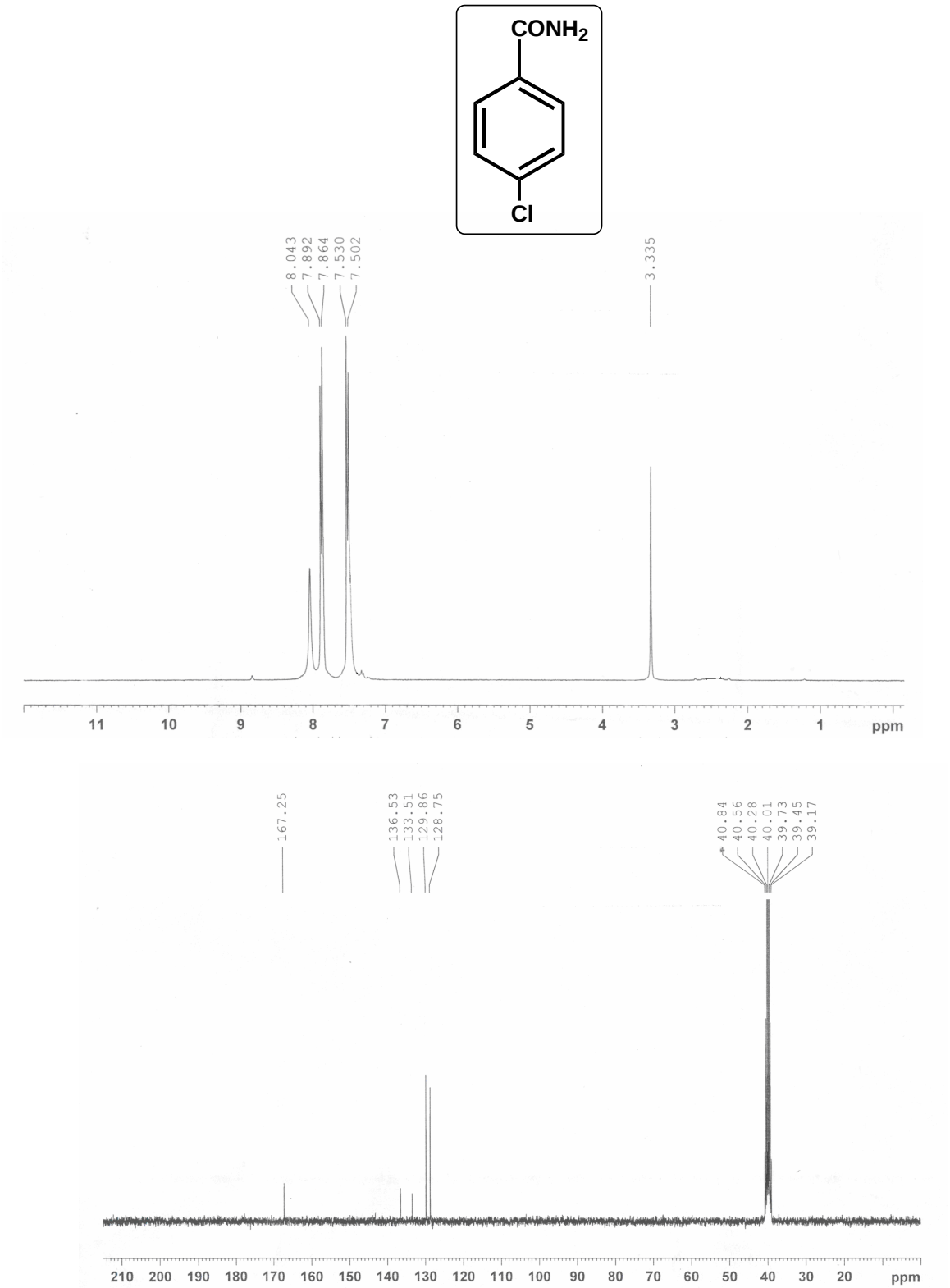
SI Figure 15. ^{1}H & ^{13}C spectrum **3g**



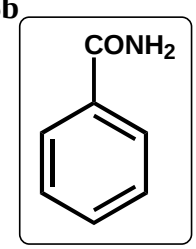


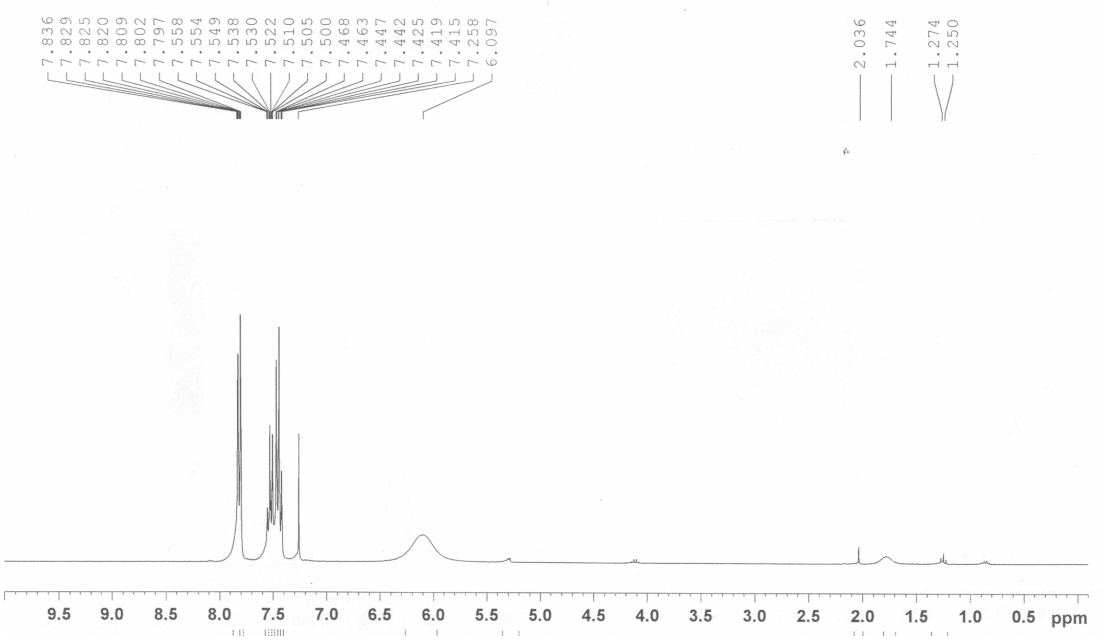


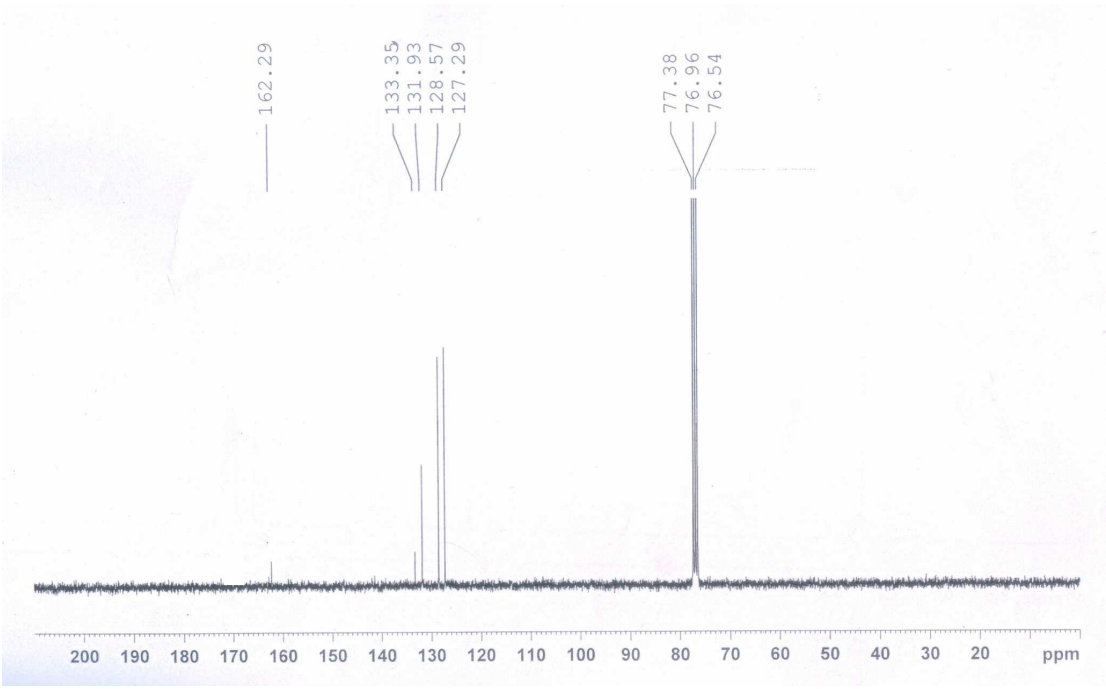
SI Figure 16. ^{1}H & ^{13}C NMR spectrum **5a**



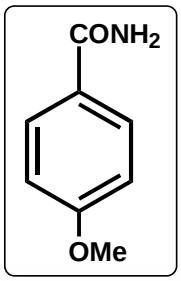
SI Figure 17. ^{1}H & ^{13}C NMR spectrum **5b**

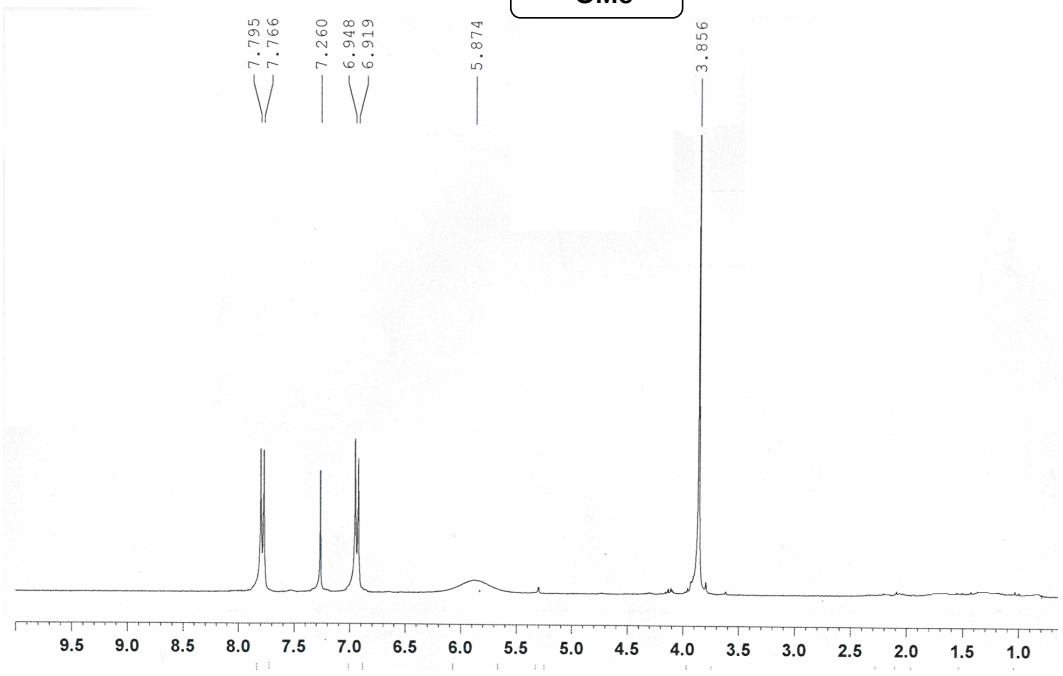


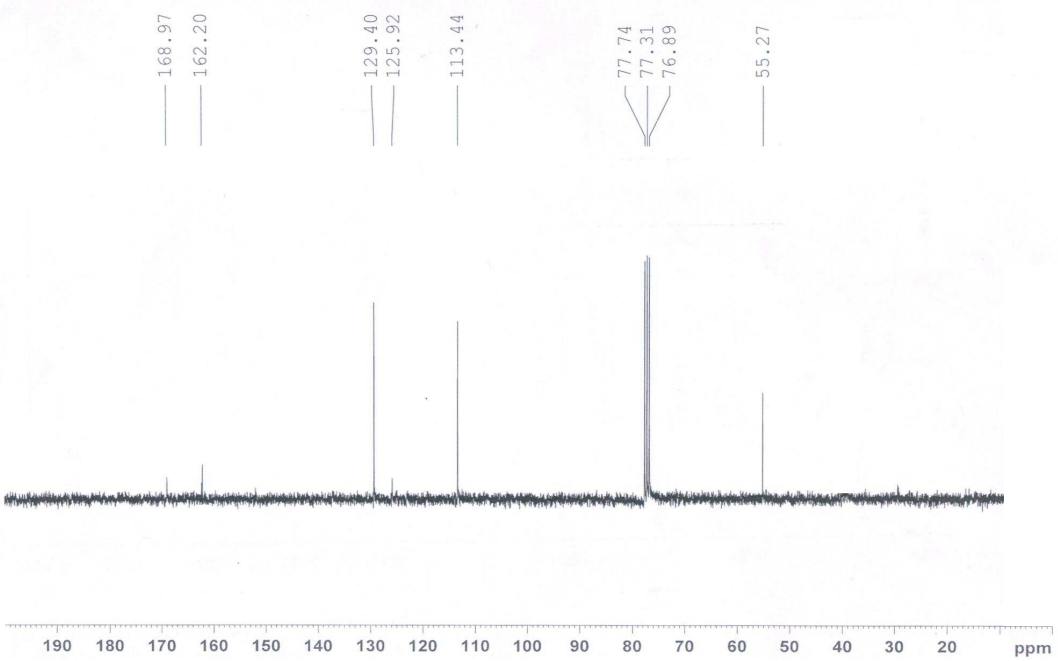




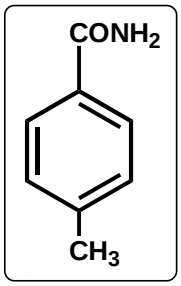
SI Figure 18. ^{1}H & ^{13}C NMR spectrum **5c**

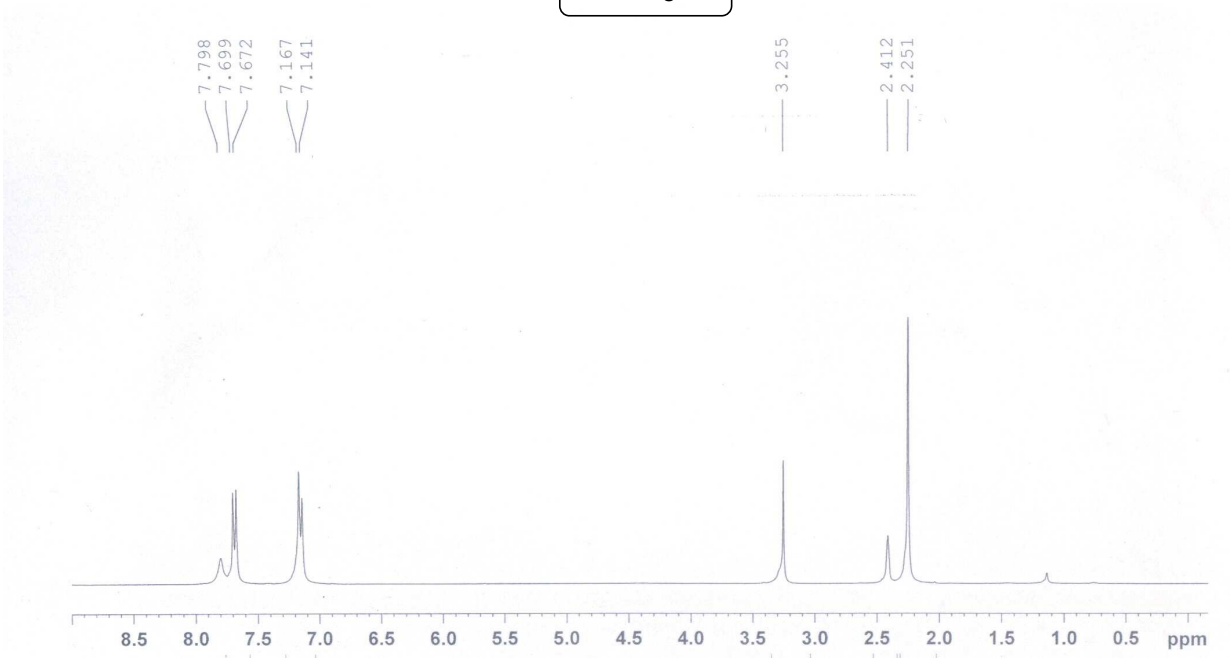


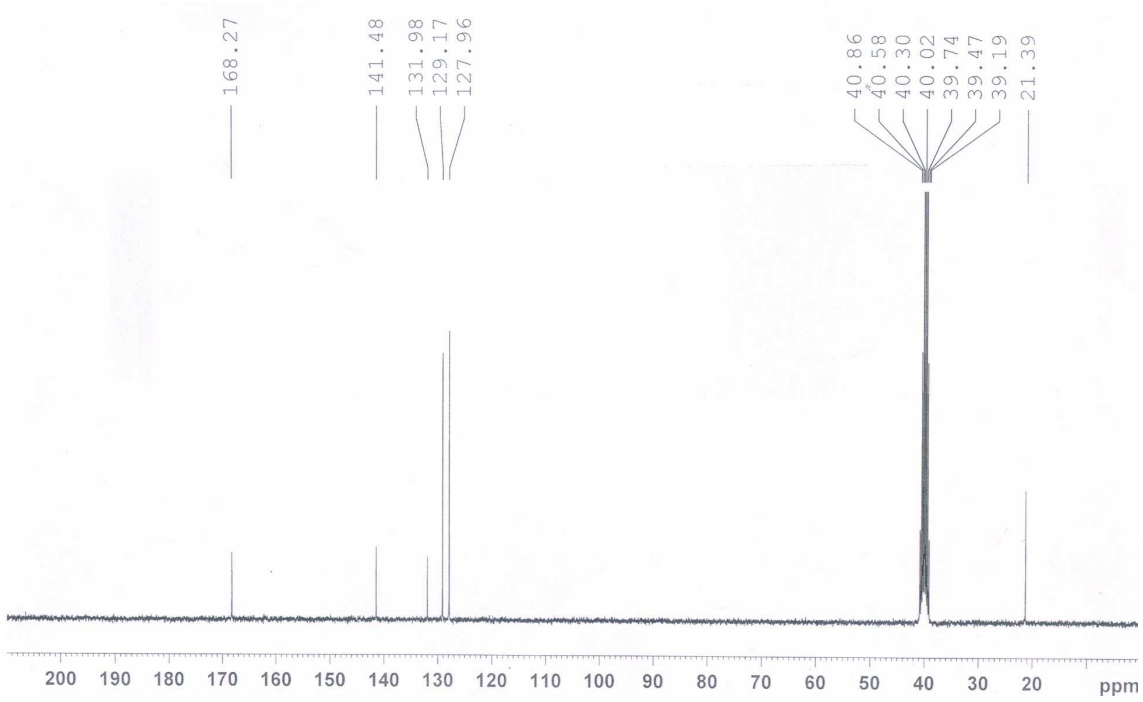




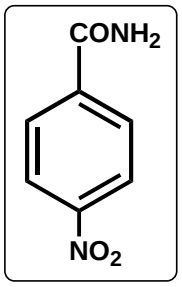
SI Figure 19. ^{1}H & ^{13}C NMR spectrum **5d**

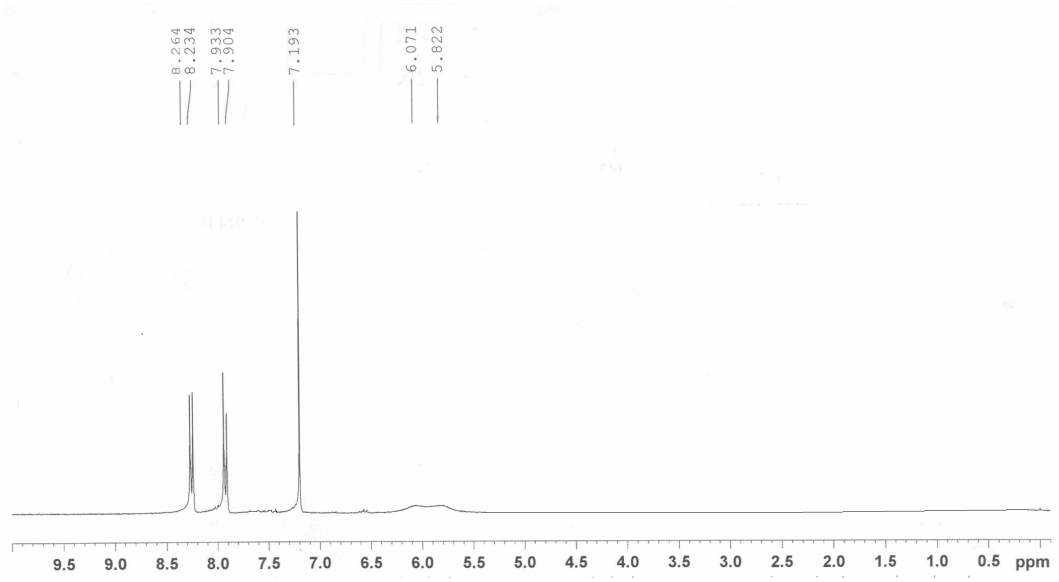


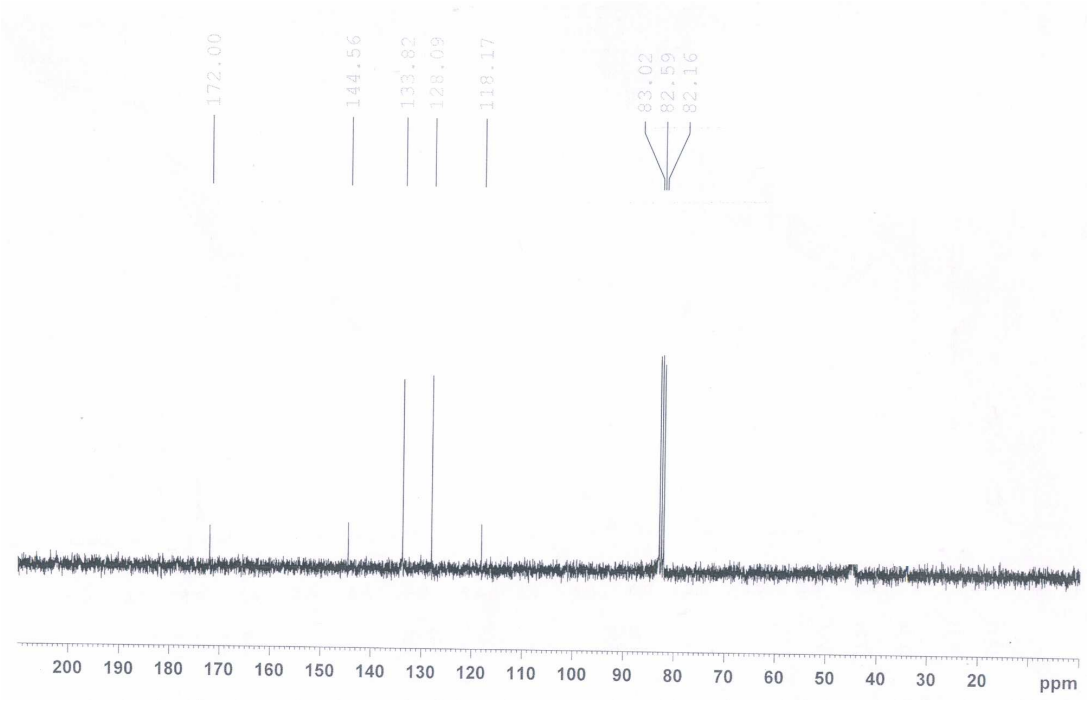




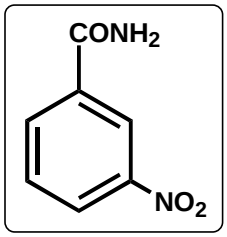
SI Figure 20. ^{1}H & ^{13}C NMR spectrum **5e**

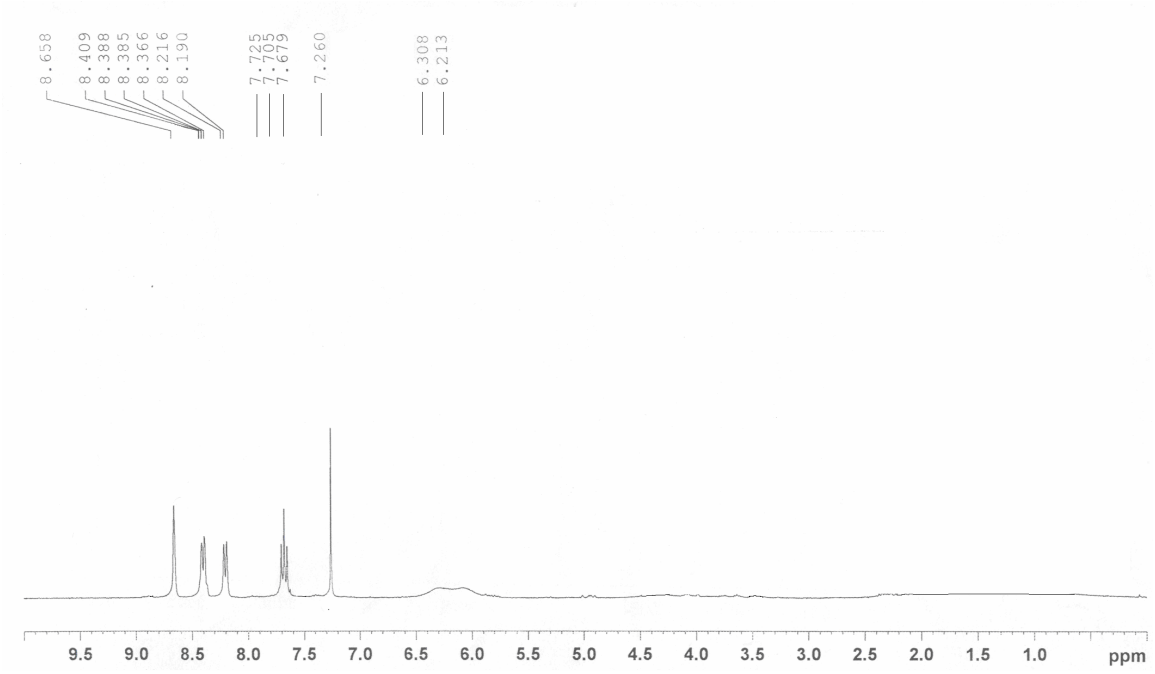


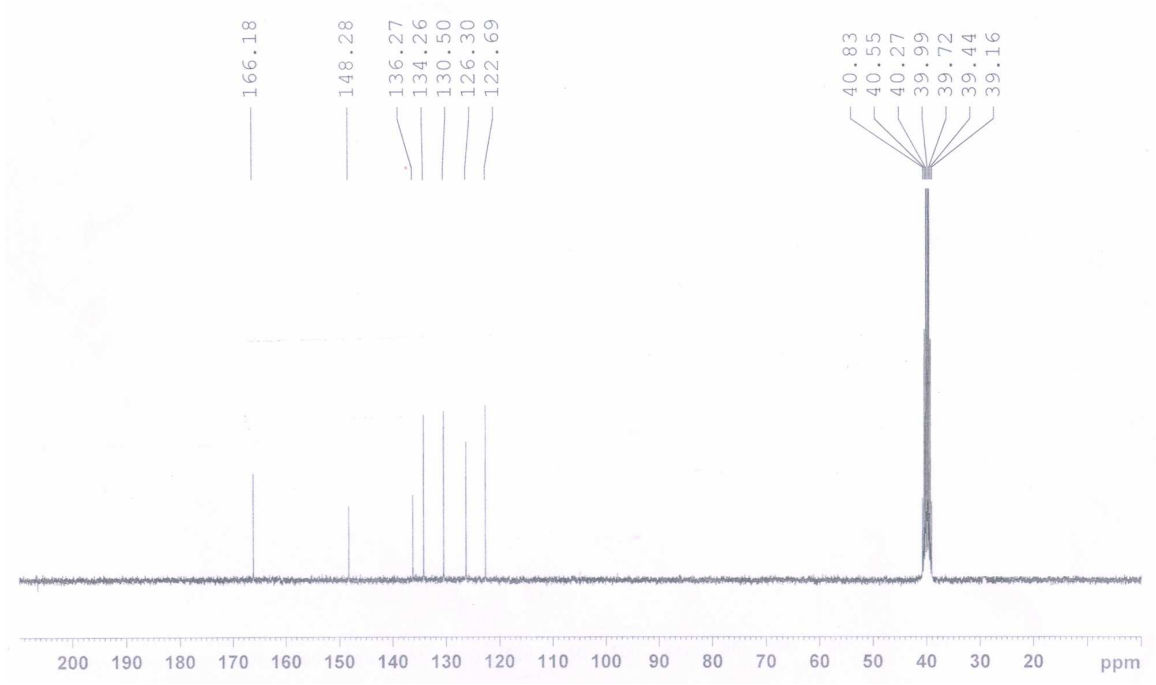




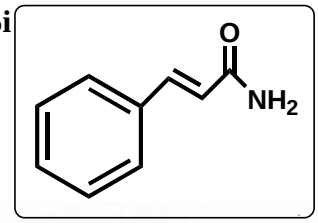
SI Figure 21. ^{1}H & ^{13}C NMR spectrum **5f**

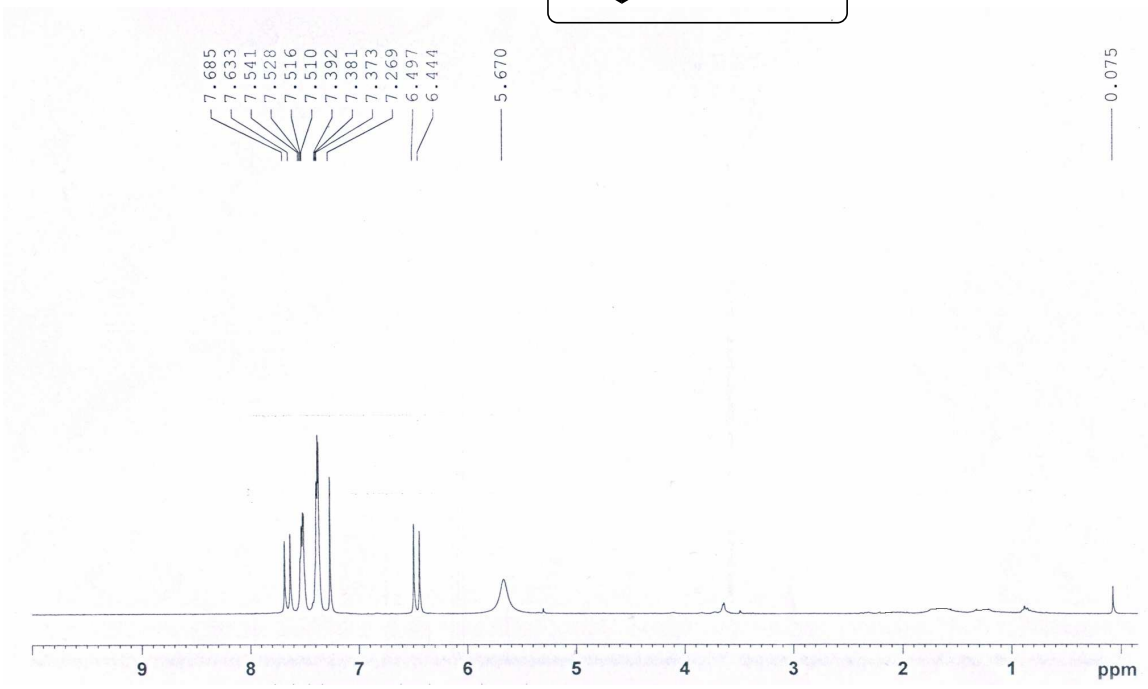


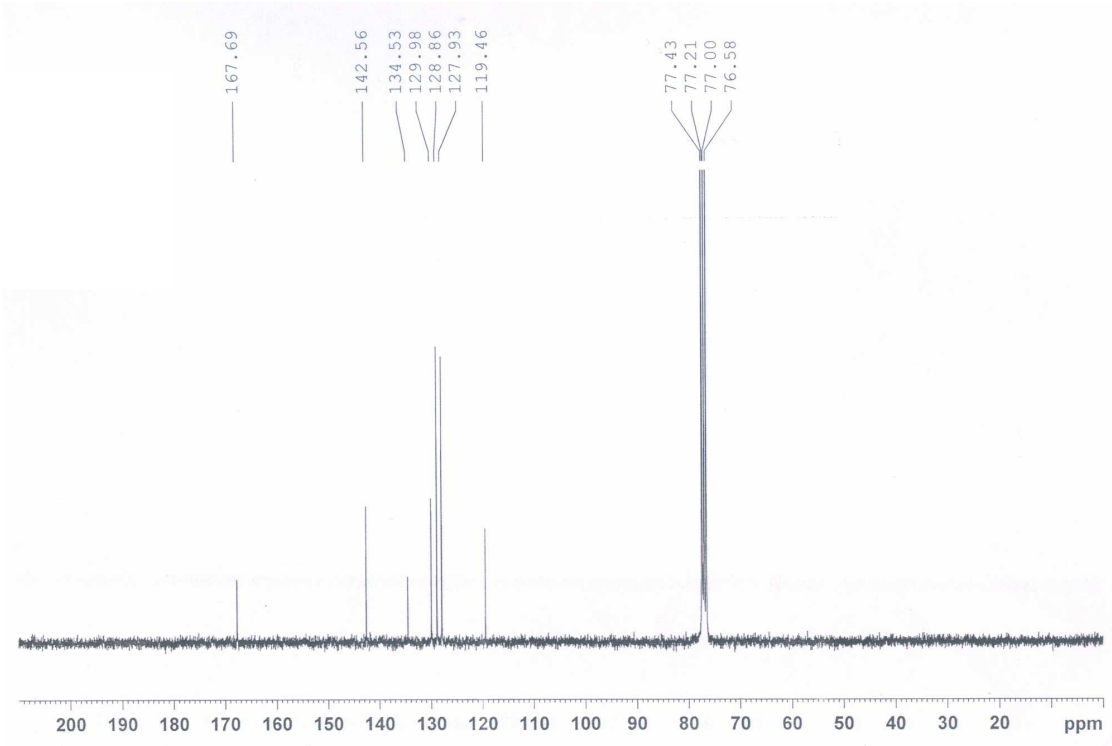




SI Figure 22. ^{1}H & ^{13}C NMR spectrum **5i**







SI Figure 23. ^{1}H & ^{13}C NMR spectrum **5j**