Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

An Eco-Economical Protocol for Direct Conversion of Baylis Hillman Alcohols to β-Chloro Aldehydes in water

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1. General Information

The starting materials and reagents were purchased from various commercial sources and used without further purification. The reactions were performed at room temperature. ACME silica gel (60-120 mesh) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates with silica gel 60-F_{254} plates and visualized by UV-light. ^{1}H NMR and ^{13}C NMR spectra were recorded, using tetramethylsilane (TMS) in the solvent of $CDCl_3$+DMSO as the internal standard on a 300, 500 MHz spectrometer (^{1}H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.0 ppm, DMSO at 39.43). Chemical shifts (δ) were recorded in ppm with respect to TMS as an internal standard and coupling constants are quoted in Hertz (Hz). Mass spectra were recorded on a mass spectrometer by the electron spray ionization (ESI) and the data acquired in positive ionization mode. HRMS spectra were determined on TOF type mass analyzer. All the starting materials of aliphatic MBH adducts[1], 2-(hydroxy(phenyl)methyl)cyclohex-2-en-1-one[2] and 1-phenylprop-2-en-1-ol[3] have been synthesized according to the reported literature.

2.1 General Procedure:

In a 25 mL round bottom flask, MBH substrates **1a-1x** (1 equiv), Oxone (1.2 equiv) and NaCl (2 equiv) were dissolved in water. The reaction mixture was stirred at room temperature for 2 h as monitored by TLC. After completion of the reaction the reaction mixture was diluted with 20 mL of ethyl acetate and then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product.

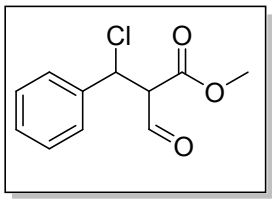
2.2 Gram-scale synthesis of 2a

In a 250 mL round bottom flask, MBH substrate **1a** (1 equiv, 26 mmol, 5g), Oxone (1.2 equiv, 31 mmol, 9.59g) and NaCl (2 equiv, 52 mmol, 3.02g) were dissolved in 100 mL of water. The reaction mixture was stirred at room temperature for 2 h as monitored by TLC. After completion of the reaction the reaction mixture was diluted with ethyl acetate and then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column

chromatography on silica gel with a gradient eluent of hexane and ethyl acetate to give the desired product **2a**.

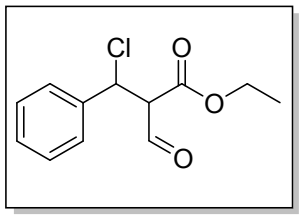
3. Characterization Data for the Products:

Methyl 3-chloro-2-formyl-3-phenylpropanoate (**2a**):



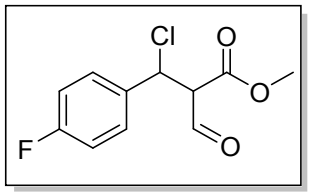
(**2a**): Colourless Liquid; Yield: 98%; IR (KBr); 3062, 2955, 1732, 1703, 1495, 1435, 1261, 1181, 1074, 937, 844,727, 695, 581 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.00 (d, *J* = 1.3 Hz, 1H), 7.43-7.37 (m, 3H), 7.20-7.17 (m, 2H), 4.31 (d, *J* = 10.6 Hz, 1H), 4.09 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.91 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 169.3, 132.7, 129.4, 129.0, 127.0, 67.1, 52.9, 43.4; Mass (ESI-MS) *m/z*: 227 $[M+H]^+$.

Ethyl 3-chloro-2-formyl-3-phenylpropanoate (**2b**):



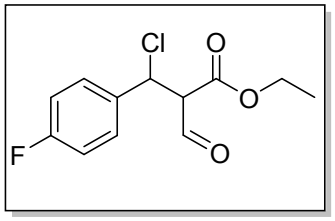
(**2b**): Colourless Liquid; Yield: 98%; IR (KBr); 3062, 2983, 1598, 1449, 1369, 1247, 1096,1036, 858, 744, 695, 581 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.00 (d, *J* = 1.3 Hz, 1H), 7.43-7.36 (m, 3H), 7.21-7.19 (m, 2H), 4.40 (q, 2H), 4.30 (d, *J* = 10.8 Hz, 1H), 4.09 (dd, *J* = 1.4, 10.8 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7, 168.7, 132.8, 128.9, 127.0, 66.9, 62.3, 43.4, 14.0.; Mass (ESI-MS) *m/z*: 241 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{14}ClO_3$ = 241.0626: $[M+H]^+$; Found = 241.0638.

Methyl 3-chloro-3-(4-fluorophenyl)-2-formylpropanoate (2c);



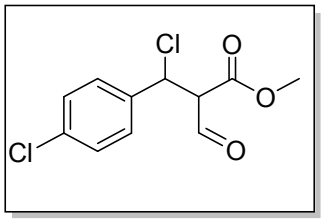
(2c): Yellow Liquid;Yield: 96%; IR (KBr): 2955, 2849, 1734, 1599, 1508, 1436,1230, 1158, 1096, 971, 834, 742, 623, 588 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.00 (d, *J* = 1.3 Hz, 1H), 7.43-7.37 (m, 3H), 7.20-7.17 (m, 2H), 4.31 (d, *J* = 10.6 Hz, 1H), 4.09 (dd, *J* = 10.8, 1.3 Hz, 1H), 3.91 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 169.0, 163.7, 161.7, 129.0, 128.5, 127.9, 66.4, 53.0, 43.4; Mass (ESI-MS) *m/z*: 245 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{11}ClFO_3$ = 245.0375, $[M+H]^+$; Found = 245.0378.

Ethyl 3-chloro-3-(4-fluorophenyl)-2-formylpropanoate (2d):



(**2d**): Yellow Liquid; Yield: 92%; IR (KBr): 3031, 2953, 2854, 1728, 1612, 1511, 1435, 1290,1194, 1095, 948, 888,738, 651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (d, *J* = 3.1 Hz, 1H), 7.42-7.36 (m, 1H), 7.21 (t, *J* = 4.7 Hz, 2H), 7.13 (q, 1H), 4.33 (q, 2H), 4.21 (d, *J* = 11.2 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7, 168.7, 132.8, 128.9, 127.0, 66.9, 62.3, 43.4, 14.0; Mass (ESI-MS) *m/z*: 259 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{13}ClFO_3$ = 259.0532, $[M+H]^+$; Found = 259.0524.

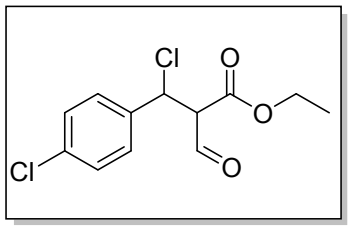
Methyl 3-chloro-3-(4-chlorophenyl)-2-formylpropanoate (2e):



(**2e**): Colourless Liquid; Yield: 92%; IR (KBr): 2955, 2853,1736, 1589, 1491, 1437, 1292, 1208, 1153, 1057, 817, 779, 757, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (d, *J* = 1.1 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 3H), 7.14 (m, *J* = 8.6 Hz, 2H), 4.25 (d, *J* = 10.8 Hz, 1H), 4.07 (dd, *J* = 10.8, 1.1 Hz, 1H), 3.90 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.2, 168.9, 135.3, 131.2, 129.6, 128.5, 127.1, 66.5, 53.1, 43.4;

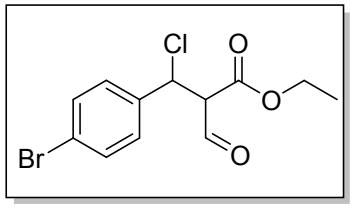
Mass (ESI-MS) *m/z*: 261 $[M+H]^+$; HRMS (ESI) (ESI) *m/z* cal for $C_{11}H_{11}Cl_2O_3$ = 261.008, $[M+H]^+$; Found = 261.0091.

Ethyl 3-chloro-3-(4-chlorophenyl)-2-formylpropanoate (2f):



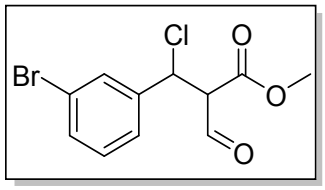
(**2f**): Colourless Liquid; Yield: 91%; IR (KBr): 2983, 2936, 1731, 1572, 1491, 1348, 1262, 1368, 1249, 1012, 858, 752, 667, 580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (d, *J* = 3.1 Hz, 1H), 7.42-7.36 (m, 1H), 7.21 (t, *J* = 4.7 Hz, 2H), 7.13 (q, 1H), 4.33 (q, 2H), 4.21 (d, *J* = 11.2 Hz, 1H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 168.4, 135.2, 131.3, 129.5, 128.8, 127.1, 66.3, 62.5, 43.4, 14.0; Mass (ESI-MS) *m/z*: 292 $[M+NH_4]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{16}Cl_2O_3N$ = 292.0502, $[M+NH_4]^+$; Found = 292.0482.

Ethyl 3-(4-bromophenyl)-3-chloro-2-formylpropanoate (2g):



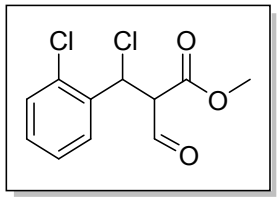
(2g): Colourless Liquid; Yield: 85%; IR (KBr): 2958, 2856, 1728, 1601, 1471, 1348, 1262, 1162, 1065, 1012, 944, 749, 698, 580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.97 (d, *J* = 1.1 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 4.40 (q, 2H), 4.24 (d, *J* = 10.8 Hz, 1H), 4.07 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.34(t, *J* = 7.0 Hz, 3H) : ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.4, 168.3, 132.5, 131.8, 131.1, 129.9, 128.8, 127.7, 123.3, 66.4, 62.5, 43.3, 13.9; Mass (ESI-MS) *m/z*: 319 $[M+H]^+$.

Methyl 3-(3-bromophenyl)-3-chloro-2-formylpropanoate (2h):



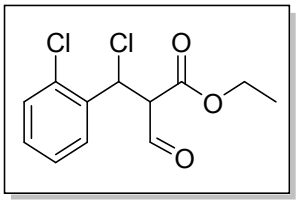
(2h): Colourless Liquid; Yield: 81%; IR (KBr): 2954,2924, 2852, 1738, 1698, 1591, 1471, 1382, 1279, 1190, 1063, 945, 787, 672, 642 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.36 (t, *J* = 1.1 Hz, 2H), 7.20 (t, *J* = 2.2 Hz, 1H), 7.09 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.26 (d, *J* = 10.9 Hz, 1H), 4.09 (dd, *J* = 10.9, 1.1 Hz, 1H), 3.92 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.6, 172.0, 137.2, 132.3, 131.9, 130.8, 128.9, 124.3, 53.9, 50.7, 29.6; Mass (ESI-MS) *m/z*: 415 $[M+H]^+$.

Methyl 3-chloro-3-(2-chlorophenyl)-2-formylpropanoate (2i):



(**2i**): Colourless Liquid; Yield: 80%; IR (KBr): 2983, 2851, 1706, 1597, 1452, 1348, 1262, 1162, 1134, 1002, 944, 749, 698, 580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.12 (s, 1H), 7.46-7.42 (m, 1H), 7.35 (t, *J* = 4.1 Hz, 2H), 7.26 (t, *J* = 4.8, 4.5 Hz, 1H), 4.30 (sp, 2H), 3.83 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 168.3, 133.4, 132.9, 130.8, 130.1, 129.9, 127.1, 66.4, 53.3, 43.2; Mass (ESI-MS) *m/z*: 261 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{11}Cl_2O_3$ = 261.0256, $[M+H]^+$; Found = 261.0260.

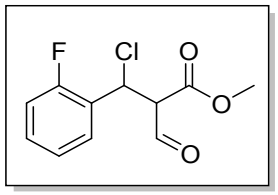
Ethyl 3-chloro-3-(2-chlorophenyl)-2-formylpropanoate(2j):



(**2j**): Colourless Liquid; Yield: 82%; IR (KBr): 2982, 2936, 1741, 1626, 1589. 1471. 1432, 1252, 1199, 1026, 955, 860, 760, 736, 688, 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.13 (d, 1H), 7.48-7.42 (m, 1H), 7.34 (t, *J* = 4.0, 3.7 Hz, 2H), 7.29-7.25 (m, 1H), 4.31(m, 4H), 1.27 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 167.7, 130.8, 130.2, 129.9, 128.7, 127.1, 126.6, 66.5, 62.7, 48.6, 13.9; Mass

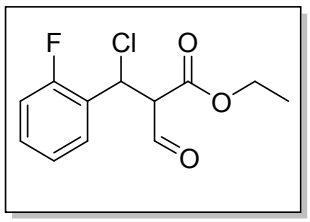
(ESI-MS) *m/z*: 275 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{13}Cl_2O_3N$ = 275.2536, $[M+H]^+$; Found = 275.2542.

Methyl 3-chloro-3-(2-fluorophenyl)-2-formylpropanoate (2k):



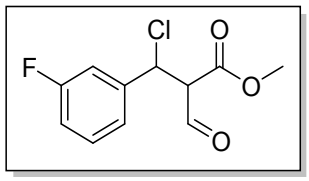
(**2k**): Yellow Liquid; Yield: 84%; IR (KBr): 2983, 2984, 2853, 1731, 1602, 1509, 1412, 1298, 1233, 1095, 1011, 835, 735, 654, 590 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.43-7.37 (m, 1H), 7.21 (t, *J* = 7.2, 6.3 Hz, 2H), 7.13 (t, *J* = 11.0, 9.2 Hz, 1H), 4.30 (d, *J* = 11.2 Hz, 1H), 4.21 (d, *J* = 11.2 Hz, 1H), 3.84(s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.2, 168.2, 161.3, 159.3, 129.0, 124.8, 116.3, 64.2, 53.2, 43.0; Mass (ESI-MS) *m/z*: 245 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{11}ClFO_3$ = 245.0265, $[M+H]^+$; Found = 245.0271.

Ethyl 3-chloro-3-(2-fluorophenyl)-2-formylpropanoate (2l):



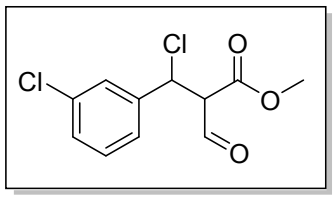
(**2l**): Yellow Liquid; Yield: 85%; IR (KBr): 2982, 2936, 1731, 1592, 1474, 1368, 1290, 1248, 1203, 1037, 889, 789, 714, 680, 584 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.0 Hz, 1H), 7.22-7.18 (m, 2H), 7.11 (t, *J* = 8.3 Hz, 2H), 4.39 (q, 2H), 4.25 (d, *J* = 10.8 Hz, 1H), 4.07 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 168.5, 163.7, 131.7, 129.0, 128.6, 116.5, 116.3, 66.2, 62.4, 43.5, 13.9; Mass (ESI-MS) *m/z*: 415 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{22}H_{27}N_2O_4S$ = 415.1657: $[M+H]^+$; Found = 415.1686.

Methyl 3-chloro-3-(3-fluorophenyl)-2-formylpropanoate (2m):



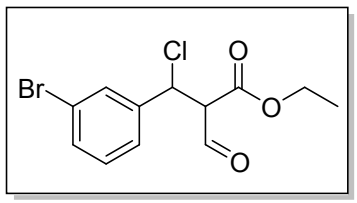
(**2m**): Yellow Liquid; Yield: 85%; IR (KBr): 2983, 2851, 1706, 1597, 1452, 1348, 1262, 1162, 1134, 1002, 944, 749, 698, 580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.99 (d, *J* = 1.2 Hz, 1H), 7.36 (t, *J* = 1.1 Hz, 2H), 7.20 (t, *J* = 2.2 Hz, 1H), 7.09 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.26 (d, *J* = 10.9 Hz, 1H), 4.09 (dd, *J* = 10.9, 1.1 Hz, 1H), 3.92 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 168.7, 135.4, 134.6, 130.5, 129.2, 127.4, 125.3, 66.6, 53.2, 43.3; Mass (ESI-MS) *m/z*: 245 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{11}ClFO_3$ = 245.0675, $[M+H]^+$; Found = 245.0678.

Methyl 3-chloro-3-(3-chlorophenyl)-2-formylpropanoate (2n):



(**2n**): Colourless Liquid; Yield: 82%; IR (KBr): 2953, 2852, 1732, 1594, 1476, 1202, 1078, 1017, 886, 788, 685 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.99 (d, *J* = 1.2 Hz, 1H), 7.36 (t, *J* = 1.1 Hz, 2H), 7.20 (t, *J* = 2.2 Hz, 1H), 7.09 (dt, *J* = 2.2, 1.1 Hz, 1H), 4.26 (d, *J* = 10.9 Hz, 1H), 4.09 (dd, *J* = 10.9, 1.1 Hz, 1H), 3.92 (s, 3H): ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.1, 168.7, 135.4, 134.6, 130.5, 129.2, 127.4, 125.3, 66.6, 53.2, 43.3; Mass (ESI-MS) *m/z*: 261 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{11}Cl_2O_3$ = 261.0180, $[M+H]^+$; Found = 261.0189.

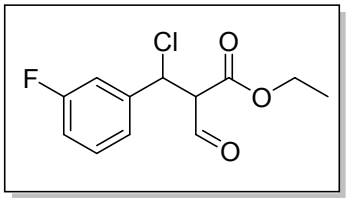
Ethyl 3-(3-bromophenyl)-3-chloro-2-formylpropanoate (2o):



(**2o**): Colourless Liquid; Yield: 80%; IR (KBr): 2982, 2936, 1730, 1585, 1487, 1397, 1248, 1096, 1054, 858, 775, 717, 570 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.1 Hz, 1H), 7.52 (dq, 1H), 7.37 (t, *J* = 1.9 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.15 (dq, 1H), 4.40 (q, 2H), 4.24 (d, *J* = 11.0 Hz, 1H), 4.08 (dd,

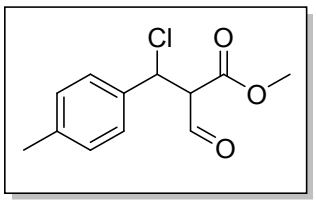
J = 10.8, 1.2 Hz, 1H), 1.34 (t, *J* = 7.2, 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.3, 168.2, 134.9, 132.1, 130.7, 125.8, 123.4, 66.4, 62.6, 43.4, 30.8, 14.0;Mass (ESI-MS) *m/z*: 319 $[M+H]^+$.

Ethyl 3-chloro-3-(3-fluorophenyl)-2-formylpropanoate (2p):



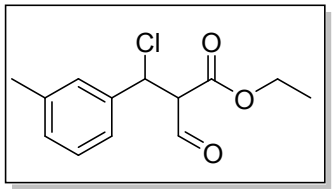
(**2p**): Yellow Liquid; Yield: 84%; IR (KBr): 2983, 2854, 1732, 1613, 1488, 1370, 1236, 1116, 1023, 879, 789, 750, 727, 687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.99 (d, *J* = 1.2 Hz, 1H), 7.42-7.36 (m, 1H), 7.09 (t, *J* = 8.3 Hz, 1H), 6.98 (t, *J* = 8.5, 7.8 Hz, 2H), 4.40 (q, 2H), 4.26 (d, *J* = 10.8 Hz, 1H), 4.09 (dd, *J* = 10.8, 1.2 Hz, 1H), 1.34 (t, *J* = 7.2, 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 168.5, 163.7, 131.7, 129.0, 128.6, 116.5, 116.3, 66.2, 62.4, 43.5, 13.9; Mass (ESI-MS) *m/z*: 259 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{13}ClFO_3$ = 259.0832, $[M+H]^+$; Found = 259.0825.

Methyl 3-chloro-2-formyl-3-p-tolylpropanoate (2q):



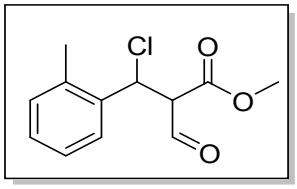
(**2q**): Colourless Liquid; Yield: 91%; IR (KBr): 3030, 2954, 2855, 1722, 1601, 1511, 1436, 1300, 1258, 1056, 955, 856, 813, 705, 584 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.21 (d, *J* = 8.06 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 4.28 (d, *J* = 10.7 Hz, 1H), 4.06 (dd, *J* =10.8, 1.3 Hz, 1H), 3.90 (s, 3H), 2.35 (s, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 169.4, 139.0, 130.1, 126.8, 66.8, 52.9, 45.4, 20.9 ; Mass (ESI-MS) *m/z*: 241 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{14}ClO_3$ = 241.0636: $[M+H]^+$; Found = 241.0638.

Ethyl 3-chloro-2-formyl-3-m-tolylpropanoate (2r):



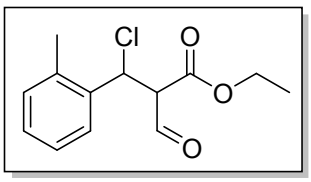
(2r): Colourless Liquid; Yield: 82%; IR (KBr): 2981, 2856, 1721, 1605, 1445, 1367, 1300, 1256, 1060, 925, 855, 698, 607 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.99 (d, *J* = 1.3 Hz, 1H), 7.29 (t, *J* = 8.3, 7.7 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.40 (q, 2H), 4.29 (d, *J* = 10.7 Hz, 1H), 2.35 (s, 3H), 1.34(t, *J* =7.2 Hz, 3H) ; ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.7, 168.8, 139.3, 132.7, 132.7, 129.6, 129.2, 127.5, 124.0, 66.9, 62.2, 43.4, 21.4, 13.9 ; Mass (ESI-MS) *m/z*: 272 $[M+NH_4]^+$; HRMS (ESI) *m/z* cal for $C_{13}H_{19}ClO_3N$ = 272.1148: $[M+NH_4]^+$; Found = 272.1164.

Methyl 3-chloro-2-formyl-3-o-tolylpropanoate (2s):



(2s): Colourless Liquid; Yield: 80%; IR (KBr): 2954, 2854, 1721, 1605, 1435, 1299, 1258, 1502, 896, 814, 745, 699, 606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.2 (s, 1H), 7.27 (t, *J* = 2.6, 2.0 Hz, 2H), 7.22 (dd, *J* = 6.8, 2.0 Hz, 1H), 7.08 (dd, *J* = 7.2, 1.8 Hz, 1H), 4.30 (q, 2H), 3.84 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.5, 169.5, 136.5, 132.7, 132.5, 128.7, 128.1, 126.5, 66.4, 53.1, 44.1, 20.8; Mass (ESI-MS) *m/z*: 241 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{12}H_{14}ClO_3$ = 241.0646: $[M+H]^+$; Found = 241.0648.

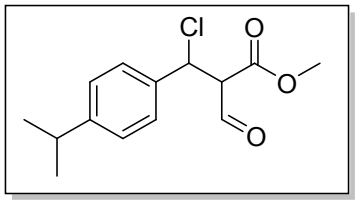
Ethyl 3-chloro-2-formyl-3-o-tolylpropanoate (2t):



(2t): Colourless Liquid; Yield: 80%; IR (KBr): 2981, 2870, 1719, 1602, 1491, 1384, 1227, 1098, 1017, 856, 743,683, 619 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.12 (s, 1H), 7.27 (t, *J* = 6.6 Hz, 1H), 7.23 (t, *J* = 6.6 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 1H), 4.34-4.28(m, 4H), 2.26 (s, 3H), 1.29 (t, *J* = 7.0 Hz, 3H); ^{13}C

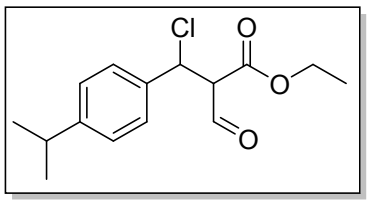
NMR (75 MHz, $CDCl_3$): δ 195.7, 168.9, 136.5, 132.8, 132.4, 128.6, 128.2, 126.4, 66.4, 62.4, 44.2, 20.9, 13.9 ; Mass (ESI-MS) *m/z*: 255 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{13}H_{16}ClO_3$ = 255.1846: $[M+NH_4]^+$; Found = 255.1852.

Methyl 3-chloro-2-formyl-3-(4-isopropylphenyl)propanoate (2u):



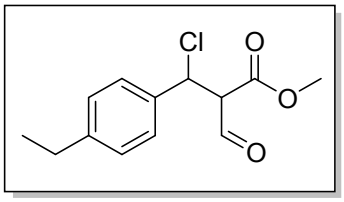
(**2u**): Colourless Liquid; Yield: 96%; IR (KBr): 2960, 2871, 2360, 1723, 1606, 1436, 1258, 1146, 1021, 896,828, 753, 685, 564 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.4 Hz, 1H), 7.26 (d, *J* = 2.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 4.29 (d, *J* = 10.7 Hz, 1H), 4.06 (dd, *J* = 10.8, 1.4 Hz, 1H), 3.91 (s, 3H), 2.90 (q, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 169.4, 149.8, 129.8, 127.5, 126.9, 126.9, 66.9, 62.2, 52.8, 33.6, 23.6; Mass (ESI-MS) *m/z*: 269 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{14}H_{18}ClO_3$ = 269.0939: $[M+H]^+$; Found = 269.0955.

Ethyl 3-chloro-2-formyl-3-(4-isopropylphenyl)propanoate (2v):



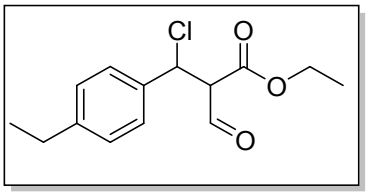
(**2v**): Colourless Liquid; Yield: 96%; IR (KBr): 2962, 2870, 1723, 1607, 1461, 1367, 1255, 1193, 1056, 1016, 898, 829, 751, 680, 564 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.26 (d, *J* = 7.1 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 4.40 (q, 2H), 4.29 (d, *J* = 10.8 Hz, 1H), 4.06 (dd, *J* = 10.8, 1.3 Hz, 3H), 2.90 (q, 1H), 1.35(t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 168.9, 149.7, 130.0, 128.4, 128.2, 126.9, 66.7, 62.2, 43.4, 33.6, 29.6, 23.7, 14.0; Mass (ESI-MS) *m/z*: 415 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{22}H_{27}N_2O_4S$ = 415.1657; $[M+H]^+$; Found = 415.1686.

Methyl 3-chloro-3-(4-ethylphenyl)-2-formylpropanoate (2w):



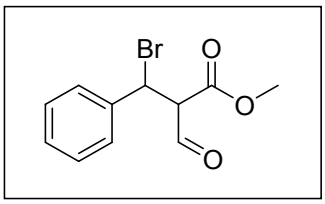
(**2w**): Colourless Liquid: 95%; IR (KBr): 2965, 2851, 1715, 1602, 1452, 1262, 1098, 1002, 944, 869, 749, 698, 580 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 4.29 (d, *J* = 10.8 Hz, 2H), 4.06 (dd, *J* = 10.8, 1.5 Hz, 1H), 3.91 (s, 3H), 2.64 (q, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 169.4, 145.3, 129.9, 128.9, 128.1, 126.9, 66.9, 52.9, 43.4, 28.3, 15.2; Mass (ESI-MS) *m/z*: 272 $[M+NH_4]^+$; HRMS (ESI) *m/z* cal for $C_{13}H_{19}ClO_3N$ = 272.1048: $[M+NH_4]^+$; Found = 272.1064.

Ethyl 3-chloro-3-(4-ethylphenyl)-2-formylpropanoate (2x):



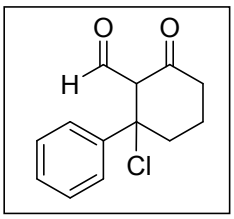
(**2x**): Colourless Liquid; Yield: 95%; IR (KBr): 2960, 2871, 1719, 1607, 1463, 1392,1225, 1180, 1068, 861, 831, 725, 626, 579 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.39 (q, 2H), 4.29 (d, *J* = 10.6 Hz, 1H), 4.06 (dd, *J* = 10.8, 1.3 Hz, 3H), 2.64 (q, 2H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.6, 169.4, 145.3, 129.9, 128.9, 128.1, 126.9, 66.9, 52.9, 43.4, 28.3, 15.2; Mass (ESI-MS) *m/z*: 269 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{14}H_{18}ClO_3$ = 269.0939, $[M+H]^+$; Found = 269.0938.

Methyl 3-bromo-2-formyl-3-phenylpropanoate (3a):



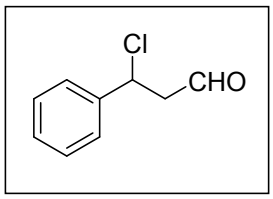
(3a); Colourless Liquid; Yield: 20% (NaBr, entry 12, Table 1) & 30% (KBr, entry 13, Table 1); IR (KBr): 3058, 2954, 2853, 1724, 1594,, 1438, 1236, 1197, 1034, 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.42-7.34 (m, 3H), 7.19 (d, *J* = 6.8 Hz, 2H), 4.13 (d, *J* = 10.0 Hz, 1H), 3.91 (s, 3H), 3.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.5, 169.3, 129.3 128.9, 128.6, 128.1, 127.9, 126.8, 66.4, 52.9, 30.4; Mass (ESI-MS) *m/z*: 270 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{12}BrO_3$ = 270.9968, $[M+H]^+$; Found = 270.9964.

2-Chloro-6-oxo-2-phenylcyclohexanecarbaldehyde (4e):



(4e); Colourless solid; m.p: 86-88 ^oC; Yield: 82%; IR (KBr): 2955, 2854, 1716, 1587, 1494, 1316,1227, 1140, 962, 663, 621 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 10.11 (s, 1H), 7.42 (t, *J* = 7.7, 6.9 Hz, 2H), 7.36 (t, *J* = 7.4, 7.2 Hz, 1H), 7.16 (d, *J* = 7.2 Hz, 2H), 5.47 (m, 1H), 2.54 (q, 2H), 2.41-2.25 (m, 2H), 2.15-2.08 (m, 1H), 1.91-1.85 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 207.0, 196.7, 132.9, 129.8, 128.7, 127.1, 70.0, 61.4, 38.6, 28.4, 20.9; Mass (ESI-MS) *m/z*: 237 $[M+H]^+$; HRMS (ESI) *m/z* cal for $C_{11}H_{14}ClO_2$ = 237.0680, $[M+H]^+$; Found = 237.0676.

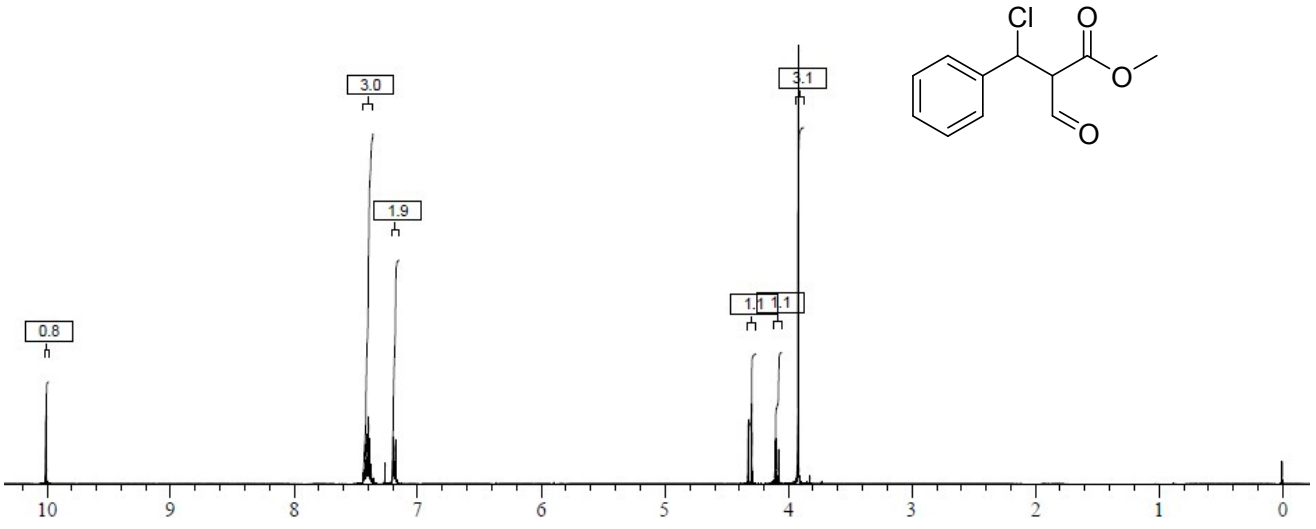
3-chloro-3-phenylpropanal (4h):[4]

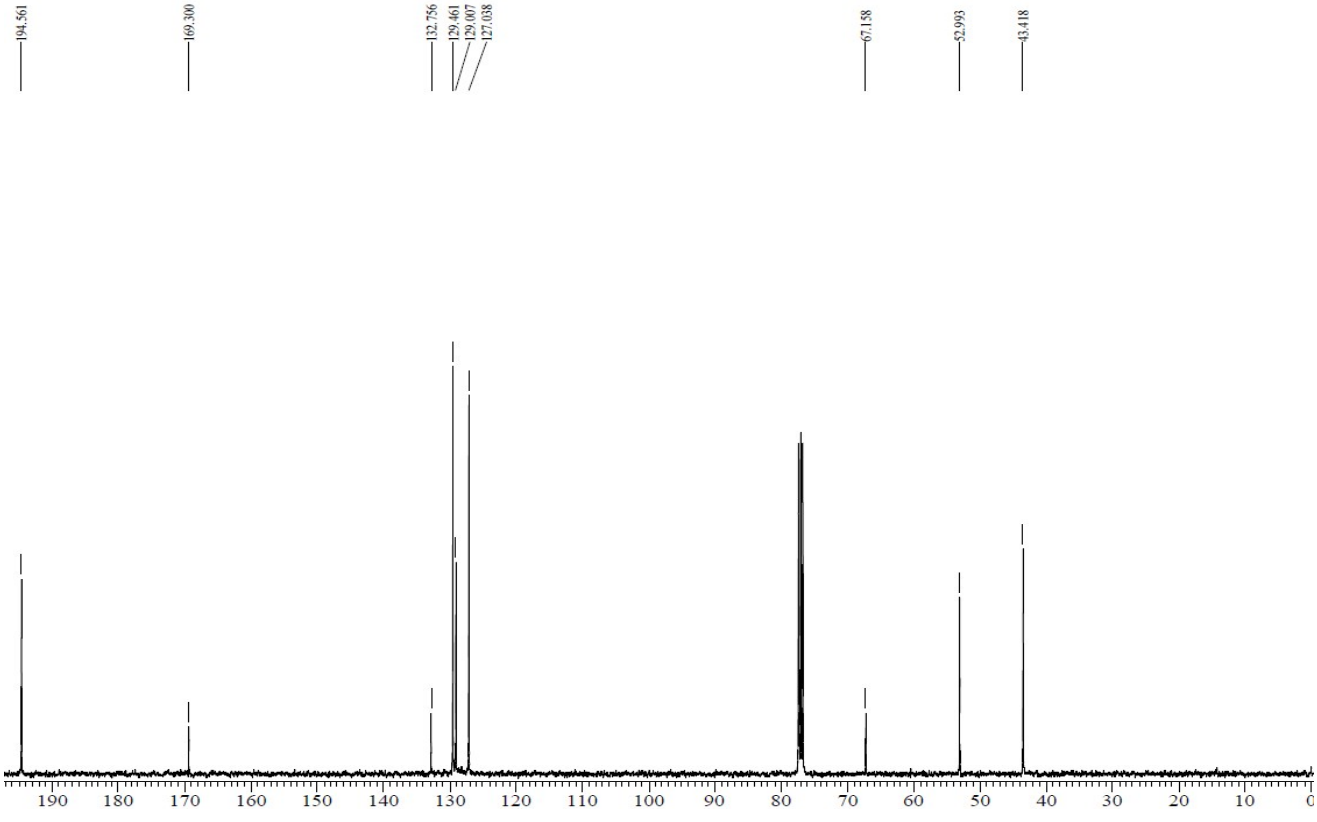


(4h); The crude reaction mixture was extracted with ethylacetate. Then the crude product was analysed by NMR spectral analysis. The resulting product has to be stored at low temperature (decomposes at room temperature). Colourless Liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 9.98 (d, *J* = 1.3 Hz, 1H), 7.42-7.34 (m, 3H), 7.19 (d, *J* = 6.8 Hz, 2H), 4.13 (d, *J* = 10.0 Hz, 1H), 3.91 (s, 3H), 3.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 129.5, 129.3, 128.9, 128.5, 128.0, 60.7, 42.3; Mass (ESI-MS) *m/z*: 168 $[M+H]^+$.

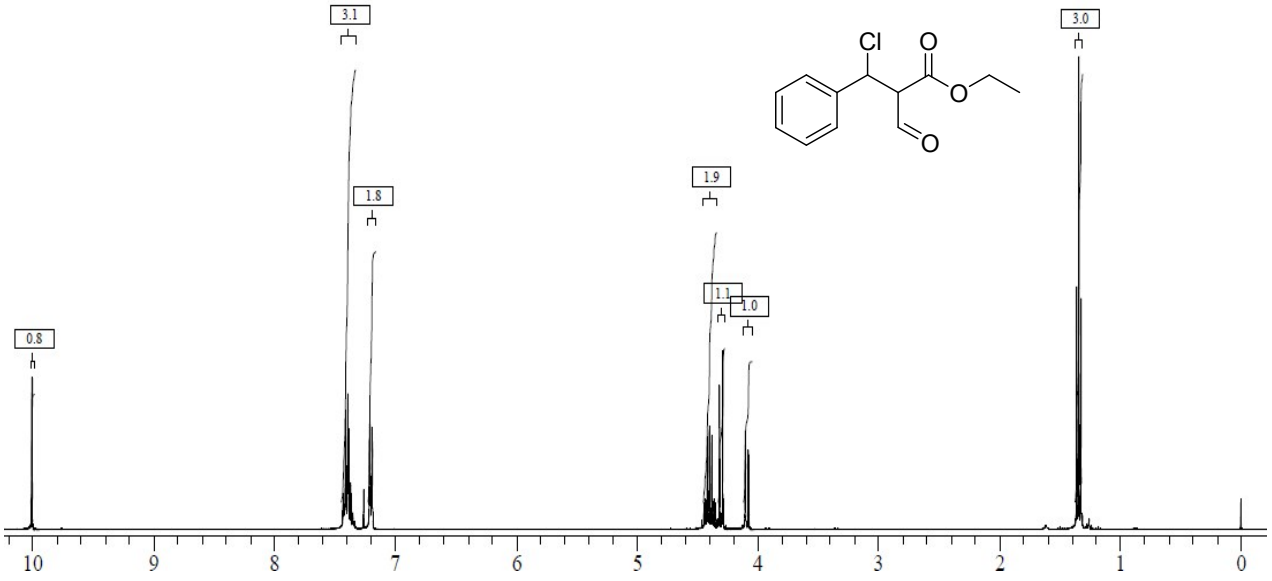
4. ^{1}H NMR and ^{13}C NMR Spectra of the Products

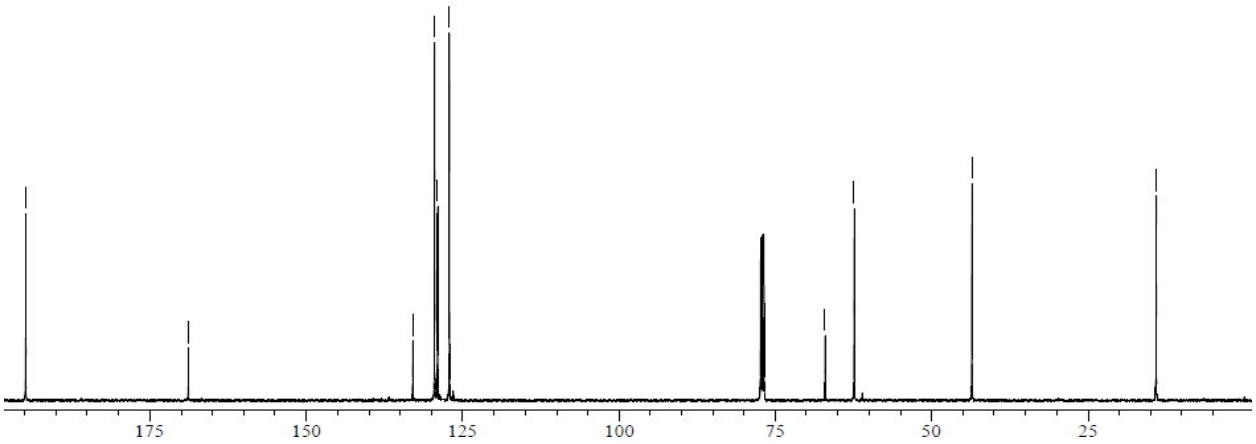
H^{1} & ^{13}C NMR of 2a:



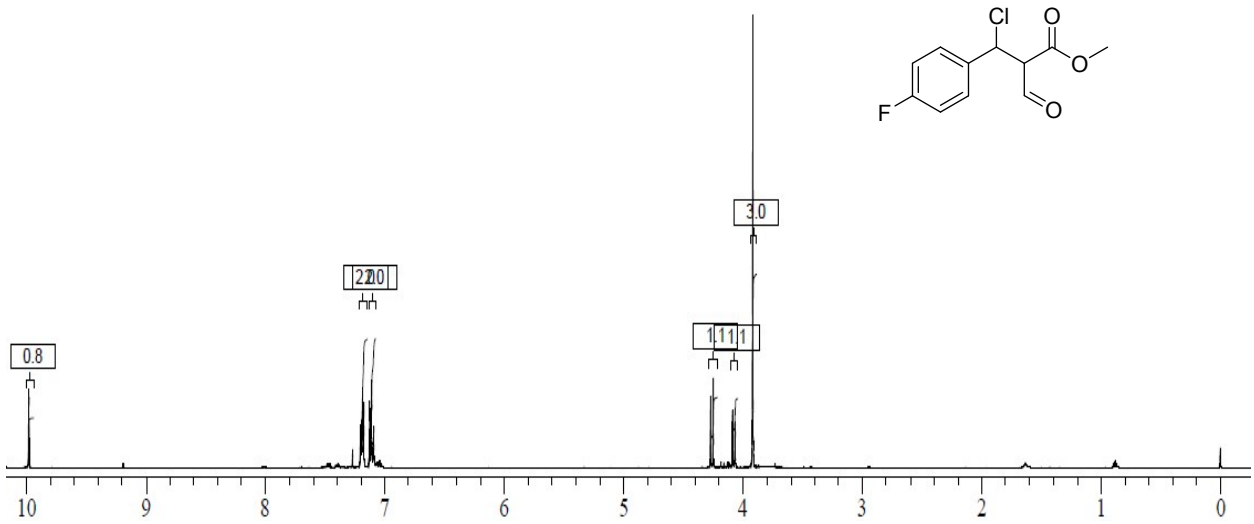


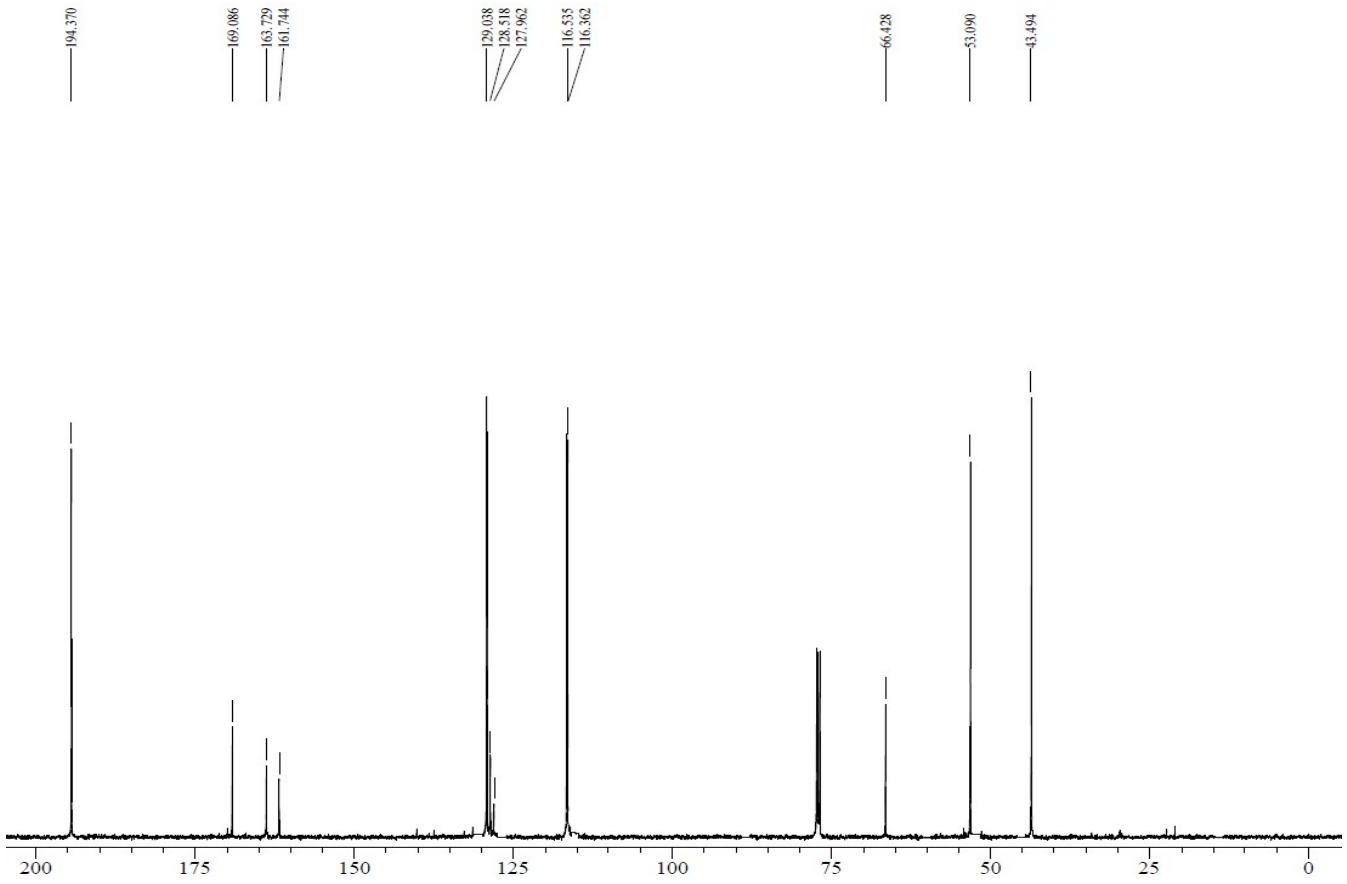
H^1 & ^{13}C NMR of 2b:



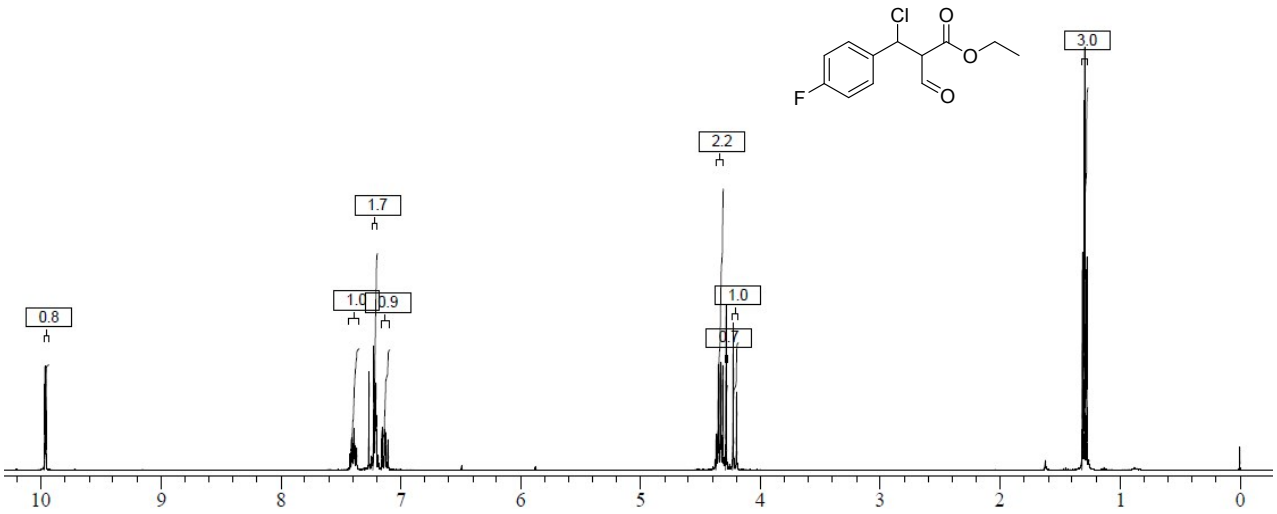


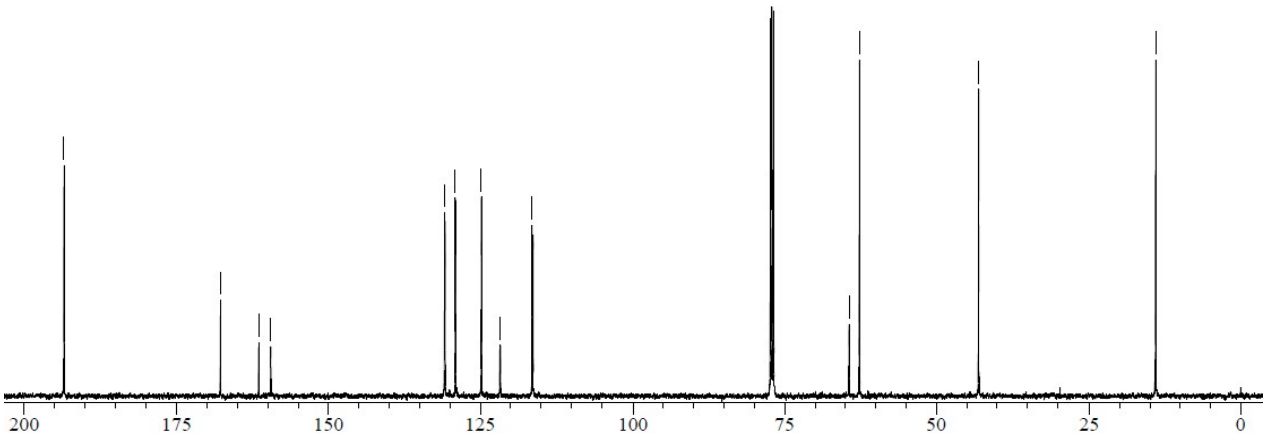
H[1] & [13]C NMR of 2c:



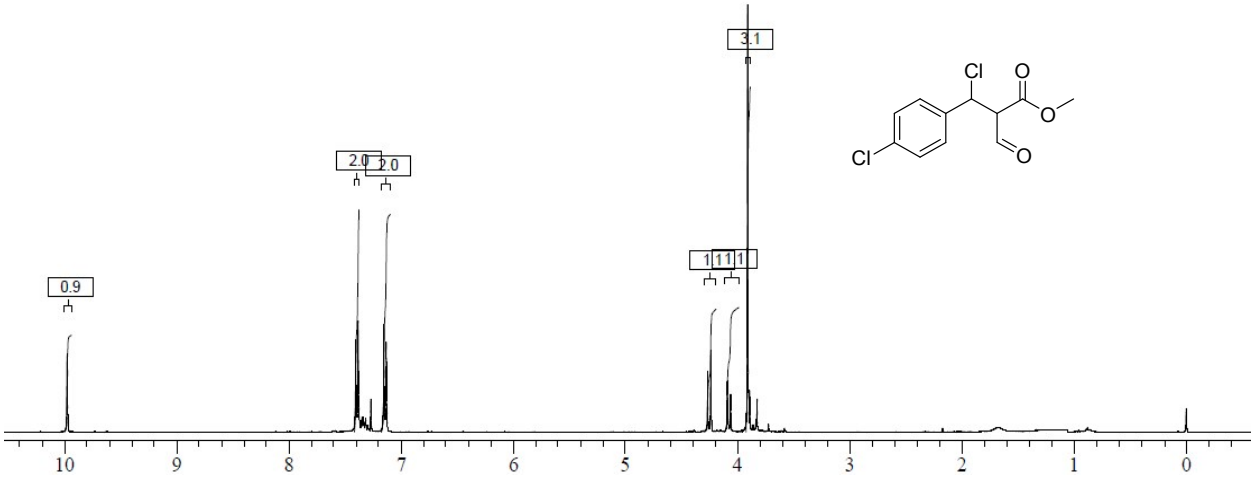


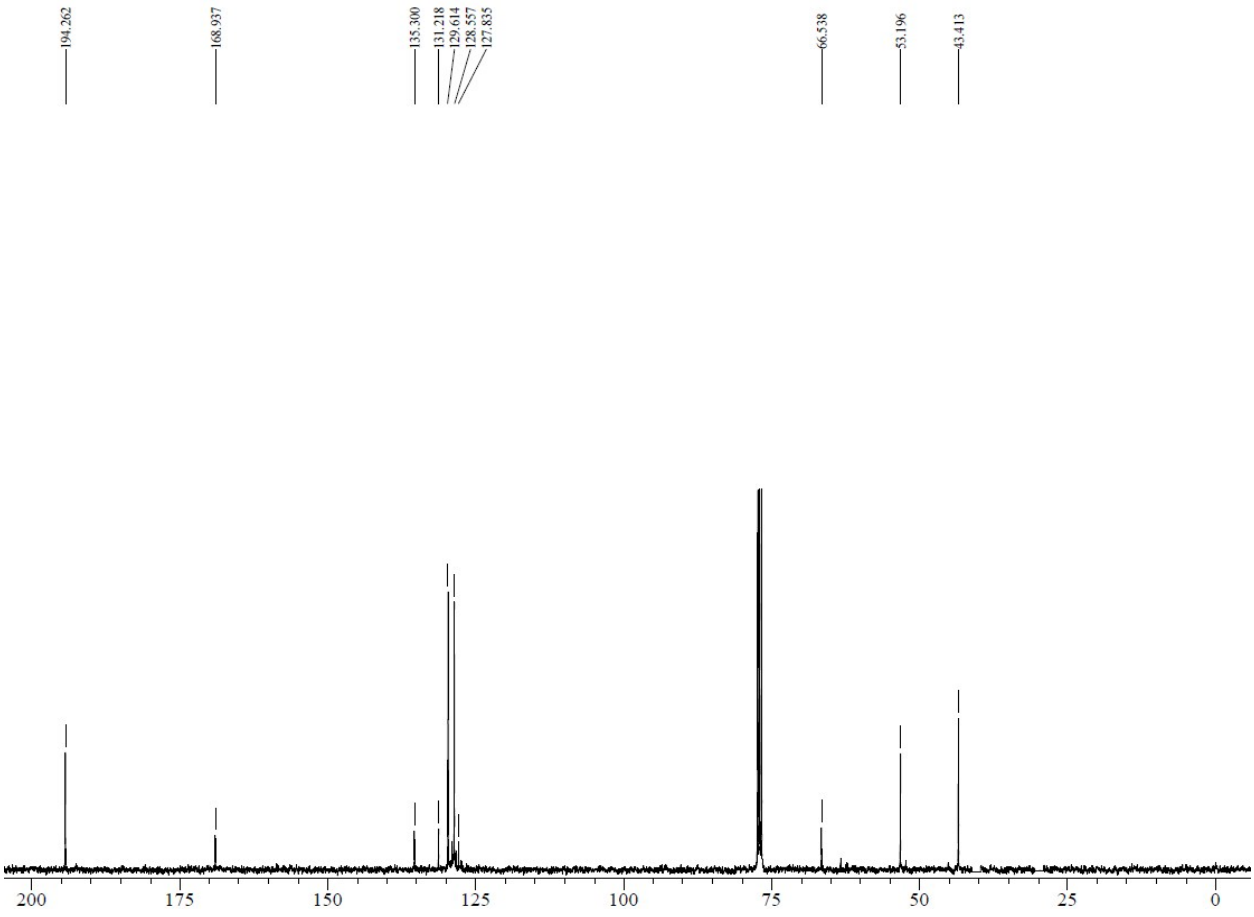
H[1] & [13]C NMR of 2d:



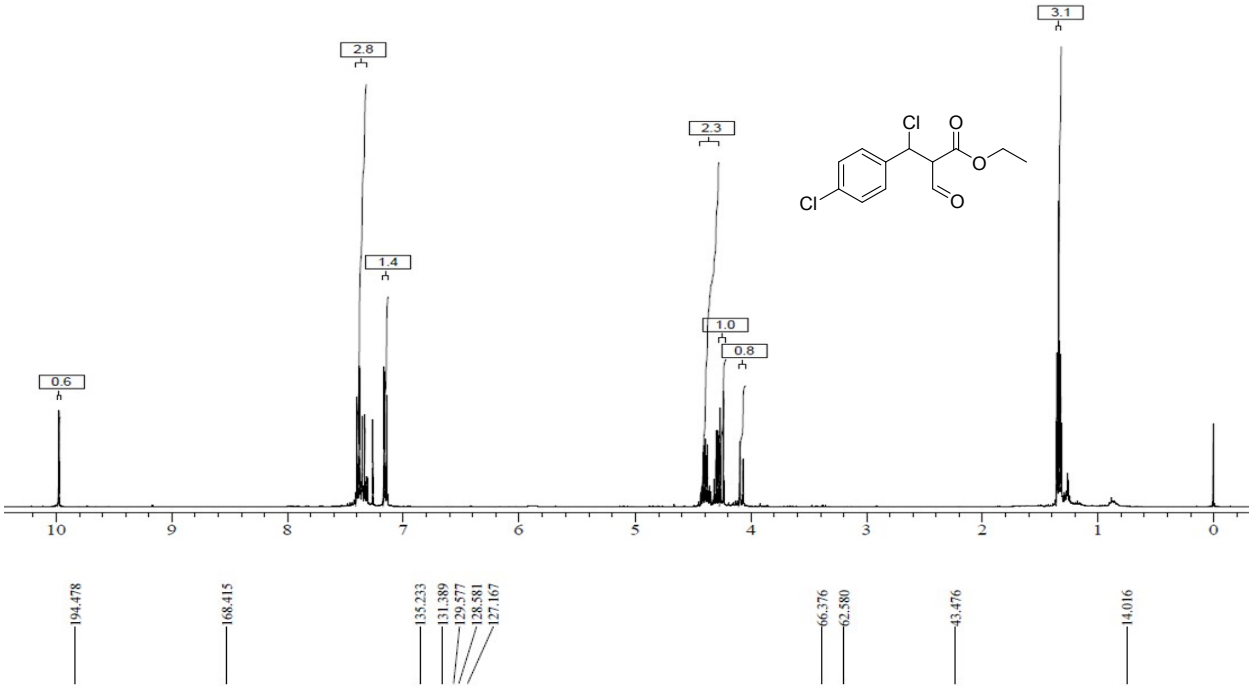


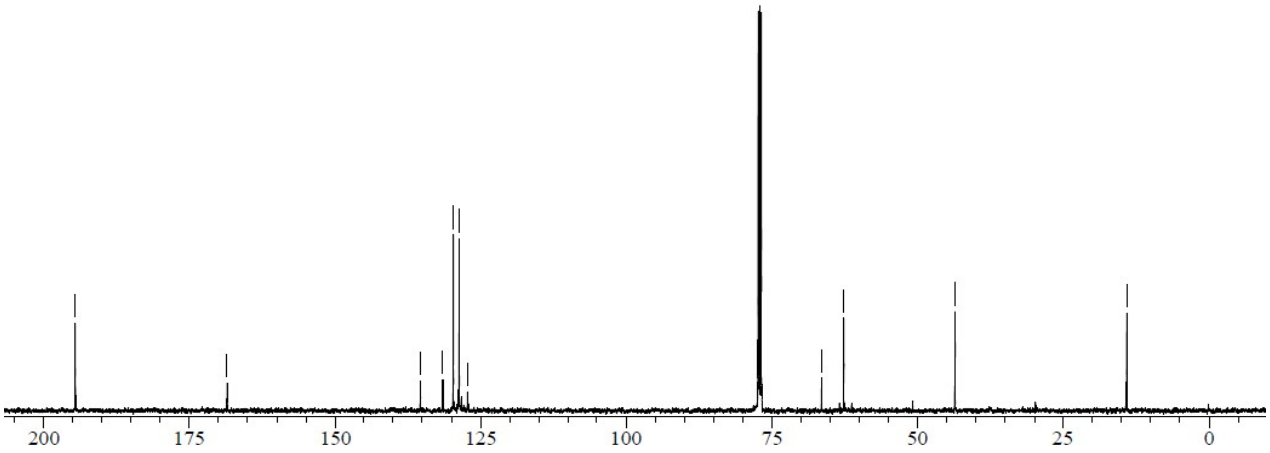
H^1 & ^{13}C NMR of 2e:



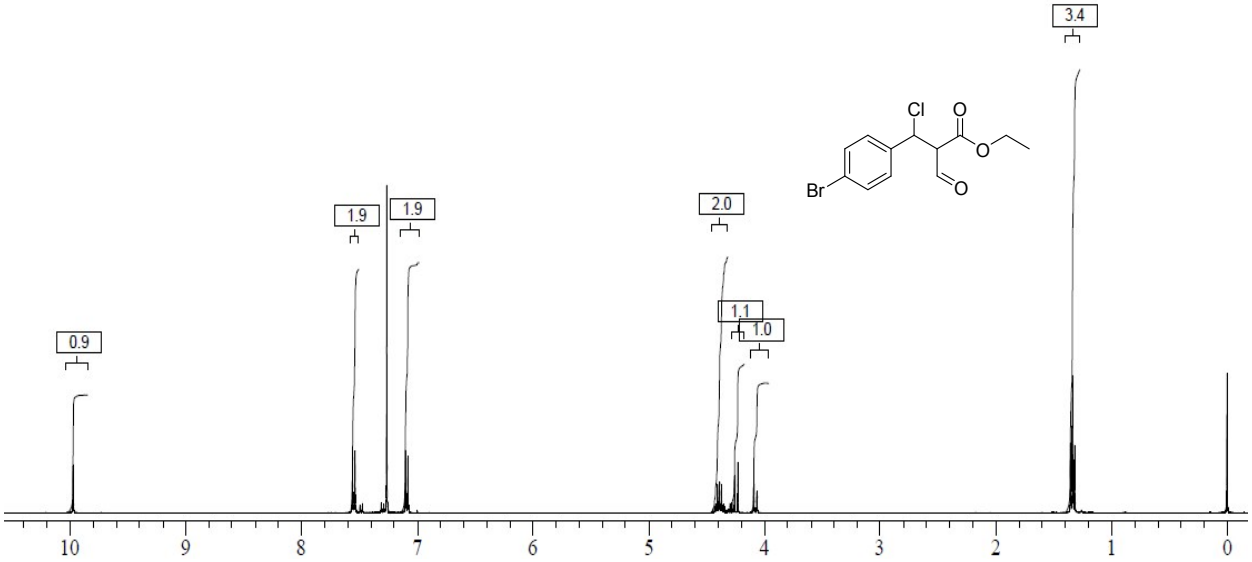


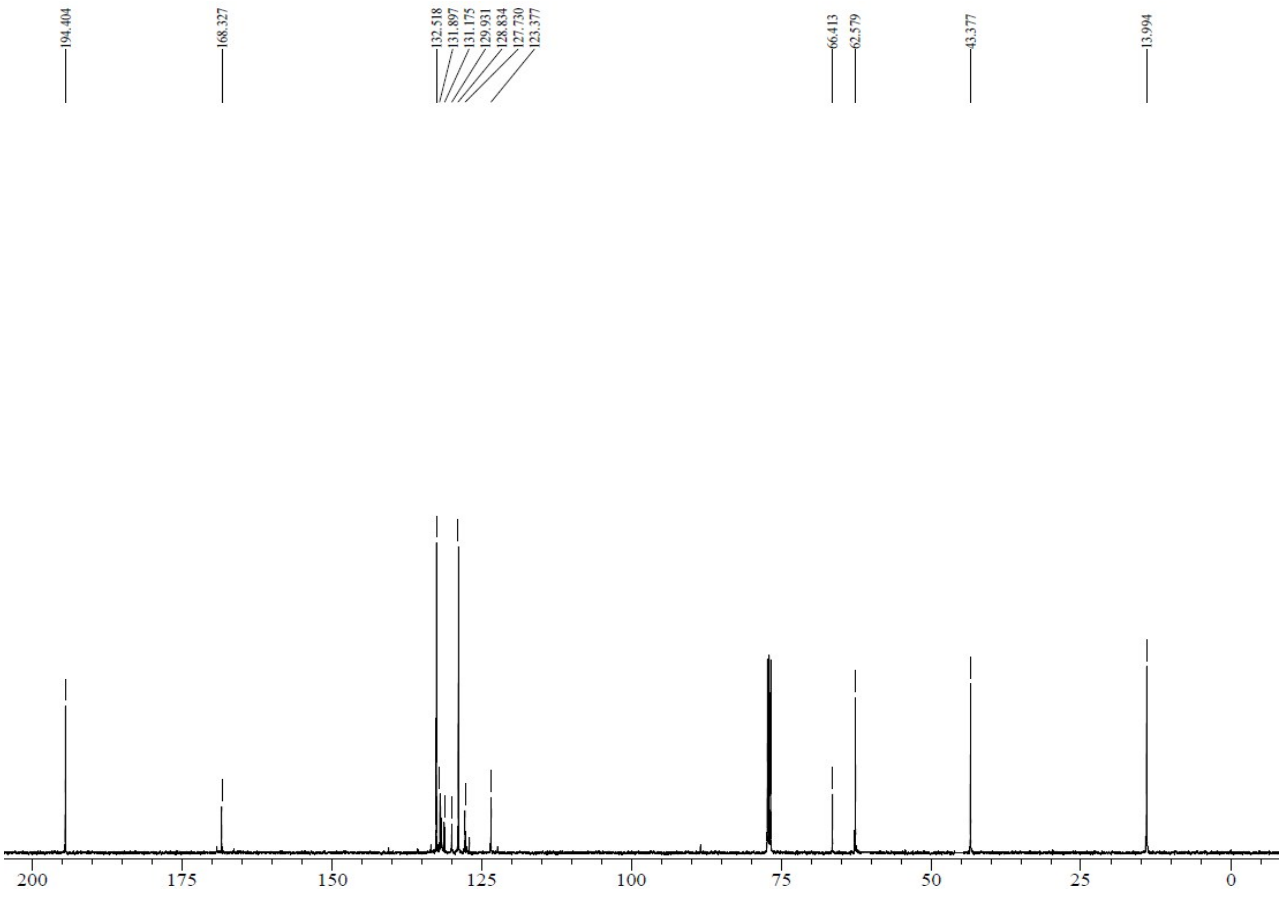
H^1 & ^{13}C NMR of 2f:



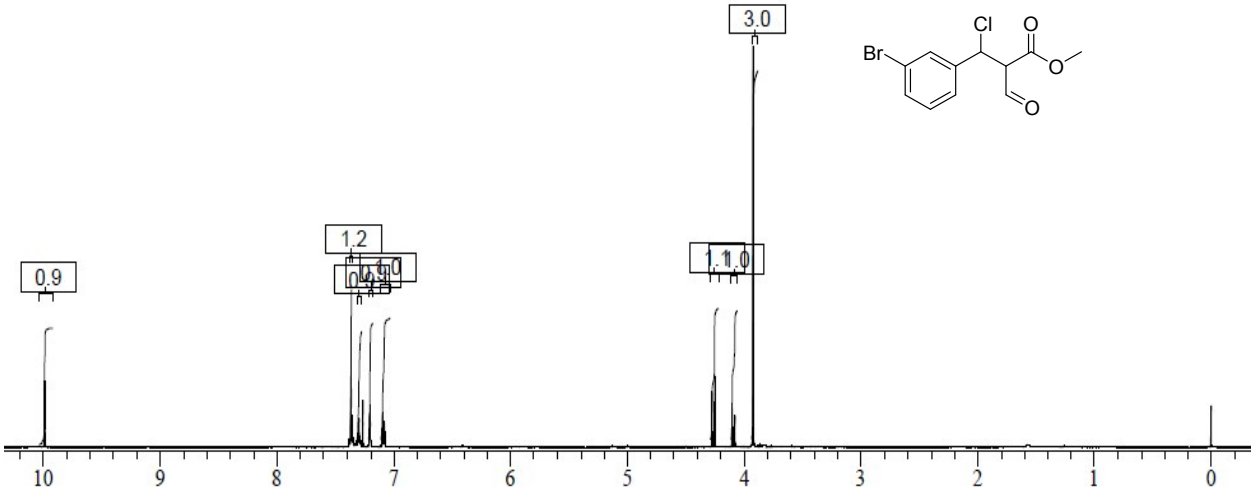


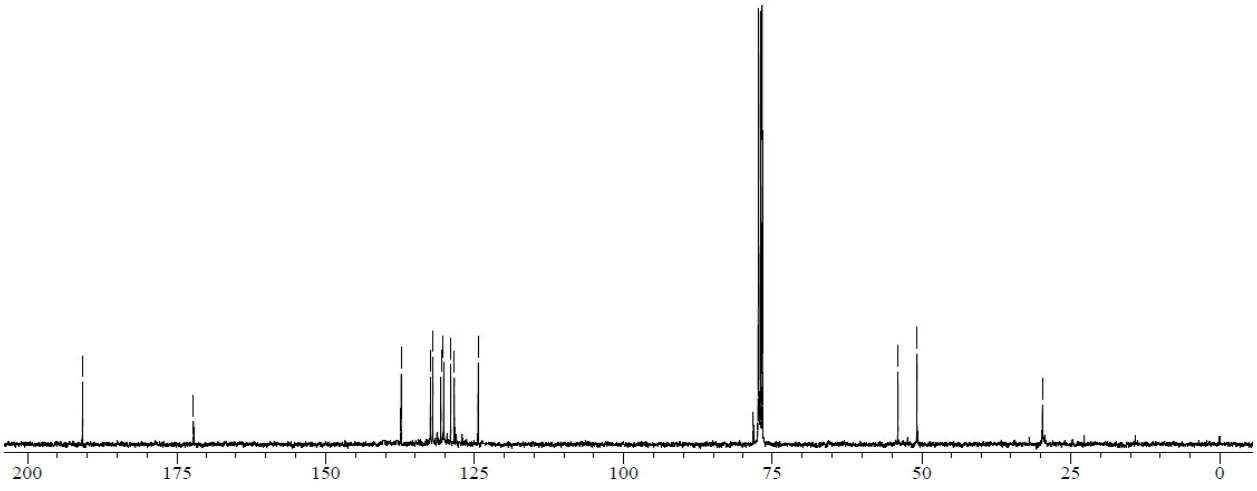
H^1 & ^{13}C NMR of 2g:



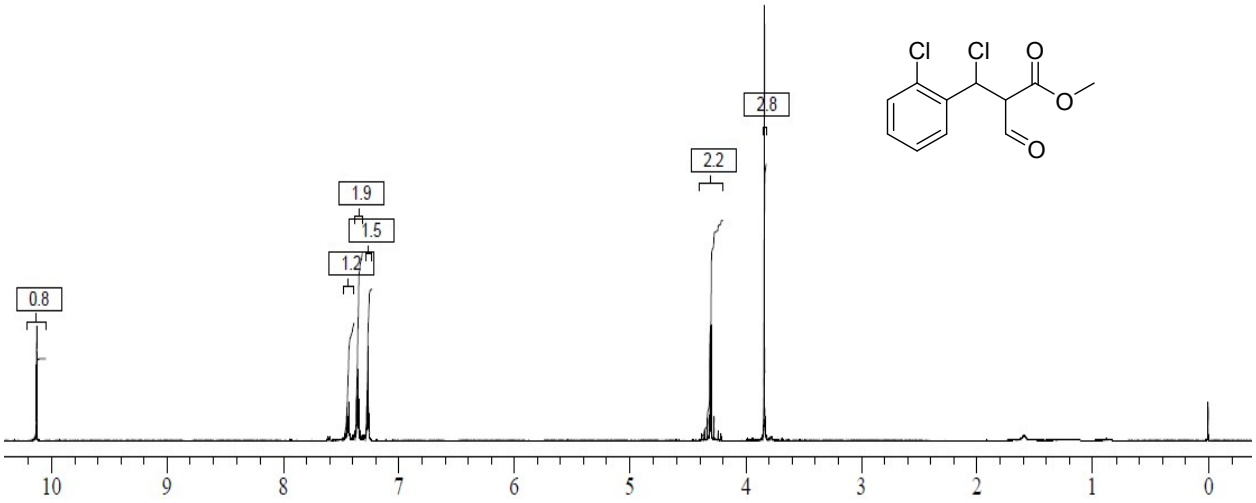


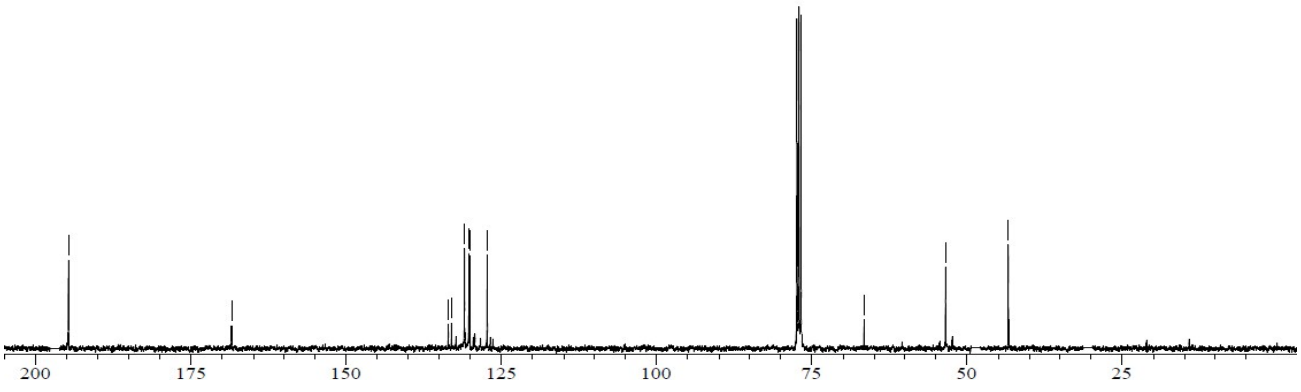
H[1] & 13C NMR of 2h:



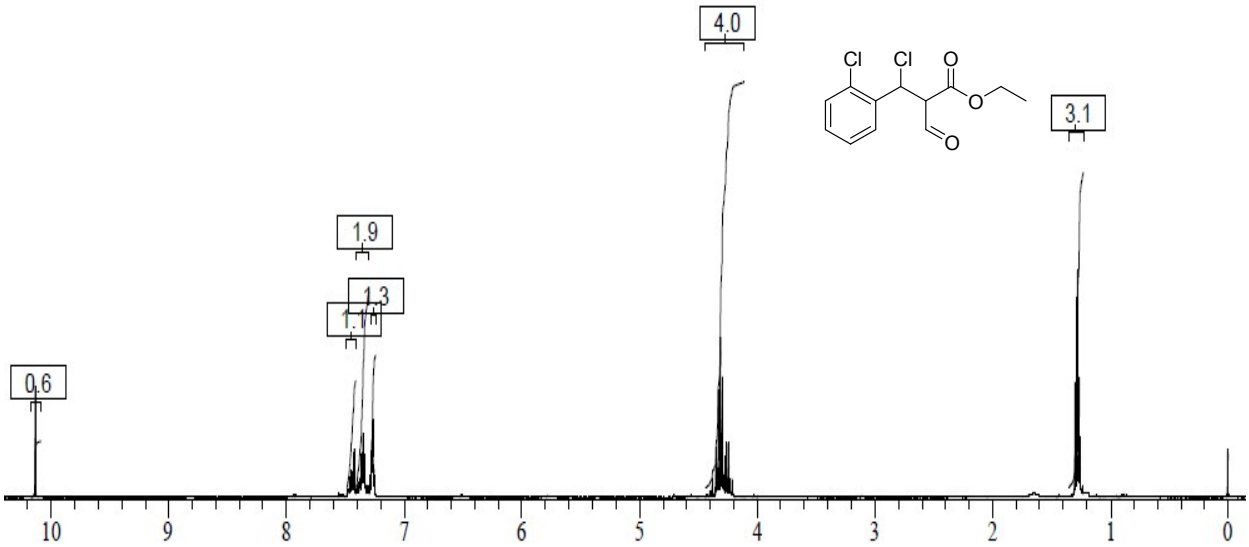


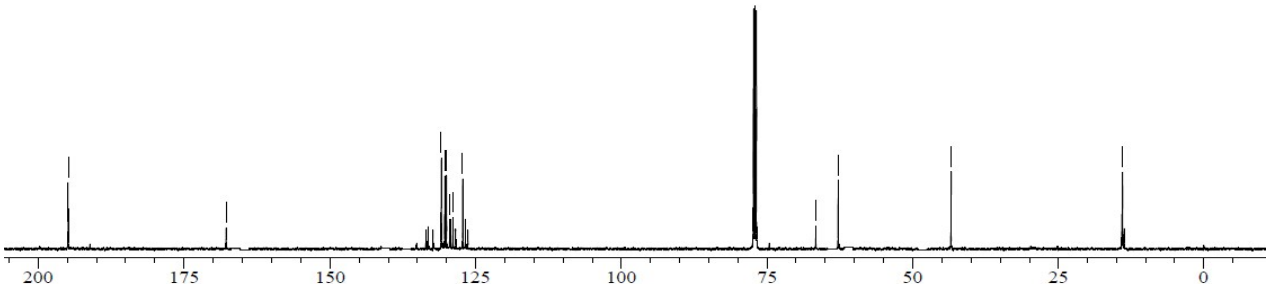
H[1] & 13C NMR of 2i:



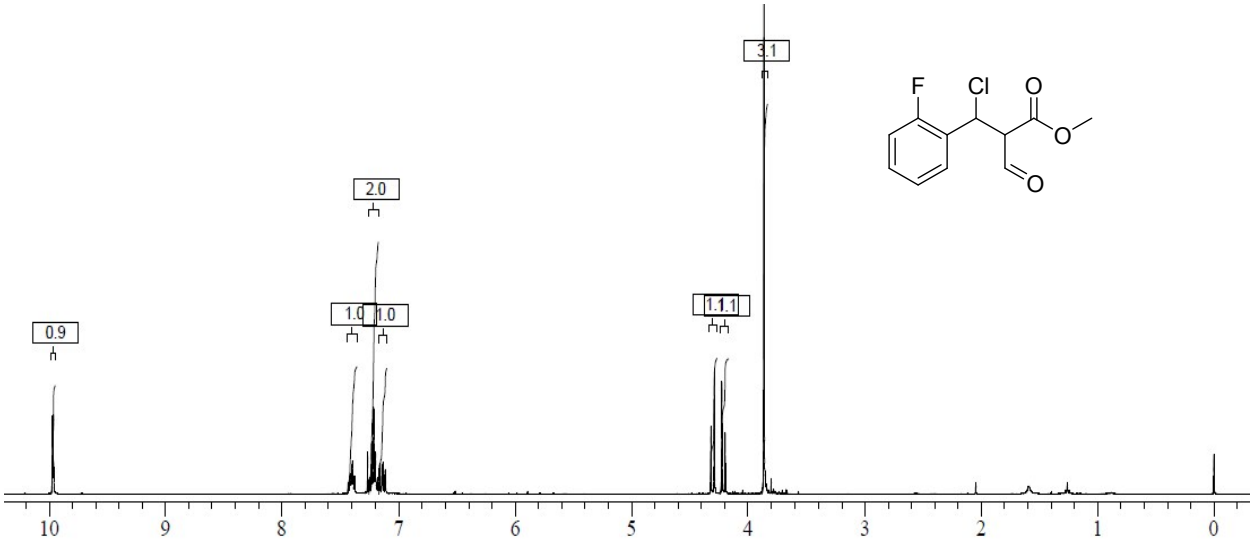


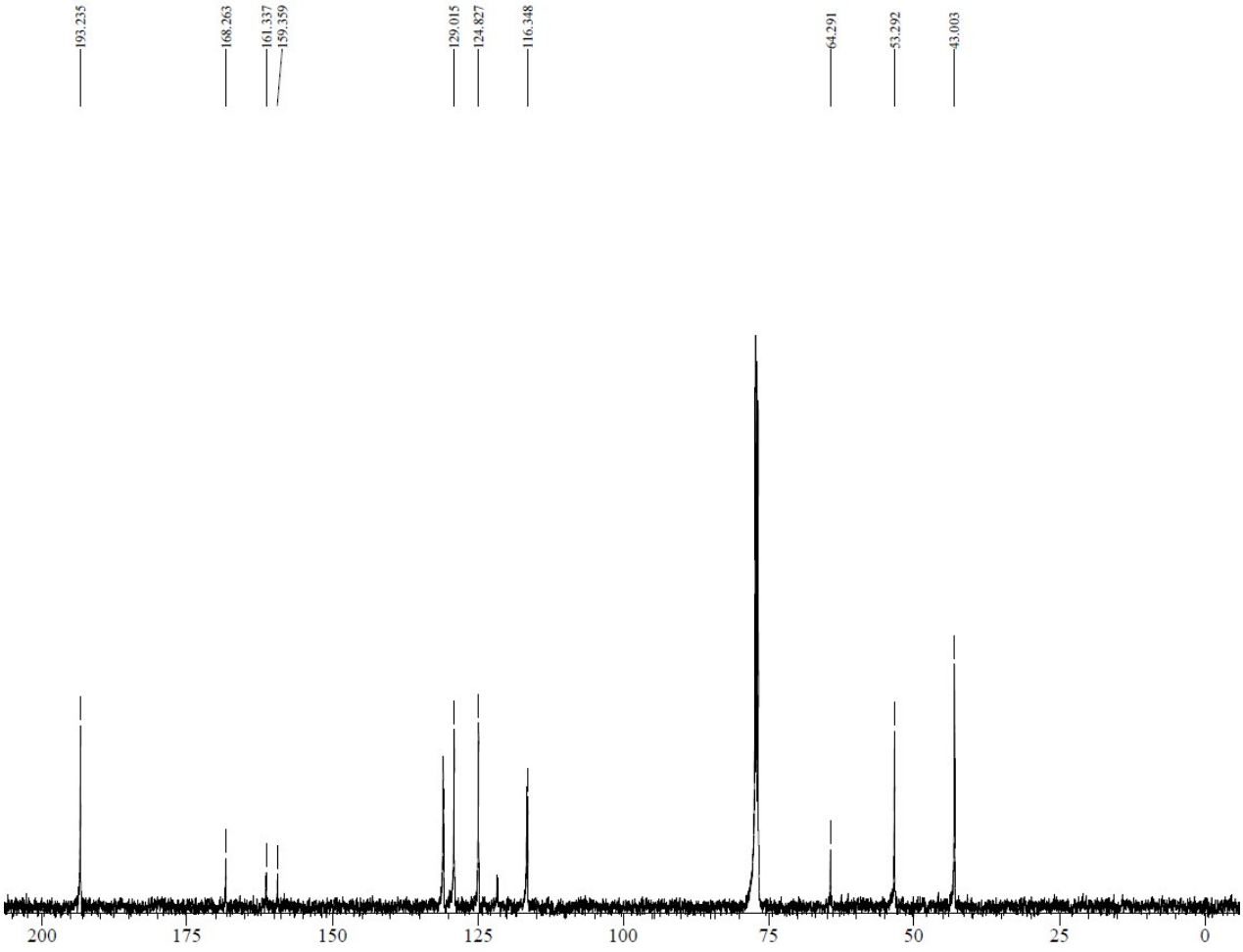
H[1] & 13C NMR of 2j:



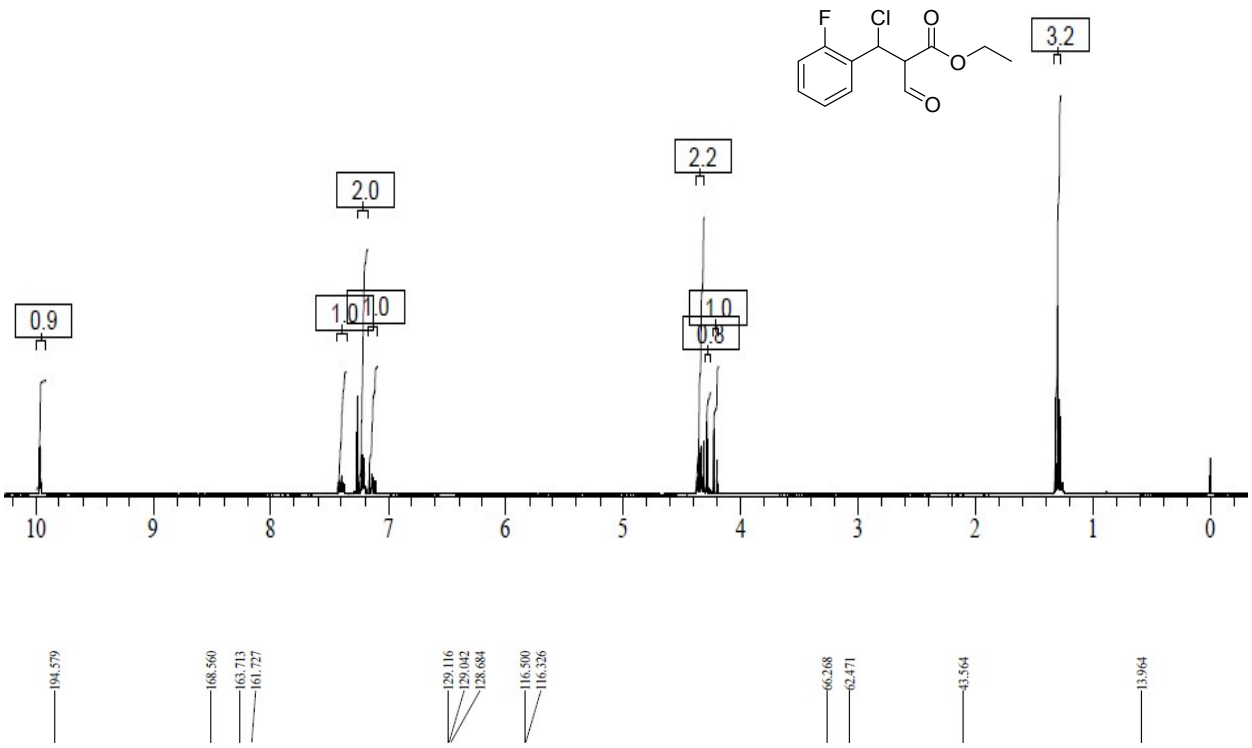


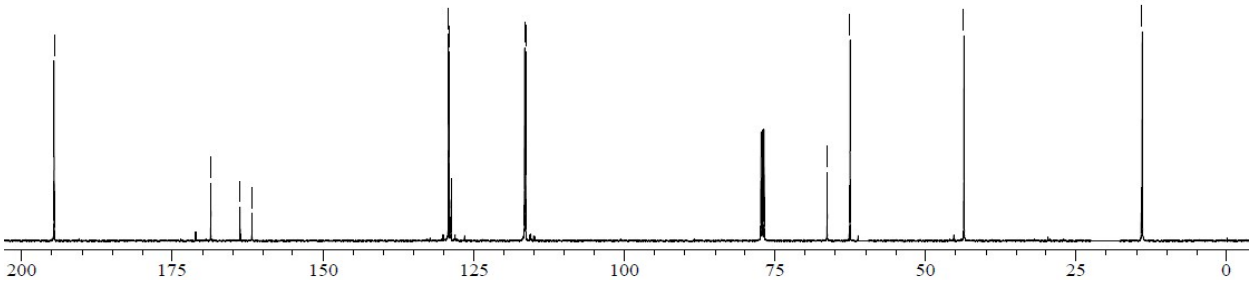
H[1] & 13C NMR of 2k:



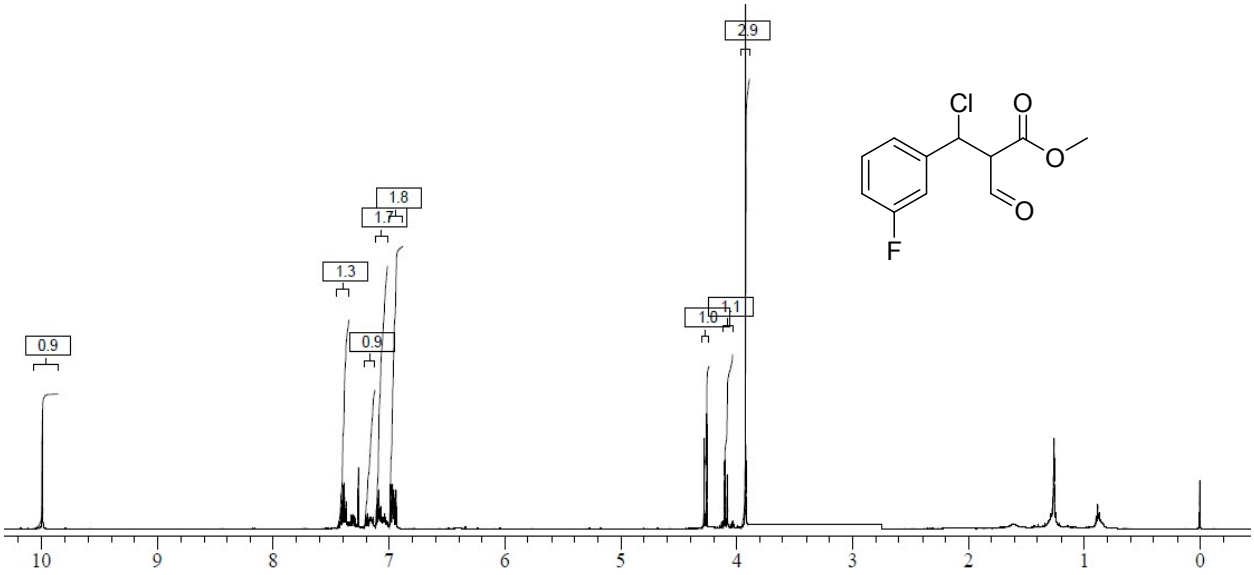


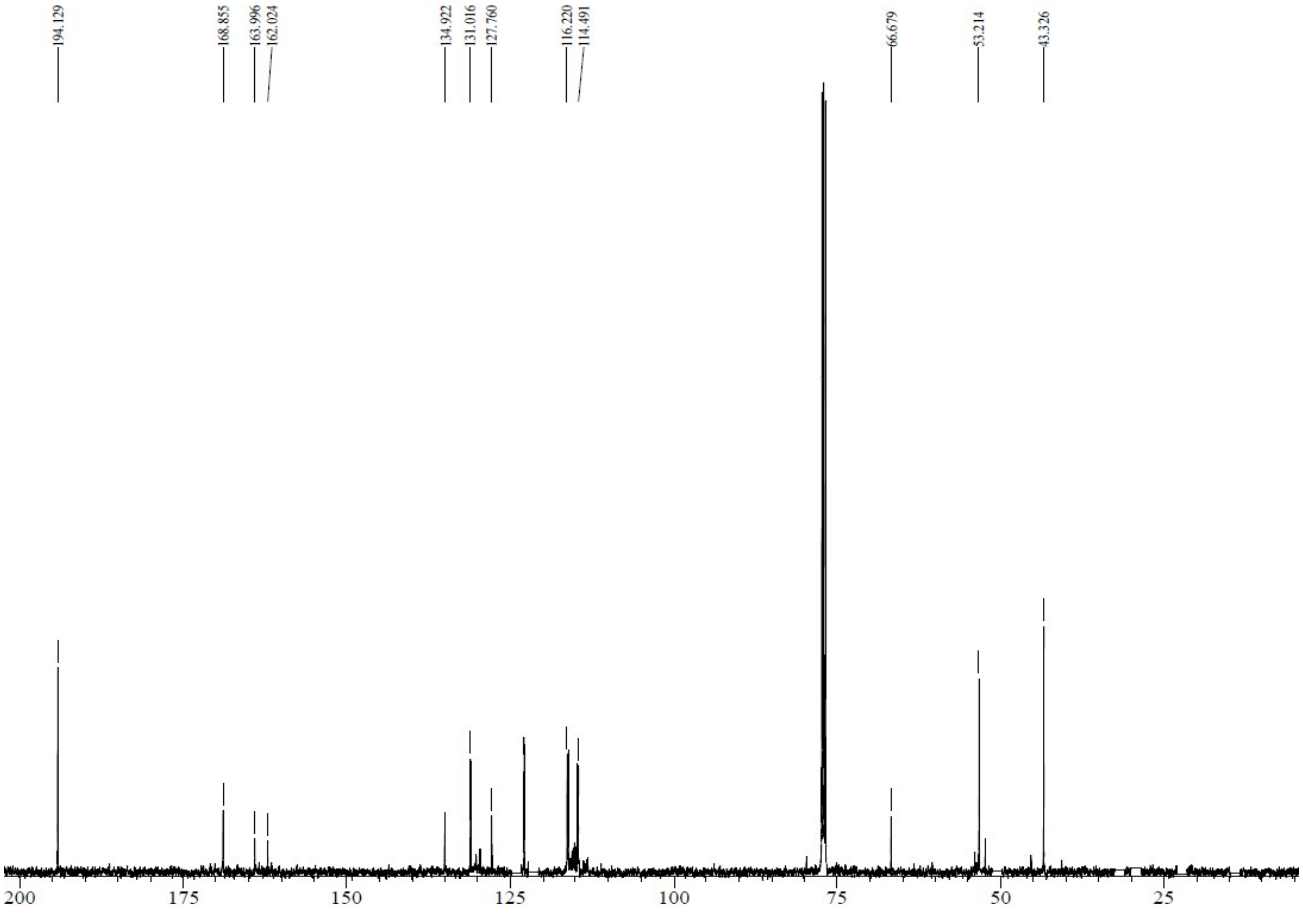
H[1] & [13]C NMR of 2l:



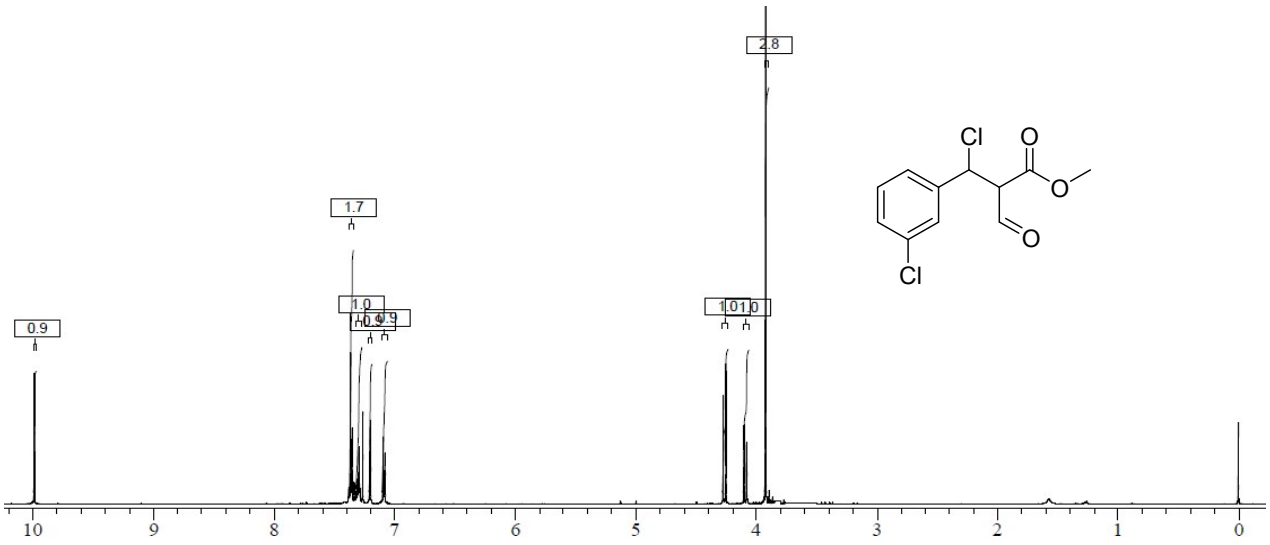


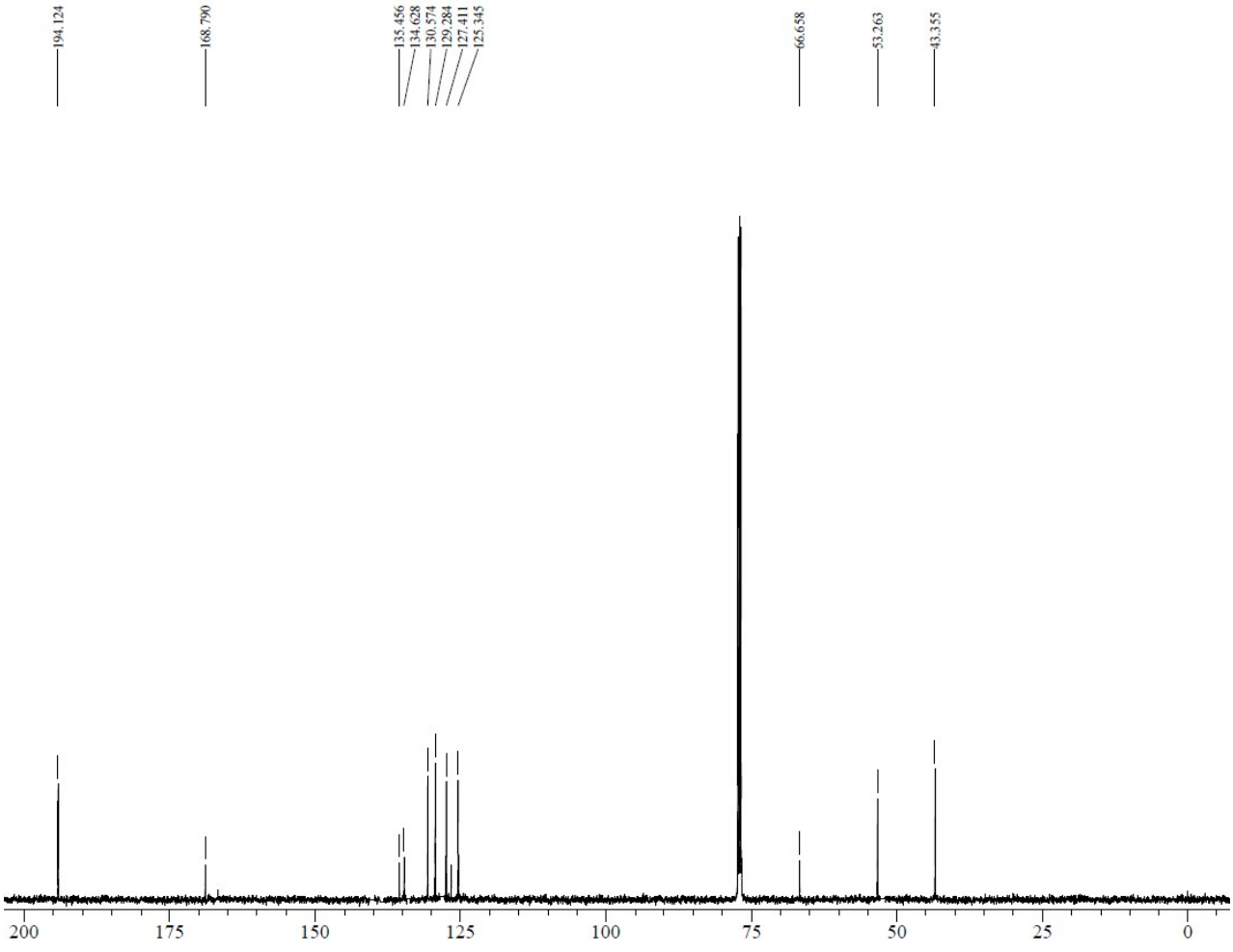
H[1] & [13]C NMR of 2m:



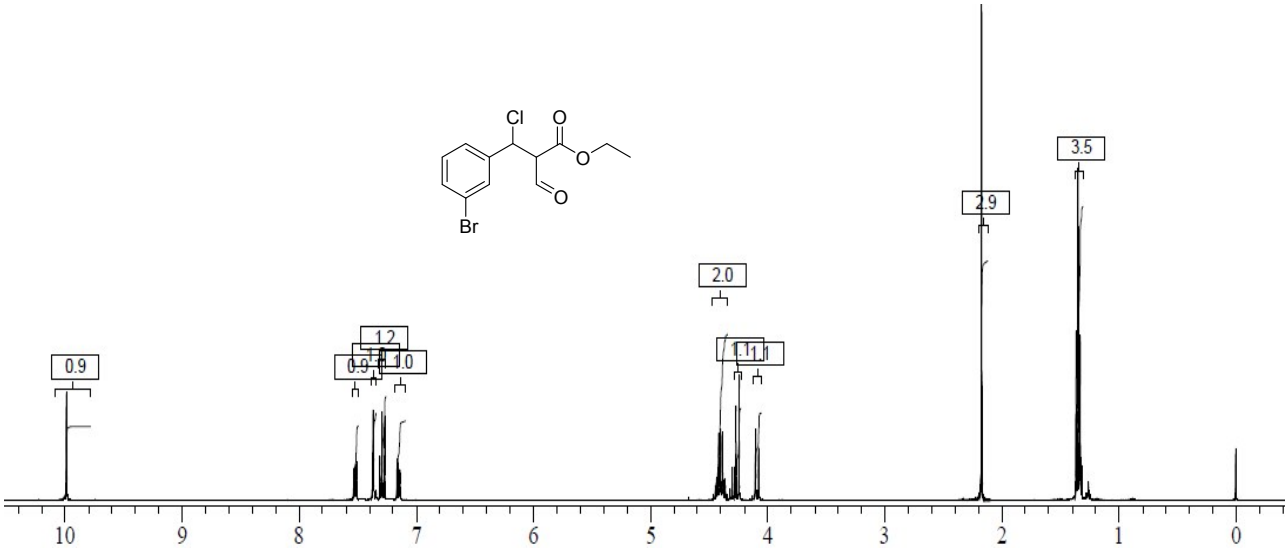


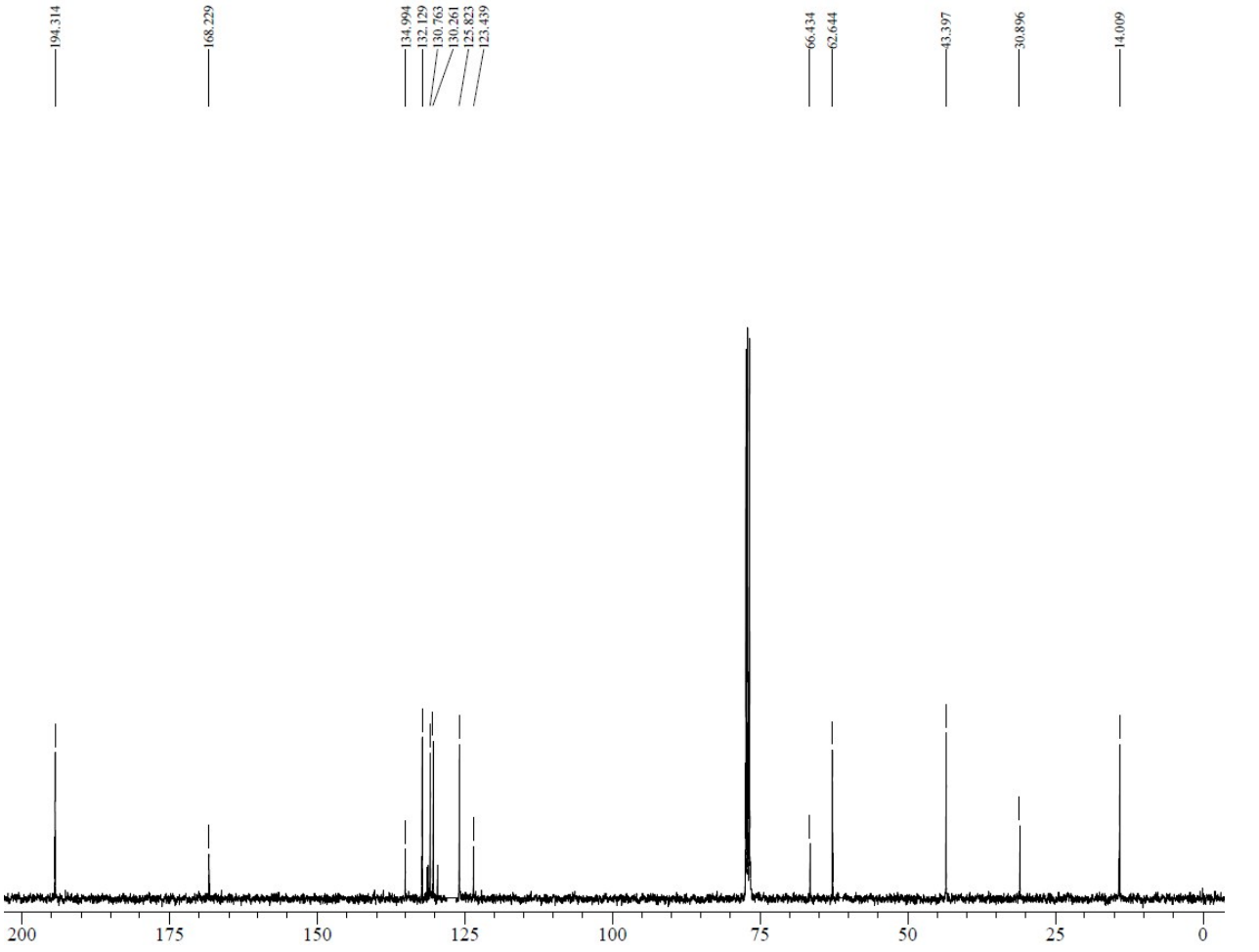
H[1] & [13]C NMR of 2n:



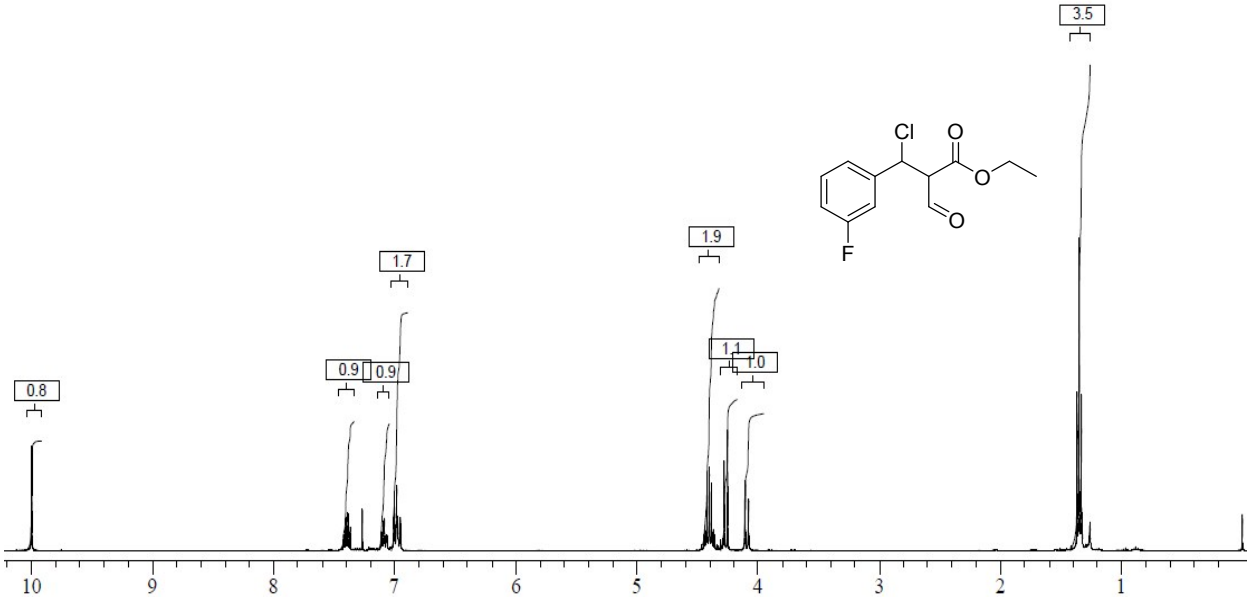


H[1] & [13]C NMR of 2o:

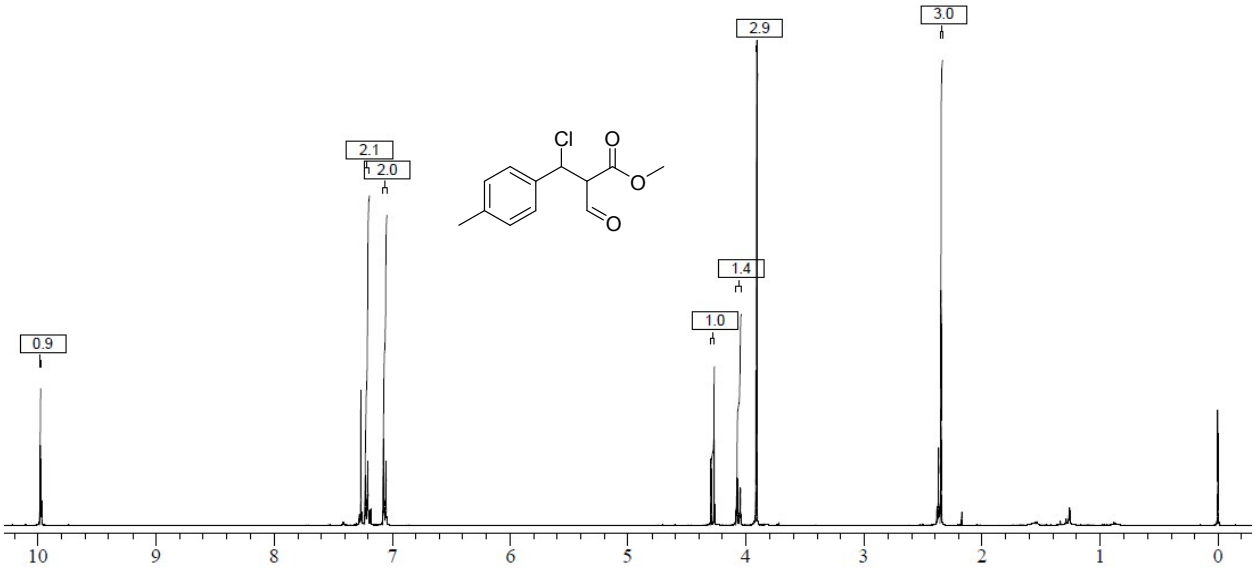


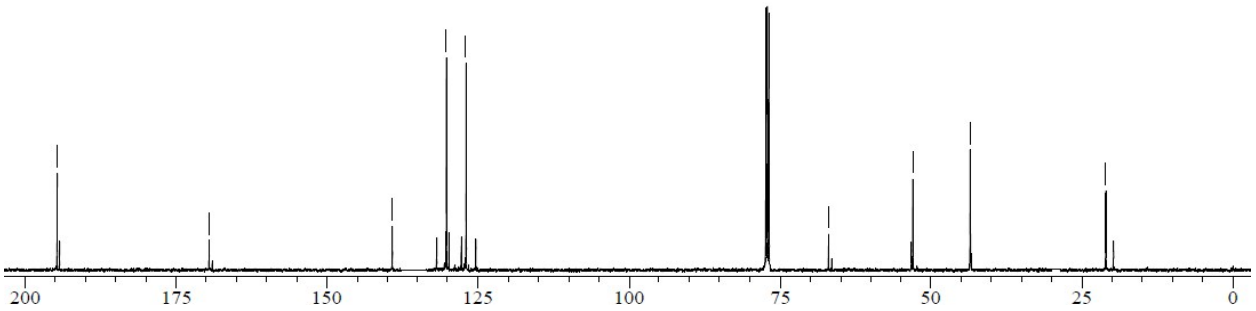


H[1] & [13]C NMR of 2p:

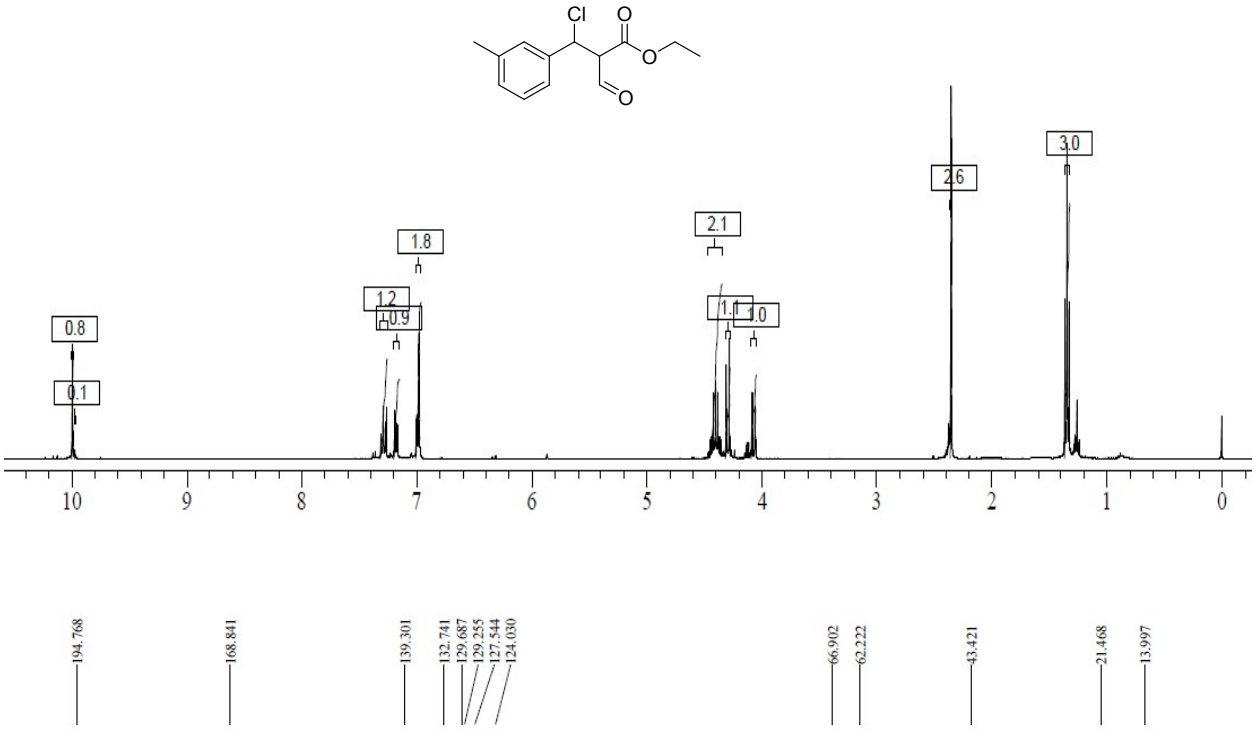


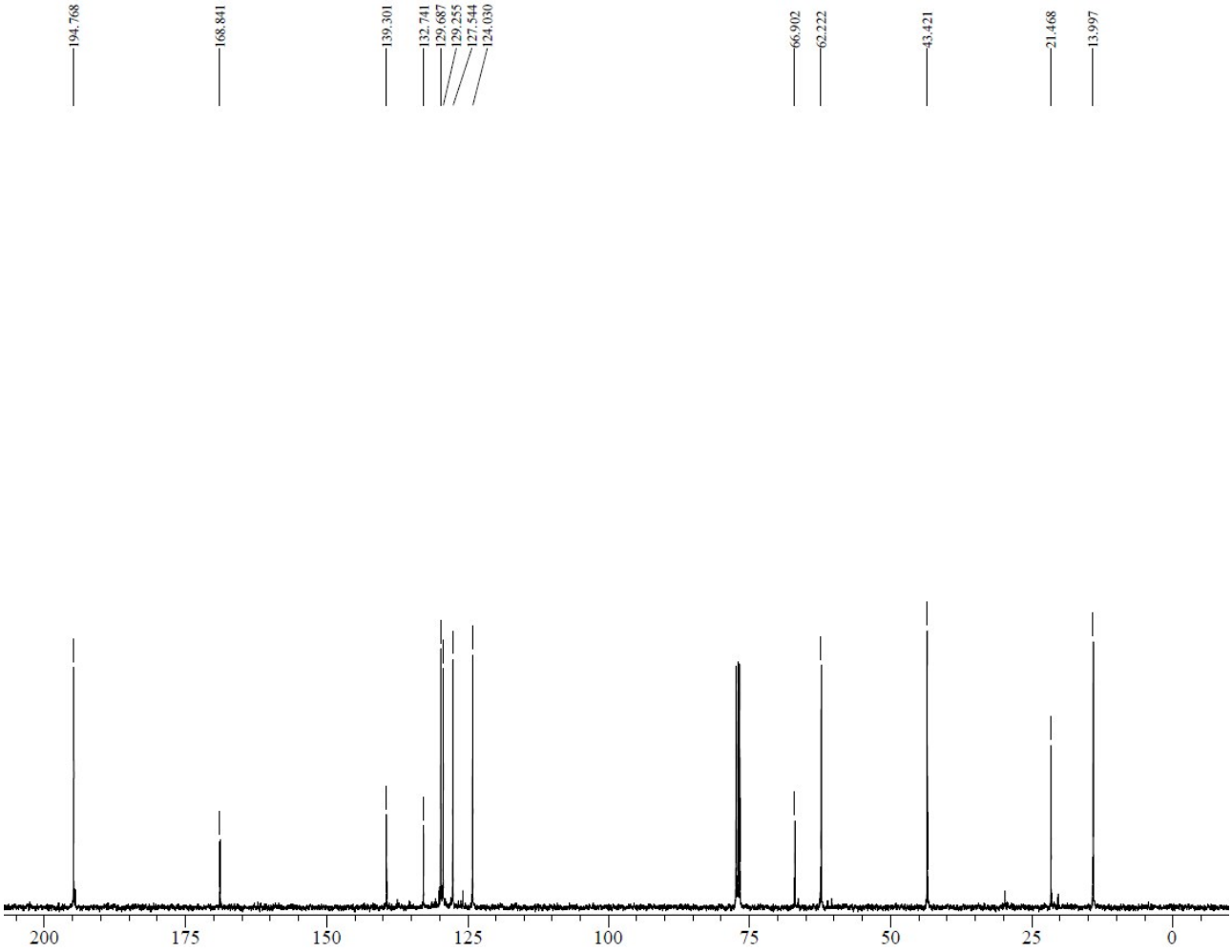
H[1] & 13C NMR of 2q:



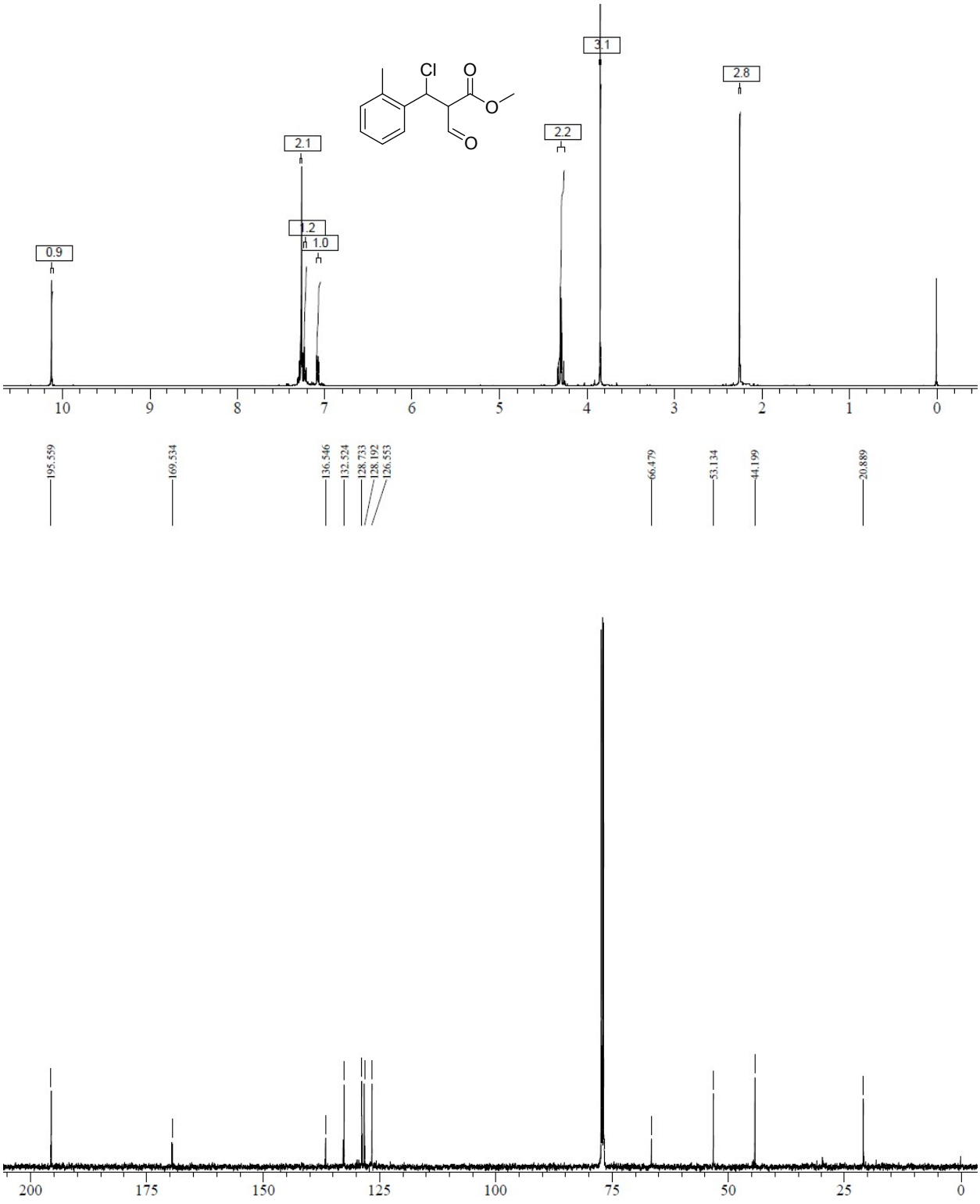


H^1 & ^{13}C NMR of 2r:

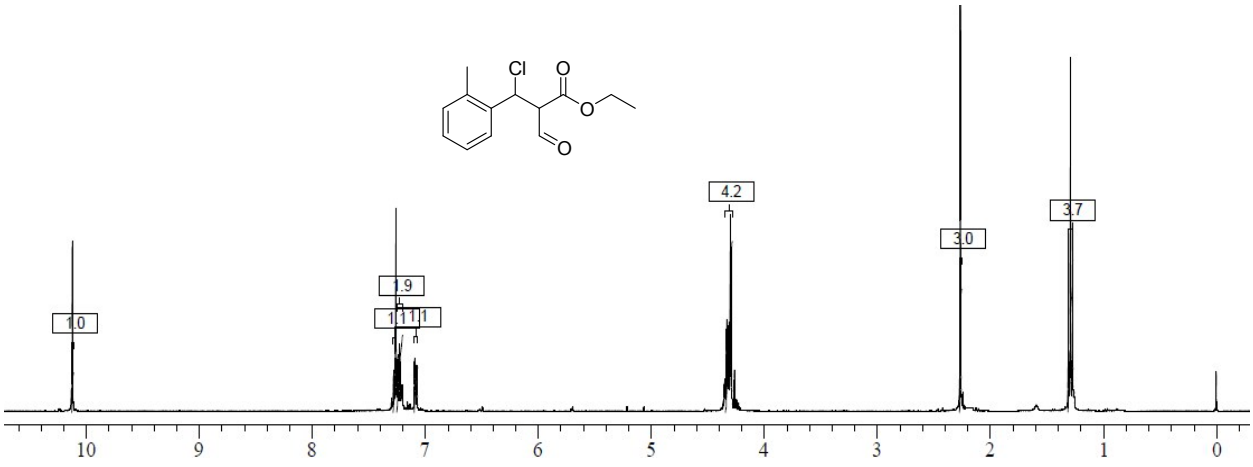


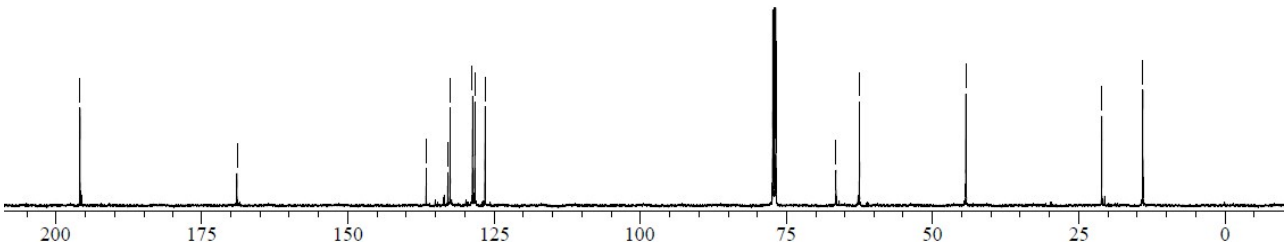


H[1] & [13]C NMR of 2s:

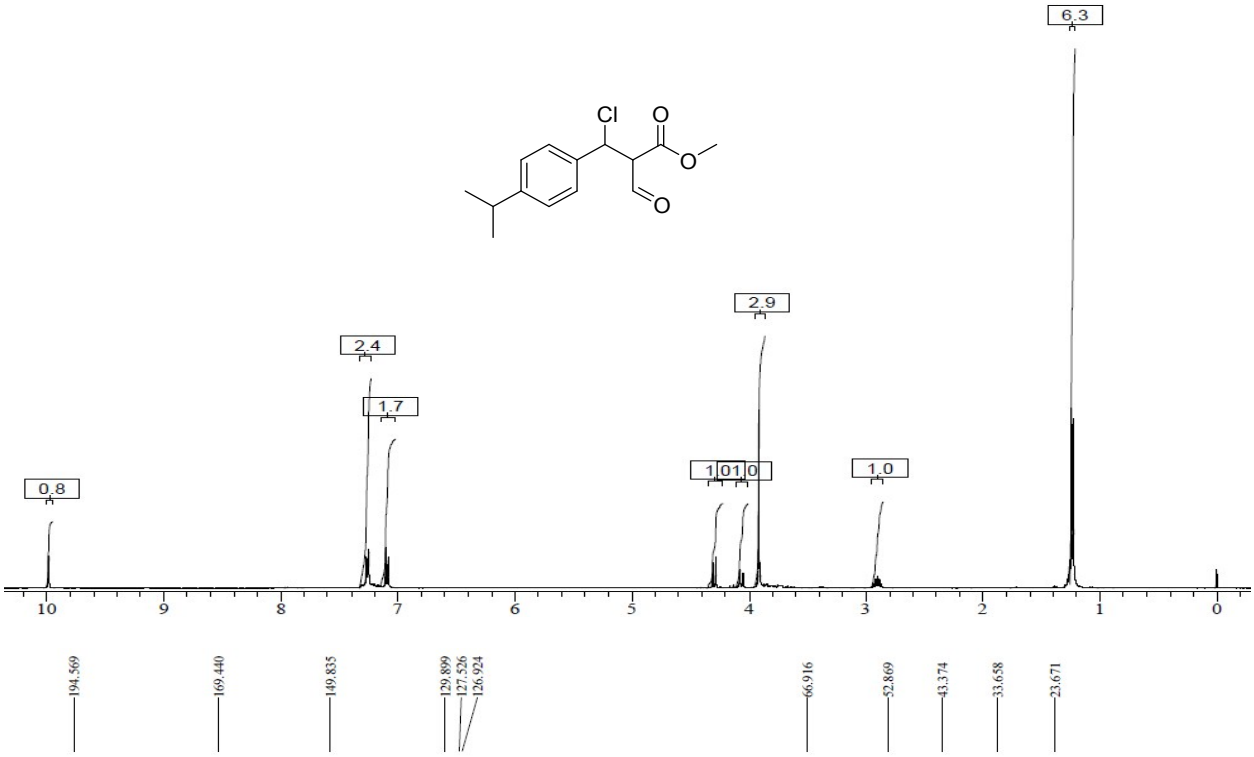


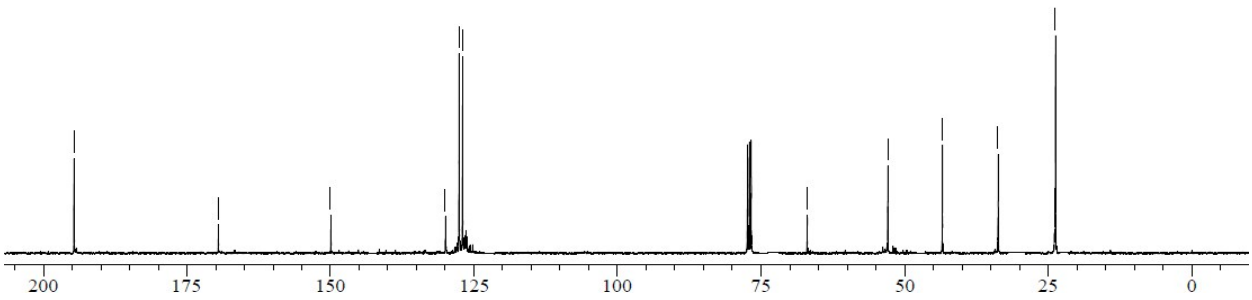
H^1 & ^{13}C NMR of 2t:



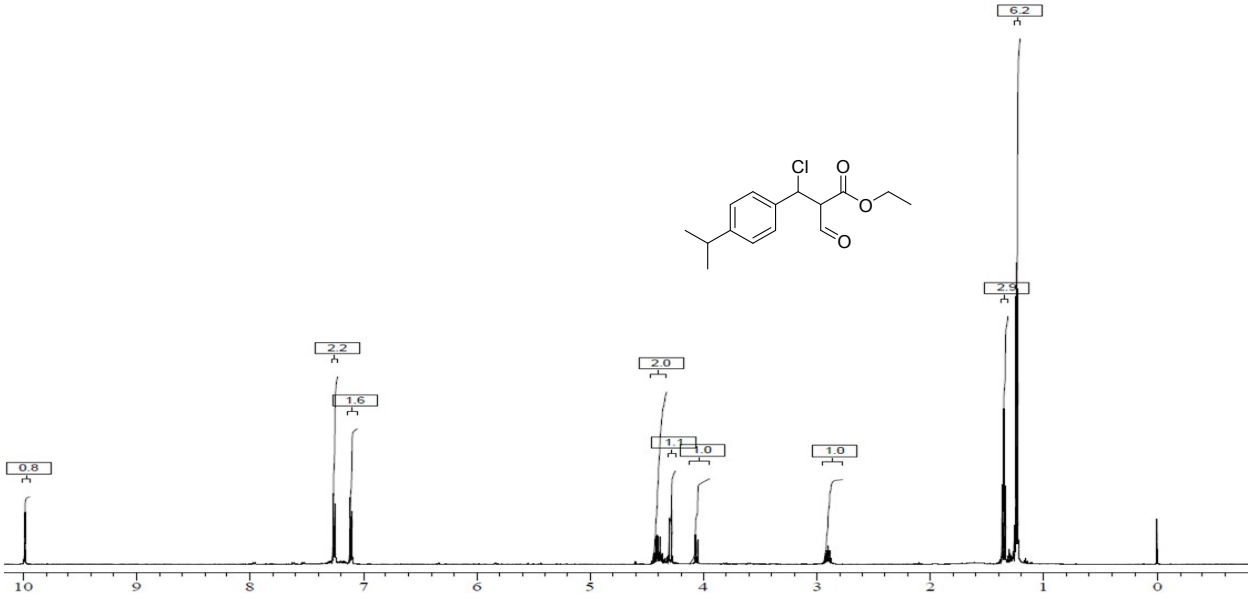


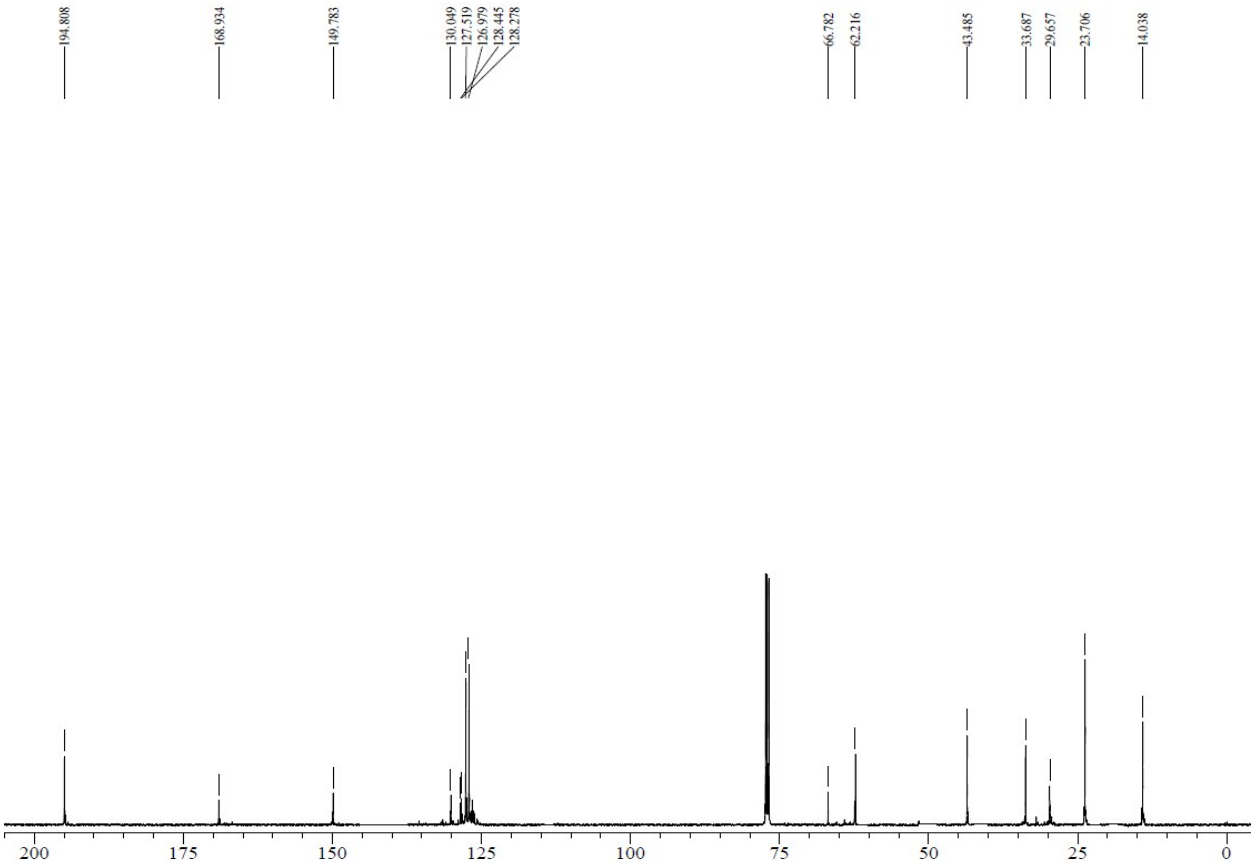
H^1 & ^{13}C NMR of 2u:



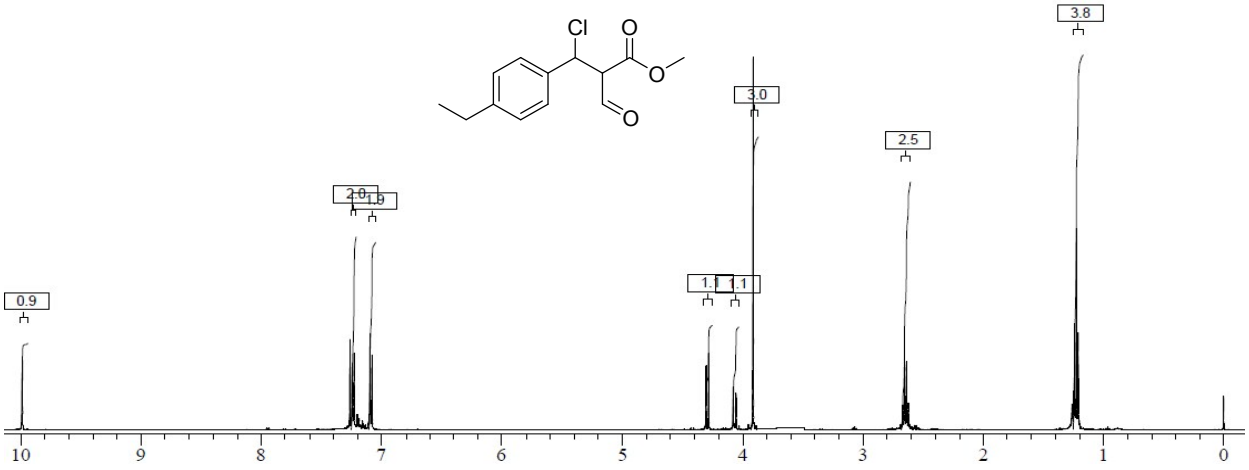


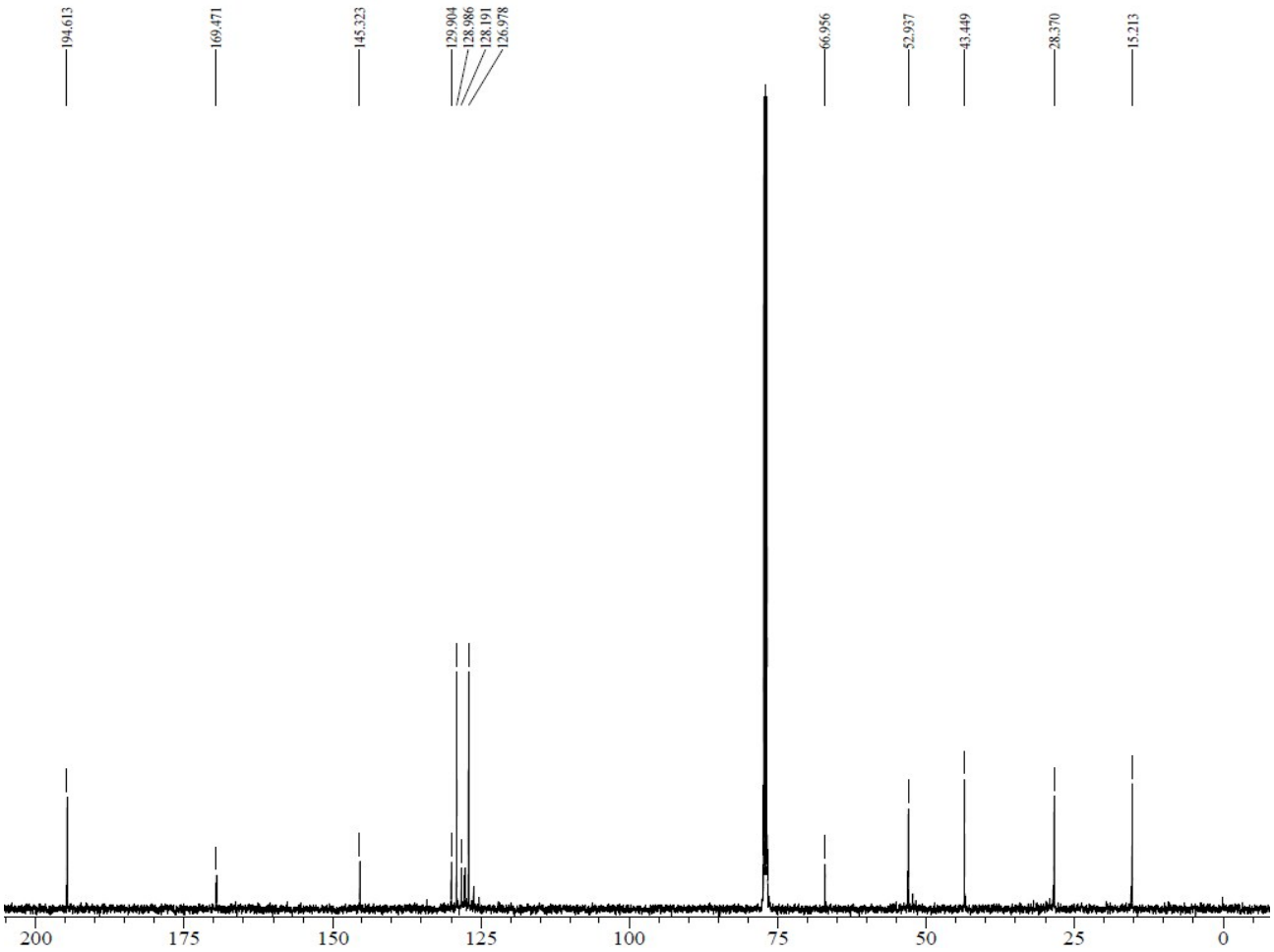
H[1] & [13]C NMR of 2v:



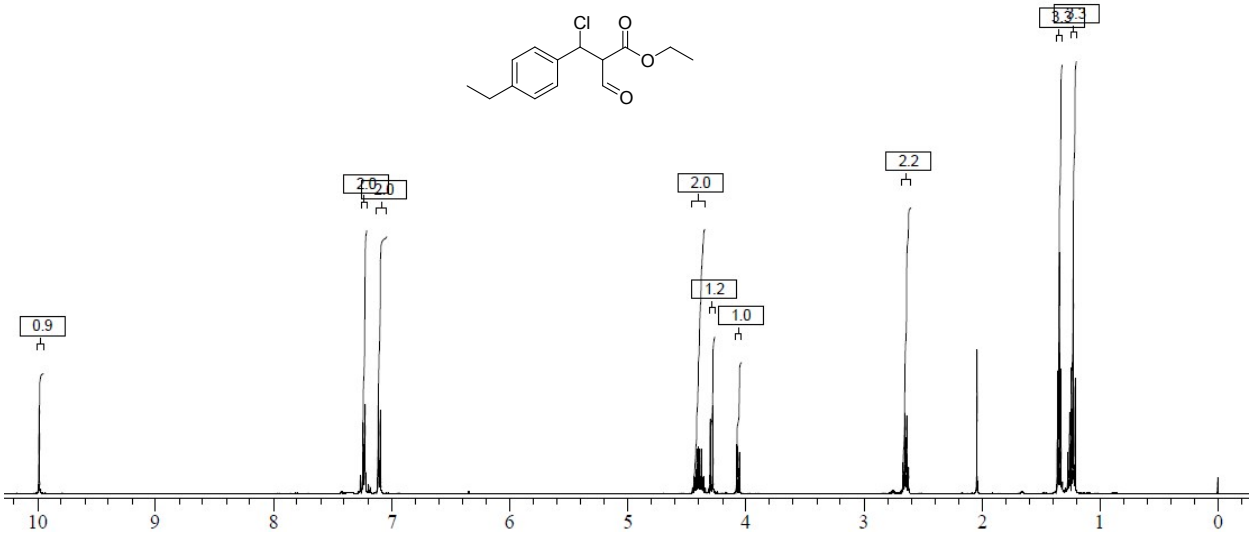


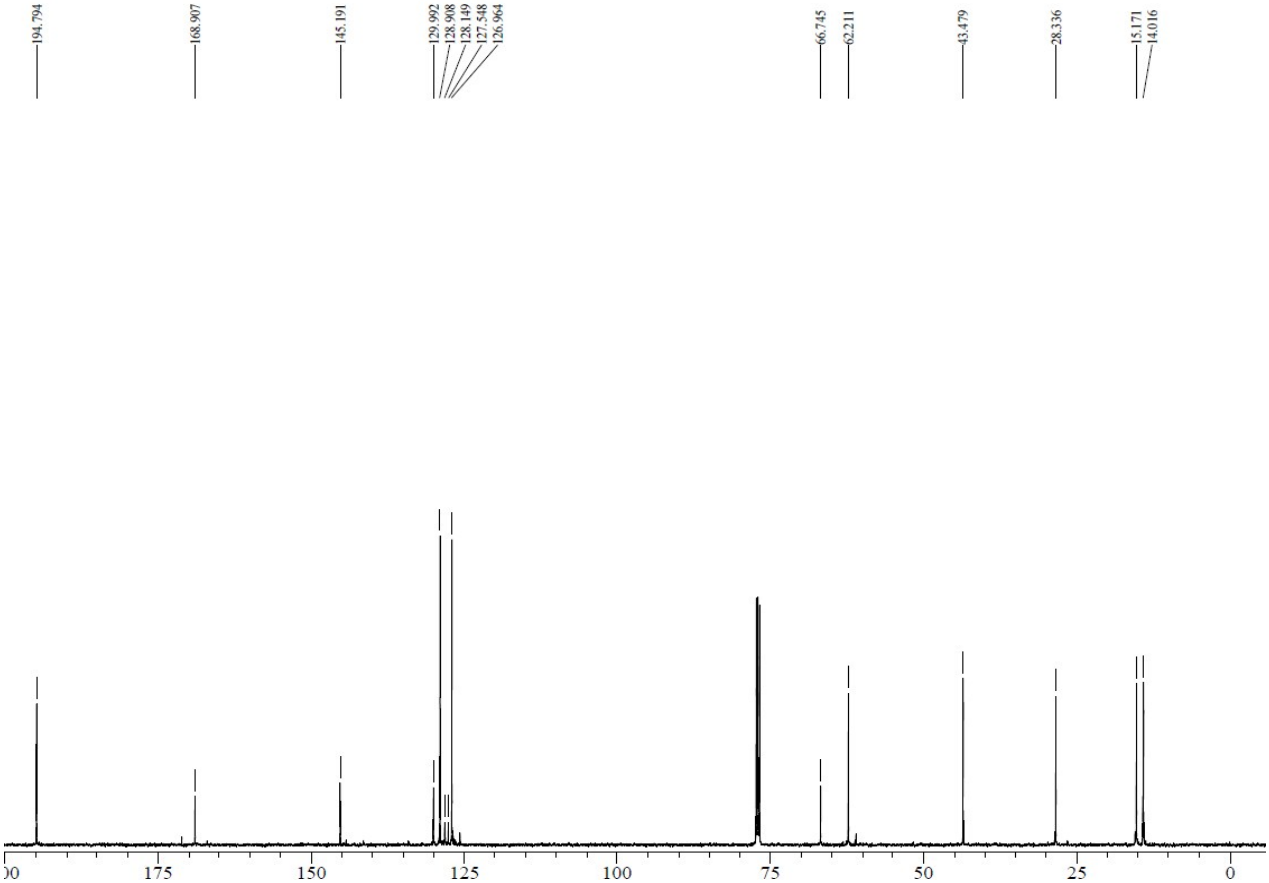
H[1] & [13]C NMR of 2w:



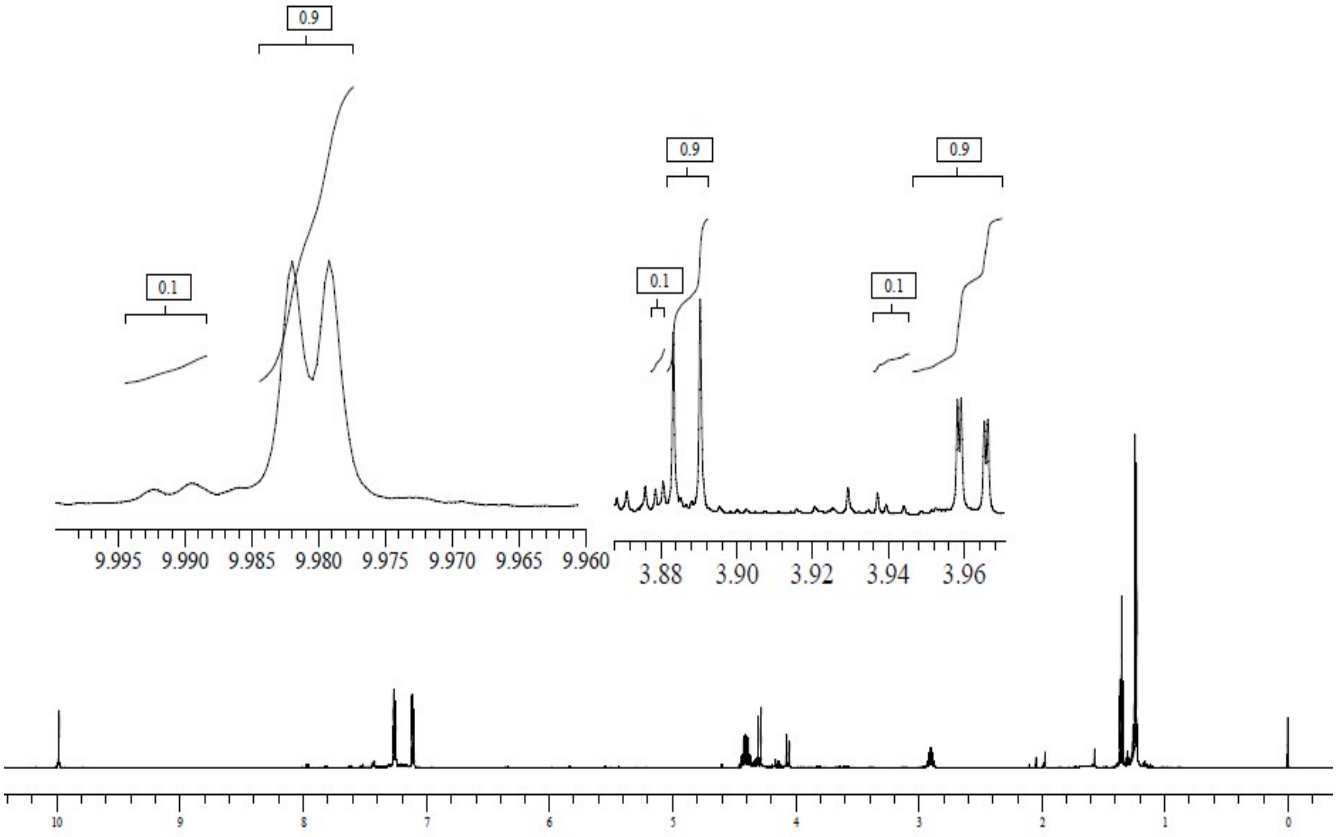


H[1] & [13]C NMR of 2x:

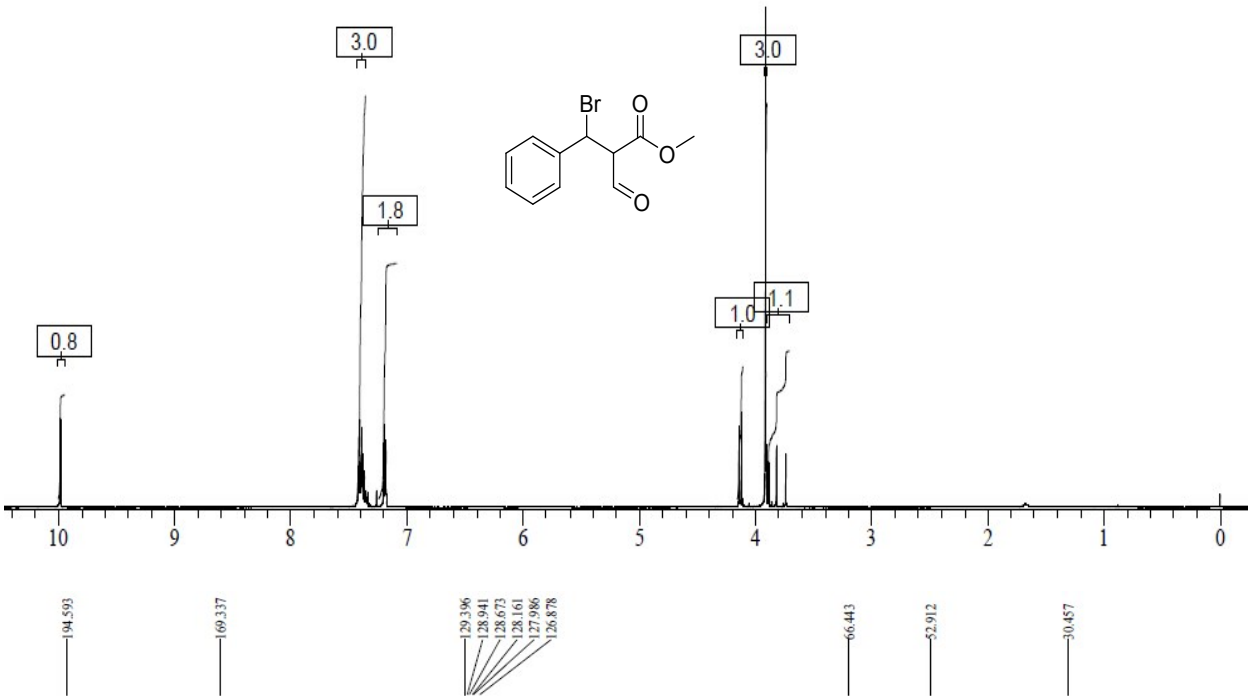


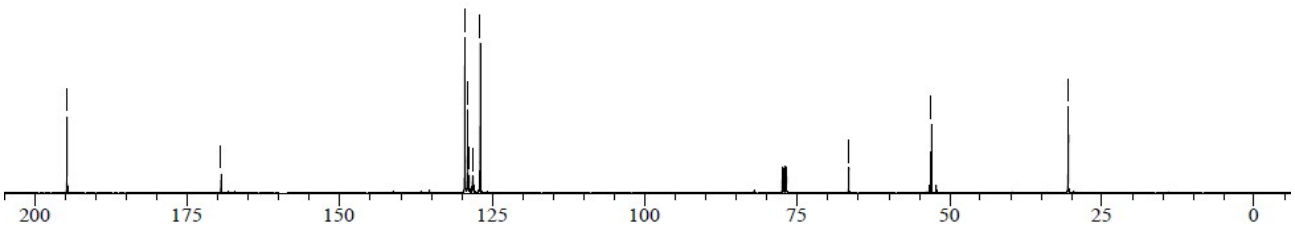


Crude H^1 NMR of 2v:

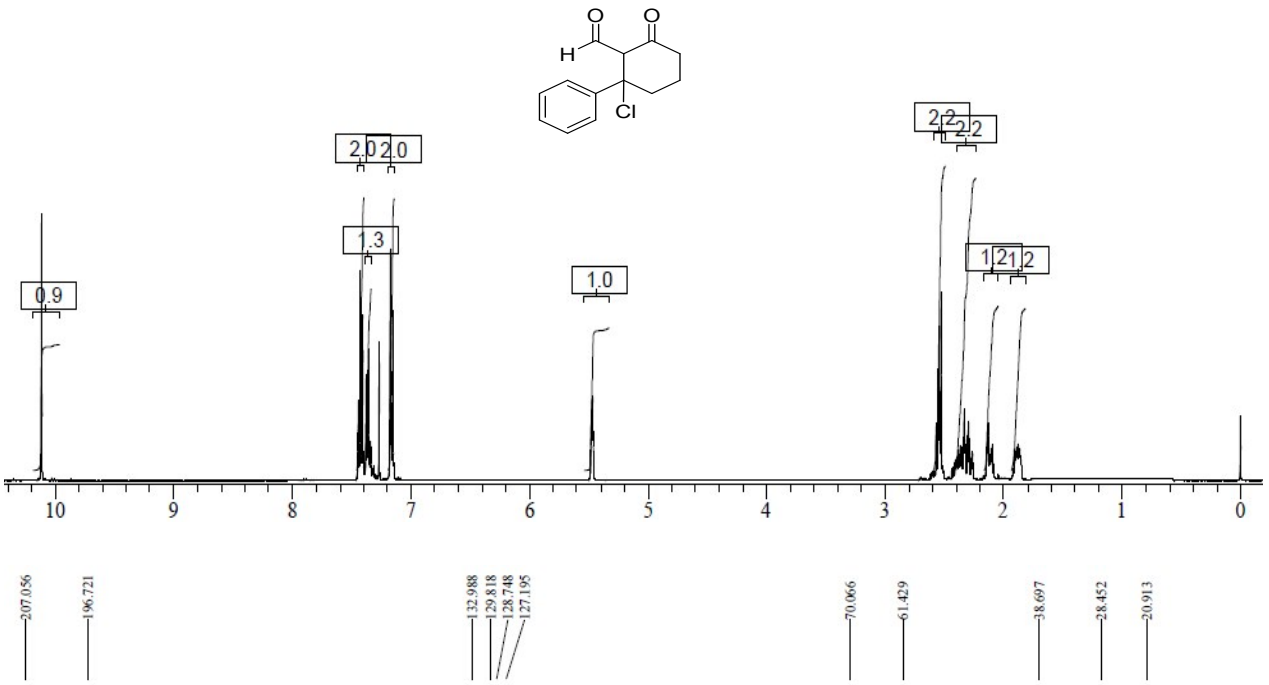


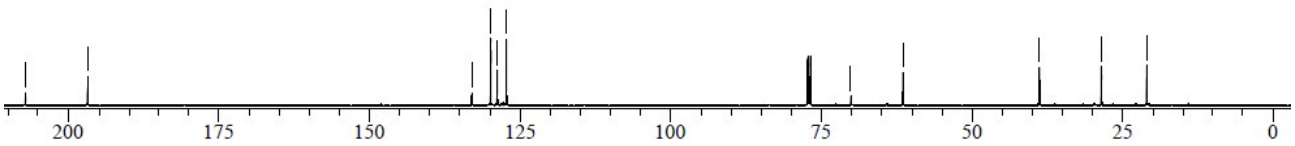
H[1] & [13]C NMR of 3a:



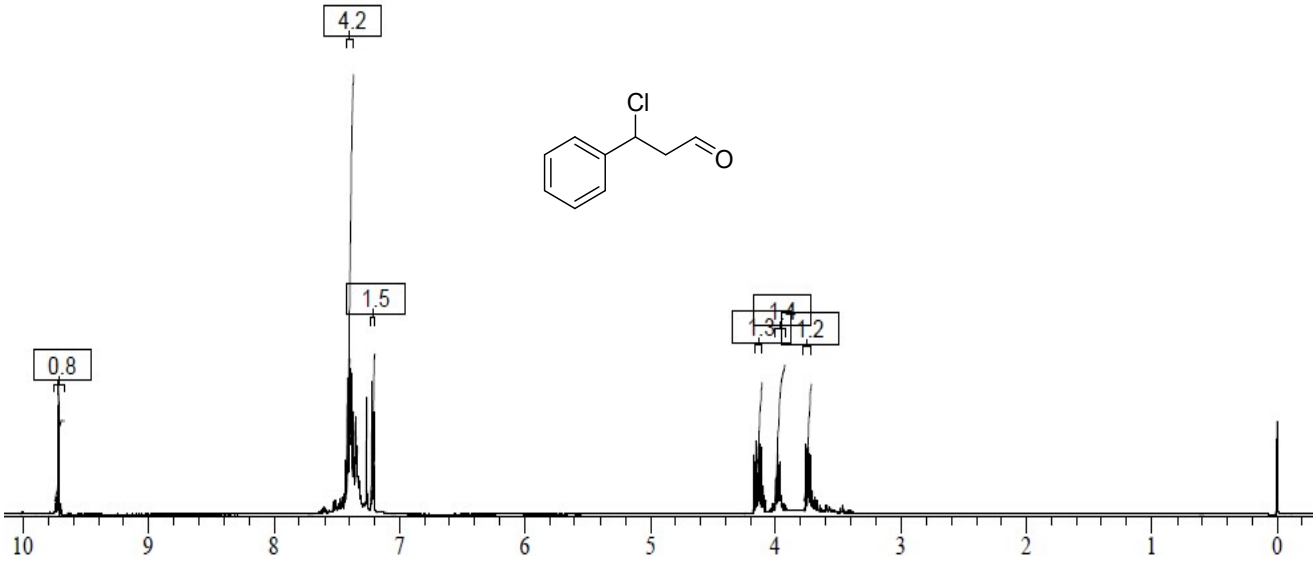


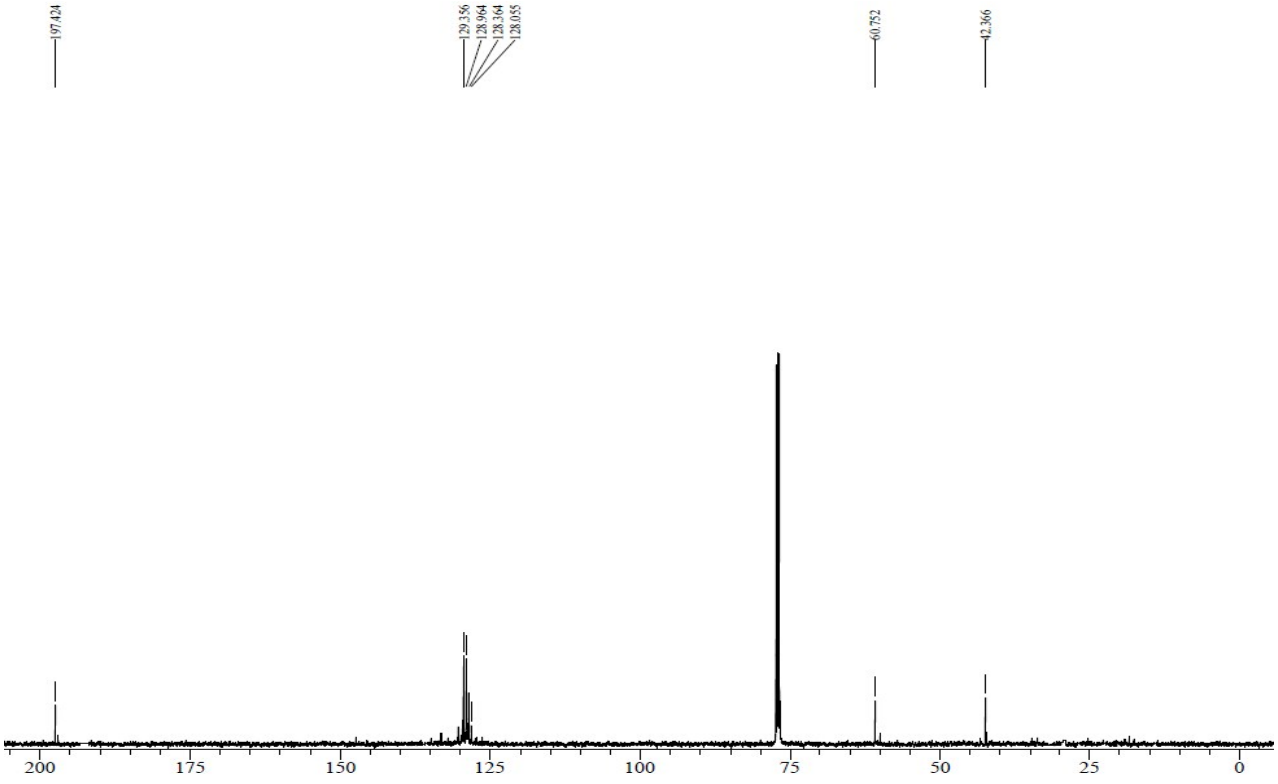
H[1] & [13]C NMR of 4e:





H^1 & ^{13}C NMR of 4h:





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2. J. C. Gomes, M. T. Rodrigues Jr., A. Moyano and F. Coelho *Eur. J. Org. Chem.* 2012, 6861–6866.

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