Electronic Supplementary Information

Efficient catalytic cyclizations of three and two imine assembly: Direct access to tetrahydroimidazo[1,5-c]imidazol-7-one and imidazole

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1. **Materials and Methods**

All solvents were dried by standard methods. Chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (60-120 mesh). TLC was done on glass sheets pre-coated with silica gel (with binder, 300 mesh, Merck). The ^{1}H- and ^{13}C-NMR spectra were taken in $CDCl_3$ with TMS as an internal reference on Bruker Supercon NMR spectrometer (Model: AV 300 Digital) which operated at 300 MHz for ^{1}H and 75 MHz for ^{13}C nuclei. The chemical shifts were reported as δ values (ppm) relative to tetramethylsilane. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer in KBr pellets and in NaCl cell (liquid sample) on a Perkin–Elmer RXI-FTIR spectrophotometer. Melting points of the samples were determined with a Fisher-John melting point apparatus and were uncorrected. HR-MS data were acquired by electrospray ionization technique on a Q-tof-micro quadriple mass spectrophotometer (Bruker). The carbonyl peaks for few compounds (e.g. **5f**) are overlapped one over another.

2. **Preparation of amino acid ester (1)**

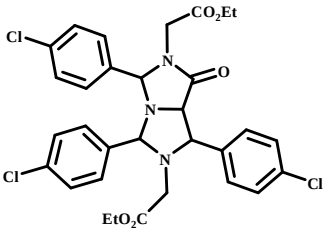
A suspension of hydrochloride salt of amino acid ester (4.0 mmol) in dichloromethane (DCM, 20 mL) was taken in a separating funnel and shaken vigorously with ammonia solution. Free amino acid ester (**1**) thus formed was dissolved in DCM layer, collected, dried with anhydrous Na_2SO_4 and evaporated to dryness in a rotary evaporator under reduced pressure at room temperature.

3. **General Procedure for the preparation of fused-tetrahydroimidazo[1,5-*c*]imidazoles (5a-l)**

A solution of amino acid ester (**1**, 3.0 mmol) and aldehyde (**2**, 3 mmol) in toluene (10 mL) was taken in a round-bottom flask (25 mL) and the reaction mixture was refluxed for 3-5 h with continuous removal of generated water using a Dean-Stark apparatus until imine formation was complete (checked by TLC). After the reaction mixture cooled down, 7 mol% of *dl*-proline was added to it and stirred magnetically. It was heated at 100^{o} C with continuous stirring until the reaction was complete (4.0-6.5 h). The progress of the reaction was checked by TLC. The post reaction mixture was cooled to room temperature and concentrated in a rotary evaporator under reduced pressure. It was transferred to a separating funnel using DCM and water, washed with 2x10 mL of saturated sodium bicarbonate solution and 1x10mL of brine solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction of glycine ethyl ester (**1a**, 309 mg, 3.0 mmol) with 4-chlorobenzaldehyde (**2a**, 420 mg, 3.0 mmol) afforded **5a** after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:13, v/v) as an eluent in an isolated yield of 81% (510 mg, 0.81 mmol). The fused-tetrahydroimidazo[1,5-*c*]imidazoles (**5a-l**) were characterized by NMR, FT-IR and HR-MS spectral analysis.

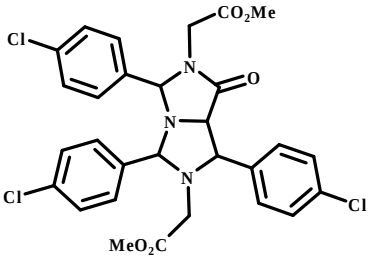
4. Characterization data of fused-tetrahydroimidazo[1,5-*c*]imidazoles (5a-l)

Characteristic data of [1,3,5-tris-(4-chlorophenyl)-6-ethoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5a)



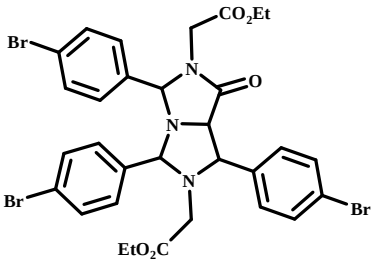
Yield: 81% (510 mg, 0.81 mmol).
Characteristic: white solid.
Melting point: 134-136° C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (3H, t, *J* = 6.9 Hz), 1.22 (3H, t, *J* = 3.0Hz), 2.98-3.23 (3H, m), 3.80 (1H, d, *J* = 5.7Hz), 3.97 (2H, q, *J* = 6.9 Hz), 4.12 (2H, q, *J* = 3.0 Hz), 4.57 (2H, s), 5.07 (1H, s), 5.38 (1H, s), 6.82 (2H, d, *J* = 7.2 Hz), 7.17 (2H, d, *J* = 8.1Hz), 7.22 (4H, d, *J* = 19.8 Hz), 7.41 (4H, d, *J* = 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 41.4, 47.0, 60.5, 61.6, 65.6, 69.1, 78.8, 84.8, 127.9, 128.9, 129.1, 129.2, 130.3, 133.9, 134.9, 135.0, 136.0, 137.3, 138.0, 168.1, 169.8, 172.6.
FT-IR (neat, cm^{-1}): 829, 953, 1084, 1716, 2926, 3437.
HR-MS (*m/z*): for $C_{31}H_{30}Cl_3N_3O_5$: Calculated 629.1251; Found 629.1260 (One of the major peaks).

Characteristic data of [1,3,5-tris-(4-chlorophenyl)-6-methoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid methyl ester (5b)



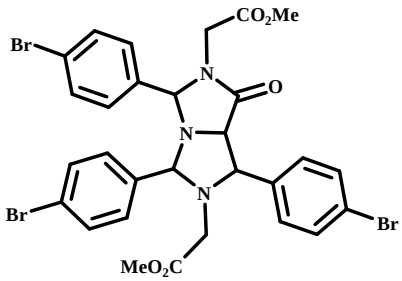
Yield: 75% (450 mg, 0.75 mmol).
Characteristic: Yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.01-3.26 (3H, m), 3.52 (3H, s), 3.72 (3H, s), 3.81 (1H, d, *J*= 5.7 Hz), 4.52-4.58 (2H, m), 5.07 (1H, s), 5.36 (1H, s), 6.81 (2H, d, *J*= 8.4 Hz), 7.14-7.19 (3H, m), 7.23-7.35 (3H, m), 7.39-7.43 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 41.3, 46.8, 51.4, 52.4, 65.6, 69.0, 78.8, 84.9, 127.9, 128.0, 128.3, 128.7, 129.0, 129.2, 129.4, 129.6, 129.8, 130.3, 130.8, 133.9, 135.0, 135.9, 137.1, 137.9, 168.6, 170.3, 172.6.
FT-IR (neat, cm^{-1}): 1089, 1211, 1436, 1725, 2360, 2924, 3427.
HR-MS (*m/z*): for $C_{29}H_{26}Cl_3N_3O_5$: Calculated 601.0938; Found 601.0942 (One of the major peaks).

Characteristic data of [1,3,5-tris-(4-bromophenyl)-6-ethoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5c)



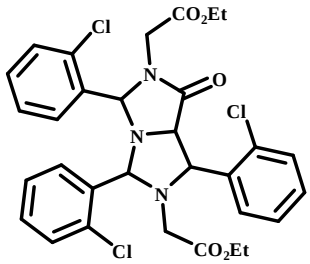
Yield: 81% (615 mg, 0.81 mmol).
Characteristic: White solid.
Melting point: 142 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, t, *J*= 7.2 Hz), 1.27 (3H, t, *J*= 7.2 Hz), 3.13 (2H, q, *J*= 17.4 Hz), 3.26 (1H, d, *J*= 18 Hz), 3.87 (1H, d, *J*= 5.7 Hz), 4.04 (2H, q, *J* = 6 Hz), 4.19 (2H, q, *J*= 3.6 Hz), 4.58-4.63 (2H, m), 5.13 (1H, s), 5.43 (1H, s), 6.82 (2H, d, *J*= 8.4 Hz), 7.38-7.61 (10H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 41.4, 46.9, 60.6, 61.6, 65.6, 69.0, 78.8, 84.8, 118.1, 122.0, 123.0, 123.2, 128.2, 129.5, 130.6, 131.7, 131.9, 132.1, 136.5, 137.8, 138.5, 162.3, 168.1, 169.9, 172.6.
FT-IR (neat, cm^{-1}): 1013, 1206, 1438, 1589, 1712, 2373, 2924, 2981.
HR-MS (*m/z*): for $C_{31}H_{30}Br_3N_3O_5$: Calculated: 760.9736; Found: 760.9745 (One of the major peaks).

Characteristic data of [1,3,5-tris-(4-bromophenyl)-6-methoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid methyl ester (5d)



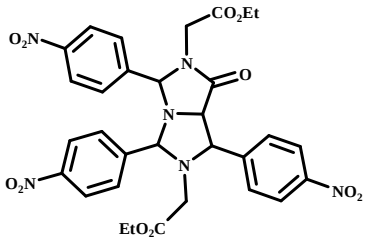
Yield: 78% (570 mg, 0.78 mmol).
Characteristic: Yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.72 (2H, d, *J*= 6.6 Hz), 3.08 (3H, s), 3.13-3.23 (2H, m), 3.31 (3H, s), 3.36 (2H, d, *J*= 6.3 Hz), 3.96 (1H, d, *J*= 6.3 Hz), 4.64 (1H, s), 6.80 (3H, s), 6.90-7.08 (9H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 47.6, 51.3, 52.4, 66.7, 68.1, 79.0, 121.9, 129.2, 129.6, 131.8, 139.1, 139.3, 170.5, 172.9.
FT-IR (neat, cm^{-1}): 1070, 1424, 1591, 1738, 2849, 2917.
HR-MS (*m/z*): for $C_{29}H_{26}Br_3N_3O_5$: Calculated 732.9423; Found: 732.9430 (One of the major peaks)

Characteristic data of [1,3,5-tris-(2-chlorophenyl)-6-ethoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5e)



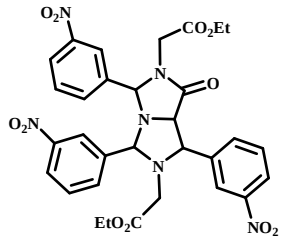
Yield: 76% (475 mg, 0.76 mmol).
Characteristic: Pale yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79 (3H, t, *J*= 6 Hz), 1.14 (3H, t, *J*= 6 Hz), 3.18 (2H, q, *J*= 15 Hz), 3.38-3.44 (2H, m), 3.68-3.74 (2H, m), 3.96 (2H, q, *J*= 6 Hz), 4.44 (1H, d, *J*= 9 Hz), 5.24 (1H, d, *J*= 9 Hz), 5.53 (2H, s), 7.16-7.41 (10H, m), 7.67 (1H, d, *J*= 6 Hz), 7.98 (1H, d, *J*= 6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.4, 14.0, 48.6, 60.5, 61.1, 63.1, 63.4, 75.9, 126.8, 127.6, 128.7, 128.8, 129.0, 129.2, 129.8, 129.9, 130.0, 135.1, 135.2, 135.8, 136.2, 170.0, 171.4.
FT-IR (neat, cm^{-1}): 1036, 1395, 1588, 1672, 1732, 2921, 3445.
HR-MS (*m/z*): for $C_{31}H_{30}Cl_3N_3O_5$: Calculated 629.1251; Found: 629.1246 (One of the major peaks).

Characteristic data of [6-ethoxycarbonylmethyl-1,3,5-tris-(4-nitrophenyl)-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5f)



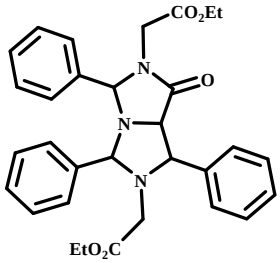
Yield: 68% (450 mg, 0.68 mmol)
Characteristic: Yellow colored viscous liquid
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (3H, t, *J* = 7.2 Hz), 1.28 (3H, t, *J* = 7.2 Hz), 3.24 (2H, d, *J*= 2.2 Hz), 3.88 (1H, d, *J*= 3.3 Hz), 4.07 (2H, q, *J*= 6.9 Hz), 4.24-4.31 (4H, m), 4.63 (1H, d, *J*= 6.3 Hz), 5.30 (1H, s), 5.33 (1H, d, *J* = 19.2 Hz), 7.69 (2H, d, *J*= 8.7 Hz), 7.79 (2H, d, *J*= 8.4 Hz), 8.24-8.27 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 48.1, 53.4, 60.8, 61.9, 66.8, 68.4, 78.7, 123.7, 123.8, 123.9, 128.5, 129.0, 147.4, 147.6, 147.9, 148.4, 169.7, 171.6.
FT-IR (neat, cm^{-1}): 1028, 1324, 1606, 1731, 2354, 2918, 3462.
HR-MS (*m/z*): for $C_{31}H_{30}N_6O_{11}$: Calculated 662.1973; Found: 662.1981.

Characteristic data of [6-ethoxycarbonylmethyl-1,3,5-tris-(3-nitrophenyl)-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5g)



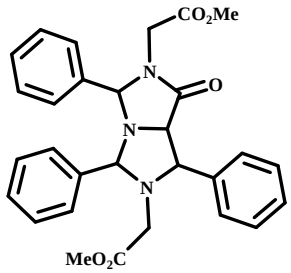
Yield: 78% (516mg, 0.78 mmol).
Characteristic: Yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17-1.40 (6H, m), 3.25 (2H, d, *J*= 5.1 Hz), 3.85 (1H, d, *J*= 5.7 Hz), 4.03-4.35 (7H, m), 4.61 (1H, d, *J*= 6.6 Hz), 5.34 (1H, s), 7.56-7.63 (4H, m), 7.89 (1H, d, *J*= 7.8 Hz), 7.96 (1H, d, *J*= 7.8 Hz), 8.18-8.27 (4H, m), 8.34 (1H, s), 8.45 (1H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 48.1, 60.8, 61.8, 66.8, 68.4, 78.7, 122.8, 123.1, 123.2, 123.8, 129.7, 129.8, 133.5, 134.2, 142.5, 142.9, 148.5, 162.3, 169.7, 171.8.
FT-IR (neat, cm^{-1}): 1196, 1350, 1531, 1736, 2923, 3437
HR-MS (*m/z*): for $C_{31}H_{30}N_6O_{11}$: Calculated 662.1973; Found: 662.1975.

Characteristic data of (6-ethoxycarbonylmethyl-7-oxo-1,3,5-triphenyl-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl)-acetic acid ethyl ester (5h)



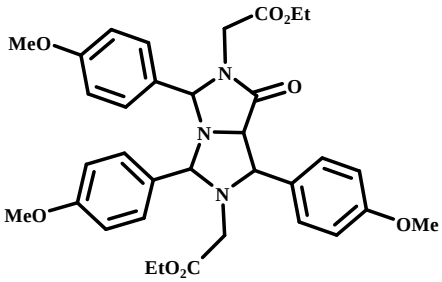
Yield: 78% (409 mg, 0.78 mmol).
Characteristic: Pale yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13 (3H, t, *J*= 7.2 Hz), 1.25 (3H, t, *J*= 7.2 Hz), 3.04-3.29 (3H, m), 3.90 (1H, d, *J*= 5.7 Hz), 4.01 (2H, q, *J*= 5.7 Hz), 4.23 (2H, q, *J*= 3.6 Hz), 4.63 (2H, d, *J*= 6 Hz), 5.13 (1H, s), 5.44 (1H, s), 6.85-6.87 (2H, m), 7.17-7.32 (9H, m), 7.52-7.54 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 41.6, 47.2, 60.3, 61.5, 66.1, 69.2, 79.2, 85.6, 126.6, 127.0, 128.3, 128.7, 128.8, 129.2, 137.6, 138.8, 140.6, 168.4, 170.4, 173.6.
FT-IR (neat, cm^{-1}): 1028, 1431, 1613, 1720, 2922, 3440.
HR-MS (*m/z*): for $C_{31}H_{33}N_3O_5$: Calculated 527.2420; Found. 527.2424.

Characteristic data of (6-methoxycarbonylmethyl-7-oxo-1,3,5-triphenyl-tetrahydro-imidazo[1,5-c]imidazol-2-yl)-acetic acid methyl ester (5i)



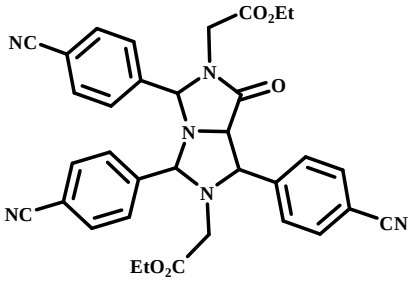
Yield: 72% (358mg, 0.72 mmol).
Characteristic: Pale yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.12-3.31 (3H, m), 3.51 (3H, s), 3.73 (3H, s), 3.91 (1H, d, *J*= 5.7 Hz), 4.57-4.63 (2H, m), 5.12 (1H, s), 5.41 (1H, s), 6.83-6.86 (2H, m), 7.16-7.32 (9H, m), 7.50-7.53 (4H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 41.5, 47.1, 51.2, 52.3, 66.2, 69.2, 79.3, 85.7, 126.5, 127.9, 128.4, 128.7, 128.8, 129.1, 129.2, 137.5, 138.8, 140.0, 168.7, 170.7, 173.3.
FT-IR (neat, cm^{-1}): 1114, 1418, 1606, 1708, 2356, 3435
HR-MS (*m/z*): for $C_{29}H_{29}N_3O_5$: Calculated 499.2107; Found: 499.2112.

Characteristic data of [6-ethoxycarbonylmethyl-1,3,5-tris-(4-methoxyphenyl)-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5j)



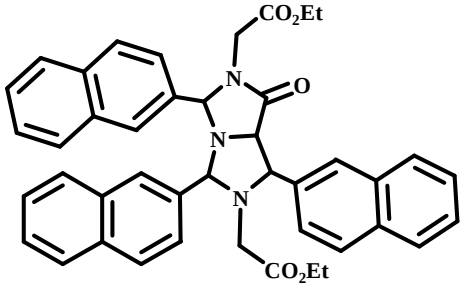
Yield: 75% (462 mg, 0.75mmol).
Characteristic: Yellow colored semisolid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 (3H, t, *J*= 7.2 Hz), 1.23 (3H, t, *J*= 7.2 Hz), 3.05-3.25 (3H, m), 3.68 (3H, s), 3.70 (3H, s), 3.73 (3H, s), 3.84 (1H, d, *J*= 5.7 Hz), 3.94 (2H, q, *J*= 5.7 Hz), 4.12 (2H, q, *J*= 3.3 Hz), 4.49-4.55 (2H, m), 4.98 (1H, s), 5.35 (1H, s), 6.69 (2H, d, *J*= 8.7 Hz), 6.78-6.84 (6H, m), 7.41 (4H, d, *J*= 8.7 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 41.5, 47.1, 55.2, 60.3, 61.4, 65.7, 69.2, 79.0, 85.1, 113.7, 114.0, 114.1, 127.8, 129.1, 129.9, 130.2, 131.0, 132.0, 159.4, 159.8, 160.1, 168.3, 170.4, 173.3.
FT-IR (neat, cm^{-1}):1028, 1250, 1611, 1735, 2364, 2851, 2926.
HR-MS (*m/z*): for $C_{34}H_{39}N_3O_8$: Calculated 617.2737; Found: 617.2744.

Characteristic data of [1,3,5-tris-(4-cyanophenyl)-6-ethoxycarbonylmethyl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5k)



Yield: 70% (420 mg, 0.70mmol).
Characteristic: Yellow solid.
Melting point: 133 °C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85, (3H, t, *J*= 6.9 Hz), 1.18 (3H, t, *J*= 9 Hz), 3.21 (2H, q, *J*= 17.4 Hz), 3.47-3.53 (2H, m), 3.73-3.81 (2H, m), 4.03 (2H, q, *J*= 7.2 Hz), 4.40 (1H, d, *J*= 9.3 Hz), 4.76 (1H, d, *J*= 9.3 Hz), 5.16 (1H, s), 5.30 (1H, s), 7.26 (2H, s), 7.53 (3H, d, *J*= 8.1 Hz), 7.64 (3H, d, *J*= 8.1 Hz), 7.76 (4H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.5, 14.1, 48.0, 53.3, 60.7, 61.3, 64.7, 67.3, 79.5, 112.0, 113.3, 128.7, 129.0, 131.9, 132.7, 143.5, 144.4, 169.7, 170.3.
IR (neat, cm^{-1}): 1080, 1731, 2228, 2365, 2926, 3437.
HR-MS (*m/z*): for $C_{34}H_{30}N_6O_5$: Calculated 602.2278; Found: 602.2269

Characteristic data of (6-ethoxycarbonylmethyl-1,3,5-tri-naphthalen-2-yl-7-oxo-tetrahydro-imidazo[1,5-*c*]imidazol-2-yl)-acetic acid ethyl ester (5l)



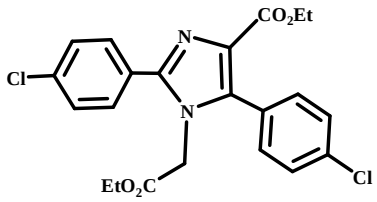
Yield: 77% (521 mg, 0.77mmol).
Characteristic: Yellow colored viscous solid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.49 (3H, t, *J*= 7.2 Hz), 1.05 (3H, t, *J*= 7.2 Hz), 3.15-3.29 (4H, m), 3.54-3.58 (2H, m), 3.90 (2H, q, *J*= 6.9 Hz), 4.38 (1H, d, *J*= 9.3 Hz), 4.86 (1H, d, *J*= 9.3 Hz), 5.24 (1H, d, *J* = 12.6 Hz), 5.26 (1H, s), 7.39-7.47 (6H, m), 7.55 (2H, dd, *J*= 8.7, 7.2 Hz), 7.75-7.92 (11H, m), 8.04 (2H, s).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.2, 14.0, 47.8, 60.3, 60.9, 64.7, 67.6, 80.0, 125.1, 125.9, 126.1, 126.3, 126.4, 127.6, 127.8, 127.9, 128.0, 128.2, 128.9, 133.2, 133.4, 134.0, 136.0, 136.4, 170.5, 171.3.
FT-IR (neat, cm^{-1}):1195, 1733, 2919, 2980, 3347.
HR-MS (*m/z*): for $C_{43}H_{39}N_3O_5$: Calculated 677.2890; Found 677.2892

4. **General Procedure for the preparation of 1,4-difunctionalized-2,5-diaryl imidazoles (7a-k)**

A solution of amino acid ester (**1**, 2.0 mmol) and aldehyde (**2**, 2 mmol) in xylene (10 mL) was taken in a round-bottom flask (25 mL) and content of the reaction mixture was refluxed for 3-5 h with continuous removal of generated water using a Dean-Stark apparatus until imine formation was complete (checked by TLC). After cooling the reaction mixture to ambient temperature 3 mol% of $Cu(OTf)_2$ and 10 mol% of Ag_2O was added and stirred magnetically. It was heated at 130^o C with continuous stirring until the reaction was complete (4.5-7.5 h). Progress of the reaction was monitored by TLC. The post reaction mixture was cooled to room temperature and concentrated by distilling out the solvent under reduced pressure. It was transferred to a separating funnel using DCM and water, washed with 2x10 mL of saturated sodium bicarbonate solution and 1x10 mL of brine solution, dried on activated sodium sulfate, and concentrated in a rotary evaporator under reduced pressure at room temperature. Thus, the reaction of glycine ethyl ester (**1a**, 206 mg, 2.0 mmol) with 4-chloro benzaldehyde (**2a**, 280 mg, 2.0 mmol) afforded **7a**, after purification by column chromatography on silica gel (60-120 mesh) with ethyl acetate-petroleum ether (1:6, v/v) as an eluent in an isolated yield of 78% (347mg, 0.78 mmol). The 1,4-difunctionalized-2,5-diaryl imidazoles (**7a-k**) were characterized by NMR, FT-IR and HR-MS spectral analysis.

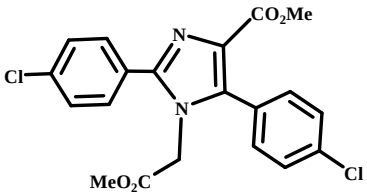
5. **Characterization data of 1,4-difunctionalized-2,5-diaryl imidazoles (7a-k)**

Characteristic data of 2,5-bis-(4-chlorophenyl)-1-ethoxycarbonylmethyl-1*H*-imidazole-4-carboxylic acid ethyl ester (7a)



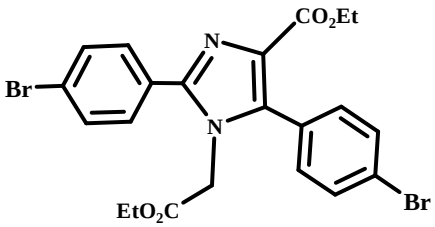
Yield: 78% (347mg, 0.78 mmol)
Characteristic: Yellow semisolid
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10-1.28 (6H, m), 4.14 (2H, q, *J* = 6.9 Hz), 4.27 (2H, q, *J* = 6.9 Hz), 4.44 (2H, s), 7.34 (2H, d, *J* = 7.5 Hz), 7.44-7.49 (4H, m), 7.56 (2H, d, *J* = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 46.8, 60.5, 62.2, 127.2, 127.8, 128.8, 129.0, 130.3, 130.6, 130.8, 131.7, 135.8, 136.1, 138.6, 139.2, 162.6, 167.4.
FT-IR (neat, cm^{-1}): 1096, 1402, 1726, 2354, 2854, 2922, 3435.
HR-MS (*m/z*): for $C_{22}H_{20}Cl_2N_2O_4$ Calculated: 446.0800; Found: 446.0808 (One of the major peaks).

Characteristic data of 2,5-bis-(4-chlorophenyl)-1-methoxycarbonylmethyl-1*H*-imidazole-4-carboxylic acid methyl ester (7b)



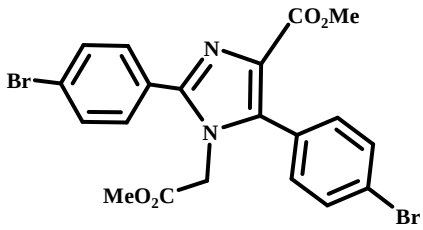
Yield: 70% (293 mg, 0.70 mmol).
Characteristic: Yellow solid.
Melting point: 86 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (3H, s), 3.73 (3H, s), 4.40 (2H, s), 7.16-7.49 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 51.9, 53.0, 53.3, 126.4, 126.8, 127.7, 128.2, 128.5, 128.7, 129.0, 129.2, 129.4, 130.7, 130.9, 131.9, 136.3, 138.8, 167.8, 168.4.
FT-IR (neat, cm^{-1}):1091, 1206, 1402, 1600, 1665, 1737, 2925, 3161.
HR-MS (*m/z*): for $C_{20}H_{16}Cl_2N_2O_4$ Calculated: 418.0487; Found: 418.0493 (One of the major peaks).

Characteristic data of 2,5-bis-(4-bromophenyl)-1-ethoxycarbonylmethyl-1*H*-imidazole-4-carboxylic acid ethyl ester (7c)



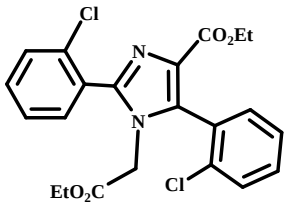
Yield: 71% (380 mg, 0.71 mmol)
Characteristic: yellow colored solid
Melting point: 122 ^{o}C
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15-1.24 (6H, m), 4.13 (2H, q, *J* = 7.2 Hz), 4.26 (2H, q, *J* = 7.2 Hz), 4.42 (2H, s), 7.26 (3H, t, *J* = 3.3 Hz), 7.46 (2H, d, *J* = 8.7 Hz), 7.59 (3H, dd, *J* = 1.5, 8.4 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 47.1, 60.7, 62.3, 124.3, 124.7, 127.8, 130.9, 131.8, 132.1, 147.8, 162.3, 167.4.
FT-IR (neat, cm^{-1}): 1111, 1384, 1621, 2346, 2363, 2926, 3446.
HR-MS (*m/z*): for $C_{22}H_{20}Br_2N_2O_4$; Calculated: 533.9790; Found: 533.9794 (One of the major peaks).

Characteristic data of 2,5-bis-(4-bromophenyl)-1-methoxycarbonylmethyl-1*H*-imidazole-4-carboxylic acid methyl ester (7d)



Yield: 78% (396 mg, 0.78 mmol).
Characteristic: yellow colored solid.
Melting point: 68 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (3H, s), 3.73 (3H, s), 4.40 (2H, s), 7.37-7.63 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 41.7, 52.0, 53.0, 125.3, 126.4, 128.3, 128.6, 131.0, 131.9, 132.0, 132.2, 132.5, 138.8, 170.3.
FT-IR (neat, cm^{-1}): 1206, 1401, 1596, 1661, 1727, 2353, 2928, 3168.
HR-MS (*m/z*): for $C_{20}H_{16}Br_2N_2O_4$ Calculated: 505.9477; Found: 505.9467 (One of the major peaks).

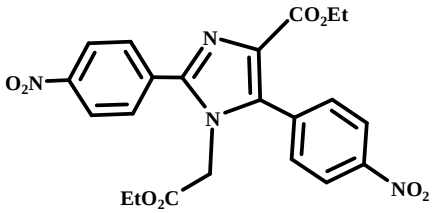
Characteristic data of 2,5-bis-(2-chloro-phenyl)-1-ethoxycarbonylmethyl-1H-imidazole-4-carboxylic acid ethyl ester (7e)



Yield: 76% (339 mg, 0.76 mmol).
Characteristic: yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.11-1.24 (6H, m), 3.88 (2H, q, *J* = 7.2 Hz), 4.13-4.34 (2H, m), 4.41 (2H, d, *J* = 6.9 Hz), 7.25-7.52 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.1, 46.5, 60.9, 62.0, 126.9, 127.2, 129.7, 131.4, 132.1, 133.2, 133.5, 134.1, 134.5, 136.0, 145.9, 166.1, 171.4.
FT-IR (KBr, cm^{-1}): 1080, 1442, 1663, 1739, 2924, 3422.

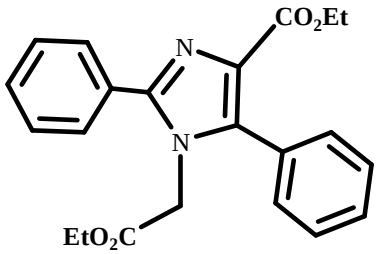
HR-MS (*m/z*): for $C_{22}H_{20}Cl_2N_2O_4$ Calculated: 446.0800; Found: 446.0807 (One of the major peaks).

Characteristic data of 1-ethoxycarbonylmethyl-2,5-bis-(4-nitrophenyl)-1*H*-imidazole-4-carboxylic acid ethyl ester (7f)



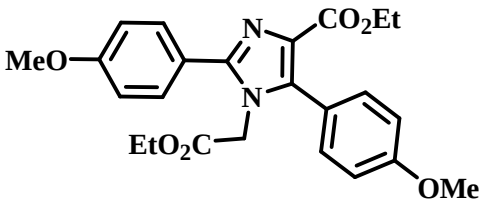
Yield: 76% (355mg, 0.76 mmol).
Characteristic: yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (3H, t, *J* = 6.9 Hz), 1.14 (3H, t, *J* = 6.9 Hz), 4.22-4.27 (2H, m), 4.45 (2H, q, *J* = 7.8 Hz), 4.88 (2H, s), 7.56 (3H, t, *J* = 9 Hz), 7.81 (1H, d, *J* = 8.7 Hz), 8.06 (3H, t, *J* = 8.7 Hz), 8.33-8.39 (1H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.2, 47.8, 61.9, 62.7, 122.9, 123.7, 123.9, 124.3, 124.8, 127.3, 127.9, 129.3, 130.4, 130.6, 131.9, 158.9, 167.9, 171.2.
FT-IR (neat, cm^{-1}): 1018, 1524, 1603, 1742, 2923, 3405.
HR-MS (*m/z*): for $C_{22}H_{20}N_4O_8$ Calculated: 468.1281; Found: 468.1275

Characteristic data of 1-ethoxycarbonylmethyl-2,5-diphenyl-1*H*-imidazole-4-carboxylic acid ethyl ester (7g)



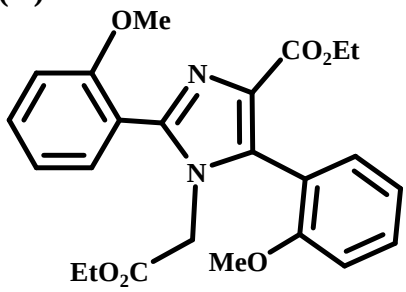
Yield: 74% (279 mg, 0.74 mmol).
Characteristic: Yellow colored viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05-1.19 (6H, m), 4.04 (2H, q, *J* = 7.2 Hz), 4.18 (2H, q, *J* = 7.2 Hz), 4.42 (2H, s), 7.19 (3H, s), 7.29-7.42 (5H, m), 7.53-7.55(2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 53.3, 128.6, 129.0, 130.4, 167.1, 171.4.
FT-IR (neat, cm^{-1}): 1094, 1199, 1401, 1608, 1736, 2856, 2924, 3157.
HR-MS (*m/z*): for $C_{22}H_{22}N_2O_4$ Calculated: 378.1580; Found: 378.1589.

Characteristic data of 1-ethoxycarbonylmethyl-2,5-bis-(4-methoxyphenyl)-1*H*-imidazole-4-carboxylic acid ethyl ester (7h)



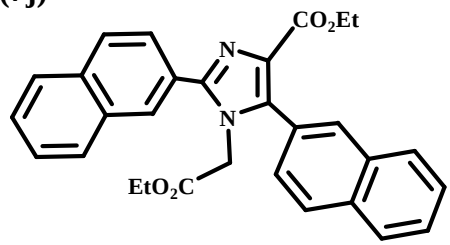
Yield: 73% (318 mg, 0.73mmol).
Characteristic: Yellow viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07-1.17 (6H, m), 3.78 (6H, s), 4.06 (2H, q, *J*=7.2 Hz), 4.19 (2H, q, *J* = 6.9 Hz), 4.43 (2H, s), 6.91 (4H, d, *J* = 4.8 Hz), 7.27 (2H, d, *J*= 8.1 Hz), 7.49 (2H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 14.1, 47.2, 55.3, 55.4, 62.2, 114.1, 114.4, 131.1, 131.8, 161.1, 161.8, 167.5.
FT-IR (neat, cm^{-1}): 1179, 1251, 1502, 1613, 1730, 2922, 3433.
HR-MS (*m/z*): for $C_{24}H_{26}N_2O_6$ Calculated: 438.1791; Found: 438.1784.

Characteristic data of 1-ethoxycarbonylmethyl-2,5-bis-(2-methoxyphenyl)-1*H*-imidazole-4-carboxylic acid ethyl ester (7i)



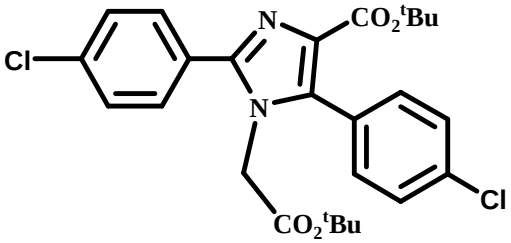
Yield: 72% (314 mg, 0.72mmol).
Characteristic: Yellow semisolid
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06-1.23 (6H, m), 3.66-3.82 (7H, m), 3.97 (3H, s), 4.19-4.27 (2H, m), 6.82-7.05 (6H, m), 7.29-7.34 (2H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 55.6, 55.9, 60.5, 111.0, 111.2, 116.9, 120.4, 121.6, 129.4, 130.2, 130.6, 132.0, 144.2, 156.2, 156.7, 167.3, 168.7.
FT-IR (neat, cm^{-1}): 1245, 1465, 1595, 1712, 2367, 2852, 2925, 3419.
HR-MS (*m/z*): for $C_{24}H_{26}N_2O_6$ Calculated: 438.1791; Found: 438.1798

Characteristic data of 1-ethoxycarbonylmethyl-2,5-di-naphthalen-2-yl-1*H*-imidazole-4-carboxylic acid ethyl ester (7j)



Yield: 73% (348 mg, 0.73 mmol).
Characteristic: yellow solid.
Melting point: 65 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15-1.95 (3H,m), 1.25 (3H, t, *J* = 7.2 Hz), 3.31 (1H, d, *J* = 17.7 Hz), 4.09-4.12 (2H, m), 4.19-4.24 (2H, m), 4.50 (1H, d, *J* = 17.7 Hz), 7.28-7.81 (14H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 14.2, 42.0, 61.6, 61.8, 126.1, 126.3, 126.6, 126.7, 126.8, 126.9, 127.5, 127.7, 127.8, 127.8, 127.9, 128.3, 128.5, 128.7, 128.8, 129.0, 129.2, 129.6, 132.5, 132.6, 133.0, 133.1, 133.3, 133.6, 142.4, 167.1, 170.2.
FT-IR (neat, cm^{-1}): 1018, 1199, 1376, 1453, 1671, 1746, 2924, 3421.
HR-MS (*m/z*): for $C_{30}H_{26}N_2O_4$ Calculated: 478.1893; Found: 478.1888.

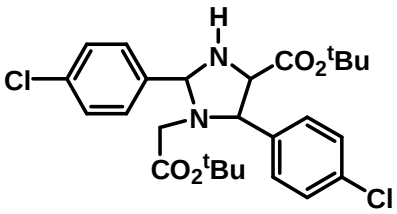
Characteristic data of 1-*tert*-butoxycarbonylmethyl-2,5-bis-(4-chlorophenyl)-1*H*-imidazole-4-carboxylic acid *tert*-butyl ester (7k)



Yield: 79% (397 mg, 0.79mmol).
Characteristic: yellow solid.
Melting point: 78 ^{o}C.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (9H, s), 1.29 (9H, s), 4.22 (2H, s), 7.24 (2H, d, *J* = 8.1 Hz), 7.35-7.37 (4H, m), 7.47 (2H, d, *J* = 8.1 Hz).
^{13}C NMR (75 MHz, $CDCl_3$): δ 27.7, 28.0, 47.8, 81.4, 83.7, 127.0, 127.5, 128.4, 128.6, 128.7, 128.9, 129.1, 129.5, 130.7, 132.0, 135.8, 136.5, 137.6, 147.5, 161.1, 166.5.
FT-IR (KBr, cm^{-1}): 1013, 1153, 1481, 1722, 2925, 2976, 3409.
HR-MS (*m/z*): for $C_{26}H_{28}Cl_2N_2O_4$ Calculated: 502.1426; Found: 502.1434 (One of the major peaks).

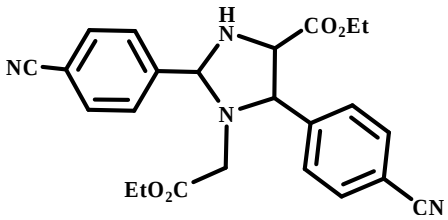
6. **Characterization data of substituted tetrahydroimidazoles** (**4a and 4b**)

Characteristic data of 1-*tert*-butoxycarbonylmethyl-4,5-bis-(4-chlorophenyl)-imidazolidine-2-carboxylic acid tert-butyl ester (4a)



Yield: 69% (347mg, 0.69 mmol)
Characteristic: Yellow viscous liquid.
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31-1.42 (18H, m), 3.03 (2H, d, *J* = 8.1Hz), 3.68 (1H, d, *J* = 6.9 Hz), 4.08 (1H, d, *J* = 6.9Hz), 4.30-4.33 (1H, m), 5.15 (1H, s), 7.32-7.52 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 28.0, 28.1, 48.5, 67.2, 68.6, 78.6, 81.3, 81.9, 128.7, 128.8, 129.2, 129.4, 130.9, 133.6, 134.3, 138.8, 139.5, 169.3, 171.5.
FT-IR (neat, cm^{-1}):1086, 1411, 1632, 1730, 2926, 3431.
HR-MS (*m/z*): for $C_{26}H_{32}Cl_2N_2O_4$ Calculated: 506.1739; Found: 506.1743 (One of the major peaks).

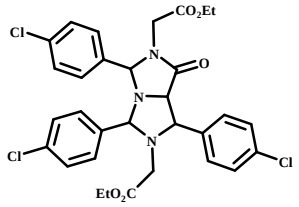
Characteristic data of 2,5-bis-(4-cyanophenyl)-1-ethoxycarbonylmethyl-imidazolidine-4-carboxylic acid ethyl ester (4b)

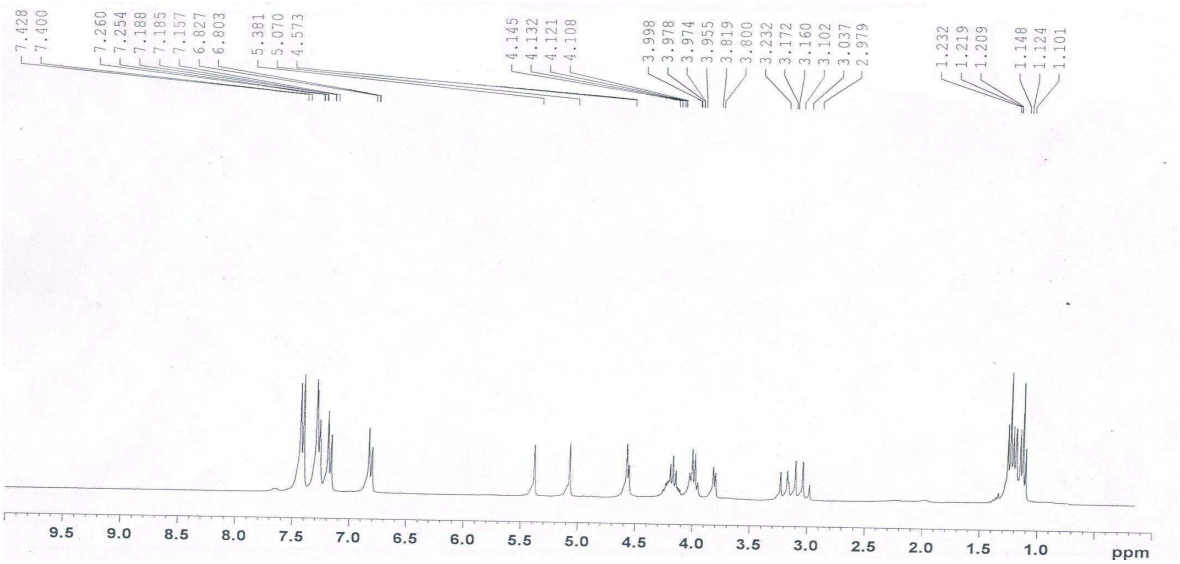


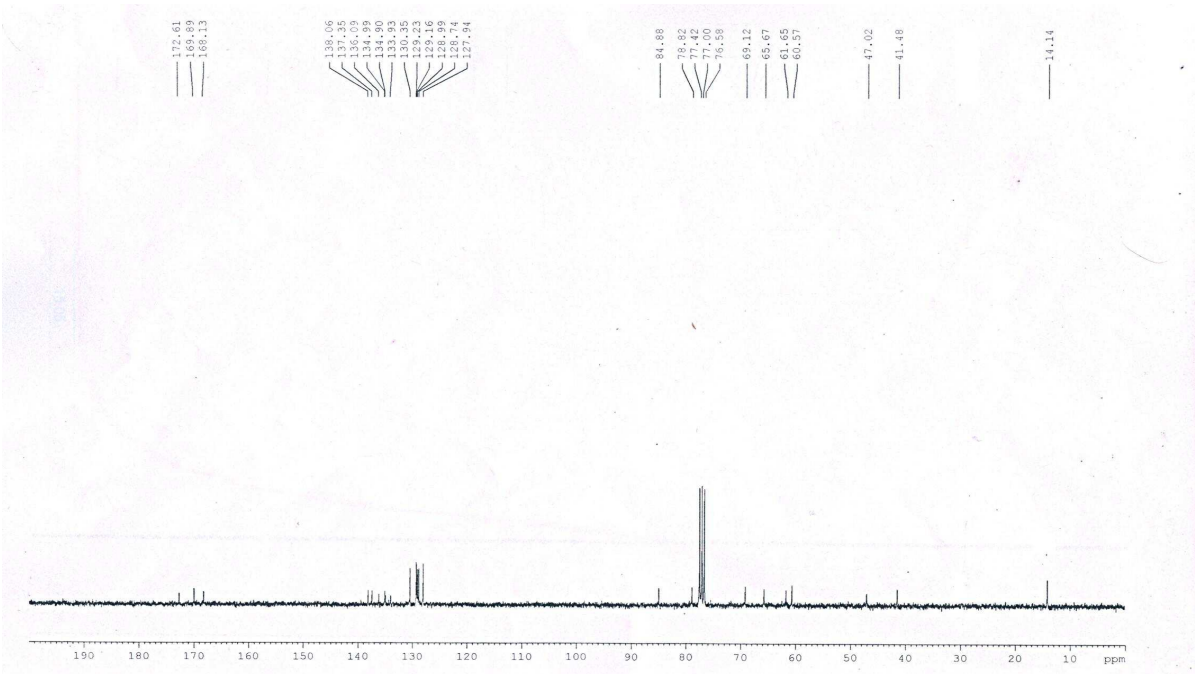
Yield: 78% (335 mg, 0.78 mmol).
Characteristic: White solid.
Melting point: 139^{o} C
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.13- 1.29 (6H, m), 3.21 (2H, d, *J* = 5.1 Hz), 3.80 (1H, d, *J* = 6.3 Hz), 4.05 (2H, q, *J* = 7.2 Hz), 4.13-4.36 (3H, m), 4.55 (1H, d, *J* = 6.3 Hz), 5.26 (1H, s), 7.56-7.86 (8H, m).
^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2, 48.1, 60.7, 61.7, 66.8, 68.7, 78.9, 112.0, 112.7, 118.6, 128.3, 128.7, 132.4, 132.5, 145.8, 169.7, 171.8.
FT-IR (neat, cm^{-1}): 1095,1409,1661,1738, 2230, 2359, 2924, 3344.
HR-MS (*m/z*): for $C_{24}H_{24}N_4O_4$ Calculated: 432.1798; Found: 432.1789.

7. ^{1}H and ^{13}C NMR spectrum of compounds 5a-l, 7a-k, 4a-b.

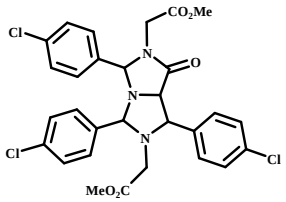
^{1}H and ^{13}C NMR of compound **5a**

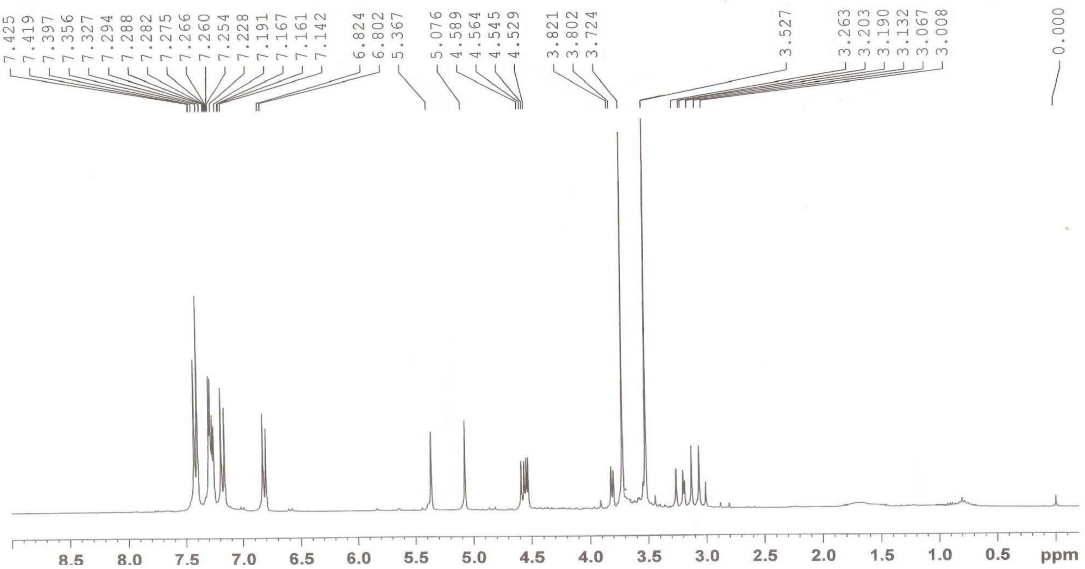


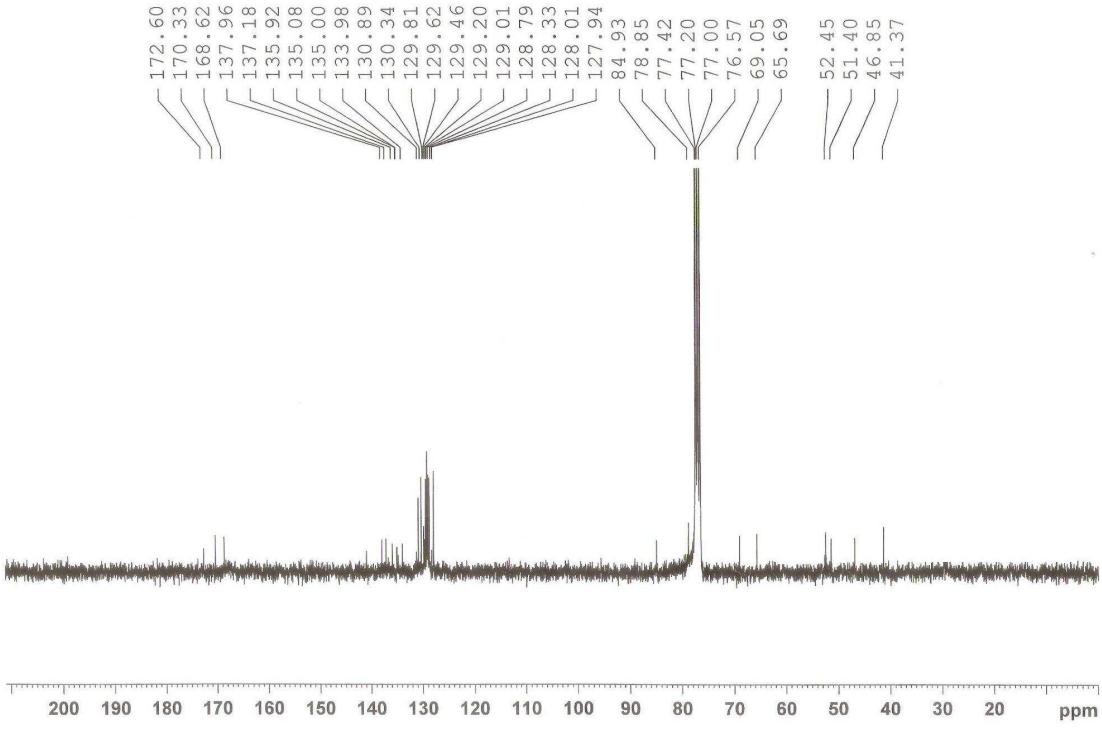




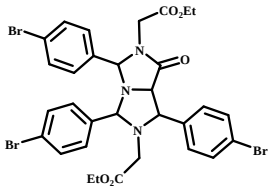
^{1}H and ^{13}C NMR of compound **5b**

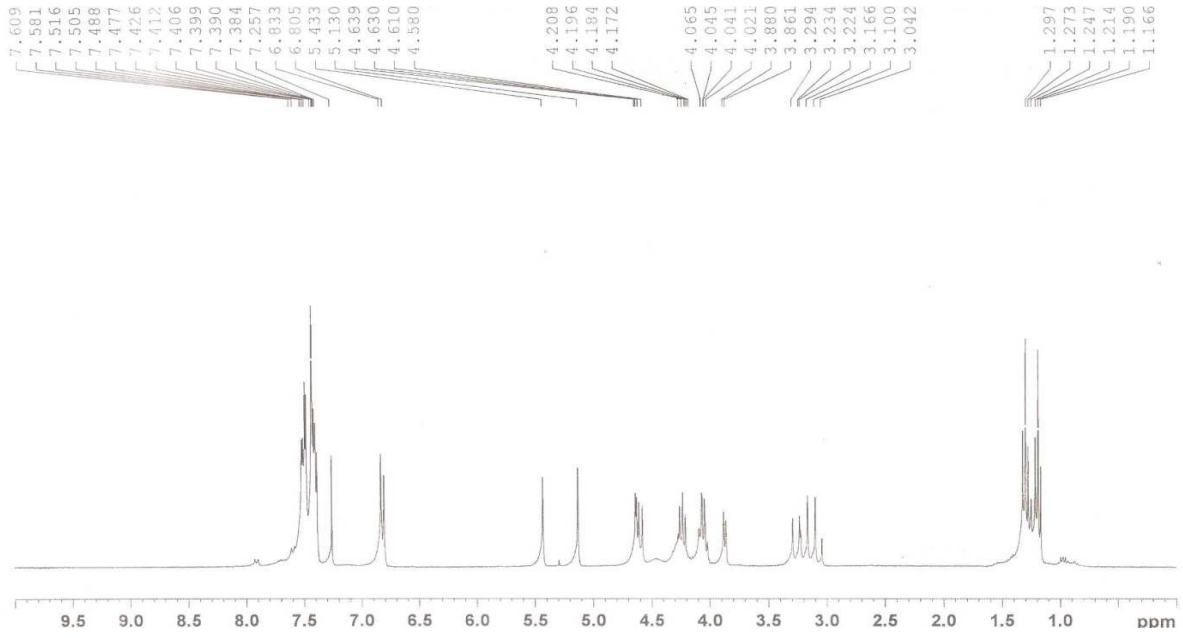


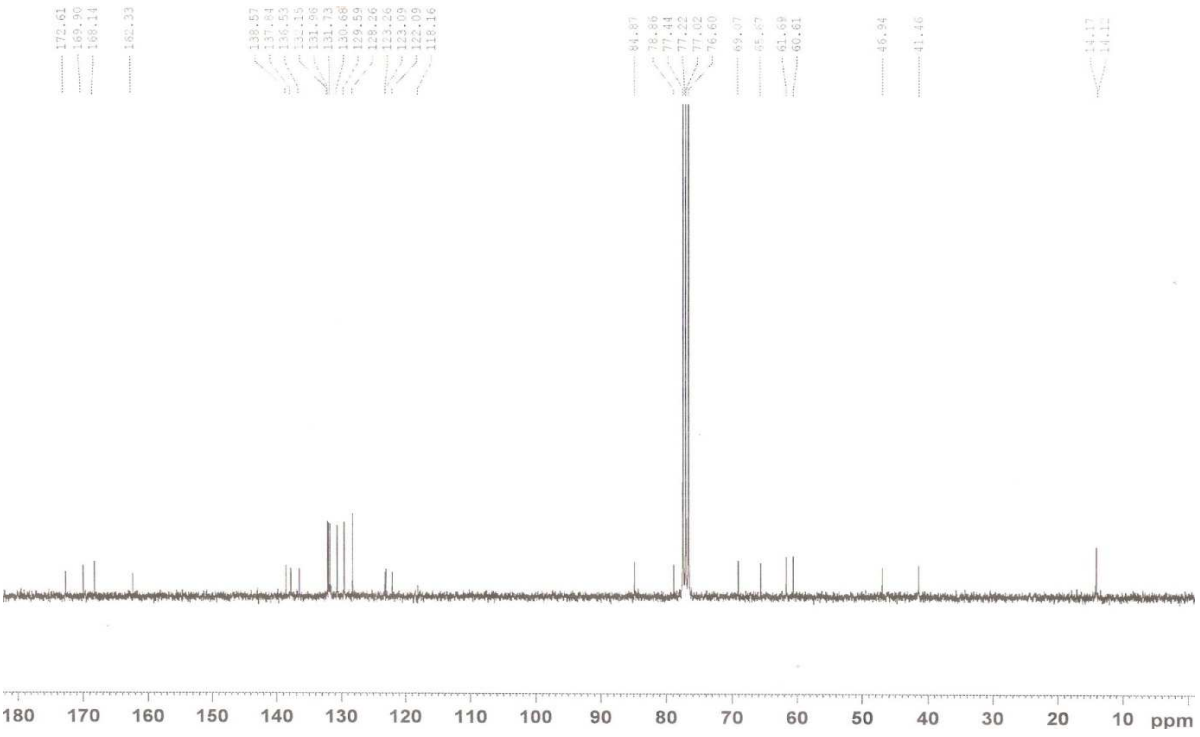




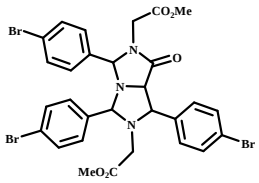
^{1}H and ^{13}C NMR of compound **5c**

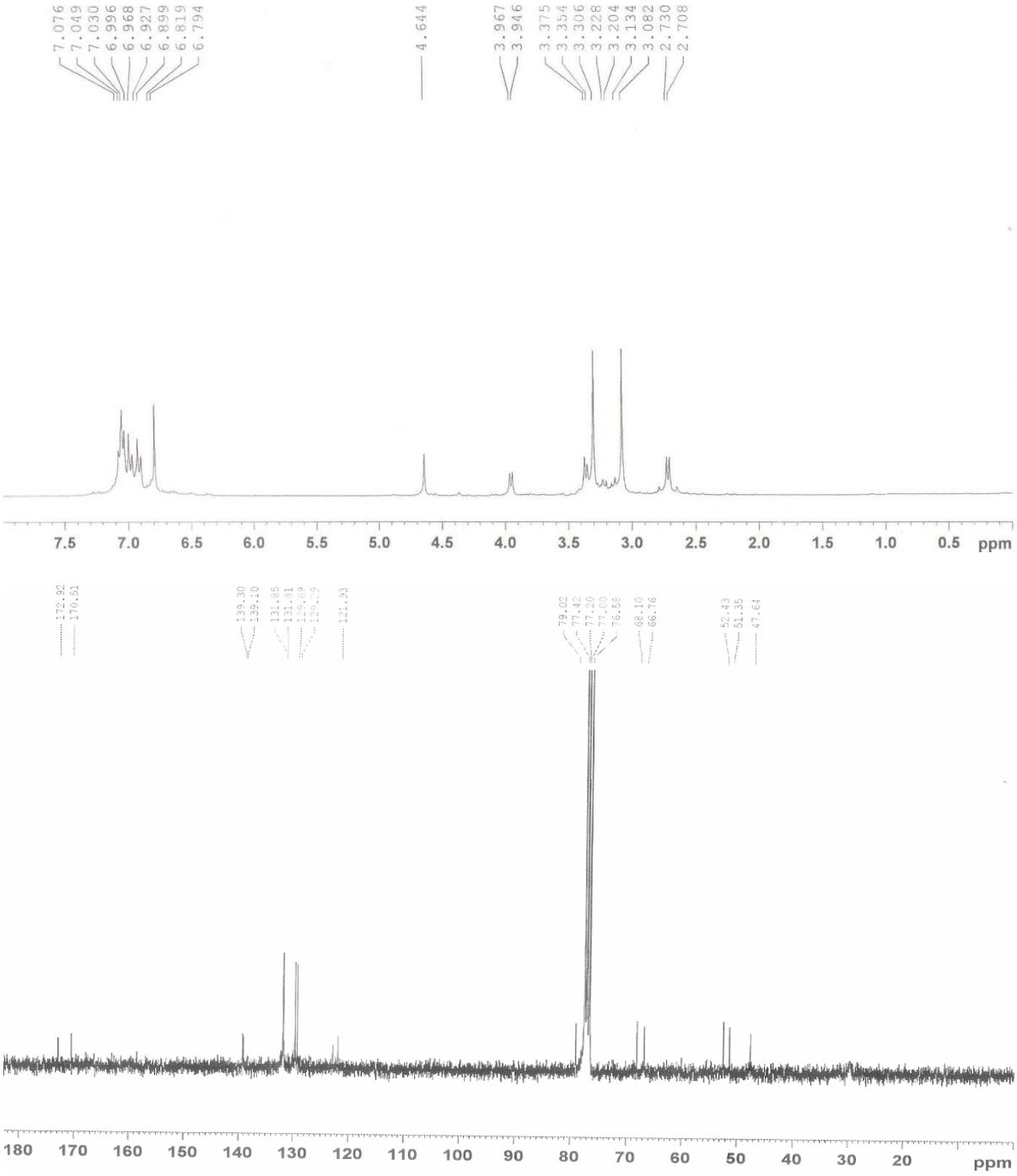




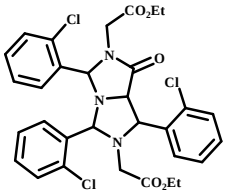


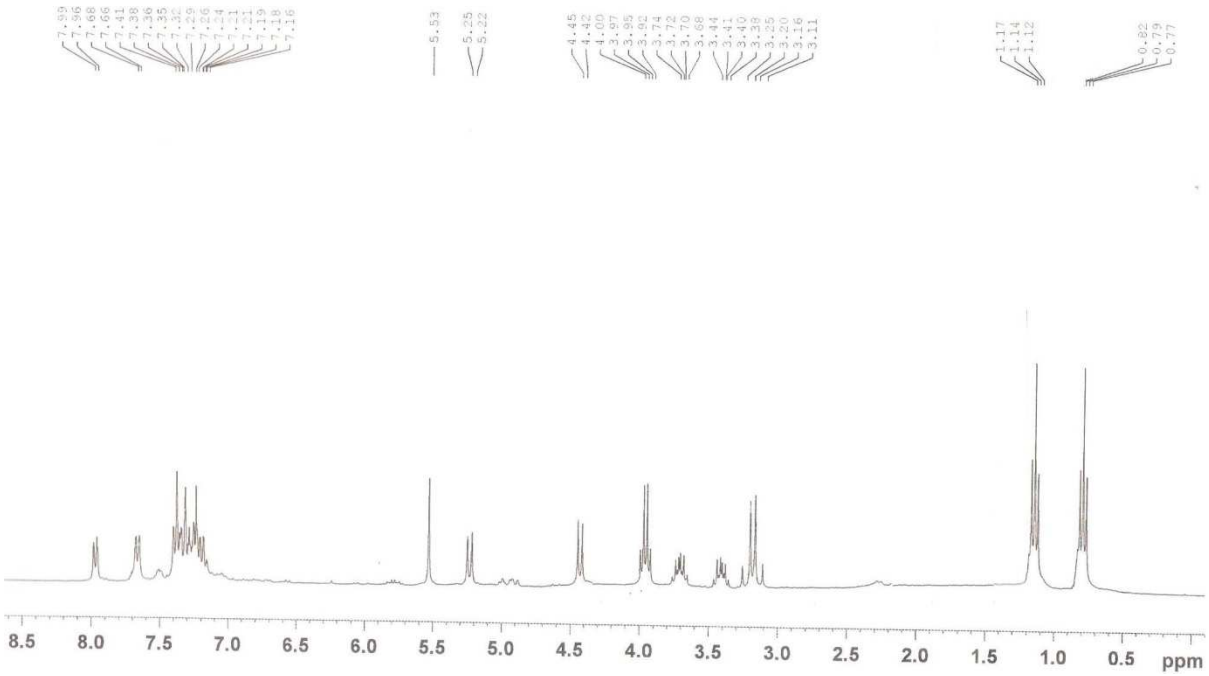
^{1}H and ^{13}C NMR of compound **5d**

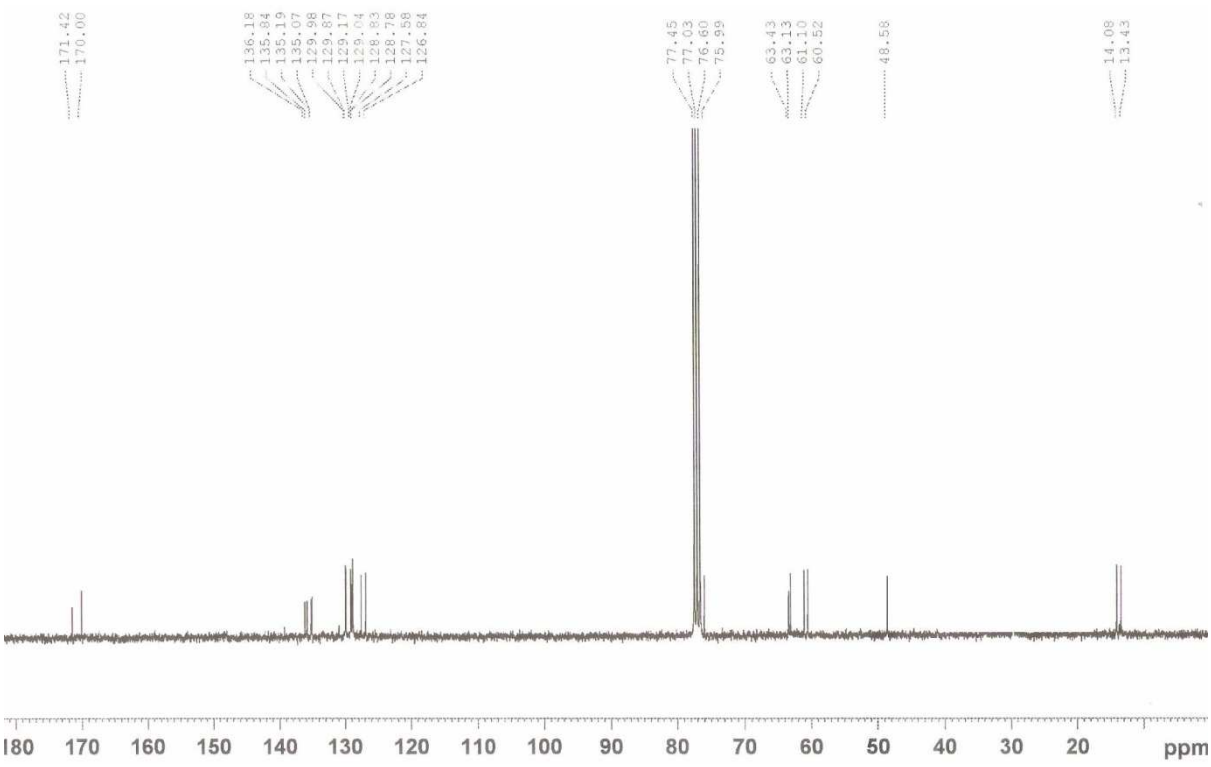




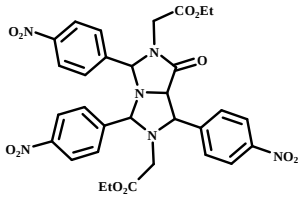
^{1}H and ^{13}C NMR of compound **5e**

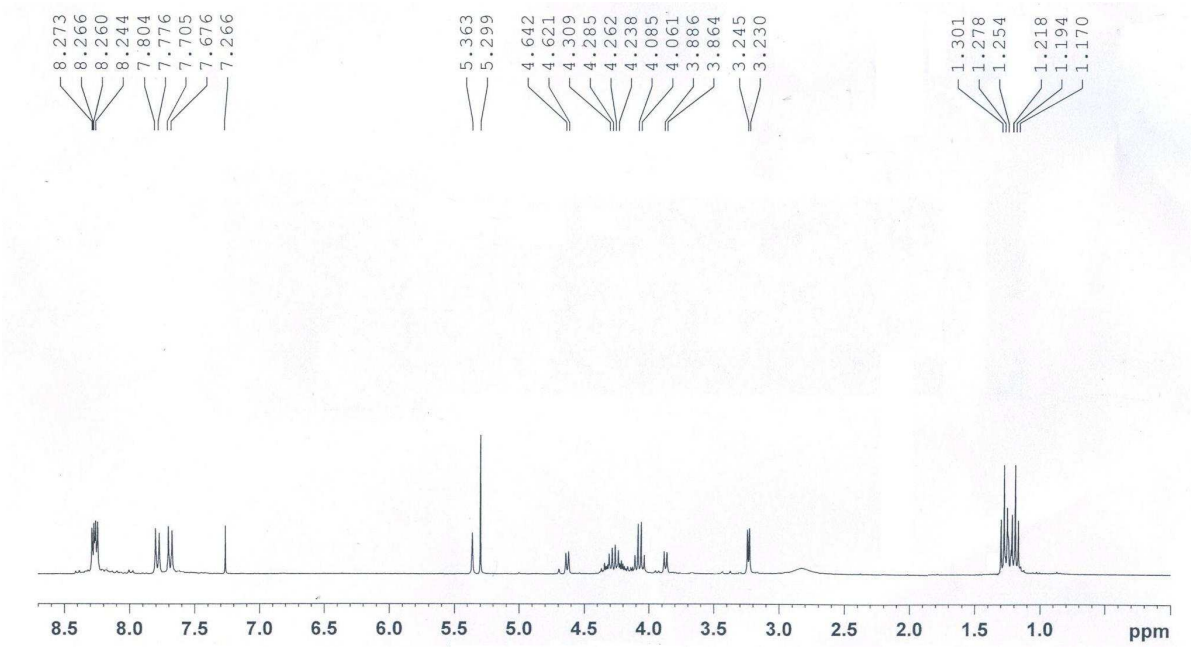


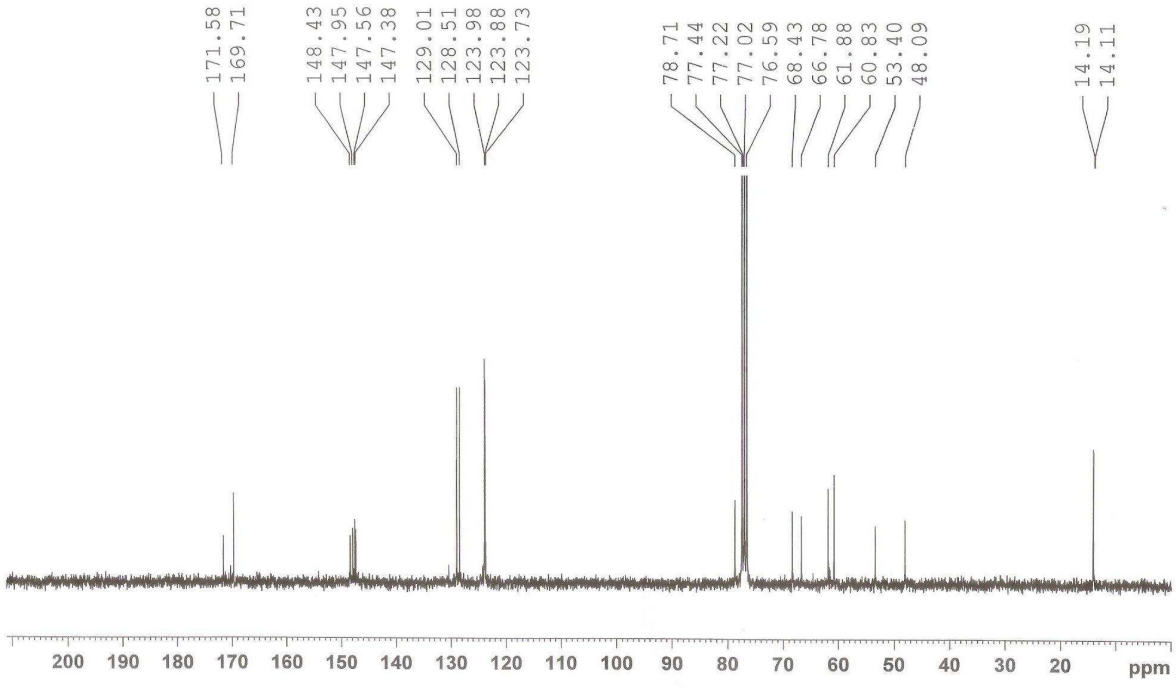




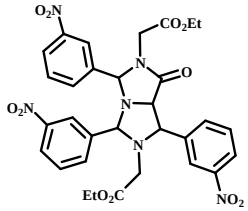
^{1}H and ^{13}C NMR of compound **5f**

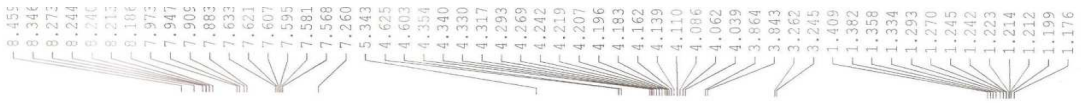


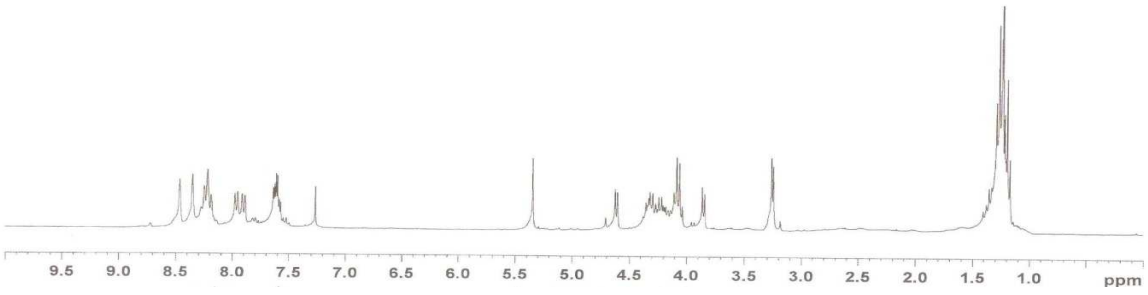


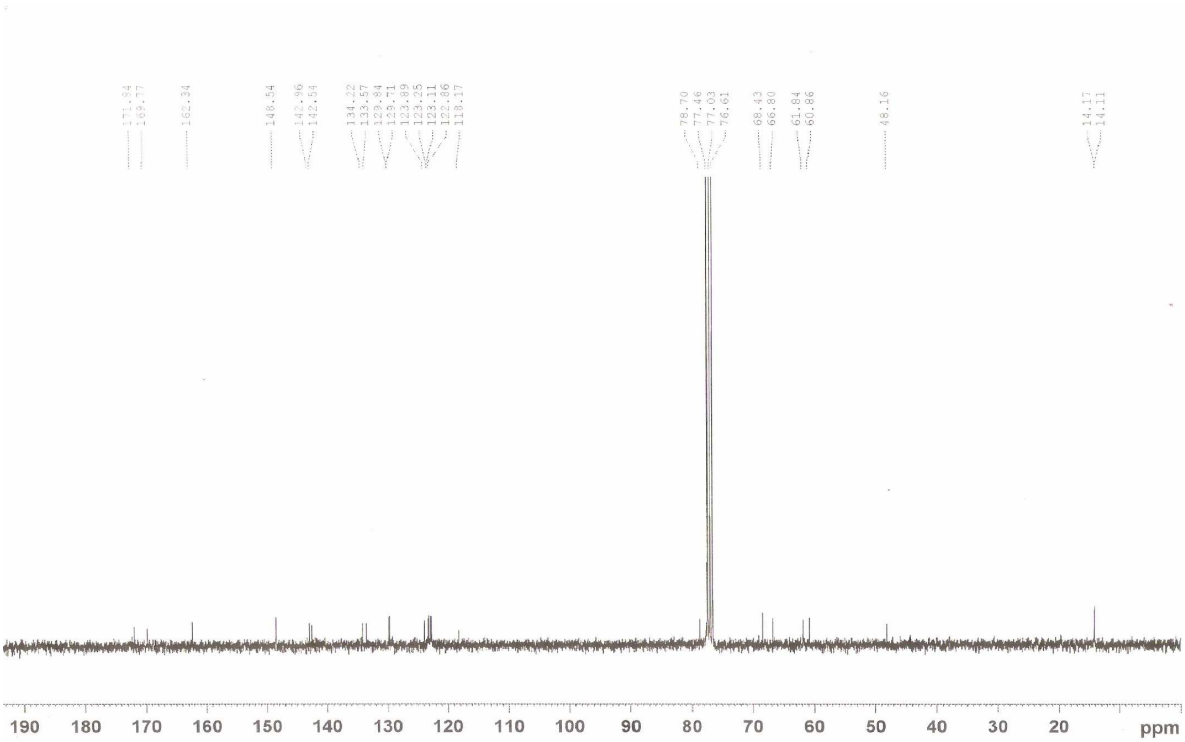


^{1}H and ^{13}C NMR of compound **5g**

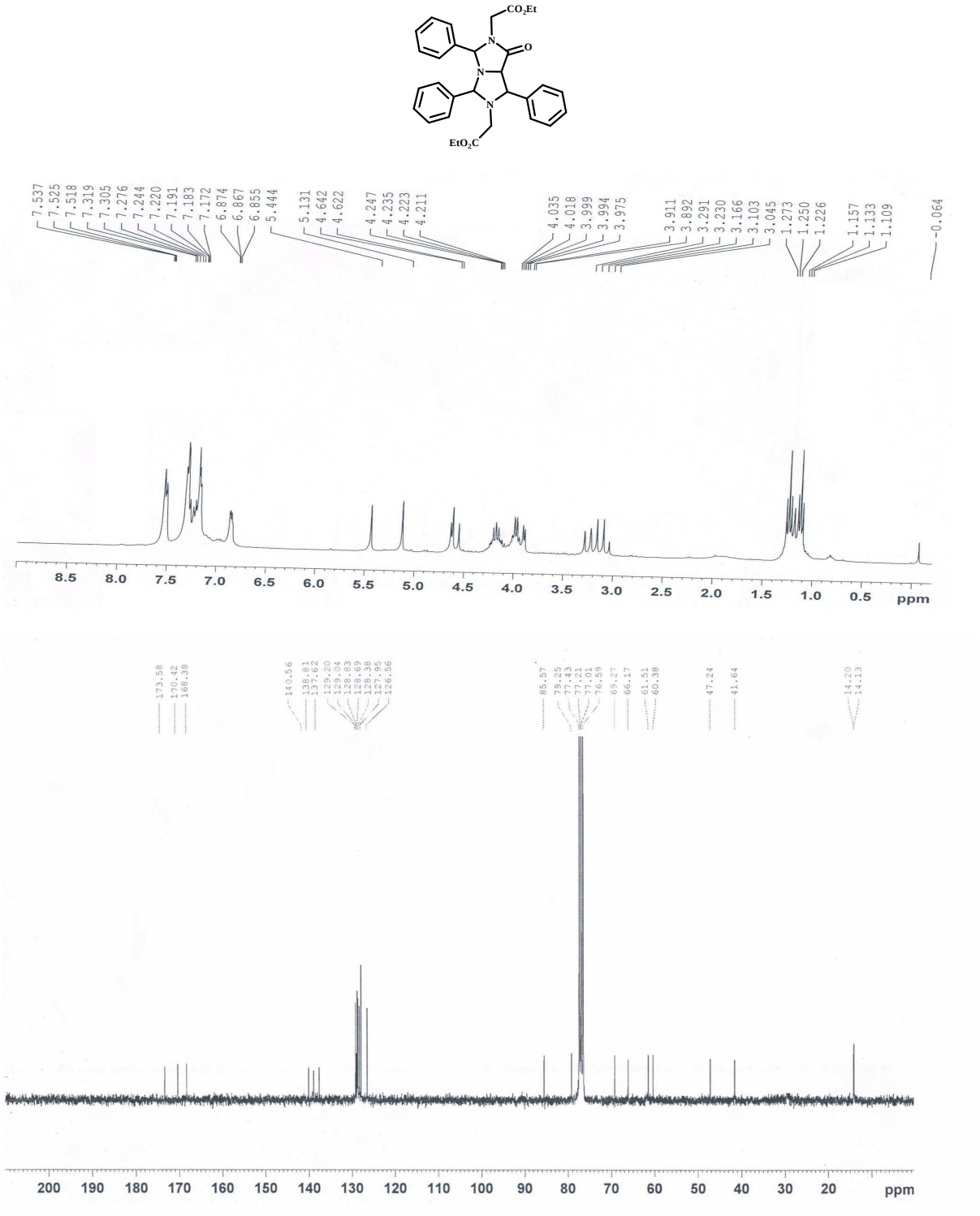




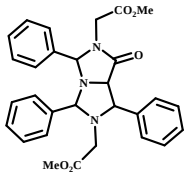


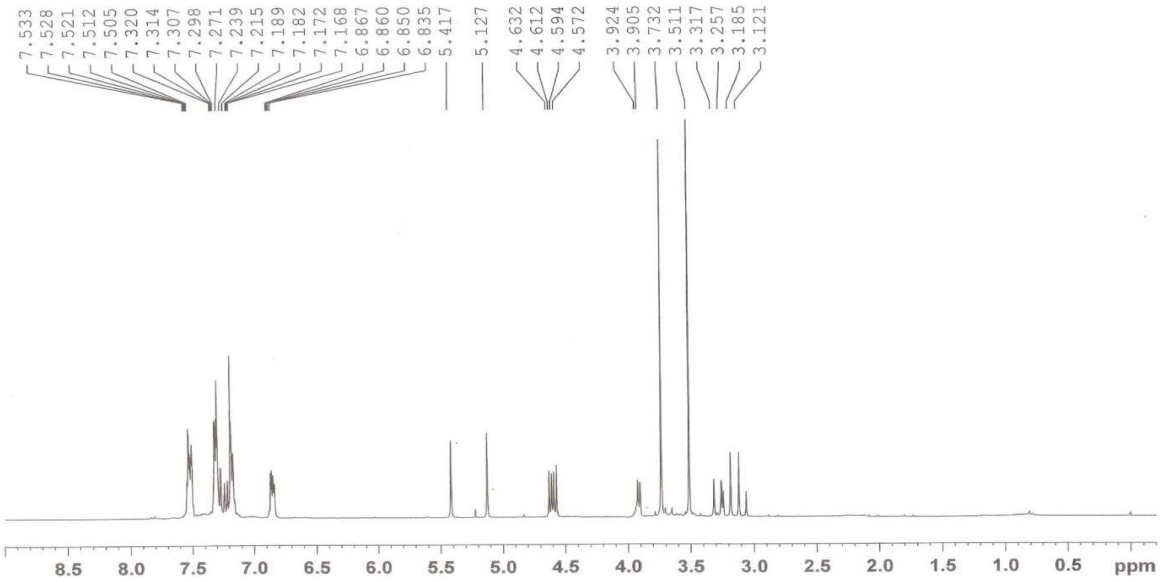


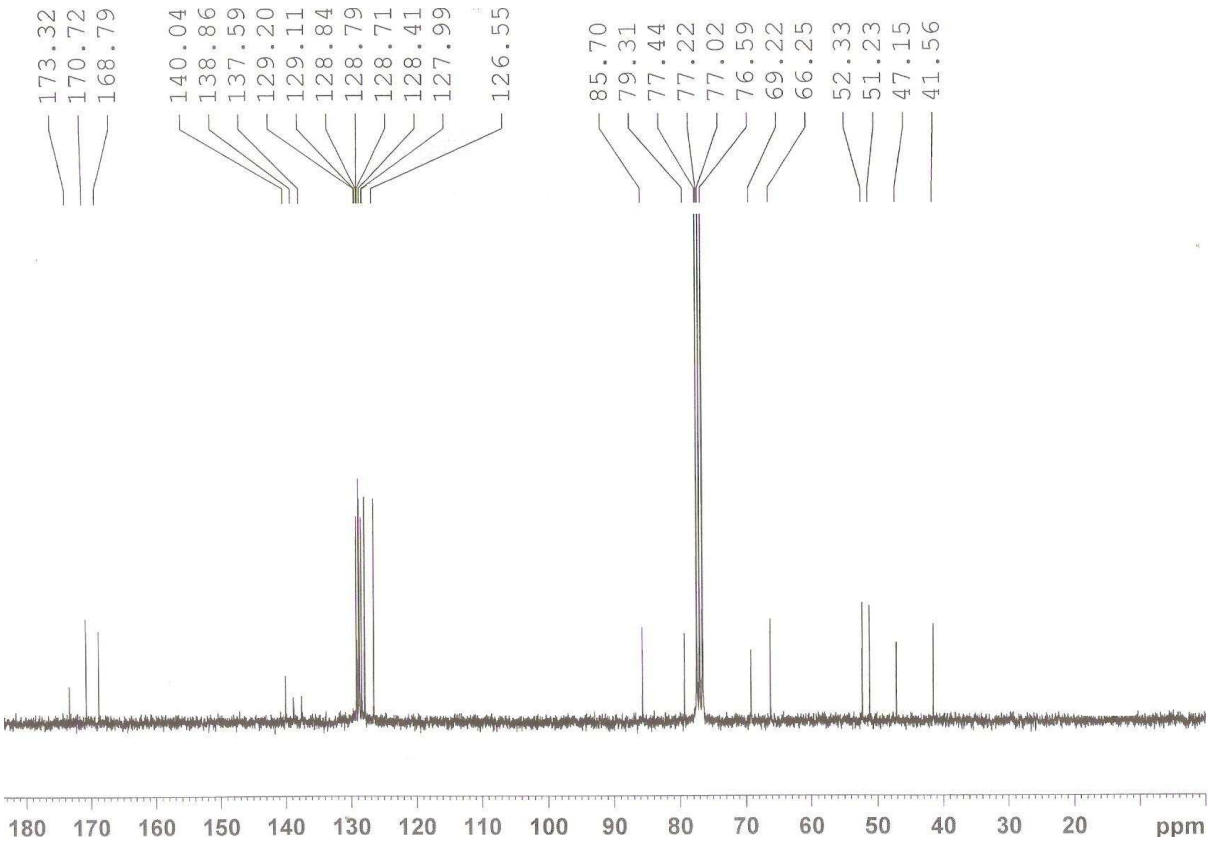
^{1}H and ^{13}C NMR of compound **5h**



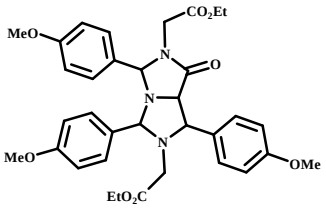
^{1}H and ^{13}C NMR of compound **5i**

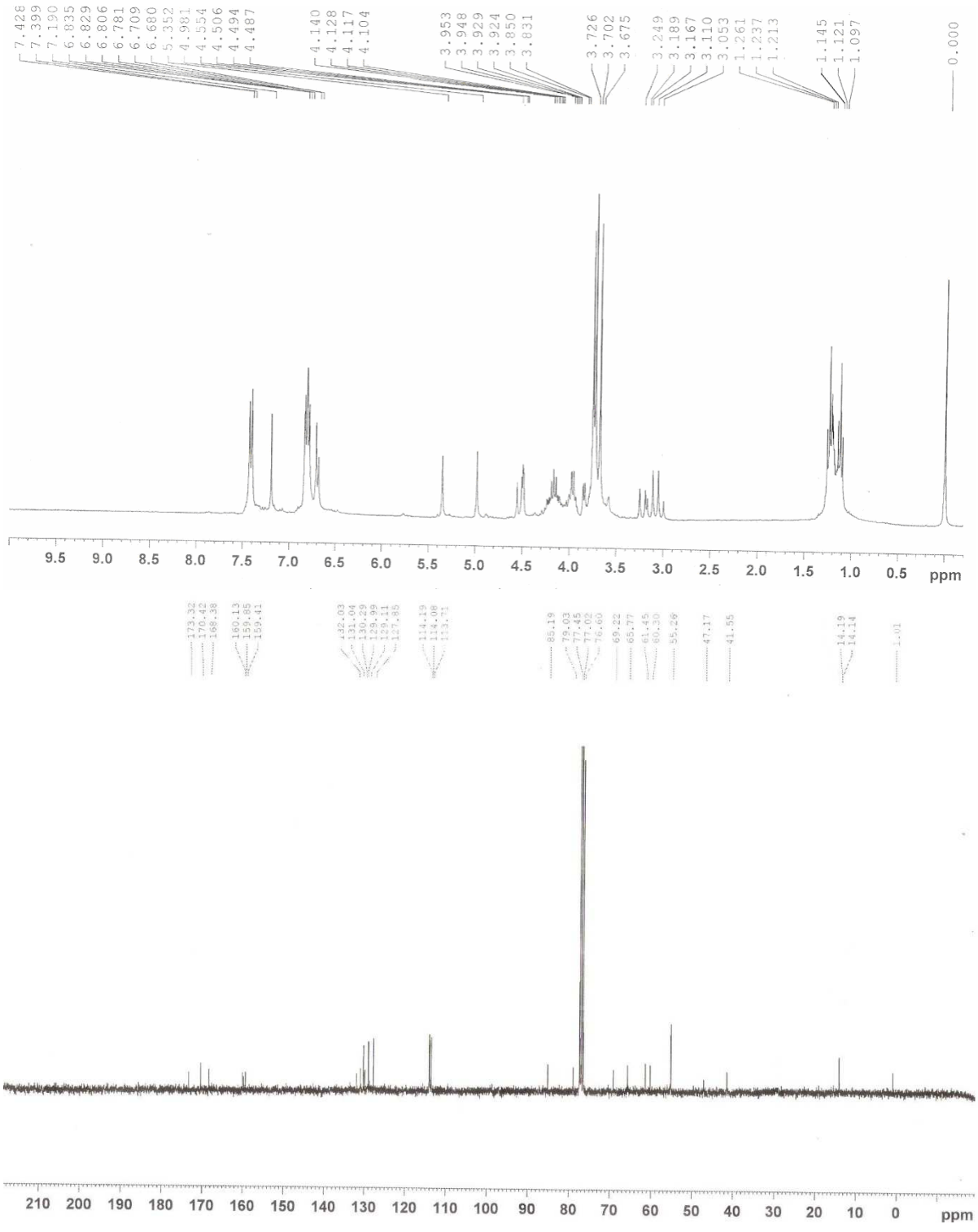




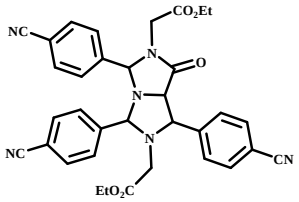


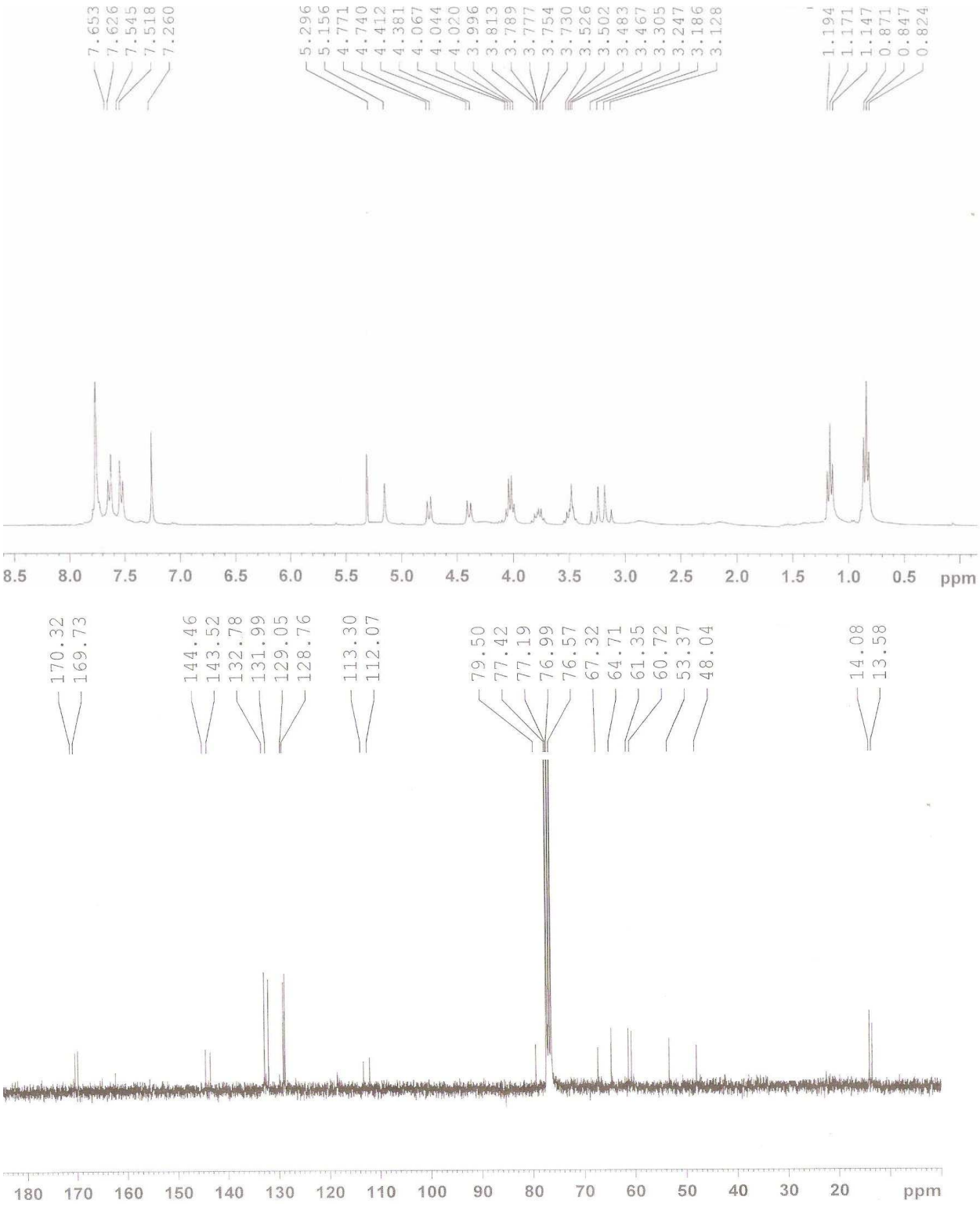
^{1}H and ^{13}C NMR of compound **5j**



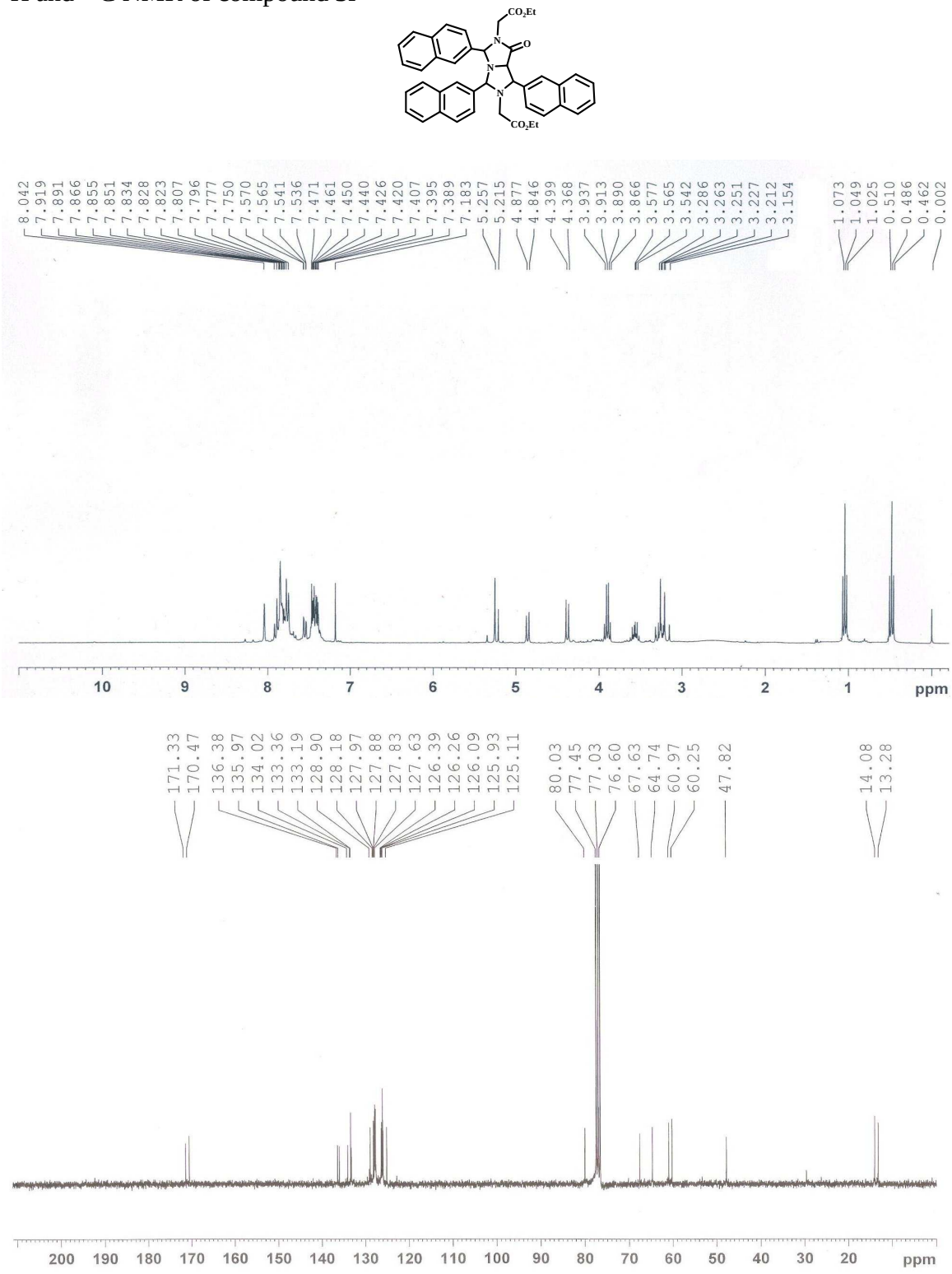


^{1}H and ^{13}C NMR of compound **5k**

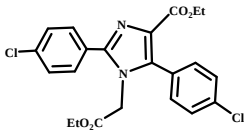


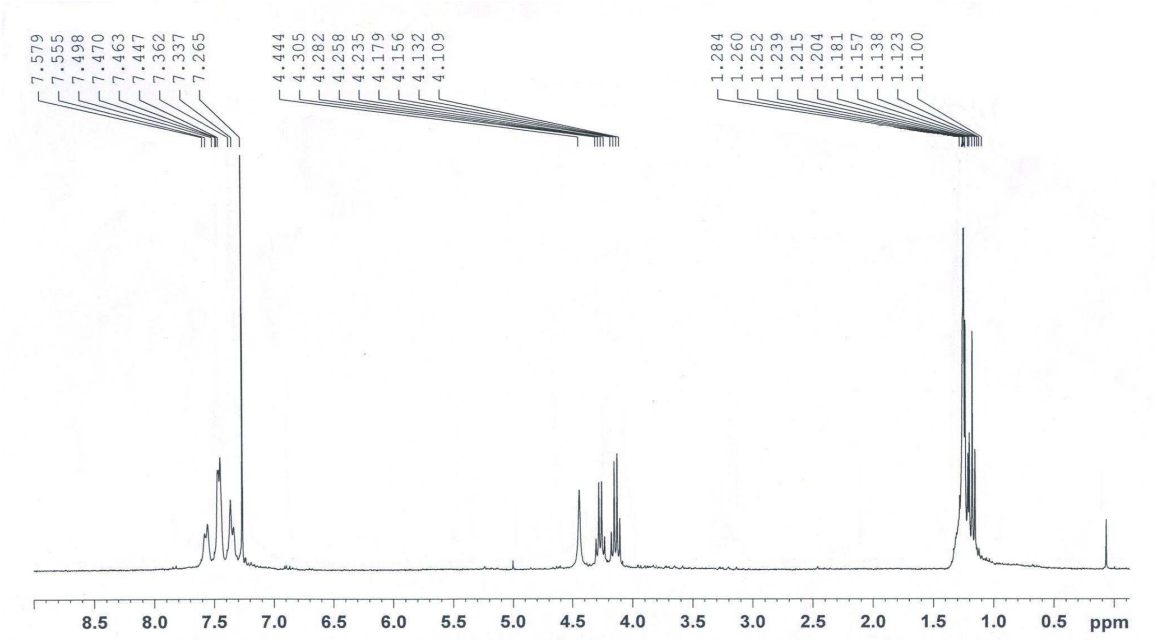


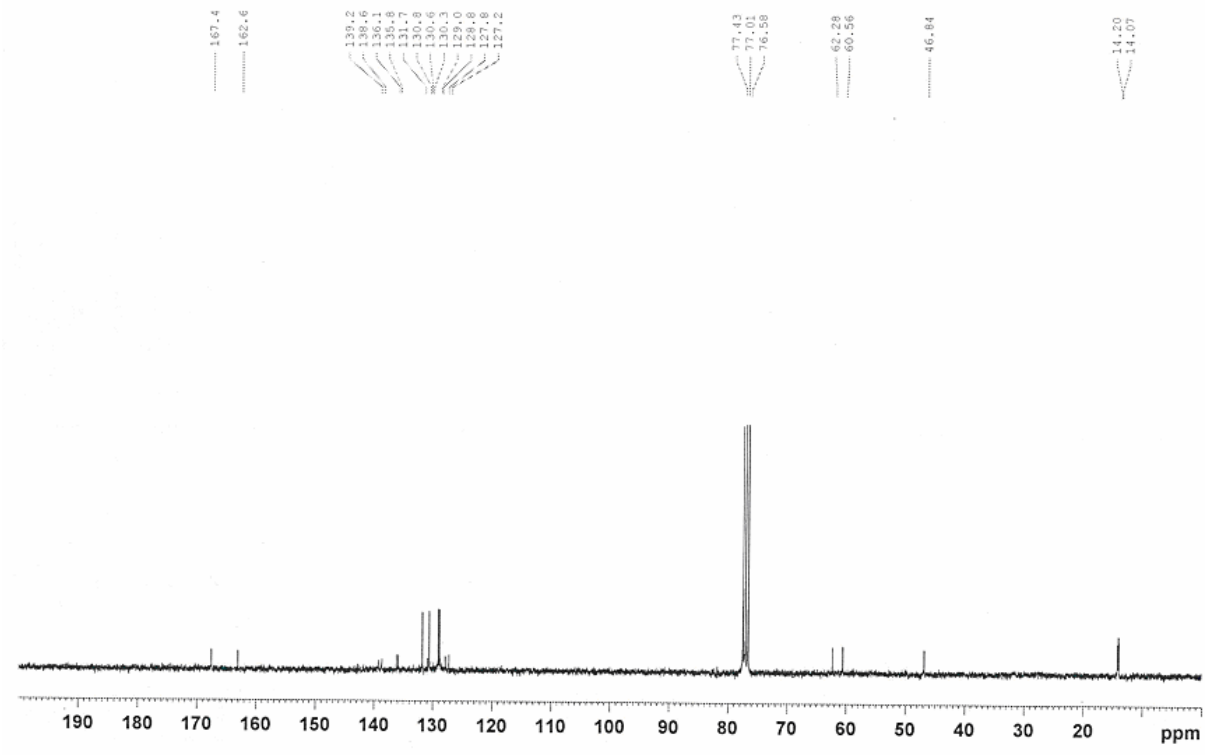
^{1}H and ^{13}C NMR of compound **5l**



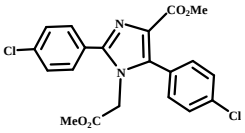
^{1}H and ^{13}C NMR of compound **7a**

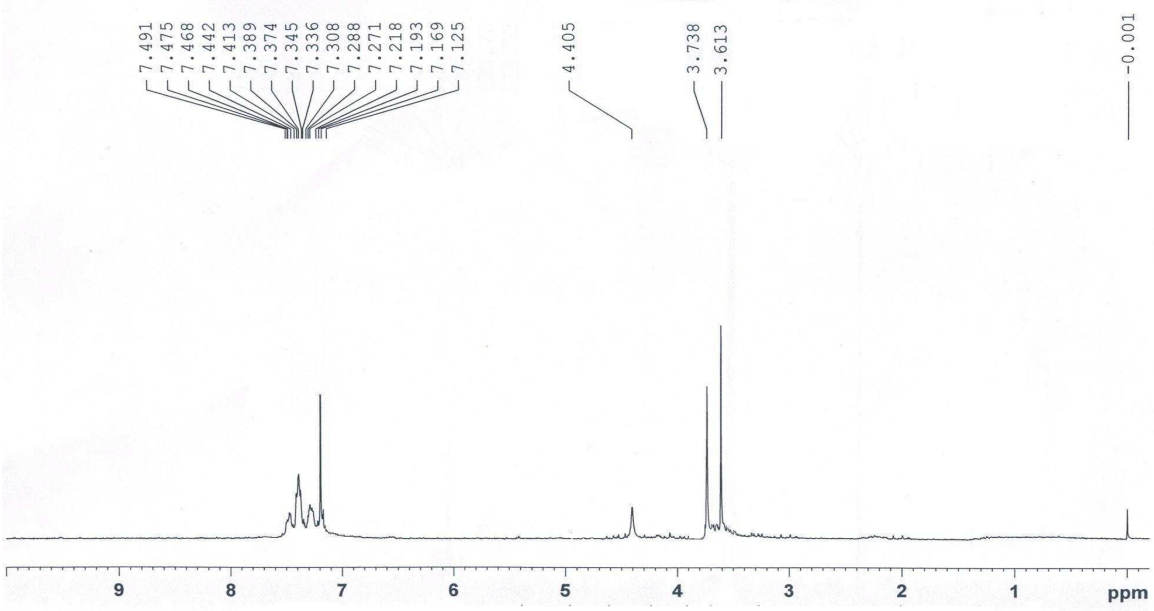


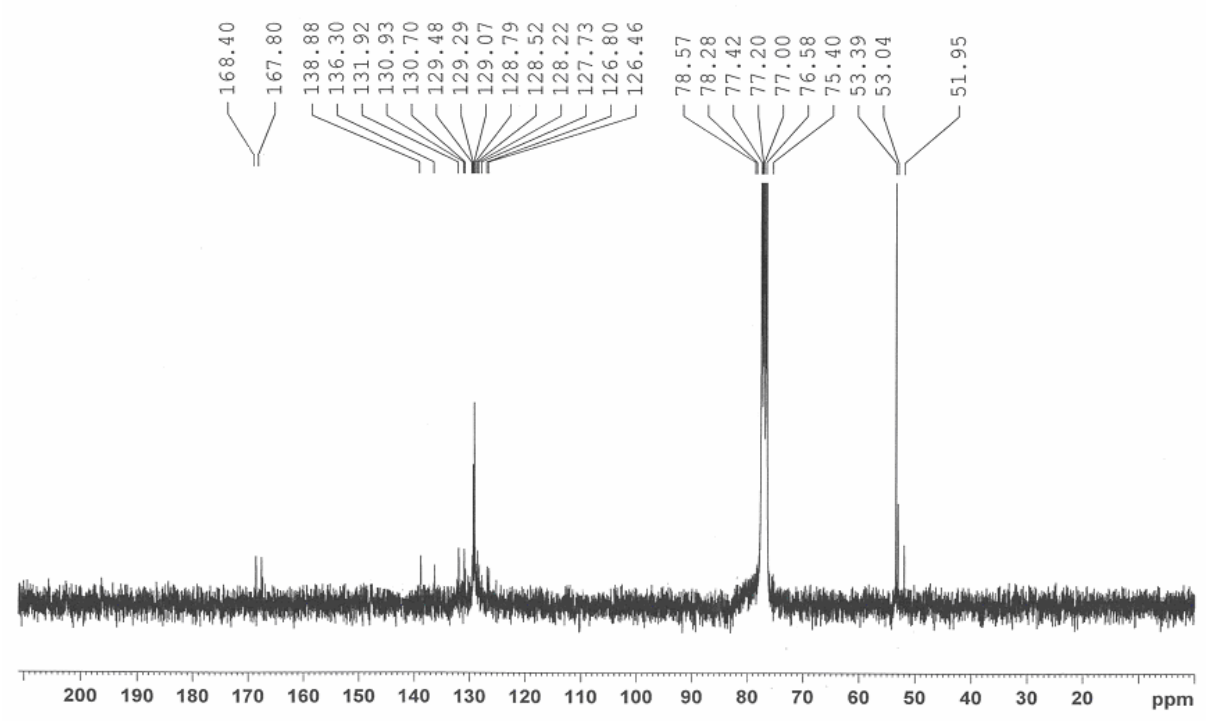




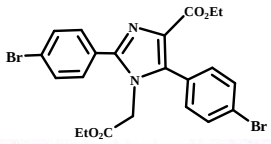
^{1}H and ^{13}C NMR of compound **7b**

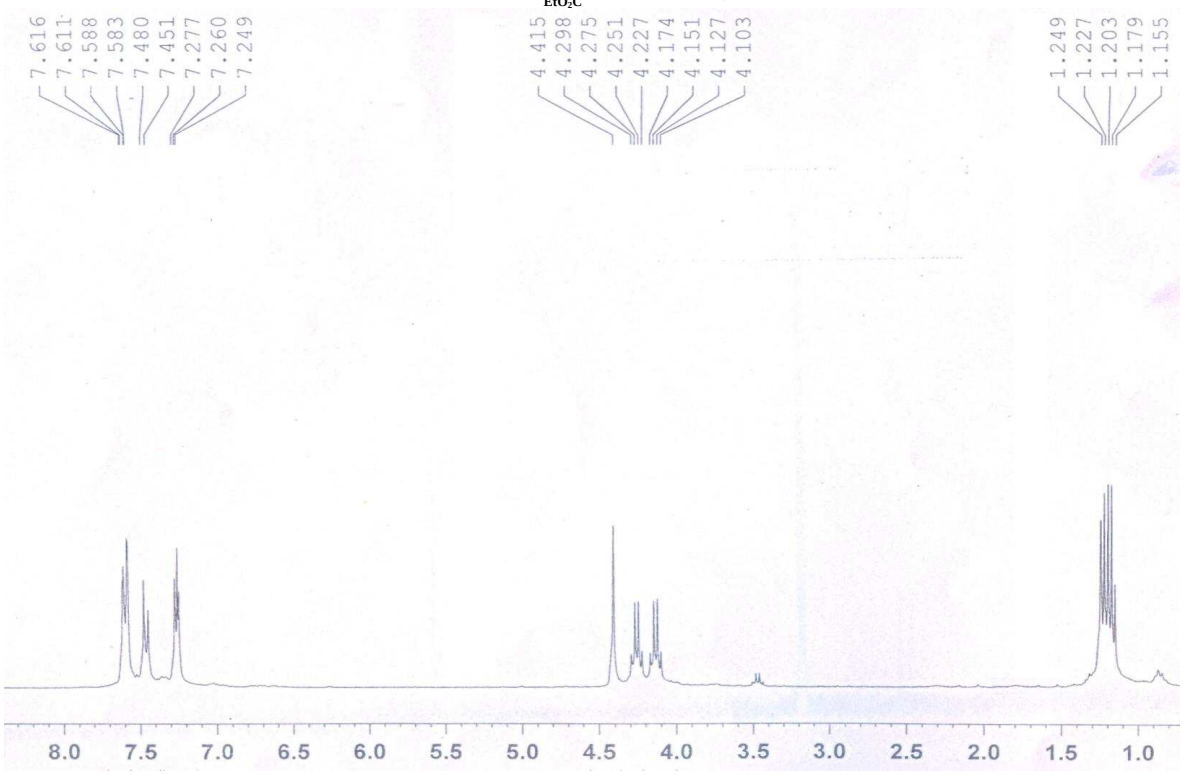


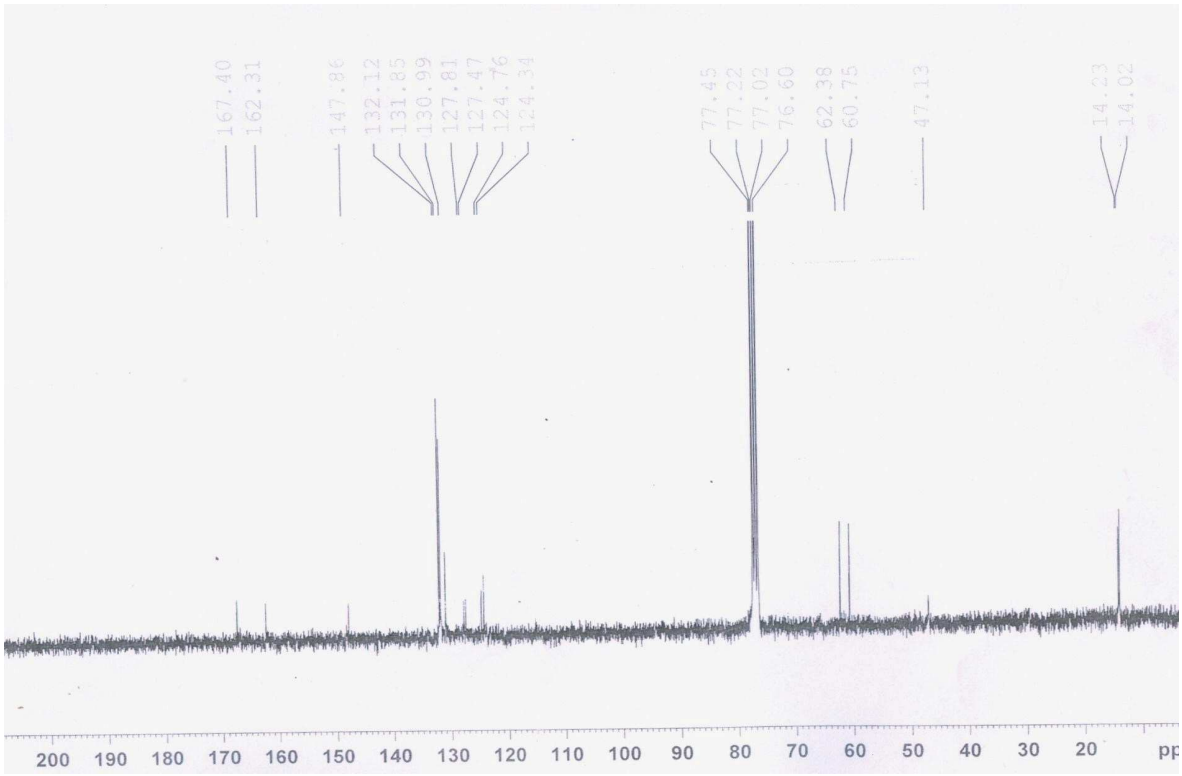




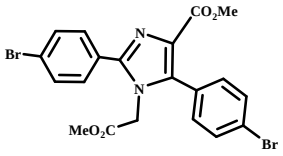
^{1}H and ^{13}C NMR of compound **7c**

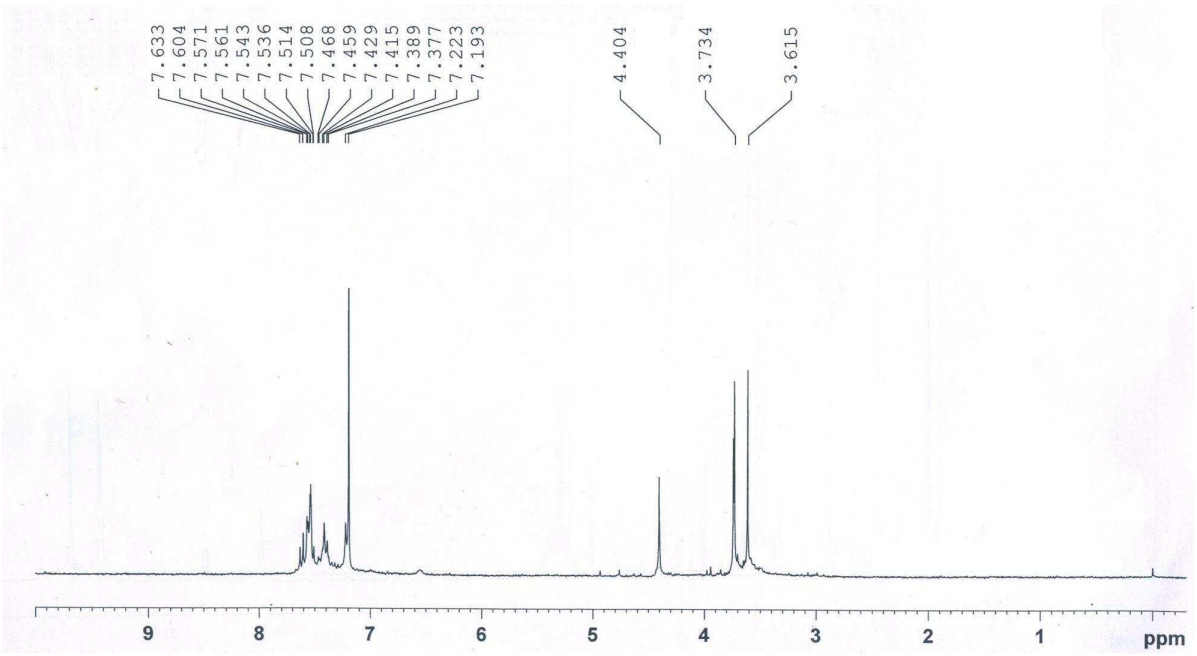


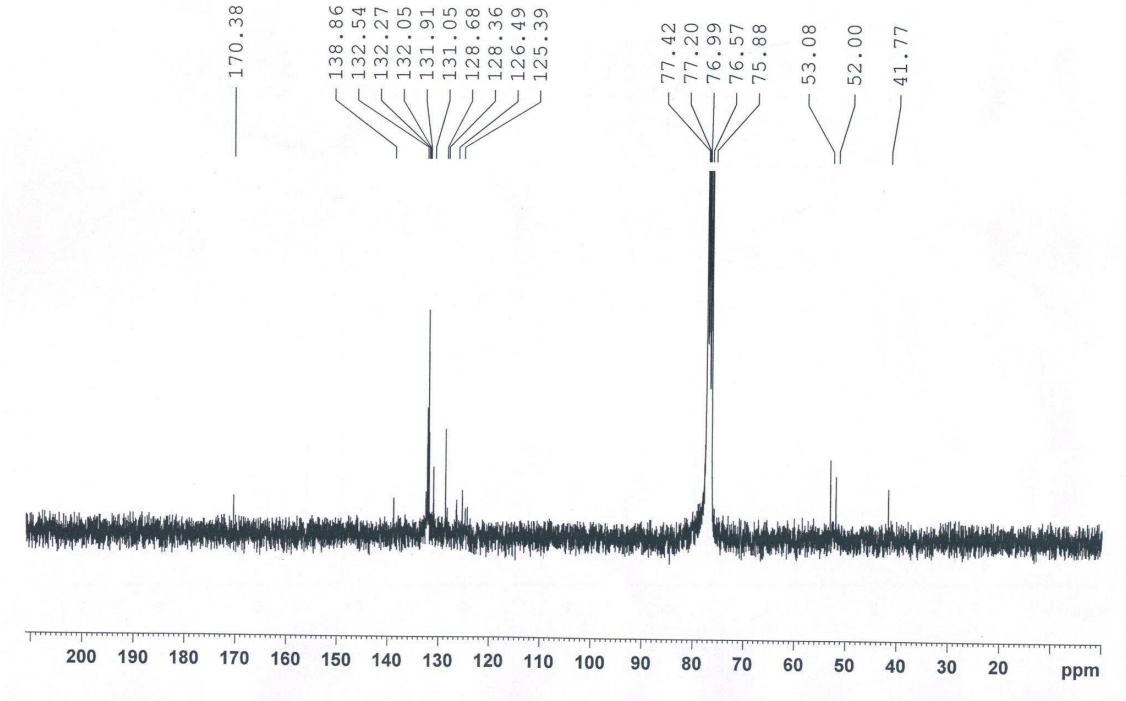




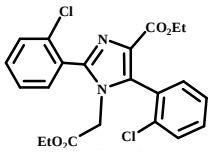
^{1}H and ^{13}C NMR of compound **7d**

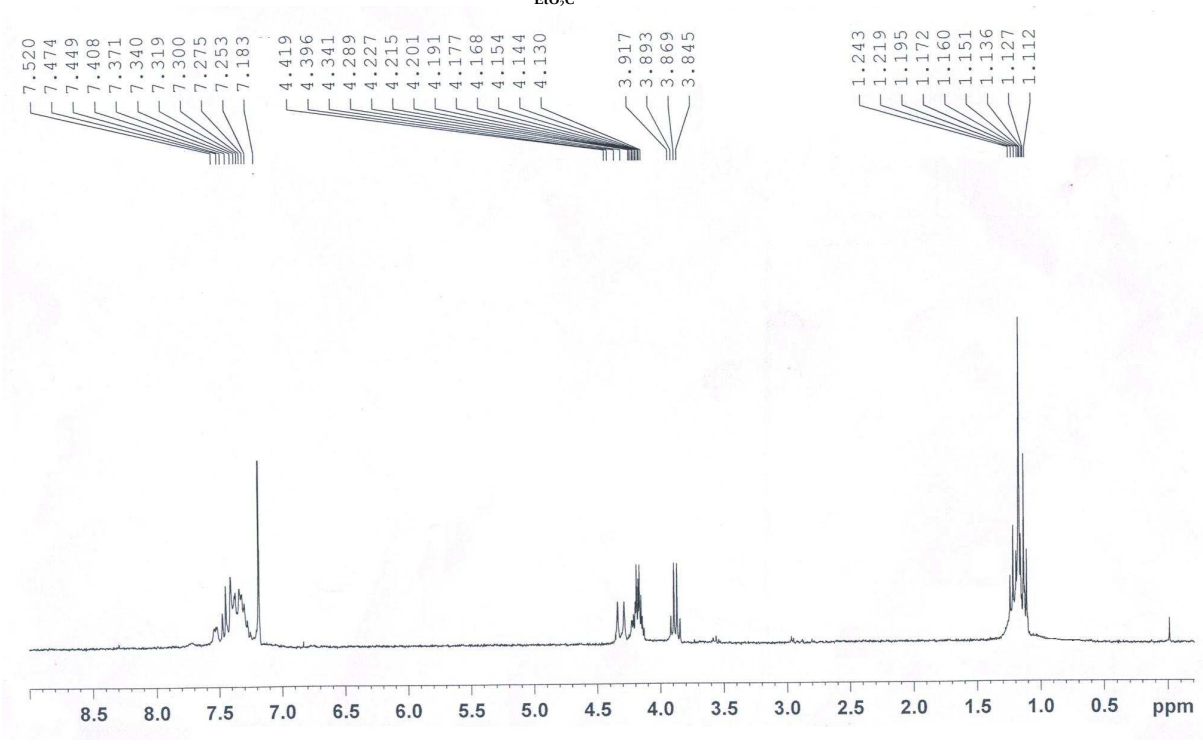


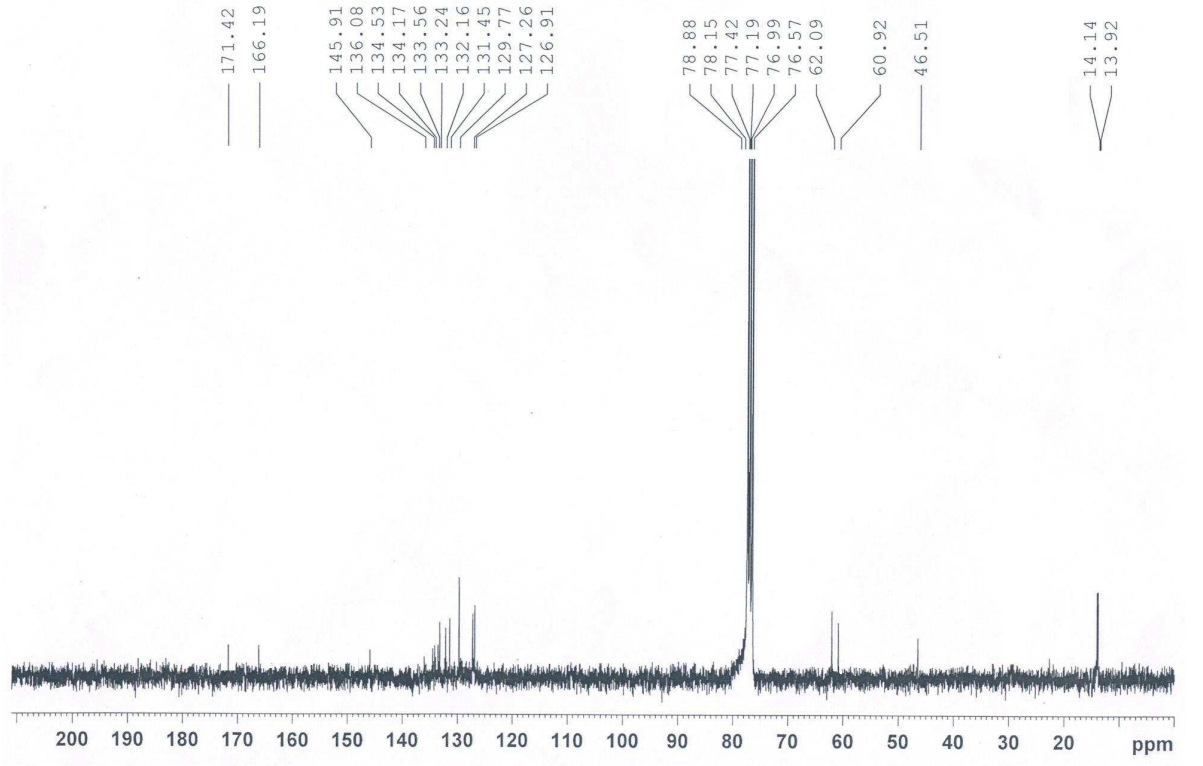




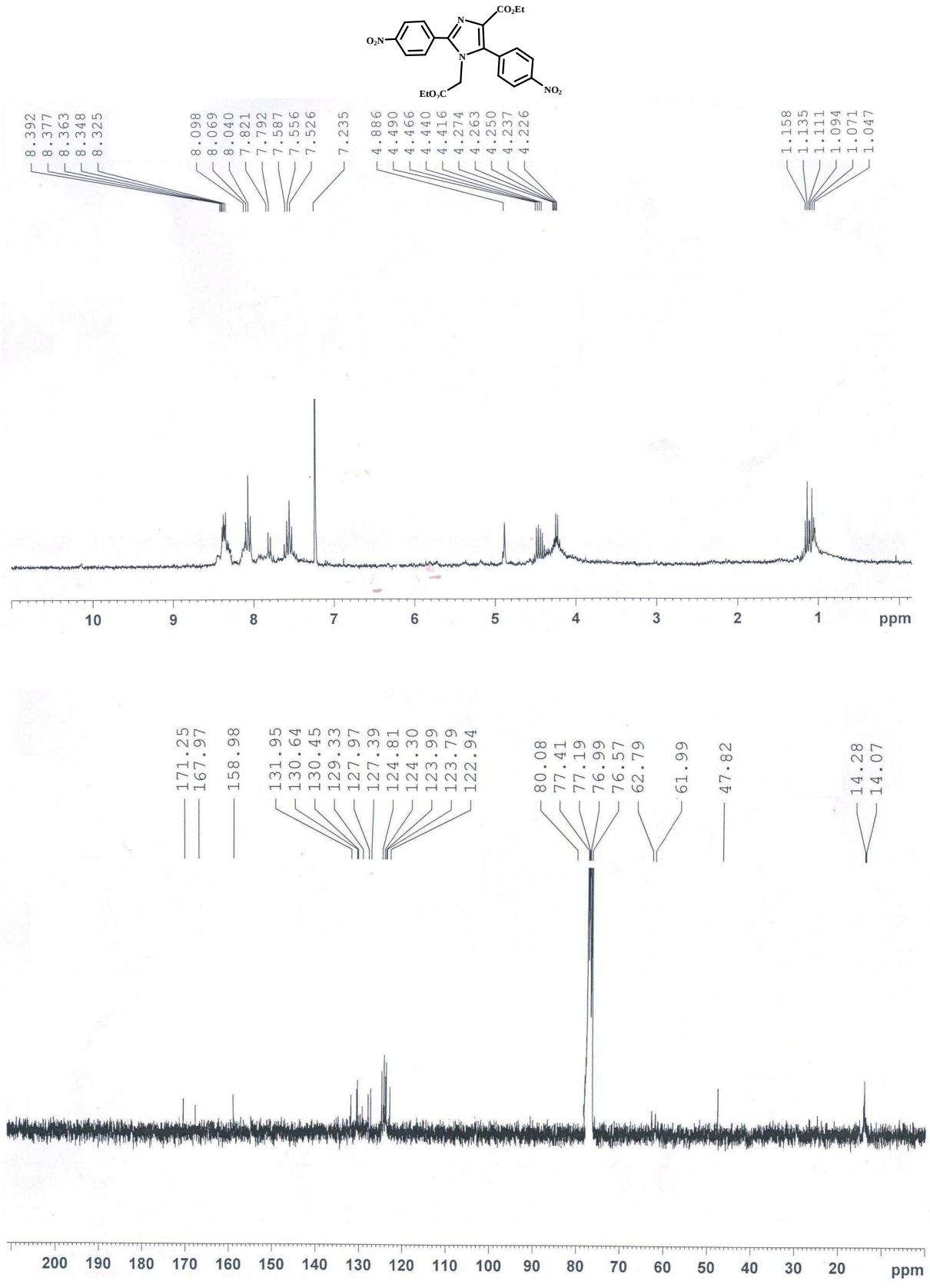
^{1}H and ^{13}C NMR of compound **7e**



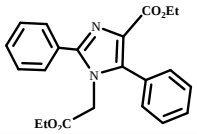


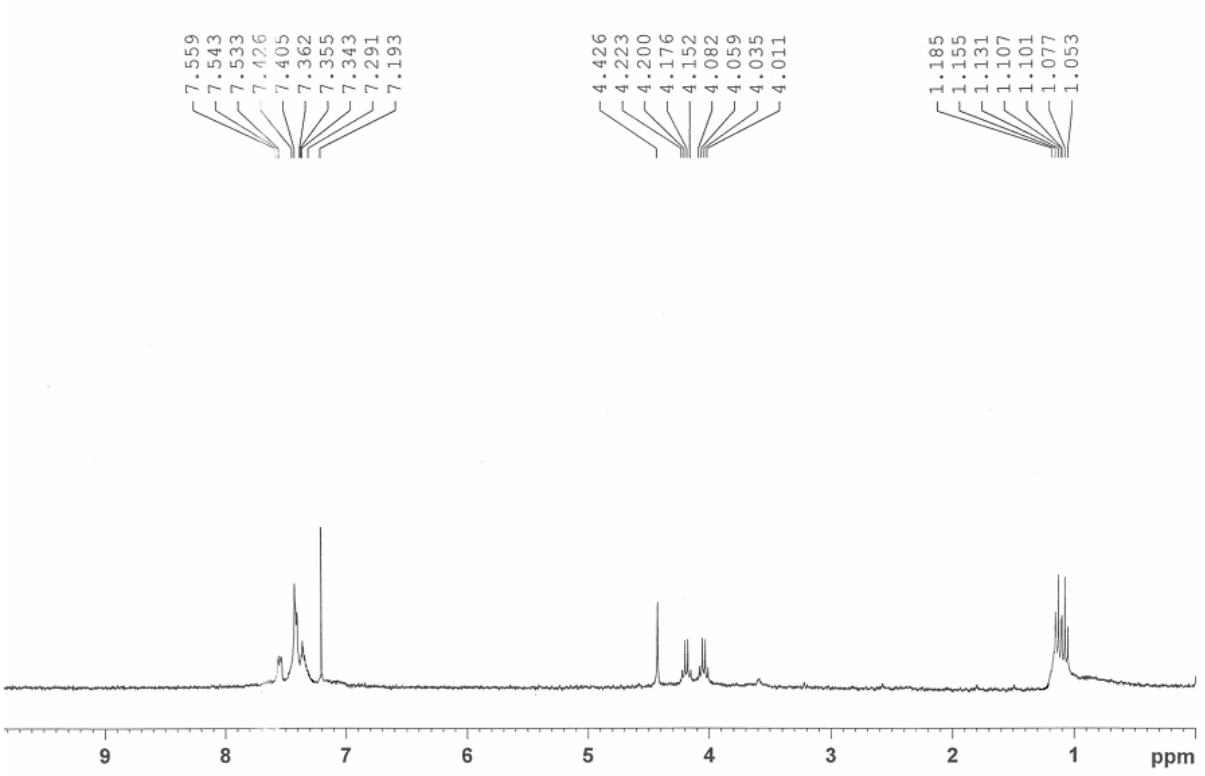


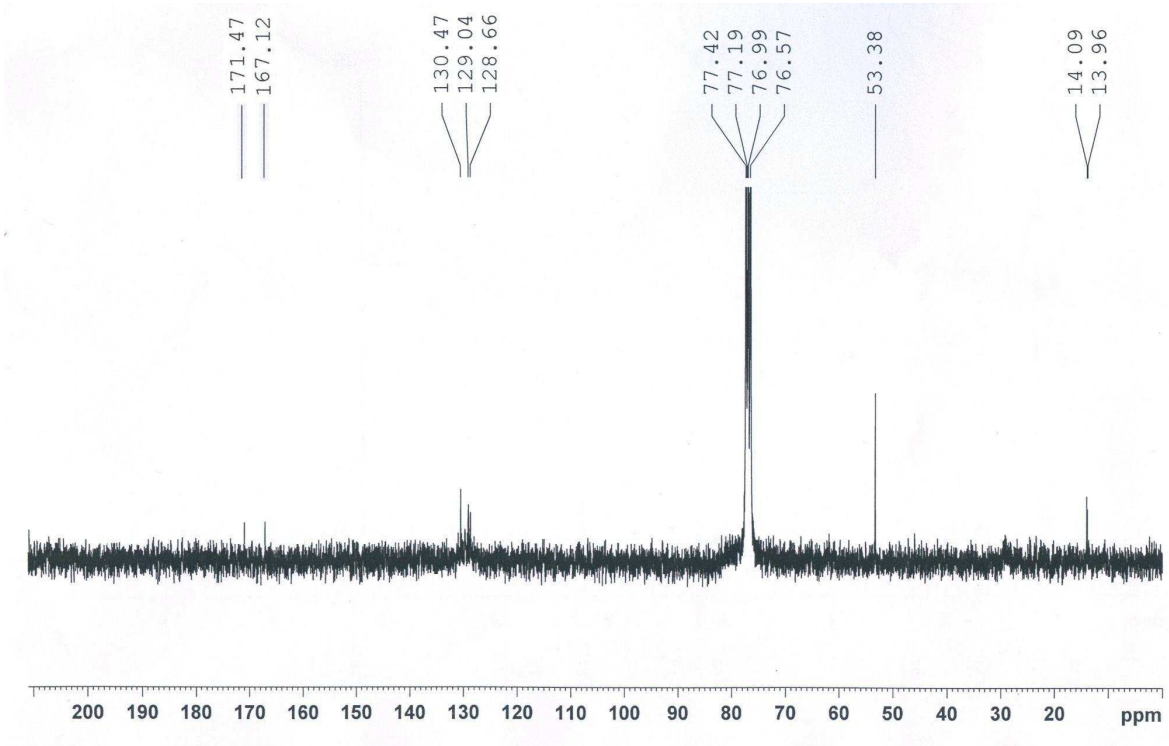
^{1}H and ^{13}C NMR of compound **7f**



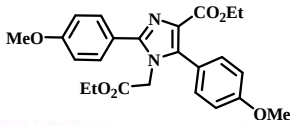
^{1}H and ^{13}C NMR of compound **7g**

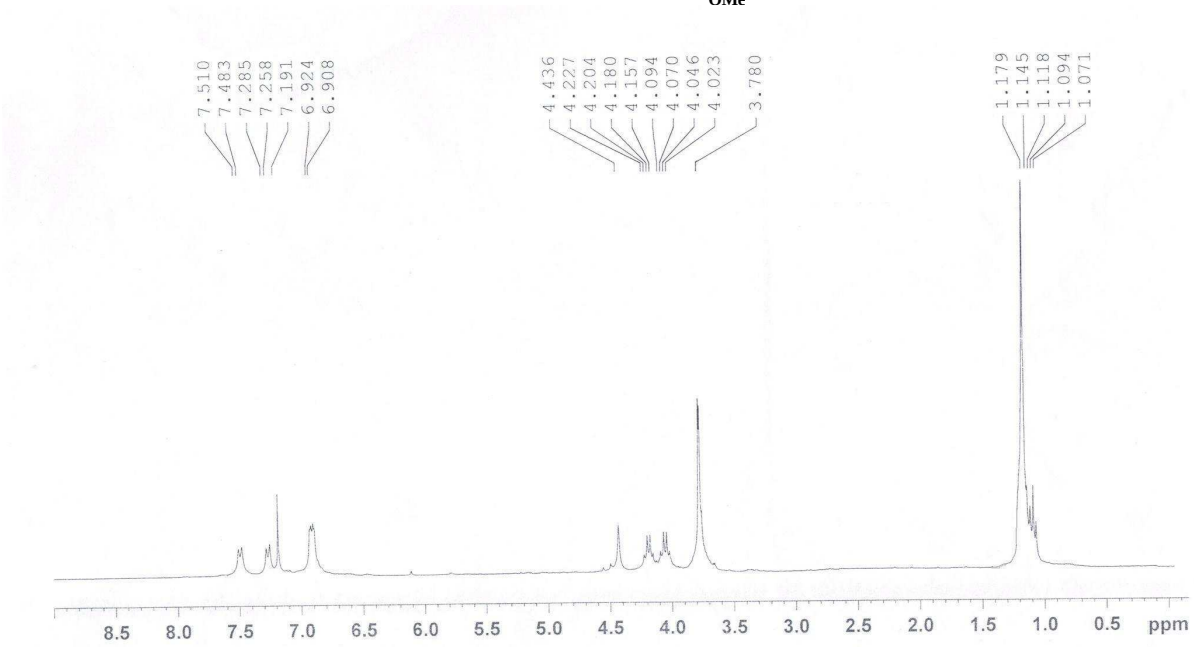


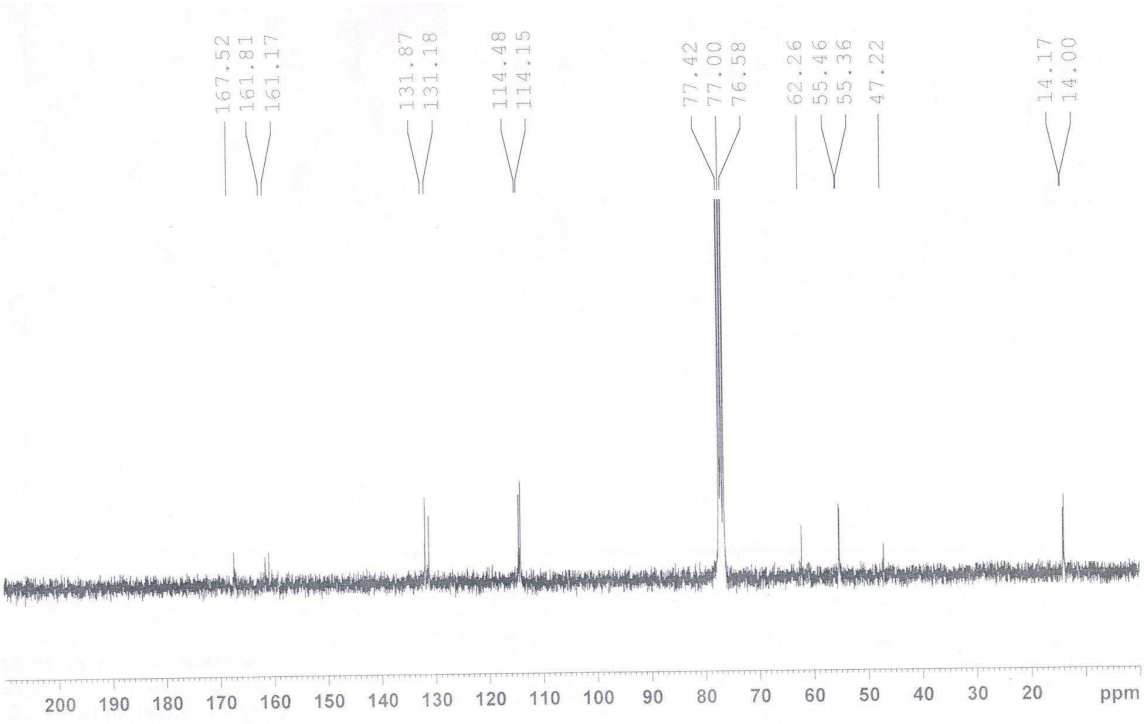




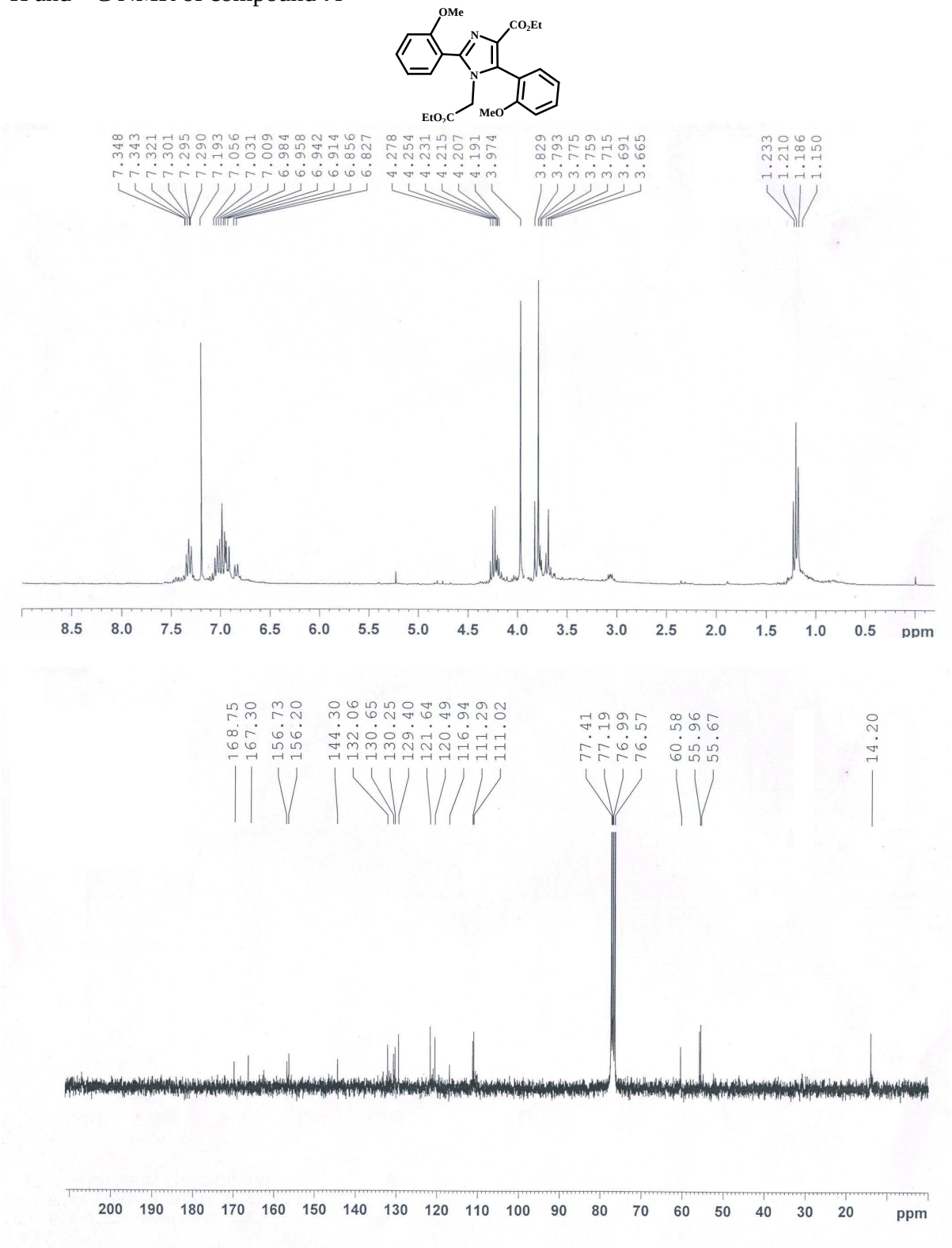
^{1}H and ^{13}C NMR of compound **7h**



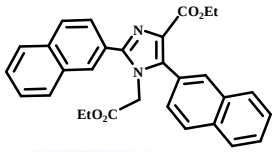


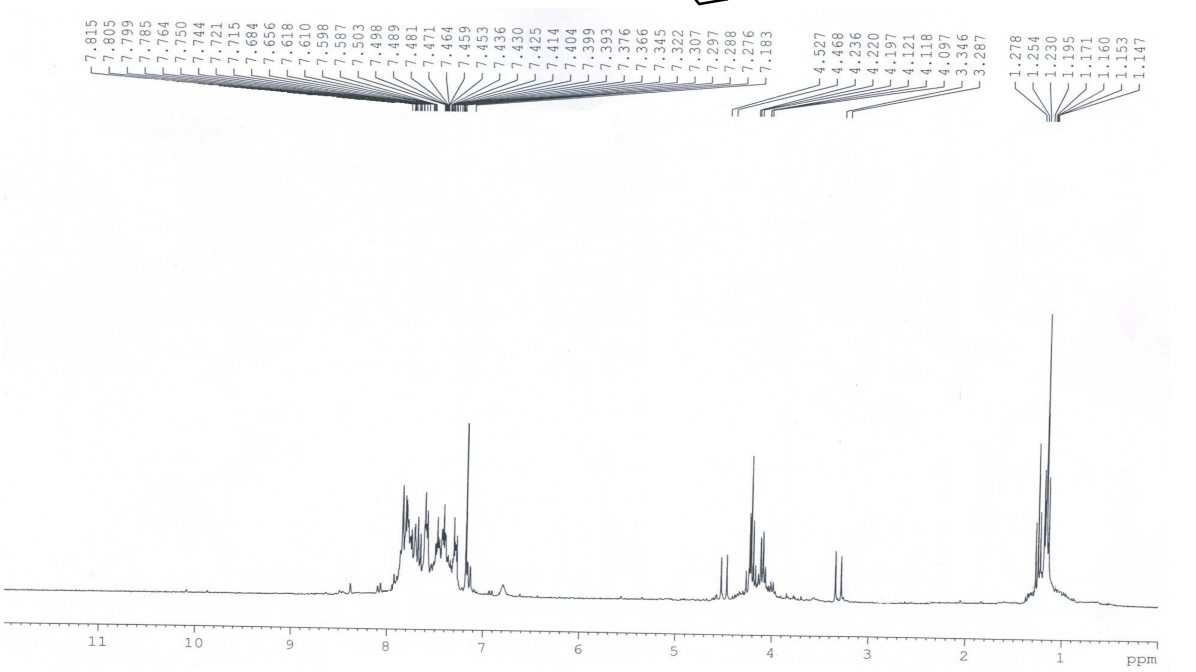


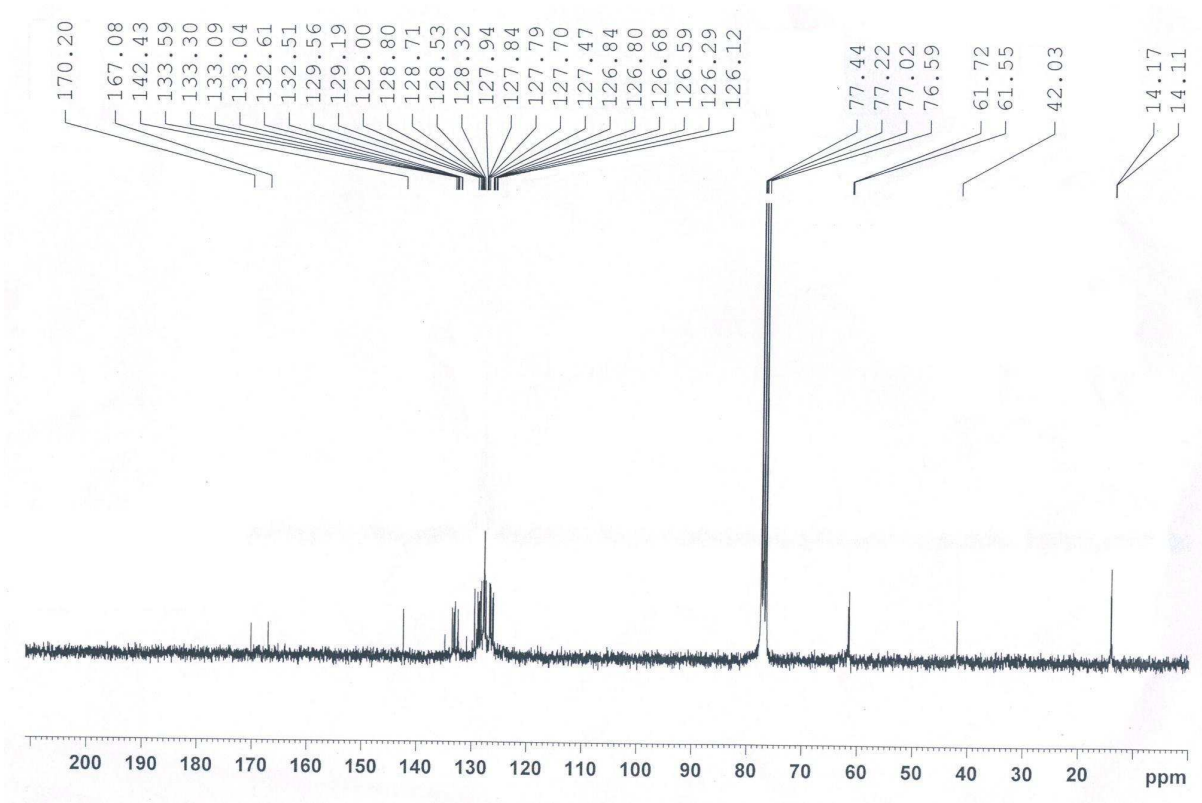
^{1}H and ^{13}C NMR of compound **7i**



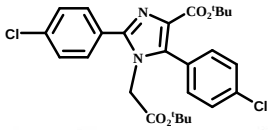
^{1}H and ^{13}C NMR of compound **7j**

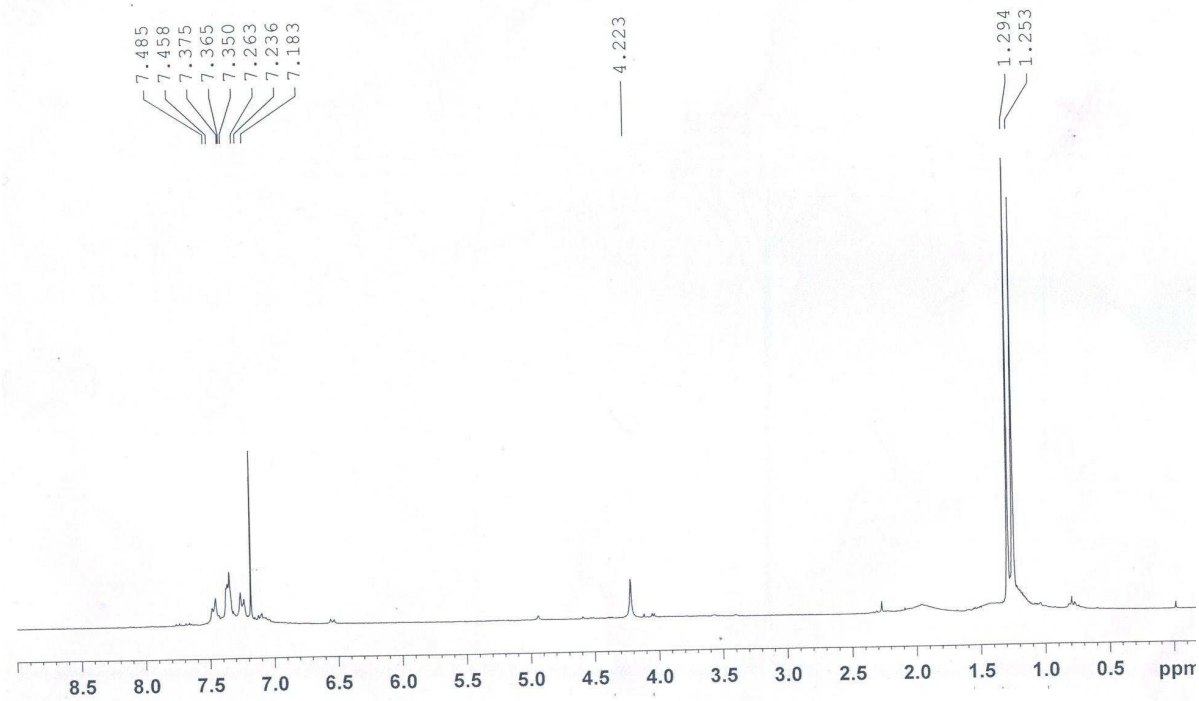


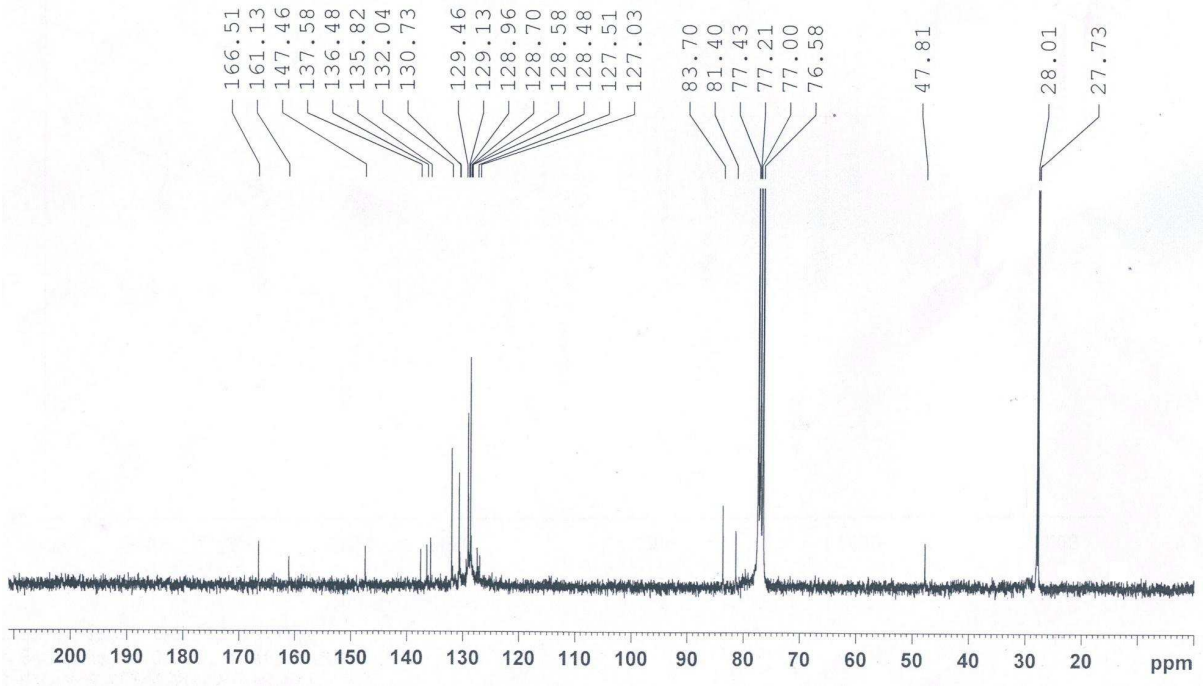




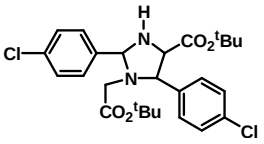
^{1}H and ^{13}C NMR of compound **7k**

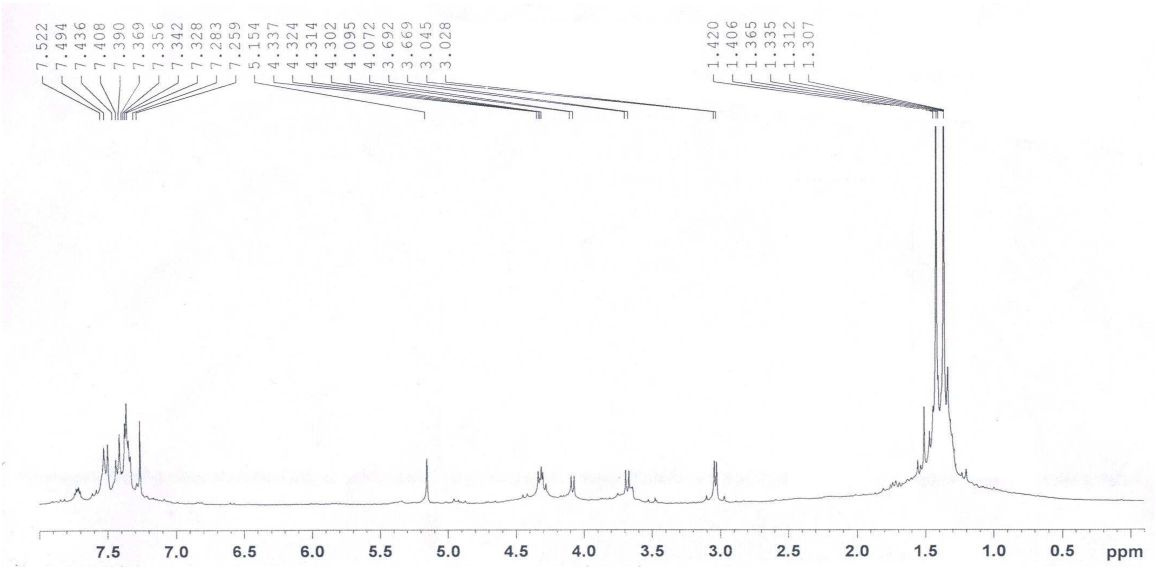


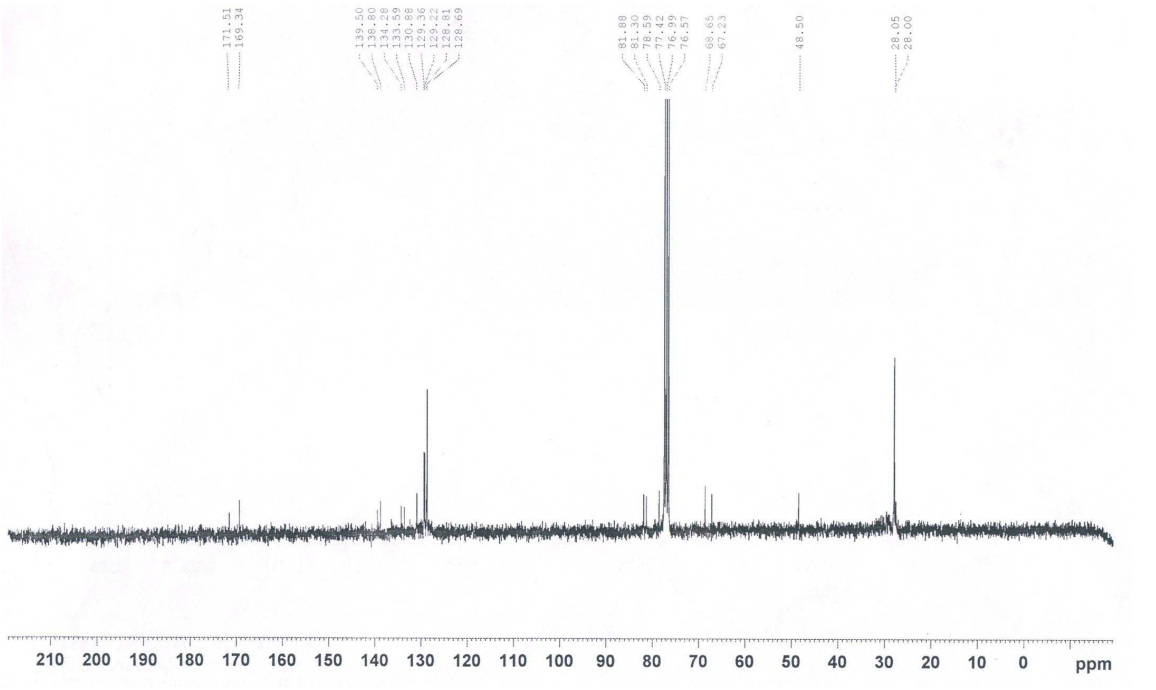




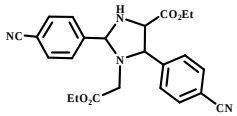
^{1}H and ^{13}C NMR of compound **4a**

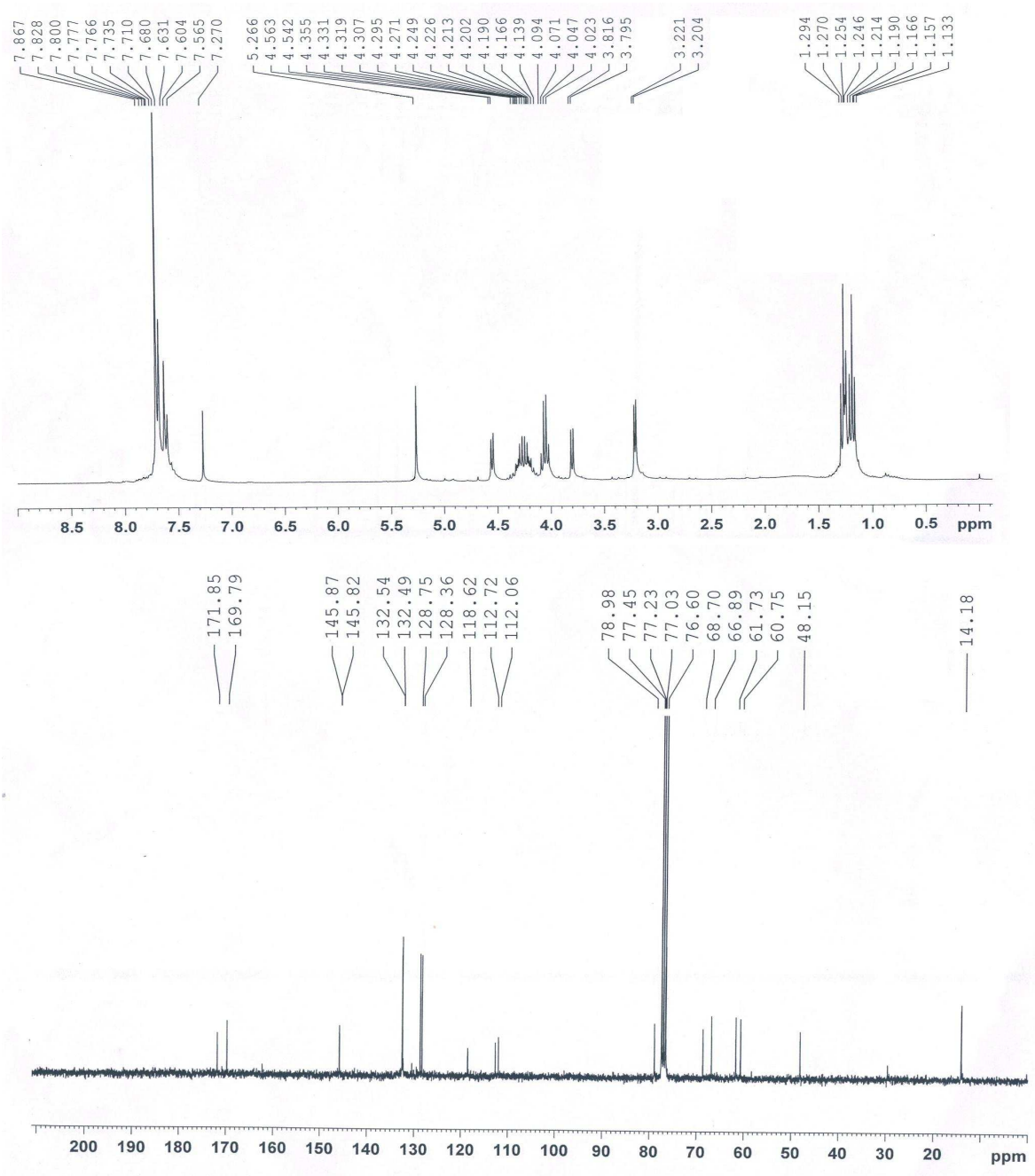




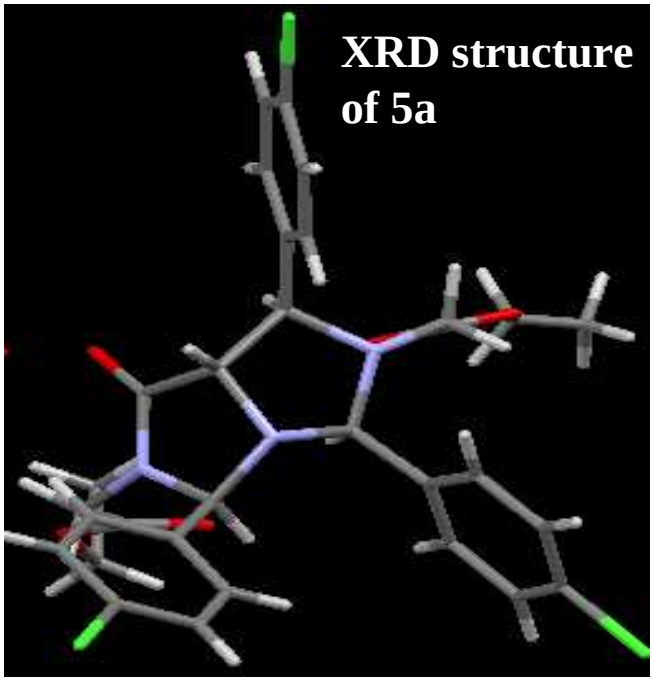


^{1}H and ^{13}C NMR of compound **4b**





9. **Single crystal structure of 1,3,5-tris-(4-chlorophenyl)-6-ethoxycarbonylmethyl-7-oxo-tetrahydroimidazo[1,5-*c*]imidazol-2-yl]-acetic acid ethyl ester (5a) and summary of data of CCDC 865937**



. Chemical formula and formula weight (M):	C31H30Cl3N3O5 and 630.93
. Crystal system:	monoclinic
. Unit-cell dimensions (angstrom or pm, degrees) and volume, with esds:	a 65.4100 b 11.6990 c 25.1520, 90.00, 95.619(5), 90.00, 19154(11)
. Temperature:	296(2)
. Space group symbol:	C2/c
. No. of formula units in unit cell (Z):	24
. Number of reflections measured and/or number of independent reflections, Rint:	6450
. Final R values (and whether quoted for all or observed data):	0.0469