Supporting Information

Title: Copper(II)-Catalyzed Carbon-Carbon Triple Bond Cleavage of Internal Alkynes for the Synthesis of Polysubstituted Indolizines Using Air as the Terminal Oxidant

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Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were measured at 400 MHz with $CDCl_3$ as solvent. The chemical shifts (δ) are reported in parts per million relative to the residual deuterated solvent signal, and coupling constants (J) are given in Hertz. ^{13}C NMR spectra were measured at 100 MHz with $CDCl_3$ as solvent. HRMS (ESI) data were obtained in the electron impact (EI) (70 eV) mode.

General Procedure for the preparation of 3

Pyridine **1a** (2.0 mmol), butynedioates **2** (1.5 mmol), and hydrated copper(II) chloride (0.1 mmol) were mixed in 15 mL acetonitrile and refluxed for 12 h under 1 atm of oxygen. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Chromatographic separation of the reaction mixture (ethyl acetate/petroleum ether, 1:6) after removal of the solvent gave product **3**.

Trimethyl indolizine-1,2,3-tricarboxylate (3a)

White solid. Mp 141–143 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (s, 6H), 4.01 (s, 3H), 7.04 (t, J = 6.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 9.49 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 163.3, 160.4, 137.8, 130.6, 127.9, 126.8, 119.9, 115.4, 111.8, 103.0, 52.9, 52.0, 51.6. HMRS (ESI) *m/z* $[M+Na]^+$ calcd for $C_{14}H_{13}NO_6Na$: 314.0641; found: 314.0645.

Triethyl indolizine-1,2,3-tricarboxylate (3b)

White solid. Mp 105–106 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36–1.45 (m, 9H), 4.35–4.48 (m, 6H), 7.01–7.05 (m, 1H), 7.34–7.38 (m, 1H), 8.35 (dd, J = 8.8, 0.8 Hz, 1H), 9.53 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.0, 160.2, 138.0, 130.6, 127.9, 126.6, 119.9, 115.3, 111.9, 103.1, 61.8, 60.8, 60.3, 14.3, 14.2, 14.1. HMRS *m/z* $[M+Na]^+$ calcd for $C_{17}H_{19}NO_6Na$: 356.1110; found: 356.1117.

Tripropyl indolizine-1,2,3-tricarboxylate (3c)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97–1.02 (m, 9H), 1.73–1.80 (m, 6H), 4.23–4.32 (m, 6H), 6.98–7.02 (m, 1H), 7.31–7.35 (m, 1H), 8.33 (d, J = 8.8 Hz, 1H), 9.52 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 163.0, 160.3, 138.0, 130.5, 127.9, 126.6, 119.9, 115.3, 111.9, 103.2, 67.5, 66.5, 66.0, 22.2, 22.1, 21.8, 10.6, 10.5, 10.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{25}NO_6Na$: 398.1580; found: 398.1580.

Triisopropyl indolizine-1,2,3-tricarboxylate (3d)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (d, J = 6.4 Hz, 12H), 1.46 (d, J = 6.4 Hz, 6H), 5.28–5.32 (m, 3H), 7.01 (t, J = 7.2 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 8.34 (d, J = 9.2 Hz, 1H), 9.56 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 162.6, 160.0, 137.8, 130.7, 128.0, 126.4, 120.0, 115.1, 112.1, 103.5, 69.7, 68.7, 67.8, 22.1, 22.0, 21.9. HMRS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{25}NO_6Na$: 398.1580; found: 398.1580.

Tributyl indolizine-1,2,3-tricarboxylate (3e)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96–1.00 (m, 9H), 1.43 – 1.50 (m, 6H), 1.71–1.79 (m, 6H), 4.30–4.38 (m, 6H), 7.03 (t, J = 7.2 Hz, 1H), 7.36 (td, J = 8.0, 1.2 Hz, 1H), 8.36 (d, J = 9.2 Hz, 1H), 9.55 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.1, 160.3, 138.0, 130.4, 127.9, 126.6, 119.9, 115.3, 111.8, 103.1, 66.0, 64.8, 64.3, 30.9, 30.8, 30.5, 19.3, 19.2, 19.1, 13.8, 13.7. HMRS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{31}NO_6Na$: 440.2049; found: 440.2044.

Tri-*tert*-butyl indolizine-1,2,3-tricarboxylate (3f)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (s, 9H), 1.63 (s, 9H), 1.65 (s, 9H), 6.91 (td, J = 6.8, 1.2 Hz, 1H), 7.22–7.26 (m, 1H), 8.15 (dt, J = 9.2, 1.2 Hz, 1H), 9.43 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 162.1, 160.0, 136.5, 131.6, 127.9, 125.4, 119.9, 114.4, 113.3, 105.4, 82.7, 82.4, 80.8, 28.6, 28.5, 28.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{31}NO_6Na$: 440.2049; found: 440.2045.

Substitued pyridine **1b**–**1g** (2.0 mmol), butynedioates **2** (1.5 mmol), and copper(II) chloride (0.1 mmol) were mixed in 15 mL acetonitrile and refluxed for 12 h under 1 atm of O_2. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Chromatographic separation of the reaction mixture (ethyl acetate/petroleum ether, 1:6) after removal of the solvent gave product **4**.

Tetramethyl indolizine-1,2,3,7-tetracarboxylate (4a)

Yellow solid. Mp 184–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 3.95 (s, 3H), 3.99 (s, 3H), 4.01 (s, 3H), 7.59 (dd, J = 7.6, 1.6 Hz, 1H), 8.99 (s, 1H), 9.53 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.6, 162.5, 159.8, 135.8, 130.8, 127.2, 127.1, 121.9, 114.0, 113.0, 105.7, 52.7, 52.4, 51.9, 51.6. HMRS *m/z* $[M+Na]^+$ calcd for $C_{16}H_{15}NO_8Na$: 372.0695; found: 372.0695.

1,2,3-Triethyl 7-methylindolizine-1,2,3,7-tetracarboxylate (4b)

Yellow solid. Mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36–1.44 (m, 9H), 3.97 (s, 3H), 4.38–4.46 (m, 6H), 7.56 (dd, J = 7.6, 2.0 Hz, 1H), 9.03 (s, 1H), 9.54 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.1, 162.4, 159.9, 136.3, 131.1, 127.4, 127.3, 122.3, 114.2, 113.4, 106.1, 61.9, 61.2, 60.7, 52.7, 14.2, 14.1, 14.0. HMRS *m/z* $[M+Na]^+$ calcd for $C_{19}H_{21}NO_8Na$: 414.1165; found: 414.1165.

1,2,3-Tripropyl 7-methylindolizine-1,2,3,7-tetracarboxylate (4c)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98–1.05 (m, 9H), 1.72–1.81 (m, 6H), 3.95 (s, 3H), 4.26–4.33 (m, 6H), 7.54 (dd, J = 7.2, 2.0 Hz, 1H), 9.02 (dd, J = 2.0, 0.8 Hz, 1H), 9.53 (dd, J = 7.2, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 165.1, 162.6, 160.0, 136.4, 131.1, 127.5, 127.3, 122.4, 114.2, 113.4, 106.2, 67.7, 66.9, 66.4, 52.7, 22.1, 22.0, 21.8, 10.6, 10.5, 10.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{22}H_{27}NO_8Na$: 456.1634; found: 456.1639.

1,2,3-trimethyl 7-ethylindolizine-1,2,3,7-tetracarboxylate (4d)

Yellow solid. Mp 147–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.45 (t, J = 7.2 Hz, 3H), 3.94 (s, 3H), 3.95 (s, 3H), 4.02 (s, 3H), 4.45 (q, J = 7.2 Hz, 2H), 7.61 (dd, J = 7.2, 1.6 Hz, 1H), 9.00 (s, 1H), 9.54 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.6, 163.0, 160.2, 136.3, 131.2, 128.0, 127.5, 122.2, 114.5, 113.3, 106.0, 62.0, 53.1, 52.4, 52.1, 14.3. HMRS *m/z* $[M+Na]^+$ calcd for $C_{17}H_{17}NO_8Na$: 386.0852; found: 386.0853.

Tetraethyl indolizine-1,2,3,7-tetracarboxylate (4e)

Yellow solid. Mp 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37–1.46 (m, 12H), 4.38–4.47 (m, 8H), 7.59 (dd, J = 7.2, 1.6 Hz, 1H), 9.04 (s, 1H), 9.55 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.7, 162.5, 159.9, 136.4, 131.2, 127.8, 127.5, 122.2, 114.3, 113.4, 106.1, 62.0, 61.9, 61.3, 60.8, 14.4, 14.3, 14.2, 14.1. HMRS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{23}NO_8Na$: 428.1321; found: 428.1321.

1,2,3-Tripropyl 7-ethylindolizine-1,2,3,7-tetracarboxylate (4f)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01–1.09 (m, 9H), 1.44 (t, J = 7.2 Hz, 3H), 1.75–1.85 (m, 6H), 4.29–4.36 (m, 6H), 4.44 (q, J = 7.2 Hz, 2H), 7.59 (dd, J = 7.2, 1.6 Hz, 1H), 9.05 (s, 1H), 9.57 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.6, 162.6, 160.1, 136.4, 131.2, 127.7, 127.5, 122.2, 114.3, 113.4, 106.2, 67.7, 66.9, 66.4, 61.8, 22.1, 22.0, 21.8, 14.3, 10.7, 10.5, 10.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{29}NO_8Na$: 470.1791; found: 470.1792.

1,2,3-Triisopropyl 7-ethylindolizine-1,2,3,7-tetracarboxylate (4g)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38–1.47 (m, 21H), 4.43 (q, J = 7.2 Hz, 2H), 5.28–5.36 (m, 3H), 7.56 (dd, J = 7.6, 2.0 Hz, 1H), 9.04 (s, 1H), 9.57 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.6, 162.1, 159.7, 136.2, 131.3, 127.5, 122.4, 114.0, 113.7, 106.6, 69.9, 69.3, 68.4, 61.8, 22.1, 22.0, 21.9, 14.2. HMRS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{29}NO_8Na$: 470.1791; found: 470.1794.

Trimethyl 7-cyanoindolizine-1,2,3-tricarboxylate (4h)

White solid. Mp 187–189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.94 (s, 3H), 3.95 (s, 3H), 4.01 (s, 3H), 7.14 (d, J = 7.2 Hz, 1H), 8.74 (s, 1H), 9.60 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 162.7, 160.2, 135.2, 131.6, 128.7, 126.4, 117.3, 115.4, 114.4, 109.7, 106.6, 53.4, 52.9, 52.5. HMRS *m/z* $[M+Na]^+$ calcd for $C_{15}H_{12}N_2O_6Na$: 339.0593; found: 339.0595.

Triethyl 7-cyanoindolizine-1,2,3-tricarboxylate (4i)

White solid. Mp 131–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38–1.45 (m, 9H), 4.38–4.49 (m, 6H), 7.12 (dd, J = 7.2, 2.0 Hz, 1H), 8.75 (s, 1H), 9.60 (dd, J = 7.2, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.1, 159.7, 135.0, 131.3, 128.3, 126.1, 117.1, 115.0, 114.2, 109.1, 106.5, 62.2, 61.6, 61.1, 14.1, 14.0. HMRS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{18}N_2O_6Na$: 381.1063; found: 381.1055.

Trimethyl 7-phenylindolizine-1,2,3-tricarboxylate (4j)

Yellow solid. Mp 181–183 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 6H), 4.01 (s, 3H), 7.33 (d, J = 7.2 Hz, 1H), 7.43–7.52 (m, 3H), 7.72 (d, J = 7.6 Hz, 2H), 8.56 (s, 1H), 9.53 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 162.4, 159.4, 138.6, 137.2, 136.7, 130.0, 128.1, 127.9, 126.9, 126.0, 115.6, 114.0, 110.6, 102.3, 51.9, 51.0, 50.7. HMRS *m/z* $[M+Na]^+$ calcd for $C_{20}H_{17}NO_6Na$: 390.0954; found: 390.0958.

Triethyl 7-phenylindolizine-1,2,3-tricarboxylate (4k)

Yellow solid. Mp 113–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29–1.38 (m, 9H), 4.28–4.41 (m, 6H), 7.24 (dd, J = 7.6, 2.0 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.2 Hz, 2H), 7.64 (dd, J = 8.4, 1.6 Hz, 2H), 8.53 (d, J = 1.2 Hz, 1H), 9.47 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.0, 159.2, 138.2, 137.4, 136.7, 129.9, 128.1, 127.9, 126.9, 125.9, 115.5, 113.7, 110.6, 102.3, 60.8, 59.8, 59.3, 13.3, 13.2, 13.1. HMRS *m/z* $[M+Na]^+$ calcd for $C_{23}H_{23}NO_6Na$: 432.1423; found: 432.1424.

Trimethyl 7-*tert*-butylindolizine-1,2,3-tricarboxylate (4l)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (s, 9H), 3.90 (s, 3H), 3.91 (s, 3H), 4.00 (s, 3H), 7.12 (dd, J = 7.2, 2.0 Hz, 1H), 8.28 (d, J = 1.6 Hz, 1H), 9.41 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 163.6, 160.5, 151.3, 138.4, 130.7, 127.4, 114.8, 114.6, 111.1, 102.2, 52.8, 51.9, 51.6, 35.1, 30.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{21}NO_6Na$: 370.1267; found: 370.1271.

Triethyl 7-*tert*-butylindolizine-1,2,3-tricarboxylate (4m)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34–1.40 (m, 18H), 4.33 (q, J = 7.2 Hz, 4H), 4.41 (q, J = 7.2 Hz, 2H), 7.06 (dd, J = 7.6, 2.0 Hz, 1H), 8.28 (dd, J = 2.0, 0.8 Hz, 1H), 9.39 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.2, 160.2, 151.0, 138.5, 130.7, 127.3, 114.6, 111.2, 102.3, 61.7, 60.7, 60.1, 35.1, 30.3, 14.3, 14.2, 14.1. HMRS *m/z* $[M+Na]^+$ calcd for $C_{21}H_{27}NO_6Na$: 412.1736; found: 412.1736.

Tripropyl 7-*tert*-butylindolizine-1,2,3-tricarboxylate (4n)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.00–1.05 (m, 9H), 1.38 (s, 9H), 1.76–1.82 (m, 6H), 4.26–4.33 (m, 6H), 7.10 (dd, J = 7.6, 2.0 Hz, 1H), 8.32 (dd, J = 2.0, 0.8 Hz, 1H), 9.45 (dd, J = 7.6, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.3, 160.4, 150.9, 138.5, 130.7, 127.4, 114.6, 114.5, 111.2, 102.4, 67.5, 66.4, 65.9, 35.1, 30.4, 22.2, 22.1, 21.8, 10.6, 10.5. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{33}NO_6Na$: 454.2206; found: 454.2205.

Triisopropyl 7-*tert*-butylindolizine-1,2,3-tricarboxylate (4o)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38–1.47 (m, 27H), 5.28–5.32 (m, 3H), 7.07 (dd, J = 7.6, 2.4 Hz, 1H), 8.32 (d, J = 1.2 Hz, 1H), 9.46 (dd, J = 7.6, 0.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 162.8, 160.0, 150.5, 138.3, 130.9, 127.4, 114.6, 114.3, 111.4, 102.8, 69.5, 68.5, 67.6, 35.0, 30.3, 22.1, 22.0, 21.9. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{33}NO_6Na$: 454.2206; found: 454.2206.

1,2,3-Triethyl 6-methylindolizine-1,2,3,6-tetracarboxylate (4p)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37–1.45 (m, 9H), 3.98 (s, 3H), 4.38–4.47 (m, 6H), 7.89 (dd, J = 9.6, 1.2 Hz, 1H), 8.37 (d, J = 9.2 Hz, 1H), 10.25 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.0, 162.6, 159.9, 138.4, 132.0, 131.6, 125.8, 119.4, 119.1, 112.9, 104.2, 62.0, 61.2, 60.6, 52.6, 14.3, 14.1, 14.0. HMRS *m/z* $[M+Na]^+$ calcd for $C_{19}H_{21}NO_8Na$: 414.1165, found: 414.1159.

1,2,3-Triethyl 8-methylindolizine-1,2,3,8-tetracarboxylate (4q)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34–1.42 (m, 9H), 3.91 (s, 3H), 4.31 (q, J = 7.2 Hz, 2H), 4.40 (q, J = 7.2 Hz, 4H), 7.07 (d, J = 7.2 Hz, 1H), 7.59 (dd, J = 7.2, 0.8 Hz, 1H), 7.68 (dd, J = 7.2, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 165.3, 162.6, 160.1, 139.3, 133.2, 130.8, 129.9, 127.7, 125.7, 114.1, 105.6, 61.8, 61.1, 60.8, 52.5, 14.2, 14.1. HMRS *m/z* $[M+Na]^+$ calcd for $C_{19}H_{21}NO_8Na$: 414.1165, found:414.1157.

Isoquinoline **5a** or quinoline **5b** (2.0 mmol), butynedioates **2** (1.5 mmol), and copper(II) chloride (0.1 mmol) were mixed in 15 mL acetonitrile and refluxed for 12 h under 1 atm of O_2. After completion of the reaction, the reaction mixture was allowed to cool to room temperature. Chromatographic separation of the reaction mixture (ethyl acetate/petroleum ether, 1:6) after removal of the solvent gave product **6** or **7**.

Trimethyl pyrrolo[2,1-*a*]isoquinoline-1,2,3-tricarboxylate (6a)

White solid. Mp 154–155 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.93 (s, 3H), 3.94 (s, 3H), 3.98 (s, 3H), 7.24 (d, J = 7.6 Hz, 1H), 7.63–7.65 (m, 2H), 7.73–7.75 (m, 1H), 9.34 (d, J = 7.2 Hz, 1H), 9.44–9.46 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 164.2, 160.3, 134.6, 130.2, 129.7, 129.2, 128.0, 127.2, 126.9, 124.3, 123.8, 116.0, 113.3, 107.7, 52.7, 52.2. HMRS *m/z* $[M+Na]^+$ calcd for $C_{18}H_{15}NO_6Na$: 364.0797; found: 364.0797.

Triethyl pyrrolo[2,1-*a*]isoquinoline-1,2,3-tricarboxylate (6b)

White solid. Mp 90–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38–1.45 (m, 9H), 4.38–4.46 (m, 6H), 7.23 (d, J = 7.6 Hz, 1H), 7.62–7.65 (m, 2H), 7.72–7.75 (m, 1H), 9.38 (d, J = 7.6 Hz, 1H), 9.37–9.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.9, 160.1, 134.5, 130.2, 129.7, 129.1, 127.9, 127.3, 126.9, 124.4, 123.9, 115.8, 113.4, 107.9, 61.6, 61.1, 14.2, 14.1, 14.0. HMRS *m/z* $[M+Na]^+$ calcd for $C_{21}H_{21}NO_6Na$: 406.1267; found: 406.1272.

Tripropyl pyrrolo[2,1-*a*]isoquinoline-1,2,3-tricarboxylate (6c)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, J = 7.6 Hz, 9H), 1.78–1.82 (m, 6H), 4.29–4.34 (m, 6H), 7.20 (d, J = 7.6 Hz, 1H), 7.60–7.63 (m, 2H), 7.69–7.71 (m, 1H), 9.36 (dd, J = 7.6, 2.0 Hz, 1H), 9.41–9.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.2, 160.3, 134.5, 130.2, 129.8, 129.2, 127.9, 127.3, 126.9, 124.5, 124.0, 115.8, 113.5, 108.1, 67.5, 66.9, 66.8, 22.1, 21.9, 10.7, 10.6, 10.5. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{27}NO_6Na$: 448.1736; found: 448.1743.

Triisopropyl pyrrolo[2,1-*a*]isoquinoline-1,2,3-tricarboxylate (6d)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39–1.47 (m, 18H), 5.26–5.38 (m, 3H), 7.18 (d, J = 7.6 Hz, 1H), 7.58–7.61 (m, 2H), 7.70–7.73 (m, 1H), 9.19–9.21 (m, 1H), 9.35 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.0, 159.9, 133.7, 129.8, 129.7, 128.9, 127.6, 127.0, 126.9, 124.4, 124.1, 115.5, 113.8, 108.8, 69.7, 69.2, 69.1, 22.1, 21.9, 21.8. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{27}NO_6Na$: 448.1736; found: 448.1745.

Trimethyl pyrrolo[1,2-*a*]quinoline-1,2,3-tricarboxylate (7a)

Yellow solid. Mp 177–179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (s, 3H), 3.97 (s, 3H), 4.00 (s, 3H), 7.51 (t, J = 7.6 Hz, 1H), 7.49–7.65 (m, 2H), 7.80 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.25 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 163.2, 161.0, 137.7, 132.6, 130.8, 128.7, 128.5, 128.4, 125.7, 125.2, 119.3, 117.5, 117.4, 105.0, 52.7, 52.3, 51.6. HMRS *m/z* $[M+Na]^+$ calcd for

$C_{18}H_{15}NO_6Na$: 364.0797; found: 364.0784.

Triethyl pyrrolo[1,2-*a*]quinoline-1,2,3-tricarboxylate (7b)

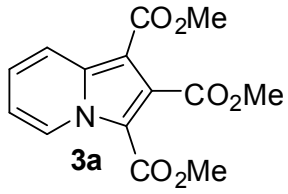
Yellow solid. Mp 113–115 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40–1.44 (m, 9H), 4.36–4.48 (m, 6H), 7.48 (td, J = 8.0, 1.2 Hz, 1H), 7.58 (t, J = 8.8 Hz, 2H), 7.76 (dd, J = 8.0, 1.2 Hz, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.26 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 163.0, 160.9, 137.9, 132.8, 131.0, 128.8, 128.5, 128.4, 125.7, 125.4, 119.7, 117.8, 117.7, 105.4, 61.8, 61.7, 60.5, 14.3, 14.1, 14.0. HMRS *m/z* $[M+Na]^+$ calcd for $C_{21}H_{21}NO_6Na$: 406.1267; found:406.1275.

Tripropyl pyrrolo[1,2-*a*]quinoline-1,2,3-tricarboxylate (7c)

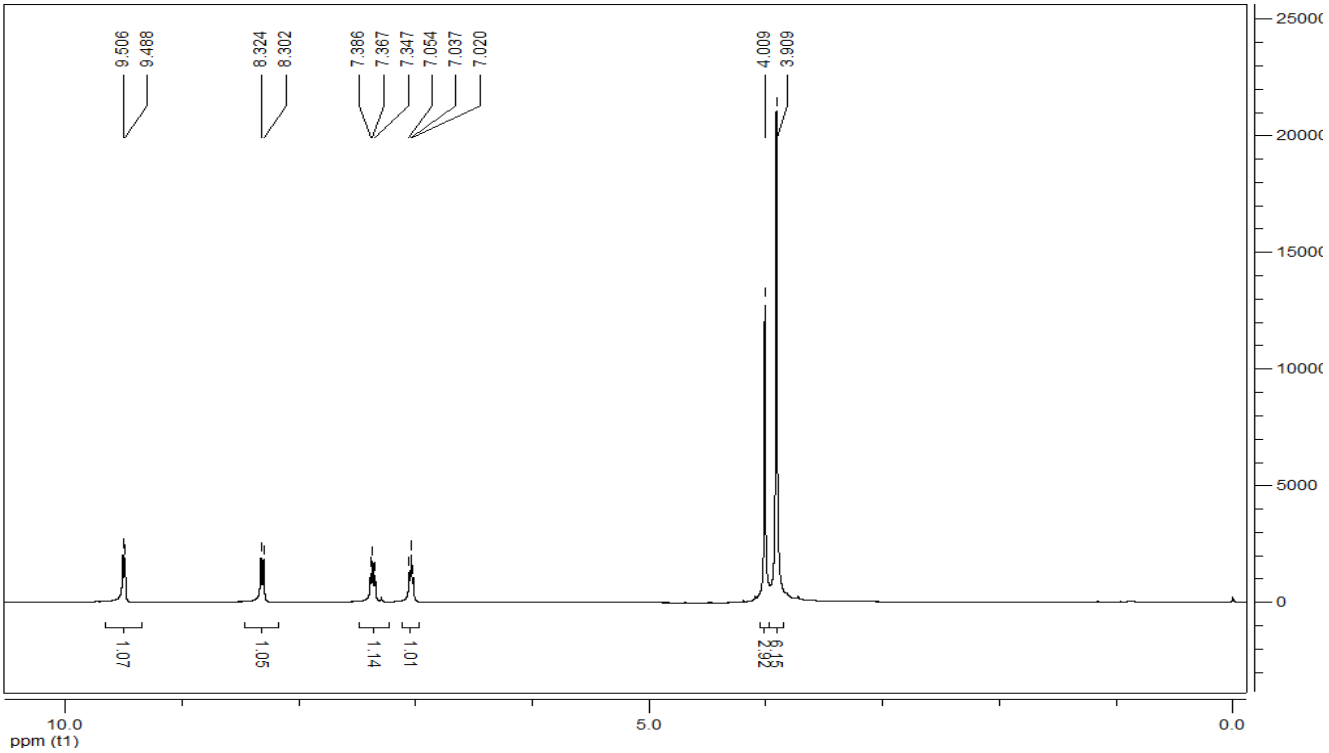
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01–1.06 (m, 9H), 1.78–1.83 (m, 6H), 4.29–4.36 (m, 6H), 7.48 (td, J = 7.6, 0.8 Hz, 1H), 7.56–7.61 (m, 2H), 7.77 (dd, J = 7.6, 1.2 Hz, 1H), 8.07 (d, J = 8.8 Hz, 1H), 8.27 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 163.1, 161.1. 137.9, 132.9, 130.8, 128.8, 128.5, 128.3, 125.7, 125.4, 119.7, 117.9, 117.7, 105.4, 67.6, 67.4, 66.2, 22.2, 22.0, 21.9, 10.6, 10.5, 10.4. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{27}NO_6Na$: 448.1736; found: 448.1738.

Triisopropyl pyrrolo[1,2-*a*]quinoline-1,2,3-tricarboxylate (7d)

Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38–1.41 (m, 12H), 1.47 (d, J = 6.0 Hz, 6H), 5.29–5.37 (m, 3H), 7.47 (t, J = 7.2 Hz, 1H), 7.55 (t, J = 8.0 Hz, 2H), 7.76 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 8.24 (d, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.6, 160.6, 137.3, 132.9, 130.7, 128.7, 128.2, 127.9, 125.6, 125.3, 119.8, 118.3, 117.9, 105.8, 69.9, 69.7, 68.1, 22.1, 22.0, 21.7. HMRS *m/z* $[M+Na]^+$ calcd for $C_{24}H_{27}NO_6Na$: 448.1736; found: 448.1744.


CO2Me
CO2Me
N
CO2Me

3a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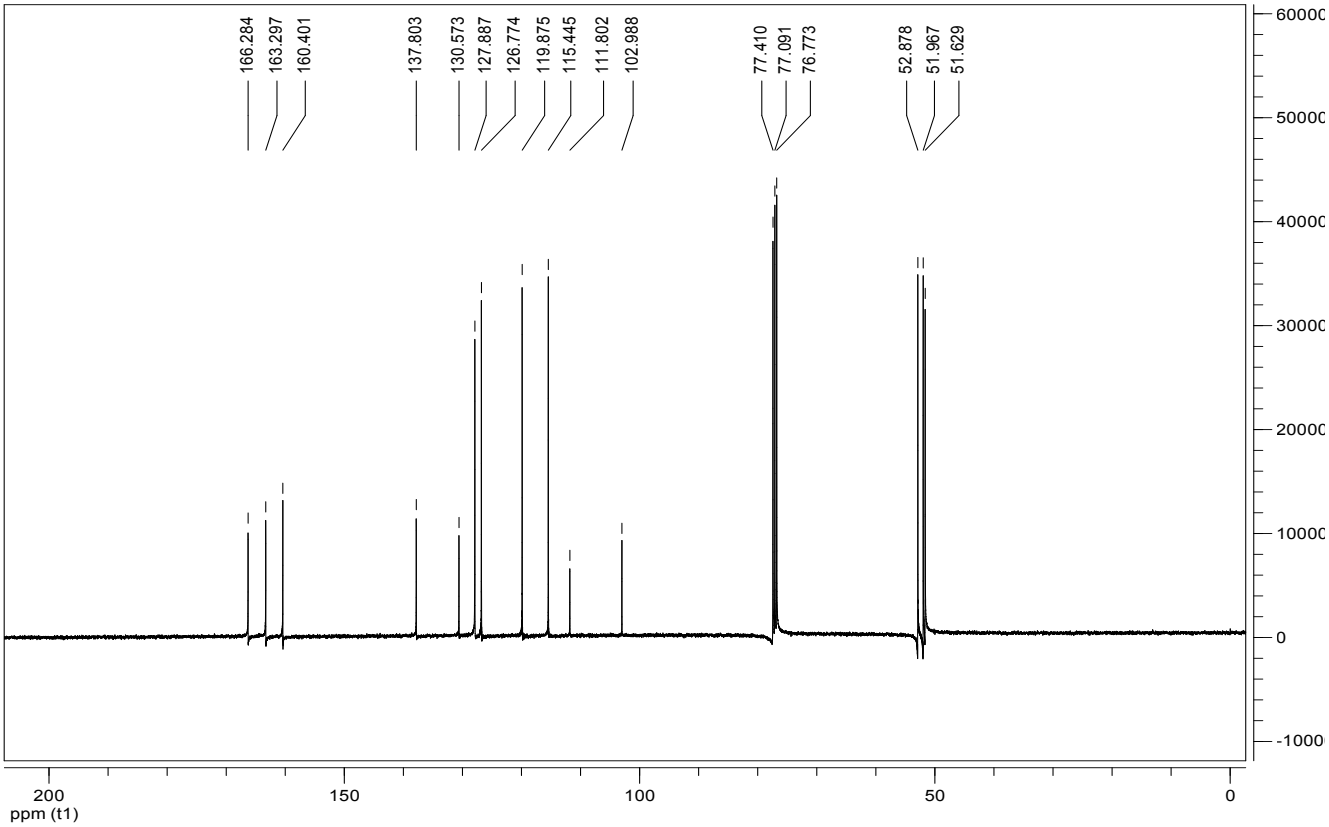
7.367
7.347
7.054
7.037
7.020
4.009
3.909
1.07
1.06
1.14
1.01
2.92
3.15
10.0
ppm (t1)
5.0
0.0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163.297
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130.573
127.887
126.774
119.875
115.445
111.802
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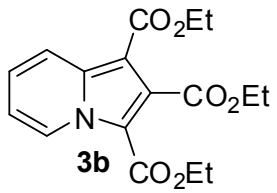
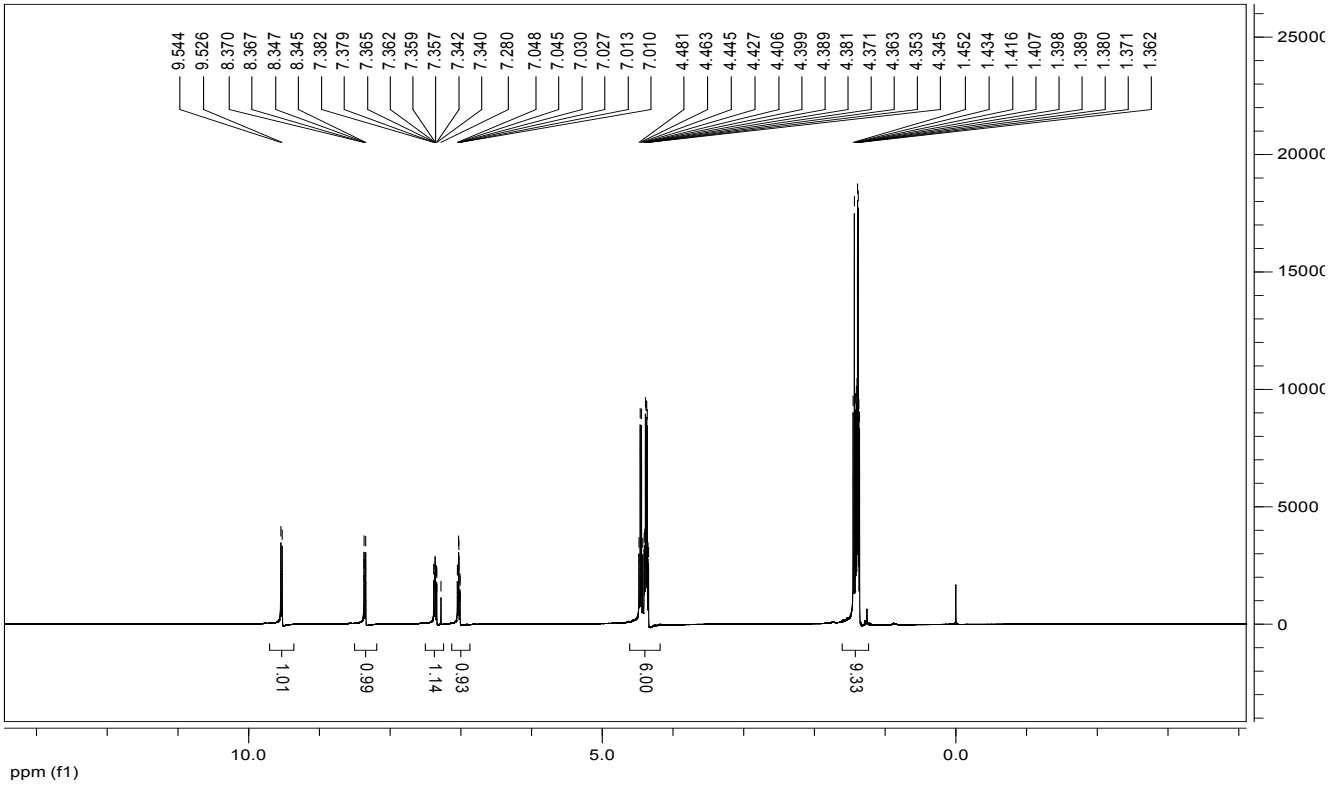
77.091
76.773
52.878
51.967
51.629
200
ppm (t1)
150
100
50
0


CO2Et
CO2Et
N
CO2Et

3b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8.345
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7.379
7.365
7.362
7.359
7.357
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7.340
7.280
7.048
7.045
7.030
7.027
7.013
7.010
4.481
4.463
4.445
4.427
4.406
4.399
4.389
4.381
4.371
4.363
4.353
4.345
1.452
1.434
1.416
1.407
1.398
1.389
1.380
1.371
1.362
1.01
0.99
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0.93
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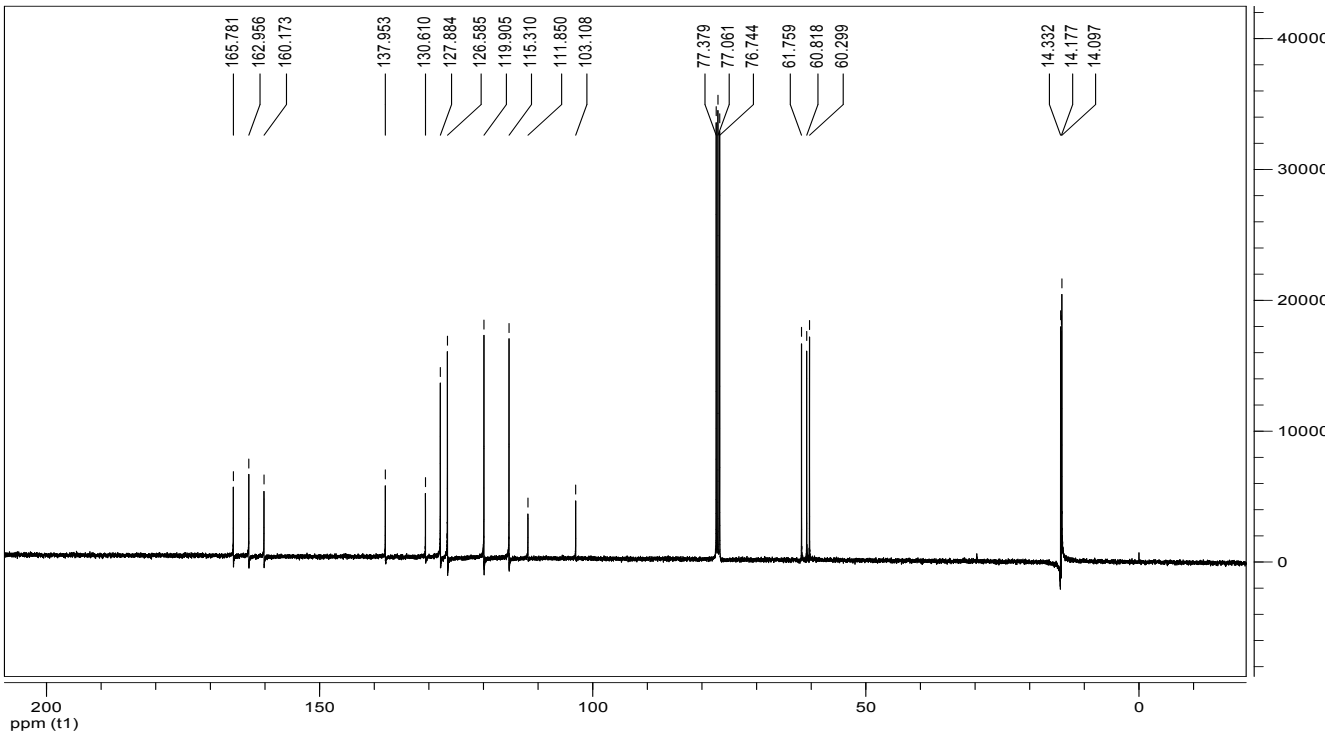
9.33
10.0
5.0
0.0
ppm (f1)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119.905
115.310
111.850
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77.379
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76.744
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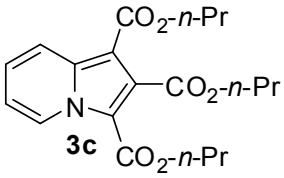
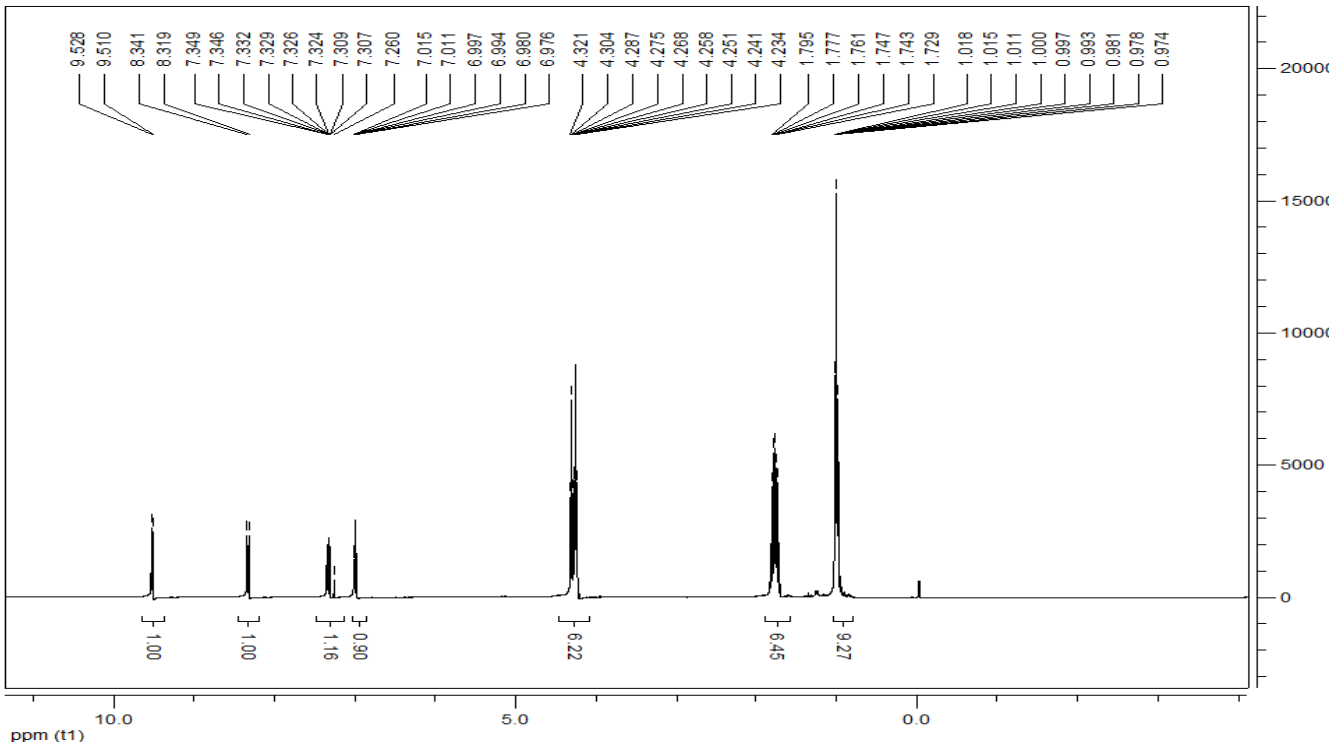
60.818
60.299
14.332
14.177
14.097
200
150
100
50
0
ppm (t1)


CO2-n-Pr
CO2-n-Pr
N
CO2-n-Pr

3c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7.346
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7.329
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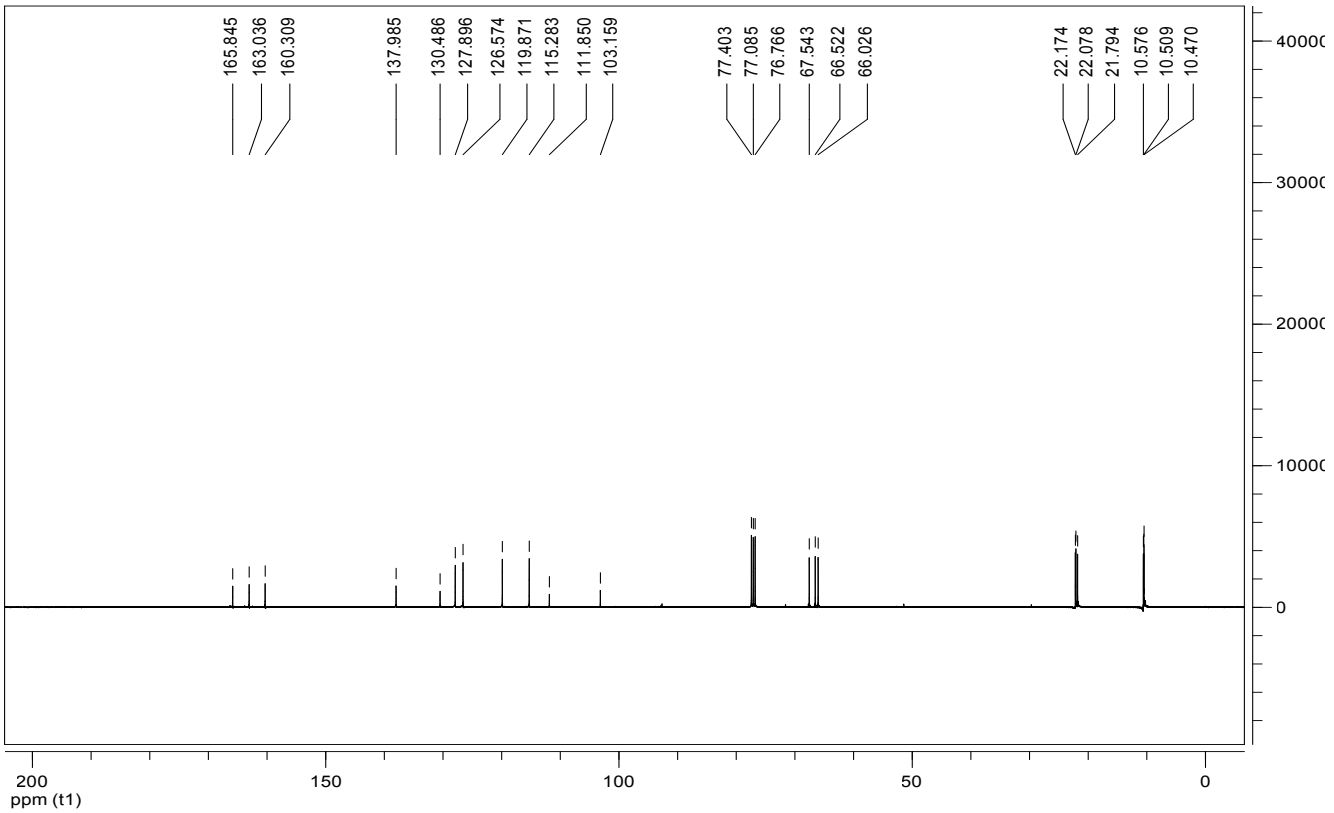
7.324
7.309
7.307
7.260
7.015
7.011
6.997
6.994
6.980
6.976
4.321
4.304
4.287
4.275
4.268
4.258
4.251
4.241
4.234
1.795
1.777
1.761
1.747
1.743
1.729
1.018
1.015
1.011
1.000
0.997
0.993
0.981
0.978
0.974
1.00
1.00
1.16
0.90
6.22
6.45
9.27
10.0
5.0
0.0
ppm (t1)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126.574
119.871
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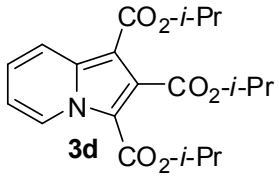
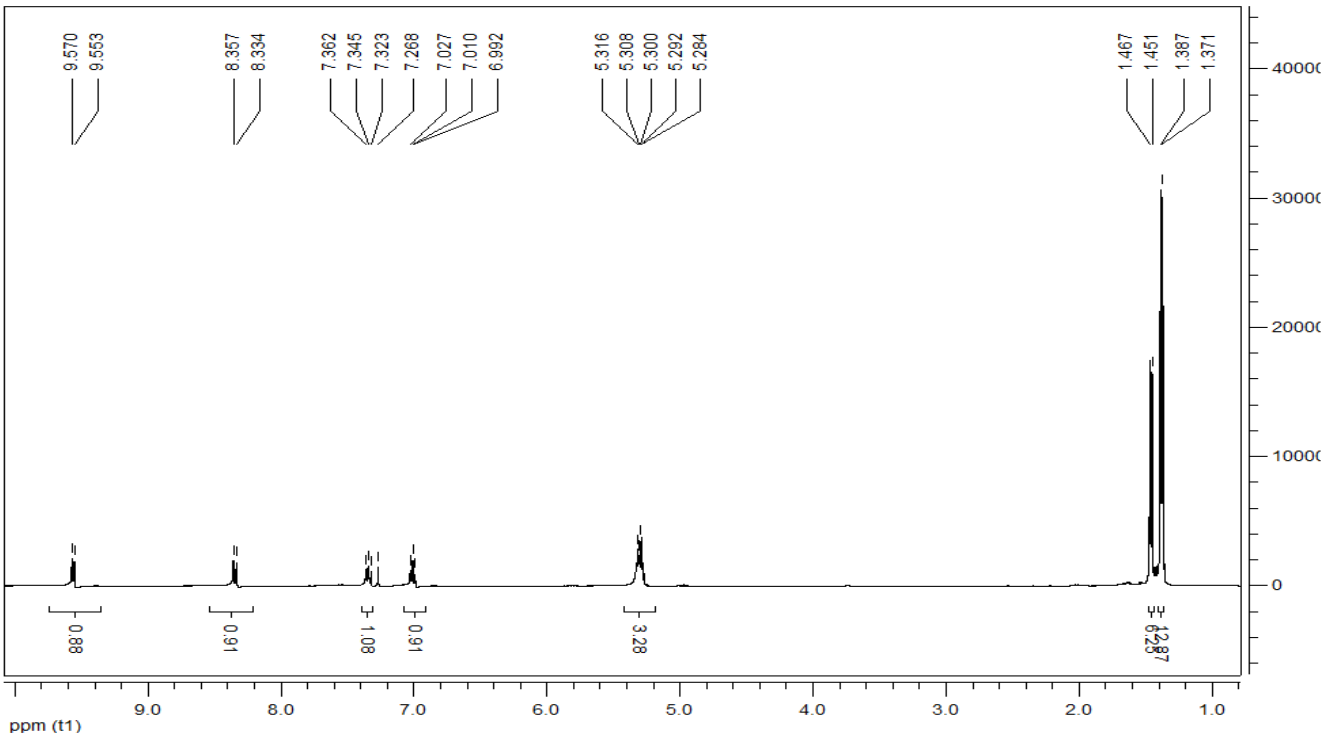
77.403
77.085
76.766
67.543
66.522
66.026
22.174
22.078
21.794
10.576
10.509
10.470
200
150
100
50
0
ppm (t1)


CO2-i-Pr
CO2-i-Pr
N
CO2-i-Pr

3d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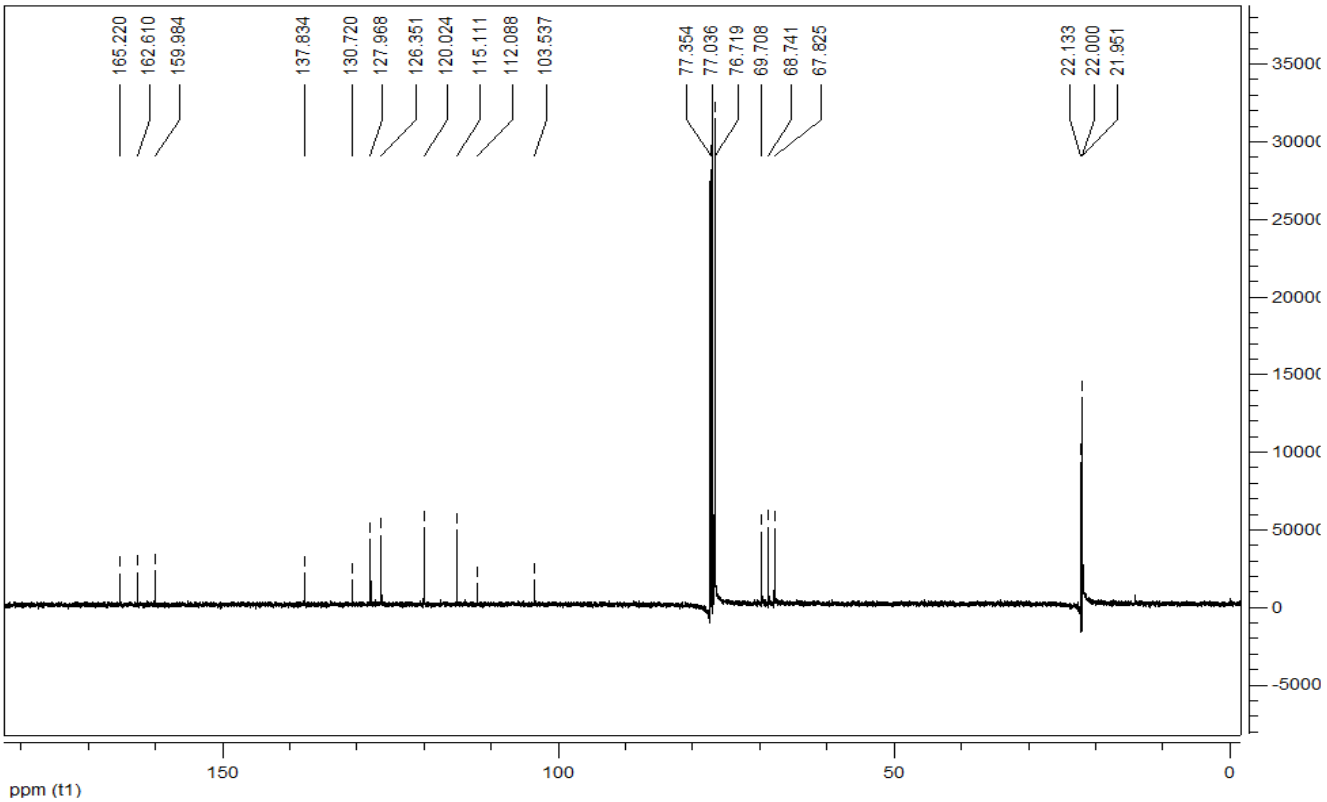
7.345
7.323
7.268
7.027
7.010
6.992
5.316
5.308
5.300
5.292
5.284
1.467
1.451
1.387
1.371
0.88
0.91
1.08
0.91
3.28
6.29
7.87
ppm (t1)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112.088
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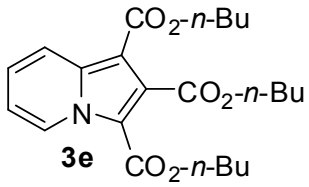
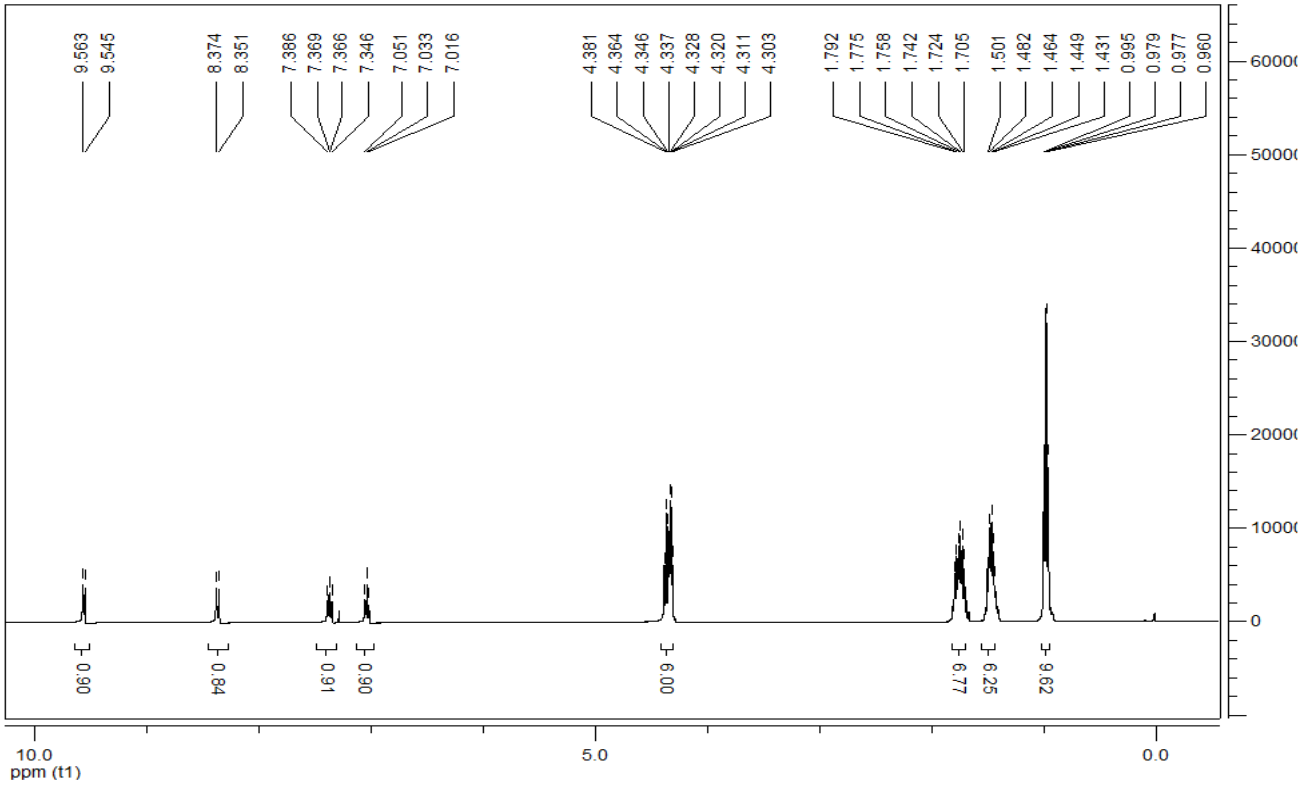
77.036
76.719
69.708
68.741
67.825
22.133
22.000
21.951
ppm (t1)


CO2-n-Bu
CO2-n-Bu
N
CO2-n-Bu

3e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7.369
7.366
7.346
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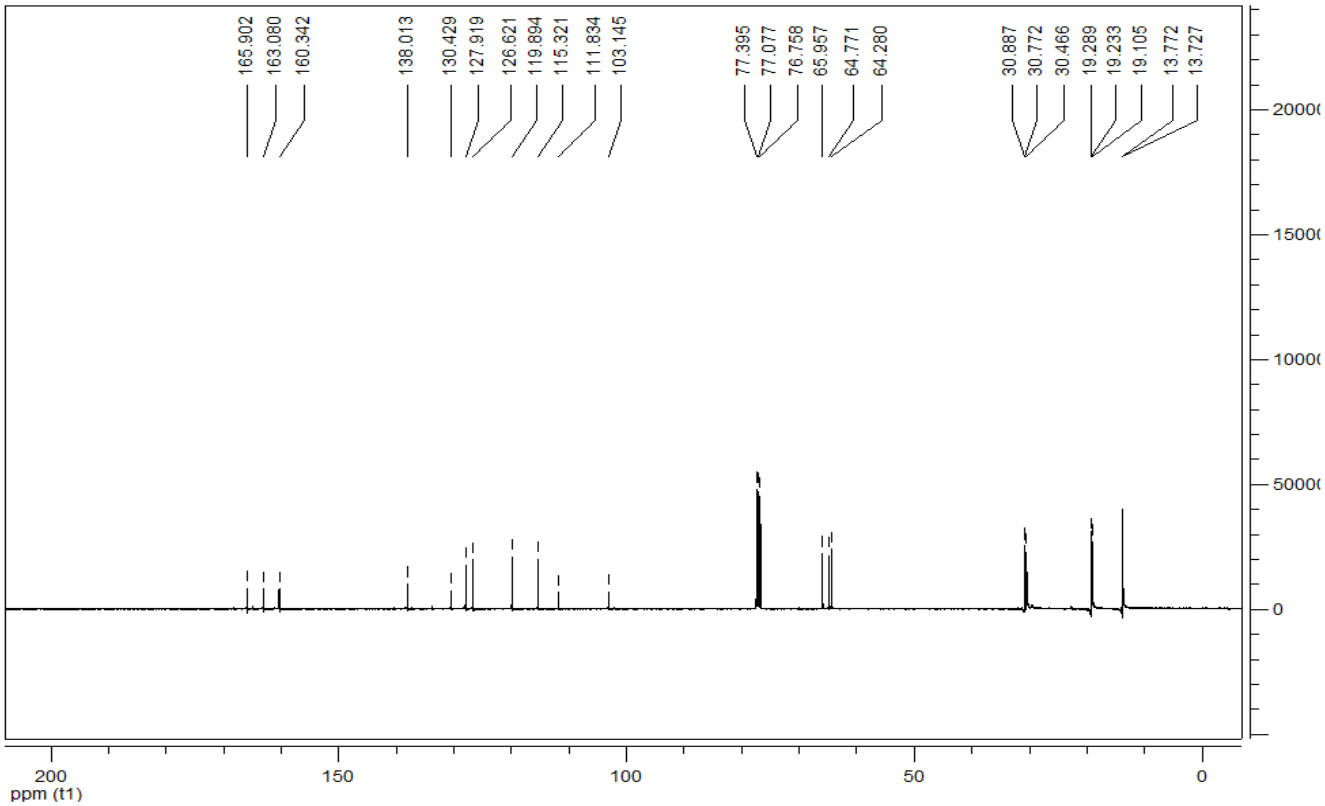
7.033
7.016
4.381
4.364
4.346
4.337
4.328
4.320
4.311
4.303
1.792
1.775
1.758
1.742
1.724
1.705
1.501
1.482
1.464
1.449
1.431
0.995
0.979
0.977
0.960
0.90
0.84
0.91
0.90
6.00
6.77
6.25
9.62
10.0
5.0
0.0
ppm (t1)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119.894
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103.145
77.395
77.077
76.758
65.957
64.771
64.280
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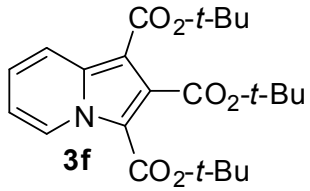
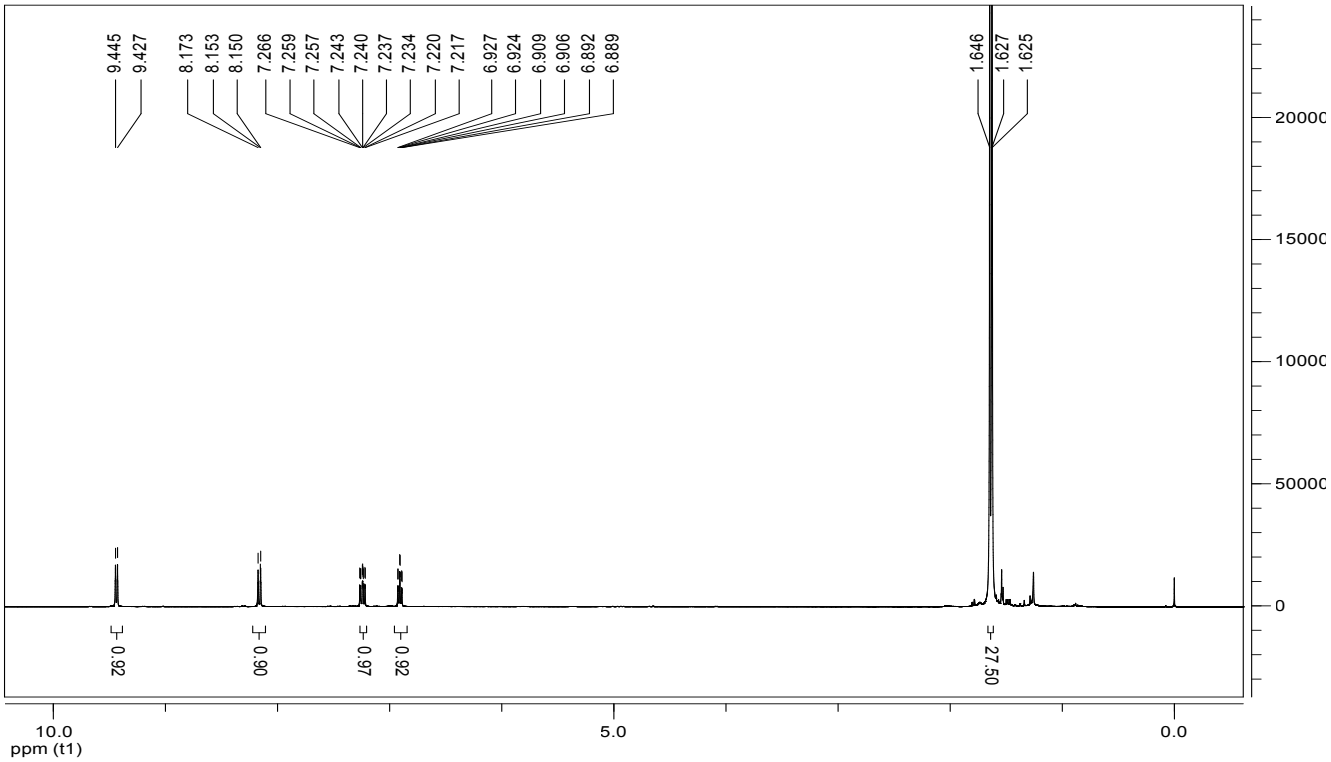
30.772
30.466
19.289
19.233
19.105
13.772
13.727
200
150
100
50
0
ppm (t1)


CO2-t-Bu
CO2-t-Bu
N
CO2-t-Bu

3f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7.257
7.243
7.240
7.237
7.234
7.220
7.217
6.927
6.924
6.909
6.906
6.892
6.889
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1.627
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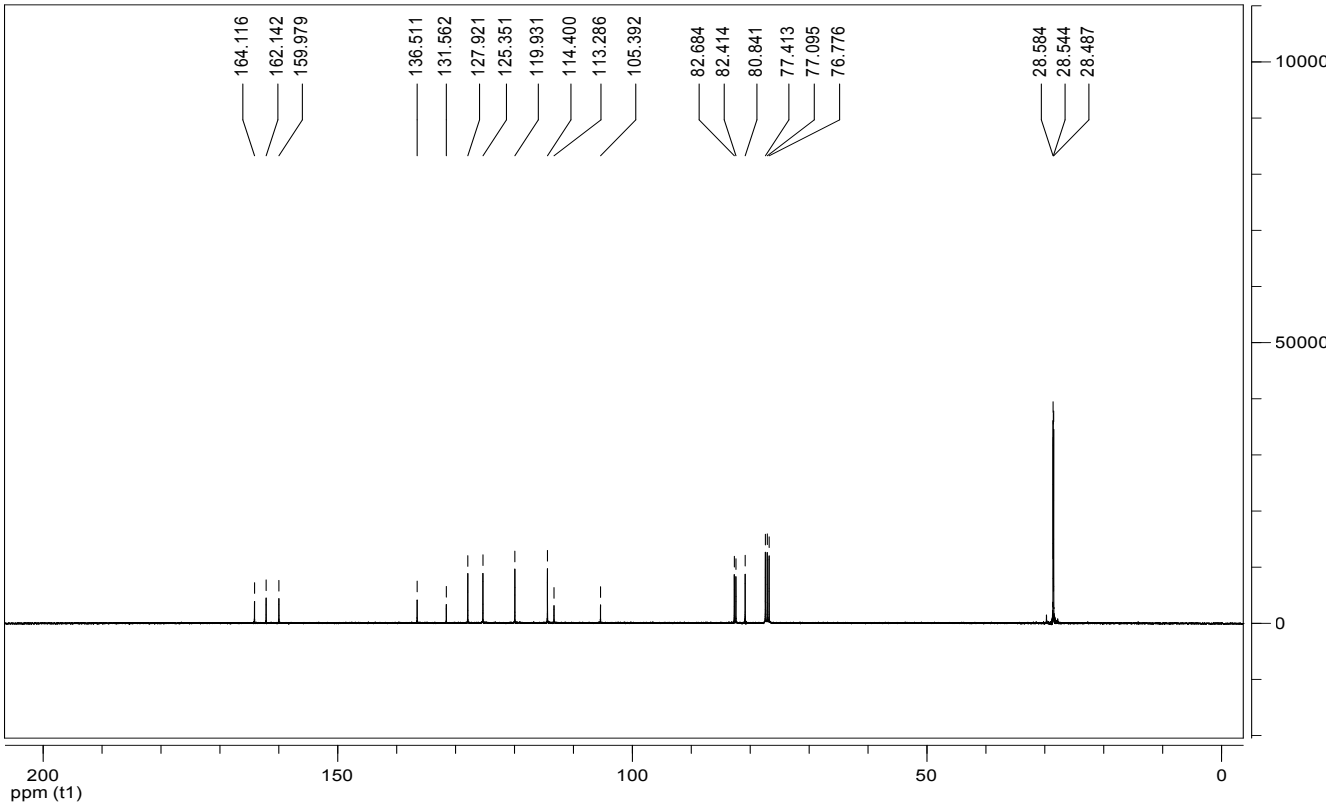
0.92
0.90
0.97
0.92
27.50
10.0
5.0
0.0
ppm (t1)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125.351
119.931
114.400
113.286
105.392
82.684
82.414
80.841
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77.095
76.776
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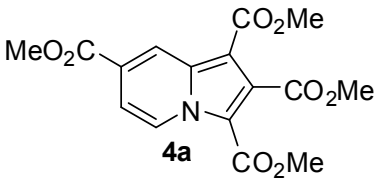
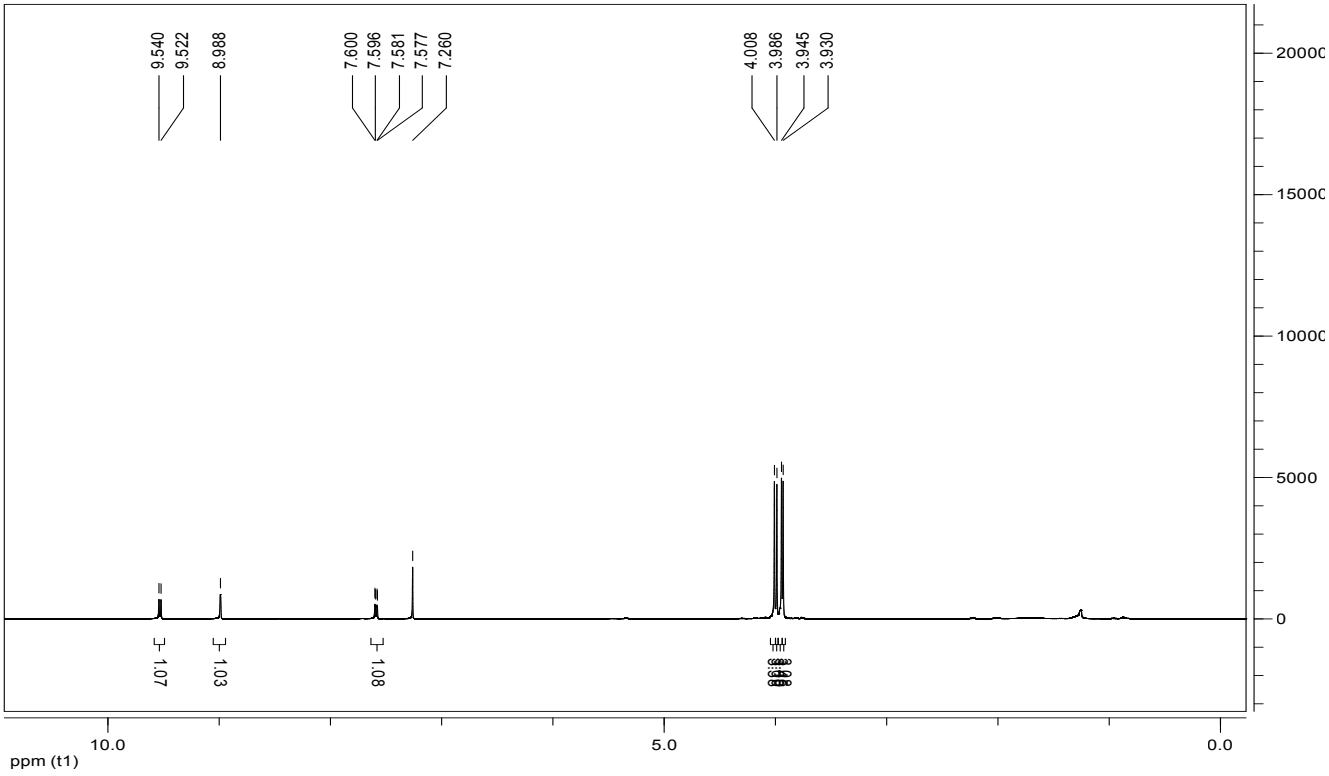
28.487
200
150
100
50
0
ppm (t1)


CO2Me
MeO2C
CO2Me
N
CO2Me

4a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7.577
7.260
4.008
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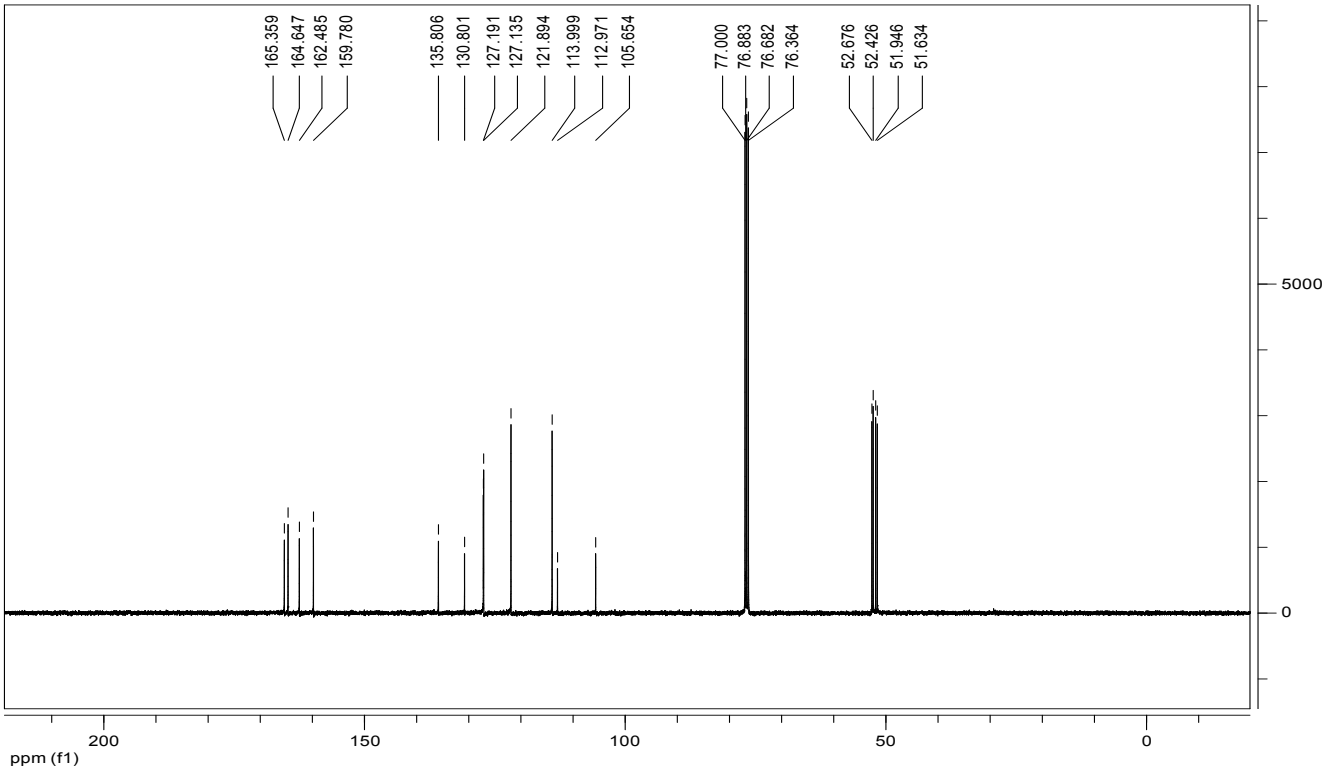
3.930
1.07
1.03
1.08
10.0
5.0
0.0
ppm (t1)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130.801
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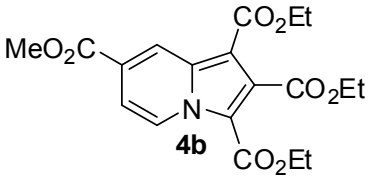
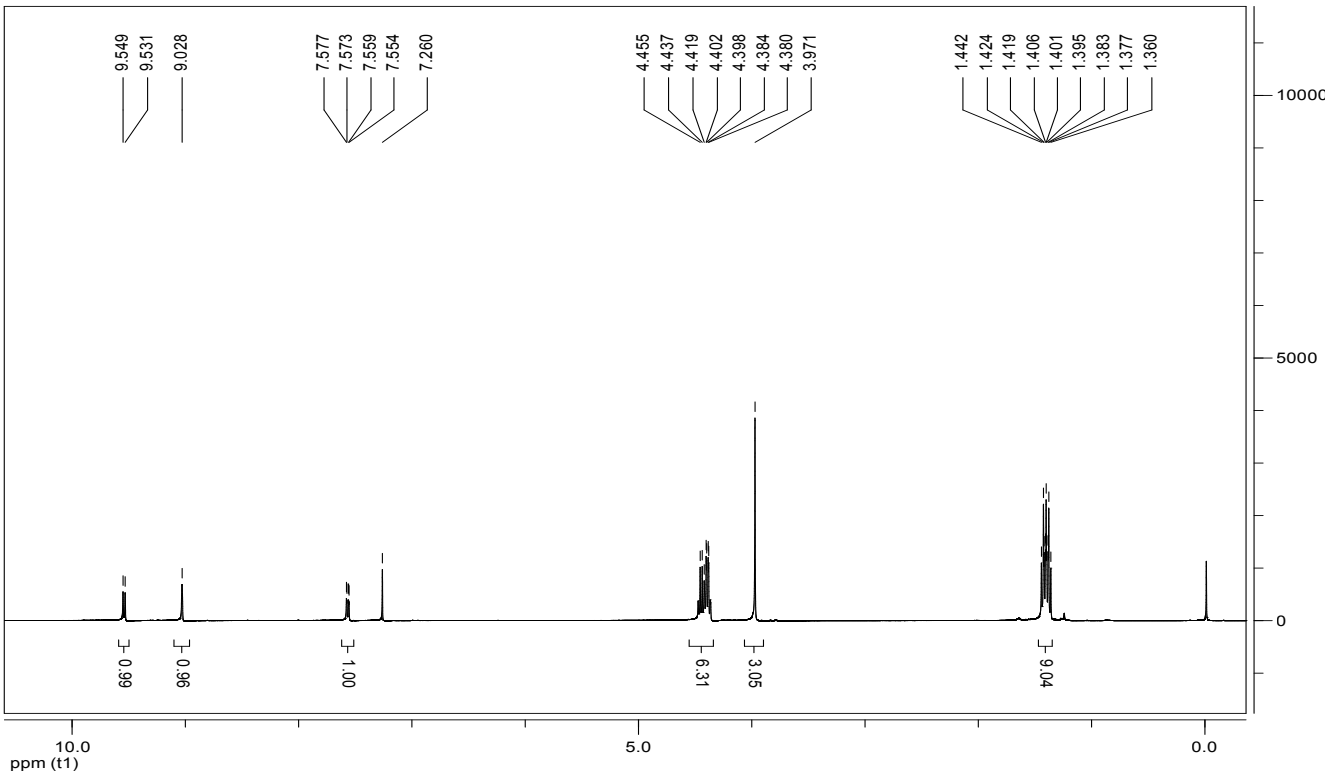
127.135
121.894
113.999
112.971
105.654
77.000
76.883
76.682
76.364
52.676
52.426
51.946
51.634
200
150
100
50
0
ppm (f1)


CO2Et
MeO2C
CO2Et
N
4b
CO2Et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7.260
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4.398
4.384
4.380
3.971
1.442
1.424
1.419
1.406
1.401
1.395
1.383
1.377
1.360
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0.96
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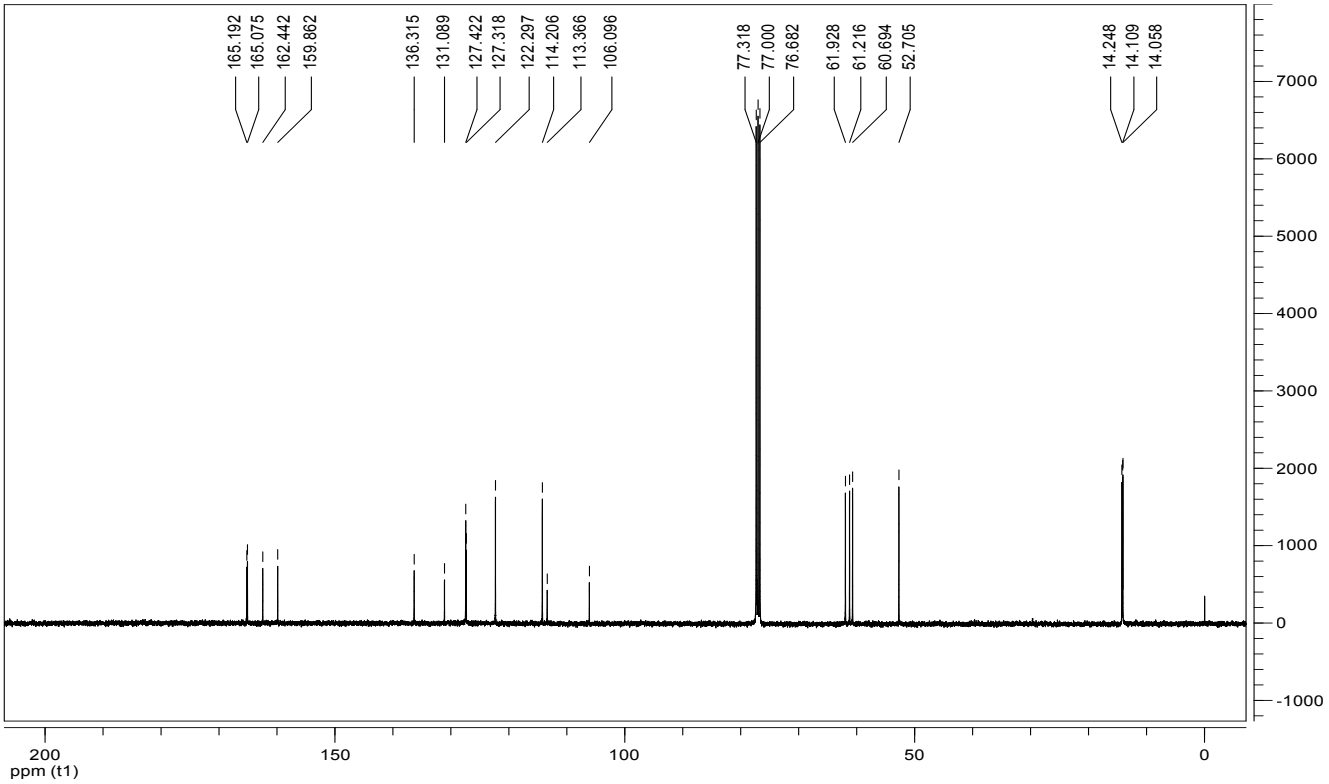
6.31
3.05
9.04
10000
5000
0
10.0
5.0
0.0
ppm (t1)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114.206
113.366
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77.000
76.682
61.928
61.216
60.694
52.705
14.248
14.109
14.058
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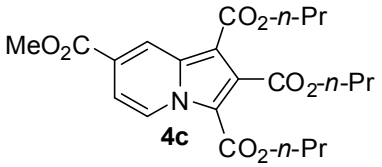
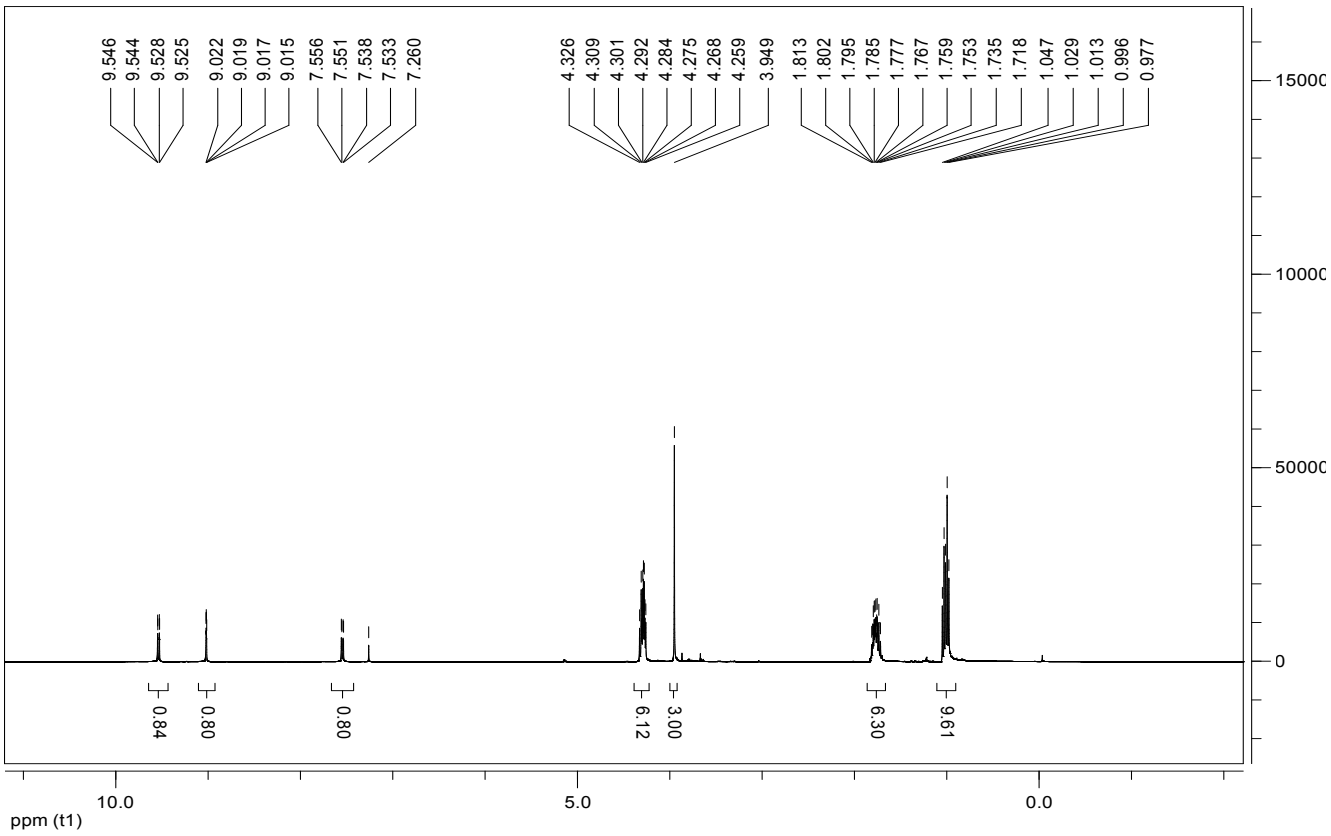
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)


CO2-n-Pr
MeO2C
CO2-n-Pr
N
4c
CO2-n-Pr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4.284
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4.259
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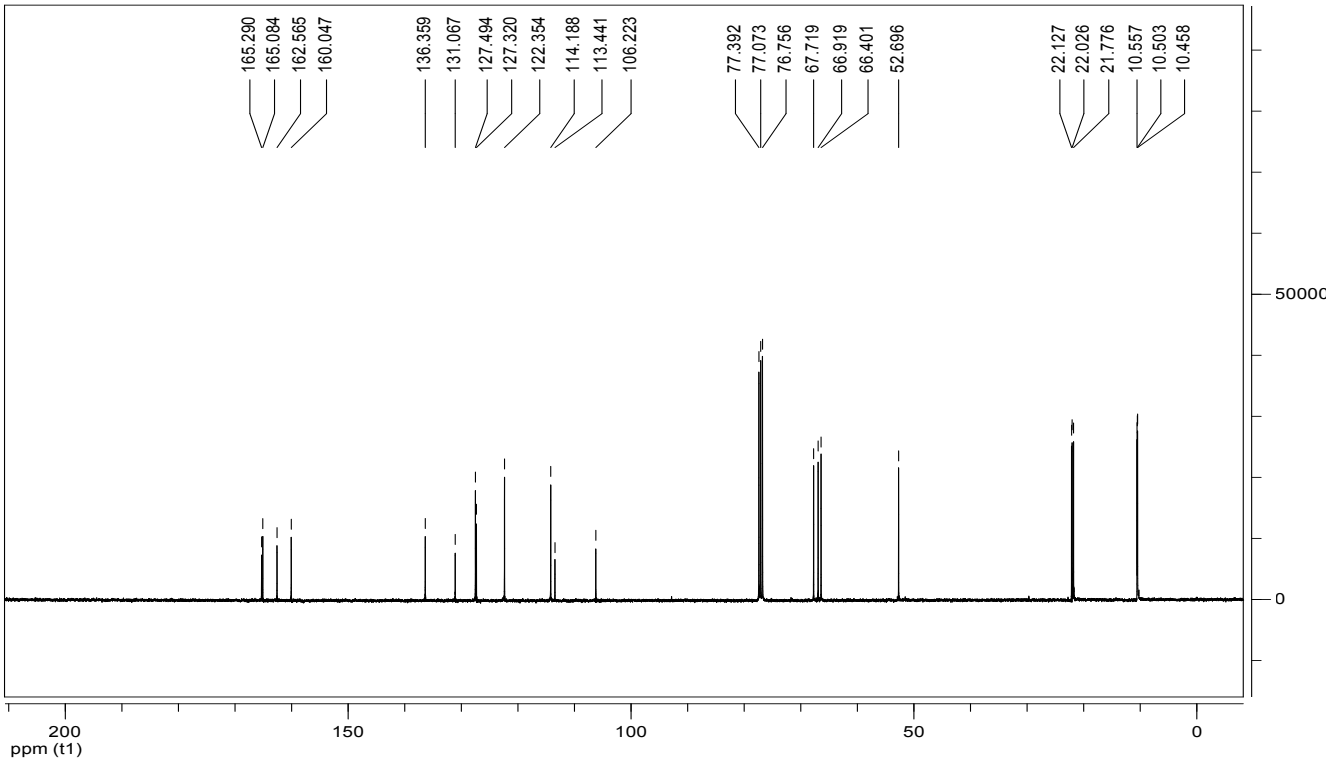
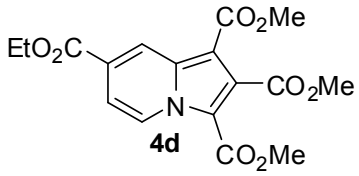
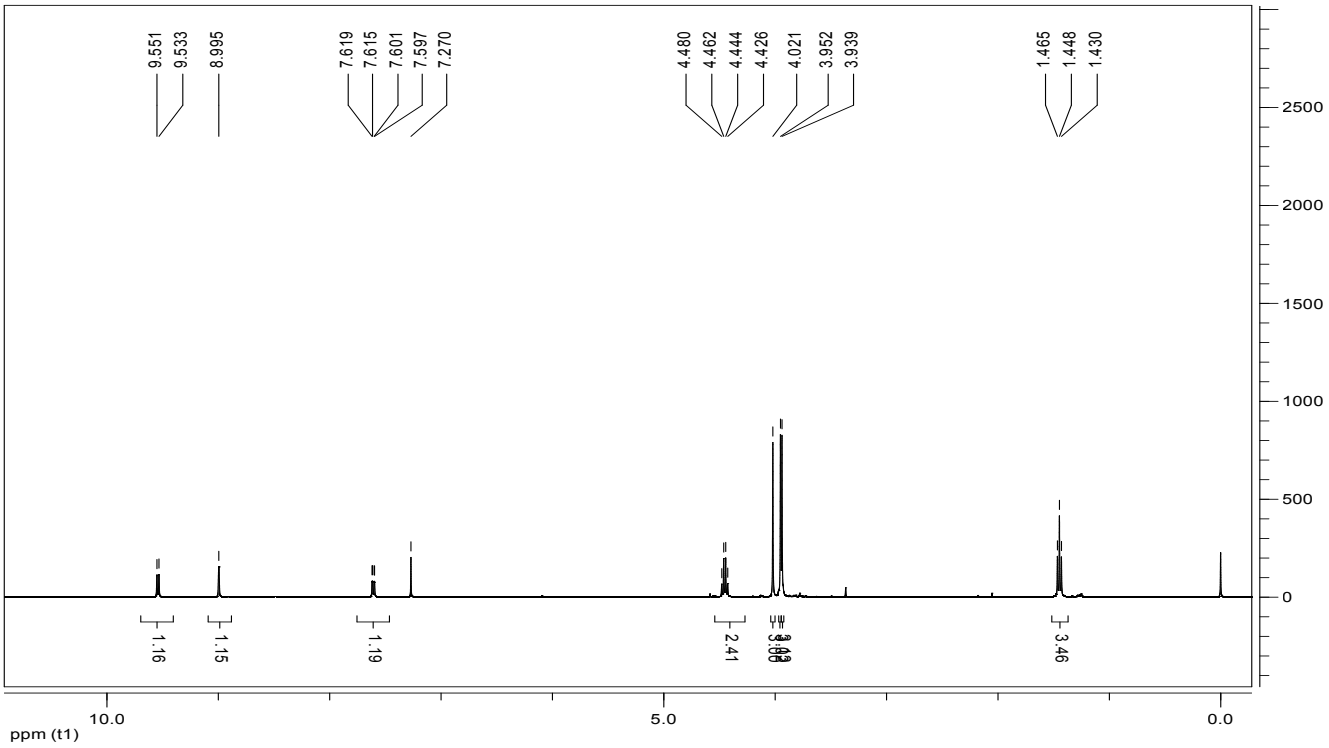
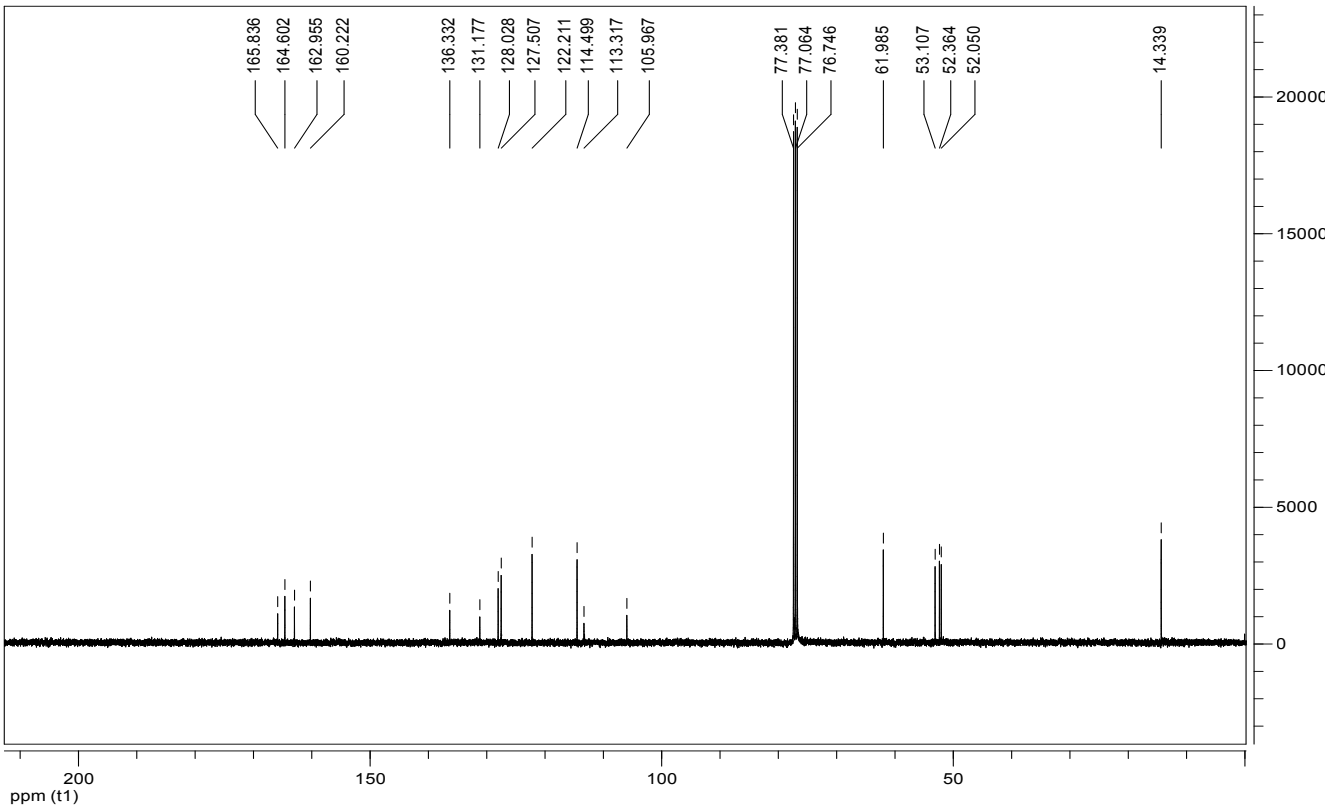
1.802
1.795
1.785
1.777
1.767
1.759
1.753
1.735
1.718
1.047
1.029
1.013
0.996
0.977
15000
10000
50000
0
0.84
0.80
0.80
6.12
3.00
6.30
9.61
10.0
5.0
0.0
ppm (t1)

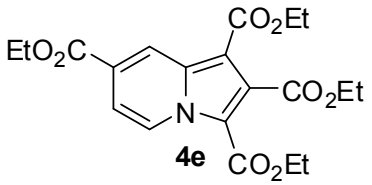

165.290
165.084
162.565
160.047
136.359
131.067
127.494
127.320
122.354
114.188
113.441
106.223
77.392
77.073
76.756
67.719
66.919
66.401
52.696
22.127
22.026
21.776
10.557
10.503
10.458
50000
0
200
150
100
50
0
ppm (t1)


CO2Me
EtO2C
CO2Me
N
CO2Me

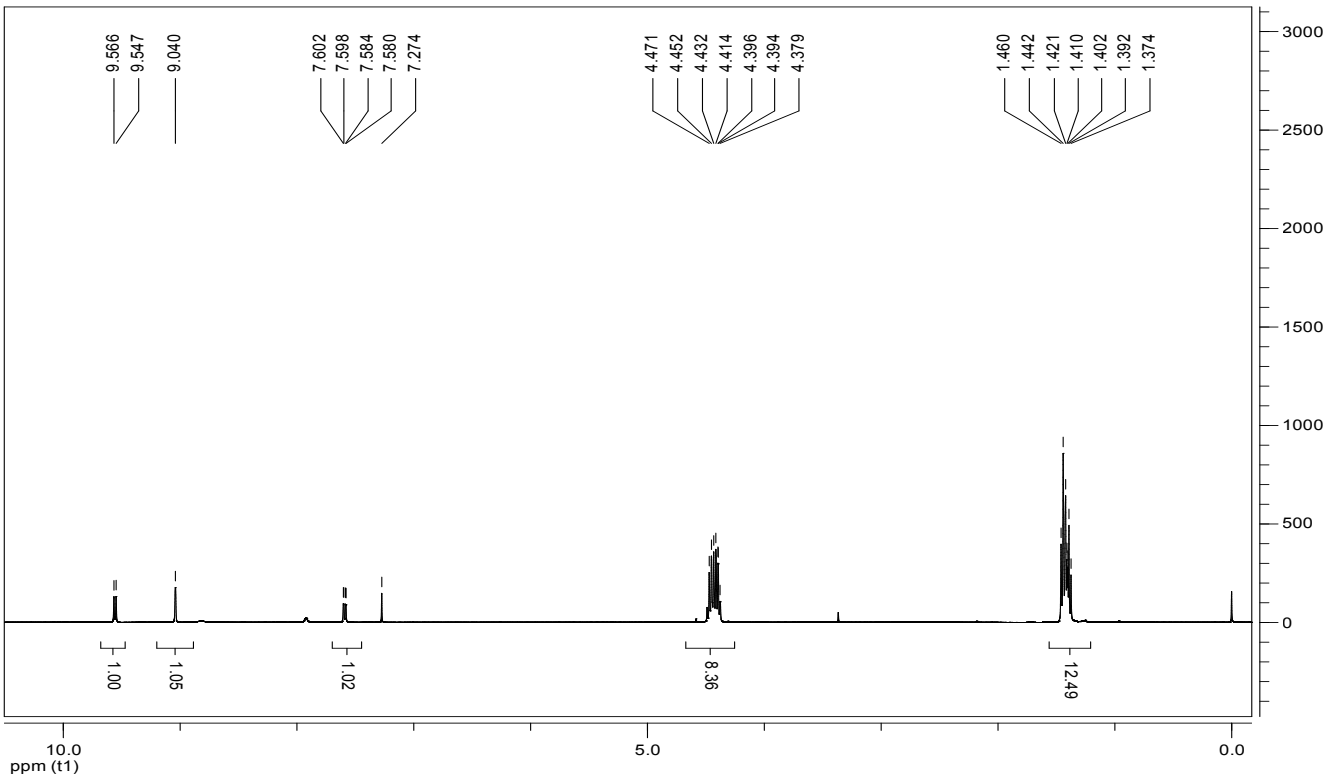
4d

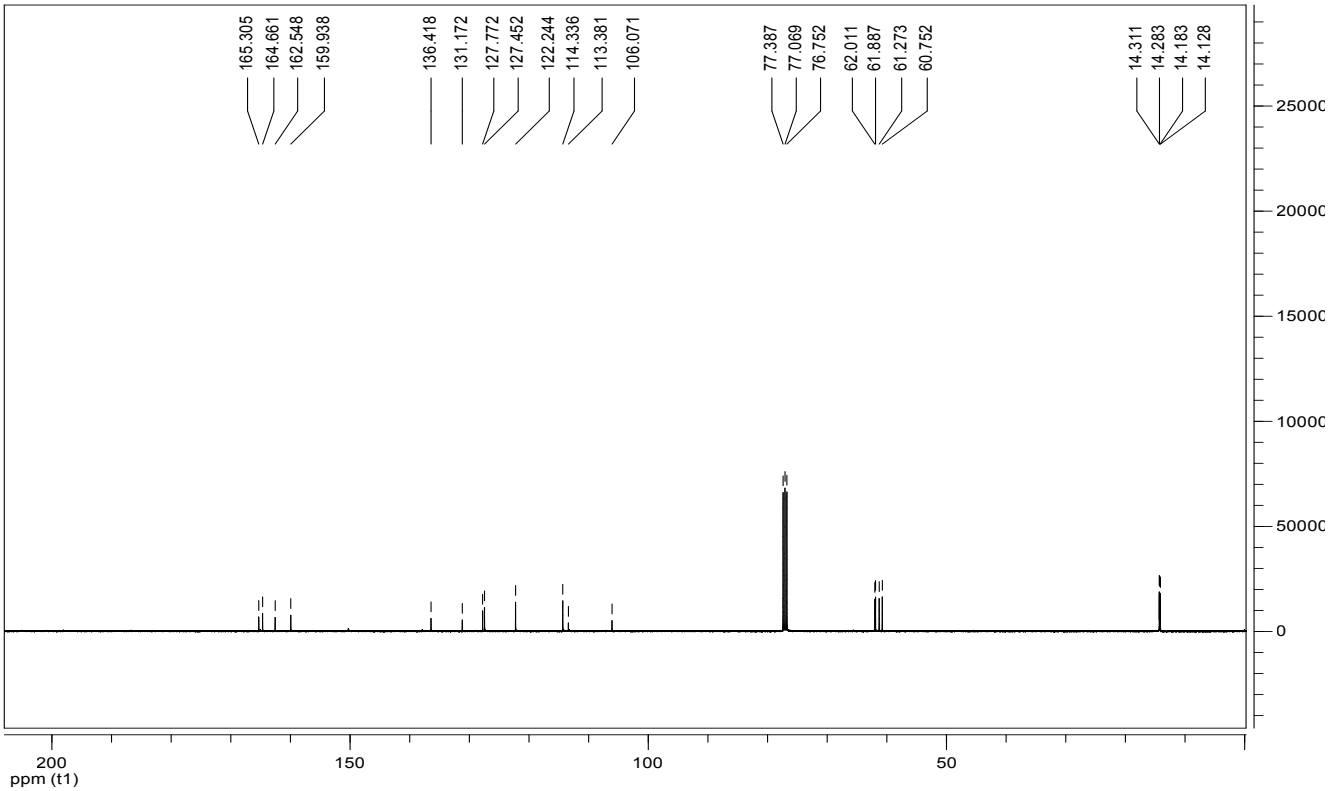

9.551
9.533
8.995
7.619
7.615
7.601
7.597
7.270
4.480
4.462
4.444
4.426
4.021
3.952
3.939
1.465
1.448
1.430
1.16
1.15
1.19
2.41
3.46
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

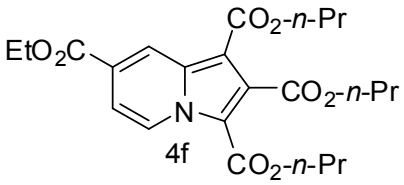

165.836
164.602
162.955
160.222
136.332
131.177
128.028
127.507
122.211
114.499
113.317
105.967
77.381
77.064
76.746
61.985
53.107
52.364
52.050
14.339
20000
15000
10000
5000
0
200
150
100
50
ppm (t1)


CO2Et
EtO2C
CO2Et
N
CO2Et

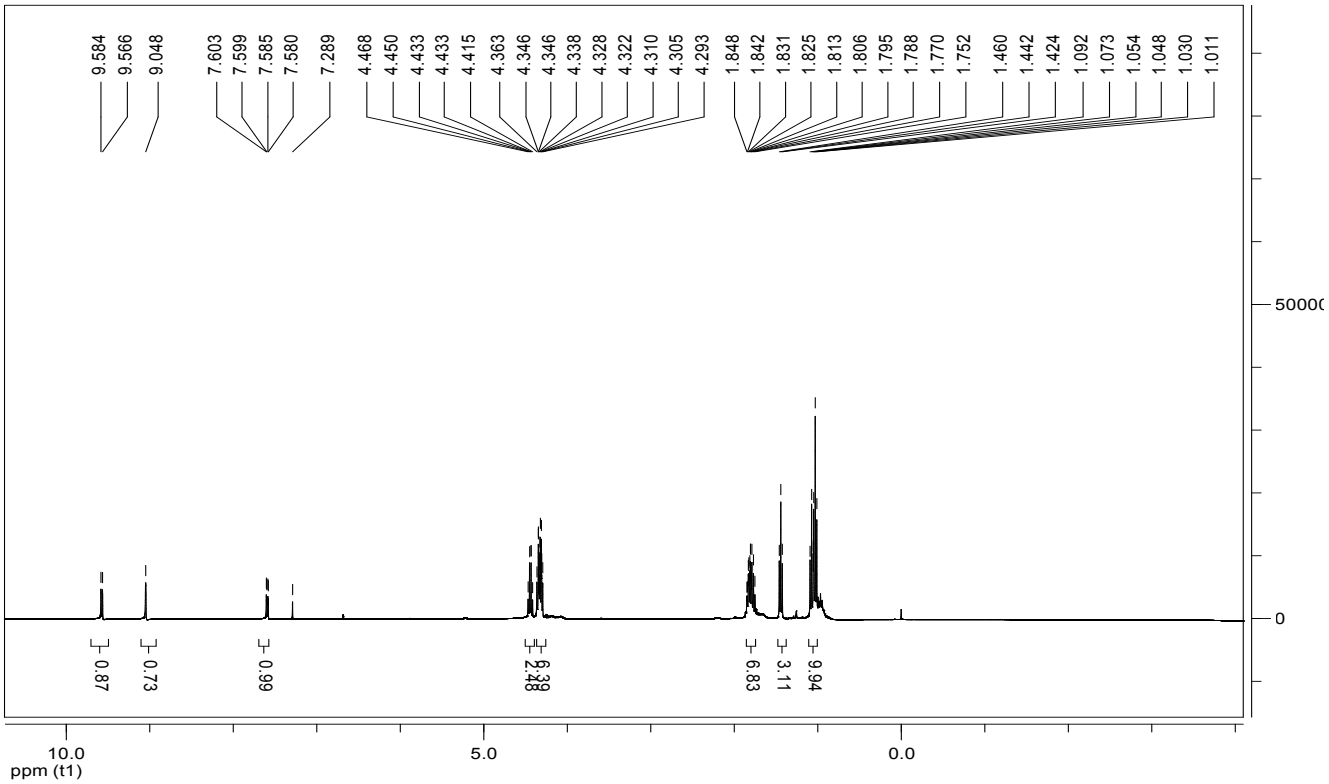
4e

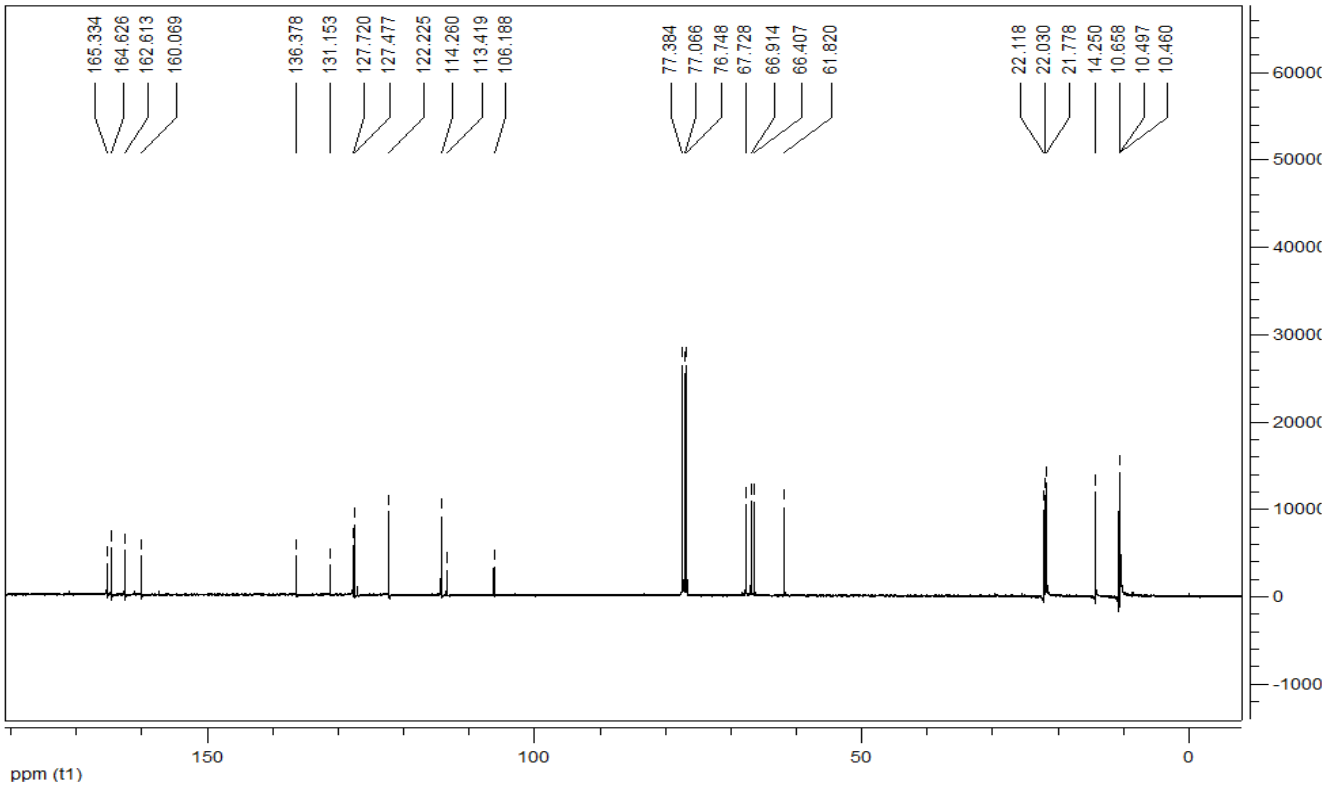

9.566
9.547
9.040
7.602
7.598
7.584
7.580
7.274
4.471
4.452
4.432
4.414
4.396
4.394
4.379
1.460
1.442
1.421
1.410
1.402
1.392
1.374
1.00
1.05
1.02
8.36
12.49
10.0
ppm (t1)
5.0
0.0

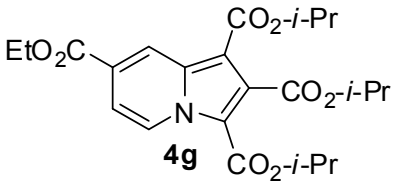

165.305
164.661
162.548
159.938
136.418
131.172
127.772
127.452
122.244
114.336
113.381
106.071
77.387
77.069
76.752
62.011
61.887
61.273
60.752
14.311
14.283
14.183
14.128
200
ppm (t1)
150
100
50


EtO2C
CO2-n-Pr
CO2-n-Pr
N
CO2-n-Pr

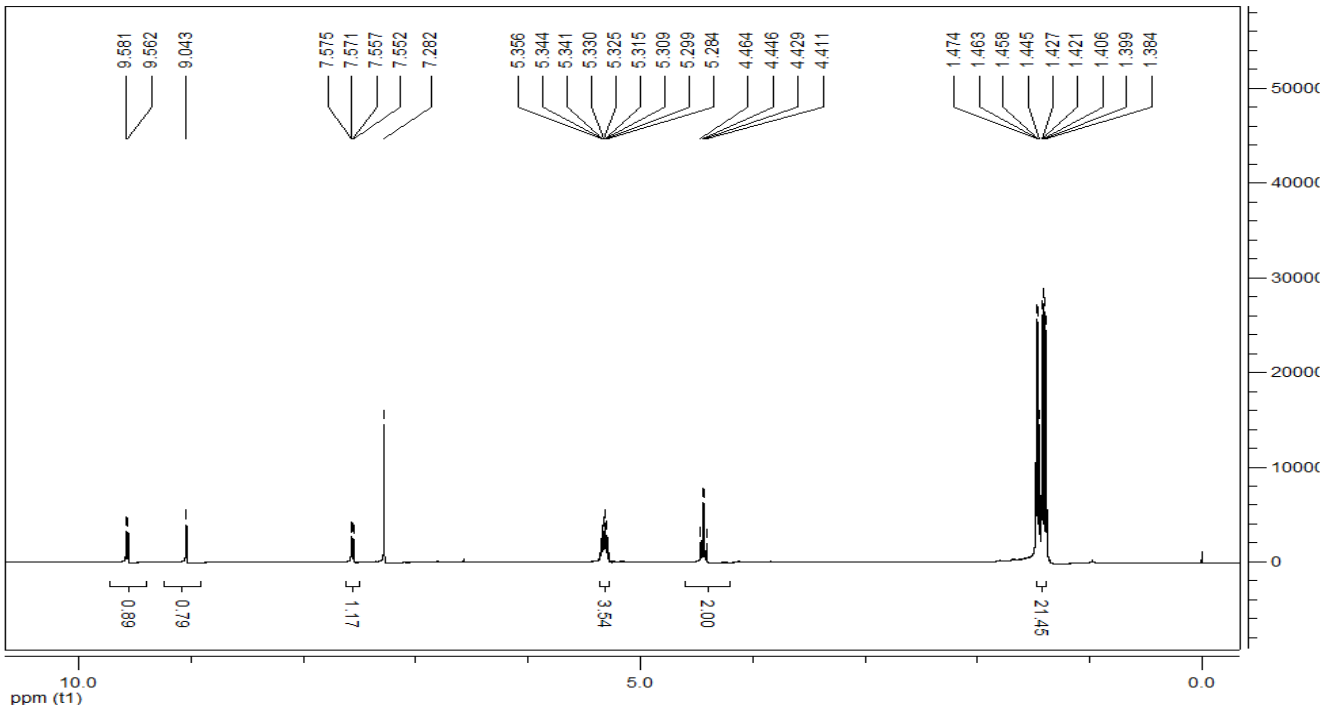
4f

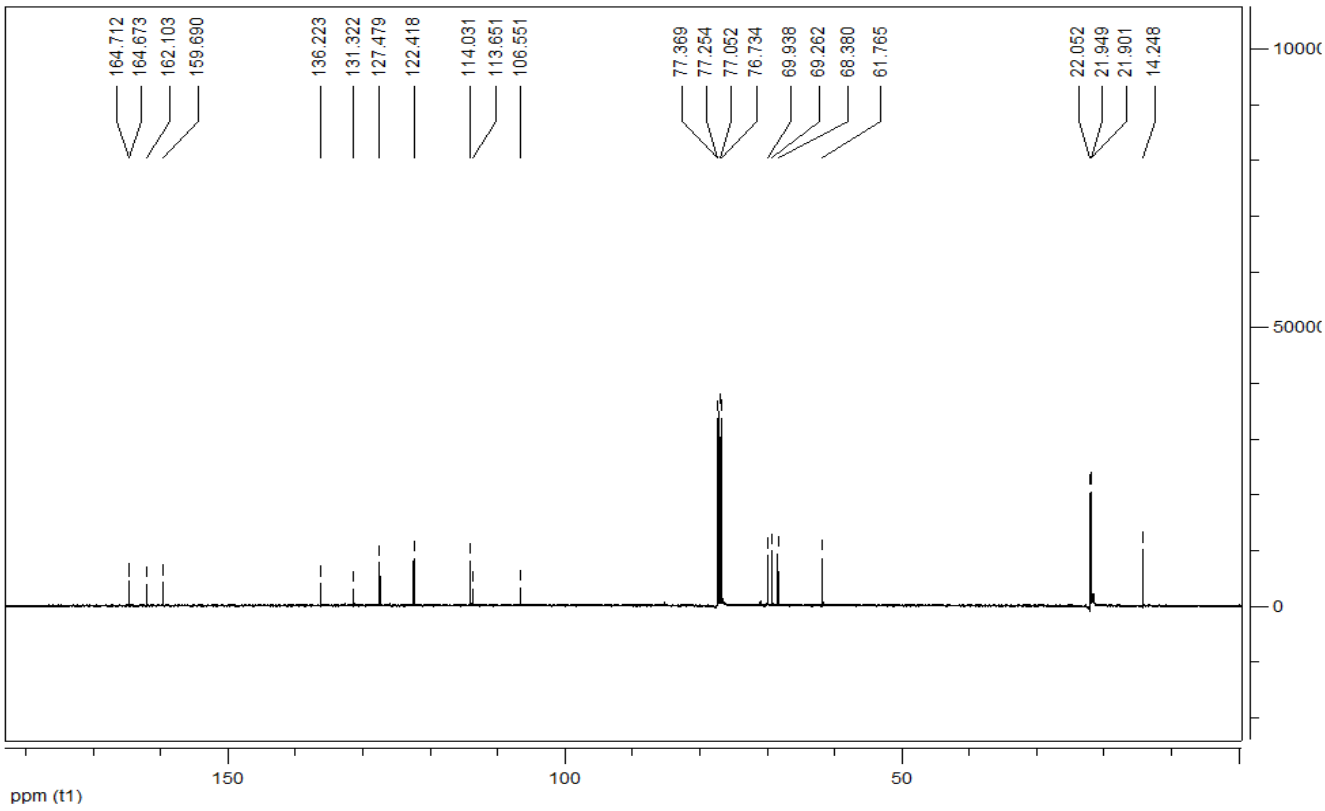

9.584
9.566
9.048
7.603
7.599
7.585
7.580
7.289
4.468
4.450
4.433
4.433
4.415
4.363
4.346
4.346
4.338
4.328
4.322
4.310
4.305
4.293
1.848
1.842
1.831
1.825
1.813
1.806
1.795
1.788
1.770
1.752
1.460
1.442
1.424
1.092
1.073
1.054
1.048
1.030
1.011
0.87
0.73
0.99
6.38
2.38
6.83
3.11
9.94
50000
0
10.0
5.0
0.0
ppm (t1)

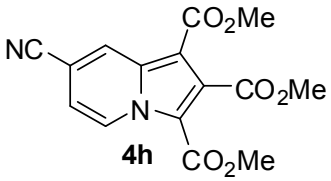

165.334
164.626
162.613
160.069
136.378
131.153
127.720
127.477
122.225
114.260
113.419
106.188
77.384
77.066
76.748
67.728
66.914
66.407
61.820
22.118
22.030
21.778
14.250
10.658
10.497
10.460
60000
50000
40000
30000
20000
10000
0
-10000
150
100
50
0
ppm (t1)


EtO2C
CO2-i-Pr
CO2-i-Pr
N
CO2-i-Pr

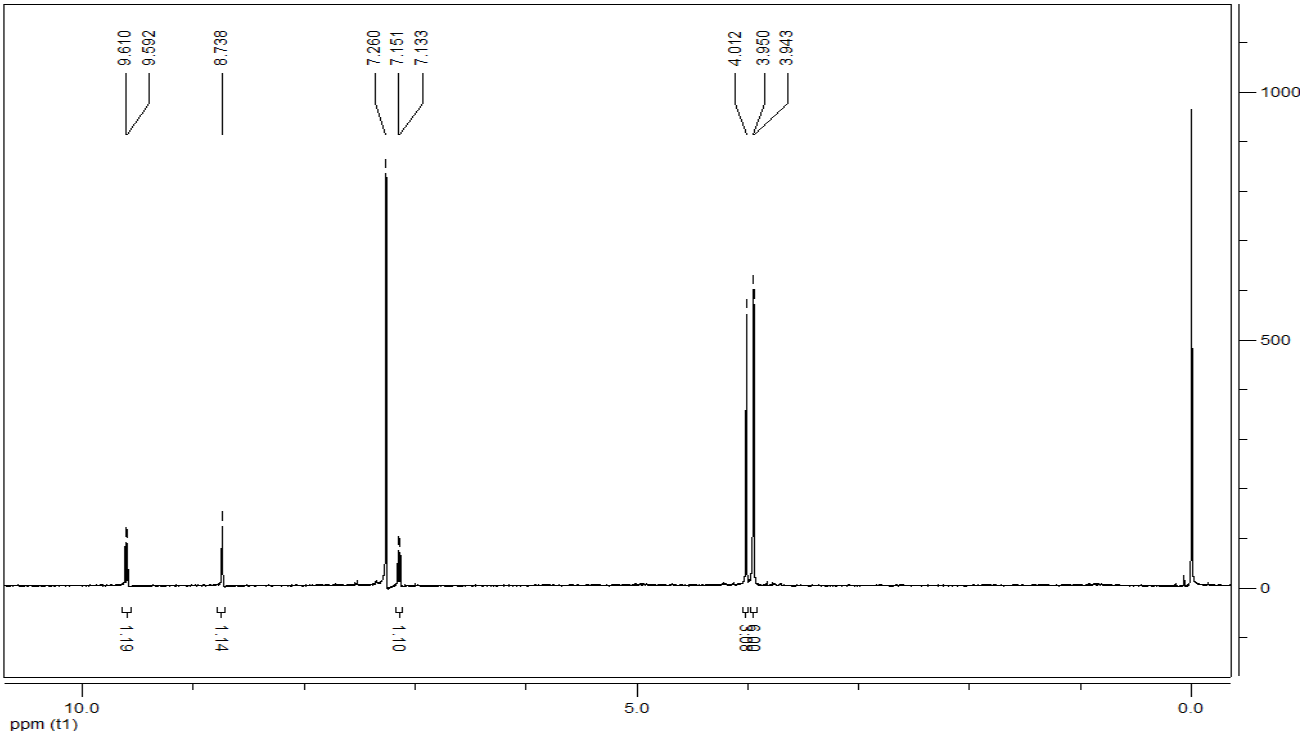
4g

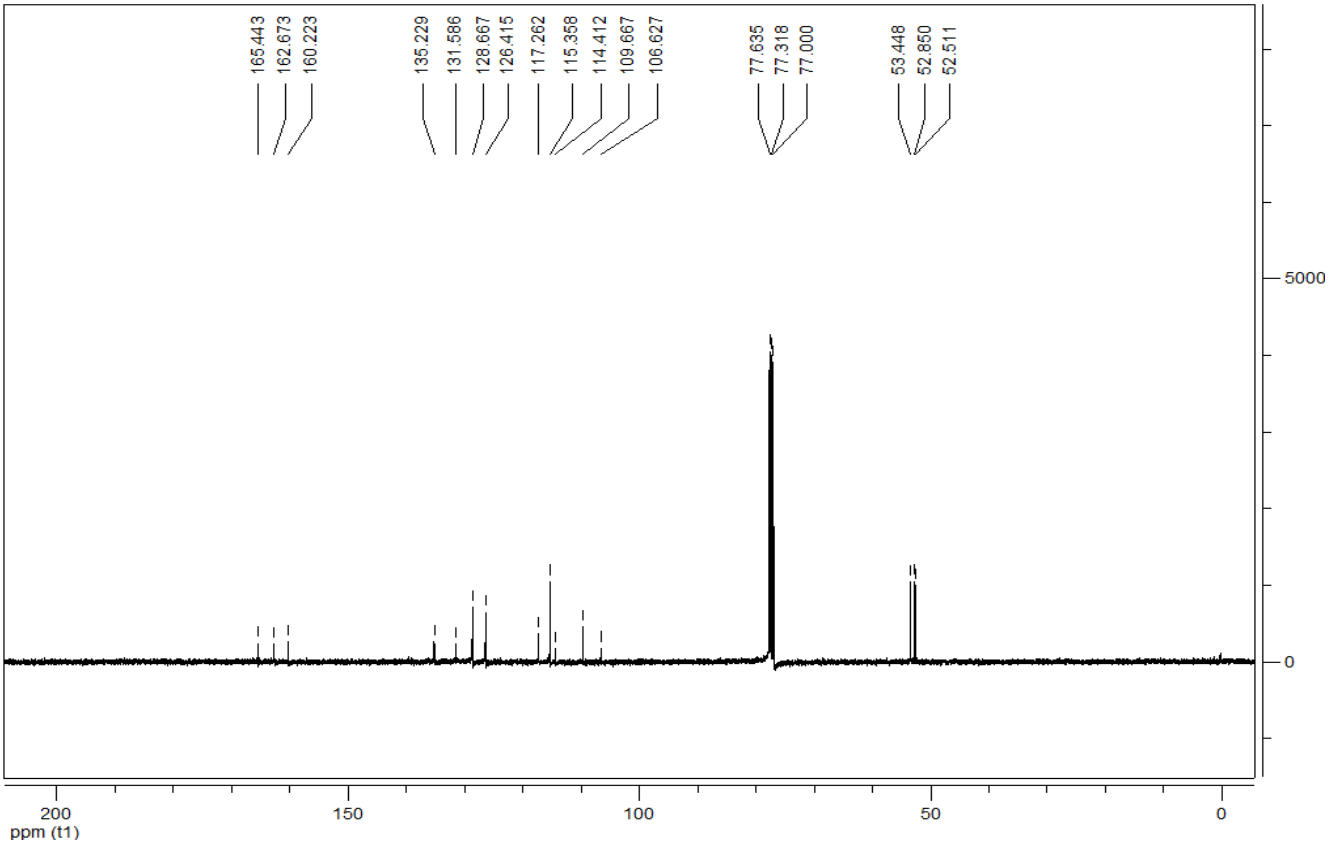

9.581
9.562
9.043
7.575
7.571
7.557
7.552
7.282
5.356
5.344
5.341
5.330
5.325
5.315
5.309
5.299
5.284
4.464
4.446
4.429
4.411
1.474
1.463
1.458
1.445
1.427
1.421
1.406
1.399
1.384
0.89
0.79
1.17
3.54
2.00
21.45
ppm (t1)

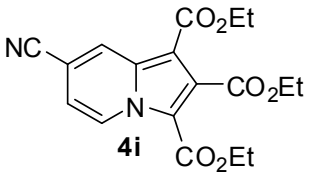

164.712
164.673
162.103
159.690
136.223
131.322
127.479
122.418
114.031
113.651
106.551
77.369
77.254
77.052
76.734
69.938
69.262
68.380
61.765
22.052
21.949
21.901
14.248
ppm (t1)


NC
CO2Me
CO2Me
N
CO2Me

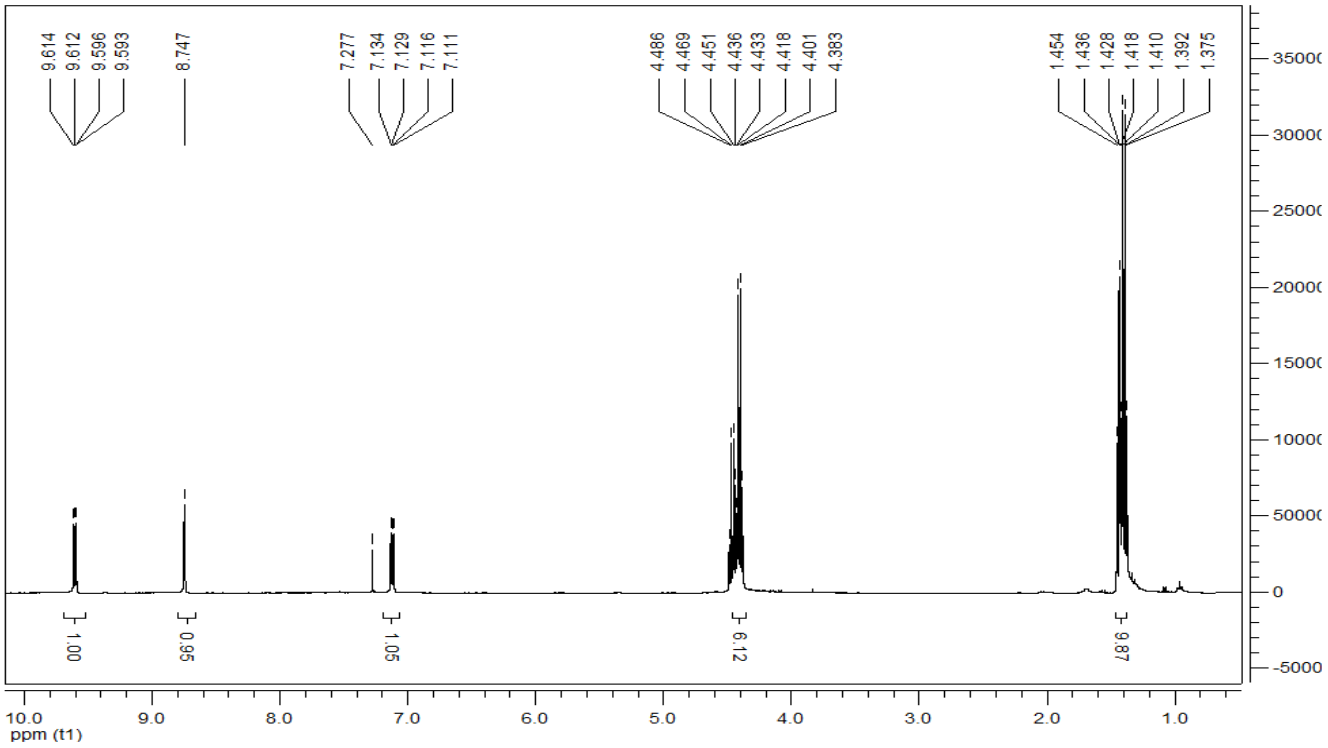
4h

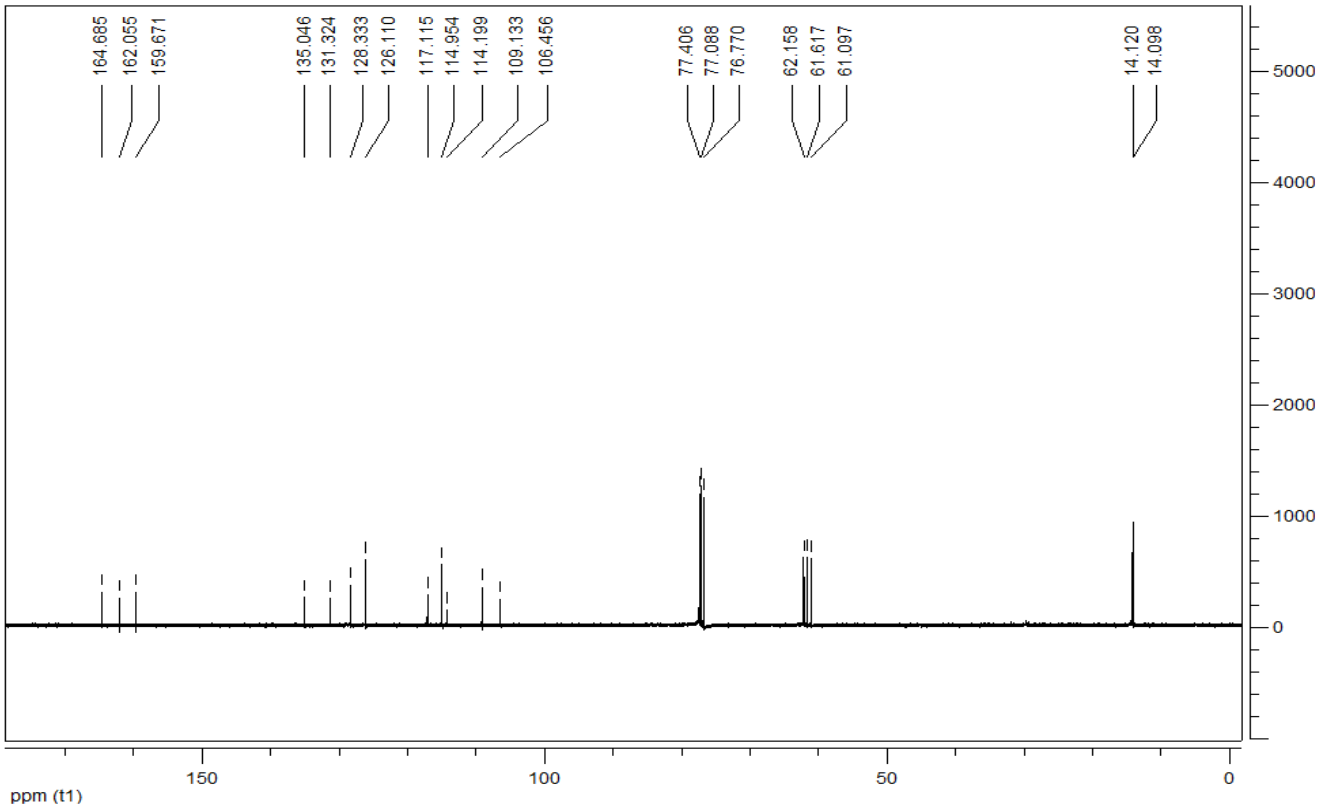

9.610
9.592
8.738
7.260
7.151
7.133
4.012
3.950
3.943
1.19
1.14
1.10
9.00
6.00
3.00
1000
500
0
10.0
5.0
0.0
ppm (t1)

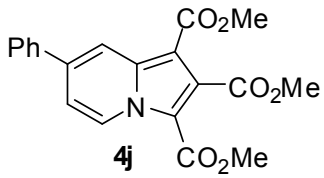

165.443
162.673
160.223
135.229
131.586
128.667
126.415
117.262
115.358
114.412
109.667
106.627
77.635
77.318
77.000
53.448
52.850
52.511
5000
0
200
150
100
50
0
ppm (t1)


NC
CO2Et
CO2Et
N
CO2Et

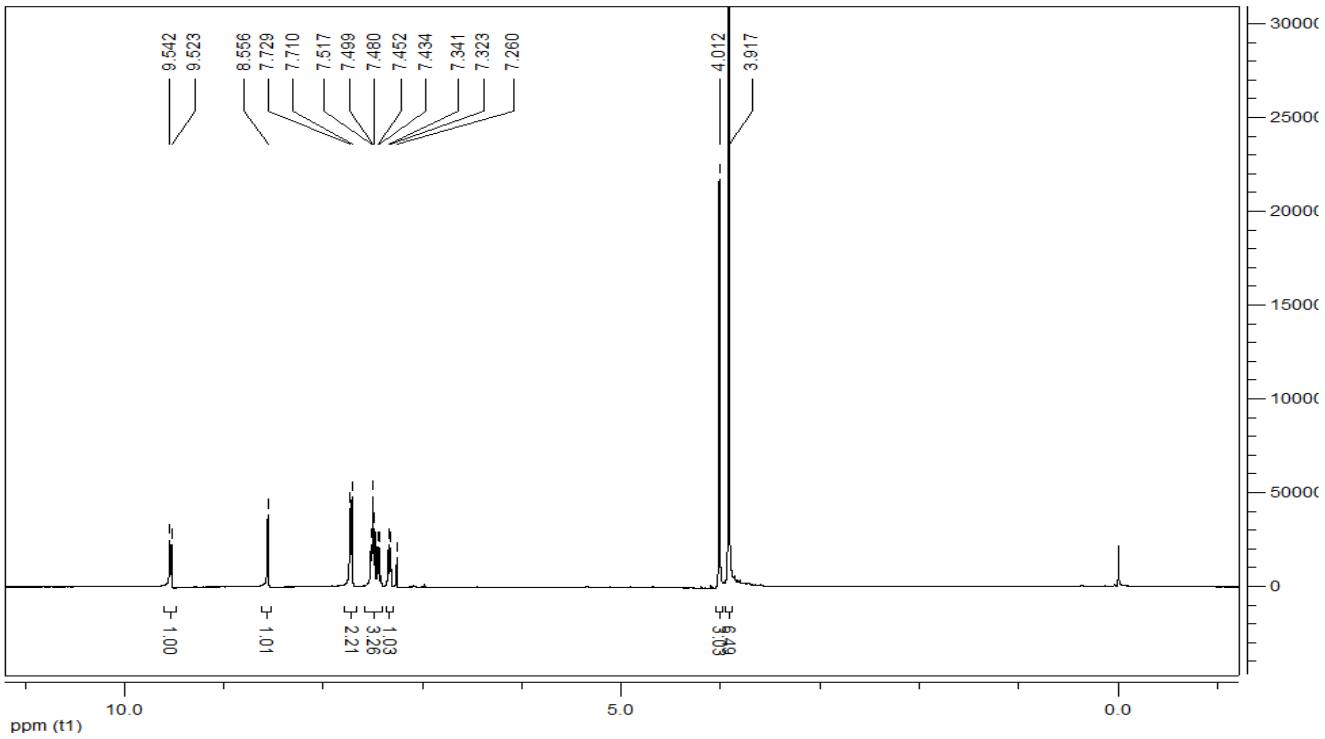
4i

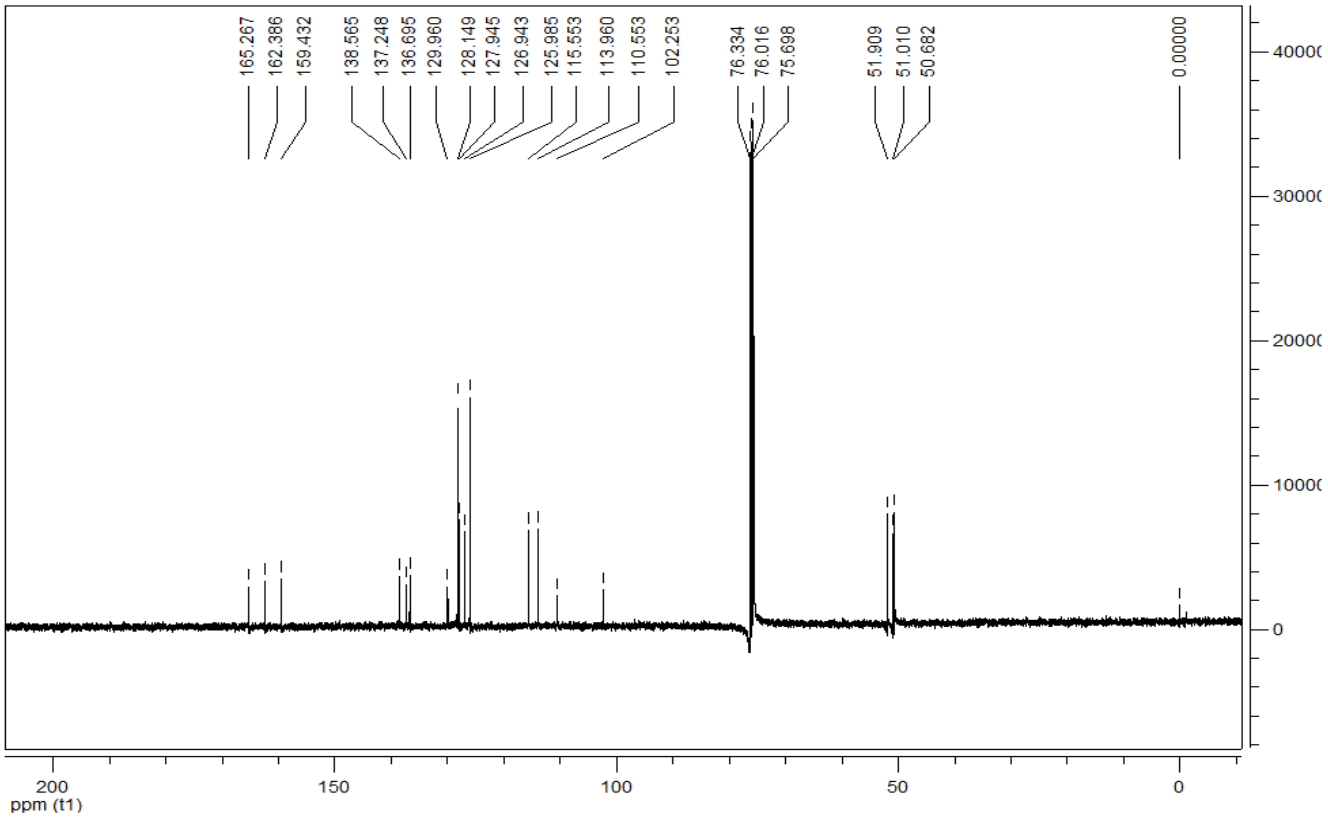

9.614
9.612
9.596
9.593
8.747
7.277
7.134
7.129
7.116
7.111
4.486
4.469
4.451
4.436
4.433
4.418
4.401
4.383
1.454
1.436
1.428
1.418
1.410
1.392
1.375
1.00
0.96
1.05
6.12
9.87
ppm (t1)

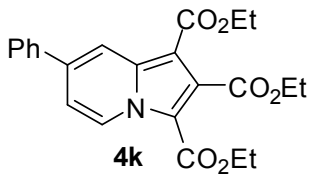

164.685
162.055
159.671
135.046
131.324
128.333
126.110
117.115
114.954
114.199
109.133
106.456
77.406
77.088
76.770
62.158
61.617
61.097
14.120
14.098
ppm (t1)


Ph
CO2Me
CO2Me
N
CO2Me

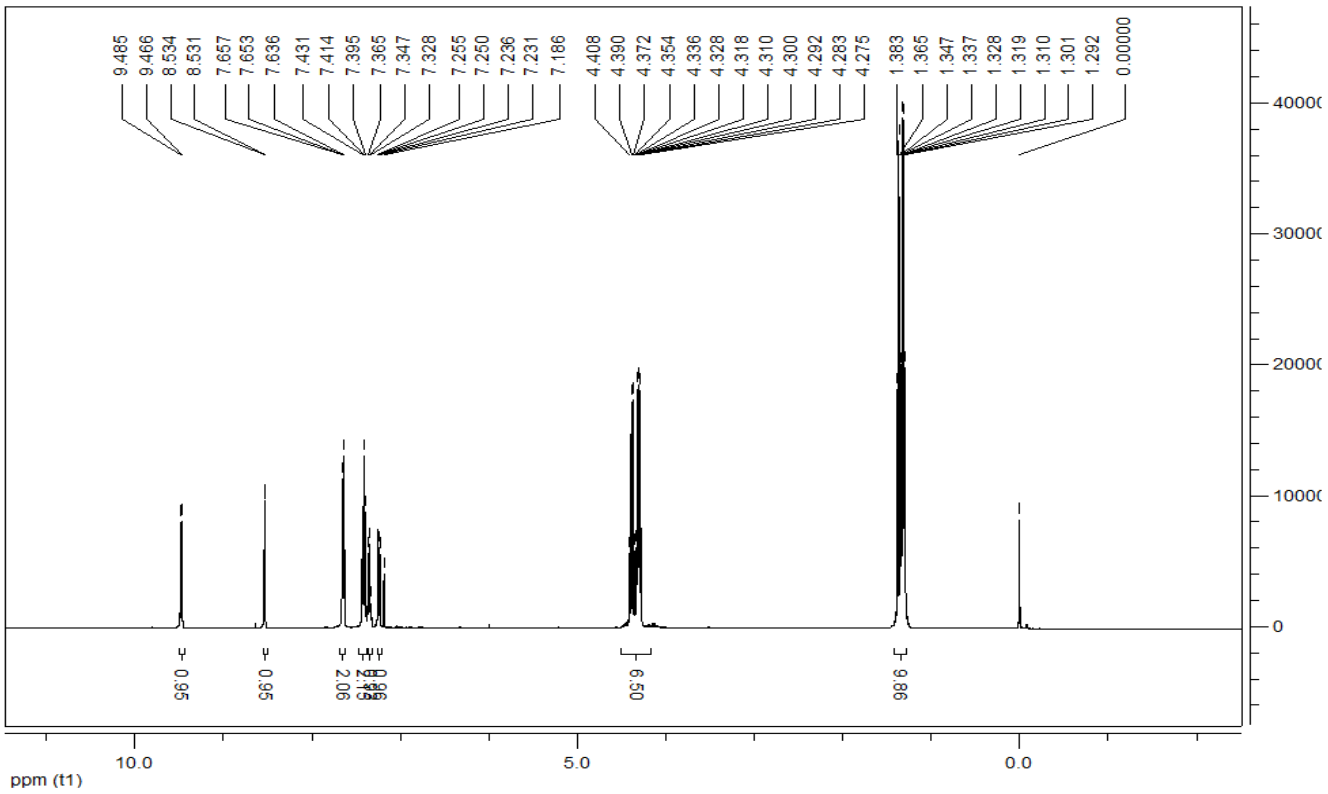
4j

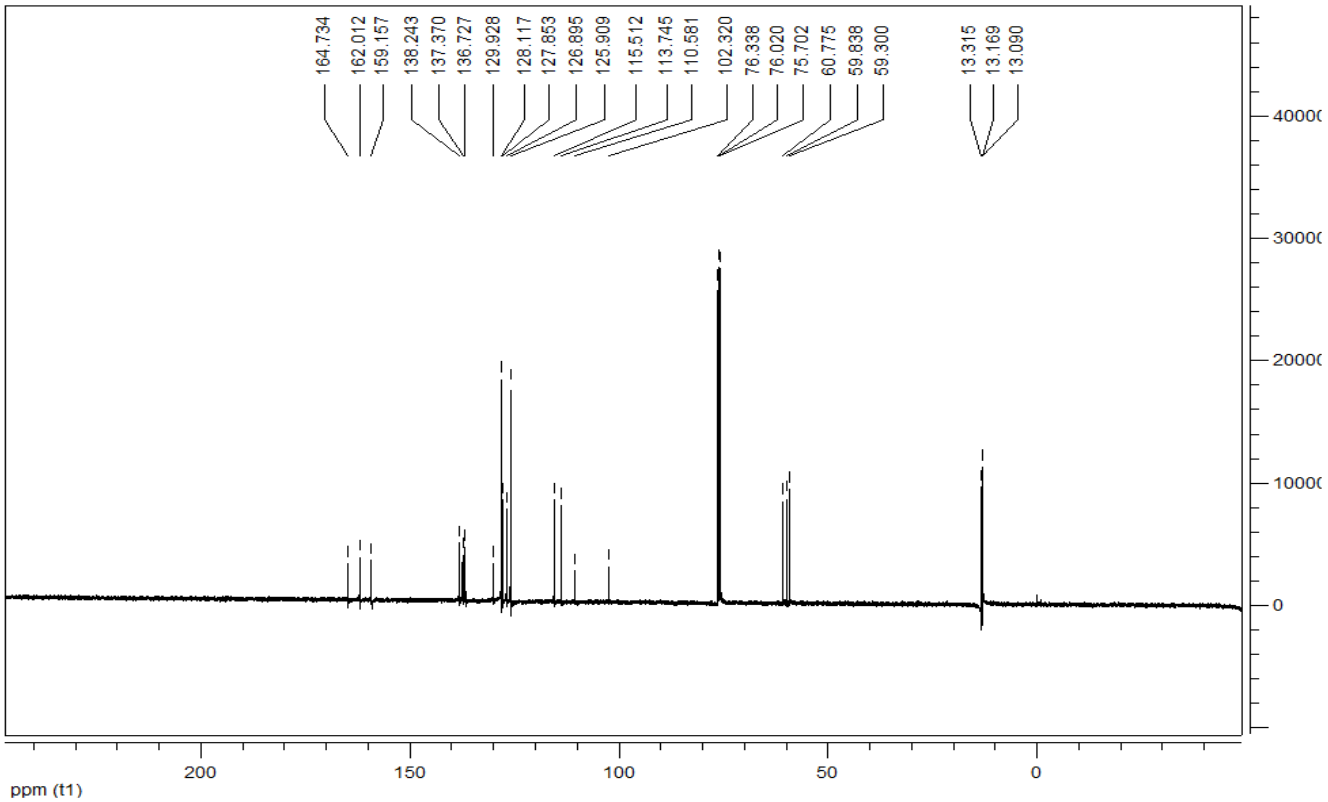

9.542
9.523
8.556
7.729
7.710
7.517
7.499
7.480
7.452
7.434
7.341
7.323
7.260
4.012
3.917
1.00
1.01
2.21
3.26
1.03
6.09
10.0
5.0
0.0
ppm (t1)

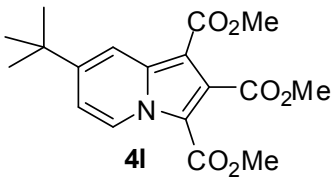

165.267
162.386
159.432
138.565
137.248
136.695
129.960
128.149
127.945
126.943
125.985
115.553
113.960
110.553
102.253
76.334
76.016
75.698
51.909
51.010
50.682
0.00000
200
150
100
50
0
ppm (t1)


Ph
CO2Et
CO2Et
N
CO2Et

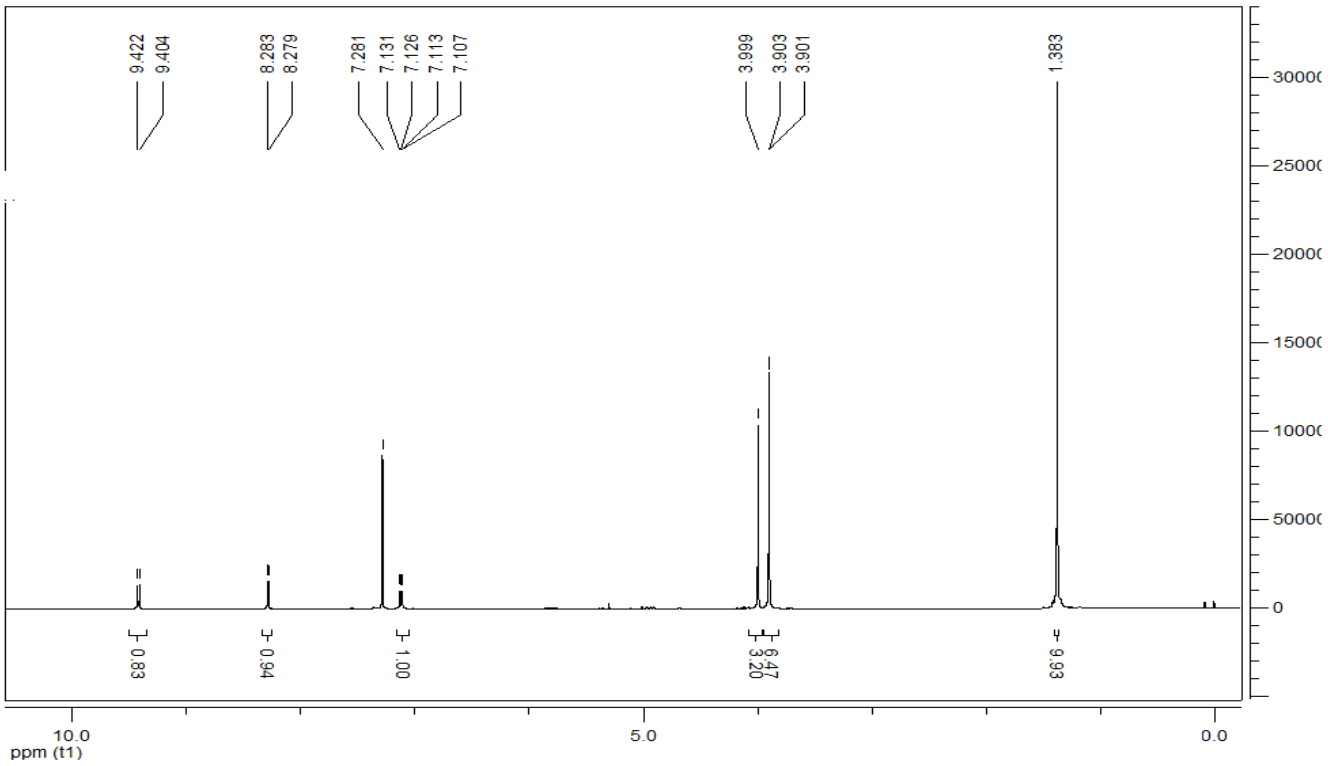
4k

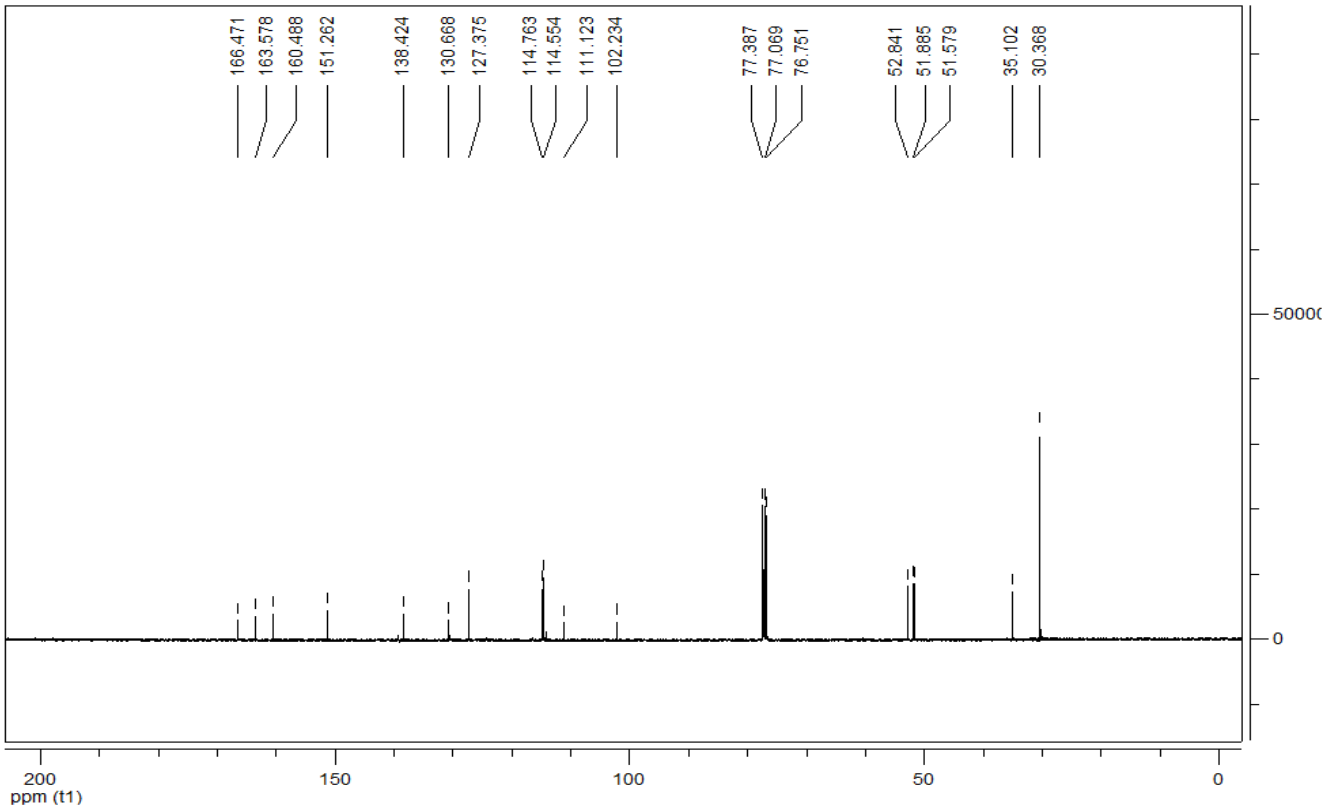

9.485
9.466
8.534
8.531
7.657
7.653
7.636
7.431
7.414
7.395
7.365
7.347
7.328
7.255
7.250
7.236
7.231
7.186
4.408
4.390
4.372
4.354
4.336
4.328
4.318
4.310
4.300
4.292
4.283
4.275
1.383
1.365
1.347
1.337
1.328
1.319
1.310
1.301
1.292
0.00000
0.95
0.95
2.06
6.50
9.86
10.0
5.0
0.0
ppm (t1)

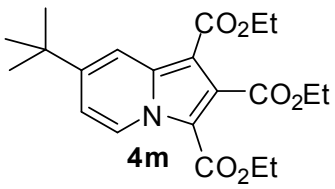

164.734
162.012
159.157
138.243
137.370
136.727
129.928
128.117
127.853
126.895
125.909
115.512
113.745
110.581
102.320
76.338
76.020
75.702
60.775
59.838
59.300
13.315
13.169
13.090
200
150
100
50
0
ppm (t1)

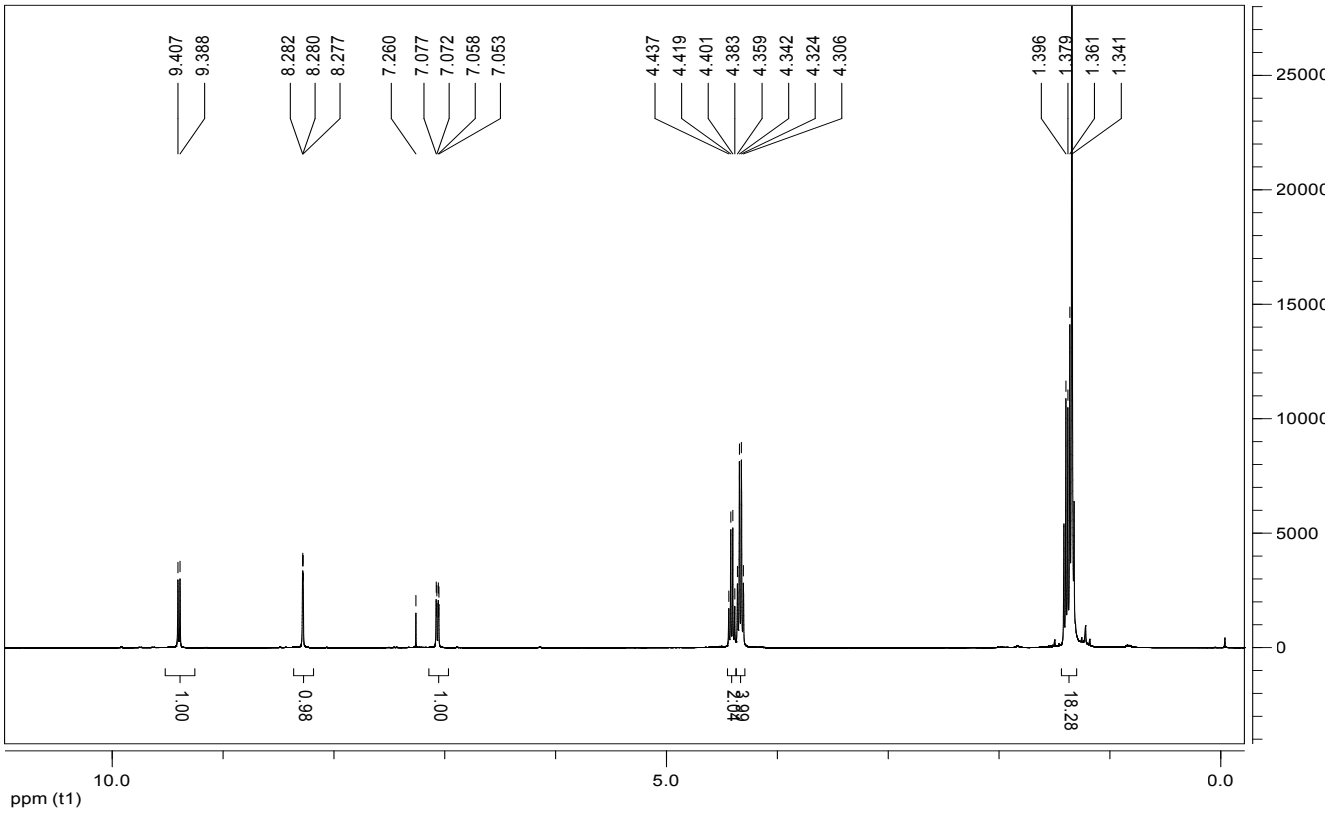

CO2Me
CO2Me
N
CO2Me

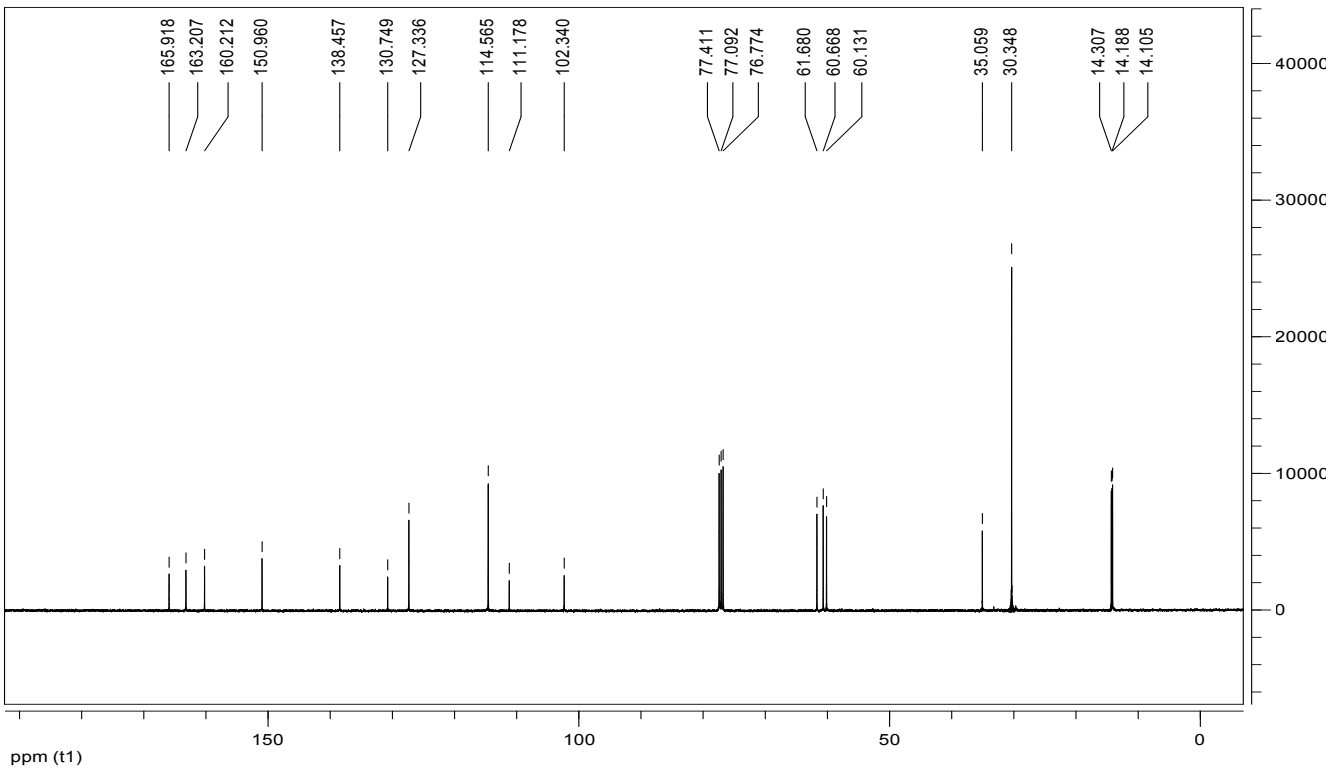
4l

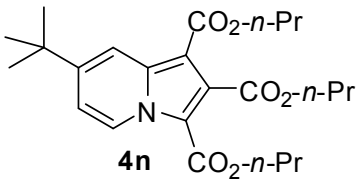

9.422
9.404
8.283
8.279
7.281
7.131
7.126
7.113
7.107
3.999
3.903
3.901
1.383
0.83
0.94
1.00
6.47
3.20
9.93
10.0
ppm (t1)
5.0
0.0


166.471
163.578
160.488
151.262
138.424
130.668
127.375
114.763
114.554
111.123
102.234
77.387
77.069
76.751
52.841
51.885
51.579
35.102
30.368
200
ppm (t1)
150
100
50
0

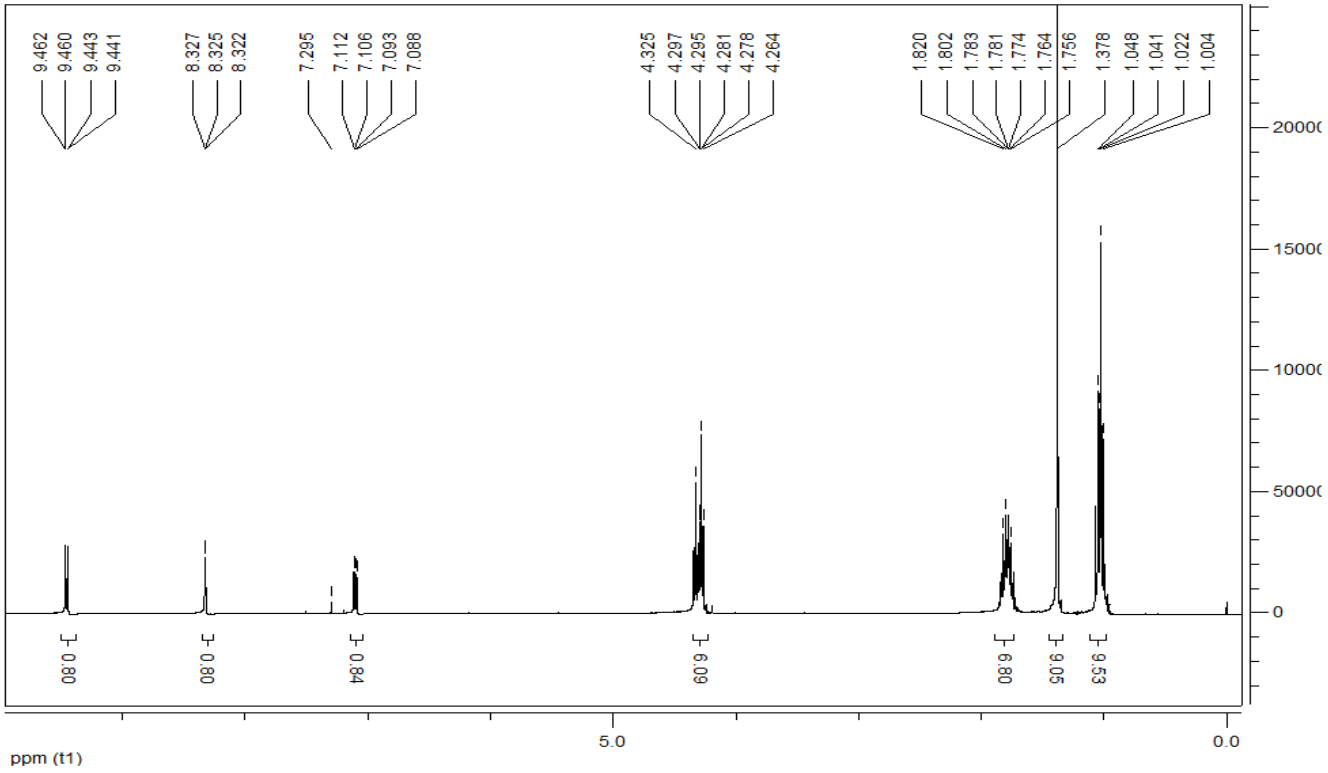

CO2Et
CO2Et
N
4m
CO2Et

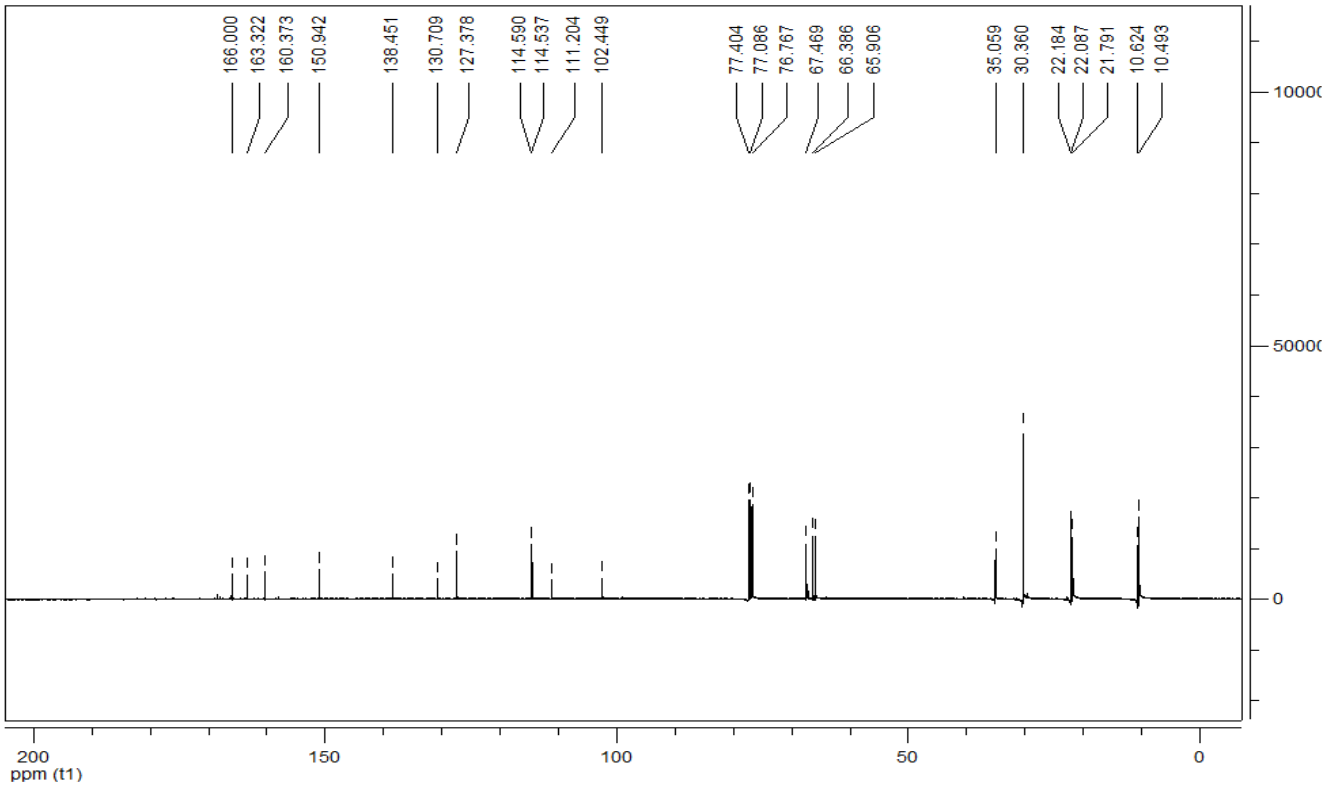

9.407
9.388
8.282
8.280
8.277
7.260
7.077
7.072
7.058
7.053
4.437
4.419
4.401
4.383
4.359
4.342
4.324
4.306
1.396
1.379
1.361
1.341
1.00
0.98
1.00
2.08
18.28
10.0
5.0
0.0
ppm (t1)

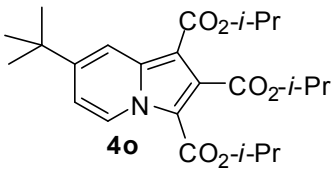

165.918
163.207
160.212
150.960
138.457
130.749
127.336
114.565
111.178
102.340
77.411
77.092
76.774
61.680
60.668
60.131
35.059
30.348
14.307
14.188
14.105
150
100
50
0
ppm (t1)


CO2-n-Pr
CO2-n-Pr
N
CO2-n-Pr

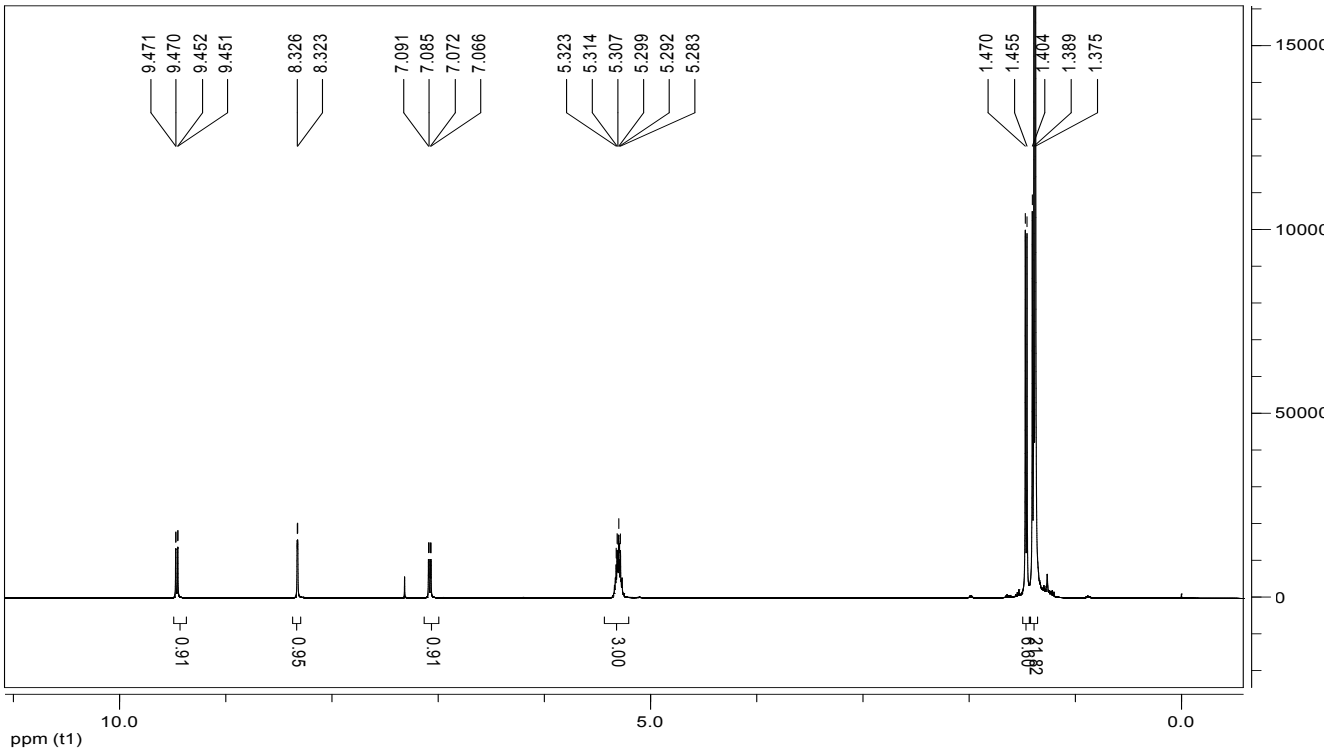
4n

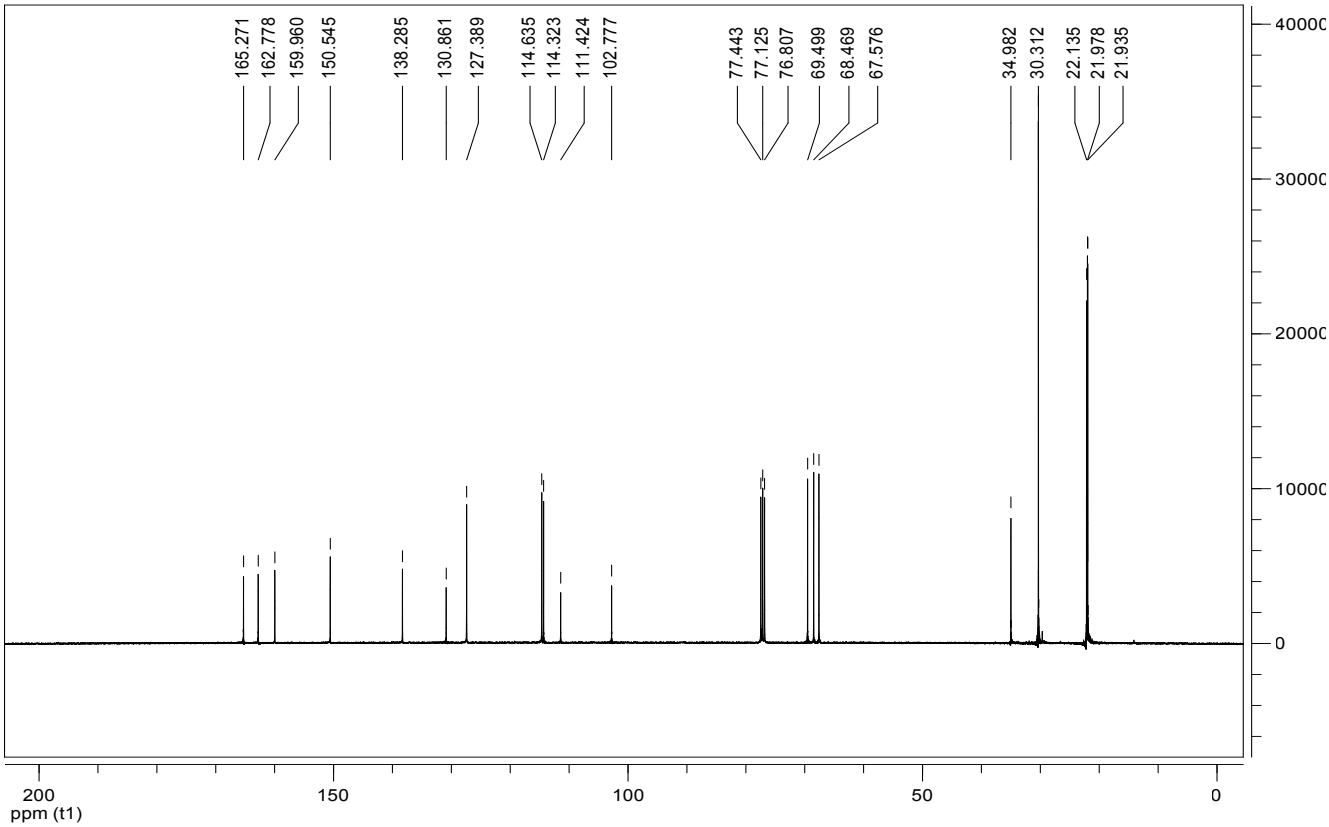

9.462
9.460
9.443
9.441
8.327
8.325
8.322
7.295
7.112
7.106
7.093
7.088
4.325
4.297
4.295
4.281
4.278
4.264
1.820
1.802
1.783
1.781
1.774
1.764
1.756
1.378
1.048
1.041
1.022
1.004
0.80
0.80
0.84
6.09
6.80
9.05
9.53
20000
15000
10000
5000
0
5.0
0.0
ppm (t1)


166.000
163.322
160.373
150.942
138.451
130.709
127.378
114.590
114.537
111.204
102.449
77.404
77.086
76.767
67.469
66.386
65.906
35.059
30.360
22.184
22.087
21.791
10.624
10.493
10000
5000
0
200
150
100
50
0
ppm (t1)


CO2-i-Pr
CO2-i-Pr
N
CO2-i-Pr

4o


9.471
9.470
9.452
9.451
8.326
8.323
7.091
7.085
7.072
7.066
5.323
5.314
5.307
5.299
5.292
5.283
1.470
1.455
1.404
1.389
1.375
0.91
0.96
0.91
3.00
6.82
10.0
5.0
0.0
ppm (t1)


165.271
162.778
159.960
150.545
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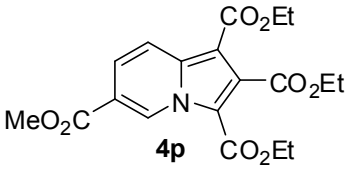
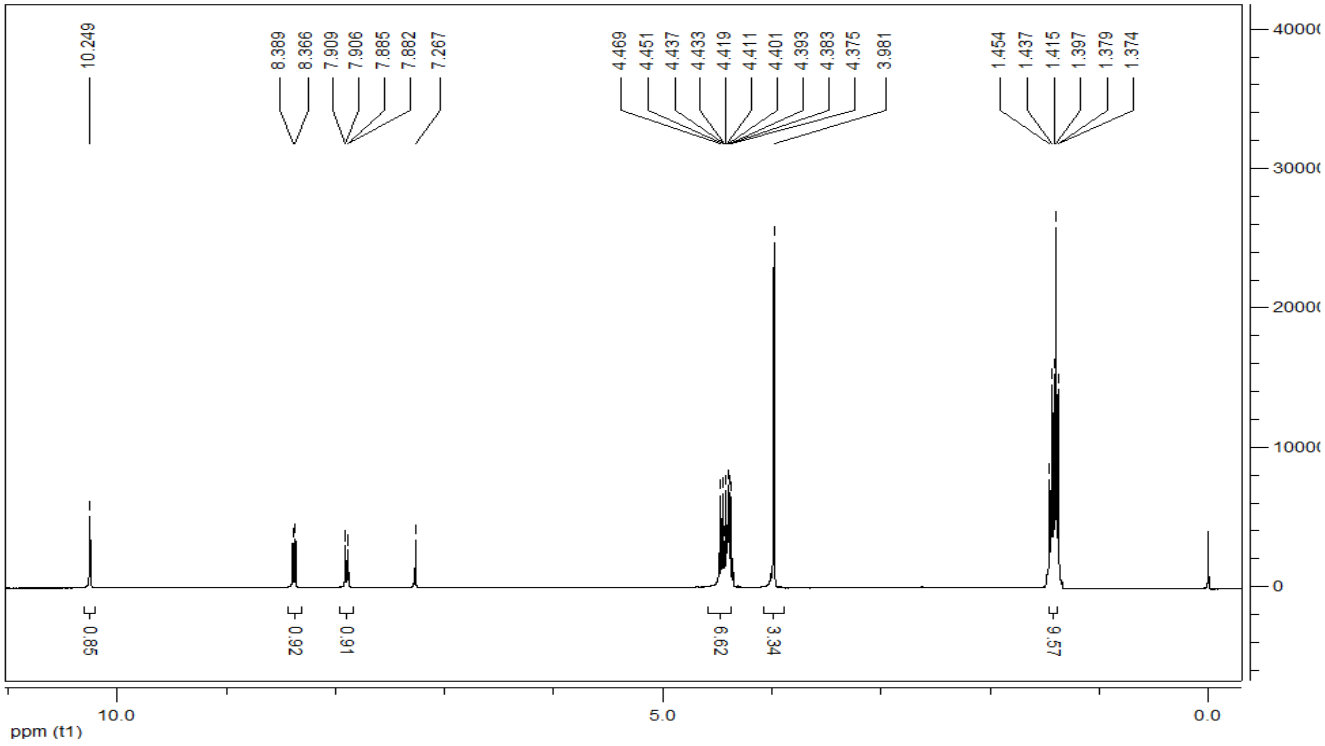
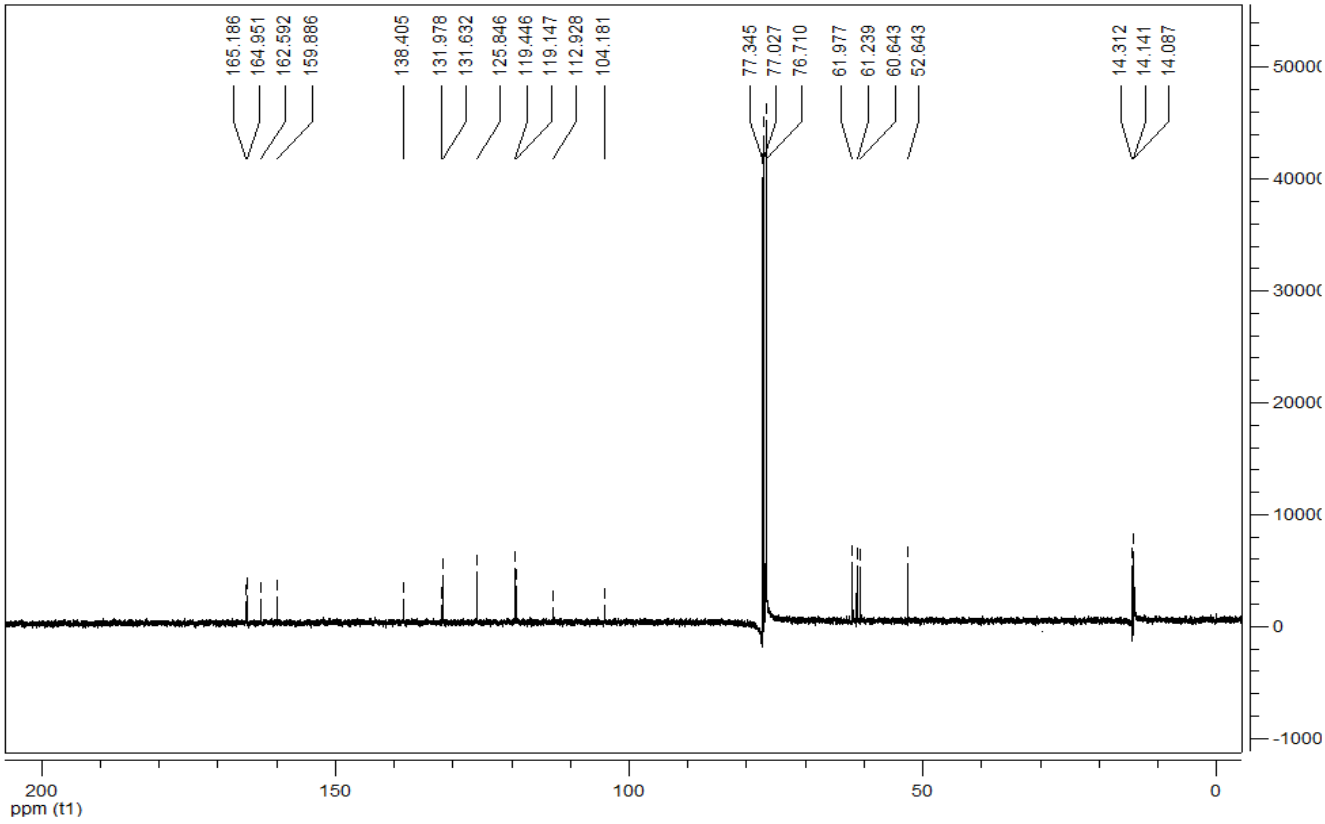
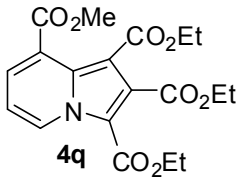
130.861
127.389
114.635
114.323
111.424
102.777
77.443
77.125
76.807
69.499
68.469
67.576
34.982
30.312
22.135
21.978
21.935
200
150
100
50
0
ppm (t1)


CO2Et
CO2Et
MeO2C
N
CO2Et

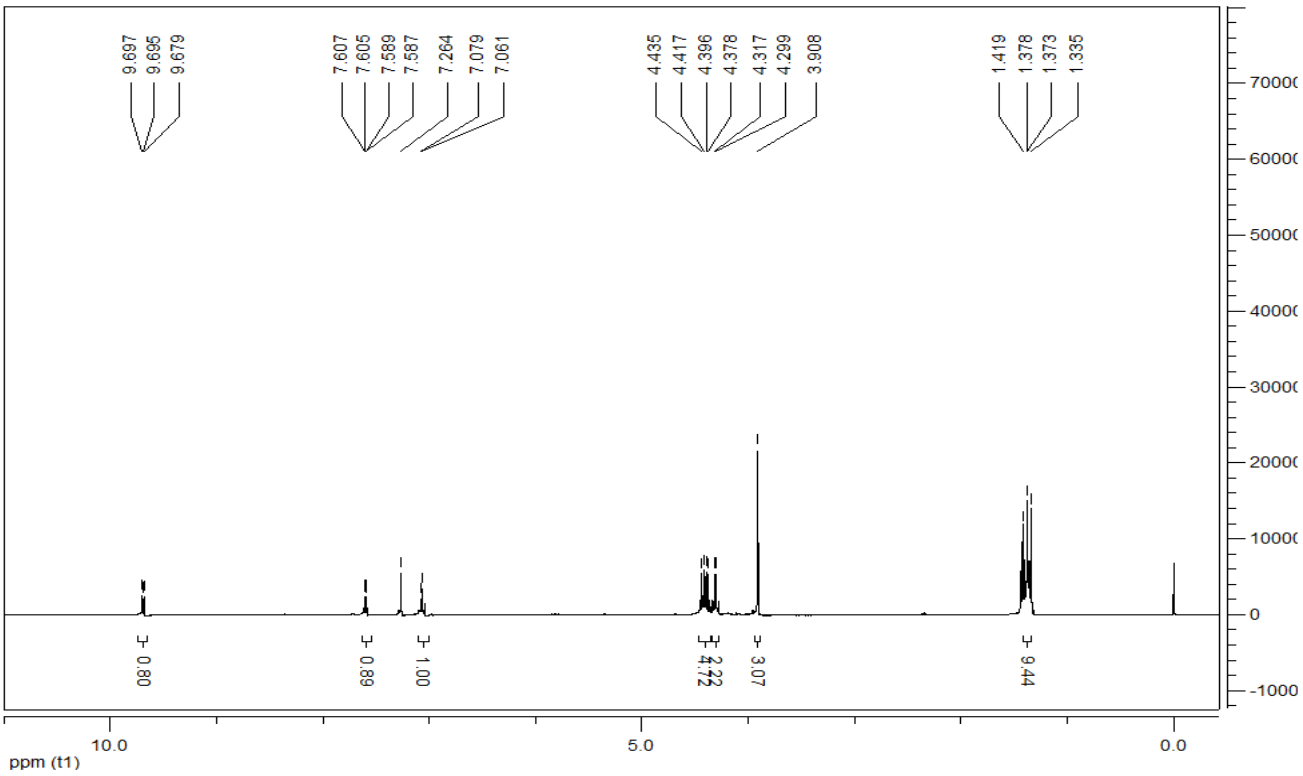
4p

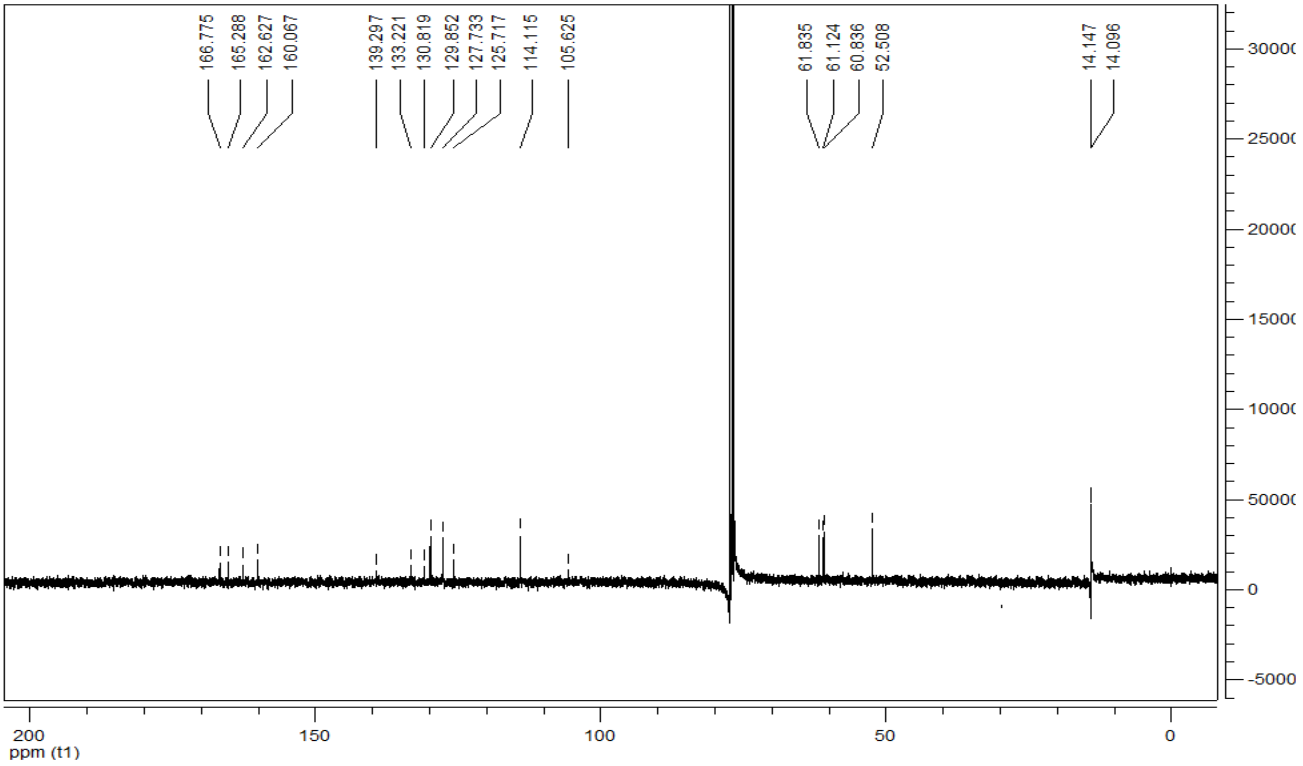

10.249
8.389
8.366
7.909
7.906
7.885
7.882
7.267
4.469
4.451
4.437
4.433
4.419
4.411
4.401
4.393
4.383
4.375
3.981
1.454
1.437
1.415
1.397
1.379
1.374
0.86
0.92
0.91
6.62
3.34
9.57
10.0
5.0
0.0
ppm (t1)

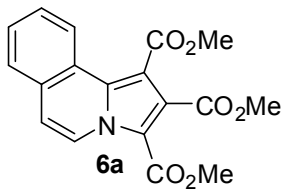

165.186
164.951
162.592
159.886
138.405
131.978
131.632
125.846
119.446
119.147
112.928
104.181
77.345
77.027
76.710
61.977
61.239
60.643
52.643
14.312
14.141
14.087
200
150
100
50
0
ppm (t1)

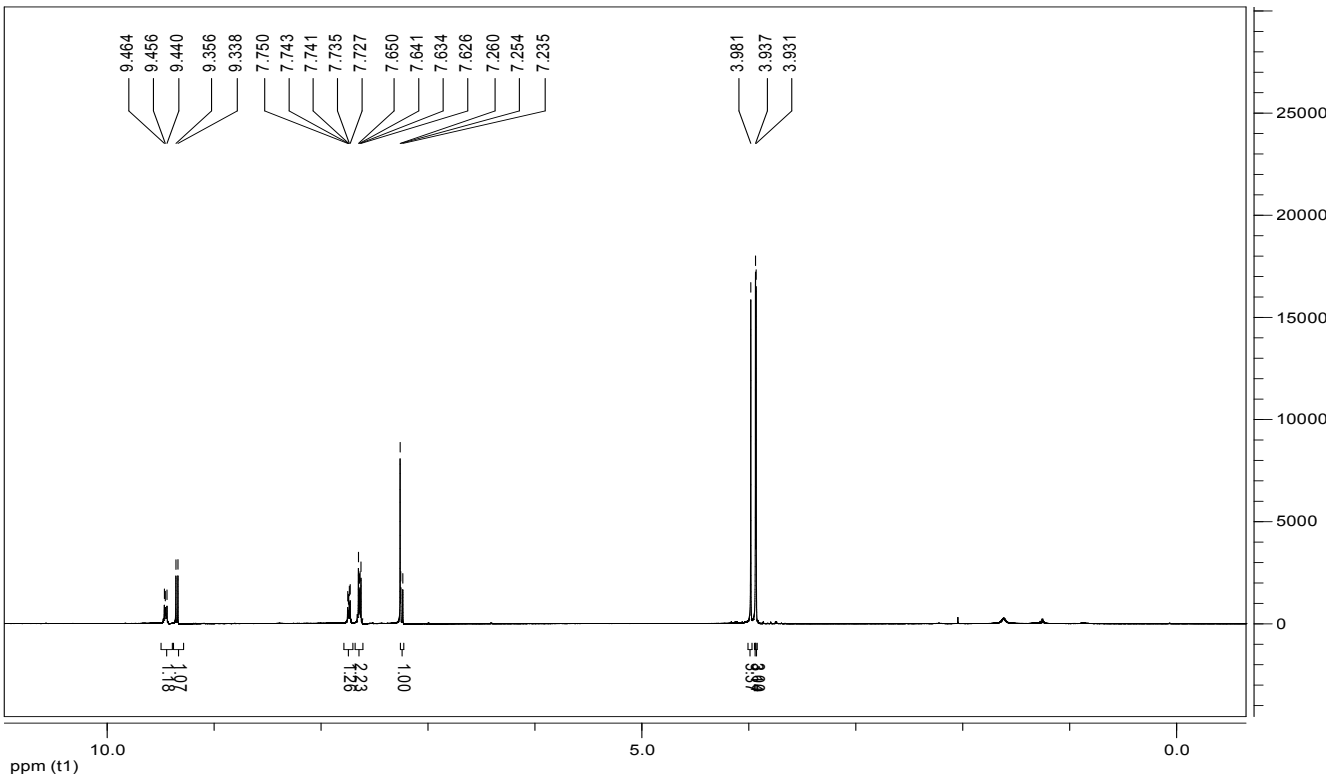

CO2Me
CO2Et
CO2Et
N
CO2Et

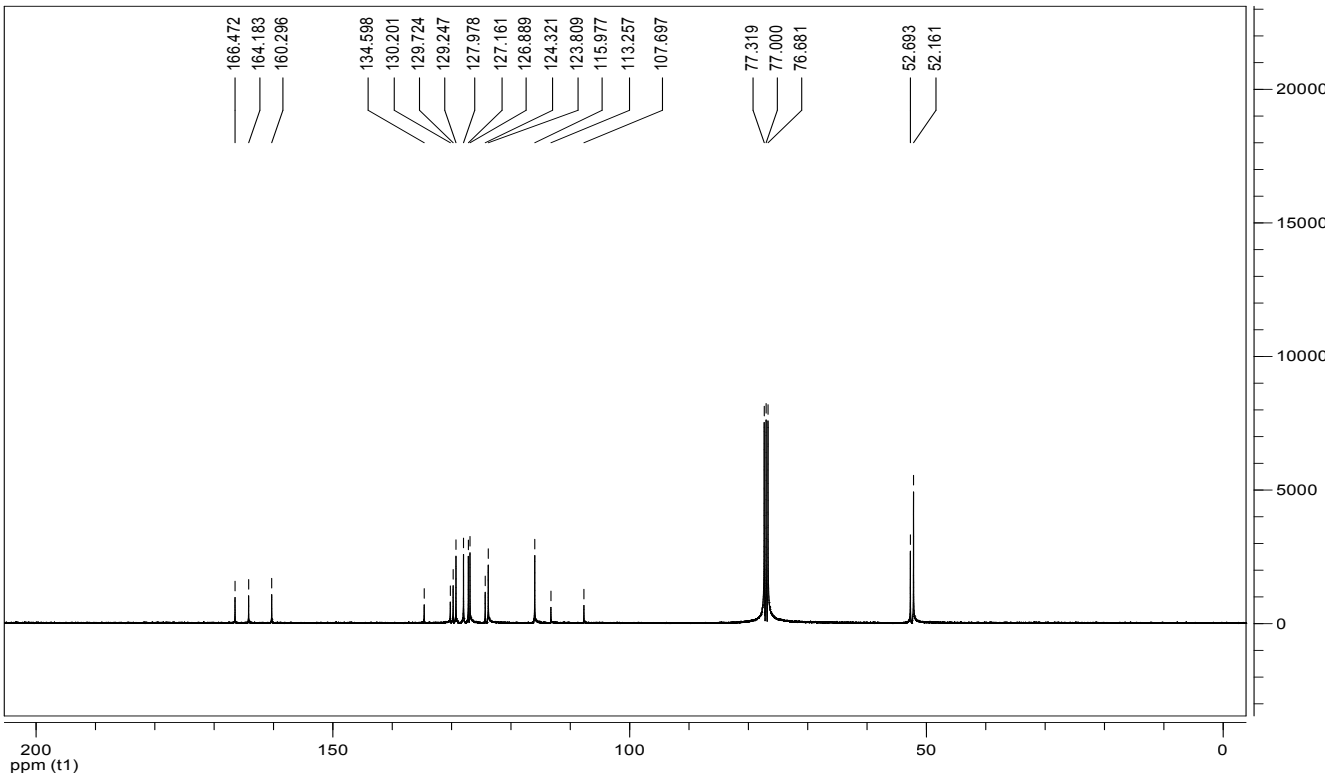
4q

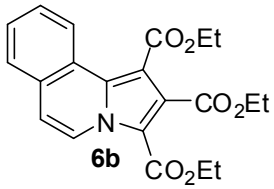

9.697
9.695
9.679
7.607
7.605
7.589
7.587
7.264
7.079
7.061
4.435
4.417
4.396
4.378
4.317
4.299
3.908
1.419
1.378
1.373
1.335
1.00
0.80
0.89
1.00
4.22
3.07
9.44
10.0
5.0
0.0
ppm (t1)


166.775
165.288
162.627
160.067
139.297
133.221
130.819
129.852
127.733
125.717
114.115
105.625
61.835
61.124
60.836
52.508
14.147
14.096
200
150
100
50
0
ppm (t1)

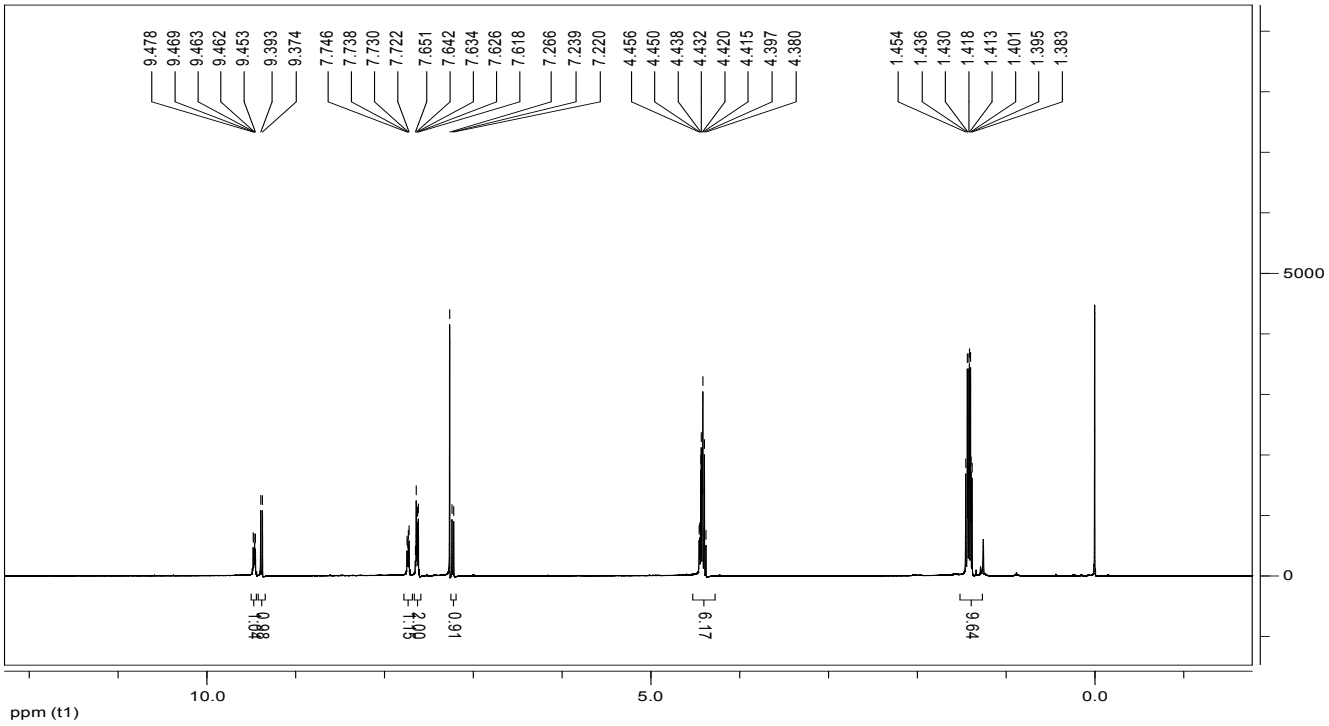

CO2Me
CO2Me
N
CO2Me
6a

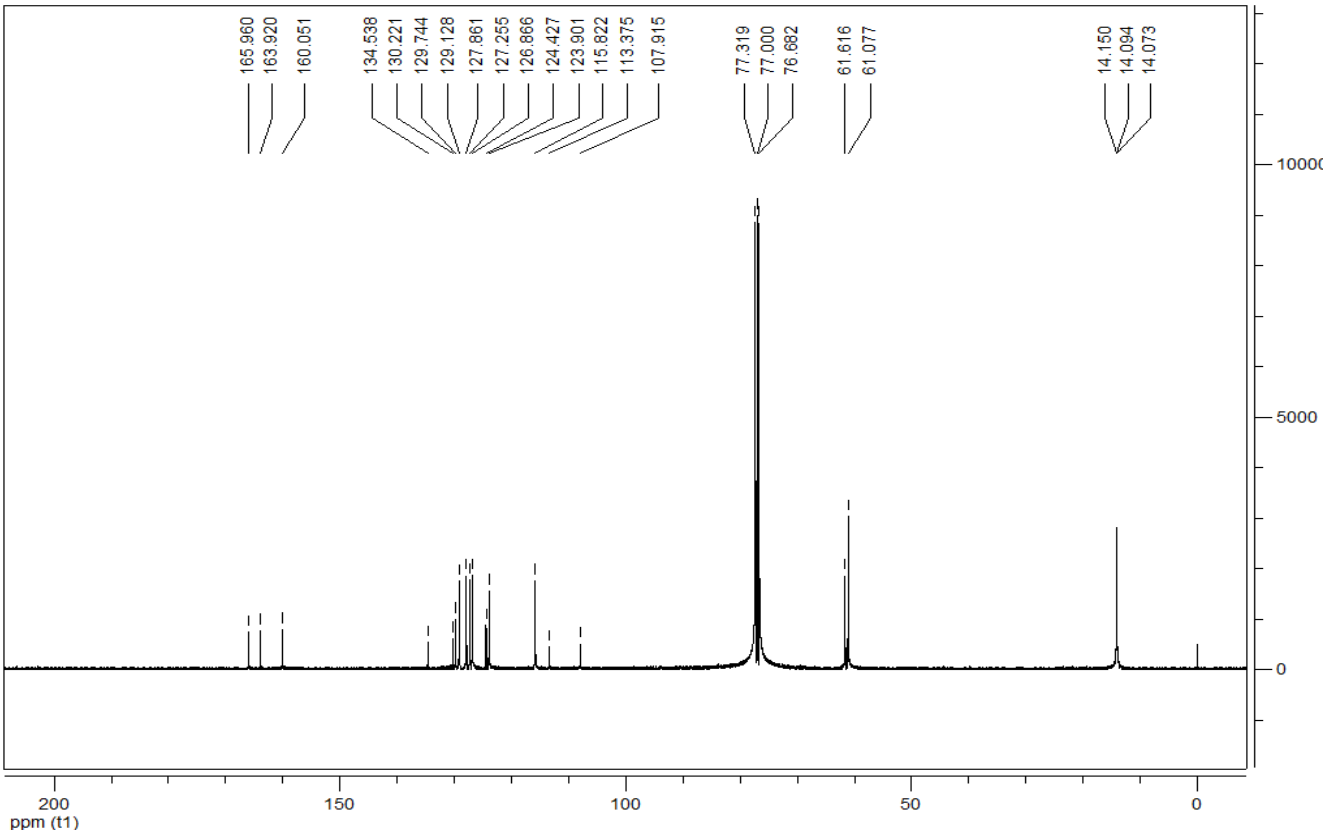

9.464
9.456
9.440
9.356
9.338
7.750
7.743
7.741
7.735
7.727
7.650
7.641
7.634
7.626
7.260
7.254
7.235
3.981
3.937
3.931
1.07
2.23
1.00
3.09
25000
20000
15000
10000
5000
0
10.0
5.0
0.0
ppm (t1)

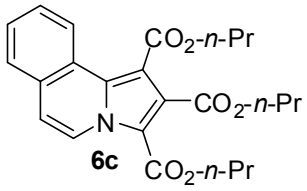

166.472
164.183
160.296
134.598
130.201
129.724
129.247
127.978
127.161
126.889
124.321
123.809
115.977
113.257
107.697
77.319
77.000
76.681
52.693
52.161
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)


CO2Et
CO2Et
N
CO2Et

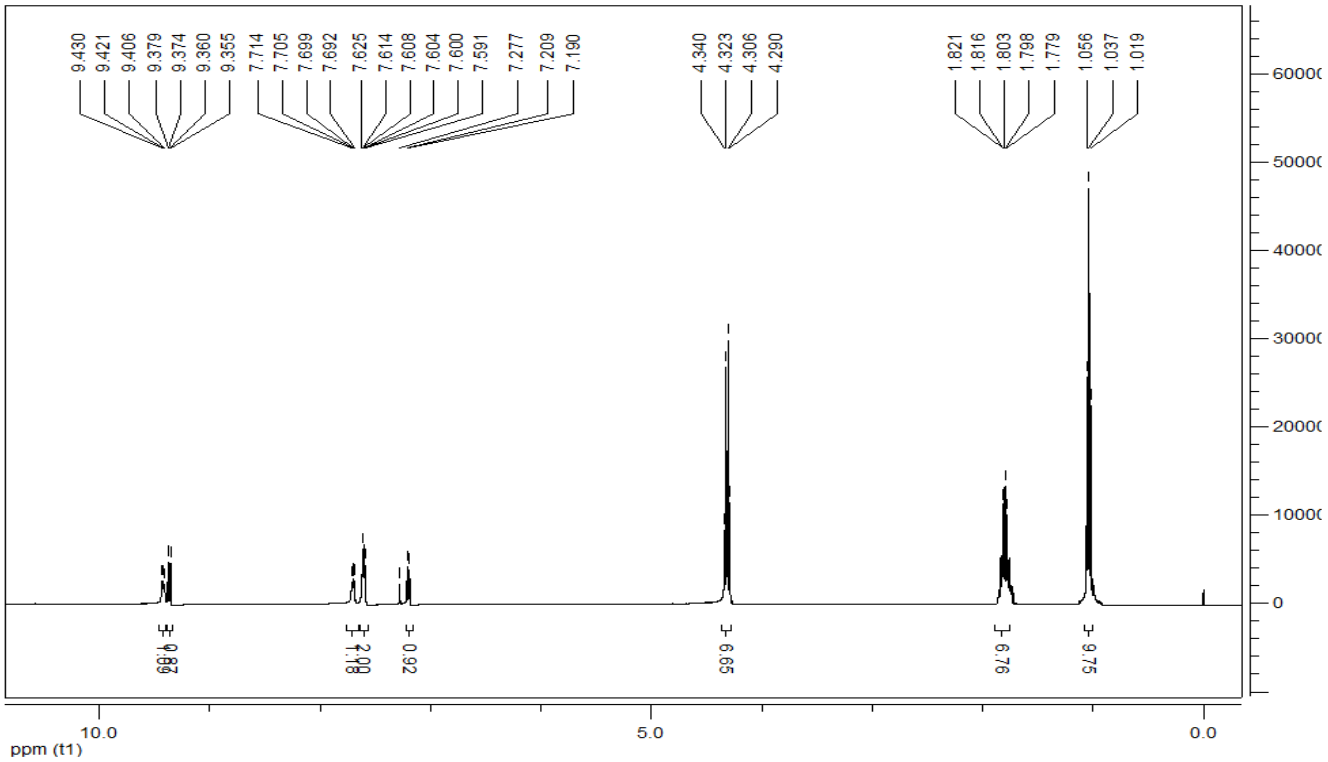
6b

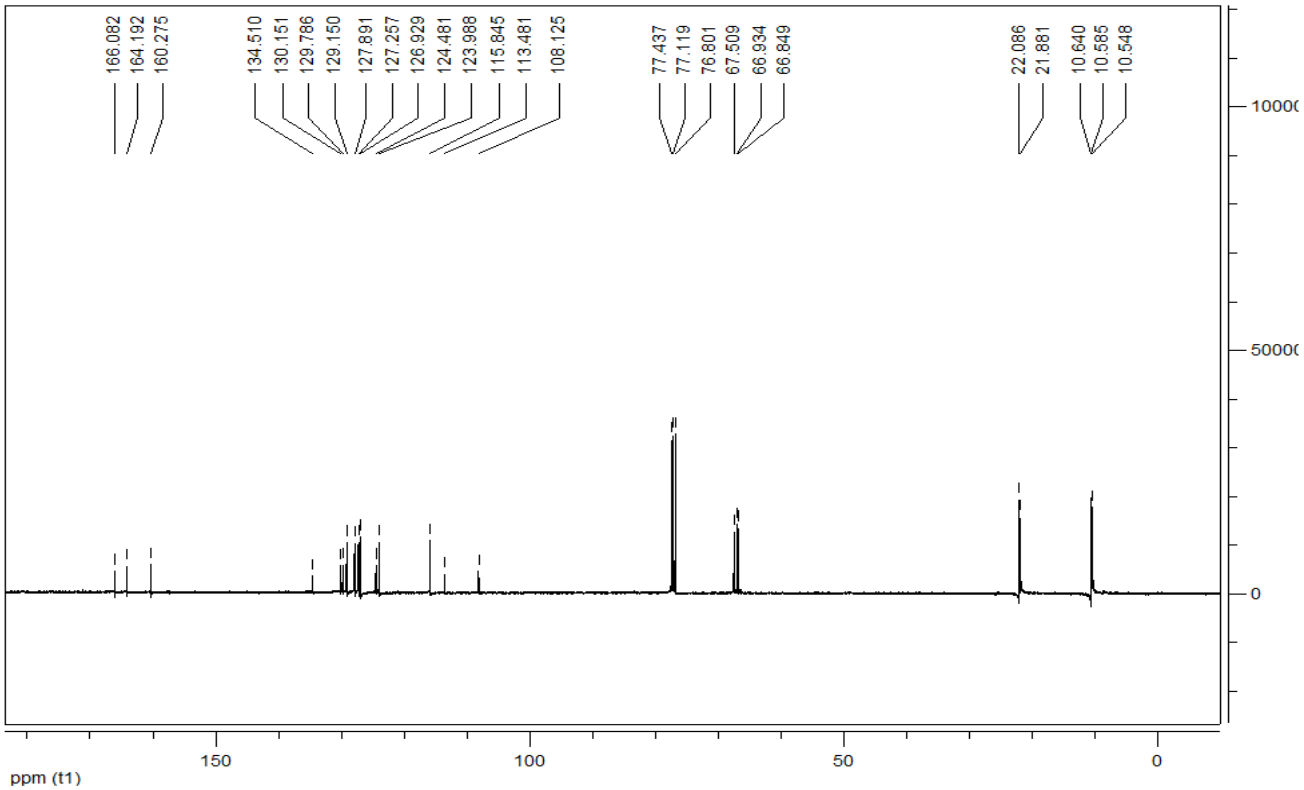

9.478
9.469
9.463
9.462
9.453
9.393
9.374
7.746
7.738
7.730
7.722
7.651
7.642
7.634
7.626
7.618
7.266
7.239
7.220
4.456
4.450
4.438
4.432
4.420
4.415
4.397
4.380
1.454
1.436
1.430
1.418
1.413
1.401
1.395
1.383
1.08
2.00
0.91
6.17
9.64
5000
0
10.0
5.0
0.0
ppm (t1)

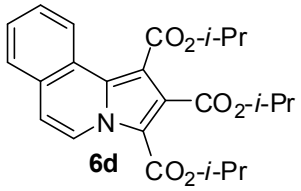

165.960
163.920
160.051
134.538
130.221
129.744
129.128
127.861
127.255
126.866
124.427
123.901
115.822
113.375
107.915
77.319
77.000
76.682
61.616
61.077
14.150
14.094
14.073
10000
5000
0
200
150
100
50
0
ppm (t1)


CO2-n-Pr
CO2-n-Pr
N
CO2-n-Pr

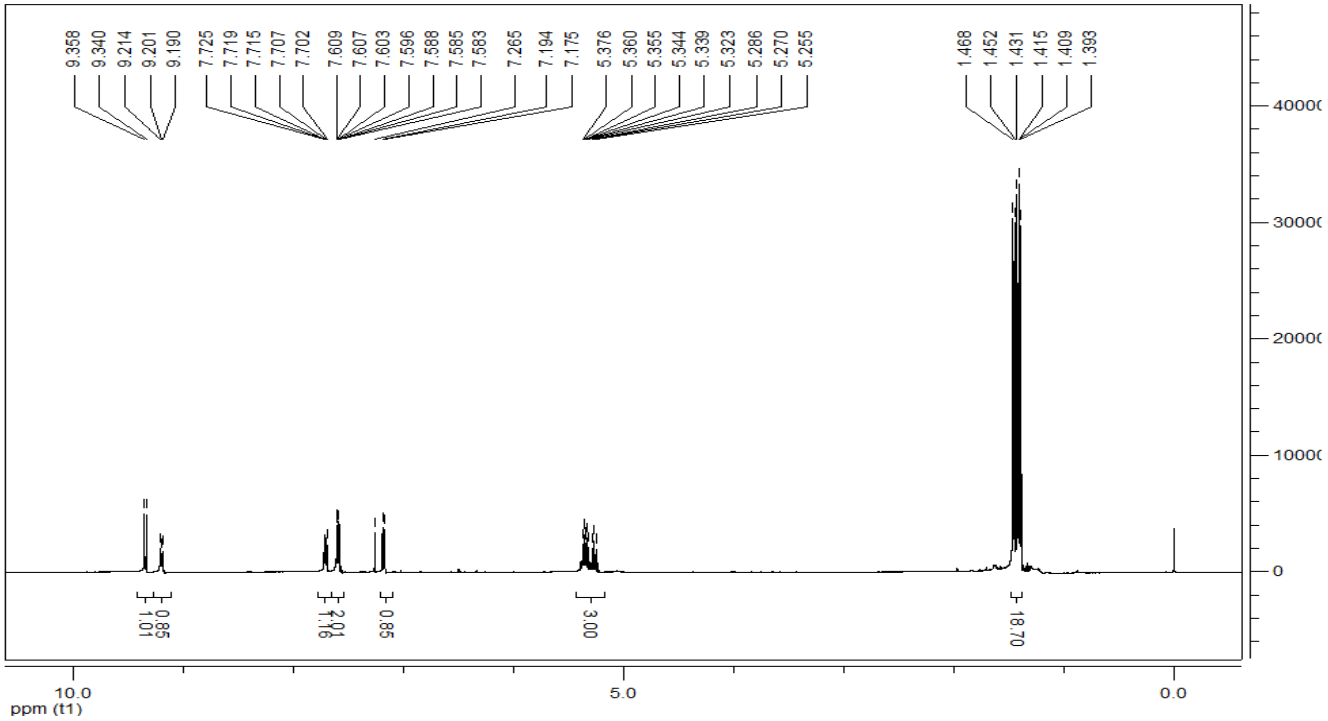
6c

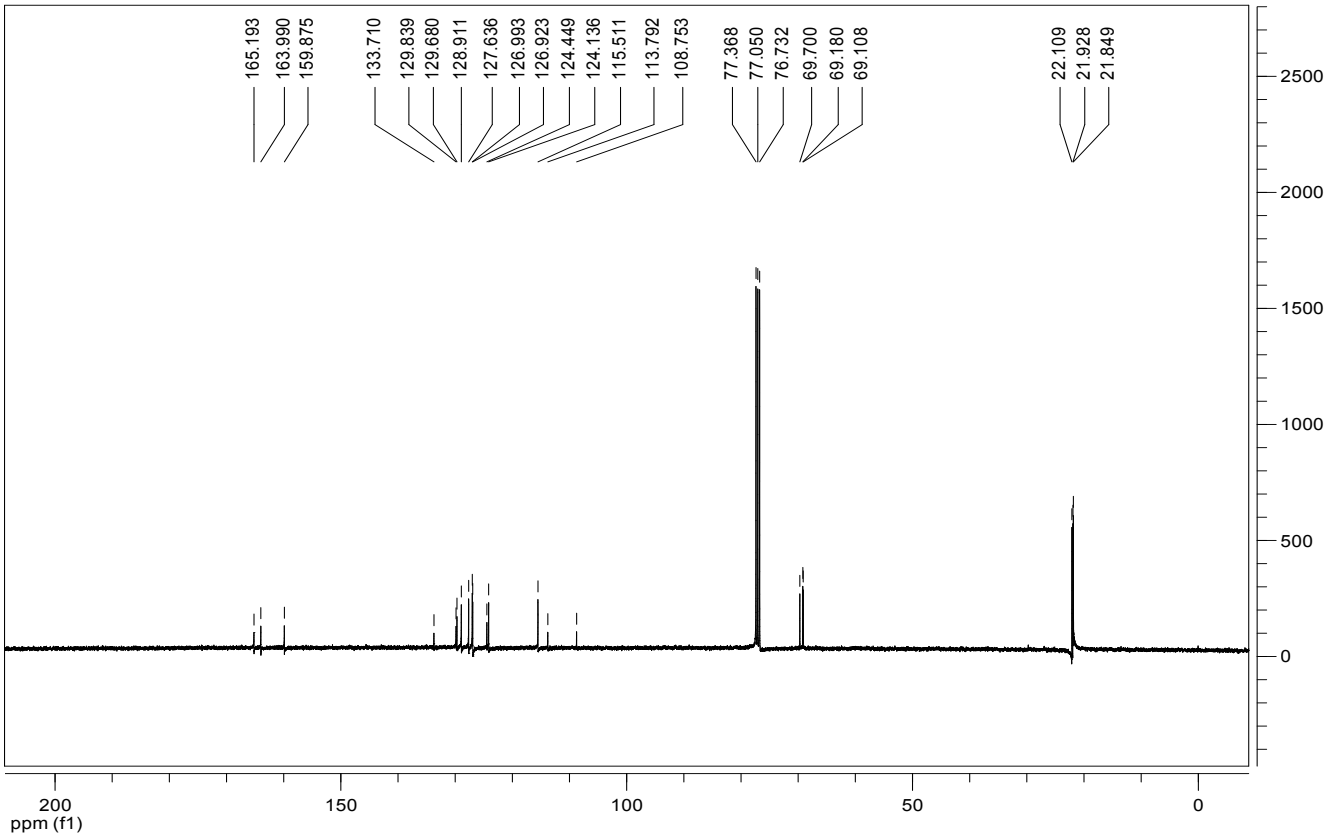

9.430
9.421
9.406
9.379
9.374
9.360
9.355
7.714
7.705
7.699
7.692
7.625
7.614
7.608
7.604
7.600
7.591
7.277
7.209
7.190
4.340
4.323
4.306
4.290
1.821
1.816
1.803
1.798
1.779
1.056
1.037
1.019
0.92
6.65
6.76
9.75
10.0
5.0
0.0
ppm (t1)

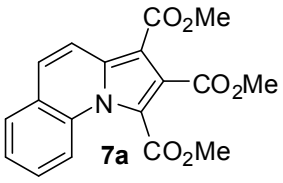

166.082
164.192
160.275
134.510
130.151
129.786
129.150
127.891
127.257
126.929
124.481
123.988
115.845
113.481
108.125
77.437
77.119
76.801
67.509
66.934
66.849
22.086
21.881
10.640
10.585
10.548
150
100
50
0
ppm (t1)

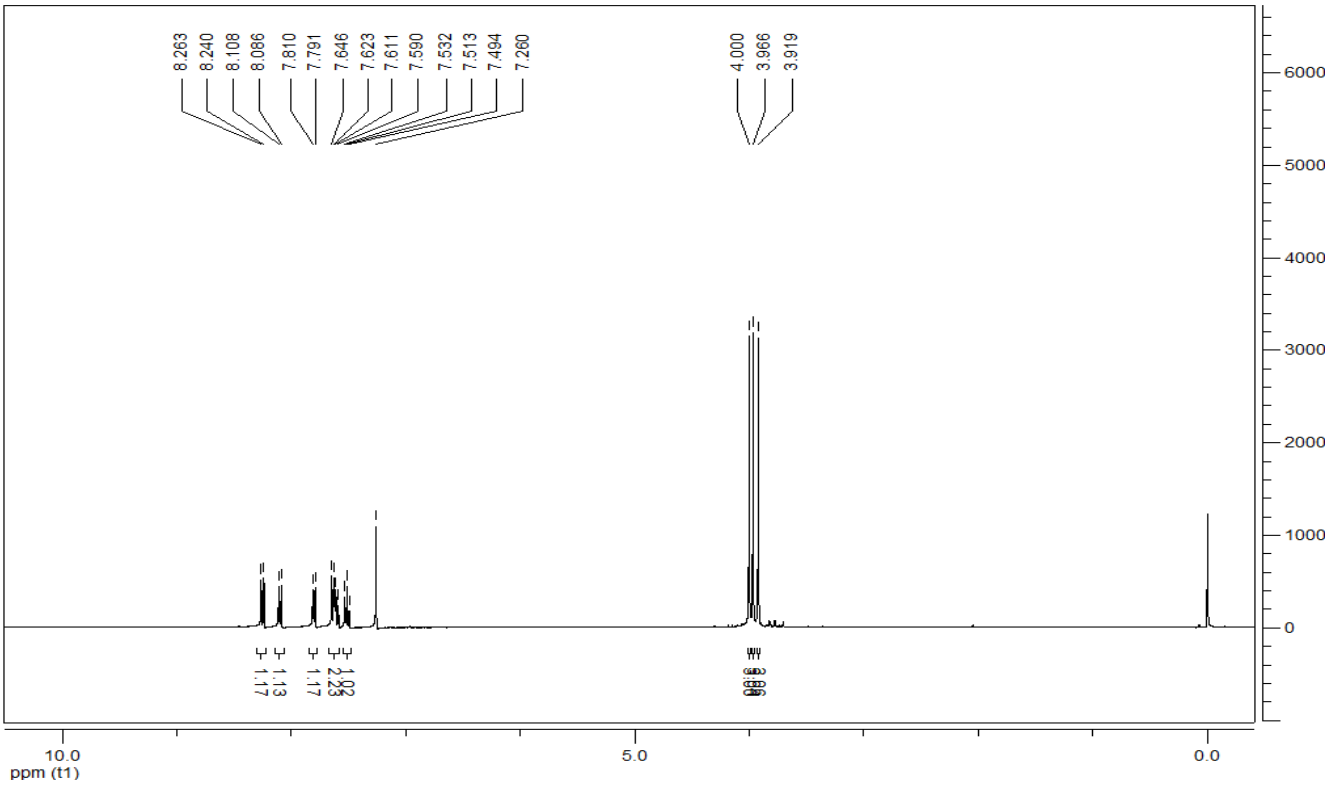

CO2-i-Pr
CO2-i-Pr
N
CO2-i-Pr

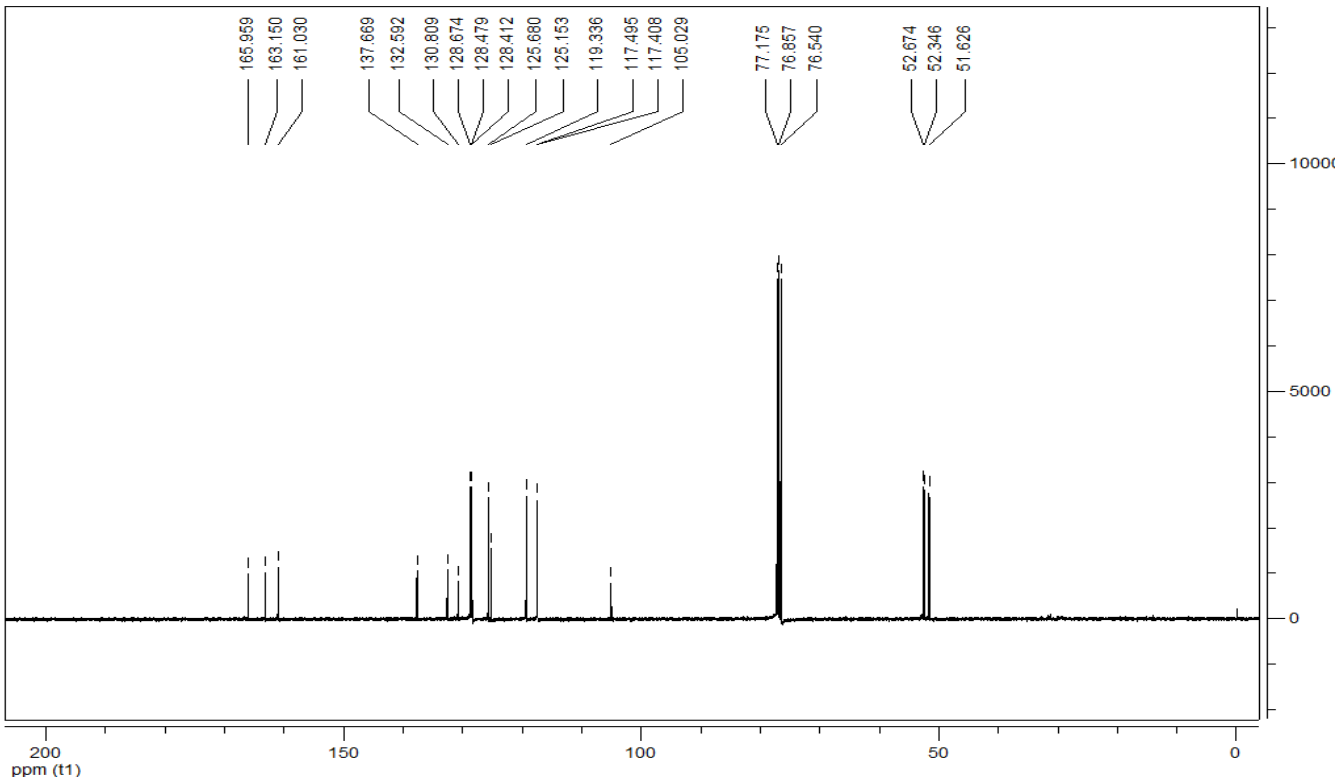
6d


9.358
9.340
9.214
9.201
9.190
7.725
7.719
7.715
7.707
7.702
7.609
7.607
7.603
7.596
7.588
7.585
7.583
7.265
7.194
7.175
5.376
5.360
5.355
5.344
5.339
5.323
5.286
5.270
5.255
1.468
1.452
1.431
1.415
1.409
1.393
1.01
0.85
2.16
2.01
0.85
3.00
18.70
10.0
5.0
0.0
ppm (t1)


165.193
163.990
159.875
133.710
129.839
129.680
128.911
127.636
126.993
126.923
124.449
124.136
115.511
113.792
108.753
77.368
77.050
76.732
69.700
69.180
69.108
22.109
21.928
21.849
200
150
100
50
0
ppm (f1)


CO2Me
CO2Me
N
7a
CO2Me


8.263
8.240
8.108
8.086
7.810
7.791
7.646
7.623
7.611
7.590
7.532
7.513
7.494
7.260
4.000
3.966
3.919
6000
5000
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (t1)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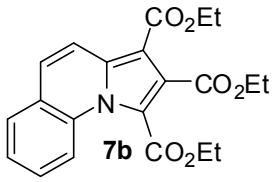
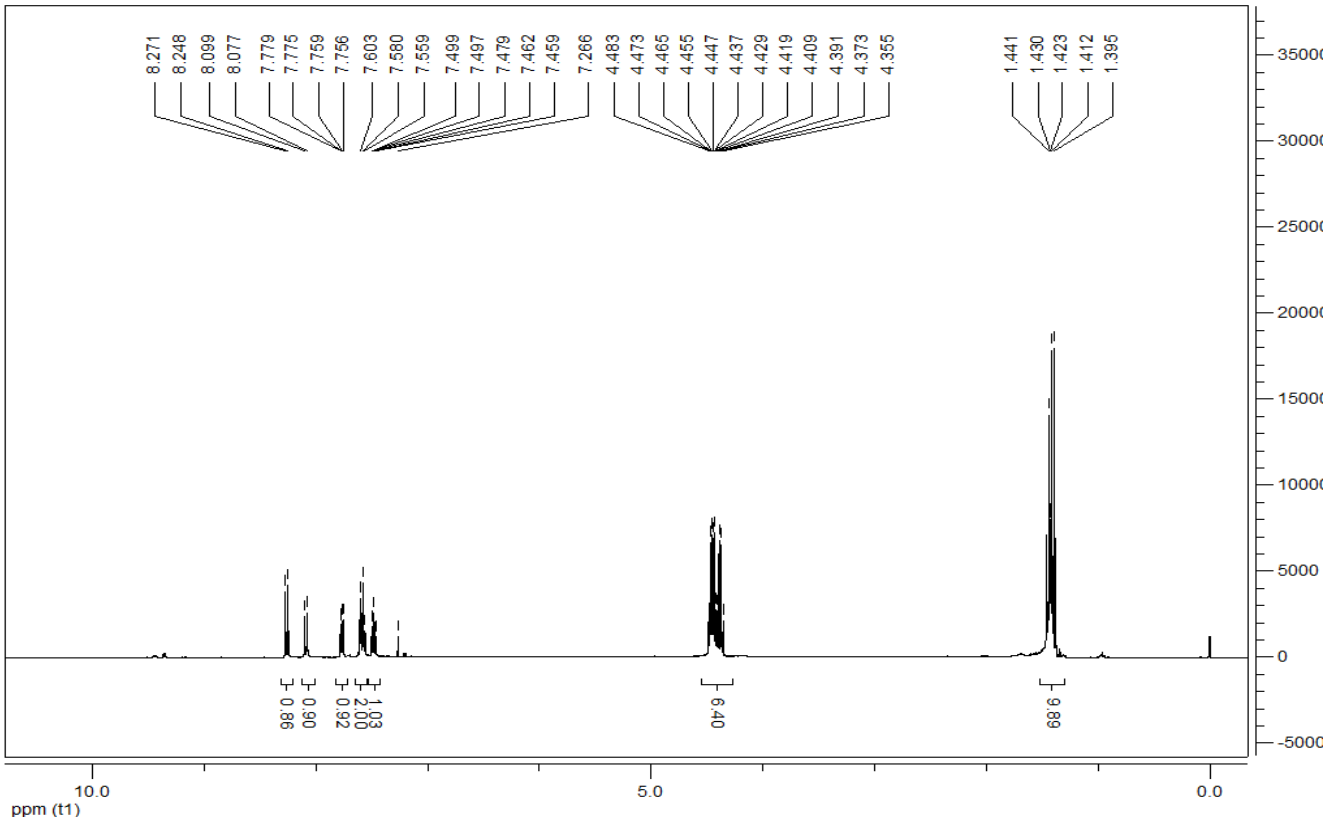
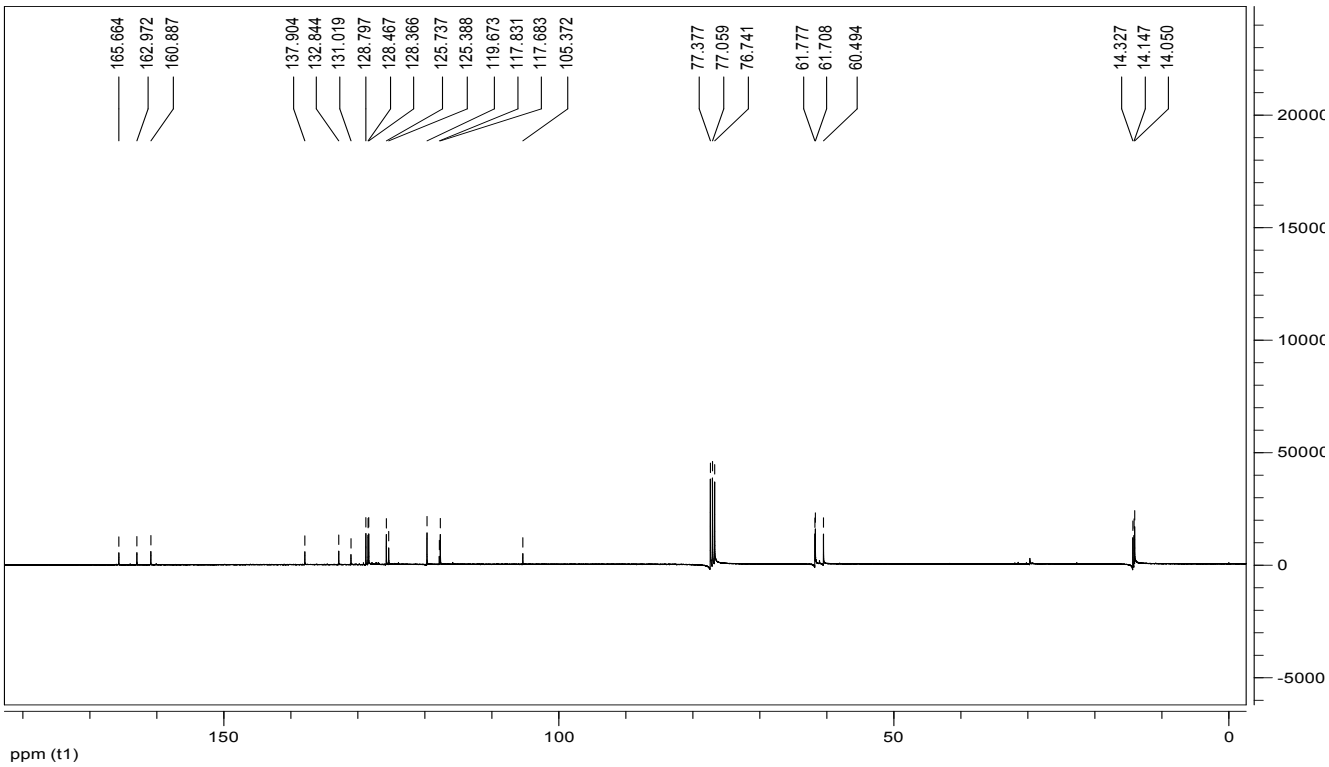
161.030
137.669
132.592
130.809
128.674
128.479
128.412
125.680
125.153
119.336
117.495
117.408
105.029
77.175
76.857
76.540
52.674
52.346
51.626
5000
0
200
150
100
50
0
ppm (t1)


CO2Et
CO2Et
N
7b
CO2Et


8.271
8.248
8.099
8.077
7.779
7.775
7.759
7.756
7.603
7.580
7.559
7.499
7.497
7.479
7.462
7.459
7.266
4.483
4.473
4.465
4.455
4.447
4.437
4.429
4.419
4.409
4.391
4.373
4.355
1.441
1.430
1.423
1.412
1.395
0.86
0.90
0.92
2.00
1.03
6.40
9.89
ppm (t1)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160.887
137.904
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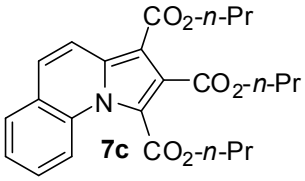
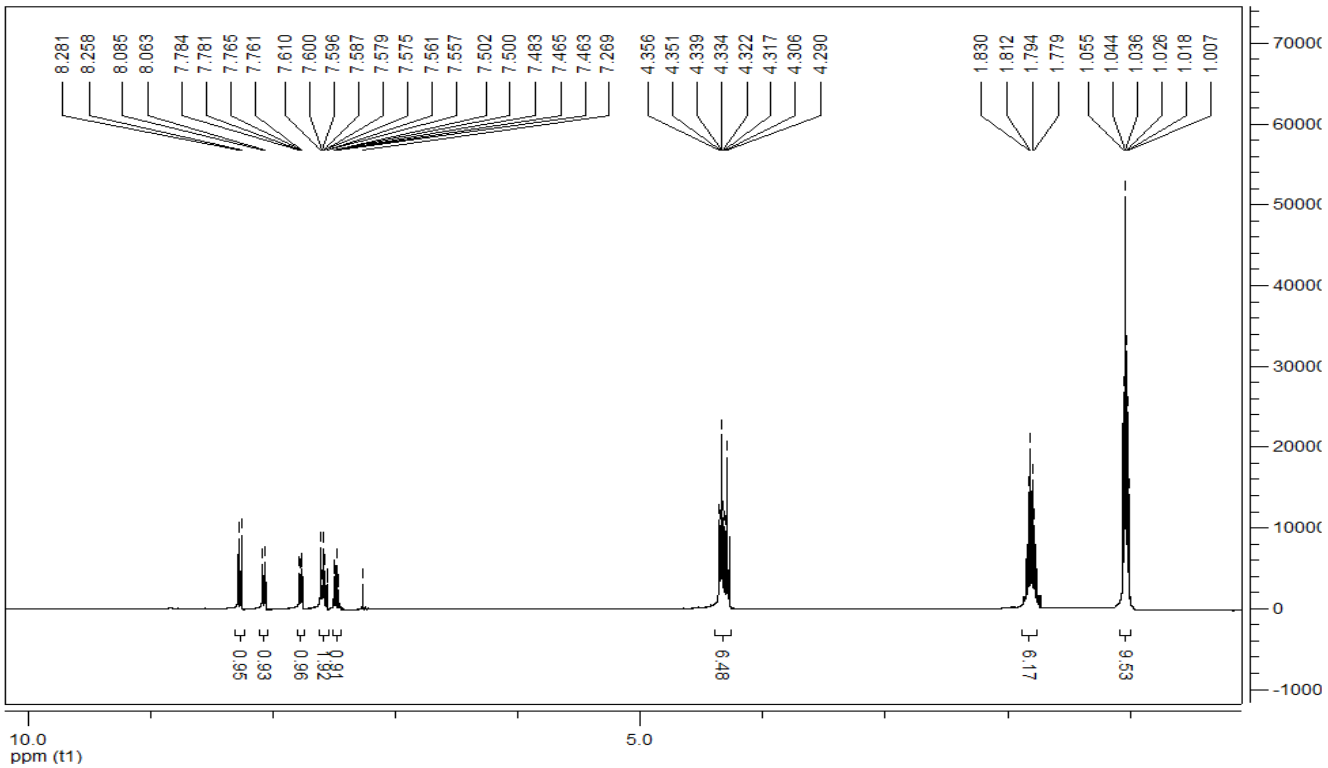
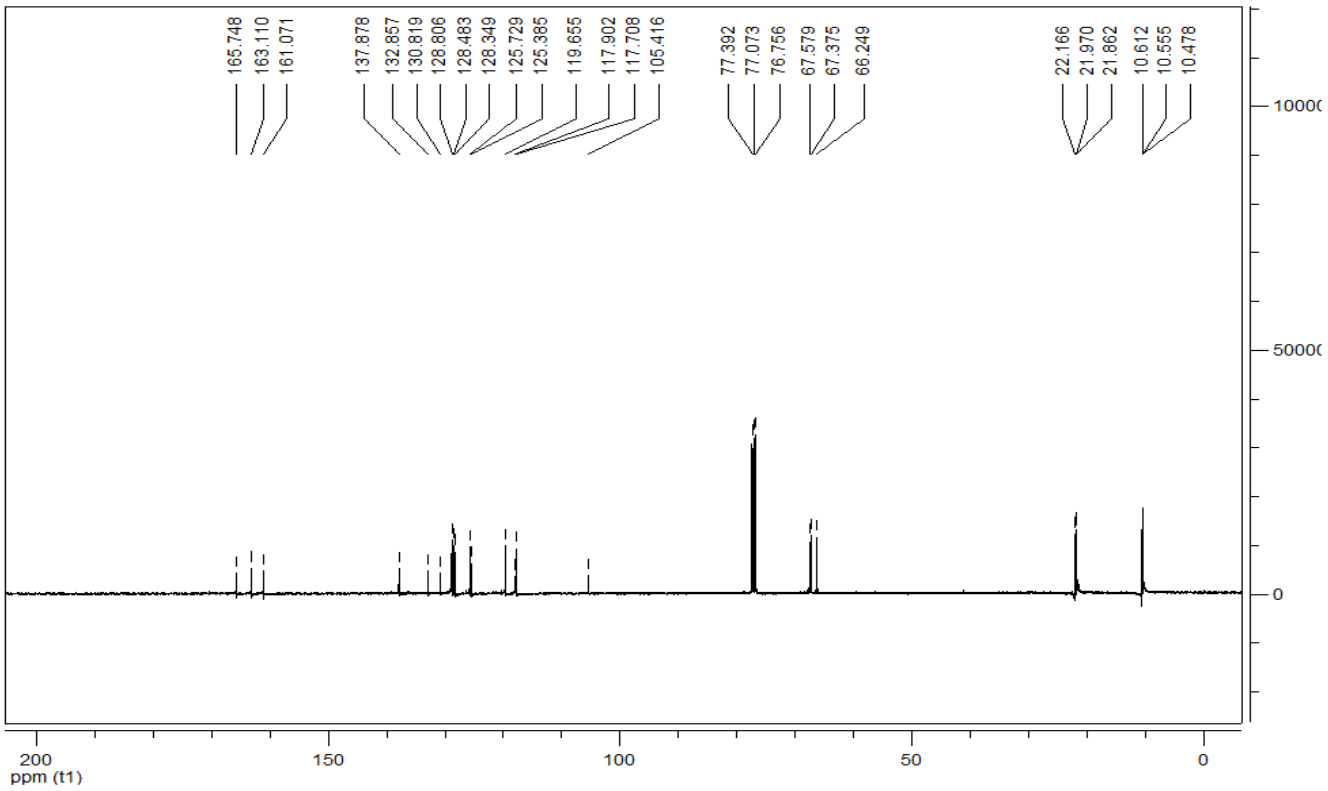
131.019
128.797
128.467
128.366
125.737
125.388
119.673
117.831
117.683
105.372
77.377
77.059
76.741
61.777
61.708
60.494
14.327
14.147
14.050
ppm (t1)


CO2-n-Pr
CO2-n-Pr
N
7c
CO2-n-Pr


8.281
8.258
8.085
8.063
7.784
7.781
7.765
7.761
7.610
7.600
7.596
7.587
7.579
7.575
7.561
7.557
7.502
7.500
7.483
7.465
7.463
7.269
4.356
4.351
4.339
4.334
4.322
4.317
4.306
4.290
1.830
1.812
1.794
1.779
1.055
1.044
1.036
1.026
1.018
1.007
0.96
0.93
0.96
0.92
0.91
6.48
6.17
9.63
70000
60000
50000
40000
30000
20000
10000
0
-1000
10.0
ppm (t1)
5.0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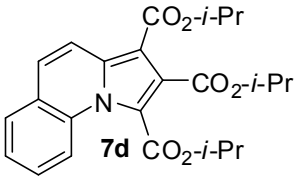
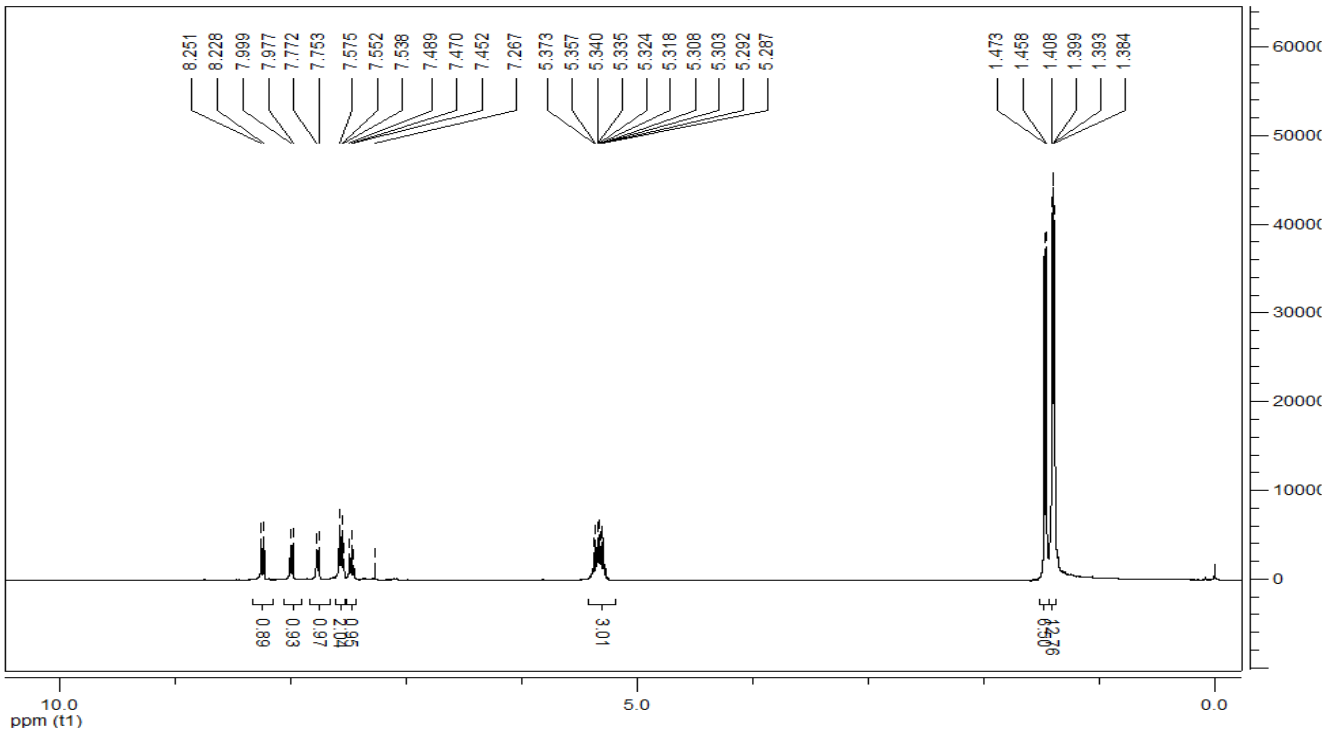
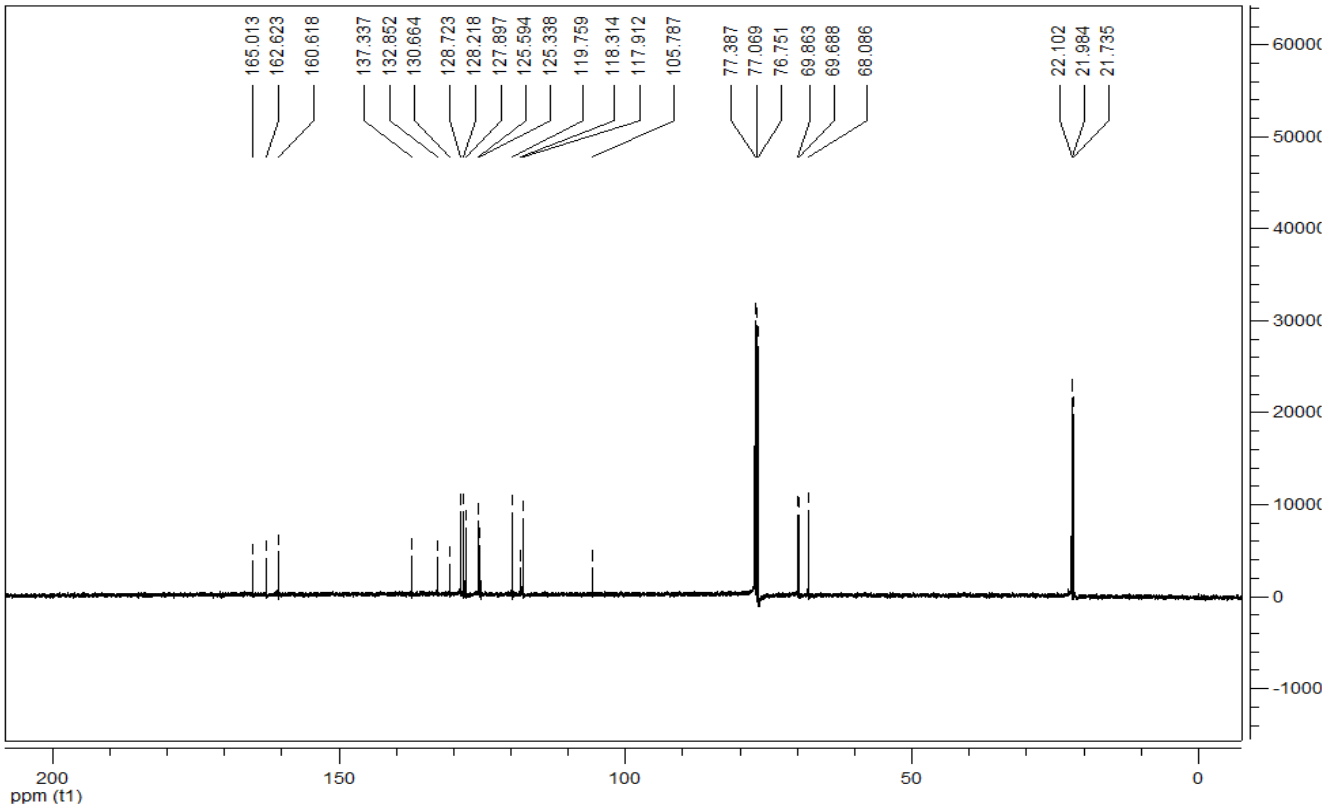
161.071
137.878
132.857
130.819
128.806
128.483
128.349
125.729
125.385
119.655
117.902
117.708
105.416
77.392
77.073
76.756
67.579
67.375
66.249
22.166
21.970
21.862
10.612
10.555
10.478
10000
5000
0
200
ppm (t1)
150
100
50
0


CO2-i-Pr
CO2-i-Pr
N
CO2-i-Pr

7d


8.251
8.228
7.999
7.977
7.772
7.753
7.575
7.552
7.538
7.489
7.470
7.452
7.267
5.373
5.357
5.340
5.335
5.324
5.318
5.308
5.303
5.292
5.287
1.473
1.458
1.408
1.399
1.393
1.384
0.89
0.93
0.97
2.04
2.06
3.01
6.26
10.0
ppm (t1)
5.0
0.0


165.013
162.623
160.618
137.337
132.852
130.664
128.723
128.218
127.897
125.594
125.338
119.759
118.314
117.912
105.787
77.387
77.069
76.751
69.863
69.688
68.086
22.102
21.984
21.735
200
ppm (t1)
150
100
50
0

X-ray crystallographic data of compound 4d

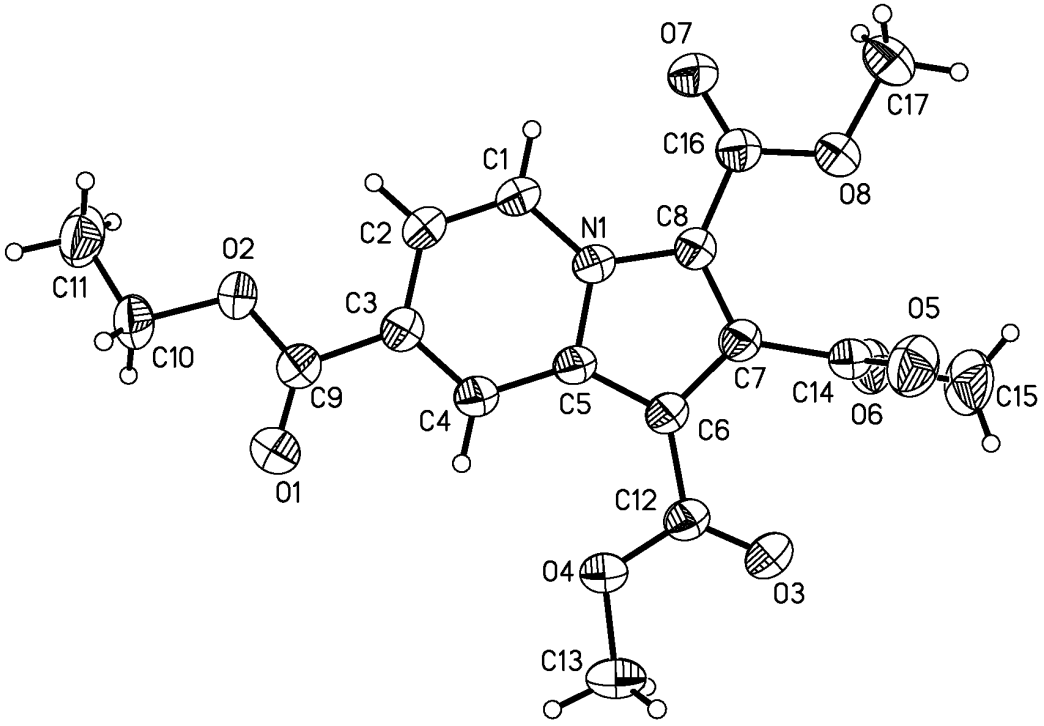


Figure 1. ORTEP drawing of **4d (**CCDC 1000659)