

Supplementary data

A simple and green approach for the synthesis of polyfunctionalized mono- and bis-dihydro-2-oxopyrroles catalyzed by trityl chloride

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Methyl 2,5-dihydro-2-oxo-1-phenyl-3-(phenylamino)-1H-pyrrole-4-carboxylate (5a). White solid, mp: 153-155 °C; ¹H NMR (400 MHz, CDCl₃): δ = 3.76 (s, 3H, OCH₃), 4.57 (s, 2H, CH₂), 7.16-7.23 (m, 4H, ArH), 7.34 (t, *J* = 8.0 Hz, 2H, ArH), 7.42 (t, *J* = 8.0 Hz, 2H, ArH), 7.81 (d, *J* = 8.0 Hz, 2H, ArH), 8.05 (br s, 1H, NH).

Ethyl 2,5-dihydro-2-oxo-1-phenyl-3-(phenylamino)-1H-pyrrole-4-carboxylate (5b). White solid, mp: 137-139 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.24 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 4.24 (t, *J* = 7.2 Hz, 2H, OCH₂CH₃), 4.52 (s, 2H, CH₂), 7.15-7.23 (m, 4H, ArH), 7.35 (d, 2H, *J* = 7.6 Hz, ArH), 7.41 (d, 2H, *J* = 7.6 Hz, ArH), 7.82 (d, 2H, *J* = 7.6 Hz, ArH), 8.01 (1H, br s, NH).

Methyl 3-(4-fluorophenylamino)-1-(4-fluorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5c). White solid, mp 163-165 °C; IR (KBr, cm⁻¹): ν = 3284 (NH), 1676 (C=O), 1649 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 3.79 (s, 3H, OCH₃), 4.52 (s, 2H, CH₂), 7.01-7.16 (m, 6H, ArH), 7.73-7.76 (m, 2H, ArH), 8.05 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ = 48.3, 51.4, 115.1 (d, *J*_{CF} = 23.0 Hz), 115.9 (d, *J*_{CF} = 22.0 Hz), 121.0 (d, *J*_{CF} = 7.0 Hz), 125.1 (d, *J*_{CF} = 8.0 Hz), 134.4 (d, *J*_{CF} = 3.0 Hz), 134.7 (d, *J*_{CF} = 2.0 Hz), 143.4, 153.7 (d, *J*_{CF} = 33.0 Hz), 161.2 (d, *J*_{CF} = 32.0 Hz), 163.5, 164.8.

Ethyl 3-(4-chlorophenylamino)-1-(4-chlorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5d). White solid, mp 168-170 °C; IR (KBr, cm⁻¹): ν = 3320 (NH), 1698 (C=O), 1640 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 1.29 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 4.27 (t, *J* = 7.2 Hz, 2H, OCH₂CH₃), 4.52 (s, 2H, CH₂), 7.09 (d, *J* = 8.8 Hz, 2H, ArH), 7.29 (d, *J* = 8.4 Hz, 2H, ArH), 7.37 (d, *J* = 8.8 Hz, 2H, ArH), 7.76 (d, *J* = 8.8 Hz, 2H, ArH), 8.07 (br s, 1H, NH); ¹³C NMR (100 MHz, CDCl₃): δ = 14.2, 48.1, 60.6, 104.2, 120.2, 123.9, 128.4, 129.2, 129.9, 130.2, 137.1, 137.2, 142.6, 163.6, 164.4.

Methyl 3-(4-bromophenylamino)-1-(4-bromophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5e). Yellow solid, mp: 175-177 °C; ¹H NMR (400 MHz, CDCl₃): δ = 3.78 (s, 3H, OCH₃), 4.50 (s, 2H, CH₂), 7.08 (d, *J* = 8.8 Hz, 2H, ArH), 7.30 (d, *J* = 8.4 Hz, 2H, ArH), 7.35 (d, *J* = 8.8 Hz, 2H, ArH), 7.72 (d, *J* = 8.8 Hz, 2H, ArH), 8.03 (br s, 1H, NH).

Ethyl 3-(4-bromophenylamino)-1-(4-bromophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5f). White solid, mp: 170-172 °C; ¹H NMR (400 MHz, CDCl₃): δ = 1.24 (t, *J* = 7.2 Hz, 3H, OCH₂CH₃), 4.24 (t, *J* = 7.2 Hz, 2H, OCH₂CH₃), 4.49 (s, 2H, CH₂), 7.09 (d, *J* = 8.0 Hz, 2H, ArH), 7.26-7.75 (m, 6H, ArH), 8.04 (br s, 1H, NH).

Ethyl 3-(4-methoxyphenylamino)-1-(4-methoxyphenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5g). Pall yellow solid, mp: 152-154 °C; IR (KBr, cm^{-1}): ν = 3264 (NH), 1692 (C=O), 1640 (C=O); ^1H NMR (400 MHz, CDCl_3): δ = 1.26 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 4.23 (q, J = 7.2 Hz, 2H, OCH_2CH_3), 4.49 (s, 2H, $\text{CH}_2\text{-N}$), 6.87 (d, J = 9.2 Hz, 2H, ArH), 6.93 (d, J = 9.2 Hz, 2H, ArH), 7.12 (d, J = 8.8 Hz, 2H, ArH), 7.69 (d, J = 9.2 Hz, 2H, ArH), 8.03 (s, 1H, NH); ^{13}C NMR (100 MHz, CDCl_3): δ = 14.3, 48.4, 55.4, 55.5, 60.1 (OCH_2CH_3), 101.3, 113.5, 114.2, 120.9, 124.8, 131.7, 132.0, 143.7, 156.8, 157.0, 163.5, 164.8.

Methyl 3-(p-tolylamino)-2,5-dihydro-2-oxo-1-p-tolyl-1H-pyrrole-4-carboxylate (5h). White solid, mp: 175-177 °C; ^1H NMR (400 MHz, CDCl_3): δ = 2.35 (s, 6H, 2CH_3), 3.79 (s, 3H, OCH_3), 4.41 (s, 2H, CH_2), 7.08 (d, J = 8.0 Hz, 2H, ArH), 7.15 (d, J = 8.2 Hz, 2H, ArH), 7.22 (d, J = 8.4 Hz, 2H, ArH), 7.63 (d, J = 8.4 Hz, 2H, ArH), 8.04 (br s, 1H, NH).

Ethyl 3-(p-tolylamino)-2,5-dihydro-2-oxo-1-p-tolyl-1H-pyrrole-4-carboxylate (5i). Yellow solid, mp: 133-135 °C; ^1H NMR (400 MHz, CDCl_3): δ = 1.25 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 2.36 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 4.23 (t, J = 7.2 Hz, 2H, OCH_2CH_3), 4.52 (s, 2H, $\text{CH}_2\text{-N}$), 7.06 (d, J = 8.4 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.21 (d, J = 8.4 Hz, 2H, ArH), 7.69 (d, J = 8.8 Hz, 2H, ArH), 8.01 (br s, 1H, NH).

Methyl 3-(benzylamino)-2,5-dihydro-2-oxo-1-phenyl-1H-pyrrole-4-carboxylate (5j). White solid, mp: 138-140 °C; ^1H NMR (400 MHz, CDCl_3): δ = 3.80 (s, 3H, OCH_3), 4.48 (s, 2H, $\text{CH}_2\text{-N}$), 5.10 (d, J = 6.4 Hz, 2H, $\text{CH}_2\text{-NH}$), 6.95 (br s, 1H, NH), 7.18-7.41 (m, 8H, ArH), 7.73 (d, J = 8.0 Hz, 2H, ArH).

Ethyl 3-(benzylamino)-2,5-dihydro-2-oxo-1-phenyl-1H-pyrrole-4-carboxylate (5k). White solid, mp: 127-129 °C; ^1H NMR (400 MHz, CDCl_3): δ = 1.27 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 4.24 (t, J = 7.2 Hz, 2H, OCH_2CH_3), 4.44 (s, 2H, $\text{CH}_2\text{-N}$), 5.11 (d, J = 6.4 Hz, 2H, $\text{CH}_2\text{-NH}$), 6.92 (br s, 1H, NH), 7.17-7.38 (m, 8H, ArH), 7.73-7.75 (m, 2H, ArH).

Methyl 3-(benzylamino)-1-p-tolyl-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5l). White solid, mp 144-146 °C; IR (KBr, cm^{-1}): ν = 3310 (NH), 1696 (C=O), 1646 (C=O); ^1H NMR (400 MHz, CDCl_3): δ = 1.34 (t, J = 7.2 Hz, 3H, OCH_2CH_3), 4.27 (t, J = 7.2 Hz, 2H, OCH_2CH_3), 4.41 (s, 2H, $\text{CH}_2\text{-N}$), 5.12 (d, J = 6.5 Hz, 2H, $\text{CH}_2\text{-NH}$), 6.90 (br s, 1H, NH), 7.28-7.37 (m, 5H, ArH),

7.52 (d, $J = 8.8$ Hz, 2H, ArH), 7.70 (d, $J = 8.8$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 20.9, 46.6, 48.0, 51.0, 97.1, 119.4, 127.3, 127.5, 128.7, 129.6, 134.8, 136.2, 139.5, 164.3, 165.6$.

Methyl 3-(benzylamino)-1-(4-chlorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5m). White solid, mp: 145-147 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.80$ (s, 3H, OCH_3), 4.43 (s, 2H, $\text{CH}_2\text{-N}$), 5.12 (d, $J = 6.0$ Hz, 2H, $\text{CH}_2\text{-NH}$), 6.95 (br s, 1H, NH), 7.28-7.39 (m, 7H, ArH), 7.73 (d, $J = 8.8$ Hz, 2H, ArH).

Methyl 3-(benzylamino)-1-(4-bromophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5n). Yellow solid, mp: 117-118 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 3.77$ (s, 3H, OCH_3), 4.41 (s, 2H, $\text{CH}_2\text{-N}$), 5.11 (d, $J = 6.4$ Hz, 2H, $\text{CH}_2\text{-NH}$), 6.85 (br s, 1H, NH), 7.28-7.37 (m, 5H, ArH), 7.52 (d, $J = 8.4$ Hz, 2H, ArH), 7.69 (d, $J = 8.8$ Hz, 2H, ArH).

Methyl 3-(benzylamino)-1-(4-fluorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5o). White solid; mp: 166-168 °C; IR (KBr, cm^{-1}) $\nu = 3316$ (NH), 1701 (C=O), 1644 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.80$ (s, 3H, OCH_3), 4.42 (s, 2H, $\text{CH}_2\text{-N}$), 5.13 (d, $J = 6.4$ Hz, 2H, $\text{CH}_2\text{-NH}$), 8.90 (br s, 1H, NH), 7.09-7.13 (m, 2H, ArH), 7.29-7.38 (m, 5H, ArH), 7.72-7.75 (m, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 46.5, 48.2, 51.1, 97.3, 115.1, 115.7, 116.0, 121.1, 125.1, 127.4, 127.5, 128.7, 134.8$ (d, $J = 8.0$ Hz), 139.4, 159.8 (d, $J = 243.0$ Hz), 164.3, 165.4.

Methyl 3-((pyridin-2-yl)methylamino)-1-(4-chlorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5p). White solid; mp: 156-158 °C; IR (KBr, cm^{-1}) $\nu = 3306$ (NH), 1698 (C=O), 1628 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 3.84$ (s, 3H, OCH_3), 4.45 (s, 2H, $\text{CH}_2\text{-N}$), 5.25 (d, $J = 5.2$ Hz, 2H, $\text{CH}_2\text{-NH}$), 7.23-7.77 (m, 9H, NH and ArH), 8.64 (d, $J = 4.4$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 47.1, 48.0, 51.2, 120.3, 122.0, 122.4, 129.1, 130.1, 137.2, 137.3, 148.7, 157.1, 164.7, 169.5$; MS (EI, 70 eV): m/z (%) = 359 ($\text{M}+2$, 21), 357 (M^+ , 65), 327 (17), 325 (48), 298 (10), 279 (4), 247 (5), 192 (24), 190 (32), 171 (33), 158 (82), 144 (88), 111 (19), 93 (100), 65 (36); Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{ClN}_3\text{O}_3$: C, 60.42; H, 4.51; N, 11.74. Found: C, 60.71, H, 4.60, N, 11.87.

Methyl 3-((pyridin-2-yl)methylamino)-2,5-dihydro-2-oxo-1-p-tolyl-1H-pyrrole-4-carboxylate (5q). White solid, mp 106-108 °C; IR (KBr, cm^{-1}) $\nu = 3306$ (NH), 1693 (C=O), 1628 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 2.36$ (s, 3H, CH_3), 3.82 (s, 3H, OCH_3), 4.44 (s, 2H, $\text{CH}_2\text{-N}$), 5.25 (d, $J = 5.6$ Hz, 2H, $\text{CH}_2\text{-NH}$), 7.21 (d, $J = 8.8$ Hz, 3H, ArH), 7.33 (d, $J = 7.6$ Hz, 1H, ArH), 7.65-7.70 (m, 4H, NH and ArH), 8.63 (d, $J = 4.4$ Hz, 1H, ArH); ^{13}C NMR (100

MHz, CDCl₃): δ = 20.9, 47.5, 48.1, 51.1, 119.4, 121.7, 122.2, 129.6, 134.8, 136.2, 136.7, 149.1, 154.4, 164.5, 165.5.

Methyl 3-(butylamino)-2,5-dihydro-2-oxo-1-phenyl-1H-pyrrole-4-carboxylate (5r). White solid, mp: 62-63 °C; ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, J = 7.2 Hz, 3H, CH₃), 1.42 (sextet, J = 7.2 Hz, 2H, CH₂), 1.64 (quintet, J = 7.2 Hz, 2H, CH₂), 3.82 (s, 3H, OCH₃), 3.85 (t, J = 7.2 Hz, 2H, CH₂-NH), 4.45 (s, 2H, CH₂-N), 6.85 (br s, 1H, NH), 7.18 (d, J = 7.6 Hz, 1H, ArH), 7.40 (d, J = 7.6 Hz, 2H, ArH), 7.73 (d, J = 7.6 Hz, 2H, ArH).

Methyl 1-(4-bromophenyl)-3-(butylamino)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5s). Pale yellow solid, mp: 103-105 °C; ¹H NMR (400 MHz, CDCl₃): δ = 0.96 (t, J = 7.2 Hz, 3H, CH₃), 1.41 (sextet, J = 7.2 Hz, 2H, CH₂), 1.61 (quintet, J = 7.2 Hz, 2H, CH₂), 3.80 (s, 3H, OCH₃), 3.86 (t, J = 7.2 Hz, 2H, CH₂-NH), 4.41 (s, 2H, CH₂-N), 6.77 (br s, 1H, NH), 7.50 (d, J = 8.4 Hz, 2H, ArH), 7.73 (d, J = 8.4 Hz, 2H, ArH).

Ethyl 1-(4-bromophenyl)-3-(butylamino)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5t): White solid, m.p. 94-96 °C; IR (KBr, cm⁻¹) ν = 3323 (NH), 1698 (C=O), 1645 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, J = 7.2 Hz, 3H, CH₃), 1.35 (t, J = 7.2 Hz, 3H, OCH₂CH₃), 1.43 (sextet, J = 7.6 Hz, 2H, CH₂), 1.61 (quintet, J = 7.6 Hz, 2H, CH₂), 3.87 (t, J = 7.2 Hz, 2H, CH₂-NH), 4.28 (t, J = 7.2 Hz, 2H, OCH₂CH₃), 4.40 (s, 2H, CH₂-N), 6.72 (br s, 1H, NH), 7.52 (d, J = 8.8 Hz, 2H, ArH), 7.71 (d, J = 8.8 Hz, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 13.8, 14.5, 19.8, 33.4, 42.8, 47.8, 59.8, 98.1, 117.7, 120.6, 132.0, 137.9, 164.6, 165.5.

Methyl 3-(butylamino)-1-(4-fluorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5u). White solid, mp 81-83 °C; IR (KBr, cm⁻¹) ν = 3346 (NH), 1694 (C=O), 1638 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, J = 7.2 Hz, 3H, CH₃), 1.43 (sextet, J = 7.2 Hz, 2H, CH₂), 1.62 (quintet, J = 7.2 Hz, 2H, CH₂), 3.81 (s, 3H, OCH₃), 3.88 (t, J = 7.2 Hz, 2H, CH₂-NH), 4.40 (s, 2H, CH₂-N), 6.69 (br s, 1H, NH), 7.09-7.13 (m, 2H, ArH), 7.71-7.75 (m, 2H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 13.8, 19.8, 33.3, 42.5, 48.2, 51.0, 97.0, 115.8 (d, J = 23.0 Hz), 121.2 (d, J = 8.0 Hz), 134.8, 159.8 (d, J = 243.0 Hz), 164.5, 165.5;

Methyl 3-(butylamino)-1-(3,4-dichlorophenyl)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5v). White solid; mp: 97-99 °C; IR (KBr, cm⁻¹) ν = 3335 (NH), 1711 (C=O), 1642 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 0.97 (t, J = 7.2 Hz, 3H, CH₃), 1.44 (sextet, J = 7.2 Hz, 2H, CH₂), 1.63 (quintet, J = 7.2 Hz, 2H, CH₂), 3.82 (s, 3H, OCH₃), 3.87 (t, J = 7.2 Hz, 2H, CH₂-NH), 4.39 (s, 2H, CH₂-N), 6.75 (br s, 1H, NH), 7.46 (d, J = 8.8 Hz, 1H, ArH), 7.67 (dd, J = 9.0, 2.8 Hz, 1H,

m, ArH), 8.00 (d, $J = 2.8$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 13.8, 19.8, 33.3, 42.6, 47.6, 51.0, 96.1, 117.9, 120.5, 128.1, 130.5, 133.0, 138.2, 144.0, 164.5, 165.5$.

Methyl 3-(butylamino)-1-p-tolyl-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5w). White solid; mp: 89-91 °C; IR (KBr, cm^{-1}) $\nu = 3353$ (NH), 1685 (C=O), 1634 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 0.97$ (t, $J = 7.2$ Hz, 3H, CH_3), 1.44 (sextet, $J = 7.2$ Hz, 2H, CH_2), 1.62 (quintet, $J = 7.2$ Hz, 2H, CH_2), 2.36 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.89 (t, $J = 6.8$ Hz, 2H, $\text{CH}_2\text{-NH}$), 4.39 (s, 2H, $\text{CH}_2\text{-N}$), 6.76 (br s, 1H, NH), 7.21 (d, $J = 8.4$ Hz, 2H, ArH), 7.64 (d, $J = 8.4$ Hz, 2H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 13.8, 19.8, 20.8, 33.4, 42.5, 48.0, 50.9, 97.5, 119.4, 129.6, 134.7, 136.3, 164.3, 165.5$; MS (EI, 70 eV): m/z , (%) = 302 (M^+ , 74), 287 (4), 271 (8), 259 (57), 243 (100), 241 (62), 227 (73) 199 (14), 187 (17), 172 (9), 159 (19), 118 (30), 91 (42), 80 (21), 66 (34), 55 (19); Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3$: C, 67.53; H, 7.33; N, 9.26. Found: C, 67.42, H, 7.39, N, 9.33.

Ethyl 2,5-dihydro-2-oxo-1-phenyl-3-(propylamino)-1H-pyrrole-4-carboxylate (5x). White solid; mp: 76-78 °C; ^1H NMR (400 MHz, CDCl_3): $\delta = 0.99$ (t, $J = 7.2$ Hz, 3H, CH_3), 1.36 (t, $J = 7.2$ Hz, 3H, OCH_2CH_3), 1.62 (quintet, $J = 7.0$ Hz, 2H, CH_2), 3.83-3.86 (m, 2H, $\text{CH}_2\text{-NH}$), 4.27 (t, $J = 7.2$ Hz, 2H, OCH_2CH_3), 4.41 (s, 2H, $\text{CH}_2\text{-N}$), 6.79 (br s, 1H, NH), 7.20 (d, $J = 8.0$ Hz, 1H, ArH), 7.34-7.41 (m, 2H, ArH), 7.69-7.73 (m, 2H, ArH).

Methyl 1-(3,4-dichlorophenyl)-3-(propylamino)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate (5y). White solid; mp: 125-127 °C; IR (KBr, cm^{-1}) $\nu = 3328$ (NH), 1707 (C=O), 1643 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.00$ (t, $J = 7.2$ Hz, 3H, CH_3), 1.64 (sextet, $J = 7.2$ Hz, 2H, CH_2), 3.81 (s, 3H, OCH_3), 3.81-3.83 (m, 2H, $\text{CH}_2\text{-NH}$), 4.37 (s, 2H, $\text{CH}_2\text{-N}$), 6.72 (br s, 1H, NH), 7.45 (d, $J = 8.8$ Hz, 1H, ArH), 7.66 (dd, $J = 8.4, 2.4$ Hz, 1H, ArH), 8.00 (d, $J = 2.4$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, CDCl_3): $\delta = 11.1, 24.5, 44.4, 47.7, 51.0, 96.3, 117.9, 120.5, 128.1, 130.5, 133.0, 138.2, 164.5, 165.5$; MS (EI, 70 eV): m/z , (%) = 344 (M^+ , 34), 315 (26), 313 (45), 295 (15), 285 (47), 283 (100), 241 (10), 226 (5), 187 (10), 174 (15), 172 (18), 145 (13), 112 (16), 80 (23), 66 (33), 53 (16); Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{Cl}_2\text{N}_2\text{O}_3$: C, 52.49; H, 4.70; N, 8.16. Found: C, 52.76, H, 4.81, N, 8.23.

Bis-(ethyl 3-(methyleneamino)-1-phenyl-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate) (7a). White solid; mp: 159-161 °C; IR (KBr, cm^{-1}) $\nu = 3295$ (NH), 1698 (C=O), 1638 (C=O); ^1H NMR (400 MHz, CDCl_3): $\delta = 1.27$ (t, $J = 6.8$ Hz, 6H, $2\text{OCH}_2\text{CH}_3$), 4.12-4.16 (m, 8H, $2\text{OCH}_2\text{CH}_3$ and $2\text{CH}_2\text{-NH}$), 4.36 (s, 4H, $2\text{CH}_2\text{-N}$), 6.74 (br s, 2H, 2NH), 7.19 (t, $J = 7.6$ Hz, 2H, ArH), 7.39 (t, $J = 8.0$ Hz, 4H, ArH), 7.75 (d, $J = 7.6$ Hz, 4H, ArH); ^{13}C NMR (100 MHz,

CDCl₃): δ = 14.4, 43.8, 47.9, 59.8, 98.0, 119.3, 124.9, 129.0, 138.7, 164.5, 165.0; MS (EI, 70 eV): m/z , (%) = 518 (M⁺, 6), 472 (4), 426 (6), 272 (100), 259 (26), 213 (68), 199 (58), 187 (36), 173 (13), 158 (9), 104 (25), 66 (32), 55 (20); Anal. Calcd for C₂₈H₃₀N₄O₆: C, 64.85; H, 5.83; N, 10.80. Found: C, 65.04, H, 5.90, N, 10.95.

Bis-(methyl 2,5-dihydro-3-(methyleneamino)-2-oxo-1-phenyl-1H-pyrrole-4-carboxylate) (7b). White solid, mp 150-152 °C; IR (KBr, cm⁻¹) ν = 3308 (NH), 1698 (C=O), 1637 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 3.67 (s, 6H, 2OCH₃), 4.16-4.18 (m, 4H, 2CH₂-NH), 4.34 (s, 4H, 2CH₂-N), 6.71-6.78 (br m, 2H, 2NH), 7.19 (t, J = 7.6 Hz, 2H, ArH), 7.39 (t, J = 7.6 Hz, 4H, ArH), 7.74 (d, J = 7.6 Hz, 4H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 43.7, 47.9, 51.0, 115.1, 119.3, 125.0, 129.1, 138.6, 164.4, 165.3.

Bis-(ethyl 1-(4-methoxyphenyl)-3-(methyleneamino)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate) (7c). White solid; mp: 222-224 °C; IR (KBr, cm⁻¹) ν = 3306 (NH), 1695 (C=O), 1634 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (t, J = 7.2 Hz, 6H, 2OCH₂CH₃), 3.84 (s, 6H, 2OCH₃), 4.16-4.19 (m, 8H, 2OCH₂CH₃ and 2CH₂-NH), 4.33 (s, 4H, 2CH₂-N), 6.70 (br s, 2H, 2NH), 6.92 (d, J = 9.2 Hz, 4H, ArH), 7.63 (d, J = 9.2 Hz, 4H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 14.4, 41.5, 49.0, 55.5, 59.7, 114.2, 121.3, 131.9, 156.9, 164.1, 165.0; MS (EI, 70 eV): m/z , (%) = 578 (M⁺, 1), 368 (1), 272 (5), 213 (5), 149 (5), 123 (66), 108 (100), 80 (56), 65 (11), 53 (26); Anal. Calcd for C₃₀H₃₄N₄O₈: C, 62.27; H, 5.92; N, 9.68. Found: C, 62.59, H, 6.05, N, 9.80.

Bis-(ethyl 2,5-dihydro-3-(methyleneamino)-2-oxo-1-p-tolyl-1H-pyrrole-4-carboxylate) (7d). White solid, mp 210-212 °C; IR (KBr, cm⁻¹) ν = 3308 (NH), 1698 (C=O), 1636 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 1.28 (t, J = 7.2 Hz, 6H, 2OCH₂CH₃), 2.36 (s, 6H, 2OCH₃), 4.13-4.18 (m, 8H, 2OCH₂CH₃ and 2CH₂-NH), 4.33 (s, 4H, 2CH₂-N), 6.73 (br s, 2H, 2NH), 7.19 (d, J = 8.4 Hz, 4H, ArH), 7.62 (d, J = 8.4 Hz, 4H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 14.4, 20.9, 30.9, 43.8, 48.0, 59.8, 98.5, 119.4, 129.5, 134.6, 136.2, 164.3, 165.1

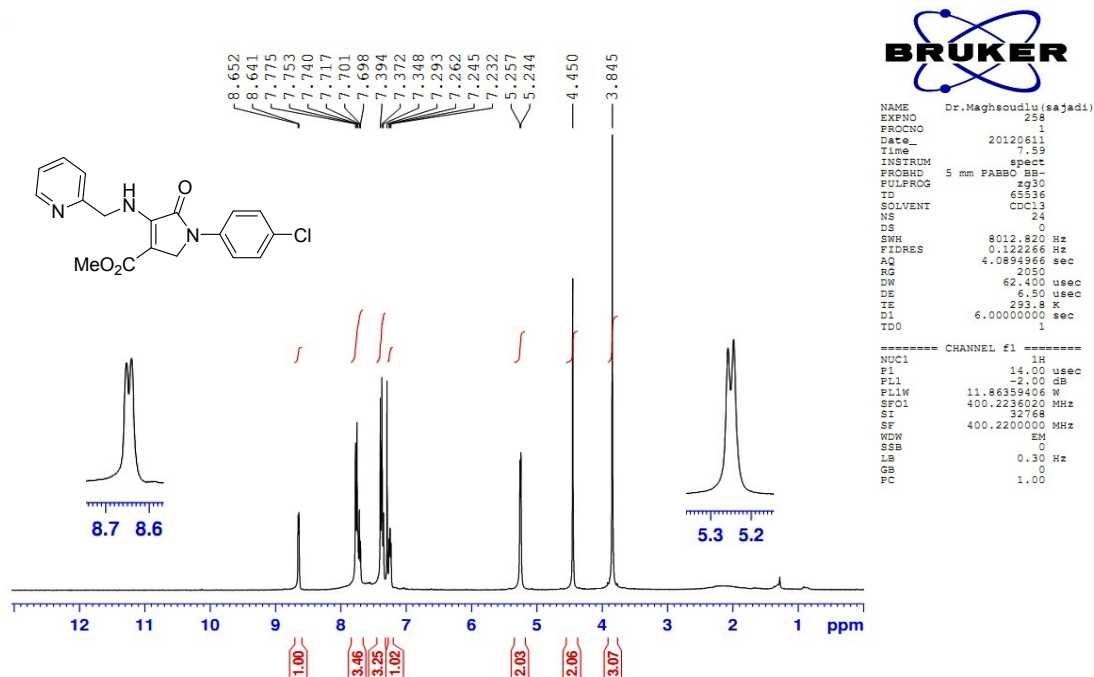
Bis-(methyl 1-(4-chlorophenyl)-3-(methyleneamino)-2,5-dihydro-2-oxo-1H-pyrrole-4-carboxylate) (7e). White solid; mp: 202-204 °C; IR (KBr, cm⁻¹) ν = 3308 (NH), 1698 (C=O), 1637 (C=O); ¹H NMR (400 MHz, CDCl₃): δ = 3.69 (s, 6H, 2OCH₃), 4.14-4.16 (m, 4H, 2CH₂-NH), 4.29 (s, 4H, 2CH₂-N), 6.75 (br s, 2H, 2NH), 7.34 (d, J = 8.8 Hz, 4H, ArH), 7.69 (d, J = 8.8 Hz, 4H, ArH); ¹³C NMR (100 MHz, CDCl₃): δ = 43.5, 47.9, 51.1, 98.0, 120.2, 129.1, 130.1, 137.2, 164.4, 165.2; MS (EI, 70 eV): m/z , (%) = 560 (M+2, 1), 558 (M⁺, 2), 441 (10), 336 (34), 304 (21), 292 (35), 280 (34), 266 (38), 247 (60), 221 (100), 138 (30), 111 (35), 91 (77), 69 (48),

57 (82), 55 (60); Anal. Calcd for $C_{26}H_{24}Cl_2N_4O_6$: C, 55.82; H, 4.32; N, 10.02. Found: C, 56.10, H, 4.40, N, 9.13.

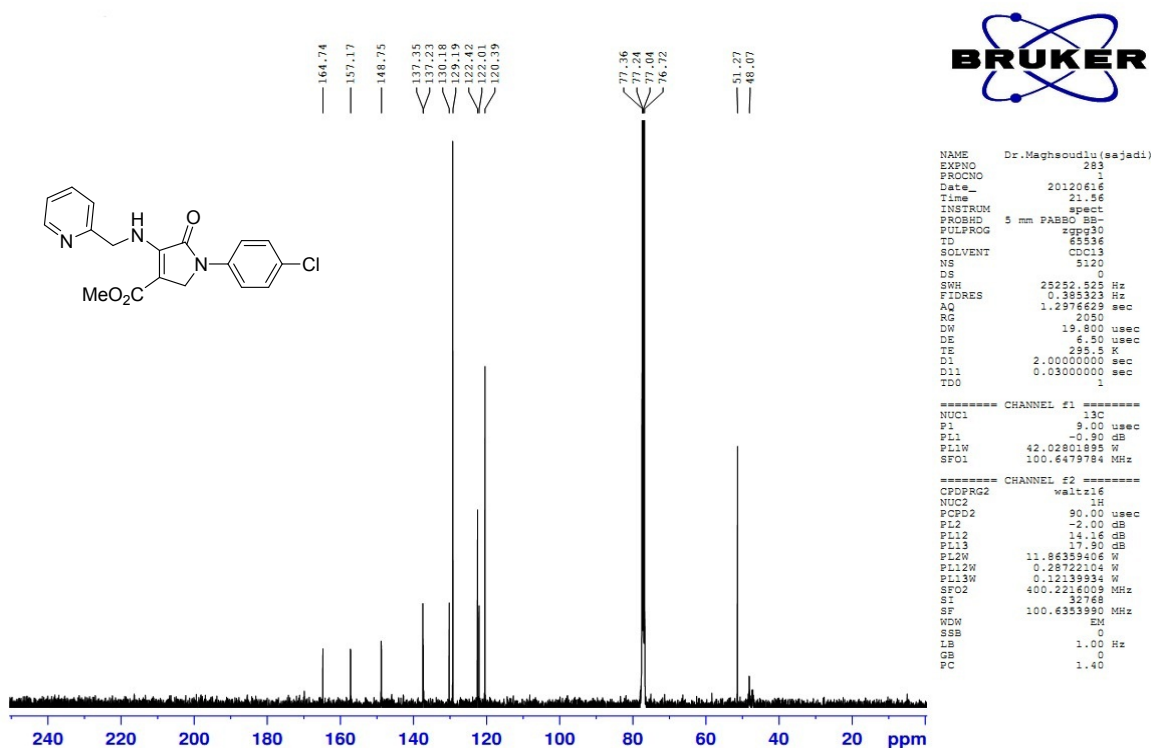
Bis-(ethyl 1-(3,4-dichlorophenyl)-2,5-dihydro-3-(methyleneamino)-2-oxo-1H-pyrrole-4-carboxylate) (7f). White solid, mp 206-208 °C; IR (KBr, cm^{-1}) ν = 3324 (NH), 1705 (C=O), 1642 (C=O); 1H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, J = 7.2 Hz, 6H, $2OCH_2CH_3$), 4.12-4.20 (br s, 8H, $2OCH_2CH_3$ and $2CH_2-NH$), 4.30 (s, 4H, $2CH_2-N$), 6.74 (br s, 2H, 2NH), 7.43 (d, J = 8.8 Hz, 2H, ArH), 7.59 (dd, J = 8.8, 2.4 Hz, 2H, ArH), 7.97 (d, J = 2.4 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 43.8, 47.6, 60.0, 98.5, 117.8, 120.5, 128.2, 130.5, 133.0, 138.1, 164.5, 165.4.

Bis-(methyl 1-(4-fluorophenyl)-2,5-dihydro-3-(methyleneamino)-2-oxo-1H-pyrrole-4-carboxylate) (7g). White solid, mp 198-200 °C; IR (KBr, cm^{-1}) ν = 3310 (NH), 1696 (C=O), 1637 (C=O); 1H NMR (400 MHz, $CDCl_3$): δ = 3.68 (s, 6H, $2OCH_3$), 4.15-4.16 (m, 4H, $2CH_2-NH$), 4.30 (s, 4H, $2CH_2-N$), 6.75 (br s, 2H, 2NH), 7.08 (t, J = 8.2 Hz, 4H, ArH), 7.67-7.71 (m, 4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.7, 48.2, 51.0, 98.0, 115.7 (d, J = 22.0 Hz), 120.9 (d, J = 7.0 Hz), 134.7 (d, J = 2.0 Hz), 159.7 (d, J = 243.0 Hz), 164.3, 165.2

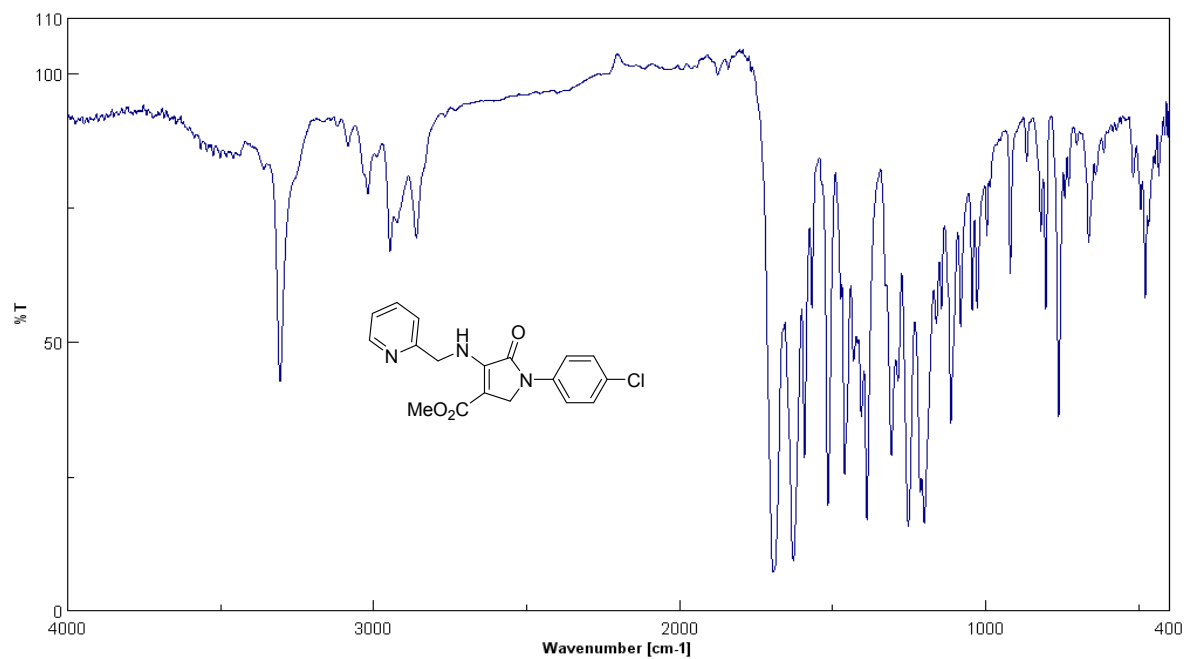
¹H NMR spectrum of **5p**



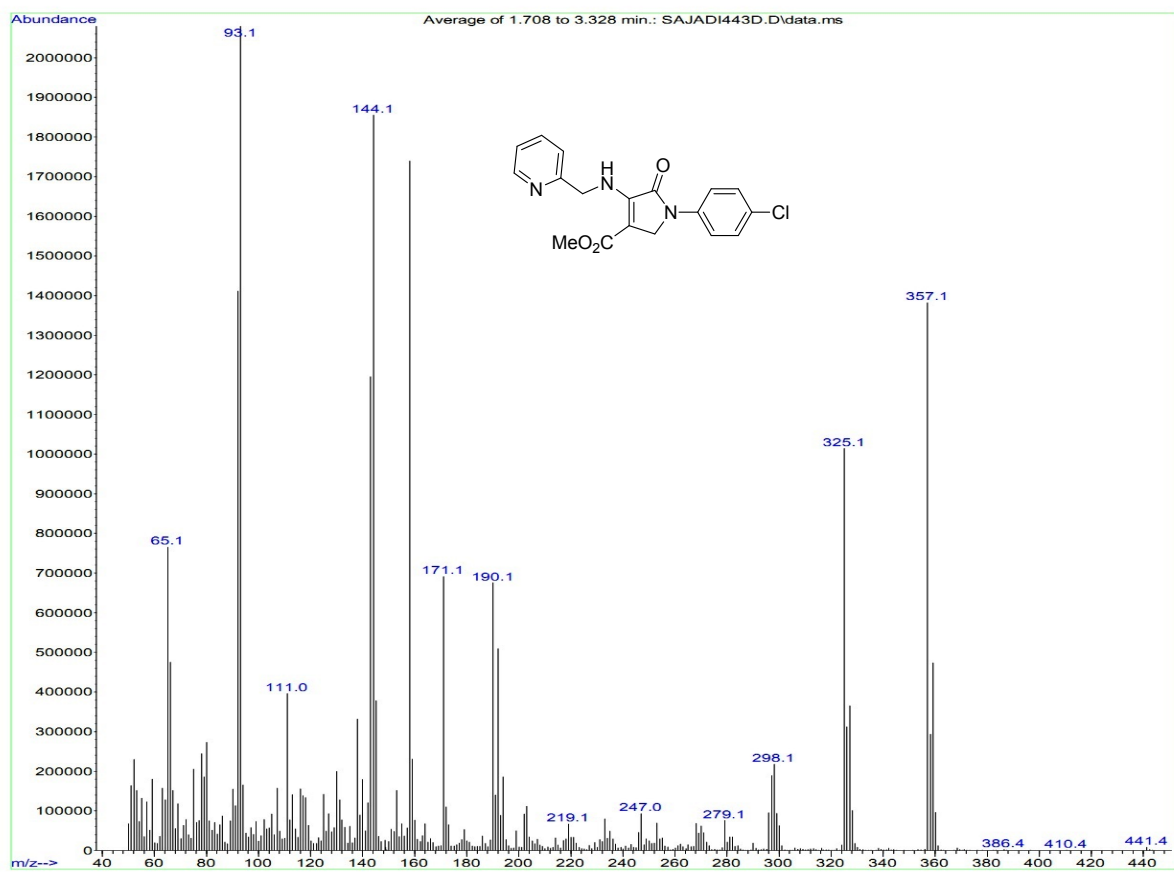
¹³C NMR spectrum **5p**



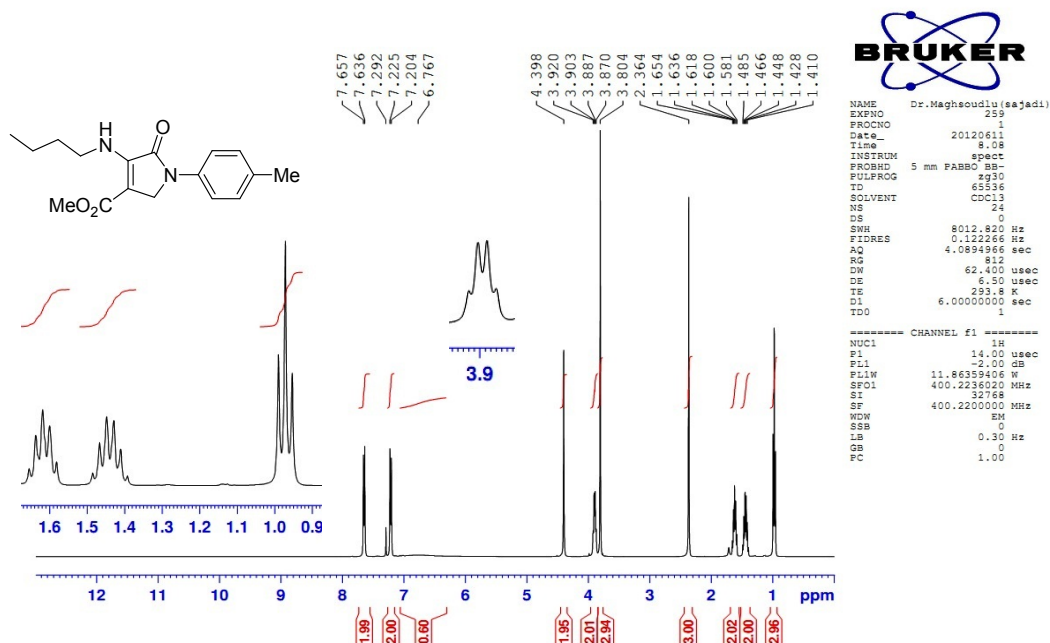
FT-IR spectrum of **5p**



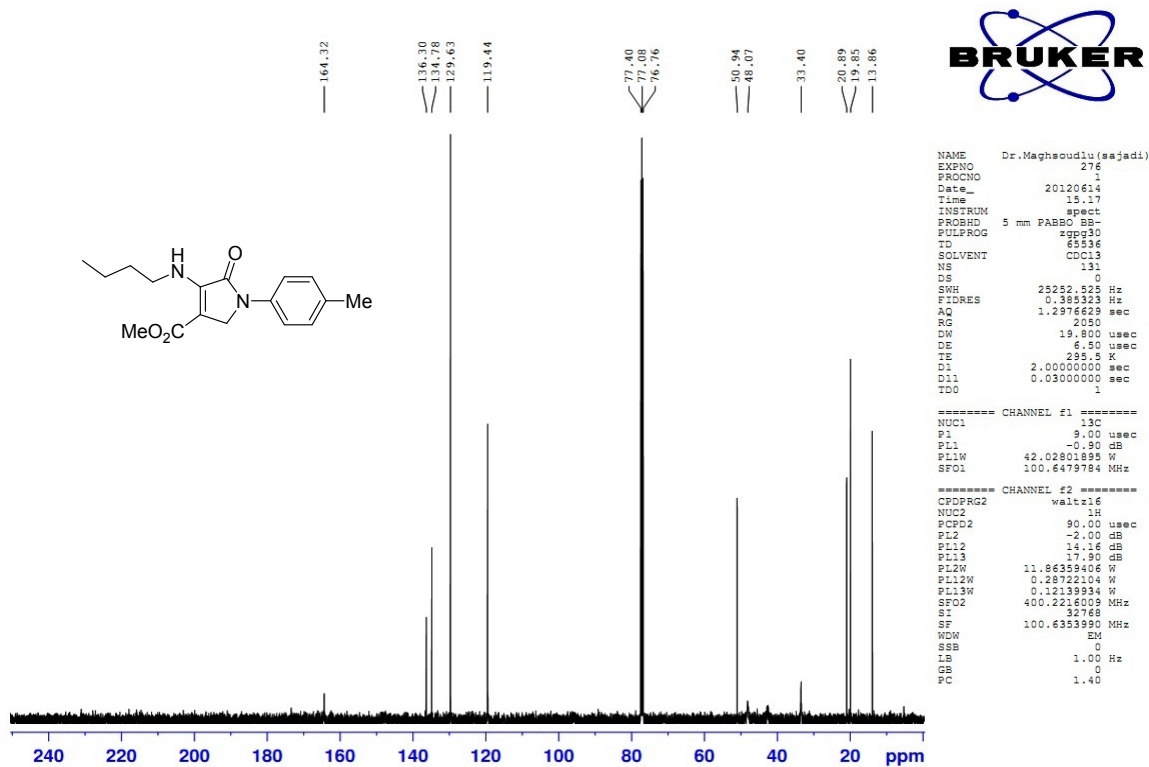
Mass spectrum of **5p**



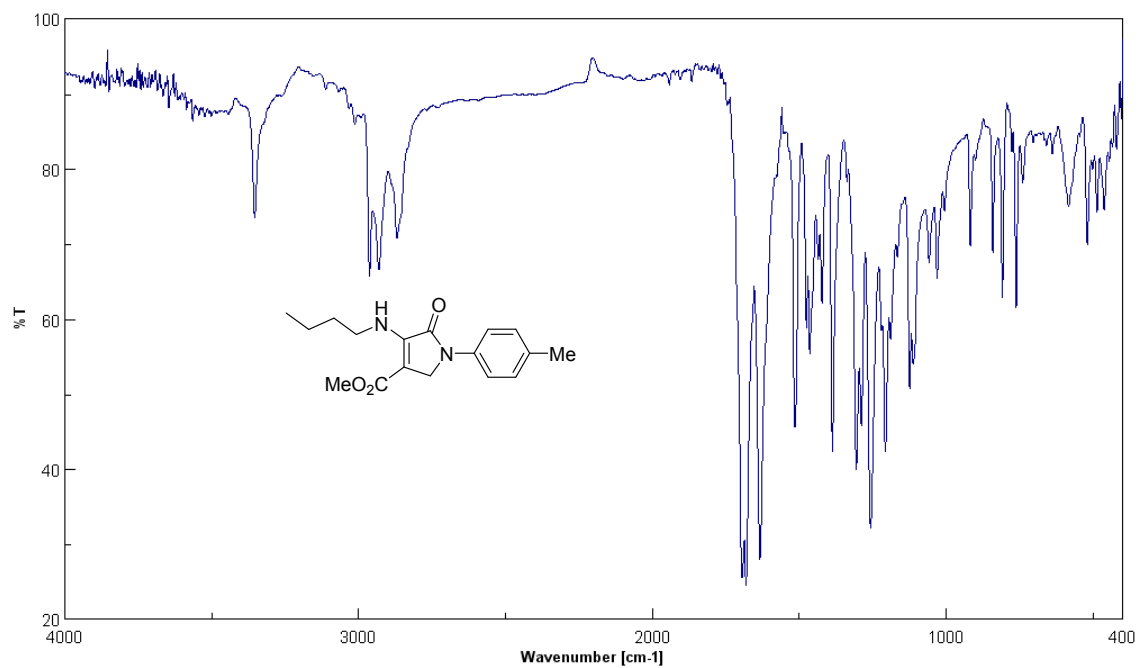
¹H NMR spectrum of **5w**



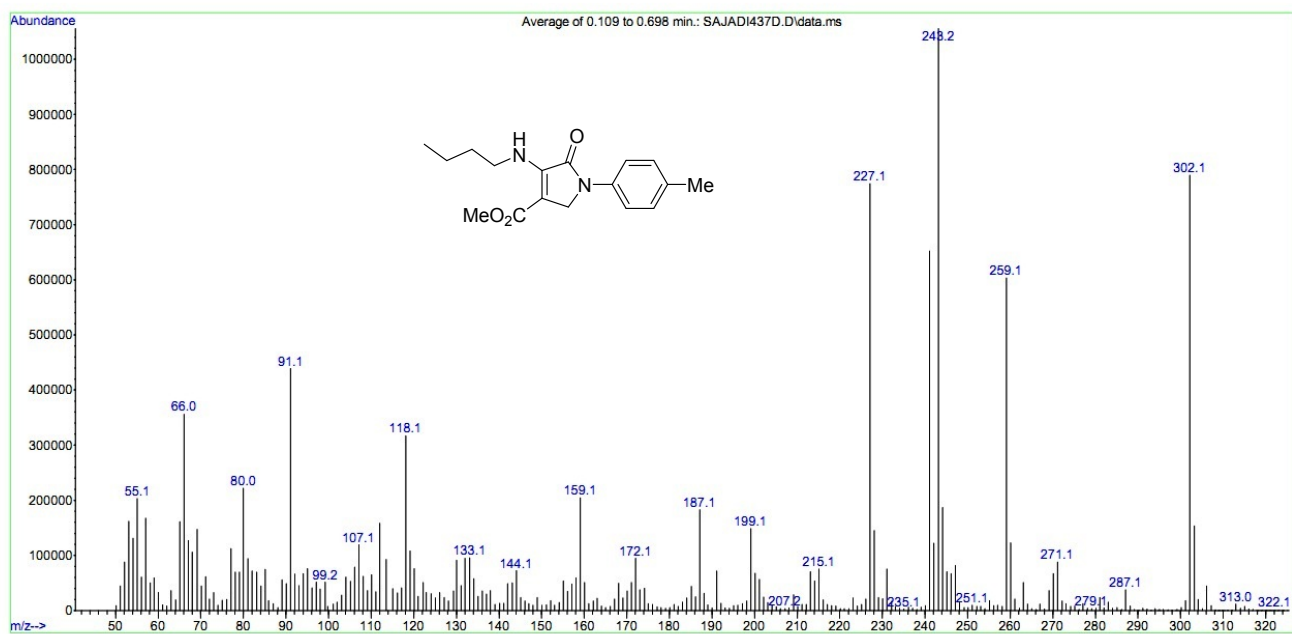
¹³C NMR spectrum **5w**



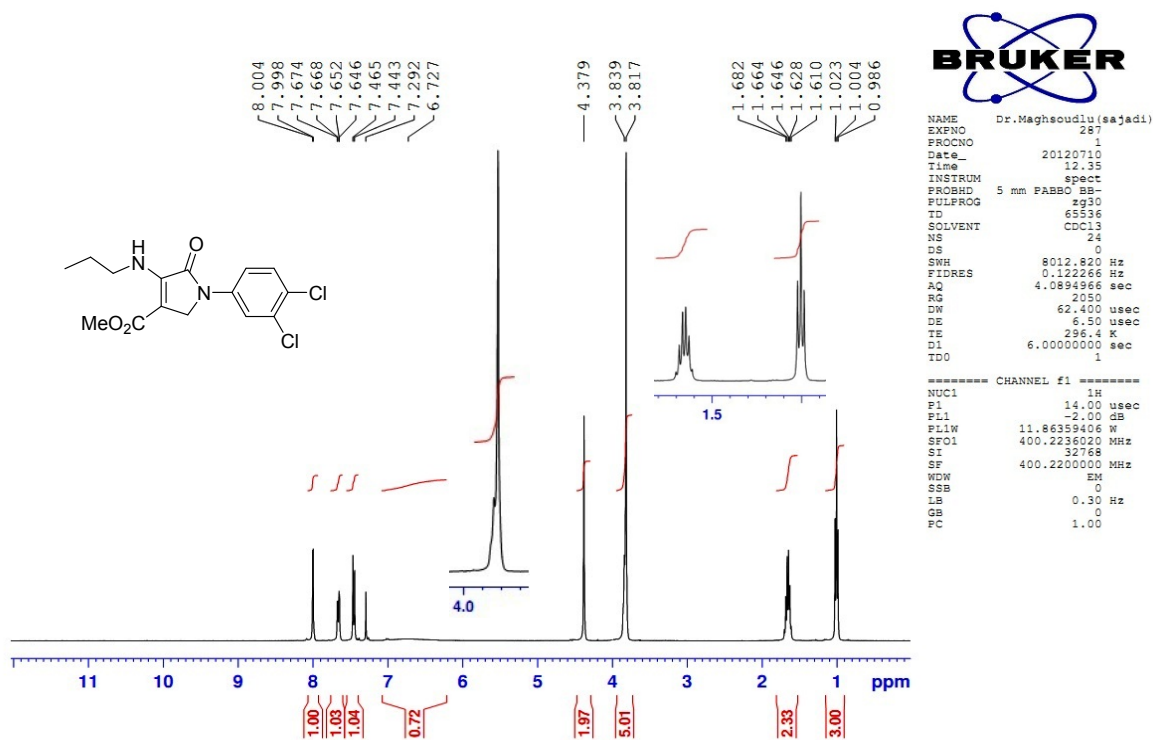
FT-IR spectrum of **5w**



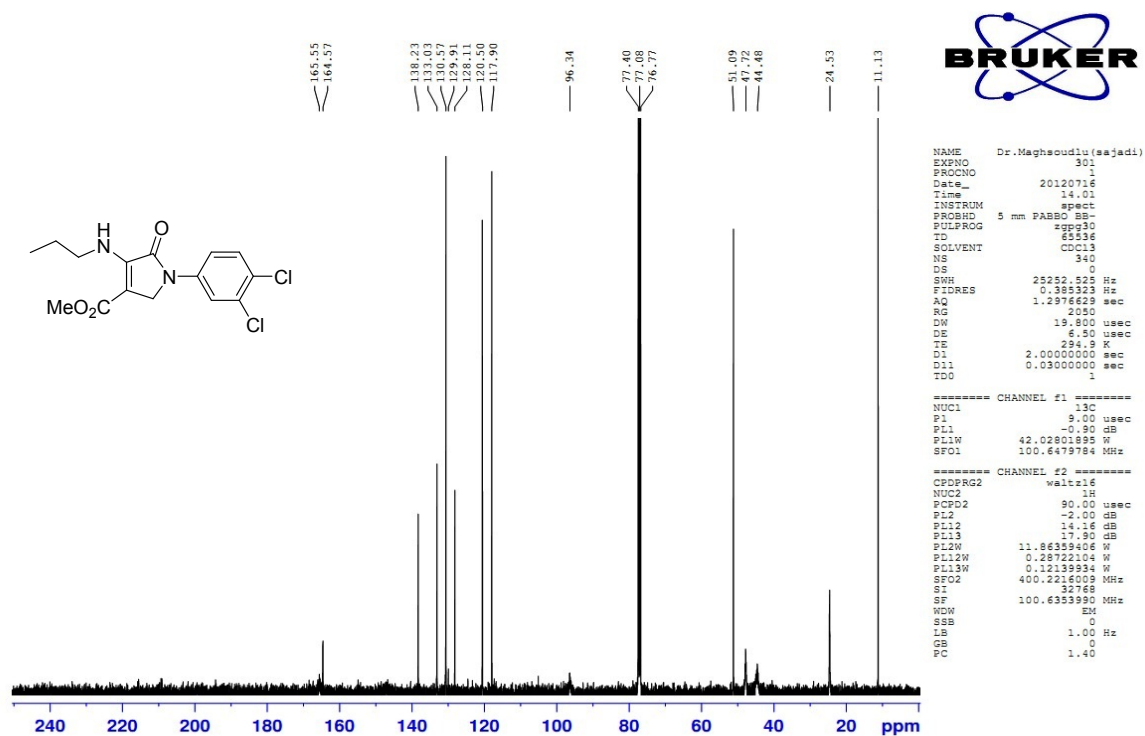
Mass spectrum of **5w**



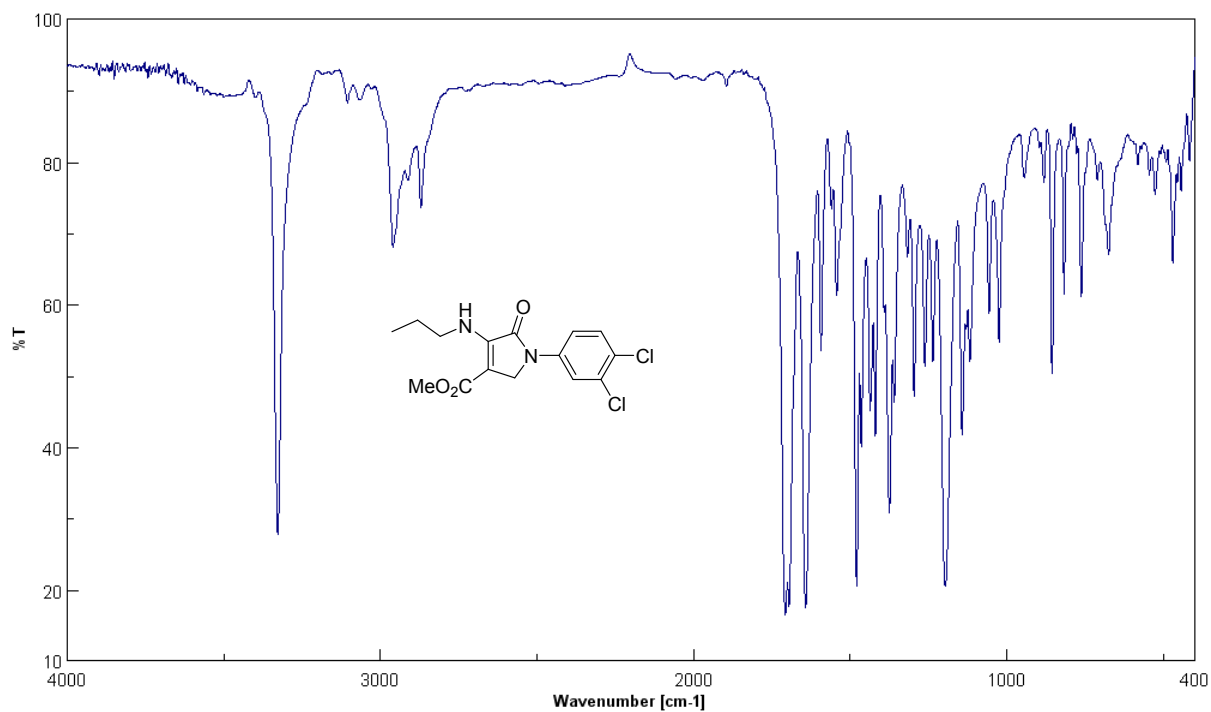
¹H NMR spectrum of **5y**



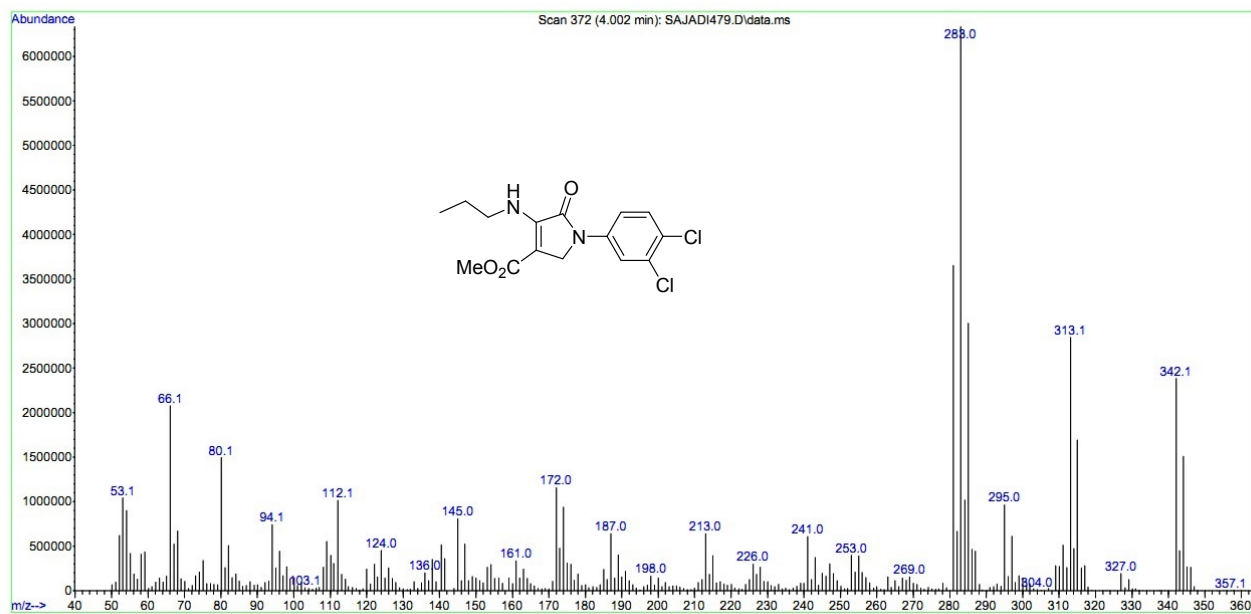
¹³C NMR spectrum **5y**



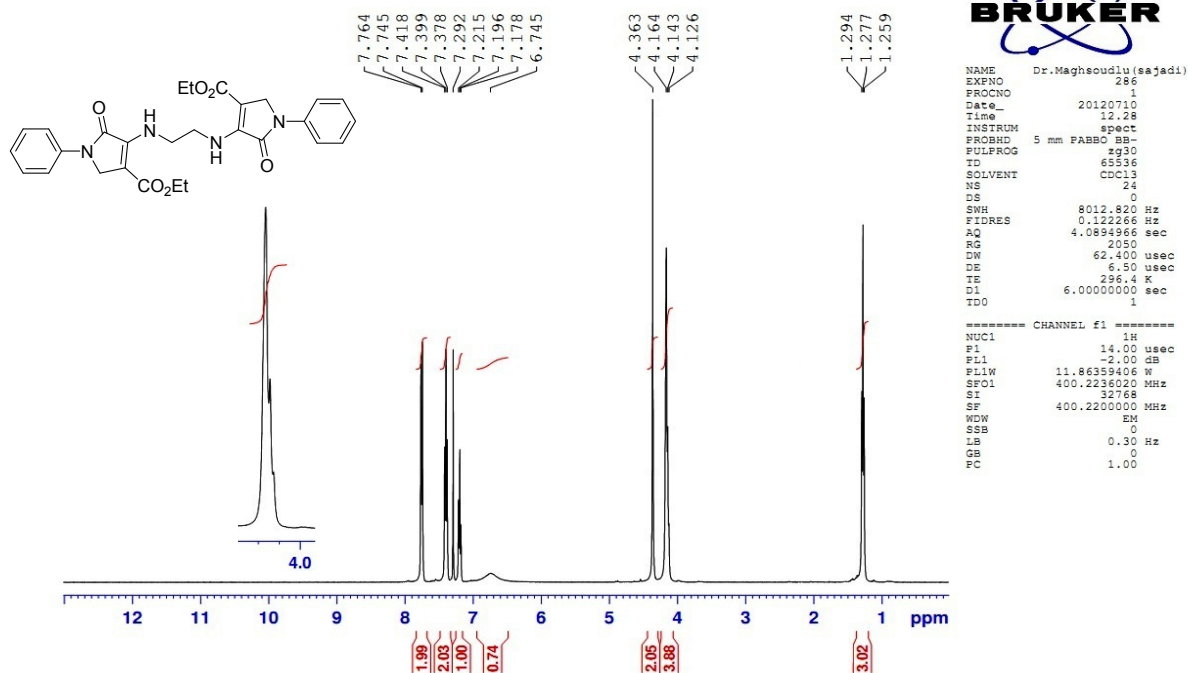
FT-IR spectrum of **5y**



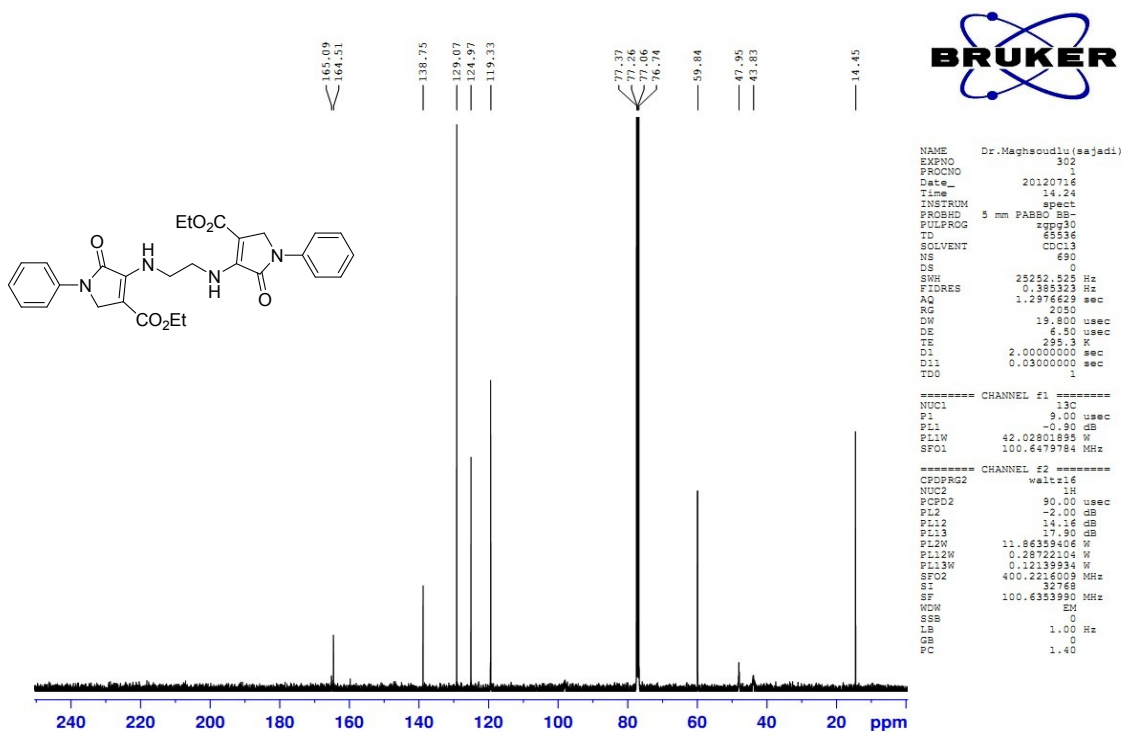
Mass spectrum of **5y**



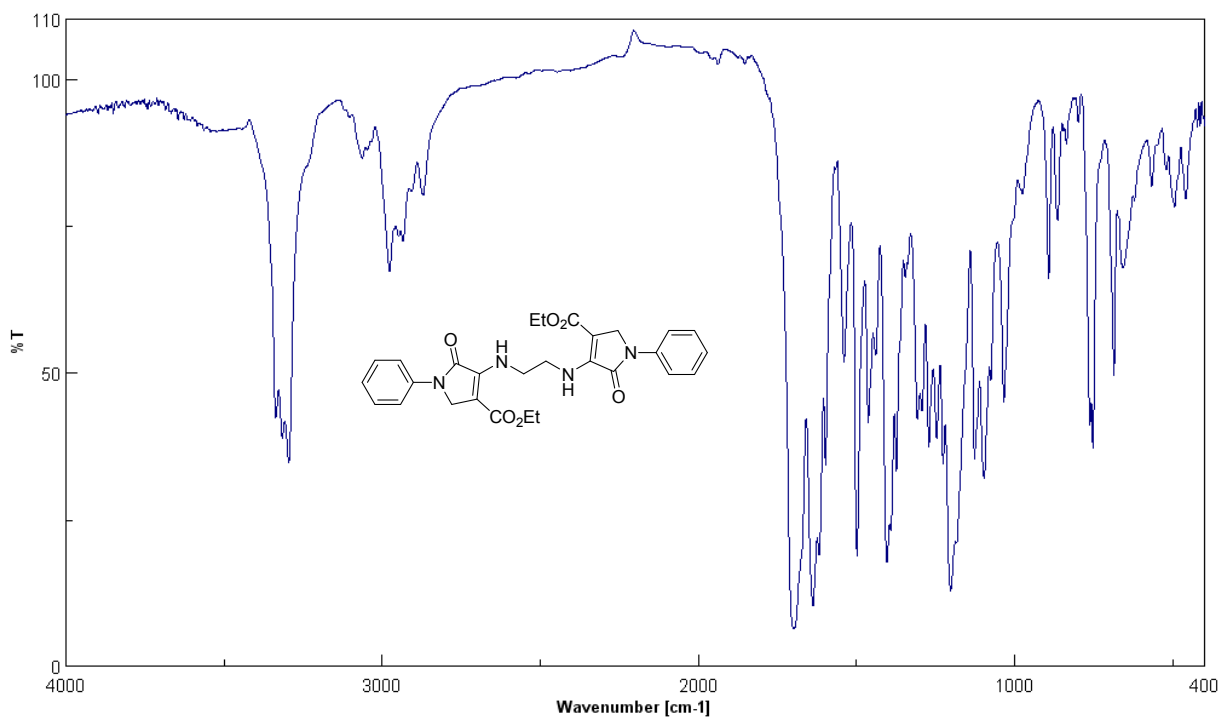
¹H NMR spectrum of **7a**



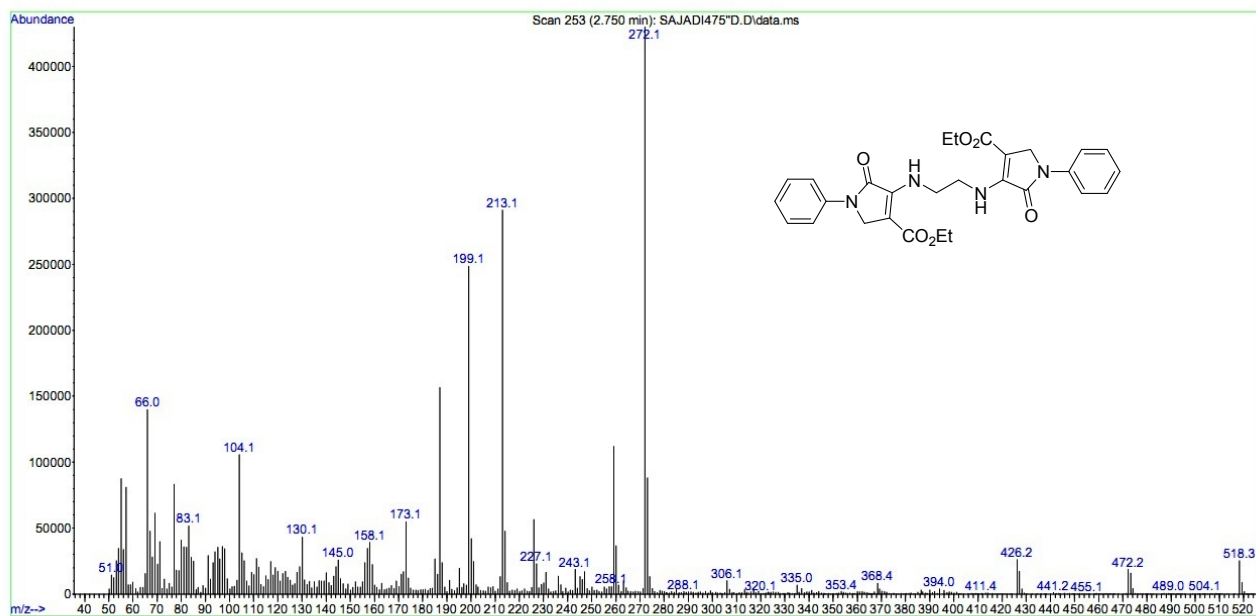
¹³C NMR spectrum **7a**



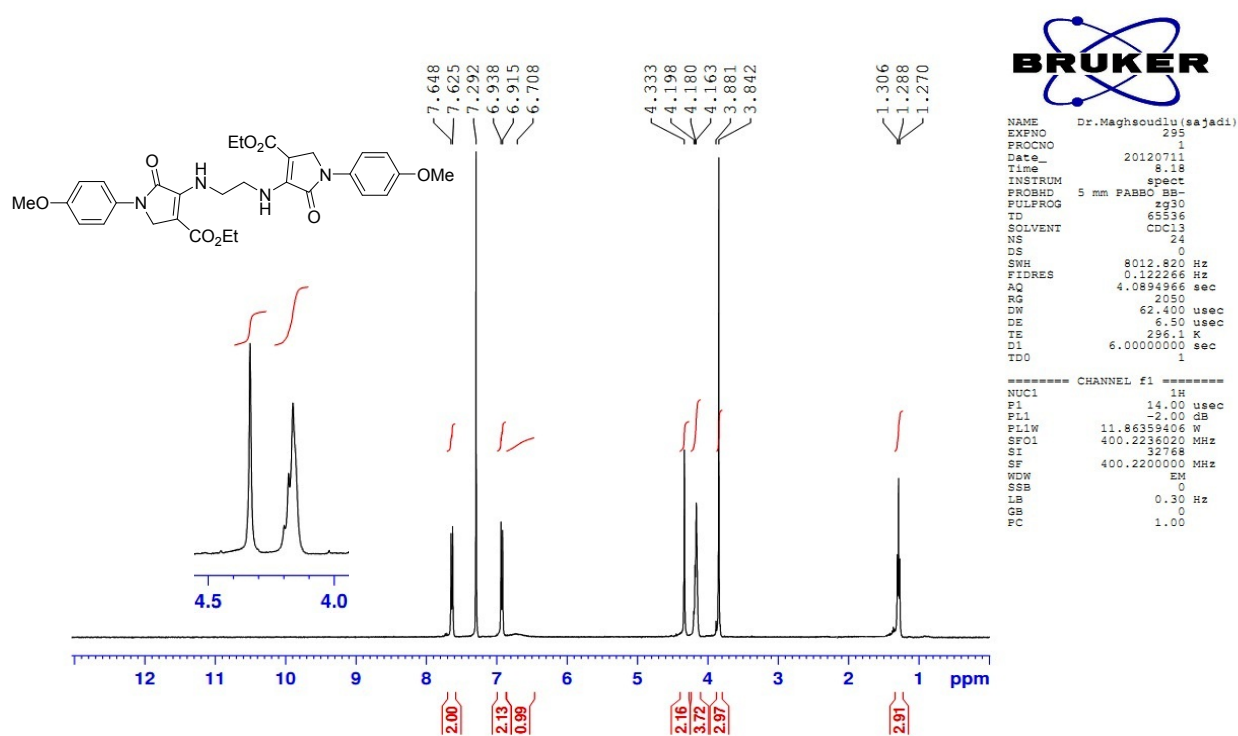
FT-IR spectrum of **7a**



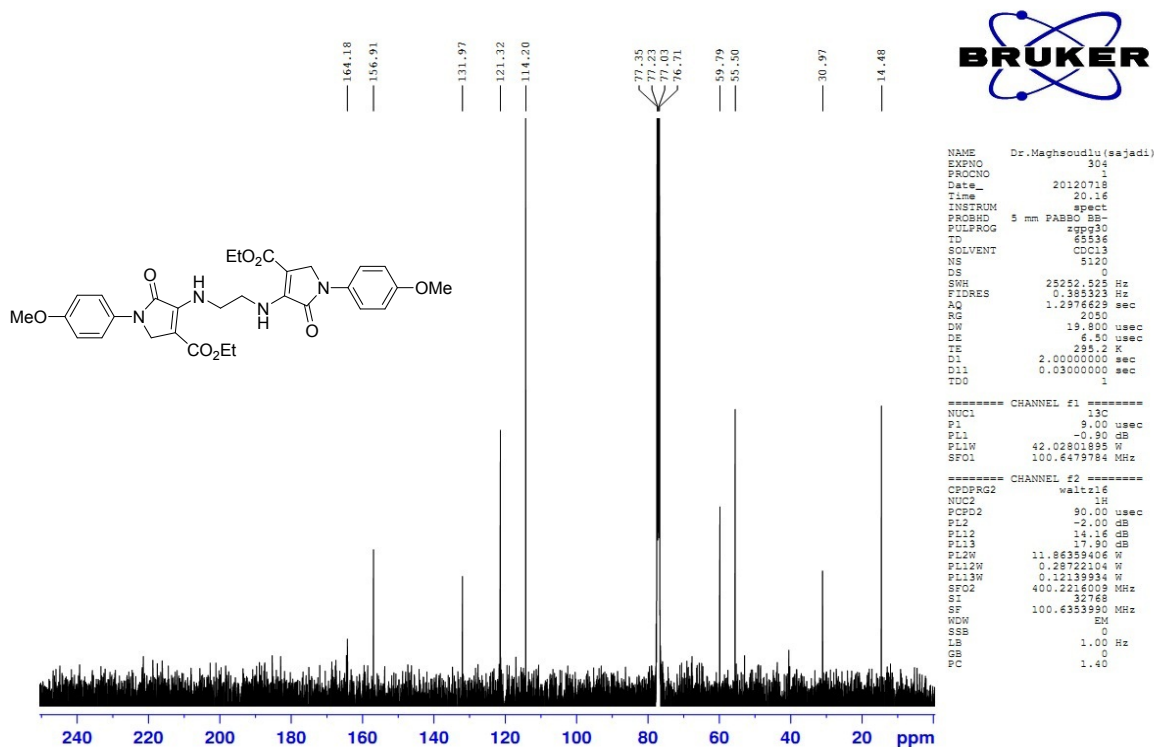
Mass spectrum of **7a**



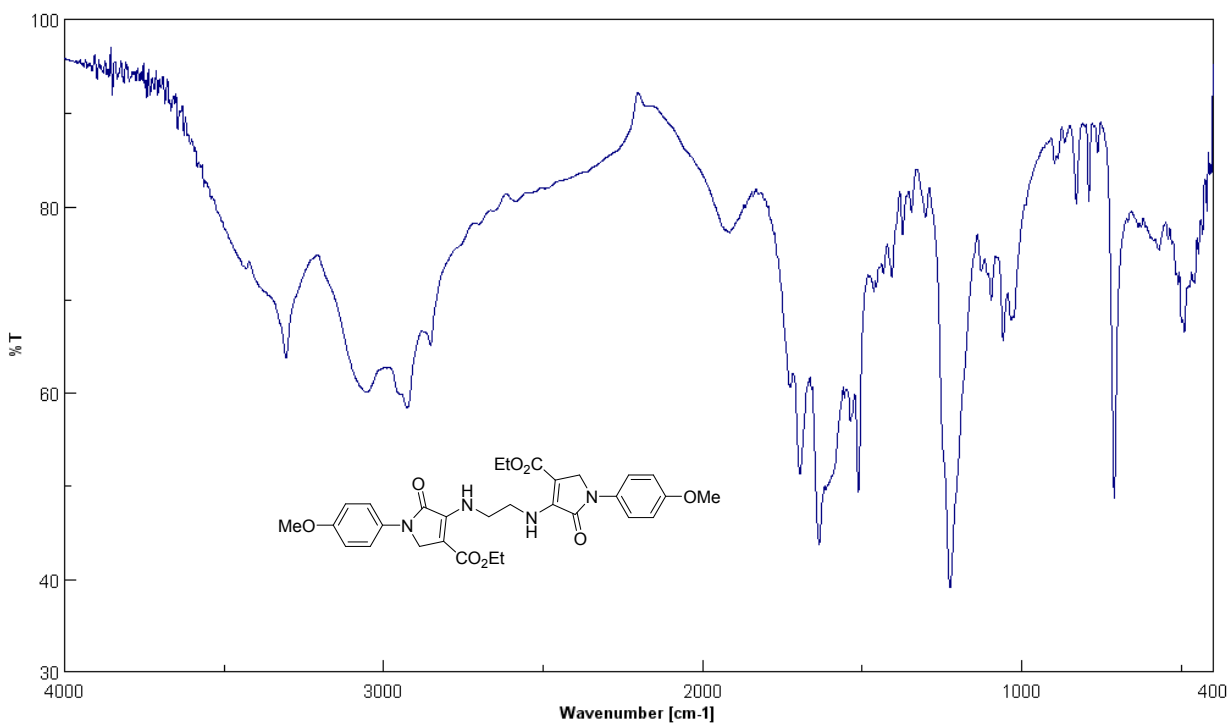
¹H NMR spectrum of **7c**



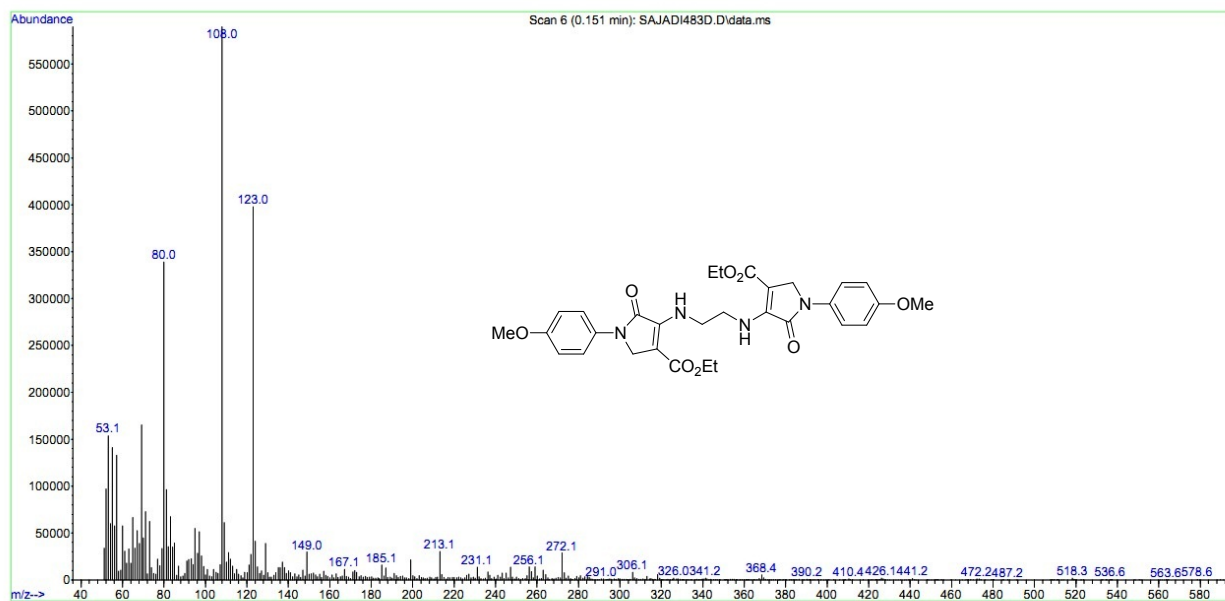
¹³C NMR spectrum **7c**



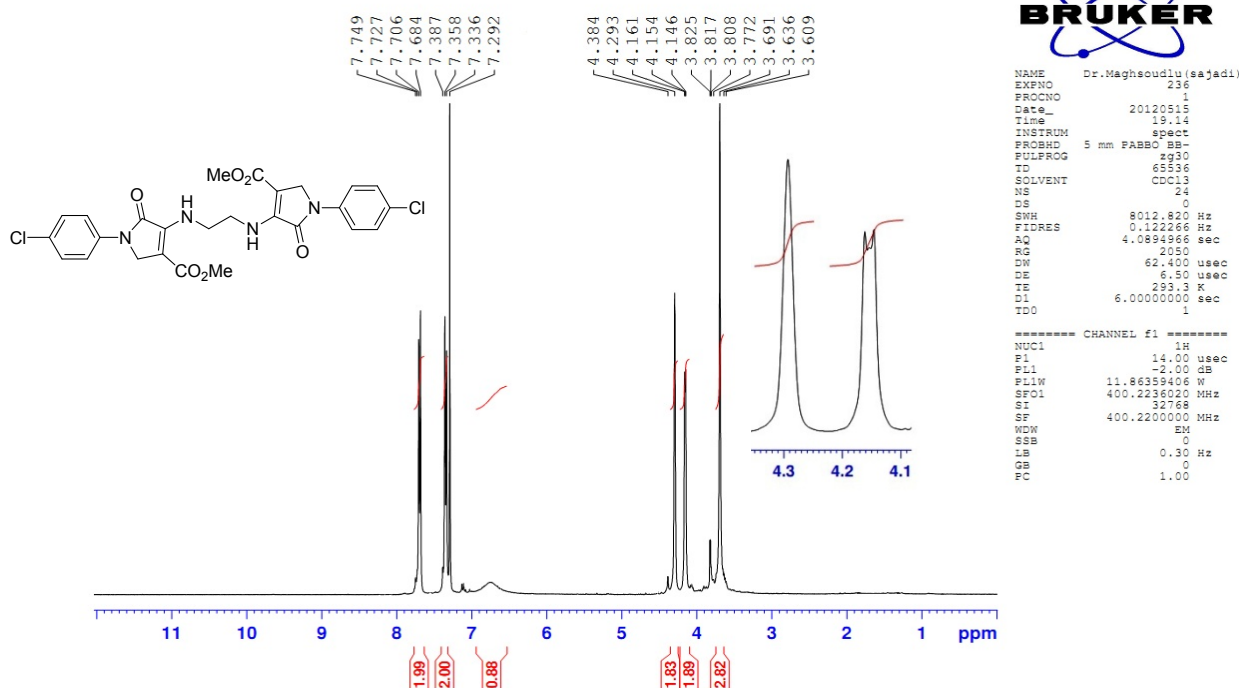
FT-IR spectrum of **7c**



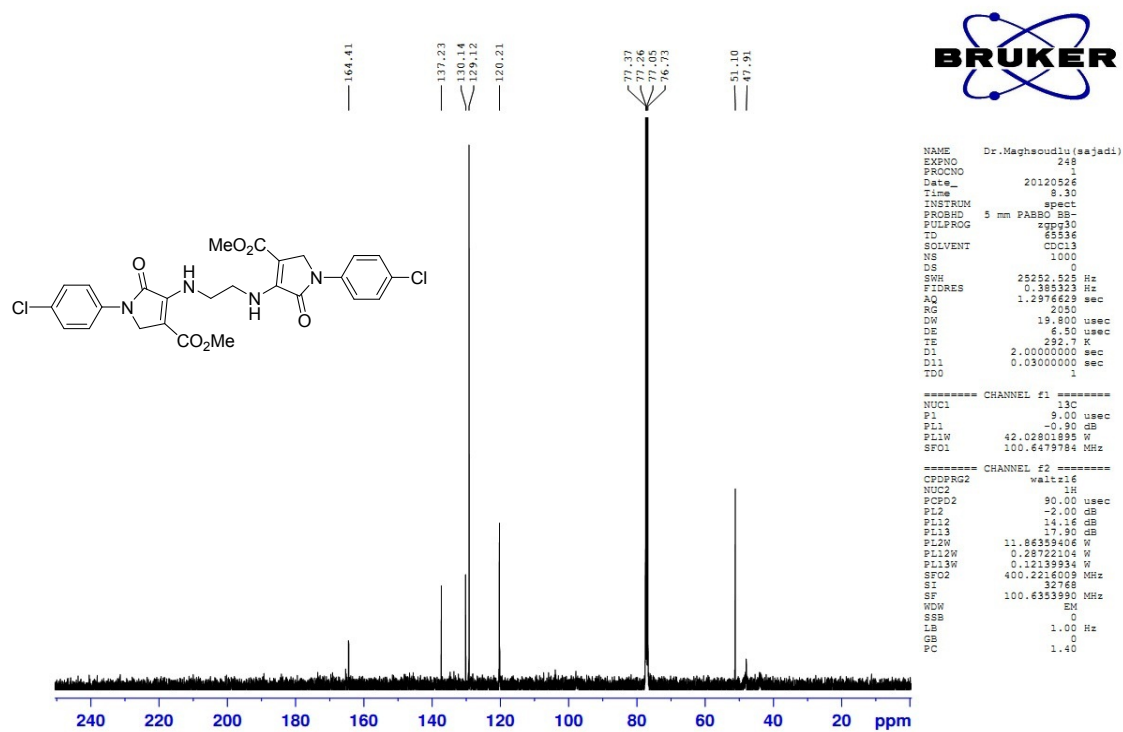
Mass spectrum of **7c**



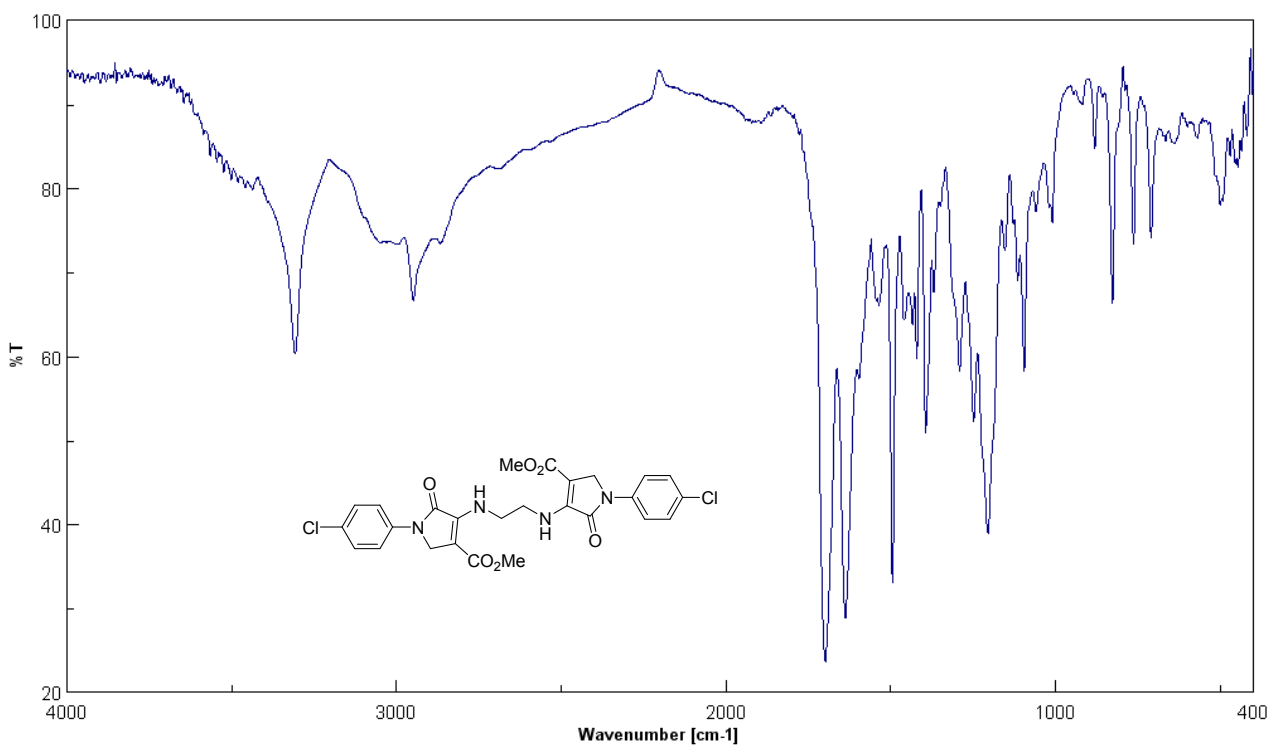
¹H NMR spectrum of **7e**



¹³C NMR spectrum **7e**



FT-IR spectrum of **7e**



Mass spectrum of **7e**

