Supporting Information

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Chitosan nanoparticles as a green and renewable catalyst in synthesis of 1,4-dihydropyridine under solvent-free conditions

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Figure 1. SEM micrograph of synthesized chitosan NPs

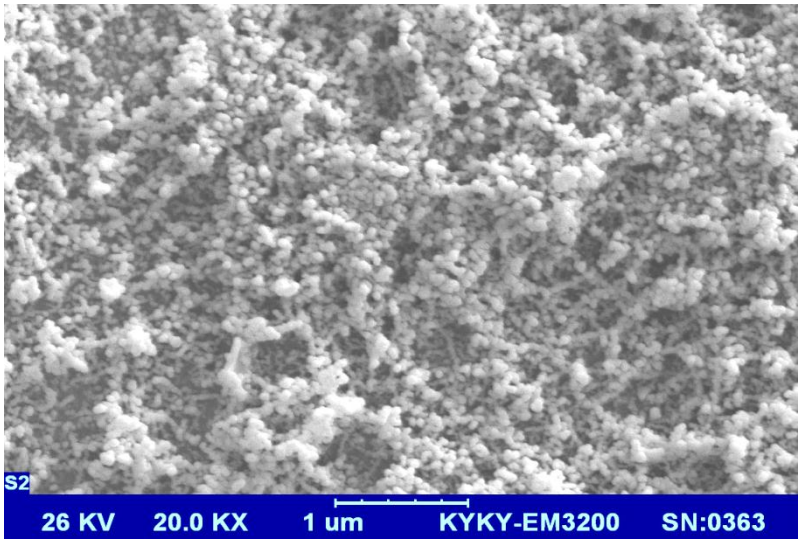


Figure 2. XRD of Chitosan

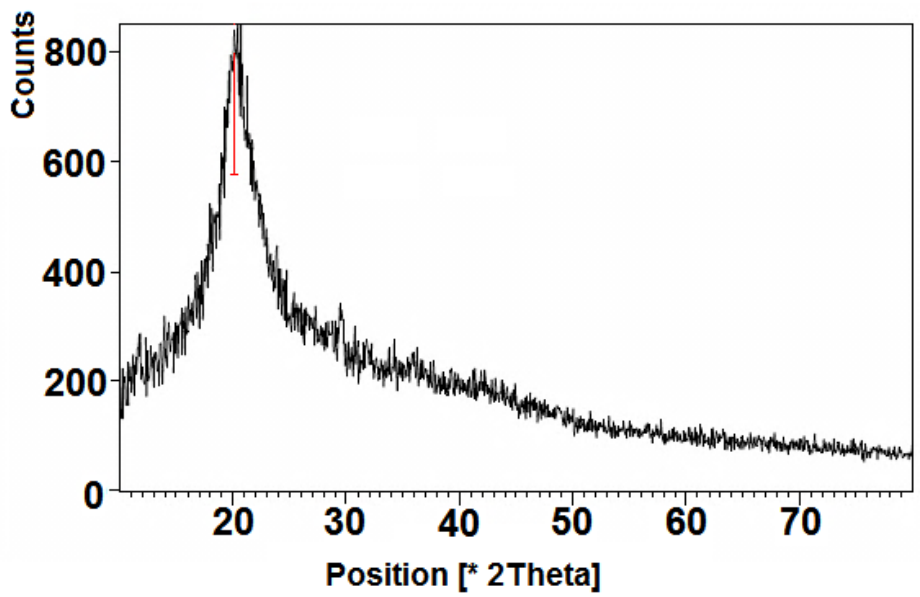


Figure 4. FT-IR spectra of sulfonated Chitosan

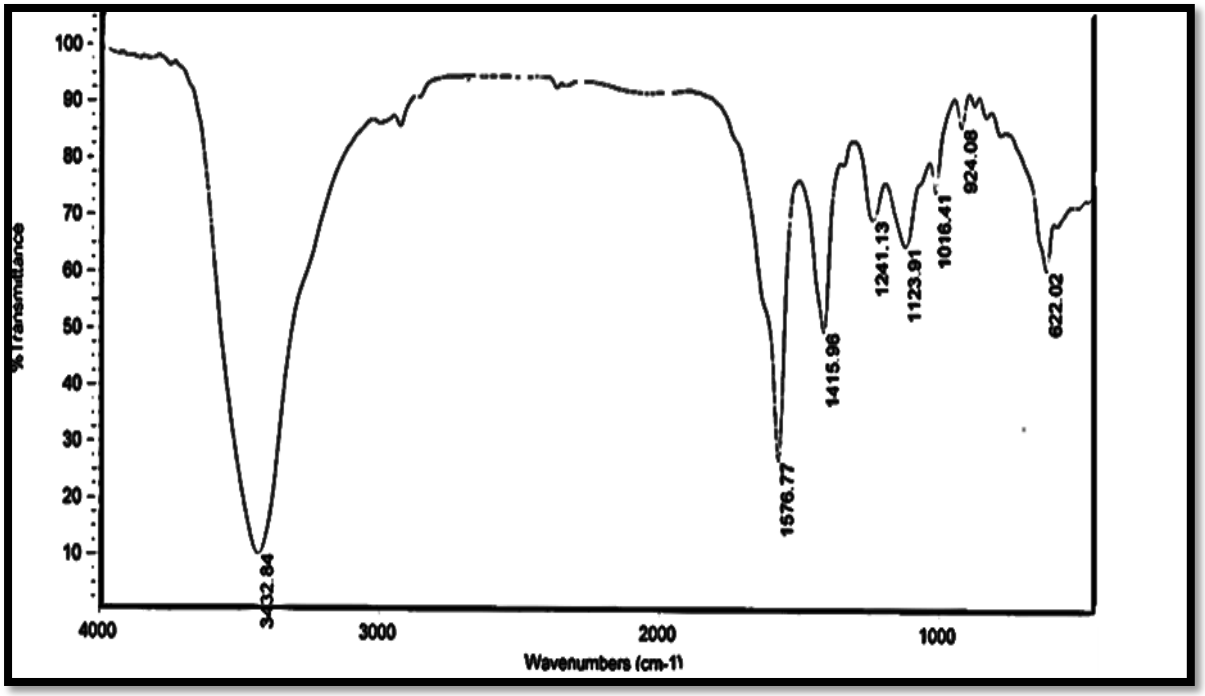


Figure 5. Raman spectra of Chitosan

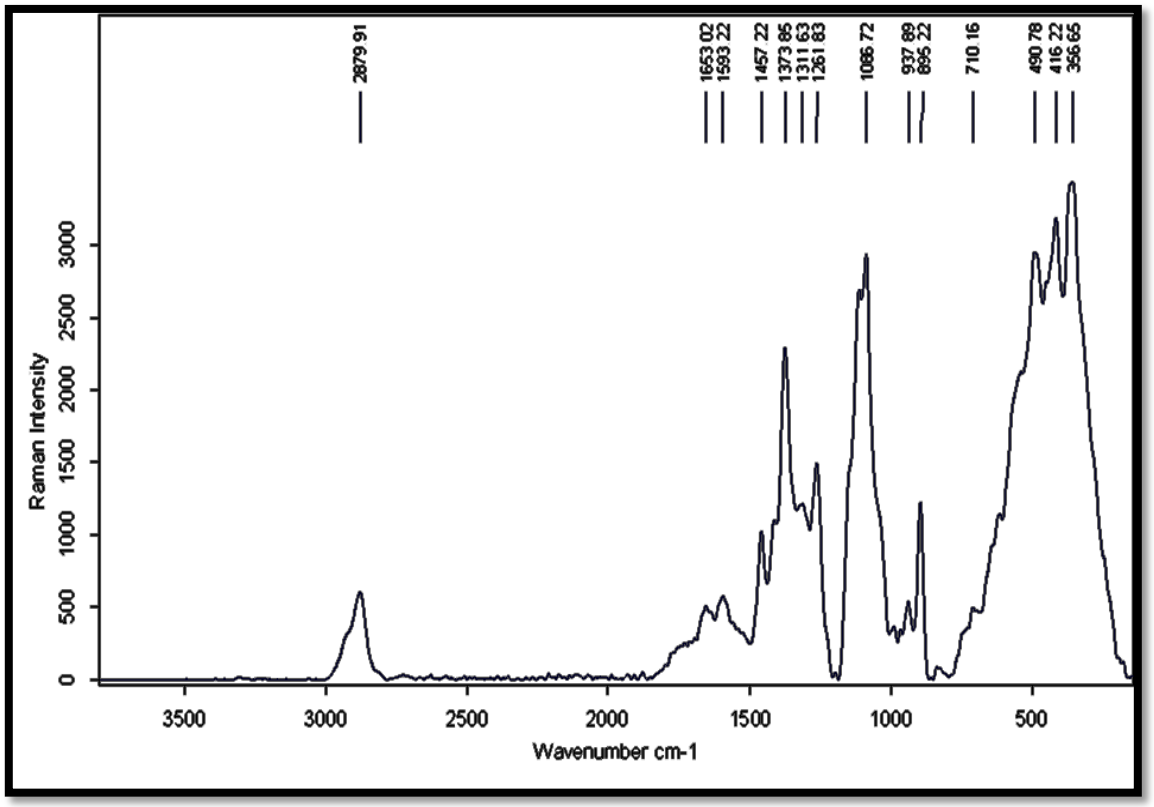


Figure 6. Raman spectra of Sulfonated Chitosan

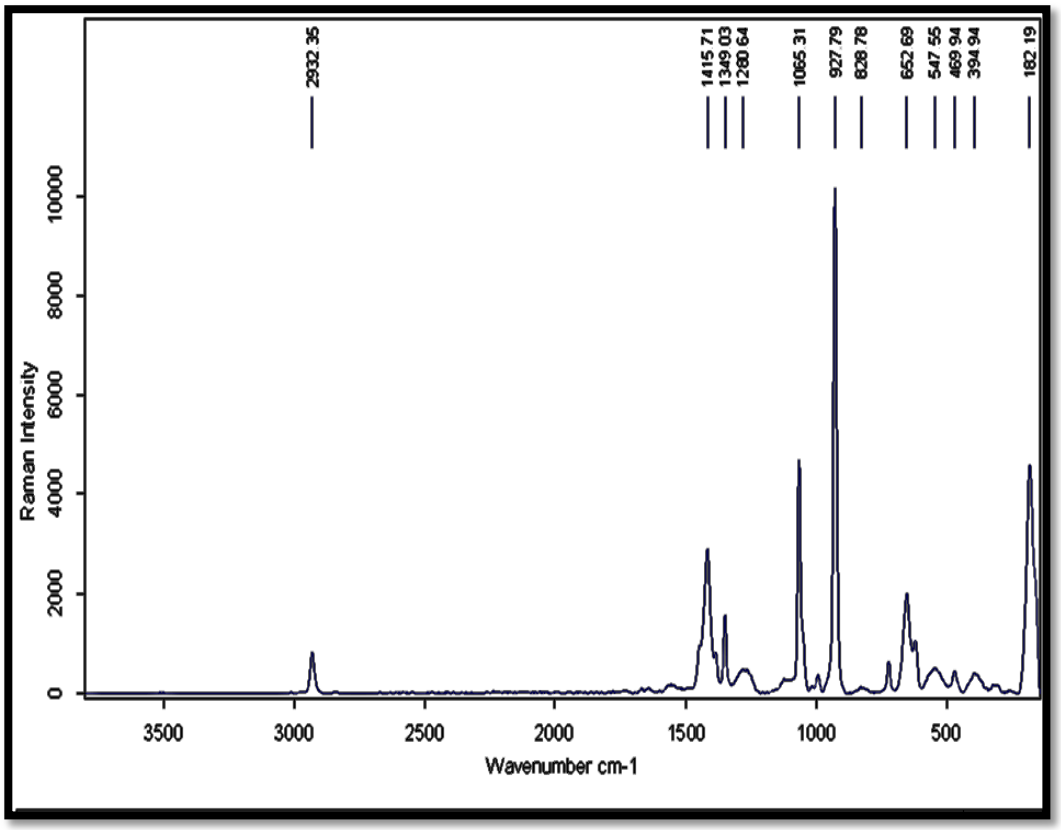
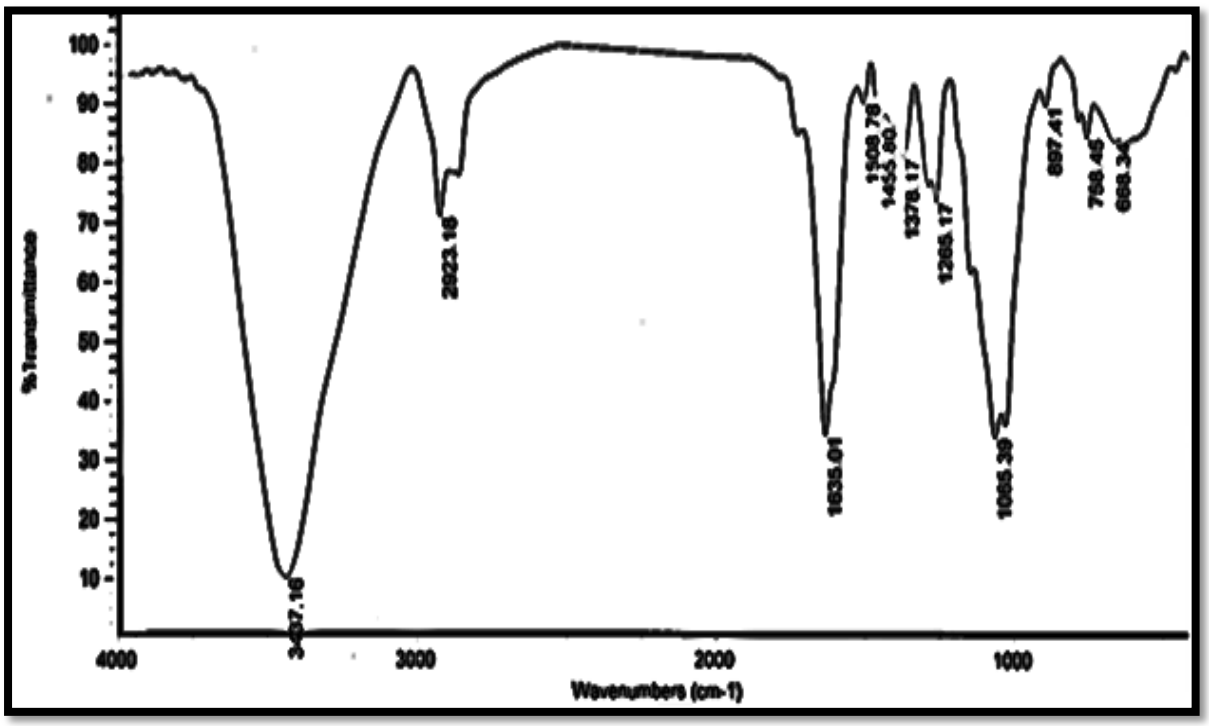
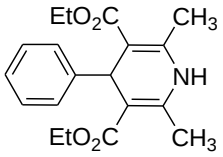


Figure 7. FT-IR spectra of Chitosan after four reaction run



1,4-dihydropyridines spectroscopic Data:



M.P. $_{Found}$ (℃): 157-158

M.P. $_{Reported}$ [Lit.] (℃) : 157-159 [101]

R_f (Petrolyom ether: Ethyl acethat, 3:2): 0.79

M. F.: $C_{19}NO_4H_{23}$

M.W. $_{extract}$ (amu): 329

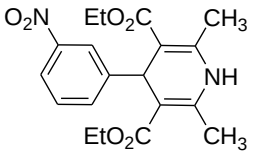
IR (KBr) υ (Cm^{-1}): 3341 (N-H), 1689 (2C=O),1650 (C=C), 1488 (N-H), 1374,1470 (C-H Bending CH3), 1211 (C-O), 701 (C-H Bending aromatic).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.19 (t, J=7.2 Hz, 6H, 2CH3CH2), 2.33 (s, 6H, $2CH_3$), 4.08 (q, J=7.0 Hz, 4H, $2CH_3CH_2$), 4.96 (s, 1H, CH), 5.97 (s, 1H, NH), 7.16–7.33 (m, 5H, Ar-H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.0, 19.4, 39.6, 59.5, 104.0, 121.8, 129.0, 131.0, 144.4, 146.5, 166.8 ppm.

MS (ESI): m/z 330 (M+H)+.

Anal. Calcd. for $C_{19}H_{23}NO_4$ (%): C, 69.30; H, 6.99; N, 4.25. **Found**: C, 69.22; H, 6.94; N, 4.23



M.P. $_{Found}$ (℃): 162-164

M.P. $_{Reported}$ [Lit.] (℃): 162 – 164 [101]

R_f (Petrolyom ether: Ethyl acethat, 3:2): 0.89

M. F.: $C_{19}H_{22}N_2O_{23}$

M.W. $_{extract}$ (amu): 374

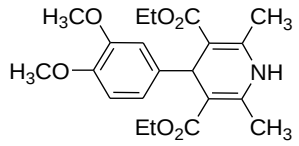
IR (KBr) υ (Cm^{-1}): 3344 (N-H), 1705 (2C=O), 1646 (C=C), 1486 (N-H), 1212 (C-O), 1346,1446 (C-H Bending CH_3), 704 (C-H Bending aromatic).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.22 (t, J=7.2 Hz, 6H, $2CH_3CH_2$), 2.36 (s, 6H, $2CH_3$), 4.08 (q, J=7.0 Hz, 4H, $2CH_3CH_2$), 5.09 (s, 1H, CH), 5.82 (s, 1H, NH), 7.66–8.13 (m, 4H, Ar-H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.23, 19.47, 39.96, 59.98, 103.20, 121.3, 123.0, 128.0, 134.52, 144.95, 148.14, 149.99, 167.19 ppm.

MS (ESI): m/z 375 $(M+ H)^+$

Anal. Calcd. for C19H22N2O6 (%): C, 60.96; H, 5.88; N, 7.49. **Found**: C, 60.88; H, 5.88; N, 7.47



M.P. $_{Found}$ (℃): 147 - 148

M.P. $_{Reported}$ [Lit.] (℃): 146 -149 [101]

R $_f$ (Petrolyom ether: Ethyl acethat, 3:2): 0.89

M. F.: $C_{23}H_{27}NO_6$

M.W. $_{extract}$ (amu): 389

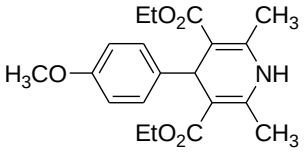
IR (KBr) υ (Cm^{-1}): 3342 (N-H), 1688 (2C=O), 1649 (C=C), 1480 (N-H), 1209 (C-O), 691(C-H)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.22 (t, J=7.2 Hz, 6H, 2CH3CH2), 2.34 (s, 6H, 2CH3), 3.68 (s, 6H, 2OCH3), 4.08 (q, J=7.2 Hz, 4H, $2CH_2CH_3$), 4.95 (s, 1H, CH), 5.60 (s, 1H, NH), 6.7–6.8 (m, 3H, Ar-H).

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.30, 19.60, 38.74, 55.14, 59.71, 104.40, 113.18, 128.97, 140.34, 143.58, 157.87, 167.71

MS (EI): m/z 399 (M^+).

Anal. Calcd. For $C_{23}H_{29}NO_5$ (%): C, 69.17; H, 7.27; N, 3.51. **Found:** C, 69.20; H, 7.30; N, 3.46



M.P. $_{Found}$ (℃): 157-159

M.P. $_{Reported}$ [Lit.] (℃): 156- 159 [101]

R $_f$ (Petrolyom ether: Ethyl acethat, 3:2): 0.85

M. F. : $C_{20}H_{25}NO_5$

M.W. $_{extract}$ (amu): 359

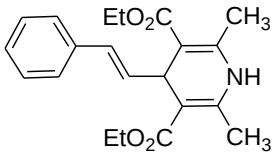
IR (KBr) υ (Cm^{-1}): 3338 (N-H), 1690 (2C=O), 1680 (C=C), 1501 (N-H), 1213 (C-O), 751(C-H Bending aromatic)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.21 (t, *J* =7.4 Hz, 6H, $2CH_3CH_2$), 2.29 (s, 6H, $2CH_3$), 4.10 (q, *J* =7.0 Hz, 4H, $2CH_3CH_2$), 4.99 (s, 1H, CH), 6.07 (s, 1H, NH), 6.96–7.12(m, 4H, Ar-H), 3.62 (s, 3H, OCH_3)

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 15.0, 20.0, 40.3, 59.5, 104.4, 118.8,
131.0, 131.5, 144.4, 147.3, 166.5

MS (ESI): m/z 360 $(M+H)^+$

Anal. Calcd. for $C_{20}H_{25}NO_5$ (%): C, 66.85; 6.96; N, 3.90. **Found**: C, 66.77; H, 6.97; N, 3.88.



M.P. $_{Found}$ (°C): 145- 146

M.P. $_{Reported}$ [Lit.] (°C) : 147 – 149 [102]
R (Petrolyom ether: Ethyl acethat, 3:2)$_f$: 0.86
M. F.: $C_{21}H_{25}NO_4$
M.W. $_{extract}$ (amu): 355

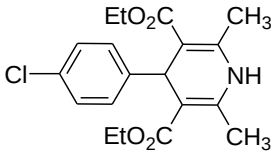
IR (KBr) υ (Cm^{-1}): 3337 (N-H), 1690, 1645 (2C=O), 1489 (N-H), 1218 (C-O), 718(C-H Bending aromatic)

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): δ 1.20 (t, 6H, J = 8.2 Hz), 2.45 (s, 6H), 4.15 (q, 4H, *J* = 8.2 Hz), 5.15 (d, 1H, *J* = 5.4 Hz), 5.75 (brs, 1H), 6.19 (t, 1H, J = 6.0 Hz), 7.20 (d, 1H, *J* = 16.6 Hz), 7.25 (m, 5H).

^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 14.2, 19.3, 36.2, 51.1, 102.2, 126.3, 126.9, 128.0, 128.3, 131.8, 137.7, 145.4,168.1

MS (EI): m/z 365 (M^+).

Anal.Calcd. for $C_{23}H_{27}NO_3$ (%): C, 75.62; H, 7.40; N, 3.83. **Found:** C, 75.60; H, 7.45; N, 3.85%.



M.P. $_{Found}$ (°C): 144 – 146

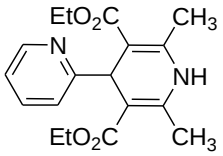
M.P. $_{Reported}$ [Lit.] (°C): 146 – 148 [102]
R $_f$ (Petrolyom ether: Ethyl acethat, 3:2): 0.9
M. F.: $C_{19}NO_4H_{22}Cl$
M.W. $_{extract}$ (amu): 363
IR (KBr) υ (Cm^{-1}): 3335 (N-H), 1695, 1651 (2C=O), 1501 (N-H), 1213 (C-O), 744(C-H Bending aromatic)

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 1.19 (t, *J* =7.2 Hz, 6H, $2CH_3CH_2$), 2.34 (s, 6H, $2CH_3$), 4.10 (q, *J*= 7.2 Hz, 4H, $2CH_3CH_2$), 5.09 (s, 1H, CH), 5.94 (s, 1H, NH), 7.22–7.48 (m, 4H, Ar-H)

^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 14.6, 19.4, 39.8, 59.4, 103.6, 119.0, 130.4, 131.4, 144.5, 146.6, 166.8

MS (ESI): m/z 364.45 $(M + H)^+$.

for $C_{19}H_{22}ClNO_4$ (%): C, 62.73; H, 6.05; N, 3.85. **Found**: C 62.64; H, 6.01; N, 3.80, **Anal. Calcd**



M.P. $_{Found}$ (℃) : 192 -194

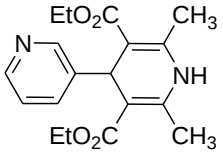
M.P. $_{Reported}$ [Lit.] (℃): 148-150 [103]
R $_f$ (Petrolyom ether: Ethyl acethat, 3:2): 0.4
M. F.: $C_{18}H_{22}N_2O_4$
M.W. $_{extract}$ (amu): 331

IR (KBr) υ (Cm^{-1}): 3324 (N-H), 1694 (C=O), 1654 (C=C), 1481(N-H), 1211 (C-O), 701 (C-H Bending aromatic)

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 1.23 (t, *J* = 7.11 Hz, 6H, 2 CH_3–CH2), 2.28 (s, 6H, 2 CH_3), 4.06–4.12 (m, 4H, OCH_2CH_3), 5.22 (s, 1H, CH), 7.16 (t, *J* = 4.88, 0.63 Hz,1H), 7.43 (d, *J* = 7.77, 1H), 7.61 (t, J = 7.66, 1.69 Hz, 1H), 8.53 (d, J = 3.98 Hz, 1H), 8.62 (brs, 1H, NH)

^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 14.71, 19.31, 43.24, 59.96, 102.15, 122.19, 124.71, 136.11, 146.73, 148.65, 165.63, 168.14

MS (EI): m/z: 330
Anal. Calcd for C19H23NO5 (%): C, 66.07; H, 6.71; and N,4.06, **Found**: C, 66.04; H, 6.67; and N, 4.00



M.P. $_{Found}$ (℃): 190-192

M.P. $_{Reported}$ [Lit.] (℃) :190-192 [103]
R $_f$ (Petrolyom ether: Ethyl acethat, 3:2): 0.37
M. F.: $C_{18}H_{22}N_2O_4$
M.W. $_{extract}$ (amu): 331

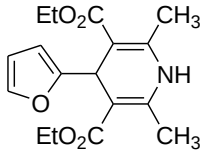
IR (KBr) υ (Cm^{-1}) : 3324 (N-H), 1694 (C=O), 1654 (C=C), 1481(N-H), 1211 (C=O), 770 (C-H Bending aromatic)

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm) : 1.24 (t, *J* = 7.13 Hz, 6H, 2 CH_3–CH_2), 2.36 (s, 6H, 2CH_3), 4.07–4.14 (m, 4H, O–CH_2CH_3), 5.01 (s, 1H, CH), 6.61 (s, 1H, NH), 7.19 (dd, *J* = 7.83, 4.98 Hz, 1H), 7.64–7.66 (m, 1H), 8.39 (dd, *J* = 4.79, 1.57 Hz, 1H), 8.55 (d, *J* = 1.94 Hz, 1H)

^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm) : 14.68, 19.75, 38.23, 60.27, 103.57, 123.55, 136.27, 144.00, 145.39, 147.40, 149.80, 167.64

MS (EI): m/z: 330 (M^+, 40)

Anal. Calcd for $C_{19}H_{23}NO_5$ (%) : C, 66.07; H, 6.71; and N,, 4.06 **Found**: C, 66.04; H, 6.67; and N, 4.00



M.P. Found (ºC): 149 -152

M.P. Reported [Lit.] (ºC): 148 – 150 [103]
R f (Petrolyom ether: Ethyl acethat, 3:2): 0.9
M. F.: $C_{17}NO_5H_{21}$
M.W. extract (amu): 321

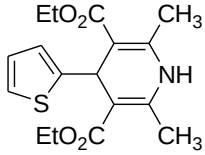
IR (KBr) υ (Cm^{-1}): 3345(N-H), 1700 (C=O), 1649(C=C), 1486(N-H), 1208 (C-O), 732 (C-H Bending aromatic)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.30 (t, 6H, *J* = 8.2 Hz), 2.40 (s, 6H), 4.30 (q, 4H, *J* = 8.2 Hz), 5.30 (s, 1H), 5.80 (brs, 1H), 6.80–7.05 (m, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 19.8, 41.0, 56.4, 105.7, 129.3, 130.7, 143.6, 149.0, 167.1 ppm

MS (ESI): m/z 320 $(M+ H)^+$

Anal. Calcd. for $C_{17}H_{21}NO_5$ (%): C, 63.95; H, 6.58; N, 4.39**. Found**: C, 63.88; H, 6.55; N, 4.36



M.P. Found (ºC): 169 - 171
M.P. Reported [Lit.] (ºC): 172 – 174 [103]
R_f (Petrolyom ether: Ethyl acethat, 3:2): 0.62
M. F.: $C_{17}H_{21}NO_4S$
M.W.extract (amu): 335

IR (KBr) V (Cm-1): 3344 (N-H), 1692(C=O), 1645(N-H), 1486 (N-H), 1212 (C-O), 721 (C-H Bending aromatic)

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.19 (t, *J*= 7.4 Hz, 6H, $2CH_3CH_2$), 2.28 (s, 6H, $2CH_3$), 4.08 (q, *J*= 7.2 Hz, 4H, $2CH_3CH_2$), 5.04 (s, 1H, CH), 6.07 (s, 1H, NH), 6.08–6.13 (m, 2H, Thienyl-H), 6.89 (m, 1H, Thienyl-H) ppm.

^{13}C NMR ($CDCl_3$, 100 MHz) δ (ppm): 14.3, 19.4, 37.3, 59.8, 103.6, 118.8, 132.0, 133.8, 144.5, 147.9, 167.5 ppm

MS (ESI): m/z 336 $(M +H)^+$.

Anal. Calcd. for $C_{17}H_{21}NO_4S$ (%): C, 60.89; H, 6.27; N, 4.18. **Found**: C, 60.80; H, 6.28; N, 4.17