Supplementary Information

N-methyl pyridinium tosylate (NMPyTs) and Ultrasound Promoted One-Pot Multicomponent Synthesis of Highly Functionalized Tetrahydropyridine Derivatives.

Amol V. Sapkal[1], Jaysing M. Dinore[2], Ajeet A. Yelwande[2], Manoj P. Palve[2], Balaji R. Madje[3]

[1]Phulsing Naik Mahavidyalaya, Department of Chemistry, Pusad Dist: Yavatmal, (Maharashtra), India
[2]Indraraj Arts, Commerce & Science College, Department of Chemistry, Sillod, Dist: Aurangabad (Maharashtra), India
[3]Vasantrao Naik Mahavidyalaya, Department of Chemistry, Aurangabad (Maharashtra), India

*Corresponding Author: Amol V. Sapkal **Email: -** ***sapkalamol9chem@gmail.com***

Compound Spectroscopic data (4a-h)

(2 R,6S)-methyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate (4a).Yield: 93%; M.180–182 _C; IR (KBr) 2919, 2849, 1743, 1647, 1595, 1374, 1246, 1188 cm_1; HRMS Calculated for C31H28N2O2: 460.2150, found: 460.2162, 1H NMR (300 MHz, CDCl3): 2.76–2.78 (m,1H), 3.95 (s,3H), 6.23 (s,1H), 5.16 (s, 1H, NH), 6.56 to 6.53 (m,1H), 7.06 to 7.37 (m, 20H); 13C NMR (100 MHz, CDCl3): 33.68, 51.11, 55.15, 58.24, 97.90, 113.92, 116.21, 125.81, 125.83, 126.34, 126.34, 127.19, 128.23, 128.66, 128.89, 128.91, 137.85, 142.77, 143.93, 146.91, 156.34, 168.60.

(2R, 6S)-ethyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4b).**Yield: 95%; M.P.173-175°C; HRMS (ESI): Calculated for $C_{32}H_{30}N_2O_2$: 474.2307, found: 474.2317, ^{1}H NMR (300 MHz, $CDCl_3$): 1.4-1.6 (t, 3H), 2.8-3.0 (m, 2H), 4.2-4.6 (q, 2H), 5.26 (S, 1H, NH), 6.34 (m,1H), 6.42 (s, 1H), 6.7 to 7.9 (m, 20H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): 14.87, 34.68, 55.15, 58.29, 59.72, 98.34, 112.02, 118.21, 126.71, 124.83, 125.33, 125.45, 126.66, 127.13, 126.29, 127.65, 126.83, 128.95, 138.12, 143.82, 145.12, 146.05, 155.11.

(2R,6S)-ethyl1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4(phenylamino)pyridine-3-carboxylate **(4c).** Yield: 86%; M.P. 180-182°C; IR (KBr) 2925, 2838, 1712, 1648, 1586, 1503, 1245, 1175, 1112 cm^{-1}; HRMS (ESI): Calculated for $C_{31}H_{28}N_2O_2$: 460.2150, found: 460.2162, ^{1}H NMR (300 MHz, $CDCl_3$): 1.47 (t, 3H), 2.75 to 2.86 (m, 2H), 3.75 (s, 3H), 4.27 to 4.46 (q, 2H), 5.10 (s,1H, NH), 6.37 (m,1H), 6.53 (s, 1H), 6.62 to 7.27 (m,18H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$): 14.84, 33.72, 54.63, 55.34, 57.64, 59.63, 98.43, 112.90, 113.53, 113.99, 116.031, 126.58, 126.81, 127.43, 128.76, 135.67, 139.01, 148.01, 157.17, 159.03, 158.58, 168.30.

(2R,6S)-methyl 1,2,5,6-tetrahydro-2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4d).** Yield: 84%; M.P. 225-227°C; IR (KBr) 2919, 1721,1657, 1593, 1441, 1357, 1259, 1194 cm^{-1}; HRMS (ESI):

Calculated for $C_{31}H_{26}N_4O_6$: 550.1852, found: 550.1856, ^{1}H NMR (300 MHz, $CDCl_3$): 2.96 to 3.01 (m,2H), 3.78 (s,3H), 6.66 to 6.68 (m,1H), 6.86 (s,1H), 7.09 to 7.94 (m,18H), 10.5 (s,1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$): 31.35, 51.10, 52.97, 53.65, 94.88, 115.20, 118.81, 124.64, 124.19, 125.41, 126.86, 127.24, 128.62, 129.18, 129.26, 129.54, 131.68, 133.57, 137.34, 137.32, 137.79, 145.73, 148.29, 150.12, 155.72, 168.14

(2R, 6S)-ethyl 2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4e).** Yield: 89%; M.P.190-192°C; IR (KBr) 2921, 1718, 1649, 1595, 1368, 1250, 1174 cm^{-1}; HRMS (ESI): Calculated for $C_{32}H_{28}Cl_2N_2O2$: 542.1528, found: 542.1537, ^{1}H NMR (300 MHz, $CDCl_3$): 1.46 (t, 3H), 2.77 to 2.86 (m,2H), 4.34 to 4.46 (q, 2H), 5.09 (s, 1H, NH), 6.35 to 6.45 (m,1H), 6.53 to 6.63 (s,1H), 7.08 to 7.45 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): 14.82, 33.72, 54.74, 57.35, 59.87, 97.72, 112.87, 116.84, 126.68, 125.86, 127.68, 128.13, 128.42, 128.74, 129.11, 129.16, 132.14, 132.76, 137.77, 140.95, 142.48, 146.40, 155.84, 167.91.

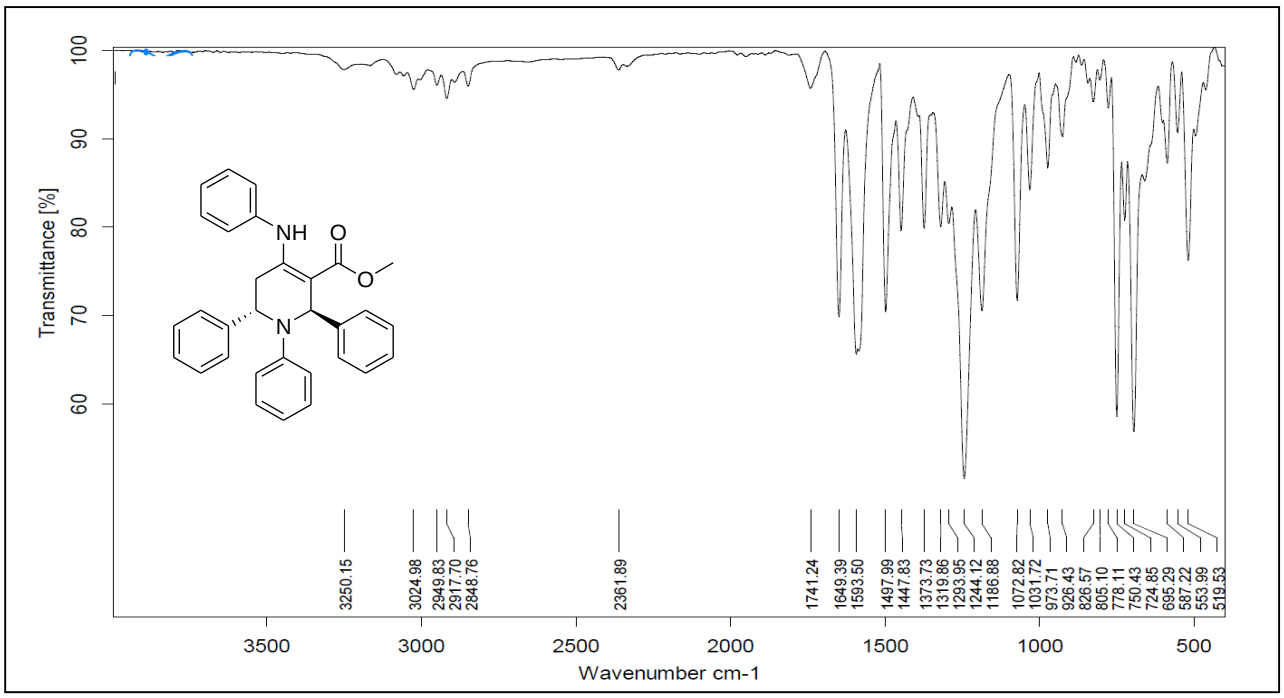
(2R,6S)-methyl,4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate **(4f).** Yield: 92%; M.P. 204-205°C) IR (KBr) 3253, 3064, 1645, 1596, 1497, 1378, 1259, 1188 cm^{-1}; HRMS (ESI): Calculated for $C_{31}H_{26}C_{l2}N_2O_2$: 528.1371, found: 528.1345, ^{1}H NMR (300 MHz, $CDCl_3$): 2.66-2.86(m,2H), 3.96 (s,3H), 5.05 (s,1H, NH), 6.16-6.18 (s,1H), 6.35-6.44 (m,1H), 6.91 to 7.30 (m,18H); ^{13}C NMR (100 MHz, $CDCl_3$): 33.49, 51.24, 55.25, 58.21, 98.33, 114.01, 121.23, 126.26, 126.52, 126.62, 127.12, 127.50, 128.40, 128.75, 128.87, 129.14, 131.44, 137.34, 142.28, 144.15, 145.43, 155.51, 168.45.

(2R,6S)-ethyl4-(4-chlorophenylamino)-1,2,6-tris(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4g).** Yield: 87%; M.P. 213-215°C; IR (KBr,) 3591, 2952, 1652, 1597, 1493, 1373, 1258, 1186 cm^{-1}; HRMS (ESI): Calculated for $C_{32}H_{26}C_{l4}N_2O_2$: 610.0748, found: 610.075, ^{1}H NMR (300 MHz, $CDCl_3$): 1.23-1.26 (t, 3H), 2.66-2.84 (m,2H), 3.68-3.73 (q,2H), 5.06 (s, 1H, NH), 6.32-6.36 (m,1H), 6.37 (s, 1H), 6.96 to 7.23 (m, 16H); ^{13}C NMR (100 MHz, $CDCl_3$): 18.46, 33.60, 51.46, 54.86, 57.37, 98.01, 114.07, 121.90, 126.98, 127.64, 127.95, 128.53, 128.90, 128.93, 129.26, 131.76, 132.43, 133.22, 136.15, 140.39, 141.60, 144.99, 155.34, 168.21.

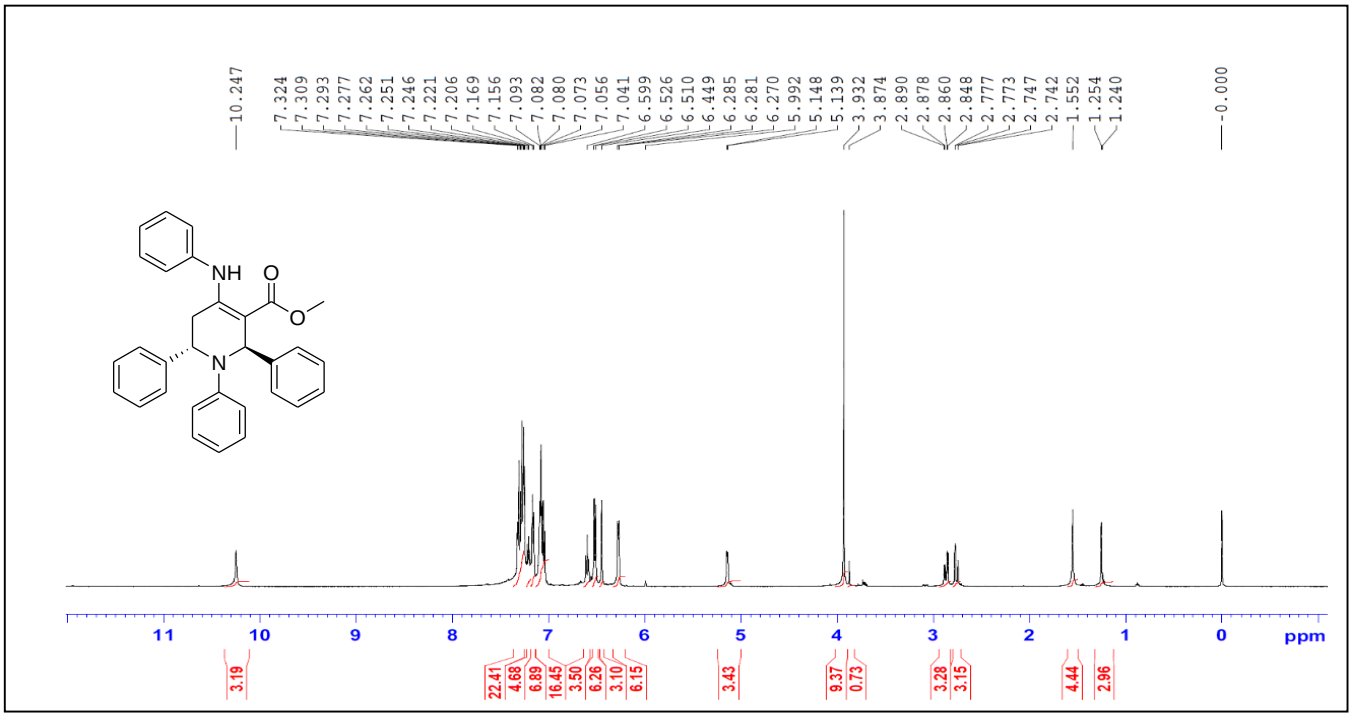
(2R,6S)-methyl4-(4-chlorophenylamino)-1-(4-chlorophenyl)1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl) pyridine-3-carboxylate (**4h**). Yield: 85%; M.P. 195-197°C; IR (KBr) 2952, 2833, 1644, 1605, 1496, 1377, 1248, 1177 cm^{-1}; HRMS (ESI): Calculated for $C_{33}H_{30}C_{l2}N_2O_4$: 588.1583, found: 588.1598, ^{1}H NMR (300 MHz, $CDCl_3$): 2.67 to 2.87 (m,2H), 3.76 (s,3H), 3.94 (s,3H), 5.04 (s, 1H, NH), 6.27 to 6.29 (m, 1H), 6.43 to 6.44 (s,1H), 6.85 to 7.26 (m, 16 H); ^{13}C NMR (100 MHz, $CDCl_3$): 33.66, 51.18, 55.28, 55.33, 57.65, 98.66, 113.65, 114.65, 114.18, 121.17, 126.91, 127.33, 127.60, 128.70, 129.07, 131.33, 134.04, 135.03, 136.40, 144.53, 154.68, 158.34, 158.82, 169.50.

Spectral Data of Compounds (4a- 4h)

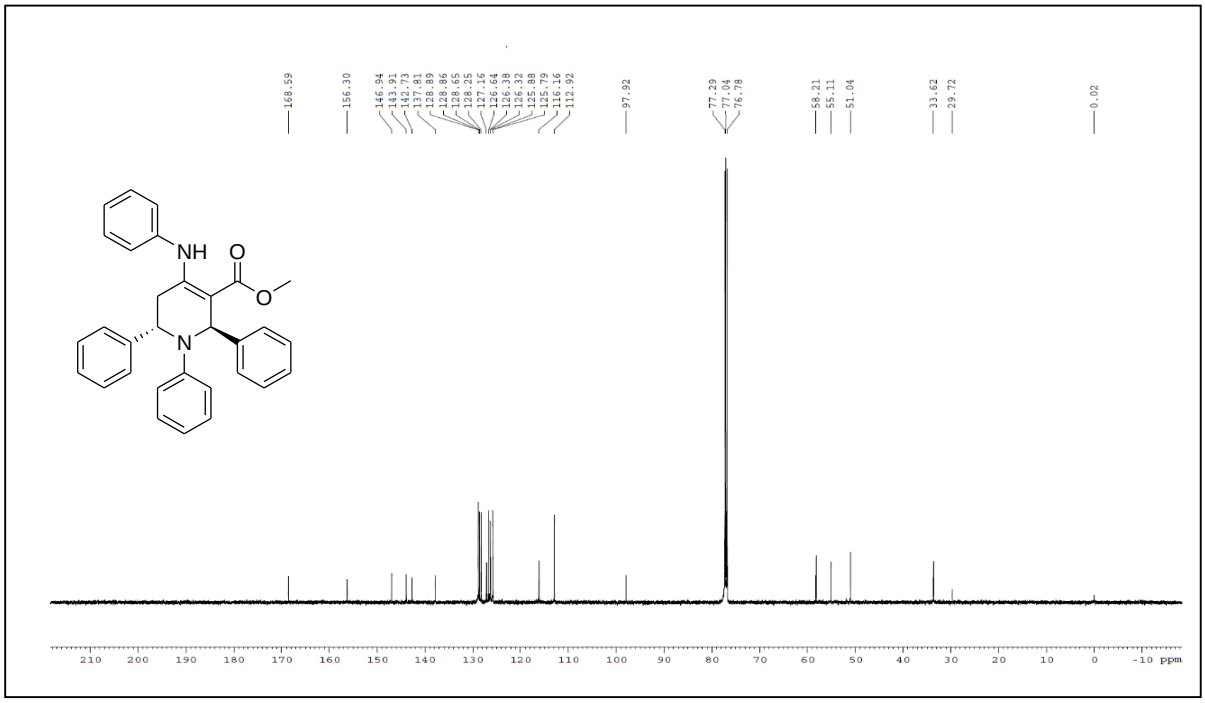
IR (2R,6S)-methyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4a).**



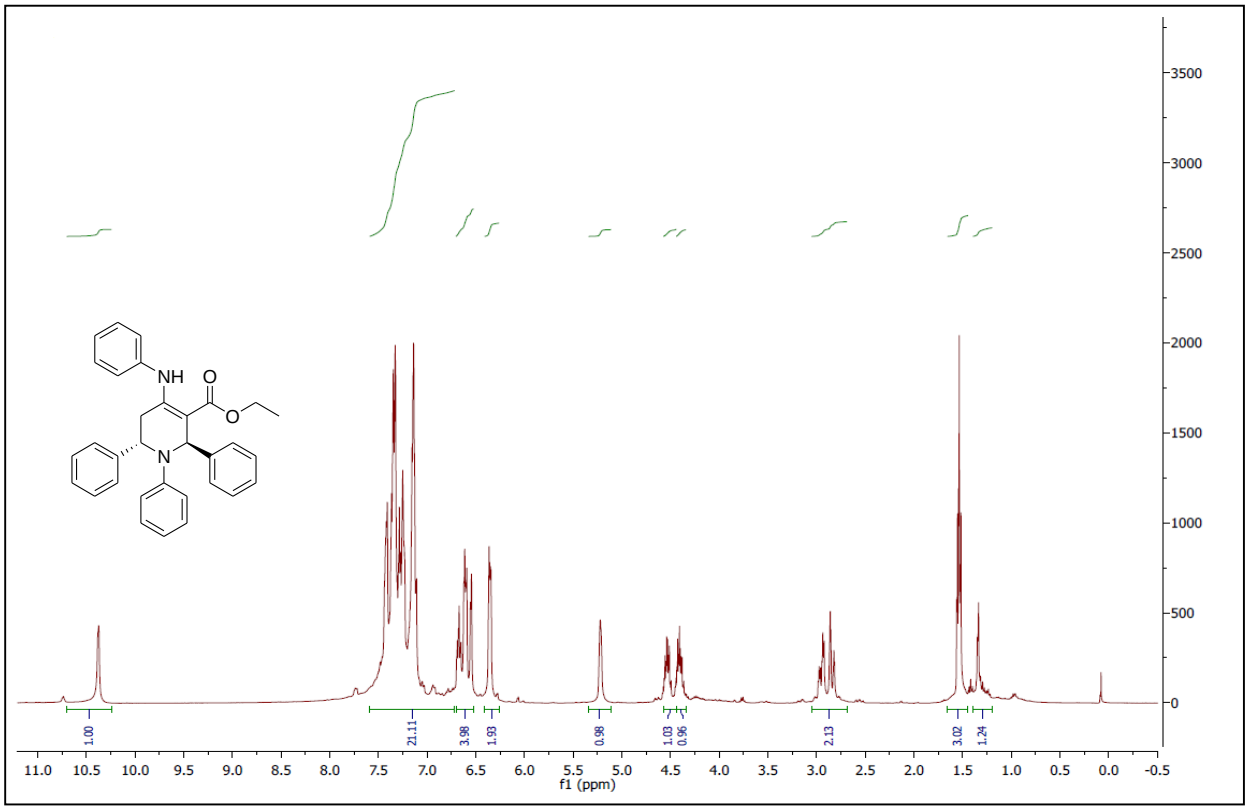
^{1}H NMR (2R,6S)-methyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4a).**



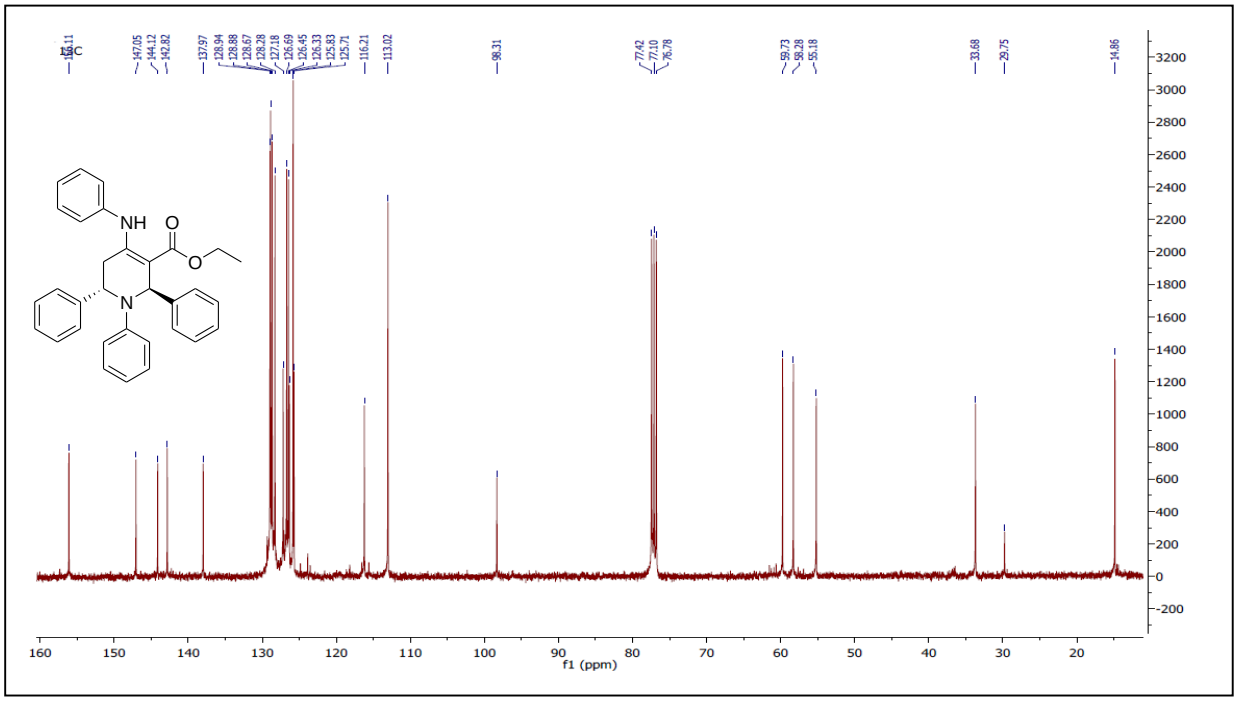
^{13}C NMR (2R,6S)-methyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4a).**



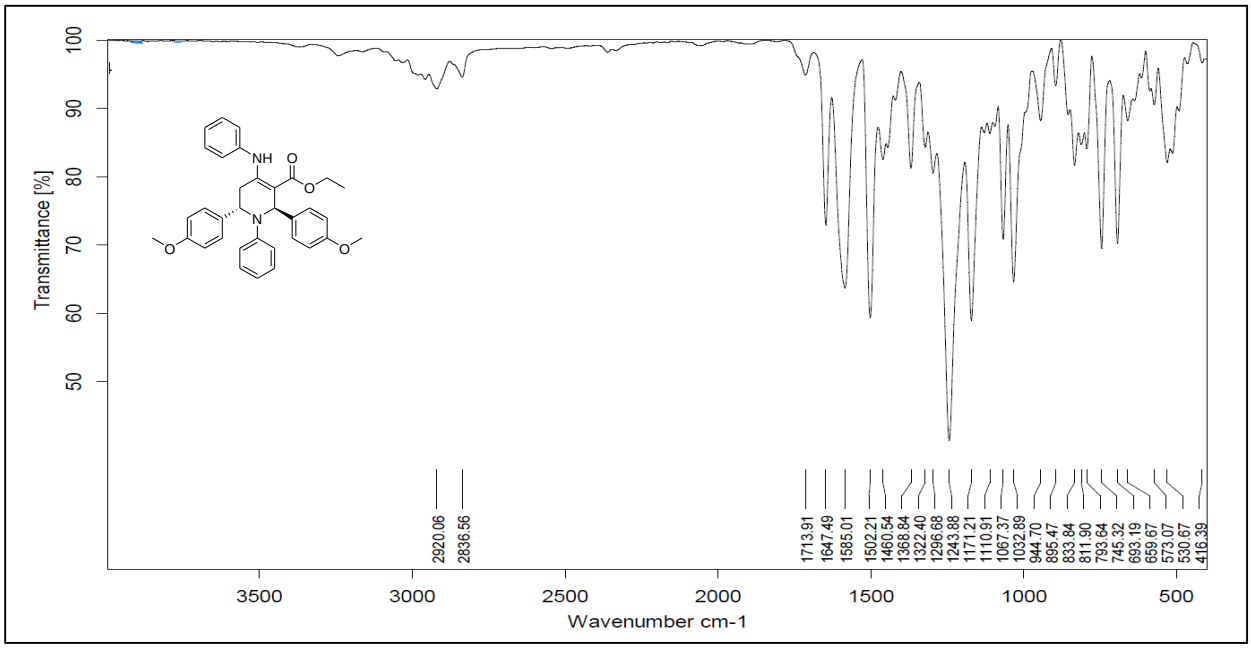
^{1}H NMR (2R,6S)-ethyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4b).**



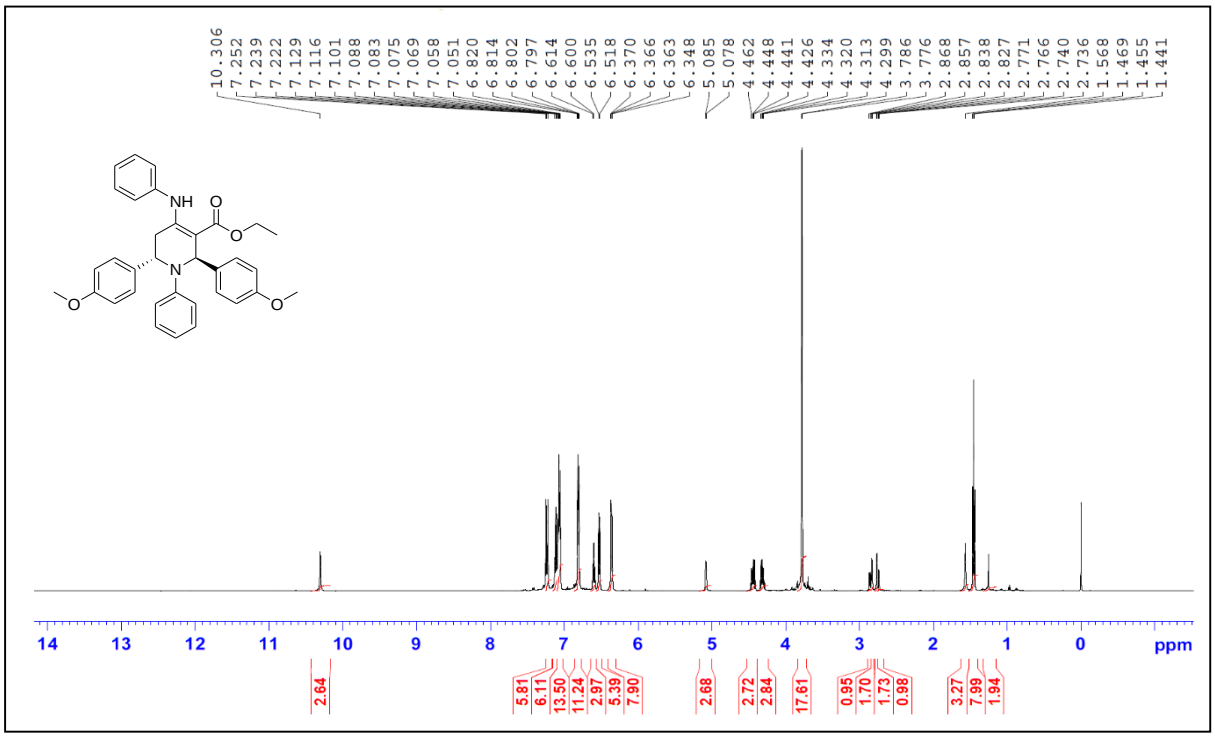
^{13}C NMR (2R,6S)-ethyl 1,2,5,6-tetrahydro-1,2,6-triphenyl-4-(phenylamino)pyridine-3-carboxylate **(4b).**



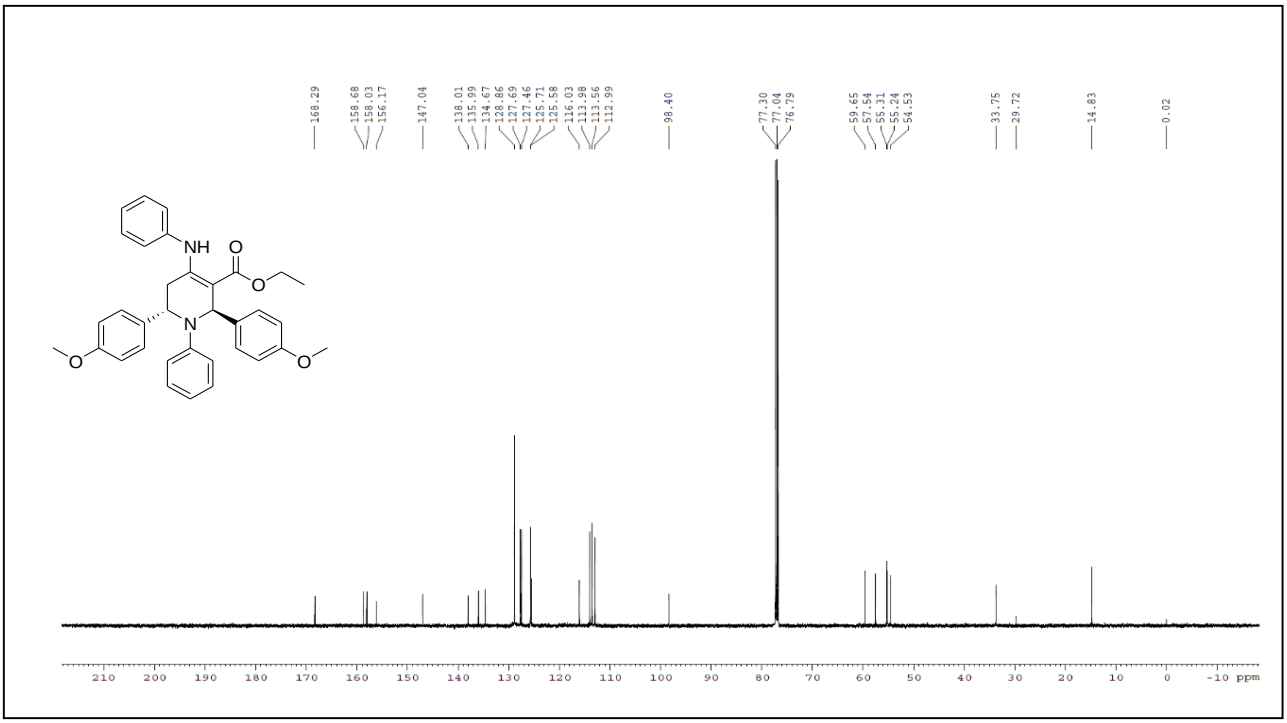
IR (2R,6S)-ethyl1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4(phenylamino)pyridine-3-carboxylate **(4c)**



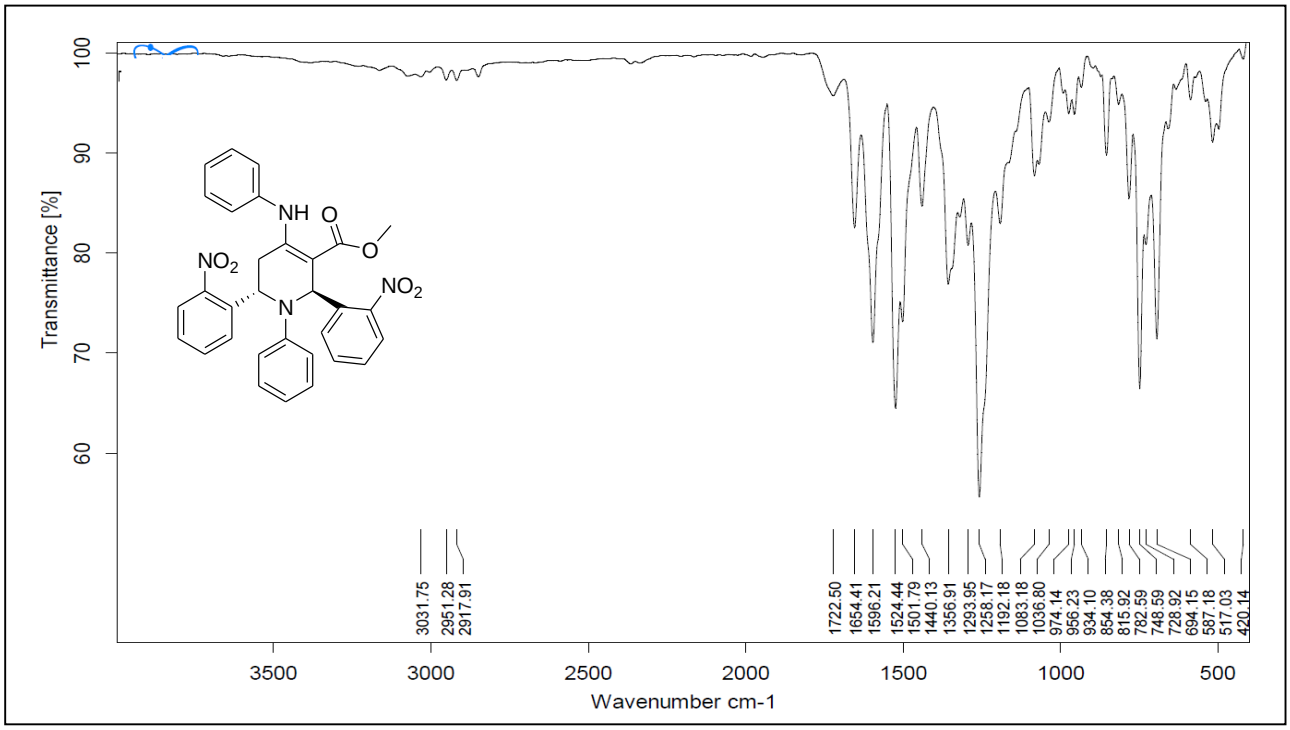
[1]H NMR (2R,6S)-ethyl1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4(phenylamino)pyridine-3-carboxylate **(4c)**



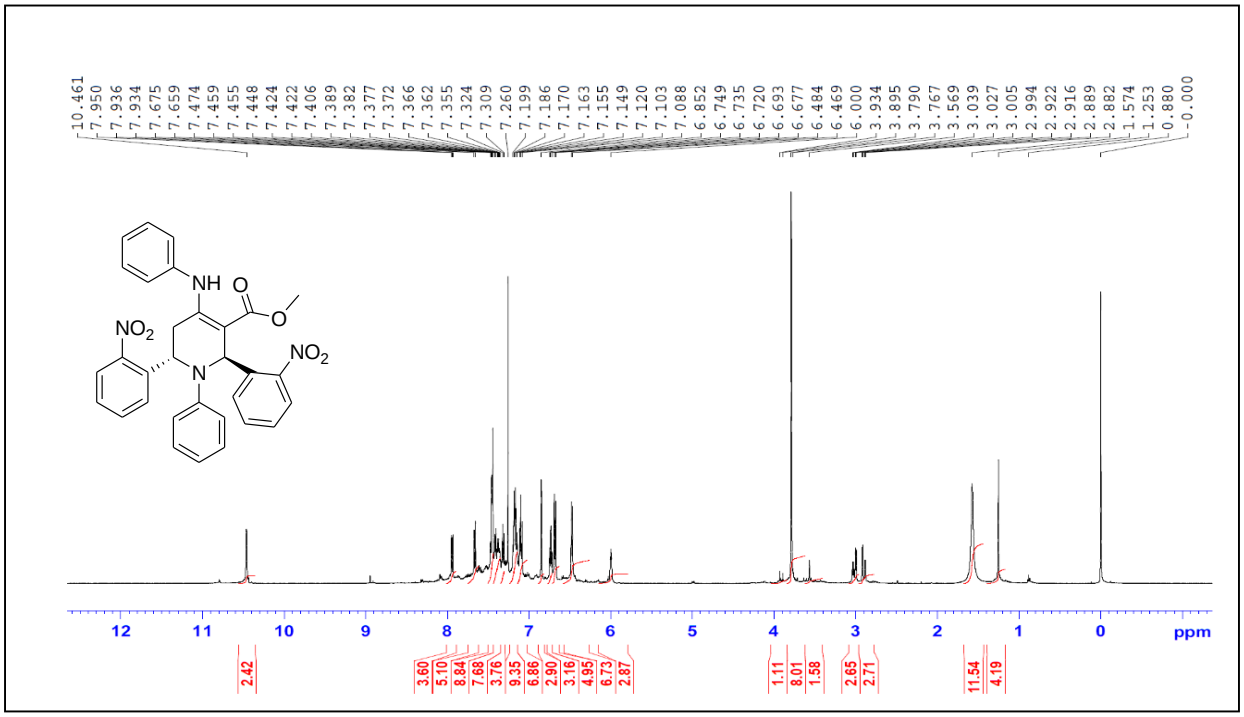
[13]C NMR (2R,6S)-ethyl1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)-1-phenyl-4(phenylamino)pyridine-3-carboxylate **(4c)**



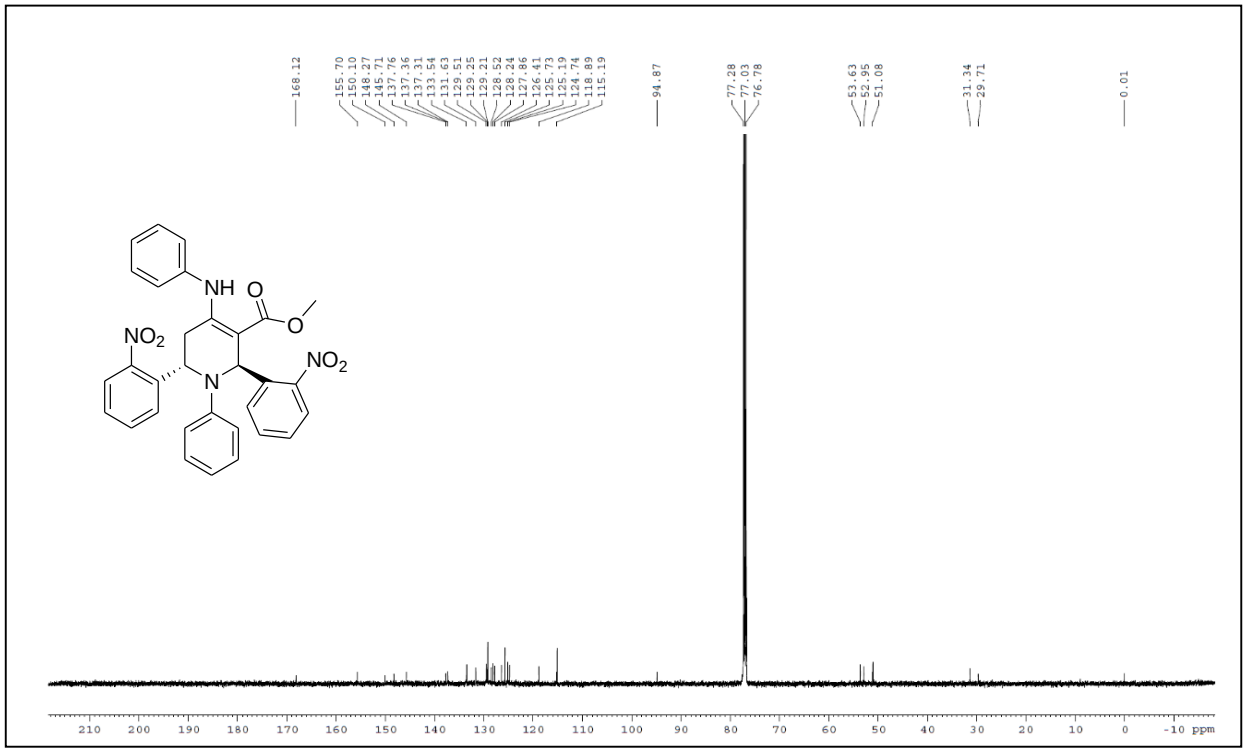
IR (2R,6S)-methyl 1,2,5,6-tetrahydro-2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4d).**



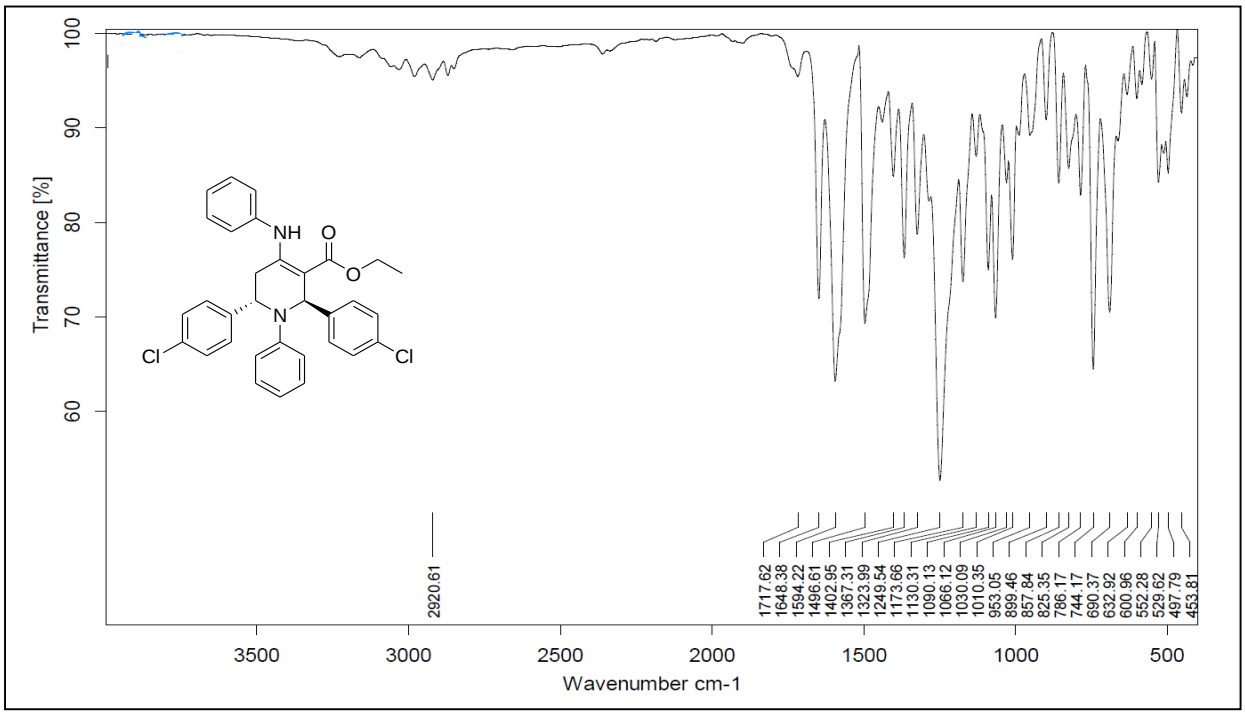
^{1}H NMR (2R,6S)-methyl 1,2,5,6-tetrahydro-2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4d).**



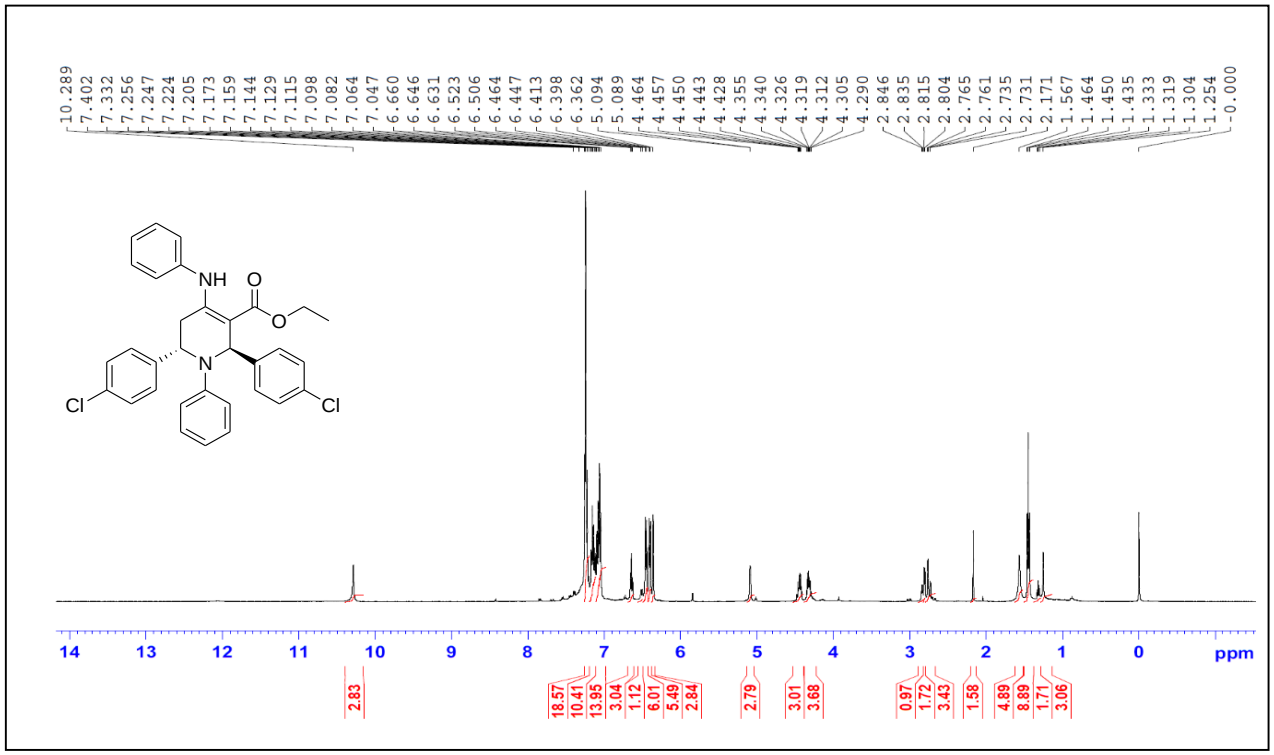
^{13}C NMR (2R,6S)-methyl 1,2,5,6-tetrahydro-2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4d).**



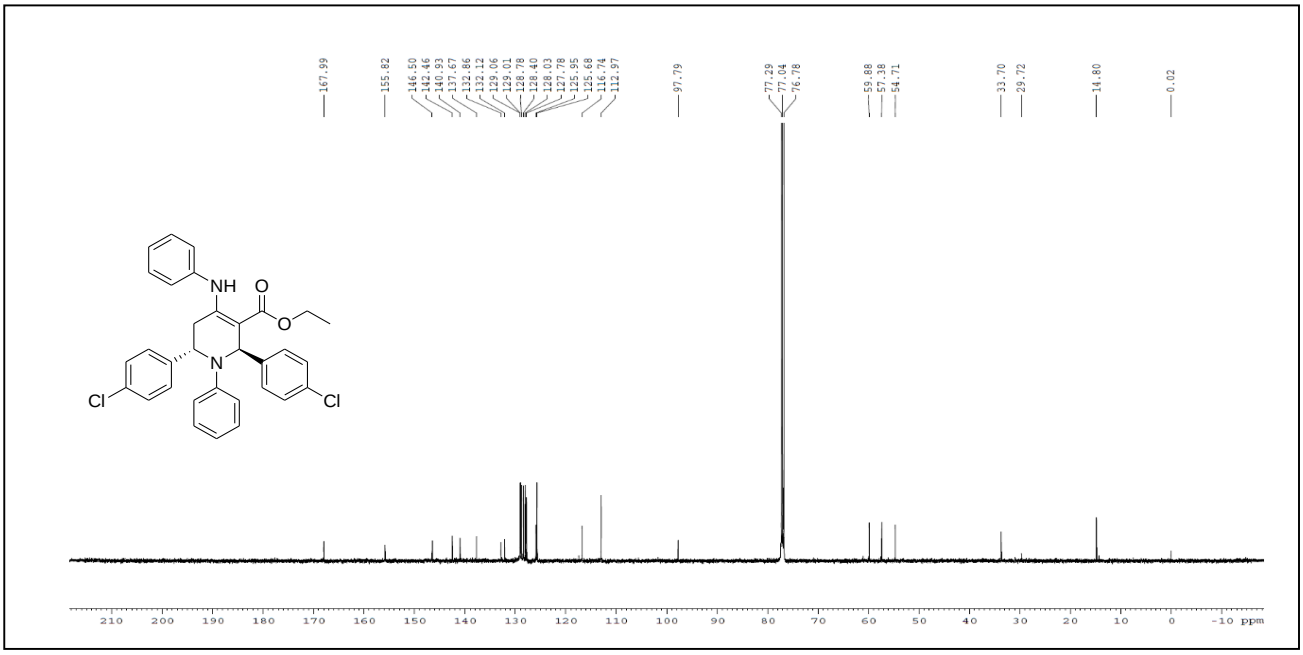
IR (2R, 6S)-ethyl 2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4e).**



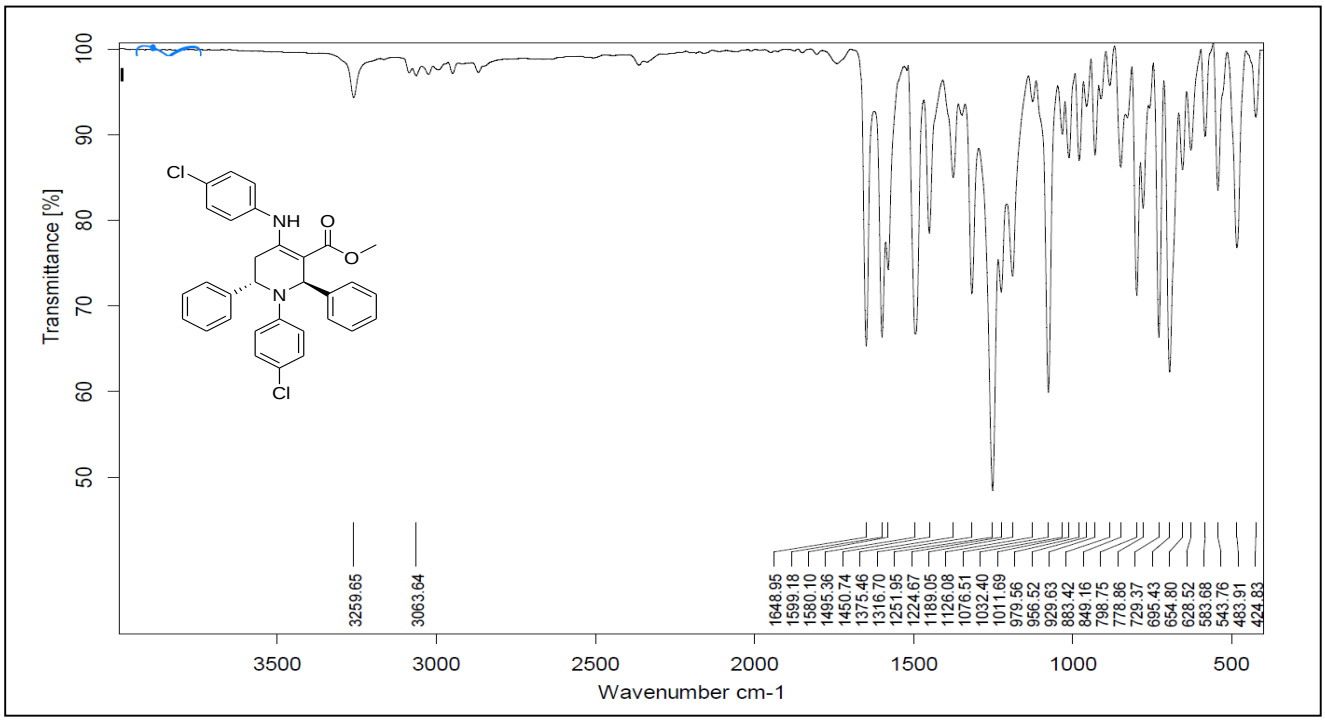
[1]H NMR (2R, 6S)-ethyl 2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4e).**



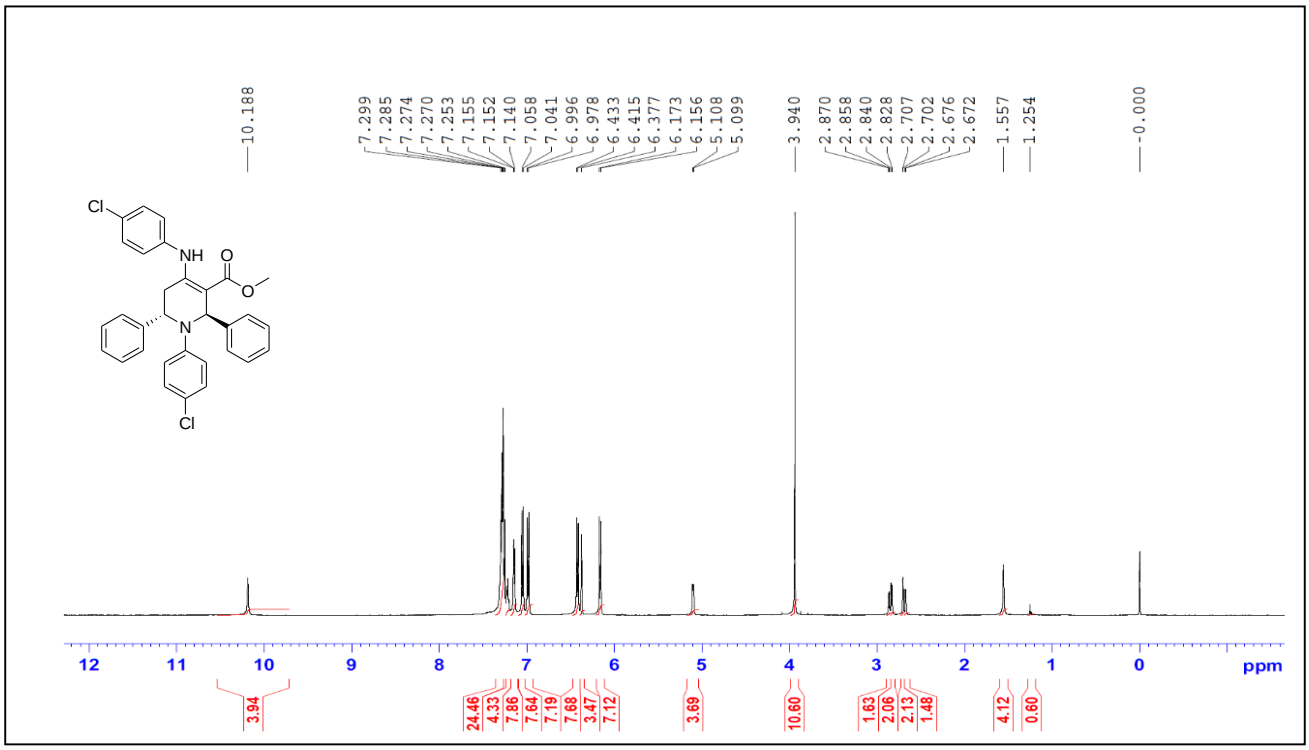
[13]C NMR (2R, 6S)-ethyl 2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydro-1-phenyl-4-(phenylamino)pyridine-3-carboxylate **(4e).**



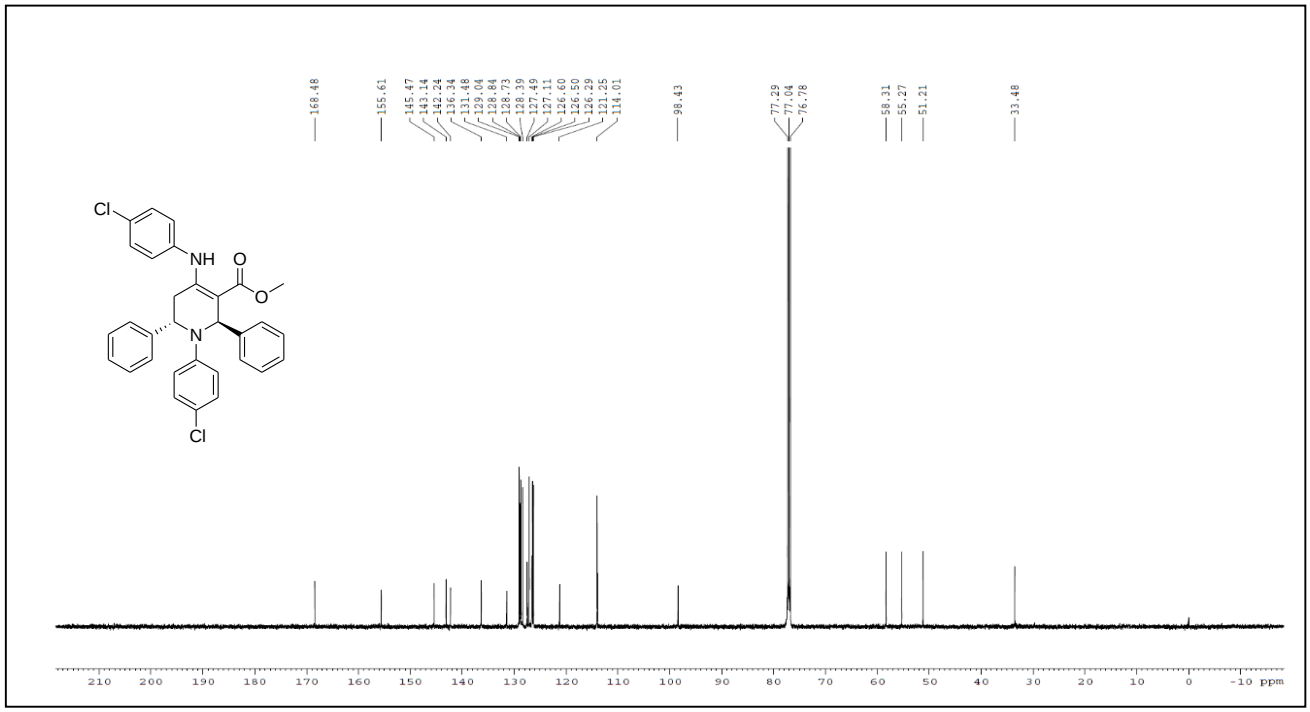
IR (2R,6S)-methyl,4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate **(4f).**



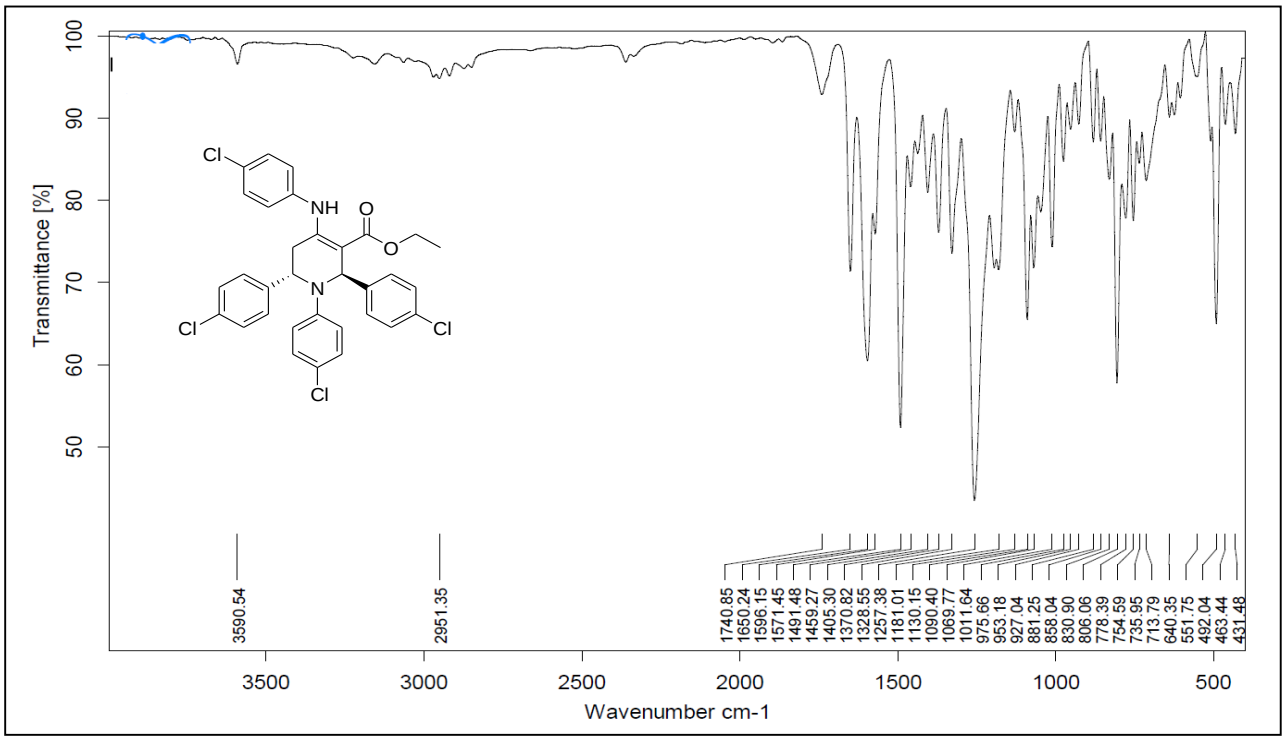
^{1}H NMR (2R,6S)-methyl,4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate **(4f).**



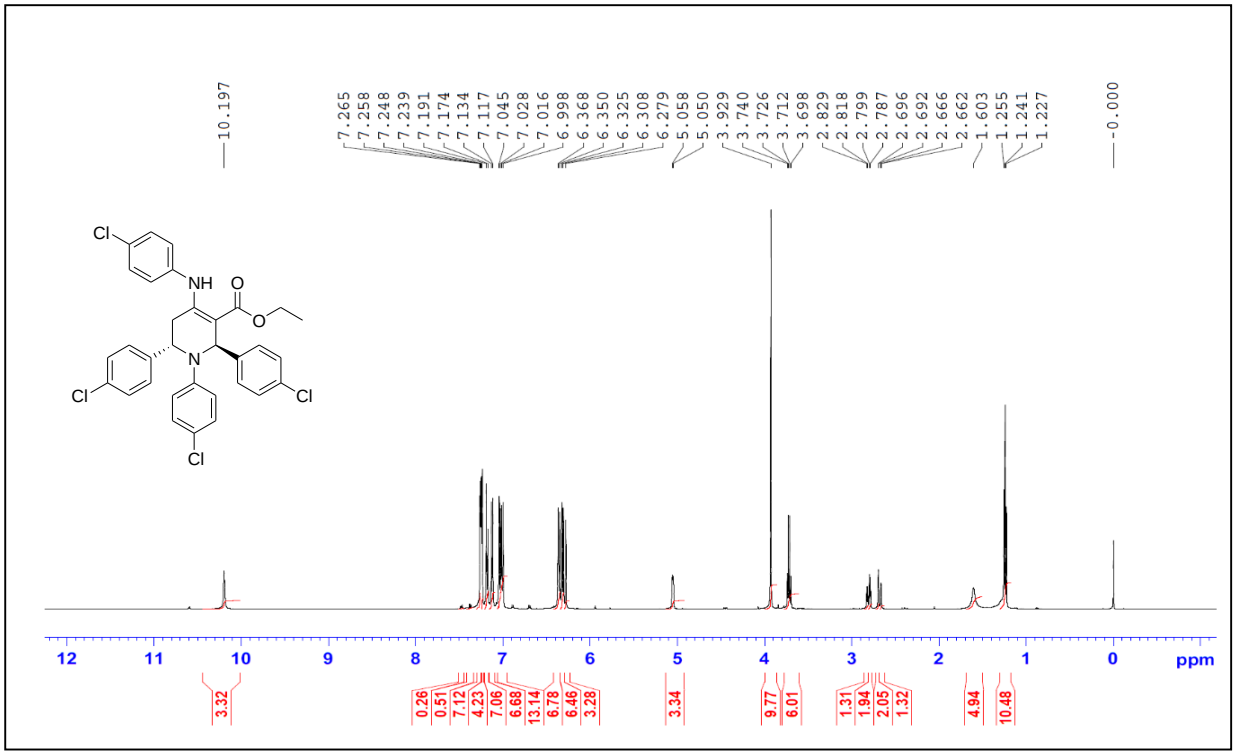
^{13}C NMR (2R,6S)-methyl,4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-diphenylpyridine-3-carboxylate **(4f).**



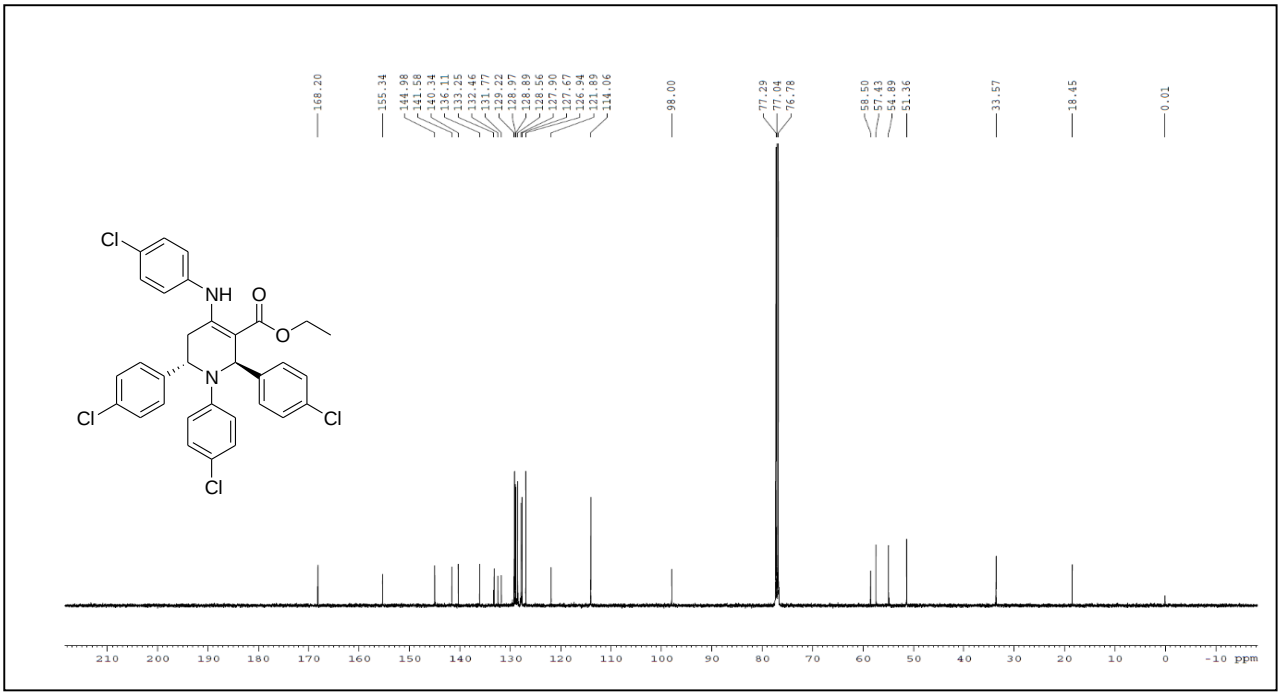
IR (2R,6S)-ethyl4-(4-chlorophenylamino)-1,2,6-tris(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4g).**



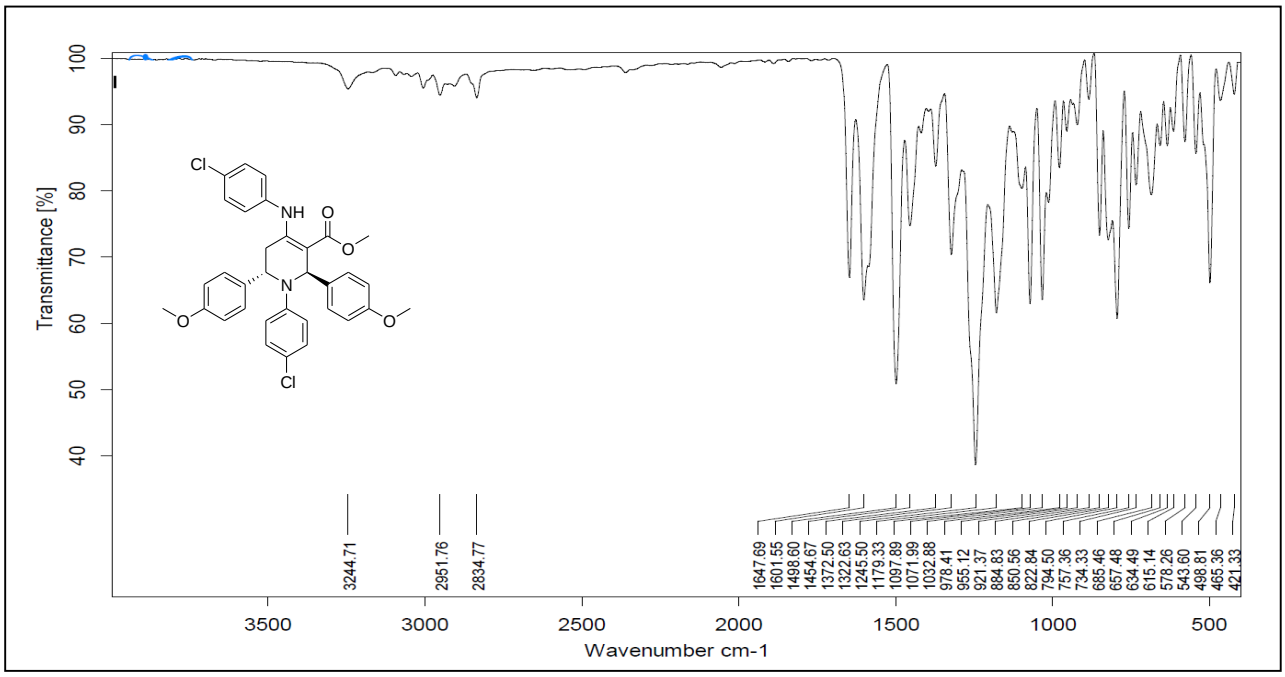
^{1}H NMR (2R,6S)-ethyl4-(4-chlorophenylamino)-1,2,6-tris(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4g).**



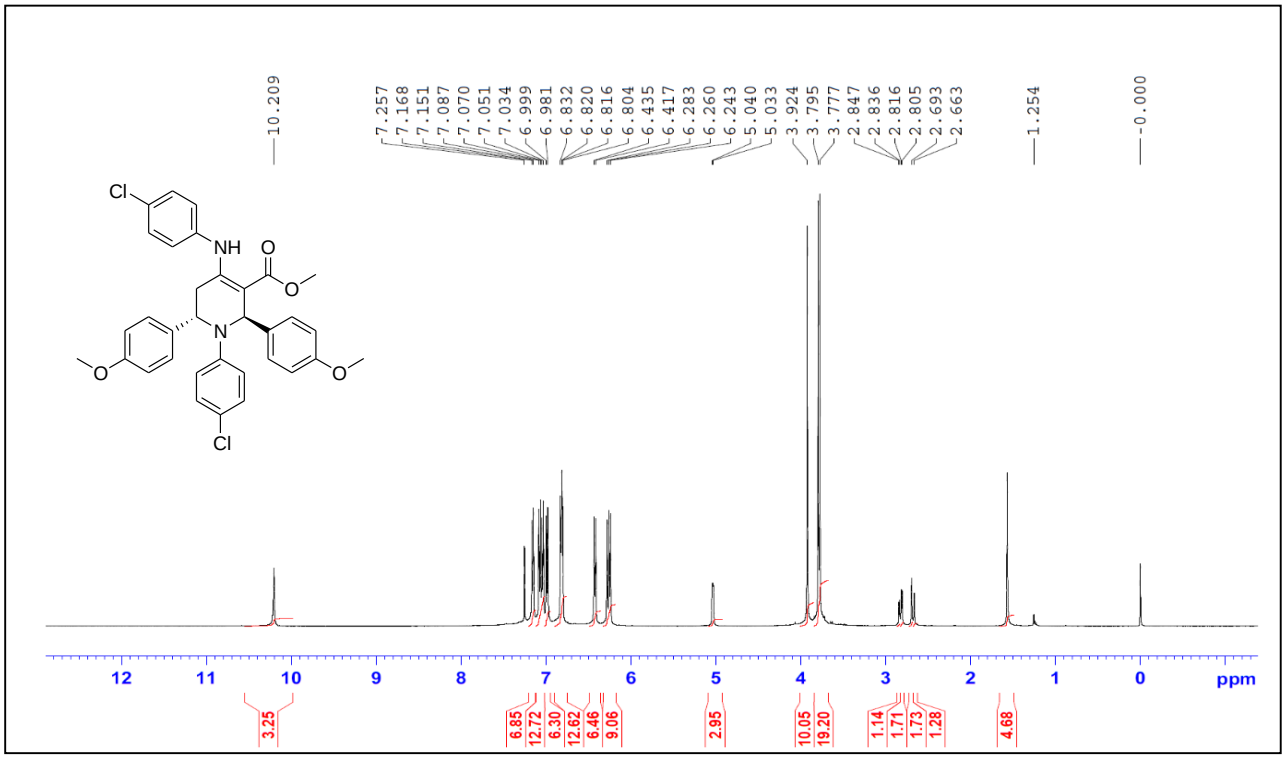
^{13}C NMR (2R,6S)-ethyl4-(4-chlorophenylamino)-1,2,6-tris(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4g).**



IR (2R,6S)-methyl4-(4-chlorophenylamino)-1-(4-chlorophenyl)1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl) pyridine-3-carboxylate **(4h).**



^{1}H NMR (2R,6S)-methyl4-(4-chlorophenylamino)-1-(4-chlorophenyl)1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl) pyridine-3-carboxylate **(4h).**



^{13}C NMR (2R,6S)-methyl4-(4-chlorophenylamino)-1-(4-chlorophenyl)1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl) pyridine-3-carboxylate **(4h).**