Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Cu(II)-grafted SBA-15 functionalized S-methylisothiourea aminated epibromohydrin (SBA-15/E-SMTU-Cu^{II}): a novel and efficient heterogeneous mesoporous catalyst for the green, one-pot, pseudo five-component synthesis of tetrahydropyridine derivatives at room temperature

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Experimental

General

The purity determinations of the products and the progress of the reactions were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of the products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on pressed KBr pellets using an AVATAR 370 FT-IR spectrometer (Therma Nicolet spectrometer, USA) at room temperature in the range between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}. The NMR spectra were recorded on a NMR Bruker Avance spectrometer at 300 MHz in $CDCl_3$ as solvent in the presence of tetramethylsilane as the internal standard and the coupling constants (*J* values) are given in Hz. Elemental analyses were performed using a Thermo Finnigan Flash EA 1112 Series instrument (furnace: 900 ˚C, oven: 65 ˚C, flow carrier: 140 mL min^{-1}, flow reference: 100 mL min^{-1}). Mass spectra were recorded with a CH7A Varianmat Bremem instrument at 70 eV electron impact ionization, in *m/z* (rel%). All yields refer to isolated products after purification by recrystallization.

Ethyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4a): (0.46 g, 98%); white solid; mp 170–171 ˚C (from EtOH) (Lit.[1] 169–171 ˚C); MS*, m/z* 474 (M^+, 18%), 476 (13, M

+ 2), 397 (30, M – $C_6H_5^{\bullet}$), 271 (24, M – $C_{12}H_{13}NO_2^{2\bullet}$), 203 (37, M – $C_{20}H_{17}N^{2\bullet}$), 77 (19, M – $C_{26}H_{25}N_2O_2^{\bullet}$), 28 (100, M – $C_{30}H_{26}N_2O_2^{\bullet}$).

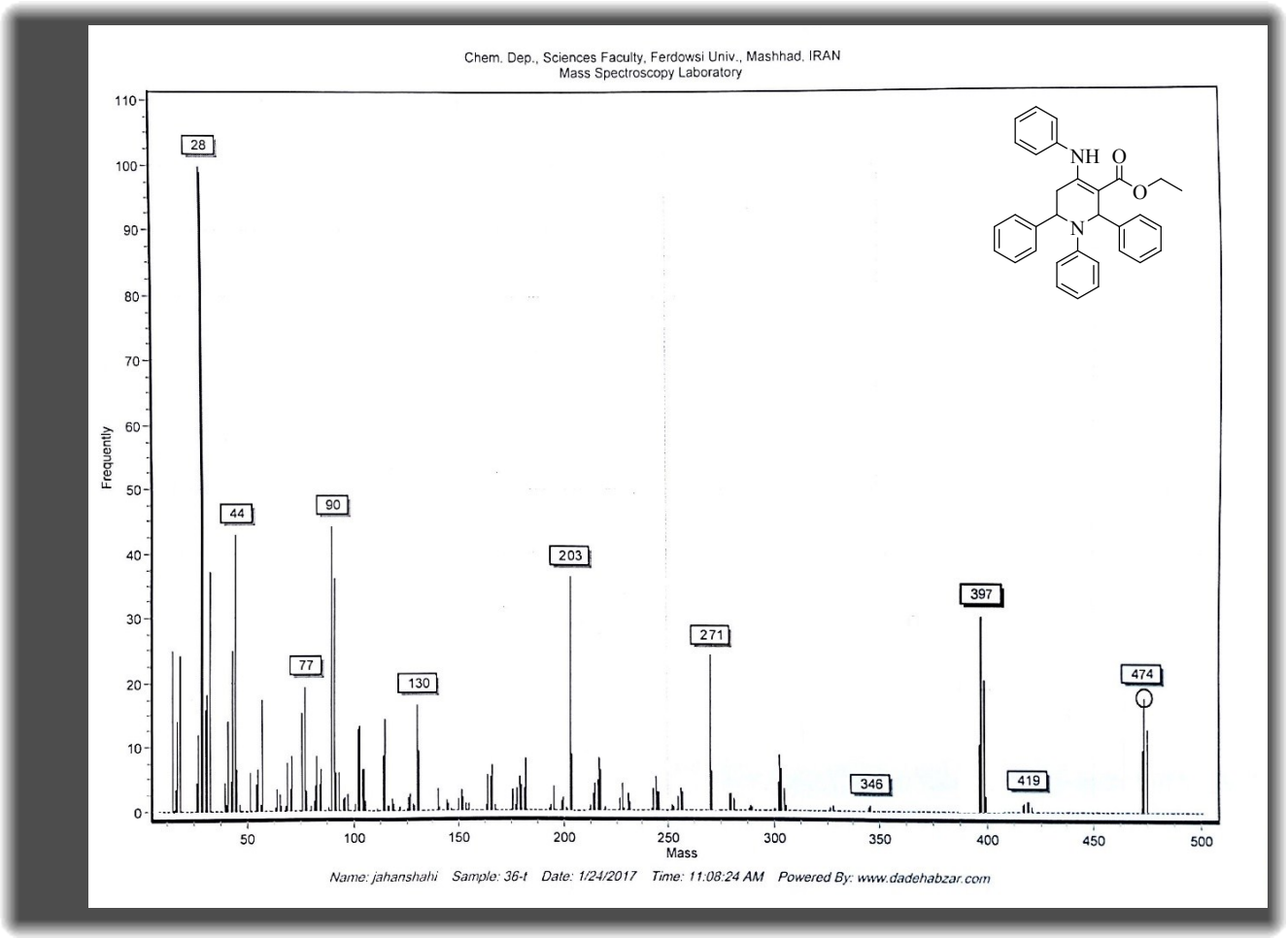

Figure 1: Mass spectrum of ethyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4a)**.

Ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4b): (0.50 g, 89%); pale yellow solid; mp 246–248 ˚C (from EtOH) (Lit.[2] 247–249 ˚C); FT-IR (KBr): ν_{max}/cm^{-1} 3235, 3043, 2973, 2851, 1656, 1592, 1502, 1344, 1254, 1069; ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.52 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.92 (2 H, br d, *J* = 3.9 Hz, 5-H', 5-H''), 4.35-4.46 (1 H, m, OCH_aH_b), 4.47-4.58 (1 H, m, OCH_aH_b), 5.31 (1 H, br s, 6-H), 6.43-6.48 (4 H, m, Ph), 6.52 (1 H, s, 2-H), 6.73 (1 H, t, *J* = 7.2 Hz, Ph), 7.11-7.23 (5 H, m, Ph), 7.29-7.35 (1 H, m, Ph), 7.56 (2 H, d, *J* = 8.7 Hz, Ph), 8.18 (5 H, t, *J* = 8.4 Hz, Ph), 10.37 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 14.84, 33.63,

55.23, 57.37, 60.30, 96.91, 112.95, 117.68, 123.81, 123.97, 125.46, 126.38, 127.37, 127.40, 129.24, 129.39, 137.21, 145.82, 146.81, 147.32, 149.80, 151.71, 155.35, 167.64; MS, *m/z* 564 (M^+, 28%), 565 (34, M + 1), 491 (13, M – $C_3H_5O_2^•$), 441 (97, M – $C_6H_5NO_2^•$), 334 (72), 223 (75), 77 (56, M – $C_{26}H_{23}N_4O_6^•$), 28 (90, M – $C_{30}H_{24}N_4O_6^•$).

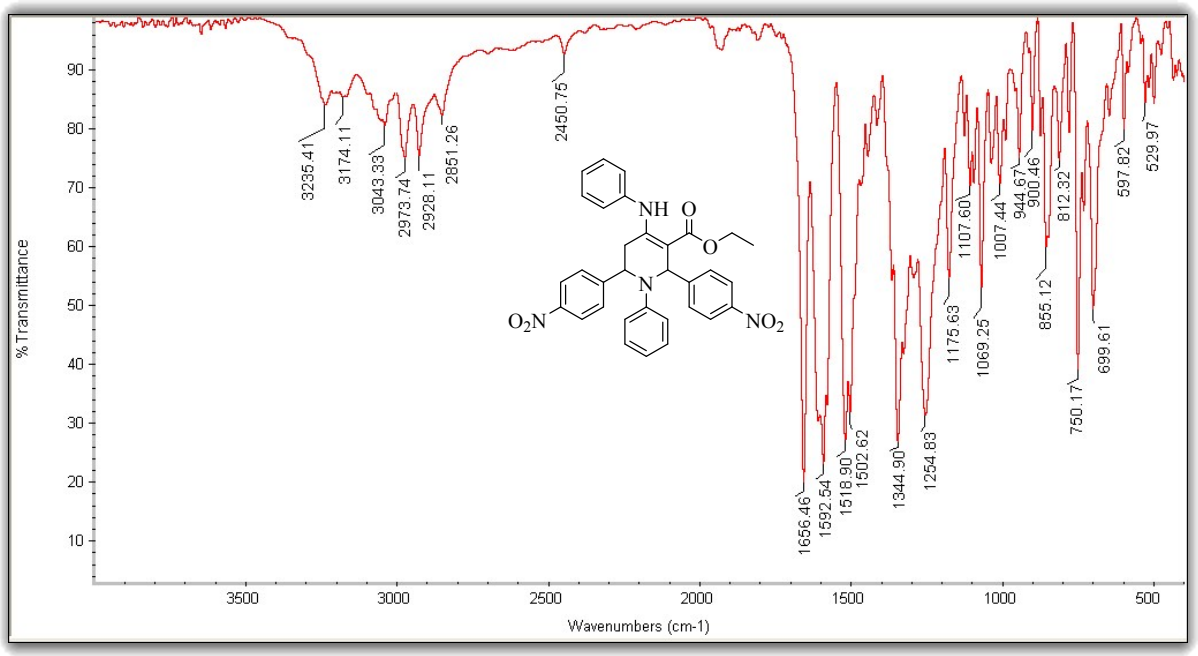

Figure 2: FT-IR spectrum (KBr) of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)**.

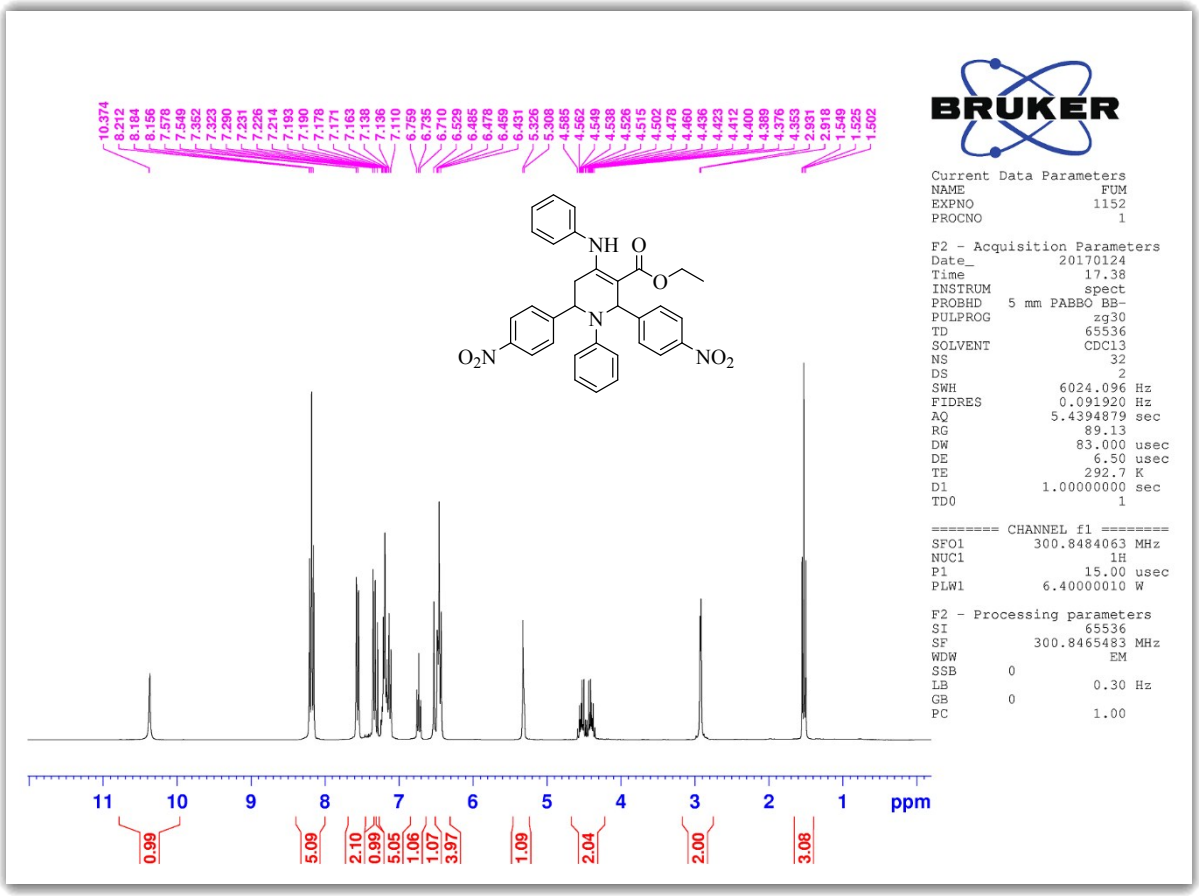

Figure 3: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)**.

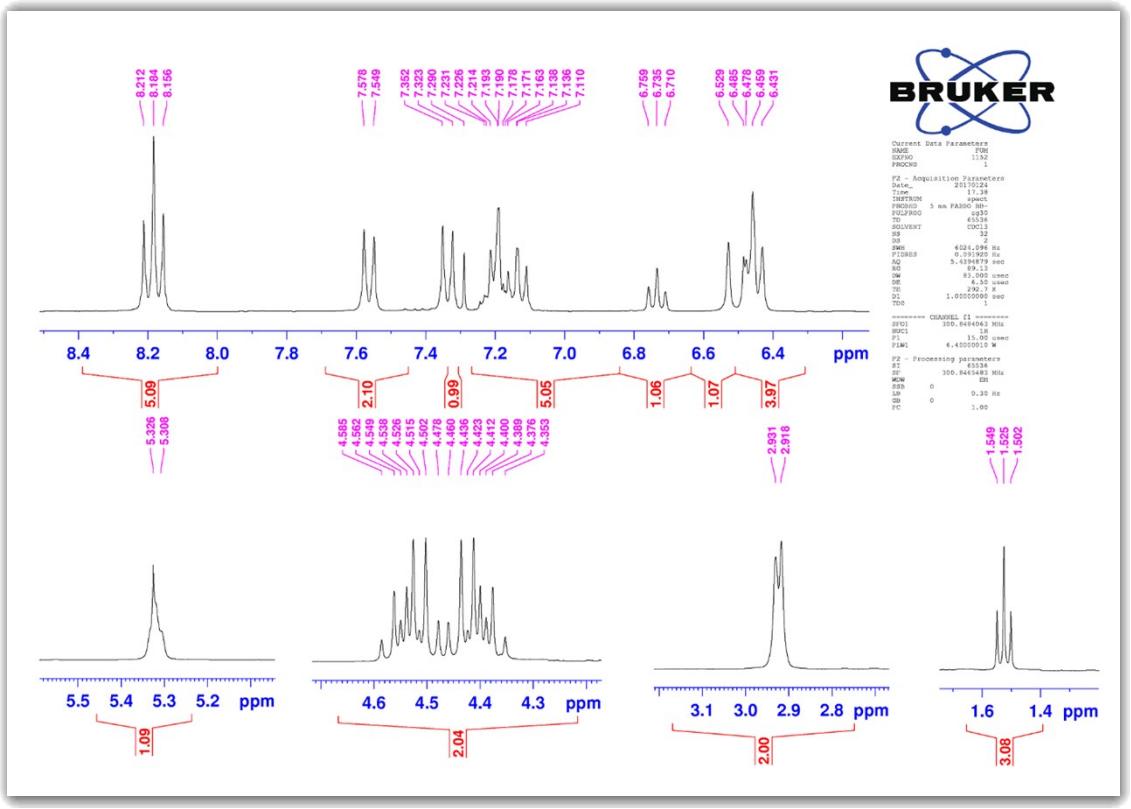

Figure 4: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)**; expanded form.

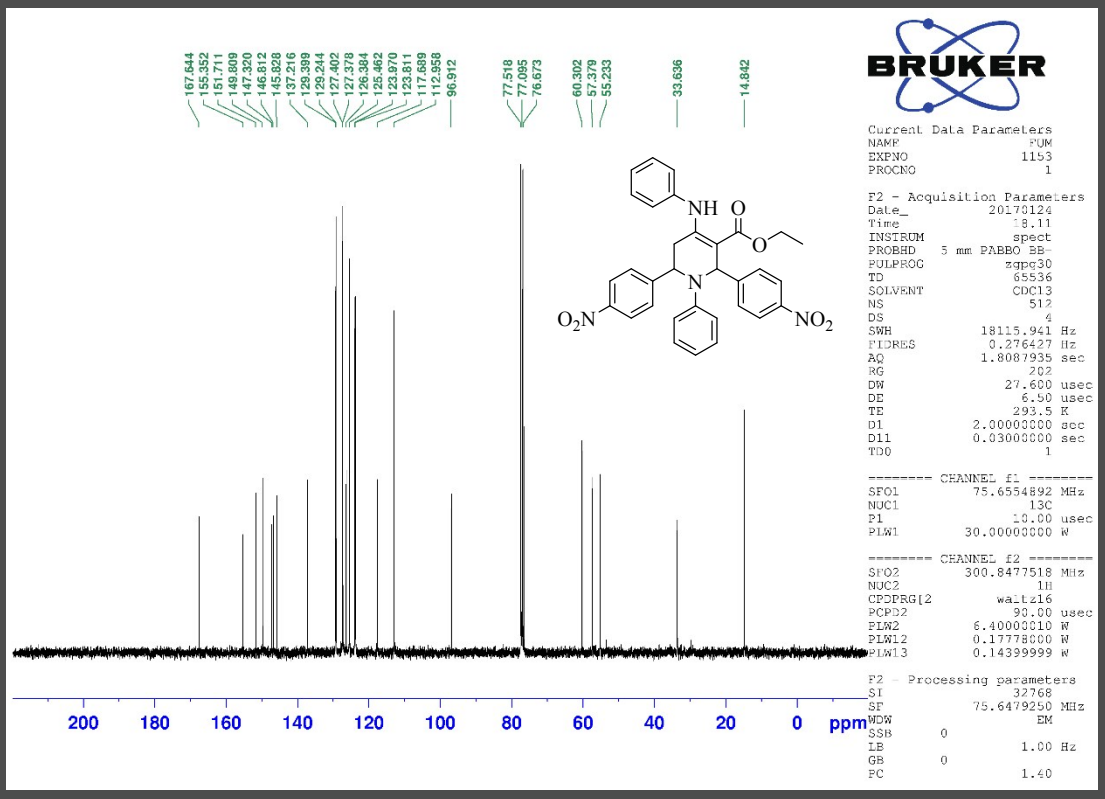

Figure 5: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)**.

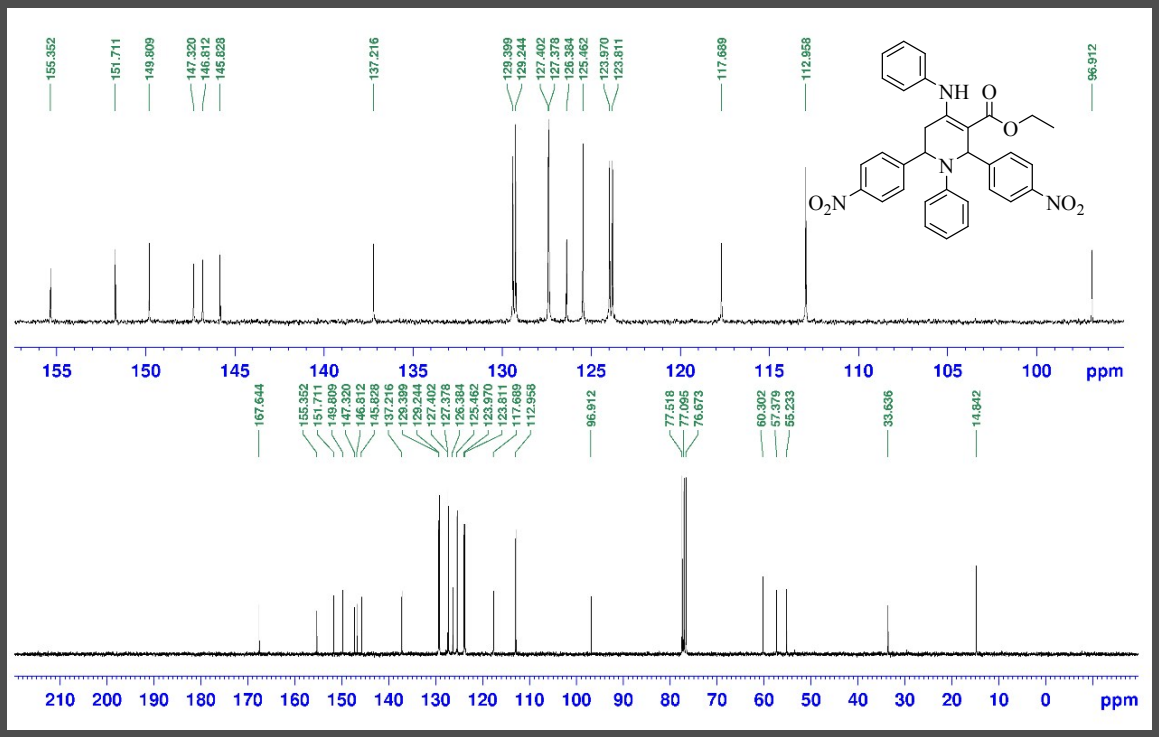

Figure 6: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)** and its expanded form.

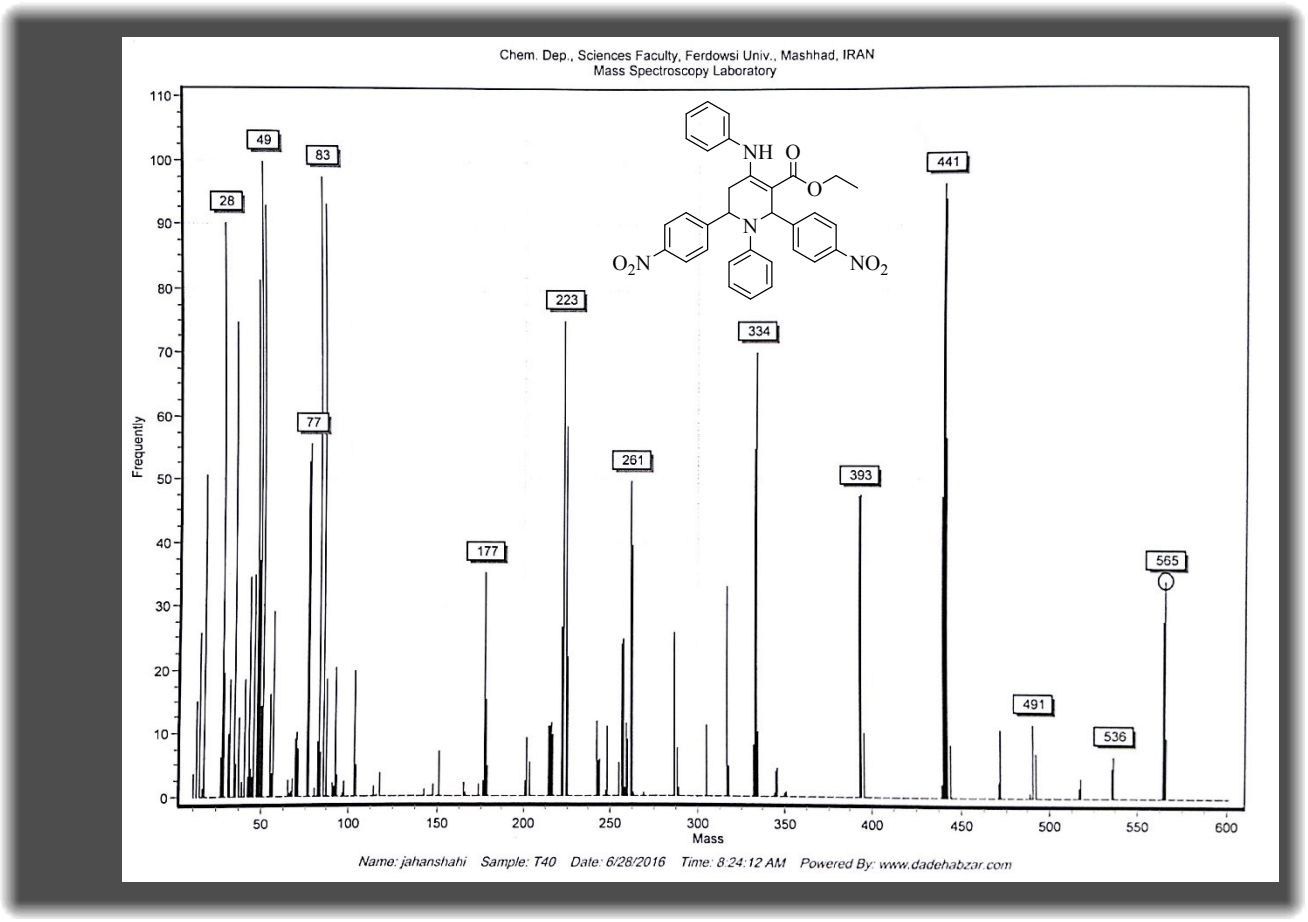

Figure 7: Mass spectrum of ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4b)**.

Ethyl 2,6-bis(4-cyanophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4c): (0.50 g, 97%); white solid; mp 191–192 ˚C (from EtOH) (Lit.[3] 190–193 ˚C); MS*, m/z* 525 (M^+, 20%), 527 (9, M + 2), 422 (95, M – $C_7H_4N^•$), 204 (82, M – $C_{22}H_{14}N_3^{2•}$), 93 (90, M – $C_{28}H_{21}N_3O_2^•$), 77 (94, M – $C_{28}H_{23}N_4O_2^•$), 29 (93, M – $C_{32}H_{23}N_4O_2^•$).

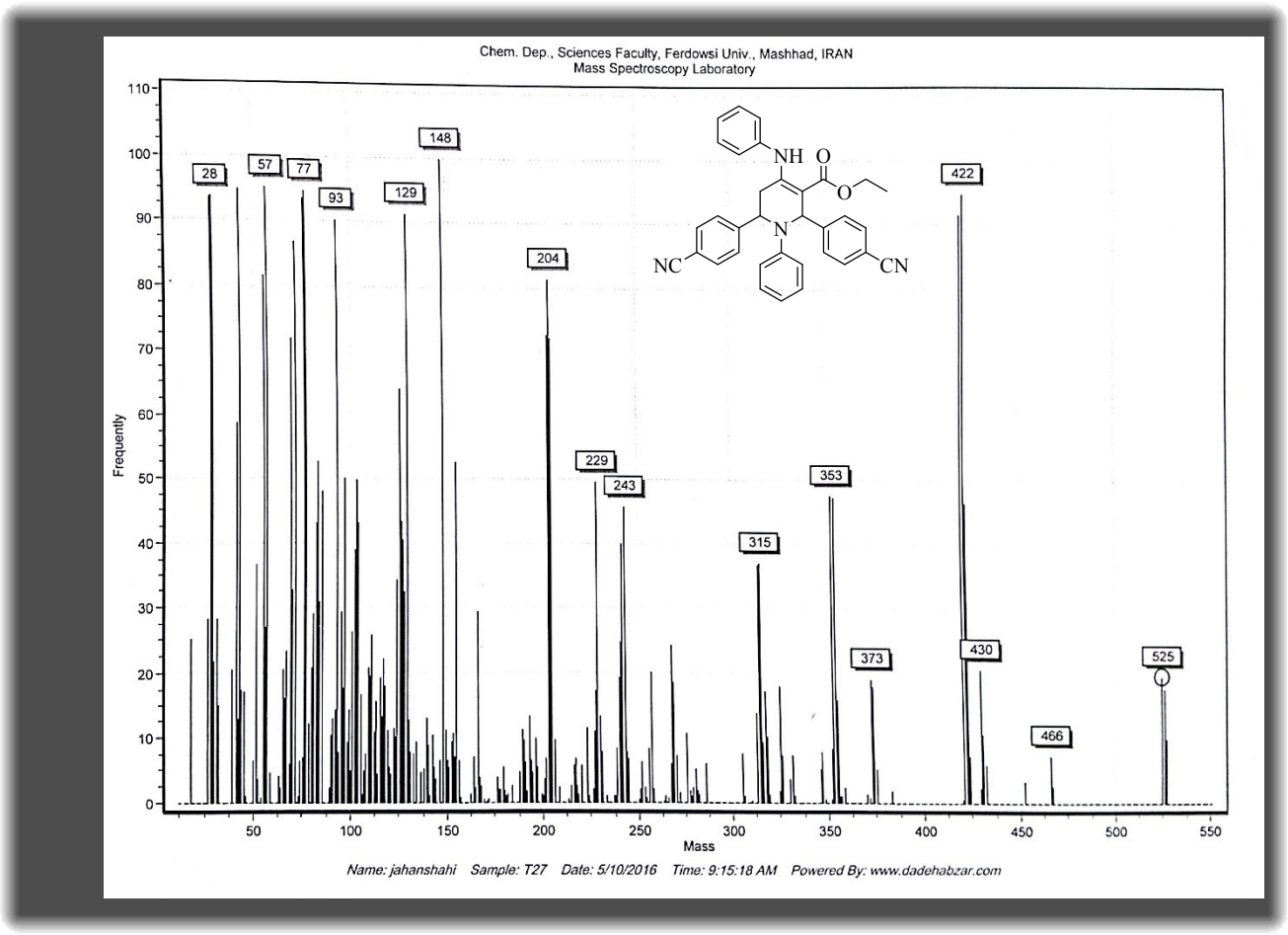

Figure 8: Mass spectrum of ethyl 2,6-bis(4-cyanophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4c)**.

Ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4d): (0.49 g, 96%); white solid; mp 202–203 ˚C (from EtOH) (Lit.[4] 203–204 ˚C), ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.38 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.67 (1 H, dd, *J* = 2.7, 2.7 Hz, 5-H'), 2.76 (1 H, dd, *J* = 5.1, 5.4 Hz, 5-H''), 4.19-4.30 (1 H, m, OCH_aH_b), 4.32-4.43 (1 H, m, OCH_aH_b), 5.03 (1 H, br s, 6-H), 6.30 (1 H, s, 2-H), 6.33 (1 H, s, Ph), 6.40 (2 H, d, *J* = 8.4 Hz, Ph), 6.56 (1 H, t, *J* = 7.2 Hz, Ph), 6.88 (4 H, t, *J* = 7.9 Hz, Ph), 6.98-7.22 (10 H, m, Ph), 10.23 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 14.80, 33.80, 54.62, 57.34, 59.82, 98.05, 113.01, 114.87, 115.15, 115.32, 115.60, 116.58, 125.65, 125.86, 127.84, 127.95, 128.06, 128.16, 129.00, 137.75, 138.08, 139.50, 146.63, 155.89, 159.89, 160.35, 163.12, 163.59, 168.06; MS, *m/z* 510 (M^+, 75%), 512 (95, M + 2), 437 (28, M

– $C_3H_5O_2^{\bullet}$), 415 (100, M – $C_6H_4F^{\bullet}$), 307 (95, M – $C_{12}H_{13}NO_2^{2\bullet}$), 77 (96, M – $C_{26}H_{23}F_2N_2O_2^{\bullet}$), 28 (94, M – $C_{30}H_{24}F_2N_2O_2^{\bullet}$).

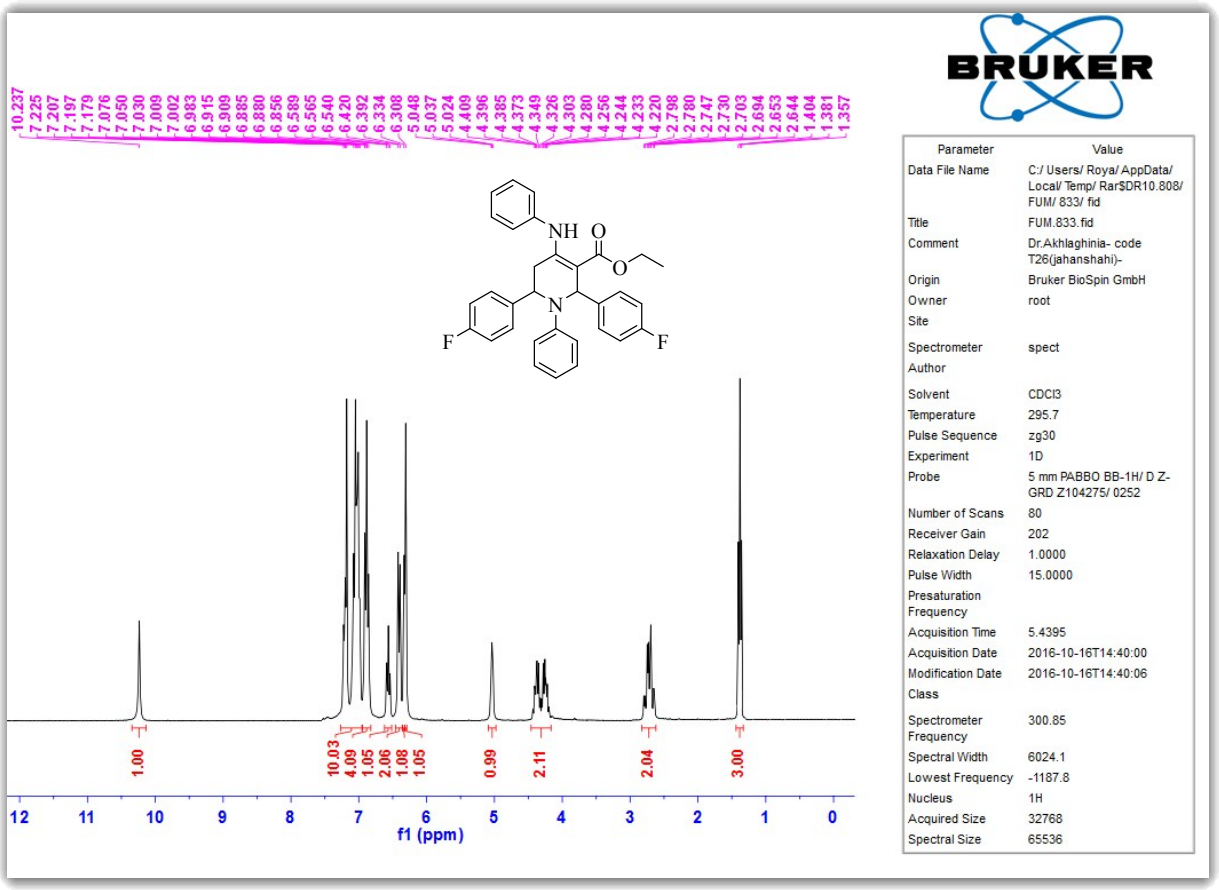

Figure 9: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4d**).

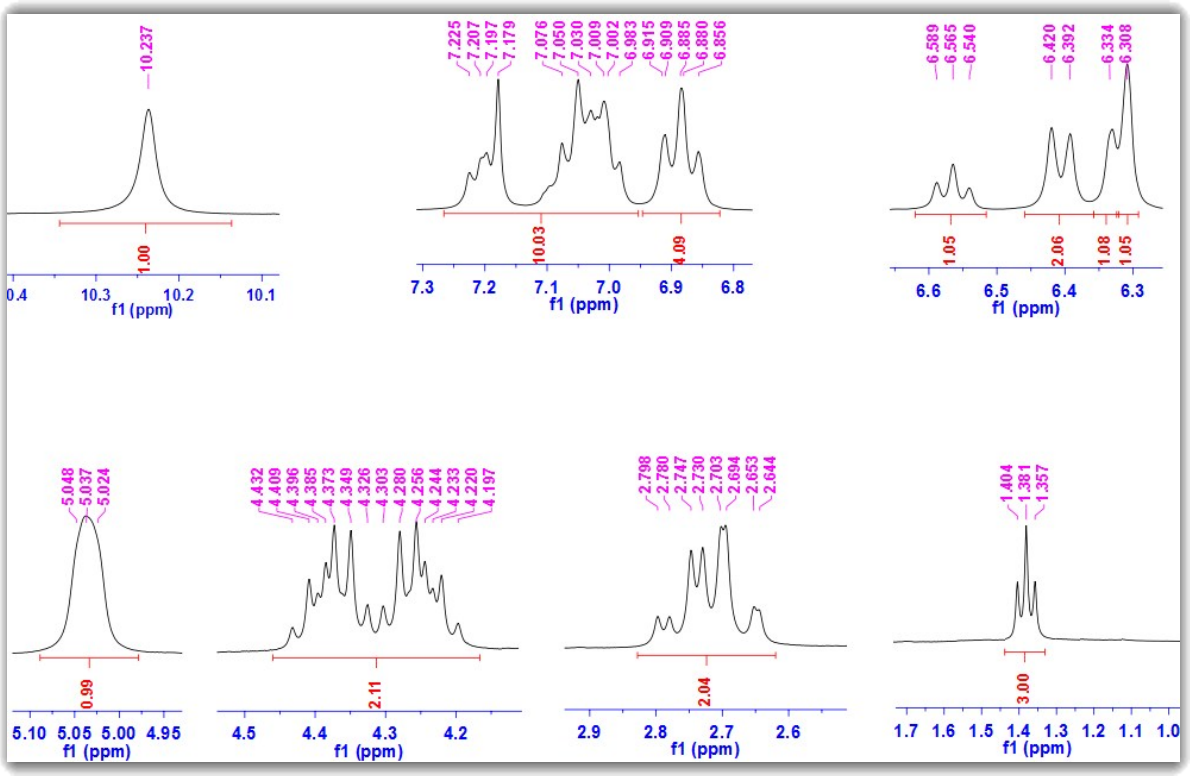

Figure 10: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4d**); expanded form.

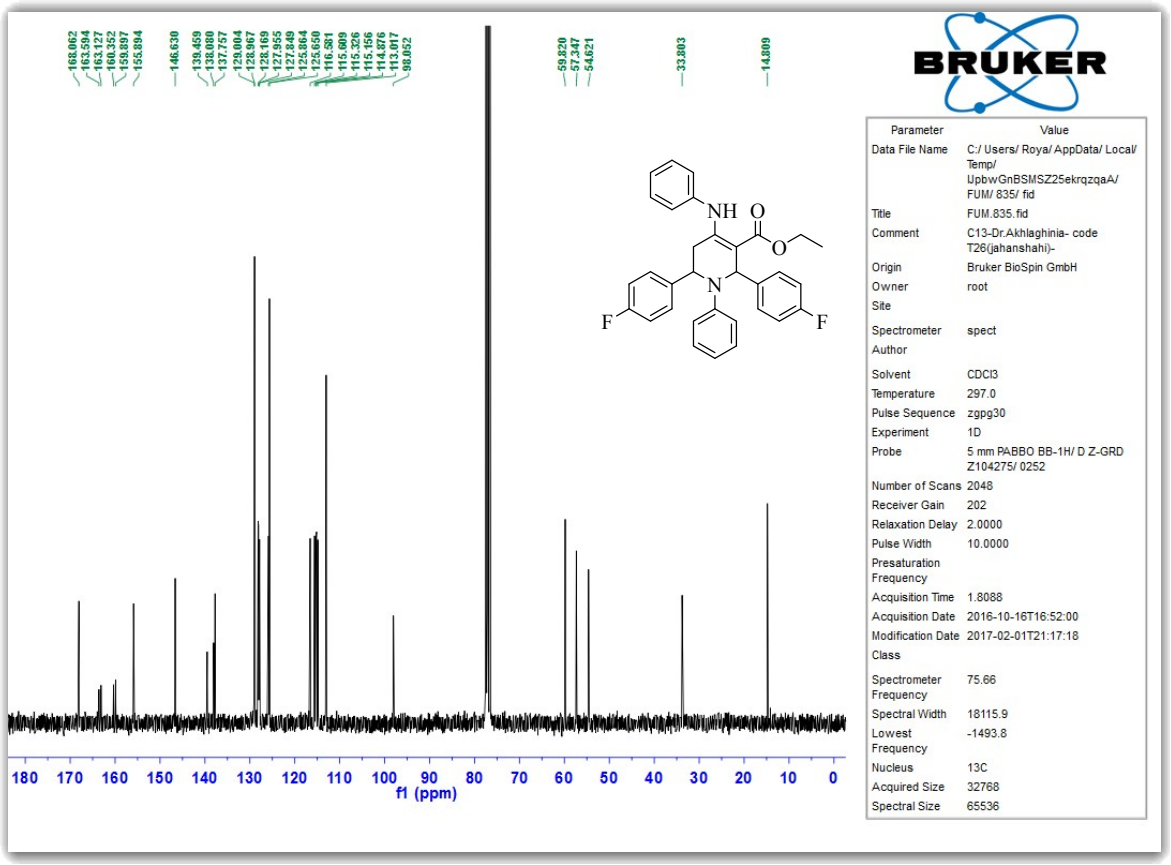

Figure 11: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4d**).

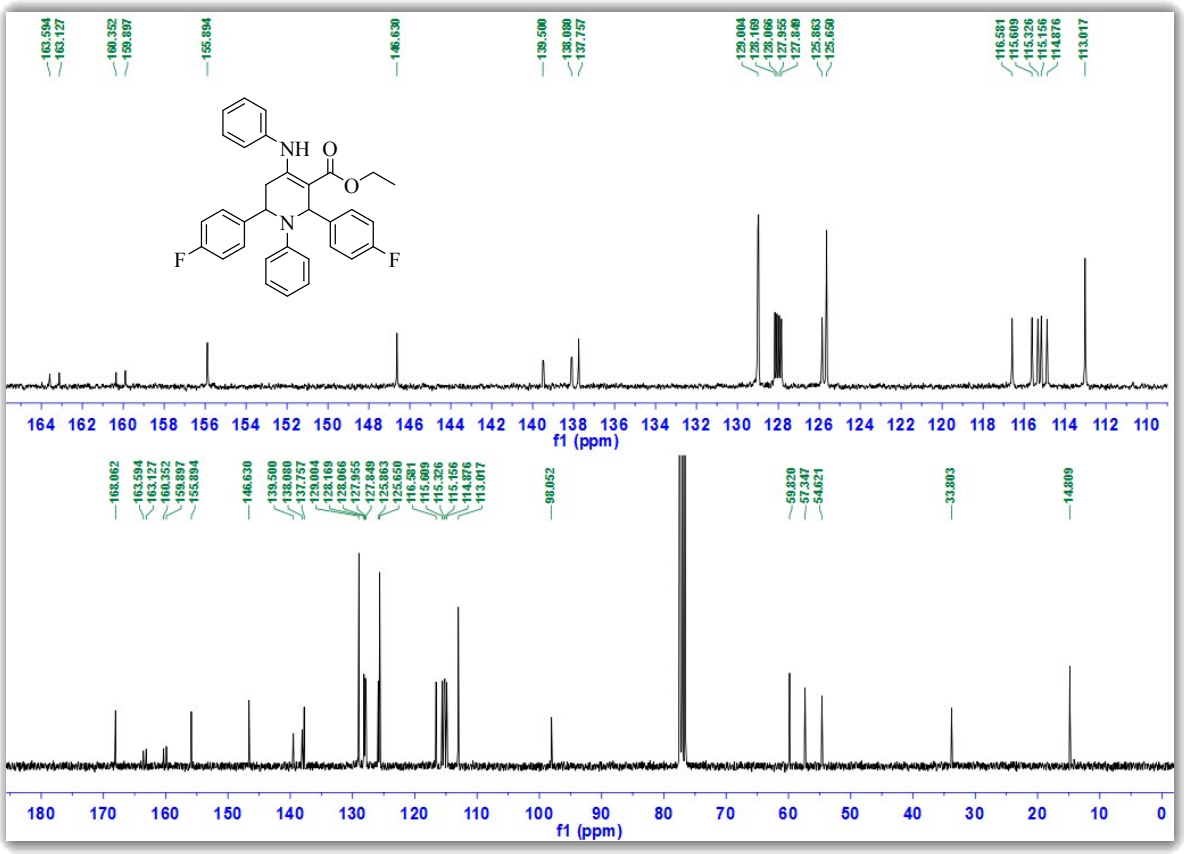

Figure 12: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4d**) and its expanded form.

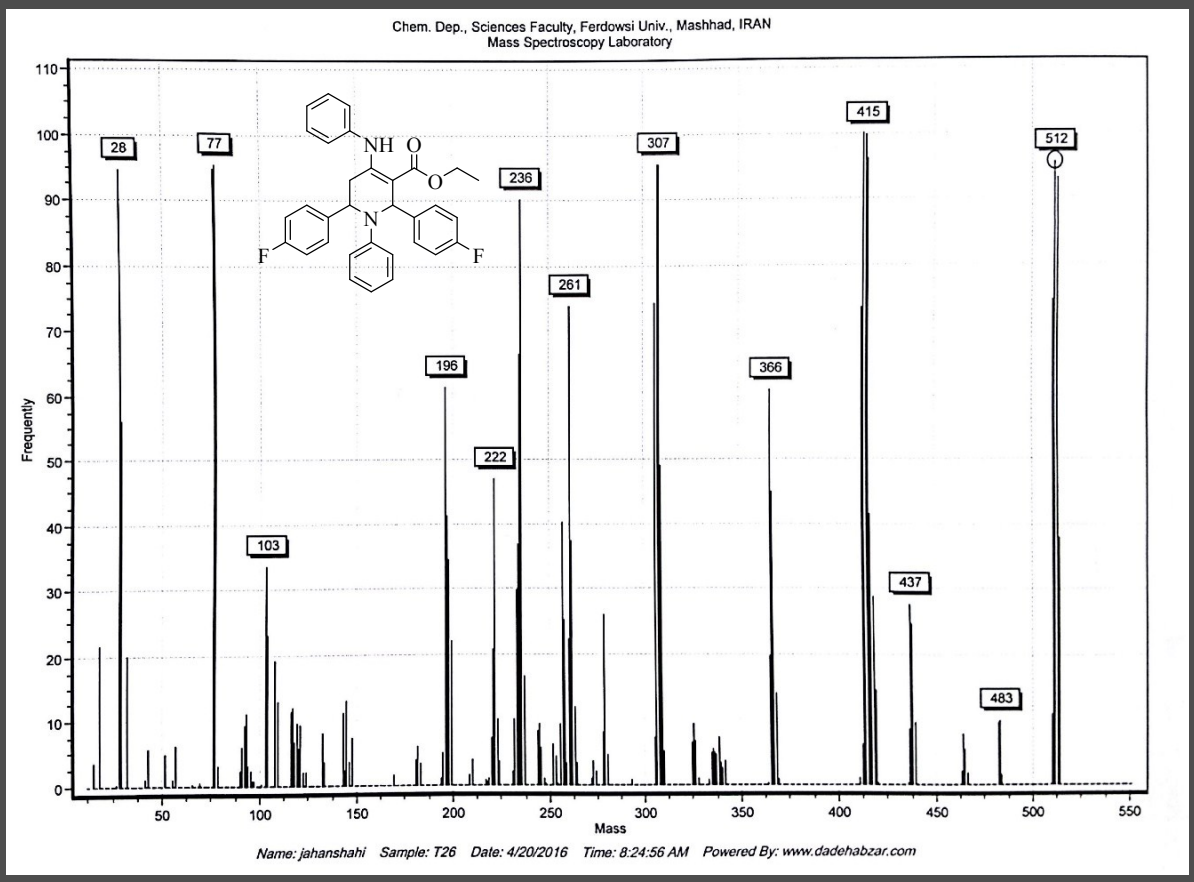

Figure 13: Mass spectrum of ethyl 2,6-bis(4-fluorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**4d**).

Ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4e): (0.50 g, 93%); white solid; 200-201 ˚C (from EtOH) (Lit.[5] 199-201 ˚C); FT-IR (KBr): ν_{max}/cm^{-1} 3235, 3056, 2982, 2876, 1651, 1595, 1500, 1368, 1254, 1091, 1011; ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.78 (1 H, br d, *J* = 13.2 Hz, 5-H'), 2.87 (1 H, dd, *J* = 5.1, 5.1 Hz, 5-H''), 4.27-4.39 (1 H, m, OCH_aH_b), 4.41-4.54 (1 H, m, OCH_aH_b), 5.13 (1 H, br s, 6-H), 6.40 (1 H, s, 2-H), 6.44 (2 H, d, *J* = 7.2 Hz, Ph), 6.49 (2 H, d, *J* = 8.4 Hz, Ph), 6.73 (1 H, t, *J* = 7.2 Hz, Ph), 7.08-7.20 (7 H, m, Ph), 7.26-7.29 (6 H, m, Ph), 10.33 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 14.82, 33.71, 54.70, 57.38, 59.89, 97.77, 112.96, 116.74, 125.69, 125.96, 127.78, 128.03, 128.41, 128.79, 129.02, 129.07, 132.12, 132.86, 137.66, 140.93, 142.45, 146.49, 155.83, 167.99; MS, *m/z* 542 (M^+, 2%), 540 (14, M – 2), 465 (25, M – $C_6H_5^\bullet$), 252 (86), 166 (90), 77 (90, M – $C_{26}H_{23}Cl_2N_2O_2^\bullet$), 28 (100, M – $C_{30}H_{24}Cl_2N_2O_2^\bullet$).

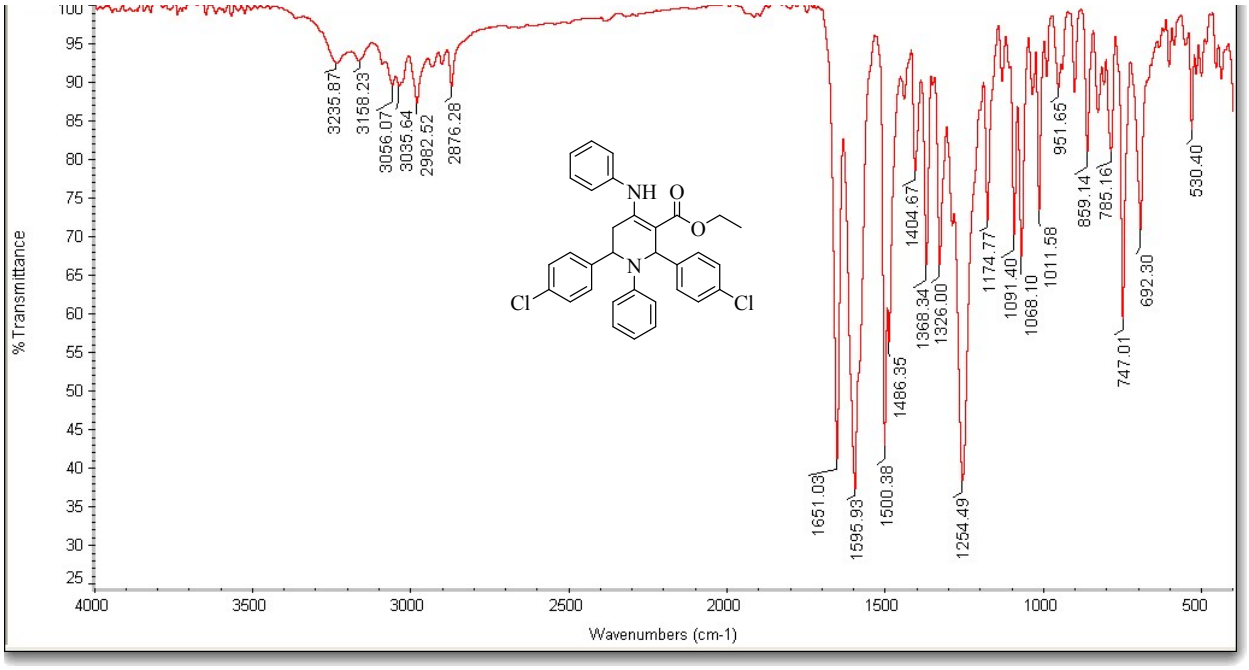

Figure 14: FT-IR spectrum (KBr) of ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)**.

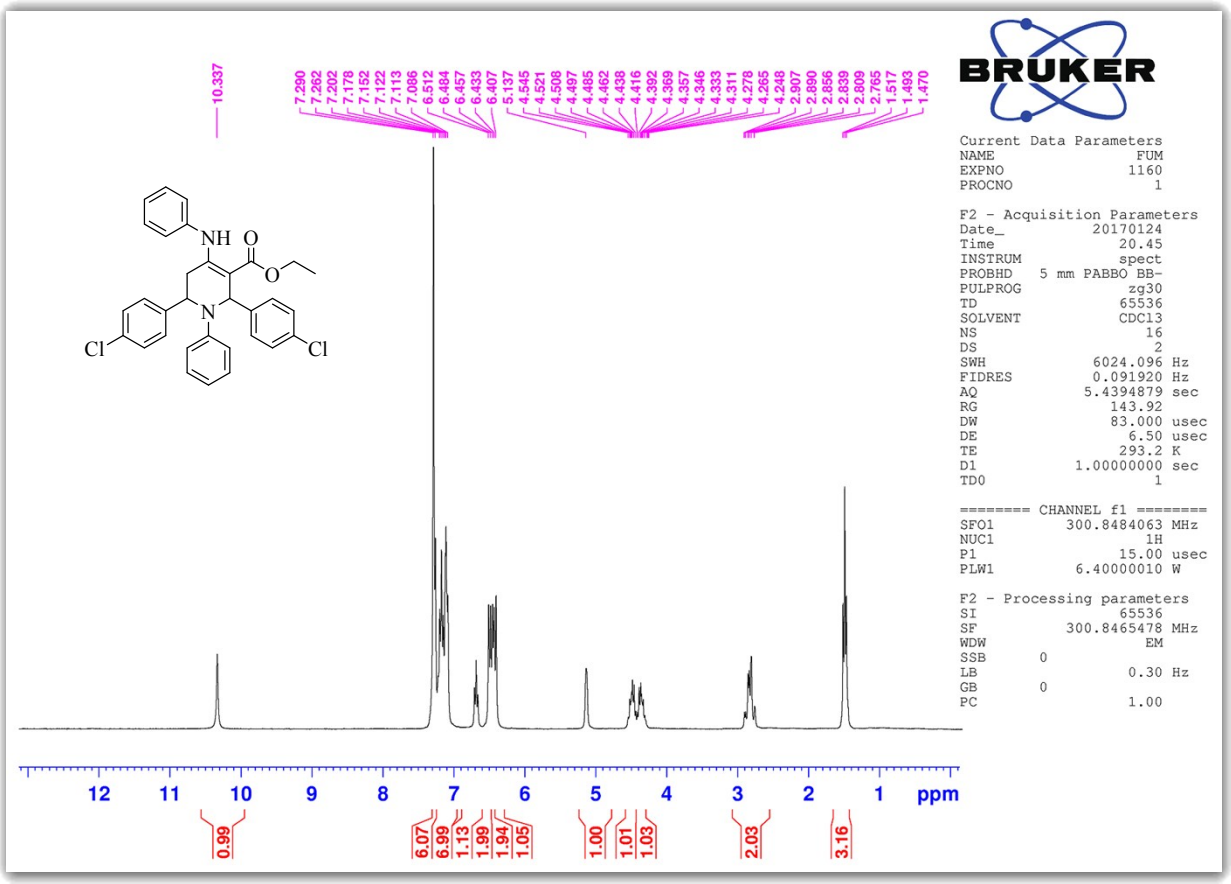

Figure 15: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)**.

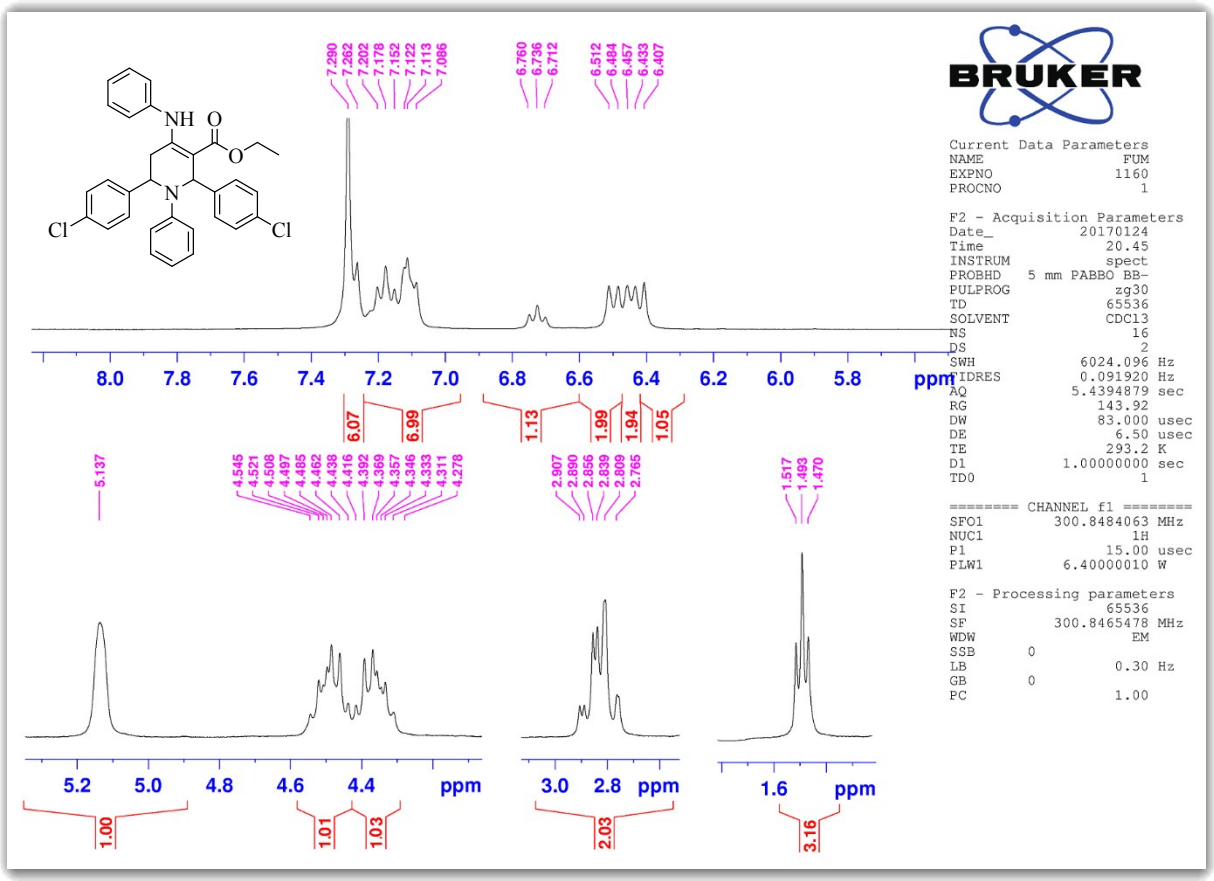

Figure 16: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)**; expanded form.

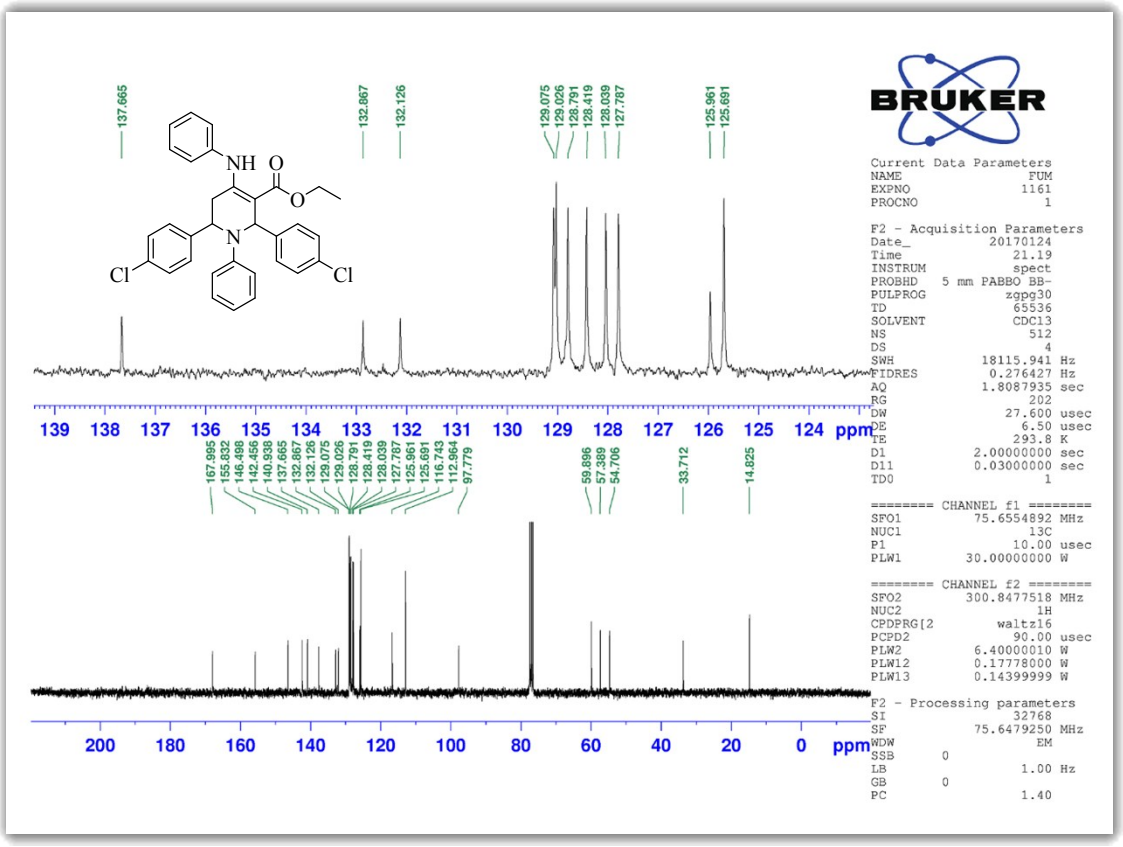

Figure 17: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)** and its expanded form.

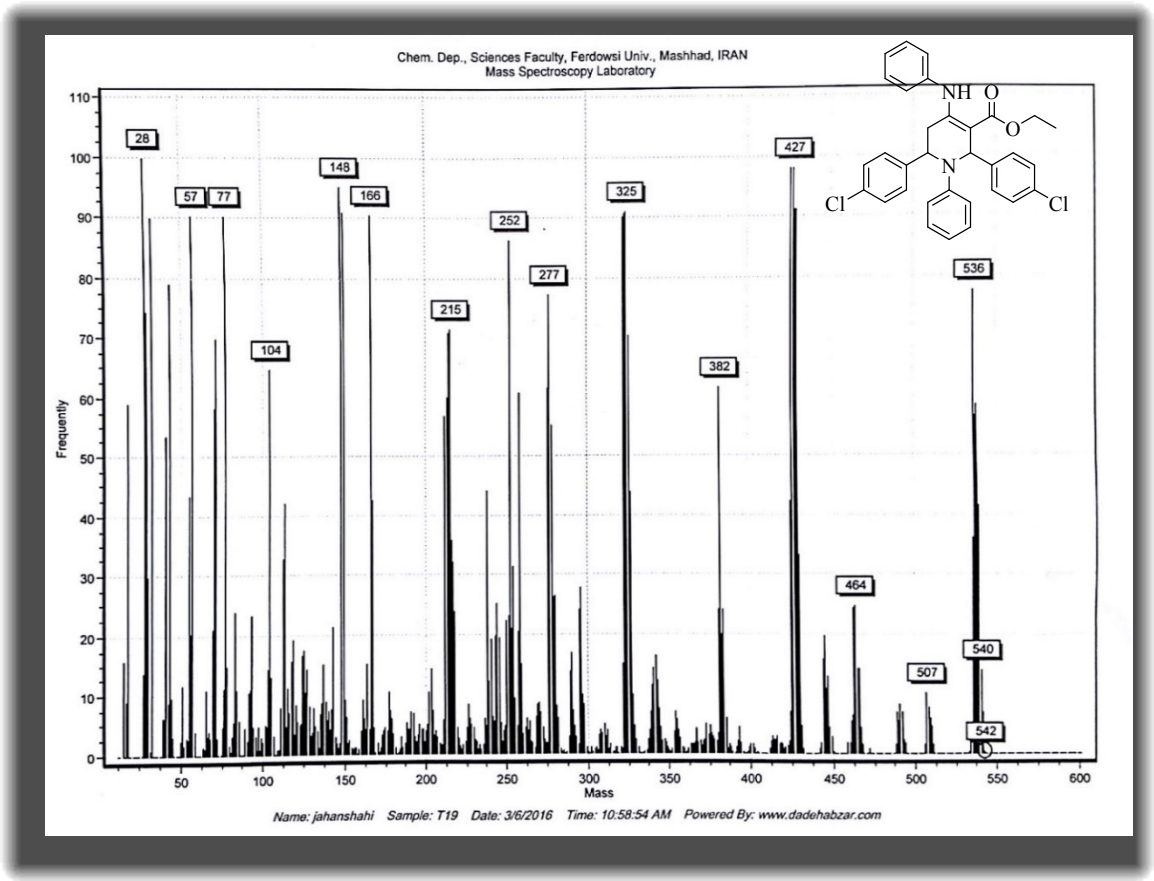

Figure 18: Mass spectrum of ethyl 2,6-bis(4-chlorophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4e)**.

Ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4f): (0.46 g, 93%); white solid; mp 229–230 ˚C (from EtOH) (Lit.[5] 227–230 ˚C); ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.38 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.24 (3 H, s, CH_3), 2.25 (3 H, s, CH_3), 2.68 (1 H, dd, *J* = 2.7, 2.7 Hz, 5-H'), 2.79 (1 H, dd, *J* = 5.4, 5.4 Hz, 5-H''), 4.18-4.29 (1 H, m, OCH_aH_b), 4.32-4.42 (1 H, m, OCH_aH_b), 5.03 (1 H, br s, 6-H), 6.21-6.23 (4 H, m, Ph), 6.33 (1 H, s, 2-H), 6.45 (2 H, d, *J* = 8.4 Hz, Ph), 6.51 (2 H, t, *J* = 7.2 Hz, Ph), 6.95-7.16 (10 H, m, Ph), 10.21 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 14.83, 21.04, 21.14, 33.67, 54.89, 57.96, 59.64, 98.38, 112.91, 115.96, 125.53, 125.75, 126.33, 126.56, 128.79, 128.86, 128.93, 129.27, 135.75, 136.60, 138.01, 139.71, 141.06, 147.09, 156.08, 168.28; MS, *m/z* 502 (M^+, 9%), 504 (38, M + 2), 429 (9, M – $C_3H_5O_2^•$), 411 (100, M – $C_7H_7^•$), 71 (26, M – $C_{31}H_{31}N_2^•$), 28 (100, M – $C_{32}H_{30}N_2O_2^•$).

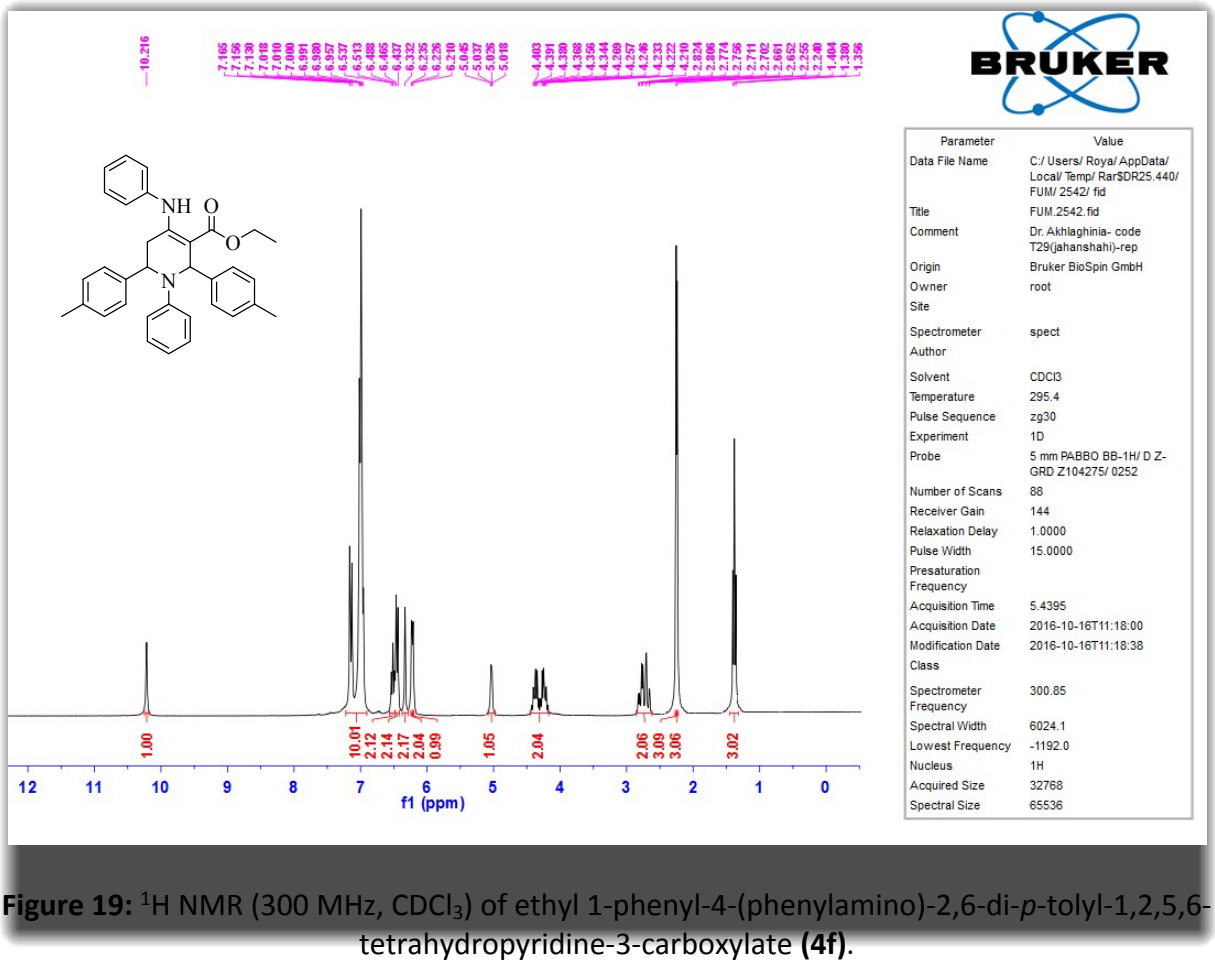

Figure 19: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4f)**.

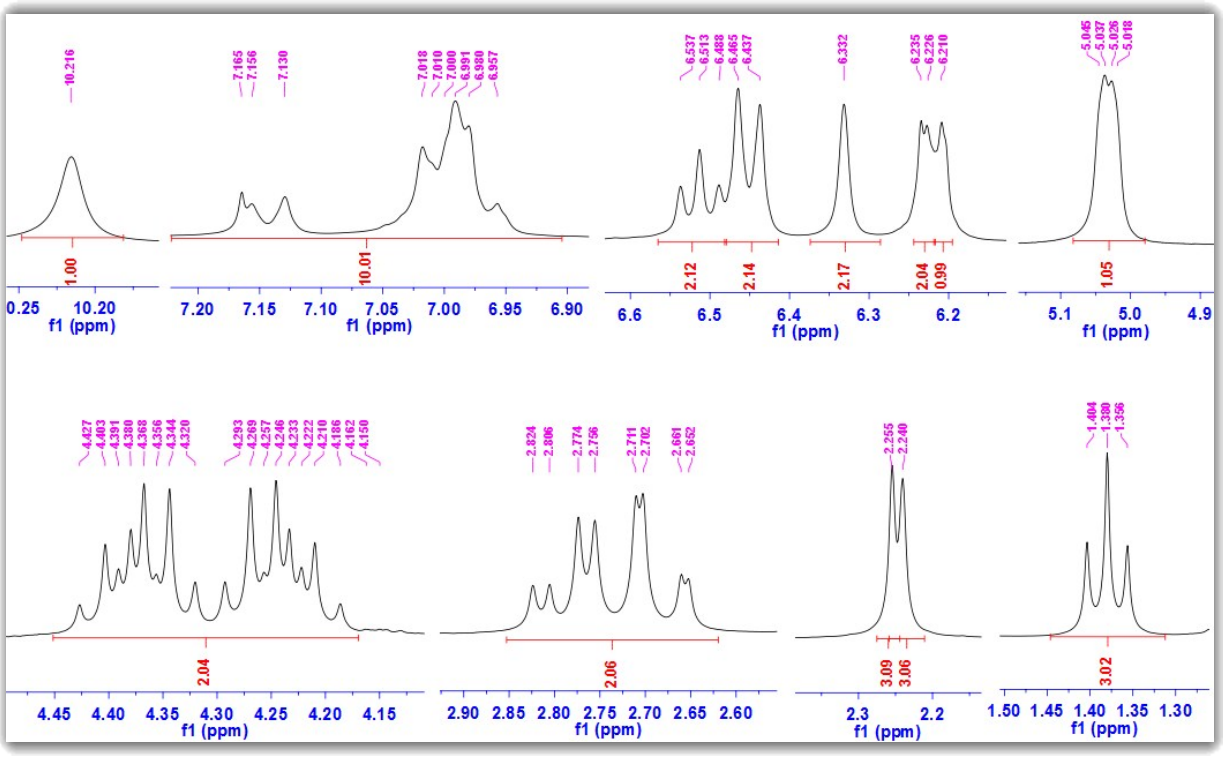

Figure 20: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4f)**; expanded form.

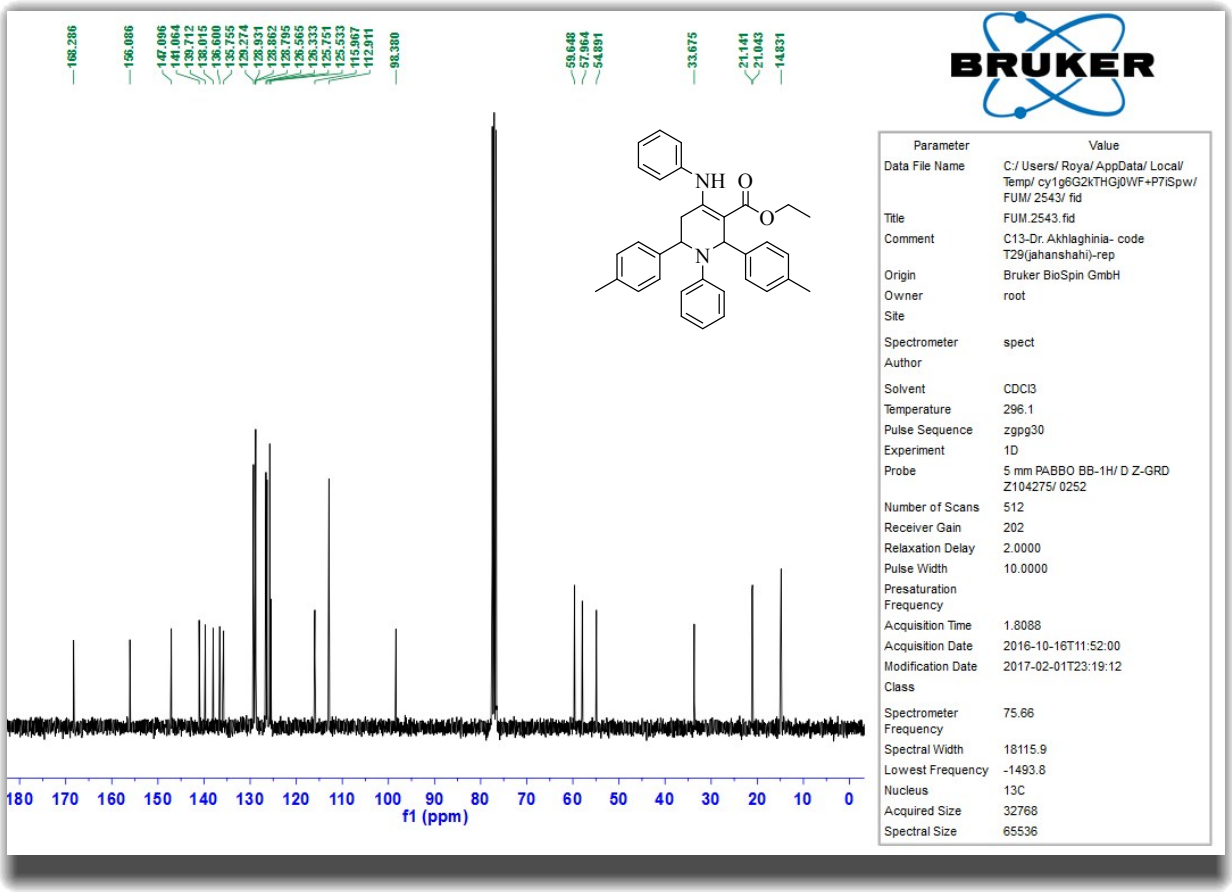

Figure 21: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4f)**.

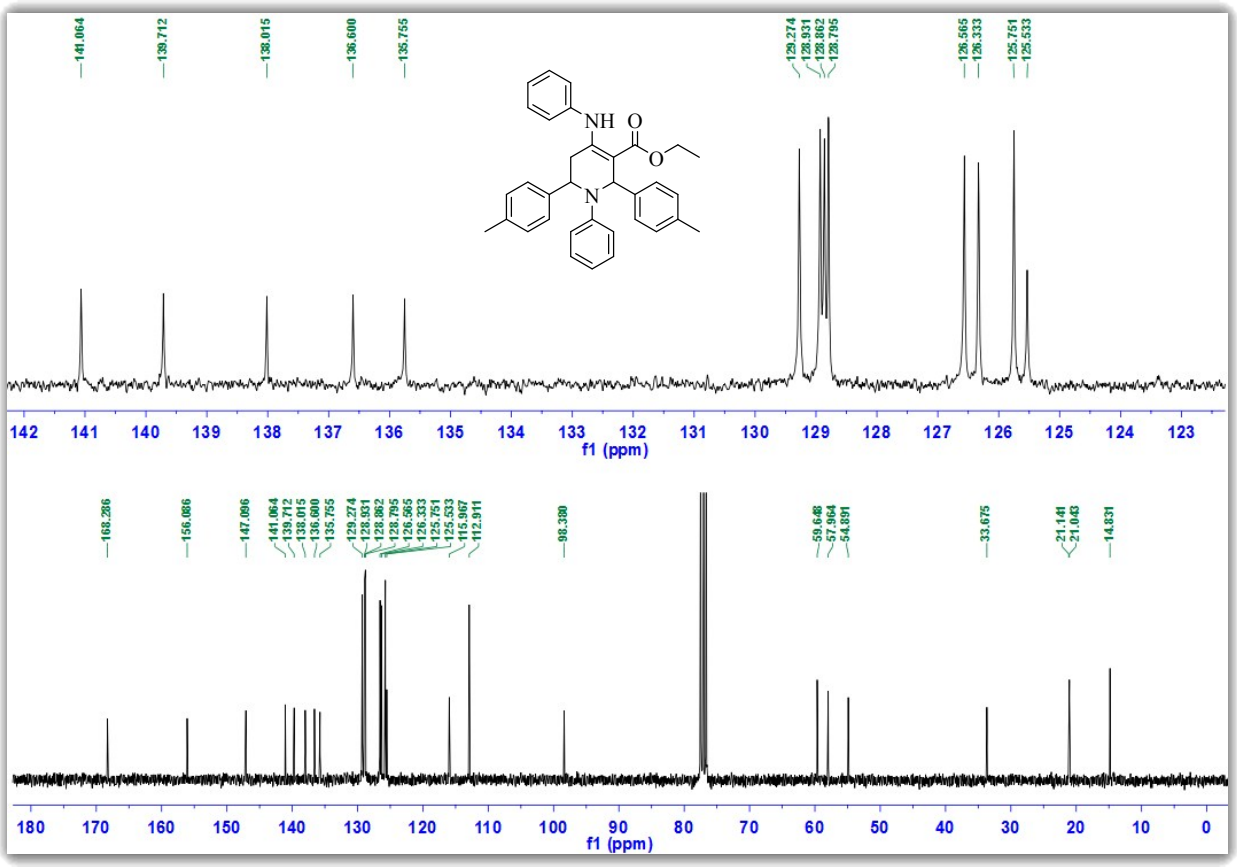

Figure 22: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4f)** and its expanded form.

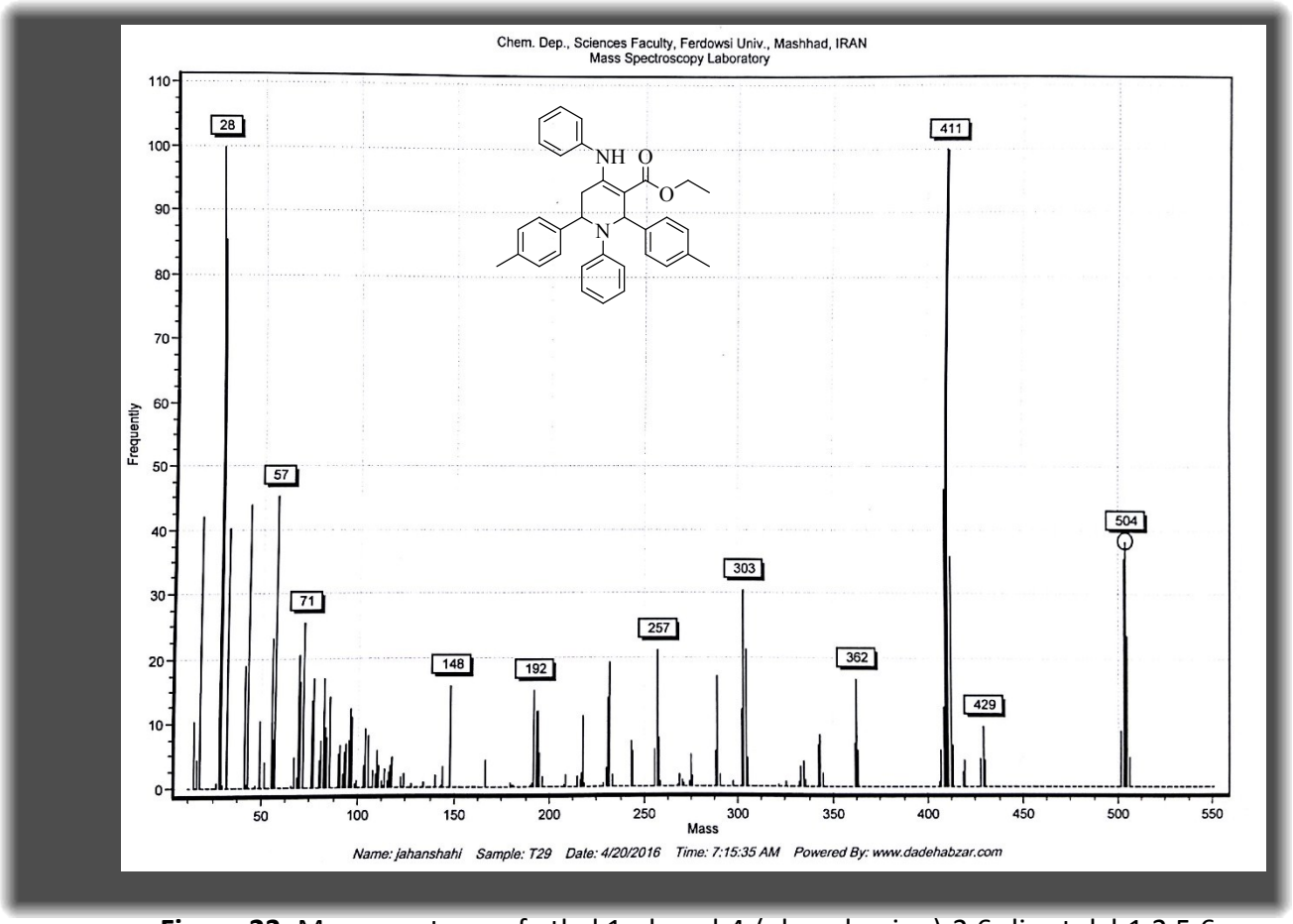

Figure 23: Mass spectrum of ethyl 1-phenyl-4-(phenylamino)-2,6-di-*p*-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4f)**.

Ethyl 1-phenyl-4-(phenylamino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4g): (0.45 g, 94%); white solid; mp 204–205 ˚C (from EtOH) (Lit.[6] 205–206 ˚C); MS*, m/z* 487 (M^+, 4%), 410 (55, M – $C_6H_4^{\bullet}$), 335 (100), 187 (54, M – $C_{17}H_{17}NO_2S^{2\bullet}$), 110 (88), 77 (98, M – $C_{22}H_{21}N_2O_2S_2^{\bullet}$), 29 (98, M – $C_{26}H_{21}N_2O_2S_2^{\bullet}$).

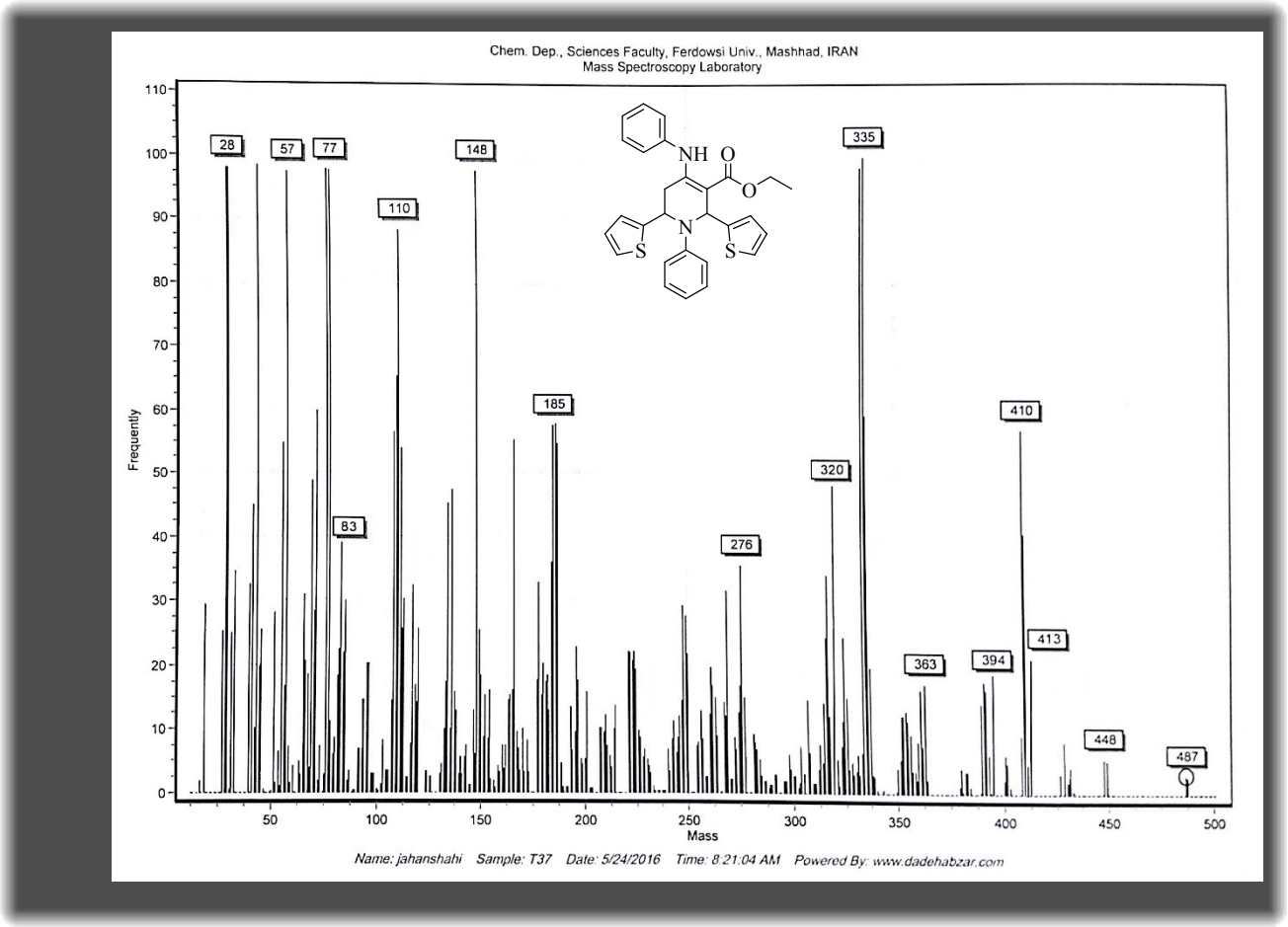

Figure 24: Mass spectrum of ethyl 1-phenyl-4-(phenylamino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4g)**.

Ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4h): (0.51 g, 92%); pale yellow solid; mp, 251–252 ˚C (from EtOH) (Lit.[7] 250–252 ˚C); ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.51 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.72 (1 H, dd, *J* = 5.7, 5.7 Hz, 5-H'), 2.97 (1 H, dd, *J* = 10.2, 10.5 Hz, 5-H''), 4.34-4.45 (1 H, m, OCH_aH_b), 4.47-4.57 (1 H, m, OCH_aH_b), 5.29 (1 H, br s, 6-H), 6.42-6.46 (4 H, m, Ph), 6.51 (1 H, s, 2-H), 6.73 (2 H, t, *J* = 7.2 Hz, Ph), 7.10-7.33 (8 H, m, Ph), 7.55 (2 H, d, *J* = 8.4 Hz, Ph), 8.18 (2 H, t, *J* = 9 Hz, Ph), 10.35 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 14.81, 33.62, 55.25, 57.38, 60.27, 96.94, 112.96, 117.72, 123.78, 123.94, 125.46, 126.37, 127.33, 127.37, 129.22, 129.38, 137.20, 145.81, 146.84, 147.34, 149.75, 151.66, 155.28, 167.60; MS, *m/z* 564 (M^+, 84%), 566 (70, M + 2), 519 (13, M – $NO_2^{4\bullet}$), 473 (41, M – $2NO_2$), 442 (100, M – $C_6H_4NO_2^{\bullet}$), 269 (83), 45 (12, M – $C_{32}H_{29}N_3O_4$).

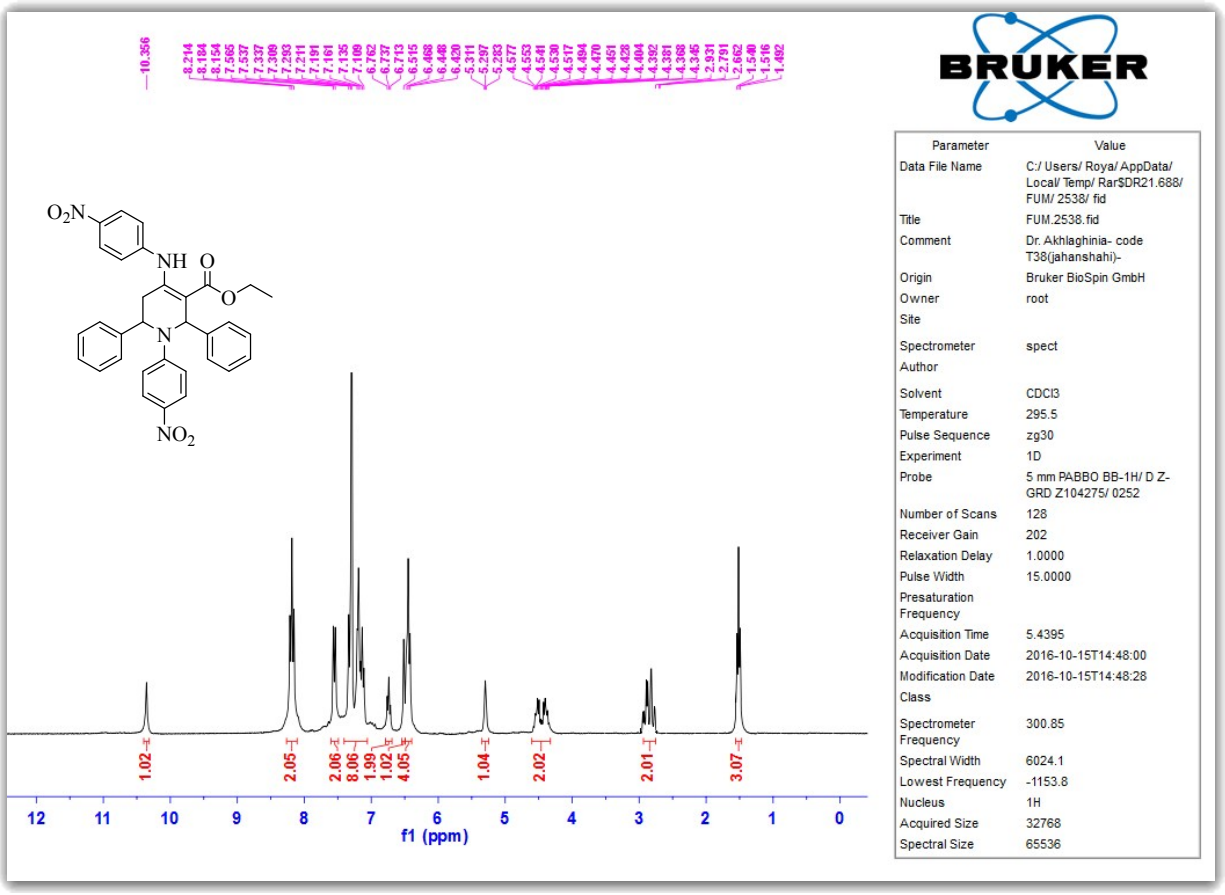

Figure 25: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4h)**.

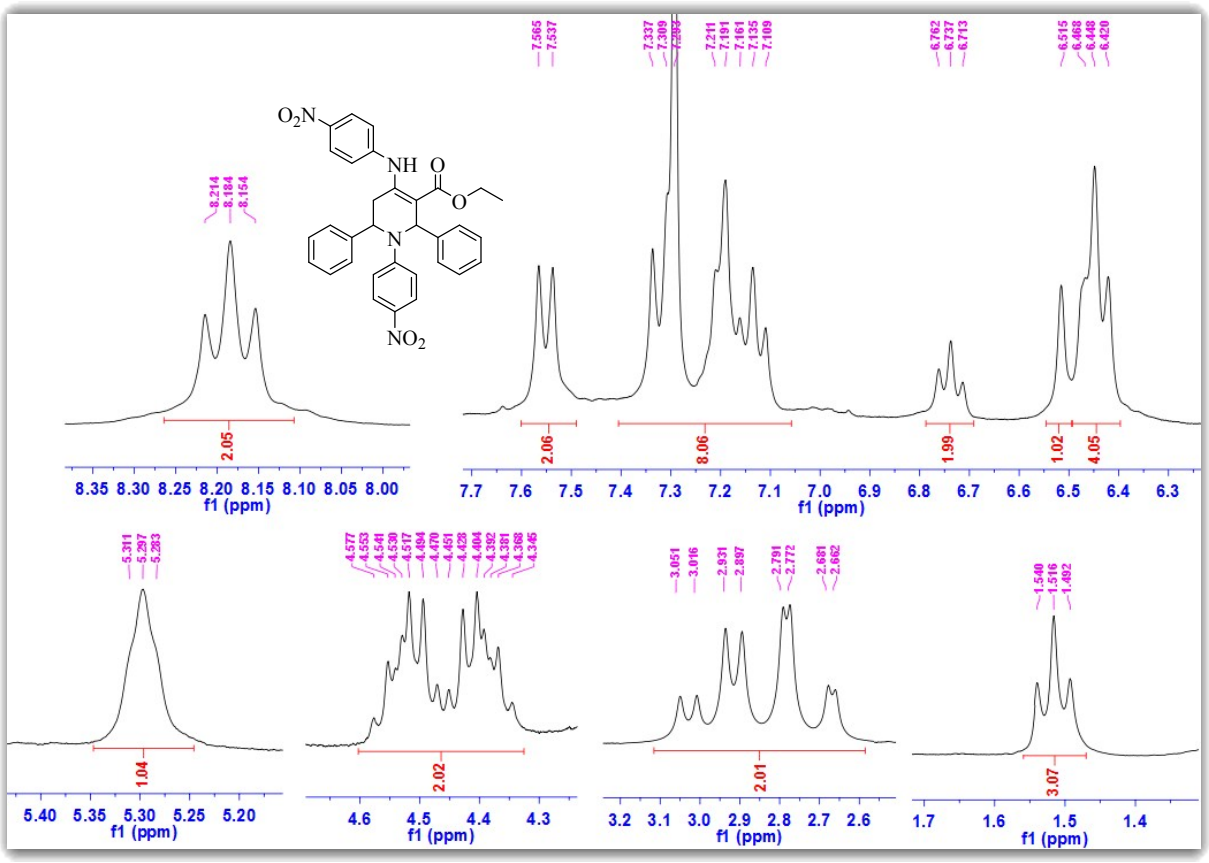

Figure 26: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4h)**; expanded form.

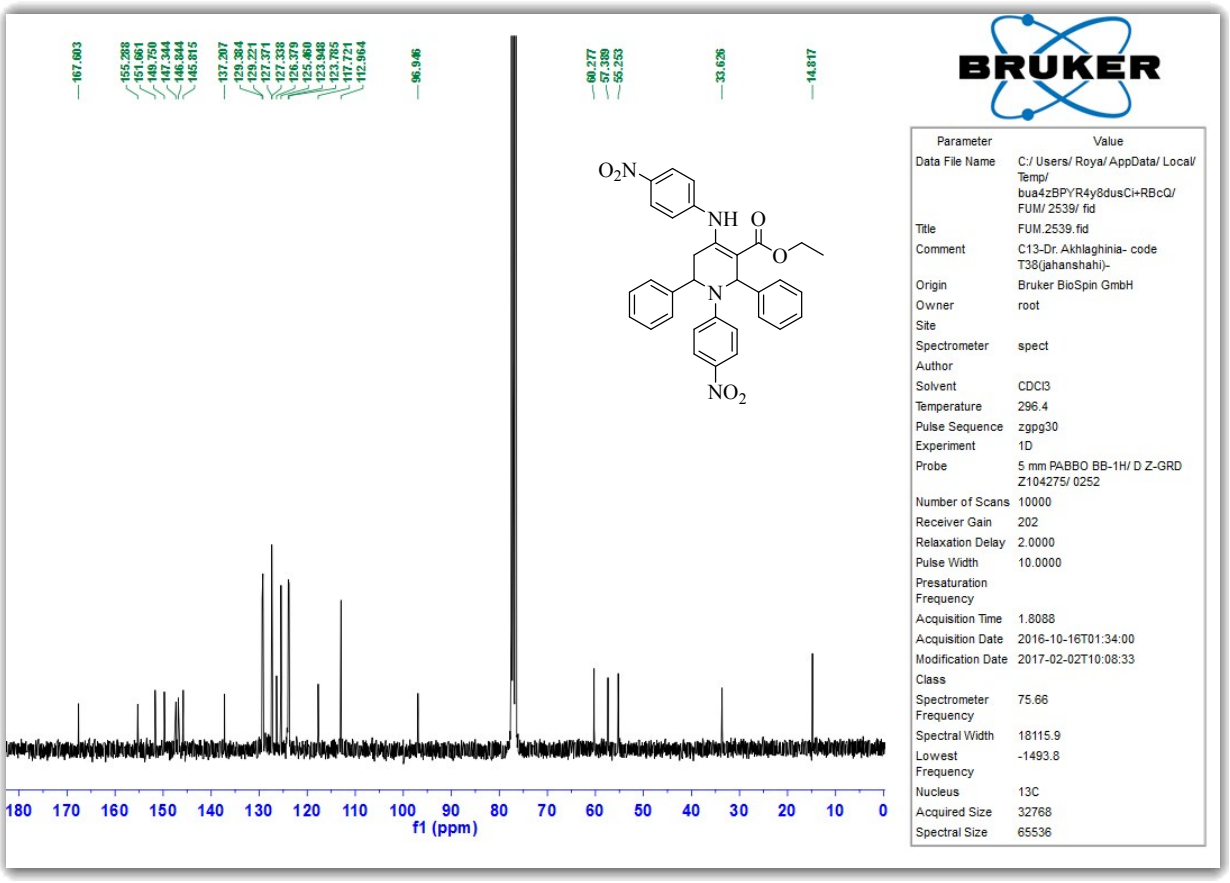

Figure 27: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4h)**.

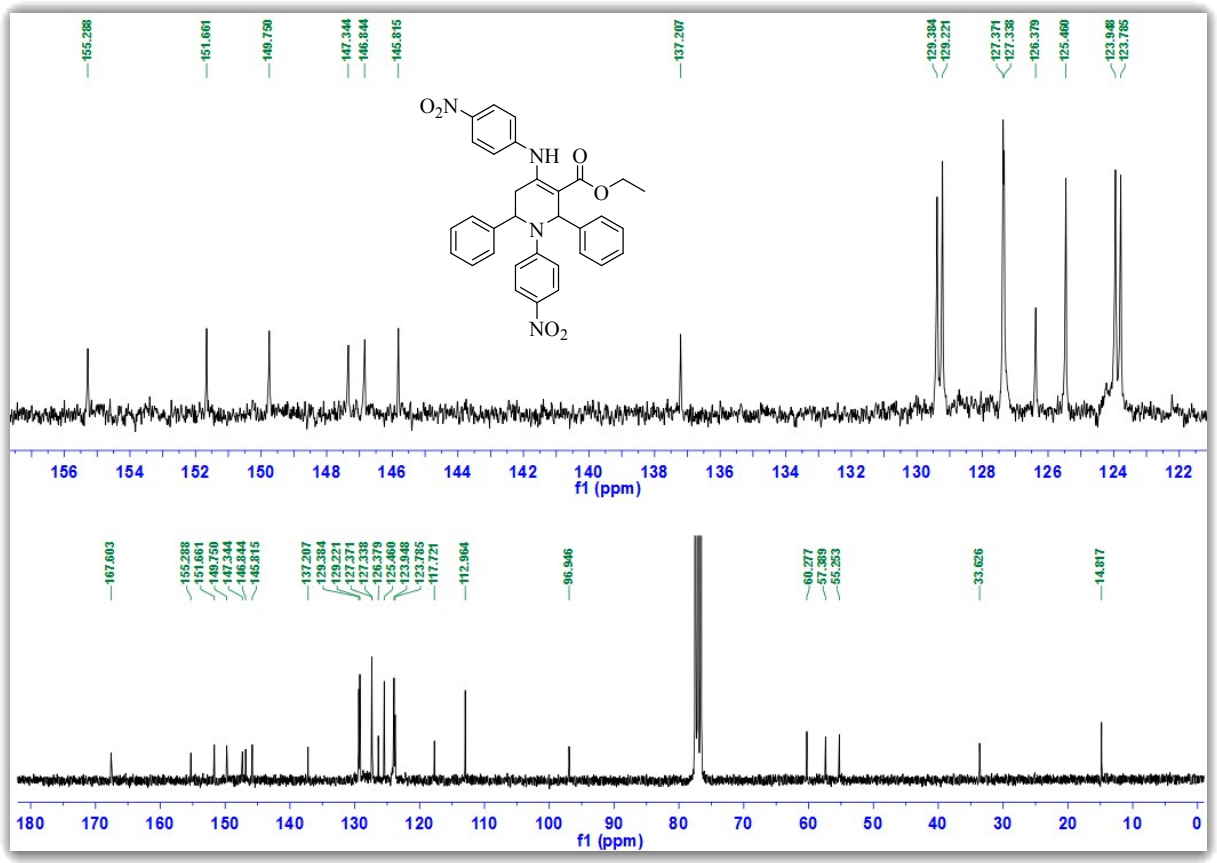

Figure 28: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4h)** and its expanded form.

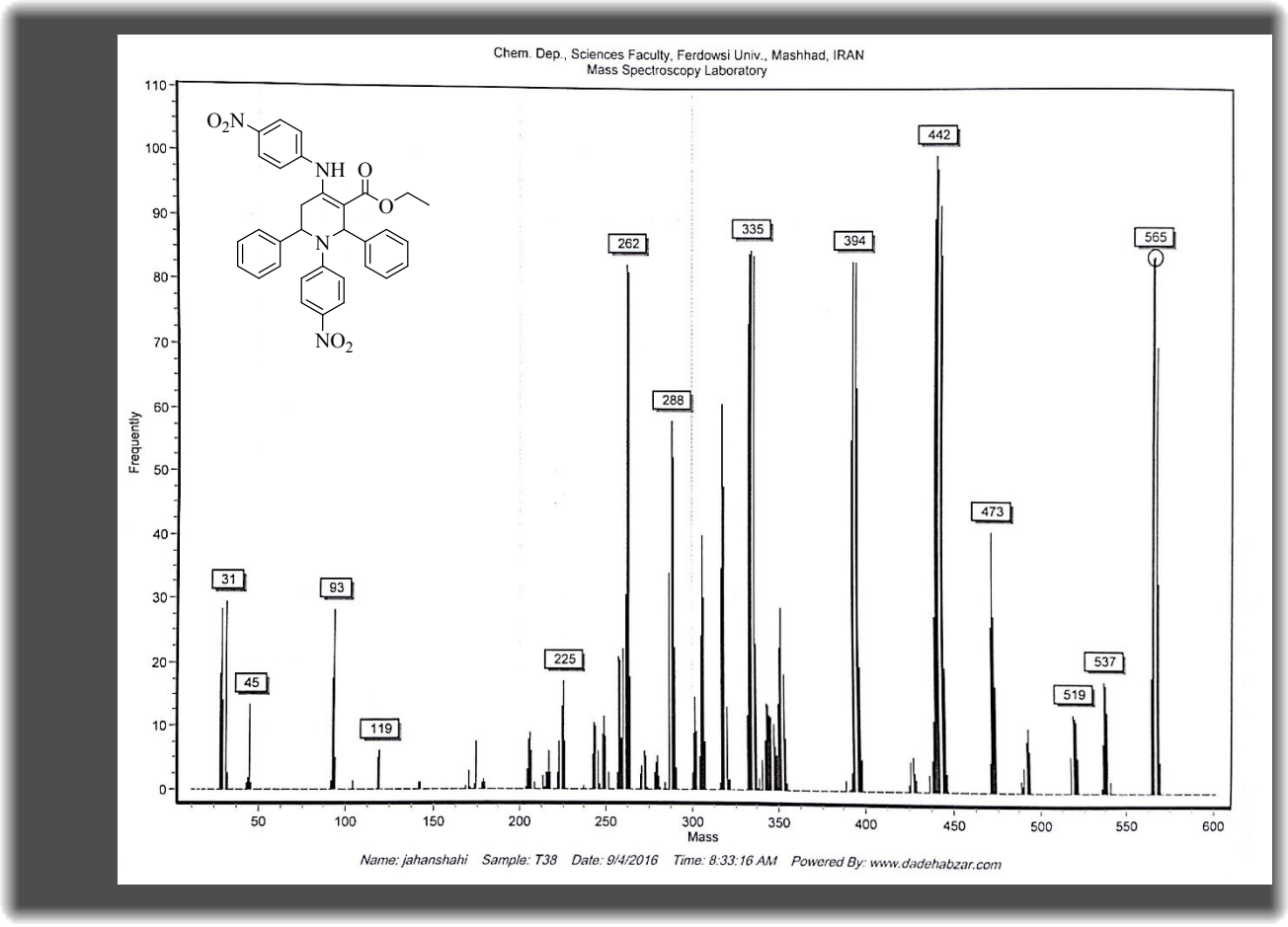

Figure 29: Mass spectrum of ethyl 1-(4-nitrophenyl)-4-((4-nitrophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4h)**.

Ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4i): (0.51 g, 95 %); white solid; mp 201–203 ˚C (from EtOH) (Lit.[2] 202–204 ˚C); FT-IR (KBr): ν_{max}/cm^{-1}; 3370, 3051, 2983, 2896, 1708, 1603, 1493, 1397, 1245, 1072, 1008; ^1H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.35 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.67 (1 H, dd, *J* = 2.7, 2.7 Hz, 5-H'), 2.80 (1 H, dd, *J* = 5.1, 5.4 Hz, 5-H''), 4.15-4.26 (1 H, m, OCH_aH_b), 4.29-4.40 (1 H, m, OCH_aH_b), 4.98 (1 H, br s, 6-H), 6.32 (1 H, s, 2-H), 6.47-6.62 (4 H, m, Ph), 6.92-6.95 (4 H, m, Ph), 7.06-7.23 (10 H, m, Ph), 10.27 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 13.73, 33.49, 55.27, 59.48, 60.32, 97.25, 126.525, 127.00, 127.03, 127.52, 128.31, 129.17, 129.98, 131.43, 138.50, 139.00, 139.36, 141.24, 143.07,

145.50, 155.41, 159.93, 168.15; MS, *m/z* 543 (M^+, 20%), 545 (12, M + 2), 465 (77, M – $C_6H_5^•$), 322 (46), 110 (36, M – $C_{26}H_{25}ClN_2O_2^•$), 28 (100, M – $C_{30}H_{24}Cl_2N_2O_2^•$).

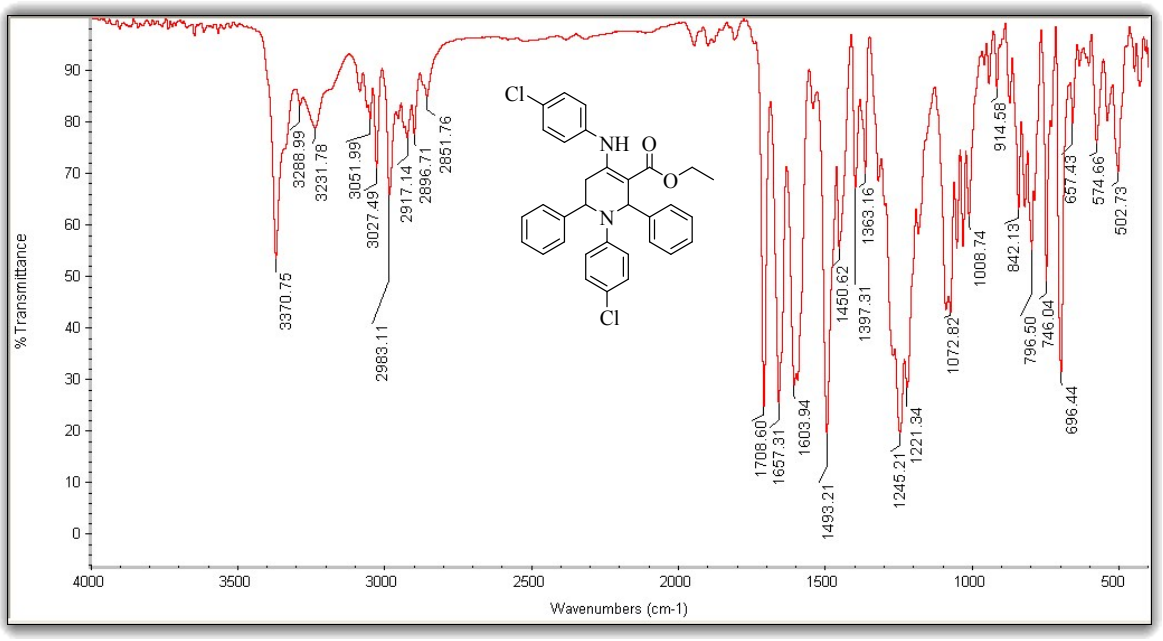

Figure 30: FT-IR spectrum (KBr) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)**.

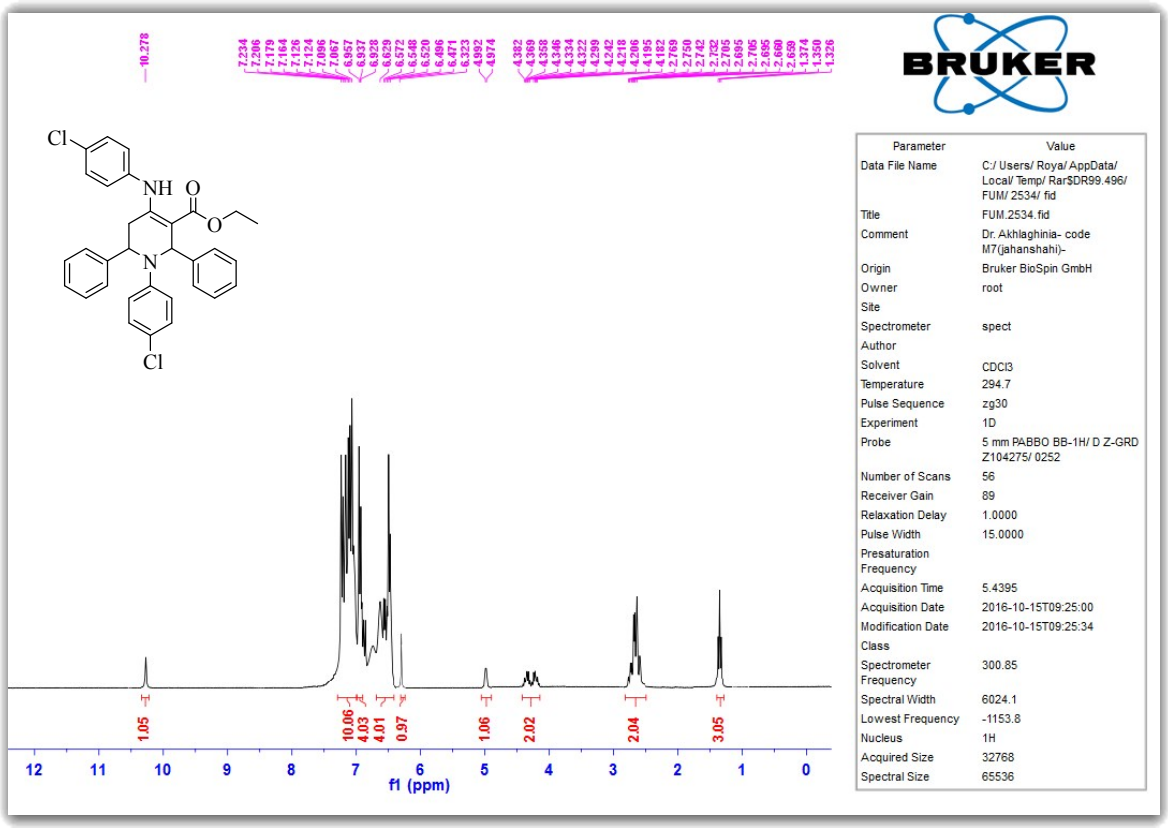

Figure 31: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)**.

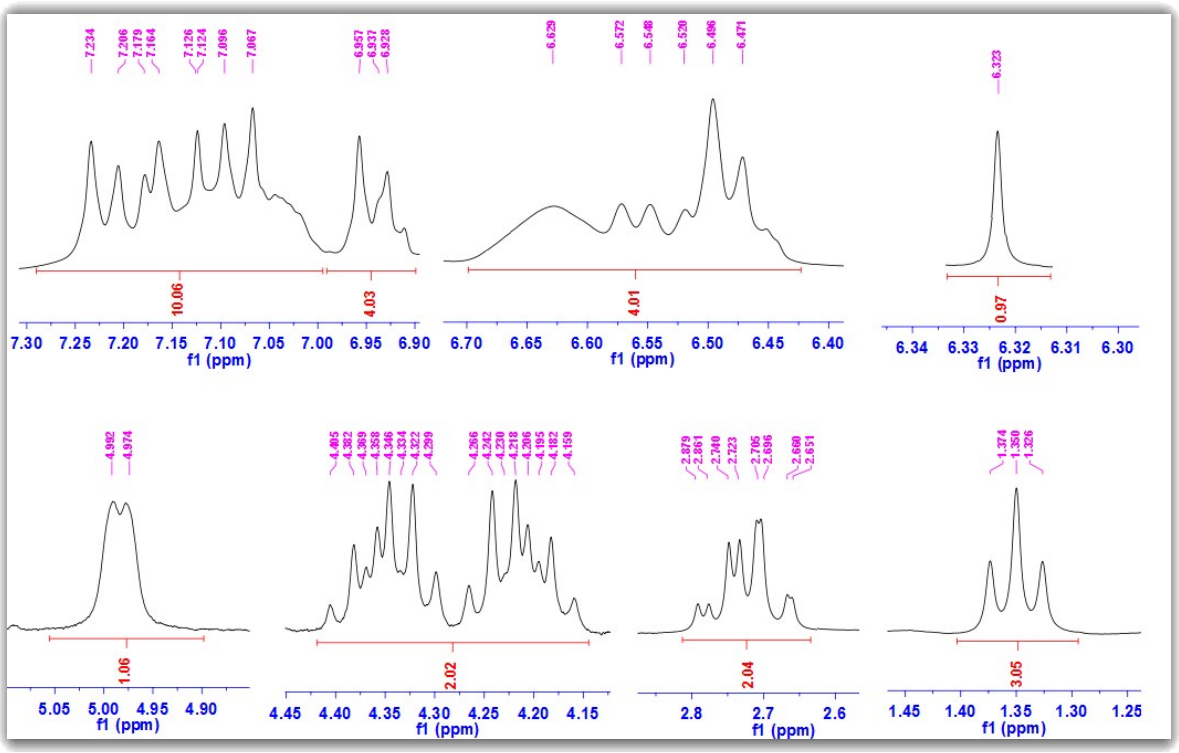

Figure 32: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)**; expanded form.

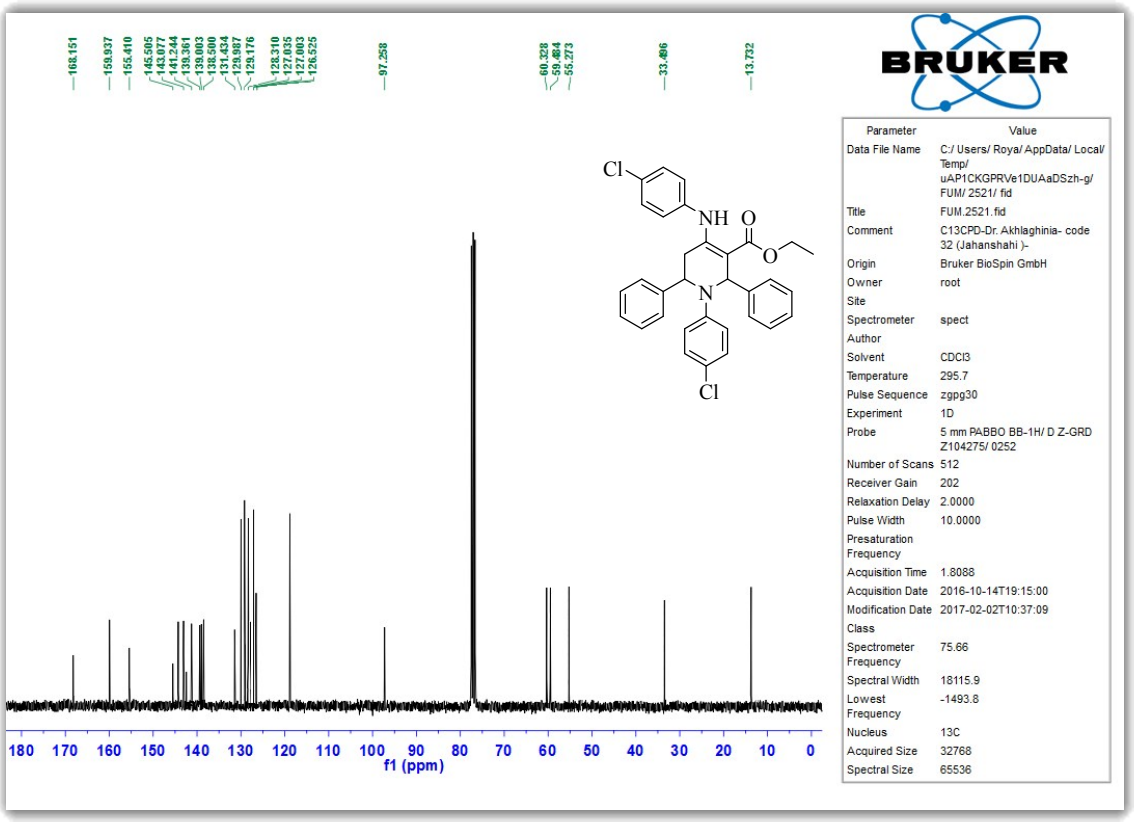

Figure 33: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)**.

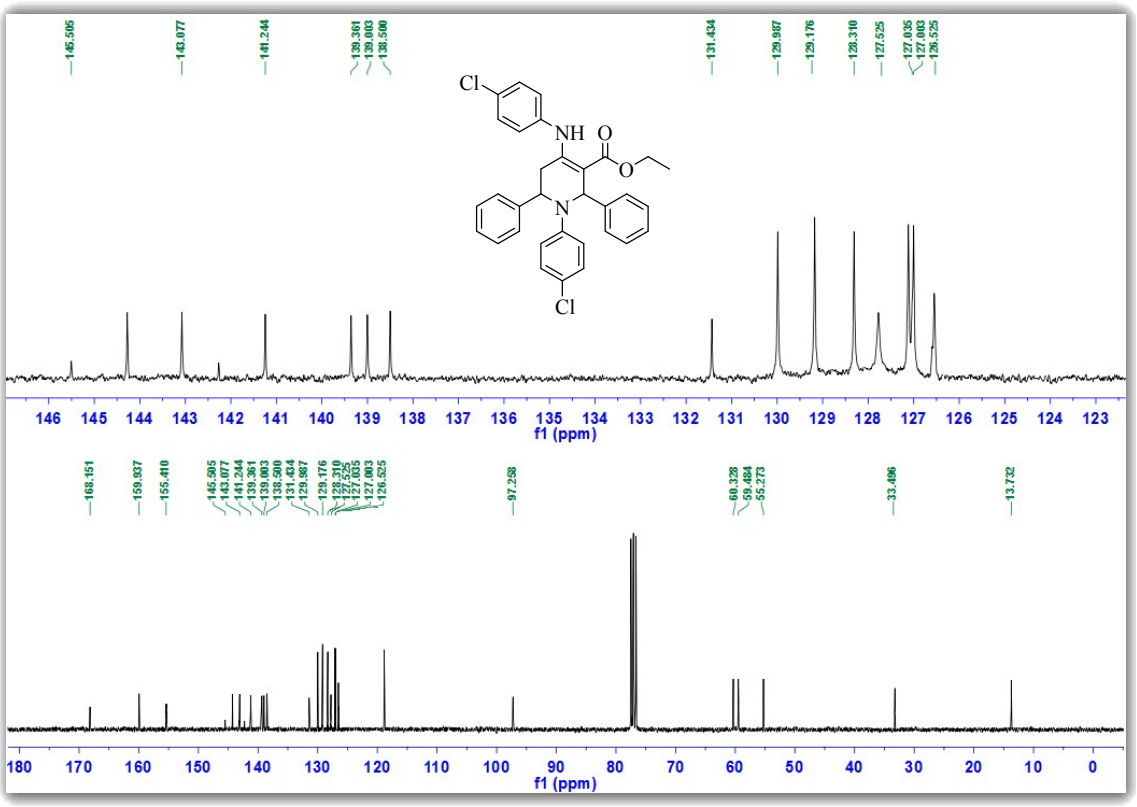

Figure 34: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)** and its expanded form.

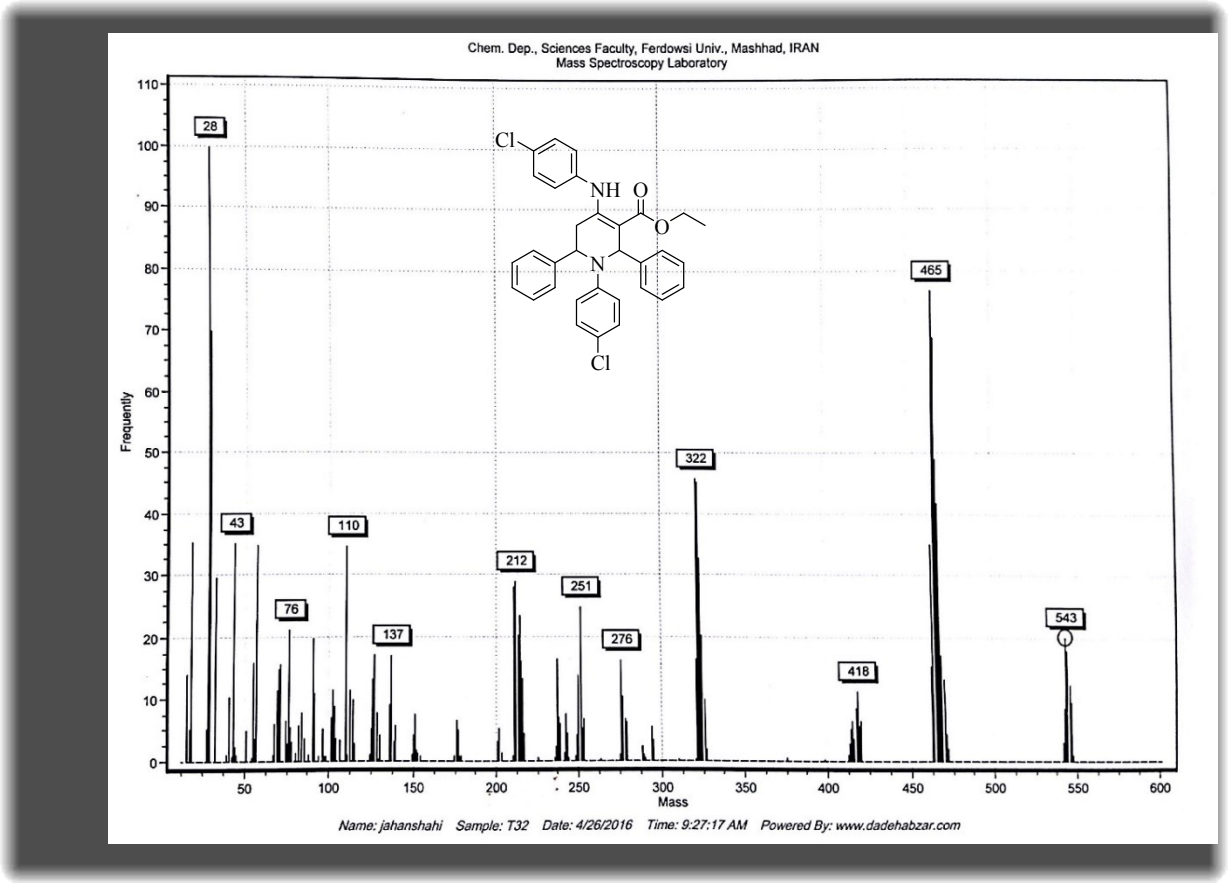

Figure 35: Mass spectrum of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4i)**.

Ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4j): (0.56 g, 95 %); pale yellow solid; mp 219–220 ˚C (from EtOH) (Lit.[3] 222–224 ˚C); MS*, m/z* 593 (M^+, 11%), 595 (20, M + 2), 596 (16, M + 3), 520 (6, M – $C_3H_4O_2^{\bullet}$), 493 (68), 348 (100), 238 (95, M – $C_{22}H_{13}ClN_3^{2\bullet}$), 111 (38, M – $C_{28}H_{22}ClN_4O_2^{\bullet}$), 29 (33, M – $C_{32}H_{21}Cl_2N_4O_2^{\bullet}$).

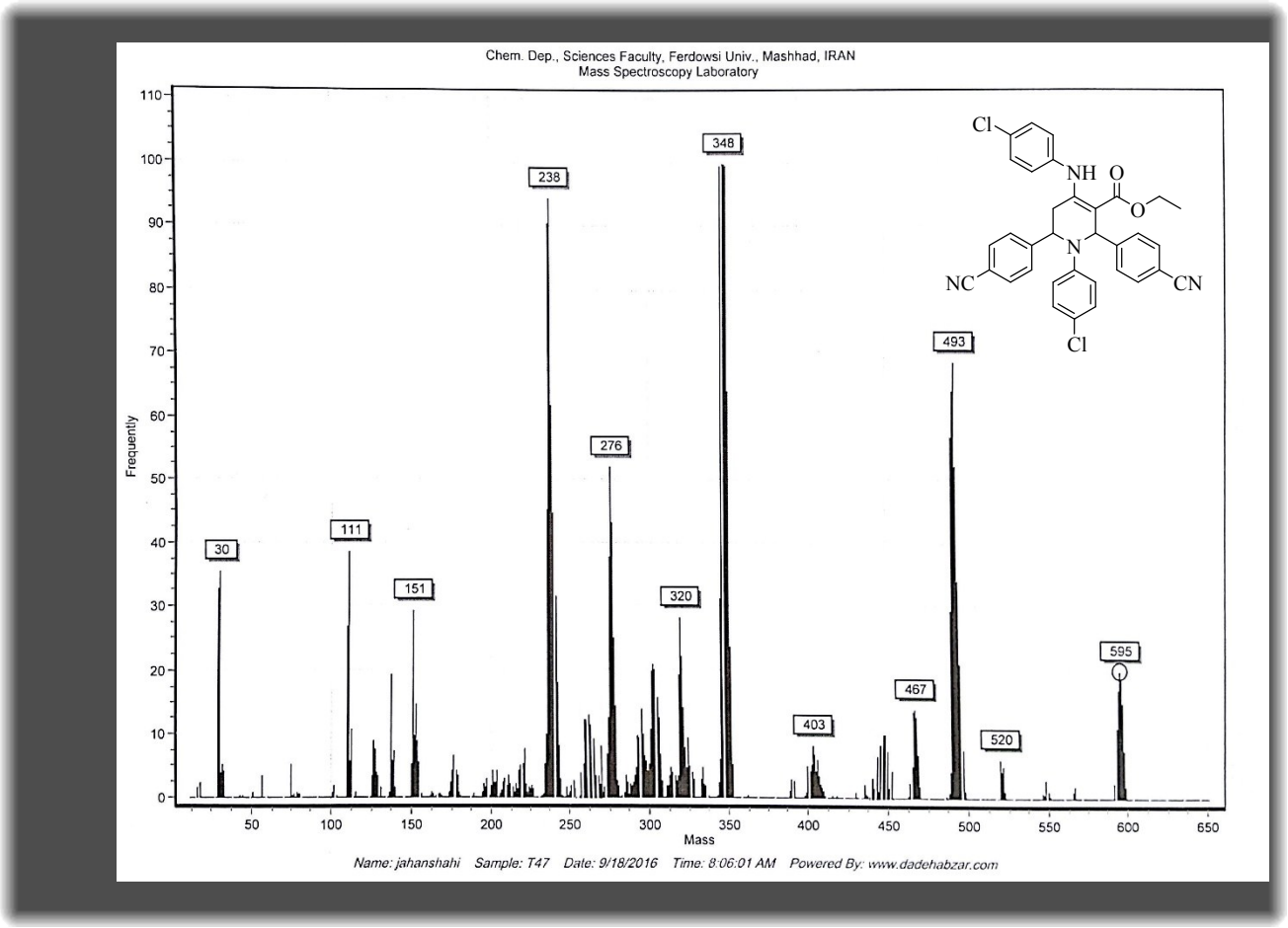

Figure 36: Mass spectrum of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4j)**.

Ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4k): (0.53 g, 93 %); white solid; mp 206–207 ˚C (from EtOH) (Lit.[7] 208–209 ˚C); ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si), 1.48 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.71 (1 H, dd, *J* = 2.1, 2.1 Hz, 5-H'), 2.85 (1 H, dd, *J* = 5.4, 5.4 Hz, 5-H''), 4.30-4.40 (1 H, m, OCH_aH_b), 4.43-4.54 (1 H, m, OCH_aH_b), 5.10 (1 H, br s, 6-H), 6.32 (2 H, d, *J* = 2.7 Hz, Ph), 6.34 (1 H, s, 2-H), 6.41 (2 H, d, *J* = 9 Hz,

Ph), 6.97-7.06 (6 H, m, Ph), 7.09-7.15 (4 H, m, Ph), 7.23-7.29 (2 H, m, Ph), 10.29 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si); 14.77, 33.67, 54.79, 57.41, 60.06, 98.51, 114.13, 115.06, 115.34, 115.55, 115.83, 121.73, 126.83, 127.78, 127.89, 127.96, 128.06, 128.85, 129.17, 131.56, 136.26, 137.53, 138.76, 145.14, 155.23, 167.97; MS, *m/z* 580 (M^+, 38%), 581 (35, M + 1), 582 (26, M + 2), 583 (24, M + 3), 471 (30, M – [2F + 2Cl]), 341 (52, M – $C_{12}H_{12}ClNO_2^{2\bullet}$), 232 (68, M – $C_{19}H_{18}ClFNO_2^{2\bullet}$), 111 (38, M – $C_{26}H_{22}ClF_2N_2O_2^{\bullet}$), 29 (88, M – $C_{30}H_{21}Cl_2F_2N_2O_2^{\bullet}$).

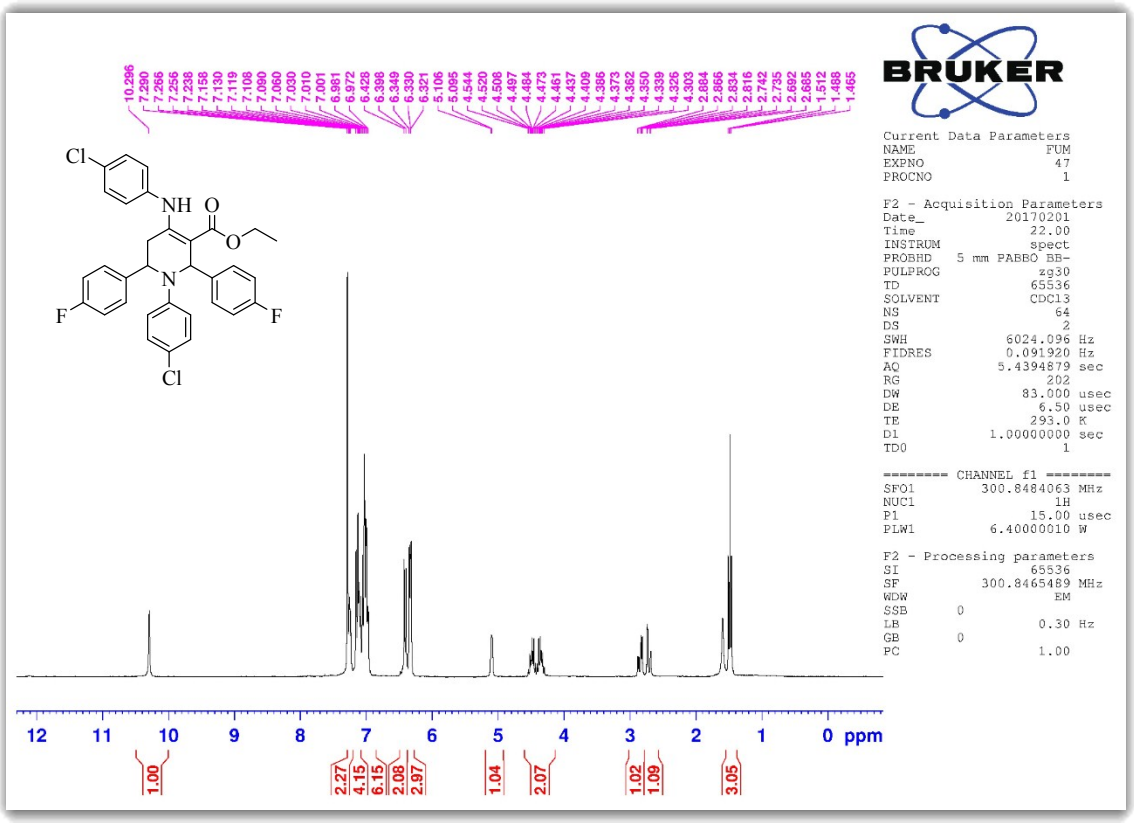

Figure 37: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4k)**.

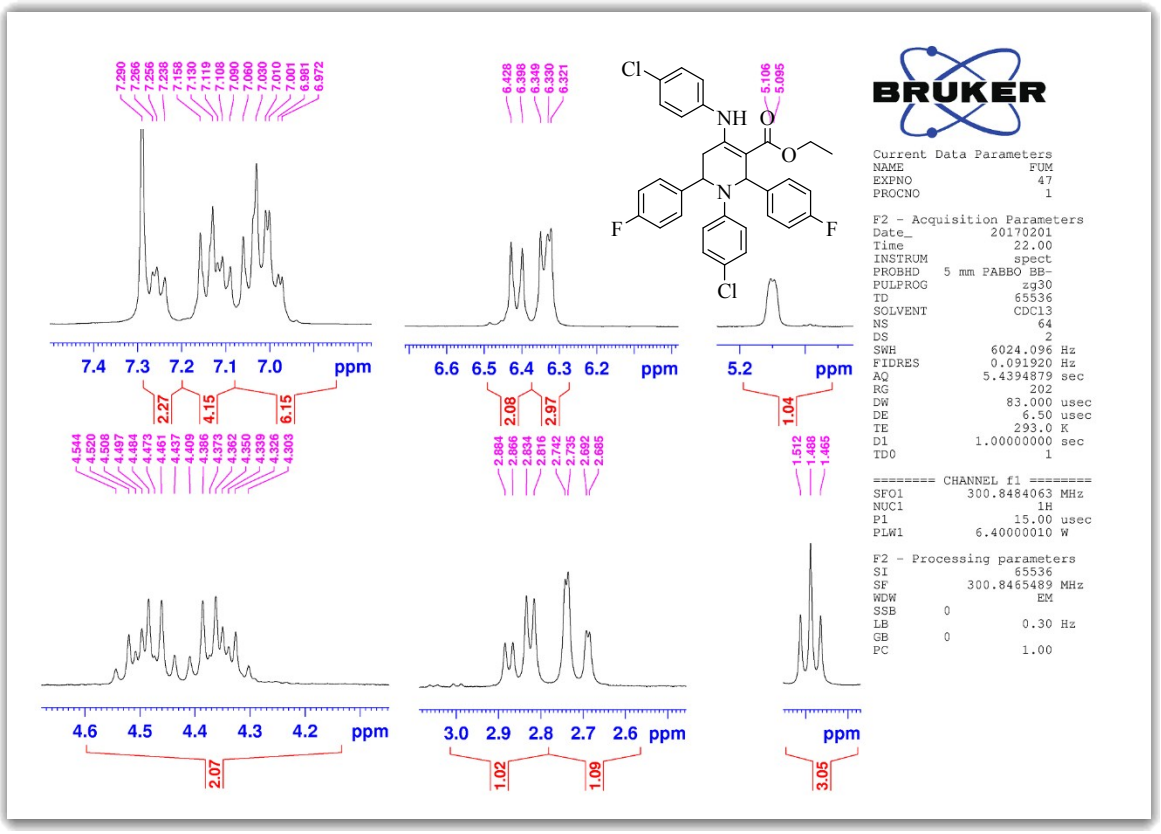

Figure 38: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4k)**; expanded form.

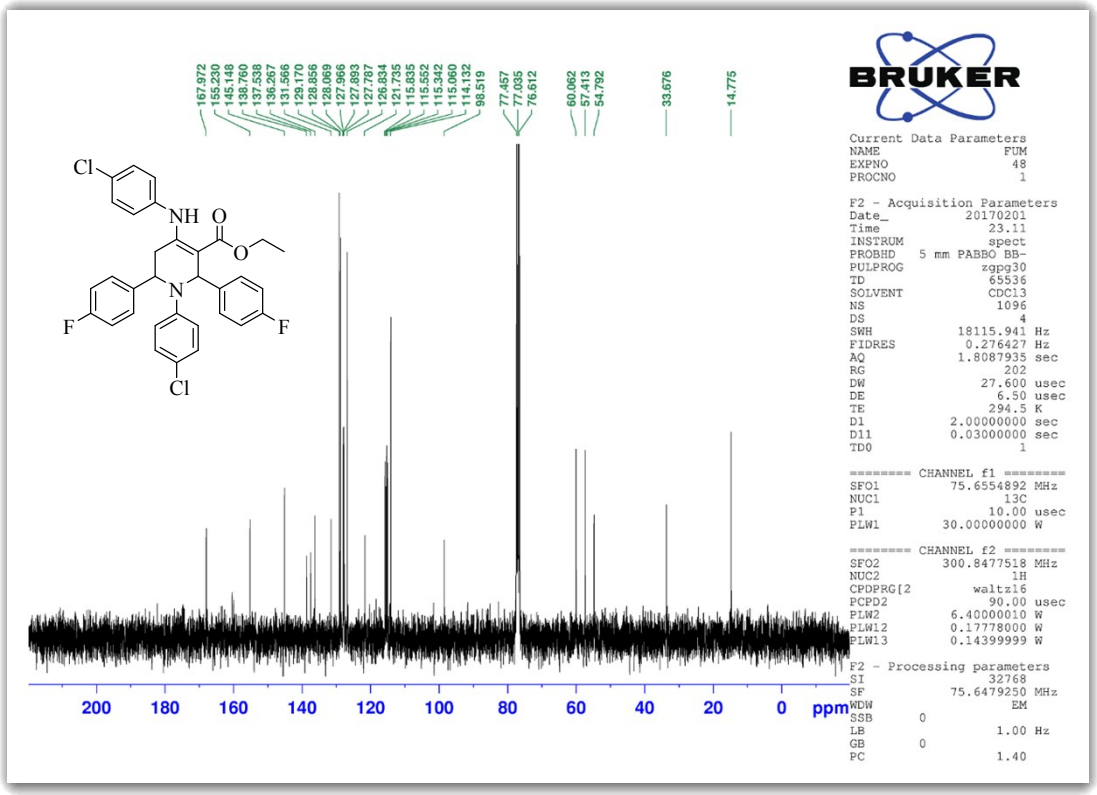

Figure 39: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4k)**.

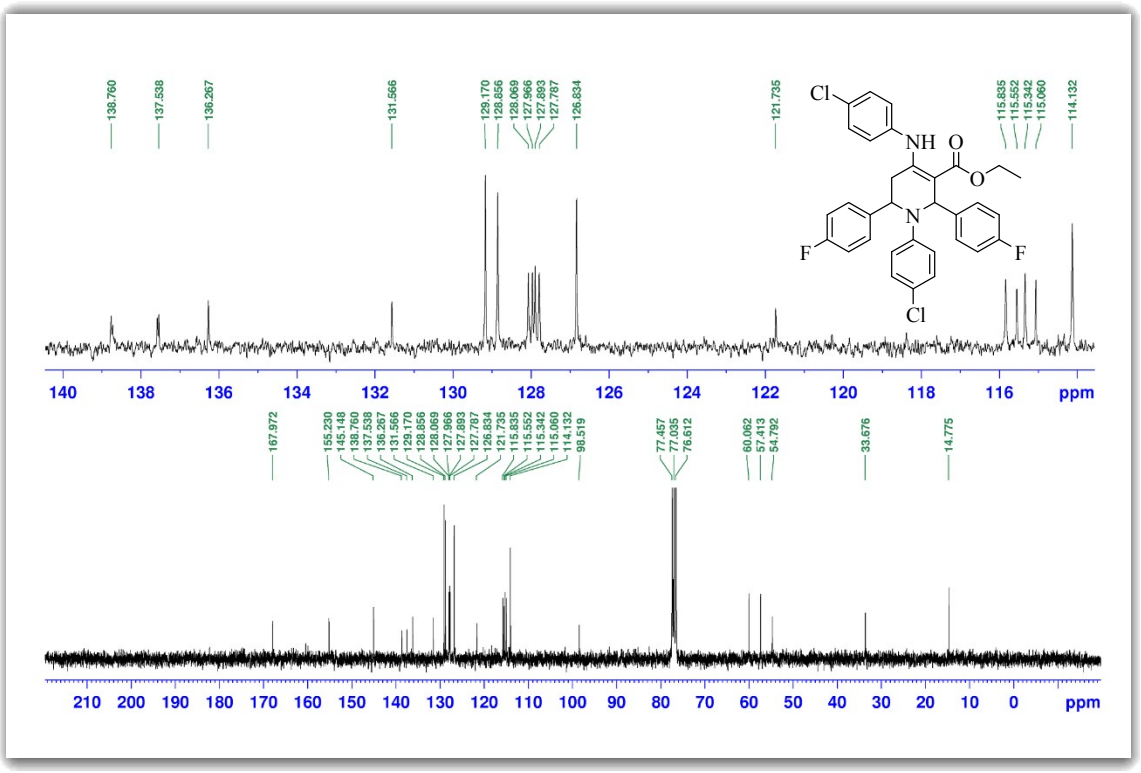

Figure 40: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4k)** and its expanded form.

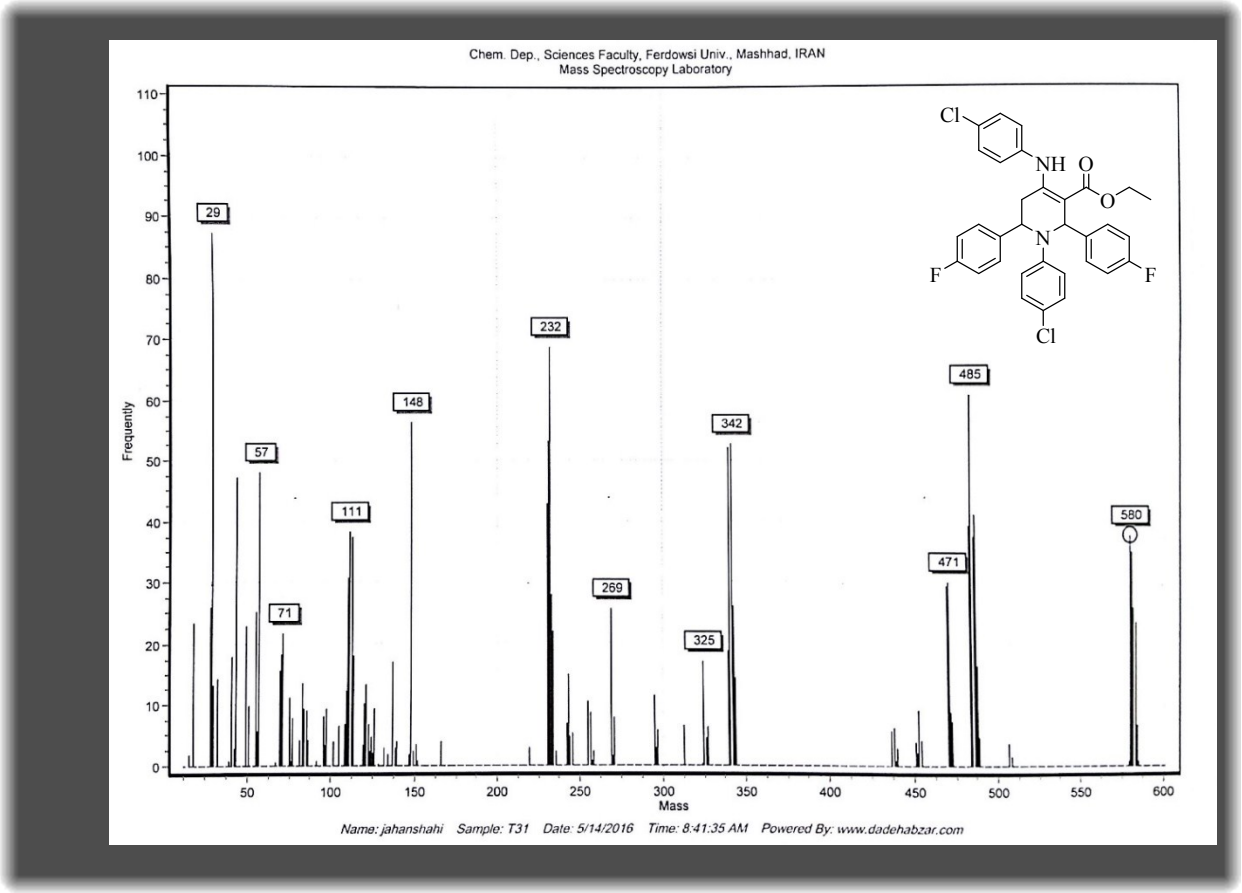

Figure 41: Mass spectrum of ethyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4k)**.

Ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4l): (0.58 g, 95 %); white solid; 212–213 ˚C (from EtOH) (Lit.[8] 214–215 ˚C); FT-IR (KBr): ν_{max}/cm^{-1} 3231, 3063, 2979, 2871, 1653, 1601, 1494, 1369, 1256, 1090, 1012; ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.38 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.60 (1 H, dd, *J* = 2.4, 2.7 Hz, 5-H'), 2.74 (1 H, dd, *J* = 5.7, 5.4 Hz, 5-H''), 4.19-4.30 (1 H, m, OCH_aH_b), 4.33-4.43 (1 H, m, OCH_aH_b), 4.98 (1 H, br s, 6-H), 6.22 (2 H, d, *J* = 6.6 Hz, Ph), 6.26 (2 H, d, *J* = 3.9 Hz, Ph), 6.30 (1 H, s, 2-H), 6.92-6.97 (4 H, m, Ph), 7.03-7.06 (2 H, m, Ph), 7.11-7.19 (6 H, m, Ph), 10.17 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si); 14.79, 33.59, 54.88, 57.45, 60.14, 98.24, 114.09, 121.86, 126.87, 127. 69, 127.90, 128.57, 128.91, 128.97, 129.21, 131.63, 132.42, 133.22, 136.18, 140.37, 141.69, 145.02, 155.16, 167.89; MS, *m/z* 613 (M^+, 27%), 615 (18, M + 2), 358 (54, M – $C_{13}H_{12}C_{l2}N^{\bullet}$), 248 (14, M – $C_{19}H_{18}C_{l2}NO_2^{2\bullet}$), 111 (14, M – $C_{26}H_{22}C_{l3}N_2O_2^{\bullet}$), 29 (98, M – $C_{30}H_{21}C_{l4}N_2O_2^{\bullet}$).

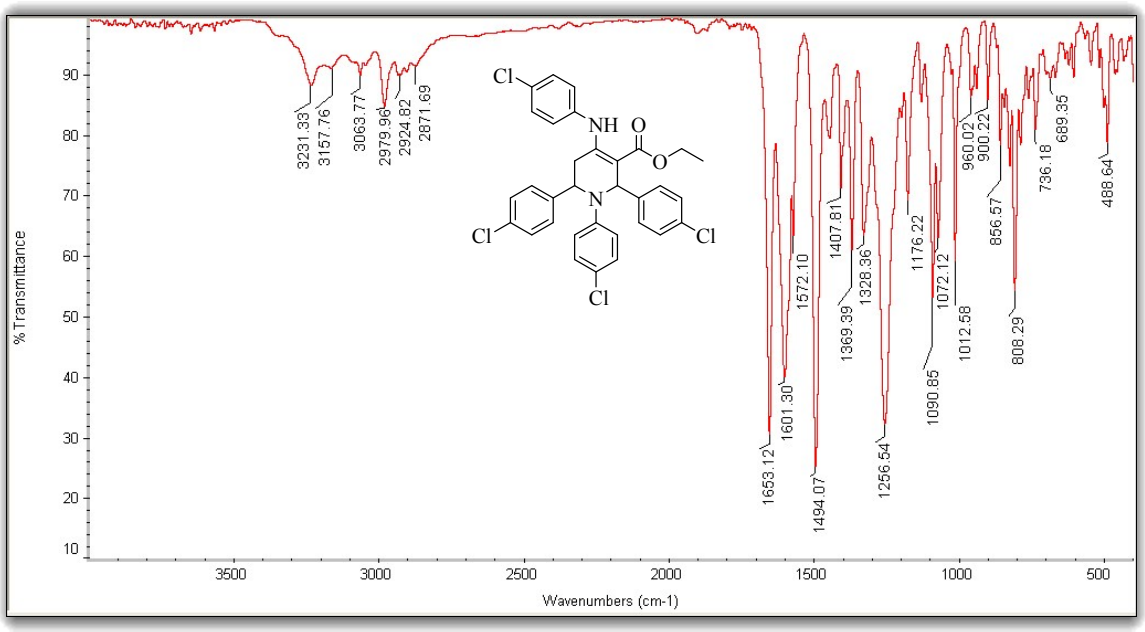

Figure 42: FT-IR spectrum (KBr) of ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4l)**.

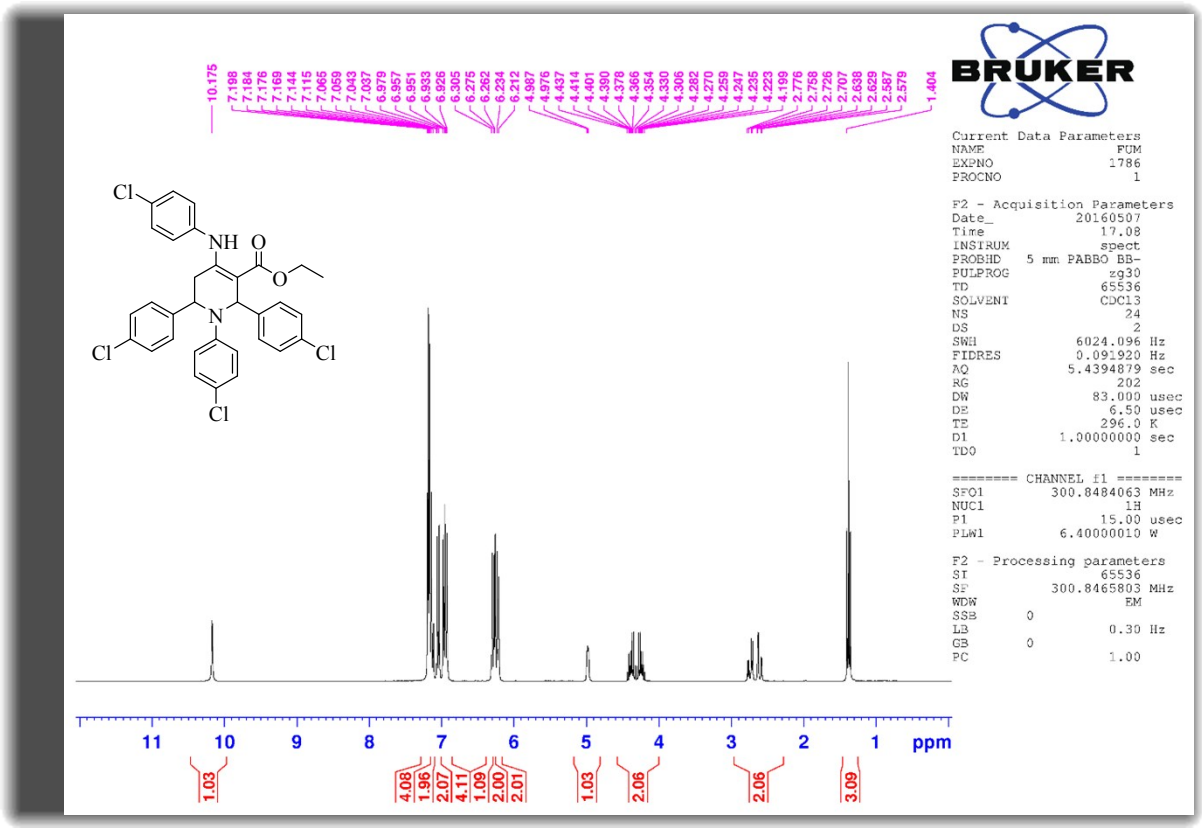

Figure 43: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4l)**.

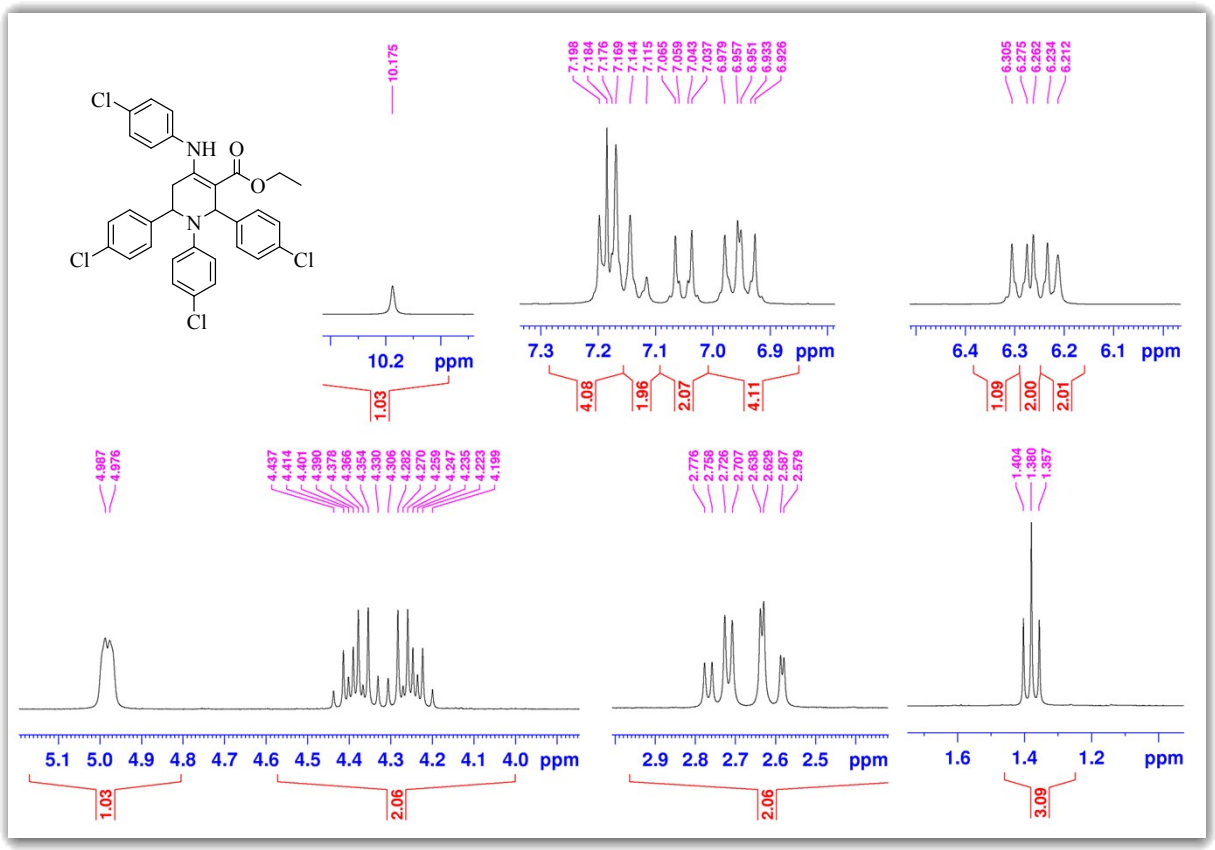

Figure 44: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4l)**; expanded form.

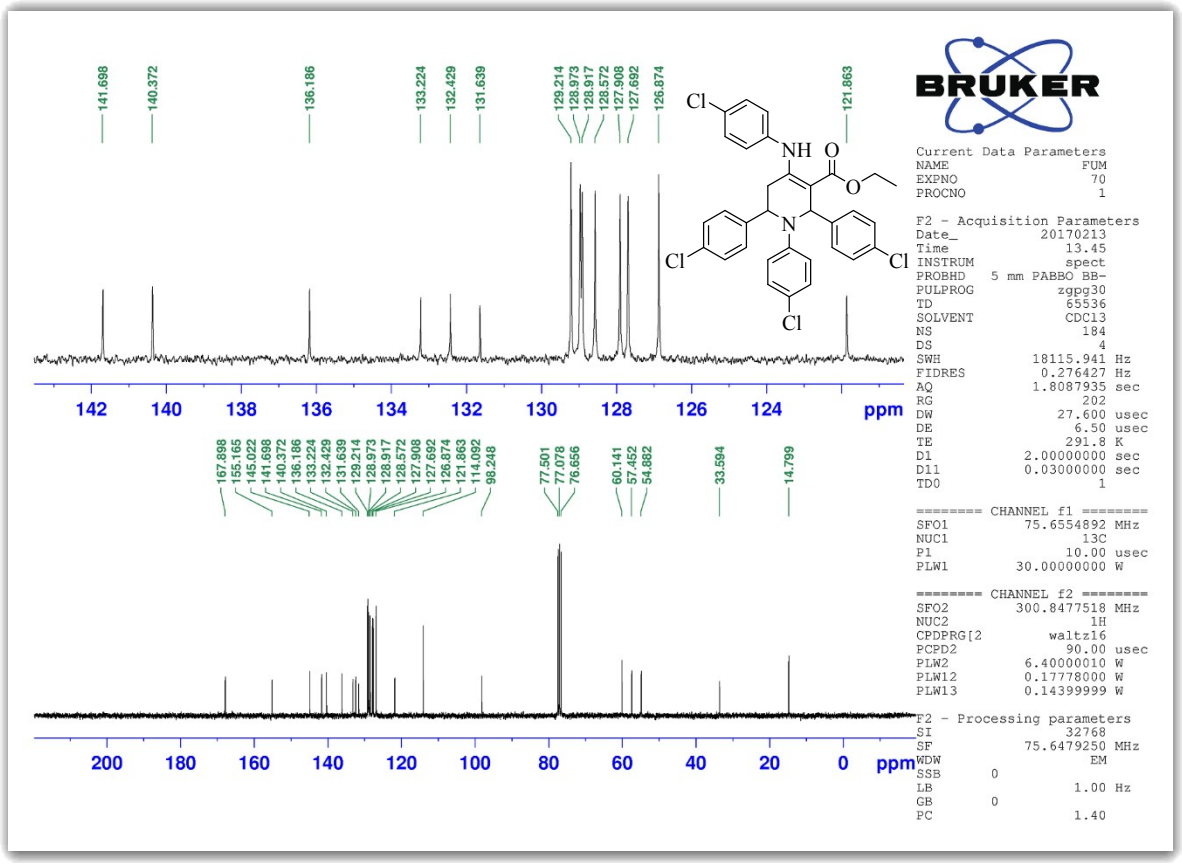

Figure 45: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4l)** and its expanded form.

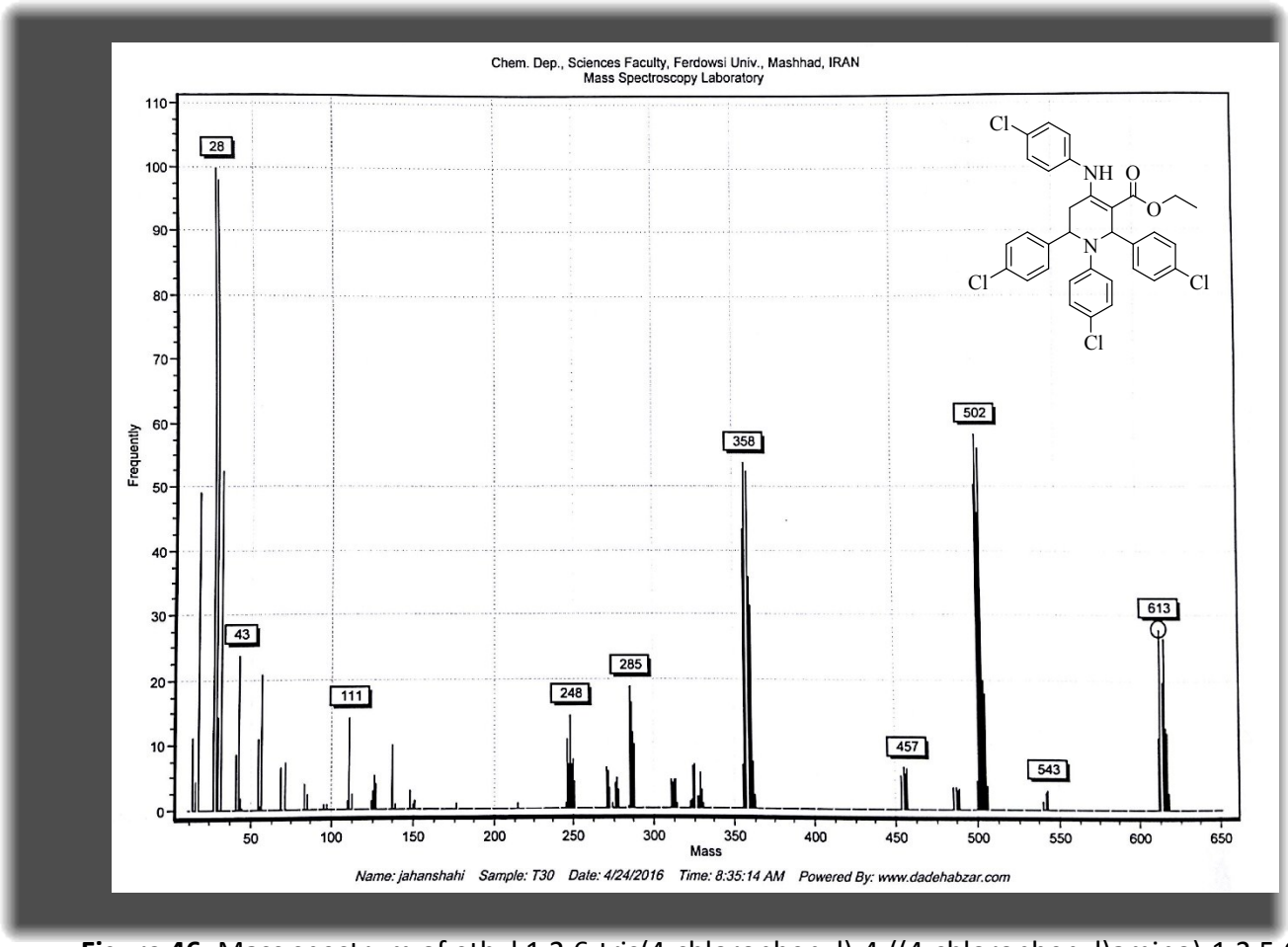

Figure 46: Mass spectrum of ethyl 1,2,6-tris(4-chlorophenyl)-4-((4-chlorophenyl)amino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4l)**.

Ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4m): (0.59 g, 93%); white solid; mp 204–205 ˚C (from EtOH); FT-IR (KBr): ν_{max}/cm^{-1} 3246, 3084, 2924, 2855, 1651, 1607, 1491, 1369, 1261, 1065; ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si) 1.49 (3 H, t, *J* = 7.2 Hz, CH_2CH_3), 2.88 (1 H, br d, *J* = 15 Hz, 5-H'), 3.14 (1 H, dd, *J* = 5.1, 5.1 Hz, 5-H''), 4.31-4.39 (1 H, m, OCH_aH_b), 4.43-4.51 (1 H, m, OCH_aH_b), 5.39 (1 H, br s, 6-H), 6.40 (1 H, s, 2-H), 6.44 (1 H, d, *J* = 8.1 Hz, Ph), 6.65 (2 H, d, *J* = 8.7 Hz, Ph), 6.86-6.95 (4 H, m, Ph), 7.17 (2 H, d, *J* = 4.8 Hz, Ph), 7.23 (2 H, d, *J* = 8.7 Hz, Ph), 7.29 (1 H, s, Ph), 7.34 (2 H, d, *J* = 8.1 Hz, Ph), 10.45 (1 H, br s, NH); δC (75 MHz; $CDCl_3$; Me_4Si) 14.733, 34.15, 52.56, 53.77, 60.08, 98.14, 109.50, 114.92, 118.05, 119.12, 123.84, 124.14, 124.47, 124.57, 124.90, 125.34, 126.55, 126.67, 126.82, 127.07, 127.20, 131.50, 131.63, 132.20, 132.44, 137.05, 145.08, 146.57, 148.22, 155.20, 167.58; MS*, m/z*

645 (M^+, 23%), 647 (19, M + 2), 475 (27, M – 2[$C_4H_3S^•$]), 473 (37, M – $C_6H_4BrN^•$), 347 (89, M – $C_{13}H_{13}BrNS^{3•}$), 154 (90, M – $C_{22}H_{20}BrN_2O_2S_2^•$), 29 (90, M – $C_{26}H_{19}Br_2N_2O_2S_2^•$); Elemental analysis: Found: C, 52.22; H, 3.79; H, 4.37. Calc. for $C_{28}H_{24}Br_2N_2O_2S_2$: C, 52.19; H, 3.75; N, 4.35%.

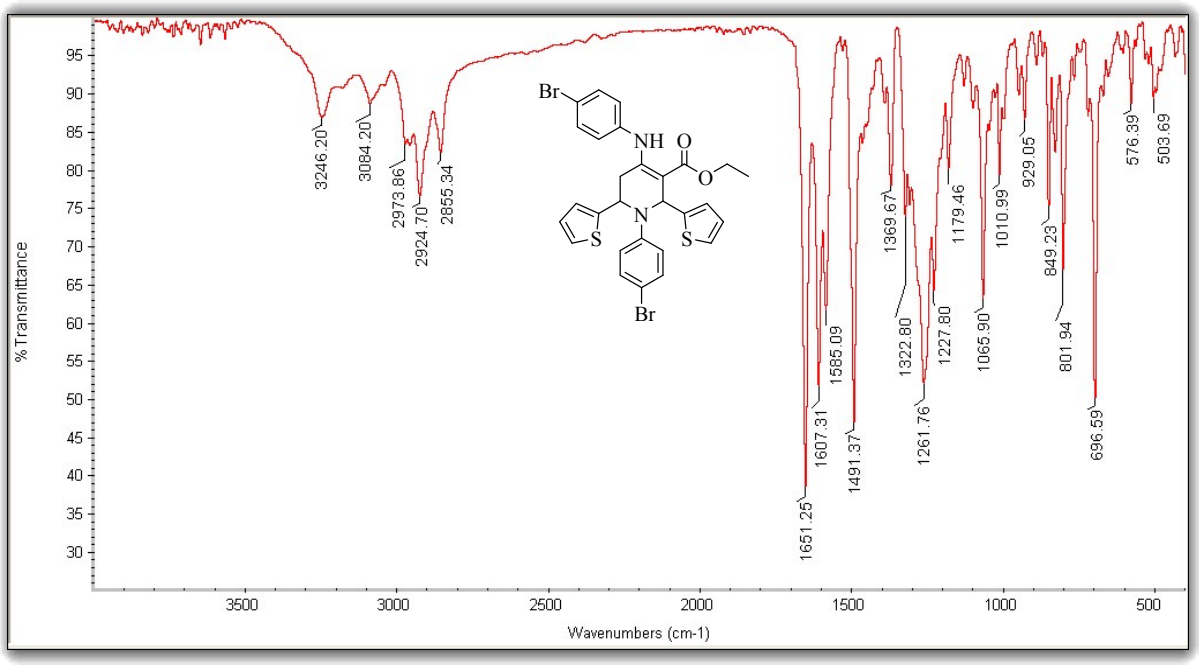

Figure 47: FT-IR spectrum (KBr) of ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4m)**.

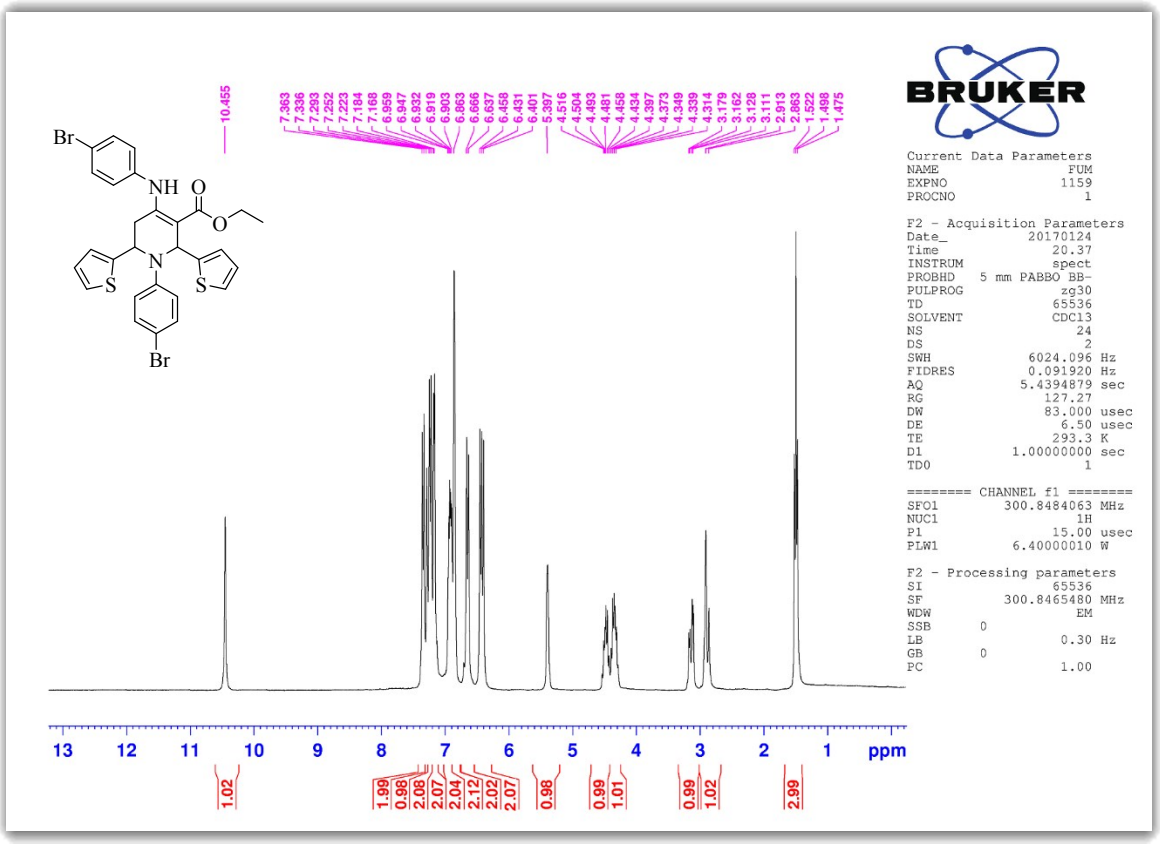

Figure 48: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4m)**.

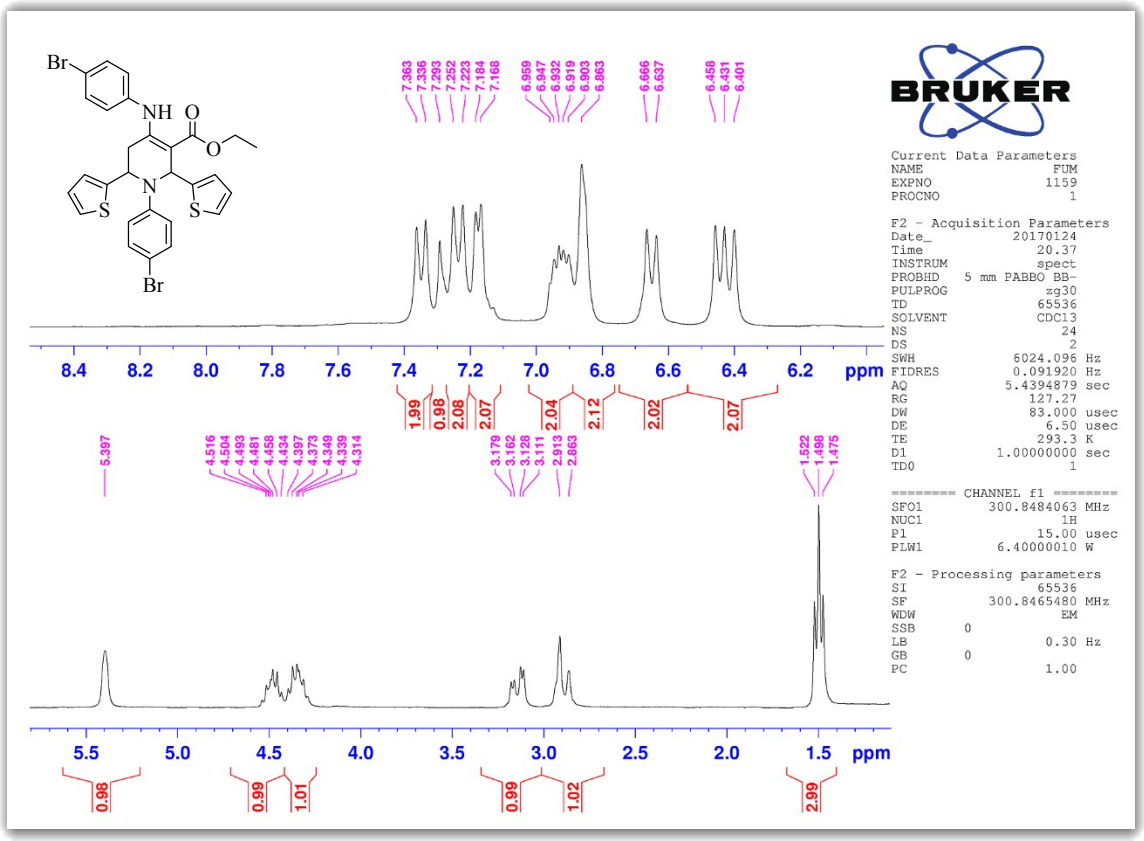

Figure 49: ^{1}H NMR (300 MHz, $CDCl_3$) of ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4m)**; expanded form.

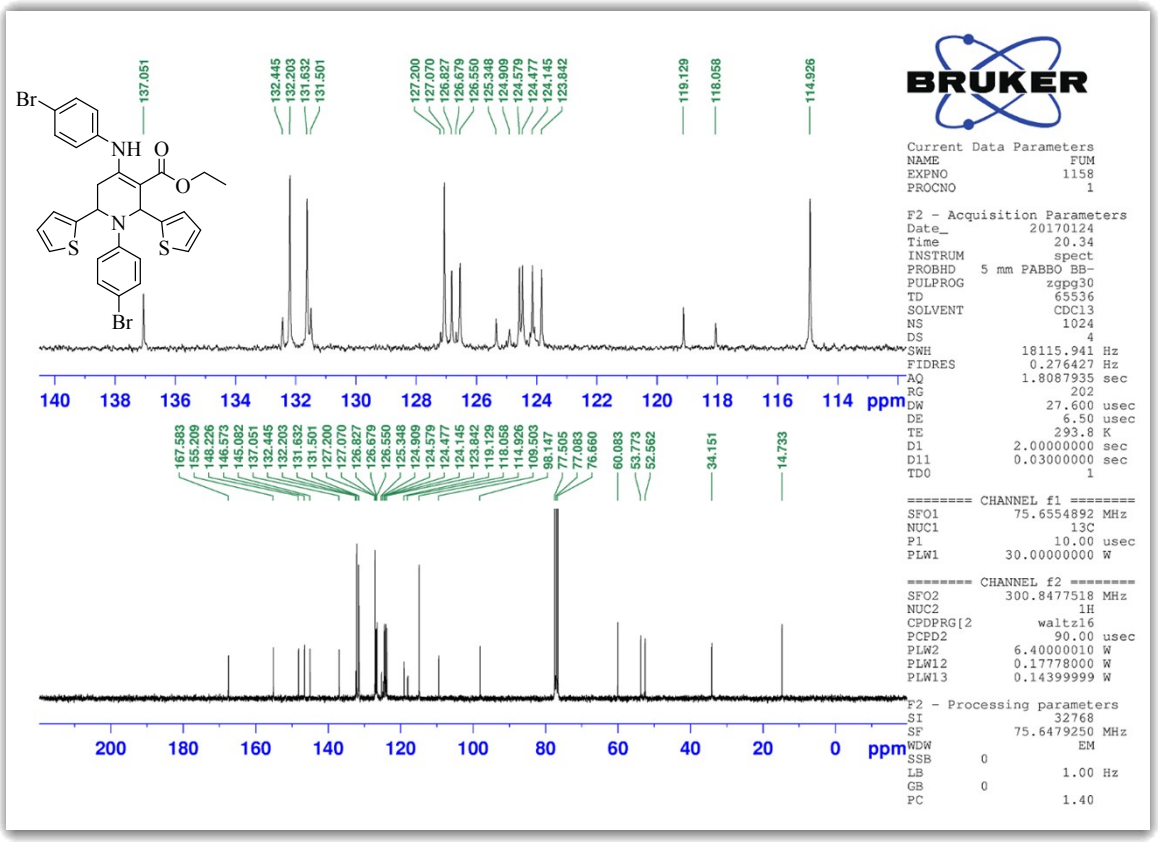

Figure 50: ^{13}C NMR (75MHz, $CDCl_3$) of ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4m)** and its expanded form.

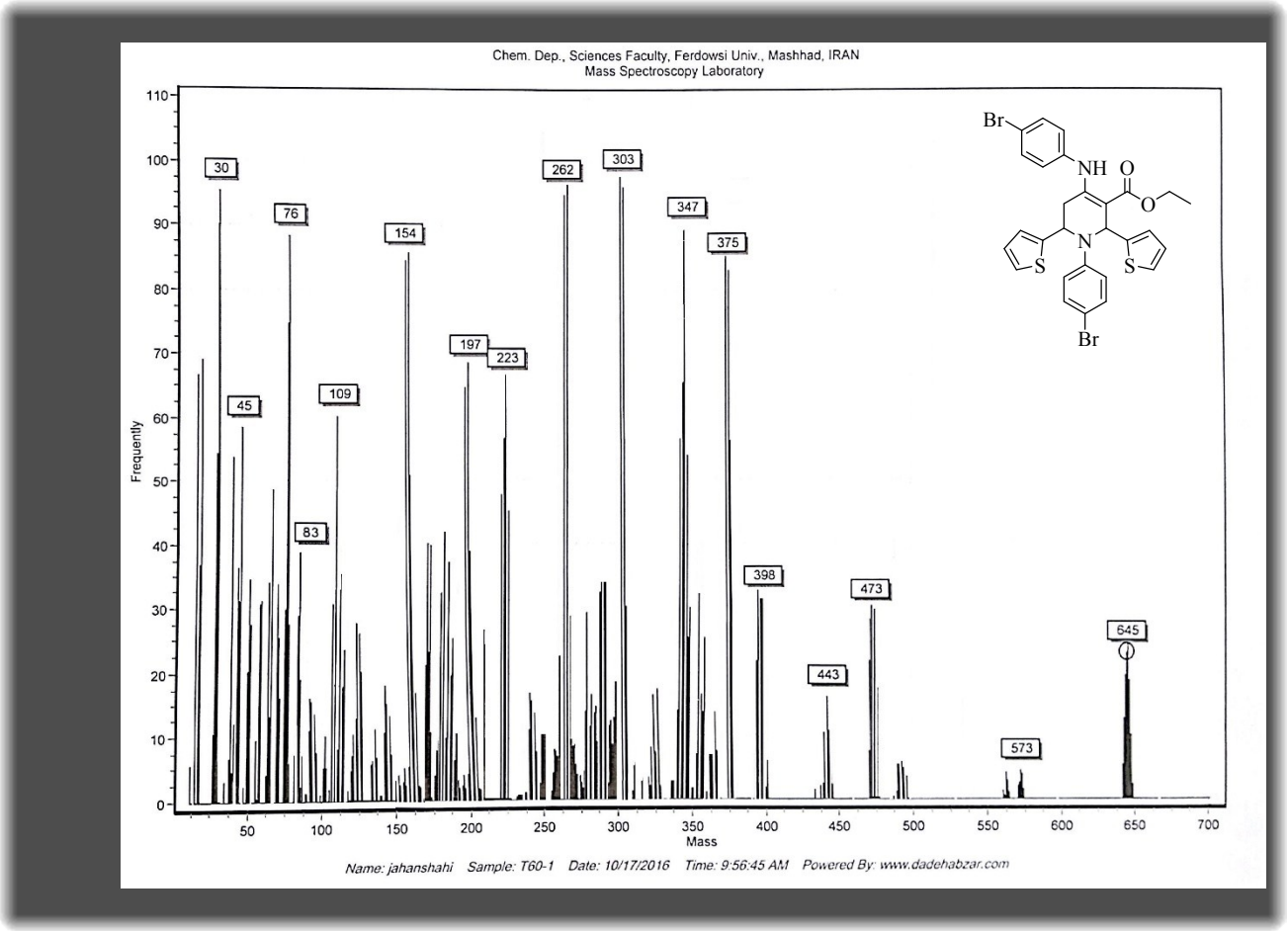

Figure 51: Mass spectrum of ethyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-di(thiophen-2-yl)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4m)**.

Methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4n): (0.44 g, 97%); white solid; mp 198–199 ˚C (from EtOH) (Lit.[9] 200–202 ˚C); MS, m/z 460 (M^+, 7%), 461 (38, M + 1), 181 (100, M – $C_{18}H_{17}NO_2^{2\bullet}$), 92 (70, M – $C_{25}H_{22}NO_2^{\bullet}$), 77 (85, M – $C_{25}H_{23}N_2O_2^{\bullet}$), 57 (43, M – $C_{29}H_{27}N_2^{\bullet}$).

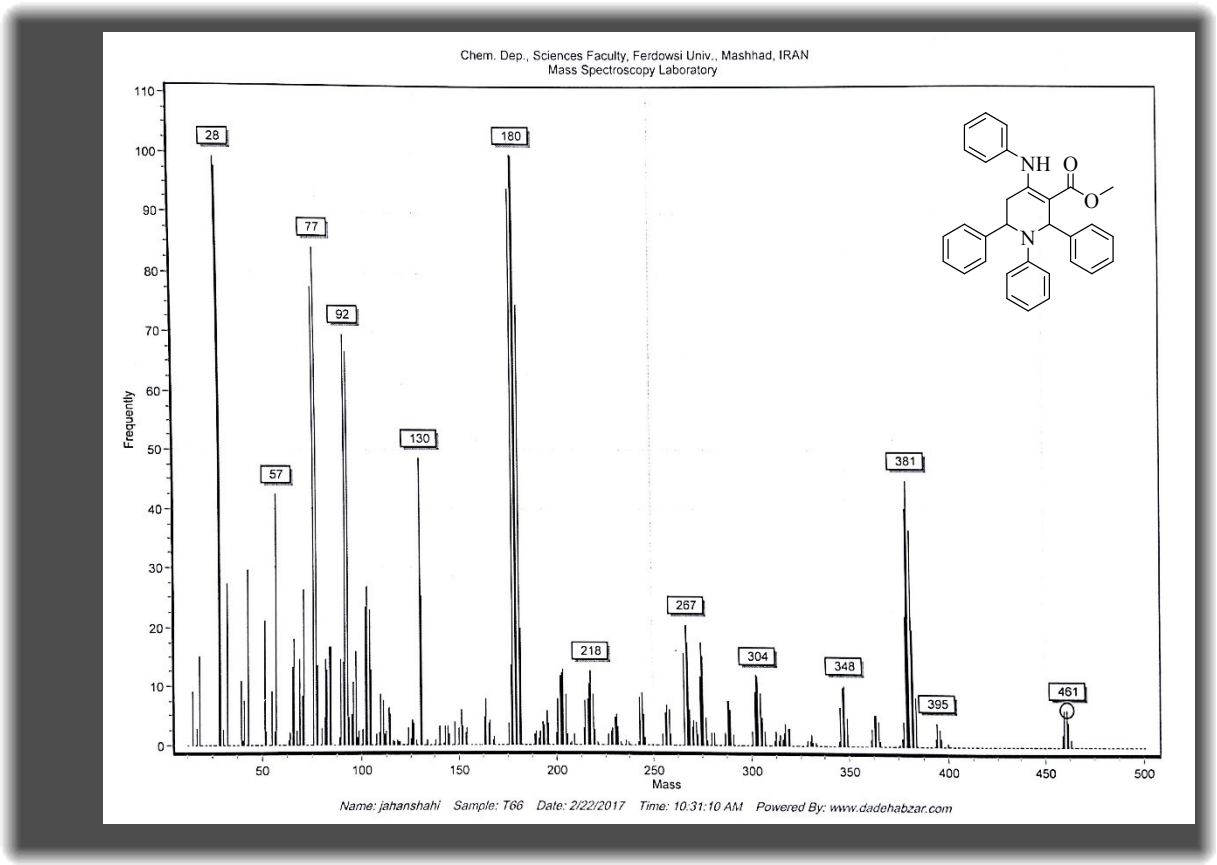

Figure 52: Mass spectrum of methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4n)**.

Methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4o): (0.50 g, 96%); white solid; mp 200–201 ˚C (from EtOH) (Lit.[1] 202–204 ˚C); FT-IR (KBr): ν_{max}/cm^{-1} 3258, 3084, 3023, 2949, 2872, 1651, 1600, 1492, 1318, 1254, 1077; ^{1}H NMR: δH (300 MHz; $CDCl_3$; Me_4Si), 2.74 (1 H, dd, *J* = 1.8, 1.8 Hz, 5-H'), 2.91 (1 H, dd, *J* = 5.7, 5.7 Hz, 5-H''), 3.99 (3 H, s, OCH_3), 5.16 (1 H, br s, 6-H), 6.20 (1 H, s, 2-H), 6.22 (1 H, s, Ph), 6.44 (1 H, s, Ph), 6.47 (1 H, s, Ph), 6.50 (1 H, s, Ph), 7.02 (1 H, s, Ph), 7.05 (1 H, s, Ph), 7.09 (1 H, s, Ph), 7.11 (1 H, s, Ph), 7.19-7.22 (2 H, m, Ph), 7.25-7.33 (8 H, m, Ph), 10.26 (1 H, br s, NH); ^{13}C NMR: δC (75 MHz; $CDCl_3$; Me_4Si) 33.50, 51.26, 55.28, 58.33, 98.43, 114.03, 121.25, 126.32, 126.53, 126.64, 127.13, 127.52, 128.43, 128.76, 128.87, 129.07, 131.49, 136.35, 142.25, 143.15, 145.48, 155.64, 168.50; MS*, m/z* 529 (M^+, 57%), 531 (38, M + 2), 451 (98, M – $C_6H_5^{\bullet}$), 417 (27, M – $C_6H_4Cl^{\bullet}$), 214 (94), 77 (61, M – $C_{25}H_{21}Cl_2N_2O_2^{\bullet}$), 59 (100, M – $C_{29}H_{23}Cl_2N_2^{\bullet}$).

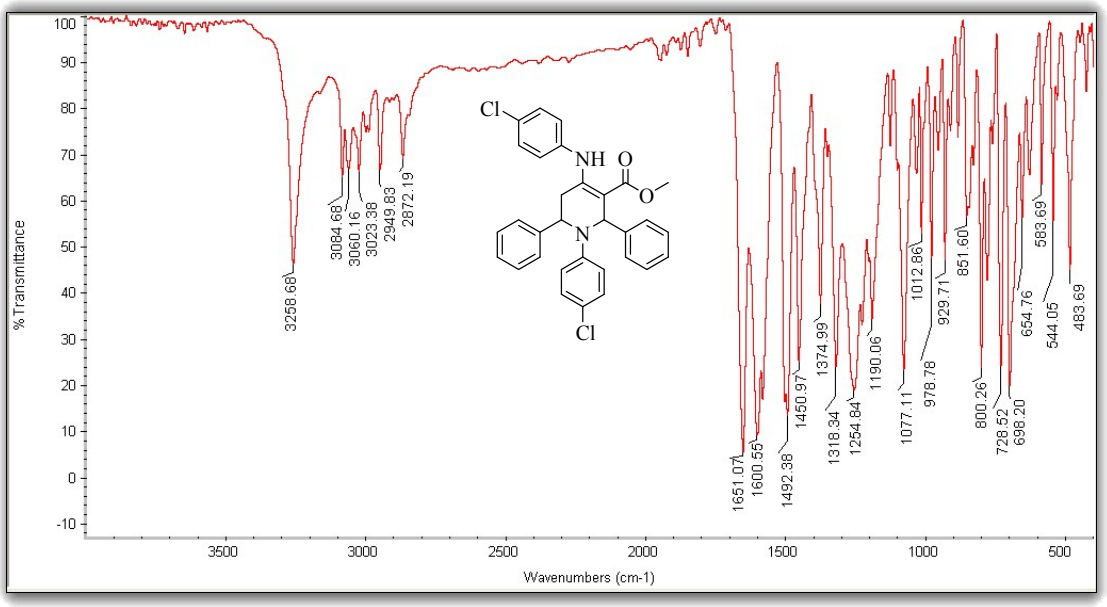

Figure 53: FT-IR spectrum (KBr) of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)**.

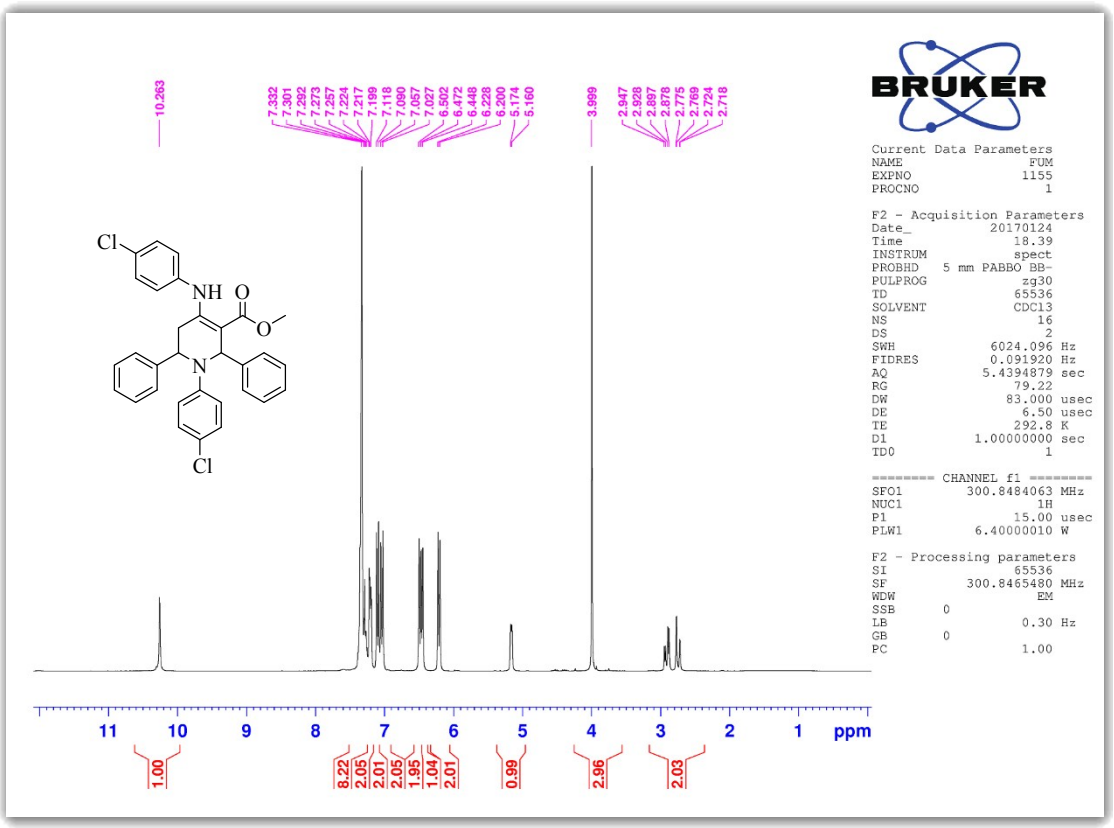

Figure 54: ^{1}H NMR (300 MHz, $CDCl_3$) of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)**.

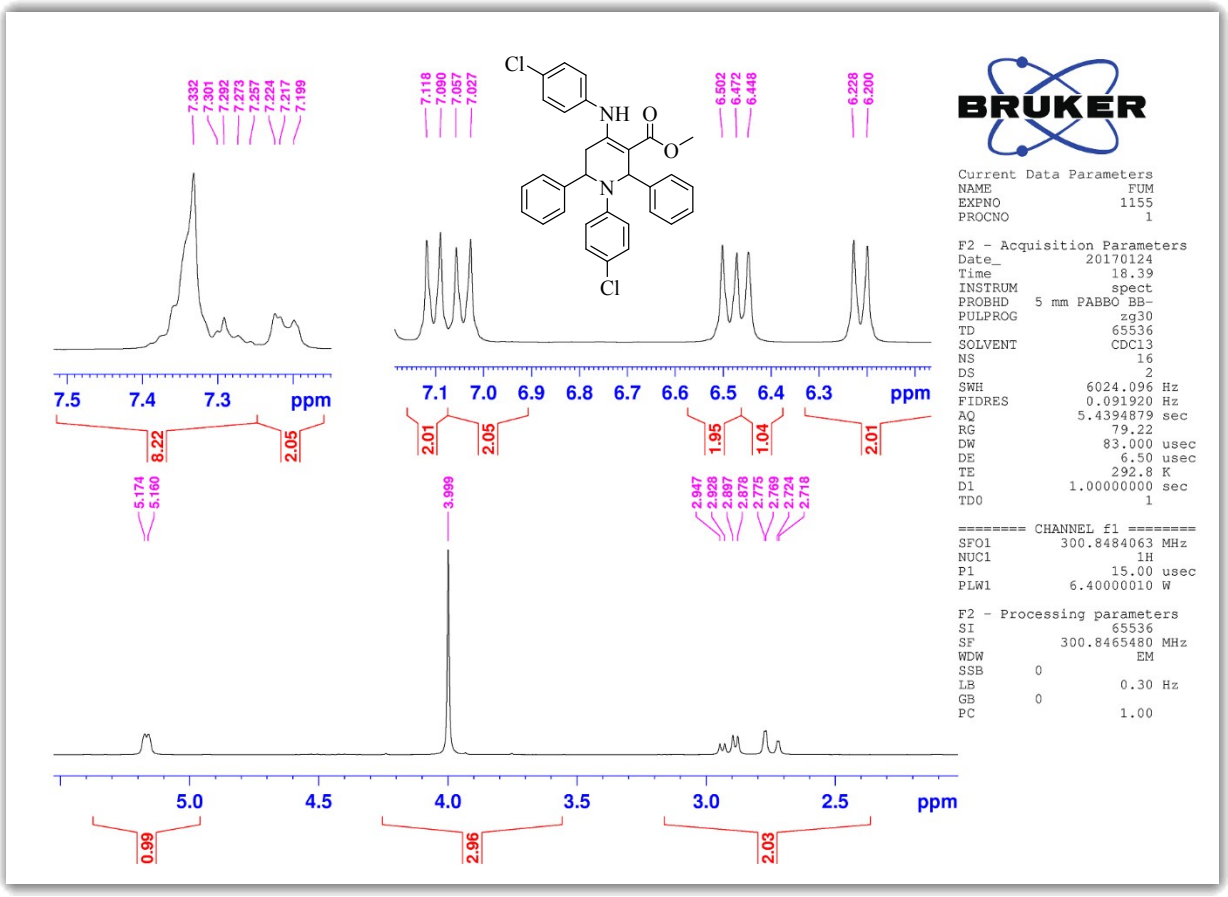

Figure 55: ^{1}H NMR (300 MHz, $CDCl_3$) of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)**; expanded form.

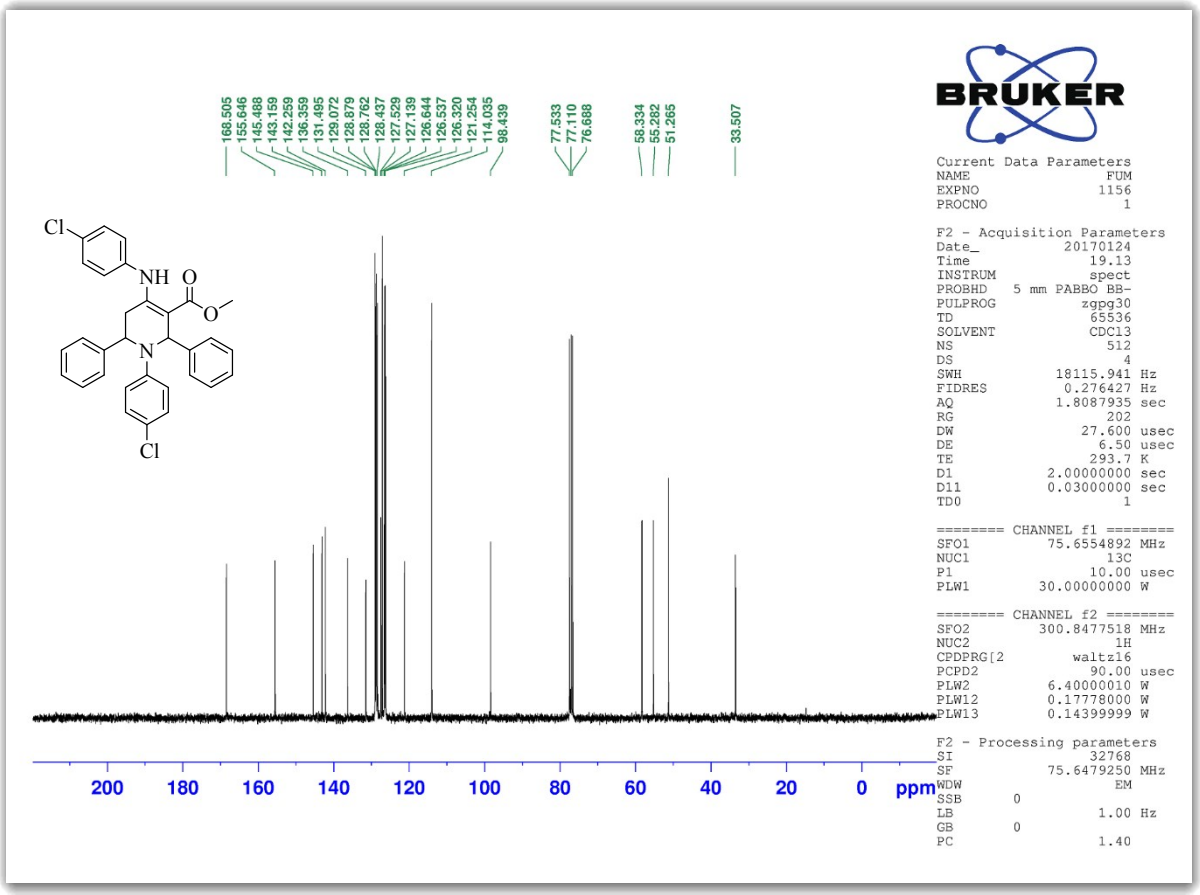

Figure 56: ^{13}C NMR (75MHz, $CDCl_3$) of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)**.

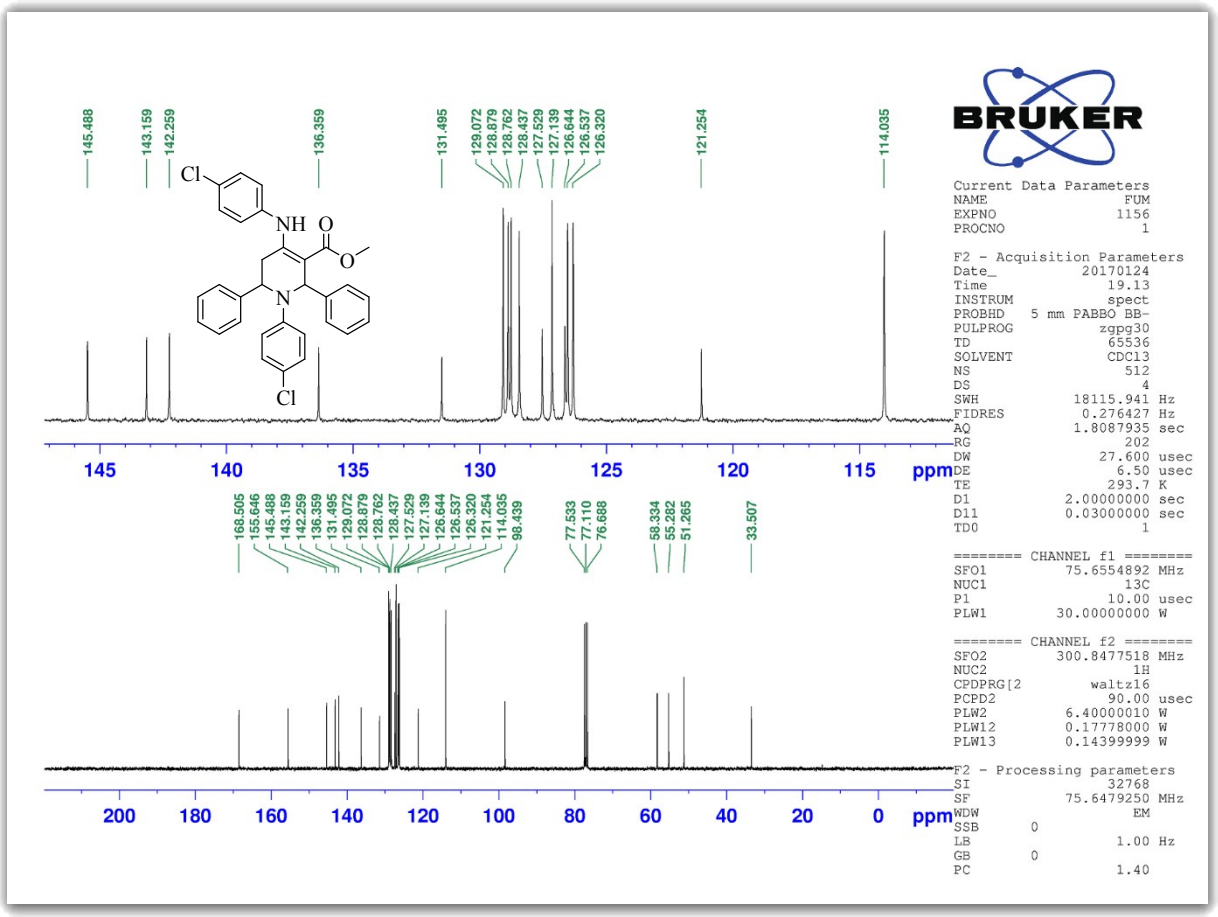

Figure 57: ^{13}C NMR (75MHz, $CDCl_3$) of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)** and its expanded form.

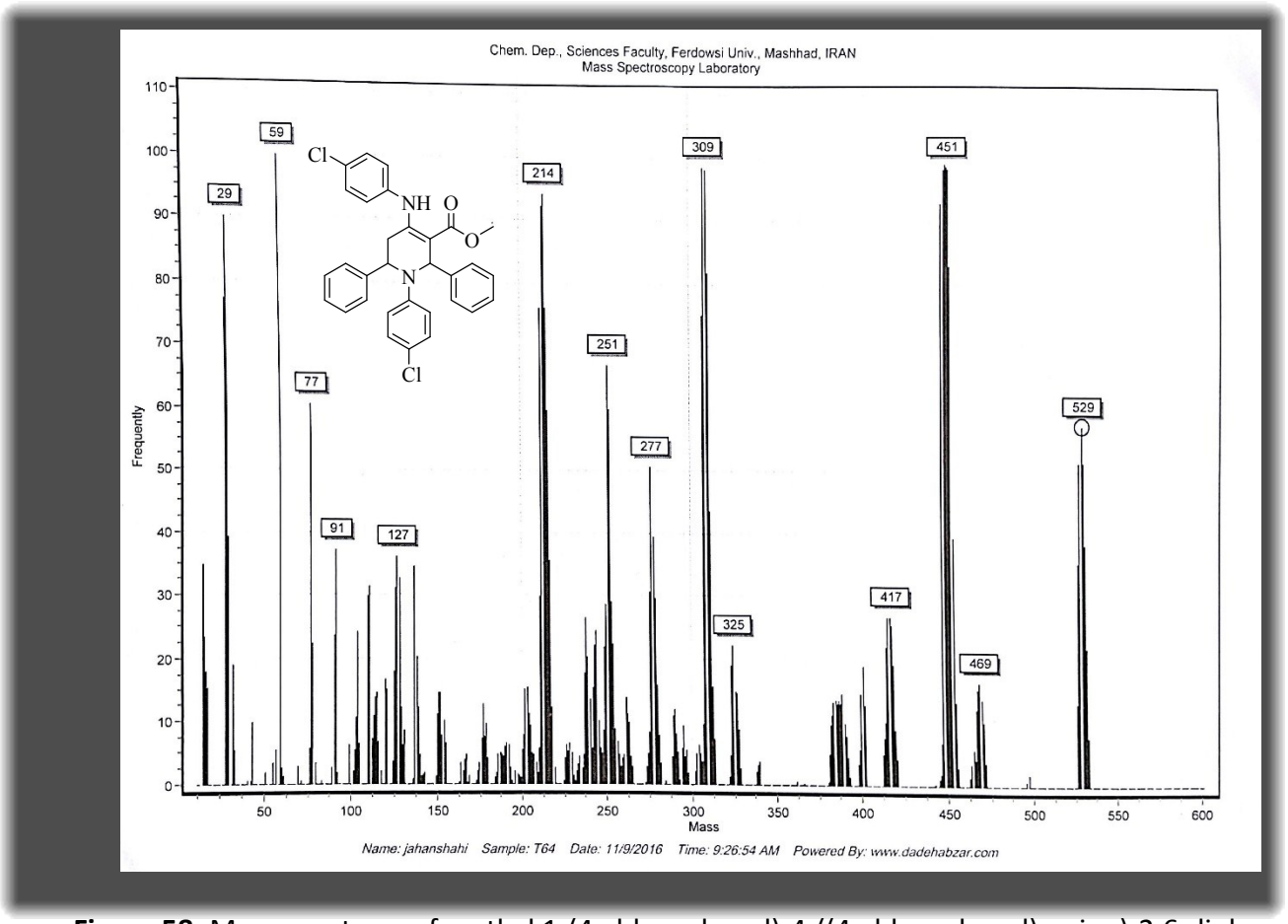

Figure 58: Mass spectrum of methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4o)**.

Methyl 2,6-diphenyl-1-(*p*-tolyl)-4-(*p*-tolylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4p): (0.46 g, 96%); white solid; mp 218–219 ˚C (from EtOH) (Lit.[1] 218–220 ˚C); MS, *m/z* 488 (M^+, 37%), 489 (22, M + 1), 461 (23, M – $C_2H_4^{2\bullet}$), 285 (17, M – $C_{12}H_{13}NO_2^{2\bullet}$), 203 (14, M – $C_{21}H_{19}N^{2\bullet}$), 28 (87, M – $C_{31}H_{29}N_2O_2^{3\bullet}$).

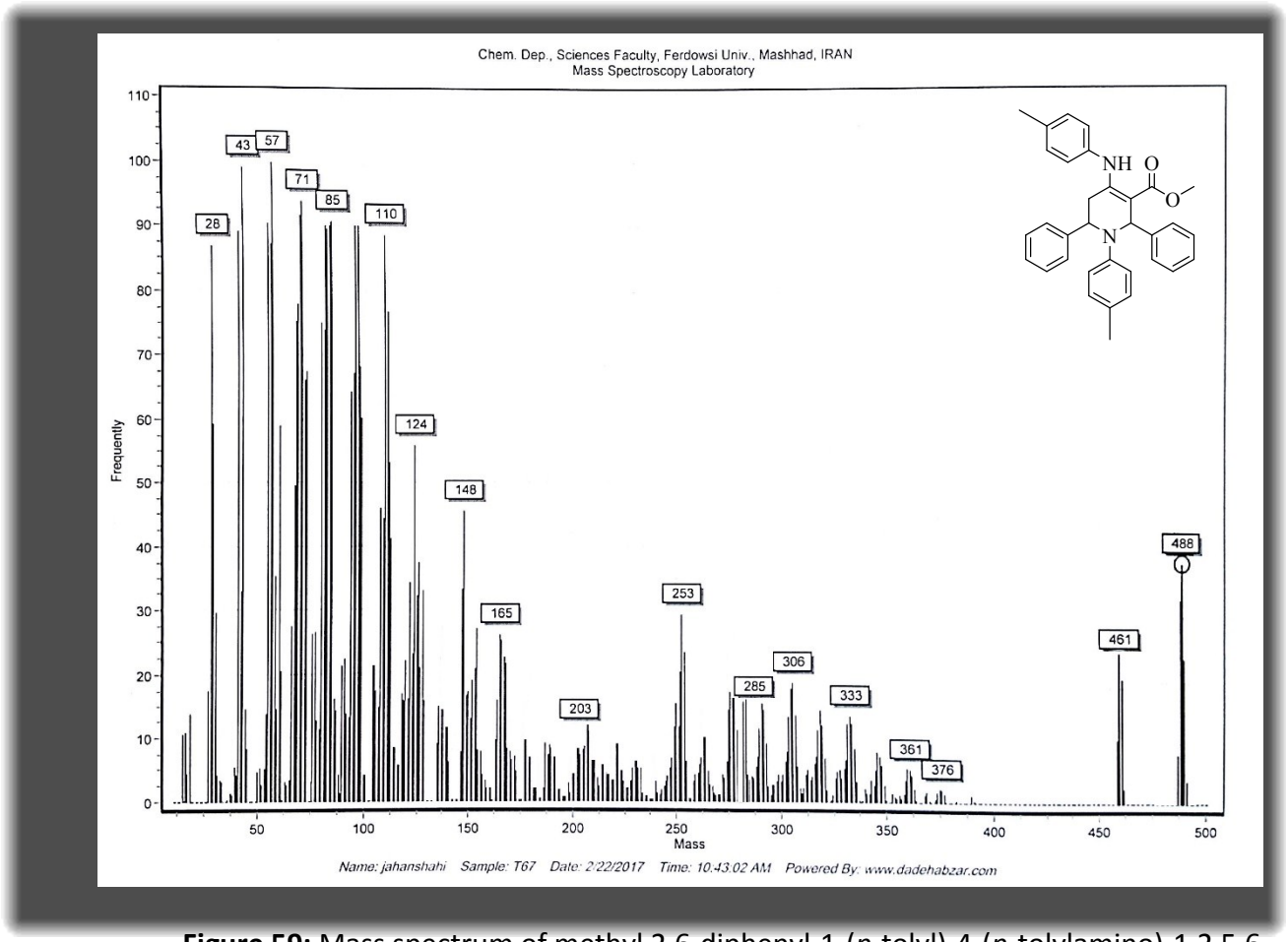

Figure 59: Mass spectrum of methyl 2,6-diphenyl-1-(*p*-tolyl)-4-(*p*-tolylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate **(4p)**.

Methyl 1-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-2,6-diphenyl-1,2,5,6 tetrahydropyridine-3-carboxylate (4q): (0.50 g, 97%); white solid; mp 220–221 ˚C (from EtOH) (Lit.[10], 220–222 ˚C); MS, *m/z* 520 (M^+, 15%), 522 (10, M + 2), 301 (35, M – $C_{12}H_{13}NO_3^{2\bullet}$), 219 (15, M – $C_{21}H_{19}NO^{2\bullet}$), 205 (20, M – $C_{22}H_{21}NO^{2\bullet}$), 69 (95, M – $C_{29}H_{27}N_2O_3^{3\bullet}$), 32 (100, M – $C_{32}H_{28}N_2O_3^{\bullet}$).

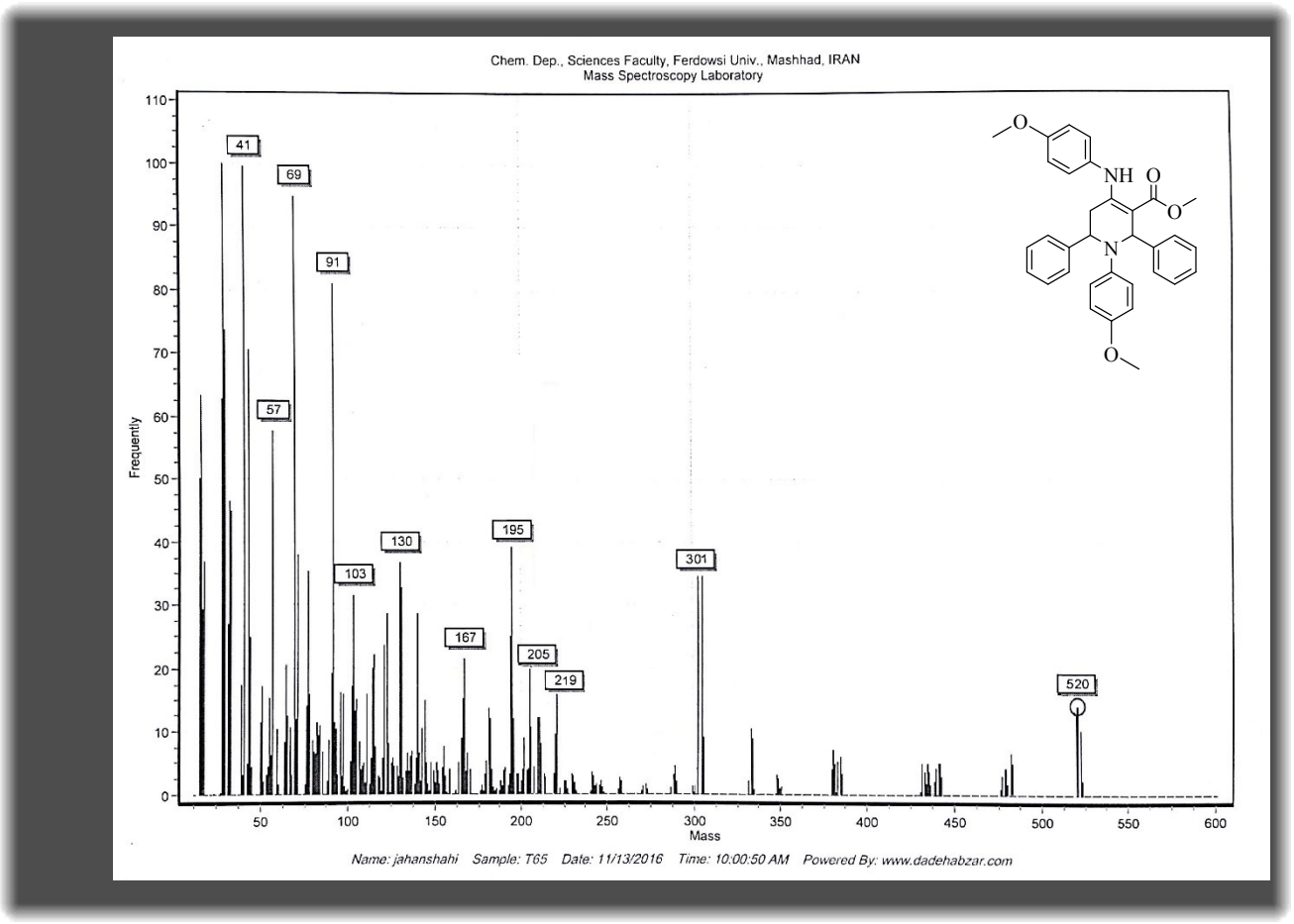

Figure 60: Mass spectrum of methyl 1-(4-methoxyphenyl)-4-((4-methoxyphenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate **(4q)**.

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