

MIL-101-SO₃H metal-organic framework as a Brønsted acid catalyst in Hantzsch reaction: an efficient and sustainable methodology for one-pot synthesis of 1,4-Dihydropyridine

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1. Characterization of MIL-101-SO₃H:

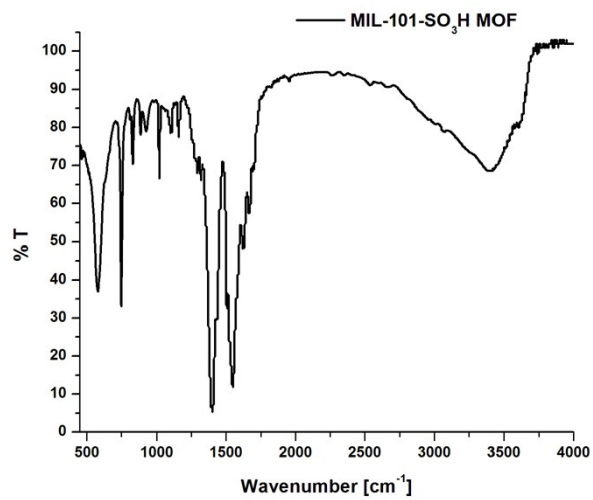


Figure S1. FT-IR spectrum of MIL-101-SO₃H MOF.

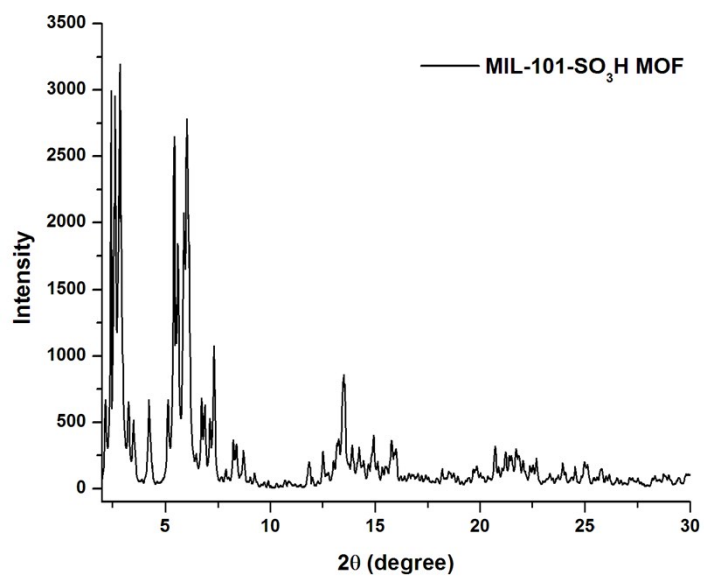


Figure S2. Powder XRD pattern of MIL-101-SO₃H MOF.

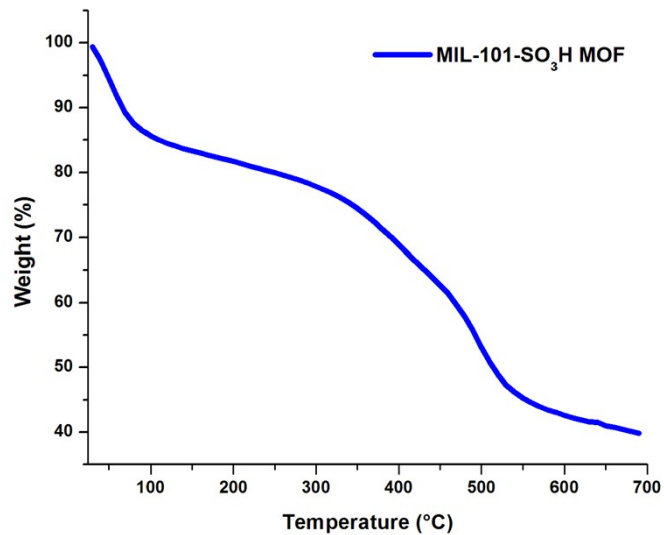


Figure S3. TGA analysis of MIL-101-SO₃H MOF.

Element	Weight %	Atomic %	Error %	Net Int.	K Ratio	Z	R	A	F
C K	49.77	62.85	8.92	308.86	0.21	1.0514	0.9708	0.4014	1
O K	33.33	31.6	12.04	221.49	0.0631	1.0061	0.9911	0.1882	1
S K	3.42	1.62	6.25	150.87	0.0293	0.8958	1.0465	0.9351	1.0201
Cr K	13.47	3.93	5.05	244.71	0.1113	0.7748	1.0783	1.0236	1.0418

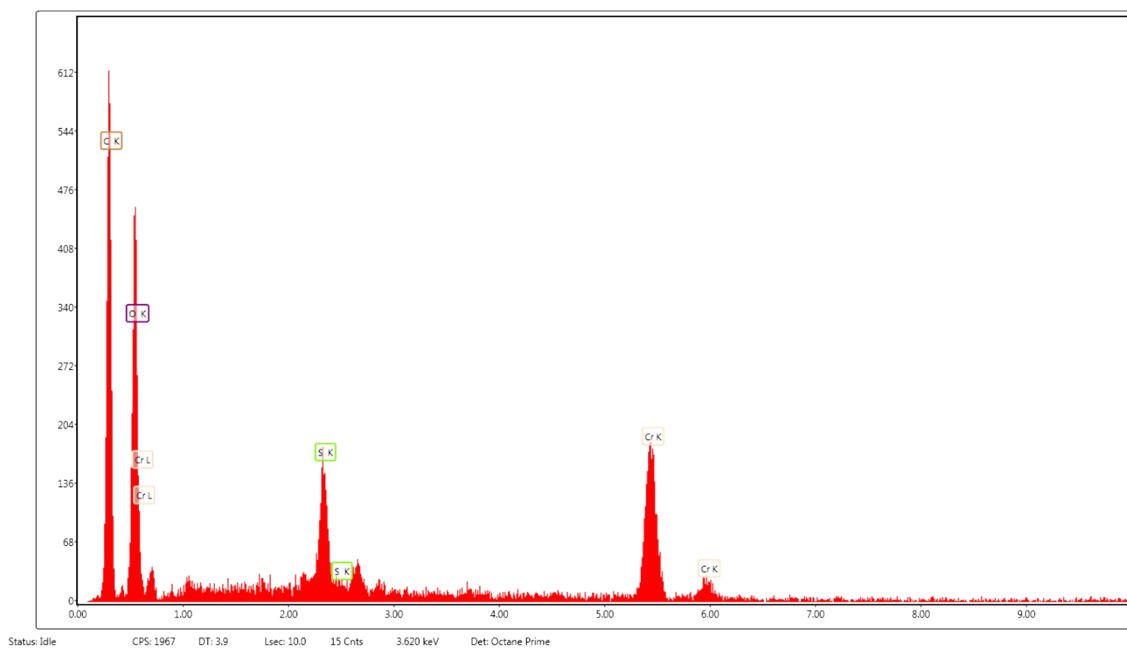
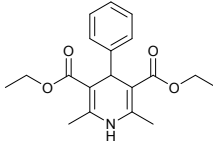
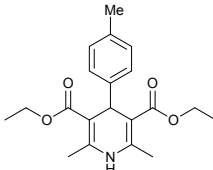
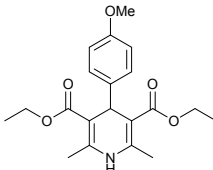
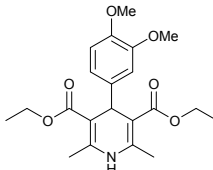
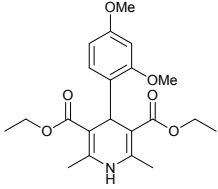
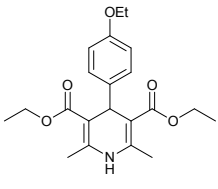
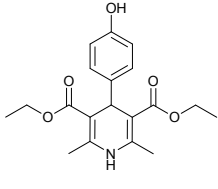
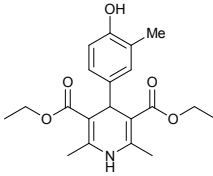
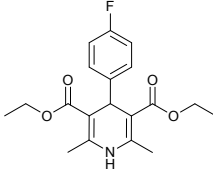
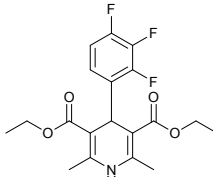


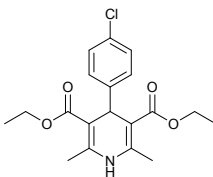
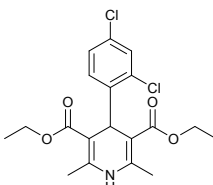
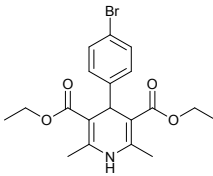
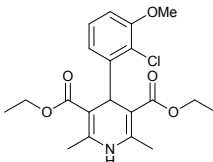
Figure S4. EDAX analysis of MIL-101-SO₃H MOF.

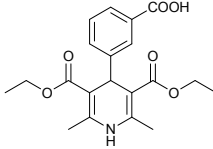
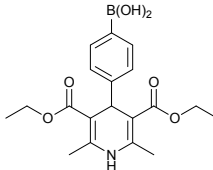
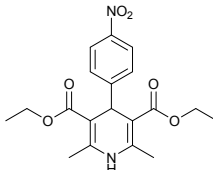
2. NMR, ESI-Mass and HR Mass data:

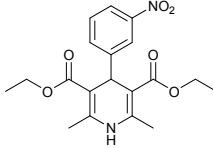
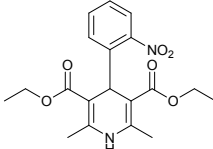
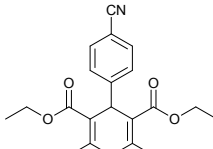
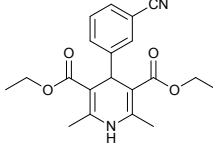
<p><u>Diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (5a)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.22 (t, 6H, <i>J</i> = 6.0 Hz), 2.33 (s, 6H), 4.03–4.12 (m, 4H), 4.99 (s, 1H), 5.67 (s, 1H), 7.09–7.32 (m, 5H). (Fig. S5)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 14.18, 19.38, 39.55, 59.66, 103.92, 126.02, 127.75, 127.90, 144.02, 147.73, 167.67. (Fig. S6)</p> <p>Mass (ESI): 328.16 (M-1) (Fig. S69)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(<i>p</i>-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate (5b)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.23 (t, 6H, <i>J</i> = 6.0 Hz), 2.27 (s, 3H), 2.32 (s, 6H), 4.09 (quar, 4H, <i>J</i> = 6.0 Hz), 4.95 (s, 1H), 5.62 (s, 1H), 7.01 (d, 2H, <i>J</i> = 9.0 Hz), 7.17 (d, 2H, <i>J</i> = 6.0 Hz). (Fig. S7)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 14.12, 19.13, 20.88, 38.95, 59.57, 103.69, 127.62, 128.40, 135.32, 144.19, 144.84, 167.77. (Fig. S8)</p> <p>Mass (ESI): 342.16 (M-1) (Fig. S70)</p>	
<p><u>Diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5c)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.23 (t, 6H, <i>J</i> = 6.0 Hz), 2.32 (s, 6H), 3.75 (s, 3H), 4.05–4.13 (m, 4H), 4.93 (s, 1H), 5.65 (s, 1H), 6.75 (d, 2H, <i>J</i> = 9.0 Hz), 7.20 (d, 2H, <i>J</i> = 9.0 Hz). (Fig. S9)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 14.26, 19.58, 38.70, 55.12, 59.68, 104.35, 113.14, 128.93, 140.30, 143.51, 157.83, 167.65. (Fig. S10)</p> <p>Mass (ESI): 358.23 (M-1) (Fig. S71)</p>	
<p><u>Diethyl 4-(3,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5d)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.24 (t, 6H, <i>J</i> = 6.0 Hz), 2.34 (s, 6H), 3.83 (d, 6H, <i>J</i> = 5.5 Hz), 4.07–4.15 (m, 4H), 4.94 (s, 1H), 5.60 (s, 1H), 6.75 (dd, 1H, <i>J</i> = 9.0, 3.0 Hz), 6.88 (d, 1H, <i>J</i> = 3.0 Hz). (Fig. S11)</p>	

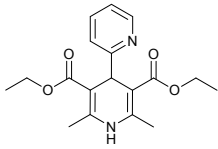
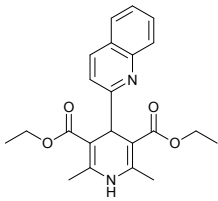
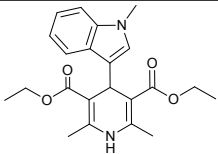
<p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.34, 19.64, 39.05, 55.76, 59.71, 104.30, 110.79, 111.73, 119.77, 140.67, 143.50, 147.31, 148.13, 167.64. (Fig. S12)</p> <p>Mass (ESI): 388.26 (M-1) (Fig. S72)</p>	
<p><u>Diethyl 4-(2,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5e)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.20 (t, 6H, $J = 6.0$ Hz), 2.28 (s, 6H), 3.76 (s, 6H), 4.05 (quar, 4H, $J = 6.0$ Hz), 5.18 (s, 1H), 5.56 (s, 1H), 6.35 (d, 2H, $J = 9.0$ Hz), 7.11 (d, 1H, $J = 9.0$ Hz). (Fig. S13)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.22, 19.40, 34.61, 55.21, 55.17, 59.43, 98.15, 103.35, 103.83, 128.45, 130.94, 143.36, 157.98, 159.07, 168.11. (Fig. S14)</p> <p>Mass (ESI): 388.11 (M-1) (Fig. S73)</p> <p>HRMS: Calculated for $\text{C}_{21}\text{H}_{27}\text{NO}_6 + \text{Na}$: 412.1730, Observed: 412.1727 (Fig. S101)</p>	
<p><u>Diethyl 4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5f)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 1.37 (t, 3H, $J = 6.0$ Hz), 2.32 (s, 6H), 3.97 (quar, 2H, $J = 6.0$ Hz), 4.08 (quar, 4H, $J = 3.0$ Hz), 4.92 (s, 1H), 5.61 (s, 1H), 6.73 (d, 2H, $J = 9.0$ Hz), 7.18 (d, 2H, $J = 9.0$ Hz). (Fig. S15)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.23, 14.86, 19.42, 38.78, 59.61, 63.27, 104.39, 113.82, 128.88, 140.18, 143.49, 157.27, 167.69. (Fig. S16)</p> <p>Mass (ESI): 372.22 (M-1) (Fig. S74)</p>	
<p><u>Diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5g)</u></p> <p>^1H NMR (300 MHz, DMSO) δ: 1.13 (t, 6H, $J = 6.0$ Hz), 2.23 (s, 6H), 3.98 (quar, 4H, $J = 3.0$ Hz), 4.74 (s, 1H), 6.57 (d, 2H, $J = 9.0$ Hz), 6.92 (d, 2H, $J = 9.0$ Hz), 8.72 (s, 1H), 9.09 (s, 1H). (Fig. S17)</p> <p>^{13}C NMR (75 MHz, DMSO) δ: 14.62, 18.62, 38.28, 59.31, 102.72,</p>	

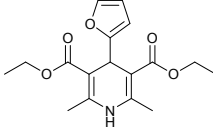
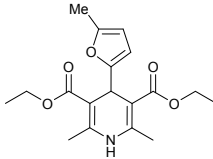
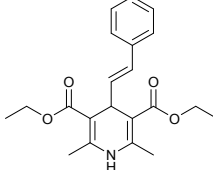
<p>114.94, 128.70, 139.34, 145.19, 155.85, 167.53. (Fig. S18)</p> <p>Mass (ESI): 344.20 (M-1) (Fig. S75)</p>	
<p><u>Diethyl 4-(4-hydroxy-3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5h)</u></p> <p>^1H NMR (300 MHz, DMSO) δ: 1.11 (t, 6H, $J = 6.0$ Hz), 2.00 (s, 3H), 2.21 (s, 6H), 3.97 (quar, 4H, $J = 6.0$ Hz), 4.69 (s, 1H), 6.55 (d, 1H, $J = 9.0$ Hz), 6.72 (d, 1H, $J = 6.0$ Hz), 6.80 (s, 1H), 8.67 (s, 1H), 8.95 (s, 1H). (Fig. S19)</p> <p>^{13}C NMR (75 MHz, DMSO) δ: 15.01, 17.06, 19.06, 38.77, 59.71, 103.21, 114.82, 123.48, 126.40, 130.56, 139.71, 145.49, 154.32, 168.02. (Fig. S20)</p> <p>Mass (ESI): 358.14 (M-1) (Fig. S76)</p> <p>HRMS: Calculated for $\text{C}_{20}\text{H}_{25}\text{NO}_5 + \text{Na}$: 382.1624, Observed: 382.1614 (Fig. S102)</p>	
<p><u>Diethyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5i)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.33 (s, 6H), 4.05–4.14 (m, 4H), 4.96 (s, 1H), 5.63 (s, 1H), 6.88 (t, 2H, $J = 8.8$ Hz), 7.21–7.26 (m, 2H). (Fig. S21)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.21, 19.48, 38.99, 59.74, 104.03, 114.30, 114.57, 129.33, 129.43, 144.62, 144.66, 143.87, 159.67, 162.90, 167.53. (Fig. S22)</p> <p>Mass (ESI): 346.23 (M-1) (Fig. S77)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(2,3,4-trifluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (5j)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.21 (t, 6H, $J = 6.0$ Hz), 2.33 (s, 6H), 4.07 (quar, 4H, $J = 6.0$ Hz), 5.20 (s, 1H), 5.65 (s, 1H), 6.82 (m, 1H), 7.01 (m, 1H). (Fig. S23)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.41, 19.82, 34.78, 60.22, 103.01, 111.55, 111.75, 124.53, 144.85, 167.51. (Fig. S24)</p> <p>Mass (ESI): 382.09 (M-1) (Fig. S78)</p>	

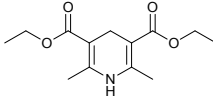
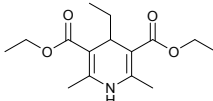
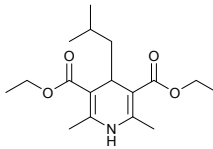
<p><u>Diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5k)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.33 (s, 6H), 4.06–4.14 (m, 4H), 4.95 (s, 1H), 5.68 (s, 1H), 7.15–7.23 (m, 4H). (Fig. S25)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.20, 19.43, 39.17, 59.77, 103.66, 127.85, 129.32, 131.59, 144.12, 146.29, 167.44. (Fig. S26)</p> <p>Mass (ESI): 362.30 (M-1) (Fig. S79)</p>	
<p><u>Diethyl 4-(2,4-dichlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5l)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.21 (t, 6H, $J = 6.0$ Hz), 2.31 (s, 6H), 4.08 (quar, 4H, $J = 6.0$ Hz), 5.35 (s, 1H), 5.67 (s, 1H), 7.11 (d, 1H, $J = 9.0$ Hz), 7.26–7.33 (m, 2H). (Fig. S27)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.26, 19.41, 37.27, 59.80, 103.29, 126.92, 128.79, 132.01, 132.43, 133.07, 144.23, 167.45. (Fig. S28)</p> <p>Mass (ESI): 396.18 (M-1) (Fig. S80)</p>	
<p><u>Diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5m)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.33 (s, 6H), 4.03–4.14 (m, 4H), 4.94 (s, 1H), 5.61 (s, 1H), 7.16 (d, 2H, $J = 9.0$ Hz), 7.32 (d, 2H, $J = 9.0$ Hz). (Fig. S29)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.17, 19.32, 39.20, 59.74, 103.45, 119.73, 129.69, 130.76, 144.25, 146.78, 167.44. (Fig. S30)</p> <p>Mass (ESI): 406.33 (M-1) (Fig. S81)</p>	
<p><u>Diethyl 4-(2-chloro-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5n)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.20 (t, 6H, $J = 6.0$ Hz), 2.30 (s, 6H), 3.86 (s, 3H), 4.01–4.13 (m, 4H), 5.48 (s, 1H), 5.65 (s, 1H), 6.71 (dd, 1H, $J = 6.0, 3.0$ Hz), 7.01–7.11 (m, 2H). (Fig. S31)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.14, 18.94, 37.33, 56.02, 59.57, 103.25, 109.32, 120.89, 123.12, 126.51, 144.22, 147.07, 154.30,</p>	

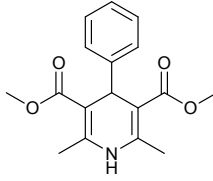
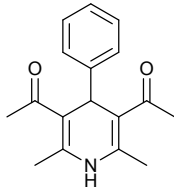
<p>167.78. (Fig. S32)</p> <p>Mass (ESI): 392.18 (M-1) (Fig. S82)</p> <p>HRMS: Calculated for C₂₀H₂₄ClNO₅+Na: 416.1235,</p> <p>Observed: 416.1260 (Fig. S103)</p>	
<p><u>3-(3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)benzoic acid (5o)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.22 (t, 6H, <i>J</i> = 6.0 Hz), 2.36 (s, 6H), 4.00–4.16 (m, 4H), 5.05 (s, 1H), 5.75 (s, 1H), 7.32 (t, 1H, <i>J</i> = 6.0 Hz), 7.56 (d, 1H, <i>J</i> = 9.0 Hz), 7.89 (d, 1H, <i>J</i> = 6.0 Hz), 8.02 (s, 1H). (Fig. S33)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 14.60, 19.88, 40.20, 60.29, 104.05, 128.34, 128.48, 129.35, 130.33, 134.18, 144.96, 148.87, 167.92, 172.48. (Fig. S34)</p> <p>Mass (ESI): 372.16 (M-1) (Fig. S83)</p>	
<p><u>4-(3,5-Bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)phenylboronic acid (5p)</u></p> <p>¹H NMR (300 MHz, DMSO) δ: 1.14 (t, 6H, <i>J</i> = 6.0 Hz), 2.26 (s, 6H), 3.98 (quar, 4H, <i>J</i> = 6.0 Hz), 4.86 (s, 1H), 7.11 (d, 2H, <i>J</i> = 9.0 Hz), 7.61 (d, 2H, <i>J</i> = 6.0 Hz), 8.81 (s, 1H). (Fig. S35)</p> <p>¹³C NMR (75 MHz, DMSO) δ: 14.54, 18.61, 39.38, 59.37, 102.18, 126.89, 132.02, 134.16, 145.72, 150.38, 167.36. (Fig. S36)</p> <p>Mass (ESI): 372.15 (M-1) (Fig. S84)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (5q)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 1.22 (t, 6H, <i>J</i> = 6.0 Hz), 2.36 (s, 6H), 4.06–4.12 (m, 4H), 5.09 (s, 1H), 5.70 (s, 1H), 7.45 (d, 2H, <i>J</i> = 9.0 Hz), 8.09 (d, 2H, <i>J</i> = 9.0 Hz). (Fig. S37)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 14.23, 19.53, 40.17, 59.95, 103.23, 123.24, 128.84, 144.59, 146.40, 155.06, 167.02. (Fig. S38)</p> <p>Mass (ESI): 373.27 (M-1) (Fig. S85)</p>	

<p><u>Diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (5r)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.36 (s, 6H), 4.01–4.17 (m, 4H), 5.09 (s, 1H), 5.93 (s, 1H), 7.38 (t, 1H, $J = 9.0$ Hz), 7.65 (d, 1H, $J = 6.0$ Hz), 8.01 (d, 1H, $J = 6.0$ Hz), 8.13 (s, 1H). (Fig. S39)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.07, 19.16, 39.78, 59.84, 102.80, 121.12, 122.89, 128.49, 134.39, 145.15, 147.91, 149.91, 167.17. (Fig. S40)</p> <p>Mass (ESI): 373.13 (M-1) (Fig. S86)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate (5s)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.37 (s, 6H), 4.03–4.14 (m, 4H), 5.09 (s, 1H), 5.79 (s, 1H), 7.38 (t, 1H, $J = 9.0$ Hz), 7.65 (dd, 1H, $J = 3.0, 6.0$ Hz), 8.01 (dd, 1H, $J = 6.0, 3.0$ Hz), 8.13 (s, 1H). (Fig. S41)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.18, 19.51, 39.91, 59.94, 103.20, 121.26, 123.05, 128.54, 134.47, 144.78, 148.07, 149.89, 167.10. (Fig. S42)</p> <p>Mass (ESI): 373.15 (M-1) (Fig. S87)</p>	
<p><u>Diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5t)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.21 (t, 6H, $J = 6.0$ Hz), 2.35 (s, 6H), 4.03–4.16 (m, 4H), 5.03 (s, 1H), 5.80 (s, 1H), 7.40 (d, 2H, $J = 9.0$ Hz), 7.51 (d, 2H, $J = 9.0$ Hz). (Fig. S43)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.08, 19.10, 40.06, 59.75, 102.62, 109.28, 119.17, 128.69, 131.62, 145.03, 153.17, 167.15. (Fig. S44)</p> <p>Mass (ESI): 353.26 (M-1) (Fig. S88)</p>	
<p><u>Diethyl 4-(3-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5u)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.22 (t, 6H, $J = 6.0$ Hz), 2.35 (s,</p>	

<p>6H), 4.04–4.15 (m, 4H), 5.00 (s, 1H), 5.80 (s, 1H), 7.27–7.35 (m, 1H), 7.43 (d, 1H, $J = 6.0$ Hz), 7.55 (d, 2H, $J = 6.0$ Hz). (Fig. S45)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.25, 19.65, 39.79, 59.93, 103.40, 111.80, 128.47, 129.83, 131.90, 132.81, 144.45, 149.17, 167.07. (Fig. S46)</p> <p>Mass (ESI): 353.24 (M-1) (Fig. S89)</p>	
<p><u>Diethyl 2',6'-dimethyl-1',4'-dihydro-[2,4'-bipyridine]-3',5'-dicarboxylate (5v)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.20 (t, 6H, $J = 6.0$ Hz), 2.27 (s, 6H), 4.06 (quar, 4H, $J = 6.0$ Hz), 5.17 (s, 1H), 7.08–7.15 (m, 1H), 7.37 (d, 1H, $J = 9.0$ Hz), 7.53–7.61 (m, 1H), 8.09 (s, 1H), 8.49 (d, 1H, $J = 3.0$ Hz). (Fig. S47)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.13, 18.37, 42.76, 59.32, 101.32, 121.74, 124.39, 135.57, 146.62, 147.81, 165.14, 167.60. (Fig. S48)</p> <p>Mass (ESI): 329.13 (M-1) (Fig. S90)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(quinolin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (5w)</u></p> <p>^1H NMR (300 MHz, DMSO) δ: 1.11 (t, 6H, $J = 6.0$ Hz), 2.28 (s, 6H), 3.93–4.04 (m, 4H), 5.21 (s, 1H), 7.38 (d, 1H, $J = 6.0$ Hz), 7.51 (dd, 1H, $J = 6.0, 3.0$ Hz), 7.63–7.69 (m, 1H), 7.82 (d, 1H, $J = 6.0$ Hz), 7.87 (d, 1H, $J = 9.0$ Hz), 8.18 (d, 1H, $J = 9.0$ Hz), 8.86 (s, 1H). (Fig. S49)</p> <p>^{13}C NMR (75 MHz, DMSO) δ: 14.62, 18.76, 42.59, 59.40, 100.89, 121.69, 126.07, 127.07, 127.99, 129.16, 129.38, 135.74, 146.46, 147.74, 166.48, 167.49. (Fig. S50)</p> <p>Mass (ESI): 379.13 (M-1) (Fig. S91)</p> <p>HRMS: Calculated for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_4 + \text{H}$: 381.1809, Observed: 381.1813 (Fig. S104)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(1-methyl-1H-indol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (5x)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.19 (t, 6H, $J = 6.0$ Hz), 2.33 (s,</p>	

<p>6H), 3.68 (s, 3H), 4.00–4.10(m, 4H), 5.32 (s, 1H), 5.76 (s, 1H), 6.85 (s, 1H), 7.01–7.07 (m, 1H), 7.14 (dd, 1H, $J = 6.0, 9.0$ Hz), 7.22 (d, 1H, $J = 9.0$ Hz), 7.68 (d, 1H, $J = 9.0$ Hz). (Fig. S51)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.27, 19.51, 30.78, 32.58, 59.62, 104.26, 108.87, 118.41, 120.32, 120.72, 121.72, 126.71, 127.61, 136.67, 142.81, 167.92. (Fig. S52)</p> <p>Mass (ESI): 381.16 (M-1) (Fig. S92)</p> <p>HRMS: Calculated for $\text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_4 + \text{Na}$: 405.1785, Observed: 405.1808 (Fig. S105)</p>	
<p><u>Diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (5y)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.26 (t, 6H, $J = 6.0$ Hz), 2.34 (s, 6H), 4.17 (quar, 4H, $J = 6.0$ Hz), 5.20 (s, 1H), 5.74 (s, 1H), 5.95 (d, 1H, $J = 3.0$ Hz), 6.21 (dd, 1H, $J = 3.0, 3.0$ Hz), 7.22 (s, 1H). (Fig. S53)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.28, 19.42, 33.36, 59.77, 100.61, 104.37, 109.94, 140.78, 145.11, 158.64, 167.46. (Fig. S54)</p> <p>Mass (ESI): 318.16 (M-1) (Fig. S93)</p>	
<p><u>Diethyl 2,6-dimethyl-4-(5-methylfuran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (5z)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.27 (t, 6H, $J = 6.0$ Hz), 2.19 (s, 3H), 2.33 (s, 6H), 4.10–4.24 (m, 4H), 5.13 (s, 1H), 5.69 (s, 1H), 5.78 (s, 2H). (Fig. S55)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 13.65, 14.32, 19.44, 33.43, 59.69, 101.08, 105.01, 105.83, 144.68, 150.21, 157.03, 167.56. (Fig. S56)</p> <p>Mass (ESI): 332.19 (M-1) (Fig. S94)</p>	
<p><u>Diethyl 2,6-dimethyl-4-styryl-1,4-dihydropyridine-3,5-dicarboxylate (5aa)</u></p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.29 (t, 6H, $J = 7.0$ Hz), 2.32 (s, 6H), 4.20 (quar, 4H, $J = 9.0$ Hz), 4.63 (s, 1H), 5.74 (s, 1H), 6.10–6.26 (m, 2H), 7.16–7.33 (m, 5H). (Fig. S57)</p>	

<p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.36, 19.36, 36.43, 59.70, 101.27, 126.12, 126.77, 127.95, 128.27, 131.73, 137.69, 144.99, 167.59. (Fig. S58)</p> <p>Mass (ESI): 354.12 (M-1) (Fig. S95)</p>	
<p><u>Diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate</u> (5ab)</p> <p>^1H NMR (300 MHz, CDCl_3) δ: 1.29 (t, 6H, $J = 6.0$ Hz), 2.19 (s, 6H), 3.26 (s, 2H), 4.17 (quar, 4H, $J = 6.0$ Hz), 5.17 (s, 1H). (Fig. S59)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.24, 24.86, 61.38, 123.13, 140.96, 162.16, 165.95. (Fig. S60)</p> <p>Mass (ESI): 252.21 (M-1) (Fig. S96)</p>	
<p><u>Diethyl 4-ethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate</u> (5ac)</p> <p>^1H NMR (300 MHz, CDCl_3) δ: 0.75 (t, 3H, $J = 6.0$ Hz), 1.29 (t, 6H, $J = 6.0$ Hz), 1.34–1.38 (m, 2H), 2.29 (s, 6H), 3.91 (t, 1H, $J = 6.0$ Hz), 4.12–4.25 (m, 4H), 5.60 (s, 1H). (Fig. S61)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 9.05, 14.25, 19.07, 29.14, 33.87, 59.41, 102.17, 145.24, 168.25. (Fig. S62)</p> <p>Mass (ESI): 280.16 (M-1) (Fig. S97)</p>	
<p><u>Diethyl 4-isobutyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate</u> (5ad)</p> <p>^1H NMR (300 MHz, CDCl_3) δ: 0.88 (d, 6H, $J = 6.0$ Hz), 1.09–1.14 (m, 2H), 1.30 (t, 6H, $J = 6.0$ Hz), 1.41 (d, 1H, $J = 6.0$ Hz), 2.30 (s, 6H), 3.95 (t, 1H, $J = 6.0$ Hz), 4.13–4.25 (m, 4H), 5.68 (s, 1H). (Fig. S63)</p> <p>^{13}C NMR (75 MHz, CDCl_3) δ: 14.71, 19.76, 23.40, 24.13, 31.03, 47.38, 60.01, 104.43, 145.10, 168.61. (Fig. S64)</p> <p>Mass (ESI): 308.25.08 (M-1) (Fig. S98)</p>	

<p><u>Dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (5ae)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 2.34 (s, 6H), 3.65 (s, 6H), 5.00 (s, 1H), 5.65 (s, 1H), 7.11–7.28 (m, 5H). (Fig. S65)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 19.84, 39.75, 51.27, 104.32, 126.54, 127.97, 128.38, 144.52, 147.78, 168.41. (Fig. S66)</p> <p>Mass (ESI): 300.19 (M-1) (Fig. S99)</p>	
<p><u>1,1'-(2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone (5af)</u></p> <p>¹H NMR (300 MHz, CDCl₃) δ: 2.27 (s, 6H), 2.33 (s, 6H), 5.11 (s, 1H), 5.91 (s, 1H), 7.17–7.26 (m, 5H). (Fig. S67)</p> <p>¹³C NMR (75 MHz, CDCl₃) δ: 20.27, 29.99, 40.21, 113.75, 126.59, 127.39, 128.48, 142.93, 146.03, 197.99. (Fig. S68)</p> <p>Mass (ESI): 268.22 (M-1) (Fig. S100)</p>	

3. NMR Spectra of isolated Compounds from 5a – 5af:

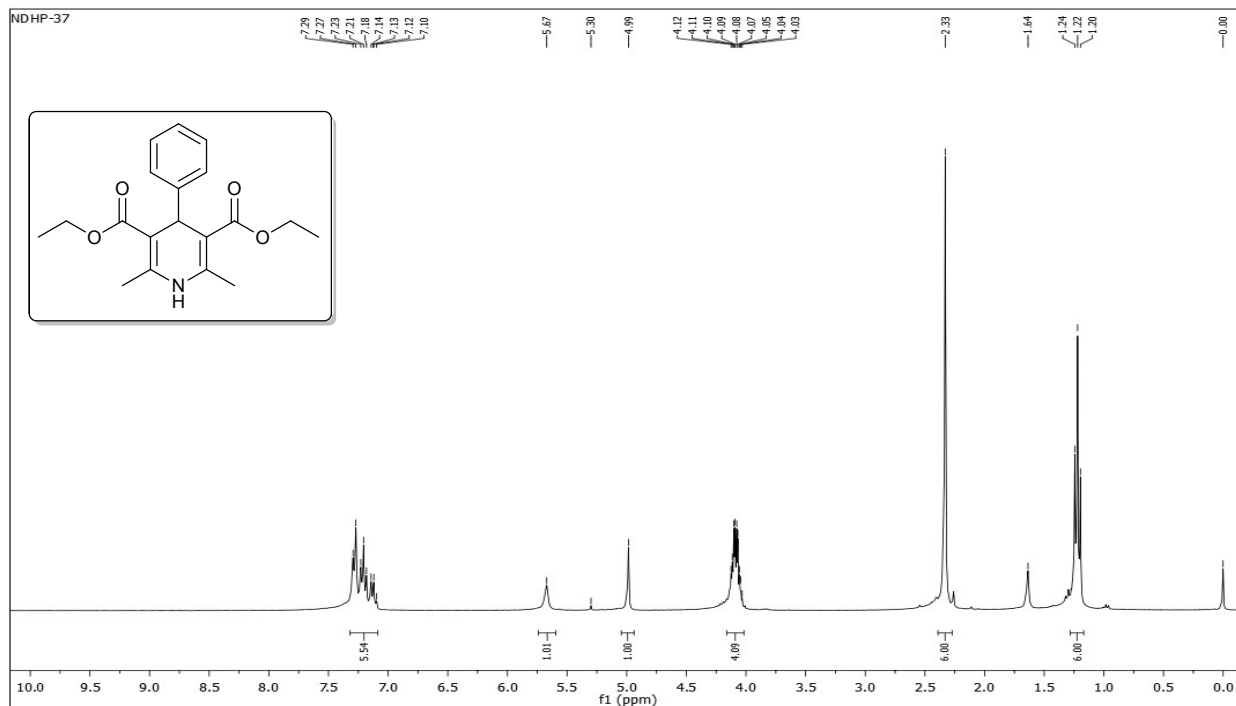


Fig. S5 ¹H NMR spectrum of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5a** (300 MHz, CDCl₃)

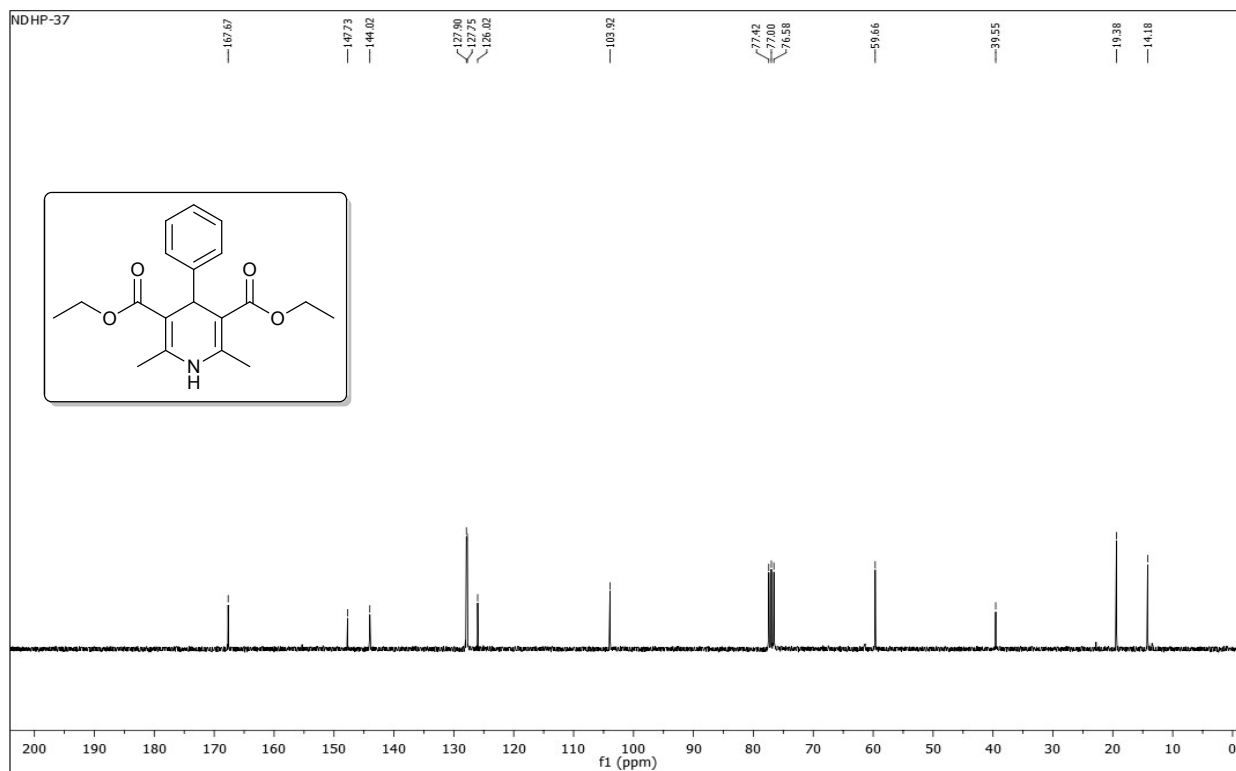


Fig. S6 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5a** (75 MHz, CDCl₃)

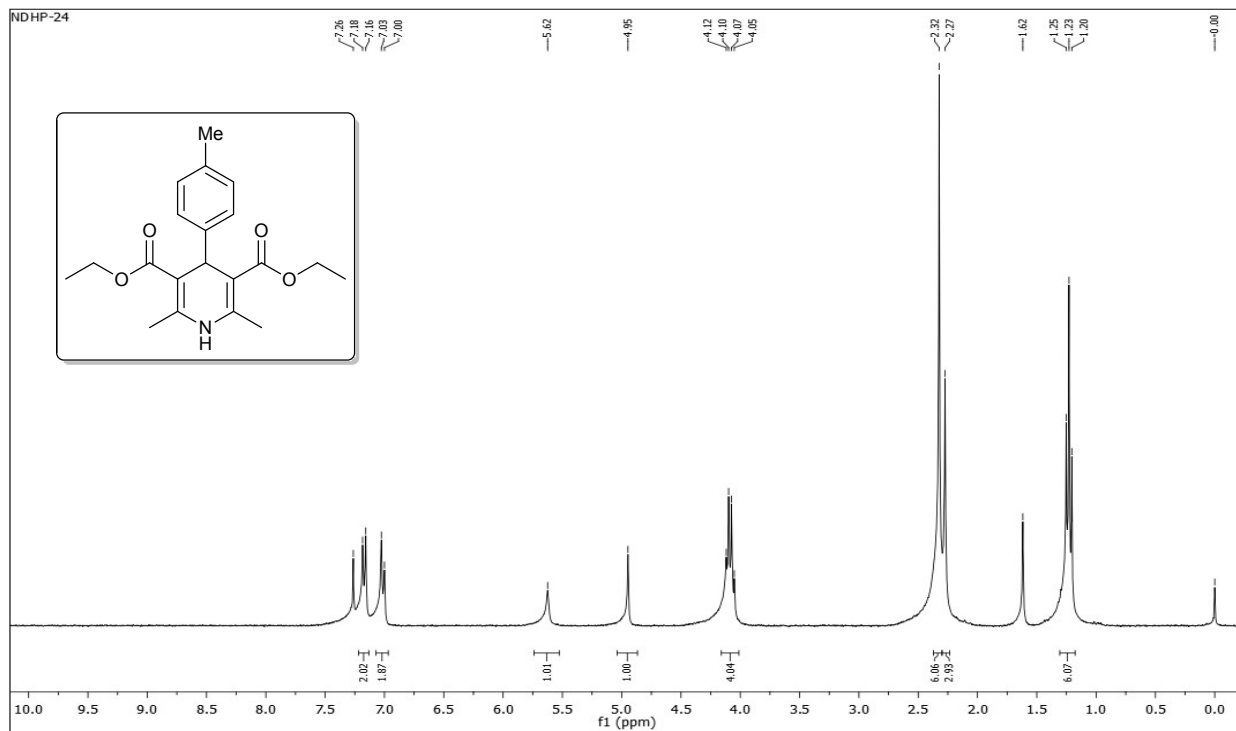


Fig. S7 ¹H NMR spectrum of diethyl 2,6-dimethyl-4-(*p*-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate **5b** (300 MHz, CDCl₃)

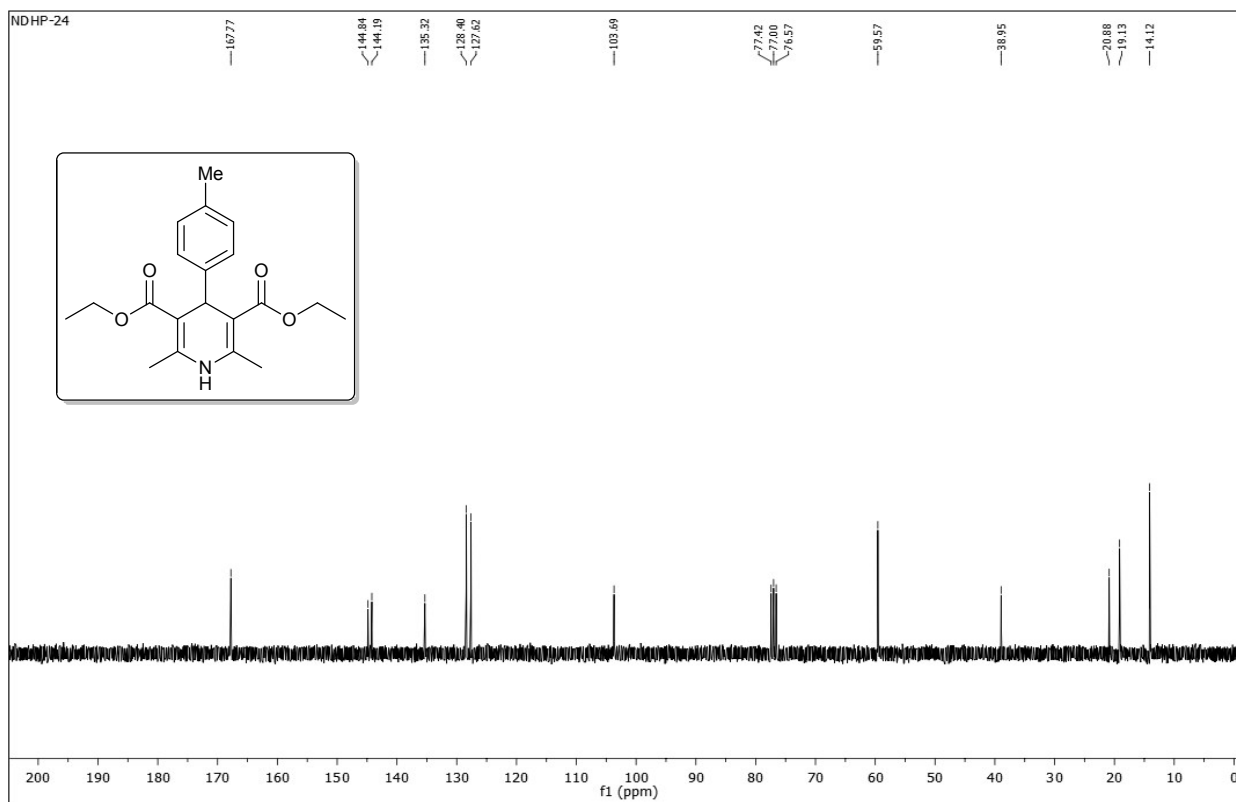


Fig. S8 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-(*p*-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate **5b** (75 MHz, CDCl₃)

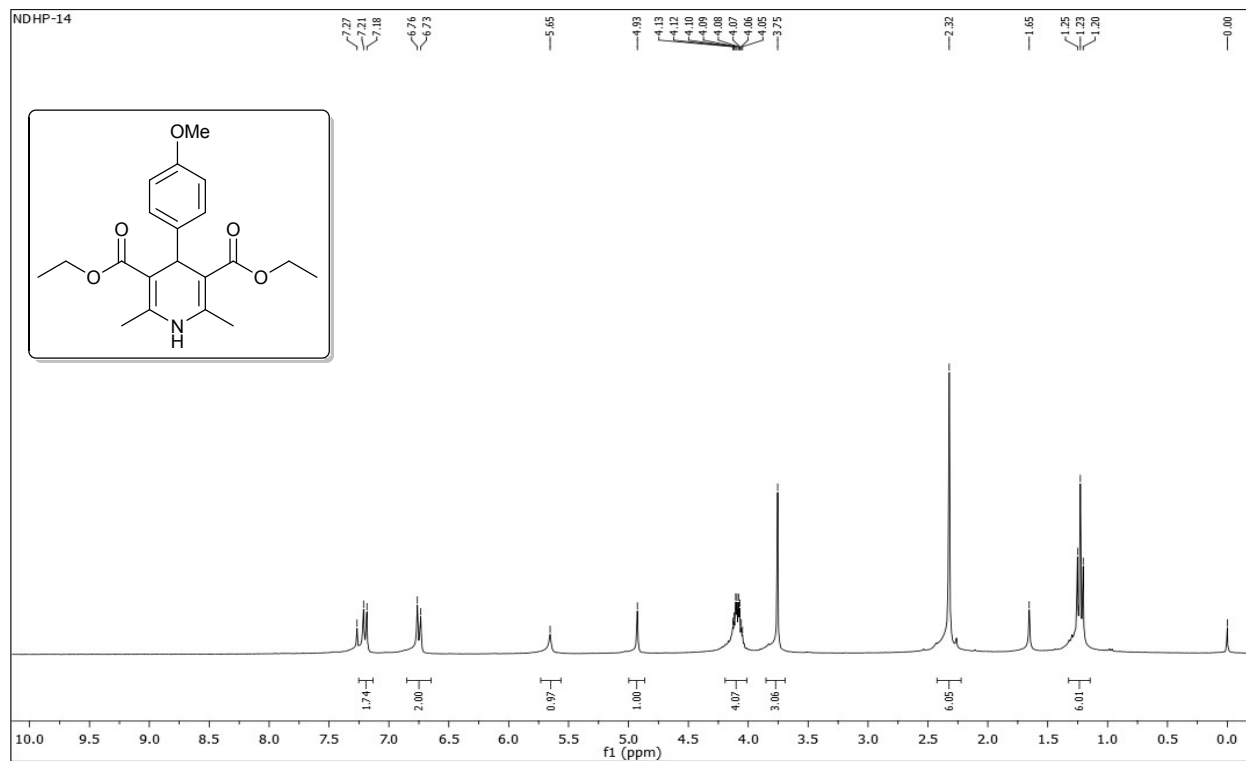


Fig. S9 ¹H NMR spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5c** (300 MHz, CDCl₃)

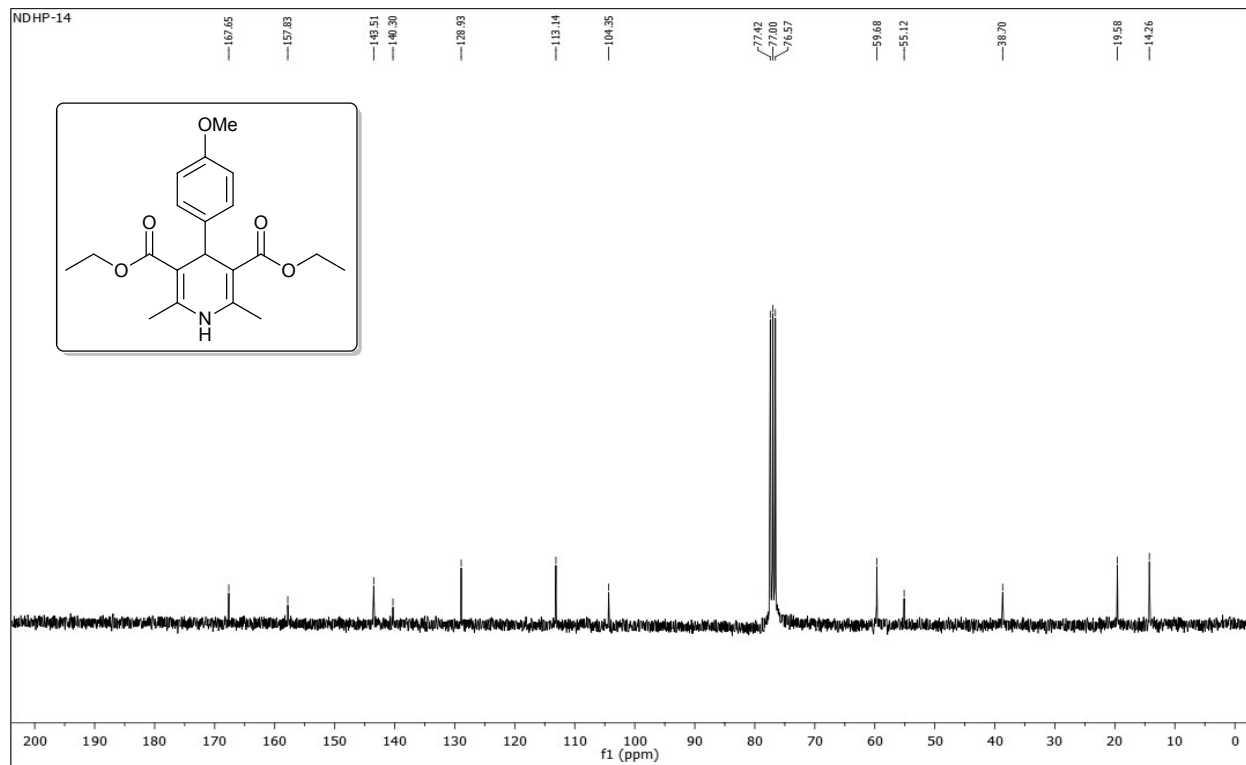


Fig. S10 ¹³C NMR spectrum of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5c** (75 MHz, CDCl₃)

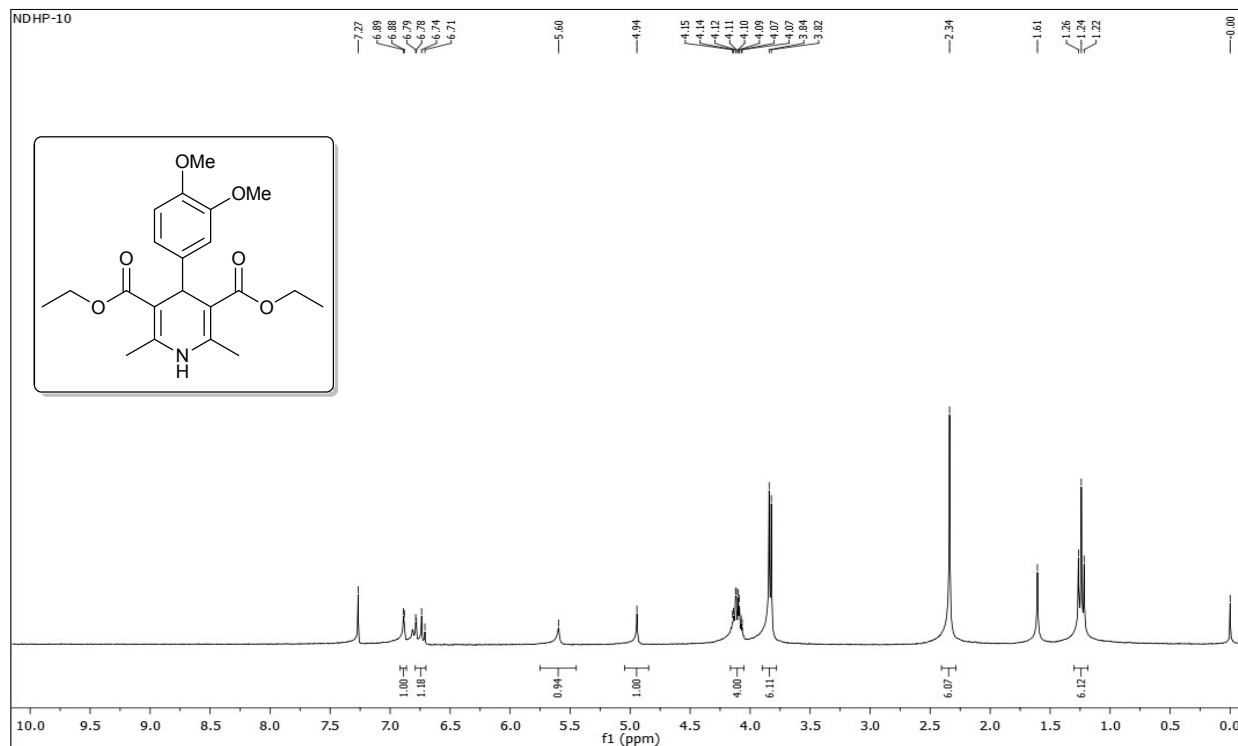


Fig. S11 ¹H NMR spectrum of diethyl 4-(3,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5d** (300 MHz, CDCl₃)

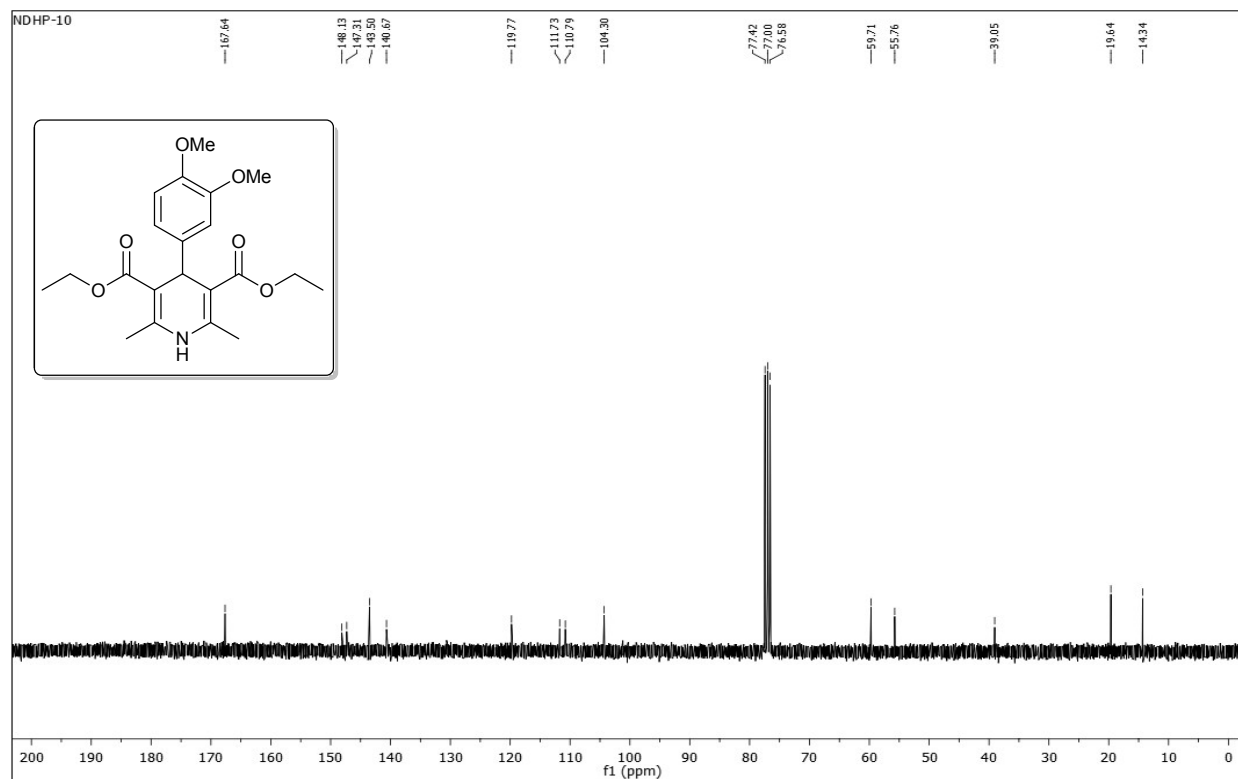


Fig. S12 ¹³C NMR spectrum of diethyl 4-(3,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5d** (75 MHz, CDCl₃)

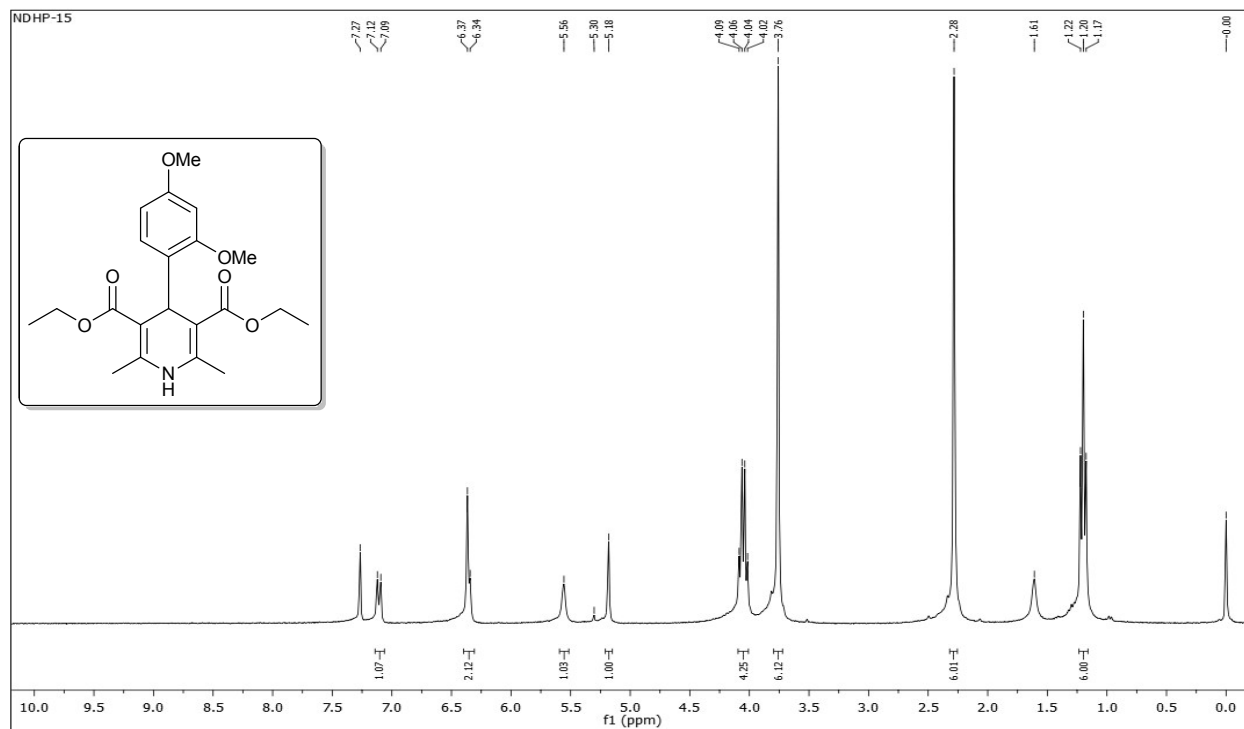


Fig. S13 ¹H NMR spectrum of diethyl 4-(2,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5e** (300 MHz, CDCl₃)

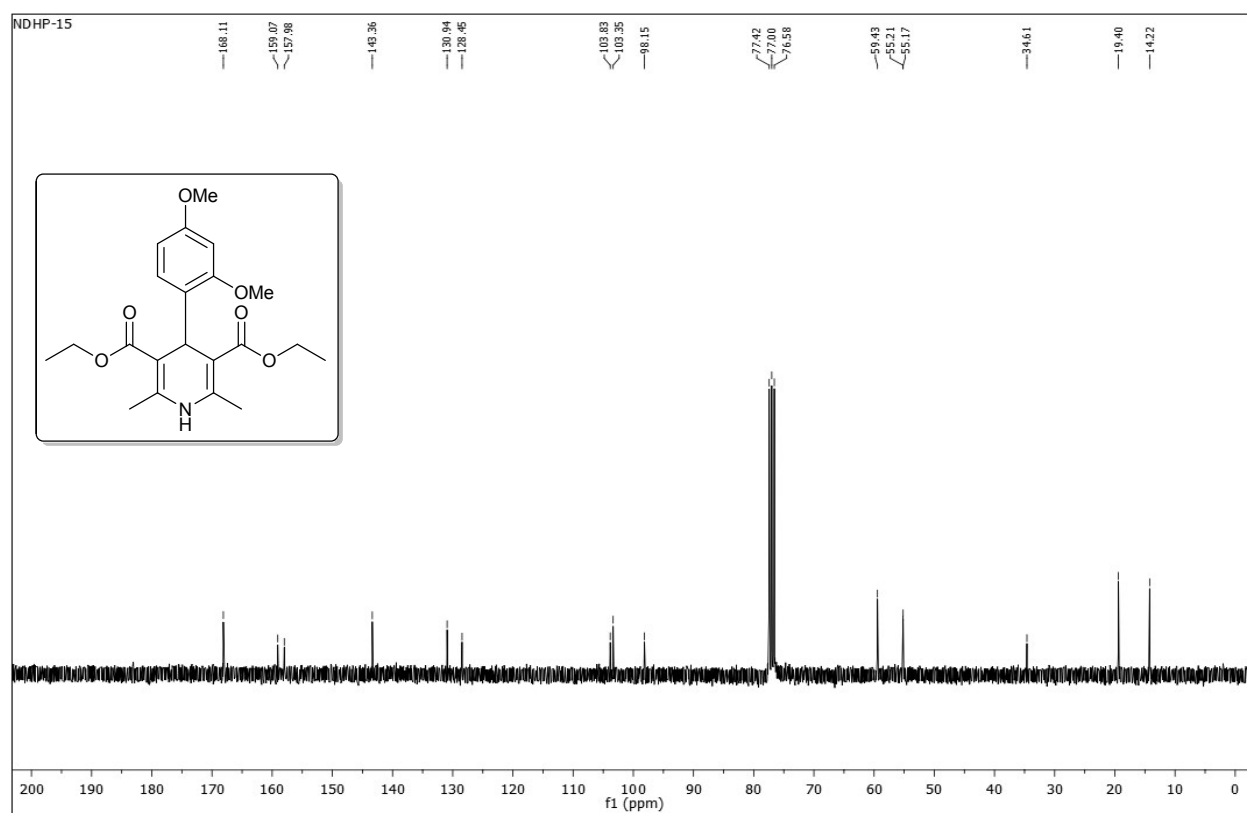


Fig. S14 ¹³C NMR spectrum of diethyl 4-(2,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5e** (75 MHz, CDCl₃)

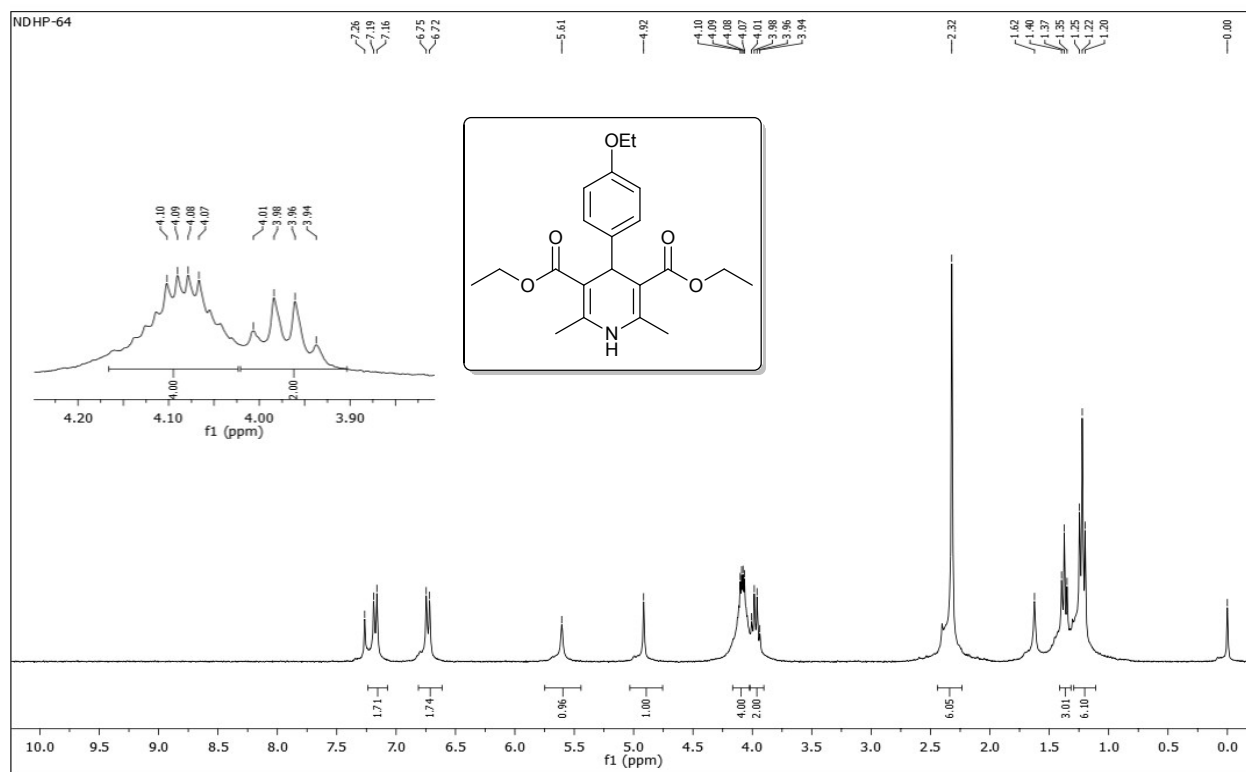


Fig. S15 ¹H NMR spectrum of diethyl 4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5f** (300 MHz, CDCl₃)

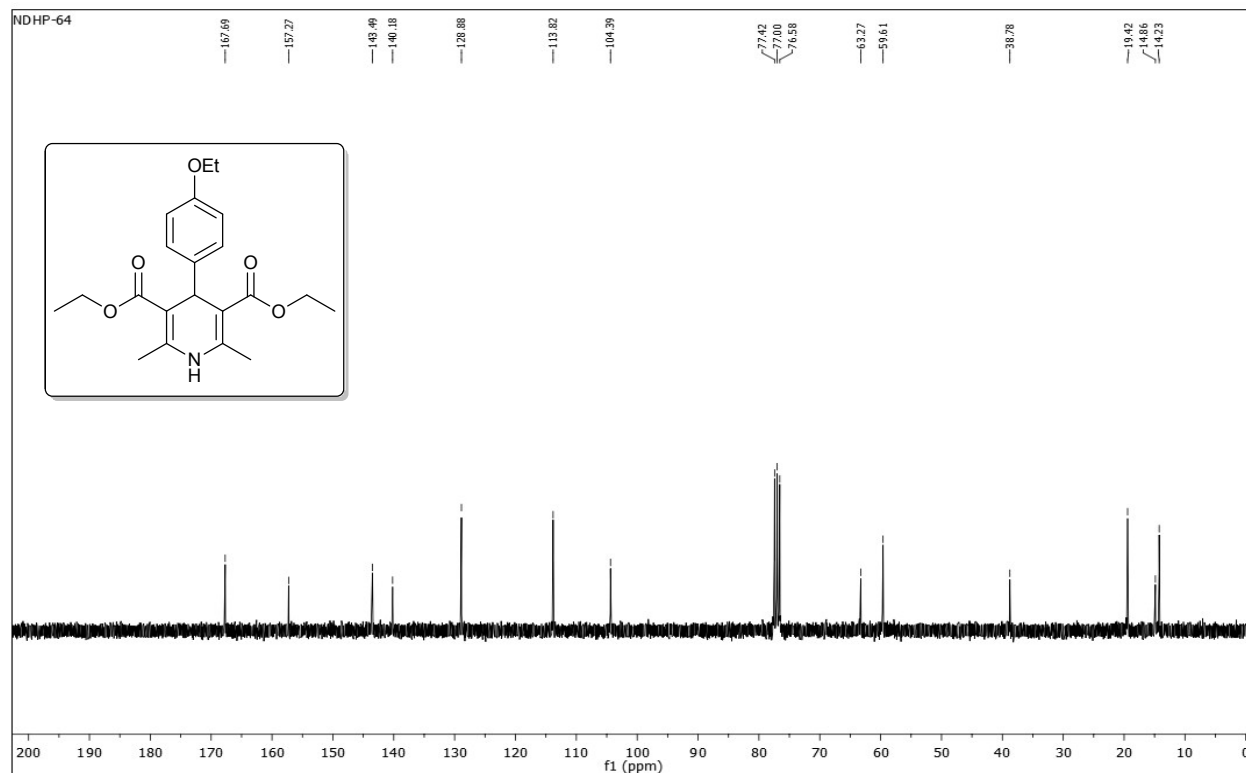


Fig. S16 ¹³C NMR spectrum of diethyl 4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5f** (75 MHz, CDCl₃)

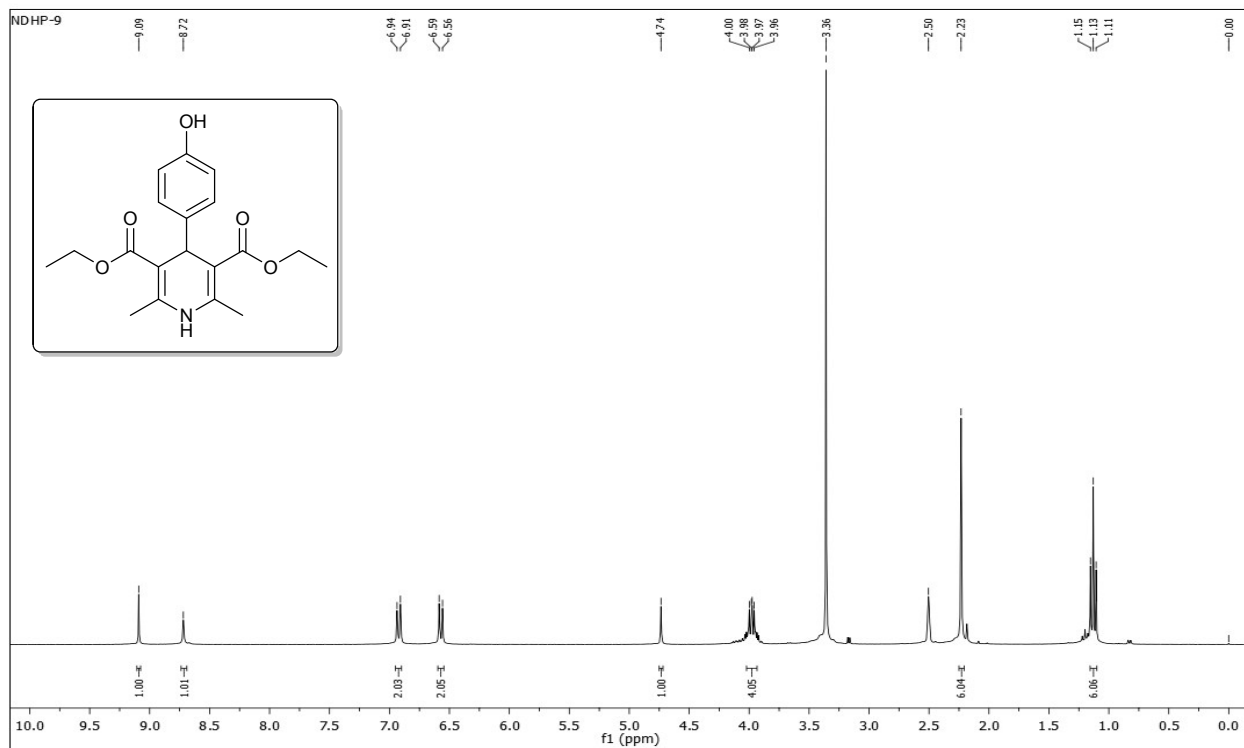


Fig. S17 ^1H NMR spectrum of diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5g** (300 MHz, DMSO)

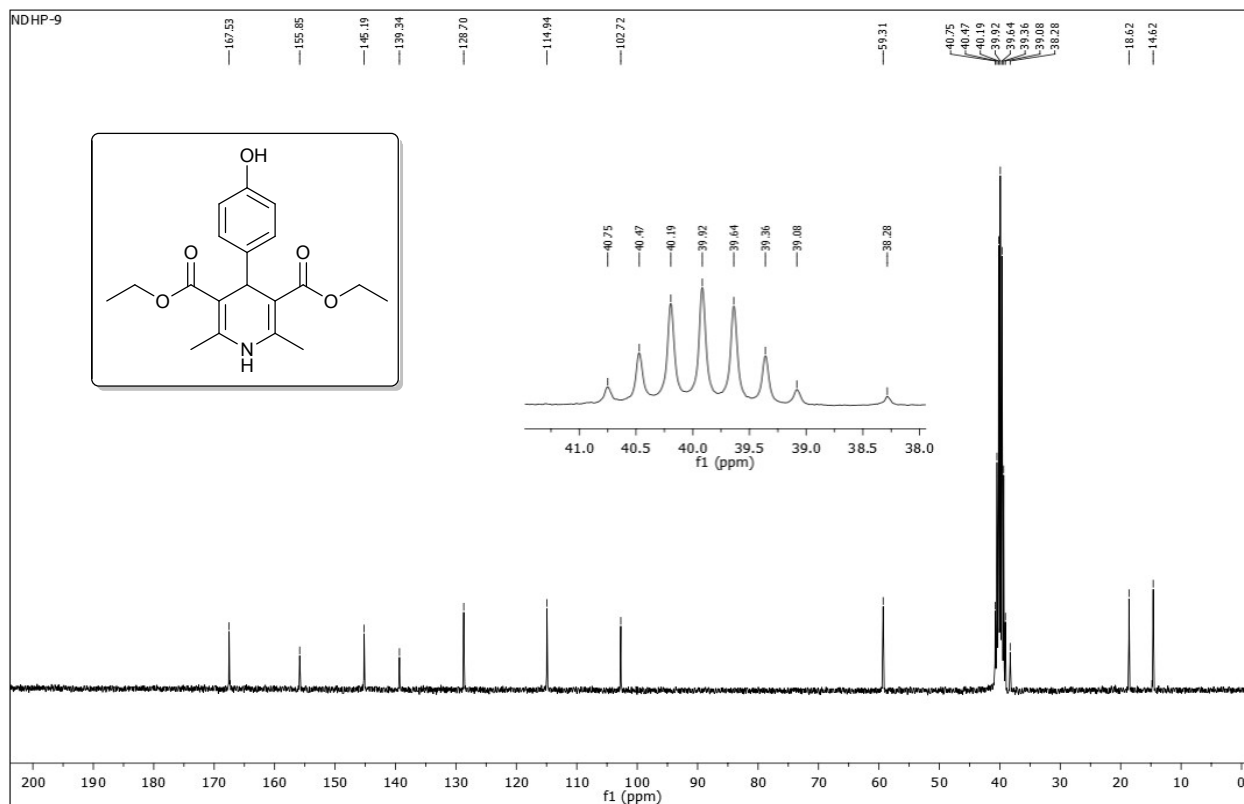


Fig. S18 ^{13}C NMR spectrum of diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5g** (75 MHz, DMSO)

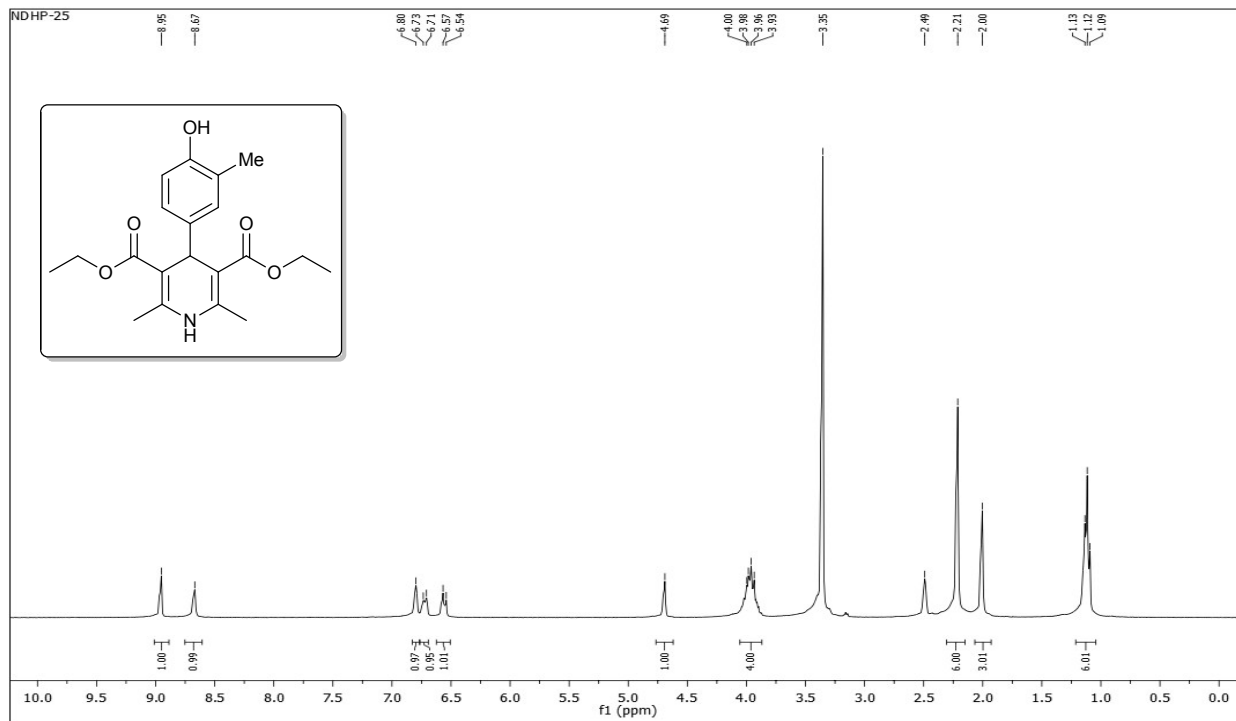


Fig. S19 ¹H NMR spectrum of diethyl 4-(4-hydroxy-3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5h** (300 MHz, DMSO)

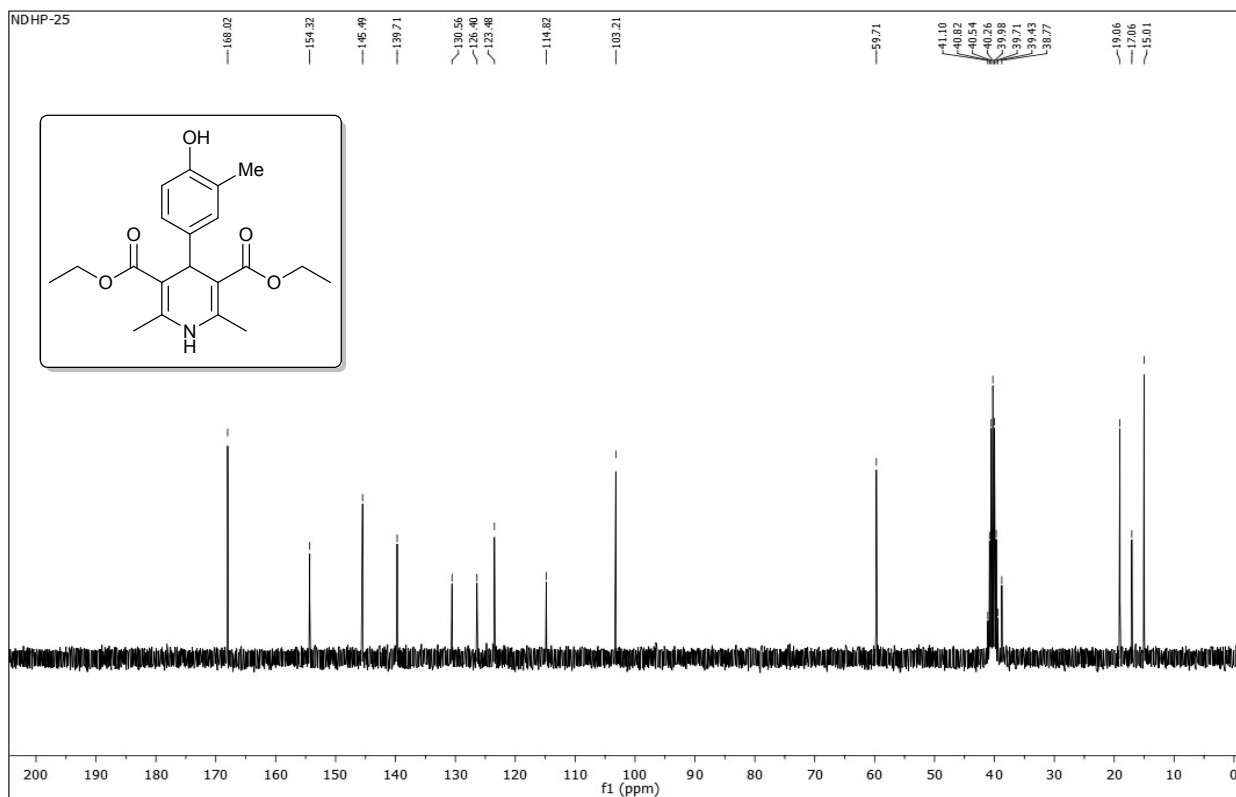


Fig. S20 ¹³C NMR spectrum of diethyl 4-(4-hydroxy-3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5h** (75 MHz, DMSO)

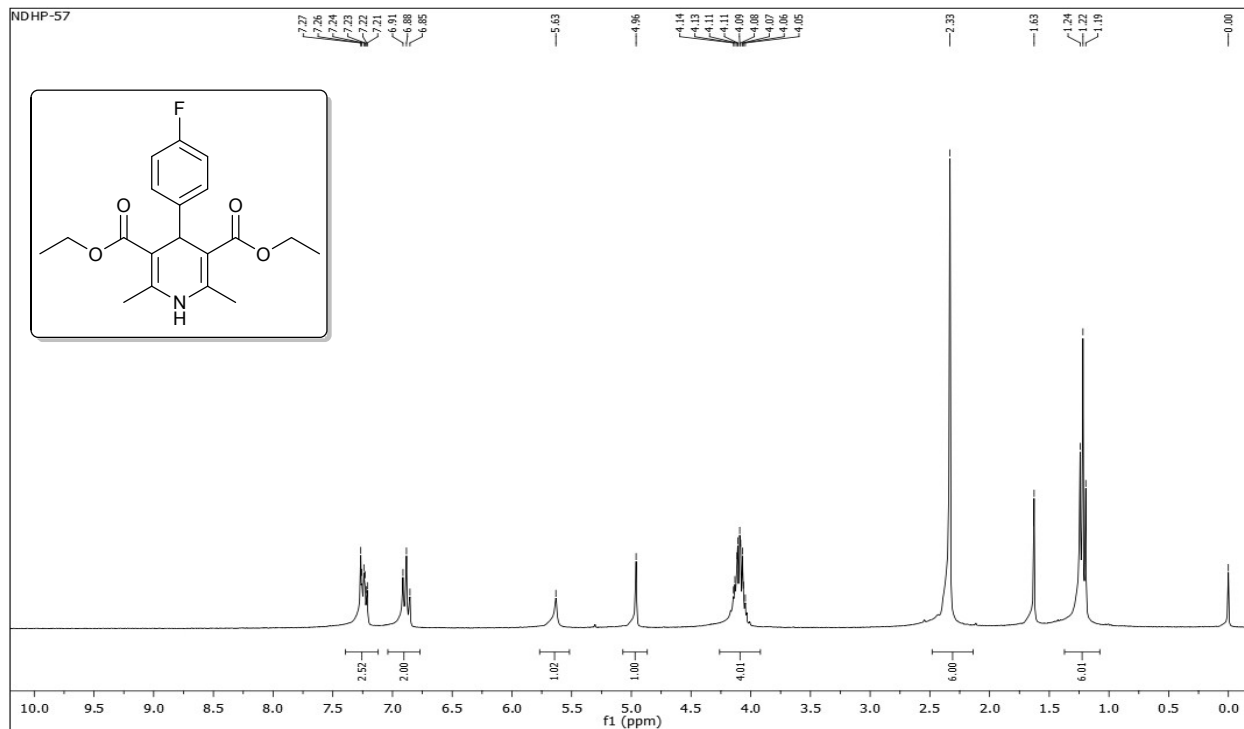


Fig. S21 ¹H NMR spectrum of diethyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5i** (300 MHz, CDCl₃)

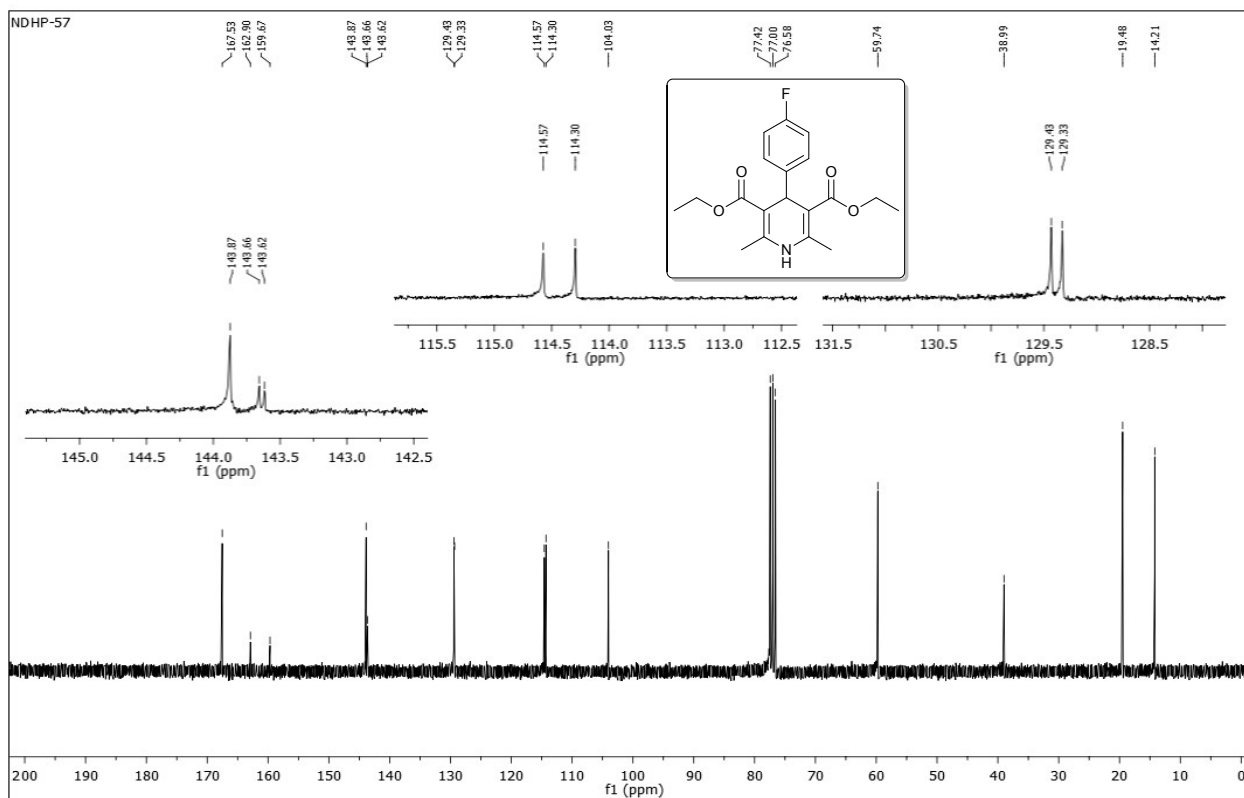


Fig. S22 ¹³C NMR spectrum of diethyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5i** (75 MHz, CDCl₃)

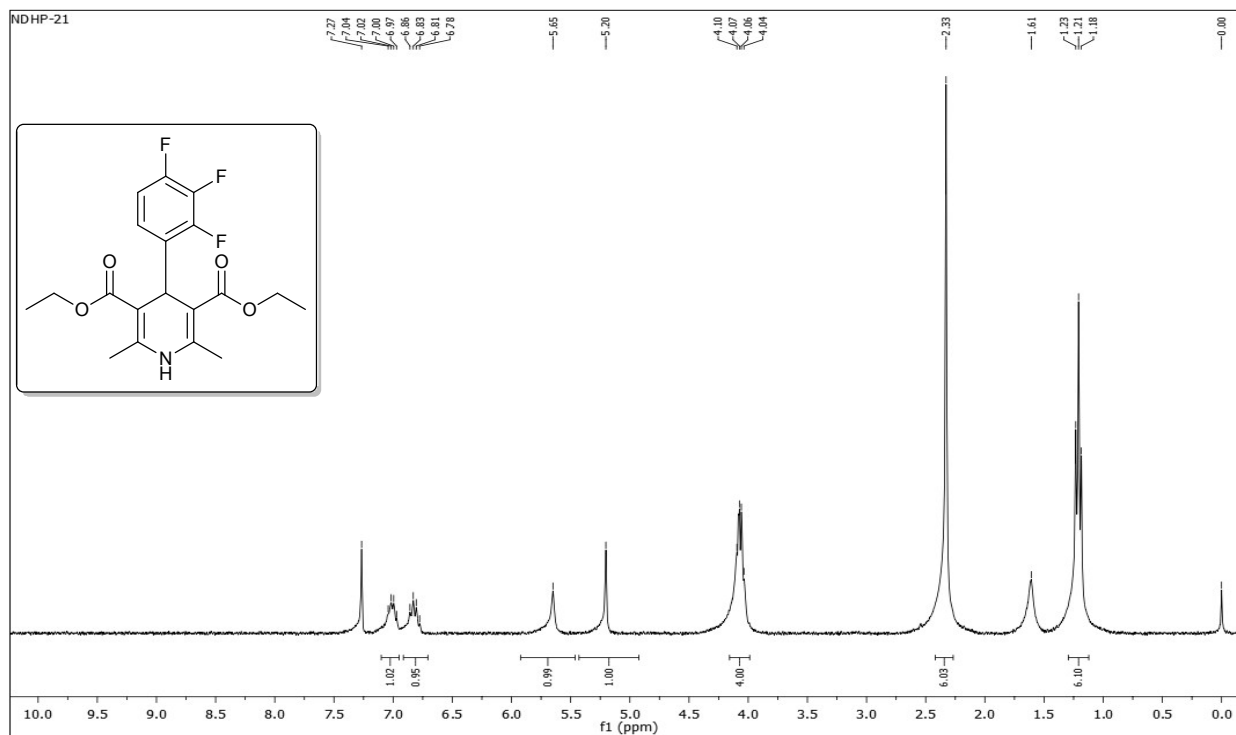


Fig. S23 ¹H NMR spectrum of diethyl 2,6-dimethyl-4-(2,3,4-trifluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5j** (300 MHz, CDCl₃)

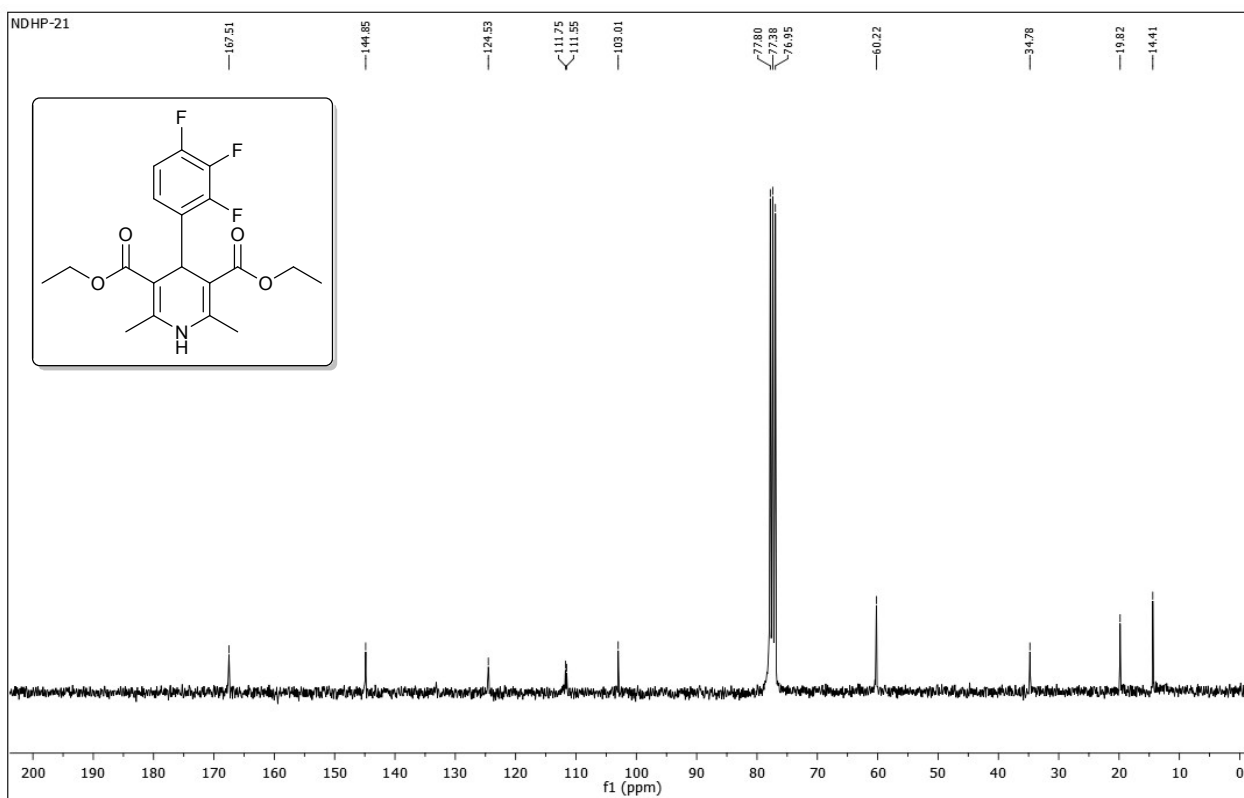


Fig. S24 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-(2,3,4-trifluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5j** (75 MHz, CDCl₃)

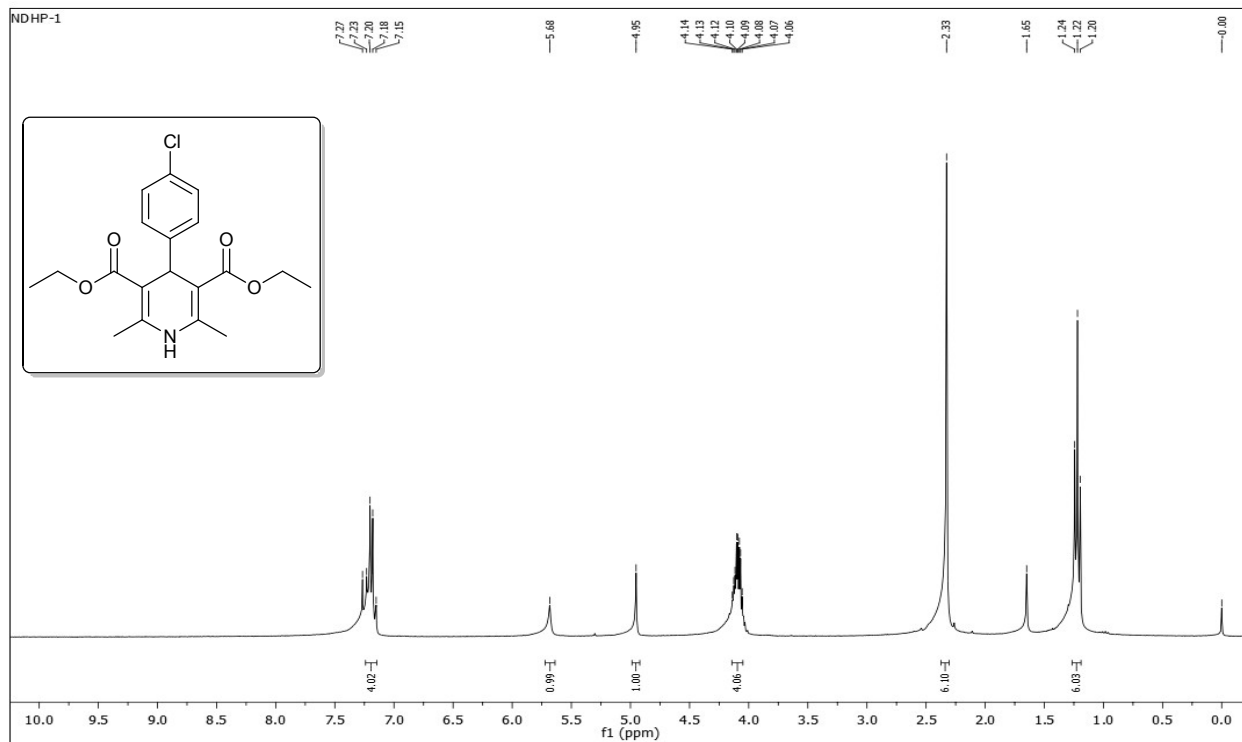


Fig. S25 ^1H NMR spectrum of diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5k** (300 MHz, CDCl_3)

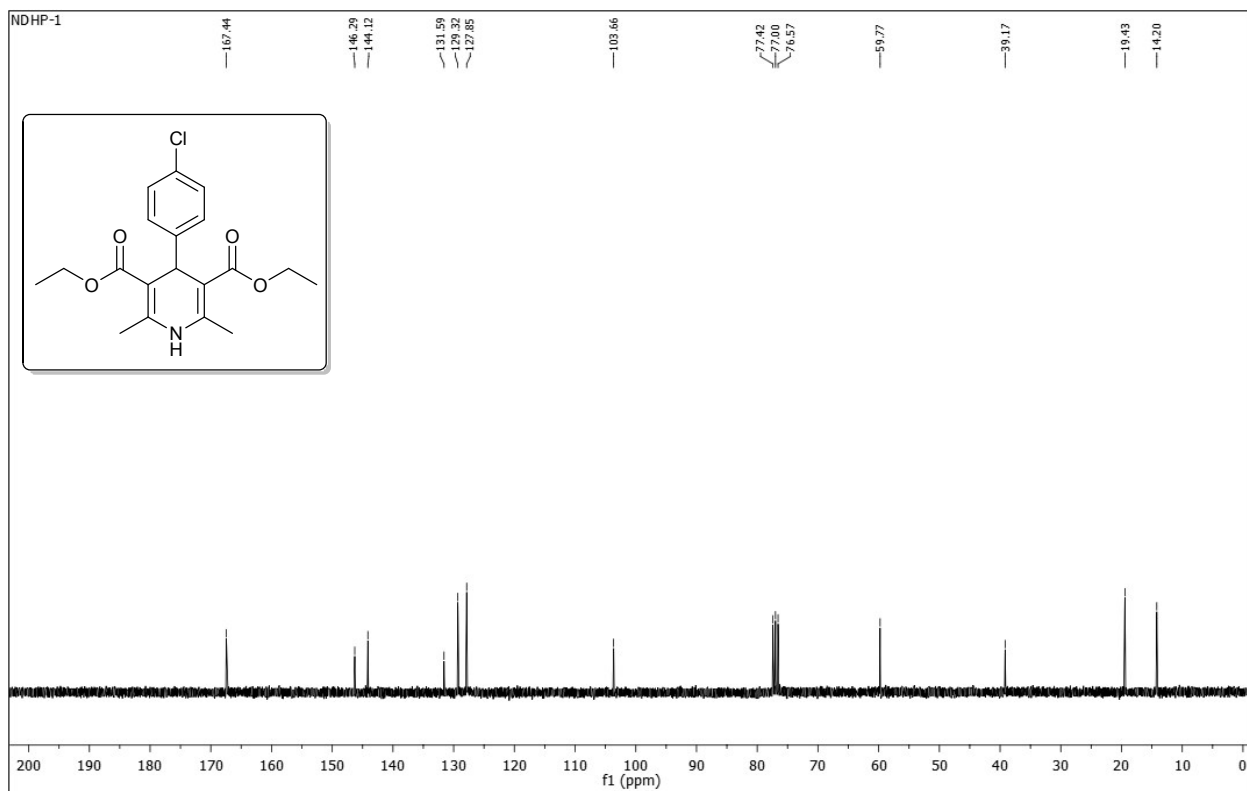


Fig. S26 ^{13}C NMR spectrum of diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5k** (75 MHz, CDCl_3)

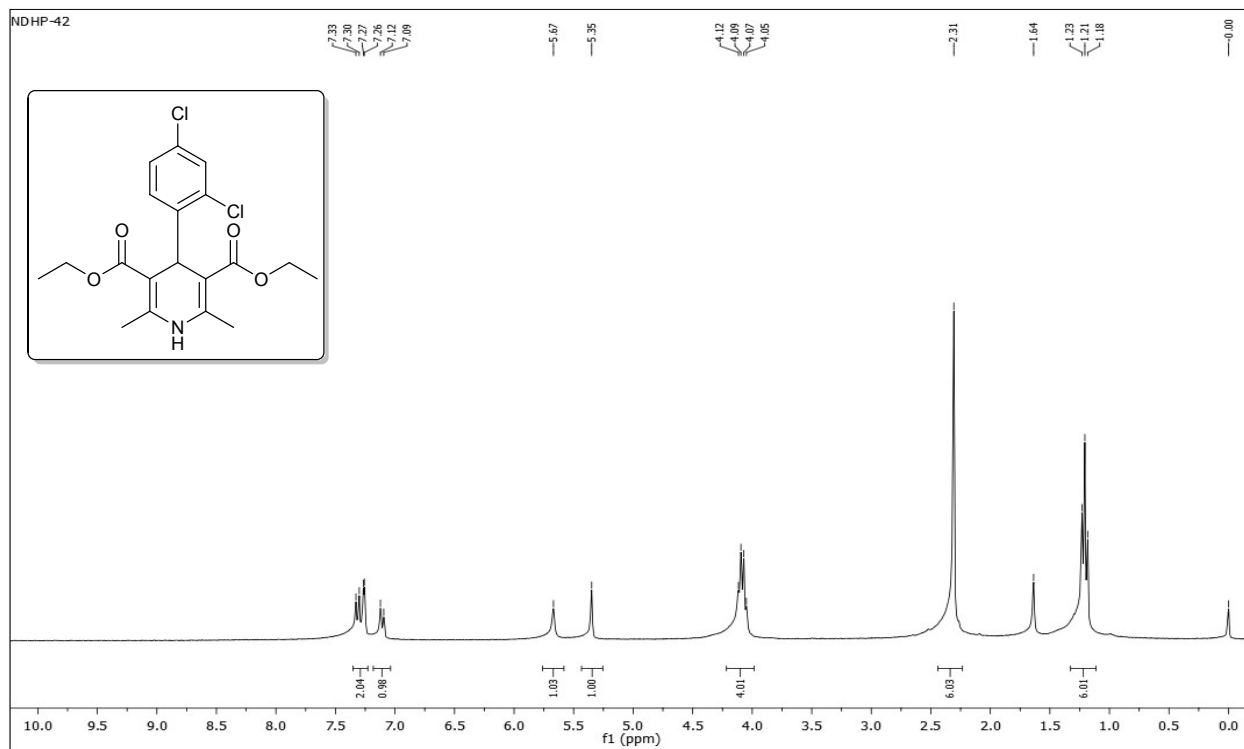


Fig. S27 ^1H NMR spectrum of diethyl 4-(2,4-dichlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5I** (300 MHz, CDCl_3)

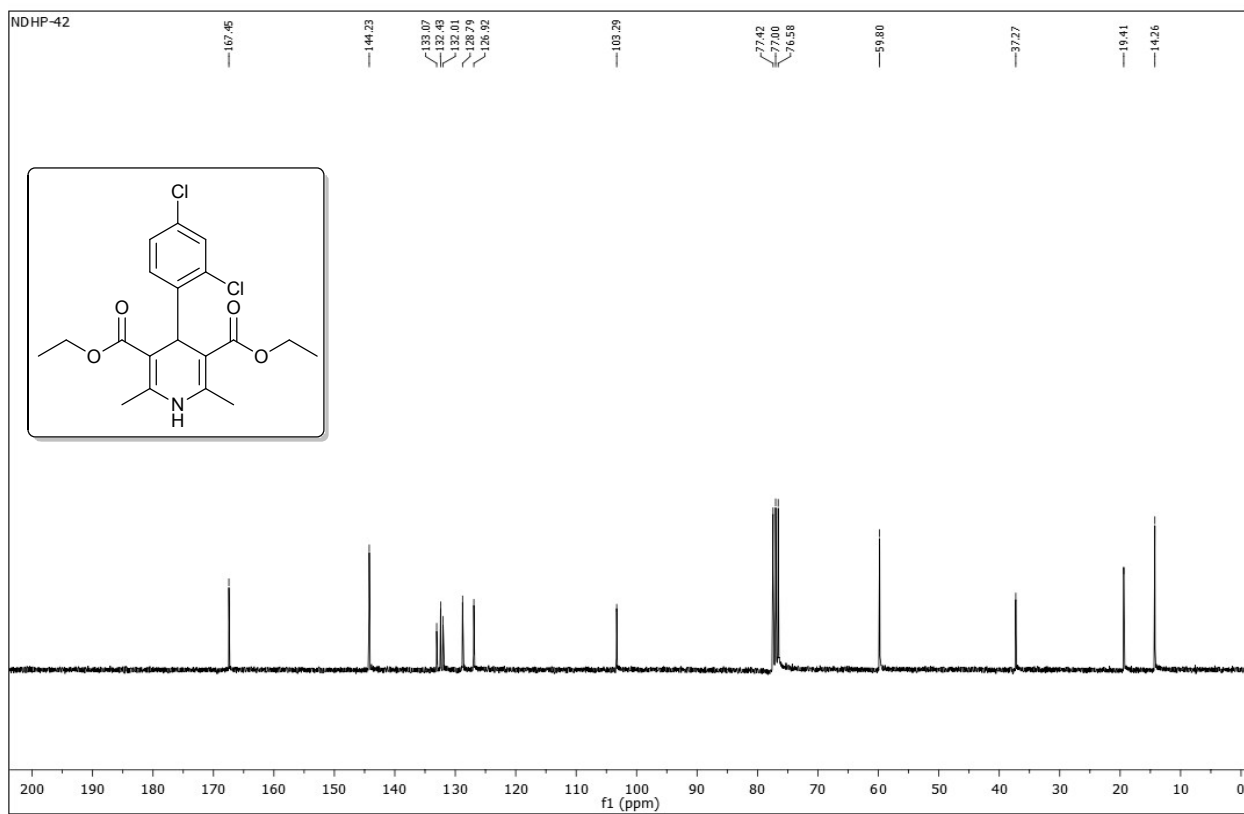


Fig. S28 ^{13}C NMR spectrum of diethyl 4-(2,4-dichlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5I** (75 MHz, CDCl_3)

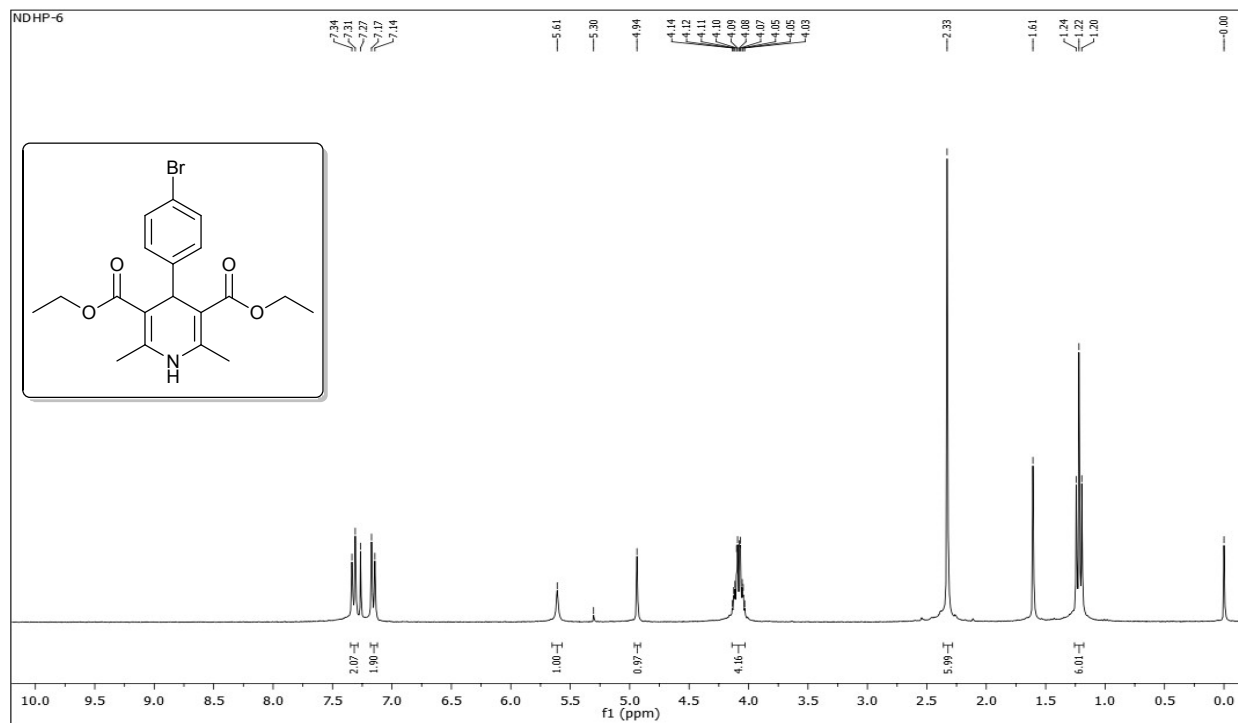


Fig. S29 ¹H NMR spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5m** (300 MHz, CDCl₃)

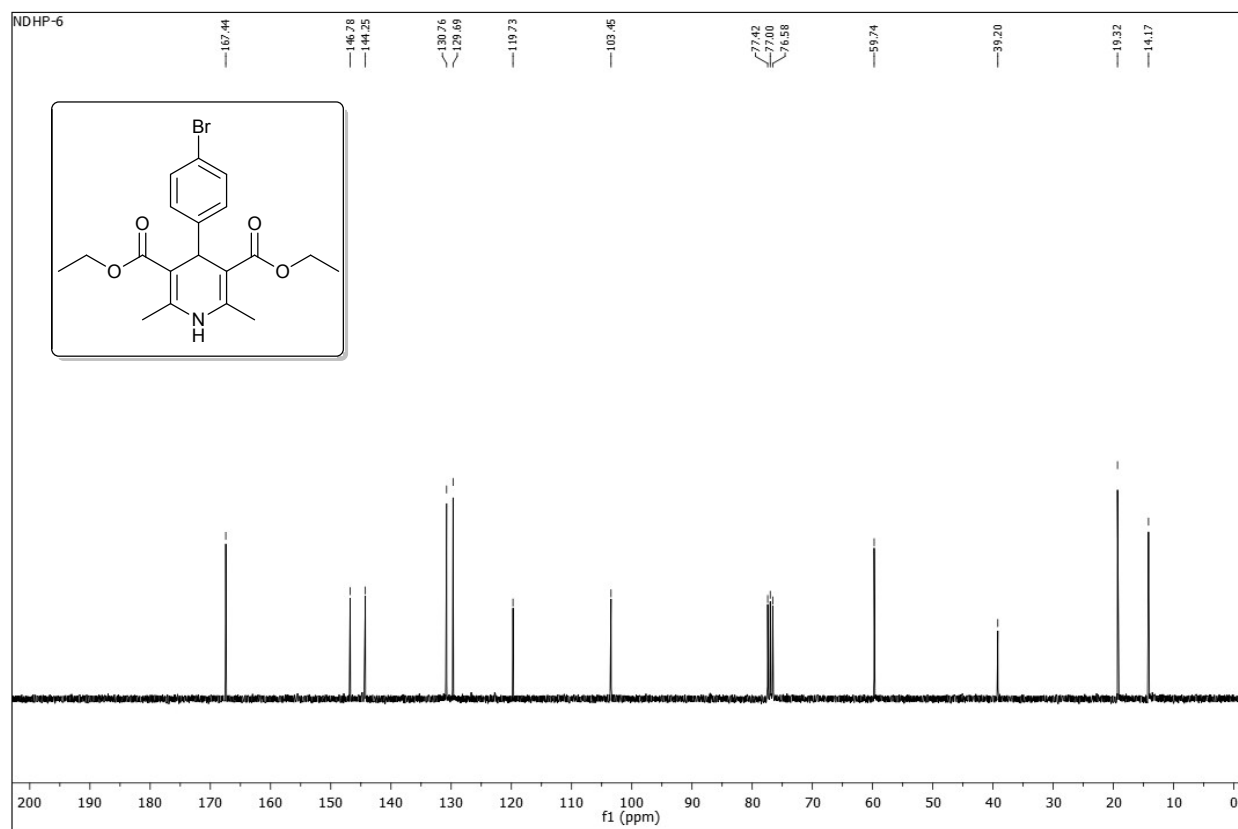


Fig. S30 ¹³C NMR spectrum of diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5m** (75 MHz, CDCl₃)

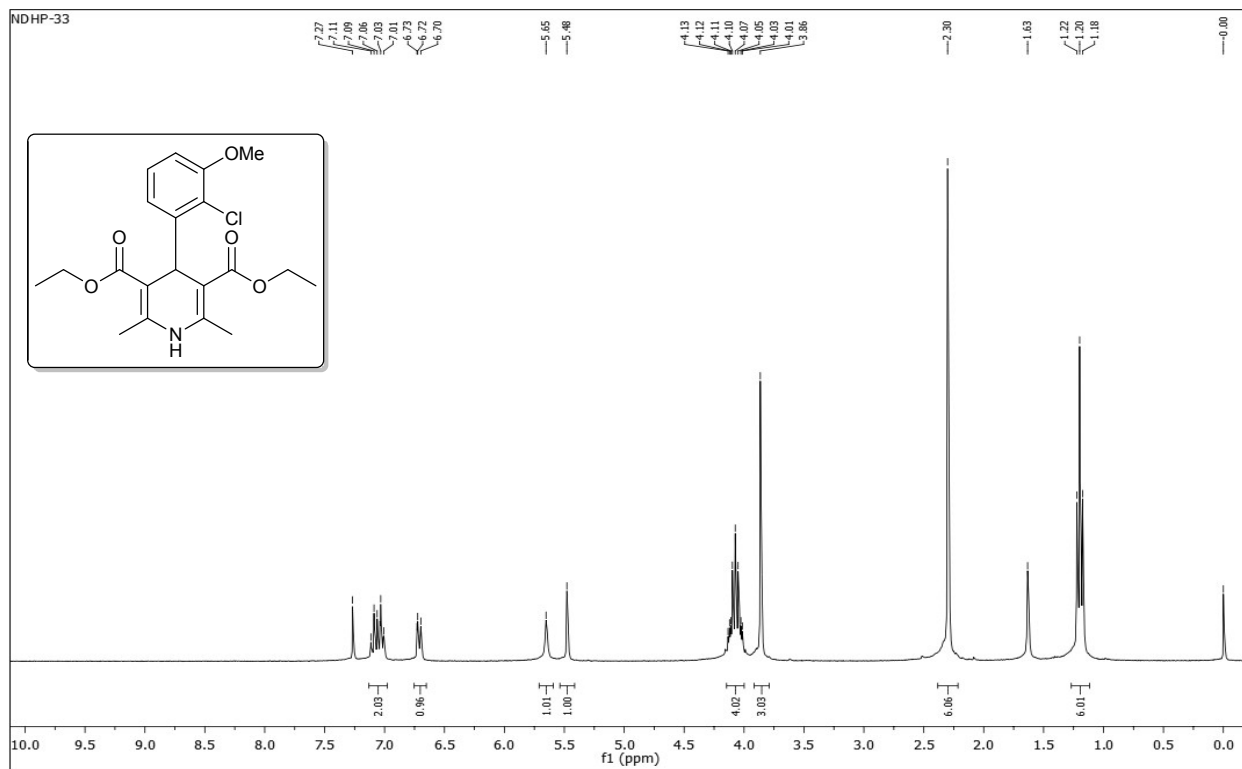


Fig. S31 ^1H NMR spectrum of diethyl 4-(2-chloro-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5n** (300 MHz, CDCl_3)

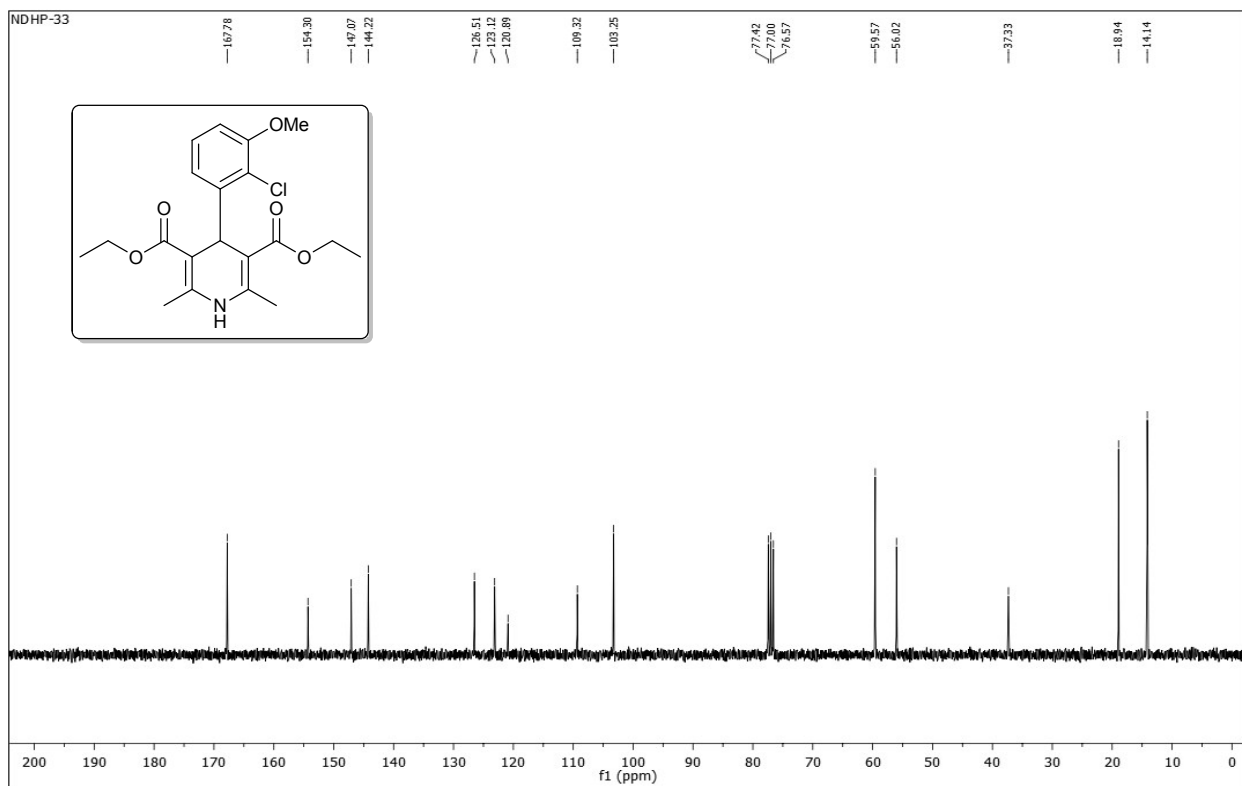


Fig. S32 ^{13}C NMR spectrum of diethyl 4-(2-chloro-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5n** (75 MHz, CDCl_3)

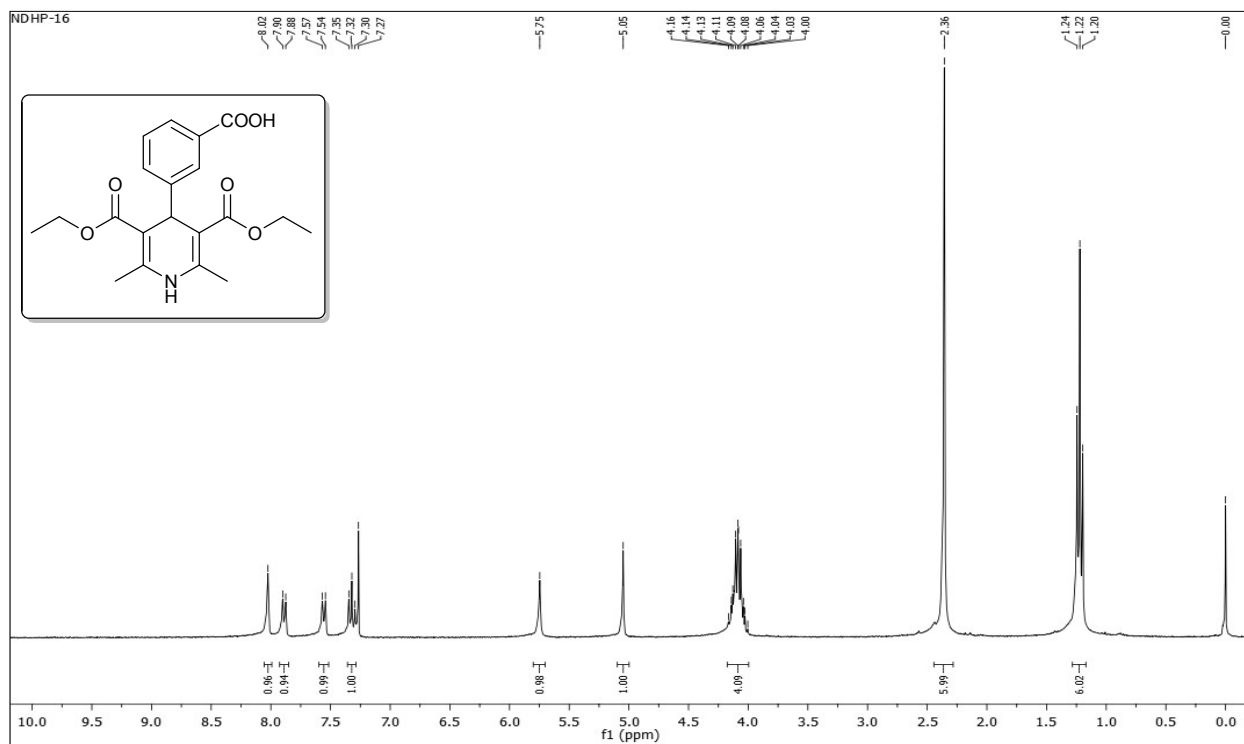


Fig. S33 ^1H NMR spectrum of 3-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)benzoic acid **50** (300 MHz, CDCl_3)

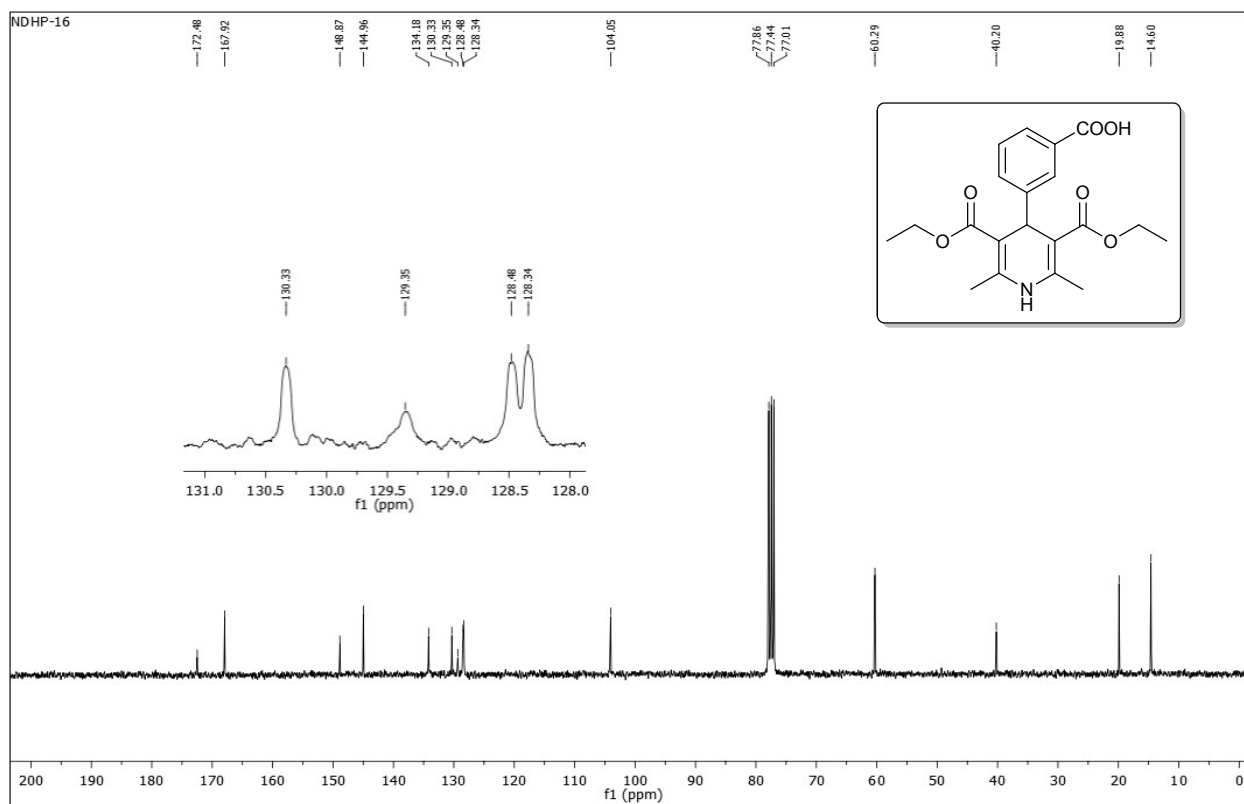


Fig. S34 ^{13}C NMR spectrum of 3-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)benzoic acid **50** (75 MHz, CDCl_3)

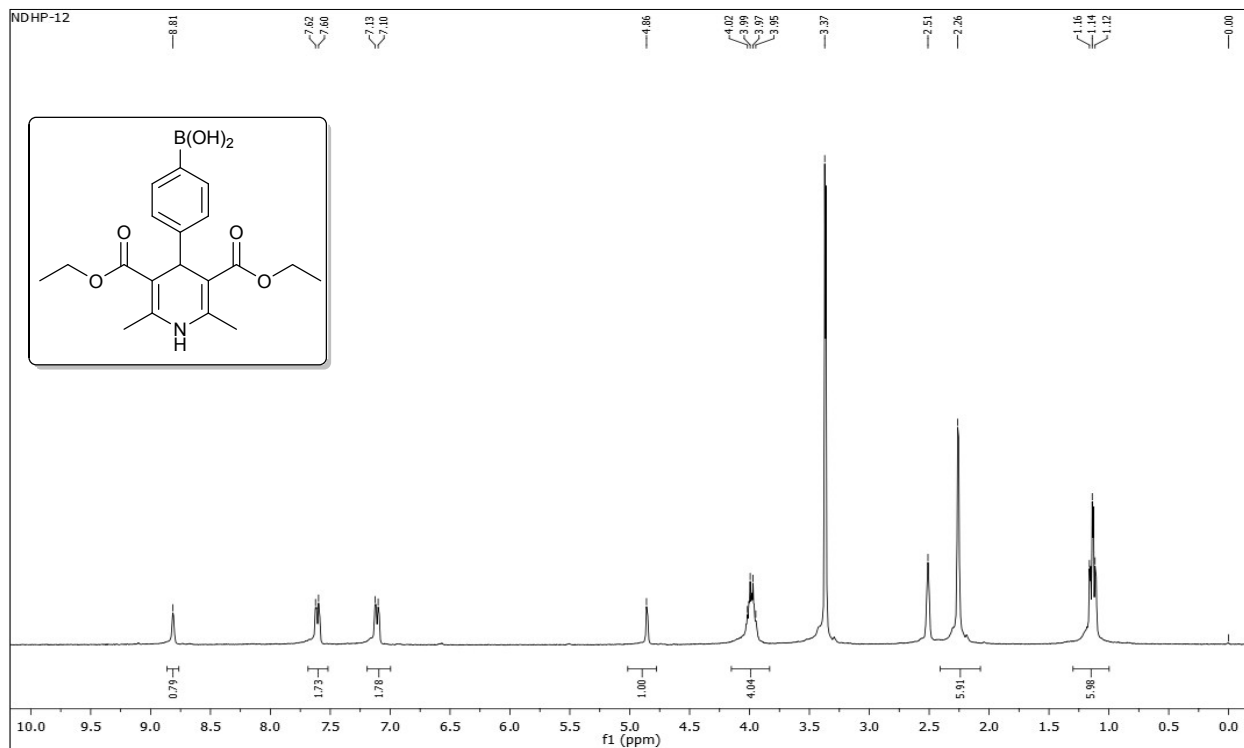


Fig. S35 ^1H NMR spectrum of (4-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)phenyl)boronic acid **5p** (300 MHz, DMSO)

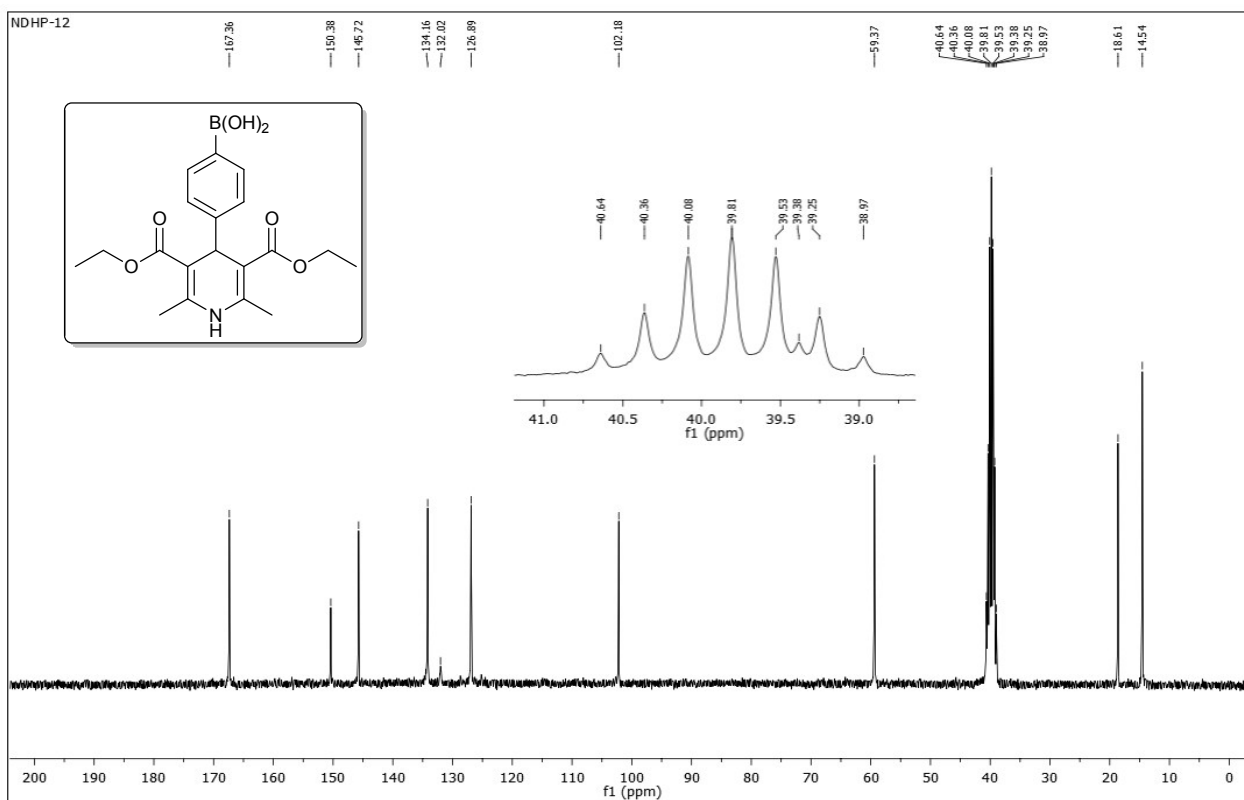
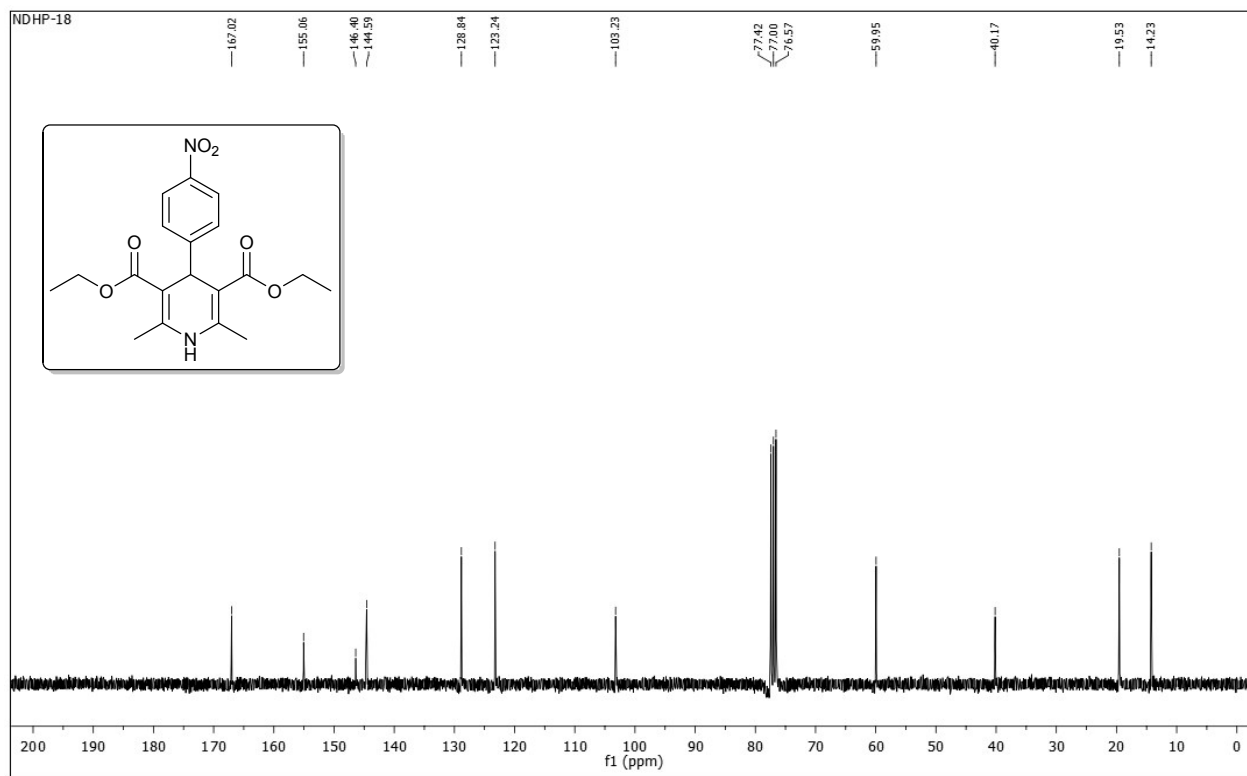
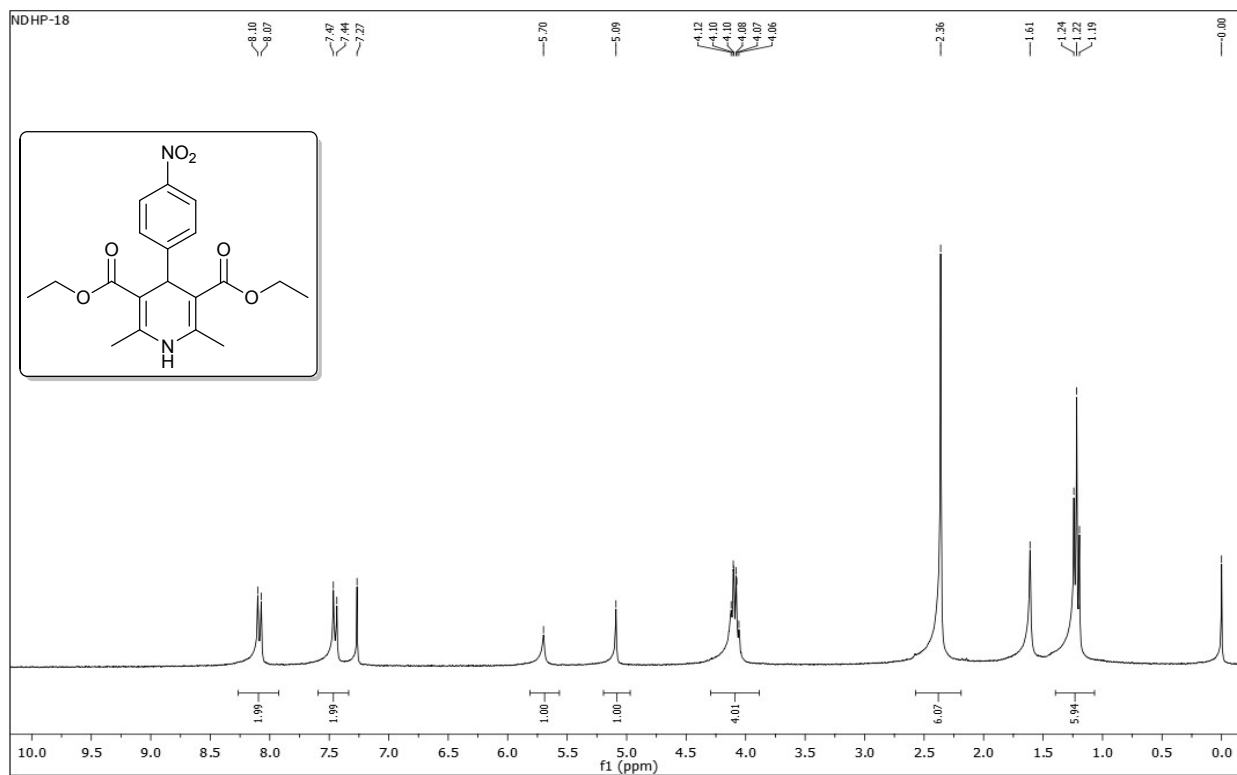


Fig. S36 ^{13}C NMR spectrum of (4-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)phenyl)boronic acid **5p** (75 MHz, DMSO)



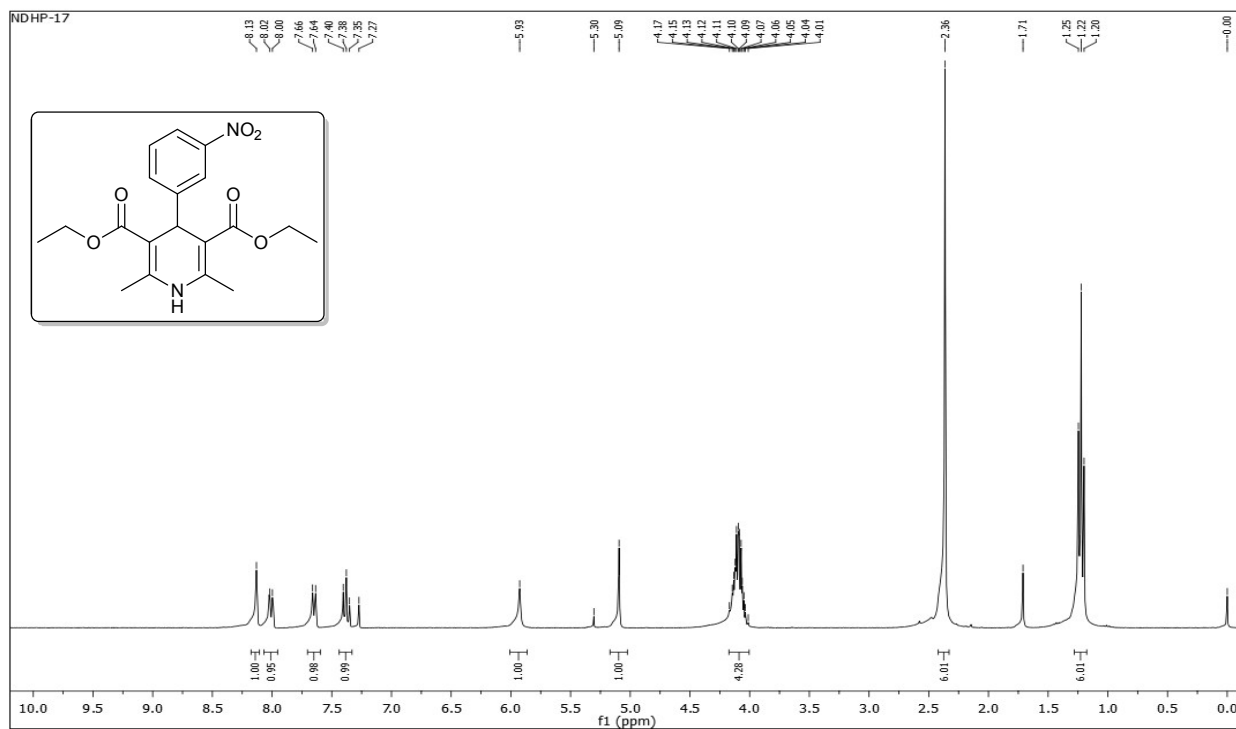


Fig. S39 ¹H NMR spectrum of diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5r** (300 MHz, CDCl₃)

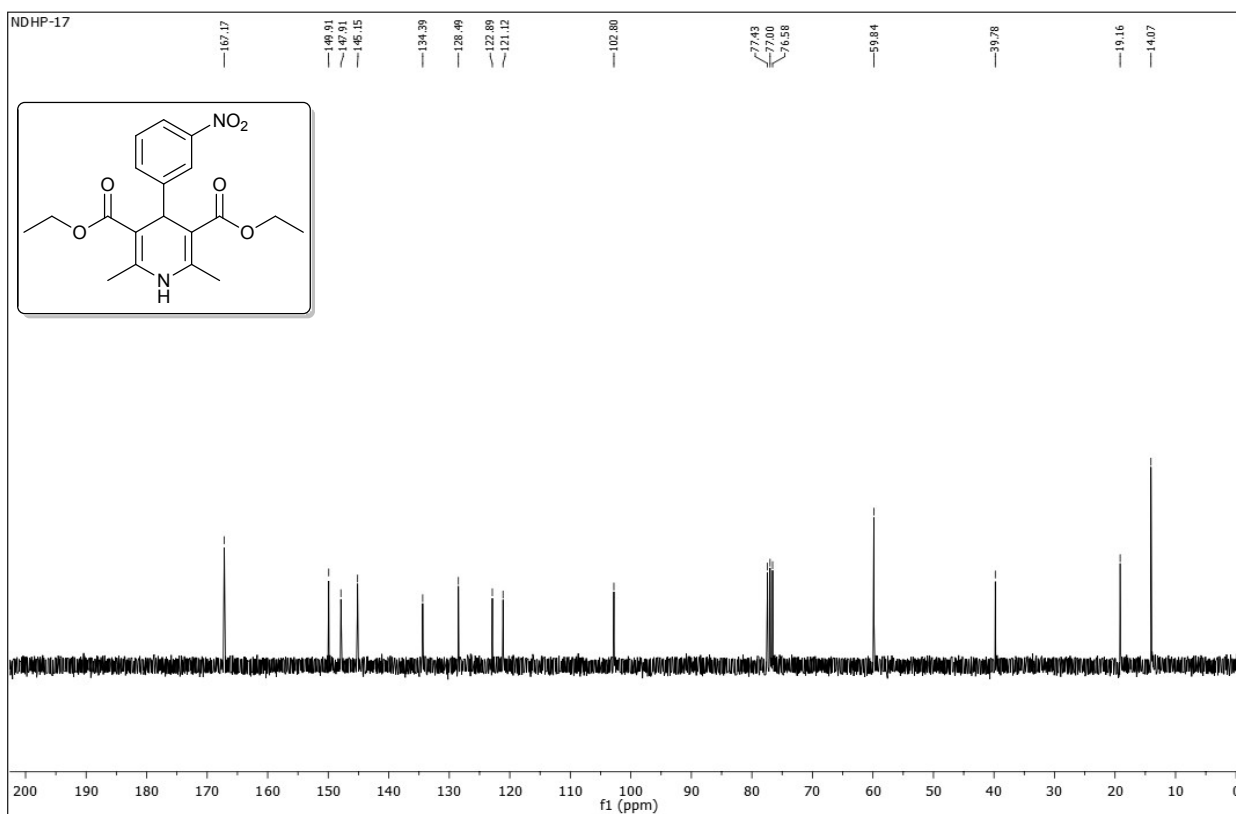


Fig. S40 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5r** (75 MHz, CDCl₃)

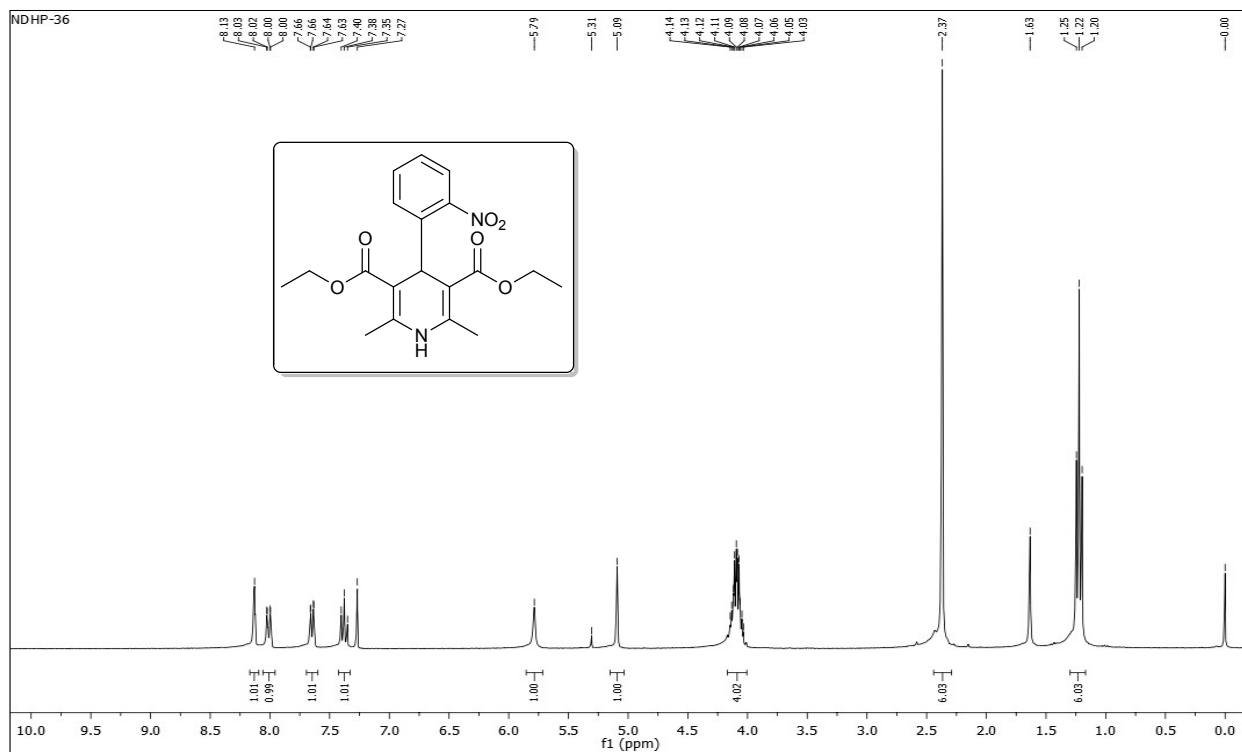


Fig. S41 ^1H NMR spectrum of diethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5s** (300 MHz, CDCl_3)

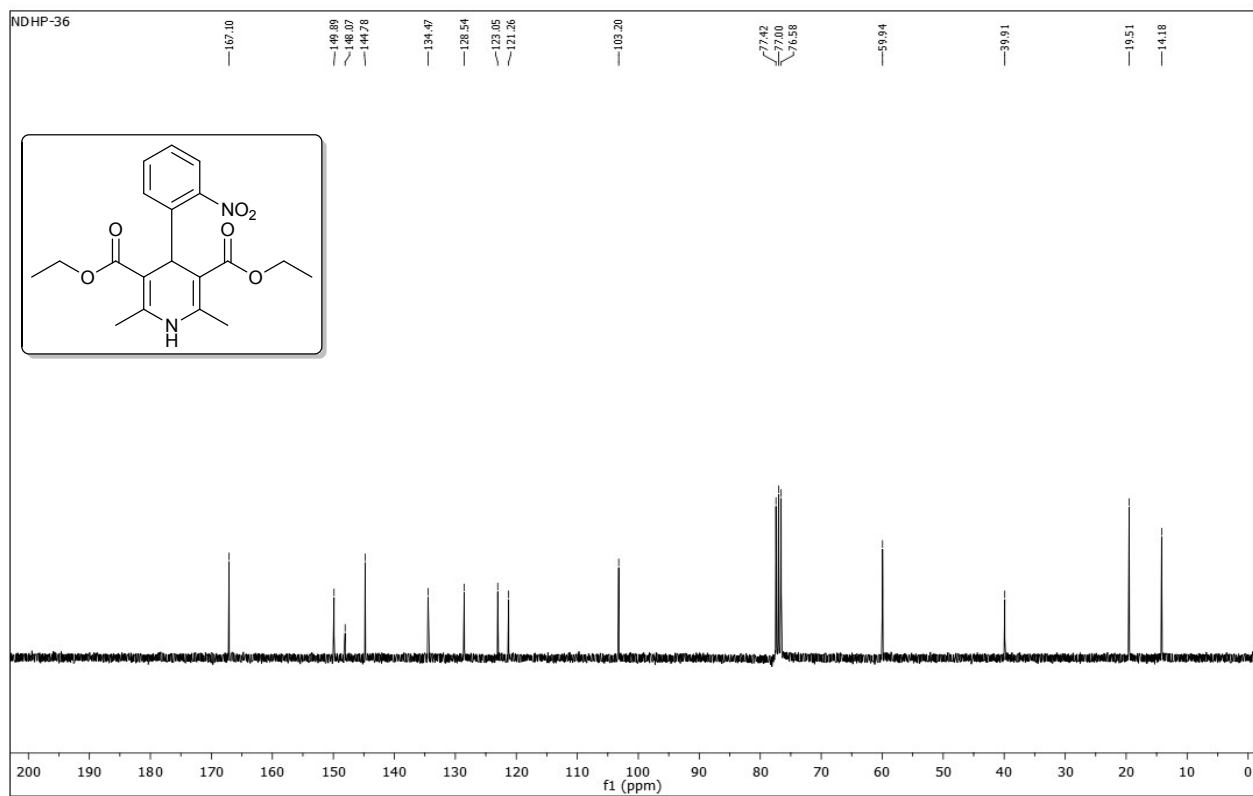


Fig. S42 ^{13}C NMR spectrum of diethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5s** (75 MHz, CDCl_3)

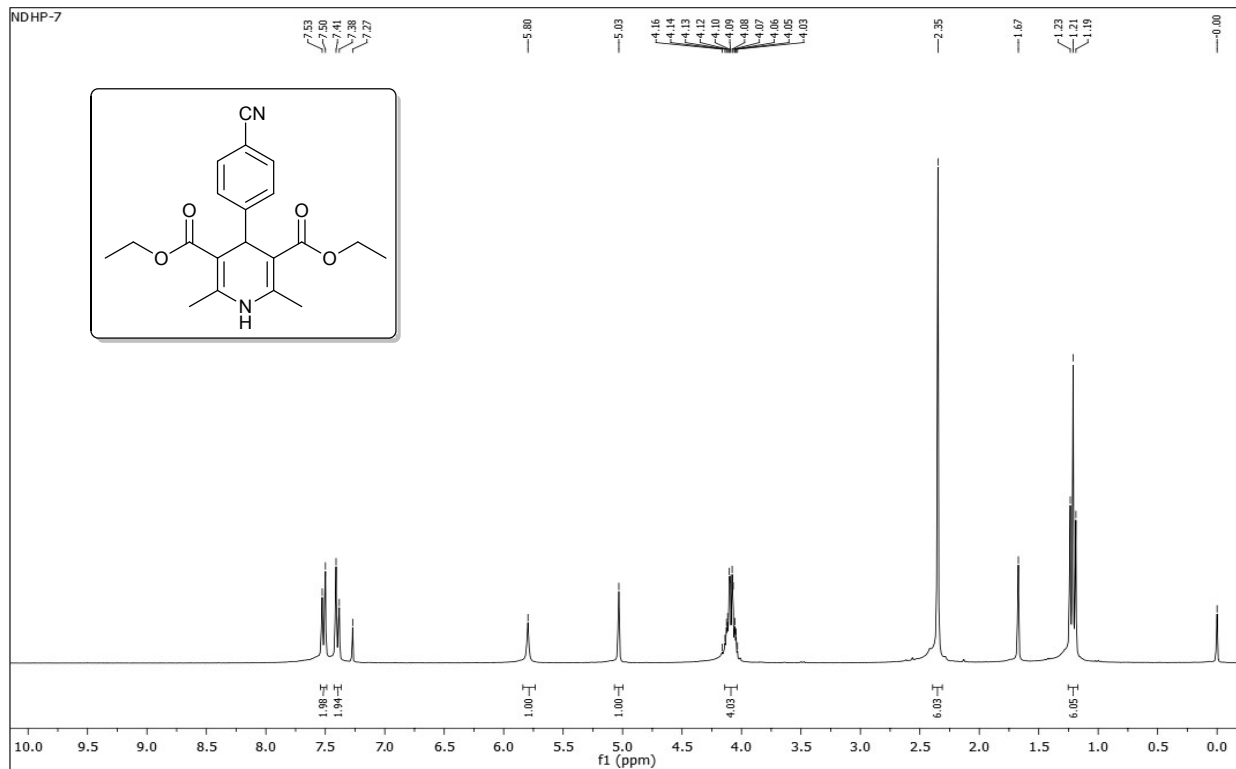


Fig. S43 ¹H NMR spectrum of diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5t** (300 MHz, CDCl₃)

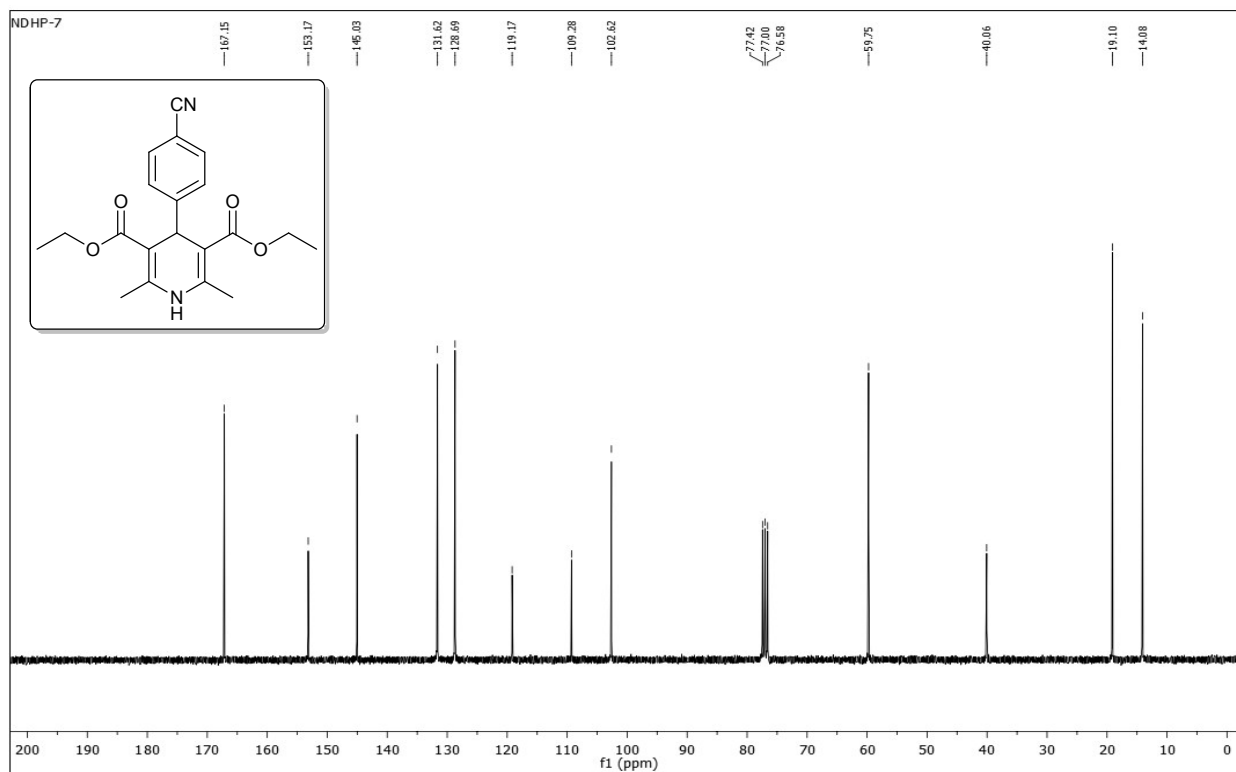


Fig. S44 ¹³C NMR spectrum of diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5t** (75 MHz, CDCl₃)

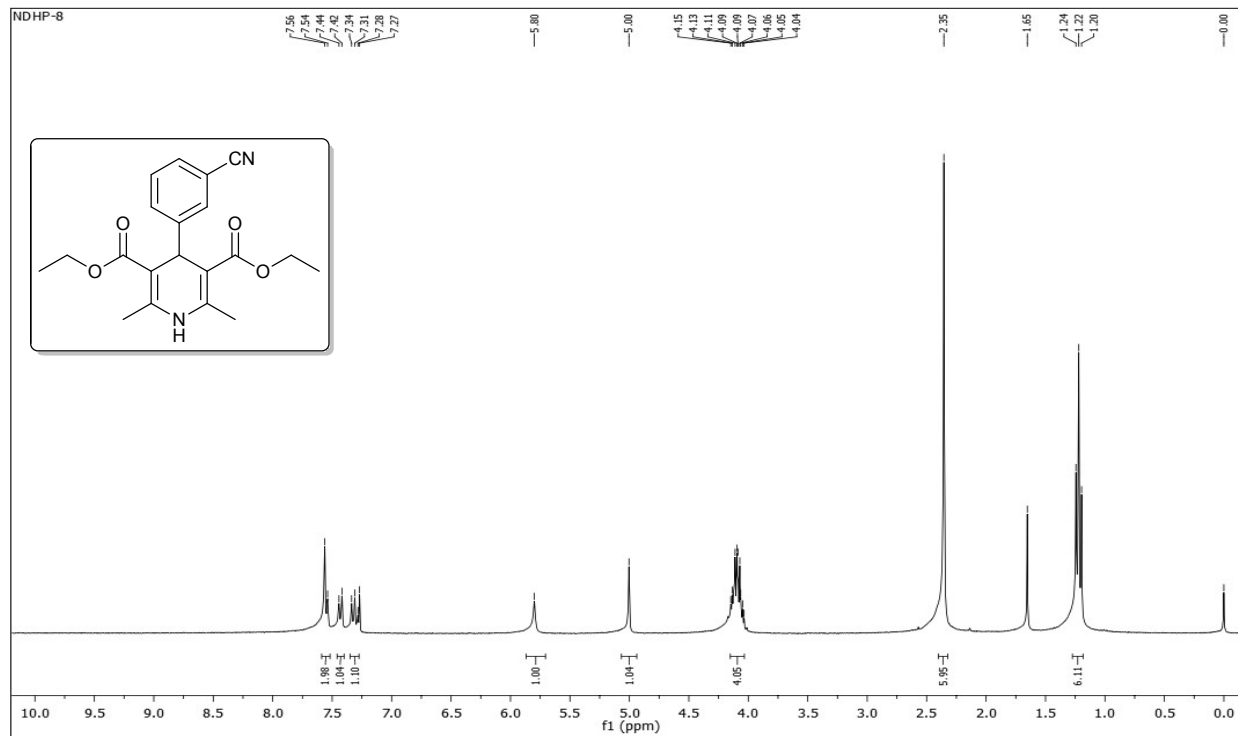


Fig. S45 ¹H NMR spectrum of diethyl 4-(3-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5u** (300 MHz, CDCl₃)

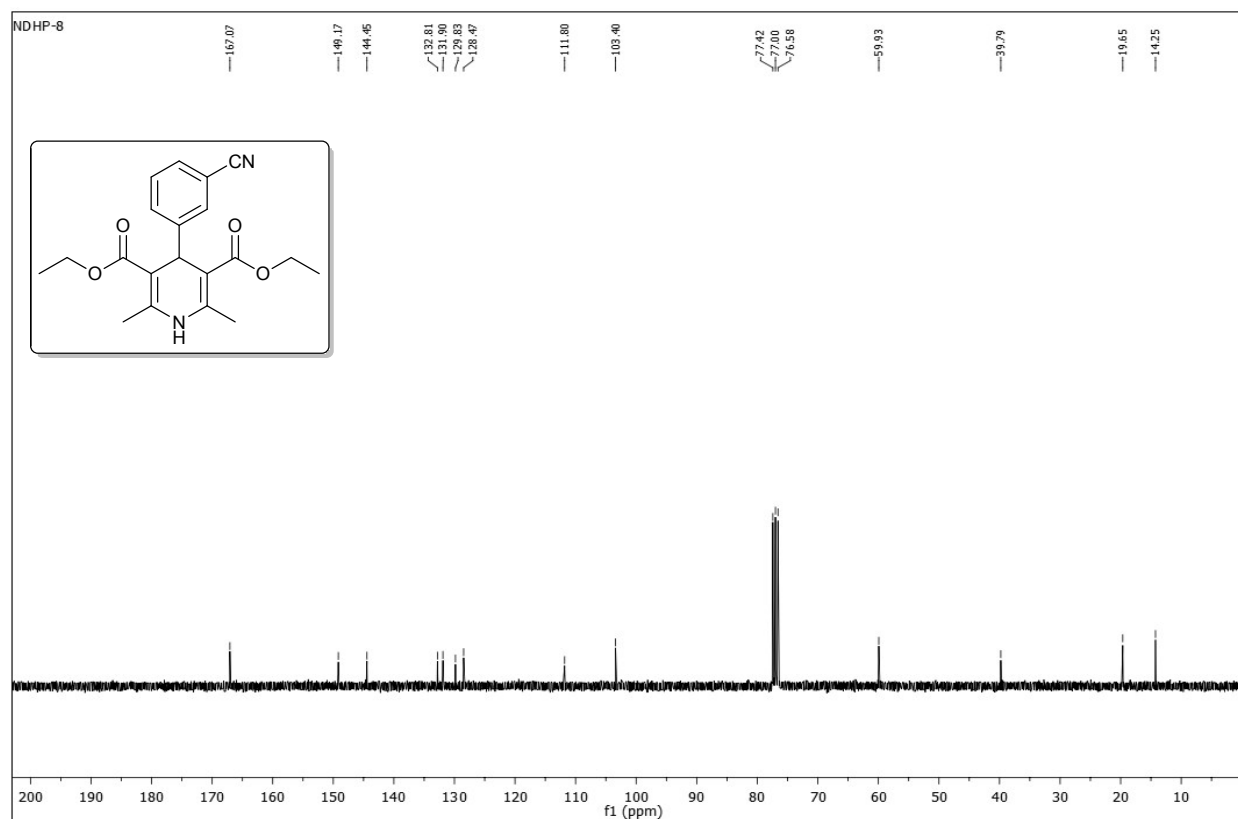


Fig. S46 ^{13}C NMR spectrum of diethyl 4-(3-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5u** (75 MHz, CDCl_3)

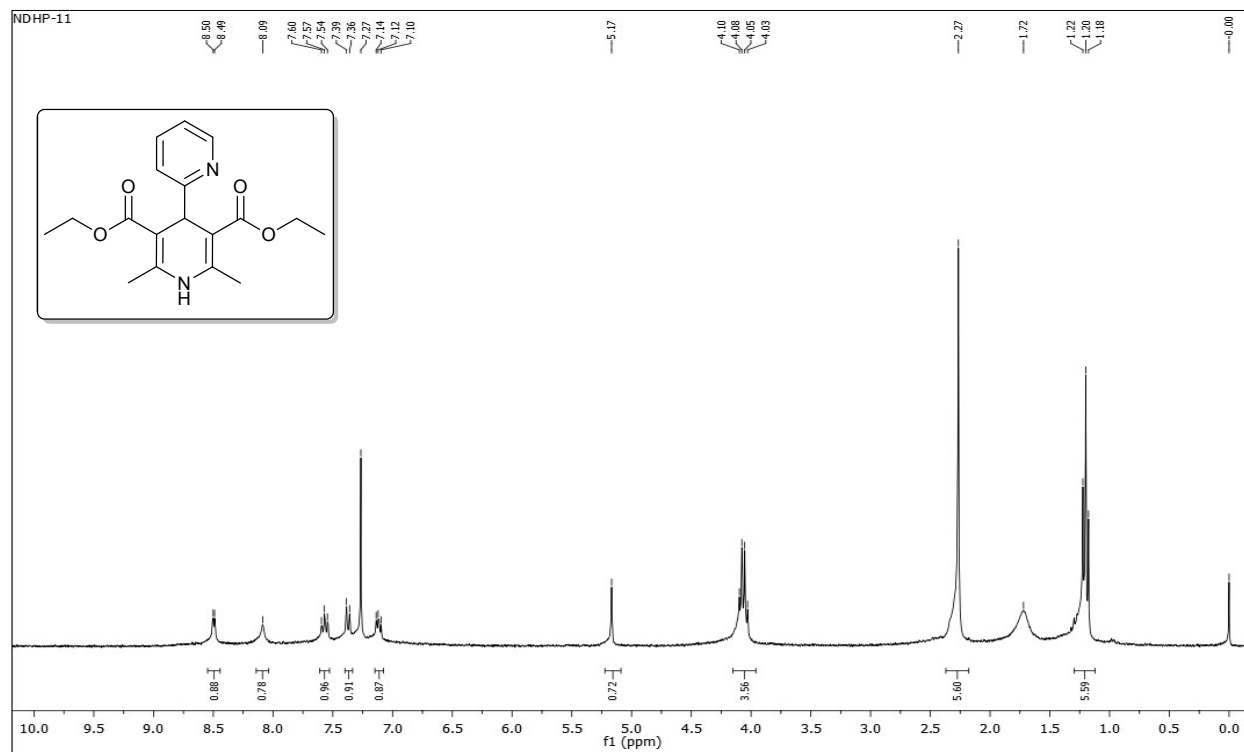


Fig. S47 ^1H NMR spectrum of diethyl 2',6'-dimethyl-1',4'-dihydro-[2,4'-bipyridine]-3',5'-dicarboxylate **5v** (300 MHz, CDCl_3)

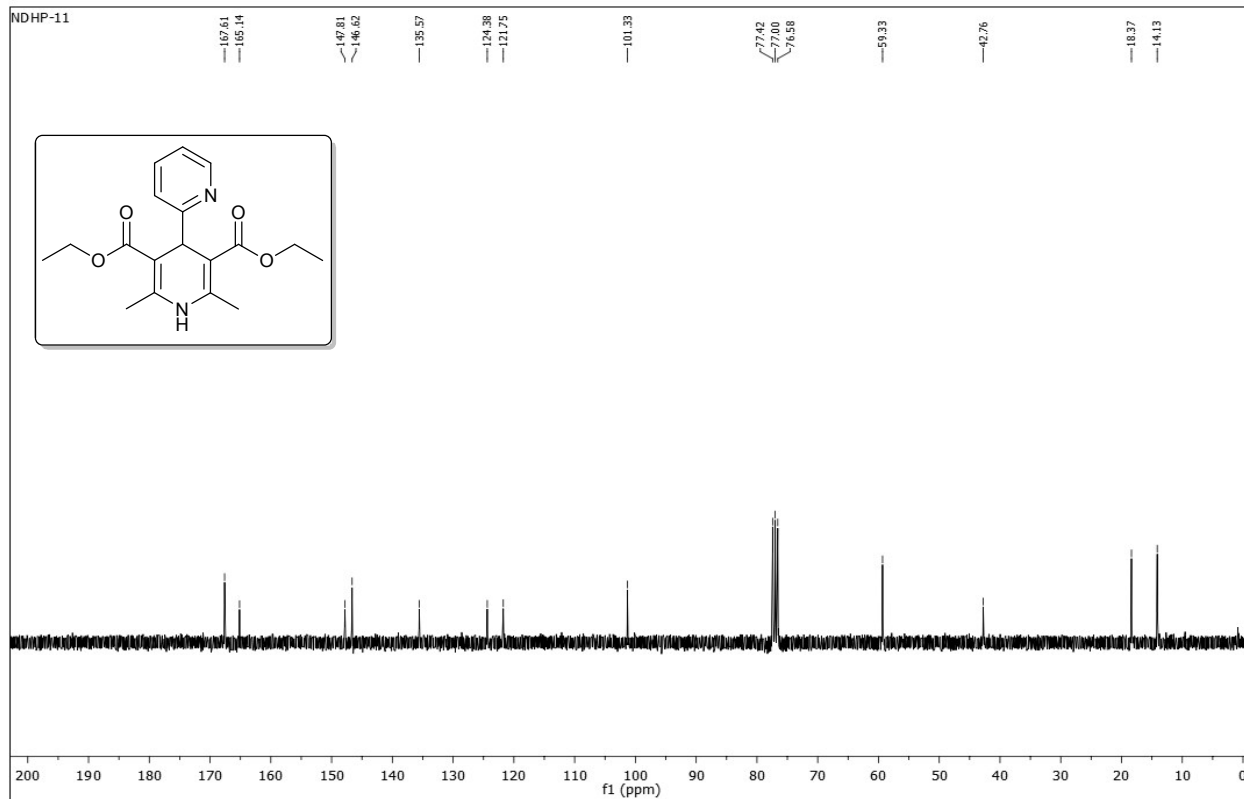


Fig. S48 ^{13}C NMR spectrum of diethyl 2',6'-dimethyl-1',4'-dihydro-[2,4'-bipyridine]-3',5'-dicarboxylate **5v** (75 MHz, CDCl_3)

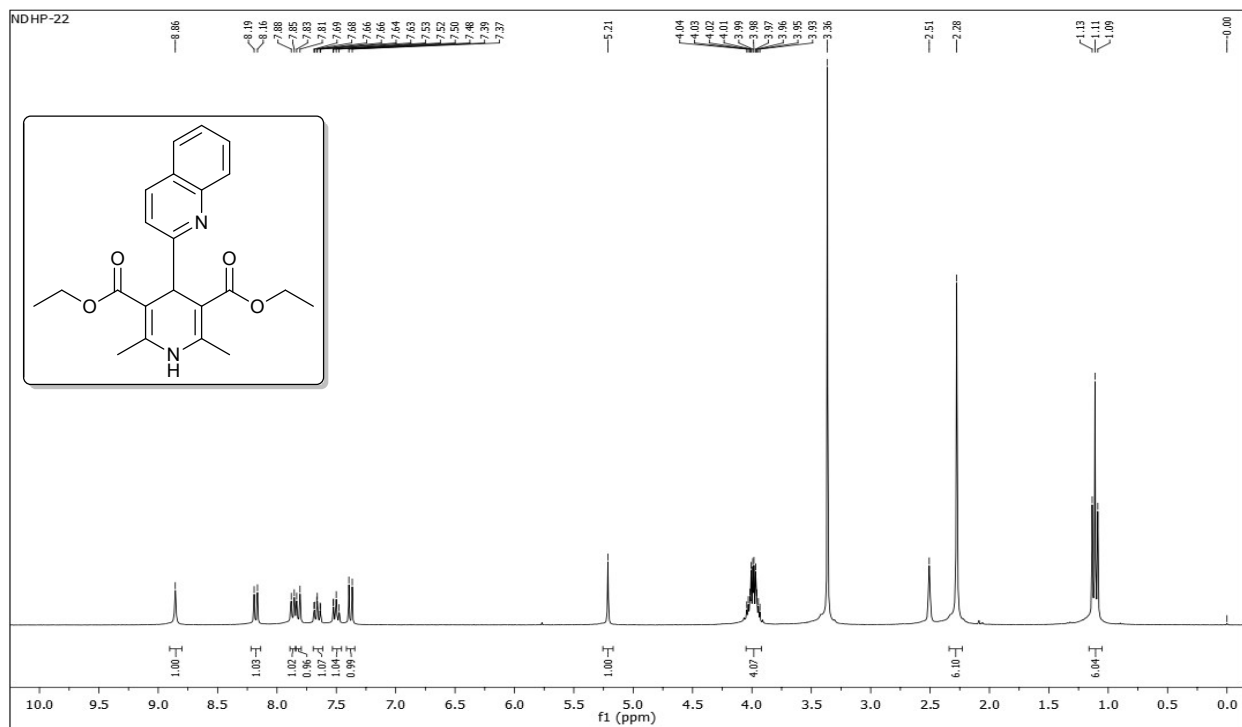


Fig. S49 ^1H NMR spectrum of diethyl 2,6-dimethyl-4-(quinolin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5w** (300 MHz, DMSO)

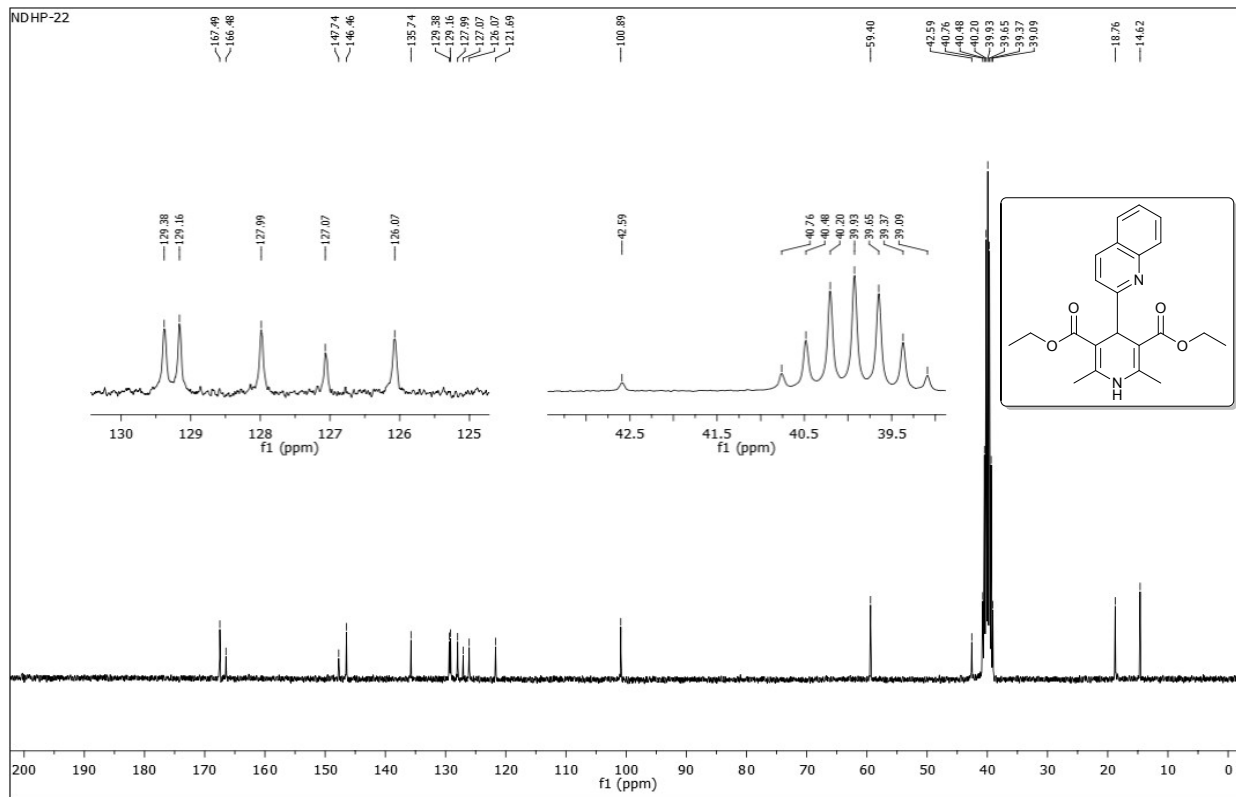


Fig. S50 ^{13}C NMR spectrum of diethyl 2,6-dimethyl-4-(quinolin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5w** (300 MHz, DMSO)

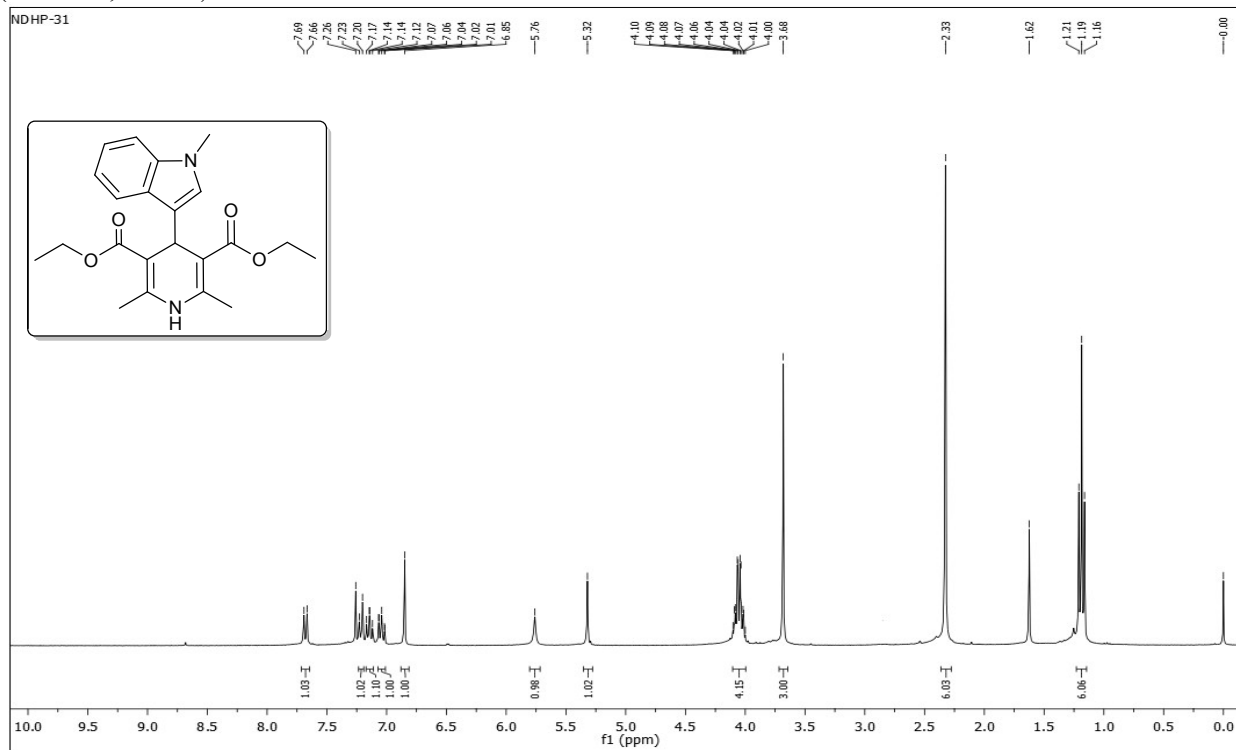


Fig. S51 ^1H NMR spectrum of diethyl 2,6-dimethyl-4-(1-methyl-1*H*-indol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5x** (300 MHz, CDCl_3)

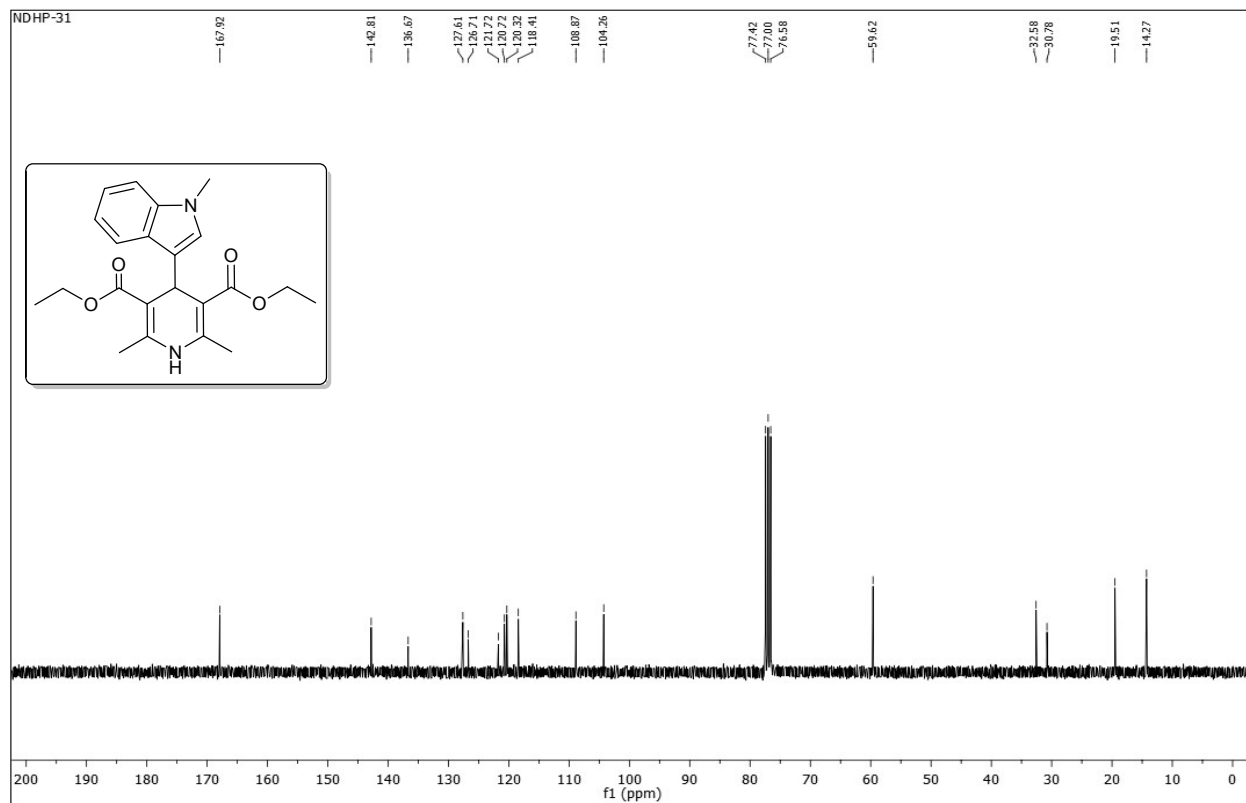


Fig. S52 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-(1-methyl-1*H*-indol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5x** (75 MHz, CDCl₃)

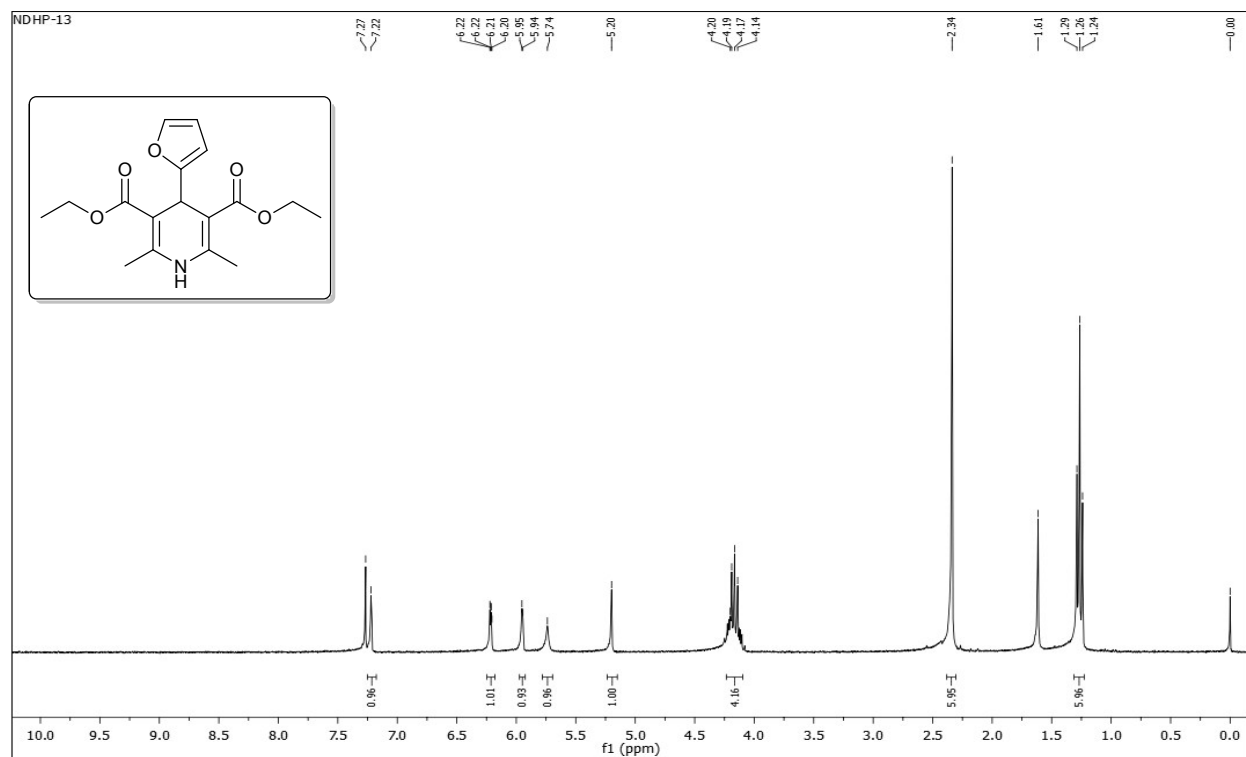


Fig. S53 ¹H NMR spectrum of diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5y** (300 MHz, CDCl₃)

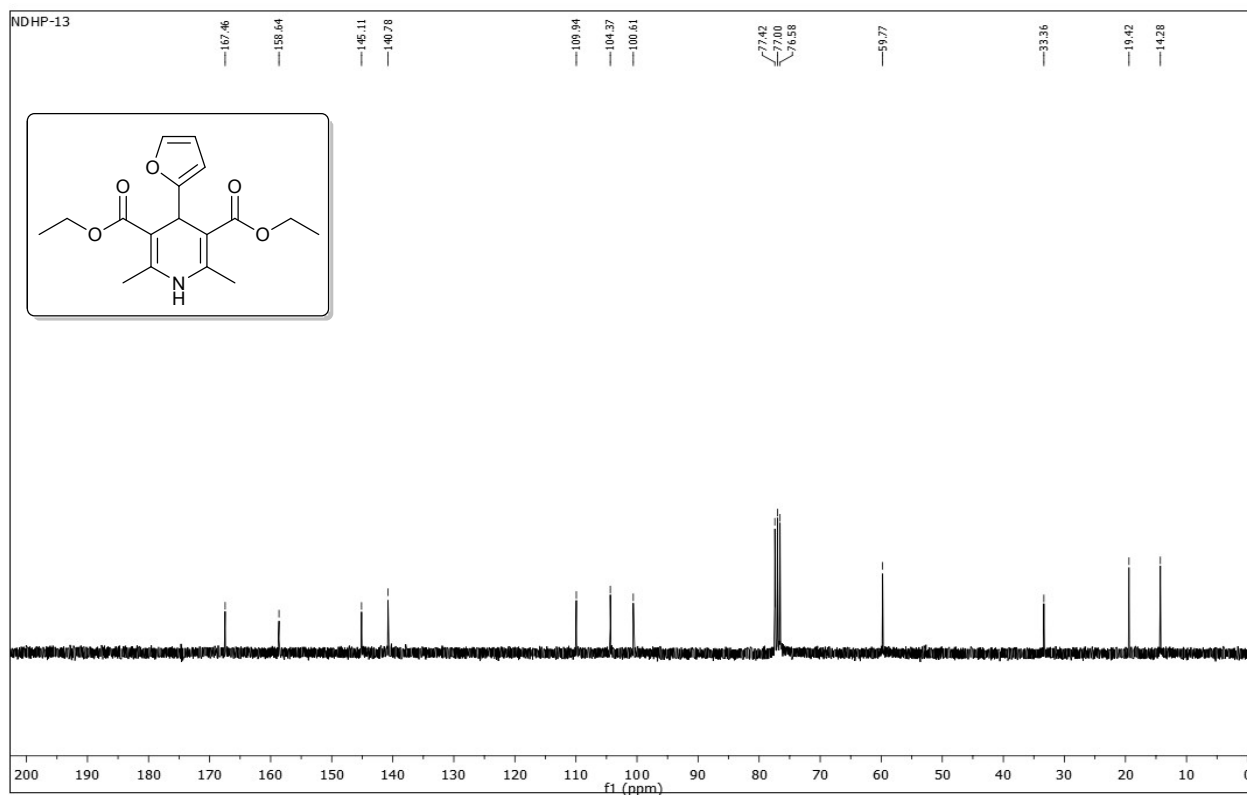


Fig. S54 ^{13}C NMR spectrum of diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5y** (75 MHz, CDCl_3)

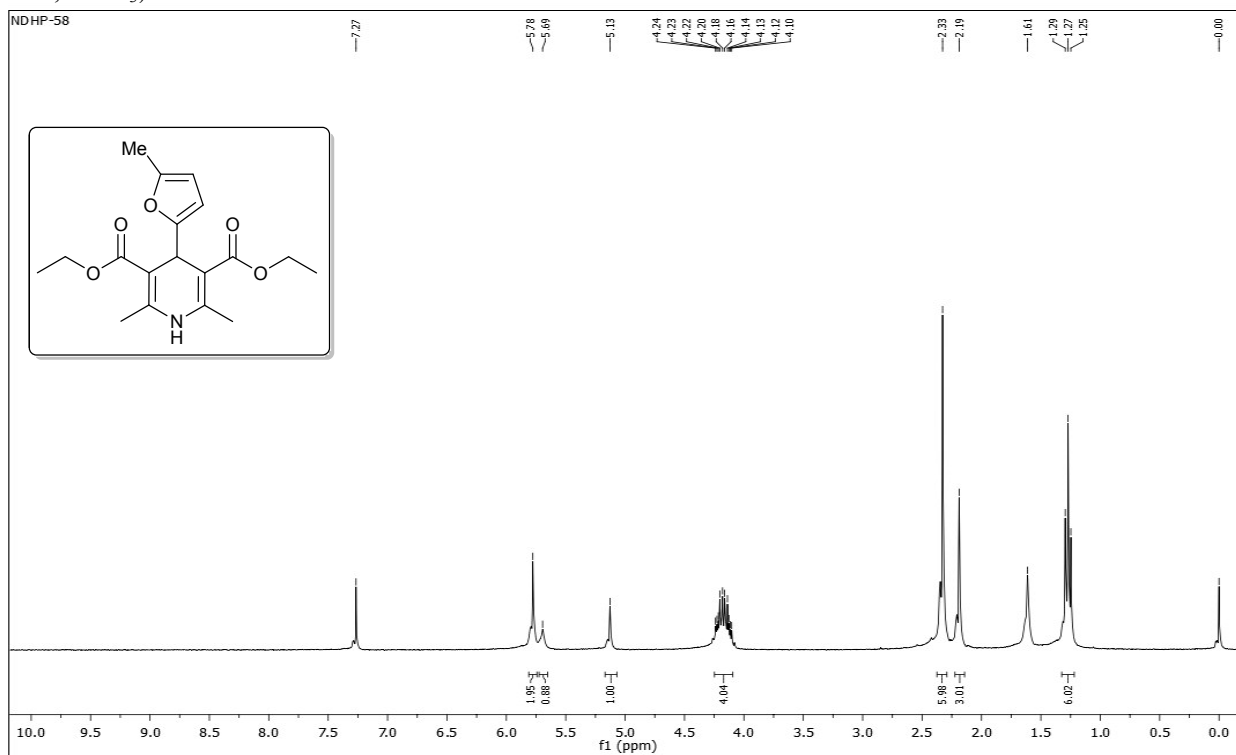


Fig. S55 ^1H NMR spectrum of diethyl 2,6-dimethyl-4-(5-methylfuran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5z** (300 MHz, CDCl_3)

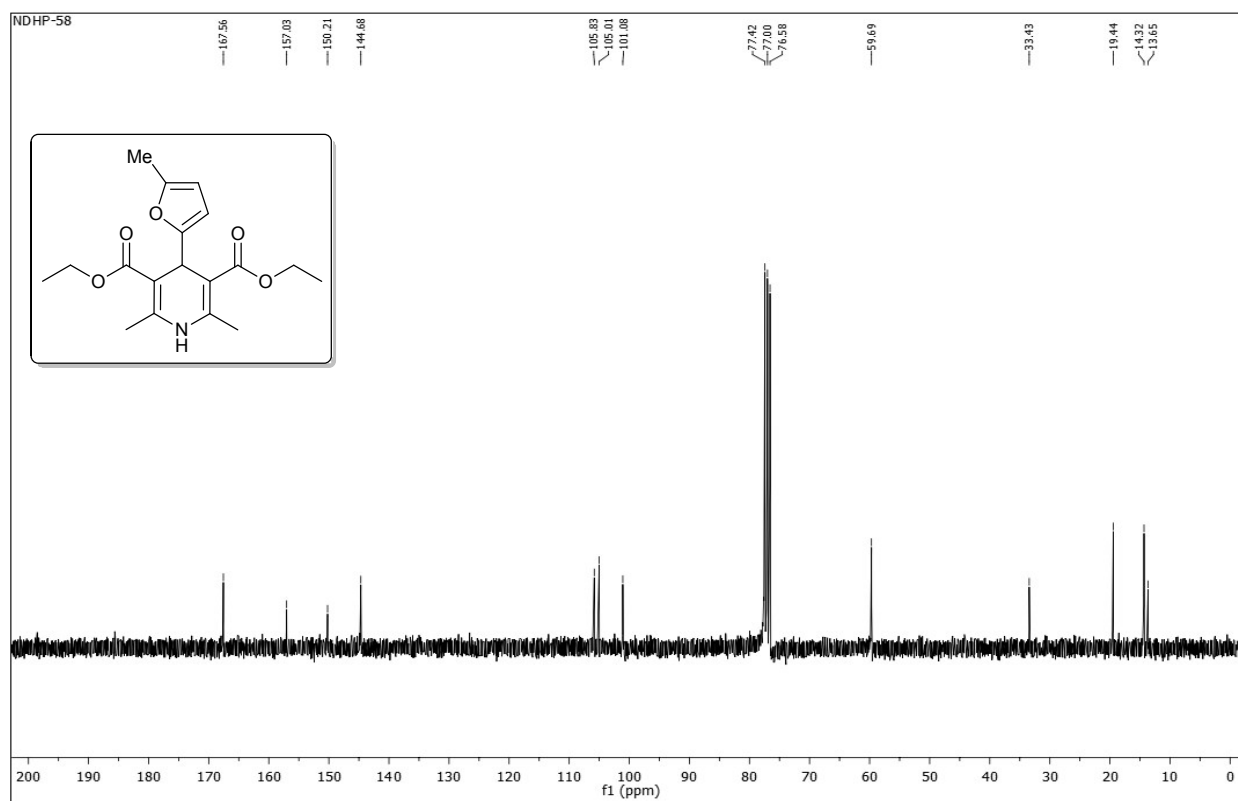


Fig. S56 ¹³C NMR spectrum of diethyl 2,6-dimethyl-4-(5-methylfuran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5z** (75 MHz, CDCl₃)

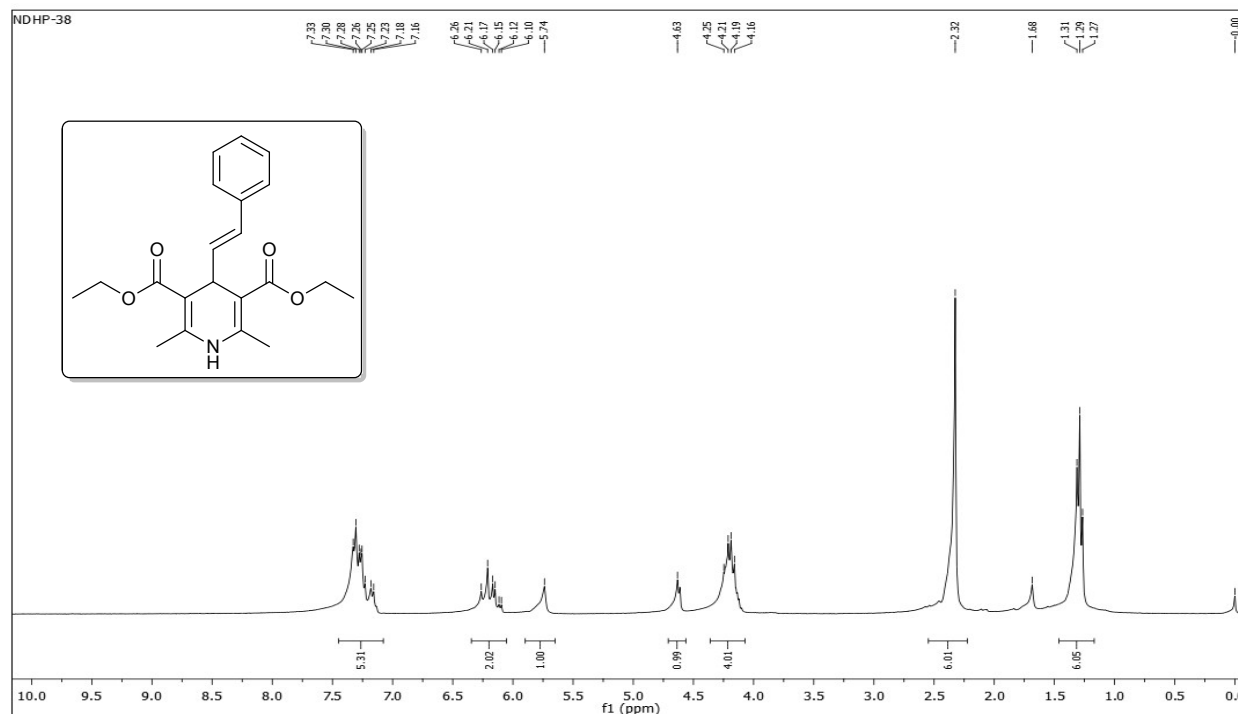


Fig. S57 ¹H NMR spectrum of diethyl 2,6-dimethyl-4-styryl-1,4-dihydropyridine-3,5-dicarboxylate **5aa** (300 MHz, CDCl₃)

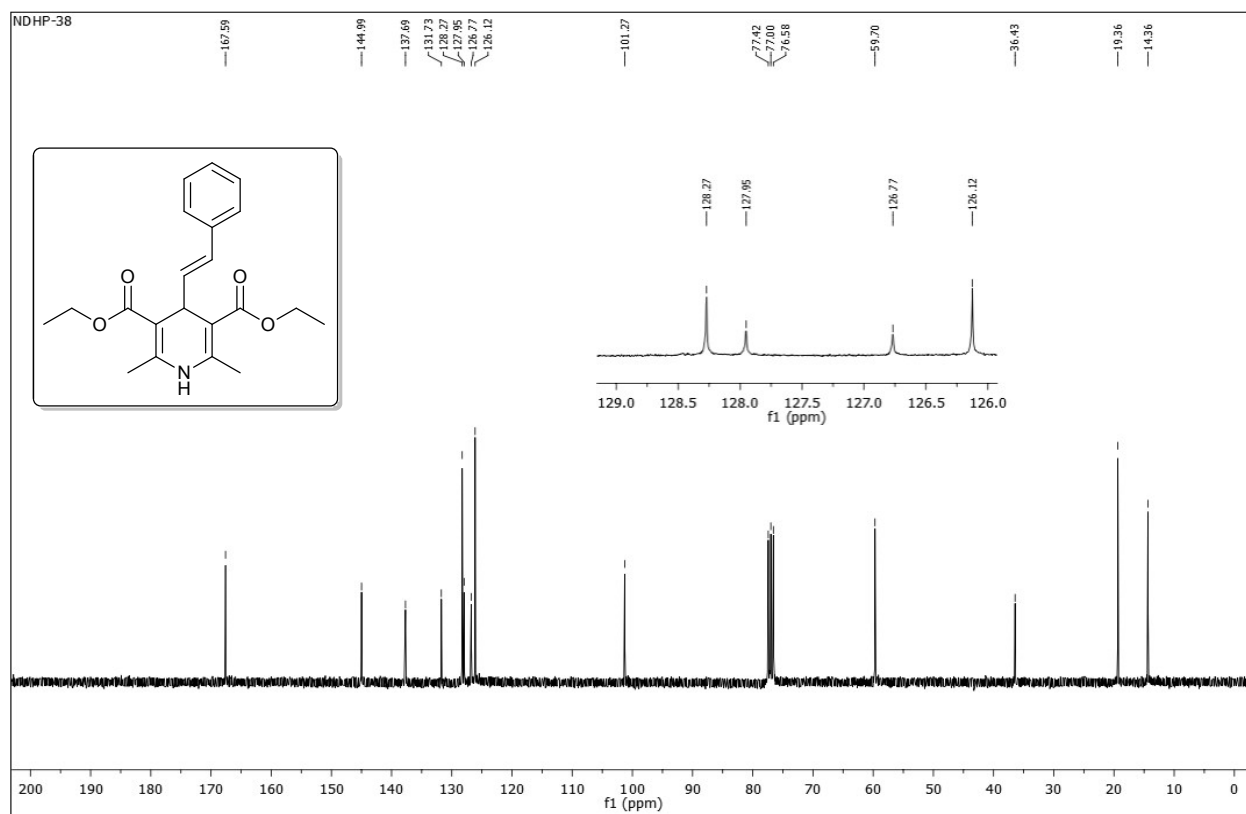


Fig. S58 ^{13}C NMR spectrum of diethyl 2,6-dimethyl-4-styryl-1,4-dihydropyridine-3,5-dicarboxylate **5aa** (75 MHz, CDCl_3)

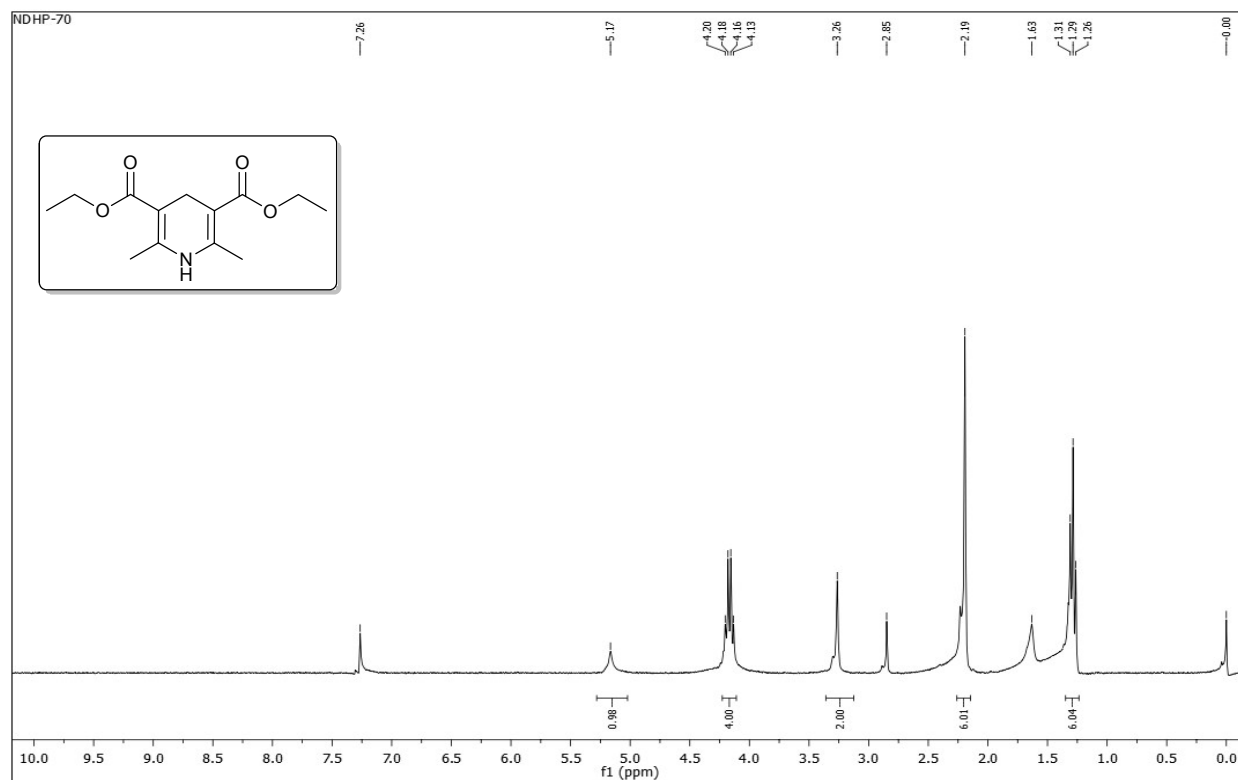


Fig. S59 ^1H NMR spectrum of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ab** (300 MHz, CDCl_3)

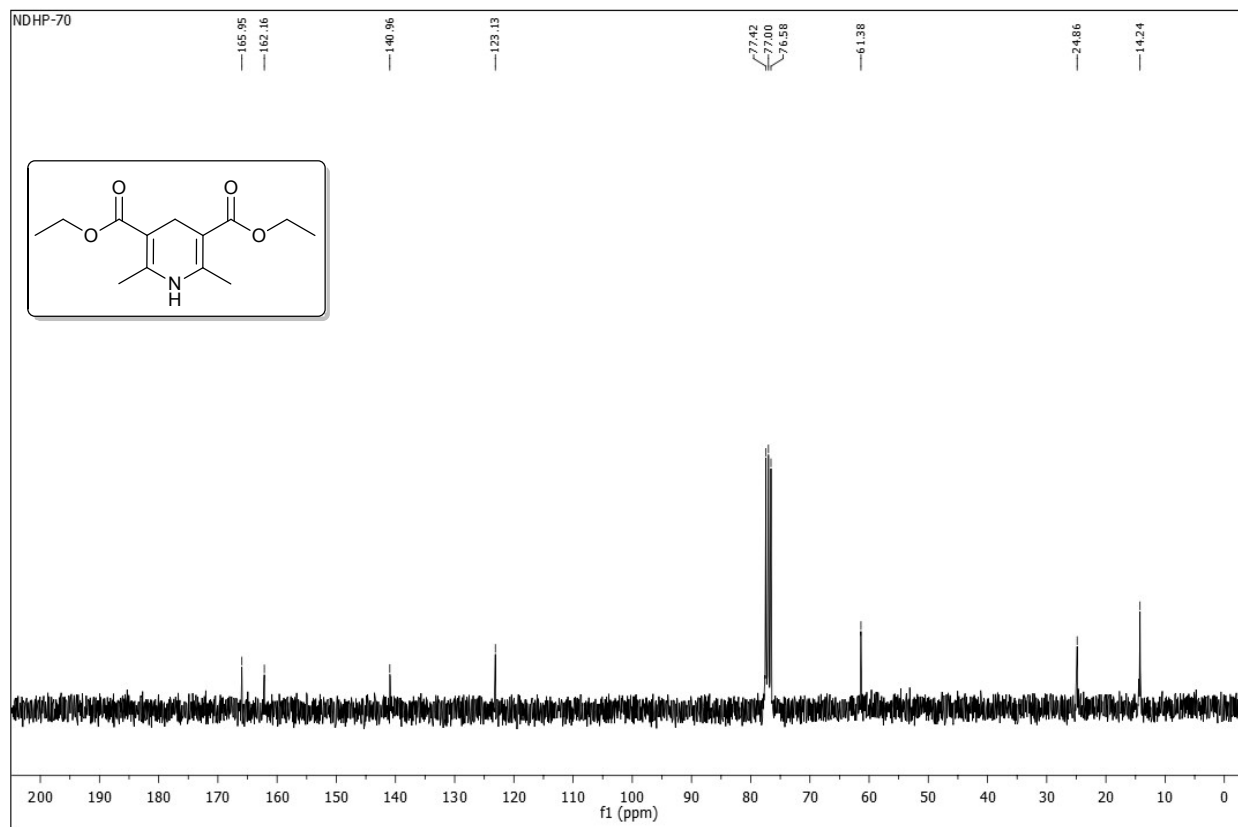


Fig. S60 ^{13}C NMR spectrum of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ab** (75 MHz, CDCl_3)

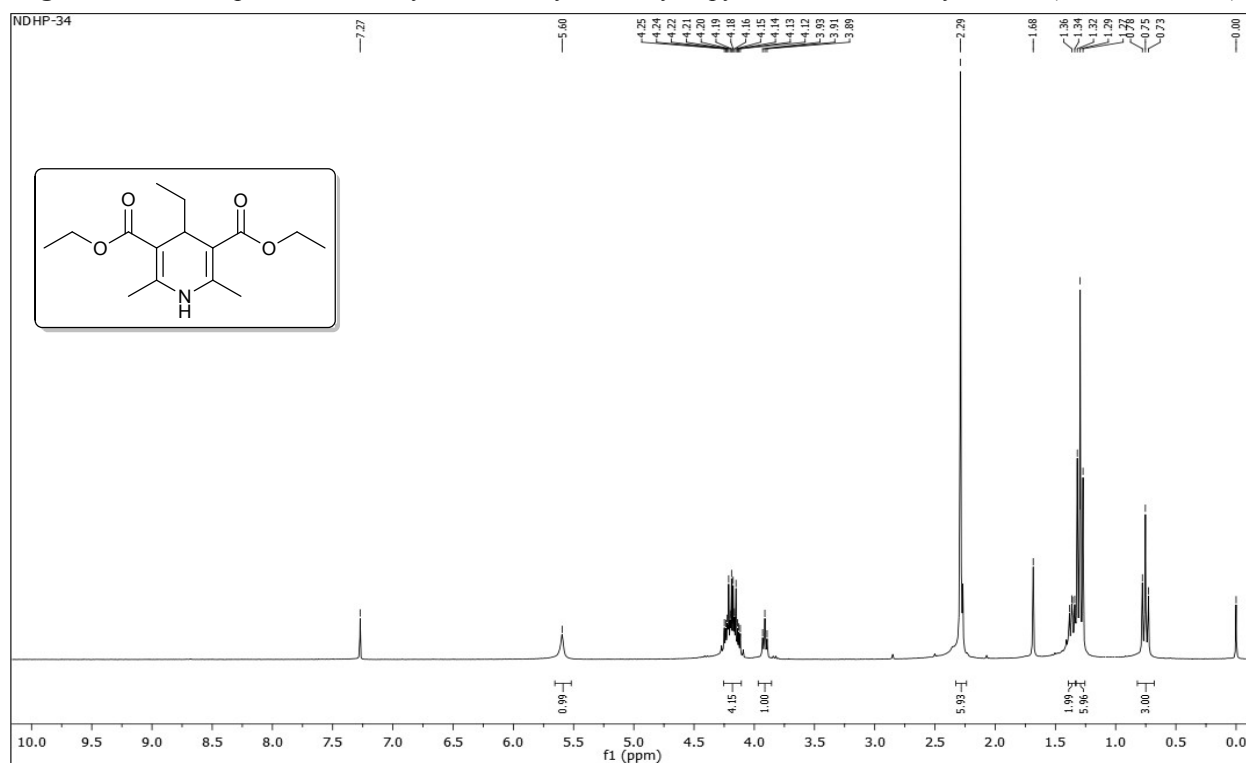


Fig. S61 ^1H NMR spectrum of diethyl 4-ethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ac** (300 MHz, CDCl_3)

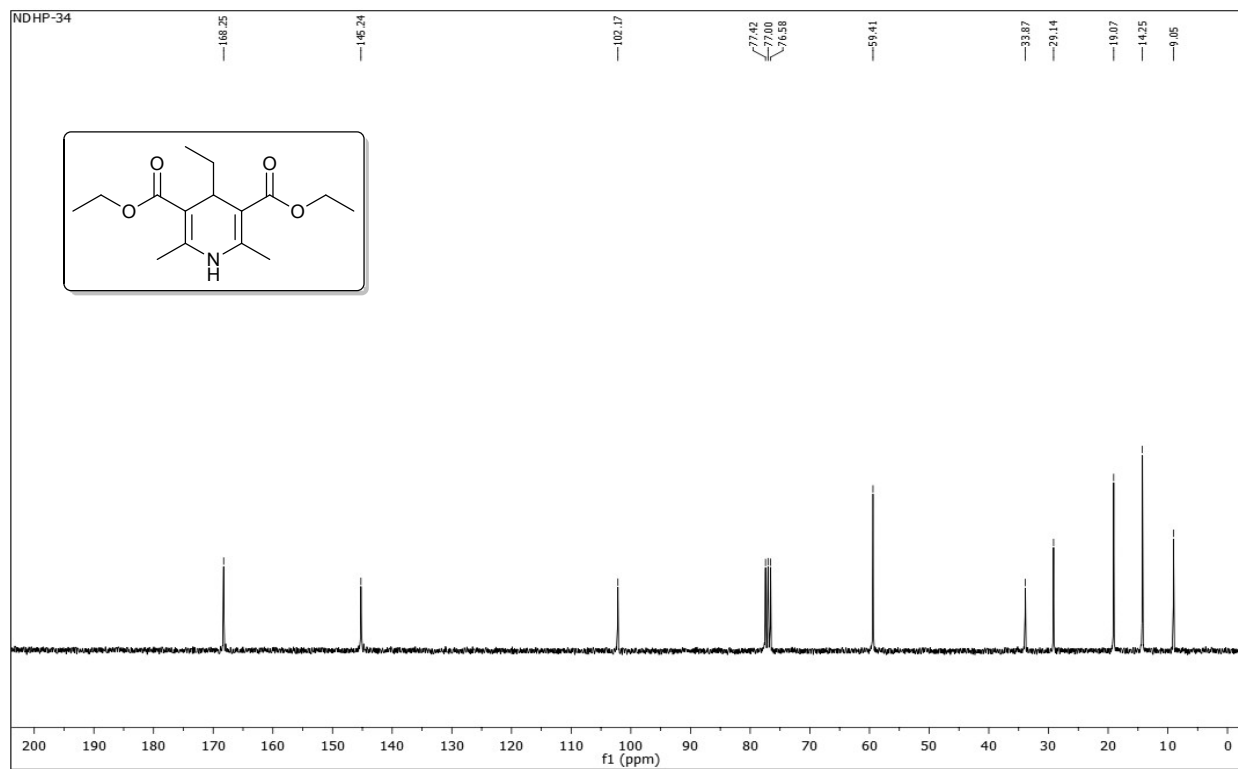


Fig. S62 ^{13}C NMR spectrum of diethyl 4-ethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ac** (75 MHz, CDCl_3)

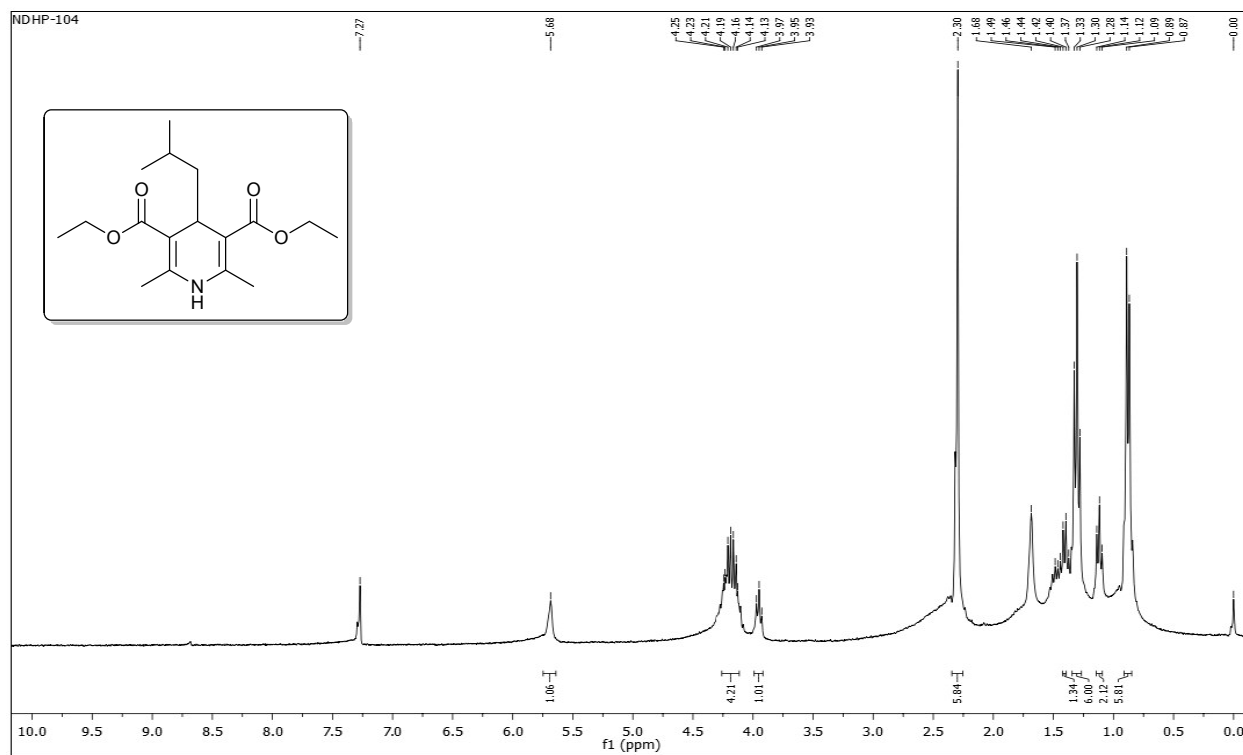


Fig. S63 ¹H NMR spectrum of diethyl 4-isobutyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ad** (300 MHz, CDCl₃)

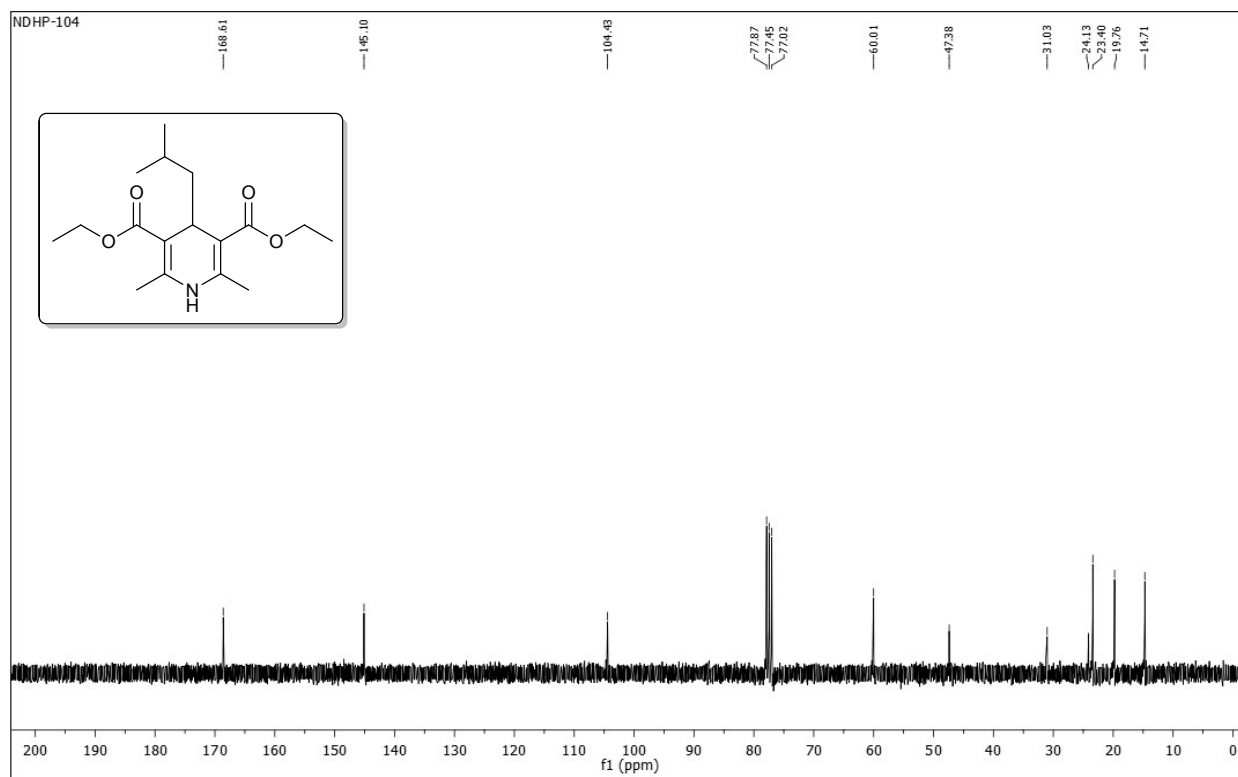


Fig. S64 ¹³C NMR spectrum of diethyl 4-isobutyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ad** (75 MHz, CDCl₃)

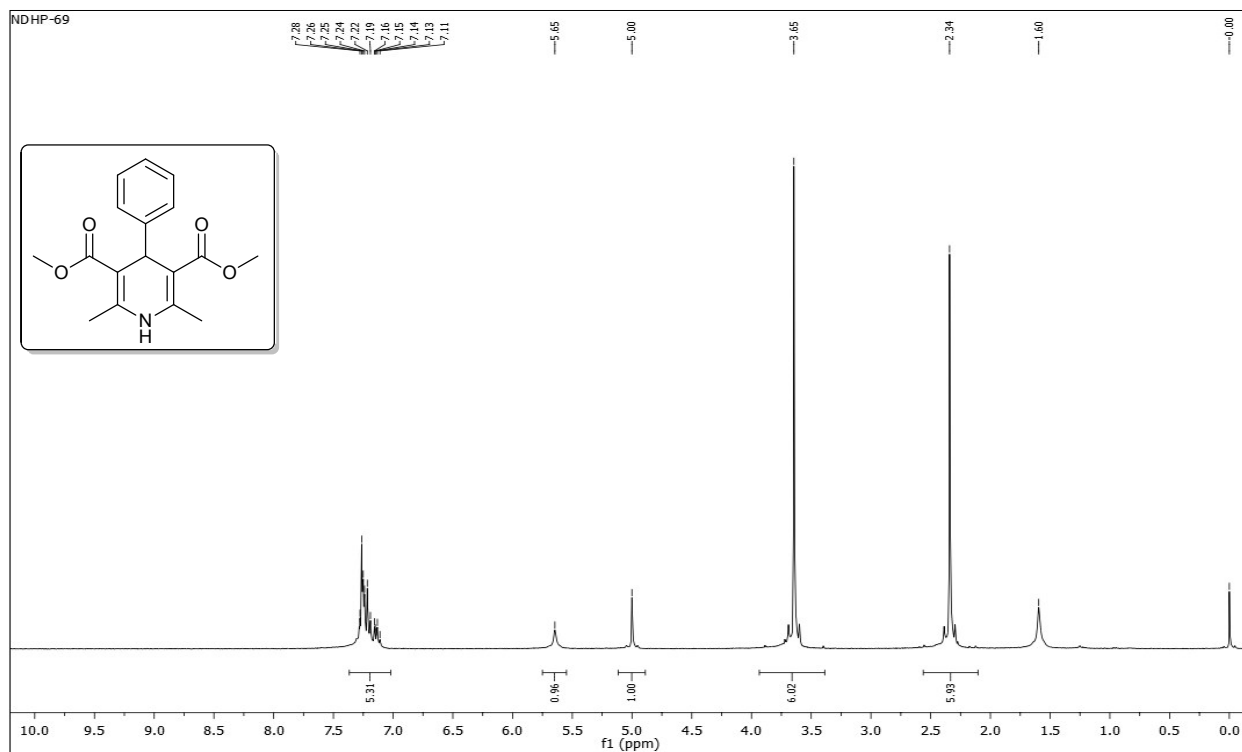


Fig. S65 ¹H NMR spectrum of dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5ae** (300 MHz, CDCl₃)

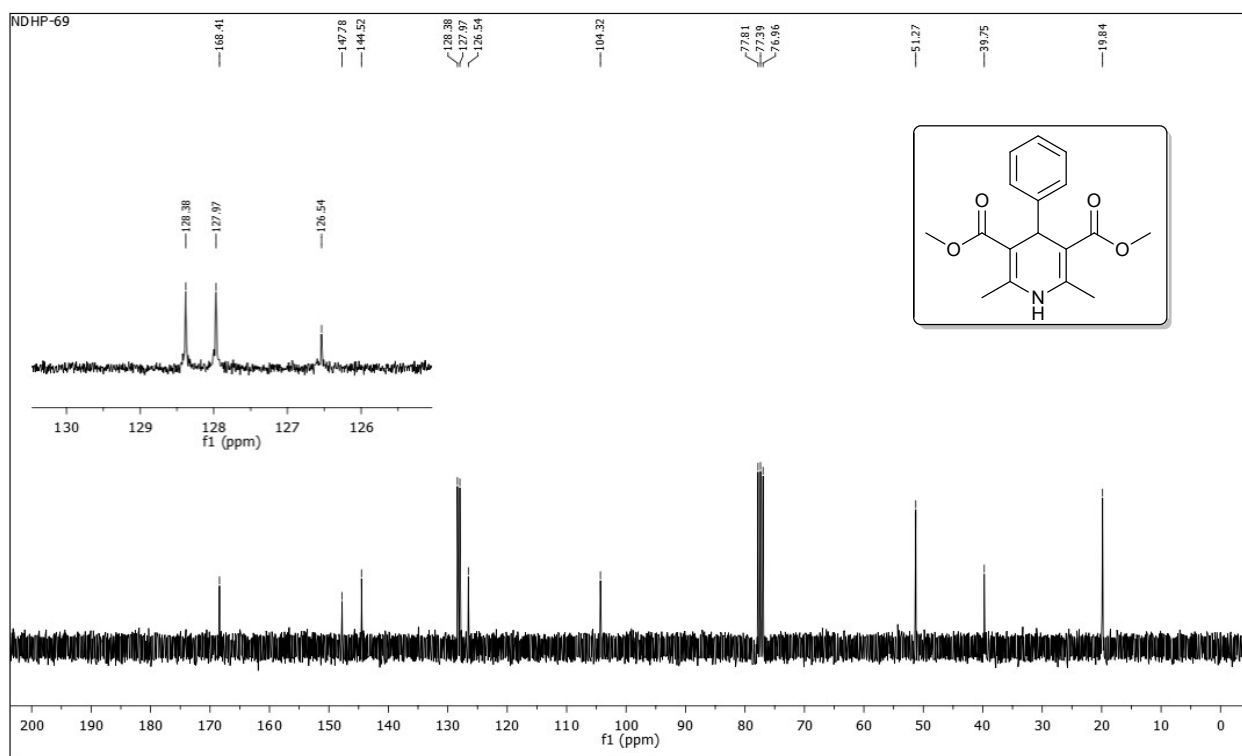


Fig. 66 ¹³C NMR spectrum of dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5ae** (75 MHz, CDCl₃)

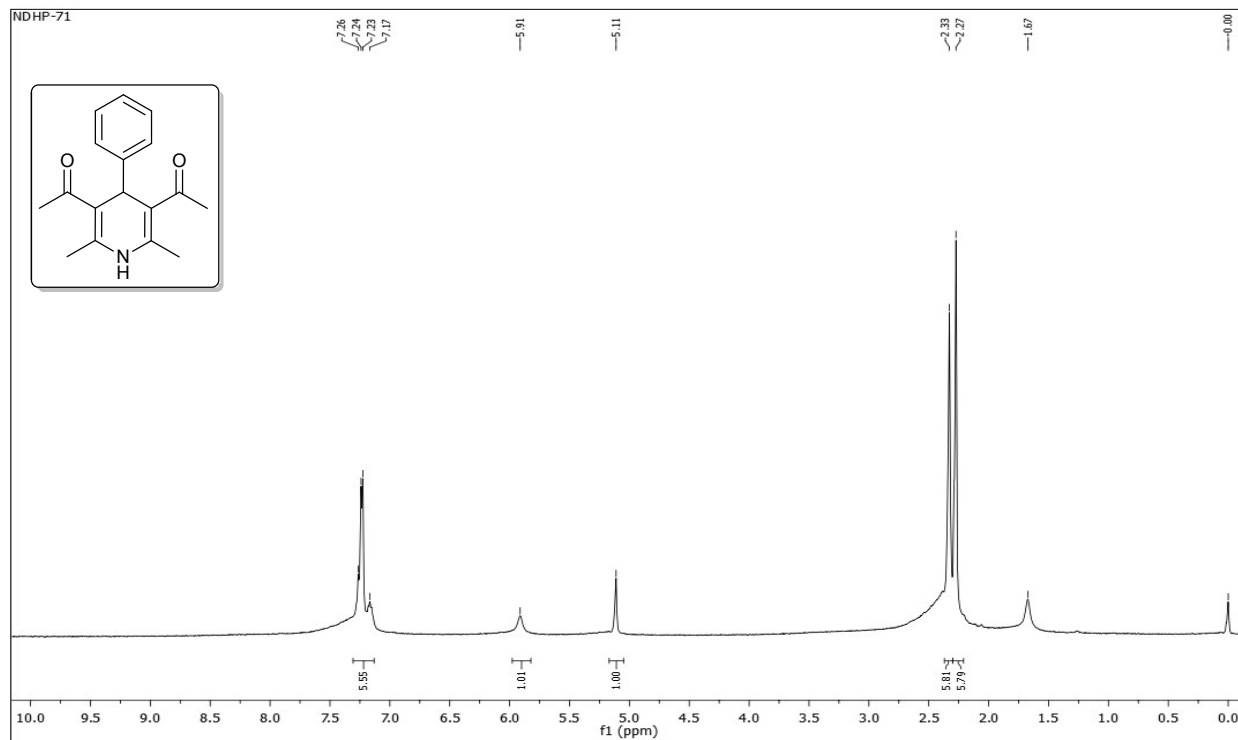


Fig. S67 ^1H NMR spectrum of 1,1'-(2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone **5af** (300 MHz, CDCl_3)

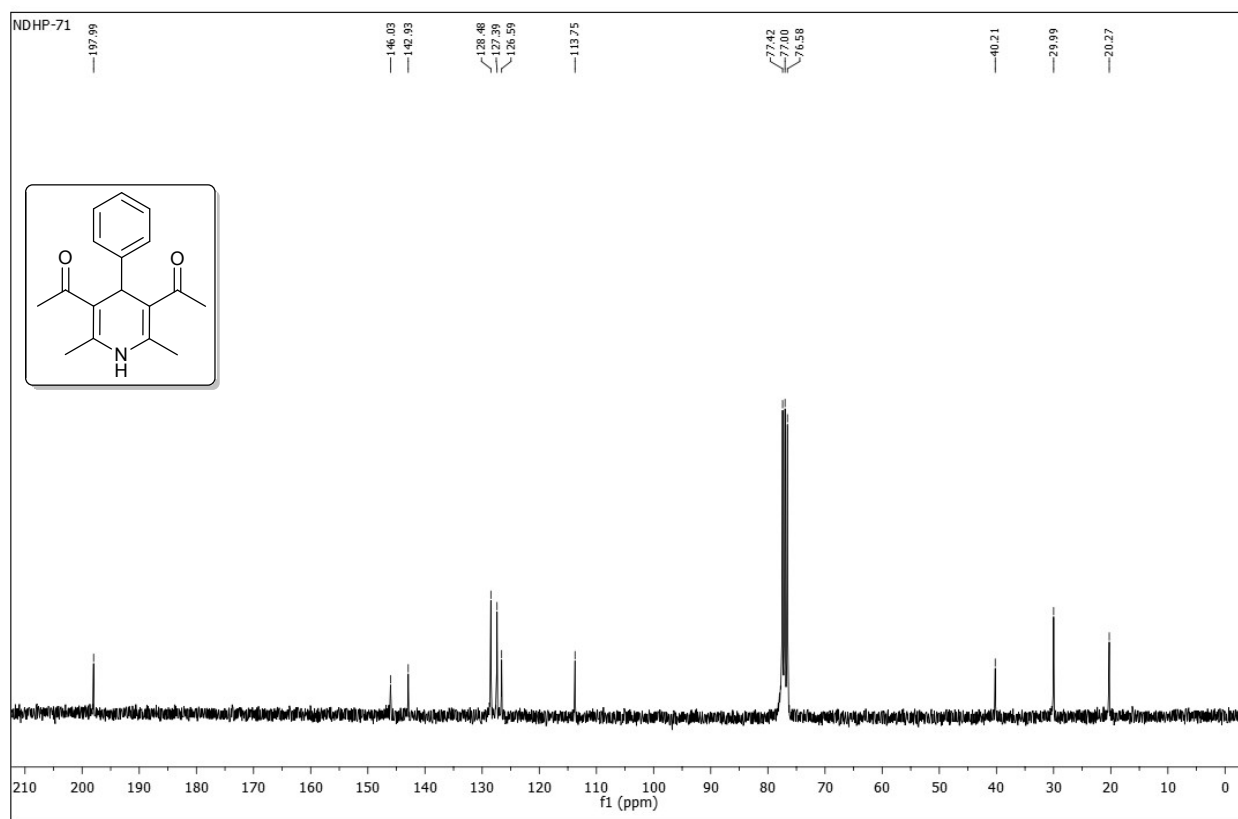


Fig. S68 ^{13}C NMR spectrum of 1,1'-(2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone **5af** (75 MHz, CDCl_3)

4. ESI-MS Spectra of isolated Compounds from 5a – 5af:

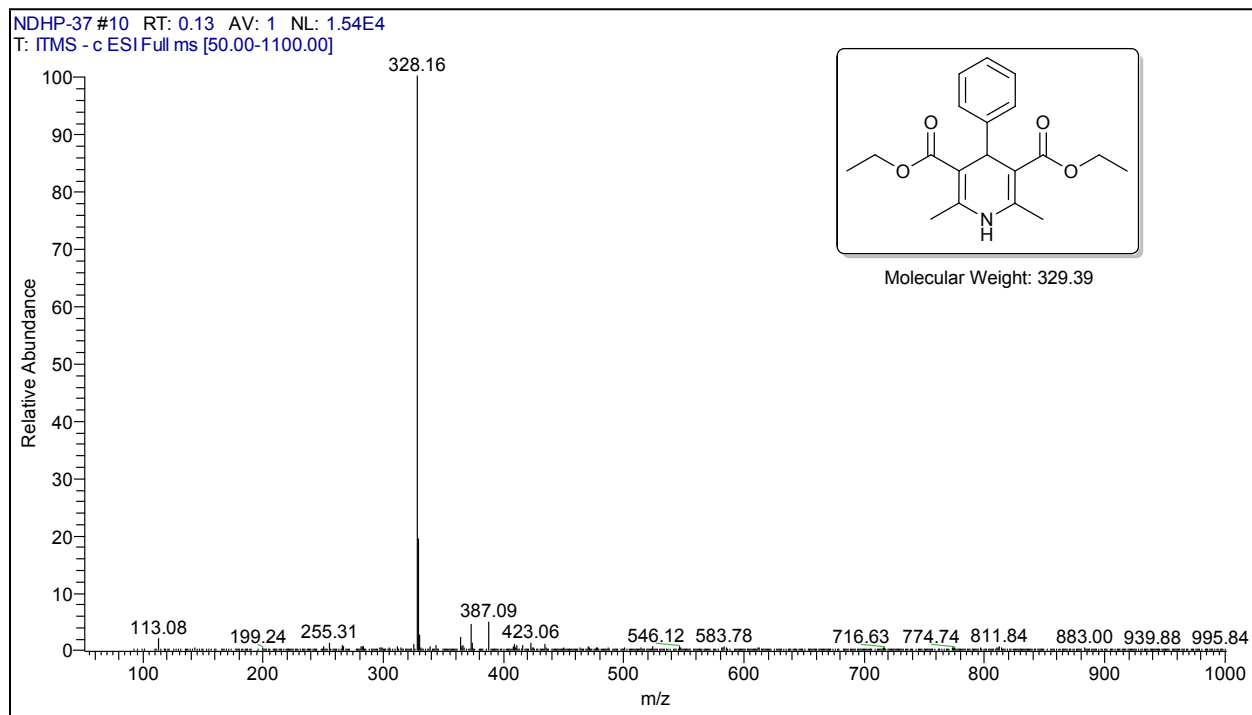


Fig. S69 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5a** (M-1)

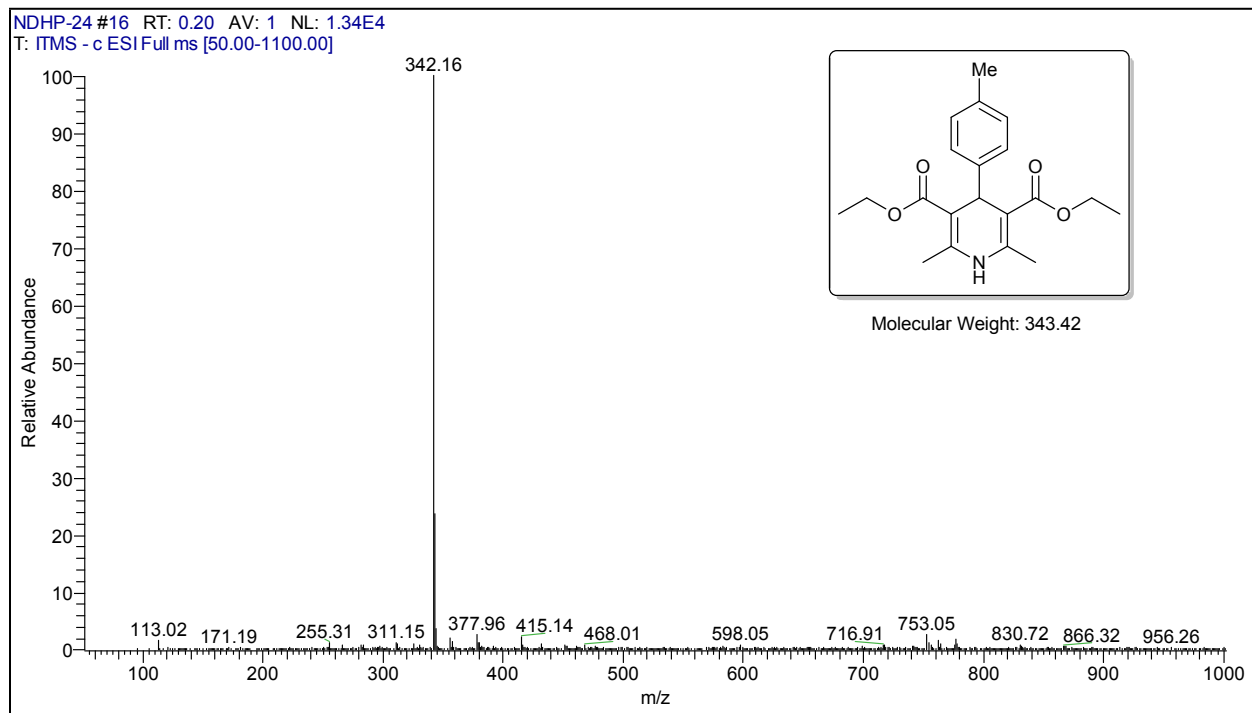


Fig. S70 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(*p*-tolyl)-1,4-dihydropyridine-3,5-dicarboxylate **5b** (M-1)

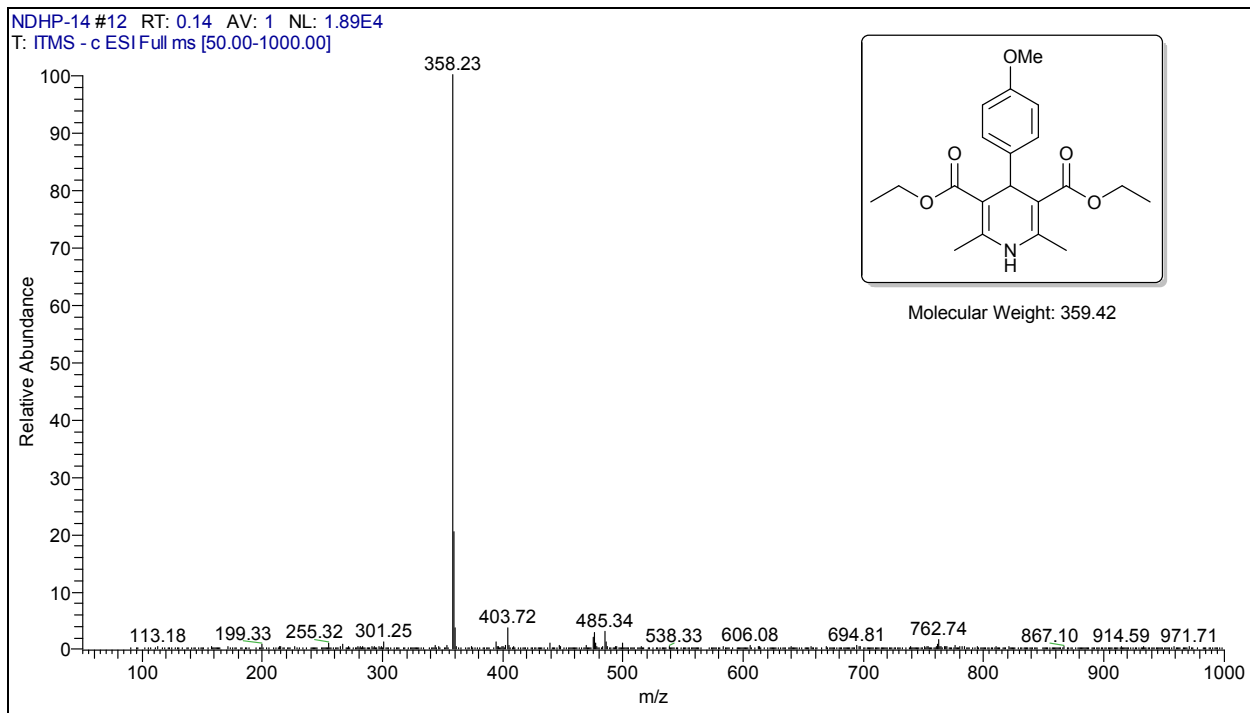


Fig. S71 Mass Spectrum (ESI) of diethyl 4-(4-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5c** (M-1)

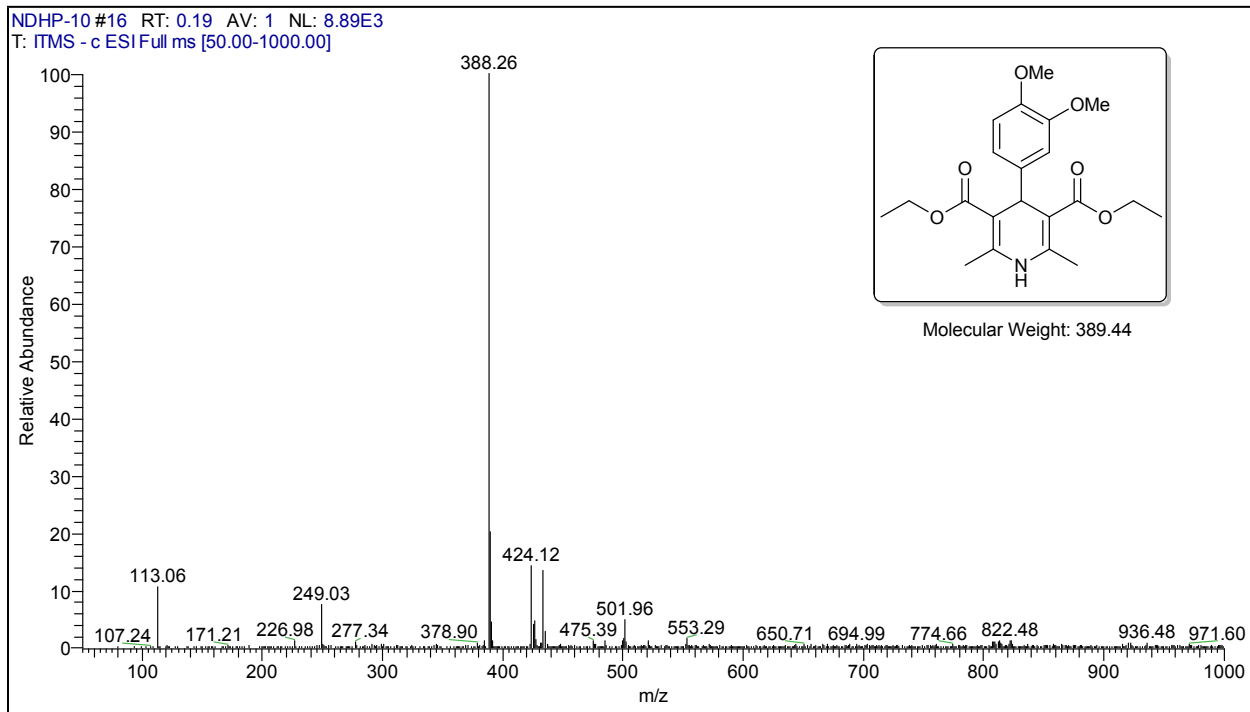


Fig. S72 Mass Spectrum (ESI) of diethyl 4-(3,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5d** (M-1)

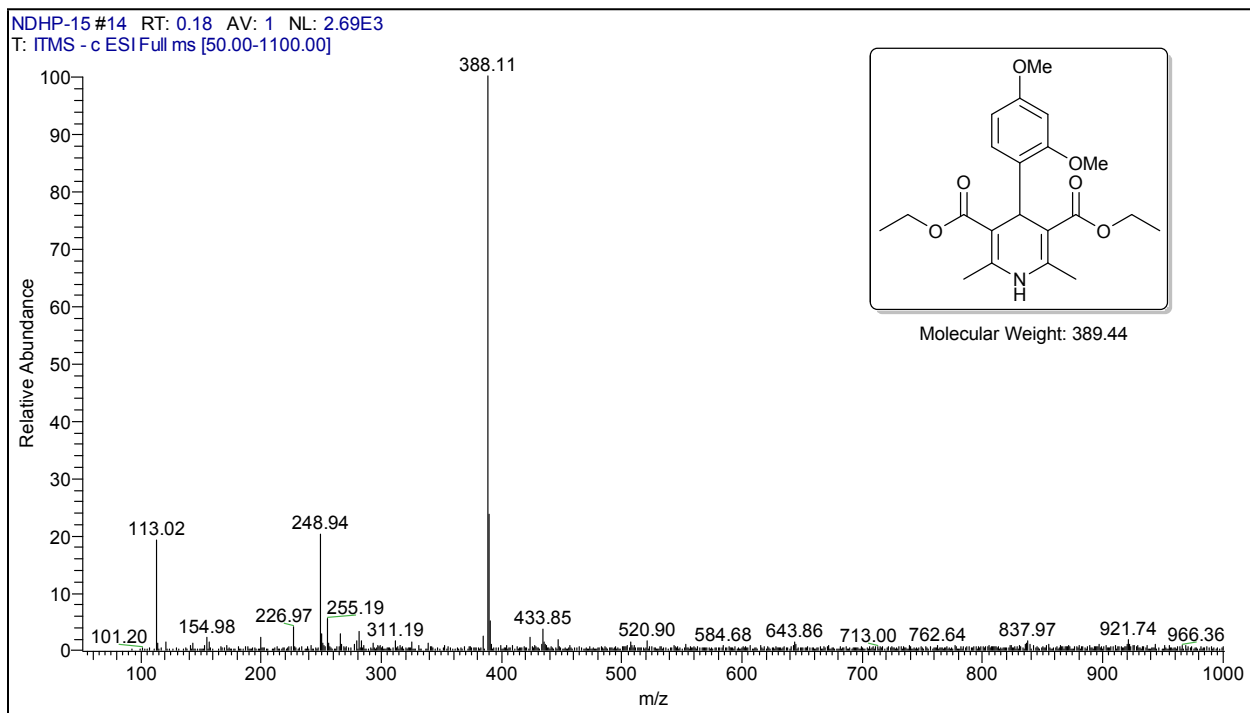


Fig. S73 Mass Spectrum (ESI) of diethyl 4-(2,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5e** (M-1)

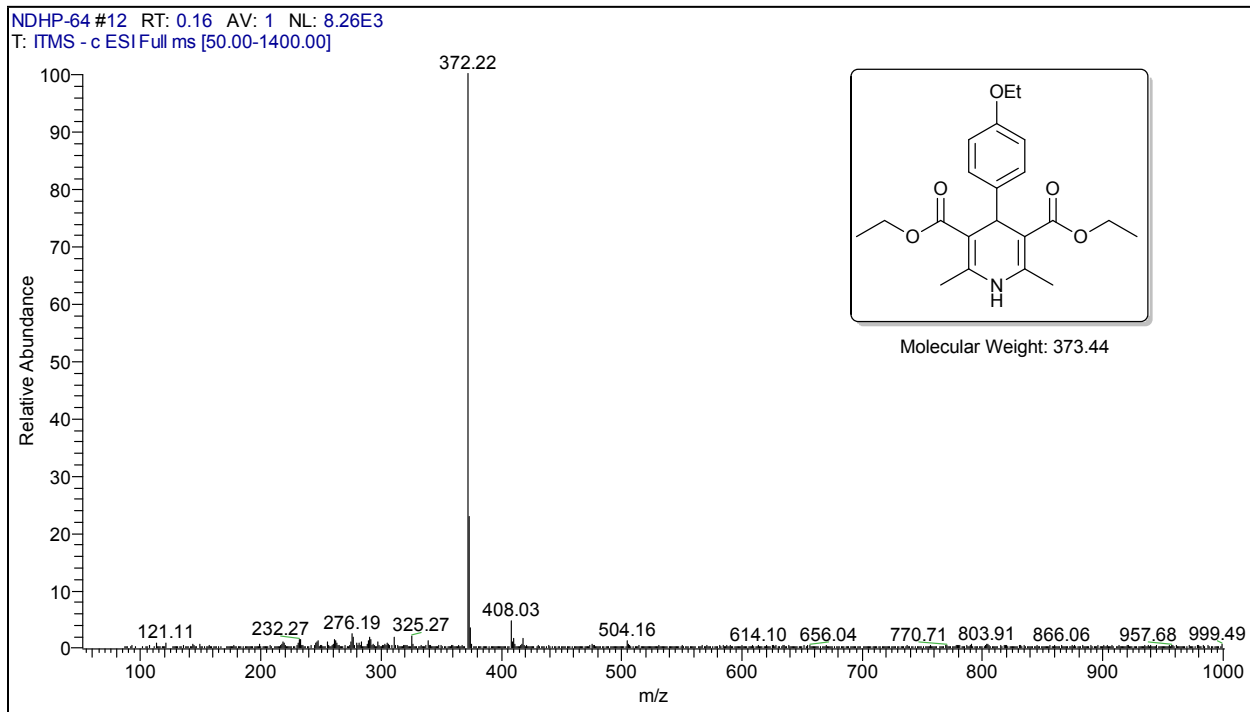


Fig. S74 Mass Spectrum (ESI) of diethyl 4-(4-ethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5f** (M-1)

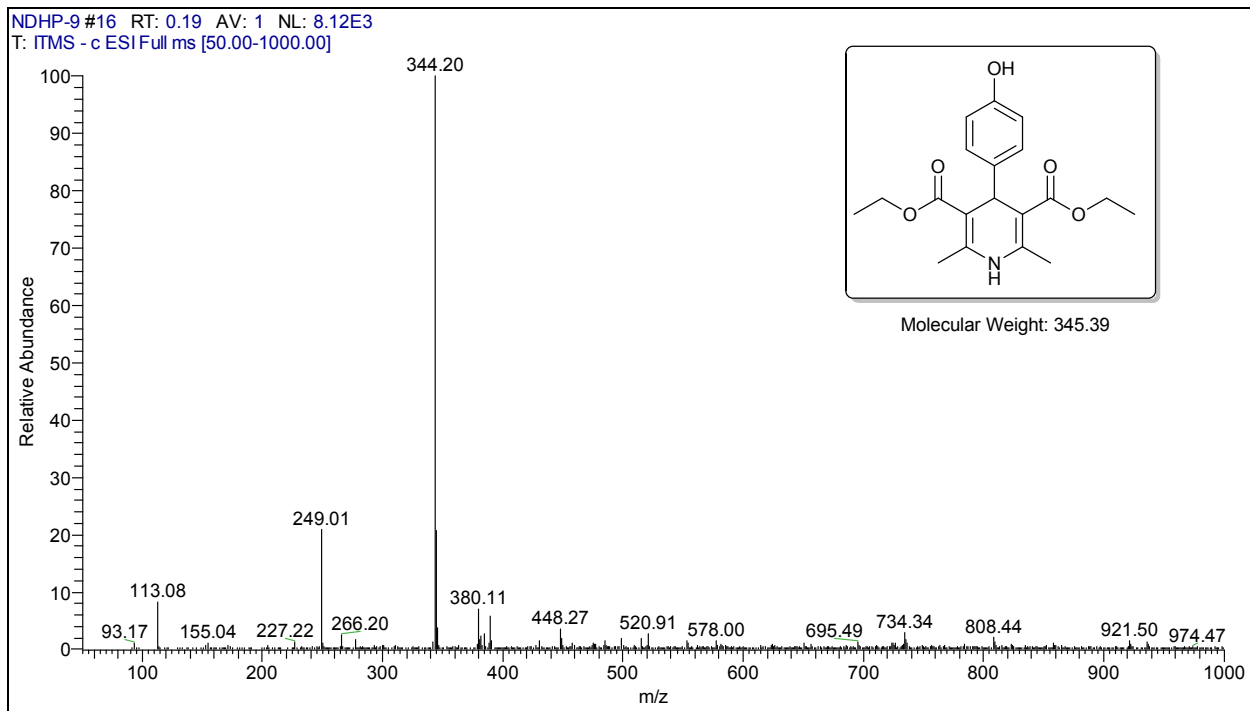


Fig. S75 Mass Spectrum (ESI) of diethyl 4-(4-hydroxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5g** (M-1)

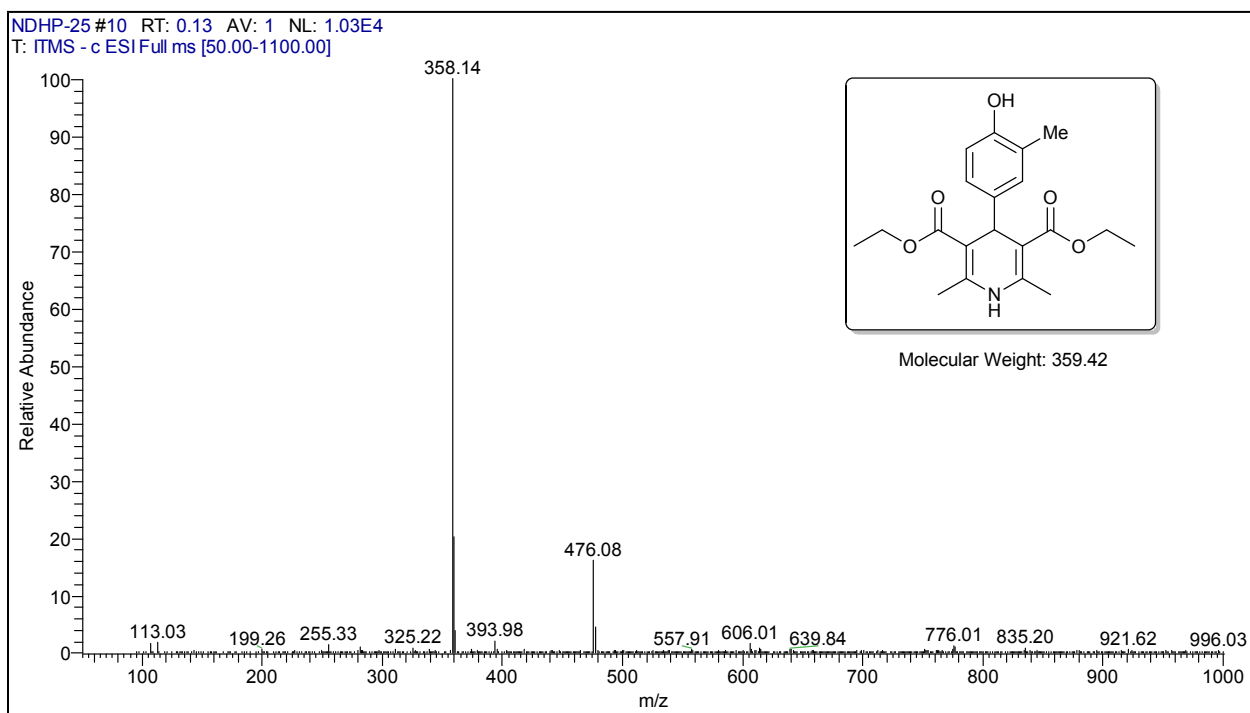


Fig. S76 Mass Spectrum (ESI) of diethyl 4-(4-hydroxy-3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5h** (M-1)

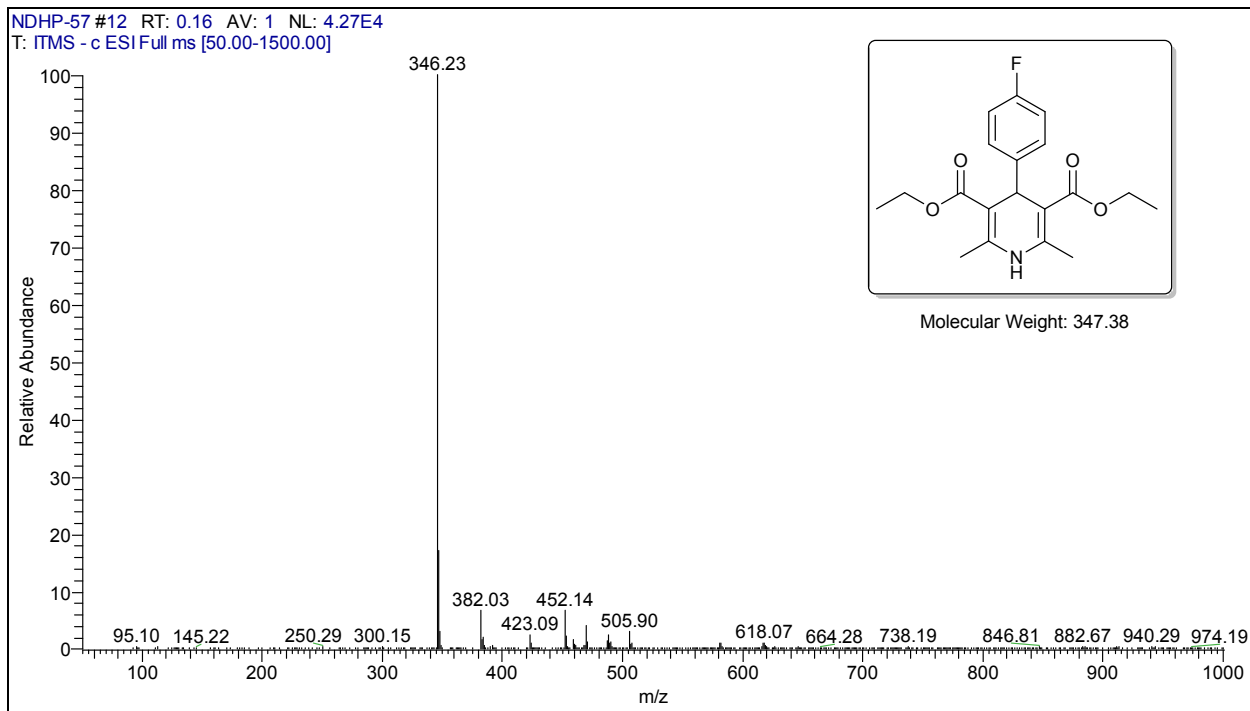


Fig. S77 Mass Spectrum (ESI) of diethyl 4-(4-fluorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5i** (M-1)

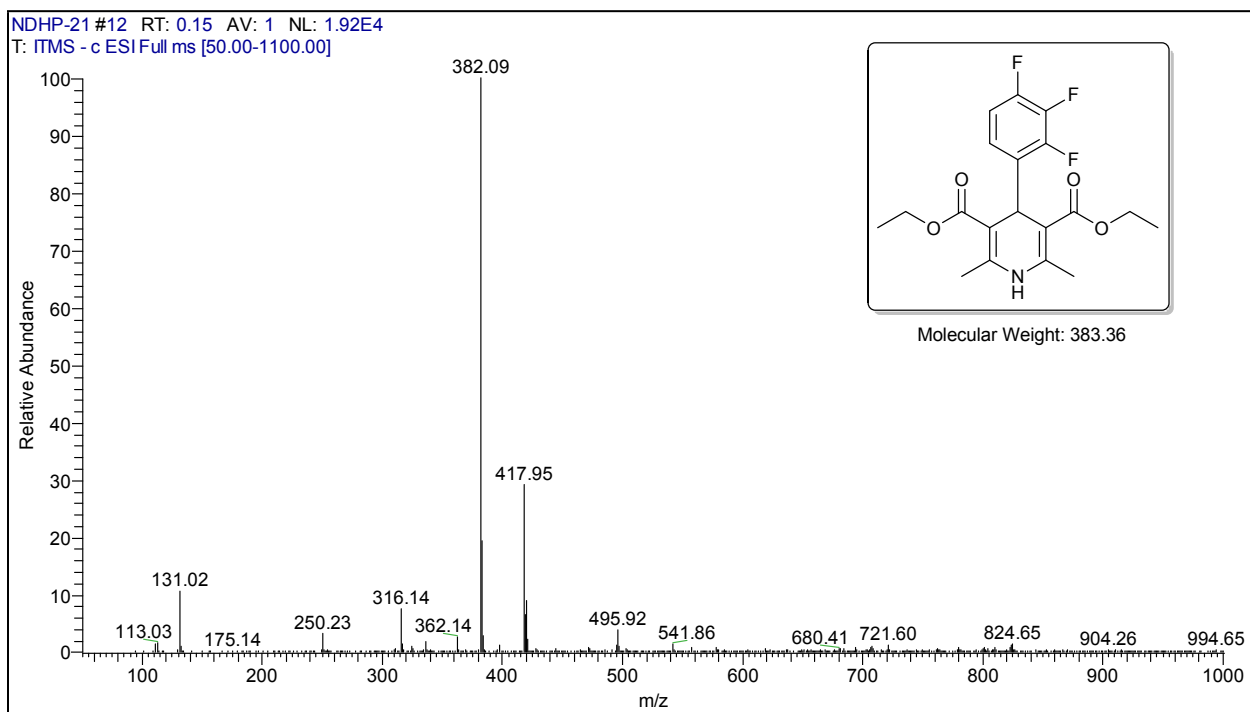


Fig. S78 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(2,3,4-trifluorophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5j** (M-1)

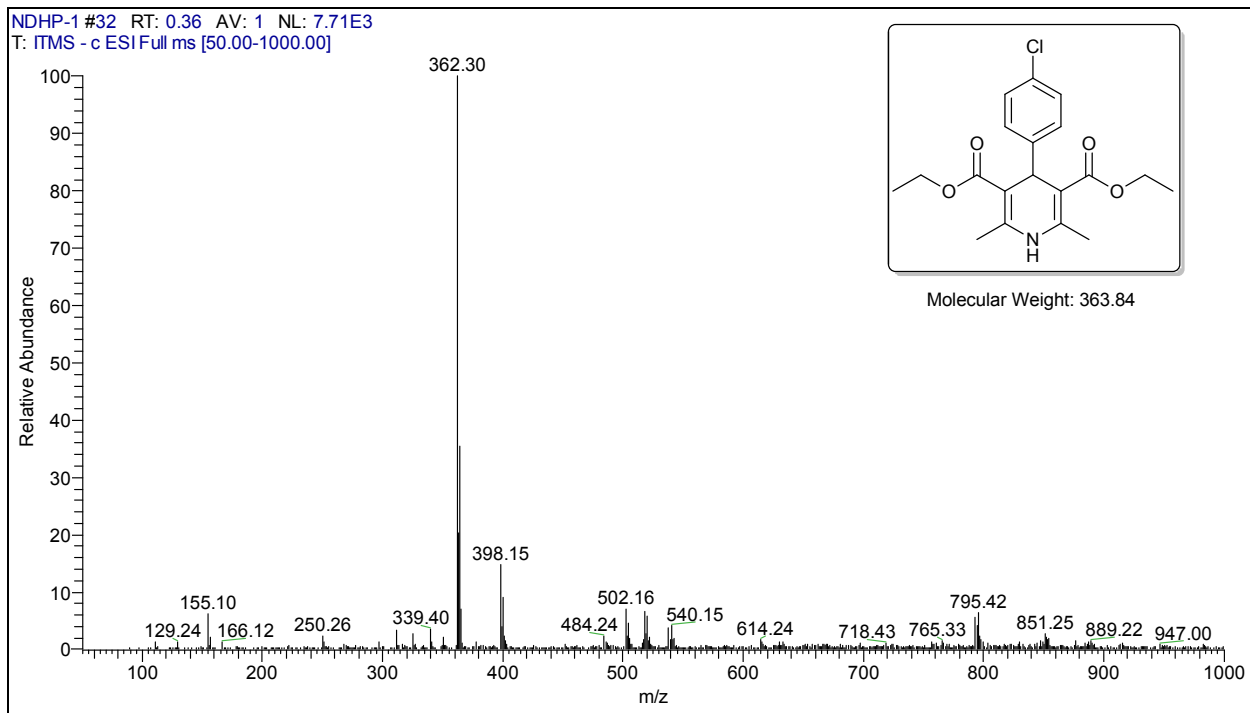


Fig. S79 Mass Spectrum (ESI) of diethyl 4-(4-chlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5k** (M-1)

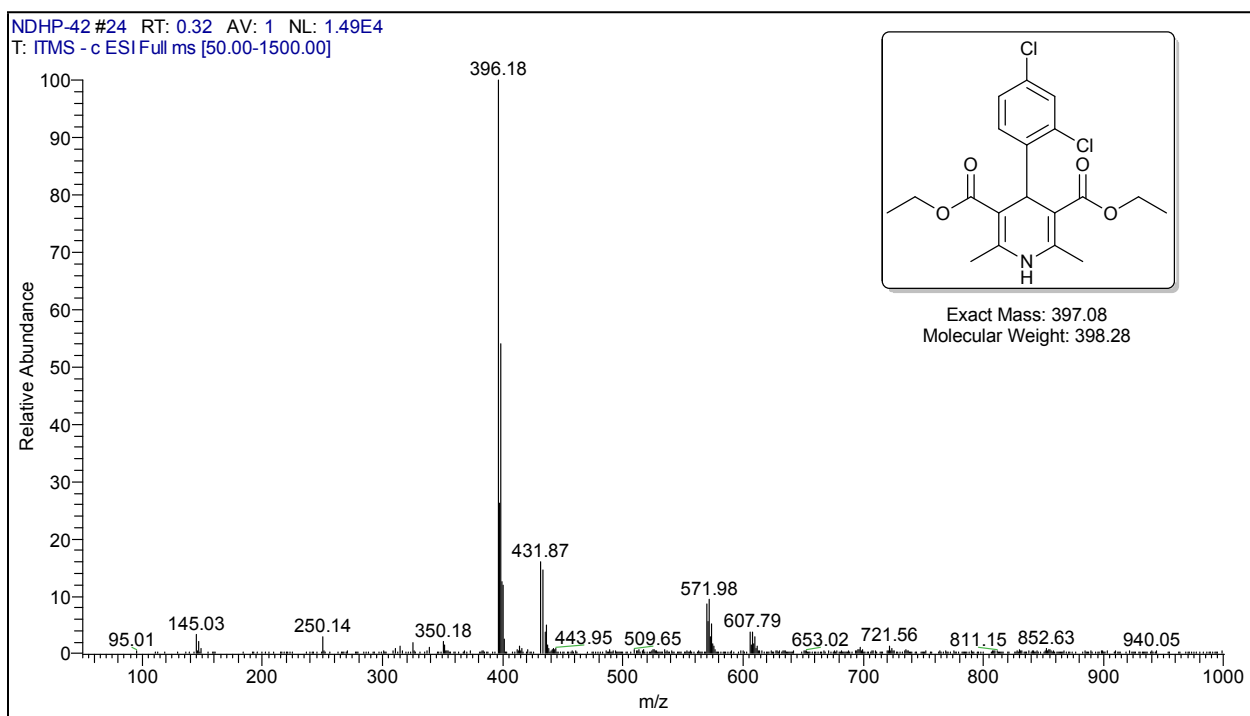


Fig. S80 Mass Spectrum (ESI) of diethyl 4-(2,4-dichlorophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5l** (M-1)

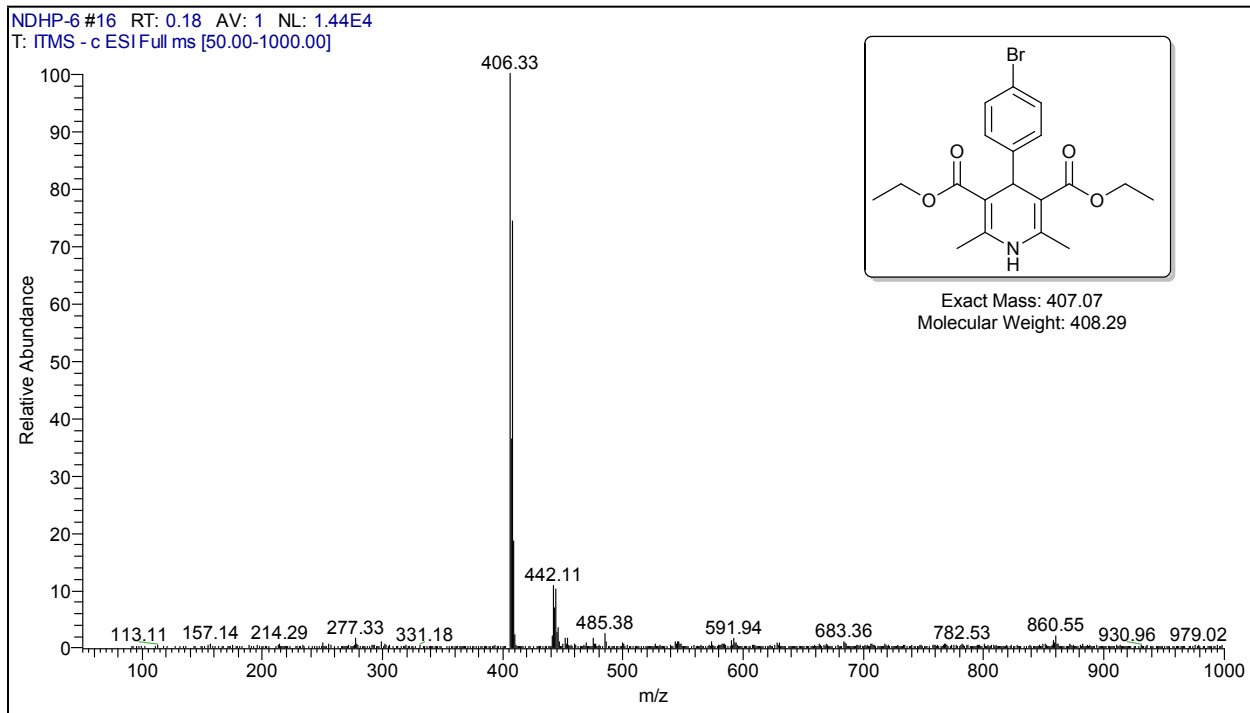


Fig. S81 Mass Spectrum (ESI) of diethyl 4-(4-bromophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5m** (M-1)

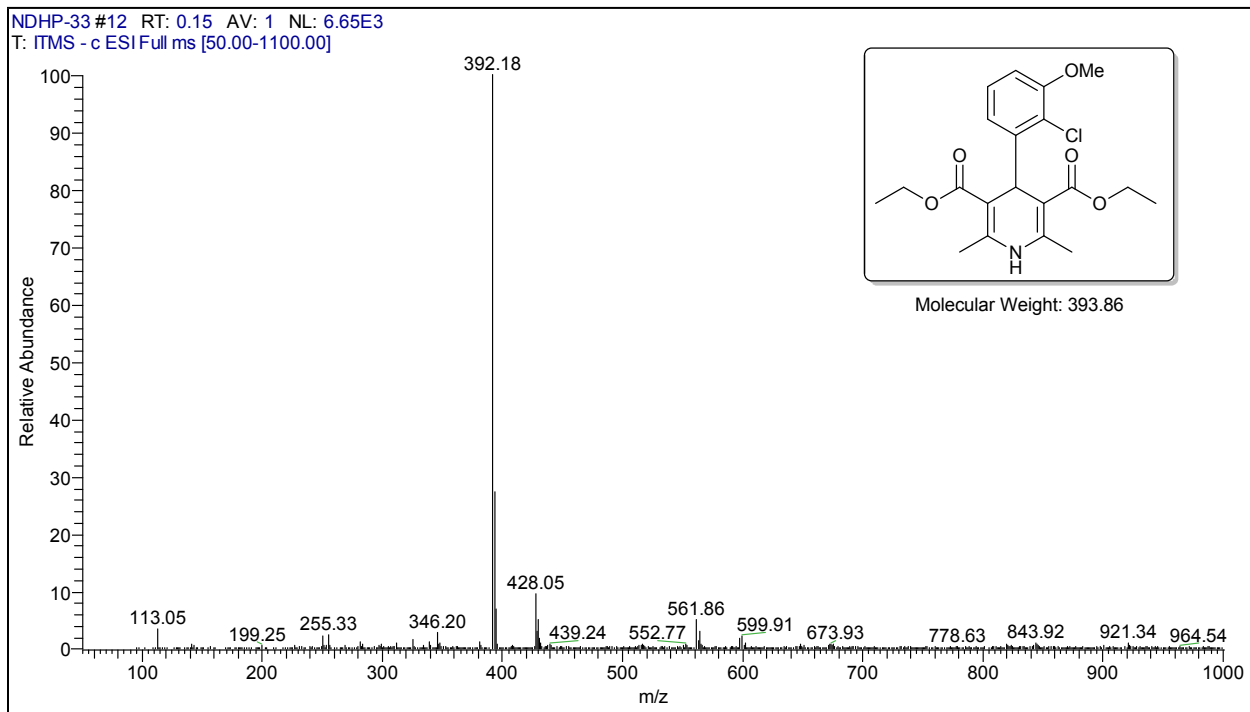


Fig. S82 Mass Spectrum (ESI) of diethyl 4-(2-chloro-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5n** (M-1)

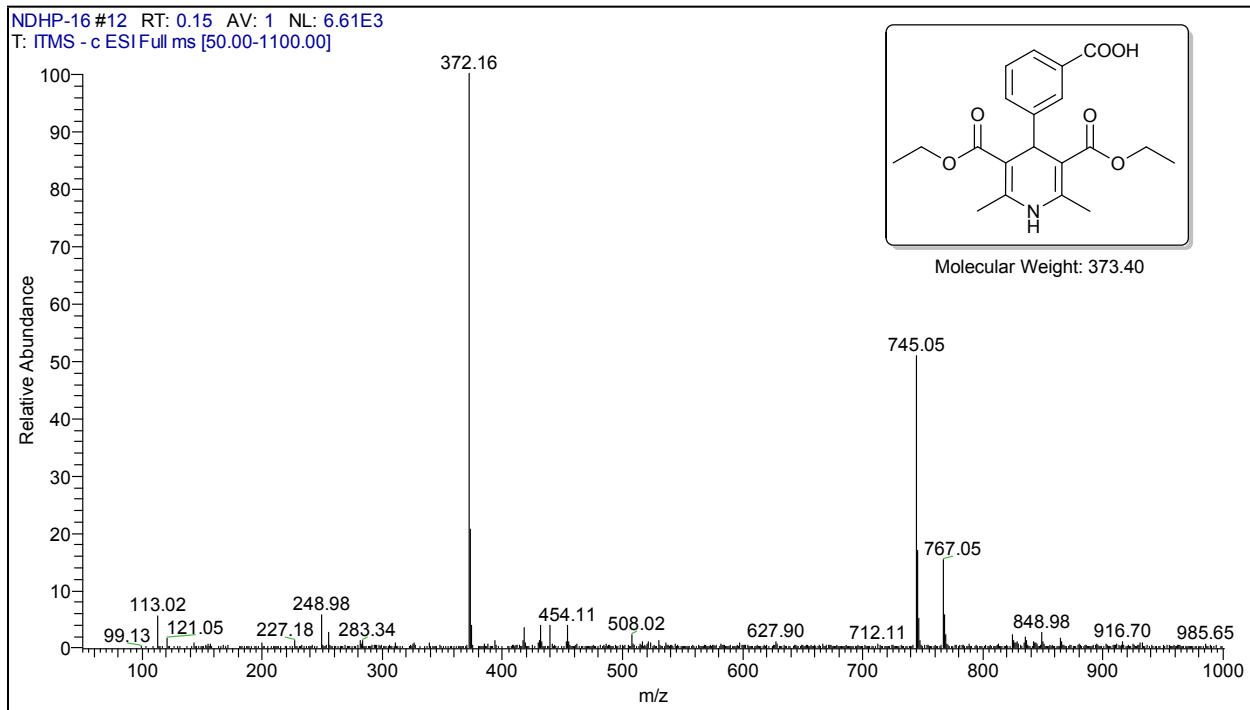


Fig. S83 Mass Spectrum (ESI) of 3-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)benzoic acid **5o** (M-1)

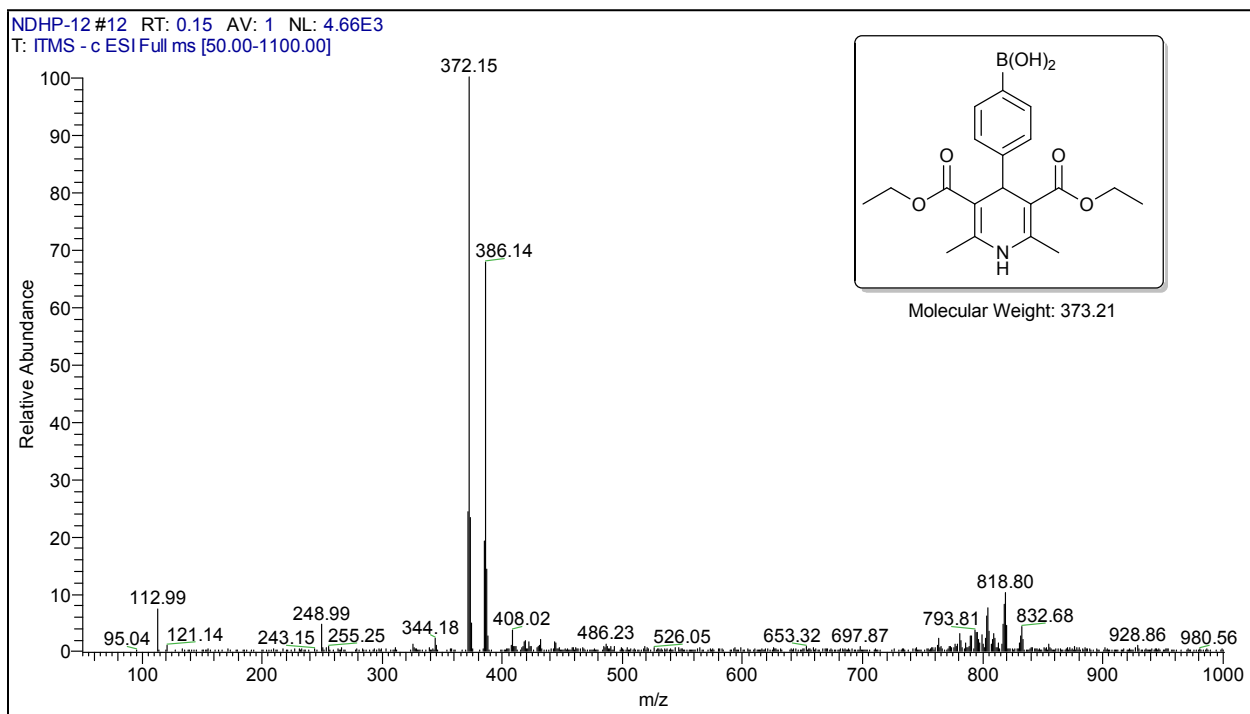


Fig. S84 Mass Spectrum (ESI) of (4-(3,5-bis(ethoxycarbonyl)-2,6-dimethyl-1,4-dihydropyridin-4-yl)phenyl)boronic acid **5p** (M-1)

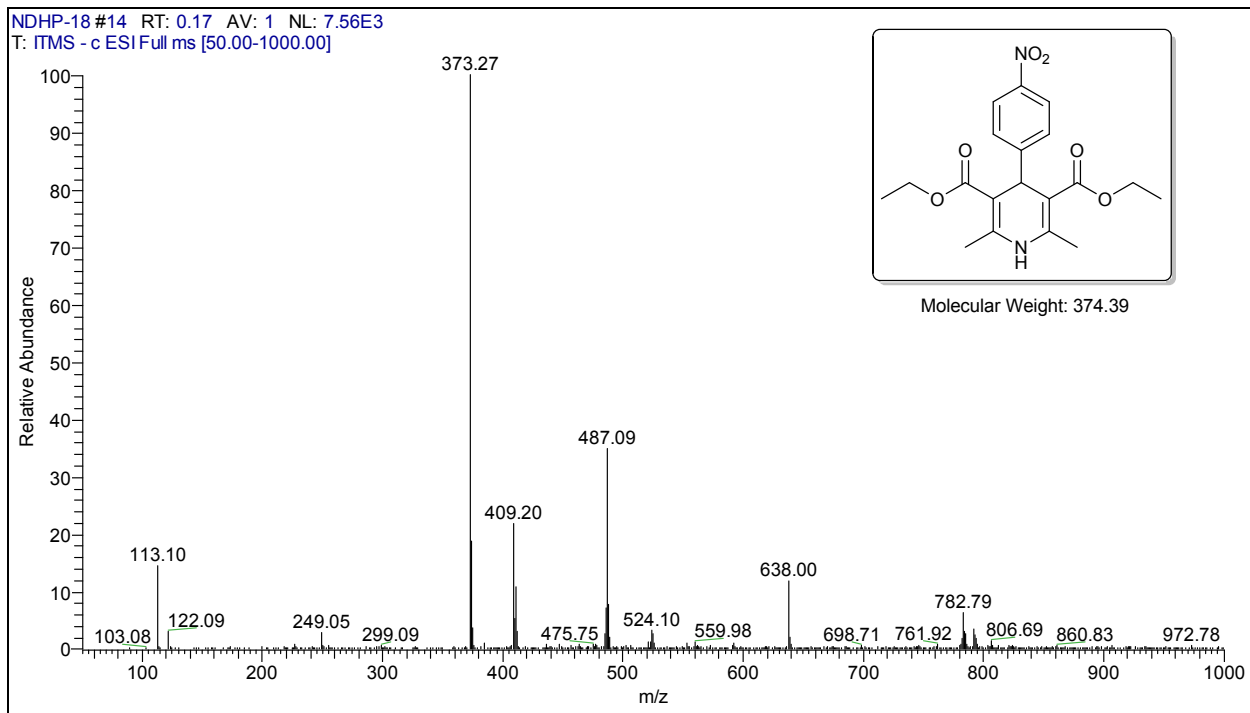


Fig. S85 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5q** (M-1)

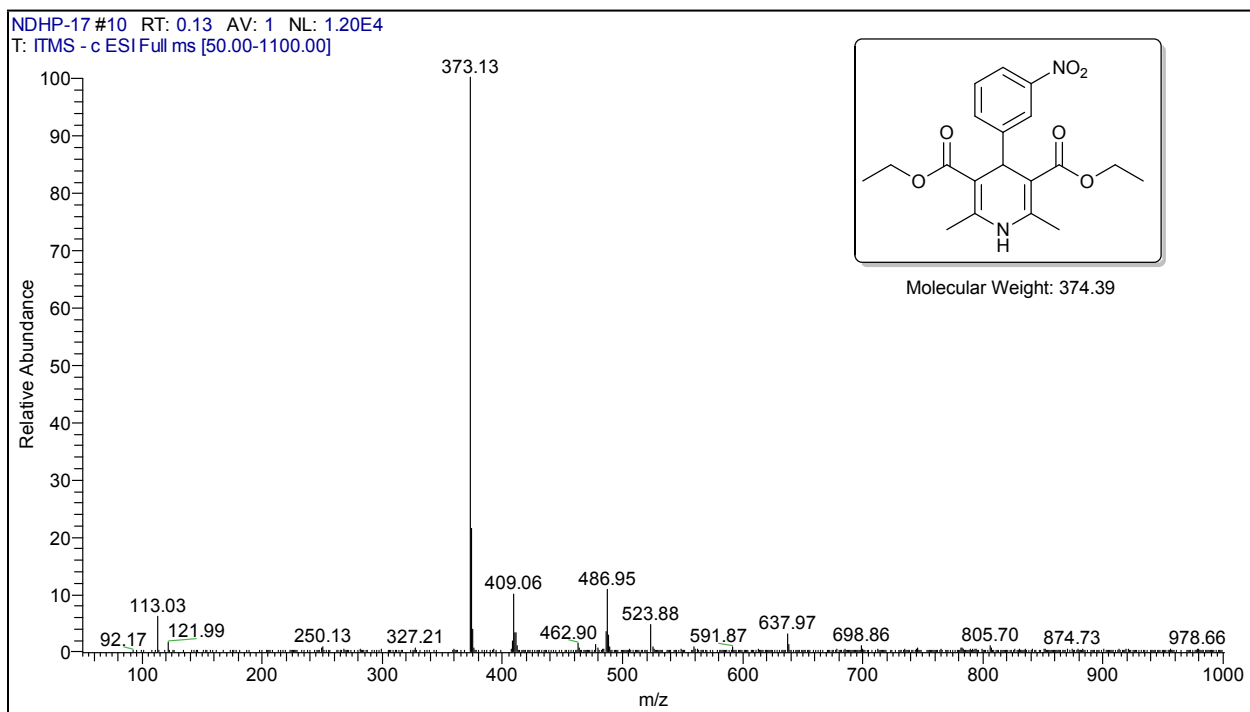


Fig. S86 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(3-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5r** (M-1)

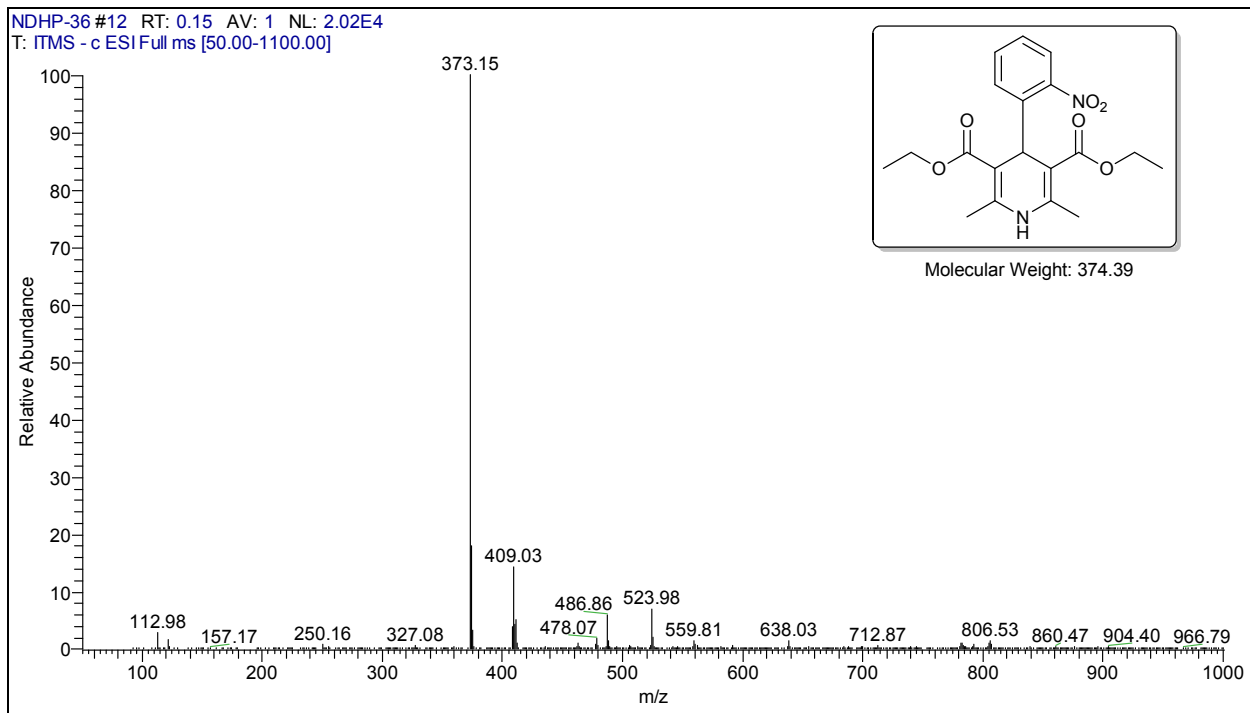


Fig. S87 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate **5s** (M-1)

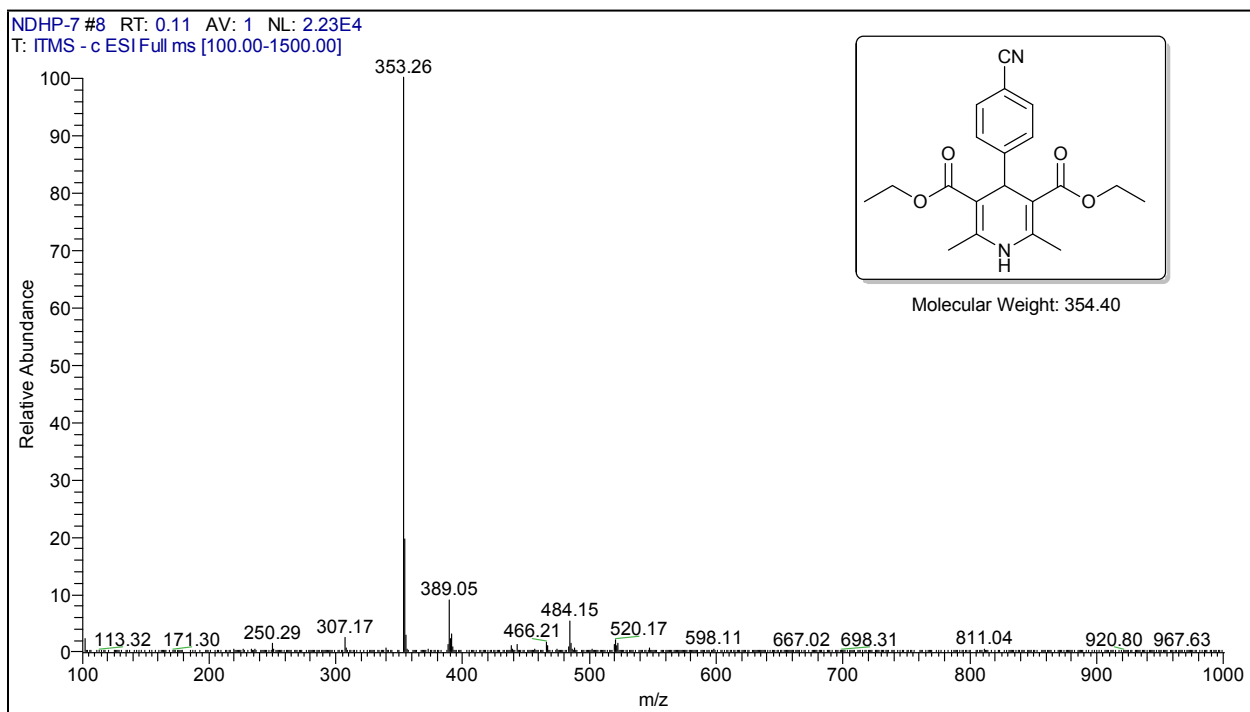


Fig. S88 Mass Spectrum (ESI) of diethyl 4-(4-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5t** (M-1)

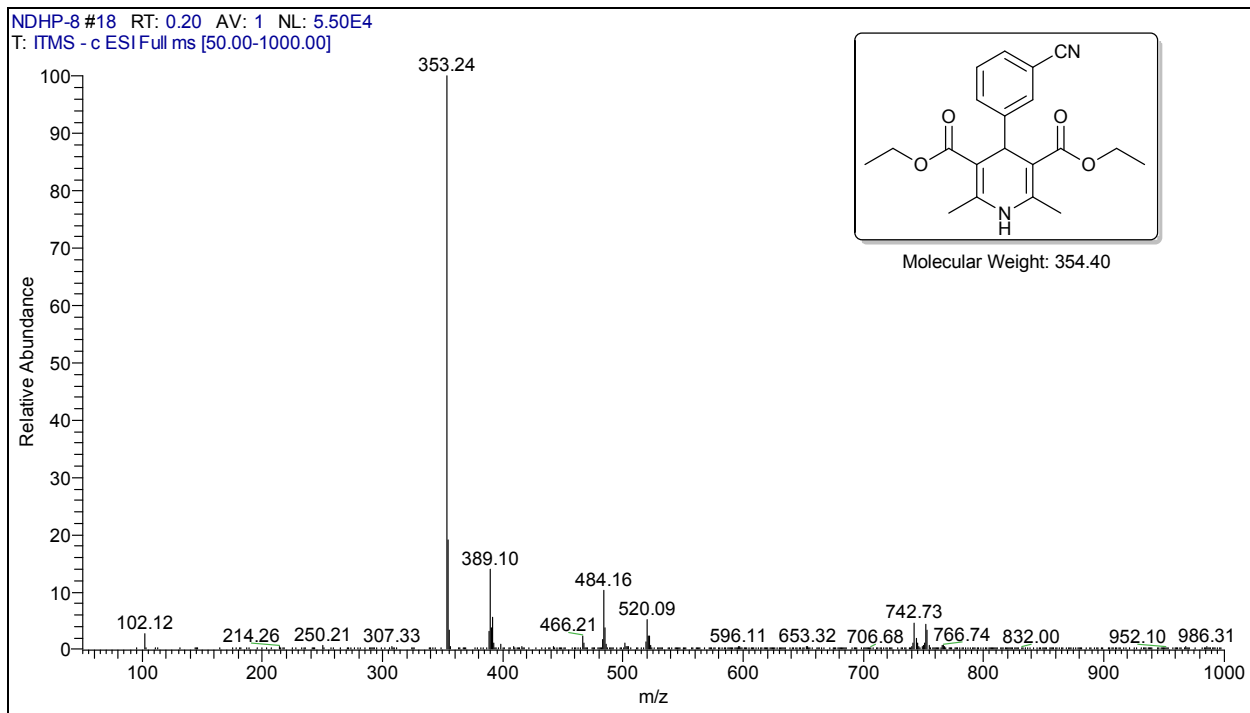


Fig. S89 Mass Spectrum (ESI) of diethyl 4-(3-cyanophenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5u** (M-1)

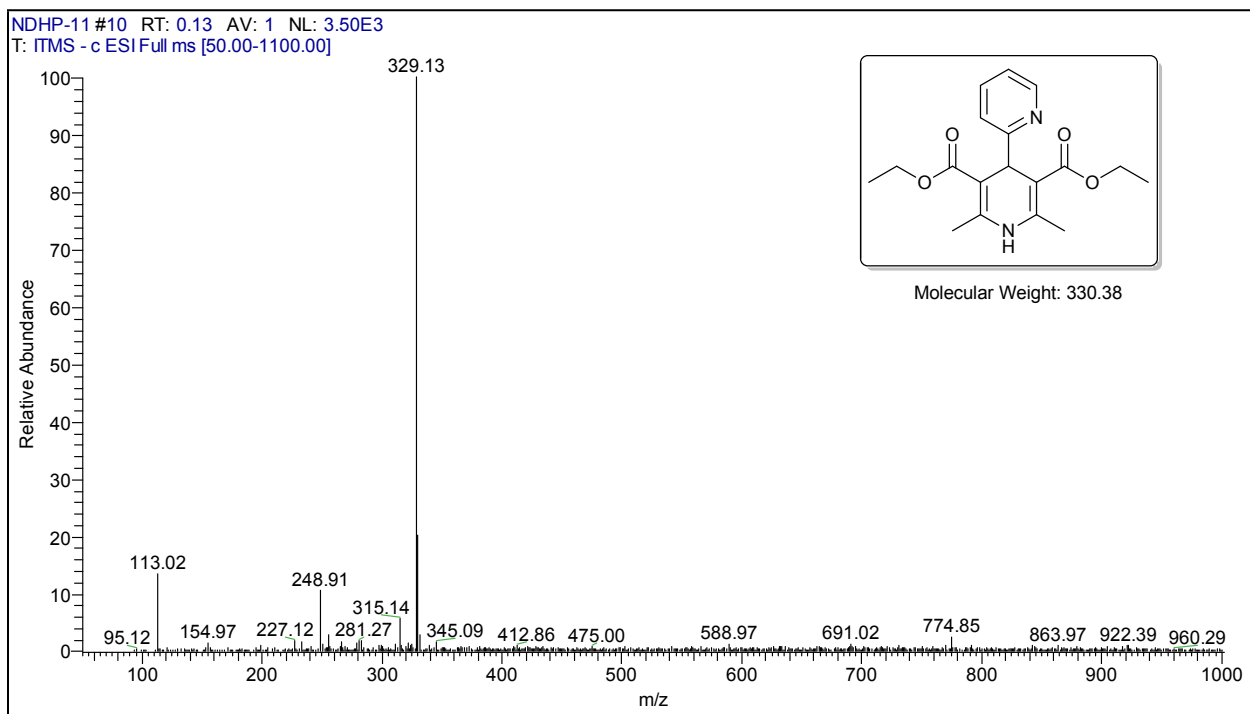


Fig. S90 Mass Spectrum (ESI) of diethyl 2',6'-dimethyl-1',4'-dihydro-[2,4'-bipyridine]-3',5'-dicarboxylate **5v** (M-1)

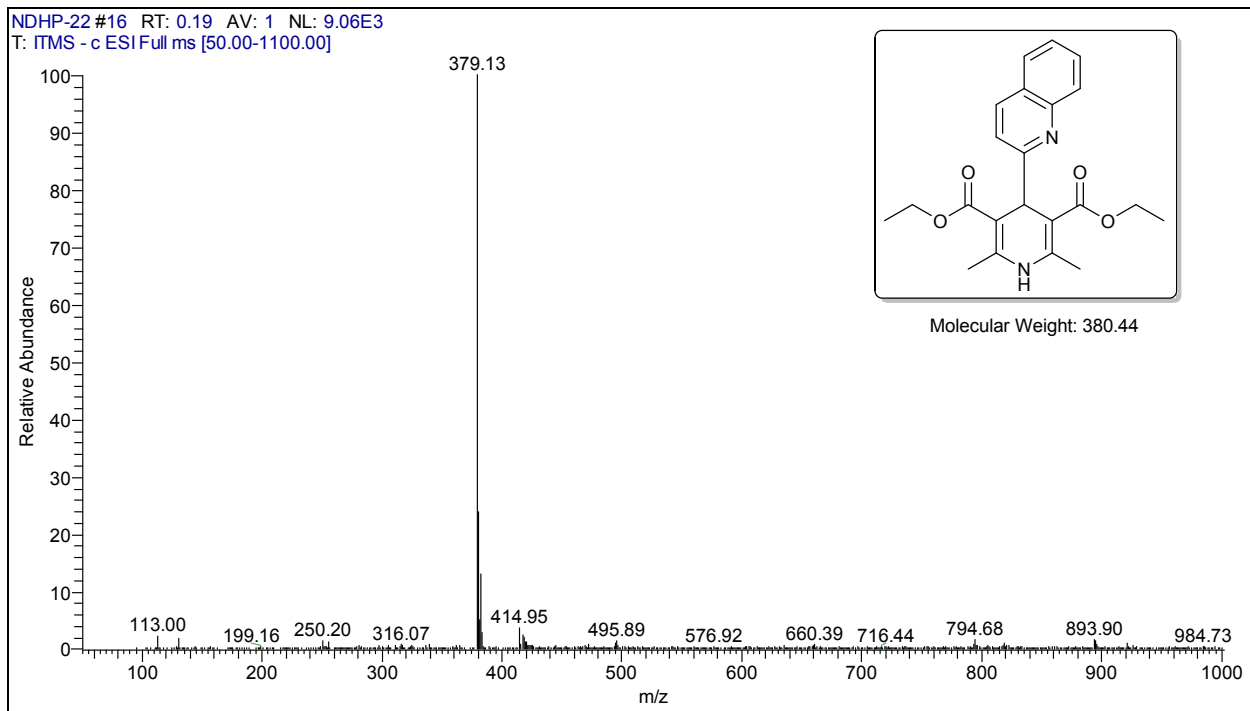


Fig. S91 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(quinolin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5w** (M-1)

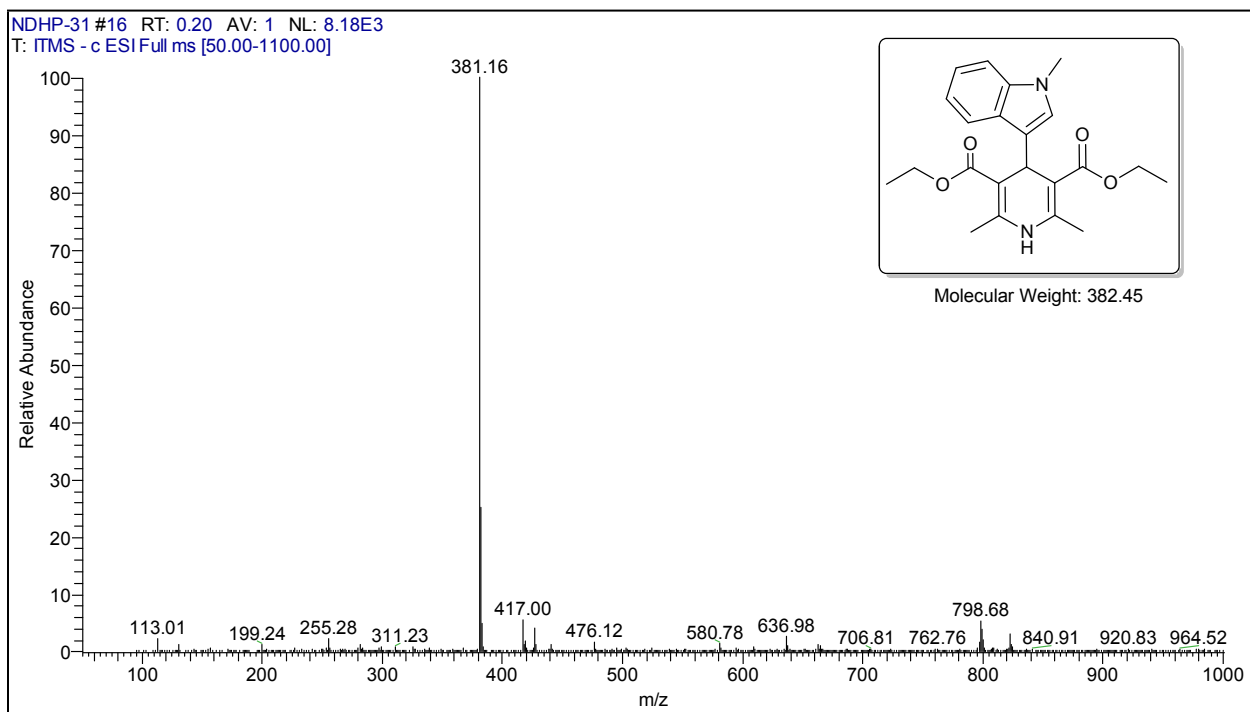


Fig. S92 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(1-methyl-1H-indol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5x** (M-1)

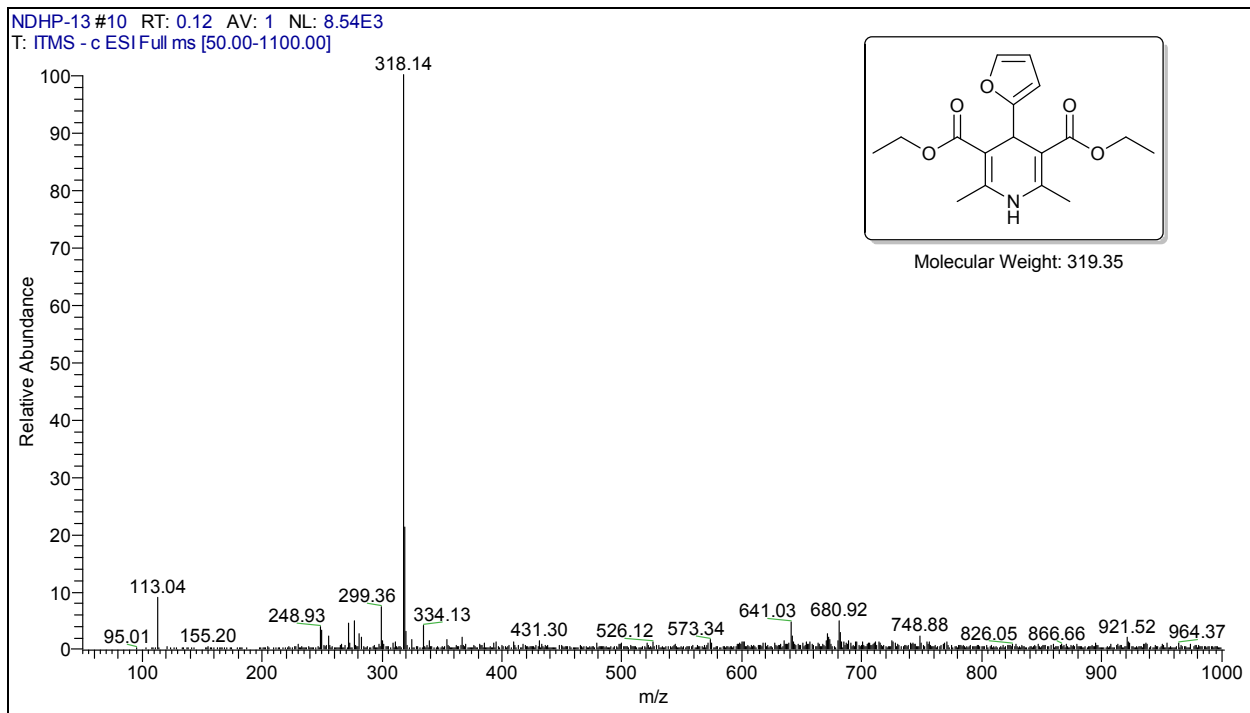


Fig. S93 Mass Spectrum (ESI) of diethyl 4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5y** (M-1)

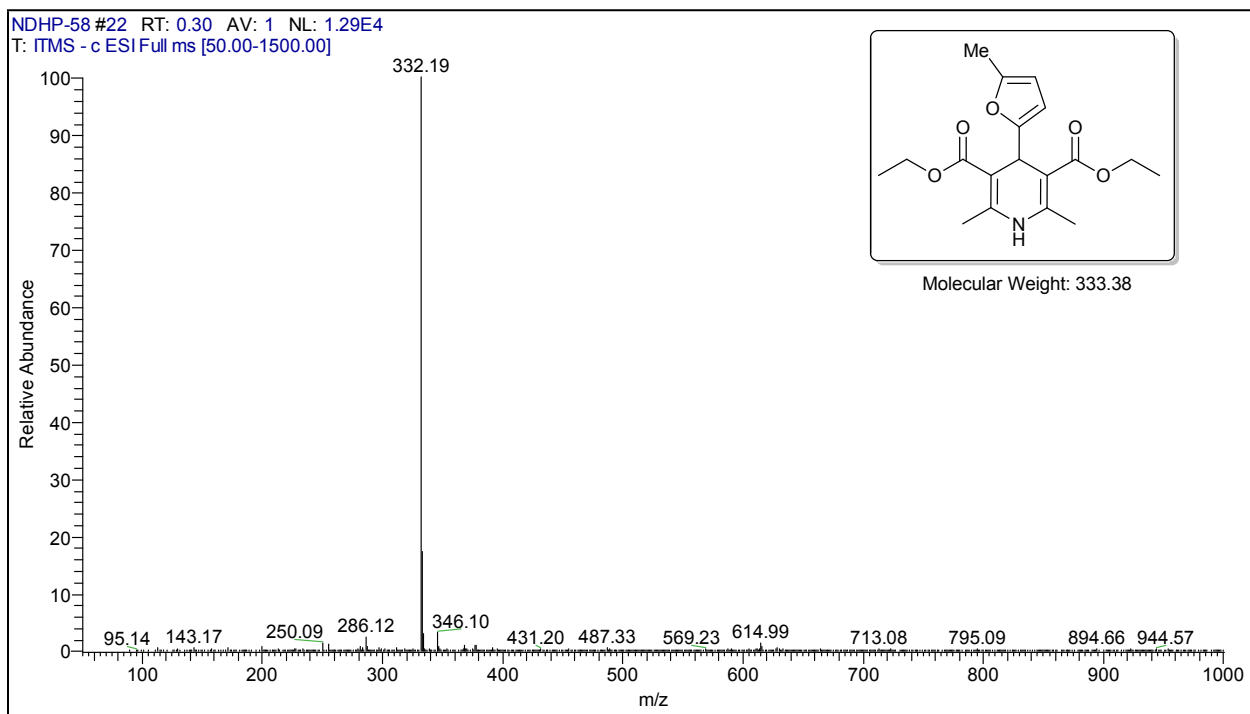


Fig. S94 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-(5-methylfuran-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5z** (M-1)

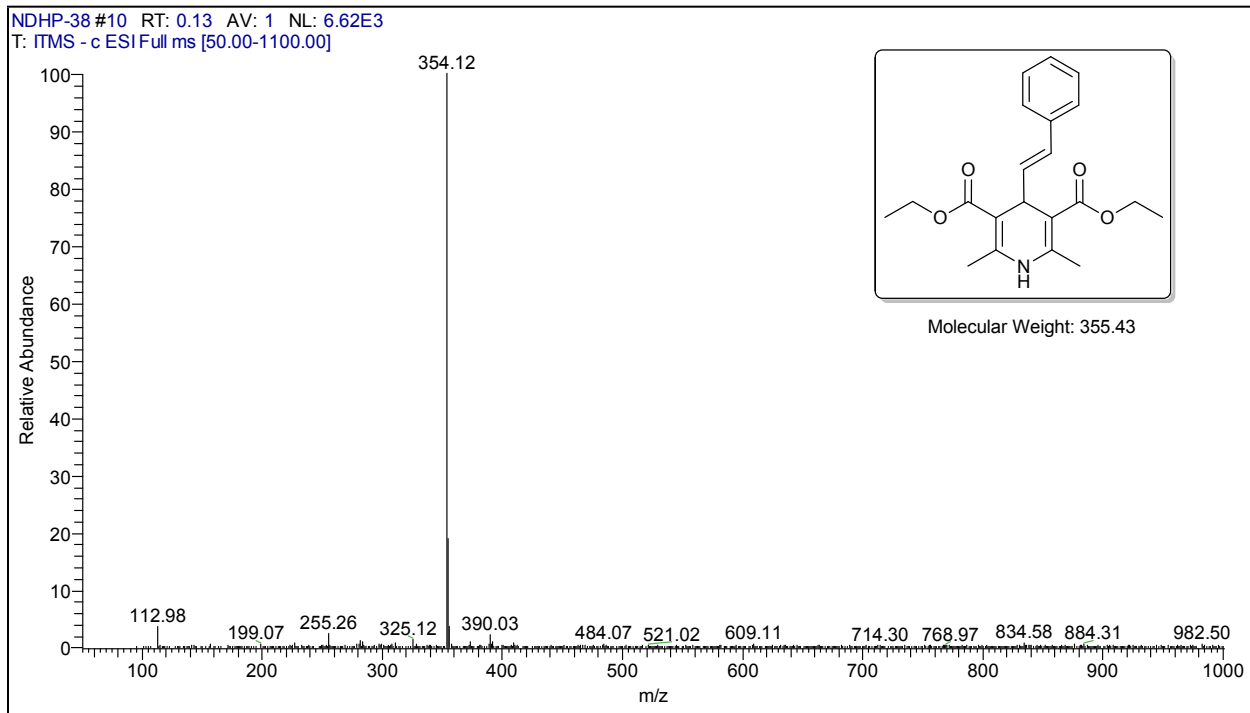


Fig. S95 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-4-styryl-1,4-dihydropyridine-3,5-dicarboxylate **5aa** (M-1)

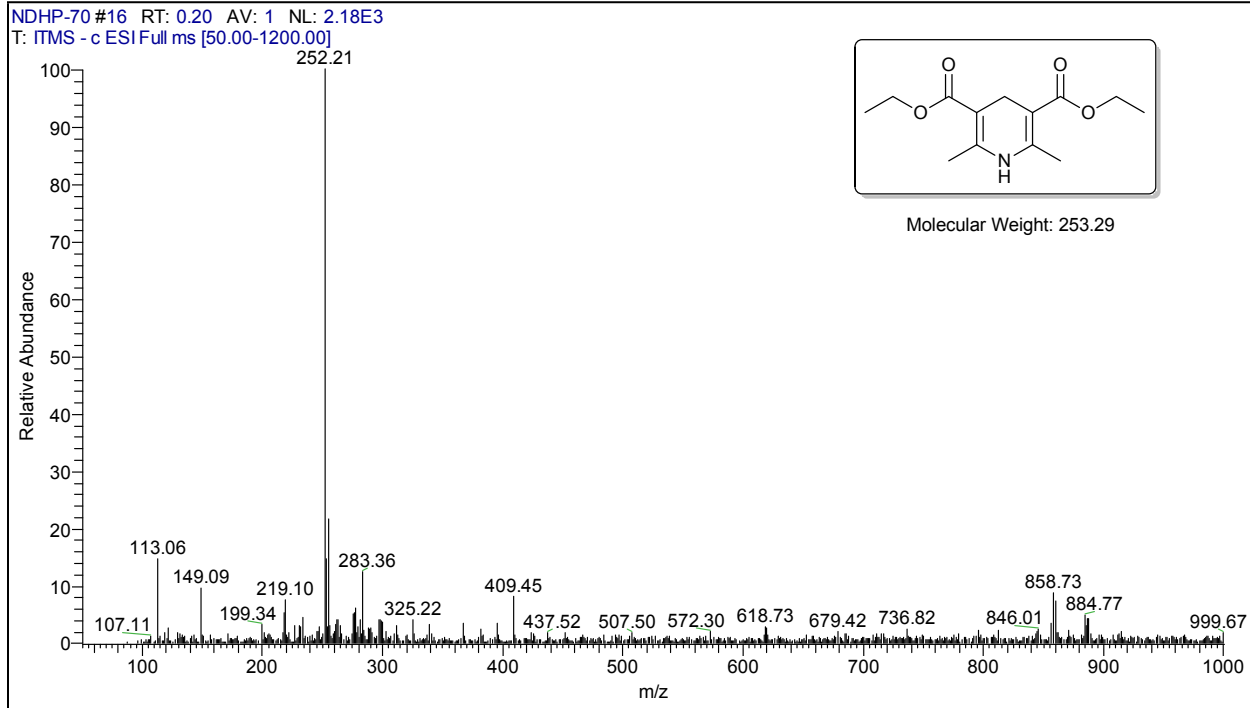


Fig. S96 Mass Spectrum (ESI) of diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ab** (M-1)

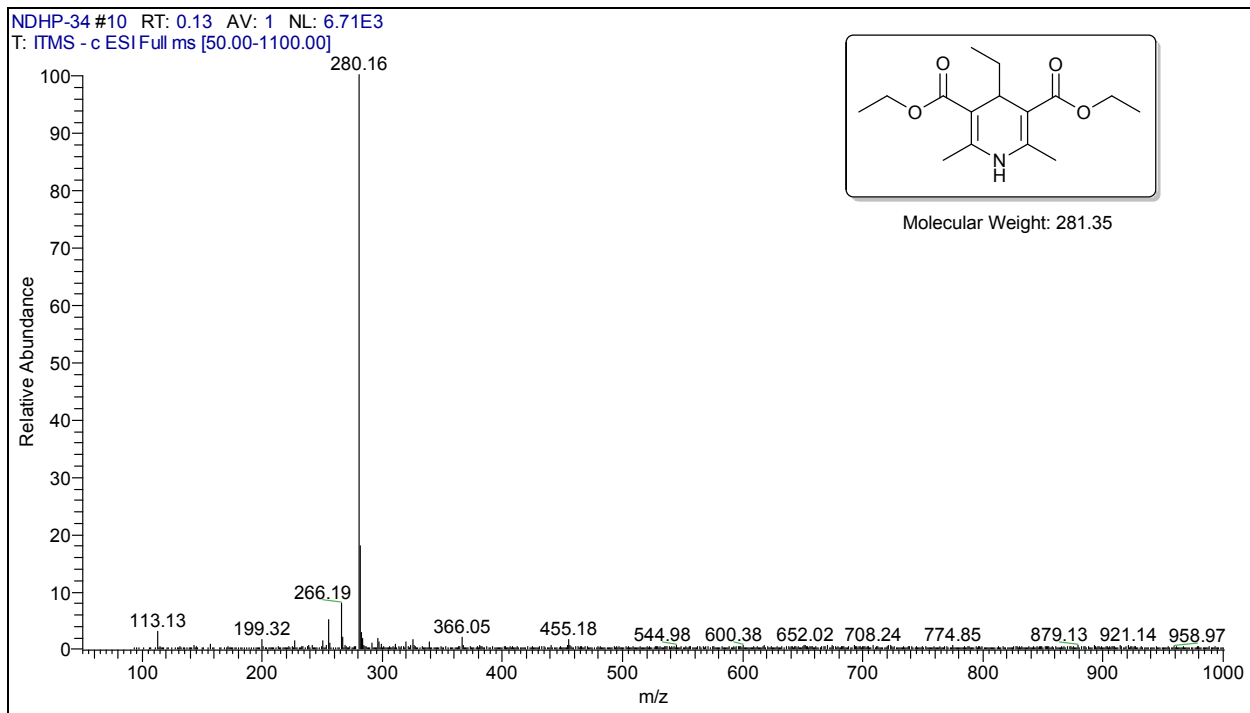


Fig. S97 Mass Spectrum (ESI) of diethyl 4-ethyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ac** (M-1)

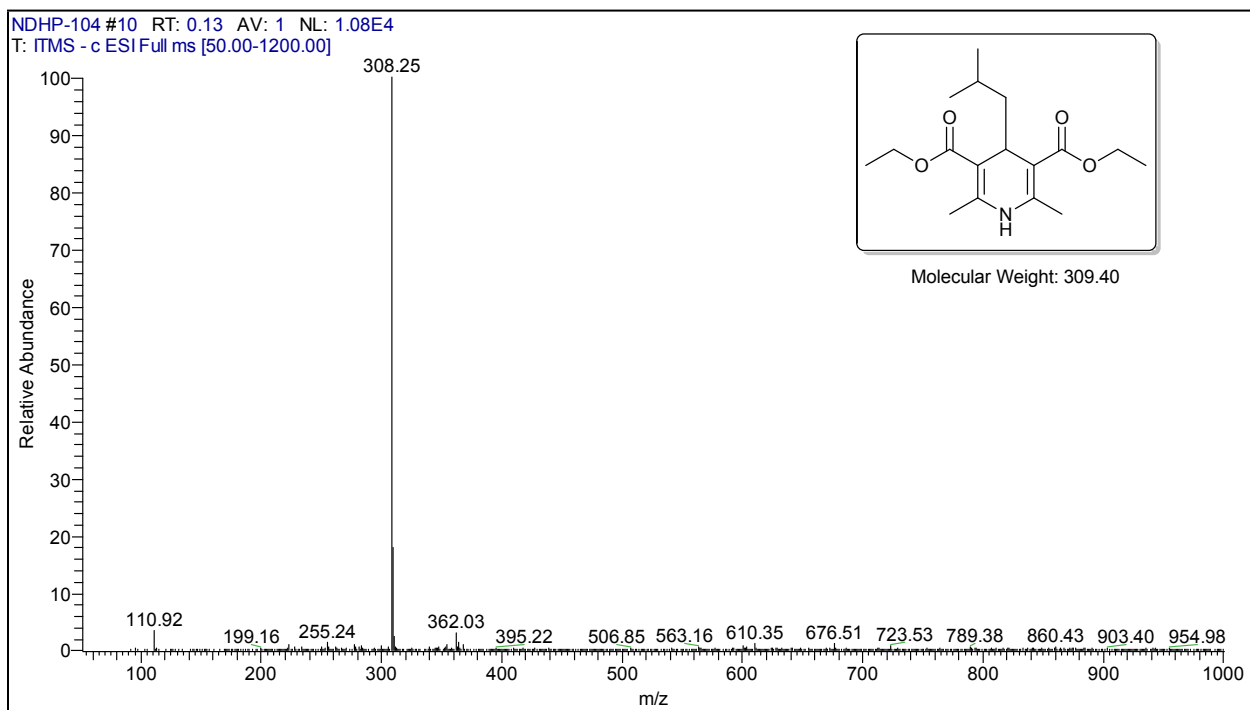


Fig. S98 Mass Spectrum (ESI) of diethyl 4-isobutyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5ad** (M-1)

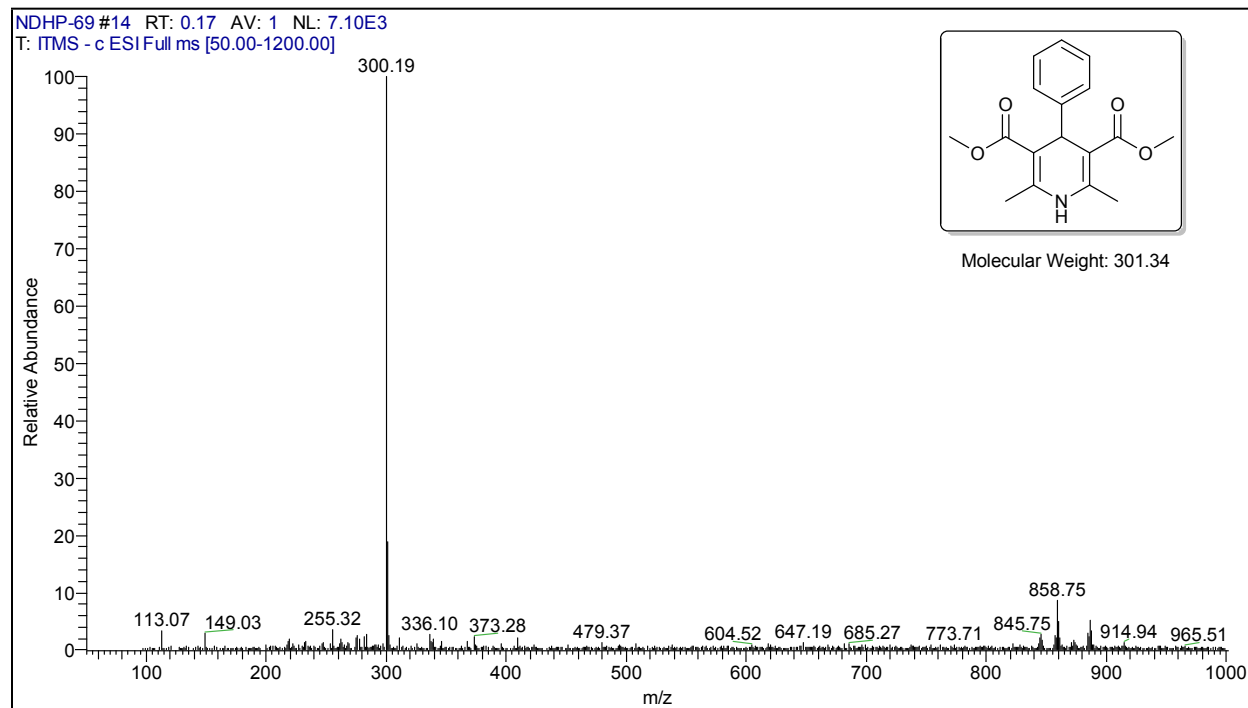


Fig. S99 Mass Spectrum (ESI) of dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate **5ae** (M-1)

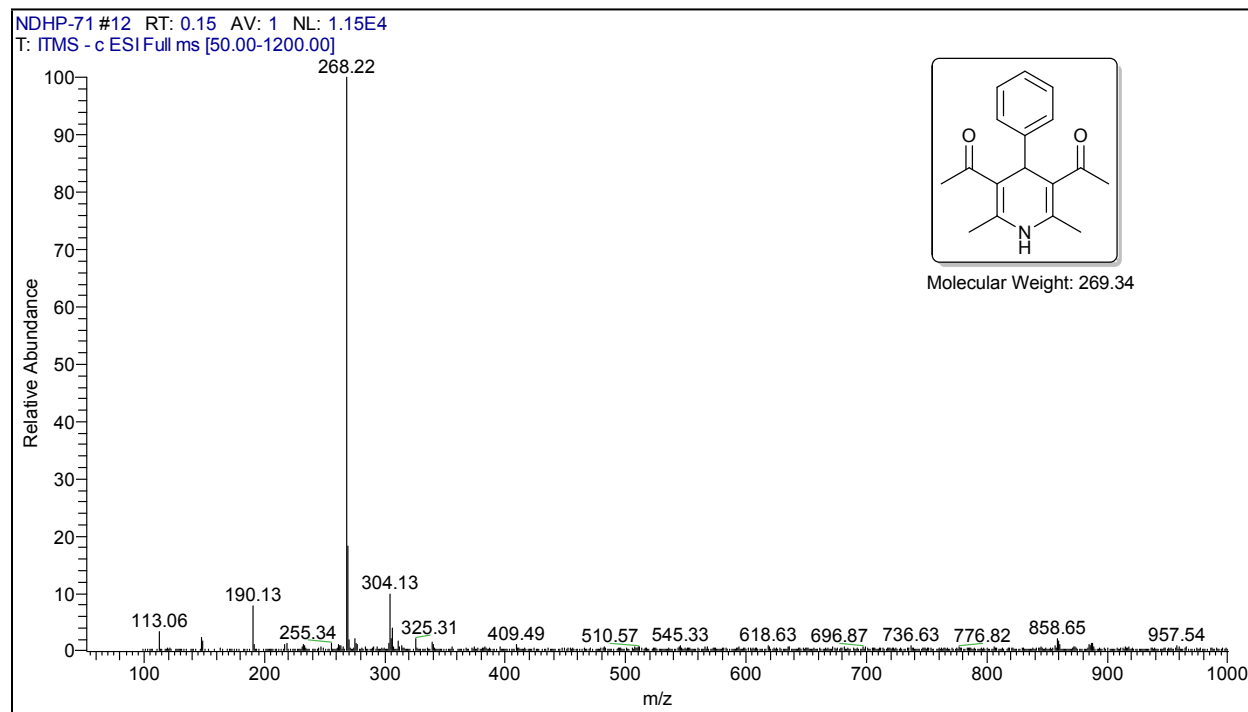


Fig. S100 Mass Spectrum (ESI) of 1,1'-(2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-diyl)diethanone **5af** (M-1)

5. HR-Mass (ESI) of selected (isolated) compounds:

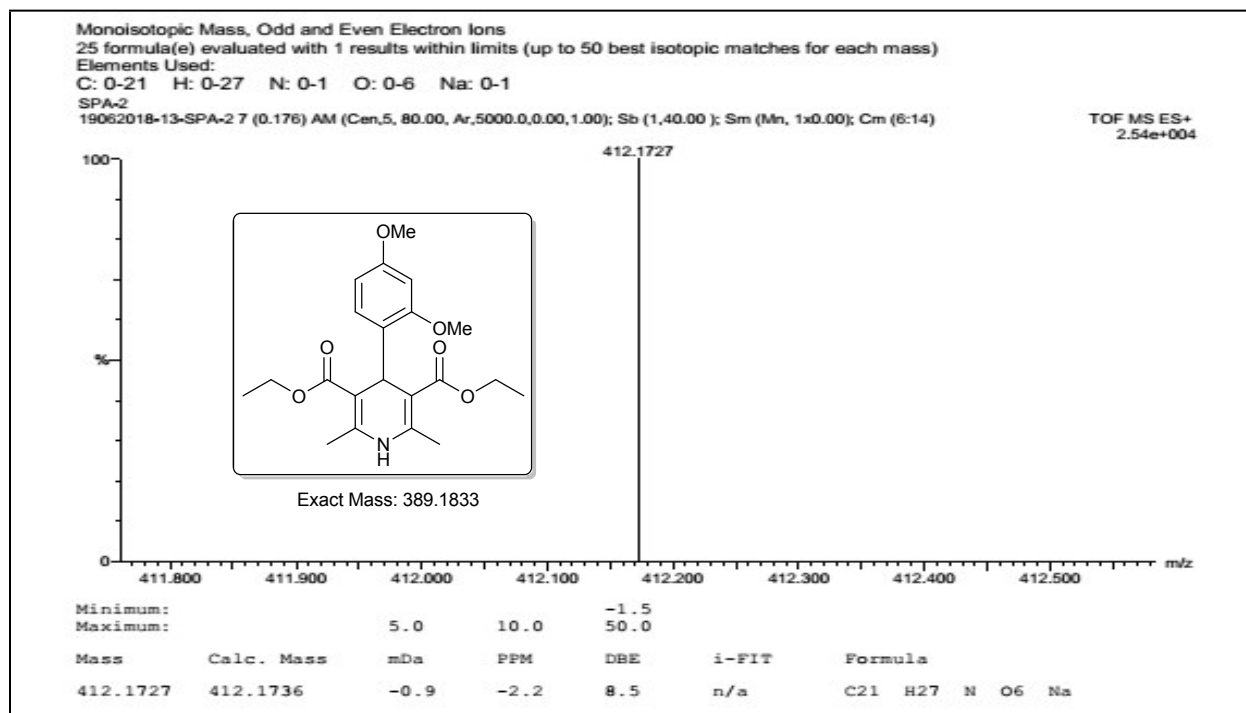


Fig. S101 HR-Mass Spectrum of diethyl 4-(2,4-dimethoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5e** (M+Na)

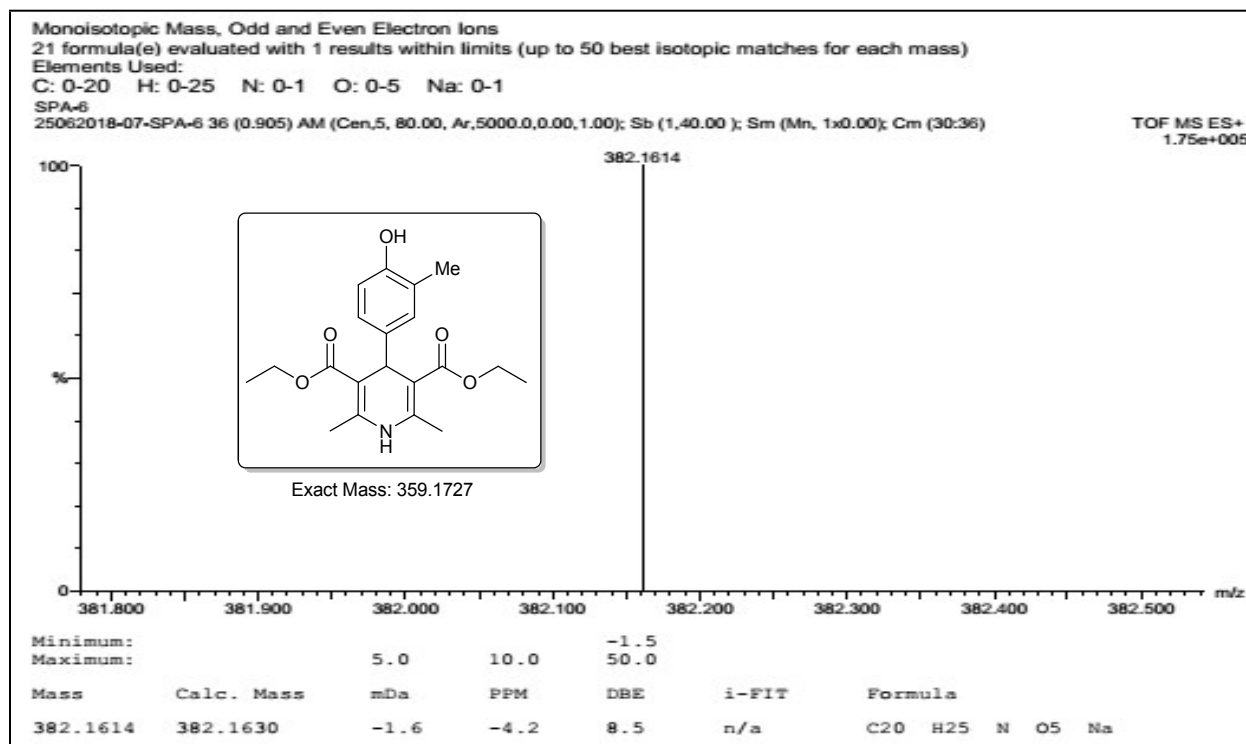


Fig. S102 HR-Mass Spectrum of diethyl 4-(4-hydroxy-3-methylphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5h** (M+Na)

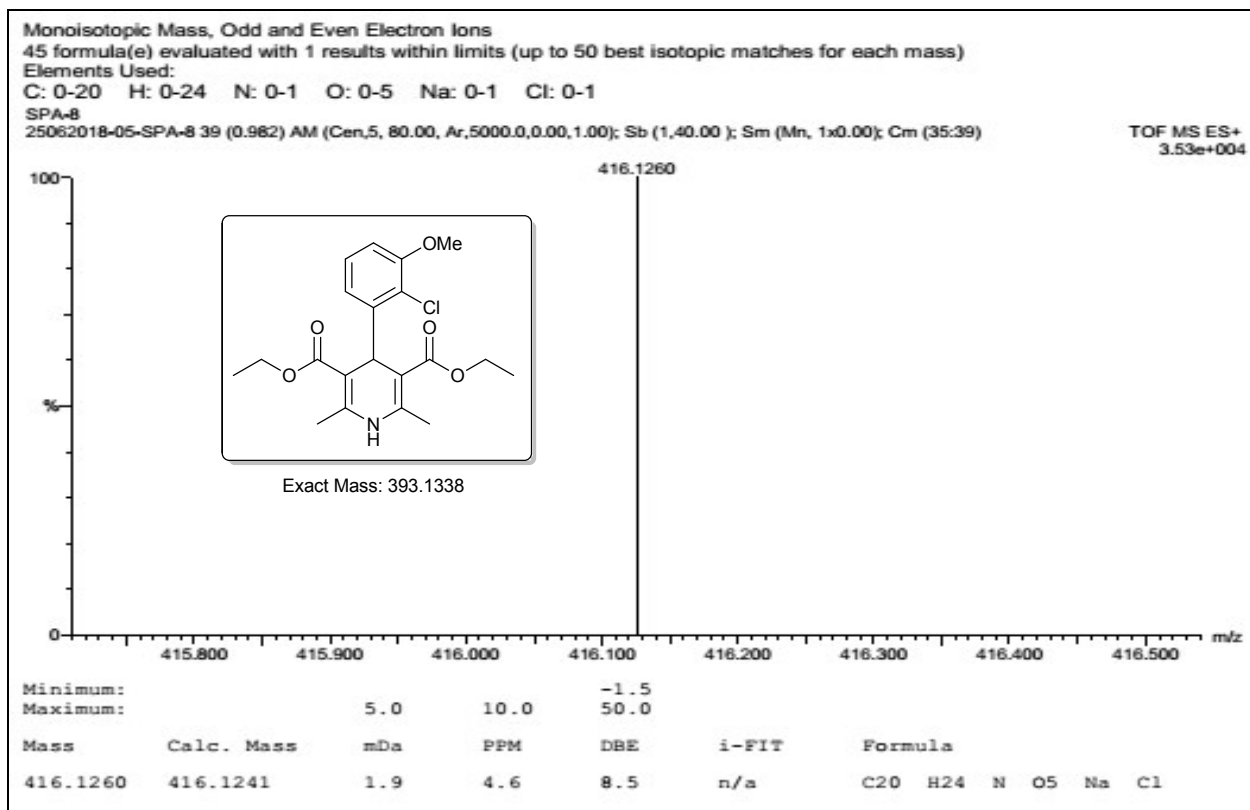


Fig. S103 HR-Mass Spectrum of diethyl 4-(2-chloro-3-methoxyphenyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate **5n** (M+Na)

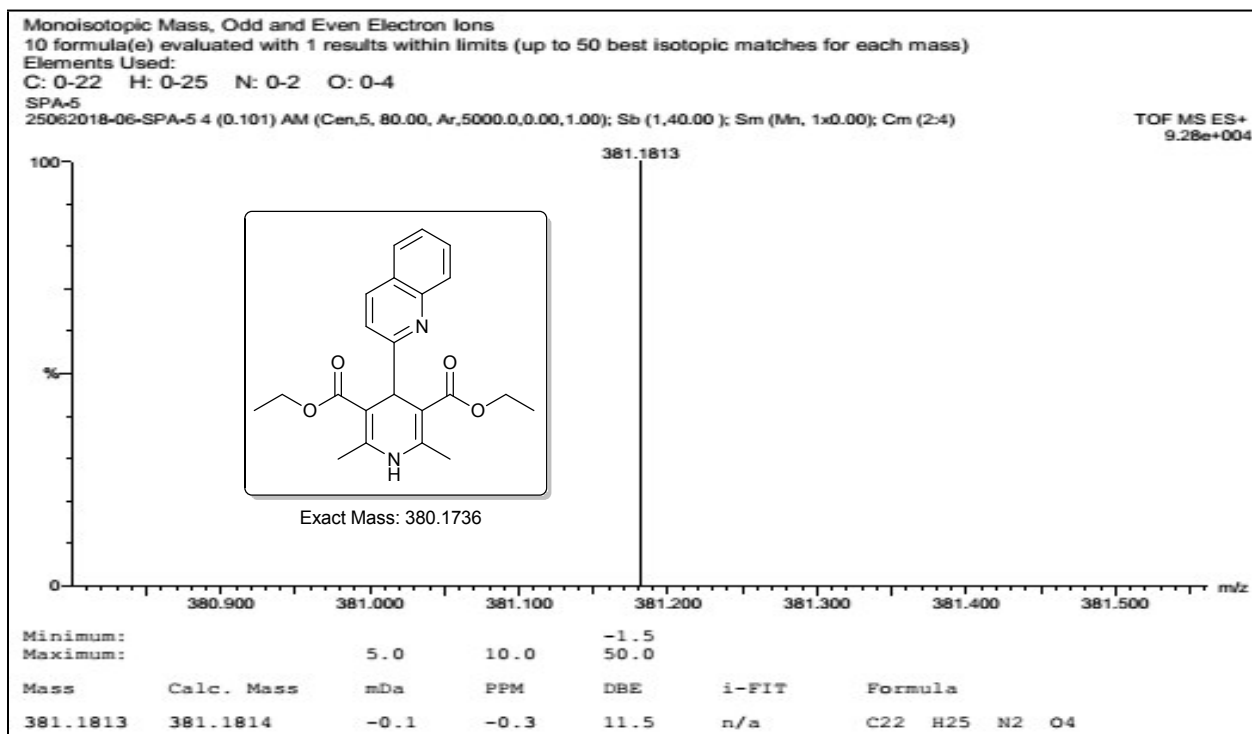


Fig. S104 HR-Mass Spectrum of diethyl 2,6-dimethyl-4-(quinolin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate **5w** (M+1)

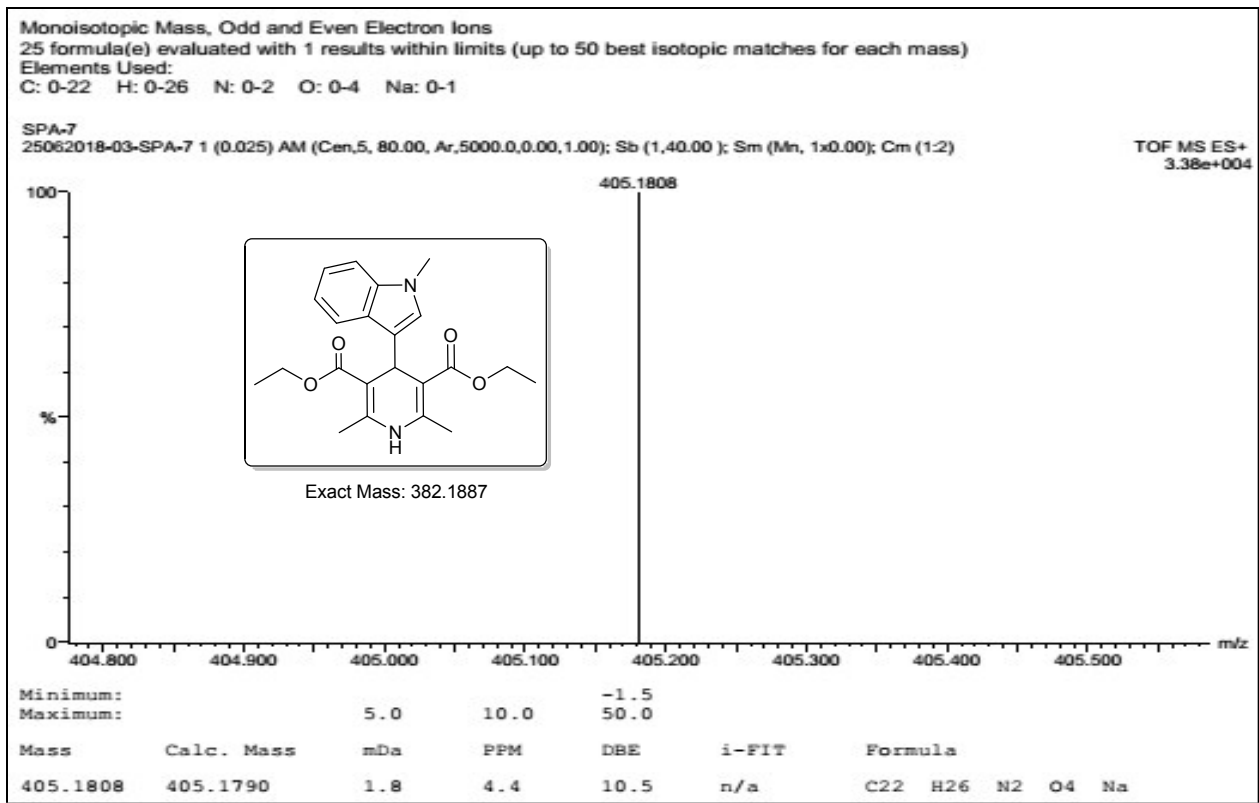


Fig. S105 HR-Mass Spectrum of diethyl 2,6-dimethyl-4-(1-methyl-1*H*-indol-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**5x**) (**M+Na**)