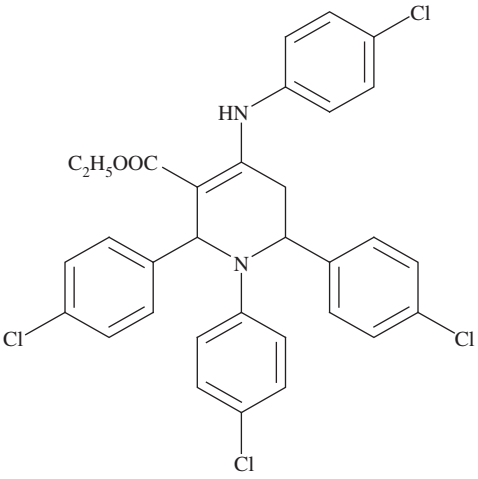
 DOI 10.1515/hc-2012-0105SUP — Heterocycl. Commun. 2012; 18(5-6): Ad1–Ad9

Supplemental data

Characterization of products

Ethyl 4-(4-chlorophenylamino)-1,2,6-tris(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4a):

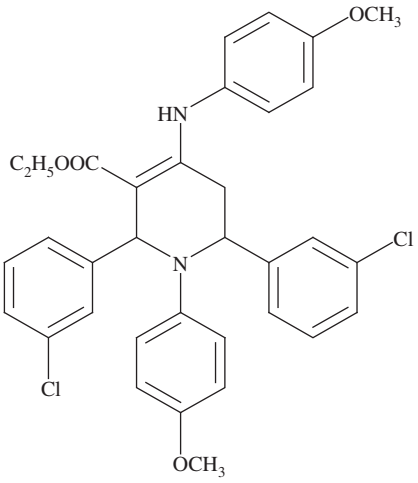


Scheme 2

White solid, yield 89%, mp 168–169°C, Reaction time 14 h; ^{1}H NMR: δ 1.25–1.35 (t, 3H), 2.70–2.85 (d, 2H) 4.15–4.30 (q, 2H) 5.25 (s, 1H), 6.05 (t, 1H), 7.05–7.25 (m, 5H), 7.30–7.50 (m, 8H), 7.75–7.90 (m, 4H), 9.72 (s, 1H); ^{13}C NMR: δ 21.1, 39.6, 57.4, 62.8, 66.3, 106.3, 112.3, 121.5, 124.6, 125.8, 128.2, 131.7, 132.0, 132.2, 132.3, 133.0, 133.9, 134.2, 134.4, 134.8, 135.2, 136.3, 138.7, 139.3, 140.2, 147.5, 149.4, 149.6, 171.3; Mass LC-MS (m/z): 614.6692 [M+]; Elemental analysis for $C_{32}H_{26}Cl_4N_2O_2$: C, 62.76; H, 4.28; N, 4.57; Found: C, 62.79; H, 4.25; N, 4.59.

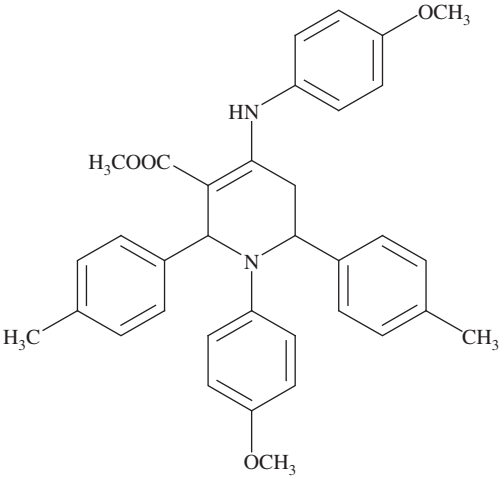
Ethyl 2,6-bis(3-chlorophenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4b):

Yellow solid, yield 86%, mp 170–171°C, lit mp 167–170°C, Reaction time 15 h, ^{1}H NMR: δ 1.50 (t, 3H), 2.69 (d, 1H), 2.80 (d, 1H), 3.75 (s, 6H), 4.30–4.59 (q, 2H), 5.10 (s, 1H), 6.30–6.44 (m, 5H), 6.70–6.81 (m, 5H), 7.12–7.39 (m, 7H), 10.24 (s, 1H); ^{13}C NMR: δ 15.5, 34.1, 55.5, 55.9, 56.3, 57.8, 60.2, 97.1, 113.9, 114.6, 115.3, 125.1, 125.4, 127.0, 127.5, 127.9, 128.6, 129.7, 130.7, 134.8, 140.0, 141.4, 145.9, 147.2, 152.1, 156.7, 158.6, 167.9; Mass LC-MS (m/z):602.5125[M+]. Elemental analysis for $C_{34}H_{32}Cl_2N_2O_4$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.64; H, 5.38; N, 4.67.



Scheme 3

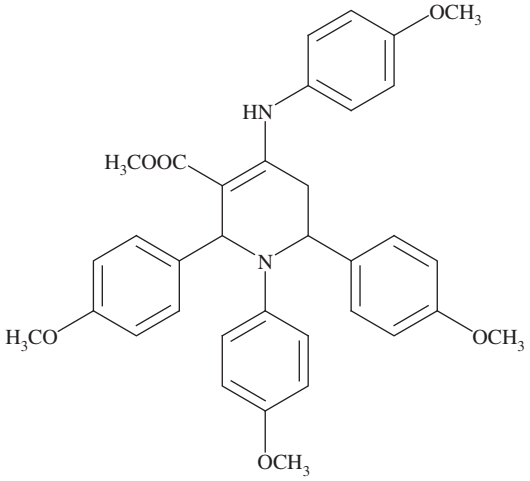
Methyl 2,6-bis(4-methylphenyl)-1-(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4c):



Scheme 4

White solid, yield 89%, mp 224–226°C, lit mp 226–228°C, Reaction time 16 h, ^{1}H NMR: δ 2.39 (s, 6H), 2.66 (d, 1H), 2.75 (d, 1H), 3.68 (s, 3H), 3.82 (s, 6H), 5.05 (d, 1H), 6.24 (d, 2H), 6.29 (s, 1H), 6.49 (d, 2H), 6.64 (d, 2H), 6.86 (d, 2H), 7.02–7.10 (m, 6H), 7.16 (d, 2H), 10.15 (s, 1H); ^{13}C NMR: δ 21.6, 21.8, 33.6, 51.6, 55.9, 56.1, 56.3, 58.5, 97.9, 114.6, 126.2, 126.8, 128.5, 129.2, 129.8, 131.6, 135.8, 136.7, 139.8, 141.6, 142.2, 151.6, 157.8, 158.6, 168.2; Mass LC-MS (m/z): 549.2753 [M+]; Elemental analysis for $C_{34}H_{32}Cl_2N_2O_4$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.68; H, 5.30; N, 4.68.

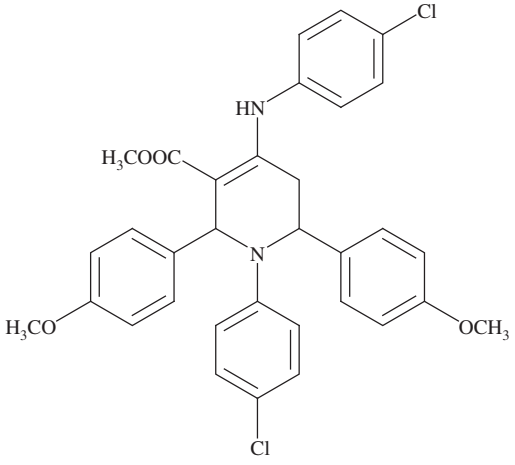
Methyl 1,2,6-tris(4-methoxyphenyl)-4-(4-methoxyphenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4d):



Scheme 5

White solid, yield 88%, mp 160–161°C, lit mp 158–160°C, Reaction time 14 h, ^{1}H NMR: δ 2.59 (d, 1H), 2.72 (d, 1H), 3.66 (s, 6H), 3.89 (s, 6H), 3.92 (s, 3H), 4.98 (s, 1H), 6.25 (s, 1H), 6.32 (d, 2H), 6.43 (d, 2H), 6.68 (d, 4H), 6.75–6.82 (m, 4H), 7.10 (d, 2H), 7.18 (d, 2H), 10.18 (s, 1H); ^{13}C NMR: δ 34.4, 51.5, 55.2, 55.3, 55.7, 56.1, 57.9, 97.2, 113.6, 114.1, 114.4, 114.6, 114.9, 128.1, 128.4, 128.6, 131.4, 135.7, 136.8, 141.7, 151.6, 157.2, 158.3, 158.5, 159.1, 168.7; Mass LC-MS (m/z): 580.2132 [M+]. Elemental analysis for $C_{35}H_{36}N_2O_6$: C, 72.39; H, 6.25; N, 4.82; Found: C, 72.37; H, 6.27; N, 4.85.

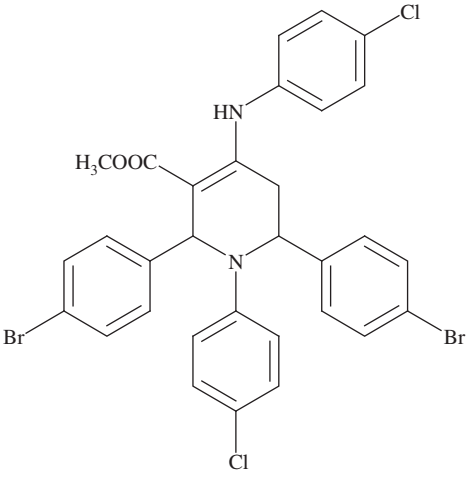
Methyl (4-chlorophenyl)-4-(4-chlorophenylamino)-2,6-bis(methoxyphenyl)-1,2,5,6-tetra hydropyridine-3-carboxylate (4e):



Scheme 6

Yellow solid, yield 90%, mp 194–196°C, lit mp 195°C, Reaction time 14 h, ^{1}H NMR: δ 2.68 (d, 1H), 2.82 (d, 1H), 3.82 (s, 6H), 3.92 (s, 3H), 5.10 (s, 1H), 6.22–6.30 (m, 3H), 6.41–6.44 (d, 2H), 6.78–6.84 (m, 5H), 7.10–7.28 (m, 7H), 10.18 (s, 1H); ^{13}C NMR: δ 33.9, 51.5, 55.3, 55.4, 55.8, 57.8, 97.6, 113.5, 117.3, 120.9, 121.6, 125.9, 126.4, 128.6, 128.5, 129.6, 131.3, 132.3, 138.2, 141.6, 143.4, 146.7, 156.2, 168.7; Mass LC-MS (m/z): 588.3562 [M+]; Elemental analysis for $C_{33}H_{30}N_2O_4Cl_2$: C, 67.23; H, 5.13; N, 4.75. Found: C, 67.26; H, 5.10; N, 4.78.

Methyl 2,6-bis(4-bromophenyl)-1-(4-chlorophenyl)-4-(4-chlorophenylamino) -1,2,5,6-tetra hydropyridine-3-carboxylate (4f):

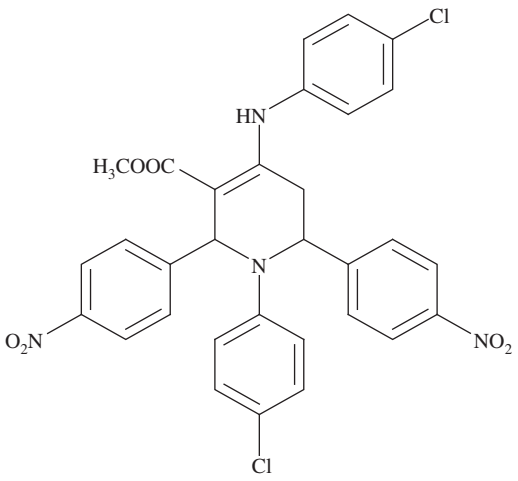


Scheme 7

Yellow solid, yield 80%, mp 163–164°C, lit mp 160–163°C, Reaction time 15 h, ^{1}H NMR: δ 2.71 (d, 1H), 2.83 (d, 1H), 3.96 (s, 3H), 5.12 (s, 1H), 6.28–6.39 (m, 5H), 6.92–6.98 (m, 4H), 7.10–7.24 (m, 4H), 7.35–7.43 (m, 4H), 10.21 (s, 1H); ^{13}C NMR: δ 33.7, 51.9, 55.1, 57.5, 98.4, 114.6, 121.1, 121.8, 122.5, 127.1, 128.5, 128.9, 129.2, 129.7, 132.0, 132.3, 132.7, 136.3, 141.4, 142.1, 145.5, 155.9, 167.8; Mass LC-MS (m/z): 683.1685 [M+]. Elemental analysis for $C_{31}H_{24}Br_2Cl_2N_2O_2$: C, 67.23; H, 5.13; N, 4.75. Found: C, 67.25; H, 5.11; N, 4.78.

Methyl 4-(4-chlorophenylamino)-1-(4-chlorophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-nitro phenyl)pyridine-3-carboxylate (4g):

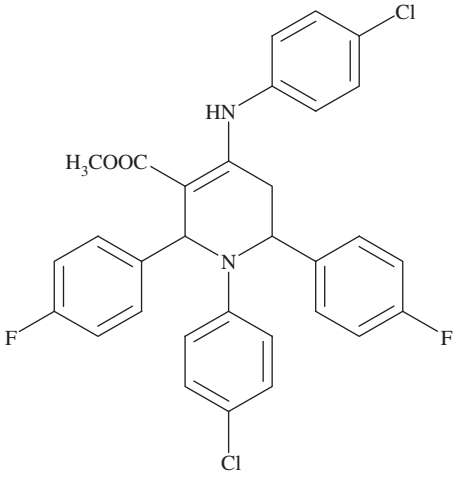
White solid, yield 78%, mp 195–196°C, Reaction time 16 h, ^{1}H NMR: δ 2.95 (d, 2H), 4.05 (s, 3H), 4.95 (s, 1H), 5.90 (t, 1H), 6.70–6.85 (m, 4H), 7.08–7.20 (m, 4H), 7.75–8.10 (m, 8H), 10.05 (s, 1H); ^{13}C NMR: δ 32.2, 33.6, 52.5, 55.4, 58.2, 113.5, 117.5, 120.1, 121.6, 122.1, 123.6, 125.1, 126.2, 128.4, 129.3, 129.4,



Scheme 8

130.2, 132.8, 141.5, 144.3, 150.1, 153.6, 178.2; Mass LC-MS (m/z): 620.7535 [M+]; Elemental analysis for $C_{34}H_{32}Cl_2N_2O_4$: C, 67.66; H, 5.34; N, 4.64. Found: C, 67.63; H, 5.37; N, 4.67.

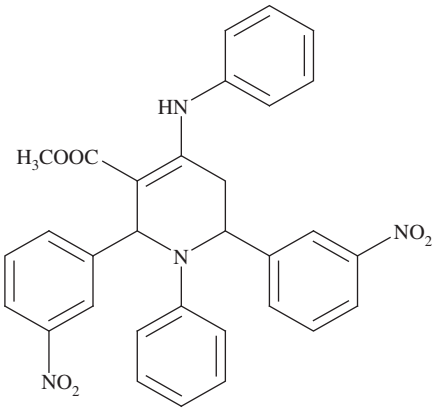
Methyl (4-chlorophenyl)-4-(4-chlorophenylamino)-2,6-bis(4-fluorophenyl)-1,2,5,6-tetra hydropyridine-3-carboxylate (4h):



Scheme 9

White solid, yield 77%, mp 178°C, lit mp 176°C, Reaction time 14 h, ^{1}H NMR: δ 2.74 (d, 1H), 2.85 (d, 1H), 4.02 (s, 3H), 5.01 (s, 1H), 5.90–6.31 (m, 6H), 6.85–7.28 (m, 11H), 10.22 (s, 1H); ^{13}C NMR: δ 34.2, 51.4, 55.7, 57.2, 97.3, 114.6, 114.9, 115.2, 115.6, 115.8, 116.3, 128.0, 128.3, 128.5, 128.7, 129.1, 131.2, 139.2, 139.8, 141.6, 151.7, 156.5, 158.6, 159.2, 164.6, 168.1; Mass LC-MS (m/z): 565.4452 [M+]; Elemental analysis for $C_{31}H_{24}Cl_2F_2N_2O_2$: C, 65.85; H, 4.28; N, 4.95; Found: C, 65.87; H, 4.24; N, 4.97.

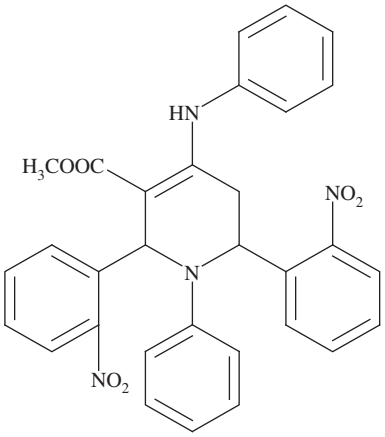
Methyl 2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4i):



Scheme 10

White solid, yield 80%, mp 178–180°C, lit mp 180°C, Reaction time 15 h, ^{1}H NMR: δ 2.75 (d, 2H), 4.21 (s, 3H), 5.21 (s, 1H), 6.05 (t, 1H), 6.60–6.71 (m, 5H), 7.05–7.15 (m, 5H), 7.72–7.95 (m, 8H), 10.48 (s, 1H); ^{13}C NMR: δ 32.0, 33.1, 51.2, 55.9, 57.2, 113.1, 118.2, 121.1, 121.6, 122.4, 122.6, 126.3, 127.1, 129.2, 129.6, 129.8, 130.1, 132.5, 137.5, 144.3, 146.5, 149.3, 155.5, 168.2; Mass LC-MS (m/z): 551.7634 [M+]; Elemental analysis for $C_{31}H_{26}N_4O_6$: C, 67.63; H, 4.76; N, 10.18; Found: C, 67.66; H, 4.73; N, 10.14.

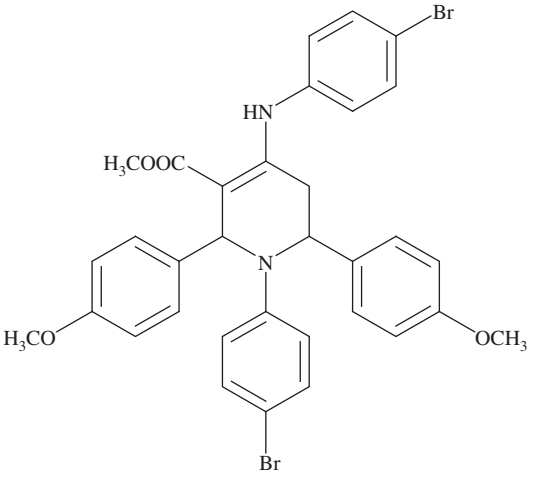
Methyl 1,2,5,6-tetrahydro-2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino) pyridine-3-carboxylate (4j):



Scheme 11

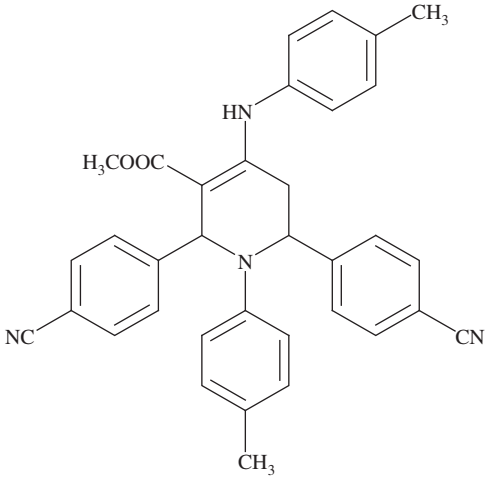
White solid, yield 80%, mp 216°C, lit mp 218–219°C, Reaction time 15 h.; ^{1}H NMR: δ 2.80 (d, 2H), 4.39 (s, 3H), 5.10 (s, 1H), 6.29 (t, 1H), 6.80–6.85 (m, 5H), 7.12–7.23 (m, 5H), 7.82–8.05 (m, 8H), 10.23 (s, 1H); ^{13}C NMR: δ 34.1, 35.3, 52.3, 55.4, 59.2, 114.3, 119.1, 122.3, 122.6, 122.8, 123.3, 127.2, 127.4, 129.6, 129.8, 130.2, 132.3, 133.7, 138.2, 146.1, 148.3, 151.1, 157.4, 165.5; Mass LC-MS (m/z): 551.4231 [M+]; Elemental analysis for $C_{31}H_{26}N_4O_6$: C, 67.63; H, 4.76; N, 10.18; Found: C, 67.65; H, 4.78; N, 10.16.

Methyl 4-(4-bromophenylamino)-1-(4-bromophenyl)-1,2,5,6-tetrahydro-2,6-bis(4-methoxyphenyl)pyridine-3-carboxylate (4k):



Scheme 12

Yellow solid, yield 84%, mp 179°C, lit mp 178°C, Reaction time 14 h. ^{1}H NMR: δ 2.84 (d, 1H), 2.90 (d, 1H), 3.72 (s, 3H), 3.91 (s, 6H), 5.12 (s, 1H), 6.20–6.27 (m, 3H), 6.38 (d, 2H), 6.78–6.86 (m, 4H), 7.02–7.18 (m, 8H), 10.20 (s, 1H); ^{13}C NMR: δ 34.3, 50.3, 54.4, 58.1, 63.2, 111.7, 114.4, 115.1, 116.7, 116.9, 123.2, 126.3, 128.4, 128.6, 128.8, 129.1, 129.5, 129.7, 129.9, 133.2, 135.7, 137.2, 139.2, 146.4, 154.3, 160.8, 165.5, 166.8; Mass LC-MS (m/z): 562.3433 Elemental analysis for $C_{33}H_{30}N_2O_4Br_2$: Calcd C, 58.42; H, 4.46; N, 4.13. Found: C, 58.46; H, 4.49; N, 4.10.

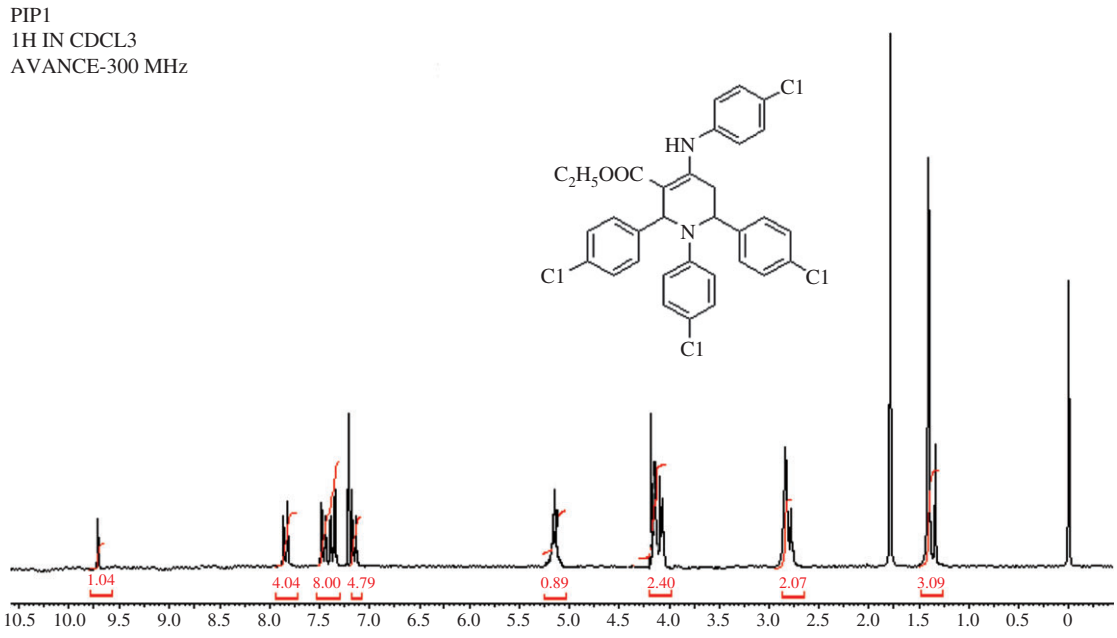


Scheme 13

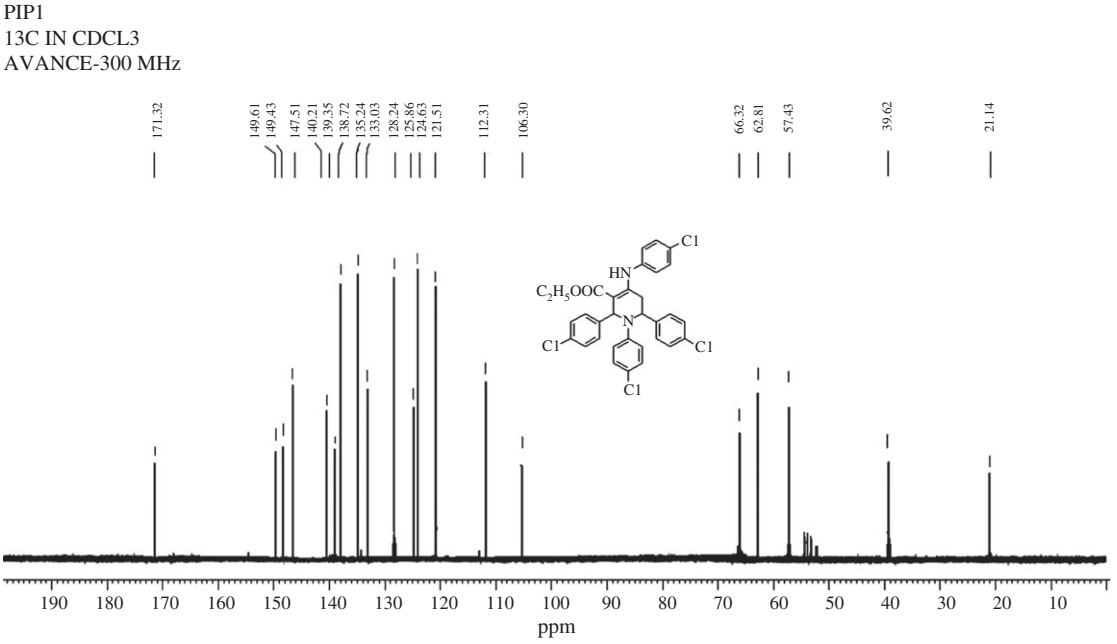
Methyl 4-(*p*-tolylamino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydro-1-*p*-tolylpyridine-3-carboxylate (4l):

White solid, yield 82%, mp 210–212°C, lit mp 214°C, Reaction time 16 h. ^{1}H NMR: δ 2.81 (d, 2H), 3.12 (s, 6H), 4.16 (s, 3H), 5.02 (s, 1H), 5.85 (t, 1H), 6.73–6.84 (m, 4H), 7.08–7.21 (m, 4H), 7.89–8.20 (m, 8H), 10.18 (s, 1H); ^{13}C NMR: δ 33.1, 34.4, 50.2, 54.8, 59.3, 110.1, 116.3, 120.6, 122.3, 124.1, 124.5, 125.7, 126.9, 129.2, 130.1, 130.4, 130.6, 134.1, 140.2, 145.5, 150.7, 155.2, 176.3; Mass LC-MS (m/z): 538.5176 [M+]; Elemental analysis for $C_{35}H_{30}N_4O_2$: C, 78.04; H, 5.61; N, 10.40; Found: C, 78.02; H, 5.63; N, 10.44.

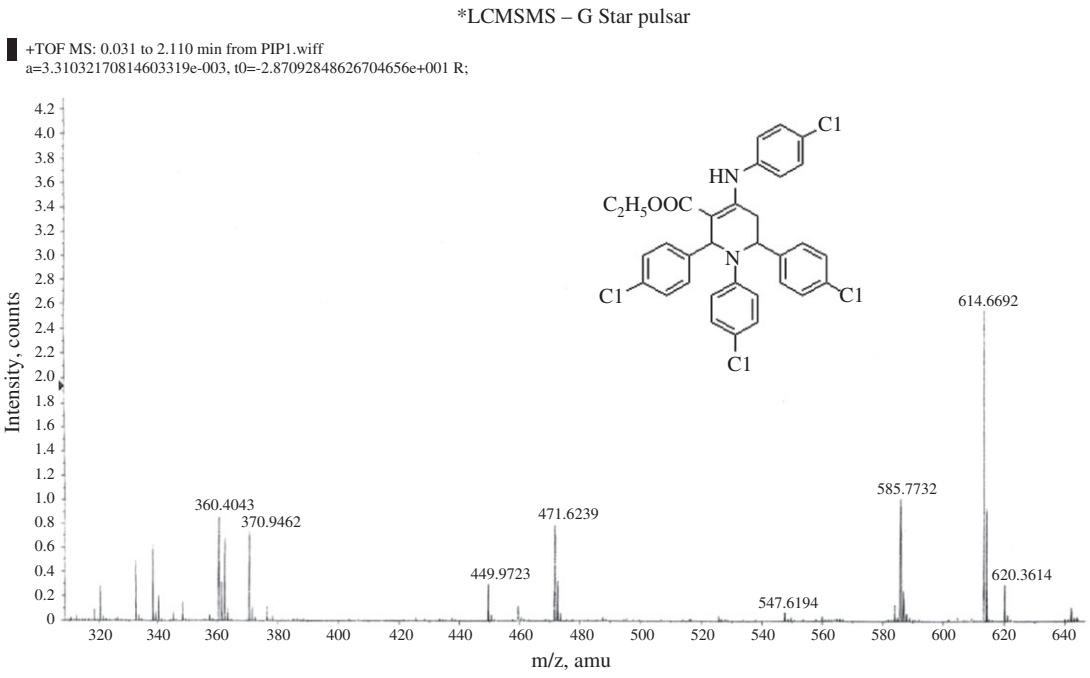
^{1}H NMR, ^{13}C NMR, and LC-MS of compound 4a



Scheme 14

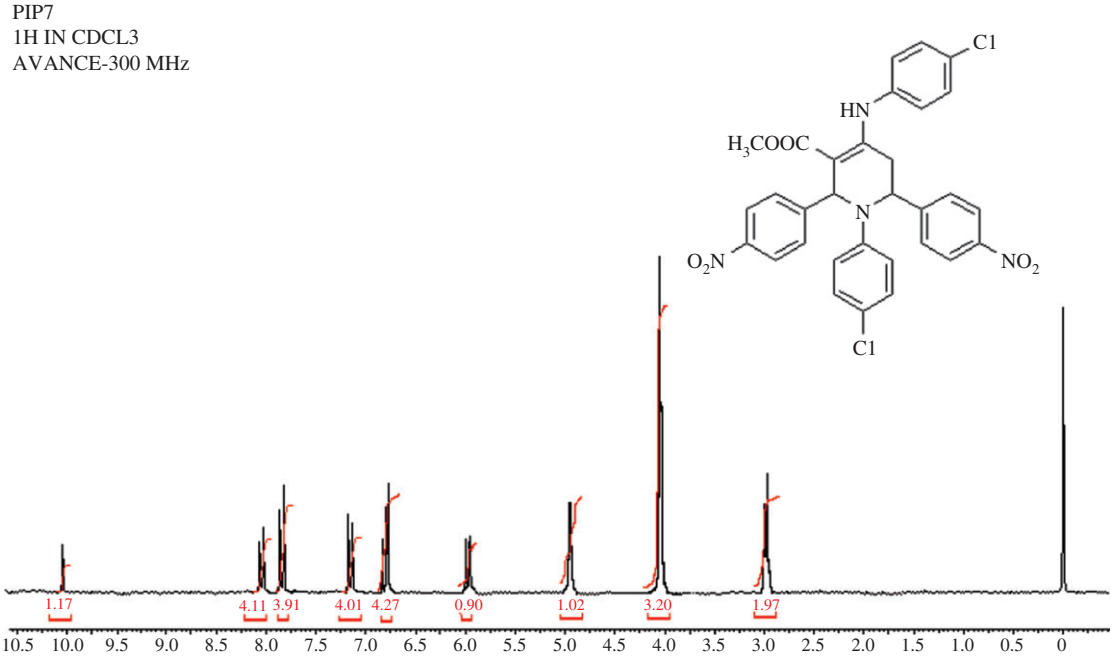


Scheme 15

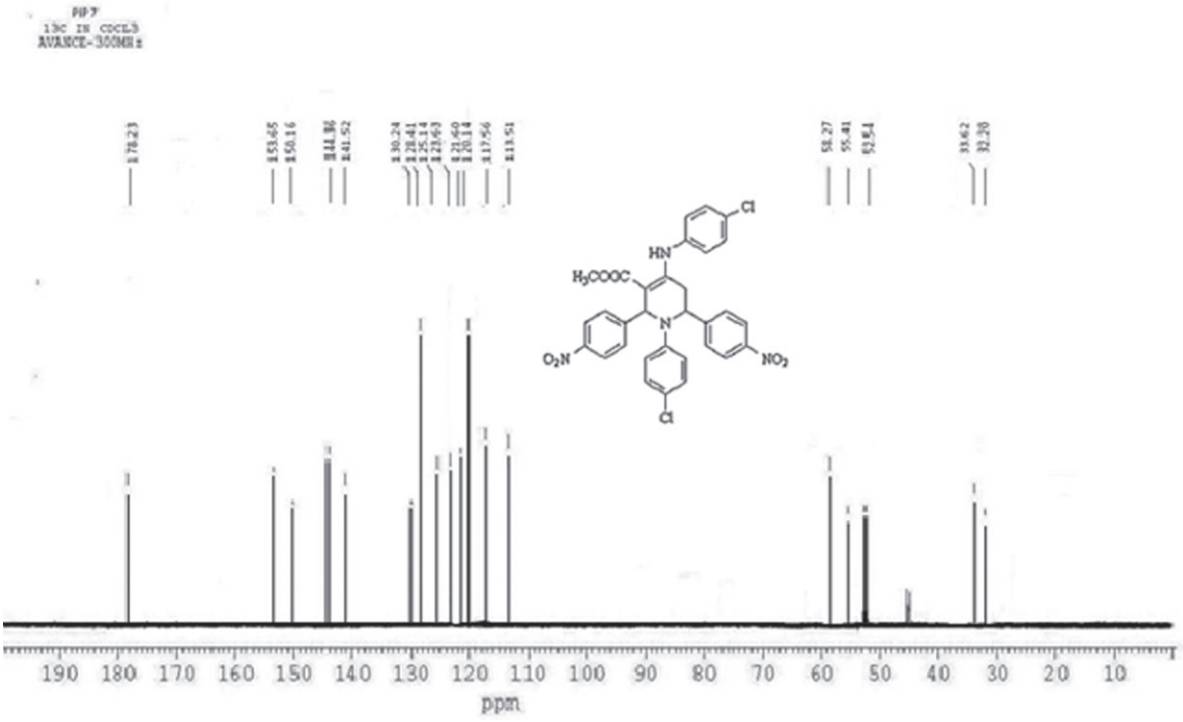


Scheme 16

^{1}H NMR, ^{13}C NMR, and LC-MS of compound 4g

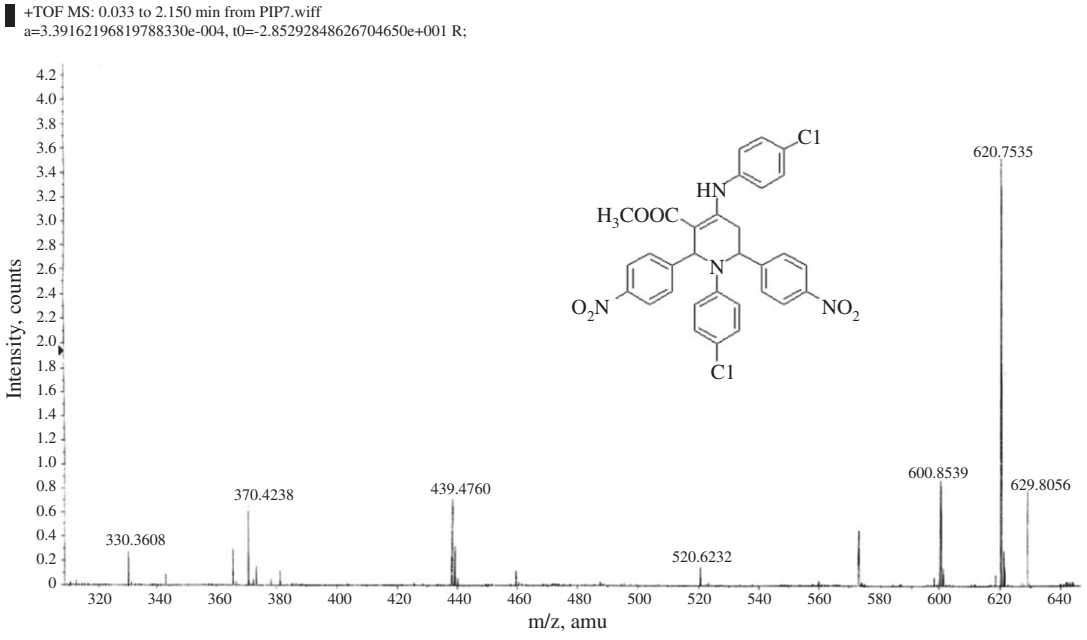


Scheme 17



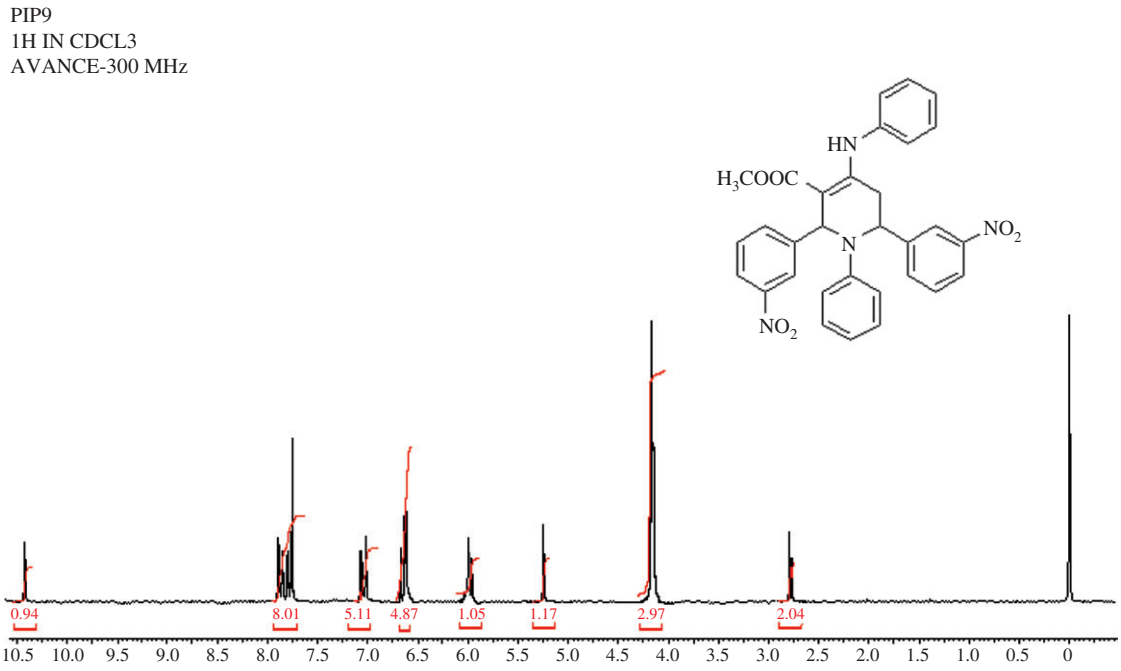
Scheme 18

*LCMSMS – Q-Star pulsar

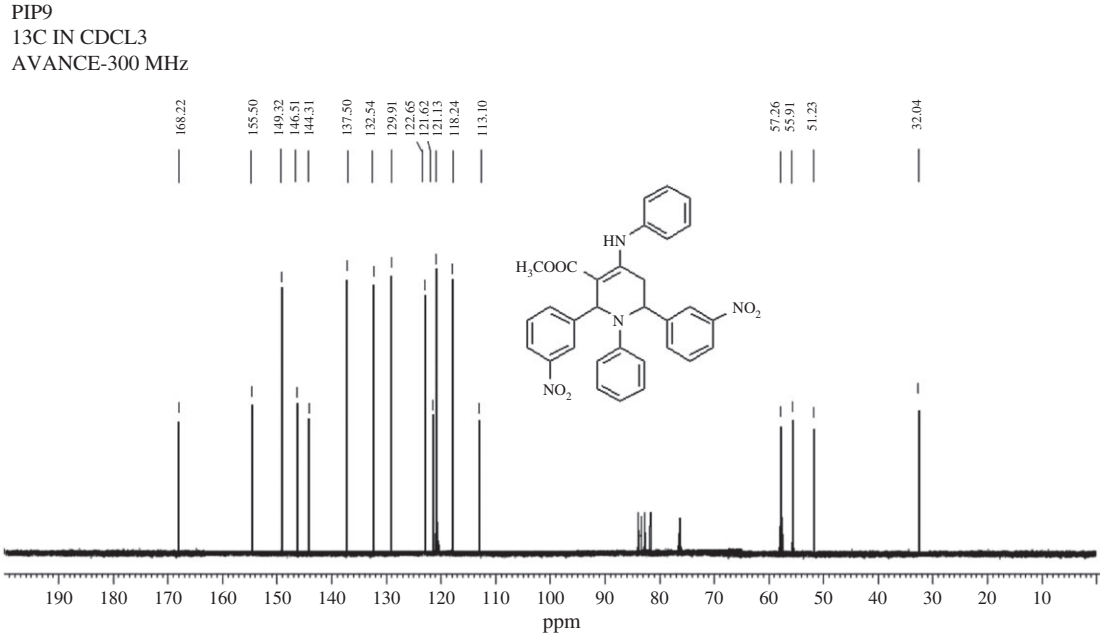


Scheme 19

^{1}H NMR, ^{13}C NMR, and LC-MS of compound 4i

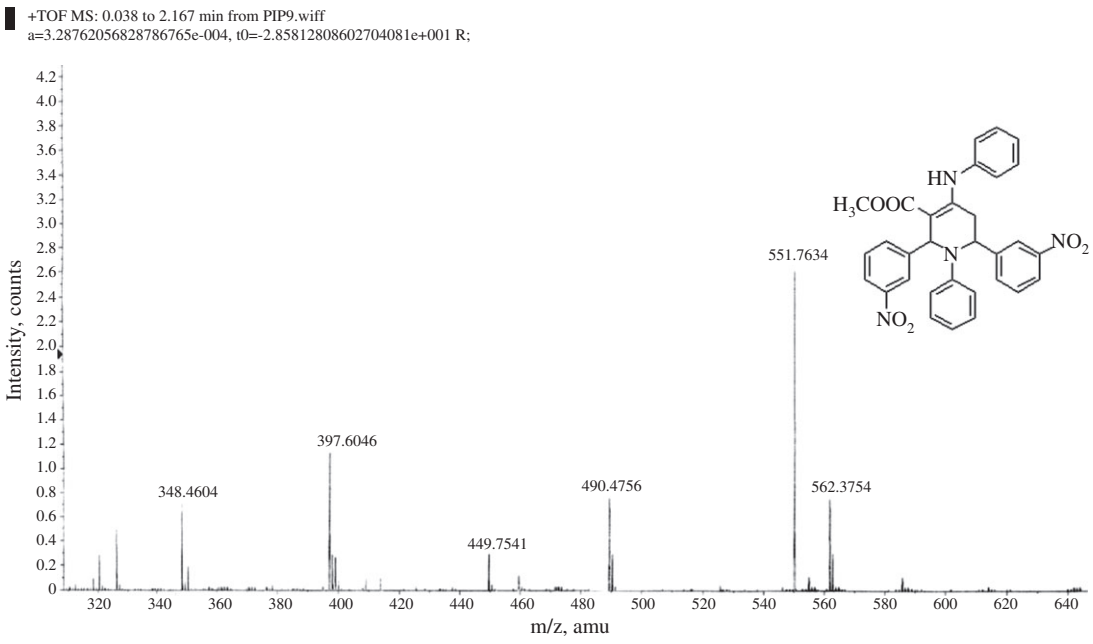


Scheme 20



Scheme 21

*LCMSMS – Q-Star pulsar



Scheme 22