Enantioselective Organocatalytic Domino Synthesis of Tetrahydropyridin-2-ols

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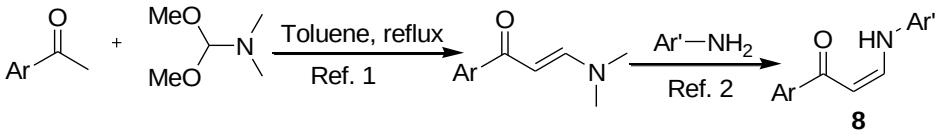
Contents

Experimental information

General information

The enaminones were prepared in two steps following a literature procedure (Scheme 1).[1-2] The chiral amine catalyst IV was synthesized according to a literature procedure.[3,4] All other chemicals and solvents were obtained from commercial sources and used without further purification. Preparative flash column chromatography was performed on Merck silica gel 60 (particle size 0.040-0.063 mm, 230-240 mesh), SIL G-25 UV_{254} plates were used for TLC analysis and indicated with ultraviolet irradiation (254 nm). ^{1}H and ^{13}C NMR spectra were recorded on 300 Varian Mercury or 400 MHz (VNMRS-400) instruments, the chemical shifts are given in ppm with TMS as internal standard.



Scheme 1

Mass spectra and high resolution mass spectra were acquired on a Finnigan SSQ7000 (EI 70 eV) spectrometer and Thermo Fisher Scientific Orbitrap XL spectrometer, respectively. FT-IR spectra were recorded on a Perkin-Elmer FT-IR Spectrum 100 instrument. HPLC analysis was performed with a Hewlett-Packard 1100 Series instrument using chiral stationary phases. Optical rotation values were measured by a Perkin-Elmer 241 polarimeter. Melting points were acquired from a Büchi apparatus without temperature correction.

General procedure for the enantioselective synthesis of 1,4,5,6-tetrahydropyridin-2-ols. Cinnamaldehyde **1** (0.9 mmol) and chiral amine catalyst IV (39 mg, 0.12 mmol) were charged in a vessel with EtOAc or 2:1 EtOAc/Et_2O (6 mL). Enaminone **8** (0.6 mmol) and benzoic acid (7 mg, 0.06 mmol) were then added and the mixture was stirred at 0 ^oC for 4 days. Upon completion, the solvent of the reaction mixture was removed and the residue was subjected to flash column chromatography with eluent of 3:1 to 1:1 mixed EtOAc/petroleum ether to provide the pure product.

References

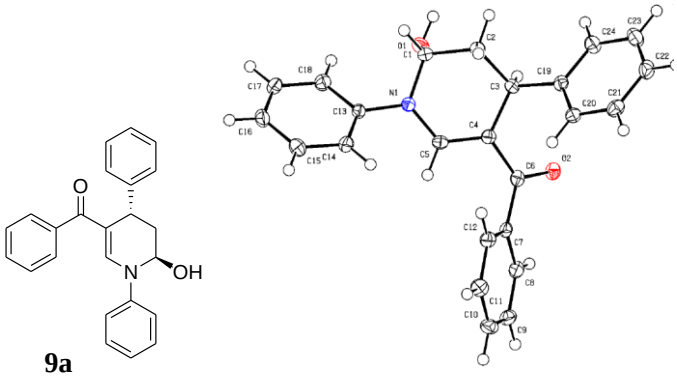
1. F. M. A. A. El-Taweel and M. H. Elnagdi, *J. Heterocyclic Chem.* 2001, **38**, 981.

2. Z.-Z. Zhou, F.-S. Liu, D.-S. Shen, C. Tan and L.-Y. Luo, *Inorg. Chem. Commun.* 2011, **14**, 659.

3. J. V. B. Kanth and M. Periasamy, *Tetrahedron* 1993, **49**, 5127.

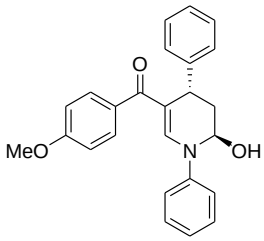
4. M. Marigo, T. C. Wabnitz, D. Fielenbach and K. A. Jørgensen, *Angew. Chem. Int. Ed.* 2005, **44**, 794.

X-ray structure of **9a**

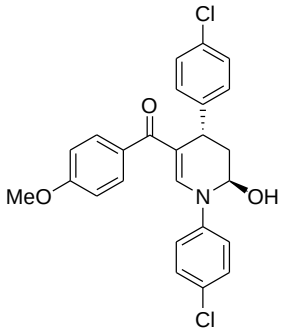


9a

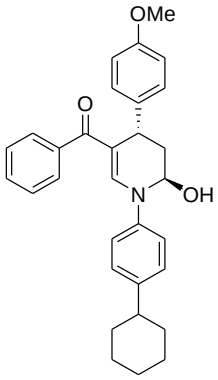
((*4S,6R*)-6-Hydroxy-1,4-diphenyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9a). Pale yellow solid, m.p. 143-145 ^{o}C; > 99:1 er from HPLC on chiral stationary phase (Chiralpak AS, n-heptane : EtOH = 9 : 1, 1.0 mL/min), t_R = 8.31 min (minor), t_R = 11.06 min (major); $[\alpha]^{D}_{23}$ = -182 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.60 (d, 2 H, *J* = 8.0 Hz), 7.45 (s, 1 H), 7.41 (t, 1 H, *J* = 8.0 Hz), 7.36-7.29 (m, 6 H), 7.24 (t, 2 H, *J* = 8.0 Hz), 7.17-7.09 (m, 4 H), 5.30 (s, 1 H), 4.24 (dd, 1 H, J_1 = 8.0 Hz, J_2 = 12.0 Hz), 3.35 (s, 1 H), 2.43-2.37 (m, 1 H), 2.15-2.08 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 194.2, 144.8, 144.5, 144.2, 139.4, 130.8, 129.6, 128.7, 128.5, 128.2, 127.2, 126.1, 124.5, 119.6, 116.5, 78.4, 39.6, 34.4; IR (KBr, cm^{-1}): ν 3337, 2925, 1557, 1493, 1259, 1050, 890; EI-MS $[M]^+$: 355; Elemental anal. calcd. for $C_{24}H_{21}NO_2$: C 81.10, H 5.96, N 3.94; found: C 81.07, H 5.92, N 3.86.



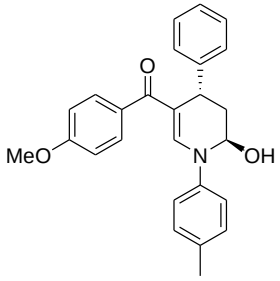
((*4S,6R*)-6-Hydroxy-1,4-diphenyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9b). Colorless solid, m.p. 119-121 ^{o}C; 96:4 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : EtOH = 9 : 1, 0.7 mL/min), t_R = 13.43 min (minor), t_R = 15.76 min (major); $[\alpha]^{D}_{23}$ = -147 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.62 (d, 2 H, *J* = 8.0 Hz), 7.42 (s, 1 H), 3.35-7.28 (m, 3 H), 7.25-7.17 (m, 5 H), 7.13 (dd, 2H, J_1 = 8.0 Hz, J_2 = 12.0 Hz), 6.84 (d, 2 H, *J* = 8.0 Hz), 5.33 (s, 1 H), 4.27-4.22 (m, 1 H), 3.81 (s, 3 H), 3.25 (brs, 1 H), 2.44-2.37 (m, 1 H), 2.13-2.10 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 193.1, 161.9, 144.5, 144.4, 143.5, 131.8, 131.0, 129.6, 128.4, 127.1, 126.1, 124.2, 119.2, 116.7, 113.4, 78.4, 55.1, 39.6, 34.4; IR (KBr, cm^{-1}): ν 3265, 1547, 1249, 1165, 749, 692; EI-MS $[M]^+$: 385; HRMS (ESI): calcd for $C_{25}H_{24}NO_3[M+H]^+$: 386.1756; found: 386.1750.



((*4S,6R*)-1,4-Bis(4-chlorophenyl)-6-hydroxy-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9c). Pale yellow solid, m.p. 90-91 ^{o}C; 96:4 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : EtOH = 7 : 3, 0.7 mL/min), t_R = 15.11 min (major), t_R = 17.23 min (minor); $[\alpha]^{D}_{23}$ = -119 (*c* 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.60 (d, 1 H, *J* = 8.0 Hz), 7.33-7.24 (m, 5 H), 7.19 (s, 3 H), 7.11 (t, 2 H, *J* = 8.0 Hz), 6.86 (d, 2 H, *J* = 8.0 Hz), 5.27 (s, 1 H), 4.18 (dd, 1 H, J_1 = 8.0 Hz, J_2 = 12.0 Hz), 3.82 (t, 4 H, OMe+OH), 2.41-2.36 (m, 1 H), 2.05 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 193.1, 162.3, 143.1, 142.8, 140.2, 131.8, 131.3, 130.8, 129.6, 128.5, 121.0, 120.4, 116.7, 113.6, 78.4, 55.6, 39.6, 33.9; IR (KBr, cm^{-1}): ν 3291, 1563, 1484, 1247, 1014, 820, 770; EI-MS $[M]^{+}$: 453; Elemental anal. calcd. for $C_{25}H_{21}Cl_2NO_3$: C 66.09, H 4.66, N 3.08; found: C 65.76, H 4.73, N 3.00.

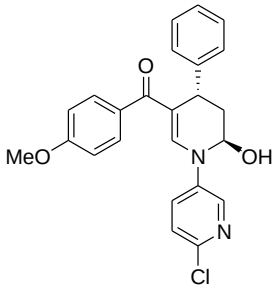


((*4S,6R*)-1-(4-Cyclohexylphenyl)-6-hydroxy-4-(4-methoxyphenyl)-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9d). Pale green solid, m.p. 160-162 ^{o}C; 98:2 er from HPLC on chiral stationary phase (s,s-WhelkO1, n-heptane : EtOH = 7 : 3, 0.7 mL/min), t_R = 10.03 min (minor), t_R = 25.98 min (major); $[\alpha]^{D}_{23}$ = -102 (*c* 0.81, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.59 (d, 2 H, *J* = 8.0 Hz), 7.40 (brs, 2 H), 7.34 (t, 2 H, *J* = 8.0 Hz), 7.21 (d, 2 H, *J* = 8.0 Hz), 7.15 (d, 2 H, *J* = 8.0 Hz), 7.08 (d, 2 H, *J* = 8.0 Hz), 6.09 (d, 2 H, *J* = 8.0 Hz), 5.27 (s, 1 H), 4.18 (dd, 1 H, J_1 = 4.0 Hz, J_2 = 12.0 Hz), 3.73 (s, 3 H), 3.23 (brs, 1 H), 2.45 (brs, 1 H), 2.39-2.32 (m, 1 H), 2.08 (t, 1 H, *J* = 12.0 Hz), 1.82 (d, 4 H, J = 12.0 Hz), 1.73 (d, 1 H, *J* = 12.0 Hz), 1.36 (brs, 4 H), 1.23 (brs, 1 H); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 193.8, 157.8, 145.3, 144.7, 142.0, 139.6, 136.6, 128.7, 128.1, 127.9, 119.9, 116.2, 113.9, 78.5, 55.2, 43.8, 39.5, 33.5, 26.8, 26.0; IR (KBr, cm^{-1}): ν 2920, 1637, 1549, 1247, 1042, 819; EI-MS $[M]^{+}$: 467; Elemental anal. calcd. for $C_{31}H_{33}NO_3$: C 79.63, H 7.11, N 3.00; found: C 79.23, H 7.07, N 2.74.

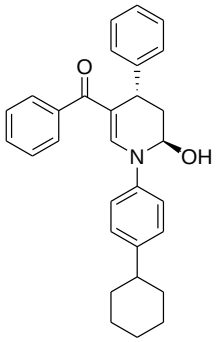


((*4S,6R*)-6-Hydroxy-4-phenyl-1-p-tolyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9e). Pale green solid, m.p. 142-143 ^{o}C; 97:3 er from HPLC on chiral stationary phase (Chiralpak AD, n-heptane : EtOH = 7 : 3, 1.0 mL/min), t_R = 9.38 min (major), t_R = 11.41 min (minor); $[\alpha]^{D}_{23}$ = -141 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.62 (d, 2 H, *J* = 9.0 Hz), 7.40 (s, 1 H), 7.31-7.21 (m, 4 H), 7.15-7.07 (m, 5 H), 6.84 (d, 2 H, *J* = 9.0 Hz), 5.27 (s, 1

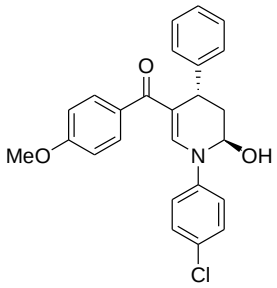
H), 4.29-4.22 (m, 1 H), 3.82 (s, 3 H), 3.51 (brs, 1 H), 2.42-2.31 (m, 4 H, CH + CH_3), 2.10 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.0, 161.8, 144.7, 144.3, 142.0, 134.2, 130.9, 130.1, 128.4, 127.6, 127.2, 126.1, 119.7, 116.1, 113.4, 78.5, 55.3, 39.6, 34.4, 20.7; IR (KBr, cm^{-1}): ν 3315, 1581, 1508, 1250, 1017, 756, 698; EI-MS $[M]^+$: 399; HRMS (ESI) calcd for $C_{26}H_{26}NO_3[M+H]^+$: 400.1913; found: 400.1907.



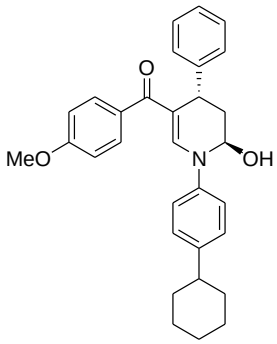
((*4S,6R*)-1-(6-Chloropyridin-3-yl)-6-hydroxy-4-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9f). Colorless solid, m.p. 169-171 °C; > 99:1 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 0.7 mL/min), t_R = 16.03 min (major), t_R = 19.41 min (minor); $[\alpha]^D_{23}$ = -162 (*c* 0.78, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 8.21 (d, 1 H, *J* = 4.0 Hz), 7.54 (d, 2 H, *J* = 8.0 Hz), 7.31 (t, 1 H, *J* = 8.0 Hz), 7.26-7.18 (m, 6 H), 7.12 (t, 1 H, *J* = 8.0 Hz), 6.81 (d, 2 H, *J* = 8.0 Hz), 5.17 (s, 1 H), 4.50 (brs, 1 H), 4.26 (dd, 1 H, J_1 = 4.0 Hz, J_2 = 12.0 Hz), 3.81 (s, 3 H), 2.44-2.38 (m, 1 H), 2.10 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 193.4, 162.3, 145.8, 143.9, 142.1, 140.2, 140.0, 131.1, 130.8, 128.5, 127.2, 126.7, 126.3, 124.5, 118.3, 113.6, 78.4, 55.1, 39.6, 34.4; IR (KBr, cm^{-1}): ν 2913, 2847, 1594, 1465, 1257, 1022, 761, 703; EI-MS $[M]^+$: 420; Elemental anal. calcd. for $C_{24}H_{21}ClN_2O_3$: C 68.49, H 5.03, N 6.66; found: C 68.22, H 4.69, N 6.29.



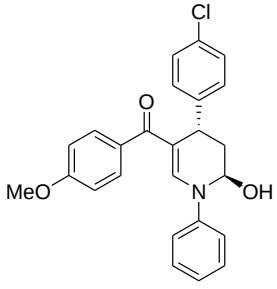
((*4S,6R*)-1-(4-Cyclohexylphenyl)-6-hydroxy-4-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9g). Colorless solid, m.p. 151-153 °C; 92:8 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 8.90 min (major), t_R = 13.72 min (minor); $[\alpha]^D_{23}$ = -138 (*c* 0.86, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.79 (d, 2 H, *J* = 9.0 Hz), 7.65-7.59 (m, 3 H), 7.56-7.43 (m, 6 H), 7.37-7.27 (m, 4 H), 5.55 (s, 1 H), 4.45 (dd, 1 H, J_1 = 6.0 Hz, J_2 = 12.0 Hz), 3.24 (brs, 1 H), 2.65-2.57 (m, 2 H), 2.32 (t, 1 H, *J* = 12.0 Hz), 1.04-1.92 (m, 5 H), 1.62-1.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 194.1, 145.4, 144.8, 142.0, 139.6, 130.6, 128.8, 128.5, 128.1, 127.9, 127.2, 126.9, 126.1, 119.9, 116.0, 78.7, 43.9, 39.3, 34.3, 26.8, 26.0; IR (KBr, cm^{-1}): ν 3343, 2923, 1638, 1546, 1251, 1038, 692; EI-MS $[M]^+$: 437; HRMS (ESI) calcd for $C_{30}H_{32}NO_2[M+H]^+$: 438.2433; found: 438.2427.



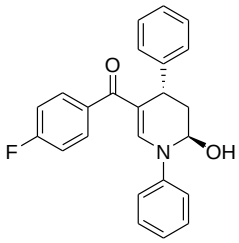
((*4S,6R*)-1-(4-Chlorophenyl)-6-hydroxy-4-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9h). Pale green solid, m.p. 156-158 ^{o}C; 91:9 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 0.7 mL/min), t_R = 13.68 min (major), t_R = 15.15 min (minor); $[\alpha]^{D}_{23}$ = -135 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.62 (d, 2 H, *J* = 9.0 Hz), 7.34 (s, 1 H), 7.29-7.21 (m, 6 H), 7.13 (t, 3 H, *J* = 9.0 Hz), 6.85 (d, 2 H, *J* = 9.0 Hz), 5.26 (s, 1 H), 4.24 (dd, 1 H, J_1 = 6.0 Hz, J_2 = 12.0 Hz), 3.83 (s, 3 H), 3.56 (brs, 1 H), 2.45-2.36 (m, 1 H), 2.11 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.3, 162.1, 144.3, 142.9, 131.6, 130.9, 129.6, 129.4, 128.5, 127.6, 127.2, 126.2, 120.4, 117.2, 113.5, 78.4, 55.2, 39.6, 34.3; IR (KBr, cm^{-1}): ν 3315, 1557, 1250, 1014, 759, 696; EI-MS $[M]^+$: 437; Elemental anal. calcd. for $C_{25}H_{22}ClNO_3$: C 71.51, H 5.28, N 3.34; Found: C 71.13, H 5.34, N 3.23.



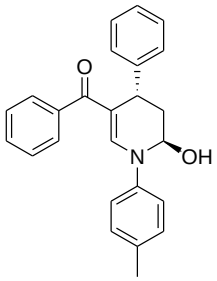
((*4S,6R*)-1-(4-Cyclohexylphenyl)-6-hydroxy-4-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9i). Pale yelllow solid, m.p. 160-162 ^{o}C; 90:10 er from HPLC on chiral stationary phase (Chiralpak AD, n-heptane : EtOH = 7 : 3, 1.0 mL/min), t_R = 7.07 min (major), t_R = 8.43 min (minor); $[\alpha]^{D}_{23}$ = -131 (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.57 (d, 2 H, *J* = 8.0 Hz), 7.37 (s, 1 H), 7.30 (d, 2 H, *J* = 8.0 Hz), 7.25-7.21 (m, 2 H), 7.15-7.08 (m, 5 H), 6.80 (d, 2 H), 5.27 (s, 1 H), 4.27 (dd, 1 H, J_1 = 4.0 Hz, J_2 = 12.0 Hz), 3.79 (s, 3 H), 2.45-2.38 (m, 2 H), 2.07 (t, 1 H, *J* = 12.0 Hz), 1.82 (d, 4 H, *J* = 8.0 Hz), 1.42-1.33 (m, 5 H), 1.27-1.18 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 193.1, 161.6, 144.8, 144.2, 142.1, 131.9, 130.9, 129.4, 128.4, 127.8, 127.3, 126.0, 119.4, 116.2, 113.4, 78.4, 55.3, 43.8, 39.5, 34.5, 26.8, 26.2; IR (KBr, cm^{-1}): ν 3356, 2926, 1584, 1250, 1166, 1033, 828, 770; EI-MS $[M]^+$: 467; HRMS (ESI) calcd for $C_{31}H_{34}NO_3[M+H]^+$: 468.2539; found: 468.2535.



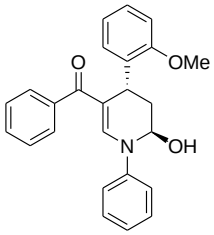
((*4S,6R*)-4-(4-Chlorophenyl)-6-hydroxy-1-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(4-methoxyphenyl)methanone (9j). Pale yellow solid, m.p. 125-127 ^{o}C; 89:11 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : EtOH = 7 : 3, 0.7 mL/min), t_R = 14.24 min (minor), t_R = 16.32 min (major); $[\alpha]^{D}_{23}$ = -93 (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.64 (d, 2 H, *J* = 9.0 Hz), 7.44 (s, 1 H), 7.36 (t, 2 H, *J* = 9.0 Hz), 7.26-7.14 (m, 7 H), 6.87 (d, 2 H, *J* = 9.0 Hz), 5.35 (s, 1 H), 4.23 (dd, 1 H, J_1 = 12.0 Hz, J_2 = 6.0 Hz), 3.83, (s, 3 H), 3.21 (brs, 1 H), 2.44-2.38 (m, 1 H), 2.08 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 192.6, 162.0, 144.5, 143.6, 143.3, 131.4, 130.8, 129.6, 128.7, 127.7, 124.6, 119.4, 116.4, 113.8, 78.5, 55.2, 39.1, 33.9; IR (KBr, cm^{-1}): ν 3322, 2929, 1571, 1493, 1248, 1024, 898, 755; EI-MS $[M]^{+}$: 419; HRMS (ESI) calcd for $C_{25}H_{23}ClNO_3[M+H]^{+}$: 420.1366; found: 420.1356.



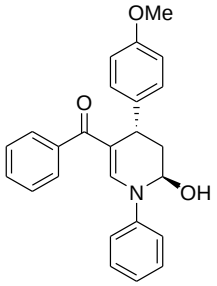
((*4S,6R*)-(4-Fluorophenyl)-6-hydroxy-1,4-diphenyl-1,4,5,6-tetrahydropyridin-3-yl)methanone (9k). Colorless solid, m.p. 159-160 ^{o}C; 89:11 er from HPLC on chiral stationary phase (Chiralpak AS, n-heptane : EtOH = 9 : 1, 1.0 mL/min), t_R = 8.56 min (minor), t_R = 11.58 min (major); $[\alpha]^{D}_{23}$ = -109 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.63 (dd, 2 H J_1 = 9.0 Hz, J_2= 12.0 Hz), 7.42 (s, 1 H), 7.35 (t, 2 H, *J* = 9.0 Hz), 7.28 (d, 4 H, *J* = 9.0 Hz), 7.19-7.12 (m, 4 H), 7.02 (t, 2 H, *J* = 9.0 Hz), 5.33 (s, 1 H), 4.27-4.21 (m, 1 H), 3.46 (brs, 1 H), 2.45-2.37 (m, 1 H), 2.17-2.07 (m, 1 H); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 192.5, 166.0, 162.6, 144.6, 135.7, 130.9, 129.7, 128.5, 127.2, 126.1, 124.7, 119.6, 116.5, 115.4, 115.1, 78.3, 39.7, 34.3; IR (KBr, cm^{-1}): ν 3278, 2926, 1564, 1499, 1243, 1036, 754; EI-MS $[M]^{+}$: 373; Elemental ana. calcd for $C_{24}H_{20}FNO_2$: C 77.19, H 5.40, N 3.75; found: C 76.79 , H 5.41 , N 3.58.



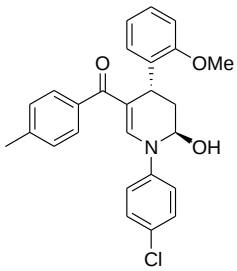
((*4S,6R*)-6-Hydroxy-4-phenyl-1-*p*-tolyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9l). Pale green solid, m.p. 97-99 ^{o}C; 87:13 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 9.50 min (major), t_R = 10.71 min (minor); $[\alpha]^{D}_{23}$ = -103 (*c* 0.89, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.77 (d, 2 H, *J* = 6.0 Hz), 7.61 (brs, 2 H), 7.54-7.43 (m, 6 H), 7.36-7.29 (m, 3 H), 7.24 (d, 2 H, *J* = 9.0 Hz), 5.44 (s, 1 H), 4.45 (dd, 1 H, J_1 = 6.0 Hz, J_2 = 12.0 Hz), 3.77 (brs, 1 H), 2.63-2.55 (m, 1 H), 2.50 (s, 3 H), 2.30 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.6, 145.6, 144.7, 141.9, 139.6, 134.4, 130.6, 130.1, 128.7, 128.4, 128.1, 127.2, 126.1, 119.8, 115.9, 78.5, 39.6, 34.3, 20.6; IR (KBr, cm^{-1}): ν 3347, 2923, 1560, 1257, 1051, 756, 704; EI-MS $[M]^{+}$: 369; HRMS (ESI) calcd for $C_{25}H_{24}NO_2[M+H]^{+}$: 370.1807; found: 370.1808.



((*4S,6R*)-6-Hydroxy-4-(2-methoxyphenyl)-1-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9m). Pale yellow solid, m.p. 51-53 ^{o}C; 86:14 er from HPLC on chiral stationary phase (Chiralpak AD, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 7.60 min (major), t_R = 9.95 min (minor); $[\alpha]^{D}_{23}$ = -160 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.63 (d, 2 H, *J* = 9.0 Hz), 7.48 (s, 1 H), 7.43-7.30 (m, 5 H), 7.21-7.17 (m, 3 H), 7.11 (t, 2 H, *J* = 9.0 Hz), 6.85 (t, 2 H, *J* = 6.0 Hz), 5.32 (s, 1 H), 6.65 (dd, 1 H, J_1 = 6.0 Hz, J_2 = 12.0 Hz), 3.86 (s, 3 H), 3.18 (brs, 1 H), 2.44-2.37 (m, 1 H), 2.17 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.8, 157.0, 144.8, 144.3, 139.6, 132.2, 130.6, 129.6, 128.8, 128.1, 127.5, 127.2, 124.3, 120.7, 119.6, 116.6, 110.7, 78.7, 55.2, 37.0, 28.2; IR (KBr, cm^{-1}): ν 3350, 2930, 1560, 1491, 1248, 1026, 893, 750; EI-MS $[M]^{+}$: 385; HRMS (ESI) calcd for $C_{25}H_{24}NO_3[M+H]^{+}$: 386.1756; found: 386.1757.

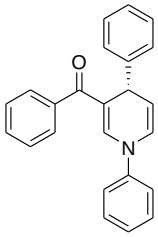


((*4S,6R*)-6-Hydroxy-4-(4-methoxyphenyl)-1-phenyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (9n). Colorless solid, m.p. 139-141 ^{o}C; 86:15 er from HPLC on chiral stationary phase (Chiralpak AD, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 8.64 min (minor), t_R = 11.03 min (major); $[\alpha]^{D}_{23}$ = -108 (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.59 (d, 2 H, *J* = 8.0 Hz), 7.42-7.39 (m, 2 H), 7.35-7.29 (m, 4 H), 7.21 (d, 2 H, *J* = 8.0 Hz), 7.16 (d, 2 H, *J* = 8.0 Hz), 7.10 (t, 1 H, *J* = 8.0 Hz), 6.79 (d, 2 H, *J* = 8.0 Hz), 5.30 (s, 1 H), 4.20 (dd, 1 H, J_1 = 8.0 Hz, J_2 = 12.0 Hz), 3.72 (s, 3 H), 3.41 (brs, 1 H), 2.40-2.35 (m, 1 H), 2.13-2.10 (m, 1 H); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 194.1, 158.1, 144.6, 144.1, 139.4, 136.3, 130.8, 129.6, 128.8, 128.1, 124.4, 119.5, 116.8, 113.9, 78.6, 55.1, 39.5, 33.5; IR (KBr, cm^{-1}): ν 3342, 2957, 1643, 1556, 1248, 1171, 1042, 814, 700; EI-MS $[M]^{+}$: 385; HRMS (ESI) calcd for $C_{25}H_{24}NO_3[M+H]^{+}$: 386.1756; found: 386.1757.

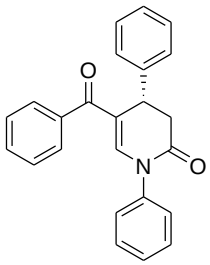


((*4S,6R*)-1-(4-Chlorophenyl)-6-hydroxy-4-(2-methoxyphenyl)-1,4,5,6-tetrahydropyridin-3-yl)(p-tolyl)methanone (9o). Colorless solid, m.p. 143-145 ^{o}C; 85:15 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 7.36 min (major), t_R = 10.40 min (minor); $[\alpha]^{D}_{23}$ = -109 (*c* 0.77, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.53

(d, 2 H, *J* = 9.0 Hz), 7.37 (s, 1 H), 7.24 (d, 2 H, *J* = 9.0 Hz), 7.18-7.08 (m, 6 H), 6.85-6.80 (m, 2 H), 5.23 (s, 1 H), 4.62 (dd, 1 H, J_1 = 6.0 Hz, J_2 = 12.0 Hz), 3.84 (s, 3 H), 3.38 (brs, 1 H), 2.42-2.34 (m, 4 H, CH+CH_3), 2.14 (t, 1 H, *J* = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.7, 157.0, 143.7, 143.0, 141.2, 136.5, 132.1, 129.4, 129.3, 129.0, 128.8, 127.5, 127.2, 120.6, 117.2, 110.7, 78.7, 55.2, 37.0, 28.1, 21.5; IR (KBr, cm^{-1}): ν 3293, 2935, 1562, 1492, 1250, 1059, 903, 749; EI-MS $[M]^+$: 433; Elemental anal. calcd. for $C_{26}H_{24}ClNO_3$: C 71.97, H 5.57, N 3.23; Found: C 71.64, H 5.57, N 3.16.

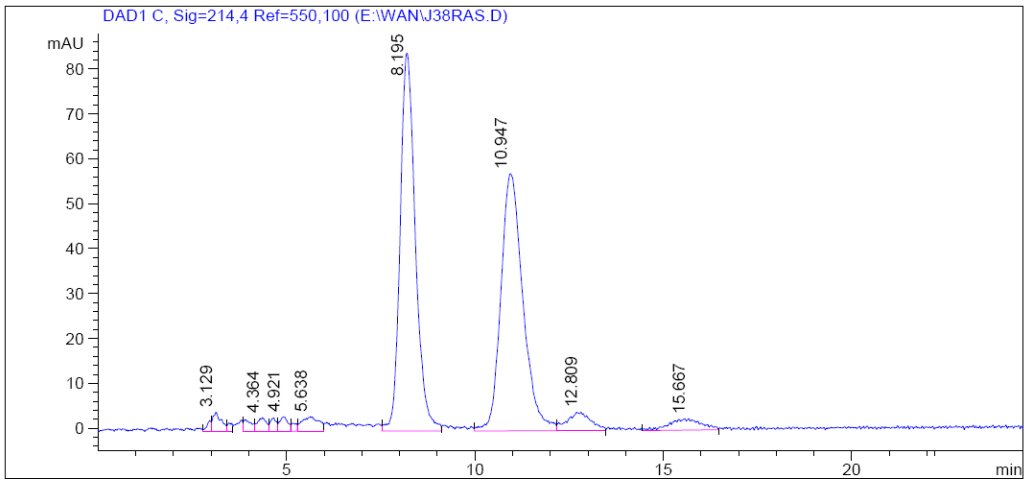


(*S*)-(1,4-Diphenyl-1,4-dihydropyridin-3-yl)(phenyl)methanone (10).[1] Pale yellow solid, m.p. 127-129 °C; 85:15 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : EtOH = 8 : 2, 0.7 mL/min), t_R = 9.98 min (minor), t_R = 11.60 min (major); $[\alpha]^D_{23}$ = -123 (*c* 0.69, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 Mz): δ 7.51 (d, 2 H, *J* = 8.0 Hz), 7.43-7.28 (m, 10 H), 7.17 (t, 2 H, *J* = 8.0 Hz), 7.11 (d, 2 H, *J* = 8.0 Hz), 6.51 (d, 1 H, *J* = 8.0 Hz), 5.26 (dd, 1 H, J_1 = 8.0 Hz, J_2 = 4.0 Hz), 4.95 (d, 1 H, *J* = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 Mz): δ 195.3, 146.7, 143.6, 141.7, 139.7, 130.5, 129.8, 128.4, 128.1, 128.0, 126.4, 125.3, 125.2, 119.9, 115.8, 111.5, 38.1; IR (KBr, cm^{-1}): ν 2040, 1671, 1569, 1255, 1134, 720; EI-MS $[M]^+$: 337.

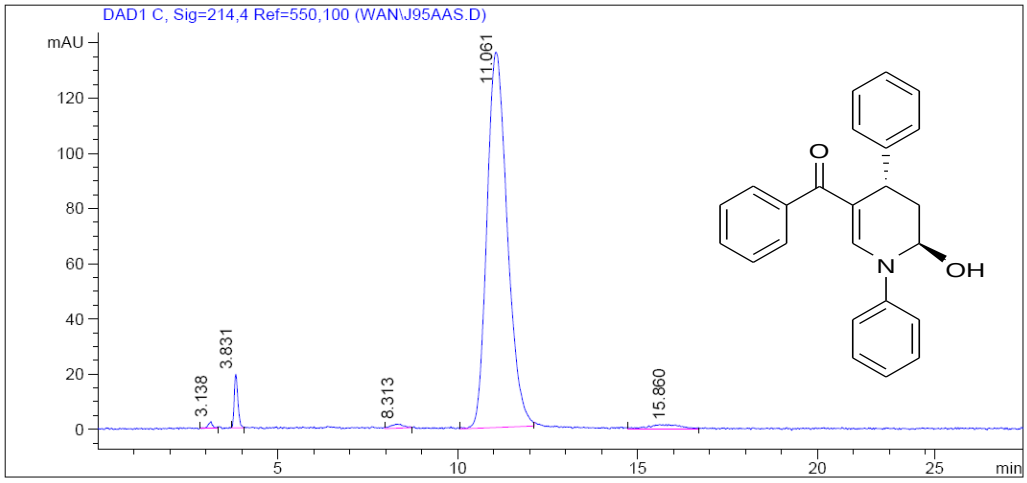


(*S*)-5-Benzoyl-1,4-diphenyl-3,4-dihydropyridin-2(1H)-one (11). Brown solid, m.p. 58-59 °C; 90:10 er from HPLC on chiral stationary phase (Chiralpak IA, n-heptane : isopropanol = 7 : 3, 1.0 mL/min), t_R = 7.36 min (major), t_R = 10.40 min (minor); $[\alpha]^D_{23}$ = -109 (*c* 0.77, $CHCl_3$);^{1}H NMR ($CDCl_3$, 300 Mz): δ 7.59 (d, 2 H, *J* = 9.0 Hz), 7.50-7.40 (m, 5 H), 7.38-7.31 (m, 6 H), 7.24 (d, 3 H, *J* = 8.0 Hz), 4.62 (dd, 1 H, J_1 = 3.0 Hz, J_2 = 9.0 Hz), 3.24 (dd, 1 H, J_1 = J_2 = 9.0 Hz), 3.06 (dd, J_1 = 3.0 Hz, J_2 = 12.0 Hz); ^{13}C NMR ($CDCl_3$, 75 Mz): δ 193.7, 168.5, 144.5, 141.2, 139.5, 138.4, 131.5, 129.5, 129.0, 128.6, 128.4, 128.0, 127.2, 126.6, 126.2, 121.5, 38.9, 36.0; EI-MS $[M]^+$: 353; IR (KBr, cm^{-1}): ν 3062, 1705, 1620, 1492, 1259, 694; EI-MS $[M]^+$: 353; HRMS (ESI) calcd for $C_{24}H_{20}NO_2[M+H]^+$: 354.1494; found: 354.1488.

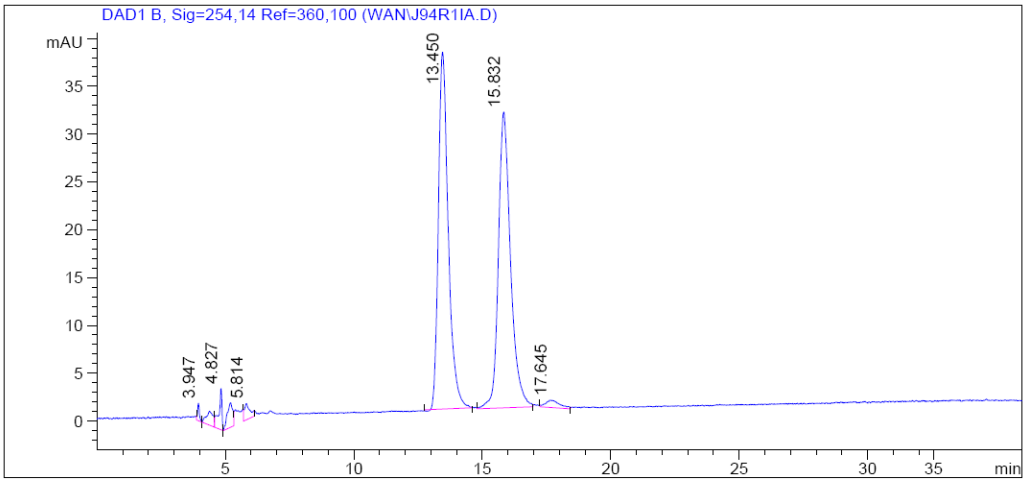
[1] J.-P. Wan, S.-F. Gan, G.-L. Sun, Y.-J. Pan, *J. Org. Chem.* **2009**, *74*, 2862-2865.



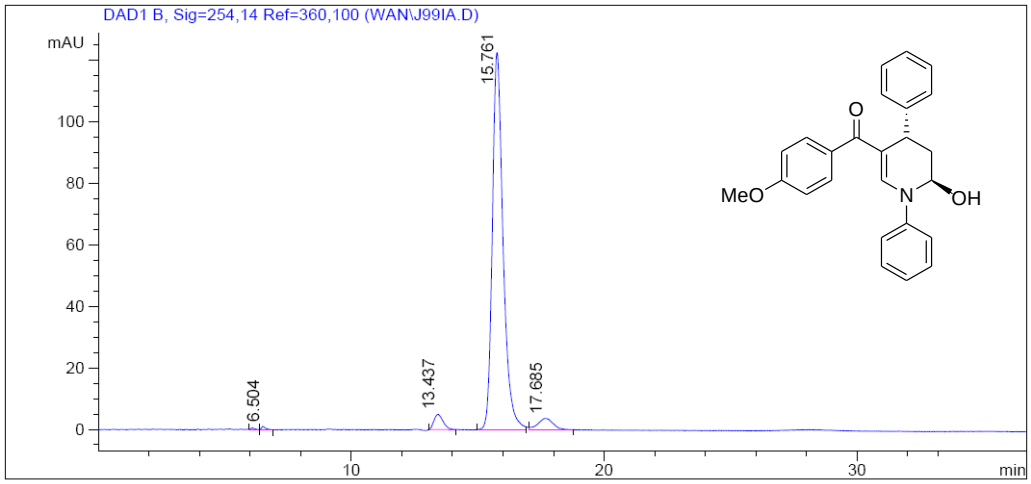
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	2.96	0.10	2.46	18.13	0.33
2	3.13	0.20	4.35	67.27	1.24
3	3.47	0.11	1.90	16.98	0.31
4	3.91	0.19	2.60	37.73	0.70
5	4.36	0.20	3.11	50.93	0.94
6	4.65	0.16	2.97	34.88	0.64
7	4.92	0.20	3.22	48.62	0.90
8	5.17	0.13	1.84	17.78	0.33
9	5.64	0.38	3.25	102.41	1.89
10	8.19	0.42	84.17	2369.66	43.66
11	10.95	0.60	57.23	2327.76	42.89
12	12.81	0.55	4.15	182.73	3.37
13	15.67	0.70	2.58	152.44	2.81
Total				5427.32	100.00



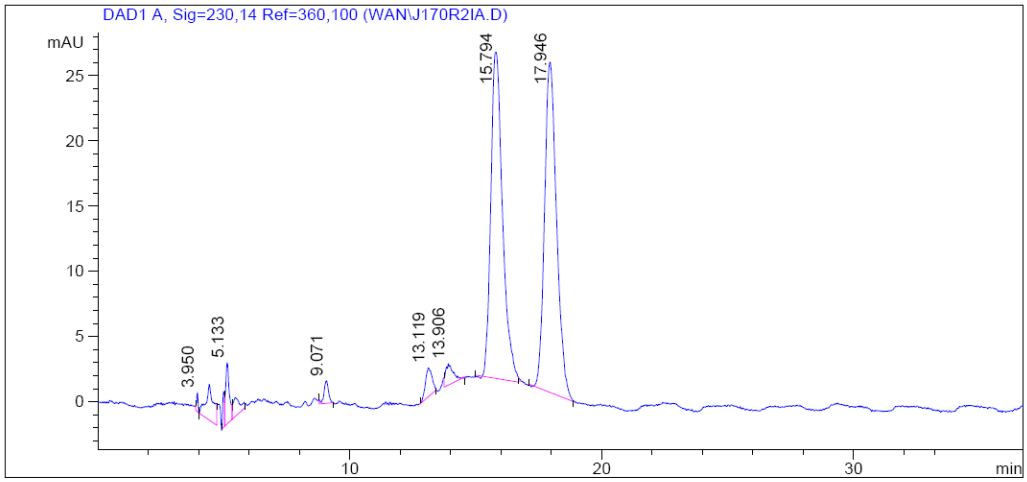
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.14	0.11	2.38	19.12	0.34
2	3.83	0.11	19.46	138.09	2.44
3	8.31	0.41	1.53	37.78	0.67
4	11.06	0.54	136.09	5362.91	94.94
5	15.86	0.96	1.58	91.11	1.61
Total				5649.01	100.00



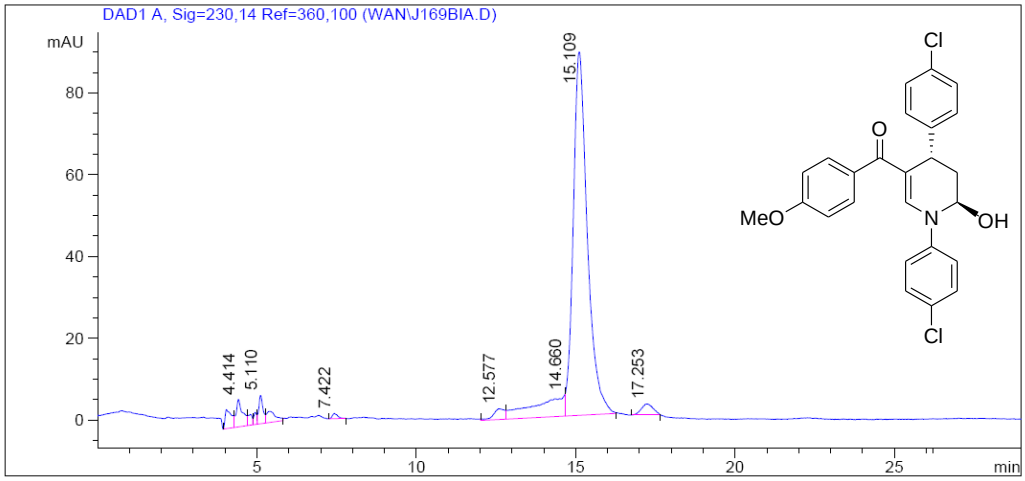
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.95	0.07	1.85	9.19	0.42
2	4.38	0.24	1.47	27.45	1.26
3	4.83	0.12	4.35	36.68	1.68
4	5.20	0.20	2.57	37.92	1.74
5	5.81	0.20	1.72	26.04	1.19
6	13.45	0.44	37.33	996.56	45.71
7	15.83	0.55	30.93	1016.31	46.62
8	17.64	0.65	0.76	29.88	1.37
Total				2180.03	100.00



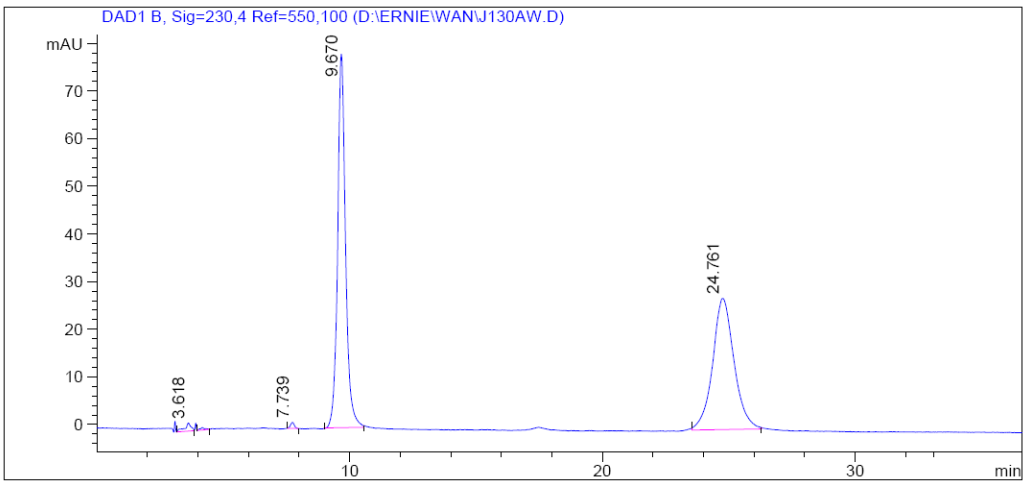
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.10	0.15	0.68	8.17	0.21
2	6.50	0.16	1.14	14.04	0.36
3	13.44	0.32	5.00	127.61	3.24
4	15.76	0.44	122.58	3625.01	92.17
5	17.69	0.50	3.74	158.22	4.02
Total				3933.06	100.00



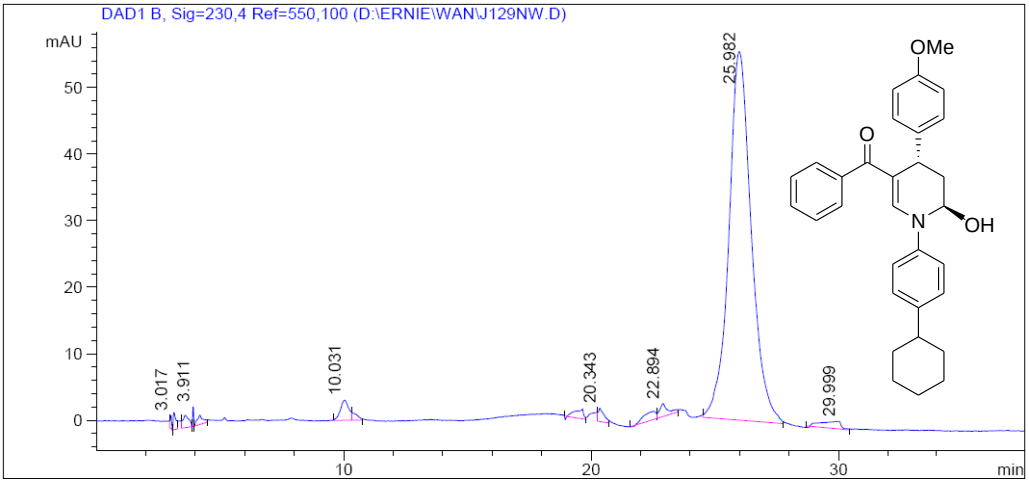
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.95	0.06	1.46	5.84	0.31
2	4.42	0.26	2.77	57.87	3.05
3	4.99	0.08	2.76	13.43	0.71
4	5.13	0.15	4.70	47.90	2.53
5	5.45	0.24	1.46	26.87	1.42
6	9.07	0.17	1.73	21.47	1.13
7	13.12	0.30	2.23	40.02	2.11
8	13.91	0.33	1.66	32.82	1.73
9	15.79	0.54	25.01	807.90	42.63
10	17.95	0.55	25.32	840.87	44.37
Total				1894.98	100.00



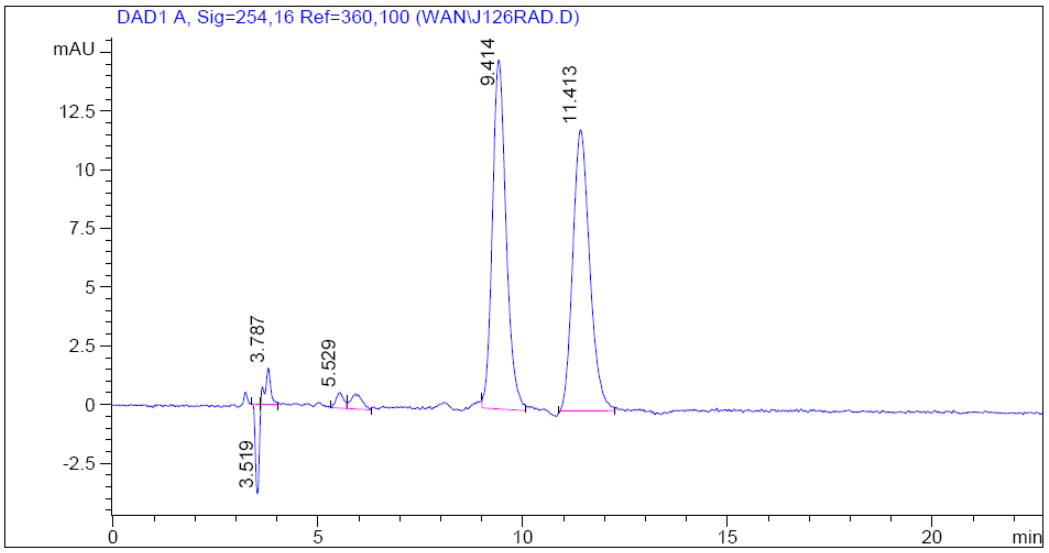
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.04	0.18	4.68	64.72	1.82
2	4.41	0.19	6.77	98.65	2.77
3	4.79	0.13	2.64	24.22	0.68
4	4.94	0.10	2.97	19.28	0.54
5	5.11	0.14	6.98	65.97	1.85
6	5.40	0.25	2.69	54.70	1.54
7	7.42	0.15	1.29	14.72	0.41
8	12.58	0.41	2.67	66.42	1.87
9	14.66	1.12	5.26	353.66	9.94
10	15.11	0.51	89.01	2730.70	76.74
11	17.25	0.30	2.61	65.44	1.84
Total				3558.48	100.00



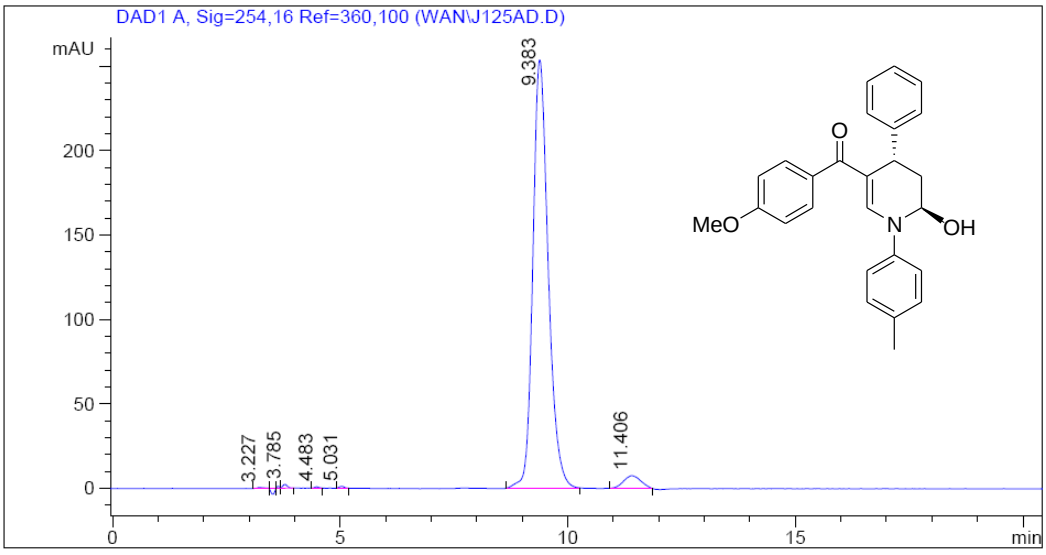
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.62	0.23	1.71	30.94	0.92
2	4.17	0.20	0.51	7.32	0.22
3	7.74	0.15	1.28	13.43	0.40
4	9.67	0.32	78.50	1700.89	50.44
5	24.76	0.78	27.56	1619.62	48.03
Total				3372.20	100.00



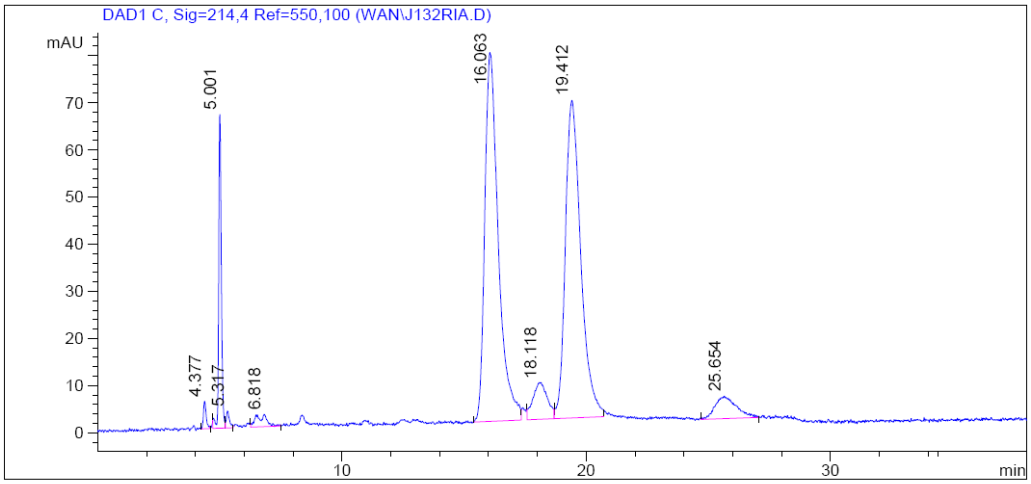
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.02	0.07	2.01	7.99	0.21
2	3.14	0.11	2.61	19.49	0.50
3	3.59	0.22	1.89	31.58	0.81
4	3.91	0.04	3.02	8.19	0.21
5	4.18	0.21	1.41	22.65	0.58
6	10.03	0.39	3.06	72.29	1.86
7	10.33	0.25	1.15	17.08	0.44
8	19.64	0.31	1.51	35.75	0.92
9	20.34	0.21	2.04	33.36	0.86
10	22.50	0.42	1.27	45.43	1.17
11	22.89	0.30	1.97	45.71	1.17
12	25.98	0.86	55.38	3491.98	89.69
13	30.00	0.90	1.15	62.03	1.59
Total				3893.51	100.00



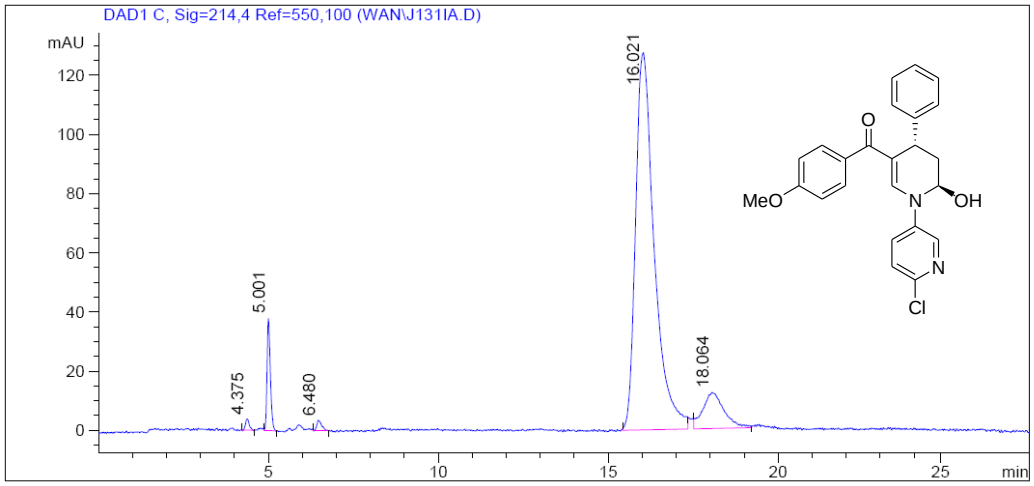
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.52	0.10	3.80	23.13	3.09
2	3.79	0.14	1.54	14.63	1.96
3	5.53	0.22	0.66	8.67	1.16
4	5.92	0.32	0.66	12.65	1.69
5	9.41	0.36	14.86	345.89	46.22
6	11.41	0.45	11.97	343.43	45.89
Total				748.40	100.00



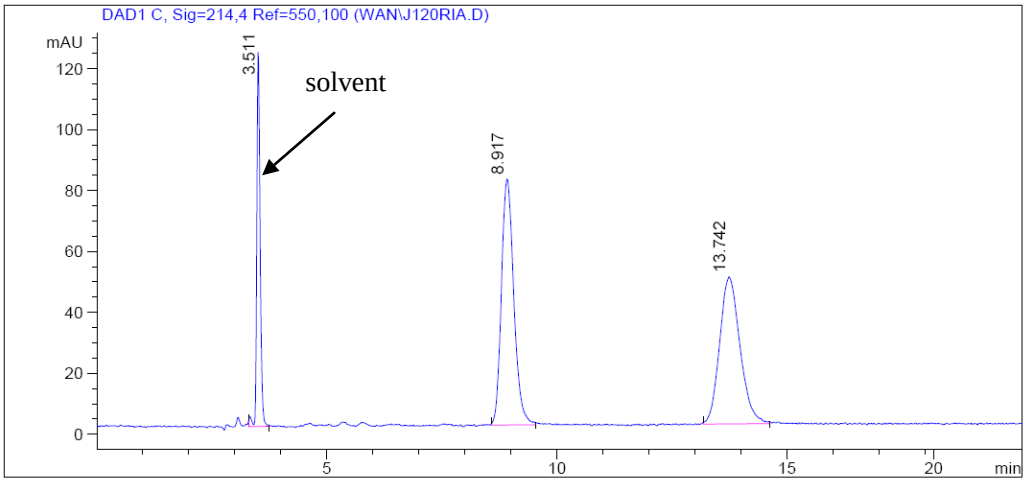
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.23	0.14	0.67	6.59	0.11
2	3.52	0.10	3.46	19.70	0.32
3	3.64	0.08	1.13	5.08	0.08
4	3.78	0.12	2.34	17.44	0.28
5	4.48	0.10	0.78	5.11	0.08
6	5.03	0.12	1.08	8.13	0.13
7	9.38	0.35	253.88	5967.30	95.79
8	11.41	0.38	7.55	200.04	3.21
Total				6229.40	100.00



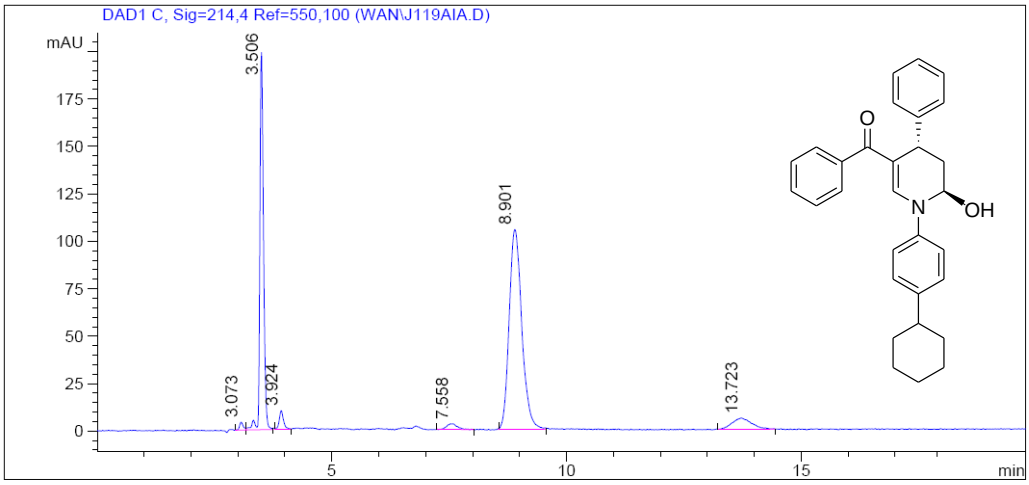
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.38	0.13	5.83	46.59	0.64
2	5.00	0.12	66.57	498.22	6.88
3	5.32	0.14	3.57	33.44	0.46
4	6.82	0.40	2.61	81.28	1.12
5	16.06	0.57	78.30	3011.70	41.56
6	18.12	0.51	7.73	322.13	4.45
7	19.41	0.69	67.41	2965.53	40.92
8	25.65	1.00	4.80	287.78	3.97
Total				7246.67	100.00



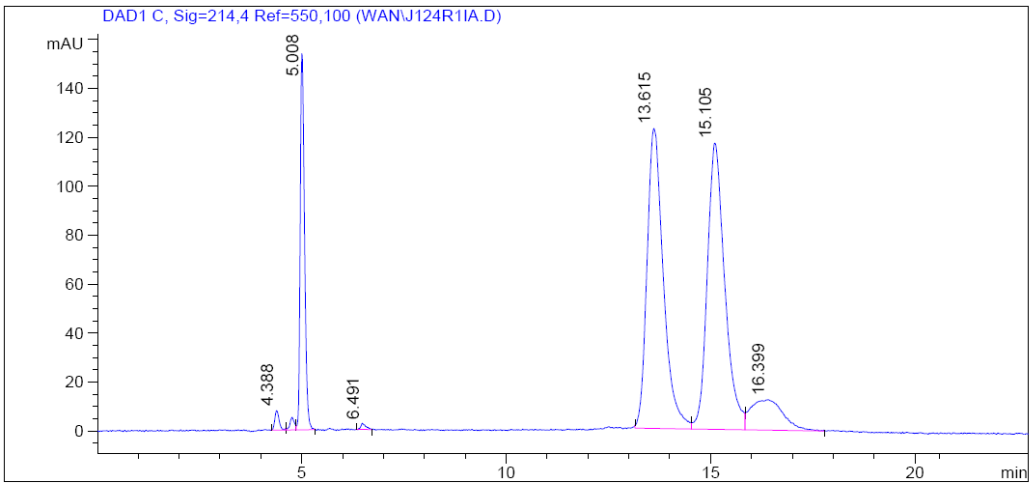
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.37	0.12	3.72	28.34	0.50
2	5.00	0.11	38.12	255.28	4.46
3	6.48	0.15	3.58	37.58	0.66
4	16.02	0.55	127.47	4863.56	85.05
5	18.06	0.53	12.25	533.91	9.34
Total				5718.67	100.00



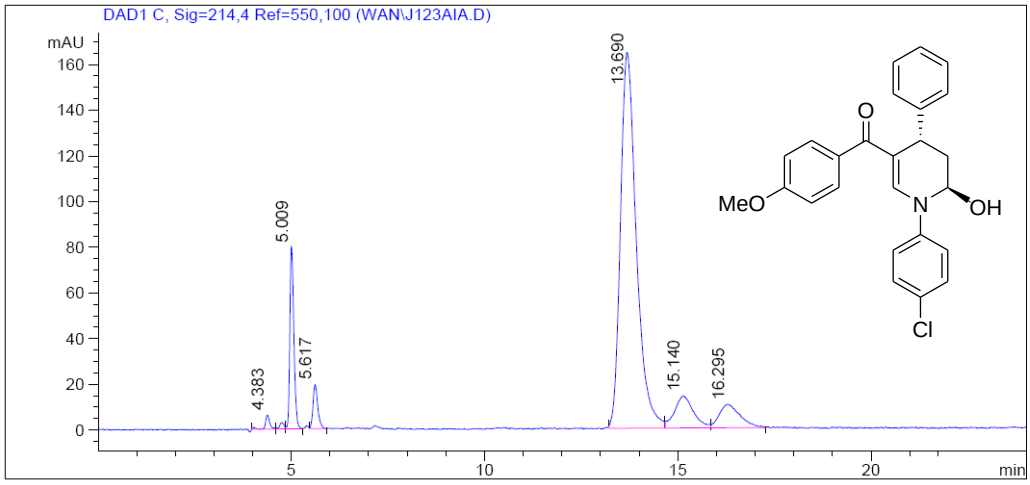
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.51	0.08	121.08	626.34	17.29
2	8.92	0.29	80.77	1510.64	41.70
3	13.74	0.47	48.34	1485.61	41.01
Total				3622.59	100.00



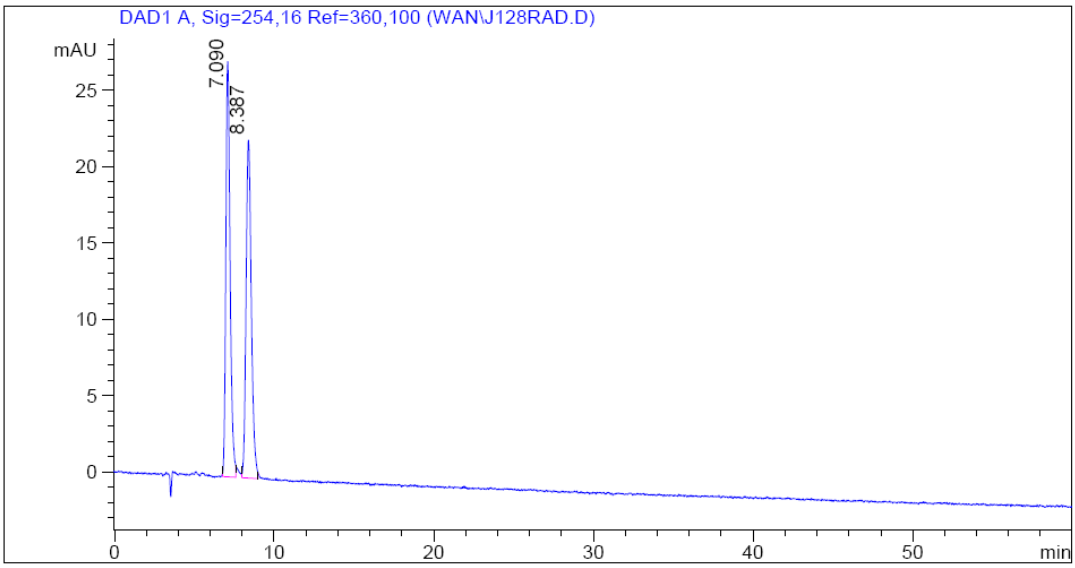
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.07	0.09	4.15	23.48	0.70
2	3.51	0.09	198.83	1066.90	31.89
3	3.92	0.10	9.95	63.06	1.88
4	7.56	0.25	2.83	46.12	1.38
5	8.90	0.30	105.32	1971.97	58.94
6	13.72	0.39	6.02	174.44	5.21
Total				3345.96	100.00



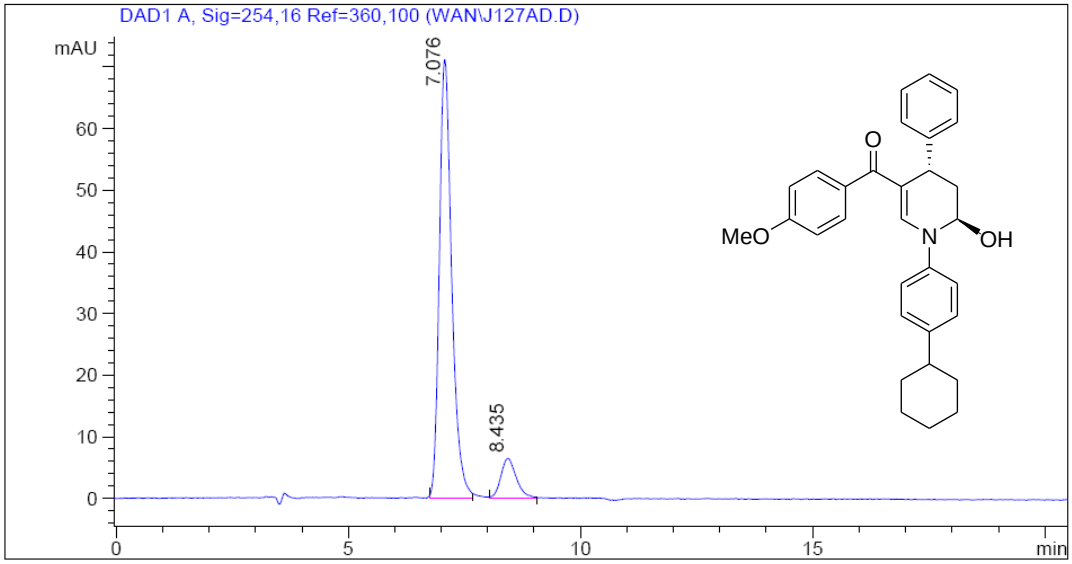
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.39	0.12	8.02	59.37	0.67
2	4.76	0.11	5.20	38.43	0.43
3	5.01	0.12	153.04	1133.65	12.83
4	6.49	0.14	2.41	21.97	0.25
5	13.61	0.41	122.63	3410.94	38.59
6	15.11	0.46	116.92	3484.84	39.42
7	16.40	0.68	12.50	690.11	7.81
Total				8839.32	100.00



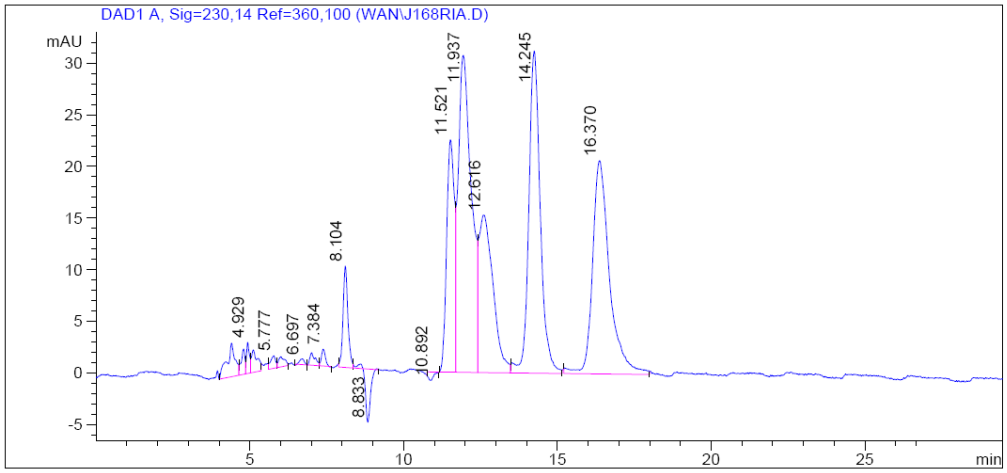
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.38	0.12	6.17	49.82	0.78
2	4.76	0.13	2.67	22.60	0.35
3	5.01	0.12	79.56	575.83	9.04
4	5.62	0.13	19.42	163.60	2.57
5	13.69	0.43	164.51	4693.15	73.68
6	15.14	0.50	14.10	477.94	7.50
7	16.29	0.52	10.36	386.87	6.07
Total				6369.80	100.00



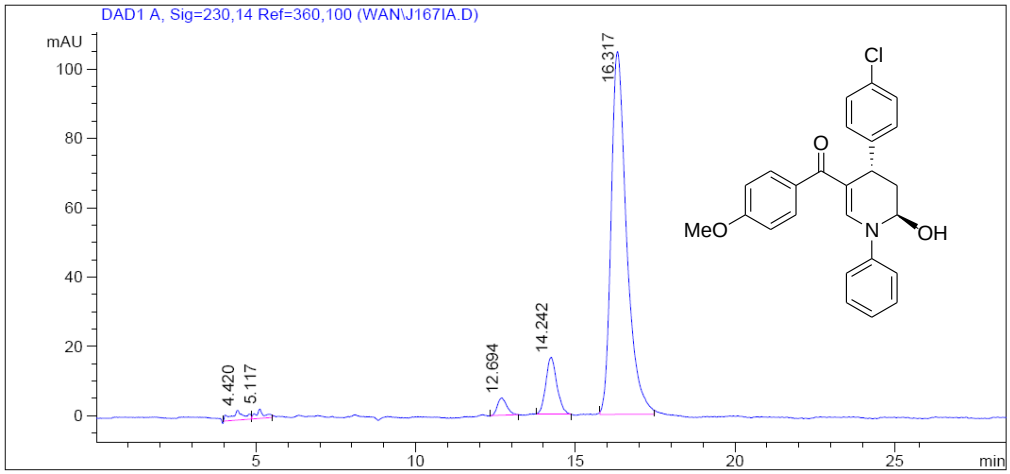
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.09	0.29	27.20	506.37	49.97
2	8.39	0.35	22.13	507.04	50.03
Total				1013.40	100.00



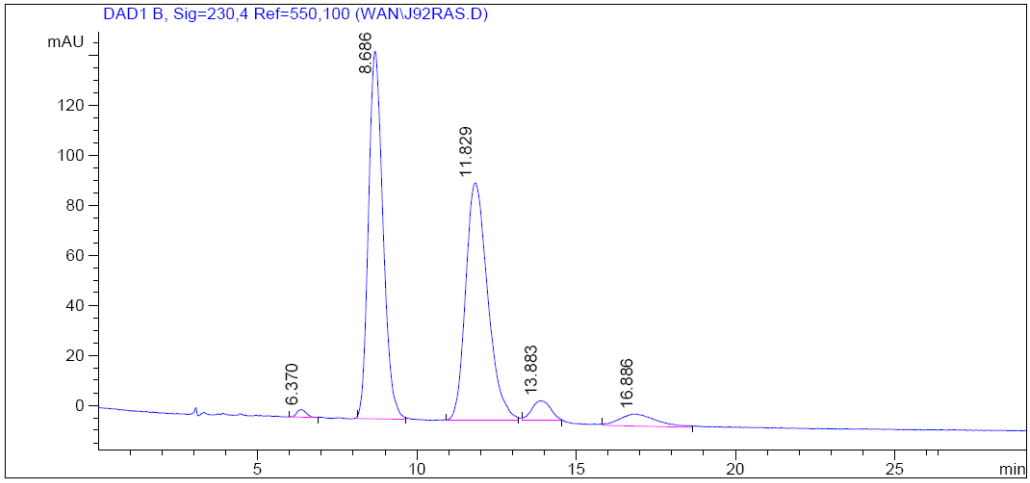
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	7.08	0.28	71.09	1316.60	89.91
2	8.43	0.36	6.42	147.77	10.09
Total				1464.37	100.00



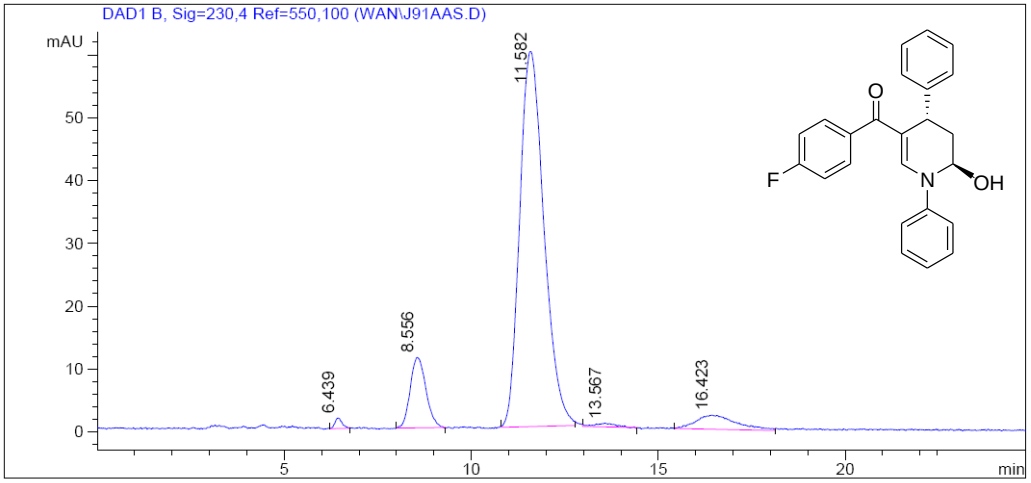
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.40	0.24	3.27	60.41	1.61
2	4.80	0.12	2.46	21.18	0.56
3	4.93	0.09	3.03	20.02	0.53
4	5.11	0.18	2.20	29.36	0.78
5	5.78	0.14	1.22	14.25	0.38
6	6.01	0.18	0.99	13.68	0.36
7	6.70	0.13	0.56	5.77	0.15
8	7.01	0.16	1.22	14.59	0.39
9	7.38	0.12	1.64	14.43	0.38
10	8.10	0.17	9.83	108.45	2.88
11	8.83	0.15	5.15	47.84	1.27
12	10.89	0.20	0.81	9.55	0.25
13	11.52	0.26	22.54	394.34	10.48
14	11.94	0.49	30.72	912.03	24.23
15	12.62	0.54	15.26	490.04	13.02
16	14.24	0.43	31.22	812.33	21.58
17	16.37	0.55	20.68	795.20	21.13
Total				3763.47	100.00



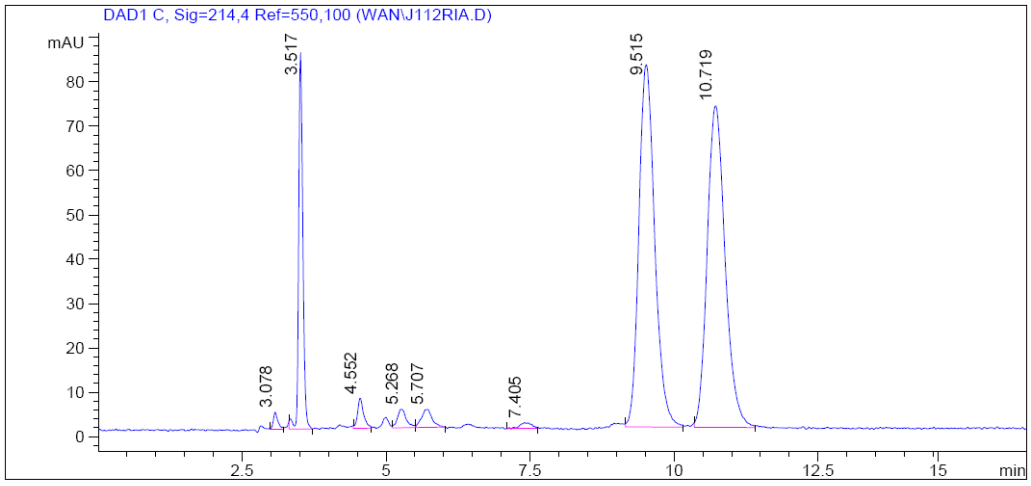
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.42	0.35	2.82	76.88	1.85
2	5.12	0.23	2.69	48.23	1.16
3	12.69	0.26	5.01	102.71	2.47
4	14.24	0.37	16.47	399.61	9.61
5	16.32	0.46	104.77	3528.80	84.90
Total				4156.23	100.00



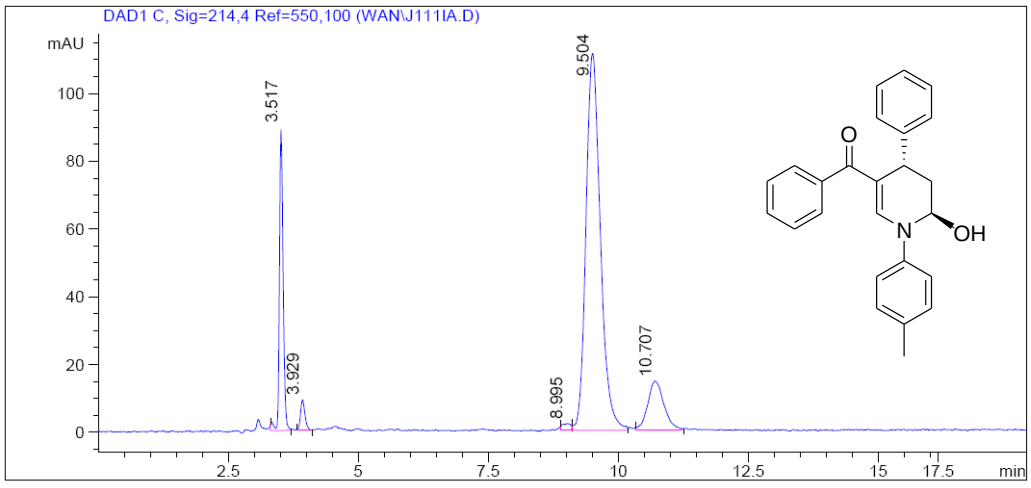
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.37	0.27	3.03	64.45	0.65
2	8.69	0.47	146.83	4648.35	46.58
3	11.83	0.72	94.83	4561.42	45.71
4	13.88	0.54	7.72	312.50	3.13
5	16.89	1.35	4.85	392.61	3.93
Total				9979.33	100.00



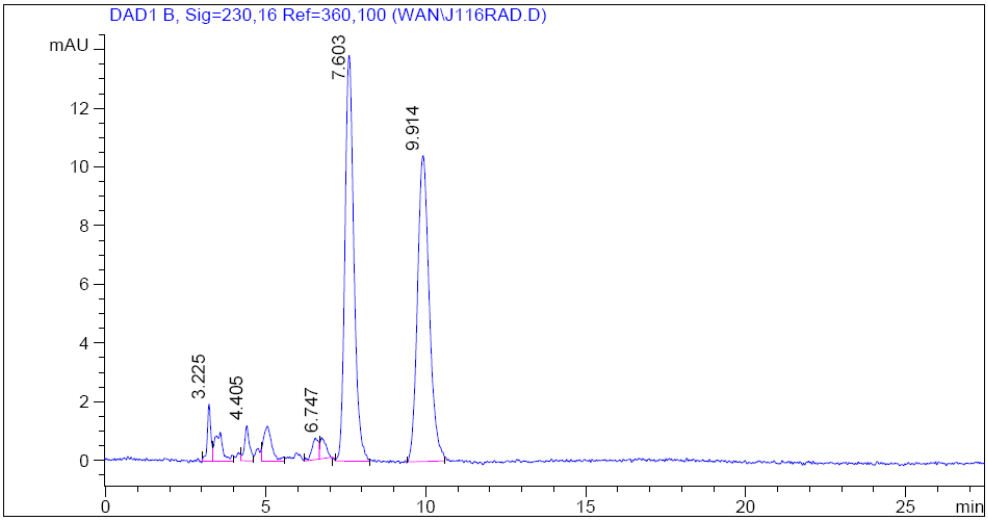
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	6.44	0.20	1.69	22.73	0.70
2	8.56	0.44	11.19	327.50	10.10
3	11.58	0.64	59.71	2698.72	83.23
4	13.57	0.64	0.60	22.99	0.71
5	16.42	1.26	2.26	170.52	5.26
Total				3242.46	100.00



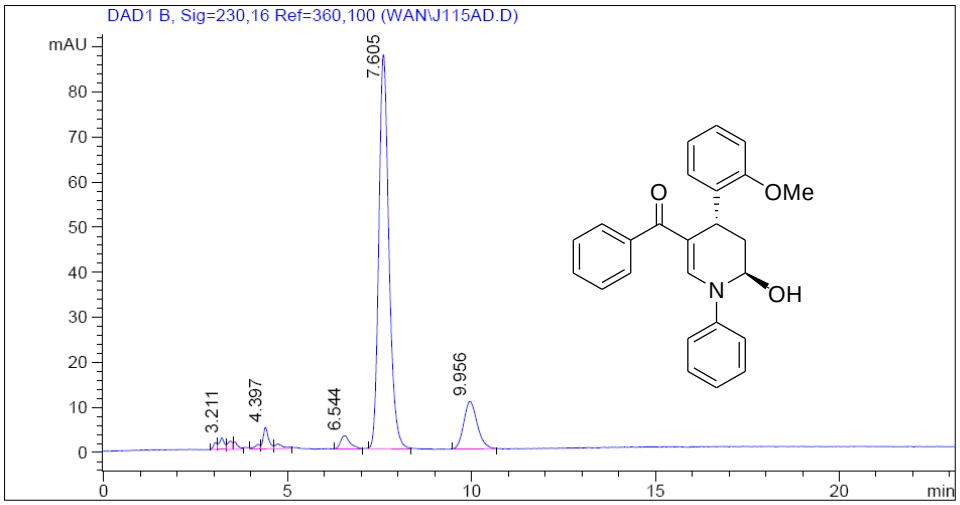
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.08	0.09	3.90	21.87	0.58
2	3.52	0.08	84.91	423.85	11.30
3	4.55	0.11	6.75	49.56	1.32
4	5.27	0.16	4.18	45.27	1.21
5	5.71	0.19	3.99	52.58	1.40
6	7.41	0.25	1.43	21.50	0.57
7	9.52	0.30	81.69	1564.18	41.72
8	10.72	0.33	72.50	1570.63	41.89
Total				3749.43	100.00



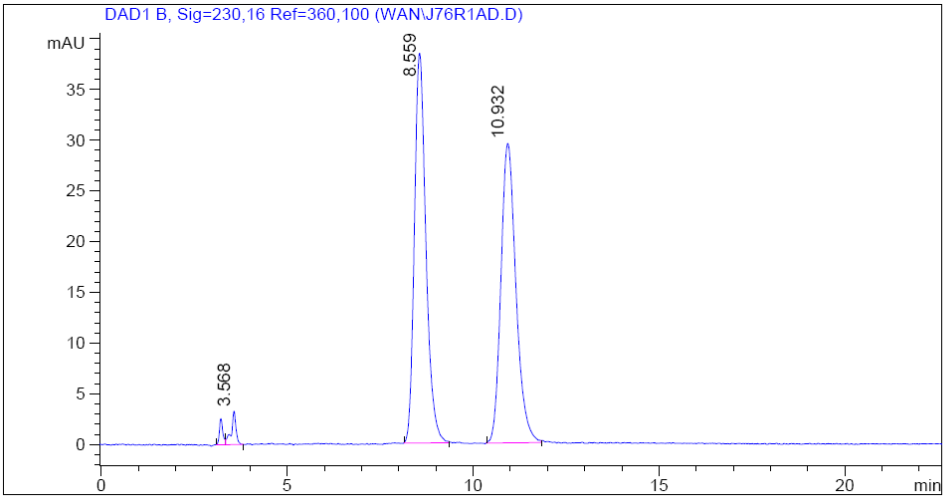
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.52	0.08	89.41	439.13	14.79
2	3.93	0.09	9.02	52.64	1.77
3	9.00	0.19	1.99	22.99	0.77
4	9.50	0.32	111.34	2141.70	72.11
5	10.71	0.32	14.48	313.64	10.56
Total				2970.10	100.00



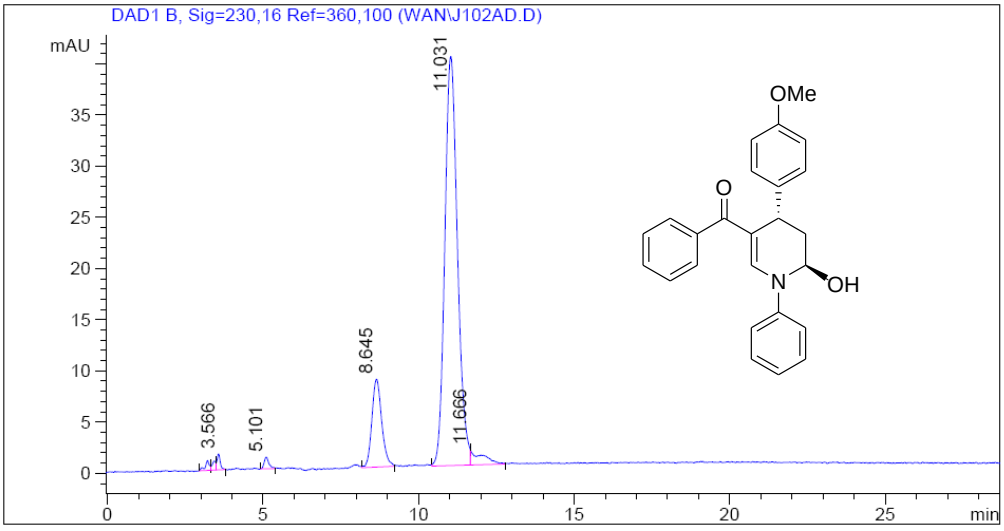
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.22	0.11	1.93	14.72	2.37
2	3.58	0.22	0.97	17.03	2.74
3	4.40	0.15	1.20	13.03	2.09
4	5.05	0.30	1.18	21.26	3.42
5	6.55	0.25	0.74	10.90	1.75
6	6.75	0.21	0.73	8.96	1.44
7	7.60	0.30	13.83	268.45	43.15
8	9.91	0.39	10.42	267.73	43.04
Total				622.10	100.00



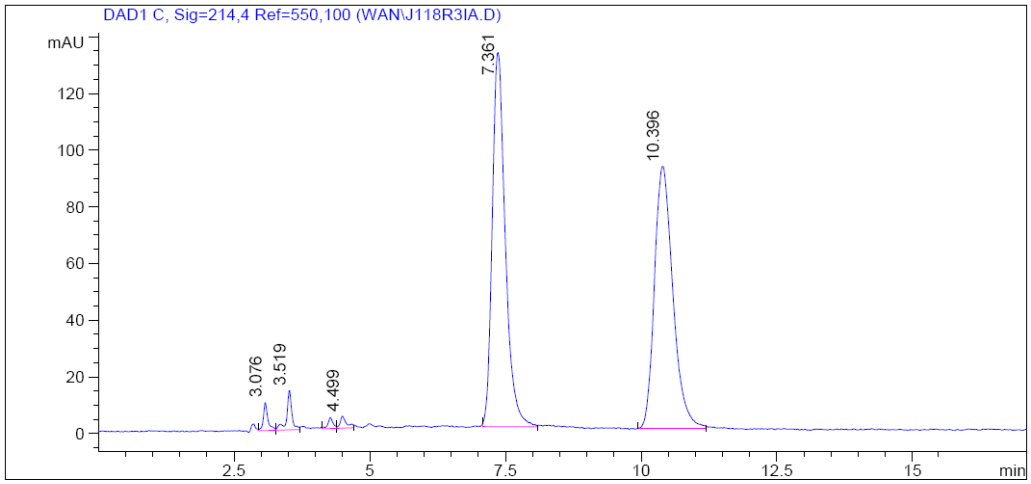
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.03	0.10	1.55	10.31	0.48
2	3.21	0.14	2.57	24.29	1.14
3	3.45	0.14	1.83	17.52	0.82
4	3.56	0.12	1.63	14.50	0.68
5	4.19	0.15	1.02	10.83	0.51
6	4.40	0.15	4.81	48.58	2.28
7	4.74	0.22	1.06	16.75	0.79
8	6.54	0.26	2.90	51.93	2.43
9	7.60	0.29	87.53	1669.47	78.23
10	9.96	0.40	10.55	269.87	12.65
Total				2134.06	100.00



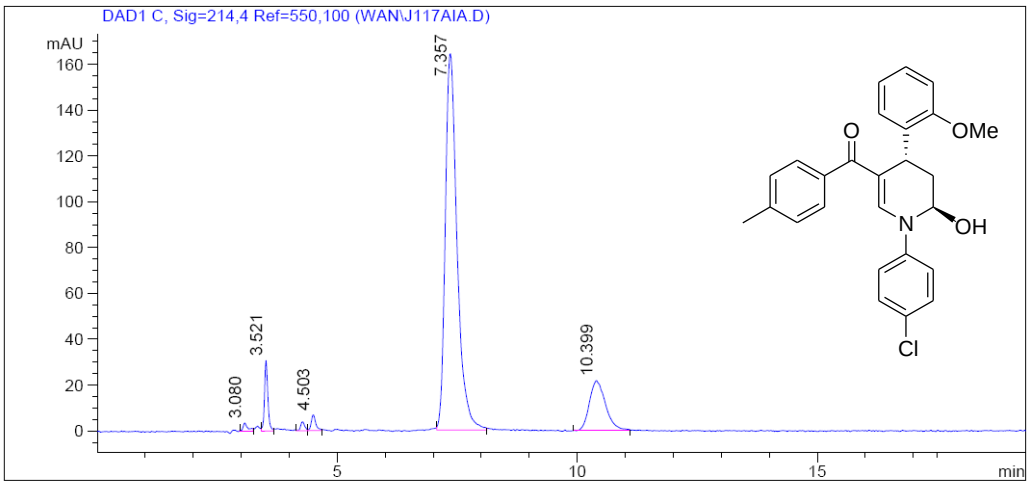
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.21	0.10	2.60	16.73	0.98
2	3.57	0.13	3.30	29.30	1.72
3	8.56	0.33	38.45	829.20	48.59
4	10.93	0.42	29.52	831.43	48.72
Total				1706.66	100.00



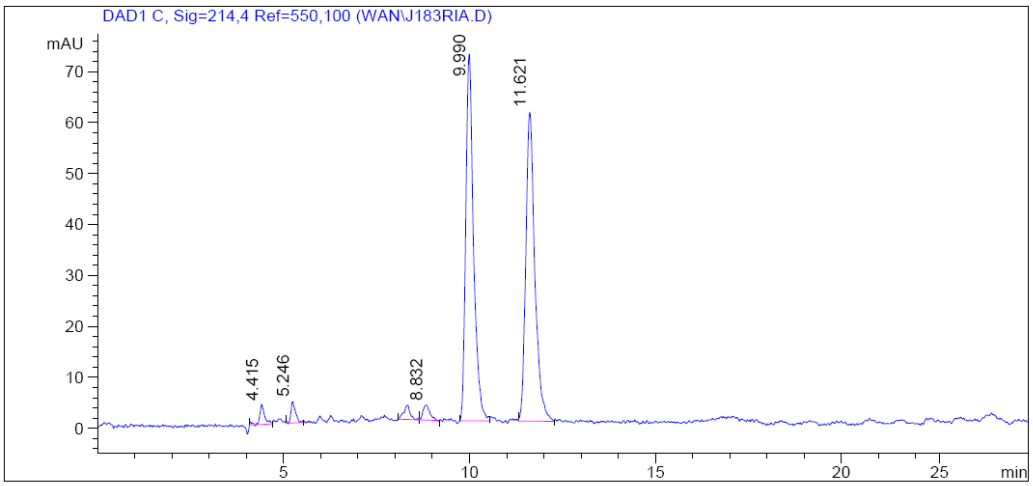
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.21	0.13	0.97	9.43	0.67
2	3.43	0.12	0.87	6.91	0.49
3	3.57	0.11	1.56	11.38	0.81
4	5.10	0.16	1.14	11.92	0.85
5	8.65	0.33	8.60	188.93	13.50
6	10.86	0.00	24.19	0.00	0.00
7	11.03	0.47	39.99	1130.80	80.83
8	11.67	0.45	1.47	39.61	2.83
9	11.77	0.00	0.82	0.00	0.00
10	11.83	0.00	0.72	0.00	0.00
11	12.28	0.00	0.42	0.00	0.00
12	12.48	0.00	0.07	0.00	0.00
13	12.62	0.00	0.10	0.00	0.00
Total				1398.98	100.00



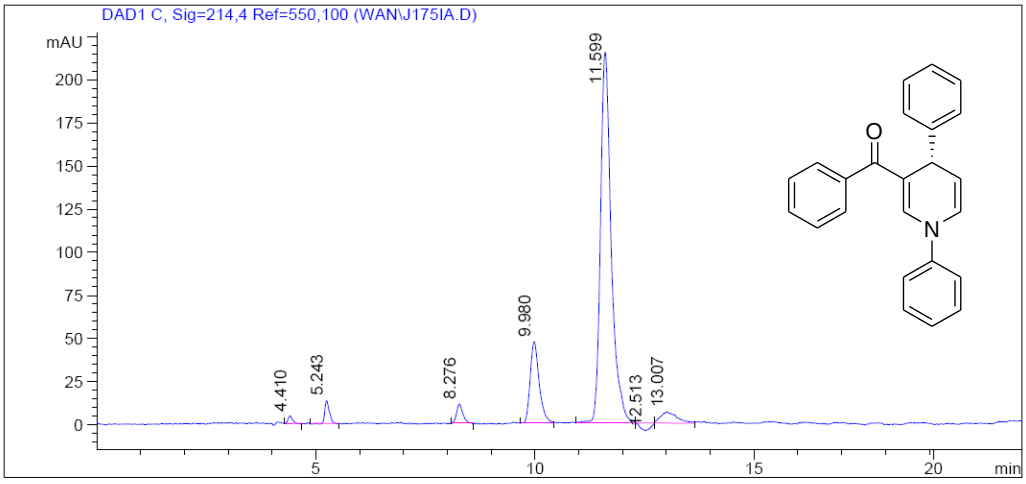
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.08	0.09	9.96	57.12	1.24
2	3.52	0.10	13.92	93.05	2.02
3	4.27	0.10	3.88	25.98	0.56
4	4.50	0.12	4.25	35.21	0.76
5	7.36	0.25	132.14	2212.62	47.99
6	10.40	0.38	92.55	2186.62	47.43
Total				4610.60	100.00



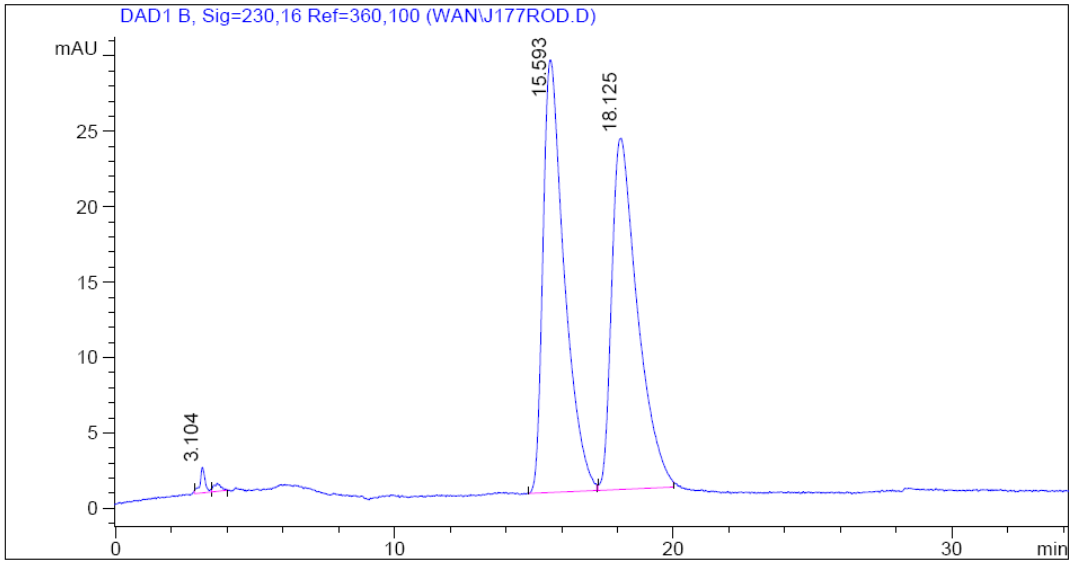
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.08	0.10	3.63	26.23	0.74
2	3.52	0.08	30.81	151.62	4.25
3	4.28	0.10	3.96	24.03	0.67
4	4.50	0.10	6.94	46.49	1.30
5	7.36	0.26	164.44	2803.82	78.62
6	10.40	0.38	21.98	514.19	14.42
Total				3566.37	100.00



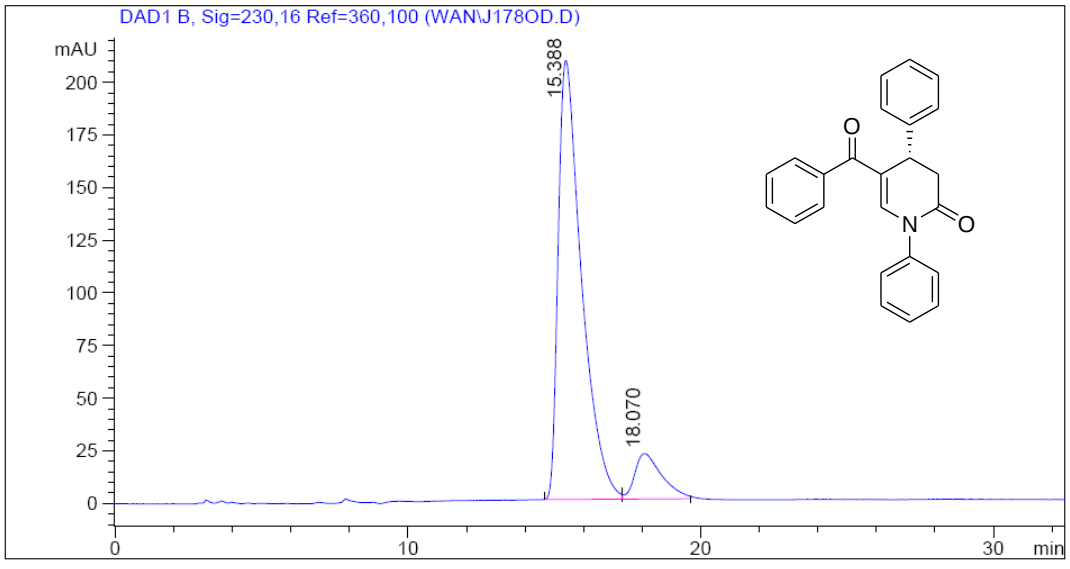
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.42	0.15	3.83	37.74	1.70
2	5.25	0.12	4.18	35.76	1.62
3	8.33	0.17	2.79	33.20	1.50
4	8.83	0.20	2.92	37.41	1.69
5	9.99	0.22	72.12	1044.23	47.18
6	11.62	0.25	60.67	1024.96	46.31
Total				2213.30	100.00



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.41	0.12	4.43	31.54	0.66
2	5.24	0.11	13.31	91.58	1.91
3	8.28	0.14	11.08	107.05	2.24
4	9.98	0.23	47.10	661.65	13.83
5	11.60	0.25	214.81	3655.53	76.41
6	12.51	0.19	4.39	65.79	1.38
7	13.01	0.32	6.41	170.81	3.57
Total				4783.95	100.00

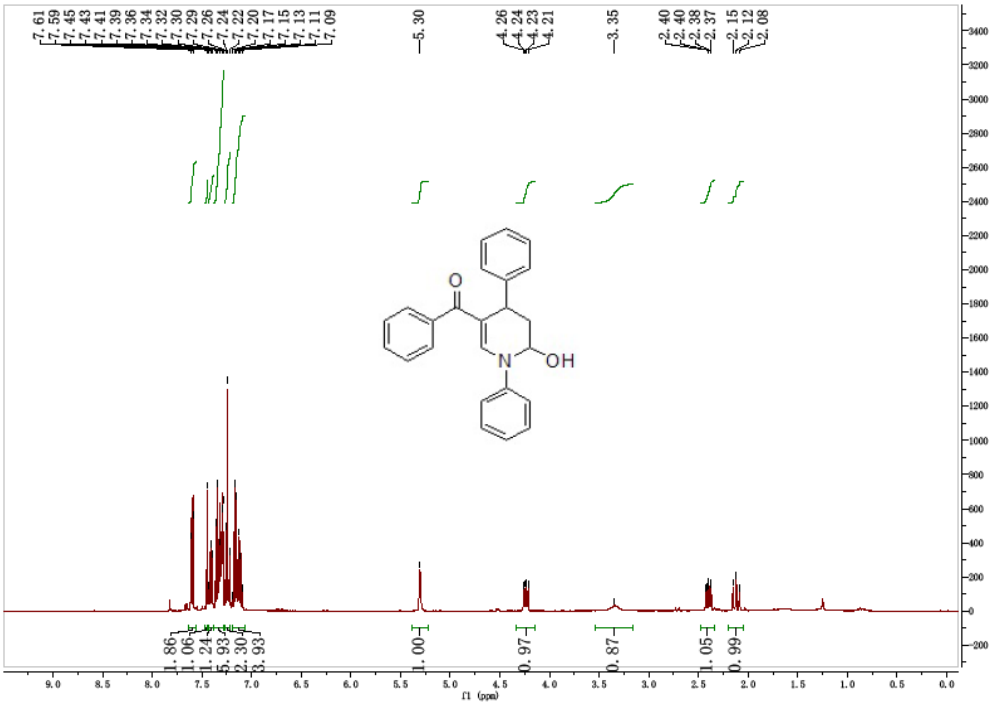


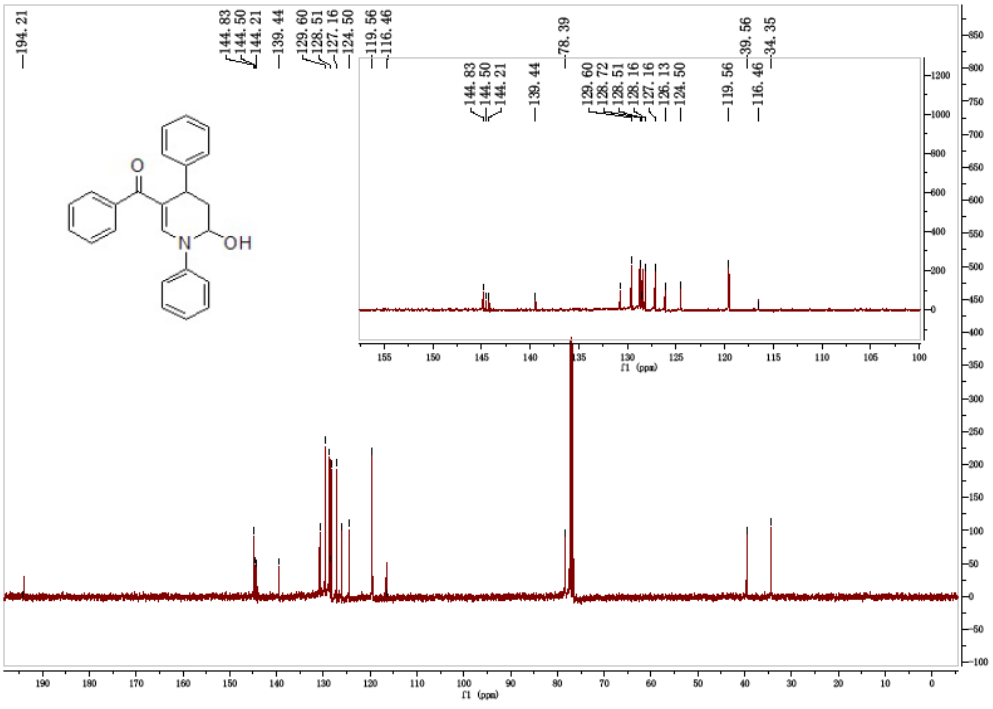
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.10	0.19	1.69	22.13	0.72
2	3.64	0.23	0.54	9.77	0.32
3	15.59	0.75	28.70	1530.34	49.93
4	18.13	0.90	23.28	1502.88	49.03
Total				3065.13	100.00



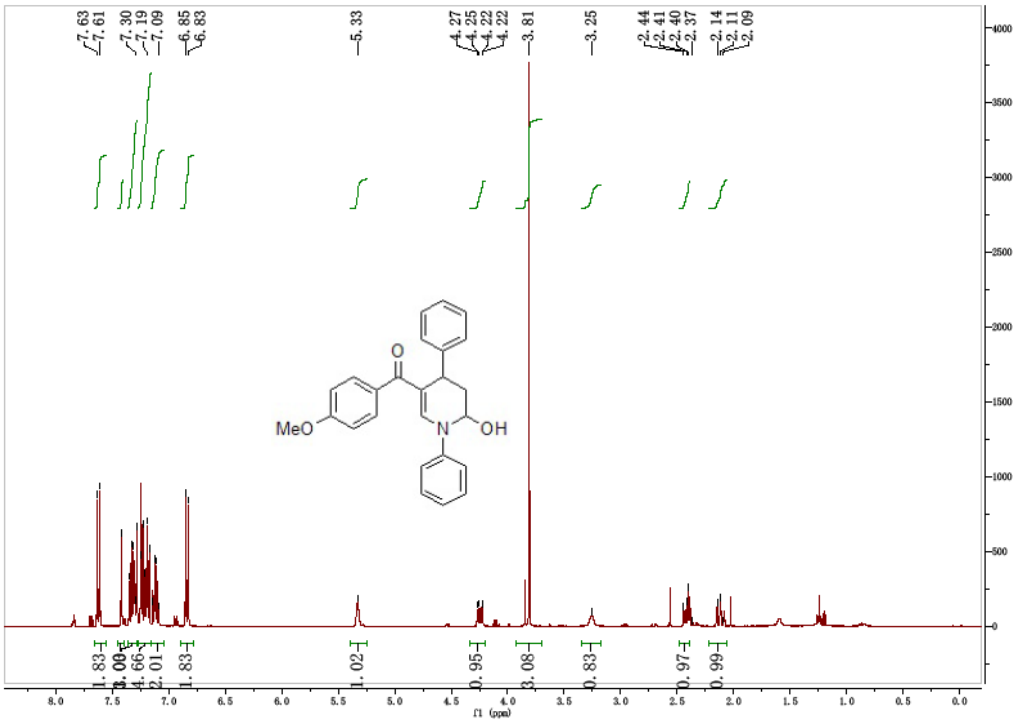
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	15.39	0.82	208.48	11578.70	89.24
2	18.07	0.89	21.61	1395.72	10.76
Total				12974.42	100.00

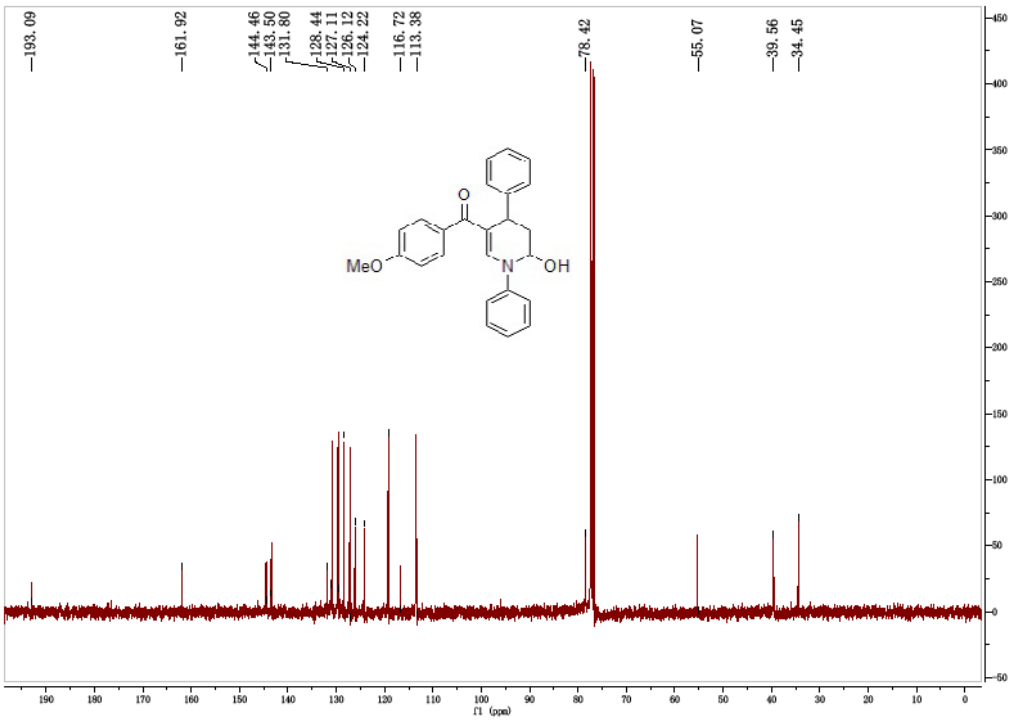
9a


7.61
7.59
7.45
7.43
7.41
7.39
7.36
7.34
7.32
7.30
7.29
7.26
7.24
7.22
7.20
7.17
7.15
7.13
7.11
7.09
5.30
4.26
4.24
4.23
4.21
3.35
2.40
2.40
2.38
2.37
2.15
2.12
2.08
O
N
OH
1.86
1.06
1.24
5.93
2.30
3.93
1.00
0.97
0.87
1.05
0.99
f1 (ppm)

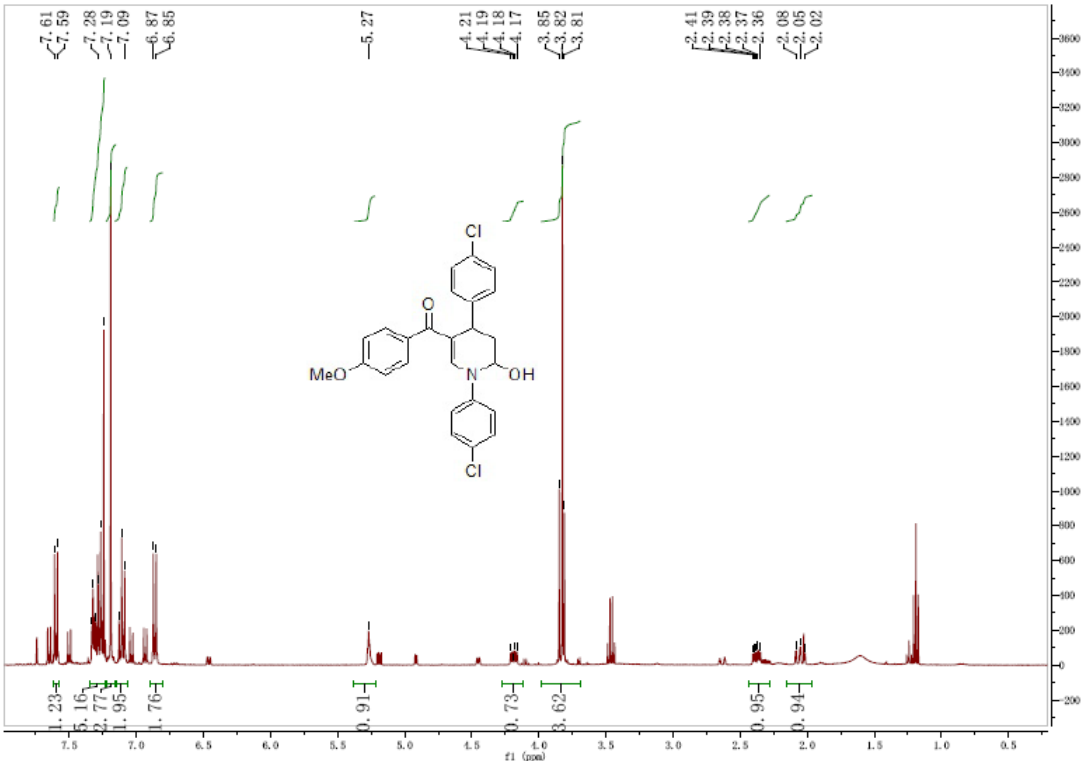

194.21
144.83
144.50
144.21
139.44
129.60
128.72
128.51
128.16
127.16
126.13
124.50
119.56
116.46
78.39
39.56
34.35
O
N
OH
f1 (ppm)

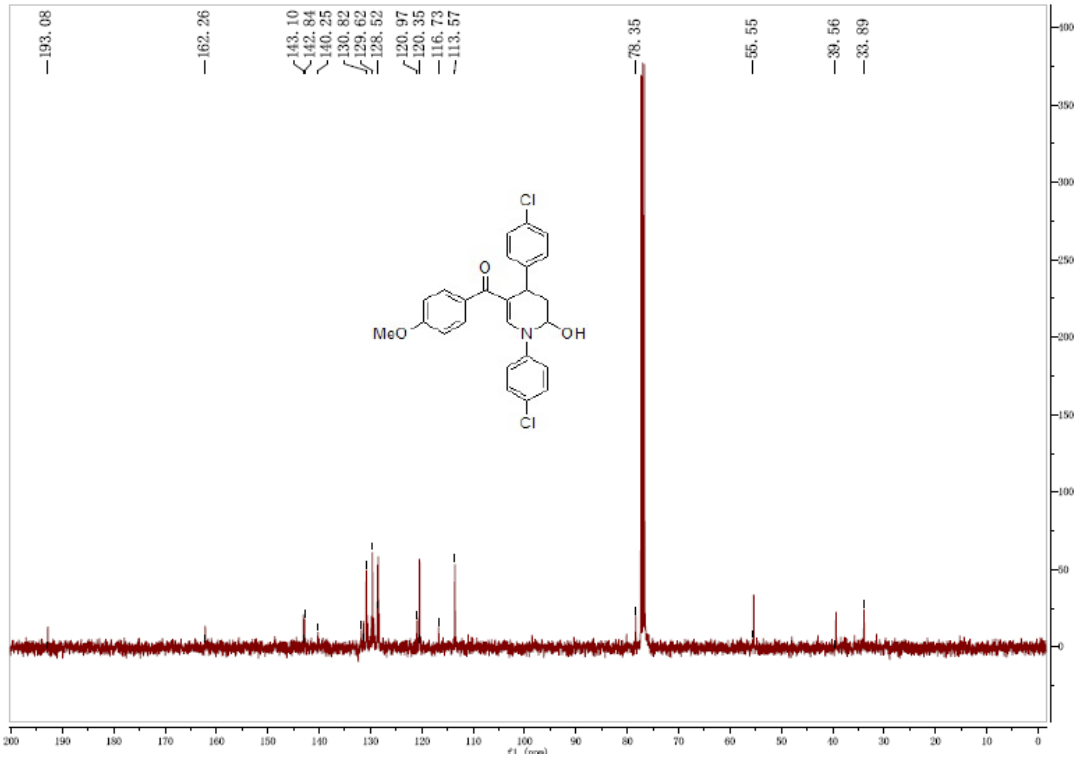
9b


7.63
7.61
7.30
7.19
7.09
6.85
6.83
5.33
4.27
4.25
4.22
4.22
3.81
3.25
2.44
2.41
2.40
2.37
2.14
2.11
2.09
MeO
O
N
OH
1.83
3.00
4.66
2.01
1.83
1.02
0.95
3.08
0.83
0.97
0.99
f1 (ppm)

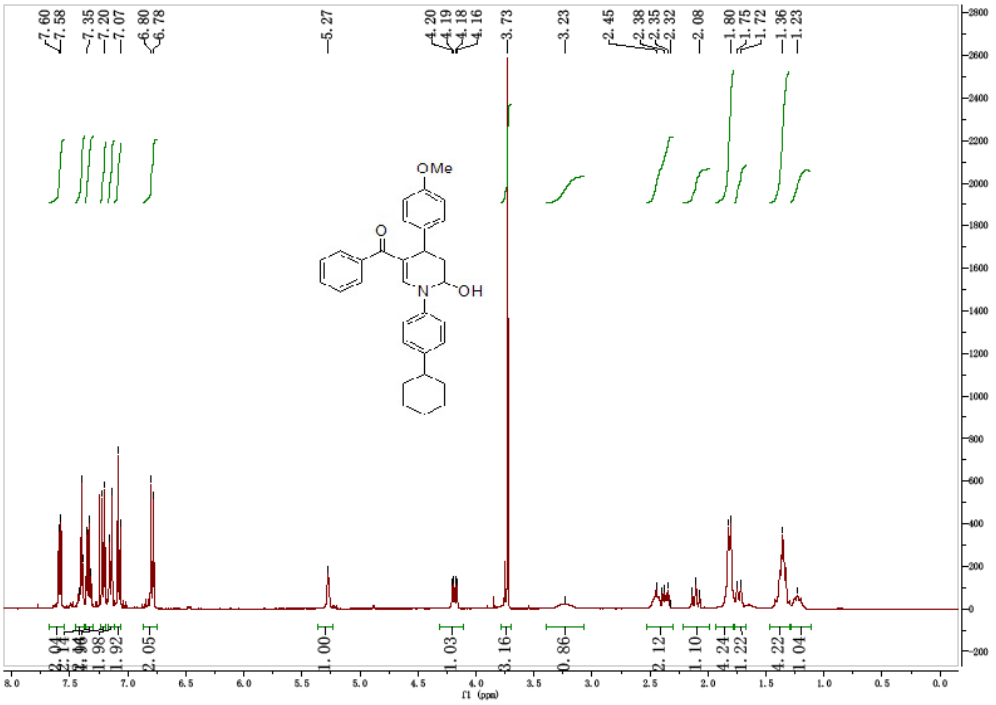

193.09
161.92
144.46
143.50
131.80
128.44
127.11
126.12
124.22
116.72
113.38
78.42
55.07
39.56
34.45
MeO
O
N
OH
f1 (ppm)

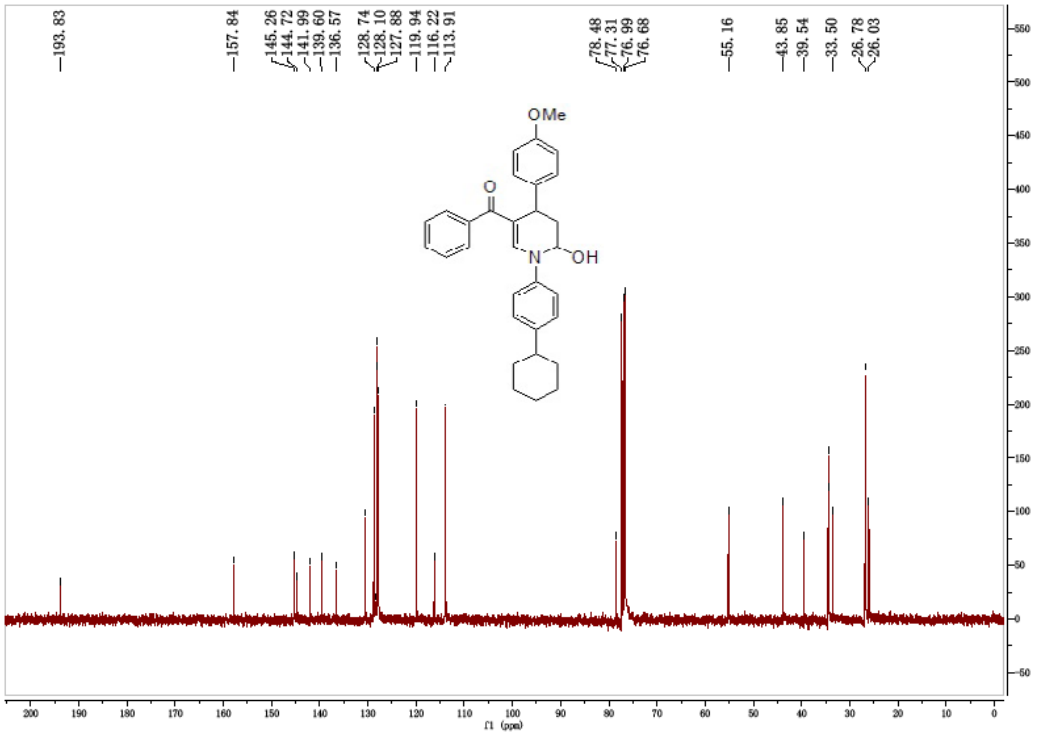
9c


7.61
7.59
7.28
7.19
7.09
6.87
6.85
5.27
4.21
4.19
4.18
4.17
3.85
3.82
3.81
2.41
2.39
2.38
2.37
2.36
2.08
2.05
2.02
Cl
O
MeO
N
OH
Cl
1.23
5.16
2.77
1.95
1.76
0.91
0.73
3.62
0.95
0.94
f1 (ppm)

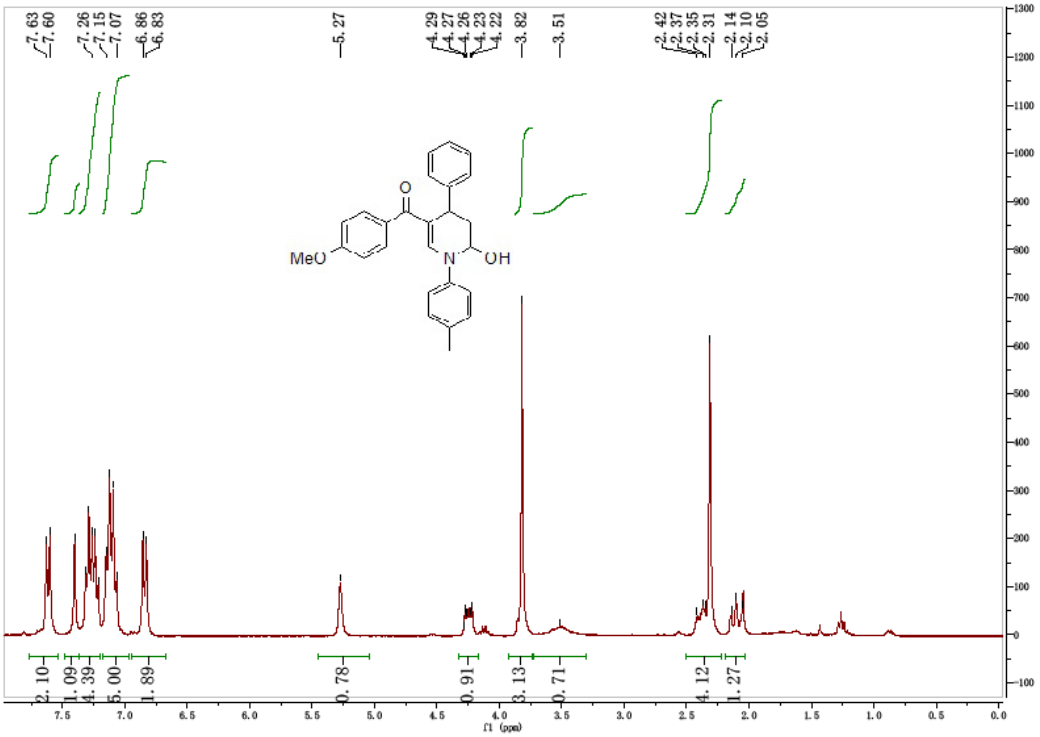

193.08
162.26
143.10
142.84
140.25
130.82
129.62
128.52
120.97
120.35
116.73
113.57
78.35
55.55
39.56
33.89
Cl
O
MeO
N
OH
Cl
f1 (ppm)

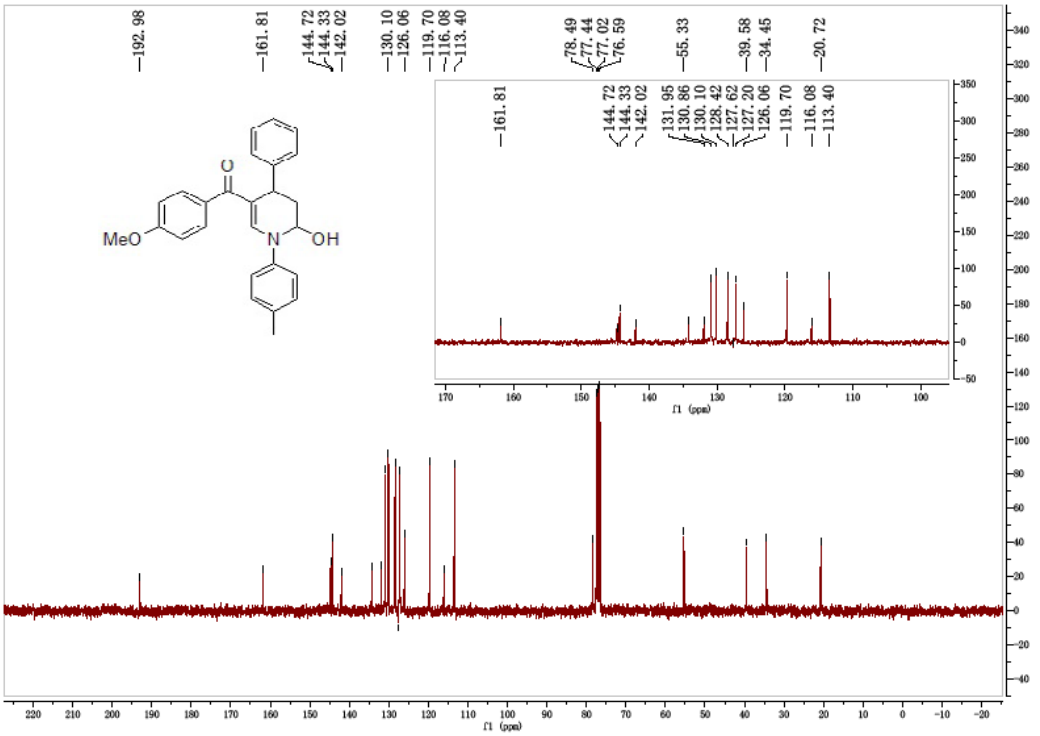
9d


7.60
7.58
7.35
7.20
7.07
6.80
6.78
5.27
4.20
4.19
4.18
4.16
3.73
3.23
2.45
2.38
2.35
2.32
2.08
1.80
1.75
1.72
1.36
1.23
OMe
O
N
OH
2.04
2.14
1.98
1.92
2.05
1.00
1.03
3.16
0.86
2.12
1.10
4.24
1.22
4.22
1.04
f1 (ppm)

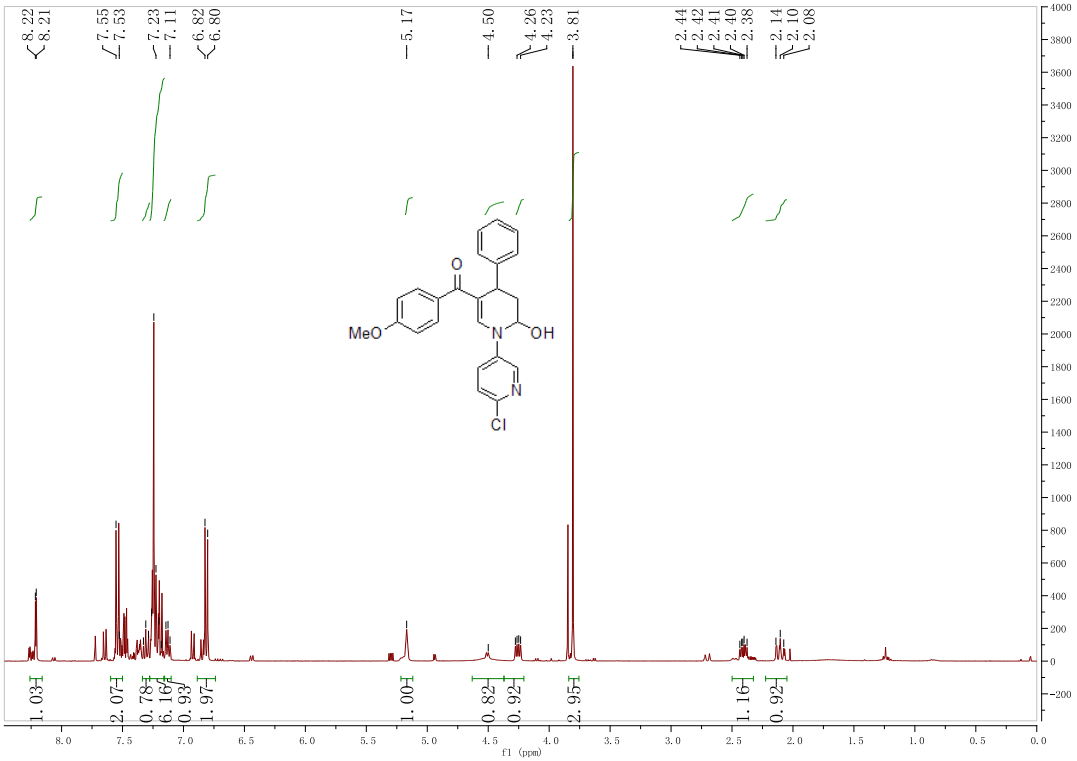

193.83
157.84
145.26
144.72
141.99
139.60
136.57
128.74
128.10
127.88
119.94
116.22
113.91
78.48
77.31
76.99
76.68
55.16
43.85
39.54
33.50
26.78
26.03
OMe
O
N
OH
f1 (ppm)

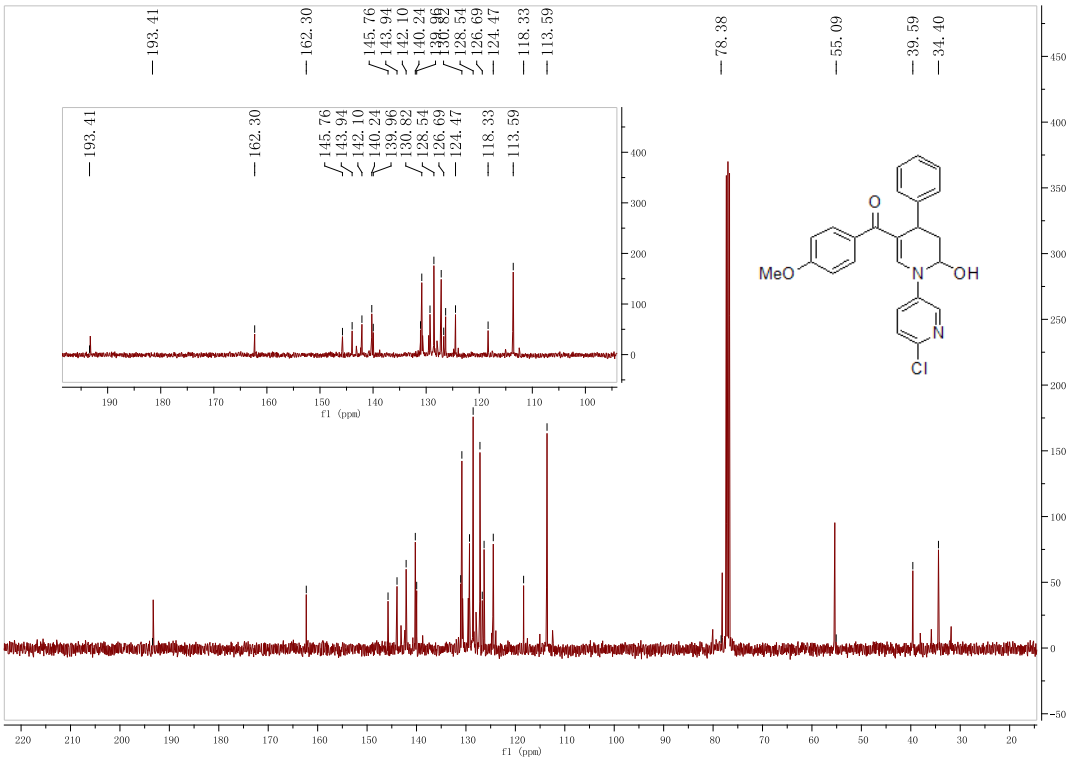
9e


7.63
7.60
7.26
7.15
7.07
6.86
6.83
5.27
4.29
4.27
4.26
4.23
4.22
3.82
3.51
2.42
2.37
2.35
2.31
2.14
2.10
2.05
MeO
O
N
OH
2.10
1.09
4.39
5.00
1.89
0.78
0.91
3.13
0.71
4.12
1.27
f1 (ppm)

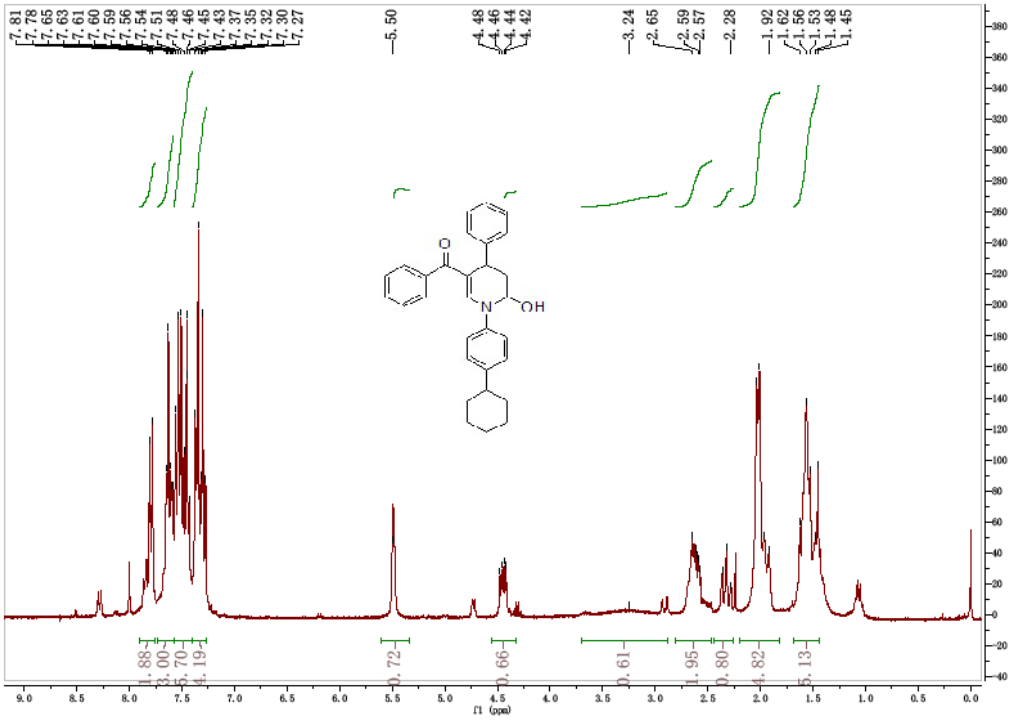

192.98
161.81
144.72
144.33
142.02
130.10
126.06
119.70
116.08
113.40
78.49
77.44
77.02
76.59
55.33
39.58
34.45
20.72
MeO
O
N
OH
131.95
130.86
128.42
127.62
127.20
f1 (ppm)

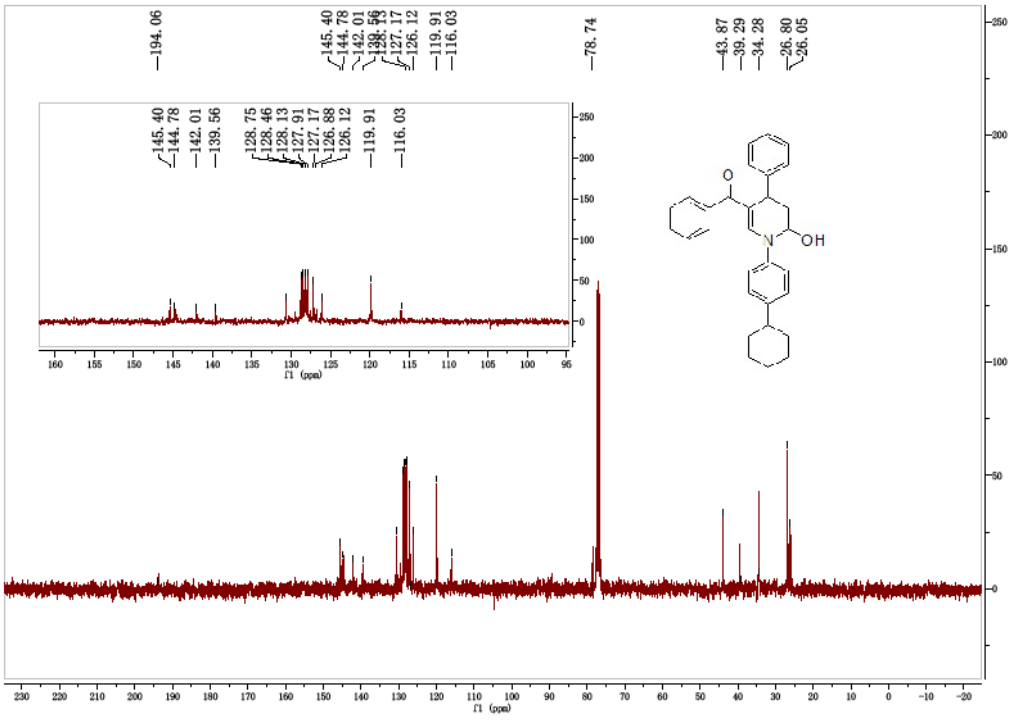
9f


8.22
8.21
7.55
7.53
7.23
7.11
6.82
6.80
5.17
4.50
4.26
4.23
3.81
2.44
2.42
2.41
2.40
2.38
2.14
2.10
2.08
MeO
O
N
OH
N
Cl
1.03
2.07
0.78
6.16
0.93
1.97
1.00
0.82
0.92
2.95
1.16
0.92
f1 (ppm)

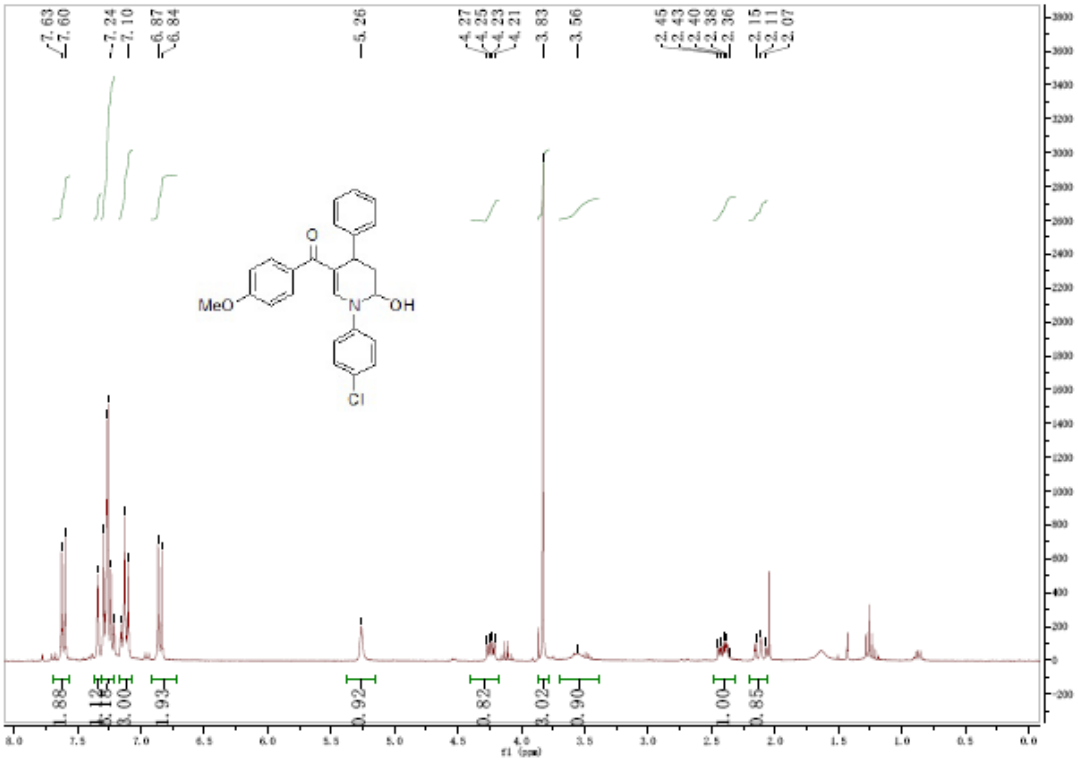

193.41
162.30
145.76
143.94
142.10
140.24
139.96
130.82
128.54
126.69
124.47
118.33
113.59
78.38
55.09
39.59
34.40
MeO
O
N
OH
N
Cl
f1 (ppm)

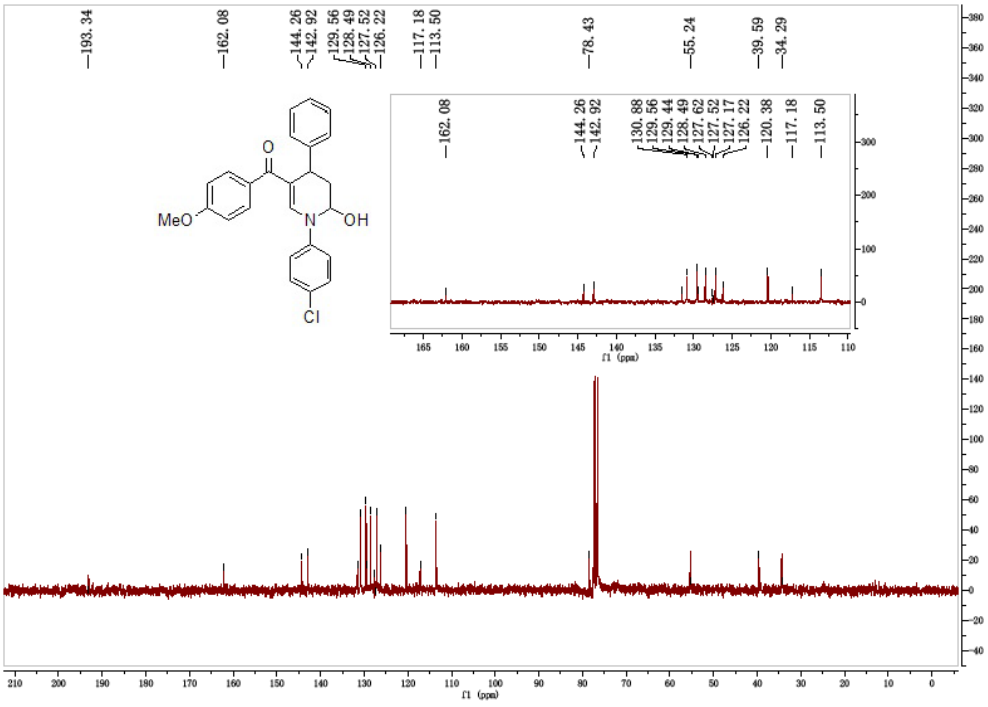
9g


7.81
7.78
7.65
7.63
7.61
7.60
7.59
7.56
7.54
7.51
7.48
7.46
7.45
7.43
7.37
7.35
7.32
7.30
7.27
5.50
4.48
4.46
4.44
4.42
3.24
2.65
2.59
2.57
2.28
1.92
1.62
1.56
1.53
1.48
1.45
O
N
OH
1.88
3.00
5.70
4.19
0.72
0.66
0.61
1.95
0.80
4.82
5.13
f1 (ppm)

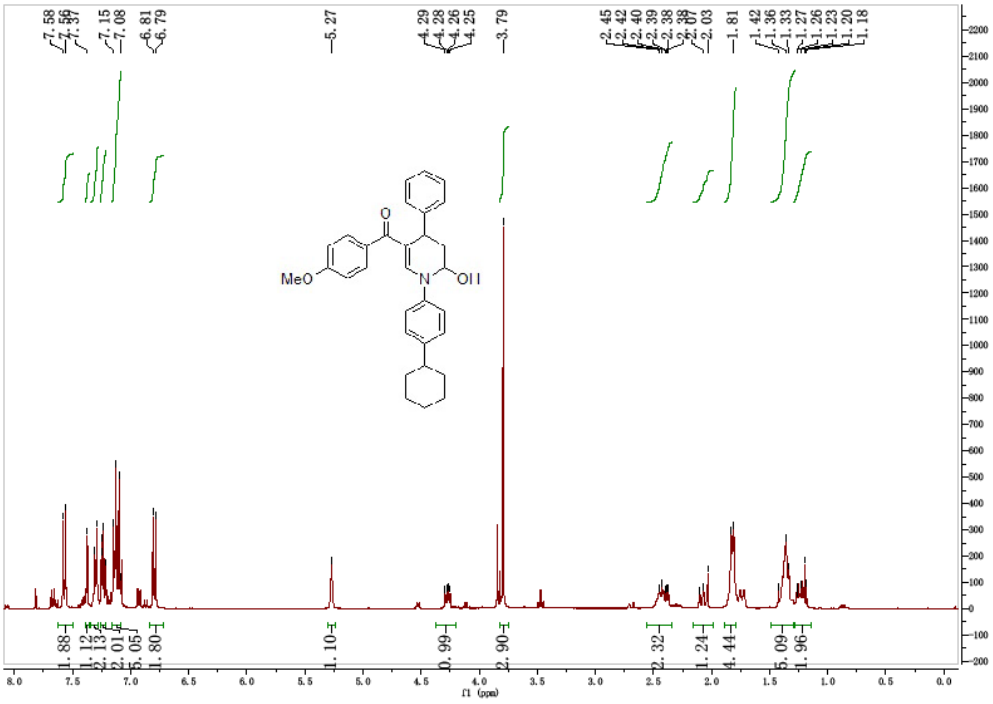

194.06
145.40
144.78
142.01
139.56
128.75
128.46
128.13
127.91
127.17
126.88
126.12
119.91
116.03
78.74
43.87
39.29
34.28
26.80
26.05
O
N
OH
f1 (ppm)

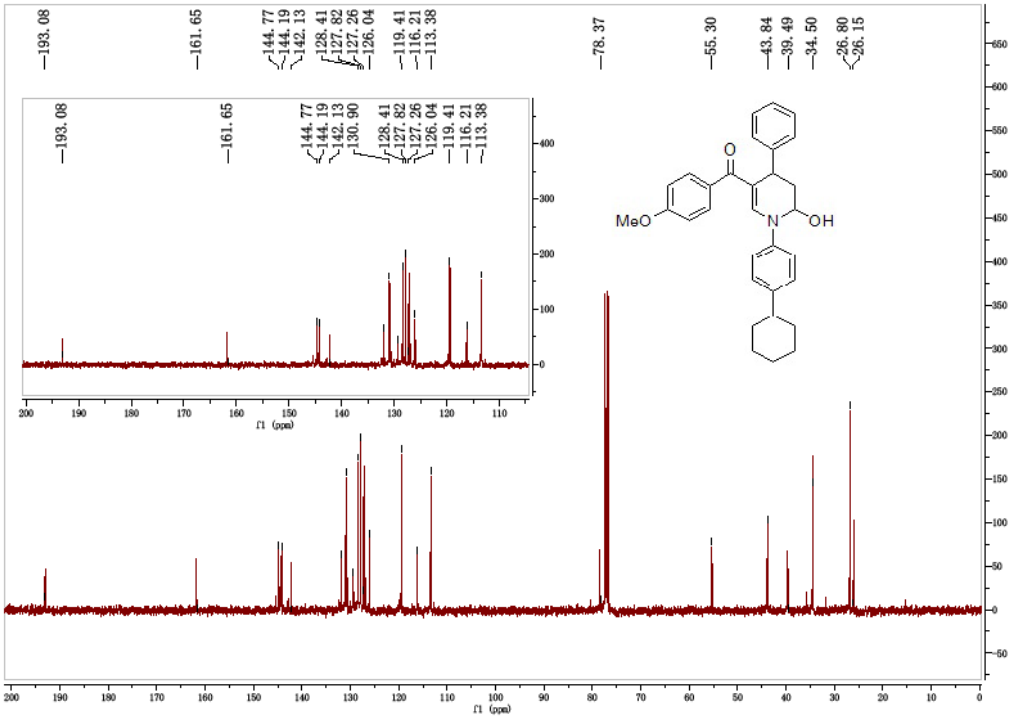
9h


7.63
7.60
7.24
7.10
6.87
6.84
5.26
4.27
4.25
4.23
4.21
3.83
3.56
2.45
2.43
2.40
2.38
2.36
2.15
2.11
2.07
MeO
OH
N
O
Cl
1.88
1.12
3.00
1.93
0.92
0.82
3.02
0.90
1.00
0.85
f1 (ppm)

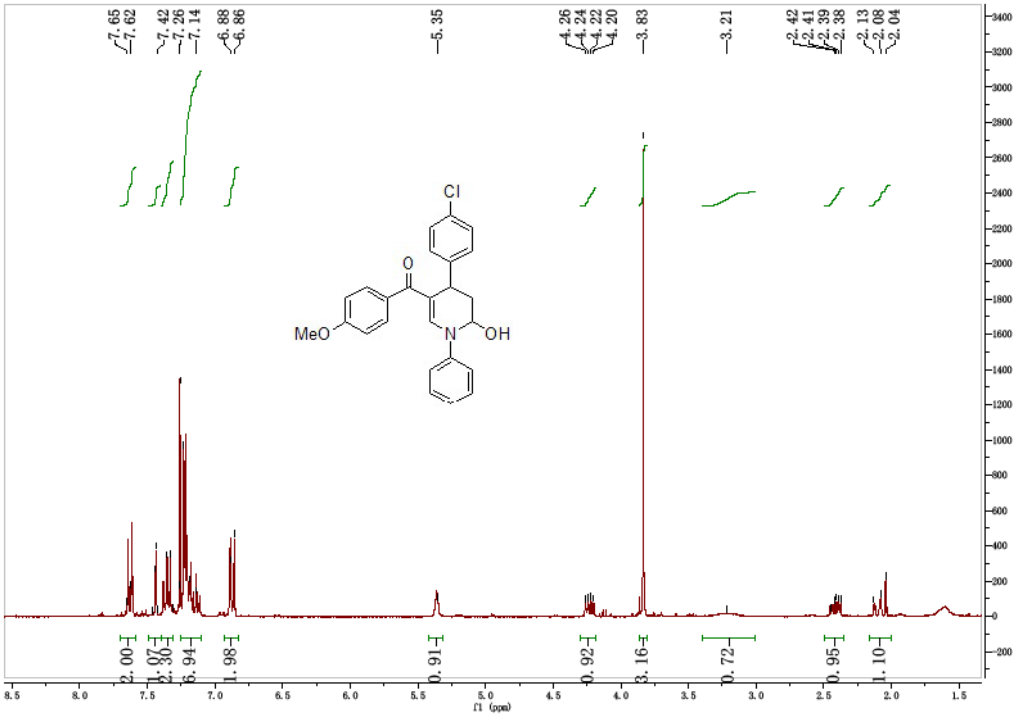

193.34
162.08
144.26
142.92
129.56
128.49
127.52
126.22
117.18
113.50
78.43
55.24
39.59
34.29
MeO
OH
N
O
Cl
130.88
129.44
127.62
127.17
120.38
f1 (ppm)

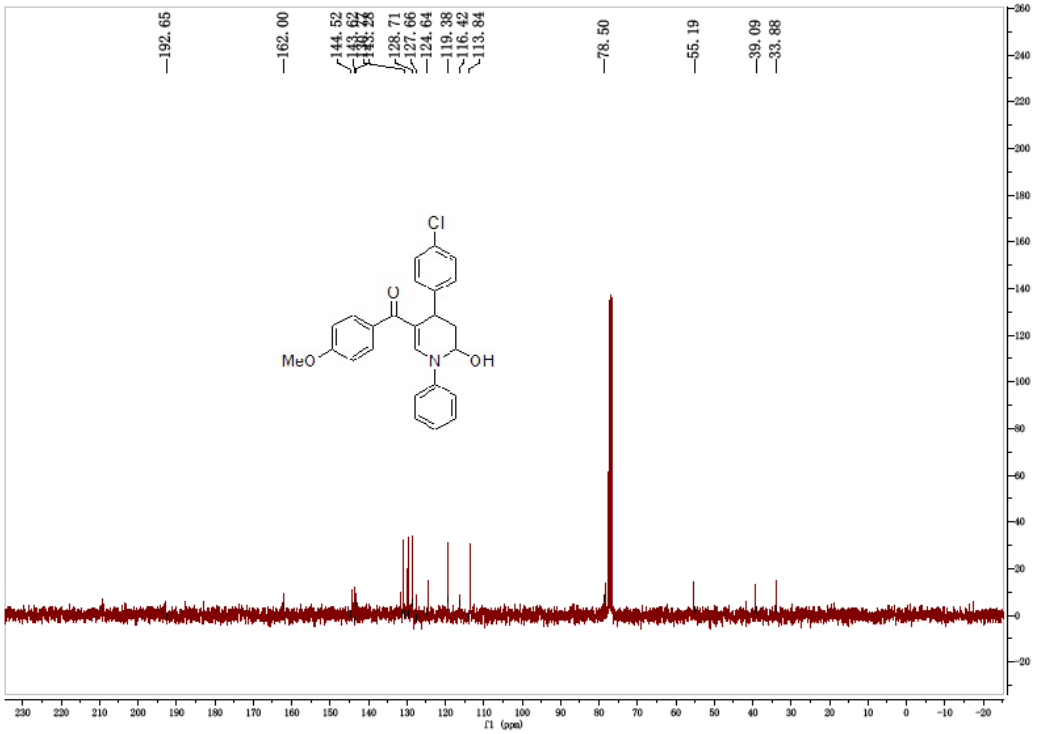
9i



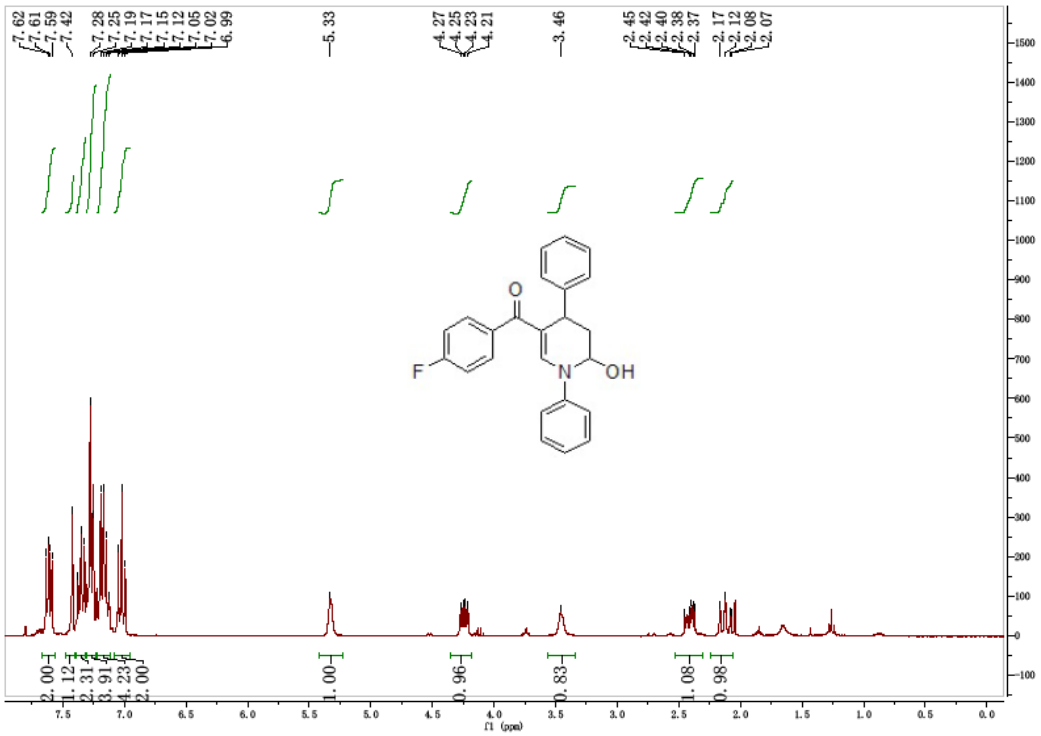


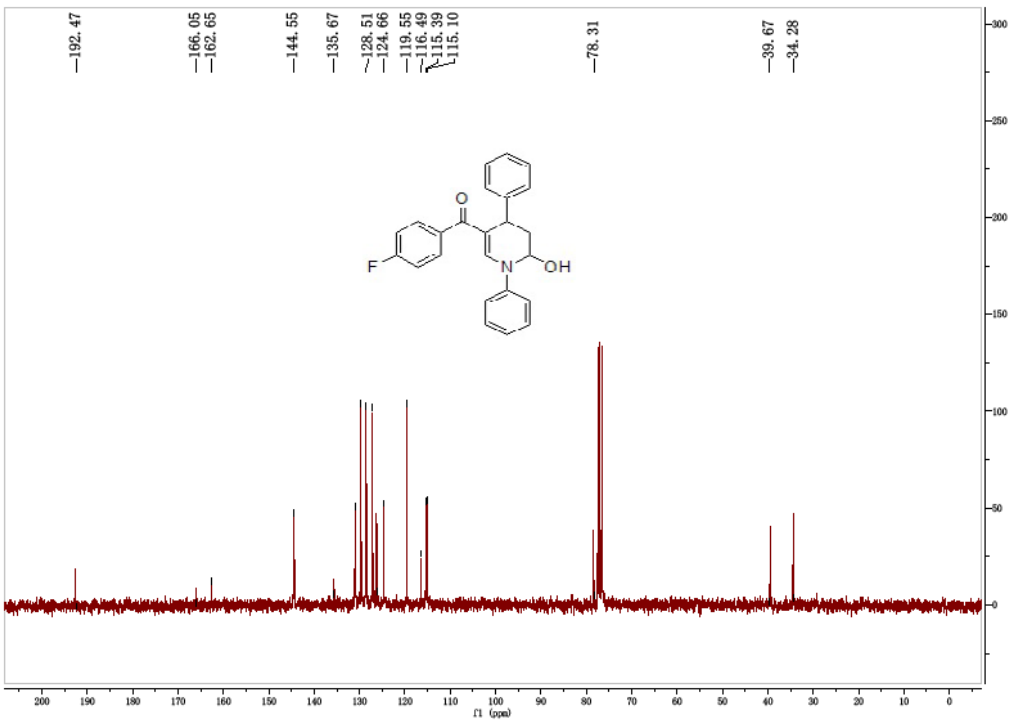
9j


7.65
7.62
7.42
7.26
7.14
6.88
6.86
5.35
4.26
4.24
4.22
4.20
3.83
3.21
2.42
2.41
2.39
2.38
2.13
2.08
2.04
Cl
O
MeO
N
OH
2.00
1.07
3.30
6.94
1.98
0.91
0.92
3.16
0.72
0.95
1.10
f1 (ppm)

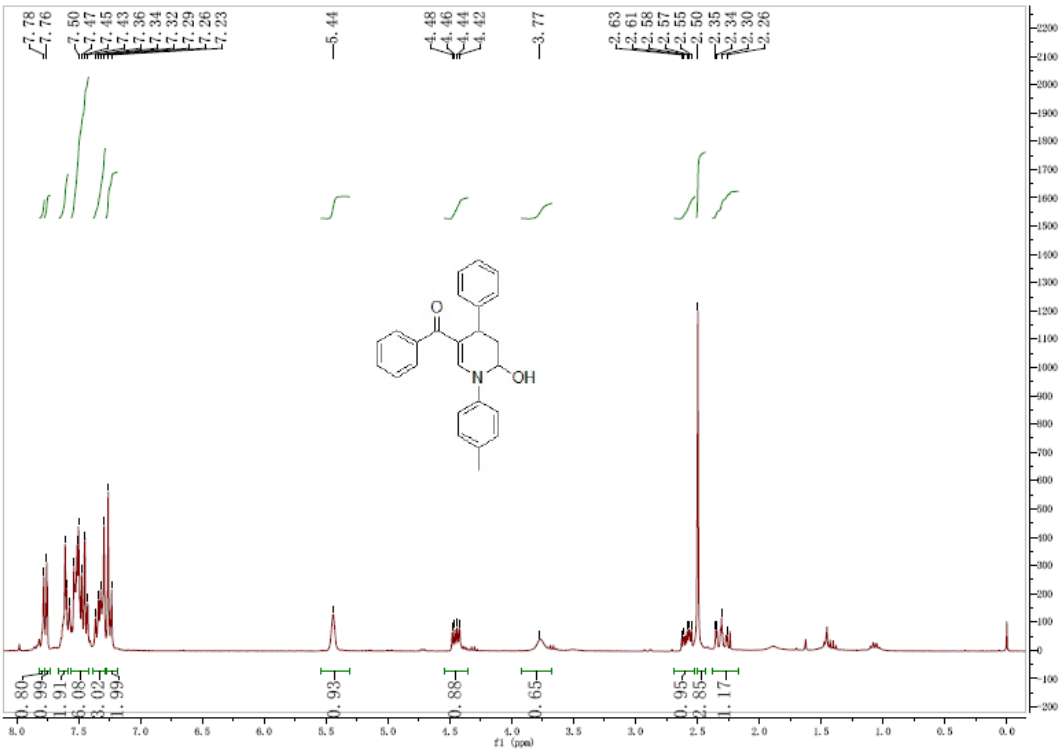

192.65
162.00
144.52
128.71
127.66
124.64
119.38
116.42
113.84
78.50
55.19
39.09
33.88
Cl
O
MeO
N
OH
f1 (ppm)

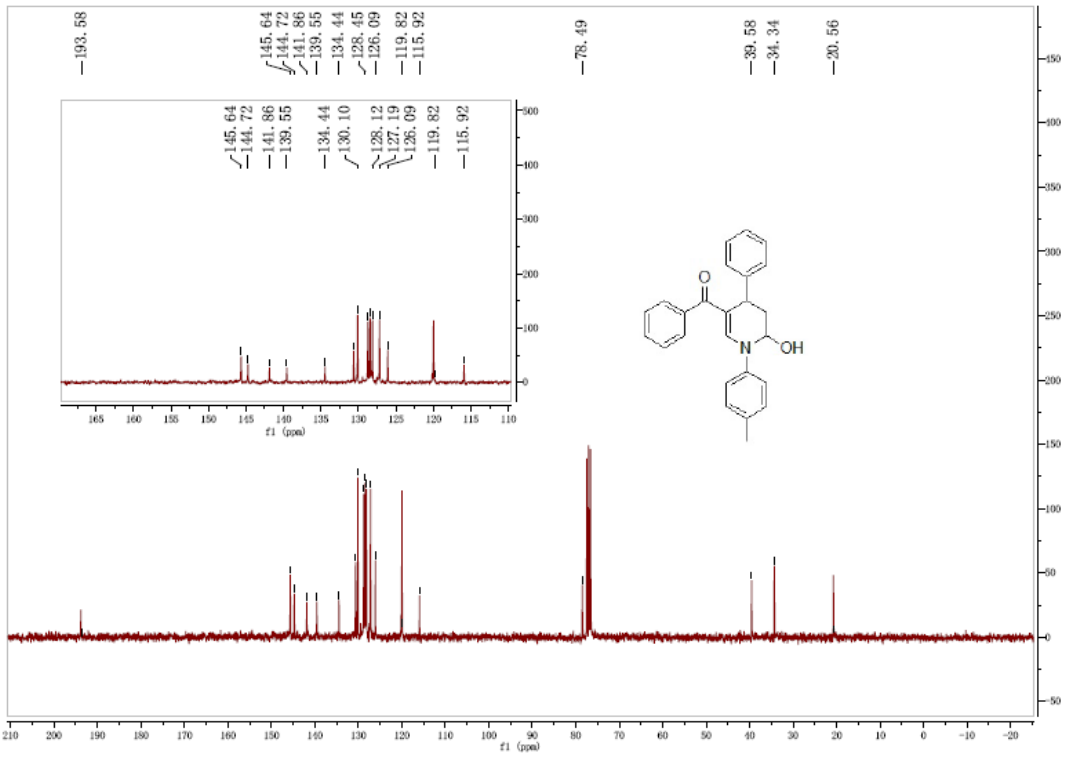
9k


7.62
7.61
7.59
7.42
7.28
7.25
7.19
7.17
7.15
7.12
7.05
7.02
6.99
5.33
4.27
4.25
4.23
4.21
3.46
2.45
2.42
2.40
2.38
2.37
2.17
2.12
2.08
2.07
O
F
N
OH
2.00
1.12
2.31
3.91
4.23
2.00
1.00
0.96
0.83
1.08
0.98
f1 (ppm)

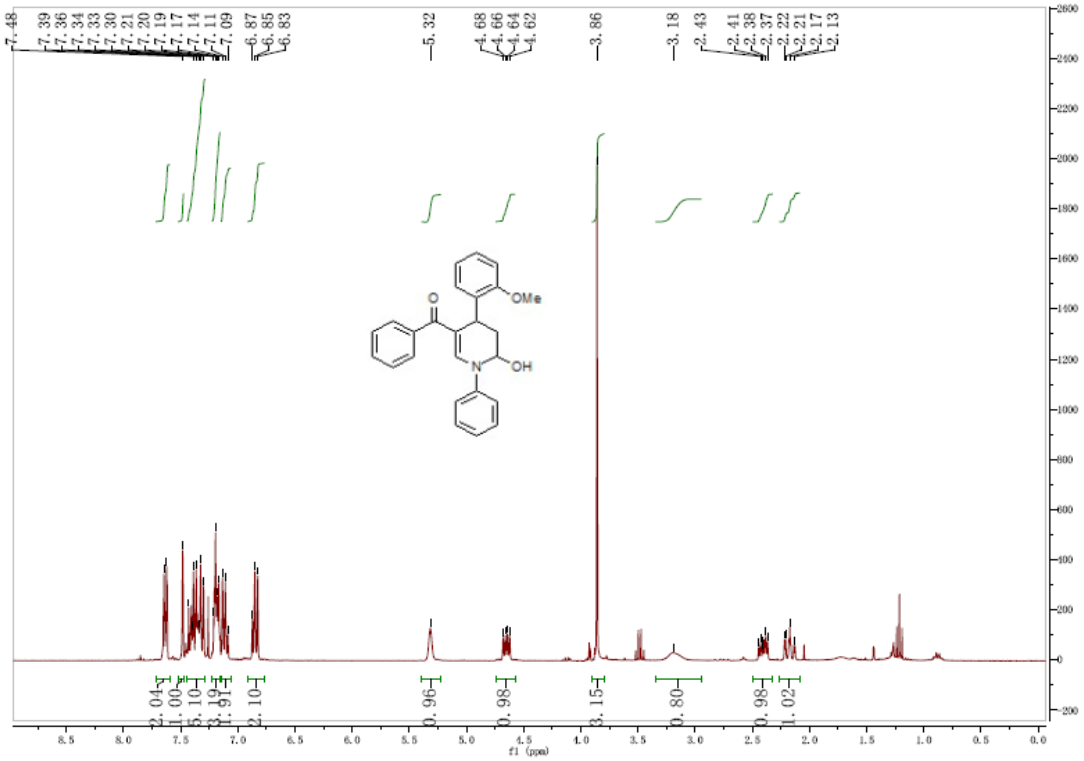

192.47
166.05
162.65
144.55
135.67
128.51
124.66
119.55
116.49
115.39
115.10
78.31
39.67
34.28
O
F
N
OH
f1 (ppm)

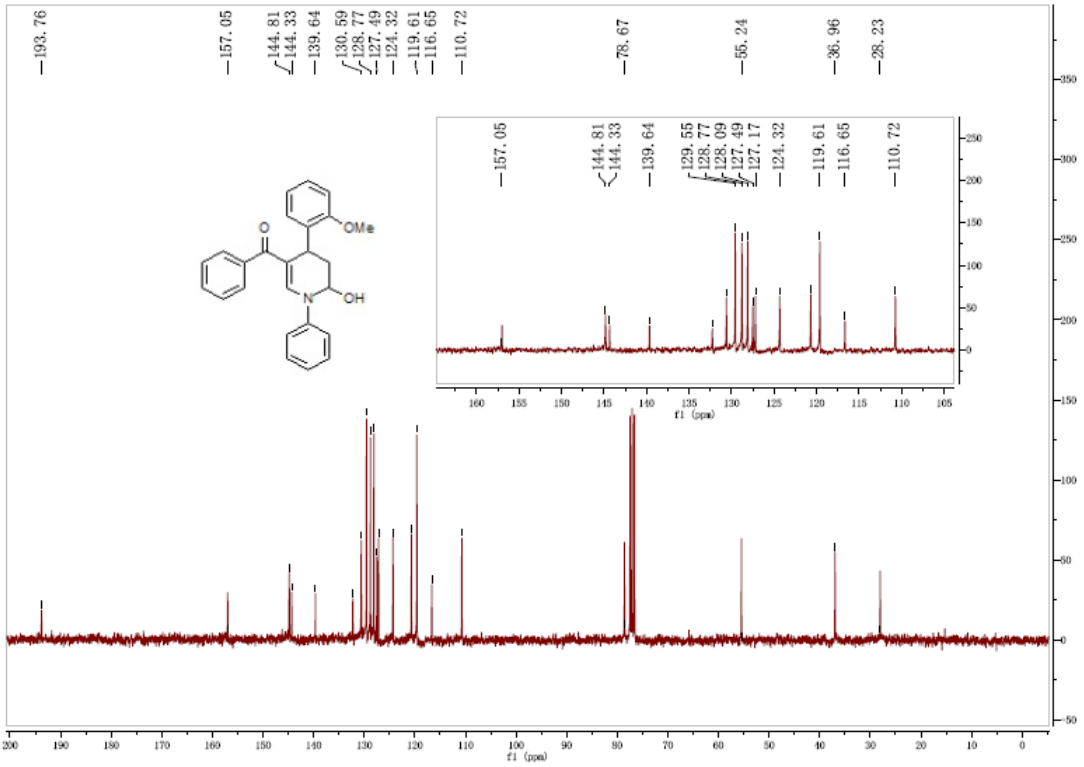
9l


7.78
7.76
7.50
7.47
7.45
7.43
7.36
7.34
7.32
7.29
7.26
7.23
5.44
4.48
4.46
4.44
4.42
3.77
2.63
2.61
2.58
2.57
2.55
2.50
2.35
2.34
2.30
2.26
O
N
OH
0.80
0.99
1.91
6.08
3.02
1.99
0.93
0.88
0.65
0.95
2.85
1.17
f1 (ppm)

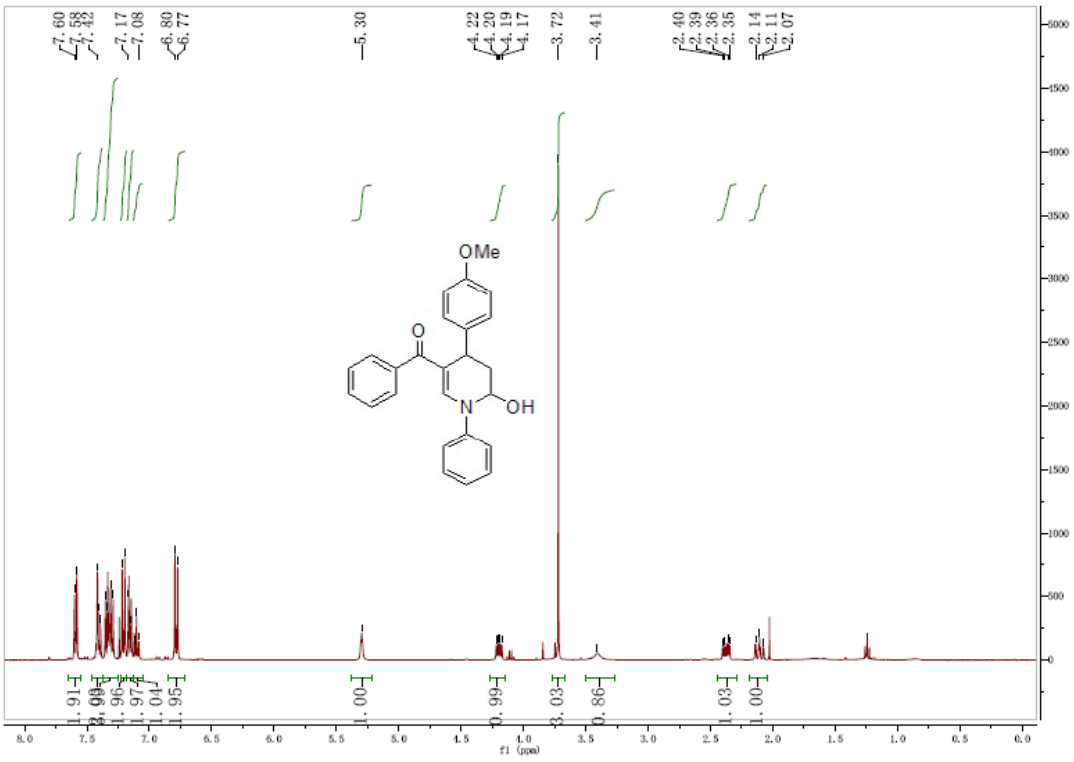

193.58
145.64
144.72
141.86
139.55
134.44
128.45
126.09
119.82
115.92
78.49
39.58
34.34
20.56
130.10
128.12
127.19
O
N
OH
f1 (ppm)

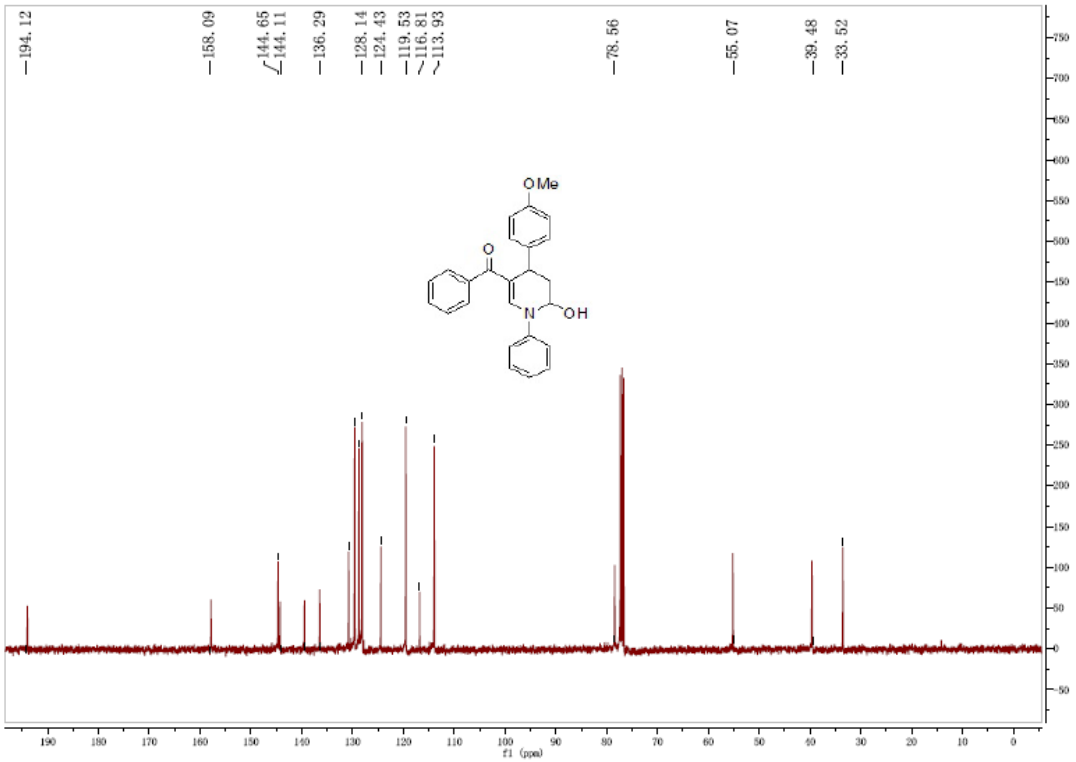
9m


7.48
7.39
7.36
7.34
7.33
7.30
7.21
7.20
7.19
7.17
7.14
7.11
7.09
6.87
6.85
6.83
5.32
4.68
4.66
4.64
4.62
3.86
3.18
2.43
2.41
2.38
2.37
2.22
2.21
2.17
2.13
OMe
O
N
OH
2.04
1.00
5.10
3.19
1.91
2.10
0.96
0.98
3.15
0.80
0.98
1.02
f1 (ppm)

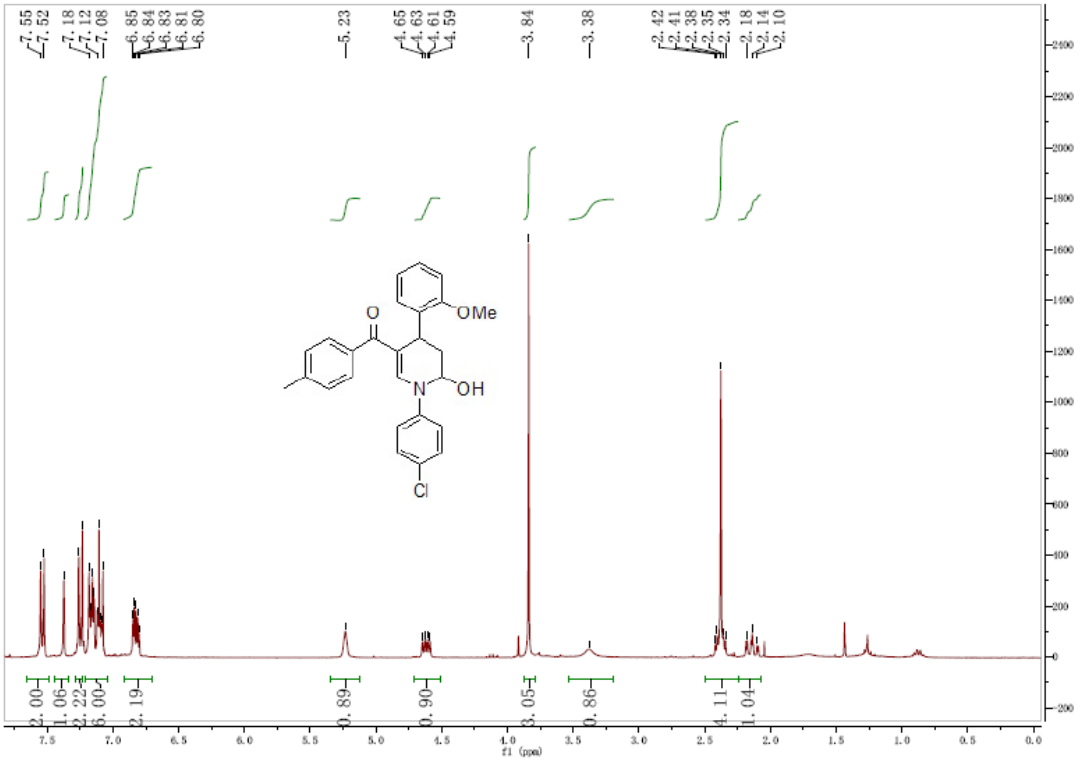

193.76
157.05
144.81
144.33
139.64
130.59
128.77
127.49
124.32
119.61
116.65
110.72
78.67
55.24
36.96
28.23
OMe
O
N
OH
129.55
128.09
127.17
f1 (ppm)

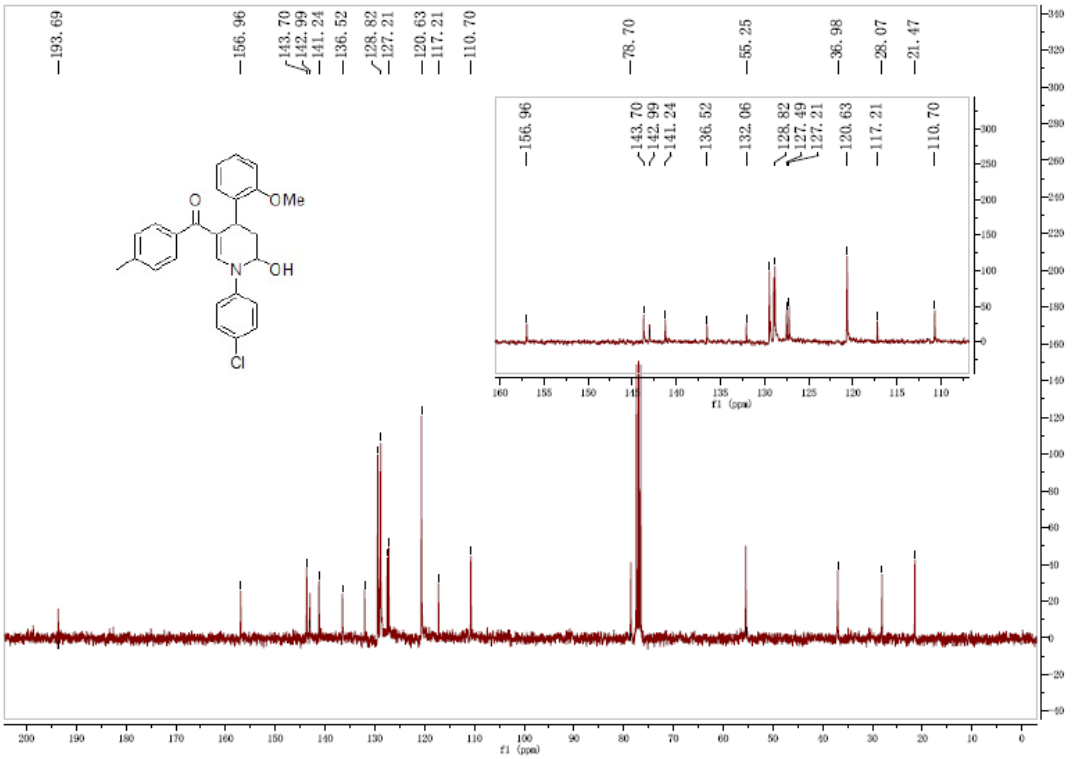
9n


7.60
7.58
7.42
7.17
7.08
6.80
6.77
5.30
4.22
4.20
4.19
4.17
3.72
3.41
2.40
2.39
2.36
2.35
2.14
2.11
2.07
OMe
O
N
OH
1.91
1.99
1.96
1.97
1.04
1.95
1.00
0.99
3.03
0.86
1.03
1.00
f1 (ppm)

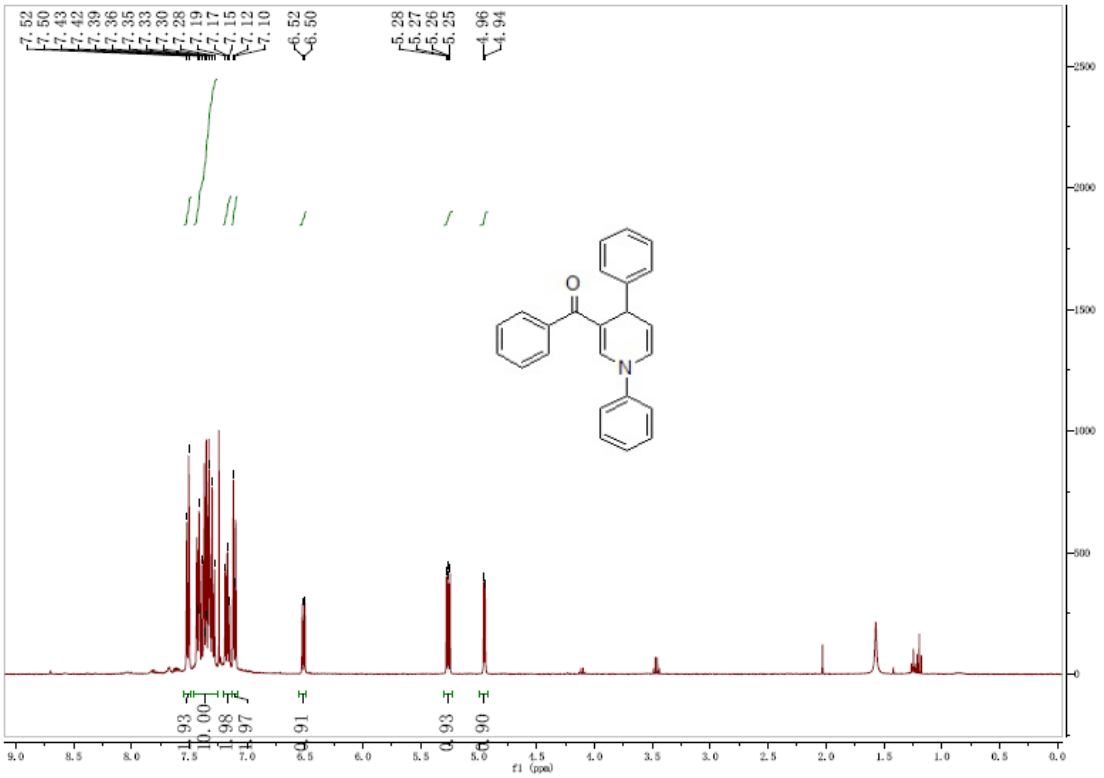

194.12
158.09
144.65
144.11
136.29
128.14
124.43
119.53
116.81
113.93
78.56
55.07
39.48
33.52
OMe
O
N
OH
f1 (ppm)

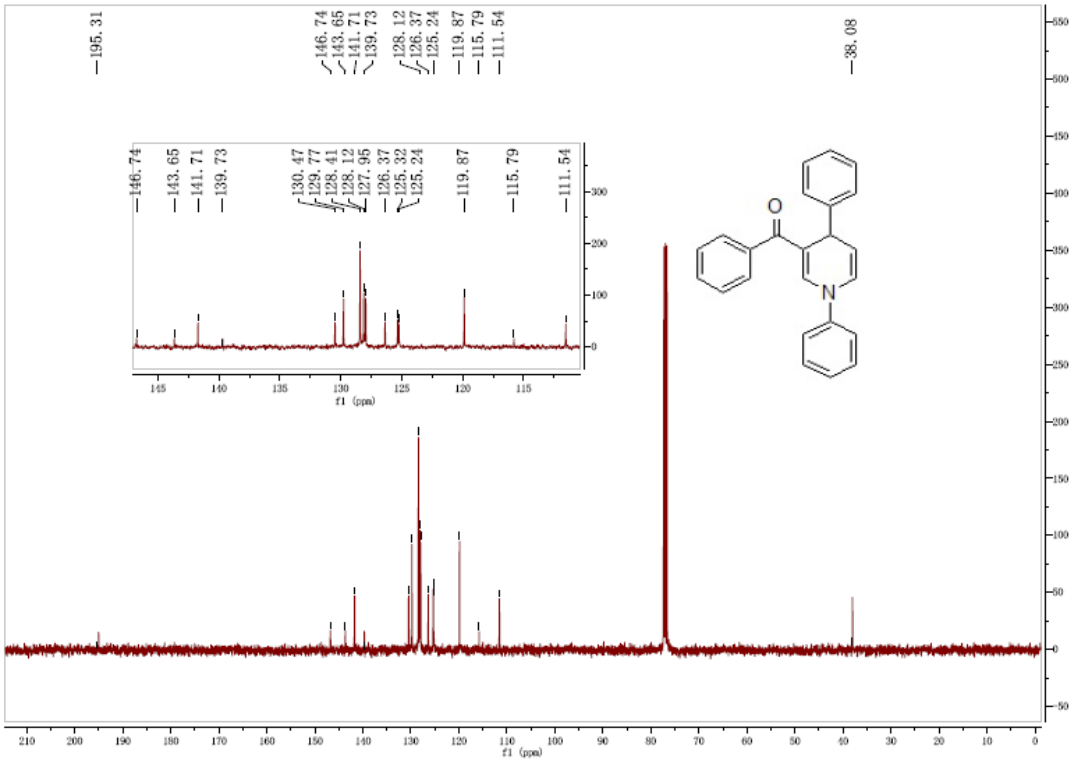
9o


7.55
7.52
7.18
7.12
7.08
6.85
6.84
6.83
6.81
6.80
5.23
4.65
4.63
4.61
4.59
3.84
3.38
2.42
2.41
2.38
2.35
2.34
2.18
2.14
2.10
OMe
O
N
OH
Cl
2.00
1.06
2.22
6.00
2.19
0.89
0.90
3.05
0.86
4.11
1.04
f1 (ppm)

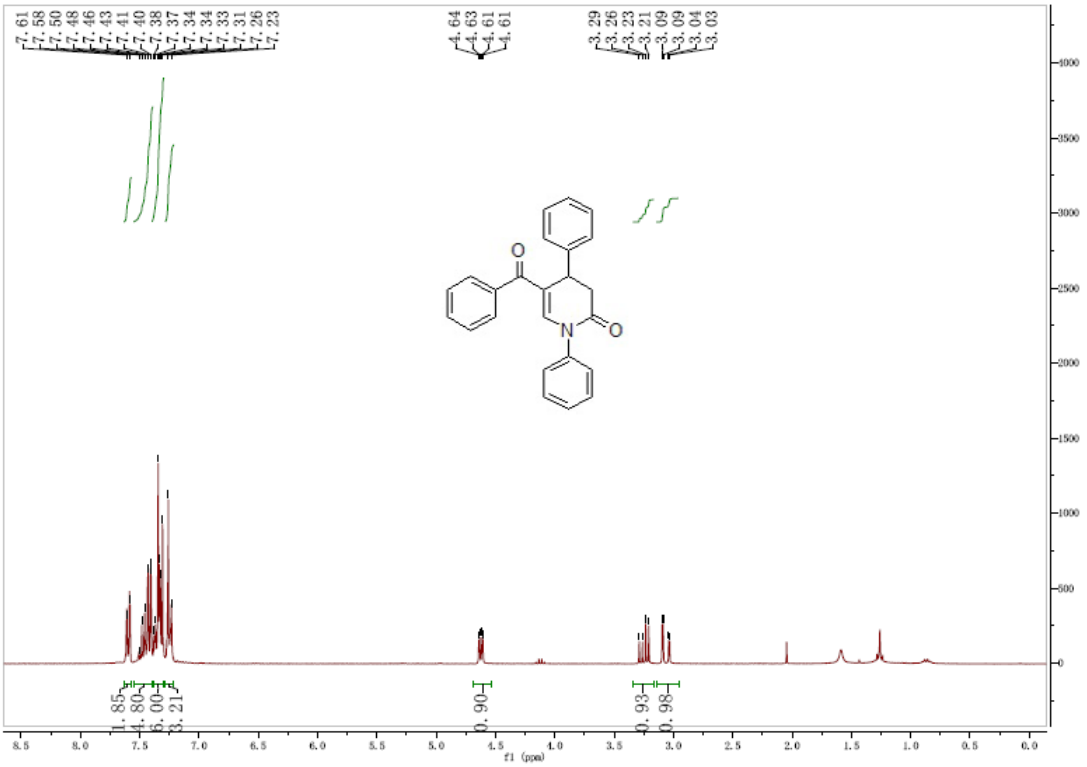

193.69
156.96
143.70
142.99
141.24
136.52
128.82
127.21
120.63
117.21
110.70
78.70
55.25
36.98
28.07
21.47
OMe
O
N
OH
Cl
f1 (ppm)

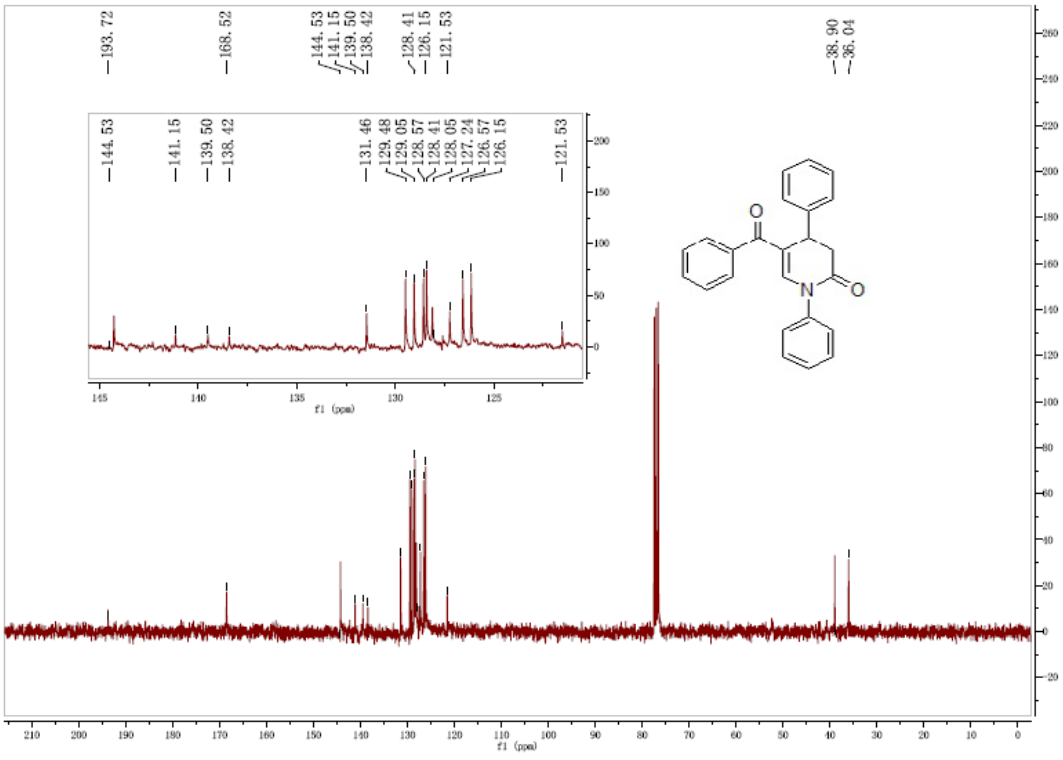
10a


7.52
7.50
7.43
7.42
7.39
7.36
7.35
7.33
7.30
7.28
7.19
7.17
7.15
7.12
7.10
6.52
6.50
5.28
5.27
5.26
5.25
4.96
4.94
O
N
1.93
10.00
1.98
1.97
0.91
0.93
0.90
f1 (ppm)


195.31
146.74
143.65
141.71
139.73
128.12
126.37
125.24
119.87
115.79
111.54
38.08
O
N
f1 (ppm)

11a


7.61
7.58
7.50
7.48
7.46
7.43
7.41
7.40
7.38
7.37
7.34
7.34
7.33
7.31
7.26
7.23
4.64
4.63
4.61
4.61
3.29
3.26
3.23
3.21
3.09
3.09
3.04
3.03
O
N
O
1.85
4.80
6.00
3.21
0.90
0.93
0.98
f1 (ppm)


193.72
168.52
144.53
141.15
139.50
138.42
128.41
126.15
121.53
38.90
36.04
131.46
129.48
129.05
128.57
128.41
128.05
127.24
126.57
126.15
O
N
O
f1 (ppm)