Supporting Information For：

Organocatalytic asymmetric multicomponent reactions of aromatic aldehydes and anilines with β-ketoesters: A facile and atom-economical access to chiral tetrahydropyridines

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CONTENTS

1. General Information

All reactions were carried out in oven-dried glassware with magnetic stirring under dry argon atmosphere unless otherwise mentioned. The corresponding carboxylic acid is an efficient catalyst for this reaction and the ee immediately drops when this acid is present, so aldehydes were all freshly distilled or dissolved in diethyl ether, washed with saturated aqueous $NaHCO_3$ for three times, dried over Na_2SO_4, filtered through a pad of silica, concentrated, and subjected to high vacuum (<0.2 Torr) before use. Solvents were purified and dried according to standard methods prior to use. Powdered 4Å molecular sieves were activated at 200 °C for 2 h under vacuum (<0.2 Torr). Catalysts **5a**-**5d** were prepared according to the methods reported in the literature[1] and washed with 4N HCl before use.

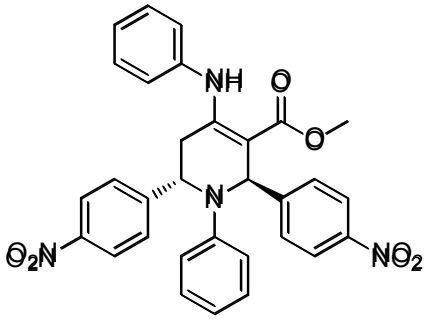
^{1}H NMR spectra were recorded on 400 MHz or 500 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in $CDCl_3$ or 2.5 in DMSO-d6. The following abbreviations were used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants were reported in Hertz (Hz). ^{13}C NMR spectra were recorded on 100 MHz or 125 MHz spectrometer, referred to the internal solvent signals (77.0 for $CDCl_3$ or 40.0 for DMSO-d6). Infrared spectra were recorded on a ATR-FTIR spectrometer. Optical rotations were determined using a Perkin Elmer Model 341 polarimeter at 20 °C. The enantiomeric excesses (ee) were determined by chiral HPLC analysis on Daicel Chiralpak AD-H and Chiralcel OD-H columns. HRMS were obtained using EI ionization.

2. General Procedure

General Procedure for synthesis of chiral functionalized Tetrahydropyridines 4.

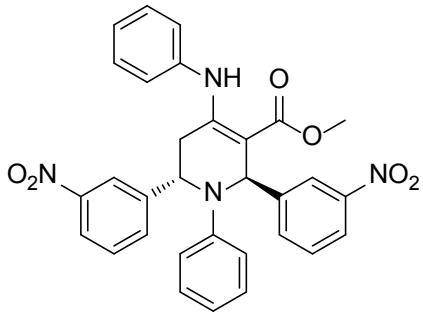
To a solution of aromatic aldehyde **1** (0.2 mmol), aniline **2** (0.2 mmol) and β-ketoester **3** (0.1 mmol) in toluene (3 mL) was added powdered 4Å molecular sieves (0.1 g) and the chiral SPINOL-phosphoric acid **5c** (0.01 mmol). The resulting mixture was stirred under an argon atmosphere at -30 ^{o}C for 3 days. Solvent was removed *in vacuum*, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the corresponding tetrahydropyridine **4**.

(2R,6S)-methyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4a)



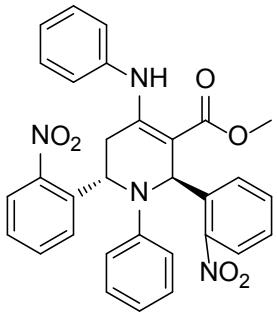
According to general procedure: the product was obtained as yellow solid, mp 254-256 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), ＞99% ee. HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min), tR (major) 23.0 min, tR (minor) 31.6 min. [α]D20 = -7° (c = 0.27, CHCl3), 1H NMR (400 MHz, CDCl3) δ (ppm) 10.28 (s, 1H), 8.15 (t, J = 9.3 Hz, 4H), 7.50 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.19 (dd, J = 10.2, 5.2 Hz, 3H), 7.10 (t, J = 7.9 Hz, 2H), 6.70 (t, J = 7.3 Hz, 1H), 6.48 (s, 1H), 6.43 (m, 3H), 6.39 (s, 1H), 5.28 (s, 1H), 3.97 (s, 3H), 2.88 (d, J = 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.89, 155.45, 151.50, 149.68, 147.26, 146.78, 145.70, 137.06, 129.31, 129.18, 127.35, 127.29, 126.41, 125.46, 123.90, 123.73, 117.63, 112.83, 96.60, 57.29, 55.14, 51.44, 33.53; IR (KBr) γ, 3448, 3244, 2946, 1654, 1595, 1519. 1500, 1346, 749 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{26}N_4O_6$ 550.1852, found 550.1862.

(2R,6S)-methyl 2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4b)



According to general procedure: the product was obtained as yellow solid, mp 218-219 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 90% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 1.0 mL/min), t_R (major) 8.8 min, t_R (minor) 30.9 min, $[\alpha]_D^{20}$ = -4° (c = 0.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.30 (s, 1H), 8.21 (s, 1H), 8.12 (dd, *J* = 8.7 Hz, 5.1, 2H), 7.94 (s, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.52-7.41 (m, 3H), 7.11 (ddd, *J* = 21.9, 10.3, 6.1 Hz, 5H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.49 (s, 1H), 6.44 (d, *J* = 8.2 Hz, 2H), 6.39 (dd, *J* = 6.5, 2.6 Hz, 2H), 5.33 (s, 1H), 3.98 (s, 3H), 2.88 (d, *J* = 3.9 Hz, 2H)； ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.99, 155.50, 148.59, 148.50, 146.24, 145.66, 144.37, 137.06, 132.51, 129.66, 129.31, 129.20, 126.55, 125.62, 122.46, 121.84, 121.47, 121.32, 117.65, 113.01, 96.69, 56.98, 55.10, 51.43, 33.70; IR (KBr) γ, 3452, 3238, 2949, 1654, 1652, 1616. 1528, 1497, 1349, 1255, 1051 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{26}N_4O_6$ 550.1852, found 550.1846.

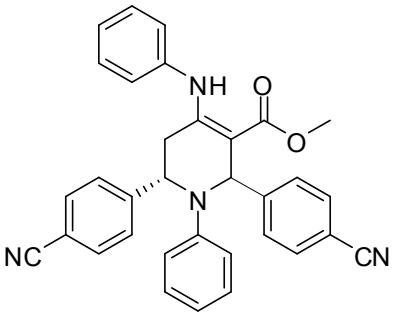
(2R,6S)-methyl 2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4c)



According to general procedure: the product was obtained as yellow solid, mp 232-234 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 87% ee. HPLC analysis: Chiralpak OD-H (hexane/i-

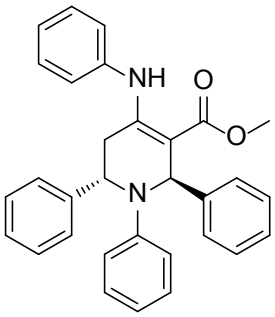
PrOH = 90/10, 0.8 mL/min), t_R (major) 19.4 min, t_R (minor) 25.4min, $[\alpha]_D^{20}$ = -2° (c = 0.29, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.46 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.66-7.68 (d, *J* = 8 Hz, 1H), 7.45-7.48 (m, 3H), 7.31 -7.40(m, 3H), 7.15 -7.20 (m, 3 H), 7.10 (t, *J* = 7.6 Hz, 2H), 6.85 (s, 1H), 6.73 (t, 14. 6 1H), 6.68 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 6.8 Hz, 2H), 6.00 (s, 1H), 3.79 (s, 3H), 3.02 (dd, *J* = 6, 5.6 Hz, 1H), 2.90 (dd, *J* = 3.2, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.08, 155.67, 150.05, 148.21, 145.66, 137.72, 137.30, 137.26, 133.50, 131.60, 129.46, 129.21, 129.17, 128.49, 128.19, 127.82, 126.36, 125.68, 125.15, 124.70, 118.84, 115.13, 94.81, 53.58, 52.91, 51.04, 31.28; IR (KBr) γ, 3448, 2944, 1653, 1597, 1529, 1367, 1498, 1261, 745 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{26}N_4O_6$ 550.1852, found 550.1854.

(2R,6S)-methyl 2,6-bis(4-cyanophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4d)



According to general procedure: the product was obtained as white solid, mp 185-187°C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 87% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH =65/35, 1 mL/min), t_R (major) 7.7 min, t_R (minor) 19.9 min, $[\alpha]_D^{20}$ = 5.4° (c = 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.26 (s, 1H), 7.57 (t, *J* = 8.2 Hz, 4H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 2H), 7.17 (d, *J* = 7.1 Hz, 3H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.1 Hz, 1H), 6.41 (dd, *J* = 14.1, 8.6 Hz, 5H), 5.20 (s, 1H), 3.94 (s, 3H), 2.82 (d, *J* = 2.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.93, 155.51, 149.36, 147.72, 145.79, 137.11, 132.63, 132.34, 129.23, 129.11, 127.27, 127.11, 126.34, 125.49, 118.84, 118.59, 117.41, 112.75, 111.20, 110.46, 96.70, 57.47, 55.10, 51.32, 33.43; IR (KBr) γ, 3059, 2950, 2227, 1660, 1593, 1500, 1319, 1256, 1891, 745 cm^{-1}; HRMS (EI-TOF): calcd for $C_{33}H_{26}N_4O_6$ 510.12056, found 510.2066.

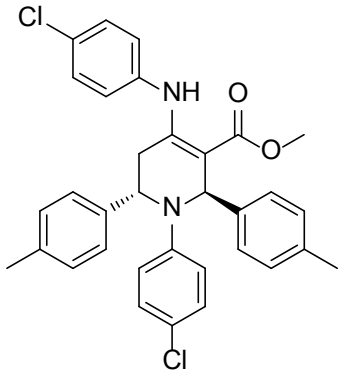
(2R,6S)-methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate(4e)



According to general procedure: the product was obtained as white solid, mp 200-202 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 88% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 85/15, 0.8 mL/min), t_R (major) 6.6 min, t_R (minor) 21.2 min, $[\alpha]_D^{20}$ = +29° (c = 0.09, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.28 (s, 1H), 7.30 (m, 7H), 7.20 (dd, *J* = 12.7, 6.2 Hz, 3H), 7.07 (m, 5H), 6.61 (dd, *J* = 14.0, 7.0 Hz, 1H), 6.53 (t, *J* = 8.2 Hz, 2H), 6.47 (d, *J* = 9.1 Hz, 1H), 6.28 (d, *J* = 7.2 Hz, 2H), 5.16 (s, 1H), 3.94 (d, *J* = 6.5 Hz, 3H), 2.83 (m, 2H); ^{13}C NMR (100 MHz,

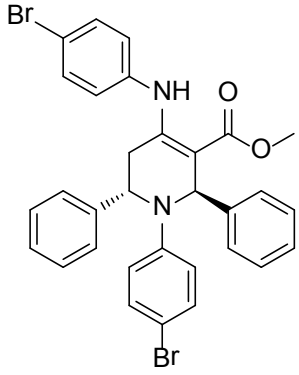
$CDCl_3$) δ (ppm) 168.48, 156.20, 146.84, 143.81, 142.63, 137.70, 128.81, 128.77, 128.56, 128.17, 127.07, 126.55, 126.28, 125.77, 125.70, 116.08, 112.82, 97.82, 58.10, 55.00, 50.96, 33.53. IR (KBr) γ, 3246, 3058, 2948, 1656, 1580, 1500, 1449, 1375, 1324, 1072 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{28}N_2O_2$ 460.2151, found 460.2154.

(2R,6S)-methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4f)



According to general procedure: the product was obtained as white solid, mp 234-236 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 41% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 7.9 min, t_R (minor) 18.7 min, $[\alpha]_D^{20}$ = 8.6° (c = 0.38, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.19 (s, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 7.12 – 6.99 (m, 8H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 8.2 Hz, 2H), 6.32 (s, 1H), 6.18 (d, *J* = 7.8 Hz, 2H), 5.06 (s, 1H), 3.89 (d, *J* = 24.2 Hz, 3H), 2.99 – 2.60 (m, 2H), 2.32 (d, *J* = 9.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.45, 155.52, 145.53, 140.14, 139.14, 137.01, 136.43, 136.08, 131.26, 129.41, 129.03, 128.94, 128.63, 126.99, 126.38, 126.20, 121.03, 113.96, 98.58, 57.99, 55.06, 51.11, 33.45, 21.06, 20.97; IR (KBr) γ, 3241, 3173, 2950, 1659, 1574, 1494 1321, 1257, 1188, 1092,1072 cm^{-1}; HRMS (EI-TOF): calcd for $C_{33}H_{30}Cl_2N_2O_2$ 556.1684, found 556.1676.

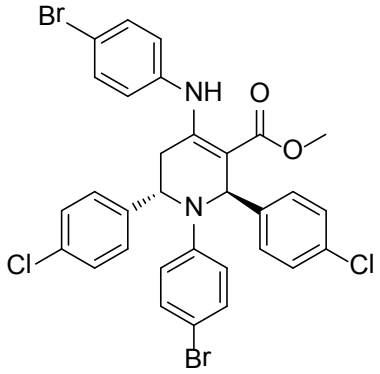
(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4g)



According to general procedure: the product was obtained as white solid, mp 220-214 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 97% ee. HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 90/10, 0.7 mL/min), t_R (major) 7.6 min, t_R (minor) 14.6 min, $[\alpha]_D^{20}$ = +29° (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.92 (s, 1H), 7.35-7.18 (m, 11H), 7.13 (dd, *J* = 18.4, 8.1 Hz, 5H), 6.41 (d, *J* = 8.9 Hz, 2H), 5.94 (s, 1H), 5.09 (t, *J* = 4.8 Hz, 1H), 3.89 (s, 3H), 3.10 (dd, *J* = 16.4, 5.8 Hz, 1H), 2.71 (dd, *J* = 16.3, 4.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.05, 170.35, 145.93, 141.99, 141.56, 131.96, 131.40, 128.69, 128.43, 127.31, 127.08, 126.61, 126.22, 117.72, 114.50, 110.41, 101.86, 57.37, 56.89, 51.91, 36.63; IR (KBr) γ, 3367, 3060, 2953, 1660, 1591,

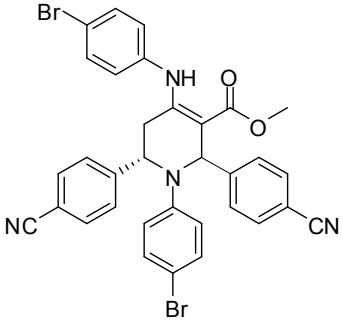
1493. 1446, 1372, 1324, 1072 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{26}Br_2N_2O_6$ 616.0361, found 616.0361.

(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4h)



According to general procedure: the product was obtained as white solid, mp 169-171 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 91% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 75/25, 1.0 mL/min), t_R (major) 4.8 min, t_R (minor) 14.4 min, $[\alpha]_D^{20}$ = +30° (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.20 (s, 1H), 7.25 (dd, *J* = 8, 3.2 Hz, 6H), 7.15 (d, *J* = 12.8 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 2H), 6.31 (d, *J* = 9.2 Hz, 2H), 6.26 (d, *J* = 5.2 Hz, 2H), 6.24 (s, 1H), 5.05 (d, *J* = 3.2 Hz, 1H), 3.92 (s, 3H), 2.81 (dd, *J* = 5.6, 5.6 Hz, 1H), 2.69 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 168.12, 155.13, 145.34, 141.44, 140.17, 136.57, 133.21, 132.43, 132.13, 131.72, 128.92, 128.52, 127.83, 127.61, 127.12, 119.47, 114.53, 109.12, 98.05, 57.34, 54.79, 51.32 , 33.49; IR (KBr) γ, 3446, 2943, 1658, 1608, 1587, 1489, 1319, 1255, 1090,1069 cm^{-1}; HRMS (EI-TOF): calcd for $C_{31}H_{24}Br_2Cl_2N_2O_2$ 683.9582, found 683.9577.

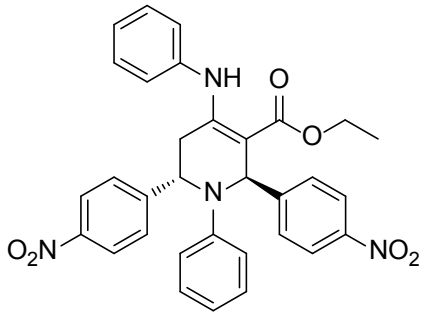
(2R,6S)-methyl 1-(4-bromophenyl)-4-(4-bromophenylamino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4i)



According to general procedure: the product was obtained as white solid, mp 242-243 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 92% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 55/45, 1 mL/min), t_R (major) 6.2 min, t_R (minor) 26.9min, $[\alpha]_D^{20}$ = -6.3° (c = 0.67, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.22 (s, 1H), 7.59 (dd, *J*=8.1, 3.8, 4H), 7.39 (d, *J*=8.2, 2H), 7.30 (d, *J*=8.5, 2H), 7.21 (d, *J*=8.2, 2H), 7.16 (d, *J*=8.9, 2H), 6.35 (s, 1H), 6.29 (s, 1H), 6.27 (d, *J*=2.4, 2H), 6.24 (s, 1H), 5.16 (s, 1H), 3.95 (s, 3H), 2.79 (dd, *J*=15.4, 3.9, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 167.85, 154.74, 148.53, 146.99, 144.79, 136.18, 132.64, 132.41, 132.36, 132.04, 127.19, 127.05, 126.91, 119.90, 118.69, 118.38, 114.45, 111.65, 110.86, 109.86, 97.35, 57.54, 55.27, 51.57, 33.38; IR (KBr) γ, 3238, 2959, 2230, 1659, 1611, 1492, 1254, 1191, 1069, 736 cm^{-1}; HRMS (EI-TOF): calcd for $C_{33}H_{24}Br_2N_4O_6$ 666.0266, found 666.0621.

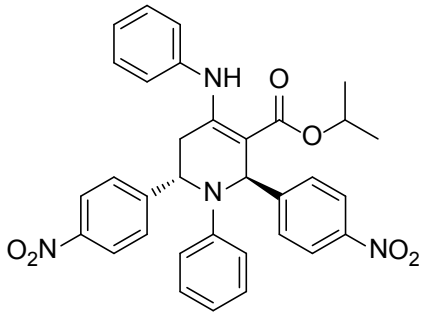
(2R,6S)-ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-

tetrahydropyridine-3-carboxylate (4j)



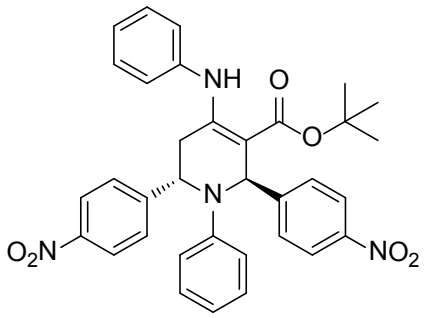
According to general procedure: the product was obtained as yellow solid, mp 247-249 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), ＞99% ee. HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 90/10, 0.7 mL/min), t_R (major) 32.7 min, t_R (minor) 42.5 min, $[\alpha]_D^{20}$ = -35.3° (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.33 (s, 1H), 8.15 (dd, *J* = 12.8, 8.5 Hz, 4H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.26 (s, 1H), 7.17 (d, *J* = 6.9 Hz, 2H), 7.10 (t, *J* = 7.8 Hz, 2H), 6.71 (t, *J* = 7.1 Hz, 1H), 6.48 (s, 1H), 6.44 (s, 1H), 6.41 (s, 2H), 6.39 (s, 1H), 5.27 (s, 1H), 4.43 (m, 2H), 2.87 (d, *J* = 3.7 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.58, 155.27, 151.64, 149.73, 147.30, 146.79, 145.78, 137.17, 129.35, 129.19, 127.33, 126.34, 125.42, 123.91, 123.75, 117.67, 112.92, 96.89, 60.24, 57.34, 55.20, 33.58, 14.77; IR (KBr) γ, 2971, 2931, 1653, 1594, 1581, 1519，1501, 1346, 1246, 750 cm^{-1}; HRMS (EI-TOF): calcd for $C_{32}H_{28}N_4O_6$ 564.2009, found 564.2015.

(2R,6S)-isopropyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4k)



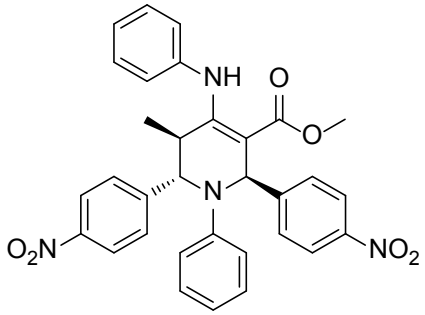
According to general procedure: the product was obtained as yellow solid, mp 198-200 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 96% ee. HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 85/15, 0.8 mL/min), t_R (major) 13.1 min, t_R (minor) 17.7 min, $[\alpha]_D^{20}$ = -50.8° (c = 0.81, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.37 (s, 1H), 8.18 (s, 1H), 8.15 (d, *J* = 6.2 Hz, 2H), 8.12 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.29 (s, 1H), 7.27 (d, *J* = 4.8 Hz, 2H), 7.14 (m, 5H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.42 (dd, *J* = 15.6, 9.0 Hz, 5H), 5.30 (m, 2H), 2.88 (d, *J* = 3.8 Hz, 2H), 1.48 (d, *J* = 6.2 Hz, 3H), 1.43 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.16, 155.06, 151.71, 149.73, 147.23, 146.71, 145.81, 137.20, 129.33, 129.15, 127.29, 126.20, 125.31, 123.86, 123.71, 117.64, 112.97, 97.14, 67.63, 57.27, 55.21, 33.58, 22.33, 22.24; IR (KBr) γ, 3451, 2974, 1654, 1593, 1519, 1501, 1248, 1180, 1108, 751 cm^{-1}; HRMS (EI-TOF): calcd for $C_{33}H_{30}N_4O_6$ 578.2165, found 578.2171.

(2R,6S)-tert-butyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4l)



According to general procedure: the product was obtained as yellow solid, mp 219-221 °C,, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 91% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 1 mL/min), t_R (major) 5.0 min,t_R (minor) 13.1min; >99% ee (after single recrystallization from hexane/EtOAc), $[\alpha]_D^{20}$ = -88° (c = 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.30 (s, 1H), 8.15 (dd, *J* = 17.0, 8.6 Hz, 4H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.13 (ddd, *J* = 22.3, 15.0, 7.3 Hz, 5H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 7.7 Hz, 3H), 6.39 (d, *J* = 8.3 Hz, 2H), 5.24 (s, 1H), 2.85 (d, *J* = 4.0 Hz, 2H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 167.47, 154.39, 151.84, 149.82, 147.25, 146.71, 145.87, 137.38, 129.35, 129.05, 127.32, 127.26, 126.00, 125.18, 123.83, 123.71, 117.62, 112.98, 98.37, 81.01, 57.30, 55.60, 53.40, 33.59, 28.73; IR (KBr) γ, 3451, 2968, 1650, 1593, 1522, 1501, 1340, 1250, 1063 cm^{-1}; HRMS (EI-TOF): calcd for $C_{34}H_{32}N_4O_6$ 592.2322, found 592.2326.

(2R,5R,6S)-methyl 5-methyl-2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4m)



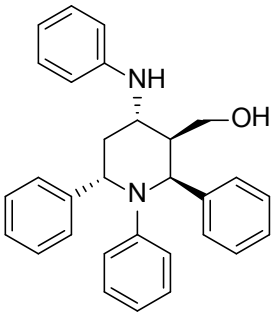
According to general procedure: the product was obtained as yellow solid, mp 249-251 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 93% ee. HPLC analysis: Chiralpak OD-H (hexane/i-PrOH = 97.5/2.5, 0.8 mL/min), t_R (major) 41.5 min,t_R (minor) 51.5 min, $[\alpha]_D^{20}$ = -50.8° (c = 0.89, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.40 (s, 1H), 8.12 (dd, *J*=11.0, 8.8 Hz, 4H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.23 (dd, *J* = 8.8, 6.3 Hz, 5H), 7.10 (t, *J* = 7.9 Hz, 2H), 6.74 (t, *J*=7.2 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 4H), 6.29 (s, 1H), 5.02 (s, 1H), 3.89 (s, 3H), 3.08 (dt, *J* = 13.0, 6.4 Hz, 1H), 1.13 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 168.73, 159.53, 151.62, 150.38, 147.00, 146.57, 146.23, 137.39, 129.26, 129.12, 128.57, 127.78, 127.07, 127.95, 123.73, 123.21, 118.68, 115.35, 94.33 , 63.96, 55.80, 51.33, 38.10, 19.22; IR (KBr) γ, 3366, 2950, 1661, 1516, 1506, 1346, 1247, 1108, 1013, 855, 747 cm^{-1}; HRMS (EI-TOF): calcd for $C_{32}H_{28}N_4O_6$ 564.2009, found 564.2015.

Procedure for reduction of 4e to 7[2]

The tetrahydropyridine **4e (**0.2 mmol) dissolved in a mixture of i-PrOH (0.5 mL) and THF (0.5 mL) was treated with an excess of sodium wire (0.05 g) and magnetically stirred 50℃ for the time required

for complete reduction (5 h) as monitored by TLC. After the removal of the unreacted sodium, the reaction mixture was poured into saturated aqueous NH_4Cl (5 mL) and extracted with CH_2Cl_2. The organic layer was dried and evaporated under reduced pressure, Column chromatographic separation of the crude material, afforded white solid **7**.

((2S,3R,4S,6S)-1,2,6-triphenyl-4-(phenylamino)piperidin-3-yl)methanol (7)



The product was obtained as white solid, mp 171-173 °C, from flash chromatography (hexane/EtOAc = 10:1 to 6:1), 88% ee. HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 8.2 min, t_R (minor) 13.5min, $[\alpha]_D^{20}$ = 34.5° (c = 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 (dd, *J* = 12.3, 4.3 Hz, 4H), 7.31 (d, *J* = 4.4 Hz, 4H), 7.29-7.27 (m, 2H), 7.16-7.09 (m, 2H), 7.00 (dd, *J* = 8.7, 7.3 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.46 (d, *J* = 8.0 Hz, 2H), 6.41-6.34 (m, 2H), 5.32 (d, *J* = 5.1 Hz, 1H), 5.15 (t, *J* = 4.9 Hz, 1H), 3.83 (m, 2H), 3.50 (brs, 1H), 2.84 (ddd, *J* = 14.8, 6.7, 5.2 Hz, 1H), 2.81-2.76 (m, 2 H), 2.71 (dd, *J* = 10.8, 5.2 Hz, 1H), 2.36 (ddd, *J* = 14.8, 4.6, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.85, 146.16, 143.35, 139.22, 129.25, 128.67, 128.62, 128.34, 127.20, 126.90, 126.84, 126.75, 119.03, 117.72, 115.54, 115.40, 64.95, 60.84, 56.27, 49.66, 47.74, 36.98. IR (KBr) γ, 3413, 3060, 2931, 1600, 1599, 1501, 1447, 1308, 1182, 1034, 745 cm^{-1}; HRMS (EI-TOF): calcd for $C_{30}H_{30}N_2O$ 434.2358, found 434.2367.

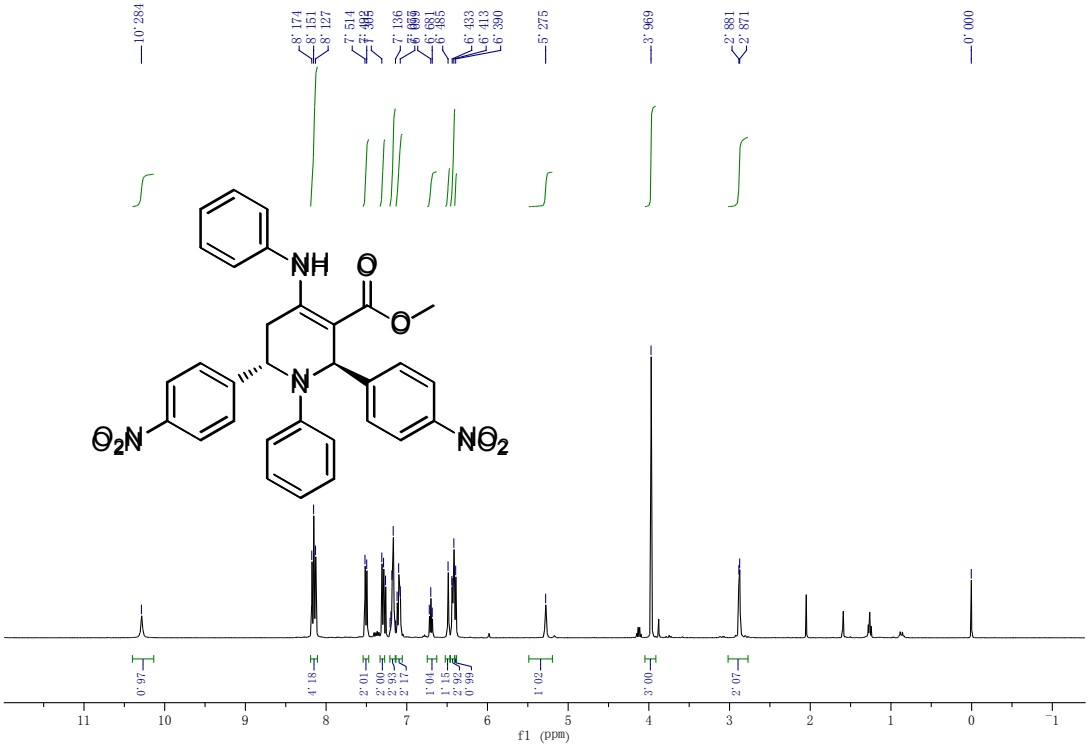
3. References

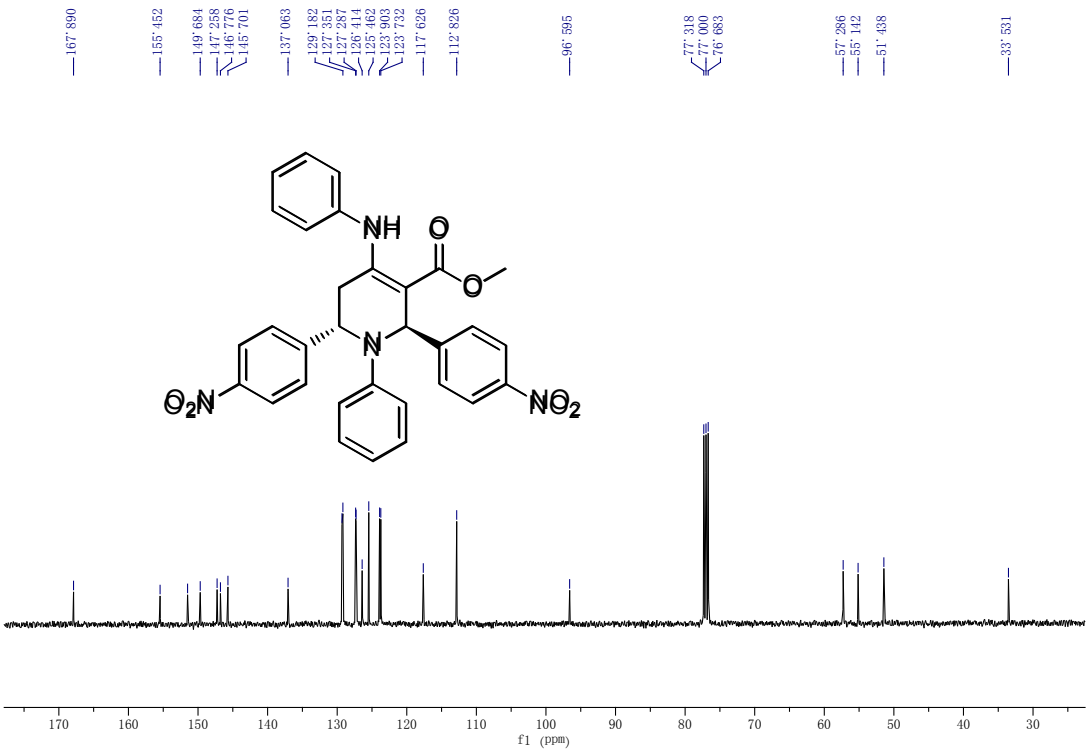
[1] F. X. Xu, D. Huang, C. Han, W. Shen, X. F. Lin, Y. G. Wang, *J. Org. Chem.* **2010**, *75*, 8677-8680.

[2] G. Bartoli, C. Cimarelli, E. Marcantoni, G. Palmieri, and M. Petrini, *J.* Org. Chem. **1994,** *59*, 5328-5335

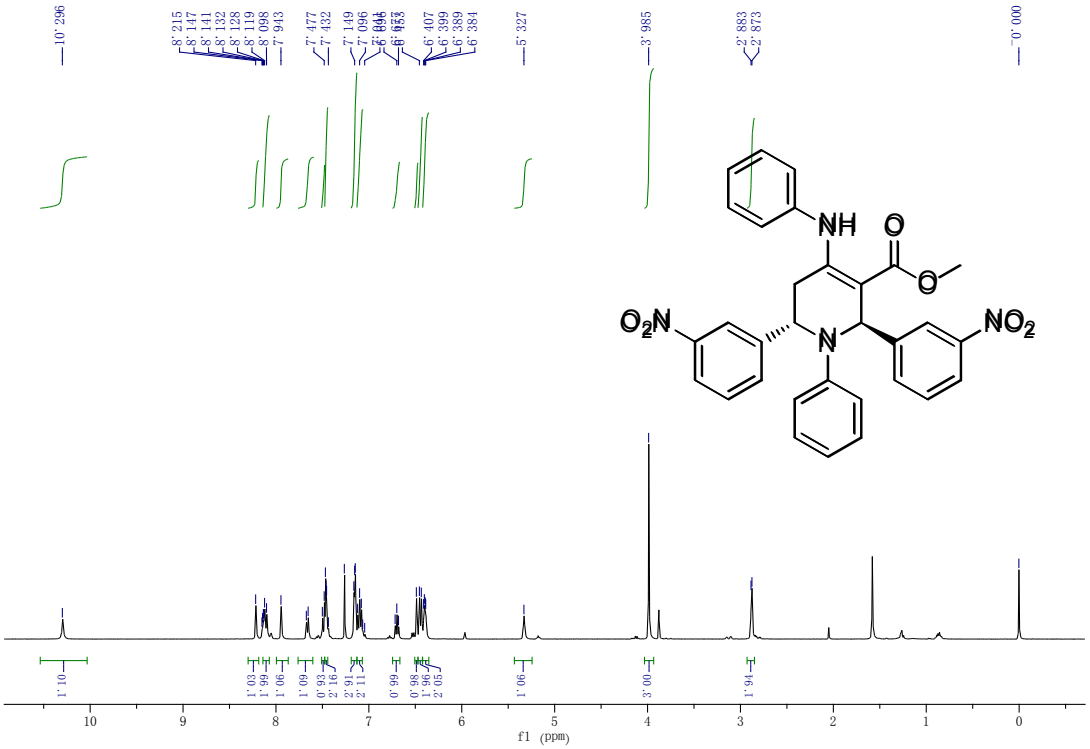
4. ^{1}H and ^{13}C NMR spectra

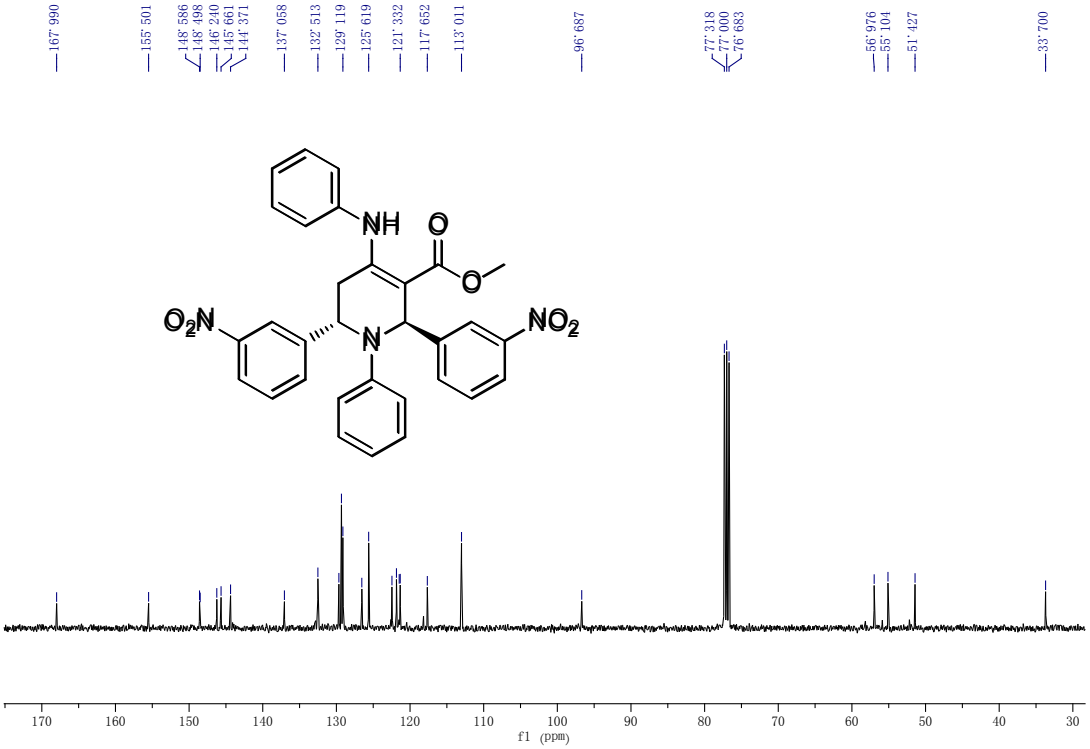
(2R,6S)-methyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4a)



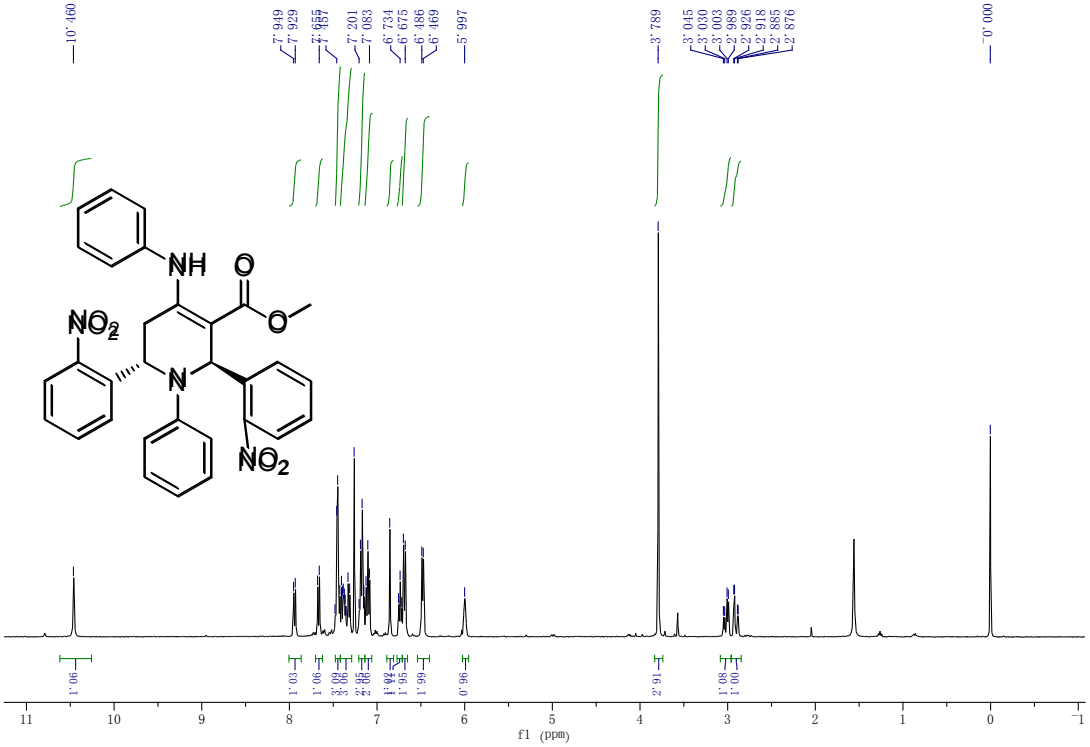


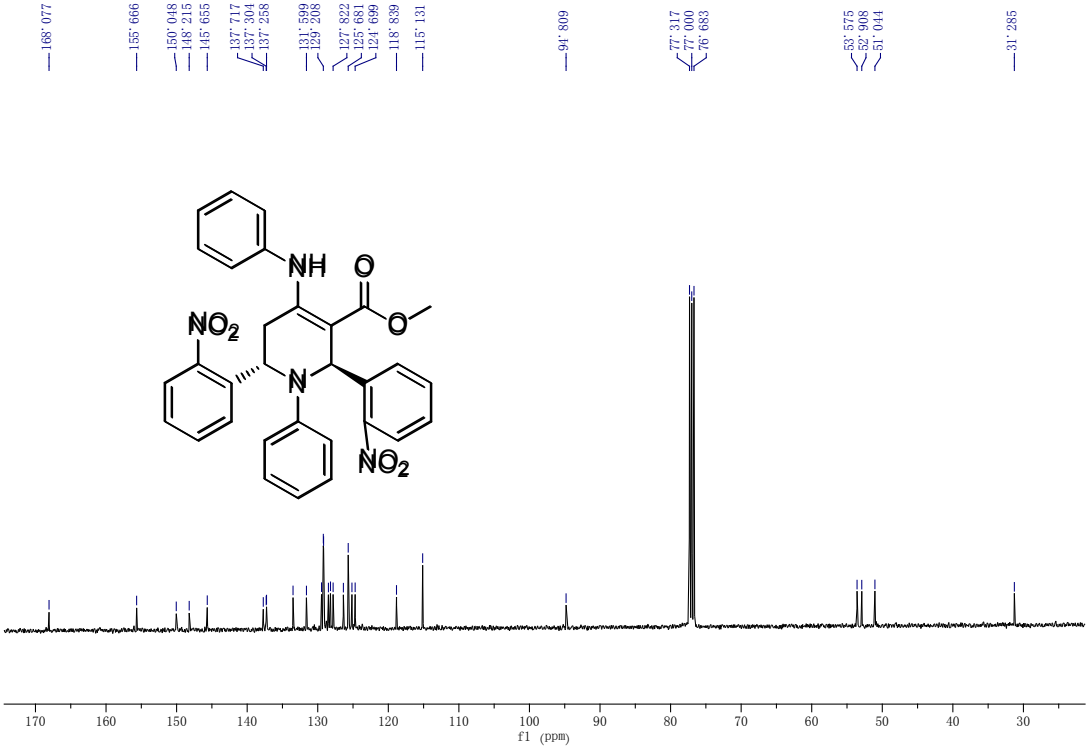
(2R,6S)-methyl 2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4b)



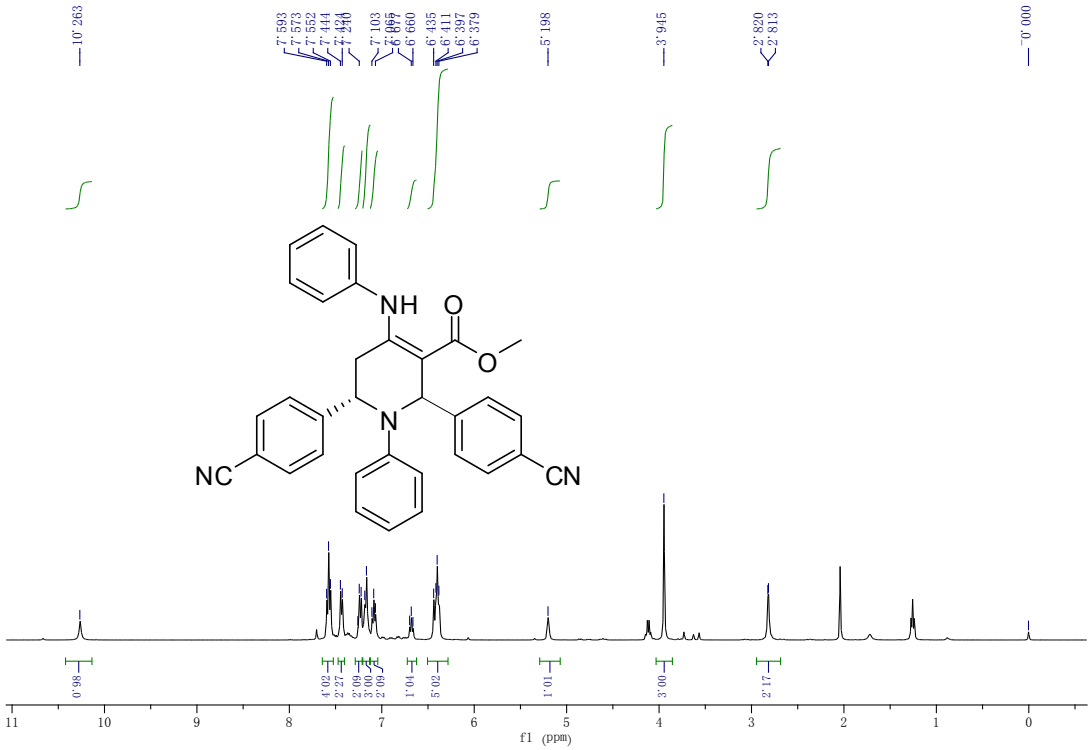


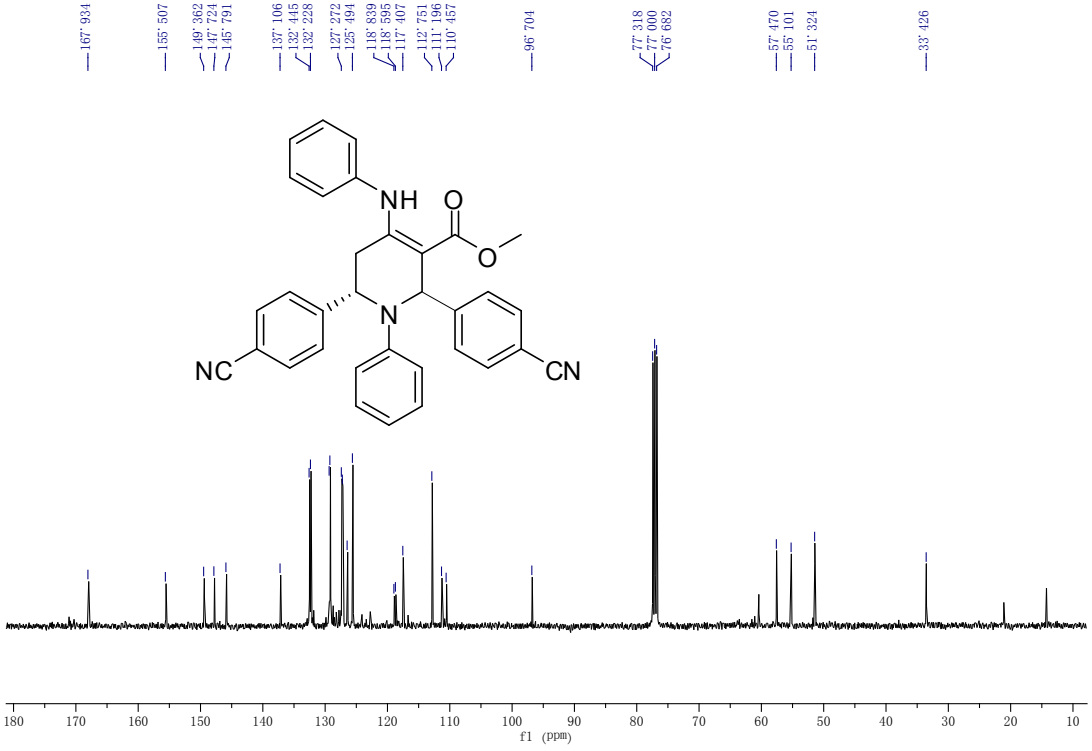
(2R,6S)-methyl 2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4c)



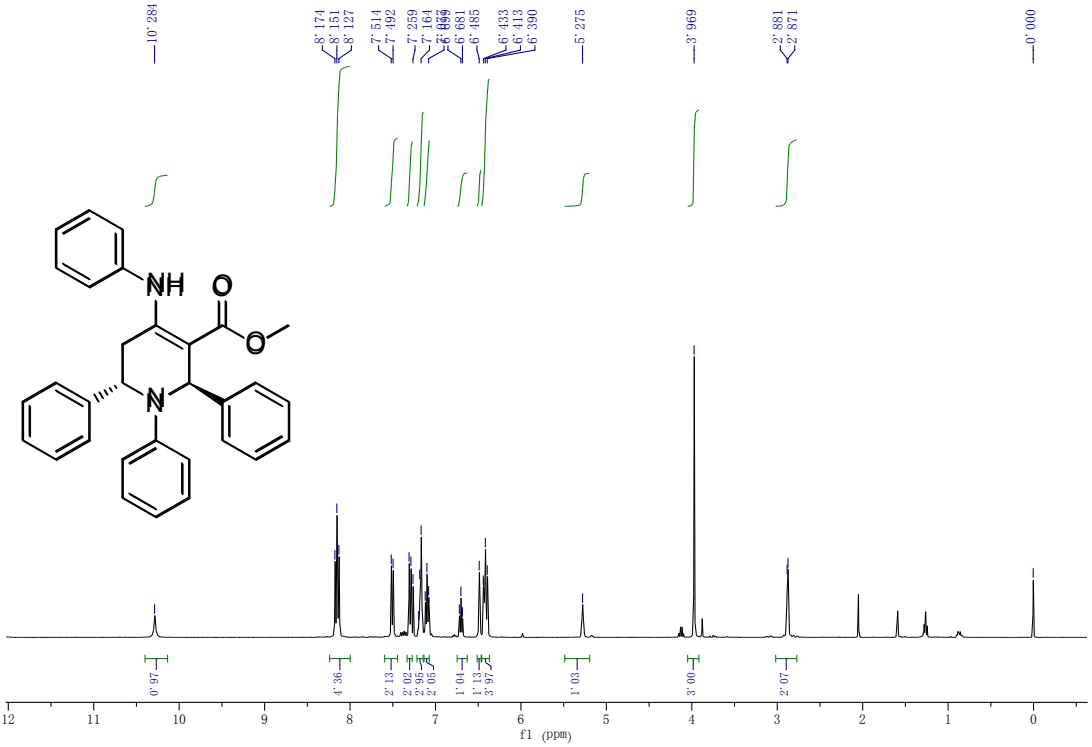


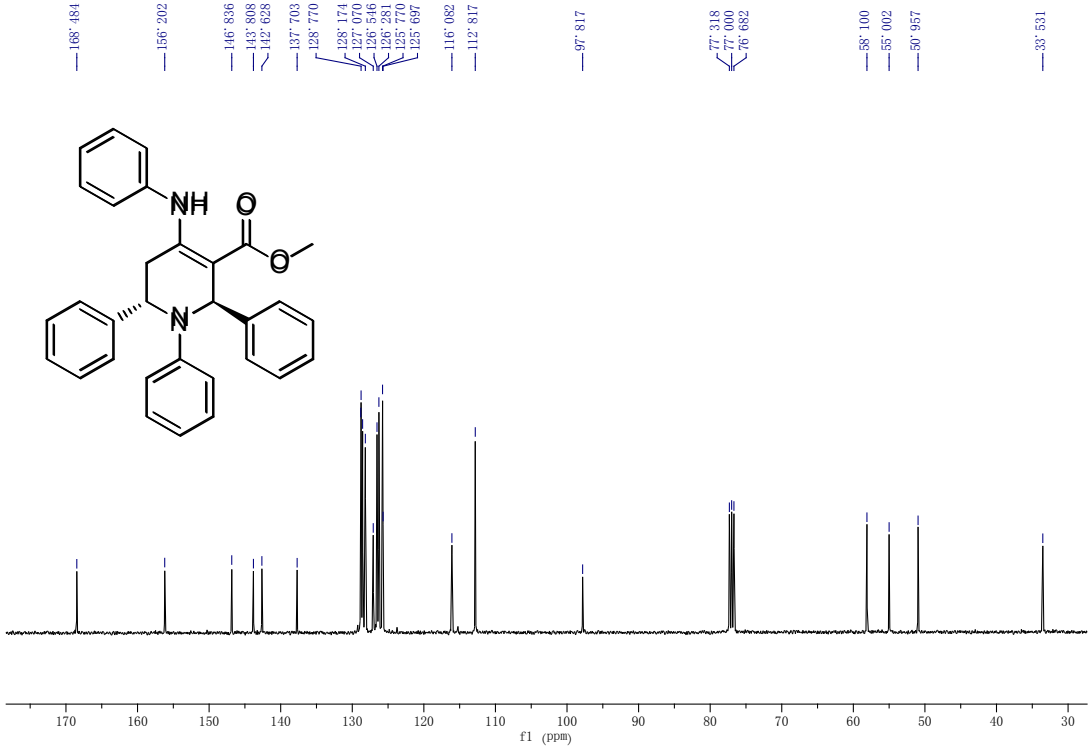
(2R,6S)-methyl2,6-bis(4-cyanophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4d)



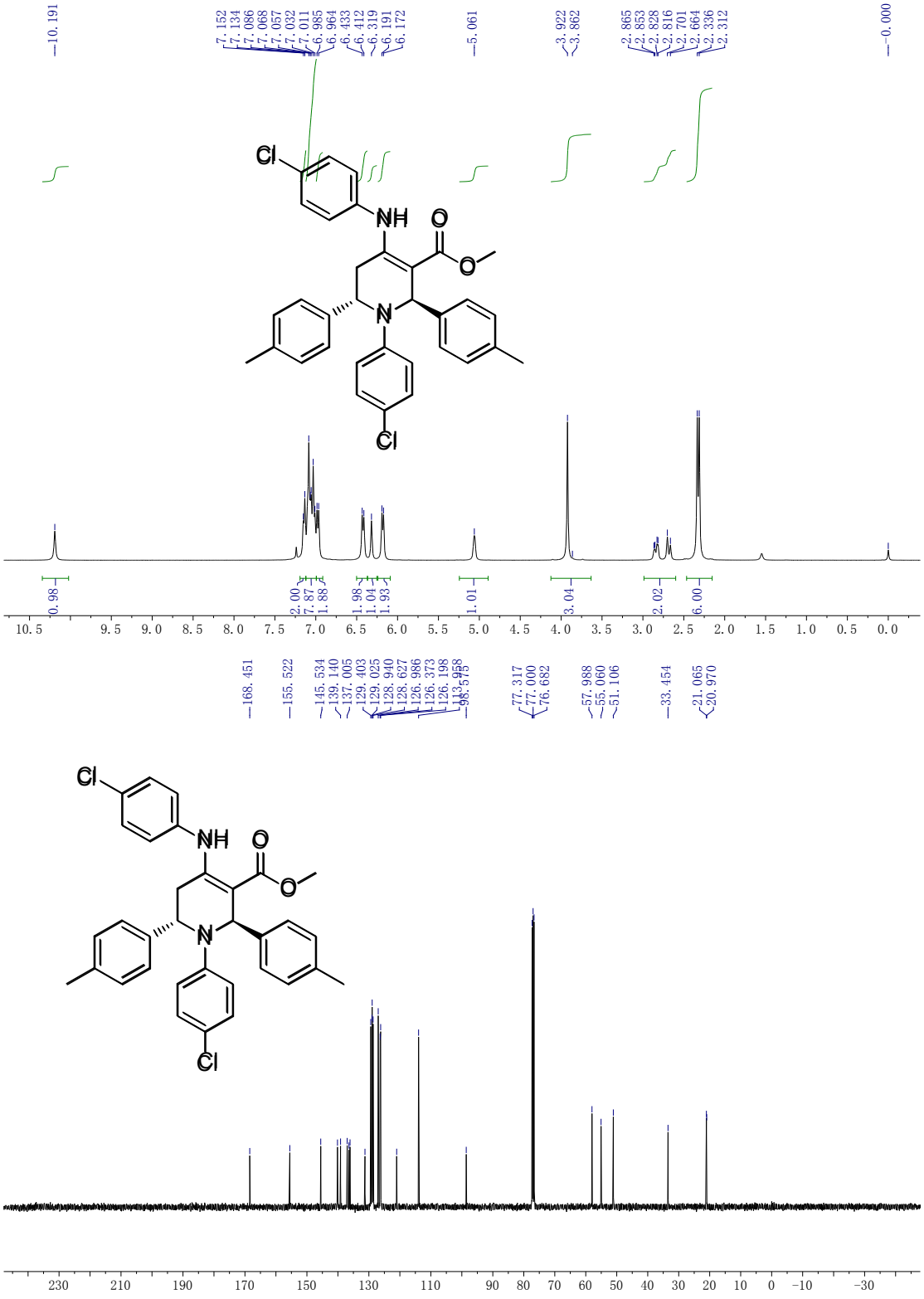


(2R,6S)-methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4e)

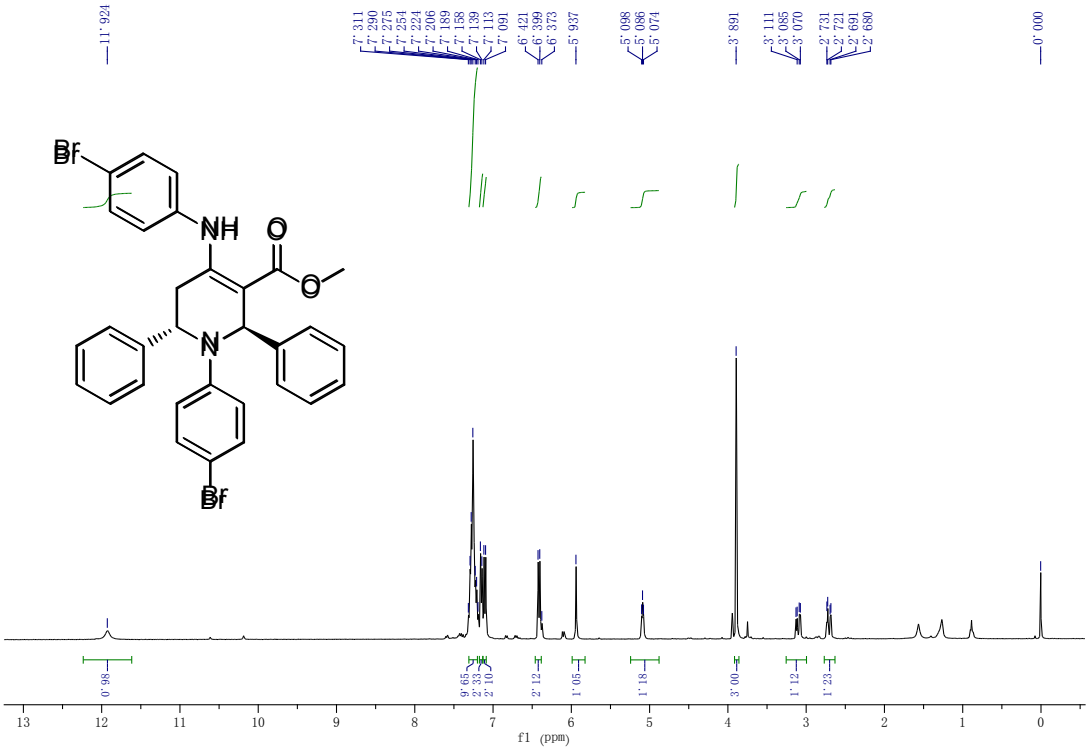




(2R,6S)-methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4f)



(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4g)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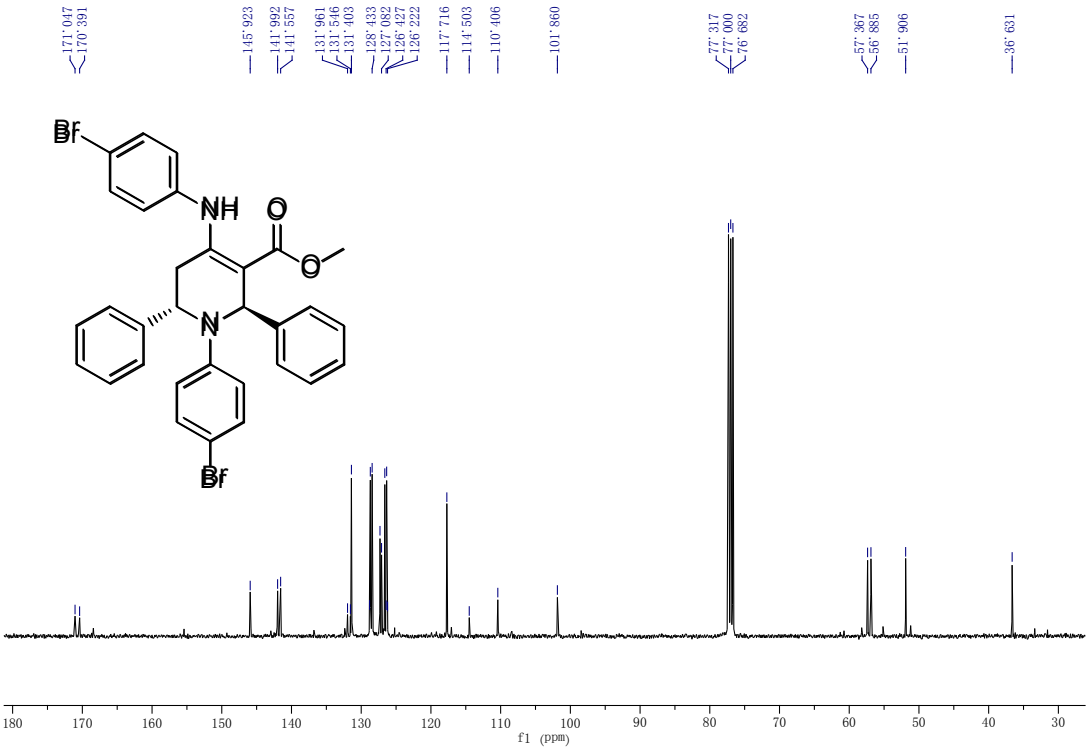
7.311
7.290
7.275
7.254
7.224
7.206
7.189
7.158
7.139
7.113
7.091
6.421
6.399
6.373
5.937
5.098
5.086
5.074
3.891
3.111
3.085
3.070
2.731
2.721
2.691
2.680
0.000
Br
NH
O
O
N
Br
0.98
9.65
2.33
2.10
2.12
1.05
1.18
3.00
1.12
1.23
f1 (ppm)


171.047
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131.961
131.546
131.403
128.433
127.082
126.427
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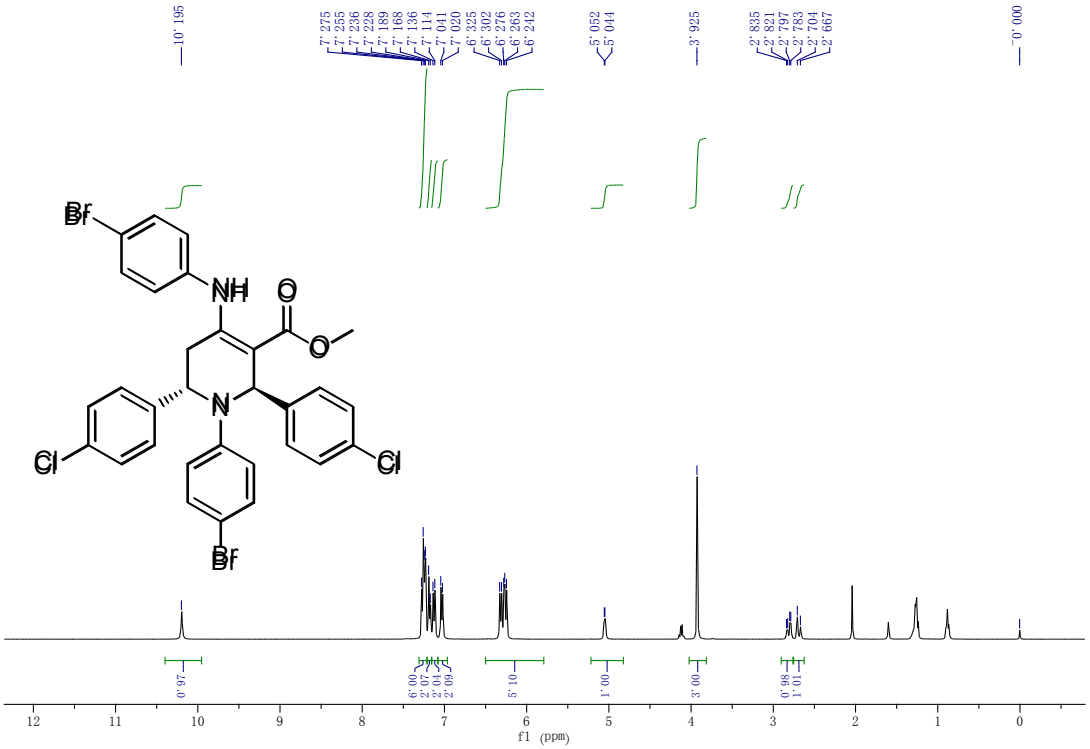
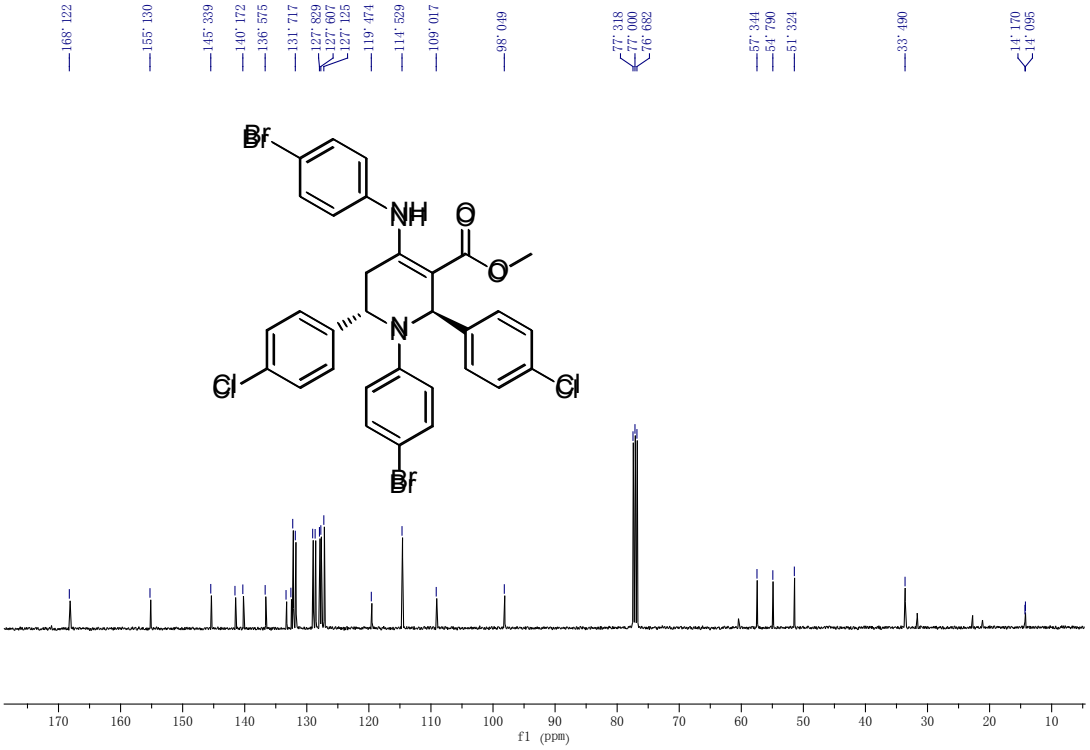
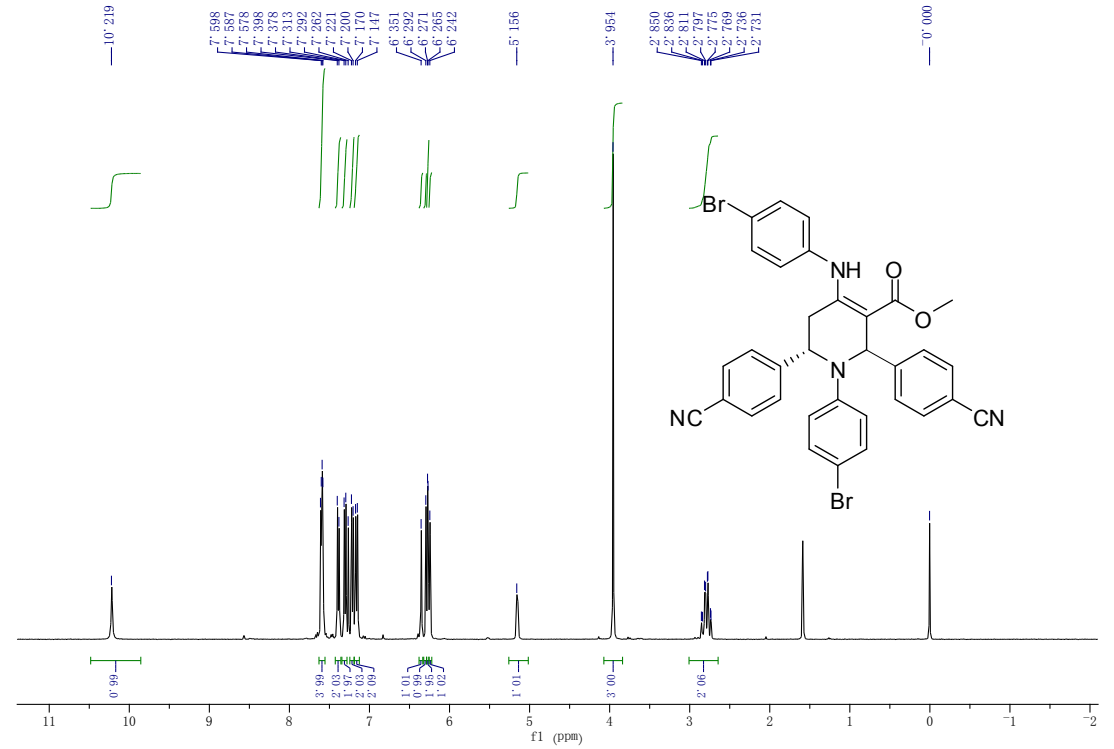
114.503
110.406
101.860
77.317
77.000
76.682
57.967
56.885
51.906
36.631
Br
NH
O
O
N
Br
f1 (ppm)

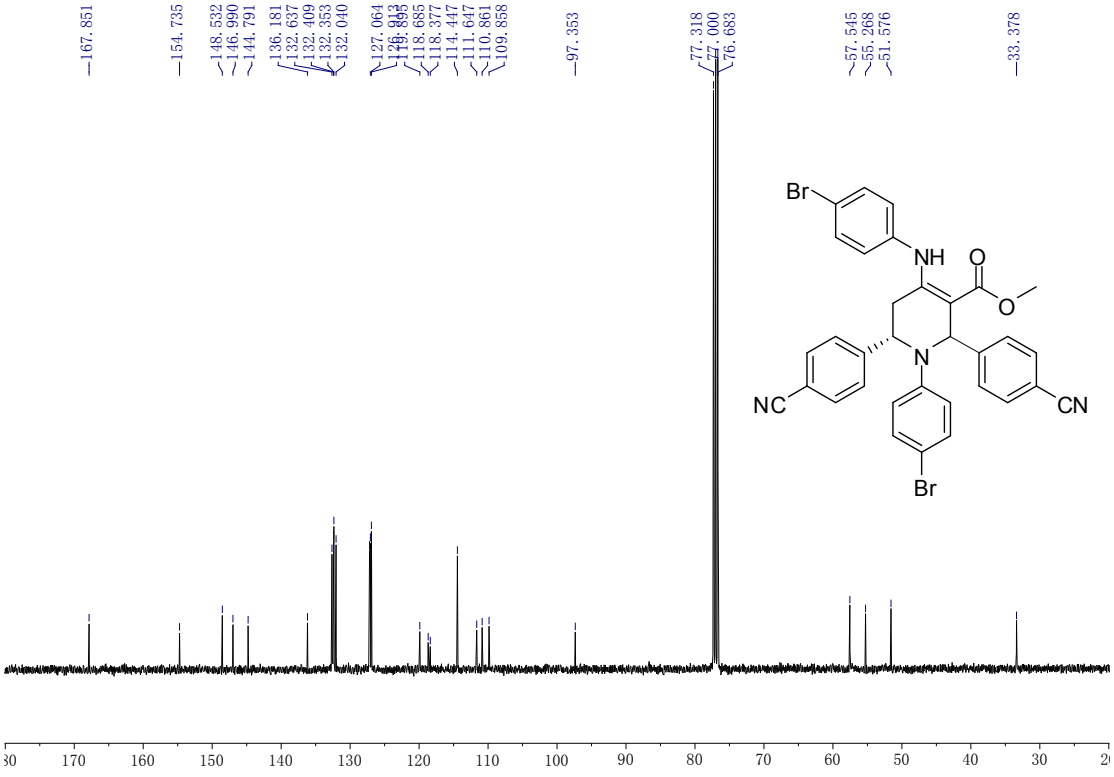
(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4h)



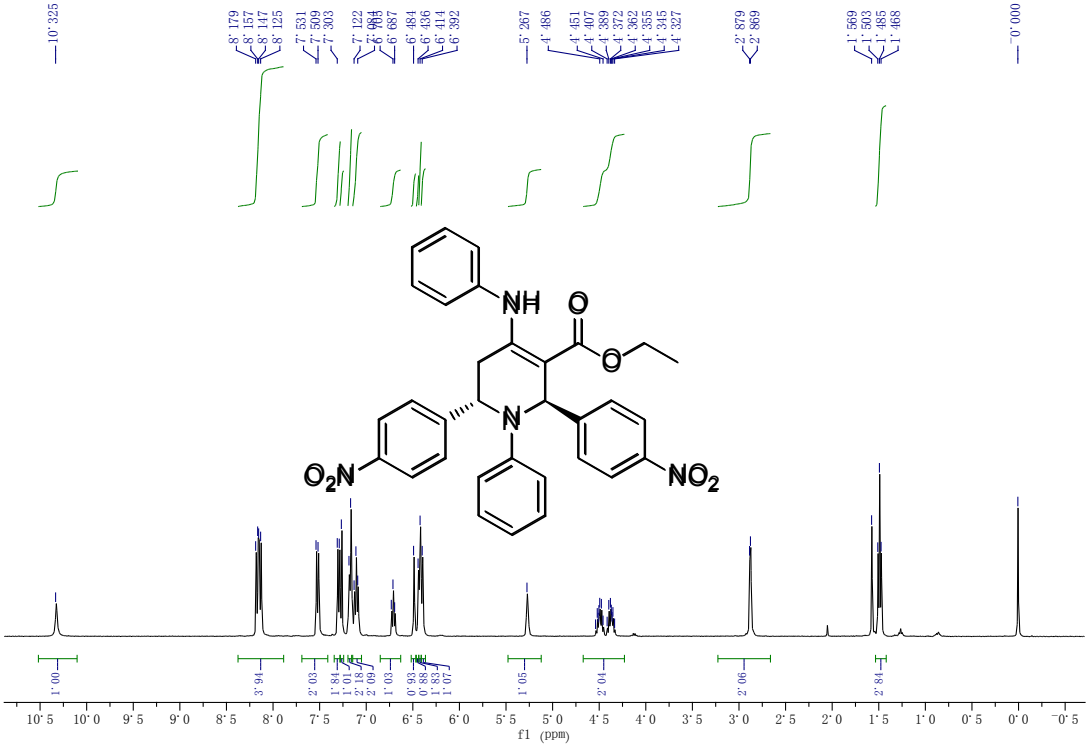


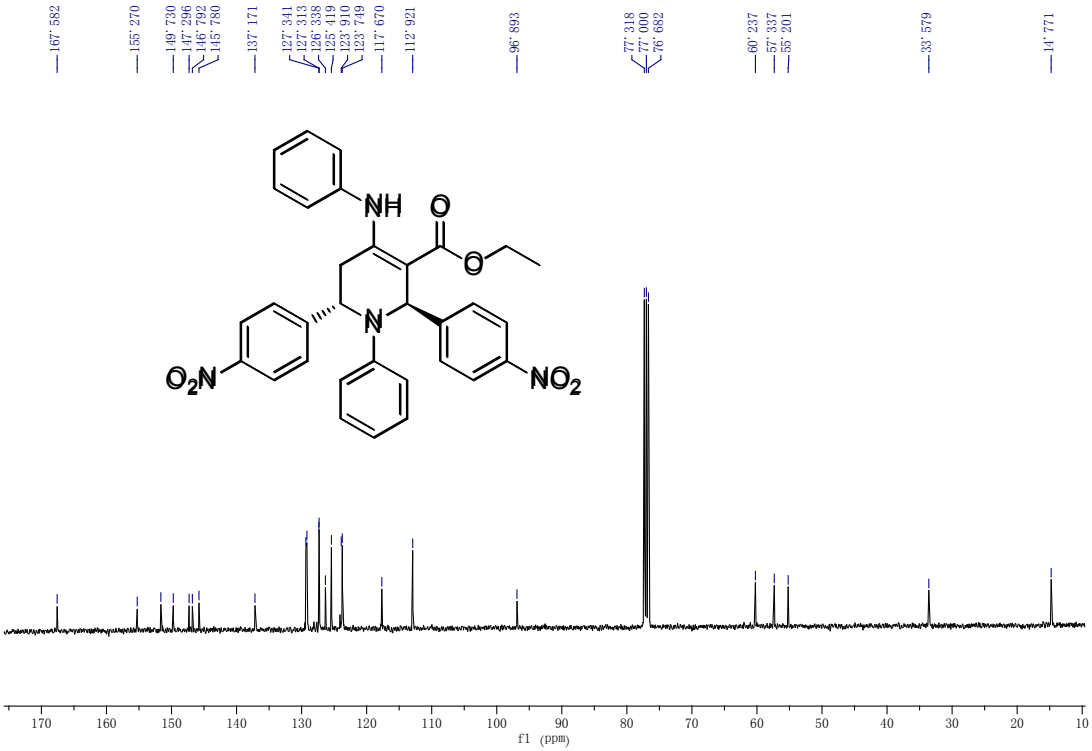
(2R,6S)-methyl1-(4-bromophenyl)-4-(4-bromophenylamino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4i)



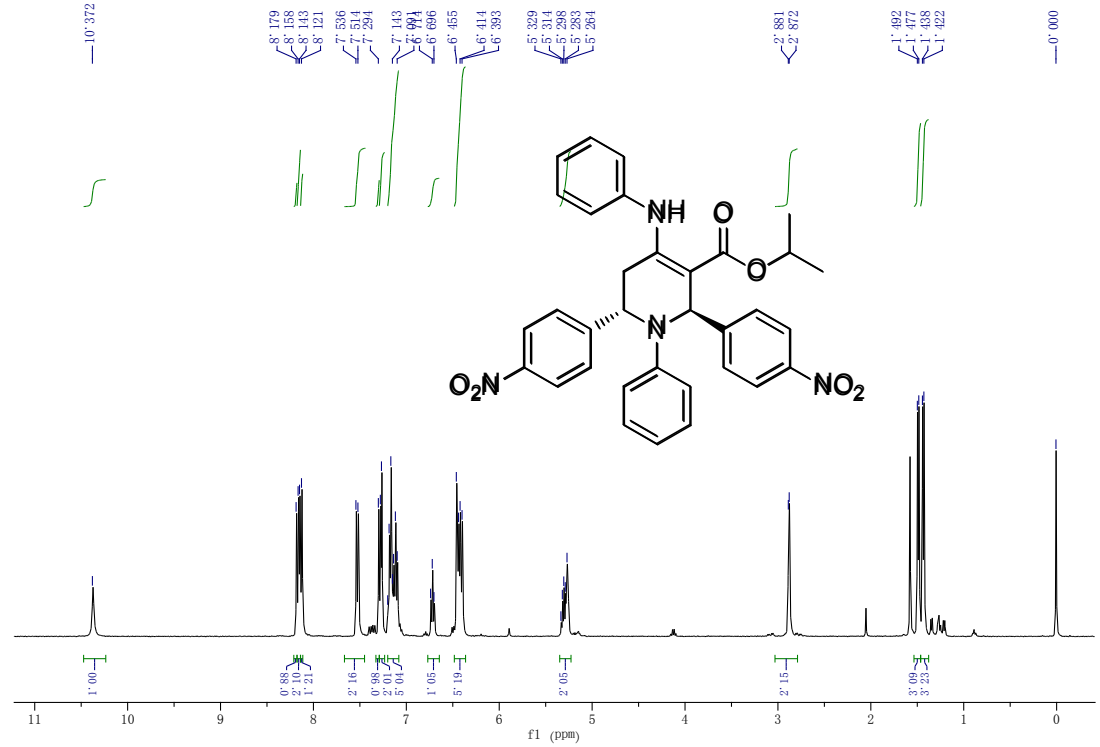


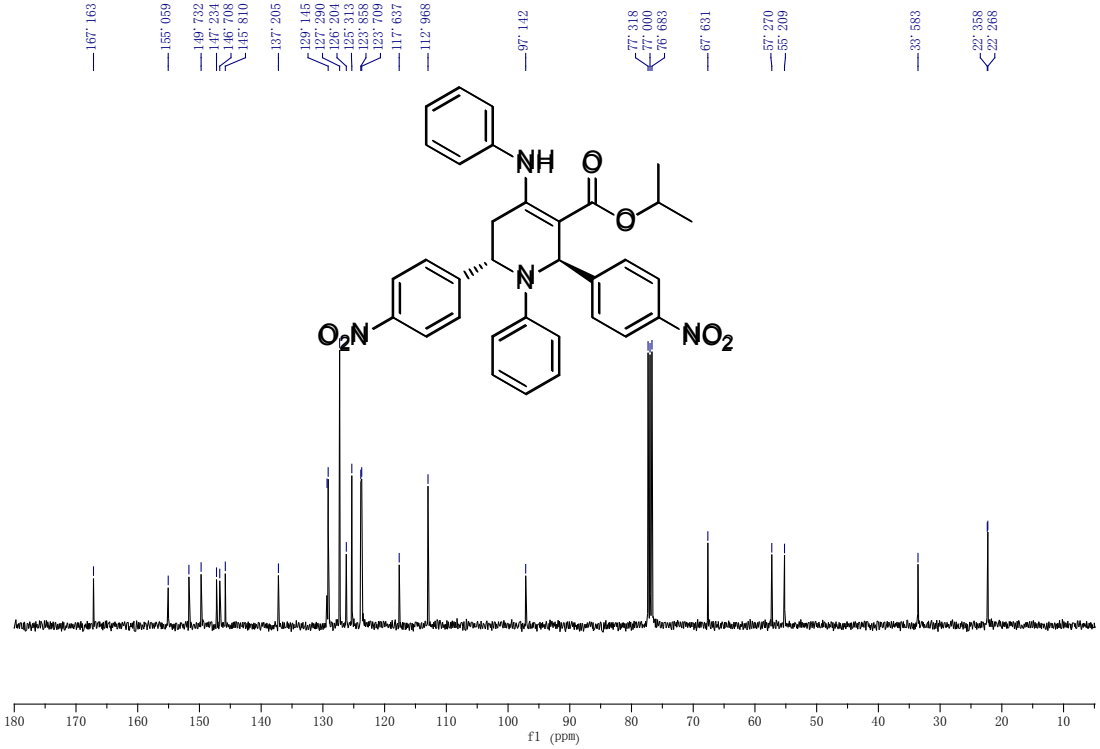
(2R,6S)-ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4j)



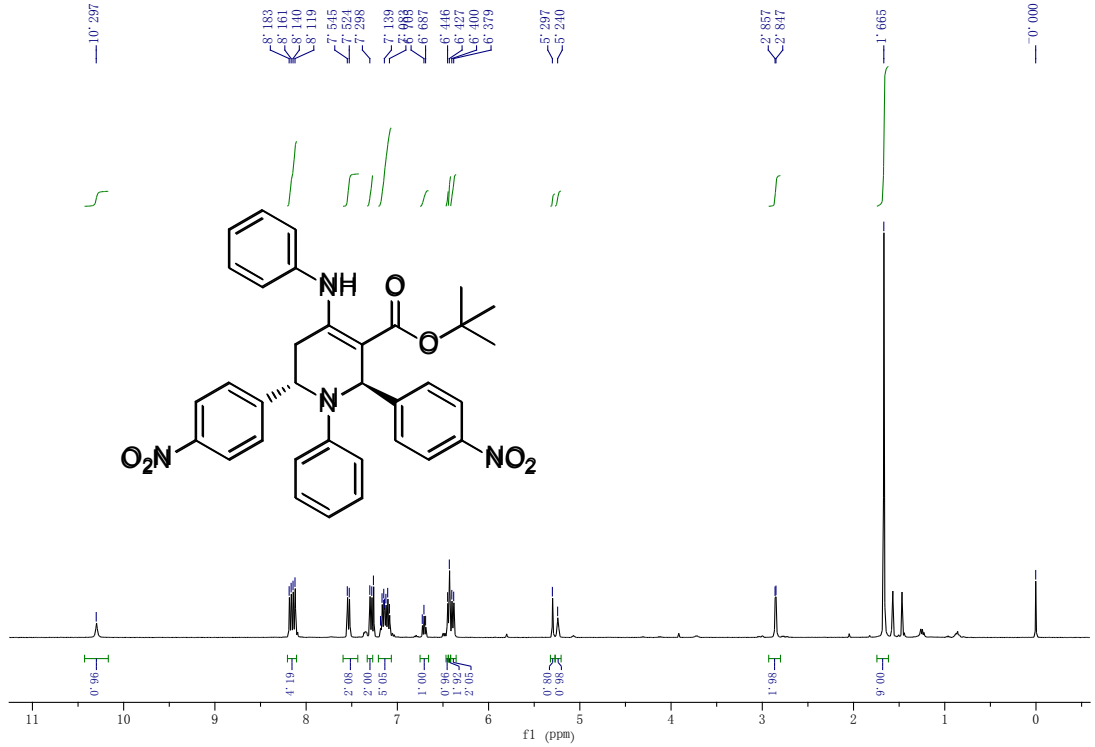


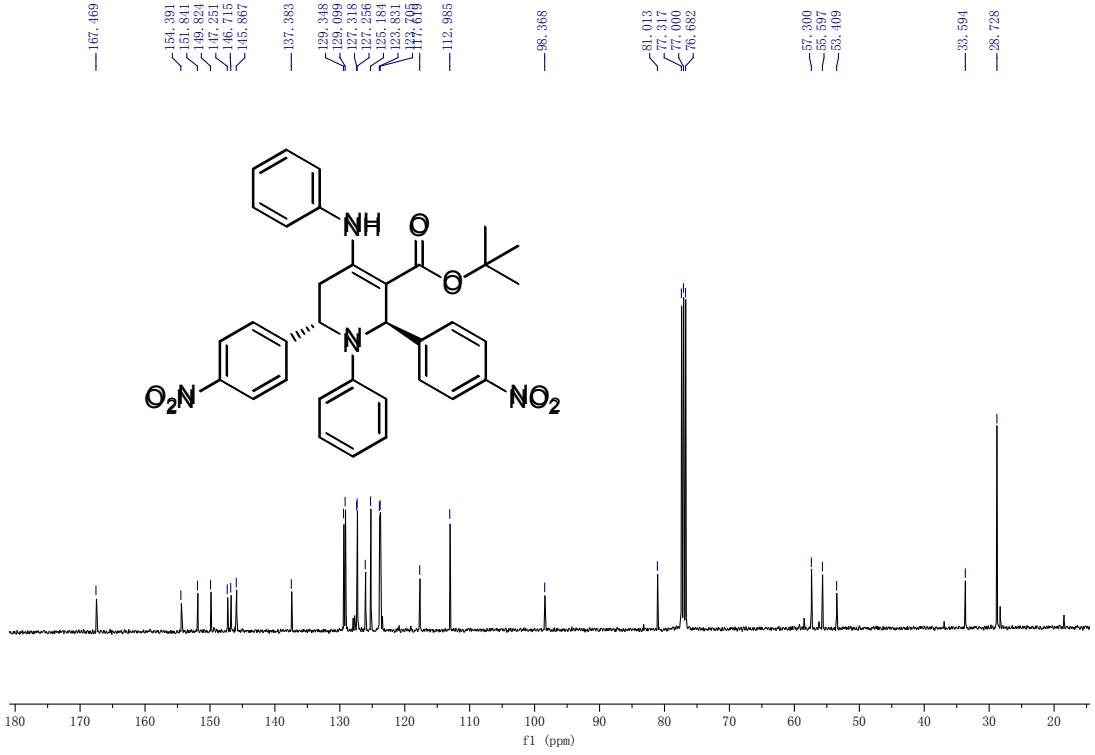
(2R,6S)-isopropyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4k)



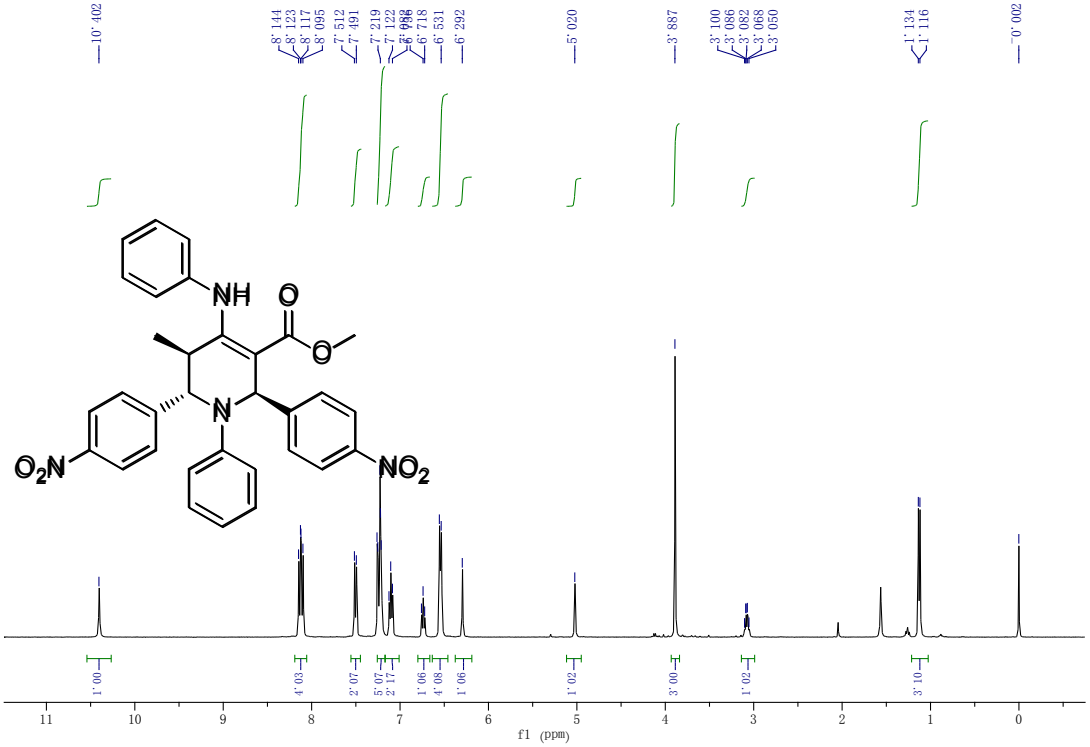


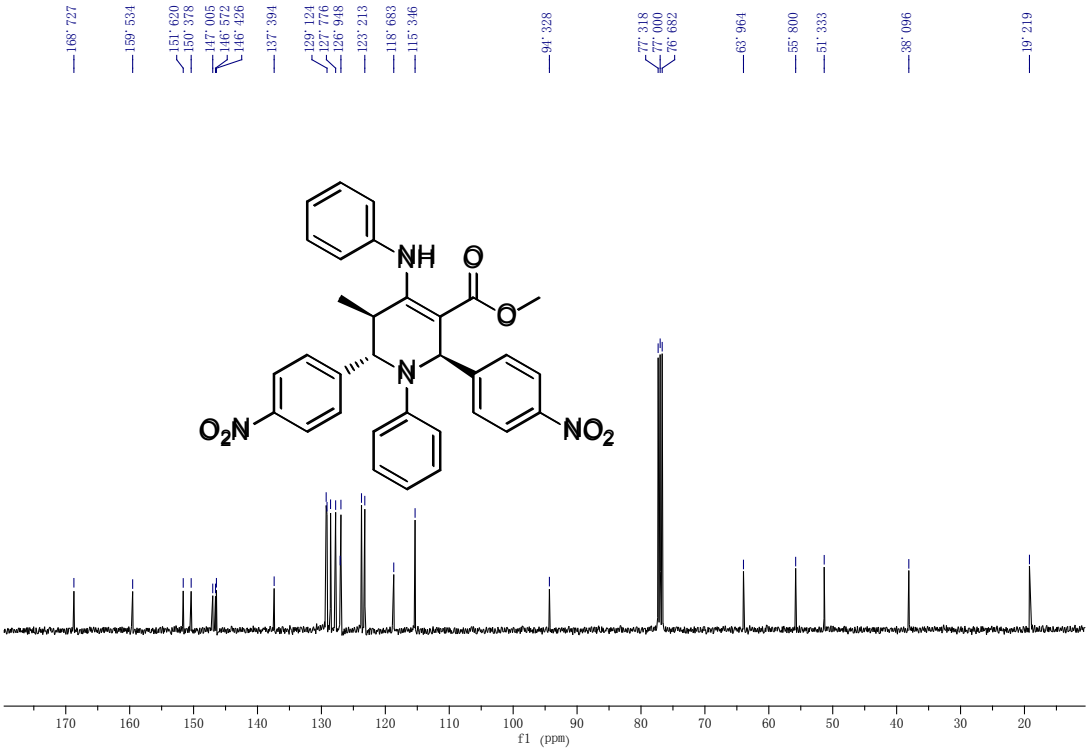
(2R,6S)-tert-butyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4l)



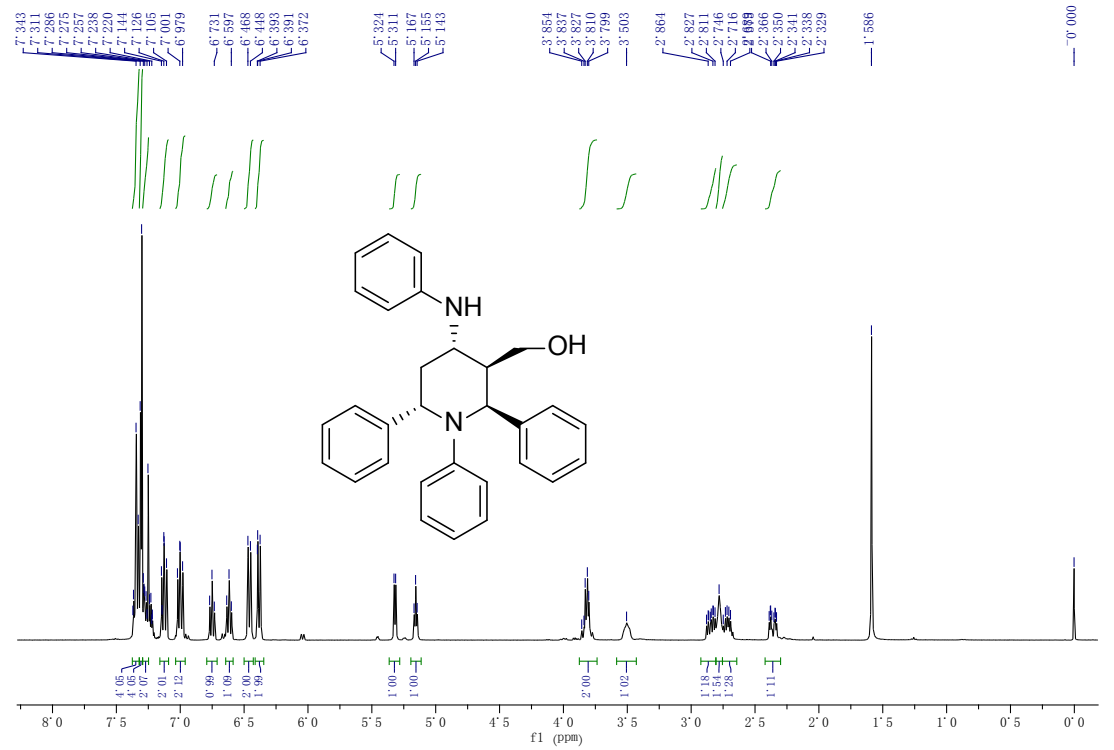


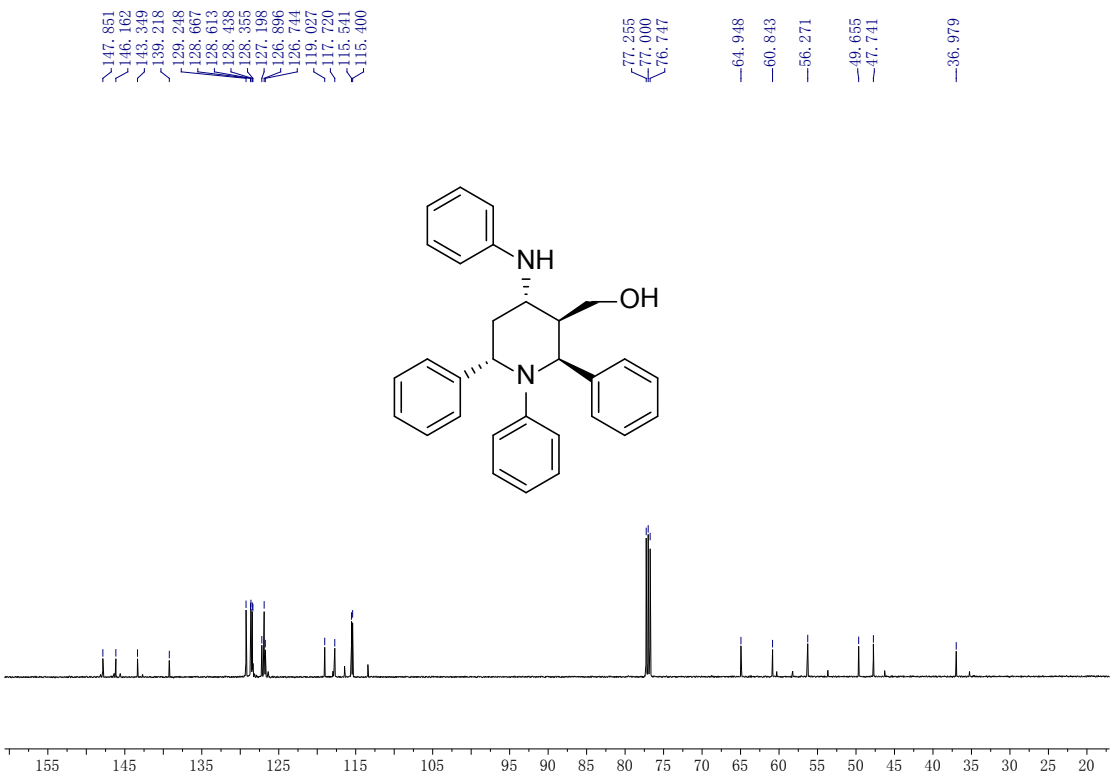
(2R,5R,6S)-methyl 5-methyl-2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4m)





((2S, 3R, 4S, 6S)-1,2,6-triphenyl-4-(phenylamino)piperidin-3-yl)methanol (7)





5. Absolute configuration assignments and a proposed mechanism

The crystal structure of enantiopure **4l** was obtained (Figure 1), and a single crystal X-ray analysis determined its configuration as (2*R*, 6*S*). CCDC 885330 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data_request/cif.

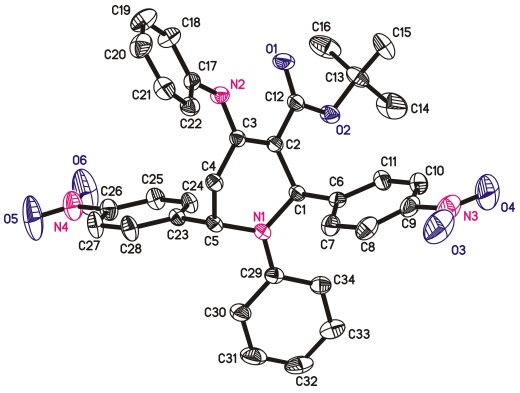
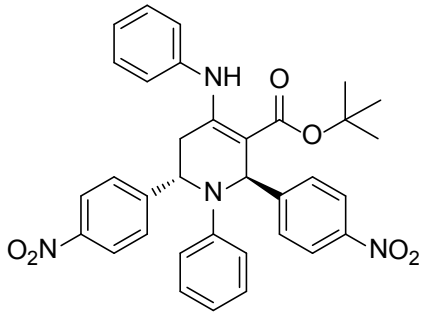


Figure 1. X-ray crystal structure of **4l**

(2*R*,6*S*)-tert-butyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4l)



Molecular structure of **4l**

The absolute configuration of product **7** was assigned by X-ray crystallographic analysis of *rac*-7 (Figure 2), which was prepared from *rac*-**4e** with Na/*i*-PrOH. The relative stereochemistry of *rac*-7 was assigned as (2,3-*cis*, 4,6-*cis*, 3,4-*trans*). As no reaction occurred at the stereogenic center in **4e** with (2*R*, 6*S*) during its transformation into **7**, thus product **7** was assigned as (2*S*, 3*R*, 4*S*, 6*S*). CCDC 898709 contains the supplementary crystallographic data for this compound *rac*-**7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/ data_request/cif.

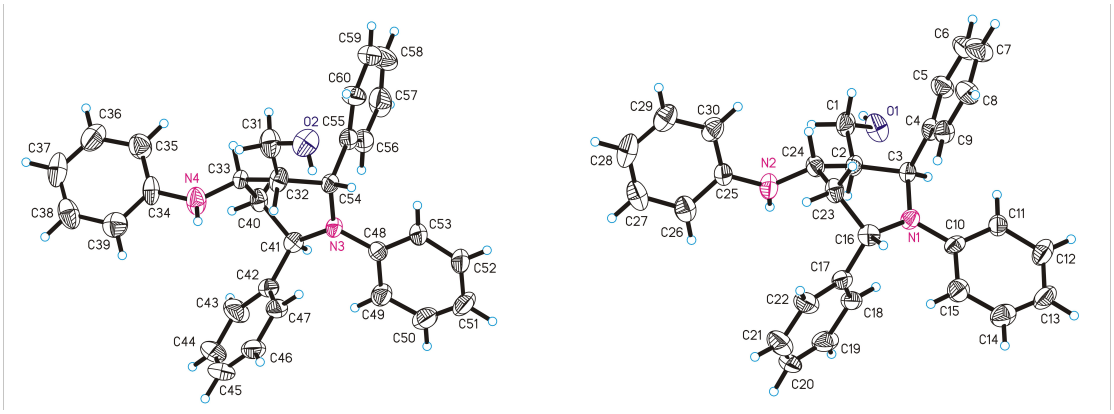
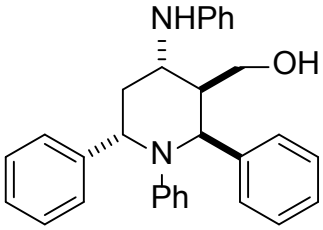
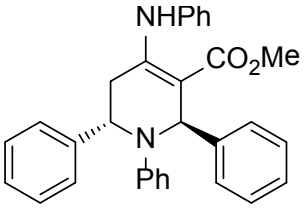


Figure 2. X-ray crystal structure of *rac*-**7**



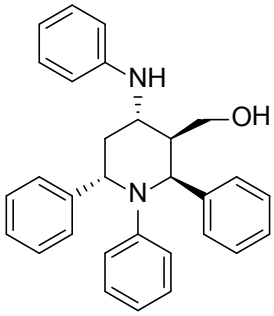
Molecular structure of *rac*-**7**

(2*R*,6*S*)-methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4e)



Molecular structure of **4e**

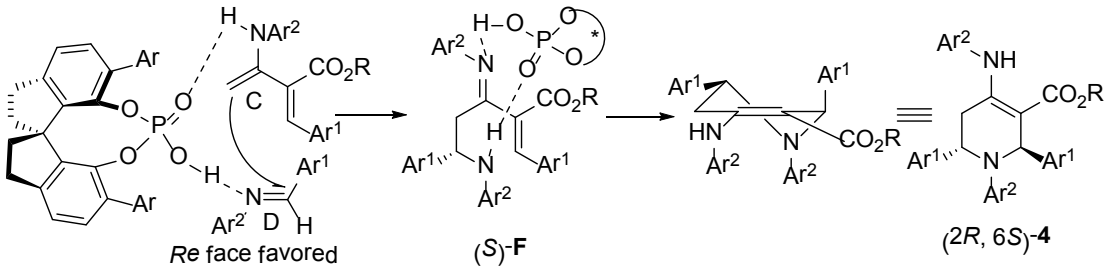
((2*S*, 3*R*, 4*S*, 6*S*)-1,2,6-triphenyl-4-(phenylamino)piperidin-3-yl)methanol (7)



Molecular structure of **7**

A proposed mechanism for the observed enantioselectivity

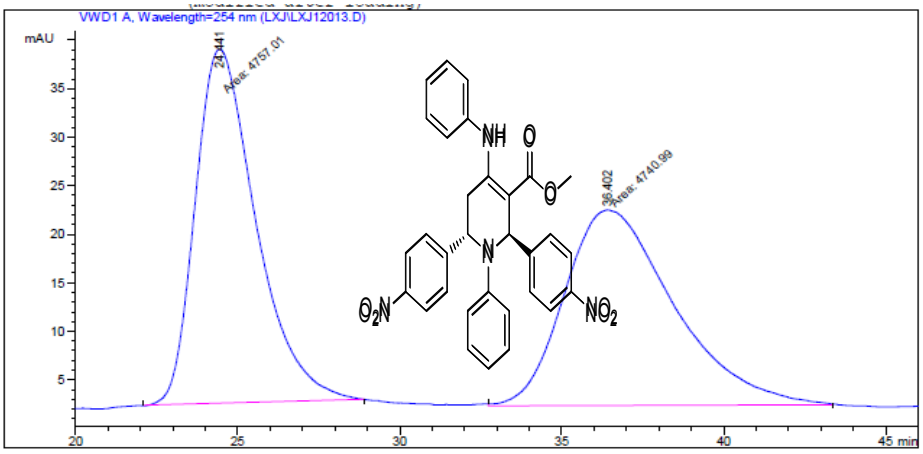
The exact mechanism of the reaction is not known at this stage; however a proposed mechanism for the observed enantioselectivity may involve the activation through hydrogen bonding between SPINOL-PA and substrates. We propose a possible model for the asymmetric induction of our catalytic system as shown in Scheme I. Phosphoric acid (S)-**5a** as a bifunctional catalyst combines two intermediates **C** and **D** through hydrogen bonding. In this model, **C** attacks imine **D** from the *Re* face preferentially, leading to a *S*-configuration adduct **F**. The resulting intermediate **F** undergoes an intramolecular 1,4-addition reaction via the sterically less congested conformer would afford the observed 2,6-trans-substituted tetrahydronpyridine **4** with defined absolute configuration (2*R*, 6*S*).



Scheme I

6. HPLC spectra of products

(2R,6S)-methyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4a)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  24.441 MM    2.1740 4757.00977   36.46817  50.0843
   2  36.402 MM    3.9163 4740.99023   20.17611  49.9157
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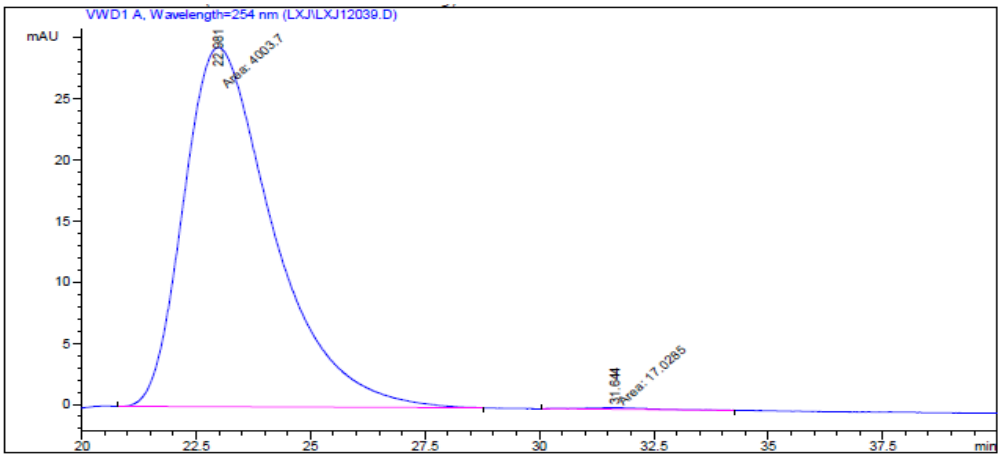


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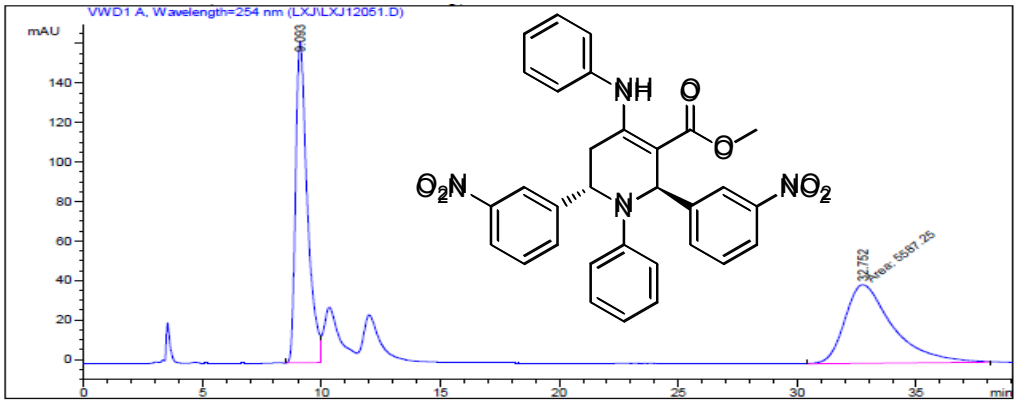
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  22.981 MM    2.2680 4003.69824   29.42196  99.5765
   2  31.644 MM    1.9381   17.02847 1.46432e-1   0.4235
```

(2R,6S)-methyl 2,6-bis(3-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine

-3-carboxylate (4b)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   9.093 PV    0.5076 5585.54102  162.98126  49.9923
   2  32.752 MM    2.3346 5587.25195   39.88652  50.0077
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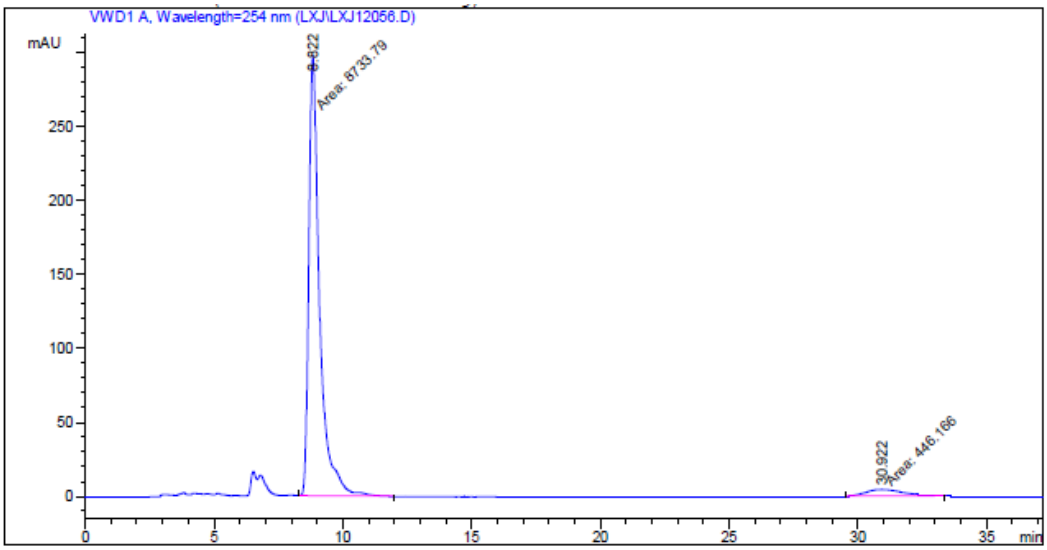


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.822 MM    0.4900 8733.79395  297.04550  95.1398
   2  30.922 MM    1.6687  446.16611    4.45630   4.8602
```
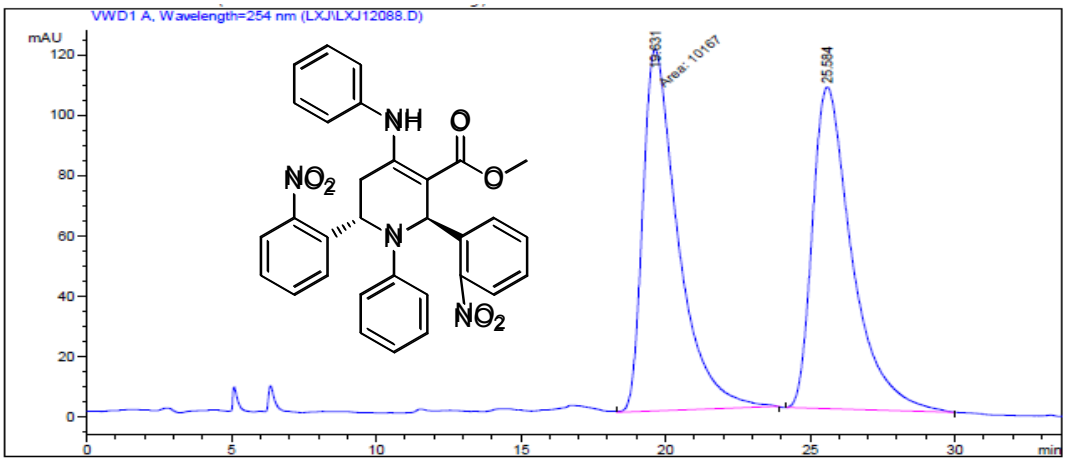

(2R,6S)-methyl 2,6-bis(2-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-

3-carboxylate (4c)

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]      [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  19.631 MM    1.4113 1.01670e4   120.06236  50.0593
   2  25.584 BB    1.3867 1.01429e4   106.60125  49.9407
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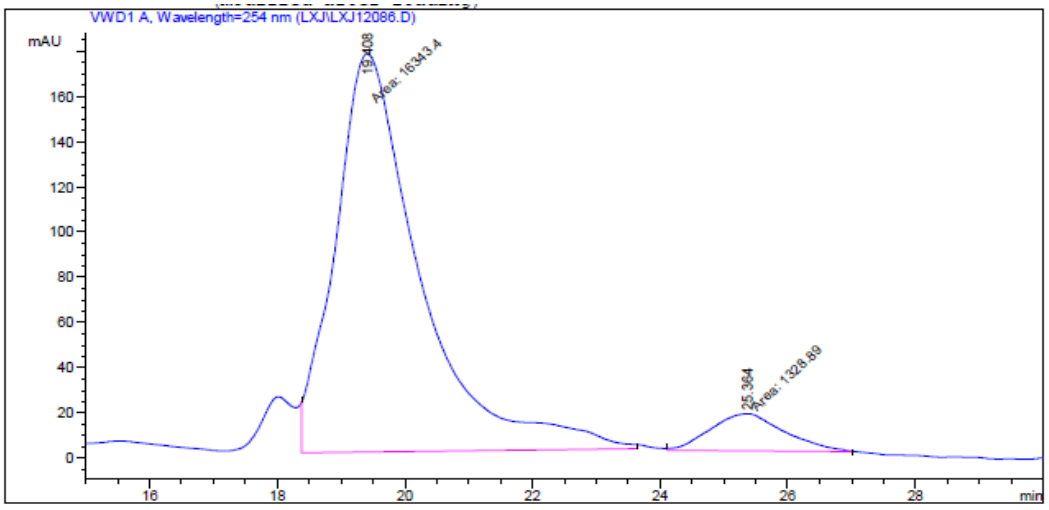


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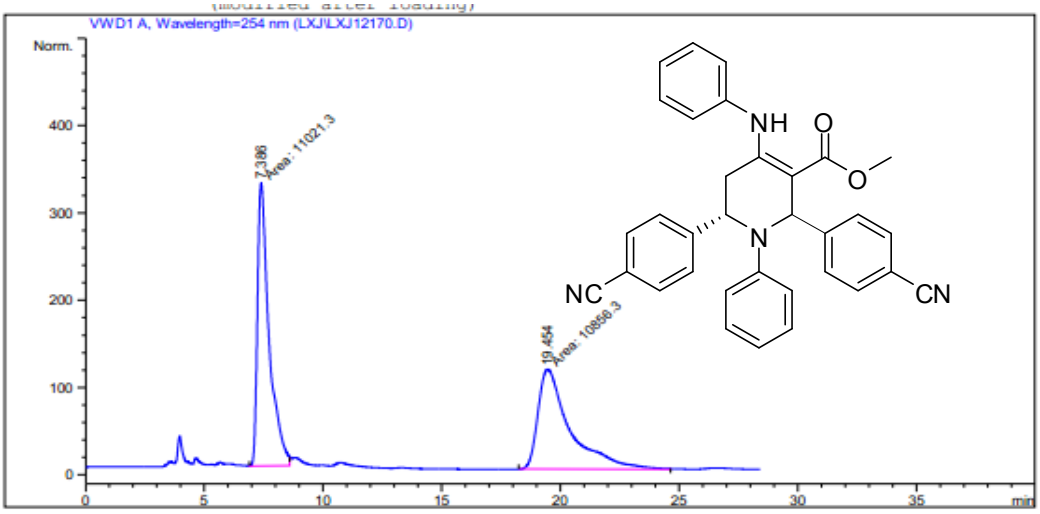
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]      [min]  mAU   *s    [mAU   ]       %
----|-------|----|-------|----------|----------|--------|
   1  19.408 MM    1.5447 1.63434e4   176.33850  92.4804
   2  25.364 MM    1.3404 1328.88916   16.52313   7.5196
```

(2R,6S)-methyl2,6-bis(4-cyanophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-

tetrahydropyridine-3-carboxylate (4d)



Area Percent Report

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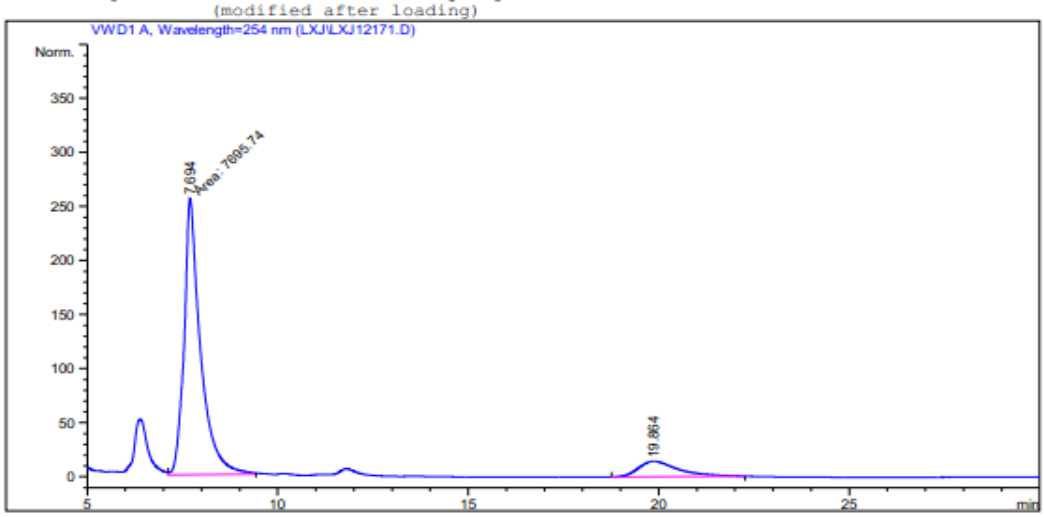
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.386	MM	0.5666	1.10213e4	324.19376	50.3771
2	19.454	MM	1.5803	1.08563e4	114.49797	49.6229

(modified after loading)



Area Percent Report

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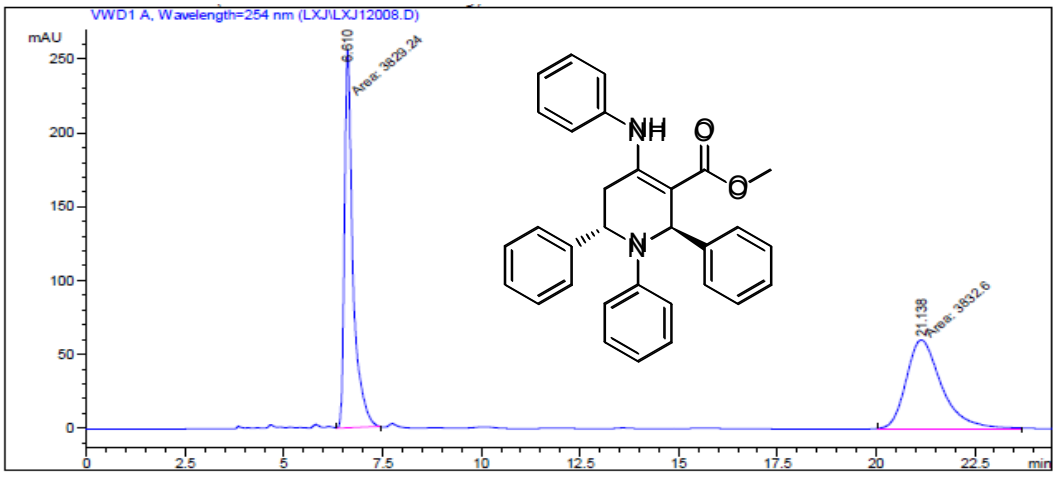
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.694	MM	0.5015	7695.73926	255.75510	87.9067
2	19.864	BB	1.0631	1058.70447	14.32628	12.0933

(2R,6S)-methyl 1,2,6-triphenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4e)

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Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.610 MM    0.2491 3829.24463  256.21384  49.9781
   2  21.138 MM    1.0567 3832.60303   60.44820  50.0219
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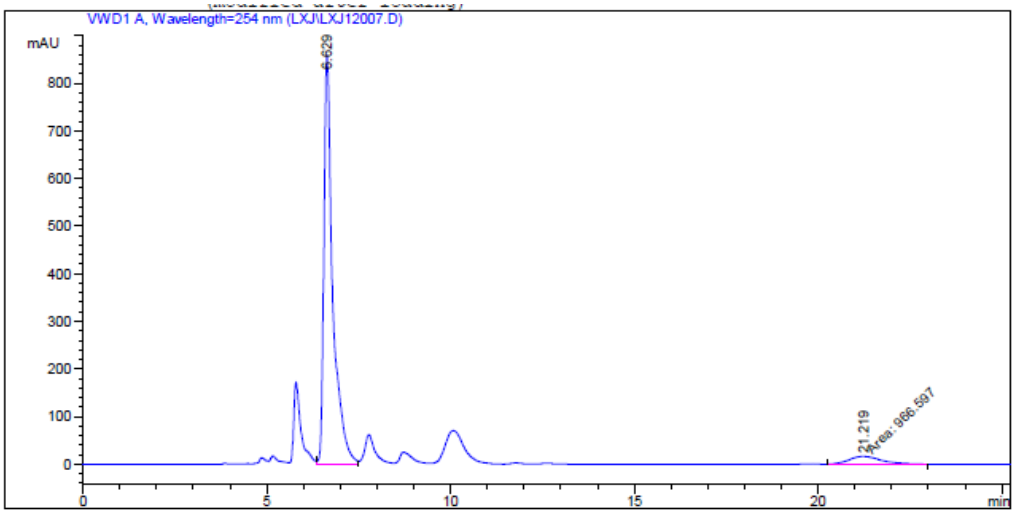


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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.629 VV    0.2425 1.45161e4   858.21716  93.7569
   2  21.219 MM    0.9938  966.59680   16.21015   6.2431
```
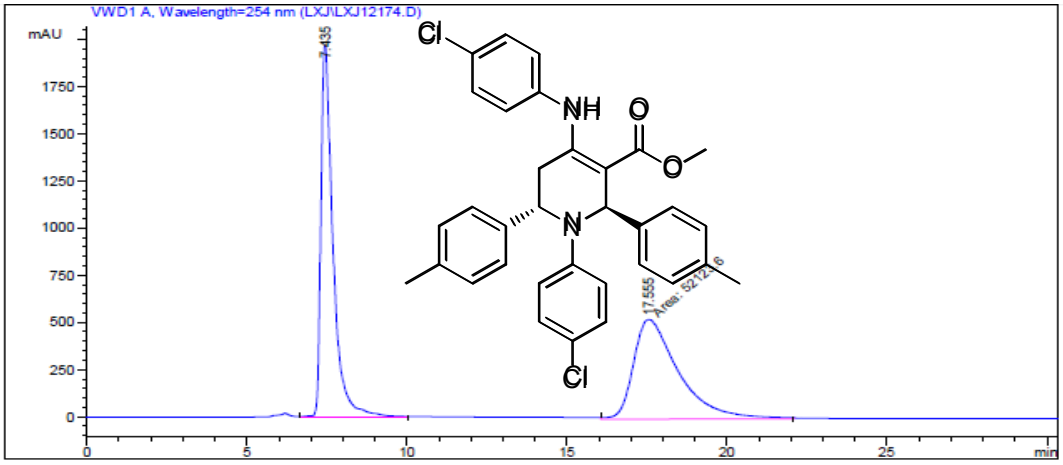

(2R,6S)-methyl 1-(4-chlorophenyl)-4-((4-chlorophenyl)amino)-2,6-di-p-tolyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4f)

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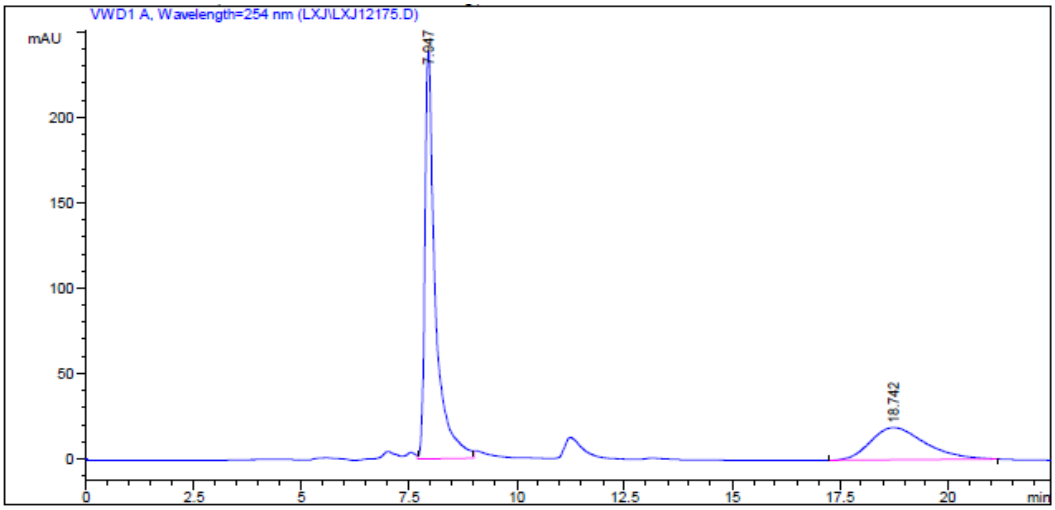
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.435 VB    0.3608 5.20428e4  1968.97961  49.9612
   2  17.555 MM    1.6412 5.21236e4   529.31439  50.0388
```

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.947 VB    0.2387 4056.69287  239.10611  70.6314
   2  18.742 BB    1.1295 1686.78027   18.98994  29.3686
```
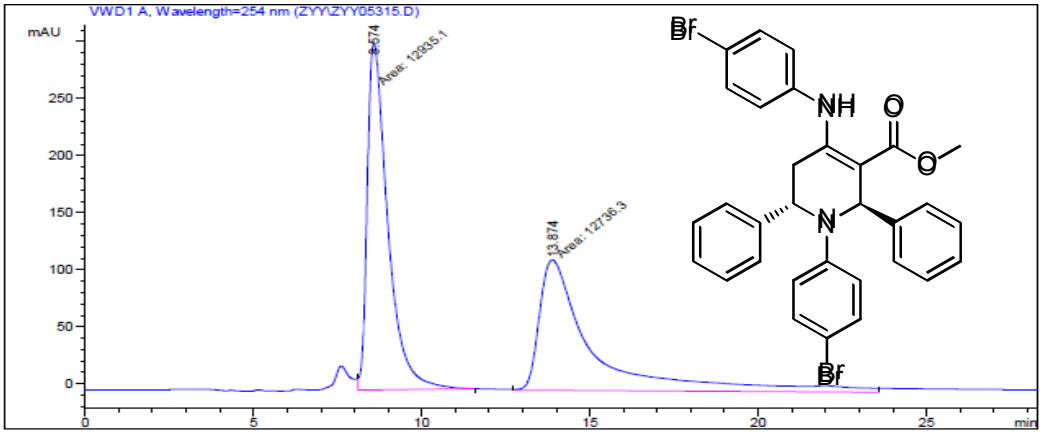

(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-diphenyl-1,2,5,6-tetrahydropyridine-3-carboxylate (4g)

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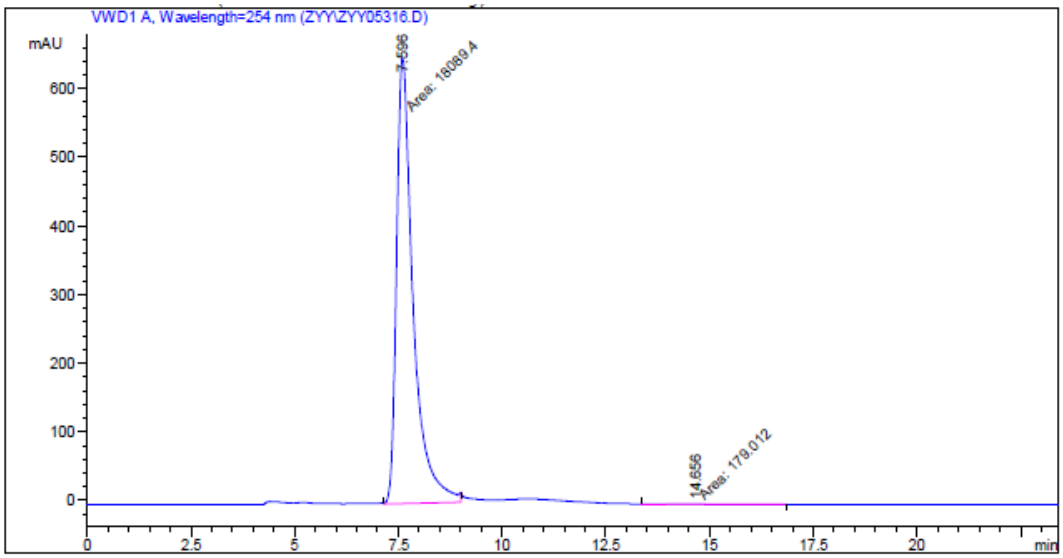
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.574 FM    0.7083 1.29351e4   304.37094  50.3872
   2  13.874 MM    1.8555 1.27363e4   114.40390  49.6128
```

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Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]      [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.596 MM    0.4635 1.80894e4   650.40875  99.0201
   2  14.656 MM    2.4590  179.01154    1.21332   0.9799
```
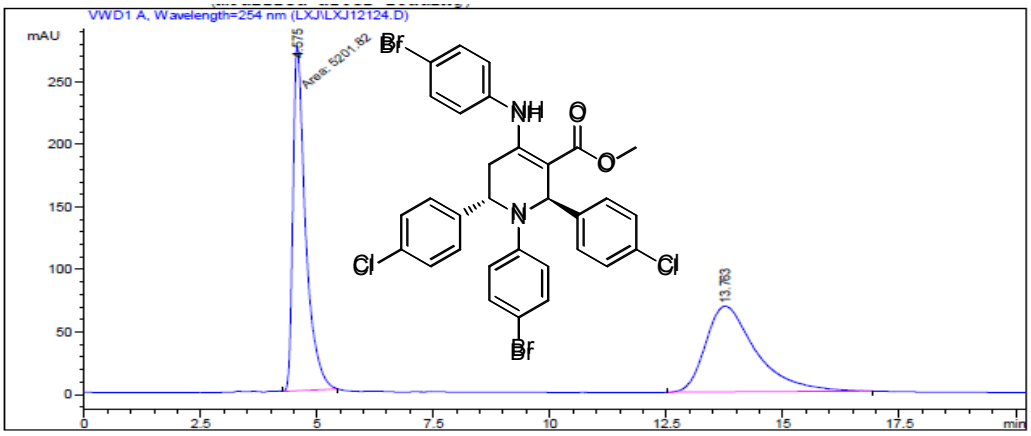

(2R,6S)-methyl 1-(4-bromophenyl)-4-((4-bromophenyl)amino)-2,6-bis(4-chlorophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4h)

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   4.575 MM    0.3147 5201.82373  275.53149  50.0930
   2  13.763 BB    1.1066 5182.50000   68.63498  49.9070
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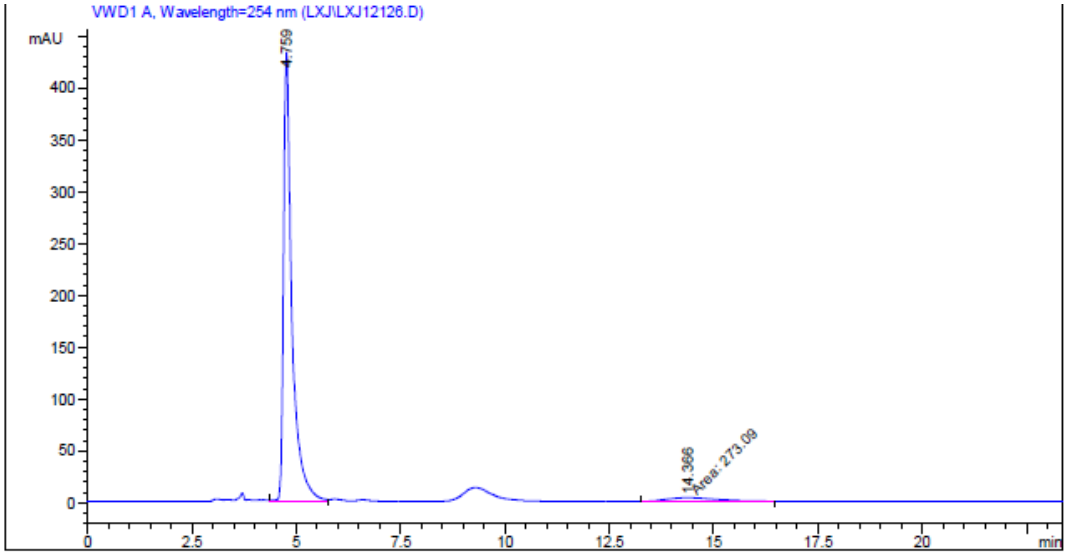


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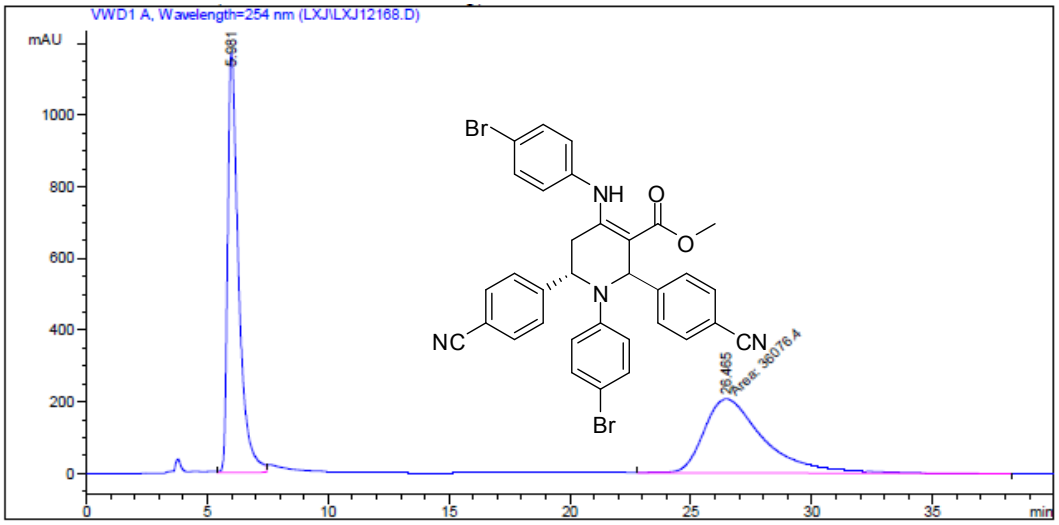
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height      Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   4.759 VV    0.2008 6050.39502  433.15567  95.6813
   2  14.366 MM    1.3179  273.08963    3.45356   4.3187
```

(2R,6S)-methyl1-(4-bromophenyl)-4-(4-bromophenylamino)-2,6-bis(4-cyanophenyl)-1,2,5,6-tetrahydropyridine-3-carboxylate (4i)

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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   5.981 VV    0.4615 3.70410e4  1173.23401  50.6596
   2  26.465 MM    2.8996 3.60764e4   207.36261  49.3404
```

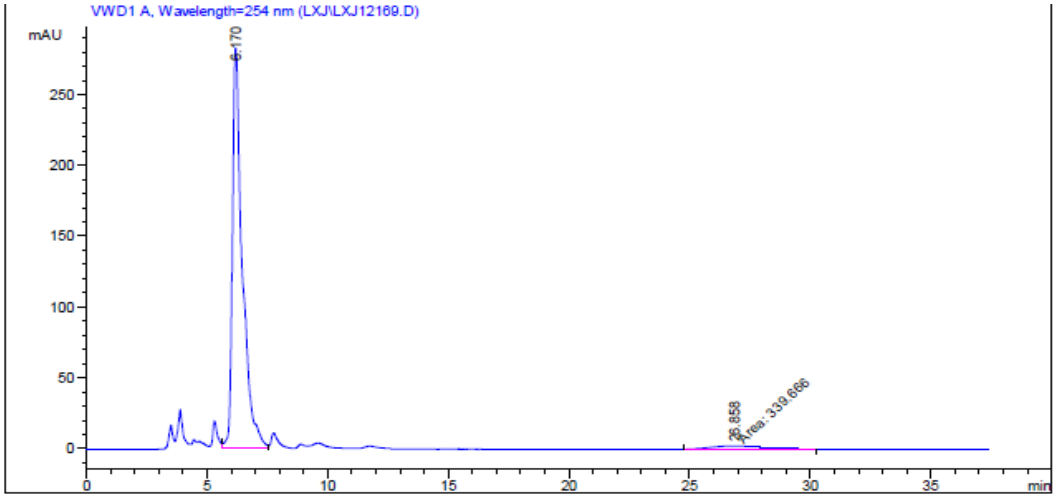


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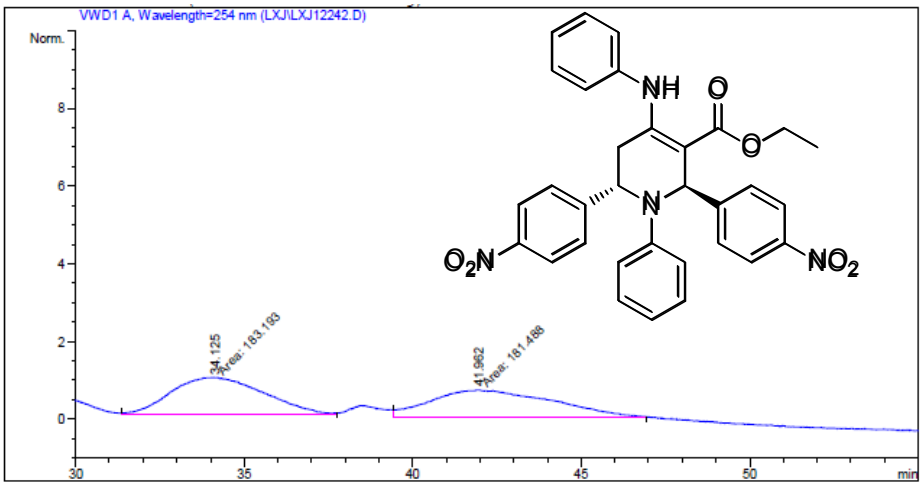
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   6.170 VV    0.4065 8144.86621  283.48550  95.9966
   2  26.858 MM    2.4583  339.66638    2.30281   4.0034
```

(2R,6S)-ethyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine -3-carboxylate (4j)

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                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  34.125 MM    3.2095  183.19328 9.51314e-1  50.2338
   2  41.962 MM    4.2533  181.48778 7.11157e-1  49.7662
```
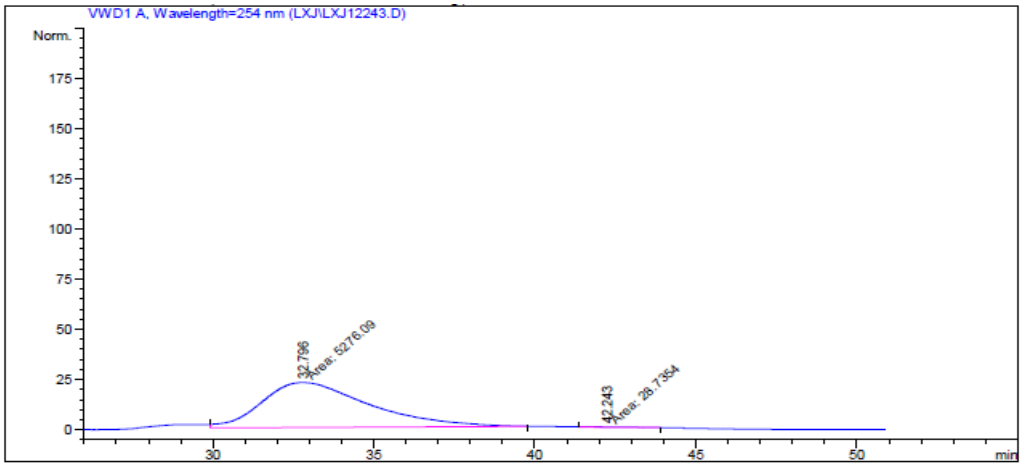
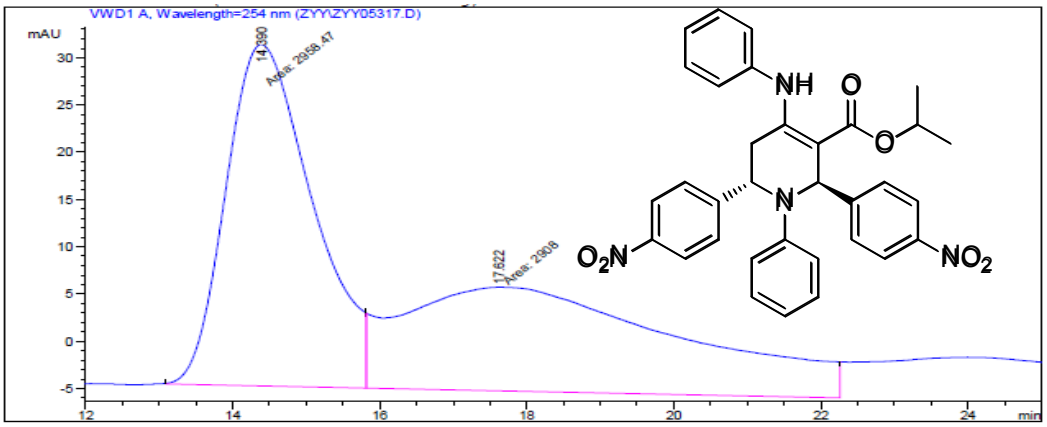
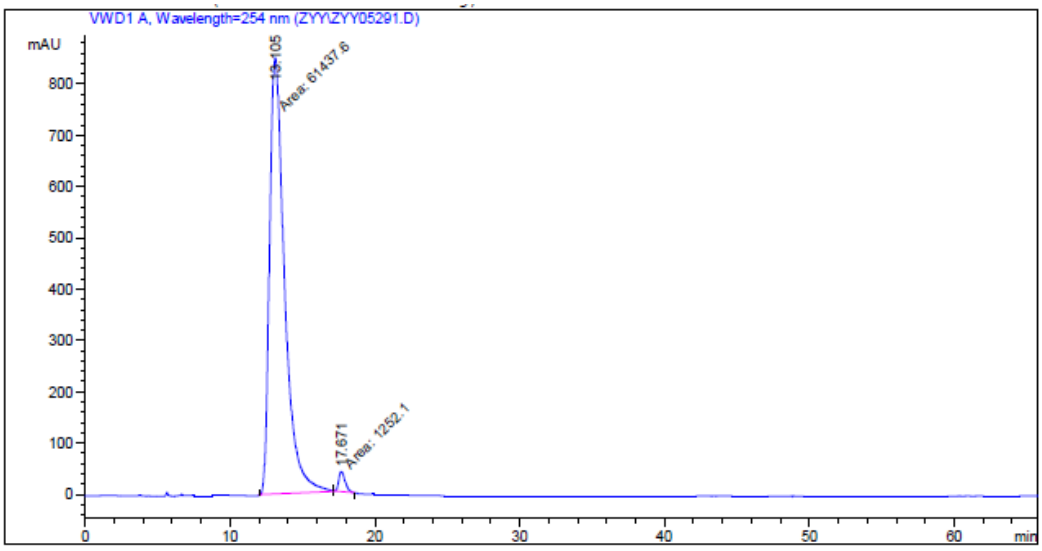




```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  32.796 MM    3.8940 5276.08594   22.58231  99.4583
   2  42.243 MM    2.1168   28.73544 2.26248e-1   0.5417
```

(2R,6S)-isopropyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4k)

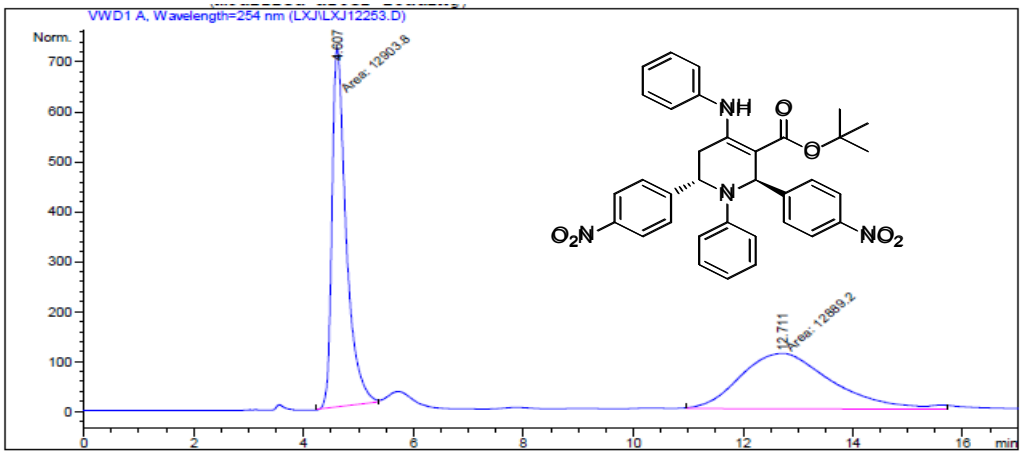



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  14.390 MF    1.3646 2958.46606   36.13251  50.4301
   2  17.622 FM    4.4071 2907.99976   10.99738  49.5699
```

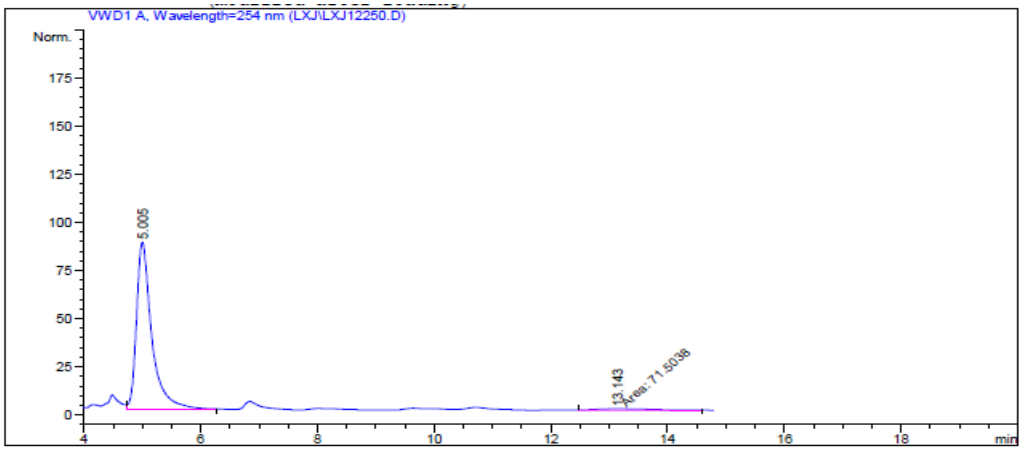



```
=====================================================================
                      Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  13.105 MM    1.2035 6.14376e4   850.81238  98.0027
   2  17.671 MM    0.5275 1252.09668   39.55929   1.9973
```

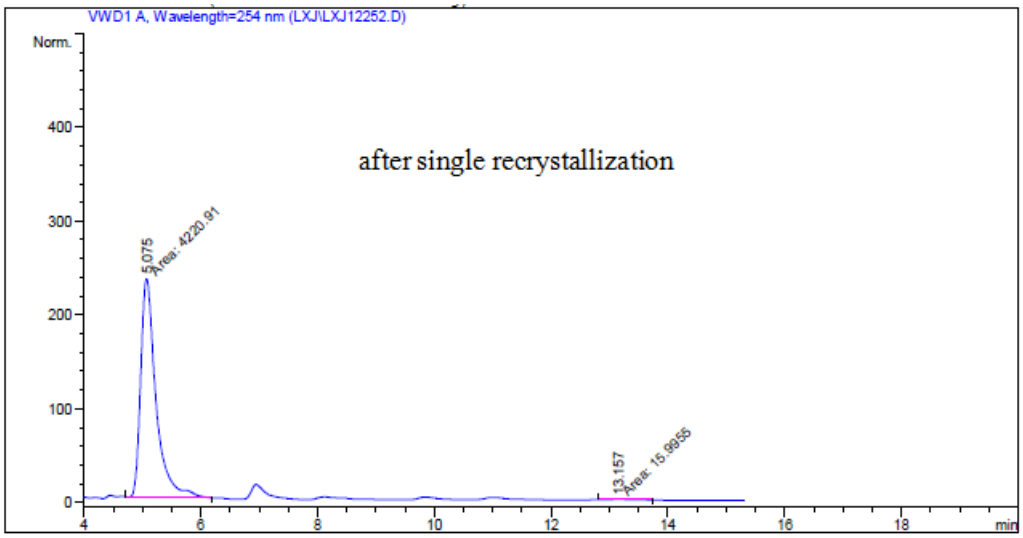
(2R,6S)-tert-butyl 2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4l)




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|--------|----------|----------|--------|
   1   4.607 MM    0.2995 1.29038e4   718.08630  50.0283
   2  12.711 MM    1.9377 1.28892e4   110.86466  49.9717
```




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|--------|----------|----------|--------|
   1   5.005 VB    0.2727 1623.80005   87.16333  95.7822
   2  13.143 MM    1.3729   71.50379 8.68013e-1   4.2178
```

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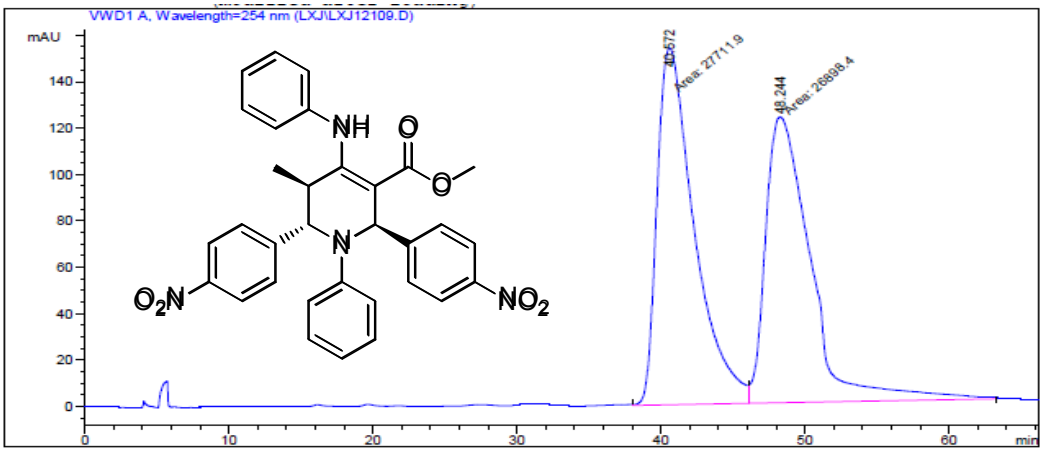
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   5.075 MM    0.3016 4220.91357  233.23302  99.6225
   2  13.157 MM    0.5078   15.99546 5.24993e-1   0.3775
```

(2R,5R,6S)-methyl 5-methyl-2,6-bis(4-nitrophenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (4m)

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================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  40.572 MF    3.0021 2.77119e4   153.84604  50.7449
   2  48.244 FM    3.6340 2.68984e4   123.36295  49.2551
```
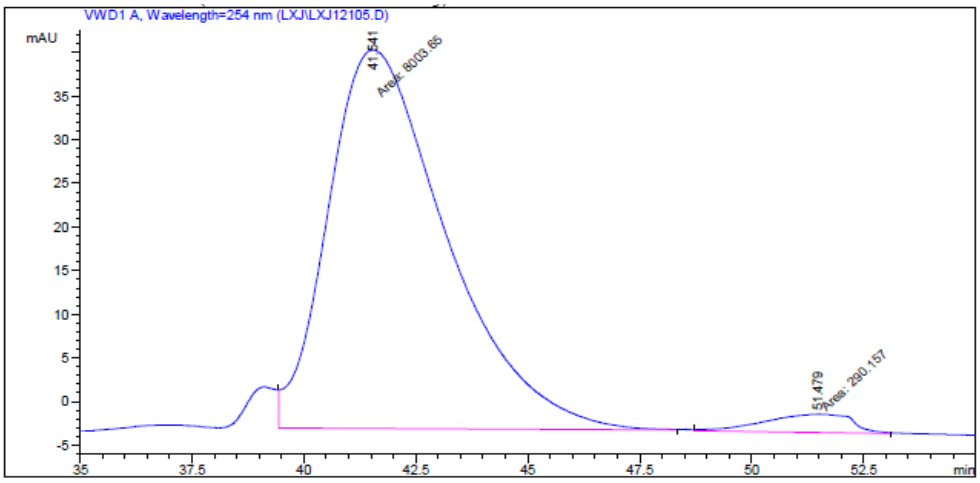
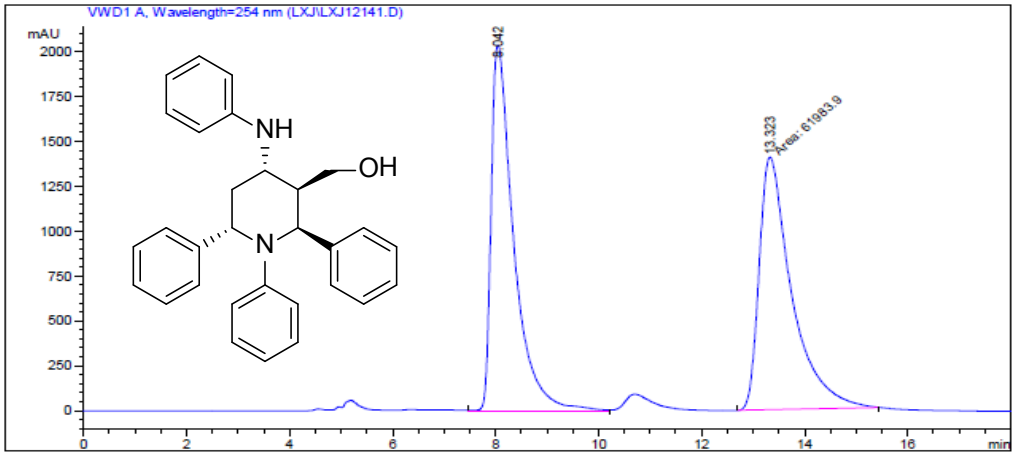
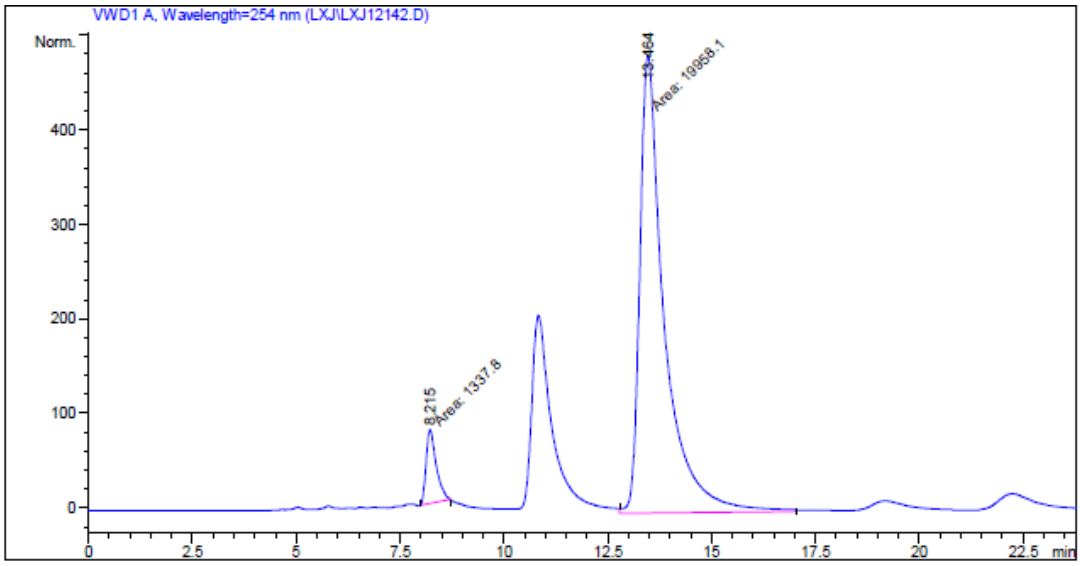




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  41.541 FM    3.0704 8003.65137   43.44580  96.5015
   2  51.479 MM    2.2970  290.15692    2.10534   3.4985
```

((2S,3R,4S,6S)-1,2,6-triphenyl-4-(phenylamino)piperidin-3-yl)methanol (7)




```
=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1   8.042 VV    0.4421 6.20321e4  2039.98657  50.0195
   2  13.323 MM    0.7335 6.19839e4  1408.41968  49.9805
```




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s    [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   8.215 MM    0.2854 1337.80103   78.12661   6.2820
   2  13.464 MM    0.6879 1.99581e4   483.57904  93.7180
```