Evolution of Chiral Lewis Basic *N*-Formamide as Highly Effective Organocatalyst for Asymmetric Reduction of Both Ketones and Ketimines with an Unprecedented Substrate Scope

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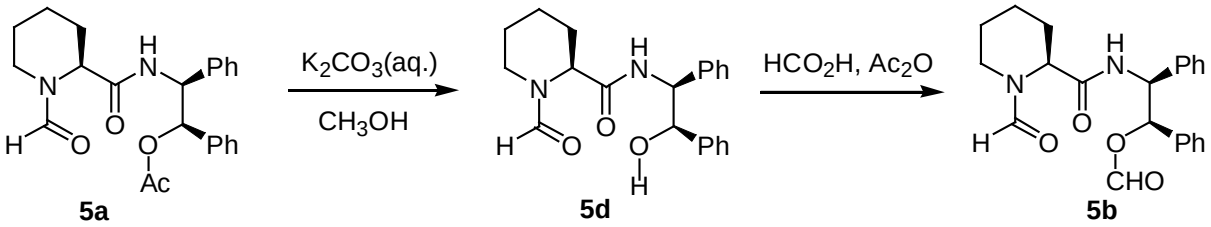
(Supporting Information)

General: All starting materials were of the highest commercially available grade and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography using silica gel HSGF254 plates. Flash chromatography was performed using silica gel HG/T2354-92. ^{1}H - and ^{13}C NMR (300 or 600 and 75 or 150 MHz, respectively) spectra were recorded in $CDCl_3$ or DMSO-d_6. ^{1}H NMR chemical shifts are reported in ppm (**δ**) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, **δ** 7.26 ppm; DMSO-d_6, **δ** 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, **δ** 77.0 ppm; DMSO-d_6, **δ** 39.7 ppm). ESIMS spectra were recorded on BioTOF Q. HPLC analyses were performed on PerkinElmer (Series 200 UV/VIS Detector and Series 200 Pump). Chiralpak OD-H, AD-H and OJ-H columns were purchased from Daicel Chemical Industries, LTD. All enantiomer ratios have been controlled by co-injections of the pure sample with the racemic substrates. All imines were prepared according to the general procedure.[1] Alcohols **7a-m**[2] and amines **9a-i**[1] are all known compounds and their ^{1}H NMR data matched the literature data. Chemical yields refer to pure isolated substances.

[1] Wang, Z.; Ye, X.; Wei, S.; Wu, P.; Zhang, A.; Sun, J. *Org. Lett.* **2006**, *8*, 999.
[2] (a) Iwasaki, F.; Onomura, O.; mishima, K.; Maki, T.; Matsumoto, Y. Tetrahedron Lett., **1999**, *40*, 7507. (b) Reetz, M. T.; Li, X. *J. Am. Chem. Soc.* **2006**, *128*, 1044. (c) Matharu, D. S.; Morris, D. J.; Kawamoto, A. M.; Clarkson, G. J.; Wils, M. *Org. Lett.* **2005**, *7*, 5489. (d) Malkov, A. V.; Stewart Liddon, A. J. P.; Ramírez-López, P.; Bendová,L.; Haigh, D.; Kočovský, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 1432. (e) Du, D.; Fang, T.; Xu, J.; Zhang, S. *Org. Lett.* **2006**, *8*, 1327.

Scheme for the synthesis of 5b and 5d:



Procedure for the synthesis of 5d: To a solution of **5a**[1a] (606 mg, 1.54 mmol) in methanol (5 mL) was added saturated aqueous K_2CO_3 solution (2 mL). The mixture was allowed to stir at room temperature for 0.5 h, and was then diluted with EtOAc (20 mL). The organic phase was separated, washed with brine (10 mL), and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to give pure **5d** (536 mg) as white solid**.**

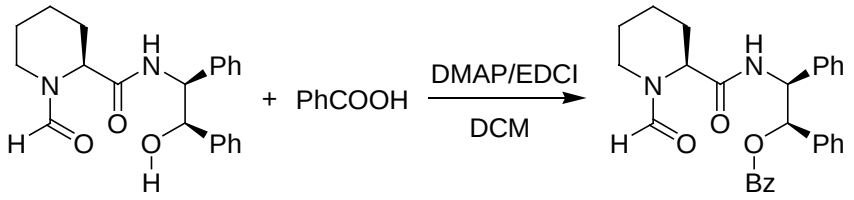
(2*S*,1'*S*,2'*R*)-1-Formyl-piperidine-2-carboxyl acid (2-hydroxy-1,2-diphenyl-ethyl)–amide (5d): white solid; yield: 98%; $[\alpha]_D^{20}$ = -31.5 (c = 0.108, MeOH); mp 195 – 197 ℃; ^{1}H NMR (600 MHz, DMSO): δ = 1.13 – 1.79 (m, 6H), 3.21 (dt, *J* = 3.14, 12.92 Hz, 1H), 3.41 (dd, *J* = 3.60, 12.60 Hz, 1H), 4.63 (d, *J* = 5.10 Hz, 1H), 4.70 (dd, *J* = 5.25, 8.67 Hz, 1H), 4.93 – 4.98 (m, 1H), 5.40 (m, 1H), 7.20 – 7.23 (m, 2H), 7.26 – 7.30 (m, 4H), 7.32 – 7.37 (m, 4H), 7.94 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 25.5, 27.6, 50.3, 58.5, 75.6, 127.2, 127.4, 127.5, 128.1, 128.6, 128.7, 141.8, 143.8, 162.4, 169.1; ESI HRMS exact mass calcd. for $(C_{21}H_{24}N_2O_3 + Na)^+$ requires m/z 375.1679, found m/z 375.1687.

Procedure for the synthesis of 5b: To a solution of **5d** (536 mg, 1.52 mmol) in formic acid (1.5 mL) was added acetic anhydride (1 mL, 10.66 mmol) at 0 ℃. The mixture was allowed to stir at room temperature overnight. After concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford pure **5b** (560 mg) as white solid.

(2*S*,1'*S*,2'*R*)-formic acid 2-[(1-formyl-piperidine-2-carbonyl)-amino]-1,2-diphenyl-ethyl ester (5b): white solid; yield: 95%; $[\alpha]_D^{20}$ = -56.3 (c = 0.096, MeOH); mp 65 – 67 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.36 – 1.68 (m, 5H), 2.18 (m, 1H), 2.97 (dt, *J* = 2.62, 13.14 Hz, 1H), 3.42 (dd, *J* = 4.17, 13.05 Hz, 1H), 4.96 (d, *J* = 5.46 Hz, 1H), 5.46 (dd, *J* = 5.16, 9.00 Hz, 1H), 6.20 (d, *J* = 5.04 Hz, 1H), 6.75 (d, *J* = 8.70 Hz, 1H), 7.01 – 7.04 (m, 2H), 7.05 – 7.31 (m, 10H), 8.07 (s, 1H), 8.09 (s, 1H); ^{13}C NMR (150 MHz,

$CDCl_3$): δ = 20.8, 24.9, 25.5, 44.3, 50.8, 56.7, 127.2, 127.5, 128.0, 128.3, 128.4, 128.6, 135.2, 137.0, 159.8, 162.6, 169.4; ESI HRMS exact mass calcd. for $(C_{22}H_{24}N_2O_4 + Na)^+$ requires m/z 403.1628, found m/z 403.1631.

Scheme for the synthesis of 5c:

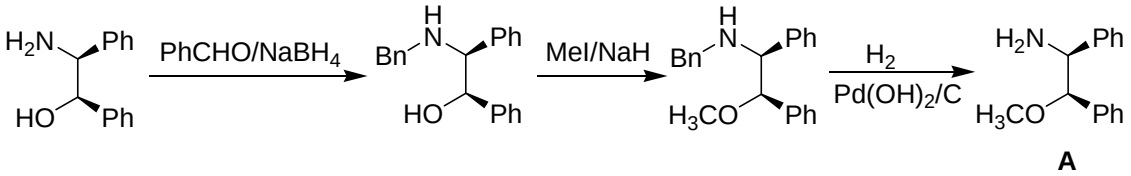


5d **5c**

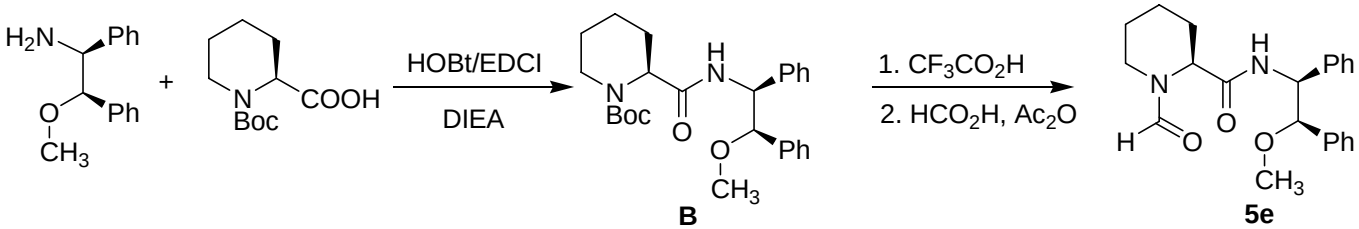
Procedure for the synthesis of 5c: To a solution of **5d** (530 mg, 1.52 mmol) and PhCOOH (463 mg, 3.8 mmol) in DCM (5 mL) was added DMAP (366 mg, 3.04 mmol) and EDCI (734 mg, 3.8 mmol) at 0 ℃. The mixture was allowed to stir at room temperature overnight. The volatiles were removed under reduced pressure, the residue was diluted with EtOAc (20 mL), washed with saturated aqueous $NaHCO_3$ (10 mL), aqueous HCl (1.0 N, 10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to give pure **5c** (575 mg) as white solid, yield: 83%.

(2*S*,1'*S*,2'*R*)-benzoic acid 2-[(1-formyl-piperidine-2-carbonyl)-amino]-1,2-diphenyl-ethyl ester (5c): white solid; yield: 65%; $[\alpha]_D^{20}$ = -5.7 (c = 0.122, MeOH); mp 204 – 206 ℃; ^{1}H NMR (600 MHz, CDCl3): δ = 1.24 – 1.67 (m, 5H), 2.18 (d, J = 13.62 Hz, 1H), 3.04 (dt, J = 2.76, 13.13 Hz, 1H), 3.44 (dd, J = 3.69, 13.41 Hz, 1H), 4.99 (d, J = 5.64 Hz, 1H), 5.56 (dd, J = 4.83, 8.67 Hz, 1H), 6.32 (d, J = 4.80 Hz, 1H), 6.90 (d, J = 8.58 Hz, 1H), 7.06 (m, 2H), 7.14 (m, 2H), 7.25 – 7.30 (m, 5H), 7.45 (m, 2H), 7.57 (m, 1H), 8.03 (m, 2H), 8.08 (s, 1H); ^{13}C NMR (150 MHz, CDCl3): δ = 20.9, 25.0, 25.5, 44.3, 50.9, 57.3, 77.9, 126.9, 127.0, 127.5, 127.8, 128.2, 128.3, 128.4, 128.5, 129.8, 133.3, 136.0, 137.2, 162.6, 165.6, 169.4; ESI HRMS exact mass calcd. for $(C_{28}H_{28}N_2O_4 + Na)$+ requires m/z 479.1941, found m/z 479.1942.

Scheme for the synthesis of 5e:



A



B **5e**

Procedure for the synthesis of 5e: To a solution of (1*R*,2*S*)-2-amino-1,2-diphenylethanol (2.13 g, 10.0 mmol) in ethanol (20 mL) was added benzaldehyde (1.06 g, 10.0 mmol). The reaction mixture was stirred at room temperature for 3 h, sodium borohydride (0.7 g, 15 mmol) was then added. After the resulting solution was stirred at room temperature for 1 h, aqueous HCl (2.0 N) was added at 0 ℃ to adjust the pH to 1. The volatiles were removed under reduced pressure. Aqueous NaOH (2.0 N) solution was then added to adjust the pH to 10. The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined extracts was washed with brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure.The residue was subjected to crystallization from ethanol to afford pure (1*R*,2*S*)-2-benzylamino-1,2-diphenylethanol (2.7 g) as white crystal, yield: 89%.

To an anhydrous THF (10 mL) solution of (1*R*,2*S*)-2-benzylamino-1,2-diphenylethanol (700 mg) obtained above was added sodium hydride (500 mg) at 0 ℃, followed by the addition of iodomethane (3 mL) dropwise. The reaction mixture was allowed to warm to room temperature and stir for 0.5 h. Upon completion, the reaction was quenched with saturated aqueous ammonium chloride and diluted with EtOAc. The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) to give pure (1*R*,2*S*)-2-benzylamino-1,2-diphenylethyl methyl ether (659 mg) as white solid, yield: 90%.

A solution of (1*R*,2*S*)-2-benzylamino-1,2-diphenylethyl methyl ether (659 mg, 2.1 mmol) in MeOH and 10% $Pd(OH)_2/C$ were charged in a two-neck flask. The mixture was stirred under hydrogen (1 atm) at 45 ℃ for 12 h, and was then filtered through Celite. The filtrate was concentrated to dryness to give **A** as white solid (448 mg), yield: 95%.

To a solution of Boc-L-pipecolinic acid (458 mg, 2.0 mmol) in DCM (20 mL) was added **A** (545 mg, 2.4 mmol), followed by HOBt (350 mg, 2.4 mmol), DIEA (700 μL) and EDCI (460 mg, 2.4 mmol) at 0 ℃. The mixture was stirred at room temperature for 12 h. The volatiles were removed under reduced

pressure, the residue was diluted with EtOAc (20 mL), washed with saturated aqueous $NaHCO_3$ (10 mL), aqueous HCl (1.0 N, 10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 5/1) to give as pure **B** (832 mg) as white solid, yield: 95%.

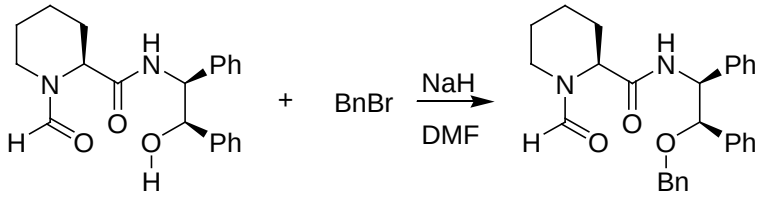
Compound **B** (832 mg, 1.9 mmol) was treated with 20 v% TFA in CH_2Cl_2 (20 mL). After stirring at room temperature for 1 h, the solution was concentrated under reduced pressure. The residue was then dissolved in formic acid (1.5 mL) and the resulting solution was cooled to 0 ℃. Acetic anhydride (1 mL, 10.66 mmol) was added dropwise and the mixture was allowed to stir at room temperature overnight. After concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford pure 5e (625 mg) as white solid, yield: 90%.

(2*S*,1'*S*,2'*R*)-1-Formyl-piperidine-2-carboxylic acid (2-methoxy-1,2-diphenyl-ethyl)–amide (5e): white solid; yield: 90%; $[\alpha]_D^{20}$ = -59.3 (c = 0.108, MeOH); mp 47 – 50 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.29 – 1.65 (m, 5H), 2.23 (d, J = 13.92 Hz, 1H), 2.98 (dt, J = 2.28, 13.20 Hz, 1H), 3.28 (s, 3H), 3.45 (dd, J = 3.24, 13.20 Hz, 1H), 4.52 (d, J = 4.44 Hz, 1H), 5.02 (d, J = 5.70 Hz, 1H), 5.16 (dd, J = 4.59, 8.79 Hz, 1H), 6.95 (m, 4H), 7.16 – 7.24 (m, 6H), 8.14 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9, 24.9, 25.6, 44.3, 50.9, 57.4, 58.0, 85.7, 127.3, 127.5, 127.8, 127.9, 128.0, 128.2, 137.3, 137.9, 162.4, 168.9; ESI HRMS exact mass calcd. for $(C_{22}H_{26}N_2O_3 + Na)^+$ requires m/z 389.1836, found m/z 389.1831.

Procedure for the synthesis of 5f is similar to that for the synthesis of 5e

(2*S*,1'*S*,2'*R*)-1-Formyl-piperidine-2-carboxyl acid (2-ethoxy-1,2-diphenyl-ethyl)–amide (5f): Colorless oil; yield: 61%; $[\alpha]_D^{20}$ = -40.5 (c = 0.111, MeOH); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.16 – 1.67 (m, 5H), 1.20 (t, J = 7.02 Hz, 3H), 2.25 (d, J = 13.86 Hz, 1H), 2.98 (dt, J = 2.62, 13.10 Hz, 1H), 3.34 – 3.37 (m, 1H), 3.46 – 3.49 (m, 2H), 4.63 (d, J = 4.38 Hz, 1H), 5.04 (d, J = 5.64 Hz, 1H), 5.11 (dd, J = 4.38, 8.76 Hz, 1H), 6.95 (m, 3H), 7.03 (m, 1H), 7.13 – 7.21 (m, 6H), 8.17 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9, 24.9, 25.6, 29.7, 44.3, 50.9, 58.0, 65.0, 83.5, 127.1, 127.2, 127.6, 127.9, 128.0, 128.2, 138.0, 138.1, 162.3, 168.8; ESI HRMS exact mass calcd. for $(C_{23}H_{28}N_2O_3 + Na)^+$ requires m/z 403.1992, found m/z 403.1996.

Scheme for the synthesis of 5g:



5d **5g**

Procedure for the synthesis of 5g: To a solution of **5d** (536 mg, 1.52 mmol) in DMF (5.0 mL) was added NaH (73 mg, 3.04 mmol) at 0 ℃, followed by the addition of BnBr (0.19 mL, 1.52 mmol) dropwise. The mixture was allowed to stir at room temperature overnight. Upon completion, the reaction was quenched with water and diluted with Et_2O. The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford pure **5g** (578 mg), yield: 86%.

(2*S*,1'*S*,2'*R*)-2-Formyl-piperidine-2-carboxyl acid (2-benzyloxy-1,2-diphenyl-ethyl)–amide (5g): white solid; yield: 65%; $[\alpha]_D^{20}$ = -61.3 (c = 0.106, MeOH); mp 168 – 170 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.26 – 1.63 (m, 5H), 2.14 (d, J = 13.32 Hz, 1H), 2.96 (dt, J = 2.40, 13.02 Hz, 1H), 3.4 (dd, J = 3.42, 9.72 Hz, 1H), 4.25 (d, J = 11.94 Hz, 1H), 4.56 (d, J = 5.10 Hz, 1H), 4.69 (d, J = 4.68 Hz, 1H), 4.94 (d, J = 5.64 Hz, 1H), 5.14 (dd, J = 4.80, 8.70 Hz, 1H), 6.92 –7.02 (m, 5H), 7.15 – 7.20 (m, 3H), 7.20 – 7.24 (m, 4H), 7.27 – 7.37 (m, 4H), 8.09 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9, 25.0, 25.6, 29.7, 44.2, 50.8, 58.2, 70.7, 82.7, 127.3, 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4, 128.6, 137.6, 137.9, 162.4, 168.9; ESI HRMS exact mass calcd. for $(C_{28}H_{30}N_2O_3 + Na)^+$ requires m/z 465.2149, found m/z 465.2142.

Scheme for the synthesis of 5h:

5d **5h**

Procedure for the synthesis of 5h: To a solution of **5d** (352 mg, 1.0 mmol) in DCM (5.0 mL) was added DIEA (0.9 mL, 5.0 mmol) at 0 ℃, followed by the addition of MOMCl (242 mg, 3.0 mmol) dropwise. The mixture was allowed to stir at room temperature overnight. The volatiles were removed under

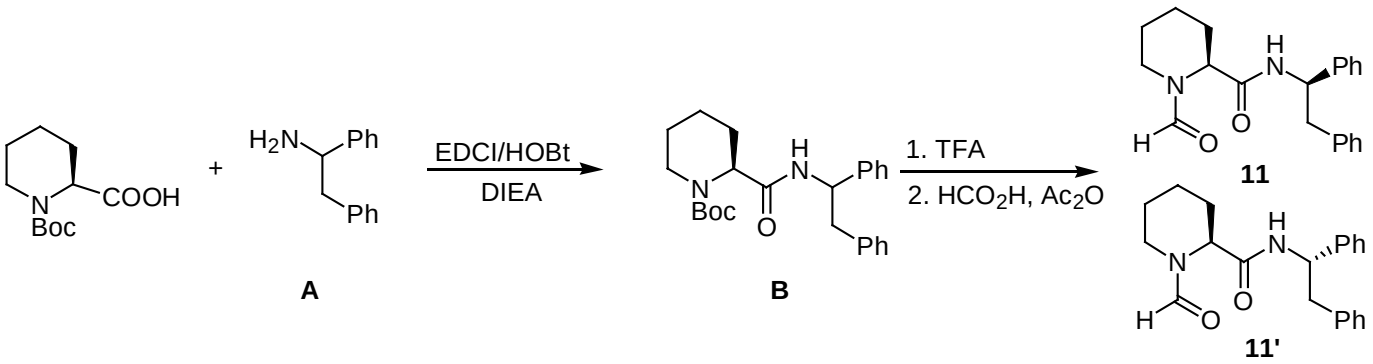
reduced pressure, the residue was diluted with EtOAc (20 mL), washed with saturated aqueous $NaHCO_3$ (10 mL), aqueous HCl (1.0 N, 10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to give as pure **5h** (349 mg), yield: 88%.

(2*S*,1'*S*,2'*R*)-1-Formyl-piperidine-2-carboxyl acid (2-methoxymethoxy-1,2-diphenyl-ethyl)–amide (5h): white solid; yield: 68%; $[\alpha]_D^{20}$ = -102.4 (c = 0.104, MeOH); mp 43 – 46 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.24 – 1.73 (m, 5H), 2.16 (d, J = 13.50 Hz, 1H), 2.99 (dt, J = 1.62, 12.78 Hz, 1H), 3.25 (s, 3H), 3.43 (d, J = 13.08 Hz, 1H), 4.49 – 4.55 (m, 2H), 4.95 (dd, J = 5.16, 19.86 Hz, 2H), 5.16 – 5.20 (m, 1H), 6.90 – 6.95 (m, 1H), 7.04 (m, 3H), 7.20 – 7.23 (m, 6H), 8.11 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 25.0, 25.6, 29.7, 44.3, 50.8, 55.8, 57.9, 80.3, 94.6, 127.4, 127.5, 127.9, 128.0, 128.1, 128.2, 137.6, 138.3, 162.4, 169.0; ESI HRMS exact mass calcd. for $(C_{23}H_{28}N_2O_4 + Na)^+$ requires m/z 419.1941, found m/z 419.1931.

The procedure for the syntheses of 10 is similar to that for the synthesis of 5e

(*S*,*S*,*S*)-1-Formyl-piperidine-2-carboxylic acid (2-methoxy-1,2-diphenyl-ethyl)–amide (10): white solid; yield: 67%; $[\alpha]_D^{20}$ = -29.0 (c = 0.100, MeOH); mp 145 – 146 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.25 – 1.65 (m, 5H), 2.14 (d, J = 13.56 Hz, 1H), 3.09 (dt, J = 2.96, 13.16 Hz, 1H), 3.21 (s, 3H), 3.49 (dd, J = 3.06, 12.90 Hz, 1H), 4.42 (d, J = 3.72 Hz, 1H), 4.99 (d, J = 5.82 Hz, 1H), 5.06 (dd, J = 3.66, 8.40 Hz, 1H), 6.90 (d, J = 7.92 Hz, 1H), 7.19 – 7.24 (m, 4H), 7.27 – 7.30 (m, 3H), 7.31 – 7.35 (m, 2H), 8.18 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.9, 25.1, 25.7, 29.7, 44.3, 50.8, 57.5, 58.7, 85.5, 126.9, 127.0, 127.3, 128.0, 128.3, 128.4, 138.4, 140.4, 162.4, 169.3; ESI HRMS exact mass calcd. for $(C_{22}H_{26}N_2O_3 + Na)^+$ requires m/z 389.1836, found m/z 389.1845.

Scheme for the synthesis of 11:



Procedure for the synthesis of 11: To a solution of Boc-L-pipecolinic acid (458 mg, 2.0 mmol) in DCM (20 mL) was added **A**[3](475 mg, 2.4 mmol), HOBt (350 mg, 2.4 mmol), DIEA (700 μL) and EDCI (460 mg, 2.4 mmol) at 0 ℃. The mixture was allowed to stir at room temperature overnight. The volatiles were removed under reduced pressure, the residue was diluted with EtOAc (20 mL), washed with saturated aqueous $NaHCO_3$ (10 mL), aqueous HCl (1.0 N, 10 mL) and brine (10 mL), and dried over anhydrous Na_2SO_4. After removal of solvents under reduced pressure, the residue was purified through column chromatography on silica gel (eluent: hexane/EtOAc = 6/1) to give pure **B** (734 mg), yield: 90%.

Compound **B** (734 mg, 1.8 mmol) was treated with 20 v% TFA in CH_2Cl_2 (20 mL). After stirring at room temperature for 1 h, the solution was concentrated under reduced pressure. The residue was then dissolved in formic acid (1.5 mL) and the resulting solution was cooled to 0 ℃. Acetic anhydride (1 mL, 10.66 mmol) was added dropwise and the mixture was allowed to stir at room temperature overnight. After concentration under reduced pressure, the crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc = 1/1) to afford pure 11 (490 mg) and **11'** (135 mg)yield: 90%.

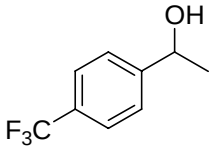
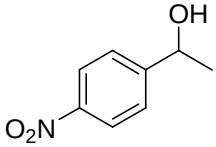
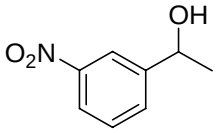
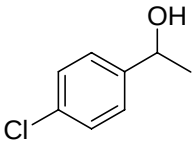
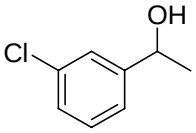
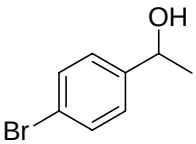
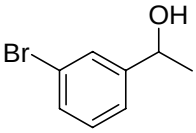
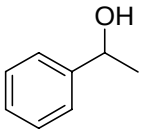
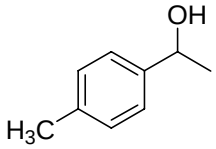
(*S*,*S*)-1-Formyl-piperidine-2-carboxylic acid (1,2-diphenyl-ethyl)–amide (11): pale yellow solid; yield: 71%; $[\alpha]_D^{20}$ = -34.4 (c = 0.16, EtOAc); mp 95 – 98 ℃; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.25 – 1.65 (m, 5H), 2.12 (d, J = 13.62 Hz, 1H), 2.99 (dt, J = 2.64, 15.84 Hz, 1H), 3.00 – 3.09 (m, 2H), 3.44 (dd, J = 3.84, 13.02 Hz, 1H), 4.91 (d, J = 5.70 Hz, 1H), 5.20 (q, J = 7.68 Hz, 1H), 6.44 (d, J = 7.80 Hz, 1H), 7.04 – 7.07 (m, 2H), 7.13 (d, J = 7.26 Hz, 2H), 7.17 – 7.21 (m, 1H), 7.22 – 7.34 (m, 5H), 8.09 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 20.8, 24.9, 25.5, 42.9, 44.3, 50.8, 54.6, 126.4, 126.6, 127.3, 128.3, 128.5, 129.4, 133.3, 137.1, 141.7, 162.4, 169.2; ESI HRMS exact mass calcd. for $(C_{21}H_{24}N_2O_2 + Na)^+$ requires m/z 359.1730, found m/z 359.1713.

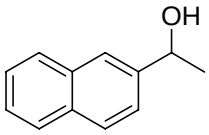
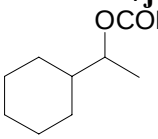
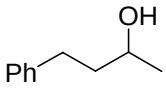
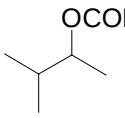
General procedure for the catalytic reduction of ketones 6a–m:

Under an argon atmosphere, trichlorosilane (40 μL, 0.4 mmol) was added dropwise to a stirred solution of ketone **6** (0.20 mmol) and catalyst **5e** (7.3 mg, 0.02 mmol) in anhydrous toluene at -20 °C. The mixture was allowed to stir at the same temperature for 16 h. The reaction was then quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL) and was extracted with EtOAc. The combined extracts was washed with brine and dried over anhydrous $MgSO_4$. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc) to afford pure alcohol **7**. The ee values were determined using established HPLC techniques with chiral stationary phases.

[3] Gyenes, F.; Bergmann, K. E.; Welch, J. T. J. Org. Chem **1998,** *63*, 2824.

Chiral-phase HPLC Data

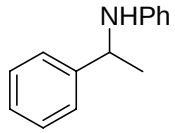
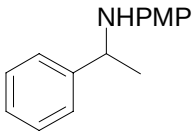
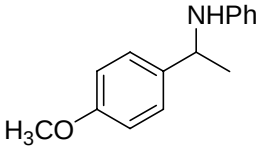
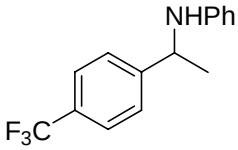
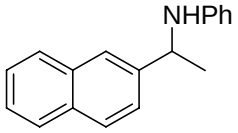
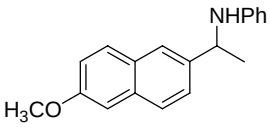
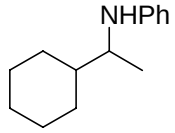
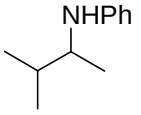
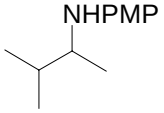
Compound	Daicel column	Flow (ml/mi)	λ (nm)	i-PrOH/Hexanes	t_R (min)	Temperature (℃)
 **7a**	OJ-H	1.0	220	5:95	7.9 8.6 (major)	25
 **7b**	OJ-H	1.0	254	10:90	16.6 18.0 (major)	25
 **7c**	OD-H	1.0	220	2:98	29.5 31.4 (major)	25
 **7d**	OJ-H	1.0	220	2:98	17.7 19.3 (major)	25
 **7e**	OJ-H	1.0	220	5:95	11.1 12.6 (major)	25
 **7f**	OD-H	1.0	220	5:95	9.8 10.6 (major)	25
 **7g**	OJ-H	1.0	220	10:90	7.7 8.7 (major)	25
 **7h**	OD-H	1.0	220	10:90	6.6 (major) 7.2	25
 **7i**	OJ-H	1.0	254	10:90	8.2 9.2 (major)	25

 **7j**	OJ-H	1.0	220	10:90	17.4 22.6 (major)	25
 **7k**	AD-H	1.0	220	1:99	8.5 9.0 (major)	26
 **7l**	OD-H	1.0	220	10:90	7.6 (major) 10.0	25
 **7m**	OJ-H	1.0	220	1:99	8.9 10.1 (major)	26

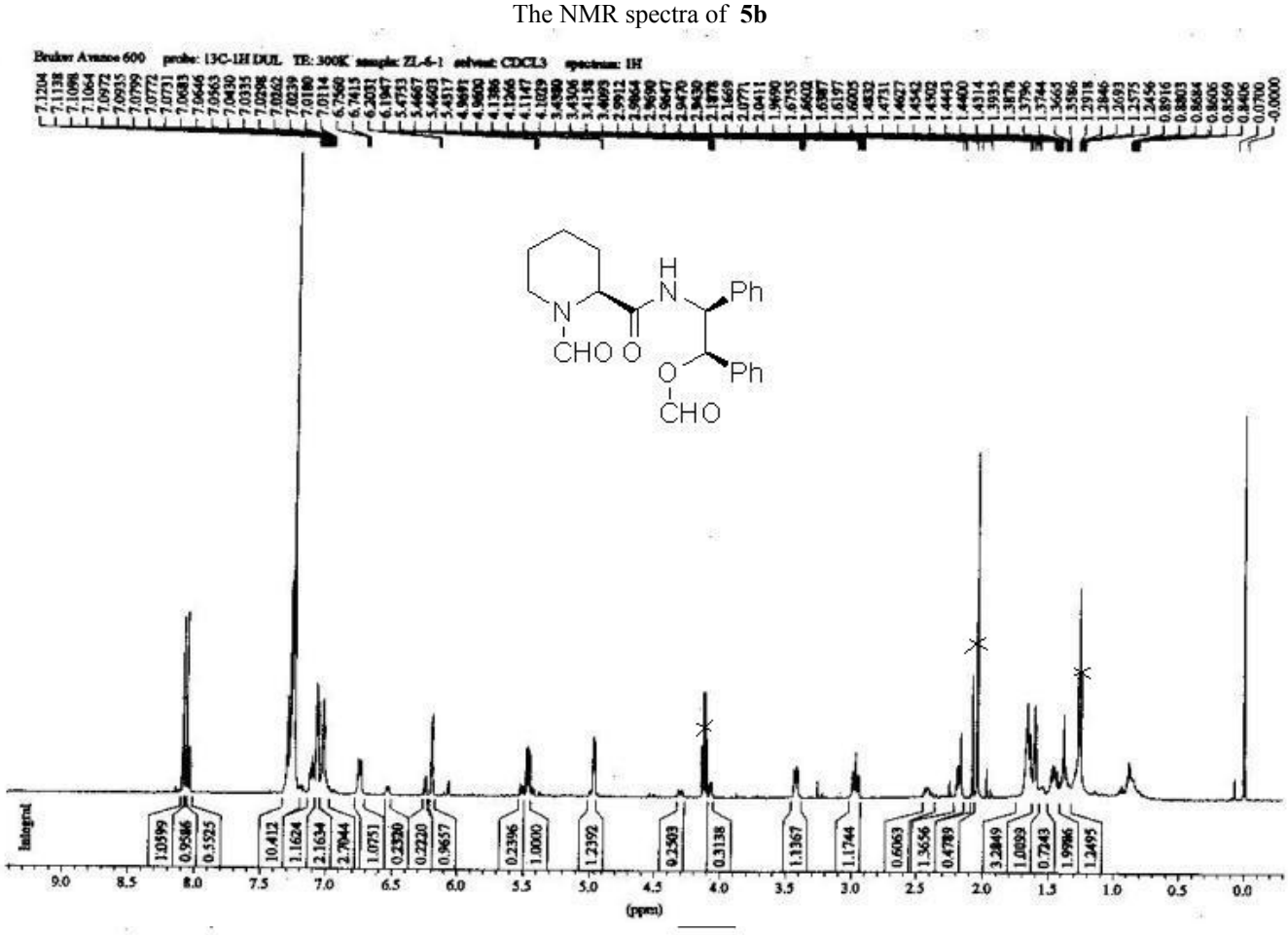
General procedure for the catalytic reduction of imines 8a – i:

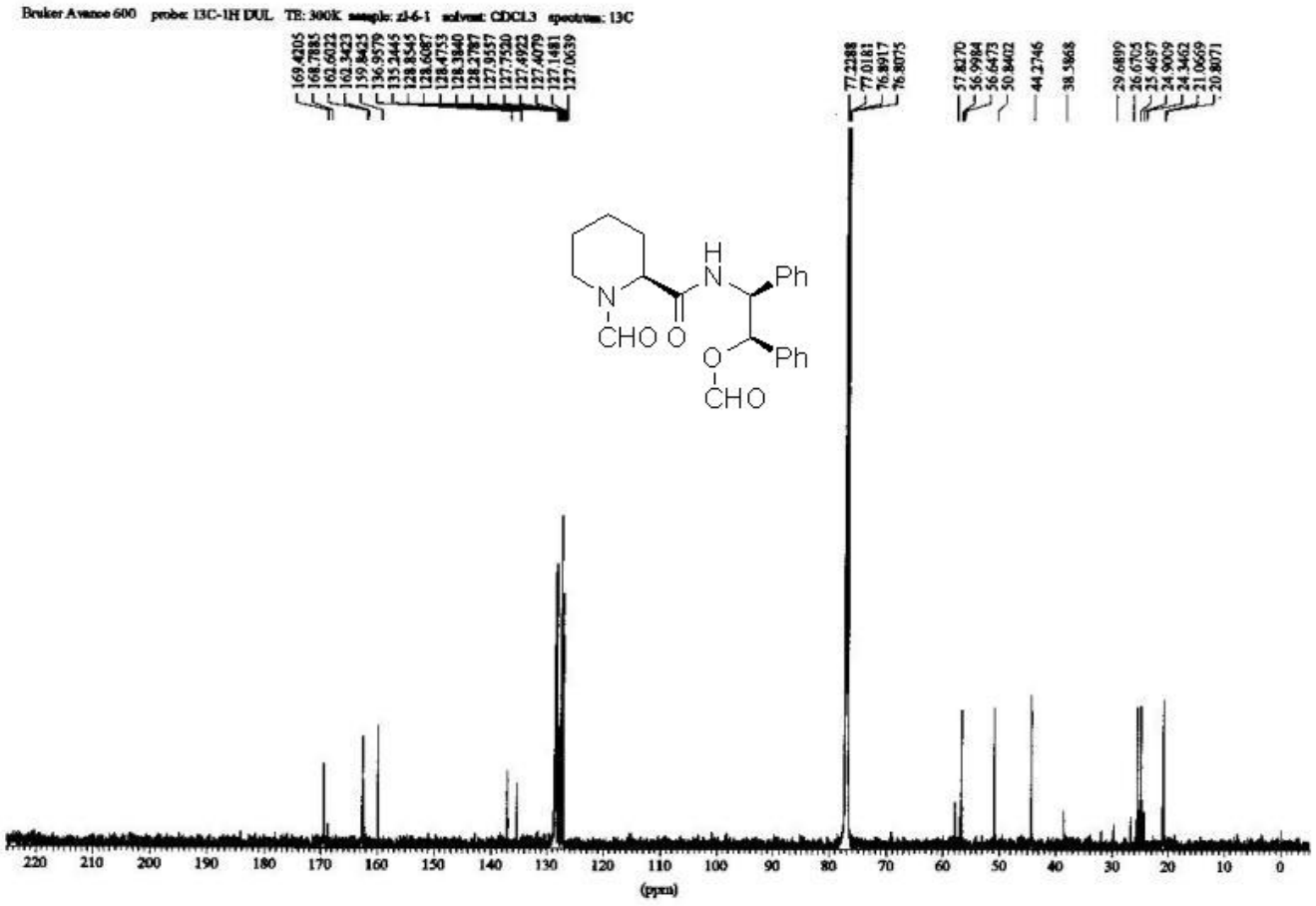
Under an argon atmosphere, trichlorosilane (40 μL, 0.4 mmol) was added dropwise to a stirred solution of imine **8** (0.20 mmol) and catalyst **5e** (7.9 mg, 0.02 mmol) in anhydrous toluene at -20 °C. The mixture was allowed to stir at the same temperature for 24 h. The reaction was quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL) and was extracted with EtOAc. The combined extracts was washed with brine and dried over anhydrous $MgSO_4$. Solvents were evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane/EtOAc) to afford pure amine **9**. The ee values were determined using established HPLC techniques with chiral stationary phases.

Chiral-phase HPLC Data

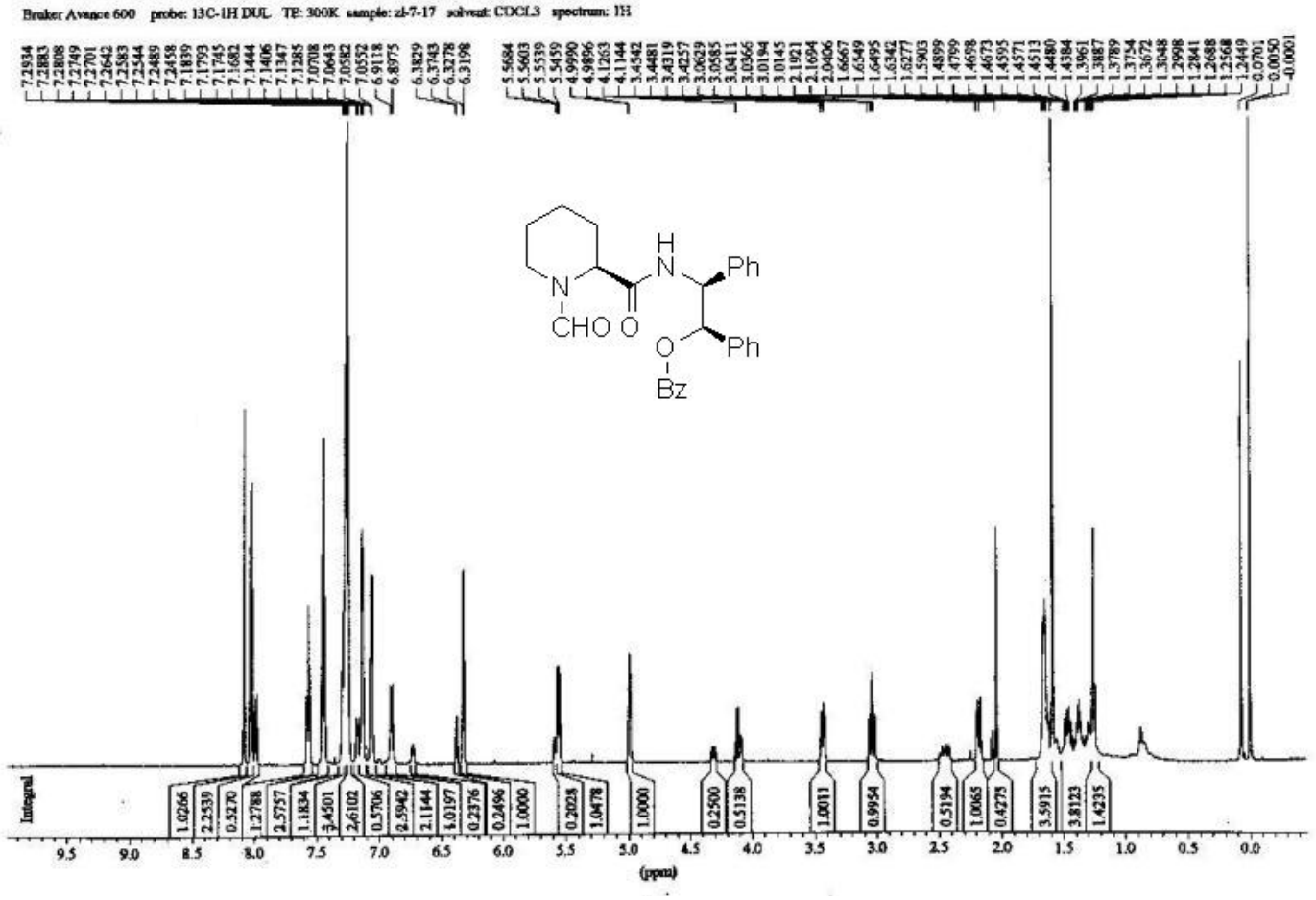
Compound	Daicel column	Flow (ml/min)	λ (nm)	i-PrOH/Hexanes	t_R (min)	Temperature (℃)
 **9a**	OD-H	1.0	254	1:99	10.6 11.0 (major)	25
 **9b**	AD-H	1.0	254	2:98	9.7 10.9 (major)	25
 **9c**	OD-H	1.0	254	1:99	12 14 (major)	25
 **9d**	OD-H	1.0	254	10:90	9.6 14.0 (major)	25
 **9e**	OD-H	1.0	254	2:98	15.4 19.0 (major)	25
 **9f**	OD-H	1.0	254	2:98	18 24 (major)	25
 **9g**	OJ-H	0.5	254	1:99	25.5 (major) 28.0	28
 **9h**	OJ-H	1.0	254	1:99	10.1 (major) 11.0	25
 **9i**	OD-H	1.0	254	1:99	6.2 (major) 6.9	25

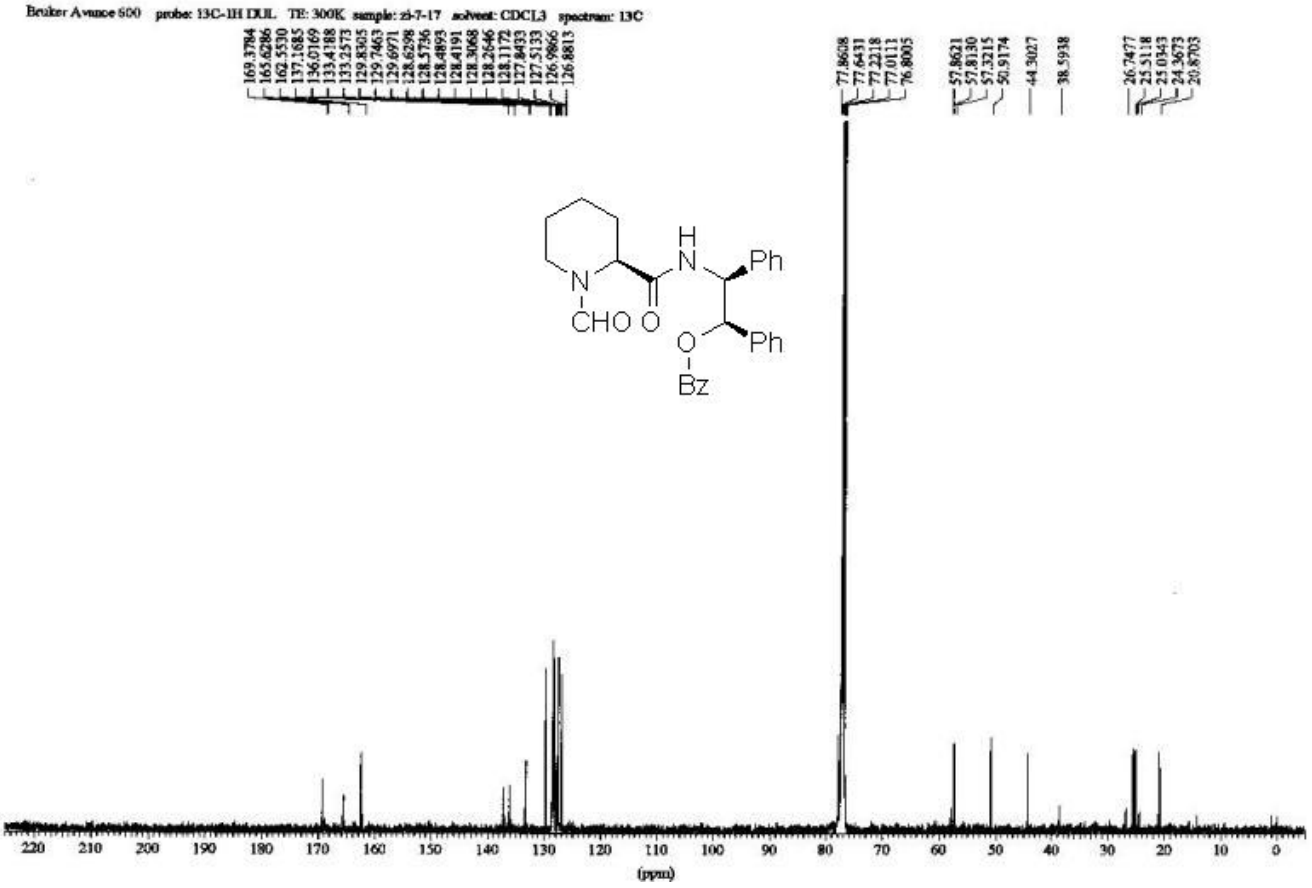
The NMR spectra of **5b**



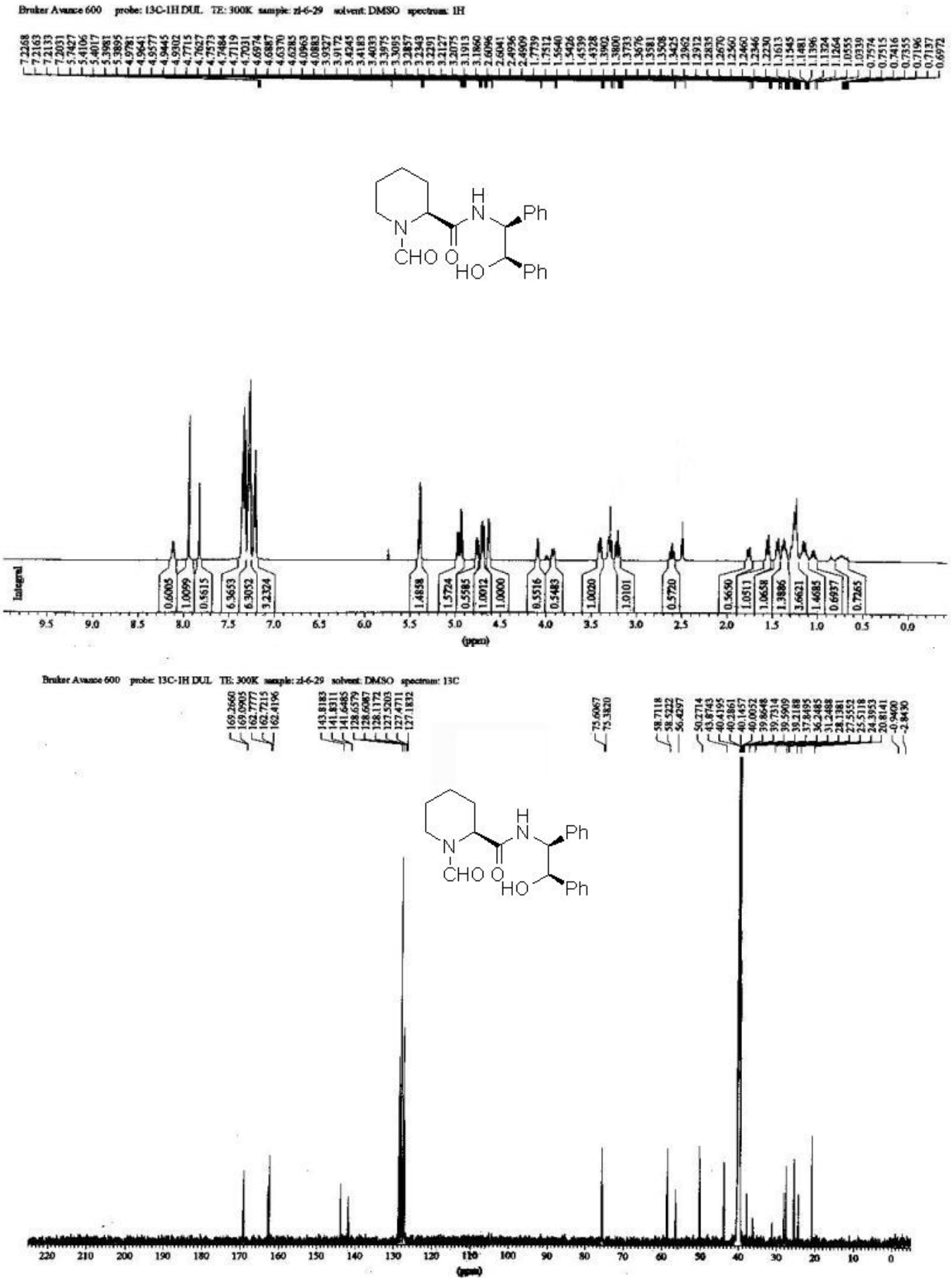


The NMR spectra of **5c**

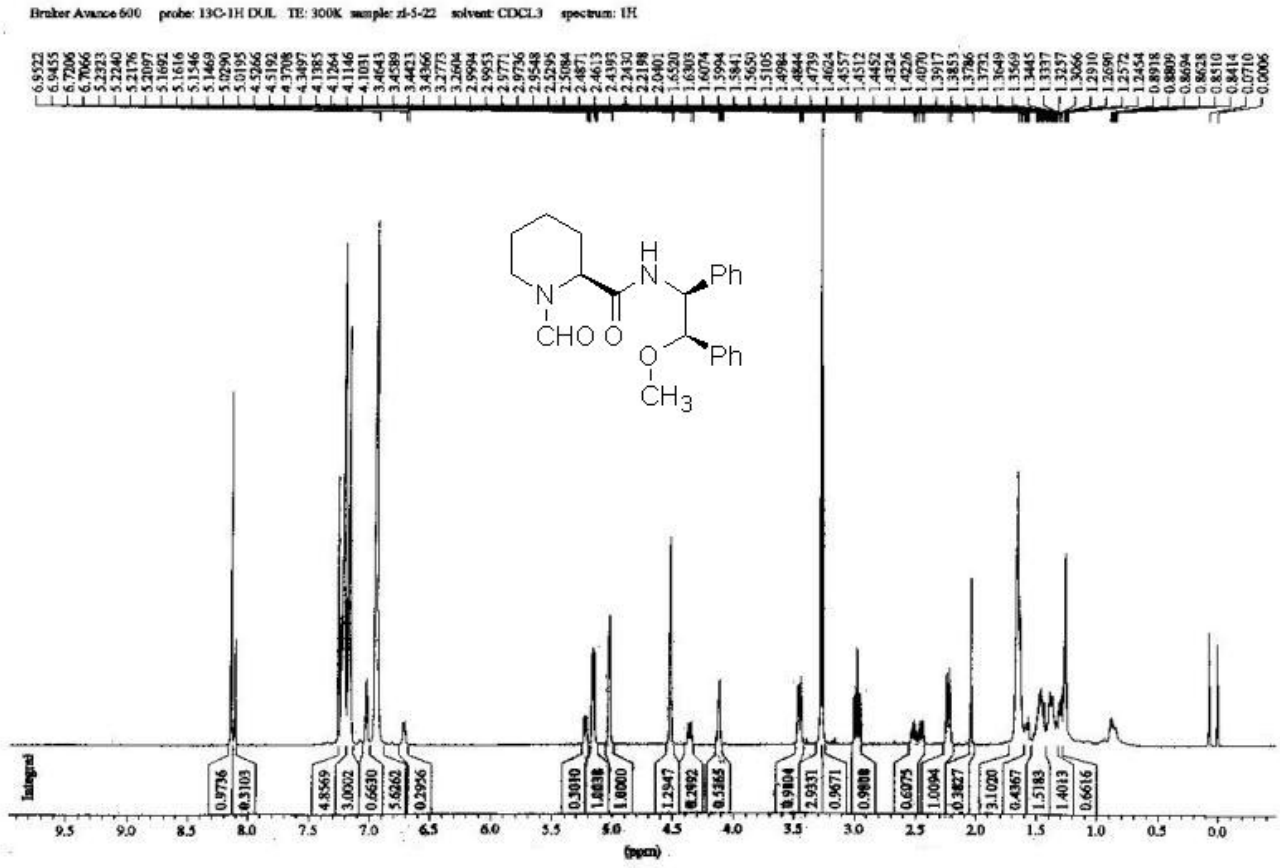


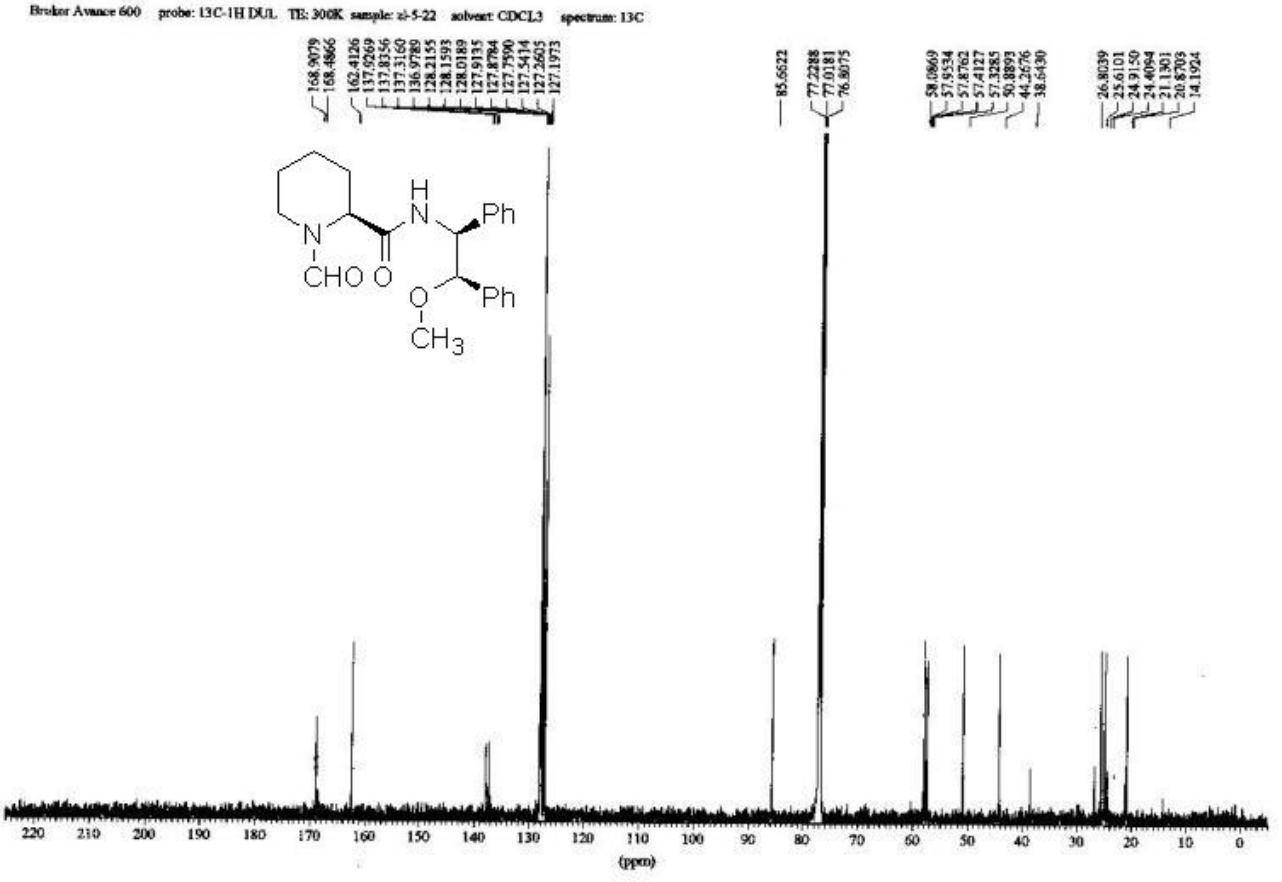


The NMR spectra of **5d**

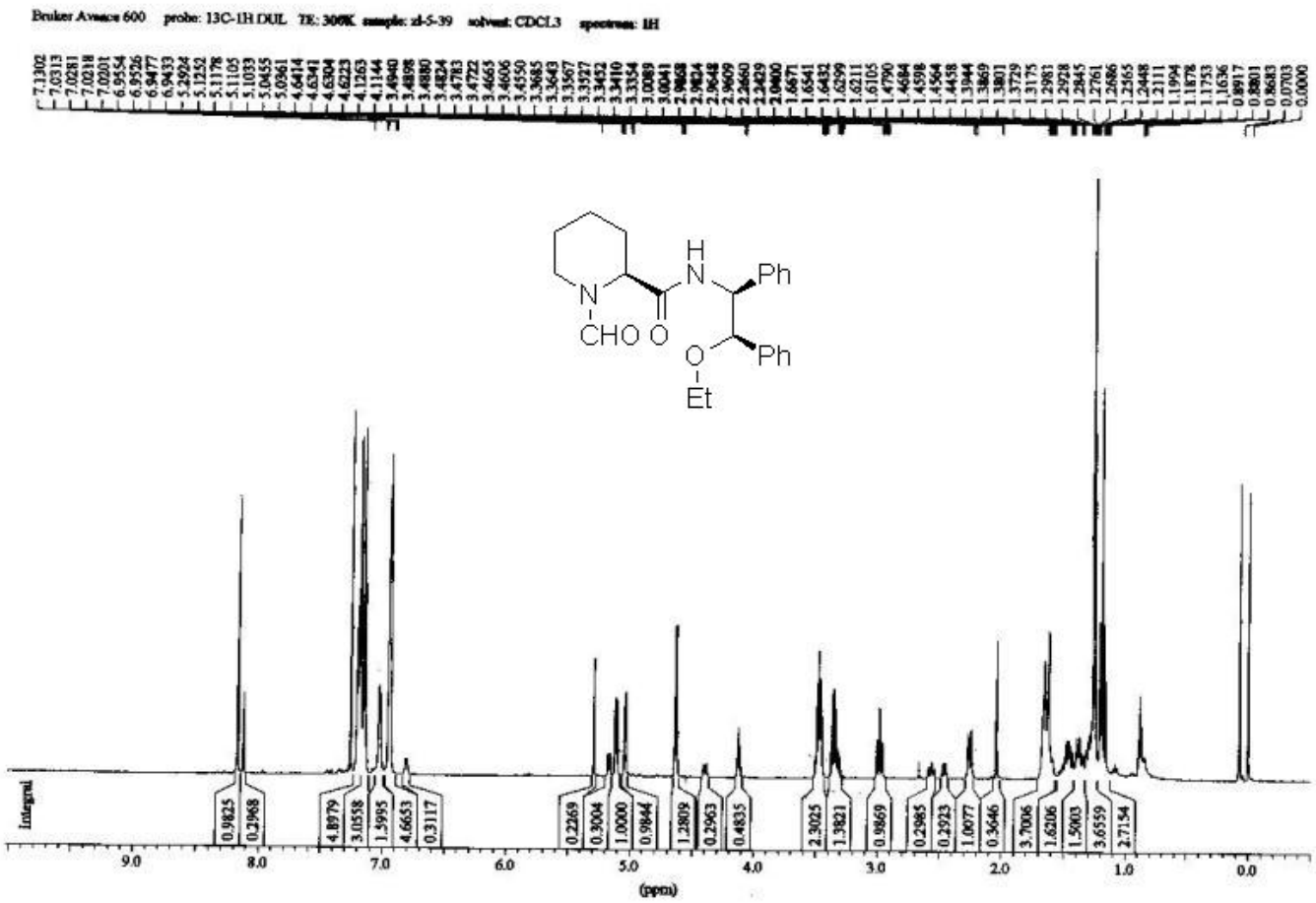


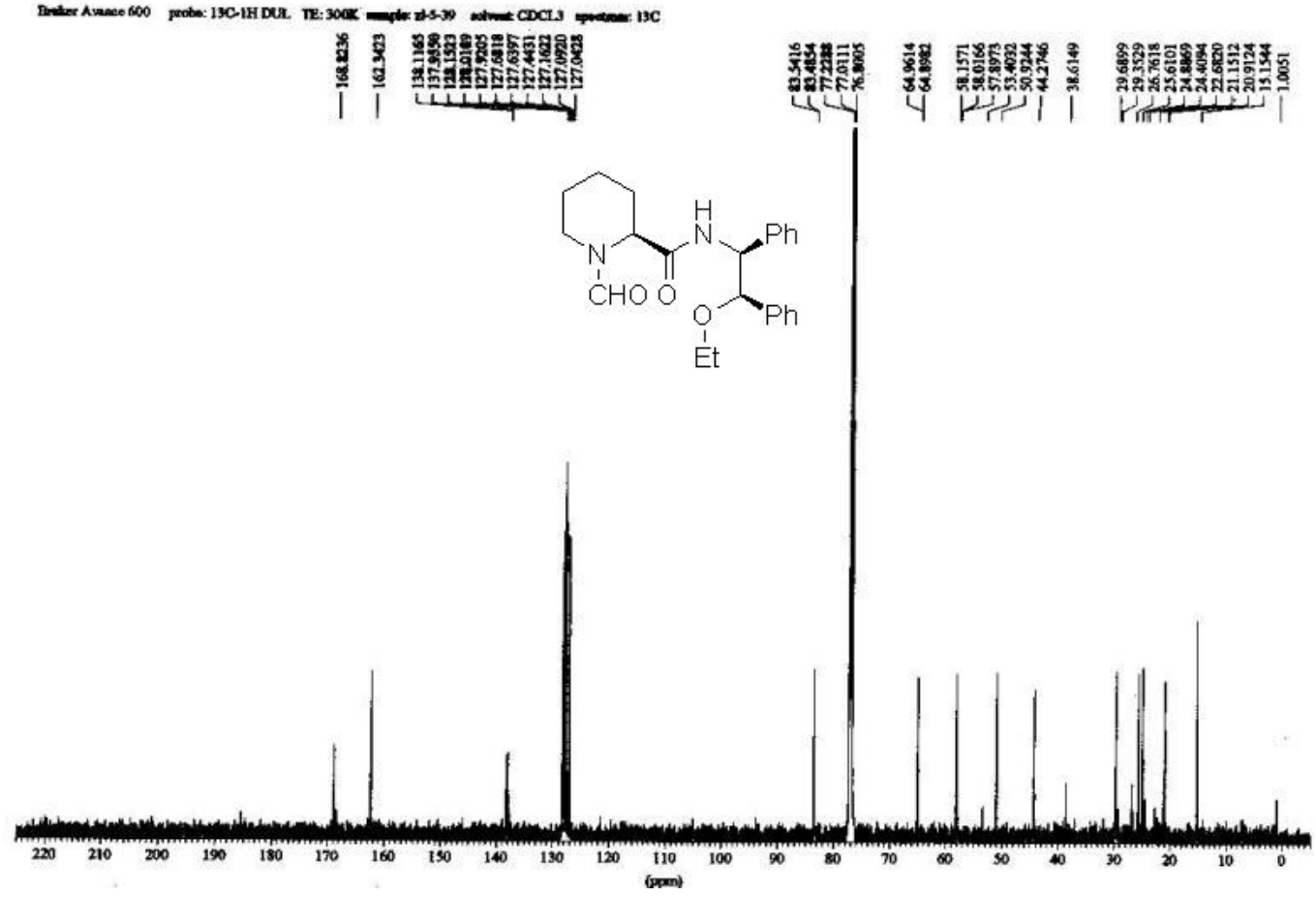
The NMR spectra of **5e**



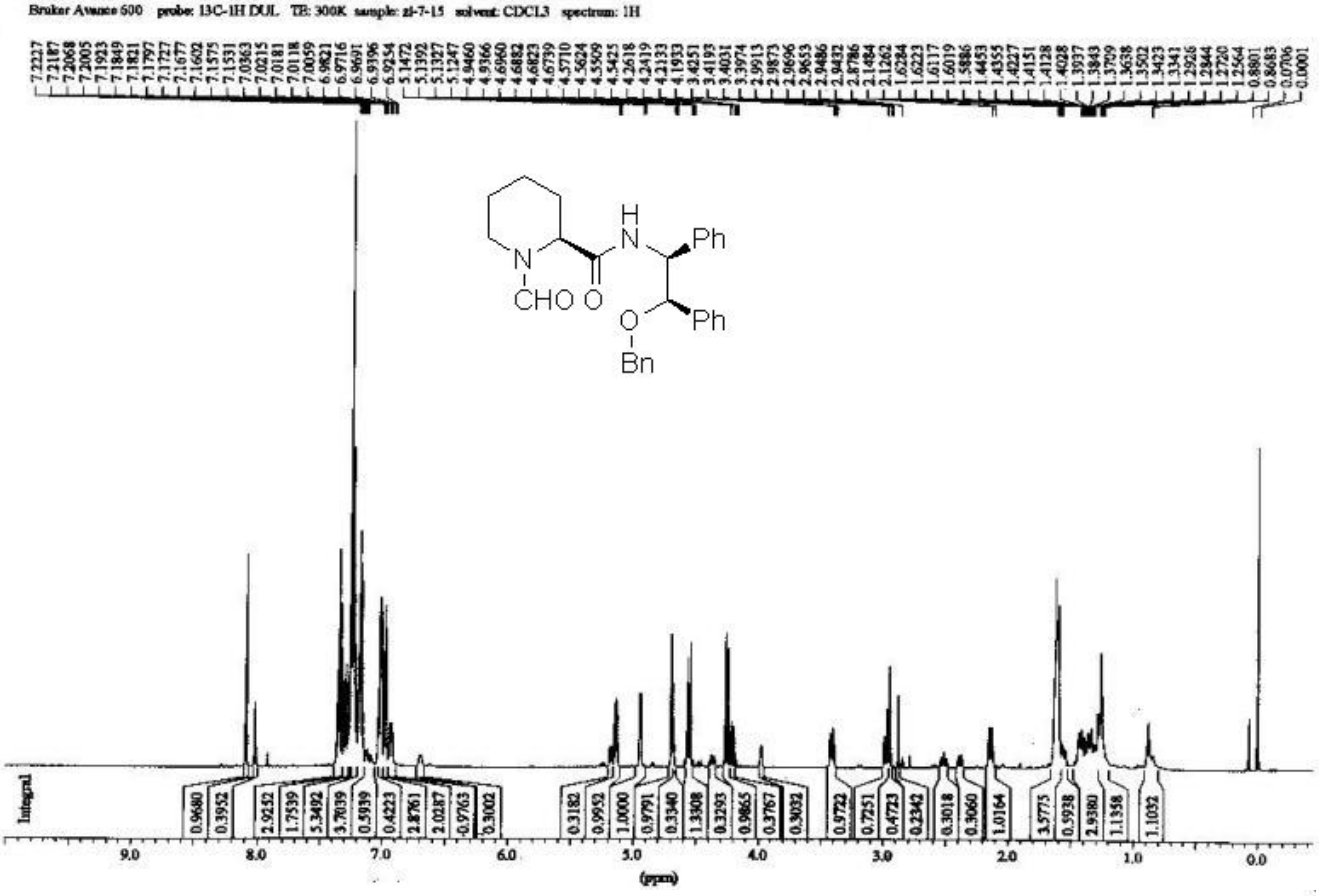


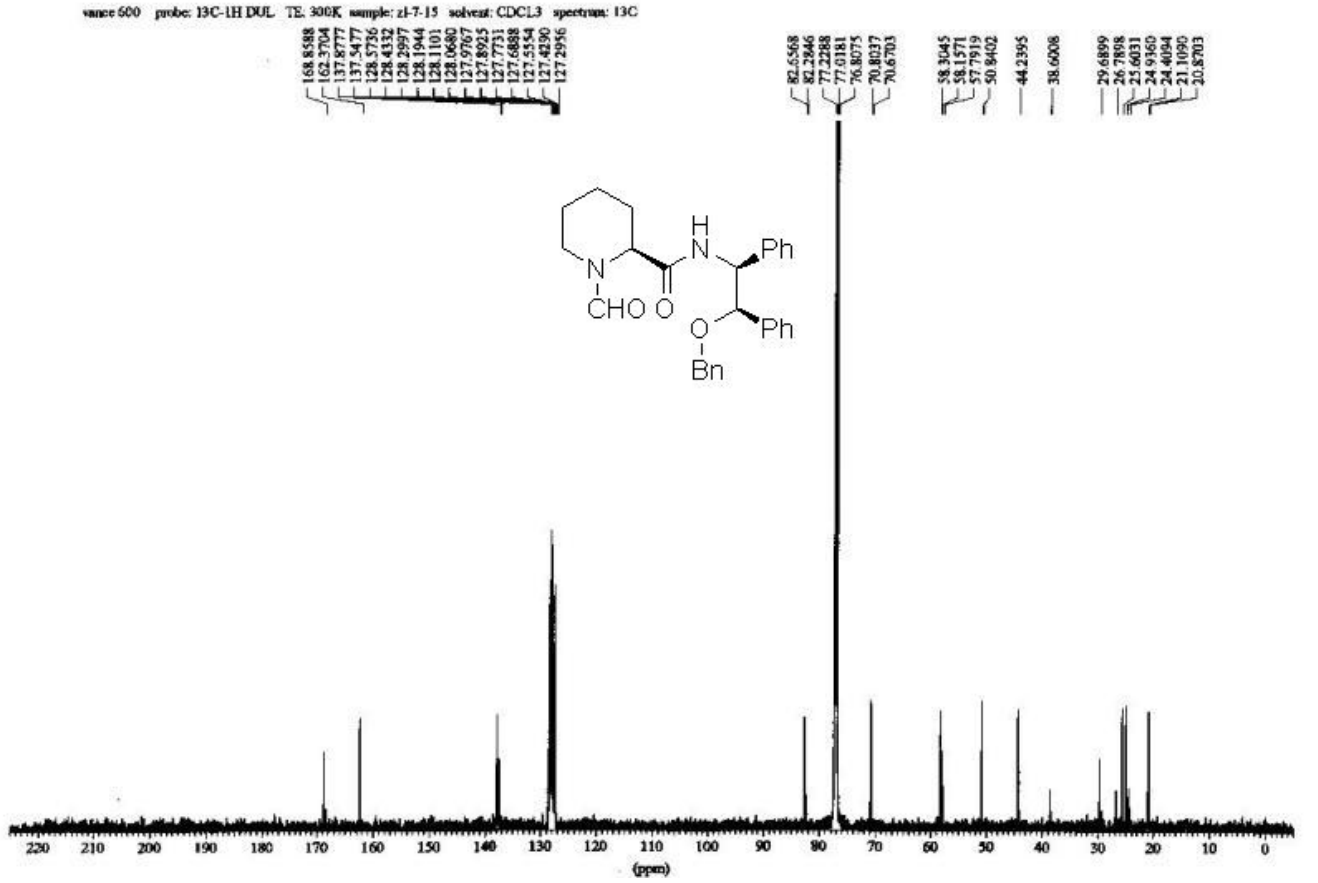
The NMR spectra of **5f**



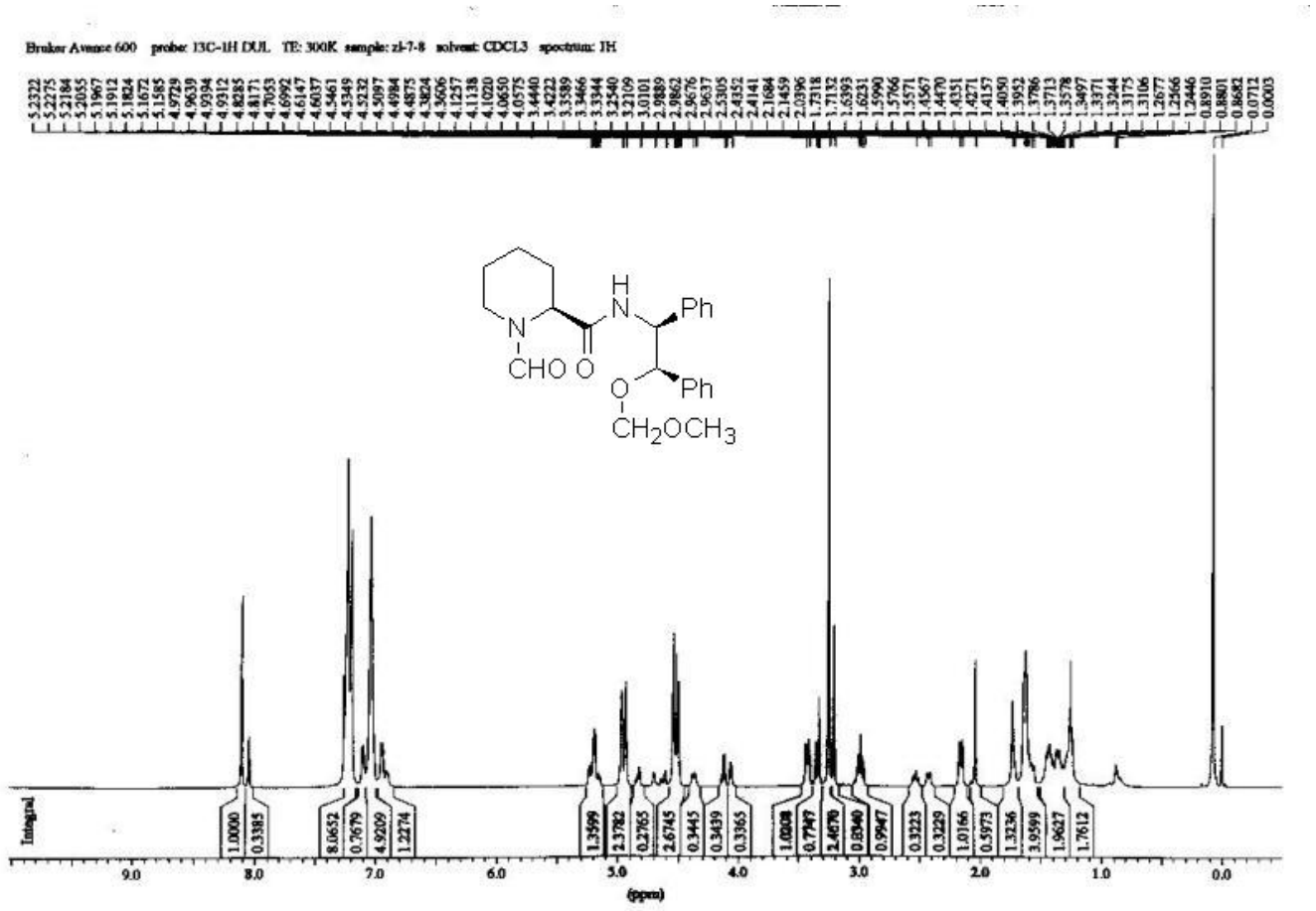


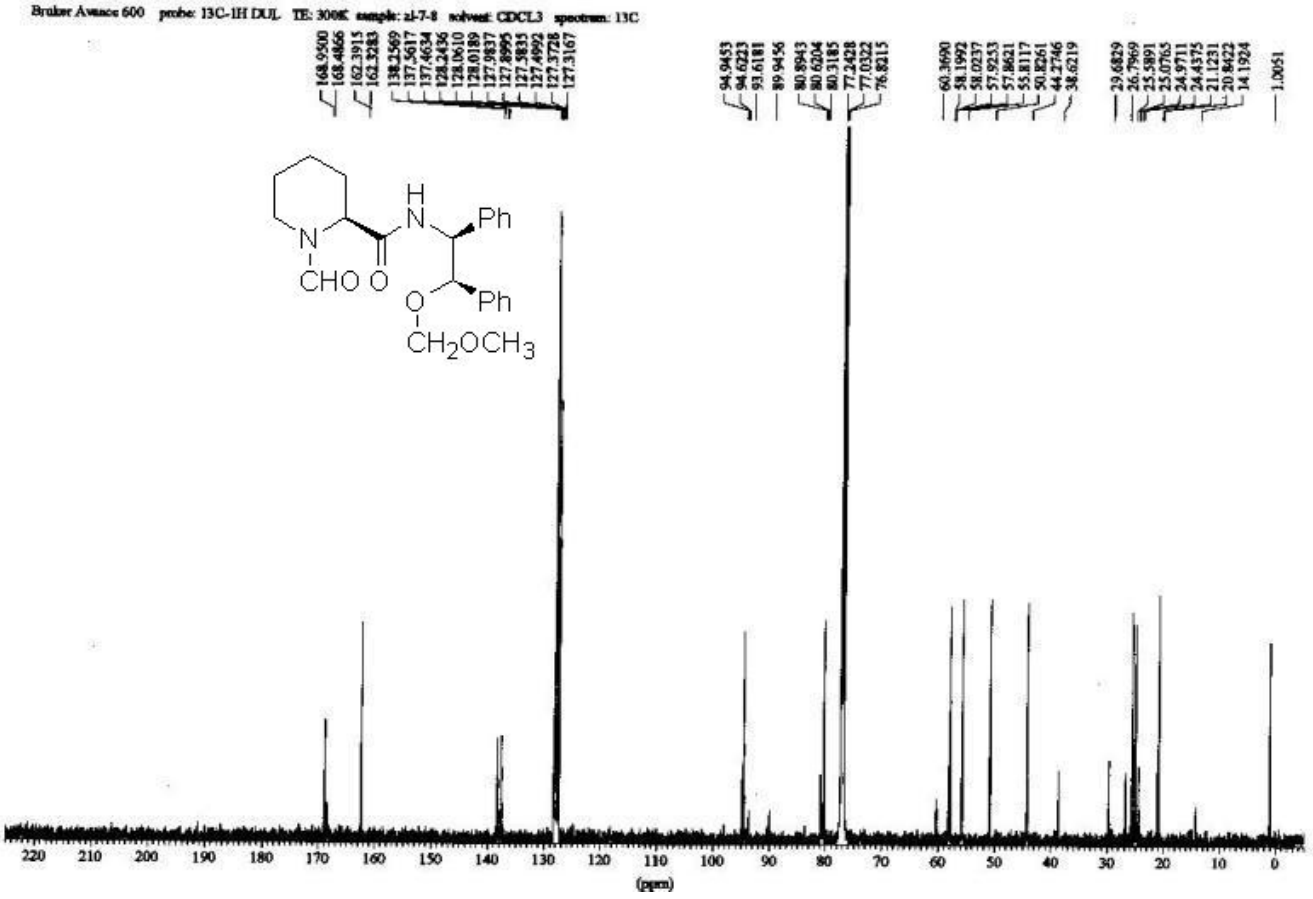
The NMR spectra of **5g**



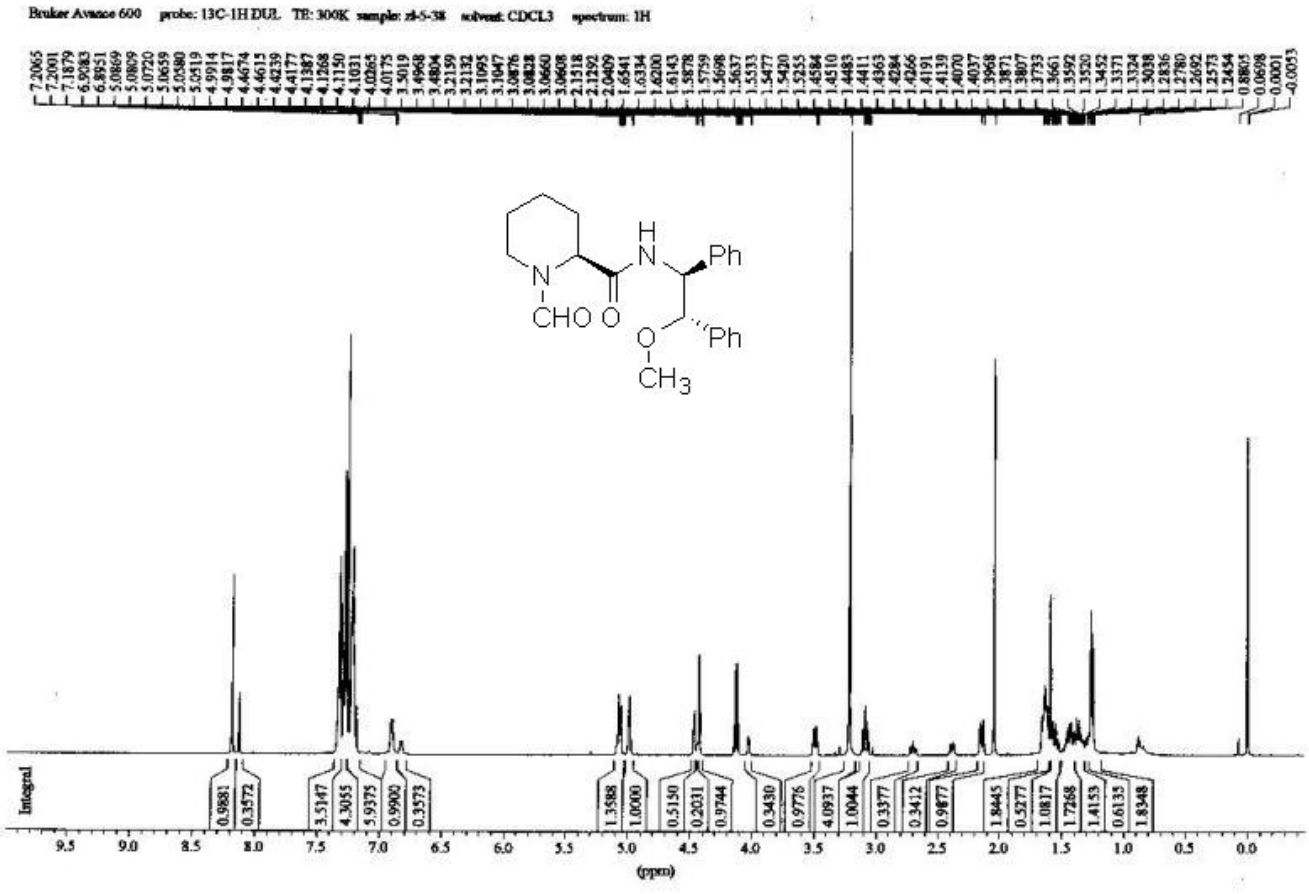


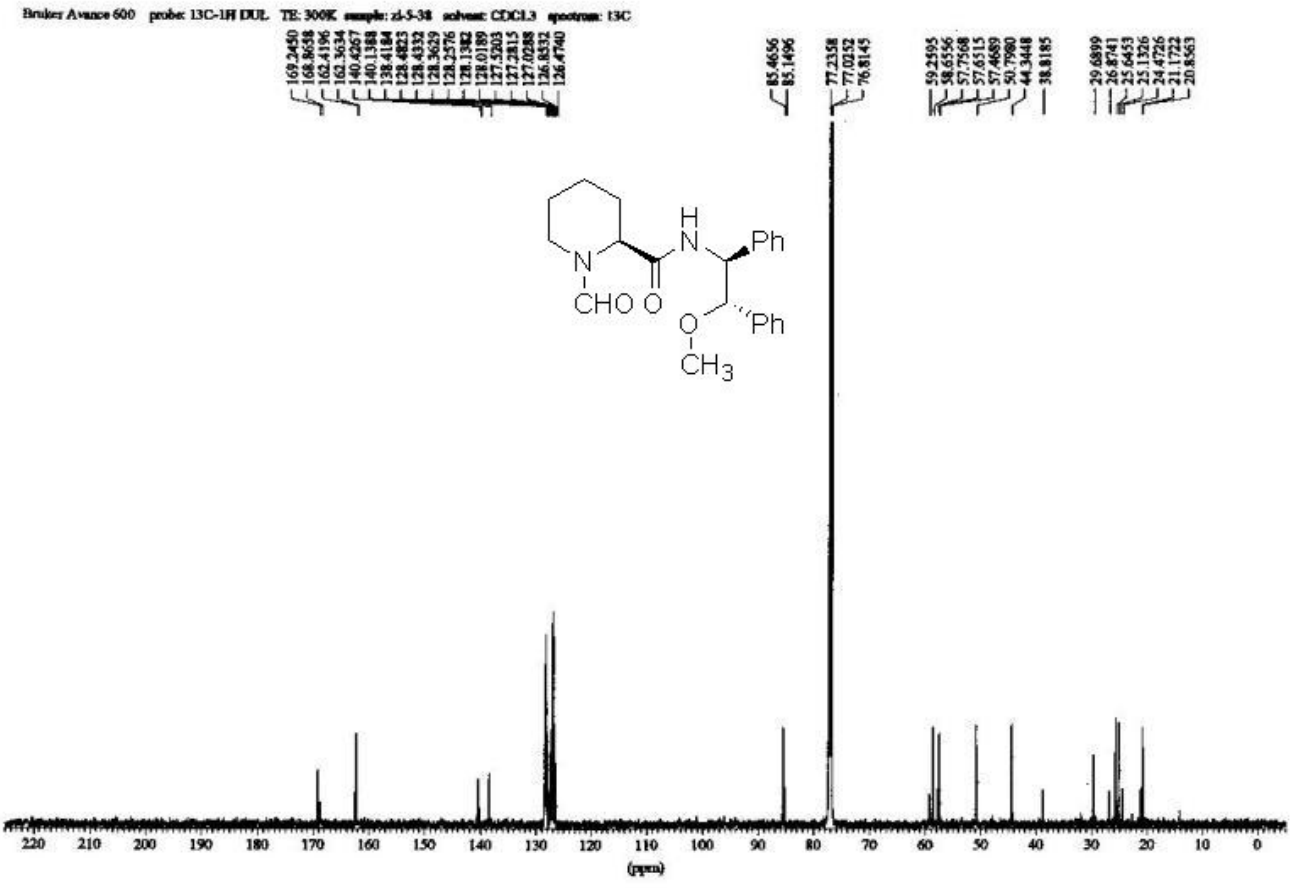
The NMR spectra of **5h**



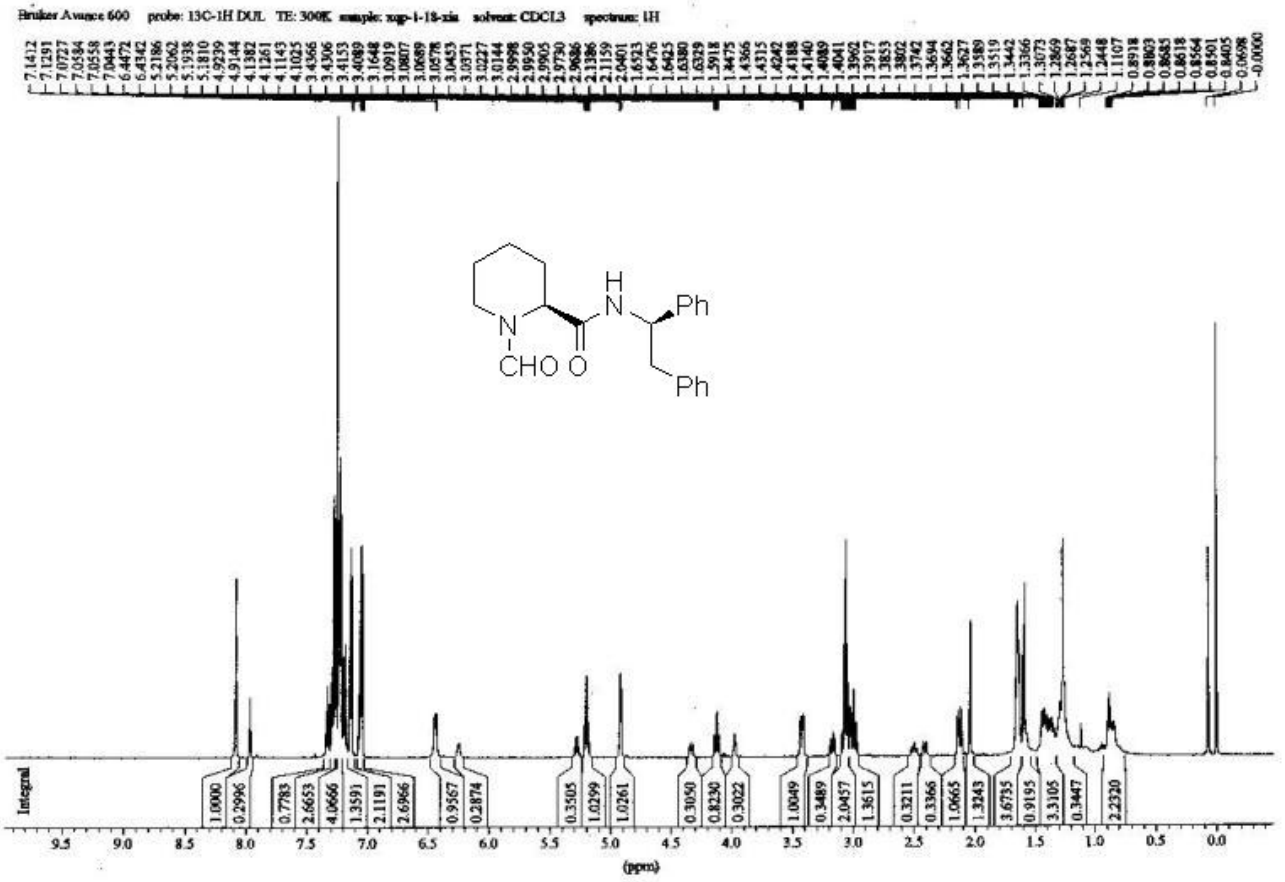


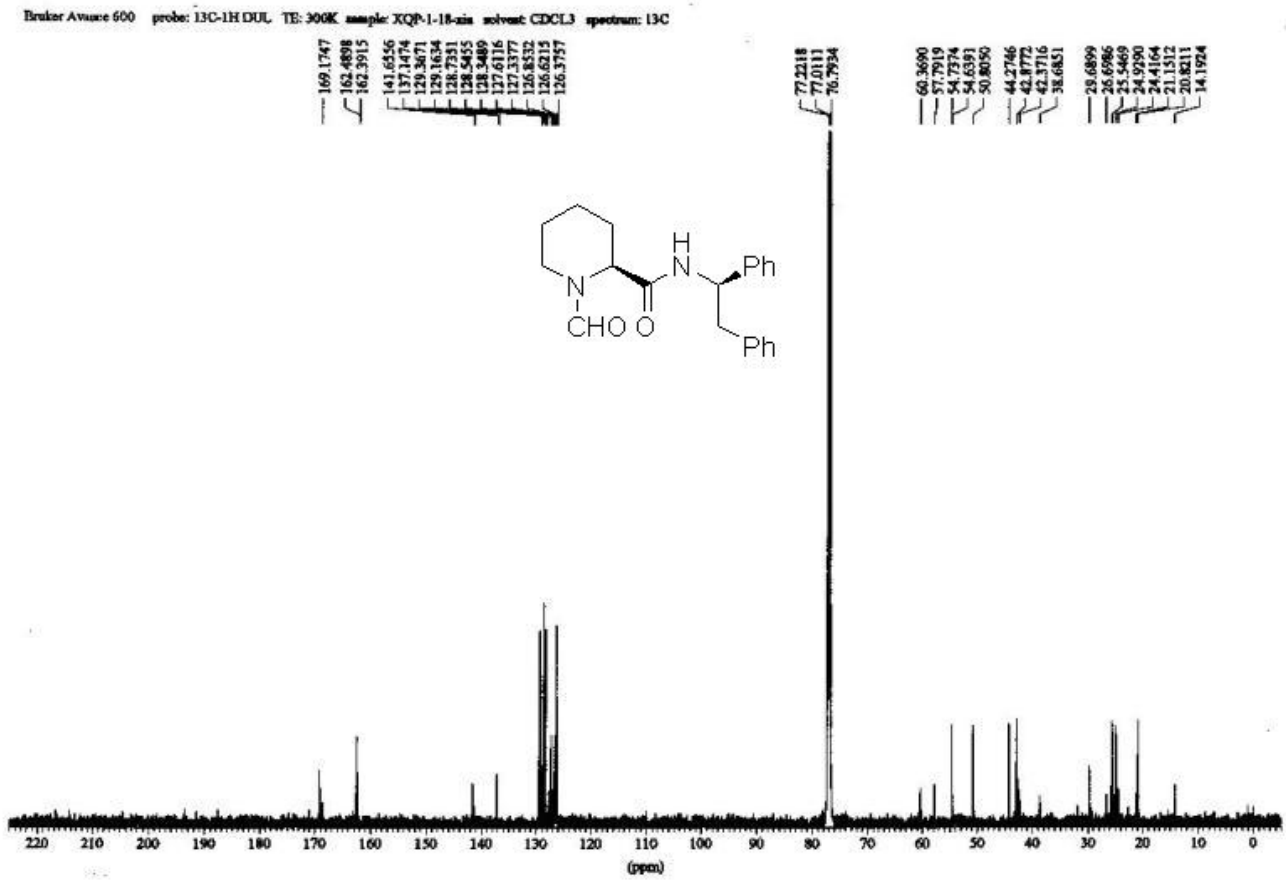
The NMR spectra of **10**





The NMR spectra of **11**



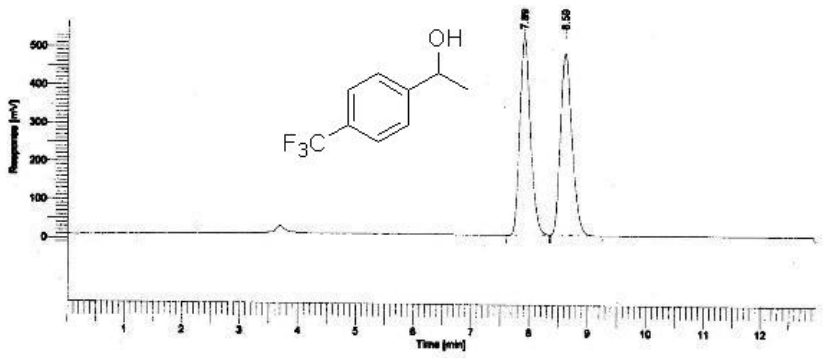


The HPLC spectra of **7a**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-5 10:23:48
Data Acquisition Time : 2006-2-27 17:54:06
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-CF3)Ph-CH(OH)-CH3\060227-5-12-2xx-oj5.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060227-5-12-2xx-oj5.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	7.886	6560888.32	516212.52	50.05
2	8.569	6548864.28	475558.32	49.95
		13109929.60	991770.84	100.00

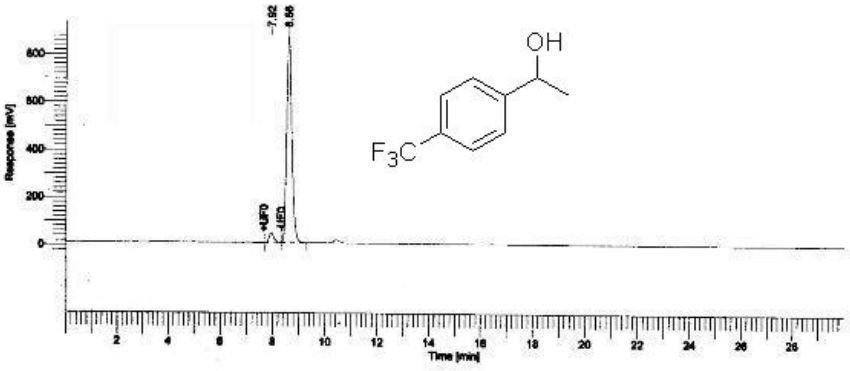
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-16-1
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-10 14:21:25
Data Acquisition Time : 2006-4-10 12:16:14
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-CF3)Ph-CH(OH)-CH3\060410-6-16-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060410-6-16-1.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	7.920	516602.56	41981.57	4.16
2	8.564	11898637.57	868470.89	95.84
		12415240.13	910452.46	100.00

Missing Component Report

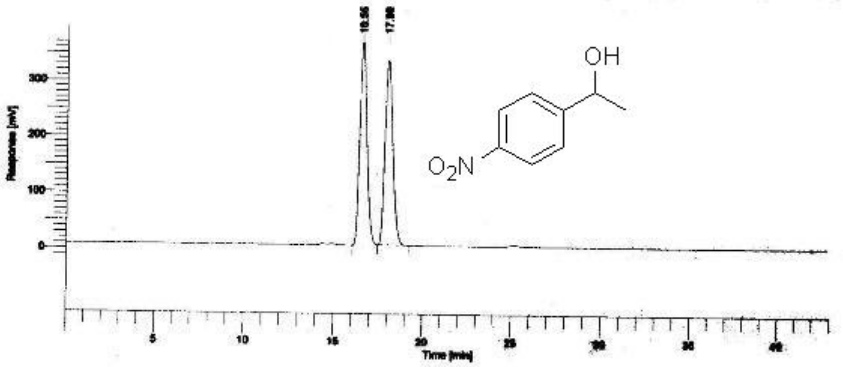
Component	Expected Retention (Calibration File)
PE series200	0.001

The HPLC spectra of **7b**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-5 10:26:05
Data Acquisition Time : 2005-12-22 15:48:06
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\wzy\(4-NO2)Ph-CH(OH)-CH3\051222-9-38-2XX-OJ10.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051222-9-38-2XX-OJ10.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	16.552	10081049.50	363819.92	50.00
2	17.991	10082797.62	330427.24	50.00
		20163847.12	694247.15	100.00

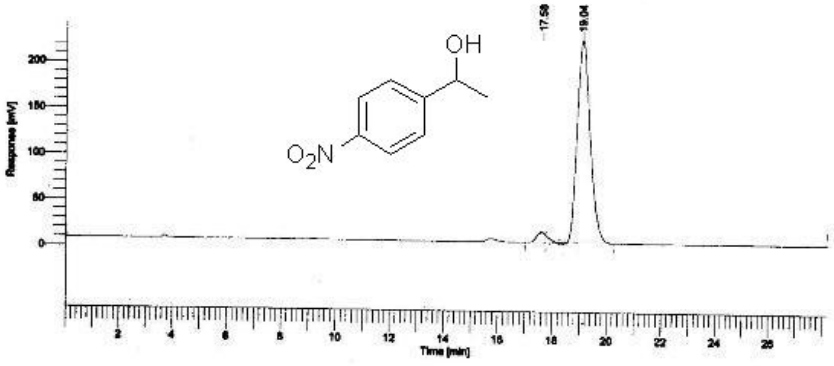
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-23-2
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-19 10:33:37
Data Acquisition Time : 2006-4-19 10:04:22
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-NO2)Ph-CH(OH)-CH3\060419-6-23-2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060419-6-23-2.seq



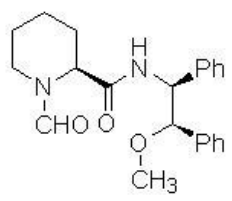
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	17.585	326621.97	11241.17	4.30
2	19.042	7274499.30	220255.65	95.70
		7601121.27	231496.83	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

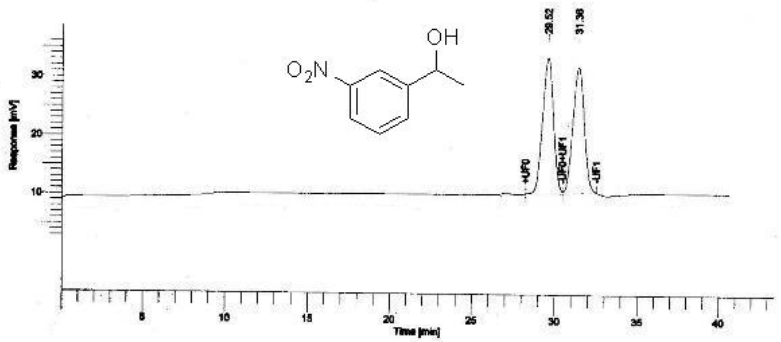


The HPLC spectra of **7c**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-8 10:24:24
Data Acquisition Time : 2006-6-8 9:39:15
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-NO2)Ph-CH(OH)-CH3\060608-7-10-1-od2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060608-7-10-1-od2.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	29.520	1052723.34	23198.15	50.75
2	31.387	1021552.31	21528.46	49.25
		2074275.65	44726.62	100.00

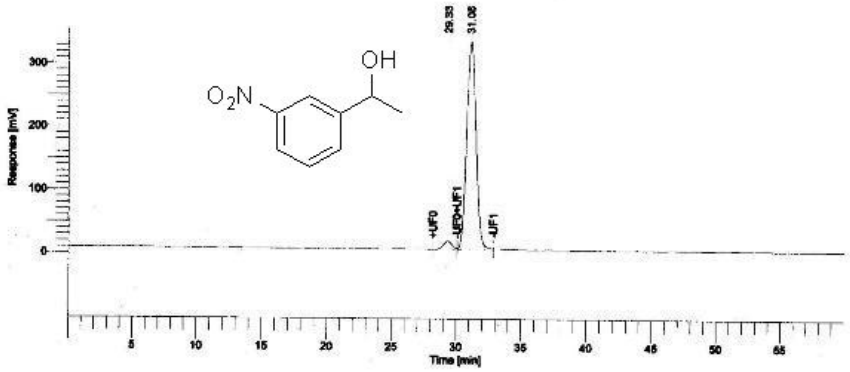
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-11-1
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-8 14:13:26
Data Acquisition Time : 2006-6-8 11:51:34
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-NO2)Ph-CH(OH)-CH3\060608-re7-11-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060608-re7-11-1.seq

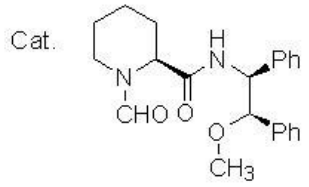


DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	29.327	617959.80	13104.53	3.61
2	31.078	16499339.38	328846.95	96.39
		17117299.18	341951.48	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

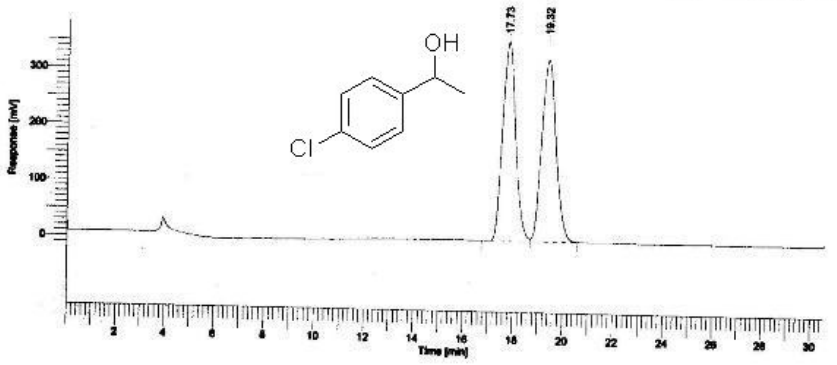


The HPLC spectra of **7d**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-7 15:10:29
Data Acquisition Time : 2006-6-7 14:39:09
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zf\(4-Cl)Ph-CH(OH)-CH3\060607-7-18xx-oj2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060607-7-18xx-oj2.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	17.727	12842085.99	354767.26	50.03
2	19.323	12829043.06	325034.75	49.97
		25671129.06	679802.01	100.00

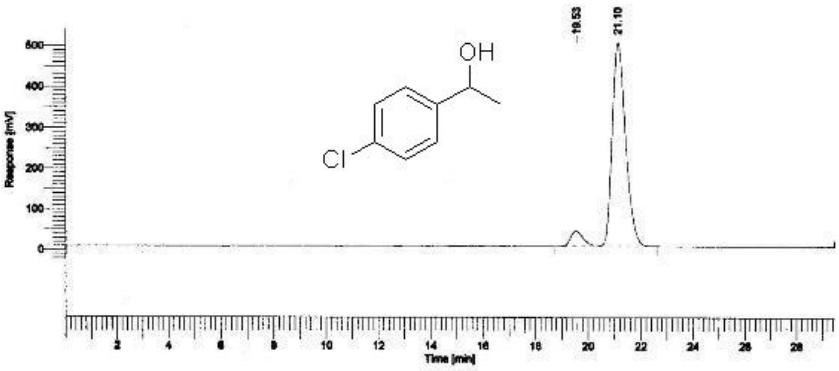
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-20-2
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-13 10:52:01
Data Acquisition Time : 2006-6-13 10:21:21
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zf\(4-Cl)Ph-CH(OH)-CH3\060613-7-20-2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060613-7-20-2.seq



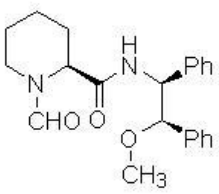
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	19.534	1282963.41	38329.03	6.75
2	21.100	17714392.77	498887.33	93.25
		18997356.18	537216.35	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

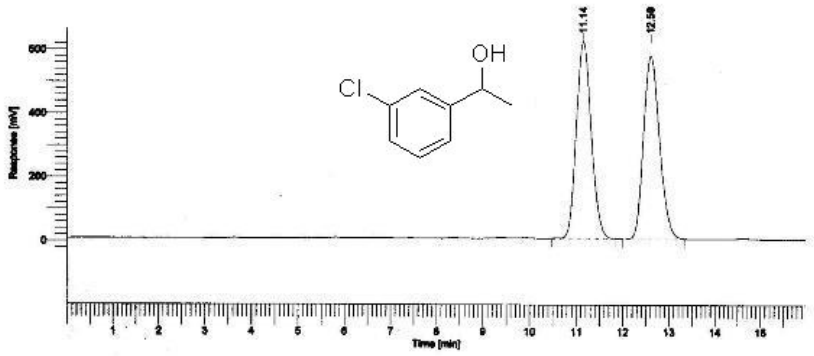


The HPLC spectra of **7e**

Software Version : 6.2.1.0.104:0104
Sample Name : ﾗｰｼｾﾐｯﾄ
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-26 16:32:20
Data Acquisition Time : 2006-4-26 16:15:33
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-Cl)Ph-CH(OH)-CH3\060426-6-38-4xx-oj5.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060426-6-38-4xx-oj5.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	11.138	13775658.96	617459.62	49.91
2	12.589	13826140.25	573482.16	50.09
		27601799.21	1.19e+06	100.00

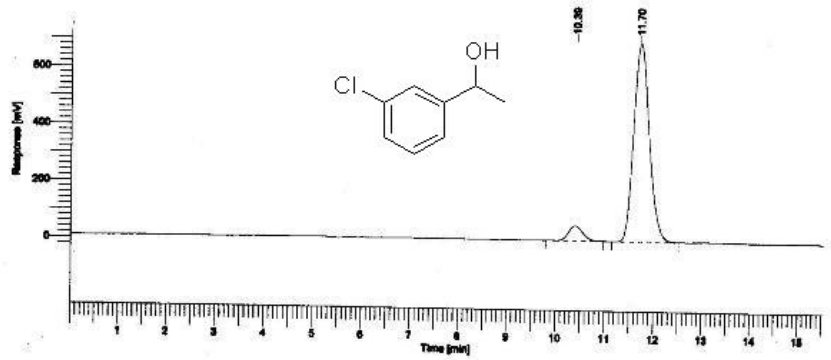
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-1-6
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-5-18 19:08:55
Data Acquisition Time : 2006-5-18 18:52:34
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-Cl)Ph-CH(OH)-CH3\060518-7-1-6.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060518-7-1-6.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	10.389	1082654.68	52754.70	6.42
2	11.696	15484916.01	694716.73	93.58
		16567570.69	747471.43	100.00

Missing Component Report

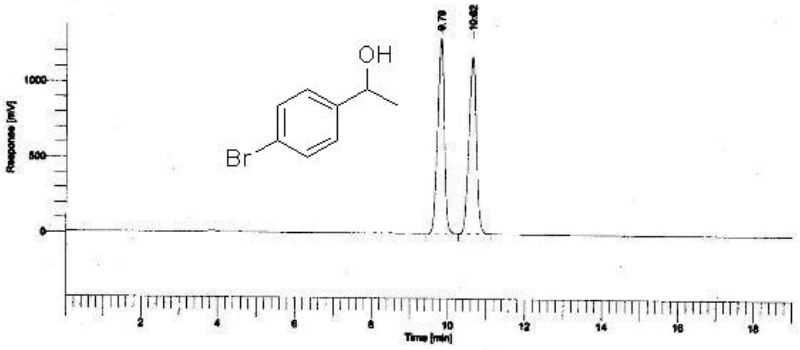
Component	Expected Retention (Calibration File)
PE series200	0.001

The HPLC spectra of **7f**

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-21
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-8 11:05:15
Data Acquisition Time : 2006-6-8 10:45:45
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-Br)Ph-CH(OH)-CH3\060608-re7-21xx-od5.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060608-re7-21xx-od5.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	9.787	15810911.28	1.29e+06	50.02
2	10.616	15796165.52	1.17e+06	49.98
		31607076.80	2.46e+06	100.00

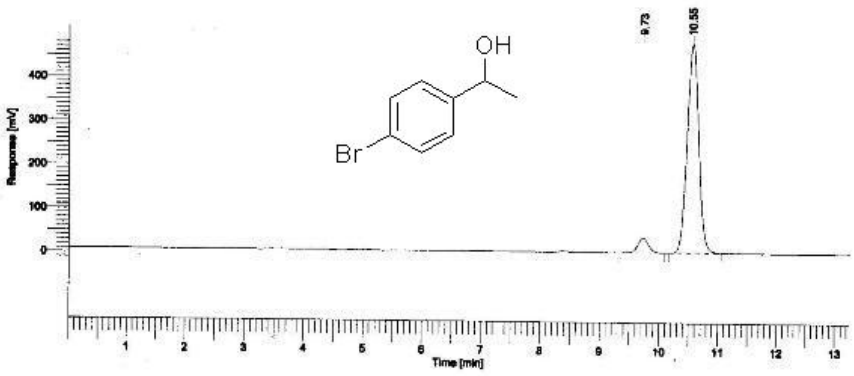
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-9 16:44:08
Data Acquisition Time : 2006-6-9 16:28:33
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-Br)Ph-CH(OH)-CH3\060609-re7-20-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060609-re7-20-1.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	9.728	412115.08	32900.49	5.94
2	10.552	6529718.43	477351.91	94.06
		6941833.52	510252.40	100.00

Missing Component Report

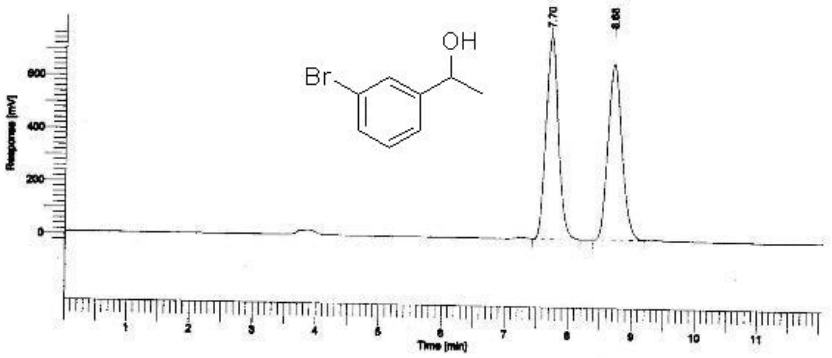
Component	Expected Retention (Calibration File)
PE series200	0.001

The HPLC spectra of **7g**

Software Version : 6.2.1.0.104:0104
Sample Name : ｸﾞﾗﾌ-2
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-26 12:37:21
Data Acquisition Time : 2006-4-26 12:24:36
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-Br)Ph-CH(OH)-CH3\060426-6-38-2xx-oj10.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060426-6-38-2xx-oj10.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	7.695	10353356.44	763881.78	50.37
2	8.683	10201700.00	663576.16	49.63
		20555056.44	1.43e+06	100.00

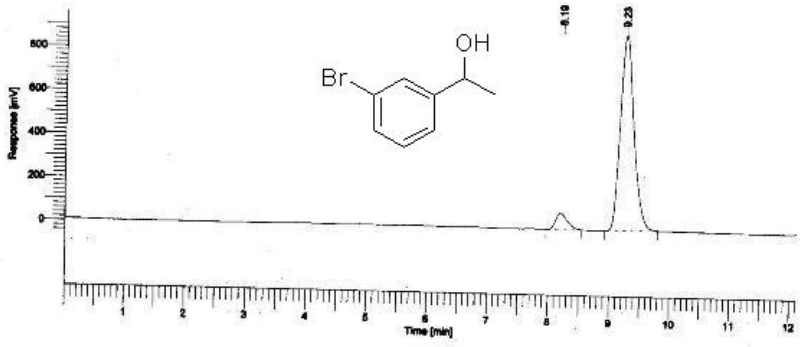
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-1-5
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-5-18 17:53:59
Data Acquisition Time : 2006-5-18 17:40:56
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(3-Br)Ph-CH(OH)-CH3\060518-7-1-5.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060518-7-1-5.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.188	979621.88	75711.49	6.57
2	9.226	13926668.48	897808.39	93.43
		14906290.36	973519.89	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

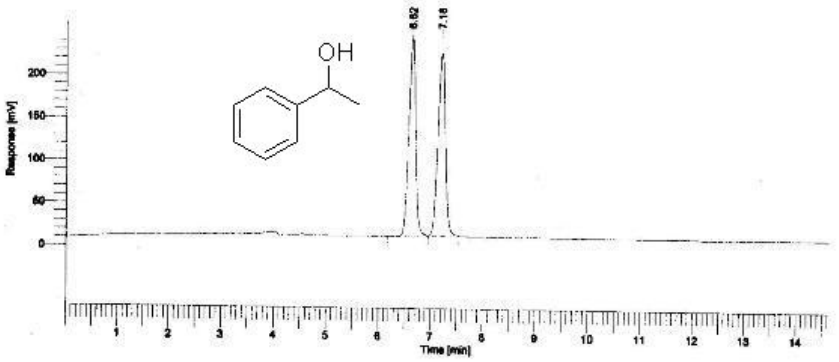
Cat.

The HPLC spectra of **7h**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-5 10:25:23
Data Acquisition Time : 2006-1-19 14:26:38
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\Ph-CH(OH)-CH3\060119-xx-od10.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060119-xx-od10.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	6.816	2145076.63	233035.60	50.05
2	7.184	2141217.61	214811.17	49.95
		4286294.24	447846.77	100.00

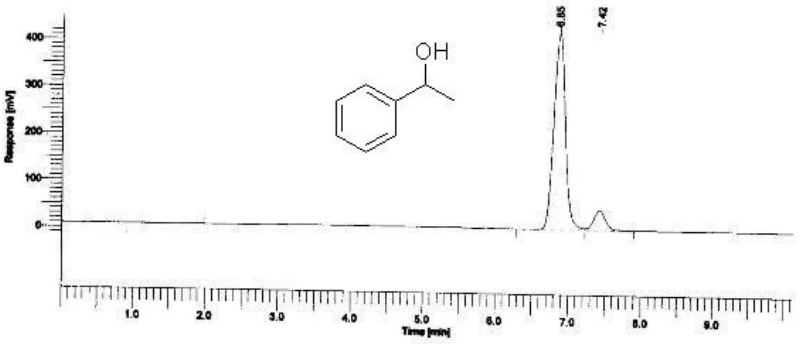
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-23-4
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-18 15:22:38
Data Acquisition Time : 2006-4-18 15:10:06
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\Ph-CH(OH)-CH3\060418-6-23-4.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060418-6-23-4.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	6.852	4554430.17	415575.58	90.57
2	7.421	474072.21	41944.64	9.43
		5028502.38	457520.23	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

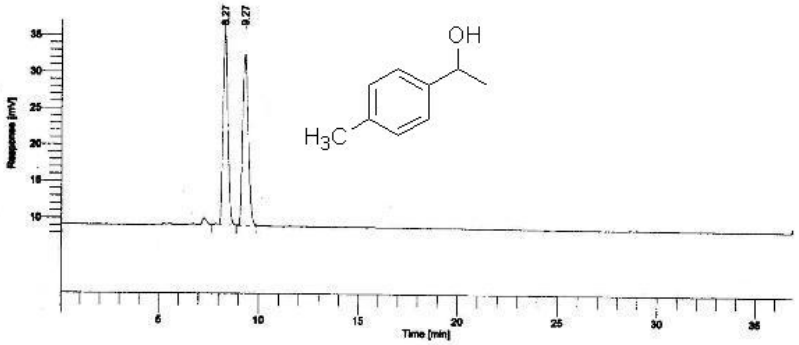
Cat.

The HPLC spectra of **7i**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-13 16:18:53
Data Acquisition Time : 2006-4-13 15:40:47
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-CH3)Ph-CH(OH)-CH3\060413-6-20xx-oj10.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060413-6-20xx-oj10.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.273	445454.83	26208.91	49.41
2	9.270	454135.65	23451.81	50.59
		897590.48	49660.72	100.00

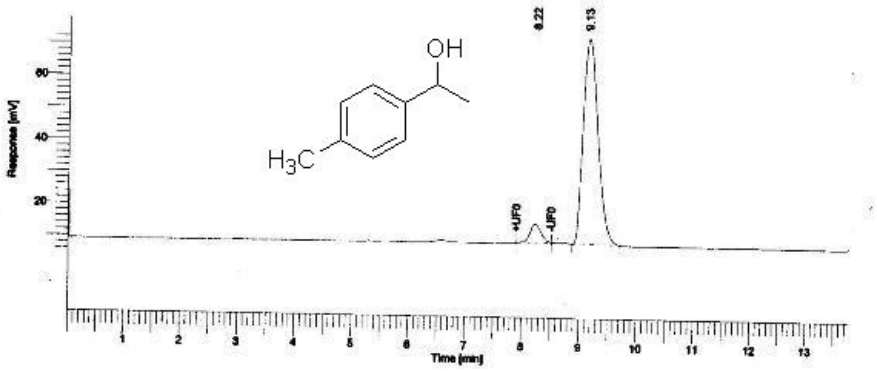
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-23-1
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-19 10:51:55
Data Acquisition Time : 2006-4-19 10:37:07
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-CH3)Ph-CH(OH)-CH3\060419-6-23-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060419-6-23-1.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.222	79432.04	5815.98	6.49
2	9.131	1144002.84	63929.81	93.51
		1223434.88	69745.79	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

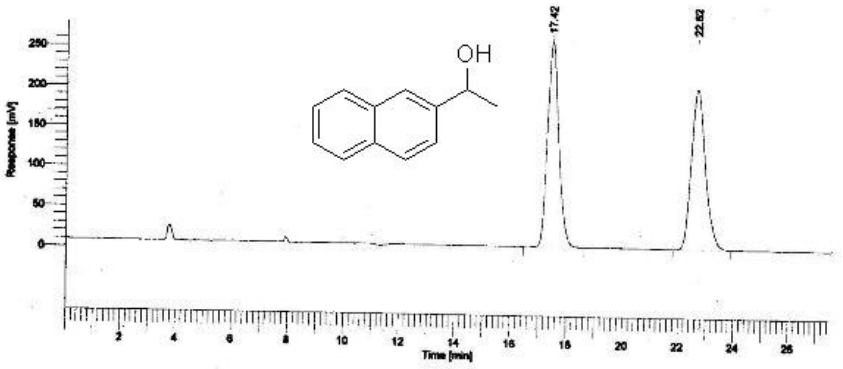
Cat.

The HPLC spectra of **7j**

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-34-1
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-4-26 10:31:45
Data Acquisition Time : 2006-4-26 10:03:28
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\NaP-CH(OH)-CH3\060426-6-34-1xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060426-6-34-1xx.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	17.425	6059129.35	255292.83	49.93
2	22.621	6079057.18	199015.09	50.07
		12138186.53	454307.92	100.00

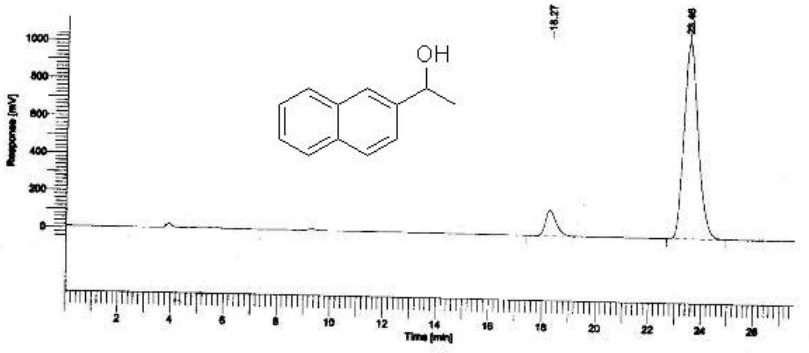
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-1-1
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-5-18 18:25:17
Data Acquisition Time : 2006-5-18 17:57:08
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\NaP-CH(OH)-CH3\060518-7-1-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060518-7-1-1.seq



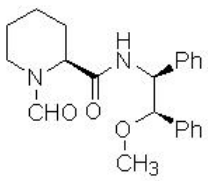
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	18.268	3869822.43	138155.08	8.89
2	23.461	39673463.36	1.05e+06	91.11
		43543285.79	1.19e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

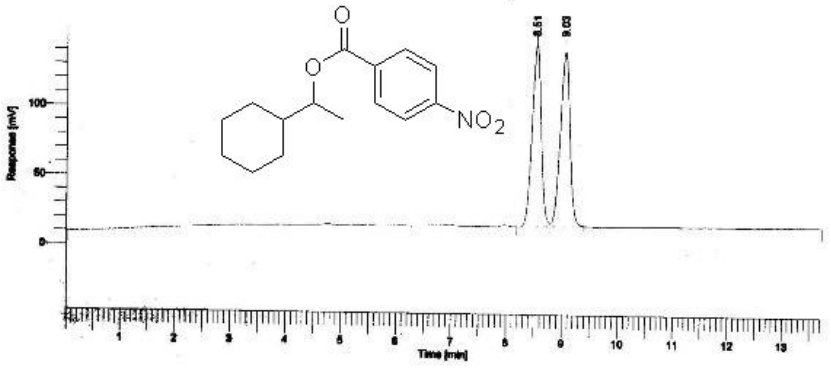


The HPLC spectra of the *para*-nitrobenzoic acid ester of **7k**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-22 20:15:23
Data Acquisition Time : 2006-6-22 19:53:55
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\cyclohexane-CH(OOC-Ph-4-NO2)-CH3\060622-xx-ad1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060622-xx-ad1.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.515	1493236.77	130793.76	49.89
2	9.028	1499869.64	125267.04	50.11
		2993106.41	256060.80	100.00

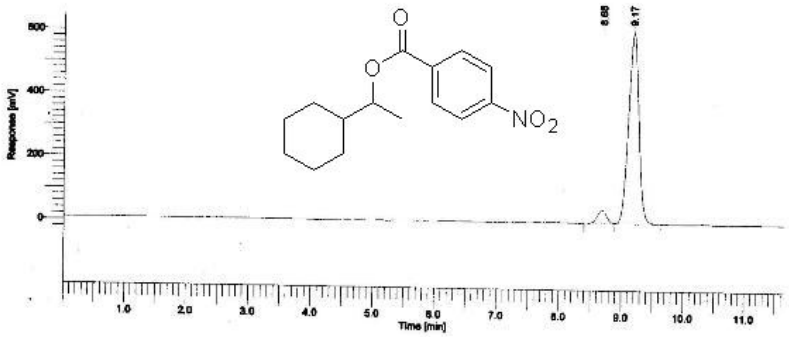
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-42
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-6-26 18:24:07
Data Acquisition Time : 2006-6-26 18:11:46
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\cyclohexane-CH(OOC-Ph-4-NO2)-CH3\060626-7-42.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060626-7-42.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.679	446636.76	42178.68	6.04
2	9.169	6949243.39	599269.09	93.96
		7395880.15	641447.77	100.00

Missing Component Report

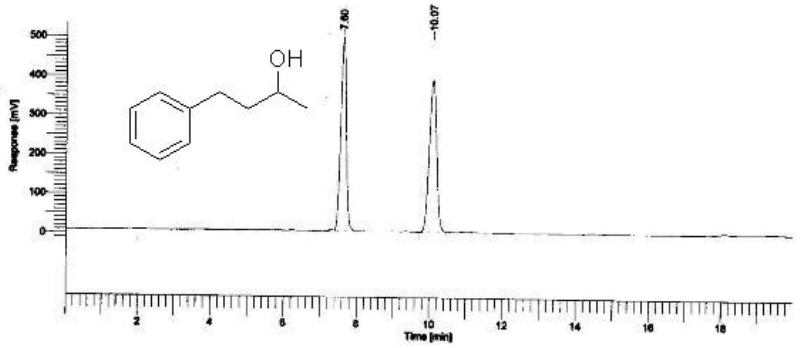
Component	Expected Retention (Calibration File)
PE series200	0.001

The HPLC spectra of **7l**

Software Version : 6.2.1.0.104:0104
Sample Name : zl6-34-5
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-5-16 15:39:30
Data Acquisition Time : 2006-5-16 15:18:10
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\Ph-C2H2-CH(OH)-CH3\060516-6-34-5xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060516-6-34-5xx.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	7.802	5243365.80	491563.71	49.29
2	10.072	5394428.02	388091.12	50.71
		10637793.83	879654.82	100.00

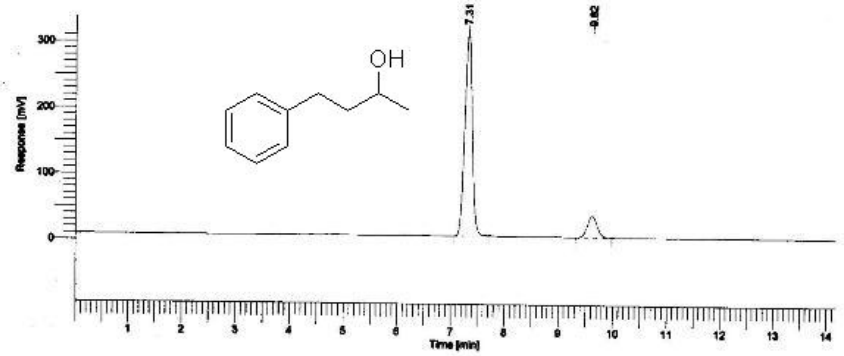
Missing Component Report

Instrument	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl7-2-2
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-5-22 17:01:03
Data Acquisition Time : 2006-5-22 16:46:04
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\Ph-C2H4-CH(OH)-CH3\060522-7-2-2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060522-7-2-2.seq



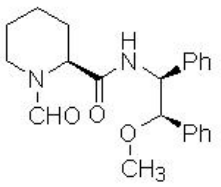
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	7.307	2981426.57	308274.55	87.89
2	9.615	412138.19	32774.89	12.11
		3403564.75	341049.43	100.00

Missing Component Report

Instrument	Expected Retention (Calibration File)
PE series200	0.001

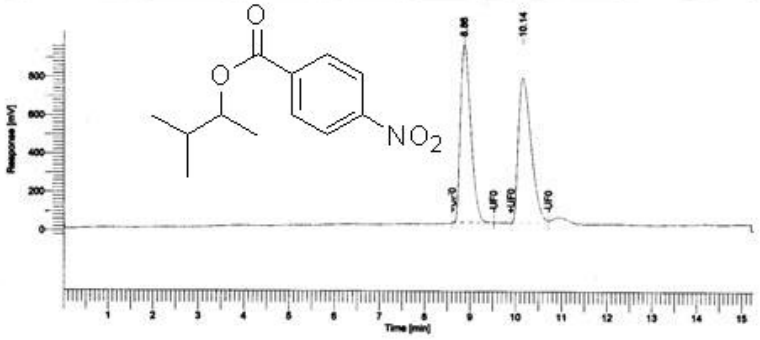
Cat.



The HPLC spectra the *para*-nitrobenzoic acid ester of **7m**

Software Version	: 6.2.1.0.104:0104	Date	: 2006-6-27 18:21:29
Sample Name	:	Data Acquisition Time	: 2006-6-27 18:04:59
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\(CH3)2CH-CH(OOC-Ph-4-NO2)-CH3\060627-xx-oj1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060627-xx-oj1.seq



DEFAULT REPORT

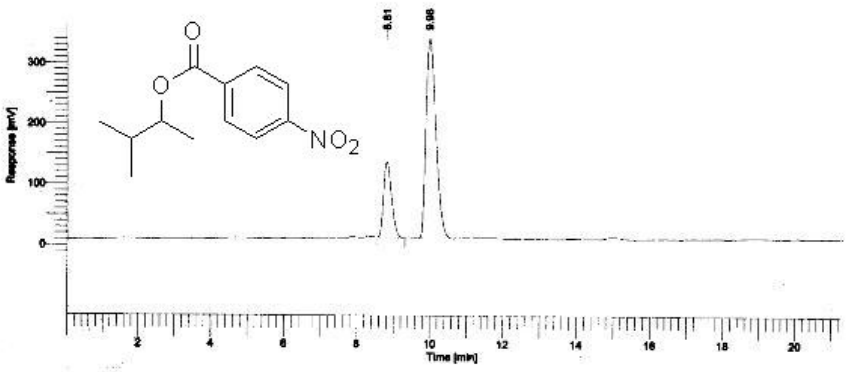
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.857	14600175.19	927571.35	49.91
2	10.142	14654790.61	755771.99	50.09
		29254965.80	1.68e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-6-30 14:17:32
Sample Name	: zl7-48	Data Acquisition Time	: 2006-6-30 12:52:38
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\(CH3)2CH-CH(OOC-Ph-4-NO2)-CH3\060630-7-48.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060630-7-48.seq



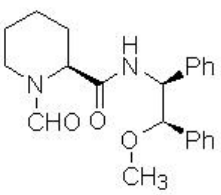
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	8.808	1925727.76	124894.27	23.54
2	9.981	6254022.12	329584.89	76.46
		8179749.88	454479.15	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

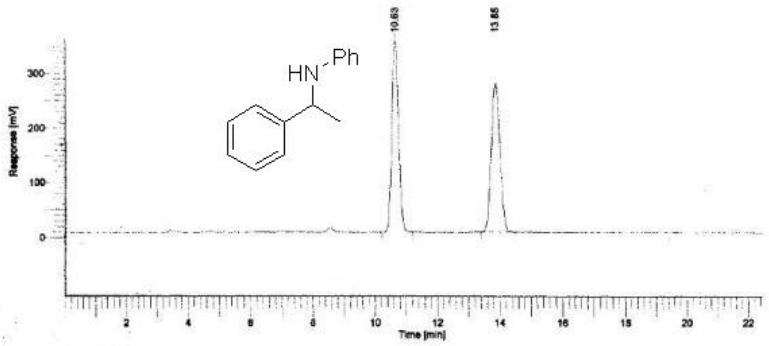


The HPLC spectra of **9a**

Software Version : 6.2.1.0.104:0104
Sample Name : wzy5-13-2
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2005-11-2 13:56:20
Data Acquisition Time : 2005-5-18 9:57:42
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\wzy\Ph-CH(NH-Ph)-CH3\050518-5-13-2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\050518-5-13-1-20050518-095515.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	10.630	5214192.14	350277.69	50.06
2	13.854	5200859.45	272623.31	49.94
		10415051.58	622901.00	100.00

Missing Component Report

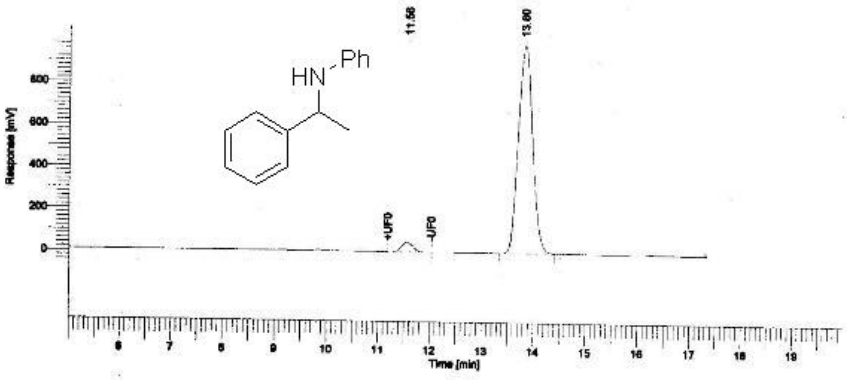
Component	Expected Retention (Calibration File)
PE serise200	0.001

Time [min]

Software Version : 6.2.1.0.104:0104
Sample Name : zl8-8-6
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-10 11:50:41
Data Acquisition Time : 2006-7-10 11:32:20
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\Ph-CH(NH-Ph)-CH3\060710-8-8-6.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060710-8-8-6.seq



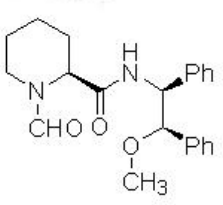
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	11.557	694773.14	45718.76	3.59
2	13.803	18675364.43	986086.96	96.41
		19370137.57	1.03e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

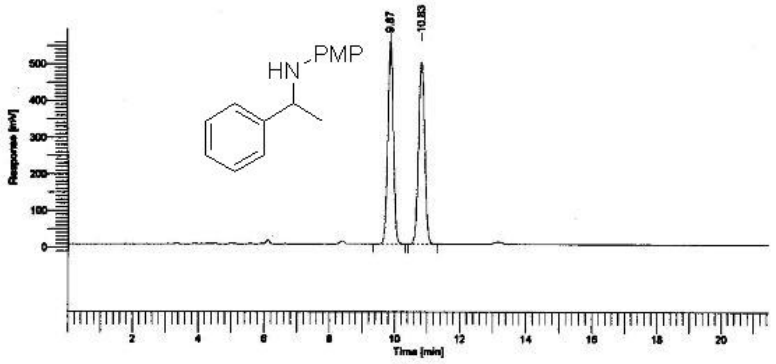
Cat.



The HPLC spectra of **9b**

Software Version	: 6.2.1.0.104:0104	Date	: 2006-11-21 15:16:24
Sample Name	:	Data Acquisition Time	: 2005-7-4 17:10:59
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\wzy\Ph-CH(NH-Ph-4-OMe)-CH3\050704-xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\050704-xx-20050704-165620.seq



DEFAULT REPORT

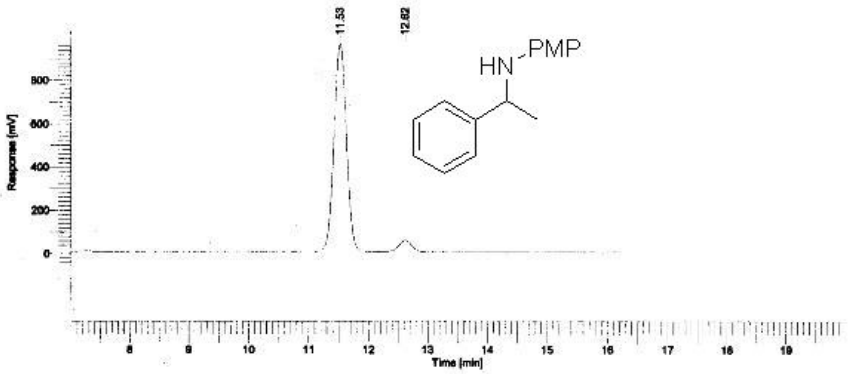
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	9.875	6656863.03	552813.80	50.12
2	10.831	6624389.39	496336.67	49.88
		13281252.42	1.05e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-7-13 9:57:34
Sample Name	: zl8-10-1	Data Acquisition Time	: 2006-7-13 9:40:37
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\Ph-CH(NH-Ph-4-OMe)-CH3\060713-8-10-1.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060713-8-10-1.seq



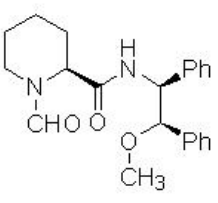
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	11.530	13857581.40	960684.65	94.29
2	12.621	838545.15	53363.91	5.71
		14696126.55	1.01e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

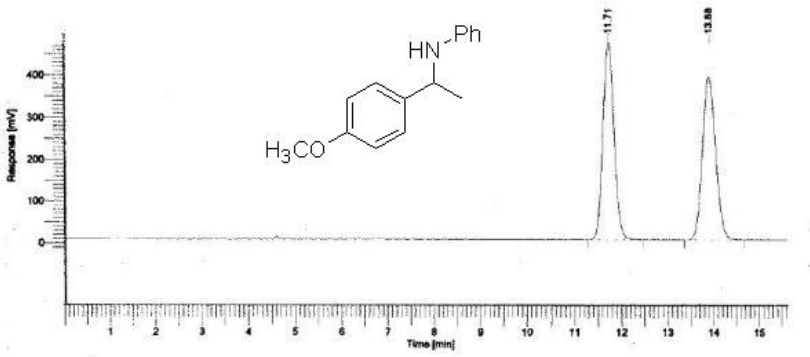


The HPLC spectra of **9c**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2005-10-9 14:52:37
Data Acquisition Time : 2005-10-9 10:39:04
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\wzy\(4-O-CH3)Ph-CH(NH-Ph)-CH3\051009-3-45-3xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051009-3-45-3xx.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	11.706	7756574.26	468946.10	49.91
2	13.880	7785965.39	386293.01	50.09
		15542539.65	855239.11	100.00

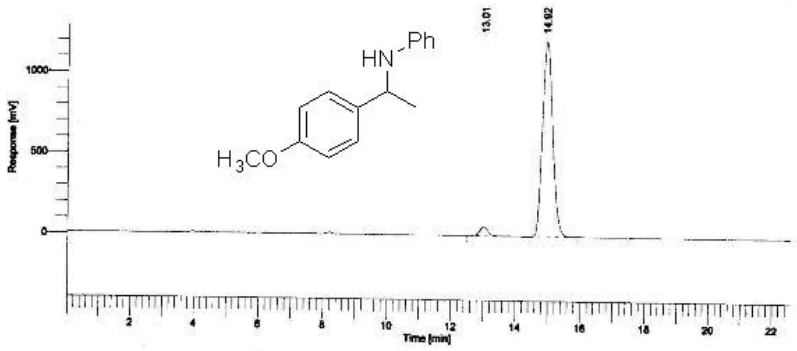
Missing Component Report

Component	Expected Retention (Calibration File)
PE serise200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl8-17-4
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-31 17:05:15
Data Acquisition Time : 2006-7-31 16:42:17
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(4-OCH3)Ph-CH(NH-Ph)-CH3\060731-8-17-4.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060731-8-17-4.seq



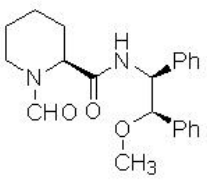
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	13.012	[illegible]	57329.07	3.74
2	14.921	26497550.41	1.21e+06	96.26
		27484885.01	1.27e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

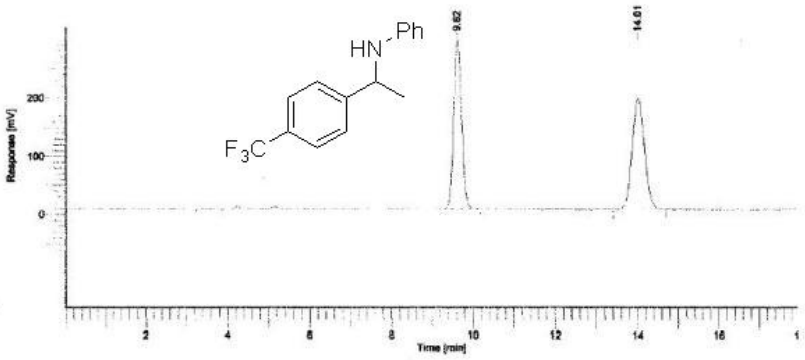
Cat.



The HPLC spectra of **9d**

Software Version	: 6.2.1.0.104:0104	Date	: 2005-11-2 9:52:16
Sample Name	:	Data Acquisition Time	: 2005-11-2 9:30:03
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\wzy\(4-CF3)Ph-CH(NH-Ph)-CH3\051102-9-3-2xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051102-9-3-2xx.seq



DEFAULT REPORT

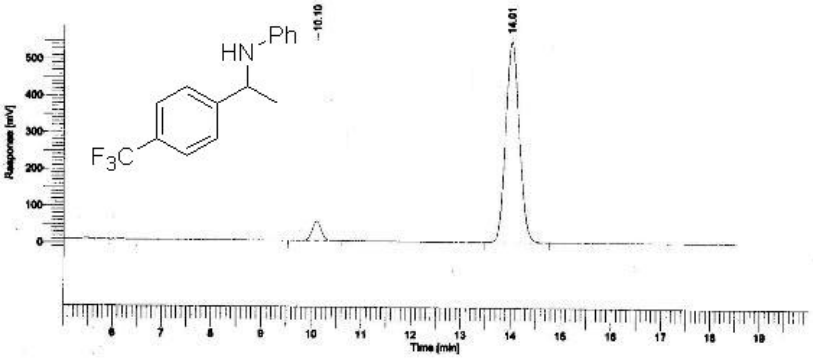
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	9.623	3932457.03	289134.89	49.77
2	14.010	3968977.67	190546.55	50.23
		7901434.70	479681.44	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-7-13 11:57:17
Sample Name	: zl8-10-2	Data Acquisition Time	: 2006-7-13 11:38:20
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\(4-CF3)Ph-CH(NH-Ph)-CH3\060713-8-10-2.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060713-8-10-2.seq



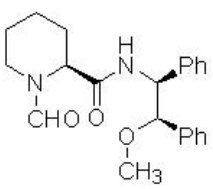
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	10.101	672913.57	52762.01	6.14
2	14.008	10295306.96	546284.99	93.86
		10968220.53	599047.00	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

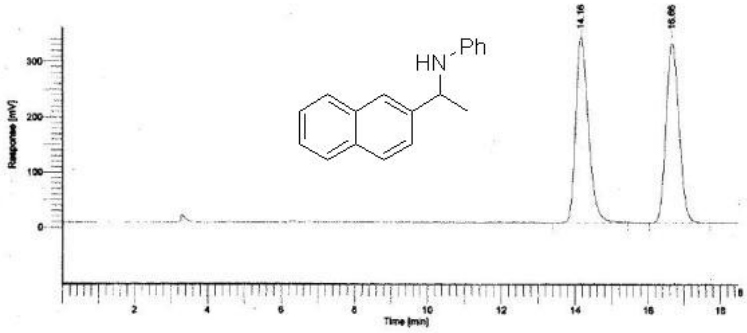
Cat.



The HPLC spectra of **9e**

Software Version	: 6.2.1.0.104:0104	Date	: 2005-10-9 14:49:39
Sample Name	:	Data Acquisition Time	: 2005-10-9 11:47:33
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\wzy\NaP-CH(NH-Ph)-CH3\051009-3-45-4xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051009-3-45-4xx.seq



DEFAULT REPORT

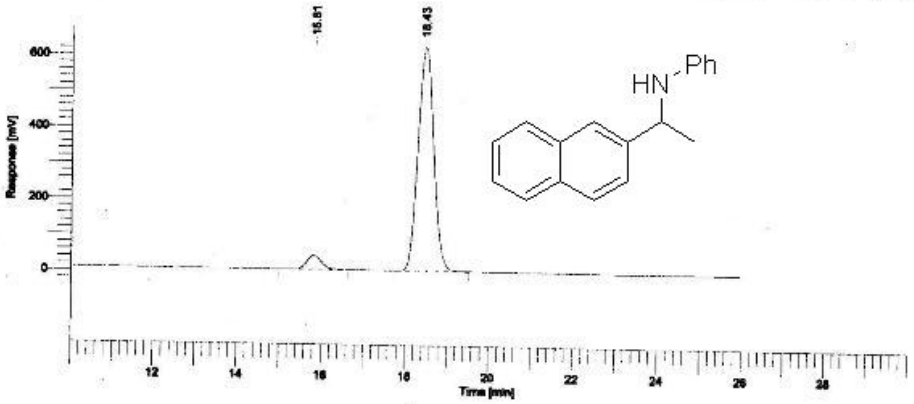
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	14.162	8026022.88	334356.45	49.64
2	16.659	8140874.05	323943.46	50.36
		16166896.93	658299.91	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE serise200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-7-13 13:06:07
Sample Name	: zl8-10-3	Data Acquisition Time	: 2006-7-13 12:39:34
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\NaP-CH(NH-Ph)-CH3\060713-8-10-3.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060713-8-10-3.seq



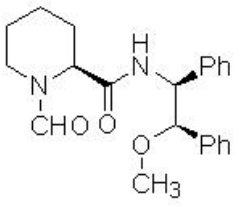
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	15.812	929595.90	38439.88	5.42
2	18.428	16215642.78	624621.37	94.58
		17145238.68	663061.25	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

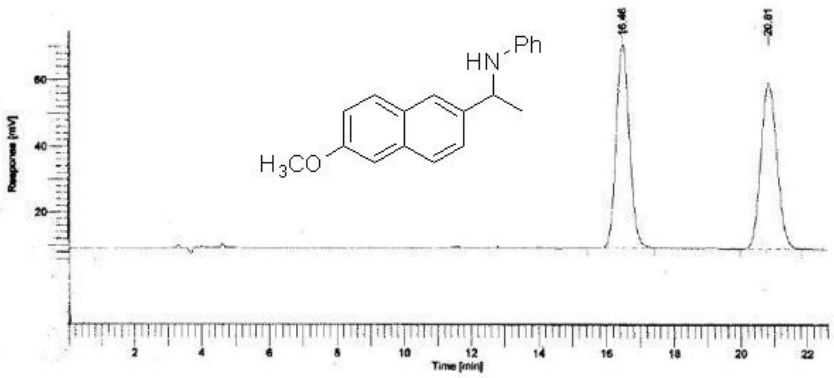
Cat.



The HPLC spectra of **9f**

Software Version	: 6.2.1.0.104:0104	Date	: 2005-10-9 16:04:58
Sample Name	:	Data Acquisition Time	: 2005-10-9 15:38:24
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\wzy\(6-O-CH3)NaP-2-CH(NH-Ph)-CH3\051009-3-45-1xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051009-3-45-1xx.seq



DEFAULT REPORT

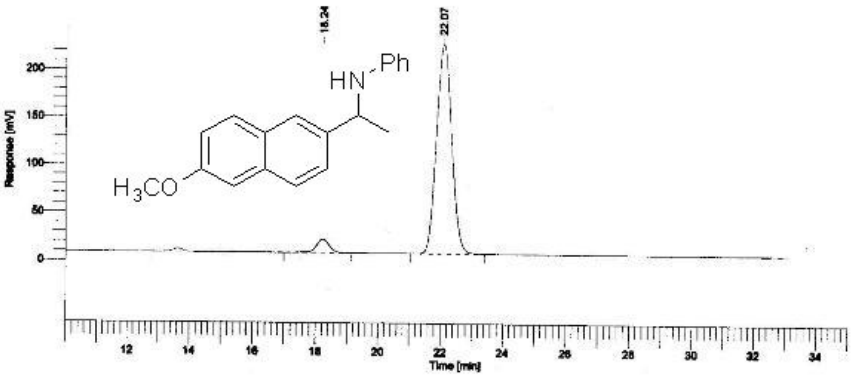
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	16.461	1659845.52	61167.70	49.57
2	20.811	1688588.54	49848.62	50.43
		3348434.05	111016.32	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-7-18 10:50:11
Sample Name	: zl8-12-4	Data Acquisition Time	: 2006-7-18 10:16:30
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\(6-O-CH3)NaP-2-CH(NH-Ph)-CH3\060718-8-12-4.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060718-8-12-4.seq



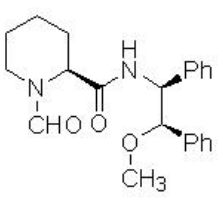
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	18.236	389760.97	13774.57	4.97
2	22.073	7452271.19	220293.89	95.03
		7842032.16	234068.46	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

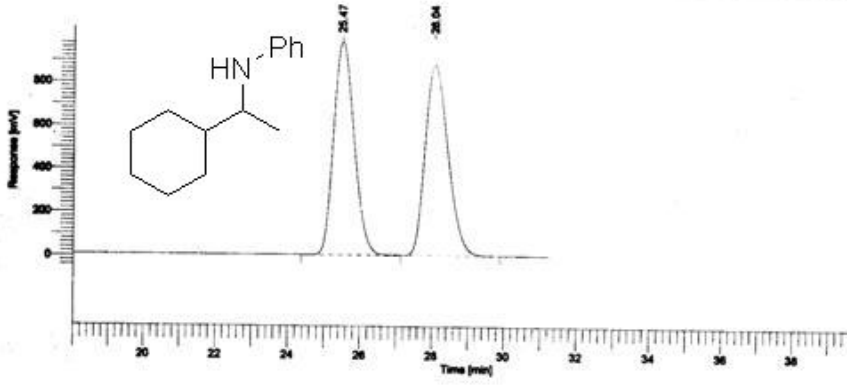


The HPLC spectra of **9g**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-8-17 12:17:53
Data Acquisition Time : 2006-8-17 11:46:13
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\pd\cyclohexane-CH(NH-Ph)-CH3\060817-xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060817-xx-20060817-112657.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	25.469	38802444.51	982078.85	49.97
2	28.039	38855869.46	879252.53	50.03
		77658313.97	1.86e+06	100.00

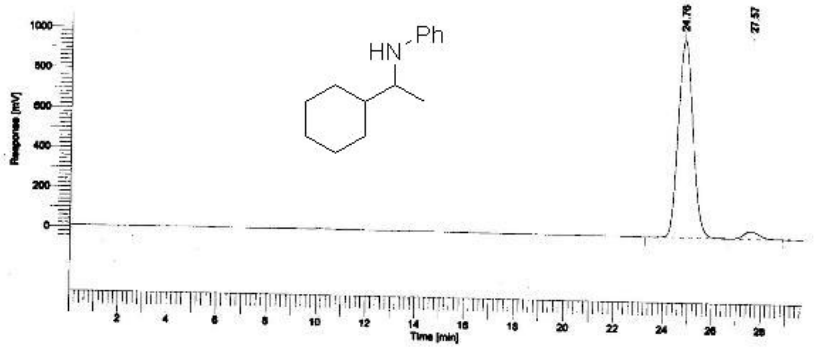
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl8-10-4
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-13 16:51:04
Data Acquisition Time : 2006-7-13 16:20:38
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\cyclohexane-CH(NH-Ph)-CH3\060713-8-10-4.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060713-8-10-4.seq



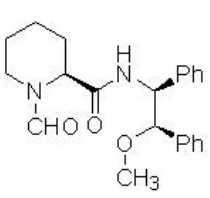
DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	24.759	41435452.37	992064.85	96.09
2	27.566	1687173.02	37487.35	3.91
		43122625.39	1.03e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.

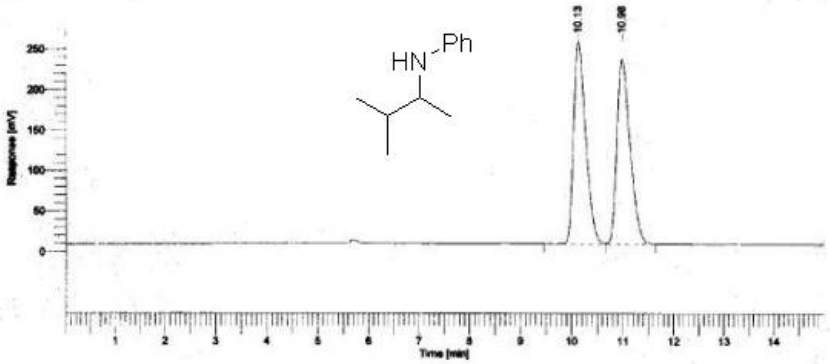


The HPLC spectra of **9h**

Software Version : 6.2.1.0.104:0104
Sample Name :
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2005-12-9 12:03:22
Data Acquisition Time : 2005-12-9 11:45:51
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\wzy\(CH3)2CH-CH(NH-Ph)-CH3\051209-xx.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051209-xx.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	10.126	4071384.72	249188.98	50.05
2	10.979	4062742.86	227372.81	49.95
		8134127.58	476561.79	100.00

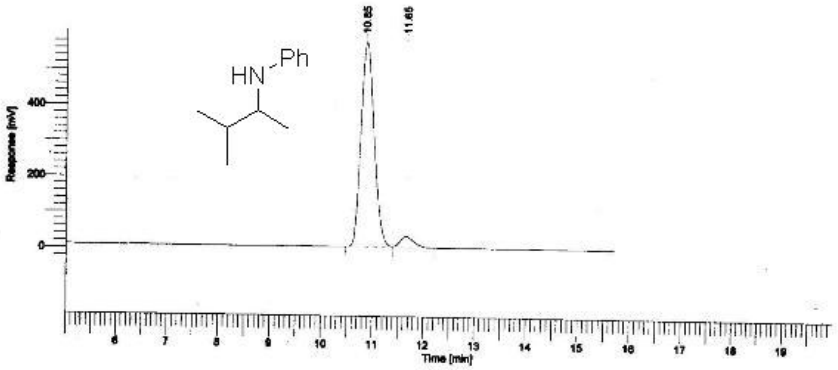
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version : 6.2.1.0.104:0104
Sample Name : zl8-15-3
Instrument Name : HPLC
Rack/Vial : 0/0
Sample Amount : 1.000000
Cycle : 1

Date : 2006-7-27 17:15:05
Data Acquisition Time : 2006-7-27 16:58:48
Channel : A
Operator : manager
Dilution Factor : 1.000000

Result File : D:\LC\zl\(CH3)2CH-CH(NH-Ph)-CH3\060727-8-15-3.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060727-8-15-3.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	10.890	10230634.31	573314.97	94.69
2	11.652	574090.69	30757.92	5.31
		10804725.00	604072.89	100.00

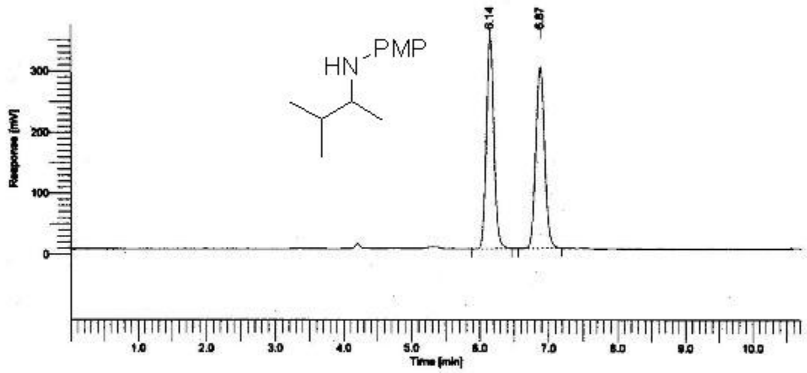
Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

The HPLC spectra of **9i**

Software Version	: 6.2.1.0.104:0104	Date	: 2006-11-14 11:55:07
Sample Name	:	Data Acquisition Time	: 2005-12-13 15:59:53
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\wzy\(CH3)2CH-CH(NH-Ph-4-OCH3)-CH3\051213-XX.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\051213-XX.seq



DEFAULT REPORT

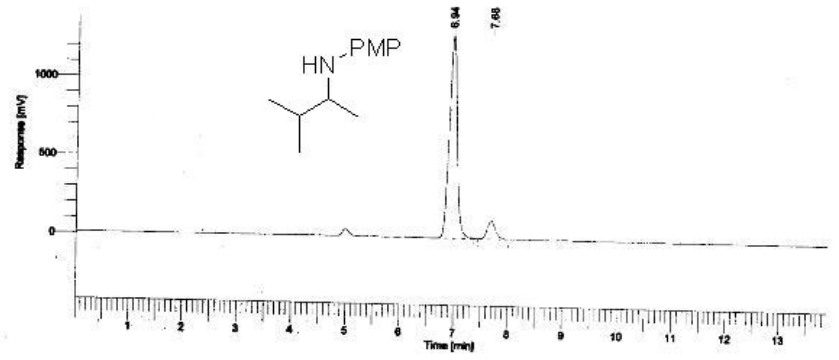
Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	6.142	2656384.40	344477.80	50.07
2	6.870	2648834.80	297252.66	49.93
		5305219.21	641730.46	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Software Version	: 6.2.1.0.104:0104	Date	: 2006-7-26 16:09:51
Sample Name	: zl8-15-4	Data Acquisition Time	: 2006-7-26 15:55:19
Instrument Name	: HPLC	Channel	: A
Rack/Vial	: 0/0	Operator	: manager
Sample Amount	: 1.000000	Dilution Factor	: 1.000000
Cycle	: 1		

Result File : D:\LC\zl\(CH3)2CH-CH(NH-Ph-4-OCH3)-CH3\060726-8-15-4.rst
Sequence File : C:\PenExe\TcWS\Ver6.2.1\Examples\060726-8-15-4.seq



DEFAULT REPORT

Peak #	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1	6.939	12904538.06	1.29e+06	91.57
2	7.680	1188461.17	112506.55	8.43
		14092999.22	1.40e+06	100.00

Missing Component Report

Component	Expected Retention (Calibration File)
PE series200	0.001

Cat.