A Strategy to Synthesize Taxol Side Chain and (-)-*epi*-Cytoxazone via Chiral Brønsted Acid-$Rh_2(OAc)_4$ Co-catalyzed Enantioselective Three-Component Reactions

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1. General information & Materials

1.1 General information: HRMS (ESI) Mass spectra were recorded on IonSpec FT-ICR mass spectrometer at State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University. NMR spectra were recorded on a Brucker-400 MHz spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump) & Shimadzu (SPD-20AV UV-VIS Detector and LC-20AT Liquid Chromatograph Pump). Chiralpak IA was purchased from Daicel Chemical Industries, LTD. The racemic standards used in HPLC studies were prepared according to the general procedure by using racemic BINOL derivatived phosphoric acid catalyst.

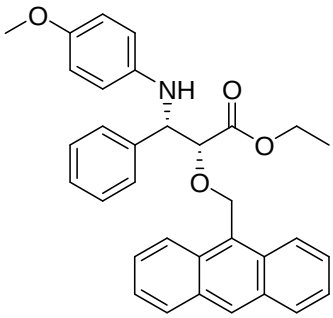
1.2 Materials: Dichloromethane was distilled over calcium hydride. Aldimines **4** and **6** were prepared from condensation of the corresponding aldehydes with amines according to the literature method.[1] chiral phosphoric acid **1a-f** were prepared according to the literature.[2] Solvents for the column chromatography were distilled before use. All reactions were carried out under argon atmosphere in a well-dried glassware.

2. General Procedure for the Enantioselective Three-Component Reactions ：

A suspension of $Rh_2(OAc)_4$ (2.2 mg, 2 mmol%), chiral phosphoric acid **1** (5 mmol%), alcohol **3** (0.275 mmol, 1.1 eq) , imine **3** or **6** (0.25 mmol, 1 eq) and 4Å MS (0.1 g) in 2 mL CH_2Cl_2 under argon atmosphere was cooled to 0℃, and then diazo compound 1 (0.3 mmol, 1.2 eq) in 1 mL CH_2Cl_2 was added over 1 h via a syringe pump. After completion of the addition, the reaction was stirred for another 0.5 h and followed by addition of saturated aqueous $NaHCO_3$ (0.1 mL) to quench the reaction. Solvent was removed and the crude products were purified by flash chromatography on silica gel (eluent: EtOAc/light petroleum ether = 1:40~ 1:20) to give the three-component reaction products. Diastereoselectivity was determined by 1H NMR spectroscopy of the crude reaction mixture.

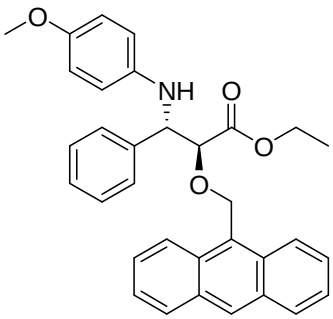
3. NMR and HRMS(ESI) analysis data of compounds 5b,d-h, 7a-i(5a, see [ref 4a], 5c see [ref 4b])

(2*R*,3*S*)-ethyl-2-(anthracen-10-ylmethoxy)-3-(4-methoxyphenylamino)-3-phenylprop



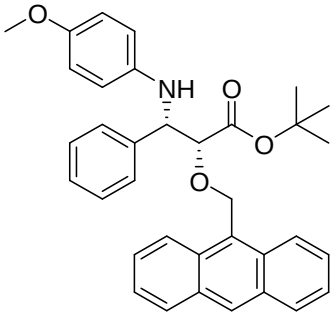
5b (*syn*)

anoate (5b *syn*): 62% yield; 37:63 dr (*syn*:*anti*); 37% *ee* (*syn*), determined by HPLC Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 8.4 min, t_{major} = 11.9 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.25 (t, 3H), 3.62 (s, 3H), 4.25 (q, 2H), 4.35 (d, *J* = 3.0 Hz, 1H), 4.47 (br, 1H), 4.89 (s, 1H), 5.16 (d, *J* = 10.7 Hz, 2H), 5.66 (d, *J* = 10.7 Hz, 2H), 6.35 (d, *J* = 8.8 Hz, 2H), 6.57 (d, *J* = 8.8 Hz, 2H), 7.20-7.22 (m, 5H), 7.37-7.45 (m, 4H), 7.97 (d, 8.0 Hz, 2H), 8.03 (d, 8.8 Hz, 2H), 8.45 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 55.6, 60.2, 61.4, 65.6, 82.2, 114.6, 114.8, 124.4, 124.9, 126.3, 127.2, 127.2, 127.2, 128.3, 128.8, 131.2, 131.3, 139.7, 140.8, 152.0,170.9; HRMS (ESI) calcd for $C_{33}H_{32}NO_4$ $[M + H]^+$ = 506.2331, found 506.2326.



5b (*anti*)

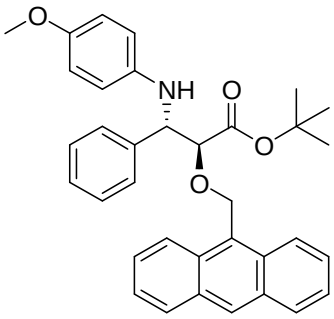
(2*S*,3*S*)-ethyl-2-(anthracen-10-ylmethoxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5b *anti*): 55% *ee*(*anti*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: tminor = 18.9 min, tmajor = 17.7 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.89 (t, 3H), 3.64 (s, 3H), 4.15 (q, 2H), 4.40 (d, *J* = 4.4 Hz, 1H), 4.67 (d, *J* = 4.4 Hz, 1H), 5.45 (d, *J* = 11.7 Hz, 2H), 5.72 (d, *J* = 11.7 Hz, 2H), 6.15 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 7.19-7.25 (m, 5H), 7.48-7.56 (m, 4H), 8.03 (d, 8.0 Hz, 2H), 8.33 (d, 8.8 Hz, 2H), 8.49 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.2, 55.6, 59.8, 61.1, 64.7, 79.9, 114.6, 115.0, 124.2, 125.1, 126.5, 127.5, 127.6, 127.9, 128.2, 128.9, 129.1, 131.3, 131.4, 138.4, 152.1, 156.1, 170.7.



5d (*syn*)

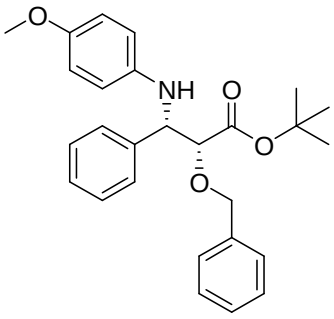
(2*R*,3*S*)-tert-butyl-2-(anthracen-10-ylmethoxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5d *syn*): 55% yield; 45:55 dr (*syn*:*anti*); 49% *ee* (*syn*) reacted with **1a**, 52% *ee* (*syn*) reacted with **1b**, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol =

90:10, 254 nm, Retention time: t_{minor} = 7.1 min, t_{major} = 8.3 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (s, 9H), 3.67 (s, 3H), 4.18 (br, 1H), 4.32 (d, *J* = 4.5 Hz, 1H), 4.66 (d, *J* = 4.5 Hz, 1H), 5.50 (d, *J* = 11.7 Hz, 1H), 5.74 (d, *J* = 11.7 Hz, 1H), 6.19 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 7.23-7.34 (m, 5H), 7.51-7.58 (m, 4H), 8.06 (d, 8.2 Hz, 2H), 8.38 (d, 8.2 Hz, 2H), 8.51 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 55.6, 59.8, 64.6, 80.2, 82.1, 114.6, 114.9, 124.3, 125.0, 126.4, 127.5, 127.8, 128.0, 128.2, 128.8, 129.1, 131.3, 131.4, 138.7, 140.4, 152.0, 169.8; HRMS (ESI) calcd for $C_{35}H_{36}NO_4$ $[M + H]^+$ = 534.2644, found 534.2639.



5d (*anti*)

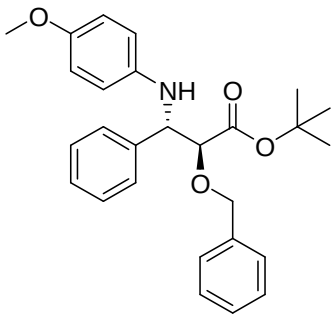
(2S,3S)-tert-butyl-2-(anthracen-10-ylmethoxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5d *anti*): 72% *ee* (*anti*) reacted with **1a**, 32% *ee* (*anti*) reacted with **1b**, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol= 90:10, 254 nm, Retention time: t_{minor} = 10.5 min, t_{major} = 9.2 min.); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.46 (s, 9H), 3.63 (s, 3H), 4.22 (d, *J* = 3.4 Hz, 1H), 4.44 (br, 1H), 4.80 (d, *J* = 3.6 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 2H), 5.64 (d, *J* = 11.0 Hz, 2H), 6.34 (d, *J* = 9.8 Hz, 2H), 6.57 (d, *J* = 9.8 Hz, 2H), 7.14-7.19 (m, 5H), 7.36-7.45 (m, 4H), 7.96 (d, 7.8 Hz, 2H), 8.05 (d, 7.8 Hz, 2H), 8.44 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.1, 55.6, 60.3, 65.2, 82.2, 82.2, 114.6, 114.6, 124.4, 124.9, 126.3, 127.1, 127.2, 127.4, 128.2, 128.7, 128.8, 131.3, 131.3, 139.8, 141.2, 151.8, 170.0.



5e (*syn*)

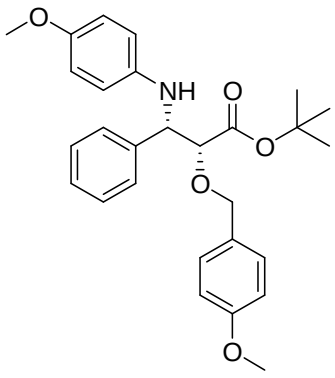
(2*R*,3*S*)-tert-butyl-2-(benzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate(5e *syn*): 56% yield; 54:46 dr (*syn*:*anti*), 84% *ee* (*syn*); determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 6.2 min, t_{major} = 5.8 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (s, 9H), 3.66 (s, 3H), 4.06 (d, *J* = 3.4 Hz, 1H), 4.28 (d, *J* = 12.0 Hz, 1H), 4.57 (br, 1H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.80 (d, *J* = 3.4 Hz, 1H),

6.45 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 7.00 (m, 2H), 7.20-7.36 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 55.6, 60.4, 72.7, 81.8, 82.1, 114.6, 114.7, 127.2, 127.3, 127.7, 127.8, 128.2, 128.3, 137.1, 140.0, 141.2, 151.9, 169.7; HRMS (ESI) calcd for $C_{27}H_{32}NO_4$ $[M + H]^+$ = 434.2331, found 434.2326.



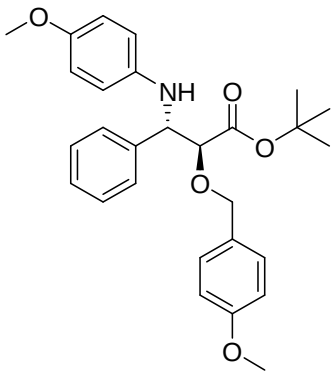
5e (*anti*)

(2*S*,3*S*)-tert-butyl-2-(benzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate(5e *anti*): 16% *ee* (*anti*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 9.3 min, t_{major} = 7.1 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.24 (s, 9H), 3.60 (s, 3H), 4.11 (d, *J* = 5.0 Hz, 1H), 4.29 (d, *J* = 11.7 Hz, 1H), 4.36 (br, 1H), 4.62 (m, 2H), 6.41 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 8.6 Hz, 2H), 7.15-7.31 (m, 10H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.6, 60.4, 72.6, 81.0, 82.0, 114.7, 115.3, 127.5, 127.9, 127.9, 128.0, 128.1, 128.4, 137.4, 138.8, 140.8, 152.3, 169.5.



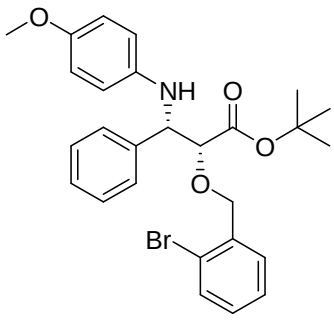
5f (*syn*)

(2*R*,3*S*)-tert-butyl-2-(4-methoxybenzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5f *syn*): 45% yield; 47:53 dr (*syn*:*anti*), 86% *ee* (*syn*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ EtOH= 30:1, 254 nm, Retention time: t_{minor} = 10.7 min, t_{major} = 11.3 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.39 (s, 9H), 3.66 (s, 3H), 3.77 (s, 3H), 4.03 (d, *J* = 3.6 Hz, 1H), 4.22 (d, *J* = 11.5 Hz, 1H), 4.57 (br, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.78 (m, 1H), 6.45 (d, *J* = 8.8 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 7.27-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 55.2, 55.6, 60.4, 72.4, 81.4, 82.0, 113.6, 114.6, 127.2, 127.3, 128.2, 129.2, 129.5, 140.1, 141.2, 151.9, 159.2, 169.8; HRMS (ESI) calcd for $C_{28}H_{34}NO_5$ $[M + H]^+$ = 464.2437, found 464.2431.



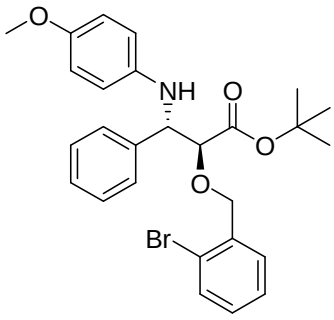
5f (*anti*)

(2*S*,3*S*)-tert-butyl-2-(4-methoxybenzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5f *anti*): 18% *ee* (*anti*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 13.2 min, t_{major} = 9.6 min.); ^{1}HNMR ($CDCl_3$, 400 MHz) δ 1.31 (s, 9H), 3.67 (s, 3H), 3.79 (s, 3H), 4.16 (d, *J* = 4.3 Hz, 1H), 4.30 (d, *J* = 11.5 Hz, 1H), 4.42 (br, 1H), 4.65 (m, 2H), 6.48 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.19-7.28 (m, 5H), 7.35 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.2, 55.6, 60.3, 72.2, 80.5, 81.9, 113.8, 114.6, 115.2, 127.5, 127.9, 128.1, 129.4, 129.6, 138.8, 140.8, 152.2, 159.3, 169.6.



5g (*syn*)

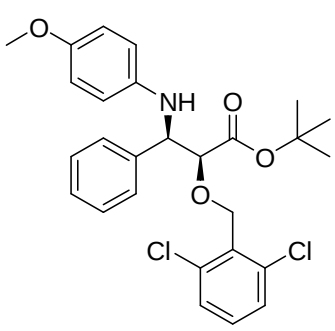
(2*R*,3*S*)-tert-butyl-2-(2-bromobenzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5g *syn*): 52% yield; 52:48 dr (*syn*:*anti*); 86% *ee* (*syn*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 11.1 min, t_{major} = 6.3 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.40 (s, 9H), 3.67 (s, 3H), 4.12 (d, *J* = 3.9 Hz, 1H), 4.43 (d, *J* = 13.0 Hz, 1H), 4.61 (br, 1H), 4.73 (d, *J* = 13.0 Hz, 2H), 4.79 (d, *J* = 3.6 Hz, 1H), 6.48 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 8.6 Hz, 2H), 7.03-7.47 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 55.7, 60.6, 71.9, 82.2, 82.6, 114.7, 114.8, 122.8, 127.3, 127.3, 127.4, 128.4, 129.0, 129.5, 132.4, 136.6, 139.8, 141.2, 152.1, 169.5; HRMS (ESI) calcd for $C_{27}H_{31}BrNO_4$ $[M + H]^+$ = 512.1436, found 512.1431.



5g (*anti*)

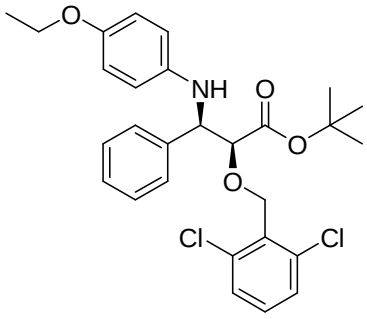
(2*S*,3*S*)-tert-butyl-2-(2-bromobenzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5g *anti*): 33% *ee* (*anti*), determined by HPLC (DaicelChirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 90:10, 254 nm, Retention time: t_{minor} = 9.4 min, t_{major} = 7.1 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (s, 9H), 3.61 (s, 3H), 4.18 (d, *J* = 4.9 Hz,

1H), 4.46 (m, 2H), 4.68 (m, 2H), 6.43 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 7.08-7.48 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.7, 60.3, 71.9, 81.3, 82.2, 114.7, 115.2, 123.0, 127.5, 127.6, 128.1, 128.2, 129.3, 129.9, 132.6, 136.8, 138.7, 140.8, 152.2, 169.3.



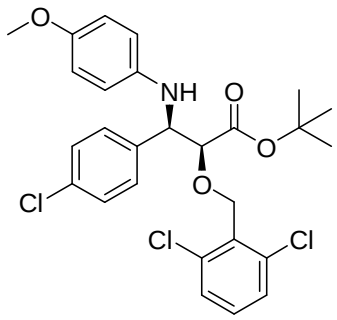
5h (*syn*)

(2S,3R)-tert-butyl2-(2,6-dichlorobenzyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (5h *syn*): 68% yield; 88% *ee* (*syn*), determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20：1, 254 nm, Retention time: t_{minor} = 7.6 min, t_{major} = 12.7 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.31 (s, 9H), 3.57 (s, 3H), 3.99 (d, *J* = 4.0 Hz, 1H), 4.62 (m, 2H), 4.87 (d, *J* = 8.0 Hz, 1H), 6.37 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 7.01-7.05 (m, 1H), 7.08-7.16 (m, 5H), 7.19-7.21 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.6, 60.5, 66.8, 82.0, 82.2, 114.5, 114.9, 127.1, 127.2, 128.1, 128.2, 130.0, 132.2, 136.9, 139.5, 141.3, 151.9, 169.3; HRMS (ESI) calcd for $C_{27}H_{29}Cl_2NNaO_4$ $[M + Na]^+$ = 524.1371, found 524.1362.



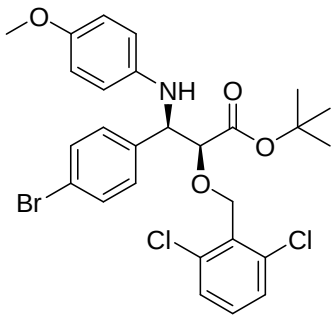
7a

(2S,3R)-tert-butyl2-(2,6-dichlorobenzyloxy)-3-(4-ethoxyphenylamino)-3-phenylpropanoate (7a): 73% yield; 87% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 9.6 min, t_{major} = 17.4 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.21 (t, 3H), 1.27 (s, 9H) ,3,75 (f, 2H), 4.12 (d, *J* = 4.0 Hz, 1H), 4.51 (br, 1H), 4.61 (br, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.94 (d, *J* = 12.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 7.05-7.29 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.9, 27.9, 60.5, 63.8, 66.8, 82.0, 82.2, 114.8, 115.4, 127.1, 127.2, 128.1, 128.2, 130.0, 132.2, 136.9, 139.6, 141.3, 151.2, 169.3; HRMS (ESI) calcd for calcd for $C_{28}H_{31}Cl_2NNaO_4$ $[M + Na]^+$ = 538.1528, found 538.1519.



7b

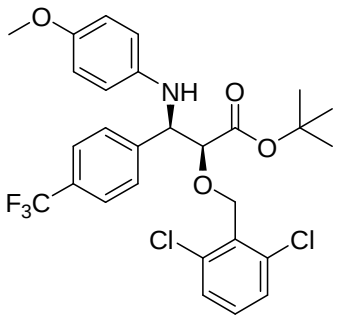
(2S,3R)-tert-butyl-2-(2,6-dichlorobenzyloxy)-3-(4-chlorophenyl)-3-(4-methoxyphenylamino)propanoate (7b): 64% yield; 82% *ee*, result after recrystallization $[\alpha]^{D}_{20}$ = -16.9° (c = 1.0 in CH_2Cl_2), >99% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 8.1 min, t_{major} = 11.8 min.); mp 149–151°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 9H), 3.66 (s, 3H), 4.03 (d, *J* = 4.0 Hz, 1H), 4.69 (m, 2H), 4.96 (d, *J* = 12.0 Hz, 1H), 6.41 (d, *J* = 12.0 Hz, 2H), 6.63 (d, *J* = 12.0 Hz, 2H), 7.11-7.20 (m, 3H), 7.21-7.25 (m, 4H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 28.0, 55.6, 59.8, 66.7, 81.7, 82.3, 114.6, 114.8, 128.2, 128.3, 128.5, 130.1, 132.0, 132.7, 136.9, 138.2, 140.8, 152.1, 169.2; HRMS (ESI) calcd for $C_{27}H_{28}Cl_3NNaO_4$ $[M + Na]^+$ = 558.0982, found 558.0973.



7c

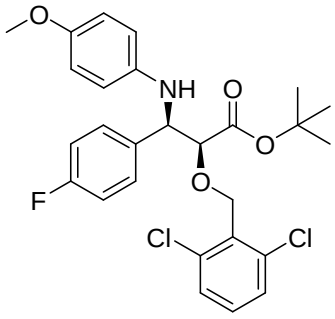
(2S,3R)-tert-butyl-2-(2,6-dichlorobenzyloxy)-3-(4-bromopheny)-3-(4-methoxyphenylamino) propanoate (7c): 72% yield; 83% *ee*, result after recrystallization $[\alpha]^{D}_{20}$ = -21.0° (c = 1.0 in CH_2Cl_2), >99% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 8.6 min, t_{major} = 12.5 min.); mp 151– 153°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.42 (s, 9H), 3.67 (s, 3H), 4.02 (d, *J* = 4.0 Hz, 1H), 4.54 (br, 1H), 4.67 (br, 1H), 4.67 (d, *J* = 16.5 Hz, 2H), 4.96 (d, *J* = 16.5 Hz, 1H), 6.41 (d, *J* = 9.0 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 7.10-7.16 (m, 3H), 7.20-7.23 (m, 2H), 7. 26 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 55.7, 59.1, 60.2, 66.7, 79.7, 82.3, 114.7, 115.0, 121.5, 128.5, 128.5, 130.0, 130.3, 131.1, 132.4, 137.0, 137.6, 140.1, 152.2, 168.9; HRMS (ESI) calcd for $C_{27}H_{28}BrCl_2NNaO_4$ $[M + Na]^+$ = 602.0476, found 602.0462.

(2S,3R)-tert-butyl2-(2,6-dichlorobenzyloxy)-3-(4-methoxyphenylamino)-3-(4-(trifluoromethyl)phenyl)propanoate (7d): 70% yield; 91% *ee*, result after recrystallization $[\alpha]^{D}_{20}$ = -15.0° (c = 1.0 in CH_2Cl_2); >99:1 *ee*, determined by HPLC (Daicel Chirapak IA,



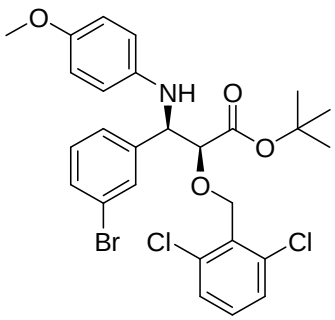
7d

flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 7.3 min, t_{major} = 9.4 min.); mp 157–158°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.36 (s, 9H), 3.60 (s, 3H), 3.98 (d, *J* = 4.0 Hz, 1H), 4.51 (br, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.73 (bs, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 7.04-7.09 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.2431 (d, *J* = 8.0 Hz, 2H); ^{13}CNMR ($CDCl_3$, 100MHz) δ 28.0, 55.6, 59.9, 66.6, 81.1, 82.5, 114.6, 114.7, 125.0, 125.0, 127.3, 128.2, 130.2, 131.8, 136.8, 140.6, 152.1, 169.1; HRMS (ESI) calcd for $C_{28}H_{28}Cl_2F_3NNaO_4$ $[M + Na]^+$ = 592.1245, found 592.1237.



7e

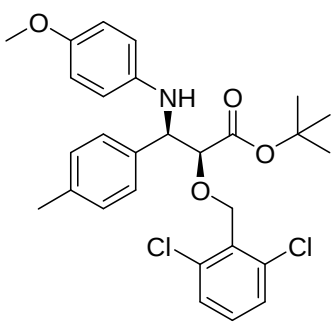
(2S,3R)-tert-butyl-2-(2,6-dichlorobenzyloxy)-3-(4-fluorophenyl)-3-(4-methoxyphenylamino)propanoate (7e): 61% yield; 81% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 11.3 min, t_{major} = 19.0 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (s, 9H), 3.57 (s, 3H), 4.11 (d, *J* = 4.0 Hz, 1H), 4.48 (br, 1H), 4.60 (br, 1H), 4.76 (d, *J* = 12.0 Hz, 1H), 4.96 (d, *J* = 12.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 2H), 6.83-6.88 (m, 2H), 7.09-7.27 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.6, 58.7, 66.6, 79.6, 82.1, 100.5, 114.6, 114.8, 114.9, 115.0, 128.5, 129.8, 129.9, 130.3, 132.4, 134.1, 137.0, 140.2, 152.0, 161.0, 169.0; HRMS (ESI) calcd for $C_{27}H_{28}Cl_2FNNaO_4$ $[M + Na]^+$ = 542.1277, found 542.1260.



7f

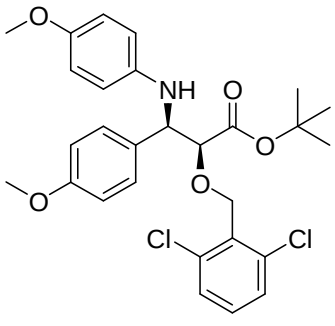
(2S,3R)-tert-butyl2-(2,6-dichlorobenzyloxy)-3-(3-bromophenyl)-3-(4-methoxyphenylamino)propanoate (7f): 65% yield; 70% *ee*, determinedmby HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 8.1 min, t_{major} = 10.6 min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.35 (s, 9H), 3.60 (s, 3H), 3.94 (d, *J* =

4.0 Hz 1H), 4.60 (d, *J* = 4.0 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 6.35 (d, *J* = 8.0 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.98-7.29 (m, 7H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.0, 29.7, 55.6, 59.9, 66.7, 81.5, 82.3, 114.6, 114.7, 114.9, 122.4, 125.9, 128.3, 129.7, 130.1, 130.2, 130.3, 131.9, 136.9, 140.8, 142.3, 153.1, 169.1; HRMS (ESI) calcd for $C_{27}H_{28}BrCl_2NNaO_4$ $[M + Na]^+$ = 602.0476, found 602.0460.



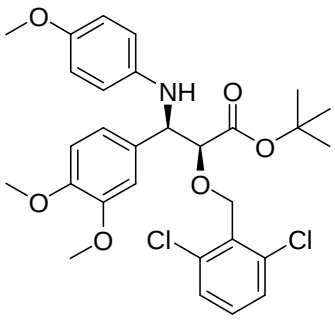
7g

(2S,3R)-tert-butyl-2-(2,6-dichlorobenzyloxy)-3-(4-methoxyphenylamino)-3-p-tolylpropanoate (7g): 63% yield; 88% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 8.0 min, t_{major} = 11.4 min.); mp 97– 98°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (s, 9H), 2.20 (s, 3H), 3.58 (s, 3H), 3.97 (d, *J* = 4.0 Hz, 1H), 4.49 (br, 1H), 4.57 (br, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 6.37 (d, *J* = 12.0 Hz, 2H), 6.54 (d, *J* = 12.0 Hz, 2H), 6.91-7.10 (m, 4H), 7.13-7.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.6, 60.3, 66.9, 81.9, 82.6, 114.5, 114.9, 127.1, 128.2, 128.8, 123.0, 132.3, 136.4, 136.6, 137.0, 141.5, 151.9, 169.4; HRMS (ESI) calcd for $C_{28}H_{31}Cl_2NNaO_4$ $[M + Na]^+$ = 538.1528, found 538.1519.



7h

(2S,3R)-tert-butyl-2-(2,6-dichlorobenzyloxy)-3-(4-methoxyphenyl)-3-(4-methoxyphenylamino)propanoate (7h): 61% yield; 82% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 6.4 min, t_{major} = 10.0min.); mp 94– 95°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.32 (s, 9H), 3.59 (s, 3H), 3.67 (s, 3H), 3.94 (d, *J* = 8.0 Hz, 1H), 4.49 (br, 1H), 4.55 (d, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 8.0 Hz, 1H), 4.88 (d, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 2H), 6.855 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 7.06-7.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.9, 55.2, 55.6, 60.0, 66.8, 82.0, 82.5, 113.6, 114.5, 115.0, 128.3, 128.3, 130.1, 131.5, 132.3, 136.9, 141.4, 151.9, 158.7, 169.4; HRMS (ESI) calcd for $C_{28}H_{31}Cl_2NNaO_5$ $[M + Na]^+$ = 554.1477, found 554.1476.

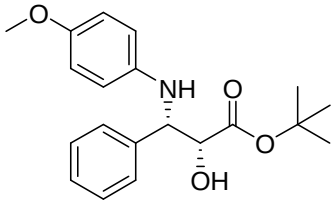


7i

(2S,3R)-tert-butyl2-(2,6-dichlorobenzyloxy)-3-(3,4-dimethoxyphenyl)-3-(4-methoxyphenylamino)propanoate (7i): 67% yield; 80% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 20: 1, 254 nm, Retention time: t_{minor} = 15.9 min, t_{major} = 27.2min.); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.26 (s, 9H), 3.72 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 5.05 (d, *J* = 4.0 Hz, 1H), 5.08 (d, *J* = 4.0 Hz, 1H), 6.74-6.91 (m, 5H), 7.09-7.26 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 29.7, 31.9, 55.4, 55.9, 62.4, 67.4, 76.7, 77.0, 77.3, 84.0, 110.8, 111.1, 114.2, 118.8, 120.9, 125.8, 128.2, 130.1, 130.7, 132.2, 136.9, 149.0, 149.2, 156.3, 163.4; HRMS (ESI) calcd for $C_{29}H_{33}Cl_2NNaO_6$ $[M + Na]^+$ = 584.1583, found 584.1578.

4. Procedure of the synthesis of taxol side chain and (-)-*epi*-cytoxazone and the analysis data of compounds 8-15

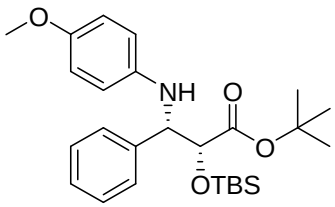
4.1 Procedure of the synthesis of taxol side chain



8

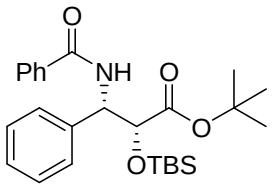
(2R,3S)-tert-butyl-2-hydroxy-3-(4-methoxyphenylamino)-3-phenylpropanoate (8): The protected phenylpropanoate **5e** (84% *ee*) was hydrogenolyzed separately using ammonium formate (3 equivalents) and 10% Pd/C (1 equivalent) in methanol (15 mL/g) for 12 h at 35℃. The catalyst was filtered and washed with methanol twice. The combined washings and filtrate were evaporated in vacuo and the residue taken into $CHCl_3$, washed with water, and dried over Na_2SO_4. The solvent was removed under reduced pressure and get the white solid product, and recrystallized by the solvent (EA:n-hex = 1:50) in the yield of 48% (two steps). $[\alpha]^D_{20}$ = -9.5° (c = 1.0 in CH_2Cl_2), >99% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 70:30, 254 nm, Retention time: t_{minor} = 15.5 min, t_{major} = 7.7 min.); mp 140– 141°C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.41 (s, 9H), 3.23 (d, *J* = 4.0 Hz, 1H) , 3.67 (s, 3H), 4.38 (br, 1H), 4.46 (br,

1H), 4.80 (br, 1H), 6.50 (d, *J* = 12.0 Hz, 2H), 6.66 (d, *J* = 12.0 Hz, 2H), 7.23-7.38 (m,5H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 27.9, 55.6, 59.9, 74.6, 83.4, 114.7, 114.9, 127.0, 127.3, 128.4, 139.6, 140.8, 152.1, 172.2; HRMS (ESI) calcd for $C_{20}H_{25}NNaO_4$ $[M + Na]^+$ = 366.1681, found 366.1676.



9

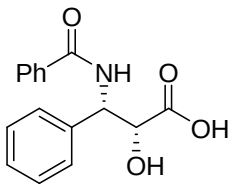
(2R,3S)-tert-butyl-2-(tert-butyldimethylsilyloxy)-3-(4-methoxyphenylamino)-3-phenylpropanoate (9): To a solvent of the hydroxyl phenylpropanoate **8** and TBSCl (1.5 equivalents) in CH_3CN (20 mL/g) was stirred at room temperature and DBU (1.2 equivalents) was added dropwise to the solution. After the reaction mixture was stirred for 10 h, the solvent was removed under reduced pressure and the remains washed with water and extracted with ethyl acetate. After a usual work, the crude product was chromatographed on flash silica gel to afford the desired protected phenylpropanoate **9** in quant yield. ^{1}H NMR ($CDCl_3$, 400 MHz) δ -0.22 (s, 3H), 0.00 (s, 3H), 0.93 (s, 9H), 1.55 (s, 9H), 3.82 (d, *J* = 4.0 Hz, 1H), 3.67 (s, 3H), 4.38 (br, 1H), 4.46 (br, 1H), 4.80 (br, 1H), 6.50 (d, *J* = 12.0 Hz, 2H), 6.66 (d, *J* = 12.0 Hz, 2H), 7.23-7.38 (m,5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ -6.1, -5.5, 1.0, 18.2, 25.5, 28.0, 55.6, 61.1, 81.6, 114.4, 114.6, 127.2, 127.3, 128.2, 140.3, 141.2, 151.7, 170.8.



10

(2R,3S)-tert-butyl-3-benzamido-2-hydroxy-3-phenylpropanoate (10): To a solution of (2R,3S)-tert-butyl-2-(tert-butyldimethylsilyloxy)-3-(4-methoxyphenylamino)-3- phenyl-propanoate (457 mg, 1 mmol) in the wet CH_3CN (20 mL) was added the solution of cerium ammonium nitrate (CAN, 2.19 g, 4 mmol) in wet CH_3CN (5 mL) at 0℃. After the reaction mixture was stirred for 1h, the mixture was added saturated $NaHCO_3$ aqueous till the PH of the solution became >7. Insoluble materials were filtered and the aqueous layer was extracted with ethyl acetate and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product directly dissolved in the CH_2Cl_2 (20 mL), then the Triethylamine (3.03 g, 3 mmol) was added dropwise to the solution and the mixture stirred for 15min at room temperature.

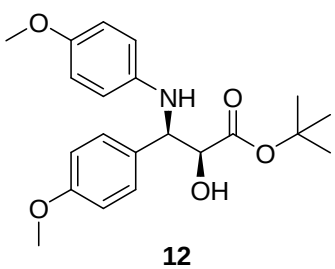
Freshly distilled benzoyl chloride (140 mg, 1 mmol) in the CH_2Cl_2 (2 mL) was added dropwise to the resultant solution and stirring was continued at room temperature for 2h. The solution was then diluted with CH_2Cl_2 (20 mL) and water (20 mL) was added. The organic layer was separated and aqueous layer extracted with further CH_2Cl_2 (2 × 20 mL). The combined organic extracts were dried (MgSO4), filtered and evaporated under reduced pressure, the crude product was chromatographed on flash silica gel to afford the desired product. To a solution of the product in anhydrous tetrahydrofuran (10 mL) was treated with TBAF (260 mg, 1 mmol). After the mixture was stirred for 2 h at room temperature, the mixture was evaporated and the crude product was chromatographed on flash silica gel to afford the desired compound **10** as a white solid (156 mg, 46%, three steps). $[\alpha]^{D}_{20}$ = -21.3° (c = 1.0 in CH_2Cl_2), >99% *ee*, determined by HPLC (Daicel Chirapak IA, flow rate 1.0 mL/min, hexane/ isopropanol = 70:30, 254 nm, Retention time: t_{minor} =13.7 min, t_{major} = 6.9 min.); mp 111– 112°C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (s, 9H), 3.34 (br, 1H), 4.54 (s, 1H), 5.77 (dd, J_1 = 1.6 Hz, J_2 = 10.9 Hz, 1H), 6.98 (br, 1H), 7.26-7.51(m, 8H), 7.76-7.78 (m, 2H); ^{13}CNMR ($CDCl_3$, 100MHz) δ 27.8, 54.5, 73.4, 84.1, 126.8, 127.0, 127.6, 128.5, 128.6, 131.6, 134.2, 138.8, 166.8, 172.0; HRMS (ESI) calcd for $C_{20}H_{23}NNaO_4$ $[M + Na]^+$ = 364.1525, found 364.1520.



11

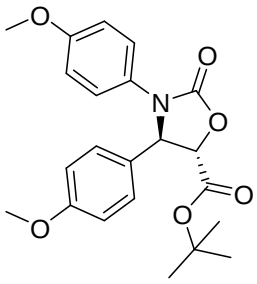
(2R,3S)-3-benzamido-2-hydroxy-3-phenylpropanoic acid (11) A solution of the *tert*-butyl ester **10** (68.0 mg, 0.2 mmol) and trifluoroacetic acid (0.4 mL) in CH_2Cl_2 (1 mL) was stirred at room temperature for 6 h. The solvent was evaporated and the residue crystallized from ethyl acetate (2 mL) to give the acid **11** (47.4 mg, 83%).[3] $[\alpha]^{D}_{20}$ = -37.0° (c = 1.0 in EtOH) ($[\alpha]^{D}_{20}$ = -38.6° (c = 1.05 in EtOH))[3]; mp 158– 160°C; ^{1}H NMR (DMSO-d^6, 500 MHz) δ 4,39 (br, 1H), 5.46 (dd, J_1 =4.0 Hz, J_2 = 13.0 Hz, 1H), 5.53 (br, 1H), 7.23-7.57 (m, 8H), 7.84 (m, 2H), 8.53 (d, J =9.0 Hz, 1H), 12.73 (s, 1H); ^{13}C NMR ($CDCl_3$, 100MHz) δ 55.8, 73.6, 127.0, 127.2, 127.4, 128.1, 128.4, 131.4, 134.4, 140.3, 166.1, 173.5; HRMS (ESI) calcd for $C_{16}H_{16}NO_4$ $[M + H]^+$ = 286.1079, found 286.1079.

(2*S*,3*R*)-tert-butyl2-hydroxy-3-(4-methoxyphenyl)-3-(4-methoxyphenylamino)



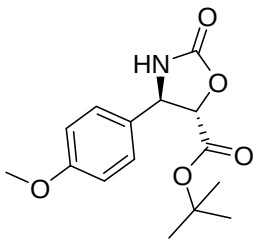
12

propanoate (12): The compound **12** was synthesized from the compound **7h** by employing a procedure similar to that described for the synthesis of the compound **8**, in an 84% yield. Notably, with a longer reaction time, a lower yield was afforded (after 20 h, a 42% yield was afforded); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.43 (s, 9H), 3.20 (br, 1H), 3.69 (s, 3H), 3.77 (s, 3H), 4.35 (s, 1H), 4.76 (s, 3H), 6.52 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.9, 55.2, 55.6, 59.4, 74.7, 83.4, 113.9, 114.7, 115.0, 128.1, 131.6, 140.8, 152.1, 158.9, 172.2; HRMS (ESI) calcd for $C_{21}H_{27}NNaO_5$ $[M + Na]^+$ = 396.1787, found 396.1776.



13

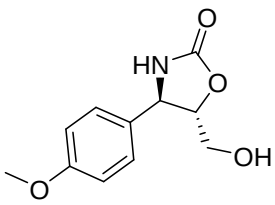
(4*R*,5*S*)-tert-butyl-3,4-bis(4-methoxyphenyl)-2-oxooxazolidine-5-carboxylate (13): To a solution of the amino ester **12** (230 mg, 0.61 mmol) in anhydrous CH_2Cl_2 (10 mL) at 0°C was added DIPEA (0.3 mL, 1.83 mmol) dropwise and a solution of triphoshene (220 mg, 0.73 mmol) in anhydrous CH_2Cl_2 (5 mL) was added over a time of 0.5 h via a syringe pump. After completion of the addition, the reaction was stirred for another 0.5 h and the product was washed with water and brine and dried over Na_2SO_4, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography to yield the oxazolidinone **13** (215 mg, 87%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.52 (s, 9H), 3.71 (s, 3H), 3.76 (s, 3H), 4.62 (d, *J* = 5.0 Hz, 1H), 5.20 (d, *J* = 5.0 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 7.22 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.9, 55.2, 55.3, 63.8, 78.2, 83.8, 114.2, 114.6, 123.4, 127.7, 129.4, 129.5, 154.6, 157.0, 159.9, 167.2; HRMS (ESI) calcd for $C_{22}H_{26}NO_6$ $[M + H]^+$ = 400.1760, found 400.1756.



14

(4*R*,5*S*)-tert-butyl-4-(4-methoxyphenyl)-2-oxooxazolidine-5-carboxylate (14): To a solution of **13** (200 mg, 0.5 mmol) in CH_3CN and water (15 mL, 2:1) was added the solution of cerium ammonium nitrate (CAN, 825 mg, 1.5 mmol) in water (5.0 mL)

over a time of 0.5 h via a syringe pump at 0°C. After the mixture was stirred for another 1 h, saturated $NaHCO_3$ aqueous was added till the PH of the solution exceeded 7. Then, the insoluble materials were filtered and the aqueous layer was extracted with ethyl acetate and dried over Na_2SO_4. The crude product was purified by flash column chromatography to afford the compound **14** (91 mg, 62%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.53 (s, 9H), 3.83 (s, 3H), 4.61 (d, *J* = 5.5 Hz, 1H), 4.87 (d, *J* = 5.5 Hz, 1H), 5.75 (s, 1H), 6.93 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 28.0, 55.4, 58.8, 81.0, 83.7, 114.5, 127.3, 130.9, 132.6, 160.1, 167.2; HRMS (ESI) calcd for $C_{15}H_{19}NNaO_5$ $[M + Na]^+$ = 316.1161, found 316.1160.



15
(-)-epi-Cytoxazone

(4*R*,5*S*)-5-(hydroxymethyl)-4-(4-methoxyphenyl)oxazolidin-2-one (15): To a stirred solution of 14 (29.0 mg, 0.1 mmol) in aqueous THF (2.5 mL) at 0°C was added Superhydride (1.0 M in THF, 1.0 mL, 1.0 mmol) over a time of 1 h via a syringe pump at 0°C, and the reaction mixture was allowed to warm to room temperature over a time of 6 h before the addition of a saturated aqueous NH_4Cl solution. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product was purified by flash column chromatography in order to afford alcohol **15** (10.5 mg, 69%) as a white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.13 (t, 1H), 3.70 (m, 1H), 3.81 (s, 3H), 3.94 (m, 1H), 4.38 (m, 1H), 4.87 (d, *J* = 7.0 Hz, 1H), 5.27 (s, 1H), 6.92 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H); HRMS (ESI) calcd for $C_{11}H_{13}NNaO_4$ $[M + H]^+$ = 246.0742, found 246.0744.

5. References

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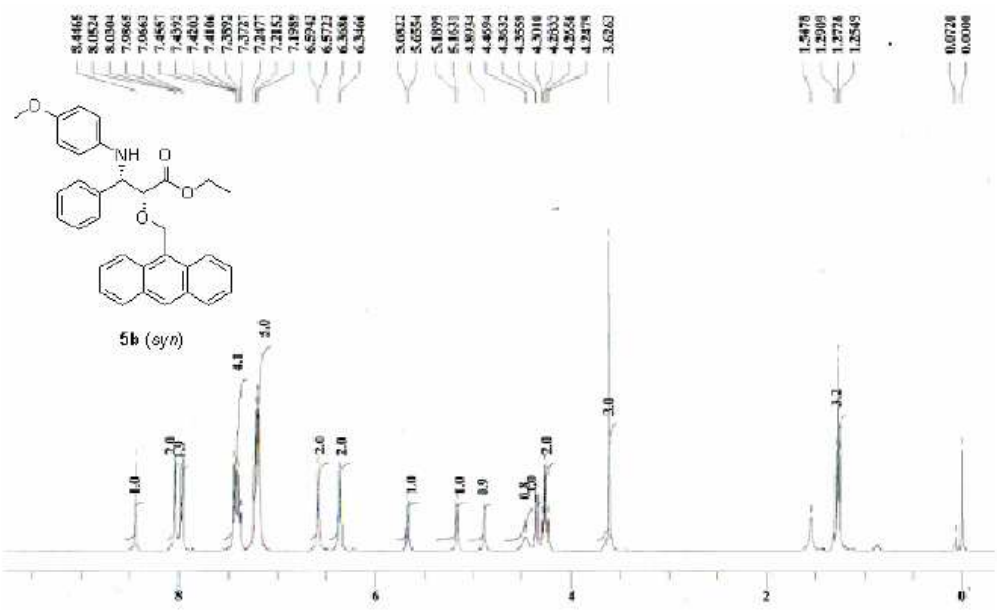
[2] (a) Uraguchi, D.; Terada, M.; *J. Am. Chem. Soc.* **2004**, *126*, 5356-5357. (b) Akiyama, T.; Morita, H.; Itoh, J.; uchibe, K. *Org. Lett.* **2005**, *7*, 2583-2585. (c) Storer, R. I.; Carrera, D. E.; Ni, Y.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2006**, *128*, 84- 86. (d) Uraguchi, D.; Sorimachi, K.; Terada, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 2254- 2257. (e) Yamanaka, M.; Junji Itoh, M.; Fuchibe, K.; Akiyama, T. *J. Am Chem. Soc.* **2007**, *129*, 6756- 6764. (f)

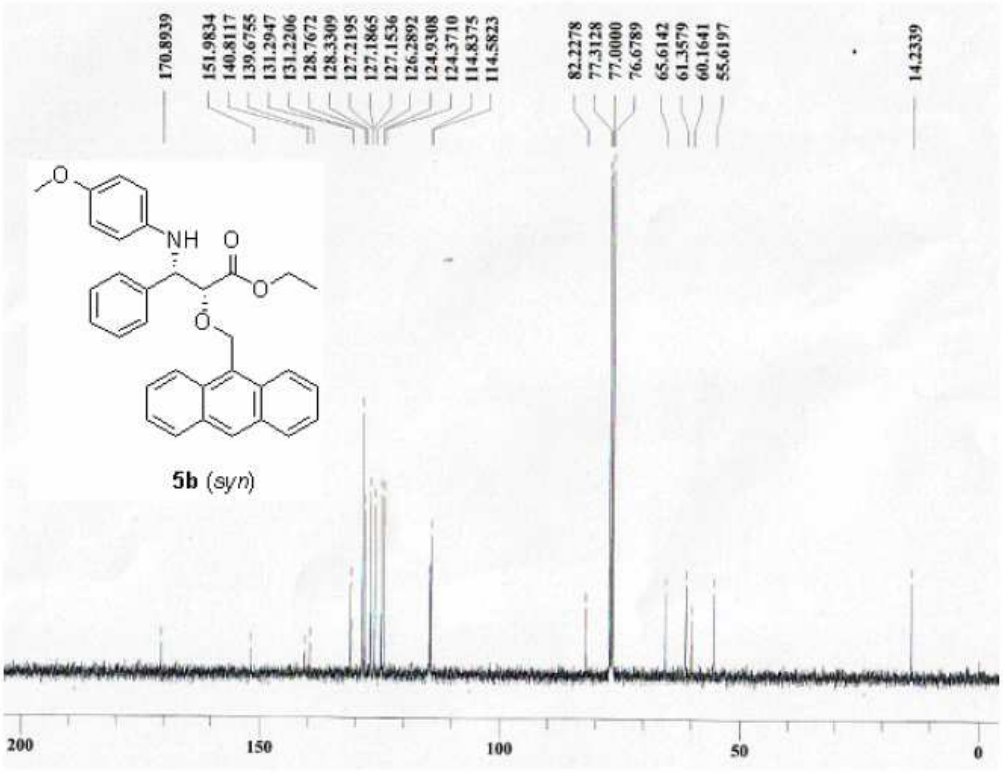
Guo, Q.; Liu, H.; Luo, S.; Guo, C.; Gu, Y.; Gong, L. *J. Am.Chem. Soc.* **2007**, *129*, 3790-3791; (g) Jiang, J.; Yu, J.; Sun, X.; Rao, Q.; Gong, L. *Angew. Chem., Int. Ed.* **2008**, *47*, 2458- 2462; (h) Masahiro, T.; Daisuke, U.; Keiichi, S.; Hideo, S. *PCT Int. Appl.* **2005** WO2005070875.

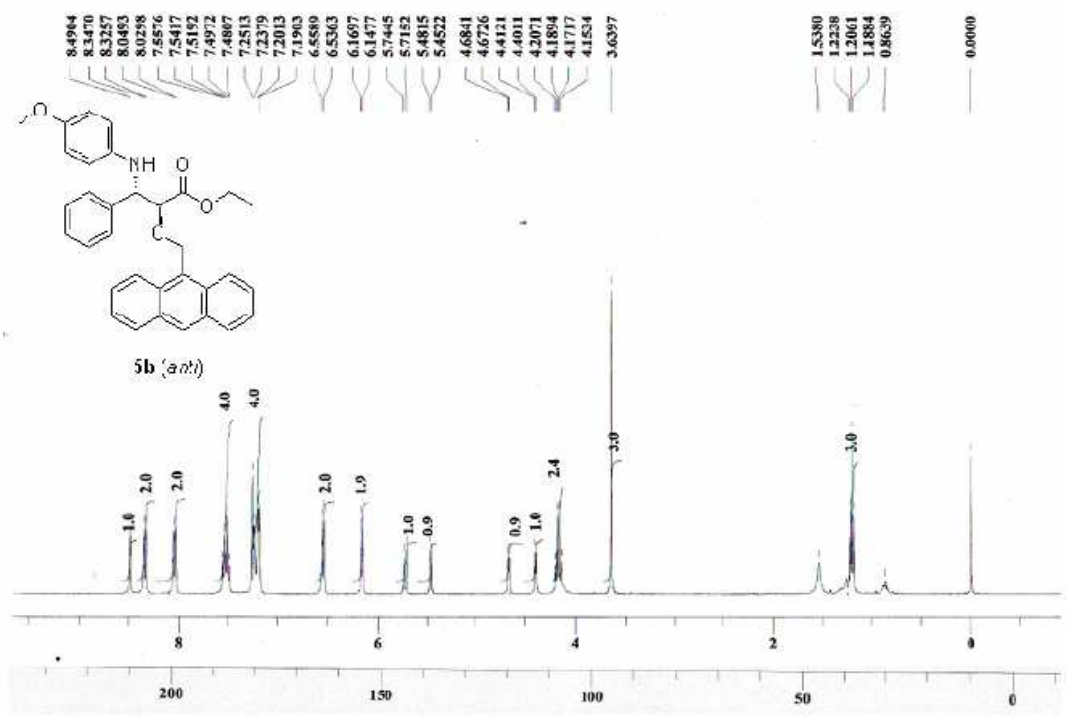
[3] Adger, B. M.; Barkley, J. V.; Bergeron, S.; Cappi, M. W.; Flowerdew, B. E.; Jackson, M. P.; McCague, R. T.; Nugent, C.; Roberts, S. M. *J. Chem. Soc., Perkin Trans. 1*, **1997**, 3501- 3507.

[4] (a) Guo, Z.; Shi, T.; Jiang, J.; Yang, L.; Hu, W. *Org. Biomol. Chem.* **2009**, *7*, 5028–5033. (b) Hu,W.; Xu, X.; Zhou, J.; Liu, W.; Huang, H.; Hu, J.; Yang, L.; Gong, L. Z. *J. Am. Chem. Soc***. 2008**, *130*, 7782-7783.

6. NMR analysis spectra for 5b,d-h, 7a-i, 8-15 (5a, see[ref 5a], 5c see[ref 5b])



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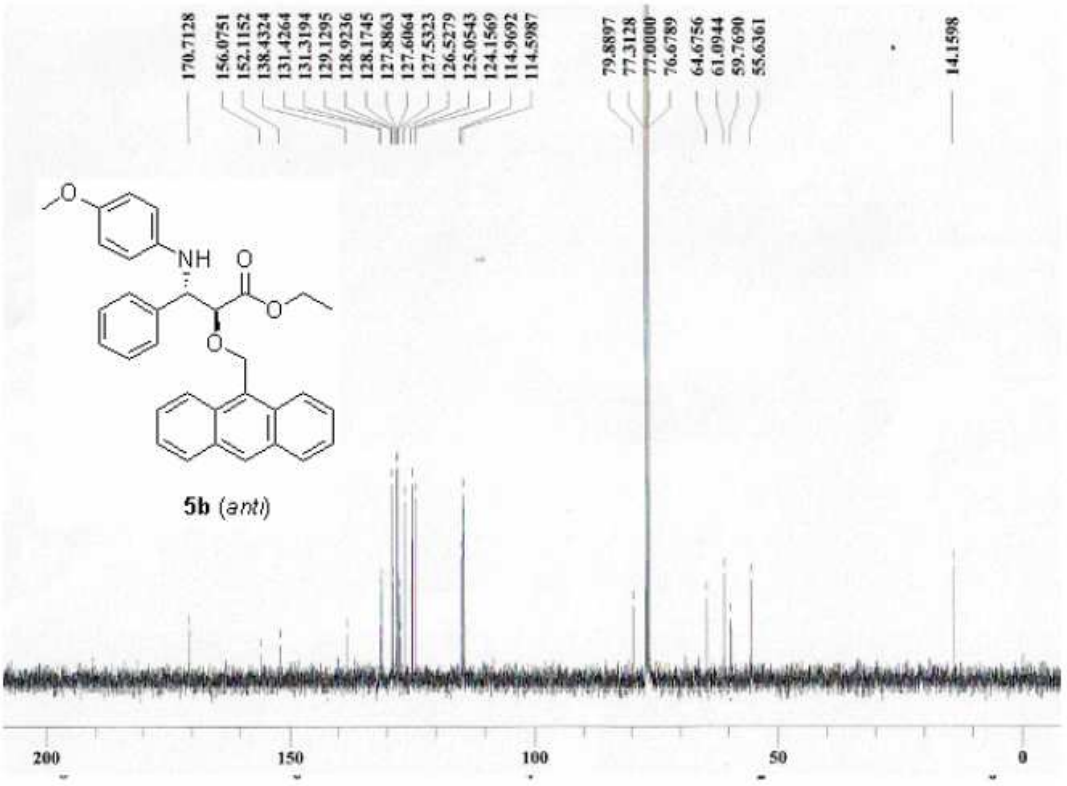
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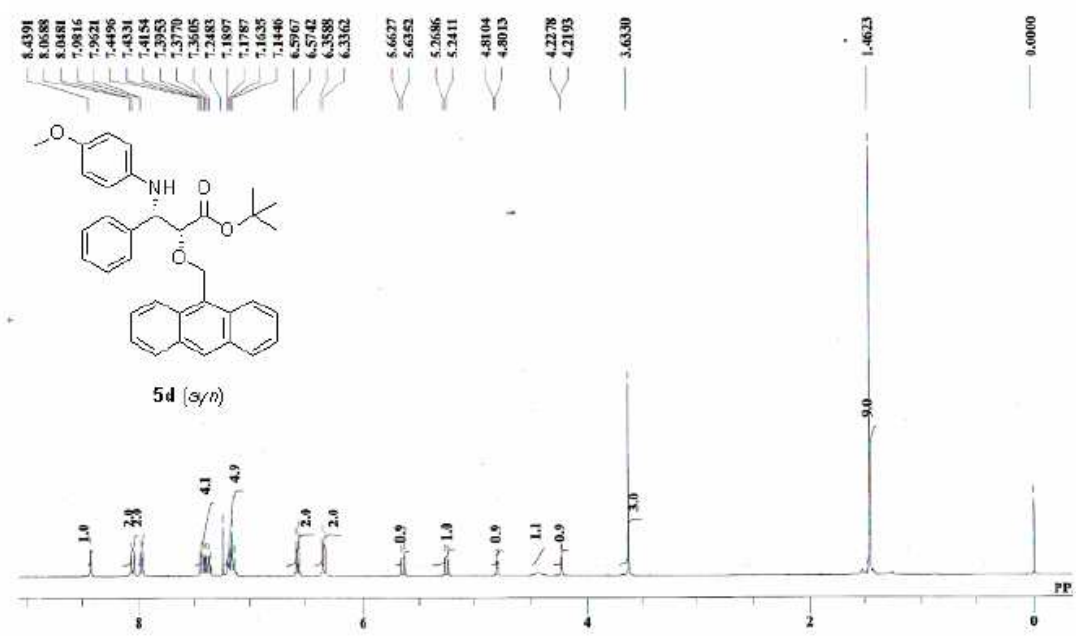
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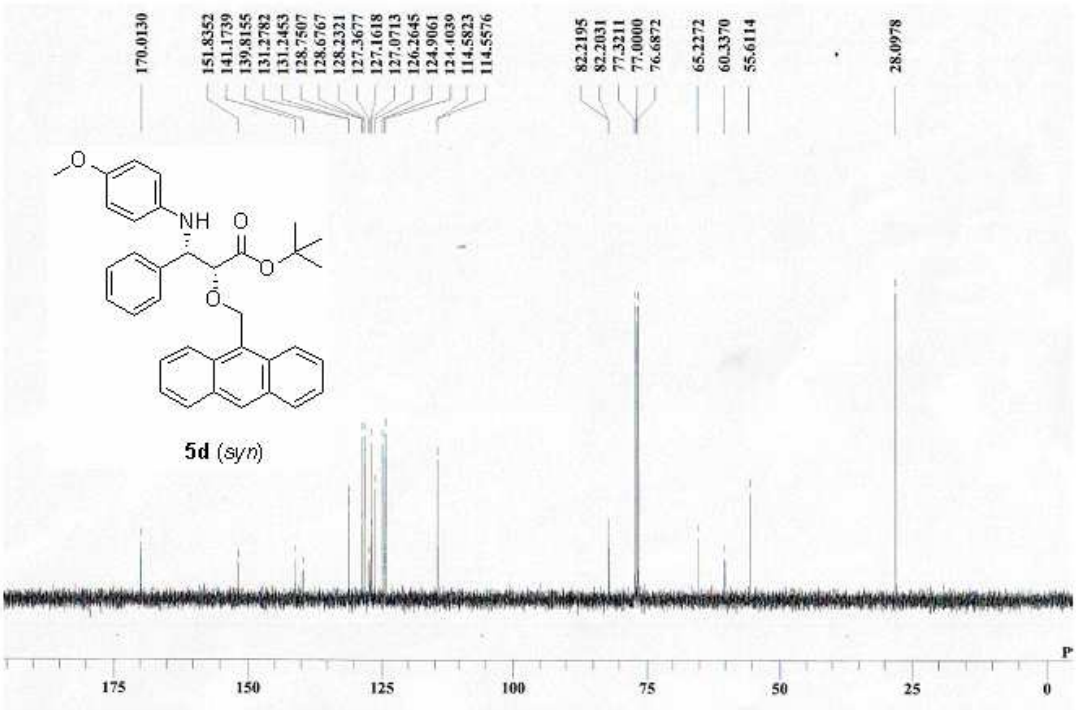
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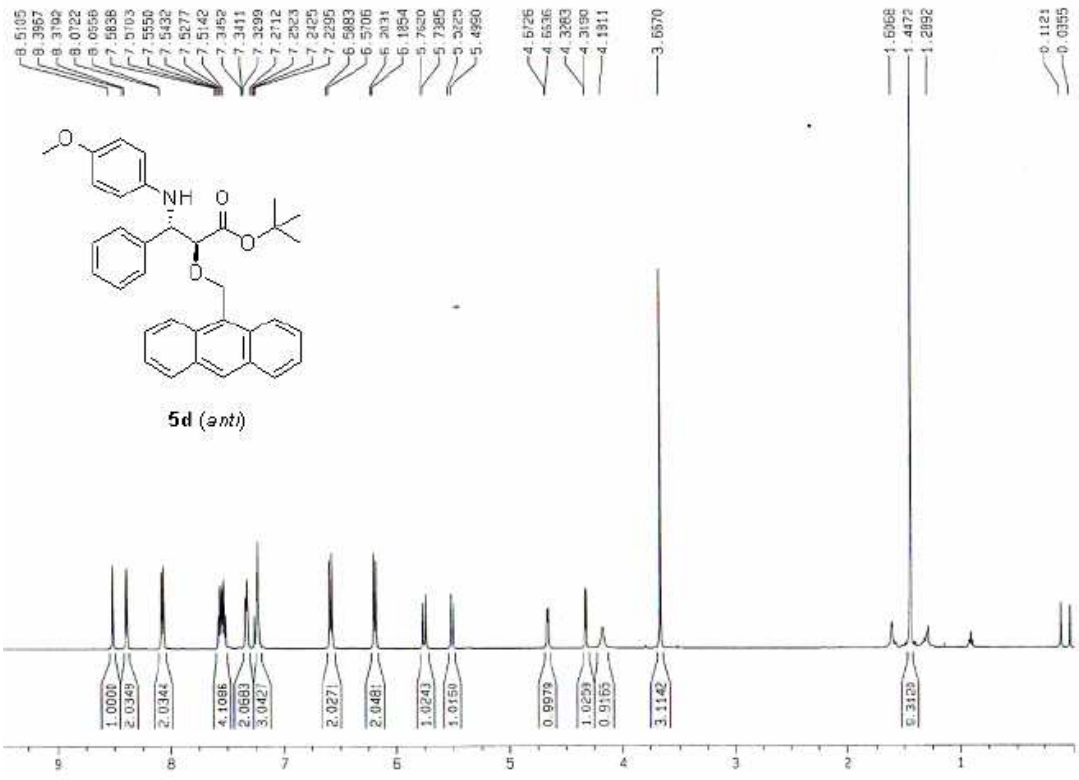
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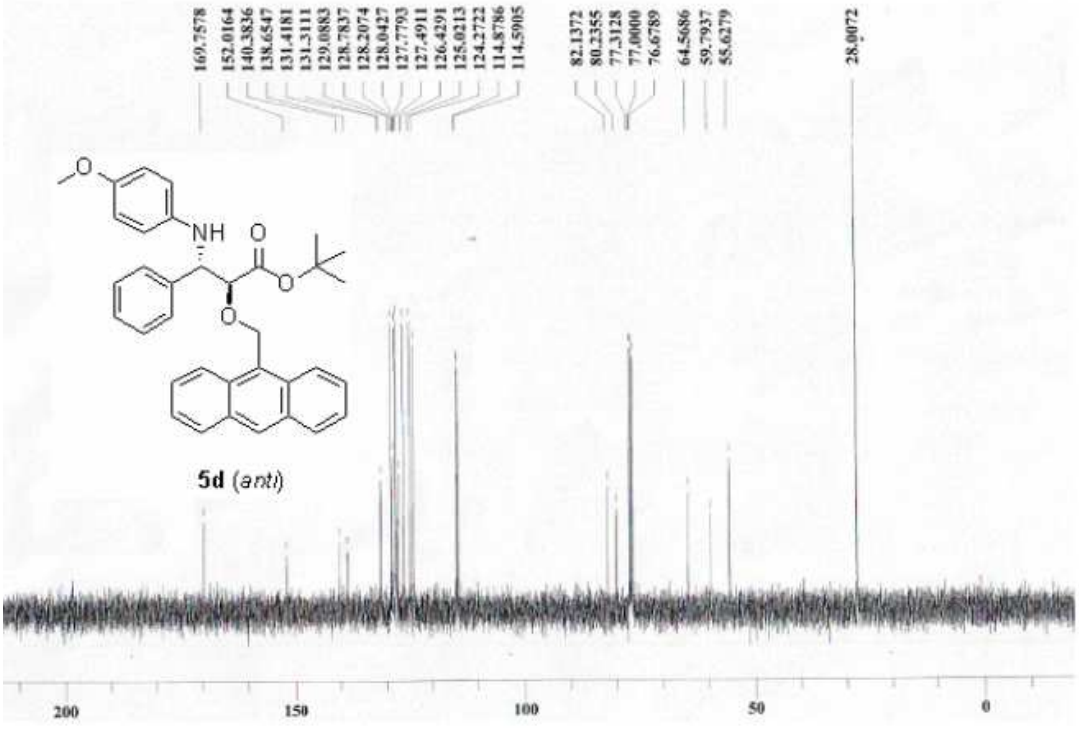
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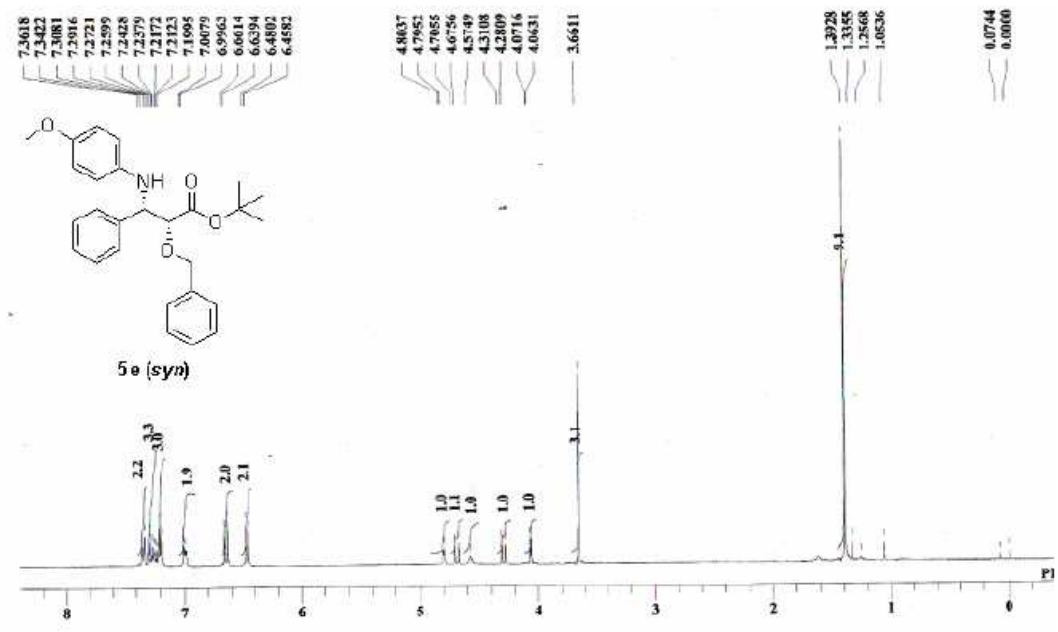
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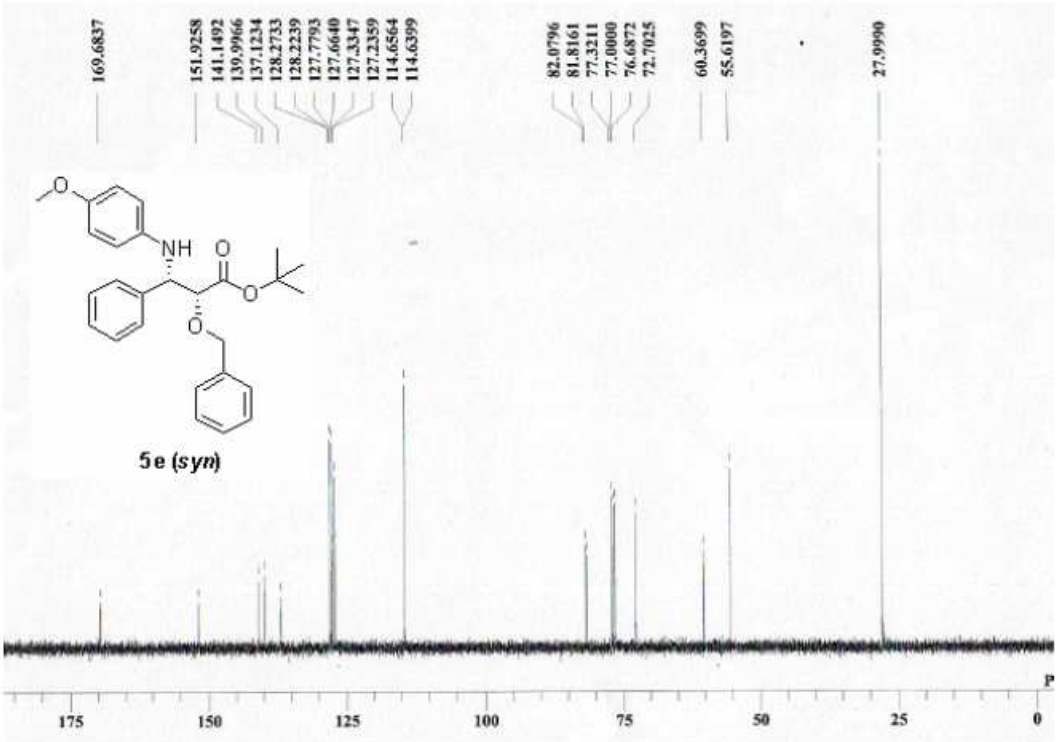
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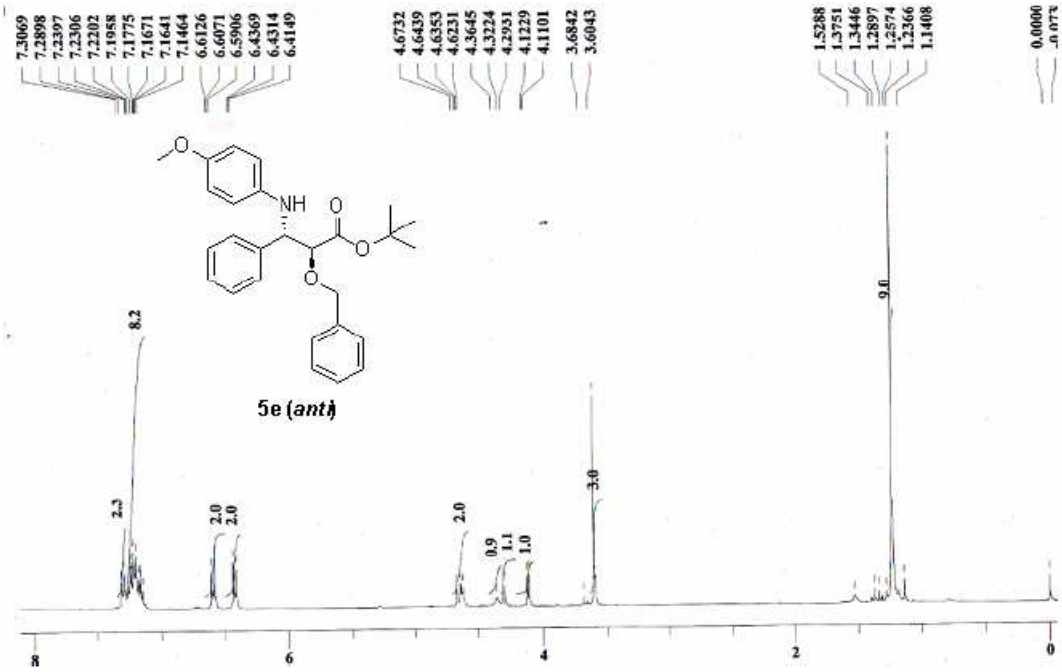
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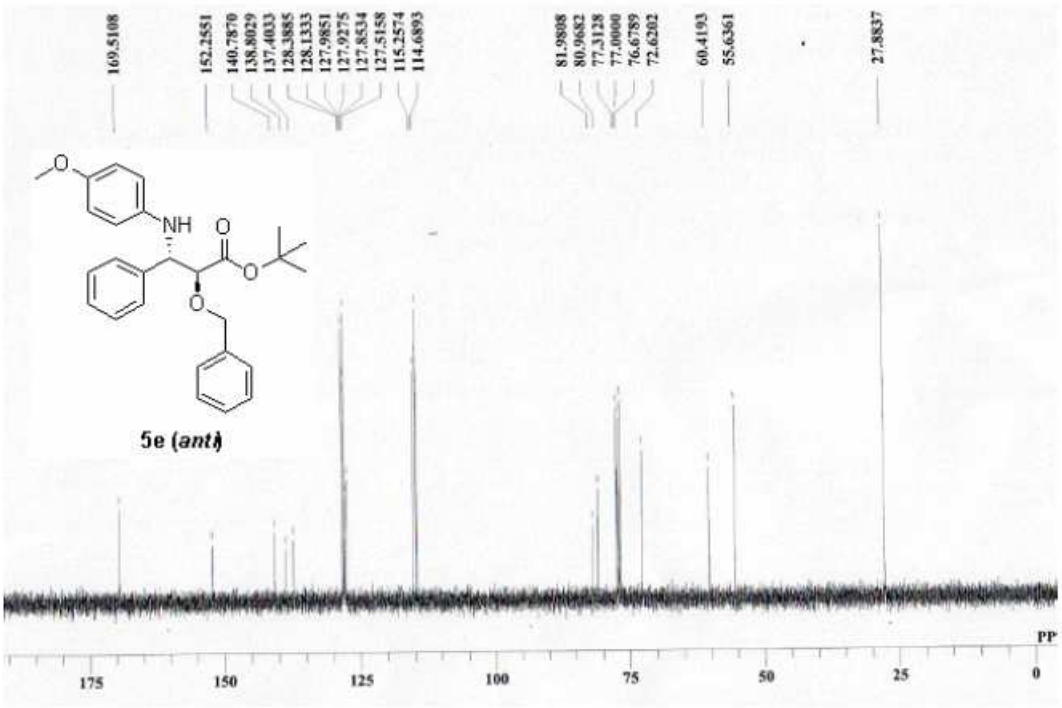
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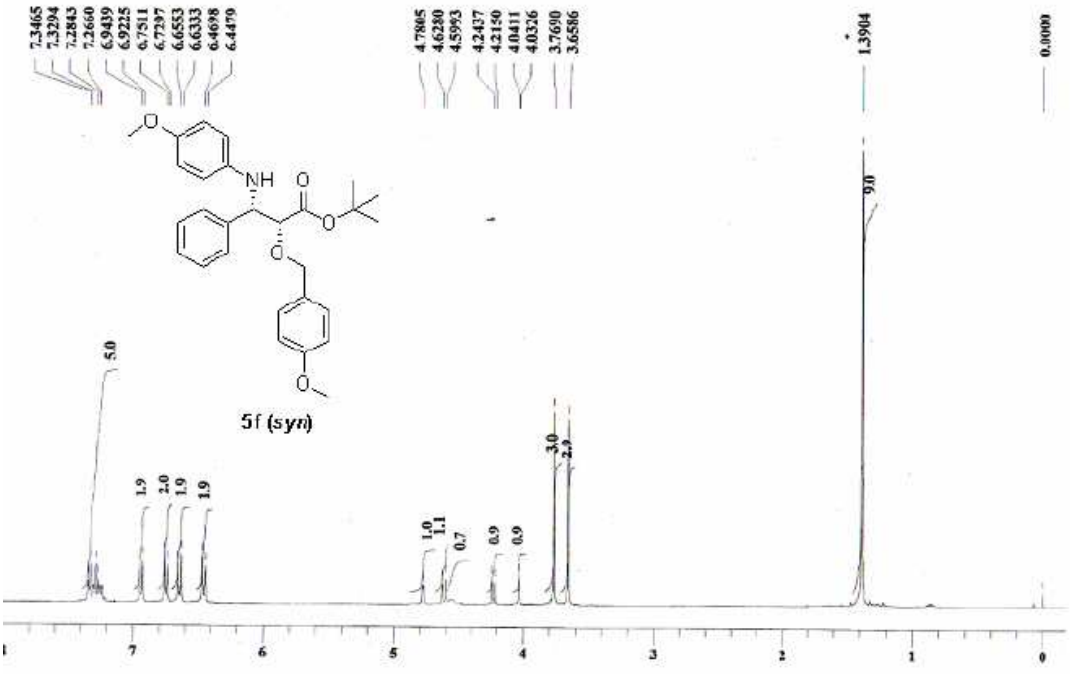
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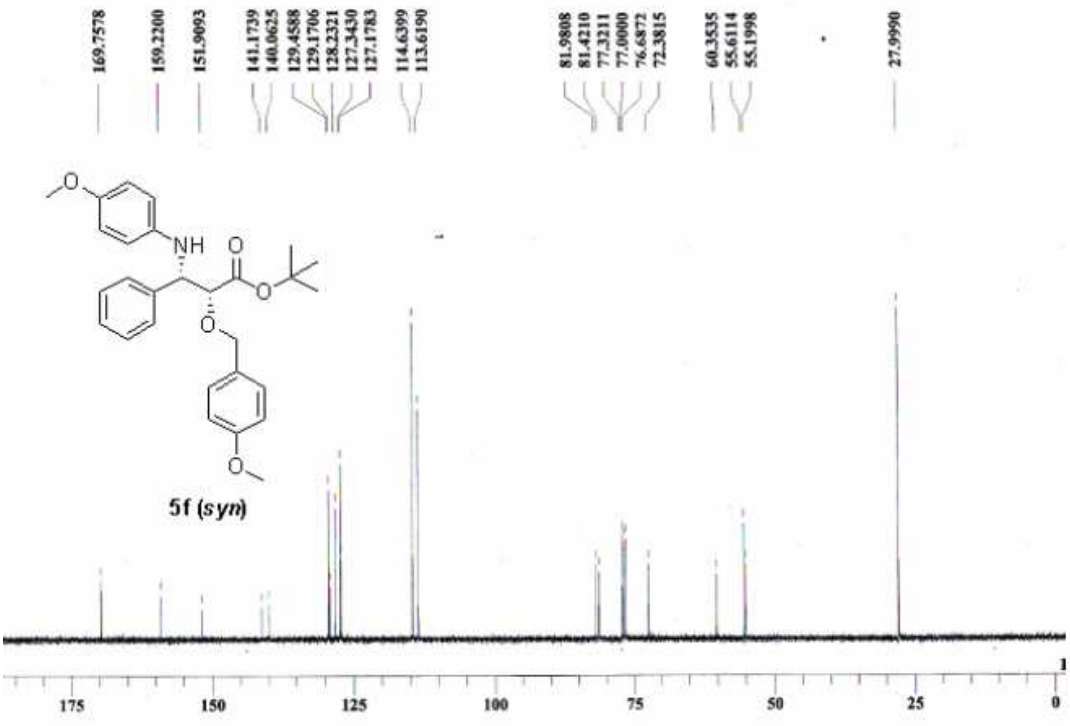
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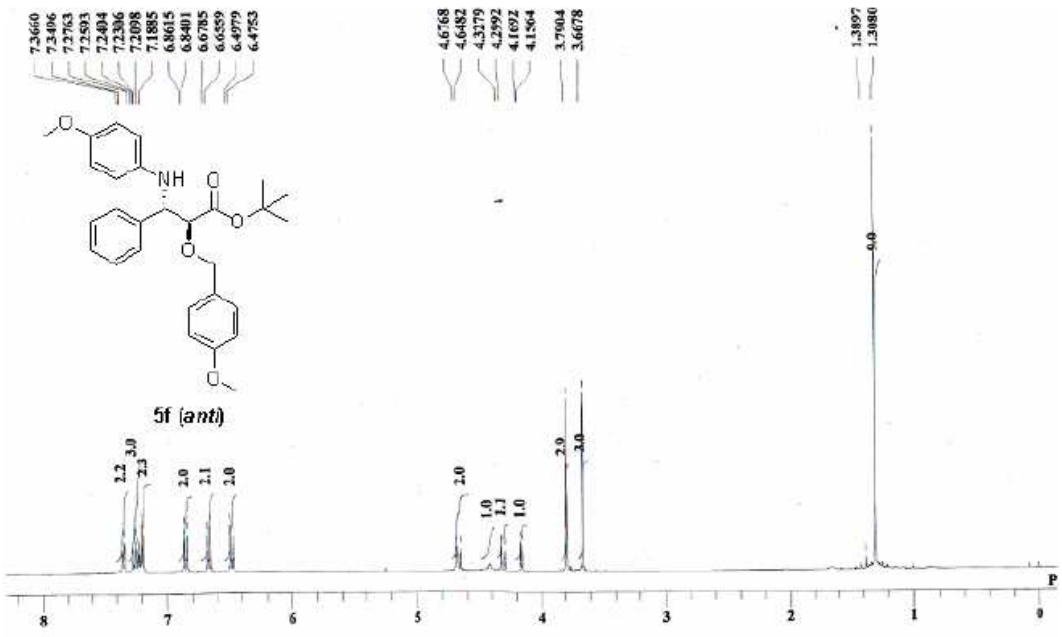
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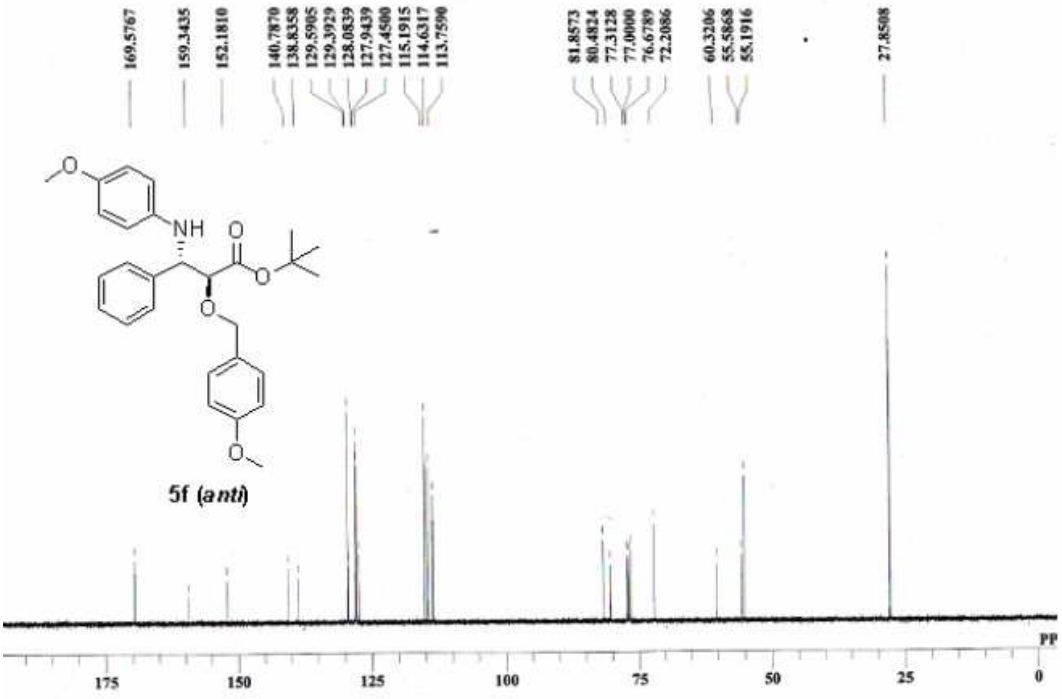
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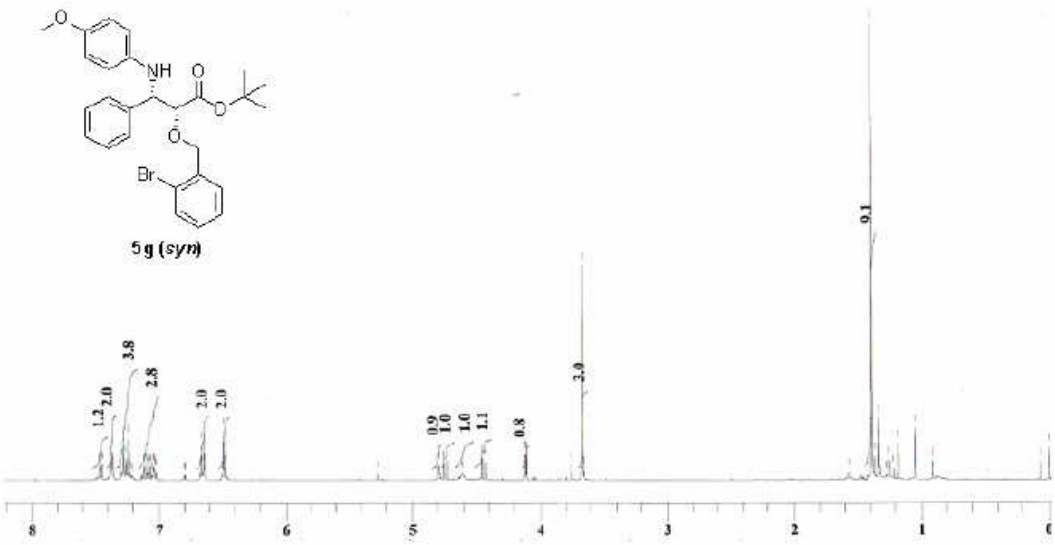
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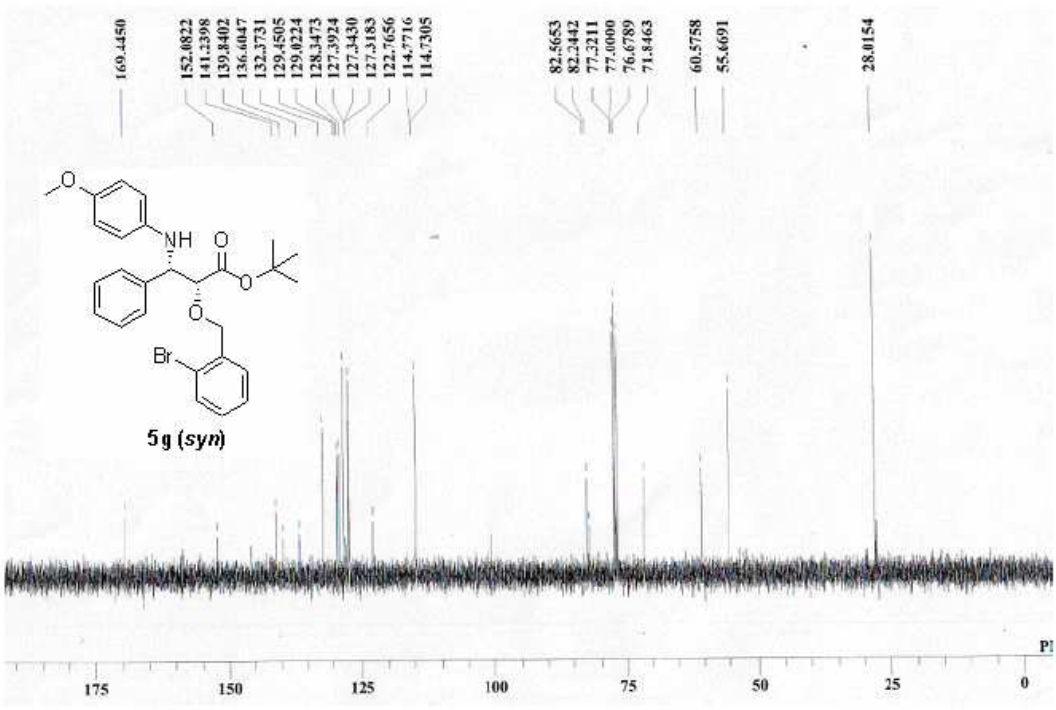
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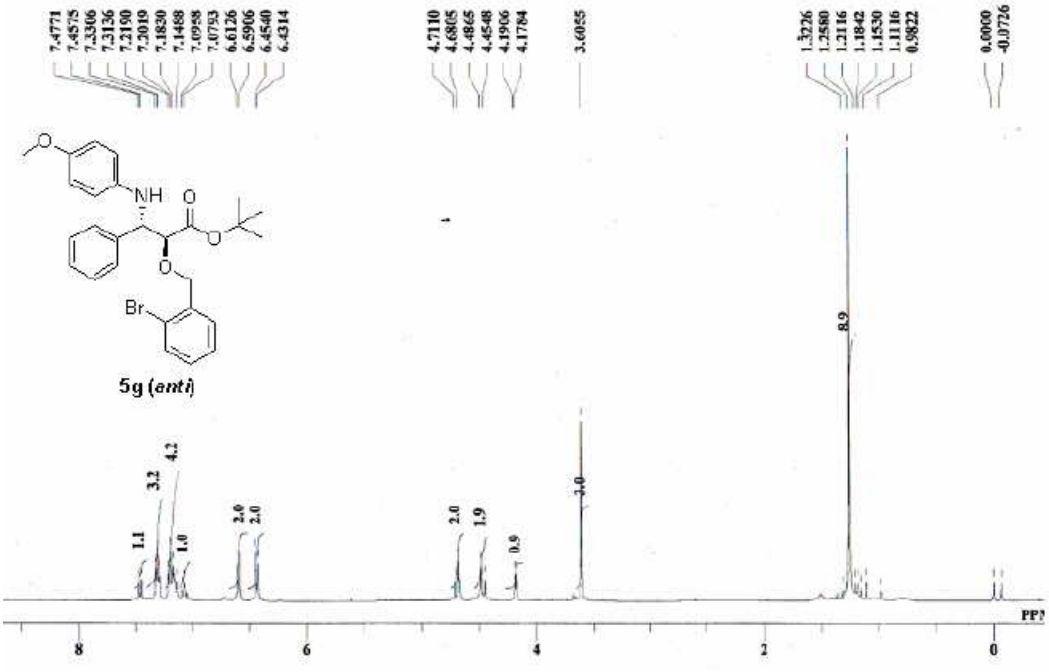
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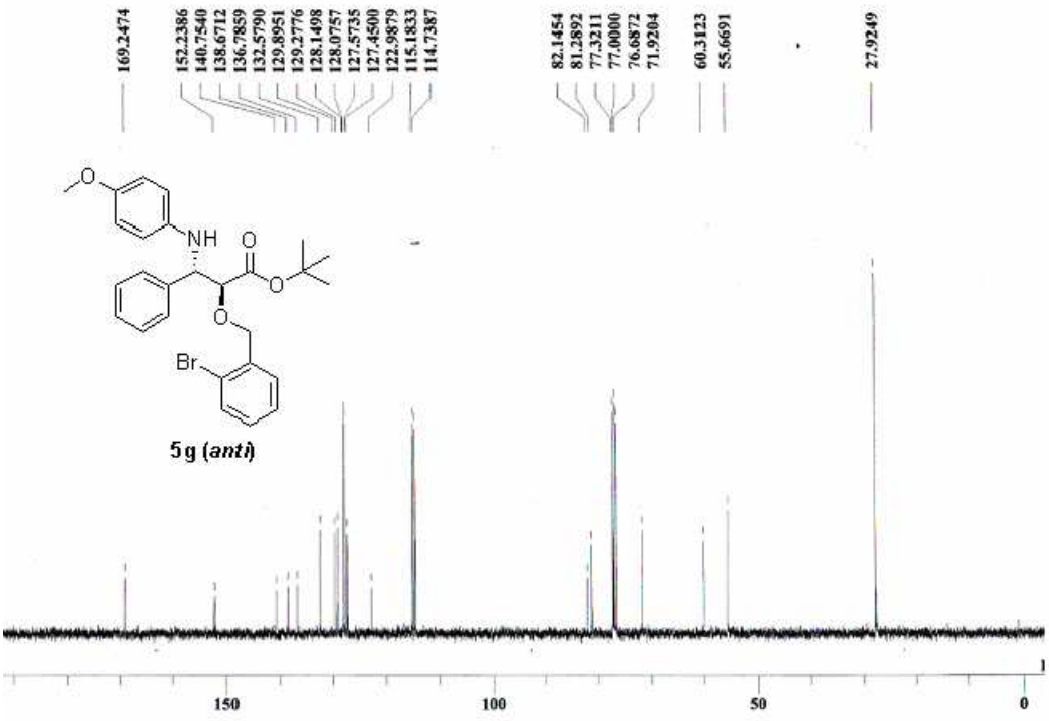
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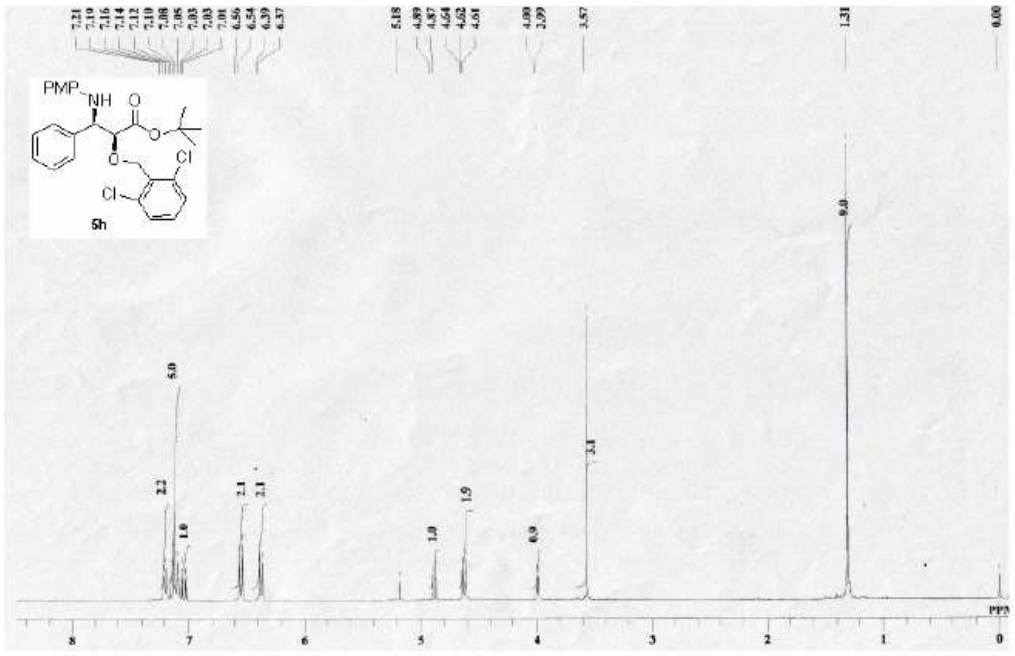
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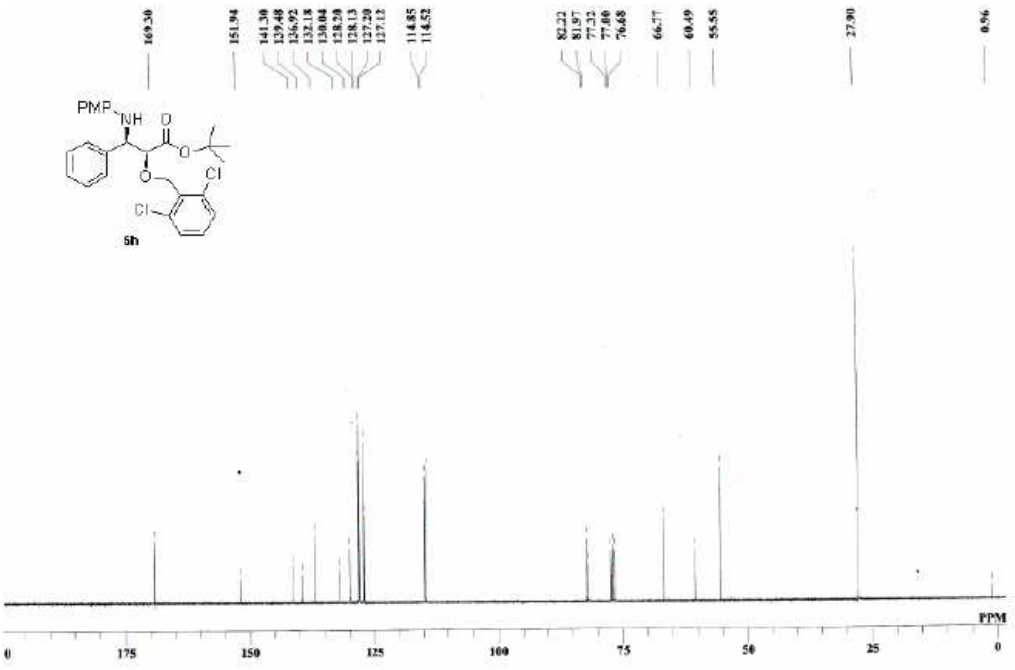
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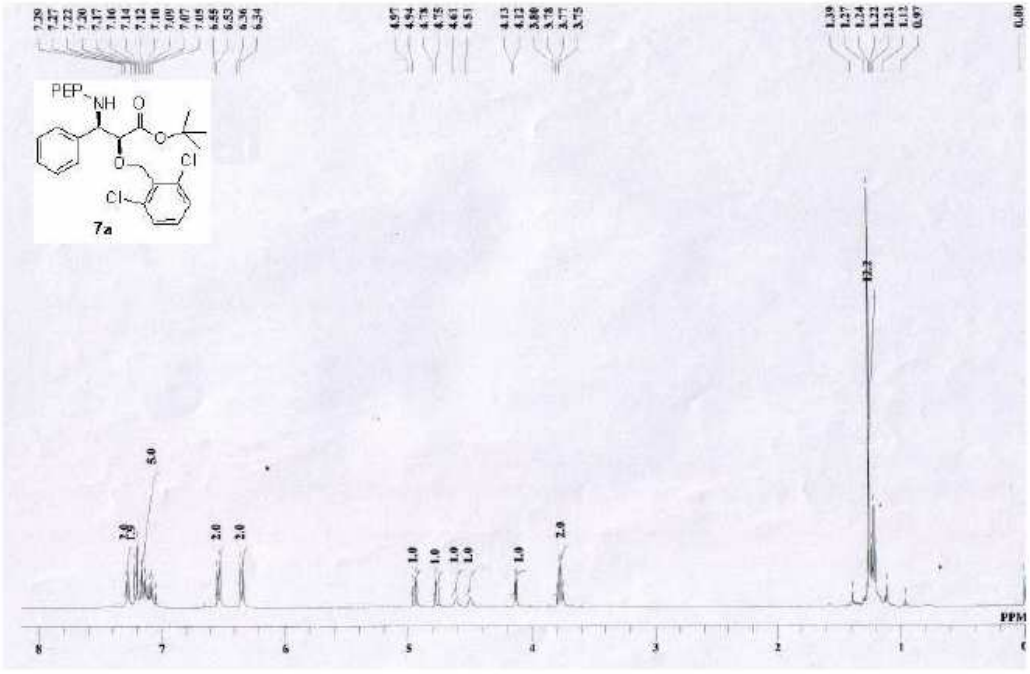
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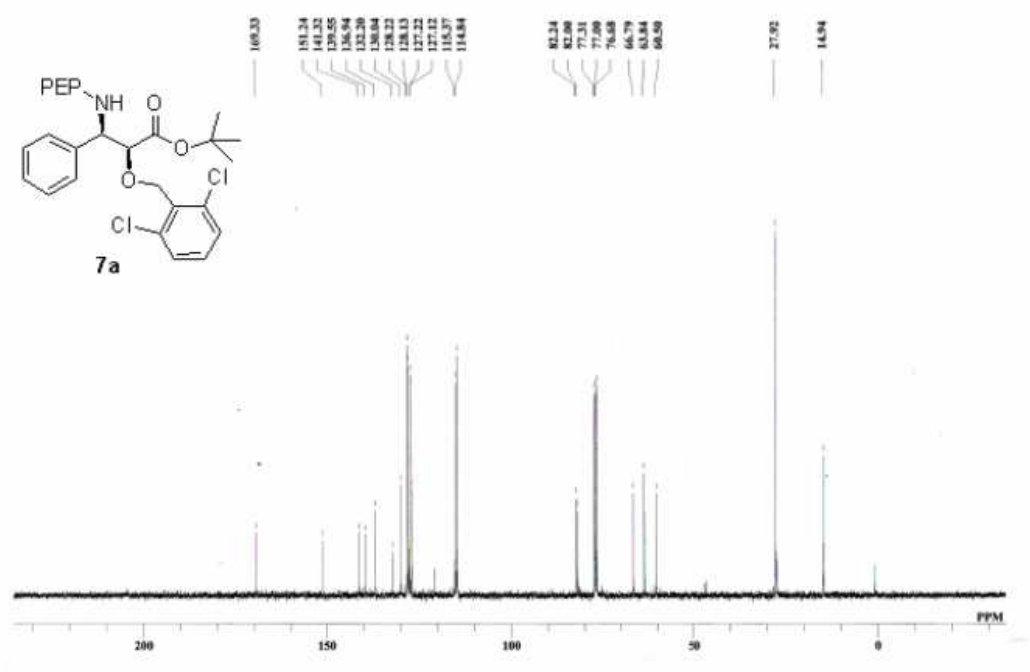
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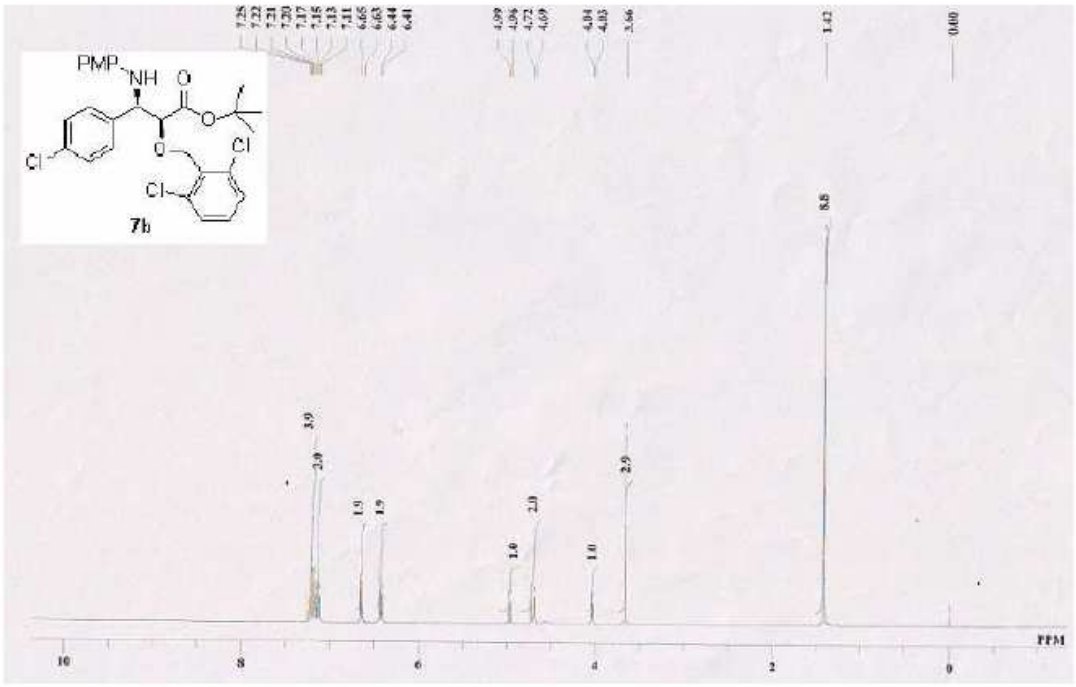
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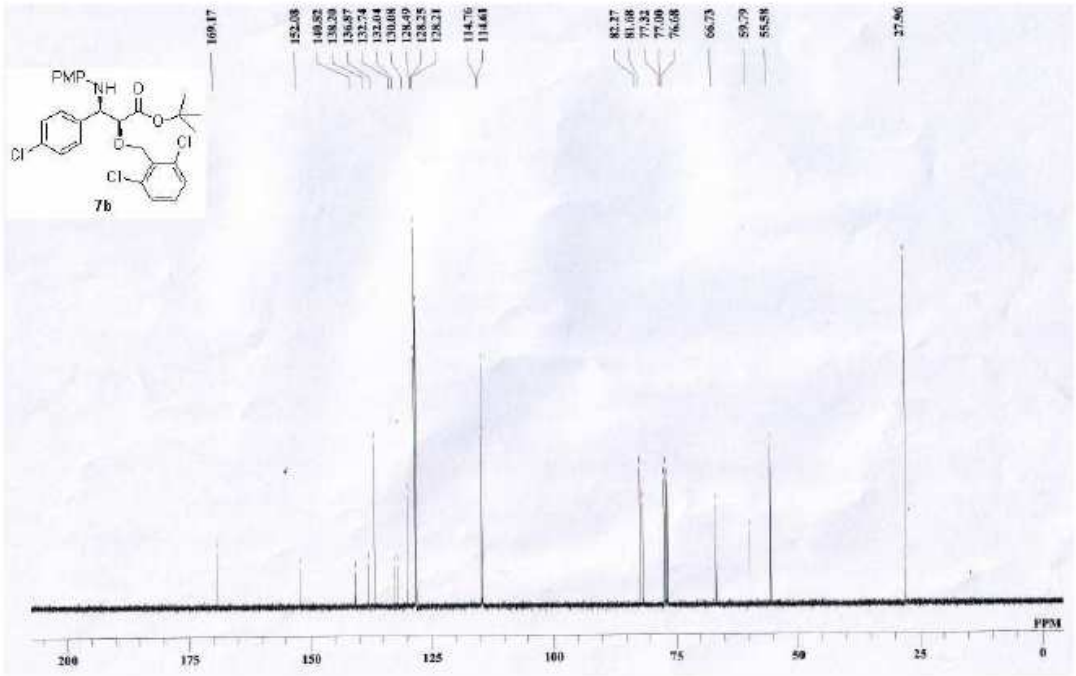
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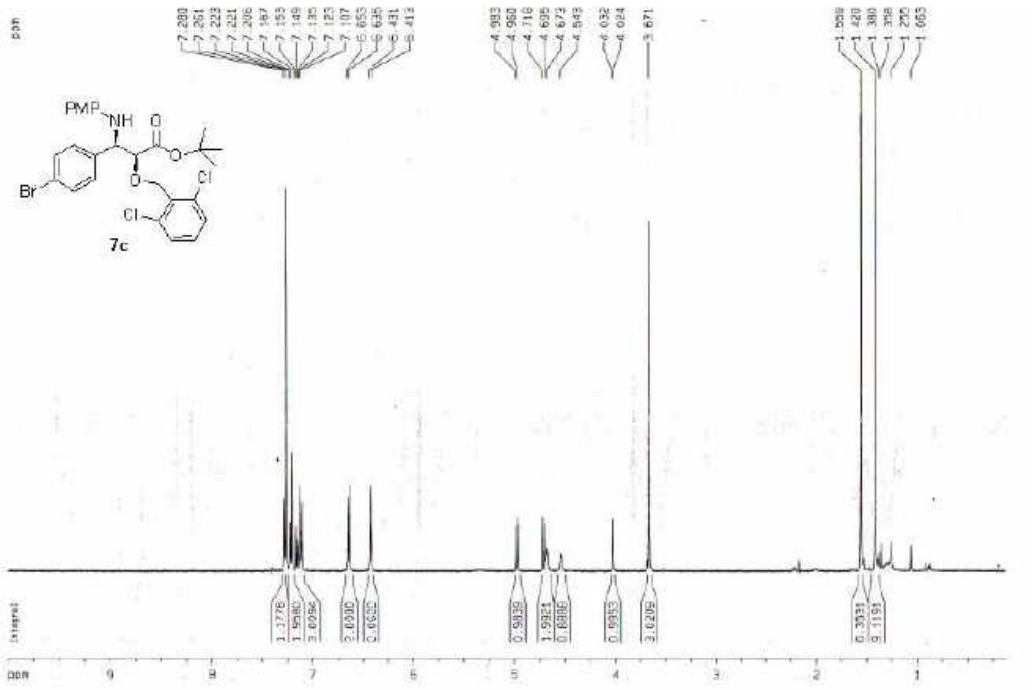
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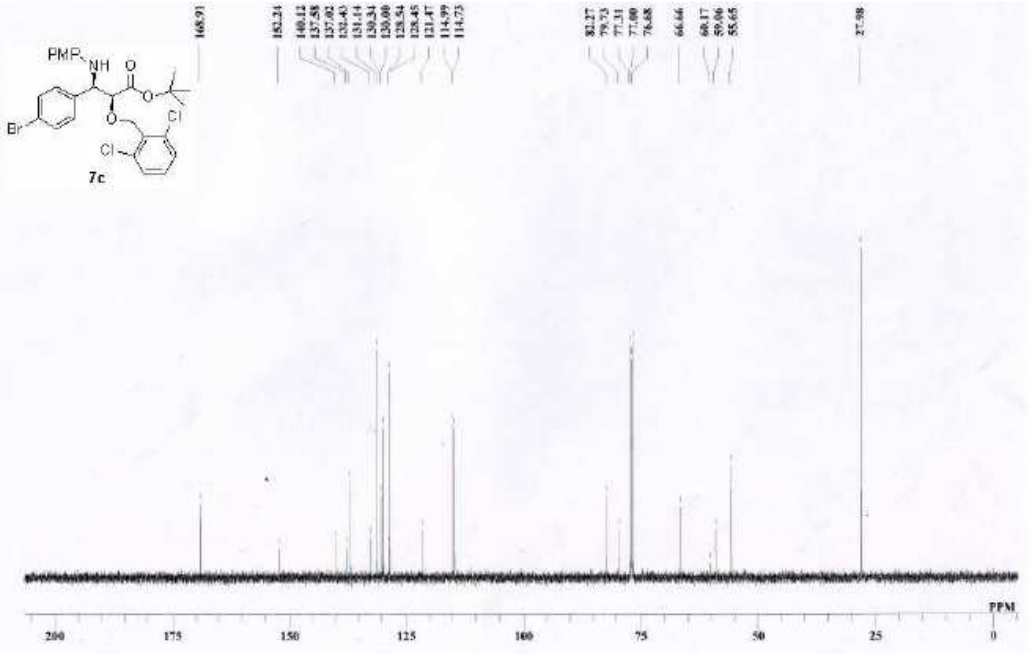
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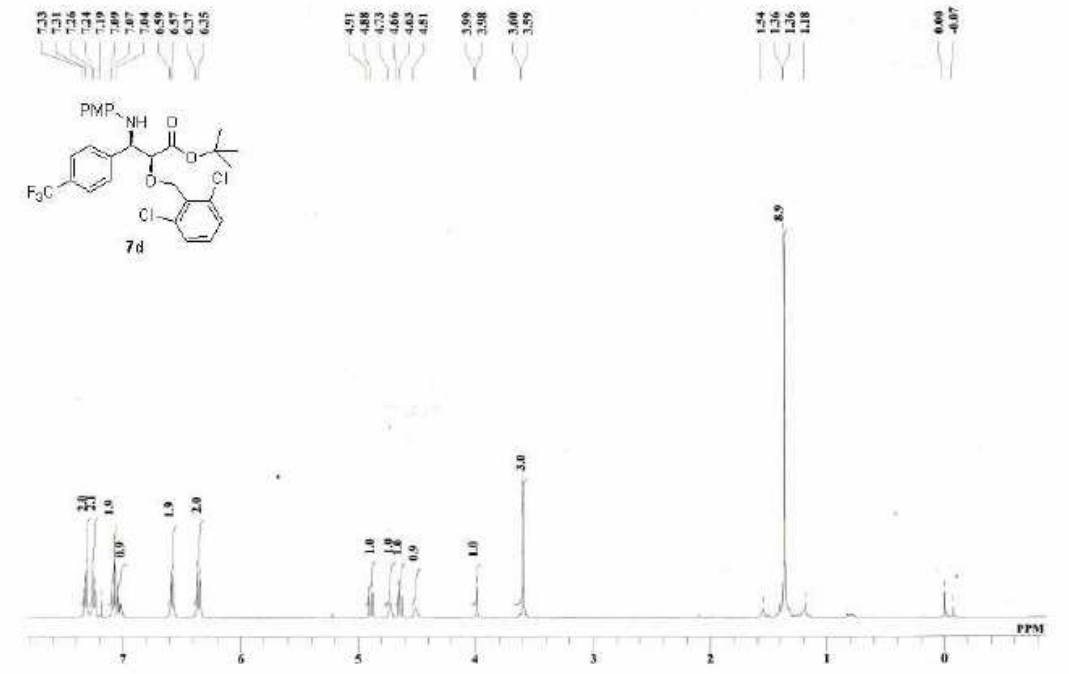
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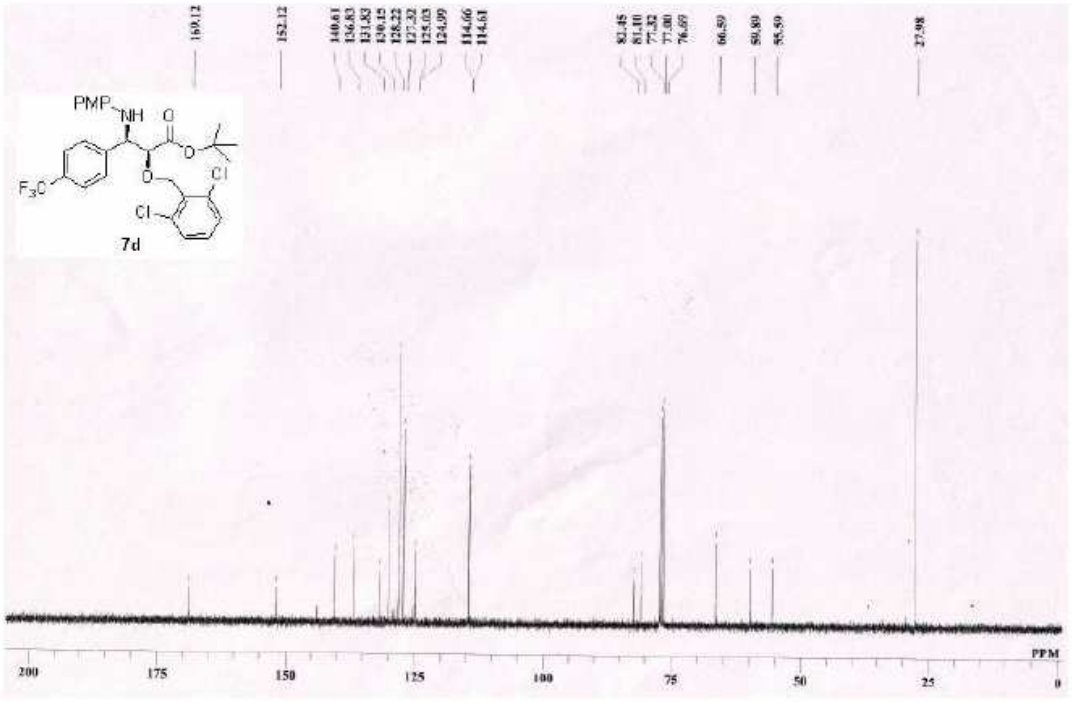
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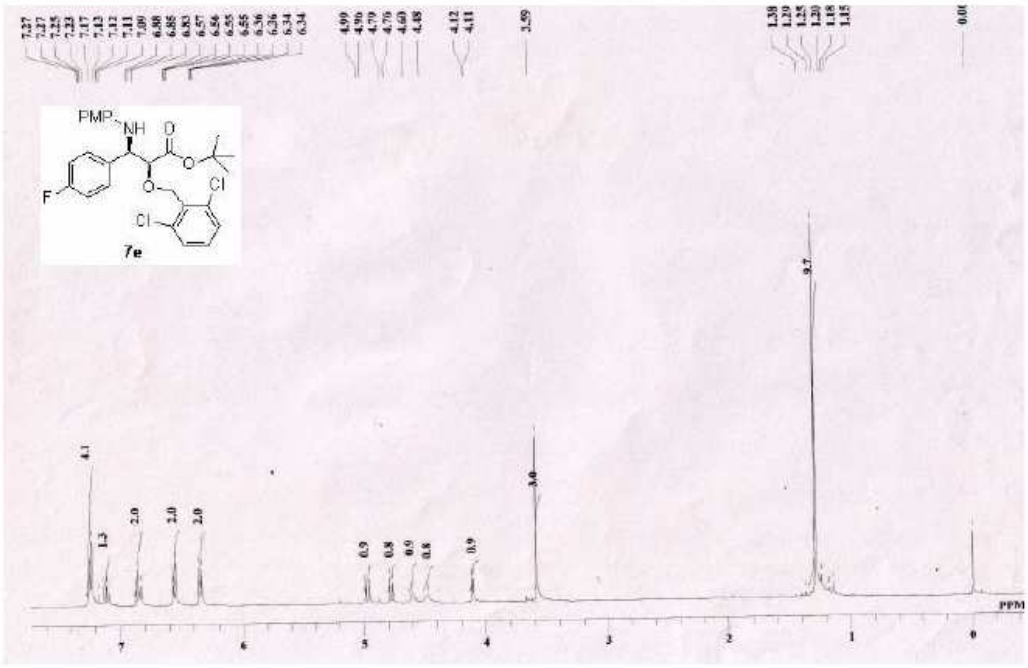
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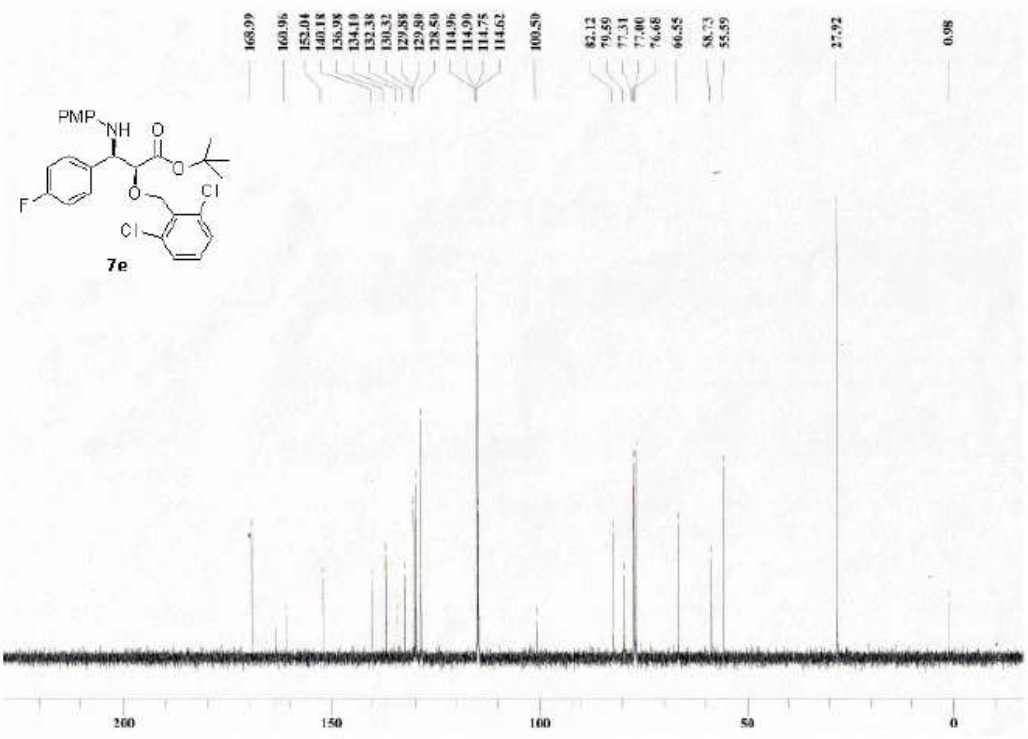
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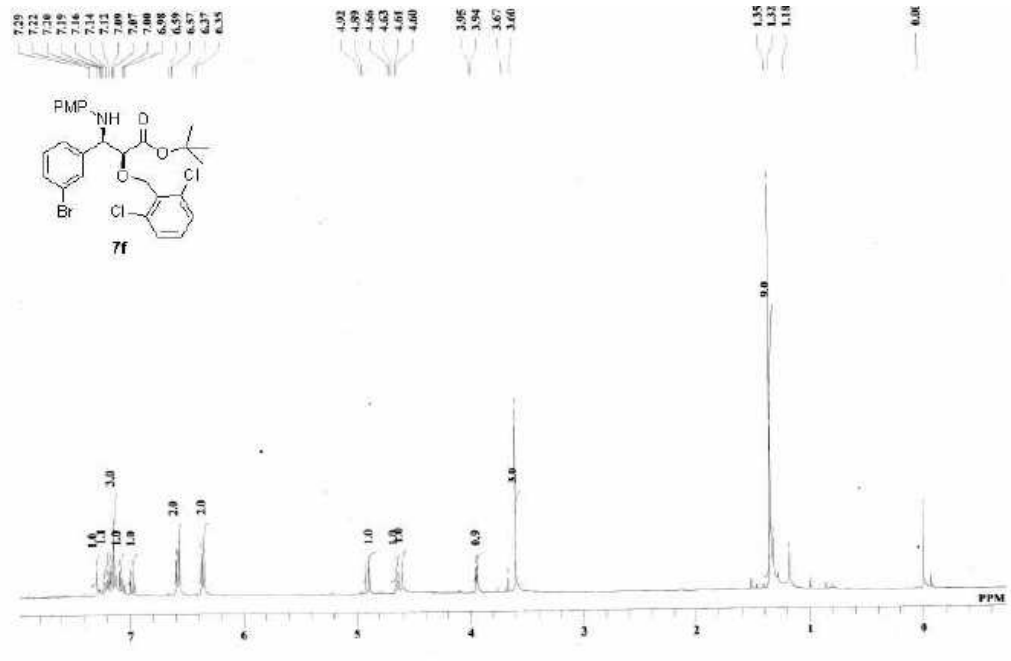
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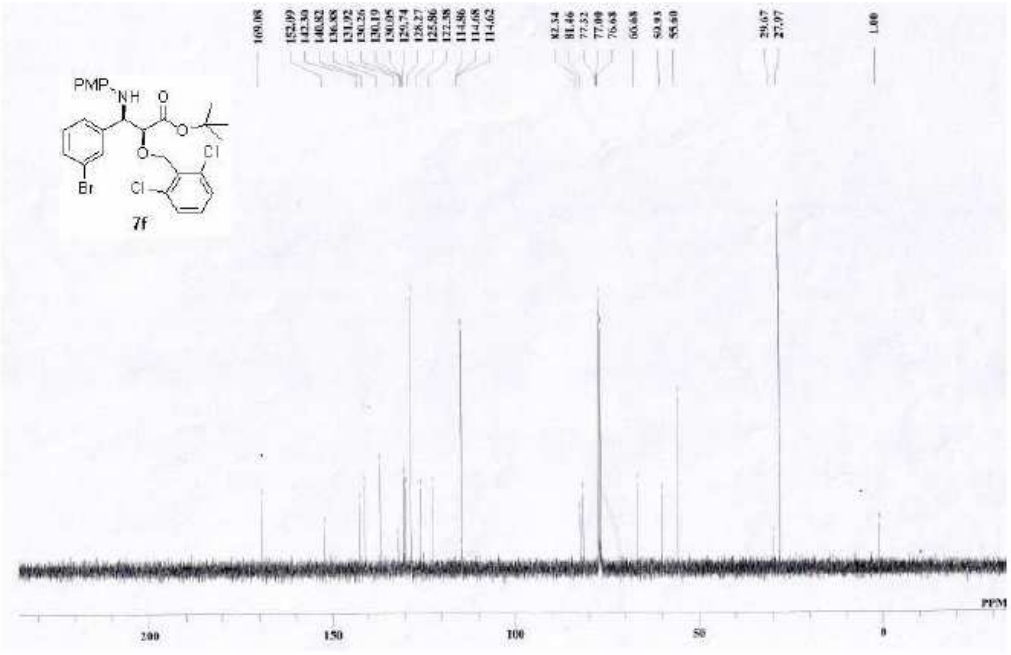
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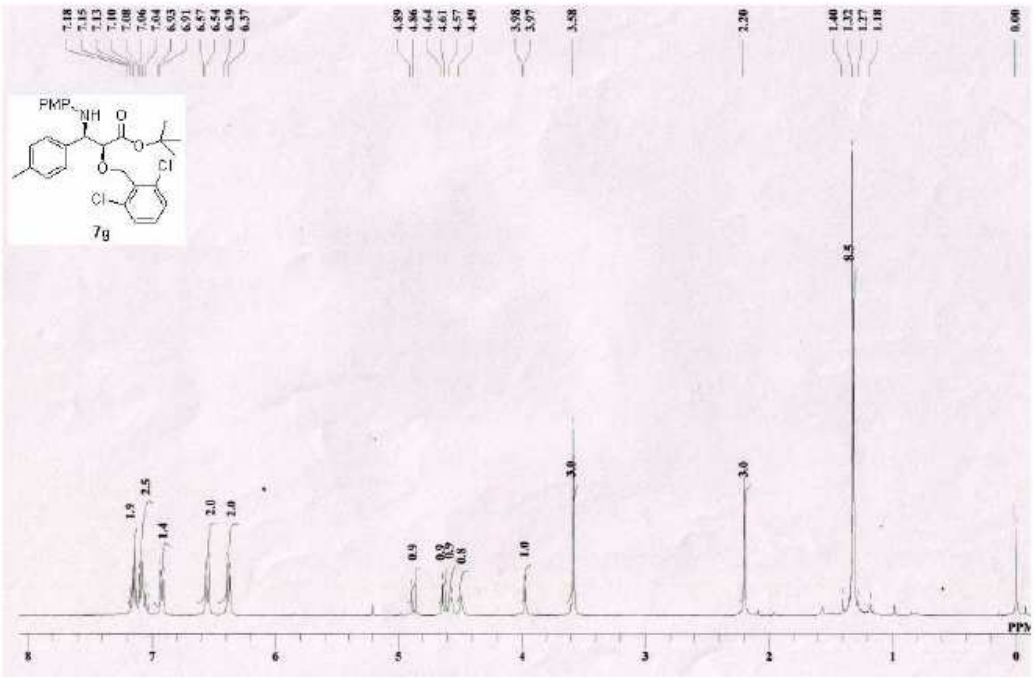
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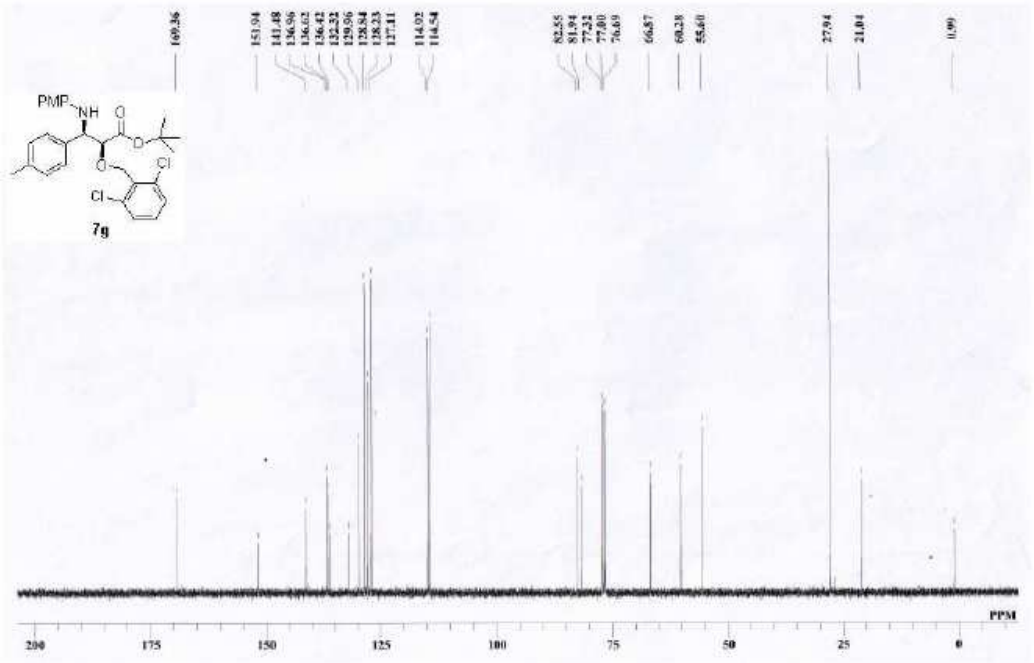
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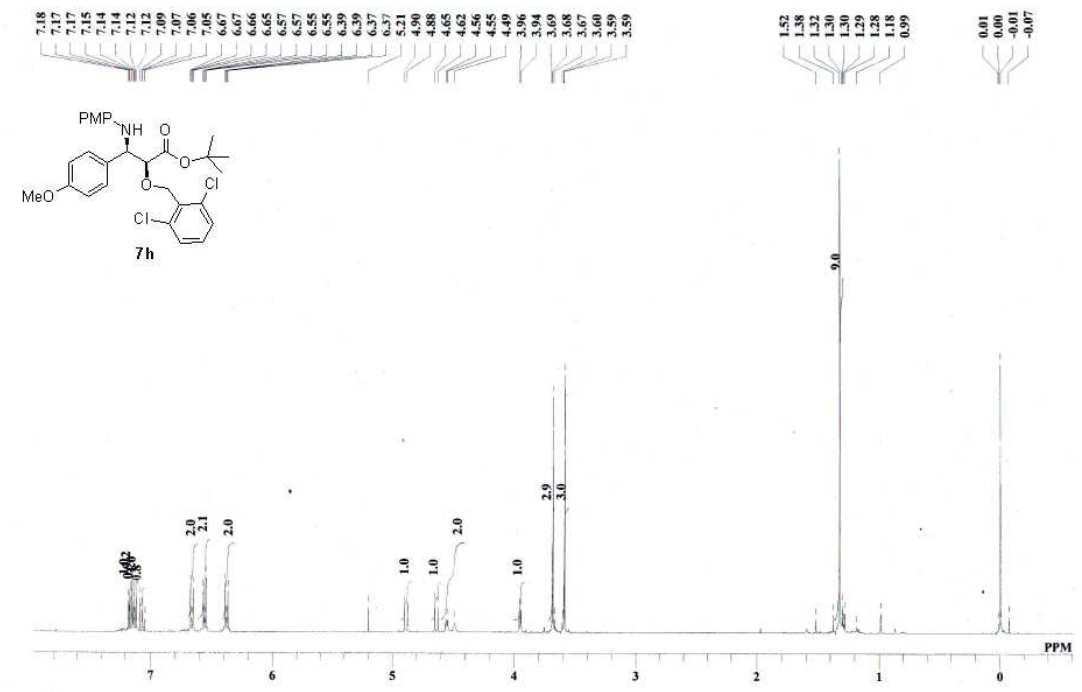
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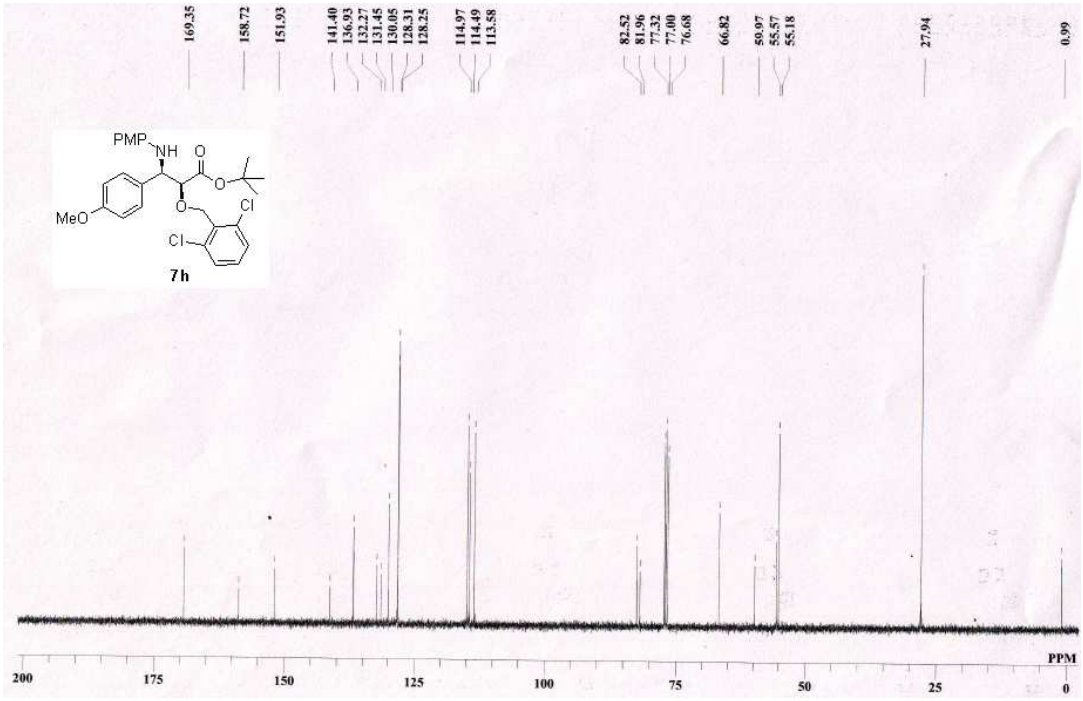
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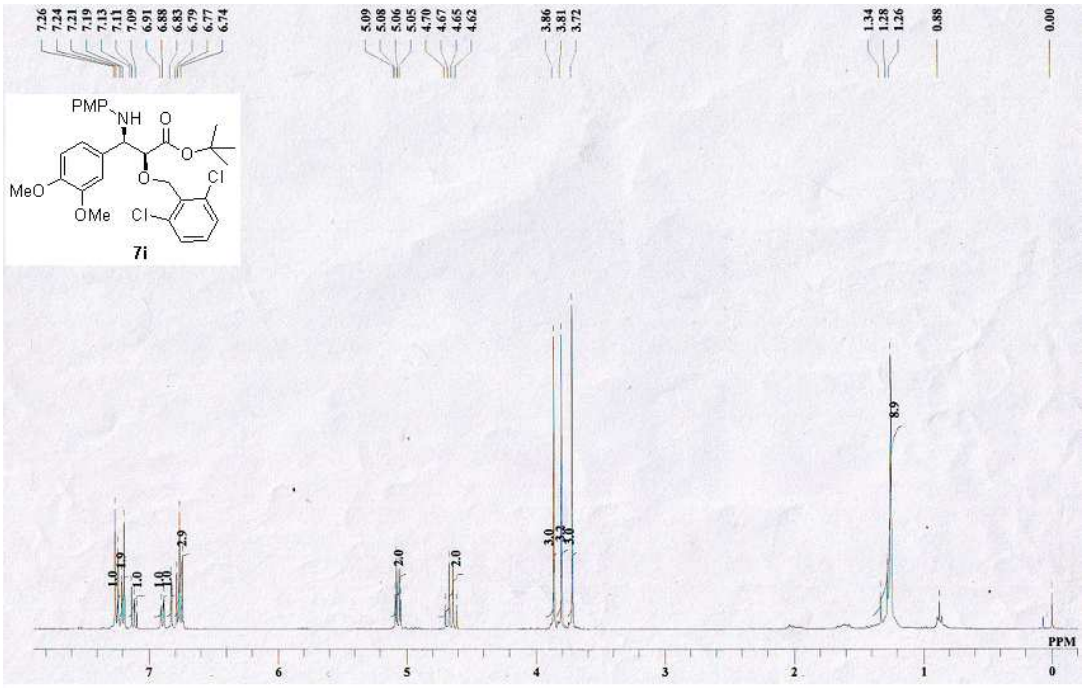
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5.06
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OMe
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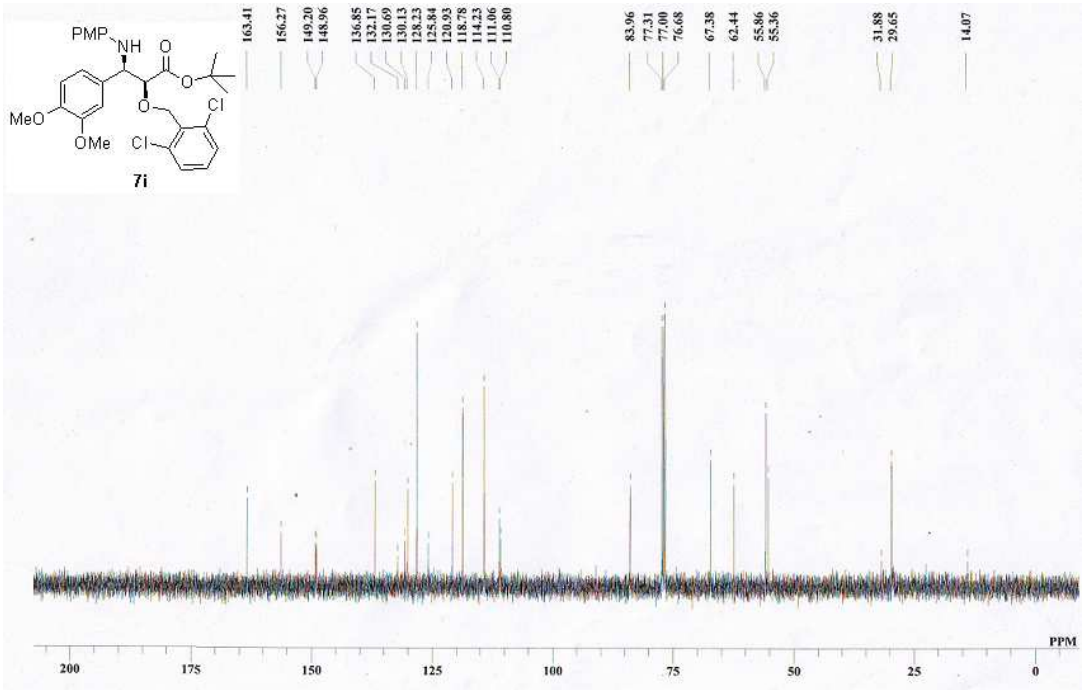
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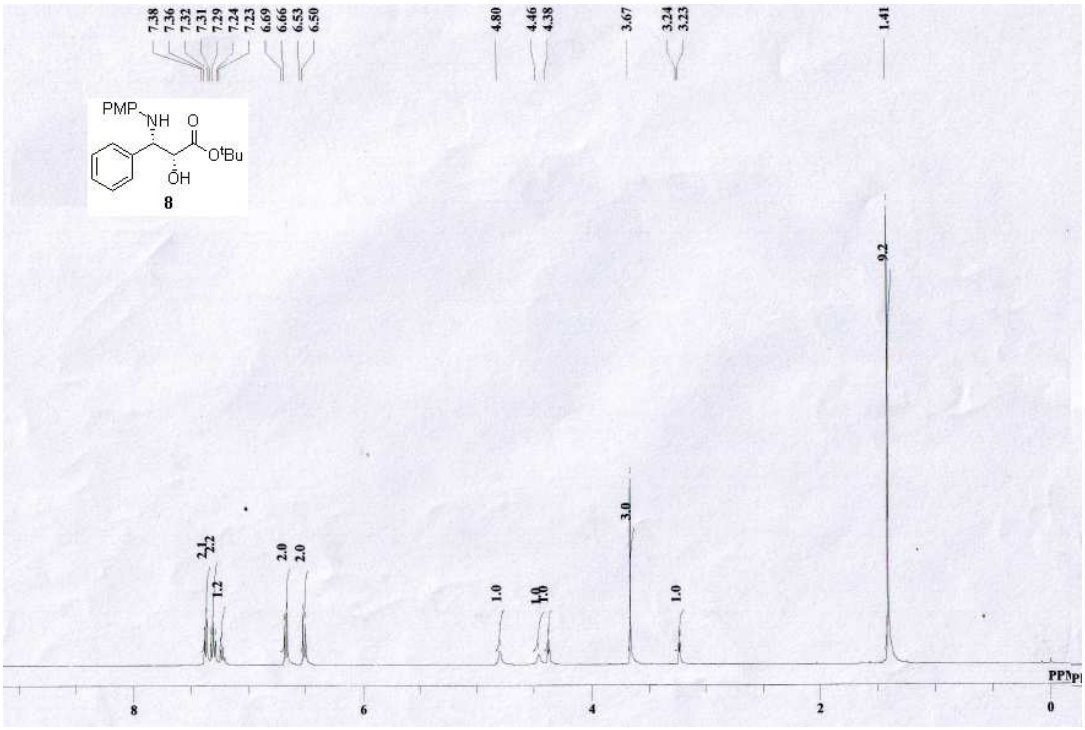
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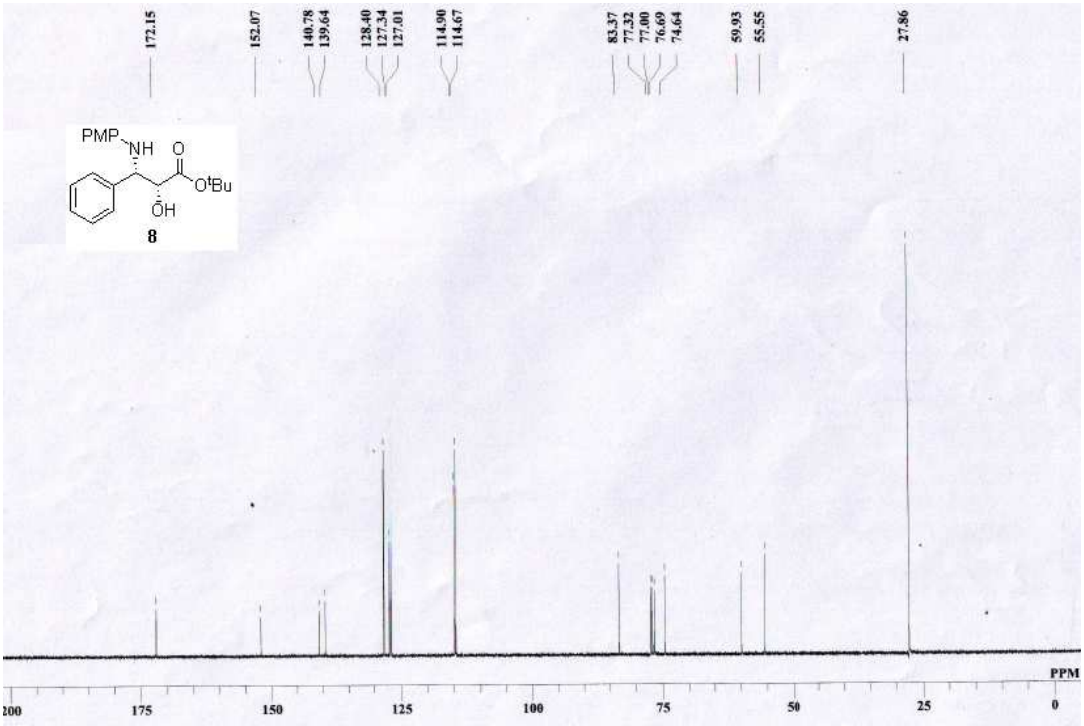
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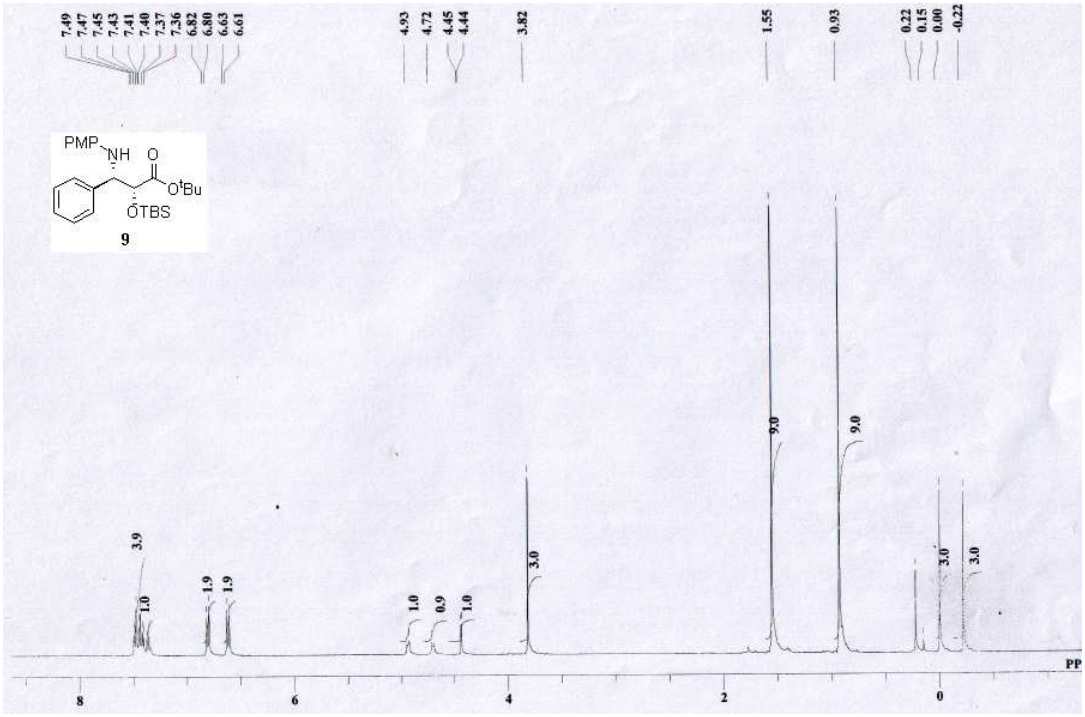
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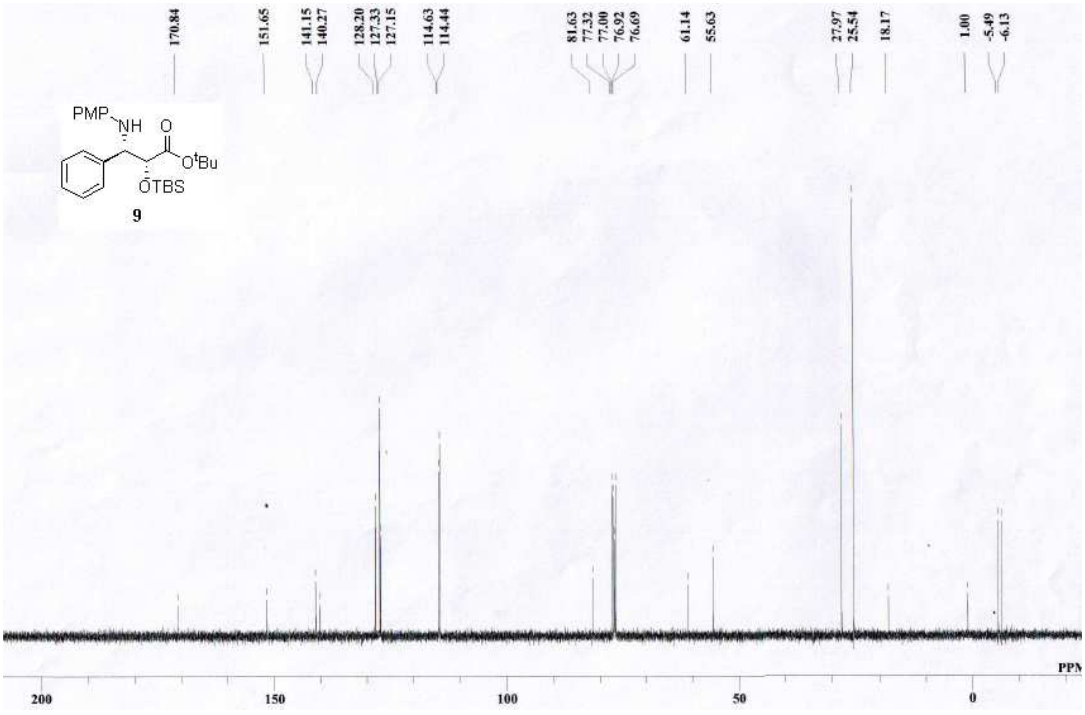
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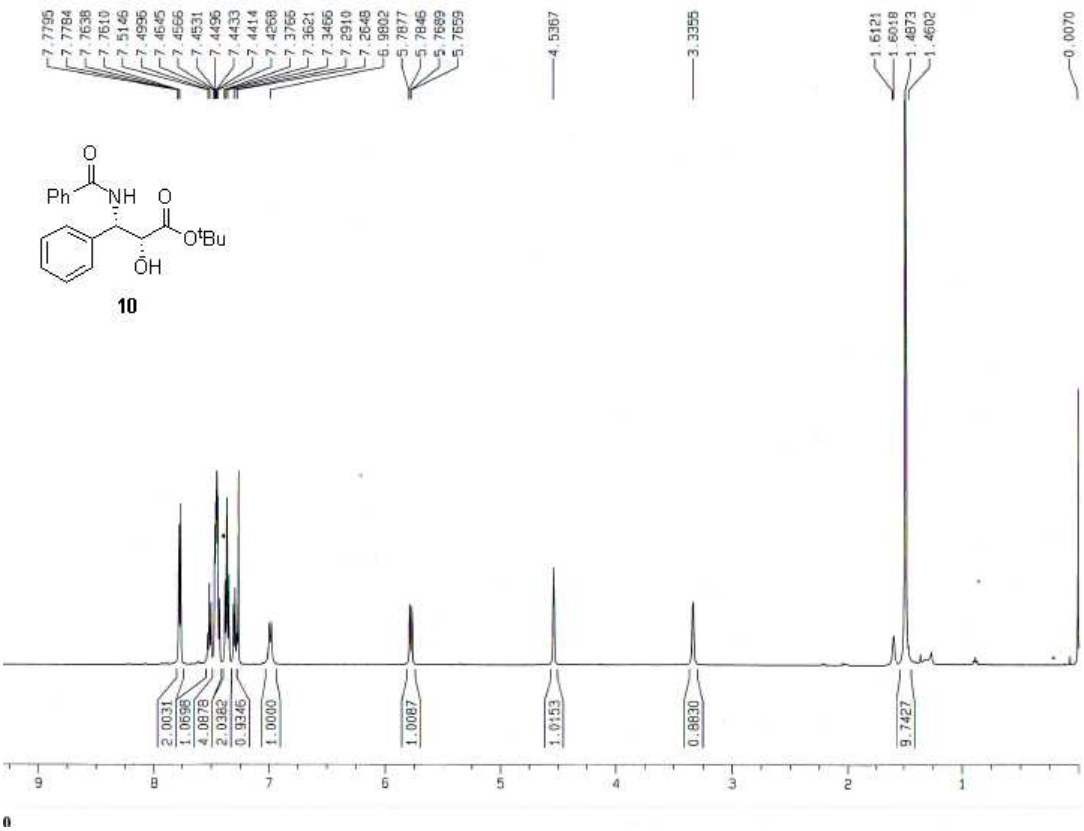
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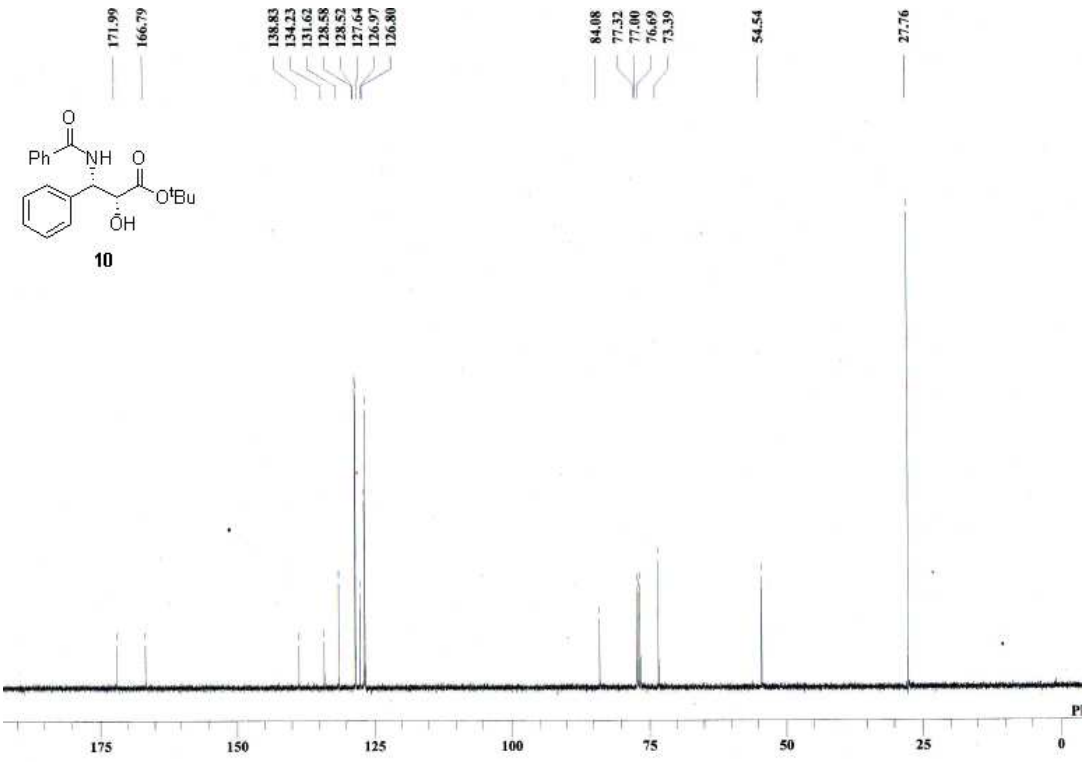
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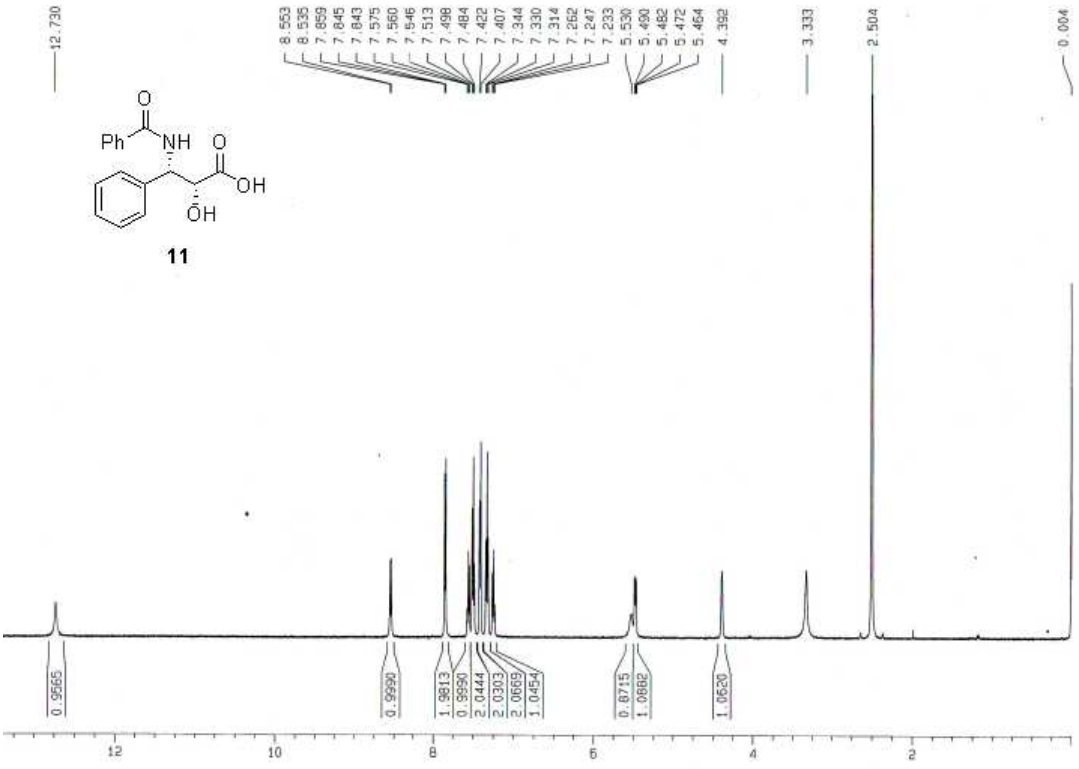
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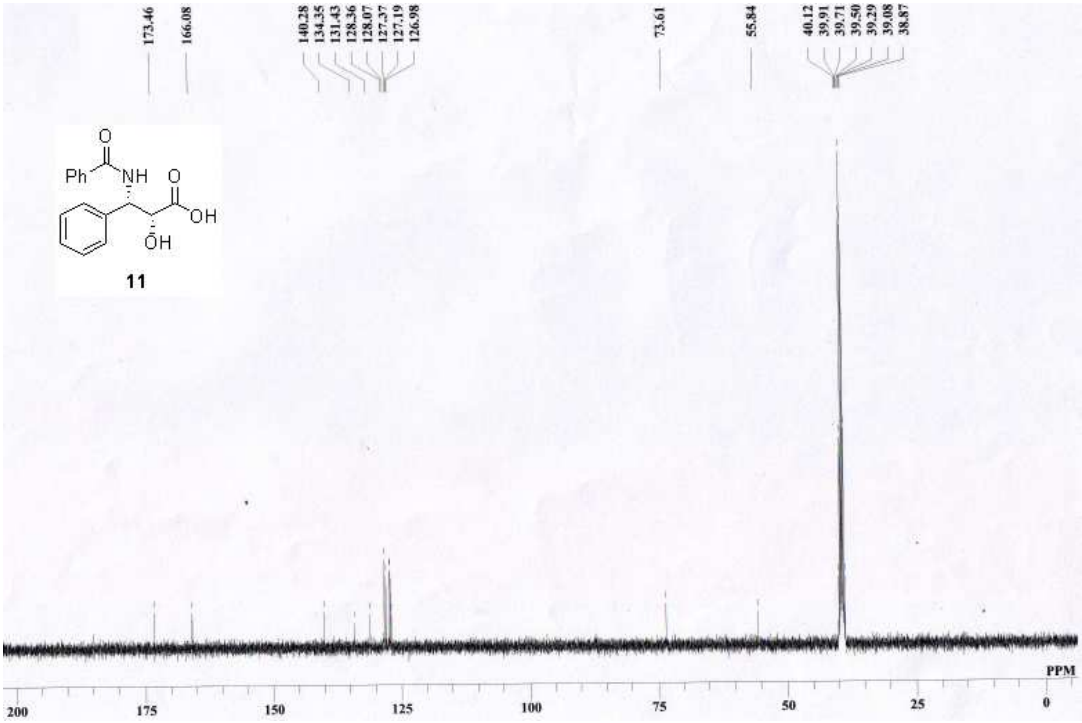
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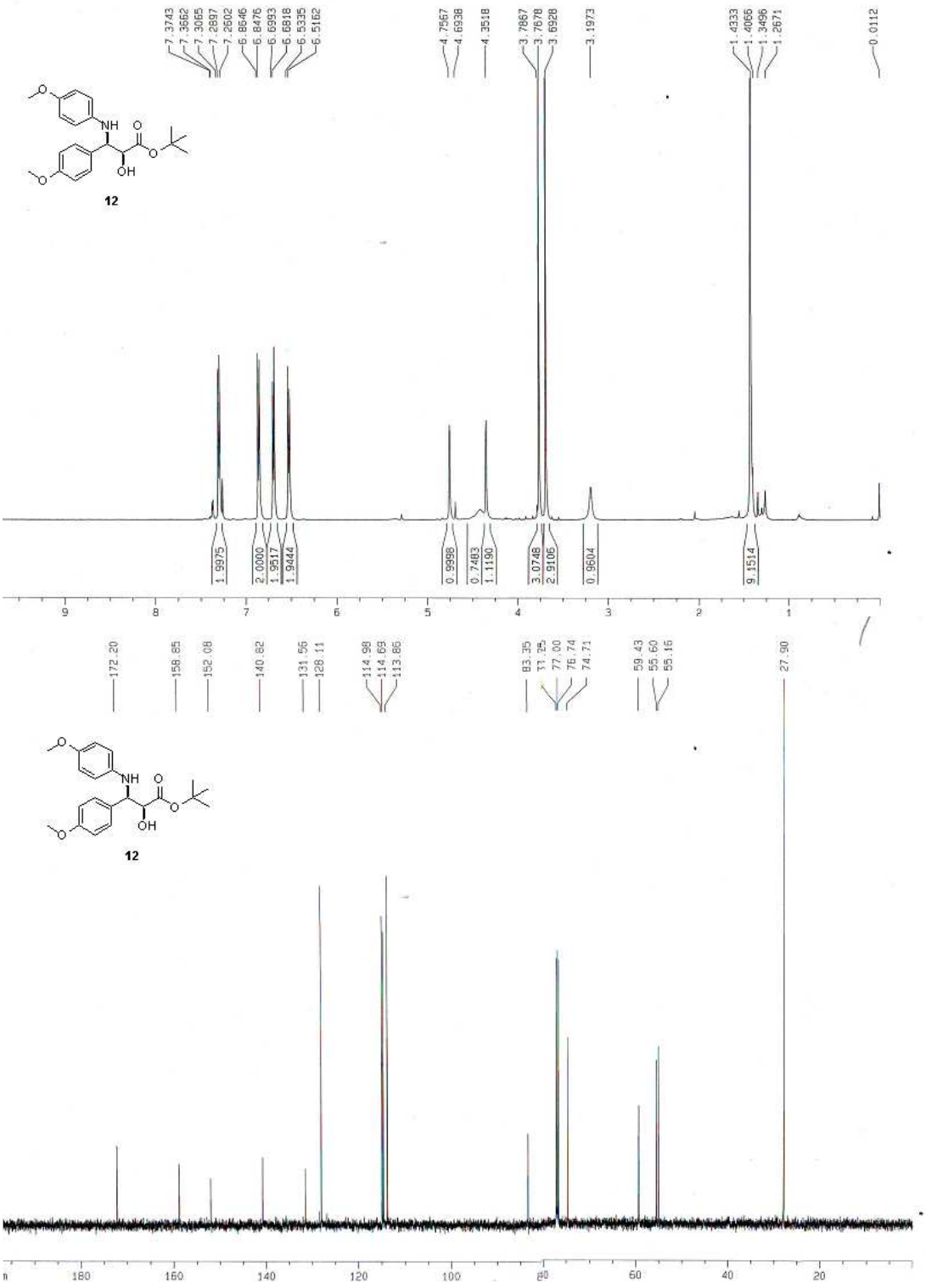
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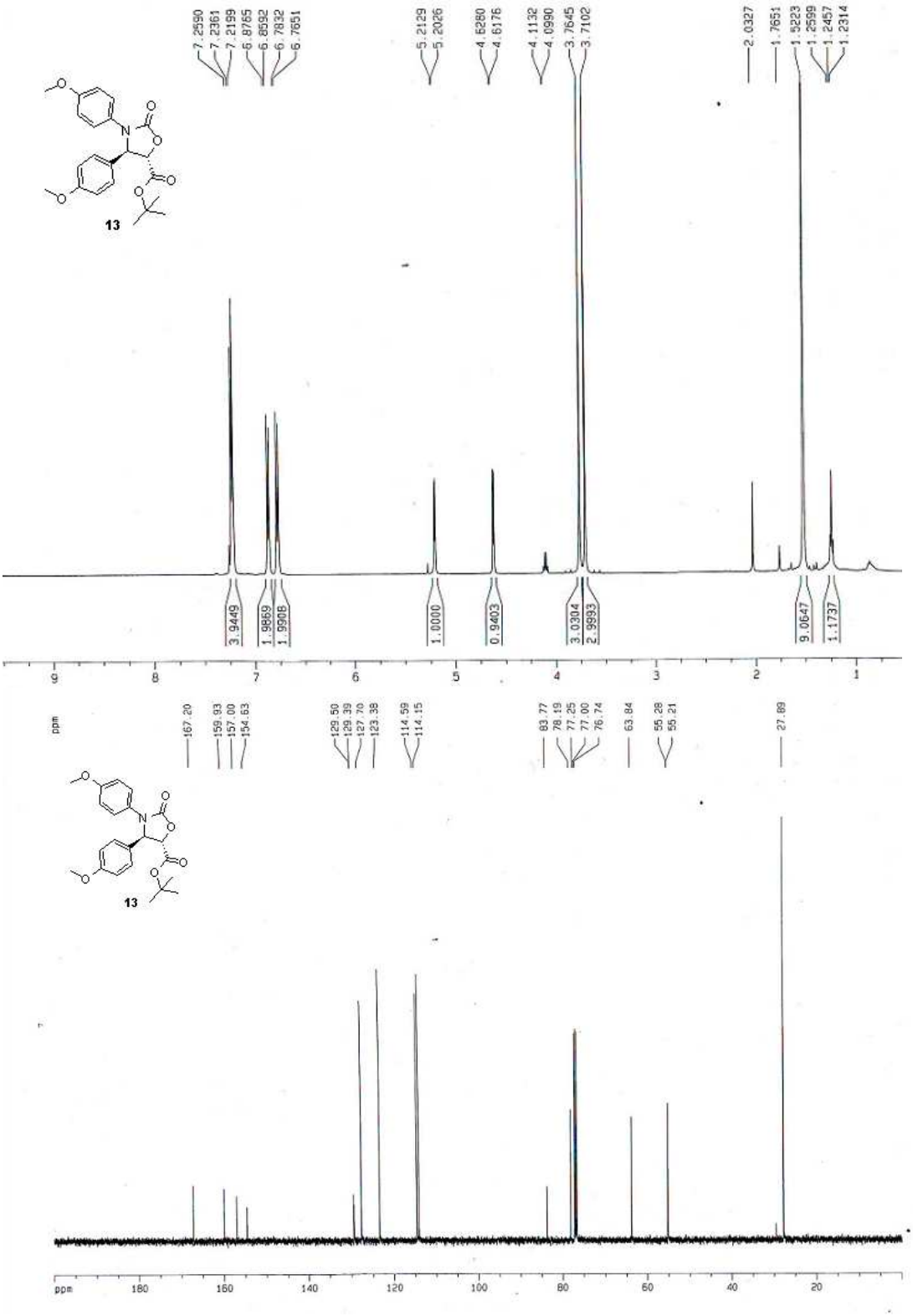
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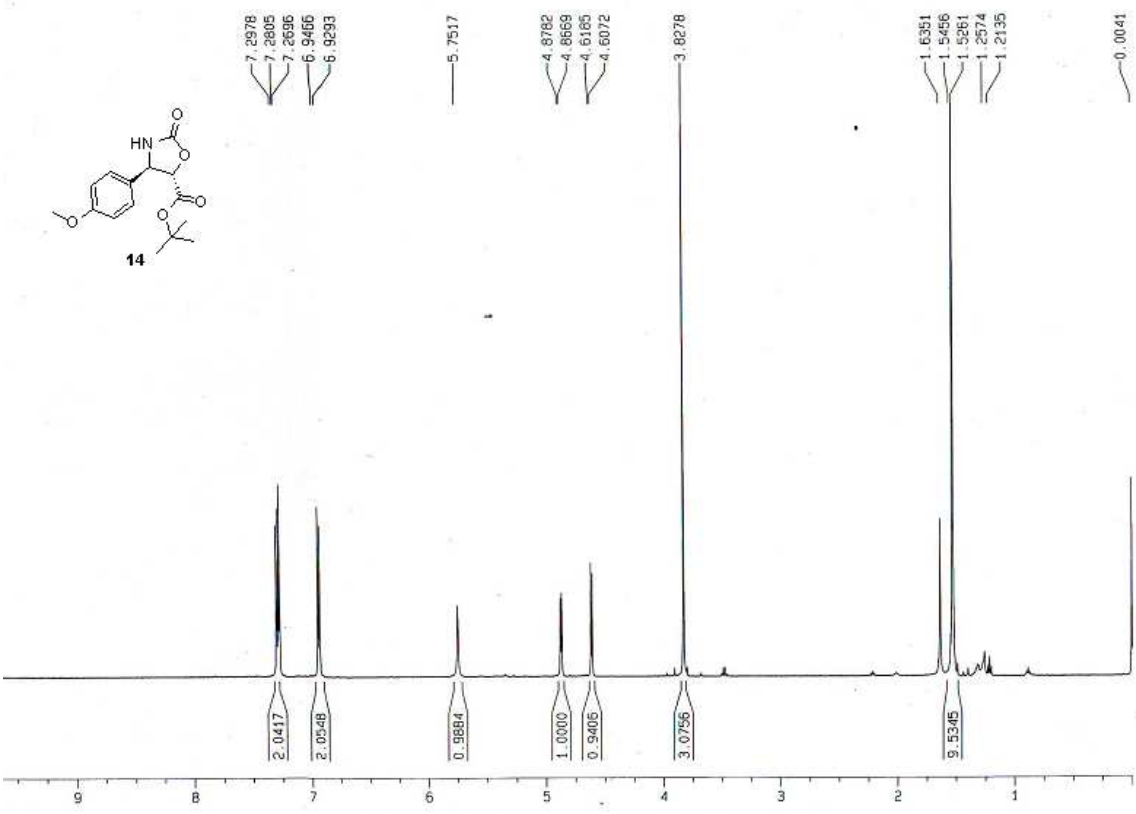
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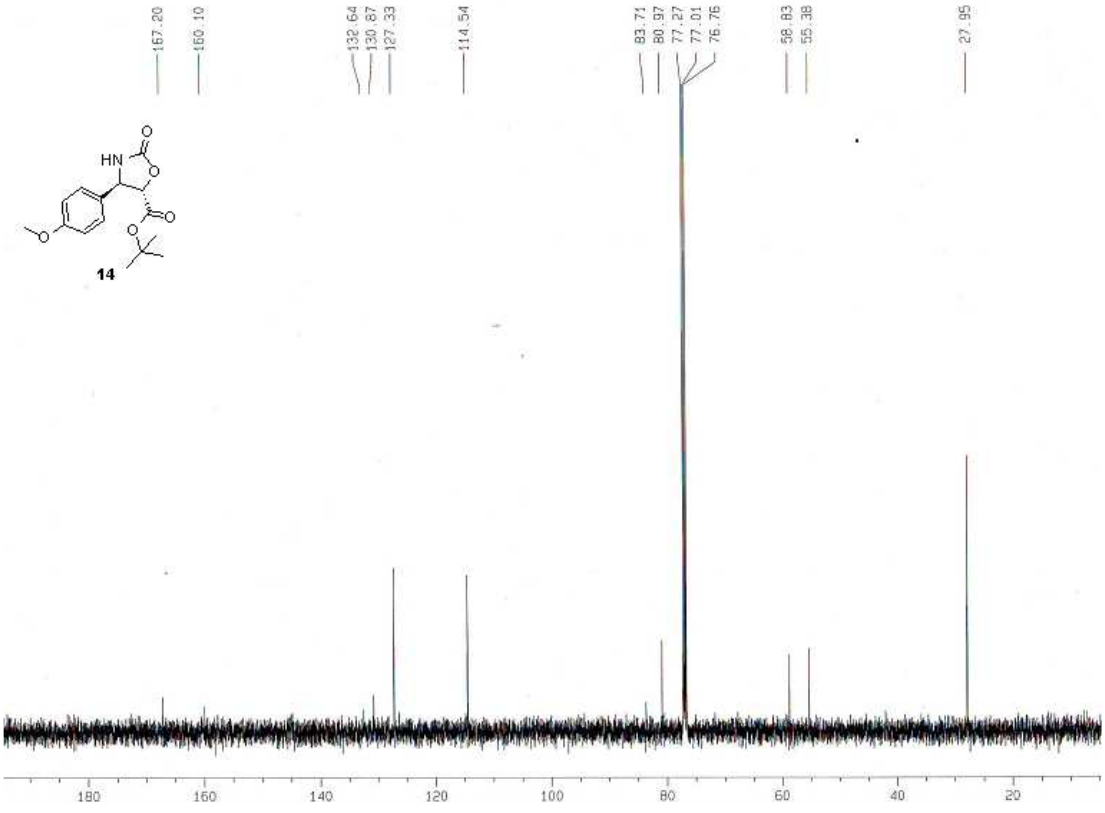
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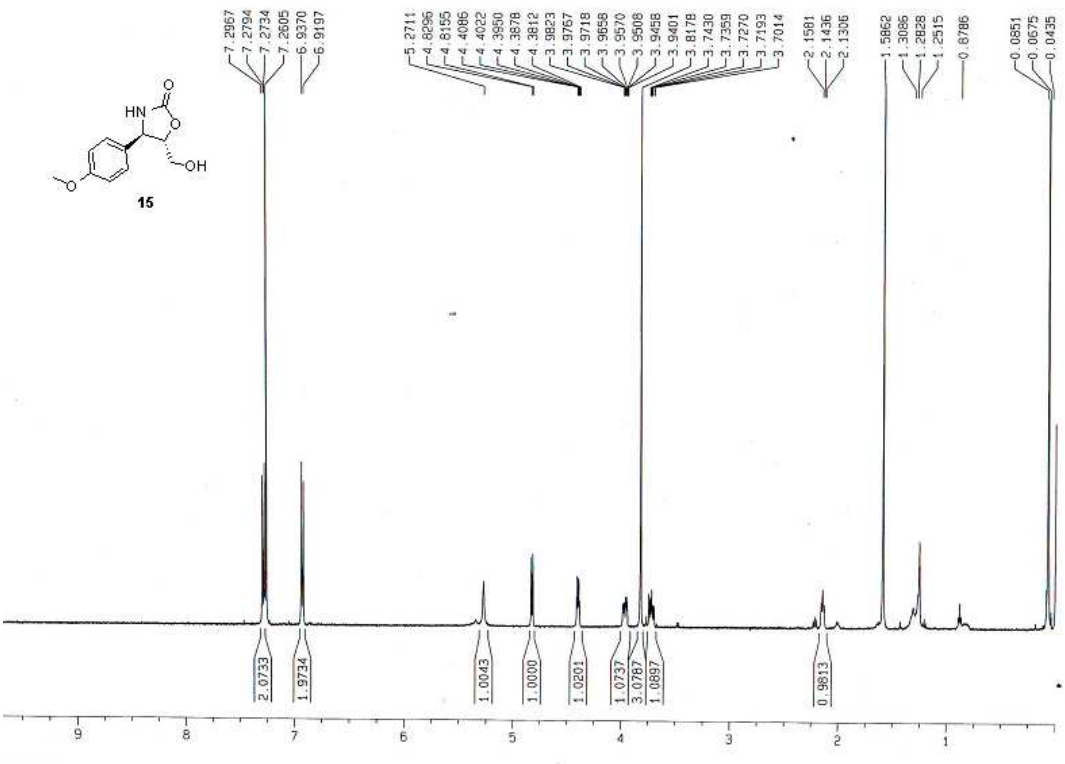
14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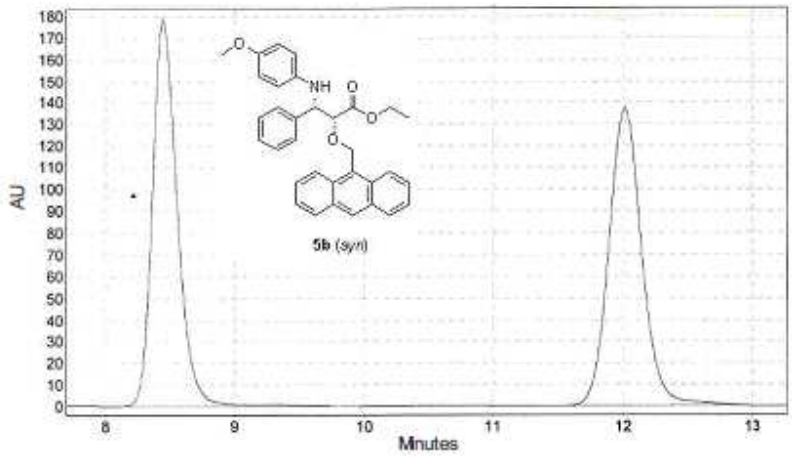
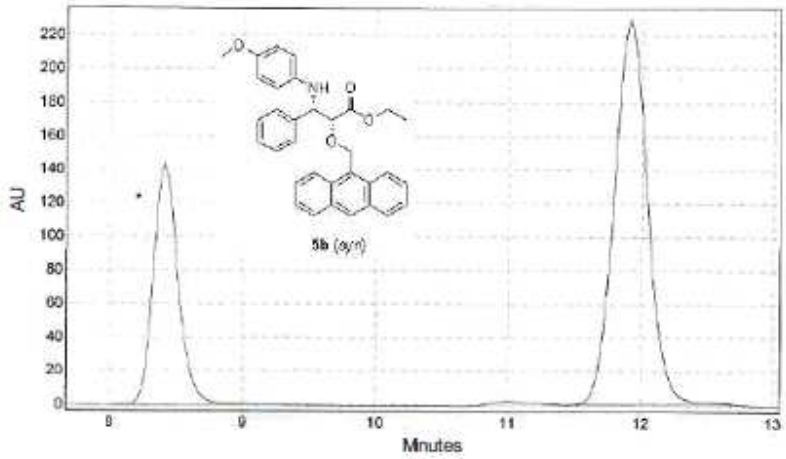
15

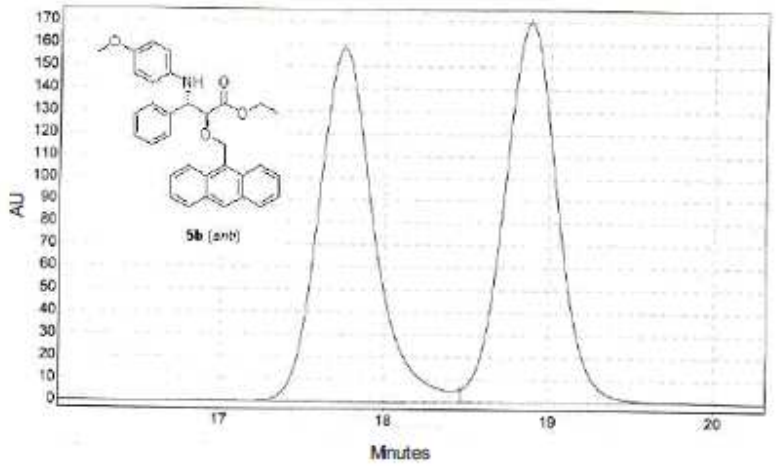
7. Chiral HPLC analysis figures of 5b, 5d-h, 7a-i, 8, 10



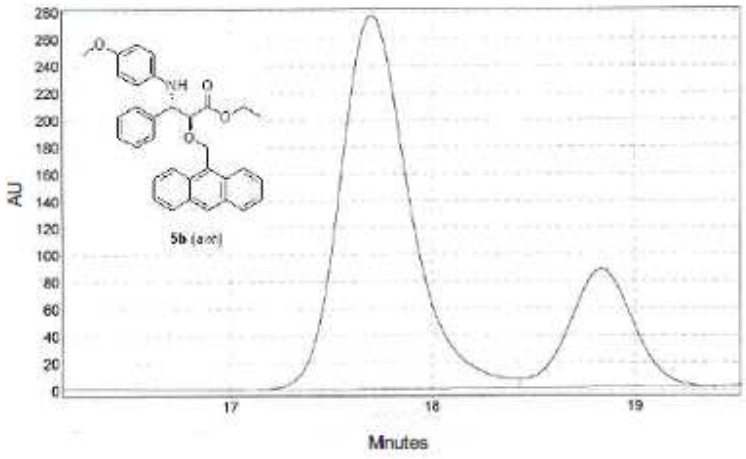
Name	Retention Time	Height	Area	% Area
1	8.452	177703.891	2358060.500	49.7674
2	12.013	136060.547	2380101.000	50.2326
Total		313764.438	4738161.500	100.0000



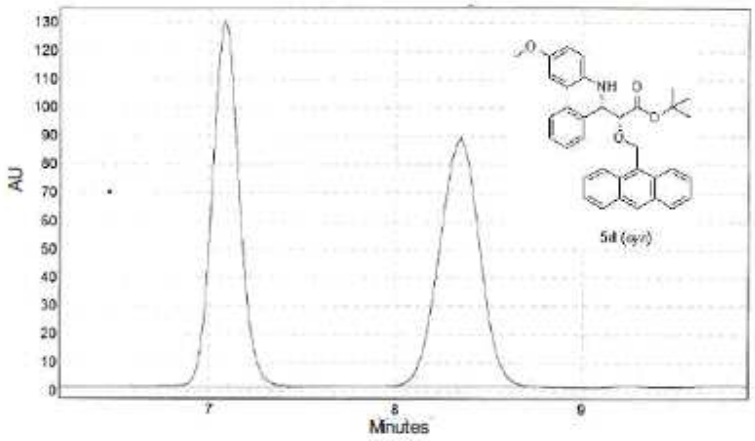
Name	Retention Time	Height	Area	% Area
1	8.408	141536.125	1835295.250	31.5723
2	11.915	226611.516	3977692.000	68.4277
Total		368147.641	5812987.250	100.0000



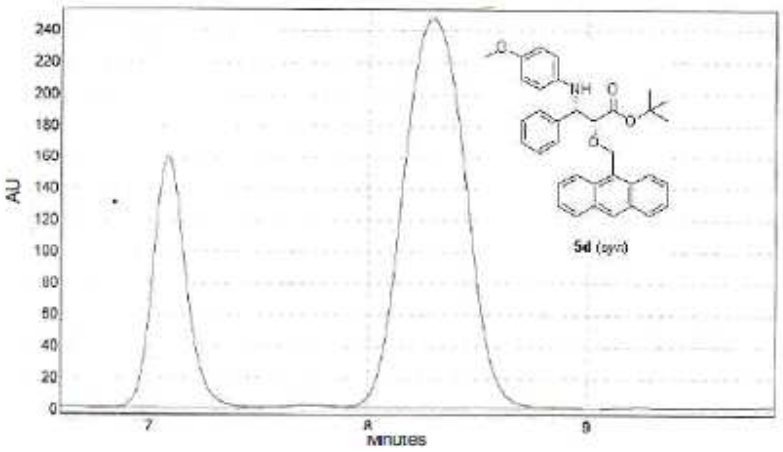
Name	Retention Time	Height	Area	% Area
1	17.745	158160.859	3717758.750	49.5275
2	18.883	170030.469	3788692.500	50.4725
Total		328191.328	7506451.250	100.0000



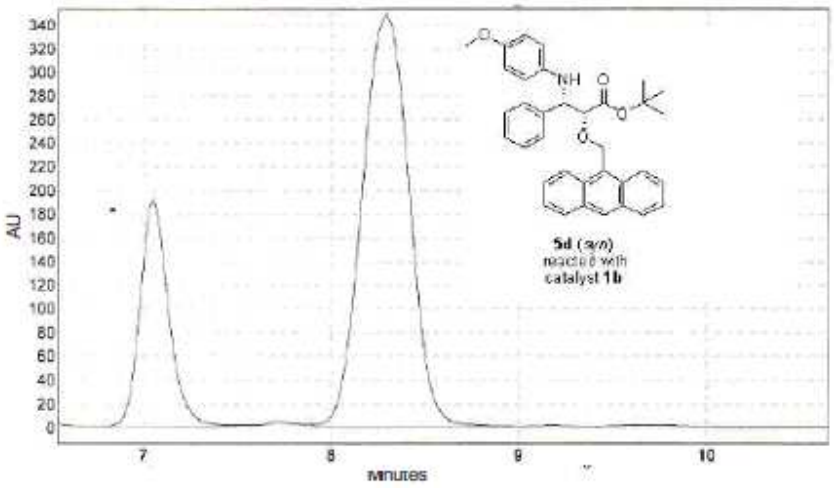
Name	Retention Time	Height	Area	% Area
1	17.732	274671.406	6612672.500	77.4487
2	18.865	87147.516	1934199.250	22.5513
Total		361818.922	8576871.750	100.0000



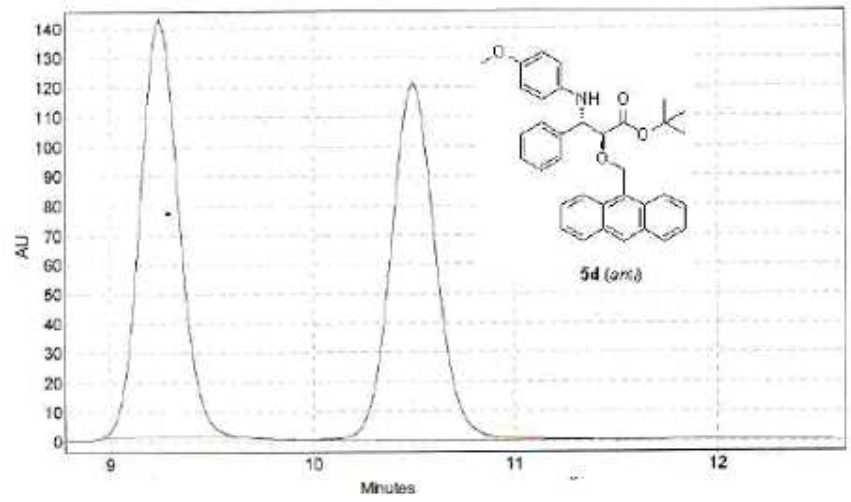
Name	Retention Time	Height	Area	% Area
1	7.082	128637.609	1305713.750	49.9223
2	8.348	86693.938	1309775.875	50.0777
Total		215331.547	2615489.625	100.0000



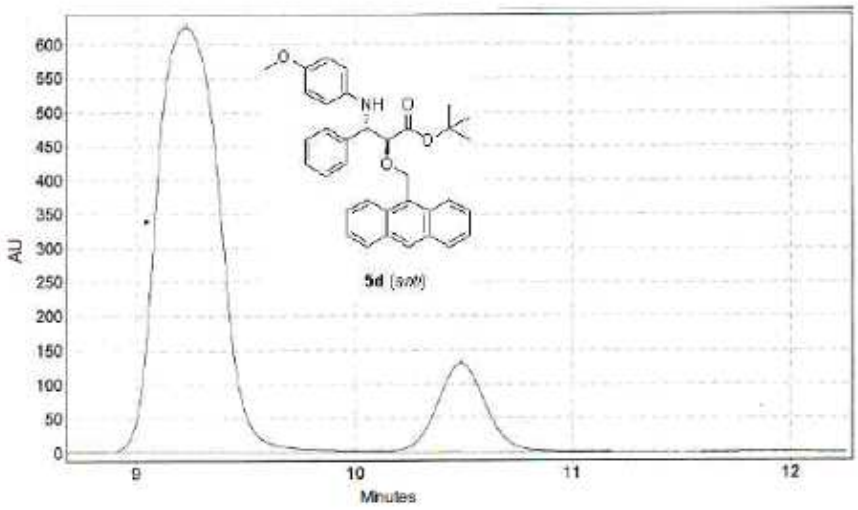
Name	Retention Time	Height	Area	% Area
1	7.098	157770.000	1655932.500	25.5009
2	8.298	245374.313	4837683.000	74.4991
Total		403144.313	6493615.500	100.0000



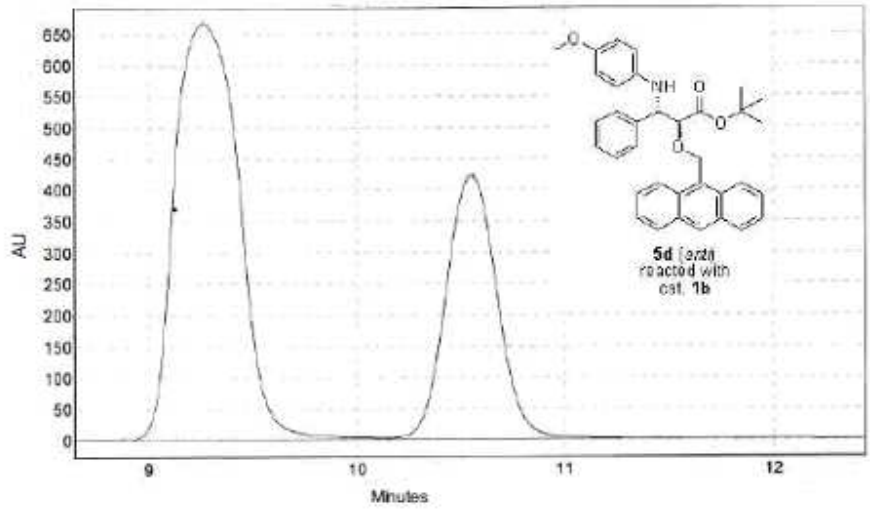
Name	Retention Time	Height	Area	% Area
1	7.048	189242.234	1979966.000	24.7037
2	8.288	345901.844	6034899.000	75.2963
Total		535144.078	8014865.000	100.0000



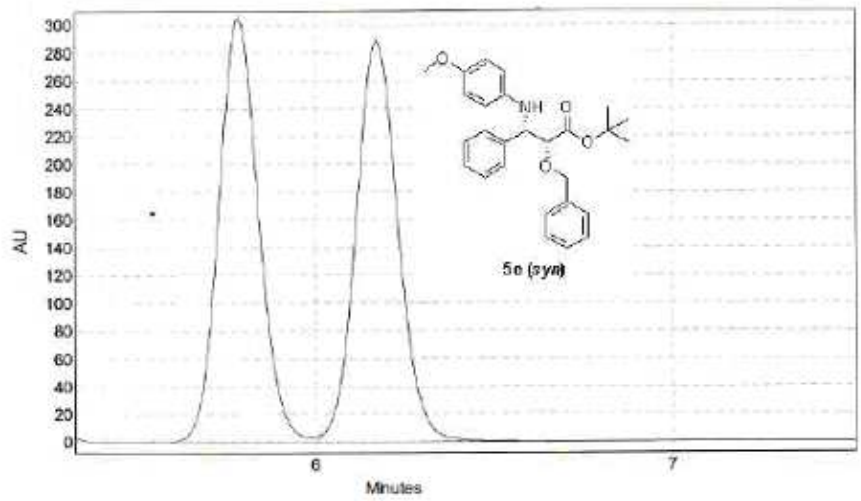
Name	Retention Time	Height	Area	% Area
1	9.243	140737.938	1855522.375	50.2700
2	10.497	120407.164	1836580.000	49.7300
Total		261145.102	3693102.375	100.0000



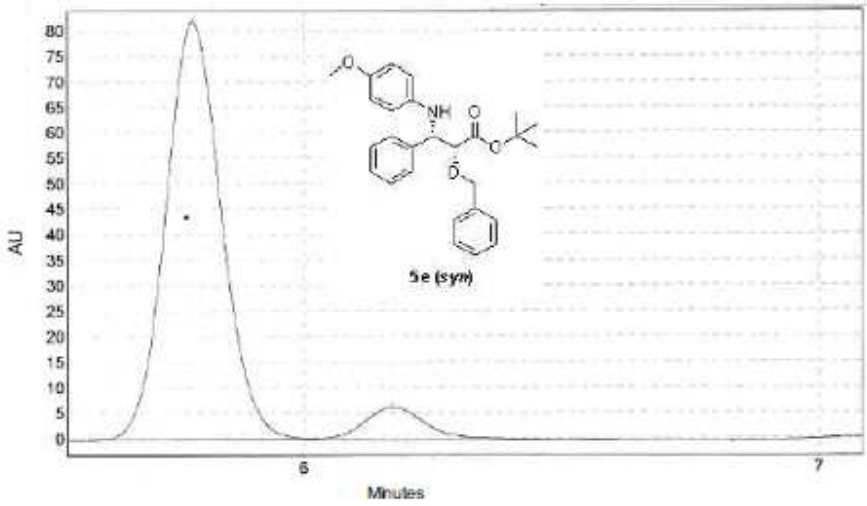
Name	Retention Time	Height	Area	% Area
1	9.225	622684.813	12089528.000	85.8669
2	10.490	129748.469	1989851.250	14.1331
Total		752433.281	14079379.250	100.000



Name	Retention Time	Height	Area	% Area
1	9.265	663891.000	14100933.000	66.1756
2	10.565	419972.469	7207417.500	33.8244
Total		1083863.469	21308350.500	100.0000



Name	Retention Time	Height	Area	% Area
1	5.785	304383.938	2345468.750	49.8125
2	6.172	288083.406	2363124.750	50.1875
Total		592467.344	4708593.500	100.0000



Name	Retention Time	Height	Area	% Area
1	5.785	81912.469	610745.875	91.8808
2	6.173	6339.055	53969.469	8.1192
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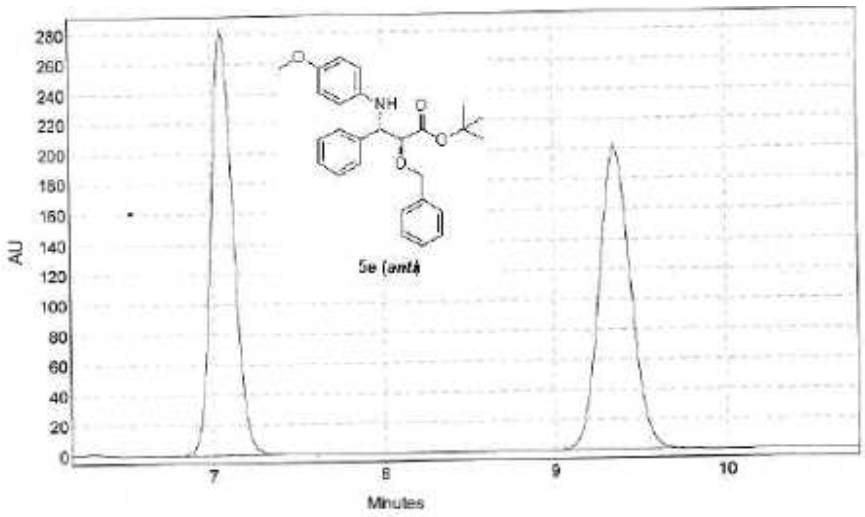

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1	7.060	280986.000	2513811.250	49.8133
2	9.355	199723.484	2532659.750	50.1867
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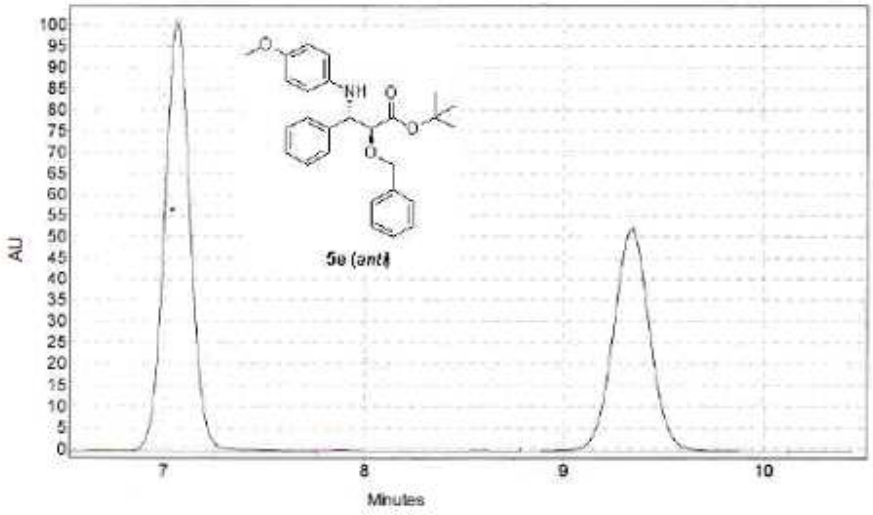
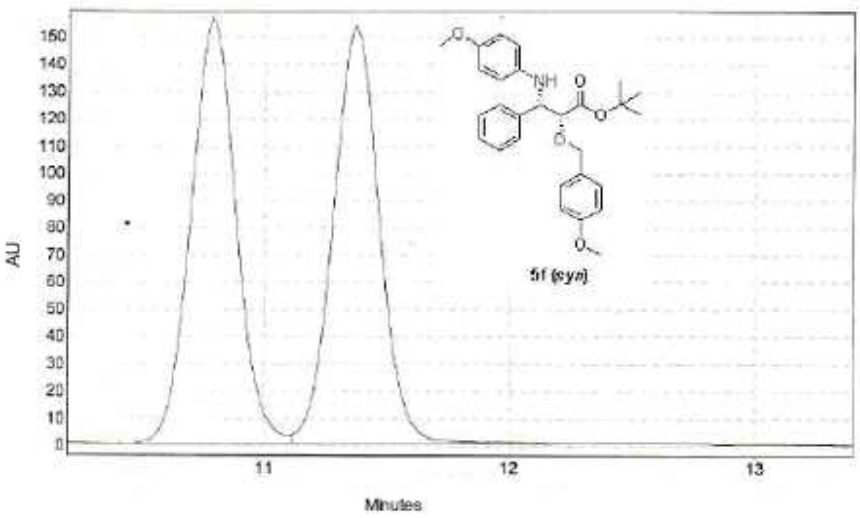
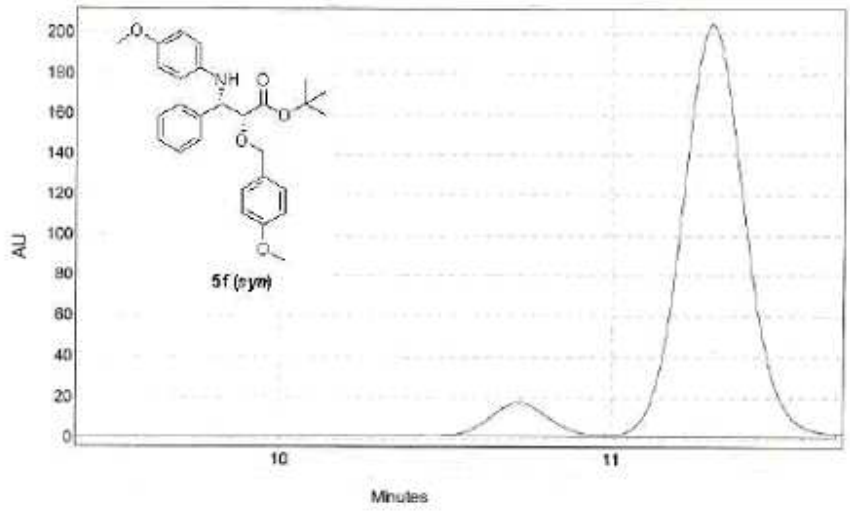


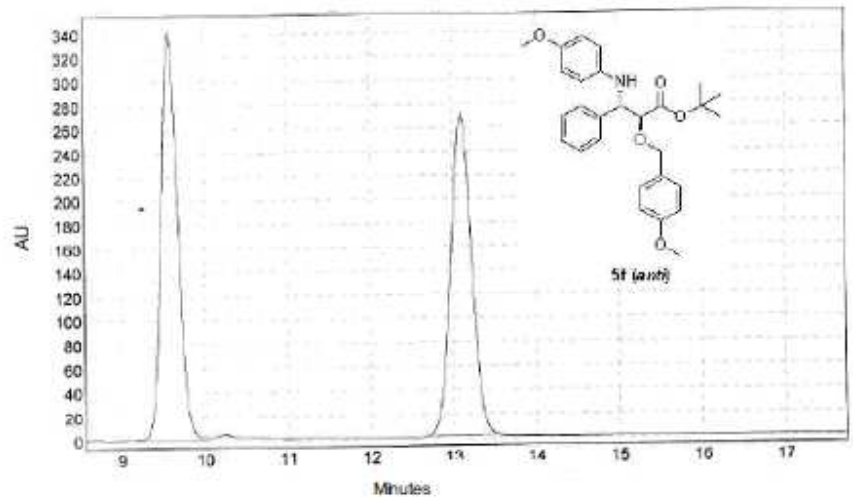
Name	Retention Time	Height	Area	% Area
1	7.065	100352.898	901171.125	57.9075
2	9.348	52112.758	655053.875	42.0925
Total		152465.656	1556225.000	100.0000



Name	Retention Time	Height	Area	% Area
1	10.788	155185.516	1986030.500	49.8402
2	11.368	152489.906	1998766.375	50.1598
Total		307675.422	3984796.875	100.0000



Name	Retention Time	Height	Area	% Area
1	10.722	16587.777	205402.922	7.2207
2	11.297	203188.297	2639243.750	92.7793
Total		219776.074	2844646.672	100.0000



Name	Retention Time	Height	Area	% Area
1	9.585	339649.406	4639116.000	49.8889
2	13.103	266356.250	4659787.500	50.1111
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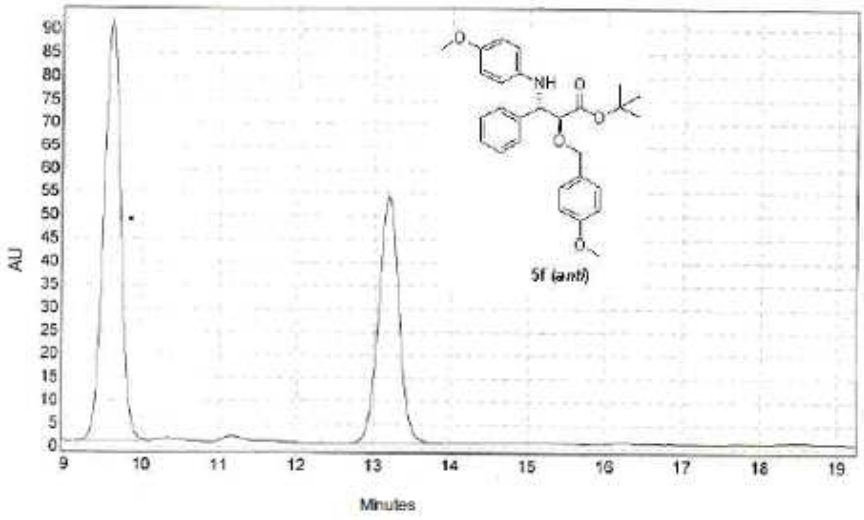

Name	Retention Time	Height	Area	% Area
1	9.607	90391.625	1384572.500	59.0039
2	13.187	52997.766	962004.500	40.9961
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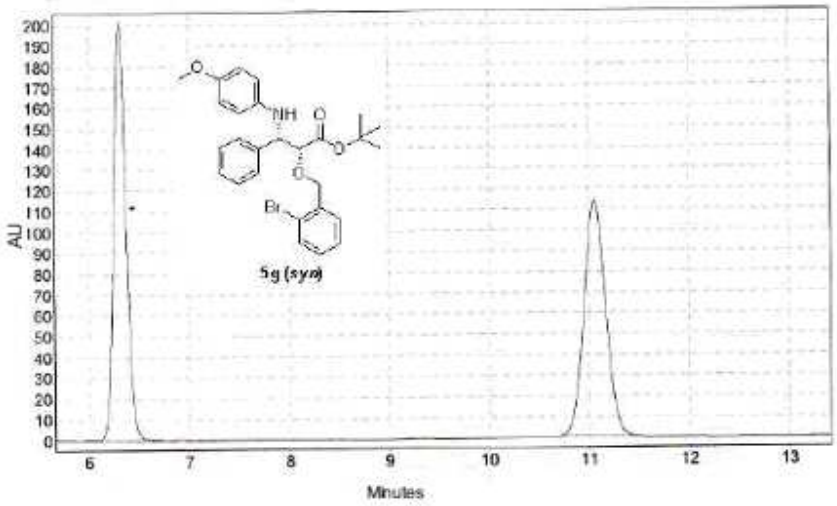
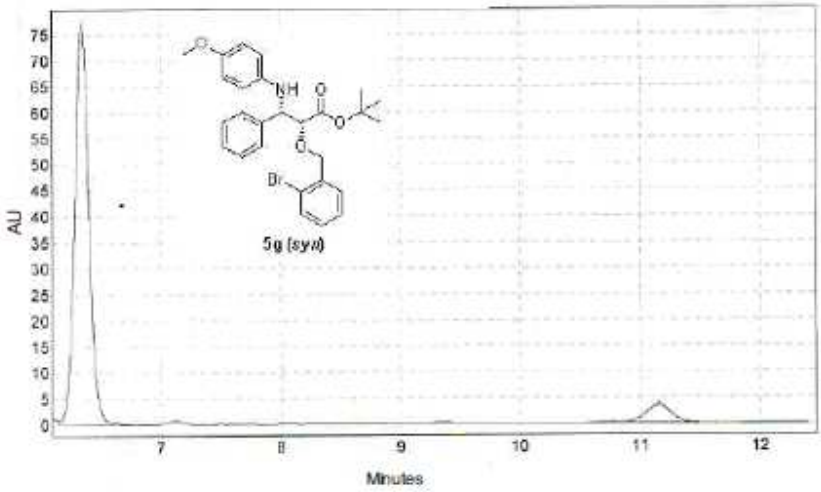
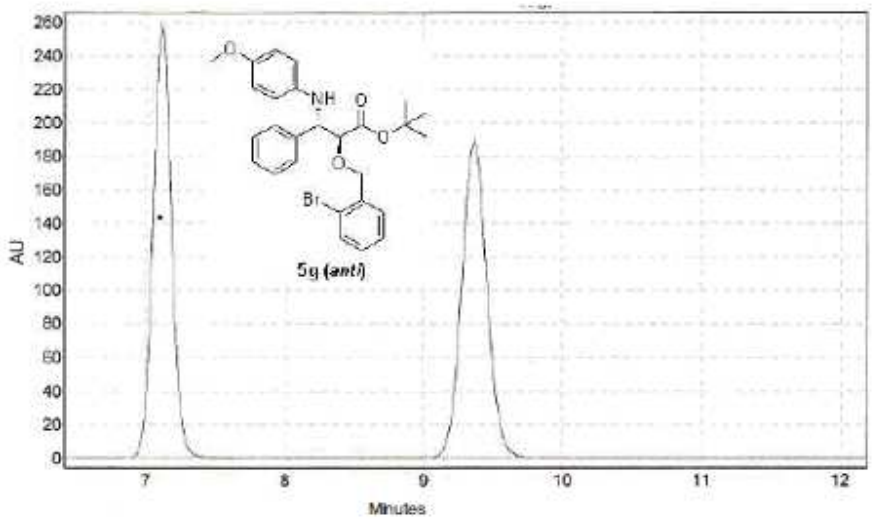


Name	Retention Time	Height	Area	% Area
1	6.313	199622.781	1683511.625	50.0531
2	11.060	112697.500	1679936.500	49.9469
Total		312320.281	3363448.125	100.0000



Name	Retention Time	Height	Area	% Area
1	6.343	76801.078	639679.563	93.2229
2	11.148	3227.649	46503.148	6.7771
Total		80028.728	686182.711	100.0000



Name	Retention Time	Height	Area	% Area
1	7.118	257471.891	2377930.750	49.8250
2	9.365	187265.141	2394638.750	50.1750
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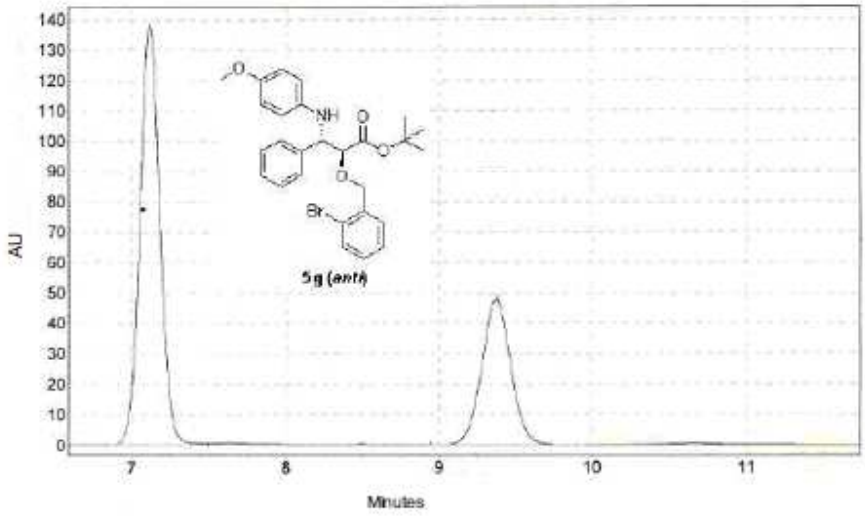
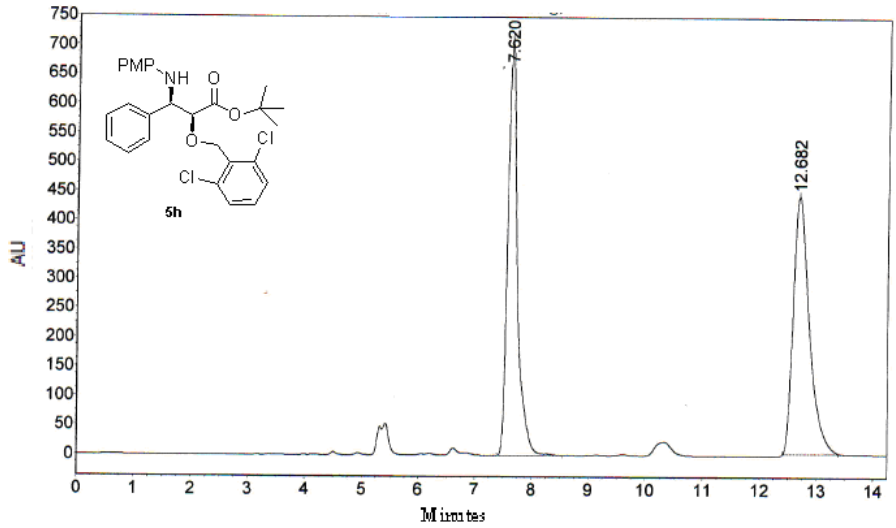
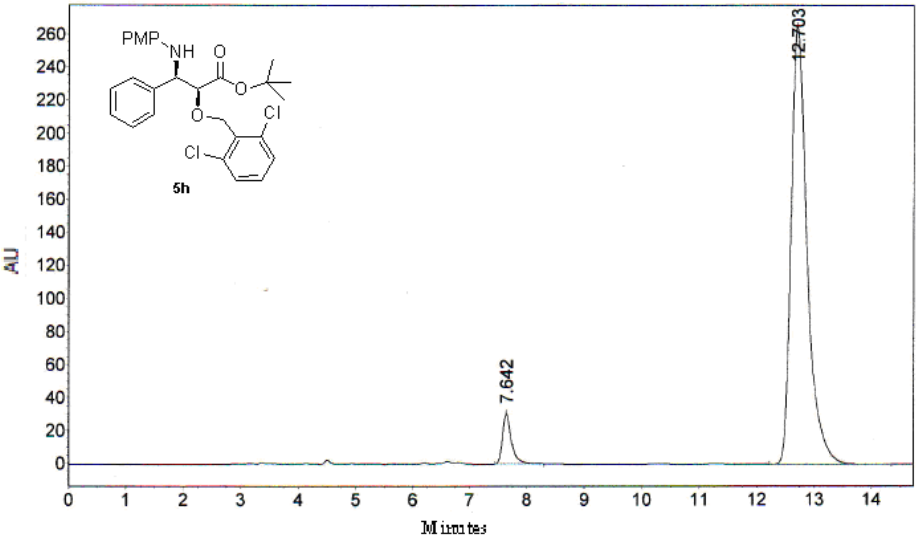


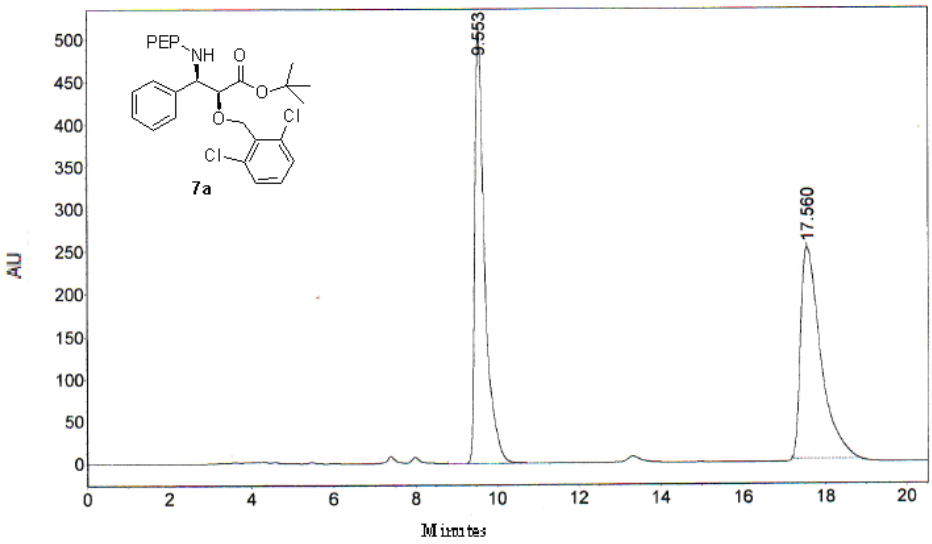
Name	Retention Time	Height	Area	% Area
1	7.132	136924.547	1253708.750	66.6085
2	9.382	47669.824	628497.250	33.3915
Total		184594.371	1882206.000	100.0000



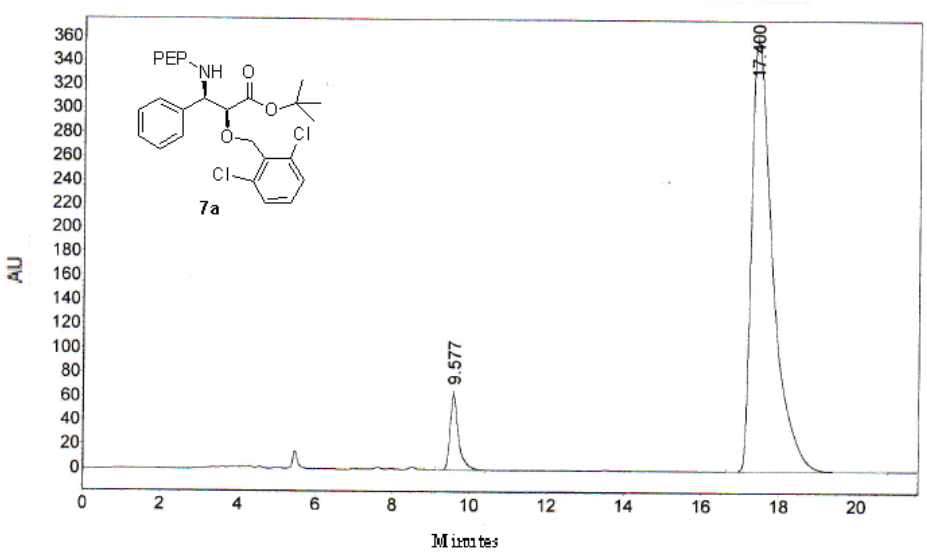
Name	Retention Time	Height	Area	%Area
1	7.620	714692.375	8607811.000	49.9169
2	12.682	441007.719	8636488.000	50.0831
Total		1155700.094	17244299.000	100.0000



Name	Retention Time	Height	Area	%Area
1	7.642	30058.783	328917.344	6.0200
2	12.703	265207.031	5134866.500	93.9800
Total		295265.814	5463783.844	100.0000



Name	Retention Time	Height	Area	%Area
1	9.553	510490.438	8606724.000	50.0921
2	17.560	249653.656	8575069.000	49.9079
Total		760144.094	17181793.000	100.0000



Name	Retention Time	Height	Area	%Area
1	9.577	62231.664	960979.375	6.5877
2	17.400	358186.563	13626518.000	93.4123
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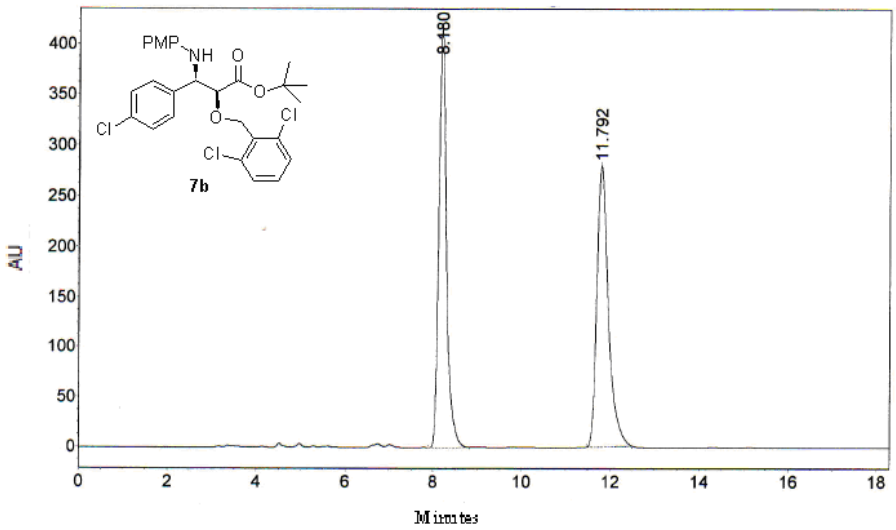
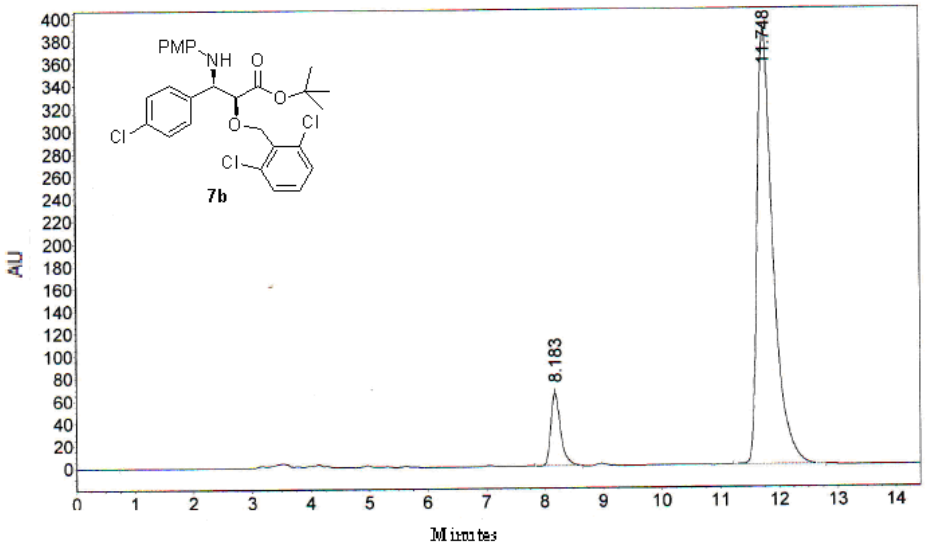
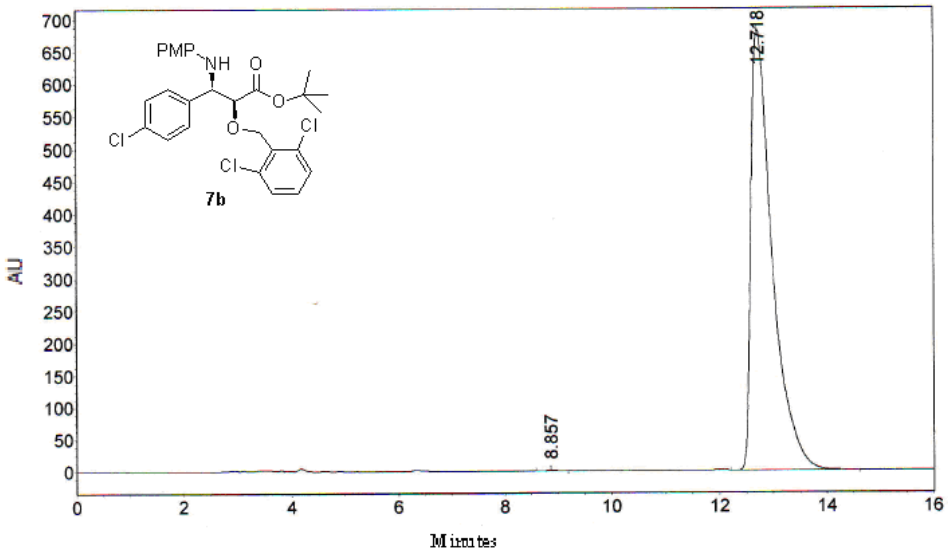


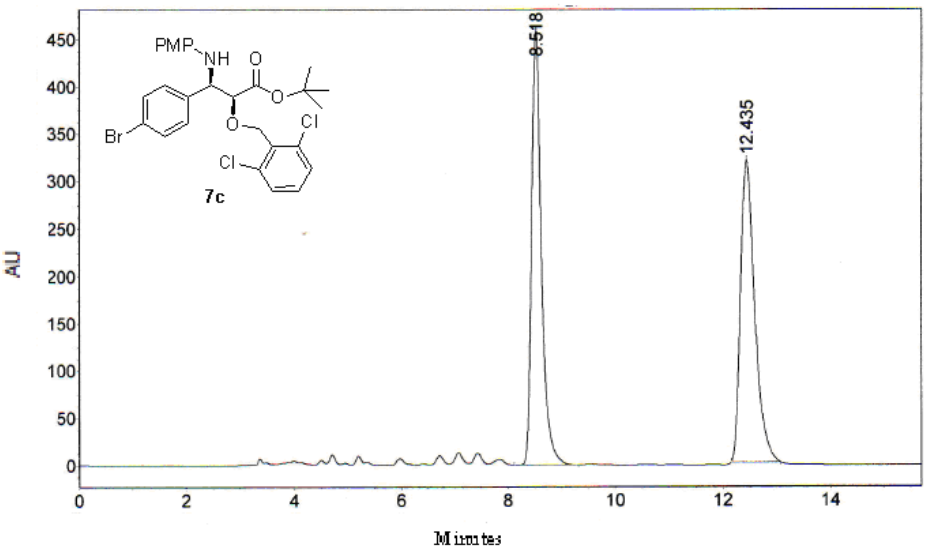
Name	Retention Time	Height	Area	%Area
1	8.180	414517.031	5035677.000	49.7432
2	11.792	279206.313	5087670.000	50.2568
Total		693723.344	10123347.000	100.0000



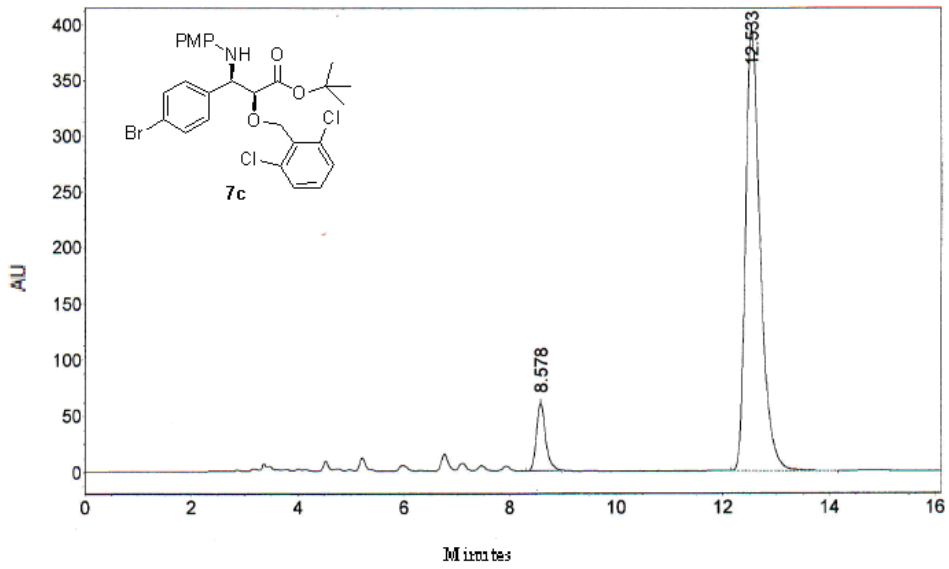
Name	Retention Time	Height	Area	%Area
1	8.183	64857.449	744687.063	9.2531
2	11.748	387153.469	7303311.500	90.7469
Total		452010.918	8047998.563	100.0000



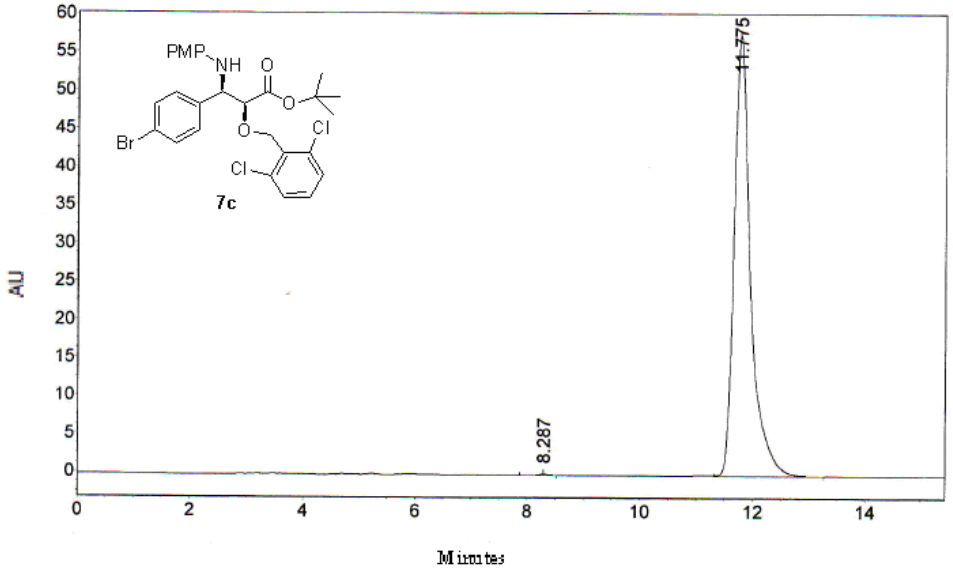
Name	Retention Time	Height	Area	%Area
1	8.857	824.412	11501.200	0.0615
2	12.718	682397.000	18698742.000	99.9385
Total		683221.412	18710243.200	100.0000



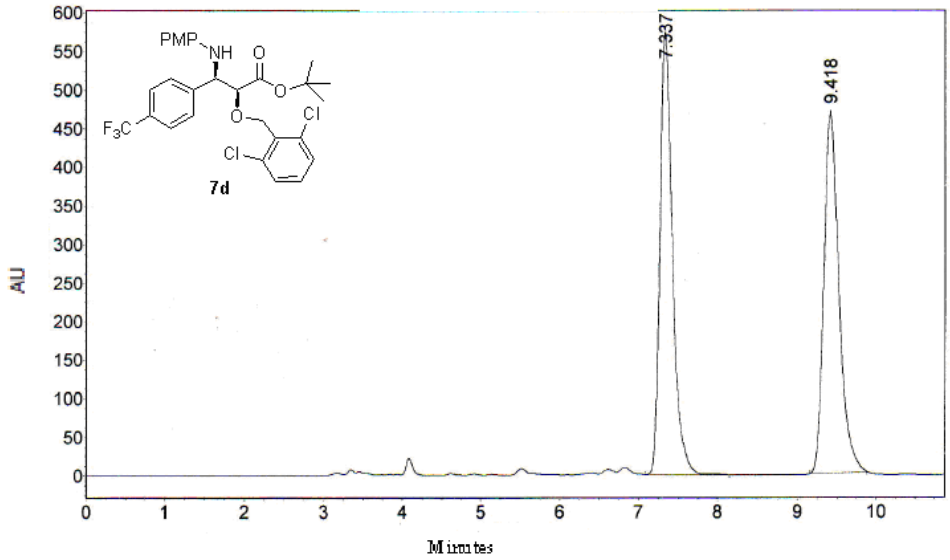
Name	Retention Time	Height	Area	%Area
1	8.518	458579.094	5818624.000	49.9158
2	12.435	318841.469	5838254.000	50.0842
Total		777420.563	11656878.000	100.0000



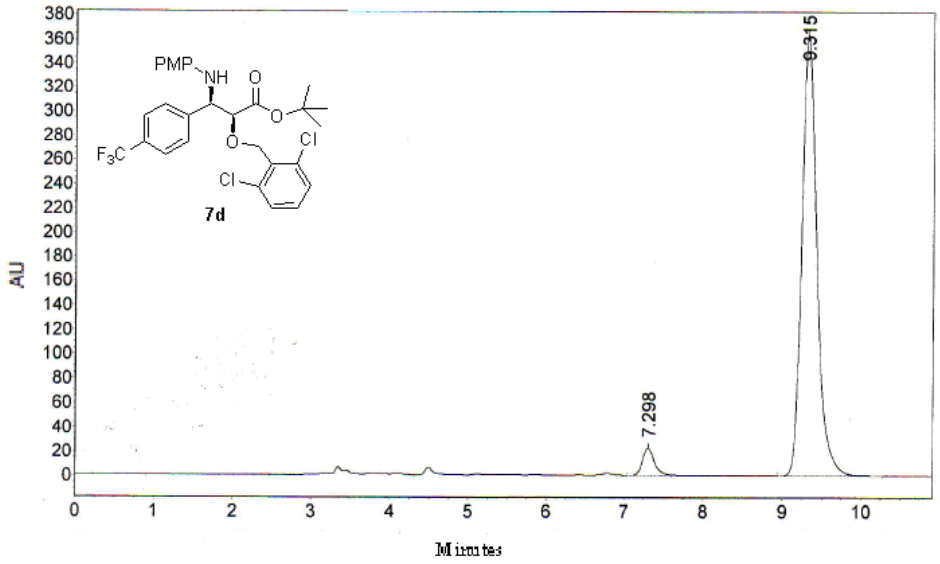
Name	Retention Time	Height	Area	%Area
1	8.578	59143.875	703950.313	8.5853
2	12.533	393845.625	7495566.000	91.4147
Total		452989.500	8199516.313	100.0000



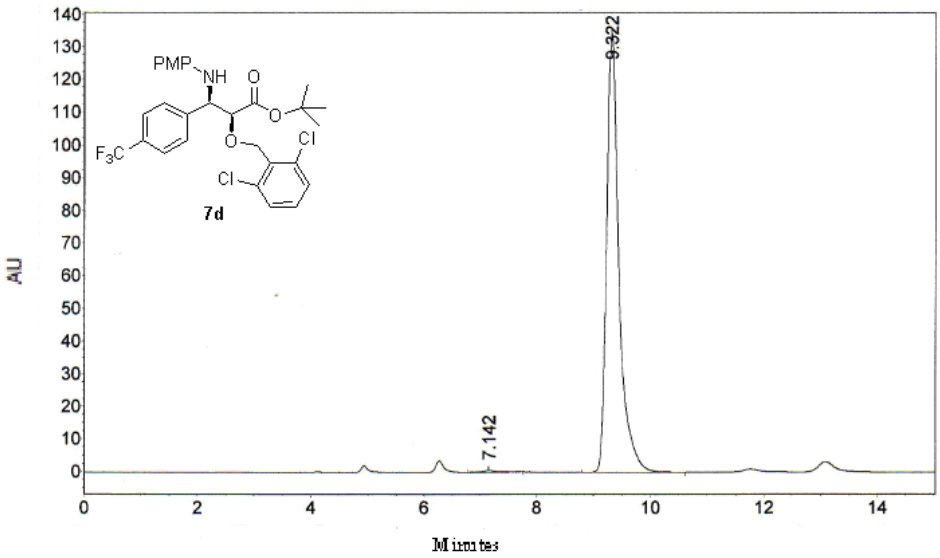
Name	Retention Time	Height	Area	%Area
1	8.287	127.858	1490.500	0.1282
2	11.775	57656.059	1161074.500	99.8718
Total		57783.916	1162565.000	100.0000



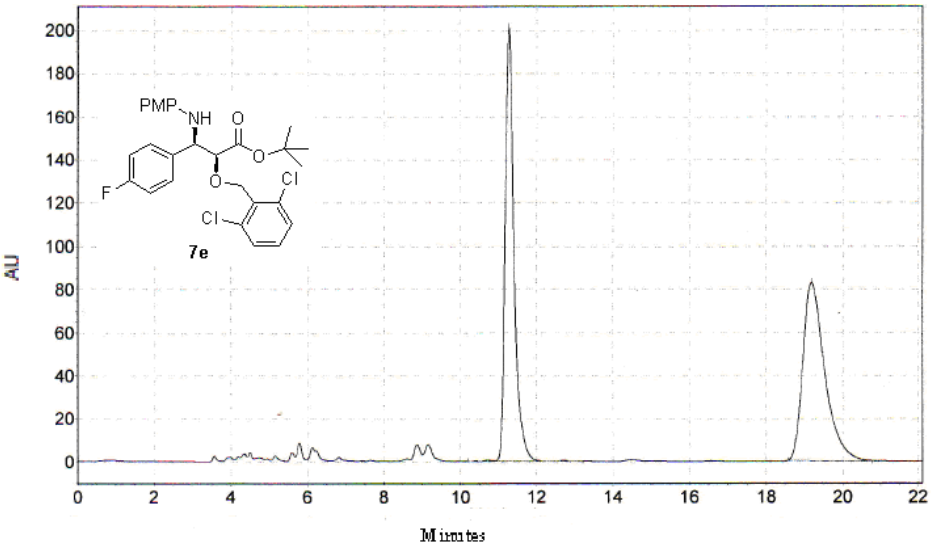
Name	Retention Time	Height	Area	%Area
1	7.337	572763.750	6231988.000	49.8661
2	9.418	464196.469	6265446.000	50.1339
Total		1036960.219	12497434.000	100.0000



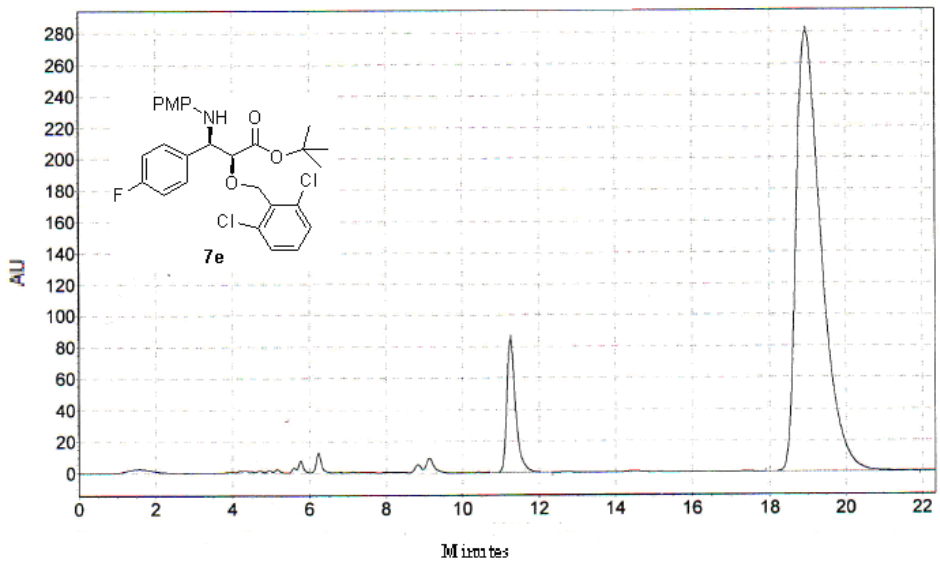
Name	Retention Time	Height	Area	%Area
1	7.298	22383.555	219169.047	4.3114
2	9.315	363968.531	4864311.500	95.6886
Total		386352.086	5083480.547	100.0000



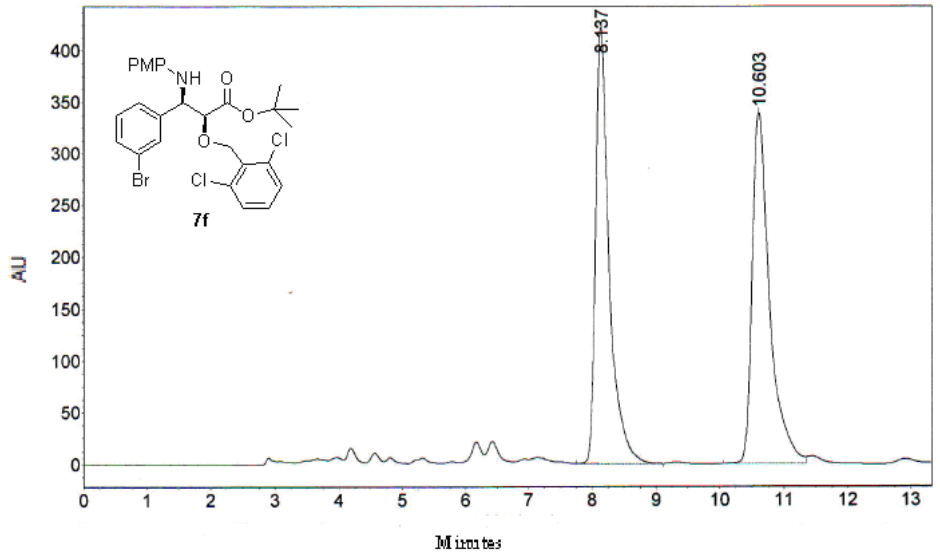
Name	Retention Time	Height	Area	%Area
1	7.142	515.499	7851.350	0.3852
2	9.322	134373.422	2030581.875	99.6148
Total		134888.921	2038433.225	100.0000



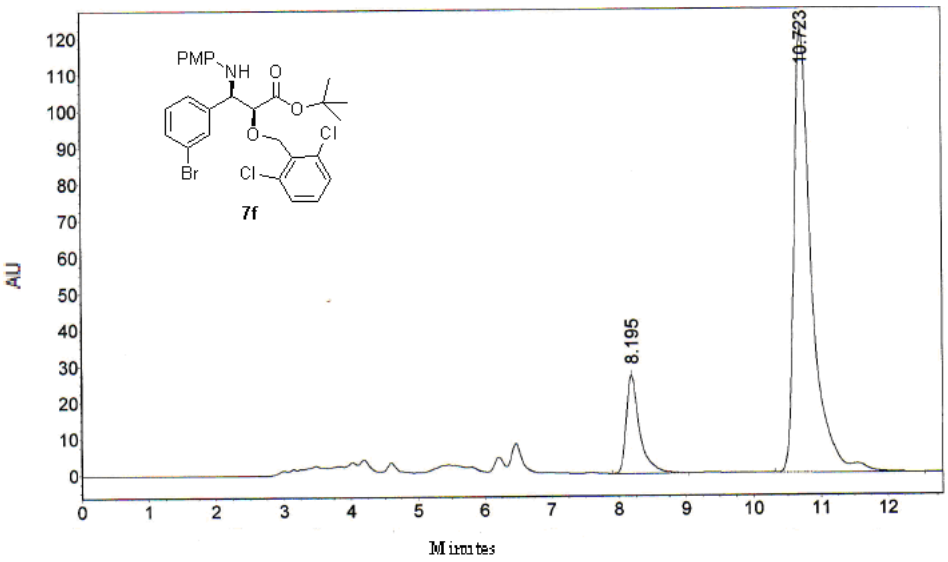
Name	Retention Time	Height	Area	%Area
1	11.278	200813.031	3259838.000	49.9181
2	19.185	82598.805	3270533.500	50.0819
Total		283411.836	6530371.500	100.0000



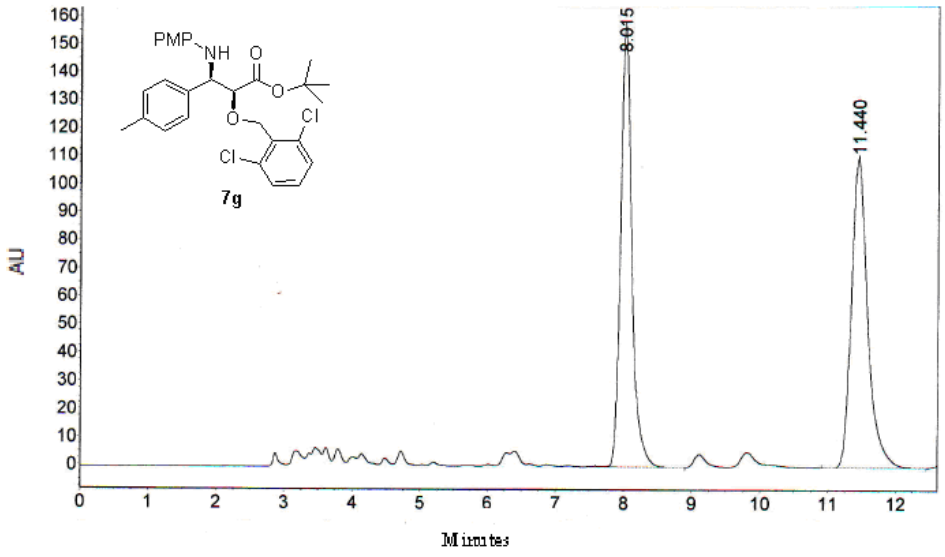
Name	Retention Time	Height	Area	%Area
1	11.265	83669.555	1359848.375	9.6528
2	18.965	279631.750	12727724.000	90.3472
Total		363301.305	14087572.375	100.0000



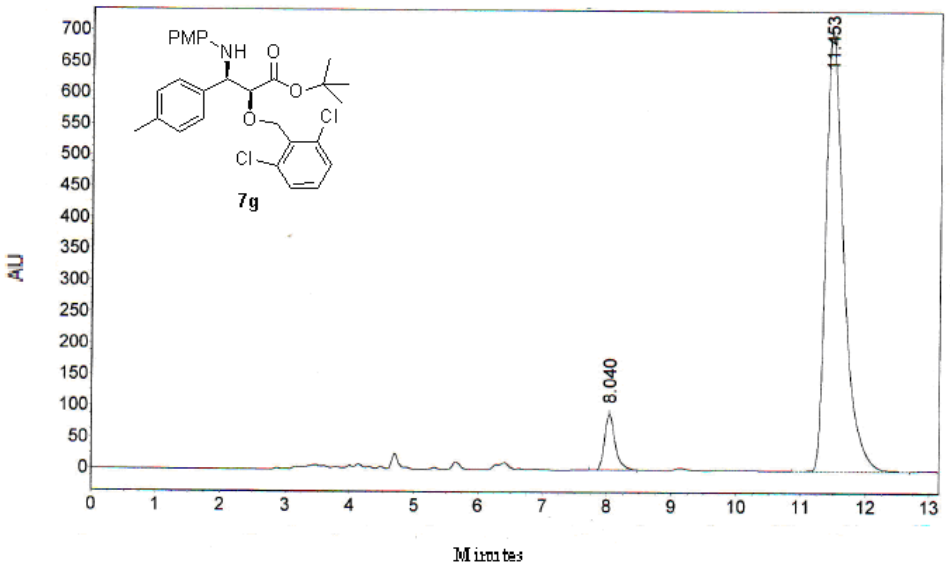
Name	Retention Time	Height	Area	%Area
1	8.137	421235.875	6251290.000	49.4402
2	10.603	338786.188	6392857.500	50.5598
Total		760022.063	12644147.500	100.0000



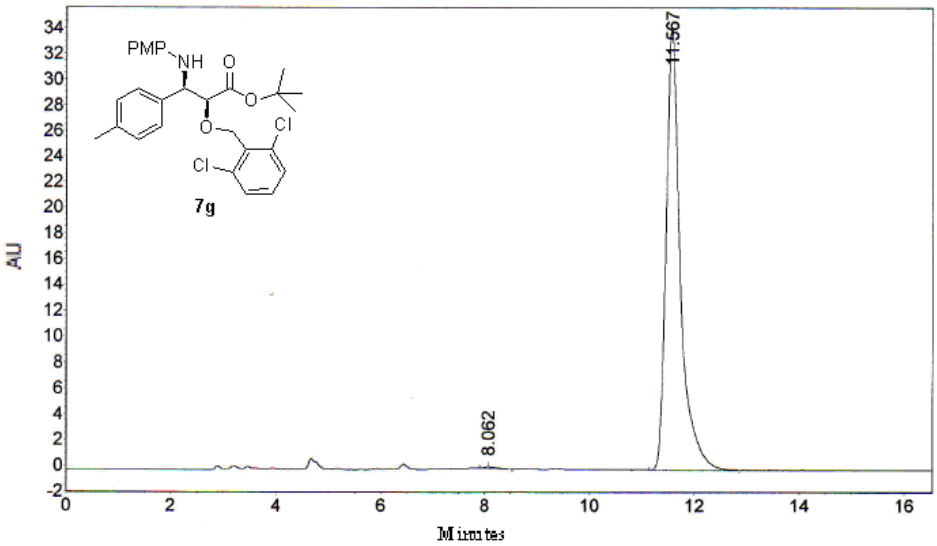
Name	Retention Time	Height	Area	%Area
1	8.195	27185.195	371193.344	14.4129
2	10.723	121911.117	2204234.000	85.5871
Total		149096.313	2575427.344	100.0000



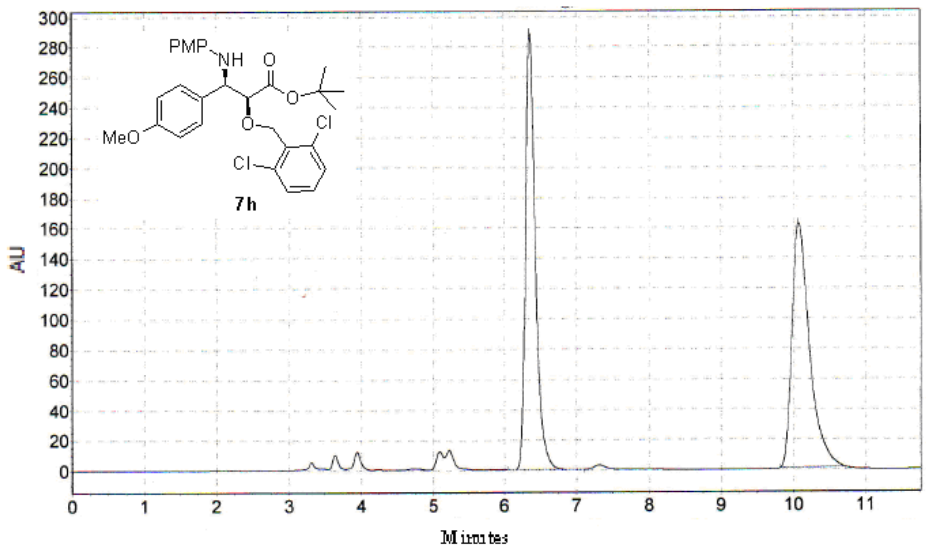
Name	Retention Time	Height	Area	%Area
1	8.015	157163.500	1818902.500	49.8269
2	11.440	109655.539	1831544.000	50.1731
Total		266819.039	3650446.500	100.0000



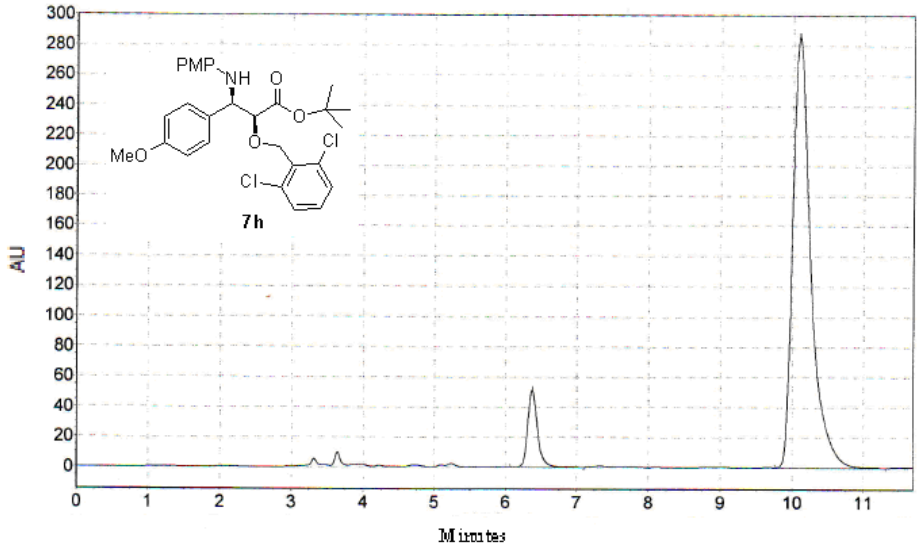
Name	Retention Time	Height	Area	%Area
1	8.040	88831.516	1006706.188	6.8570
2	11.453	699634.688	13674739.000	93.1430
Total		788466.203	14681445.188	100.0000



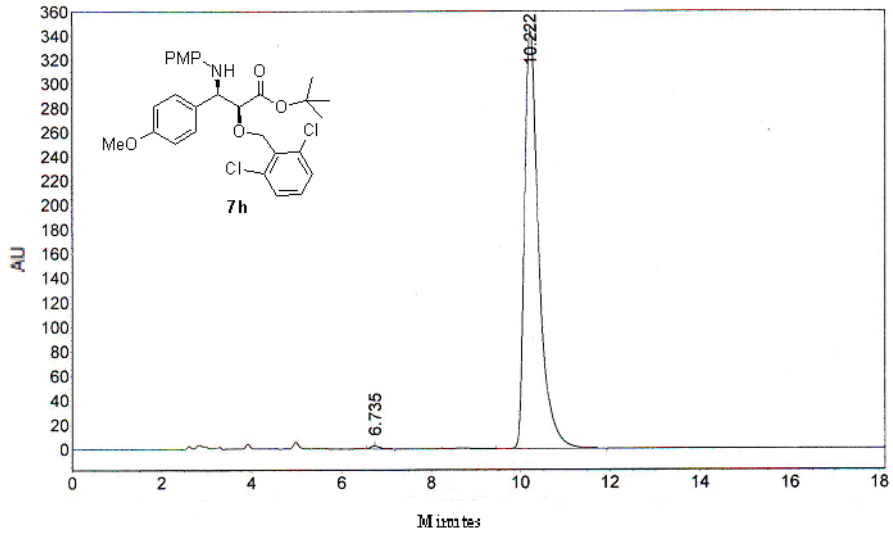
Name	Retention Time	Height	Area	%Area
1	8.062	97.287	1511.600	0.2314
2	11.567	34235.180	651733.938	99.7686
Total		34332.467	653245.538	100.0000



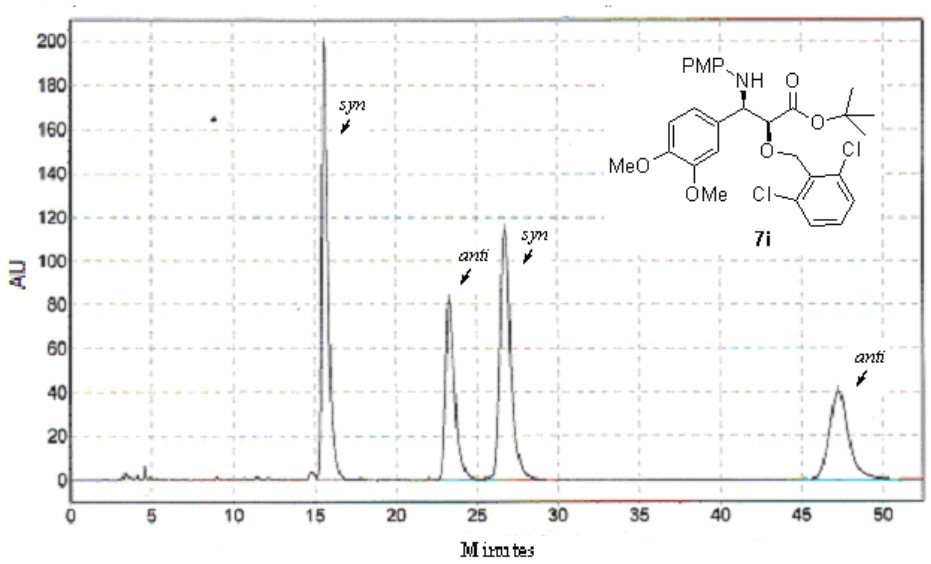
Name	Retention Time	Height	Area	%Area
1	6.355	288811.781	2718897.500	49.8952
2	10.070	161112.063	2730323.500	50.1048
Total		449923.844	5449221.000	100.0000



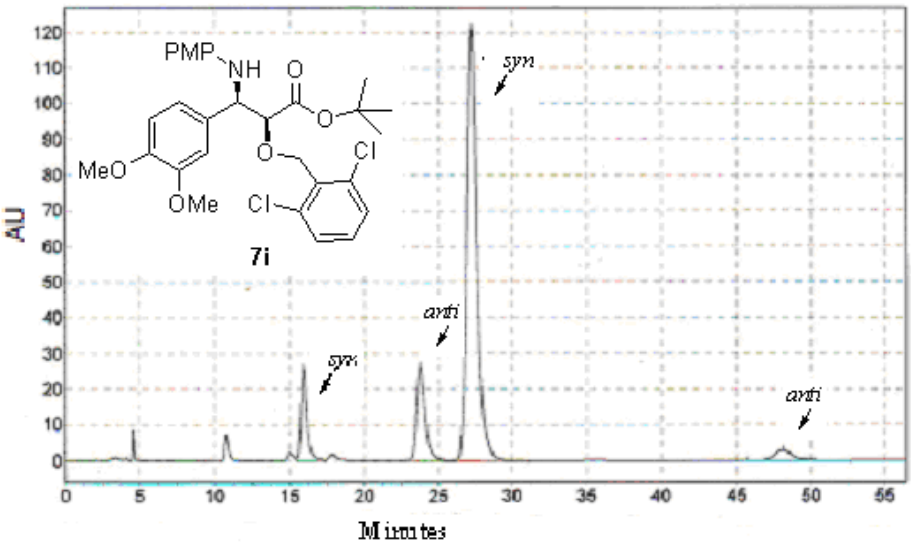
Name	Retention Time	Height	Area	%Area
1	6.382	51374.680	492332.531	8.9693
2	10.098	285489.375	4996751.000	91.0307
Total		336864.055	5489083.531	100.0000



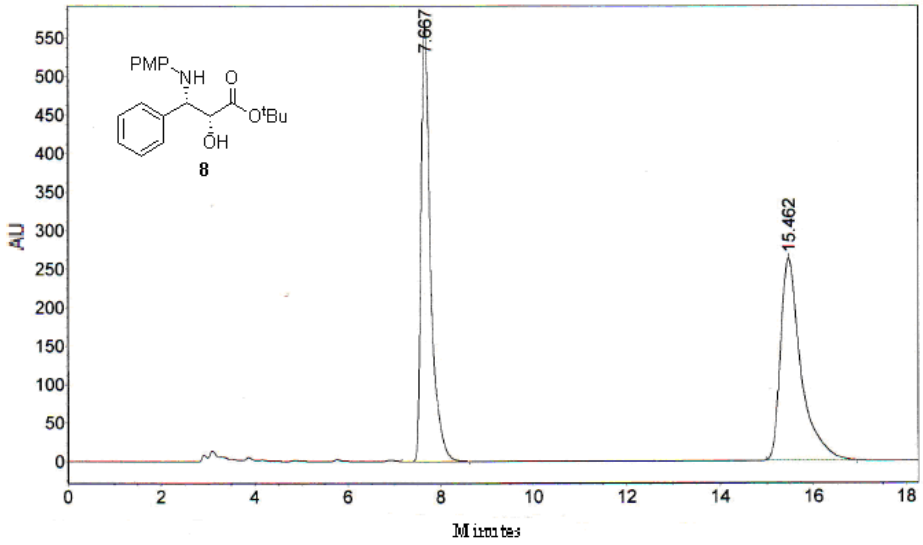
Name	Retention Time	Height	Area	%Area
1	6.735	2227.283	27489.299	0.3631
2	10.222	342984.375	7544034.000	99.6369
Total		345211.658	7571523.299	100.0000



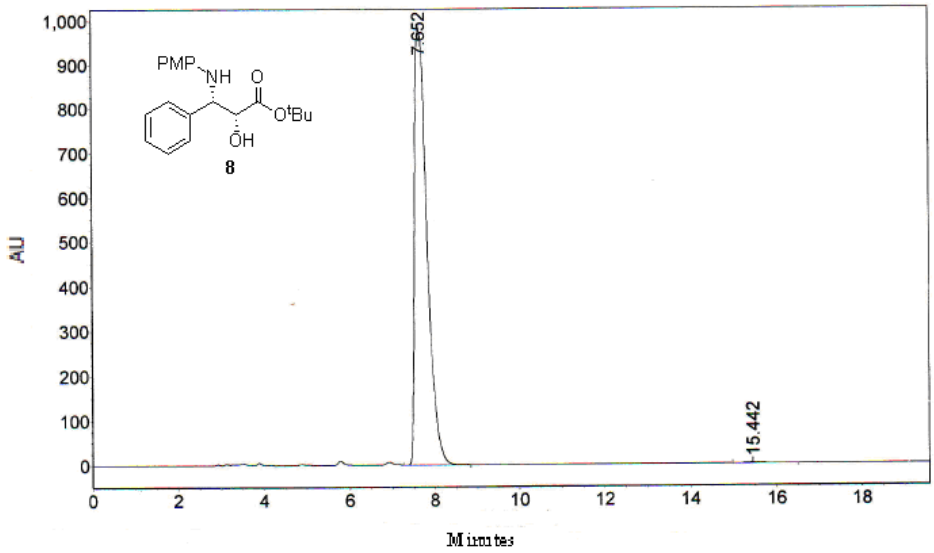
Name	Retention Time	Height	Area	%Area
1	15.613	199513.203	5232783.000	30.7190
2	23.303	82421.563	3261137.000	19.1445
3	26.755	114017.469	5262987.000	30.8963
4	47.243	40184.695	3277455.750	19.2403
Total		436136.930	17034362.750	100.0000



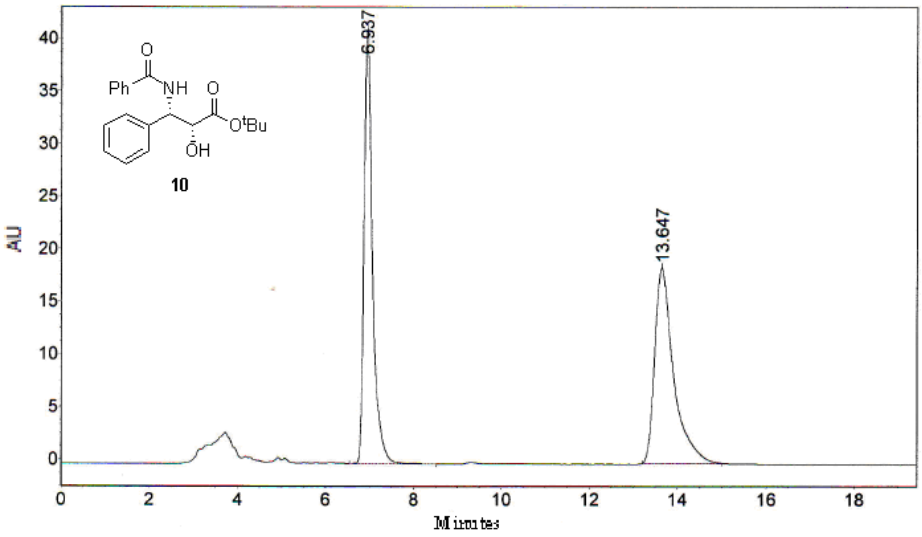
Name	Retention Time	Height	Area	%Area
1	15.927	25975.988	702109.688	9.1655
2	23.762	26473.113	1062129.375	13.8653
3	27.238	120893.703	5655535.000	73.8290
4	48.092	2892.451	240546.297	3.1402
Total		176235.256	7660320.359	100.0000



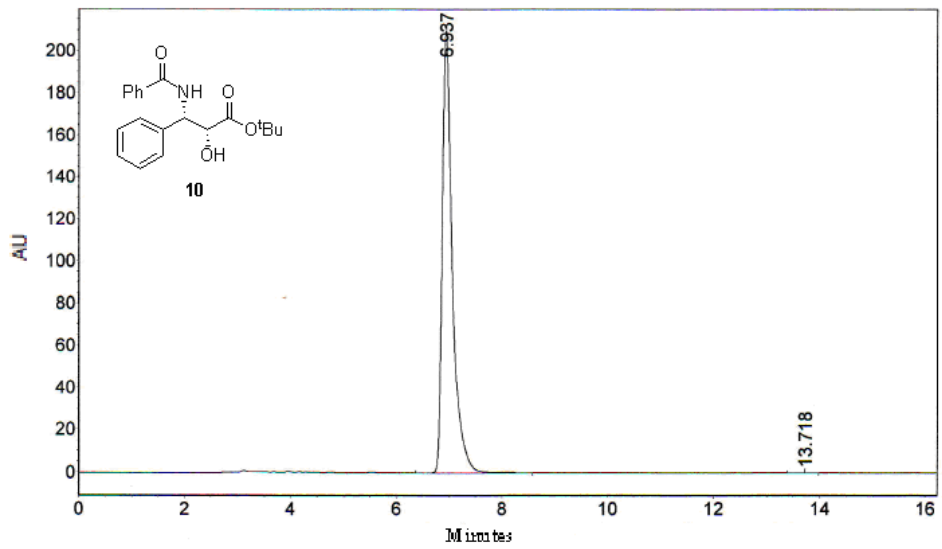
Name	Retention Time	Height	Area	%Area
1	7.667	563772.250	8042232.000	49.9843
2	15.462	263097.375	8047297.500	50.0157
Total		826869.625	16089529.500	100.0000



Name	Retention Time	Height	Area	%Area
1	7.652	977442.438	20052778.000	99.7189
2	15.442	2013.812	56531.250	0.2811
Total		979456.250	20109309.250	100.0000



Name	Retention Time	Height	Area	%Area
1	6.937	41399.801	543270.500	49.6054
2	13.647	18524.533	551914.625	50.3946
Total		59924.334	1095185.125	100.0000



Name	Retention Time	Height	Area	%Area
1	6.937	209790.109	2810081.750	99.9838
2	13.718	27.121	456.500	0.0162
Total		209817.231	2810538.250	100.0000