Catalytic Asymmetric *endo*-Selective [3+2] Cycloaddition Reactions of Schiff Bases of α-Aminophosphonates with Olefins Using Chiral Metal Amides

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Electronic Supplementary Information

General Experimental Procedures

All reactions were conducted in flame-dried glassware with magnetic stirring. Reaction temperatures refer to external bath temperatures. Specific rotations were recorded on JASCO P-2100 polarimeter. IR Spectra were recorded as neat between NaCl plates on JASCO FT/IR-4200 spectrometer. Selected bands (ν_{max}) reported herein. All NMR spectra were recorded on JEOL JNM-ECX400, JNM-ECA500 and JNM-ECX600 spectrometers in chloroform-d. All signals are reported in parts per million (ppm) with reference to tetramethylsilane as the internal standard at 0 ppm (^{1}H) and 77.0 ppm (^{13}C); 85% phosphoric acid as the internal standard at 0 ppm (^{31}P). Data is reported as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet), with coupling constants reported to nearest 0.1 Hz. *J* refers to proton-proton coupling unless otherwise stated. High resolution mass spectra were recorded on JEOL JMS-T100TD spectrometer (DART). Solvents used for reactions were distilled under argon as specified – Et_2O, THF, toluene, mesitylene, were distilled from sodium benzophenone ketyl; CH_2Cl_2 was distilled from calcium hydride; BTF and xylenes were distilled and dried over molecular sieves followed by freeze-pump-thaw method. Silver triflate (AgOTf), copper(I) triflate ½-toluene complex (CuOTf•½($CH_3C_6H_5$)), lithium dimethyl amide ($LiNMe_2$), lithium diisopropylamide (LDA), lithium tetramethylpiperidide (LiTMP) were purchased from Aldrich Co. Ltd. and used without purification; potassium hexamethyldisilazane (KHMDS) was purchased from Aldrich Co. Ltd. and purified by sublimation; triphenylphosphine (PPh_3) was purchased from Wako Pure Chemical Industries Ltd. and recrystallised prior to use; diethylamine ($HNEt_2$), bis(trimethylsilyl)amine (H-HMDS), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), triethylamine (NEt_3) were purchased from Wako Pure Chemical Industries Ltd. and Tokyo Chemical Industry

Co. Ltd. and distilled prior to use. Ligands were purchased from or supplied by commercial suppliers (Strem Chemicals Inc., Aldrich Co. Ltd., Tokyo Chemical Industry Co. Ltd.) and used as received. Fesulphos (**L5**) was synthesised according to the literature[1)] and characterised by NMR. Dipolarophiles (**2a**-**2e**) were purchased from commercial suppliers (Wako Pure Chemical Industries Ltd., Tokyo Chemical Industry Co. Ltd.) and purified by distillation (liquids) or recrystallization (solids) prior to use. Schiff bases (**1a**-**1l**) were synthesised according to the literature.[2)] Thin layer chromatography was performed on pre-coated silica gel 60 glass-backed plates and visualized under UV (254 nm) and/or staining by potassium permanganate followed by gentle heating with a heat gun. Preparative thin layer chromatography was performed on glass plates coated with Wakogel B-5F. High performance liquid chromatography was carried out on Shimadzu LC10ATvp or LC-20AB (liquid chromatograph), Shimadzu SPD-M20A (photo diode array detector) or SPD-10Avp (UV detector).

[3+2] Cycloaddition of α-Aminophosphonate Schiff Bases

Typical Procedure for [3+2] Cycloaddition by CuHMDS:

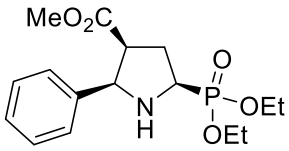
To a dried 5 mL microwave vial, KHMDS (4.0 mg, 0.020 mmol), CuOTf•½($CH_3C_6H_5$) (5.7 mg, 0.022 mmol) and (*R*)-Fesulphos **L5** (10.1 mg, 0.022 mmol) was added in the glovebox under Ar atmosphere and sealed with a rubber septum. Dry mesitylene (1 mL) was added and the mixture was allowed to stir until all the solids have dissolved. It was then stirred at 40 ^oC for 1 hour and transferred to a 25 ^oC water bath. To the catalyst mixture, Schiff base **1a** (102.1 mg, 0.40 mmol), methyl acrylate **2a** (45 µL, 0.50 mmol), H-HMDS (4.2 µL, 0.020 mmol) was transferred *via* cannula by dry mesitylene (1 mL). The mixture was stirred at 25 ^oC for 48 hours. The reaction was quenched with saturated NH_4Cl (3 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude sample was purified by preparative TLC (Et_2O/MeOH: 200/1) to afford the desired product. The enantiomeric excess of the product was analysed by HPLC. Absolute configuration of **3aa** was confirmed by X-ray crystallographic analysis of a single crystal (CCDC number: 1409067).[3)] The absolute configurations of the other products were determined by analogy to **3aa**.

Typical Procedure for [3+2] Cycloaddition by AgHMDS:

To a dried 5 mL microwave vial, KHMDS (4.0 mg, 0.020 mmol), AgOTf (5.7 mg, 0.022 mmol) and (*R*)-Fesulphos **L5** (10.1 mg, 0.022 mmol) was added in the glovebox under Ar atmosphere and sealed with a rubber septum. Dry mesitylene (1 mL) was added and the mixture was allowed to stir until all the solids have dissolved. It was then stirred at 40 ^oC for 1 hour and transferred to a -40 ^oC bath. To the catalyst mixture, Schiff base **1a** (102.1 mg, 0.40 mmol), H-HMDS (42 µL, 0.20 mmol) was transferred *via* cannula by dry mesitylene (0.9 mL) and allowed to stir for 10 minutes. Methyl acrylate **2a** (45 µL, 0.50 mmol) was then added directly to the mixture and followed by dry mesitylene (0.1 mL). The mixture was stirred at -40 ^oC for 18 hours. The reaction was quenched

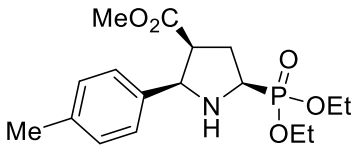
with saturated NH_4Cl (3 mL) and extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude sample was purified by preparative TLC (Et_2O/MeOH: 200/1) to afford the desired product. The enantiomeric excess of the product was analysed by HPLC.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-phenylpyrrolidine-3-carboxylate (**3aa**):



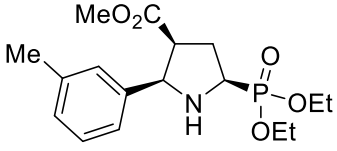
colourless oil; **[α]$_D$** +22 (*c* 1.00, $CHCl_3$, 95% *ee*); **IR** (neat) ν_{max} 3326, 2983, 1738, 1453, 1234, 1053, 1029, 966, 703 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 2.16-2.22 (m, 1H), 2.28 (br. s, 1H), 2.43-2.53 (m, 1H), 3.08 (s, 3H), 3.27 (ddd, J = 8.9, 8.5, 8.3 Hz, 1H), 3.39-3.44 (m, 1H), 4.15-4.26 (m, 4H), 4.45 (d, J = 9.2 Hz, 1H), 7.13-7.16 (m, 1H), 7.19-7.22 (m, 2H), 7.26-7.28 (m, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, J_{P-C} = 5.8 Hz), 16.7 (d, J_{P-C} = 5.8 Hz), 30.1, 49.9 (d, J_{P-C} = 13.9 Hz), 51.3, 54.9 (d, J_{P-C} = 165.2 Hz), 62.6 (d, J_{P-C} = 6.9 Hz), 63.0 (d, J_{P-C} = 6.5 Hz), 65.8 (d, J_{P-C} = 18.6 Hz), 124.4, 127.6, 128.1, 139.9, 172.8; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.2; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 9/1, 0.6 mL/min, 210 nm, t_R : 23.7 min (2*R*,3*S*,5*R*), 33.2 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{16}H_{25}NO_5P$: 342.1470 $[M+H]^+$, found: 342.1483 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(*p*-tolyl)pyrrolidine-3-carboxylate (**3ba**): off-



white solid; **mp** 73-75 °C, **[α]$_D$** +28 (*c* 1.00, $CHCl_3$, 97% *ee*); **IR** (neat) ν_{max} 2983, 1738, 1233, 1052, 1028, 965 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.30 (t, J = 7.5 Hz, 3H), 1.32 (t, J = 7.5 Hz, 3H), 2.15-2.26 (m, 1H), 2.22 (s, 3H), 2.36 (br. s, 1H), 2.40-2.50 (m, 1H), 3.11 (s, 3H), 3.24 (ddd, J = 8.8, 8.3, 8.3 Hz, 1H), 3.37-3.41 (m, 1H), 4.13-4.25 (m, 4H), 4.41 (d, J = 9.2 Hz, 1H), 7.00 (d, J = 7.7 Hz, 2H), 7.14 (d, J = 7.7 Hz, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 16.6 (d, J_{P-C} = 4.8 Hz), 16.7 (d, J_{P-C} = 4.8 Hz), 21.1, 30.1, 49.8 (d, J_{P-C} = 13.8 Hz), 51.2, 54.8 (d, J_{P-C} = 167 Hz), 62.5 (d, J_{P-C} = 7.3 Hz), 62.9 (d, J_{P-C} = 7.1 Hz), 65.6 (d, J_{P-C} = 19.3 Hz), 127.2, 128.7, 137.1, 136.8, 172.8; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.3; **HPLC** Diacel Chiralpak AD-H column (Hexane /^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 6.9 min (2*R*,3*S*,5*R*), 10.6 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{17}H_{27}NO_5P$: 356.1627 $[M+H]^+$, found: 356.1627 $[M+H]^+$.

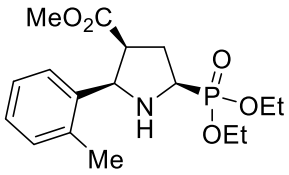
(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(*m*-tolyl)pyrrolidine-3-carboxylate (**3ca**): pale



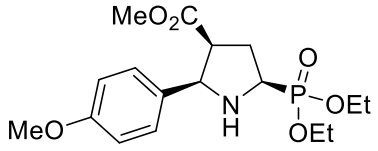
yellow oil; **[α]$_D$** +23 (*c* 1.00, $CHCl_3$, 90% *ee*); **IR** (neat) ν_{max} 3369, 2983, 1738, 1438, 1232, 1053, 1029, 965, 789 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.32 (t, J = 7.4 Hz, 3H), 1.33 (t, J = 7.5 Hz, 3H), 2.17-2.23 (m, 1H), 2.25 (s, 3H), 2.41-2.51 (m, 1H), 3.11 (s, 3H), 3.26 (ddd, J = 8.4, 8.4, 8.4 Hz, 1H), 3.39-3.43 (m, 1H), 4.15-4.27 (m, 4H), 4.41 (d, J = 9.3 Hz, 1H), 6.96-6.97 (m, 1H), 7.05-7.11 (m, 3H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, J_{P-C} = 4.7 Hz), 16.7 (d, J_{P-C} =

4.7 Hz), 21.5, 30.3, 49.9 (d, $J_{P\text{-}C}$ = 13.6 Hz), 51.3, 54.9 (d, $J_{P\text{-}C}$ = 164.4 Hz), 62.6 (d, $J_{P\text{-}C}$ = 6.8 Hz), 63.0 (d, $J_{P\text{-}C}$ = 6.5 Hz), 66.0 (d, $J_{P\text{-}C}$ = 18.6 Hz), 124.5, 128.0, 128.1, 128.4, 137.6, 139.8, 172.9; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.3; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R : 6.6 min (2*R*,3*S*,5*R*), 10.5 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{17}H_{27}NO_5P$: 356.1627 $[M+H]^+$, found: 356.1613 $[M+H]^+$.

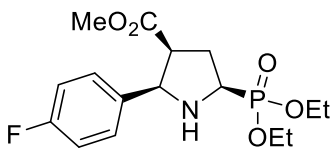
(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(*o*-tolyl)pyrrolidine-3-carboxylate (**3da**): pale yellow oil; **[α]$_D$** +64 (*c* 1.00, $CHCl_3$, 93% *ee*); **IR** (neat) ν_{max} 3462, 3293, 2983, 1739, 1438, 1231, 1165, 1053, 1029, 966, 752 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 2.24-2.28 (m, 1H), 2.31 (s, 3H), 2.51-2.57 (m, 1H), 3.00 (s, 3H), 3.36 (ddd, *J* = 6.9, 8.5, 9.3 Hz, 1H), 3.42 (ddd, *J* = 4.7, 7.1, 10.8 Hz, 1H), 4.19-4.34 (m, 4H), 4.56 (d, *J* = 9.1 Hz, 1H), 7.05-7.11 (m, 3H), 7.41-7.43 (m, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.9 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.9 Hz), 19.6, 30.2, 47.6 (d, $J_{P\text{-}C}$ = 13.6 Hz), 51.2, 54.7 (d, $J_{P\text{-}C}$ = 166.4 Hz), 62.6 (d, $J_{P\text{-}C}$ = 7.0 Hz), 63.0 (d, $J_{P\text{-}C}$ = 21.7 Hz), 63.2 (d, $J_{P\text{-}C}$ = 6.5 Hz), 125.9, 126.3, 127.4, 129.9, 135.8, 137.3, 173.1; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak AD-H column (Hexane /^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R : 5.6 min (2*R*,3*S*,5*R*), 6.8 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{17}H_{27}NO_5P$: 356.1627 $[M+H]^+$, found: 356.16211 $[M+H]^+$.



(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(4-methoxy-phenyl)-pyrrolidine-3-carboxylate (**3ea**): colourless oil; **[α]$_D$** +22 (*c* 1.00, $CHCl_3$, 99% *ee*); **IR** (neat) ν_{max} 3364, 2982, 1737, 1515, 1250, 1032, 967 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.1 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 2.19-2.24 (m, 1H), 2.29 (br. s, 1H), 2.46-2.54 (m, 1H), 3.17 (s, 3H), 3.27 (ddd, *J* = 8.6, 8.6, 8.6 Hz, 1H), 3.44 (ddd, *J* = 4.8, 6.7, 11.1 Hz, 1H), 4.18-4.28 (m, 4H), 4.46 (d, *J* = 9.2 Hz, 1H), 6.8 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.8 Hz), 16.8 (d, $J_{P\text{-}C}$ = 5.8 Hz), 30.1, 50.0 (d, $J_{P\text{-}C}$ = 13.9 Hz), 51.4, 54.9 (d, $J_{P\text{-}C}$ = 166.3 Hz), 55.4, 62.6 (d, $J_{P\text{-}C}$ = 7.0 Hz), 63.0 (d, $J_{P\text{-}C}$ = 6.6 Hz), 65.4 (d, $J_{P\text{-}C}$ = 19.5 Hz), 113.5, 128.6, 132.1, 159.2, 172.9; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.3; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R : 9.7 min (2*R*,3*S*,5*R*), 14.9 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{17}H_{27}NO_6P$: 372.1576 $[M+H]^+$, found: 372.1563 $[M+H]^+$.

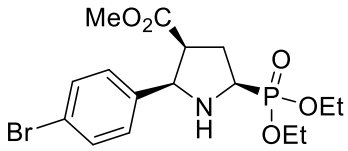


(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(4-fluorophenyl)-pyrrolidine-3-carboxylate (**3fa**): white solid; **mp** 83-85 ^{o}C, **[α]$_D$** +29 (*c* 0.50, $CHCl_3$, 99% *ee*); **IR** (neat) ν_{max} 2983, 1731, 1510, 1231, 1028, 967 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.38 (t, *J* = 7.1 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 2.22-2.28 (m, 1H), 2.41 (br. s, 1H), 2.49-2.57 (m, 1H), 3.20 (s, 3H), 3.33 (ddd, *J* = 8.4, 8.9, 8.9 Hz, 1H), 3.44-3.54 (m, 1H), 4.21-4.32 (m, 4H), 4.54 (d, *J* = 9.3 Hz, 1H),



6.95-6.99 (m, 2H), 7.32-7.35 (m, 2H); **^{13}C-NMR** (125 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.3 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.3 Hz), 29.8, 49.9 (d, $J_{P\text{-}C}$ = 14.0 Hz), 51.4, 54.8 (d, $J_{P\text{-}C}$ = 168.9 Hz), 62.5 (d, $J_{P\text{-}C}$ = 6.9 Hz), 63.0 (d, $J_{P\text{-}C}$ = 6.6 Hz), 64.8 (d, $J_{P\text{-}C}$ = 18.9 Hz), 114.9 (d, $J_{F\text{-}C}$ = 21.6 Hz), 129.1 (d, $J_{F\text{-}C}$ = 8.0 Hz), 136.0 (d, $J_{F\text{-}C}$ = 2.5 Hz), 162.3 (d, $J_{F\text{-}C}$ = 246.6 Hz), 172.5; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 6.9 min (2*R*,3*S*,5*R*), 12.4 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{16}H_{24}FNO_5P$: 360.1376 $[M+H]^+$, found: 360.1367 $[M+H]^+$.

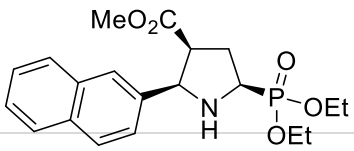
(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(4-bromophenyl)-pyrrolidine-3-carboxylate



(**3ga**): white solid; **mp** 133-135 ^{o}C, **$[\alpha]_D$** +23 (*c* 1.00, $CHCl_3$, 99% *ee*); **IR** (neat) ν_{max} 3299, 2981, 1729, 1229, 1048, 1025, 970 cm^{-1}; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 6.8 Hz, 3H), 1.38 (t, *J* = 6.8 Hz, 3H), 2.20-2.27 (m, 1H), 2.36 (br. s, 1H), 2.45-2.55 (m, 1H), 3.20 (s, 3H), 3.35 (ddd, *J* = 8.7, 8.7, 8.7 Hz, 1H), 3.45-3.50 (m, 1H), 4.18-4.31 (m, 4H), 4.49 (d, *J* = 9.3 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H); **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.1 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.1 Hz), 29.7, 49.7 (d, $J_{P\text{-}C}$ = 14.3 Hz), 51.4, 54.7 (d, $J_{P\text{-}C}$ = 170.3 Hz), 62.5 (d, $J_{P\text{-}C}$ = 7.7 Hz), 63.0 (d, $J_{P\text{-}C}$ = 6.6 Hz), 64.6 (d, $J_{P\text{-}C}$ = 19.3 Hz), 121.5, 129.2, 131.1, 139.4, 172.34; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 7.0 min (2*R*,3*S*,5*R*), 13.4 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{16}H_{24}BrNO_5P$: 420.0576 $[M+H]^+$, found: 420.0579 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(4-(trifluoro-methyl)phenyl)pyrrolidine-3-carboxylate (**3ha**): colourless oil; **$[\alpha]_D$** +11 (*c* 1.00, $CHCl_3$, 98% *ee*); **IR** (neat) ν_{max} 3322, 2986, 1739, 1327, 1234, 1165, 1122, 1066, 1054, 1029, 965, 850 cm^{-1}; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.34 (t, *J* = 7.3 Hz, 3H), 1.36 (t, *J* = 7.3 Hz, 3H), 2.21-2.26 (m, 1H), 2.43 (br. s, 1H), 2.45-2.55 (m, 1H), 3.13 (s, 3H), 3.35 (ddd, *J* = 8.3, 8.7, 9.0 Hz, 1H), 3.47-3.51 (m, 1H), 4.17-4.27 (m, 4H), 4.57 (d, *J* = 9.3 Hz, 1H), 7.45-7.51 (m, 4H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.7 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.7 Hz), 29.7, 50.0 (d, $J_{P\text{-}C}$ = 13.9 Hz), 51.4, 54.8 (d, $J_{P\text{-}C}$ = 169.1 Hz), 62.6 (d, $J_{P\text{-}C}$ = 6.9 Hz), 63.1 (d, $J_{P\text{-}C}$ = 6.6 Hz), 64.7 (d, $J_{P\text{-}C}$ = 18.7 Hz), 124.3 (d, $J_{F\text{-}C}$ = 271.8 Hz), 124.9 (d, $J_{F\text{-}C}$ = 3.0 Hz), 128.0, 130.0 (d, $J_{F\text{-}C}$ = 32.5 Hz), 144.6, 172.2; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 25.9; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 6.2 min (2*R*,3*S*,5*R*), 9.1 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{17}H_{24}F_3NO_5P$: 410.1344 $[M+H]^+$, found: 410.1364 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(naphthalen-2-yl)pyrrolidine-3-carboxylate



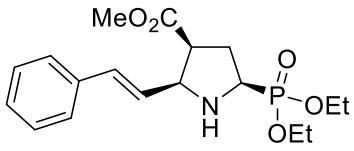
(**3ia**): yellow oil; **$[\alpha]_D$** +27 (*c* 1.00, $CHCl_3$, 88% *ee*); **IR** (neat) ν_{max} 3324, 2982, 1737, 1438, 1234, 1050, 1028, 965, 823, 749 cm^{-1}; **^{1}H-**

NMR (600 MHz, $CDCl_3$) δ 1.38 (t, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H), 2.26-2.31 (m, 1H), 2.54-2.62 (m, 1H), 3.02 (s, 3H), 3.40 (ddd, J = 8.6, 8.6, 8.6 Hz, 1H), 3.52 (ddd, J = 4.8, 6.9, 11.0 Hz, 1H), 4.22-4.35 (m, 4H), 4.65 (d, J = 9.2 Hz, 1H), 7.40-7.44 (m, 3H), 7.73 (d, J = 8.6 Hz, 1H), 7.76-7.78 (m, 2H), 7.79 (s, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 6.0 Hz), 16.8 (d, $J_{P\text{-}C}$ = 6.0 Hz), 30.2, 49.9 (d, $J_{P\text{-}C}$ = 13.7 Hz), 51.3, 55.0 (d, $J_{P\text{-}C}$ = 167.0 Hz), 62.6 (d, $J_{P\text{-}C}$ = 7.0 Hz), 63.0 (d, $J_{P\text{-}C}$ = 6.6 Hz), 65.9 (d, $J_{P\text{-}C}$ = 19.5 Hz), 125.7, 125.9, 126.1, 126.2, 127.6, 127.7, 128.1, 133.1, 133.2, 137.5, 172.8; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.2; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 10.1 min (2*R*,3*S*,5*R*), 20.7 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{20}H_{27}NO_5P$: 392.1627 $[M+H]^+$, found: 392.1614 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(naphthalen-1-yl)pyrrolidine-3-carboxylate (**3ja**): yellow oil; **[α]$_D$** +117 (*c* 1.00, $CHCl_3$, 91% *ee*); **IR** (neat) ν_{max} 3280, 2983, 1737, 1437, 1233, 1047, 1028, 967, 793 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.36 (t, J = 7.1 Hz, 3H), 1.38 (t, J = 7.1 Hz, 3H), 2.28-2.33 (m, 1H), 2.48 (br. s, 1H), 2.55-2.64 (m, 1H), 2.69 (s, 3H), 3.51-3.55 (m, 2H), 4.21-4.35 (m, 4H), 5.16 (d, J = 8.9 Hz, 1H), 7.38 (dd, J = 7.2, 8.2 Hz, 1H), 7.41 (dd, J = 7.2, 8.1 Hz, 1H), 7.46 (dd, J = 6.6, 8.6 Hz, 1H), 7.69 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 7.3 Hz, 1H), 7.78 (d, J = 8.2 Hz, 1H), 7.96 (d, J = 8.5 Hz, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.8 (d, $J_{P\text{-}C}$ = 7.7 Hz), 16.8 (d, $J_{P\text{-}C}$ = 7.7 Hz), 30.3, 48.8 (d, $J_{P\text{-}C}$ = 13.3 Hz), 51.0, 54.7 (d, $J_{P\text{-}C}$ = 167.0 Hz), 62.2 (d, $J_{P\text{-}C}$ = 21.0 Hz), 62.7 (d, $J_{P\text{-}C}$ = 7.0 Hz), 63.3 (d, $J_{P\text{-}C}$ = 6.4 Hz), 123.2, 124.4, 125.4, 125.5, 126.0, 128.1, 128.9, 131.4, 131.8, 133.5, 135.1, 173.0; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak OD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 10.7 min (2*S*,3*R*,5*S*), 18.3 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{20}H_{27}NO_5P$: 392.1627 $[M+H]^+$, found: 392.1618 $[M+H]^+$.

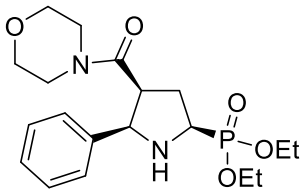
(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-(furan-2-yl)pyrrolidine-3-carboxylate (**3ka**): yellow oil; **[α]$_D$** -6 (*c* 1.00, $CHCl_3$, 97% *ee*); **IR** (neat) ν_{max} 3327, 2984, 1739, 1439, 1369, 1235, 1027, 965, 743 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.31 (t, J = 7.1 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 2.20-2.25 (m, 1H), 2.38 (br. s, 1H), 2.43-2.51 (m, 1H), 3.22 (ddd, J = 8.9, 8.9, 7.7 Hz, 1H), 3.40 (s, 3H), 4.14-4.19 (m, 4H), 4.52 (d, J = 8.8 Hz, 1H), 6.24-6.26 (m, 2H), 7.25-7.27 (m, 1H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.6 (d, $J_{P\text{-}C}$ = 5.8 Hz), 30.2, 48.7 (d, $J_{P\text{-}C}$ = 13.1 Hz), 51.9, 54.6 (d, $J_{P\text{-}C}$ = 164.1 Hz), 59.6 (d, $J_{P\text{-}C}$ = 17.6 Hz), 62.7 (d, $J_{P\text{-}C}$ = 6.8 Hz), 62.9 (d, $J_{P\text{-}C}$ = 6.8 Hz), 107.4, 110.4, 141.9, 153.3, 172.4; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 16.0 min (2*S*,3*R*,5*S*), 19.6 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{14}H_{23}NO_6P$: 332.1263 $[M+H]^+$, found: 332.1279 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-2-((*E*)-styryl)-pyrrolidine-3-carboxylate (**3la**):



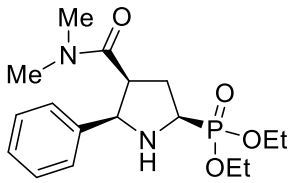
yellow oil; **[α]$_D$** -11 (*c* 0.50, $CHCl_3$, 96% *ee*); **IR** (neat) ν_{max} 2983, 1736, 1439, 1370, 1232, 1027, 965, 748 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.29 (t, J = 7.1 Hz, 3H), 1.30 (t, J = 7.1 Hz, 3H), 2.18 (br. s, 1H), 2.19-2.24 (m, 1H), 2.34-2.42 (m, 1H), 3.14 (ddd, J = 8.7, 8.7, 7.8 Hz, 1H), 3.52 (ddd, J = 6.9, 6.9, 10.9 Hz, 1H), 3.52 (s, 3H), 3.98 (dd, J = 7.7, 8.7 Hz, 1H), 4.13-4.17 (m, 4H), 6.06 (dd, J = 7.8, 15.8 Hz, 1H), 6.49 (d, J = 15.8 Hz, 1H), 7.14-7.16 (m, 1H), 7.20-7.23 (m, 2H), 7.24-7.26 (m, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.6 Hz), 30.6, 49.1 (d, $J_{P\text{-}C}$ = 12.3 Hz), 51.9, 54.8 (d, $J_{P\text{-}C}$ = 162.6 Hz), 62.7 (d, $J_{P\text{-}C}$ = 7.0 Hz), 62.9 (d, $J_{P\text{-}C}$ = 6.8 Hz), 64.3 (d, $J_{P\text{-}C}$ = 16.1 Hz), 126.7, 127.5, 127.9, 128.7, 132.5, 136.9, 173.0; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.5; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 14.7 min (2*S*,3*R*,5*S*), 22.8 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{18}H_{27}NO_5P$: 368.1627 $[M+H]^+$, found: 368.1642 $[M+H]^+$.

Diethyl ((2*R*,4*S*,5*R*)-4-(morpholine-4-carbonyl)-5-phenylpyrrolidin-2-yl)phosphonate (**3ab**):



yellow oil; **[α]$_D$** -26 (*c* 1.00, $CHCl_3$, 88% *ee*); **IR** (neat) ν_{max} 3448, 2980, 2907, 2859, 1643, 1455, 1441, 1240, 1116, 1027, 968, 702 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.32 (t, J = 6.4 Hz, 6H), 2.14-2.19 (m, 1H), 2.53 (br. s, 1H), 2.70-2.78 (m, 2H), 2.90-2.93 (m, 1H), 2.98-3.01 (m, 1H), 3.11-3.15 (m, 1H), 3.18-3.24 (m, 2H), 3.34-3.45 (m, 4H), 4.15-4.24 (m. 4H), 4.26 (d, J = 8.9 Hz, 1H), 7.18-7.30 (m, 5H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.0 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.0 Hz), 31.6, 41.9, 45.7 (d, $J_{P\text{-}C}$ = 13.2 Hz), 45.8, 55.0 (d, $J_{P\text{-}C}$ = 163.4 Hz), 62.9 (d, $J_{P\text{-}C}$ = 10.6 Hz), 62.9 (d, $J_{P\text{-}C}$ = 9.1 Hz), 64.0, 66.1, 66.4, 67.4 (d, $J_{P\text{-}C}$ = 20.2 Hz), 128.1, 128.3, 128.4, 139.1, 170.6; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.7; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 11.6 min (2*S*,3*R*,5*S*), 13.3 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{19}H_{30}N_2O_5P$: 397.1892 $[M+H]^+$, found: 397.1877 $[M+H]^+$.

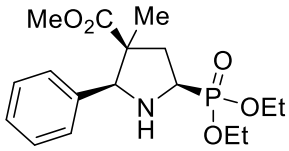
Diethyl ((2*R*,4*S*,5*R*)-4-(dimethylcarbamoyl)-5-phenylpyrrolidin-2-yl)phosphonate (**3ac**):



yellow oil; **[α]$_D$** -13 (*c* 0.50, $CHCl_3$, 85% *ee*); **IR** (neat) ν_{max} 3421, 2982, 1641, 1233, 1051, 1029, 965, 702 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.32 (t, J = 7.1 Hz, 6H), 2.11-2.16 (m, 1H), 2.44 (s, 3H), 2.64 (s, 3H), 2.65-2.72 (m, 1H), 3.35-3.39 (m, 1H), 3.49 (dd, J = 8.2, 8.6 Hz, 1H), 4.13-4.24 (m, 4H), 4.34 (d, J = 9.0 Hz, 1H), 7.15-7.27 (m, 5H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, $J_{P\text{-}C}$ = 5.2 Hz), 16.7 (d, $J_{P\text{-}C}$ = 5.2 Hz), 31.4, 35.4, 37.2, 46.4 (d, $J_{P\text{-}C}$ = 13.4 Hz), 55.0 (d, $J_{P\text{-}C}$ = 163.4 Hz), 55.3 (d, $J_{P\text{-}C}$ = 13.1 Hz), 62.8 (d, $J_{P\text{-}C}$ = 8.0 Hz), 62.9 (d, $J_{P\text{-}C}$ = 7.9 Hz), 64.0, 66.8 (d, $J_{P\text{-}C}$ = 19.5 Hz), 127.7, 128.0, 128.1, 139.5, 171.6; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.6; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R: 8.7 min (2*S*,3*R*,5*S*),

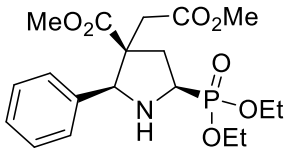
10.1 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{17}H_{28}N_2O_4P$: 355.1787 $[M+H]^+$, found: 355.1774 $[M+H]^+$.

(2*R*,3*S*,5*R*)-Methyl-5-(diethoxyphosphoryl)-3-methyl-2-phenyl-pyrrolidine-3-carboxylate



(**3ad**): white solid; **mp** 86-88 °C, **$[\alpha]_D$** -24 (*c* 0.50, $CHCl_3$, 98% *ee*); **IR** (neat) ν_{max} 3309, 2990, 1721, 1456, 1232, 1027, 963 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.32 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.39 (s, 3H), 1.82 (ddd, J = 6.7, 12.9 Hz, 1H), 1.46 (br. s, 1H), 2.80-2.87 (m, 1H), 3.06 (s, 3H), 3.51 (ddd, J = 5.1, 6.7, 11.3 Hz, 1H), 3.95 (s, 1H), 4.16-4.27 (m, 4H), 7.14-7.17 (m, 1H), 7.19-7.22 (m, 2H), 7.25-7.26 (m, 2H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (d, J_{P-C} = 4.8 Hz), 16.7 (d, J_{P-C} = 4.8 Hz), 24.3, 38.1, 51.5, 53.9 (d, J_{P-C} = 167.0 Hz), 55.3 (d, J_{P-C} = 13.1 Hz), 62.6 (d, J_{P-C} = 6.9 Hz), 62.9 (d, J_{P-C} = 6.7 Hz), 74.6 (d, J_{P-C} = 18.2 Hz), 127.3, 127.8, 128.0, 139.9, 174.7; **^{31}P-NMR** (243 MHz, $CDCl_3$) δ 26.5; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R : 6.4 min (2*S*,3*R*,5*S*), 7.4 min (2*R*,3*S*,5*R*); **DART-HRMS** calcd. for $C_{17}H_{27}NO_5P$: 356.1627 $[M+H]^+$, found: 356.1611 $[M+H]^+$.

Methyl (2*S*,3*S*,5*R*)-5-(diethoxyphosphoryl)-3-(2-methoxy-2-oxoethyl)-2-phenylpyrrolidine-3-carboxylate (**3ae**): colourless oil; **mp** °C, **$[\alpha]_D$** -19 (*c* 0.25, $CHCl_3$, 93% *ee*); **IR** (neat) ν_{max} 3312, 2994, 1722, 1699, 1521, 1027 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$) δ 1.33 (m, 6H), 1.77 (br. s, 3H), 2.11-2.15 (m, 1H), 2.59 (d_{AB}, J_{AB} 17.0Hz, 1H), 3.04-3.38 (m, 4H), 3.43-3.51 (m, 1H), 3.64 (s, 3H), 3.99 (s, 1H), 4.18-4.35 (m, 4H), 7.24-7.29 (m, 5H); **^{13}C-NMR** (151 MHz, $CDCl_3$) δ 16.7 (t, J_{P-C} = 5.9 Hz), 36.0, 41.1, 51.8 (d, J_{P-C} = 23.0 Hz), 53.8 (d, J_{P-C} = 166.8 Hz), 56.8 (d, J_{P-C} = 6.8 Hz), 62.5 (d, J_{P-C} = 7.1 Hz), 63.1 (d, J_{P-C} = 6.7 Hz),72.9, 73.1, 127.3, 128.1, 128.2, 138.3, 171.53, 172.9; **^{31}P-NMR** (200 MHz, $CDCl_3$) δ 26.0; **HPLC** Diacel Chiralpak AD-H column (Hexane/^{i}PrOH: 4/1, 1.0 mL/min, 210 nm, t_R : 7.3 min (2*R*,3*S*,5*R*), 11.1 min (2*S*,3*R*,5*S*); **DART-HRMS** calcd. for $C_{19}H_{29}NO_7P$: 414.1660 $[M+H]^+$, found: 414.1682 $[M+H]^+$.



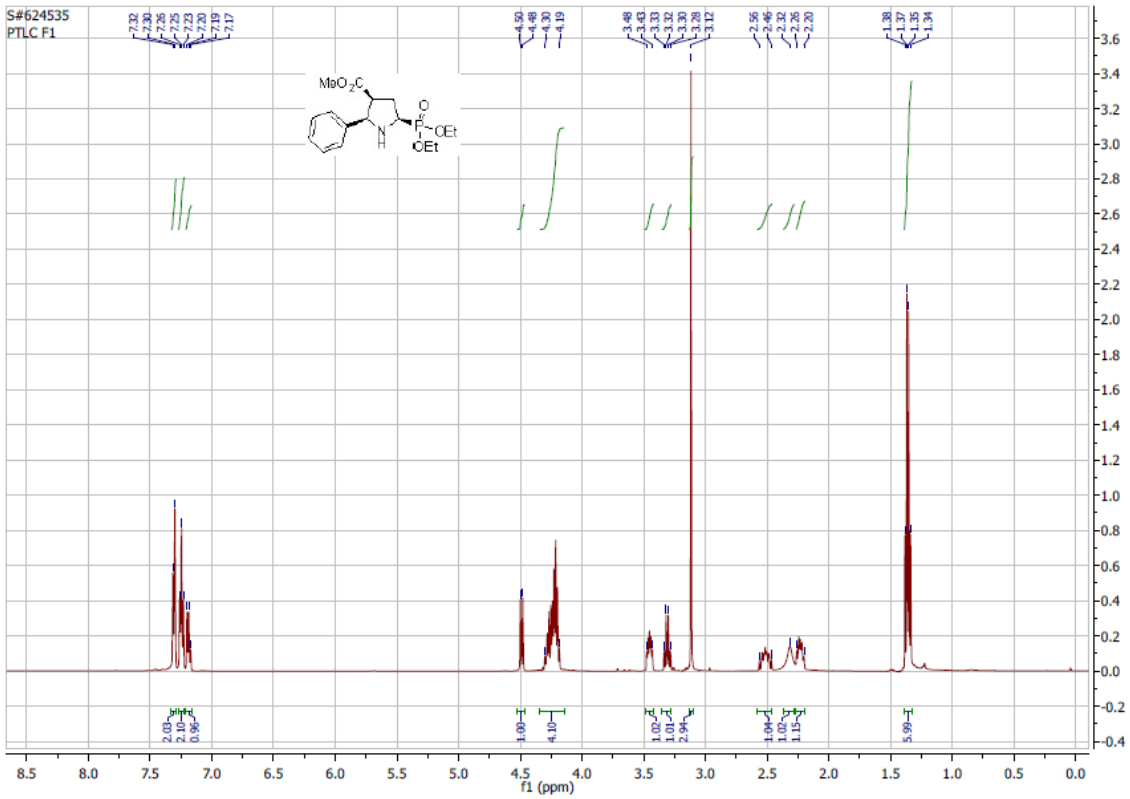
Reference

1) Mancheno, O. G.; Priego, J.; Cabrera, S.; Arrayás, R. G.; Llamas, T.; Caretero, J. C. *J. Org. Chem.* **2003**, *68*, 3679.

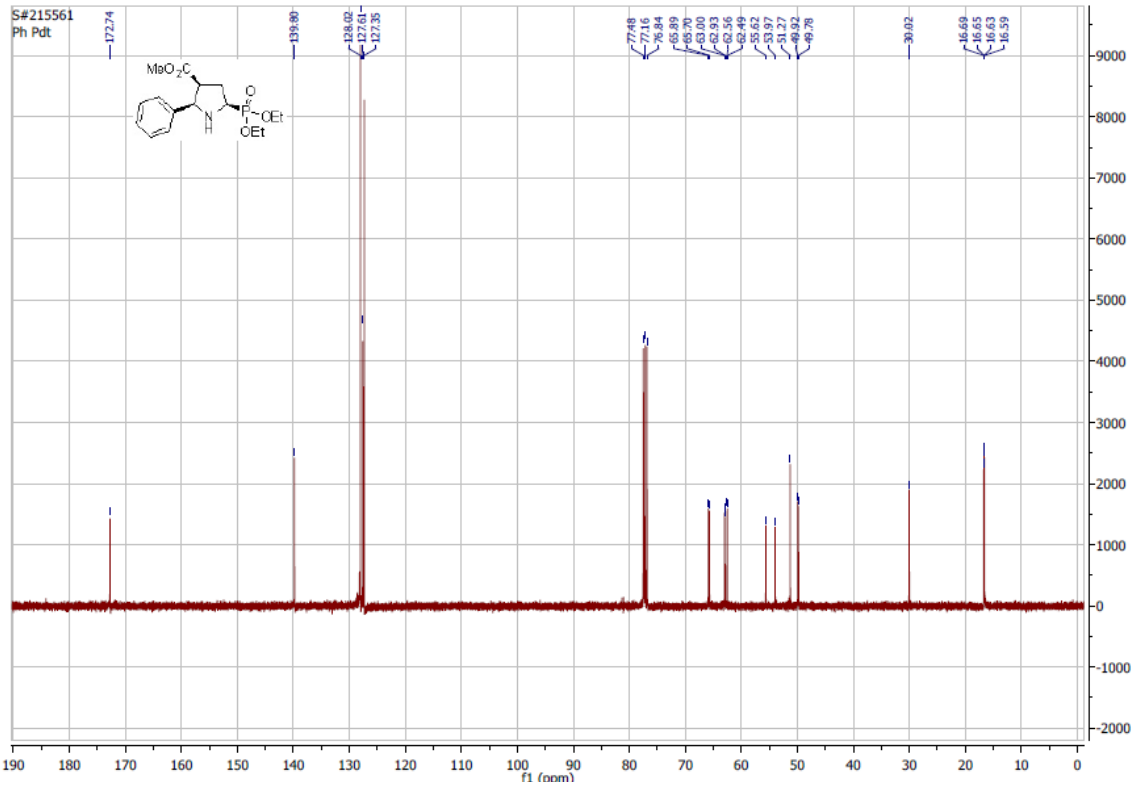
2) Davidsen, S. K.; Phlips, G. W.; Martin, S. F. *Org. Synth.* **1993**, 8, 451.

3) The data have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1409067. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +448(0)12238336033 or deposit@ccdc.cam.ac.uk). As the Flack parameter of the data was 0.95(14), the actual structure of the product is the opposite enantiomer of the structure in the analysis.

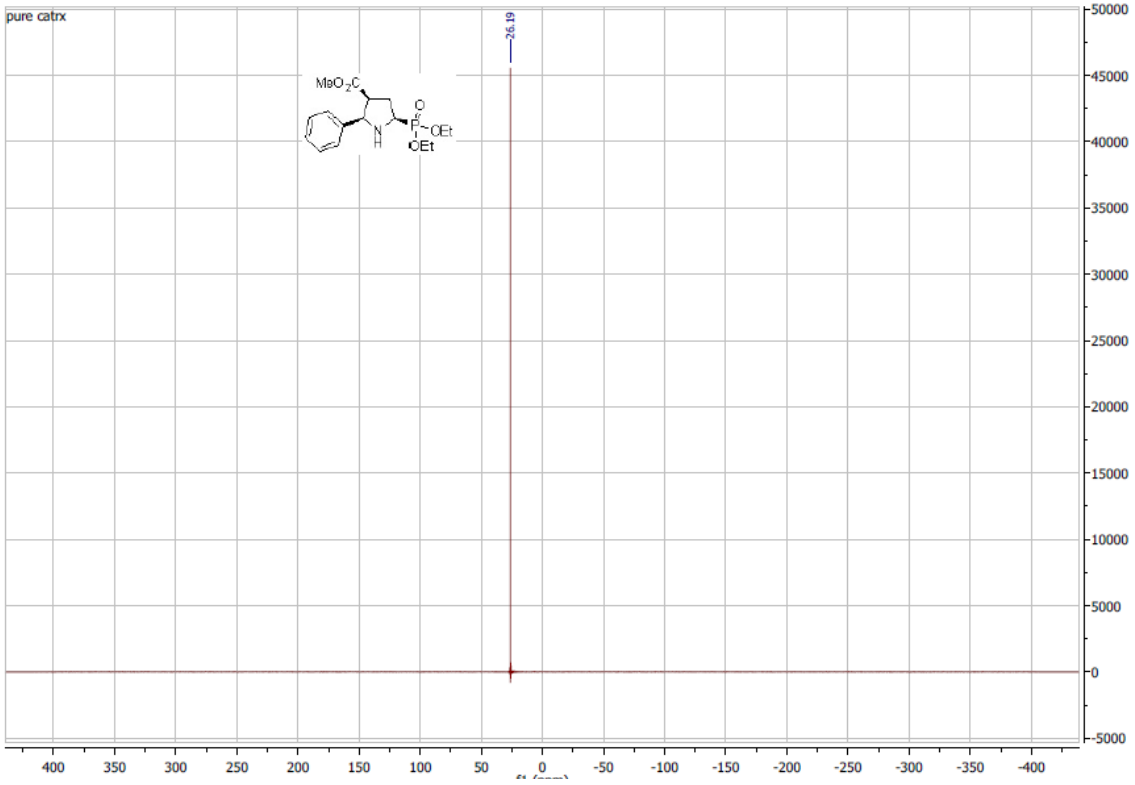
Compound 3aa ^{1}H NMR



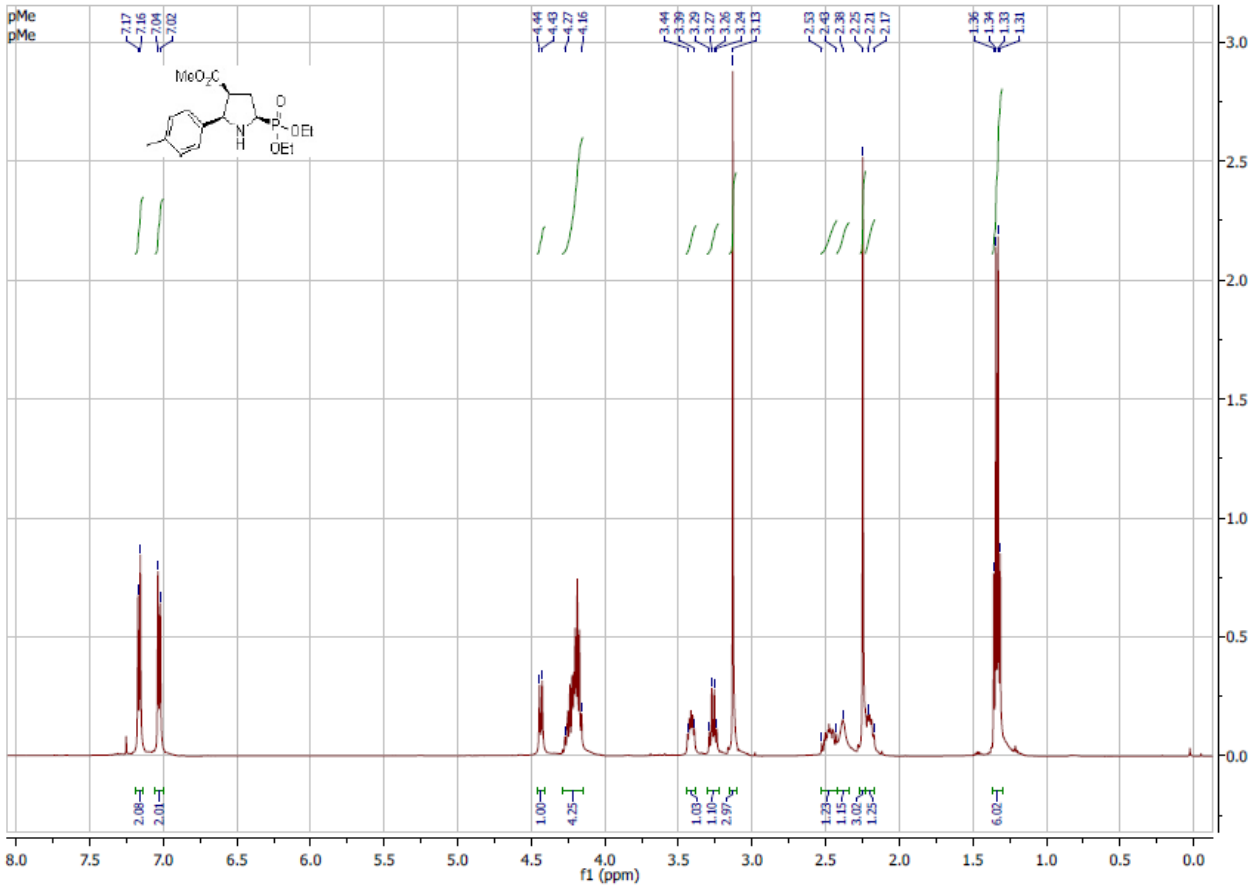
Compound 3aa ^{13}C NMR



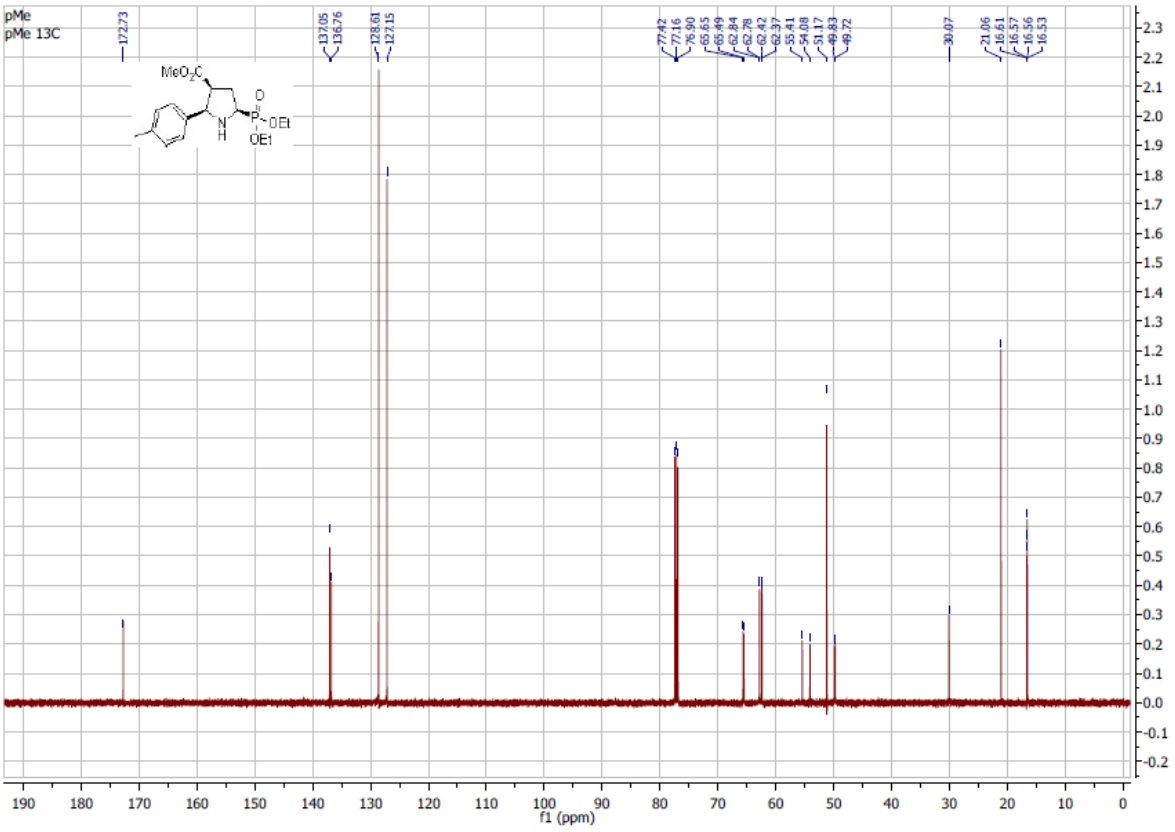
Compound 3aa ^{31}P NMR



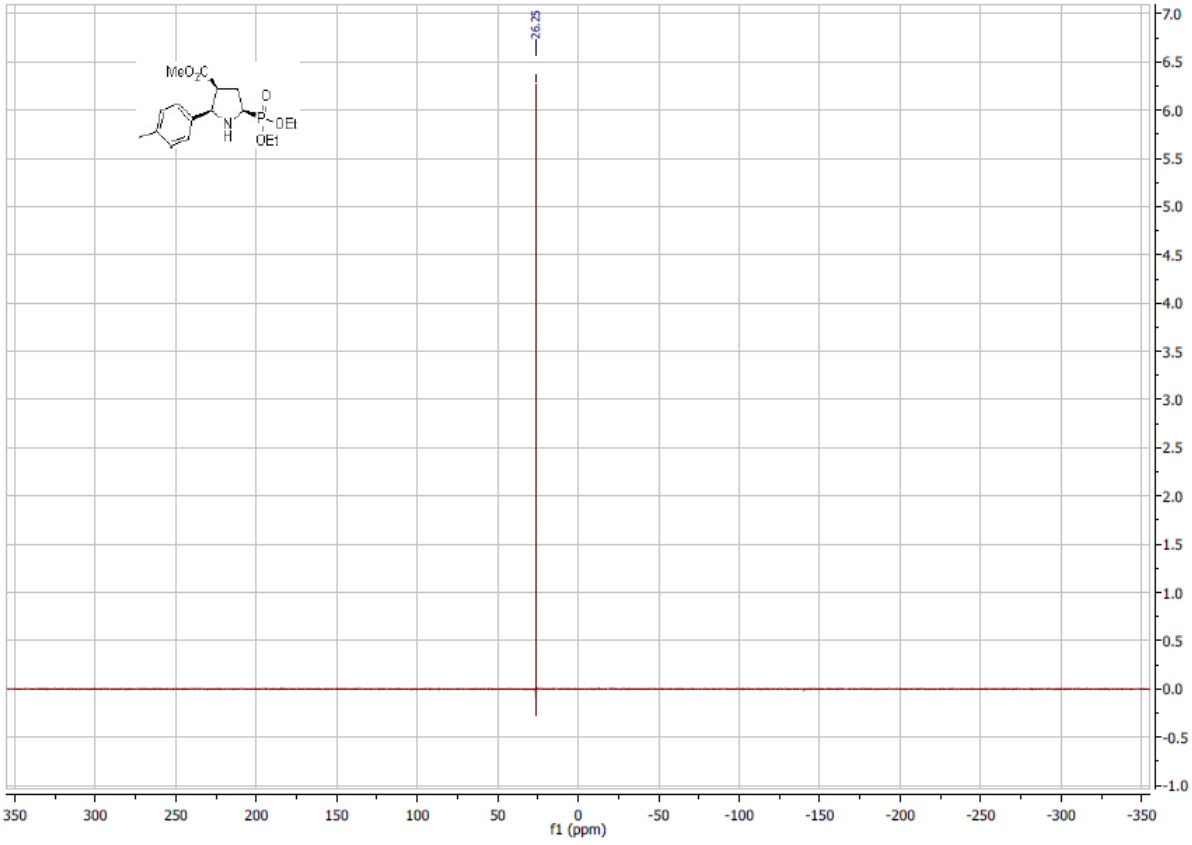
Compound 3ba ^{1}H NMR



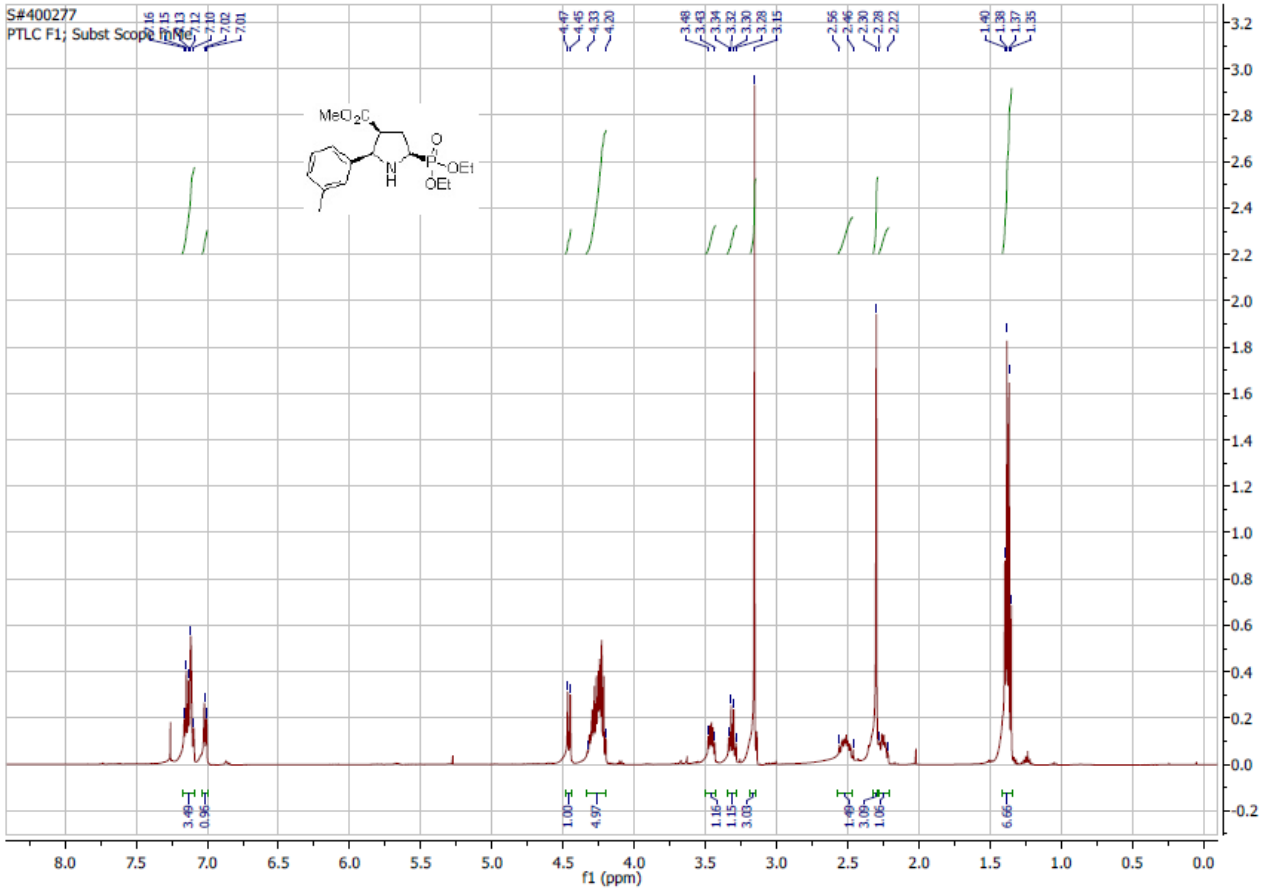
Compound 3ba ^{13}C NMR



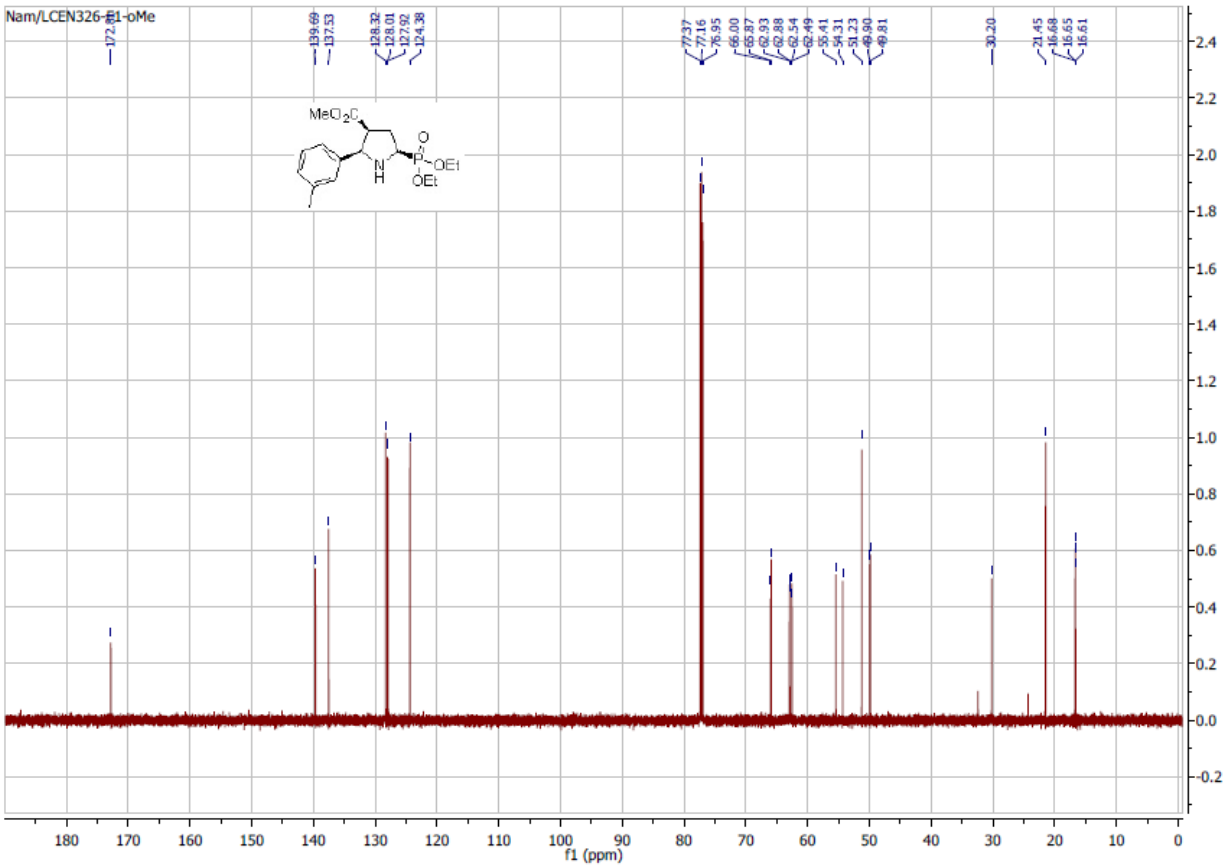
Compound 3ba ^{31}P NMR



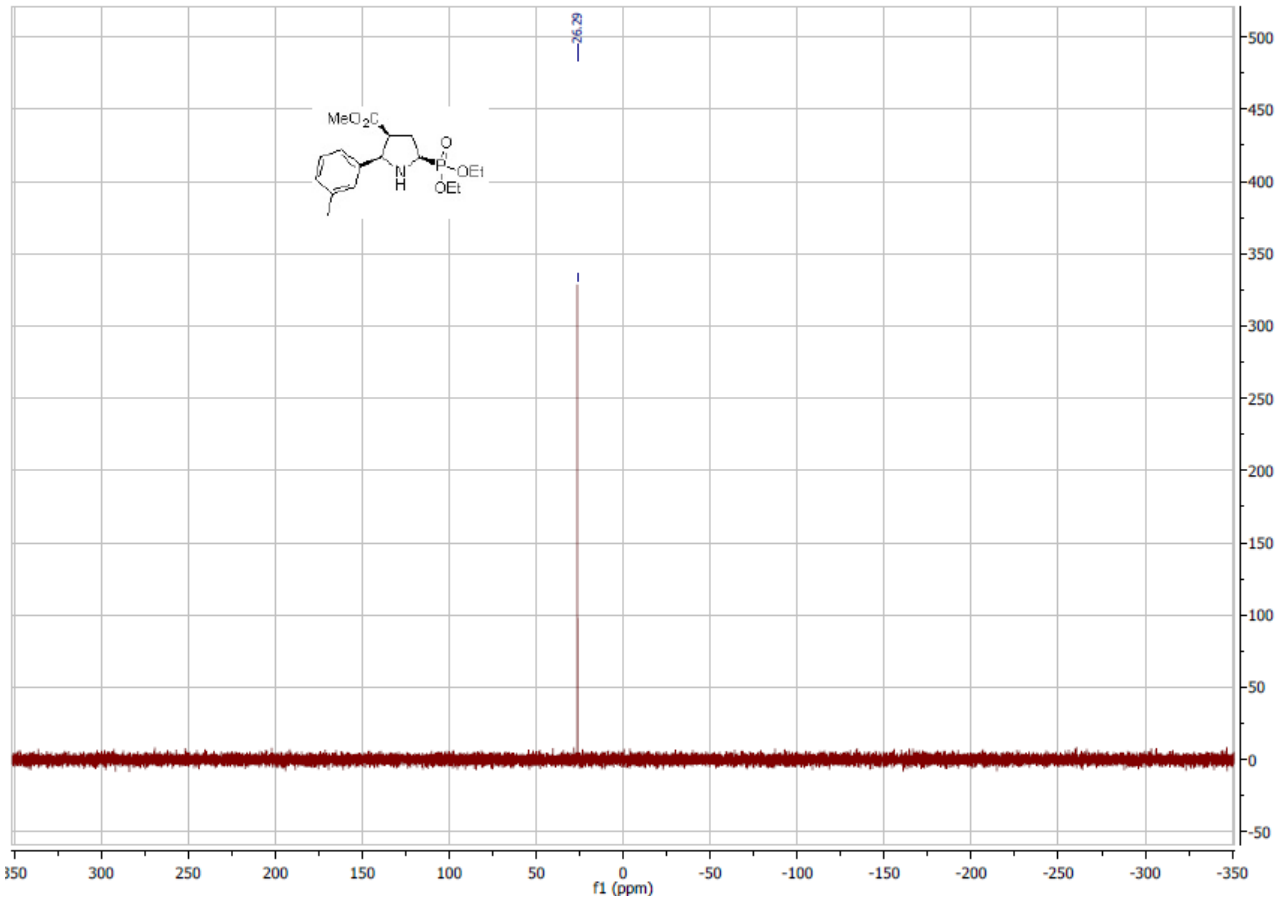
Compound 3ca ^{1}H NMR



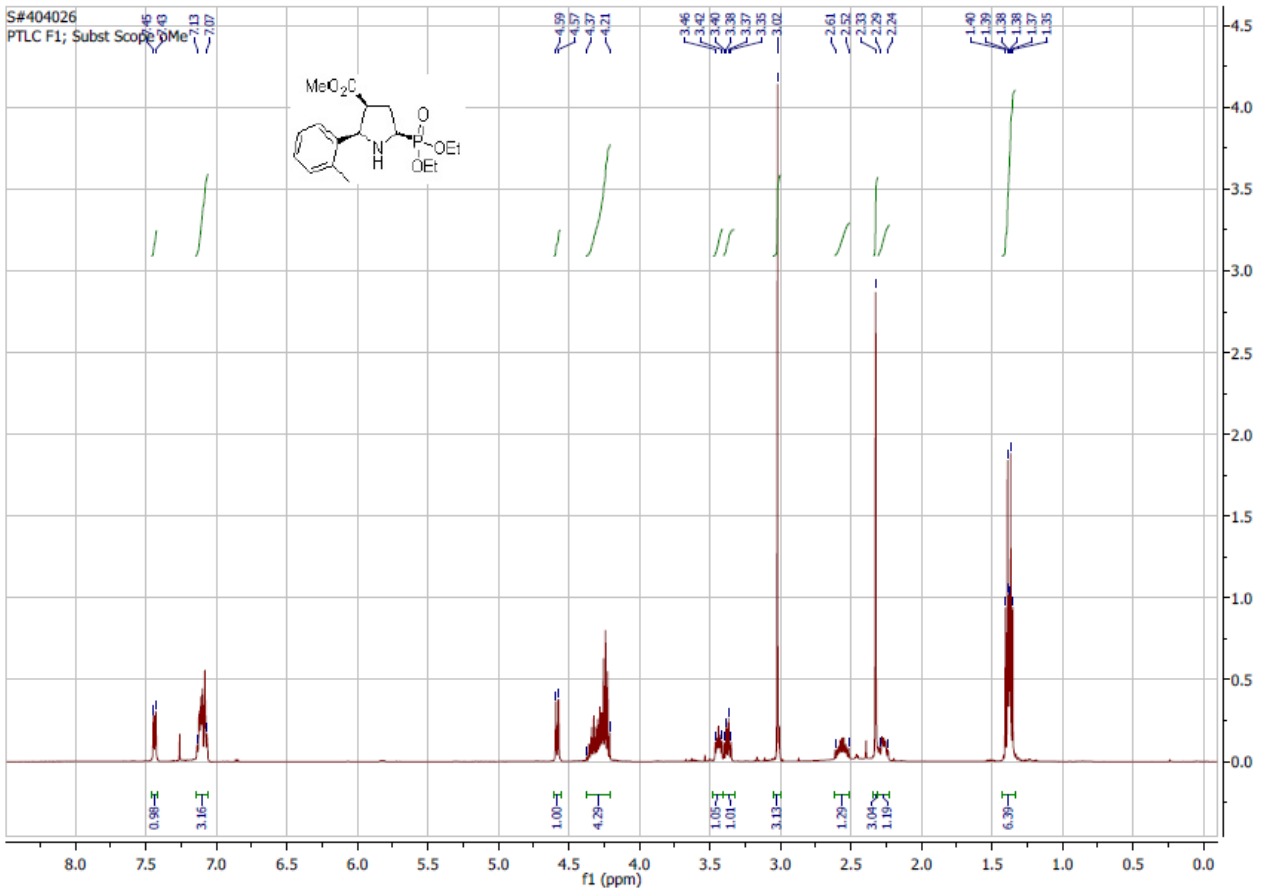
Compound 3ca ^{13}C NMR



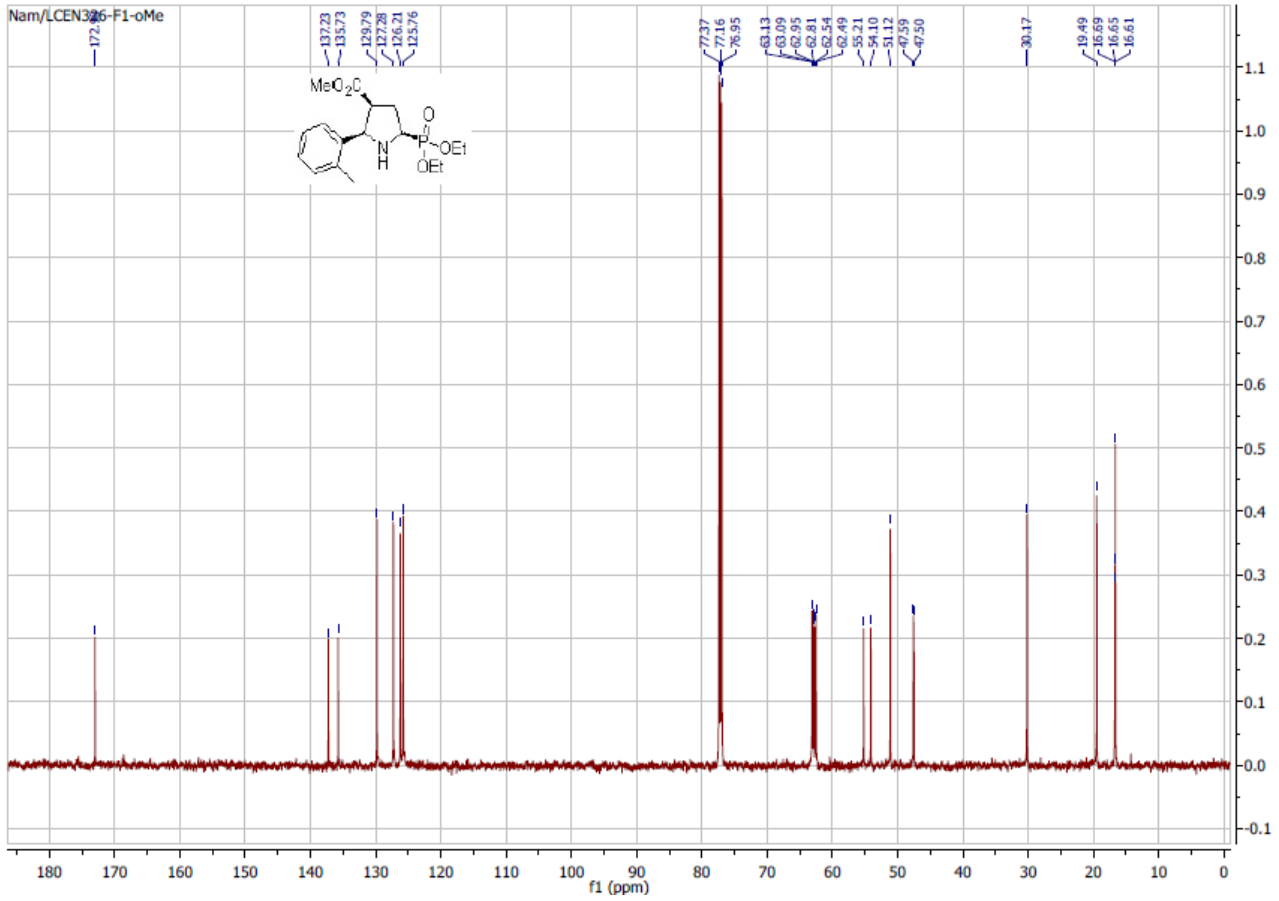
Compound 3ca ^{31}P NMR



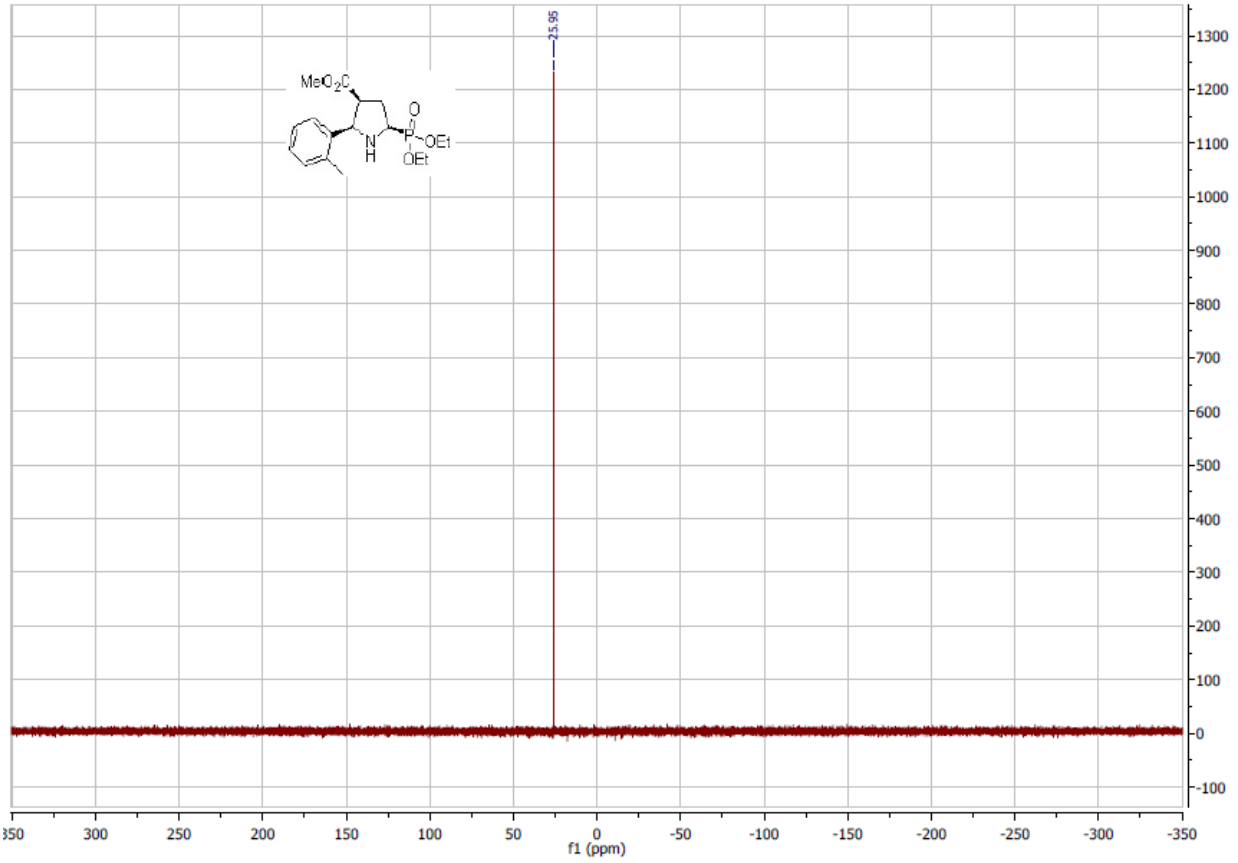
Compound 3da ^{1}H NMR



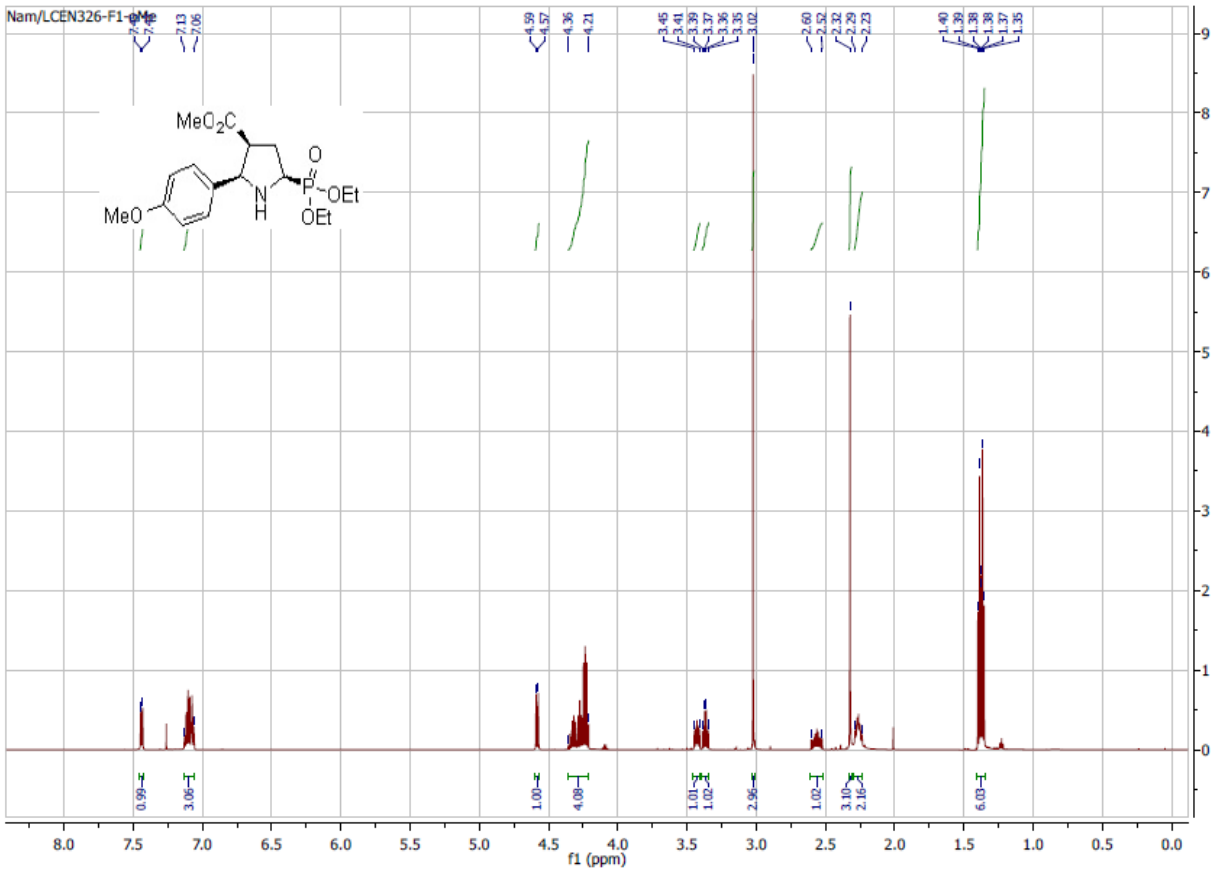
Compound 3da ^{13}C NMR



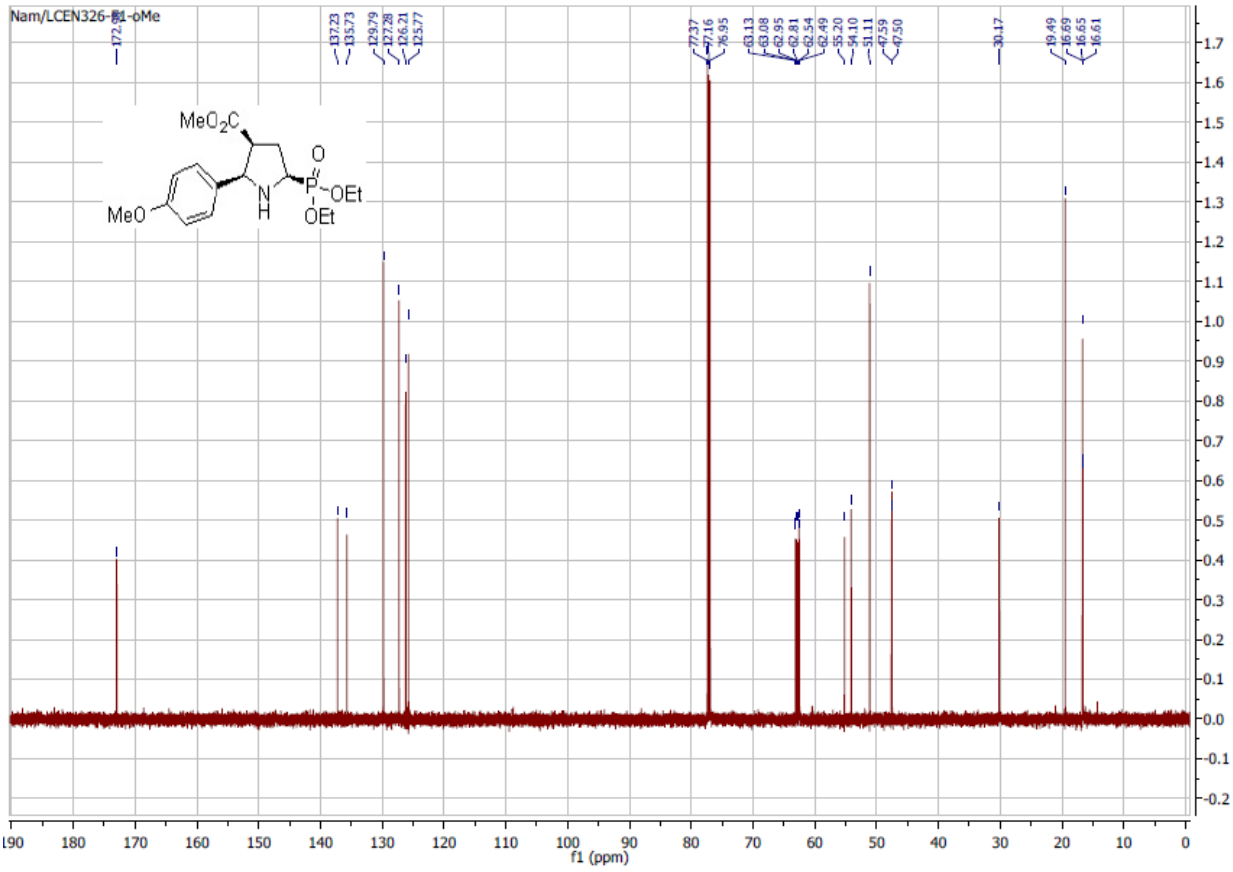
Compound 3da ^{31}P NMR



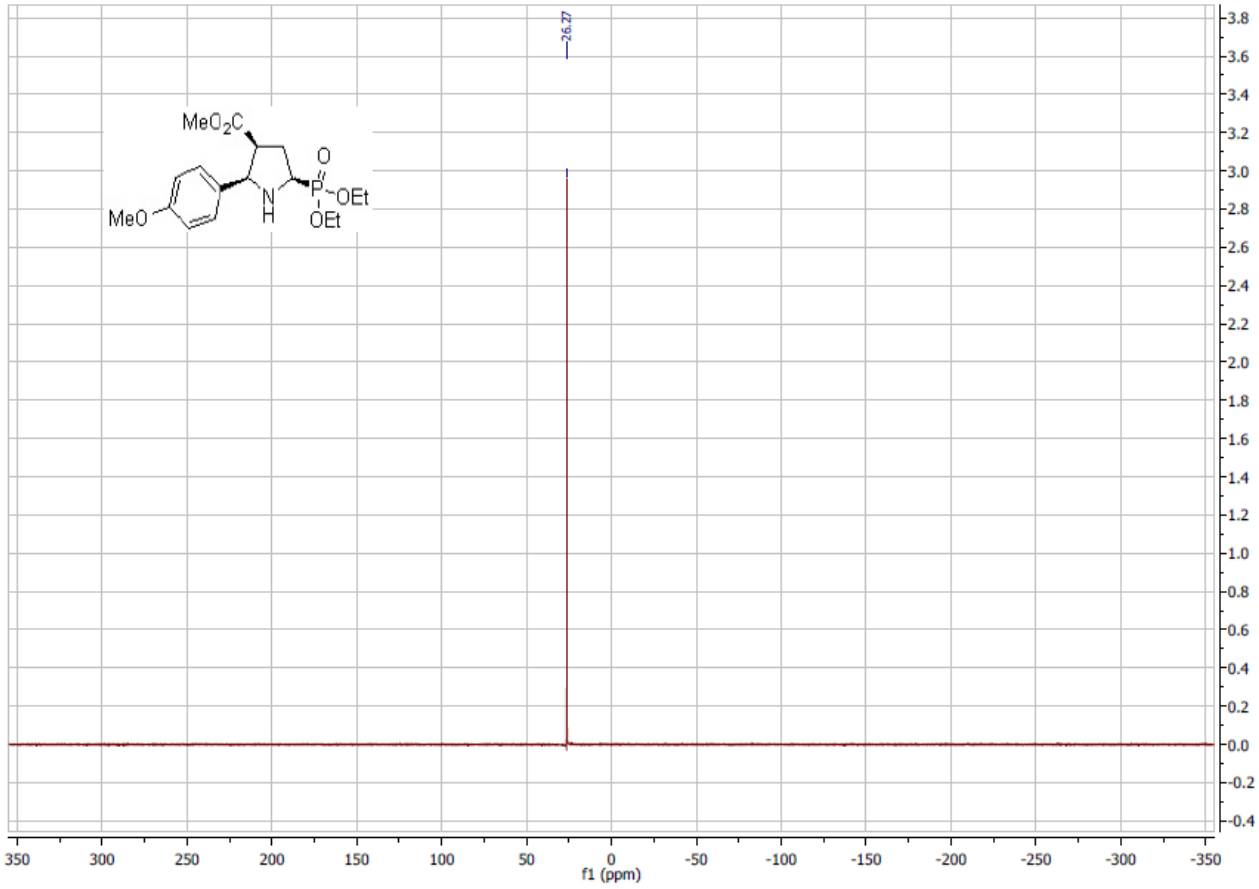
Compound 3ea ^{1}H NMR



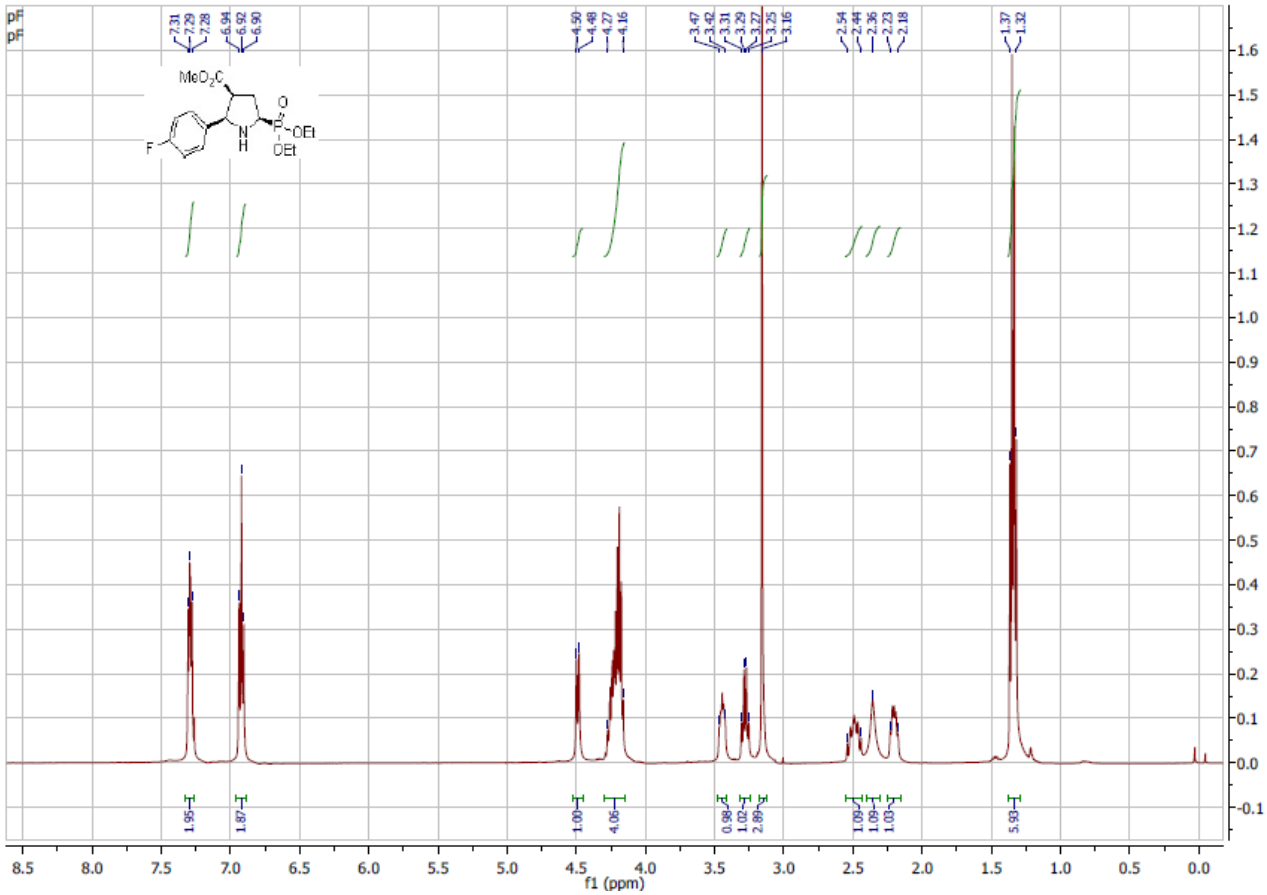
Compound 3ea ^{13}C NMR



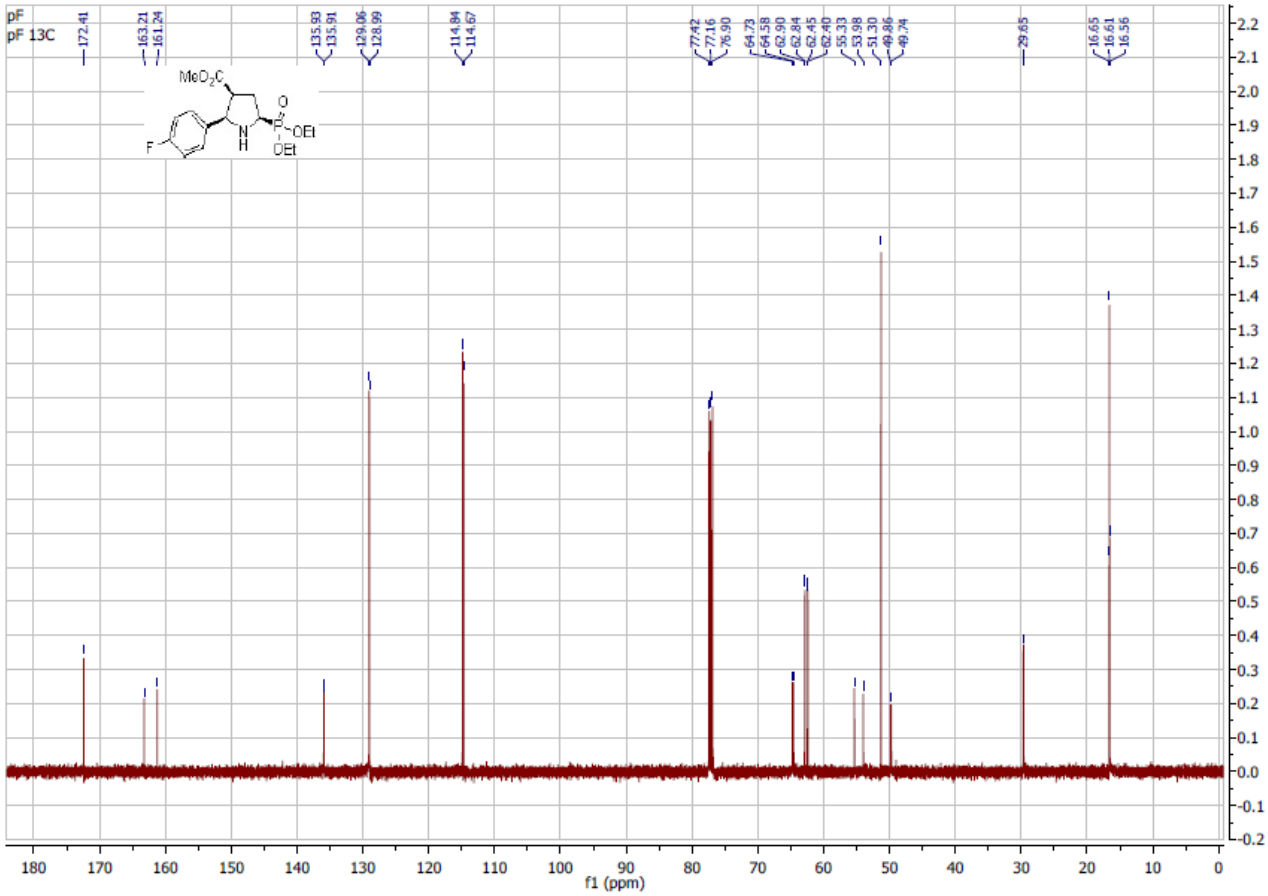
Compound 3ea ^{31}P NMR



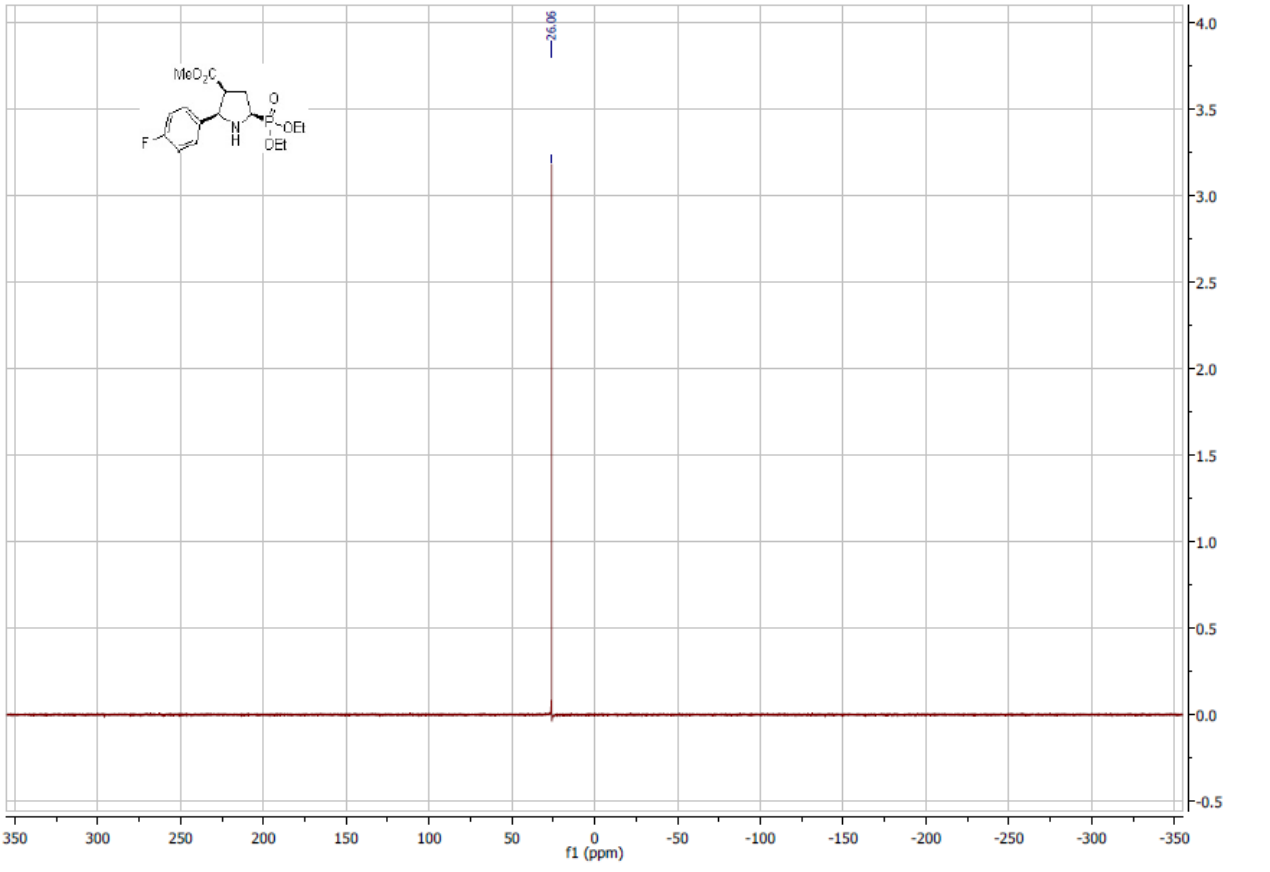
Compound 3fa ^{1}H NMR



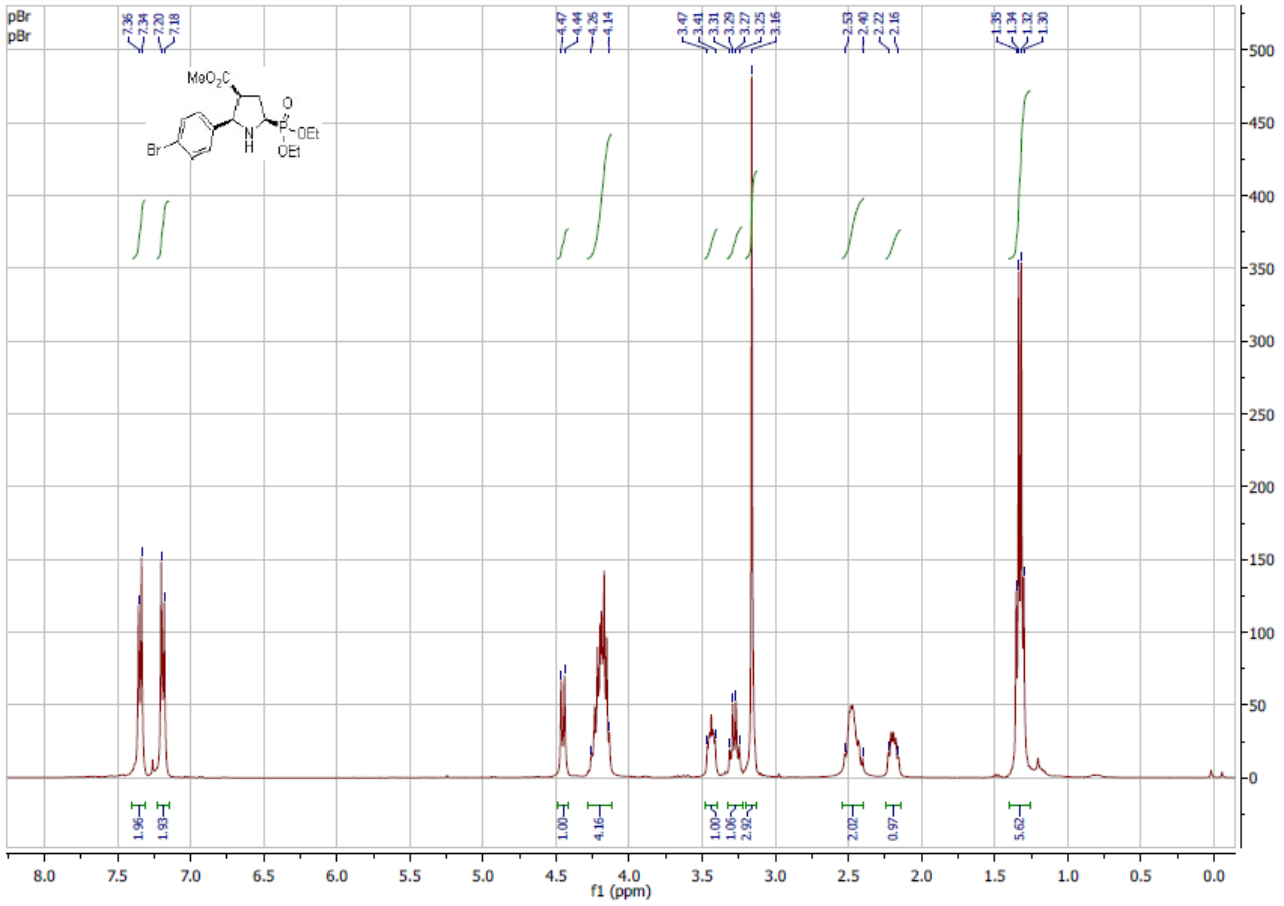
Compound 3fa ^{13}C NMR



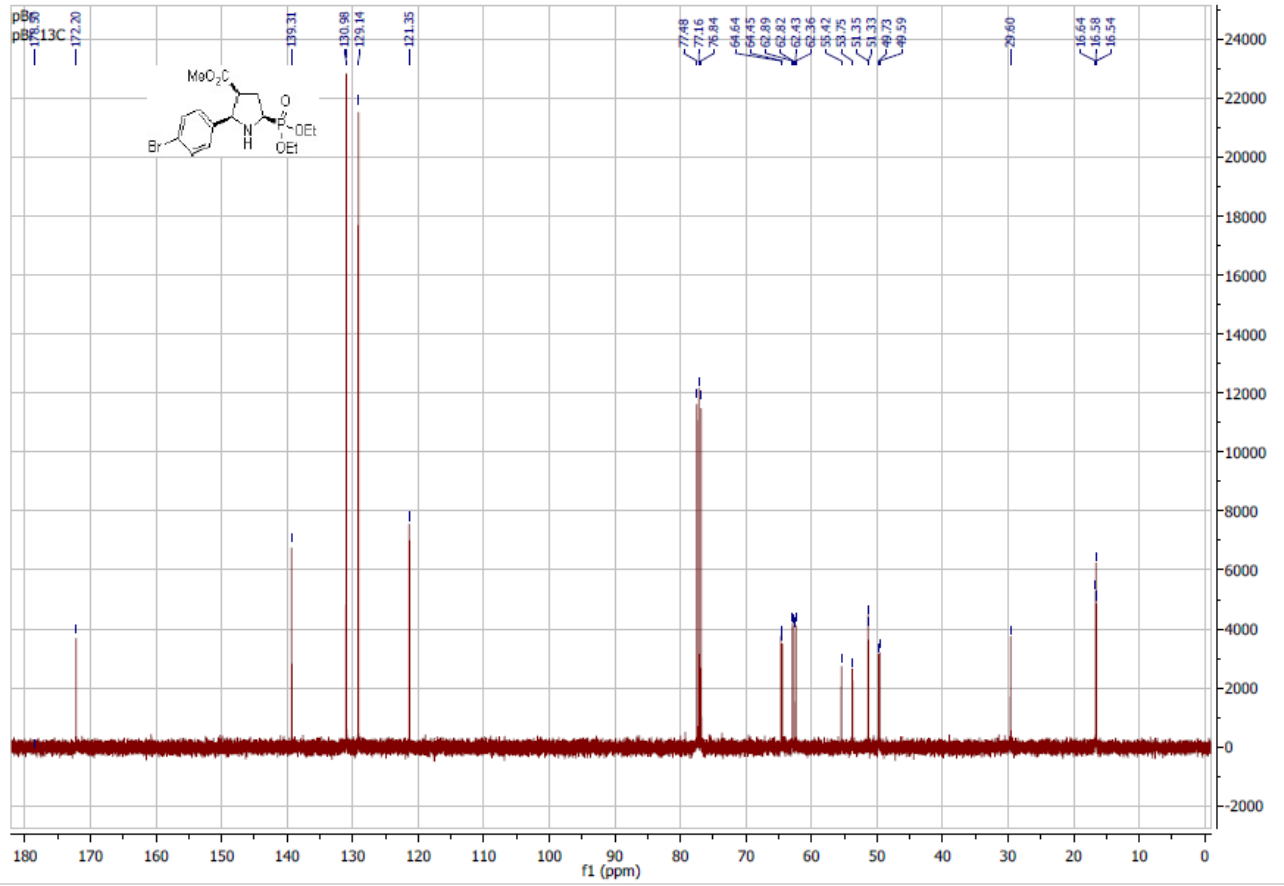
Compound 3fa ^{31}P NMR



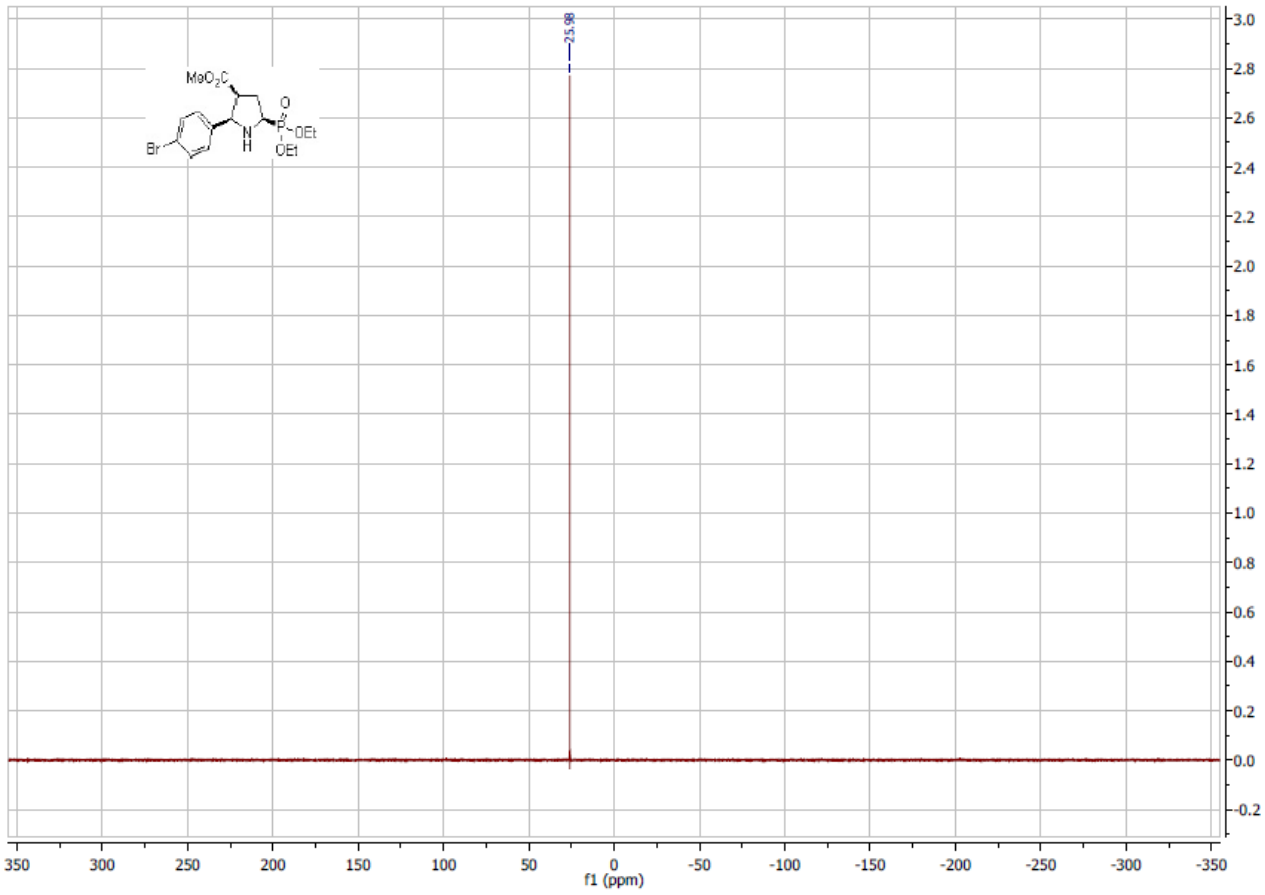
Compound 3ga ^{1}H NMR



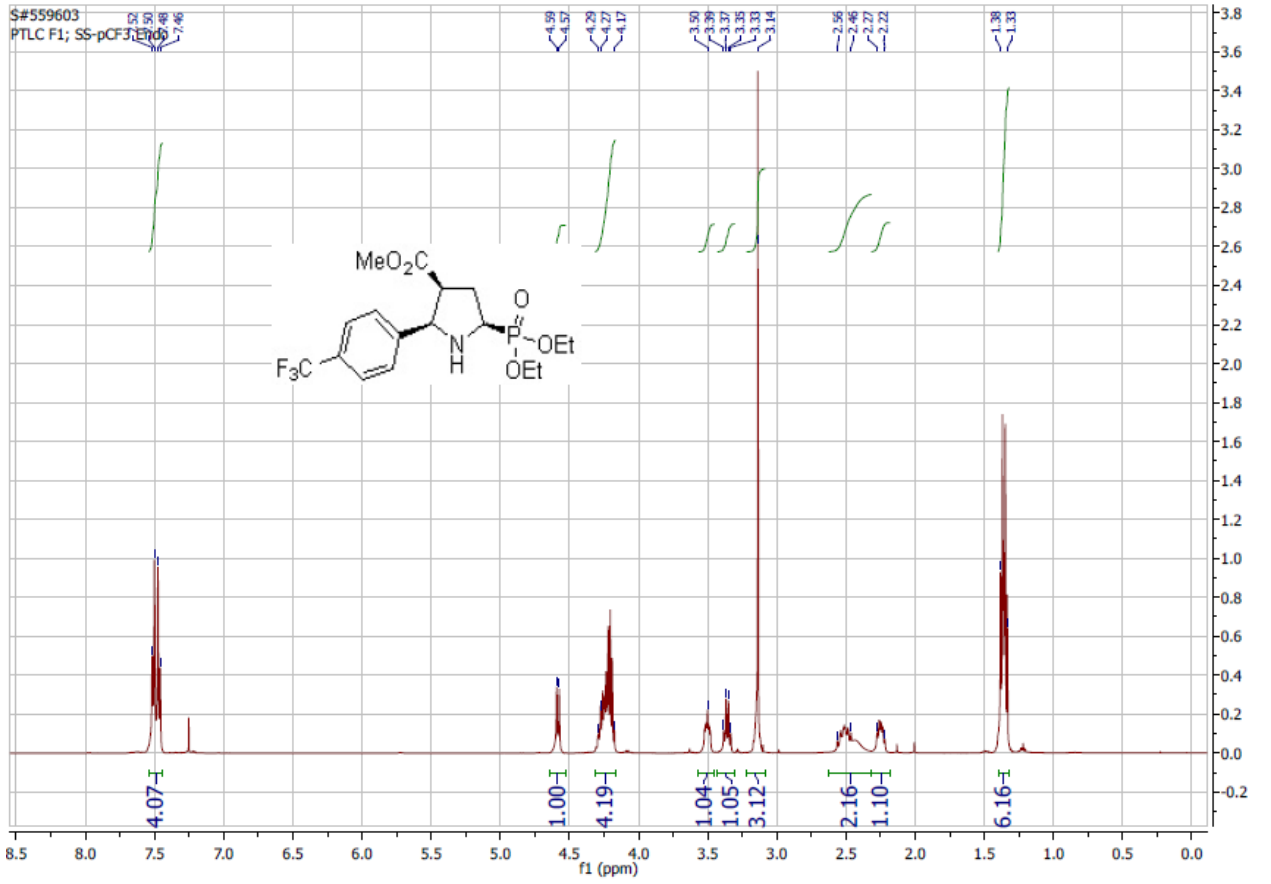
Compound 3ga ^{13}C NMR



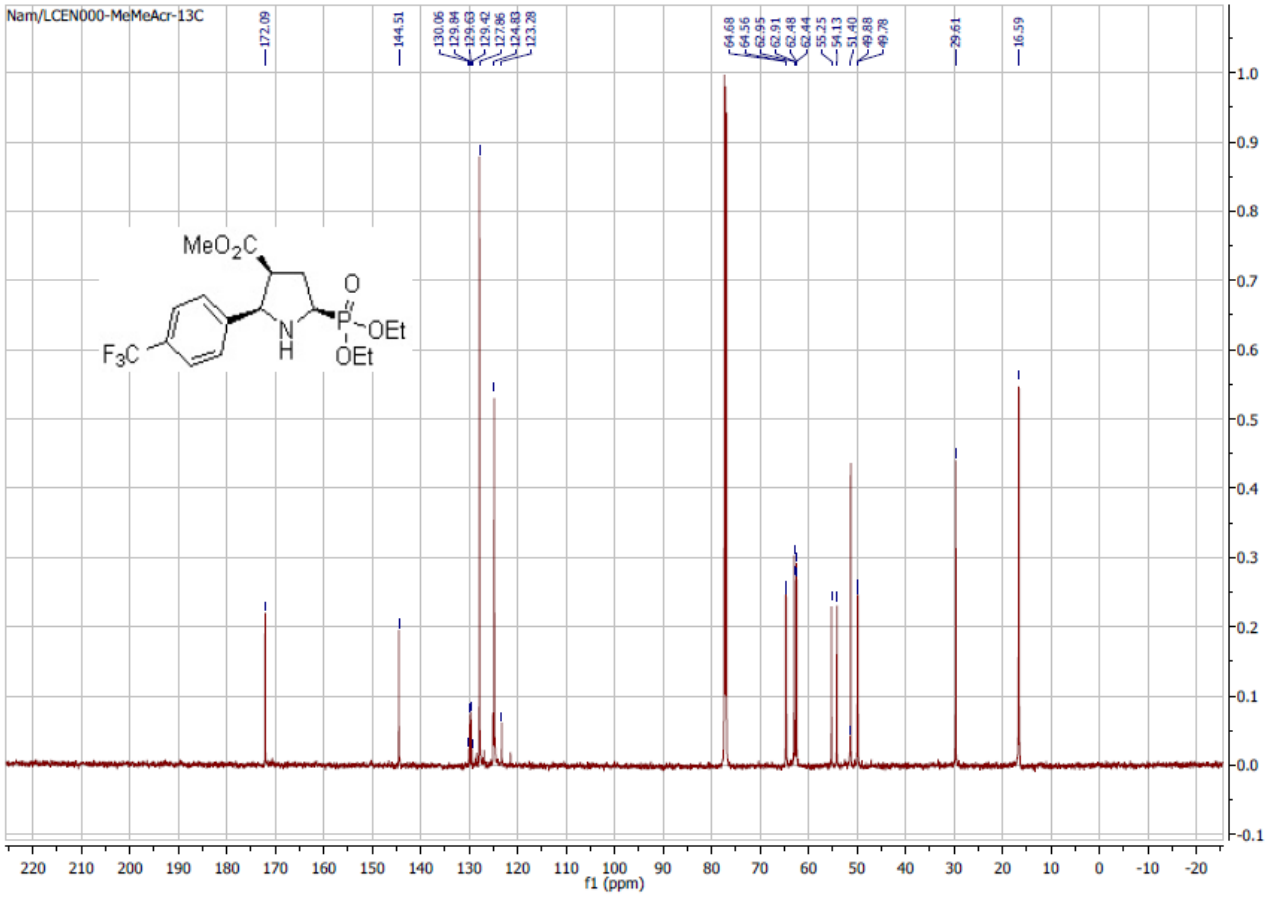
Compound 3ga ^{31}P NMR



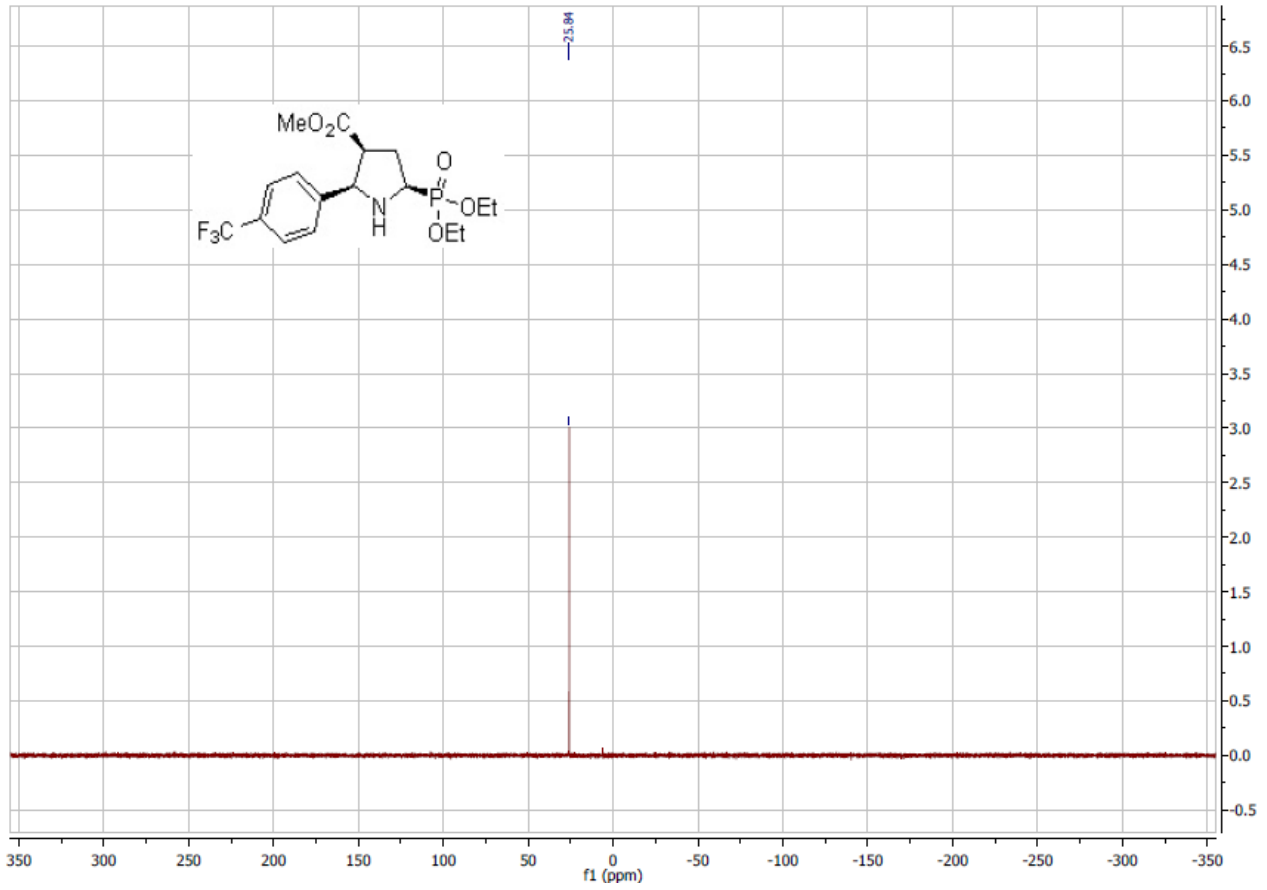
Compound 3ha ^{1}H NMR



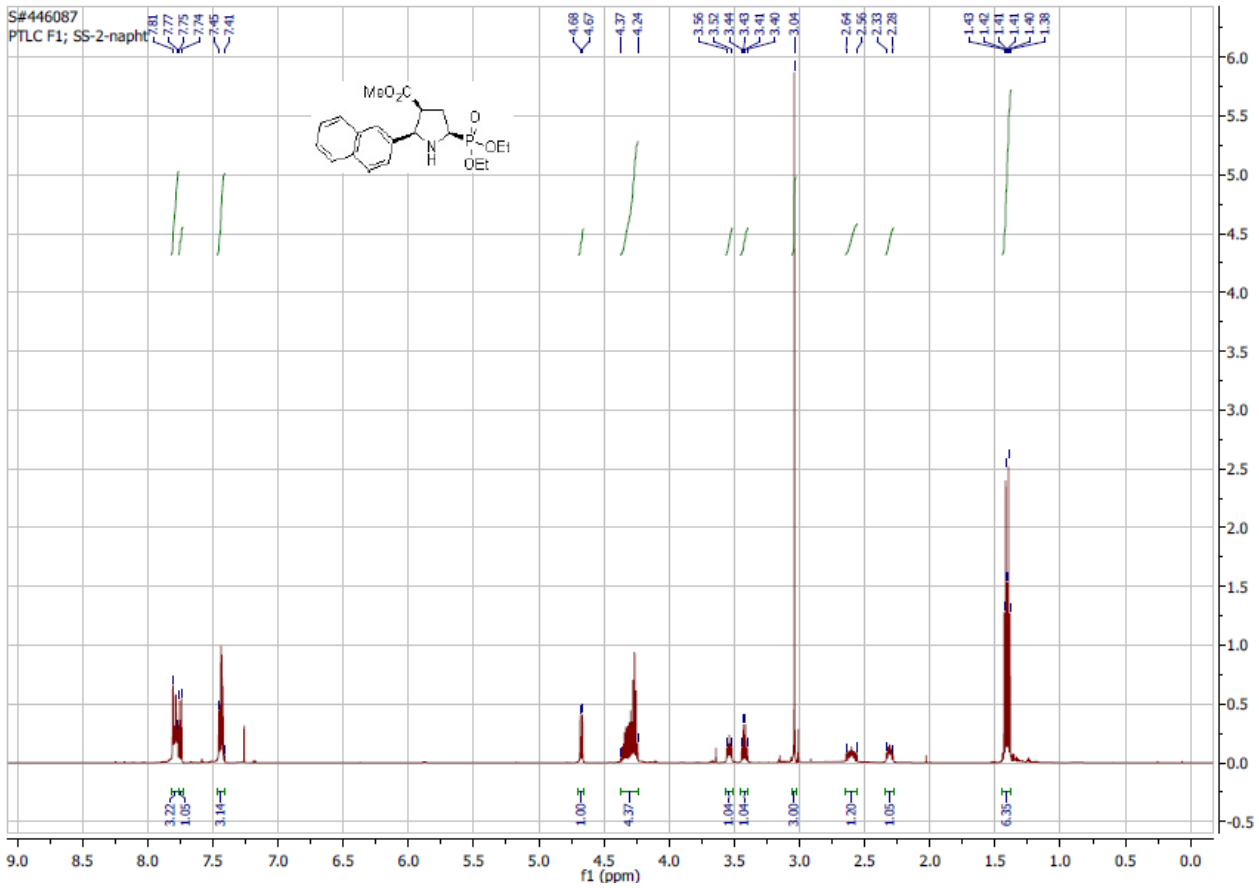
Compound 3ha ^{13}C NMR



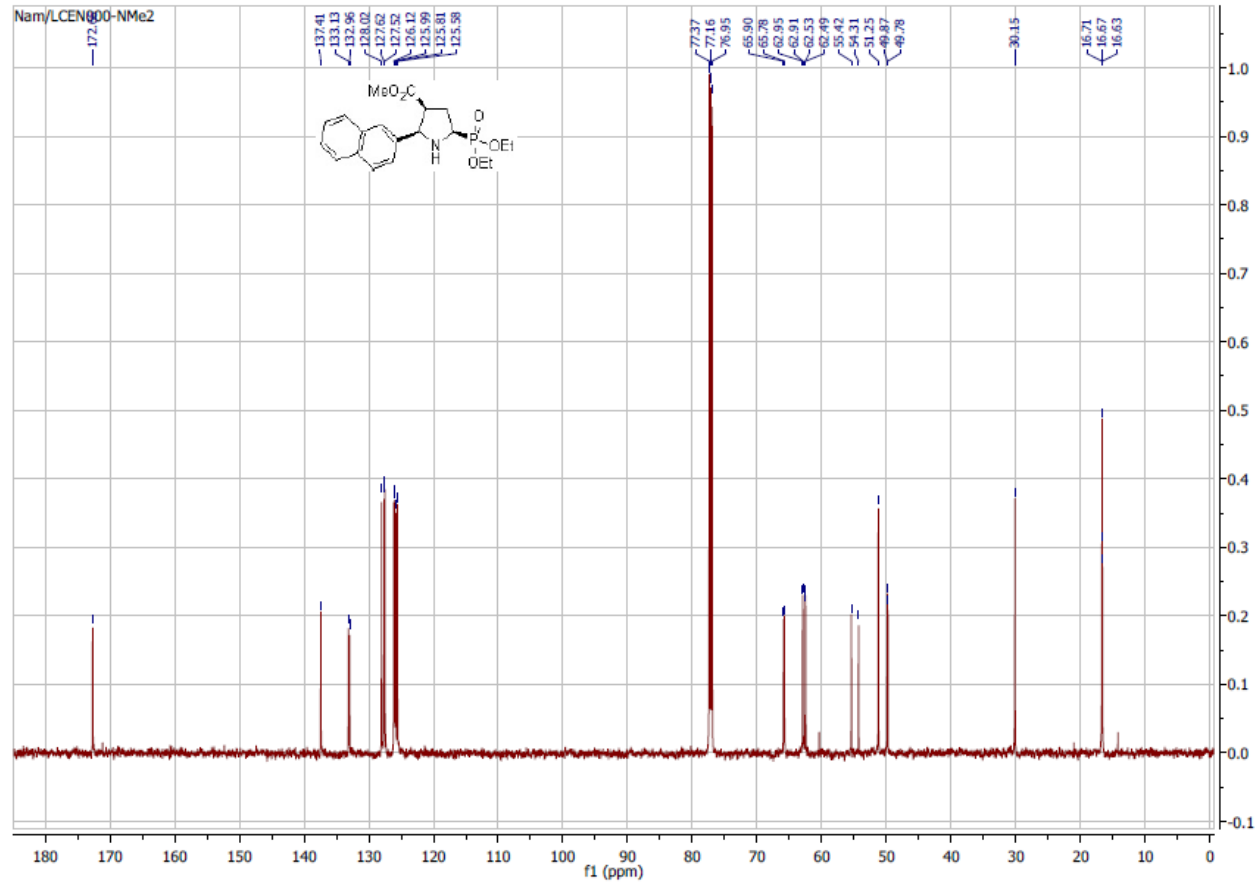
Compound 3ha ^{31}P NMR



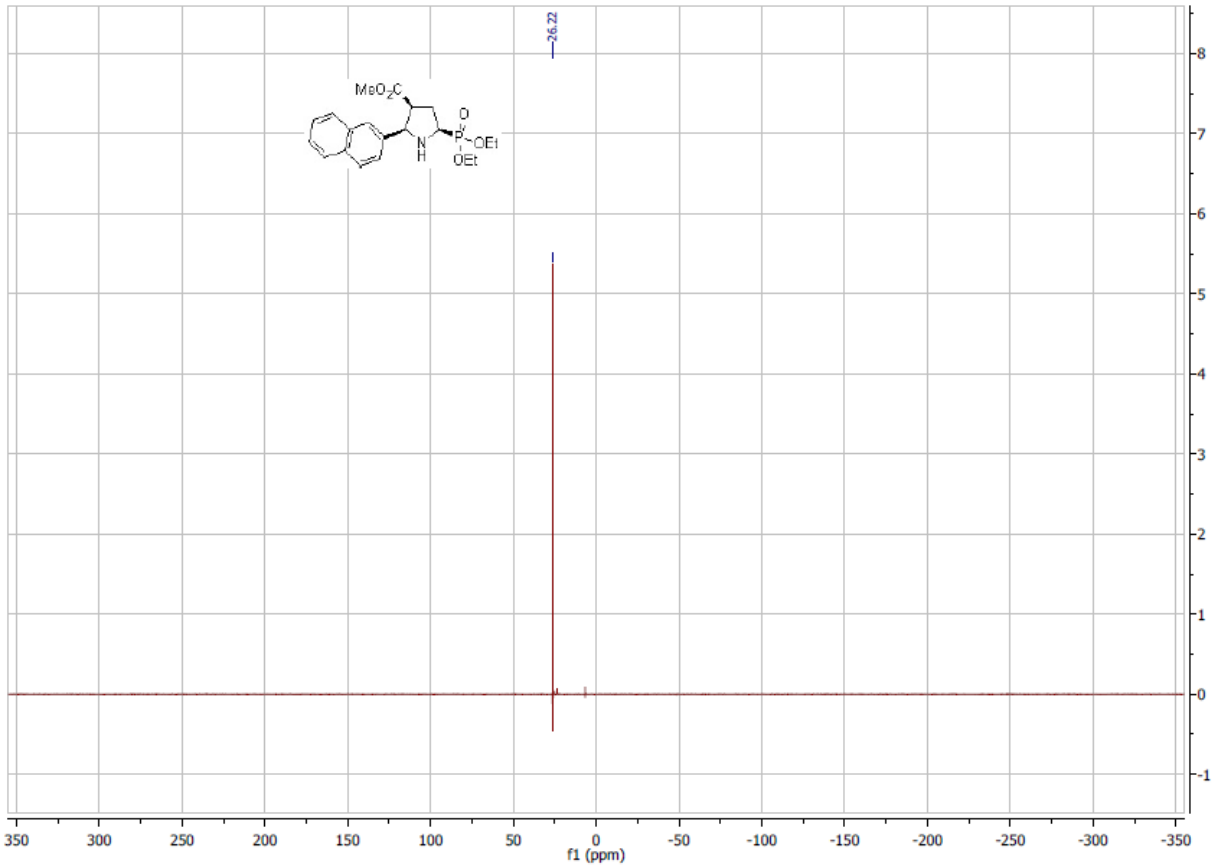
Compound 3ia ^{1}H NMR



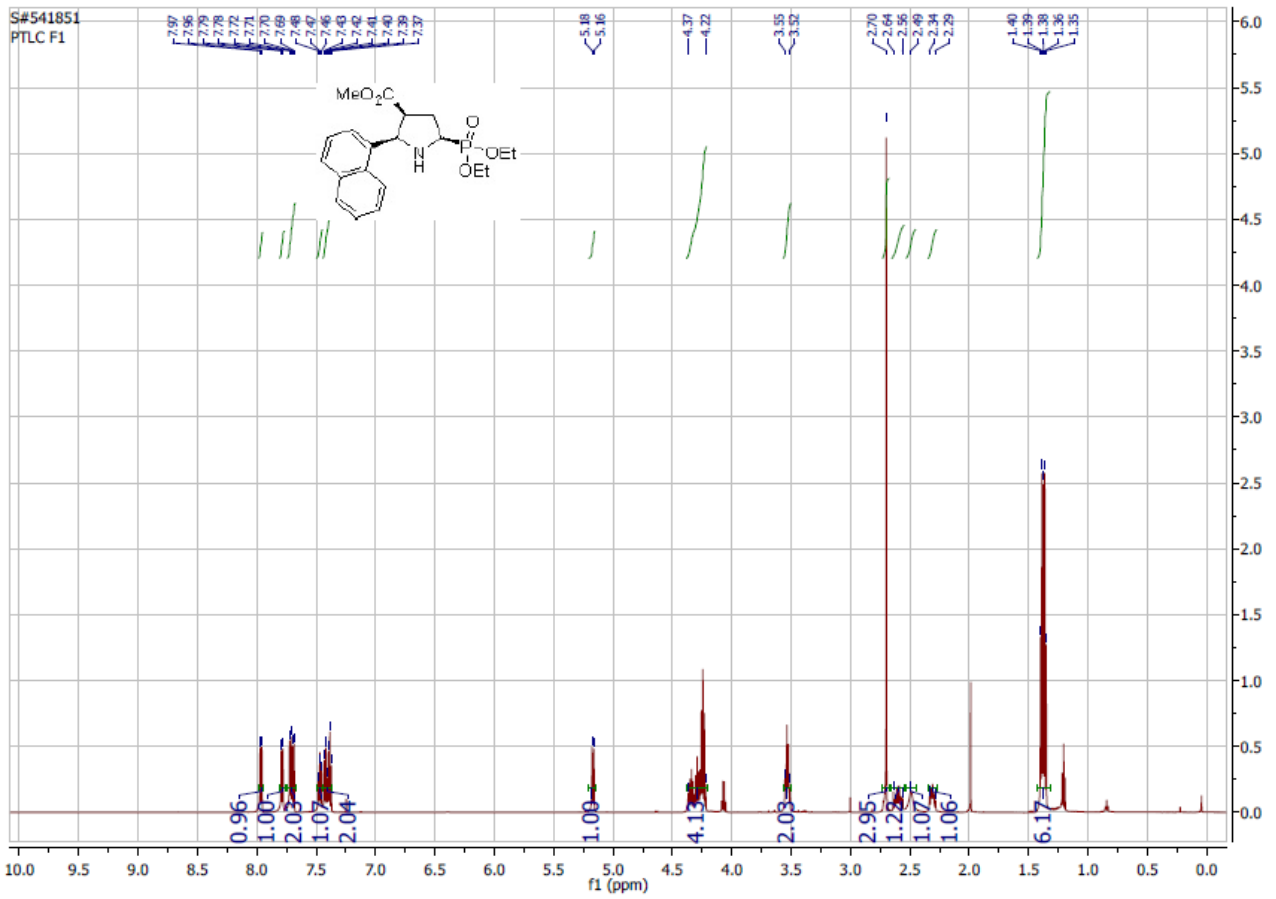
Compound 3ia ^{13}C NMR



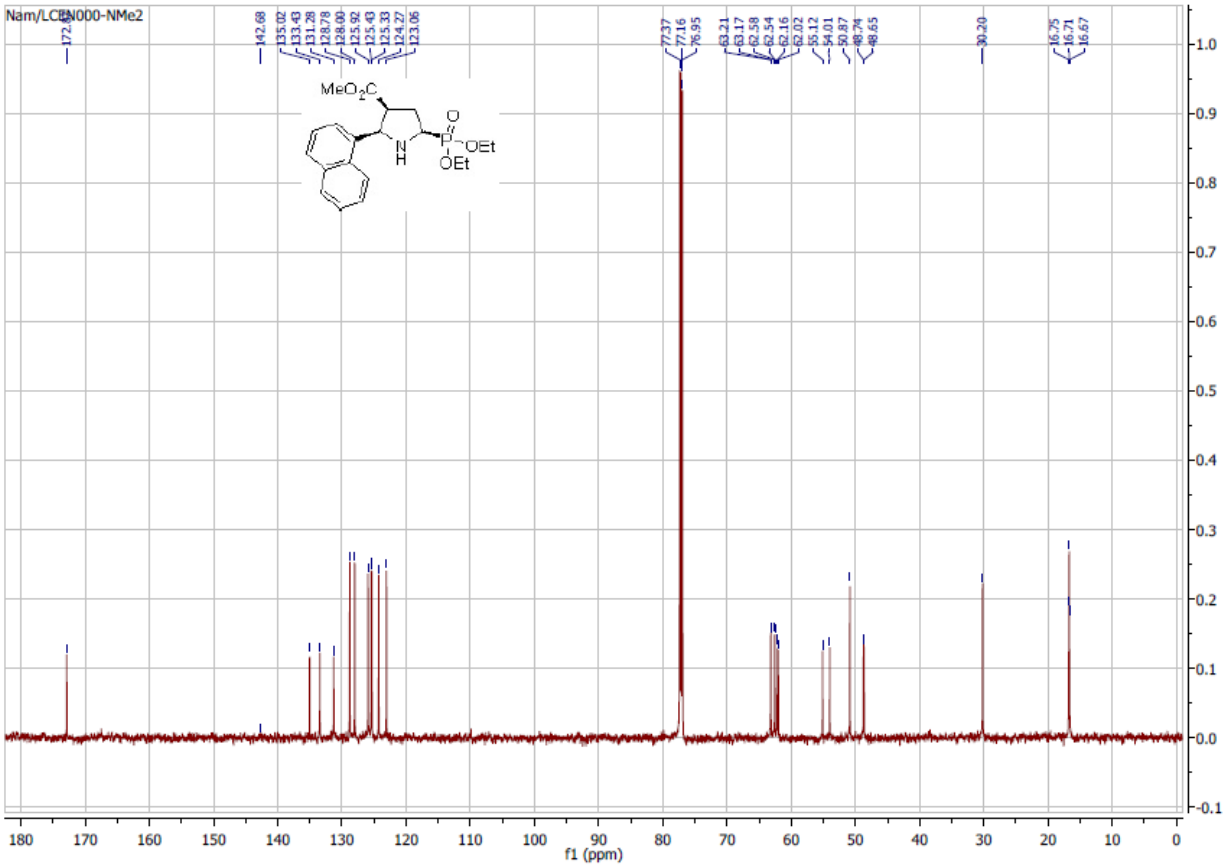
Compound 3ia ^{31}P NMR



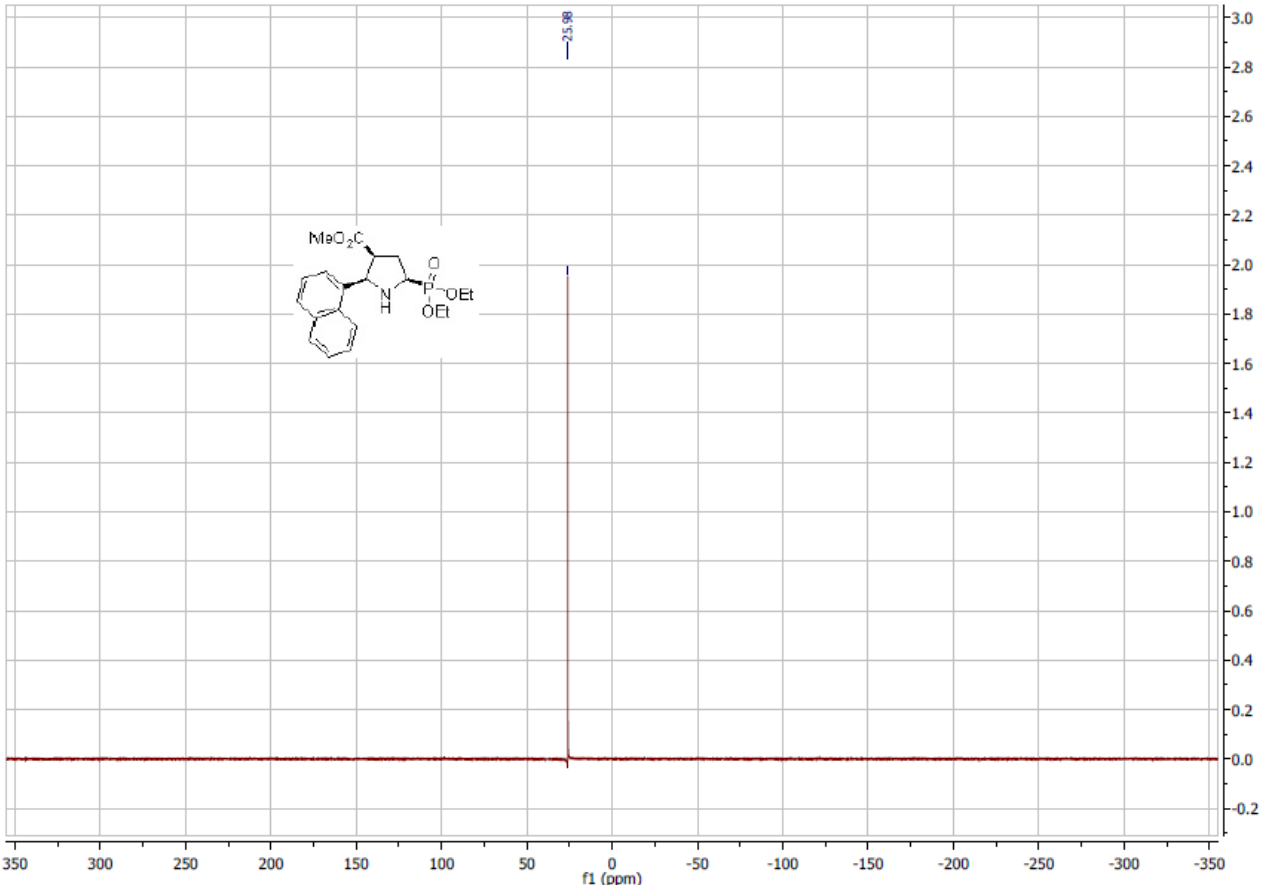
Compound 3ja ^{1}H NMR



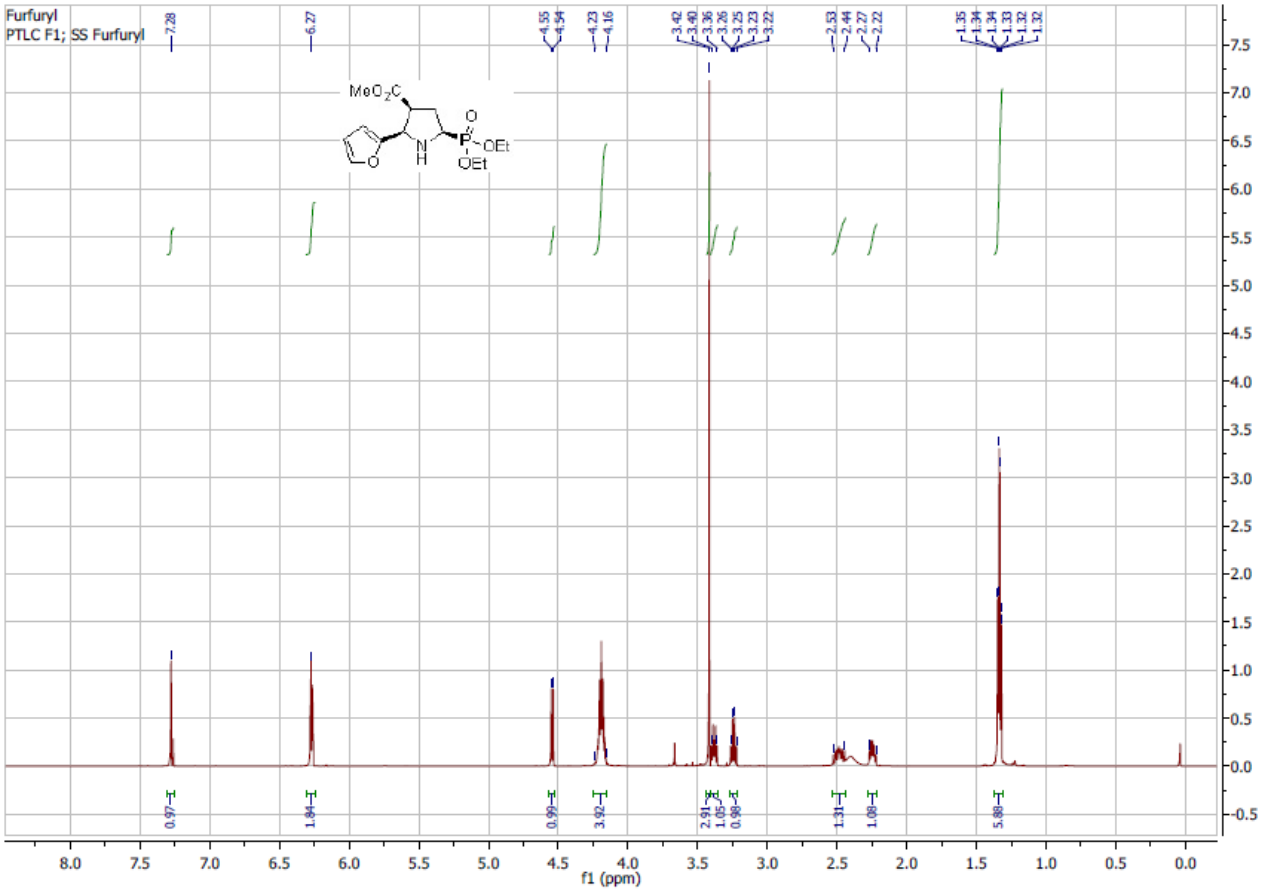
Compound 3ja ^{13}C NMR



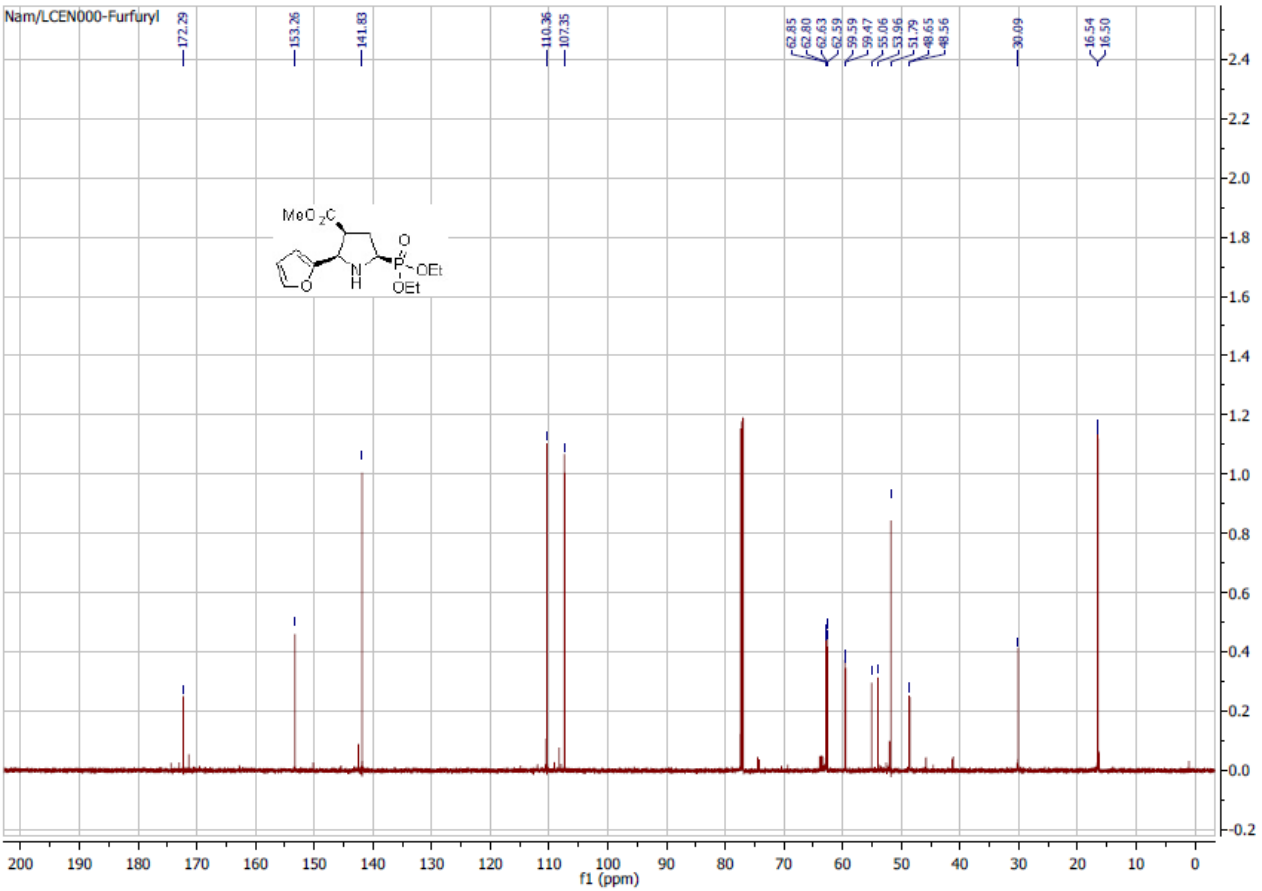
Compound 3ja ^{31}P NMR



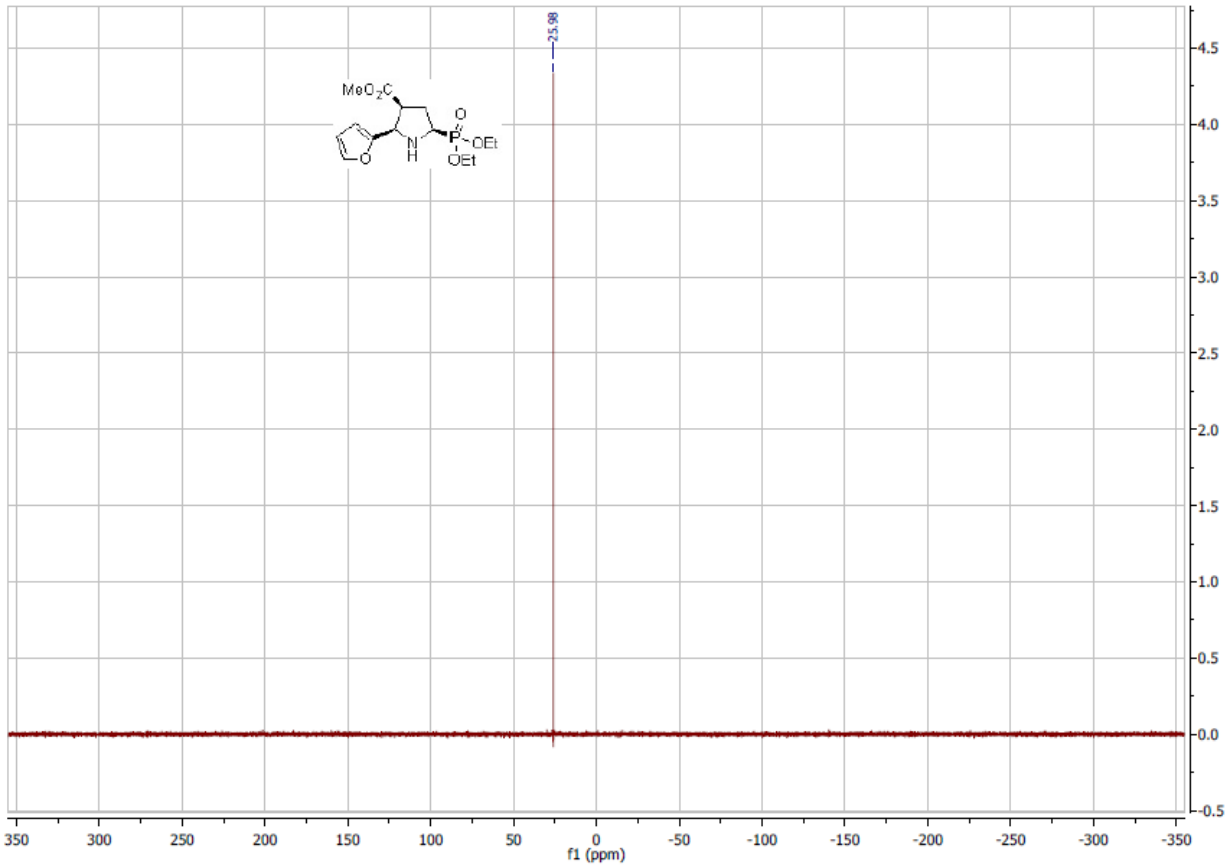
Compound 3ka ^{1}H NMR



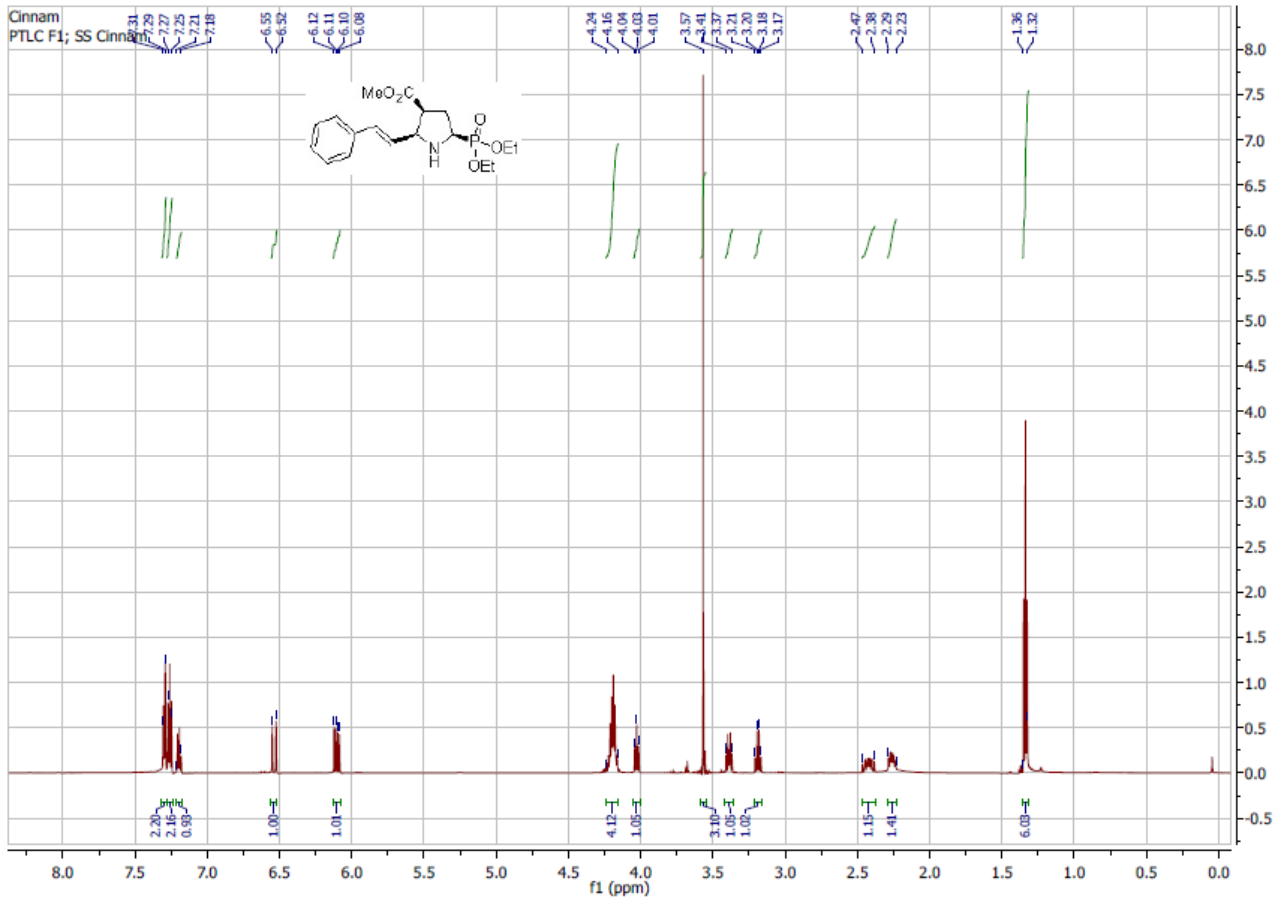
Compound 3ka ^{13}C NMR



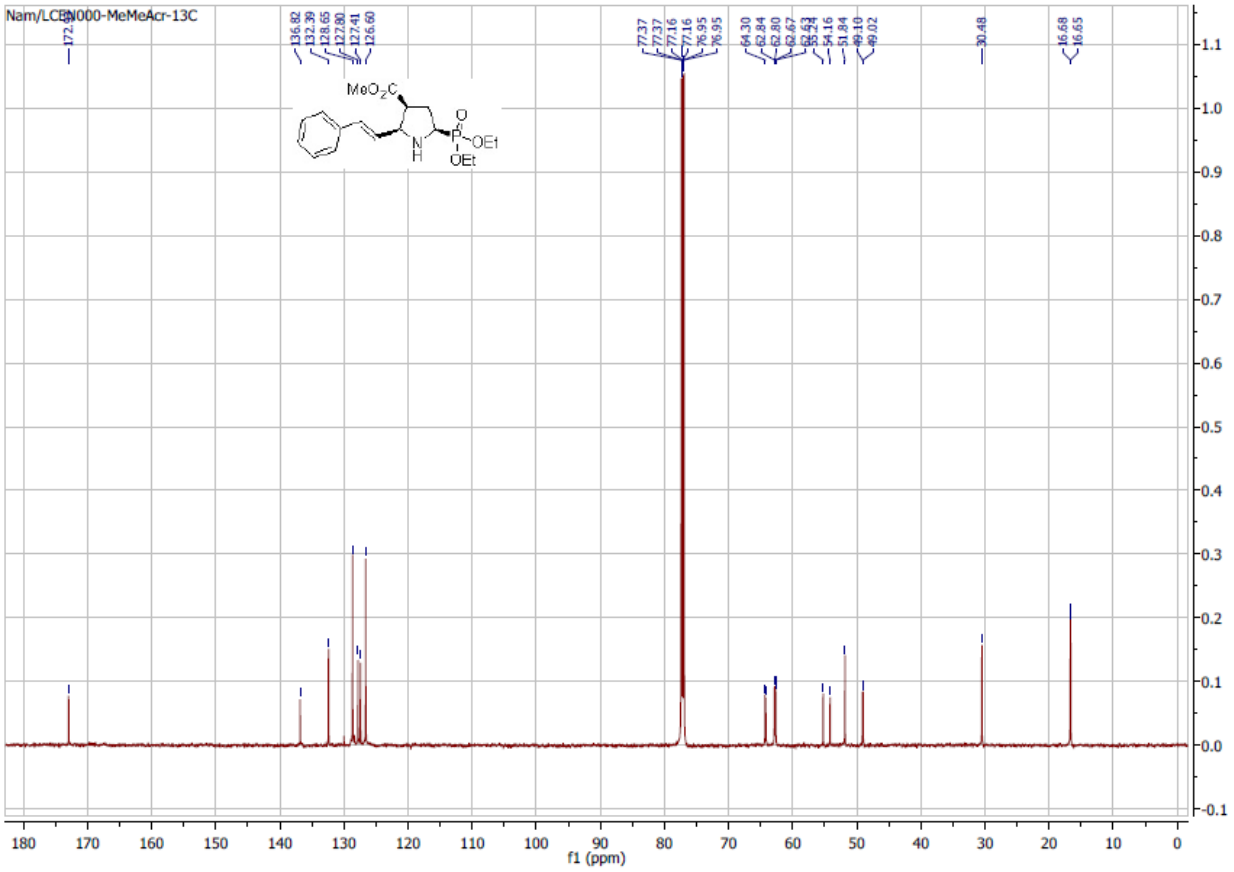
Compound 3ka ^{31}P NMR



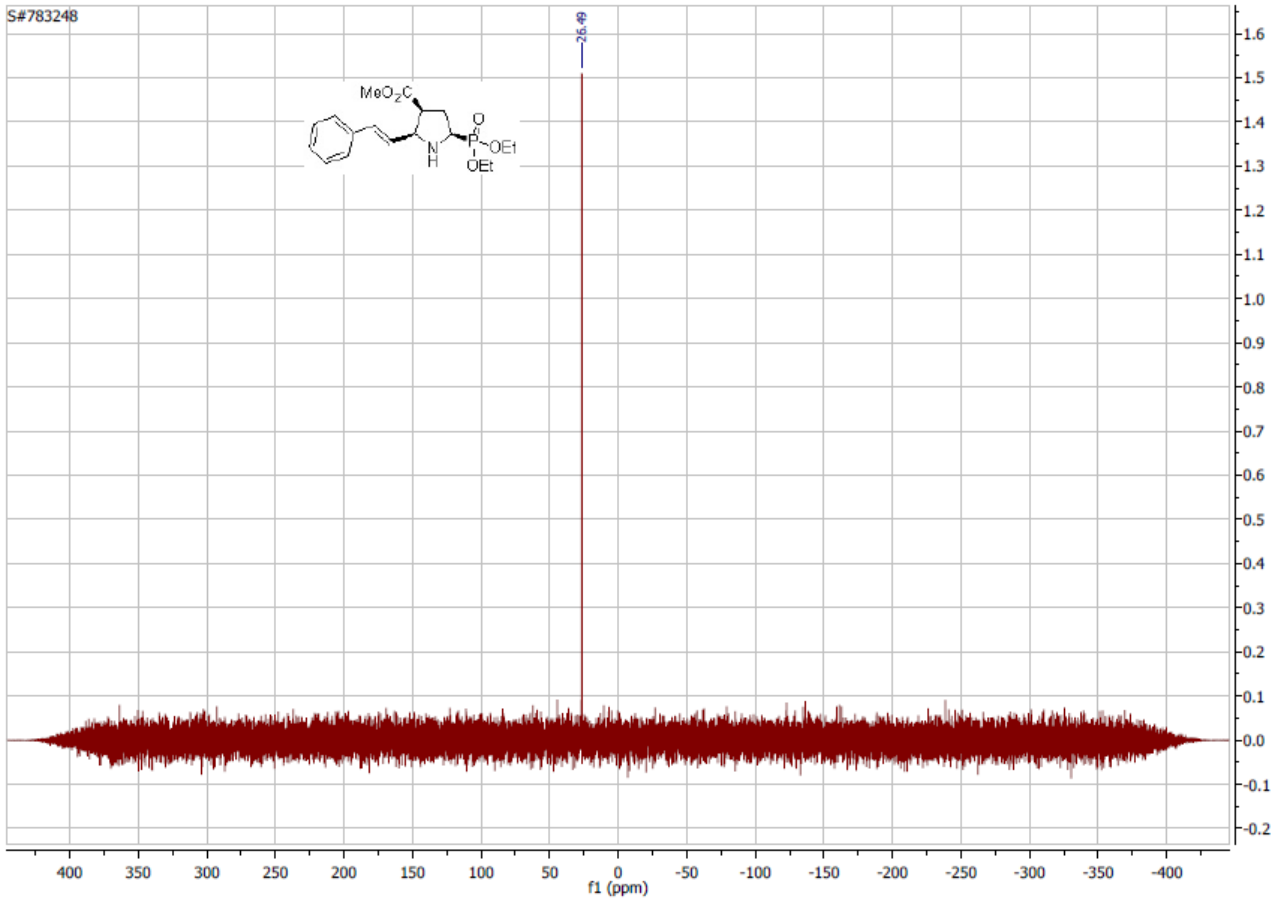
Compound 3la ^{1}H NMR



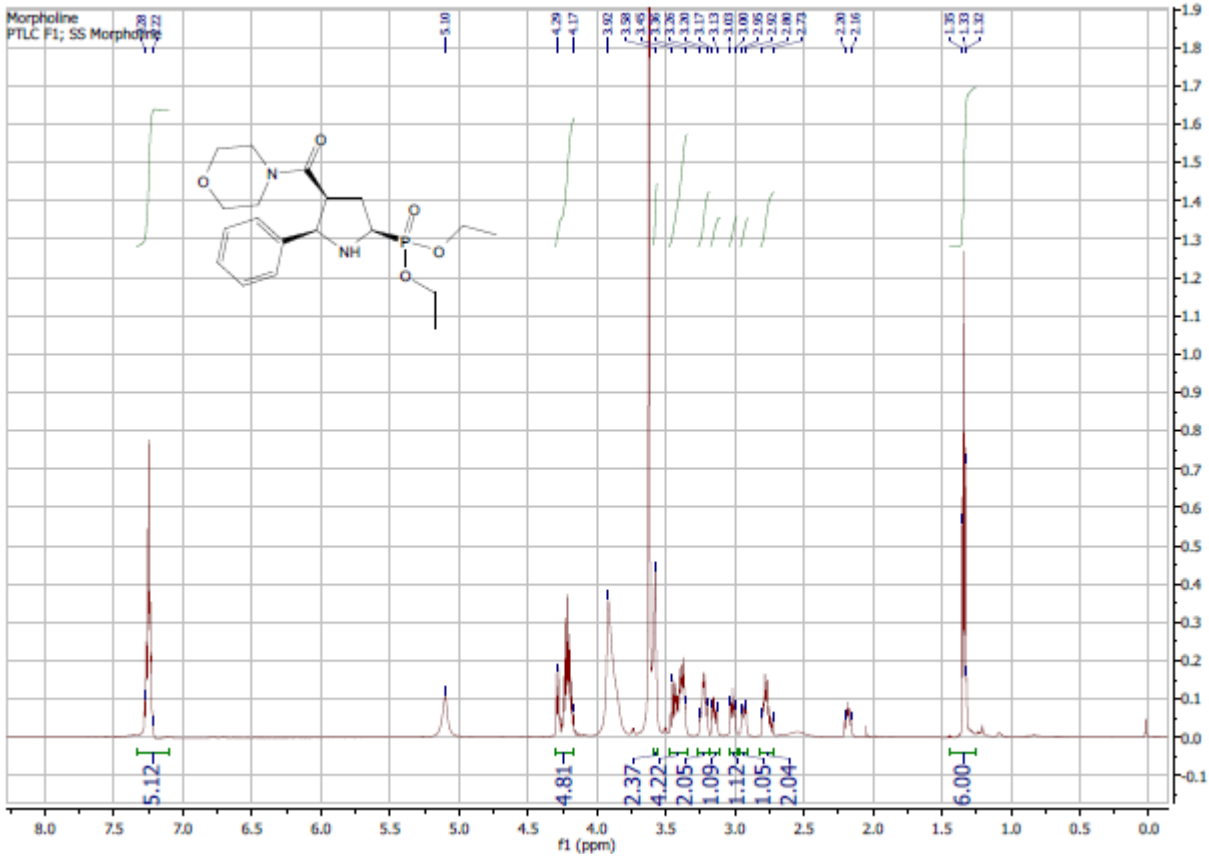
Compound 3la ^{13}C NMR



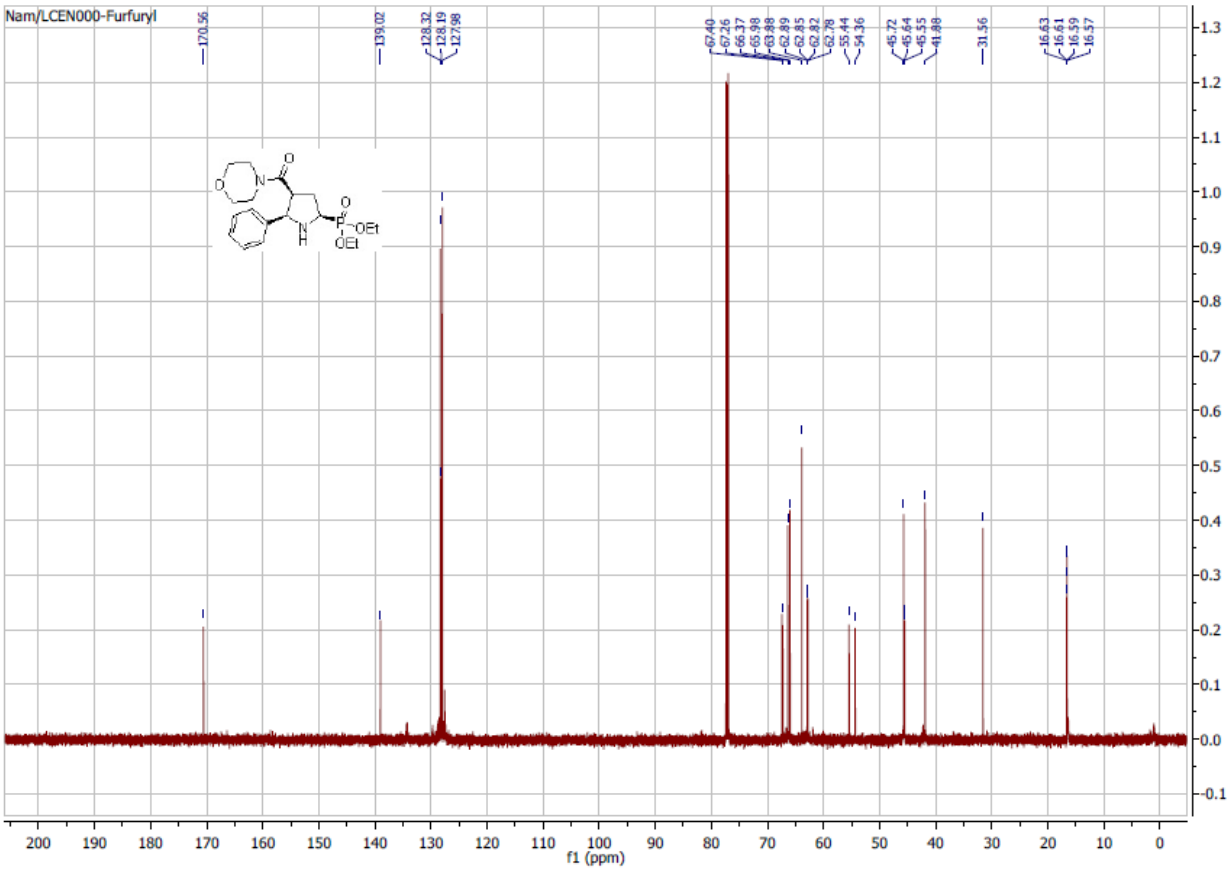
Compound 3la ^{31}P NMR



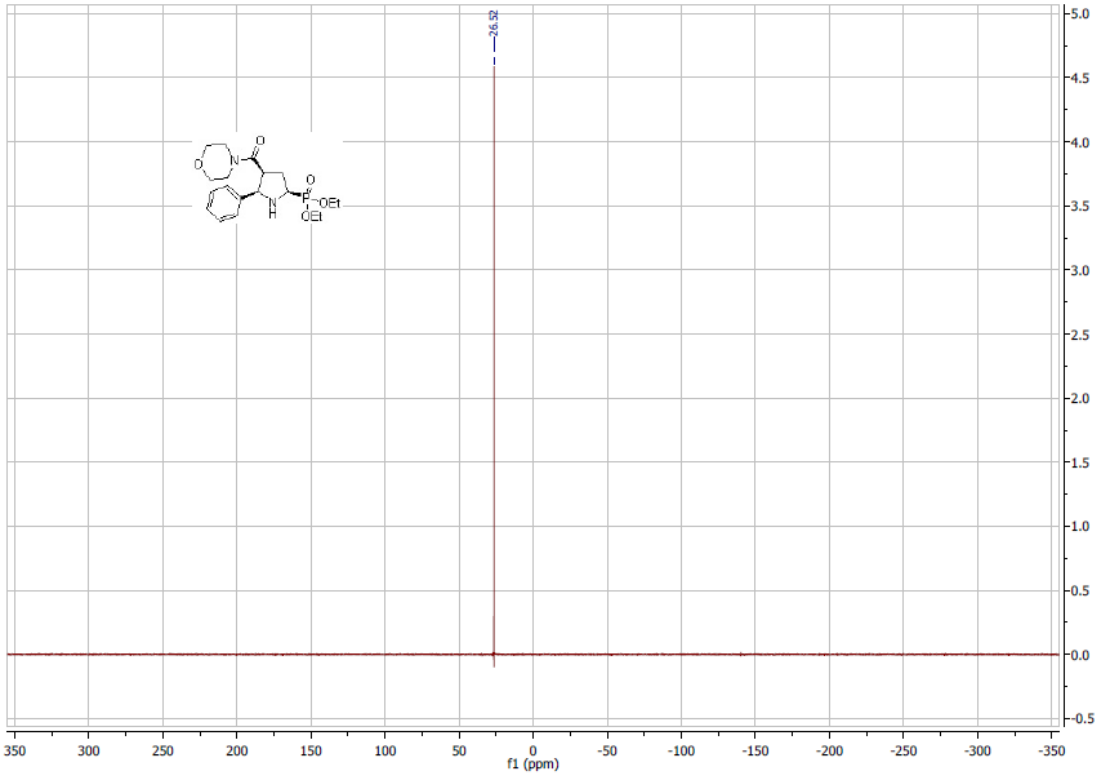
Compound 3ab ^{1}H NMR



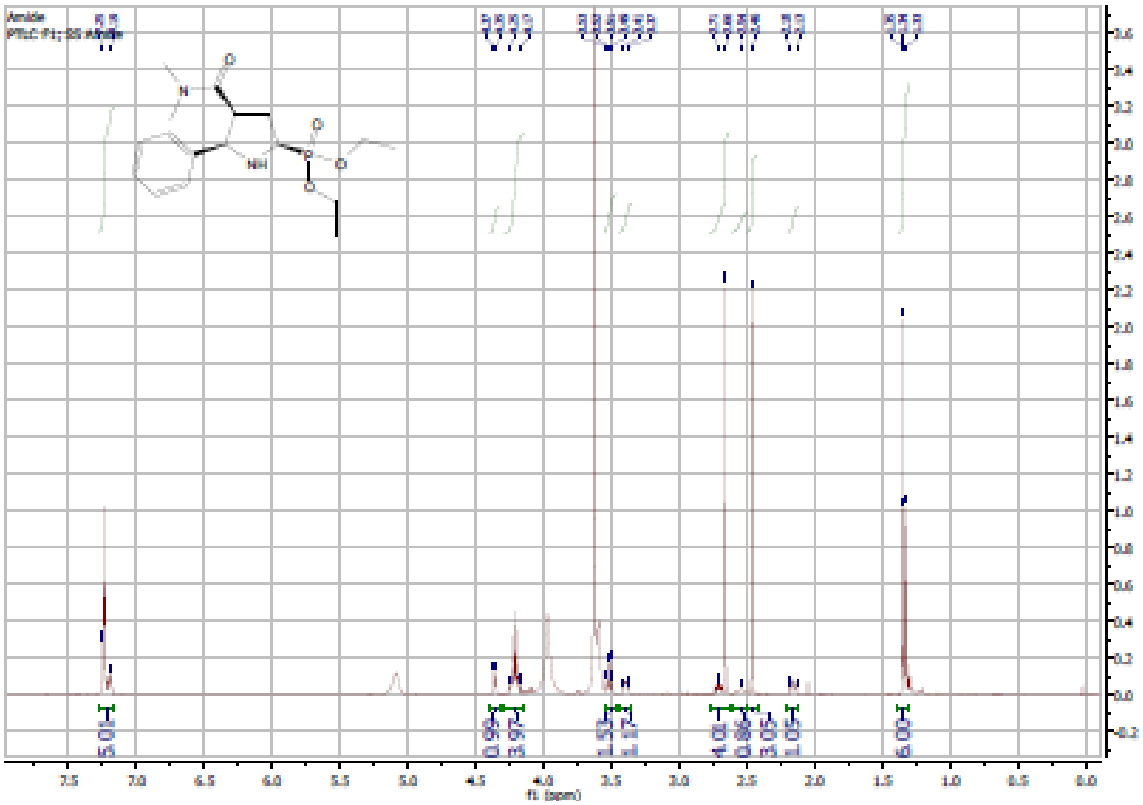
Compound 3ab ^{13}C NMR



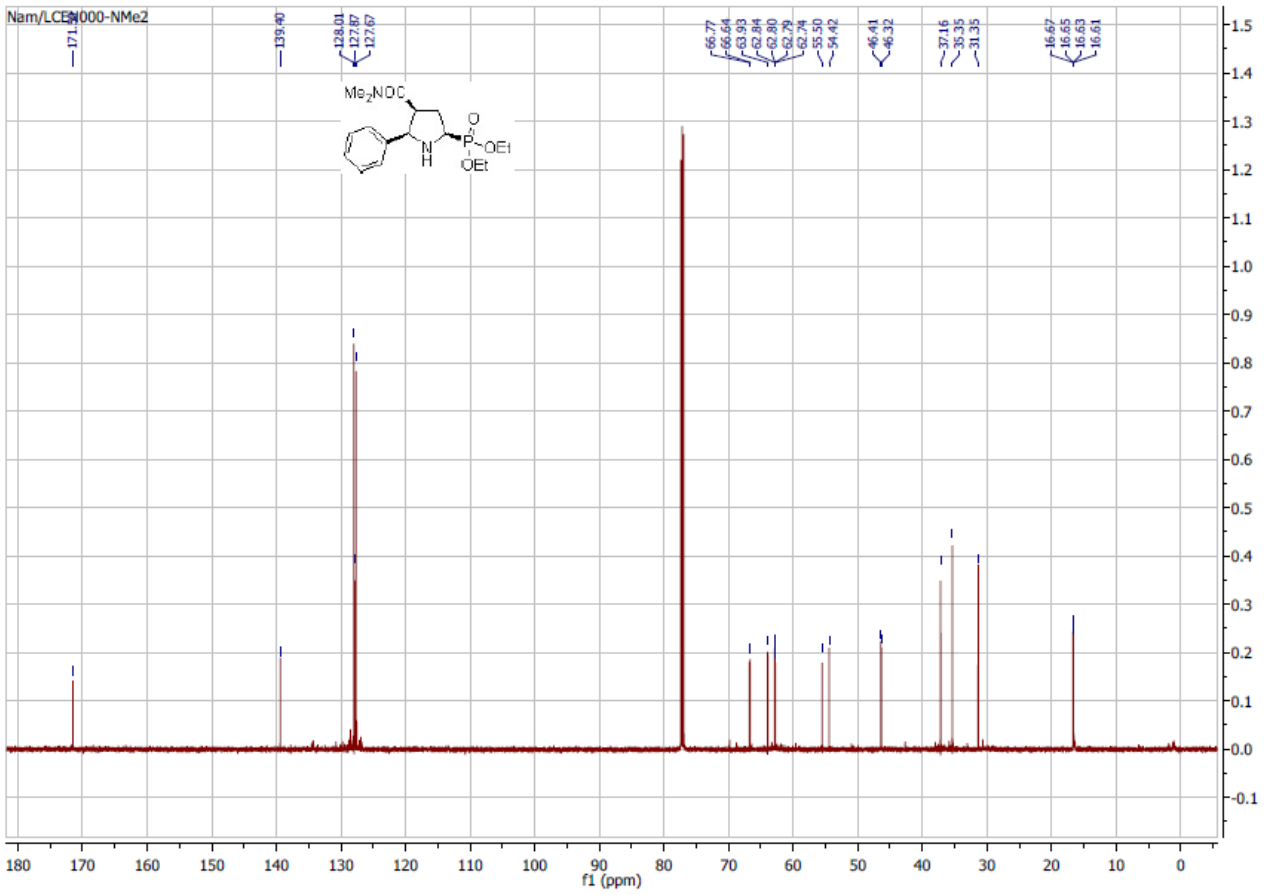
Compound 3ab ^{31}P NMR



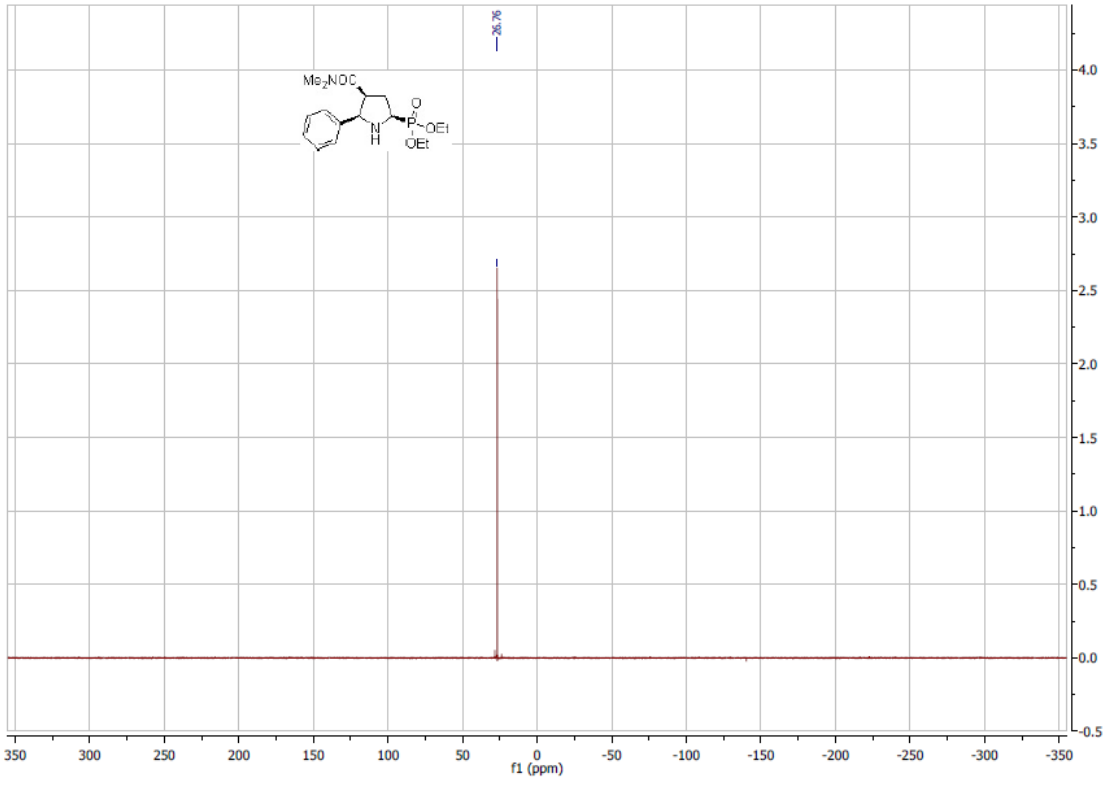
Compound 3ac ^{1}H NMR



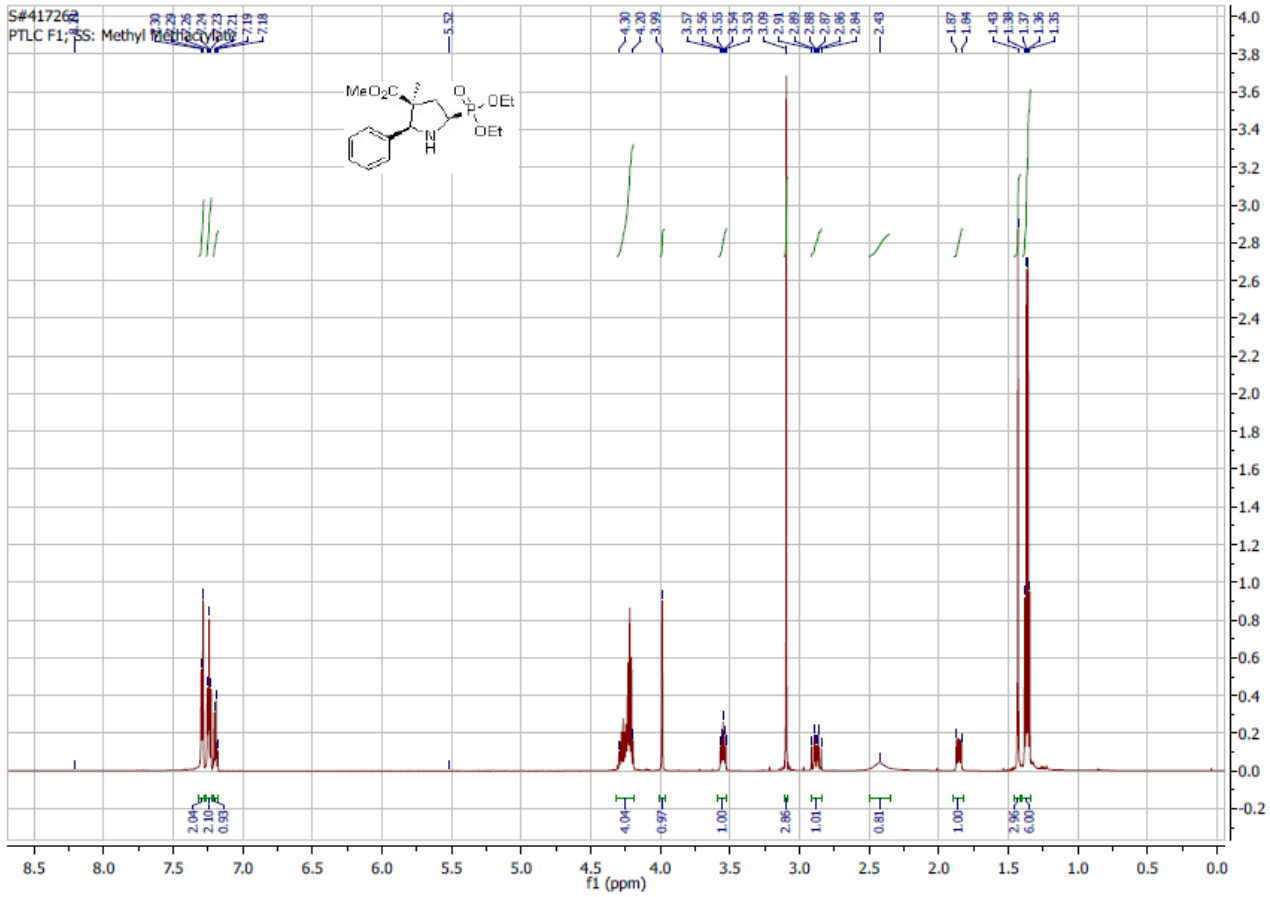
Compound 3ac ^{13}C NMR



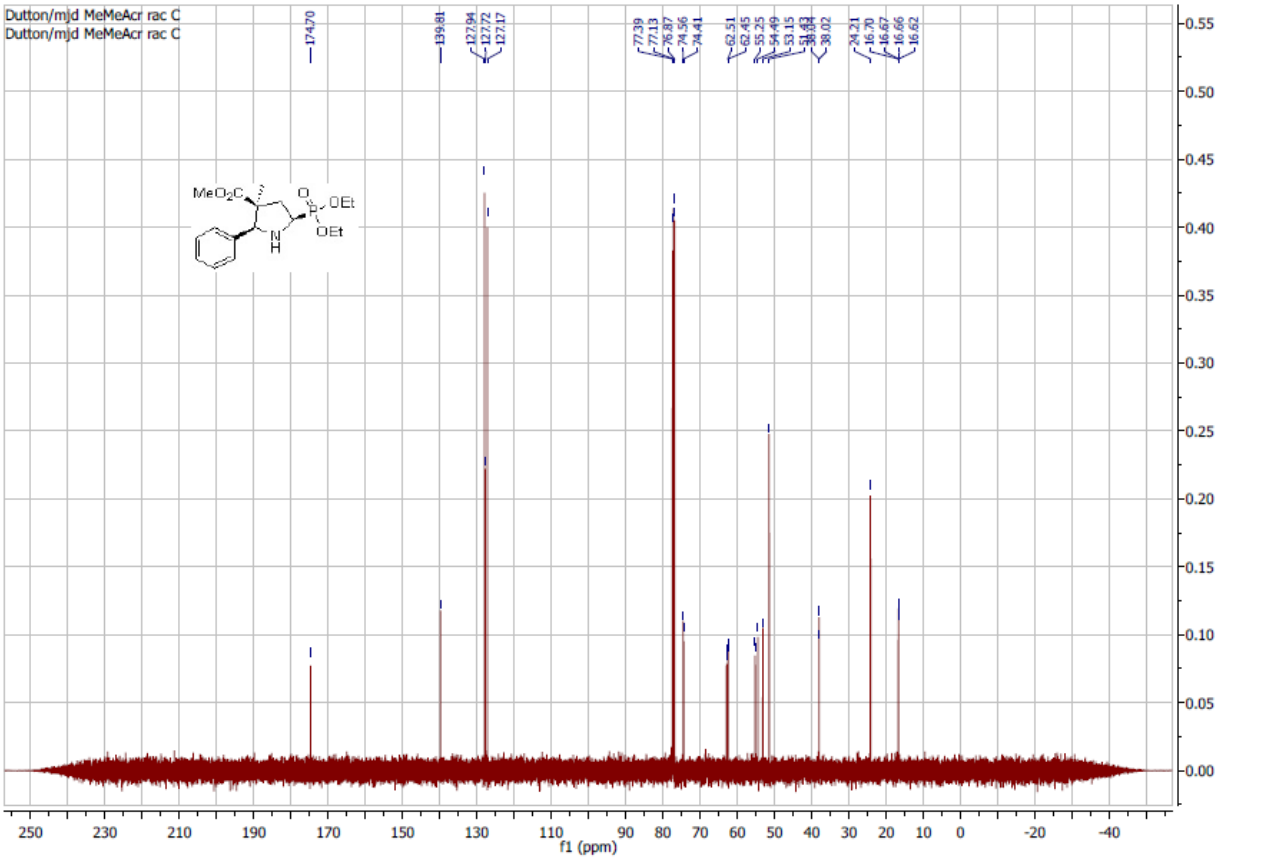
Compound 3ac ^{31}P NMR



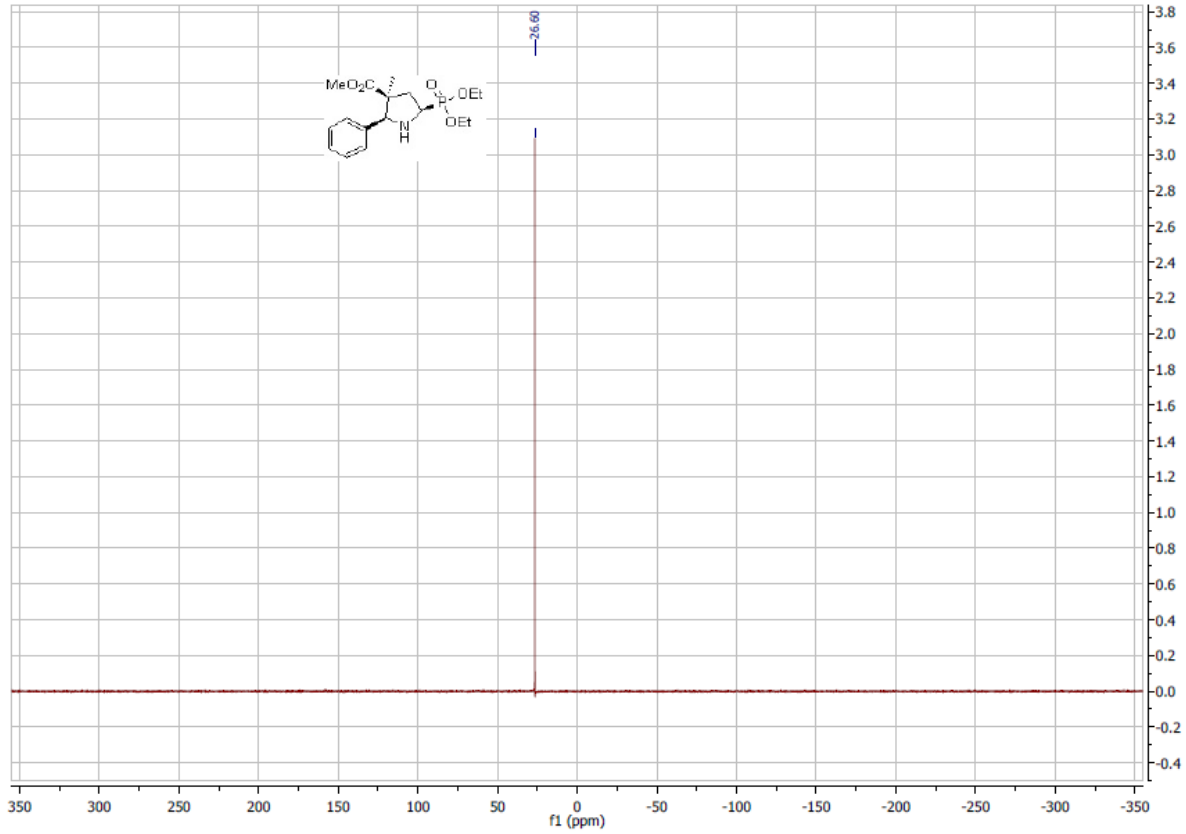
Compound 3ad ^{1}H NMR



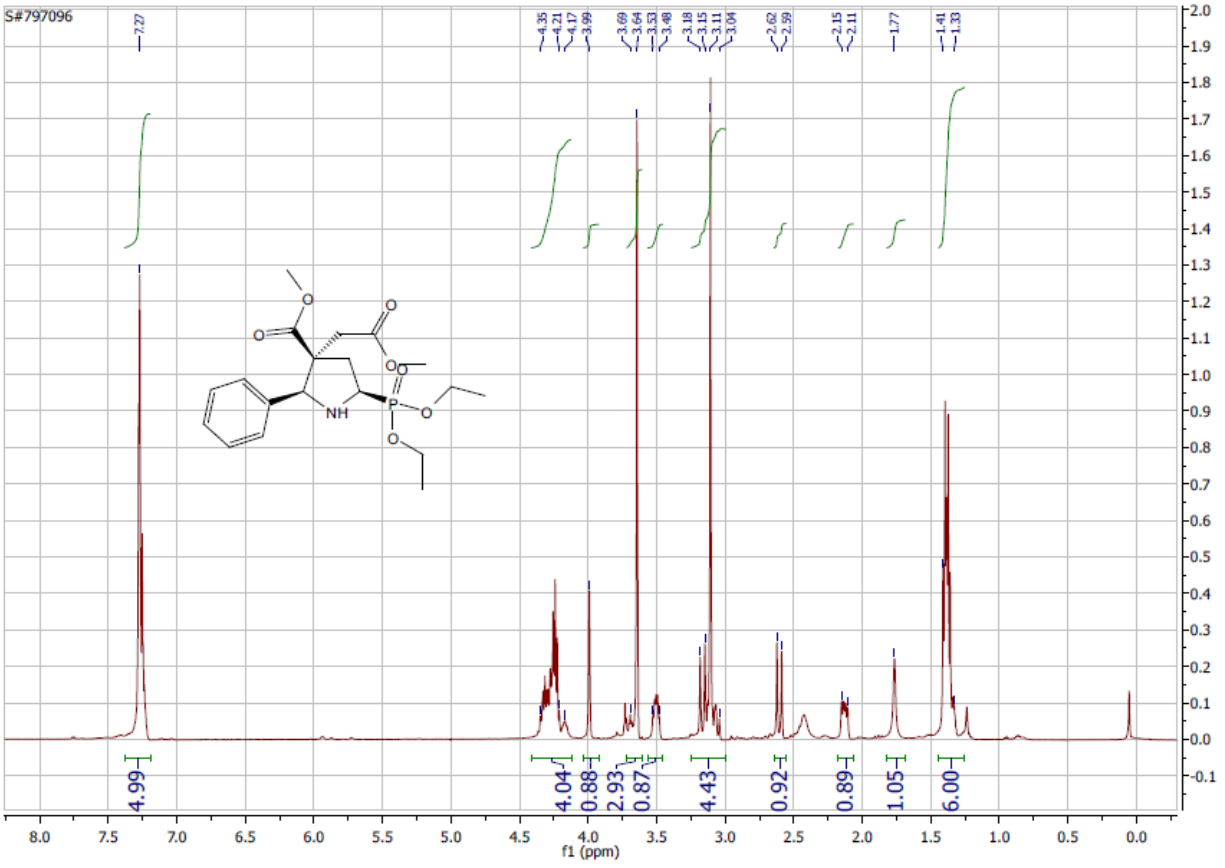
Compound 3ad ^{13}C NMR



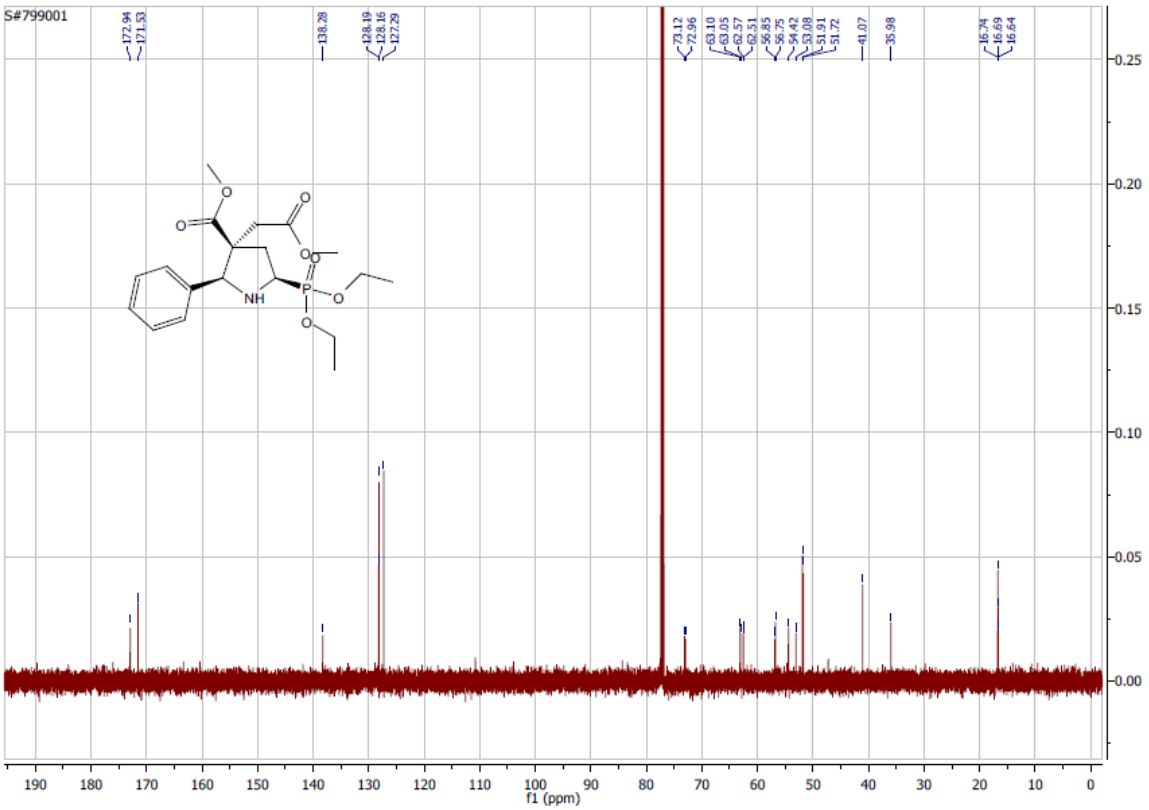
Compound 3ad ^{31}P NMR



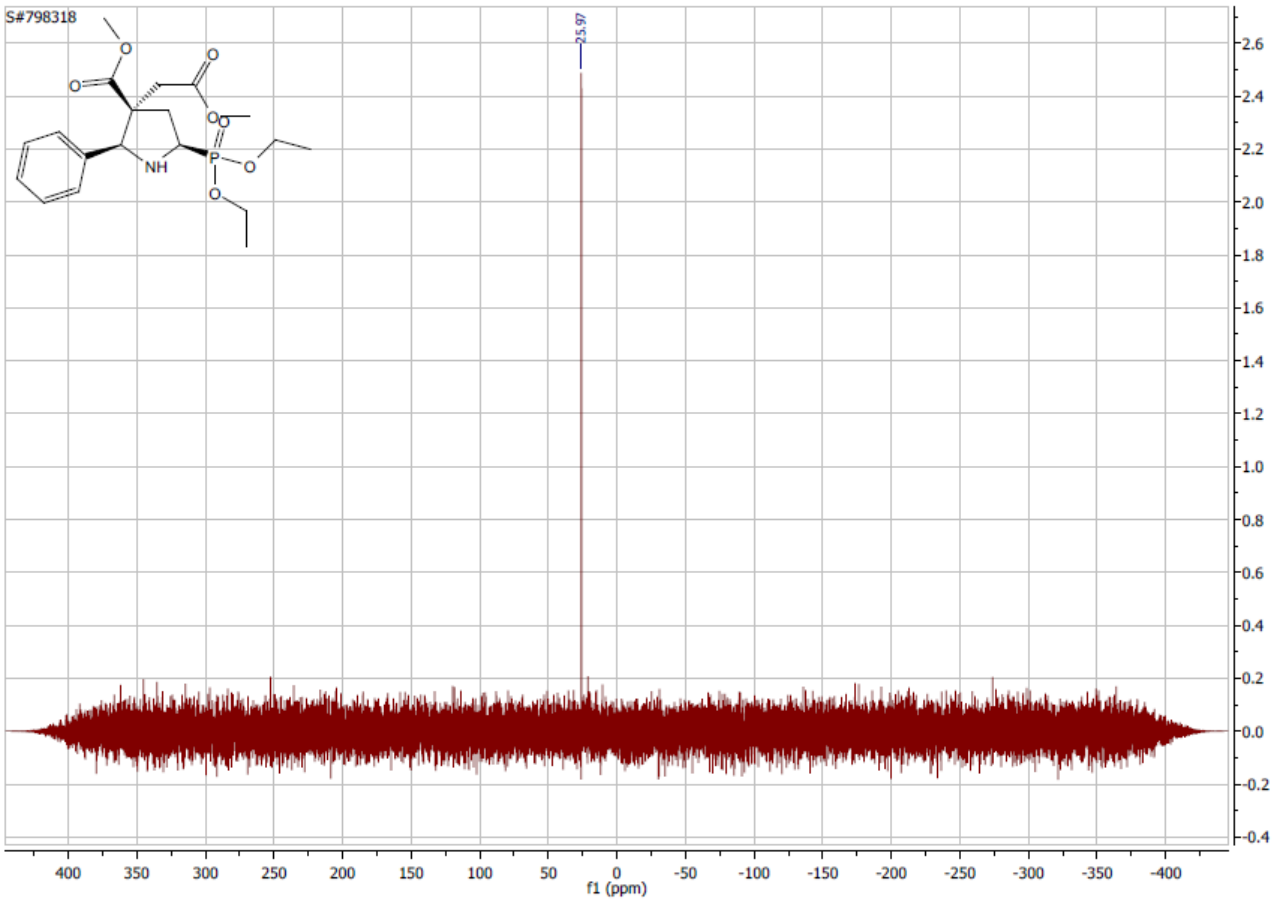
Compound 3ae ^{1}H NMR



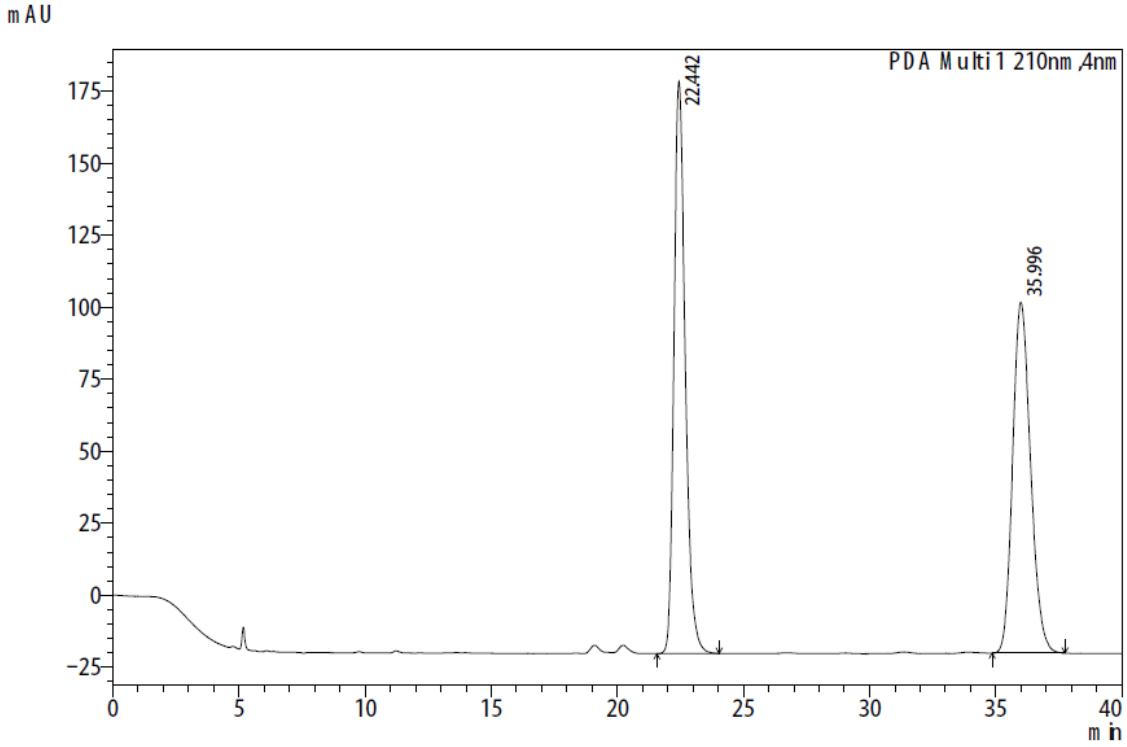
Compound 3ae ^{13}C NMR



Compound 3ae ^{31}P NMR



Compound 3aa HPLC (Racemic)

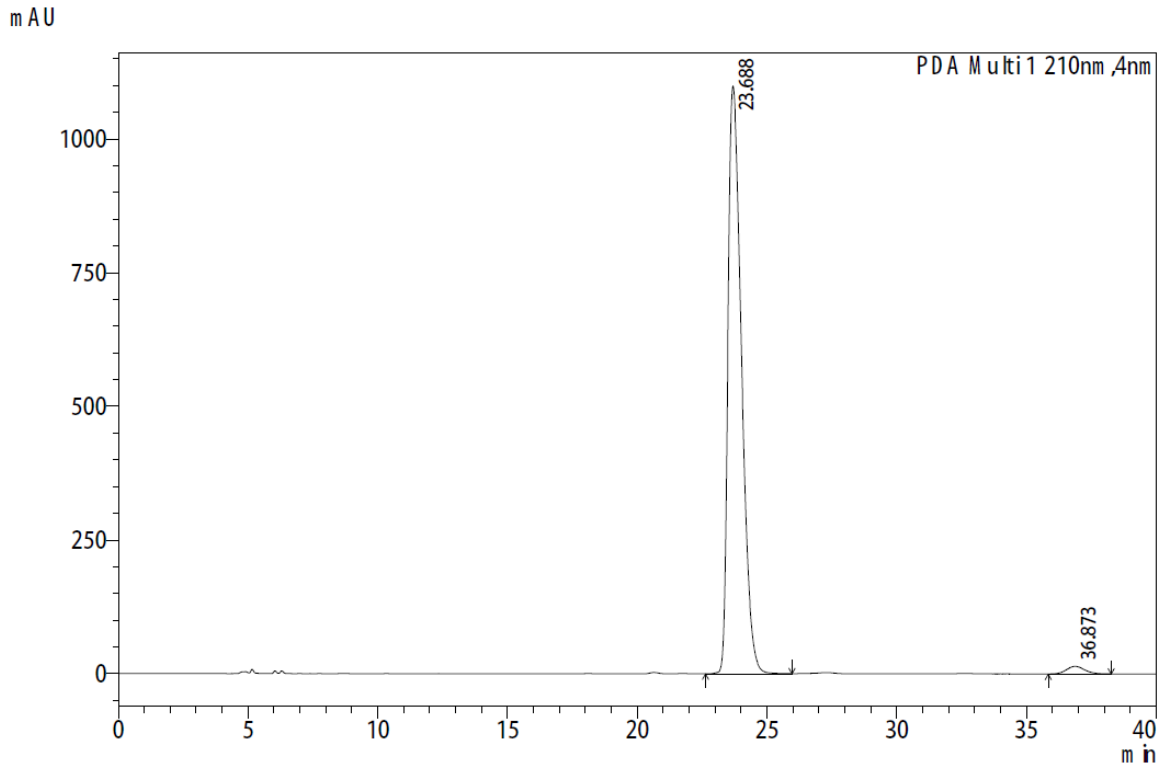


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	22.442	6178416	198596	50.637
2	35.996	6022978	121773	49.363
Total		12201393	320369	100.000

Compound 3aa HPLC Silver

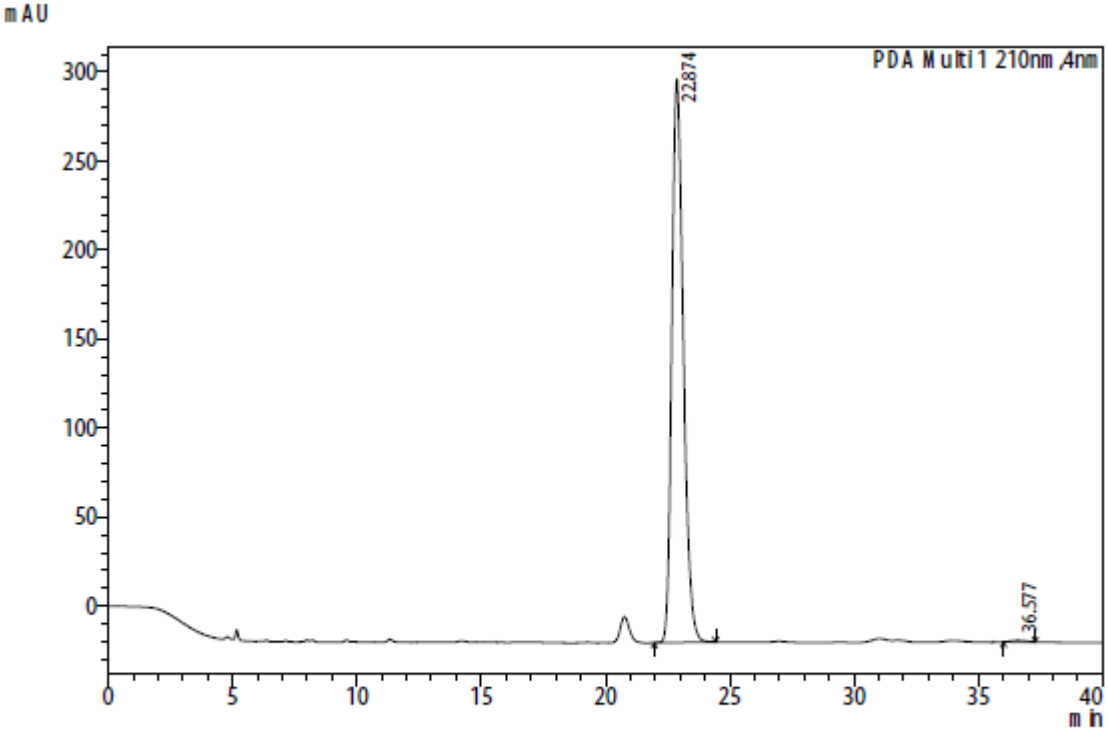


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	23.688	39708334	1099110	98.250
2	36.873	707248	14327	1.750
Total		40415581	1113438	100.000

Compound 3aa HPLC Copper

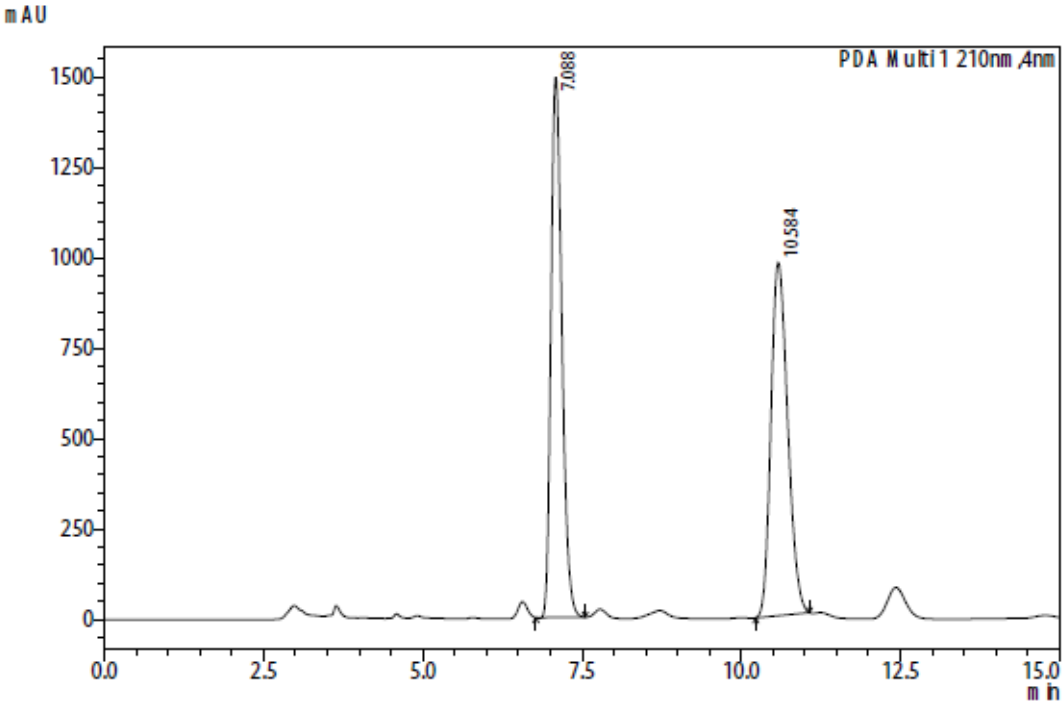


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	22.874	10155044	316438	99.611
2	36.577	39636	968	0.389
Total		10194680	317407	100.000

Compound 3ba HPLC (Racemic)

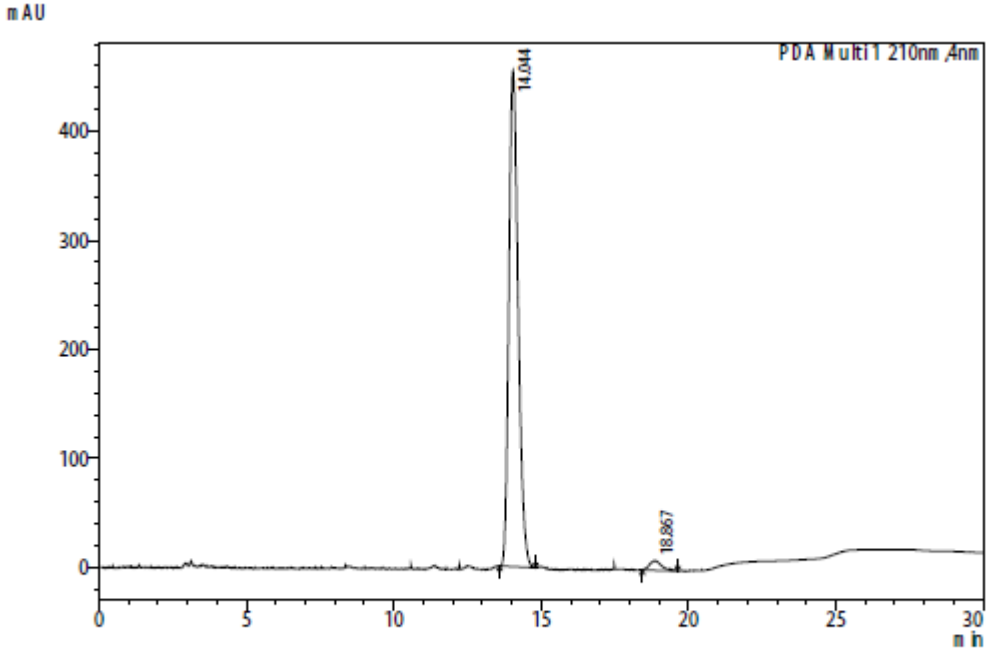


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.088	17821874	1492184	49.915
2	10.584	17882741	975796	50.085
Total		35704615	2467980	100.000

Compound 3ba HPLC Silver

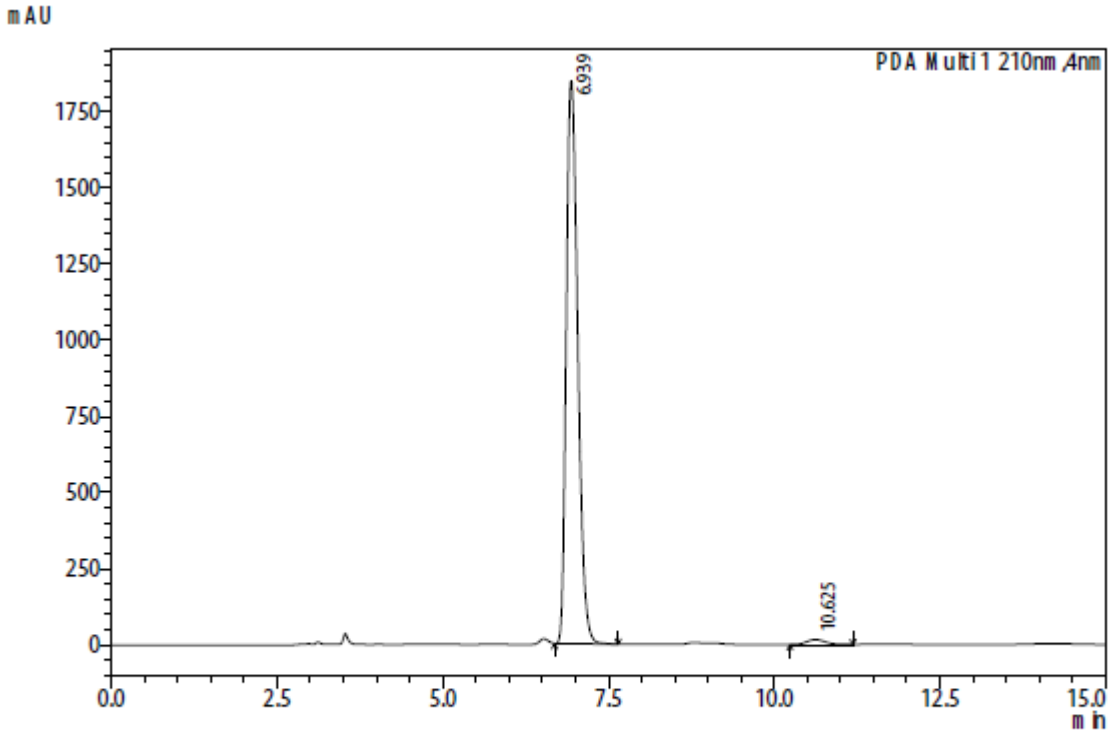


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.044	9951705	455715	97.526
2	18.867	252439	8945	2.474
Total		10204144	464660	100.000

Compound 3ba HPLC Copper

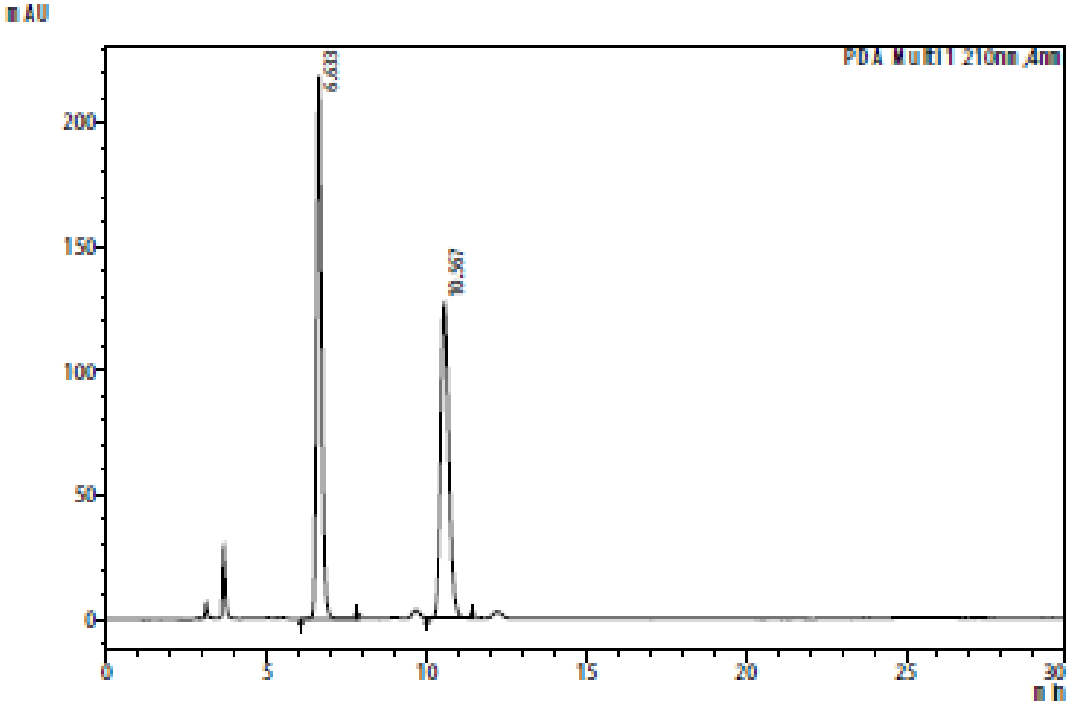


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.939	22279886	1846290	98.607
2	10.625	314676	16739	1.393
Total		22594562	1863029	100.000

Compound 3ca HPLC (Racemic)

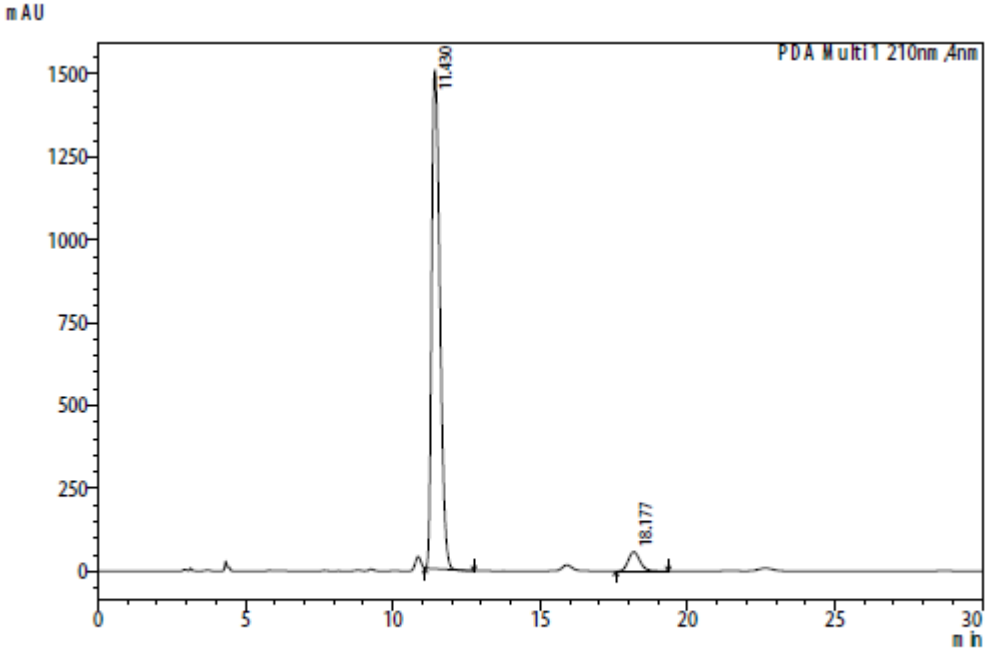


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.633	2343511	218832	50.805
2	10.567	2269284	126775	49.195
Total		4612795	345607	100.000

Compound 3ca HPLC Silver

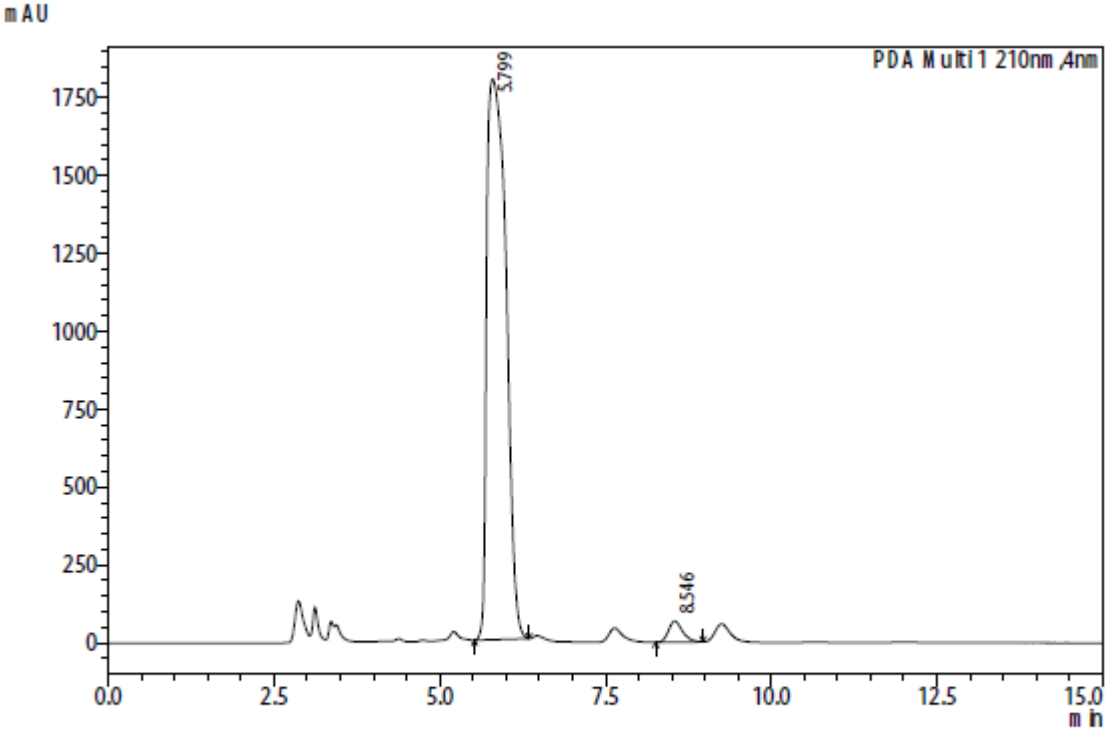


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	11.430	29157816	1304483	94.773
2	18.177	1608047	58186	5.227
Total		30765863	1362669	100.000

Compound 3ca HPLC Copper

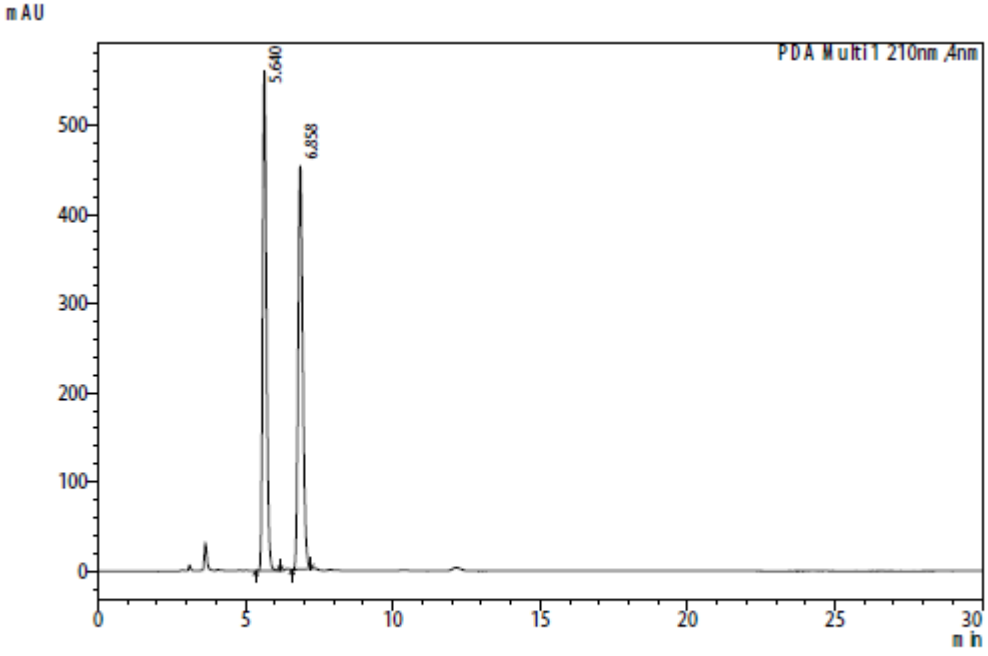


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.799	36254714	1799034	97.330
2	8.546	994414	67490	2.670
Total		37249128	1866524	100.000

Compound 3da HPLC (Racemic)

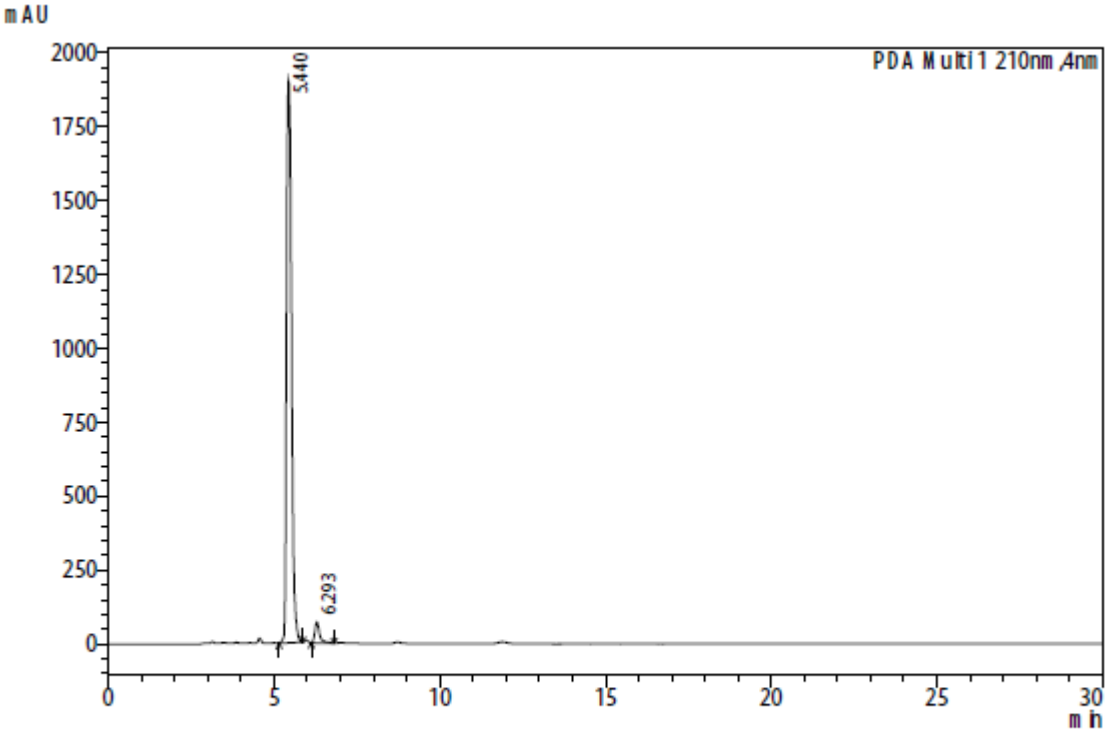


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.640	4980737	360619	50.075
2	6.858	4965751	451932	49.925
Total		9946488	1012371	100.000

Compound 3da HPLC Silver

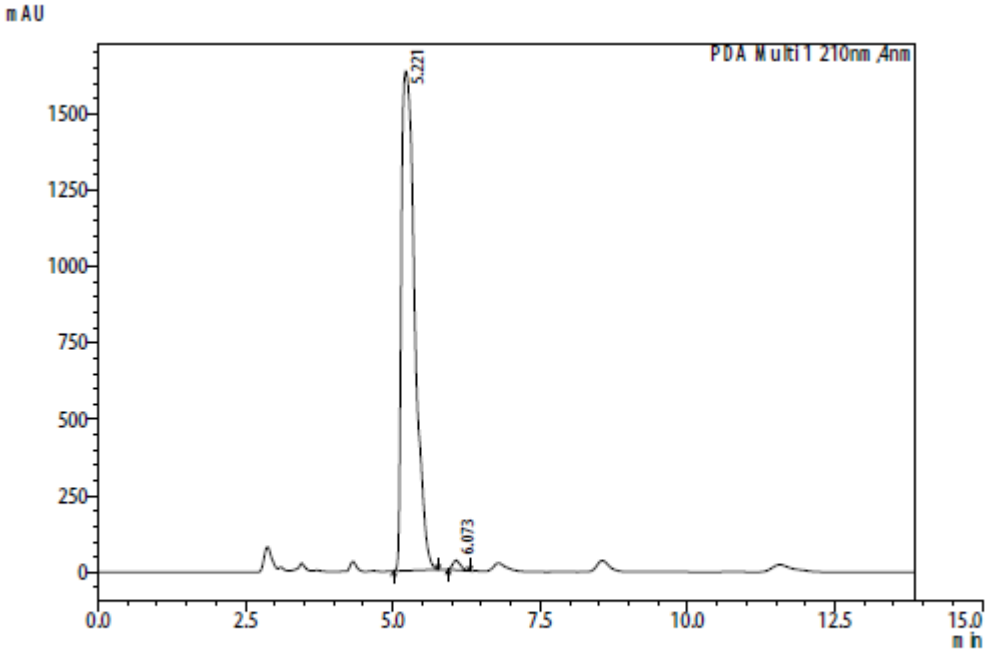


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.440	20019197	1904271	96.519
2	6.293	721983	70635	3.481
Total		20741180	1974906	100.000

Compound 3da HPLC Copper

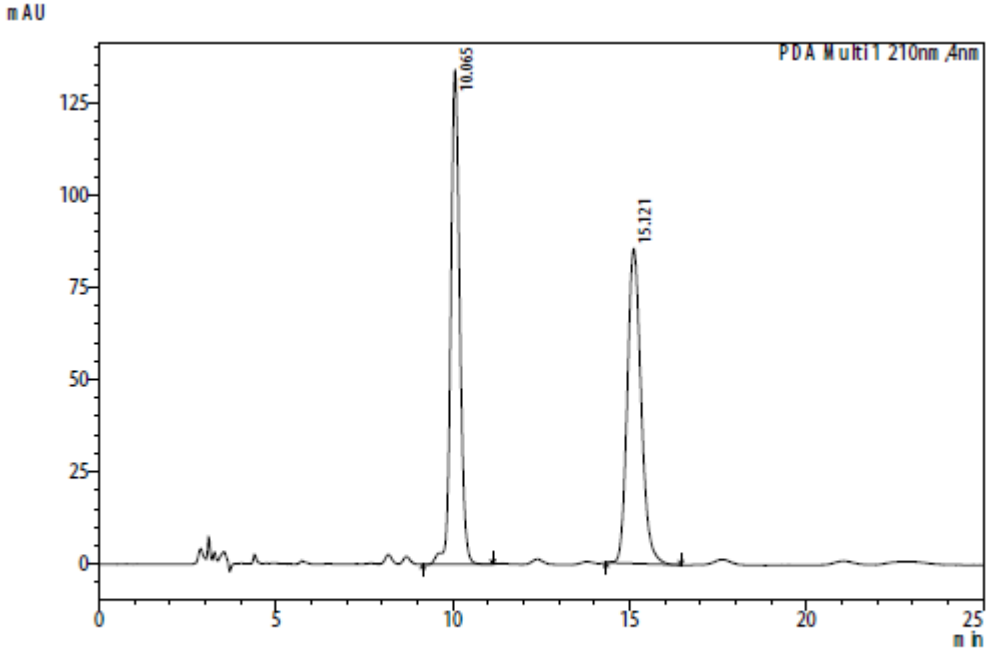


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	5.221	25860353	1634368	98.895
2	6.073	288917	31245	1.105
Total		26149272	1665613	100.000

Compound 3ea HPLC (Racemic)

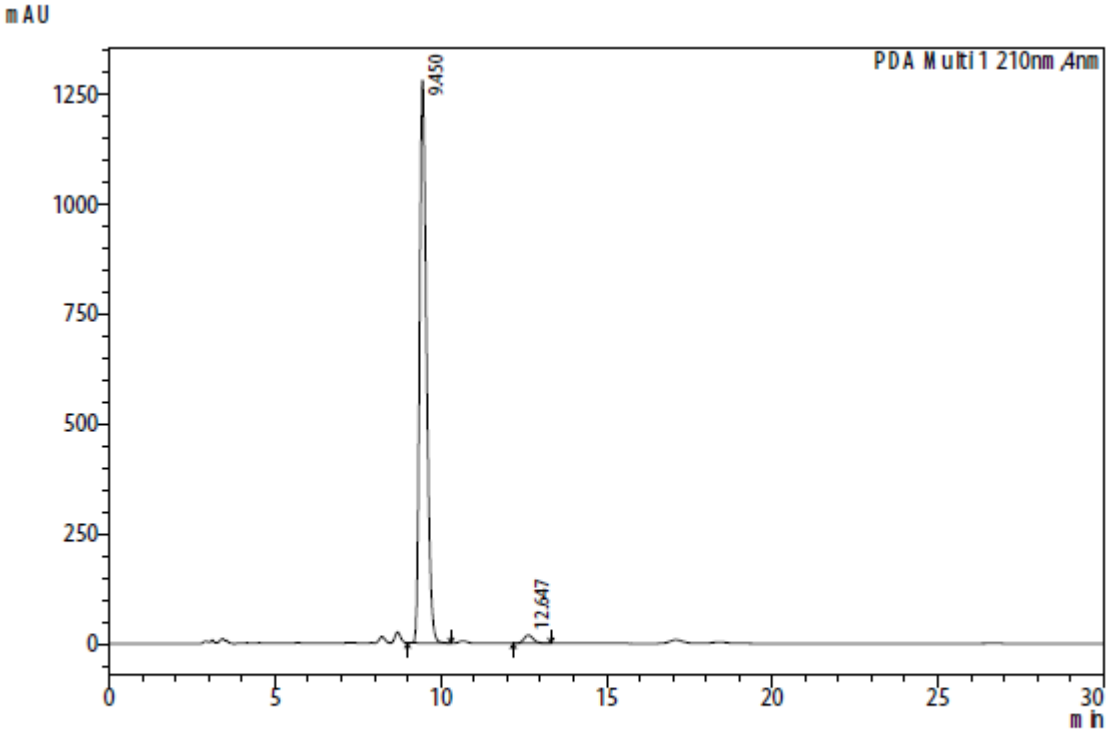


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	10.065	2364221	133863	50.515
2	15.121	2316046	85247	49.485
Total		4680266	219110	100.000

Compound 3ea HPLC Silver

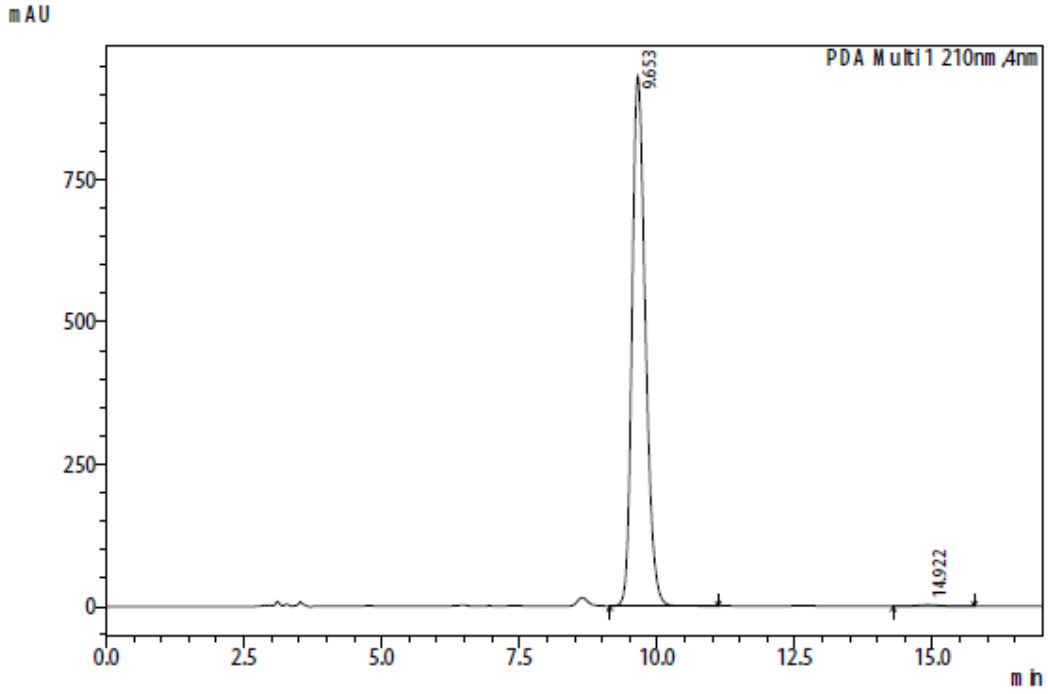


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	9.450	18695953	1280301	98.085
2	12.647	365014	18879	1.915
Total		19060967	1299180	100.000

Compound 3ea HPLC Copper

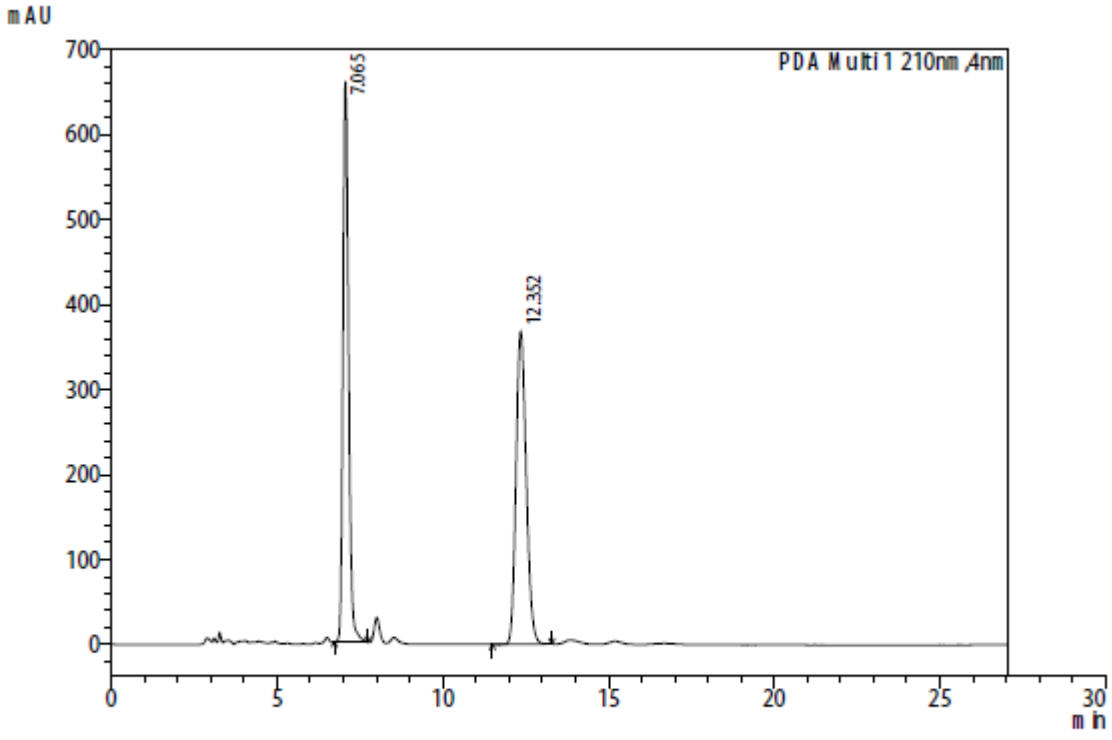


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	9.653	15719566	930886	99.613
2	14.922	61034	2327	0.387
Total		15780600	933213	100.000

Compound 3fa HPLC (Racemic)

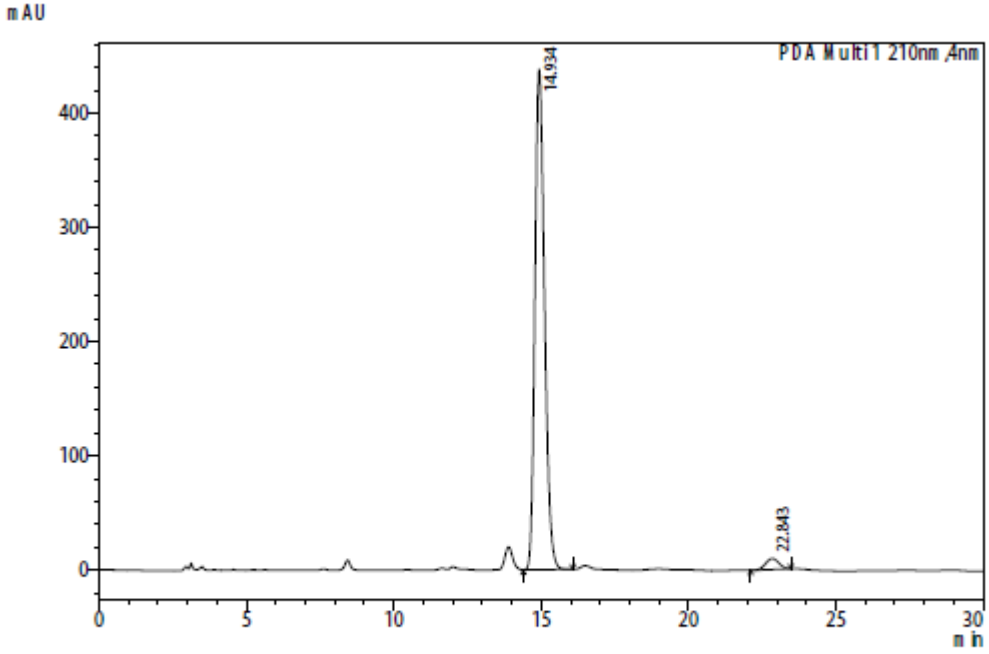


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.065	7734700	659564	49.592
2	12.352	7861869	368208	50.408
Total		15596569	1027771	100.000

Compound 3fa HPLC Silver

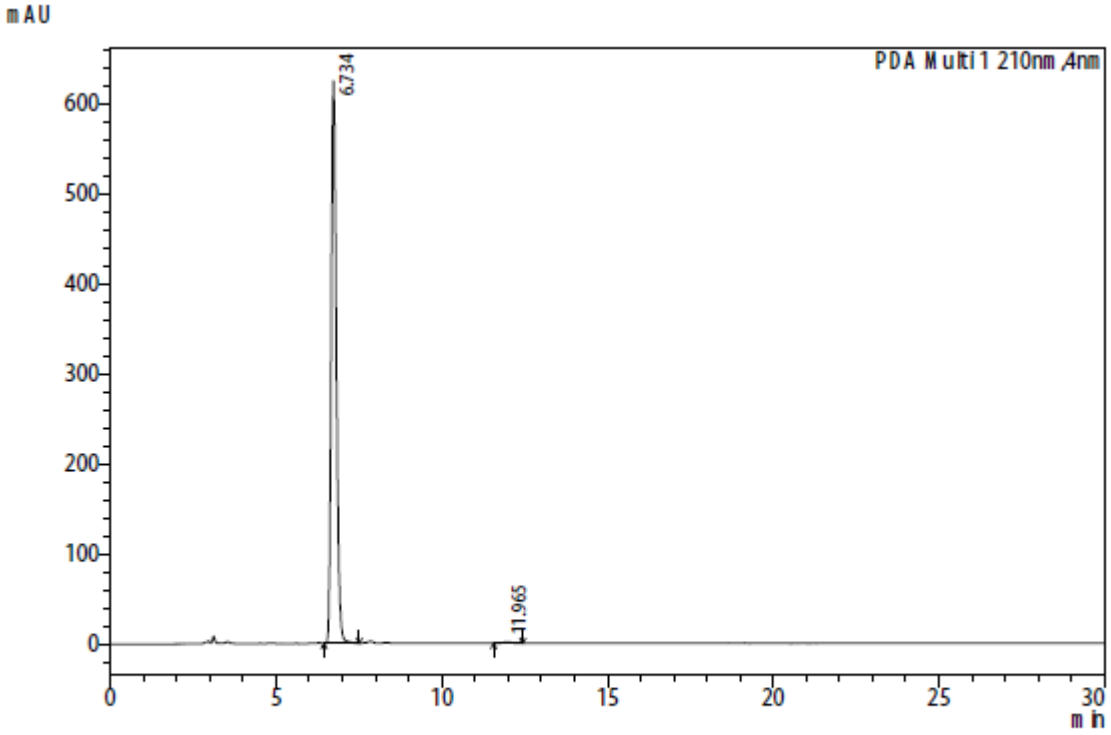


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.934	9923829	437163	97.093
2	22.843	297166	9548	2.907
Total		10222995	446711	100.000

Compound 3fa HPLC Copper

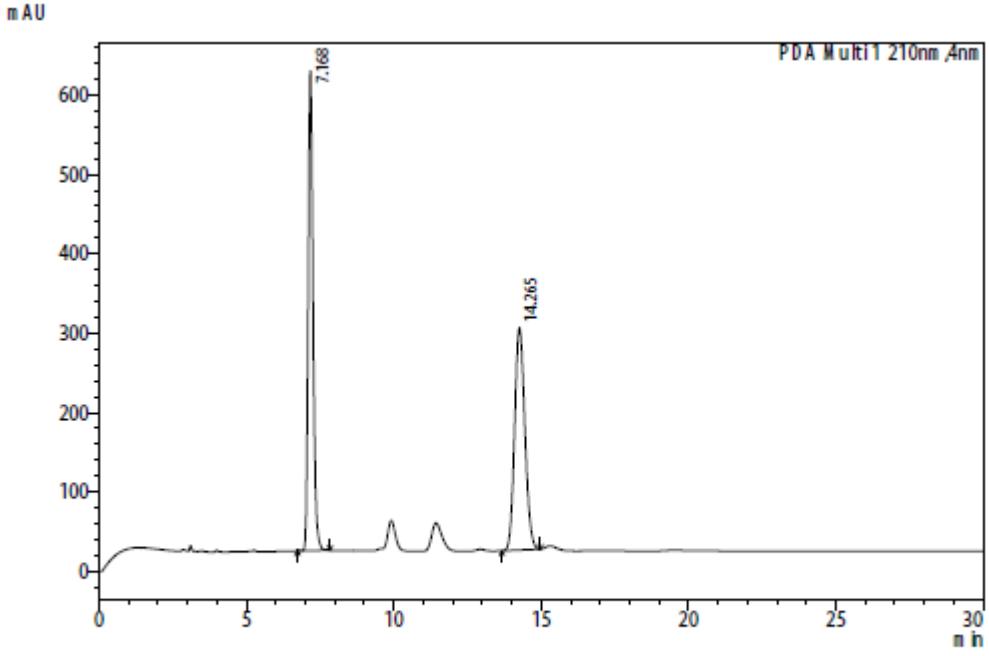


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.734	6746392	625654	99.570
2	11.965	29104	1430	0.430
Total		6775496	627084	100.000

Compound 3ga HPLC (Racemic)

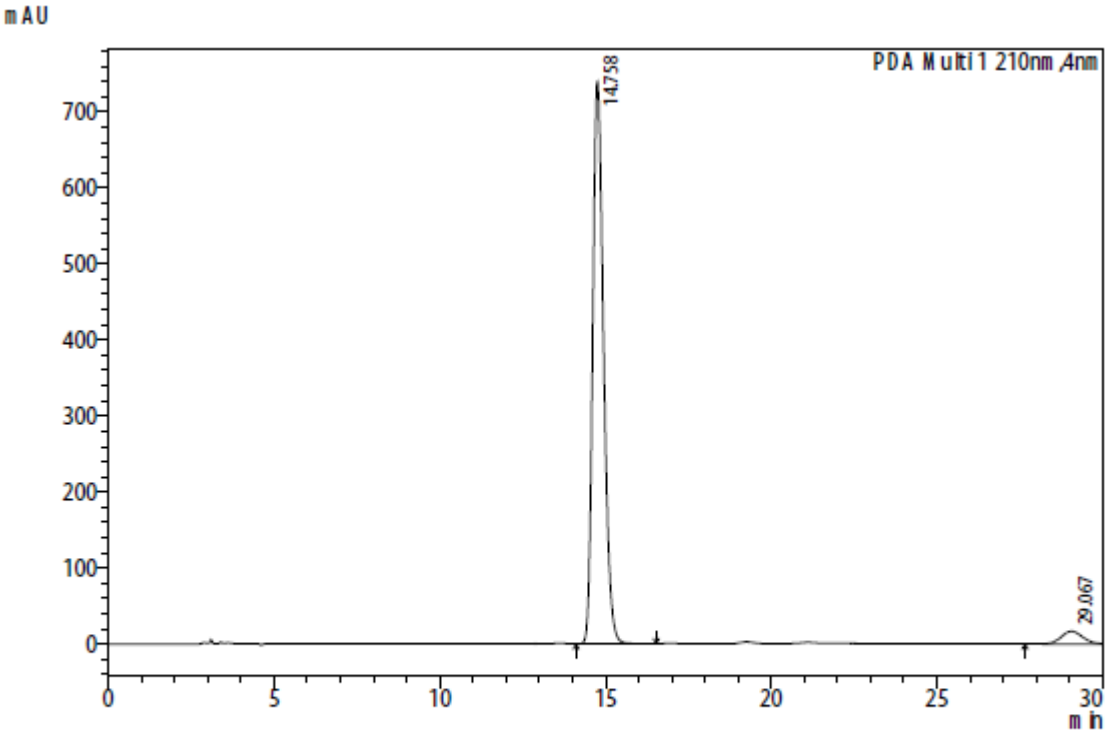


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.168	6922753	605234	50.518
2	14.265	6780870	279948	49.482
Total		13703624	885202	100.000

Compound 3ga HPLC Silver

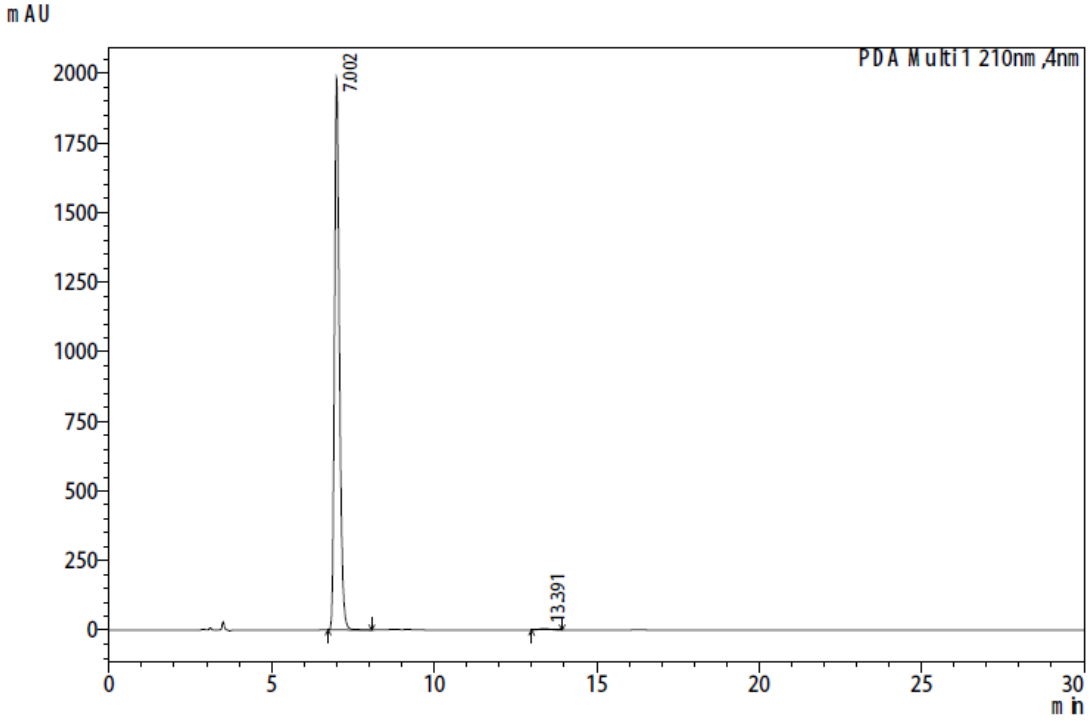


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.758	16897554	739952	95.702
2	29.067	758957	16784	4.298
Total		17656511	756737	100.000

Compound 3ga HPLC Copper

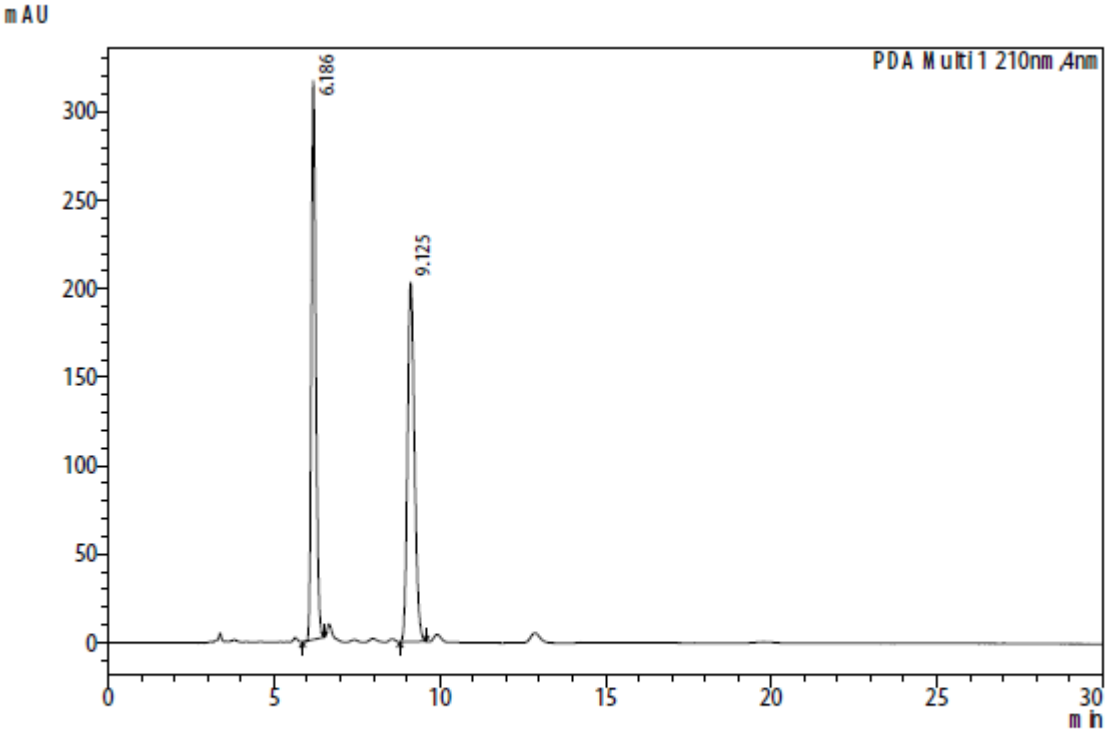


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.002	20940598	1981611	99.401
2	13.391	126200	5745	0.599
Total		21066798	1987356	100.000

Compound 3ha HPLC (Racemic)

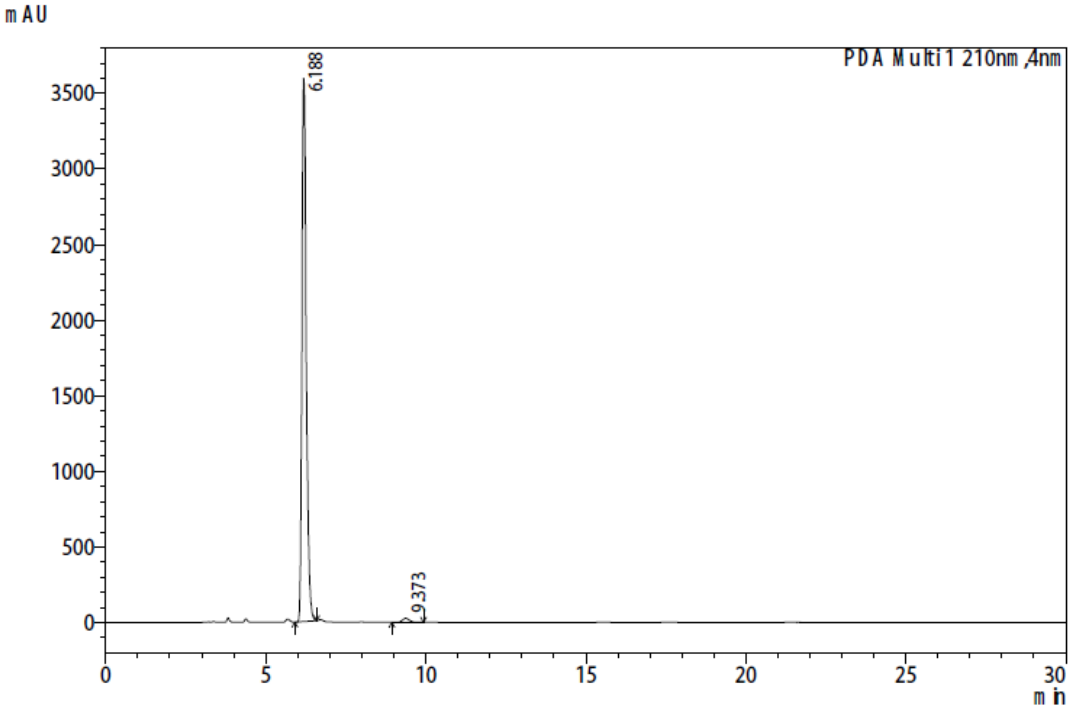


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.186	2944708	316212	49.776
2	9.125	2971231	202883	50.224
Total		5915939	519096	100.000

Compound 3ha HPLC

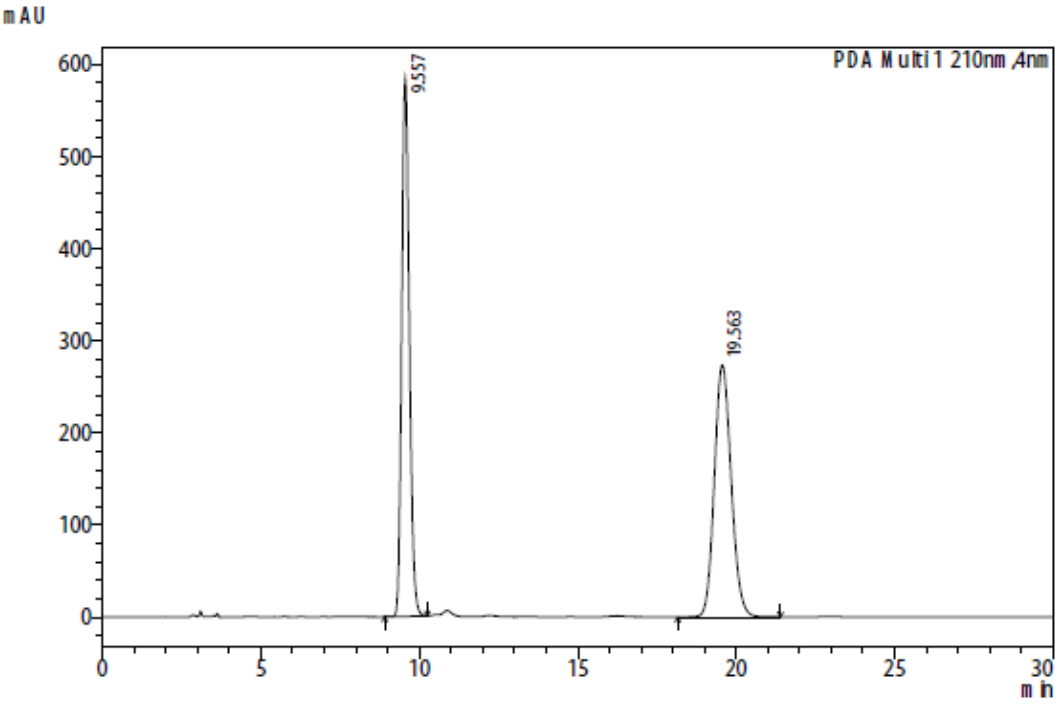


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.188	33910818	3597495	98.799
2	9.373	412161	26766	1.201
Total		34322979	3624261	100.000

Compound 3ia HPLC (Racemic)

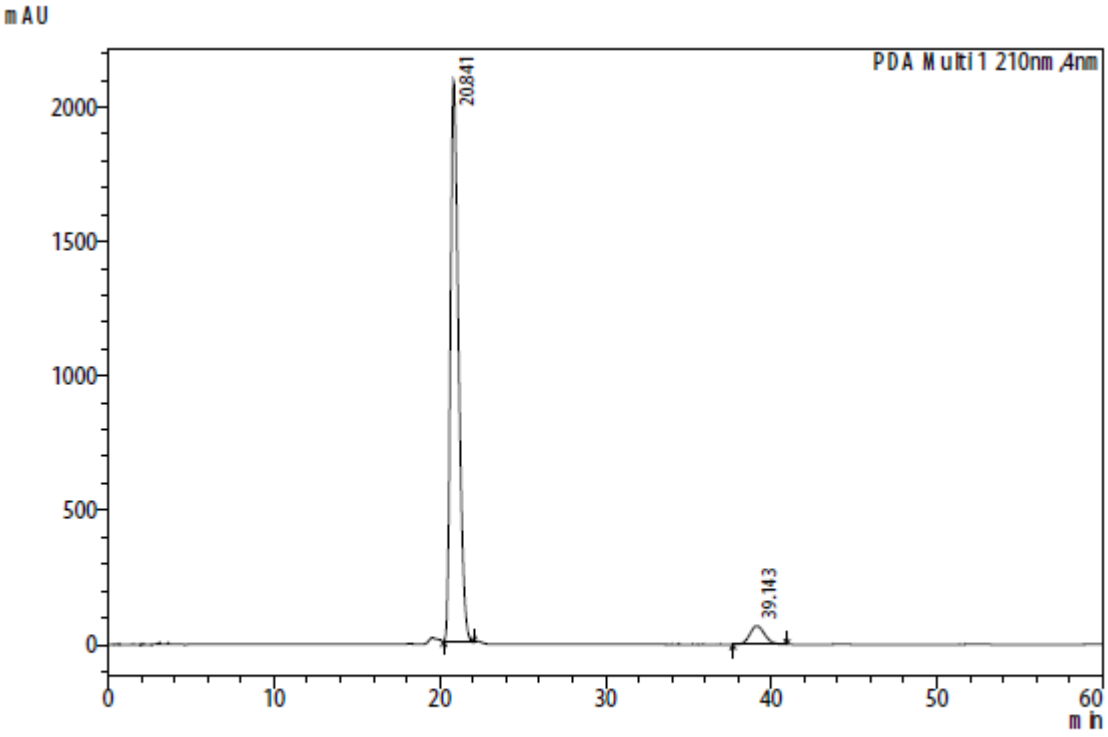


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	9.557	9783556	584171	49.183
2	19.563	10108739	273769	50.817
Total		19892295	857940	100.000

Compound 3ia HPLC Silver

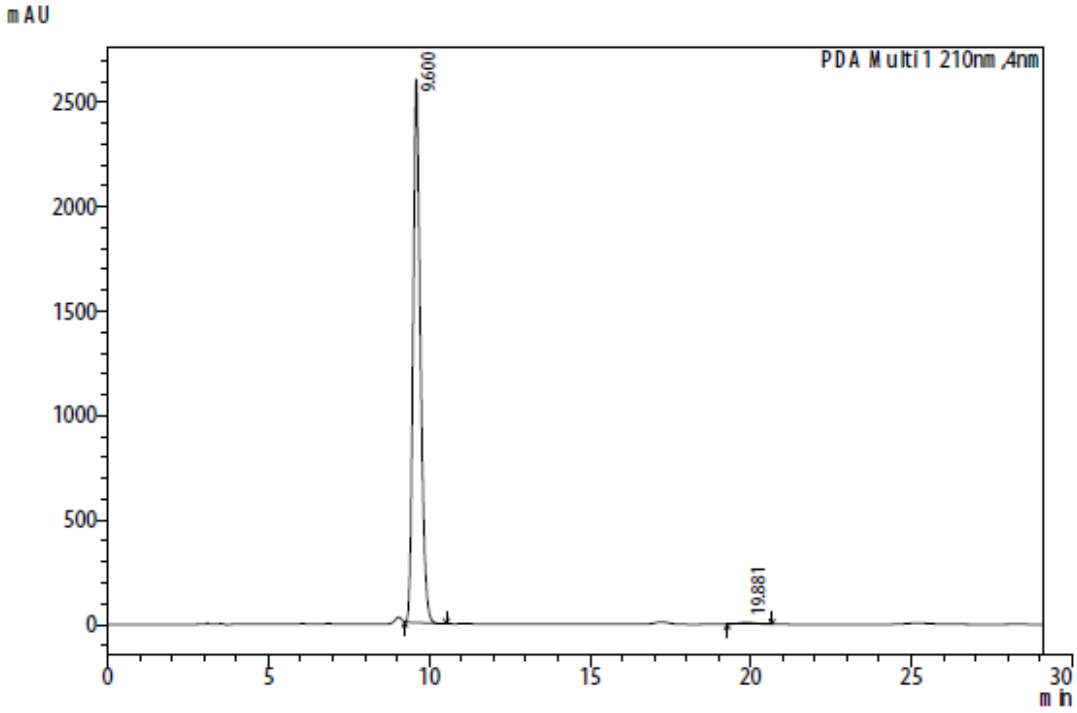


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	20.841	70926937	2085355	94.191
2	39.143	4374594	69489	5.809
Total		75301530	2154844	100.000

Compound 3ia HPLC Copper

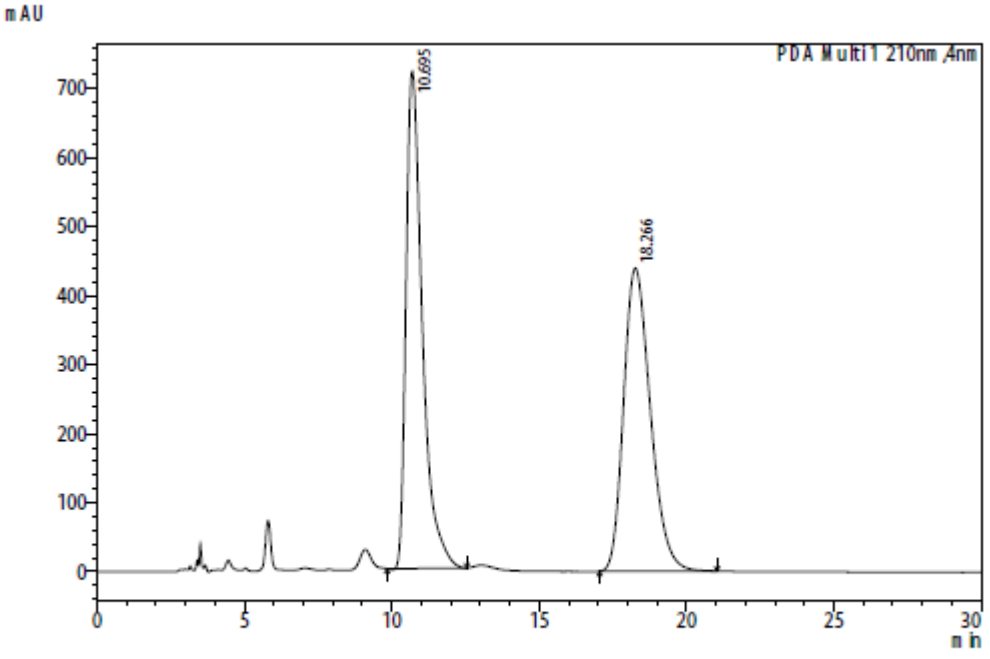


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	9.600	41386204	2605581	99.292
2	19.881	294908	8469	0.708
Total		41681112	2614051	100.000

Compound 3ja HPLC (Racemic)

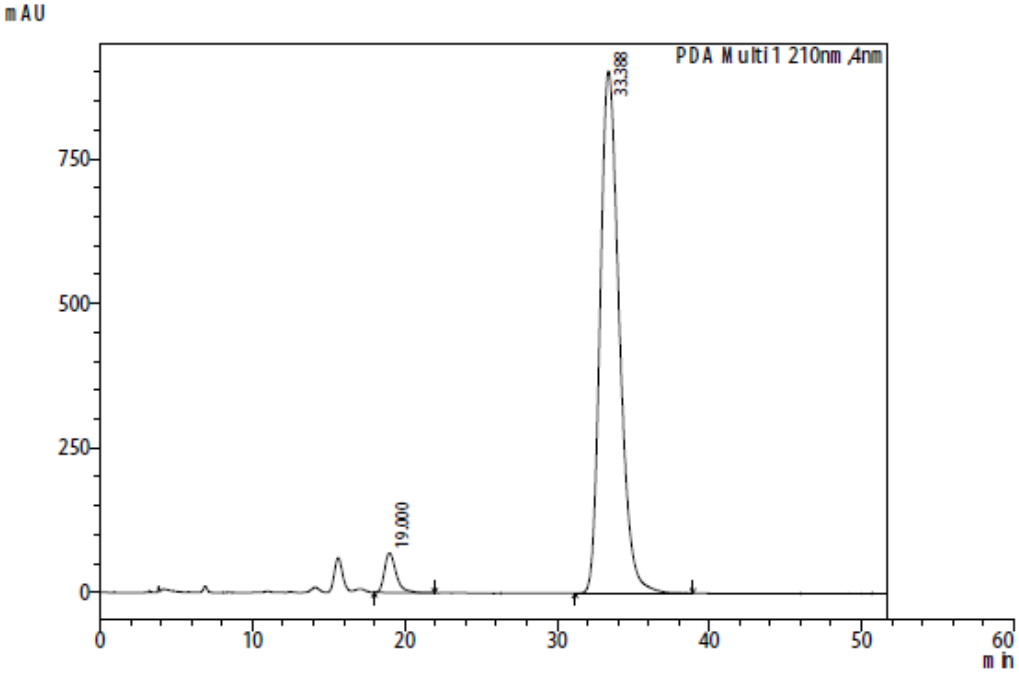


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	10.695	27756531	720336	50.011
2	18.266	27743800	438977	49.989
Total		55500331	1159313	100.000

Compound 3ja HPLC Silver

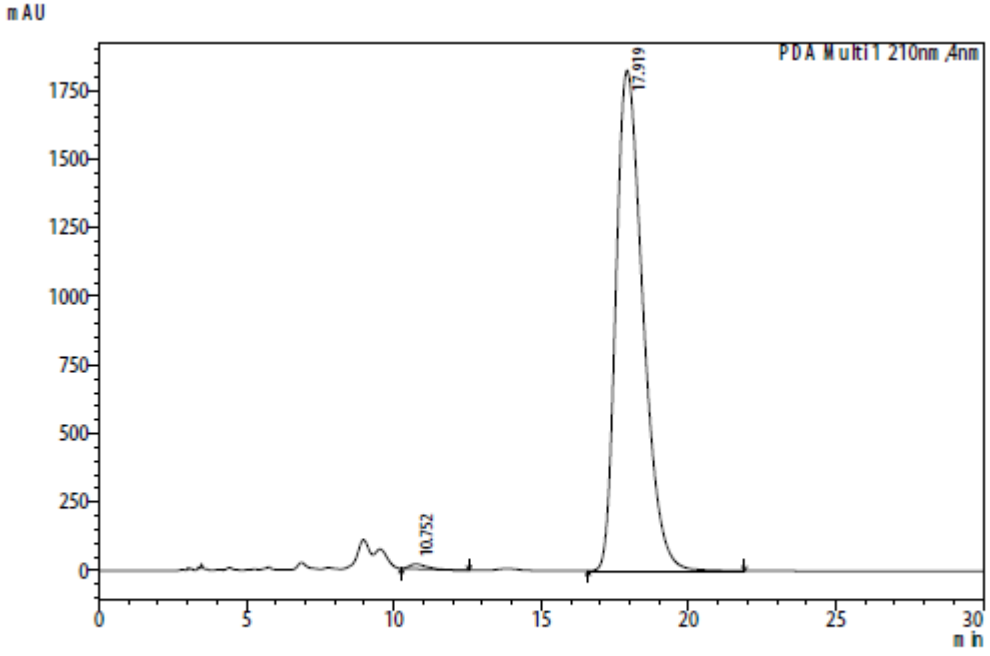


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	19.000	3643343	68531	4.430
2	33.388	78603773	903273	95.570
Total		82247115	971804	100.000

Compound 3ja HPLC Copper

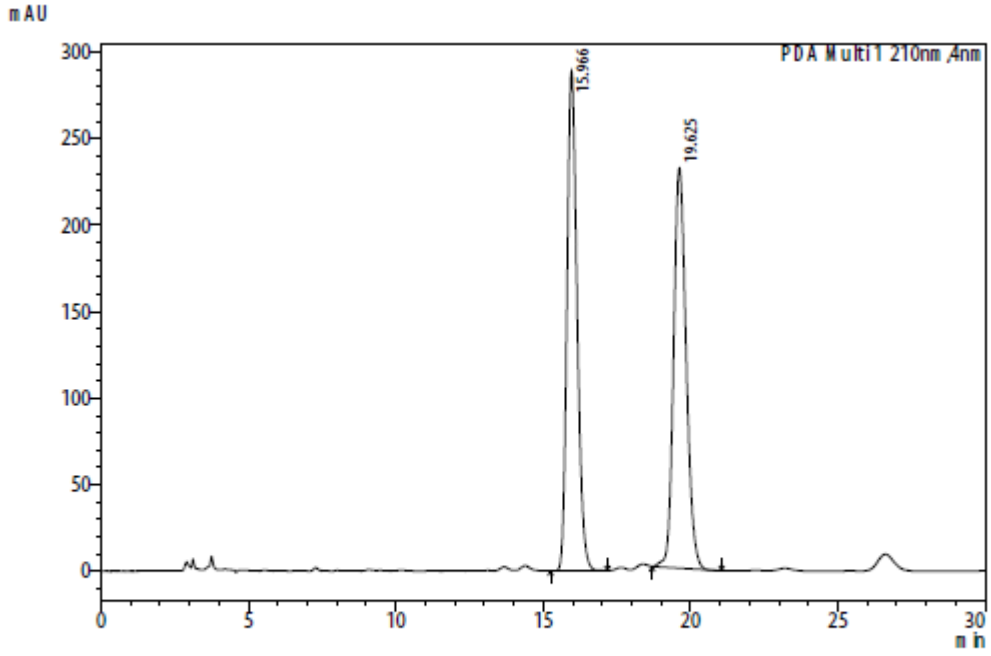


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	10.752	660382	17460	0.565
2	17.919	116182458	1824653	99.435
Total		116842840	1842113	100.000

Compound 3ka HPLC (Racemic)

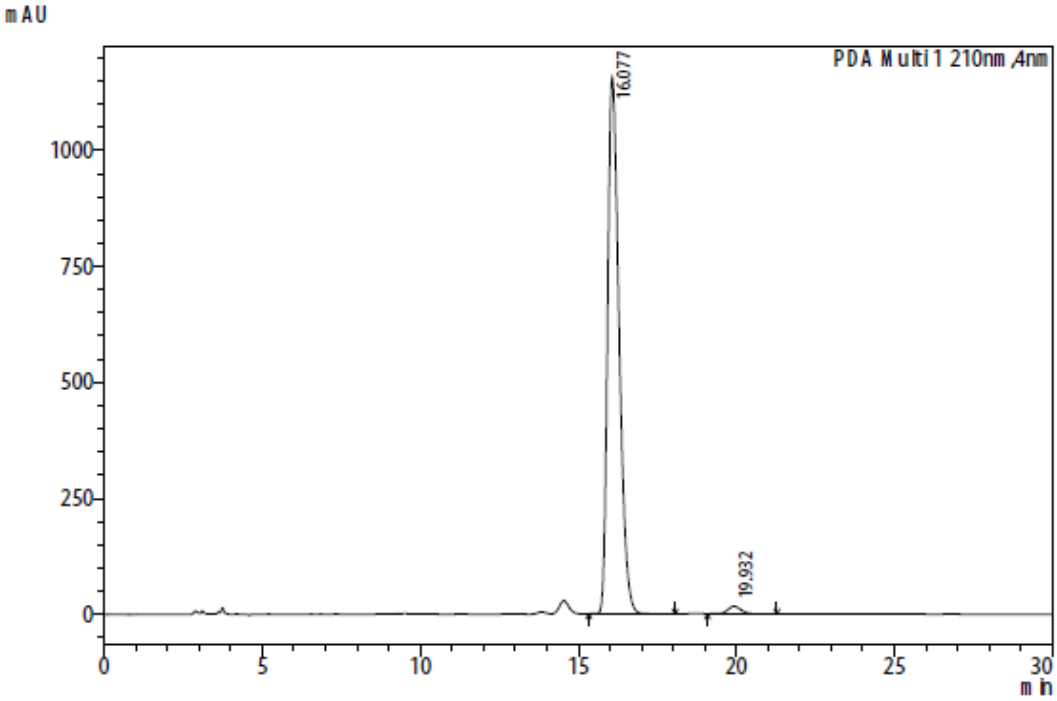


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	15.966	6873351	288849	50.109
2	19.625	6843362	231348	49.891
Total		13716712	520197	100.000

Compound 3ka HPLC Copper

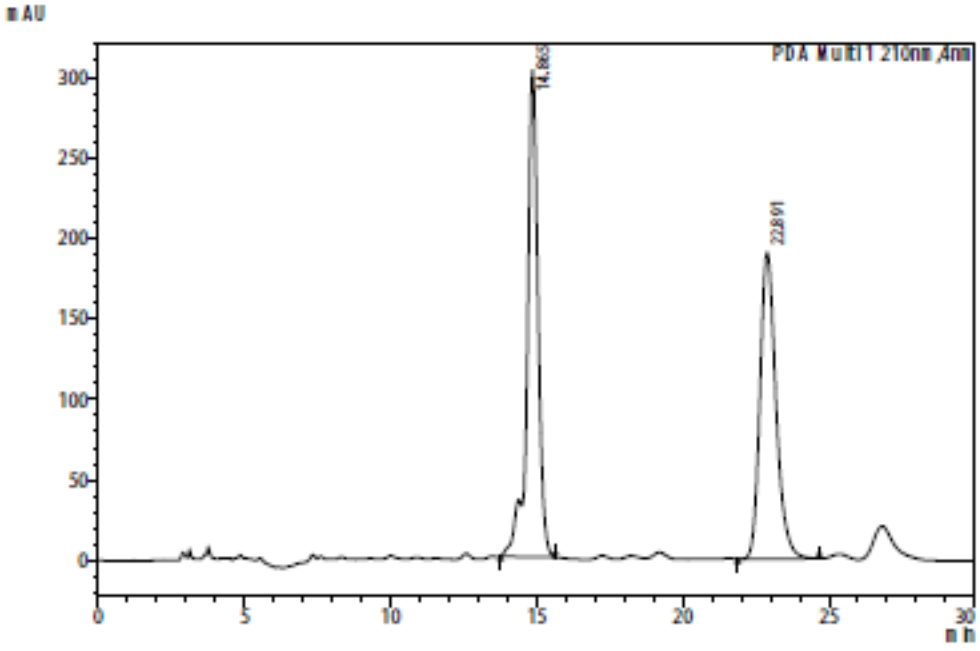


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	16.077	29002396	1156066	98.395
2	19.932	473001	16364	1.605
Total		29475398	1172430	100.000

Compound 3la HPLC (Racemic)

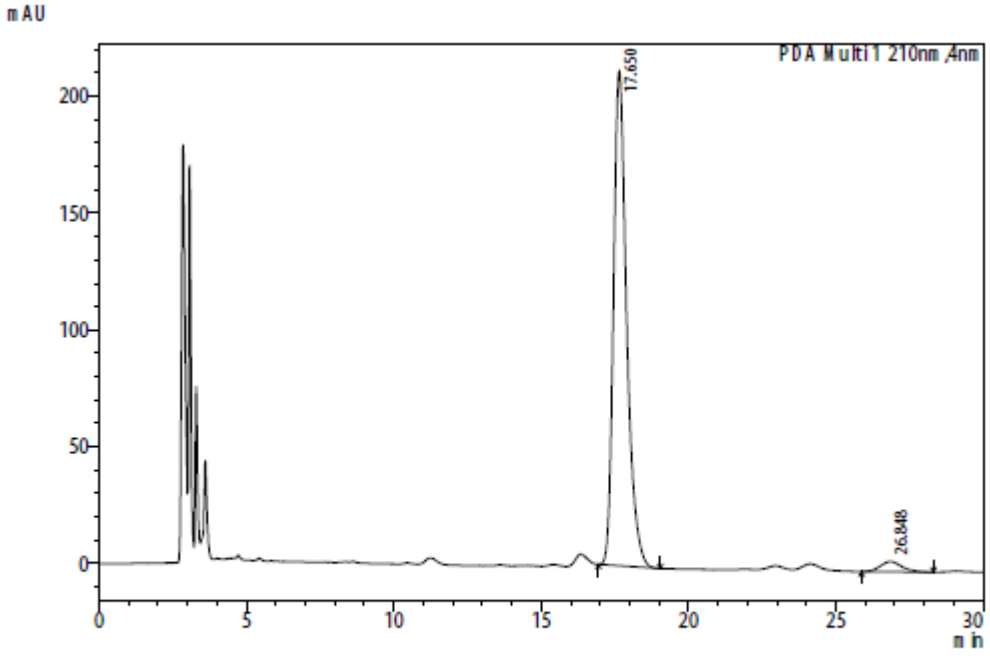


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	14.865	7804793	301710	51.921
2	22.891	7227288	190106	48.079
Total		15032081	491816	100.000

Compound 3la HPLC

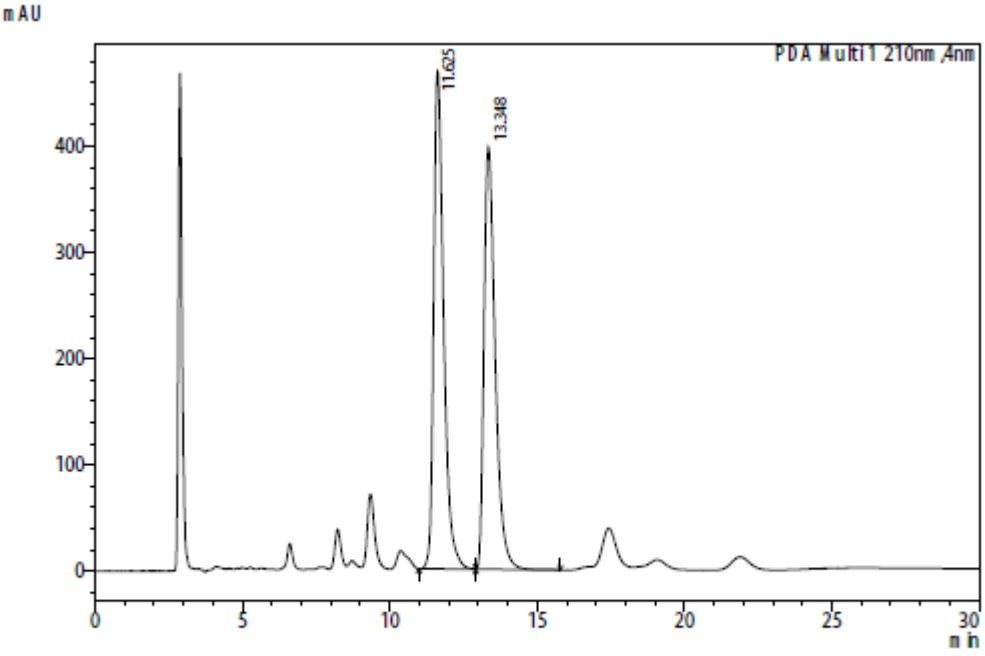


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	17.650	6556745	211632	96.691
2	26.848	224404	4383	3.309
Total		6781149	216016	100.000

Compound 3ab HPLC (Racemic)

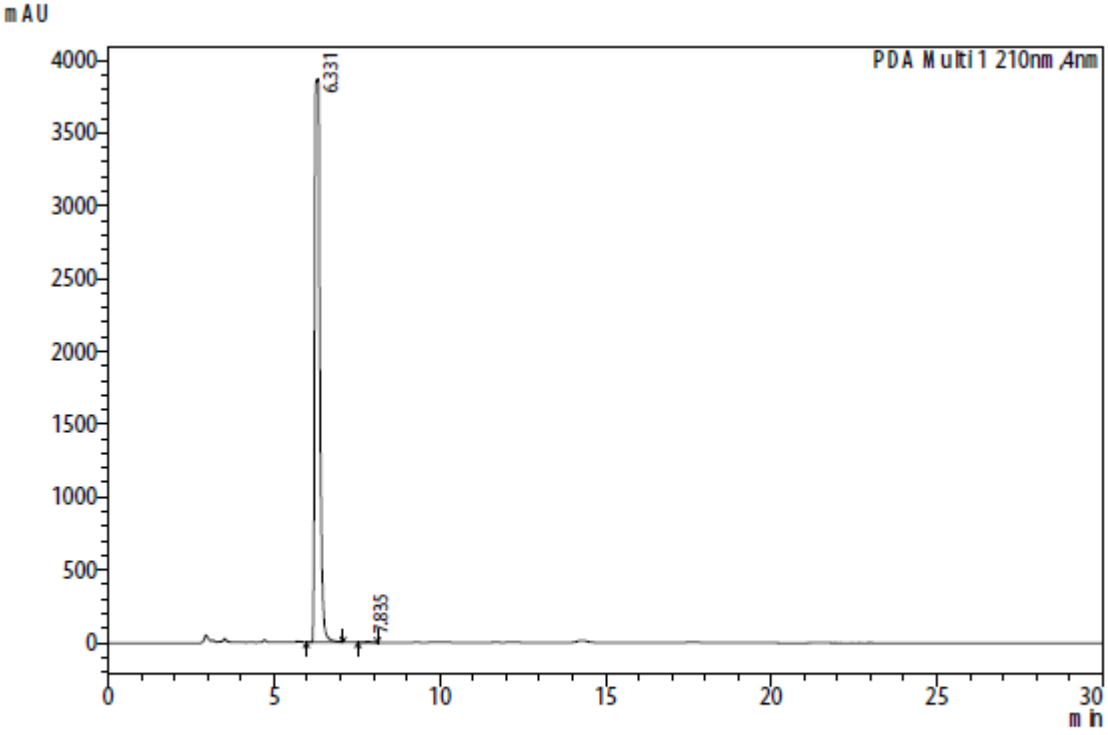


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	11.625	11061078	468583	51.260
2	13.348	10517142	397763	48.740
Total		21578220	866347	100.000

Compound 3ab HPLC Silver

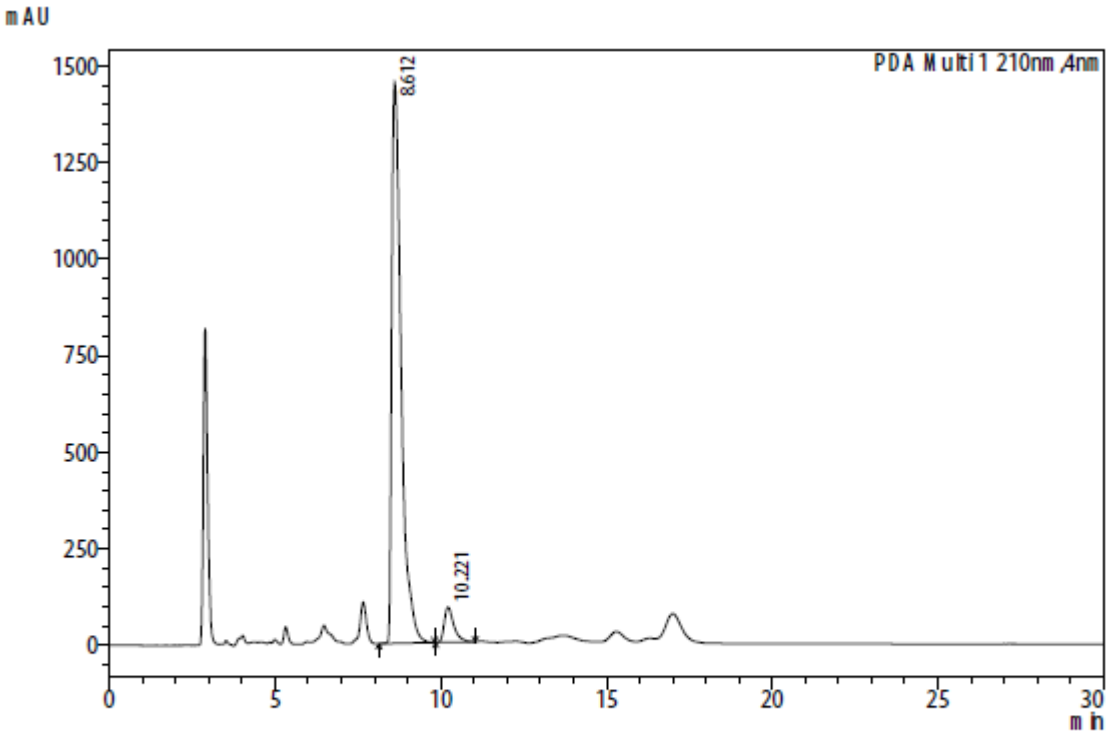


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.331	42755770	3864393	99.831
2	7.835	72356	6147	0.169
Total		42828126	3870540	100.000

Compound 3ab HPLC Copper

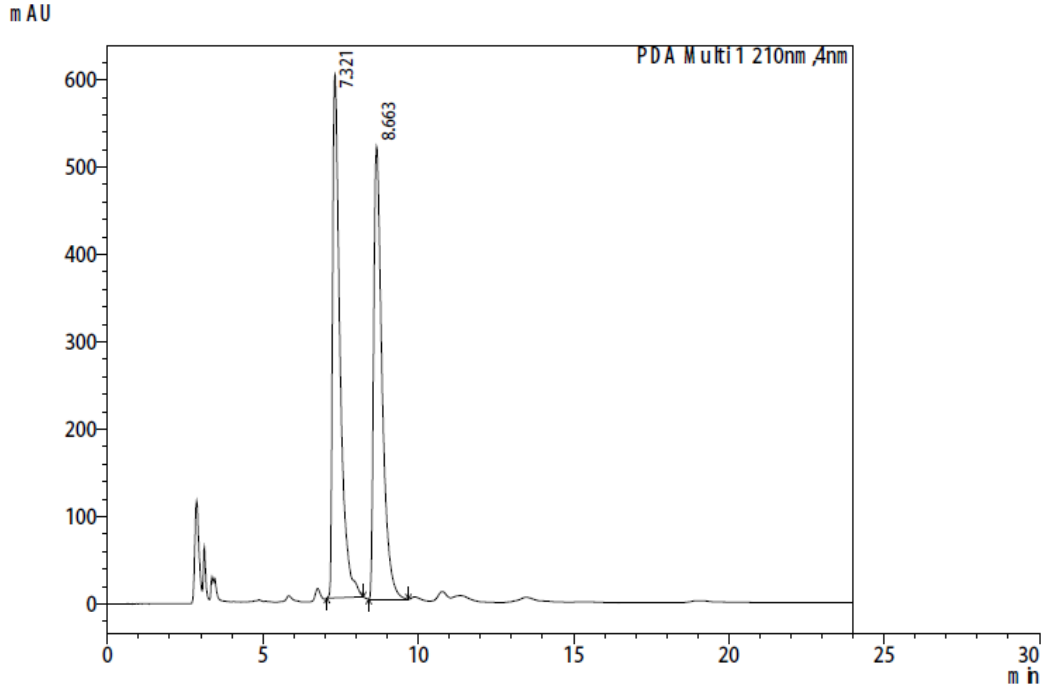


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	8.612	28574386	1452248	93.997
2	10.221	1824823	90984	6.003
Total		30399209	1543232	100.000

Compound 3ac HPLC (Racemic)

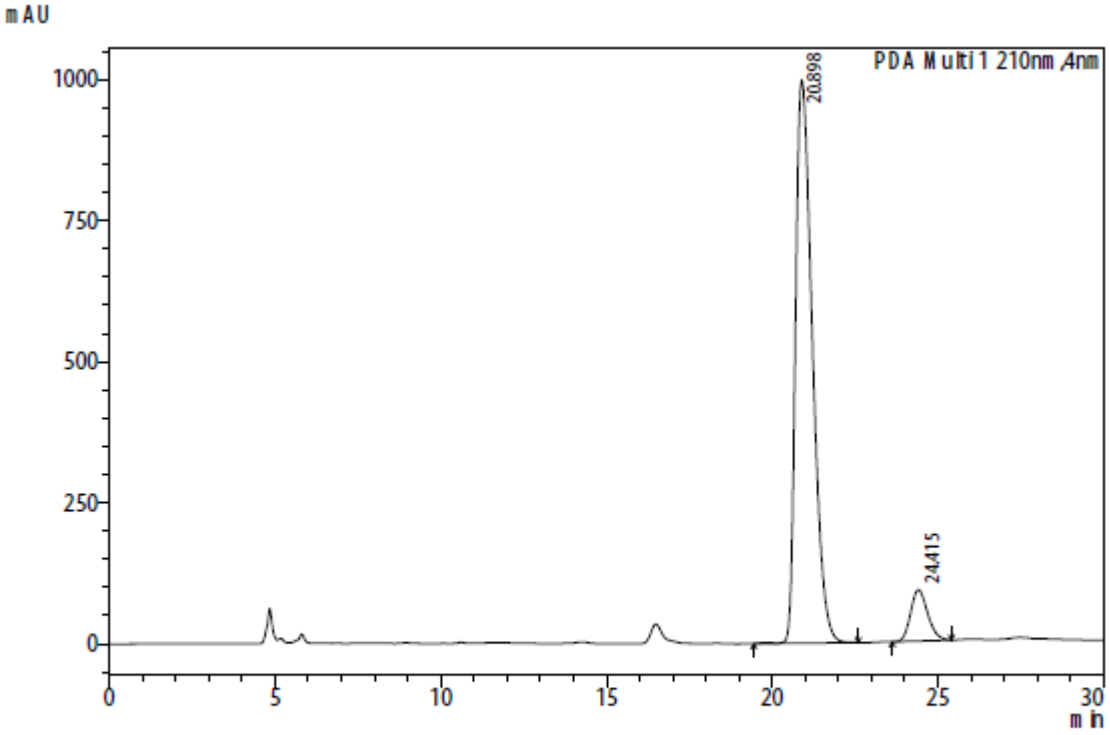


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.321	10140840	598779	50.917
2	8.663	9775760	518662	49.083
Total		19916600	1117441	100.000

Compound 3ac HPLC Silver

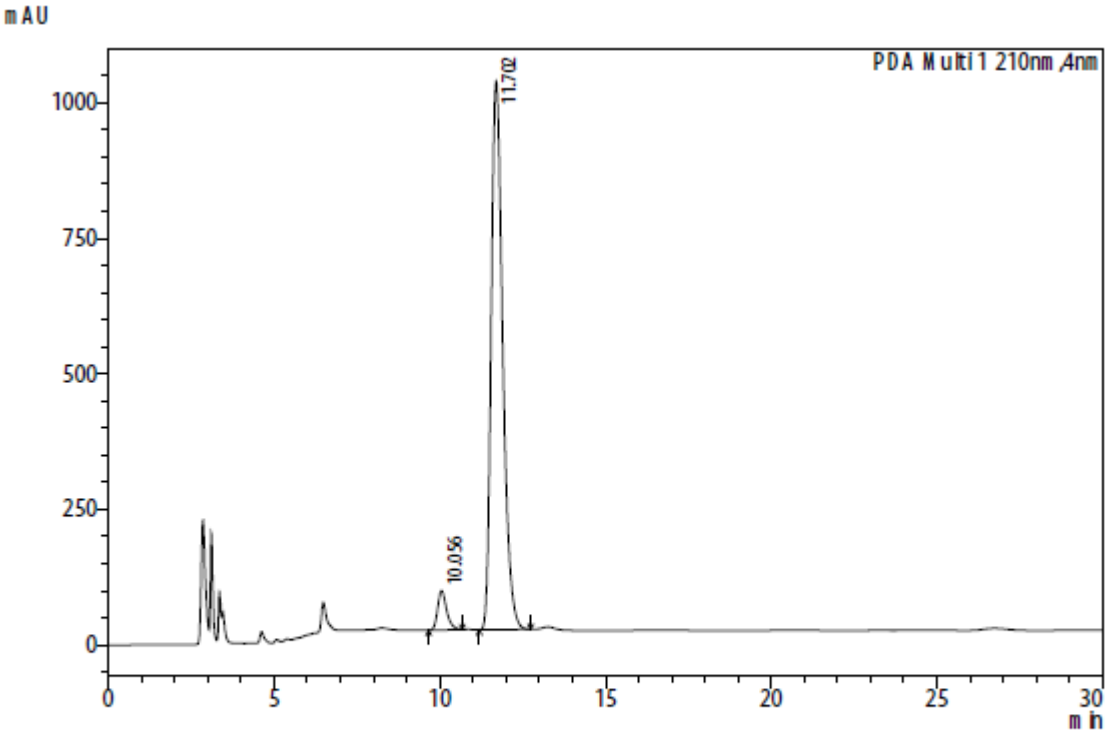


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	20.898	35161827	997027	91.586
2	24.415	3230349	90456	8.414
Total		38392176	1087483	100.000

Compound 3ac HPLC Copper

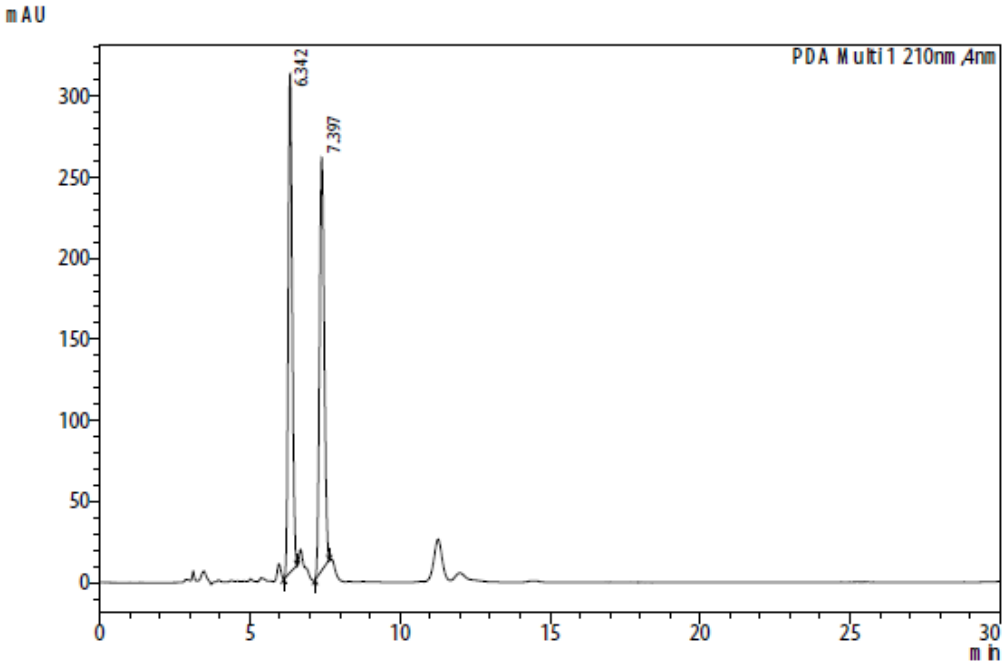


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	10.056	1372983	72500	5.290
2	11.702	24582539	1011693	94.710
Total		25955521	1084193	100.000

Compound 3ad HPLC (Racemic)

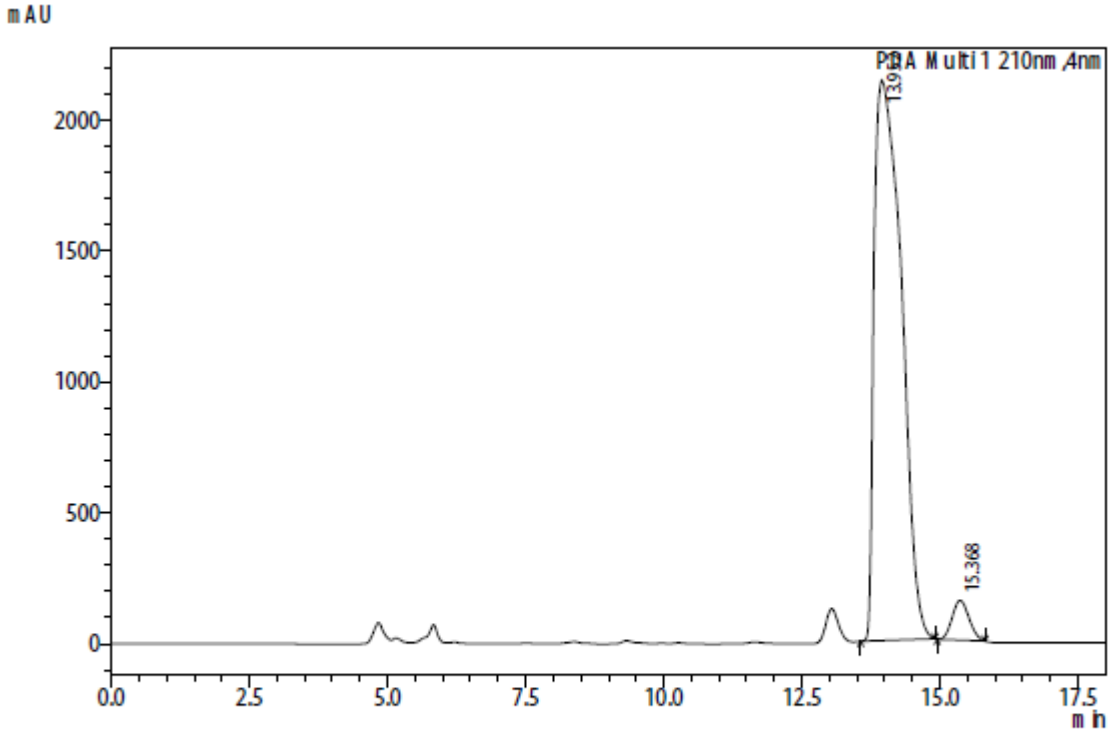


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.342	2866347	307301	50.528
2	7.397	2806489	254826	49.472
Total		5672837	562127	100.000

Compound 3ad HPLC Silver

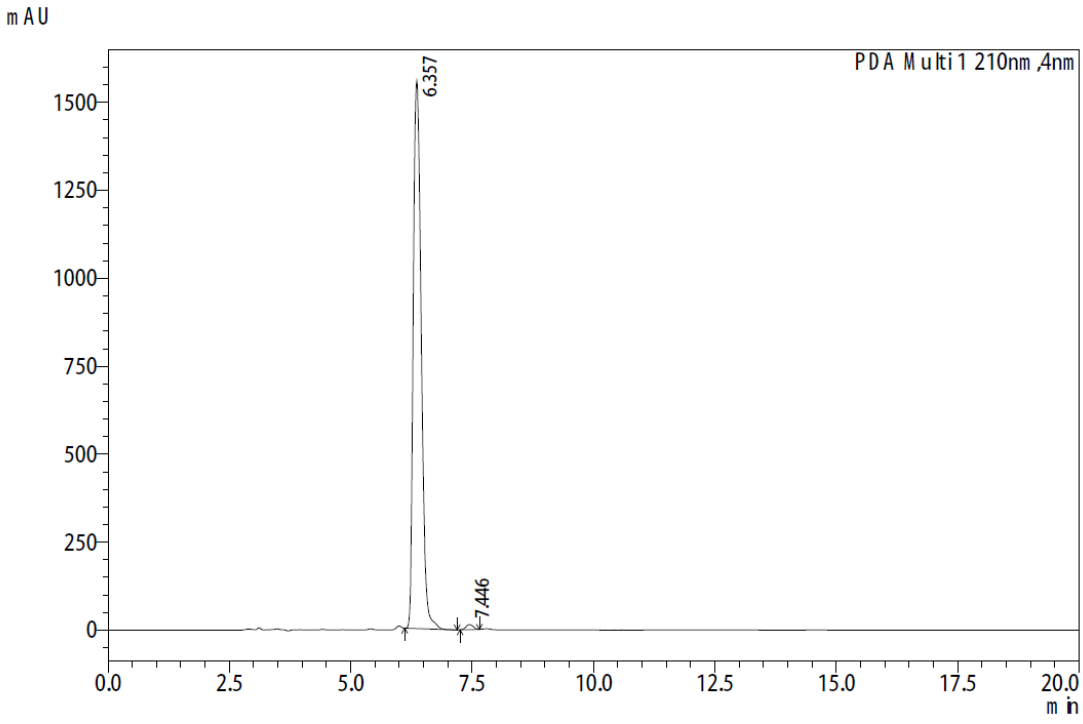


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	13.952	73070794	2139926	95.765
2	15.368	3231770	151605	4.235
Total		76302564	2291531	100.000

Compound 3ad HPLC Copper

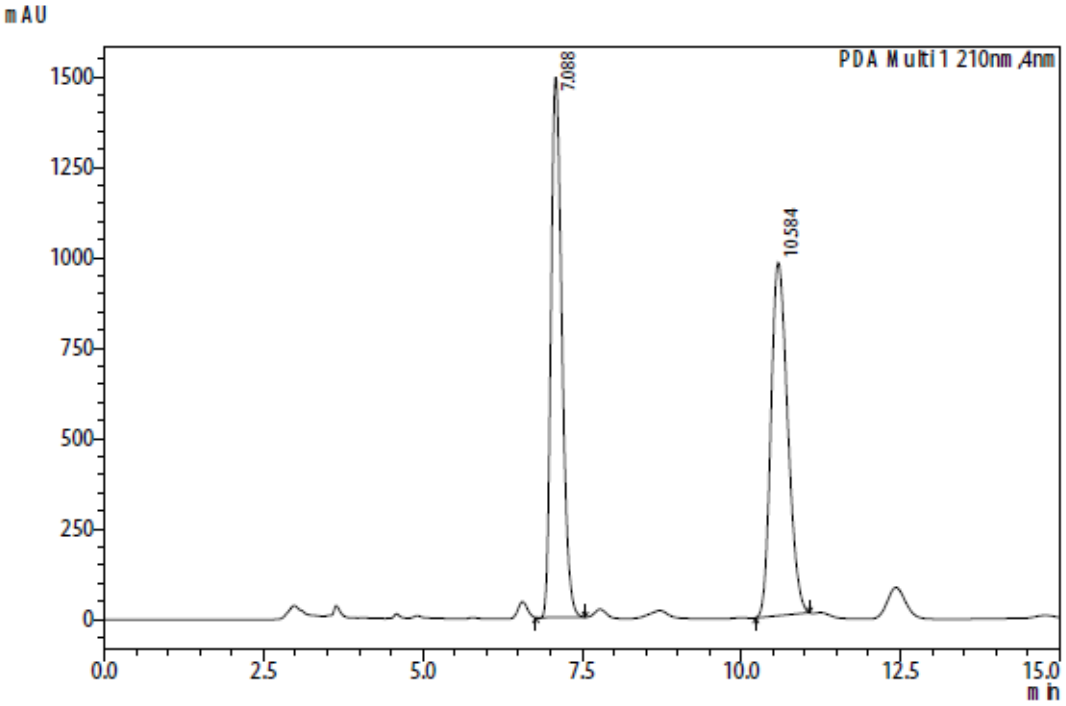


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	6.357	17772552	1556132	99.173
2	7.446	148275	14002	0.827
Total		17920828	1570134	100.000

Compound 3ae HPLC (racemic)

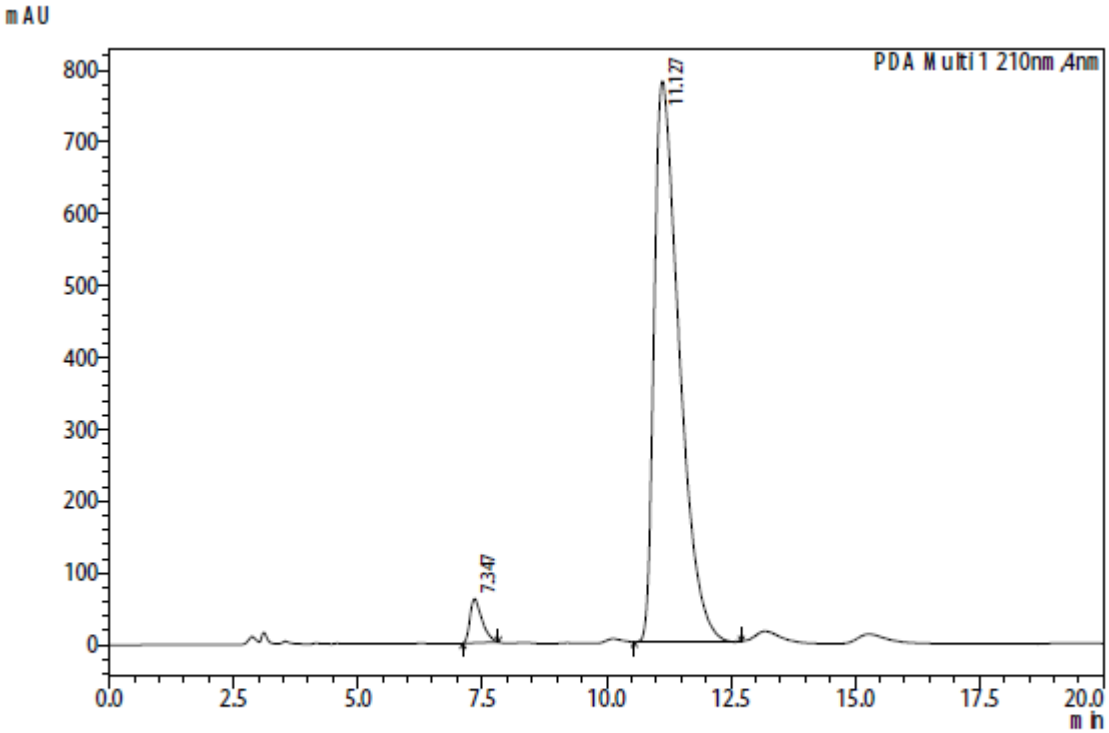


Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.088	17821874	1492184	49.915
2	10.584	17882741	975796	50.085
Total		35704615	2467980	100.000

Compound 3ae HPLC Silver



Peak Table

SPD-M20A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	7.347	1036656	60962	3.645
2	11.127	27399973	780236	96.355
Total		28436629	841198	100.000