A True Brønsted Acid Catalyst for the Enantioselective Protonation Reaction

Cheol Hong Cheon and Hisashi Yamamoto*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

General Procedures:

All reactions were carried out in oven- or flame-dried glassware under an atmosphere of dry argon unless otherwise noted. Except as otherwise indicated, all reactions were magnetically stirred and monitored by analytical thin layer chromatography (TLC) using Whatman pre-coated silica gel flexible plates (0.25 mm) with F254 indicator or Merck pre-coated silica gel plates with F254 indicator. Visualization was accomplished by UV light (254 nm), with combination of potassium permanganate and/or phosphomolybdic acid, solution as an indicator. Flash column chromatography was performed according to the method of Still using silica gel 60 (mesh 230-400) supplied by Silicycle. Yields refer to chromatographically and spectrographically pure compounds, unless otherwise noted.

Commercial grade reagents and solvents were used without further purification except as indicated below. Toluene (anhydrous, 99.8 %, 18 L in Pure-Pac^{TM}), dichloromethane (anhydrous, 99.9%, 18L in Pure-Pac^{TM}), hexanes (anhydrous, 99.9%, 18L in Pure-Pac^{TM}), and THF (anhydrous, 99.9%, 18L in Pure-Pac^{TM}) purchased from Aldrich were purified by M. BRAUN solvent purification system (A2 Alumina). Propionitrile was dried over 4 Å MS.

^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded on a Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C, 471 MHz ^{19}F, 202 MHz ^{31}P). Tetramethylsilane was used as an internal standard for ^{1}H NMR (δ: 0.0 ppm), $CDCl_3$ for ^{13}C NMR (δ: 77.0 ppm), $CFCl_3$ for ^{19}F NMR (δ: 0.0 ppm) as an external standard, and H_3PO_4 for ^{31}P NMR (δ: 0.0 ppm) as an external standard. The proton spectra are reported as follows δ (position of proton, multiplicity, coupling constant *J*, number of protons). Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (quintet), h (septet), m (multiplet) and br (broad). High-performance liquid chromatography (HPLC) was performed on a Varian ProStar Series equipped with a variable wavelength detector using chiral stationary columns (0.46 cm x 25 cm) from Daicel. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter.

1. Synthesis of Chiral Brønsted Acids

Synthesis of (*S*)-BINOL derivatives

All 3,3'-diaryl-2,2'-dihydroxy-1,1'-dinaphthyls were prepared following the reported procedure, except (*S*)-3,3'-bis-(4-*t*-butyl-2,6-diisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl.

(*S*)-3,3'-Di-(2-phenyl)-2,2'-dihydroxy-1,1'-dinaphthyl[1]

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 5.36 (s, 2H), 7.15-7.42 (m, 12H), 7.45 (m, 4H), 7.93 (d, *J* = 7.7 Hz, 2H), 8.03 (s, 2H).

(*S*)-3,3'-Bis-(2-mesityl)-2,2'-dihydroxy-1,1'-dinaphthyl[2]

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.06 (s, 6H), 2.13 (s. 6H), 2.31 (s, 6H), 5.00 (s, 2H), 7.98 (s, 4H), 7.23-7.36 (m, 6H), 7.72 (s, 2H), 7.84 (d, *J* = 8.1Hz, 2H).

(*S*)-3,3'-Bis-(2,4,6-triisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl[3]

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.06 (s, 6H), 2.13 (s. 6H), 2.31 (s, 6H), 5.00 (s, 2H), 7.98 (s, 4H), 7.23-7.36 (m, 6H), 7.72 (s, 2H), 7.84 (d, *J* = 8.1Hz, 2H).

(*S*)-3,3'-Bis-(4-(1-admantyl)-2,6-diisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl[4]

^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.06 (d, *J* = 6.9 Hz, 6H), 1.10 (d, *J* = 6.9 Hz, 6H), 1.12 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.80 (m, 18H), 1.99 (m, 12H), 2.12 (m, 6H), 2.72 (m, 2H), 2.88 (m, 2H), 4.92 (s, 2H), 7.26 (m, 2H), 7.29 (m, 2H), 7.31 (m, 4H), 7.36 (m, 2H), 7.78 (s, 2H), 7.86 (d, *J* = 8.1Hz, 2H).

(*S*)-3,3'-Bis-(4-*t*-butyl-2,6-diisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl

1-Bromo-4-*t*-butyl-2,6-diisopropylbenzene To a mixture of 1,3-diisopropylbenzene (2.91 eq, 170 g, 1.05 mol) and $FeCl_3$ (0.44 eq, 26 g, 0.16 mol) was added *t*-BuCl (1 eq, 33 g, 0.36 mol) dropwise over a period of 60 min at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 2 h. After 2 h, H_2O (200 mL) was carefully added to the reaction mixture at 0 ^{o}C. The organic layer was extracted with ethyl acetate (200 mL x 2), dried over Na_2SO_4, and concentrated. The dark mixture was distilled under vacuum. Unreacting starting material was first distilled out (69-71 ^{o}C at 5 mmHg). The desired product (27.2 g, 0.12 mol) was obtained as colorless oil at 98-100 ^{o}C at 5 mmHg. The above product (1 eq, 27.2 g, 0.12 mol), Fe (0.19 eq, 1.3 g, 23 mmol) and CCl_4 (120 mL) were added to a flask, which was wrapped with aluminum foil. A bromine (1.1 eq, 22 g, 136 mmol) in CCl_4 (20 mL) was added to the reaction mixture through an addition funnel over a period of 60 min at 0 ^{o}C. The resulting mixture was allowed to stir at 0 ^{o}C for additional 3 h. After 3h, 15 % of Na_2SO_3 aqueous solution (100 mL) and CH_2Cl_2 (50 mL) were added to the reaction mixture. The mixture was stirred until red color disappeared. The aqueous layer was extracted with CH_2Cl_2 (100 mL x 2), dried over Na_2SO_4, and concentrated in vacuo. A brown liquid was distilled under vacuum. Colorless oil was obtained at 130-135 ^{o}C at 5 mmHg (25 g, 84 mmol, 23 %).^{1}H NMR (CDCl3, 500 MHz) δ: 1.25 (d, J = 5.8 Hz, 12H), 1.32 (s, 9H), 3.49 (m, 2H), 7.15 (s, 2H); MS (EI) Exact mass calcd for $C_{16}H_{25}Br$ (M+1): 297.2 Found: 297.9.

(4-*t*-Butyl-2,6-diisopropylphenyl)magnesium bromide. A three neck round-bottom flask containing Mg (2 eq, 0.82 g, 34 mmol) was equipped with a condenser and an addition funnel. A 5 mL portion of a 1-bromo-4-*t*-butyl-2,6-diisopropylbenzene (1 eq, 5.0 g, 17 mmol) in Et_2O (30 mL) was added to the flask through the addition funnel. 1,2-Dibromoethane (0.20 mL, 0.002 mmol) was added and waited until the reaction mixture was refluxing. After starting refluxing, the remaining solution was added dropwise over a period of 30 min. The resulting mixture was refluxing under a nitrogen atmosphere for 12 h. The resulting Grignard reagent was titrated and stored in a Schreck tube. (0. 28 M, 30 mL, 8.4 mmol, 50 %).

(*S*)-{3,3'-Bis-(4-*t*-butyl-2,6-diisopropylphenyl)-2,2'-dihydroxy-1,1'-binaphthyl. (*S*)-3,3'-Diiodo-2,2'-dimethoxy-1,1'-binaphthyl(1 eq, 1.27 g, 2.25 mmol) and $NiCl_2(PPh_3)_2$ (0.11 eq, 0.16 g, .25 mmol) were suspended in Et_2O (20 mL). To this suspension was added the above Grignard reagent (4 eq, 0.28 M, 30 mL, 8.4 mmol) slowly at room temperature. The reaction mixture was allowed to stir for 10 min. The resulting dark green solution was refluxed for 24 h. The reaction mixture was cooled to 0 ^{o}C and quenched slowly by the addition of 1*N* HCl solution (10 mL). The aqueous layer was extracted with ether (50 mL)

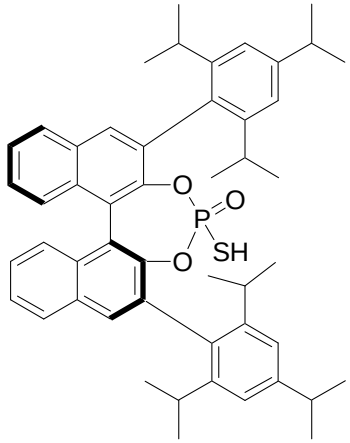
twice, dried over Na_2SO_4, and concentrated. Without further purification, to a solution of this crude product in CH_2Cl_2 (20 mL) was added BBr_3 (1 M in CH_2Cl_2) (3 eq, 6.7 mL, 6.7 mmol) slowly at 0 ^oC. The resulting mixture was allowed to warm up to room temperature and stirred for 6 h. The mixture was then cooled to 0 ^oC, and the reaction was quenched by the slow addition of 25 mL water. Aqueous layer was extracted with CH_2Cl_2 (25 mL X 2), dried over Na_2SO_4, and concentrated. Chromatography on silica (hexanes/EtOAc, 50/1) gave 0.89 g (1.24 mmol, 55 %) of the desired product as an foamy solid. ^1H NMR ($CDCl_3$, 500 MHz) δ: 1.03 (d, *J* = 6.8 Hz, 6H), 1.08-1.12 (m, 12H), 1.21 (d, *J* = 6.8 Hz, 6H), 1.38 (s, 18H), 2.68-2.71 (m, 2H), 2.84-2.88 (m, 2H), 4.91 (s, 2H), 7.28-7.31 (m, 8H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.77 (s, 2H), 7.86 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.9, 24.1, 24.5, 31.1 (2C), 31.6, 35.1, 113.2, 120.2, 123.9, 124.7, 126.8, 128.4, 129.2 (2C), 130.2, 130.8, 133.6, 147.4 (2C), 150.8, 151.5; $[\alpha]^{23.9}_D$ = -64.6 (c 1.29, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{52}H_{61}O_2$ (M-1): 717.4 Found: 717.2.

Synthesis of Chiral Brønsted Acids (1-5)

(*S*)-{3,3'-Bis-(2,4,6-triisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}phosphoric acid (1)[5]

This compound was prepared following the reported procedure and ^1H NMR data was in agreement with the literature. After purification by column chromatography on silica gel (hexanes/EtOAc, 1/1), the product in Et_2O was washed with 4 *N* HCl (aq) twice, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Foam-like solid was obtained. ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.92 (d, *J* = 6.7 Hz, 12H), 0.99 (d, *J* = 6.6 Hz, 6H), 1.11 (d, *J* = 6.8 Hz, 6H), 1.20-1.25 (m, 12H), 2.54-2.60 (m, 4H), 2.81-2.86 (m, 2H), 6.94 (s, 2H), 6.97 (s, 2H), 7.26-7.32 (m, 4H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.82 (s, 2H), 7.87 (d, J = 8.2 Hz, 2H); ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 3.68.

(*S*)-{3,3'-Bis-(2,4,6-triisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}thiophosphoric acid (2)



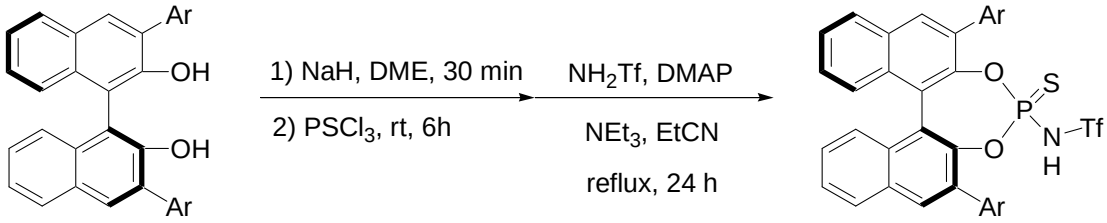
To a solution of (*S*)-3,3'-bis-(2,4,6-triisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl in dimethoxyethane was added NaH at 0 ^oC. The resultant mixture was stirred for 30 min at room temperature. $PSCl_3$ was added to the reaction mixture droppwise. The reaction mixture was stirred at room temperature for 6 h. After 6 h, H_2O was added to the reaction mixture, and the reaction mixture was allowed to reflux for 12 h. The reaction mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ aqueous solution, extracted with Et_2O, dried over Na_2SO_4, and concentrated. After purification by column chromatography on silica gel (hexanes/EtOAc, 2/1), the product was re-dissolved in Et_2O was washed with 4 *N* HCl (aq) twice, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Foam-like solid was obtained in 85 % yield. ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.86 (d, *J* = 6.5 Hz, 3H), 0.97-1.00 (m, 6H), 1.04-1.15 (m, 6H), 1.21-1.43 (m, 21H), 2.65-3.02 (m, 4H), 3.33-3.40 (m, 2H), 6.99 (s, 4H), 7.07-7.11 (m, 3H), 7.22-7.34 (m, 4H), 7.47-7.50 (m, 2H), 7.87 (s, 1H), 7.90-7.93 (dd, *J* = 3.8, 8.2 Hz, 1H), 7.95 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 23.2 (2C), 23.8, 24.0, 24.2 (2C), 25.2 (2C), 26.8, 27.5, 30.4, 30.8, 31.0, 31.1, 31.4, 34.4, 120.2, 120.8, 121.2, 121.6, 122.5, 122.9, 125.7, 125.8, 126.2 (2C), 127.4,

127.6, 128.3, 128.4, 131.1, 131.6, 131.9, 132.3, 132.6, 132.7, 133.0, 145.7, 145.8, 147.0, 147.1, 147.3, 147.9, 148.0, 148.2, 148.4, 148.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 68.4; $[\alpha]^{24.3}_D$ = +2.6 (c 1.20, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{50}H_{56}O_3PS$ (M-1): 767.3 Found: 767.1.

(*S*)-{3,3'-Bis-(2,4,6-triisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflylphosphoramide (3)[6]

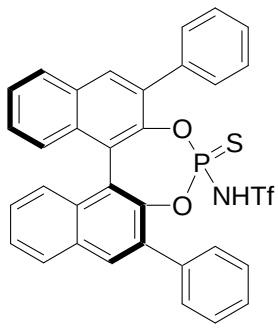
This compound was prepared following the reported procedure and ^{1}H NMR data was in agreement with the literature. After purification by Column chromatography on silica gel (hexanes/EtOAc, 2/1), the product in Et_2O was washed with 4 *N* HCl (aq) twice, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Foam-like solid was obtained in high yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.94 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 6.5 Hz, 3H), 1.16 (t, *J* = 6.5 Hz, 6H), 1.20 (d, *J* = 6.5 Hz, 3H), 1.24-1.30 (m, 18H), 2.55-2.65 (m, 1H), 2.65-2.80 (m, 3H), 2.90-3.00 (m, 2H), 7.04 (s, 1H), 7.11 (s, 2H), 7.16 (s, 1H), 7.27-7.34 (m, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.97 (s, 2H); ^{31}P NMR ($CDCl_3$, 202 MHz) δ: -2.57.

Synthesis of Chiral N-triflylthiophosphamides (4a-4e)



General procedures: To a solution of BINOL derivatives in dimethoxyethane was added NaH at 0 °C. The resultant mixture was stirred for 30 min at room temperature. $PSCl_3$ was added to the reaction mixture dropwise. The reaction mixture was stirred at room temperature for 6 h. After 6 h, the reaction mixture was quenched with saturated $NaHCO_3$ aqueous solution, extracted with Et_2O, dried over Na_2SO_4, and concentrated. The resultant crude mixture was used for amidation reaction without further purification. The resultant crude mixture was dissolved in EtCN. NH_2Tf, DMAP, and NEt_3 were added into the reaction mixture. The resultant reaction mixture was allowed to reflux for 24 h. The reaction mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ aqueous solution, extracted with Et_2O, dried over Na_2SO_4, and concentrated. After purification by column chromatography on silica gel (hexanes/EtOAc, 3/1), the product was re-dissolved in Et_2O was washed with 4 *N* HCl (x 2), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Foam-like solid was obtained.

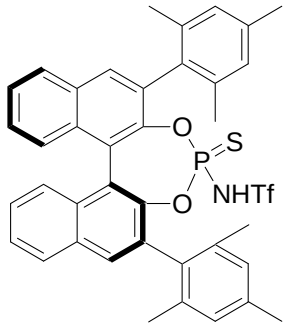
(*S*)-{3,3'-diphenyl-1,1'-binaphthalen-2,2'-yl}-*N*-triflyl-thiophosphoramide (4a)



Thiophosphoramide (**4a**) was obtained as a foamy solid in 70 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 7.32-7.38 (m, 4H), 7.41-7.47 (m, 6H), 7.50-7.54 (m, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.98-8.01 (m, 2H), 8.06 (s, 1H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 119.7 (q, J = 322.5 Hz), 123.5 (2C), 123.9 (2C), 126.0, 126.1, 126.6 (2C), 127.2, 127.5, 128.0, 128.2, 128.6 (2C), 130.5, 131.2, 131.4, 131.7, 131.9, 132.3, 132.4, 134.5 (2C),

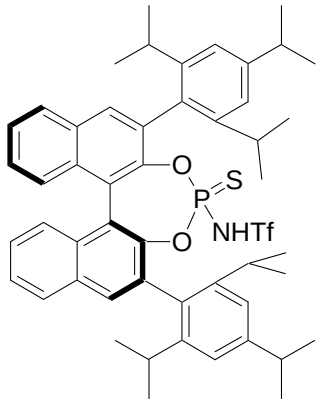
134.9 (2C), 137.6, 137.8, 144.3, 144.4, 145., 145.8, 164.1; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-77.44; ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 64.4; $[\alpha]^{24.3}_D$ = +223.8 (c 1.25, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{33}H_{20}F_3NO_4PS_2$ (M-1): 646.0 Found: 645.8.

(*S*)-{3,3'-Bis(2,4,6-trimethylphenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflyl-thiophosphoramide (4b)



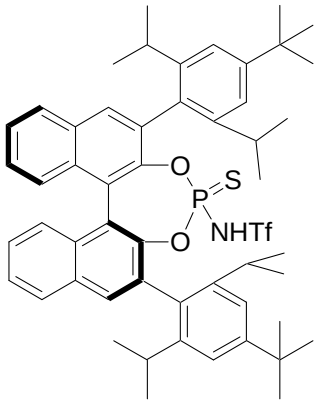
Thiophosphoramide (**4b**) was obtained as a foamy solid in 45 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 2.05 (s, 3H), 2.06 (s, 3H), 2.16 (s, 3H), 2.24 (s, 3H), 2.31 (s, 6H), 6.91-7.00 (m, 4H), 7.27-7.29 (m, 4H), 7.47-7.49 (m, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.90-7.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 20.1, 20.5, 21.3, 22.4, 29.9, 30.5, 123.1 (q, *J* = 112 Hz), 125.7, 125.8, 126.2, 126.5, 127.3, 127.4, 127.7, 127.8, 128.4, 128.6, 128.7, 131.4, 131.5, 131.8, 132.0, 132.2, 132, 3, 133.2 (2C), 133.7, 134.9, 137.1, 137.3, 137.5, 137.6, 145.4, 145.5, 146.8, 147.0; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-78.43; ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 67.7; $[\alpha]^{22.7}_D$ = +72.4 (c 0.27, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{39}H_{32}F_3NO_4PS_2$ (M-1): 730.1 Found: 729.9.

(*S*)-{3,3'-Bis(2,4,6-triisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflyl-thiophosphoramide (4c)



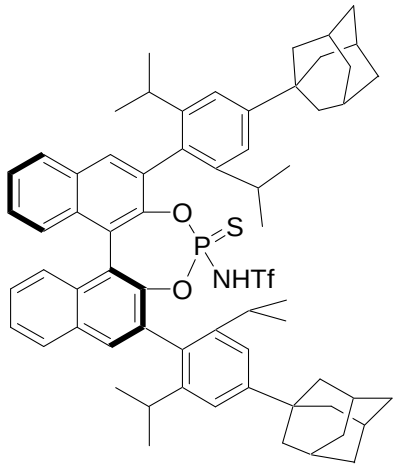
Thiophosphoramide (**4c**) was obtained as a foamy solid in 52 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.85 (d, *J* = 6.5 Hz, 3H), 0.99 (d, *J* = 6.5 Hz, 3H), 1.10 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.25-1.35 (m, 24H), 2.54-2.59 (m, 1H), 2.69-2.82 (m, 2H), 2.90-3.06 (m, 3H), 7.03 (s, 1H), 7.12-7.18 (m, 4H), 7.26-7.34 (m, 3H), 7.53 (t, *J* = 7 Hz, 2H), 7.95 (d, *J* = 8 Hz, 2H), 7.98 (s, 1H), 8.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 22.4, 23.3, 23.7, 23.8, 24.0 (2C), 24.1, 24.3, 25.3, 25.6, 27.1, 27.6, 30.5, 31.0 (2C), 31.7, 34.6, 34.7, 120.3, 121.3, 121.9, 122.1, 122.2 (q, *J* = 106 Hz), 126.4 (2C), 126.7, 126.9, 127.4, 127.5, 128.5 (2C), 129.8, 130.2 (2C), 130.6, 131.3, 131.5, 132.5, 132.6, 133.0, 133.5, 144.9, 145.0, 146.1, 146.4, 146.5, 147.0, 147.5, 148.7, 149.0, 150.0; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-75.34; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 52.7; $[\alpha]^{24.3}_D$ = +15.5 (c 1.04, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{51}H_{56}F_3NO_4PS_2$ (M-1): 898.3 Found: 898.0.

(*S*)-{3,3'-Bis(4-*t*-butyl-2,6-diisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}-*N*-triflyl-thiophosphoramide (4d)



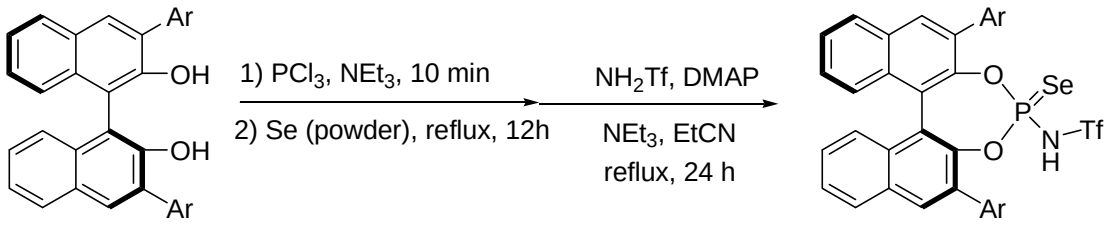
Thiophosphoramide (**4d**) was obtained as a foamy solid in 57 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz) ; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.80 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 1.12-1.25 (m, 18H), 1.28 (s, 9H), 1.31 (s, 9H), 2.59-2.65 (m, 1H), 2.75-2.81 (m, 1H), 3.00-3.06 (m, 1H), 3.10-3.15 (m, 1H), 7.05-7.10 (m, 2H), 7.16 (s, 1H), 7.23 (t, J = 7.5 Hz, 3H), 7.27 (s, 1H), 7.31 (s, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.83 (s, 1H), 7.87 (d, J = 7.5 Hz, 2H), 7.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 21.7, 23.6, 23.9, 24.2, 24.9 (2C), 26.6, 27.3, 30.3, 30.7, 30.8 (2C), 31.1, 31.4, 34.7, 34.8, 118.9, 119.3, 119.8, 120.2, 122.5 (q, J = 153 Hz), 125.3, 125.4, 125.5, 126.0, 126.2, 126.9, 127.0, 128.0, 128.1, 130.6, 130.7, 131.2, 131.4, 131.9, 132.3, 132.4, 132.6, 132.8, 145.5, 145.6, 147.1, 147.2 (2C), 147.3, 147.8, 148.2, 150.4, 151.3; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-78.37; ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 67.0; $[\alpha]^{24.7}_{D}$ = +38.5 (c 1.43, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{53}H_{60}F_3NO_4PS_2$ (M-1): 926.2 Found: 926.1.

(*S*)-{3,3'-Bis(4-adamantyl-2,6-diisopropylphenyl-1,1'-binaphthalen-2,2'-yl}-N-triflyl-thiophosphoramide (4e)

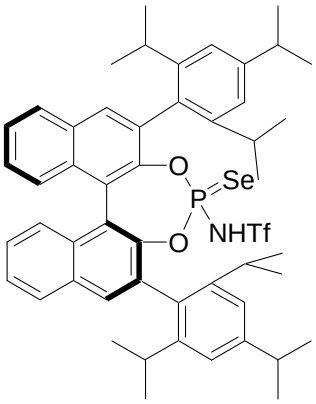


Thiophosphoramide (**4e**) was obtained as a foamy solid in 42 % yield. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.81 (d, *J* = 7.0 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.21-1.24 (m, 6H), 1.33 (d, *J* = 6.5 Hz, 6H), 1.66 (s, 3H), 1.68 (s, 3H), 1.76 (s, 6H), 1.91 (s, 6H), 1.94 (s, 6H), 2.01 (s, 3H), 2.08 (s, 3H), 2.57-2.63 (m, 1H), 2.79-2.85 (m, 1H), 3.00-3.12 (m, 2H), 7.05 (d, *J* = 8.5 Hz, 1H), 7.11 (d, *J* = 9.0 Hz, 1H), 7.14 (s, 1H), 7.21-7.24 (m, 3H), 7.26 (s, 1H), 7.29 (s, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.83 (s, 1H), 7.86-7.88 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 22.0, 23.5, 23.8, 24.0, 24.4, 25.3, 27.0, 27.5, 29.0, 29.2, 30.5, 31.0, 31.1, 36.7, 37.0, 43.1, 43.3, 118.8, 119.0, 119.6, 119.9, 122.8 (q, J = 156 Hz), 125.5, 125.6, 125.7, 126.2, 126.4, 127.2, 128.2, 128.3, 129.0, 130.8, 130.9, 131.2, 131.4, 131.6, 132.1, 132.5, 132.7, 132.9, 133.0, 133.1, 145.6, 145.7, 147.3, 148.3, 148.6, 150.9, 151.9; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-78.37; ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 67.0; $[\alpha]^{25.2}_{D}$ = +29.4 (c 1.57, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{65}H_{72}F_3NO_4PS_2$ (M-1): 1082.3 Found: 1082.2.

(*S*)-{3,3'-Bis-(2,4,6-triisopropylphenyl)-1,1'-binaphthalen-2,2'-yl}-N-triflyl-selenophosphoramide (5)



Ar = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$



To a solution of PCl_3 in toluene was added NEt_3 at 0 ^oC with vigorous stirring under nitrogen atmosphere. To the resultant solution was added (*S*)-3,3'-bis-(2,4,6-triisopropylphenyl)-2,2'-dihydroxy-1,1'-dinaphthyl in toluene at 0 ^oC, the reaction mixture was stirred at the same temperature for 10 min. After the addition of elemental selenium, the mixture was warmed to 110 ^oC and stirred for an additional 12 h. After 12 h, the reaction mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ aqueous solution, extracted with Et_2O, dried over Na_2SO_4, and concentrated.[7] The resultant crude mixture was used for amidation reaction without further purification. The resultant crude mixture was dissolved in EtCN. NH_2Tf, DMAP, and NEt_3 were added into the reaction mixture. The resultant reaction mixture was allowed to reflux for 24 h. The reaction mixture was cooled to room temperature, quenched with saturated $NaHCO_3$ aqueous solution, extracted with Et_2O, dried over Na_2SO_4, and concentrated. After purification by Column chromatography on silica gel (hexanes:EtOAc, 3:1), the product was re-dissolved in Et_2O was washed with 4 *N* HCl (aq) twice, dried over anhydrous Na_2SO_4, and concentrated in vacuo. Selenophosphoramide (5) was obtained as a foamy solid in 42 % yield. ^{1}H NMR ($CDCl_3$) δ: 0.78 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 1.12 (d, *J* = 6.5 Hz, 3H), 1.16 (d, *J* = 6.5 Hz, 3H), 1.21-1.28 (m, 18H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.34 (d, *J* = 7.0 Hz, 3H), 2.54-2.60 (m, 1H), 2.79-2.85 (m, 1H), 2.87-2.95 (m, 2H), 2.98-3.04 (m, 1H), 3.12- 3.18 (m, 1H), 7.00 (s, 1H), 7.03-7.08 (m, 2H), 7.10 (s, 1H), 7.13 (s, 1H), 7.20 (s, 1H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.44-7.48 (m, 2H), 7.82 (s, 1H), 7.89 (t, *J* = 7.5 Hz, 2H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ: 21.5, 23.7, 23.8, 24.0, 24.2, 24.3, 24.4, 25.0 (2C), 26.8, 27.7, 29.8, 30.5, 30.8, 30.9, 31.0, 33.8, 34.3, 120.1, 120.7, 121.5, 121.6,122.9 (q, J = 180 Hz), 125.5, 125.7, 126.2, 126.6, 127.0, 127.2, 128.2, 128.4, 130.7 (2C), 130.9, 131.6, 132.4 (2C), 132.6, 132.7, 132.9, 133.2 (2C), 145.3, 145.4, 147.4, 147.5, 147.6, 148.4, 148.9, 149.5, 149.60; ^{19}F NMR ($CDCl_3$, 471 MHz) δ:-78.7; ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 62.4; $[\alpha]^{21.7}_D$ = +23.6 (c 1.36, $CHCl_3$); MS (APCI) Exact mass calcd for $C_{51}H_{56}F_3NO_4PSSe$ (M-1): 946.2 Found: 946.0.

2. Structure determination by X-ray crystallography

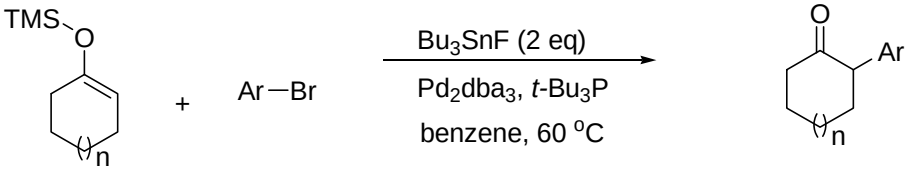
X-ray crystallographic analysis of **4c** reveals that P-N bond (1.60 Å) is almost as same as the P-N bond (1.61 Å) in the phosphoramide.[4] In addition, the observed P-S bond (1.92 Å) is much shorter than P-S

bond (2.09 Å) and almost as same as P=S bond (1.93 Å).[8] Thus, as suggested in the molecular structures of 4a-e above, P-S bond has double bond character and the proton is located on the nitrogen atom, instead of the sulfur atom bonded to the phosphorus atom.

3. Synthesis of 2-substituted cyclic ketones

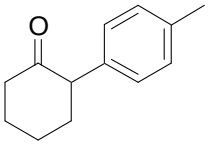
3-1. Synthesis of 2-aryl cyclic ketones

All α-aryl cyclic ketones were prepared by α-arylation of trimethylsilyl (TMS) enol ethers with aryl halides.[9]

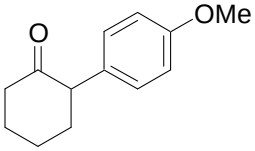


n = 1, 2

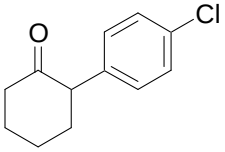
General Procedures: To a solution of TMS enol ether of cyclic ketone (20 mmol), $Pd_2(dba)_3$ (0.23 g, 0.25 mmol), and Bu_3SnF (6.18 g, 20 mmol) under nitrogen was added a solution of $^tBu_3P$ (1.0 M, 0.6 mL) in benzene (40 mL) at room temperature. The resultant mixture was heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was diluted with ether (200 mL) (when tin residue precipitated, it was removed by decantation with ether), washed with 1 *N* aqueous NaOH twice, followed by brine (50 mL x 2), dried over Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc, 10/1) on silica gel.



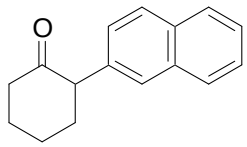
2-(4-Methylphenyl)cyclohexanone was obtained as a white solid (1.34 g, 72 % yield) and ^{1}H NMR was in agreement with the literature.[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.78-1.84 (m, 2H), 1.95-2.05 (m, 2H), 2.12-2.17 (m, 1H), 2.22-2.27 (m, 1H), 2.22 (s, 3H), 2.39-2.56 (m, 2H), 3.56 (dd, *J* = 5.4, 12.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H).



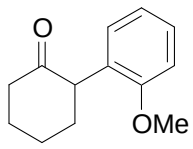
2-(4-Methoxyphenyl)cyclohexanone was obtained as a white solid (1.34 g, 72 % yield) and ^{1}H NMR was in agreement with the literature.[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.75-1.85 (m, 2H), 1.94-2.02 (m, 2H), 2.10-2.15 (m, 1H), 2.22-2.26 (m, 1H), 2.49-2.53 (m, 2H), 3.56 (dd, *J* = 5.5, 12.5 Hz, 1H), 3.78 (s, 3H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H).



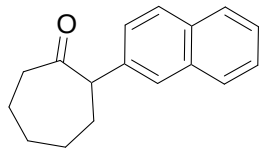
2-(4-Chlorophenyl)cyclohexanone was obtained as a white solid (1.29 g, 62 % yield), and ^{1}H NMR was in agreement with the literature.[10] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.79-1.91 (m, 2H), 1.95-2.02 (m, 2H), 2.15-2.28 (m, 2H), 2.41-2.54 (m, 2H), 3.59 (dd, *J* = 5.4, 12.4 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H).



2-(2-naphthyl)cyclohexanone was obtained as a white solid (1.54 g, 70 % yield) and ^{1}H NMR was in agreement with the literature.[11] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.81-1.91 (m, 2H), 2.00-2.07 (m,1H), 2.12-2.21 (m, 2H), 2.31-2.36 (m, 1H), 2.46-2.58 (m, 2H), 3.77 (dd, *J* = 5.6, 12.2 Hz, 1H), 7.27 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.41-7.46 (m, 2H), 7.60 (s, 1H), 7.77-7.83 (m, 3H).



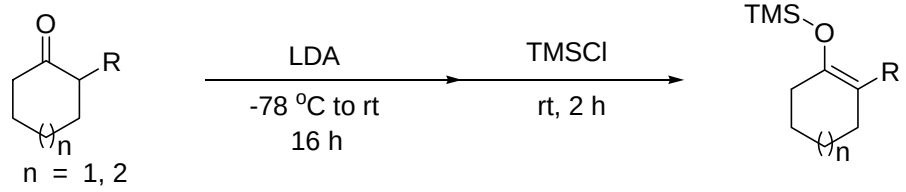
2-(2-Methoxyphenyl)cyclohexanone was obtained as oil (1.02 g, 50 %) and ^{1}H NMR was in agreement with the literature.[9] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.73-1.84 (m, 2H), 1.98-2.05 (m, 2H), 2.13-2.21 (m, 2H), 2.44-2.53 (m, 2H), 3.78 (s, 3H), 3.94 (dd, *J* = 5.5, 12.5 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H), 6.96 (t, *J* = 8 Hz, 1H), 7,12 (d, *J* = 8 Hz, 1H), 7.24 (t, *J* = 8 Hz, 1H).



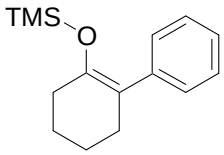
2-(2-Naphthyl)cyclohexanone was obtained as oil (1.37 g, 57 %). ^{1}H NMR ($CDCl_3$, 500 MHz,) δ: 1.49-1.53 (m, 2H), 1.66-1.73 (m, 1H), 1.99-2.15 (m, 4H), 2.20-2.23 (m, 1H), 2.55-2.58 (m, 1H), 2.72-2.78 (td, *J* = 12.8, 3.1 Hz, 1H), 3.88 (dd, *J* = 4.2, 11.4 Hz, 1H), 7.37 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.42-7.48 (m, 2H), 7.67 (s, 1H), 7.79-7.81 (m, 3H); ^{13}C NMR ($CDCl_3$) δ: 25.5, 28.8, 30.3, 32.1, 43.0, 59.1, 125.9, 126.2, 126.4, 127.8, 128.0, 128.3, 129.8, 132.6, 133.6, 138.0, 213.8; MS (APCI) Exact mass calcd for $C_{17}H_{19}O$ (M+1): 239.2 Found: 239.1.

3-2. Synthesis of silyl enol ethers of 2-substituted cyclic ketones (6a-j)

All silyl enol ethers of 2-substituted cyclic ketones were synthesized by the following method, except **6j**.

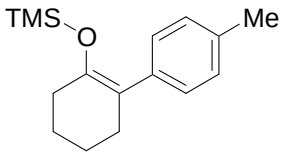


General procedures of 6a-i: To a solution of lithium diisopropylamide (LDA) (4.8 mmol) in THF was added 2-substituted cyclic ketone (5.0 mmol) at -78 °C. The reaction mixture was warmed up to room temperature and stirred for 16 h. After 16h, trimethylsilyl chloride (TMSCl) was added to the reaction mixture. The reaction mixture was allowed to stir for additional 2 h. After then, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with ether, followed by brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (hexanes/EtOAc, 20:1) on silica gel.

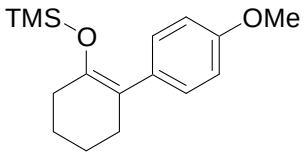


The silyl enol ether (**6a**) was obtained as oil (1.15 g, 93 %) and ^{1}H NMR was in agreement with the literature.[12,13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.05 (s, 9H), 1.64-

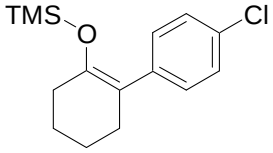
1.77 (m, 4H), 2.15-2.19 (m, 2H), 2.34-2.38 (m, 2H), 7.12-7.15 (m, 1H), 7.25-7.28 (m, 2H), 7.34-7.36 (dd, *J* = 1.3, 8.2 Hz, 2H).



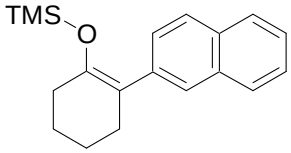
The silyl enol ether (**6b**) was obtained as oil (1.10 g, 84 %) and ^{1}H NMR was in agreement with the literature.[13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.04 (s, 9H), 1.65-1.76 (m, 4H), 2.15-2.18 (m, 2H), 2.31 (s, 3H), 2.32-2.36 (m, 2H), 7.07-7.09 (d, *J* = 7.9 Hz, 2H), 7.25-7.26 (d, *J* = 7.9 Hz, 2H).



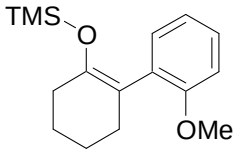
The silyl enol ether (**6c**) was obtained as oil (1.18 g, 85 %) and ^{1}H NMR was in agreement with the literature.[12,13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.04 (s, 9H), 1.65-1.77 (m, 4H), 2.14-2.17 (m, 2H), 2.31-2.35 (m, 2H), 3.80 (s, 3H), 6.80-6.85 (d, *J* = 8.8 Hz, 2H), 7.28-7.31 (d, *J* = 8.8 Hz, 2H).



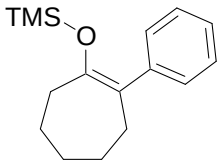
The silyl enol ether (**6d**) was obtained as oil (1.13 g, 80 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.02 (s, 9H), 1.67-1.75 (m,4H), 2.15-2.18 (m, 2H), 2.31-2.34 (m, 2H), 7.22-7.24 (d, *J* = 8.6 Hz, 2H), 7.30-7.32 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 0.78, 23.4, 23.5, 29.4, 30.5, 31.2, 114.6, 127.9, 128.4, 128.7, 130.0, 131.1, 140.0, 146.6; MS (EI) Exact mass calcd for $C_{15}H_{21}ClOSi$ (M): 280.1 this compound is not stable in this condition. Instead, the corresponding ketone was observed. Exact mass calcd for the ketone $C_{12}H_{14}ClO$ (M+1):209.1 Found: 209.2.



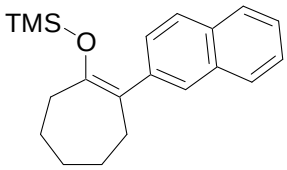
The silyl enol ether (**6e**) was obtained as oil (1.24 g, 84 %) and ^{1}H NMR was in agreement with the literature.[12,13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.06 (s, 9H), 1.72-1.82 (m, 4H), 2.21-2.24 (m, 2H), 2.47-2.49 (m, 2H), 7.38-7.43 (m, 2H), 7.57-7.59 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.73-7.80 (m, 4H).



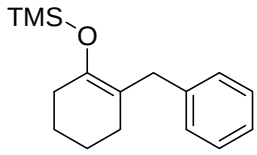
The silyl enol ether (**6f**) was obtained as oil (1.05 g, 76 %). ^{1}H NMR ($CDCl_3$, 500 MHz)) δ: -0.12 (s, 9H), 1.64-1.68 (m, 2H), 1.74-1.79 (m, 2H), 2.13-2.16 (m, 2H), 2.26-2.28 (m, 2H), 3.78 (s, 3H), 6.84-6.90 (m, 2H), 7.11-7.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 1.38, 24.3, 24.7, 30.3, 31.9, 56.5, 111.9, 116.5, 121.3, 128.4, 131.7, 132.5, 146.2, 158.3; MS (APCI) Exact mass calcd for $C_{16}H_{24}O_2Si$ (M): 276.2 this compound is not stable in this condition. Instead, the corresponding ketone was observed. Exact mass calcd for the ketone $C_{13}H_{17}O_2$ (M+1):205.2 Found: 205.1.



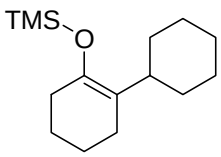
The silyl enol ether (**6g**) was obtained as oil (1.06 g, 81 %) and ^{1}H NMR was in agreement with the literature.[12,13] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.07 (s, 9H), 1.63-1.70 (m, 4H), 1.78-1.82 (m, 2H), 2.42-2.47 (m, 4H), 7.11-7.14 (t, , *J* = 7.2 Hz, 1H), 7.25-7.32 (m, 4H).



The silyl enol ether (**6h**) was obtained as a white solid (1.12 g, 72 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: -0.09 (s, 9H), 1.67-1.76 (m, 4H), 1.82-1.87 (m, 2H), 2.45-2.50 (m, 2H), 2.56-2.62 (m, 2H), 7.39-7.45 (m, 2H), 7.50-7.54 (d, *J* = 8.5 Hz, 1H), 7.68-7.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ: 0.65, 25.4, 27.8, 32.4, 33.3, 36.5, 121.5, 125.1, 125.7, 126.8, 126.9, 127.6, 127.9, 128.0, 131.8, 133.6, 140.6, 151.8; MS (APCI) Exact mass calcd for $C_{20}H_{26}OSi$ (M): 310.2 this compound is not stable in this condition. Instead, the corresponding ketone was observed. Exact mass calcd for the ketone $C_{17}H_{19}O$ (M+1): 239.2 Found: 239.1.



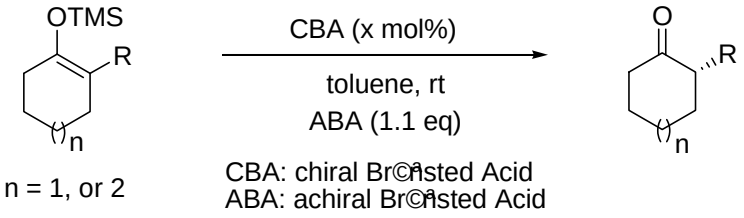
The mixture of thermodynamic (**6i**) and kinetic silyl enol ethers (94:6) was obtained as oil (0.60 g, 46 %) and ^{1}H NMR was in agreement with the literature.[14] ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.20 (s, 9H), 1.51-1.53 (m, 2H), 1.65-1.68 (m, 2H), 1.87-1.89 (m, 2H), 2.11-2.13 (m, 2H), 3.39 (s, 2H), 7.15-7,19 (m, 3H), 7.25-7.28 (m, 2H).



The silyl enol ether (**6j**) was synthesized by the method developed by Cazeau *et al.*.[15]

To a solution of the ketone (0.90 g, 5 mmol), pyridine (0.49 g, 6.25 mmol), and TMSCl (0.65 g, 6 mmol) in acetonitrile (6 mL) was added NaI (0.94 g, 6.25 mmol) in acetonitrile (5 mL) at room temperature. Anhydrous pentane (10 mL) was added to the reaction mixture. The reaction mixture was allowed to stir at room temperature for 24 h. After 24 h, the reaction mixture was extracted with pentane. The organic layer was collected, washed with H_2O and brine, dried over Na_2SO_4, and concentrated under reduced pressure. After column chromatography on silica (pentane:diethyl ether, 40:1), the mixture of thermodynamic and kinetic silyl enol ethers (96:4) was obtained as oil (1.08 g, 85 %). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.17 (s, 9H), 1.20-1.30 (m, 6H), 1.42-1.45 (m, 2H), 1.48-1.53 (m, 2H), 1.57-1.62 (m, 2H), 1.71-1.74 (m, 2H), 1.90-1.93 (m, 2H), 2.00-2.03 (m, 2H), 2.58-2.63 (m, 1H).

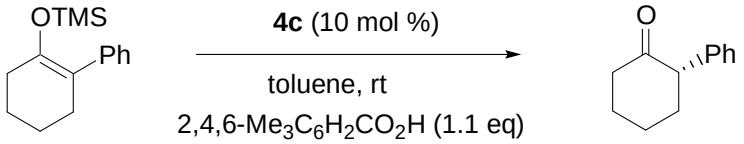
4. **Catalytic Asymmetric Protonation Reactions of Silyl Enol Ethers with Chiral Brønsted Acid**



General Procedures: To a solution of catalytic amount of chiral Brønsted acid and achiral Brønsted source (1.1 eq) in toluene was added silyl enol ether dropwise. The reaction mixture was monitored by thin layer chromatography (TLC). When the silyl enol ether was completely consumed, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, extracted with ether, followed by brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by flash column chromatography (EtOAc/hexanes, 1/10) on silica gel. Enantiomeric ratio (e.r.) was determined by HPLC or GC with a chiral column.

Optimization of Reaction Conditions

1) Solvent effect

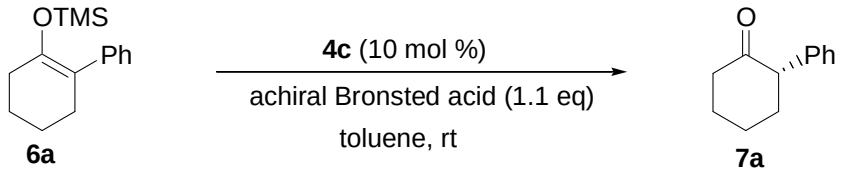


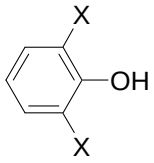
6a **7a**

Solvent	time	% yield	er (config.)
CH_2Cl_2	3 h	>99	83.5:16.5 (*S*)
Et_2O	32 h	80	81:19 (*S*)
THF	32 h	50	76:24 (*S*)
CH_3CN	3 h	>99	58:42 (*S*)
toluene	3 h	>99	89:11 (*S*)
Hexanes	8 h	>99	85.5:14.5 (*S*)

The reactivity and enantioselectivity of **4c** showed dependence on the solvent. High enantioselectivity could be achieved in non-polar solvents, such as toluene, hexanes, and methylene chloride (entries 1,5,6), whereas polar solvents, such as acetonitrile and ether solvent gave rise to lower enantioselectivity (entries 2-4). In addition, the reactivity of **4c** was decreased in ethereal solvents, such as ether and THF (entries 2-3). Among the various solvents tested, toluene was found to be best in terms of enantioselectivity and reactivity.

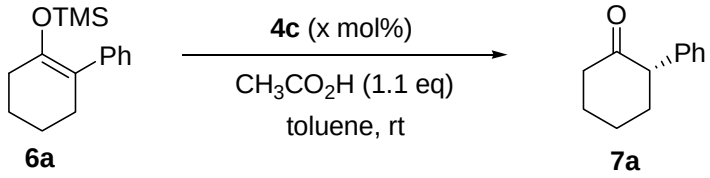
2) Survey of Achiral Brønsted Acids



entry	achiral Brosted acid		time	% yield	er (config.)
1		MeOH	4 h	>99	65:35 (*S*)
2		EtOH	5 h	>99	66:34 (*S*)
3		*i*-PrOH	5 h	>99	84.5:15.5 (*S*)
4		*t*-BuOH	5 h	>99	87:13 (*S*)
5		X = H	3 h	>99	89:11 (*S*)
6		X =Me	3 h	>99	88.5:11.5 (*S*)
7		X = *i*-Pr	3 h	>99	86.5:13.5 (*S*)
8		X = *t*-Bu	48 h	< 1	N. D.
9		X = Ph	24 h	>99	70.5:29.5 (*S*)
10	RCO_2H	$R = CH_3$	3 h	>99	89:11 (*S*)
11		R = Ph	3 h	>99	89:11 (*S*)
12		$R = 2,4,6\text{-}(Me)_3C_6H_2$	3 h	>99	89:11 (*S*)

The steric bulk of the achiral Brønsted acids exhibited a dramatic effect on both reactivity and enantioselectivity. Enantioselectivity increased with the increase in the steric demand of alkyl moiety in alcohols (entries 1-4), whereas bulkier phenols had deleterious effect on both enantioselectivity and reactivity (entries 5-9). Especially, 2,6-di-t-butylphenol gave almost no reaction even after long reaction times (entry 8). Various aliphatic and non-hindered aromatic carboxylic acids showed almost same reactivity and enantioselectivity (entries 10-12). The best enantioselectivity could be achieved with non-hindered phenols and carboxylic acids (entries 5-6, 10-12). Either phenol or acetic acid was suitable as an achiral proton source for asymmetric protonation reaction.

3) Survey catalyst loading

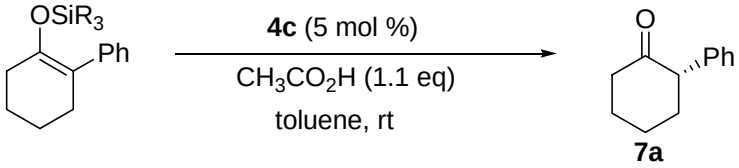


6a **7a**

entry	amount of **4c**	time	% yield	er (config)
1	1 mol%	48 h	>99	88:11 (*S*)
2	3 mol%	7 h	>99	89:11 (*S*)
3	5 mol%	5 h	>99	89:11 (*S*)
4	10 mol%	3.5 h	>99	89:11 (*S*)

Next, we surveyed the catalyst loading with **4c**. Gratifyingly, we could decrease the catalyst loading to 1 mol% without any loss of enantioselectivity. Such a low catalyst loading was an unprecedented example of phosphoric acid catalysis. Even though high enantioselectivity and high yield could be obtained with only 1 mol% of **4c**, 5 mol% of **4c** was used for next experiments in order to get reasonable reactivity of **4c**.

4) Survey of size of silyl groups

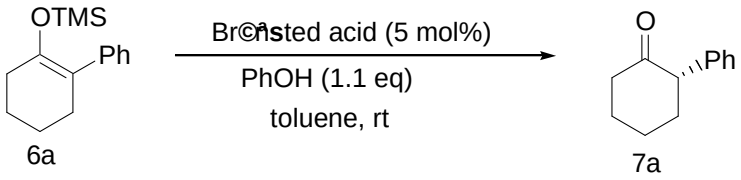


7a

entry	SiR_3	time	% yield	er (config.)
1	TMS	5 h	>99	89:11 (*S*)
2	TBS	8 h	>99	82:18 (*S*)
3	$SiMe_2TMS$	6 h	>99	88:12 (*S*)
4	TIPS	12 h	>99	76:24 (*S*)

Next, the effect of silyl groups on the enantioselectivity with **4c** was investigated. The size of silyl group affected the enantioselectivity. Enantioselectivity decreased with the increase in the size of silyl groups (entries 1-4). Hence, TMS group was chosen as a suitable silyl group.

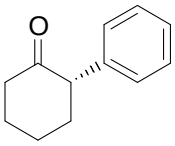
5) Survey of substituents at the 3,3'-positions of the binaphthyl scaffold



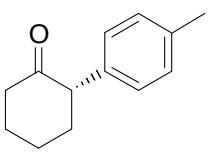
entry	Bronsted acid	time	% yield	er (config.)
1	**4a**	12 h	>99	56:44 (*S*)
2	**4b**	8 h	>99	86:14 (*S*)
3	**4c**	5 h	>99	89:11 (*S*)
4	**4d**	5 h	>99	91:9 (*S*)
5	**4e**	7 h	>99	89:11 (*S*)

With the optimized condition with **4c**, we tested the effect of substituents at the 3,3'-positions of the binaphthyl scaffold. Both enantioselectivity and reactivity highly depended on the substituents at 3,3'-position of BINOL scaffold (entries 1-5). We found that alkyl substituents at 2,6-positions of aromatic substituents at 3,3'-position of the binaphthyl scaffold are crucial for enantioselectivity (entries 1-2). In addition, the substituent at 4-position of aromatic substituents could tune the electronic properties of thiophosphoric acids, which had slight influence on the enantioselectivity (entries 3-5). Enantioselectivity as high as 91:1 er was obtained using **4d** as the catalyst (entry 4).

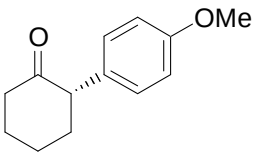
Substrate scope



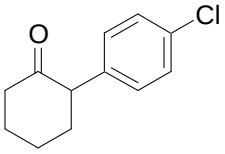
The product (7a)[12,13] was obtained as a white solid in 97 % yield (17.0 mg; 0.098 mmol) and 91:9 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.80-1.84 (m, 2H), 1.99-2.05 (m, 2H), 2.14-2.15 (m, 1H), 2.26-2.30 (m, 1H), 2.45-2.55 (m, 2H), 3.59-3.64 (dd, *J* = 5.0, 12.5 Hz, 1H), 7.11-7.16 (d, *J* = 7.5 Hz, 2H), 7.23-7.27 (t, *J* = 7.5 Hz, 1H), 7.31-7.35 (t, *J* = 7.5 Hz, 2H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes: 2-propanol = 99:1, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major, *S*) = 15.7 min., t_r(minor, *R*) = 17.8 min.



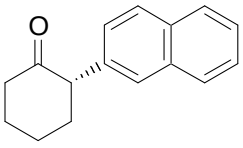
The product (**7b**)[12,13] was obtained as a white solid in 96 % yield (18.1 mg; 0.096 mmol) and 93:7 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.78-1.84 (m, 2H), 1.95-2.05 (m, 2H), 2.12-2.17 (m, 1H), 2.22-2.27 (m, 1H), 2.22 (s, 3H), 2.39-2.56 (m, 2H), 3.56 (dd, *J* = 5.4, 12.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major, *S*) = 14.9 min., t_r(minor, *R*) = 16.2 min.



The product (**7c**)[12,13] was obtained as a white solid in 98 % yield (20.0 mmol; 0.098 mmol) and 92:8 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.75-1.85 (m, 2H), 1.94-2.02 (m, 2H), 2.10-2.15 (m, 1H), 2.22-2.26 (m, 1H), 2.49-2.53 (m, 2H), 3.56 (dd, *J* = 5.5, 12.5 Hz, 1H), 3.78 (s, 3H), 6.87 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major, *S*) = 12.2 min., t_r(minor, *R*) = 15.5 min.

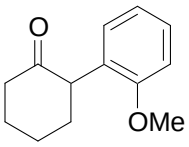


The product (**7d**)[16] was obtained as a white solid in 95 % yield (19.9 mg; 0.095 mmol) and 92:8 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.79-1.91 (m, 2H), 1.95-2.02 (m, 2H), 2.15-2.28 (m, 2H), 2.41-2.54 (m, 2H), 3.59 (dd, *J* = 5.4, 12.4 Hz, 1H), 7.07 (d, *J* = 9.0 Hz, 2H), 7.30 (d, *J* = 9.0 Hz, 2H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OJ column equipped with an OJ guard column (hexanes:2-propanol = 90:10, flow rate = 0.7 mL/min, λ= 210 nm), t_r(major) = 32.3 min., t_r(minor) = 23.1 min.

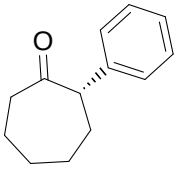


The product (**7e**)[12,13] was obtained as a white solid in 99 % yield (22.2 mg; 0.099 mmol) and 93:7 er. ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ: 1.81-1.91 (m, 2H), 2.00-2.07 (m,1H), 2.12-2.21 (m, 2H), 2.31-2.36 (m, 1H), 2.46-2.58 (m, 2H), 3.77 (dd, *J* = 5.6, 12.2 Hz, 1H), 7.27 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.41-7.46 (m, 2H), 7.60 (s,

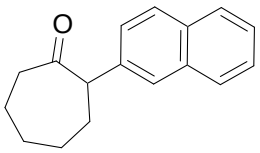
1H), 7.77-7.83 (m, 3H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major, *S*) = 25.9 min., t_r(minor, *R*) = 32.1 min.



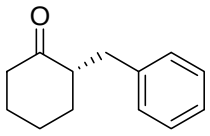
The product (**7f**) was obtained as oil in 97 % yield (19.8 mg; 0.097 mmol) and 86:14 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.73-1.84 (m, 2H), 1.98-2.05 (m, 2H), 2.13-2.21 (m, 2H), 2.44-2.53 (m, 2H), 3.78 (s, 3H), 3.94 (dd, *J* = 5.5, 12.5 Hz, 1H), 6.88 (d, *J* = 8 Hz, 1H), 6.96 (t, *J* = 8 Hz, 1H), 7,12 (d, *J* = 8 Hz, 1H), 7.24 (t, *J* = 8 Hz, 1H); Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OD-H column equipped with an OD-H guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major) = 8.6 min., t_r(minor) = 14.2 min; $[\alpha]^{24.3}_D$ = -14.1 (c 1.20, $CHCl_3$)



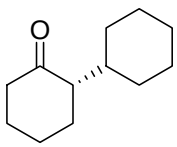
The product (7g)[12,13] was obtained as oil in 99 % yield (18.6 mg; 0.099 mmol) and 95:5 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.43-1.48 (m, 2H), 1.60-1.69 (m, 1H), 1.95-2.18 (m, 4H), 2.47-2.54 (m, 1H), 2.67-2.72 (m, 1H), 3.70-3.73 (dd, *J* = 4, 11 Hz, 1H), 7.20-7.26 (m, 3H), 7.30-7.33 (t, *J* = 7 Hz,2H). Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS column equipped with an AS guard column (hexanes:2-propanol = 95:5, flow rate = 1.0 mL/min, λ= 210 nm), t_r(major, *S*) = 9.8 min., t_r(minor, *R*) = 7.9 min.



The product (**7h**) was obtained as oil in 98 % yield (23.3 mg; 0.098 mmol) and 95:5 er. ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.49-1.53 (m, 2H), 1.66-1.73 (m, 1H), 1.99-2.15 (m, 4H), 2.10-2.23 (m, 1H), 2.55-2.58 (m, 1H), 2.72-2.78 (td, *J* = 12.8, 3.1 Hz, 1H), 3.88 (dd, *J* = 4.2, 11.4 Hz, 1H), 7.37 (dd, *J* = 1.7, 8.5 Hz, 1H), 7.42-7.48 (m, 2H), 7.67 (s, 1H), 7.79-7.81 (m, 3H); Enantiomeric ratio (er) was determined by HPLC with a Chiralcel AS column equipped with an AS guard column (hexanes:2-propanol = 99:1, flow rate = 1.0 mL/min, λ= 230 nm), t_r(major) = 18.9 min., t_r(minor) = 15.5 min; $[\alpha]^{24.3}_D$ = -134.0 (c 1.15, $CHCl_3$).



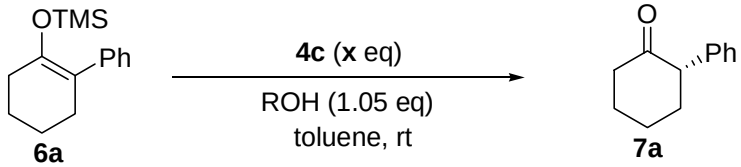
The product (**7i**)[17] was obtained as oil in 97 % yield (18.3 mg; 0.097 mmol) and 77:23 er. ^{1}H NMR (CDCl3, 500 MHz) δ: 1.32-1.38 (m, 1H), 1.54-1.73 (m, 2H), 1.81-1.88 (m, 1H), 2.01-2.08 (m, 2H), 2.30-2.36 (m, 1H), 2.39-2.45 (m, 2H), 2.52-2.56 (m, 1H), 3.22-3.26 (dd, *J* = 5.0, 14 Hz, 1H); Enantiomeric ratio (er) was determined by HPLC with a Chiralcel OJ-H column equipped with an OJ-H guard column (hexanes:2-propanol = 95:5, flow rate = 0.7 mL/min, λ= 210 nm), t_r(major) = 17.1 min., t_r(minor) = 15.5 min.



The product (**7j**)[18] was obtained as oil in 96 % (17.3 mg; 0.096 mmol) and 82:18 er. ^{1}H NMR (CDCl3, 500 MHz) δ: 0.68-1.26 (m, 5H), 1.34-1.88 (m, 12H), 1.90-2.02 (m, 1H), 2.07-2.32 (m, 2H); Enantiomeric ratio (er) was determined by GC with a Chlorosil-B column (injection temperature: 160 ^{o}C, column temperature: 140 ^{o}C, pressure: 100kPa),

t_r(major) = 28.3 min., t_r(minor) = 29.4 min. $[\alpha]^{24.3}_D$ = -38.1 (c 1.58, CH_3OH).

Survey of the Role of Achiral Brønsted Acids



entry	**4c** (eq)	ROH	time	% yield	er (config.)
1	1.05 eq	-	48 h	<1 %	N. D.
2	1.05 eq	CH_3CO_2H	2 h	100 %	88:12 (*S*)
3	0.1 eq	2,6-(^{t}Bu)$_2C_6H_3OH$	48 h	<1 %	N. D.
4	0.1 eq	CH_3CO_2H	3.5 h	100 %	89:11 (*S*)

Preliminary studies into the mechanism of the Brønsted acid catalyzed asymmetric protonation reaction of silyl enol ethers indicate that achiral proton sources play an important role in determining reactivity. In the absence of an achiral proton source, even though a stoichiometric amount of chiral Brønsted acid was used, no reaction was observed even after 2 days (entry 1). However, when the same reaction was carried out in the presence of stoichiometric amount of CH_3CO_2H as an achiral proton source, the reaction was completed within 2 h with almost the same enantioselectivity as the catalytic one (entries 2 and 4). When 2,6-di-(*t*-butyl)phenol, sterically hindered achiral Brønsted acid, was used as an achiral proton source, protonation was still very slow, however (entry 3).

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Crystal Structure Report for Chch03

$C_{55}H_{65}F_3NNaO_6PS_2 + 1/2C_6H_{14}$

Report Prepared for:

Cheol Hong Cheon and Mr. H. Yamamoto

May, 2008

Ian Steele (steele@geosci.uchicago.edu)
X-ray Laboratory, Jones 305, 773-834-5861
Department of Chemistry
The University of Chicago
5735 S. Ellis Ave.
Chicago, Il 60637

Crystallographic Experimental Section

Data Collection

An irregular broken fragment (0.20 x 0.12 x 0.10 mm) was selected under a stereo-microscope while immersed in Fluorolube oil to avoid possible reaction with air. The crystal was removed from the oil using a tapered glass fiber that also served to hold the crystal for data collection. The crystal was mounted and centered on a Bruker SMART APEX system at 100 K. Rotation and still images showed the diffractions to be sharp. Frames separated in reciprocal space were obtained and provided an orientation matrix and initial cell parameters. Final cell parameters were obtained from the full data set.

A "full sphere" data set was obtained which samples approximately all of reciprocal space to a resolution of 0.75 Å using 0.3^{o} steps in ω using 10 second integration times for each frame. Data collection was made at 100 K. Integration of intensities and refinement of cell parameters were done using SAINT [1]. Absorption corrections were applied using SADABS [1] based on redundant diffractions.

Structure solution and refinement

The space group was determined as P1(bar) based on systematic absences and intensity statistics. Direct methods were used to locate S, P and many C atoms from the E-map. Repeated difference Fourier maps allowed recognition of all expected C, N, O and F atoms. Following anisotropic refinement of all non-H atoms, ideal H-atom positions were calculated. Electron density clearly indicated yet another unexpected atom. Trial and error of occupancy factor indicated that Na was present. One Na bond was to the O atom of C_4OH_{10} solvent. Another solvent group thought to be C_6H_{14} was present and yet another disordered solvent molecule was indicated. Program SQUEEZE was uses to remove the contribution from the latter ($84e^{-}$/cell, void =115ang^3). Considerable positional disorder is present as indicated by large displacement parameters on unconstrained terminal groups. Final refinement was anisotropic for all non-H atoms, and isotropic-riding for H atoms. No other anomalous bond lengths or thermal parameters were noted. All ORTEP diagrams have been drawn with 50% probability ellipsoids.

Equations of interest:

$R_{int} = \Sigma \mid F_o^2 - \langle F_o^2 \rangle \mid / \Sigma \mid F_o^2 \mid$ $\quad\quad$ $R1 = \Sigma \mid \mid F_o \mid - \mid F_c \mid \mid / \Sigma \mid F_o \mid$

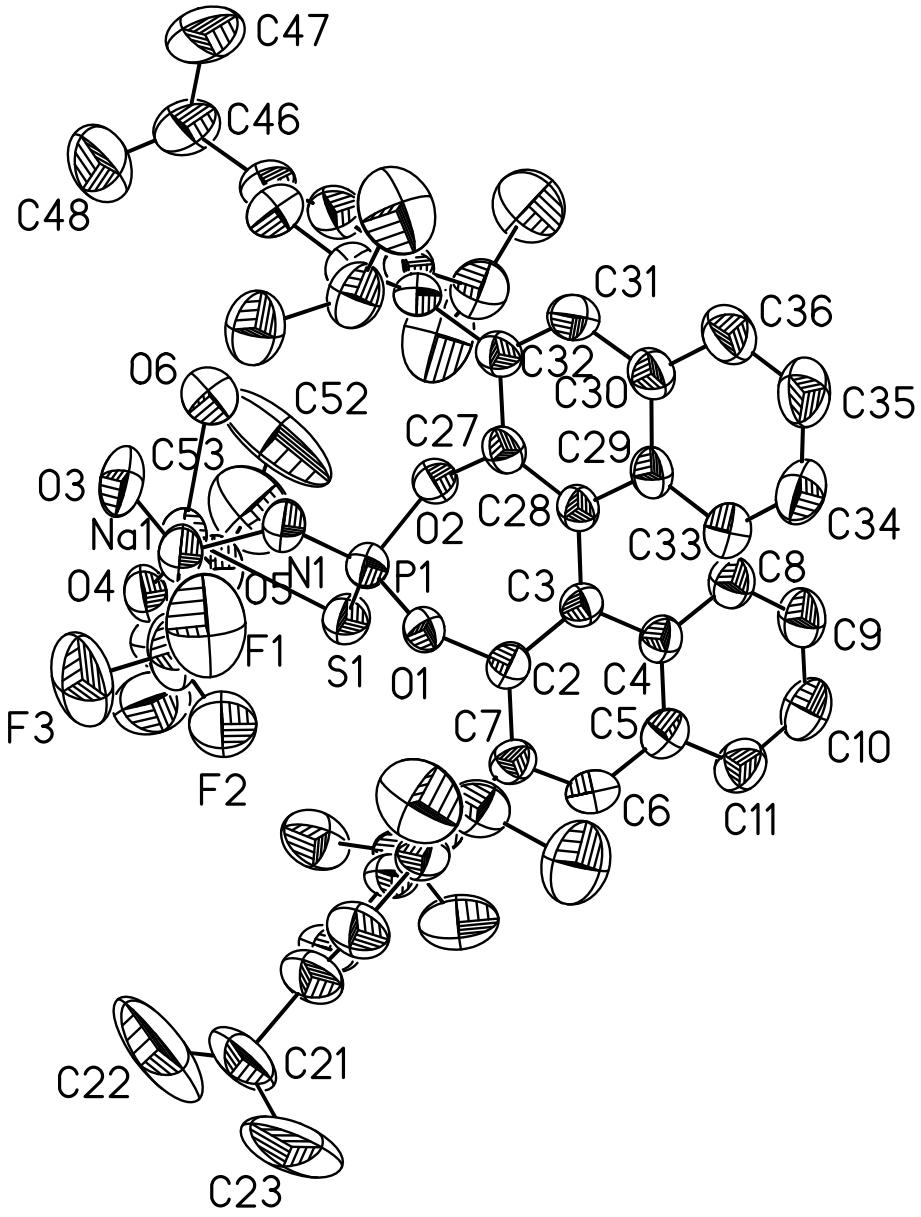
$wR2 = [\Sigma [w (F_o^2 - F_c^2)^2] / \Sigma [w (F_o^2)^2]]^{1/2}$ $\quad\quad$ $GooF = S = [\Sigma [w (F_o^2 - F_c^2)^2] / (n-p)^{1/2}$

where: $w = q / \sigma^2 (F_o^2) + (aP)^2 + bP$; $\quad\quad$ n = number of independent reflections;

q, a, b, P as defined in [1] $\quad\quad$ p = number of parameters refined.

References

[1] All software and sources of scattering factors are contained in the SHELXTL (version 5.1) program library (G. Sheldrick, Bruker Analytical X-ray Systems, Madison, WI).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Na1
O2
C33
O4
O5
N1
P1
C3
C8
C9
F1
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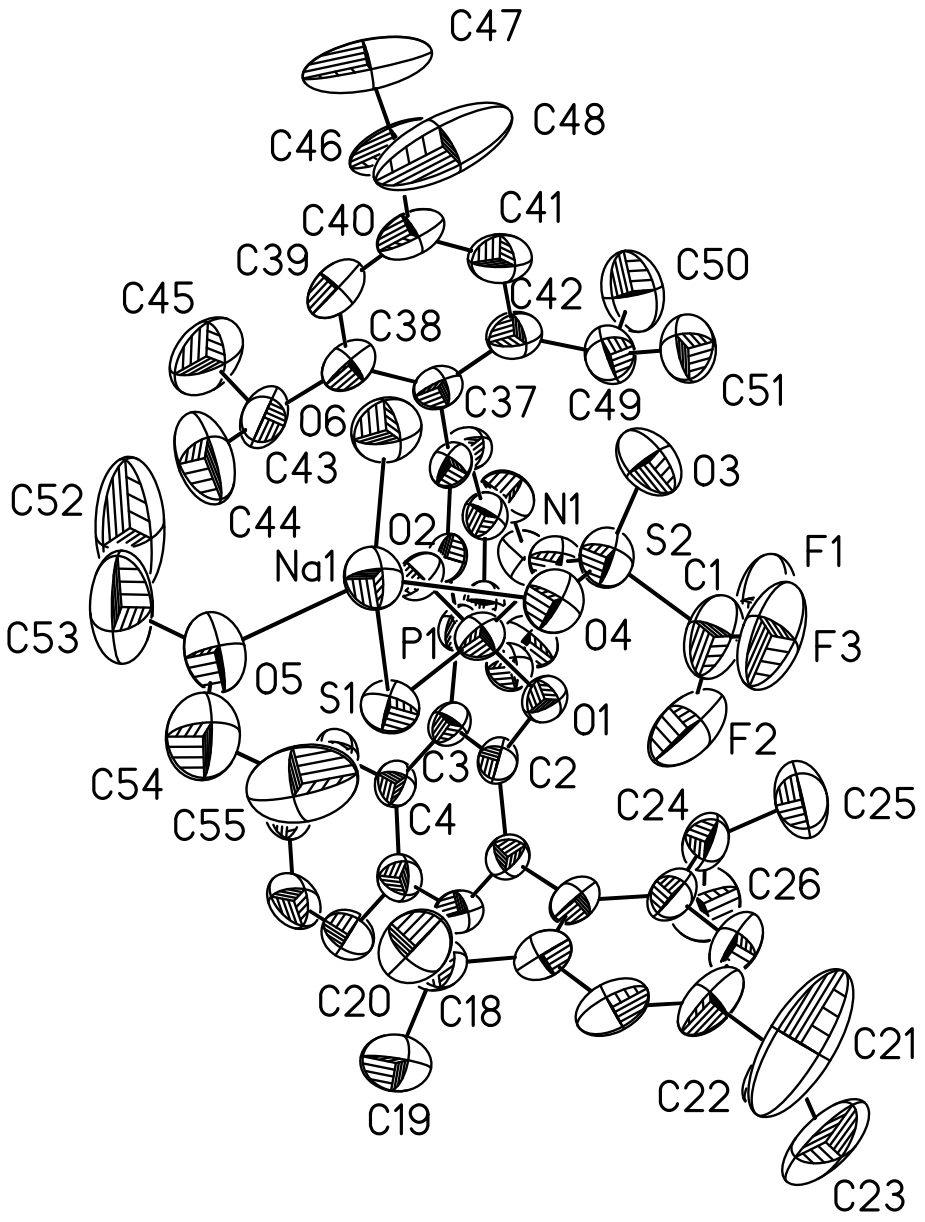
C22
C21
C23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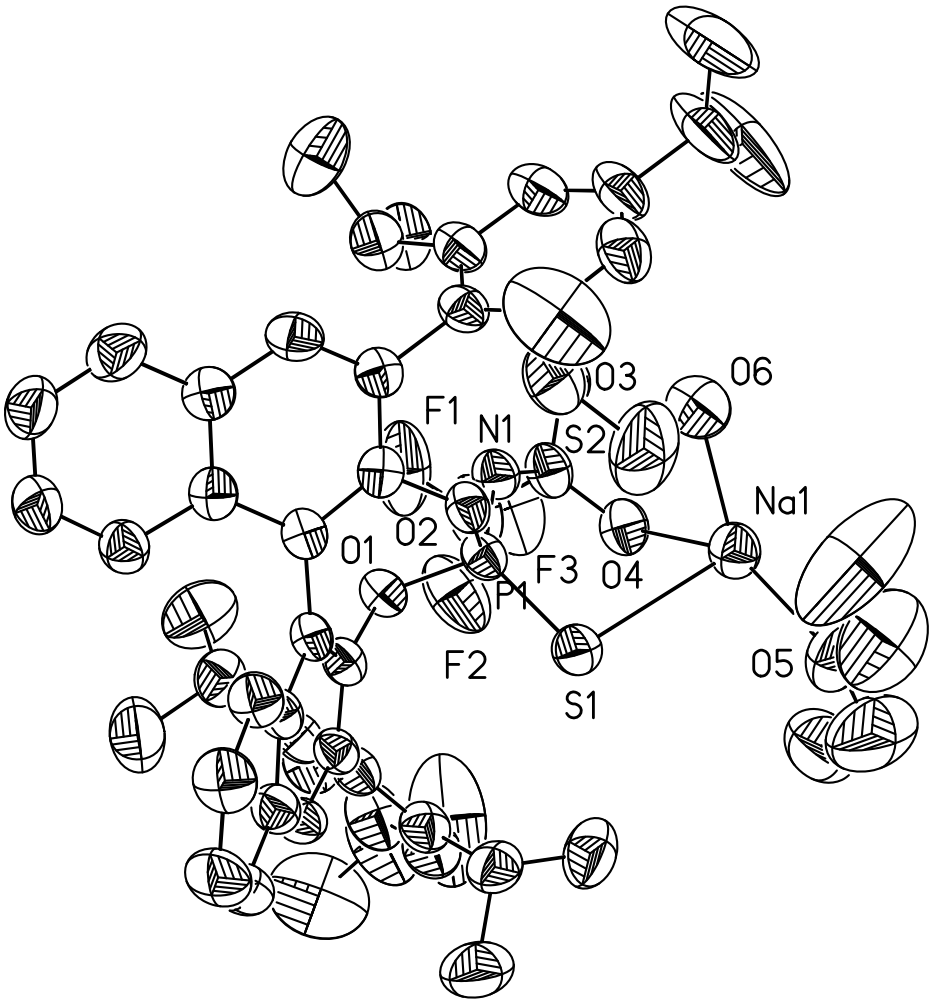
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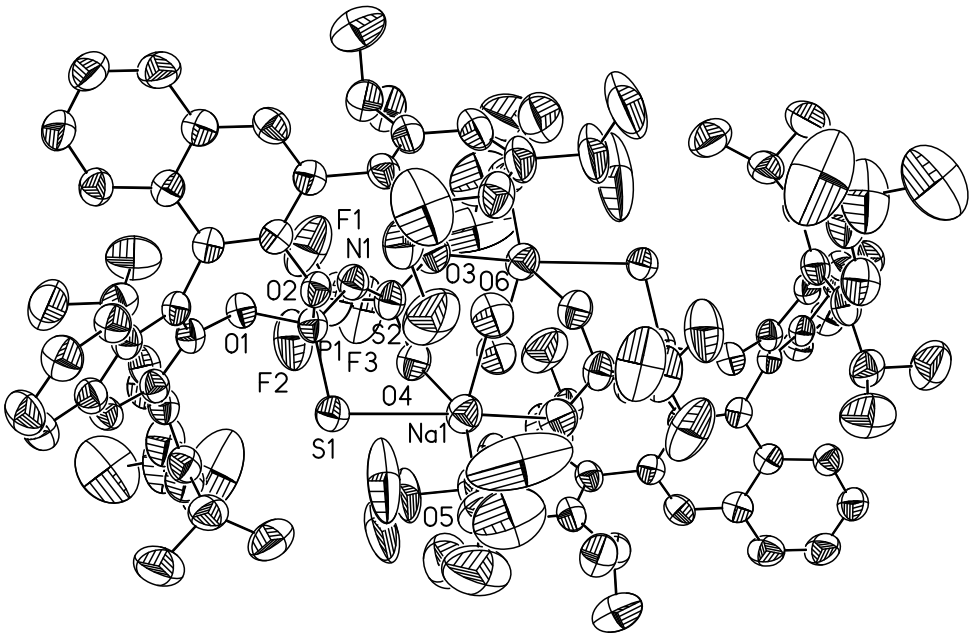
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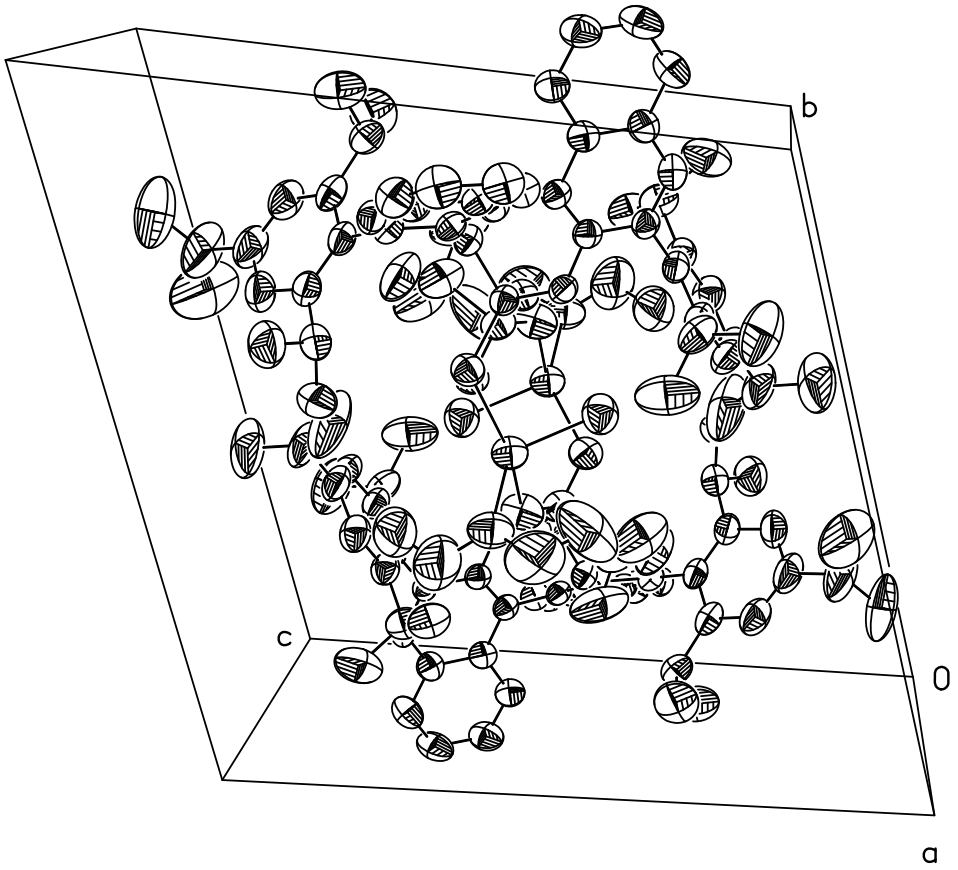
b
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Table 1. Crystal and structure refinement for Chch03.

Identification Code	Chch03	
Empirical formula	$C_{55}H_{65}F_3NNaO_6PS_2 + 1/2C_6H_{14}$	
Formula weight	1054.25	
Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space Group	P1(bar)	
Unit cell dimensions	*a* = 13.010(2) Å	α = 66.982(3) ^{o}
	b = 16.696(3) Å	β = 69.797(4) ^{o}
	c = 17.141(3) Å	γ = 79.001(3) ^{o}
Volume	3209.1(10) $Å^3$	
Z	2	
Density (calculated)	1.091 Mg/m^3	
Absorption coefficient	0.166 mm^{-1}	
F(000)	1120	
Crystal size, color, habit	0.20 x 0.12 x 0.10 mm, transparent, fragment	
Theta range for data collection	1.33 – 28.31 ^{o}	
Index ranges	$-17 \le h \le 17$, $-22 \le k \le 22$, $-22 \le l \le 22$	
Reflections collected	38,168	
Independent reflections	15,071 (R_{int} = 0.0265)	
Reflections with $I > 4\sigma(F_o)$	5,626	
Absorption correction	SADABS based on redundant diffractions	
Max. and min. transmission	1.0, 0.852	
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = q [\sigma^2 (F_o^2) + (aP)^2 + bP]^{-1}$ where:	
	$P = (F_o^2 + 2 F_c^2)/3$, a = 0.0772, b = 0.0, q =1	
Data / restraints / parameters	15071 / 0 / 665	
Goodness-of-fit on F^2	0.767	
Final R indices [I > 2 sigma(I)]	R1 = 0.0620, wR2 = 0.1445	
R indices (all data)	R1 = 0.1507, wR2 = 0.1693	
Largest diff. peak and hole	0.506, -0.283 $eÅ^{-3}$	

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for Chch03. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)	SOF
C(1)	3997(4)	6926(3)	5900(4)	94(1)	
C(2)	7576(2)	8141(2)	5167(2)	43(1)	
C(3)	8385(2)	8555(2)	4412(2)	42(1)	
C(4)	9353(2)	8734(2)	4522(2)	45(1)	
C(5)	9381(3)	8565(2)	5396(2)	52(1)	
C(6)	8451(3)	8242(2)	6120(2)	54(1)	
C(7)	7555(2)	8004(2)	6043(2)	46(1)	
C(8)	10306(2)	9033(2)	3804(2)	54(1)	
C(9)	11208(3)	9182(2)	3948(3)	67(1)	
C(10)	11220(3)	9040(2)	4803(3)	74(1)	
C(11)	10329(3)	8744(2)	5509(3)	66(1)	
C(12)	6594(3)	7687(2)	6850(2)	52(1)	
C(13)	6668(3)	6894(2)	7521(2)	61(1)	
C(14)	5778(4)	6671(3)	8315(2)	82(1)	
C(15)	4843(4)	7225(3)	8426(3)	89(1)	
C(16)	4794(3)	7992(3)	7748(3)	78(1)	
C(17)	5633(3)	8249(2)	6959(2)	60(1)	
C(18)	7651(3)	6241(2)	7454(2)	70(1)	
C(19)	8355(4)	6237(3)	8016(3)	106(2)	
C(20)	7332(4)	5319(2)	7704(3)	96(1)	
C(21)	3890(5)	6992(4)	9281(3)	147(2)	
C(22)	3414(6)	6313(5)	9506(5)	244(5)	
C(23)	3836(5)	7495(5)	9815(3)	186(3)	
C(24)	5535(3)	9137(2)	6259(2)	67(1)	
C(25)	4361(3)	9429(3)	6220(3)	115(2)	
C(26)	6011(4)	9824(3)	6403(3)	115(2)	
C(27)	7930(2)	8272(2)	3239(2)	44(1)	
C(28)	8233(2)	8837(2)	3519(2)	43(1)	
C(29)	8339(2)	9729(2)	2938(2)	46(1)	
C(30)	8273(2)	9970(2)	2061(2)	52(1)	
C(31)	8033(2)	9330(2)	1813(2)	55(1)	
C(32)	7823(2)	8502(2)	2380(2)	45(1)	
C(33)	8485(2)	10404(2)	3195(2)	55(1)	
C(34)	8596(3)	11240(2)	2609(3)	68(1)	
C(35)	8579(3)	11470(2)	1743(3)	75(1)	
C(36)	8416(3)	10845(2)	1477(2)	69(1)	
C(37)	7486(3)	7865(2)	2109(2)	49(1)	
C(38)	8236(3)	7198(2)	1908(2)	59(1)	
C(39)	7910(3)	6623(2)	1646(2)	70(1)	
C(40)	6874(4)	6669(3)	1592(2)	73(1)	
C(41)	6149(3)	7342(2)	1781(2)	72(1)	
C(42)	6432(3)	7949(2)	2043(2)	58(1)	
C(43)	9418(3)	7115(3)	1920(3)	76(1)	
C(44)	9709(4)	6213(3)	2533(4)	134(2)	
C(45)	10221(4)	7318(4)	987(3)	142(2)	
C(46)	6521(5)	6017(3)	1324(3)	114(2)	
C(47)	6843(6)	6203(4)	422(3)	177(3)	
C(48)	5667(6)	5510(4)	1922(4)	206(4)	
C(49)	5594(3)	8666(2)	2230(3)	69(1)	
C(50)	5534(4)	9403(3)	1375(3)	113(2)	
C(51)	4437(3)	8347(2)	2779(3)	83(1)	

C(52)	9287(5)	3993(5)	4166(5)	235(5)
C(53)	9195(5)	3515(5)	5005(5)	167(3)
C(54)	8144(6)	3123(5)	6524(5)	178(3)
C(55)	7196(6)	3367(4)	7138(4)	147(2)
C(56)	231(5)	5122(5)	9557(3)	136(2)
C(57)	489(8)	6027(6)	9223(6)	213(4)
C(58)	1133(8)	6212(6)	8266(8)	283(5)
F(1)	3678(2)	7735(2)	5467(2)	140(1)
F(2)	4495(2)	6951(2)	6437(2)	118(1)
F(3)	3113(2)	6487(2)	6387(2)	142(1)
N(1)	5831(2)	7012(2)	4571(2)	54(1)
Na(1)	6803(1)	4676(1)	5237(1)	64(1)
O(1)	6693(1)	7867(1)	5066(1)	45(1)
O(2)	7821(2)	7400(1)	3781(1)	47(1)
O(3)	4222(2)	6420(2)	4615(2)	76(1)
O(4)	5166(2)	5554(1)	5698(1)	62(1)
O(5)	8250(2)	3705(2)	5636(2)	88(1)
O(6)	6811(2)	5405(2)	3772(2)	85(1)
P(1)	6955(1)	7043(1)	4744(1)	47(1)
S(1)	7641(1)	6028(1)	5442(1)	59(1)
S(2)	4895(1)	6405(1)	5127(1)	59(1)

Table 3. Bond lengths [Å] and angles [°] for Chch03.

C(1)-F(2)	1.310(5)	C(31)-C(32)	1.357(4)
C(1)-F(3)	1.318(4)	C(32)-C(37)	1.499(4)
C(1)-F(1)	1.327(5)	C(33)-C(34)	1.364(4)
C(1)-S(2)	1.823(5)	C(34)-C(35)	1.386(5)
C(2)-C(3)	1.378(4)	C(35)-C(36)	1.365(5)
C(2)-O(1)	1.400(3)	C(37)-C(42)	1.390(4)
C(2)-C(7)	1.419(4)	C(37)-C(38)	1.401(4)
C(3)-C(4)	1.435(4)	C(38)-C(39)	1.389(4)
C(3)-C(28)	1.487(4)	C(38)-C(43)	1.524(5)
C(4)-C(8)	1.415(4)	C(39)-C(40)	1.369(5)
C(4)-C(5)	1.425(4)	C(40)-C(41)	1.387(5)
C(5)-C(6)	1.408(4)	C(40)-C(46)	1.527(5)
C(5)-C(11)	1.414(4)	C(41)-C(42)	1.407(4)
C(6)-C(7)	1.363(4)	C(42)-C(49)	1.512(5)
C(7)-C(12)	1.497(4)	C(43)-C(45)	1.523(5)
C(8)-C(9)	1.364(4)	C(43)-C(44)	1.527(5)
C(9)-C(10)	1.396(5)	C(46)-C(47)	1.374(6)
C(10)-C(11)	1.354(5)	C(46)-C(48)	1.377(6)
C(12)-C(13)	1.387(4)	C(49)-C(50)	1.517(5)
C(12)-C(17)	1.417(4)	C(49)-C(51)	1.540(5)
C(13)-C(14)	1.417(5)	C(52)-C(53)	1.319(7)
C(13)-C(18)	1.518(5)	C(53)-O(5)	1.409(6)
C(14)-C(15)	1.386(6)	C(54)-O(5)	1.426(7)
C(15)-C(16)	1.361(5)	C(54)-C(55)	1.429(7)
C(15)-C(21)	1.523(6)	C(56)-C(56)#1	1.346(10)
C(16)-C(17)	1.381(5)	C(56)-C(57)	1.452(9)
C(17)-C(24)	1.516(5)	C(57)-C(58)	1.497(11)
C(18)-C(20)	1.527(5)	N(1)-S(2)	1.527(2)
C(18)-C(19)	1.539(5)	N(1)-P(1)	1.603(2)
C(21)-C(22)	1.256(7)	Na(1)-O(6)	2.321(3)
C(21)-C(23)	1.445(7)	Na(1)-O(5)	2.344(3)
C(24)-C(25)	1.528(5)	Na(1)-O(3)#2	2.351(2)
C(24)-C(26)	1.536(5)	Na(1)-O(4)	2.420(3)
C(27)-C(28)	1.379(4)	Na(1)-S(1)	2.8671(15)
C(27)-O(2)	1.390(3)	O(1)-P(1)	1.612(2)
C(27)-C(32)	1.419(4)	O(2)-P(1)	1.598(2)
C(28)-C(29)	1.433(4)	O(3)-S(2)	1.429(2)
C(29)-C(33)	1.423(4)	O(3)-Na(1)#2	2.351(2)
C(29)-C(30)	1.425(4)	O(4)-S(2)	1.436(2)
C(30)-C(31)	1.413(4)	P(1)-S(1)	1.9175(12
C(30)-C(36)	1.415(4)		
)			

F(2)-C(1)-F(3)	108.1(4)	C(6)-C(5)-C(4)	118.8(3)
F(2)-C(1)-F(1)	108.7(4)	C(11)-C(5)-C(4)	119.1(3)
F(3)-C(1)-F(1)	108.0(4)	C(7)-C(6)-C(5)	123.6(3)
F(2)-C(1)-S(2)	111.0(3)	C(6)-C(7)-C(2)	116.0(3)
F(3)-C(1)-S(2)	110.0(3)	C(6)-C(7)-C(12)	119.7(3)
F(1)-C(1)-S(2)	110.9(4)	C(2)-C(7)-C(12)	124.2(3)
C(3)-C(2)-O(1)	118.1(3)	C(9)-C(8)-C(4)	120.6(3)
C(3)-C(2)-C(7)	124.3(3)	C(8)-C(9)-C(10)	121.1(3)
O(1)-C(2)-C(7)	117.6(2)	C(11)-C(10)-C(9)	120.1(3)
C(2)-C(3)-C(4)	117.7(3)	C(10)-C(11)-C(5)	120.9(3)
C(2)-C(3)-C(28)	120.7(3)	C(13)-C(12)-C(17)	119.9(3)
C(4)-C(3)-C(28)	121.5(3)	C(13)-C(12)-C(7)	121.1(3)
C(8)-C(4)-C(5)	118.0(3)	C(17)-C(12)-C(7)	118.7(3)
C(8)-C(4)-C(3)	123.1(3)	C(12)-C(13)-C(14)	118.7(3)
C(5)-C(4)-C(3)	118.8(3)	C(12)-C(13)-C(18)	123.6(3)
C(6)-C(5)-C(11)	122.1(3)	C(14)-C(13)-C(18)	117.6(3)

C(15)-C(14)-C(13)	121.4(4)	C(37)-C(42)-C(41)	117.9(3)
C(16)-C(15)-C(14)	118.2(4)	C(37)-C(42)-C(49)	122.8(3)
C(16)-C(15)-C(21)	120.3(5)	C(41)-C(42)-C(49)	119.3(3)
C(14)-C(15)-C(21)	121.5(5)	C(45)-C(43)-C(38)	111.4(3)
C(15)-C(16)-C(17)	123.3(4)	C(45)-C(43)-C(44)	110.6(4)
C(16)-C(17)-C(12)	118.4(3)	C(38)-C(43)-C(44)	111.5(3)
C(16)-C(17)-C(24)	119.8(3)	C(47)-C(46)-C(48)	124.4(5)
C(12)-C(17)-C(24)	121.7(3)	C(47)-C(46)-C(40)	113.8(4)
C(13)-C(18)-C(20)	112.9(3)	C(48)-C(46)-C(40)	118.2(4)
C(13)-C(18)-C(19)	111.5(3)	C(42)-C(49)-C(50)	111.1(3)
C(20)-C(18)-C(19)	110.2(3)	C(42)-C(49)-C(51)	113.4(3)
C(22)-C(21)-C(23)	128.3(5)	C(50)-C(49)-C(51)	109.1(3)
C(22)-C(21)-C(15)	118.2(5)	C(52)-C(53)-O(5)	116.0(6)
C(23)-C(21)-C(15)	111.9(5)	O(5)-C(54)-C(55)	111.2(5)
C(17)-C(24)-C(25)	113.4(3)	C(56)#1-C(56)-C(57)	107.9(9)
C(17)-C(24)-C(26)	110.3(3)	C(56)-C(57)-C(58)	104.8(7)
C(25)-C(24)-C(26)	110.2(3)	S(2)-N(1)-P(1)	130.39(17)
C(28)-C(27)-O(2)	119.6(3)	O(6)-Na(1)-O(5)	122.81(12)
C(28)-C(27)-C(32)	123.9(3)	O(6)-Na(1)-O(3)#2	91.15(10)
O(2)-C(27)-C(32)	116.3(3)	O(5)-Na(1)-O(3)#2	94.28(10)
C(27)-C(28)-C(29)	117.7(3)	O(6)-Na(1)-O(4)	89.25(9)
C(27)-C(28)-C(3)	122.0(3)	O(5)-Na(1)-O(4)	147.01(12)
C(29)-C(28)-C(3)	120.3(3)	O(3)#2-Na(1)-O(4)	92.41(9)
C(33)-C(29)-C(30)	117.3(3)	O(6)-Na(1)-S(1)	97.46(8)
C(33)-C(29)-C(28)	123.4(3)	O(5)-Na(1)-S(1)	90.28(8)
C(30)-C(29)-C(28)	119.2(3)	O(3)#2-Na(1)-S(1)	166.04(9)
C(31)-C(30)-C(36)	122.1(3)	O(4)-Na(1)-S(1)	76.80(6)
C(31)-C(30)-C(29)	118.7(3)	C(2)-O(1)-P(1)	116.22(17)
C(36)-C(30)-C(29)	119.2(3)	C(27)-O(2)-P(1)	125.54(17)
C(32)-C(31)-C(30)	123.0(3)	S(2)-O(3)-Na(1)#2	129.96(14)
C(31)-C(32)-C(27)	117.0(3)	S(2)-O(4)-Na(1)	122.89(13)
C(31)-C(32)-C(37)	121.2(3)	C(53)-O(5)-C(54)	113.7(4)
C(27)-C(32)-C(37)	121.8(3)	C(53)-O(5)-Na(1)	122.7(4)
C(34)-C(33)-C(29)	120.8(3)	C(54)-O(5)-Na(1)	122.3(3)
C(33)-C(34)-C(35)	122.0(3)	O(2)-P(1)-N(1)	105.49(12)
C(36)-C(35)-C(34)	119.0(3)	O(2)-P(1)-O(1)	102.75(10)
C(35)-C(36)-C(30)	121.5(3)	N(1)-P(1)-O(1)	101.83(12)
C(42)-C(37)-C(38)	120.3(3)	O(2)-P(1)-S(1)	107.34(9)
C(42)-C(37)-C(32)	119.6(3)	N(1)-P(1)-S(1)	122.09(10)
C(38)-C(37)-C(32)	120.0(3)	O(1)-P(1)-S(1)	115.40(8)
C(39)-C(38)-C(37)	119.1(3)	P(1)-S(1)-Na(1)	100.68(5)
C(39)-C(38)-C(43)	118.9(3)	O(3)-S(2)-O(4)	115.08(14)
C(37)-C(38)-C(43)	121.9(3)	O(3)-S(2)-N(1)	111.69(15)
C(40)-C(39)-C(38)	122.6(3)	O(4)-S(2)-N(1)	116.92(14)
C(39)-C(40)-C(41)	117.3(3)	O(3)-S(2)-C(1)	103.3(2)
C(39)-C(40)-C(46)	121.9(4)	O(4)-S(2)-C(1)	103.6(2)
C(41)-C(40)-C(46)	120.7(4)	N(1)-S(2)-C(1)	104.19(17)
C(40)-C(41)-C(42)	122.7(3)		

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for Chch03. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+ ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	61(3)	92(4)	122(4)	-55(3)	10(3)	-26(3)
C(2)	36(2)	47(2)	52(2)	-26(2)	-10(2)	-1(1)
C(3)	44(2)	40(2)	45(2)	-21(2)	-10(2)	-3(1)
C(4)	40(2)	46(2)	54(2)	-24(2)	-11(2)	-3(1)
C(5)	49(2)	52(2)	61(2)	-26(2)	-21(2)	1(2)
C(6)	61(2)	60(2)	47(2)	-25(2)	-20(2)	1(2)
C(7)	45(2)	48(2)	49(2)	-25(2)	-13(2)	0(2)
C(8)	42(2)	59(2)	62(2)	-23(2)	-14(2)	-5(2)
C(9)	43(2)	76(3)	79(3)	-27(2)	-11(2)	-13(2)
C(10)	55(2)	86(3)	98(3)	-36(2)	-36(2)	-9(2)
C(11)	58(2)	78(3)	74(3)	-32(2)	-27(2)	-7(2)
C(12)	53(2)	61(2)	44(2)	-28(2)	-3(2)	-9(2)
C(13)	71(2)	65(2)	47(2)	-26(2)	-10(2)	-6(2)
C(14)	105(3)	85(3)	47(2)	-23(2)	-3(2)	-23(3)
C(15)	88(3)	101(3)	67(3)	-47(3)	19(2)	-24(3)
C(16)	63(2)	92(3)	71(3)	-44(3)	7(2)	-7(2)
C(17)	53(2)	74(2)	59(2)	-40(2)	-4(2)	-6(2)
C(18)	84(3)	70(3)	51(2)	-20(2)	-21(2)	3(2)
C(19)	123(4)	123(4)	83(3)	-43(3)	-52(3)	22(3)
C(20)	125(4)	63(3)	75(3)	-14(2)	-18(3)	2(2)
C(21)	153(5)	166(5)	90(4)	-70(4)	72(3)	-90(4)
C(22)	217(8)	184(7)	209(8)	-88(6)	148(6)	-96(6)
C(23)	145(5)	296(9)	91(4)	-102(5)	46(4)	-34(5)
C(24)	62(2)	66(2)	68(2)	-33(2)	-11(2)	10(2)
C(25)	70(3)	134(4)	123(4)	-40(3)	-31(3)	23(3)
C(26)	131(4)	79(3)	141(4)	-43(3)	-42(3)	-12(3)
C(27)	37(2)	44(2)	45(2)	-16(2)	-4(1)	-3(1)
C(28)	36(2)	45(2)	45(2)	-19(2)	-4(1)	-6(1)
C(29)	36(2)	48(2)	52(2)	-17(2)	-7(2)	-8(1)
C(30)	45(2)	55(2)	50(2)	-15(2)	-9(2)	-9(2)
C(31)	55(2)	67(2)	43(2)	-19(2)	-12(2)	-9(2)
C(32)	41(2)	49(2)	43(2)	-19(2)	-5(1)	-3(1)
C(33)	52(2)	53(2)	62(2)	-21(2)	-18(2)	-8(2)
C(34)	78(3)	52(2)	86(3)	-21(2)	-37(2)	-12(2)
C(35)	85(3)	50(2)	90(3)	-7(2)	-40(2)	-14(2)
C(36)	73(2)	63(2)	60(2)	-4(2)	-23(2)	-15(2)
C(37)	53(2)	55(2)	41(2)	-20(2)	-9(2)	-8(2)
C(38)	64(2)	62(2)	51(2)	-29(2)	-3(2)	-10(2)
C(39)	78(3)	68(2)	63(2)	-38(2)	-1(2)	-7(2)
C(40)	94(3)	76(3)	59(2)	-40(2)	-10(2)	-20(2)
C(41)	80(3)	83(3)	68(2)	-34(2)	-27(2)	-14(2)
C(42)	63(2)	62(2)	55(2)	-25(2)	-16(2)	-13(2)
C(43)	59(2)	86(3)	89(3)	-54(2)	-7(2)	5(2)
C(44)	101(4)	97(4)	218(6)	-61(4)	-78(4)	32(3)
C(45)	80(3)	223(6)	123(4)	-100(4)	29(3)	-39(4)
C(46)	172(5)	114(4)	82(3)	-65(3)	-14(3)	-50(3)
C(47)	306(9)	177(6)	91(4)	-57(4)	-48(5)	-114(6)
C(48)	297(9)	217(7)	122(5)	-107(5)	60(5)	-189(7)
C(49)	58(2)	67(2)	90(3)	-35(2)	-26(2)	1(2)
C(50)	100(4)	84(3)	131(4)	-16(3)	-39(3)	10(3)
C(51)	66(3)	78(3)	109(3)	-42(2)	-22(2)	-3(2)

C(52)	133(6)	229(8)	133(6)	38(6)	49(5)	68(5)
C(53)	88(4)	182(7)	190(7)	-70(6)	-13(5)	38(4)
C(54)	171(6)	221(8)	146(6)	-97(6)	-73(5)	96(6)
C(55)	222(7)	122(4)	112(4)	-41(4)	-57(5)	-33(5)
C(56)	132(5)	153(5)	135(5)	-68(6)	-49(5)	17(4)
C(57)	265(10)	205(9)	154(7)	-69(7)	-3(7)	-86(8)
C(58)	236(11)	197(9)	386(17)	-113(11)	-47(11)	-10(8)
F(1)	103(2)	97(2)	212(3)	-83(2)	-16(2)	16(2)
F(2)	115(2)	141(2)	108(2)	-83(2)	15(2)	-39(2)
F(3)	79(2)	150(2)	182(3)	-97(2)	41(2)	-40(2)
N(1)	53(2)	52(2)	59(2)	-18(1)	-16(1)	-15(1)
Na(1)	58(1)	60(1)	74(1)	-23(1)	-18(1)	-10(1)
O(1)	38(1)	53(1)	45(1)	-21(1)	-5(1)	-11(1)
O(2)	52(1)	44(1)	46(1)	-21(1)	-7(1)	-6(1)
O(3)	62(2)	71(2)	104(2)	-22(1)	-37(1)	-20(1)
O(4)	56(1)	57(1)	67(2)	-18(1)	-8(1)	-20(1)
O(5)	72(2)	74(2)	114(2)	-30(2)	-29(2)	3(2)
O(6)	85(2)	91(2)	74(2)	-28(2)	-15(1)	-20(2)
P(1)	48(1)	49(1)	47(1)	-20(1)	-9(1)	-11(1)
S(1)	65(1)	55(1)	60(1)	-18(1)	-22(1)	-10(1)
S(2)	50(1)	58(1)	73(1)	-28(1)	-12(1)	-13(1)

Table 5. Hydrogen coordinates [x 10^4] and isotropic displacement parameters [$Å^2$ x 10^3] for Chch03.

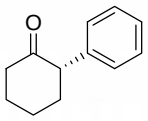
	x	y	z	U(eq)
H(6)	8448	8186	6694	65
H(8)	10317	9131	3217	65
H(9)	11839	9386	3457	80
H(10)	11854	9151	4890	89
H(11)	10341	8656	6088	79
H(14)	5823	6130	8779	99
H(16)	4149	8369	7820	94
H(18)	8118	6430	6820	83
H(19A)	8581	6827	7833	159
H(19B)	9007	5838	7928	159
H(19C)	7925	6043	8645	159
H(20A)	6955	5083	8343	144
H(20B)	7994	4946	7556	144
H(20C)	6842	5335	7373	144
H(22A)	3732	5826	9921	366
H(22B)	3508	6176	8978	366
H(22C)	2630	6407	9794	366
H(23A)	3827	8117	9454	279
H(23B)	4479	7332	10032	279
H(23C)	3167	7377	10322	279
H(24)	5987	9099	5669	80
H(25A)	4073	8995	6110	172
H(25B)	4357	9993	5739	172
H(25C)	3900	9486	6787	172
H(26A)	5580	9880	6976	172
H(26B)	5984	10387	5925	172
H(26C)	6775	9644	6399	172
H(31)	8017	9487	1221	66
H(33)	8504	10270	3782	65
H(34)	8687	11678	2799	82
H(35)	8680	12053	1342	90
H(36)	8399	11002	886	83
H(39)	8428	6180	1497	84
H(41)	5433	7395	1730	86
H(43)	9490	7554	2159	91
H(44A)	9673	5771	2301	202
H(44B)	9187	6095	3130	202
H(44C)	10453	6195	2561	202
H(45A)	10086	6961	700	213
H(45B)	10974	7189	1023	213
H(45C)	10120	7937	639	213
H(46)	7123	5560	1448	136
H(47A)	6899	5665	303	265
H(47B)	7560	6456	153	265
H(47C)	6301	6620	167	265
H(48A)	5153	5511	1617	309
H(48B)	5284	5746	2396	309
H(48C)	5955	4911	2179	309
H(49)	5841	8908	2581	83
H(50A)	6261	9628	1037	169
H(50B)	5014	9872	1516	169
H(50C)	5286	9185	1020	169
H(51A)	3967	8811	2970	124

H(51B)	4482	7832	3302	124
H(51C)	4126	8194	2414	124
H(52A)	8807	3785	3961	352
H(52B)	10049	3945	3803	352
H(52C)	9072	4603	4110	352
H(53A)	9848	3584	5139	200
H(53B)	9208	2894	5079	200
H(54A)	8807	3126	6682	214
H(54B)	8089	2523	6567	214
H(55A)	7238	3968	7082	221
H(55B)	7165	2975	7745	221
H(55C)	6535	3325	7008	221
H(56A)	-284	5058	9277	163
H(56B)	907	4750	9416	163
H(57A)	931	6111	9551	255
H(57B)	-190	6414	9281	255
H(58A)	1875	5933	8223	424
H(58B)	1176	6843	7956	424
H(58C)	769	5980	7992	424

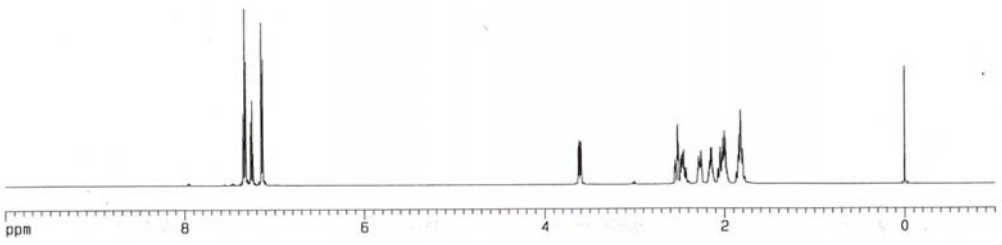
Table 6. Torsion angles [°] for Chch03.

O(1)-C(2)-C(3)-C(4)	-172.2(2)	C(33)-C(29)-C(30)-C(31)	-174.5(3)
C(7)-C(2)-C(3)-C(4)	10.3(4)	C(28)-C(29)-C(30)-C(31)	4.1(4)
O(1)-C(2)-C(3)-C(28)	10.3(4)	C(33)-C(29)-C(30)-C(36)	3.6(4)
C(7)-C(2)-C(3)-C(28)	-167.2(3)	C(28)-C(29)-C(30)-C(36)	-177.8(3)
C(2)-C(3)-C(4)-C(8)	170.2(3)	C(36)-C(30)-C(31)-C(32)	-175.7(3)
C(28)-C(3)-C(4)-C(8)	-12.3(4)	C(29)-C(30)-C(31)-C(32)	2.4(5)
C(2)-C(3)-C(4)-C(5)	-6.7(4)	C(30)-C(31)-C(32)-C(27)	-4.4(4)
C(28)-C(3)-C(4)-C(5)	170.8(3)	C(30)-C(31)-C(32)-C(37)	175.2(3)
C(8)-C(4)-C(5)-C(6)	-178.1(3)	C(28)-C(27)-C(32)-C(31)	-0.2(4)
C(3)-C(4)-C(5)-C(6)	-1.1(4)	O(2)-C(27)-C(32)-C(31)	-173.8(2)
C(8)-C(4)-C(5)-C(11)	3.3(4)	C(28)-C(27)-C(32)-C(37)	-179.7(3)
C(3)-C(4)-C(5)-C(11)	-179.7(3)	O(2)-C(27)-C(32)-C(37)	6.7(4)
C(11)-C(5)-C(6)-C(7)	-175.2(3)	C(30)-C(29)-C(33)-C(34)	-2.3(4)
C(4)-C(5)-C(6)-C(7)	6.2(5)	C(28)-C(29)-C(33)-C(34)	179.1(3)
C(5)-C(6)-C(7)-C(2)	-3.1(4)	C(29)-C(33)-C(34)-C(35)	-0.4(5)
C(5)-C(6)-C(7)-C(12)	-178.5(3)	C(33)-C(34)-C(35)-C(36)	1.9(6)
C(3)-C(2)-C(7)-C(6)	-5.5(4)	C(34)-C(35)-C(36)-C(30)	-0.5(5)
O(1)-C(2)-C(7)-C(6)	177.1(2)	C(31)-C(30)-C(36)-C(35)	175.8(3)
C(3)-C(2)-C(7)-C(12)	169.7(3)	C(29)-C(30)-C(36)-C(35)	-2.2(5)
O(1)-C(2)-C(7)-C(12)	-7.8(4)	C(31)-C(32)-C(37)-C(42)	-73.7(4)
C(5)-C(4)-C(8)-C(9)	-2.2(4)	C(27)-C(32)-C(37)-C(42)	105.8(3)
C(3)-C(4)-C(8)-C(9)	-179.1(3)	C(31)-C(32)-C(37)-C(38)	105.2(4)
C(4)-C(8)-C(9)-C(10)	0.3(5)	C(27)-C(32)-C(37)-C(38)	-75.3(4)
C(8)-C(9)-C(10)-C(11)	0.5(6)	C(42)-C(37)-C(38)-C(39)	-0.2(5)
C(9)-C(10)-C(11)-C(5)	0.7(6)	C(32)-C(37)-C(38)-C(39)	-179.1(3)
C(6)-C(5)-C(11)-C(10)	178.8(3)	C(42)-C(37)-C(38)-C(43)	176.4(3)
C(4)-C(5)-C(11)-C(10)	-2.6(5)	C(32)-C(37)-C(38)-C(43)	-2.5(5)
C(6)-C(7)-C(12)-C(13)	-68.7(4)	C(37)-C(38)-C(39)-C(40)	-1.4(5)
C(2)-C(7)-C(12)-C(13)	116.3(4)	C(43)-C(38)-C(39)-C(40)	-178.1(3)
C(6)-C(7)-C(12)-C(17)	105.4(3)	C(38)-C(39)-C(40)-C(41)	2.3(5)
C(2)-C(7)-C(12)-C(17)	-69.6(4)	C(38)-C(39)-C(40)-C(46)	-178.5(3)
C(17)-C(12)-C(13)-C(14)	-1.2(5)	C(39)-C(40)-C(41)-C(42)	-1.8(5)
C(7)-C(12)-C(13)-C(14)	172.8(3)	C(46)-C(40)-C(41)-C(42)	179.0(3)
C(17)-C(12)-C(13)-C(18)	178.4(3)	C(38)-C(37)-C(42)-C(41)	0.6(5)
C(7)-C(12)-C(13)-C(18)	-7.5(5)	C(32)-C(37)-C(42)-C(41)	179.5(3)
C(12)-C(13)-C(14)-C(15)	0.4(5)	C(38)-C(37)-C(42)-C(49)	-178.6(3)
C(18)-C(13)-C(14)-C(15)	-179.2(4)	C(32)-C(37)-C(42)-C(49)	0.3(5)
C(13)-C(14)-C(15)-C(16)	0.6(6)	C(40)-C(41)-C(42)-C(37)	0.4(5)
C(13)-C(14)-C(15)-C(21)	-179.5(4)	C(40)-C(41)-C(42)-C(49)	179.6(3)
C(14)-C(15)-C(16)-C(17)	-0.8(6)	C(39)-C(38)-C(43)-C(45)	65.5(5)
C(21)-C(15)-C(16)-C(17)	179.2(4)	C(37)-C(38)-C(43)-C(45)	-111.2(4)
C(15)-C(16)-C(17)-C(12)	0.1(6)	C(39)-C(38)-C(43)-C(44)	-58.7(4)
C(15)-C(16)-C(17)-C(24)	-176.6(4)	C(37)-C(38)-C(43)-C(44)	124.7(4)
C(13)-C(12)-C(17)-C(16)	1.0(5)	C(39)-C(40)-C(46)-C(47)	-81.2(6)
C(7)-C(12)-C(17)-C(16)	-173.2(3)	C(41)-C(40)-C(46)-C(47)	98.0(6)
C(13)-C(12)-C(17)-C(24)	177.6(3)	C(39)-C(40)-C(46)-C(48)	119.2(6)
C(7)-C(12)-C(17)-C(24)	3.3(4)	C(41)-C(40)-C(46)-C(48)	-61.6(7)
C(12)-C(13)-C(18)-C(20)	-130.2(3)	C(37)-C(42)-C(49)-C(50)	99.5(4)
C(14)-C(13)-C(18)-C(20)	49.5(4)	C(41)-C(42)-C(49)-C(50)	-79.7(4)
C(12)-C(13)-C(18)-C(19)	105.2(4)	C(37)-C(42)-C(49)-C(51)	-137.2(3)
C(14)-C(13)-C(18)-C(19)	-75.2(4)	C(41)-C(42)-C(49)-C(51)	43.6(4)
C(16)-C(15)-C(21)-C(22)	119.5(8)	C(56)#1-C(56)-C(57)-C(58)	172.4(8)
C(14)-C(15)-C(21)-C(22)	-60.4(9)	C(3)-C(2)-O(1)-P(1)	71.8(3)
C(16)-C(15)-C(21)-C(23)	-73.7(7)	C(7)-C(2)-O(1)-P(1)	-110.5(2)
C(14)-C(15)-C(21)-C(23)	106.3(6)	C(28)-C(27)-O(2)-P(1)	63.1(3)
C(16)-C(17)-C(24)-C(25)	-34.2(5)	C(32)-C(27)-O(2)-P(1)	-123.0(2)
C(12)-C(17)-C(24)-C(25)	149.3(3)	O(6)-Na(1)-O(4)-S(2)	-25.69(15)
C(16)-C(17)-C(24)-C(26)	90.0(4)	O(5)-Na(1)-O(4)-S(2)	141.53(17)
C(12)-C(17)-C(24)-C(26)	-86.5(4)	O(3)#2-Na(1)-O(4)-S(2)	-116.81(15)
O(2)-C(27)-C(28)-C(29)	179.8(2)	S(1)-Na(1)-O(4)-S(2)	72.15(14)
C(32)-C(27)-C(28)-C(29)	6.4(4)	C(52)-C(53)-O(5)-C(54)	175.0(7)
O(2)-C(27)-C(28)-C(3)	-3.8(4)	C(52)-C(53)-O(5)-Na(1)	7.8(9)
C(32)-C(27)-C(28)-C(3)	-177.1(3)	C(55)-C(54)-O(5)-C(53)	177.7(5)
C(2)-C(3)-C(28)-C(27)	-52.1(4)	C(55)-C(54)-O(5)-Na(1)	-15.0(8)
C(4)-C(3)-C(28)-C(27)	130.5(3)	O(6)-Na(1)-O(5)-C(53)	0.0(4)
C(2)-C(3)-C(28)-C(29)	124.3(3)	O(3)#2-Na(1)-O(5)-C(53)	94.1(4)
C(4)-C(3)-C(28)-C(29)	-53.1(4)	O(4)-Na(1)-O(5)-C(53)	-164.8(4)
C(27)-C(28)-C(29)-C(33)	170.3(3)	S(1)-Na(1)-O(5)-C(53)	-99.1(4)
C(3)-C(28)-C(29)-C(33)	-6.2(4)	O(6)-Na(1)-O(5)-C(54)	-166.1(4)
C(27)-C(28)-C(29)-C(30)	-8.2(4)	O(3)#2-Na(1)-O(5)-C(54)	-72.0(4)
C(3)-C(28)-C(29)-C(30)	175.3(3)	O(4)-Na(1)-O(5)-C(54)	29.2(5)

S(1)-Na(1)-O(5)-C(54)	94.8(4)
C(27)-O(2)-P(1)-N(1)	82.2(2)
C(27)-O(2)-P(1)-O(1)	-24.1(2)
C(27)-O(2)-P(1)-S(1)	-146.2(2)
S(2)-N(1)-P(1)-O(2)	149.4(2)
S(2)-N(1)-P(1)-O(1)	-103.6(2)
S(2)-N(1)-P(1)-S(1)	26.8(3)
C(2)-O(1)-P(1)-O(2)	-63.1(2)
C(2)-O(1)-P(1)-N(1)	-172.21(19)
C(2)-O(1)-P(1)-S(1)	53.3(2)
O(2)-P(1)-S(1)-Na(1)	-96.54(8)
N(1)-P(1)-S(1)-Na(1)	25.19(13)
O(1)-P(1)-S(1)-Na(1)	149.62(8)
O(6)-Na(1)-S(1)-P(1)	36.23(9)
O(5)-Na(1)-S(1)-P(1)	159.41(9)
O(3)#2-Na(1)-S(1)-P(1)	-91.4(3)
O(4)-Na(1)-S(1)-P(1)	-51.23(7)
Na(1)#2-O(3)-S(2)-O(4)	14.0(2)
Na(1)#2-O(3)-S(2)-N(1)	150.40(17)
Na(1)#2-O(3)-S(2)-C(1)	-98.2(2)
Na(1)-O(4)-S(2)-O(3)	91.53(17)
Na(1)-O(4)-S(2)-N(1)	-42.5(2)
Na(1)-O(4)-S(2)-C(1)	-156.44(19)
P(1)-N(1)-S(2)-O(3)	-161.8(2)
P(1)-N(1)-S(2)-O(4)	-26.3(3)
P(1)-N(1)-S(2)-C(1)	87.3(3)
F(2)-C(1)-S(2)-O(3)	178.9(3)
F(3)-C(1)-S(2)-O(3)	59.3(4)
F(1)-C(1)-S(2)-O(3)	-60.2(3)
F(2)-C(1)-S(2)-O(4)	58.5(4)
F(3)-C(1)-S(2)-O(4)	-61.1(4)
F(1)-C(1)-S(2)-O(4)	179.4(3)
F(2)-C(1)-S(2)-N(1)	-64.3(4)
F(3)-C(1)-S(2)-N(1)	176.1(4)
F(1)-C(1)-S(2)-N(1)	56.7(4)



7a

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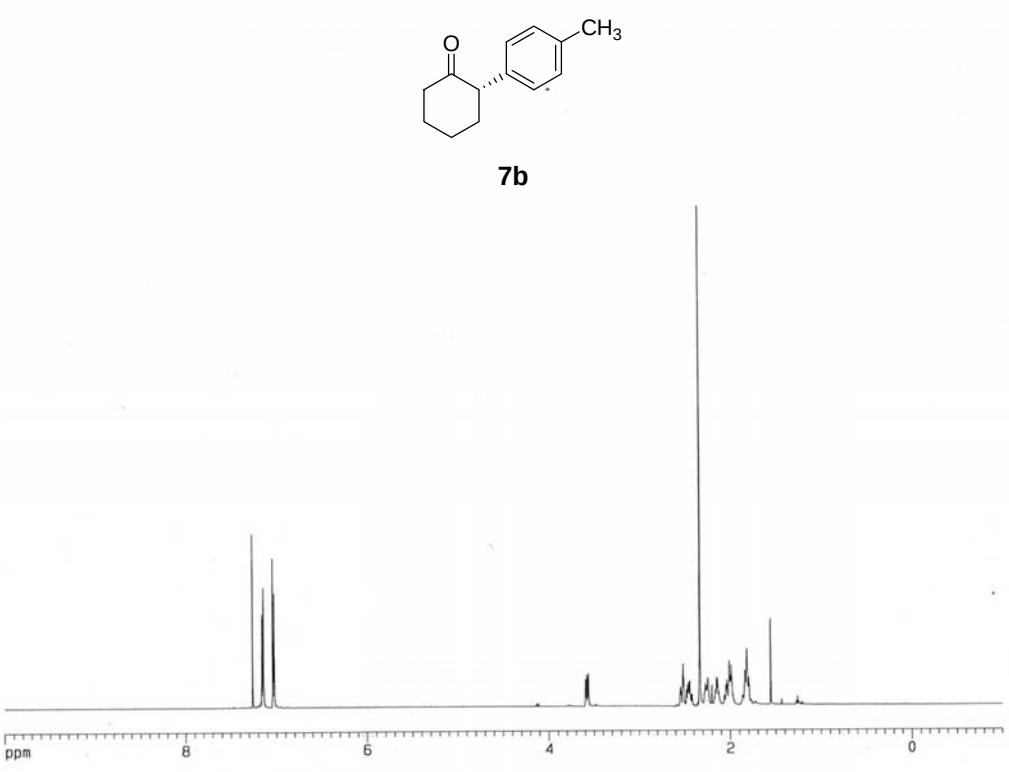
Current Data Parameters
NAME                  6Ph
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              20080210
Time                 23.33
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG                 zg
TD                   48076
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8012.820 Hz
FIDRES               0.166670 Hz
AQ                2.9999924 sec
RG                      64
DW                  62.400 usec
DE                   4.50 usec
TE                  300.0 K
D1                3.00000000 sec

============ CHANNEL f1 ========
NUC1                    1H
P1                   9.50 usec,
PL1                  0.00 dB
SFO1             500.1325006 MHz

F2 - Processing parameters
SI                      65536
SF               500.1300191 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 10.000 ppm
F1                 5001.30 Hz
F2P                 -1.000 ppm
F2                 -500.13 Hz
PPMCM                0.55000 ppm/cm
HZCM               275.07150 Hz/cm
```



7b

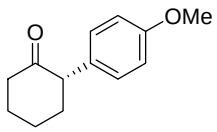
```
Current Data Parameters
NAME                  4Me-sub
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20080202
Time                   0.40
INSTRUM                spect
PROBHD   5 mm BBI 1H-BB
PULPROG                   zg
TD                     45044
SOLVENT                CDCl3
NS                         8
DS                         0
SWH               7507.507 Hz
FIDRES           0.166671 Hz
AQ               2.9999804 sec
RG                       256
DW                  66.600 usec
DE                   4.50 usec
TE                   300.0 K
D1               1.00000000 sec

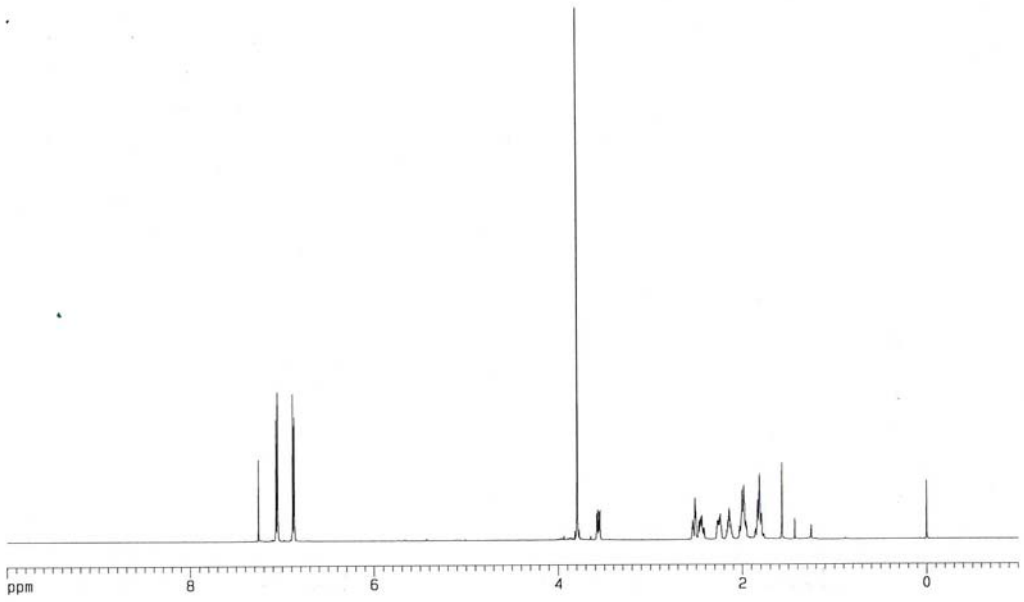
======== CHANNEL f1 ========
NUC1                      1H
P1                   5.80 usec
PL1                   0.00 dB
SFO1           499.8779993 MHz

F2 - Processing parameters
SI                     32768
SF             499.8750146 MHz
WDW                       EM
SSB                        0
LB                   0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                   20.00 cm
CY                   10.00 cm
F1P                 10.000 ppm
F1                 4998.75 Hz
F2P                 -1.000 ppm
F2                 -499.87 Hz
PPMCM             0.55000 ppm/cm
HZCM             274.93124 Hz/cm
```



7c




```
Current Data Parameters
NAME                  6-phome
EXPNO                       1
PROCNO                      1

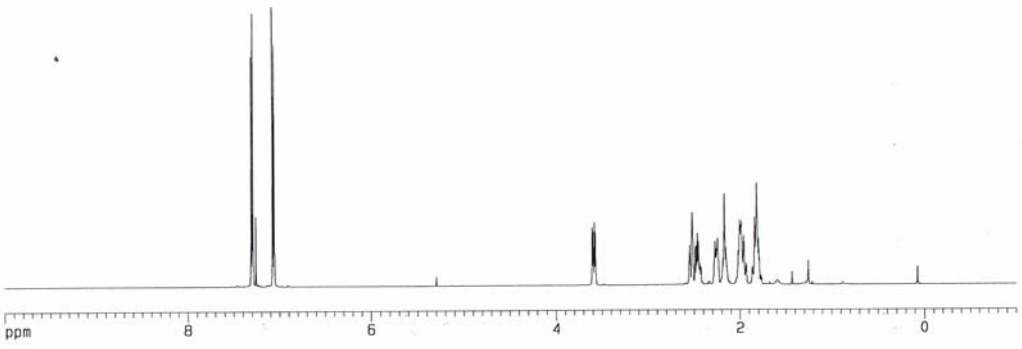
F2 - Acquisition Parameters
Date_              20080529
Time                  14.02
INSTRUM               spect
PROBHD   5 mm BBI 1H-BB
PULPROG                 zg
TD                   45044
SOLVENT              CDCl3
NS                       8
DS                       0
SWH              7507.507 Hz
FIDRES          0.166671 Hz
AQ              2.9999804 sec
RG                    90.5
DW                66.600 usec
DE                 4.50 usec
TE                 300.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 5.80 usec
PL1                0.00 dB
SFO1         499.8779993 MHz

F2 - Processing parameters
SI                   32768
SF           499.8750142 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00

1D NMR plot parameters
CX                 20.00 cm
CY                 15.00 cm
F1P               10.000 ppm
F1              4998.75 Hz
F2P               -1.000 ppm
F2              -499.87 Hz
PPMCM           0.55000 ppm/cm
HZCM          274.93124 Hz/cm
```

7d




```
Current Data Parameters
NAME                  4Cl-sub
EXPNO                       1
PROCNO                      1

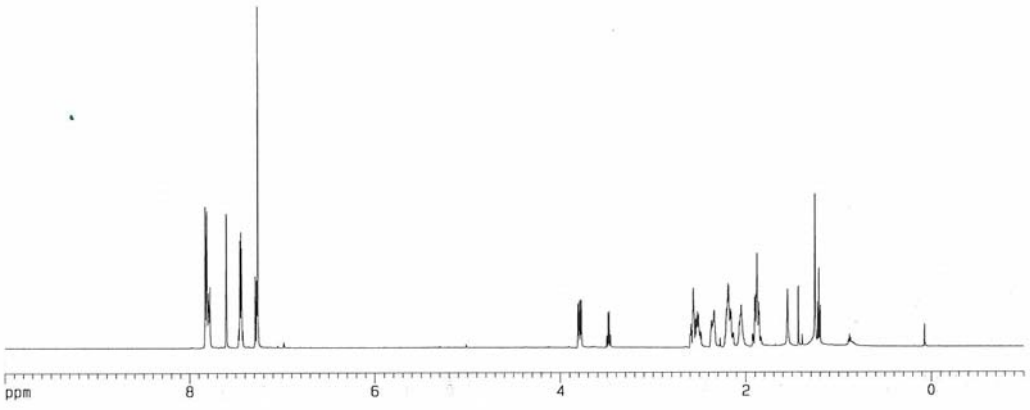
F2 - Acquisition Parameters
Date_              20080201
Time                  22.32
INSTRUM               spect
PROBHD   5 mm BBI 1H-BB
PULPROG                   zg
TD                     45044
SOLVENT                CDCl3
NS                         8
DS                         0
SWH                7507.507 Hz
FIDRES            0.166671 Hz
AQ                2.9999804 sec
RG                      90.5
DW                   66.600 usec
DE                    4.50 usec
TE                   300.0 K
D1                1.00000000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                    5.80 usec
PL1                    0.00 dB
SFO1            499.8779993 MHz

F2 - Processing parameters
SI                       32768
SF              499.8750146 MHz
WDW                       EM
SSB                        0
LB                     0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     20.00 cm
CY                      2.00 cm
F1P                   10.000 ppm
F1                  4998.75 Hz
F2P                   -1.000 ppm
F2                  -499.87 Hz
PPMCM                0.55000 ppm/cm
HZCM               274.93124 Hz/cm
```

7e

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Current Data Parameters
NAME                  2Naph-sub
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_                  20080201
Time                      23.33
INSTRUM                   spect
PROBHD   5 mm BBI 1H-BB
PULPROG                      zg
TD                        45044
SOLVENT                   CDCl3
NS                            8
DS                            0
SWH                    7507.507 Hz
FIDRES                 0.166671 Hz
AQ                     2.9999804 sec
RG                          362
DW                        66.600 usec
DE                         4.50 usec
TE                        300.0 K
D1                    1.00000000 sec

======== CHANNEL f1 ========
NUC1                          1H
P1                         5.80 usec
PL1                        0.00 dB
SFO1                499.8779993 MHz

F2 - Processing parameters
SI                        32768
SF                  499.8750140 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00

1D NMR plot parameters
CX                        20.00 cm
CY                         3.00 cm
F1P                       10.000 ppm
F1                      4998.75 Hz
F2P                       -1.000 ppm
F2                      -499.87 Hz
PPMCM                  0.55000 ppm/cm
HZCM                 274.93124 Hz/cm
```
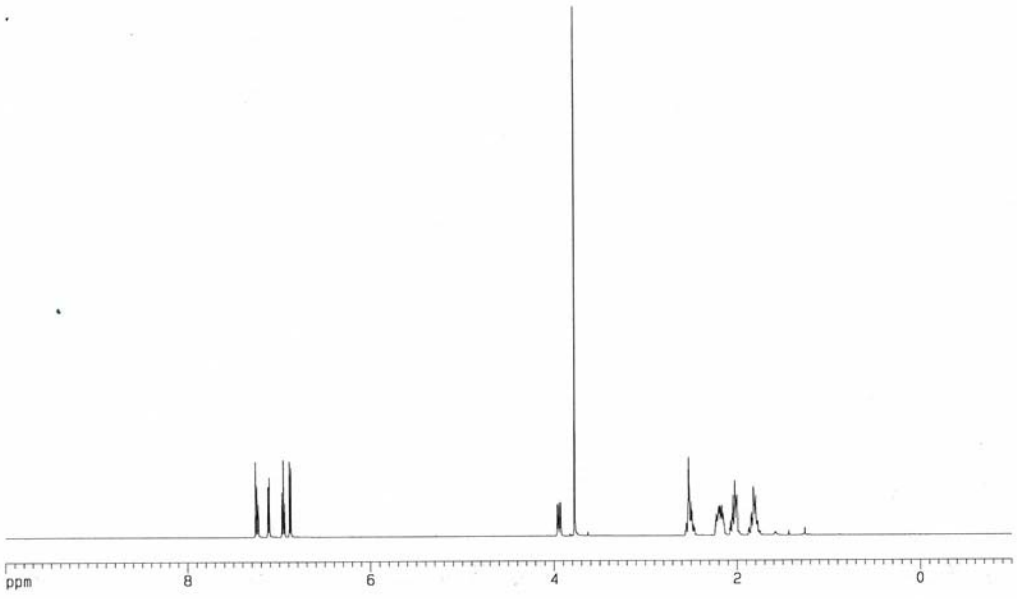

7f




```
Current Data Parameters
NAME                  2MeO-sub
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20080201
Time                     20.46
INSTRUM                  spect
PROBHD    5 mm BBI 1H-BB
PULPROG                     zg
TD                       45044
SOLVENT                  CDCl3
NS                           8
DS                           0
SWH                 7507.507 Hz
FIDRES              0.166671 Hz
AQ                  2.9999804 sec
RG                       101.6
DW                    66.600 usec
DE                     4.50 usec
TE                     300.0 K
D1                  1.00000000 sec

======== CHANNEL f1 ========
NUC1                        1H
P1                       5.80 usec
PL1                      0.00 dB
SFO1               499.8779993 MHz

F2 - Processing parameters
SI                       32768
SF                 499.8750146 MHz
WDW                         EM
SSB                          0
LB                       0.30 Hz
GB                           0
PC                        1.00

1D NMR plot parameters
CX                       20.00 cm
CY                       15.00 cm
F1P                     10.000 ppm
F1                    4998.75 Hz
F2P                     -1.000 ppm
F2                    -499.87 Hz
PPMCM                 0.55000 ppm/cm
HZCM                274.93124 Hz/cm
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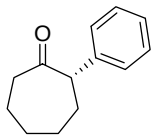
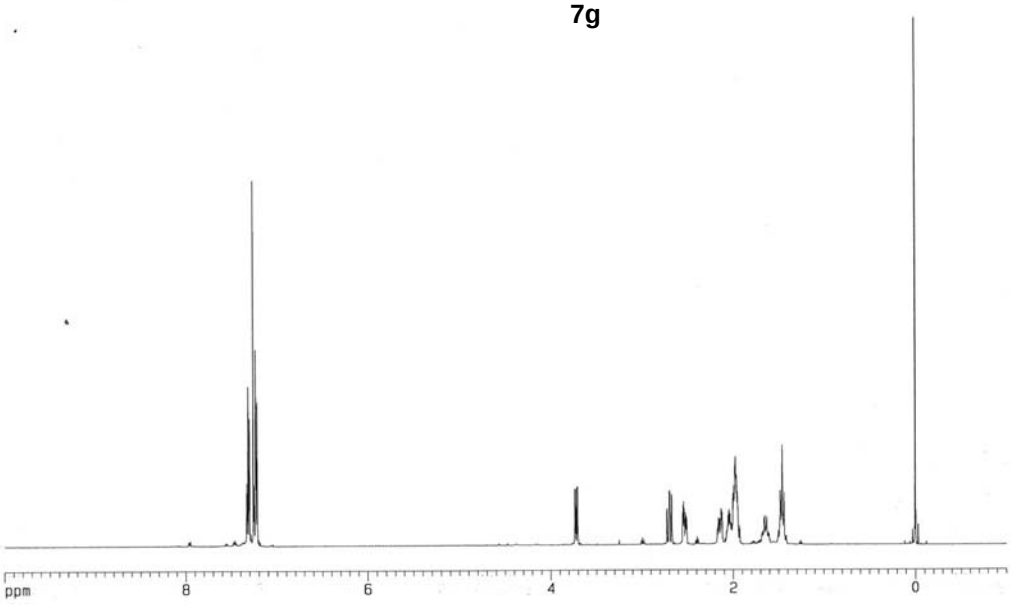


7g



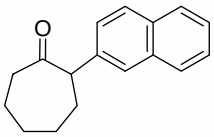

```
Current Data Parameters
NAME                  7Ph
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_              20080210
Time                 23.44
INSTRUM              spect
PROBHD     5 mm QNP  1H
PULPROG                 zg
TD                   48076
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8012.820 Hz
FIDRES               0.166670 Hz
AQ                2.9999924 sec
RG                     256
DW                  62.400 usec
DE                   4.50 usec
TE                  300.0 K
D1                3.00000000 sec

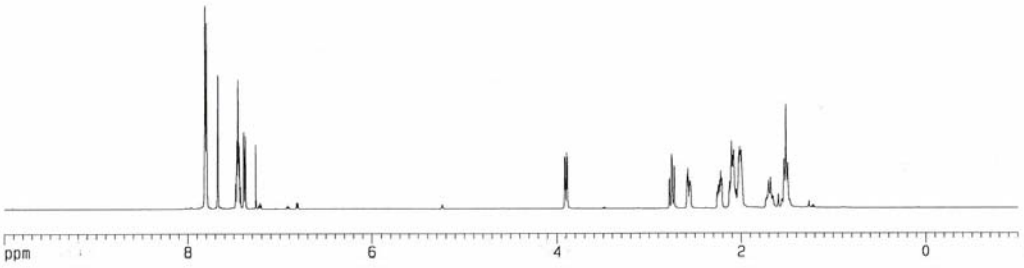
============ CHANNEL f1 ========
NUC1                    1H
P1                   9.50 usec
PL1                  0.00 dB
SFO1            500.1325006 MHz

F2 - Processing parameters
SI                      65536
SF              500.1300141 MHz
WDW                     EM
SSB                      0
LB                   0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                   20.00 cm
F1P                 10.000 ppm
F1                5001.30 Hz
F2P                 -1.000 ppm
F2                -500.13 Hz
PPMCM              0.55000 ppm/cm
HZCM             275.07150 Hz/cm
```



7h

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Current Data Parameters
NAME          2Naph7-sub
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20080202
Time                0.47
INSTRUM            spect
PROBHD   5 mm BBI 1H-BB
PULPROG              zg
TD                45044
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            7507.507 Hz
FIDRES        0.166671 Hz
AQ            2.9999804 sec
RG                 80.6
DW               66.600 usec
DE                4.50 usec
TE               300.0 K
D1            1.00000000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 5.80 usec
PL1                0.00 dB
SFO1         499.8779993 MHz

F2 - Processing parameters
SI                32768
SF           499.8750146 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                20.00 cm
CY                 4.00 cm
F1P              10.000 ppm
F1             4998.75 Hz
F2P              -1.000 ppm
F2             -499.87 Hz
PPMCM          0.55000 ppm/cm
HZCM          274.93124 Hz/cm
```
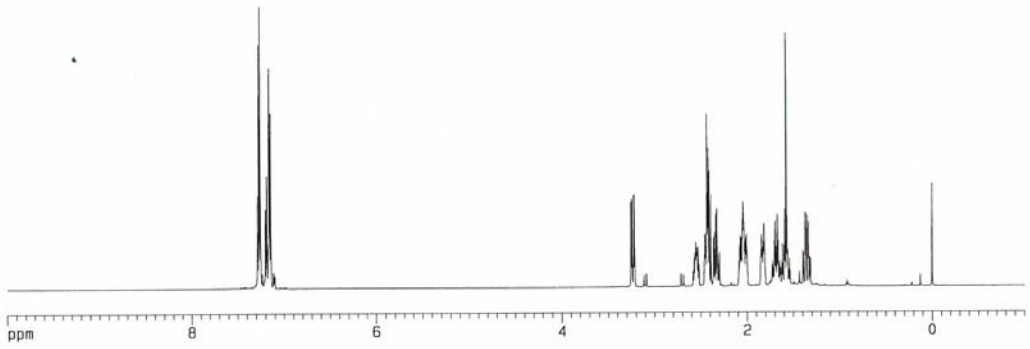
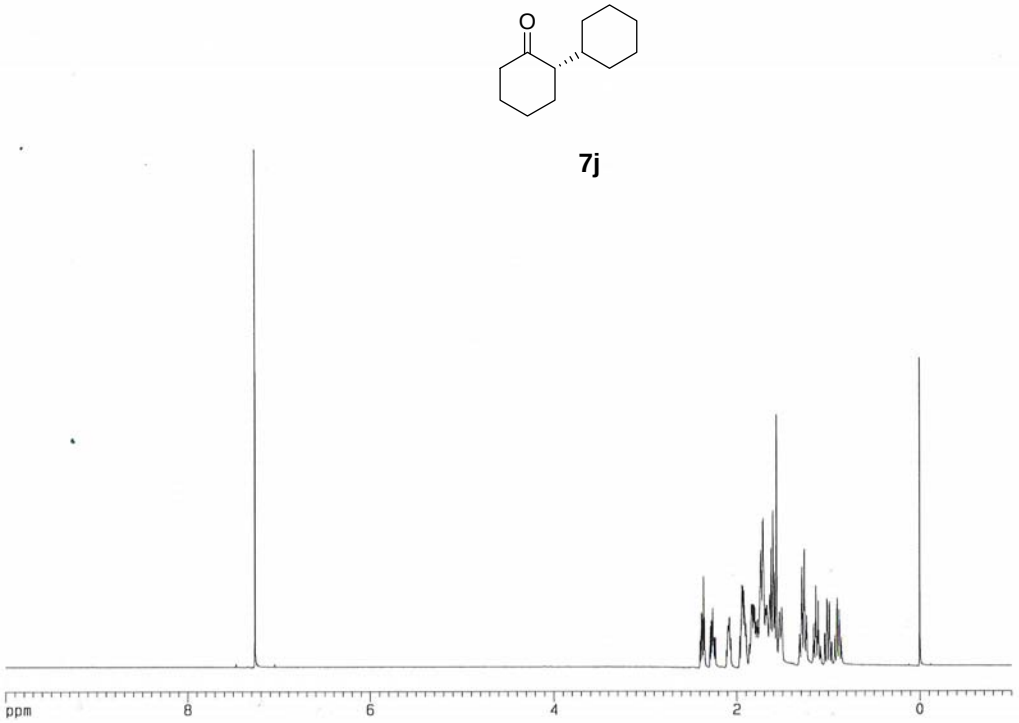

7i




```
Current Data Parameters
NAME                  6-bn
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20080529
Time                 10.40
INSTRUM              spect
PROBHD   5 mm BBI 1H-BB
PULPROG                 zg
TD                   45044
SOLVENT              CDCl3
NS                       8
DS                       0
SWH             7507.507 Hz
FIDRES          0.166671 Hz
AQ              2.9999804 sec
RG                    90.5
DW                66.600 usec
DE                 4.50 usec
TE                 300.0 K
D1             1.00000000 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                  5.80 usec
PL1                 0.00 dB
SFO1          499.8779993 MHz

F2 - Processing parameters
SI                   32768
SF            499.8750144 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                  20.00 cm
CY                   5.00 cm
F1P                10.000 ppm
F1                4998.75 Hz
F2P                -1.000 ppm
F2                -499.87 Hz
PPMCM             0.55000 ppm/cm
HZCM            274.93124 Hz/cm
```



7j

```
Current Data Parameters
NAME                  6-cy
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_              20080529
Time                 10.49
INSTRUM              spect
PROBHD   5 mm BBI 1H-BB
PULPROG                zg
TD                  45044
SOLVENT             CDCl3
NS                       8
DS                       0
SWH             7507.507 Hz
FIDRES          0.166671 Hz
AQ              2.9999804 sec
RG                    90.5
DW                66.600 usec
DE                 4.50 usec
TE                 300.0 K
D1              1.00000000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 5.80 usec
PL1                0.00 dB
SFO1          499.8779993 MHz

F2 - Processing parameters
SI                    32768
SF            499.8750126 MHz
WDW                   EM
SSB                      0
LB                 0.30 Hz
GB                       0
PC                    1.00

1D NMR plot parameters
CX                20.00 cm
CY                 5.00 cm
F1P               10.000 ppm
F1              4998.75 Hz
F2P               -1.000 ppm
F2              -499.87 Hz
PPMCM          0.55000 ppm/cm
HZCM          274.93124 Hz/cm
```