Supporting Information

Enantioselective Acylation of 1,2- and 1,3-Diols Catalyzed by Aminophosphinite Derivatives of (1*S*,2*R*)-1-Amino-2-indanol

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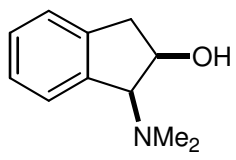
General Information

Reactions were run in dried glassware under a nitrogen or argon atmosphere. Flash column chromatography was carried out on silica gel 60 (Cica-MERCK). Column chromatography using alumina gel was performed on Merck aluminum oxide 90 active basic. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 400 spectrometer using $CDCl_3$ as a solvent. Chemical shifts are reported in δ from TMS as an internal standard for the ^{1}H NMR. For the ^{13}C NMR spectra, the signal of $CDCl_3$ (77.0 ppm) was employed as a standard of their chemical shifts. ^{31}P chemical shifts were recorded relative to a signal for 85% phosphoric acid which was used as an external reference. Mass spectra and HRMS were obtained by EI or FAB ionization mode at 70 eV or voltages indicated in parentheses. Melting points are uncorrected.

Typical procedure for the preparation of aminoindanol derivatives

(*1S,2R*) -1-Dimethylamino-2-indanol [1]

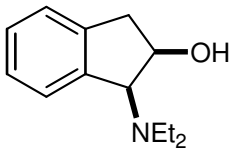


Formic acid (90% purity, 209 μL, 5 mmol) and 35% aqueous formaldehyde solution (1.57 mL, 20 mmol) were added to (1*S*,2*R*)-1-amino-2-indanol (149 mg, 1 mmol). After heated to reflux for 6.5 h, the solution was cooled to room temperature and treated with saturated aqueous Na_2CO_3 to make the solution weak alkaline. Then, the mixture was extracted with CH_2Cl_2, and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation (0.38 mmHg, 120 ℃) to give the corresponding aminoindanol derivative as a white solid (161 mg, 91%); ^{1}H NMR δ 2.29 (s, 6H), 2.80 (dd, *J* = 8 and 16 Hz, 1H), 3.26 (dd, *J* = 8 and 16 Hz, 1H), 4.07 (d, *J* = 8 Hz, 1H), 4.44 (q, *J* = 8 Hz, 1H), 4.71 (brs, 1H), 7.19-7.33 (m, 4H); ^{13}C NMR δ 41.2, 43.1, 69.6, 69.8, 125.4, 126.29, 126.34, 128.4, 138.3,

141.6; IR (KBr) ν 3060, 2950, 2880, 1450, 1330, 1055, 1040 cm^{-1}; MS *m/z* 177 (M^+).

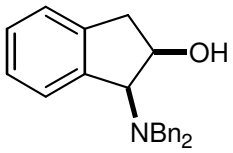
The other aminoindanol derivatives were prepared by alkylation reaction using appropriate halogenated alkanes in the presence of Na_2CO_3 or $NaHCO_3$.[2] Representative procedure is as follows.

(*1S,2R*) -1-Diethylamino-2-indanol



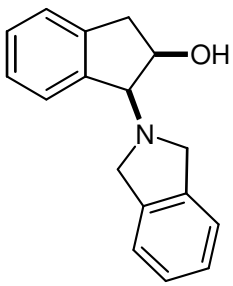
Ethyl iodide (0.48 mL, 6 mmol) was added to a solution of (1*S*, 2*R*)-1-amino-2-indanol (448 mg, 3 mmol) and Na_2CO_3 (636 mg, 6 mmol) in dry EtOH (3 mL). After the solution was heated to reflux for 16 h under nitrogen atmosphere, the reaction was quenched with water at room temperature. After evaporation of volatile solvent, the residue was extracted with diethyl ether. The combined organic layers was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel eluting with ethyl acetate / MeOH (5 / 1) to give the desired product as a colorless oil (411 mg, 67%); ^{1}H NMR δ 1.09 (t, *J* = 7 Hz, 6H), 2.41 (dq, *J* = 7 and 13 Hz, 2H), 2.56 (dq, *J* = 7 and 13 Hz, 2H), 2.73 (dd, *J* = 7 and 16 Hz, 1H), 3.27 (dd, *J* = 8 and 16 Hz, 1H), 4.29 (d, *J* = 8 Hz, 1H), 4.36 (dt, *J* = 7 and 8 Hz, 1H), 4.87 (brs, 1H), 7.17-7.31 (m, 4H); ^{13}C NMR δ 13.6, 41.4, 45.6, 67.0, 69.0, 125.4, 126.1, 126.4, 128.2, 139.6, 142.0; IR (neat) ν 3410, 3270, 2990, 2950, 2860, 1485, 1410, 1385, 1300, 1215, 1180, 1090 cm^{-1}; MS *m/z* 205 (M^+)

(*1S,2R*) -1-Dibenzylamino-2-indanol



^{1}H NMR δ 2.79-2.87 (m, 1H), 3.21-3.29 (m, 1H), 3.52 (d, *J* = 14 Hz, 2H), 3.73 (d, *J* = 14 Hz, 2H), 4.35- 4.42 (m, 3H), 7.20-7.36 (m, 14H); ^{13}C NMR δ 41.5, 56.1, 64.8, 70.3, 125.6, 126.0, 126.6, 127.3, 128.4, 128.6, 128.9, 138.8, 139.4, 141.6; IR (neat) ν 3390, 3040, 2940, 2850, 1955, 1880, 1815, 1740, 1610, 1590, 1500, 1480, 1450, 1360, 1210, 1160, 1080 cm^{-1}; MS *m/z* 329 (M^+); HRMS *m/z* calcd for $C_{23}H_{23}ON$ 329.1779, found 329.1800.

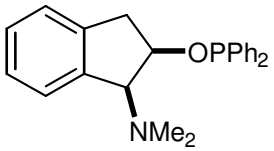
(*1S,2R*) -1-(Isoindolin-2-yl) -2-indanol [3]



^{1}H NMR δ 2.87 (dd, *J* = 7 and 16 Hz, 1H), 3.26 (dd, *J* = 7 and 16 Hz, 1H), 3.64 (brs, 1H), 4.01 (d, *J* = 11 Hz, 2H), 4.19 (d, *J* = 11 Hz, 2H), 4.47 (d, *J* = 7 Hz, 1H), 4.52 (q, *J* = 7 Hz, 1H), 7.15-7.36 (m, 8H); ^{13}C NMR δ 40.6, 56.1, 66.8, 70.8, 122.2, 125.5, 126.75, 126.84, 128.6, 139.0, 139.3, 141.7; IR (KBr) ν 3340, 2940, 2810, 1465, 1395, 1365, 1090, 1065 cm^{-1}; HRMS (20 eV) *m/z* calcd for $C_{17}H_{17}ON$ 251.1310, found 251.1294.

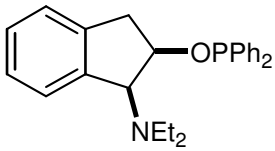
Typical procedure for the preparation of phosphinite derivatives 3a-d

Phosphinite derivative 3a



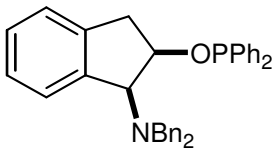
To a solution of *N*,*N*-dimethylaminoindanol (531 mg, 3 mmol) in dry CH_2Cl_2 (12 mL), *N*,*N*-diisopropylethylamine (538 μL, 3 mmol), and chlorodiphenylphosphine (538 μL, 3 mmol) were added dropwise under argon atmosphere. After the mixture was heated to reflux for 13 h, the reaction was quenched with water at rt. The resulting solution was extracted with CH_2Cl_2 and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on alumina gel eluting with *n*-hexane / ethyl acetate (5 / 1) to give the corresponding phosphinite derivative as a white solid (1.02 g, 94%); ^{1}H NMR δ 2.36 (s, 6H), 3.05-3.15 (m, 2H), 4.22 (d, *J* = 7 Hz, 1H), 4.81-4.88 (m, 1H), 7.15-7.18 (m, 1H), 7.20-7.25 (m, 2H), 7.28-7.36 (m, 7H), 7.44-7.48 (m, 2H), 7.53-7.58 (m, 2H); ^{13}C NMR δ 39.3 (J_{CP} = 6.1 Hz), 41.9, 70.0 (J_{CP} = 6.1 Hz), 81.4 (J_{CP} = 16.9 Hz), 124.8-142.9 (aromatic carbons); ^{31}P NMR (162 MHz) δ 110.2; IR (KBr) ν 3060, 2940, 2880, 1480, 1430, 1350, 1075, 1030 cm^{-1}; MS (20 eV) *m/z* 361 (M^+); HRMS (20 eV) *m/z* calcd for $C_{23}H_{24}ONP$ 361.1596, found 361.1573.

Phosphinite derivative 3b



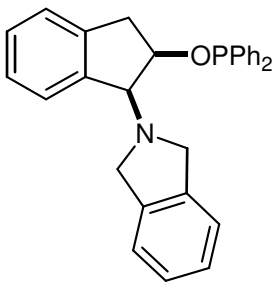
3b was obtained as a colorless oil in 98% yield; ^{1}H NMR δ 0.99 (t, *J* = 7 Hz, 6H), 2.63-2.80 (m, 4H), 2.97 (dd, *J* = 6 and 16 Hz, 1H), 3.07 (dd, *J* = 3 and 16 Hz, 1H), 4.44 (d, *J* = 6 Hz, 1H), 4.82-4.88 (m, 1H), 7.12-7.39 (m, 12H), 7.49-7.54 (m, 2H); ^{31}P NMR (162 MHz) δ 109.6; IR (neat) ν 3060, 2980, 2940, 2860, 1730, 1590, 1435, 1370, 1070, 1040 cm^{-1}; HRMS *m/z* calcd for $C_{25}H_{28}ONP$ 389.1908, found 389.1927.

Phosphinite derivative 3c



3c was obtained as a colorless oil in 88% yield; ^{1}H NMR δ 2.95 (dd, *J* = 6 and 17 Hz, 1H), 3.09 (dd, *J* = 3 and 17 Hz, 1H), 3.80 (d, *J* = 14 Hz, 2H), 3.90 (d, *J* = 14 Hz, 2H), 4.34 (d, *J* = 5 Hz, 1H), 4.90-4.96 (m, 1H), 7.12-7.48 (m, 22H), 7.60-7.66 (m, 2H); ^{31}P NMR (162 MHz) δ 111.7; IR (neat) ν 3040, 2920, 1950, 1880, 1815, 1740, 1600, 1440, 1360, 1160, 1070, 1030 cm^{-1}.

Phosphinite derivative 3d

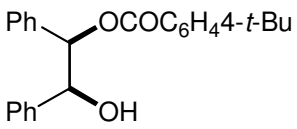


3d was obtained as a colorless oil in 79% yield; ^{1}H NMR δ 3.13-3.25 (m, 2H), 4.17-4.28 (m, 4H), 4.60 (d, *J* = 6 Hz, 1H), 4.91-4.98 (m, 1H), 7.02-7.41 (m, 18H); ^{31}P NMR (162 MHz) δ 111.1; HRMS (20 eV) *m/z* calcd for $C_{29}H_{26}ONP$ 435.1752, found 435.1767.

Typical procedure for the 3a-catalyzed desymmetrization of *meso*-diols

A solution of aminophosphinite **3a** (18.1 mg, 0.05 mmol) in dry toluene (4 mL), *N, N*-diisopropylethyl amine (129 mg, 1.0 mmol), and 4-*tert*-butylbenzoyl chloride (293 μL, 1.5 mmol) were added to the mixture of diol (1.0 mmol) and dried 4 Å molecular sieves (0.2 g) in dry toluene (8 mL) under argon atmosphere at 0 ℃. After being stirred at 0 ℃ for 6-24 h (see Table 3), the reaction was quenched with water. After the molecular sieves were removed by suction filter, the filtrate was extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n* – hexane / ethyl acetate. Absolute configuration of products was not determined except for a 4-*tert*-butylbenzoate of *meso*-hydrobenzoin.

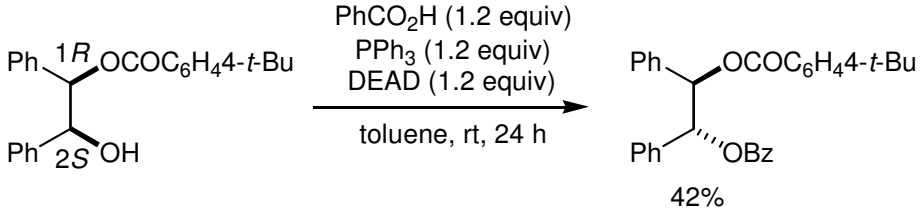
4-*tert*-butylbenzoate of *meso*-hydrobenzoin



361 mg (97% yield); 95% ee; a white solid; $[\alpha]_D^{27}$ = +43.5 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 1.33 (s, 9H), 2.28 (brd, 1H), 5.13 (dd, *J* = 3 and 6 Hz, 1H), 6.14 (d, *J* = 6 Hz, 1H), 7.24-7.32 (m, 10H), 7.43-7.45 (m, 2H), 7.92-7.95 (m, 2H); ^{13}C NMR (100 MHz) δ 31.1, 35.1, 76.6, 79.3, 125.4, 127.0, 127.2, 127.5, 128.05, 128.10, 128.3, 128.4, 129.5, 136.7, 139.5, 156.8, 165.5; IR (KBr) ν 3550, 2970, 1700, 1610, 1450, 1320, 1280, 1175, 1120, 1100 cm^{-1}; MS *m/z* 374 (M^+); HRMS *m/z* calcd for $C_{25}H_{26}O_3$ 374.1882, found 374.1911; HPLC (CHIRALPAK AD-H, *n*-hexane / 2-propanol (80 / 20), λ = 254 nm, flow rate 1.0 mL / min) retention time 13.6 min (minor) and 19.3 min (major).

The above 4-*tert*-butylbenzoate of hydrobenzoin was transformed to (*R,R*)-hydrobenzoin by the Mitsunobu reaction of the monoester followed by the hydrolysis of the resulting diester. Therefore, the initial product was assigned to be a (1*R*,2*S*) adduct.

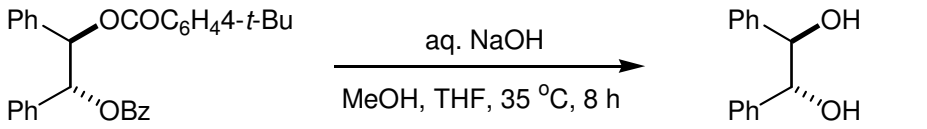
Mitsunobu reaction using benzoic acid



Triphenyl phosphine (162 mg, 0.6 mmol), benzoic acid (73 mg, 0.6 mmol), and diethyl azodicarboxylate (40% in toluene, 261 mg, 0.6 mmol) were added to a solution of 4-*tert*-butylbenzoate (187 mg, 0.5 mmol) in dry toluene (3 mL) at 0 ℃ under nitrogen atmosphere. After being stirred at rt for 24 h, the solution was treated with water and extracted with CH_2Cl_2. The extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n*-hexane / ethyl acetate (15 / 1) to

afford the corresponding diester as a white solid (101 mg, 42%); ^{1}H NMR δ 1.31 (s, 9H), 6.43 (s, 2H), 7.21-7.28 (m, 10H), 7.38-7.43 (m, 4H), 7.50-7.54 (m, 1H), 7.96-7.99 (m, 2H), 8.03-8.07 (m, 2H).

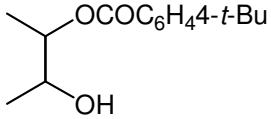
Hydrolysis of the diester



(*R, R*)-hydrobenzoin
93%

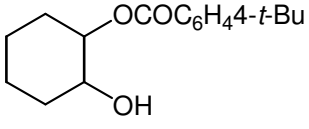
A solution of the diester (101 mg, 0.21 mmol) in MeOH (7 mL), THF (7 mL), and aqueous 10% NaOH (7 mL) was stirred at 35 ℃ for 8 h. After the mixture was concentrated under reduced pressure, the residue was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n*-hexane / ethyl acetate (2 / 1) to afford the corresponding diol as a white solid (42 mg, 93%); ^{1}H NMR δ 2.82 (s, 2H), 4.72 (s, 2H), 7.10-7.16 (m, 4H), 7.21-7.27 (m, 6H); $[\alpha]_D^{26}$ = +91.2 (c = 0.5, $CHCl_3$) [commercially available (*R,R*)-hydrobenzoin (>99% ee), $[\alpha]_D^{29}$ = +92.0 (c=0.5, $CHCl_3$)], HPLC (CHIRALPAK AD-H, *n*-hexane / 2-propanol (95 / 5), λ = 254 nm, flow rate 1.0 mL / min) retention time 33.1 min.

4-*tert*-Butylbenzoate of *meso*-2,3-butanediol



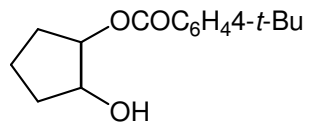
206 mg (82% yield); 89% ee; a colorless oil; $[\alpha]_D^{29}$ = −10.0 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 1.25 (d, *J* = 6 Hz, 3H), 1.33-1.35 (m, 12H), 2.1 (brs, 1H), 4.01 (dq, *J* = 3 and 6 Hz, 1H), 5.12 (dq, *J* = 3 and 6 Hz, 1H), 7.45-7.48 (m, 2H), 7.96-7.99 (m, 2H); ^{13}C NMR (100 MHz) δ 14.5, 18.0, 31.1, 35.1, 69.9, 74.9, 125.4, 127.5, 129.5, 156.8, 166.3; IR (neat) ν 3450, 2950, 1700, 1600, 1450, 1400, 1270, 1180, 1120, 1080 cm^{-1}; MS *m/z* 250 (M^+); HRMS (40 eV) *m/z* calcd for $C_{15}H_{22}O_3$ 250.1569, found 250.1555; HPLC (CHIRALPAK AD-H, *n*-hexane / 2-propanol (95 / 5), λ = 254 nm, flow rate 1.0 mL / min) retention time 10.9 min (minor) and 13.3 min (major).

4-*tert*-Butylbenzoate of *cis*-1,2-cyclohexanediol



228 mg (83% yield); 93% ee; a white solid; $[\alpha]_D^{27}$ = −9.8 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 1.34-1.50 (m, 11H), 1.61-1.88 (m, 5H), 1.96-2.04 (m, 2H), 3.92-3.99 (m, 1H), 5.20-5.22 (m, 1H), 7.45-7.48 (m, 2H), 7.97-8.00 (m, 2H); ^{13}C NMR (100 MHz) δ 21.6, 21.8, 27.4, 30.4, 31.1, 35.1, 69.7, 74.4, 125.4, 127.6, 129.5, 156.8, 166.2; IR (KBr) ν 3280, 2950, 1715, 1610, 1280, 1190, 1130, 1110, 1080 cm^{-1}; MS *m/z* 276 (M^+); HRMS (40 eV) *m/z* calcd for $C_{17}H_{24}O_3$ 276.1725, found 276.1718; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (95 / 5), λ = 254 nm, flow rate 1.0 mL / min) retention time 7.0 min (minor) and 9.6 min (major).

4-*tert*-Butylbenzoate of *cis*-1,2-cyclopentanediol



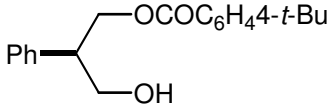
251 mg (96% yield); 59% ee; a colorless oil ; $[\alpha]_D^{27}$ = −6.0 (c = 1.0, $CHCl_3$); ^{1}H NMR δ 1.34 (s, 9H), 1.56-1.69 (m, 1H), 1.75-1.83 (m, 1H), 1.87-2.00 (m, 4H), 2.04-2.14 (m, 1H), 4.27-4.33 (m, 1H), 5.20-5.25 (m, 1H), 7.44-7.48 (m, 2H), 7.96-8.00 (m, 2H); ^{13}C NMR (100 MHz) δ 19.5, 28.2, 30.9, 31.1, 35.1, 73.4, 77.2, 125.4, 127.3, 129.5, 156.8, 166.4; IR (neat) ν 3470, 2960, 1710, 1610, 1280, 1185, 1120 cm^{-1}; MS *m/z* 262 (M^+); HRMS *m/z* calcd for $C_{16}H_{22}O_3$ 262.1569, found 262.1526; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (90/10), λ = 254 nm, flow rate 1.0 mL / min) retention time 5.7 min (minor) and 7.4 min (major).

Typical procedure for the 3a-catalyzed desymmetrization of 1,3-propanediol derivatives

To a suspension of phosphinite derivative **3a** (0.025 mmol, 2.5 mol%) and dried 4 Å molecular sieves (0.5 g) in toluene (12 mL), *N*,*N*-diisopropylethylamine (129 mg, 1.0 mmol), 1,3-propanediol (1.0 mmol), and 4-*tert*-butylbenzoyl chloride (293 μL, 1.5 mmol) were added at 0 ℃ under nitrogen atmosphere. The resulting suspension was stirred for the time indicated in Table 4 and the reaction was quenched with water. After the molecular sieves were removed by suction filter, the filtrate was extracted with Et_2O and the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with *n*-hexane / ethyl acetate to give the desired monoester and diester. Enantiomeric excess was determined by HPLC analysis.

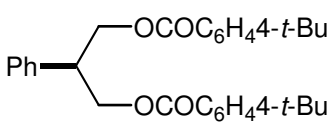
4-*tert*-Butylbenzoylation of 2-phenyl-1,3-propanediol

Monoester



223 mg (71% yield); 63% ee (for 2.5 mol % cat.); a colorless oil; $[\alpha]_D^{26}$ = +4.9 (c = 1.01, $CHCl_3$); ^{1}H NMR δ 1.34 (s, 9H), 2.03 (brs, 1H), 3.29 (quint, *J* = 8 Hz, 1H), 3.89-3.98 (m, 2H), 4.58-4.68 (m, 2H), 7.27-7.39 (m, 5H), 7.44-7.47 (m, 2H), 7.92-7.95 (m, 2H); ^{13}C NMR(100 MHz) δ 31.1, 35.1, 47.6, 63.8, 65.2, 125.4, 127.1, 127.3, 128.2, 128.8, 129.5, 139.1, 156.9, 166.9; IR (neat) ν 3450, 2980, 1720, 1610, 1410, 1280, 1190, 1120 cm^{-1}; MS *m/z* 297 (M^+-Me); HRMS (20 eV) *m/z* calcd for $C_{20}H_{24}O_3$ 312.1726, found 312.1752; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (90 / 10), λ = 254 nm, flow rate 1.0 mL / min) retention time 12.7 min (major) and 17.4 min (minor).

Diester

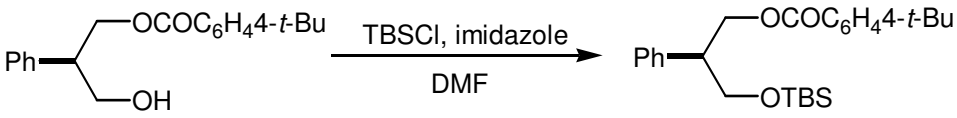


52 mg (11% yield for 2.5 mol % cat.); a white solid; ^{1}H NMR δ 1.32 (s, 18H), 3.61 (quint, *J* = 7 Hz, 1H), 4.63-4.70 (m, 4H), 7.27-7.31 (m, 1H), 7.34-7.44 (m, 8H), 7.89-7.92 (m, 4H); ^{13}C NMR(100 MHz) δ 31.1, 35.1, 44.2, 65.3, 125.3, 127.2, 127.4, 128.0, 128.7, 129.5, 138.6, 156.7, 166.4;

IR (KBr) ν 2980, 1720, 1610, 1410, 1270, 1190, 1115, 1100 cm^{-1}; HRMS (15 eV) *m/z* calcd for $C_{31}H_{36}O_4$ 472.2614, found 472.2632.

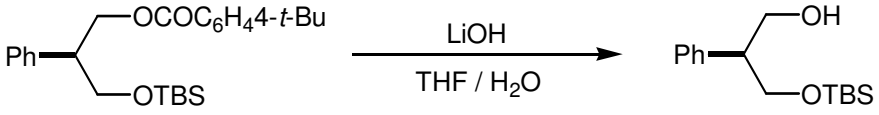
The absolute configuration was determined by the specific rotation of a *tert*-butyldimethylsilyloxy alcohol. [4]

Protection of hydroxyl group with *tert*-butyldimethylsilylchloride (TBSCl)



To a solution of the ester (526 mg, 1.68 mmol) in dry DMF (5 mL), imidazole (189 mg, 2.78 mmol) and TBSCl (279 mg, 1.85 mmol) were added under nitrogen atmosphere. After being stirred at rt for 2 h, the mixture was treated with water and extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n*-hexane / ethyl acetate to afford the corresponding TBS ether; 571 mg (80% yield); $[\alpha]_D^{26} = -5.3$ (c = 1.1, $CHCl_3$); ^{1}H NMR δ -0.02 (s, 6H), 0.86 (s, 9H), 1.32 (s, 9H), 3.25 (quint, *J* = 6 Hz, 1H), 3.92 (d, *J* = 6 Hz, 2H), 4.58 (dd, *J* = 6 and 11 Hz, 1H), 4.66 (dd, *J* = 6 and 11 Hz, 1H), 7.21-7.27 (m, 1H), 7.28-7.34 (m, 4H), 7.41-7.43 (m, 2H), 7.87-7.91 (m, 2H); ^{13}C NMR(100 MHz) δ –5.6, 18.2, 25.8, 31.1, 35.0, 47.3, 64.3, 65.3, 125.3, 126.9, 127.6, 128.28, 128.34, 129.4, 140.0, 156.4, 166.5; IR (KBr) ν 2970, 1725, 1615, 1470, 1280, 1260, 1190, 1100 cm^{-1}.

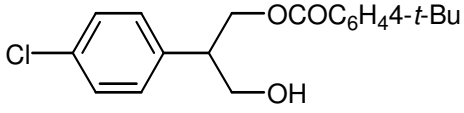
Hydrolysis of silyloxy ester



A mixture of silyloxy ester (479 mg, 1.12 mmol) and LiOH monohydrate (0.10 g, 2.4 mmol) in THF (3 mL) and H_2O (1.5 mL) was heated to reflux for 25 h. After evaporation of volatile solvent under reduced pressure, the residual solution was extracted with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n*-hexane / ethyl acetate to afford the corresponding alcohol; 72 mg (24% yield); $[\alpha]_D^{26} = -7.5$ (c = 1.36, $CHCl_3$) (lit.[4] $[\alpha]_D$ = +14.7 (c=1.00, $CHCl_3$) for *R* isomer); ^{1}H NMR δ 0.06 (s, 6H), 0.90 (s, 9H), 2.68 (brs, 1H), 3.05-3.12 (m, 1H), 3.86-3.93 (m, 3H), 4.06-4.09 (m, 1H), 7.20-7.33 (m, 5H).

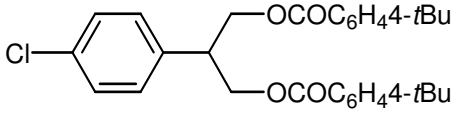
4-*tert*-Butylbenzoate of 2-(4-chlorophenyl)-1,3-propanediol

Monoester



250 mg (72% yield); 67% ee (for 5 mol % cat.); a colorless oil; $[\alpha]_D^{25}$ = +1.4 (c = 0.70, $CHCl_3$); ^{1}H NMR δ 1.34 (s, 9H), 2.04 (s, 1H), 3.29 (quint, *J* = 6 Hz, 1H), 3.90 (d, *J* = 6 Hz, 2H), 4.56-4.65 (m, 2H), 7.26-7.28 (m, 2H), 7.31-7.34 (m, 2H), 7.44-7.47 (m, 2H), 7.90-7.93 (m, 2H); ^{13}C NMR(100 MHz) δ 31.1, 35.1, 47.0, 63.5, 64.8, 125.5, 126.9, 128.9, 129.5, 129.6, 133.1, 137.7, 157.0, 166.8; IR (neat) ν 3440, 2970, 1710, 1610, 1490, 1270, 1190, 1110 cm^{-1}; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (97 / 3), λ = 254 nm, flow rate 1.0 mL / min) retention time 32.6 min (major) and 37.8 min (minor).

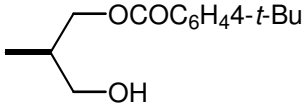
Diester



65 mg (13% yield for 5 mol % cat.); a white solid; ^{1}H NMR δ 1.33 (s, 18H), 3.60 (quint, *J* = 7 Hz, 1H), 4.64 (d, *J* = 7 Hz, 4H), 7.30-7.35 (m, 4H), 7.41-7.44 (m, 4H), 7.88-7.91 (m, 4H); ^{13}C NMR(100 MHz) δ 31.1, 35.1, 43.7, 65.0, 125.4, 127.0, 128.9, 129.4, 129.5, 133.3, 137.1, 156.8, 166.3; IR (KBr) ν 2970, 1710, 1610, 1410, 1270, 1190, 1120 cm^{-1}.

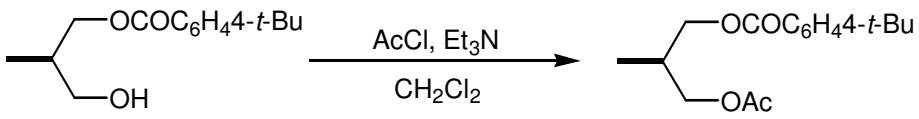
4-*tert*-Butylbenzoate of 2-methyl-1,3-propanediol

Monoester



187 mg (75% yield for 5 mol % cat.); a colorless oil; $[\alpha]_D^{26}$ = +1.1 (c = 0.71, $CHCl_3$) (lit.[5] $[\alpha]_D$ = +2.03 (c = 1.0, $CHCl_3$) for *R* isomer (96% ee)); ^{1}H NMR δ 1.04 (d, *J* = 7 Hz, 3H), 1.34 (s, 9H), 1.60 (brs, 1H), 2.07-2.18 (m, 1H), 3.56 (dd, *J* = 6 and 11 Hz, 1H), 3.62 (dd, *J* = 5 and 11 Hz, 1H), 4.29 (dd, *J* = 6 and 11 Hz, 1H), 4.39 (dd, *J* = 5 and 11 Hz, 1H), 7.45-7.48 (m, 2H), 7.95-7.99 (m, 2H); IR (neat) ν 3450, 2980, 1730, 1615, 1470, 1415, 1280, 1190, 1120 cm^{-1}. The ee was determined by HPLC analysis of the acetate derivative.

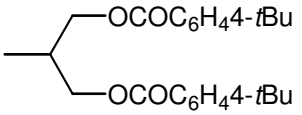
Preparation of the acetate derivative



To a solution of 4-*tert*-butylbenzoate (0.18 g, 0.72 mmol) in CH_2Cl_2 (12 mL), triethylamine (0.20 mL, 1.4 mmol) and acetyl chloride (0.10 mL, 1.4 mmol) were added under nitrogen atmosphere. After being stirred at rt for 44 h, the mixture was treated with water and extracted with

CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography eluting with *n*-hexane / ethyl acetate to afford the corresponding acetate; 170 mg (81% yield); 47% ee (the derivative of the 4-*tert*-butylbenzoate obtained from the reaction using 5.0 mol % catalyst); a colorless oil; ^{1}H NMR δ 1.08 (d, *J* = 7 Hz, 3H), 1.34 (s, 9H), 2.06 (s, 3H), 2.28-2.37 (m, 1H), 4.11 (d, *J* = 6 Hz, 2H), 4.26 (d, *J* = 6 Hz, 2H), 7.45-7.47 (m, 2H), 7.95-7.97 (m, 2H); ^{13}C NMR(100 MHz) δ 13.9, 20.8, 31.1, 32.6, 35.0, 65.96, 66.03, 125.3, 127.3, 129.4, 156.7, 166.4, 171.0; MS *m/z* 277 (M^+ - Me); IR (neat) ν 2980, 1740, 1720, 1610, 1470, 1360, 1270, 1240, 1190, 1120 cm^{-1}; HPLC (CHIRALPAK OD-H, *n*-hexane / 2-propanol (99 / 1), λ = 254 nm, flow rate 1.0 mL / min) retention time 10.3 min (minor) and 12.4 min (major).

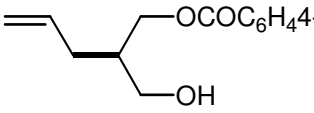
Diester



53 mg (13% yield for 5 mol % cat.); a white solid; ^{1}H NMR δ 1.16 (d, *J* = 7 Hz, 3H), 1.33 (s, 18H), 2.40-2.52 (m, 1H), 4.36 (d, *J* = 6 Hz, 4H), 7.43-7.46 (m, 4H), 7.96-7.99 (m, 4H); ^{13}C NMR(100 MHz) δ 14.0, 31.1, 32.9, 35.0, 66.2, 125.3, 127.3, 129.5, 156.6, 166.5; IR (KBr) ν 2980, 1730, 1615, 1470, 1410, 1280, 1190, 1120 cm^{-1}; MS *m/z* 410 (M^+).

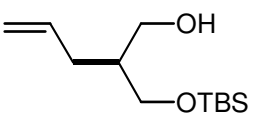
4-*tert*-Butylbenzoate of 2-allyl-1,3-propanediol

Monoester



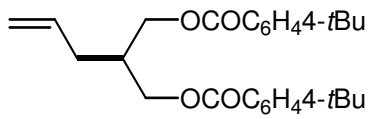
210 mg (76% yield); 60% ee (for 5 mol % cat.); a colorless oil; $[\alpha]_D^{26}$ = +5.2 (c = 0.71, $CHCl_3$); ^{1}H NMR δ 1.34 (s, 9H), 2.01-2.12 (m, 2H), 2.19-2.23 (m, 2H), 3.60 (dd, *J* = 6 and 11 Hz, 1H), 3.68 (dd, *J* = 5 and 11 Hz, 1H), 4.33 (dd, *J* = 6 and 11 Hz, 1H), 4.47 (dd, *J* = 5 and 11 Hz, 1H), 5.07-5.15 (m, 2H), 5.85 (ddt, *J* = 7, 10 and 17 Hz, 1H), 7.45-7.48 (m, 2H), 7.95-7.98 (m, 2H); ^{13}C NMR(100 MHz) δ 31.1, 32.7, 35.1, 40.6, 62.4, 64.2, 117.1, 125.4, 127.2, 129.5, 135.7, 156.8, 167.1; IR (neat) ν 3450, 3080, 2970, 1720, 1640, 1610, 1280, 1190, 1120 cm^{-1}; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (99 / 1), λ = 254 nm, flow rate 1.0 mL / min) retention time 31.4 min (minor) and 34.1 min (major). The absolute configuration was determined by the specific rotation of the *tert*-butyldimethylsilyloxy propanol derivative prepared by the reactions similar as 2-phenyl-1,3-propanediol mono 4-*tert*-butylbenzoate (see above).

***tert*-Butyldimethylsilyloxy propanol derivative**



^{1}H NMR δ 0.07 (s, 6H), 0.90 (s, 9H), 1.78-1.87 (m, 1H), 2.03-2.07 (m, 2H), 2.68 (dd, *J* = 5 and 6 Hz, 1H), 3.60-3.68 (m, 2H), 3.72-3.81 (m, 2H), 5.01-5.08 (m, 2H), 5.79 (ddt, *J* = 7, 10 and 17 Hz, 1H); $[\alpha]_D^{22}$ = – 2.7(c = 0.52, $CHCl_3$) [lit.[6] $[\alpha]_D$ = +3.73 (c = 1.76, $CHCl_3$) for *R* isomer]

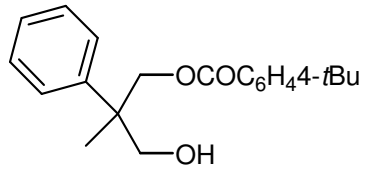
Diester



46 mg (11% yield for 5 mol % cat.); a white solid; ^{1}H NMR δ 1.34 (s, 18H), 2.32-2.43 (m, 3H), 4.38 (dd, *J* = 6 and 11 Hz, 2H), 4.44 (dd, *J* = 5 and 11 Hz, 2H), 5.09-5.16 (m, 2H), 5.86 (ddt, *J* = 7, 10 and 17 Hz, 1H), 7.43-7.46 (m, 4H), 7.95-7.98 (m, 4H); ^{13}C NMR(100 MHz) δ 31.1, 33.0, 35.1, 37.6, 64.3, 117.7, 125.4, 127.3, 129.5, 134.9, 156.7, 166.4; IR (KBr) ν 2970, 1710, 1610, 1275, 1190, 1120 cm^{-1}.

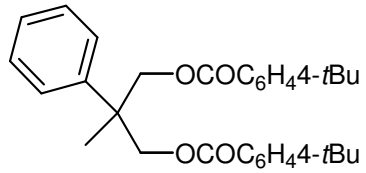
4-*tert*-Butylbenzoate of 2-metyl-2-phenyl-1,3-propanediol

Monoester



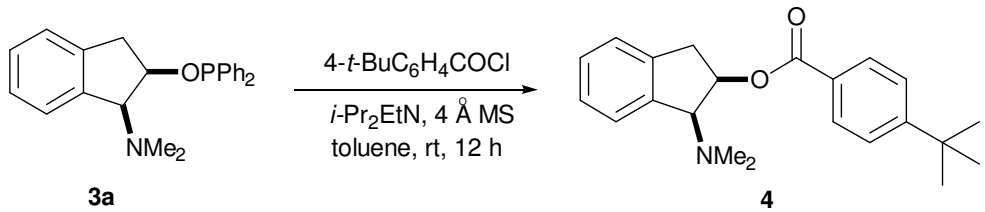
178 mg (55% yield); 42% ee (for 5 mol % cat.); a colorless oil; $[\alpha]_D^{24}$ = +3.4 (c = 0.71, $CHCl_3$); ^{1}H NMR δ 1.33 (s, 9H), 1.45 (s, 3H), 2.04 (brs, 1H), 3.82 (s, 2H), 4.59 (s, 2H), 7.25-7.29 (m, 1H), 7.36-7.40 (m, 2H), 7.42-7.47 (m, 4H), 7.90-7.93 (m, 2H); ^{13}C NMR(100 MHz) δ 20.8, 31.1, 35.1, 44.1, 67.9, 68.7, 125.4, 126.5, 126.8, 127.1, 128.6, 129.5, 142.7, 156.9, 166.9; IR (neat) ν 3460, 2970, 1720, 1610, 1280, 1190, 1120 cm^{-1};MS *m/z* 311 (M^+ - Me); HRMS (20 eV) *m/z* calcd for $C_{21}H_{26}O_3$ 326.1882, found 326.1891; HPLC (CHIRALPAK OJ-H, *n*-hexane / 2-propanol (90 / 10), λ = 254 nm, flow rate 0.5 mL / min) retention time 23.5 min (major) and 31.7 min (minor).

Diester



36 mg (7% yield for 5 mol % cat.); a white solid; ^{1}H NMR δ 1.32 (s, 18H), 1.57 (s, 3H), 4.62 (d, *J* = 11 Hz, 2H), 4.65 (d, *J* = 11 Hz, 2H), 7.26-7.29 (m, 1H), 7.36-7.43 (m, 6H), 7.48-7.51 (m, 2H), 7.87-7.90 (m, 4H); ^{13}C NMR(100 MHz) δ 30.9, 31.1, 35.1, 44.2, 65.3, 125.3, 127.2, 127.4, 128.0, 128.7, 129.5, 138.6, 156.7, 166.4; IR (KBr) ν 2960, 1720, 1610, 1260, 1180, 1110 cm^{-1}; HRMS (15 eV) *m/z* calcd for $C_{32}H_{38}O_4$ 486.2770, found 486.2775.

Reaction of 3a with 4-*tert*-butylbenzoyl chloride

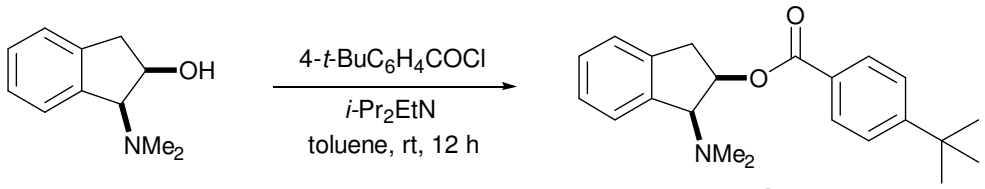


3a **4**

To a mixture of **3a** (181 mg, 0.50 mmol), dried 4 Å molecular sieves (0.1 g), and *i*-Pr_2EtN (129 mg, 1.00 mmol) in toluene (6 mL), 4-*tert*-butylbenzoyl chloride (197 mg, 1.00 mmol) was added dropwise at 0 °C under nitrogen atmosphere. After being stirred at room temperature for 12 h, the mixture was treated with water and extracted with CH_2Cl_2. The organic layer was washed with

brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified with silica gel column chromatography using *n*-hexane / ethyl acetate (10 / 1) as an eluent to afford 4-*tert*-butylbenzoate **4** in 70% yield (118 mg) as a white solid; ^{1}H NMR δ 1.33 (s, 9H), 2.46 (s, 6H), 3.13 (dd, *J* = 6 and 16 Hz, 1H), 3.28 (dd, *J* = 7 and 16 Hz, 1H), 4.44 (d, *J* = 6 Hz, 1H), 5.85-5.90 (m, 1H), 7.25-7.29 (m, 3H), 7.36-7.39 (m, 1H), 7.43-7.46 (m, 2H), 7.95-7.98(m, 2H); $[\alpha]_D^{26} = -64.8$ (c = 0.95, $CHCl_3$). ^{1}H NMR and value of specific rotation was consistent with one of the product obtained from the below reaction of *N,N*-dimethylaminoindanol with 4-*tert*-butylbenzoyl chloride.

Reaction of *N,N*-dimethylaminoindanol with 4-*tert*-butylbenzoyl chloride



4

To a mixture of *N,N*-dimethylaminoindanol (177 mg, 1.00 mmol) and *i*-Pr_2EtN (129 mg, 1.00 mmol) in toluene (3 mL), 4-*tert*-butylbenzoyl chloride (197 mg, 1.00 mmol) was added dropwise at 0 ^{o}C under nitrogen atmosphere. After being stirred at room temperature for 12 h, the mixture was treated with water and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified with silica gel column chromatography using *n*-hexane / ethyl acetate (10 / 1) as an eluent to afford 4-*tert*-butylbenzoate **4** in 97% yield (329 mg) as a white solid; $[\alpha]_D^{26} = -65.0$ (c = 1.06, $CHCl_3$).

References

(1) (a) Hirata, Y.; Yanagisawa, I.; Takeda, M.; Ino, H.; Takahashi, K.; Murakami, M. *Chem. Pharm. Bull*. **1977**, *25*, 1060-1066. (b) Rodríguez-Escrich, S.; Solà, L.; Jimeno, C.; Rodríguez-Escrich, C.; Pericàs, M. A. *Adv. Synth. Catal*. **2008**, *350*, 2250-2260.

(2) (a) Simone, B. D.; Savoia, D.; Tagliavini, E.; Umani-Ronchi, A. *Tetrahedron: Asymmetry,* **1995**, *6*, 301-306. (b) Zhao, D.; Chen, C.-y.; Xu, F.; Tan, L.; Tillyer, R.; Pierce, M. E.; Moore, J. R. *Organic Syntheses,* **1999**, *77,* (Ed.: Hart, D. J.), 12-21.

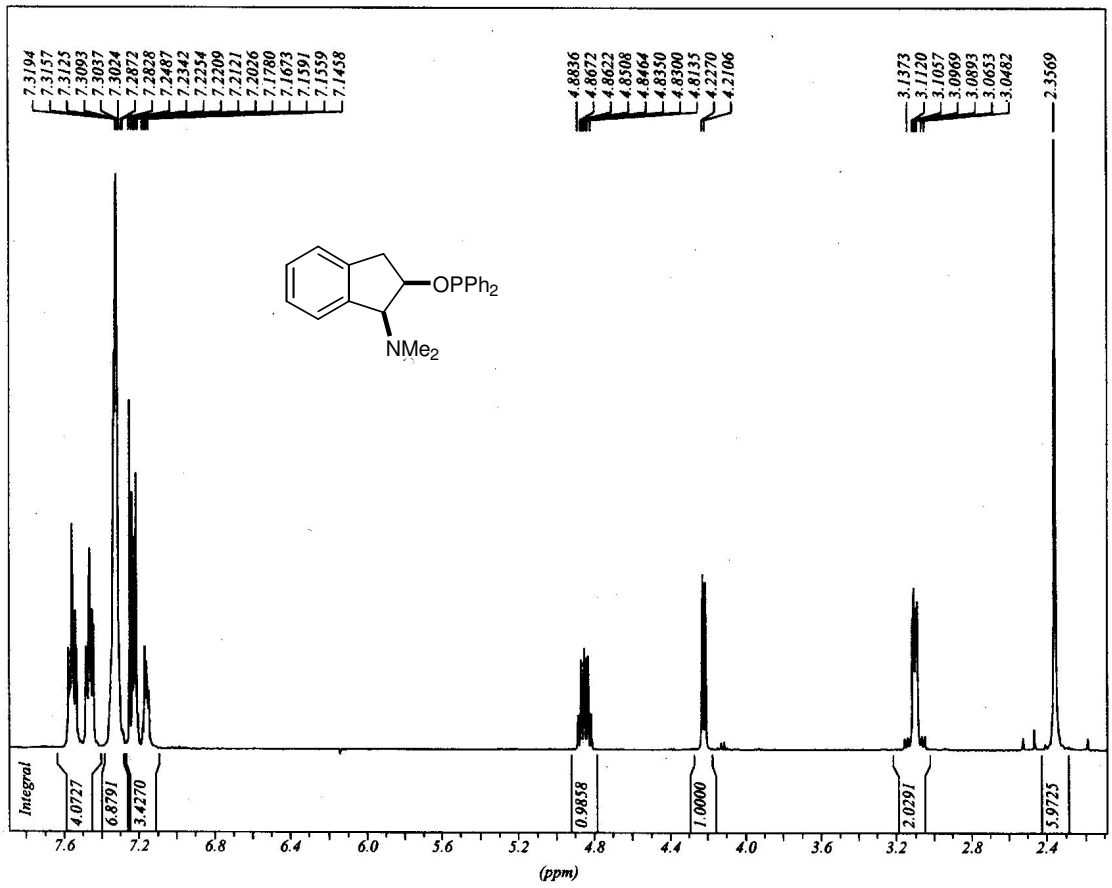
(3) Soh, J. Y.-T.; Tan, C.-H. *J. Am. Chem. Soc*. **2009**, *131*, 6904-6905.

(4) Maruoka, K.; Ooi, T.; Nagahara, S.; Yamamoto, H. *Tetrahedron*, **1991**, *47*, 6983-6998.

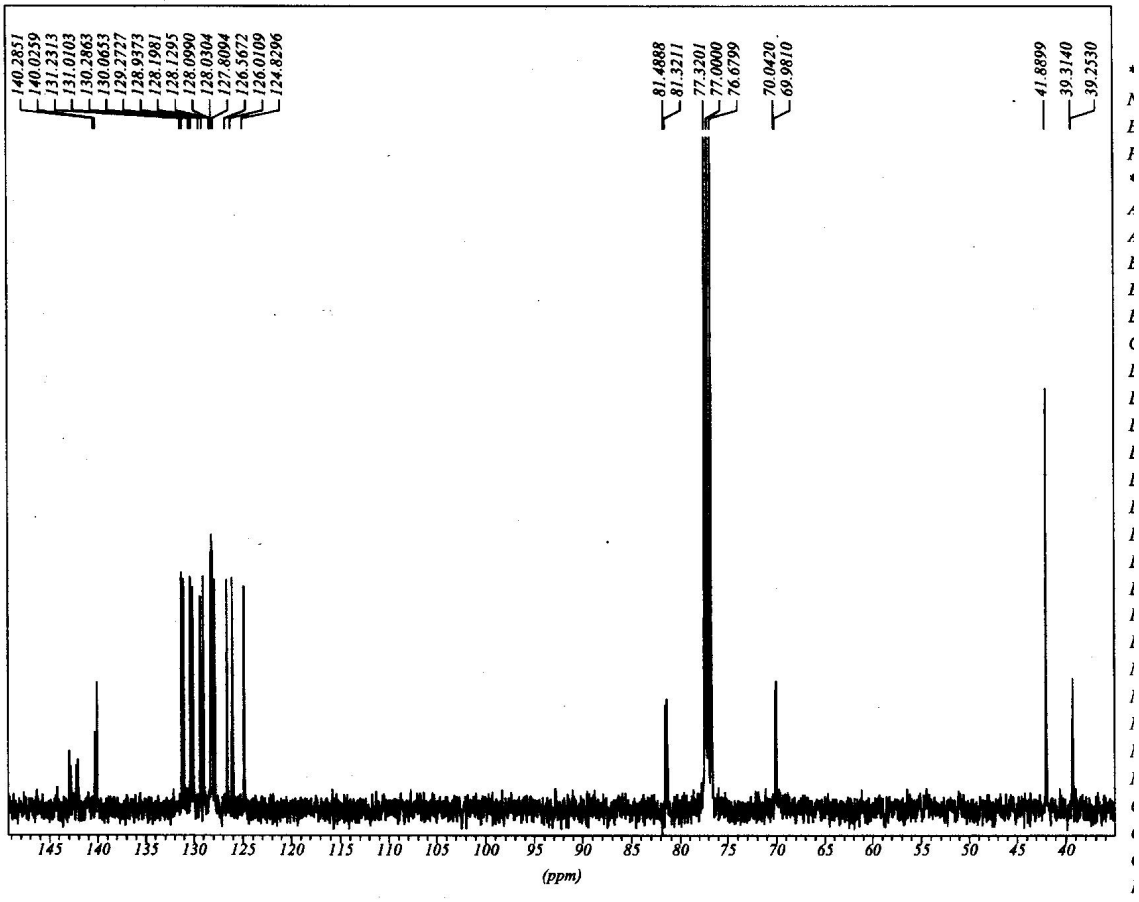
(5) Oriyama, T.; Taguchi, H.; Terakado, D.; Sano, T. *Chem. Lett*. **2002**, 26-27.

(6) Sells, T. B.; Nair, V. *Tetrahedron*, **1994**, *50*, 117-138.

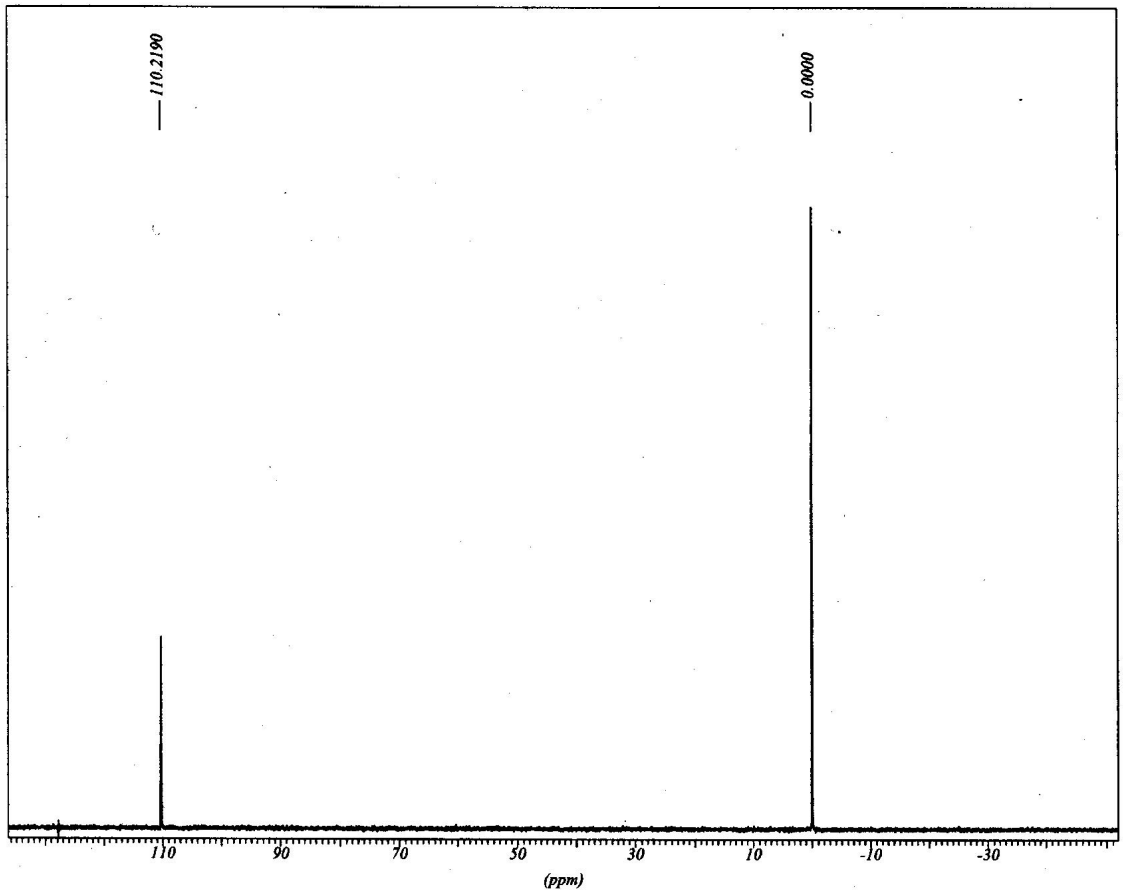
^{1}H NMR of Aminophosphinite 3a



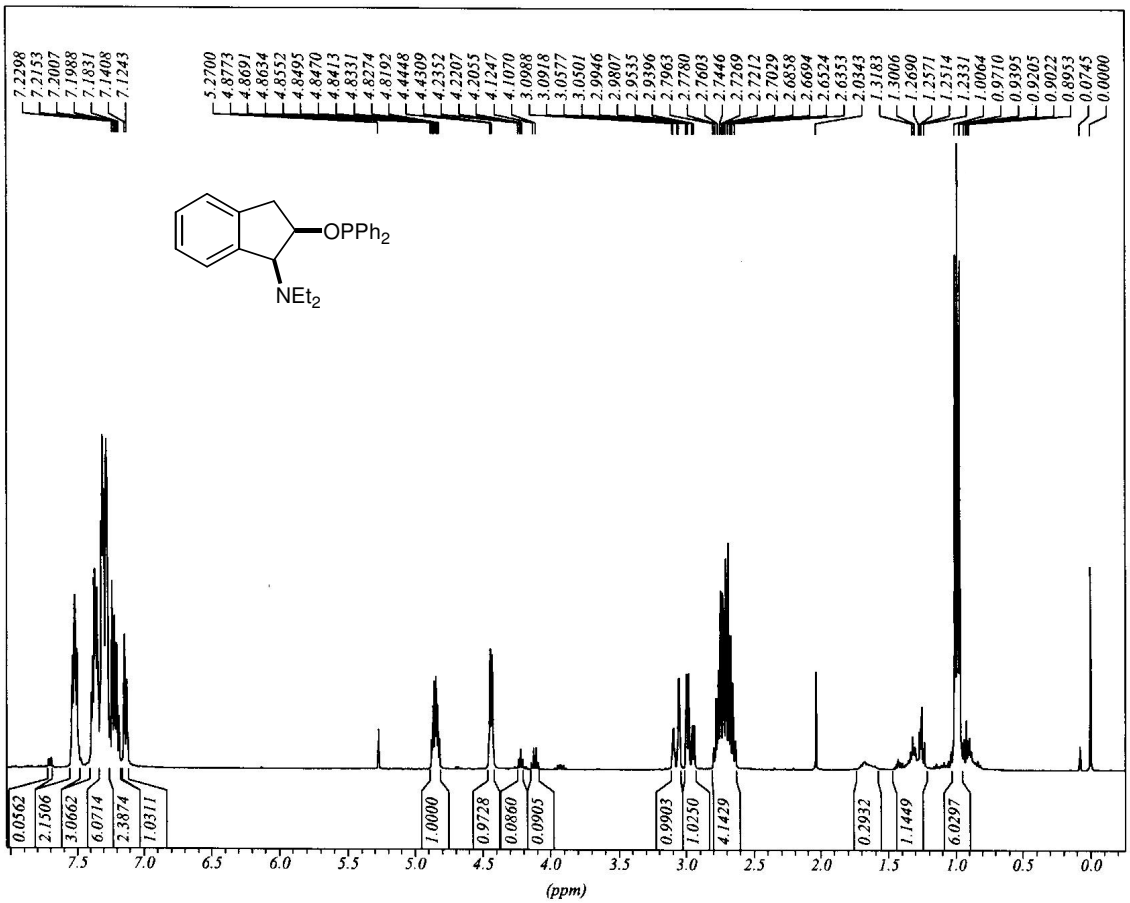
^{13}C NMR of Aminophosphinite 3a



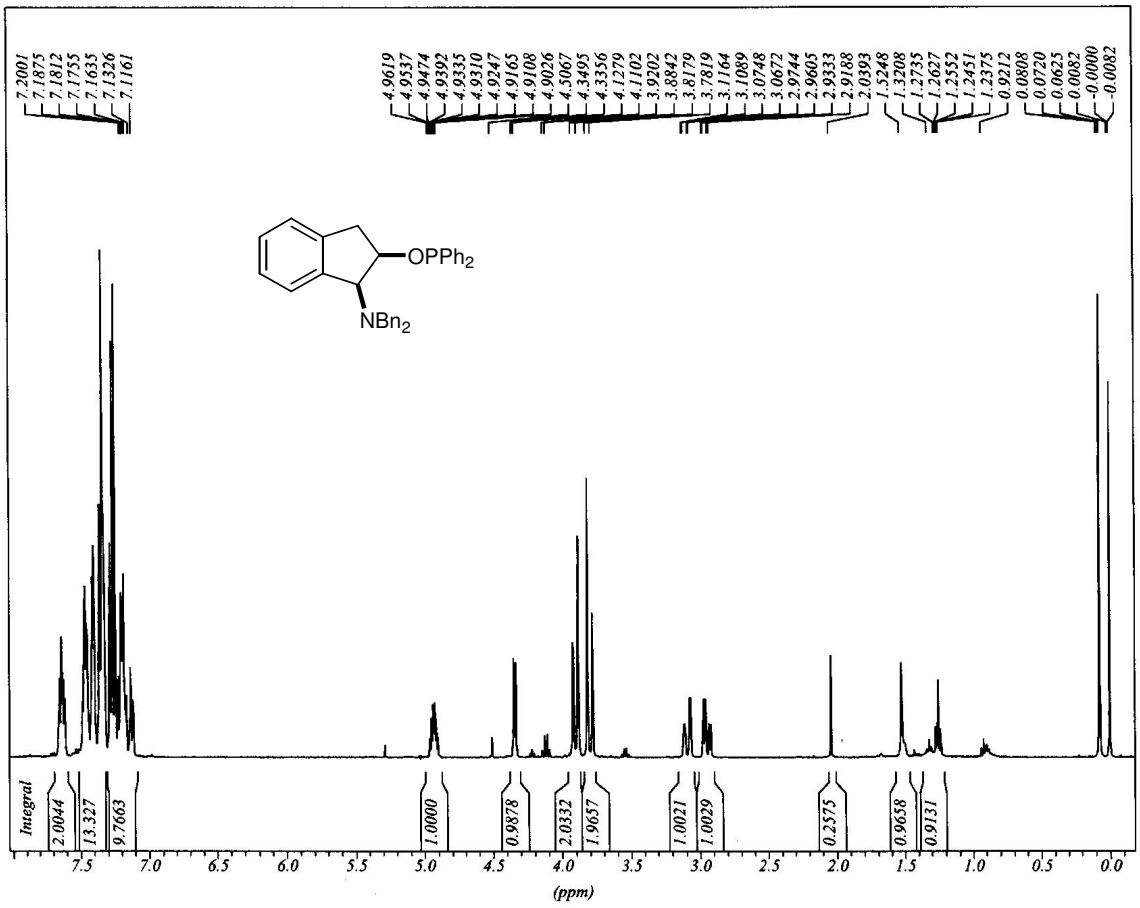
^{31}P NMR of Aminophosphinite 3a



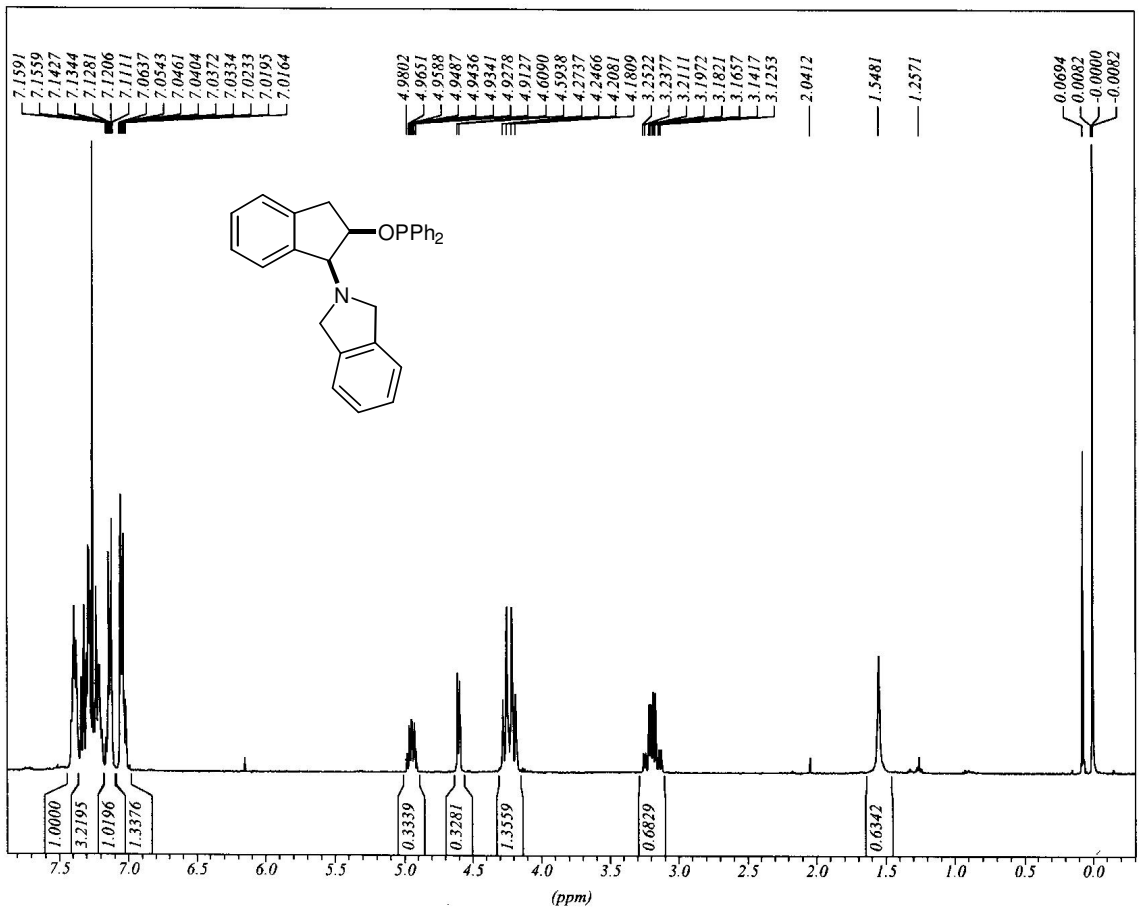
^{1}H NMR of Aminophosphinite 3b



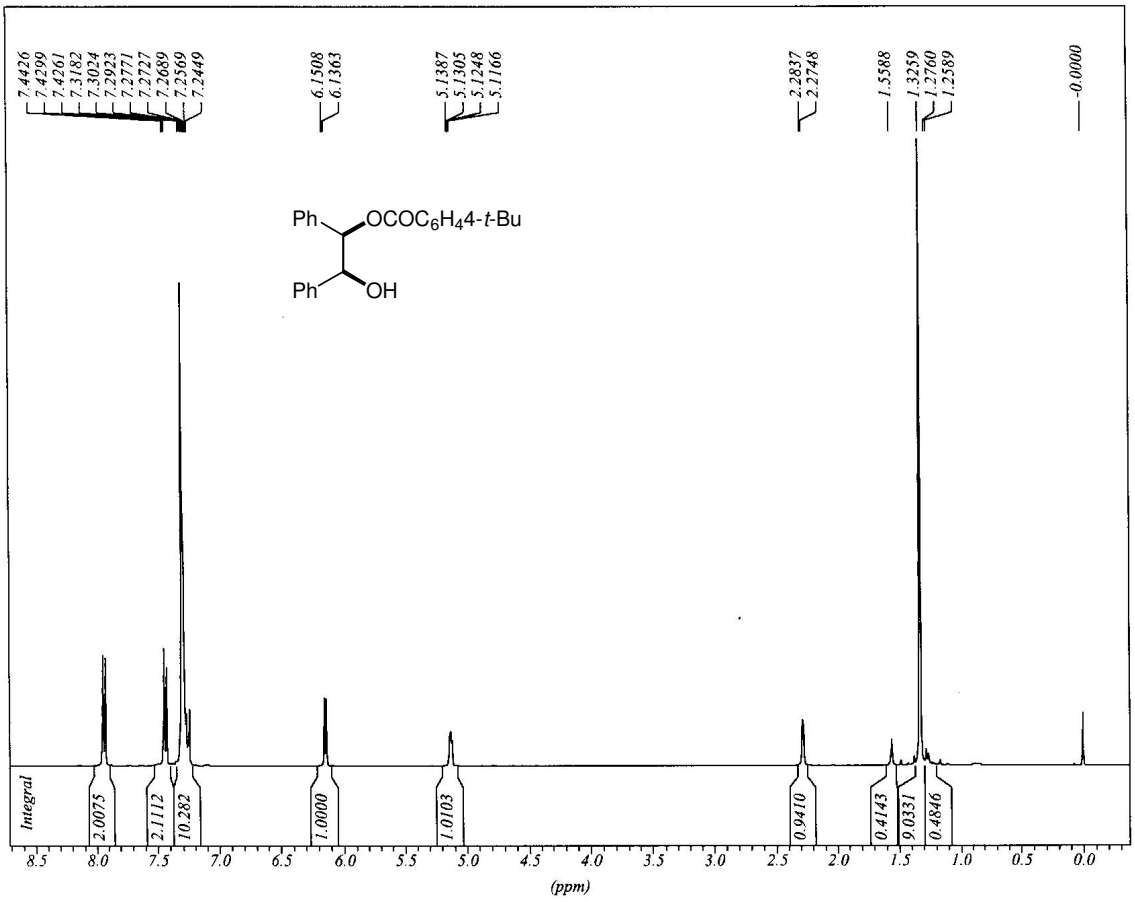
^{1}H NMR of Aminophosphinite 3c



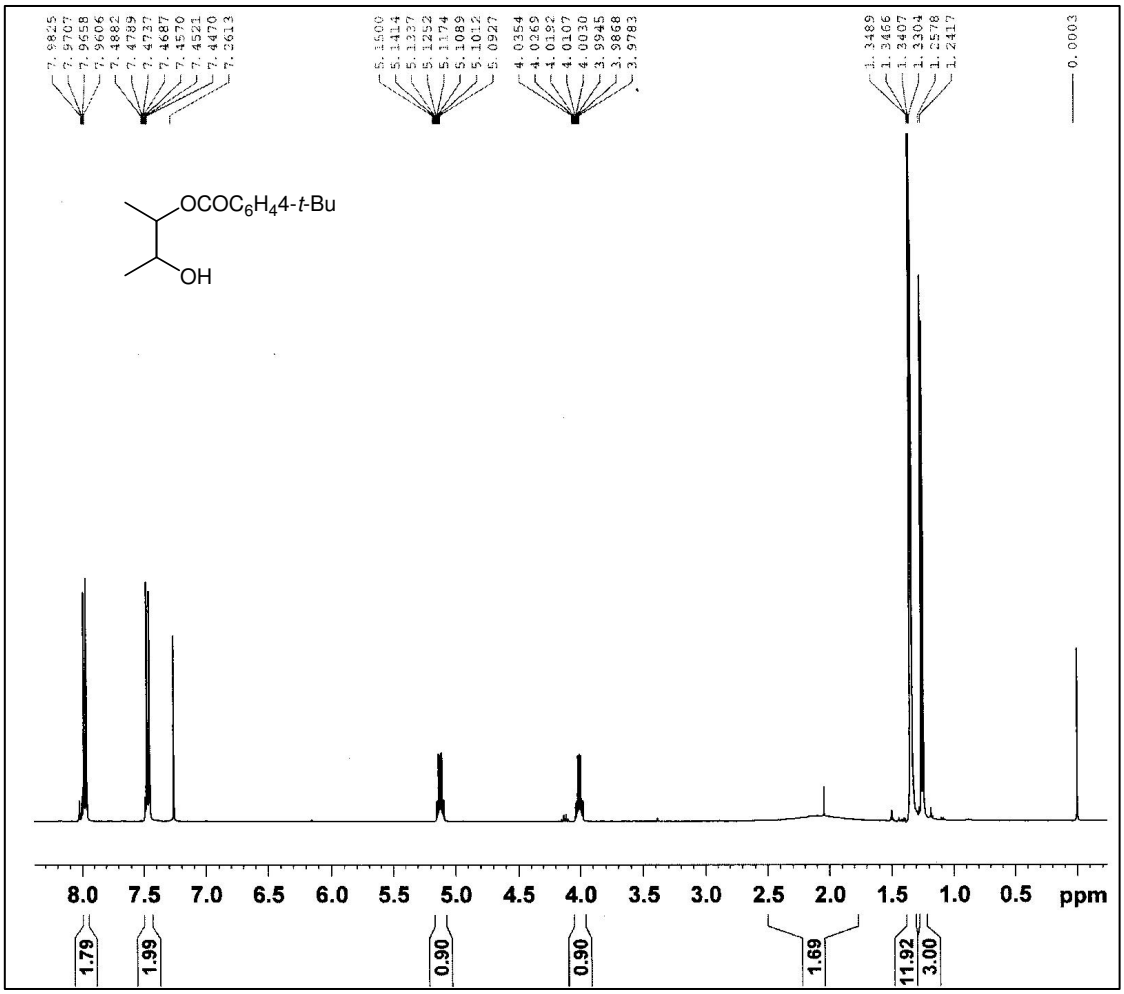
^{1}H NMR of Aminophosphinite 3d



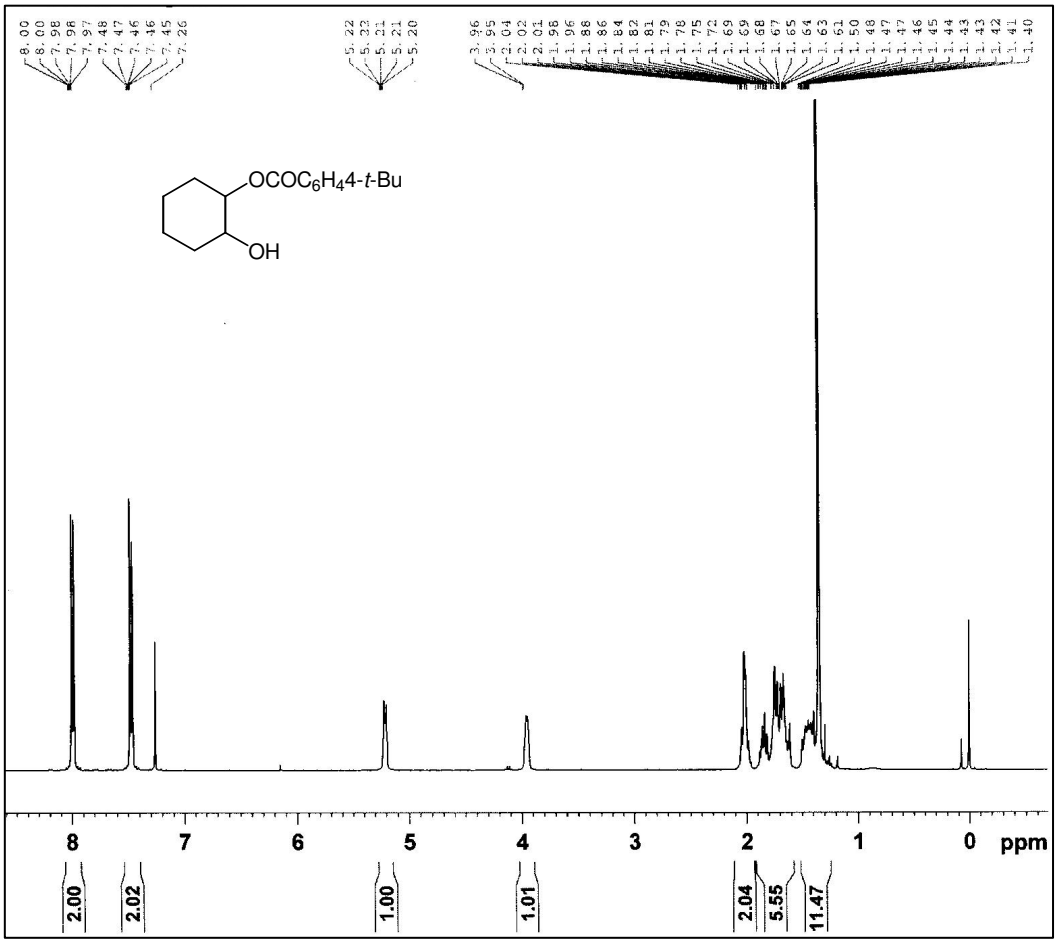
^{1}H NMR of 4-*tert*-butylbenzoate of *meso*-hydrobenzoin



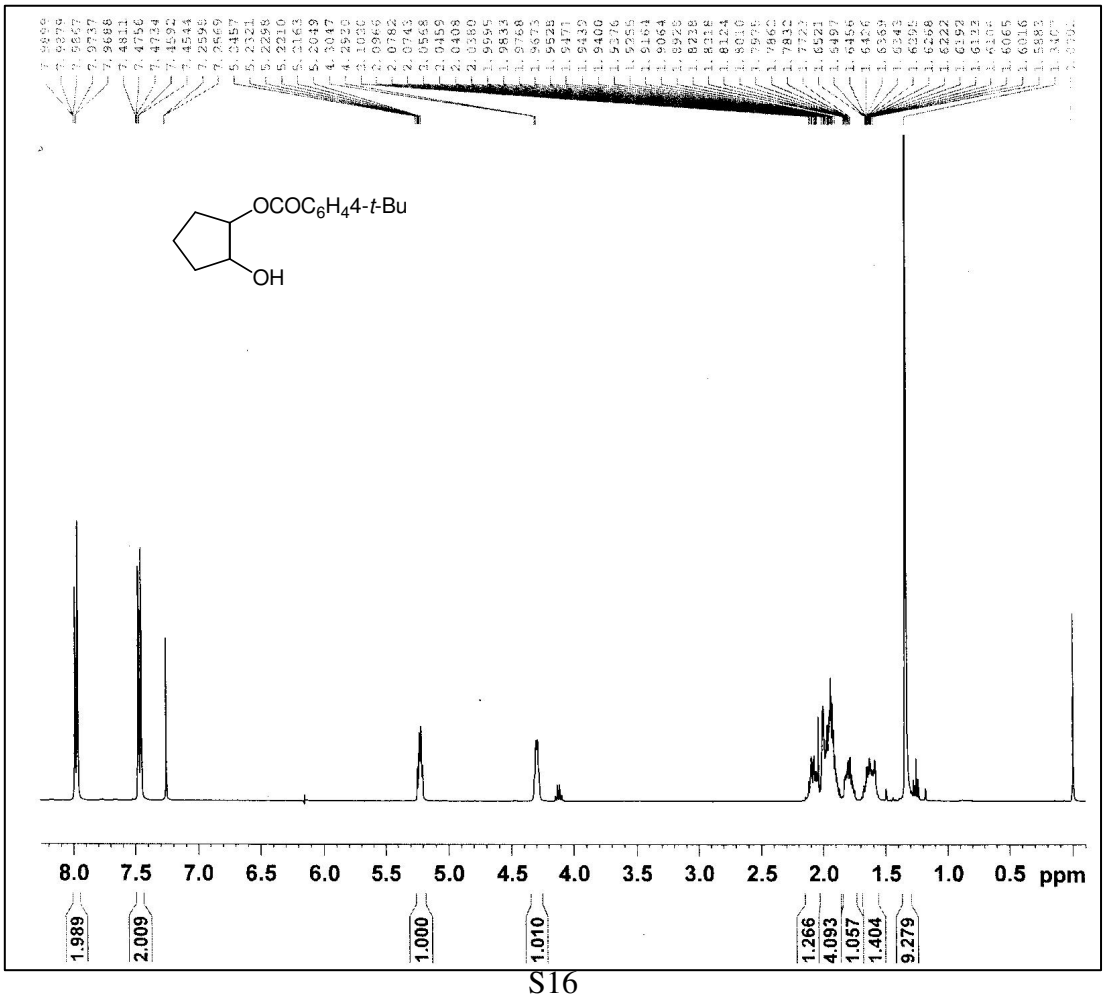
^{1}H NMR of 4-*tert*-Butylbenzoate of *meso*-2,3-butanediol



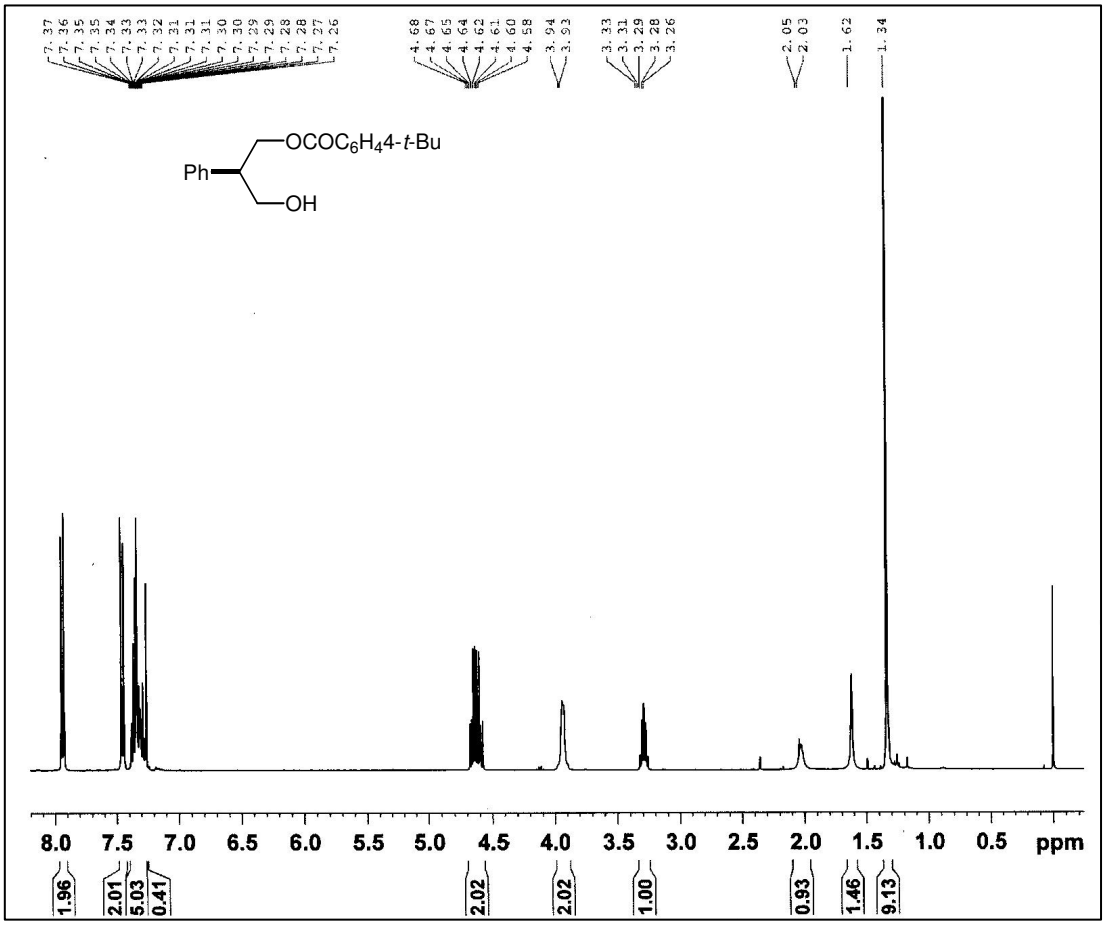
^{1}H NMR of 4-*tert*-Butylbenzoate of *cis*-1,2-cyclohexanediol



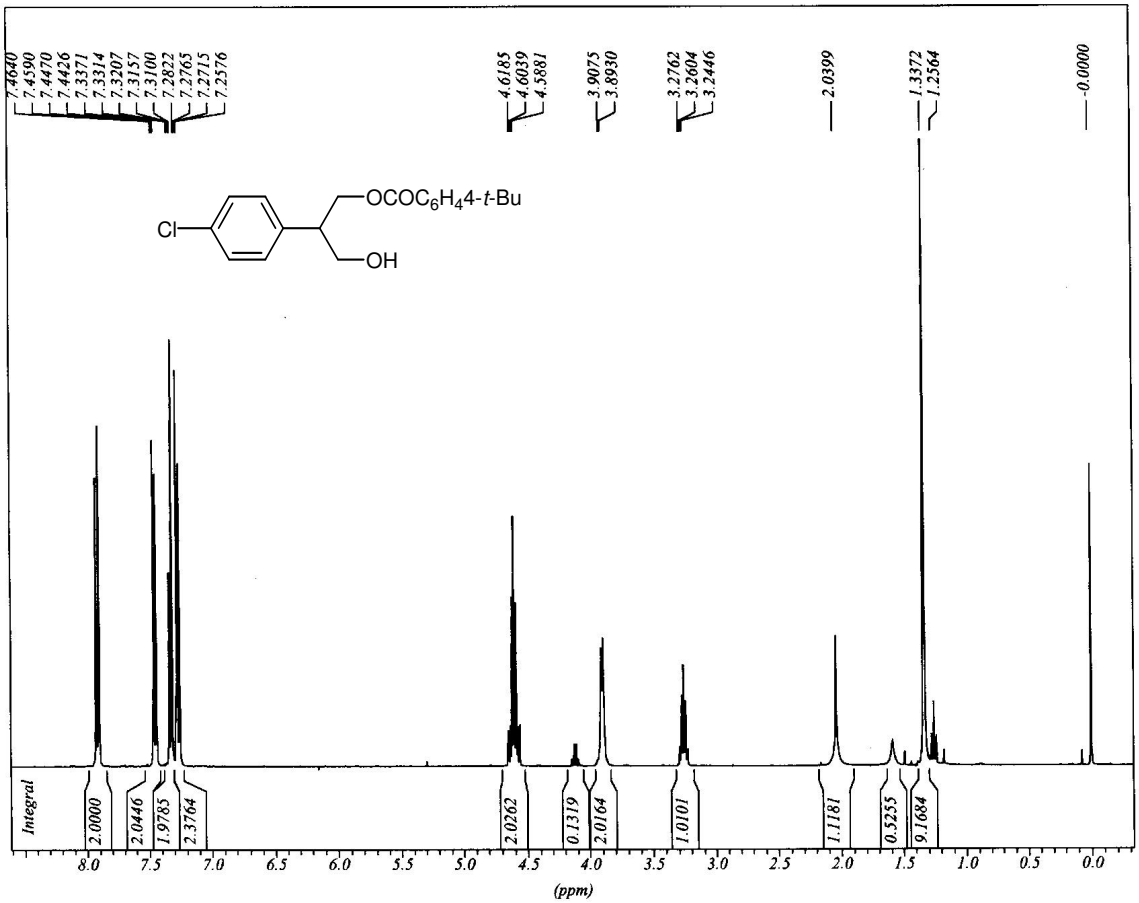
^{1}H NMR of 4-*tert*-Butylbenzoate of *cis*-1,2-cyclopentanediol



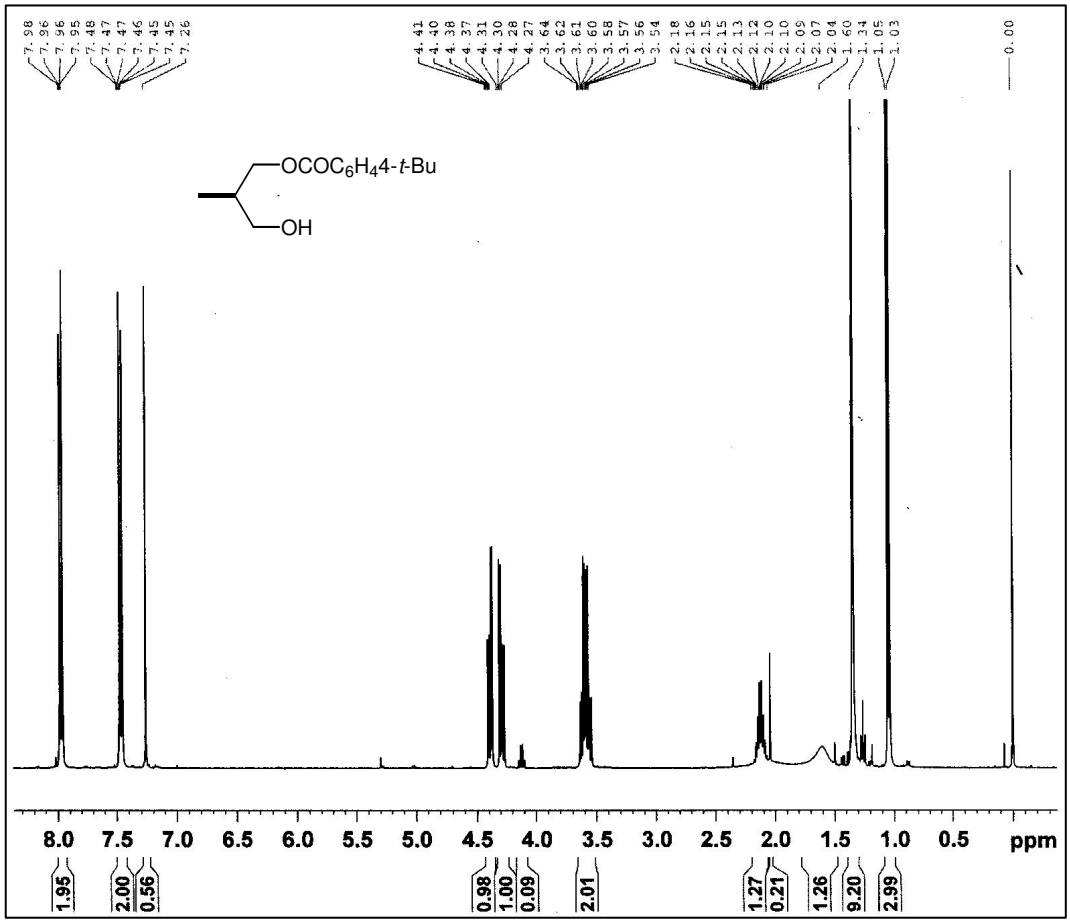
^{1}H NMR of 4-*tert*-Butylbenzoate of 2-phenyl-1,3-propanediol



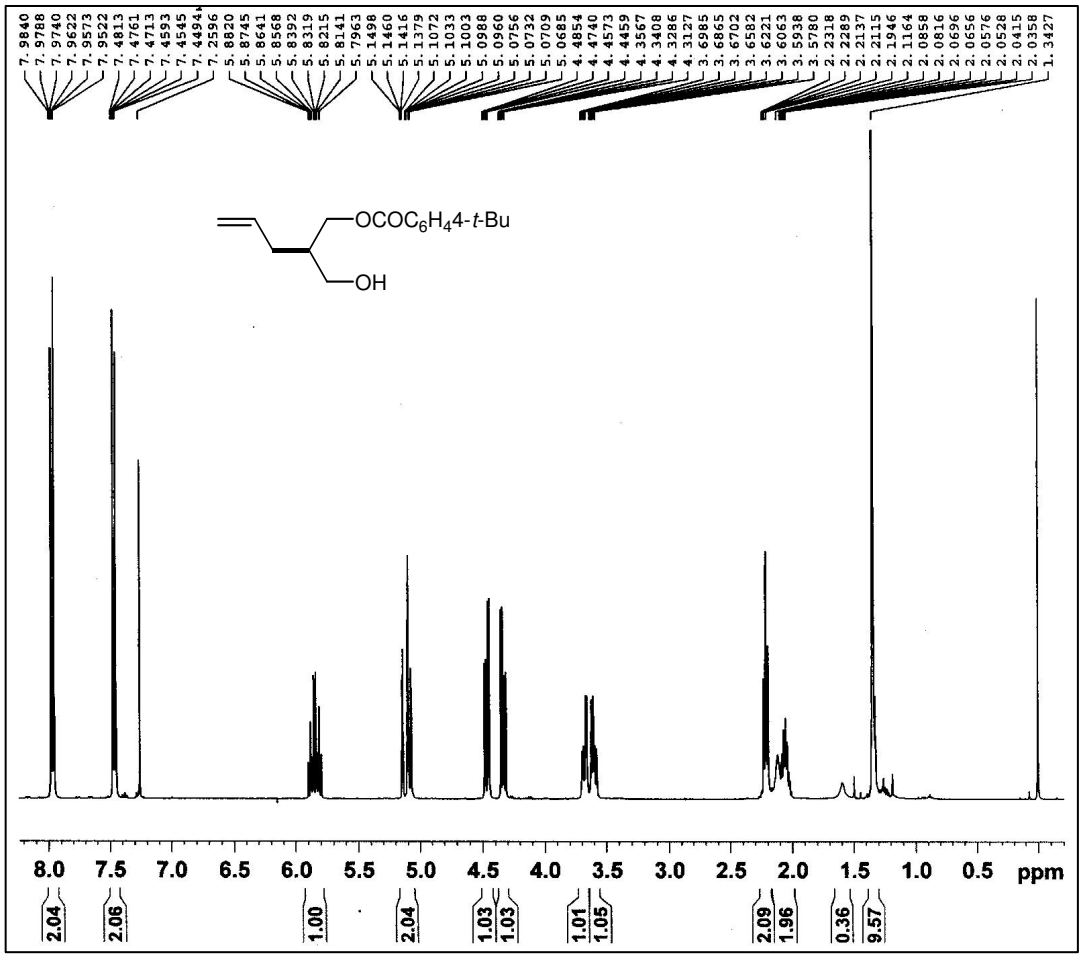
^{1}H NMR of 4-*tert*-Butylbenzoate of 2-(4-chlorophenyl)-1,3-propanediol



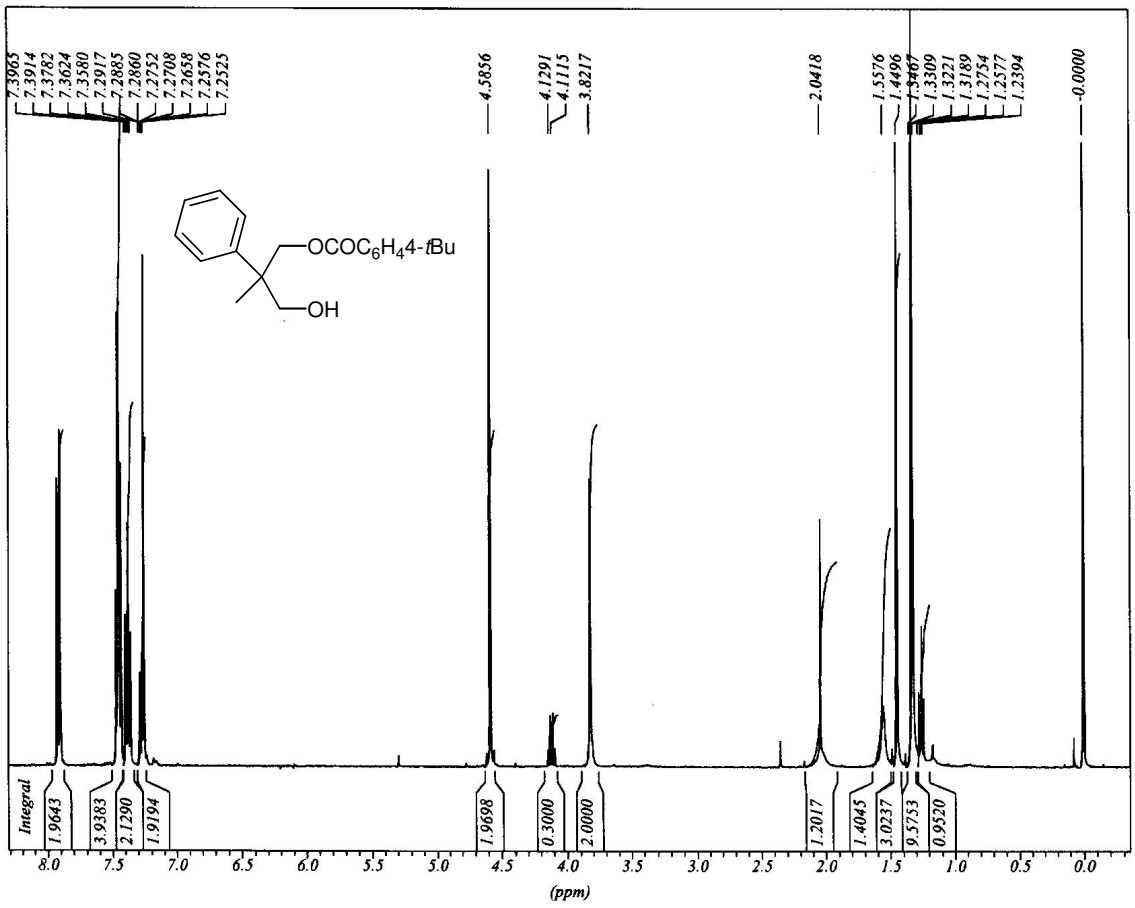
^{1}H NMR of 4-*tert*-Butylbenzoate of 2-methyl-1,3-propanediol



^{1}H NMR of 4-*tert*-Butylbenzoate of 2-allyl-1,3-propanediol



^{1}H NMR of 4-*tert*-Butylbenzoate of 2-metyl-2-phenyl-1,3-propanediol



^{1}H NMR of 4-*tert*-Butylbenzoate of *N,N*-dimethylaminoindanol 4