Supporting Information

Fluorinative Hydrolysis of Phosphorothioic Acid Esters with a Binaphthyl Group Through Axis-to-Center Chirality Transfer Leading to the Formation of *P*-Chiral Phosphorothioic Monofluoridic Acid Salts

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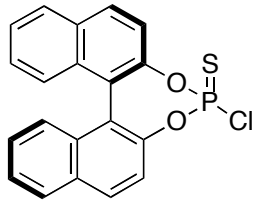
General Remarks: The IR spectra were obtained on a JASCO FT/IR 410 spectrometer. The ^{1}H NMR spectra were recorded on a JEOL α-400 (400 MHz) in $CDCl_3$. Chemical shifts of protons were reported in δ values referred to tetramethylsilane as an internal standard in $CDCl_3$, and the following abbreviations were used: s: singlet, d: doublet, t: triplet, sext: sextet, m: multiplet. The ^{13}C NMR spectra were measured on a JEOL α-400 (100 MHz) in $CDCl_3$. The ^{19}F NMR spectra were measured on a JEOL α-400 (376 MHz) in $CDCl_3$ and with CF_3COOH as an external standard. The ^{31}P NMR spectra were measured on a JEOL α-400 (162 MHz) in $CDCl_3$ and with 85% H_3PO_4 as an external standard. All spectra were acquired in the proton-decoupled mode. The mass spectra (MS), the high-resolution mass spectra (HRMS) and the fast atomic bombardment mass spectra (FAB) were taken on a JMS-700 mass spectrometer. Melting points were determined using a Yanaco seisakusho MP-S2 micro melting point apparatus and are uncorrected. Enantiomeric excess were determined by HPLC analysis (JASCO Gulliver) with CHIRALCEL OZ-Hand OD-H with MeCN/Et_3N/CF_3COOH (100/0.1/0.1) as eluent. Optical rotations were measured on a JASCO-P 1010 polarimeter. Circular Dichroism spectra were measured on a JASCO J-820 spectrometer. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University.

• Synthesis of binaphthylphosphorothioic acid chlorides

(R_{ax})-4-Chlorodinaphtho[2,1-d:1'-f][1,3,2]dioxaphophepin-4-sulfide ((R_{ax})-BISPCl)

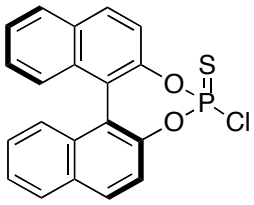


Chemical Formula: $C_{20}H_{12}ClO_2PS$
Exact Mass: 381.9984
Molecular Weight: 382.7998

To a toluene (60 mL) solution of thiophosphorylchloride (3.1 mL, 30 mmol) were added Et_3N (8.4 mL, 60 mmol) and (R_{ax})-1,1'-bi-2-naphthol (8.6 g, 30 mmol) at 0 ºC. The resulting mixture was stirred under reflux for 21 h. The reaction mixture was filtered, washed with CH_2Cl_2, and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3) to give (R_{ax})-4-chlorodinaphtho[2,1-d:1'-f][1,3,2]dioxaphophepin-4-sulfide (R_{ax})-BISPCl (10.6 g, 28 mmol, 92%) as a white solid.

mp : 218 – 219 ºC; IR (KBr) 3437, 3070, 1906, 1763, 1621, 1589, 1508, 1462, 1433, 1403, 1361, 1324, 1256, 1217, 1193, 1155, 1143, 1068, 1028, 963, 879, 849, 816, 794, 772, 751, 734, 704, 687, 652, 631, 589, 566, 525 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25-7.54 (m, 8H, Ar), 7.91-8.02 (m, 4H, Ar); ^{31}P NMR ($CDCl_3$) δ 74.8; MS (EI) *m/z* 382 (M^+); HRMS calcd for $C_{20}H_{12}ClO_2FPS$ (M^+) 381.9984, found 381.9984.

(S_{ax})-4-Chlorodinaphtho[2,1-d:1'-f][1,3,2]dioxaphophepin-4-sulfide ((S_{ax})-BISPCl)



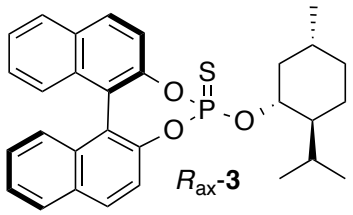
Chemical Formula: $C_{20}H_{12}ClO_2PS$
Exact Mass: 381.9984
Molecular Weight: 382.7998

To a toluene (60 mL) solution of thiophosphorylchloride (3.1 mL, 30 mmol) were added Et_3N (8.4 mL, 60 mmol) and (S_{ax})-1,1'-bi-2-naphthol (8.6 g, 30 mmol) at 0 ºC. The resulting mixture was stirred under reflux for 23.5 h. The reaction mixture was filtered, washed with CH_2Cl_2, and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3) to give (S_{ax})-4-chlorodinaphtho[2,1-d:1'-f][1,3,2]dioxaphophepin-4-sulfide (S_{ax})-BISPCl (10.6 g, 28 mmol, 92%) as a white solid.

mp : 218 – 219 ºC; IR (KBr) 3436, 3069, 2924, 1906, 1827, 1763, 1621, 1589, 1508, 1462, 1433, 1403, 1361, 1324, 1270, 1256, 1217, 1193, 1155, 1143, 1068, 1028, 964, 879, 849, 816, 794, 772, 751, 735, 704, 687, 652, 631, 589, 566, 525 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26-7.53 (m, 8H, Ar), 7.90-8.01 (4H, Ar); ^{31}P NMR ($CDCl_3$) δ 74.9; MS (EI) *m/z* 382 (M^+); HRMS calcd for $C_{20}H_{12}ClO_2FPS$ (M^+) 381.9984, found 381.9973.

• Synthesis of binaphthylphosphorothioic acid esters

(R_{ax})-4-(L)-Menthyl-dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide (R_{ax}-3)

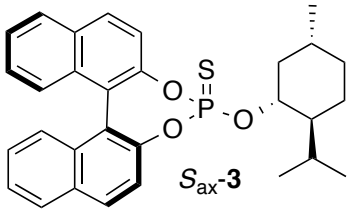


Chemical Formula: $C_{30}H_{31}O_3PS$
Exact Mass: 502.1732
Molecular Weight: 502.6088

To a CH_2Cl_2 (10 mL) solution of (R_{ax})-BISPCl (1.91 g, 5.0 mmol) was added (L)-menthol (780 mg, 5.0 mmol), DMAP (1.22 g, 10.0 mmol) under an Ar atmosphere. The resulting solution was stirred at room temperature for 3 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide R_{ax}-**3** (2.47 g, 98%) as a white solid.

mp 149-151 °C; IR (KBr): 3055, 2954, 2925, 2869, 1620, 1508, 1463, 1370, 1323, 1226, 1201, 1155, 1072, 1017, 958, 876, 845, 833, 812, 749, 721, 705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.71 (d, J = 7.3 Hz, 3H, OCHCHCH($C\underline{H}_3$)$_2$), 0.73 (d, J = 7.3 Hz, 3H, OCHCHCH($C\underline{H}_3$)$_2$), 0.96 (d, J = 6.3 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.70-0.90 (m, 1H, OCHC$\underline{H}$), 0.95-1.30 (m, 3H), 1.47-1.51 (m, $OCHCH_2C\underline{H}CH_3$, 1H), 1.60-1.68 (m, $OCHCHC\underline{H}_2$, 2H), 1.86-1.89 (m, $OCHCH_2CH(CH_3)C\underline{H}_2$, 1H), 2.40-2.43 (m, $OCHC\underline{H}_2CHCH_3$, 1H), 4.60-4.67 (m, 1H, OC$\underline{H}$), 7.18-7.98 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.8, 20.7, 22.0, 22.6, 25.4, 31.6, 33.9, 42.9, 47.9 (d, J = 8.3 Hz), 82.7 (d, J = 7.4 Hz, O$\underline{C}$H), 120.79, 121.82, 121.42, 121.45, 121.9, 122.1, 125.6, 126.5, 126.6, 127.0, 127.2, 128.3, 128.5, 130.6, 130.9, 131.5, 131.9, 132.4, 146.4, 146.5, 147.9, 148.2 (Ar) ; ^{31}P NMR ($CDCl_3$) δ 74.3; MS (EI) m/z 502 (M^+); HRMS Calcd for $C_{30}H_{31}O_3PS$ 502.6041, Found 502.1726; $[\alpha]^{25}_D$ - 320.1 (c 0.10, $CHCl_3$).

(S_{ax})-4-(L)-Menthyl-dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide (S_{ax}-3)



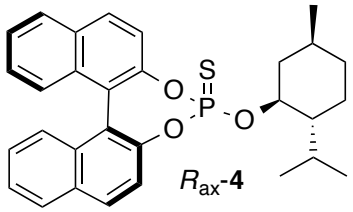
Chemical Formula: $C_{30}H_{31}O_3PS$
Exact Mass: 502.1732
Molecular Weight: 502.6088

To a CH_2Cl_2 (8 mL) solution of (S_{ax})-BISPCl (766 mg, 3.0 mmol) was added (L)-menthol (312 mg, 3.0 mmol), DMAP (488 mg, 4.0 mmol) under an Ar atmosphere. The resulting solution was stirred at room temperature for 3 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide S_{ax}-**3** (865 mg, 86%) as a white solid.

mp 107-108 ℃; IR (KBr): 2953, 2869, 1589, 1508, 1463, 1323, 1226, 1201, 1155, 1072, 1015, 982, 958, 875, 846, 833, 812, 749, 721, 678, 653, 569 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (d, J = 6.8 Hz, 3H, OCHCHCH($C\underline{H}_3$)$_2$), 0.76 (d, J = 6.8 Hz, 3H, OCHCHCH($C\underline{H}_3$)$_2$), 0.98 (d, J = 6.3 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.73-1.05 (m, 1H), 1.21-1.37 (m, 3H), 1.48-1.53 (m, $OCHCH_2C\underline{H}CH_3$, 1H), 1.59-1.66 (m, $OCHCHCH(CH_3)_2C\underline{H}_2$, 2H), 1.88-1.92 (m, $OCHCH_2CH(CH_3)C\underline{H}_2$, 1H), 2.43-2.46 (m,

OCHC$\underline{H}_2$CHCH$_3$, 1H), 4.64-4.68 (m, 1H, OC$\underline{H}$), 7.19-8.00 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.8, 20.7, 22.0, 22.6, 25.4, 31.6, 33.9, 42.9, 47.8 (d, J = 8.3 Hz), 82.7 (d, J = 6.6 Hz, O$\underline{C}$H), 120.8, 121.42, 121.45, 121.9, 122.2, 125.5, 126.5, 126.6, 127.1, 127.3, 128.3, 128.5, 130.6, 130.9, 131.6, 131.9, 132.4, 146.4, 147.8, 148.2 (Ar); ^{31}P NMR ($CDCl_3$) δ 74.4; MS (EI) m/z 502 (M^+); HRMS Calcd for $C_{30}H_{31}O_3PS$ 502.6041, Found 502.1739; $[\alpha]^{25}_D$ + 259.9 (c 0.10, $CHCl_3$).

(R_{ax})-4-(D)-Menthyl-dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide (R_{ax}-4)



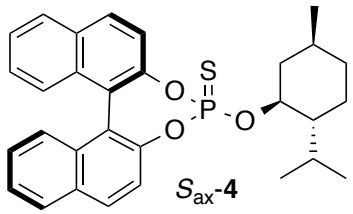
R_{ax}-**4**

Chemical Formula: $C_{30}H_{31}O_3PS$
Exact Mass: 502.1732
Molecular Weight: 502.6088

(*D*)-Menthol (234 mg, 1.5 mmol) was added to a solution of titanium *i*-propoxide (42 mg, 0.15 mmol) in CH_2Cl_2 (6 mL). DMAP (366 mg, 3.0 mmol) and (R_{ax})-BISPCl (574 mg, 1.5 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide R_{ax}-**4** (501 mg, 66%) as a white solid.

mp 107-110 ℃; IR (KBr): 2954, 2869, 1620, 1589, 1509, 1463, 1433, 1370, 1323, 1226, 1201, 1155, 1072, 1016, 982, 958, 875, 846, 833, 812, 772, 749, 721, 705 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (d, J = 6.3 Hz, 3H, OCHCHCH(C$\underline{H}_3$)$_2$), 0.88 (d, J = 7.3 Hz, 3H, OCHCHCH(C$\underline{H}_3$)$_2$), 0.90 (d, J = 7.3 Hz, 3H, OCHCH$_2$CHC$\underline{H}_3$), 0.64-1.16 (m, 1H), 1.15 (br s, 3H), 1.27-1.37 (m, 1H), 1.47-1.59 (m, 2H), 2.13-2.25 (m, 2H), 4.55-4.59 (m, 1H, OC$\underline{H}$), 7.11-7.92 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 16.2, 20.9, 21.8, 22.9, 25.9, 31.5, 33.8, 42.2, 47.9 (d, J = 8.3 Hz), 83.2 (d, J = 7.4 Hz, O$\underline{C}$H), 120.7, 121.3, 121.7, 122.2, 125.6, 127.0, 127.2, 128.3, 128.5, 130.6, 130.9, 131.5, 131.8, 132.3, 146.7, 146.8, 148.1, 148.2 (Ar); ^{31}P NMR ($CDCl_3$) δ 74.5; MS (EI) m/z 502 (M^+); HRMS Calcd for $C_{30}H_{31}O_3PS$ 502.6041, Found 502.1726; $[\alpha]^{25}_D$ - 257.5 (c 0.10, $CHCl_3$).

(S_{ax})-4-(D)-Menthyl-dinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide (S_{ax}-4)



S_{ax}-**4**

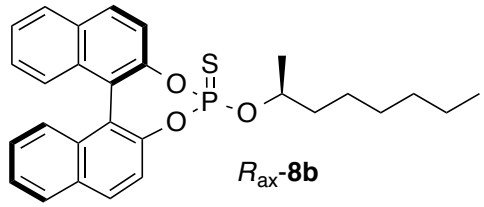
Chemical Formula: $C_{30}H_{31}O_3PS$
Exact Mass: 502.1732
Molecular Weight: 502.6088

(*D*)-Menthol (313 mg, 2.0 mmol) was added to a solution of titanium *i*-propoxide (56 mg, 0.2 mmol) in CH_2Cl_2 (8 mL). DMAP (488 mg, 4.0 mmol) and (S_{ax})-BISPCl (765 mg, 2.0 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide S_{ax}-**4** (489 mg, 48%) as a white solid.

mp 151-154 ℃; IR (KBr): 2953, 1589, 1508, 1463, 1323, 1226, 1015, 958, 875, 812, 749, 721, 678, 654, 569 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (d, J = 6.8 Hz, 3H, OCHCHCH(C$\underline{H}_3$)$_2$), 0.78 (d, J = 6.8 Hz,

3H, OCHCHCH(C<u>H</u>$_3$)$_2$), 1.01 (d, J = 6.4 Hz, 3H, OCHCH$_2$CHC<u>H</u>$_3$), 0.85-1.06 (m, 2H), 1.24-1.35 (m, 3H), 1.62-1.70 (m, 2H), 1.90-1.94 (m, 1H), 2.45-2.48 (m, 1H), 4.60-4.68 (m, 1H, OC<u>H</u>), 7.18-7.99 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 15.8, 20.7, 22.0, 22.8, 25.4, 31.6, 33.9, 42.9, 47.9 (d, J = 8.3 Hz), 82.8 (d, J = 7.4 Hz, O<u>C</u>H), 120.8, 121.4, 121.9, 122.2, 125.6, 127.0, 127.2, 128.3, 128.4, 130.6, 130.9, 131.5, 131.9, 132.4, 146.4, 147.95, 148.09 (Ar); ^{31}P NMR ($CDCl_3$) δ 74.4; MS (EI) m/z 502 (M^+); HRMS Calcd for $C_{30}H_{31}O_3PS$ 502.6041, Found 502.1727; $[\alpha]^{25}_D$ + 352.9 (c 0.10, $CHCl_3$).

(R_{ax})-4-((1*S*)-1-Methylheptyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide (R_{ax}-8b)



R_{ax}-**8b**

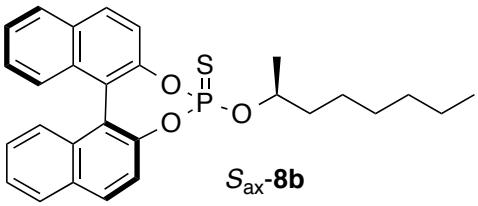
Chemical Formula: $C_{28}H_{29}O_3PS$
Exact Mass: 476.1575
Molecular Weight: 476.5708

(*S*)-(+)-Octanol (0.24 mL, 1.5 mmol) was added to a solution of titanium *i*-propoxide (42 mg, 0.15 mmol) in CH_2Cl_2 (6 mL). DMAP (366 mg, 3.0 mmol) and (R_{ax})-BISPCl (574 mg, 1.5 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide R_{ax}-**8b** (491 mg, 69%) as a white pulpy solid.

mp 137-138 ℃; IR (KBr): 3055, 2932, 2857, 1619, 1589, 1507, 1464, 1433, 1378, 1323, 1256, 1227, 1202, 1155, 1071, 1017, 957, 876, 818, 751, 705, 670, 651, 566, 528 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 6.8 Hz, 3H, OCH(CH$_2$)$_5$C<u>H</u>$_3$), 1.20 (d, J = 5.9 Hz, 3H, OCHC<u>H</u>$_3$), 1.14-1.70 (m, 10H, OCH(C<u>H</u>$_2$)$_5$), 4.84-4.91 (m, 1H, OC<u>H</u>), 7.06-7.88 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.1 ((CH$_2$)$_5$<u>C</u>H$_3$), 21.2 (d, J = 3.3 Hz, (CH$_2$)$_4$<u>C</u>H$_2$CH$_3$), 22.5 (OCH<u>C</u>H$_3$), 25.0 (<u>C</u>H$_2$(CH$_2$)$_3$CH$_3$), 29.0 (<u>C</u>H$_2$(CH$_2$)$_2$CH$_3$), 31.5 (<u>C</u>H$_2$CH$_2$CH$_3$), 37.1 (d, $J_{C\text{-}P}$ = 6.6 Hz, OCH<u>C</u>H$_2$), 79.9 (d, $J_{C\text{-}P}$ = 5.8 Hz, O<u>C</u>H), 120.6, 121.2, 121.3, 121.7, 122.1, 125.4, 126.4, 126.5, 126.9, 127.1, 128.3, 128.4, 130.6, 131.0, 131.4, 131.8, 132.3, 146.5, 147.9, 148.1 ; ^{31}P NMR ($CDCl_3$) δ 74.4; MS (EI) m/z 476; HRMS Calcd for $C_{28}H_{29}O_3PS$ 476.1575, Found: 476.1602; $[\alpha]^{25}_D$ - 329.1 (c 0.10, $CHCl_3$).

(S_{ax})-4-((1*S*)-1-Methylheptyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide (S_{ax}-8b)

(*S*)-(+)-Octanol (0.32 mL, 2.0 mmol) was added to a solution of titanium *i*-propoxide (56 mg, 0.2 mmol) in CH_2Cl_2 (8 mL). DMAP (488 mg, 4.0 mmol) and (S_{ax})-BISPCl (766 mg, 2.0 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.20) to give the corresponding sulfide



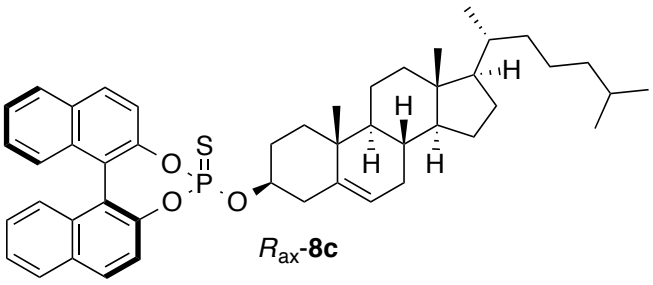
S_{ax}-**8b**

Chemical Formula: $C_{28}H_{29}O_3PS$
Exact Mass: 476.1575
Molecular Weight: 476.5708

S_{ax}-**8b** (591 mg, 62%) as a white pulpy solid.

mp 125-127 ℃; IR (KBr): 3066, 2934, 2855, 1912, 1829, 1767, 1619, 1590, 1508, 1464, 1432, 1402, 1379, 1362, 1324, 1225, 1198, 1154, 1119, 1070, 1004, 957, 909, 861, 817, 777, 748, 705, 669, 651, 630, 552, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (t, J = 6.8 Hz, 3H, $OCH(CH_2)_5C\underline{H}_3$), 1.42 (d, J = 6.3 Hz, 3H, $OCHC\underline{H}_3$), 1.08-1.63 (m, 10H, $OCH(C\underline{H}_2)_5$), 4.86-4.91 (m, 1H, OC<u>H</u>), 7.15-7.96 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.0 ($(CH_2)_5\underline{C}H_3$), 21.2 (d, J = 3.3 Hz, $(CH_2)_4\underline{C}H_2CH_3$), 22.4 ($(CH_2)_3\underline{C}H_2CH_2CH_3$), 31.5 ($\underline{C}H_2Ph$), 37.0 (d, $J_{C\text{-}P}$ = 6.6 Hz, $CH\underline{C}H_2$), 79.7 (d, $J_{C\text{-}P}$ = 5.8 Hz, O<u>C</u>H), 120.7, 121.30, 121.33, 121.8, 122.2, 125.6, 126.5, 126.7, 127.0, 127.2, 128.3, 128.4, 128.5, 130.7, 131.5, 131.6, 131.8, 132.3, 146.4, 148.1 ; ^{31}P NMR ($CDCl_3$) δ 74.2; MS (EI) m/z 476; HRMS Calcd for $C_{28}H_{29}O_3PS$ 476.1575, Found: 476.1576; $[\alpha]^{25}_D$ + 339.5 (c 0.10, $CHCl_3$).

(R_{ax})-4–Cholesteryl dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide (R_{ax}-8c)



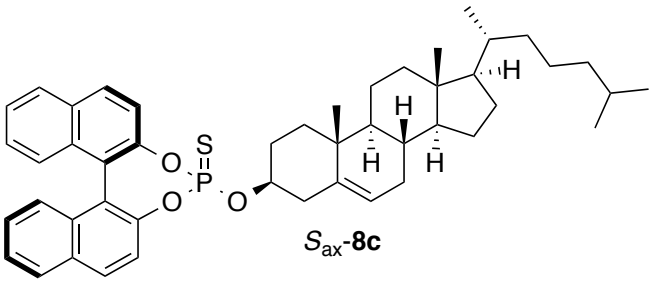
R_{ax}-**8c**

Chemical Formula: $C_{47}H_{57}O_3PS$
Exact Mass: 732.3766
Molecular Weight: 733.0038

Cholesterol (773 mg, 2.0 mmol) was added to a solution of titanium *i*-propoxide (56 mg, 0.2 mmol) in CH_2Cl_2 (8 mL). DMAP (488 mg, 4.0 mmol) and (R_{ax})-BISPCl (765 mg, 2.0 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.35) to give the corresponding sulfide R_{ax}-**8c** (933 mg, 64%) as a white solid.

mp 210-214 ℃; IR (KBr): 3066, 2940, 2865, 1619, 1591, 1509, 1466, 1363, 1326, 1227, 1200, 1155, 1072, 1020, 961, 906, 881, 814, 772, 750, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.63 (s, 3H, Me), 0.81 (d, J = 6.3 Hz, 3H, $CHCHCH_2CH_2CH_2CHC\underline{H}_3$), 0.86 (d, J = 5.9 Hz, 3H, $CHCHCH_2CH_2CH_2CHC\underline{H}_3$), 0.73-1.67 (m, 27H), 1.79-1.82 (m, 2H), 1.94-1.98 (m, 3H), 2.45-2.62 (m, 2H, $OCHC\underline{H}_2$), 4.65-4.67 (m, 1H, OC<u>H</u>), 5.44 (br s, 1H, C=C<u>H</u>), 7.19-7.99 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 11.8, 18.7, 19.2, 21.0, 22.6, 22.8, 23.8, 24.2, 28.2, 29.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 31.5, 31.7, 31.8, 35.7, 36.1, 36.3, 36.8, 39.5, 39.6, 39.6, 42.2, 49.8, 56.0, 56.5, 81.3 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, O<u>C</u>H), 120.6, 121.3, 121.8, 122.1, 126.4, 126.5, 127.0, 127.1, 128.3, 128.4, 130.7, 130.9, 131.5, 131.8, 132.3, 146.3, 147.9, 148.1 (Ar), 123.5 (C=<u>C</u>H), 139.1 (<u>C</u>=CH); ^{31}P NMR ($CDCl_3$) δ 73.7; Anal Calcd for $C_{47}H_{57}O_3PS \cdot 0.6\ CHCl_3$ C, 72.98; H, 7.41. Found: C, 76.17; H, 7.46; $[\alpha]^{25}_D$ + 148.4 (c 0.10, $CHCl_3$).

(S_{ax})-4–Cholesteryl dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide (S_{ax}-8c)



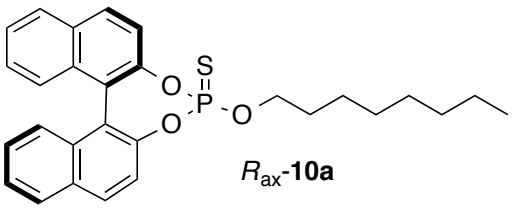
S_{ax}-**8c**

Chemical Formula: $C_{47}H_{57}O_3PS$
Exact Mass: 732.3766
Molecular Weight: 733.0038

Cholesterol (580 mg, 1.5 mmol) was added to a solution of titanium *i*-propoxide (42 mg, 0.15 mmol) in CH_2Cl_2 (6 mL). DMAP (366 mg, 3.0 mmol) and (S_{ax})-BISPCl (574 mg, 1.5 mmol) were added sequentially under an Ar atmosphere. The resulting solution was stirred at room temperature for 1.5 h and concentrated in vacuo. The reaction mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3, Rf = 0.35) to give the corresponding sulfide S_{ax}-**8c** (774 mg, 70%) as a white solid.

mp 147-149 ℃; IR (KBr): 3055, 2945, 1621, 1590, 1509, 1464, 1365, 1323, 1256, 1226, 1200, 1156, 1072, 1021, 957, 909, 876, 846, 812, 771, 749, 704, 678, 654, 568, 550, 528 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.66 (s, 3H, Me), 0.87 (d, J = 5.9 Hz, 3H, $CHCHCH_2CH_2CH_2CHC\underline{H}_3$), 0.86 (d, J = 4.9 Hz, 3H, $CHCHCH_2CH_2CH_2CHC\underline{H}_3$), 0.76-1.68 (m, 27H), 1.75-2.01 (m, 5H), 2.20-2.54 (m, 2H, $OCHC\underline{H}_2$), 4.65-4.67 (m, 1H, $OC\underline{H}$), 5.44 (br s, 1H, $C{=}C\underline{H}$), 7.19-7.99 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 11.8, 18.7, 19.2, 21.0, 22.6, 22.8, 23.8, 24.2, 28.2, 29.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 31.5, 31.7, 31.8, 35.7, 36.1, 36.3, 36.8, 39.5, 39.6, 39.6, 42.2, 49.8, 56.0, 56.5, 81.3 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, $O\underline{C}H$), 120.6, 121.3, 121.8, 122.1, 126.4, 126.5, 127.0, 127.1, 128.3, 128.4, 130.7, 130.9, 131.5, 131.8, 132.3, 146.3, 147.9, 148.1 (Ar), 123.5 ($C{=}\underline{C}H$), 139.1 ($\underline{C}{=}CH$); ^{31}P NMR ($CDCl_3$) δ 73.7; Anal Calcd for $C_{47}H_{57}O_3PS$ C, 76.73; H, 7.80. Found: C, 77.01; H, 7.84; $[\alpha]^{25}_D$ + 149.5 (c 0.10, $CHCl_3$).

(R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(octyloxy)-, 4-sulfide (R_{ax}-10a)



R_{ax}-**10a**

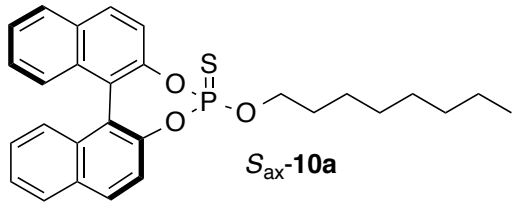
Chemical Formula: $C_{28}H_{29}O_3PS$
Exact Mass: 476.1575
Molecular Weight: 476.5708

To a CH_2Cl_2 solution (5 mL) of (R_{ax})-BISPCl (1.0 mmol, 0.38 g) were added 1-octanol (1.0 mmol, 0.16 mL) and DMAP (1.2 mmol, 0.15 g) under Ar atmosphere. The resulting solution was stirred at room temperature for 5.5 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2: hexane = 1: 3) to give the corresponding sulfide R_{ax}-**10a** (0.99 mmol 0.47 g, 99%) as colorless oil.

IR (KBr) 3061, 2957, 2923, 2851, 1955, 1902, 1840, 1761, 1620, 1589, 1508, 1463, 1433, 1402, 1361, 1323, 1272, 1225, 1201, 1156, 1070, 1023, 983, 958, 876, 845, 814, 768, 749, 703, 670, 646, 630, 568 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (t, 1H, CH_3), 1.18-1.30 (m, 10H, $(C\underline{H}_2)_5CH_3$), 1.66 (quin, 2H, $C\underline{H}_2(CH_2)_5CH_3$), 4.19-4.33 (m, 2H, OCH_2), 7.20-7.52 (m, 8H, Ar), 7.87-7.98 (m, 4H, Ar); ^{13}C

NMR ($CDCl_3$) δ 14.1, 22.6, 25.4, 29.0, 29.1, 30.1 (d, $J_{C\text{-}P}$ = 6.6 Hz), 31.7, 70.5 (d, $J_{C\text{-}P}$ = 5.8 Hz, OCH_2), 120.5, 121.2, 122.1, 125.7, 126.6, 126.7, 127.0, 127.2, 128.4, 128.5, 130.8, 131.0, 131.6, 131.9, 132.3, 132.4, 146.3, 146.4, 147.9, 148.0 (Ar); ^{31}P NMR ($CDCl_3$) δ 75.3; MS (EI) *m/z* 476 (M^+); HRMS calcd for $C_{26}H_{23}O_3PS$ (M^+) 476.1575, found 476.1575; $[\alpha]^{19}_D$ -336.6 (c 1.0, $CHCl_3$).

(S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(octyloxy)-, 4-sulfide (S_{ax}-10a)



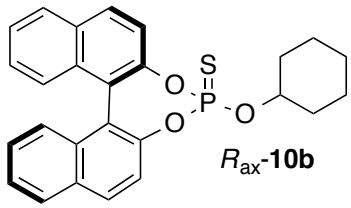
S_{ax}-**10a**

Chemical Formula: $C_{28}H_{29}O_3PS$
Exact Mass: 476.1575
Molecular Weight: 476.5708

To a CH_2Cl_2 solution (5 mL) of (S_{ax})-BISPCl (1.0 mmol, 0.38 g) were added 1-octanol (1.0 mmol, 0.16 mL) and DMAP (1.2 mmol, 0.15 g) under Ar atmosphere. The resulting solution was stirred at room temperature for 4.5 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2: hexane = 1: 3) to give the corresponding sulfide S_{ax}-**10a** (0.92 mmol 0.44 g, 92%) as colorless oil.

IR (KBr) 3059, 2958, 2925, 2851, 2331, 1955, 1901, 1840, 1762, 1689, 1620, 1589, 1508, 1463, 1433, 1402, 1361, 1323, 1272, 1225, 1201, 1155, 1070, 1021, 983, 949, 873, 844, 814, 768, 750, 704, 671, 646, 630, 568, 544, 526 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86-0.89 (t, J = 6.8 Hz, 3H, CH_3), 1.26-1.38 (m, 10H, ($C\underline{H}_2$)$_5CH_3$), 1.74 (quin, J = 6.9 Hz, 2H, $OCH_2C\underline{H}_2$), 4.28-4.42 (m, 2H, OCH_2), 7.27-7.59 (m, 8H, Ar), 7.94-8.06 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$) δ 14.1, 22.6, 25.4, 29.0, 29.1, 30.0 (d, $J_{C\text{-}P}$ = 7.4 Hz), 31.7, 70.4 (d, $J_{C\text{-}P}$ = 5.8 Hz, $O\underline{C}H_2$), 120.5, 121.2, 122.1, 125.7, 126.6, 126.7, 127.0, 127.2, 128.4, 128.5, 130.8, 131.0, 131.6, 131.9, 132.3, 132.4, 146.3, 146.4, 147.9, 148.0 (Ar); ^{31}P NMR ($CDCl_3$) δ 75.3; MS (EI) *m/z* 476 (M^+); HRMS calcd for $C_{28}H_{29}O_3PS$ (M^+) 476.1575, found 476.1576; $[\alpha]^{19}_D$ +338.7 (c 1.0, $CHCl_3$).

(R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(cyclohexyloxy)-, 4-sulfide (R_{ax}-10b)



R_{ax}-**10b**

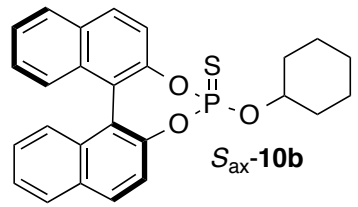
Chemical Formula: $C_{26}H_{23}O_3PS$
Exact Mass: 446.1106
Molecular Weight: 446.5008

To a CH_2Cl_2 solution (3 mL) of (R_{ax})-BISPCl (1.0 mmol, 0.38 g) were added cyclohexanol (1.0 mmol, 0.11 mL) and DMAP (1.2 mmol, 0.14 g) under Ar atmosphere. The resulting solution was stirred at room temperature for 3.0 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2: hexane = 1 : 3) to give the corresponding sulfide R_{ax}-**10b** (0.99 mmol 0.44 g, 99%) as a white solid.

mp 95-96 °C; IR (KBr) 3054, 2936, 2856, 2349, 1905, 1620, 1589, 1508, 1463, 1433, 1402, 1363, 1323, 1257, 1224, 1200, 1155, 1072, 1015, 981, 957, 876, 845, 813, 794, 772, 749, 720, 704, 678,

654, 631, 569, 553, 527 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09-1.23 (m, 1H), 1.24-1.37 (m, 2H), 1.38-1.49 (m, 2H), 1.55-1.64 (m, 2H), 1.65-1.81 (m, 1H), 1.88-1.92 (m, 1H), 2.01-2.08 (m, 1H), 4.75-4.79 (m, 1H), 7.16-7.96 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 23.4, 23.6, 25.0, 32.9 (d, J_{C-P} = 5.0 Hz), 33.3 (d, J_{C-P} = 4.1 Hz), 80.7(d, J_{C-P} = 5.8 Hz), 120.6 (d, J_{C-P} = 2.5 Hz), 121.3 (d, J_{C-P} = 2.5 Hz), 121.8 (d, J_{C-P} = 2.5 Hz), 122.2 (d, J_{C-P} = 2.5 Hz), 125.6, 126.5, 126.6, 127.0, 127.2, 128.3, 128.5, 130.6, 131.0, 131.6, 131.9, 132.4, 146.4, 146.5, 148.0, 148.1 (Ar); ^{31}P NMR ($CDCl_3$) δ 73.8; MS (EI) *m/z* 446 (M^+); HRMS calcd for $C_{28}H_{29}O_3PS$ (M^+) 446.1106, found 446.1087; $[\alpha]^{19}_D$ -340.4 (c 1.0, $CHCl_3$).

(S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(cyclohexyloxy)-, 4-sulfide (S_{ax}-10b)

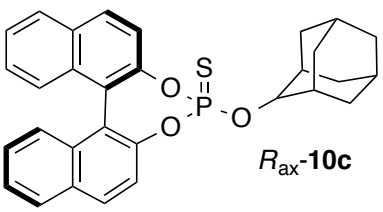


S_{ax}-**10b**

Chemical Formula: $C_{26}H_{23}O_3PS$
Exact Mass: 446.1106
Molecular Weight: 446.5008

To a CH_2Cl_2 solution (6 mL) of (S_{ax})-BISPCl (1.0 mmol, 0.38g) were added cyclohexanol (1.0 mmol, 0.11 mL) and DMAP (1.2 mmol, 0.14 g) under Ar atmosphere. The resulting solution was stirred at room temperature for 3.5 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3) to give the corresponding sulfide S_{ax}-**10b** (0.99 mmol 0.44 g, 99%) as a white solid.

mp 95-96 °C; IR (KBr) 3057, 2935, 2858, 1905, 1820, 1712, 1620, 1589, 1508, 1463, 1433, 1403, 1362, 1323, 1257, 1225, 1200, 1155, 1126, 1072, 1014, 981, 954, 865, 812, 795, 772, 750, 720, 704, 678, 653, 630, 621, 580, 568, 553, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.12-1.29 (m, 1H), 1.30-1.47 (m, 2H), 1.48-1.58 (m, 2H), 1.63-1.72 (m, 2H), 1.73-1.82 (m, 1H), 1.97-2.01 (m, 1H), 2.13-2.16 (m, 1H), 4.84-4.4.87 (m, 1H), 7.25-8.05 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 23.4, 23.6, 25.0, 32.9 (d, J_{C-P} = 5.0 Hz), 33.3 (d, J_{C-P} = 4.1 Hz), 80.7(d, J_{C-P} = 5.8 Hz), 120.6 (d, J_{C-P} = 2.5 Hz), 121.3 (d, J_{C-P} = 2.5 Hz), 121.8 (d, J_{C-P} = 2.5 Hz), 122.2 (d, J_{C-P} = 2.5 Hz), 125.6, 126.5, 126.6, 127.0, 127.2, 128.3, 128.5, 130.6, 131.0, 131.6, 131.9, 132.4, 146.4, 146.5, 148.0, 148.1 (Ar); ^{31}P NMR ($CDCl_3$) δ 73.8; MS (EI) *m/z* 446 (M^+); HRMS calcd for $C_{28}H_{29}O_3PS$ (M^+) 446.1106, found 446.1095; $[\alpha]^{19}_D$ +335.6.



R_{ax}-**10c**

Chemical Formula: $C_{30}H_{27}O_3PS$
Exact Mass: 498.1419
Molecular Weight: 498.5768

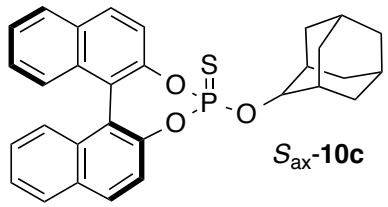
(R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(2-tricyclo[3.3.1.$1^{3,7}$]decyloxy)-, 4-sulfide (R_{ax}-10c)

To a CH_2Cl_2 solution (25 mL) of (S_{ax})-BISPCl (10 mmol, 3.9 g) were added 2-adamantanol (10 mmol, 1.5 g) and DMAP (20 mmol, 2.4 g) under Ar atmosphere. The resulting solution was stirred at

room temperature for 7.0 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3) to give the corresponding sulfide R_{ax}-**10c** (9.8 mmol 4.9 g, 98%) as a white solid.

mp 143-144 °C; IR (KBr) 3060, 2906, 2855, 2679, 2572, 2487, 2434, 2364, 2299, 2183, 1960, 1910, 1827, 1738, 1688, 1620, 1589, 1507, 1463, 1452, 1433, 1403, 1383, 1363, 1323, 1260, 1227, 1201, 1156, 1142, 1126, 1116, 1100, 1072,1013, 940, 910, 829, 813, 772, 755, 725, 704, 684, 666, 653, 631, 580, 569, 552, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34-1.37 (m, 1H), 1.48-1.53 (m, 1H), 1.64-1.76 (m, 10H), 2.08 (br, 1H), 2.23 (br, 1H), 4.95-4.97 (m, 1H), 7.18-7.98 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 26.8 (d, J_{C-P} = 29.8 Hz), 31.3 (d, J_{C-P} = 31.4 Hz), 33.1 (d, J_{C-P} = 3.3Hz), 36.2 (d, J_{C-P} = 11.6 Hz), 37.2, 85.2 (d, J_{C-P} = 5.8 Hz), 120.6, 121.4, 121.9, 122.3, 125.6, 126.5, 126.6, 127.1, 127.3, 128.4, 128.5, 130.6, 131.0, 131.5, 131.9, 132.4, 148.1, 148.3 (Ar); ^{31}P NMR ($CDCl_3$) δ 73.8; MS (EI) *m/z* 498 (M^+); HRMS calcd for $C_{28}H_{29}O_3PS$ (M^+) 498.1419, found 498.1444; $[\alpha]^{19}_D$ -314.0 (c 1.0, $CHCl_3$).

(S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(2-tricyclo[3.3.1.1^{3,7}]decyloxy)-, 4-sulfide (S_{ax}-10c)



S_{ax}-**10c**

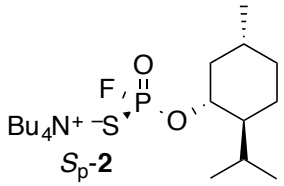
Chemical Formula: $C_{30}H_{27}O_3PS$
Exact Mass: 498.1419
Molecular Weight: 498.5768

To a CH_2Cl_2 solution (20 mL) of (S_{ax})-BISPCl (5.0 mmol, 1.9 g) were added 2-adamantanol (5.0 mmol, 0.76 g), DMAP (10 mmol, 1.2 g) under Ar atmosphere. The resulting solution was stirred at room temperature for 2.5 h and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (CH_2Cl_2 : hexane = 1 : 3) to give the corresponding sulfide S_{ax}-**10c** (4.9 mmol 2.4 g, 98%) as a white solid.

mp 143-144 °C; IR (KBr) 3055, 2909, 2854, 2673, 2351, 2237, 1903, 1839, 1736, 1620, 1588, 1508, 1462, 1451, 1433, 1403, 1383, 1361, 1323, 1270, 1255, 1226, 1200, 1155, 1143, 1127, 1115, 1100, 1071, 1015, 956, 911, 877, 812, 771, 750, 725, 704, 685, 652, 631, 580, 568, 552, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37-1.40 (m, 1H), 1.46-1.55 (m, 1H), 1.65-1.92 (m, 10H), 2.10 (br, 1H), 2.26 (br, 1H), 5.22-5.24 (m, 1H), 7.18-8.00 (m, 12H, Ar); ^{13}C NMR ($CDCl_3$) δ 26.8 (d, J_{C-P} = 28.9 Hz), 31.2 (d, J_{C-P} = 31.4 Hz), 33.1 (d, J_{C-P} = 3.3 Hz), 33.4 (d, J_{C-P} = 4.1 Hz), 36.2 (d, J_{C-P} = 10.8 Hz), 37.2, 85.2 (d, J_{C-P} = 6.6 Hz), 120.6, 121.3, 121.8, 125.6, 126.5, 127.1, 127.3, 128.4, 128.5, 130.6, 131.0, 131.5, 131.9, 132.3, 132.4, 146.5, 148.1 (Ar); ^{31}P NMR ($CDCl_3$) δ 73.8; MS (EI) *m/z* 498 (M^+); HRMS calcd for $C_{28}H_{29}O_3PS$ (M^+) 498.1419, found 498.1404; $[\alpha]^{19}_D$ +308.4 (c 1.0, $CHCl_3$).

• Fluorinative hydrolysis of binaphthylphosphorothioic acid esters

***N,N,N*-Tributyl-1-butanaminium (*L*)-menthylphosphorofluoridothioate (*S*p-2)**



S_p-**2**

Chemical Formula: $C_{26}H_{55}FNO_2PS$
Exact Mass: 495.3675
Molecular Weight: 495.7632

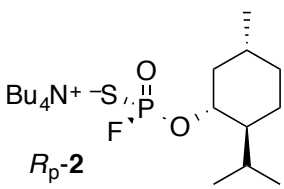
To a THF solution (10 mL) of the (R_{ax})-4-(*L*)-menthyldinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide R_{ax}-**3** (2.01 g, 4.0 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (16.0 mL, 16.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 5.5 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt *S*p-**2** (1.75 g, 88%; major : minor = 97 : 3) as a yellow oil.

IR (neat): 2960, 2872, 2205, 1711, 1459, 1384, 1199, 1110, 1021, 931, 882, 805, 775, 734, 660, 636 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.71-0.78 (m, 10H, Me and OCHC<u>H</u>), 0.90 (t, *J* = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 0.86-0.97 (m, 2H), 1.15-1.21 (m, 1H), 1.35 (sext, *J* = 7.3 Hz, 8H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.30-1.39 (m, 1H, $OCHCHCH_2C\underline{H}_2$), 1.51-1.59 (m, 10H, $NCH_2C\underline{H}_2CH_2CH_3$ and $OCHC\underline{H}_2$ and $OCHCHC\underline{H}_2$), 2.17-2.30 (m, 2H), 3.21 (t, *J* = 8.3 Hz, 8H, $NC\underline{H}_2$), 4.09-4.12 (m, 1H, OC<u>H</u>); ^{13}C NMR ($CDCl_3$) δ 13.6 ($CH_2\underline{C}H_3$), 15.9, 19.7 ($\underline{C}H_2CH_3$), 21.2, 22.1, 22.9, 24.0 (NCH_2CH_2), 25.2, 31.5, 34.5, 43.0, 48.6 (d, *J* = 8.3 Hz), 58.6 ($N\underline{C}H_2$), 77.8 (d, *J* = 6.6 Hz, O<u>C</u>H); ^{31}P NMR ($CDCl_3$) δ 51.3 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -30.9 (d, $J_{P\text{-}F$ = 1042.2 Hz); MS (FAB^-) m/z 253 (M^+-Bu_4N); HRMS calcd for $C_{10}H_{19}O_2FPS$ (M^+ -Bu_4N^+) 253.0833, found 253.0837.

$[\alpha]^{25}_D$ - 31.9 (c 0.36, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$) δ 51.7 (d, $J_{P\text{-}F}$ = 1040.0 Hz); ^{19}F NMR ($CDCl_3$) δ -30.3 (d, $J_{P\text{-}F$ = 1050.6 Hz)

***N,N,N*-Tributyl-1-butanaminium (*L*)-menthylphosphorofluoridothioate (R_p-2)**



R_p-**2**

Chemical Formula: $C_{26}H_{55}FNO_2PS$
Exact Mass: 495.3675
Molecular Weight: 495.7632

To a THF solution (5 mL) of the (S_{ax})-4-(*L*)-menthyldinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide S_{ax}-**3** (251 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 6.0 h. The reaction mixture was poured into water and extracted

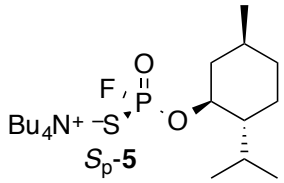
with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt R_p-**2** (199 mg, 80%; major : minor = 92 : 8) as a yellow oil.

IR (neat): 2955, 2868, 2347, 1674, 1459, 1384, 1197, 1107, 1021, 931, 881, 805, 782, 661, 636 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.62-0.81 (m, 1H), 0.76 (d, J = 6.8 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.79 (d, J = 6.8 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.80 (d, J = 6.3 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.92 (t, J = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 0.91-1.03 (m, 2H), 1.19-1.25 (m, 1H), 1.33-1.42 (m, 1H), 1.36 (sext, J = 7.3 Hz, 8H, $NCH_2CH_2C\underline{H}_2CH_3$)), 1.56-1.58 (m, 10H, $NCH_2C\underline{H}_2CH_2CH_3$ and $OCHC\underline{H}_2$ and $OCHCHC\underline{H}_2$), 2.23-2.26 (m, 2H), 3.22 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2$), 4.11-4.20 (m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.6 ($CH_2\underline{C}H_3$), 16.0, 19.6 ($\underline{C}H_2CH_3$), 21.1, 22.1, 22.8, 23.9 ($N\underline{C}H_2CH_2$), 25.1, 31.4, 34.4, 42.7, 48.5 (d, J = 8.3 Hz), 58.6 ($N\underline{C}H_2$), 77.8 (d, J = 6.6 Hz, $O\underline{C}H$); ^{31}P NMR ($CDCl_3$) δ 52.0 (d, $J_{P\text{-}F}$ = 1040.0 Hz); ^{19}F NMR ($CDCl_3$) δ -28.0 (d, $J_{P\text{-}F}$ = 1042.5 Hz); MS (FAB^-) m/z 253 (M^+-Bu_4N); HRMS calcd for $C_{10}H_{19}O_2FPS$ (M^+ -Bu_4N^+) 253.0833, found 253.0837.

$[\alpha]^{25}_D$ - 33.6 (c 0.62, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$): δ 51.5 (d, $J_{P\text{-}F}$ = 1040.0 Hz); ^{19}F NMR ($CDCl_3$): δ -29.4 (d, $J_{P\text{-}F}$ = 1050.6 Hz)

N,N,N-Tributyl-1-butanaminium (*D*)-menthylphosphorofluoridothioate (S_p-5)



S_p-**5**

Chemical Formula: $C_{26}H_{55}FNO_2PS$
Exact Mass: 495.3675
Molecular Weight: 495.7632

To a THF solution (3 mL) of the (R_{ax})-4-(*D*)-menthyldinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide R_{ax}-**4** (251 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 5.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt S_p-**5** (165 mg, 66%; major : minor = 94 : 6) as a yellow oil.

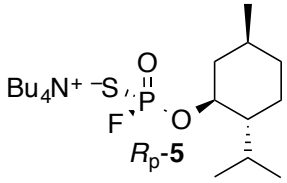
IR (neat): 2859, 1711, 1595, 1475, 1386, 1269, 1203, 1020, 930, 873, 769 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.61-0.81 (m, 1H), 0.76 (d, J = 6.8 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.78 (d, J = 7.3 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.80 (d, J = 6.3 Hz, 3H, $OCHCH_2CHC\underline{H}_3$), 0.92 (t, J = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 0.91-1.05 (m, 2H), 1.17-1.27 (m, 1H), 1.34-1.42 (m, 1H), 1.36 (sext, J = 7.3 Hz, 8H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.54-1.62 (m, 10H, $NCH_2C\underline{H}_2CH_2CH_3$ and $OCHC\underline{H}_2$ and $OCHCHC\underline{H}_2$), 2.23-2.27 (m, 2H), 3.24 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2$), 4.12-4.18 (m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.6 ($CH_2\underline{C}H_3$), 16.0, 19.6 ($\underline{C}H_2CH_3$), 21.1, 22.0, 22.8, 23.9 ($N\underline{C}H_2CH_2$), 25.0,

31.4, 34.4, 42.7, 48.5 (d, J = 8.3 Hz), 58.6 (N<u>C</u>H$_2$), 76.9 (d, J = 8.3 Hz, O<u>C</u>H); ^{31}P NMR ($CDCl_3$) δ 51.8 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -27.8 (d, $J_{P\text{-}F}$ = 1043.7 Hz); MS (FAB$^-$) m/z 253 (M^+-Bu_4N).

$[\alpha]^{25}_D$ + 34.3 (c 0.83, $CHCl_3$)

minor product ^{31}P NMR ($CDCl_3$): δ 51.4 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$): δ -29.1 (d, $J_{P\text{-}F}$ = 1052.1 Hz).

N,*N*,*N*-Tributyl-1-butanaminium (*D*)-menthylphosphorofluoridothioate (R_p-5)



Chemical Formula: $C_{26}H_{55}FNO_2PS$
Exact Mass: 495.3675
Molecular Weight: 495.7632

To a THF solution (3 mL) of the (S_{ax})-4-(*D*)-menthyldinaphtho [2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide S_{ax}-**4** (251 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 5.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt R_p-**5** (181 mg, 73%; major : minor = 97 : 3) as a yellow oil.

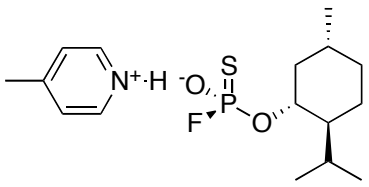
IR (neat): 2959, 2872, 2347, 1640, 1462, 1384, 1198, 1107, 1021, 931, 881, 805, 777, 663, 638 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.59-0.73 (m, 1H), 0.63 (d, J = 7.3 Hz, 3H, OCHCH$_2$CHC<u>H</u>$_3$), 0.71 (d, J = 6.3 Hz, 3H, OCHCH$_2$CHC<u>H</u>$_3$), 0.72 (d, J = 7.3 Hz, 3H, OCHCH$_2$CHC<u>H</u>$_3$), 0.84 (t, J = 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C<u>H</u>$_3$), 0.80-1.02 (m, 2H), 1.13-1.20 (m, 1H), 1.25-1.30 (m, 1H), 1.27 (sext, J = 7.3 Hz, 8H, NCH$_2$CH$_2$C<u>H</u>$_2$CH$_3$), 1.43-1.54 (m, 10H, NCH$_2$C<u>H</u>$_2$CH$_2$CH$_3$ and OCHC<u>H</u>$_2$ and OCHCHC<u>H</u>$_2$), 2.10-2.25 (m, 2H), 3.15 (t, J = 8.5 Hz, 8H, NC<u>H</u>$_2$), 4.00-4.10 (m, 1H, O<u>C</u>H); ^{13}C NMR ($CDCl_3$) δ 13.4 (CH$_2$<u>C</u>H$_3$), 15.7, 19.4 (<u>C</u>H$_2$CH$_3$), 21.0, 21.9, 22.7, 23.8 (N<u>C</u>H$_2$CH$_2$), 25.0, 31.2, 34.3, 42.8, 48.5 (d, J = 7.4 Hz), 58.5 (N<u>C</u>H$_2$), 76.4 (d, J = 8.3 Hz, O<u>C</u>H); ^{31}P NMR ($CDCl_3$) δ 51.4 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -29.6 (d, $J_{P\text{-}F}$ = 1043.7 Hz); MS (FAB$^-$) m/z 253 (M^+-Bu_4N).

$[\alpha]^{25}_D$ + 38.4 (c 0.35, $CHCl_3$)

minor product ^{31}P NMR ($CDCl_3$) δ 51.8 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -28.3 (d, $J_{P\text{-}F}$ = 1042.9 Hz)

4-Methylpyridium (*L*)-menthylphosphorofluorothoate (S_p-7)

Amberlyst 15 ion-exchange resin (5 g) was added to a CH_2Cl_2 (20 mL) solution of



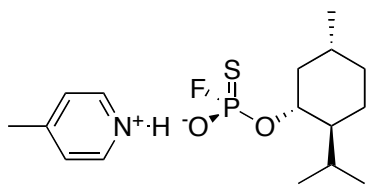
Chemical Formula: $C_{16}H_{27}FNO_2PS$
Exact Mass: 347.1484
Molecular Weight: 347.4282

tetrabutylammonium salt S_p-**2** (dr = 97 : 3) (0.56 mmol, 0.28 g) at room temperature. The mixture was stirred for 3 h at room temperature. The resulting mixture was filtered, washed with CH_2Cl_2 and concentrated *in vacuo* to give colorless oil. To a hexane solution of the oil, hexane (0.6 mL) solution of 4-methylpyridine (0.60 mmol, 0.06 mL) was added at room temperature to give the corresponding 4-methylpyridium salt S_p-**7** (dr = 96 : 4) (0.19 g, 0.55 mmol, 98%) as a white solid.

mp 87-88 ºC; IR (KBr) 3079, 2950, 2922, 2866, 2457, 2024, 1639, 1502, 1454, 1388, 1349, 1317, 1263, 1236, 1142, 802, 708, 649, 594, 514 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77-0.78 (m, 3H), 0.82-0.86 (m, 7H), 0.94-1.13 (m 3H), 1.30-1.43 (m, 2H), 1.59-1.62 (m, 2H), 2.15-2.22 (m, 1H), 2.33-2.36 (m, 1H), 2.62 (s, 3H, CH_3 (4-position of pyridine)), 4.20-4.29 (m, 1H, OCH), 7.64 (d, J = 5.8 Hz, 2H, NCCH), 8.72 (d, J = 5.8 Hz, 2H, NCH); ^{13}C NMR ($CDCl_3$) δ 15.5, 20.7, 21.7, 22.0, 22.6, 25.1, 31.1, 33.9, 42.4, 48.2 (d, $J_{C\text{-}P}$ = 5.8Hz), 78.3 (d, $J_{C\text{-}P}$ = 7.4 Hz, OC), 127.1, 141.1, 158.0; ^{19}F NMR ($CDCl_3$) δ 33.8 (d, $J_{F\text{-}P}$ = 1047 Hz), ^{31}P NMR ($CDCl_3$) δ 55.5 (d, $J_{P\text{-}F}$ = 1045 Hz); $[\alpha]^{25}_D$ -68.5 (c 1.0, $CHCl_3$).

minor product: ^{19}F NMR ($CDCl_3$) δ -30.7 (d, $J_{F\text{-}P}$ = 1047 Hz), ^{31}P NMR ($CDCl_3$) δ 56.5 (d, $J_{P\text{-}F}$ = 1045 Hz).

4-Methylpyridium (*L*)-menthylphosphorofluorothoate (R_p-7)



Chemical Formula: $C_{16}H_{27}FNO_2PS$
Exact Mass: 347.1484
Molecular Weight: 347.4282

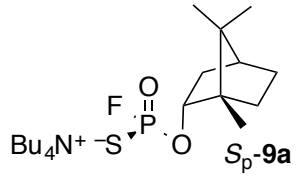
Amberlyst 15 ion-exchange resin (10 g) was added to a CH_2Cl_2 (20 mL) solution of tetrabutylammonium salt R_p-**2** (dr = 95 : 5) (1.32 mmol, 0.654 g) at room temperature. The mixture was stirred for 3 h at room temperature. The resulting mixture was filtered, washed with CH_2Cl_2 and concentrated *in vacuo* to give colorless oil. To a hexane solution of the oil, hexane (1.3 mL) solution of 4-methylpyridine (1.35 mmol, 1.35 mL) was added at room temperature to give the corresponding 4-methylpyridium salt R_p-**7** (97 : 3) (0.341 g, 0.981 mmol, 74%) as a white solid.

mp 126-127 ºC; IR (KBr) 3079, 2950, 2922, 2866, 2457, 2024, 1639, 1502, 1454, 1388, 1349, 1317, 1263, 1236, 1142, 802, 708, 649, 594, 514 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81-0.92 (m, 10H), 0.99-1.17 (m, 2H), 1.32-1.38 (m 1H), 1.44-1.52 (m, 1H), 1.64-1.66 (m, 2H), 2.20-2.22 (m, 1H), 2.26-2.29 (m, 1H), 2.66 (s, 3H, CH_3 (4-position of pyridine)), 4.28-4.36 (m, 1H, OCH), 7.67 (d, J = 5.6 Hz, 2H,

NCCH), 8.74 (d, J = 5.4 Hz, 2H, NCH); ^{13}C NMR ($CDCl_3$) δ 16.0, 20.8, 21.9, 22.2, 22.8, 25.3, 31.3, 34.0, 42.2, 48.3 (d, $J_{C\text{-}P}$ = 8.3 Hz), 78.7 (d, $J_{C\text{-}P}$ = 7.4 Hz, OCH), 127.2, 141.1, 158.3; ^{19}F NMR ($CDCl_3$) δ -30.7 (d, $J_{F\text{-}P}$ = 1050 Hz), ^{31}P NMR ($CDCl_3$) δ 56.7 (d, $J_{P\text{-}F}$ = 1051 Hz); MS (FAB$^-$) *m/z* 253 (M^- -$HNC_5H_5CH_3$); HRMS calcd for $C_{10}H_{19}FO_2PS$ 253.0833 (M^+ -$HNC_5H_5CH_3$), found 253.0808; $[\alpha]^{25}_D$ -47.6 (c 1.0, $CHCl_3$)

minor product: ^{19}F NMR ($CDCl_3$) δ -34.0 (d, $J_{F\text{-}P}$ = 1049 Hz), ^{31}P NMR ($CDCl_3$) δ 55.6 (d, $J_{P\text{-}F}$ = 1048 Hz)

***N,N,N*-Tributyl-1-butanaminium 1-endo-(1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy -phosphorofluorothioic acid (S_p-9a)**



S_p-**9a**

Chemical Formula: $C_{26}H_{53}FNO_2PS$
Exact Mass: 493.3519
Molecular Weight: 493.7472

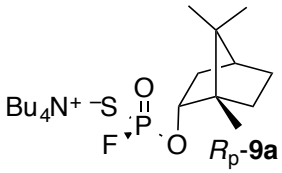
To a THF solution (2 mL) of (R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(endo-(1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-, 4-sulfide R_{ax}-**8a** (0.25 g, 0.5 mmol) was added tetrabutylammonium fluoride solution 1M in THF (2 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 4 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc, $CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt S_p-**9a** (0.33 mmol, 0.16 g, 66%, dr = 98 : 2) as a white solid.

mp 123-125 ºC; IR (KBr) 3411, 2959, 2874, 1489, 1475, 1386, 1300, 1196, 1111, 1052, 1038, 997, 981, 949, 923, 900, 871, 806, 770, 651, 634, 517 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 3H, CH_3), 0.70 (s, 3H, CH_3), 0.72 (s, 3H, CH_3), 0.84 (t, J = 7.3 Hz, 12H, $N(CH_2)_3C\underline{H}_3$), 0.98-1.10 (m, 3H), 1.29 (sext, J = 7.3 Hz, 8H, $N(CH_2)_2C\underline{H}_2CH_3$), 1.41-1.44 (m, 1H), 1.46-1.54 (m, 9H), 1.89-1.96 (m, 1H), 2.09-2.17 (m, 1H), 3.16 (t, J = 8.3 Hz, 8H, NCH_2), 4.46-4.51 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 12.9, 13.3 ($N(CH_2)_3\underline{C}H_3$), 18.5, 19.3 $N(CH_2)_2\underline{C}H_2CH_3$, 19.6, 23.7 ($NCH_2\underline{C}H_2$), 26.4, 27.8, 37.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 44.6, 47.1, 48.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 58.4 (NCH_2), 81.1 (d, $J_{C\text{-}P}$ = 6.6 Hz, OC); ^{19}F NMR ($CDCl_3$) δ -31.3 (d, $J_{P\text{-}F}$ = 1043 Hz); ^{31}P NMR ($CDCl_3$) δ 52.4 (d, $J_{P\text{-}F}$ = 1042 Hz); MS (FAB) *m/z* 251 (M^+-Bu_4N); HRMS calcd for $C_{10}H_{17}FO_2PS$ 251.0671 (M^+-Bu_4N), found 251.0668; $[\alpha]^{19}_D$ -7.84 (c 1.0, $CHCl_3$).

Minor product: ^{19}F NMR ($CDCl_3$) δ -30.7 (d, $J_{P\text{-}F}$ = 1047 Hz); ^{31}P NMR ($CDCl_3$) d 53.2 (d, $J_{P\text{-}F}$ =

1045 Hz).

***N,N,N*-Tributyl-1-butanaminium 1-endo-(1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy -phosphorofluorothioic acid (R_p-9a)**



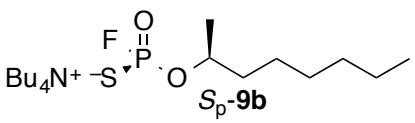
Chemical Formula: $C_{26}H_{53}FNO_2PS$
Exact Mass: 493.3519
Molecular Weight: 493.7472

To a THF solution (6 mL) of (S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(endo-(1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-, 4-sulfide S_{ax}-**8a** (0.75 g, 1.5 mmol) was added tetrabutylammonium fluoride solution 1M in THF (6 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 4.0 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc, $CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt R_p-**9a** (0.64 g, 82%, dr = 88 : 22) as a white solid.

mp 117-118 ºC; IR (KBr) 3411, 2959, 2874, 1489, 1475, 1386, 1300, 1196, 1111, 1052, 1038, 997, 981, 949, 923, 900, 871, 806, 770, 651, 634, 517 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.72-0.73 (m, 3H), 0.75-0.78 (m, 6H), 0.85-0.91 (m, 12H), 1.03-1.15 (m, 3H), 1.30-1.37 (m, 8H), 1.47-1.55 (m, 10H), 1.92-2.00 (m, 1H), 2.13-2.16 (m, 1H), 3.20 (t, J = 8.8 Hz, 8H, NCH_2), 4.54-4.58 (m, 1H, OCH); ^{13}C NMR ($CDCl_3$) d 13.1, 13.5 ($N(CH_2)_3\underline{C}H_3$), 18.7, 19.5 ($N(CH_2)_2\underline{C}H_2$), 19.8, 23.8 ($NCH_2\underline{C}H_2$), 26.6, 27.9, 36.8, 44.7, 47.1, 49.0 (d, $J_{C\text{-}P}$ = 7.4 Hz), 58.5 (NCH_2), 81.3 (d, $J_{C\text{-}P}$ = 4.9 Hz, OCH); ^{19}F NMR ($CDCl_3$) δ -30.3 (d, $J_{P\text{-}F}$ = 1042 Hz); ^{31}P NMR ($CDCl_3$) δ 53.1 (d, $J_{P\text{-}F}$ = 1042 Hz); MS (FAB) *m/z* 251 (M^- -Bu_4N); HRMS calcd for $C_{10}H_{17}FO_2PS$ 251.0671 (M^+ -Bu_4N), found 251.0668; [a] $^{19}_D$ = -9.78 (c 1.0, $CHCl_3$).

minor product: ^{19}F NMR ($CDCl_3$) δ -31.2 (d, $J_{P\text{-}F}$ = 1042 Hz); ^{31}P NMR ($CDCl_3$) δ 52.5 (d, $J_{P\text{-}F}$ = 1042 Hz).

***N,N,N*-Tributyl-1-butanaminium 4-((1*S*)-1-methylheptyloxy)phosphorofluoridothioate (S_p-9b)**



Chemical Formula: $C_{24}H_{53}FNO_2PS$
Exact Mass: 469.3519
Molecular Weight: 469.7252

To a THF solution (3 mL) of the (R_{ax})-4-((1*S*)-1-methylheptyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide R_{ax}-**8b** (238 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0

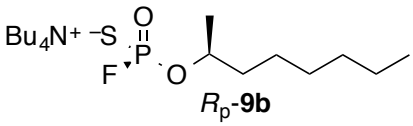
mmol) at at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 4.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt *S*p-**9b** (171 mg, 73%; major : minor = 93 : 7) as a colorless oil.

IR (neat): 2959, 2874, 2348, 1710, 1640, 1468, 1380, 1201, 1063, 984, 885, 767, 663, 628 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (t, *J* = 6.8 Hz, 3H, $(CH_2)_5C\underline{H}_3$), 0.92 (t, *J* = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.18 (d, *J* = 5.8 Hz, 3H, $OCHC\underline{H}_3$) 1.17-1.39 (m, 10H, $OCH(C\underline{H}_2)_5$), 1.34-1.39 (m, 8H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.57 (br s, 8H, $NCH_2C\underline{H}_2CH_2CH_3$), 3.24 (t, *J* = 8.3 Hz, 8H, $NC\underline{H}_2$), 4.41-4.51 (m, 1H, $OC\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.5 ($NCH_2CH_2CH_2\underline{C}H_3$), 13.9 ($(CH_2)_5\underline{C}H_3$), 19.6 ($NCH_2CH_2\underline{C}H_2CH_3$), 21.2 (d, *J* = 3.3 Hz, $(CH_2)_4\underline{C}H_2CH_3$), 22.5 ($OCH\underline{C}H_3$), 23.9 ($NCH_2\underline{C}H_2CH_2CH_3$), 25.3 ($\underline{C}H_2(CH_2)_3CH_3$), 29.3 ($\underline{C}H_2(CH_2)_2CH_3$), 31.7 ($\underline{C}H_2CH_2CH_3$), 37.7 (d, *J* = 6.6 Hz, $OCH\underline{C}H_2$), 58.6 ($N\underline{C}H_2CH_2CH_2CH_3$), 73.5 (d, *J* = 7.4 Hz, $O\underline{C}H$); ^{31}P NMR ($CDCl_3$) δ 52.0 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -29.7 (d, $J_{P\text{-}F}$ = 1041.4 Hz) ; MS (FAB^-) m/z 227(M^+-Bu_4N).

$[a]^{25}_D$ + 7.68 (c 0.25, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$): δ 51.6 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$): δ -30.3 (d, $J_{P\text{-}F}$ = 1042.9 Hz).

***N,N,N*-Tributyl-1-butanaminium 4-((1*S*)-1-methylheptyloxy)phosphorofluoridothioate (*R*p-9b)**



*R*p-**9b**

Chemical Formula: $C_{24}H_{53}FNO_2PS$
Exact Mass: 469.3519
Molecular Weight: 469.7252

To a THF solution (3 mL) of the (S_{ax})-4-((1*S*)-1-methylheptyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2] dioxaphosphepin-4-sulfide S_{ax}-**8b** (238 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0 mmol) at at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 4.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt S_p-**9b** (84 mg, 36%; major : minor = 96 : 4) as a yellow oil.

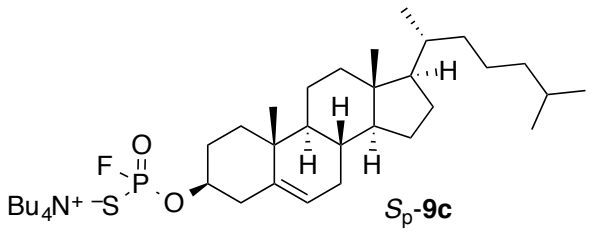
IR (neat): 2959, 2875, 2348, 1712, 1641, 1467, 1380, 1198, 1059, 982, 884, 774, 664, 627 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (t, *J* = 6.8 Hz, 3H, $(CH_2)_5C\underline{H}_3$), 0.93 (t, *J* = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$),

1.20 (d, J = 6.3 Hz, 3H, OCHC$\underline{H}_3$) 1.19-1.43 (m, 10H, OCH(C$\underline{H}_2$)$_5$), 1.38 (sext, J = 7.3 Hz, 8H, NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.55-1.63 (m, 8H, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 3.24 (t, J = 8.3 Hz, 8H, NC$\underline{H}_2$), 4.43-4.48 (m, 1H, OC$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.5 (NCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 13.9 ((CH$_2$)$_5$C$\underline{H}_3$), 19.6 (NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 21.4 (d, J = 4.1 Hz, (CH$_2$)$_4$C$\underline{H}_2$CH$_3$), 22.5 (OCH$\underline{C}$H$_3$), 23.9 (NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 25.2 (C$\underline{H}_2$(CH$_2$)$_3$CH$_3$), 29.2 (C$\underline{H}_2$(CH$_2$)$_2$CH$_3$), 31.7 (C$\underline{H}_2$CH$_2$CH$_3$), 37.6 (d, J = 5.0 Hz, OCH$\underline{C}$H$_2$), 58.6 (N$\underline{C}$H$_2$CH$_2$CH$_2$CH$_3$), 73.6 (d, J = 6.6 Hz, O$\underline{C}$H); ^{31}P NMR ($CDCl_3$) δ 51.8 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -30.4 (d, $J_{P\text{-}F}$ = 1043.7 Hz) ; MS (FAB$^-$) m/z 227 (M^+-Bu$_4$N).

$[\alpha]^{25}_D$ + 10.9 (c 0.21, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$) δ 52.2 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -29.8 (d, $J_{P\text{-}F}$ = 1046.0 Hz).

N,N,N-Tributyl-1-butanaminium cholesteryl –phosphorofluoridothioate (Sp-9c)



S_p-**9c**

Chemical Formula: $C_{43}H_{81}FNO_2PS$
Exact Mass: 725.5710
Molecular Weight: 726.1582

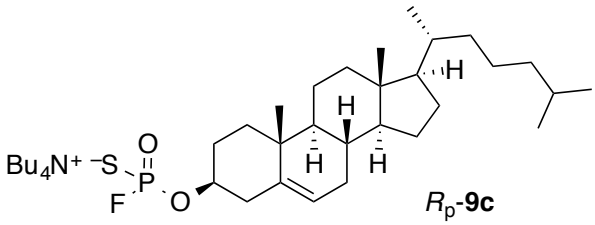
To a THF solution (3 mL) of the (R_{ax})-4–cholesteryl dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide R_{ax}-**8c** (366 mg, 0.5 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (2.0 mL, 2.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 6.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt Sp-**9c** (311 mg, 85%; major : minor = 99 : 1) as a white solid.

mp 34-42 ℃; IR (neat): 2843, 1465, 1381, 1196, 1038, 959, 891, 803 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 3H, Me), 0.78 (d, J = 6.3 Hz, 3H, Me), 0.83 (d, J = 6.3 Hz, 3H, Me), 0.91 (t, J = 7.3 Hz, 12H, NCH$_2$CH$_2$CH$_2$C$\underline{H}_3$), 1.34 (sext, J = 7.3 Hz, 8H, NCH$_2$CH$_2$C$\underline{H}_2$CH$_3$), 1.43-1.57 (m, 8H, NCH$_2$C$\underline{H}_2$CH$_2$CH$_3$), 0.93-2.08 (m, 32H), 2.28-2.41 (m, 2H), 3.21-3.23 (m, 8H, NC$\underline{H}_2$), 4.19-4.21 (m, 1H, OC$\underline{H}$), 5.24 (br s, 1H, C=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH$_2$C$\underline{H}_3$), 19.2 (C$\underline{H}_2$CH$_3$), 23.9 (NCH$_2$C$\underline{H}_2$), 58.8 (N$\underline{C}$H$_2$), 11.7, 18.6, 19.6, 20.9, 22.4, 23.6, 24.1, 27.8, 28.1, 31.8, 31.9, 35.6, 36.0, 36.3, 37.0, 39.3, 39.6, 40.0, 40.1, 42.1, 50.0, 55.9, 56.6, 76.6 (d, J = 8.3 Hz, O$\underline{C}$H), 121.5 (C=$\underline{C}$H), 140.6 ($\underline{C}$=CH); ^{31}P NMR ($CDCl_3$): δ 51.6 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -29.9 (d, $J_{P\text{-}F}$ = 1043.7 Hz); Anal Calcd for $C_{43}H_{81}FNO_2PS \cdot 0.5\ CHCl_3$ C, 66.46; H, 10.45; N, 1.78. Found: C, 67.00; H, 10.37; N, 1.79.

$[\alpha]^{25}_D$ - 20.4 (c 0.30, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$): δ 51.8 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$): δ -29.7 (d, $J_{P\text{-}F}$ = 1042.9 Hz).

***N,N,N*-Tributyl-1-butanaminium cholesteryl –phosphorofluoridothioate (*R*p-9c)**



R_p-**9c**

Chemical Formula: $C_{43}H_{81}FNO_2PS$
Exact Mass: 725.5710
Molecular Weight: 726.1582

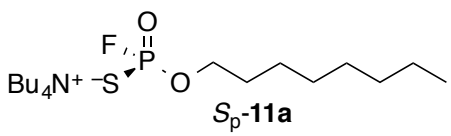
To a THF solution (3 mL) of the (S_{ax})-4–cholesteryl dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-sulfide S_{ax}-**8c** (2.93 g, 4.0 mmol) was added tetrabutylammonium fluoride (1.0 M, THF) (16.0 mL, 16.0 mmol) at room temperature under an Ar atmosphere. After the addition, the mixture was stirred for 6.0 h. The reaction mixture was poured into water and extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography on silica gel (ethyl acetate then $CHCl_3$: MeOH = 10 : 1, Rf = 0.08) to give an ammonium salt ***R*p-9c** (2.33 g, 80%; major : minor = 99 : 1) as a white solid.

mp 37-41 °C; IR (neat): 2960, 2870, 1665, 1469, 1381, 1202, 1036, 959, 927, 891,870, 765, 649, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.63 (s, 3H, Me), 0.81 (d, J = 6.8 Hz, 3H, Me), 0.83 (d, J = 6.3 Hz, 3H, Me), 0.87 (d, J = 6.8 Hz, 3H, Me), 0.97 (t, J = 7.3 Hz, 12H, $NCH_2CH_2CH_2C\underline{H}_3$), 1.45 (sext, J = 7.3 Hz, 8H, $NCH_2CH_2C\underline{H}_2CH_3$), 1.65 (quint, J = 7.9 Hz, 8H, $NCH_2C\underline{H}_2CH_2CH_3$), 0.93-2.08 (m, 29H), 2.41-2.49 (m, 2H), 3.21-3.26 (t, J = 8.3 Hz, 8H, $NC\underline{H}_2$), 4.25-4.27 (m, 1H, O$C\underline{H}$), 5.27-5.30 (m, 1H, C=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ 13.7 ($CH_2\underline{C}H_3$), 19.7 ($\underline{C}H_2CH_3$), 23.8 ($NCH_2\underline{C}H_2$), 58.8 ($NC\underline{H}_2$), 11.8, 18.7, 19.3, 21.0, 22.5, 23.7, 24.0, 27.9, 28.2, 31.8, 31.9, 35.8, 36.1, 36.4, 37.1, 39.5, 39.7, 40.1, 42.3, 50.4, 56.1, 56.7, 58.8, 76.6 (d, J = 8.3 Hz, O$\underline{C}$H), 121.4 (C=$\underline{C}$H), 140.4 ($\underline{C}$=CH); ^{31}P NMR ($CDCl_3$) δ 51.7 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$) δ -29.7 (d, $J_{P\text{-}F}$ = 1044.5 Hz); Anal Calcd for $C_{43}H_{81}FNO_2PS \cdot 0.3\ CHCl_3$ C, 68.25; H, 10.75; N, 1.84. Found: C, 68.33; H, 10.81; N, 1.83.

$[\alpha]^{25}_D$ - 19.3 (c 0.30, $CHCl_3$)

minor product: ^{31}P NMR ($CDCl_3$): δ 51.6 (d, $J_{P\text{-}F}$ = 1042.9 Hz); ^{19}F NMR ($CDCl_3$): δ -29.9 (d, $J_{P\text{-}F}$ = 1042.9 Hz).

***N,N,N*-Tributyl-1-butanaminium 1-octylphosphorofluorothioic acid (*S*p-11a)**



S_p-**11a**

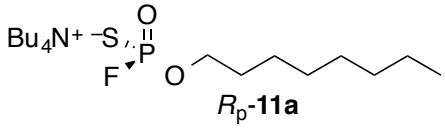
Chemical Formula: $C_{24}H_{53}FNO_2PS$
Exact Mass: 469.3519
Molecular Weight: 469.7252

To a THF solution (1.0 mL) of (R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(octyloxy)-, 4-sulfide R_{ax}-**10a** (0.25 mmol, 0.12 g) was added tetrabutylammonium fluoride solution 1M in THF

(1.0 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 5.0 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc-$CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt *S*p-**11a** (0.22 mmol, 0.10 g, 88%) as a colorless oil.

IR (neat) 2958, 2348, 1712, 1621, 1594, 1468, 1382, 1203, 1108, 1051, 922, 883, 770, 700, 663, 627, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3H, $O(CH_2)_7C\underline{H}_3$), 1.00 (t, 12H, $N(CH_2)_3C\underline{H}_3$), 1.20-1.37 (m, 10H, $O(CH_2)_2(C\underline{H}_2)_5CH_3$), 1.44 (sext, 8H, $N(CH_2)_2C\underline{H}_2CH_3$), 1.62-1.69 (m, 10H, $OCH_2C\underline{H}_2$, $NCH_2C\underline{H}_2$), 3.31 (t, 8H, NCH_2), 3.92-4.06 (m, 2H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.6 ($N(CH_2)_3\underline{C}H_3$), 14.0, 19.6 ($N(CH_2)_2\underline{C}H_2CH_3$), 22.5, 24.0 ($NCH_2\underline{C}H_2$), 25.7, 29.2, 29.3, 30.5 (d, $^3J_{C\text{-}P}$ = 7.4 Hz, $OCH_2\underline{C}H_2$), 31.7, 58.7 ($N\underline{C}H_2$), 66.5 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, OCH_2); ^{19}F NMR ($CDCl_3$) δ -5.5 (d, $^1J_{P\text{-}F}$ = 1042 Hz) ^{31}P NMR ($CDCl_3$) δ 52.4 (d, $^1J_{P\text{-}F}$ = 1039 Hz); MS (FAB) *m/z* 227 (M^- -Bu_4N) ; HRMS calcd for $C_8H_{17}O_2FPS^-$ (M^+ -Bu_4N) 227.0676, found 227.0688.

***N,N,N*-Tributyl-1-butanaminium 1-octylphosphorofluorothioic acid (*R*p-11a)**



R_p-**11a**

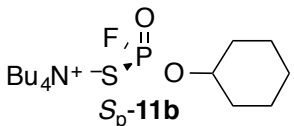
Chemical Formula: $C_{24}H_{53}FNO_2PS$
Exact Mass: 469.3519
Molecular Weight: 469.7252

To a THF solution (2.0 mL) of (S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(octyloxy)-, 4-sulfide S_{ax}-**10a** (0.5 mmol, 0.24 g) was added tetrabutylammonium fluoride solution 1M in THF (2.0 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 5.0 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc-$CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt *R*p-**11a** (0.38 mmol, 0.18 g, 77%) as a colorless oil.

IR (neat) 2958, 2874, 2348, 1712, 1640, 1468, 1382, 1201, 1069, 920, 883, 775, 662, 627, 534 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.80 (t, 3H, $O(CH_2)_7C\underline{H}_3$), 0.93 (t, 12H, $N(CH_2)_3C\underline{H}_3$), 1.12-1.30 (m, 10H, $O(CH_2)_2(C\underline{H}_2)_5CH_3$), 1.37 (sext, 8H, $N(CH_2)_2C\underline{H}_2CH_3$), 1.53-1.62 (m, 10H, $OCH_2C\underline{H}_2$, $NCH_2C\underline{H}_2$), 3.23 (t, 8H, NCH_2), 3.87-3.98 (m, 2H, OCH_2); ^{13}C NMR ($CDCl_3$) δ 13.6 ($N(CH_2)_3\underline{C}H_3$), 14.0, 19.6 ($N(CH_2)_2\underline{C}H_2CH_3$), 22.5, 23.9 ($NCH_2\underline{C}H_2$), 25.6, 29.2, 29.3, 30.5 (d, $^3J_{C\text{-}P}$ = 7.4 Hz, $OCH_2\underline{C}H_2$), 31.7, 58.6 ($N\underline{C}H_2$), 66.5 (d, $^2J_{C\text{-}P}$ = 6.6 Hz, OCH_2); ^{19}F NMR ($CDCl_3$) δ -5.5 (d, $J_{P\text{-}F}$ = 1045 Hz) ^{31}P NMR ($CDCl_3$) δ 52.7 (d, $J_{P\text{-}F}$ = 1043 Hz); MS (FAB+) *m/z* 227 (M^- -Bu_4N); HRMS calcd for

$C_8H_{17}O_2FPS^-$ (M^+ -Bu_4N) 227.0676, found 227.0678.

***N,N,N*-Tributyl-1-butanaminium cyclohexylphosphorofluorothioic acid (S_p-11b)**

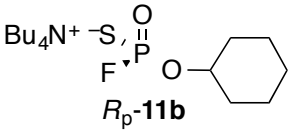


S_p-**11b**
Chemical Formula: $C_{22}H_{47}FNO_2PS$
Exact Mass: 439.3049
Molecular Weight: 439.6552

To a THF solution (5.0 mL) of (R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(cyclohexyloxy)-, 4-sulfide (R_{ax}-**10b**) (1.0 mmol, 0.45 g) was added tetrabutylammonium fluoride solution 1M in THF (4.0 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 4.5 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc, $CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt S_p-**11b** (0.86 mmol, 0.38 g, 86%) as a colorless oil.

IR (neat) 2934, 2874, 2347, 1711, 1641, 1468, 1382, 1259, 1205, 1128, 1048, 1021, 991, 926, 868, 826, 772, 699, 659, 636, 598, 547 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 12H), 1.05-1.16 (m, 2H), 1.19-1.35 (m, 2H), 1.37-1.43 (m, 11H), 1.55-1.66 (m, 10H), 1.90-1.96 (m, 2H), 3.25 (t, J = 8.3 Hz, 8H), 4.30-4.37 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 25.5, 33.6 (d, $^4J_{C\text{-}P}$ = 4.1 Hz), 33.7 (d, $^3J_{C\text{-}P}$ = 5.0 Hz), 58.8 (NCH_2), 75.2 (d, $^2J_{C\text{-}P}$ = 7.4 Hz, OCH); ^{19}F NMR ($CDCl_3$) δ -0.9 (d, $^1J_{P\text{-}F}$ = 1047 Hz); ^{31}P NMR ($CDCl_3$) δ 51.6 (d, $^1J_{P\text{-}F}$ = 1042 Hz); MS (FAB+) *m/z* 197 (M^- -Bu_4N); HRMS calcd for $C_6H_{11}O_2FPS^-$ (M^- -Bu_4N) 197.0207, found 197.0221.

***N,N,N*-Tributyl-1-butanaminium cyclohexylphosphorofluorothioic acid (R_p-11b)**

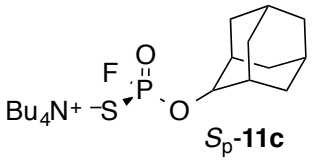


R_p-**11b**
Chemical Formula: $C_{22}H_{47}FNO_2PS$
Exact Mass: 439.3049
Molecular Weight: 439.6552

To a THF solution (3.0 mL) of (S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(cyclohexyloxy)-, 4-sulfide S_{ax}-**10b** (1.3 mmol, 0.57 g) was added tetrabutylammonium fluoride solution 1M in THF (5.1 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 3.0 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc-$CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt R_p-**11b** (0.90 mmol, 0.40 g, 70%) as a colorless oil.

IR (neat) 2935, 2874, 2386, 2348, 1640, 1468, 1382, 1258, 1197, 1127, 1048, 1021, 991, 927, 868, 827, 775, 658, 637, 597, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 12H, CH_3), 1.05-1.16 (m, 1H), 1.19-1.28 (m, 2H), 1.34-1.43 (m, 11H), 1.55-1.66 (m, 10H), 1.92-1.95 (m, 2H), 3.25 (t, J = 8.3 Hz, 8H, NCH_2), 4.29-4.37 (m, 1H, OCH); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 19.7 ($\underline{C}H_2CH_3$), 24.0 ($NCH_2\underline{C}H_2$), 25.5, 33.6 (d, $^{4}J_{C\text{-}P}$ = 4.1 Hz), 33.7 (d. $^{3}J_{C\text{-}P}$ = 5.8 Hz), 58.8 (NCH_2), 75.2 (d, $^{2}J_{C\text{-}P}$ = 7.4 Hz); ^{19}F NMR ($CDCl_3$) δ -0.9 (d, $^{1}J_{P\text{-}F}$ = 1047 Hz); ^{31}P NMR ($CDCl_3$) δ 51.8 (d, $^{1}J_{P\text{-}F}$ = 1042 Hz); MS (FAB+) *m/z* 197 (M^+ -Bu_4N) ; HRMS calcd for $C_6H_{11}O_2FPS^-$ (M^+ -Bu_4N^+) 197.0207, found 197.0178.

_N,N,N_-Tributyl-1-butanaminium 2-tricyclo[3.3.1.1^{3,7}]decylphosphorofluorothioic acid (S_p-11c)



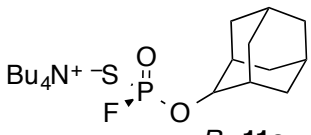
S_p-**11c**

Chemical Formula: $C_{26}H_{51}FNO_2PS$
Exact Mass: 491.3362
Molecular Weight: 491.7312

To a THF solution (8.0 mL) of (R_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(2-tricyclo[3.3.1.1^{3,7}]decyloxy)-, 4-sulfide (R_{ax}-**10c**) (2.0 mmol, 1.0 g) was added tetrabutylammonium fluoride solution 1M in THF (8.0 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 5.5 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc-$CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt S_p-**11c** (1.8 mmol, 0.86 g, 88%) as a white solid.

mp 116-117 ℃; IR (KBr) 2934, 2874, 2347, 1711, 1641, 1468, 1382, 1259, 1205, 1128, 1048, 1021, 991, 926, 868, 826, 772, 699, 659, 636, 598, 547 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 12H, CH_3), 1.33-1.42 (m, 10H), 1.55-1.62 (m, 10H), 1.65-1.74 (m, 6H), 2.05 (br, 2H), 2.13-2.16 (br, 2H), 3.37(t, J =8.3 Hz, 8H, NCH_2), 4.54-4.58 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 19.6 ($\underline{C}H_2CH_3$), 23.9 ($NCH_2\underline{C}H_2$), 27.0, 27.3, 31.3 (d, $J_{C\text{-}P}$ = 3.3 Hz), 33.0 (d, $J_{C\text{-}P}$ = 3.3 Hz), 33.1, 33.1, 36.4 (d, $J_{C\text{-}P}$ = 4.1 Hz), 37.6, 58.6 (NCH_2), 79.4 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{19}F NMR ($CDCl_3$) δ -29.4 (d, $J_{P\text{-}F}$ = 1041 Hz); ^{31}P NMR ($CDCl_3$) δ 51.4 (d, $J_{P\text{-}F}$ =1040 Hz); MS (FAB+) *m/z* 249 (M^+ -Bu_4N); Anal. Calcd for $C_{26}H_{51}FNO_2PS$: C, 63.51; H, 10.54; N, 2.85. Found: C, 63.62; H, 10.57; N, 2.73; $[\alpha]^{25}_D$ +0.61 (c 0.50, $CHCl_3$).

_N,N,N_-Tributyl-1-butanaminium 2-tricyclo[3.3.1.1^{3,7}]decylphosphorofluorothioic acid (R_p-11c) (TH096)



R_p-**11c**

Chemical Formula: $C_{26}H_{51}FNO_2PS$
Exact Mass: 491.3362
Molecular Weight: 491.7312

To a THF solution (12 mL) of (S_{ax})-Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin, 4-(2-tricyclo[3.3.1.1^{3,7}]decyloxy)-, 4-sulfide (S_{ax}-**10c**) (3.0 mmol, 1.5 g) was added tetrabutylammonium fluoride solution 1M in THF (12 mL) at 0 ℃ under Ar atmosphere. The resulting solution was stirred at room temperature for 3.0 h. The mixture was diluted with Et_2O and washed with water. The water layer was extracted with Et_2O. The organic layer was dried over $MgSO_4$, filtered, concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc-$CHCl_3$: MeOH =10: 1) to give the corresponding ammonium salt R_p-**11c** (2.6 mmol, 1.3 g, 86%) as a white solid.

mp 116-118 ℃; IR (KBr) 2935, 2874, 2386, 2348, 1640, 1468, 1382, 1258, 1197, 1127, 1048, 1021, 991, 927, 868, 827, 775, 658, 637, 597, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.3 Hz, 12H, CH_3), 1.36-1.45 (m, 10H), 1.58-1.65 (m, 10H), 1.68-1.77 (m, 6H), 2.08 (br, 2H), 2.16-2.19 (br, 2H), 3.29 (t, J = 8.6 Hz, 8H, NCH_2), 4.54-4.47 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 19.6 ($\underline{C}H_2CH_3$), 23.9 ($NCH_2\underline{C}H_2$), 27.0, 27.3, 31.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 33.0 (d, $J_{C\text{-}P}$ = 3.3 Hz), 33.1, 33.1, 36.4 (d, $J_{C\text{-}P}$ = 4.1 Hz), 37.6, 58.6 (NCH_2), 79.4 (d, $J_{C\text{-}P}$ = 7.4 Hz); ^{19}F NMR ($CDCl_3$) δ -29.3 (d, $J_{P\text{-}F}$ = 1041 Hz); ^{31}P NMR ($CDCl_3$) δ 51.4 (d, $J_{P\text{-}F}$ =1040 Hz); MS (FAB) *m/z* 249 (M^+ -Bu_4N); Anal. Calcd for $C_{26}H_{51}FNO_2PS$: C, 63.51; H, 10.54; N, 2.85. Found: C, 63.21; H, 10.54; N, 2.90; $[\alpha]^{25}_D$ -0.61 (c 0.50, $CHCl_3$).

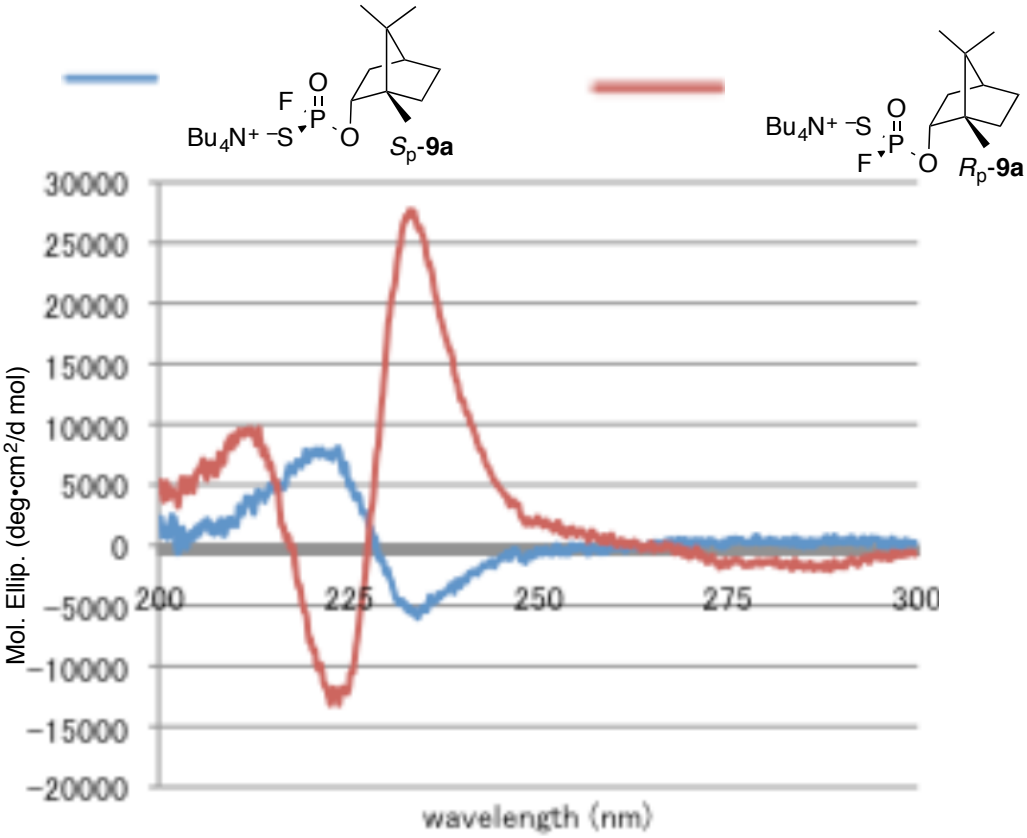


Figure S1 CD spectra of S_p-**9a** and R_p-**9a**

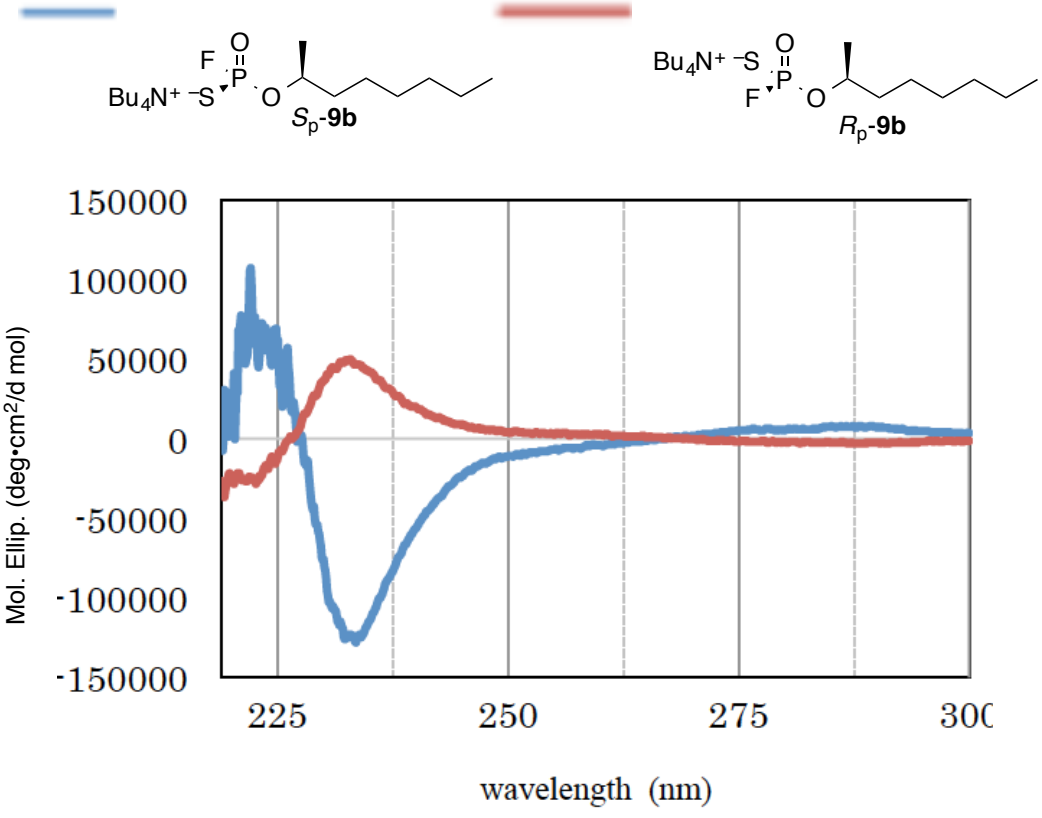


Figure S2 CD spectra of S_p-**9b** and R_p-**9b**

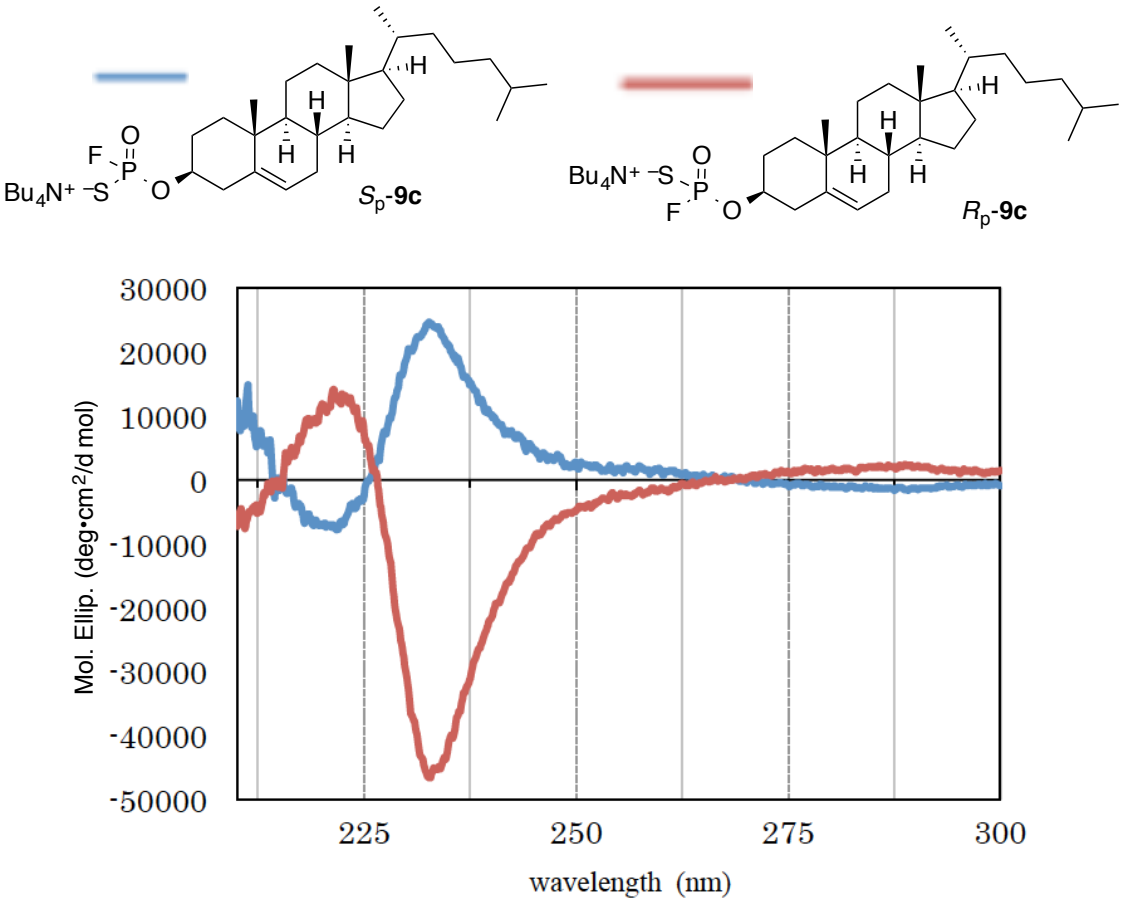


Figure S3 CD spectra of S_p-**9c** and R_p-**9c**

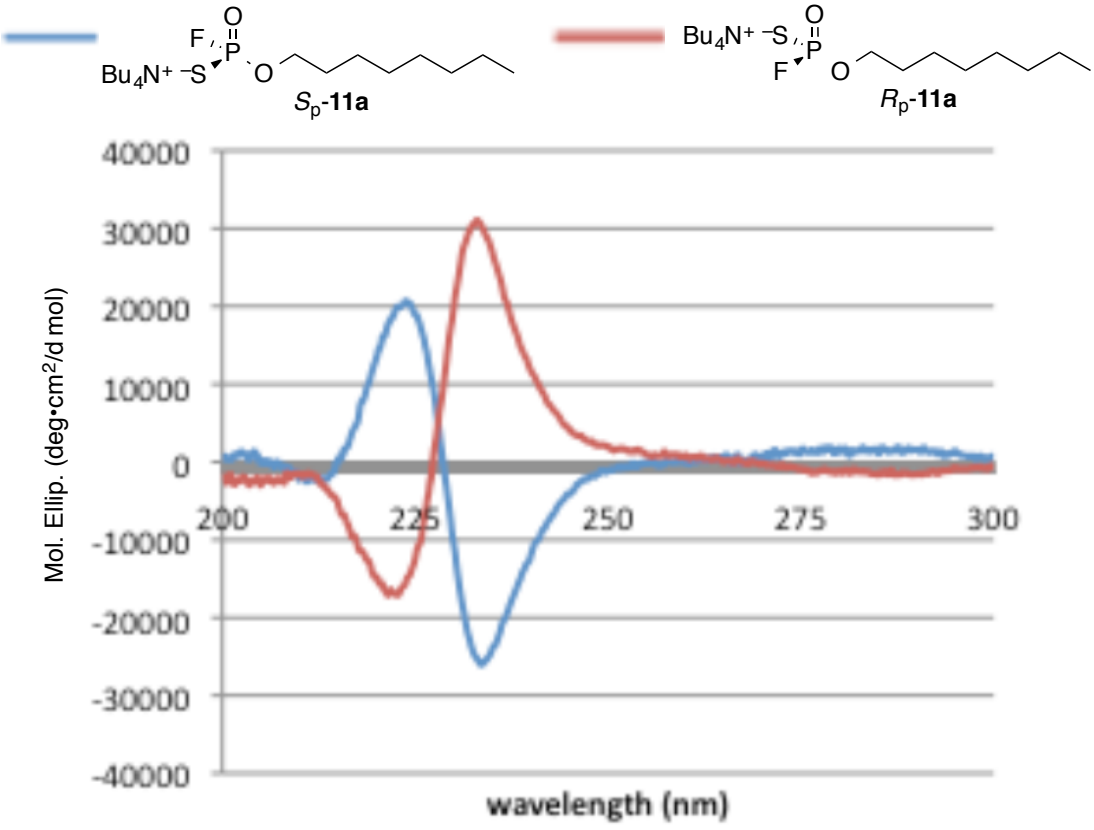


Figure S4 CD spectra of S_p-**11a** and R_p-**11a**

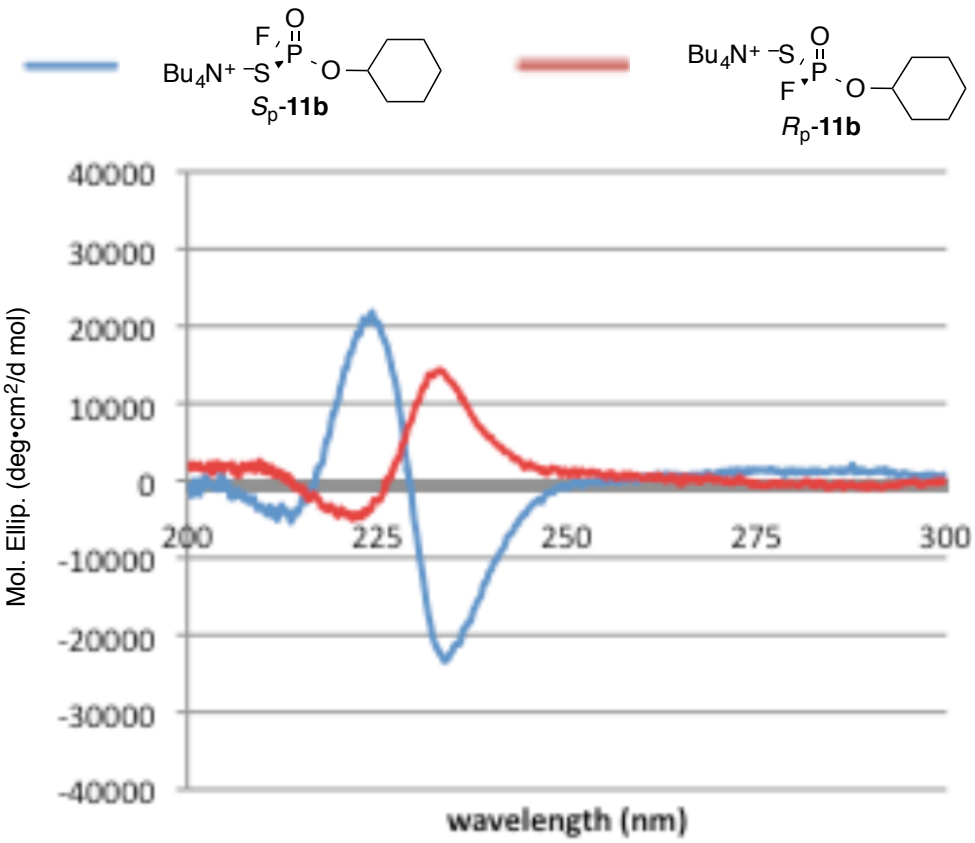


Figure S5 CD spectra of S_p-**11b** and R_p-**11b**

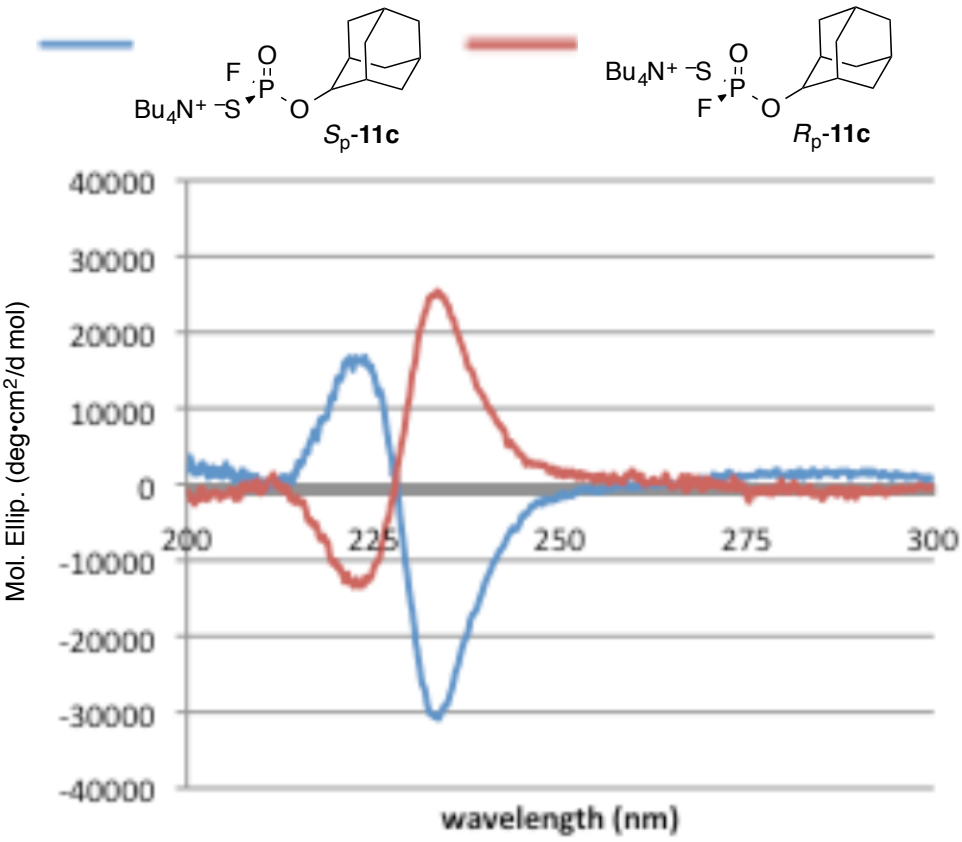


Figure S6 CD spectra of S_p-**11c** and R_p-**11c**

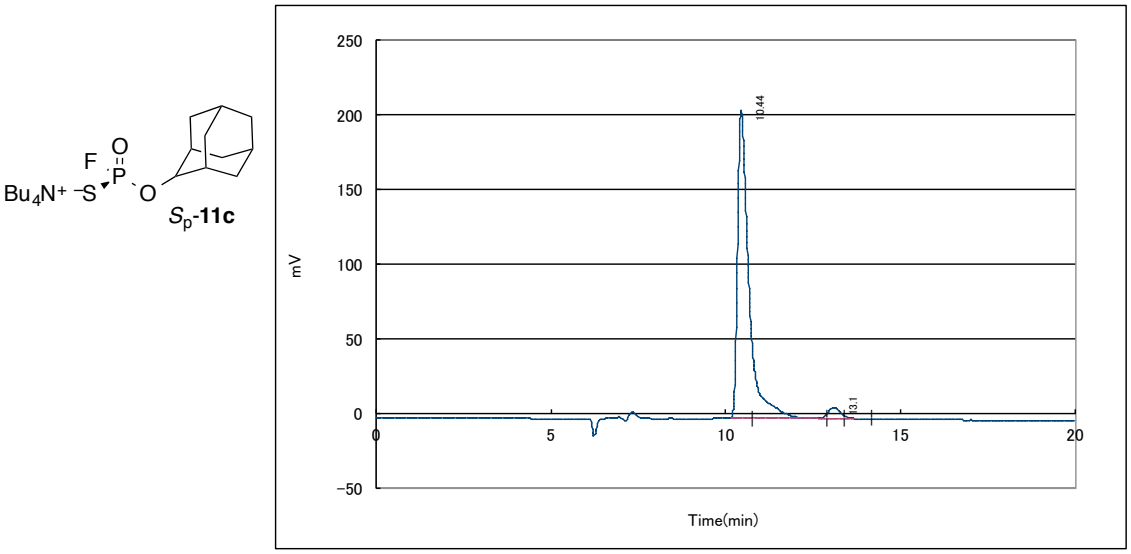


Figure S7 HPLC spectra of S_p**11c** (major) and R_p-**11c** (minor)

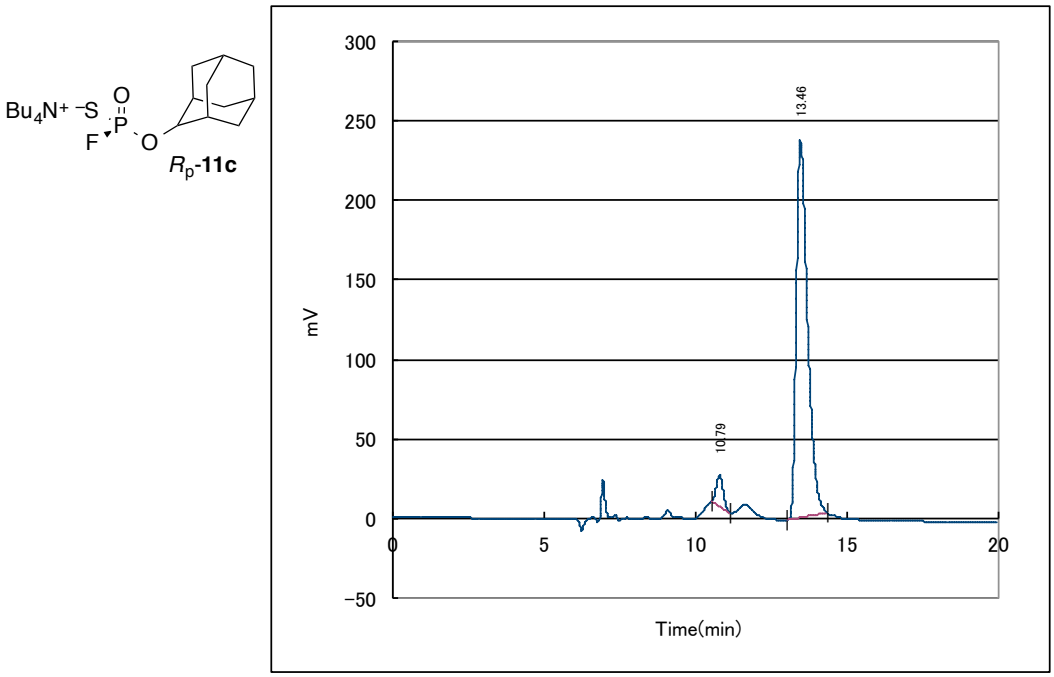


Figure S8 HPLC spectra of S_p**11c** (minor) and R_p-**11c** (major)

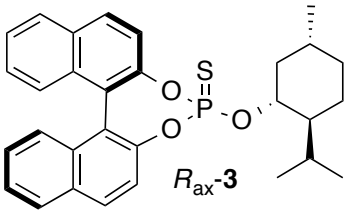
X-ray crystallography. Single crystals of Sp-**7** were obtained from solutions of AcOEt/CH_2Cl_2/hexane after slow evaporation of the solvent at room temperature. Diffraction data were collected on a Bruker Apex-II CCD diffractometer equipped with a graphite monochromated MoKα radiation source (λ = 0.71073 Å). The structure was solved by direct methods (SHELXS-97), and refined by full-matrix least-square methods on *F*2 for all reflections (SHELXL-97) [S1)] with all non-hydrogen atoms anisotropic and all hydrogen atoms isotropic. The crystal data are shown in Tables S1.

Table S1. Crystal Data and Structure Refinement for S_p-**7**

Empirical formula	$C_{16}H_{27}FNO_2PS$
Formula weight	347.41
Temperature	173 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12$
Unit cell dimensions	a = 34.891(4) Å
	b = 6.7332(7) Å
	c = 7.8957(9) Å
Volume	1854.9(4) $Å^3$
Z	4
Density (calculated)	1.244 g/cm^{-3}
Crystal size	0.50 x 0.10 x 0.02 mm^3
Reflections collected	4198
Independent reflections	4016
Flack parameter	0.03(8)
Goodness-of-fit on F^2	1.186
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0346, wR_2 = 0.0942
R indices (all data)	R_1 = 0.0378, wR_2 = 0.1018

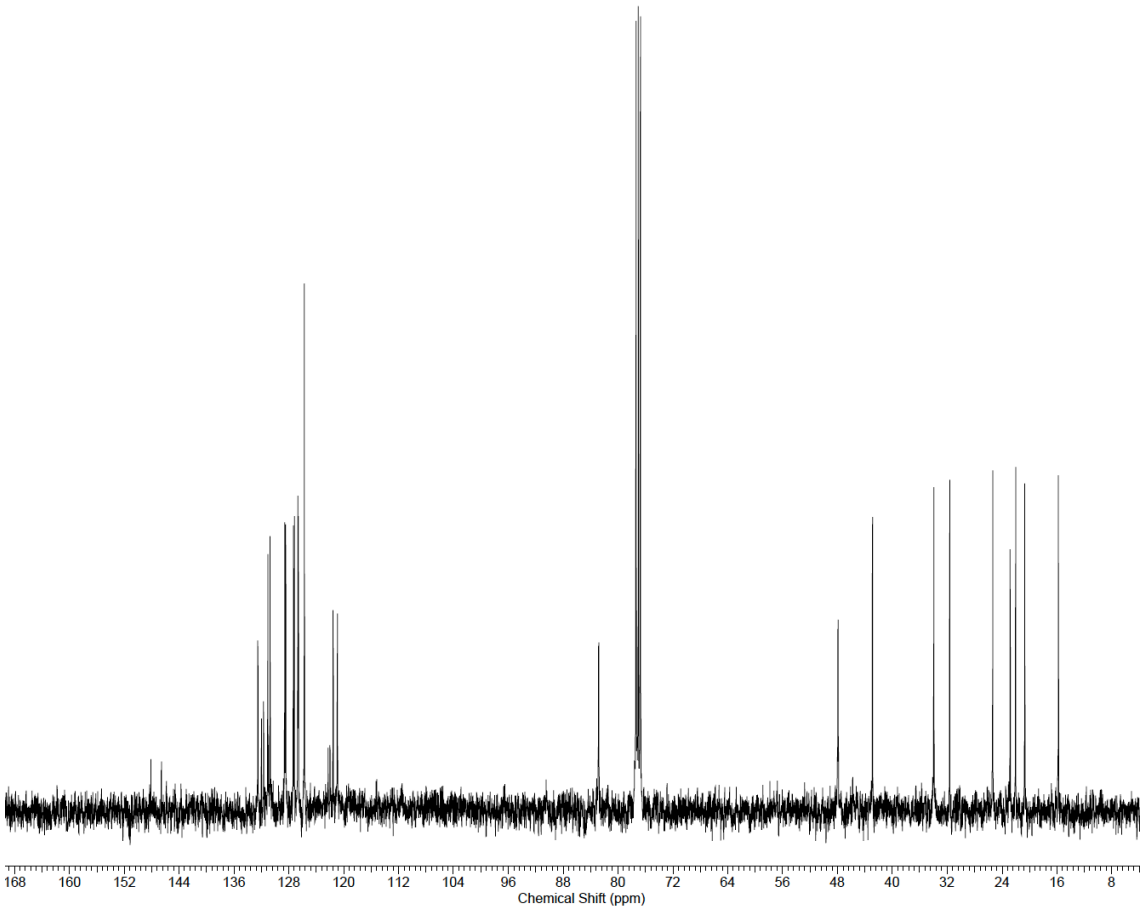
Reference

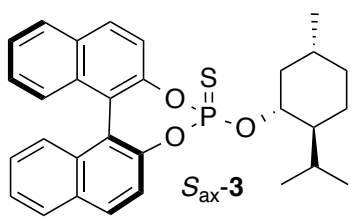
S1) G. M. Sheldrick, SHELXL-97, *A Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, **1997**.


S
O
P
O
O

R_{ax}-**3**

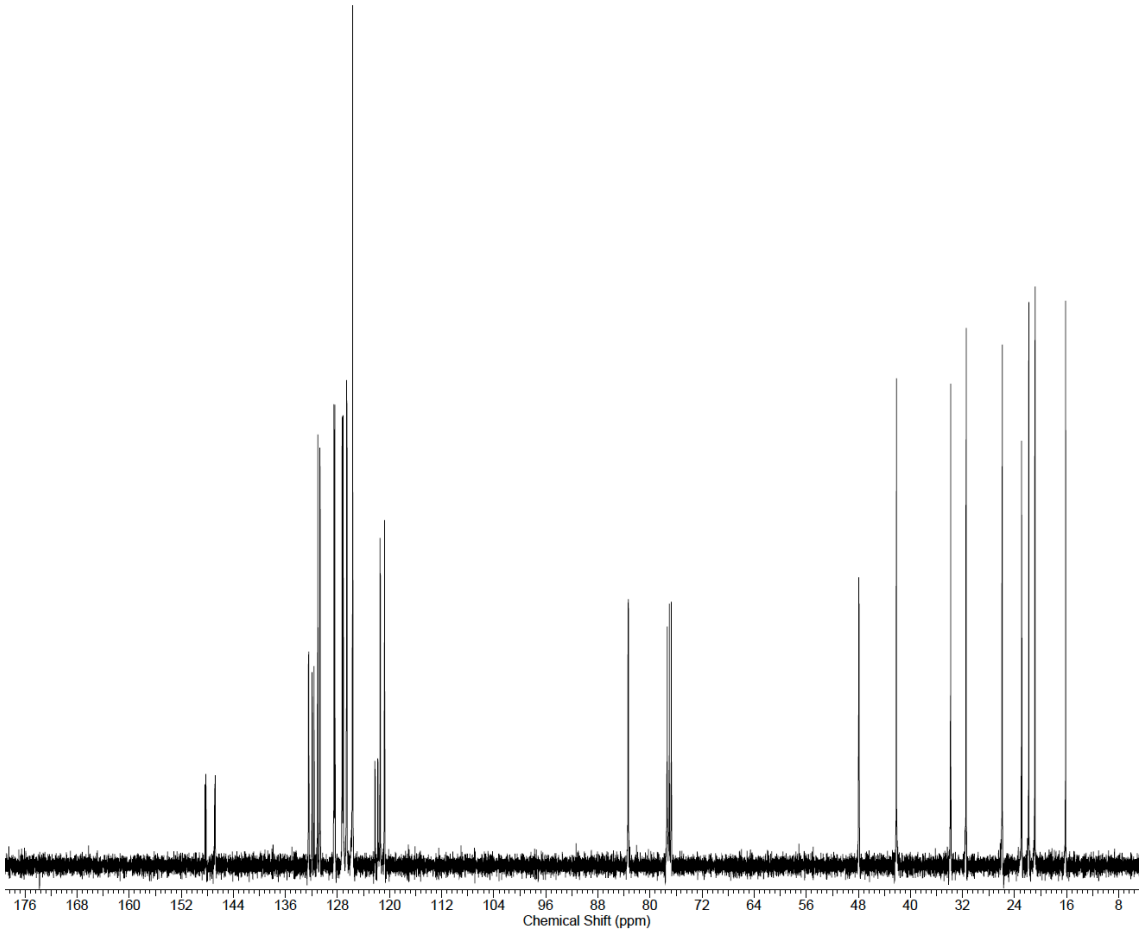
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

S_{ax}-**3**

0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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96
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64
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48
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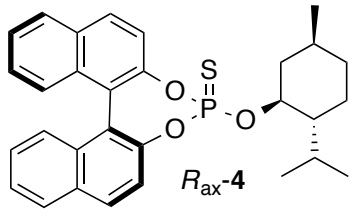
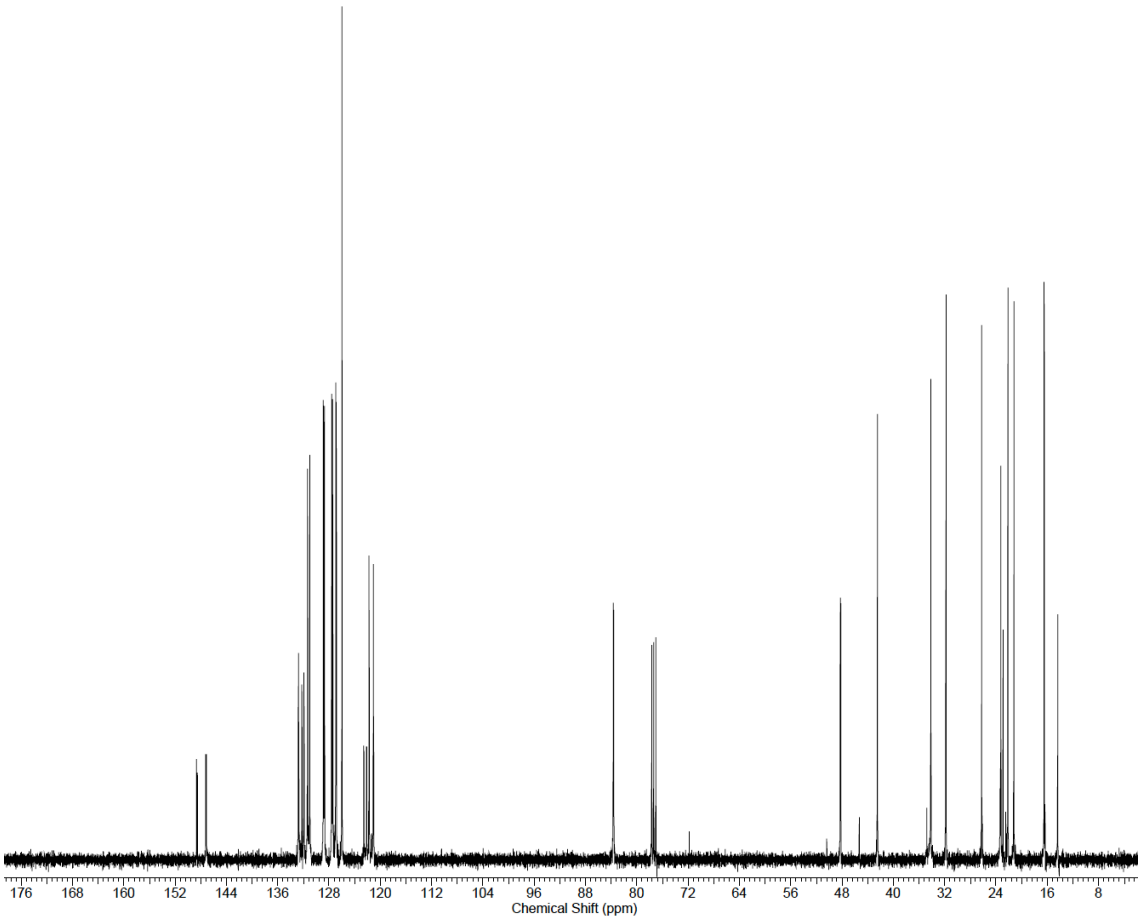
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

R_{ax}-**4**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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48
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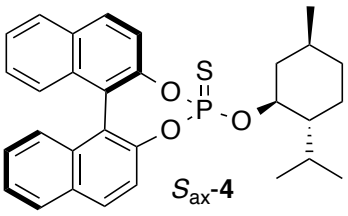
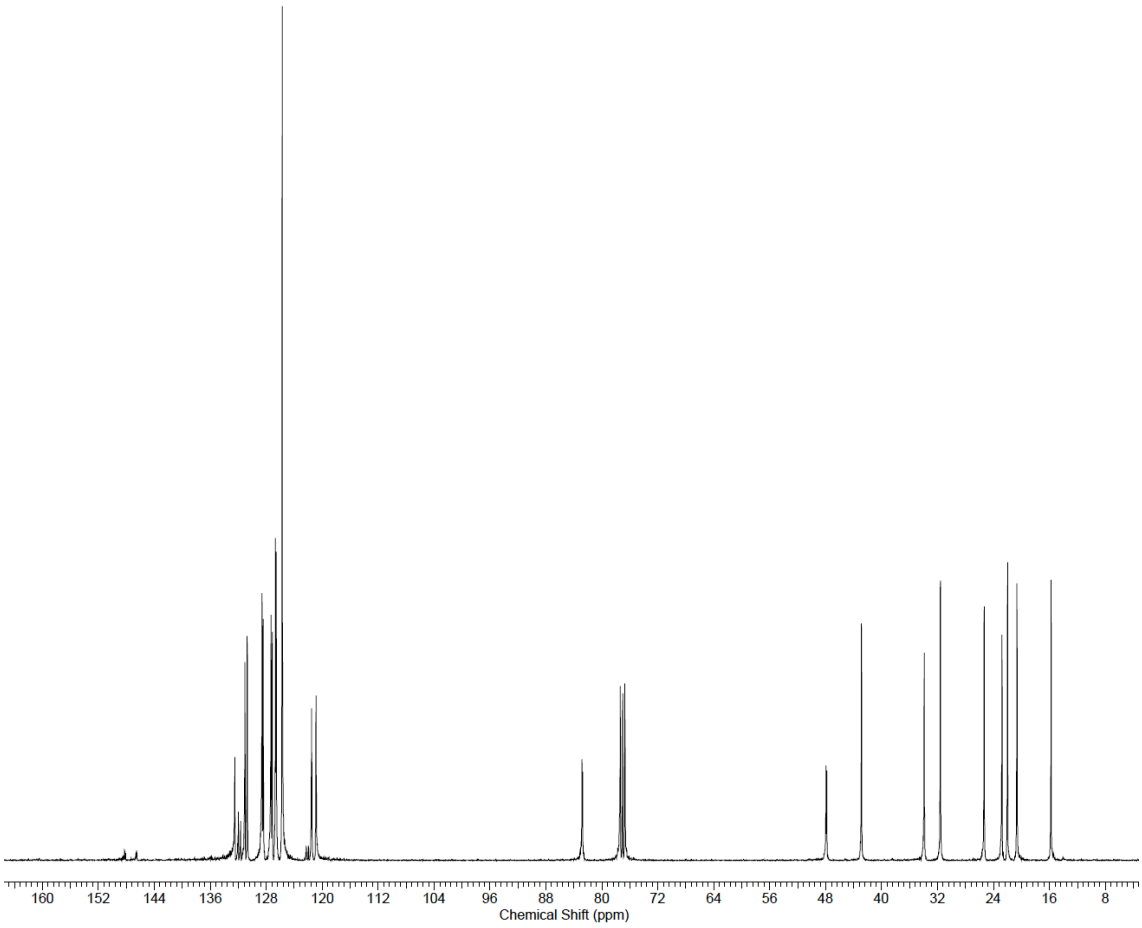
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

S_{ax}-**4**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)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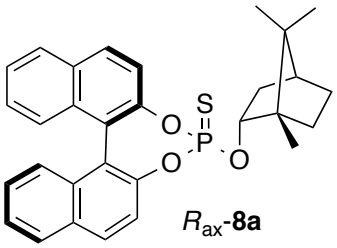
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

R_{ax}-**8a**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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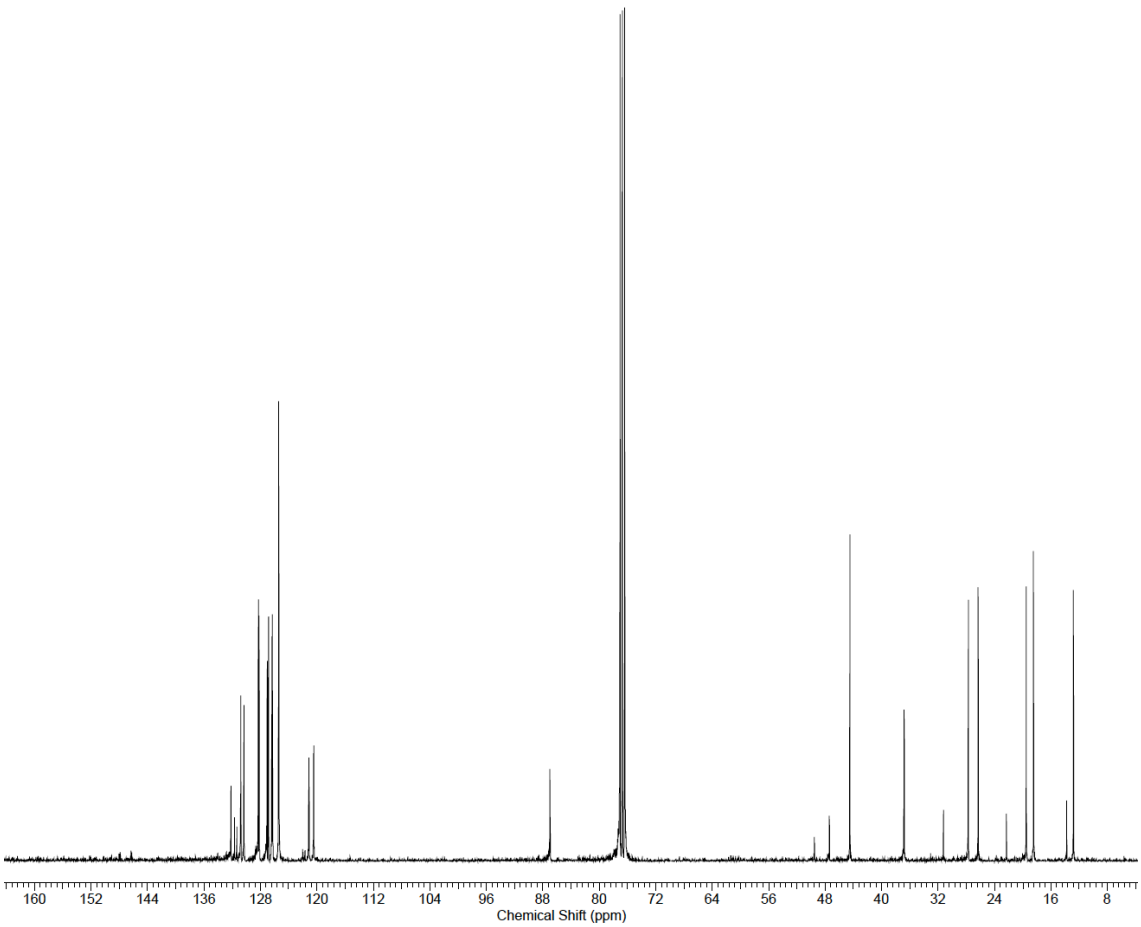
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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80
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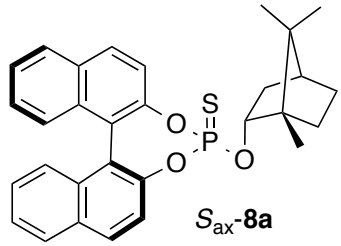
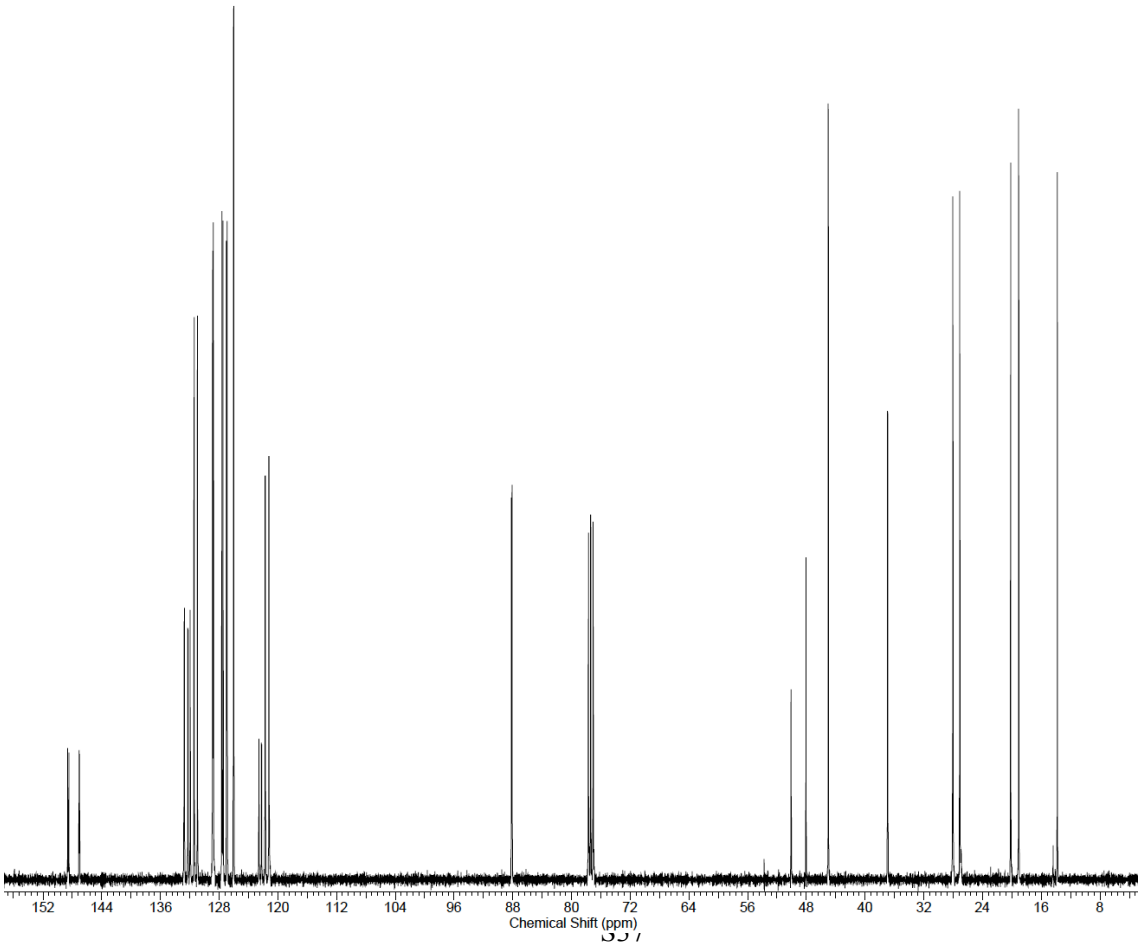
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

S_{ax}-**8a**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)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32
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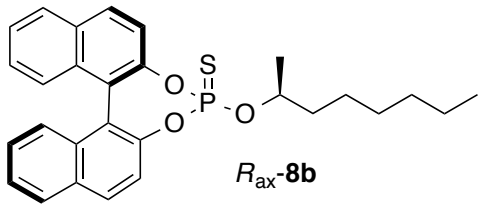
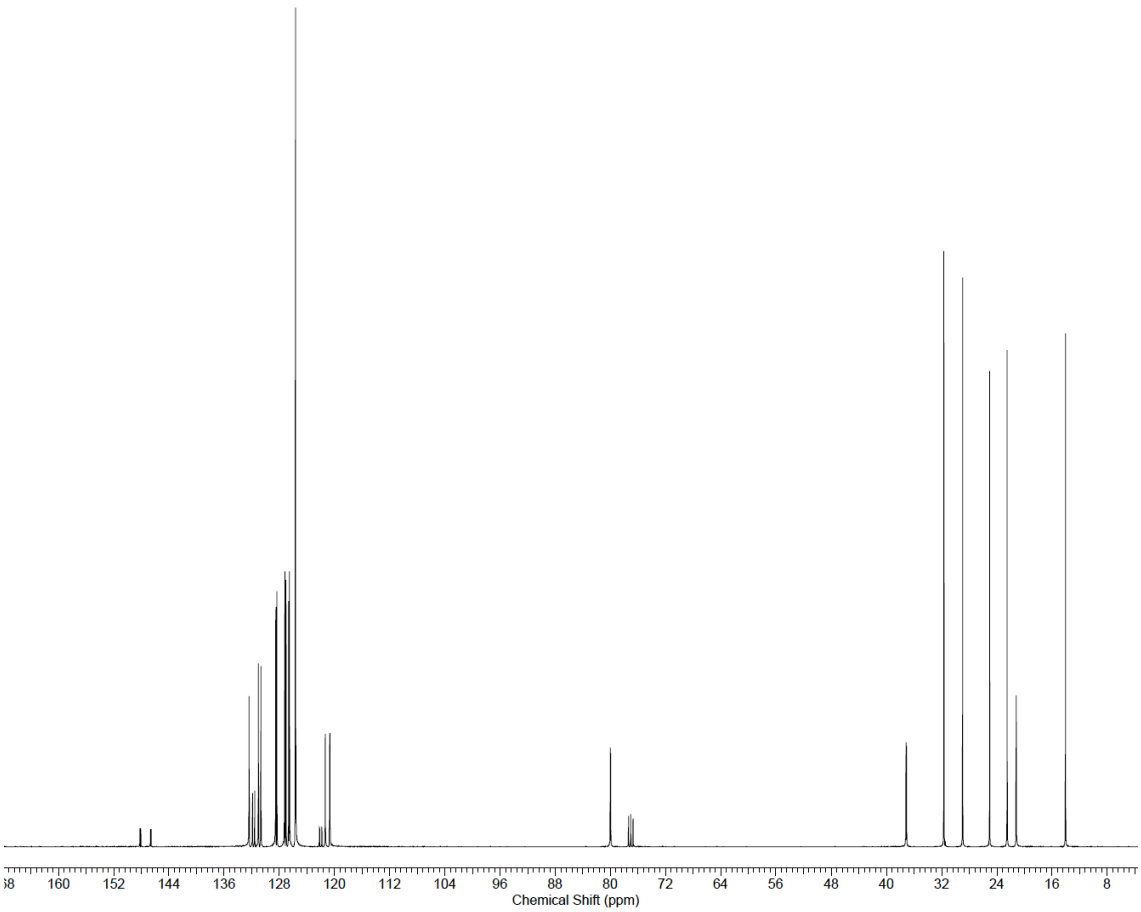
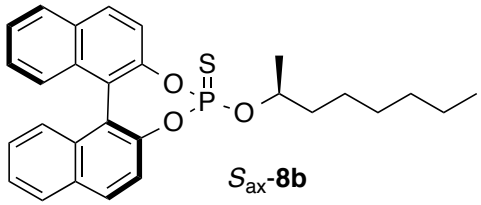
16
8
Chemical Shift (ppm)


S
O
P
O
O

R_{ax}-**8b**

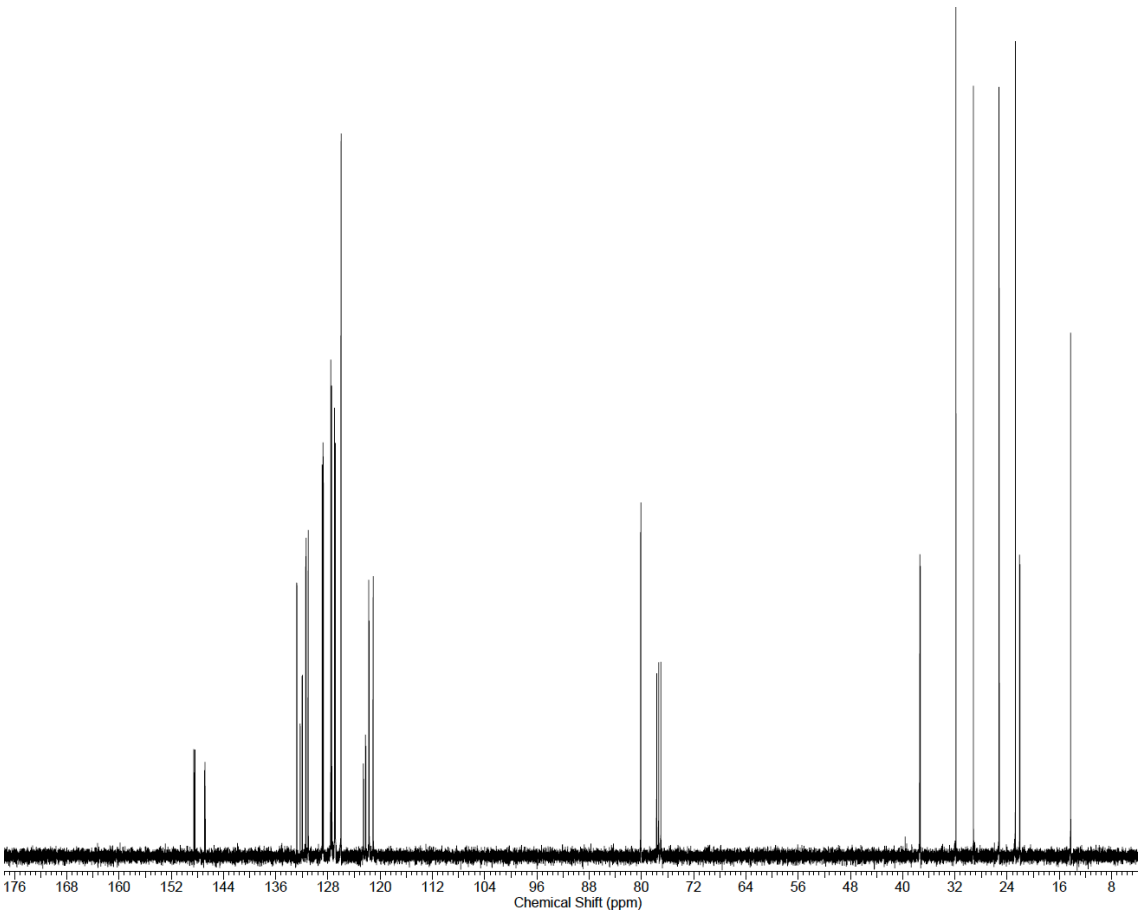
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

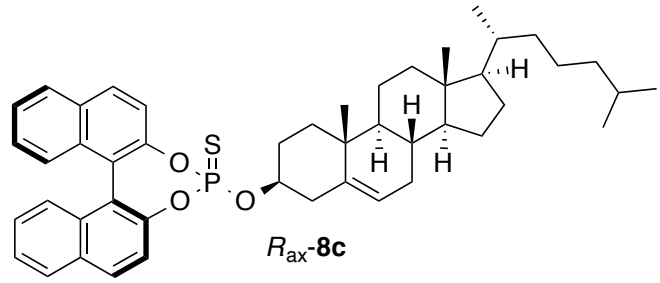

160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

S_{ax}-**8b**

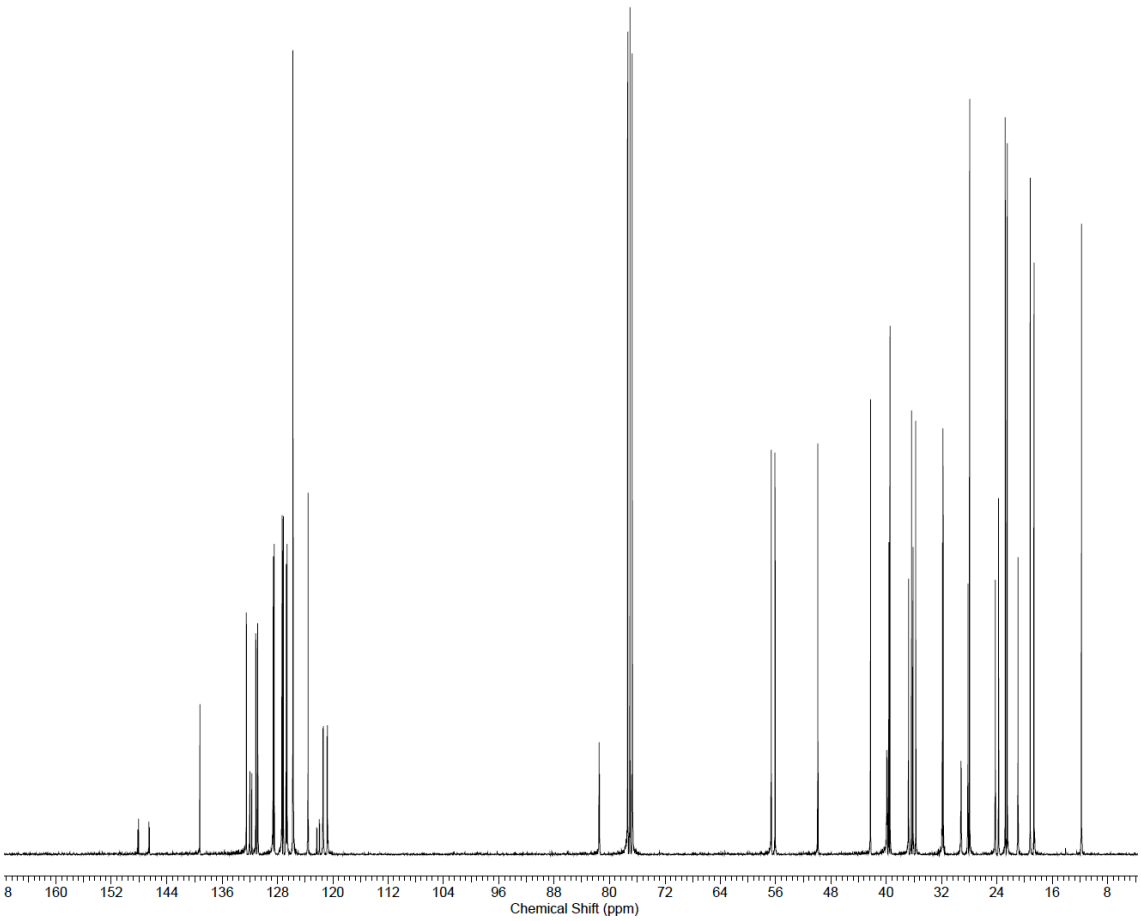
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

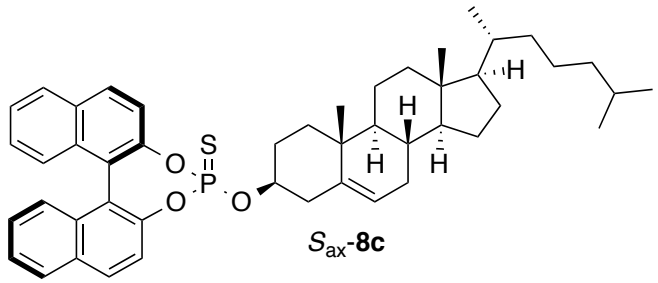

176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O
H
H
H
H

R_{ax}-**8c**

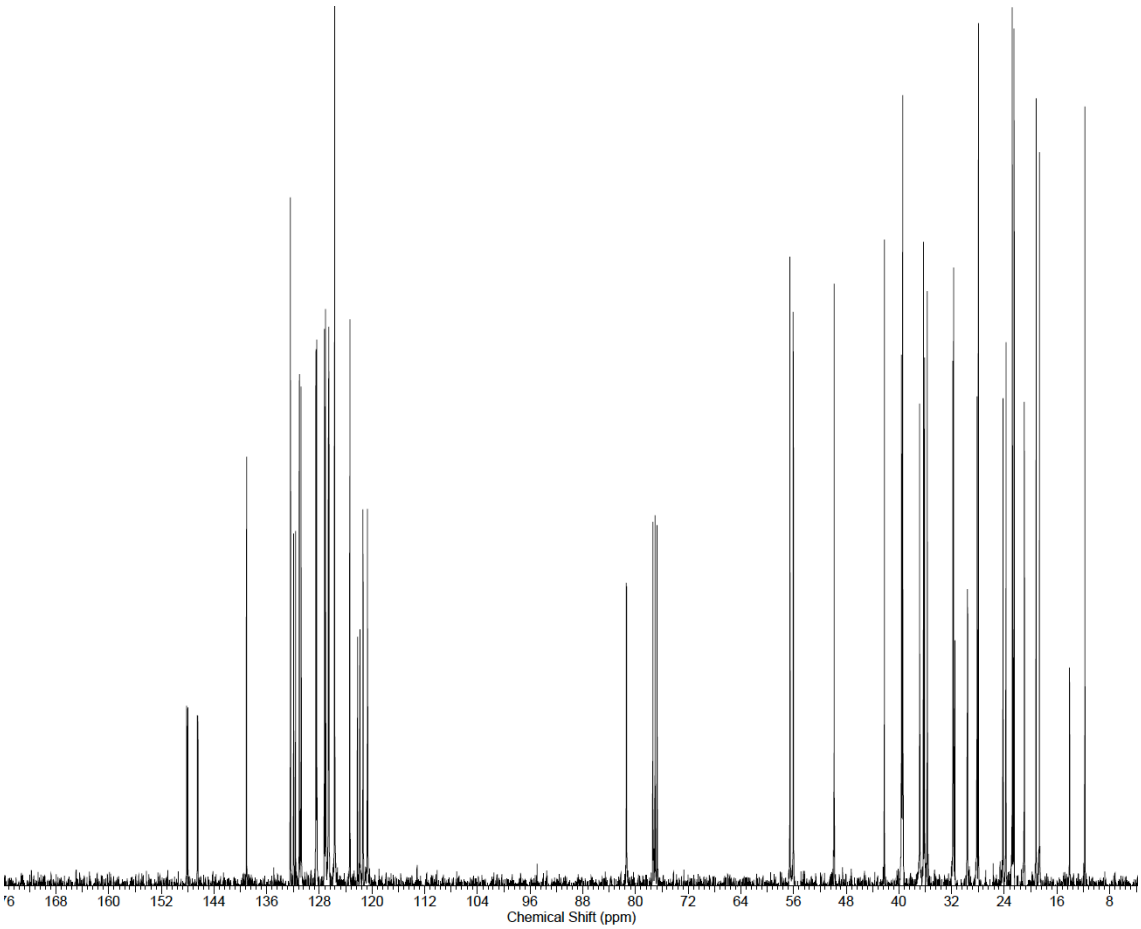
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

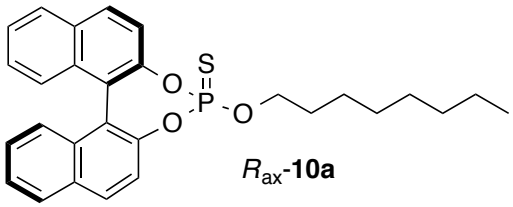

8
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O
H
H
H

S_{ax}-**8c**

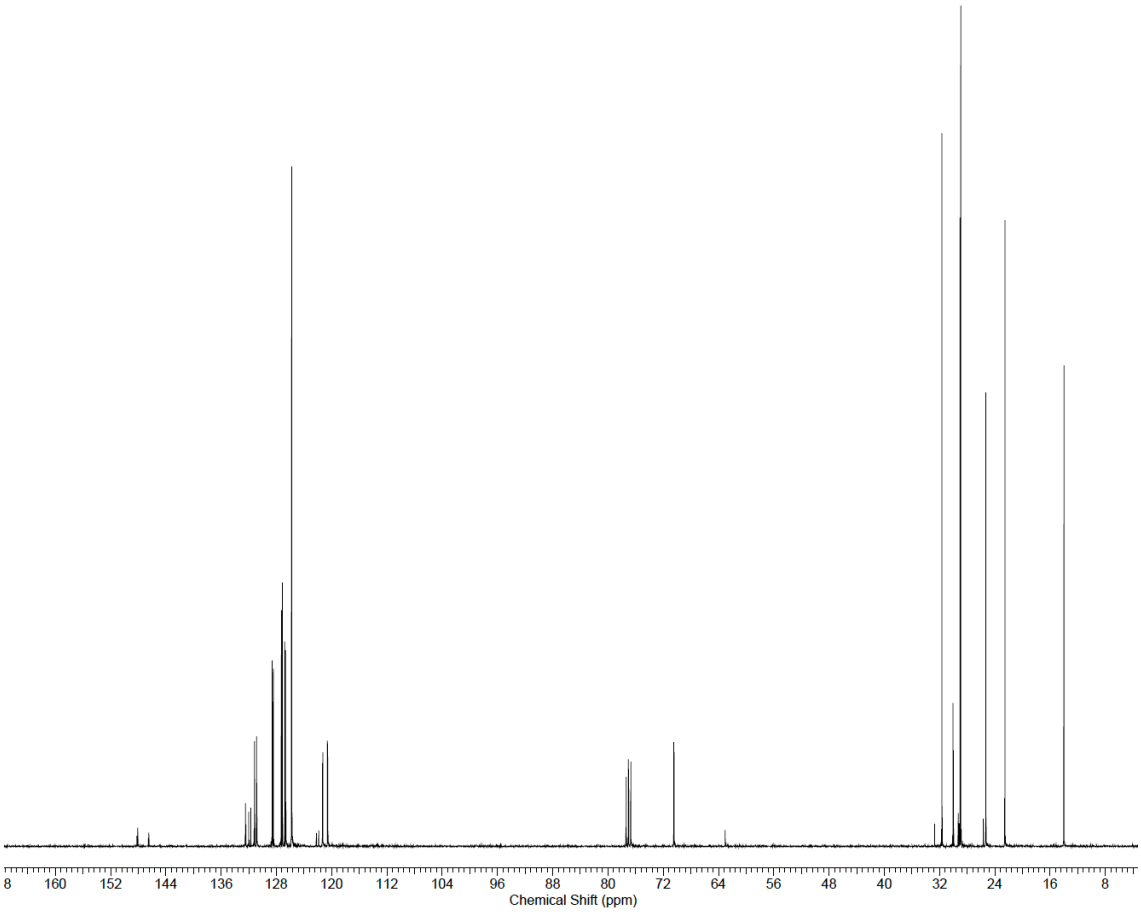
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

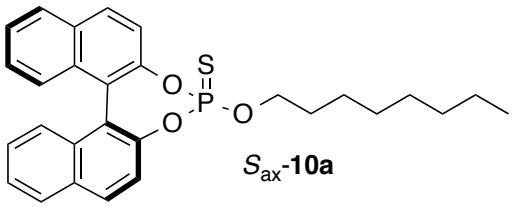

'6
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

R_{ax}-**10a**

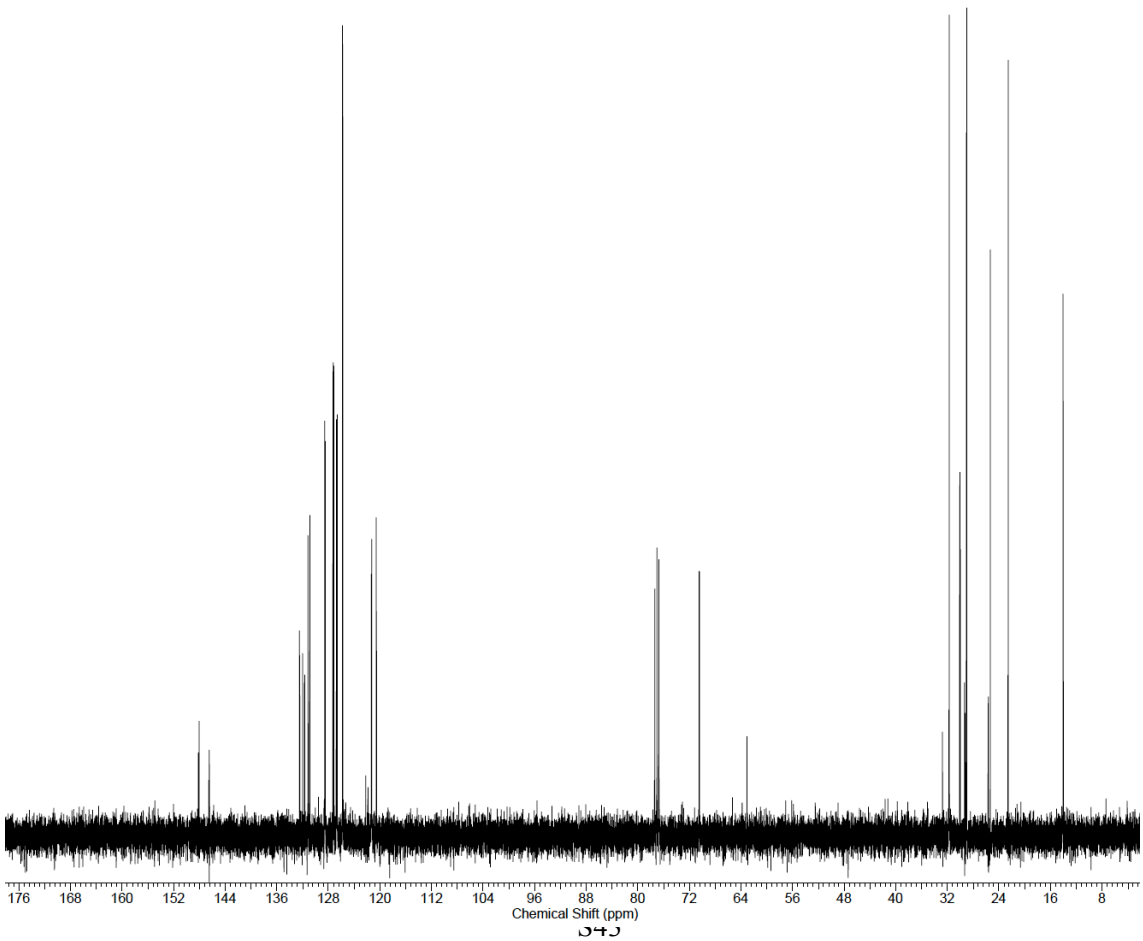
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

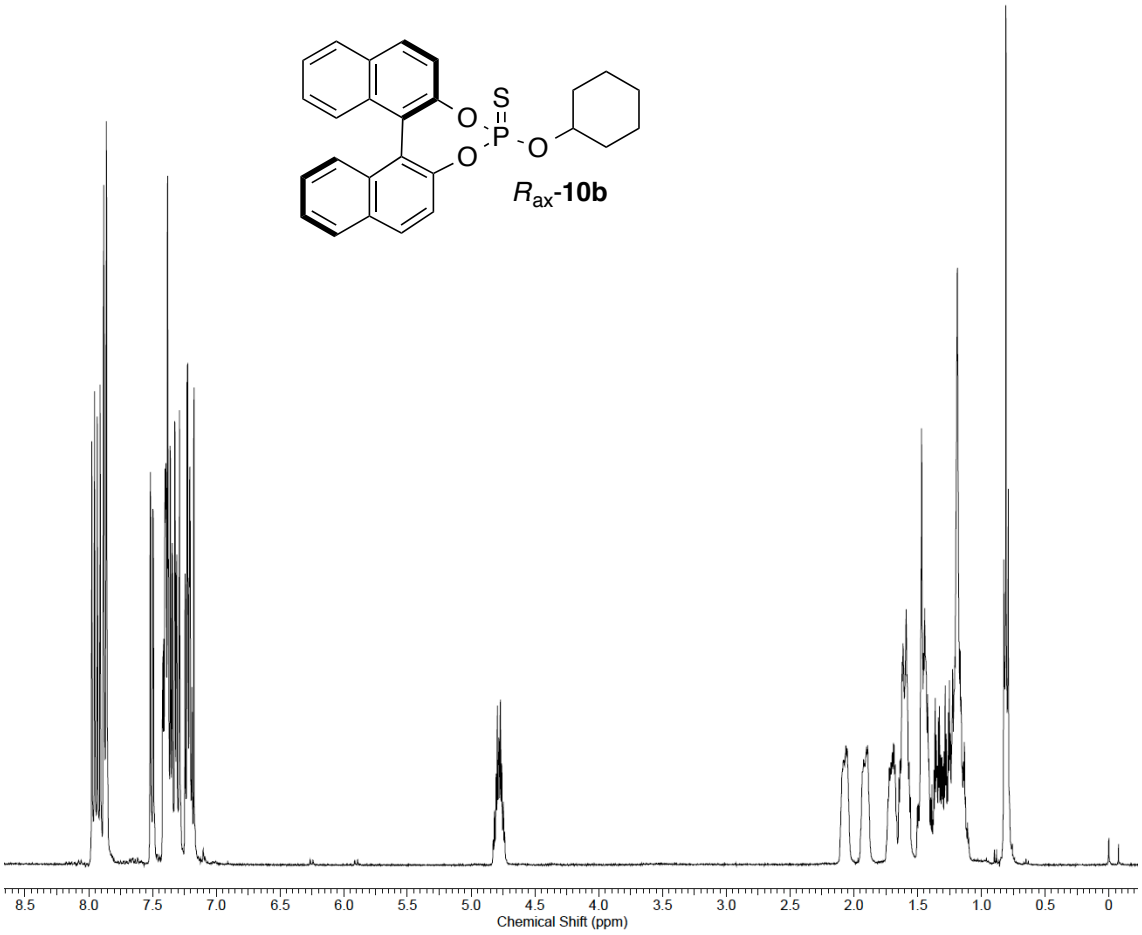

8
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

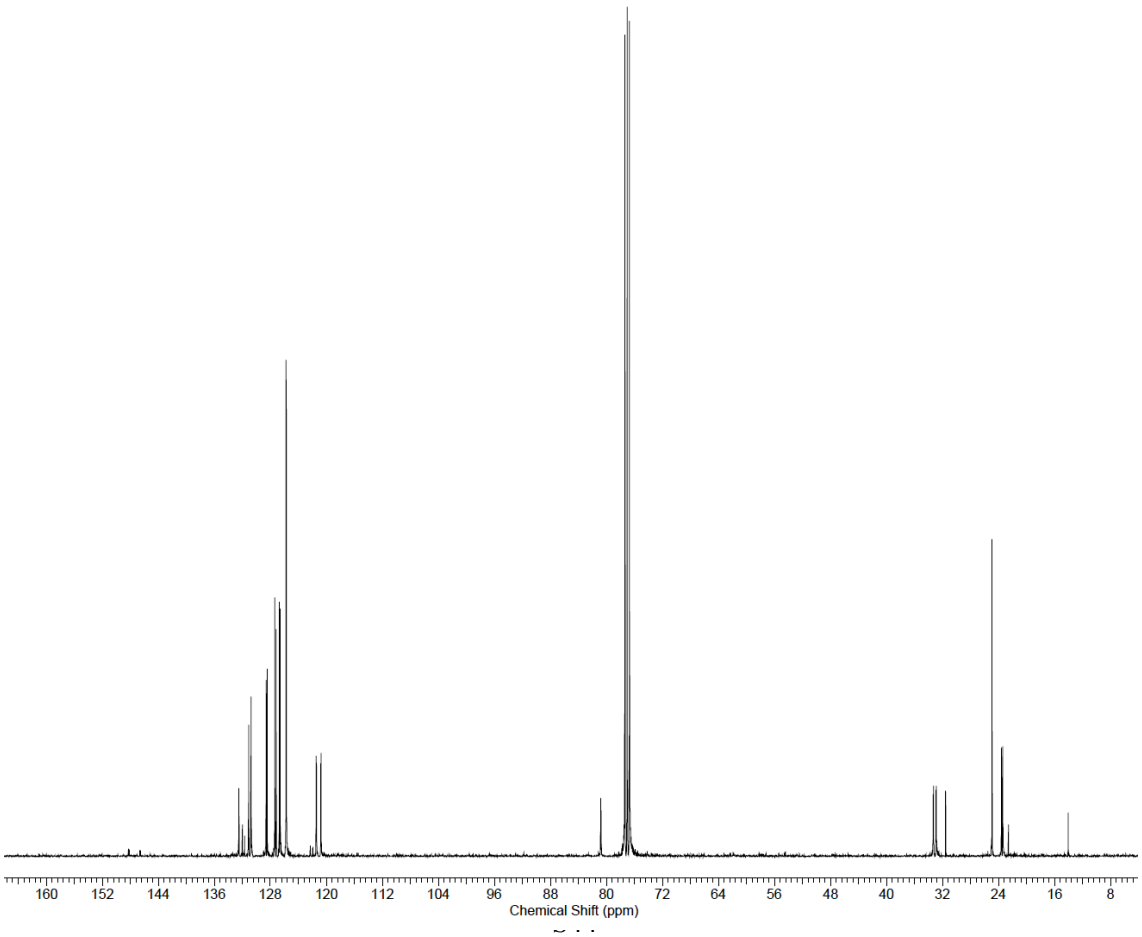
S_{ax}-**10a**

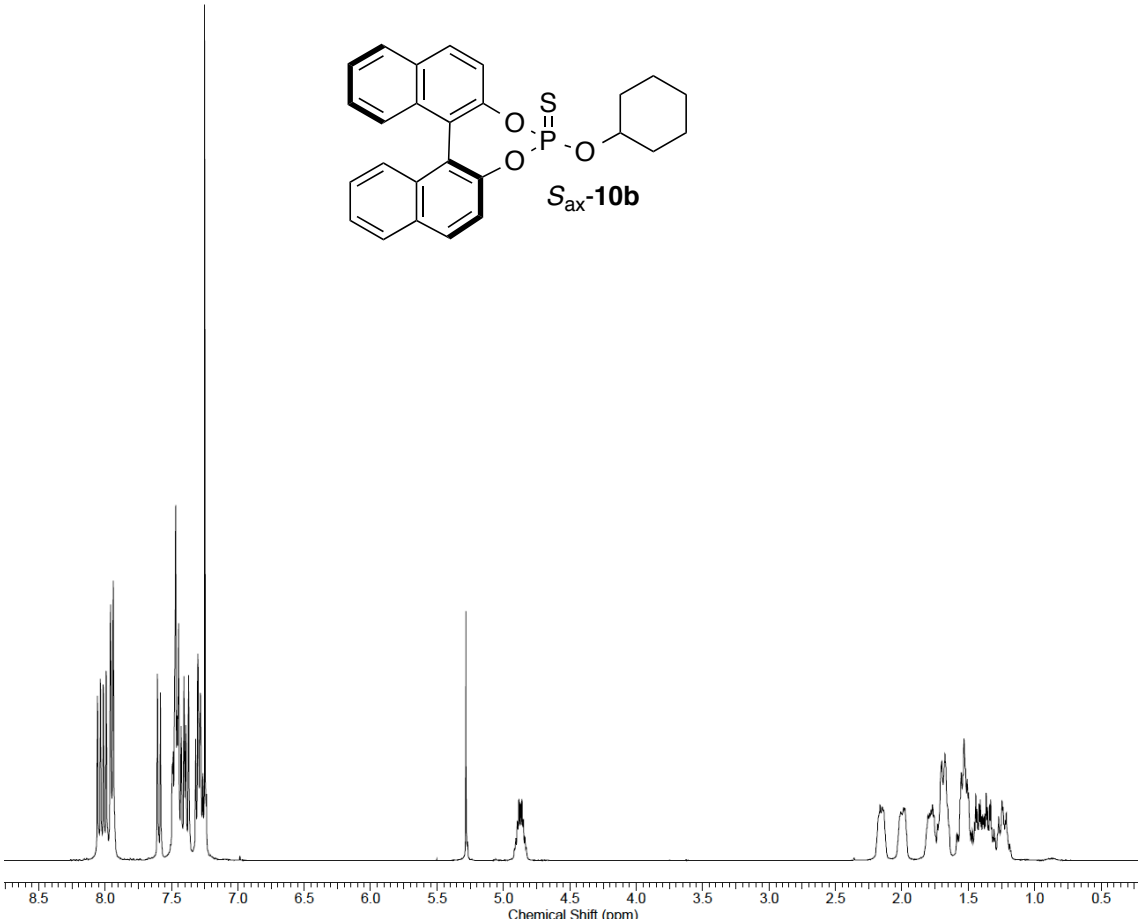
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

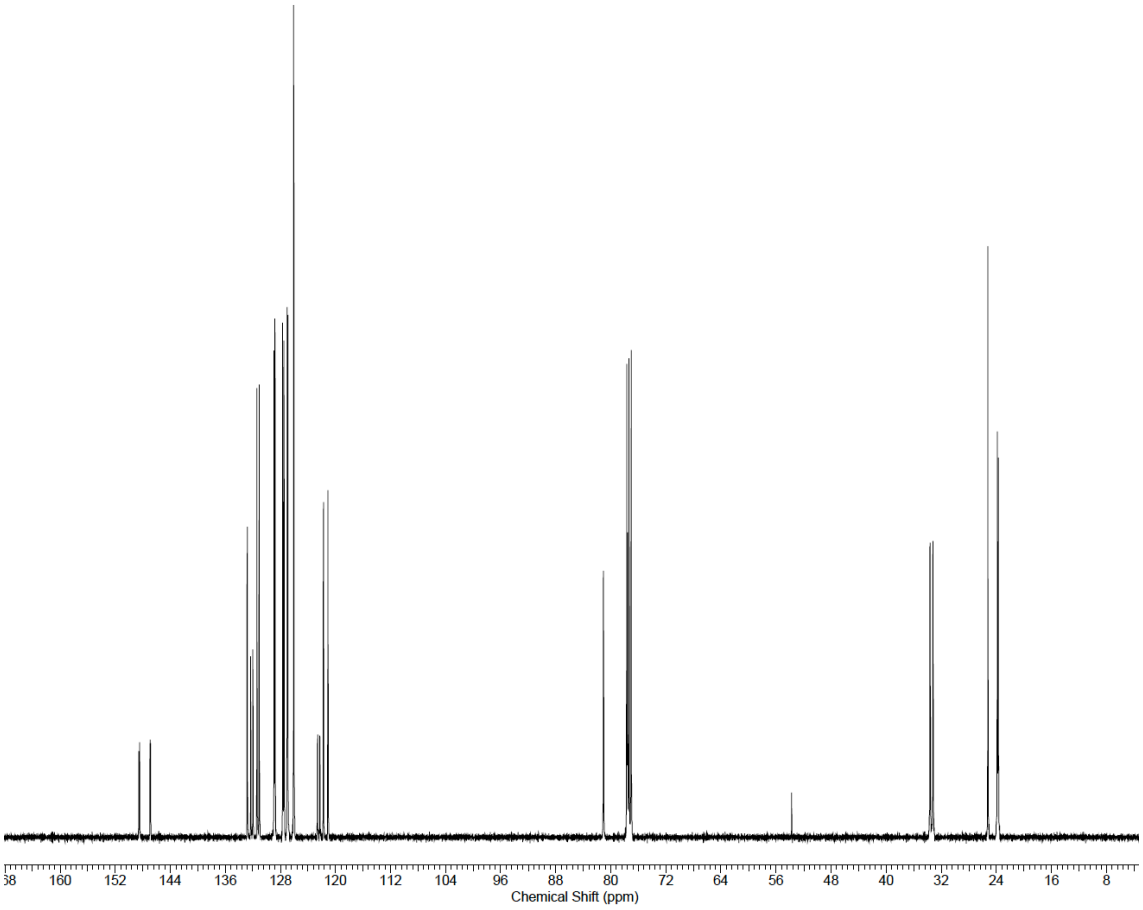

S
O
P
O
O
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

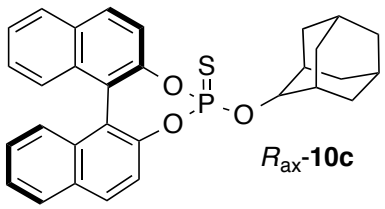
R_{ax}-**10b**


160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


S
O
P
O
O
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
Chemical Shift (ppm)

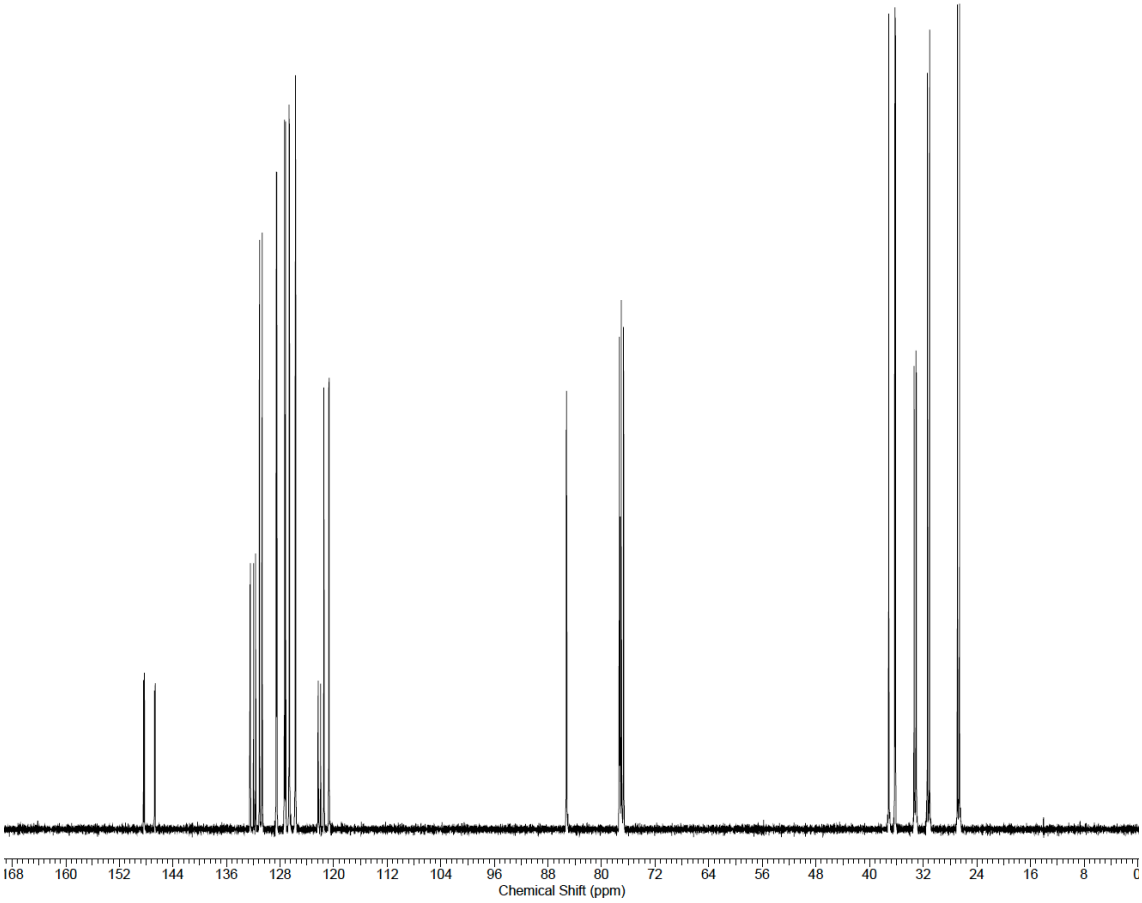
S_{ax}-**10b**

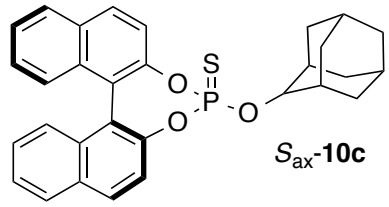

160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


S
O
P
O
O

R_{ax}-**10c**

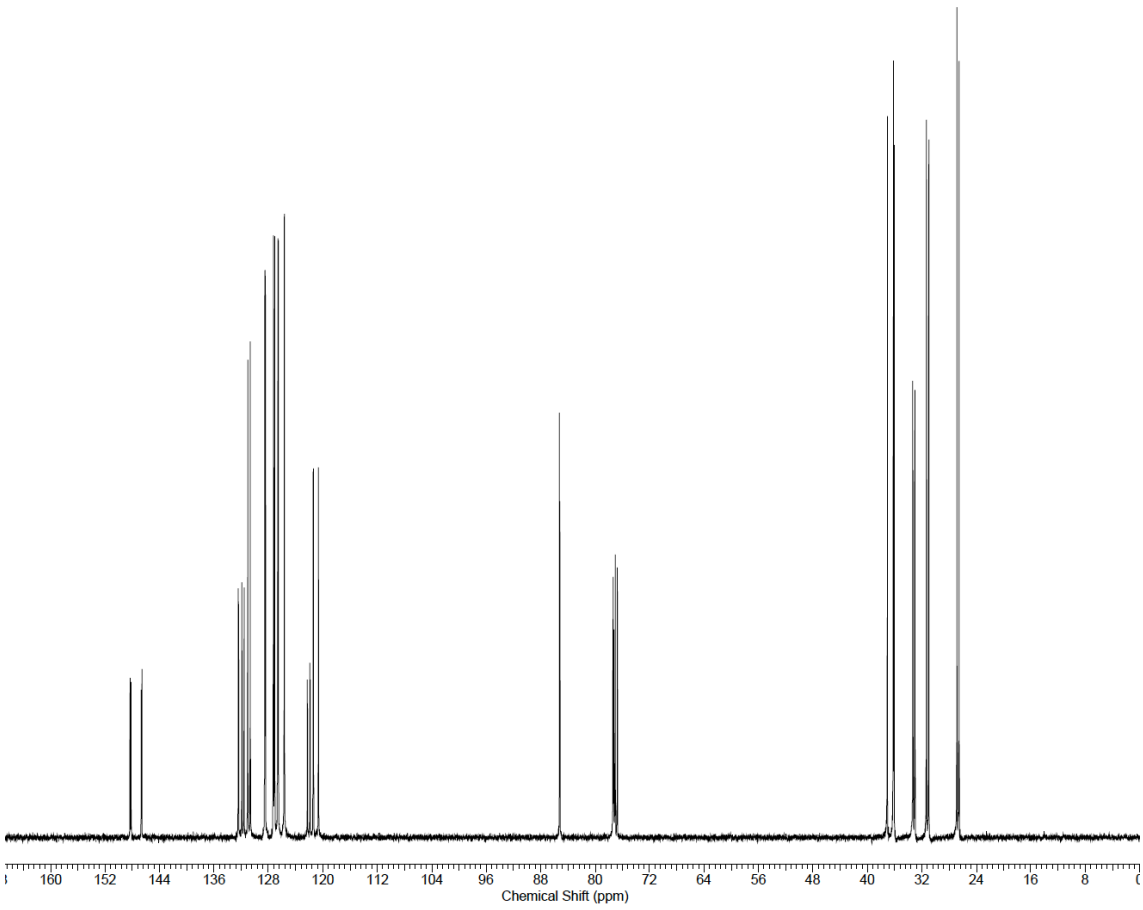
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

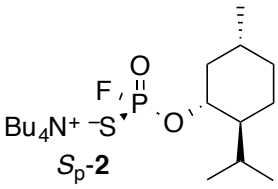

168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


S
O
P
O
O

S_{ax}-**10c**

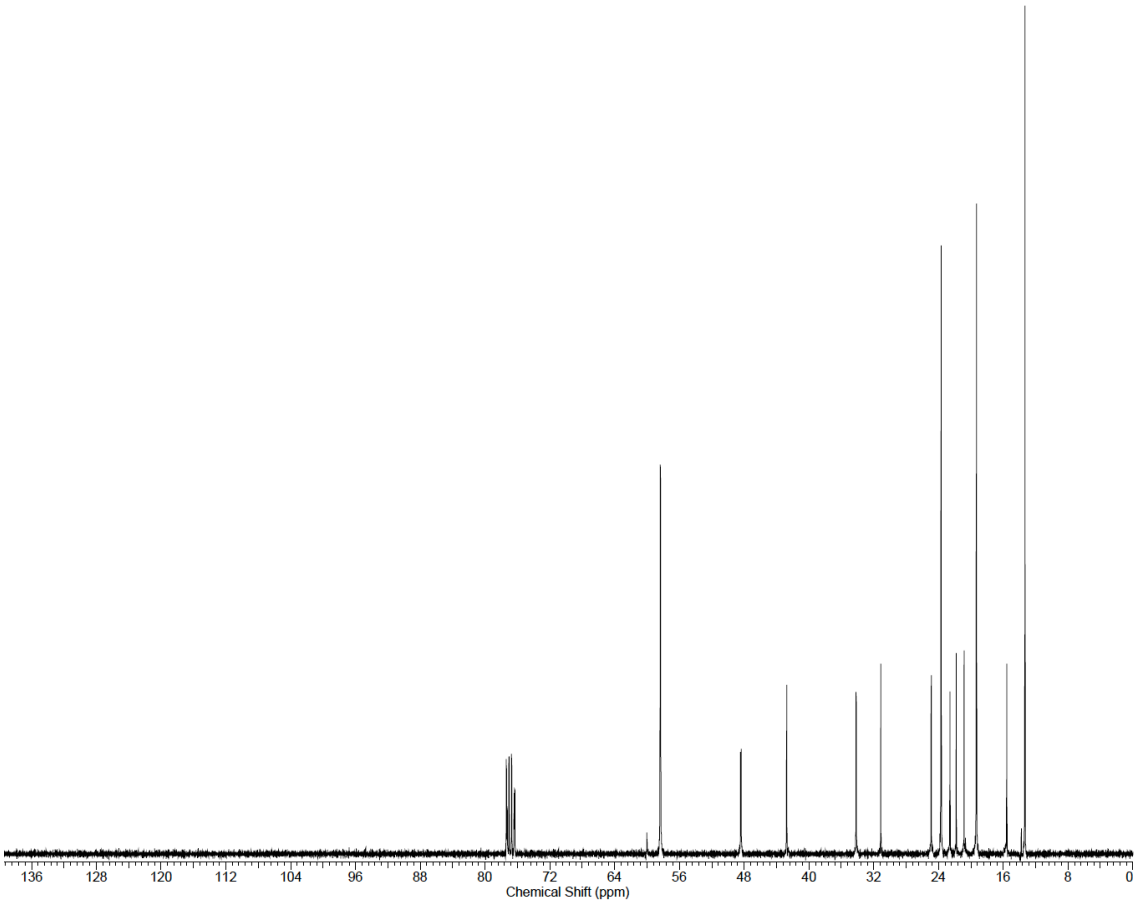
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

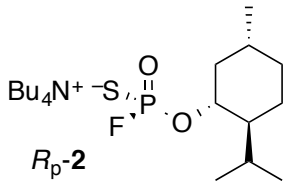

160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


O
F
P
S
O
Bu4N+ −

S_p-**2**

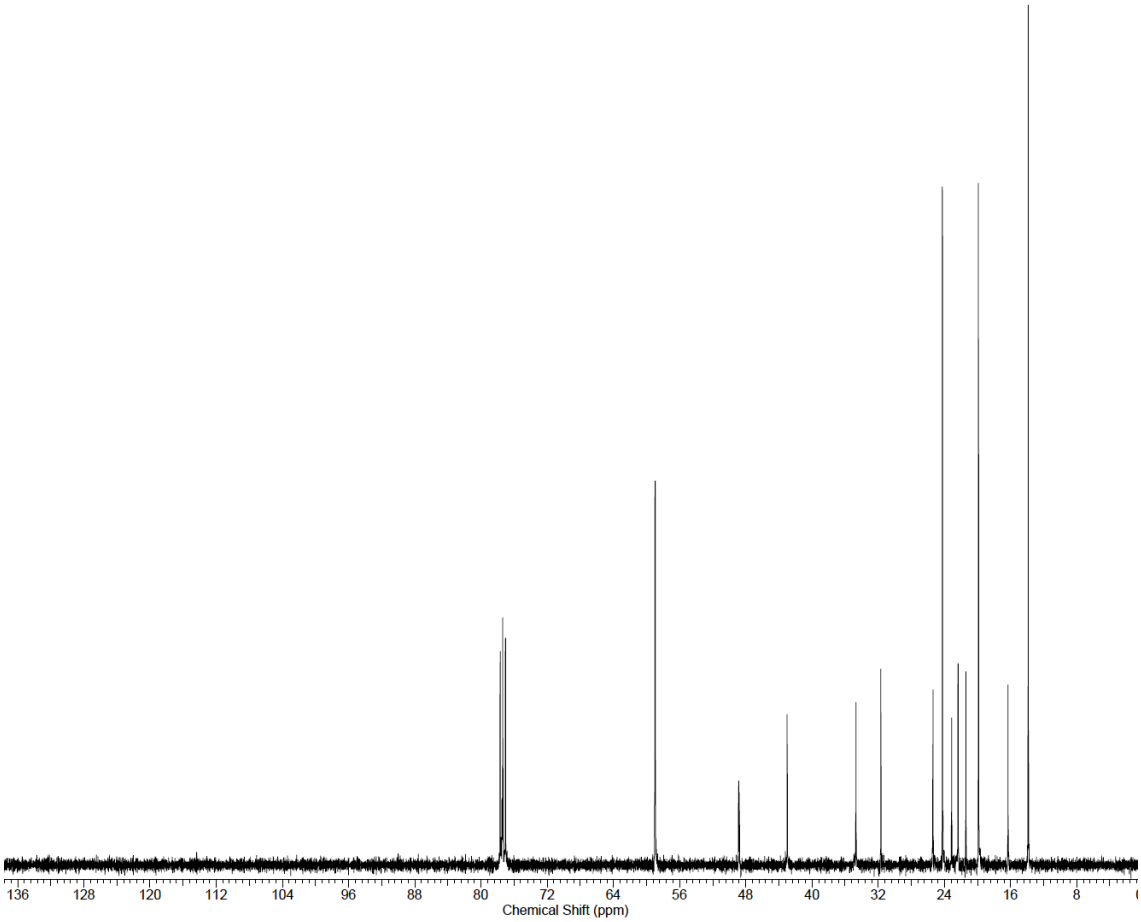
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

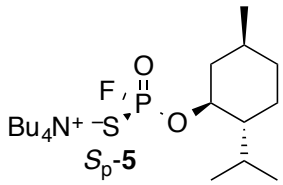

136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O

R_p-**2**

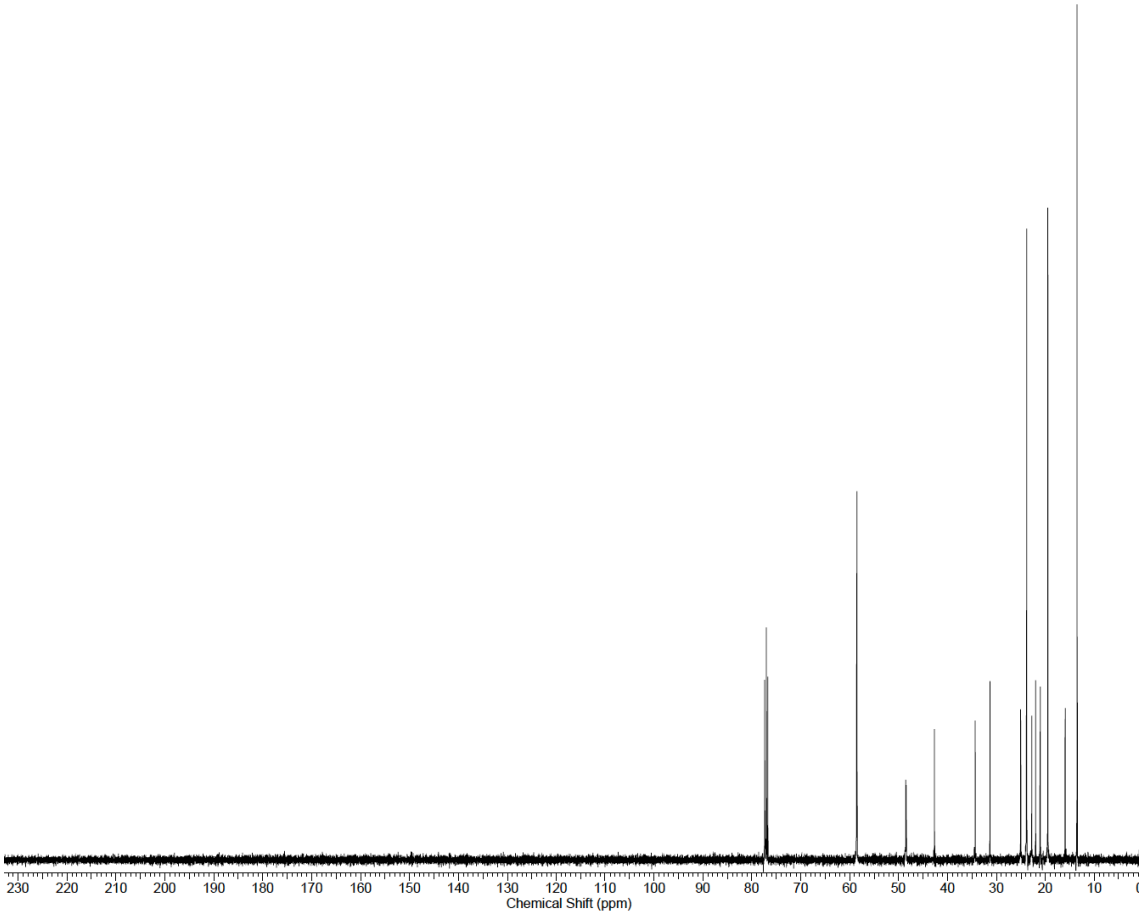
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

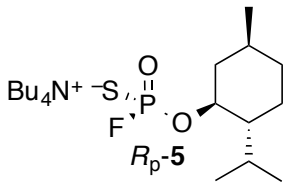

136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


O
F
P
Bu4N+ −S
O

S_p-**5**

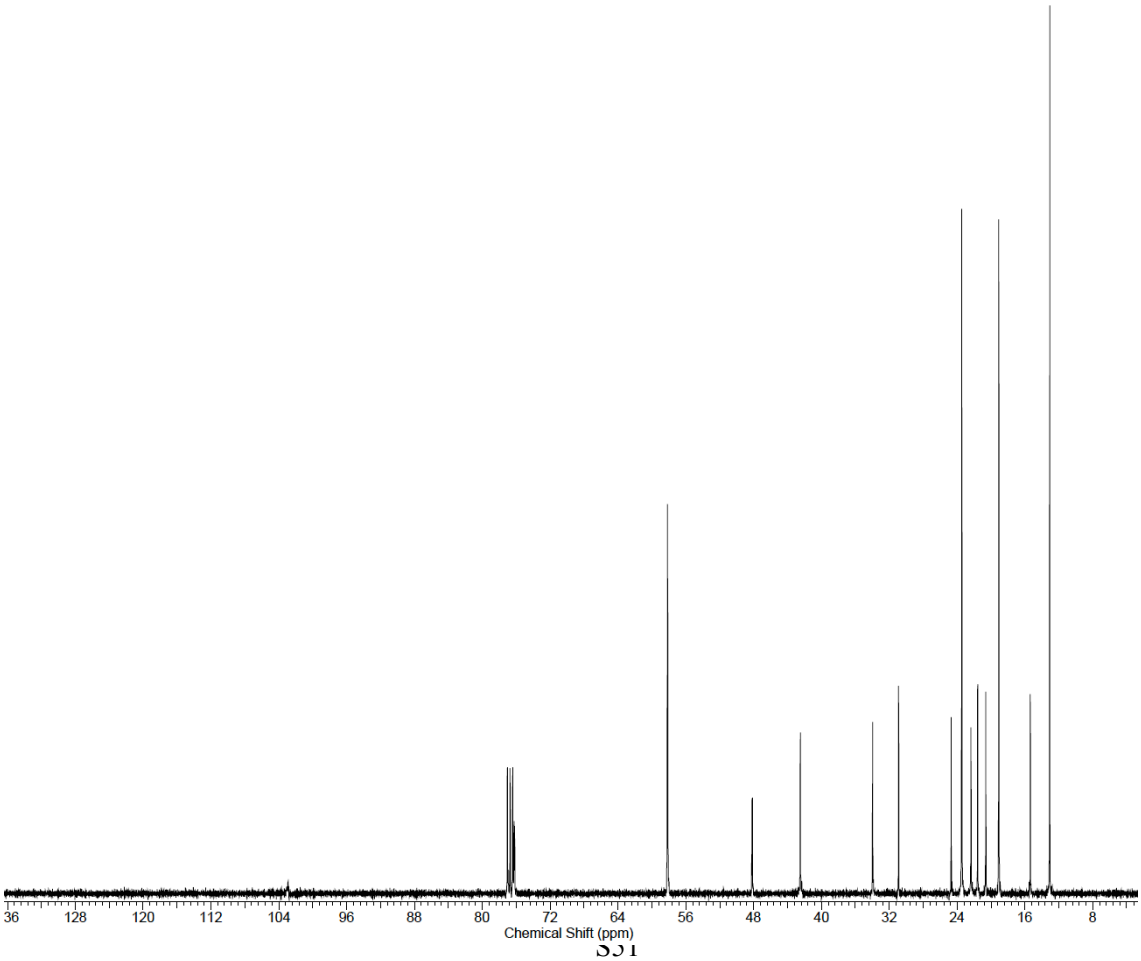
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

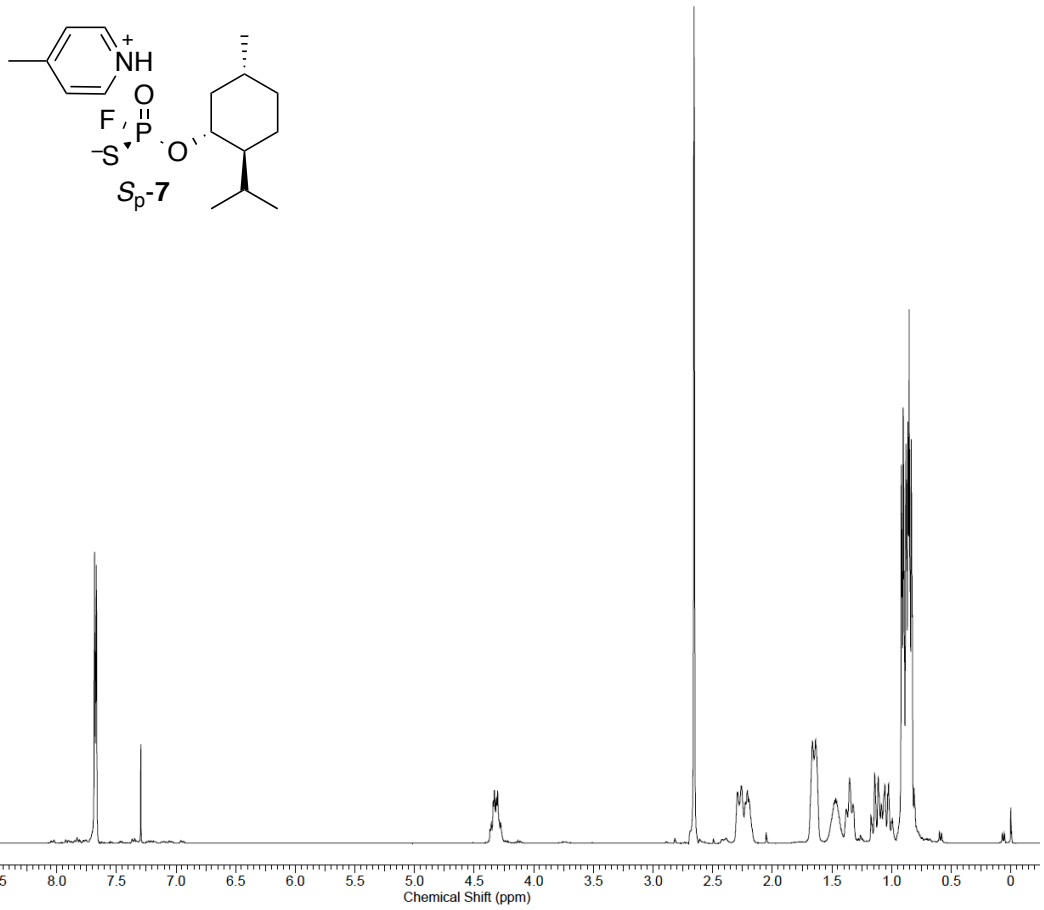

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical Shift (ppm)

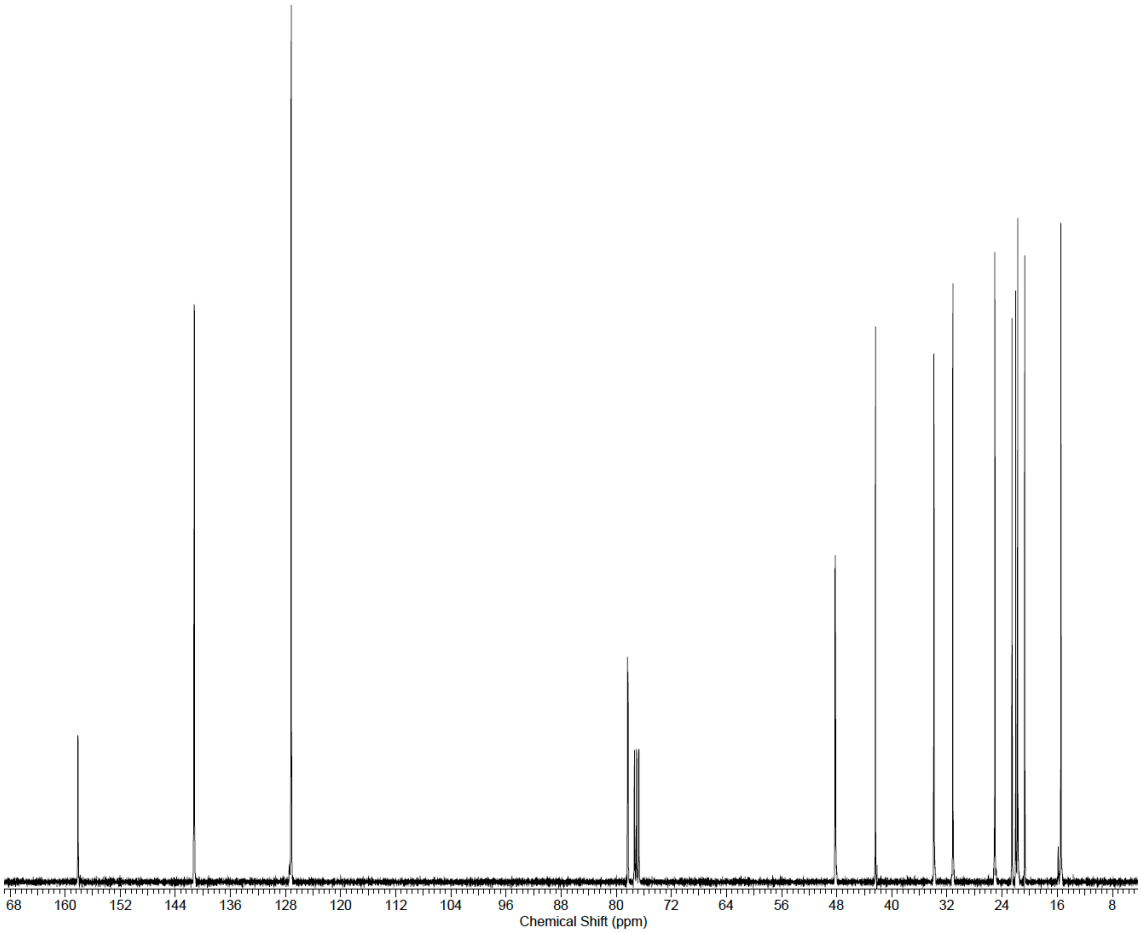

Bu4N+ −S
O
P
F
O

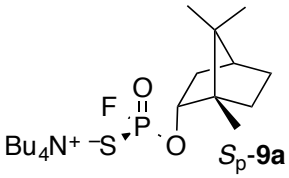
R_p-**5**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

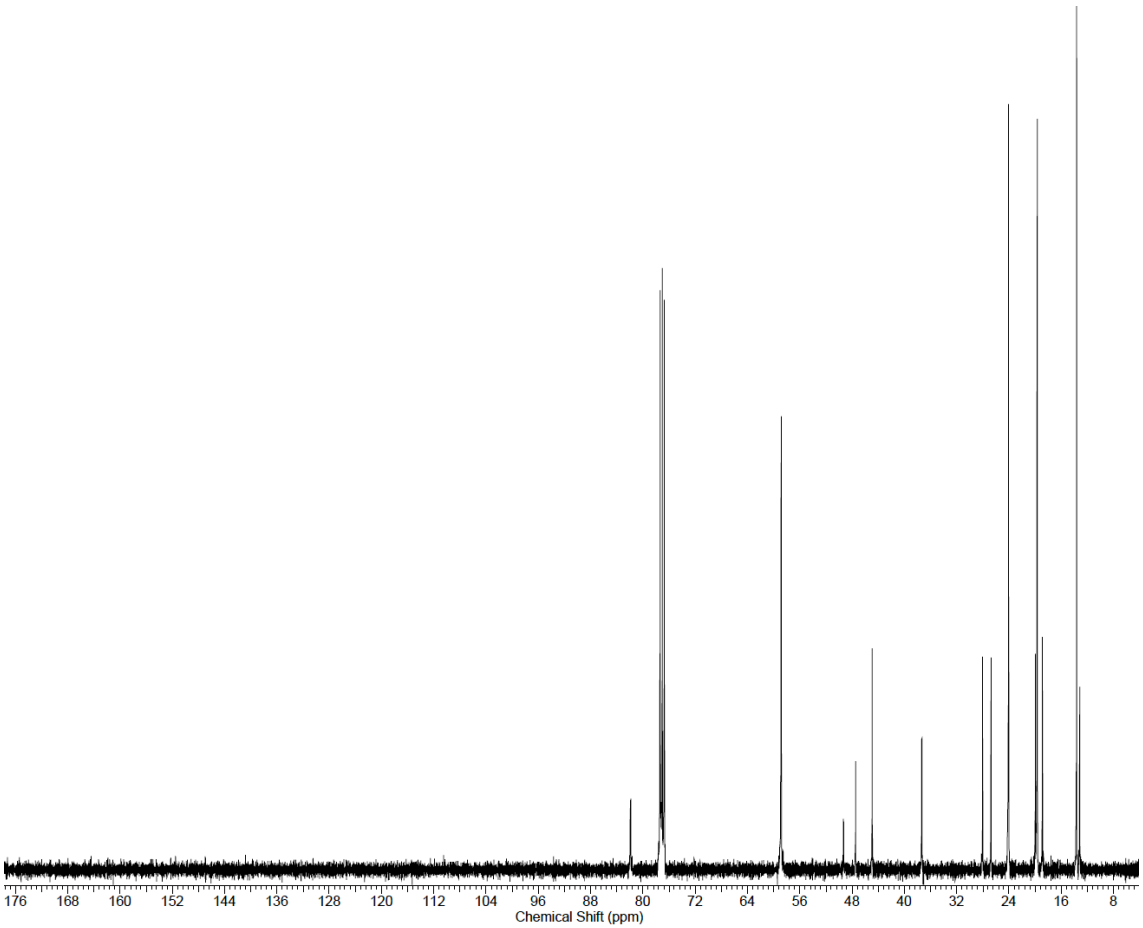

NH
O
F
P
S
O
S_p-7
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

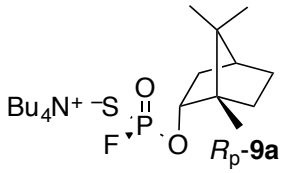

68 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


F
O
P
O
Bu_4N^+ ^-S

S_p-**9a**

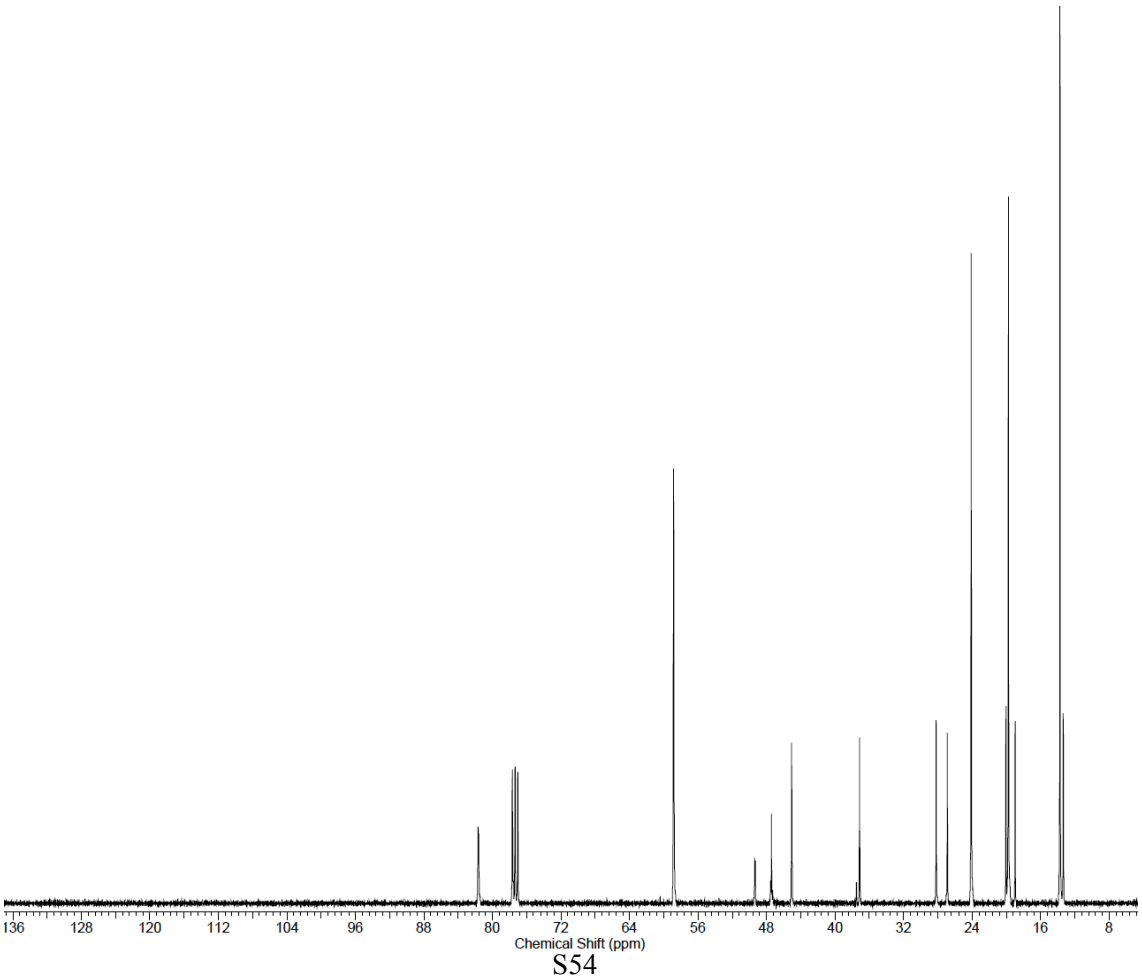
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

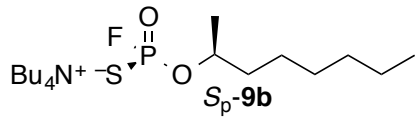

176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O

R_p-**9a**

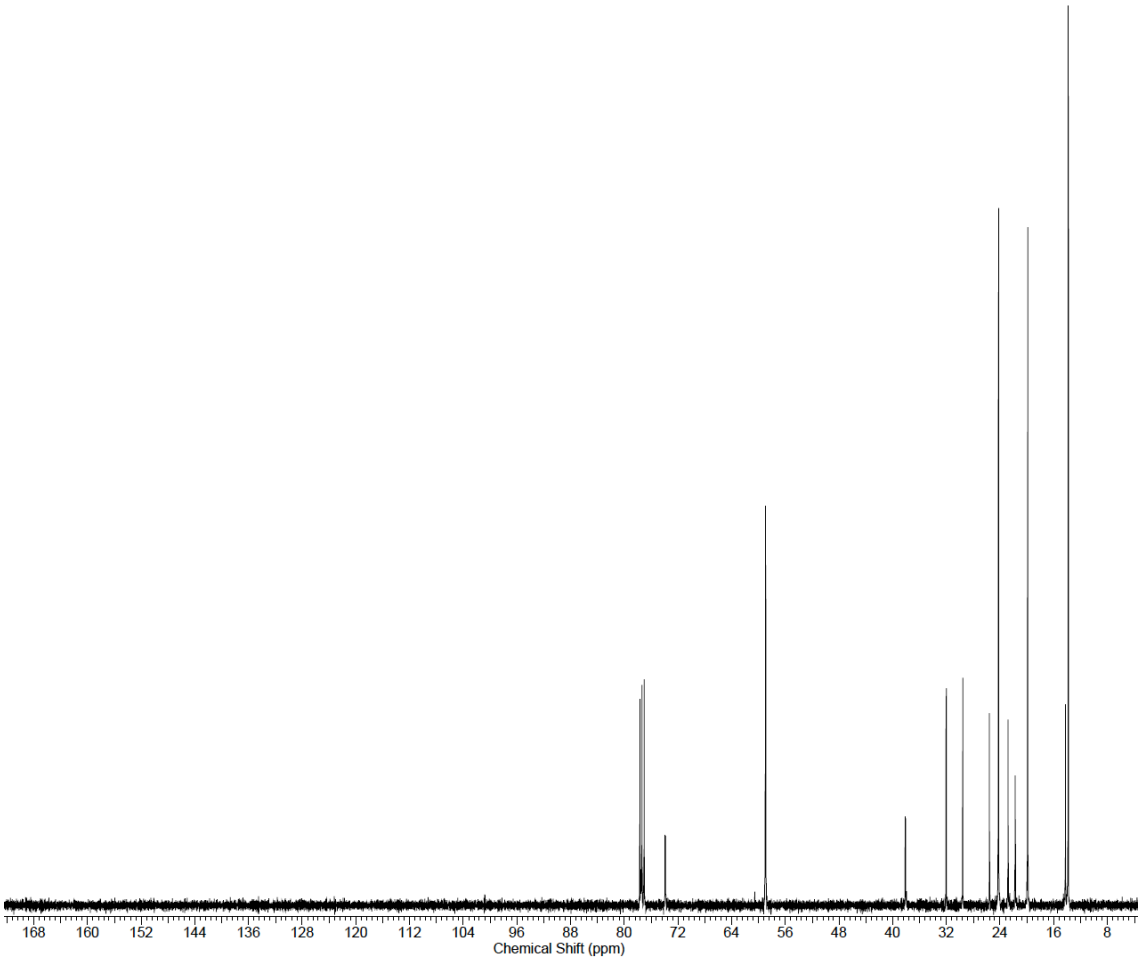
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

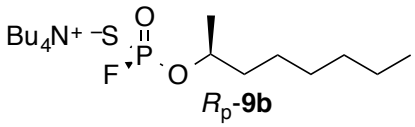

136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


F
O
P
S
O
Bu4N+ −

S_p-**9b**

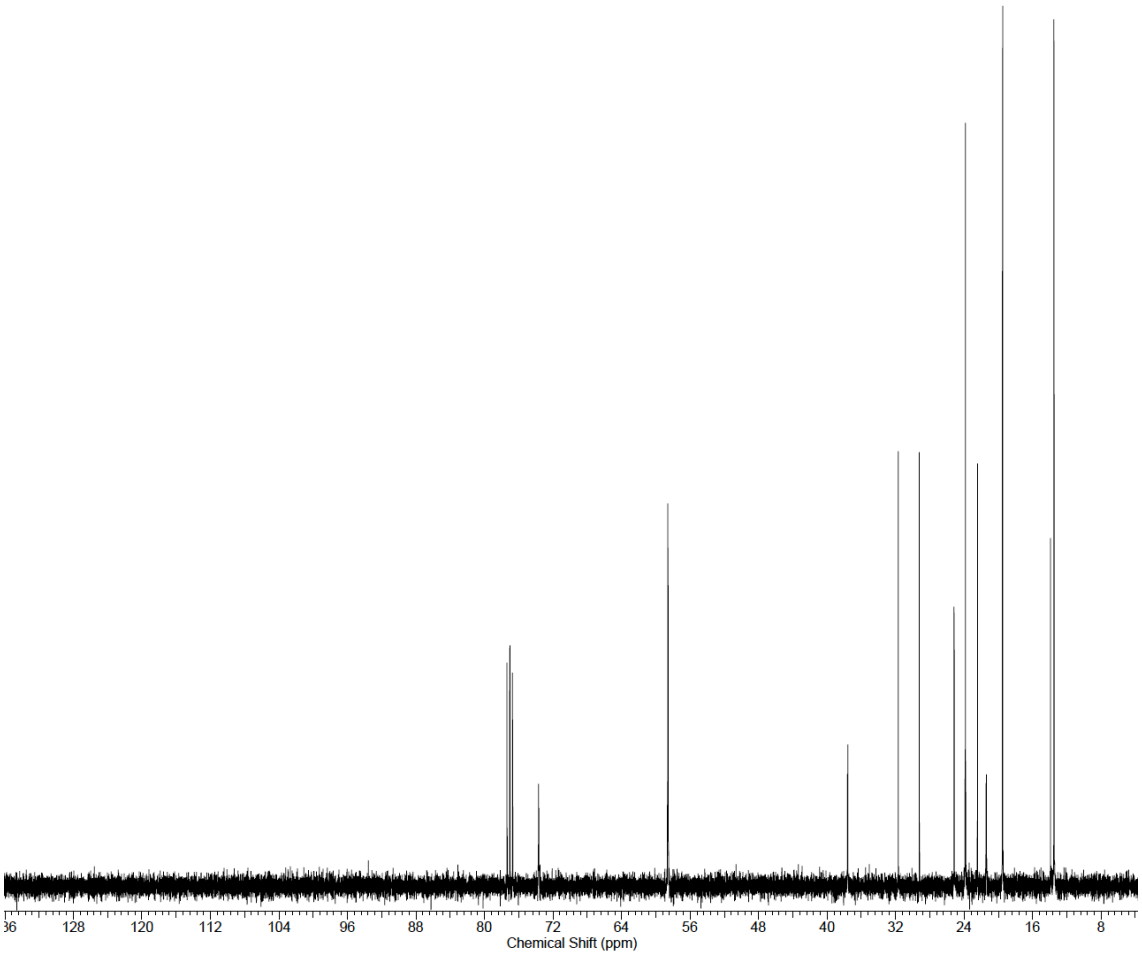
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

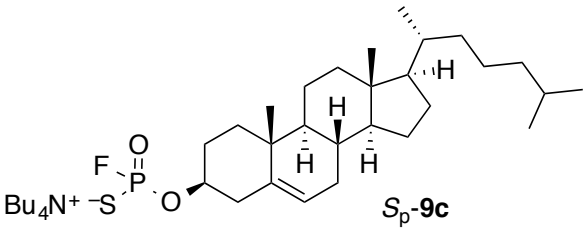

168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O

R_p-**9b**

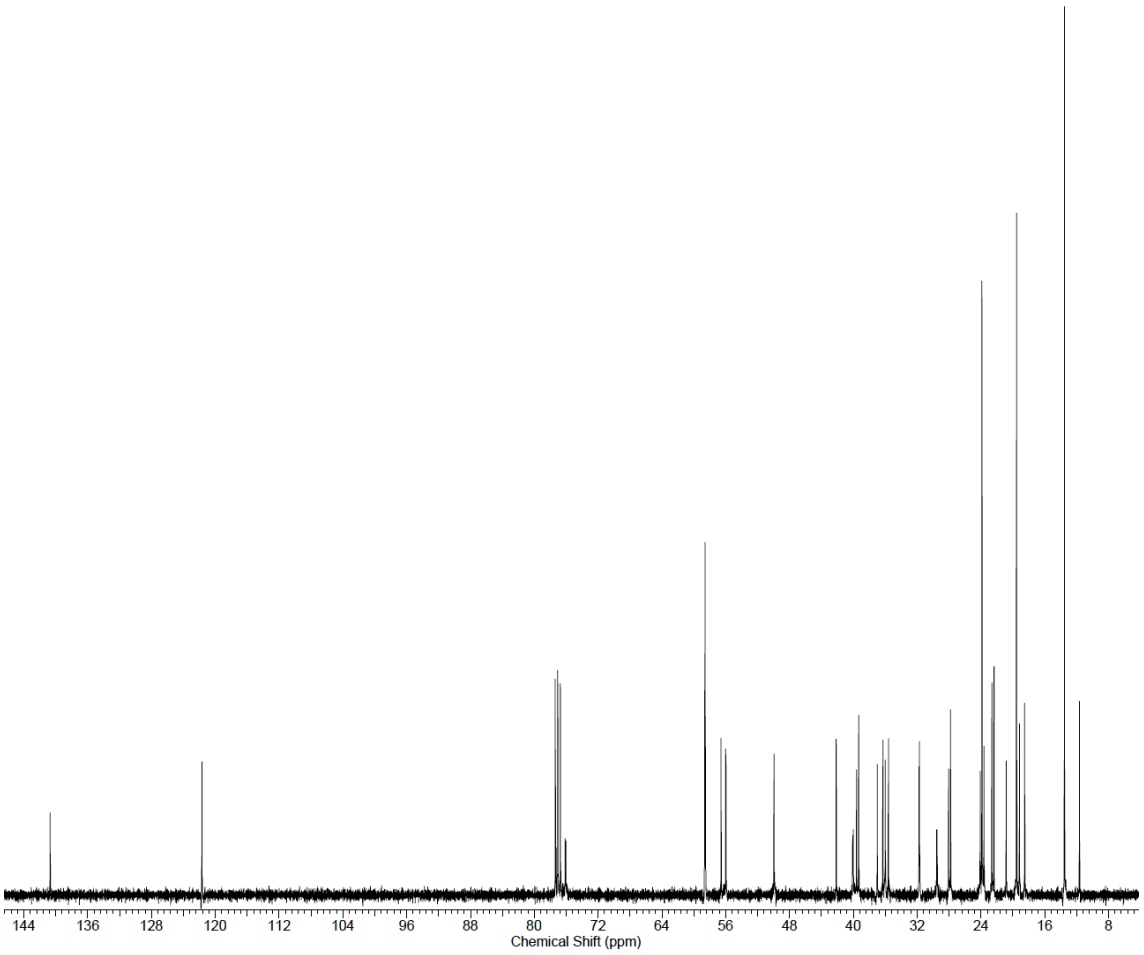
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

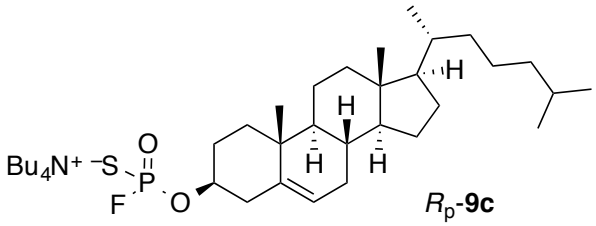

136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


F
O
P
O
Bu4N+ −S
H
H
H
H

S_p-**9c**

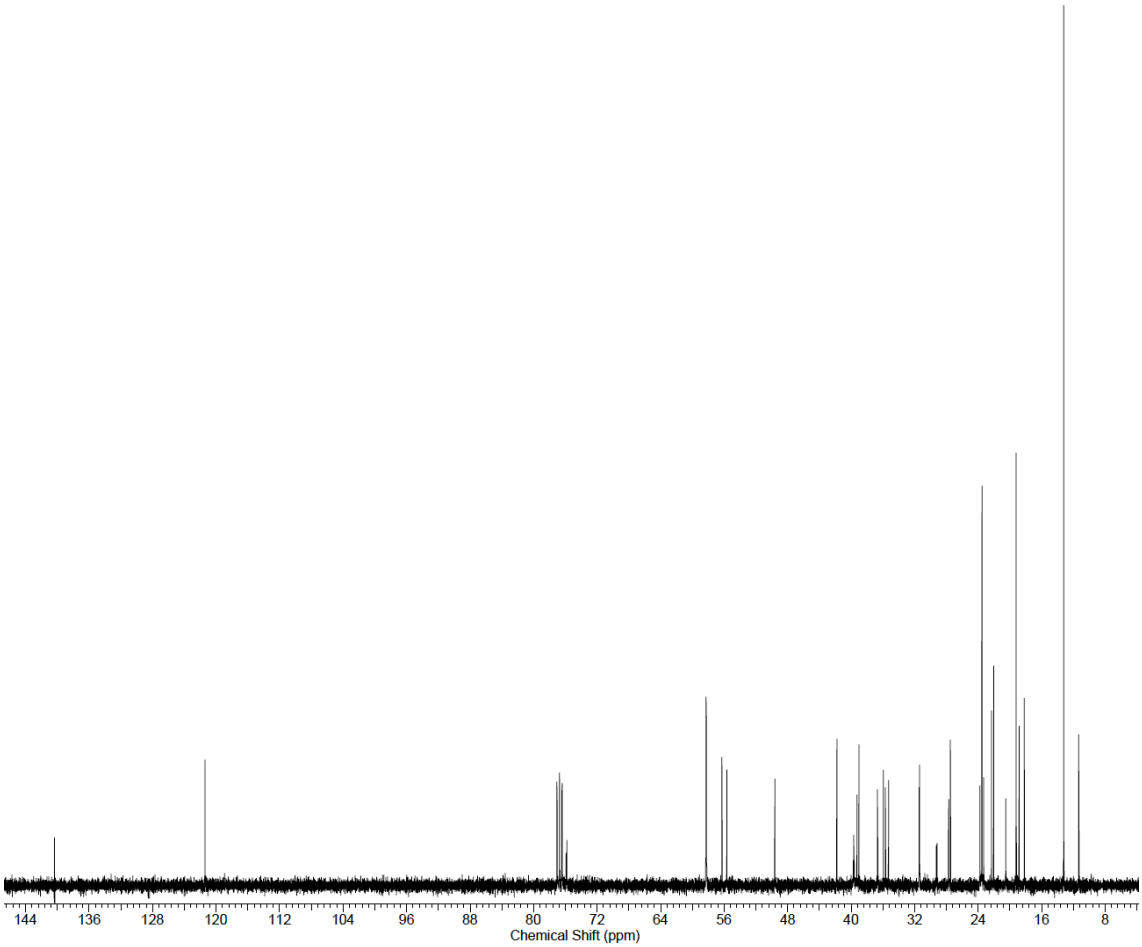
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

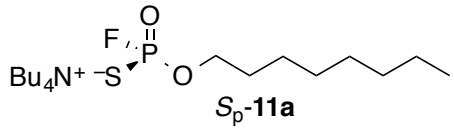

144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O
H
H
H
H

R_p-**9c**

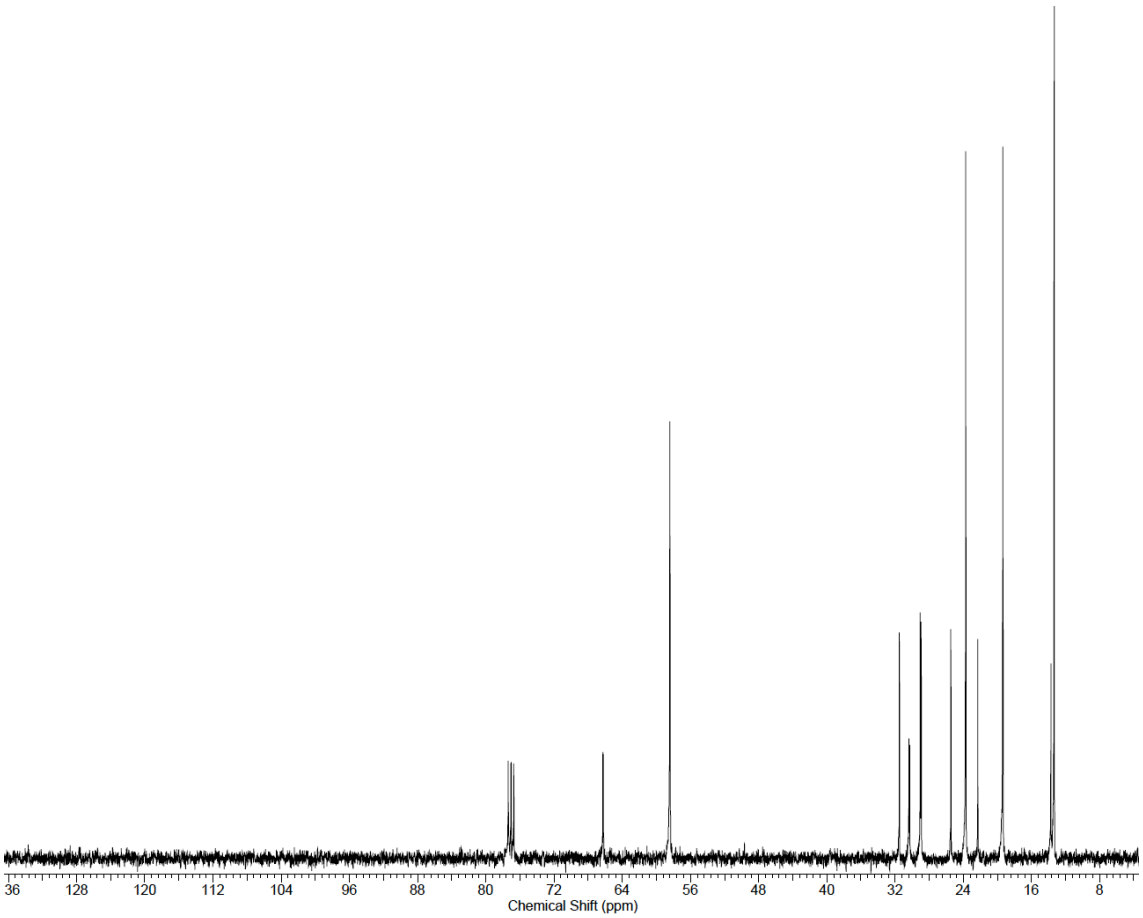
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

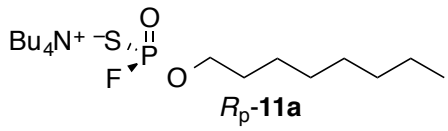

144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


O
F
P
Bu4N+ −S
O

S_p-**11a**

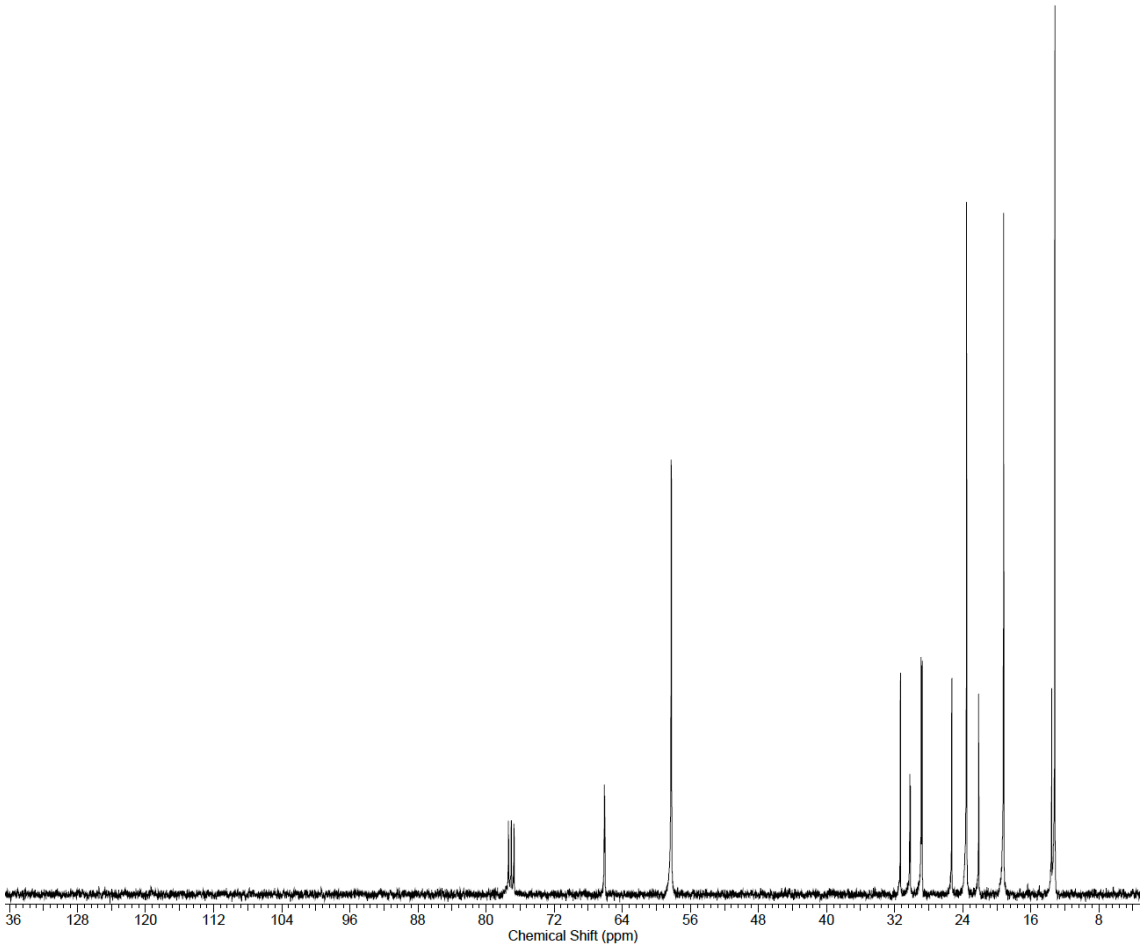
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

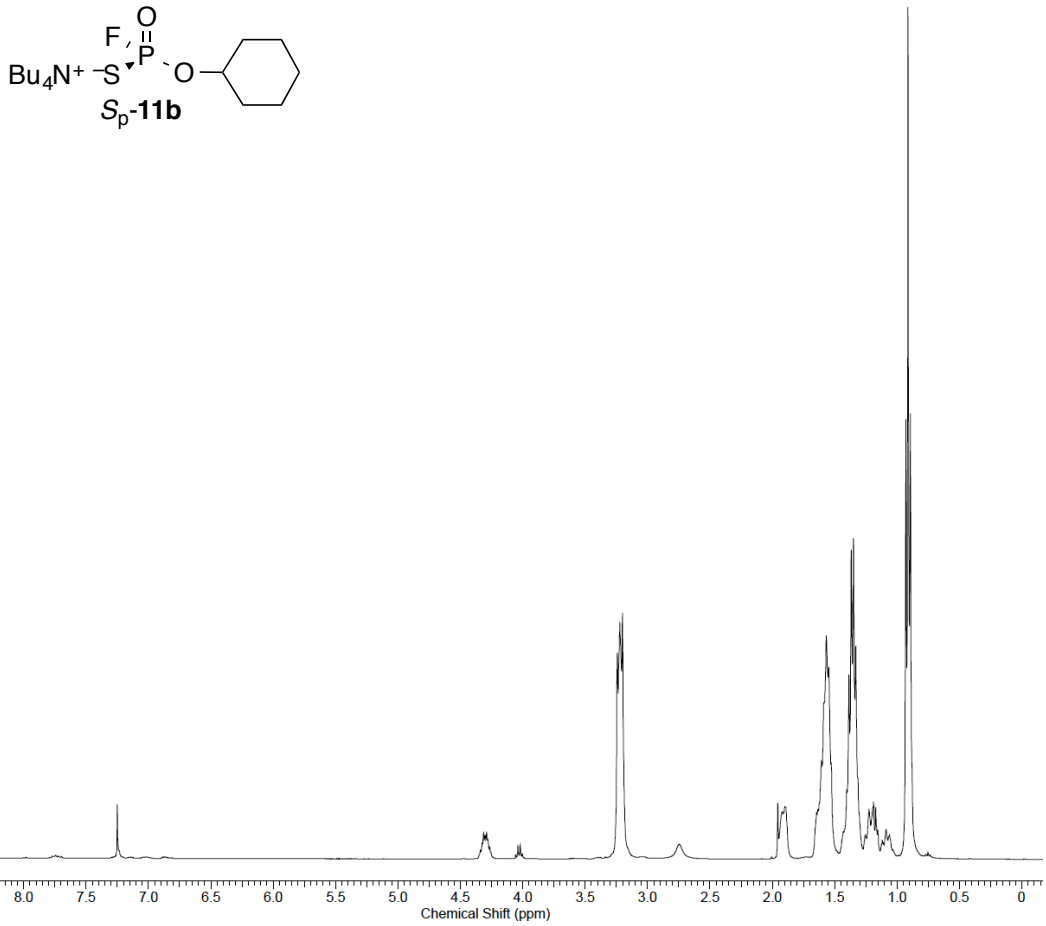

136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

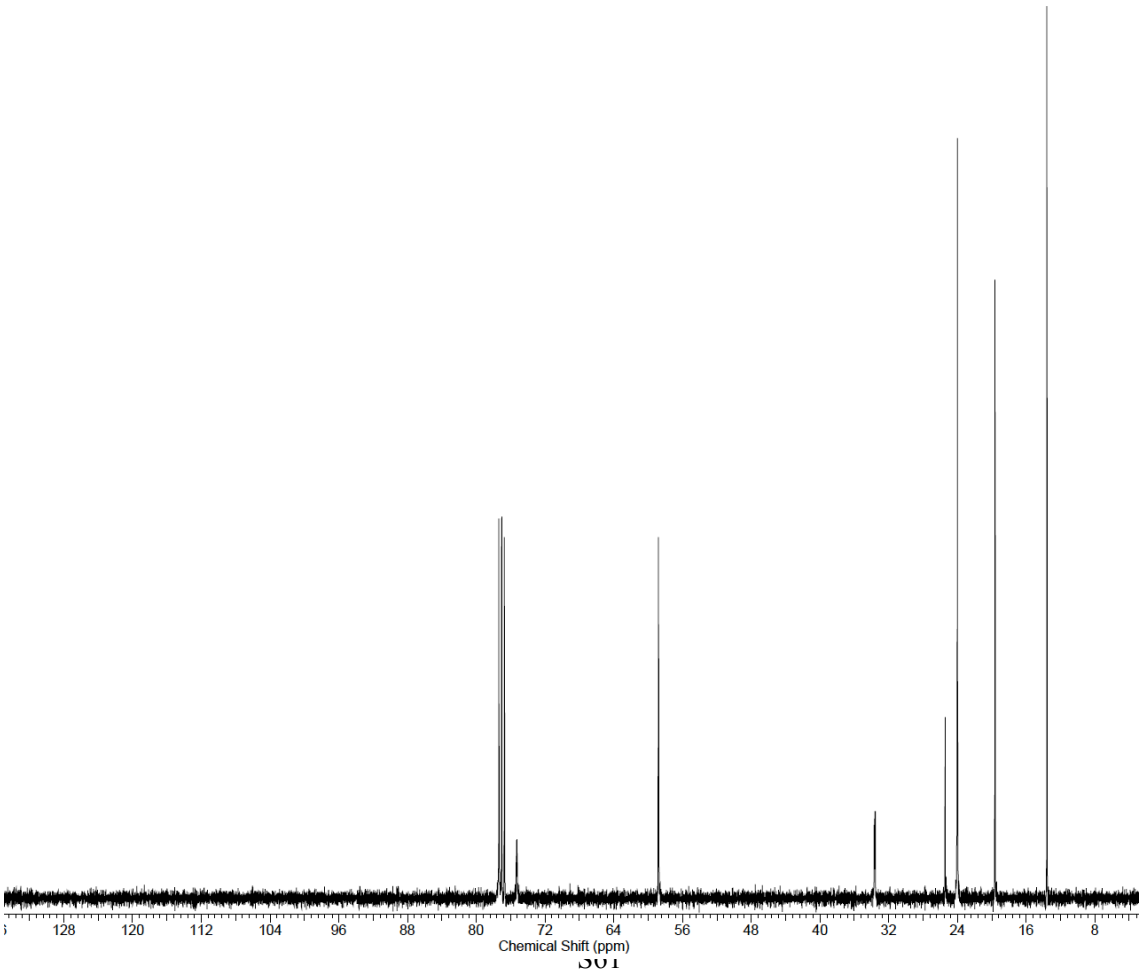

Bu4N+ −S
O
P
F
O

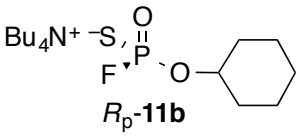
R_p-**11a**

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


36
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)

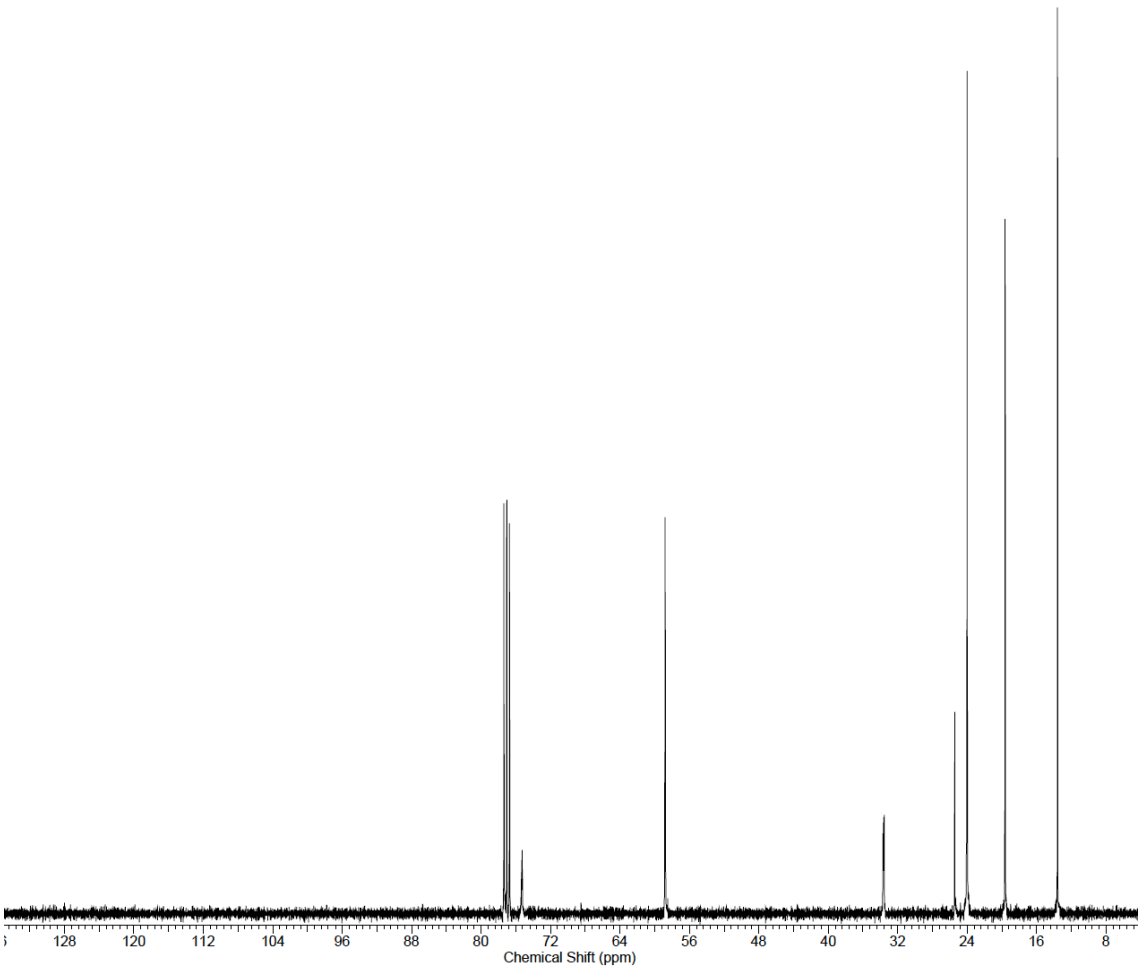

Bu4N+
F
O
P
S
O
Sp-11b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

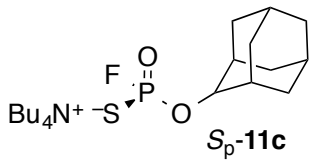

128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O

R_p-**11b**

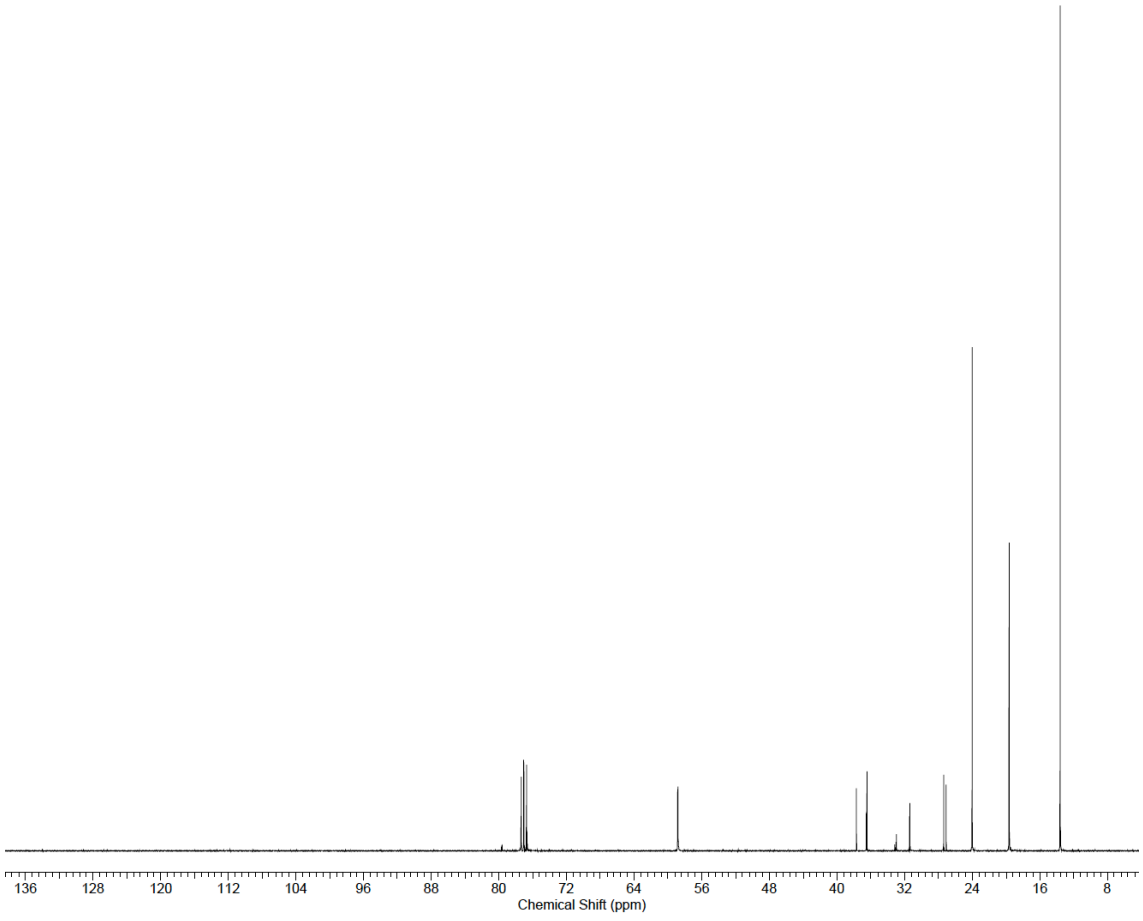
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

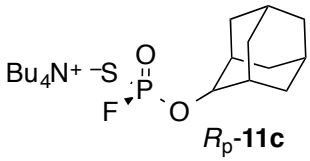

128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


F
O
P
Bu4N+ −S
O

S_p-**11c**

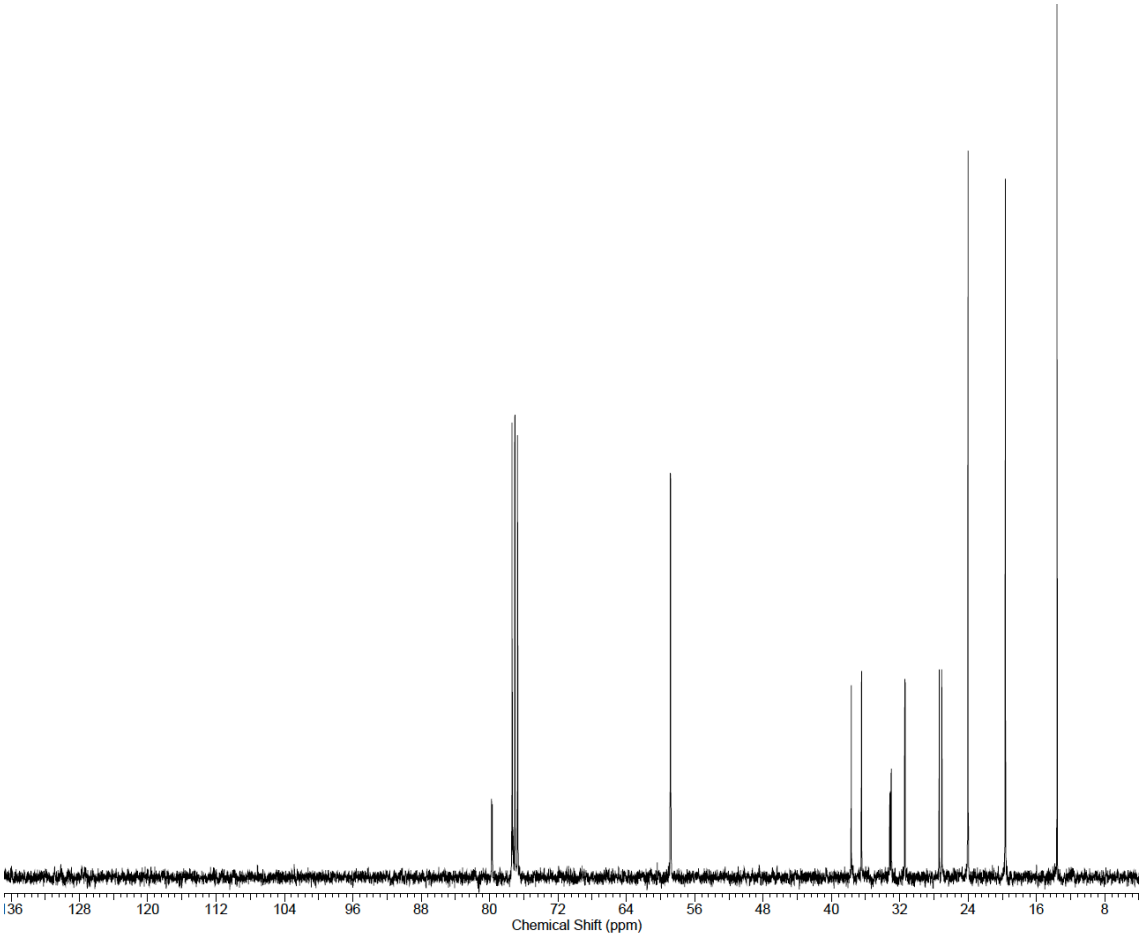
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
Chemical Shift (ppm)


Bu4N+ −S
O
P
F
O

R_p-**11c**

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)