

# Synthesis of new bicyclic *P-N* ligands and their application in asymmetric *Pd*-catalyzed $\pi$ -allyl alkylation and Heck reactions

Scott R. Gilbertson,\* Daniel G. Genov, and Arnold L. Rheingold

*Department of Chemistry, Washington University, St. Louis, Missouri 63130*

*Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716*

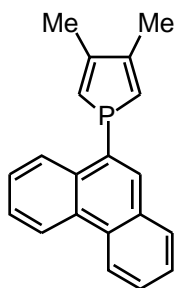
*srg@wuchem.wustl.edu*

**General information.**  $^1\text{H}$  NMR spectra were recorded on Varian Mercury 300 and Varian Unity 300 spectrometers. The spectra are of  $\text{CHCl}_3$  solutions, unless indicated otherwise. The chemical shifts are referenced to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity, coupling constants, integration.  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 300 (75 MHz) spectrometer with complete proton decoupling. The chemical shifts are referenced to tetramethylsilane.  $^{31}\text{P}$  NMR spectra were recorded on a Varian Mercury 300 (125MHz) spectrometer and the chemical shifts are referenced to 85%  $\text{H}_3\text{PO}_4$ . IR spectra of films of chloroform solutions of the compounds were recorded on a Perkin Elmer Spectrum BX spectrometer. TLC was performed on Whatman 250 $\mu\text{m}$  silica gel plates. Column chromatography was performed on ICN silica gel 60. All reactions were carried out under a  $\text{N}_2$  atmosphere. Dichloromethane, toluene and xylene were distilled from  $\text{CaH}_2$  under  $\text{N}_2$ , THF was

distilled from Na/benzophenone ketyl, C<sub>6</sub>H<sub>6</sub> was dried over Na, anhydrous DMF was purchased from Aldrich and used without further purification. Melting points are uncorrected.

**1-Phenyl-3,4-dimethylphosphole** was synthesized as previously described.

**1-(9-Phenanthryl)-3,4-dimethylphosphole.**

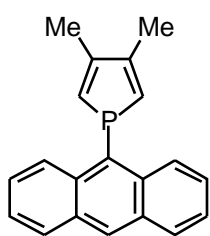


In a 500 mL three-necked flask, equipped with N<sub>2</sub> inlet and magnetic stirring bar, 1-phenyl-3,4-dimethylphosphole (6.58 g, 3.5 mmol) was dissolved in 60 mL dry THF. Li metal (0.97g, 1.4 mmol) was added at 0 °C and the solution was stirred under N<sub>2</sub> for 12h (overnight). The excess Li was removed, the brown mixture was cooled to -60 °C and AlCl<sub>3</sub> (1.55g, 1.2 mmol) was added as one portion. The mixture was stirred at RT for 30 min and then Bu<sub>3</sub>SnCl (11.37g, 0.035 mmol) was added at 0 °C. At the end of the addition, the color of the solution turns from brown to yellow. After stirring at RT for 5 min, the solvent was distilled off. The magnetic stirrer was replaced by a mechanical one and 200 mL degassed hexane was added, followed by the addition of 10 mL aqueous Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> with vigorous stirring. The mixture was filtered into a 500 mL Schlenk flask via a filter line assembly and the solid residue was washed 3 times with degassed hexane. The hexane was distilled off in vacuum to give 1-tributyltin-3,4-dimethylphosphole as yellow oil (12.38g, 3.1 mmol; <sup>31</sup>P NMR, (C<sub>6</sub>D<sub>6</sub>) -61).

9-Iodophenanthrene (9.35g, 3.1 mmol) and CuI (0.47 g, .246 mmol, 8 mol %) were added to a 500 mL Schlenk flask, equipped with magnetic stirring bar, and dissolved in 100 mL degassed anhydrous DMF under N<sub>2</sub>. Pd<sub>2</sub>(dba)<sub>3</sub> (0.56 g, .06 mmol, 2 mol %) was added to the solution

followed by the addition of  $\text{Ph}_3\text{As}$  (1.50 g, .49 mmol, 16 mol %) with stirring. The flask was immersed in an oil bath and the stirring was continued at 60 °C for 10 min. 1-Tributyltin-3,4-dimethylphosphole was dissolved in 50 mL DMF and the solution was transferred via syringe to the flask in the oil bath. The mixture was stirred overnight at 60 °C.  $^{31}\text{P}$  NMR of the mixture indicated a complete conversion to the product. After cooling of the reaction mixture the solvent was evaporated in vacuum and the residue was suspended in 200 mL degassed hexane. The hexane solution was filtered via filter line and the residue was washed with hexane and ether. The solvents were evaporated and the crude product was purified by column chromatography under  $\text{N}_2$ , using hexane as eluent to give 1-phenanthryl-3,4-dimethylphosphole as white solid (2.6 g, 26 % from the starting phosphole).  $^1\text{H}$  NMR 8.70-7.53 (m, 9H, Ar), 6.72(d,  $J_{\text{PH}} = 37.6$  Hz, 2H), 2.19(d,  $J_{\text{PH}} = 3.6$  Hz);  $^{13}\text{C}$  NMR 148.56-122.36 (m, Ar, olefinic), 18.07 (d,  $J_{\text{PC}} = 4.0$  Hz);  $^{31}\text{P}$  NMR -4.04; IR  $\text{cm}^{-1}$  3055, 3011, 2966, 2937, 2907, 2848, 1609, 1572, 1487, 1447, 1369, 1336, 1240, 1214, 1141, 1078, 1041, 986, 952, 890, 820, 750, 724; LRFAB m/z (%) 289 ( $\text{MH}^+$ , 27), HRFAB calcd for  $\text{C}_{20}\text{H}_{18}\text{P}$  m/e 289.1146, measured m/e 289.1150; TLC  $R_f$  (hexane) = 0.16.

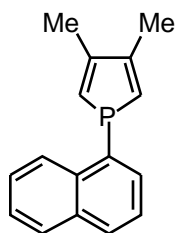
### 1-(9-Anthracyl)-3,4-dimethylphosphole.



1-Tributyltin-3,4-dimethylphosphole (12.86g, 3.20 mmol), 9-iodoanthracene (9.75g, 3.20 mmol),  $\text{CuI}$  (0.425g, 0.223 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.511 g, 0.0558 mmol),  $\text{Ph}_3\text{As}$  (1.36g, 0.0446 mmol) in 120 mL DMF were reacted as above to give phosphole the product after column chromatography using hexane as eluent, as a yellow solid (3.00g, 30%).  $^1\text{H}$  NMR 8.46-7.28 (m, 9H), 6.81 (d,  $J_{\text{PH}} = 37,1$  Hz, 2H), 2.26 (d,  $J_{\text{PH}} = 4.7$  Hz, 6H);  $^{13}\text{C}$  NMR 145.88-124. (Ar), 19.99 (d,  $J_{\text{PC}} = 4.6$  Hz);  $^{31}\text{P}$  NMR

-23.46; IR  $\text{cm}^{-1}$  3048, 3018, 2974, 2915, 2856, 1620, 1517, 1439, 1380, 1340, 1306, 1214, 1070, 1015, 897, 835, 757, 694, 669; MS HREI calcd for  $\text{C}_{20}\text{H}_{17}\text{P}$   $m/z$  288.1068, measured  $m/z$  288.1072; TLC (hexane)  $R_f$  0.34.

### 1-(1-Naphthyl)-3,4-dimethylphosphole.

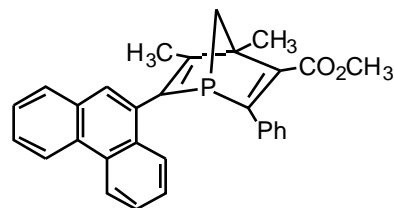
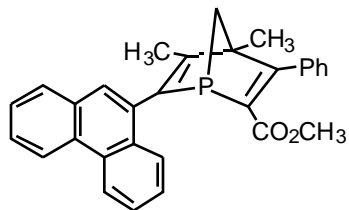


1-Tributyltin-3,4-dimethylphosphole (12.66g, 0.032 mmol), 1-iodonaphthalene (6.98g, 2.80 mmol), CuI (0.40g, 0.21 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.482g, 0.0526 mmol), tri-(2-furyl)phosphine (0.87g, 0.421 mmol) in 150 mL DMF were reacted as above to give after column chromatography using hexane as eluent the desired phosphol as an oil (2.05g, 26%).  $^1\text{H}$  NMR 8.36-7.26 (m, Ar, 7H), 6.63 (d,  $J_{\text{PH}} = 37.9$  Hz, 2H), 2.12 (d,  $J_{\text{PH}} = 3.6$  Hz, 6H);  $^{13}\text{C}$  NMR 148.32-125.37 (Ar.), 17.92 (d,  $J_{\text{PC}} = 3.7$  Hz);  $^{31}\text{P}$  NMR -6.69; IR  $\text{cm}^{-1}$  3055, 3004, 2974, 2907, 2848, 1587, 1565, 1502, 1443, 1380, 1340, 1255, 1211, 1141, 1074, 1019, 978, 860, 820, 794, 757, 665; MS LREI  $m/z$  (% intensity) 238 ( $\text{M}^+$ , 100), HREI calcd for  $\text{C}_{16}\text{H}_{15}\text{P}$   $m/z$  238.0911, measured  $m/z$  238.0906; TLC (hexane)  $R_f$  0.40.

4,5-Dimethyl-3,6-diphenyl-2-methoxycarbonyl-1-phospha-2,5-norbornadiene and 4,5-dimethyl-2,6-diphenyl-3-methoxycarbonyl-1-phospha-2,5-norbornadiene as well as the corresponding ethyl esters were synthesized and separated as previously described.

### 4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene and 4,5-dimethyl-3-methoxycarbonyl-6-phenanthryl-2-phenyl-1-phospha-2,5-norbornadiene.

In a 50 mL Schlenk tube 1-(9-Phenanthryl)-3,4-dimethylphosphole (2.45 g, 0.85 mmol) was dissolved in 15 mL freshly distilled xylene. Methyl 3-phenylpropiolate (1.39 g, 0.86 mmol) was added, the tube was sealed and the solution was heated in an oil bath at 145 °C with stirring for



20h. The products were separated by column chromatography under N<sub>2</sub>, using 10% ether in pentane to 15% ether in pentane as eluent to give the two regioisomers as white solids in more than two to one ratio (2.23 g 4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene and 0.93 g 4,5-dimethyl-3-methoxycarbonyl-6-phenanthryl-2-phenyl-1-

phospha-2,5-norbornadiene, 86% combined yield).

**4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene:**

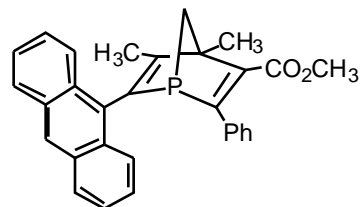
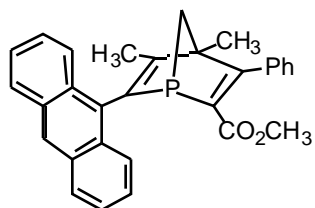
<sup>31</sup>P NMR -9.58, -10.48; <sup>1</sup>H NMR 8.75-7.11 (m, 14H), 3.63 (s, 3H), 2.38 (m, 2H), 1.88 (s, 3H), 1.39 (s, 3H); <sup>13</sup>C NMR 179.64 (s), 179.43 (s), 166.95 (d, *J*<sub>PC</sub> = 18.8 Hz), 159.14 (s), 144.41 (d, *J*<sub>PC</sub> = 32.5 Hz), 135.46 (d, *J*<sub>PC</sub> = 18.8 Hz), 137.32-125.51 (m, Ar), 72.72, 71.83 (2s), 67.83, 66.67 (2s), 51.62 (s), 20.19 (s), 15.92 (s); IR cm<sup>-1</sup> 3062, 3018, 2974, 2915, 1708, 1612, 1579, 1487, 1450, 1432, 1380, 1277, 1240, 1214, 1144, 1063, 1026, 1041, 997, 908, 890, 757, 698, 669; MS LRFAB *m/z* (rel. int. %) 455 (MLi<sup>+</sup>, 68); HRFAB calcd for C<sub>30</sub>H<sub>15</sub>O<sub>2</sub>PLi *m/e* 455.1752, measured *m/e* 455.1746; R<sub>f</sub> (15% ether in pentane) = 0.20.

**4,5-dimethyl-3-methoxycarbonyl-6-phenanthryl-2-phenyl-1-phospha-2,5-norbornadiene:**

<sup>31</sup>P NMR 2.73, 1.90; <sup>1</sup>H NMR 8.71-6.95 (m, 14H), 3.78 (s, 3H), 2.34-2.18 (m, 2H), 1.96 (s, 3H), 1.71 (s, 3H); <sup>13</sup>C NMR 168.88, 168.73 (2s), 161.48, 161.11 (2d, *J*<sub>PC</sub> = 27.4, 22.2 Hz), 151.11, 150.86 (2s), 147.88, 147.07 (3d, *J*<sub>PC</sub> = 29.03, 28.0 Hz), 136.62 (d, *J*<sub>PC</sub> = 17.6 Hz), 135.29 (d, *J*<sub>PC</sub> = 18.8 Hz), 131.54-122.32 (Ar), 70.76, 70.11 (2s), 64.75, 64.27 (2s), 51.78 (s), 18.85 (s),

15.45, 1516 (2s); IR  $\text{cm}^{-1}$  3055, 3025, 2966, 2915, 1712, 1590, 1491, 1450, 1432, 1380, 1292, 1244, 1207, 1067, 1037, 949, 890, 753, 724, 694, 669.

**6-Anthracyl-4,5-dimethyl-2-methoxycarbonyl-3-phenyl-1-phospha-2,5-norbornadiene and 6-anthracyl-4,5-dimethyl-2-phenyl-3-methoxycarbonyl-1-phospha-2,5-norbornadiene.**



1-Anthracyl-3,4-dimethylphosphole (3.00g, 1.00 mmol) and methyl 3-phenylpropiolate (1.67g, 1.00 mmol) were reacted as above to give 1.53g regioisomer 6-Anthracyl-4,5-dimethyl-2-methoxycarbonyl-3-phenyl-1-phospha-2,5-norbornadiene and 0.61g regioisomer 6-anthracyl-4,5-dimethyl-2-phenyl-3-methoxycarbonyl-1-phospha-2,5-norbornadiene (48% combined

yield).

**6-Anthracyl-4,5-dimethyl-2-methoxycarbonyl-3-phenyl-1-phospha-2,5-norbornadiene:**  $^1\text{H}$

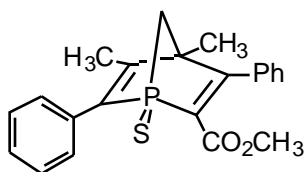
NMR 8.41-7.18 (m, 14H), 3.55 (s, 3H), 2.66-2.47 (ddd,  $J_{\text{HH}} = 10.5$ ,  $J_{\text{PH}} = 10.2$  Hz, 2H), 1.68 (d,  $J_{\text{PH}} = 0.6$  Hz, 3H), 1.43 (s, 3H);  $^{13}\text{C}$  NMR 179.33 (s), 166.59 (d,  $J_{\text{PC}} = 20.5$  Hz), 160.42 (s), 148.15 (d,  $J_{\text{PC}} = 27.6$  Hz), 137.17-125.04 (m, Ar), 72.34 (d,  $J_{\text{PC}} = 6.2$  Hz), 67.55 (d,  $J_{\text{PC}} = 2.9$  Hz), 51.56 (s), 20.30 (s), 15.95 (s);  $^{31}\text{P}$  NMR -8.83; IR  $\text{cm}^{-1}$  3048, 3025, 2966, 2915, 1712, 1624, 1583, 1517, 1487, 1432, 1380, 1347, 1273, 1244, 1203, 1059, 1030, 886, 842, 753, 735, 698, 669; MS LREI m/z (% rel int.) 448 ( $\text{M}^+$ , 29), HREI calcd for  $\text{C}_{30}\text{H}_{25}\text{O}_2\text{P}$  m/e 448.1592, measured m/e 448.1593; TLC (15%  $\text{Et}_2\text{O}$ , 75% pentane)  $R_f$  0.29.

**6-anthracyl-4,5-dimethyl-2-phenyl-3-methoxycarbonyl-1-phospha-2,5-norbornadiene:**  $^1\text{H}$

NMR 8.33-6.97 (m, 14H), 3.81 (s), 2.54-2.40 (ddd,  $J_{\text{PH}} = 10.2$ ,  $J_{\text{HH}} = 10.2$  Hz, 2H), 1.75(s,

6H);  $^{13}\text{C}$  NMR 168.99 (s), 162.53 (s), 161.32 (d,  $J_{\text{PC}} = 33.3$  Hz), 151.23 (s), 145.84 (d,  $J_{\text{PC}} = 27.6$  Hz), 136.52 (d,  $J_{\text{PC}} = 18.2$  Hz), 133.50 (d,  $J_{\text{PC}} = 17.1$  Hz), 131.41-124.98 (m, Ar), 70.69 (d,  $J_{\text{PC}} = 5.9$  Hz), 64.99 (d,  $J_{\text{PC}} = 3.2$  Hz), 51.92(s), 18.97 (s), 15.50 (s);  $^{31}\text{P}$  NMR 4.02; IR  $\text{cm}^{-1}$  3055, 3025, 2966, 2944, 2922, 1712, 1624, 1598, 1583, 1517, 1487, 1432, 1380, 1347, 1292, 1214, 1200, 1111, 1067, 1037, 1012, 953, 886, 757, 694, 669; MS LREI  $m/z$  (% int.) 448 ( $\text{M}^+$ , 40); HREI calcd for  $\text{C}_{30}\text{H}_{25}\text{O}_2\text{P}$   $m/e$  448.1592, measured  $m/e$  448.1587; TLC (15%  $\text{Et}_2\text{O}$ , 75% pentane)  $R_f$  0.42.

#### 4,5-Dimethyl-3,6-diphenyl-2-methoxycarbonyl-1-phospha-2,5-norbornadiene sulfide.



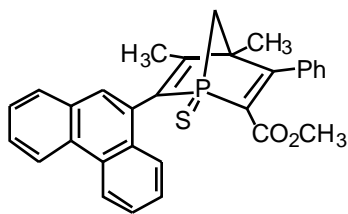
4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-

phospha-2,5-norbornadiene (2.60g, 0.747 mmol) was dissolved in 20 mL freshly distilled toluene and sulfur (0.29g, 0.896 mmol) was added

in small portions with stirring. The mixture was stirred for 12 h at 90-95 °C. The progress of the reaction was followed by  $^{31}\text{P}$  NMR. The product was purified by column chromatography using toluene as eluent first to elute the excess sulfur and then dichloromethane. In this way pure phosphine sulfide (2.54g, 90% yield) was obtained as a white solid. (3,6-Diphenyl-4,5-dimethyl-2-ethoxycarbonyl-1-phospha-2,5-norbornadiene sulfide was synthesized in the same way.)  $^1\text{H}$  NMR 7.47-7.06 (m, 10H, Ar), 3.66 (s, 3H), 2.81-2.63 (ddd,  $J_{\text{PH}} = 7.8, 6.6$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 2.07 (d,  $J_{\text{PH}} = 3.0$  Hz, 3H), 1.39 (s, 3H);  $^{13}\text{C}$  NMR 174.31 (d,  $J_{\text{PC}} = 10.5$  Hz), 163.80 (d,  $J_{\text{PC}} = 12.5$  Hz), 158.54 (d,  $J_{\text{PC}} = 14.0$  Hz), 140.66 (d,  $J_{\text{PC}} = 64.1$  Hz), 136.26 (d,  $J_{\text{PC}} = 58.6$  Hz), 133.9-126.64 (Ar), 69.70 (d,  $J_{\text{PC}} = 59.2$  Hz), 56.35 (d,  $J_{\text{PC}} = 18.5$  Hz), 51.99 (s), 18.76 (d,  $J_{\text{PC}} = 16.5$  Hz), 15.60 (d,  $J_{\text{PC}} = 12.5$  Hz);  $^{31}\text{P}$  NMR 49.83; IR  $\text{cm}^{-1}$  3062, 3025, 2959, 2924,

1716, 1620, 1609, 1487, 1435, 1384, 1306, 1288, 1240, 1211, 1152, 1063, 1026, 934, 849, 798, 761; MS HREI calcd for C<sub>22</sub>H<sub>21</sub>O<sub>2</sub>PS m/z 380.0994, measured m/z 380.0999; TLC R<sub>f</sub> (dichloromethane) 0.29.

**4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide.**

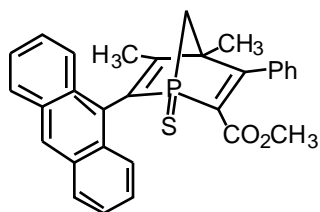


4,5-Dimethyl-2-methoxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide was prepared following the procedure for 4,5-Dimethyl-3,6-diphenyl-2-methoxycarbonyl-1-phospha-2,5-norbornadiene sulfide. 4,5-Dimethyl-2-methoxy-carbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene (2.2g, 0.49 mmol) and sulfur (0.19g, 0.5.88 mmol) in 15 mL of toluene were reacted as above to give the desired phosphine sulfide. The product was purified by column chromatography using first toluene as eluent to elute the excess sulfur and then dichloromethane and 15% EtOAc in dichloromethane to give after evaporation of the solvent 2.22 g of the sulfide as a white solid (94 %), mp 105-108 °C. <sup>31</sup>P NMR 51.07, 50.71; <sup>1</sup>H NMR 8.78-7.15 (m, 14H), 3.74, 3.64 (2s, 3H), 3.01-2.89 (m, J<sub>HH</sub> = 9.9 Hz, J<sub>PH</sub> = 6.6, 7.7 Hz, 2H), 1.92, 1.86 (2d, J<sub>PH</sub> = 2.5 Hz, J<sub>PH</sub> = 2.7Hz, 3H), 1.48, 1.43 (2s, 3H); <sup>13</sup>C NMR 175.08, 173.80 (2d, J<sub>PC</sub> = 10.8 Hz, J<sub>PC</sub> = 10.2 Hz), 164.02, 163.85 (2d, J<sub>PC</sub> = 14.4 Hz, J<sub>PC</sub> = 11.9 Hz), 162.00, 161.87 (2d, J<sub>PC</sub> = 14.2 Hz, J<sub>PC</sub> = 14.2 Hz), 141.57, 140.20 (2d, J<sub>PC</sub> = 63.7 Hz, J<sub>PC</sub> = 63.7 Hz), 137.19, 136.57 (2d, J<sub>PC</sub> = 57.5 Hz, J<sub>PC</sub> = 55.7 Hz), 134.14-122.45 (Ar), 73.04, 70.42 (2d, J<sub>PC</sub> = 58.9 Hz, J<sub>PC</sub> = 58.4Hz), 56.86, 56.58 (2d, J<sub>PC</sub> = 18.2 Hz, J<sub>PC</sub> = 18.2 Hz), 52.18, 52.10 (2s), 18.94, 18.85 (2d, J<sub>PC</sub> = 16.3 Hz, J<sub>PC</sub> = 16.2 Hz), 16.33, 16.01 (2d, J<sub>PC</sub> = 13.1 Hz, J<sub>PC</sub> = 12.8 Hz); IR cm<sup>-1</sup> 3055, 3018, 2944, 2988, 1708, 1627, 1605, 1583, 1487, 1447, 1428, 1380, 1288, 1240,



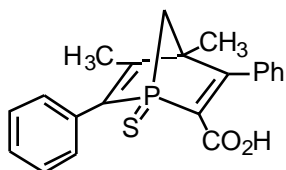
1214, 1074, 1067, 1026, 928, 905, 820, 842, 757, 720, 702, 669; MS LRFAB (rel. int. %) 487 (MLi<sup>+</sup>, 30), HRFAB calcd for C<sub>30</sub>H<sub>25</sub>O<sub>2</sub>PSLi m/e 487.1473, measured m/e 487.1491; TLC R<sub>f</sub> (DCM) = 0.39.

### 6-Anthracyl-2-methoxycarbonyl-3-phenyl-4,5-dimethyl-1-phospha-2,5-norbornadiene sulfide.



6-Anthracyl-4,5-dimethyl-2-methoxycarbonyl-3-phenyl-1-phospha-2,5-norbornadiene (1.48g, 3.30×10<sup>-3</sup> mol) and sulfur (0.13g, 3.96×10<sup>-3</sup> mol) were dissolved in 15 mL toluene were reacted as described above to give crude sulfide, which was purified by column chromatography using dichloromethane as eluent (1.39g, 89%). <sup>1</sup>H NMR 8.48-7.24 (m, 14H), 3.62 (s, 3H), 3.16-3.05 (ddd, J<sub>PH</sub> = 6.3, 7.8 Hz, J<sub>HH</sub> = 9.9Hz, 2H), 1.75 (d, J<sub>PH</sub> = 2.7 Hz, 3H), 1.49 (s, 3H); <sup>13</sup>C NMR 174.69 (d, J<sub>PC</sub> = 10.6 Hz), 163.83 (d, J<sub>PC</sub> = 11.9 Hz), 163.46 (d, J<sub>PC</sub> = 13.9 Hz), 140.27 (d, J<sub>PC</sub> = 63.2 Hz), 137.09 (d, J<sub>PC</sub> = 55.2 Hz), 134.12-125.13 (m, Ar), 72.64 (d, J<sub>PC</sub> = 58.4 Hz), 57.09 (d, J<sub>PC</sub> = 17.9Hz), 52.93 (s), 18.99 (d, J<sub>PC</sub> = 16.0Hz), 15.87 (d, J<sub>PC</sub> = 13.1 Hz); <sup>31</sup>P NMR 50.82; IR cm<sup>-1</sup> 3018, 2974, 2930, 1716, 1623, 1587, 1520, 1487, 1454, 1435, 1369, 1351, 1284, 1214, 1148, 1067, 1093, 1023, 986, 897, 827, 757, 694, 669; MS LREI m/z (% int.) 480 (M<sup>+</sup>, 95), HREI calcd for C<sub>30</sub>H<sub>25</sub>O<sub>2</sub>PS m/e 480.1319, measured m/e 480.1308, TLC (dichloromethane) R<sub>f</sub> 0.69.

### 3,6-Diphenyl-4,5-dimethyl-2-hydroxycarbonyl-1-phospha-2,5-norbornadiene sulfide.



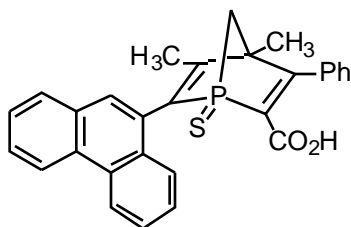
**Method A.** Anhydrous LiI (4.35 g, 0.032 mol) was added to a 100 mL Schlenk flask equipped with magnetic stirring bar. Dry pyridine (30 mL) was added and the mixture was stirred at 150 °C until LiI dissolved.

The corresponding methyl ester (2.47 g, 0.065 mmol) was dissolved in 20 mL pyridine and added via syringe to the LiI solution. The mixture was refluxed at 150 °C for 20h. The progress of the reaction was followed by TLC using 50%hexane to 50% EtOAc as eluent. After cooling the solvent was evaporated, the solid residue was dissolved in 40 mL water and the solution was acidified with 6M HCl to pH=3. The mixture was extracted with ether and CHCl<sub>3</sub>. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvents the acid was obtained quantitatively as white solid (2.3 g) and used without purification.

**Method B.** 3,6-Diphenyl-4,5-dimethyl-2-ethoxycarbonyl-1-phospha-2,5-norbornadiene sulfide (1.86g, 0.470 mmol) was dissolved in 60 mL THF and then EtOH (20 mL) was added. The solution was cooled to 0 °C and LiOH.H<sub>2</sub>O (1.00g, 2.40 mmol in 15 mL H<sub>2</sub>O) was added. The mixture was stirred at 0 °C for 3h and then at RT for 12h. TLC ( 20% EtOAc in hexane) was used to follow the progress of the reaction. After completion of the reaction the reaction mixture was acidified with 1M KHSO<sub>4</sub> to pH 3. THF was removed under reduced pressure. The aqueous mixture was extracted with EtOAc and CH<sub>2</sub>Cl<sub>2</sub>. The combined organic fractions were washed with brine and dried over MgSO<sub>4</sub>. After the removal of the solvents the acid was obtained as white solid (1.70g, 98%). Recrystallization from hexane/dichloromethane gave 0.44g pure acid, mp 221-224 °C. <sup>31</sup>P NMR 48.40; <sup>1</sup>H NMR 7.45-7.00 (m, 10H), 2.83-2.66 (ddd, *J*<sub>PH</sub> = 8.4 and 6.6 Hz, *J*<sub>HH</sub> = 9.9Hz, 2H), 2.06 (d, *J*<sub>PH</sub> = 2.7 Hz, 3H), 1.34 (s, 3H); <sup>13</sup>C NMR 178.91 (d, *J*<sub>PC</sub> = 10.6 Hz), 165.02 (d, *J*<sub>PC</sub> = 13.0 Hz), 159.21 (d, *J*<sub>PC</sub> = 13.5Hz), 140.35 (d, *J*<sub>PC</sub> = 64.1 Hz), 133.91 (d, *J*<sub>PC</sub> = 58.1 Hz), 134.16-126.34 (m), 70.39 (d, *J*<sub>PC</sub> = 58.6 Hz), 57.09 (d, *J*<sub>PC</sub> = 18.6 Hz), 18.76 (d, *J*<sub>PC</sub> = 16.6 Hz), 15.59 (d, *J*<sub>PC</sub> = 12.6 Hz); IR cm<sup>-1</sup> 3313-2738 (br), 3055, 3018,

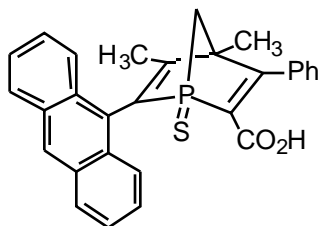
2981, 2937, 1686, 1627, 1587, 1487, 1454, 1435, 1399, 1292, 1277, 1214, 1170, 1137, 1085, 1023, 1004, 934, 882, 849, 761, 717, 698, 669; MS-LRFAB m/z (% intensity) 367.3 (MH<sup>+</sup>, 44), 349.2 (M-H<sub>2</sub>O, 100); HRFAB calcd for C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>PS (MH<sup>+</sup>) m/e 367.0922, measured m/e 367.0923; Anal. Calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>PS C, 68.84; H, 5.22. Found: C, 68.60; H, 4.93%.

**4,5-Dimethyl-2-hydroxycarbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide.**



Acid was obtained following method A. The corresponding ester (2.11 g, 0.44 mmol) and LiI (2.95 g, 2.2 mmol) in 50 mL of pyridine were reacted as described above to give the acid as a white solid, which was purified by recrystallization from hexane/CHCl<sub>3</sub> (2.0g, 95%). <sup>31</sup>P NMR (DMSO-*d*<sub>6</sub>) 56.58, 56.44; <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) 8.93-7.24 (m, 14H), 3.36 (br. s, 1H), 3.16-2.90 (m, *J*<sub>PH</sub> = 6.0 Hz, *J*<sub>PH</sub> = 6.6 Hz, *J*<sub>HH</sub> = 9.9Hz, 2H), 1.85, 1.80 (2d, *J*<sub>PH</sub> = 1.8Hz, 3H), 1.43, 1.39 (2s, 3H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>) 170.82, 170.33 (2d, *J*<sub>PC</sub> = 10.3 Hz, *J*<sub>PC</sub> = 10.3 Hz), 165.14, 165.04 (2d, *J*<sub>PC</sub> = 12.2 Hz, *J*<sub>PC</sub> = 12.2 Hz), 163.56, 163.14 (2d, *J*<sub>PC</sub> = 15.2 Hz, *J*<sub>PC</sub> = 14.6 Hz), 140.00, 136.68 (2d, *J*<sub>PC</sub> = 64.3 Hz, *J*<sub>PC</sub> = 64.0 Hz), 138.21, 137.63 (2d, *J*<sub>PC</sub> = 54.4 Hz, *J*<sub>PC</sub> = 55.2 Hz), 134.31-122.93 (m, Ar), 72.42, 69.45 (2d, *J*<sub>PC</sub> = 58.6 Hz, *J*<sub>PC</sub> = 58.6 Hz), 56.77, 56.27 (2d, *J*<sub>PC</sub> = 18.8 Hz, *J*<sub>PC</sub> = 18.5 Hz), 18.06, 17.77 (2d, *J*<sub>PC</sub> = 17.0 Hz, *J*<sub>PC</sub> = 17.3 Hz), 15.83, 15.66 (2d, *J*<sub>PC</sub> = 12.6 Hz, *J*<sub>PC</sub> = 12.5 Hz); IR cm<sup>-1</sup> 3335-2346 (br.), 3077, 3011, 2929, 2856, 1679, 1631, 1590, 1528, 1487, 1447, 1406, 1373, 1288, 1244, 1218, 1163, 1096, 1070, 1023, 908, 853, 746, 694, 672; MS LRFAB (rel. int. %) 473 (MLi<sup>+</sup>, 8), 479 (M-H, +Li)Li<sup>+</sup>, 10); HRFAB calcd for C<sub>29</sub>H<sub>23</sub>O<sub>2</sub>PSLi m/e 473.1316, measured m/e 473.1322.

**6-Anthracyl-4,5-dimethyl-2-hydroxycarbonyl-3-phenyl-1-phospha-2,5-norbornadiene sulfide.**

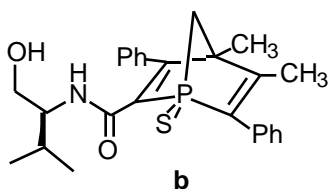
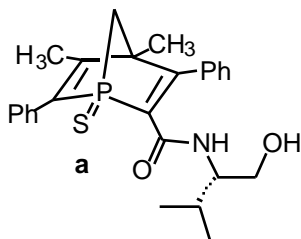


6-Anthracyl-2-methoxycarbonyl-3-phenyl-4,5-dimethyl-1-phospha-2,5-norbornadiene sulfide (1.36g,  $2.83 \times 10^{-3}$  mol) and LiI (1.89g, 1.40 mmol) in 50 mL pyridine was reacted following method A to give the

acid, which was purified by recrystallization from hexane/chloroform (yellow solid, 1.30g, 99%).

$^1\text{H}$  NMR (DMSO- $d_6$ ) 8.65-7.30 (m, 14H), 3.34-3.11 (ddd,  $J_{\text{PH}} = 7.1, 5.8$  Hz,  $J_{\text{HH}} = 7.7$  Hz, 2H), 3.36 (s, 1H), 1.66 (d,  $J_{\text{PH}} = 1.9$  Hz, 3H), 1.45 (s, 3H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ) 170.57 (d,  $J_{\text{PC}} = 10.5$  Hz), 164.67 (d,  $J_{\text{PC}} = 12.2$  Hz), 164.45 (d,  $J_{\text{PC}} = 19.1$  Hz), 138.43 (d,  $J_{\text{PC}} = 63.8$  Hz), 137.91 (d,  $J_{\text{PC}} = 55.2$  Hz), 134.19-125.33 (m, Ar), 72.02 (d,  $J_{\text{PC}} = 57.8$  Hz), 58.83 (d,  $J_{\text{PC}} = 18.5$  Hz), 18.04 (d,  $J_{\text{PC}} = 16.8$  Hz), 15.57 (d,  $J_{\text{PC}} = 12.53$  Hz);  $^{31}\text{P}$  NMR (DMSO- $d_6$ ) ; IR  $\text{cm}^{-1}$  3321-2738 (br), 3055, 3025, 2974, 1686, 1620, 1587, 1517, 1458, 1439, 1399, 1284, 1244, 1214, 1100, 1074, 1030, 1011, 905, 883, 842, 750, 698, 665; MS LREI  $m/z$  (% int.) 466.2 ( $\text{M}^+$ , 51); HREI calcd  $m/e$  for  $\text{C}_{29}\text{H}_{23}\text{O}_2\text{PS}$  466.1156, measured  $m/e$  466.1175.

**3,6-Diphenyl-4,5-dimethyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]-carbonyl-1-phospha-2,5-norbornadiene sulfide (a and b).**



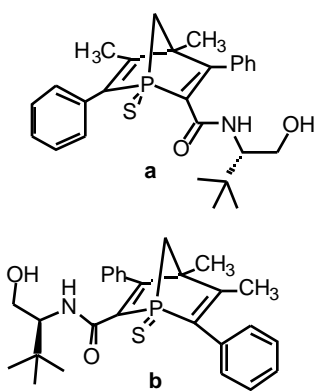
3,6-Diphenyl-4,5-dimethyl-2-hydroxycarbonyl-1-phospha-2,5-norbornadiene sulfide (0.41g, 0.110 mmol) was dissolved in 50 mL DMF. The solution was cooled to 0 °C and HOBT (0.25g, 0.160 mmol, 1.7 equiv.) and EDCI (0.30g, 0.155 mmol, 1.4 equiv.) were added with stirring. The mixture was stirred for 20 min at 0 °C until EDCI completely dissolved and then (*S*)-(+)-2-amino-3-methyl-1-

butanol was added. The reaction mixture was further stirred at 0 °C for 30 min and then at room temperature until the reaction was completed. The progress of the reaction was followed by TLC (60% EtOAc:40% Hexane) and <sup>31</sup>P NMR. After the completion of the reaction DMF was evaporated in vacuum and the residue was dissolved in CHCl<sub>3</sub>, the solution was washed with brine and the aqueous phase was back extracted with CHCl<sub>3</sub> and EtOAc. The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub>. After the removal of the solvents the two diastereomers were obtained as pale yellow oil. The separation of the diastereomers was carried out by column chromatography using mixture of 60%EtOAc and 40% hexane as eluent to give **a** (0.20g) and **b** (0.26g) as white solids (combined yield 93%).

**a**: mp 65-68 °C; <sup>31</sup>P NMR 48.10; <sup>1</sup>H NMR 7.74 (d,  $J_{\text{HH}} = 7.2$  Hz, 1H), 7.44-7.00 (m, 10H), 3.81-3.72 (m, 1H), 3.69-3.56 (ddd,  $J_{\text{HH}} = 3.6, 6.6$  and 11.4 Hz, 2H), 2.84-2.67 (ddd,  $J_{\text{PH}} = 8.1$  and 7.0 Hz,  $J_{\text{HH}} = 9.6$  Hz, 2H), 2.06 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.98-1.86 (m, 1H), 1.75 (br. s, 1H), 1.32 (s, 3H), 0.94 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.93 (d,  $J_{\text{HH}} = 6.9$  Hz); <sup>13</sup>C NMR 175.39 (d,  $J_{\text{PC}} = 11.0$  Hz), 163.13 (d,  $J_{\text{PC}} = 12.0$  Hz), 159.87 (d,  $J_{\text{PC}} = 13.5$  Hz), 140.26 (d,  $J_{\text{PC}} = 64.1$  Hz), 134.48 (d,  $J_{\text{PC}} = 51.1$  Hz), 135.51-126.14 (m), 70.92 (d,  $J_{\text{PC}} = 58.7$  Hz), 64.31 (s), 57.81 (s), 56.59 (d,  $J_{\text{PC}} = 19.5$  Hz), 28.94 (s), 19.44 (s), 18.82 (d,  $J_{\text{PC}} = 17.0$  Hz), 18.61 (s), 15.62 (d,  $J_{\text{PC}} = 12.5$  Hz); IR cm<sup>-1</sup> 3424, 3276, 3055, 2966, 2930, 2878, 1646, 1579, 1524, 1491, 1461, 1443, 1388, 1373, 1314, 1240, 1214, 1137, 1085, 1026, 930, 905, 849, 753, 698, 665; MS LRFAB m/z (% intensity) 452 (MH<sup>+</sup>, 100), HRFAB calcd for C<sub>26</sub>H<sub>31</sub>NO<sub>2</sub>PS m/z 452.1813, measured m/z 452.1815; TLC (60% EtOAc, 40% hexane) R<sub>f</sub> = 0.47.

**b**: mp 62-65 °C;  $^{31}\text{P}$  NMR 47.74;  $^1\text{H}$  NMR 7.95 (d,  $J_{\text{HH}} = 7.8$  Hz, 1H), 7.43-6.99 (m, 10H), 3.85-3.77 (m, 1H), 3.69-3.58 (ddd,  $J_{\text{HH}} = 3.9, 6.6$  and  $11.0$  Hz, 2H), 2.85-2.67 (ddd,  $J_{\text{PH}} = 8.1$  and  $6.9$  Hz,  $J_{\text{HH}} = 9.6$  Hz, 2H), 2.06 (d,  $J_{\text{PH}} = 3.0$  Hz, 3H), 1.90 (m, 1H), 1.84 (br.s, 1H), 1.31 (s, 3H), 0.94 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.93 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR 176.35 (d,  $J_{\text{PC}} = 10.5$  Hz), 163.29 (d,  $J_{\text{PC}} = 12.5$  Hz), 159.93 (d,  $J_{\text{PC}} = 13.6$  Hz), 140.35 (d,  $J_{\text{PC}} = 64.1$  Hz), 133.99 (d,  $J_{\text{PC}} = 50.1$  Hz), 135.32-126.07 (Ar), 70.81 (d,  $J_{\text{PC}} = 58.6$  Hz), 64.78 (s), 57.72 (s), 56.69 (d,  $J_{\text{PC}} = 19.6$  Hz), 28.96 (s), 19.51 (s), 18.79 (d,  $J_{\text{PC}} = 16.5$  Hz), 18.46 (s), 15.62 (d,  $J_{\text{PC}} = 13.1$  Hz); IR  $\text{cm}^{-1}$  3416, 3269, 3055, 2959, 2930, 2870, 1646, 1579, 1528, 1491, 1458, 1443, 1388, 1373, 1413, 1314, 1295, 1240, 1214, 1174, 1137, 1085, 1026, 930, 905, 846, 757, 698, 665; MS LRFAB  $m/z$  (% intensity) 452 ( $\text{MH}^+$ , 100), HRFAB calcd for  $\text{C}_{26}\text{H}_{31}\text{NO}_2\text{PS}$   $m/z$  452.1813, measured  $m/z$  452.1810; TLC (60% EtOAc, 40% hexane)  $R_f = 0.39$ .

**4,5-Dimethyl-3,6-diphenyl-2-[1-(1-hydroxymethyl-2,2-dimethylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide (a, b).**



3,6-Diphenyl-4,5-dimethyl-2-hydroxycarbonyl-1-phospha-2,5-

norbornadiene sulfide (2.05g, 0.56 mmol), HOBT (1.29g, 0.95 mmol),

EDCI (1.50g, 0.783 mmol) and (*S*)-*t*-leucinol (0.79g, 0.671 mmol)

were dissolved in 120 mL DMF and were reacted as above. The

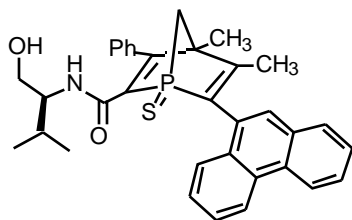
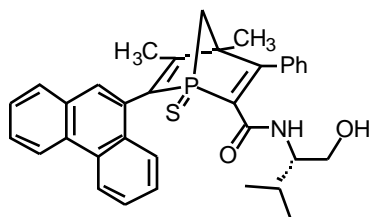
resulting diastereomers **a**, **b** were separated by column

chromatography using 60% EtOAc and 40% hexane mixture as eluent to give 0.83 g amide **a**, 0.87 g amide **b** and 0.27g mixture of **a** and **b** (79% combined yield).

**a:** mp 53-56 °C; <sup>1</sup>H NMR 7.80-7.02 (m, 10 H, Ar), 3.89-3.52 (m, 3H), 2.86-2.69 (ddd,  $J_{\text{PH}} = 7.8, 7.2$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 2.37 (br. s, 1H), 2.08 (d,  $J_{\text{PH}} = 2.4$  Hz, 3H), 1.34 (d,  $J_{\text{PH}} = 0.6$  Hz, 3H), 0.96 (s, 9H); <sup>13</sup>C NMR 175.33 (d,  $J_{\text{PC}} = 10.5$  Hz), 163.36 (d,  $J_{\text{PC}} = 12.5$  Hz), 159.84 (d,  $J_{\text{PC}} = 13.6$  Hz), 140.32 (d,  $J_{\text{PC}} = 64.7$  Hz), 134.54 (d,  $J_{\text{PC}} = 50.6$  Hz), 135.51-126.16 (Ar), 70.99 (d,  $J_{\text{PC}} = 58.6$  Hz), 63.63 (s), 60.75 (s), 56.58 (d,  $J_{\text{PC}} = 19.6$  Hz), 33.40 (s), 27.02 (s), 18.80 (d,  $J_{\text{PC}} = 16.6$  Hz), 15.60 (d,  $J_{\text{PC}} = 12.5$  Hz); <sup>31</sup>P NMR 48.55; IR cm<sup>-1</sup> 3424, 3284, 3062, 2974, 2878, 1653, 1576, 1524, 1491, 1447, 1369, 1343, 1288, 1240, 1218, 1174, 1137, 1089, 1048, 997, 930, 905, 846, 809, 754, 698; MS HREI calcd for C<sub>26</sub>H<sub>32</sub>NO<sub>2</sub>PS - CH<sub>2</sub>OH m/z 434.1703, measured m/z 434.1404; TLC (60% EtOAc, 40% hexane) R<sub>f</sub> 0.48.

**b:** mp 57-59 °C; <sup>1</sup>H NMR 8.00-7.02 (m, 10H, Ar), 3.89-3.52 (m, 3H), 2.88-2.69 (ddd,  $J_{\text{PH}} = 8.1, 7.2$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 2.61 (br. s, 1H), 2.07 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.32 (s, 3H), 0.97 (s, 9H); <sup>13</sup>C NMR 176.89 (d,  $J_{\text{PC}} = 11.0$  Hz), 163.87 (d,  $J_{\text{PC}} = 12.5$  Hz), 160.36 (d,  $J_{\text{PC}} = 14.0$  Hz), 140.62 (d,  $J_{\text{PC}} = 64.65$  Hz), 134.20 (d,  $J_{\text{PC}} = 50.0$  Hz), 136.09-126.39 (Ar), 71.07 (d,  $J_{\text{PC}} = 58.6$  Hz), 64.29 (s), 60.96 (s), 57.03 (d,  $J_{\text{PC}} = 18.9$  Hz), 33.63 (s), 27.39 (s), 19.09 (d,  $J_{\text{PC}} = 17.0$  Hz), 15.96 (d,  $J_{\text{PC}} = 13.1$  Hz); <sup>31</sup>P NMR 48.09; IR cm<sup>-1</sup> 3424, 3284, 3055, 2966, 2870, 1649, 1579, 1528, 1491, 1447, 1369, 1284, 1240, 1214, 1177, 1137, 1089, 1052, 1000, 930, 905, 842, 757, 698, 665; MS HREI calcd for C<sub>27</sub>H<sub>32</sub>NO<sub>2</sub>PS - CH<sub>2</sub>OH m/z 434.1727, measured m/z 434.1710; TLC (60% EtOAc, 40% hexane) R<sub>f</sub> 0.37.

**4,5-Dimethyl-2-(1-hydroxymethyl-1-isopropylamino)carbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfides (a, b).**



4,5-Dimethyl-2-hydroxycarbonyl-6-phenanthryl-3-phenyl-1-

phospha-2,5-norbornadiene sulfide (crude, 0.57g, 0.122 mmol),

HOBT (0.28g, 0.208 mmol), EDCI (0.33g, 0.171 mmol) and (*S*-

(+)-2-amino-3-methyl-1-butanol (0.15 g, 0.147 mmol) were reacted

as above to give diastereomers **a** and **b**. The separation of the

diastereomers was carried out by column chromatography using

mixture of 60%EtOAc and 40% hexane as eluent to give **a** (0.26g)

and **b** (0.316g) as white solids (combined yield 86%).

**a**: mp 98-103 °C;  $^{31}\text{P}$  NMR 49.60, 49.50;  $^1\text{H}$  NMR 8.75-7.08 (m, 14H), 3.87-3.81 (m, 1H),

3.73-3.60, 3.60-3.47 (2ddd,  $J_{\text{HH}} = 3.8, 6.9$  and  $11.3$  Hz,  $J_{\text{HH}} = 3.8, 6.3$  and  $11.5$  Hz, 2H), 3.31-

2.83 (m,  $J_{\text{PH}} = 7.1$  Hz,  $J_{\text{HH}} = 9.7$  Hz,  $J_{\text{PH}} = 7.1$  Hz, 2H), 2.61 (s, 1H), 1.91, 1.85 (2d,  $J_{\text{PH}} = 2.7,$

2.7Hz, 3H), 1.94-1.81 (m, 1H), 1.38, 1.35 (2s, 3H), 0.93, 0.88 (2d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.93, 0.85

(2d,  $J_{\text{HH}} = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR 176.38, 175.54 (2d,  $J_{\text{PC}} = 10.9$  Hz,  $J_{\text{PC}} = 11.0$  Hz), 163.18,

163.03 (2d,  $J_{\text{PC}} = 13.7$  Hz), 162.88, 162.65 (2d,  $J_{\text{PC}} = 13.9$  Hz), 141.70, 139.54 (2d,  $J_{\text{PC}} = 64.3$ Hz,

64.3 Hz), 134.83, 134.36 (2d,  $J_{\text{PC}} = 49.4$  Hz,  $J_{\text{PC}} = 48.5$  Hz), 135.60-122.34 (Ar), 72.44, 70.78

(2d,  $J_{\text{PC}} = 57.4$  Hz,  $J_{\text{PC}} = 57.7$  Hz), 64.31, 64.12 (2s), 57.76, 57.56 (2s), 57.03, 56.76 (2d,  $J_{\text{PC}} =$

21.3 Hz,  $J_{\text{PC}} = 19.1$  Hz), 28.73 (s), 19.36 (s), 18.78 (Me, overlaps), 18.48 (s), 16.19.15.74 (2d,

$J_{\text{PC}} = 13.1$  Hz,  $J_{\text{PC}} = 12.5$  Hz); IR  $\text{cm}^{-1}$  3417, 3276, 3055, 2966, 2929, 2870, 1653, 1579, 1528,

1491, 1450, 1428, 1391, 1373, 1262, 1240, 1159, 1144, 1082, 1037, 952, 905, 849, 768, 735,

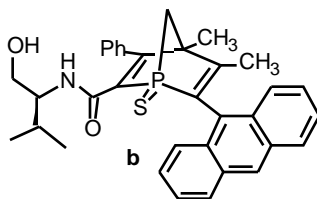
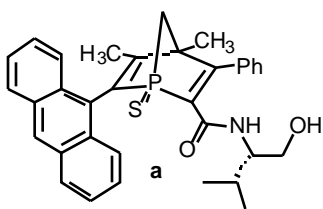
698, 665; MS LRFAB  $m/z$  (% rel. int.) 552 ( $\text{MH}^+$ , 100), HRFAB calcd for  $\text{C}_{34}\text{H}_{35}\text{NO}_2\text{PS}$   $m/e$

552.2126, measured  $m/e$  552.2132; TLC  $R_f$  (40% hexane, 60% EtOAc) = 0.25.



**b:** mp 80-82 °C;  $^{31}\text{P}$  NMR 49.48, 49.01;  $^1\text{H}$  NMR 8.75-7.07 (m, 14 H), 5.62 (br. s, 1H), 3.92-3.74 (m, 1H), 3.66-3.32 (m,  $J_{\text{HH}} = 4.1, 7.1$  and  $11.3$  Hz, 2H), 3.01-2.84 (m,  $J_{\text{PH}} = 6.0, 6.9$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 1.89, 1.86 (2d,  $J_{\text{PH}} = 2.4$  Hz,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.76-1.69 (m, 1H), 1.37, 1.33 (2s, 3H), 0.94, 0.66 (2d,  $J_{\text{HH}} = 6.6, 6.9$  Hz, 3H), 0.93, 0.65 (2d,  $J_{\text{HH}} = 6.9, 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 176.74, 176.65 (2d,  $J_{\text{PC}} = 11.6$  Hz,  $J_{\text{PC}} = 10.7$  Hz), 163.49, 163.30 (2d,  $J_{\text{PC}} = 13.7$  Hz), 163.12, 162.90 (2d,  $J_{\text{PC}} = 12.5$  Hz,  $J_{\text{PC}} = 13.9$  Hz), 141.25, 139.50 (2d,  $J_{\text{PC}} = 64.0$  Hz,  $J_{\text{PC}} = 64.3$  Hz), 134.12, 134.06 (2d,  $J_{\text{PC}} = 48.5$  Hz,  $J_{\text{PC}} = 49.7$  Hz), 135.56-111.12 (Ar), 72.61, 71.13 (2d,  $J_{\text{PC}} = 58.0$  Hz,  $J_{\text{PC}} = 57.6$  Hz), 64.14 (s), 57.65, 57.30 (2s), 57.17, 56.79 (2d,  $J_{\text{PC}} = 19.9$  Hz,  $J_{\text{PC}} = 19.1$  Hz), 28.68 (s), 19.64, 19.20 (2s), 18.62, 18.41 (2d,  $J_{\text{PC}} = 16.4$  Hz), 18.73, 18.31 (2s), 16.10, 15.80 (2d,  $J_{\text{PC}} = 13.1$  Hz,  $J_{\text{PC}} = 12.5$  Hz); IR  $\text{cm}^{-1}$  3416, 3276, 3055, 2959, 2929, 2870, 1653, 1579, 1528, 1491, 1450, 1432, 1384, 1373, 1262, 1244, 1159, 1144, 1074, 1037, 952, 905, 849, 764, 735, 698; MS LRFAB  $m/z$  (% intensity) 552 ( $\text{MH}^+$ , 100), HRFAB Calcd for  $\text{C}_{34}\text{H}_{35}\text{NO}_2\text{PS}$   $m/z$  552.2126, found  $m/z$  552.2131; TLC  $R_f$  (40% Hexane, 60 % EtOAc) = 0.16.

**6-Anthracyl-4,5-dimethyl-3-phenyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide (a and b).**



6-Anthracyl-4,5-dimethyl-2-hydroxycarbonyl-3-phenyl-1-

phospha-2,5-norbornadiene sulfide (1.35g, 0.347 mmol), HOBT

(0.66g, 0.490 mmol), EDCI (0.78g, 0.405 mmol) and (*S*)-valinol

(0.36g, 0.347 mmol) in 120 mL DMF were reacted as above. The

resulting diastereomers **a** and **b** were separated by column

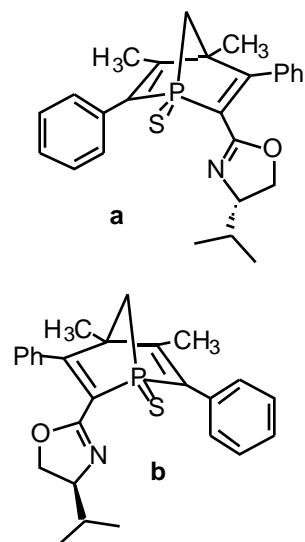
chromatography using 60% EtOAc : 40% hexane as eluent to give

0.63g amide **a** and 0.67g amide **b** (81 % combined yield).

**a:** mp 118-120 °C; <sup>1</sup>H NMR 8.48-7.16 (m, 14H), 3.84-3.76 (m, 1H), 3.55-3.41 (m, 2H), 3.18-3.04 (ddd,  $J_{\text{PH}} = 6.6, 7.8$  Hz,  $J_{\text{HH}} = 10.2$  Hz, 2H), 1.81 (m, 1H), 1.76 (d,  $J_{\text{PH}} = 2.4$  Hz, 3H), 1.44 (s, 3H), 0.86 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.81 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H); <sup>13</sup>C NMR 176.06 (d,  $J_{\text{PC}} = 10.8$  Hz), 164.05 (d,  $J_{\text{PC}} = 13.7$  Hz), 162.64 (d,  $J_{\text{PC}} = 12.2$  Hz), 139.81 (d,  $J_{\text{PC}} = 63.5$  Hz), 134.73 (d,  $J_{\text{PC}} = 47.8$  Hz), 135.58-124.41 (m, Ar), 71.98 (d,  $J_{\text{PC}} = 57.2$  Hz), 64.20 (s), 57.86 (s), 57.35 (d,  $J_{\text{PC}} = 19.1$  Hz), 28.80 (s), 19.45 (s), 18.89 (d,  $J_{\text{PC}} = 16.2$  Hz), 18.67 (s), 15.95 (d,  $J_{\text{PC}} = 13.1$  Hz); <sup>31</sup>P NMR 49.67; IR cm<sup>-1</sup> 3409, 3276, 3048, 2959, 2937, 2870, 1657, 1576, 1528, 1487, 1450, 1439, 1388, 1369, 1351, 1262, 1244, 1218, 1159, 1078, 1052, 1012, 901, 846, 779, 739, 702; MS LREI m/z (% int.) 551.2 (M<sup>+</sup>, 100), HREI calcd for C<sub>34</sub>H<sub>34</sub>NO<sub>2</sub>PS m/e 551.2048, measured m/e 551.2022, TLC (60% EtOAc, 40% hexane) R<sub>f</sub> 0.42.

**b:** mp 113-115 °C; <sup>1</sup>H NMR 8.50-7.17 (m, 14H), 3.80-3.72 (m, 1H), 3.64-3.50 (m, 2H), 3.19-3.06 (ddd,  $J_{\text{PH}} = 6.3, 7.5$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 1.77 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.73-1.62 (m, 1H), 1.44 (s, 3H), 0.61 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.60 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H); <sup>13</sup>C NMR 176.41 (d,  $J_{\text{PC}} = 11.1$  Hz), 164.19 (d,  $J_{\text{PC}} = 13.7$  Hz), 162.82 (d,  $J_{\text{PC}} = 12.0$  Hz), 139.73 (d,  $J_{\text{PC}} = 63.8$  Hz), 134.56 (d,  $J_{\text{PC}} = 47.6$  Hz), 135.68-124.40 (m, Ar), 72.11 (d,  $J_{\text{PC}} = 57.2$  Hz), 64.61 (s), 57.87 (s), 57.47 (d,  $J_{\text{PC}} = 19.1$  Hz), 28.87 (s), 19.35 (s), 18.96 (d,  $J_{\text{PC}} = 16.3$  Hz), 18.49 (s), 15.98 (d,  $J_{\text{PC}} = 13.1$  Hz); <sup>31</sup>P NMR 49.45; IR cm<sup>-1</sup> 3417, 3276, 3055, 2959, 2929, 2870, 1649, 1579, 1528, 1454, 1443, 1388, 1373, 1295, 1262, 1240, 1218, 1159, 1141, 1078, 1030, 1012, 901, 846, 779, 735, 698; MS LREI m/z (% int.) 551.5 (M<sup>+</sup>, 100), HREI calcd for C<sub>34</sub>H<sub>34</sub>NO<sub>2</sub>PS m/e 551.2048, measured m/e 551.2059, TLC (60% EtOAc, 40% hexane) R<sub>f</sub> 0.28.

**3,6-Diphenyl-4,5-dimethyl-2-(4-isopropylloxazol-2-yl)-1-phospha-2,5-norbornadiene sulfide (a and b).**



3,6-Diphenyl-4,5-dimethyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]-carbonyl-1-phospha-2,5-norbornadiene sulfide **a** (0.19g, 0.0434 mmol) was dissolved in 10 mL freshly distilled  $\text{CH}_2\text{Cl}_2$  and then DMAP (0.0027g, 0.0022 mmol) and  $\text{Et}_3\text{N}$  (0.22g, 0.220 mmol, 5 equiv.) were added. The solution was cooled to 0 °C and  $\text{MsCl}$  (0.10g, 0.0870 mmol, 2 equiv.) was added. The reaction mixture was stirred at 0 °C for 30 min and then for 24 h at room temperature. TLC

( $\text{EtOAc}:\text{hexane} = 60:40$ ) was used to follow the progress of the reaction. When the reaction was completed the reaction mixture was diluted with  $\text{CHCl}_3$  and washed with aqueous  $\text{NaHCO}_3$ . The aqueous phase was back extracted with  $\text{CHCl}_3$ . The combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ . After evaporation of the solvent the crude product was purified by column chromatography ( $\text{EtOAc}:\text{hexane}:\text{Et}_3\text{N} = 50:45:5$ ) to give the product (0.15g, 80%) as a white solid.

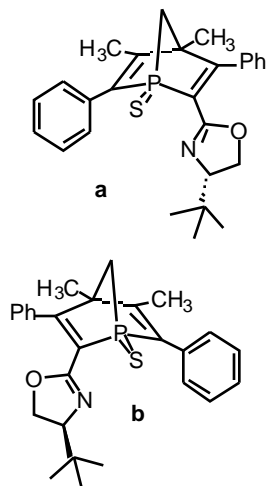
Compound **b** was synthesized in the same way. 3,6-Diphenyl-4,5-dimethyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]-carbonyl-1-phospha-2,5-norbornadiene sulfide **b** (0.13g, 0.028 mmol), DMAP (0.0017g, 0.0014 mmol),  $\text{Et}_3\text{N}$  (0.14g, 0.140 mmol) and  $\text{MsCl}$  (0.06g, 0.055 mmol) were reacted as above to give **b** as a white solid (0.11g, 93%).

**a**: mp 53-56 °C;  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ ) 50.80,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.38-7.00 (m, 10H), 4.06-3.76 (m, 2H), 3.95-3.87 (ddd,  $J_{\text{HH}} = 7.5$  and 9.3 Hz, 1H), 2.79-2.56 (ddd,  $J_{\text{PH}} = 8.1$  and 7.2 Hz,  $J_{\text{HH}} =$

9.9 Hz, 2H), 1.99 (d,  $J_{\text{PH}} = 2.4$  Hz, 3H), 1.69-1.58 (m, 1H), 1.33 (s, 3H), 0.73 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.70 (d,  $J_{\text{HH}} = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ) 171.34 (d,  $J_{\text{PC}} = 10.5$  Hz), 158.92 (d,  $J_{\text{PC}} = 14.0$  Hz), 158.39 (d,  $J_{\text{PC}} = 11.6$  Hz), 141.25 (d,  $J_{\text{PC}} = 64.6$  Hz), 132.97 (d,  $J_{\text{PC}} = 62.6$  Hz), 134.61-127.14 (m), 72.41 (s), 70.42 (d,  $J_{\text{PC}} = 59.1$  Hz), 69.46 (s), 56.00 (d,  $J_{\text{PC}} = 18.5$  Hz), 32.23 (s), 18.87 (d,  $J_{\text{PC}} = 16.1$  Hz), 18.53 (s), 17.76 (s), 15.45 (d,  $J_{\text{PC}} = 13.1$  Hz); IR  $\text{cm}^{-1}$  3055, 2966, 2930, 2870, 1664, 1616, 1491, 1461, 1443, 1410, 1384, 1354, 1306, 1240, 1258, 1214, 1200, 1170, 1141, 1089, 1048, 1019, 967, 934, 857, 779, 757, 698, 665; MS LRFAB (% intensity) 440 ( $\text{MLi}^+$ , 100), 434 ( $\text{MH}^+$ , 58); HRFAB calcd for  $\text{C}_{26}\text{H}_{28}\text{NOPSLi}$  ( $\text{MLi}^+$ ) m/e 440.1789, measured m/e 440.1786; TLC  $R_f = 0.70$  (EtOAc, hexane = 60:40).

**b:** mp 110-113 °C;  $^{31}\text{P}$  NMR 50.87;  $^1\text{H}$  NMR 7.39-7.05 (m, 10H), 4.15-3.80 (m, 2H), 3.92-3.78 (ddd,  $J_{\text{HH}} = 7.2, 7.2$  and  $8.2$  Hz, 1H), 2.77-2.54 (ddd,  $J_{\text{PH}} = 7.8$  and  $6.9$  Hz,  $J_{\text{HH}} = 9.6$  Hz, 2H), 1.99 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.52-1.46 (m, 1H), 1.34 (s, 3H), 0.64 (d,  $J_{\text{HH}} = 6.6$  Hz, 3H), 0.61 (d,  $J_{\text{HH}} = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR 171.58 (d,  $J_{\text{PC}} = 10.5$  Hz), 158.90 (d,  $J_{\text{PC}} = 14.6$  Hz), 158.31 (d,  $J_{\text{PC}} = 10.5$  Hz), 140.86 (d,  $J_{\text{PC}} = 63.5$  Hz), 133.44 (d,  $J_{\text{PC}} = 62.6$  Hz), 134.27-127.44 (m), 72.35 (d,  $J_{\text{PC}} = 57.1$  Hz), 56.01 (d,  $J_{\text{PC}} = 18.5$  Hz), 32.31 (s); IR  $\text{cm}^{-1}$  3062, 3018, 2966, 2930, 2878, 1664, 1620, 1578, 1491, 1458, 1443, 1388, 1354, 1211, 1137, 1089, 1056, 1023, 967, 930, 901, 857, 753, 698, 669; MS LRFAB m/z (% intensity) 434 ( $\text{MH}^+$ , 100), HRFAB calcd for  $\text{C}_{26}\text{H}_{29}\text{NOPS}$  m/e 434.1707, measured m/z 434.1716.

**4,5-Dimethyl-3,6-diphenyl-2-(4-*tert*-butyloxazol-2-yl)-1-phospha-2,5-norbornadiene sulfide (a and b).**



4,5-Dimethyl-3,6-diphenyl-2-[1-(1-hydroxymethyl-2,2-dimethylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide **a** (0.71g, 0.153 mmol), Et<sub>3</sub>N (0.77g, 0.763 mmol), DMAP (0.0093g, 0.007.63 mmol) and MsCl (0.35g, 0.305 mmol) in 20 mL dichloromethane were reacted as above to give 0.63g (92%) oxazoline **a**.

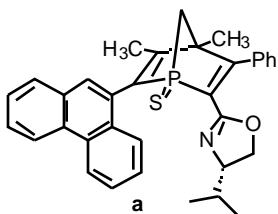
In the same way amide 4,5-dimethyl-3,6-diphenyl-2-[1-(1-hydroxymethyl-2,2-dimethylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide **b** (0.71g, 0.0153 mmol), Et<sub>3</sub>N (0.77g, 0.763 mmol), DMAP (0.0093g, 0.0153 mmol) and MsCl (0.35g, 0.03.05 mmol) were reacted as above to give oxazoline **b** (0.65g, 96%).

**a**: mp 46-48 °C; <sup>1</sup>H NMR 7.45-7.06 (m, 10H, Ar), 4.13-3.88 (m, 3H), 2.87-2.63 (ddd,  $J_{\text{PH}} = 7.8, 6.9$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 2.06 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.40 (s, 3H), 0.78 (s, 9H); <sup>13</sup>C NMR 171.32 (d,  $J_{\text{PC}} = 11.3$  Hz), 158.86 (d,  $J_{\text{PC}} = 14.0$  Hz), 158.23 (d,  $J_{\text{PC}} = 11.0$  Hz), 141.37 (d,  $J_{\text{PC}} = 64.6$  Hz), 132.87 (d,  $J_{\text{PC}} = 63.1$  Hz), 134.71-127.13 (Ar), 76, 19 (s), 70.26 (d,  $J_{\text{PC}} = 59.1$  Hz), 68.25 (s), 55.97 (d,  $J_{\text{PC}} = 18.5$  Hz), 33.71 (s), 25.69 (s), 28.16 (d,  $J_{\text{PC}} = 16.5$  Hz), 15.42 (d,  $J_{\text{PC}} = 15.5$  Hz); <sup>31</sup>P NMR 51.13; IR cm<sup>-1</sup> 3055, 2959, 2900, 2863, 1664, 1616, 1602, 1495, 1473, 1458, 1439, 1414, 1384, 1358, 1336, 1304, 1266, 1236, 1200, 1137, 1052, 1012, 964, 927, 905, 857, 757, 702, 665; MS HREI calcd for C<sub>27</sub>H<sub>30</sub>NOPS m/z 447.1786, measured m/z 447.1785; TLC (50% EtOAc, 45% hexane, 5% Et<sub>3</sub>N) R<sub>f</sub> 0.76.

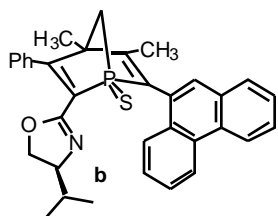
**b**: mp 112-115 °C; <sup>1</sup>H NMR 7.47-7.14 (m, Ar, 10 H), 4.23-3.87 (m, 3H), 2.85-2.62 (ddd,  $J_{\text{PH}} = 8.4, 6.9$  Hz,  $J_{\text{HH}} = 9.9$  Hz, 2H), 2.09 (d,  $J_{\text{PH}} = 2.7$  Hz, 3H), 1.41 (s, 3H), 0.66 (s, 9H); <sup>13</sup>C NMR

171.66 (s), 158.79 (d,  $J_{PC} = 13.6$  Hz), 140.98 (d,  $J_{PC} = 64.6$  Hz), 133.52 (d,  $J_{PC} = 62.1$  Hz), 134.23-127.51 (Ar), 76.17 (s), 70.25 (d,  $J_{PC} = 58.1$  Hz), 68.76 (s), 56.09 (d,  $J_{PC} = 19.1$  Hz), 33.64 (s), 25.47 (s), 18.80 (d,  $J_{PC} = 16.5$  Hz), 15.46 (d,  $J_{PC} = 12.5$  Hz);  $^{31}\text{P}$  NMR 51.34; IR  $\text{cm}^{-1}$  3062, 3018, 2967, 2870, 1664, 1624, 1590, 1491, 1476, 1454, 1440, 1414, 1384, 1366, 1351, 1307, 1244, 1215, 1192, 1141, 1089, 1074, 1052, 1023, 971, 930, 908, 857, 754, 702, 665; MS HREI calcd for  $\text{C}_{27}\text{H}_{30}\text{NOPS}$   $m/z$  447.1786, measured  $m/e$  447.1785; TLC (50% EtOAc, 45% hexane, 5%  $\text{Et}_3\text{N}$ )  $R_f$  0.66.

**4,5-Dimethyl-2-(4-isopropylloxazol-2-yl)-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide (a and b).**



4,5-Dimethyl-2-(1-hydroxymethyl-1-isopropylamino)carbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide **a** (0.205g, 0.0371 mmol), DMAP (0.0023g, 0.00185 mmol),  $\text{Et}_3\text{N}$  (0.19g, 0.0186



mmol) and  $\text{MsCl}$  (0.085g, 0.0743 mmol) were reacted as above to give oxazoline **a**. The crude product was purified by column chromatography ( $\text{EtOAc}:\text{hexane}:\text{Et}_3\text{N} = 50:45:5$ ) to give **a** (0.172 g,

93%) as a white solid.

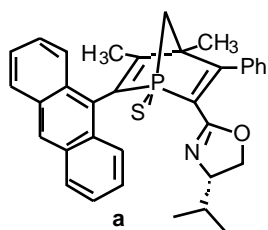
4,5-Dimethyl-2-(1-hydroxymethyl-1-isopropylamino)carbonyl-6-phenanthryl-3-phenyl-1-phospha-2,5-norbornadiene sulfide **b** (0.87g, 0.16 mmol),  $\text{Et}_3\text{N}$  (0.8g, 0.0790 mmol), DMAP (0.0096g, 0.0079 mmol) and  $\text{MsCl}$  (0.36g, 0.320 mmol) were reacted to give after column chromatography oxazoline **b** as a white solid (0.79g, 94%).

**a:** mp 77-78 °C; <sup>31</sup>P NMR 52.47, 51.88; <sup>1</sup>H NMR 8.77-7.17 (m, 14H), 4.20-3.86 (2ddd,  $J_{\text{HH}} = 7.5, 6.6$  and  $9.3$  Hz, 2H), 4.10-3.80 (m, 1H), 3.04-2.81 (2ddd,  $J_{\text{PH}} = 7.5$  and  $6.9$  Hz,  $J_{\text{HH}} = 9.6$  Hz, 2H), 1.94, 1.86 (2d,  $J_{\text{HH}} = 2.4$  Hz, 3H), 1.50, 1.47 (2s, 3H), 0.85, 0.77 (2d,  $J_{\text{HH}} = 6.9$  Hz, 3H), 0.83, 0.75 (2d,  $J_{\text{HH}} = 6.6, 6.9$  Hz, 3H); <sup>13</sup>C NMR 171.84, 171.26 (2d,  $J_{\text{PC}} = 10.9, 10.5$  Hz), 162.25, 161.95 (2d,  $J_{\text{PC}} = 14.0$  Hz), 158.36, 158.08 (2d,  $J_{\text{PC}} = 11.6, 11.0$  Hz), 142.08, 140.43 (2d,  $J_{\text{PC}} = 64.1, 63.0$  Hz), 133.58, 133.13 (2d,  $J_{\text{PC}} = 62.1, 61.6$  Hz), 134.59-122.36 (Ar), 73.44, 70.96 (2d,  $J_{\text{PC}} = 58.6, 58.1$  Hz), 72.54, 72.41 (2s), 69.38, 69.24 (2s), 56.37, 56.05 (2d,  $J_{\text{PC}} = 18.5, 18.0$  Hz), 32.16, 32.03 (2s), 18.88, 18.74 (2d,  $J_{\text{PC}} = 16.5, 16.1$  Hz), 18.48, 18.43 (2s), 17.77, 17.61 (2s), 16.04, 15.64 (2d,  $J_{\text{PC}} = 13.0, 12.5$  Hz); IR cm<sup>-1</sup> 3062, 2966, 2930, 2900, 2870, 1664, 1587, 1491, 1450, 1428, 1384, 1354, 1307, 1240, 1214, 1196, 1144, 1093, 1052, 1019, 964, 905, 860, 809, 757, 724, 698, 665; MS LRFAB m/z (rel. int.) 534 (MH<sup>+</sup>, 100), HRFAB calcd for C<sub>34</sub>H<sub>33</sub>NOPS m/e 534.2020, measured m/e 534.2019; TLC (EtOAc, Hexane, Et<sub>3</sub>N = 50 : 45 : 5) R<sub>f</sub> = 0.40.

**b:** mp 83-86 °C; <sup>1</sup>H NMR 8.74 - 7.21 (m, 14H), 4.29 - 3.82 (m, 3H), 3.01 - 2.77 (2ddd,  $J_{\text{PH}} = 7.8, 6.9$  Hz,  $J_{\text{PH}} = 9.6$  Hz, 2H), 1.89, 1.84 (2d,  $J_{\text{PH}} = 2.7, 2.4$  Hz, 3H), 1.62 (m, 1H), 1.48, 1.43 (2s, 3H), 0.78, 0.70 (2d,  $J_{\text{HH}} = 6.6$  Hz, 3H), 0.77, 0.70 (2d,  $J_{\text{HH}} = 6.6$  Hz, 3H); <sup>13</sup>C NMR 172.09, 170.93 (2d,  $J_{\text{PC}} = 11.1, 10.6$  Hz), 162.01 (d,  $J_{\text{PC}} = 13.9$  Hz), 158.21, 158.14 (2d,  $J_{\text{PC}} = 10.8, 10.5$  Hz), 141.64, 140.06 (2d,  $J_{\text{PC}} = 63.8$  Hz), 134.17, 133.46 (2d,  $J_{\text{PC}} = 62.1, 59.8$  Hz), 134.58-122.35 (Ar), 73.31, 70.81 (2d,  $J_{\text{PC}} = 58.0, 57.2$  Hz), 72.63, 72.51 (2s), 69.96, 69.68 (2s), 56.48, 56.20 (2d,  $J_{\text{PC}} = 18.5, 18.2$  Hz), 32.48, 32.27 (2s), 19.07, 18.85 (2d,  $J_{\text{PC}} = 16.2$  Hz), 18.27, 18.22 (2s), 18.20, 17.87 (2s), 16.25, 15.86 (2d,  $J_{\text{PC}} = 13.1, 12.5$  Hz); <sup>31</sup>P NMR 52.43, 52.25; IR

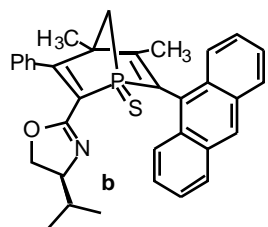
cm<sup>-1</sup> 3062, 2966, 2929, 2900, 2870, 1664, 1627, 1587, 1491, 1450, 1428, 1384, 1354, 1306, 1240, 1214, 1196, 1144, 1093, 1056, 1026, 964, 934, 905, 860, 809, 753, 728, 702, 665; MS HRFAB m/z (% intensity) 543 ([MH]<sup>+</sup>, 100), HRFAB calcd for C<sub>34</sub>H<sub>33</sub>NOPS m/z 534.2020, measured m/e 534.2015; TLC (50% EtOAc, 45% Hexane, 5% Et<sub>3</sub>N) R<sub>f</sub> = 0.50.

**6-Anthracyl-4,5-dimethyl-3-phenyl-2-(4-isopropylloxazol-2-yl)-1-phospha-2,5-norbornadiene sulfide (a and b).**



6-Anthracyl-4,5-dimethyl-3-phenyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide **a** (0.58g, 0.105 mmol), Et<sub>3</sub>N (0.53g, 0.530 mmol), DMAP (0.0064g,

0.00530 mmol) and MsCl (0.24g, 0.21 mmol) in 20 mL dichloromethane were reacted as above to give oxazoline **a** (0.51g, 91% after purification by column chromatography with 50% EtOAc, 40% hexane and 5% Et<sub>3</sub>N as eluent).



6-Anthracyl-4,5-dimethyl-3-phenyl-2-[1-(1-hydroxymethyl-2-methylpropyl)amino]carbonyl-1-phospha-2,5-norbornadiene sulfide **b** (0.53g, 0.0960 mmol), Et<sub>3</sub>N (0.49g, 0.480 mmol), DMAP (0.0060g, 0.0048 mmol) and MsCl (0.22g, 0.0192 mmol) in 20 mL dichloromethane were reacted in the same way to give oxazoline **b** (0.49g, 95% after purification by column chromatography with 50% EtOAc, 40% hexane and 5% Et<sub>3</sub>N as eluent).

**a:** mp 97-100 °C; <sup>1</sup>H NMR 8.47-7.25 (m, 14H), 4.13-3.96 (m, 1H), 4.10-3.85 (m, 2H), 3.11 (d, J<sub>PH</sub> = 6.9 Hz, 2H), 1.75 (d, J<sub>PH</sub> = 2.7 Hz, 3H), 1.73-1.65 (m, 1H), 1.52 (s, 3H), 0.75 (d, J<sub>HH</sub> = 6.9 Hz, 3H), 0.74 (d, J<sub>HH</sub> = 6.9 Hz, 3H); <sup>13</sup>C NMR 171.55 (d, J<sub>PC</sub> = 10.8 Hz), 163.47 (d, J<sub>PC</sub> =



13.7 Hz), 157.92 (d,  $J_{PC} = 11.1$  Hz), 140.48 (d,  $J_{PC} = 63.5$  Hz), 133.52 (d,  $J_{PC} = 61.2$  Hz), 134.59-125.10 (m, Ar), 73.19 (d,  $J_{PC} = 57.8$  Hz), 72.62 (s), 69.35 (s), 56.69 (d,  $J_{PC} = 17.9$  Hz), 32.20 (s), 19.19 (d,  $J_{PC} = 15.9$  Hz), 18.59 (s), 17.80 (s), 15.82 (d,  $J_{PC} = 12.8$  Hz);  $^{31}\text{P}$  NMR 52.33; IR  $\text{cm}^{-1}$  3055, 2966, 2900, 2870, 1660, 1623, 1583, 1520, 1491, 1450, 1439, 1384, 1354, 1306, 1255, 1244, 1214, 1200, 1178, 1093, 1052, 1011, 967, 953, 934, 901, 857, 805, 702, 665; MS LREI m/z (% int.) 533.3 ( $\text{M}^+$ , 100), HREI calcd for  $\text{C}_{34}\text{H}_{32}\text{NOPS}$  m/e 533.1942, measured m/e 533.1931; TLC (50% EtOAc, 40% hexane, 5% Et<sub>3</sub>N)  $R_f$  0.34.

**b:** mp 92-95 °C;  $^1\text{H}$  NMR 8.46-7.25 (m, 14H), 4.15-3.82 (m, 2H), 4.00-3.92 (m, 1H), 3.11 (d,  $J_{PH} = 6.9$  Hz, 2H), 1.73 (d,  $J_{PH} = 2.7$  Hz, 3H), 1.51 (s, 3H), 0.69 (d,  $J_{HH} = 6.9$  Hz, 3H), 0.68 d,  $J_{HH} = 6.9$  Hz, 3H);  $^{13}\text{C}$  NMR 171.96 (d,  $J_{PC} = 11.1$  Hz), 163.63 (d,  $J_{PC} = 13.7$  Hz), 158.20 (d,  $J_{PC} = 10.5$  Hz), 140.29 (d,  $J_{PC} = 63.5$  Hz), 133.96 (d,  $J_{PC} = 60.6$  Hz), 134.45-125.08 (m, Ar), 72.88 (d,  $J_{PC} = 60.6$  Hz), 72.48 (s), 69.64 (s), 56.80 (d,  $J_{PC} = 17.9$  Hz), 32.24 (s), 19.14 (d,  $J_{PC} = 15.9$  Hz), 18.22 (s), 17.81 (s), 15.80 (d,  $J_{PC} = 12.8$  Hz);  $^{31}\text{P}$  NMR 52.19; IR  $\text{cm}^{-1}$  3055, 2966, 2929, 2907, 2870, 1664, 1623, 1583, 1520, 1491, 1450, 1439, 1413, 1384, 1373, 1351, 1306, 1244, 1214, 1196, 1141, 1096, 1052, 1011, 964, 934, 901, 886, 857, 801, 750, 698, 665; MS LREI m/z (% int.) 533.3 ( $\text{M}^+$ , 100), HREI calcd for  $\text{C}_{34}\text{H}_{32}\text{NOPS}$  m/e 533.1942, measured m/e 533.1947; TLC (50% EtOAc, 40% hexane, 5% Et<sub>3</sub>N)  $R_f$  0.44.

### **General Procedure for Reduction of Phosphine Sulfides.**

Raney nickel (~25 equiv.) in a Schlenk tube was washed 3 times with  $\text{CH}_3\text{OH}$ , 3 times with  $\text{Et}_2\text{O}$  and 3 times with degassed  $\text{CH}_3\text{CN}$ . A solution of phosphine sulfide in  $\text{CH}_3\text{CN}$  is added and the

mixture is freeze-pump-thaw-degassed for three cycles. The suspension is stirred until the reduction is complete ( $^{31}\text{P}$  NMR, usually 1-1.5 h). Thus obtained phosphine (**1**, **2**, **3** or **4**) is used directly in a catalyst preparation.

### **Enantioselective allylic alkylation.**

To a 50 mL Schlenk flask containing a  $\text{C}_6\text{H}_6$  solution of the ligand (4.5 mol %) and  $[\text{Pd}(\text{allyl})\text{Cl}]_2$  (1 mol%), 1,3-diphenylpropenylacetate in 1 mL  $\text{C}_6\text{H}_6$  is added via syringe. The nucleophile is made in a separate flask where 3 mL  $\text{C}_6\text{H}_6$  and dimethyl malonate (3 equiv.), followed by TBAF (3 equiv., 1M in THF) and BSA (3 equiv.) are added. The solution is stirred for 10 min and transferred via syringe to an additional funnel. The nucleophile is added drop wise to the solution of the acetate and the catalyst over 30 min period. At the end of the addition TLC ( $\text{KMnO}_4$ ) shows complete conversion. The mixture is diluted with ether and washed twice with aqueous  $\text{NaHCO}_3$ . The organic phase is dried over  $\text{Na}_2\text{SO}_4$ . The product is purified by column chromatography, using 35% EtOAc, 65% hexane as eluent. Enantiomeric excess is determined by  $^1\text{H}$  NMR using  $\text{eu}(\text{hfc})_3$  shift reagent.

### **Enantioselective Heck reaction.**

To a solution of the ligand (8 mol %) and  $\text{Pd}_2(\text{dba})_3$  (3mol%) in a Schlenk tube, cyclohex-1-en-1-yl triflate, followed by 2,3-dihydrofuran (5equiv.) and base (3 equiv.) are added. The solution is freeze-pump-thaw degassed for three cycles. The conversion and the enantiomeric excess are determined by chiral GC using Chiraldex -CD-TFA, 30 m column.