Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

A [2+2+2] cyclization strategy for the synthesis of phosphorus embedding [6]helicene-like structures

Paul Aillard, Pascal Retailleau, Arnaud Voituriez* and Angela Marinetti*

Institut de Chimie des Substances Naturelles; CNRS UPR 2301; 1, avenue de la Terrasse, 91198 Gif-sur-Yvette Cedex, France.

arnaud.voituriez@cnrs.fr

angela.marinetti@cnrs.fr

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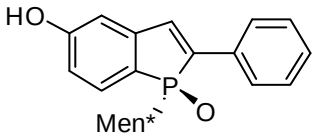
I. General information.

Reactions were run under an inert atmosphere (argon), by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O and CH_2Cl_2). All reagents and solvents were of commercial quality and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on plates precoated with silica gel (Merck 60 F_{254}). The developed chromatogram was visualized by UV absorbance. Flash column chromatography was performed using 40-63 mesh silica gel. Purifications have been performed on a CombiFlash Companion TS Chromatography system, unless otherwise stated. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded on either Brucker AV 500 or AV 300 spectrometers. Chemical shifts are reported in parts per million relative to an internal standard of residual chloroform (δ = 7.26 ppm for ^1H NMR and 77.16 ppm for ^{13}C NMR). IR spectra were recorded on a Perkin-Elmer FT-IR spectrophotometer and are reported in reciprocal centimeters (cm^{-1}). High resolution mass spectra (HRMS-ESI) were obtained on a LCT Waters equipment. Optical rotations were determined on a JASCO P-1010 polarimeter. Data are reported as follows: $[\alpha]_D^{temp}$ (*c* in g/100 mL, solvent). HPLC was performed at a column temperature of 20°C on a Waters 2695 Separations Module equipped with a diode array UV detector.

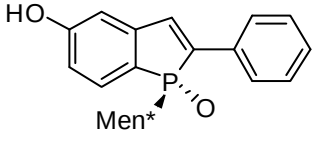
II. Experimental procedures.

I.1. 5-hydroxy-1-(*l*-menthyl)-1-oxo-2-phenyl-1*H*-phosphindoles (S_P)-**1b** and (R_P)-**1c**, (l-menthyl = (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl). To a solution of *tert*-butyllithium 1.7 M in pentane (17.9 mmol, 10.5 mL) was added (*Z*)-(4-bromo-3-(2-bromo-2-phenylvinyl)phenoxy)(*tert*-butyl)dimethylsilane (4.27 mmol, 2.0 g) in anhydrous diethyl ether (45 mL) at -78°C. The reaction mixture was then stirred for 20 min before adding dichloro((1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)phosphine (5.12 mmol, 1.24 g). The reaction mixture was stirred overnight at room temperature. A saturated solution of $NaHCO_3$ was added, the layers were separated and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was then dissolved in 50 mL of CH_2Cl_2, then H_2O_2 (33% solution, 4 equiv.) was added. After 10 min a tetrabutylammonium fluoride solution (1.0 M in THF, 12.8 mmol) was added. After 30 min stirring, the mixture was hydrolyzed with 50 mL of a saturated NH_4Cl solution. The layers were separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel with a CH_2Cl_2-MeOH gradient (0% to 3% MeOH) to afford the desired compounds **1b,c** (1.4 g, 86%). The epimers were then separated by preparative HPLC with an heptanes/AcOEt gradient (90 to 100% AcOEt), retention times: 9 min (S_P)-**1b** and 12 min (R_P)-**1c**.

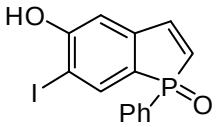
(S_P)-5-hydroxy-1-(*l*-menthyl)-1-oxo-2-phenyl-1*H*-phosphindole (**1b**) (yellow oil); R_f 0.70 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.37-7.32 (m, 1H), 7.30 (t, *J* = 8.0 Hz, 1H), 6.93 (d, J_{H-P} = 34.0 Hz, 1H), 6.71 (dt, *J* = 8.0, 2.5 Hz, 1H), 6.61 (t, *J* = 2.5 Hz, 1H), 2.97-2.88 (m, 1H), 2.35-2.25 (m, 1H), 1.77-1.41 (m, 4H), 1.22-1.08 (m, 2H), 1.06 (d, *J* = 7.0 Hz, 3H), 1.04 (d, *J* = 6.5 Hz, 3H), 0.69-0.61 (m, 1H), 0.62 (d, *J* = 6.5 Hz, 3H), 0.33-0.24 (m, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (C), 144.7 (d, J_{C-P} = 27.2 Hz, C), 137.4 (d, J_{C-P} = 89.4 Hz, C), 136.4 (d, J_{C-P} = 17.0 Hz, CH), 133.4 (d, J_{C-P} = 10.4 Hz, C), 130.9 (d, J_{C-P} = 11.0 Hz, CH), 129.2 (CH x 2), 128.8 (CH), 126.3 (d, J_{C-P} = 6.0 Hz, CH), 117.1 (d, J_{C-P} = 104.2 Hz, C), 115.7 (d, J_{C-P} = 10.9 Hz, CH), 113.6 (d, J_{C-P} = 9.8 Hz, CH), 44.6 (CH), 40.6 (d, J_{C-P} = 64.9 Hz, CH), 34.2 (CH_2), 34.1 (CH_2), 32.7 (d, J_{C-P} = 14.7 Hz, CH), 30.0 (CH), 24.9 (d, J_{C-P} = 13.1 Hz, CH_2), 22.4 (CH_3), 21.6 (CH_3), 16.1 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 60.6 ppm; IR: ν_{max} = 3041, 2953, 2926, 2869, 1604, 1586, 1558, 1454, 1370, 1268, 1248, 1200, 1148, 1130, 1117, 1061, 897, 857, 793, 759, 691 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{30}O_2P$ $[M+H]^+$: 381.1983, found: 381.1990; $[\alpha]_D^{25}$= +33 (c = 1, $CHCl_3$).



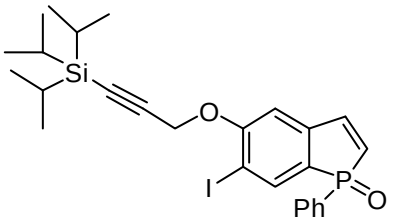
(R_P)-5-hydroxy-1-(*l*-menthyl)-1-oxo-2-phenyl-1*H*-phosphindole (**1c**) (yellow oil); R_f 0.68 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.40-7.29 (m, 4H), 6.92 (d, J_{H-P} = 34.0 Hz, 1H), 6.70-6.64 (m, 2H), 2.48-2.43 (m, 1H), 2.31-2.22 (m, 1H), 1.82-1.77 (m, 1H), 1.66-1.61 (m, 1H), 1.59-1.52 (m, 1H), 1.31-1.24 (m, 1H), 1.20-1.14 (m, 1H), 0.98-0.82 (m, 3H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.73-0.65 (m, 1H), 0.62 (d, *J* = 7.0 Hz, 3H),



0.56 (d, J = 6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 144.0 (d, $J_{C\text{-}P}$ = 26.2 Hz, C), 138.8 (d, $J_{C\text{-}P}$ = 87.2 Hz, C), 138.3 (d, $J_{C\text{-}P}$ = 17.5 Hz, CH), 134.6 (d, $J_{C\text{-}P}$ = 10.9 Hz, C), 129.9 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 129.0 (CH), 128.8 (CH), 126.6 (d, $J_{C\text{-}P}$ = 5.4 Hz, CH), 118.9 (d, $J_{C\text{-}P}$ = 106.9 Hz, C), 116.0 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 113.8 (d, $J_{C\text{-}P}$ = 9.8 Hz, CH), 43.8 (CH), 40.1 (d, $J_{C\text{-}P}$ = 63.2 Hz, CH), 34.9 (CH_2), 34.5 (CH_2), 33.2 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH), 28.3 (CH), 25.0 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH_2), 22.6 (CH_3), 21.3 (CH_3), 15.9 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 58.2 ppm; IR: ν_{max} = 3056, 2954, 2926, 2869, 1604, 1588, 1559, 1455, 1370, 1301, 1269, 1248, 1199, 1146, 1130, 1116, 1063, 899, 790, 761, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{30}O_2P$ $[M+H]^+$: 381.1983, found: 381.1986; $[\alpha]_D^{25}$= -194 (c = 1, $CHCl_3$).



I.2. 5-hydroxy-6-iodo-1-oxo-1-phenyl-1*H*-phosphindole (S1). To a solution of 5-hydroxy-1-phenyl-1*H*-phosphindole-1-oxide **1a**[1] (1.6 mmol, 385 mg) in DMF (14 mL) was added NIS (1.6 mmol, 358 mg) at -78°C. The reaction mixture was warmed to 0°C and stirred at this temperature for 1h. The reaction mixture was quenched by addition of $NH_4Cl_{sat.}$ and extracted twice with EtOAc. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel with a CH_2Cl_2-MeOH gradient (2% to 5% MeOH) to afford **S1** (432 mg, 74% yield, white powder); R_f 0.23 (EtOAc); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.31 (s, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.68-7.61 (m, 3H), 7.56-7.48 (m, 3H), 7.04 (d, J = 2.5 Hz, 1H), 6.68 (dd, $J_{H\text{-}P}$ = 26.5 Hz, $J_{H\text{-}H}$ = 9.0 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 160.8 (C), 144.6 (d, $J_{C\text{-}P}$ = 11.9 Hz, CH), 144.1 (d, $J_{C\text{-}P}$ = 33.6 Hz, C), 138.6 (d, $J_{C\text{-}P}$ = 11.9 Hz, CH), 132.2 (CH), 130.5 (d, $J_{C\text{-}P}$ = 99.3 Hz, C), 130.4 (d, $J_{C\text{-}P}$ = 10.1 Hz, CH), 128.9 (d, $J_{C\text{-}P}$ = 11.9 Hz, CH), 127.8 (d, $J_{C\text{-}P}$ = 93.0 Hz, CH), 123.7 (d, $J_{C\text{-}P}$ = 108.4 Hz, C), 111.9 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 85.1 (d, $J_{C\text{-}P}$ = 12.8 Hz, C); ^{31}P NMR (121 MHz, $CDCl_3$) δ = 37.1 ppm; IR: ν_{max} = 3056, 1718, 1604, 1542, 1437, 1269, 1174, 1143, 1111, 765, 746, 716, 692 cm^{-1}; HRMS (ESI) calcd. for $C_{14}H_{11}IO_2P$ $[M+H]^+$: 368.9541, found: 368.9559.

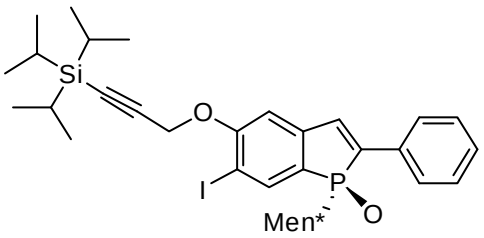


I.3. 6-iodo-1-oxo-1-phenyl-5-(3-(triisopropylsilyl)prop-2-ynyloxy)-1*H*-phosphindole (2a). To a solution of **S1** (1.09 mmol, 400 mg) in DMF (7 mL) was added K_2CO_3 (2.18 mmol, 301 mg) and (3-bromoprop-1-yn-1-yl)triisopropylsilane (1.31 mmol, 360 mg). The mixture was stirred at room temperature for 3h, quenched by addition of $NH_4Cl_{sat.}$ and extracted twice with EtOAc. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography on silica gel with a petroleum ether/EtOAc gradient (60% to 100% AcOEt), to afford the desired compound as a pale yellow oil (583 mg, 95% yield); R_f 0.59 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 7.70-7.64 (m, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.47-7.40 (m, 2H), 7.29 (dd, $J_{H\text{-}P}$ = 39.0 Hz, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.46 (dd, $J_{H\text{-}P}$ = 25.5 Hz, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 4.89 (s, 2H), 1.03 (s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1 (C), 144.1 (d, $J_{C\text{-}P}$ =

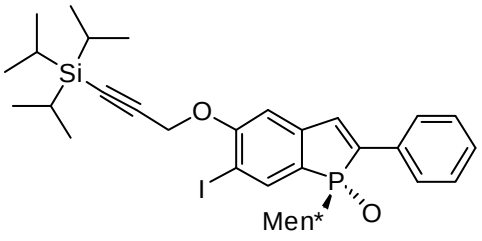
[1] K. Yavari, S. Moussa, B. Ben Hassine, P. Retailleau, A. Voituriez, A. Marinetti, *Angew. Chem. Int. Ed.* **2012**, *51*, 6748-6752.

32.2 Hz, C), 144.0 (d, J_{C-P} = 12.0 Hz, CH), 139.6 (d, J_{C-P} = 12.0 Hz, CH), 132.5 (CH), 130.8 (d, J_{C-P} = 10.9 Hz, CH), 128.9 (d, J_{C-P} = 12.5 Hz, CH), 128.8 (d, J_{C-P} = 102.0 Hz, C), 128,3 (d, J_{C-P} = 94.4 Hz, CH), 126.1 (d, J_{C-P} = 109.7 Hz, C), 110.1 (d, J_{C-P} = 11.5 Hz, CH), 100.4 (C), 91.6 (C), 87.3 (d, J_{C-P} = 12.6 Hz, C), 57.9 (CH_2), 18.5 (CH_3), 11.1 (CH); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.3 ppm; IR: ν_{max} = 2943, 2865, 1591, 1528, 1461, 1438, 1262, 1236, 1199, 1166, 1113, 1029, 989, 883, 745, 680 cm^{-1}.

I.4. 6-iodo-1-(*l*-menthyl)-1-oxo-2-phenyl-5-(3-(triisopropyl-silyl)prop-2-ynyloxy)-1*H*-phosphindoles (2b) and (2c). To a solution of **1b** or **1c** (1.0 equiv) in DMF (0.2M) was added NIS (1.0 equiv) at -78°C. Then the reaction was warmed to 0°C and stirred at this temperature for 1h. K_2CO_3 (3 equiv) and (3-bromoprop-1-yn-1-yl)triisopropylsilane (2.1 equiv) were added and the mixture was stirred at room temperature for 3h. The reaction mixture was quenched by addition of a saturated NH_4Cl solution and extracted with EtOAc. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was purified by silica gel column chromatography with a 60/40 petroleum ether /EtOAc mixture.



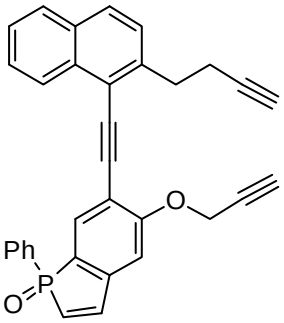
(S_P)-2b (82% yield, white powder); mp 184-186°C; R_f 0.75 (40% EtOAc / petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.0 Hz, 1H), 7.80 (d, J = 7.5 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.40-7.35 (m, 1H), 7.23 (d, J_{H-P} = 31.5 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 4.92-4.85 (m, 2H), 3.00-2.95 (m, 1H), 2.30-2.21 (m, 1H), 1.79-1.75 (m, 1H), 1.65-1.60 (m, 1H), 1.51-1.46 (m, 2H), 1.21-0.96 (m, 29 H), 0.73-0.64 (m, 1H), 0.64 (d, J = 6.5 Hz, 3H), 0.30-0.21 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9 (C), 144.8 (d, J_{C-P} = 26.2 Hz, C), 140.6 (d, J_{C-P} = 11.0 Hz, CH), 139.6 (d, J_{C-P} = 87.8 Hz, C), 134.3 (d, J_{C-P} = 16.4 Hz, CH), 133.5 (d, J_{C-P} = 10.4 Hz, C), 129.3 (CH), 129.2 (CH), 126.4 (d, J_{C-P} = 6.0 Hz, CH), 123.8 (d, J_{C-P} = 97.7 Hz, C), 109.6 (d, J_{C-P} = 9.8 Hz, CH), 100.6 (C), 91.5 (C), 85.6 (d, J_{C-P} = 11.5 Hz, C), 57.9 (CH_2), 45.1 (CH), 40.9 (d, J_{C-P} = 64.4 Hz, CH), 34.5 (CH_2), 34.2 (CH_2), 32.7 (d, J_{C-P} = 14.8 Hz, CH), 30.0 (CH), 25.1 (d, J_{C-P} = 13.1 Hz, CH_2), 22.5 (CH_3), 21.5 (CH_3), 18.7 (CH_3), 16.1 (CH_3), 11.2 (CH); ^{31}P NMR (202 MHz, $CDCl_3$) δ 57.6 ppm; IR: ν_{max} = 2944, 2865, 1578, 1460, 1368, 1265, 1206, 1163, 1076, 1034, 1018, 996, 884, 762, 680, 664 cm^{-1}; HRMS (ESI) calcd. for $C_{36}H_{51}IO_2PSi$ $[M+H]^+$: 701.2441, found: 701.2468; $[\alpha]_D^{25}$= +89 (c = 1, $CHCl_3$).



(R_P)-2c (70% yield, yellow oil); R_f 0.72 (40% EtOAc / petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.5 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.43-7.34 (m, 3H), 7.15 (d, J_{H-P} = 33.5 Hz, 1H), 7.07 (d, J = 2.5 Hz, 1H), 4.91-4.84 (m, 2H), 2.69-2.64 (m, 1H), 2.27-2.19 (m, 1H), 1.64-1.56 (m, 3H), 1.20-1.17 (m, 1H), 1.05-0.92 (m, 23 H), 0.84-0.76 (m, 1H), 0.75 (d, J = 6.5 Hz, 3H), 0.72 (d, J = 6.5 Hz, 3H), 0.71-0.63 (m, 1H), 0.62 (d, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8 (C), 144.0 (d, J_{C-P} = 26.2 Hz, C), 140.5 (d, J_{C-P} = 83.0 Hz, C), 139.2 (d, J_{C-P} = 11.5 Hz, CH), 136.3

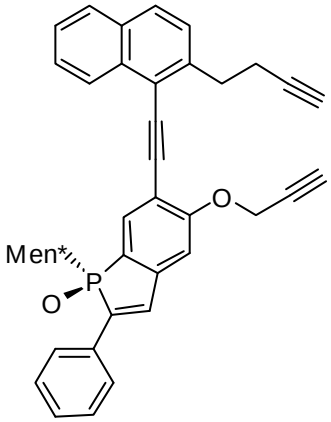
(d, $J_{C\text{-}P}$ = 17.0 Hz, CH), 134.7 (d, $J_{C\text{-}P}$ = 9.8 Hz, C), 129.0 (CH), 126.6 (d, $J_{C\text{-}P}$ = 5.4 Hz, CH), 125.7 (d, $J_{C\text{-}P}$ = 100.4 Hz, C), 109.5 (d, $J_{C\text{-}P}$ = 9.8 Hz, CH), 100.6 (C), 91.4 (C), 85.9 (d, $J_{C\text{-}P}$ = 11.4 Hz, C), 57.9 (CH_2), 43.6 (CH), 40.4 (d, $J_{C\text{-}P}$ = 63.3 Hz, CH), 35.0 (CH_2), 34.4 (CH_2), 32.9 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH), 28.3 (CH), 25.0 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH_2), 22.5 (CH_3), 21.2 (CH_3), 18.6 (CH_3), 15.9 (CH_3), 11.1 (CH); ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.0 ppm; IR: ν_{max} = 2944, 2866, 1717, 1572, 1460, 1392, 1367, 1347, 1266, 1229, 1204, 1164, 1078, 1034, 993, 884, 761, 696, 679, 666 cm^{-1}; HRMS (ESI) calcd. for $C_{36}H_{51}IO_2PSi$ $[M+H]^+$: 701.2441, found: 701.2443; $[\alpha]_D^{25}$= -168 (c = 1, $CHCl_3$).

I.5. 6-((2-(but-3-ynyl)naphthalen-1-yl)ethynyl)-1-oxo-1-phenyl-5-(prop-2-ynyloxy)-1*H*-phosphindole (4a). A Schlenk flask was charged with **2a** (1.03 mmol, 580 mg), $Pd(PPh_3)_4$ (0.021 mmol, 24 mg), CuI (0.041 mmol, 8 mg), and flushed with argon. Diisopropylamine (2 mL) and then (4-(1-ethynylnaphthalen-2-yl)but-1-ynyl)triisopropylsilane **3** (1.24 mmol, 447 mg) in diisopropylamine (2 mL) were added and the reaction mixture was stirred at 80°C for 15 min. The reaction mixture was quenched by the addition of $NH_4Cl_{sat.}$ and extracted three times with EtOAc. The combined fractions were dried, concentrated and the residue was diluted in THF. Tetrabutylammonium fluoride (1 M in THF) (2.58 mmol, 2.6 mL) was added and the mixture was stirred at room temperature for 2h. The solution was evaporated in *vacuo* to dryness and the residue was purified by flash chromatography on silica gel with a CH_2Cl_2-MeOH gradient (2% to 5% MeOH), to obtain the desired triyne **4a**. (352 mg, 71% yield, yellow oil); R_f 0.45 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.82-7.72 (m, 4H), 7.58-7.51 (m, 2H), 7.48-7.34 (m, 5H), 7.10 (bs, 1H), 6.56 (dd, $J_{H\text{-}P}$ = 25.0 Hz, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 5.00-4.93 (m, 2H), 3.29 (t, *J* = 7.5 Hz, 2H), 2.68-2.61 (m, 3H), 1.97 (t, *J* = 2.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.0 (C), 144.5 (d, $J_{C\text{-}P}$ = 12.0 Hz, CH), 143.8 (d, $J_{C\text{-}P}$ = 31.7 Hz, C), 141.7 (C), 133.52 (d, $J_{C\text{-}P}$ = 12.0 Hz, CH), 133.49 (C), 132.6 (d, $J_{C\text{-}P}$ = 2.2 Hz, CH), 132.0 (C), 131.1 (CH), 131.0 (CH), 129.09 (CH), 129.08 (d, $J_{C\text{-}P}$ = 95.4 Hz, CH), 128.9 (CH), 128.8 (CH), 128.65 (d, $J_{C\text{-}P}$ = 41.5 Hz, C), 128.1 (CH), 127.4 (CH), 127.1 (CH), 126.3 (CH), 126.0 (CH), 124.4 (d, $J_{C\text{-}P}$ = 110.7 Hz, C), 119.2 (C), 114.7 (d, $J_{C\text{-}P}$ = 12.6 Hz, C), 109.3 (d, $J_{C\text{-}P}$ = 11.0 Hz, CH), 94.3 (C), 92.9 (C), 84.2 (C), 77.7 (C), 77.0 (CH), 69.1 (CH), 56.9 (CH_2), 34.6 (CH_2), 19.7 (CH_2); ^{31}P NMR (202 MHz, $CDCl_3$) δ 40.0 ppm; IR: ν_{max} = 3297, 3057, 2929, 1721, 1593, 1524, 1438, 1411, 1292, 1265, 1195, 1166, 1113, 1033, 838, 749, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{24}O_2P$ $[M+H]^+$: 483.1514, found: 483.1521.

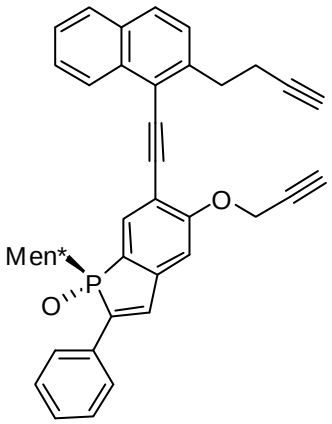


I.6. 6-((2-(but-3-ynyl)naphthalen-1-yl)ethynyl)-1-(*l*-menthyl)-1-oxo-2-phenyl-5-(prop-2-ynyloxy)-1*H*-phosphindole (4b) and (4c). A Schlenk flask was charged with **2b** or **2c** (1.0 equiv), $Pd(PPh_3)_4$ (2 mol%), CuI (4 mol%), and flushed with argon. Diisopropylamine (0.2 M) and then (4-(1-ethynylnaphthalen-2-yl)but-1-ynyl)triisopropylsilane **3** (1.2 equiv) in diisopropylamine (0.2 M) were added and the reaction mixture was stirred at 80°C for 15 min. The reaction mixture was quenched by addition of a saturated NH_4Cl solution and extracted three times with EtOAc. The combined fractions were concentrated and THF was added.

Tetrabutylammonium fluoride (2.5 equiv) was then added and the mixture was stirred at room temperature for 2h. The solution was evaporated *in vacuo* to dryness and the residue was purified on silica gel with a CH_2Cl_2-MeOH gradient (0% to 3% MeOH) to obtain the desired triyne.



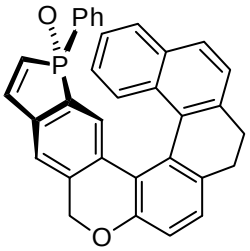
(S_P)-4b (81% yield, yellow oil); R_f 0.63 (40% EtOAc / petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.5 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 7.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.45-7.35 (m, 5H), 7.09 (d, *J* = 1.5 Hz, 1H), 5.02-4.95 (m, 2H), 3.33 (t, *J* = 7.5 Hz, 2H), 3.14-3.08 (m, 1H), 2.72 (td, *J* = 8.0, 2.5 Hz, 2H), 2.66 (t, *J* = 2.0 Hz, 1H), 2.37-2.28 (m, 1H), 2.01 (t, *J* = 2.5 Hz, 1H), 1.81-1.77 (m, 1H), 1.63-1.58 (m, 1H), 1.54-1.48 (m, 1H), 1.20 (d, *J* = 6.5 Hz, 3H), 1.19-1.11 (m, 3H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.75-0.67 (m, 1H), 0.66 (d, *J* = 6.5 Hz, 3H), 0.38-0.29 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (C), 144.6 (d, J_{C-P} = 25.6 Hz, C), 141.5 (C), 140.3 (d, J_{C-P} = 87.2 Hz, C), 134.8 (d, J_{C-P} = 15.8 Hz, CH), 134.2 (d, J_{C-P} = 10.9 Hz, CH), 133.6 (C), 133.4 (d, J_{C-P} = 10.4 Hz, C), 132.0 (C), 129.3 (CH), 129.2 (CH), 128.7 (CH), 128.2 (CH), 127.5 (CH), 127.0 (CH), 126.5 (CH), 126.4 (CH), 126.3 (CH), 126.0 (CH), 122.0 (d, J_{C-P} = 100.1 Hz, C), 119.4 (C), 113.2 (d, J_{C-P} = 11.4 Hz, C), 108.8 (d, J_{C-P} = 9.8 Hz, CH), 94.8 (C), 92.6 (C), 84.2 (C), 77.8 (C), 76.8 (CH), 69.1 (CH), 56.8 (CH_2), 45.1 (CH), 41.0 (d, J_{C-P} = 64.4 Hz, CH), 34.6 (CH_2), 34.5 (CH_2), 34.2 (CH_2), 32.7 (d, J_{C-P} = 15.3 Hz, CH), 30.1 (CH), 25.1 (d, J_{C-P} = 13.1 Hz, CH_2), 22.5 (CH_3), 21.6 (CH_3), 19.7 (CH_2), 16.2 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 58.0 ppm; IR: ν_{max} = 3305, 3055, 2953, 2869, 1591, 1447, 1249, 1205, 1154, 1069, 1039, 761, 752, 692 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2919; $[\alpha]_D^{25}$= +148 (c = 1, $CHCl_3$).



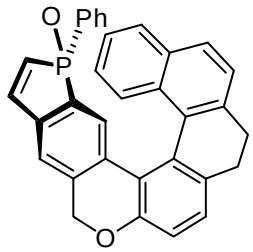
(R_P)-4c (68% yield, yellow oil); R_f 0.60 (40% EtOAc / petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.88-7.78 (m, 4H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.48-7.35 (m, 4H), 7.30 (d, J_{H-P} = 33.5 Hz, 1H), 7.06 (d, *J* = 2.0 Hz, 1H), 5.00-4.95 (m, 2H), 3.43-3.33 (m, 2H), 2.81-2.70 (m, 3H), 2.64 (t, *J* = 2.0 Hz, 1H), 2.39-2.25 (m, 1H), 2.04 (t, *J* = 2.5 Hz, 1H), 1.78-1.55 (m, 3H), 1.30-1.20 (m, 2H), 1.05-0.95 (m, 1H), 0.96-0.82 (m, 1H), 0.77 (d, *J* = 6.5 Hz, 6H), 0.76-0.65 (m, 1H), 0.66 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (C), 143.8 (d, J_{C-P} = 25.6 Hz, C), 141.6 (C), 141.4 (d, J_{C-P} = 82.9 Hz, C), 136.9 (d, J_{C-P} = 16.9 Hz, CH), 134.9 (d, J_{C-P} = 10.4 Hz, C), 133.6 (C), 133.0 (d, J_{C-P} = 10.9 Hz, CH), 132.1 (C), 129.1 (CH), 128.8 (CH), 128.2 (CH), 127.5 (CH), 127.2 (CH), 126.8 (CH), 126.7 (CH), 126.4 (CH), 126.1 (CH), 124.2 (d, J_{C-P} = 102.5 Hz, C), 119.4 (C), 113.6 (d, J_{C-P} = 12.0 Hz, C), 108.8 (d, J_{C-P} = 9.8 Hz, CH), 94.8 (C), 92.8 (C), 84.3 (C), 77.8 (C), 76.9 (CH), 69.1 (CH), 56.9 (CH_2), 43.8 (CH), 40.6 (d, J_{C-P} = 63.5 Hz, CH), 35.1 (CH_2), 34.7 (CH_2), 34.5 (CH_2), 33.1 (d, J_{C-P} = 13.6 Hz, CH), 28.5 (CH),

25.1 (d, $J_{C\text{-}P}$ = 13.7 Hz, CH_2), 22.6 (CH_3), 21.3 (CH_3), 19.8 (CH_2), 16.0 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.6 ppm; IR: ν_{max} = 3305, 2956, 2928, 2868, 1712, 1592, 1477, 1447, 1331, 1266, 1238, 1202, 1164, 1154, 1120, 1069, 1039, 761, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2906; $[\alpha]_D^{25}$= -232 (c = 1, $CHCl_3$).

I.7. Nickel catalyzed [2+2+2] cycloisomerization of 4a: A Schlenk flask was charged with $Ni(cod)_2$ (0.044 mmol, 12 mg) and triphenylphosphine (0.087 mmol, 23 mg) under inert atmosphere and THF (3 ml) was added. A degassed solution of triyne **4a** (0.22 mmol, 106 mg) in THF (3 ml) was added dropwise to the solution of the catalyst and the reaction mixture was stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel with a CH_2Cl_2-MeOH gradient (2% to 5% MeOH) to afford the desired product as a 40/60 mixture of the two diastereoisomers (R_P*, M*)-**5a** and (S_P*, M*)-**5a'** (64 mg, 60% yield). The diastereoisomers were then separated by preparative HPLC with AcOEt as the eluent (retention times: 7 min (**5a**) and 9 min (**5a'**)).



10-oxo-10-phenyl-1,2,6,10-tetrahydrophenanthro[4,3-f]-phosphindolo[5,6-c]chromene (R_P*, M*)-**5a**; mp 201-203°C; R_f 0.46 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (t, J = 8.5 Hz, 2H), 7.42 (d, J = 8.5 Hz, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.38-7.32 (m, 3H), 7.30 (d, J = 7.5 Hz, 1H), 7.26-7.18 (m, 3H), 7.11 (d, J = 7.0 Hz, 2H), 6.99 (d, J = 2.5 Hz, 1H), 6.92 (t, J = 7.3 Hz, 1H), 6.49 (d, J = 10.0 Hz, 1H), 6.23 (dd, $J_{H\text{-}P}$ = 25.0 Hz, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 5.25 (d, J = 13.0 Hz, 1H), 4.94 (d, J = 13.0 Hz, 1H), 2.95-2.83 (m, 3H), 2.71-2.64 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5 (C), 143.4 (d, $J_{C\text{-}P}$ = 12.8 Hz, CH), 142.8 (C), 142.3 (d, $J_{C\text{-}P}$ = 2.2 Hz, C), 138.3 (C), 133.9 (C), 133.6 (C), 131.8 (CH), 131.2 (C), 130.8 (CH), 130.7 (CH), 129.8 (C), 129.2 (CH), 128.9 (C), 128.70 (CH), 128.67 (d, $J_{C\text{-}P}$ = 16.4 Hz, CH), 128.6 (CH), 128.50 (d, $J_{C\text{-}P}$ = 93.9 Hz, CH), 128.49 (CH), 127.9 (C), 126.9 (CH), 126.1 (CH), 125.9 (d, $J_{C\text{-}P}$ = 11.8 Hz, C), 125.4 (CH), 124.9 (CH), 124.0 (d, $J_{C\text{-}P}$ = 111.1 Hz, C), 122.6 (CH), 114.4 (d, $J_{C\text{-}P}$ = 11.9 Hz, CH), 70.0 (CH_2), 30.8 (CH_2), 30.5 (CH_2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 32.8 ppm; IR: ν_{max} = 3252, 2928, 1603, 1526, 1436, 1292, 1262, 1242, 1201, 1143, 1113, 1038, 827, 743, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{24}O_2P$ $[M+H]^+$: 483.1514, found: 483.1536.

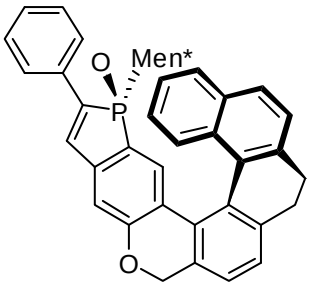


10-oxo-10-phenyl-1,2,6,10-tetrahydrophenanthro[4,3-f]-phosphindolo[5,6-c]chromene (S_P*, M*)-**5a'** (white powder); mp 220-222°C; R_f 0.42 (EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.65 (m, 1H), 7.60-7.52 (m, 1H), 7.48-7.45 (m, 1H), 7.39-7.33 (m, 4H), 7.29 (d, J = 7.5 Hz, 1H), 7.21 (dd, $J_{H\text{-}P}$ = 38.5 Hz, $J_{H\text{-}H}$ = 8.5 Hz, 1H), 7.14-7.08 (m, 3H), 7.00 (d, J = 3.0 Hz, 1H), 6.93-6.86 (m, 2H), 6.76 (d, J = 9.5 Hz, 1H), 6.22 (dd, $J_{H\text{-}P}$ = 25.0 Hz, $J_{H\text{-}H}$ = 8.0 Hz, 1H), 5.26 (d, J = 13.5 Hz, 1H), 4.95 (d, J = 13.5 Hz, 1H), 2.95-2.81 (m, 3H), 2.58 (td, J = 15.0, 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.6 (C), 144.5 (d, $J_{C\text{-}P}$ = 11.8 Hz, CH), 142.8 (C), 142.2 (d, $J_{C\text{-}P}$ = 32.8 Hz, C), 138.5 (C), 134.0 (C), 132.7 (C), 132.2 (d, $J_{C\text{-}P}$ = 10.0 Hz, CH), 132.0 (d, $J_{C\text{-}P}$ = 28.3 Hz, CH),

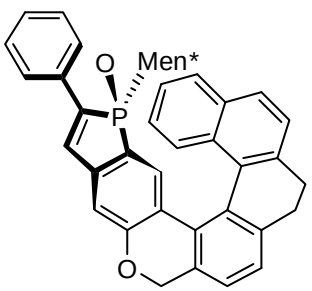
130.8 (C), 130.6 (d, J_{C-P} = 11.9 Hz, CH), 130.3 (C), 129.0 (d, J_{C-P} = 12.8 Hz, CH), 128.8 (d, J_{C-P} = 12.8 Hz, CH), 128.6 (d, J_{C-P} = 11.8 Hz, CH), 128.5 (C), 128.4 (CH), 128.24 (C), 128.18 (CH), 127.8 (d, J_{C-P} = 94.8 Hz, CH), 127.0 (CH), 126.7 (d, J_{C-P} = 11.9 Hz, C), 126.3 (CH), 125.14 (CH), 125.09 (CH), 124.23 (d, J_{C-P} = 111.1 Hz, C), 124.22 (CH), 122.6 (CH), 115.4 (d, J_{C-P} = 11.0 Hz, CH), 70.1 (CH_2), 30.8 (CH_2), 30.3 (CH_2); ^{31}P NMR (202 MHz, $CDCl_3$) δ 41.4 ppm; IR: ν_{max} = 3050, 2937, 2849, 1602, 1527, 1437, 1292, 1242, 1189, 1115, 1037, 836, 741, 727, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{33}H_{24}O_2P$ $[M+H]^+$: 483.1514, found: 483.1535.

I.8. Nickel catalyzed [2+2+2] cycloisomerization of 4b and 4c: A Schlenk flask was charged with $Ni(cod)_2$ (20 mol%) and triphenylphosphine (40 mol%) under inert atmosphere and tetrahydrofuran was added. A degassed solution of triyne **4b** or **4c** (1.0 equiv) in THF (0.1 M) was added dropwise to the solution of the catalyst and the reaction mixture was stirred at room temperature for 15 min. The solvent was removed *in vacuo* and the residue was chromatographed on silica gel to afford pure products.

Starting from the (S_P)-**4b** epimer, the cyclisation step occurred in 68% yield, giving (S_P,*P*)-**5b** and (S_P,*M*)-**5b'** in a 33 /67 ratio.



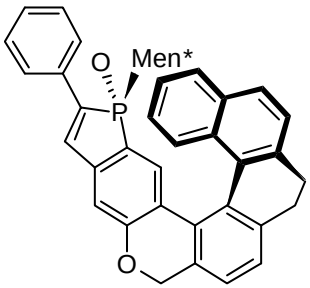
(S_P,*P*)-**5b**; R_f 0.38 (20% EtOAc / 40% petroleum ether / 40% toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.37-7.31 (m, 3H), 7.30-7.25 (m, 1H), 7.19-7.12 (m, 3H), 6.94 (d, *J* = 2.5 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.28 (d, *J* = 13.5 Hz, 1H), 5.03 (d, *J* = 13.5 Hz, 1H), 2.95-2.86 (m, 3H), 2.77-2.70 (m, 1H), 2.00-1.86 (m, 2H), 1.49-1.43 (m, 2H), 1.20-0.85 (m, 4H), 0.81 (d, *J* = 6.5 Hz, 3H), 0.62 (d, *J* = 6.5 Hz, 3H), 0.51 (d, *J* = 6.5 Hz, 3H), 0.47-0.39 (m, 1H), -0.07 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1 (C), 142.89 (d, J_{C-P} = 26.4 Hz, C), 142.86 (C), 139.2 (d, J_{C-P} = 88.2 Hz, C), 138.0 (C), 134.2 (d, J_{C-P} = 16.4 Hz, CH), 134.0 (C), 133.9 (d, J_{C-P} = 12.8 Hz, C), 133.7 (C), 131.0 (C), 130.1 (C), 129.3 (d, J_{C-P} = 10.9 Hz, CH), 129.0 (CH), 128.9 (CH), 128.8 (CH), 128.3 (C), 126.7 (CH), 126.45 (CH), 126.41 (CH), 126.1 (CH), 125.6 (CH), 125.1 (CH), 124.9 (CH), 124.5 (d, J_{C-P} = 10.9 Hz, C), 122.6 (CH), 122.2 (d, J_{C-P} = 105.6 Hz, C), 113.7 (d, J_{C-P} = 10.0 Hz, CH), 69.8 (CH_2), 44.4 (CH), 40.8 (d, J_{C-P} = 64.6 Hz, CH), 34.3 (CH_2), 32.6 (d, J_{C-P} = 14.5 Hz, CH), 30.8 (CH_2), 30.6 (CH_2), 29.3 (CH), 24.8 (d, J_{C-P} = 12.8 Hz, CH_2), 22.4 (CH_3), 21.7 (CH_3), 16.1 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 54.6 ppm; IR: ν_{max} = 2952, 2927, 2867, 1603, 1447, 1364, 1323, 1246, 1205, 1178, 1168, 1143, 1042, 810, 829, 791, 745, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2943; $[\alpha]_D^{25}$= +1506 (c = 1, $CHCl_3$).



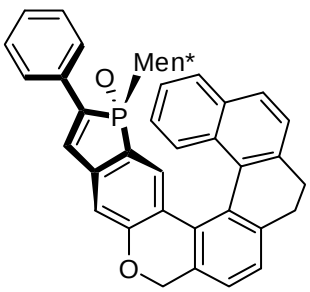
(S_P,*M*)-**5b'**; R_f 0.32 (20% EtOAc / 40% petroleum ether / 40% toluene); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.67 (m, 4H), 7.65 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 1H), 7.40-7.32 (m, 2H), 7.33-7.26 (m, 2H), 7.20-7.12 (m, 3H), 7.09-7.03 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.24 (d, *J* = 13.0 Hz, 1H), 4.88 (d, *J* = 13.0 Hz, 1H), 3.06 (td, *J* = 14.5, 4.0 Hz, 1H), 3.00-2.85 (m, 2H), 2.65-2.54 (m, 2H),

1.88-1.80 (m, 1H), 1.55-1.50 (m, 2H), 1.08-1.01 (m, 1H), 0.93-0.83 (m, 3H), 0.82 (d, *J* = 7.0 Hz, 3H), 0.65 (d, *J* = 7.0 Hz, 3H), 0.63 (d, *J* = 6.5 Hz, 3H), 0.37-0.33 (m, 1H), -0.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.7 (C), 143.6 (d, $J_{C\text{-}P}$ = 26.2 Hz, C), 142.9 (C), 139.2 (d, $J_{C\text{-}P}$ = 90.5 Hz, C), 138.6 (C), 135.4 (d, $J_{C\text{-}P}$ = 15.3 Hz, CH), 134.6 (C), 133.6 (d, $J_{C\text{-}P}$ = 9.8 Hz, C), 133.2 (C), 130.9 (C), 130.6 (C), 129.3 (CH), 129.1 (CH), 128.8 (CH), 128.3 (CH), 127.2 (CH), 127.0 (d, $J_{C\text{-}P}$ = 10.9 Hz, C), 126.7 (CH), 126.24 (CH), 126.17 (CH), 125.7 (CH), 125.6 (CH), 124.7 (CH), 123.8 (d, $J_{C\text{-}P}$ = 98.2 Hz, C), 122.6 (CH), 115.2 (d, $J_{C\text{-}P}$ = 9.8 Hz, CH), 70.2 (CH_2), 43.1 (CH), 39.6 (d, $J_{C\text{-}P}$ = 64.4 Hz, CH), 33.4 (CH_2), 32.8 (CH_2), 32.6 (d, $J_{C\text{-}P}$ = 15.2 Hz, CH), 31.1 (CH_2), 30.3 (CH_2), 29.1 (CH), 25.1 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH_2), 22.3 (CH_3), 21.3 (CH_3), 16.4 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 58.7 ppm; IR: ν_{max} = 2952, 2929, 2866, 1601, 1467, 1446, 1435, 1318, 1246, 1206, 1163, 1142, 1039, 901, 829, 811, 796, 762, 749, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2896; $[\alpha]_D^{25}$= -902 (c = 1, $CHCl_3$).

Starting from the (*R*$_P$)-**4c** epimer, the helical derivatives (*R*$_P$,*P*)-**5c** and (*R*$_P$,*M*)-**5c'** were obtained in 71% total yield (86 /14 ratio).



(*R*$_P$,*P*)-**5c**; R$_f$ 0.31 (20% EtOAc / 40% toluene / 40% petroleum ether); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 1H), 7.74-7.64 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.37-7.27 (m, 4H), 7.18-7.03 (m, 4H), 6.99 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 1H), 5.26 (d, *J* = 13.5 Hz, 1H), 4.95 (d, *J* = 13.5 Hz, 1H), 3.06 (td, *J* = 15.0, 4.5 Hz, 1H), 2.97-2.84 (m, 2H), 2.60 (td, *J* = 15.0, 4.5 Hz, 1H), 1.59-1.35 (m, 4H), 1.14-1.03 (m, 1H), 0.84-0.30 (m, 13H), 0.28-0.13 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2 (C), 143.0 (C), 139.0 (C), 136.1 (d, $J_{C\text{-}P}$ = 15.4 Hz, CH), 134.1 (C), 133.2 (C), 131.0 (C), 130.7 (C), 129.1 (C), 128.9 (CH), 128.8 (CH+C), 128.4 (CH), 128.3 (CH), 126.91 (CH), 126.86 (CH), 126.62 (CH), 126.57 (CH), 126.0 (CH), 125.7 (CH), 125.1 (CH), 122.7 (CH), 115.3 (d, $J_{C\text{-}P}$ = 7.4 Hz, CH), 70.1 (CH_2), 42.5 (CH), 39.0 (d, $J_{C\text{-}P}$ = 60.1 Hz, CH), 34.0 (CH_2), 33.7 (CH_2), 32.6 (bs, CH), 31.2 (CH_2), 30.5 (CH_2), 27.6 (CH), 25.2 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH_2), 22.5 (CH_3), 21.4 (CH_3), 15.9 (CH_3); ^{31}P NMR (121 MHz, $CDCl_3$) δ 56.9 ppm; IR: ν_{max} = 2950, 2928, 2869, 1603, 1446, 1366, 1320, 1288, 1246, 1203, 1165, 1143, 1042, 1030, 897, 830, 808, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2944; $[\alpha]_D^{25}$= + 844 (c = 0.3, $CHCl_3$).

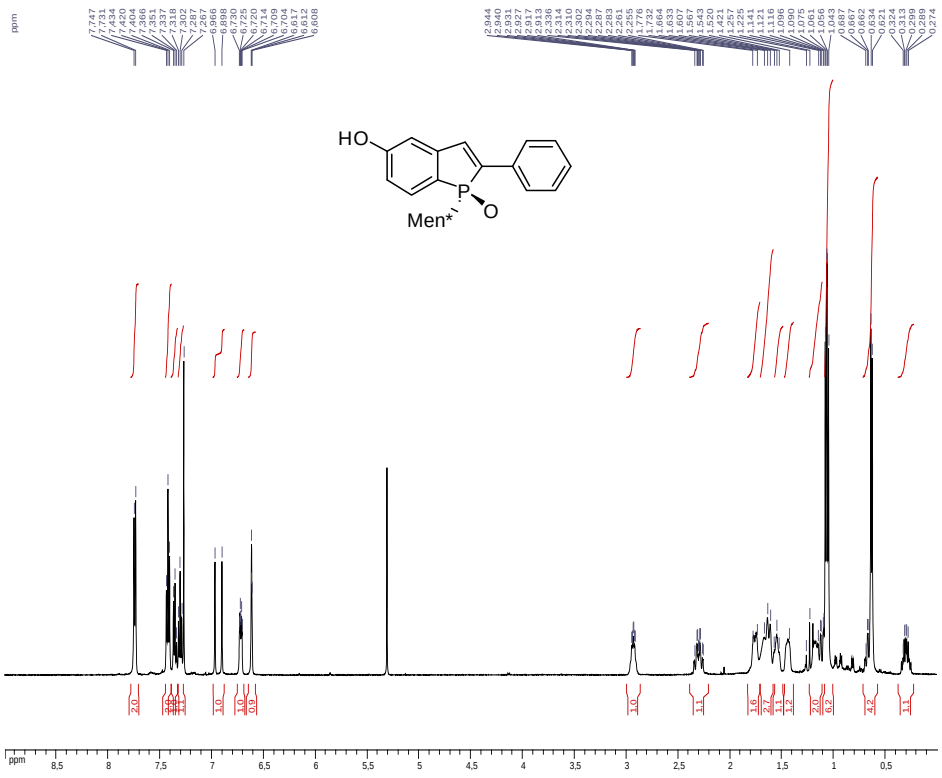


(*R*$_P$,*M*)-**5c'**; R$_f$ 0.44 (20% EtOAc / 40% toluene / 40% petroleum ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.8 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.31-7.19 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.06 (d, $J_{H\text{-}P}$ = 32.4 Hz, 1H), 6.96-6.89 (m, 2H), 6.55 (d, *J* = 9.0 Hz, 1H), 5.26 (d, *J* = 13.5 Hz, 1H), 4.96 (d, *J* = 13.5 Hz, 1H), 3.01-2.86 (m, 3H), 2.70 (td, *J* = 14.4, 5.4 Hz, 1H), 2.16-2.07 (m, 1H), 1.79-1.66 (m, 2H), 1.50-0.85 (m, 5H), 0.78-0.66 (m, 1H), 0.59 (d, *J* = 6.6 Hz, 3H), 0.48 (d, *J* = 6.9 Hz, 3H), 0.42-0.37 (m, 1H), 0.36 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$)

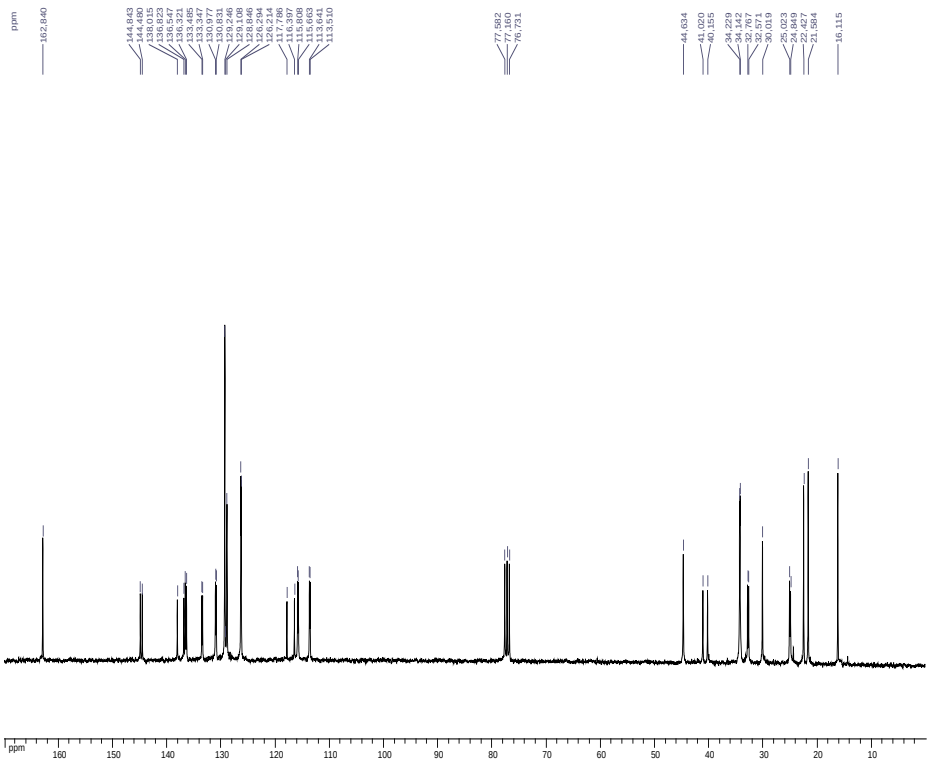
δ 158.9 (C), 142.8 (C), 142.2 (d, $J_{C\text{-}P}$ = 27.3 Hz, C), 140.6 (d, $J_{C\text{-}P}$ = 85.1 Hz, C), 138.1 (C), 135.9 (d, $J_{C\text{-}P}$ = 17.5 Hz, CH), 135.2 (d, $J_{C\text{-}P}$ = 9.8 Hz, C), 133.9 (C), 133.5 (C), 131.1 (C), 130.2 (C), 129.1 (C), 129.0 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz, CH), 128.1 (C), 126.8 (CH), 126.6 (CH), 126.5 (CH), 125.8 (CH), 125.2 (CH), 124.9 (CH), 122.6 (CH), 113.8 (d, $J_{C\text{-}P}$ = 11.4 Hz, CH), 69.9 (CH_2), 43.5 (CH), 40.5 (d, $J_{C\text{-}P}$ = 63.2 Hz, CH), 35.4 (CH_2), 34.4 (CH_2), 33.0 (d, $J_{C\text{-}P}$ = 14.2 Hz, CH), 30.8 (CH_2), 30.7 (CH_2), 28.3 (CH), 24.8 (d, $J_{C\text{-}P}$ = 13.1 Hz, CH_2), 22.5 (CH_3), 21.3 (CH_3), 15.8 (CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 52.4 ppm; IR: ν_{max} = 2959, 2928, 2869, 1604, 1447, 1260, 1092, 1040, 1026, 799, 746, 697, 663 cm^{-1}; HRMS (ESI) calcd. for $C_{43}H_{42}O_2P$ $[M+H]^+$: 621.2922, found: 621.2904; $[\alpha]_D^{25}$= -906 (c = 1, $CHCl_3$).

III. NMR Spectra (^{1}H NMR, ^{13}C NMR and ^{31}P NMR).

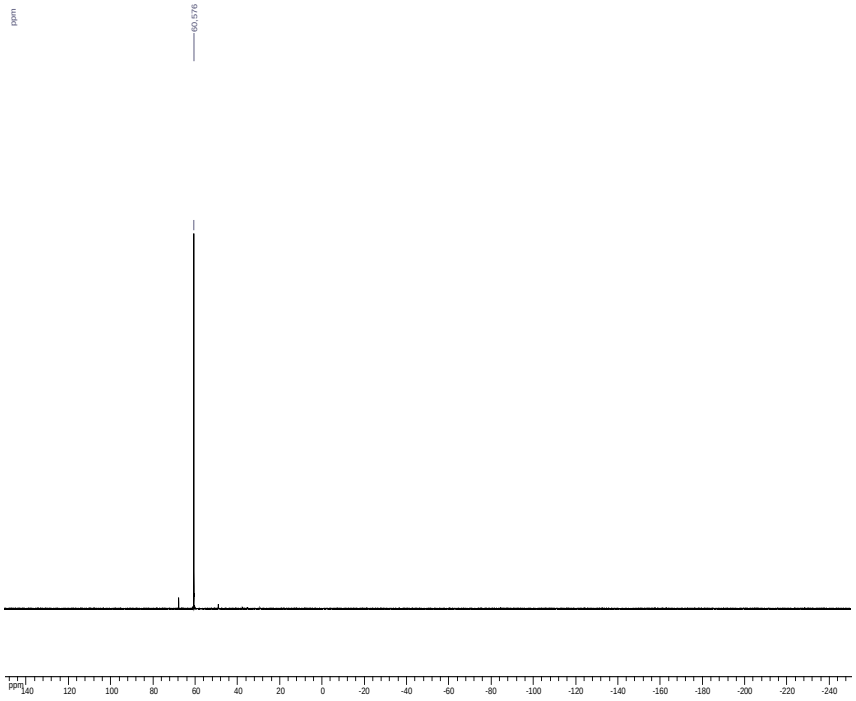
(**1b**) ^{1}H NMR (500 MHz, $CDCl_3$):



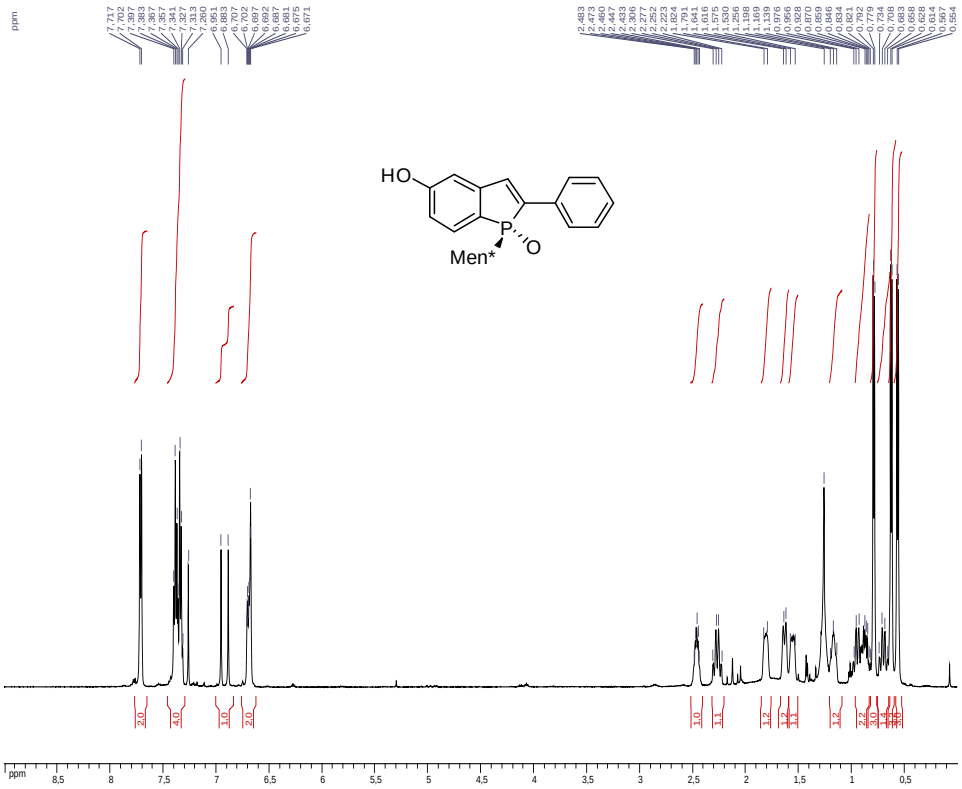
(**1b**) ^{13}C NMR (75 MHz, $CDCl_3$):



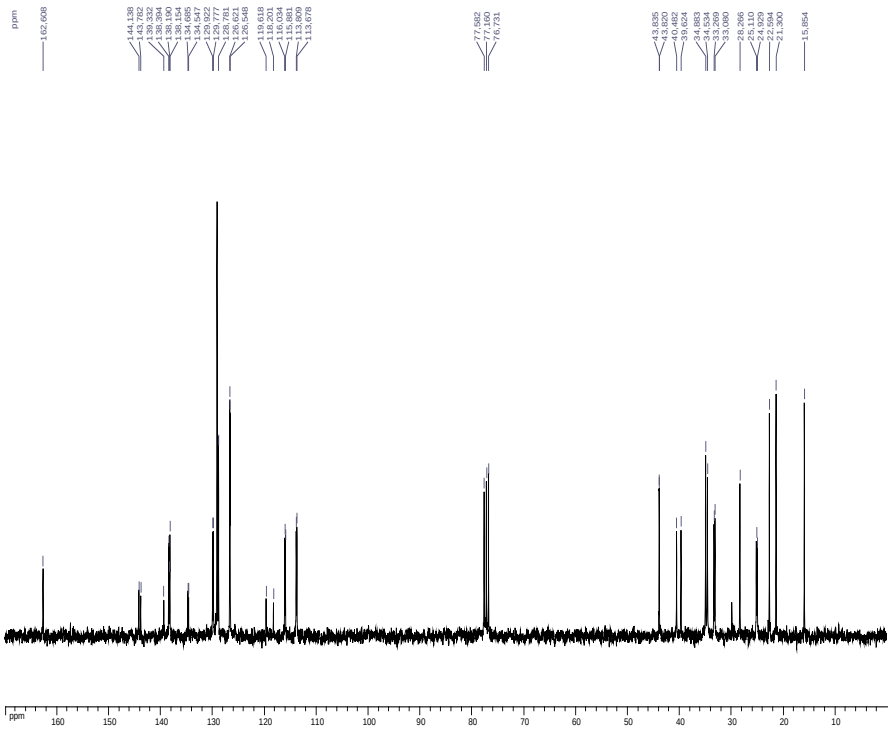
(**1b**) ^{31}P NMR (121 MHz, $CDCl_3$):



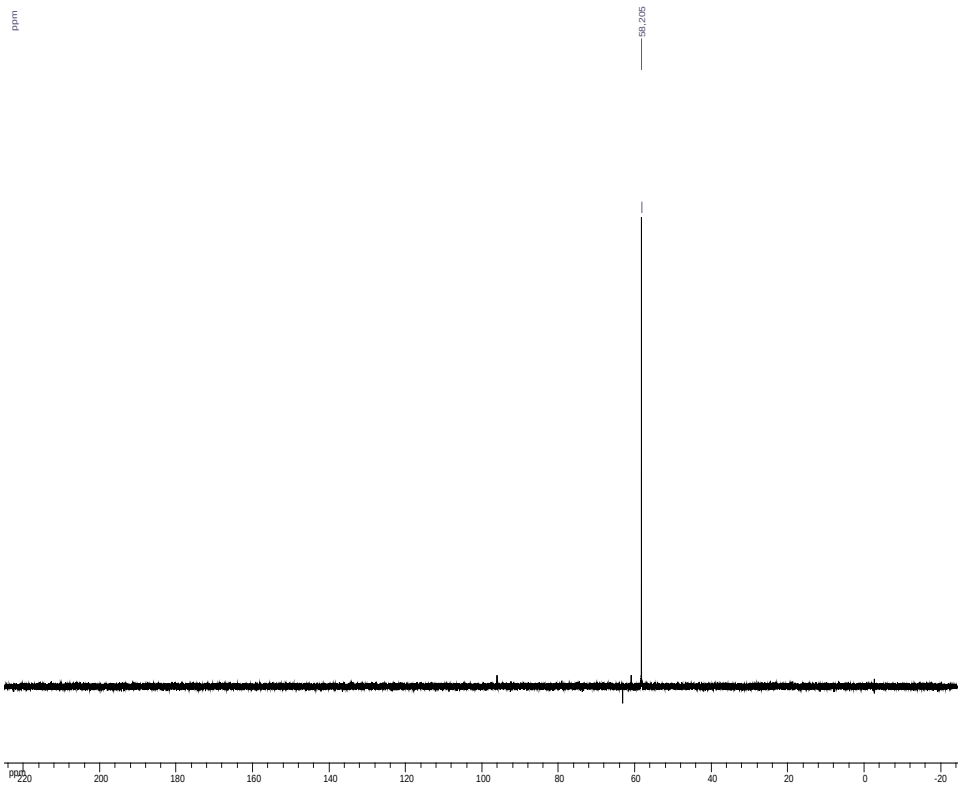
(**1c**) ^{1}H NMR (500 MHz, $CDCl_3$):



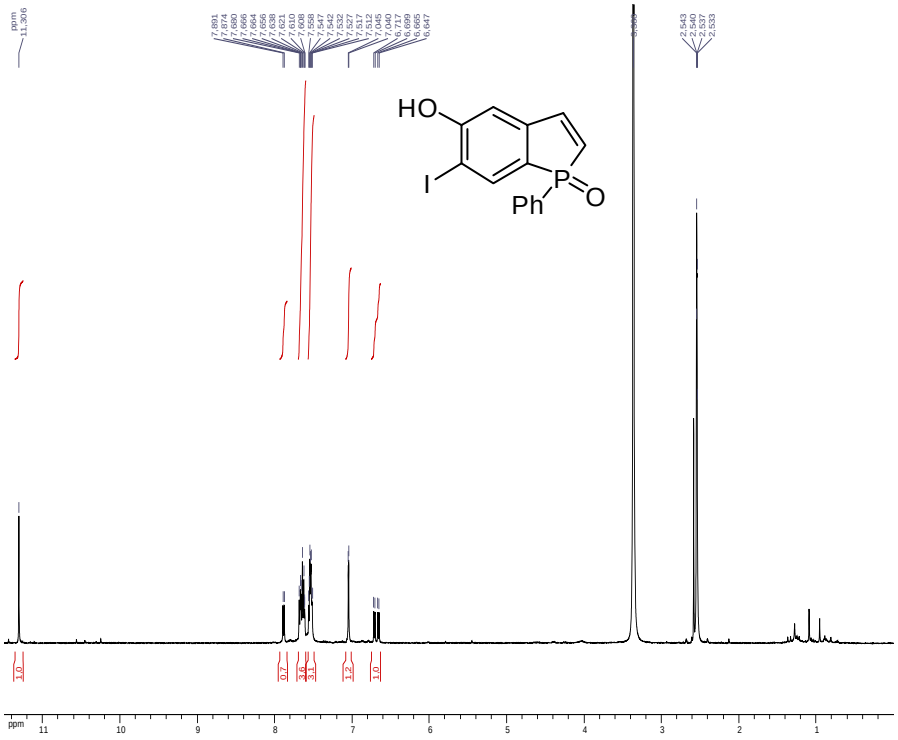
(**1c**) ^{13}C NMR (75 MHz, $CDCl_3$):



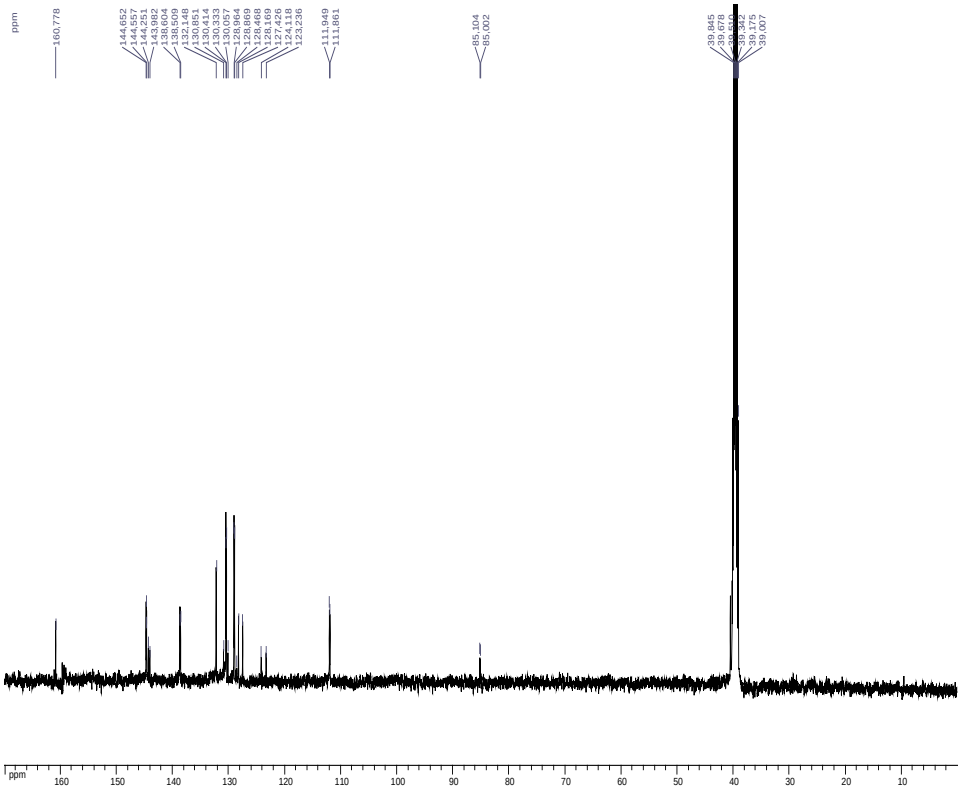
(**1c**) ^{31}P NMR (202 MHz, $CDCl_3$):



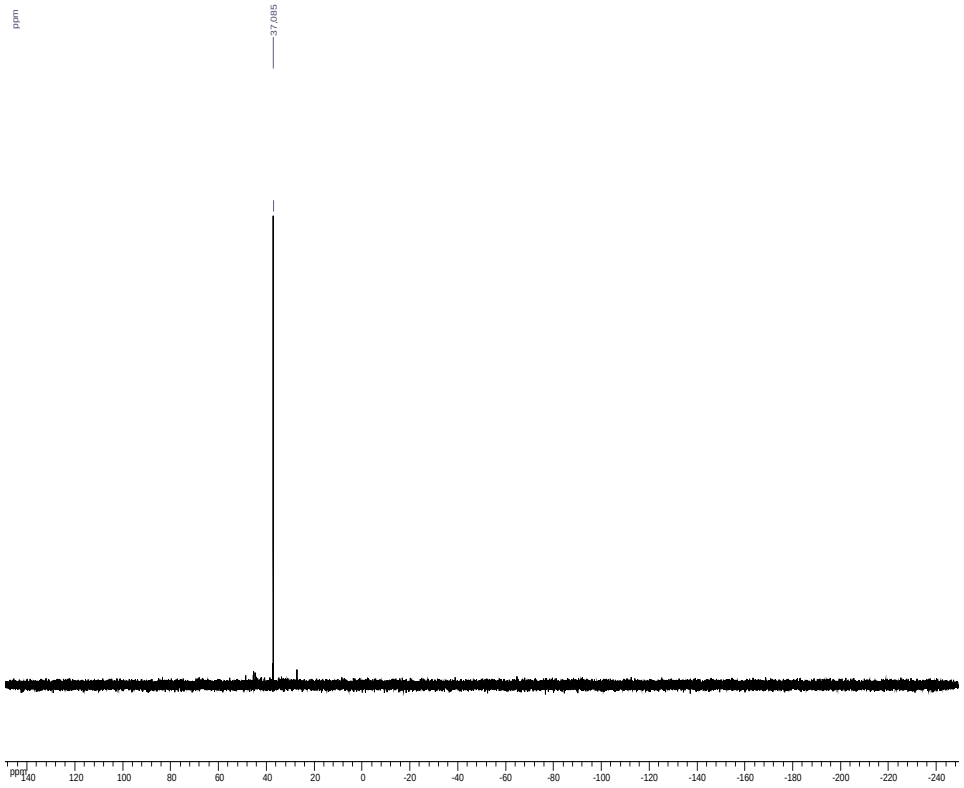
(**S1**) ^{1}H NMR (500 MHz, DMSO-d_6):



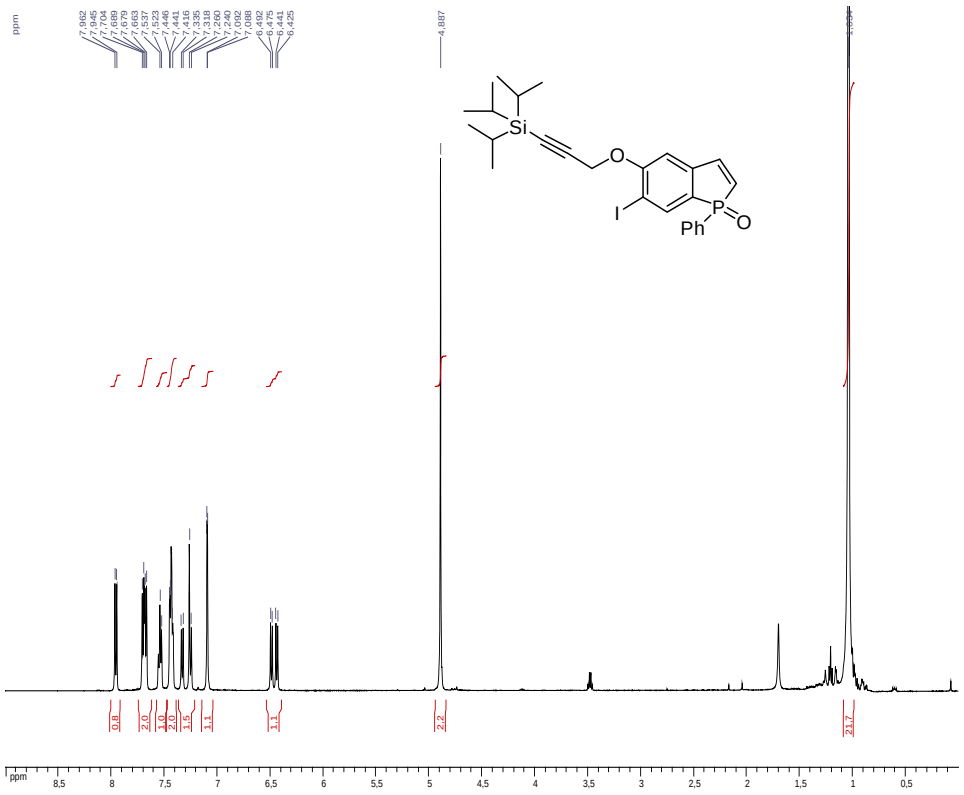
(**S1**) ^{13}C NMR (125 MHz, DMSO-d_6):



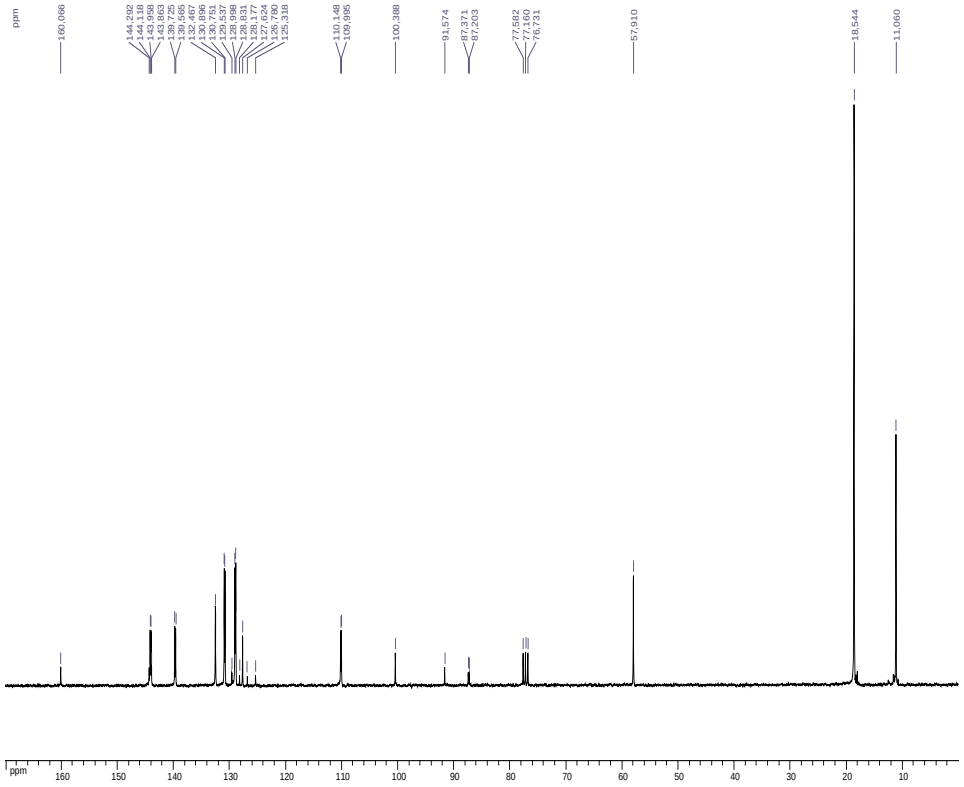
(**S1**) ^{31}P NMR (121 MHz, $CDCl_3$):



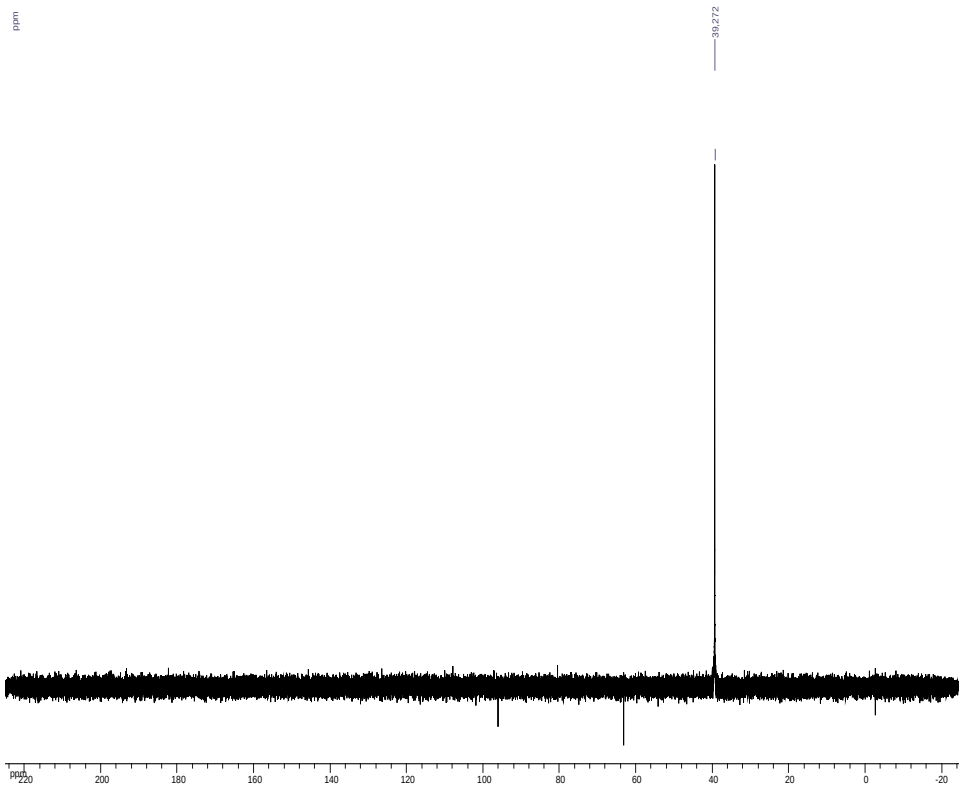
(**2a**) ^{1}H NMR (500 MHz, $CDCl_3$):



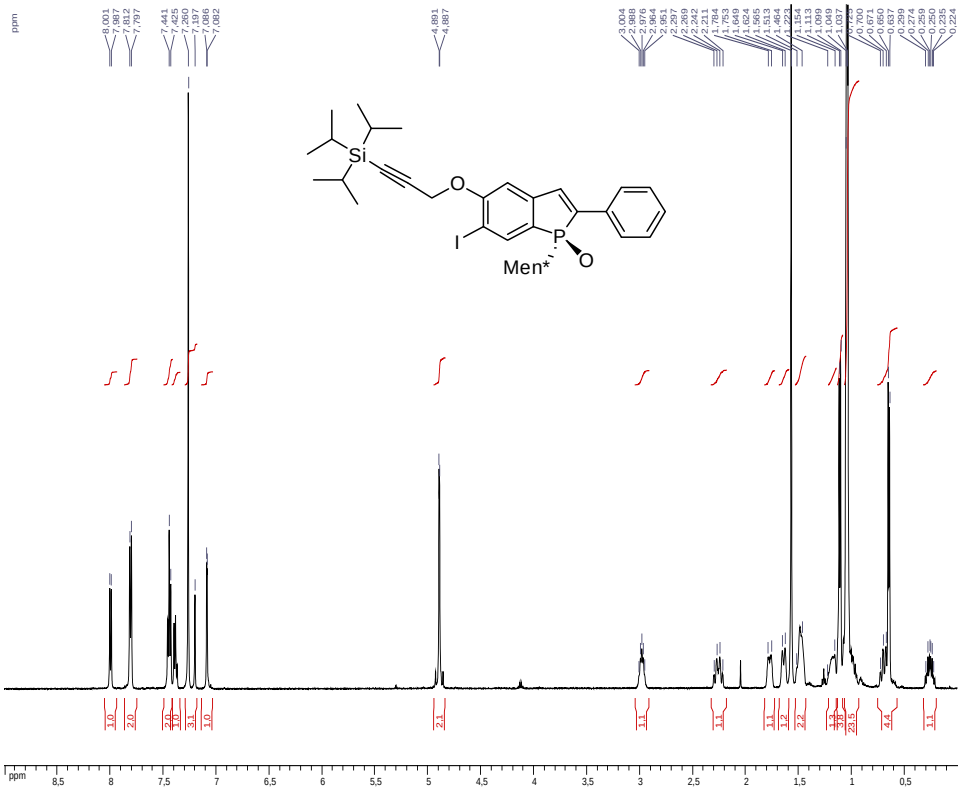
(**2a**) ^{13}C NMR (75 MHz, $CDCl_3$):



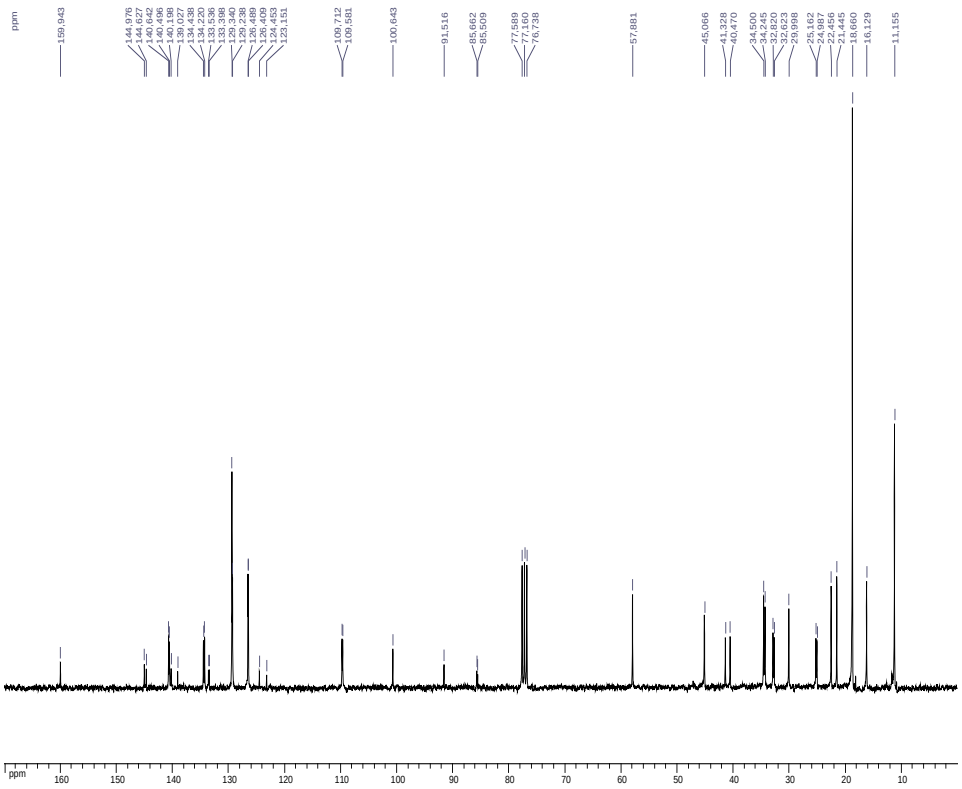
(**2a**) ^{31}P NMR (202 MHz, $CDCl_3$):



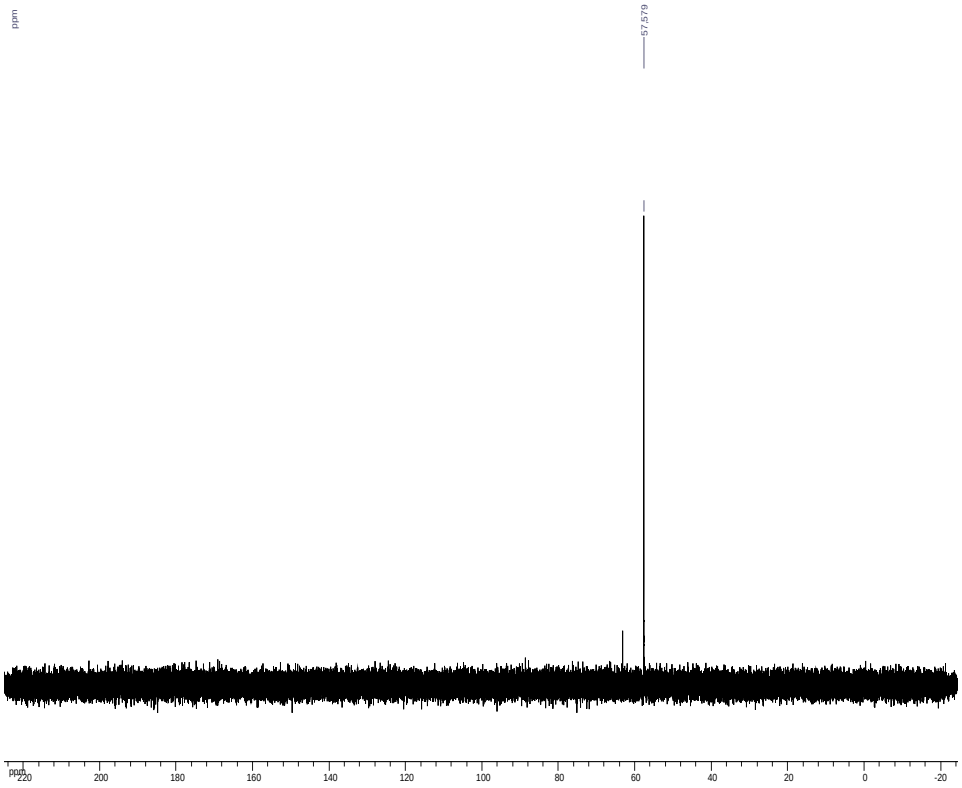
(**2b**) ^{1}H NMR (500 MHz, $CDCl_3$):



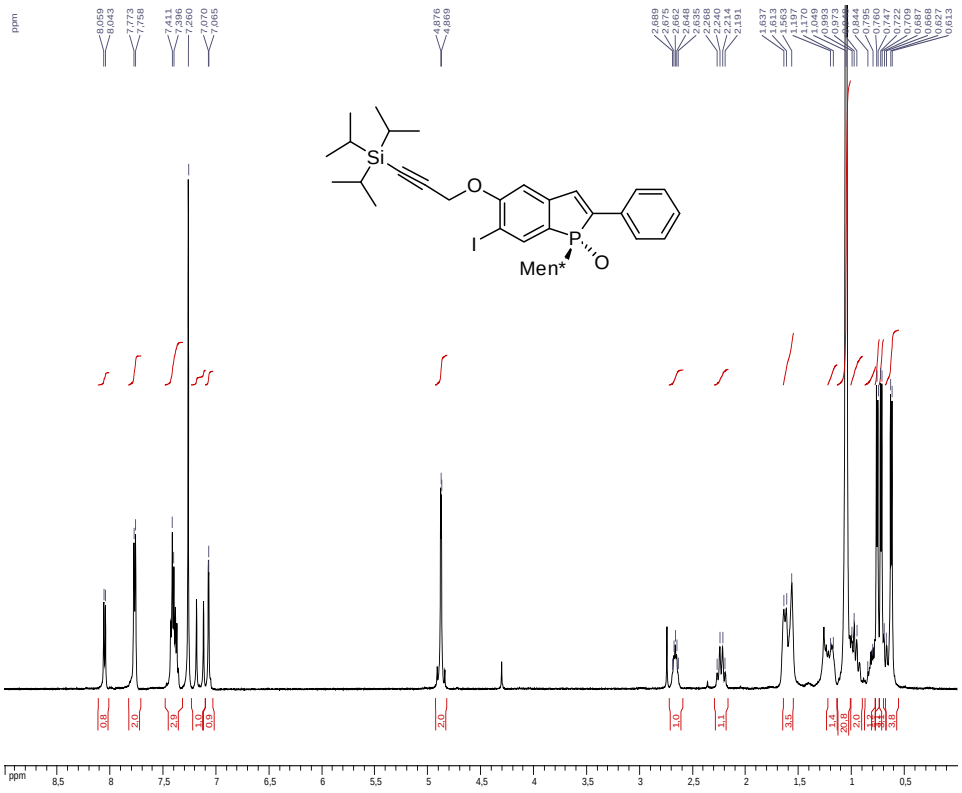
(**2b**) ^{13}C NMR (75 MHz, $CDCl_3$):



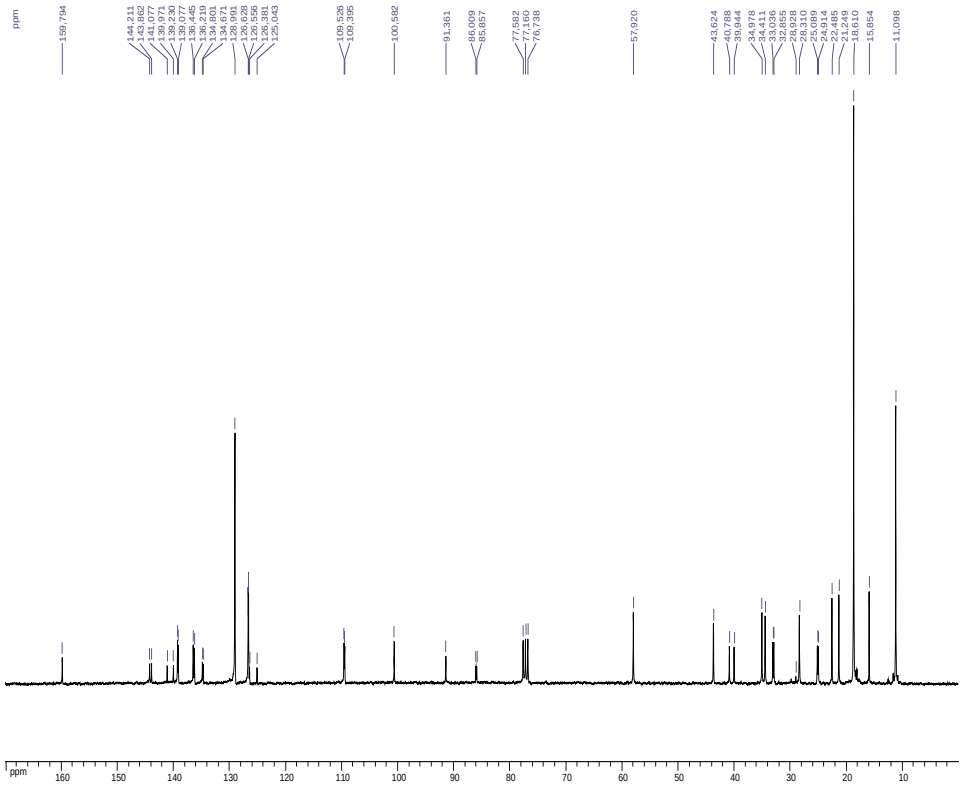
(**2b**) ^{31}P NMR (202 MHz, $CDCl_3$):



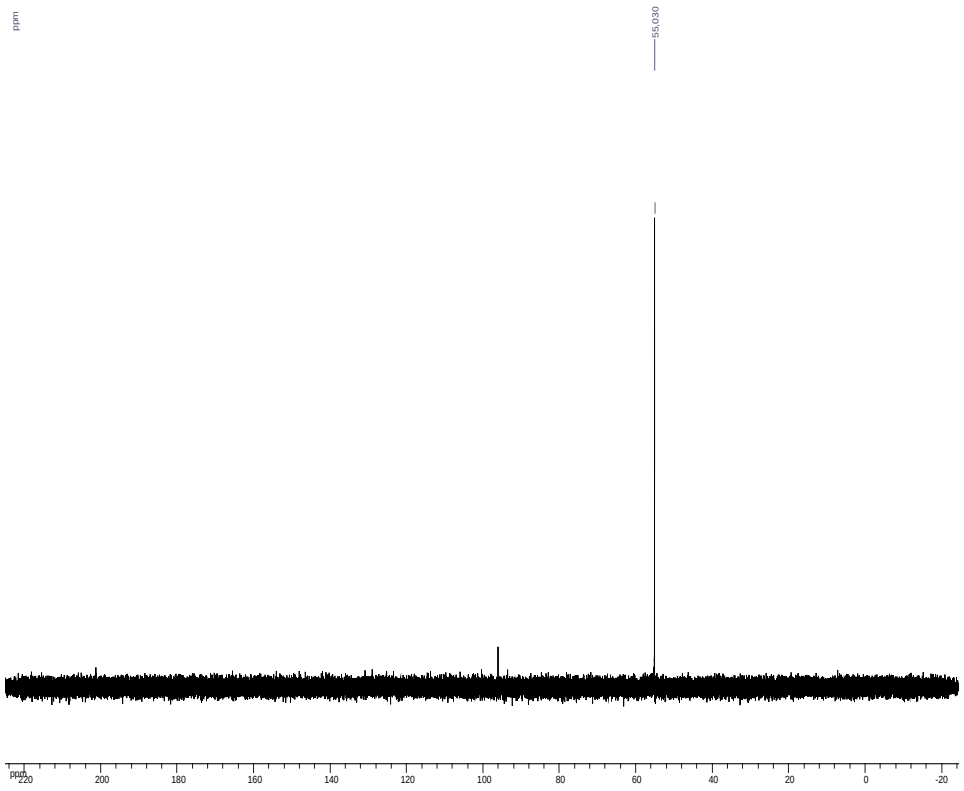
(**2c**) ^{1}H NMR (500 MHz, $CDCl_3$):



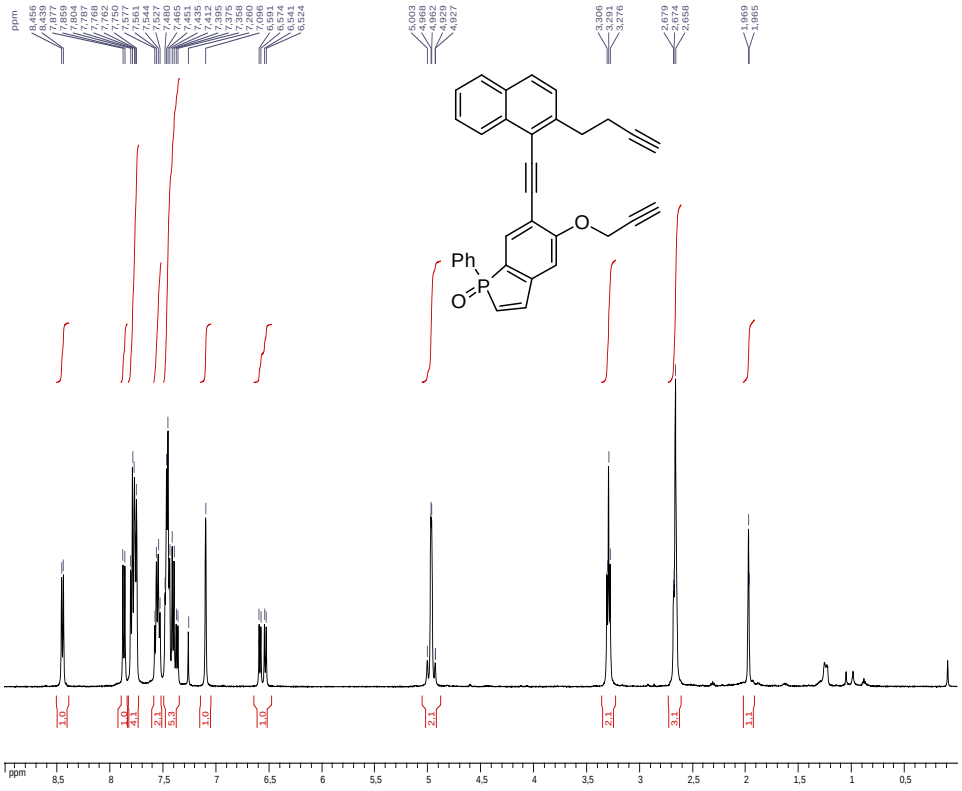
(**2c**) ^{13}C NMR (75 MHz, $CDCl_3$):



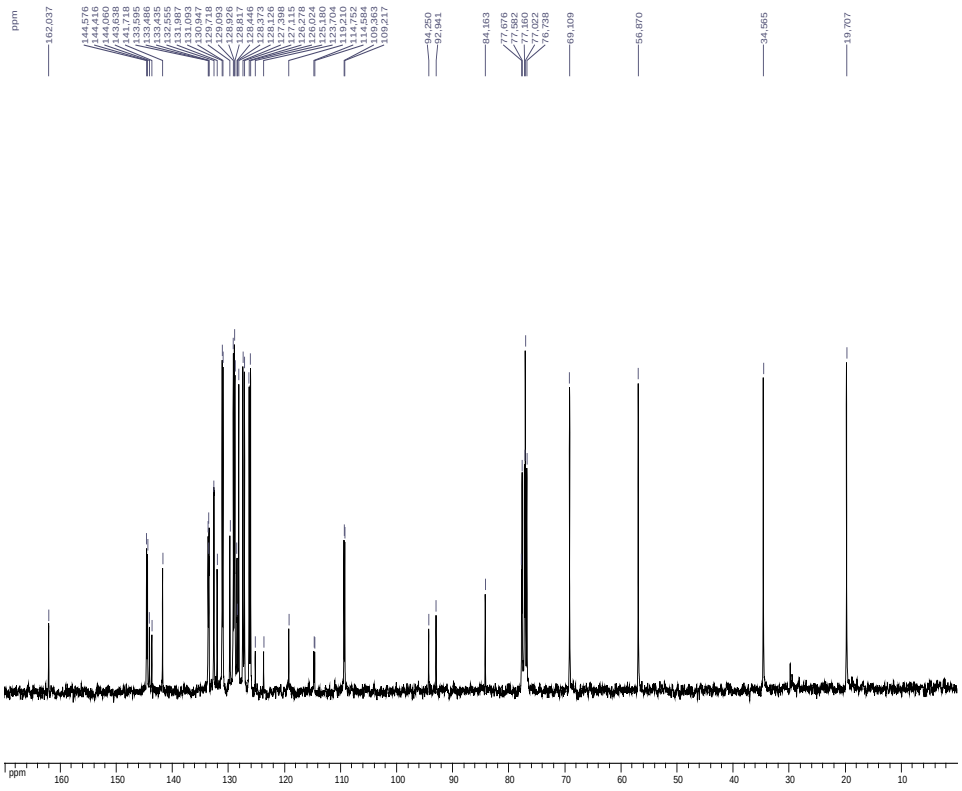
(**2c**) ^{31}P NMR (202 MHz, $CDCl_3$):



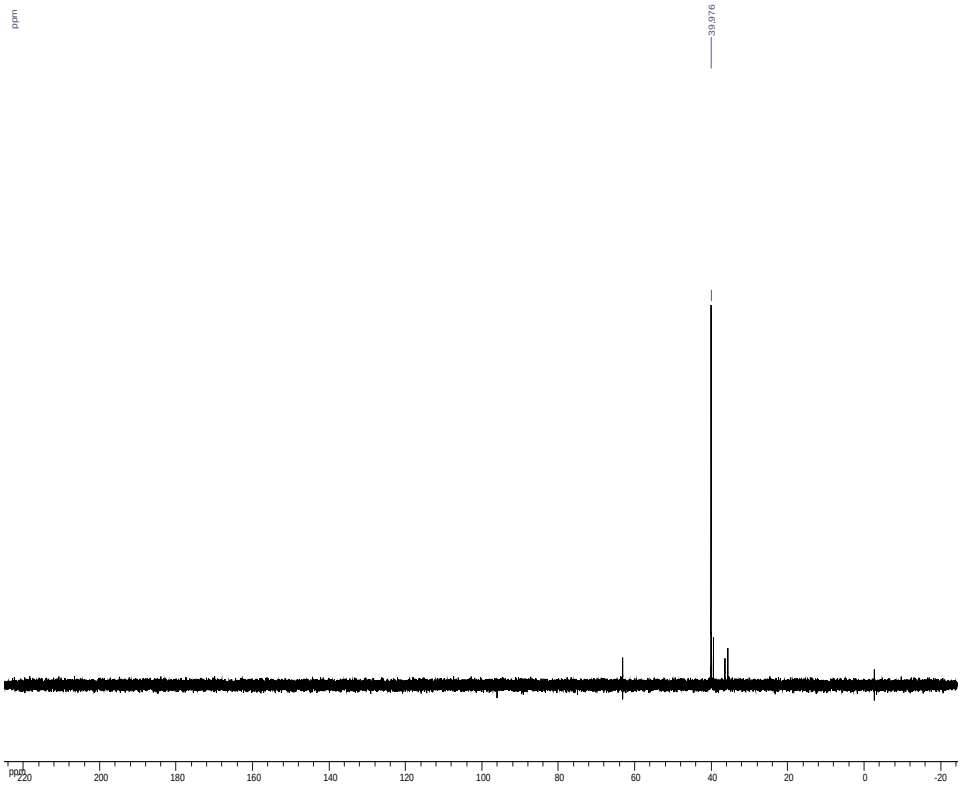
(**4a**) ^{1}H NMR (500 MHz, $CDCl_3$):



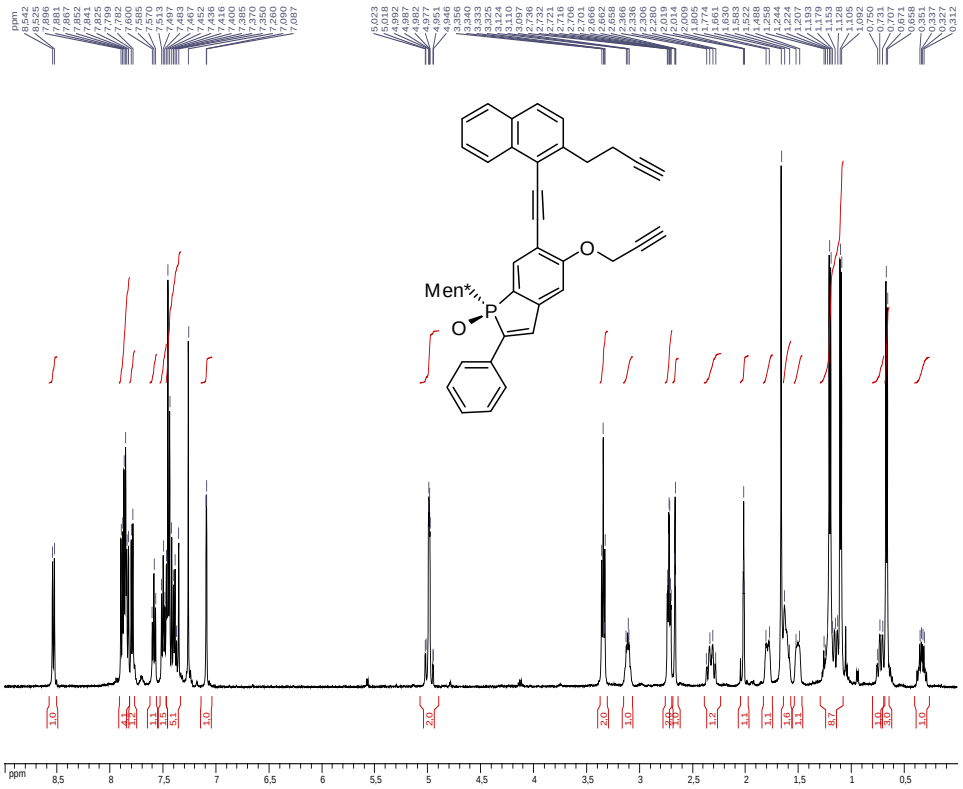
(**4a**) ^{13}C NMR (75 MHz, $CDCl_3$):



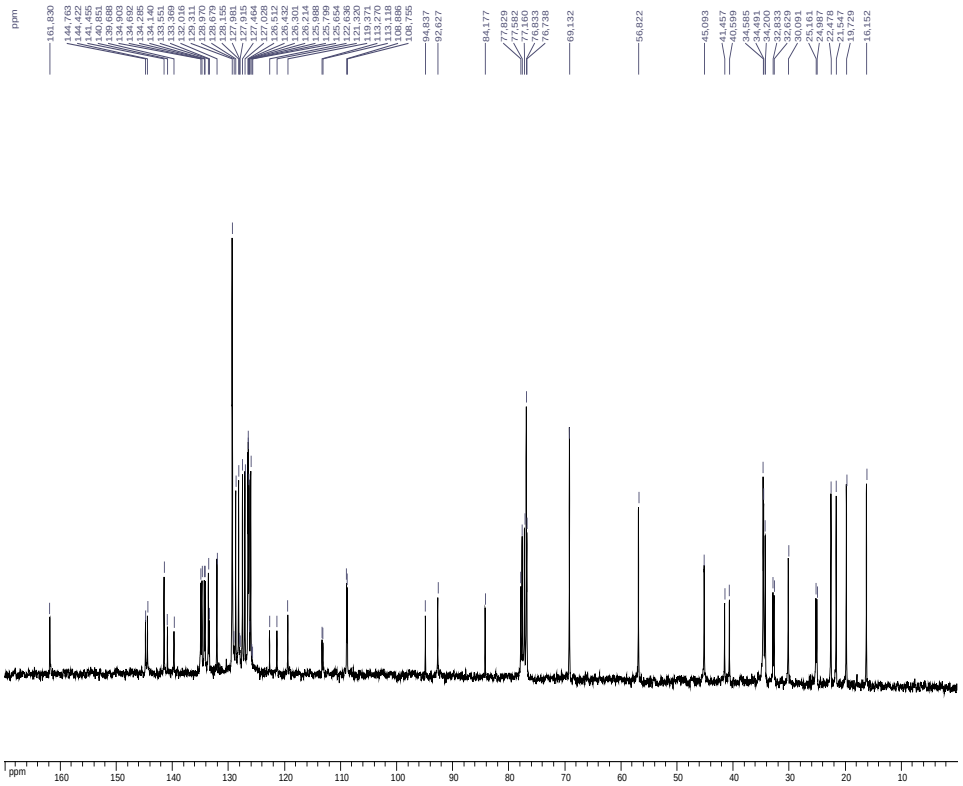
(**4a**) ^{31}P NMR (202 MHz, $CDCl_3$):



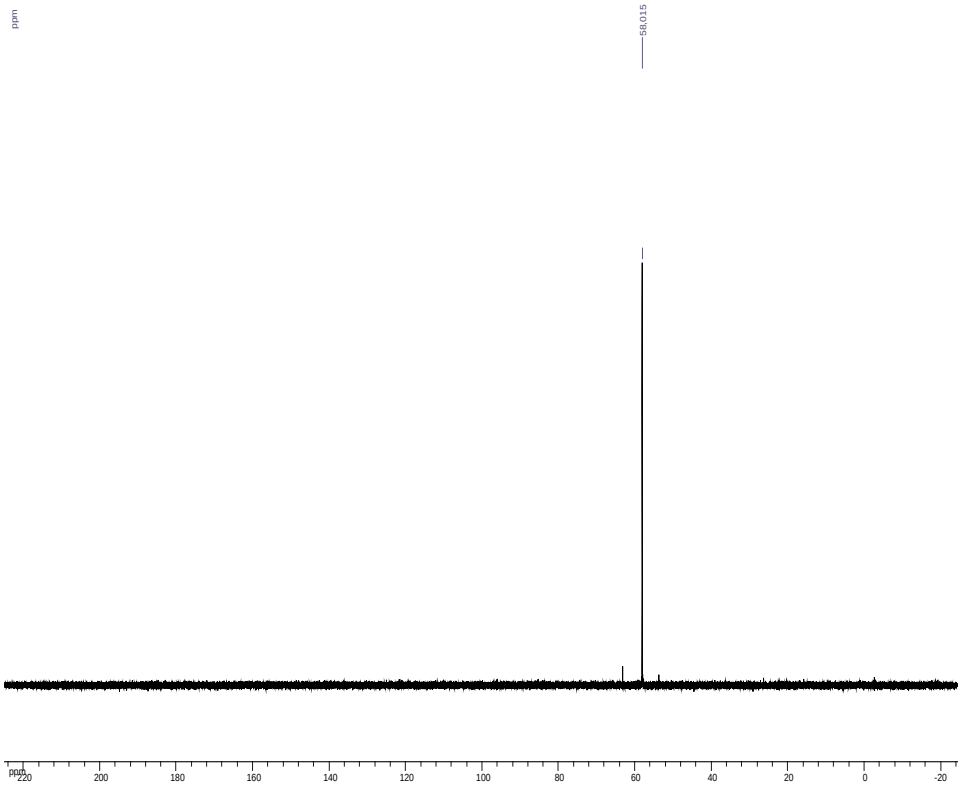
(**4b**) ^{1}H NMR (500 MHz, $CDCl_3$):



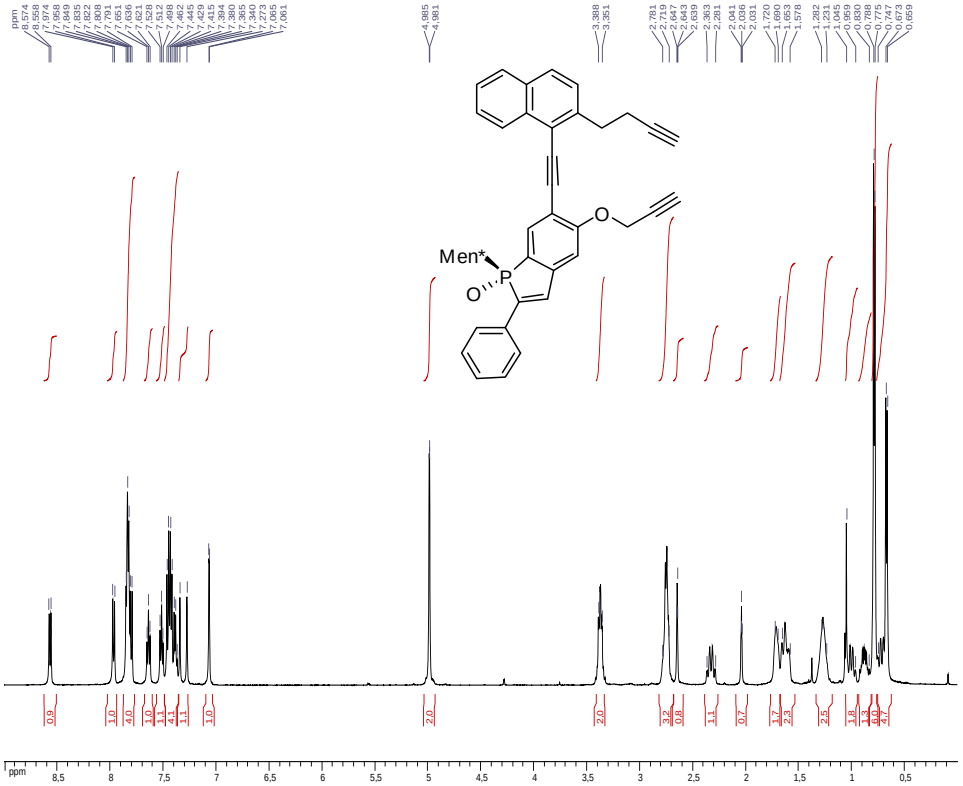
(**4b**) ^{13}C NMR (75 MHz, $CDCl_3$):



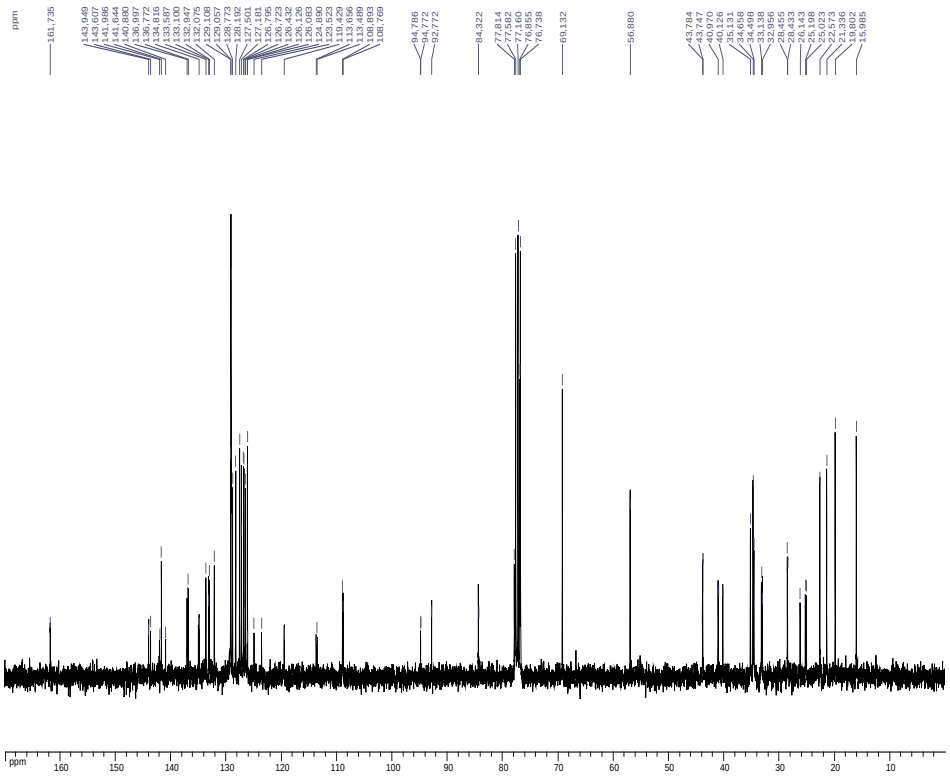
(**4b**) ^{31}P NMR (202 MHz, $CDCl_3$):



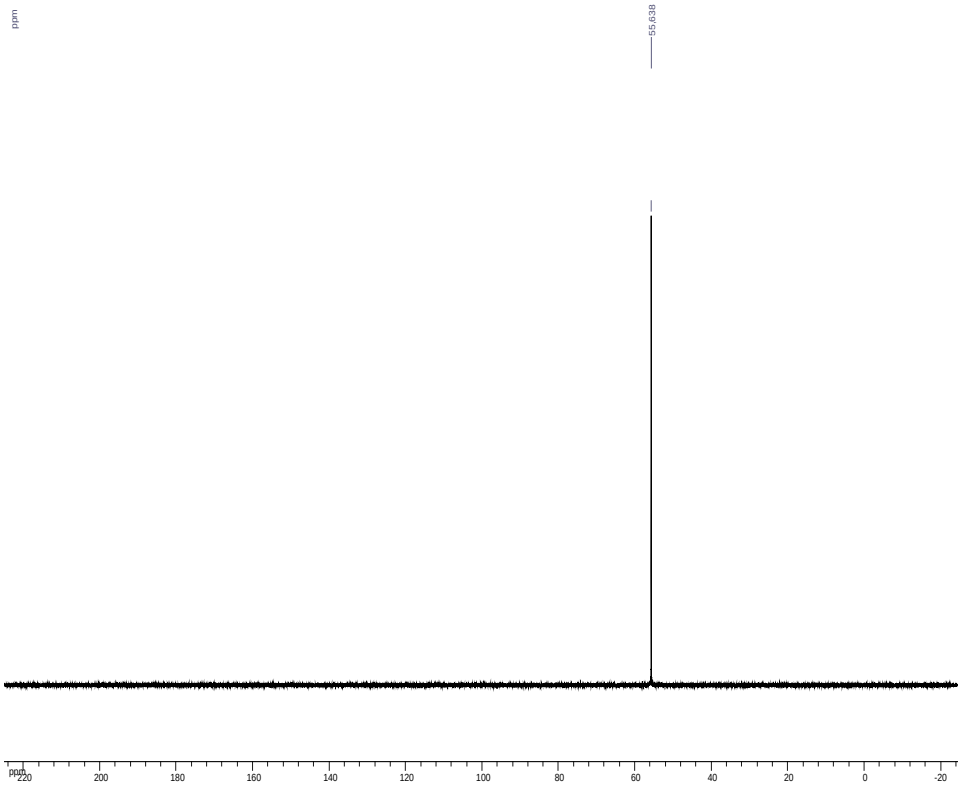
(**4c**) ^{1}H NMR (500 MHz, $CDCl_3$):



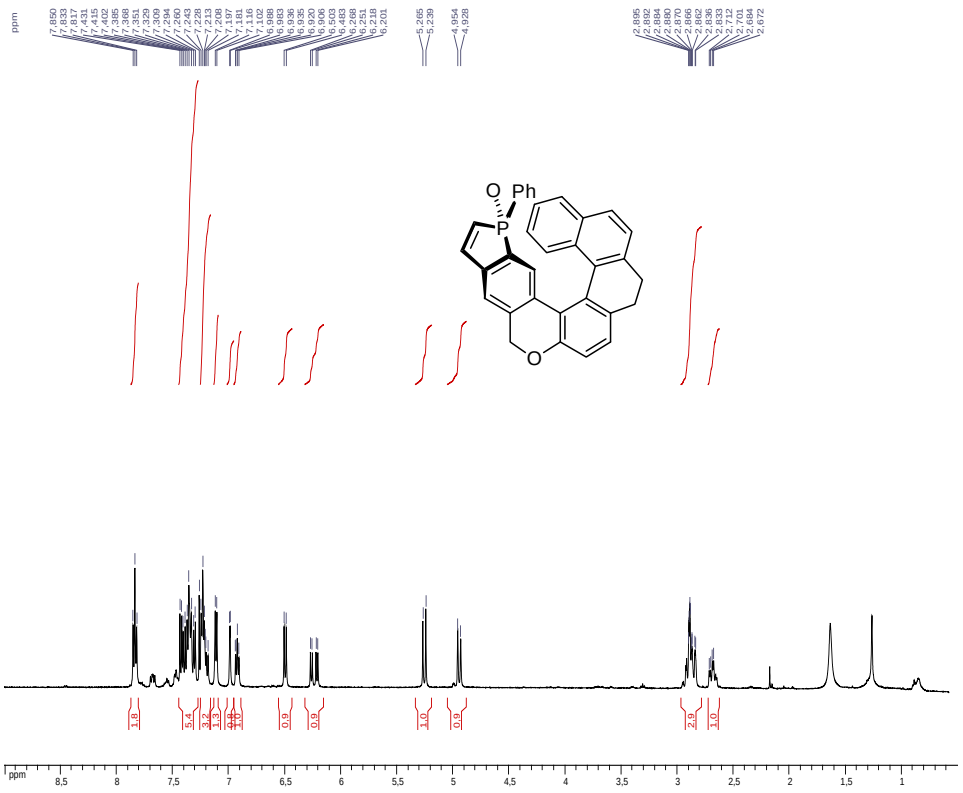
(**4c**) ^{13}C NMR (75 MHz, $CDCl_3$):



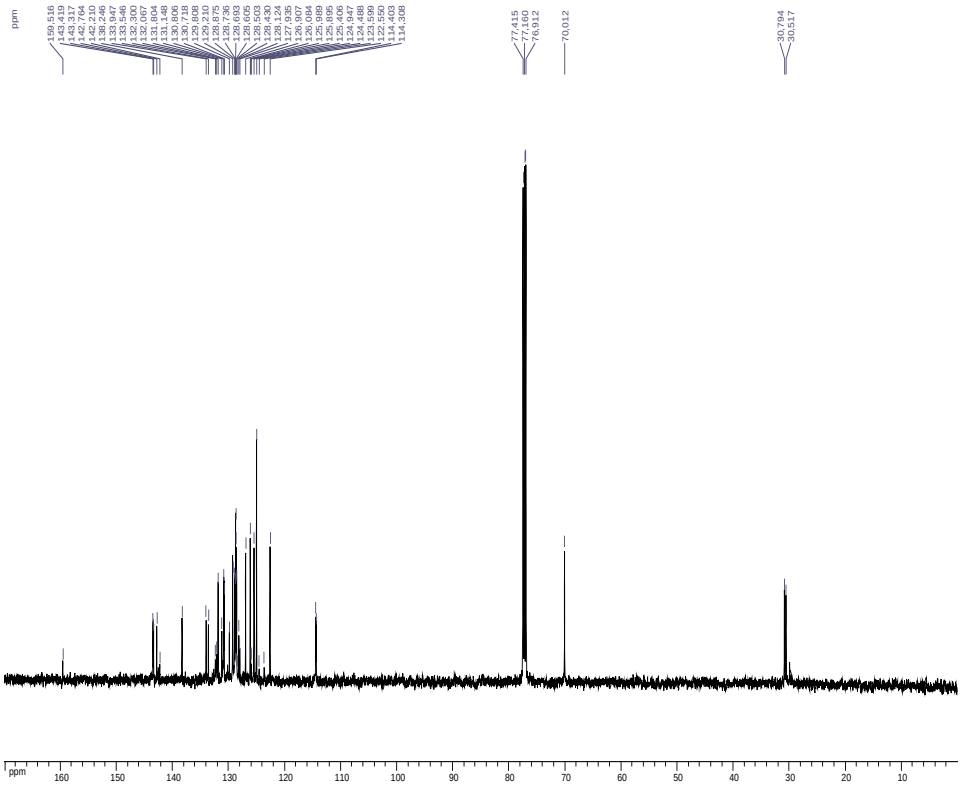
(**4c**) ^{31}P NMR (202 MHz, $CDCl_3$):



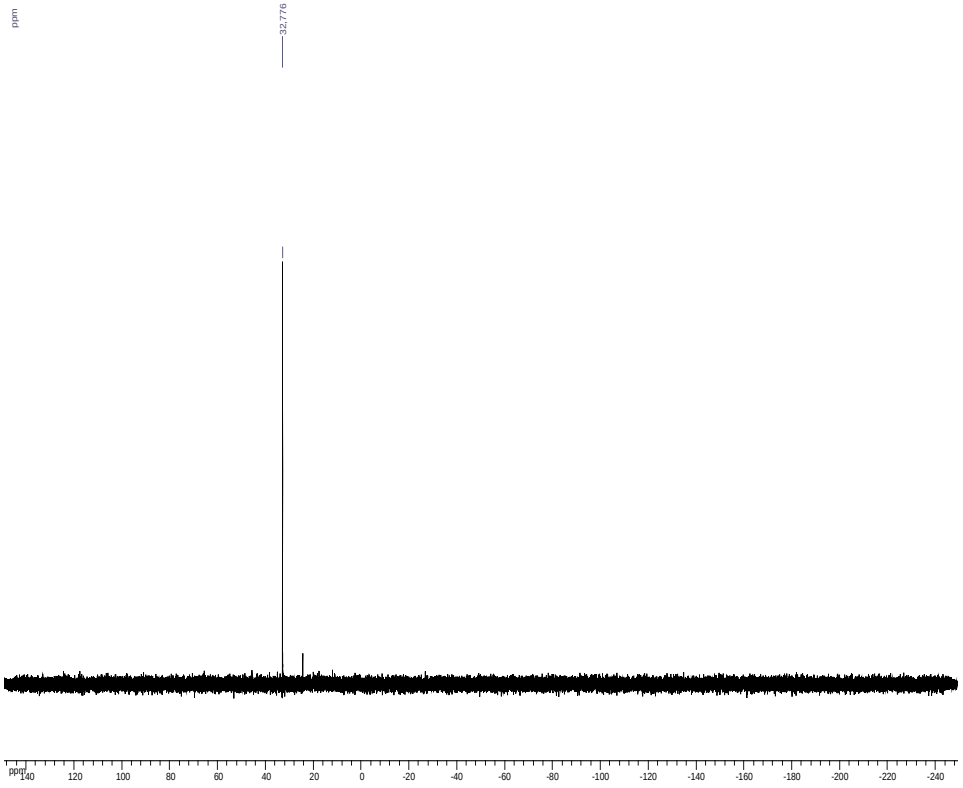
(**5a**) ^{1}H NMR (500 MHz, $CDCl_3$):



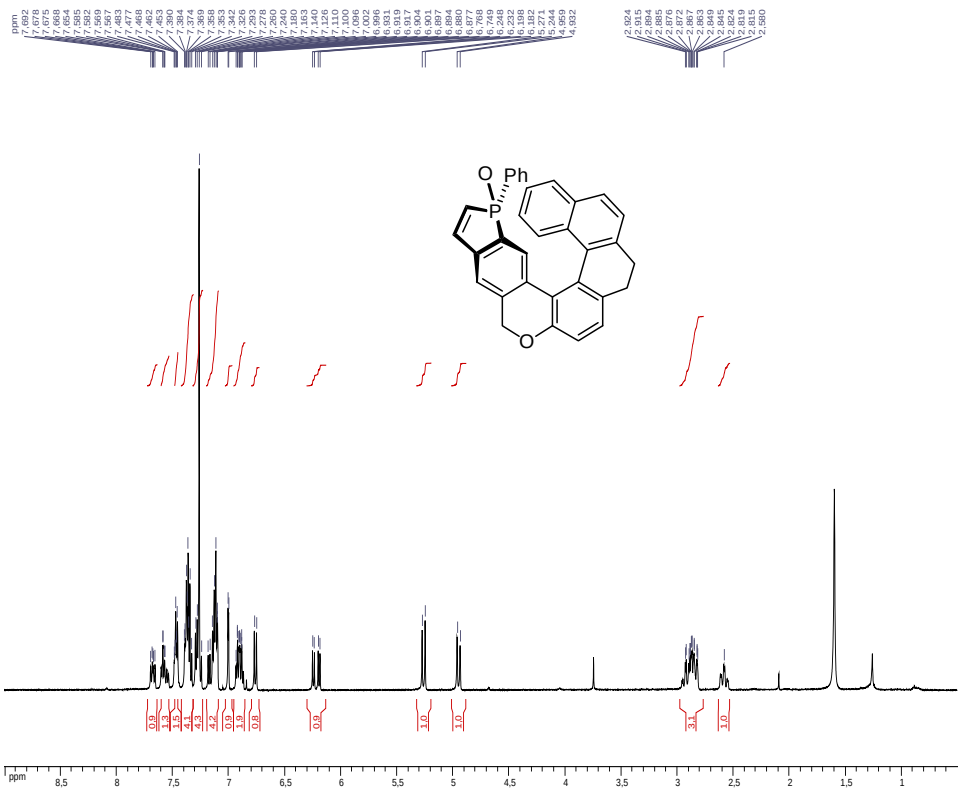
(**5a**) ^{13}C NMR (125 MHz, $CDCl_3$):



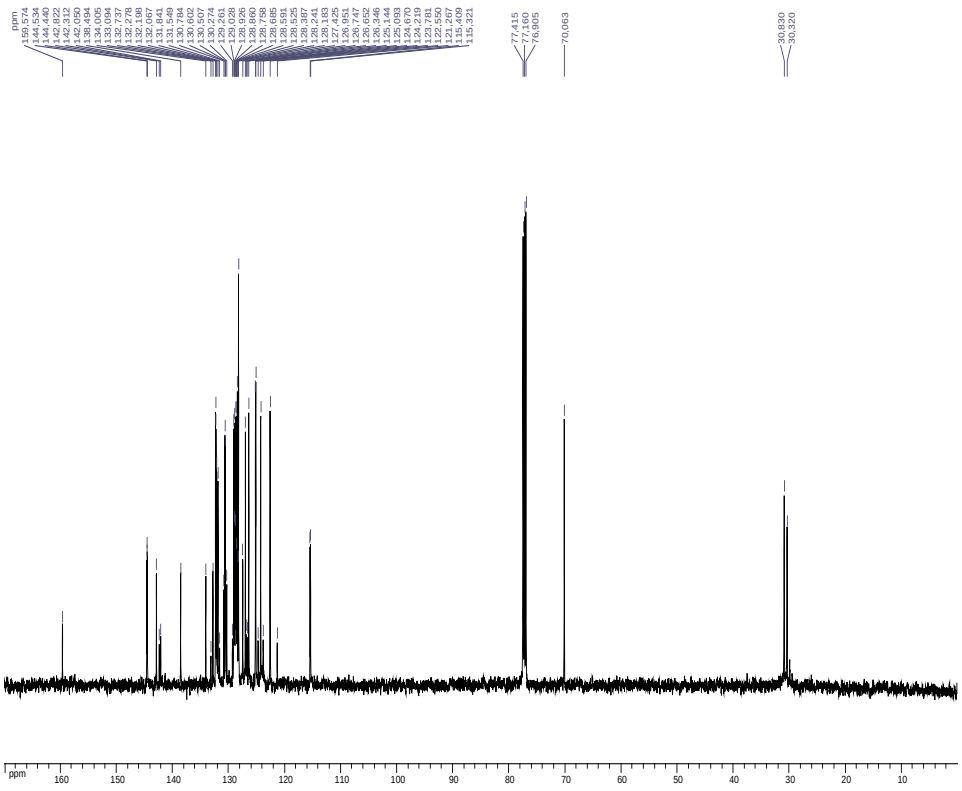
(**5a**) ^{31}P NMR (121 MHz, $CDCl_3$):



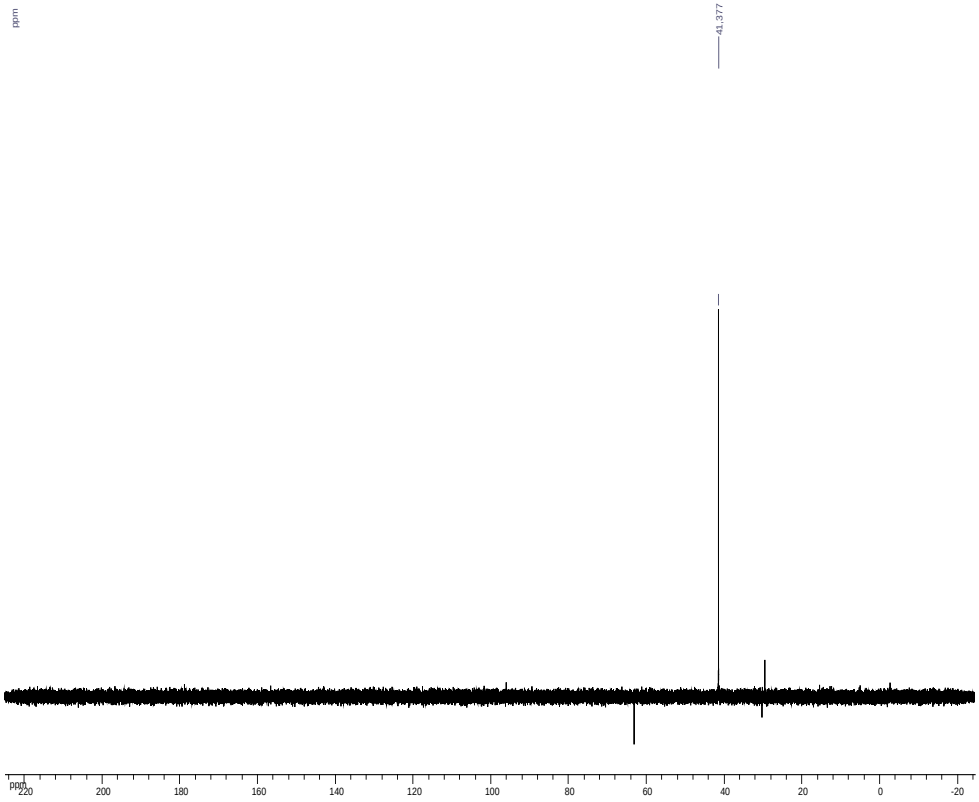
(**5a'**) ^{1}H NMR (500 MHz, $CDCl_3$):



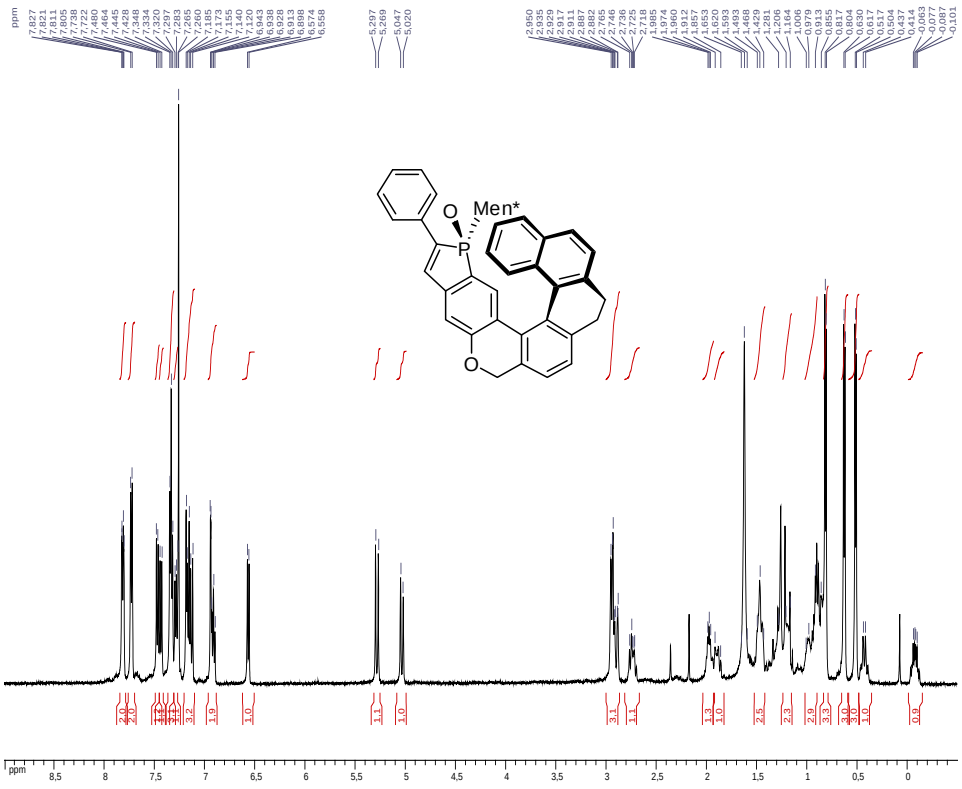
(**5a'**) ^{13}C NMR (125 MHz, $CDCl_3$):



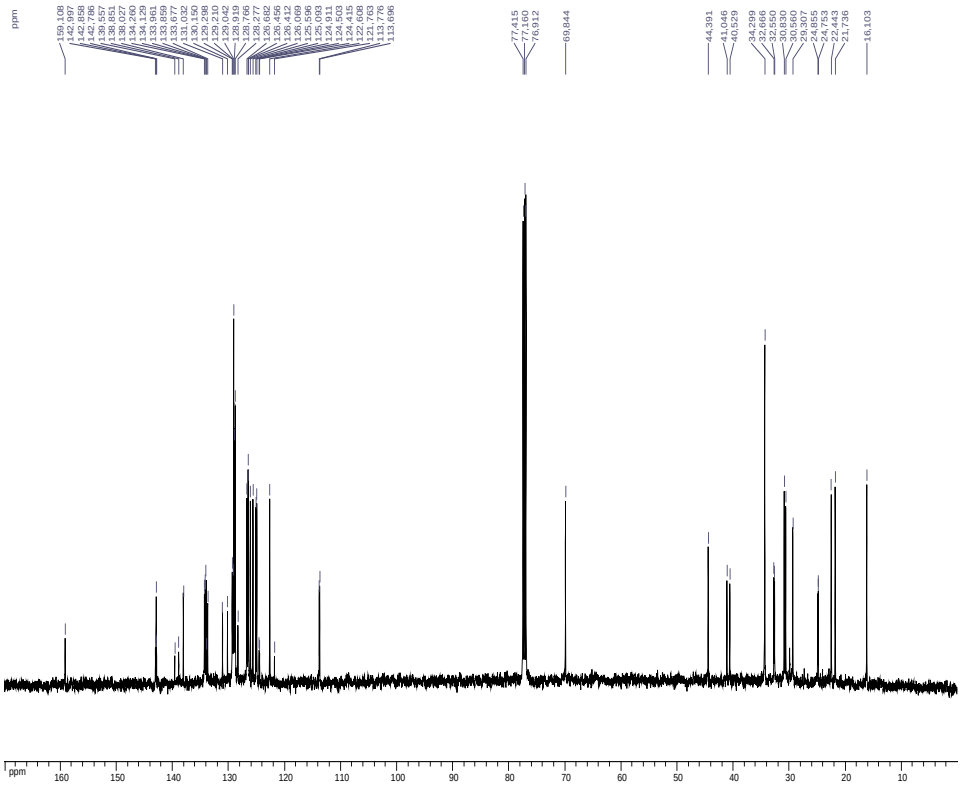
(**5a'**) ^{31}P NMR (202 MHz, $CDCl_3$):



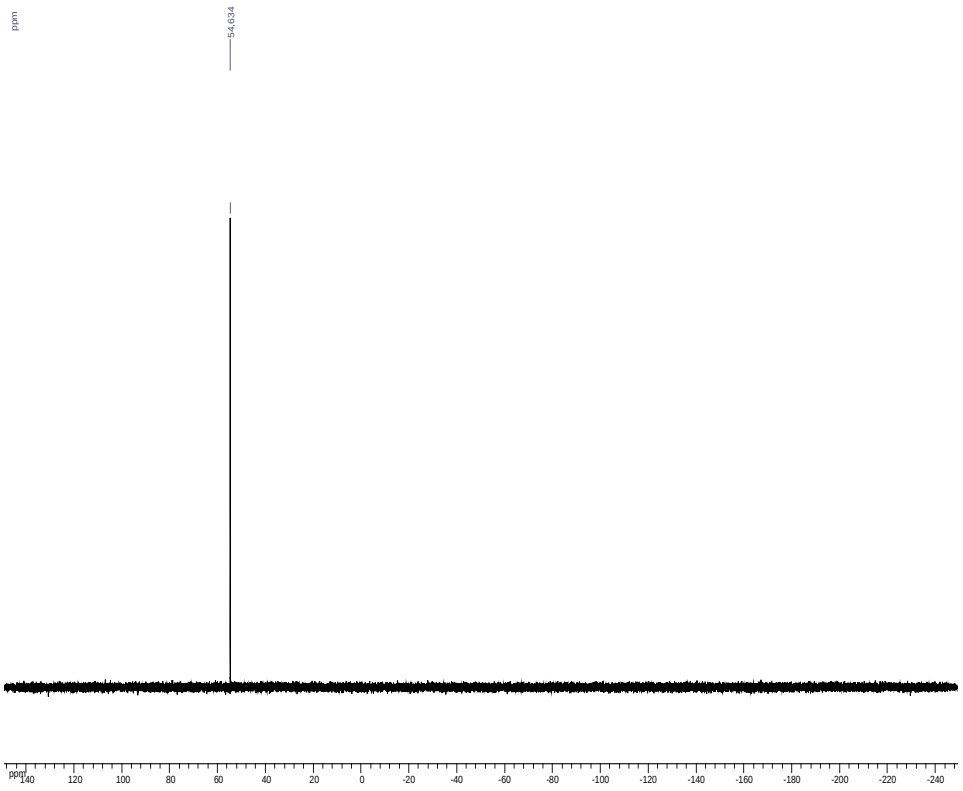
(**5b**) ^{1}H NMR (500 MHz, $CDCl_3$):



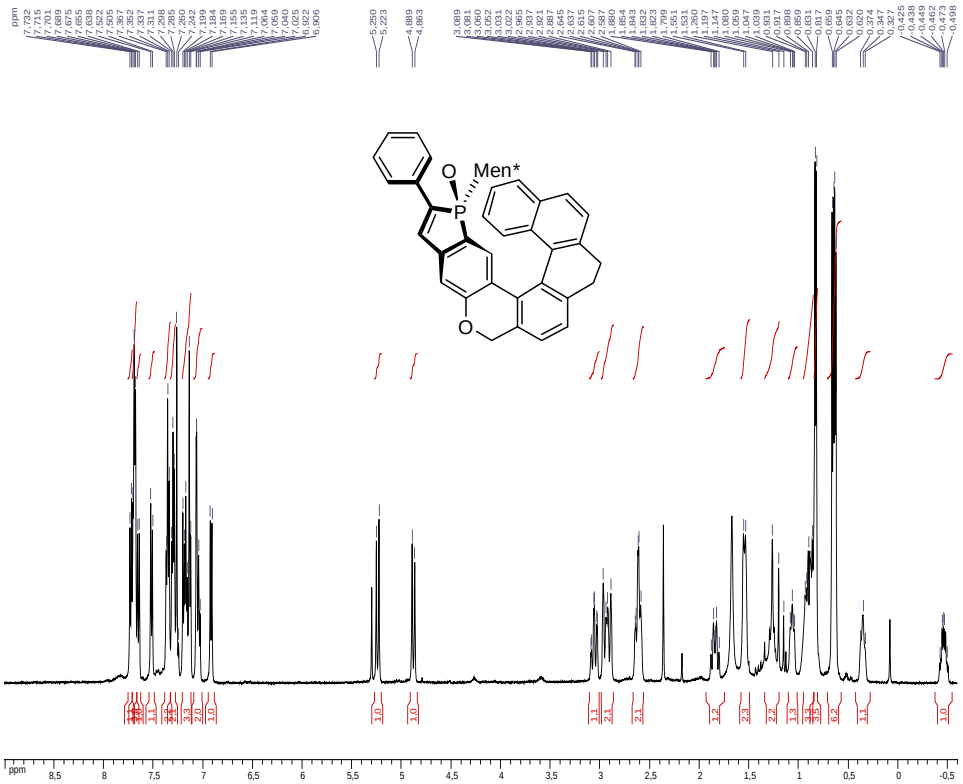
(**5b**) ^{13}C NMR (125 MHz, $CDCl_3$):



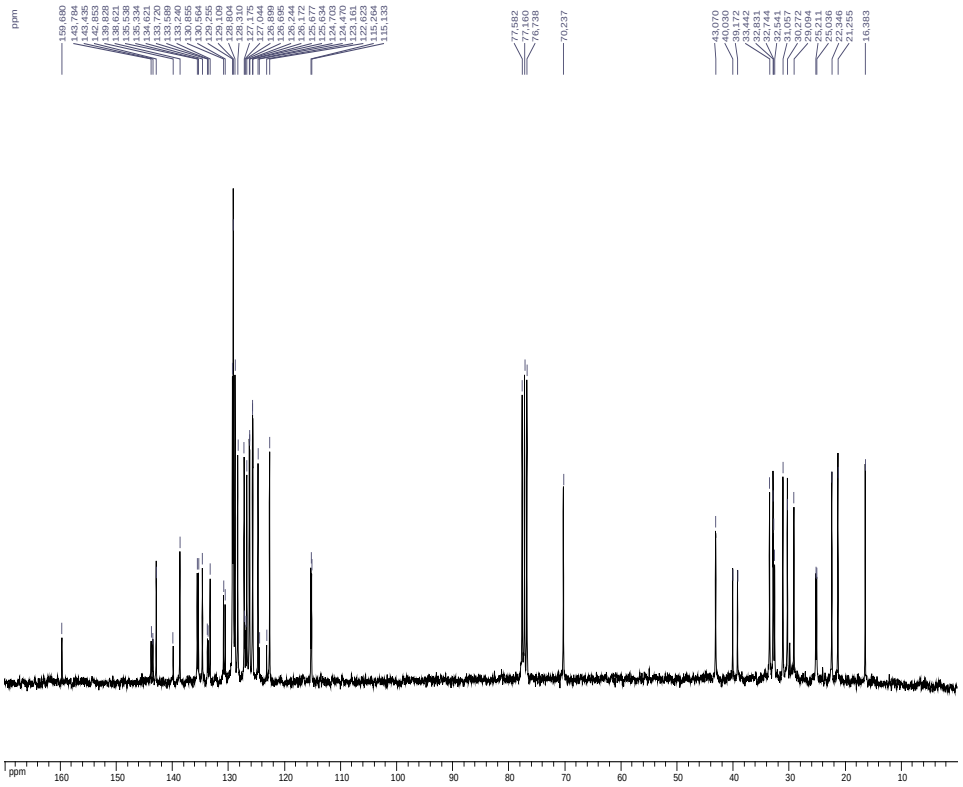
(**5b**) ^{31}P NMR (121 MHz, $CDCl_3$):



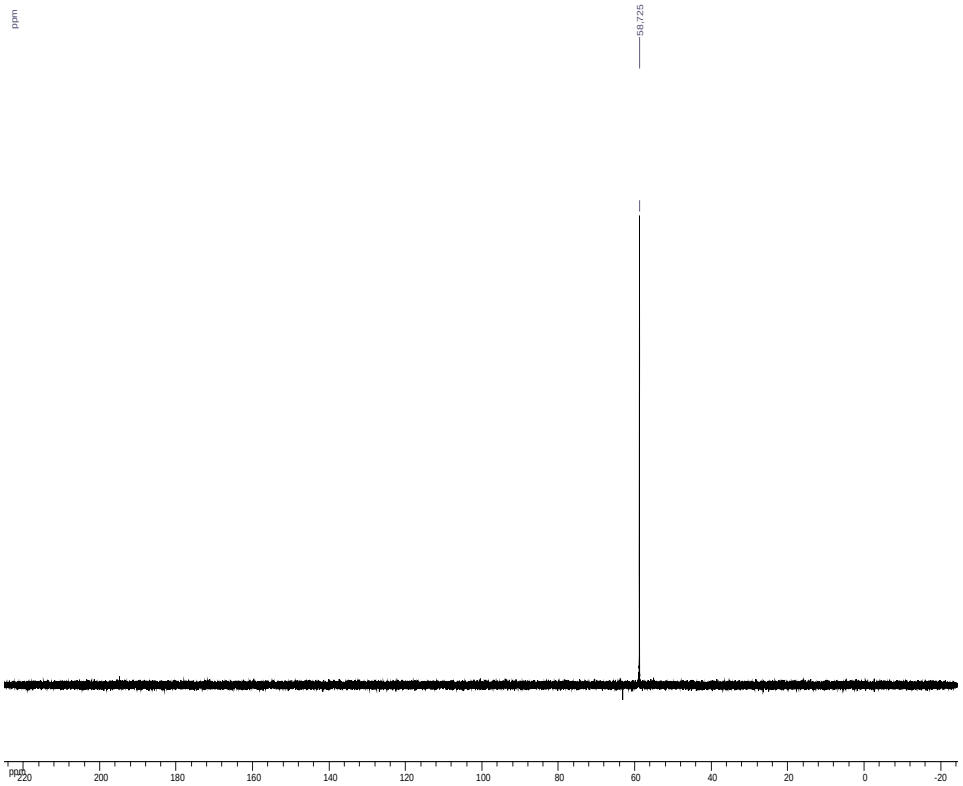
(**5b'**) ^{1}H NMR (500 MHz, $CDCl_3$):



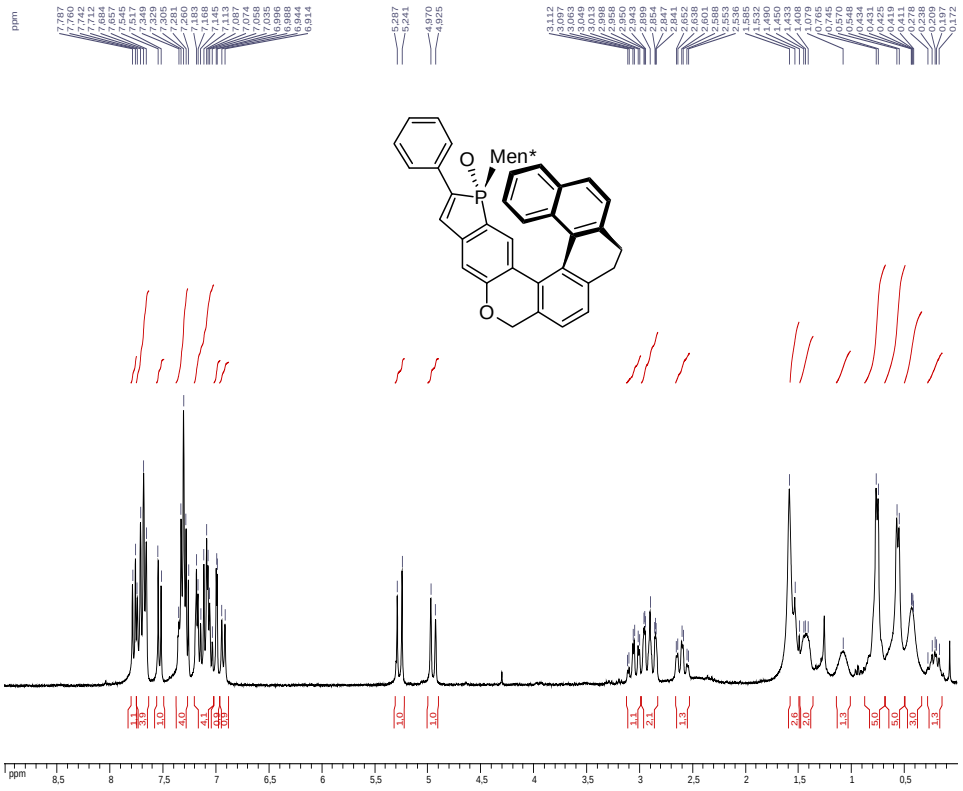
(**5b'**) ^{13}C NMR (75 MHz, $CDCl_3$):



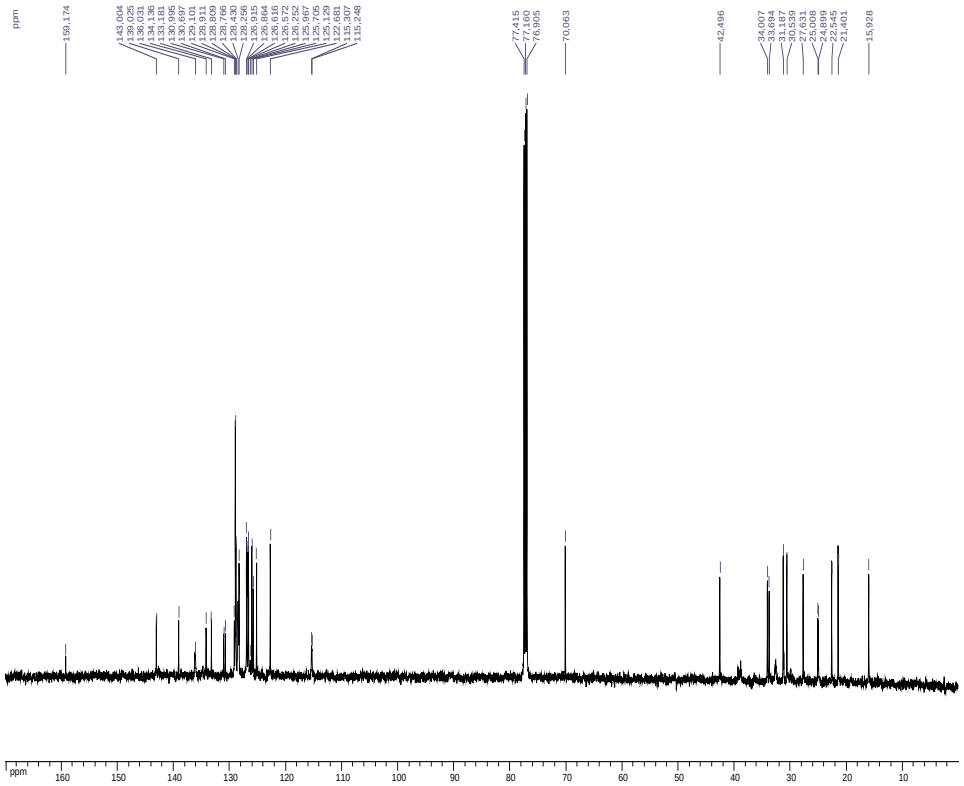
(**5b'**) ^{31}P NMR (202 MHz, $CDCl_3$):



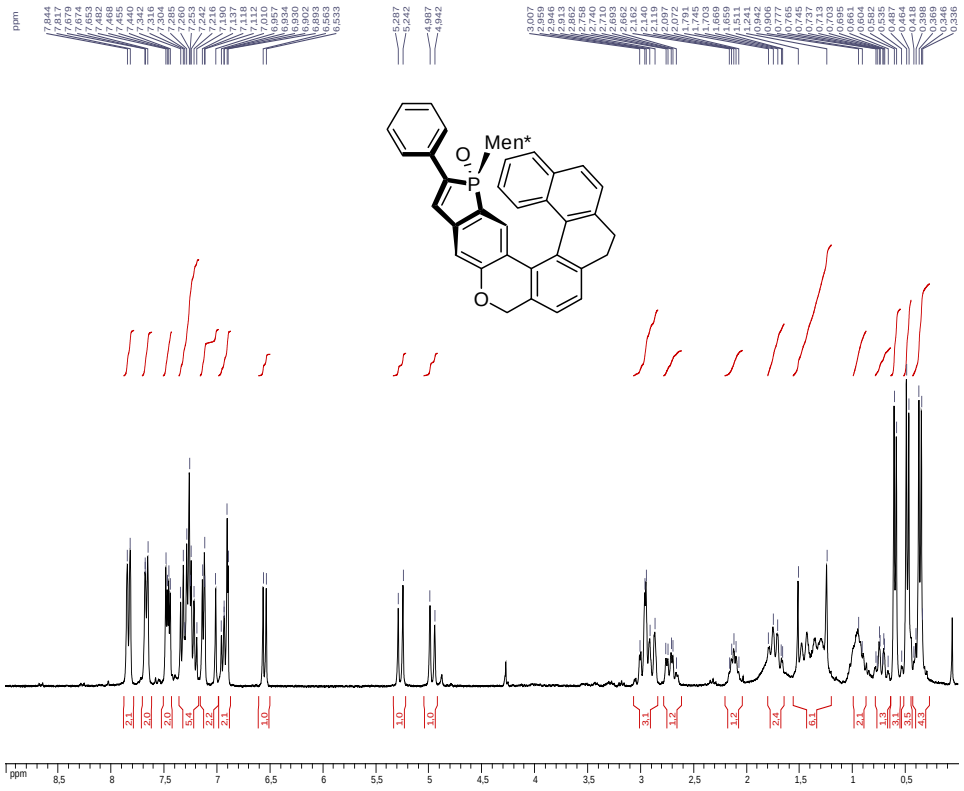
(**5c**) ^{1}H NMR (300 MHz, $CDCl_3$):



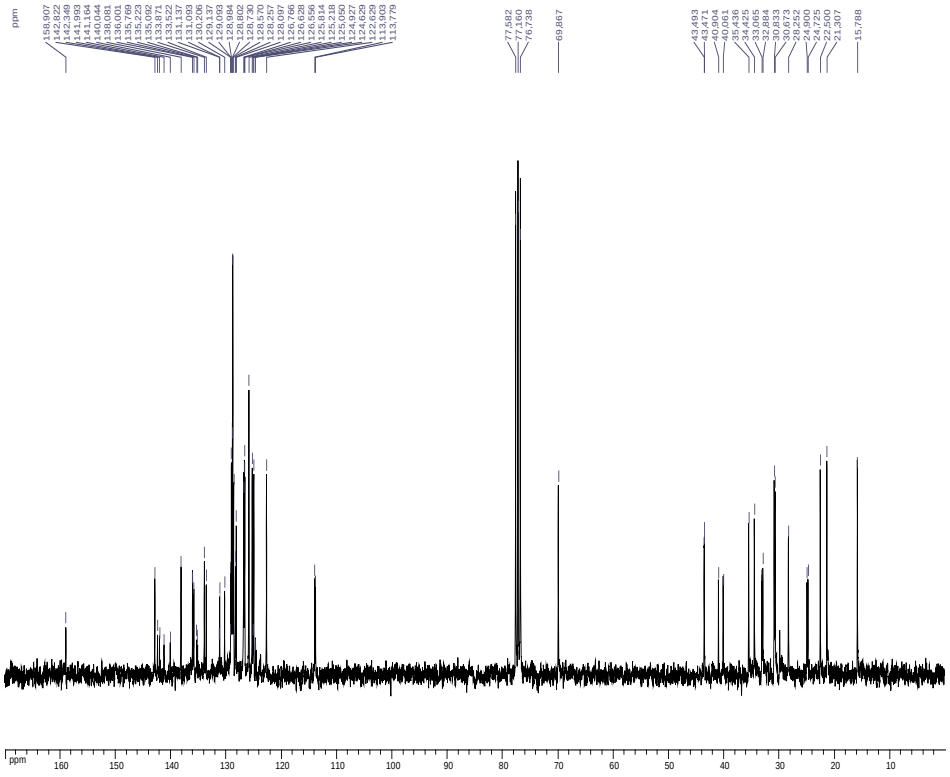
(**5c**) ^{13}C NMR (125 MHz, $CDCl_3$):



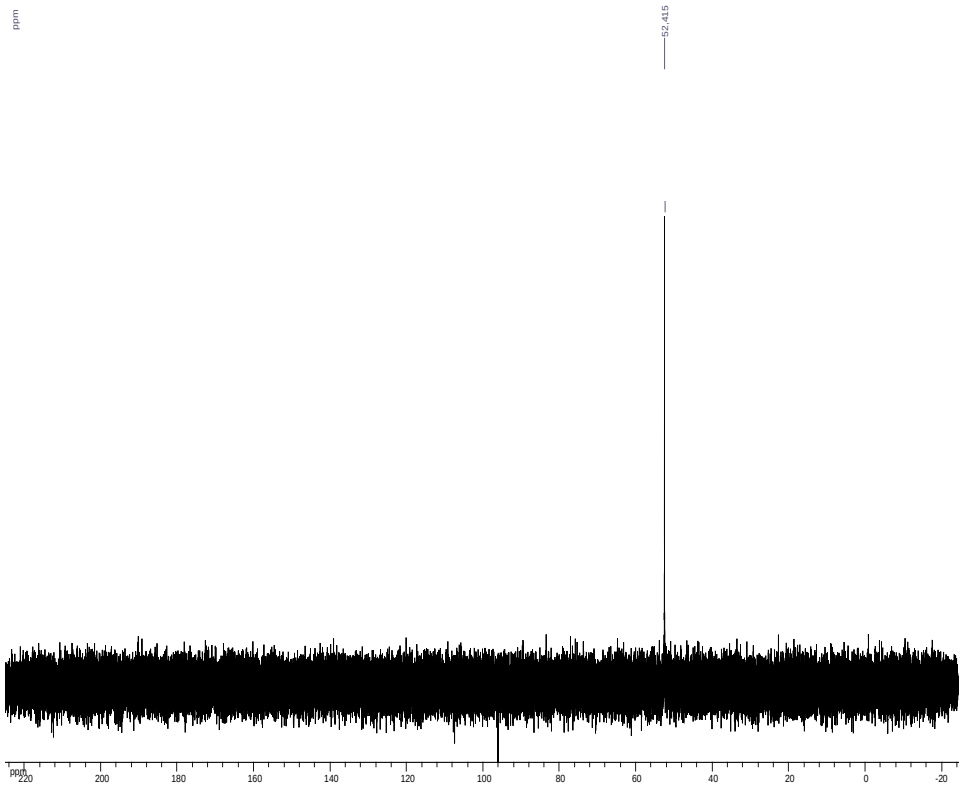
(**5c'**) ^{1}H NMR (500 MHz, $CDCl_3$):



(**5c'**) ^{13}C NMR (75 MHz, $CDCl_3$):



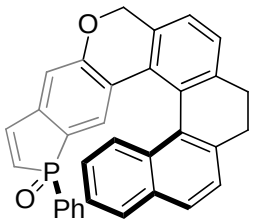
(**5c'**) ^{31}P NMR (202 MHz, $CDCl_3$):

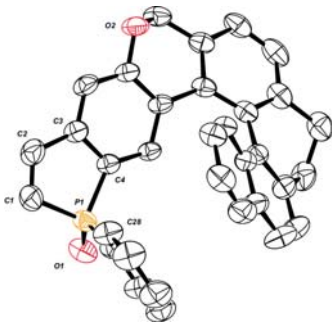


IV. X-Ray crystal structure determinations.

X-ray structure of (a) **5a'**: $C_{33}H_{23}O_2P$, $CHCl_3$, M =601.85 g.mol^{-1}, yellow rod, 0.60 x 0.12 x 0.08 mm^3, orthorhombic, P b c a, a= 9.5669(2), b=19.1416(4), c= 31.576(2) Å; V=5782.4(4) Å^3, Z=8, D=1.383 g.cm^{-3}, μ(CuKα)= 3.636mm^{-1}, CuKα radiation (λ=1.54187 Å), T=193 K, $2\theta_{max}$ 68.24°, 20524 reflections, 5197 independent, 2064 with I/2σ(I), Rint= 0.0396, mean σ(I)/I=0.0369, 32 soft restraints applied to disordered chloroform atom parameters, 399 parameters, R(F_{obs})= 0.0879, Rw(F^2)= 0.2411 (All data), S= 1.187, min. and max. residual electron density -0.798, 0.979 e.Å^{-3}; (b) **5b** : $C_{43}H_{41}O_2P$, 2($CHCl_3$), M = 859.46 g.mol^{-1}, yellow tab, 0.42 x 0.17 x 0.11 mm^3, monoclinic, P 2_1, a= 10.4867(3), b= 21.7680(9), c= 10.5830(7) Å, β= 116.312(8)° ; V= 2165.53(18) Å^3, Z=2, D= 1.318 g.cm^{-3}, μ(CuKα)= 4.249mm^{-1}, CuKα radiation (λ=1.54187 Å), T=193 K, $2\theta_{max}$ 68.24°, 19770 reflections, 7385 independent, 2064 with I/2σ(I), Rint= 0.0591, mean σ(I)/I= 0.0719, 491 parameters, R(F_{obs})= 0.1084, Rw(F^2)=0.2414 (All data), S= 1.174, Flack parameter 0.00 (3), min. and max. residual electron density -0.532, 0.460 e.Å^{-3}. Data collection by means of a Rigaku Rapid II diffractometer equipped with a rotating anode mm007 HF generator and Osmic mirrors (ω-scans), structure solution by direct methods with SHELXS-97, structure refinement with SHELXL-97. C-bound H atoms have been added geometrically treated as riding on their parent atoms, 32 soft restraints on positional and anisotropic displacement parameters for the disordered solvent chloroform molecule refined over two positions with refined occupancy factors of 0.58 :0.43; CCDC 960385 (**5a'**) and CCDC 960386 (**5b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(S_P*, *M**)-**5a' (**CCDC 960385)





(S_P,*P*)-**5b (**CCDC 960386)