Supporting Information

Asymmetric Synthesis of *P*-Stereogenic Diarylphosphinites by Palladium-Catalyzed Enantioselective Addition of Diarylphosphines to Benzoquinones

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Contents of Supporting Information:

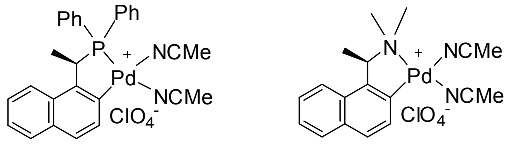
1. General information

All air-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or argon. Solvents were degassed prior to use when necessary. Low Temp PAIRSTIRRER PSL-1800 machine was used for controlling temperatures for the reactions. Column chromatography was conducted on Silica gel 60 (Merck). NMR spectra are recorded on Bruker ACF-300 spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121 MHz for ^{31}P), ACF-400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C, and 162 MHz for ^{31}P), and ACF-500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, and 202 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to an internal $SiMe_4$ standard (δ = 0 ppm) for ^{1}H NMR, chloroform-d (δ = 77.23 ppm) for ^{13}C NMR, and to an external 85% H_3PO_4 (δ = 0 ppm) standard for ^{31}P NMR. The following abbreviations were used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad. Optical rotations were measured on a Perkin-Elmer 341 polarimeter, and an ATAGO AP-300 polarimeter. HRMS(ESI) were recorded on a time-of-fligh (TOF) LC/MS instrument.

2. Materials

The commercially available solvents and chemicals listed below were used as received for the reaction without further purification: degassed dichloromethane (Alfa), degassed chloroform (Alfa), degassed THF (Alfa), degassed MeCN (Alfa), quinones **2m** (CAS:844-51-9) (Aldrich), **2n** (CAS:137-18-8) (Aldrich), **2o** (CAS:106-51-4) (Aldrich), and **2p** (CAS:615-93-0) (Aldrich).

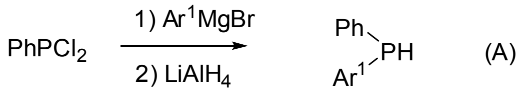
Complex PdL1* (CAS:1335292-75-5)[1] and PdL2* (CAS:142216-18-0)[2] were prepared according to the reported procedures.



PdL1* **PdL2***

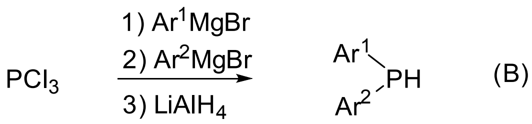
Caution! *Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.*

3. Preparation of racemic secondary phospines Ar^1Ar^2PH



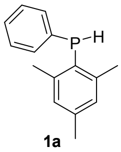
The racemic secondary phosphines **1a** (CAS: 217975-66-1),[3] **1b, 1c, 1d, 1e, 1f** (CAS: 141868-58-8),[4] **1g** (CAS: 179117-27-2)[5] were prepared according to reported procedure[5] with modifications (**eq A**). A typical procedure for the synthesis of **1a** is shown below.

To a solution of $PhPCl_2$ (4.49 g, 25.1 mmol) in THF (50 mL) was added slowly MesMgBr (25.1 mmol in 50 mL of THF, prepared from MesBr (5.00 g, 25.1 mmol) and Mg (0.72 g, 30.1 mmol) in 50 mL of THF) (Mes = 2,4,6-$Me_3C_6H_2$) at –80 °C under N_2, and the mixture was stirred at –80 °C for 2 h before it was warmed to room temperature and stirred for another 2 h. The mixture was cooled to 0 °C and $LiAlH_4$ (1.14 g, 30.1 mmol) was added slowly. The mixture was kept stirring at room temperature for 2 h. Degassed water (10 mL) was added dropwise at 0 °C and the mixture was extracted with ether (40 mL × 3). The organic layer was combined and dried over $MgSO_4$. The solvent was removed by distillation and the residue was subjected to high vacuum microdistillation to give Ph(Mes)PH (**1a**) (4.30 g, 75%).

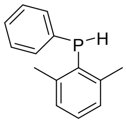


The racemic secondary phosphines **1h** and **1i** were prepared similarly with modifications (**eq B**). A typical procedure for the synthesis of **1h** is shown below.

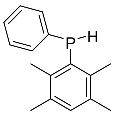
To a solution of PCl_3 (2.07 g, 15.1 mmol) in THF (40 mL) was added slowly MesMgBr (15.1 mmol in 40 mL of THF, prepared from MesBr (3.00 g, 15.1 mmol) and Mg (0.43 g, 18.1 mmol) in 40 mL of THF) at –80 °C under N_2, and the mixture was stirred at –80 °C for 2 h. 4-MeC_6H_4MgBr (15.1 mmol in 40 mL of THF, prepared from 4-MeC_6H_4Br (2.58 g, 15.1 mmol) and Mg (0.43 g, 18.1 mmol) in 40 mL of THF) was added dropwise, and the mixture was stirred at –80 °C for 2 h before it was warmed to room temperature and stirred for another 2 h. The mixture was cooled to 0 °C and $LiAlH_4$ (0.69 g, 18.1 mol) was added slowly. The mixture was kept stirring at room temperature for 2 h. Degassed water (10 mL) was added dropwise at 0 °C and the mixture was extracted with ether (40 mL × 3). The combined organic layer was dried over $MgSO_4$. The solvent was removed by distillation and the residue was subjected to high vacuum microdistillation to give (4-MeC_6H_4)(Mes)PH (**1h**) (1.57 g, 43%).



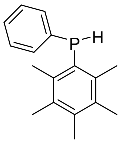
1a **Compound 1a** (CAS: 217975-66-1)[3] was prepared by the reaction of 2,4,6-$Me_3C_6H_2MgBr$ with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (75% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) δ –76.6. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.29 (s, 3H), 2.40 (s, 6H), 4.70-5.90 (br s, 1H), 6.94 (s, 2H), 7.19-7.28 (m, 5H).



1b **Compound 1b** was prepared by the reaction of 2,6-$Me_2C_6H_3MgBr$ with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (78% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ –76.0. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.43 (s, 6H), 5.39 (d, J_{HP} = 223.5 Hz, 1H), 7.09 (d, J_{HH} = 7.4 Hz, 2H), 7.18 (t, J_{HH} = 7.9 Hz, 1H), 7.19-7.29 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 23.4 (d, J_{CP} = 11.5 Hz, 2C), 128.0 (s, 1C), 128.3 (d, J_{CP} = 3.1 Hz, 2C), 128.6 (d, J_{CP} = 6.0 Hz, 2C), 129.2 (s, 1C), 132.2 (d, J_{CP} = 12.1 Hz, 1C), 132.4 (d, J_{CP} = 16.4 Hz, 2C), 134.2 (d, J_{CP} = 12.6 Hz, 1C), 143.1 (d, J_{CP} = 12.4 Hz, 2C). HRMS (ESI) calcd for $C_{14}H_{16}P$ $[M+H]^+$ 215.0991, found 215.0990.

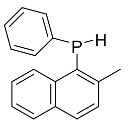


1c **Compound 1c** was prepared by the reaction of 2,3,5,6-Me_4C_6HMgBr with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (68% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) δ –72.2. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 6H), 2.36 (s, 6H), 5.45 (d, J_{HP} = 222.2 Hz, 1H), 7.01 (s, 1H), 7.18-7.27 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.5 (d, J_{CP} = 14.6 Hz, 2C), 20.9 (d, J_{CP} = 0.9 Hz, 2C), 127.7 (s, 1C), 128.5 (d, J_{CP} = 5.6 Hz, 2C), 132.1 (d, J_{CP} = 16.2 Hz, 2C), 132.3 (d, J_{CP} = 10.7 Hz, 1C), 133.2 (s, 1C), 134.2 (d, J_{CP} = 3.7 Hz, 2C), 135.2 (d, J_{CP} = 13.2 Hz, 1C), 139.0 (d, J_{CP} = 12.5 Hz, 2C). HRMS (ESI) calcd for $C_{16}H_{20}P$ $[M+H]^+$ 243.1306, found 243.1303.

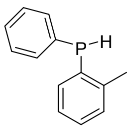


1d **Compound 1d** was prepared by the reaction of 2,3,4,5,6-Me_5C_6MgBr with $PhPCl_2$

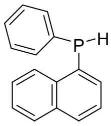
followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (65% yield). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 162 MHz) δ –69.9. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.24 (s, 6H), 2.27 (s, 3H), 2.44 (s, 6H), 5.46 (d, J_{HP}= 219.4 Hz, 1H), 7.19-7.24 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 17.4 (s, 3C), 20.8 (d, J_{CP} = 15.6 Hz, 2C), 127.5 (s, 1C), 128.5 (d, J_{CP} = 5.5 Hz, 2C), 129.2 (d, J_{CP} = 9.3 Hz, 1C), 131.9 (d, J_{CP} = 15.6 Hz, 2C), 133.2 (d, J_{CP} = 3.5 Hz, 2C), 135.8 (d, J_{CP} = 13.7 Hz, 1C), 136.8 (s, 1C), 138.8 (d, J_{CP} = 12.3 Hz, 2C). HRMS (ESI) calcd for $C_{17}H_{22}P$ $[M+H]^+$ 257.1462, found 257.1459.



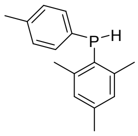
1e **Compound 1e** was prepared by the reaction of 2-Me-1-naphthylMgBr with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (53% yield). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) δ –79.6. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.68 (s, 3H), 5.68 (d, J_{HP} = 223.1 Hz, 1H), 7.16-7.19 (m, 3H), 7.22-7.26 (m, 2H), 7.37-7.46 (m, 3H), 7.80 (d, J = 8.4 Hz, 2H), 8.42 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.0 (d, J_{CP} = 13.2 Hz, 1C), 125.2 (s, 1C), 126.9 (s, 1C), 126.9 (d, J_{CP} = 15.9 Hz, 1C), 127.8 (s, 1C), 128.5 (d, J_{CP} = 12.8 Hz, 1C), 128.6 (d, J_{CP} = 5.5 Hz, 2C), 128.8 (s, 1C), 129.3 (d, J_{CP} = 3.8 Hz, 1C), 130.2 (s, 1C), 132.1 (d, J_{CP} = 16.3 Hz, 2C), 132.5 (d, J_{CP} = 3.3 Hz, 1C), 134.8 (d, J_{CP} = 12.0 Hz, 1C), 136.4 (d, J_{CP} = 10.8 Hz, 1C), 142.8 (d, J_{CP} = 13.3 Hz, 1C). HRMS (ESI) calcd for $C_{17}H_{16}P$ $[M+H]^+$ 251.0993, found 251.0990.



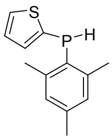
1f **Compound 1f** (CAS: 141868-58-8)[4] was prepared by the reaction of 2-MeC_6H_4MgBr with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (78% yield). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) δ –48.7. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.37 (s, 3H), 5.18 (d, J_{HP} = 220.9 Hz, 1H), 7.12 (t, J_{HH} = J_{HP} = 7.3 Hz, 1H), 7.17 (dd, J = 7.5 Hz, 3.5Hz, 1H), 7.23 (td, J = 7.5 Hz, 1.0 Hz, 1H), 7.28-7.31 (m, 3H), 7.35 (t, J = 7.5 Hz, 1H), 7.40-7.45 (m, 2H).



1g **Compound 1g** (CAS: 179117-27-2)[5] was prepared by the reaction of 1-naphthylMgBr with $PhPCl_2$ followed by reduction with $LiAlH_4$ according to the typical procedure (eq A) (48% yield). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) δ –50.3. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.51 (d, J_{HP} = 221.6 Hz, 1H), 7.24-7.28 (m, 3H), 7.43-7.49 (m, 5H), 7.80-7.85 (m, 3H), 8.23-8.25 (m, 1H).

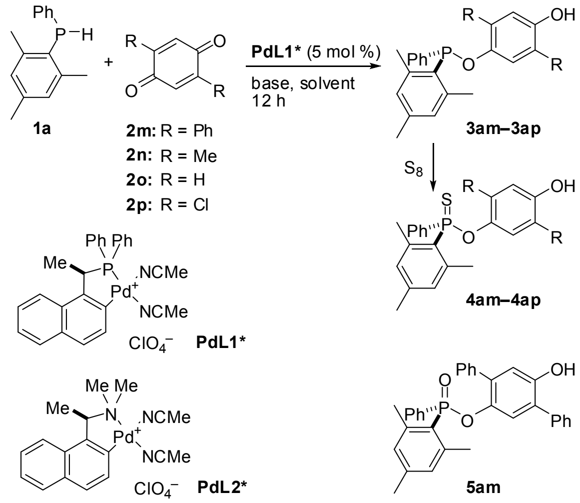


1h **Compound 1h** was prepared by the reaction of MesMgBr, 4-MeC_6H_4MgBr and PCl_3 followed by reduction with $LiAlH_4$ according to the typical procedure (eq B) (43% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ –77.6. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.28 (s, 6H), 2.39 (s, 6H), 5.33 (d, J_{HP} = 223.2 Hz, 1H), 6.92 (s, 2H), 7.03 (d, J = 7.6 Hz, 2H), 7.15 (t, J = 7.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3 (s, 1C), 21.4 (s, 1C), 23.3 (d, J_{CP} = 11.5 Hz, 2C), 128.9 (d, J_{CP} = 10.8 Hz, 1C), 129.2 (d, J_{CP} = 3.5 Hz, 2C), 129.4 (d, J_{CP} = 6.2 Hz, 2C), 132.5 (d, J_{CP} = 16.7 Hz, 2C), 134.1 (d, J_{CP} = 17.1 Hz, 1C), 137.8 (s, 1C), 138.9 (s, 1C), 142.9 (d, J_{CP} = 12.6 Hz, 2C). HRMS (ESI) calcd for $C_{16}H_{20}P$ $[M+H]^+$ 243.1304, found 243.1303.



1i **Compound 1i** was prepared by the reaction of MesMgBr, 2-thienylMgBr, and PCl_3 followed by reduction with $LiAlH_4$ according to the typical procedure (eq B) (53% yield). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ –97.1. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 2.46 (s, 6H), 5.56 (d, J_{HP} = 230.1 Hz, 1H), 6.89 (d, J = 1.6 Hz, 2H), 6.98 (td, J = 4.8 Hz, 1.2 Hz, 1H), 7.20 (t, J = 4.0 Hz, 1H), 7.40 (dd, J = 4.8 Hz, 0.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3 (s, 1C), 23.3 (d, J_{CP} = 11.3 Hz, 2C), 127.9 (d, J_{CP} = 7.5 Hz, 1C), 129.3 (d, J_{CP} = 3.3 Hz, 2C), 129.5 (d, J_{CP} = 8.9 Hz, 1C), 131.0 (s, 1C), 133.3 (d, J_{CP} = 30.3 Hz, 1C), 135.3 (d, J_{CP} = 25.2 Hz, 1C), 138.9 (s, 1C), 142.0 (d, J_{CP} = 12.4 Hz, 2C). HRMS (ESI) calcd for $C_{13}H_{16}PS$ $[M+H]^+$ 235.0711, found 235.0710.

4. Palladium-catalyzed asymmetric addition of Ph(Mes)PH (1a) to 2,5-diphenyl-1,4-benzoquinone (2m) (Table 1)



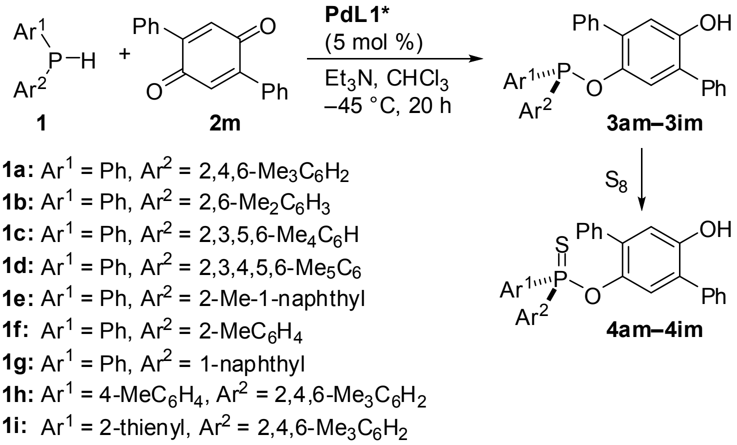
A typical prodecure (Table 1, entry 1): To a solution of phenyl(2,4,6-trimethyl)-phosphine (**1a**) (68.5 mg, 0.300 mmol) in degassed $CHCl_3$ (7 mL) was added **PdL1*** (9.4 mg, 0.015 mmol, 5 mol%). The solution was stirred at room temperature for 2 min, before it was cooled to –45 °C. 2,5-Diphenyl-1,4-benzoquinone (**2m**) (82.0 mg, 0.315 mmol) was added, followed by dropwise addition of Et_3N (30.3 mg, 0.300 mmol) in $CHCl_3$ (0.5 mL). The mixtrue was stirred at –45 °C for 12 h to give a $CHCl_3$ solution containing phosphinite **3am** as a major component. The phosphinite **3am** was found to undergo decomposition/oxidation during the isolation by silica-gel chromatography, and it was isolated and characterized as thiophosphinate **4am** or phosphinate **5am**.

For the conversion into thiophosphinate **4am**, excess sulfur powder (14.4 mg, 0.450 mmol) was added to the reaction mixture. After stirring at room temperature for 15 min, the reaction mixture was passed through a short celite pad and the solution was concentrated on a rotary evaporator. The residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/7) to give **4am** (150 mg, 96%).

For the conversion into phosphinate **5am**, excess 30% H_2O_2 (2 mL) was added to the reaction mixture in $CHCl_3$, and the mixture was stirred vigorously at room temperature for 15 min. The mixture was extracted with CH_2Cl_2 (15 mL × 3). The organic extracts were washed with H_2O, and dried over $MgSO_4$. The solvent was removed by a rotary evaporator. The residue was subjected to silica-gel chromatography (acetone/CH_2Cl_2 = 1/10) to give **5am**

(142 mg, 94%).

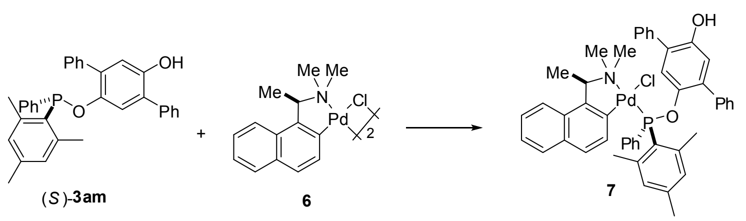
5. Palladium-catalyzed asymmetric addition of diarylphosphines 1 to benzoquinone 2m (Table 2)



A general procedure: To a solution of diarylphosphine **1** (0.300 mmol) in degassed $CHCl_3$ (7 mL) was added **PdL1*** (9.4 mg, 0.015 mmol, 5 mol%). The solution was stirred at room temperature for 2 min, before it was cooled to –45 °C. 2,5-Diphenyl-1,4-benzoquinone (**2m**) (82.0mg, 0.315 mmol) was added, followed by dropwise addition of Et_3N (30.3 mg, 0.300 mmol) in $CHCl_3$ (0.5 mL). The solution was subsequently stirred at –45 °C for 20 h to give a $CHCl_3$ solution containing phosphinite **3** as a major component.

For the conversion into thiophosphinate **4**, excess sulfur powder (14.4 mg, 0.450 mmol) was added to the reaction mixture. After stirring at room temperature for 15 min, the reaction mixture was passed through a short celite pad and the solution was concentrated on a rotary evaporator. The residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/7) to give **4**.

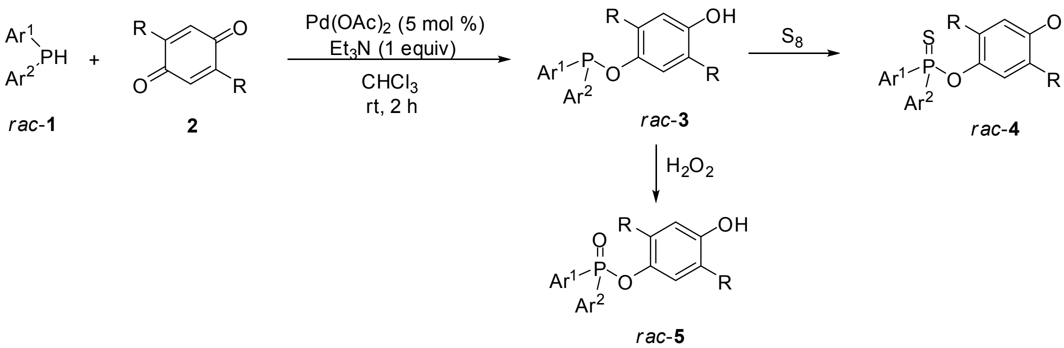
6. Determination of the absolute configuration of phosphinite 3am



To the reaction mixture containing phosphinite **3am**, which was obtained by the reaction of diarylphosphine **1a** (0.300 mmol) with benzoquinone **2m** (Table 1, entry 1), was added palladium complex (*R*)-**6** (107.2 mg, 0,157 mmol, 0.315 mol of Pd) (CAS: 80145-77-3).[6] The mixture was stirred at room temperature for 30 min and was concentrated on a rotary evaporator. The residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/4) to give the phosphinite comeplex **7** (236.2 mg, 95%).

Colorless crystals of complex **7** suitable for X-ray crystallographic analysis were obtained by recrystallization from dichloromethane/ether/hexane. The ORTEP drawing of compelx **7** is shown in Figure S1 (page S23). The X-ray analysis revealed that absolute configuration of **3am** is *S*.

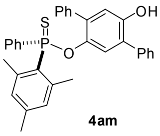
7. A typical procedure for the preparation of racemic 4 and 5



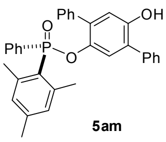
The *rac*-**4** and *rac*-**5** were prepared at room temperature employing $Pd(OAc)_2$ as a catalyst. A typical procedure for the synthesis of *rac*-**4a** and *rac*-**5a** is shown below.

To a solution of phenyl(2,4,6-trimethylphenyl)phosphine (**1a**) (68.5 mg, 0.300 mmol) in degassed $CHCl_3$ (7 mL) was added $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%) and 2,5-diphenyl-1,4-benzoquinone (**2m**) (82.0 mg, 0.315 mmol) at room temperature. Subsequently, Et_3N (30.3 mg, 0.300 mmol) in $CHCl_3$ (0.5 mL) was added dropwise. The solution was stirred at room temperature and the reaction was monitored by $^{31}P\{^1H\}$ NMR. Upon completion (about 2 h), the reaction mixture was treated with excess sulfur powder (14.4 mg, 0.450 mmol) or excess 30% H_2O_2 (2 mL) to give racemic thiophosphinate *rac*-**4am** (85%) or phosphinate *rac*-**5am** (84%), respectively, which were isolated and purified as described above for the asymmetric addition.

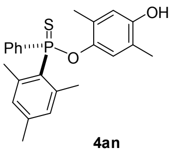
8. Characterization of the products 4 and 5

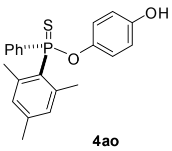


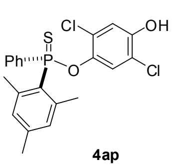
4am **Compound 4am**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 97/3, flow 1.0 mL/min, 280 nm, t_1 = 34.9 min (major), t_2 = 38.7 min (minor). $[\alpha]_D^{20}$ +202 (*c* 1.28, CH_2Cl_2) for 98% ee (*S*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) δ 85.3. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.24 (s, 3H), 2.27 (s, 6H), 5.25 (s, 1H), 6.75 (s, 1H), 6.81 (d, *J* = 4.6 Hz, 2H), 7.06 (td, *J* = 7.7 Hz, 3.5 Hz, 2H), 7.12-7.20 (m, 5H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.42-7.48 (m, 6H), 7.64 (d, *J* = 1.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.1 (s, 1C), 23.9 (d, J_{CP} = 4.5 Hz, 2C), 118.3 (s, 1C), 124.9 (d, J_{CP} = 4.9 Hz, 1C), 127.0 (s, 1C), 127.2 (s, 1C), 128.06 (s, 1C), 128.08 (d, J_{CP} = 13.5 Hz, 2C), 128.08 (s, 2C), 128.8 (d, J_{CP} = 117.0 Hz, 1C), 129.2 (s, 2C), 129.35 (s, 2C), 129.44 (s, 2C), 131.0 (d, J_{CP} = 12.4 Hz, 2C), 131.3 (d, J_{CP} = 13.3 Hz, 2C), 131.4 (d, J_{CP} = 2.8 Hz, 1C), 135.2 (d, J_{CP} = 101.0 Hz, 1C), 135.3 (d, J_{CP} = 4.6 Hz, 1C), 136.5 (s, 1C), 137.8 (s, 1C), 140.4 (d, J_{CP} = 9.3 Hz, 1C), 141.3 (d, J_{CP} = 2.8 Hz, 1C), 141.6 (d, J_{CP} = 11.7 Hz, 2C), 149.1 (s, 1C). HRMS (ESI) calcd for $C_{33}H_{30}O_2PS$ $[M+H]^+$ 521.1704, found 521.1701.



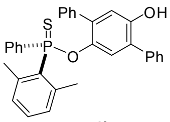
5am **Compound 5am**. The ee was measured by HPLC (Daicel Chiralpak IC), hexane/2-propanol = 90/10, flow 1.0 mL/min, 280 nm, t_1 = 16.8 min (minor), t_2 = 19.4 min (major). $[\alpha]_D^{20}$ –52 (*c* 1.16, CH_2Cl_2) for 98% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 35.0. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H), 2.36 (s, 6H), 6.12 (s, 1H), 6.85 (d, *J* = 4.2 Hz, 2H), 6.87 (s, 1H), 7.06 (d, *J* = 1.3 Hz, 1H), 7.22-7.27 (m, 5H), 7.28-7.34 (m, 5H), 7.36-7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3 (s, 1C), 23.5 (d, J_{CP} = 3.4 Hz, 2C), 118.7 (s, 1C), 121.9 (d, J_{CP} = 4.0 Hz, 1C), 124.0 (d, J_{CP} = 129.5 Hz, 1C), 127.4 (s, 1C), 127.7 (s, 1C), 127.9 (s, 1C), 128.1 (s, 2C), 128.5 (d, J_{CP} = 13.8 Hz, 2C), 129.0 (s, 2C), 129.2 (s, 2C), 129.8 (s, 2C), 130.6 (d, J_{CP} = 11.5 Hz, 2C), 131.1 (d, J_{CP} = 13.3 Hz, 2C), 131.8 (d, J_{CP} = 2.9 Hz, 1C), 134.2 (d, J_{CP} = 137.2 Hz, 1C), 134.6 (d, J_{CP} = 5.0 Hz, 1C), 136.8 (s, 1C), 137.7 (s, 1C), 141.1 (d, J_{CP} = 8.4 Hz, 1C), 142.6 (d, J_{CP} = 2.8 Hz, 1C), 144.1 (d, J_{CP} = 11.8 Hz, 2C), 149.6 (s, 1C). HRMS (ESI) calcd for $C_{33}H_{30}O_3P$ $[M+H]^+$ 505.1933, found 505.1938.


4an **Compound 4an**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 97/3, flow 1.0 mL/min, 280 nm, t_1 = 22.1 min (major), t_2 = 39.1 min (minor). $[\alpha]_D^{20}$ +112 (c 2.67, CH_2Cl_2) for 87% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 84.4. ^1H NMR ($CDCl_3$, 400 MHz) δ 1.91 (s, 3H), 2.00 (s, 3H), 2.30 (s, 3H), 2.43 (s, 6H), 6.43 (s, 1H), 6.76 (s, 1H), 6.91 (d, J = 4.6 Hz, 2H), 7.39 (td, J = 7.6 Hz, 3.4 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.86 (dd, J = 14.0 Hz, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.6 (s, 1C), 17.3 (s, 1C), 21.2 (s, 1C), 24.3 (d, J_{CP} = 4.4 Hz, 2C), 117.5 (s, 1C), 121.5 (d, J_{CP} = 1.4 Hz, 1C), 124.3 (d, J_{CP} = 4.2 Hz, 1C), 128.5 (d, J_{CP} = 13.2 Hz, 2C), 128.6 (d, J_{CP} = 115.8 Hz, 1C), 128.9 (d, J_{CP} = 4.7 Hz, 1C), 131.3 (d, J_{CP} = 11.9 Hz, 2C), 131.5 (d, J_{CP} = 13.1 Hz, 2C), 132.0 (d, J_{CP} = 2.9 Hz, 1C), 136.4 (d, J_{CP} = 100.2 Hz, 1C), 141.5 (d, J_{CP} = 3.0 Hz, 1C), 141.9 (d, J_{CP} = 11.6 Hz, 2C), 142.0 (d, J_{CP} = 9.6 Hz, 1C), 150.4 (d, J_{CP} = 1.6 Hz, 1C). HRMS (ESI) calcd for $C_{23}H_{26}O_2PS$ $[M+H]^+$ 397.1391, found 397.1386.

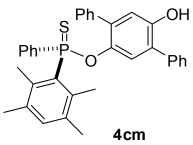

4ao **Compound 4ao**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 96/4, flow 0.8 mL/min, 280 nm, t_1 = 34.5 min (major), t_2 = 37.1 min (minor). $[\alpha]_D^{20}$ +60 (c 1.00, CH_2Cl_2) for 68% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 85.1. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.36 (s, 6H), 5.16 (s, 1H), 6.55 (d, J = 8.8 Hz, 2H), 6.67 (dd, J = 8.8 Hz, 1.7 Hz, 2H), 6.88 (d, J = 4.7 Hz, 2H), 7.43 (td, J = 7.6 Hz, 3.6 Hz, 2H), 7.52 (td, J = 7.6 Hz, 2.0 Hz, 1H), 7.91 (dd, J = 14.0 Hz, 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2 (s, 1C), 24.0 (d, J_{CP} = 4.9 Hz, 2C), 115.9 (s, 1C), 123.1 (d, J_{CP} = 4.4 Hz, 1C), 128.57 (d, J_{CP} = 13.5 Hz, 2C), 128.63 (d, J_{CP} = 118.4 Hz, 1C), 131.3 (d, J_{CP} = 13.0 Hz, 2C), 131.8 (d, J_{CP} = 11.7 Hz, 2C), 132.2 (d, J_{CP} = 2.8 Hz, 1C), 135.9 (d, J_{CP} = 99.9 Hz, 1C), 141.60 (d, J_{CP} = 3.8 Hz, 1C), 141.64 (d, J_{CP} = 11.5 Hz, 2C), 143.1 (d, J_{CP} = 9.2 Hz, 1C), 152.7 (d, J_{CP} = 1.6 Hz, 1C). HRMS (ESI) calcd for $C_{21}H_{22}O_2PS$ $[M+H]^+$ 396.1078, found 369.1080.


4ap **Compound 4ap**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 11.8 min (major), t_2 = 18.3 min

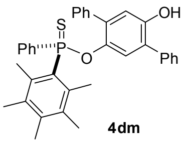
(minor). $[\alpha]_D^{20}$ –27 (*c* 1.13, CH_2Cl_2) for 7% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 87.9. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.30 (s, 3H), 2.39 (s, 6H), 6.90 (s, 1H), 6.90 (d, *J* = 3.1 Hz, 2H), 7.39 (td, *J* = 7.7Hz, 3.5 Hz, 2H), 7.48 (td, *J* = 7.1 Hz, 1.4 Hz, 1H), 7.61 (d, *J* = 1.3 Hz, 1H), 7.92 (dd, *J* = 14.4 Hz, 7.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2 (s, 1C), 24.1 (d, J_{CP} = 4.8 Hz, 2C), 117.4 (s, 1C), 117.8 (s, 1C), 122.7 (d, J_{CP} = 4.9 Hz, 1C), 125.9 (d, J_{CP} = 5.7 Hz, 1C), 128.47 (d, J_{CP} = 116.8 Hz, 1C), 128.55 (d, J_{CP} = 13.5 Hz, 2C), 131.5 (d, J_{CP} = 13.2 Hz, 2C), 131.7 (d, J_{CP} = 12.3 Hz, 2C), 132.5 (d, J_{CP} = 2.9 Hz, 1C), 134.8 (d, J_{CP} = 99.2 Hz, 1C), 140.3 (d, J_{CP} = 8.7 Hz, 1C), 141.7 (d, J_{CP} = 11.9 Hz, 2C), 141.8 (d, J_{CP} = 3.1 Hz, 1C), 148.4 (d, J_{CP} = 1.2 Hz, 1C). HRMS (ESI) calcd for $C_{21}H_{20}Cl_2O_2PS$ $[M+H]^+$ 437.0299, found 437.0292.



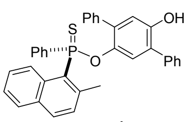
4bm **Compound 4bm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 97/3, flow 1.0 mL/min, 280 nm, t_1 = 36.6 min (minor), t_2 = 41.6 min (major). $[\alpha]_D^{20}$ +199 (*c* 1.71, CH_2Cl_2) for 98% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) δ 84.6. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.31 (s, 6H), 5.14 (s, 1H), 6.79 (s, 1H), 7.00 (dd, *J* = 7.4 Hz, 5.1 Hz, 2H), 7.10 (td, *J* = 7.7 Hz, 3.5 Hz, 2H), 7.16-7.24 (m, 6H), 7.30 (t, *J* = 6.9 Hz, 1H), 7.38-7.50 (m, 7H), 7.66 (d, *J* = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 24.0 (s, J_{CP} = 4.7 Hz, 2C), 118.4 (s, 1C), 124.9 (d, J_{CP} = 4.8 Hz, 1C), 127.1 (s, 1C), 127.3 (s, 1C), 128.16 (s, 2C), 128.17 (d, J_{CP} = 13.3 Hz, 2C), 128.23 (s, 1C), 129.2 (s, 2C), 129.50 (s, 2C), 129.54 (s, 2C), 130.4 (d, J_{CP} = 12.6 Hz, 2C), 131.1 (d, J_{CP} = 2.5 Hz, 1C), 131.2 (d, J_{CP} = 12.5 Hz, 2C), 131.6 (d, J_{CP} = 3.0 Hz, 1C), 132.1 (d, J_{CP} = 115.5 Hz, 1C), 134.9 (d, J_{CP} = 98.1 Hz, 1C), 135.3 (d, J_{CP} = 1.1 Hz, 1C), 136.5 (s, 1C), 137.8 (s, 1C), 140.4 (d, J_{CP} = 9.2 Hz, 1C), 141.6 (d, J_{CP} = 11.0 Hz, 2C), 149.1 (s, 1C). HRMS (ESI) calcd for $C_{32}H_{28}O_2PS$ $[M+H]^+$ 507.1549, found 507.1548.



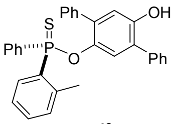
4cm **Compound 4cm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 16.7 min (minor), t_2 = 22.4 min (major). $[\alpha]_D^{20}$ +164 (*c* 1.58, CH_2Cl_2) for 97% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 84.3. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.05 (s, 6H), 2.09 (s, 6H), 5.16 (s, 1H), 6.75 (d, *J* = 0.9 Hz, 1H), 7.02 (s, 1H), 7.13 (td, *J* = 8.0 Hz, 3.6 Hz, 2H), 7.16-7.23 (m, 5H), 7.28-7.36 (m, 2H), 7.39-7.45 (m, 4H), 7.49 (dd, J = 14.0 Hz, 8.4 Hz, 2H), 7.73 (d, J = 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.1 (d, J_{CP} = 6.4 Hz, 2C), 20.2 (d, J_{CP} = 1.7 Hz, 2C), 118.1 (s, 1C), 123.3 (d, J_{CP} = 5.4 Hz, 1C), 127.0 (s, 1C), 127.2 (s, 1C), 127.9 (s, 2C), 128.0 (s, 1C), 128.1 (d, J_{CP} = 11.3 Hz, 2C), 129.1 (s, 2C), 129.4 (s, 2C), 129.5 (s, 2C), 131.3 (d, J_{CP} = 11.9 Hz, 2C), 131.4 (d, J_{CP} = 2.8 Hz, 2C), 133.1 (d, J_{CP} = 119.0 Hz, 1C), 134.5 (d, J_{CP} = 5.2 Hz, 1C), 134.6 (d, J_{CP} = 2.8.0 Hz, 1C), 135.22 (d, J_{CP} = 99.8 Hz, 1C), 135.20 (d, J_{CP} = 13.7 Hz, 2C), 137.5 (d, J_{CP} = 11.4 Hz, 2C), 137.7 (s, 1C), 141.3 (d, J_{CP} = 9.3 Hz, 1C), 148.7 (s, 1C). HRMS (ESI) calcd for $C_{34}H_{32}O_2PS$ $[M+H]^+$ 535.1861, found 535.1860.



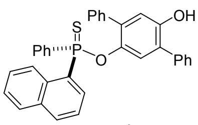
4dm **Compound 4dm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 15.7 min (minor), t_2 = 19.3 min (major). $[\alpha]_D^{20}$ +165 (c 2.55, CH_2Cl_2) for 97% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 84.3. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.07 (s, 12H), 2.24 (s, 3H), 5.11 (s, 1H), 6.76 (s, 1H), 7.11-7.25 (m, 7H), 7.29-7.47 (m, 6H), 7.51 (dd, J = 14.0 Hz, 7.6 Hz, 2H), 7.71 (d, J = 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 16.3 (d, J_{CP} = 1.7 Hz, 2C), 17.3 (s, 1C), 21.5 (d, J_{CP} = 6.8 Hz, 2C), 118.1 (s, 1C), 123.1 (d, J_{CP} = 5.6 Hz, 1C), 127.0 (s, 1C), 127.2 (s, 1C), 128.0 (s, 2C), 128.06 (d, J_{CP} = 11.5 Hz, 2C), 128.07 (s, 1C), 129.1 (s, 2C), 129.4 (s, 2C), 129.6 (s, 2C), 131.0 (d, J_{CP} = 122.6 Hz, 1C), 131.36 (d, J_{CP} = 11.8 Hz, 2C), 131.40 (d, J_{CP} = 3.1 Hz, 1C), 133.9 (d, J_{CP} = 13.2 Hz, 2C), 134.4 (d, J_{CP} = 5.3 Hz, 1C), 135.5 (d, J_{CP} = 99.0 Hz, 1C), 136.6 (s, 1C), 136.9 (d, J_{CP} = 10.8 Hz, 2C), 137.8 (s, 1C), 138.5 (d, J_{CP} = 3.4 Hz, 1C), 141.5 (d, J_{CP} = 9.0 Hz, 1C), 148.6 (s, 1C). HRMS (ESI) calcd for $C_{35}H_{34}O_2PS$ $[M+H]^+$ 549.2017, found 549.2014.



4em **Compound 4em**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 28.2 min (minor), t_2 = 30.6 min (major). $[\alpha]_D^{20}$ +213 (c 1.25, CH_2Cl_2) for 95% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 83.9. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (d, J = 1.5 Hz, 3H), 5.24 (s, 1H), 6.75 (s, 1H), 6.95 (t, J = 7.6 Hz, 2H), 7.02-7.42 (m, 16H), 7.73 (d, J = 1.3 Hz, 1H), 7.74 (dd, J = 17.4 Hz, 8.2 Hz, 2H), 8.53 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 24.4 (d, J_{CP} = 5.9 Hz, 1C), 118.1 (s, 1C), 124.0 (d, J_{CP} = 5.0 Hz, 1C), 125.3 (s, 1C), 126.2 (s, 1C), 127.1 (s, 2C), 127.2 (d, J_{CP} = 6.5 Hz, 1C), 127.8 (s, 2C), 127.99 (d, J_{CP} = 115.6 Hz, 1C), 128.04 (d, J_{CP} = 2.1 Hz, 2C), 128.2 (d, J_{CP} = 13.8 Hz, 1C), , 128.5 (s, 1C), 129.0 (s, 2C), 129.3 (s, 2C), 129.5 (s, 2C), 130.3 (d, J_{CP} = 14.5 Hz, 1C), 131.2 (d, J_{CP} = 12.3 Hz, 2C), 131.7 (d, J_{CP} = 2.4 Hz, 1C), 132.4 (d, J_{CP} = 4.0 Hz, 1C), 132.5 (d, J_{CP} = 10.4 Hz, 1C), 132.9 (d, J_{CP} = 11.0 Hz, 1C), 134.8 (d, J_{CP} = 100.9 Hz, 1C), 135.0 (d, J_{CP} = 4.9 Hz, 1C), 136.4 (s, 1C), 137.2 (s, 1C), 141.0 (d, J_{CP} = 9.9 Hz, 1C), 141.5 (d, J_{CP} = 9.9 Hz, 1C), 149.1 (s, 1C). HRMS (ESI) calcd for $C_{35}H_{28}O_2PS$ $[M+H]^+$ 543.1548, found 543.1549.

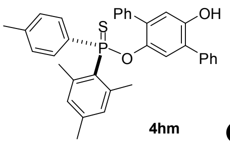


4fm **Compound 4fm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 19.5 min (minor), t_2 = 23.9 min (major). $[\alpha]_D^{20}$ +33 (*c* 1.09, CH_2Cl_2) for 43% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 80.7. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.15 (s, 3H), 5.19 (s, 1H), 6.90 (d, J = 0.5 Hz, 1H), 7.10 (d, J = 1.5 Hz, 1H), 7.11 (t, J = 6.5 Hz, 1H), 7.22-7.27 (m, 6H), 7.35-7.44 (m, 9H), 7.53 (dd, J = 14.5 Hz, 7.5 Hz, 2H), 8.03 (dd, J = 14.5 Hz, 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6 (d, J_{CP} = 4.6 Hz, 1C), 118.3 (s, 1C), 123.5 (d, J_{CP} = 4.7 Hz, 1C), 125.8 (d, J_{CP} = 12.9 Hz, 1C), 127.3 (s, 1C), 127.5 (s, 1C), 128.16 (s, 2C), 128.17 (s, 1C), 128.4 (d, J_{CP} = 13.7 Hz, 2C), 129.1 (s, 2C), 129.5 (s, 2C), 129.9 (s, 2C), 131.2 (d, J_{CP} = 12.2 Hz, 2C), 131.8 (d, J_{CP} = 2.6 Hz, 1C), 132.1 (d, J_{CP} = 12.8 Hz, 1C), 132.26 (d, J_{CP} = 109.9 Hz, 1C), 132.33 (d, J_{CP} = 3.2 Hz, 1C), 132.9 (d, J_{CP} = 10.0 Hz, 1C), 134.7 (d, J_{CP} = 106.4 Hz, 1C), 135.8 (d, J_{CP} = 4.8 Hz, 1C), 136.4 (s, 1C), 137.6 (s, 1C), 141.1 (d, J_{CP} = 12.4 Hz, 1C), 141.4 (d, J_{CP} = 8.7 Hz, 1C), 149.2 (s, 1C). HRMS (ESI) calcd for $C_{31}H_{26}O_2PS$ $[M+H]^+$ 493.1391, found 493.1387.

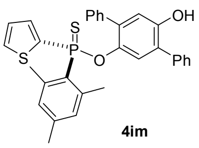


4gm **Compound 4gm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 96/4, flow 0.8 mL/min, 280 nm, t_1 = 24.1 min (major), t_2 = 28.3 min (minor). $[\alpha]_D^{20}$ –19 (*c* 1.24, CH_2Cl_2) for 24% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 81.1. ^1H NMR ($CDCl_3$, 400 MHz) δ 5.21 (s, 1H), 6.90 (d, J = 0.6 Hz, 1H), 7.12 (d, J = 1.6 Hz, 1H,), 7.16-7.29 (m, 6H), 7.30-7.42 (m, 9H), 7.45-7.49 (m, 1H), 7.56 (dd, J = 14.4 Hz, 8.4 Hz, 2H), 7.81 (d, J = 8.2 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.32 (ddd, J = 17.2 Hz,7.6 Hz, 1.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.3 (s, 1C), 123.5 (d, J_{CP} = 4.8 Hz, 1C), 124.6 (d, J_{CP} = 14.7 Hz, 1C), 126.3 (s, 1C), 126.7 (d, J_{CP} = 5.8 Hz, 1C), 127.1 (s, 1C), 127.4 (d, J_{CP} = 1.2 Hz, 1C), 127.5 (s, 1C), 128.0 (s, 2C), 128.1 (s, 1C), 128.5 (d, J_{CP} =

13.8 Hz, 2C), 129.1 (s, 2C), 129.3 (d, J_{CP} = 27.9 Hz, 1C), 129.4 (s, 2C), 129.5 (d, J_{CP} = 107.8 Hz, 1C), 129.9 (s, 2C), 131.0 (d, J_{CP} = 12.2 Hz, 2C), 131.83 (d, J_{CP} = 11.0 Hz, 1C), 131.86 (d, J_{CP} = 3.1 Hz, 1C), 133.8 (d, J_{CP} = 3.1 Hz, 1C), 131.9 (d, J_{CP} = 9.9 Hz, 1C), 134.0 (d, J_{CP} = 10.9 Hz, 1C), 135.2 (d, J_{CP} = 108.8 Hz, 1C), 135.8 (d, J_{CP} = 4.9 Hz, 1C),136.4 (s, 1C), 137.5 (s, 1C), 141.5 (d, J_{CP} = 8.8 Hz, 1C), 149.3 (s, 1C). HRMS (ESI) calcd for $C_{34}H_{26}O_2PS$ $[M+H]^+$ 529.1391, found 529.1388.

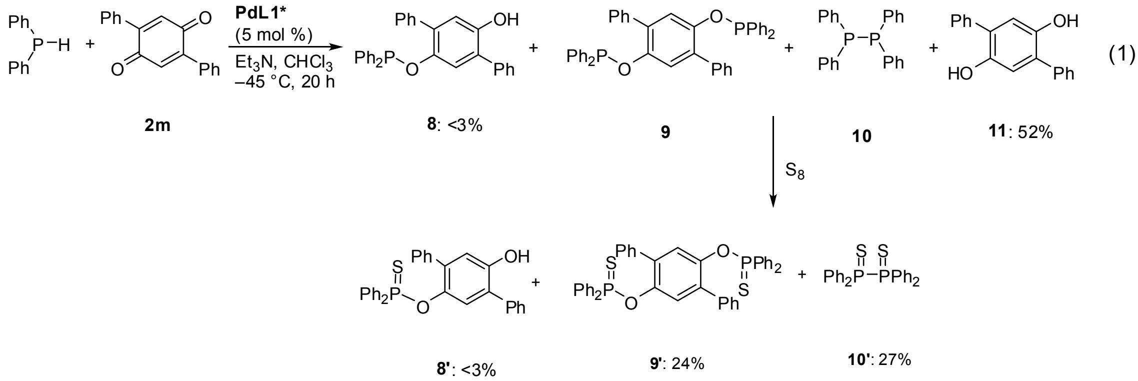


4hm **Compound 4hm**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 14.6 min (minor), t_2 = 16.9 min (major). $[\alpha]_D^{20}$ +194 (*c* 2.01, CH_2Cl_2) for 91% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 85.4. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.25 (s, 3H), 2.27 (s, 6H), 2.29 (s, 3H), 5.22 (s, 1H), 6.76 (d, *J* = 0.6 Hz, 1H), 6.81 (d, *J* = 4.6 Hz, 2H), 6.87 (dd, *J* = 7.9 Hz, 3.2 Hz, 2H), 7.13-7.22 (m, 5H), 7.29-7.38 (m, 3H), 7.43-7.49 (m, 4H), 7.61 (d, *J* = 1.5 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1 (d, J_{CP} = 1.2 Hz, 1C), 21.7 (d, J_{CP} = 1.0 Hz, 1C), 23.9 (d, J_{CP} = 4.6 Hz, 2C), 118.3 (s, 1C), 125.0 (d, J_{CP} = 4.9 Hz, 1C), 127.0 (s, 1C), 127.1 (s, 1C), 127.9 (s, 2C), 128.1 (s, 1C), 128.8 (d, J_{CP} = 14.1 Hz, 2C), 128.9 (d, J_{CP} = 114.8 Hz, 1C), 129.2 (s, 2C), 129.4 (s, 2C), 129.5 (s, 2C), 131.1 (d, J_{CP} = 12.8 Hz, 2C), 131.3 (d, J_{CP} = 13.1 Hz, 2C), 132.1 (d, J_{CP} = 103.3 Hz, 1C), 135.3 (d, J_{CP} = 4.7 Hz, 1C), 136.6 (s, 1C), 137.9 (s, 1C), 140.4 (d, J_{CP} = 9.4 Hz, 1C), 141.2 (d, J_{CP} = 3.0 Hz, 1C), 141.6 (d, J_{CP} = 11.5 Hz, 2C), 141.9 (d, J_{CP} = 2.8 Hz, 1C), 149.0 (s, 1C). HRMS (ESI) calcd for $C_{34}H_{32}O_2PS$ $[M+H]^+$ 535.1861, found 535.1860.

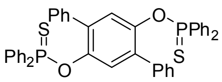


4im **Compound 4im**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 24.8 min (major), t_2 = 27.8 min (minor). $[\alpha]_D^{20}$ +118 (*c* 2.03, CH_2Cl_2) for 81% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 70.9. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.26 (s, 3H), 2.33 (s, 6H), 5.19 (s, 1H), 6.79-6.82 (m, 1H), 6.83 (d, *J* = 5.2 Hz, 2H), 6.86 (s, 1H), 6.92 (dd, *J* = 8.4 Hz, 3.6 Hz, 1H), 7.18-7.21 (m, 3H), 7.27 (dd, *J* = 6.0 Hz, 2.4 Hz, 2H), 7.35-7.39 (m, 1H), 7.45-7.50 (m, 5H), 7.62 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1 (d, J_{CP} = 1.2 Hz, 1C), 23.7 (d, J_{CP} = 4.6 Hz, 2C), 118.3 (s, 1C), 124.7 (d, J_{CP} = 5.0 Hz, 1C), 127.1 (s, 1C), 127.2 (s, 1C), 128.1 (s, 2C), 128.2 (s, 1C), 128.4 (d, J_{CP} = 15.6 Hz, 1C), 129.3 (d, J_{CP} = 123.1 Hz, 1C), 129.2 (s, 2C), 129.48 (s, 2C), 129.51 (s, 2C), 131.4 (d, J_{CP} = 13.7 Hz, 2C), 134.2 (d, J_{CP} = 6.3 Hz, 1C), 135.4 (d, J_{CP} = 4.9 Hz, 1C), 135.9 (d, J_{CP} = 12.1 Hz, 1C), 136.5 (s, 1C), 137.8 (s, 1C), 139.3 (d, J_{CP} = 112.7 Hz, 1C), 140.4 (d, J_{CP} = 9.9 Hz, 1C), 141.5 (d, J_{CP} = 3.0 Hz, 1C), 141.8 (d, J_{CP} = 12.1 Hz, 2C), 149.2 (d, J_{CP} = 1.4 Hz, 1C). HRMS (ESI) calcd for $C_{31}H_{28}O_2PS_2$ $[M+H]^+$ 527.1268, found 527.1265.

9. Addition of PhPH to 2,5-diphenyl-1,4-benzoquinone (2m)



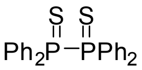
To a solution of Ph_2PH (55.9 mg, 0.300 mmol) in degassed $CHCl_3$ (8 mL) was added **PdL1*** (9.4 mg, 0.015 mmol, 5 mol%). The solution was stirred at room temperature for 2 minutes, before it was cooled to –45 °C. 2,5-Diphenyl-1,4-benzoquinone (**2m**) (82.0 mg, 0.315 mmol) was added followed by dropwise addition of Et_3N (30.3 mg, 0.300 mmol) in $CHCl_3$ (0.5 mL). The mixture was stirred at –45 °C for 20 h. The mixture was filtered immediately and the solids (20 mg of **11**, poor solubility) was collected. The filtrate was treated with excess sulfur powder (14.4 mg, 0.450 mmol) and kept stirring at room temperature for 15 min. The mixture was passed through a short celite pad and the solution was concentrated on a rotary evaporator. The residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/10 to 1/5) to give dithiophosphinate **9’** (25.0 mg, 24% yield), diphosphine disulfide **10’** (17.6 mg, 27% yield), **11** (41.0 mg, 51% yield, combined with the collected solids), and trace amount of **8’** (<3%, based on ^{31}P NMR).



9'

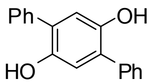
Compound 9’. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 83.2. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.24-7.33 (m, 18H), 7.38 (br s, 2H), 7.42 (t, J = 7.4 Hz, 4H), 7.63 (dd, J = 13.8

Hz, 7.8 Hz, 8H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 124.2 (d, J_{CP} = 4.6 Hz, 2C), 127.6 (s, 2C), 128.2 (s, 4C), 128.4 (d, J_{CP} = 13.8 Hz, 8C), 129.9 (s, 4C), 131.5 (d, J_{CP} = 11.7 Hz, 8C), 132.0 (s, J_{CP} = 2.7 Hz, 4C), 134.2 (d, J_{CP} = 110.2 Hz, 4C), 134.3 (d, J_{CP} = 5.6 Hz, 2C), 137.0 (s, 2C), 144.6 (d, J_{CP} = 9.2 Hz, 2C). HRMS (ESI) calcd for $C_{42}H_{33}O_2P_2S_2$ $[M+H]^+$ 695.1397, found 695.1403.



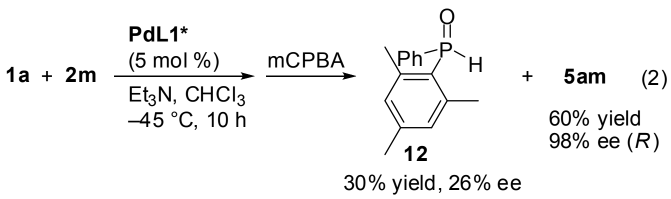
Compound 10' [1054-60-0]. ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz) δ 38.6. ^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.38 (tdd, J = 7.6 Hz, 2.4 Hz, 1.2 Hz, 8H), 7.50 (td, J = 7.2 Hz, 1.2 Hz, 4H), 8.01-8.07 (m, 8H).

Colorless crystals of compound **10'** for X-ray crystallorgraphic analysis were obtained by recrystallization from EtOAc/pentane. The ORTEP drawing of compound **10'** is shown in Figure S2 (page S25). The X-ray analysis of **10'** further confirmed the structure.



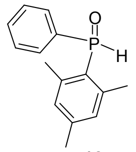
Compound 11 [5422-91-3]. ^{1}H NMR (CDCl$_3$, 500 MHz) δ 4.90 (s, 2H), 6.91 (s, 2H), 7.39-7.43 (m, 2H), 7.48-7.52 (m, 8H).

10. Studies on kinetic resolution



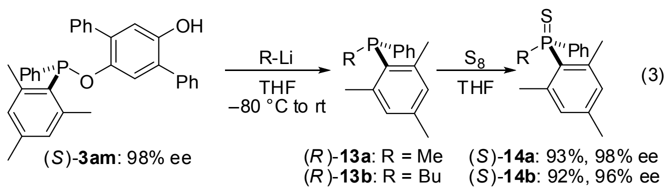
To a solution of phenyl(2,4,6-trimethylphenyl)phosphine (**1a**) (68.5 mg, 0.300 mmol) in degassed CHCl$_3$ (7 mL) was added **PdL1*** (9.4 mg, 0.015 mmol, 5 mol%). The solution was stirred at room temperature for 2 min, before it was cooled to –45 °C. 2,5-Diphenyl-1,4-benzoquinone (**2m**) (82.0 mg, 0.315 mmol) was added followed by dropwise addition of Et$_3$N (30.3 mg, 0.300 mmol) in CHCl$_3$ (0.5 mL). The solution was stirred at –45 °C for 10 h (conversion = 63% based on ^{31}P NMR). m-CPBA (0.300 mmol, 1 equiv, purified by recrystallization and titrated by the reaction with Ph$_2$PH) was added, and the mixture was kept stirring at –45 °C for 8 h. The reaction mixture was concentrated on a rotary evaporator and the residue was subjected to silica-gel chromatography (acetone/CH_2Cl_2 = 1/10 to 1/5) to give phosphinate **5am** (90.8 mg, 60% yield, 98% ee) and phosphine oxide **12** (22.0 mg, 30% recovered, 26% ee).

When the reaction was stopped at 97% conversion, phosphinate **5am** (139.3 mg, 92% yield, 98% ee) and phosphine oxide **12** (2.2 mg, 3% recovered, 84% ee) were isolated.



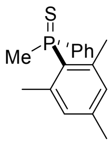
12 **Compound 12**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 98/2, flow 1.0 mL/min, 280 nm, t_1 = 145.9 min (major), t_2 = 158.9 min (minor). $[\alpha]_D^{20}$ +21 (c 0.92, CH_2Cl_2) for 26% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) δ 9.8. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.30 (s, 3H), 2.46 (s, 6H), 6.91 (d, J = 3.8 Hz, 2H), 7.45 (td, J = 7.5 Hz, 2.5 Hz, 2H), 7.52 (td, J = 7.0 Hz, 1.5 Hz, 1H), 7.63 (dd, J = 13.5 Hz, 7.0 Hz, 2H), 8.55 (d, J = 482.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 21.4 (s, 1C), 21.6 (d, J_{CP} = 8.6 Hz, 2C), 124.5 (d, J_{CP} = 102.4 Hz, 1C), 128.9 (d, J_{CP} = 12.6 Hz, 2C), 130.4 (d, J_{CP} = 10.2 Hz, 2C), 130.6 (d, J_{CP} = 11.3 Hz, 2C), 132.0 (d, J_{CP} = 3.2 Hz, 1C), 132.4 (d, J_{CP} = 99.0 Hz, 1C), 142.2 (d, J_{CP} = 9.9 Hz, 2C), 142.9 (d, J_{CP} = 1.9 Hz, 1C). HRMS (ESI) calcd for $C_{15}H_{18}OP$ $[M+H]^+$ 245.1095, found 245.1092.

11. Transformations of the products, (*S*)-3am, (*R*)-4am, and (*S*)-5am



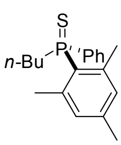
To a THF (5 mL) solution of (*S*)-**3am**, which was obtained by removal of $CHCl_3$ from the reaction mixture in entry 1 of Table 2, was added MeLi (0.94 mL, 1.6 M in diethyl ether, 1.5 mmol, 5 equiv) at –80 °C. The reaction mixture was kept stirring at –80 °C for 8 h and warmed gradually to room temperature over 8 h. After stirring at room temperature for another 2 h, degassed H_2O (0.5 mL) was added followed by addition of excess S_8. The reaction mixture was stirred for 15 min and passed through a short celite pad. The solution was extracted with EtOAc (20 mL × 3) and the organic layer was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/Hexane = 1/10) to give sulfide (*S*)-**14a** (76.5 mg, 93% yield, 98% ee).

Similarly, (*S*)-**14b** was prepared by reaction of (*S*)-**3am** with n-BuLi (0.6 mL, 2.5 M in hexane, 1.5 mmol) under otherwise the same conditions (87.3 mg, 92% yield, 96% ee).

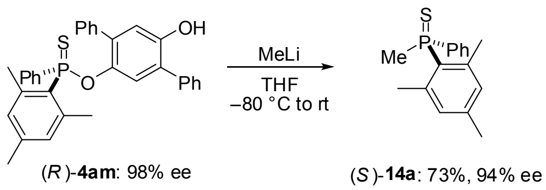


(*S*)-**14a** **Compound** (*S*)-**14a**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 98/2, flow 1.0 mL/min, 280 nm, t_1 = 11.3 min (minor), t_2 = 19.8 min (major). $[\alpha]_D^{20}$ –108 (*c* 1.94, CH_2Cl_2) for 98% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) δ 36.4. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.24 (d, *J* = 13.2 Hz, 3H), 2.27 (s, 3H), 2.30 (s, 6H), 6.84 (d, *J* = 3.9 Hz, 2H), 7.40-7.48 (m, 3H), 7.81 (dd, *J* = 13.5 Hz, 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.1 (s, 1C), 23.9 (d, J_{CP} = 5.9 Hz, 2C), 30.2 (d, J_{CP} = 57.0 Hz, 1C), 128.8 (d, J_{CP} = 12.2 Hz, 2C), 128.9 (d, J_{CP} = 83.4 Hz, 1C), 130.0 (d, J_{CP} = 10.8 Hz, 2C), 131.0 (d, J_{CP} = 2.9 Hz, 1C), 131.4 (d, J_{CP} = 11.0 Hz, 2C), 137.7 (d, J_{CP} = 80.4 Hz, 1C), 142.1 (d, J_{CP} = 2.9 Hz, 1C), 141.5 (d, J_{CP} = 10.3 Hz, 2C). HRMS (ESI) calcd for $C_{16}H_{20}PS$ $[M+H]^+$ 275.1023, found 275.1021.

Colorless crystals of phosphine sulfide **14a** suitable for X-ray crystallographic analysis were obtained by recrystallization from EtOAc/pentane. The ORTEP drawing of **14a** is shown in Figure S3 (page S27). The X-ray analysis of the crystal revealed that absolute configuration of **14a** is *S*.

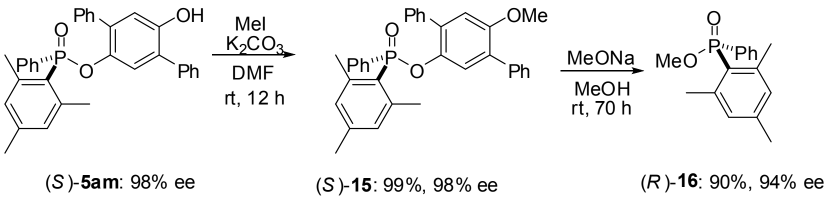


(*S*)-**14b** **Compound** (*S*)-**14b**. The ee was measured by HPLC (Daicel Chiralpak AD-H), hexane/2-propanol = 95/5, flow 0.8 mL/min, 280 nm, t_1 = 8.7 min (major), t_2 = 10.2 min (minor). $[\alpha]_D^{20}$ –77 (*c* 4.04, CH_2Cl_2) for 96% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 43.7. ^1H NMR ($CDCl_3$, 400 MHz) δ 0.69-0.82 (m, 1H), 0.79 (t, *J* = 7.3 Hz, 3H), 1.22-1.38 (m, 2H), 1.60-1.73 (m, 1H), 2.26 (s, 3H), 2.30 (s, 6H), 2.39-2.60 (m, 2H), 6.83 (d, J = 3.8 Hz, 2H), 7.40-7.50 (m, 3H), 7.76 (dd, J = 12.8 Hz, 6.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8 (s, 1C), 21.0 (s, 1C), 24.1 (d, J_{CP} = 17.6 Hz, 1C), 24.2 (d, J_{CP} = 4.8 Hz, 2C), 25.1 (d, J_{CP} = 3.2 Hz, 1C), 38.7 (d, J_{CP} = 52.8 Hz, 1C), 128.5 (d, J_{CP} = 12.1 Hz, 2C), 129.2 (d, J_{CP} = 81.4 Hz, 1C), 130.87 (d, J_{CP} = 9.7 Hz, 2C), 131.89 (d, J_{CP} = 3.9 Hz, 1C), 131.5 (d, J_{CP} = 11.0 Hz, 2C), 135.0 (d, J_{CP} = 76.9 Hz, 1C), 140.9 (d, J_{CP} = 3.0 Hz, 1C), 141.7 (d, J_{CP} = 10.0 Hz, 2C). HRMS (ESI) calcd for $C_{19}H_{26}PS$ $[M+H]^+$ 317.1493, found 317.1492.



(4)

To a solution of (R)-**4am** (100.0 mg, 0.192 mmol) in dry THF (5 mL) was added MeLi (0.60 mL, 1.6 M in diethyl ether, 0.96 mmol, 5 equiv) at –80 °C. The reaction mixture was kept stirring at –80 °C for 8 h and warmed gradually to room temperature over 8 h. After stirring at room temperature for another 2 h, the reaction mixture was quenched by H_2O (0.5 mL) and extracted with EtOAc (20 mL × 3). The organic layer was dried over $MgSO_4$ and the solvent was removed on a rotary evaporator. The residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/10) to give the phosphine sulfide (S)-**14a** (38.5 mg, 73% yield, 94% ee).

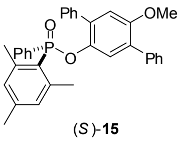


(5)

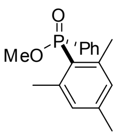
To a solution of (S)-**5am** (200 mg, 0.396 mmol, 98% ee) in dry DMF (5 mL) was added MeI (169 mg, 1.19 mmol) and K_2CO_3 (164 mg, 1.19 mol). The reaction mixture was stirred at room temperature for 12 h. Saturated aqueous NH_4Cl was added, and the mixture was extracted with EtOAc (20 mL × 3). The organic layer was dried over $MgSO_4$ and the solvent was removed by a rotary evaporator and vacuum pump. The residue was subjected to silica-gel chromatography (with acetone/CH_2Cl_2 = 1/10) to give the product (S)-1**5** (203.3 mg, 99% yield, 98% ee).

To a solution of (S)-**15** (98.5 mg, 0.190 mmol) in MeOH (5 mL) was added NaOMe (30.8

mg, 0.570 mmol) at 20 °C. The reaction mixture was kept stirring for 70 h (conversion = 92% based on ^{31}P NMR). The solvent was removed on a rotary evaporator and the residue was dissolved in CH_2Cl_2 (20 mL). It was washed with H_2O and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was subjected to silica-gel chromatography (EtOAc/hexane = 1/5) to give the product (*R*)-1**6** (46.9 mg, 90% yield, 94% ee).



(*S*)-**15** **Compound** (*S*)-**15**. The ee was measured by HPLC (Daicel Chiralpak IC, hexane/2-propanol = 90/10, flow 1.0 mL/min, 280 nm, t_1 = 27.9 min (minor), t_2 = 30.3 min (major). $[\alpha]_D^{20}$ –28 (*c* 2.12, CH_2Cl_2) for 98% ee (*S*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 34.8. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.27 (s, 3H), 2.36 (s, 6H), 3.74 (s, 3H), 6.86 (d, *J* = 4.1 Hz, 2H), 6.90 (s, 1H), 7.21 (d, *J* = 1.2 Hz, 1H), 7.21-7.28 (m, 3H), 7.30-7.42 (m, 10H), 7.51 (dd, *J* = 7.8 Hz, 1.9 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.2 (s, 1C), 23.4 (d, J_{CP} = 3.4 Hz, 2C), 56.2 (s, 1C), 114.3 (s, 1C), 122.8 (d, J_{CP} = 3.4 Hz, 1C), 124.0 (d, J_{CP} = 128.6 Hz, 1C), 127.3 (s, 1C), 127.5 (s, 1C), 128.1 (s, 2C), 128.2 (s, 2C), 128.4 (d, J_{CP} = 13.8 Hz, 2C), 129.6 (s, 2C), 129.8 (s, 2C), 130.4 (d, J_{CP} = 11.5 Hz, 2C), 130.5 (s, 1C), 131.0 (d, J_{CP} = 13.4 Hz, 2C), 131.7 (d, J_{CP} = 2.9 Hz, 1C), 134.0 (d, J_{CP} = 5.5 Hz, 1C), 134.4 (d, J_{CP} = 137.2 Hz, 1C), 137.5 (s, 1C), 138.2 (s, 1C), 141.5 (d, J_{CP} = 8.1 Hz, 1C), 142.6 (d, J_{CP} = 2.8 Hz, 1C), 144.1 (d, J_{CP} = 11.6 Hz, 2C), 153.0 (s, 1C). HRMS (ESI) calcd for $C_{34}H_{32}O_3P$ $[M+H]^+$ 519.2089, found 519.2087.



(*R*)-**16** **Compound** (*R*)-**16**. The ee was measured by HPLC (Daicel Chiralpak IC), hexane/2-propanol = 90/10, flow 1.0 mL/min, 280 nm, t_1 = 54.8 min (minor), t_2 = 68.8 min (major). $[\alpha]_D^{20}$ –28 (*c* 2.12, CH_2Cl_2) for 94% ee. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz) δ 37.2. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.29 (s, 3H), 2.49 (s, 6H), 3.73 (d, *J* = 11.2 Hz, 3H), 6.91 (d, *J* = 4.0 Hz, 2H), 7.38-7.42 (m, 2H), 7.45-7.50 (m, 1H), 7.66 (ddd, *J* = 12.8 Hz, 8.0 Hz, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3 (s, 1C), 23.5 (d, J_{CP} = 3.2 Hz, 2C), 50.8 (d, J_{CP} = 5.8 Hz, 1C), 123.6 (d, J_{CP} = 130.1 Hz, 1C), 128.6 (d, J_{CP} = 13.2 Hz, 2C), 130.7 (d, J_{CP} = 10.9 Hz, 2C), 131.0 (d, J_{CP} = 13.0 Hz, 2C), 131.8 (d, J_{CP} = 2.8 Hz, 1C), 134.2 (d, J_{CP} = 134.4 Hz, 1C), 142.3 (d, J_{CP} = 2.8 Hz, 1C), 144.1 (d, J_{CP} = 11.1 Hz, 2C). HRMS (ESI) calcd for

$C_{16}H_{20}O_2P$ [M+H]$^+$ 275.1200, found 275.1201.

12. References

(1) (a) Ng, J. K.; Tan, G. K.; Gagadese, J. V.; Leung, P. H. *Inorg. Chem*. **2003**, *42*, 7674. (b) Huang, Y.; Chew, R. J.; Li, Y.; Pullarkat, S. A.; Leung, P. H. *Org. Lett.* **2011**, *13*, 5862.

(2) Chooi, S. Y. M.; Leung, P.-H.; Chin, L. C.; Mok, K. F.; Quek, G. H.; Sim, K. Y.; Tan, M. K. *Tetrahedron: Asymmetry* **1992**, *3*, 529.

(3) Kovacik, I.; Wicht, D. K.; Grewal, N. S.; Glueck, D. S.; Incarvito, C. D.; Guzei, I. A.; Rheingold, A. L. *Organometallics* **2000**, *19*, 950.

(4) Clarke, E. F.; Rafter, E.; Müller-Bunz, H.; Higham, L. J.; Gilheany, D. G. *J. Organomet. Chem.* **2011**, *696*, 3608.

(5) (a) Peer, M.; Jong, J. C.; Kiefer, M.; Langer, T.; Rieck, H.; Schell, H.; Sennhenn, P.; Sprinz, J.; Steinhagen, H.; Wiese, B.; Helmchen, G. *Tetrahdron* **1996**, *52*, 7547.

(6) Allen, D. G.; Mclaughlin, G. M.; Robertson, G. B.; Steffen, W. L.; Salem, G.; Wild, S. B. *Inorg. Chem.* **1982**, *21*, 1007.

13. Single Crystal X-Ray Diffraction Data

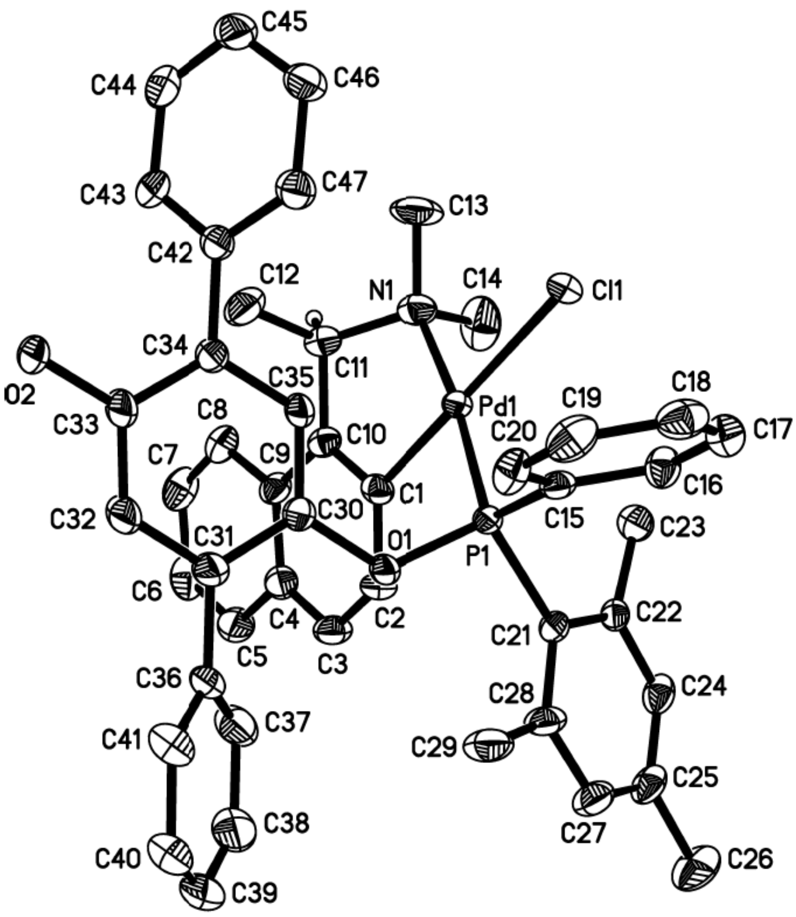


Figure S1. ORTEP illustration of compelx **7** with thermal ellipsoids drawn at 50% probability level.

Table S1. Crystal data and structure refinement for compelx 7

Empirical formula	C48.50 H48 Cl4 N O2 P Pd	
Formula weight	956.05	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2	
Unit cell dimensions	a = 12.3208(10) Å	α = 90°
	b = 35.000(3) Å	β = 90°
	c = 10.4586(8) Å	γ = 90°
Volume	4510.0(6) $Å^3$	
Z	4	
Density (calculated)	1.408 Mg/m^3	
Absorption coefficient	0.723 mm^{-1}	
F(000)	1964	
Crystal size	0.40 x 0.24 x 0.14 mm^3	
Theta range for data collection	1.16 to 30.56°.	
Index ranges	-17<=h<=17, -47<=k<=50, -13<=l<=14	
Reflections collected	41191	
Independent reflections	13755 [R(int) = 0.0477]	
Completeness to theta = 30.56°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9055 and 0.7607	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13755 / 130 / 567	
Goodness-of-fit on F^2	1.120	
Final R indices [I>2sigma(I)]	R1 = 0.0597, wR2 = 0.1646	
R indices (all data)	R1 = 0.0724, wR2 = 0.1782	
Absolute structure parameter	0.01(3)	
Largest diff. peak and hole	1.827 and -1.005 e.$Å^{-3}$	

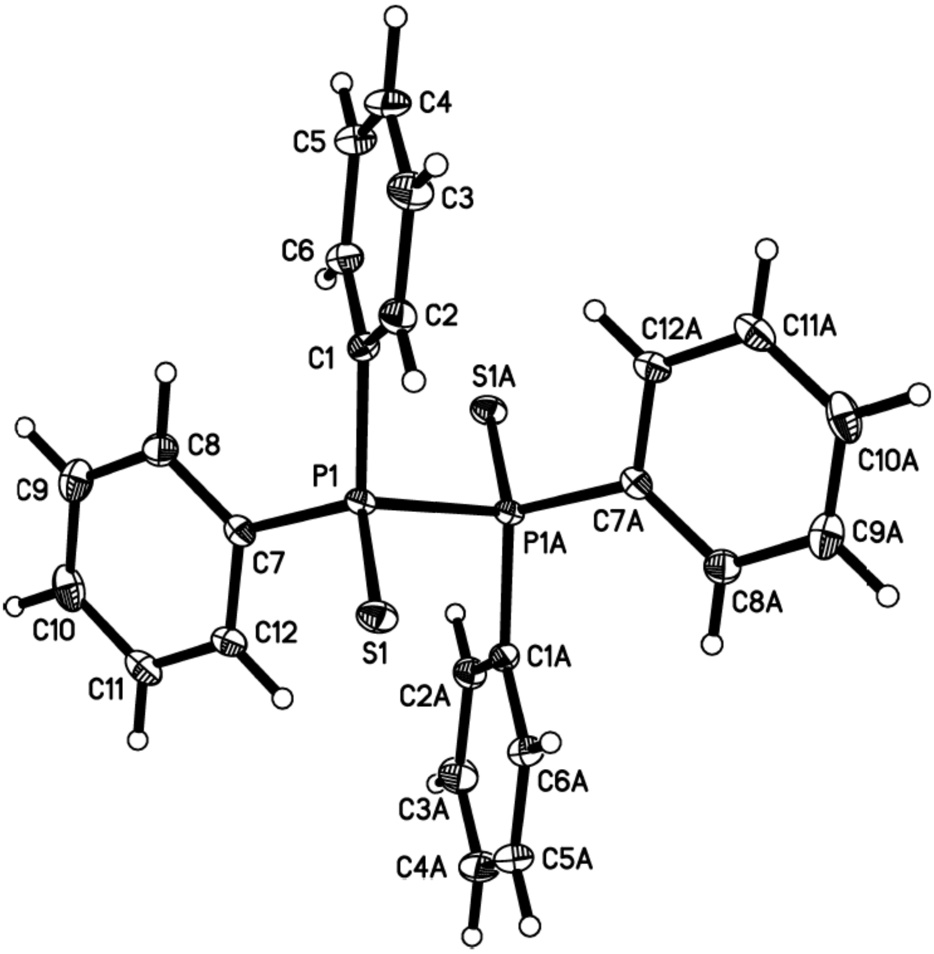


Figure S2. ORTEP illustration of **10'** with thermal ellipsoids drawn at 50% probability level.

Table S2. Crystal data and structure refinement for compound 10’

Chemical formula	$C_{24}H_{20}P_2S_2$
Formula weight	434.46
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal size	0.300 x 0.320 x 0.420 mm
Crystal habit	colorless block
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	a = 9.5656(5) Å α = 90°
	b = 15.6505(9) Å β = 96.8115(15)°
	c = 14.0777(8) Å γ = 90°
Volume	2092.6(2) $Å^3$
Z	4
Density (calculated)	1.379 g/cm^3
Absorption coefficient	0.415 mm^{-1}
F(000)	904
Theta range for data collection	2.51 to 31.49°
Index ranges	-13<=h<=14, -22<=k<=22, -20<=l<=20
Reflections collected	49831
Independent reflections	6912 [R(int) = 0.0769]
Coverage of independent reflections	99.5%
Absorption correction	multi-scan
Max. and min. transmission	0.8860 and 0.8450
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2013 (Sheldrick, 2013)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	6912 / 0 / 253
Goodness-of-fit on F2	1.123
Δ/σmax	0.001
Final R indices	5061 data; I>2σ(I) R1 = 0.0487, wR2 = 0.1078
	all data R1 = 0.0784, wR2 = 0.1237
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0458P)^2+1.7634P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.596 and -0.416 $eÅ^{-3}$
R.M.S. deviation from mean	0.099 $eÅ^{-3}$

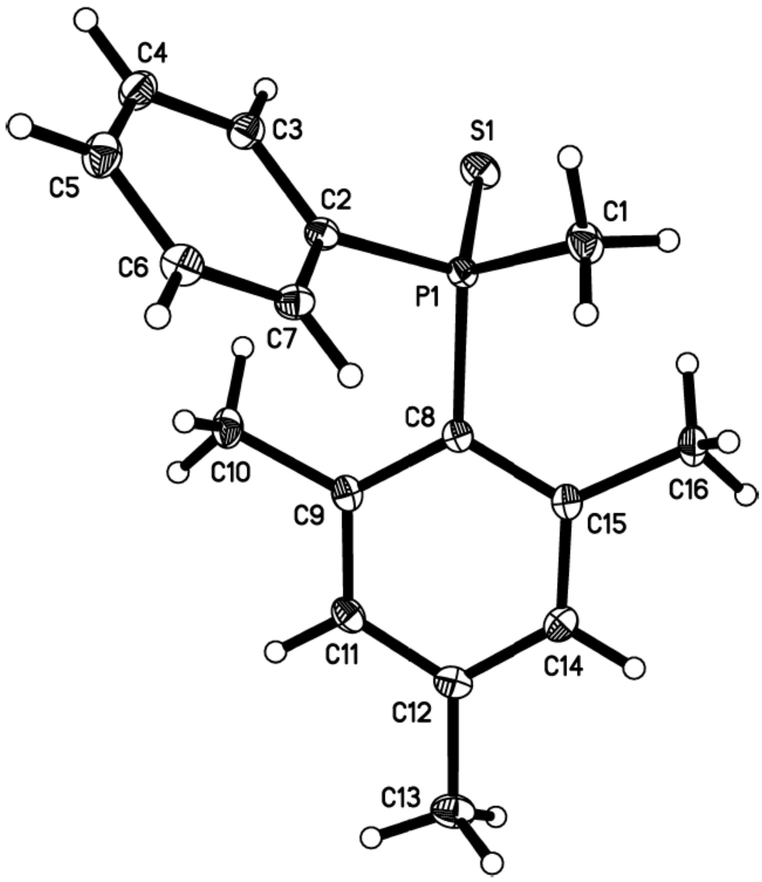
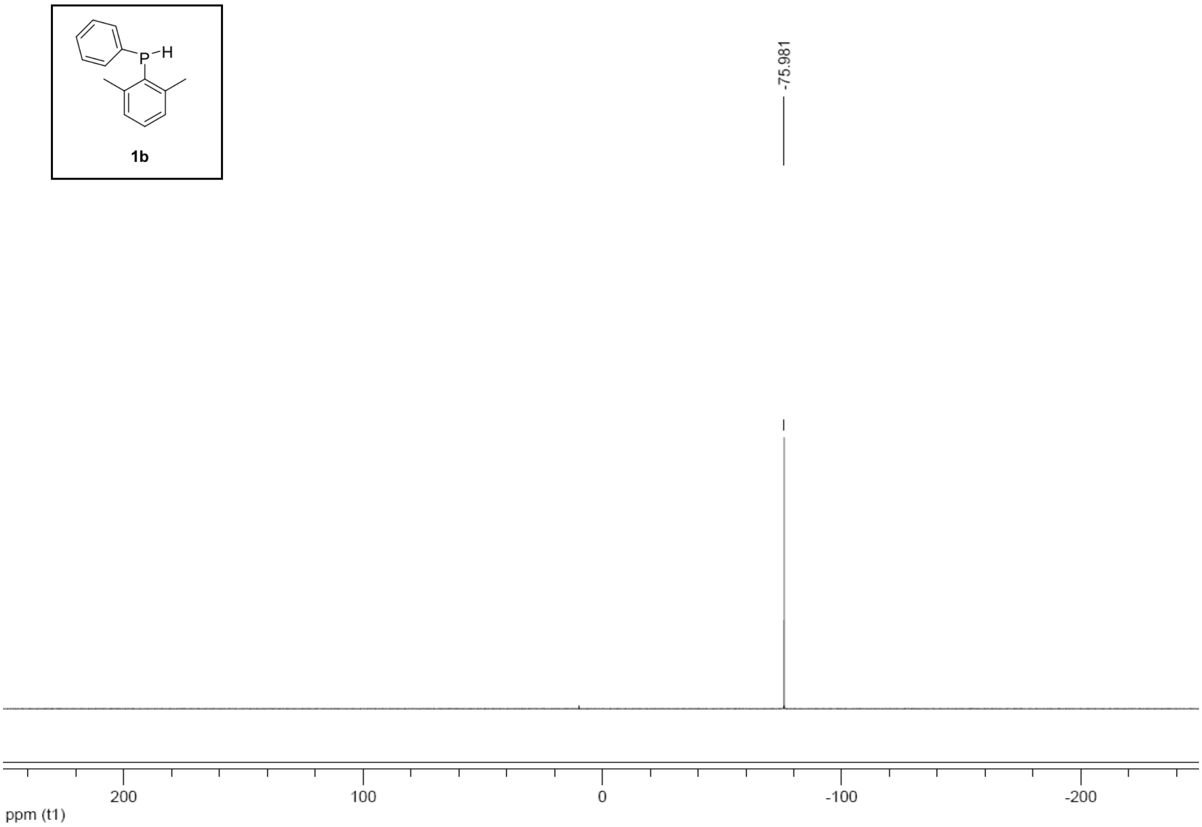


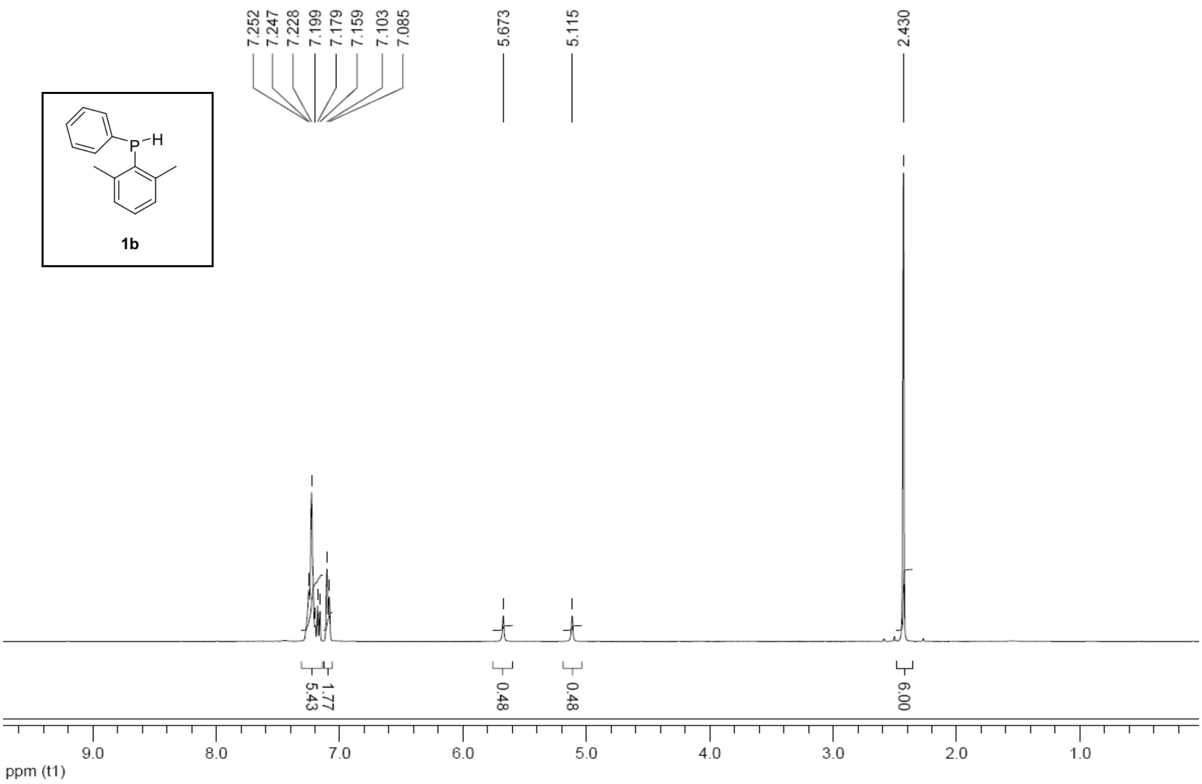
Figure S3. ORTEP illustration of (*S*)-**14a** with thermal ellipsoids drawn at 50% probability level.

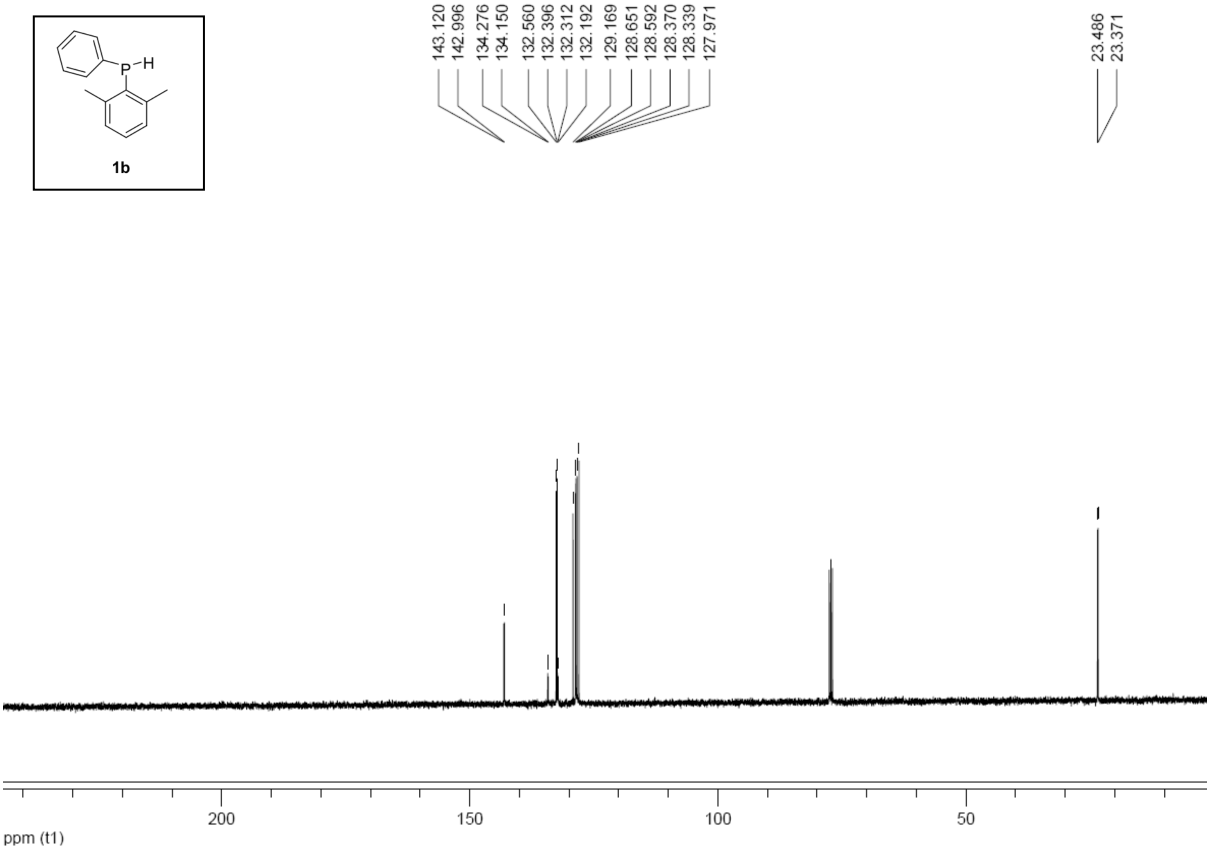
Table S3. Crystal data and structure refinement for compound (*S*)-14

Chemical formula	$C_{16}H_{19}PS$	
Formula weight	274.34	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.300 x 0.420 mm	
Crystal habit	colorless plate	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.6479(2) Å	α = 90°
	b = 9.9545(4) Å	β = 90°
	c = 16.8563(7) Å	γ = 90°
Volume	1451.08(9) $Å^3$	
Z	4	
Density (calculated)	1.256 g/cm^3	
Absorption coefficient	0.314 mm^{-1}	
F(000)	584	
Theta range for data collection	3.17 to 35.08°	
Index ranges	-12<=h<=13, -15<=k<=16, -27<=l<=10	
Reflections collected	18262	
Independent reflections	6388 [R(int) = 0.0431]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9750 and 0.8800	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6388 / 0 / 167	
Goodness-of-fit on F^2	1.029	
Δ/σ_{max}	0.001	
Final R indices	5583 data; I>2σ(I)	R1 = 0.0400, wR2 = 0.0874
	all data	R1 = 0.0497, wR2 = 0.0924
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0443P)^2+0.0499P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	0.398 and -0.297 $eÅ^{-3}$	
R.M.S. deviation from mean	0.064 $eÅ^{-3}$	

14. $^{31}P\{^{1}H\}$, ^{1}H, ^{13}C NMR spectra and chiral HPLC charts







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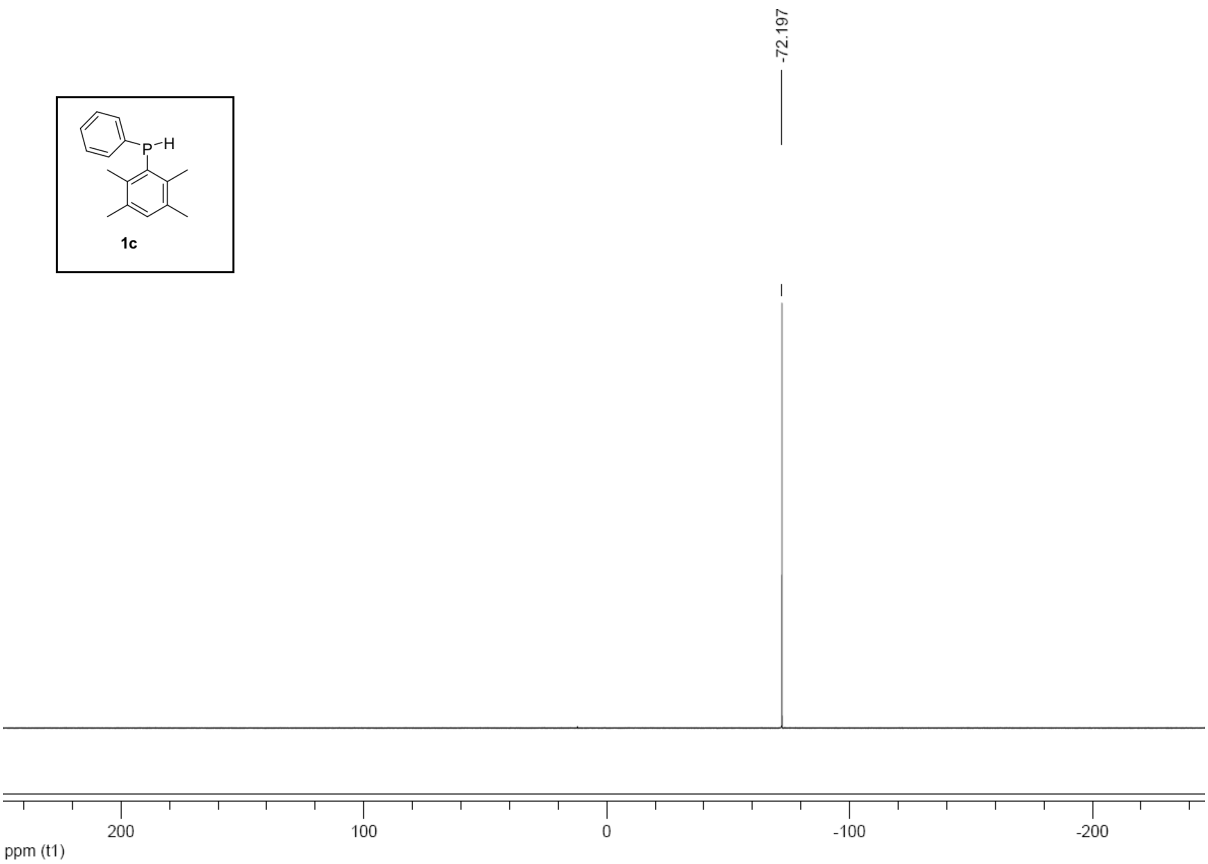
ppm (t1)



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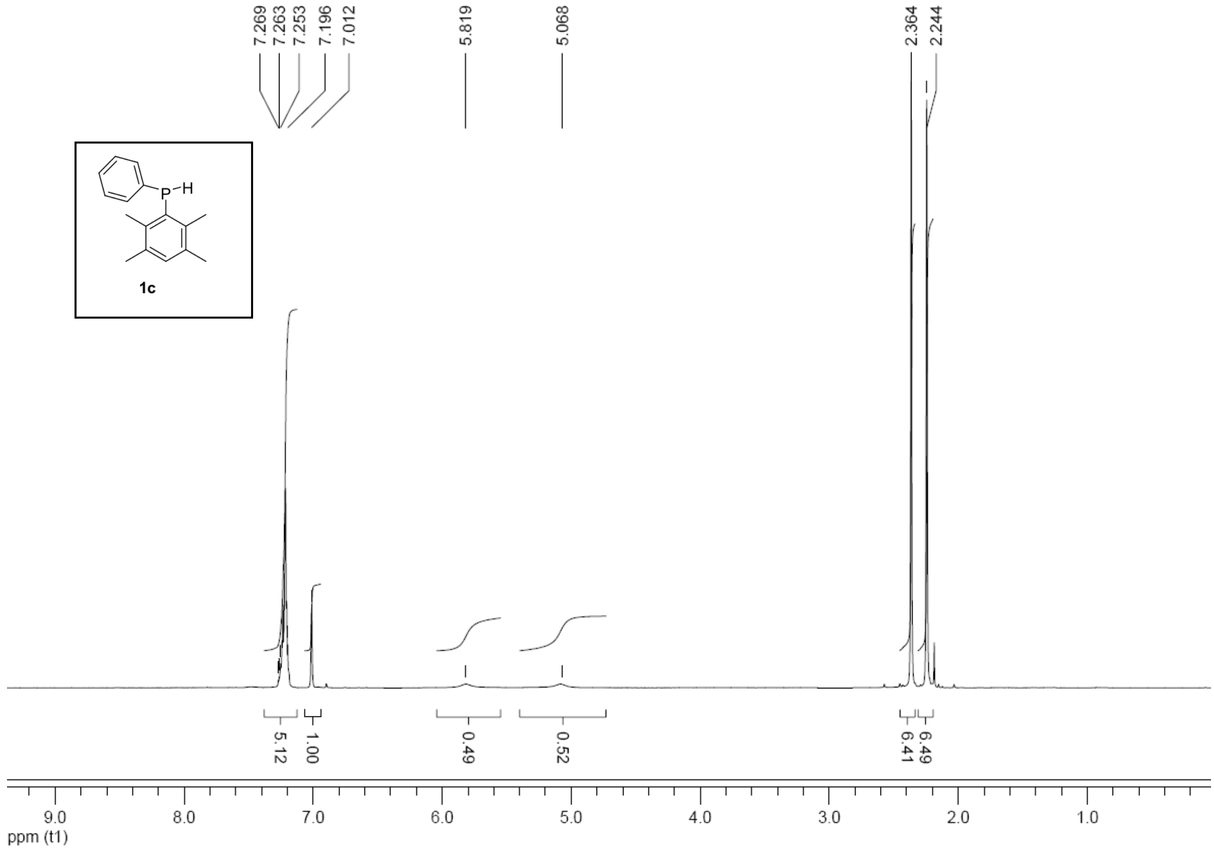
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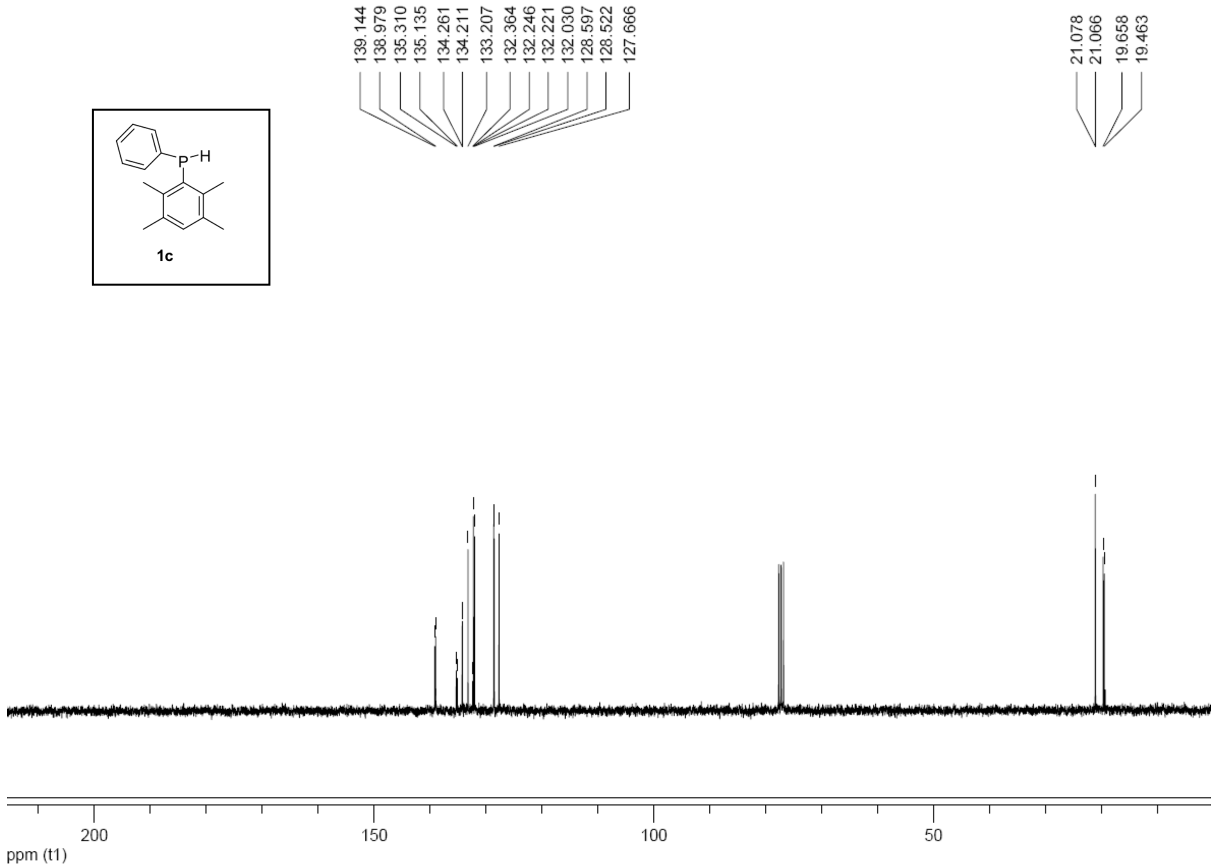
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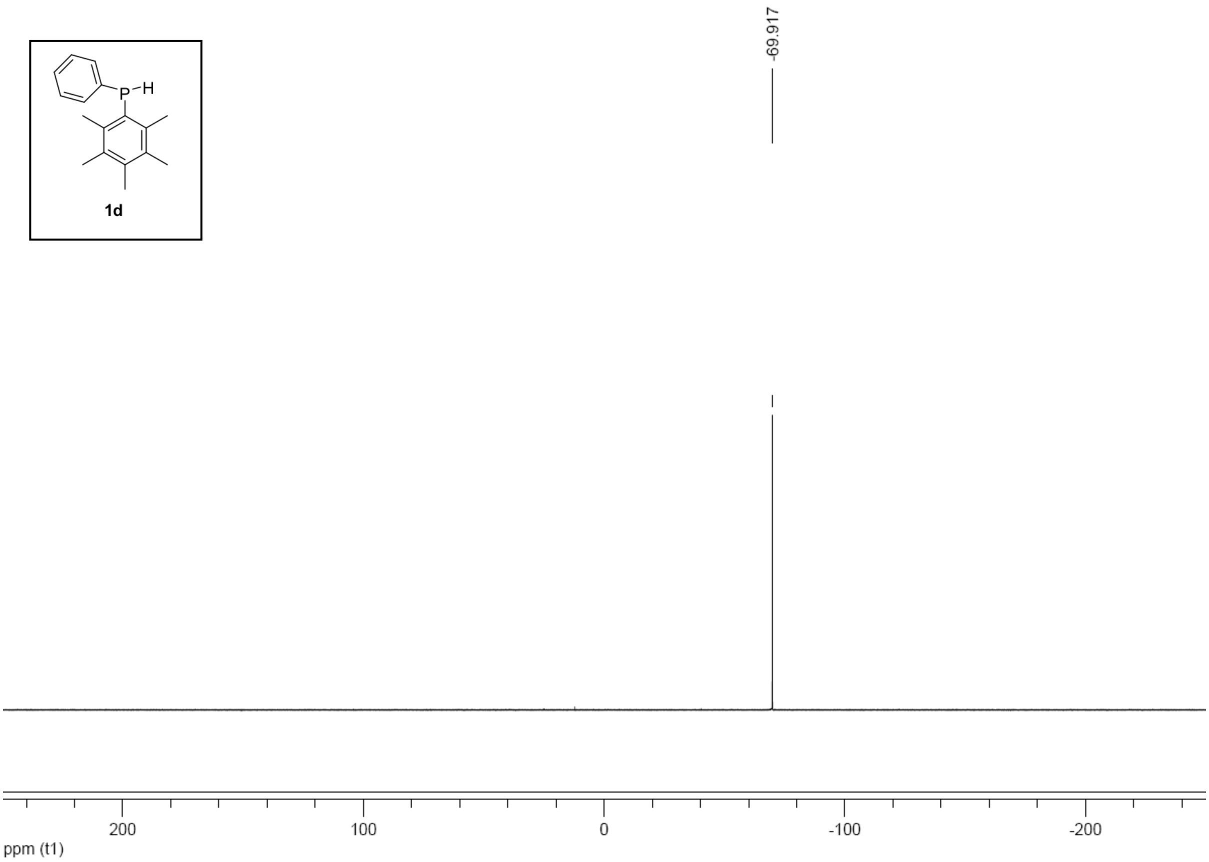
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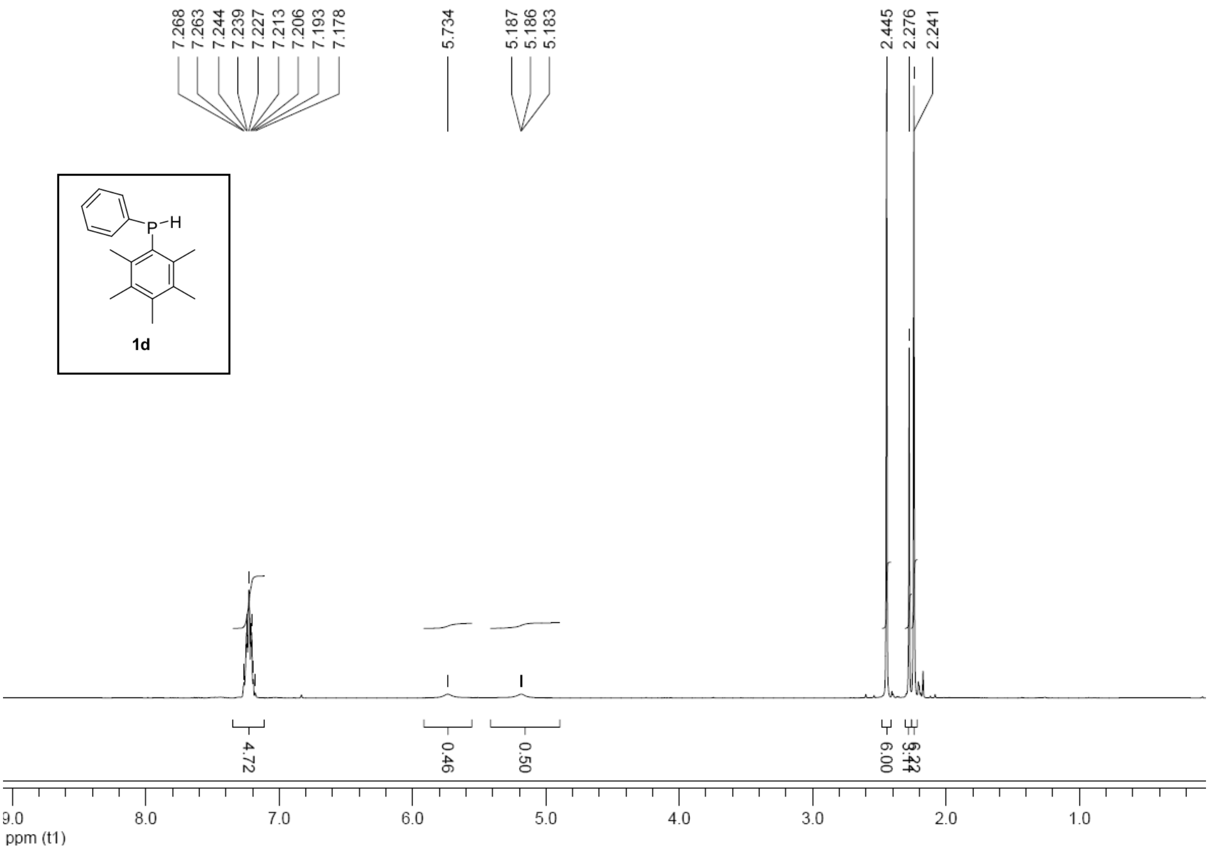
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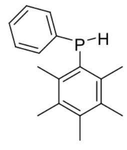

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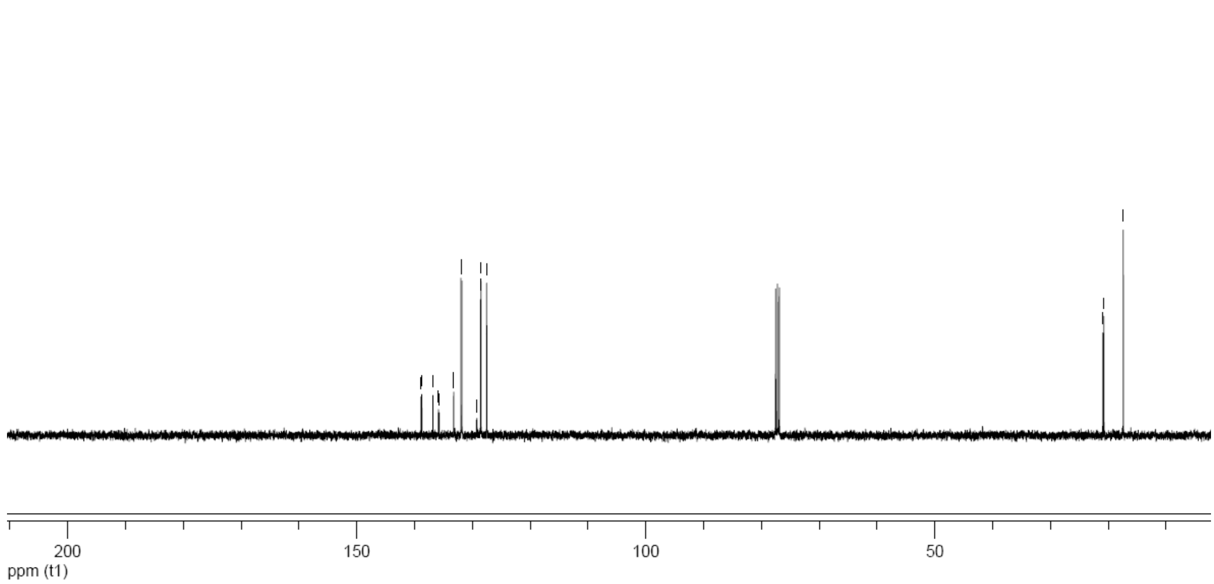

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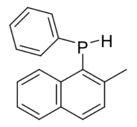

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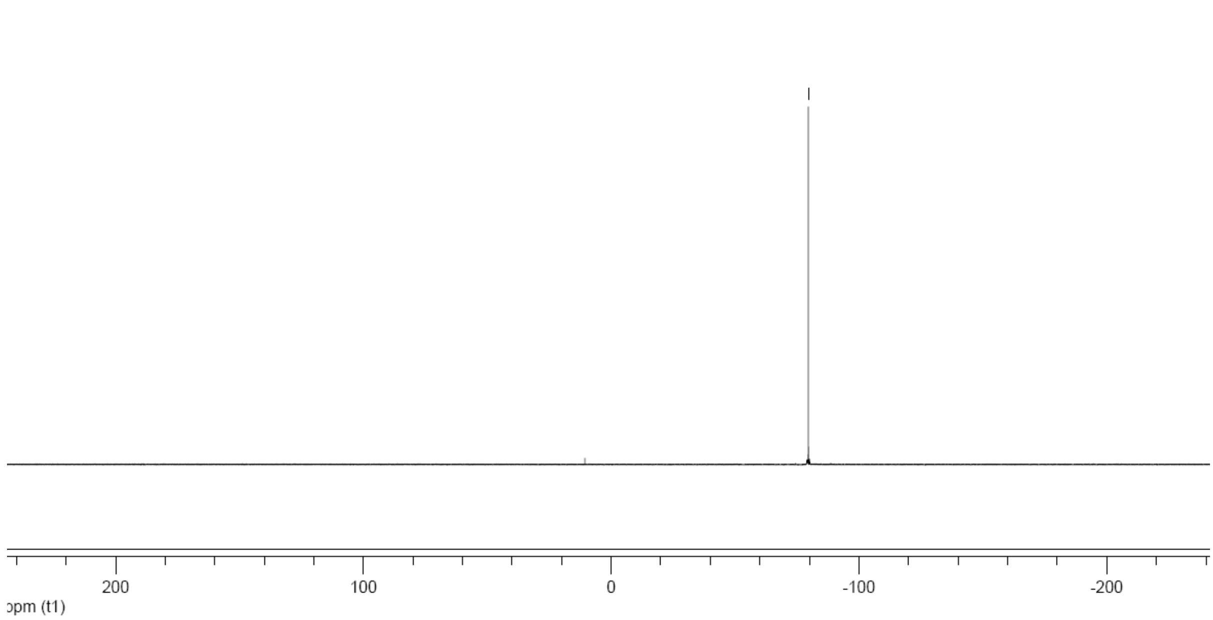

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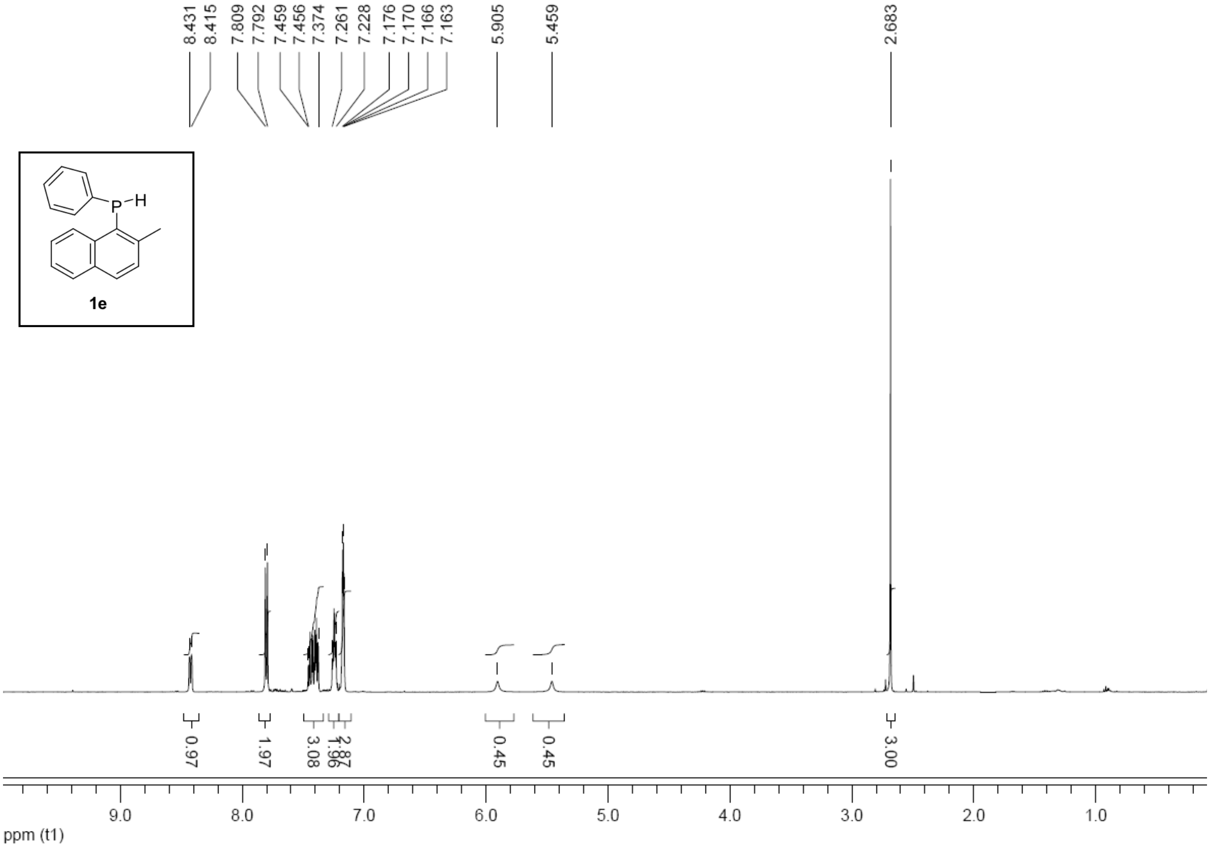
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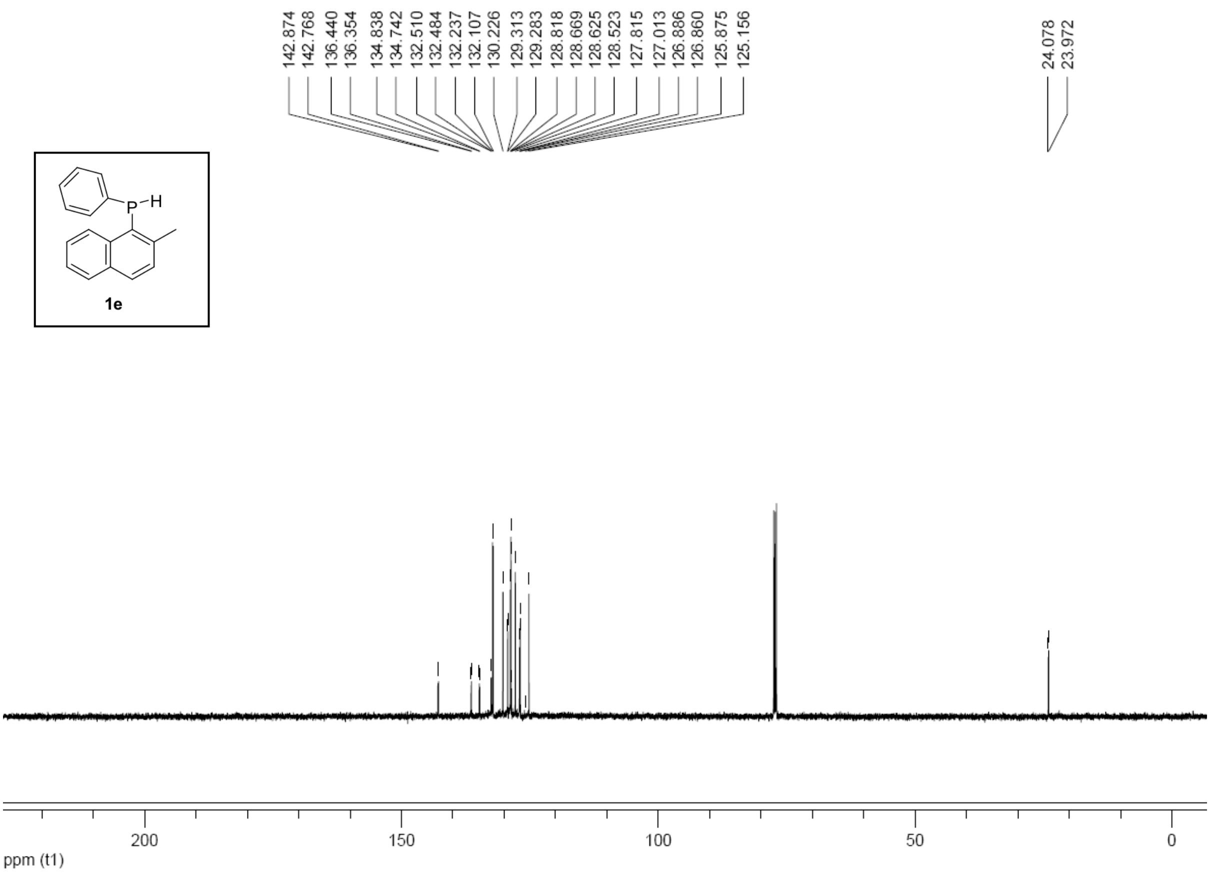
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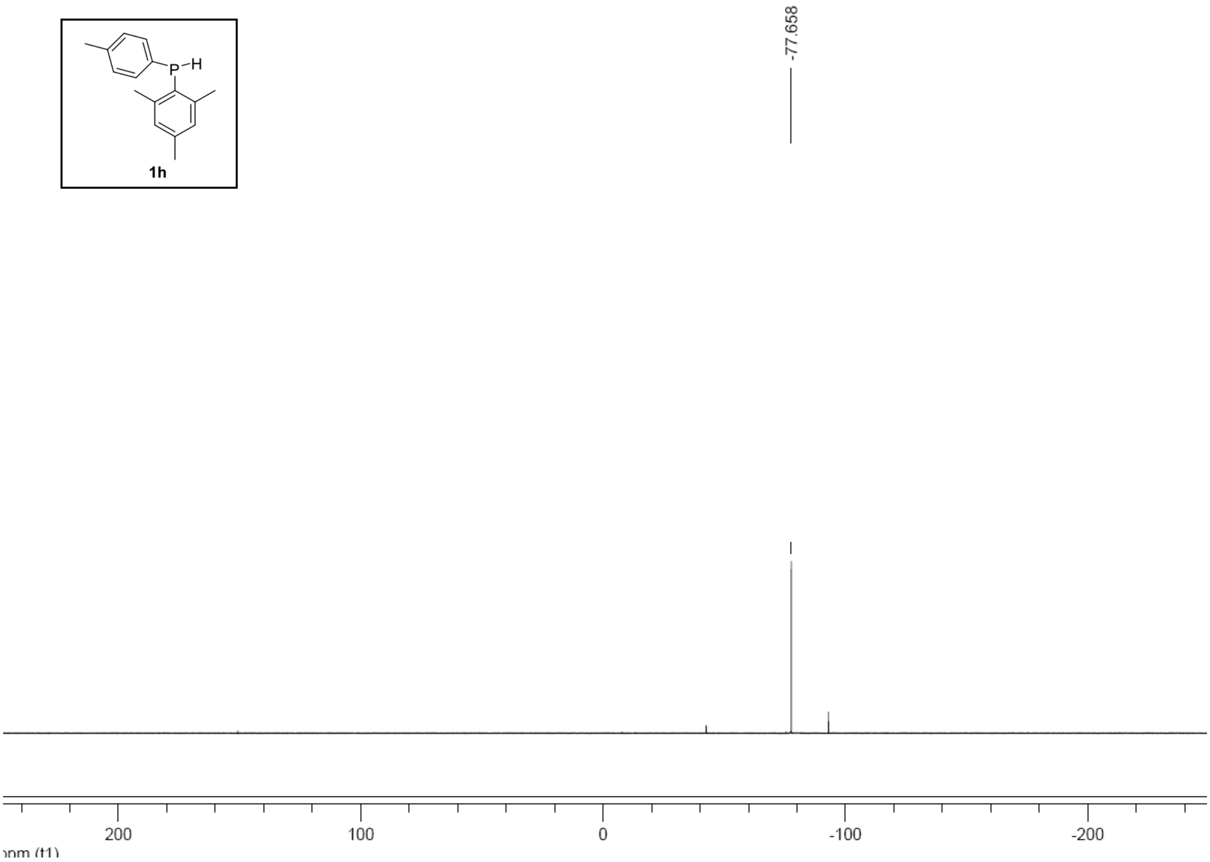
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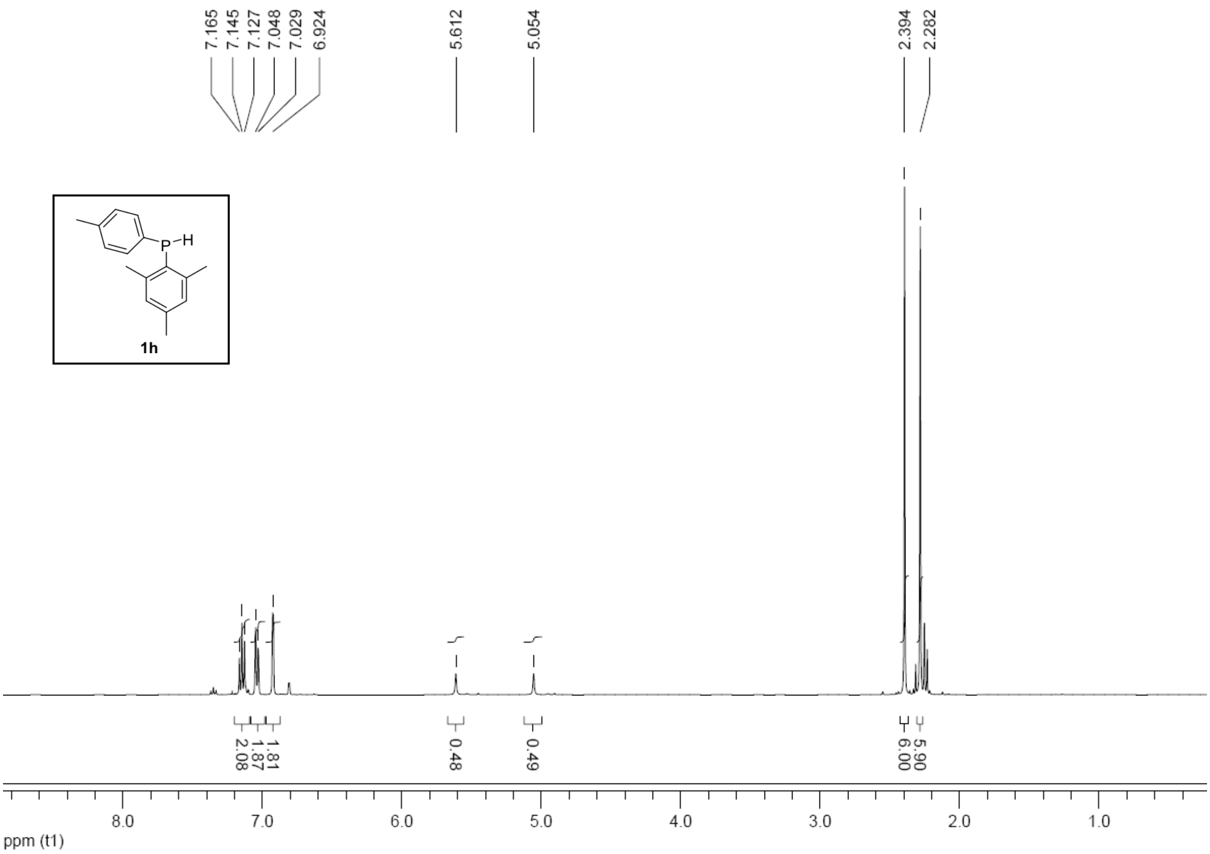
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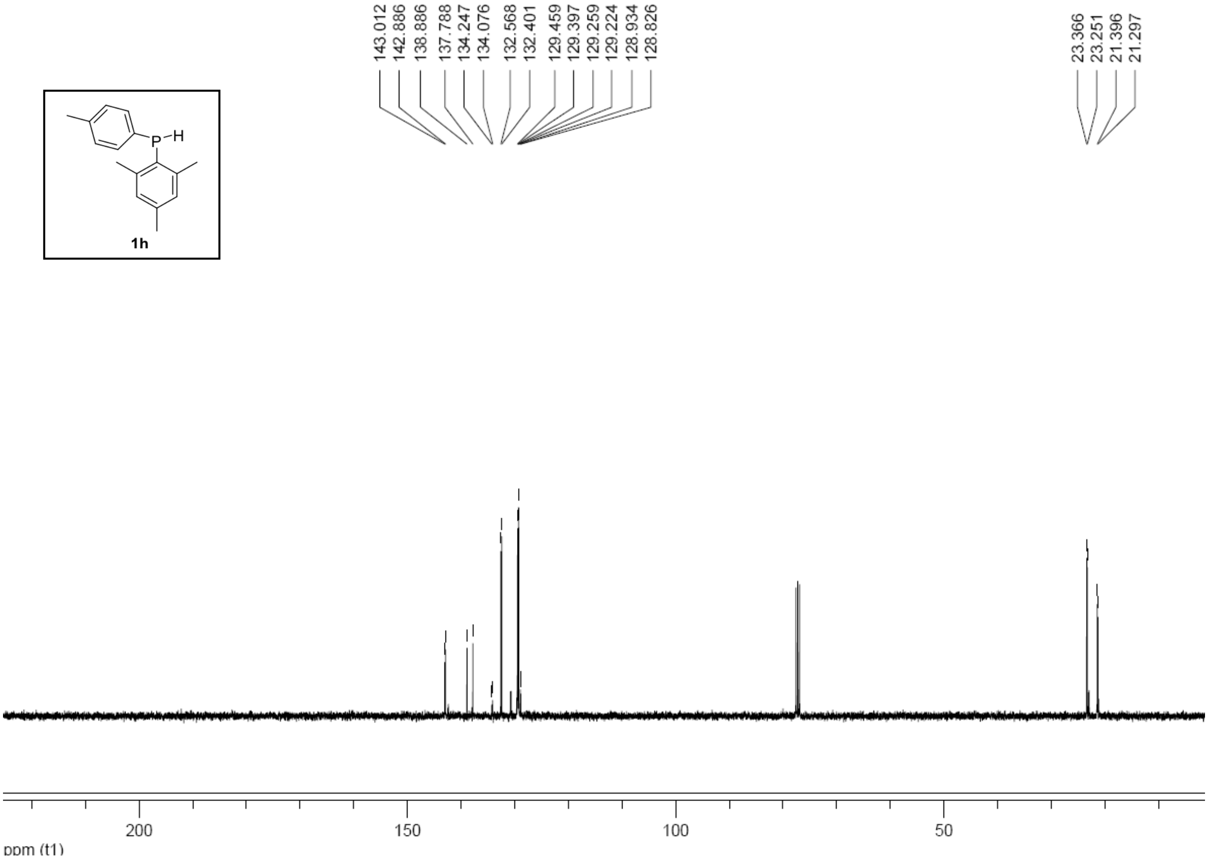
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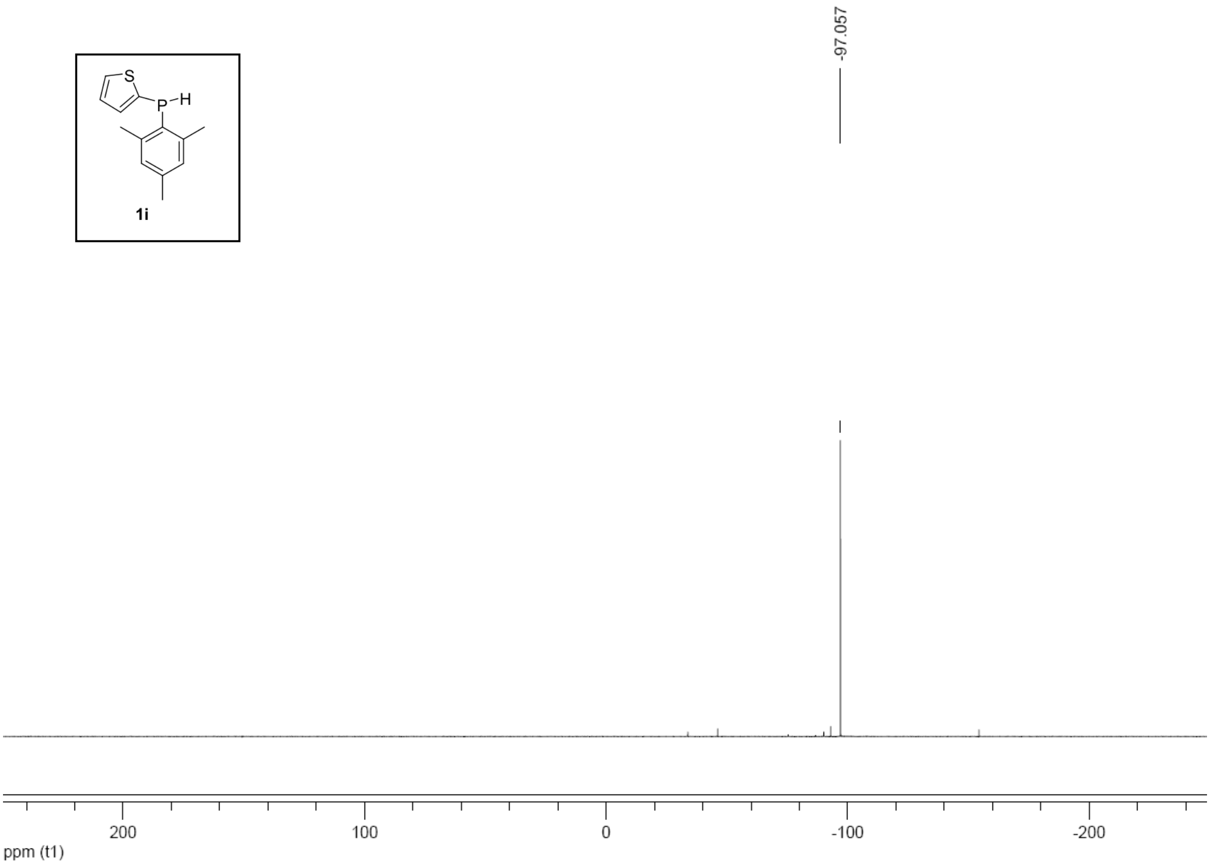
ppm (t1)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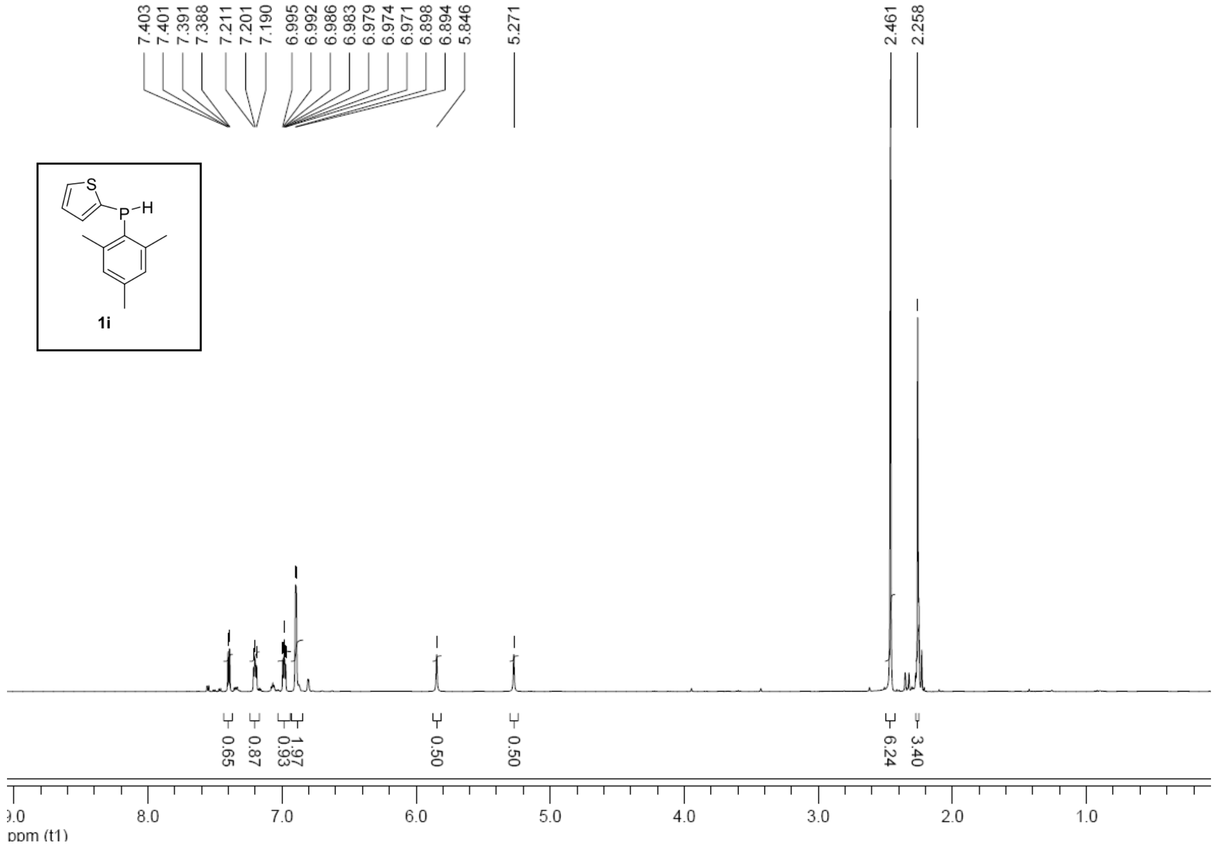

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5.846
5.271
2.461
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S
P
H
1i
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0.87
0.93
1.97
0.50
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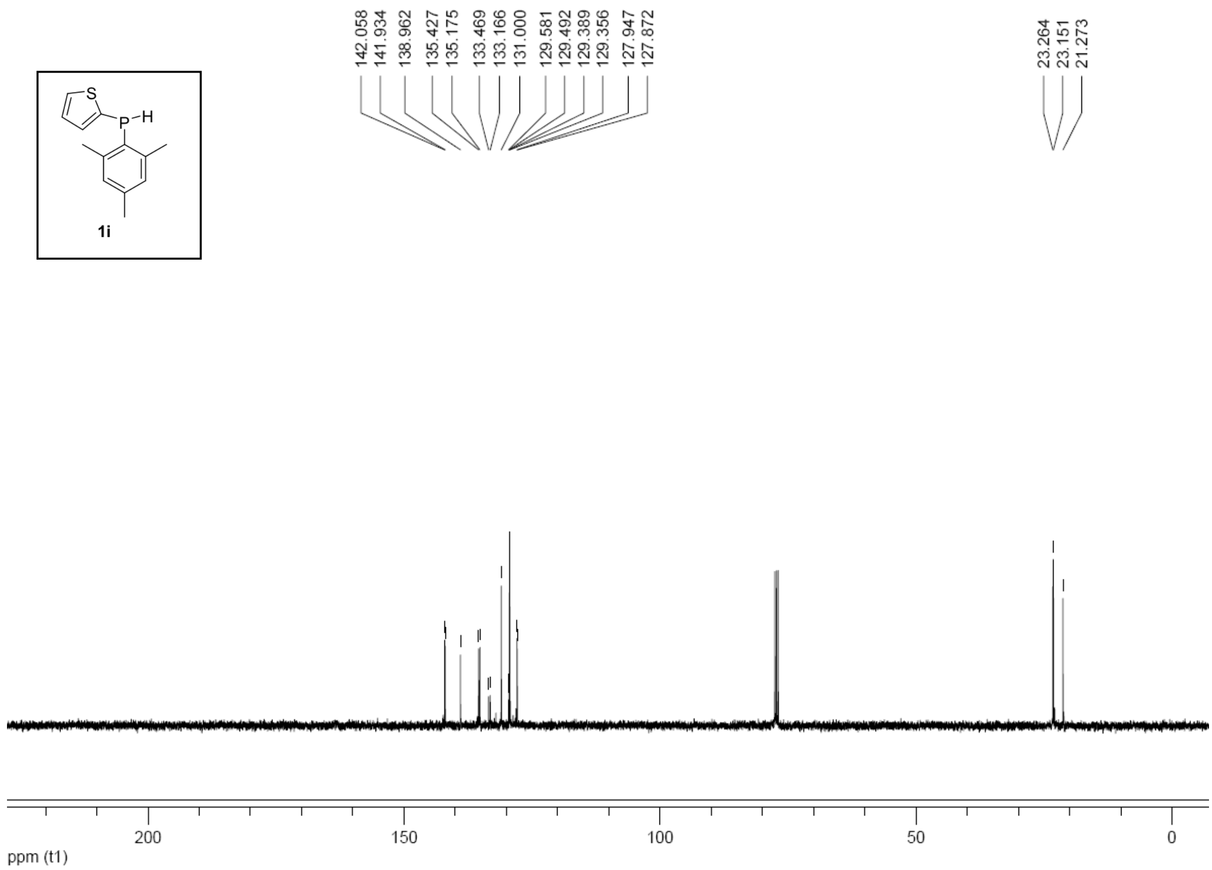

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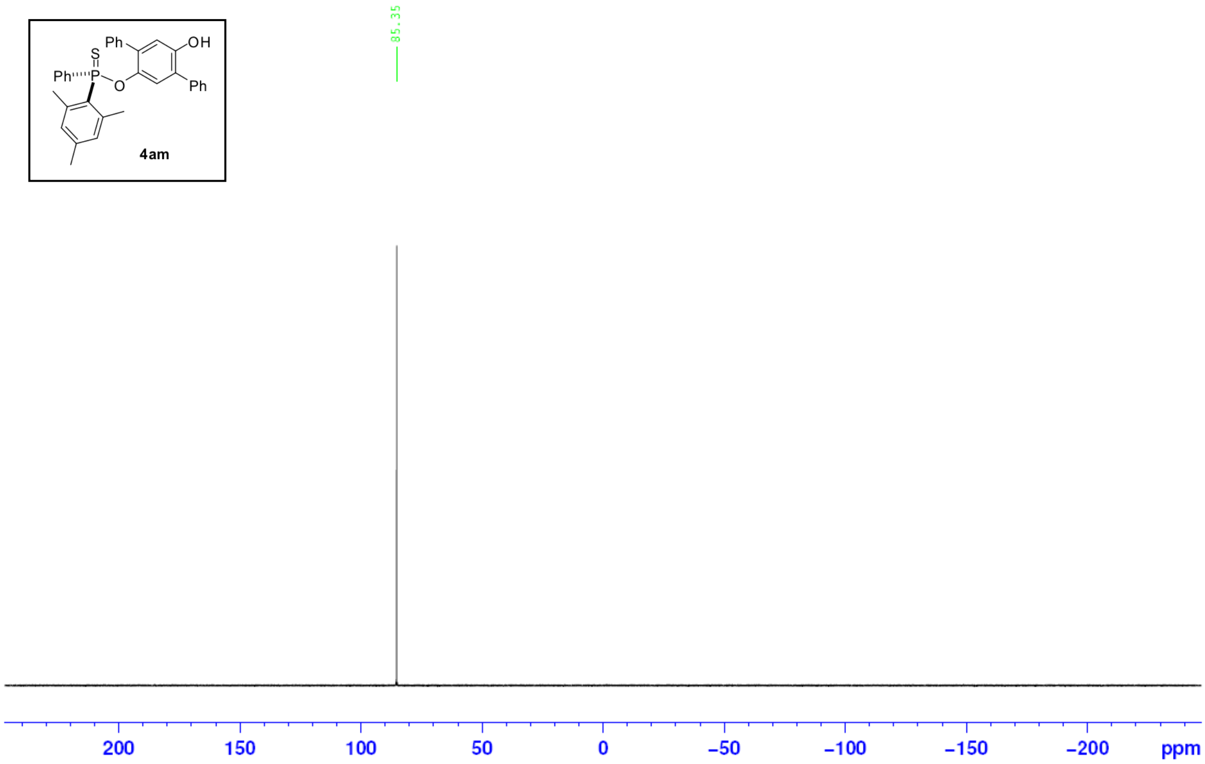
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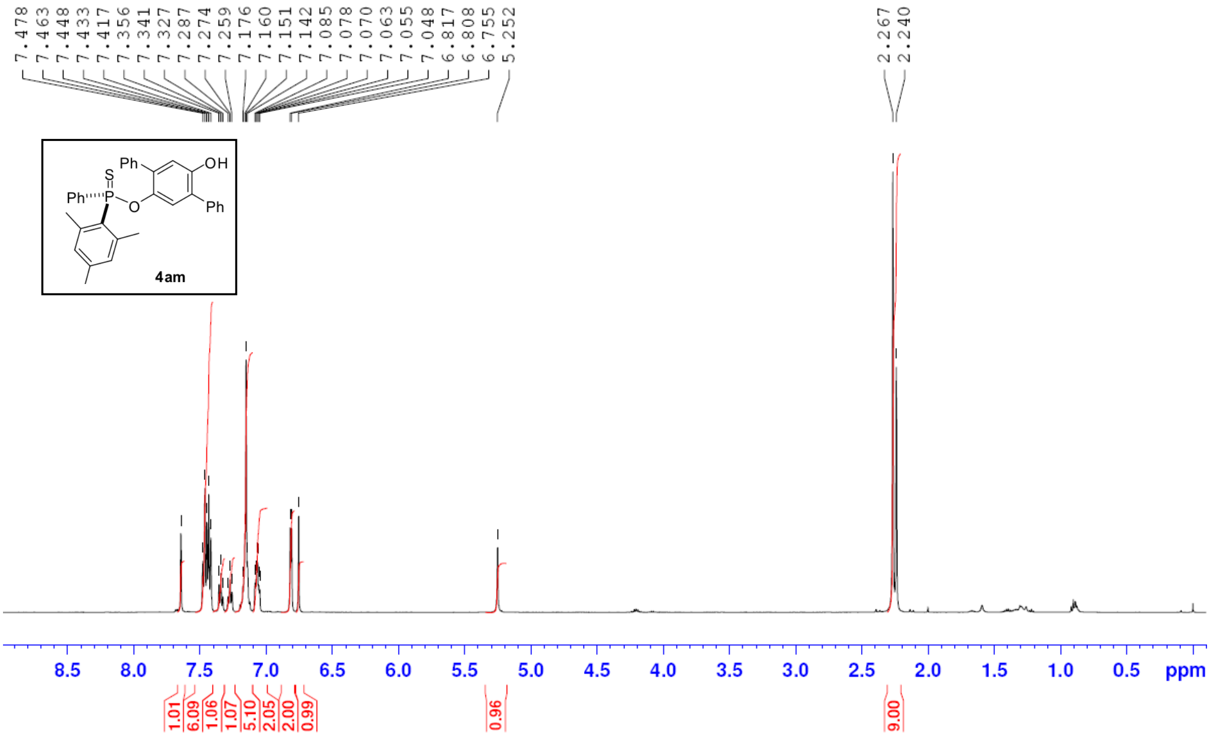
ppm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7.327
7.287
7.274
7.259
7.176
7.160
7.151
7.142
7.085
7.078
7.070
7.063
7.055
7.048
6.817
6.808
6.755
5.252
2.267
2.240
4am
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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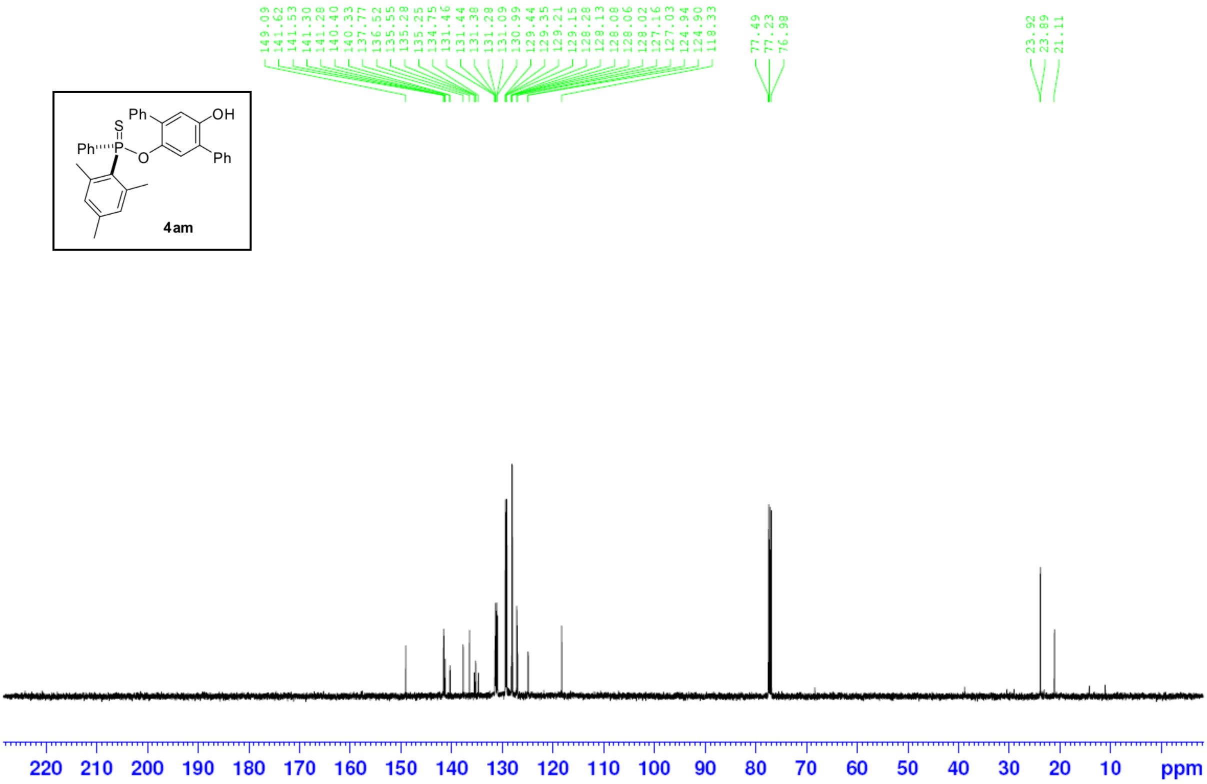
6.09
1.06
1.07
5.10
2.05
2.00
0.99
0.96
9.00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141.53
141.30
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140.40
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137.77
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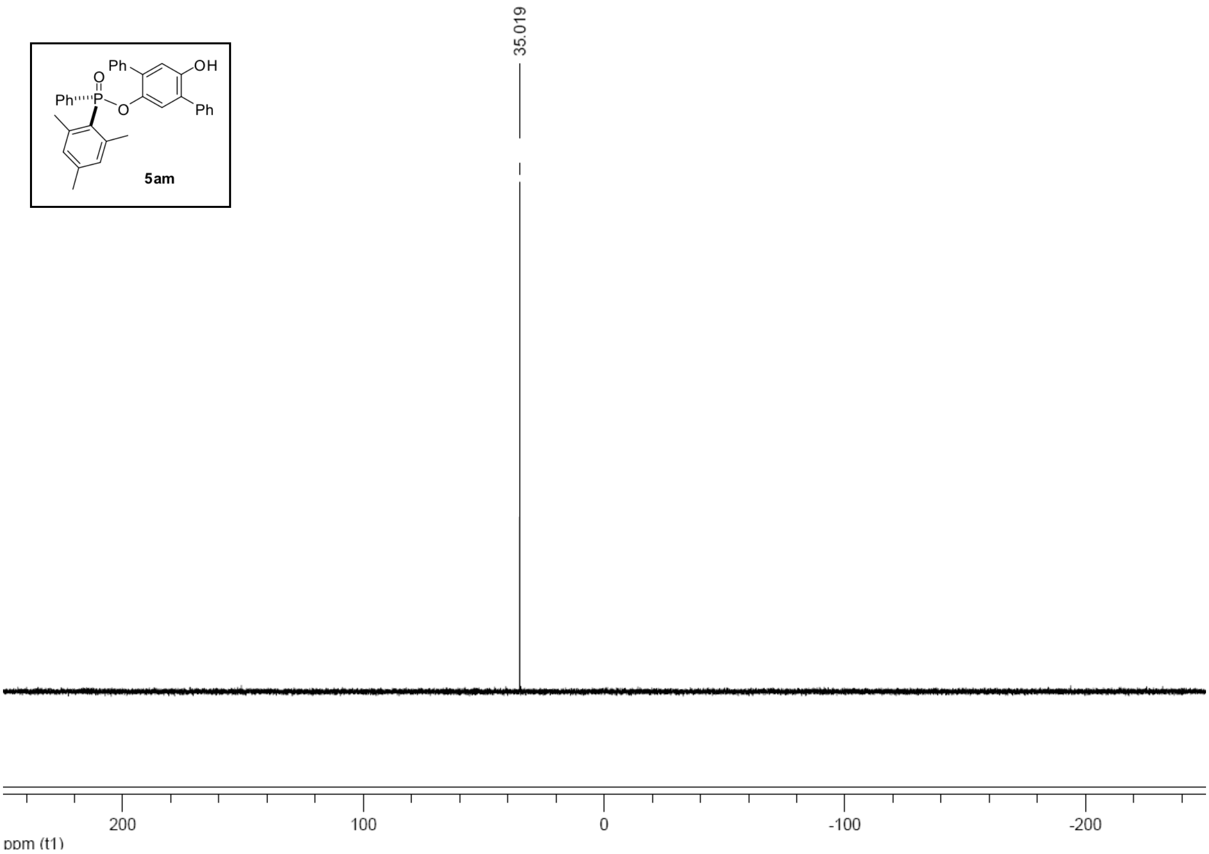
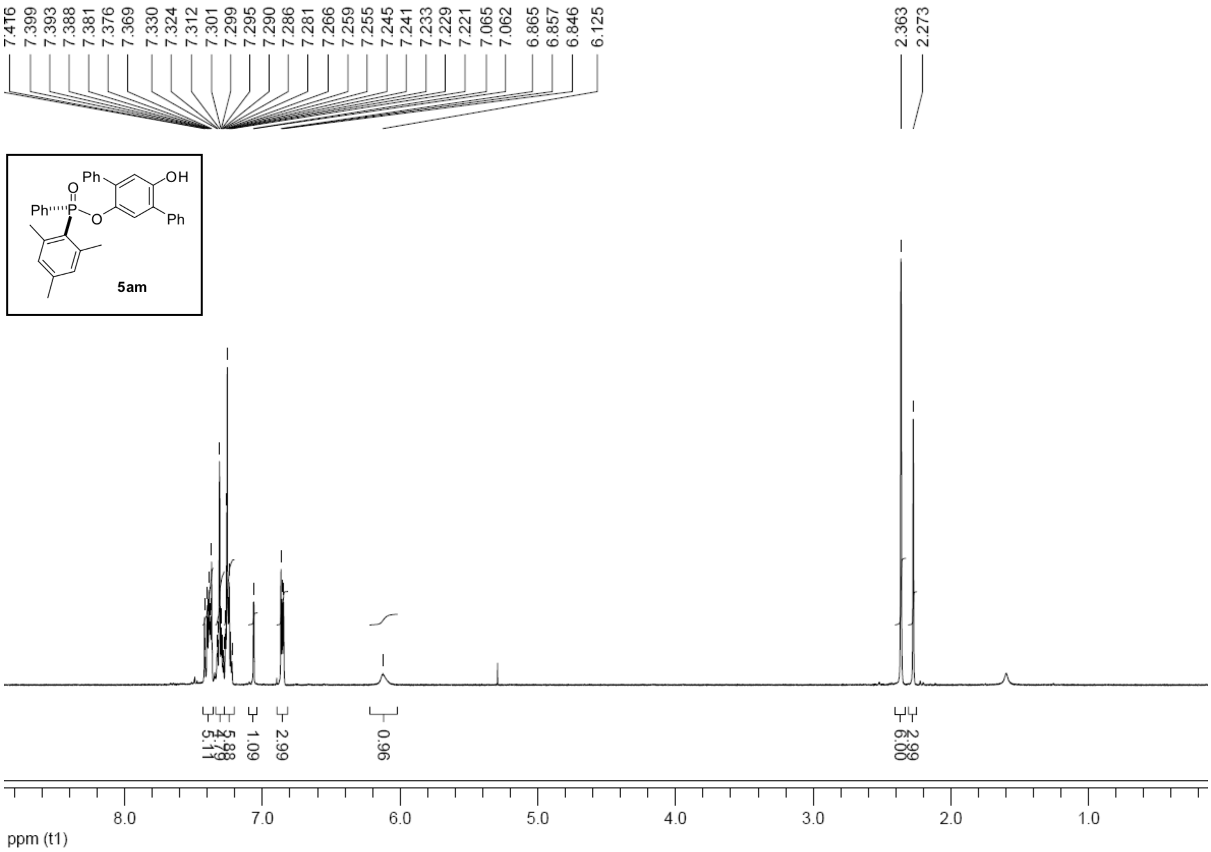
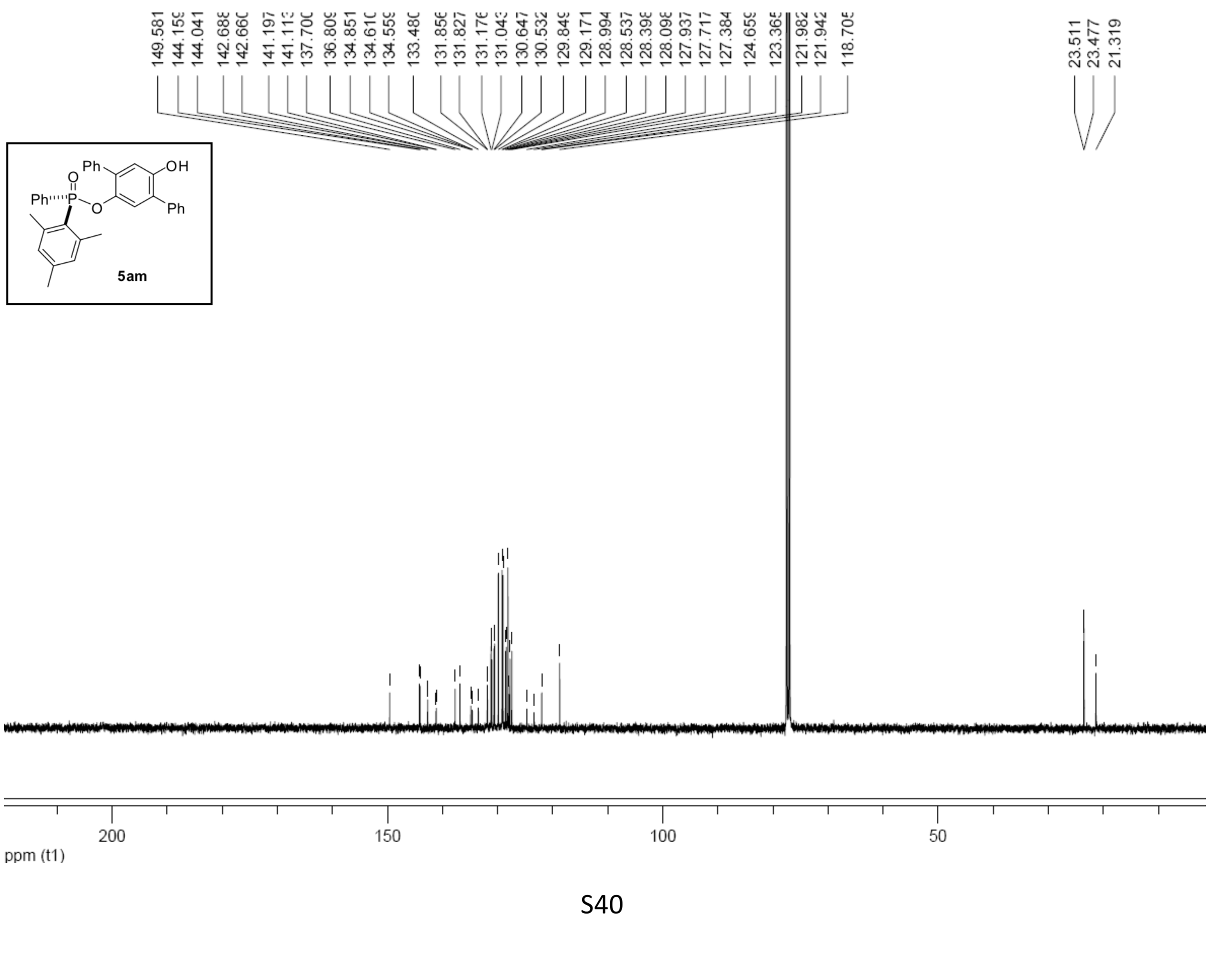
135.55
135.29
135.25
134.75
131.46
131.44
131.38
131.28
131.09
130.99
129.44
129.35
129.21
129.15
129.28
128.13
128.08
128.06
128.02
127.16
127.03
124.94
124.90
118.33
77.49
77.23
76.98
23.92
23.89
21.11
Ph
S
OH
Ph
P
O
Ph
4am
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

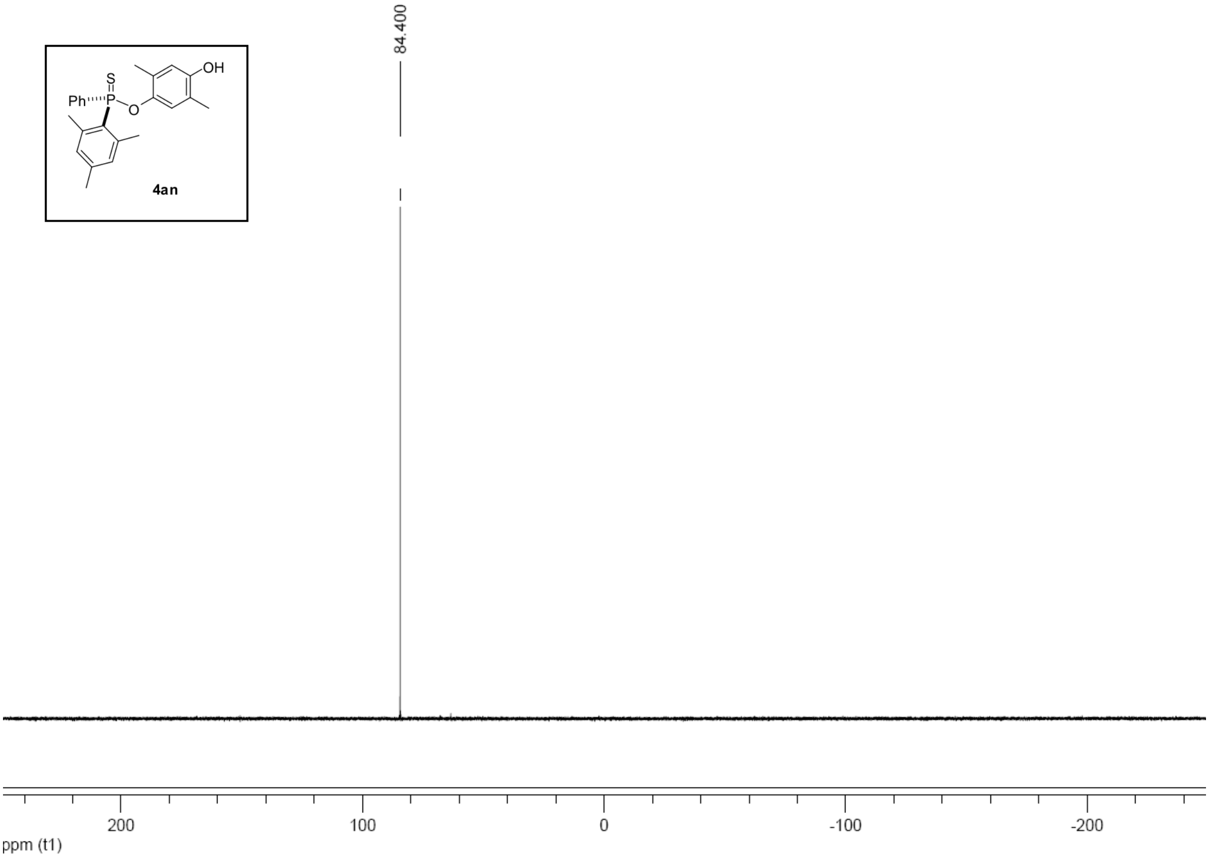

35.019
Ph
O
OH
Ph
P
O
Ph
5am
200
100
0
-100
-200
ppm (t1)



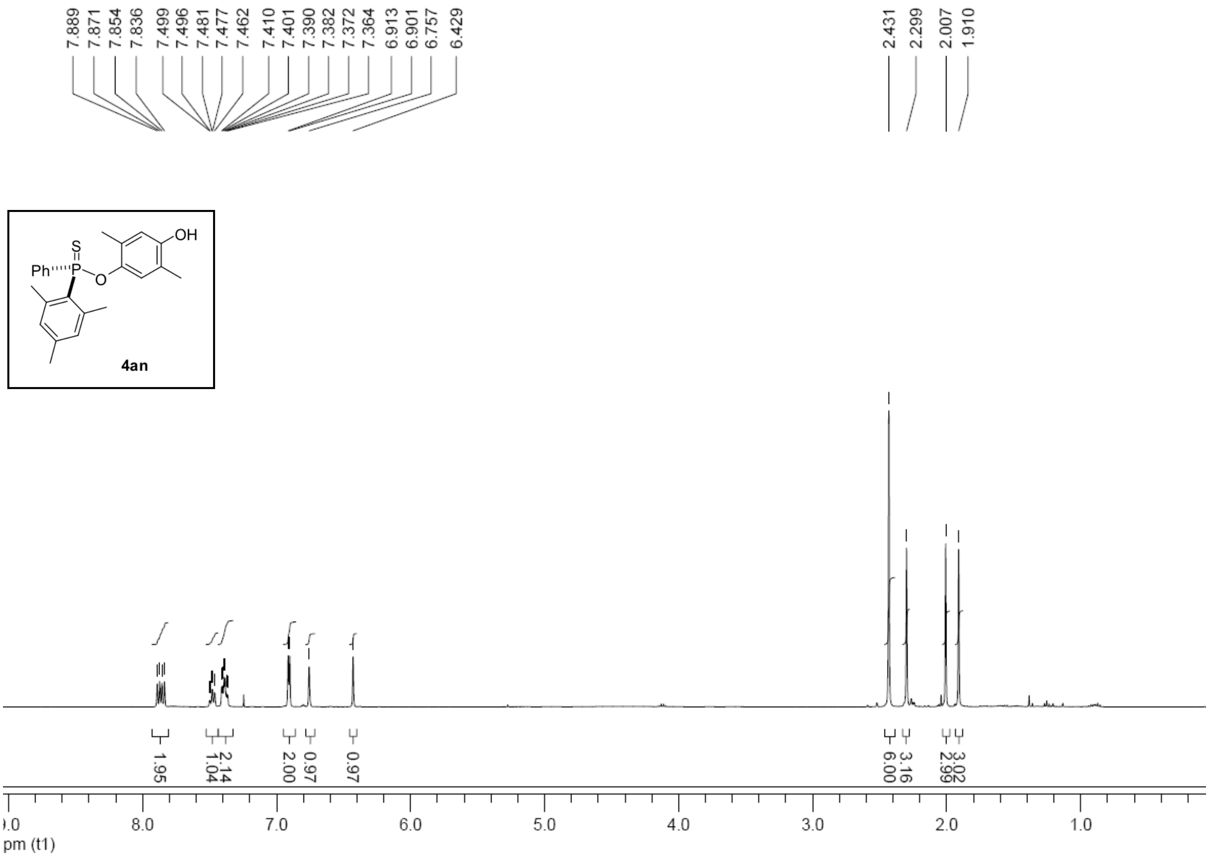
7.416
7.399
7.393
7.388
7.381
7.376
7.369
7.330
7.324
7.312
7.301
7.299
7.295
7.290
7.286
7.281
7.266
7.259
7.255
7.245
7.241
7.233
7.229
7.221
7.065
7.062
6.865
6.857
6.846
6.125
2.363
2.273
Ph
OH
O
Ph
P
O
Ph
5am
5.11
4.79
5.88
1.09
2.99
0.96
6.00
2.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



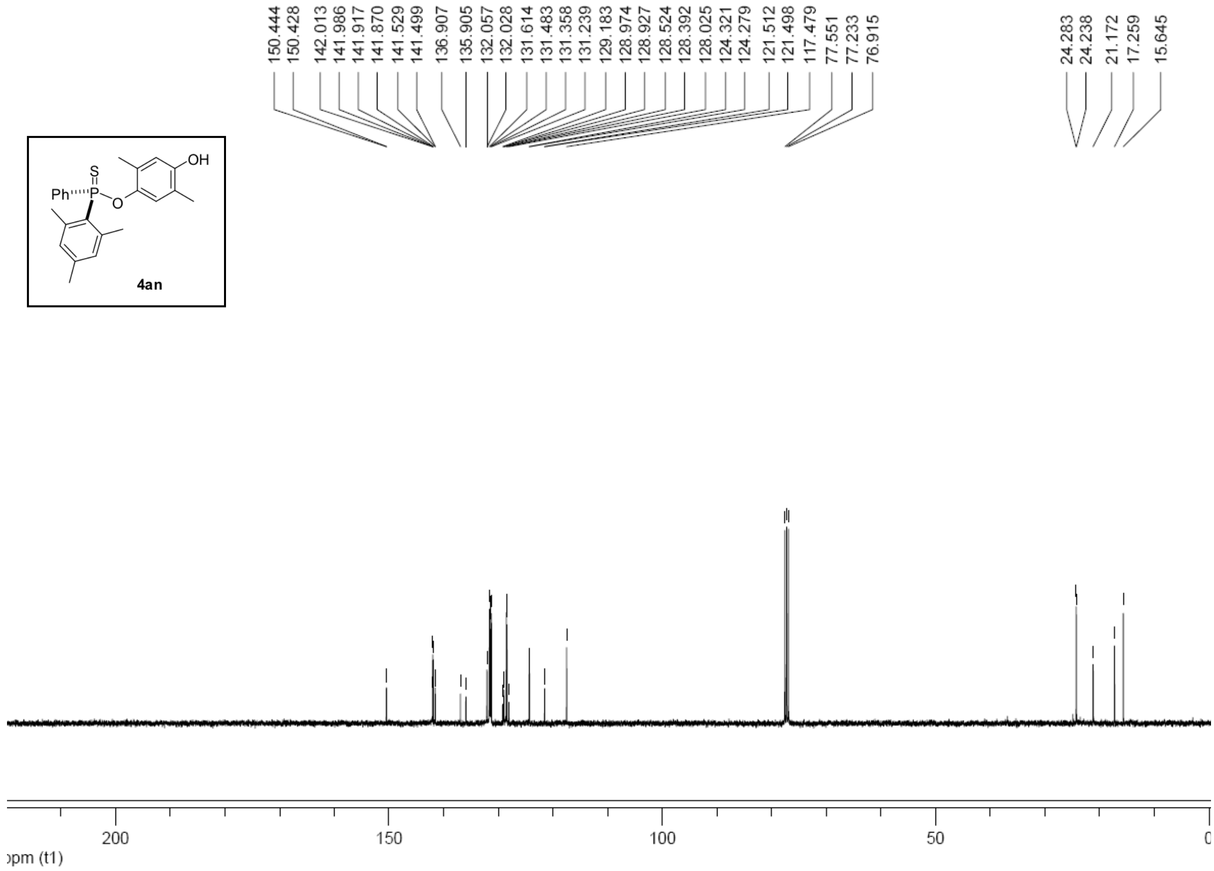
149.581
144.159
144.041
142.688
142.660
141.197
141.113
137.700
136.809
134.851
134.610
134.559
133.480
131.856
131.827
131.176
131.043
130.647
130.532
129.849
129.171
128.994
128.537
128.398
128.098
127.937
127.717
127.384
124.659
123.365
121.982
121.942
118.705
23.511
23.477
21.319
Ph
OH
O
Ph
P
O
Ph
5am
200
150
100
50
ppm (t1)

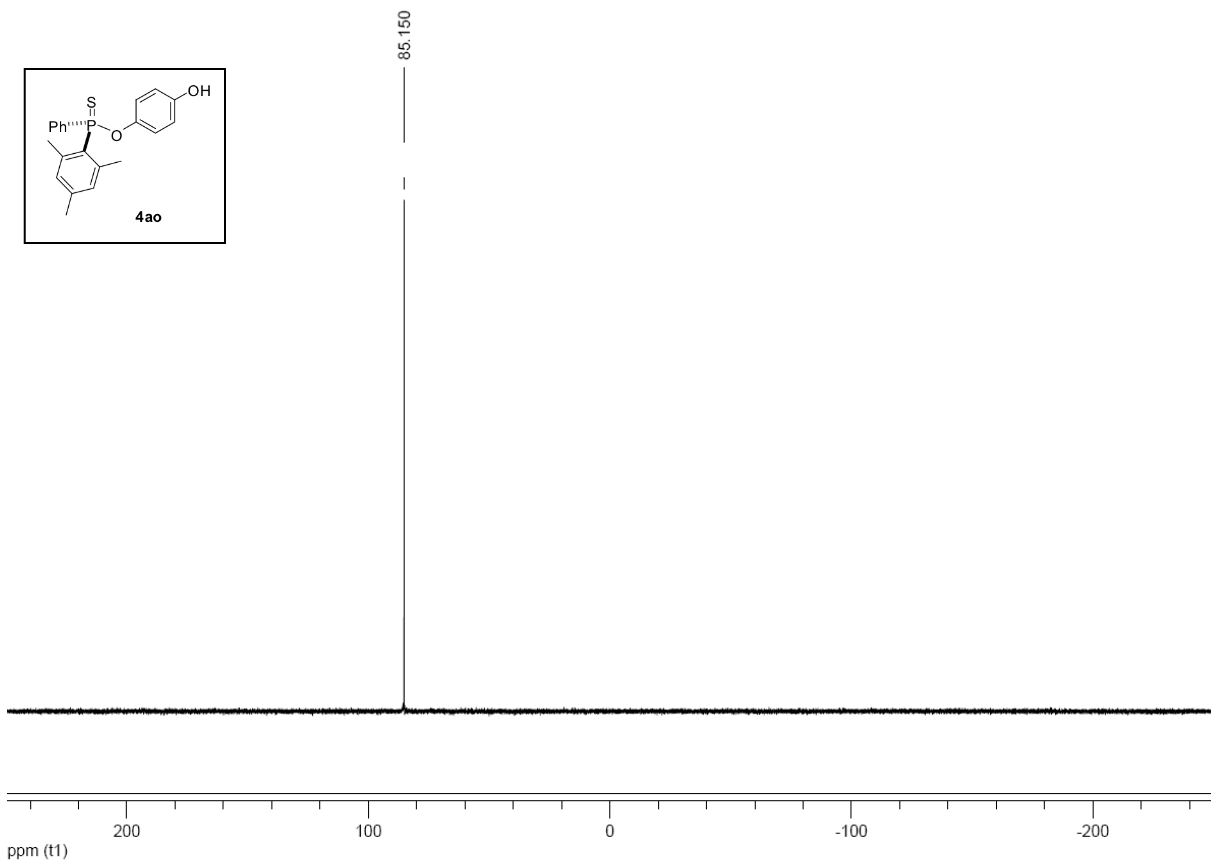


84.400
4an
ppm (t1)
200
100
0
-100
-200



7.889
7.871
7.854
7.836
7.499
7.496
7.481
7.477
7.462
7.410
7.401
7.390
7.382
7.372
7.364
6.913
6.901
6.757
6.429
2.431
2.299
2.007
1.910
4an
1.95
1.04
2.14
2.00
0.97
0.97
6.00
3.16
2.99
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


150.444
150.428
142.013
141.986
141.917
141.870
141.529
141.499
136.907
135.905
132.057
132.028
131.614
131.483
131.358
131.239
129.183
128.974
128.927
128.524
128.392
128.025
124.321
124.279
121.512
121.498
117.479
77.551
77.233
76.915
24.283
24.238
21.172
17.259
15.645
Ph
S
P
O
OH
4an
200
150
100
50
0
ppm (t1)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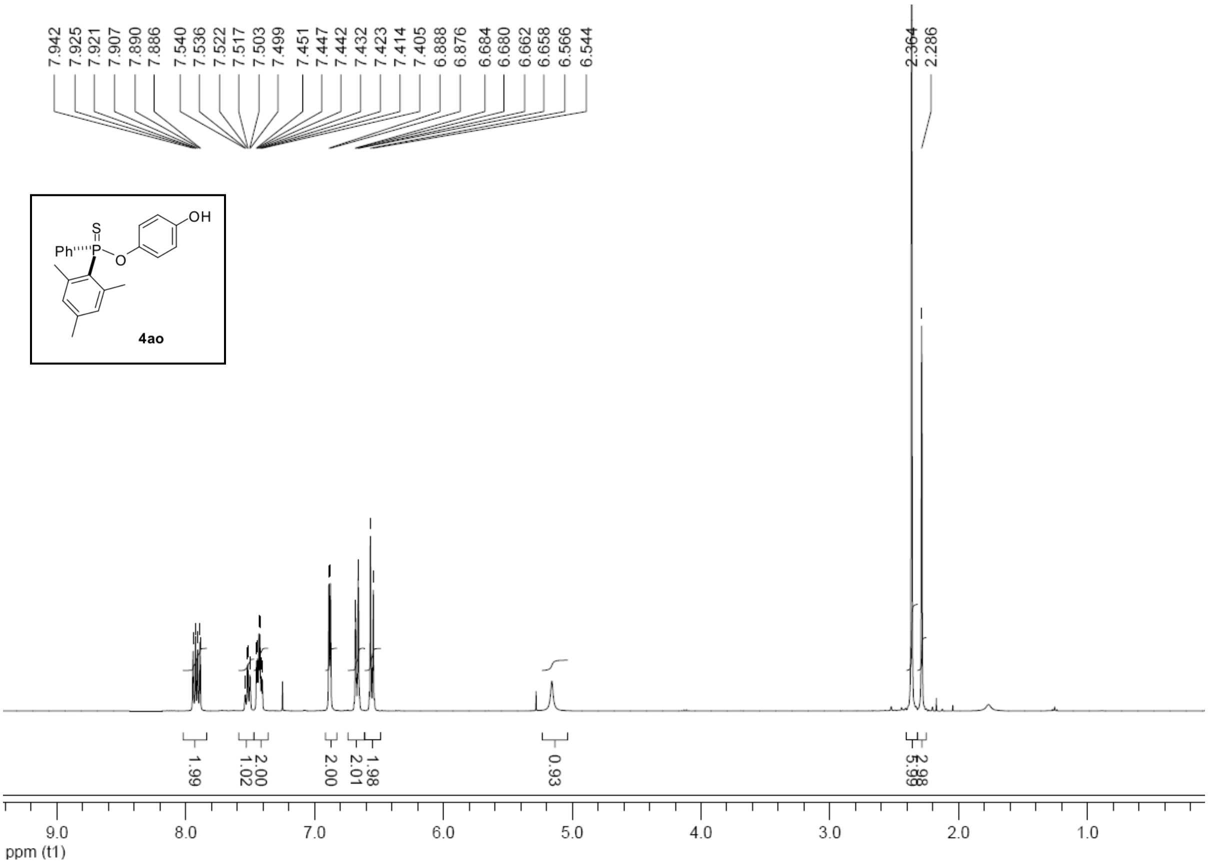
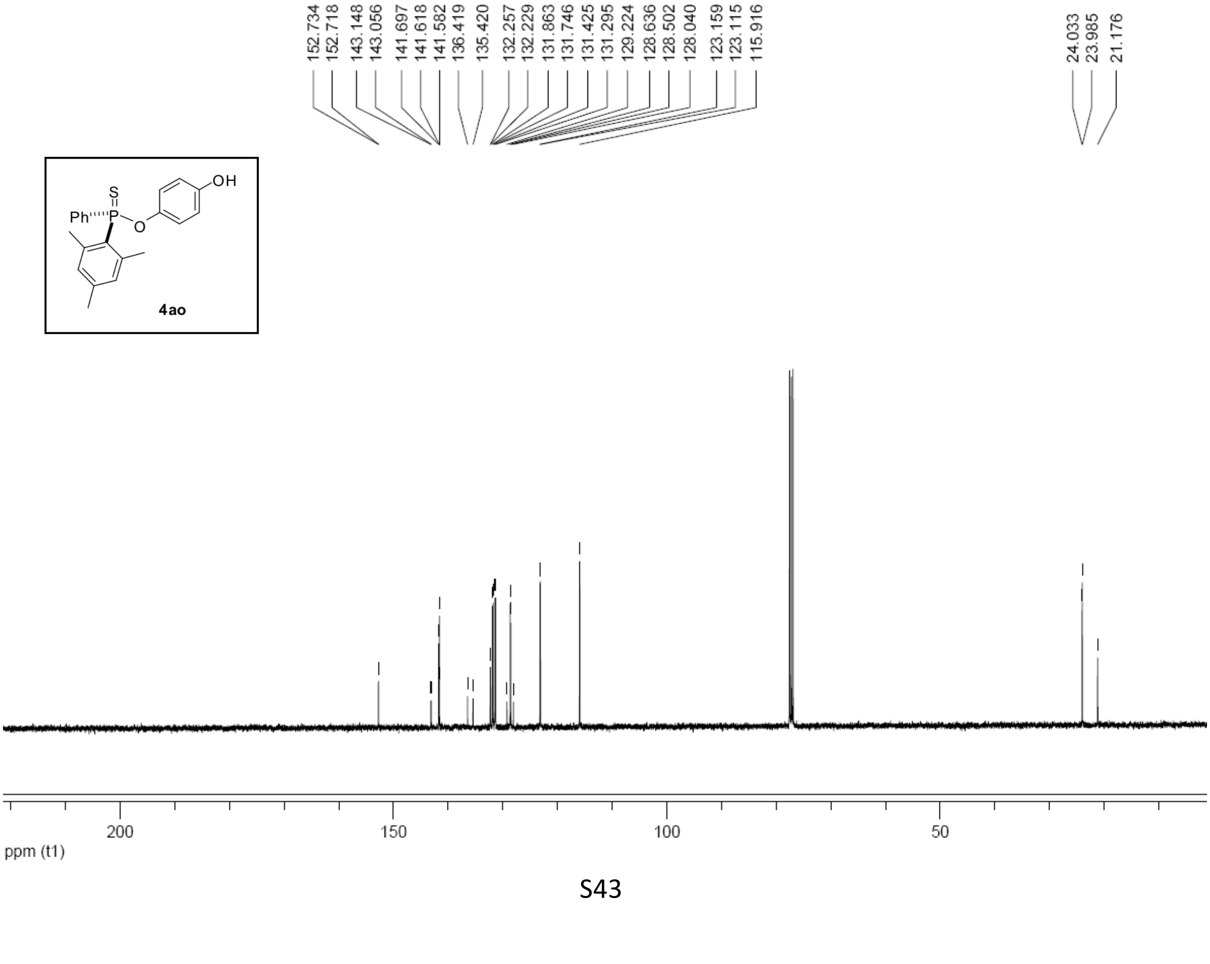
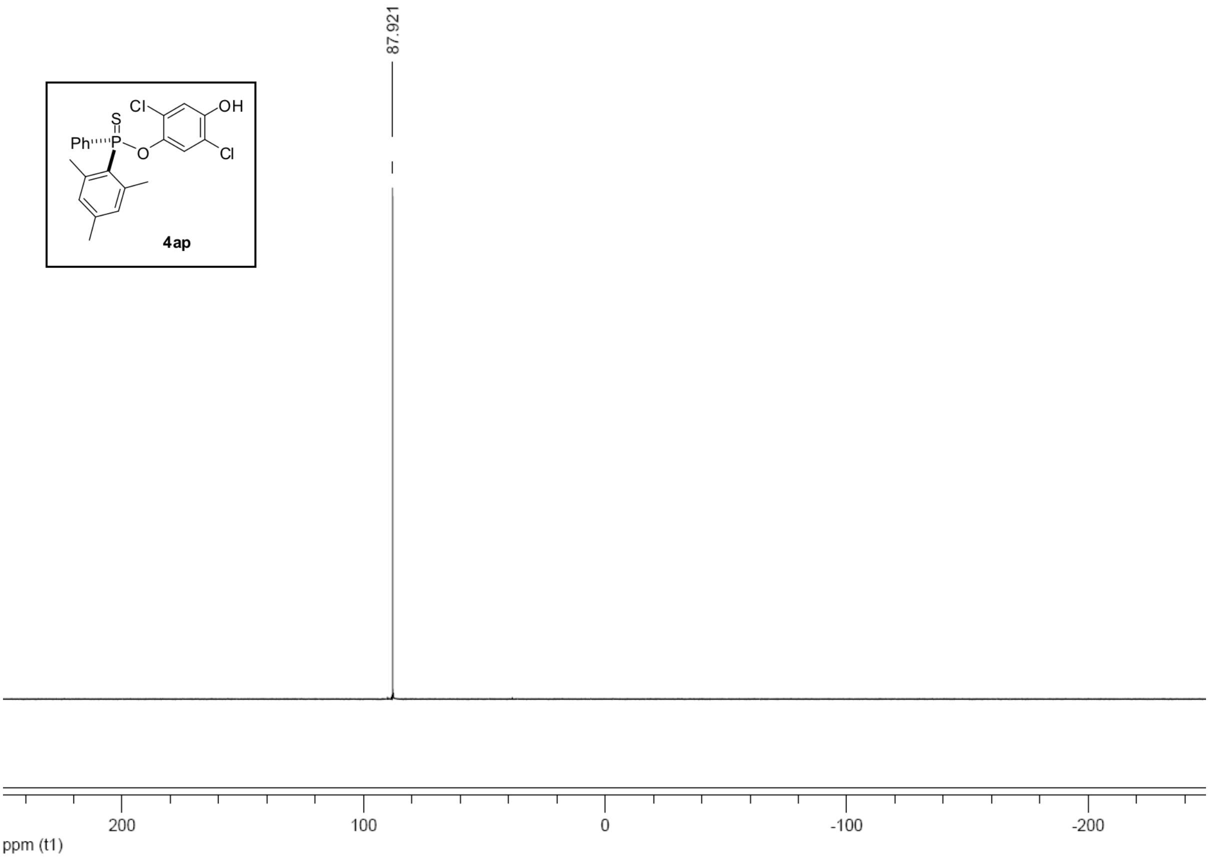
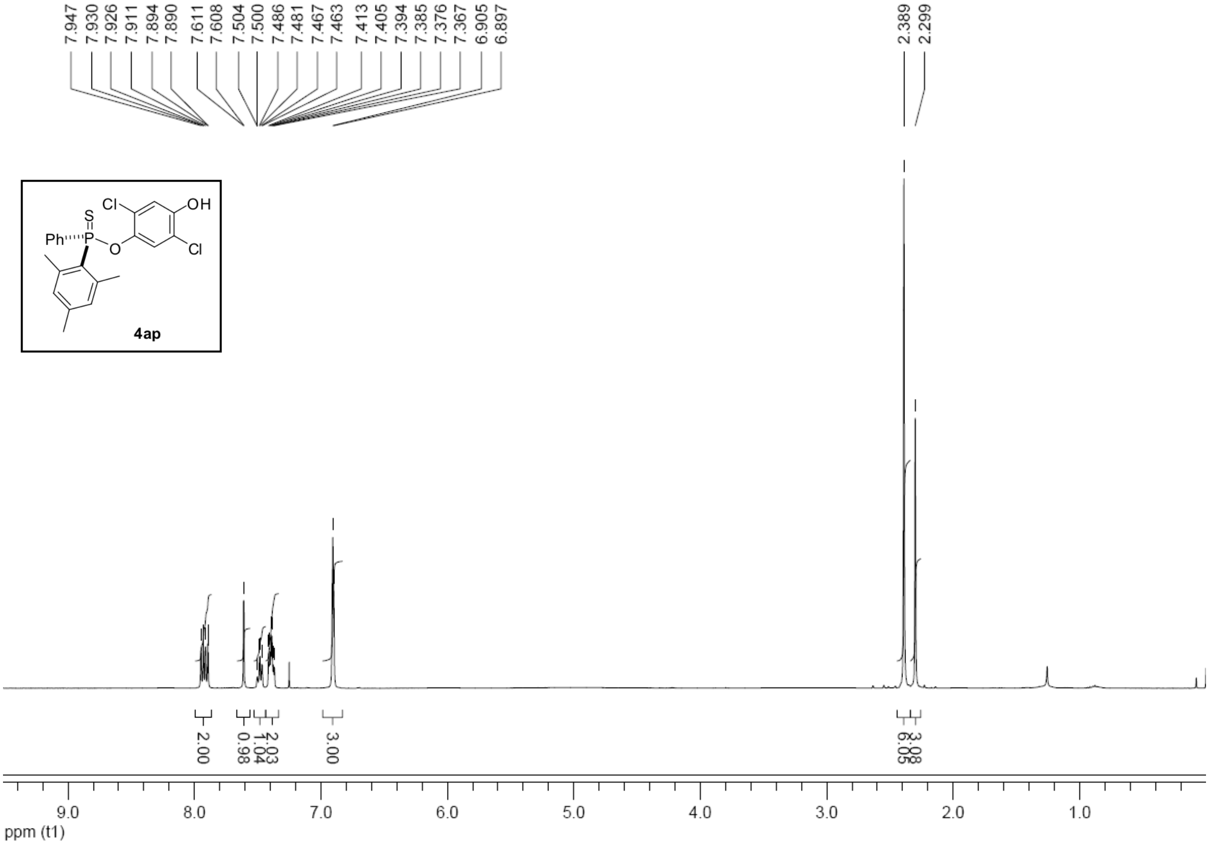
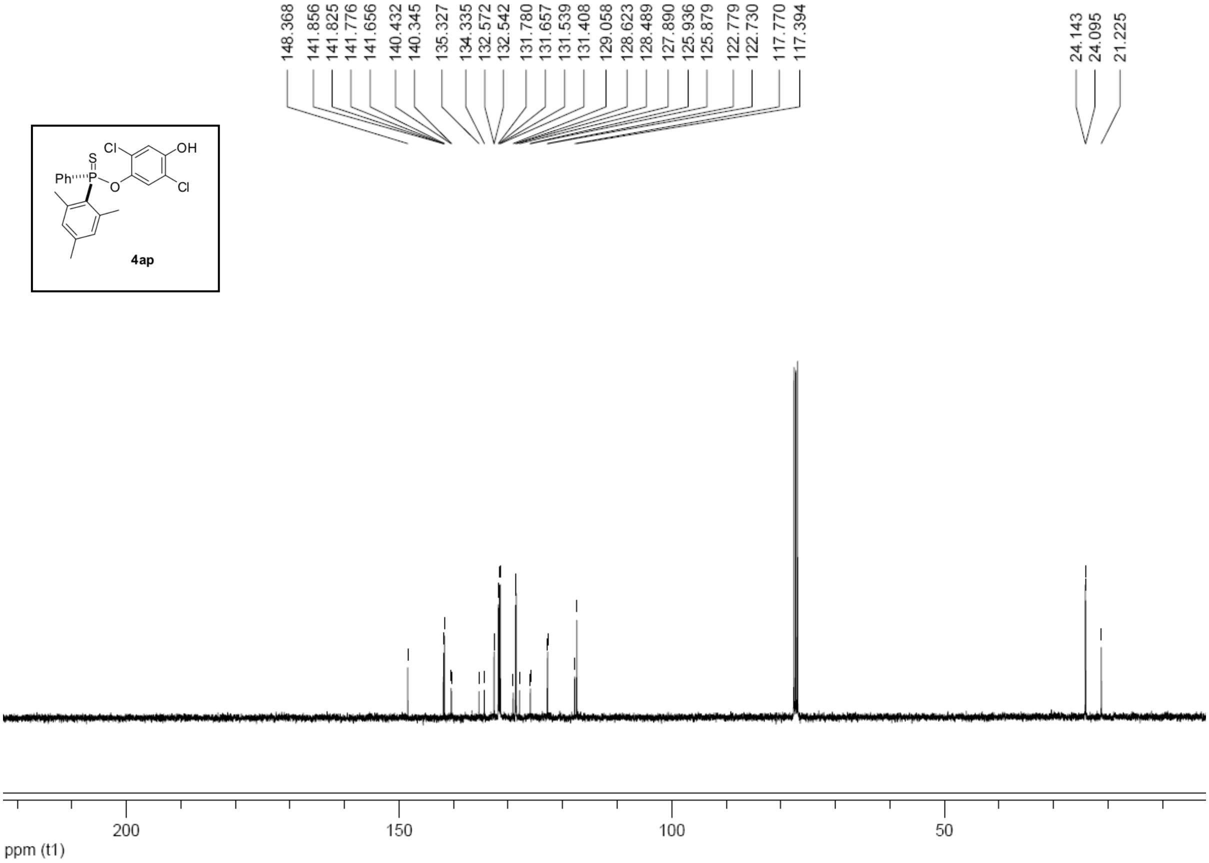
S
P
O
OH
4ao
200
100
0
-100
-200
ppm (t1)


7.942 7.925 7.921 7.907 7.890 7.886 7.540 7.536 7.522 7.517 7.503 7.499 7.451 7.447 7.442 7.432 7.423 7.414 7.405 6.888 6.876 6.684 6.680 6.662 6.658 6.566 6.544
2.364 2.286
Ph P S O OH
4ao
1.99 1.02 2.00 2.00 2.01 1.98 0.93 5.99 2.98
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (t1)


152.734 152.718 143.148 143.056 141.697 141.618 141.582 136.419 135.420 132.257 132.229 131.863 131.746 131.425 131.295 129.224 128.636 128.502 128.040 123.159 123.115 115.916
24.033 23.985 21.176
Ph P S O OH
4ao
200 150 100 50
ppm (t1)


87.921
Cl
OH
Ph
P
S
O
Cl
4ap
200
100
0
-100
-200
ppm (t1)


7.947
7.930
7.926
7.911
7.894
7.890
7.611
7.608
7.504
7.500
7.486
7.481
7.467
7.463
7.413
7.405
7.394
7.385
7.376
7.367
6.905
6.897
2.389
2.299
Cl
OH
Ph
P
S
O
Cl
4ap
2.00
0.98
1.04
2.03
3.00
6.05
3.08
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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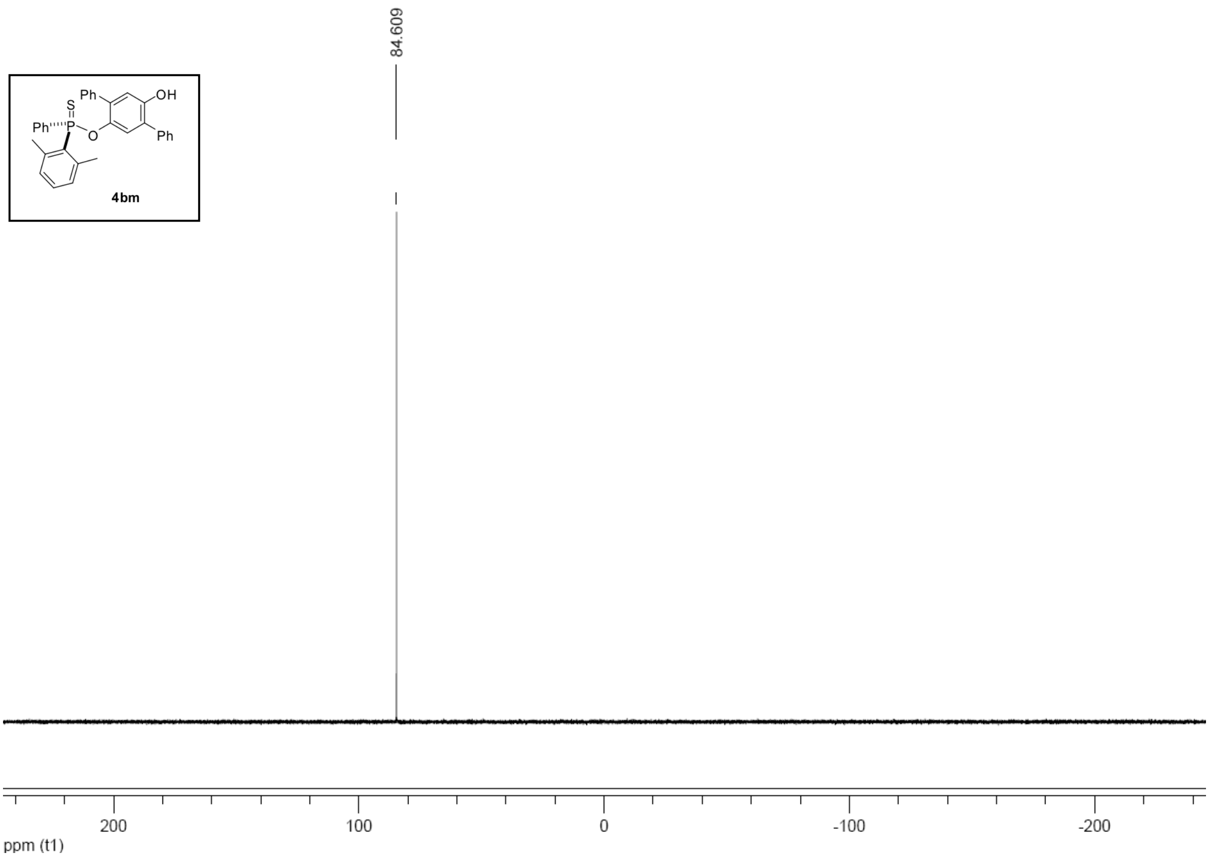
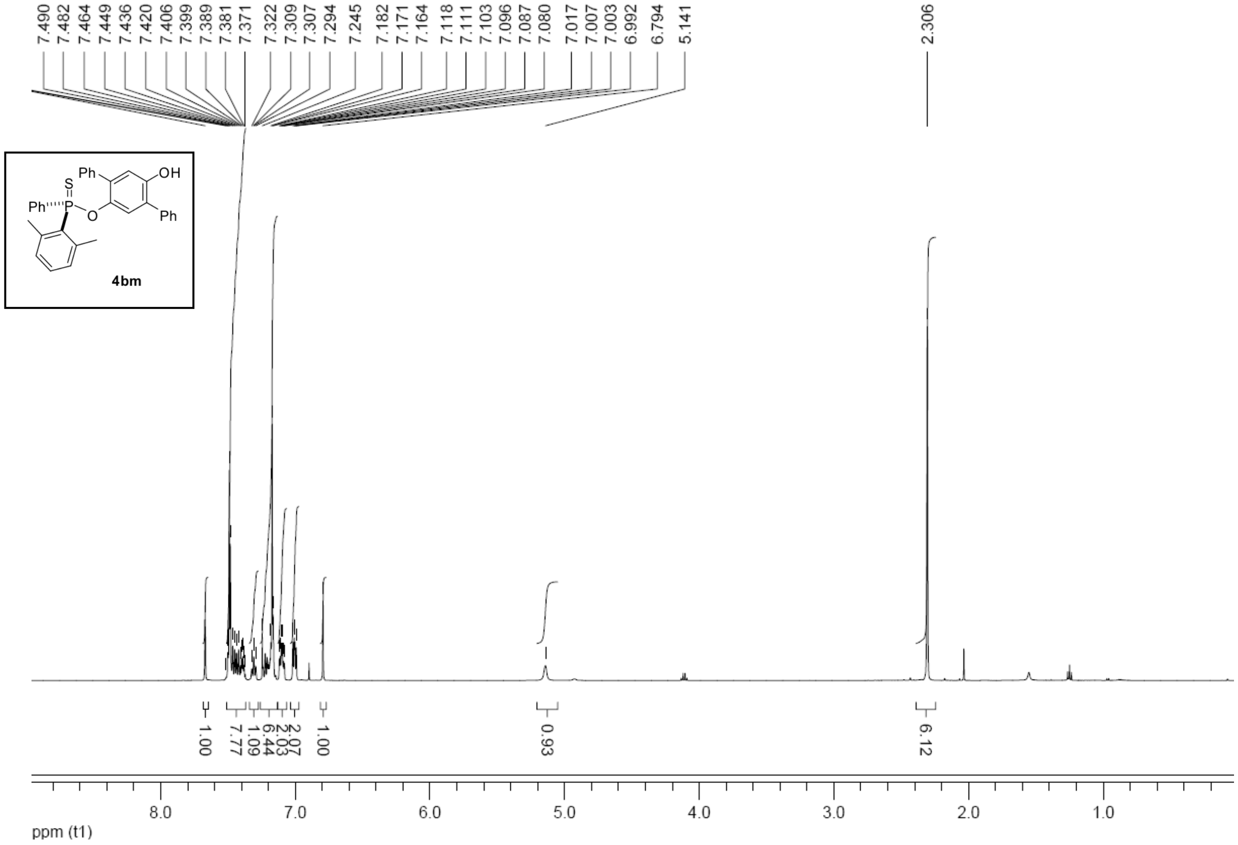
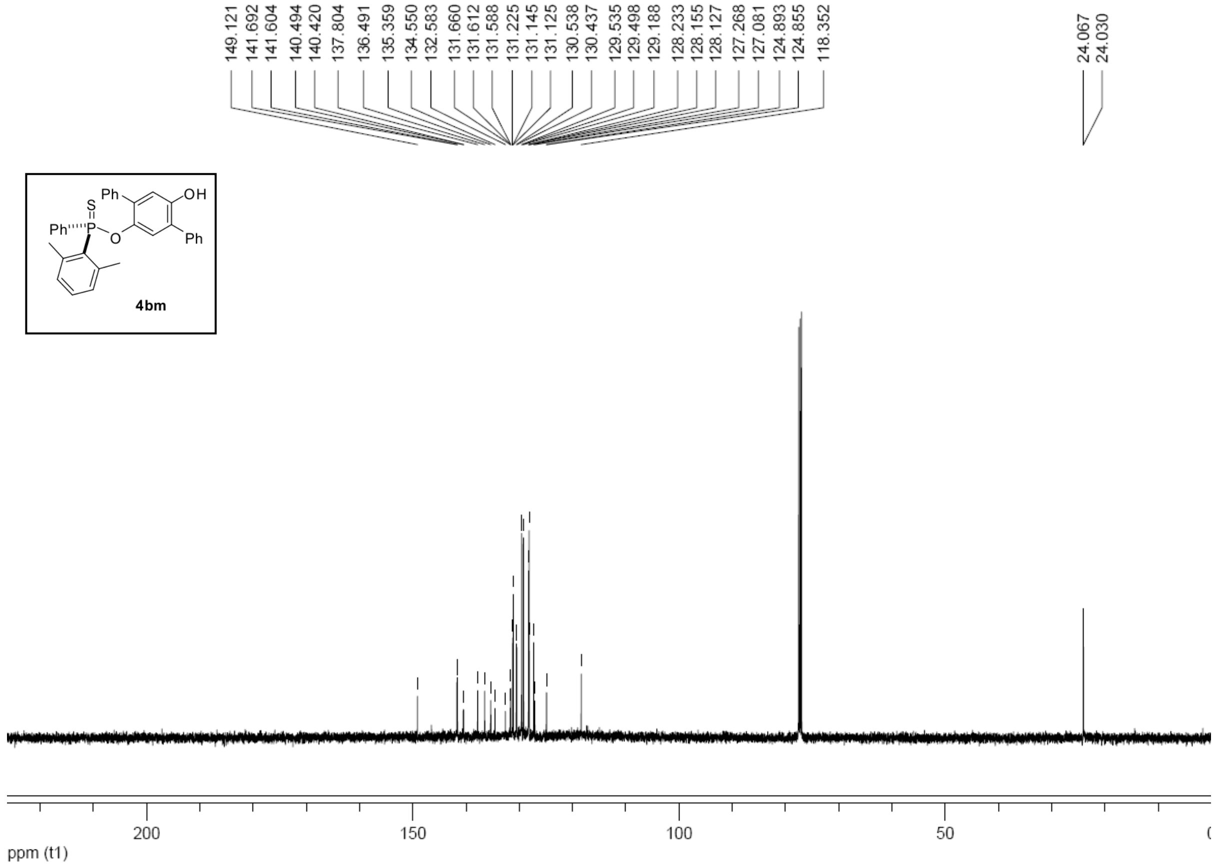
141.825
141.776
141.656
140.432
140.345
135.327
134.335
132.572
132.542
131.780
131.657
131.539
131.408
129.058
128.623
128.489
127.890
125.936
125.879
122.779
122.730
117.770
117.394
24.143
24.095
21.225
Cl
OH
S
Ph
P
O
Cl
4ap
200
150
100
50
ppm (t1)

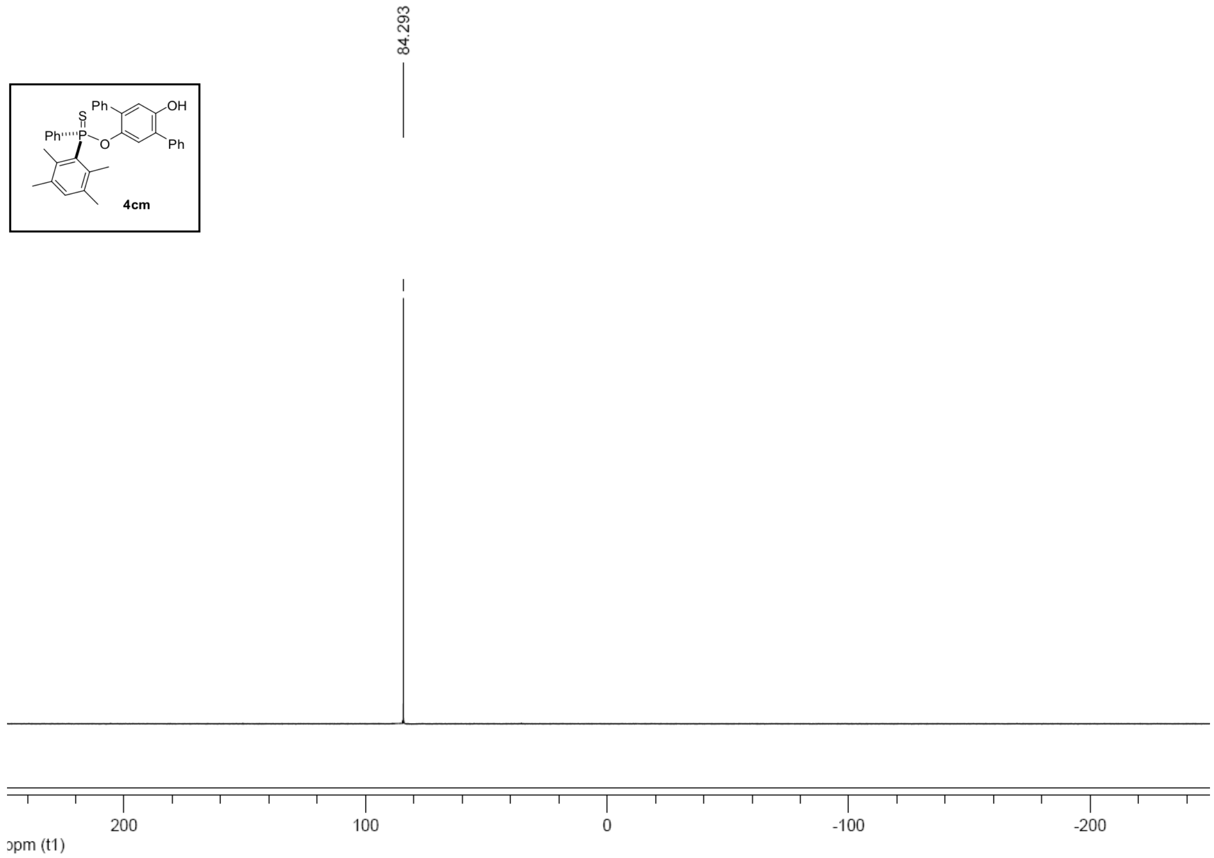

84.609
Ph
OH
S
Ph
P
O
Ph
4bm
200
100
0
-100
-200
ppm (t1)

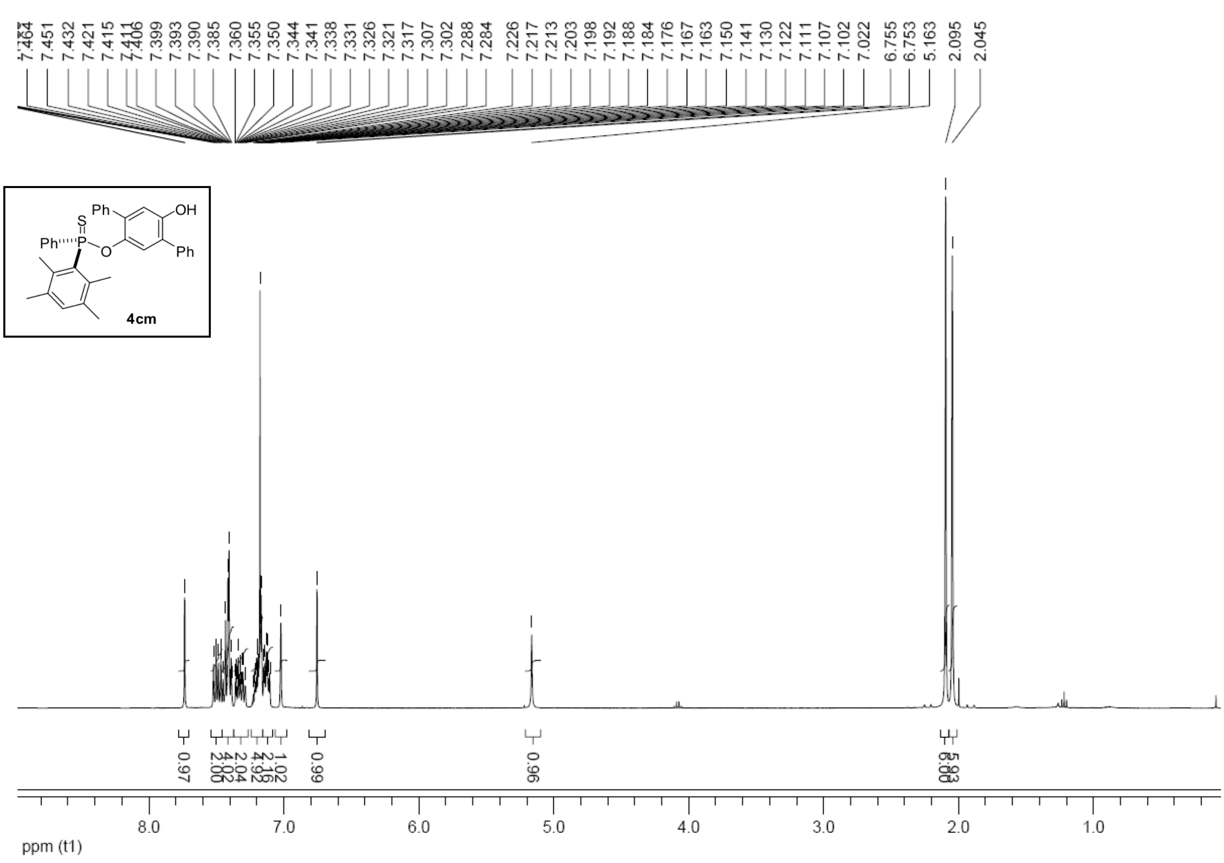


7.490
7.482
7.464
7.449
7.436
7.420
7.406
7.399
7.389
7.381
7.371
7.322
7.309
7.307
7.294
7.245
7.182
7.171
7.164
7.118
7.111
7.103
7.096
7.087
7.080
7.017
7.007
7.003
6.992
6.794
5.141
2.306
Ph
OH
S
Ph
P
O
Ph
4bm
1.00
7.77
1.09
6.44
2.03
2.07
1.00
0.93
6.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



149.121
141.692
141.604
140.494
140.420
137.804
136.491
135.359
134.550
132.583
131.660
131.612
131.588
131.225
131.145
131.125
130.538
130.437
129.535
129.498
129.188
128.233
128.155
128.127
127.268
127.081
124.893
124.855
118.352
24.067
24.030
Ph
OH
S
Ph
P
O
Ph
4bm
200
150
100
50
ppm (t1)


Ph
OH
S
Ph
P
O
Ph
4cm
84.293
200
100
0
-100
-200
ppm (t1)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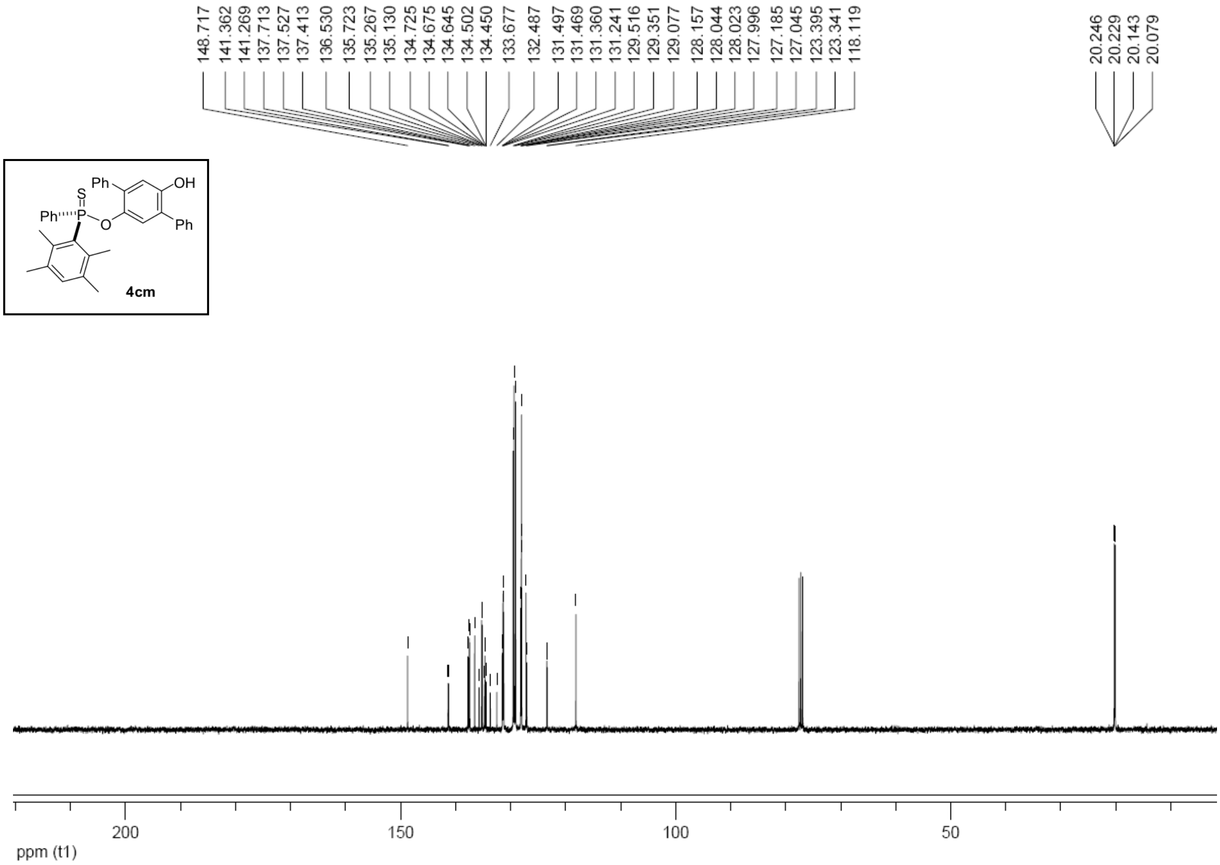
7.411
7.406
7.399
7.393
7.390
7.385
7.360
7.355
7.350
7.344
7.341
7.338
7.331
7.326
7.321
7.317
7.307
7.302
7.288
7.284
7.226
7.217
7.213
7.203
7.198
7.192
7.188
7.184
7.176
7.167
7.163
7.150
7.141
7.130
7.122
7.111
7.107
7.102
7.022
6.755
6.753
5.163
2.095
2.045
Ph
OH
S
Ph
P
O
Ph
4cm
0.97
2.00
4.02
2.04
4.92
2.16
1.02
0.99
0.96
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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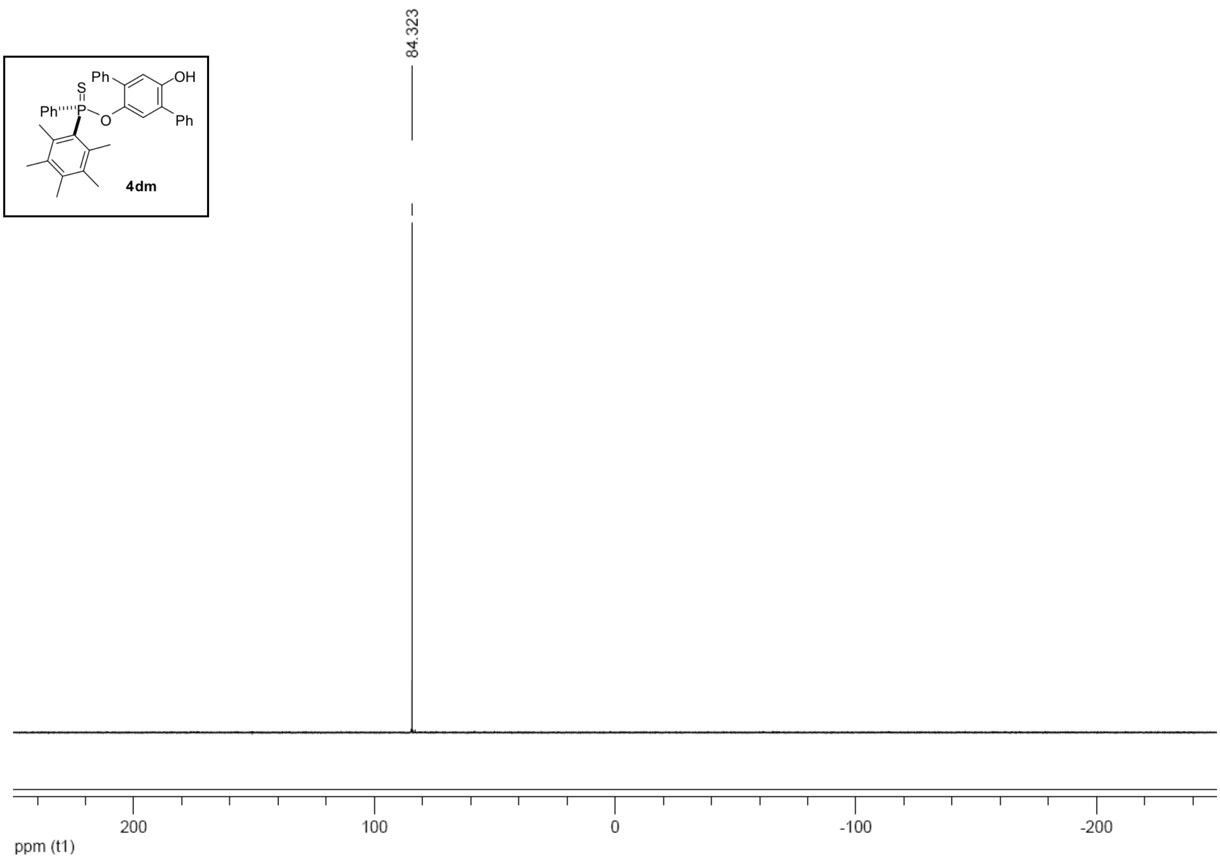
141.269
137.713
137.527
137.413
136.530
135.723
135.267
135.130
134.725
134.675
134.645
134.502
134.450
133.677
132.487
131.497
131.469
131.360
131.241
129.516
129.351
129.077
128.157
128.044
128.023
127.996
127.185
127.045
123.395
123.341
118.119
20.246
20.229
20.143
20.079
Ph
S
OH
Ph
P
O
Ph
4cm
200
150
100
50
ppm (t1)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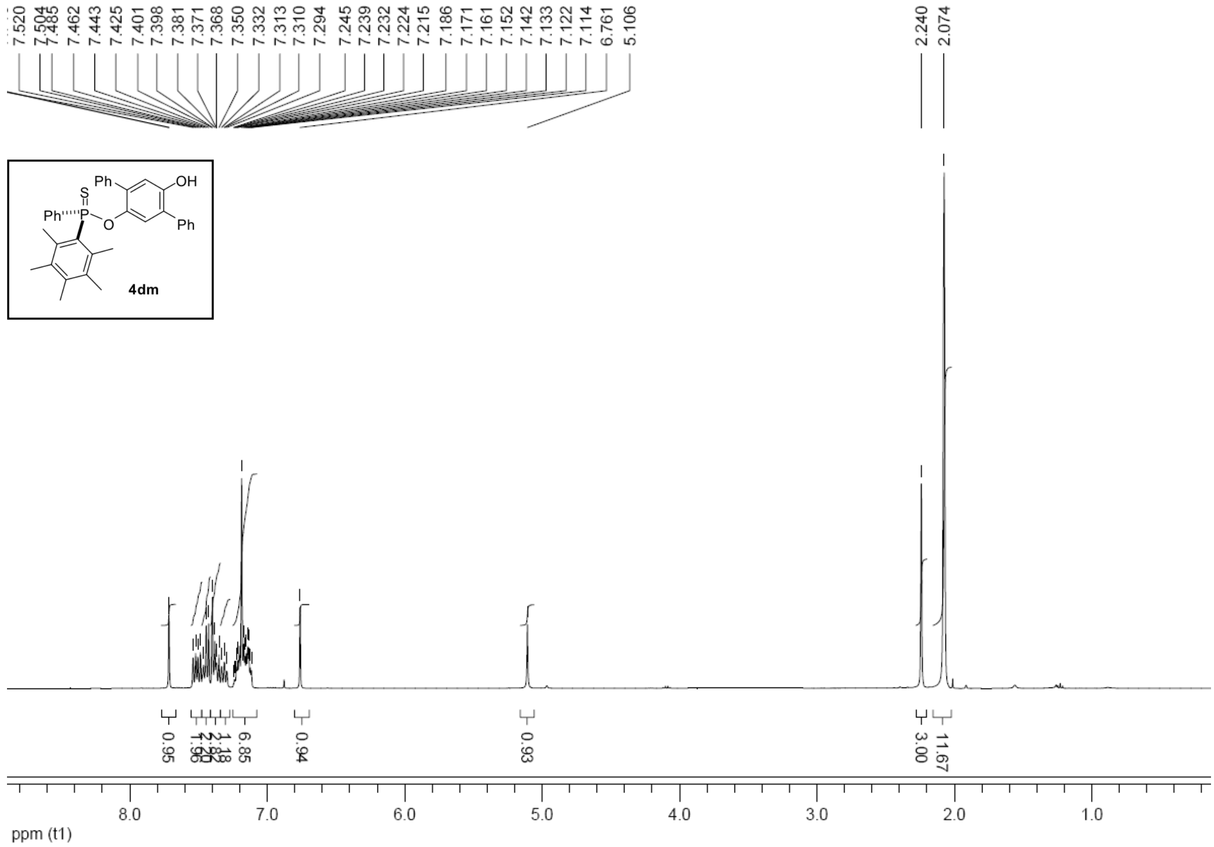
S
OH
Ph
P
O
Ph
4dm
200
100
0
-100
-200
ppm (t1)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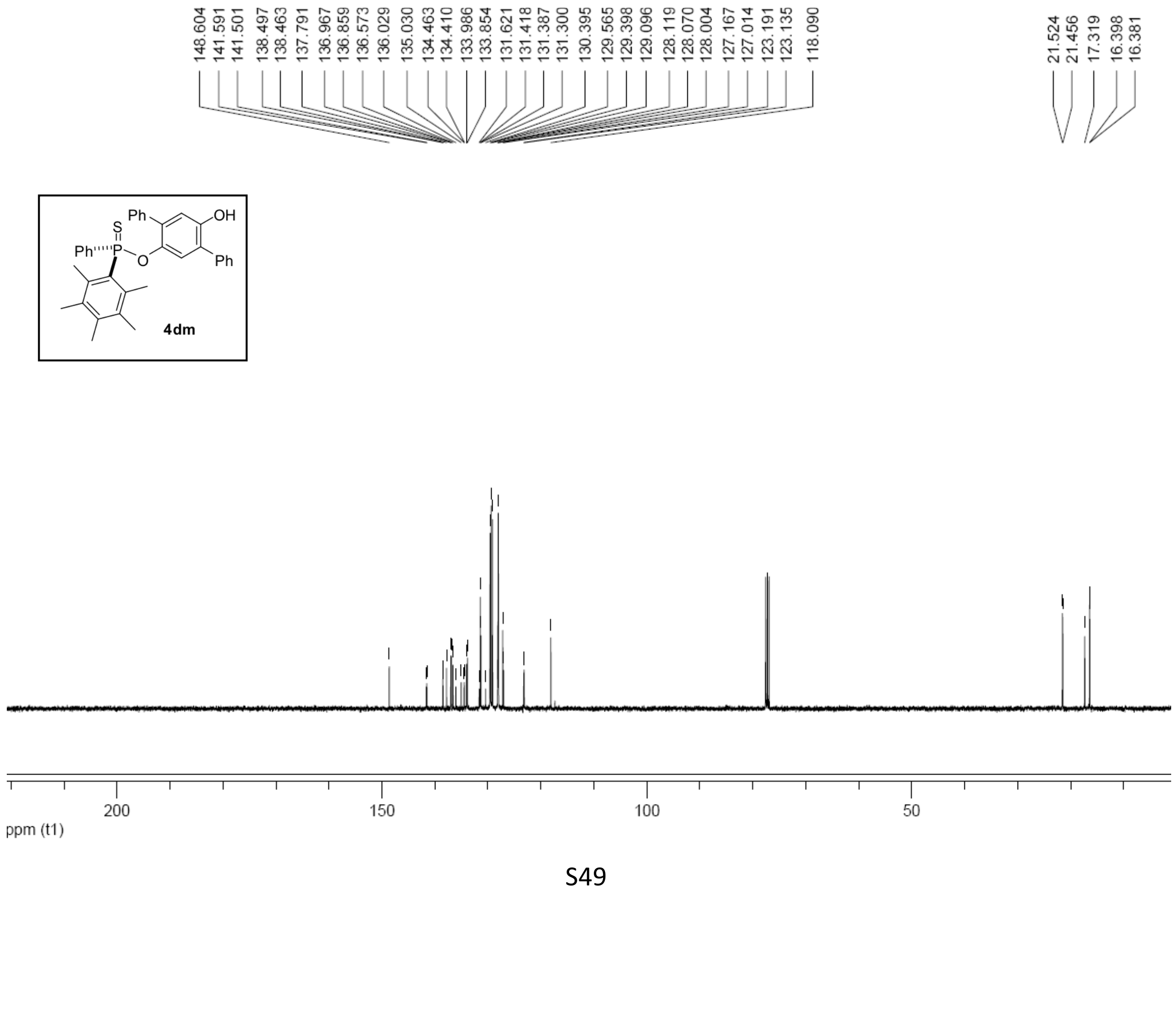
7.485
7.462
7.443
7.425
7.401
7.398
7.381
7.371
7.368
7.350
7.332
7.313
7.310
7.294
7.245
7.239
7.232
7.224
7.215
7.186
7.171
7.161
7.152
7.142
7.133
7.122
7.114
6.761
5.106
2.240
2.074
Ph
OH
S
Ph
P
O
Ph
4dm
0.95
1.18
6.85
0.94
0.93
3.00
11.67
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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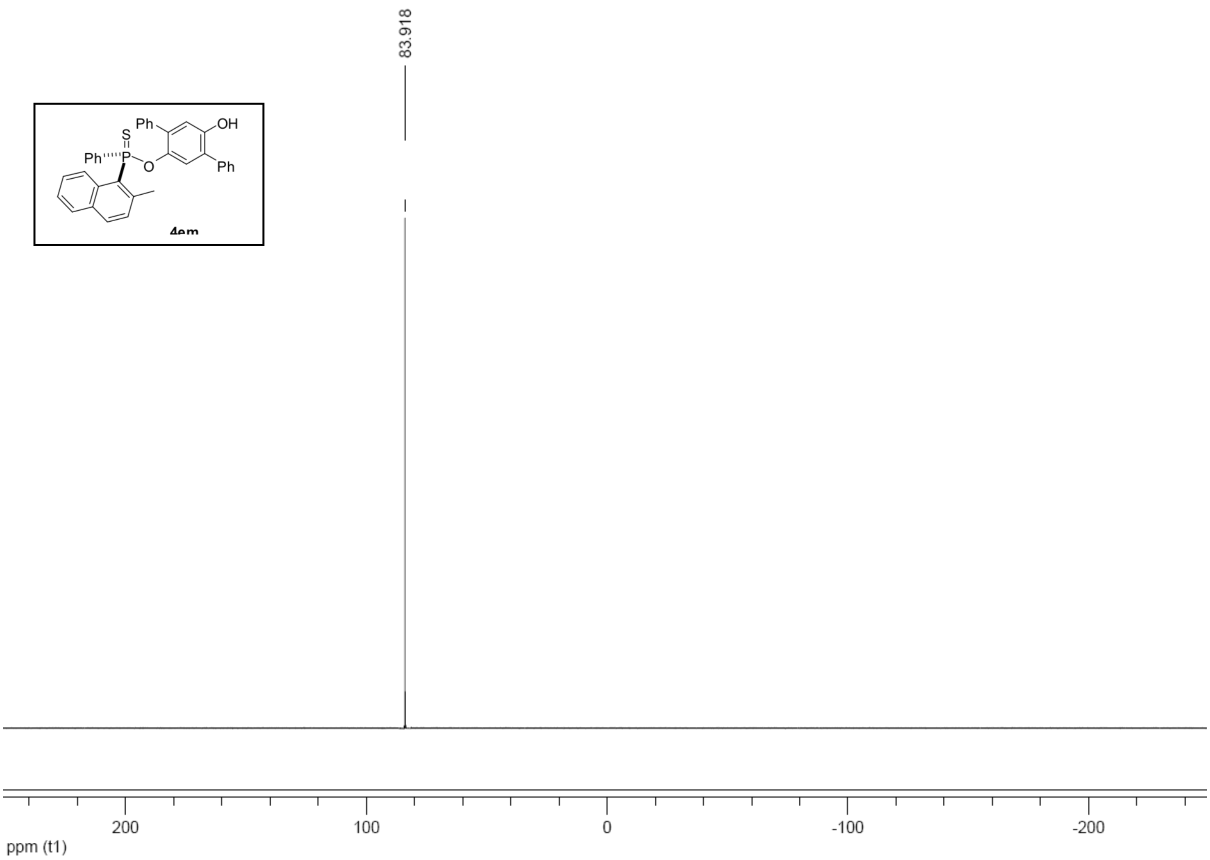
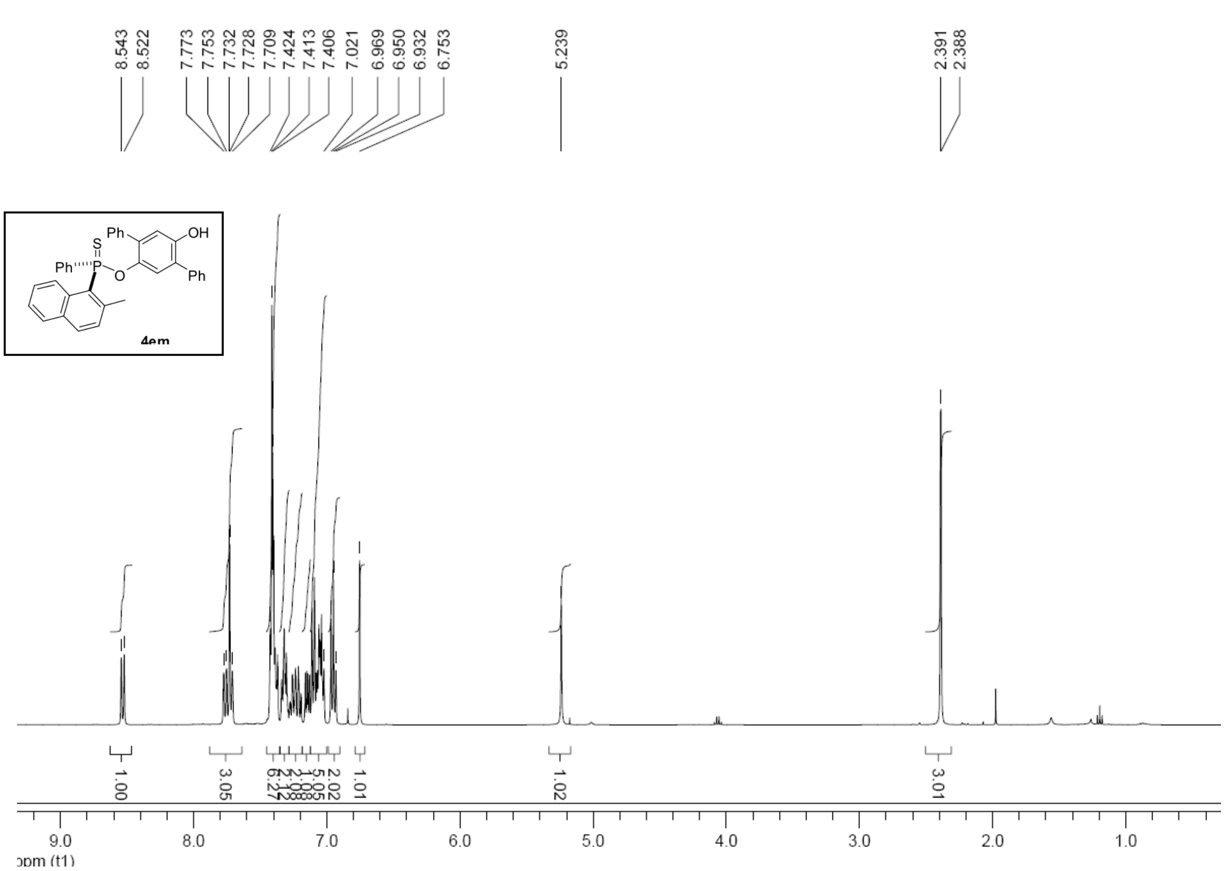
141.501
138.497
138.463
137.791
136.967
136.859
136.573
136.029
135.030
134.463
134.410
133.986
133.854
131.621
131.418
131.387
131.300
130.395
129.565
129.398
129.096
128.119
128.070
128.004
127.167
127.014
123.191
123.135
118.090
21.524
21.456
17.319
16.398
16.381
Ph
OH
S
Ph
P
O
Ph
4dm
200
150
100
50
ppm (t1)



83.918
Ph
OH
S
Ph
P
O
Ph
4em
200
100
0
-100
-200
ppm (t1)



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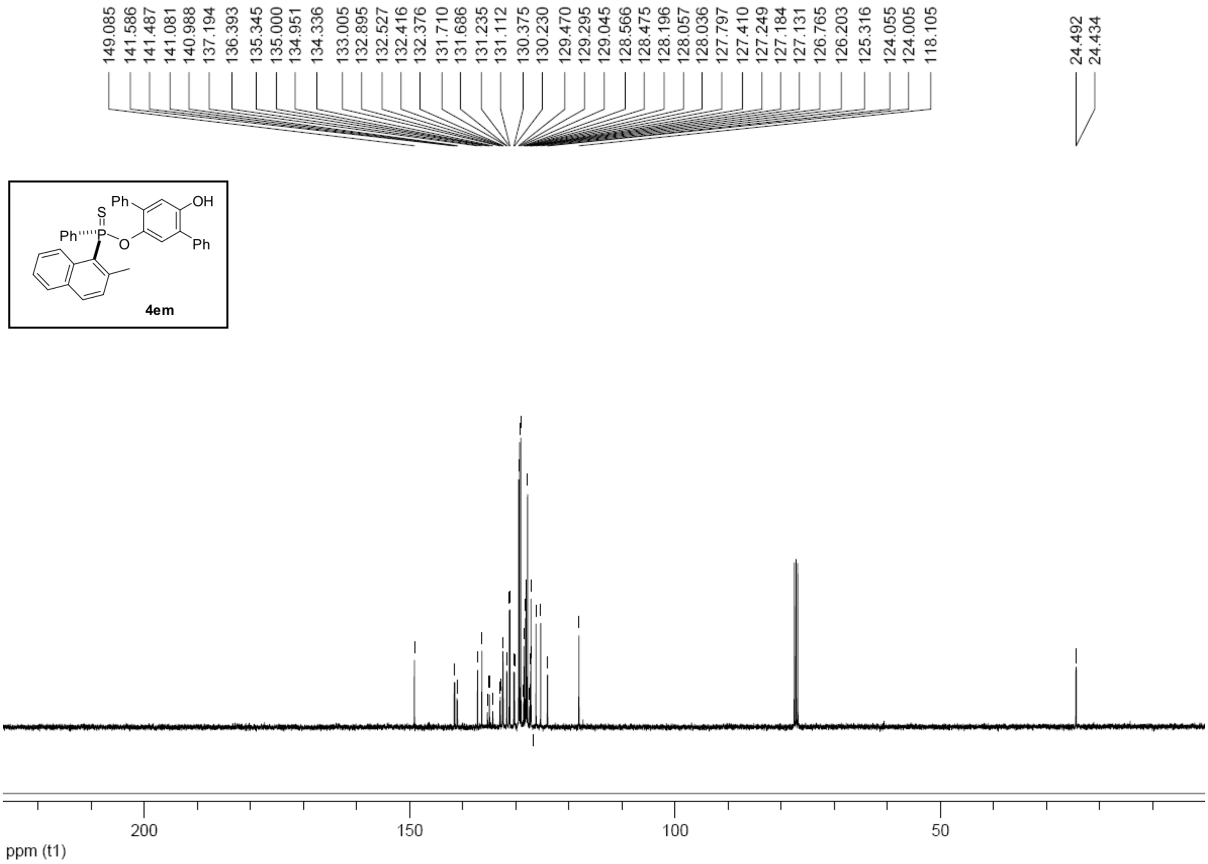
8.522
7.773
7.753
7.732
7.728
7.709
7.424
7.413
7.406
7.021
6.969
6.950
6.932
6.753
5.239
2.391
2.388
Ph
OH
S
Ph
P
O
Ph
4em
1.00
3.05
6.27
2.14
2.08
1.08
5.05
2.02
1.01
1.02
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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134.951
134.336
133.005
132.895
132.527
132.416
132.376
131.710
131.686
131.235
131.112
130.375
130.230
129.470
129.295
129.045
128.566
128.475
128.196
128.057
128.036
127.797
127.410
127.249
127.184
127.131
126.765
126.203
125.316
124.055
124.005
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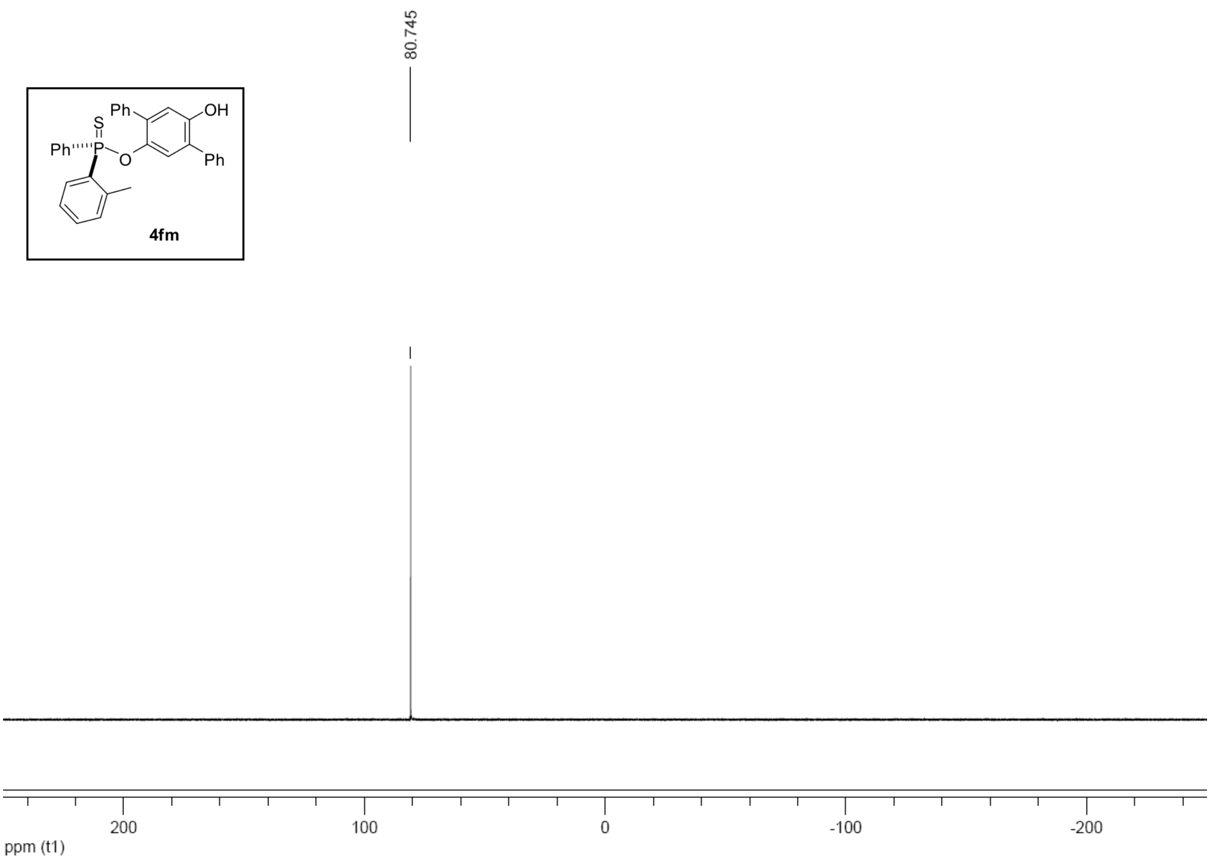
24.492
24.434
Ph
OH
S
Ph
P
O
Ph
4em
200
150
100
50
ppm (t1)


80.745
Ph
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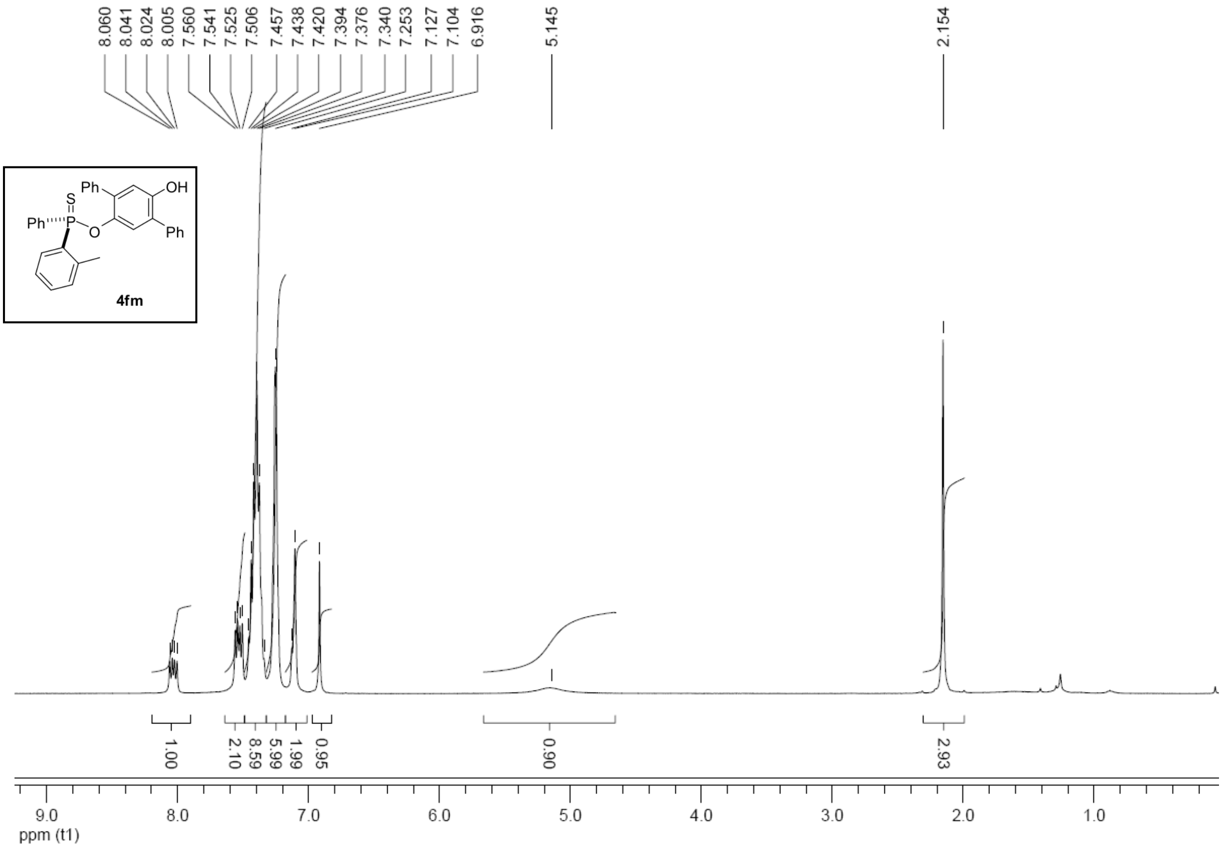
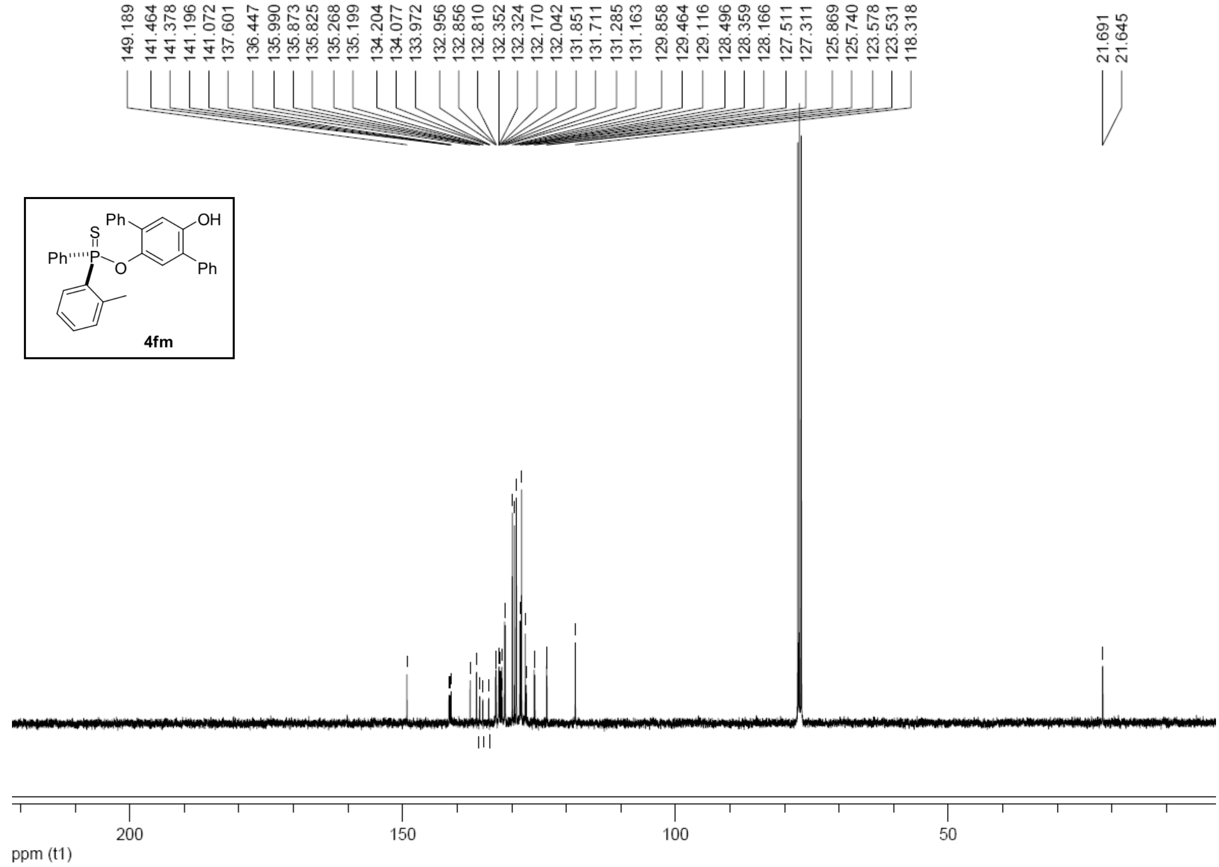
S
Ph
P
O
Ph
4fm
200
100
0
-100
-200
ppm (t1)


8.060
8.041
8.024
8.005
7.560
7.541
7.525
7.506
7.457
7.438
7.420
7.394
7.376
7.340
7.253
7.127
7.104
6.916
5.145
2.154
Ph
OH
S
Ph
O
P
Ph
4fm
1.00
2.10
8.59
5.99
1.99
0.95
0.90
2.93
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)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141.378
141.196
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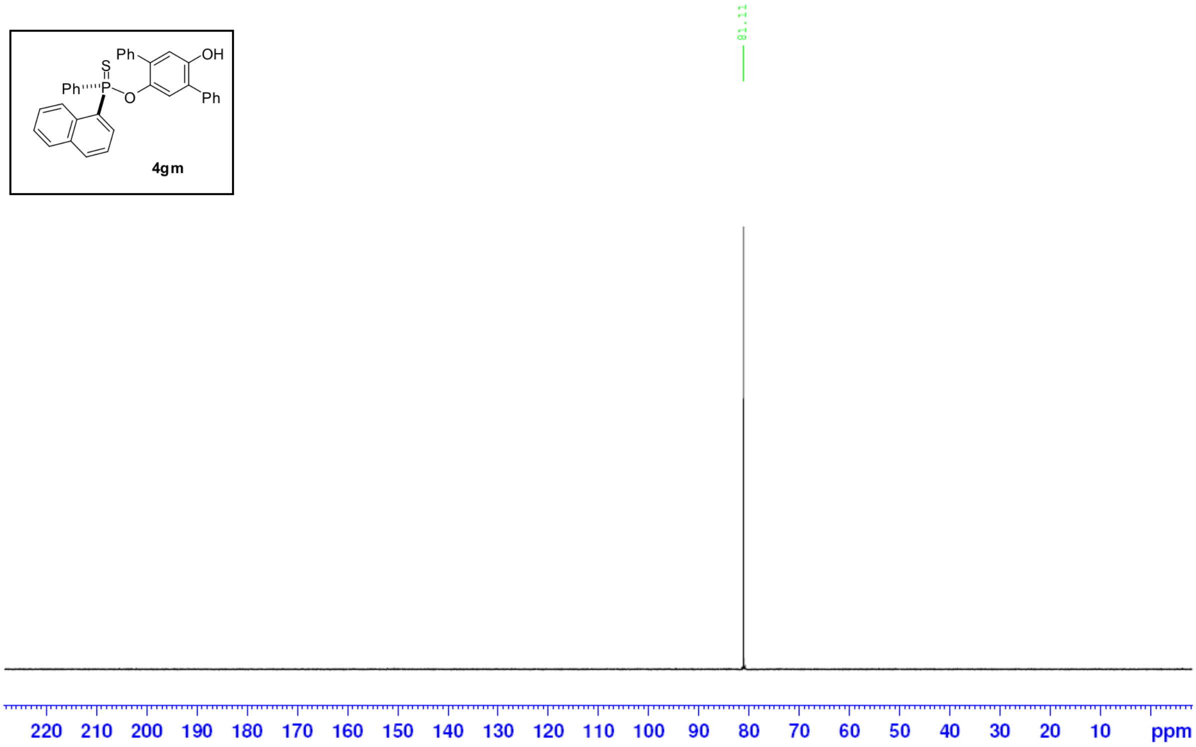
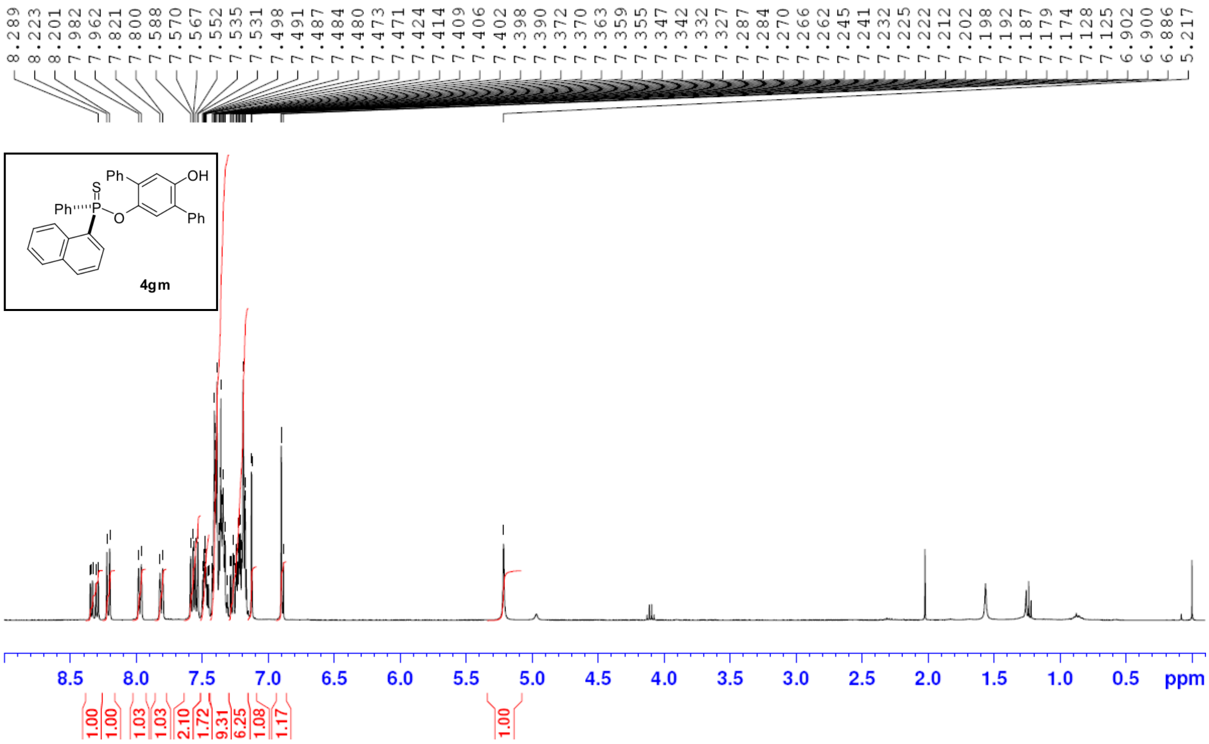
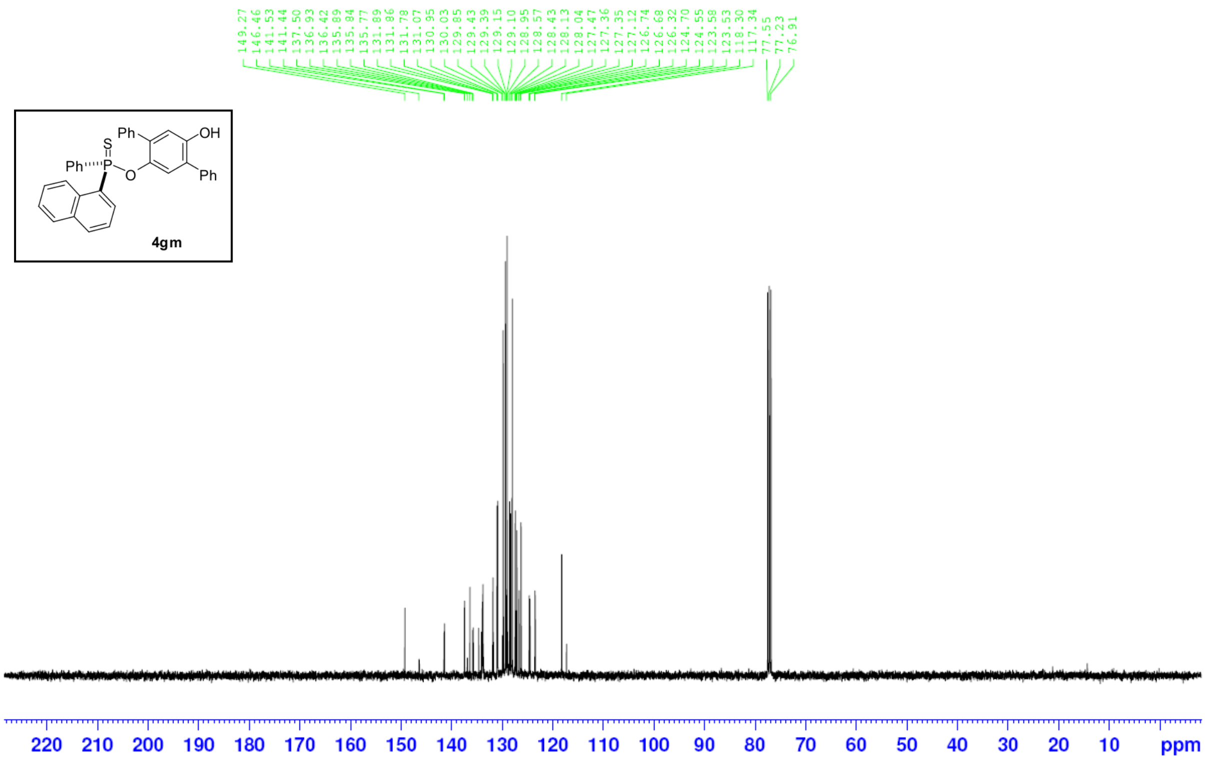
136.447
135.990
135.873
135.825
135.268
135.199
134.204
134.077
133.972
132.956
132.856
132.810
132.352
132.324
132.170
132.042
131.851
131.711
131.285
131.163
129.858
129.464
129.116
128.496
128.359
128.166
127.511
127.311
125.869
125.740
123.578
123.531
118.318
21.691
21.645
Ph
OH
S
Ph
O
P
Ph
4fm
200
150
100
50
ppm (t1)

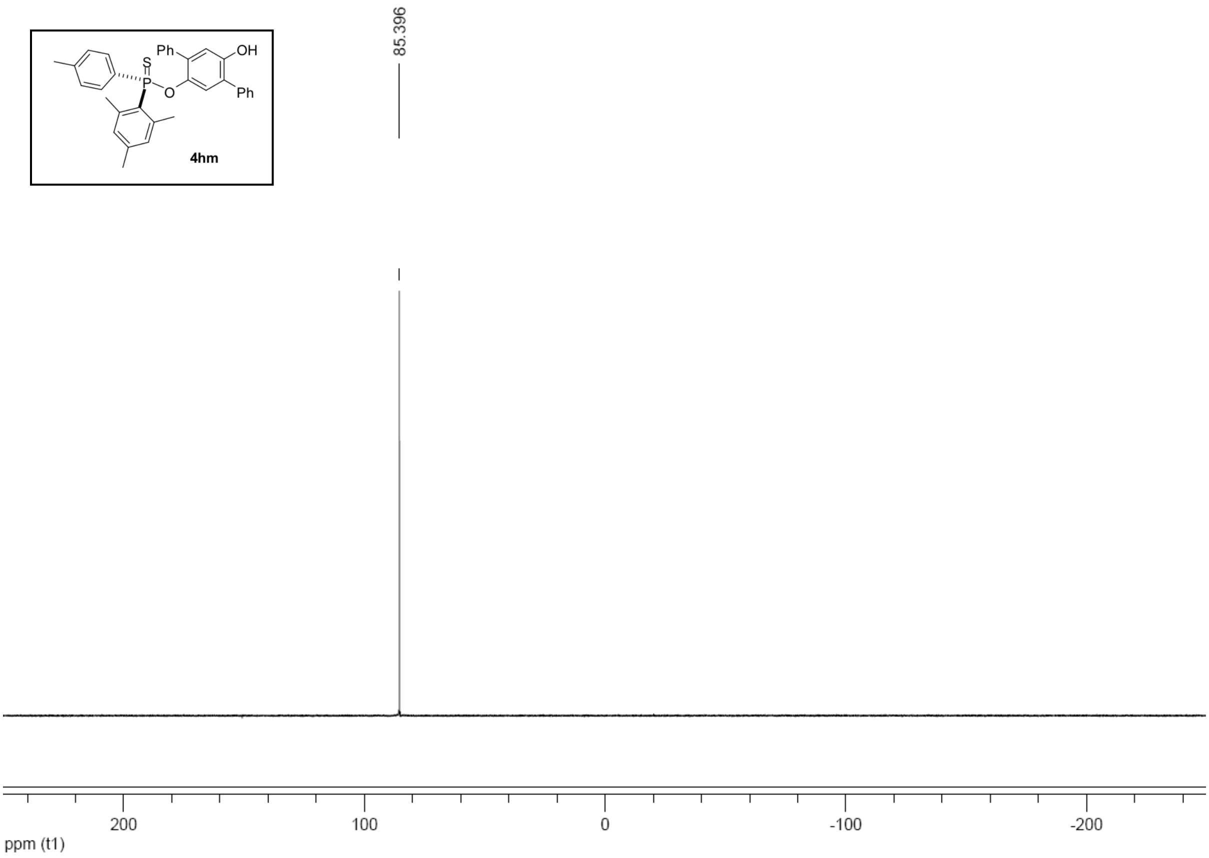


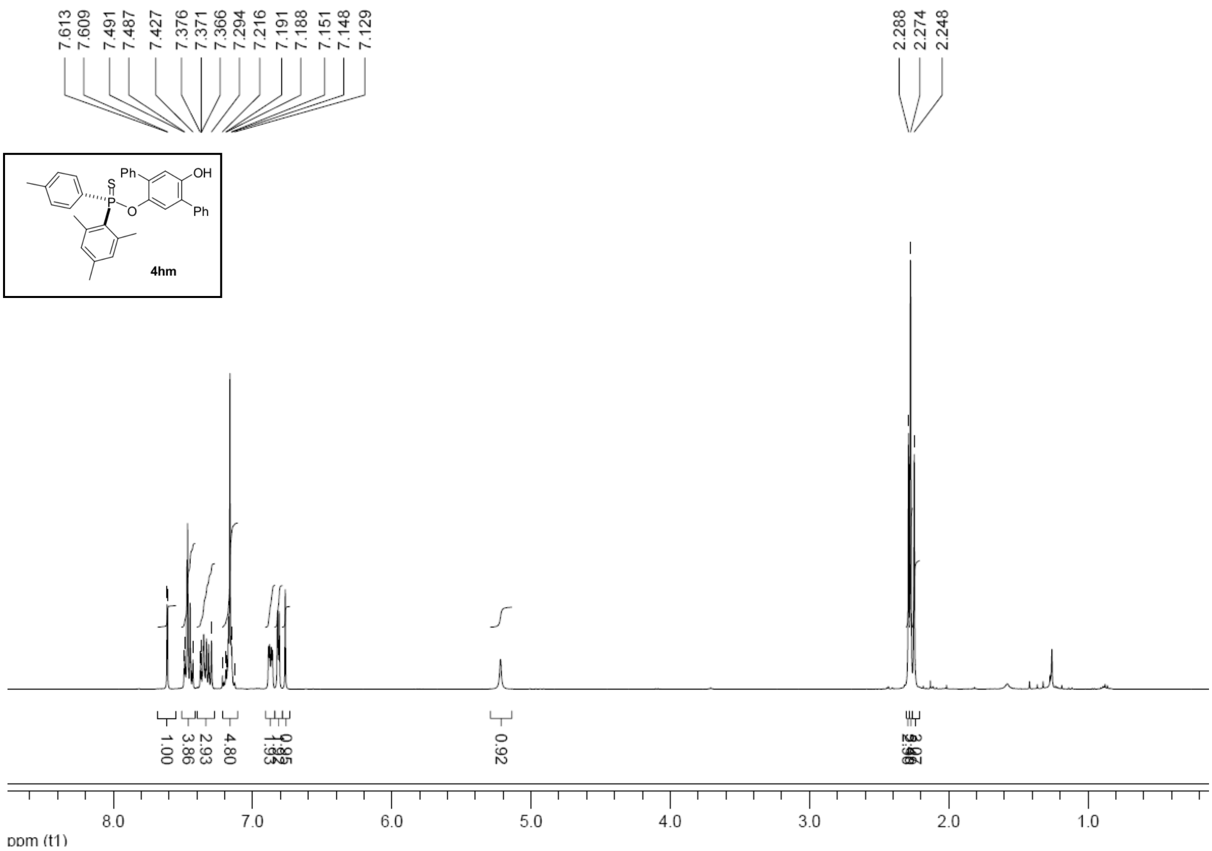
81.11
Ph
OH
S
Ph
P
O
Ph
4gm
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

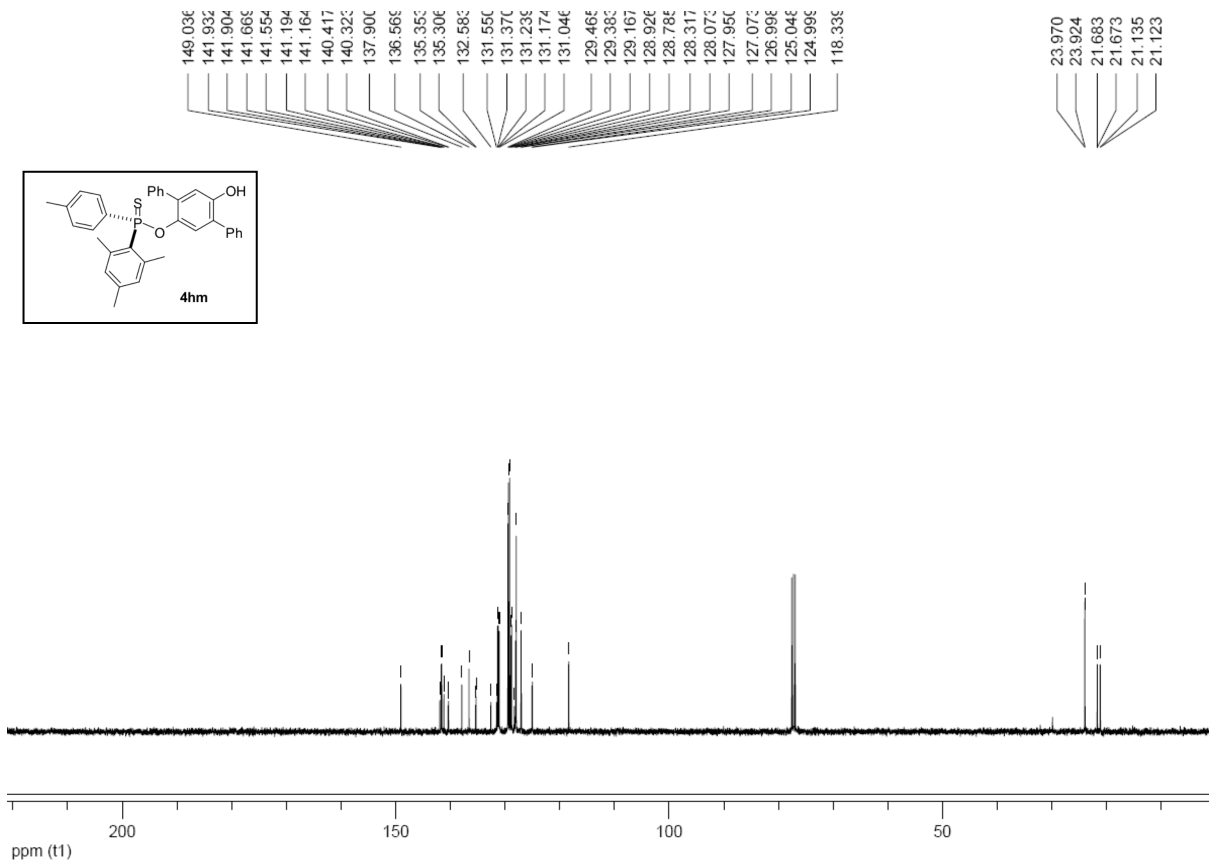


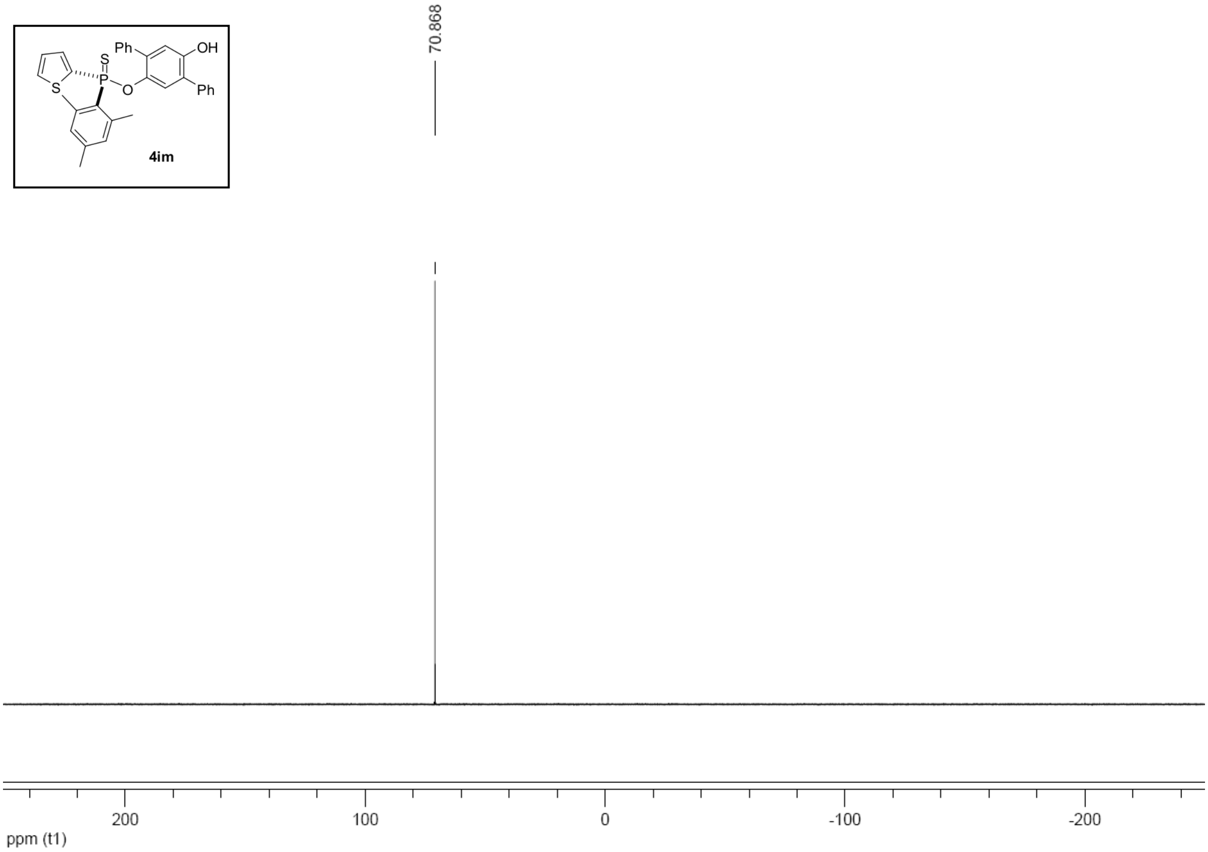
8.289
8.223
8.201
7.982
7.962
7.821
7.800
7.588
7.570
7.567
7.552
7.535
7.531
7.498
7.491
7.487
7.484
7.480
7.473
7.471
7.424
7.414
7.409
7.406
7.402
7.398
7.390
7.372
7.370
7.363
7.359
7.355
7.347
7.342
7.332
7.327
7.287
7.284
7.270
7.266
7.262
7.245
7.241
7.232
7.225
7.222
7.212
7.202
7.198
7.192
7.187
7.179
7.174
7.128
7.125
6.902
6.900
6.886
5.217
Ph
OH
S
Ph
P
O
Ph
4gm
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
1.00
1.03
1.03
2.10
1.72
9.31
6.25
1.08
1.17
1.00

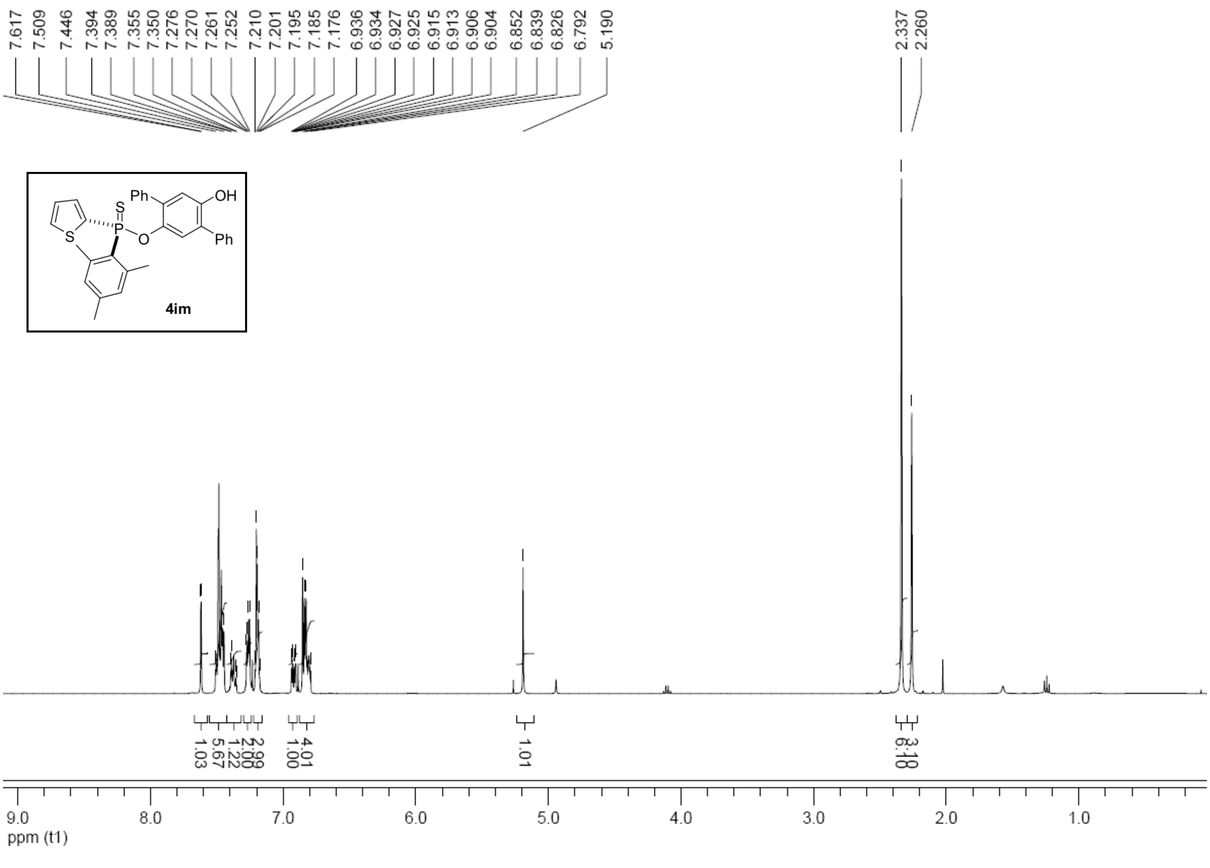

149.27
146.46
141.53
141.44
137.50
136.93
136.42
135.89
135.84
135.77
131.89
131.86
131.78
131.07
130.95
130.03
129.85
129.43
129.39
129.15
129.10
128.95
128.57
128.43
128.13
128.04
127.47
127.36
127.35
127.12
126.74
126.68
126.32
124.70
124.55
123.58
123.53
118.30
117.34
77.55
77.23
76.91
Ph
OH
S
Ph
O
Ph
4gm
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

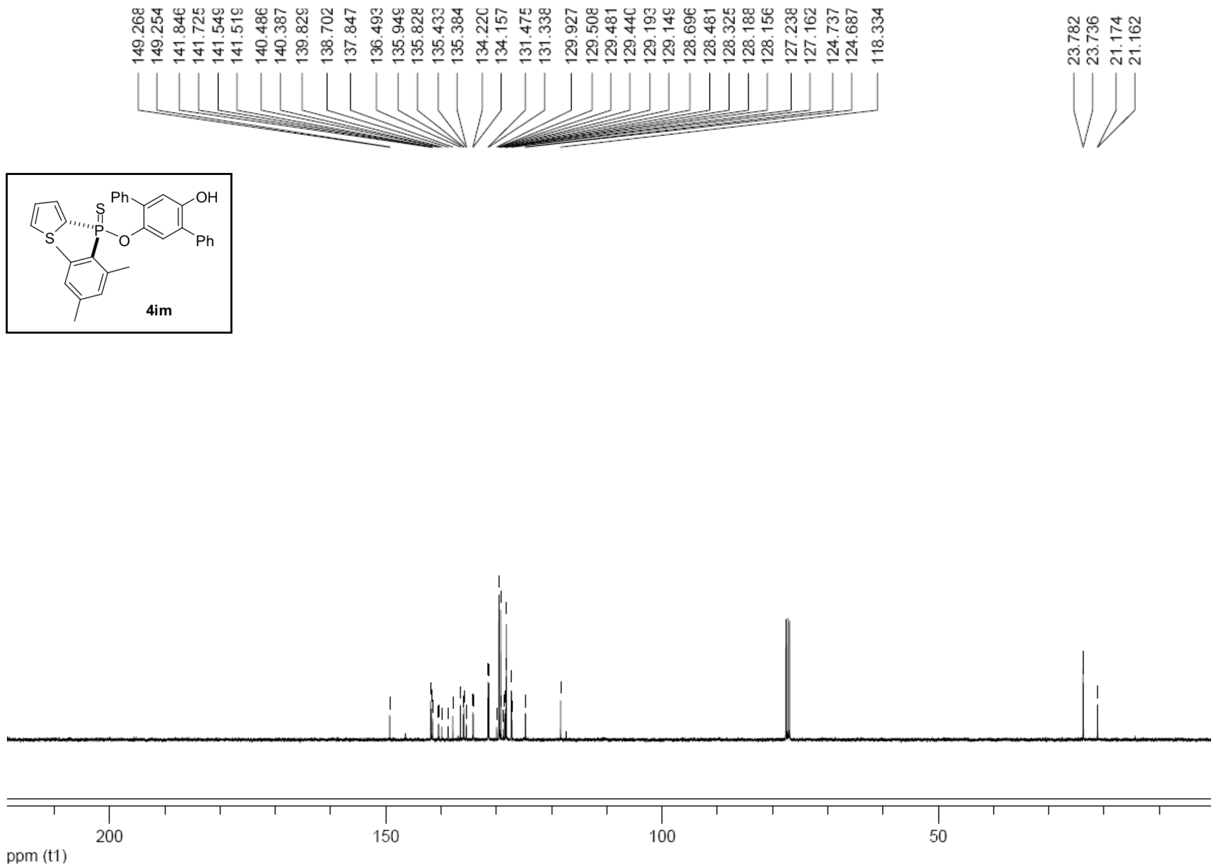

85.396
Ph
OH
S
P
O
Ph
4hm
200
100
0
-100
-200
ppm (t1)

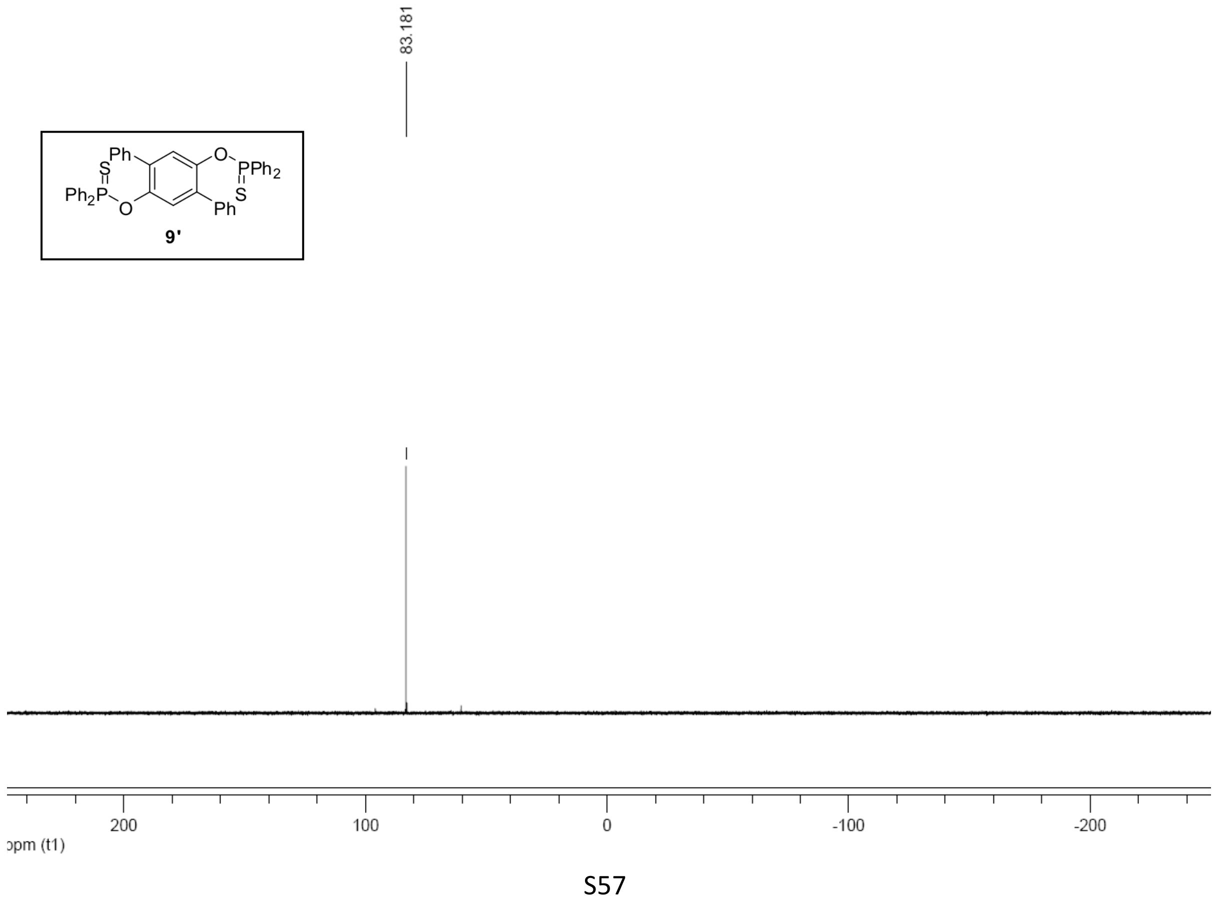

7.613
7.609
7.491
7.487
7.427
7.376
7.371
7.366
7.294
7.216
7.191
7.188
7.151
7.148
7.129
2.288
2.274
2.248
Ph
OH
S
P
O
Ph
4hm
1.00
3.86
2.93
4.80
0.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

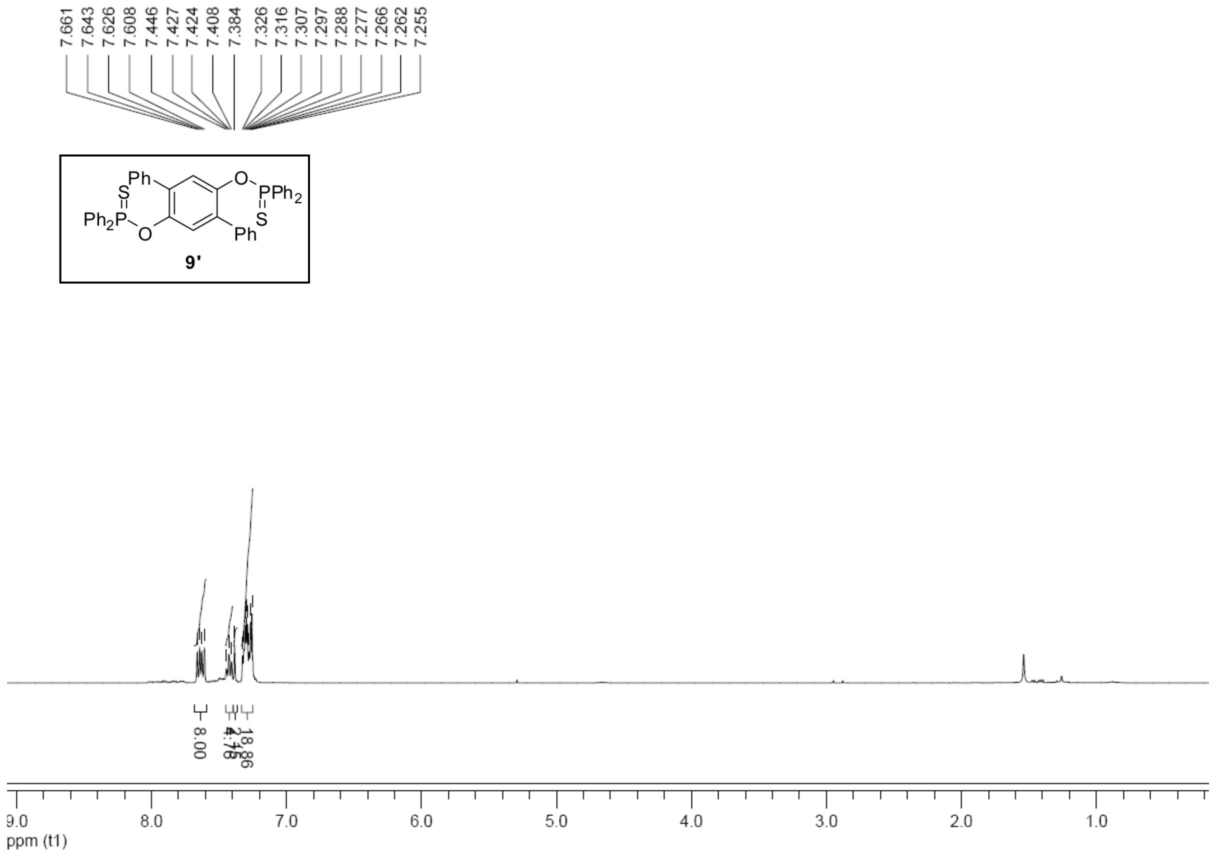

141.932
141.904
141.554
141.194
141.164
140.417
137.900
135.353
132.583
131.550
131.370
131.239
131.174
129.383
129.167
128.317
125.048
124.999
118.339
23.970
23.924
21.683
21.673
21.135
21.123
Ph
OH
S
P
O
Ph
4hm
200
150
100
50
ppm (t1)

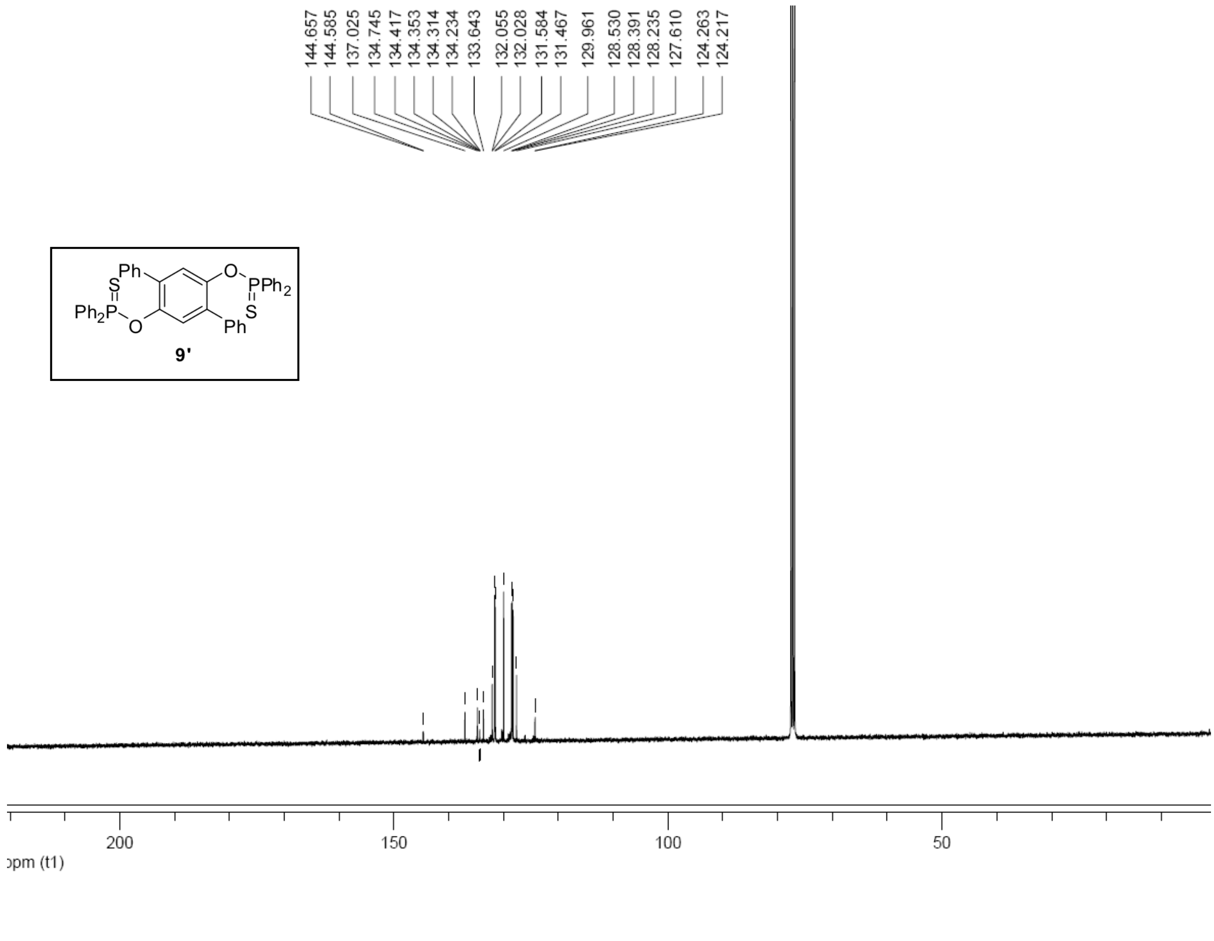

70.868
Ph
OH
S
P
O
Ph
S
4im
200
100
0
-100
-200
ppm (t1)

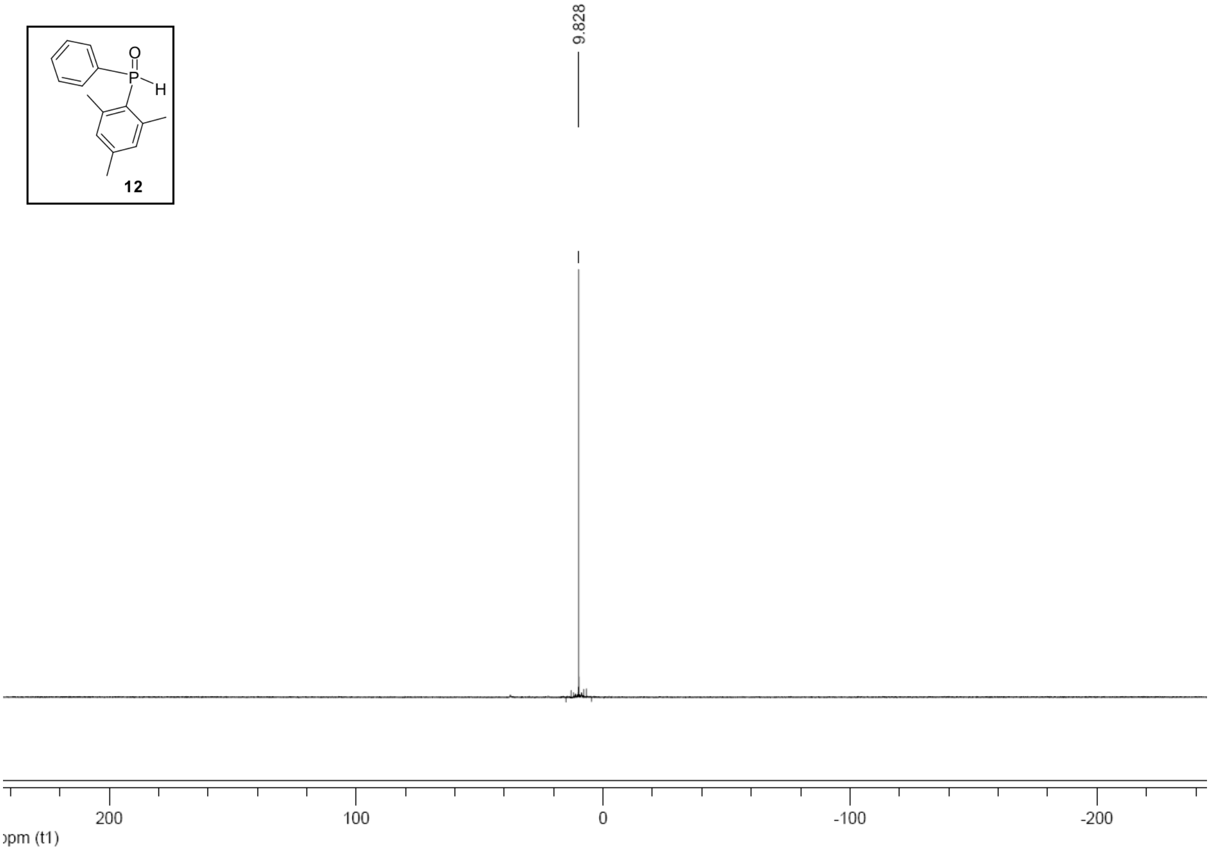

7.617
7.509
7.446
7.394
7.389
7.355
7.350
7.276
7.270
7.261
7.252
7.210
7.201
7.195
7.185
7.176
6.936
6.934
6.927
6.925
6.915
6.913
6.906
6.904
6.852
6.839
6.826
6.792
5.190
2.337
2.260
Ph
OH
S
P
O
Ph
S
4im
1.03
5.67
1.22
2.00
2.99
1.00
4.01
1.01
6.18
3.10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


4im
ppm (t1)

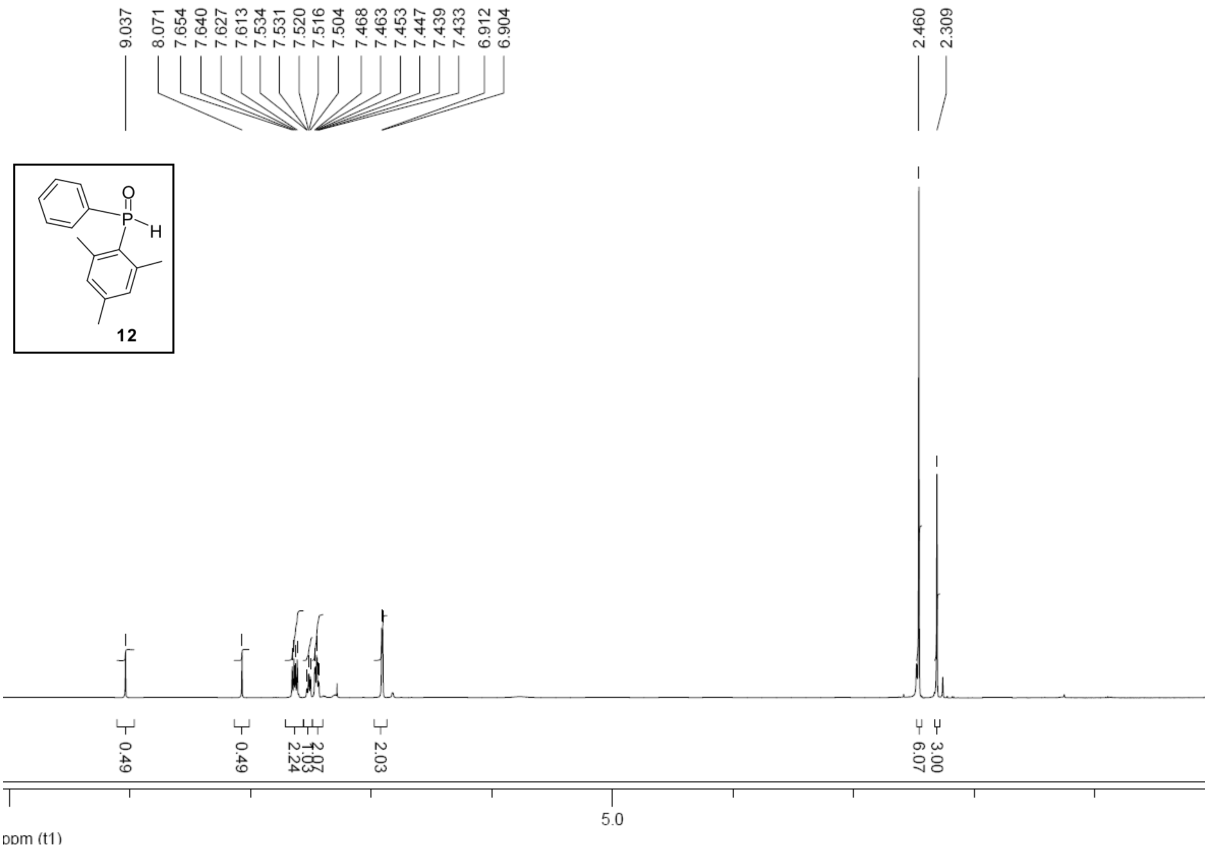

83.181
9'
ppm (t1)


7.661 7.643 7.626 7.608 7.446 7.427 7.424 7.408 7.384 7.326 7.316 7.307 7.297 7.288 7.277 7.266 7.262 7.255
9'
8.00
18.86
9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0
ppm (t1)

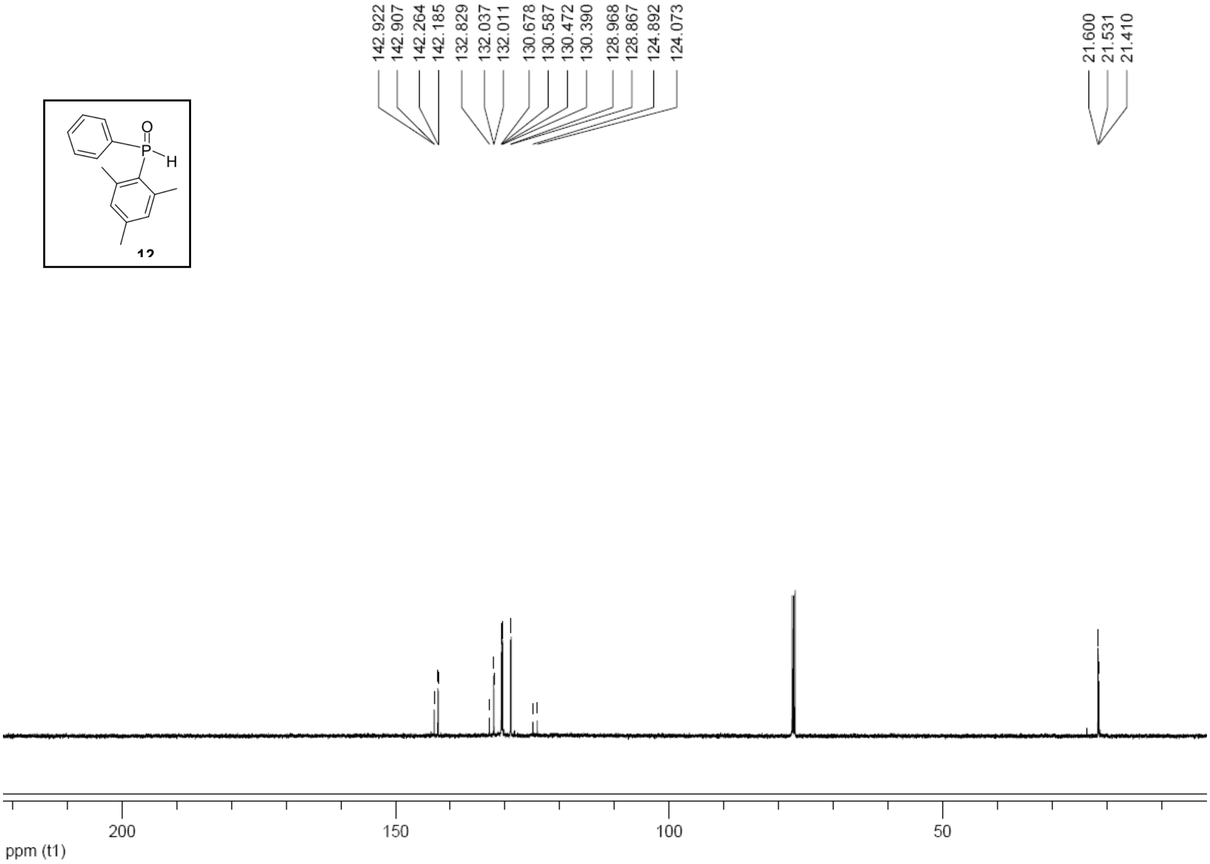

144.657 144.585 137.025 134.745 134.417 134.353 134.314 134.234 133.643 132.055 132.028 131.584 131.467 129.961 128.530 128.391 128.235 127.610 124.263 124.217
9'
200 150 100 50
ppm (t1)



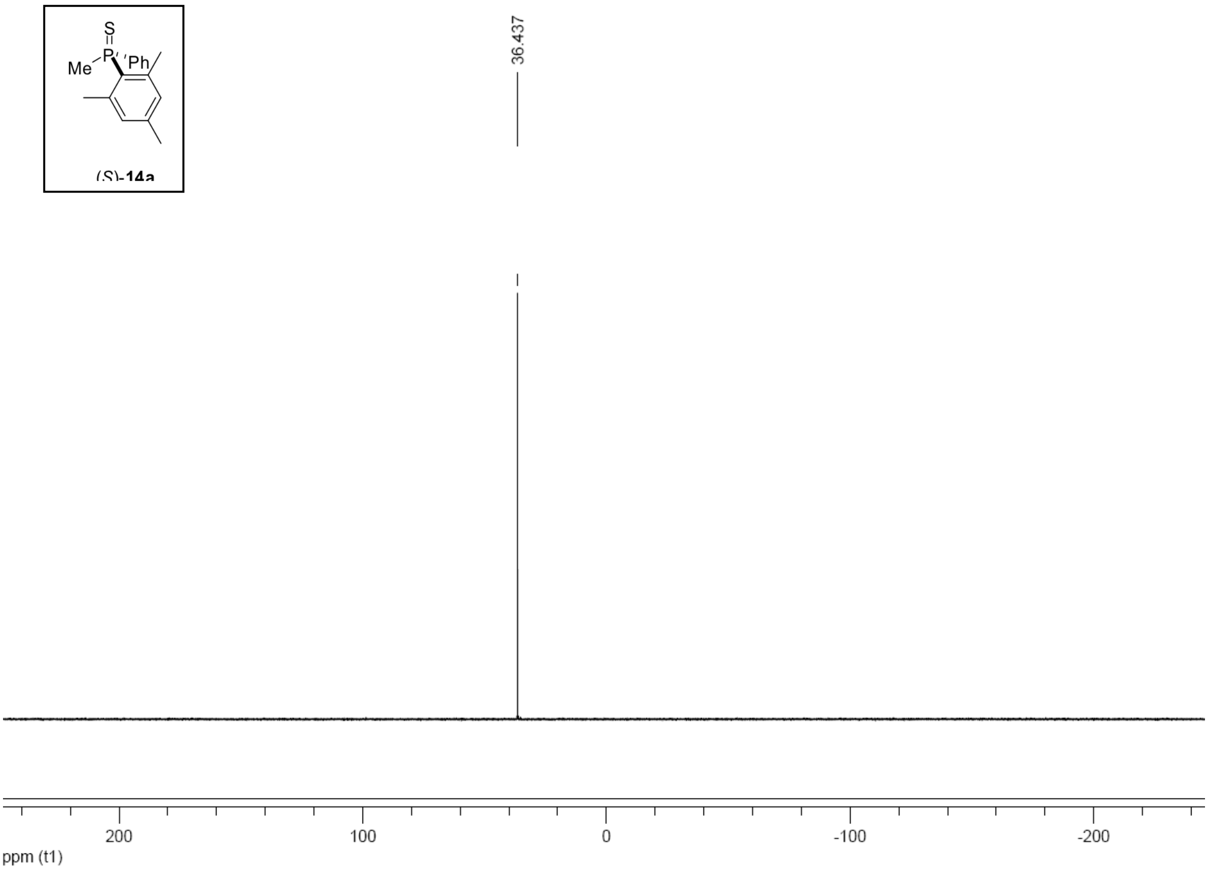
12
9.828
200
100
0
-100
-200
ppm (t1)



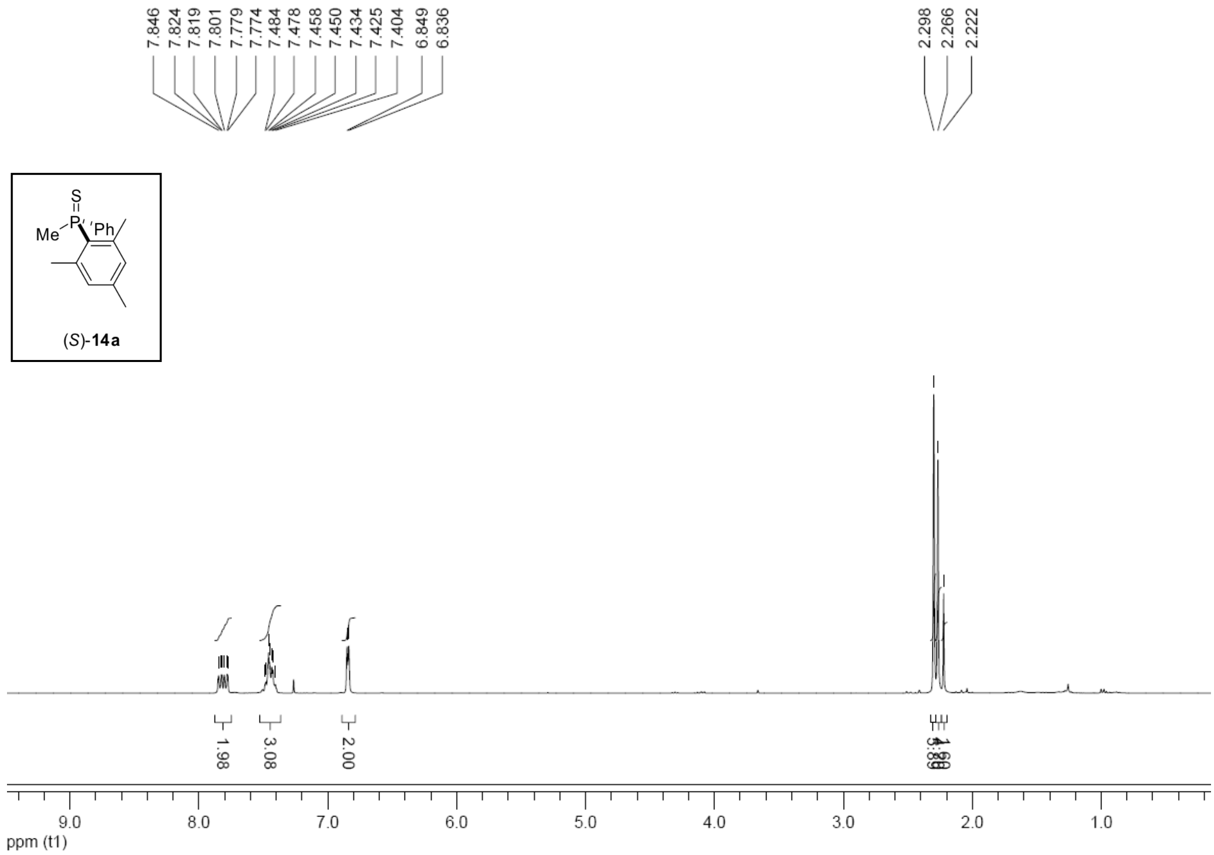
12
9.037
8.071
7.654
7.640
7.627
7.613
7.534
7.531
7.520
7.516
7.504
7.468
7.463
7.453
7.447
7.439
7.433
6.912
6.904
2.460
2.309
0.49
0.49
2.24
1.03
2.07
2.03
6.07
3.00
5.0
ppm (t1)



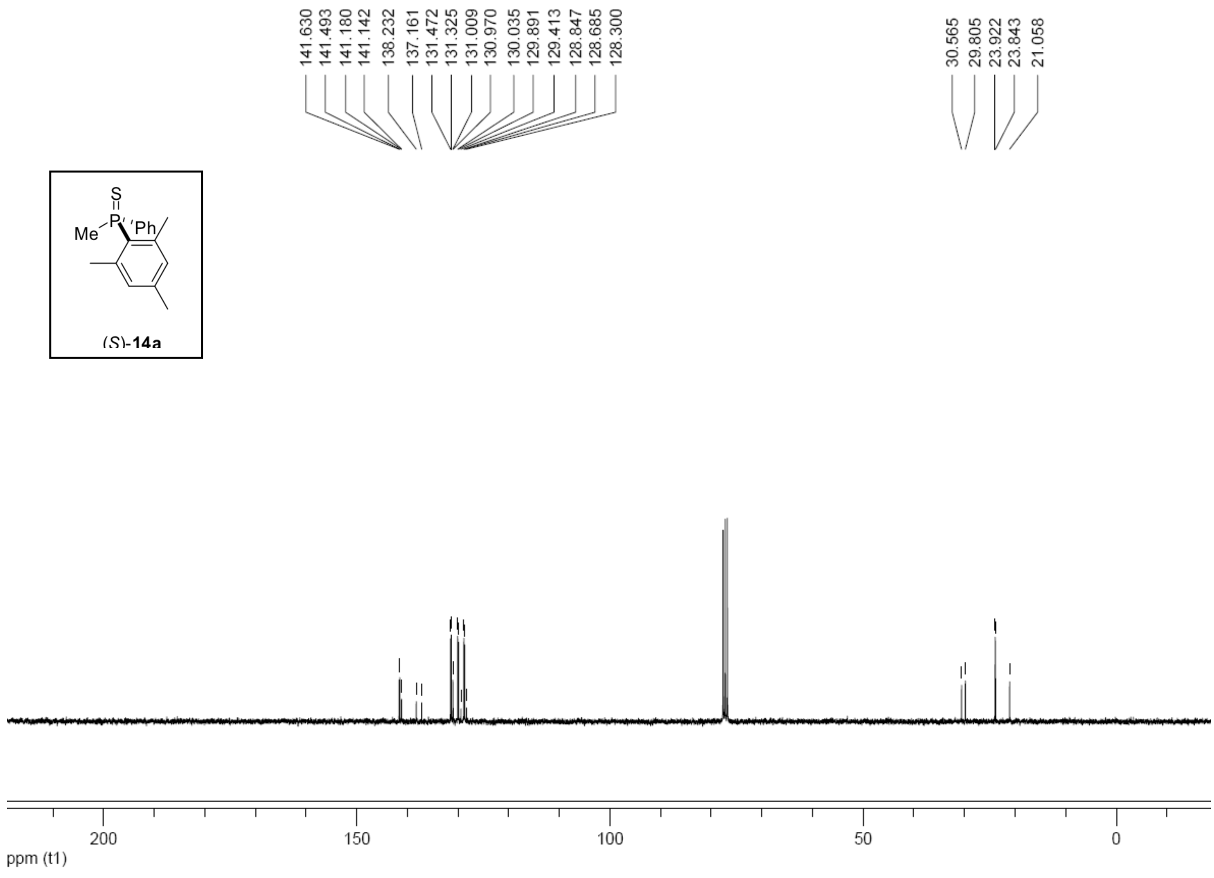
12
142.922
142.907
142.264
142.185
132.829
132.037
132.011
130.678
130.587
130.472
130.390
128.968
128.867
124.892
124.073
21.600
21.531
21.410
200
150
100
50
ppm (t1)



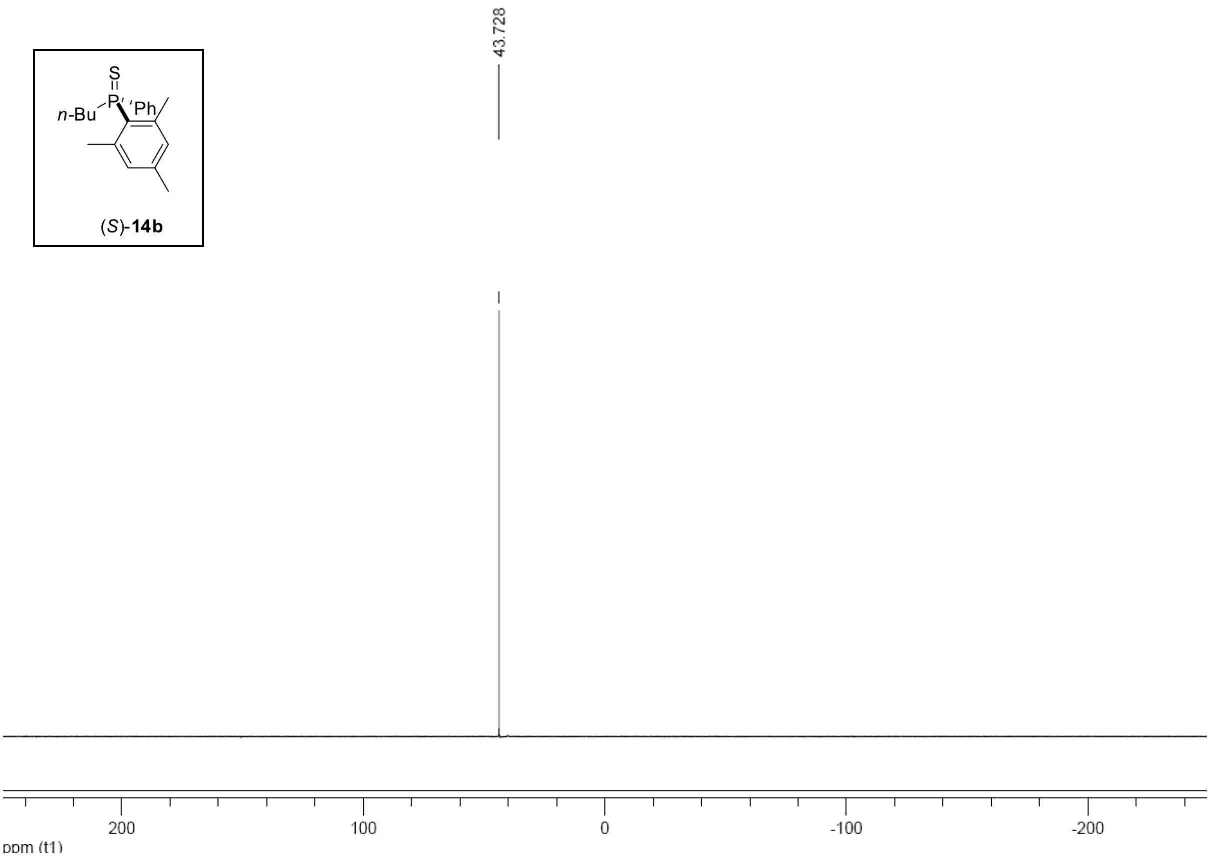
S
Me
P
Ph
(S)-14a
36.437
200
100
0
-100
-200
ppm (t1)



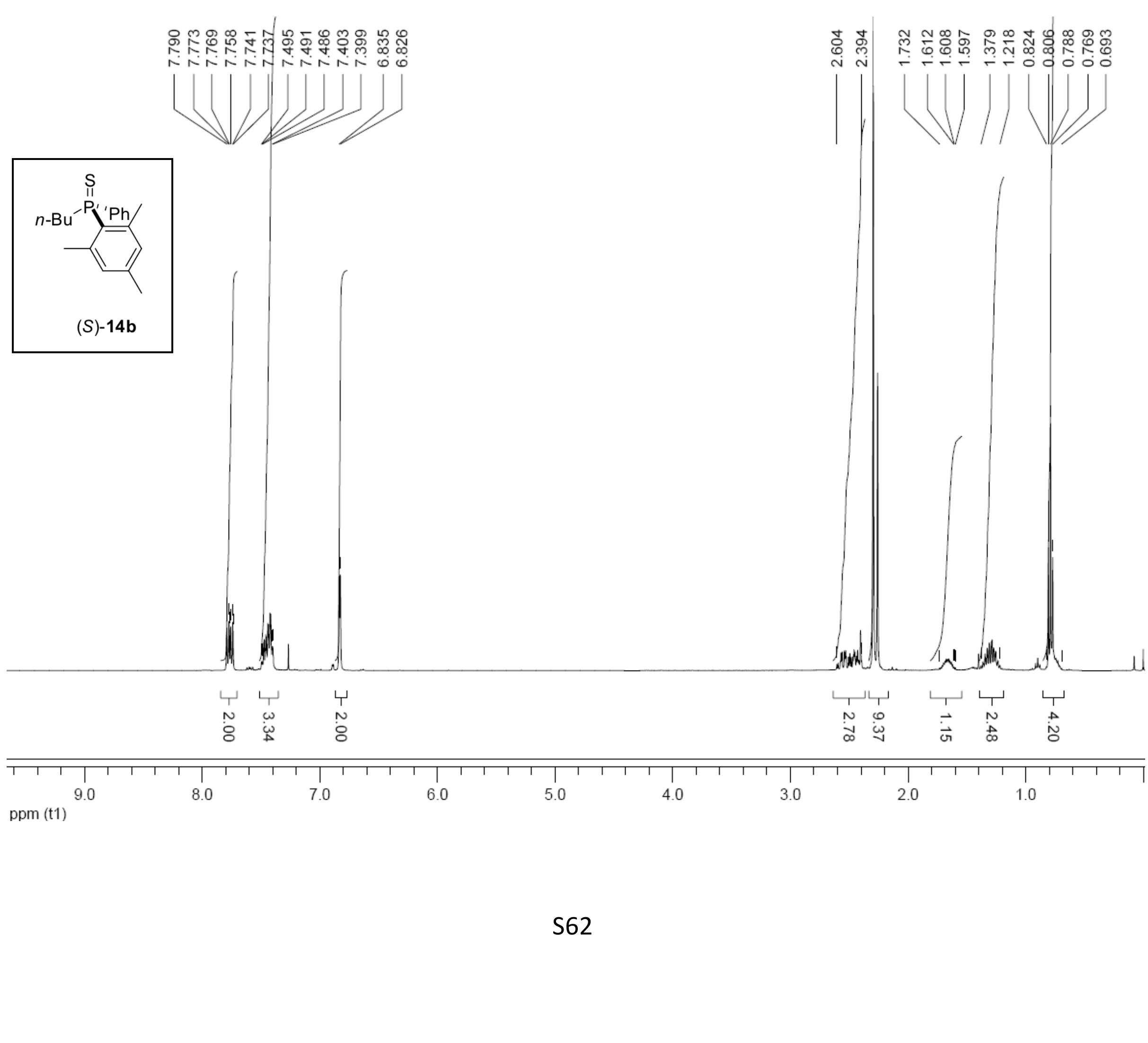
7.846
7.824
7.819
7.801
7.779
7.774
7.484
7.478
7.458
7.450
7.434
7.425
7.404
6.849
6.836
2.298
2.266
2.222
S
Me
P
Ph
(S)-14a
1.98
3.08
2.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)



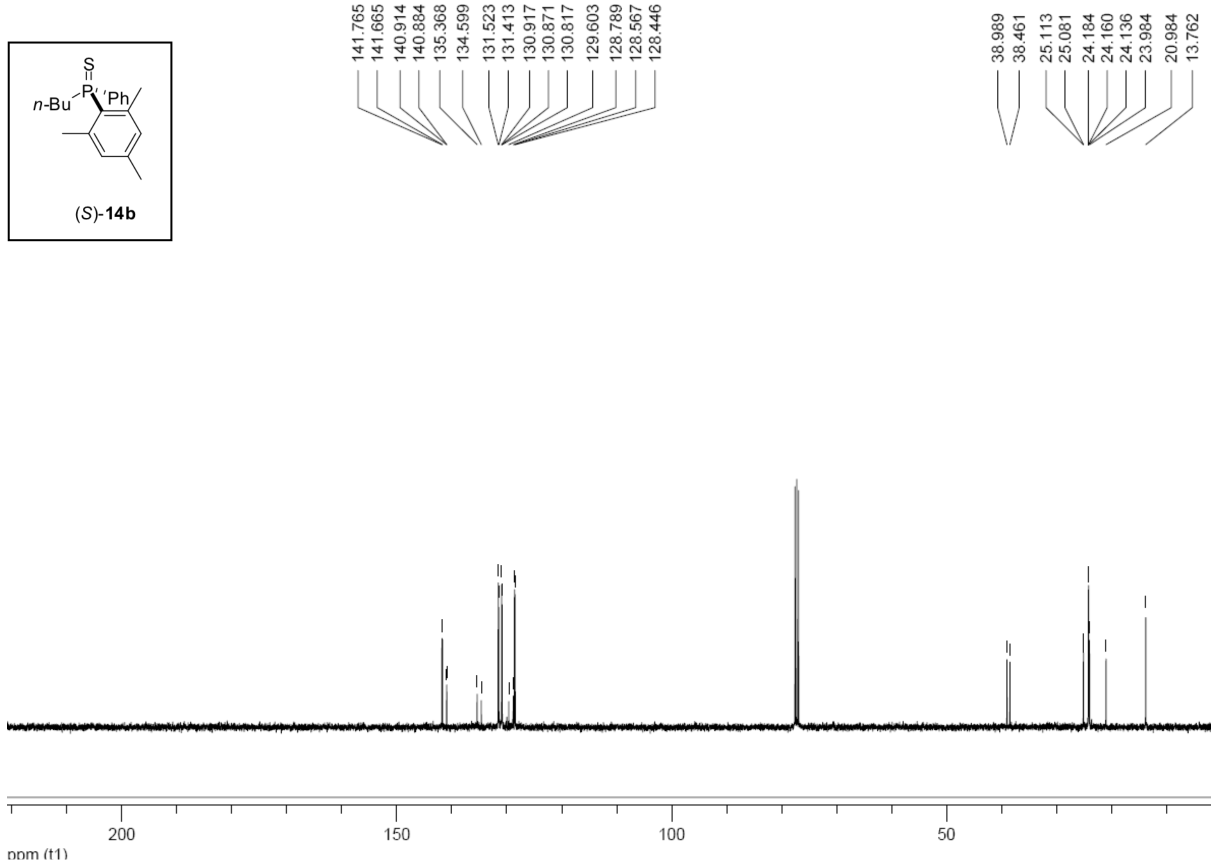
141.630
141.493
141.180
141.142
138.232
137.161
131.472
131.325
131.009
130.970
130.035
129.891
129.413
128.847
128.685
128.300
30.565
29.805
23.922
23.843
21.058
S
Me
P
Ph
(S)-14a
200
150
100
50
0
ppm (t1)

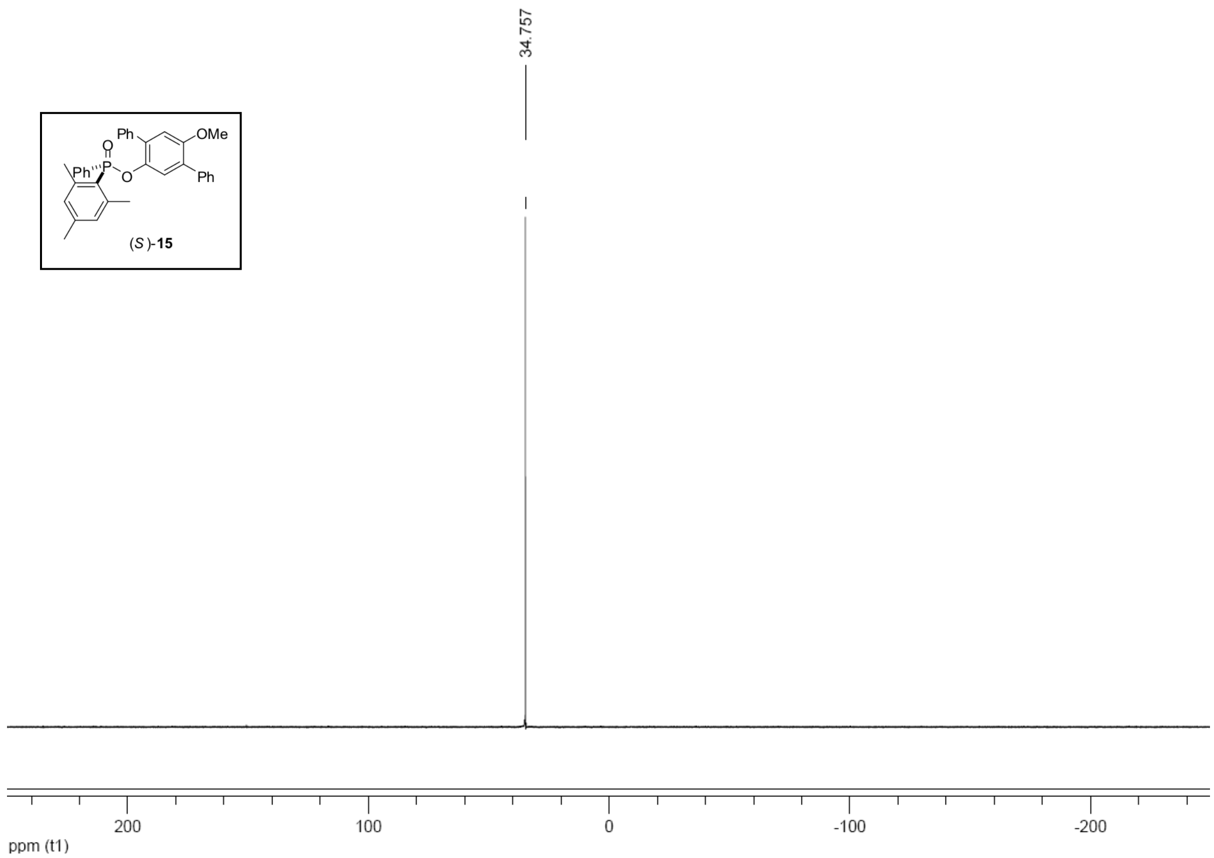


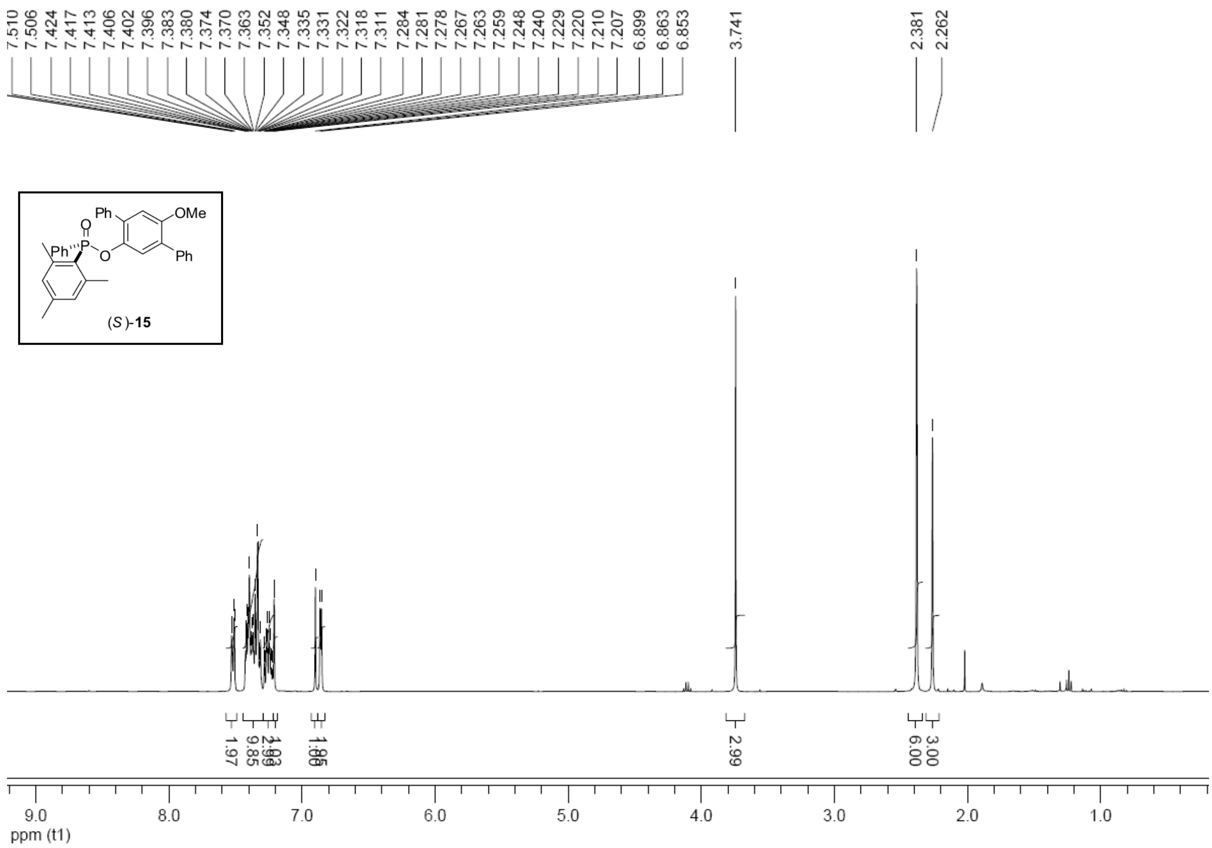
S
n-Bu
P
Ph
(S)-14b
43.728
200
100
0
-100
-200
ppm (t1)

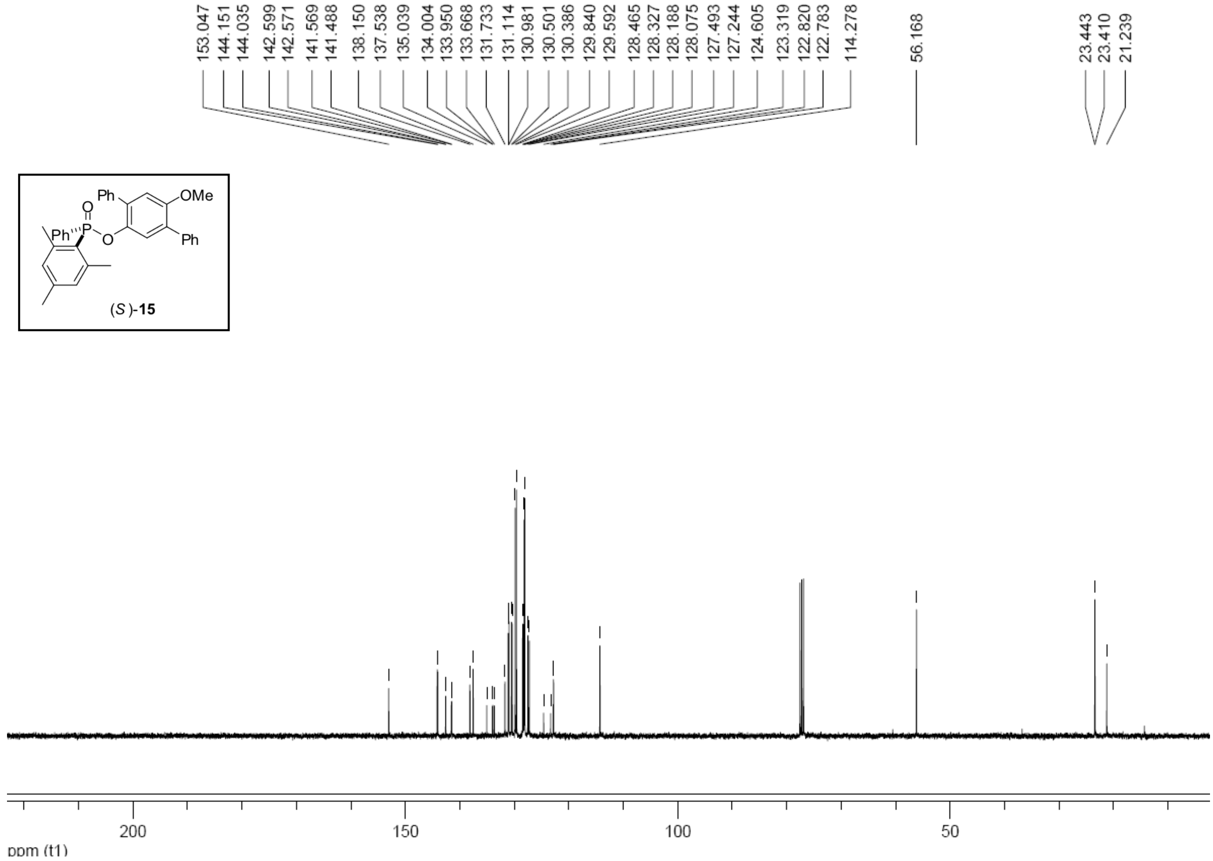


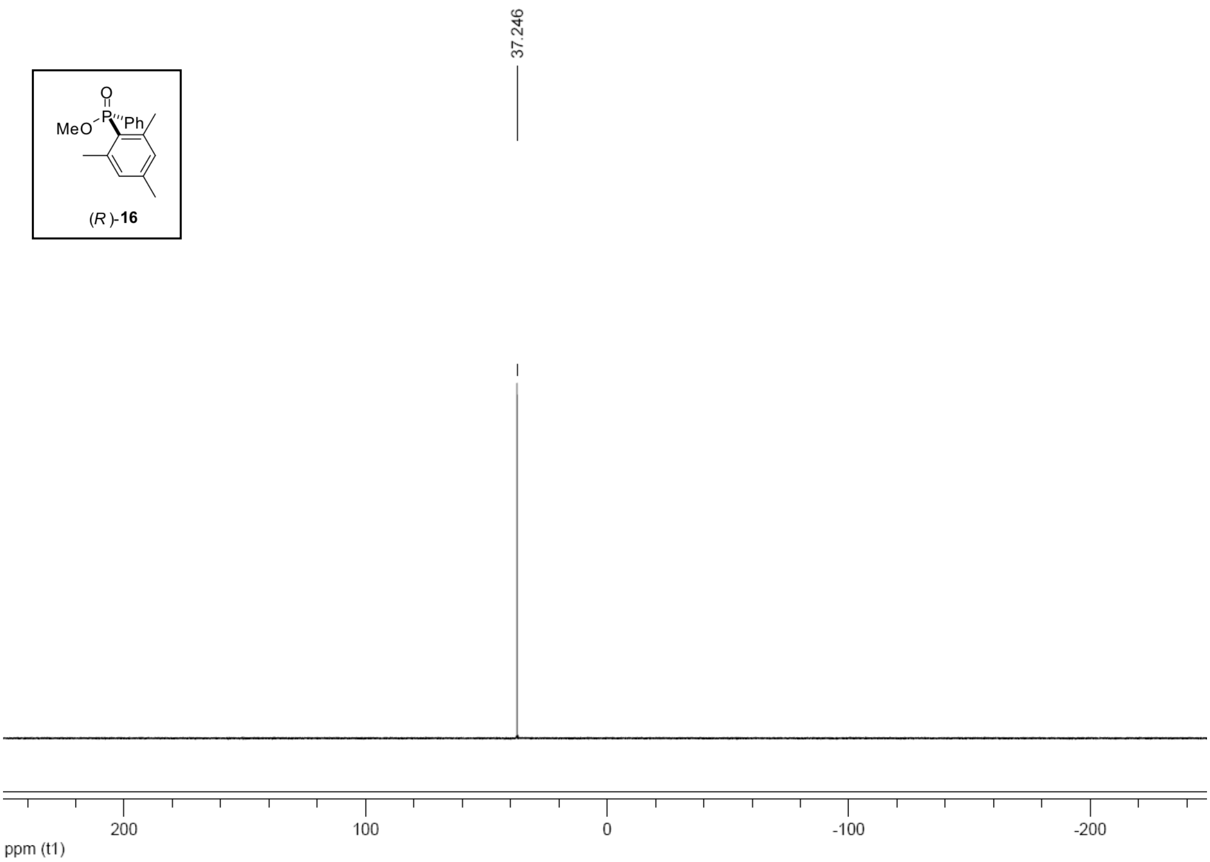
7.790
7.773
7.769
7.758
7.741
7.737
7.495
7.491
7.486
7.403
7.399
6.835
6.826
2.604
2.394
1.732
1.612
1.608
1.597
1.379
1.218
0.824
0.806
0.788
0.769
0.693
S
n-Bu
P
Ph
(S)-14b
2.00
3.34
2.00
2.78
9.37
1.15
2.48
4.20
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

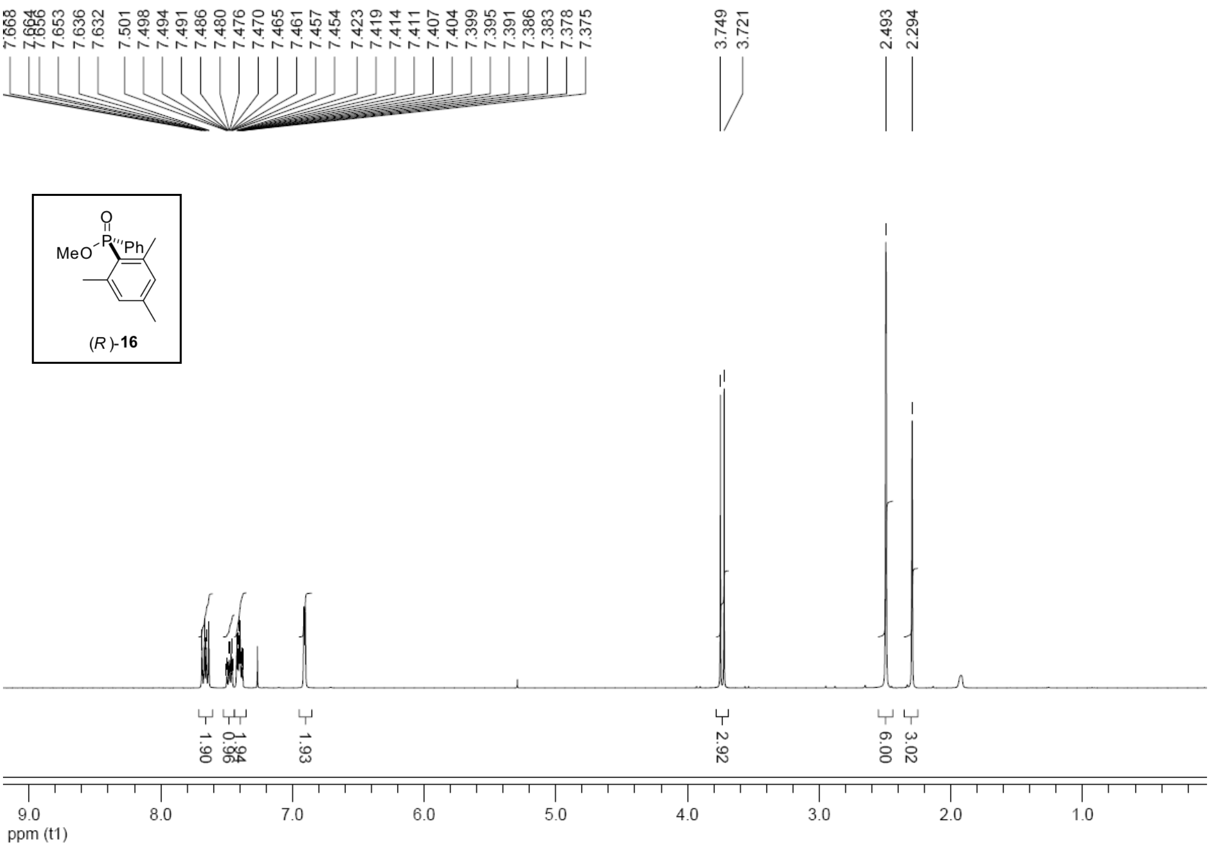

141.765
141.665
140.914
140.884
135.368
134.599
131.523
131.413
130.917
130.871
130.817
129.603
128.789
128.567
128.446
38.989
38.461
25.113
25.081
24.184
24.160
24.136
23.984
20.984
13.762
n-Bu
Ph
S
P
(S)-14b
200
150
100
50
ppm (t1)

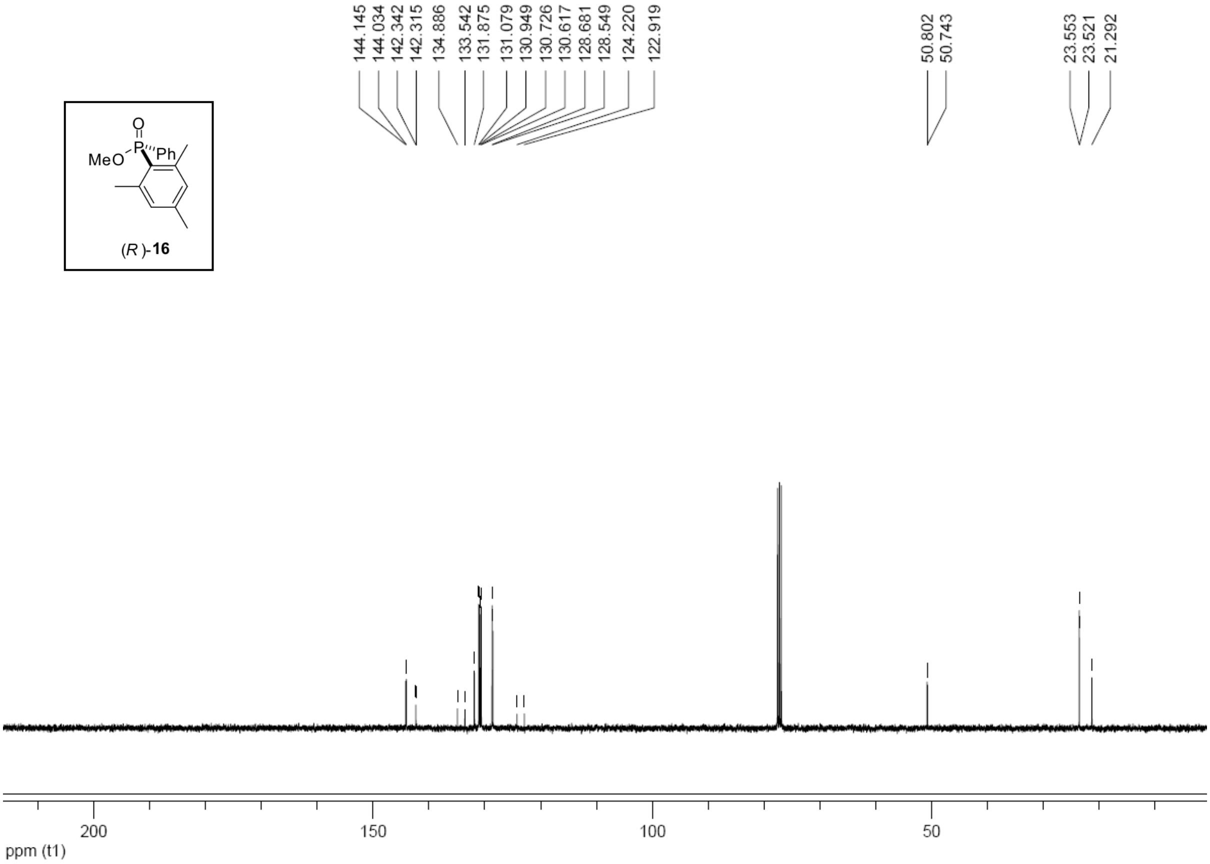

34.757
Ph
OMe
O
P
O
Ph
Ph
(S)-15
200
100
0
-100
-200
ppm (t1)

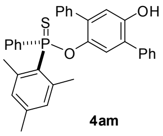

7.510
7.506
7.424
7.417
7.413
7.406
7.402
7.396
7.383
7.380
7.374
7.370
7.363
7.352
7.348
7.335
7.331
7.322
7.318
7.311
7.284
7.281
7.278
7.267
7.263
7.259
7.248
7.240
7.229
7.220
7.210
7.207
6.899
6.863
6.853
3.741
2.381
2.262
Ph
OMe
O
Ph
P
O
Ph
(S)-15
1.97
9.85
2.99
6.00
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


153.047
144.151
144.035
142.599
142.571
141.569
141.488
138.150
137.538
135.039
134.004
133.950
133.668
131.733
131.114
130.981
130.501
130.386
129.840
129.592
128.465
128.327
128.188
128.075
127.493
127.244
124.605
123.319
122.820
122.783
114.278
56.168
23.443
23.410
21.239
Ph
OMe
O
Ph
P
O
Ph
(S)-15
200
150
100
50
ppm (t1)


37.246
MeO
Ph
(R)-16
200
100
0
-100
-200
ppm (t1)

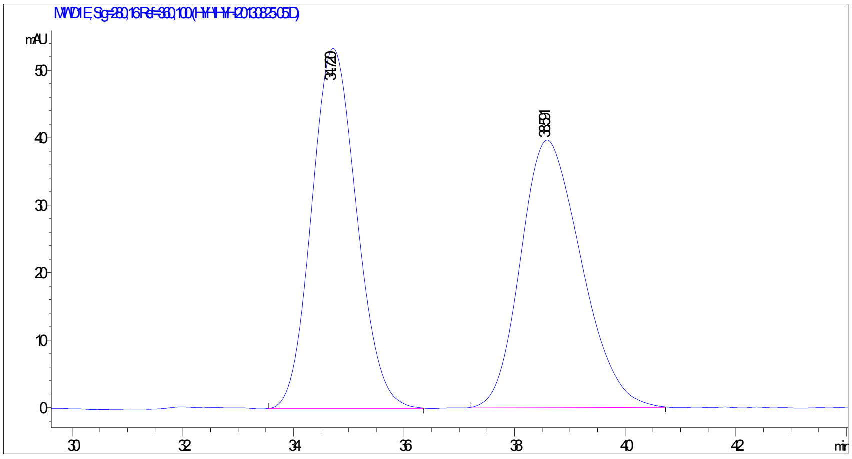

7.668 7.664 7.656 7.653 7.636 7.632 7.501 7.498 7.494 7.491 7.486 7.480 7.476 7.470 7.465 7.461 7.457 7.454 7.423 7.419 7.414 7.411 7.407 7.404 7.399 7.395 7.391 7.386 7.383 7.378 7.375
3.749 3.721
2.493 2.294
MeO
Ph
(R)-16
1.90
0.96
1.94
1.93
2.92
6.00
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


144.145
144.034
142.342
142.315
134.886
133.542
131.875
131.079
130.949
130.726
130.617
128.681
128.549
124.220
122.919
50.802
50.743
23.553
23.521
21.292
MeO
Ph
(R)-16
200
150
100
50
ppm (t1)



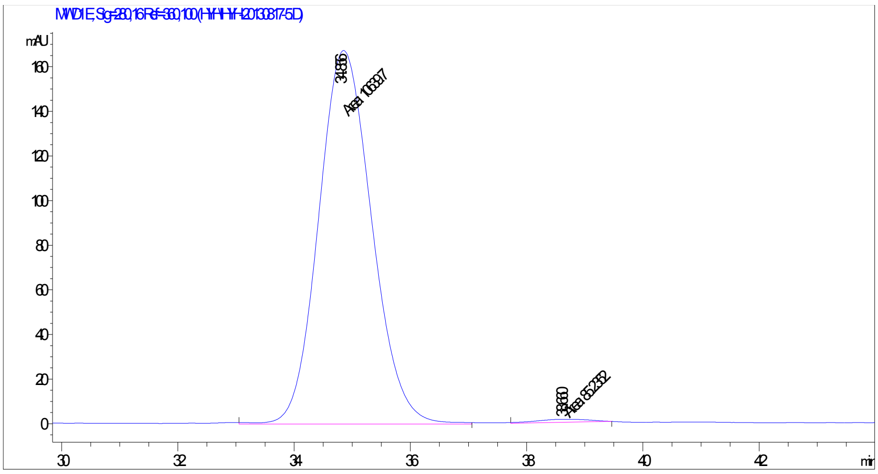
4am

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

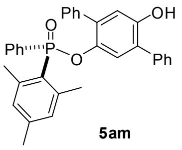


#	Time	Area	Height	Area%
1	34.720	3022.2	53.4	50.015
2	38.591	3020.4	39.7	49.985

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

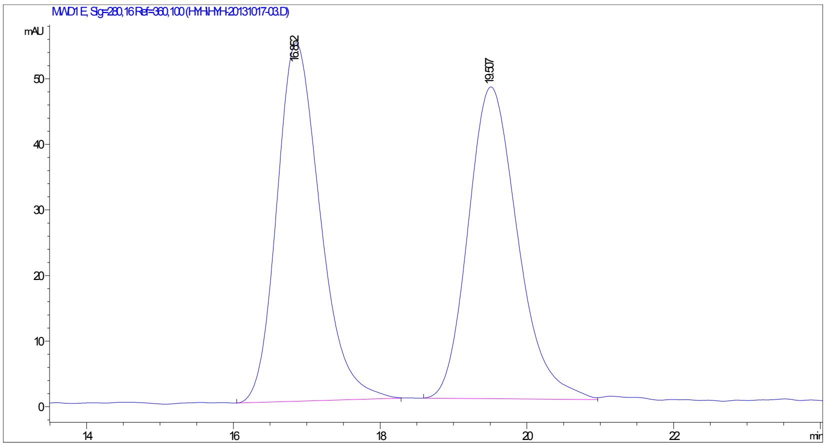


#	Time	Area	Height	Area%
1	34.856	10639.7	167.4	99.205
2	38.660	85.2	1.3	0.795



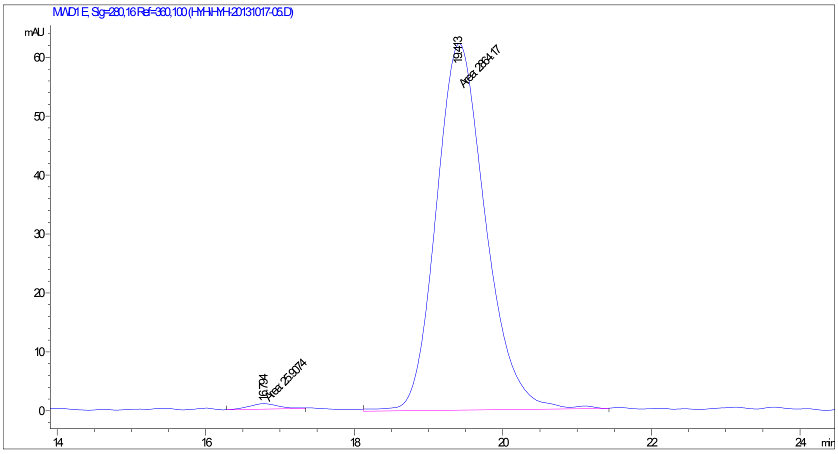
5am

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC

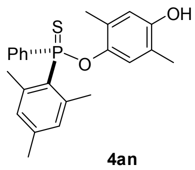


#	Time	Area	Height	Area%
1	16.852	2237.4	54.7	50.089
2	19.507	2229.4	47.5	49.911

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC

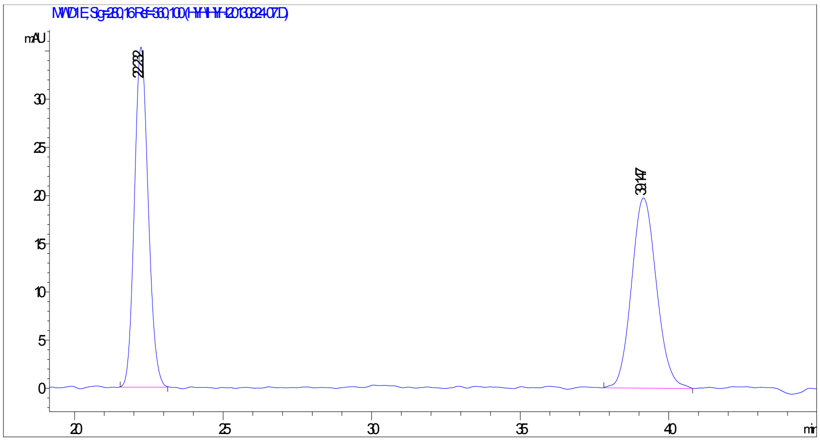


#	Time	Area	Height	Area%
1	16.794	25.9	9.2E-1	0.896
2	19.413	2864.2	62.2	99.104



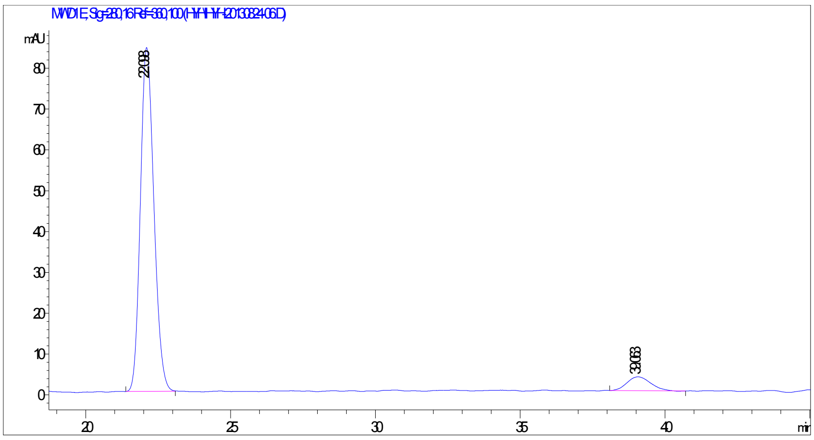
4an

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

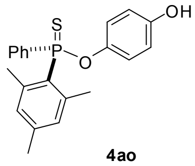


#	Time	Area	Height	Area%
1	22.232	1139.5	35.3	49.666
2	39.147	1154.8	19.7	50.334

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

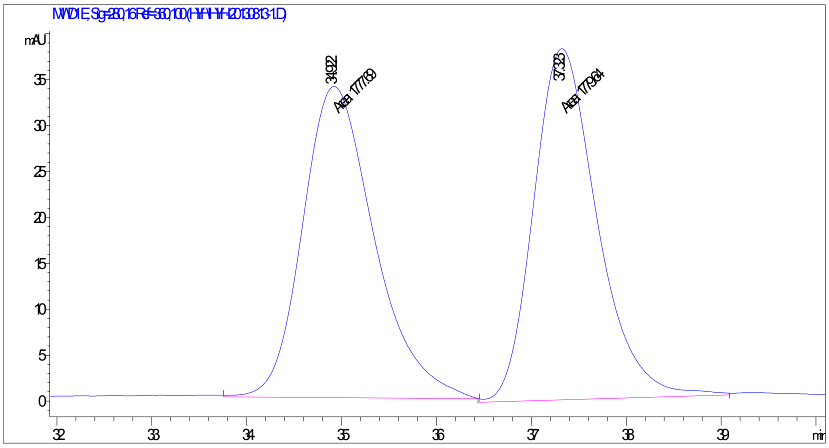


#	Time	Area	Height	Area%
1	22.098	2727.2	84.2	93.521
2	39.063	188.9	3.4	6.479



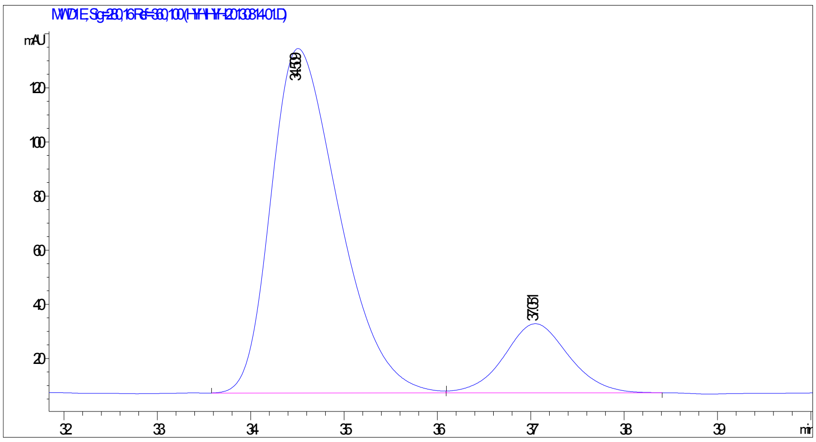
4ao

flow = 0.8 ml/m; IPA = 4%, Hexane = 96%; 280 nm; AD-H

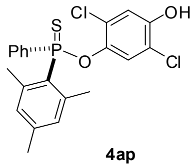


#	Time	Area	Height	Area%
1	34.922	1777.7	33.9	49.973
2	37.323	1779.6	38.2	50.027

flow = 0.8 ml/m; IPA = 4%, Hexane = 96%; 280 nm; AD-H

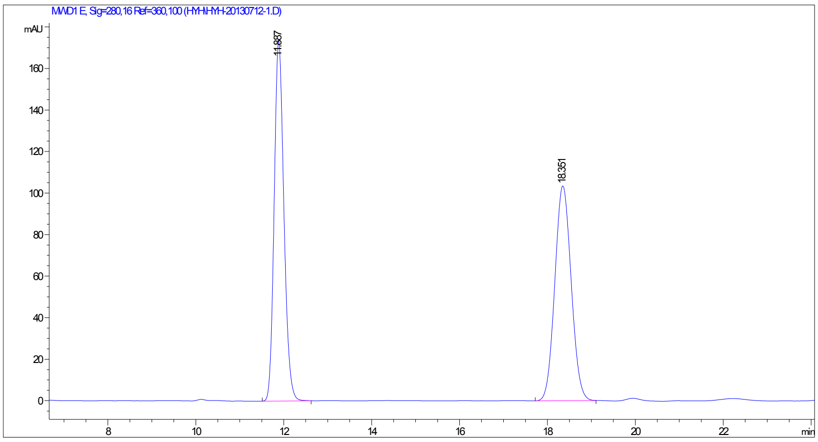


#	Time	Area	Height	Area%
1	34.509	6431.1	127.2	83.873
2	37.051	1236.6	25.6	16.127



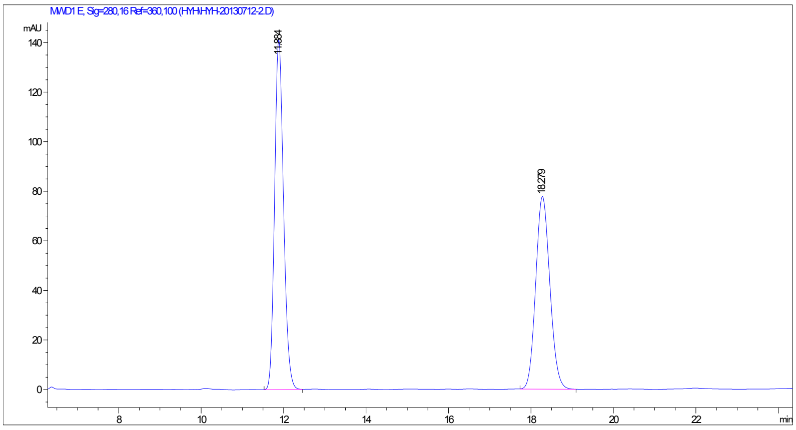
4ap

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

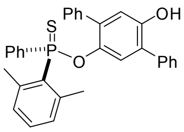


#	Time	Area	Height	Area%
1	11.887	2665.5	173.5	49.903
2	18.351	2675.9	103.4	50.097

HYH-20130712-2 flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

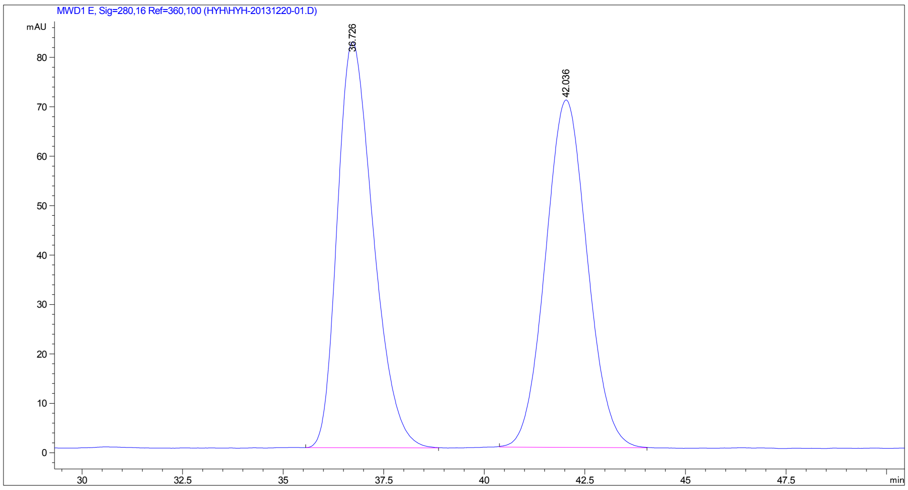


#	Time	Area	Height	Area%
1	11.884	2131.5	141.2	53.434
2	18.279	1857.5	77.7	46.566



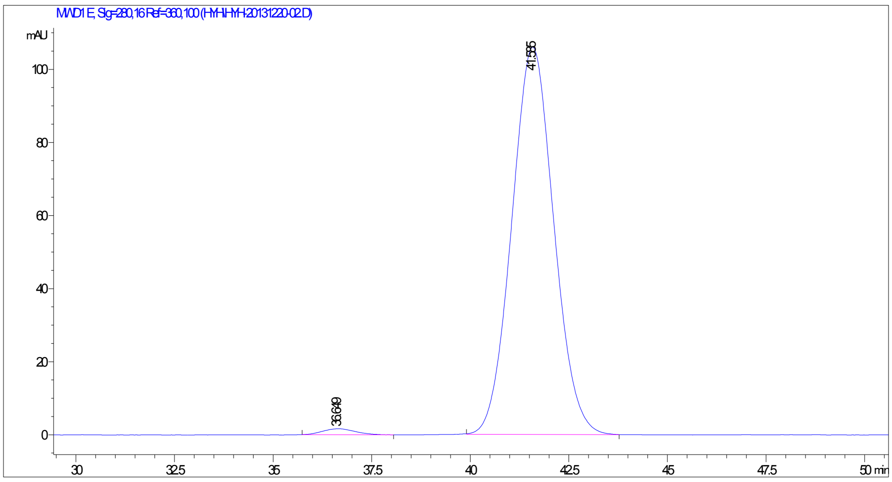
4bm

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

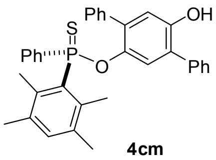


#	Time	Area	Height	Area%
1	36.726	5103.2	82.2	50.076
2	42.036	5087.8	70.3	49.924

flow = 1.0 ml/m; IPA = 3%, Hexane = 97%; 280 nm; AD-H

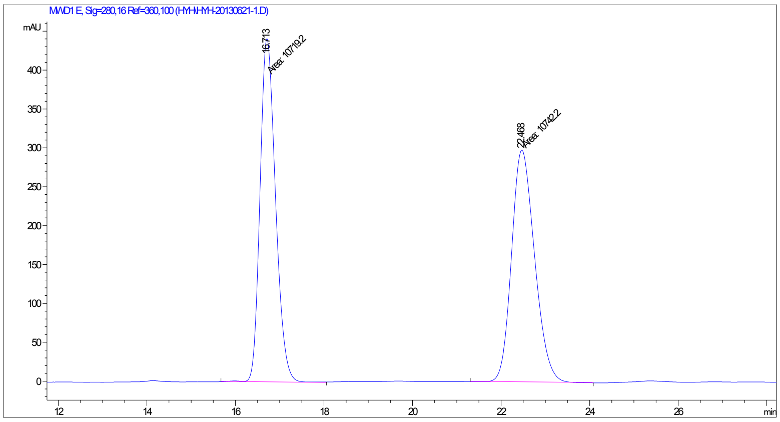


#	Time	Area	Height	Area%
1	36.649	95.8	1.7	1.206
2	41.585	7847.8	106	98.794



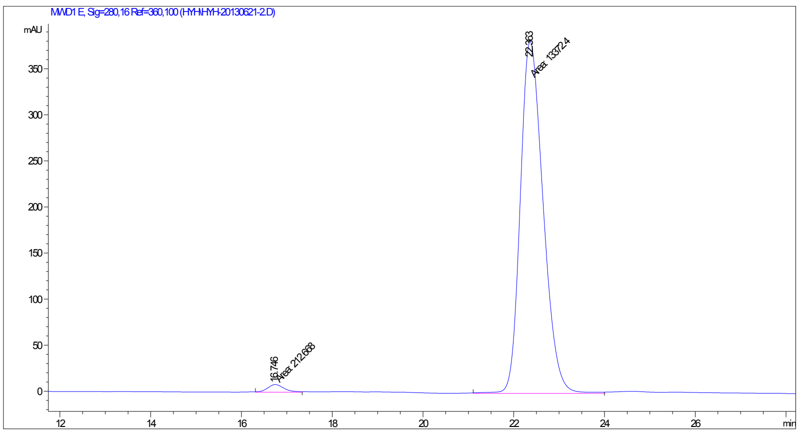
4cm

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

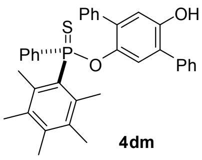


#	Time	Area	Height	Area%
1	16.713	10719.2	441	49.947
2	22.468	10742.2	297.8	50.053

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

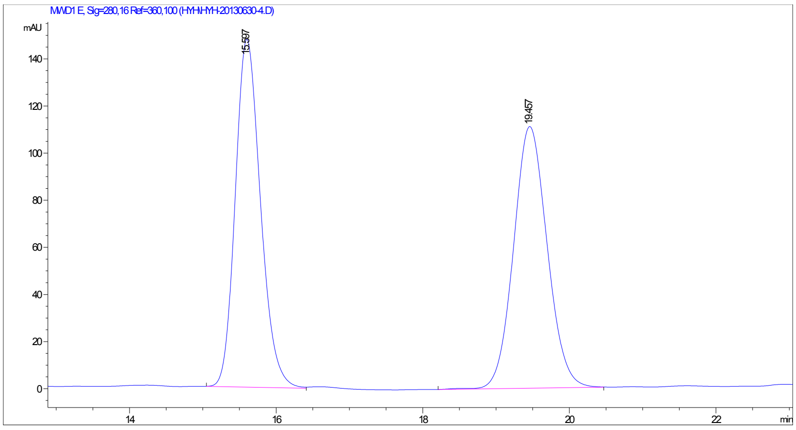


#	Time	Area	Height	Area%
1	16.746	211.5	8.3	1.557
2	22.363	13372.4	382	98.443



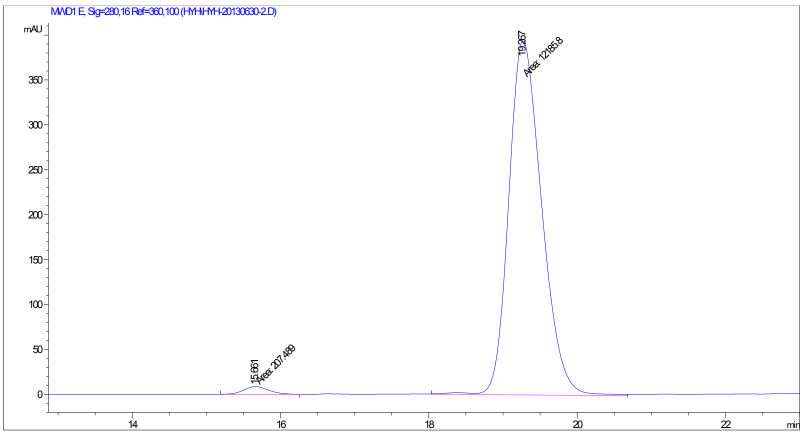
4dm

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

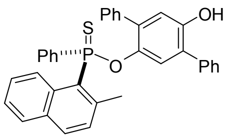


#	Time	Area	Height	Area%
1	15.597	3529.7	147.6	49.920
2	19.457	3541.1	111.1	50.080

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

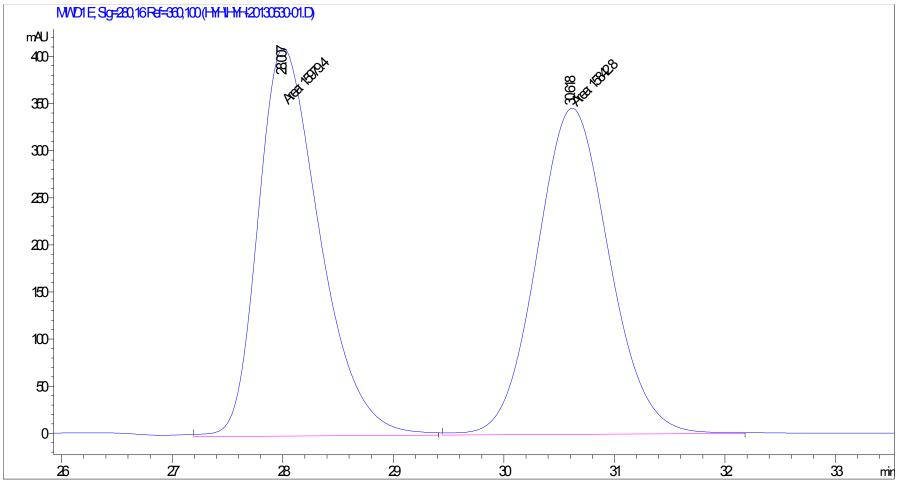


#	Time	Area	Height	Area%
1	15.661	207.5	8.7	1.674
2	19.267	12185.8	394.4	98.326



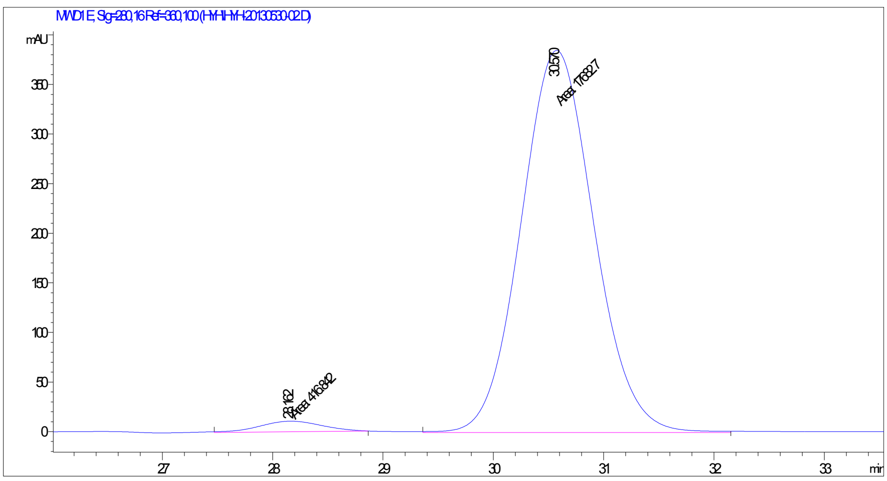
4em

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

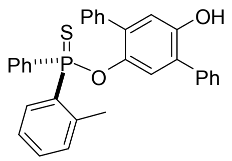


#	Time	Area	Height	Area%
1	28.007	15979.4	411.8	50.215
2	30.618	15842.8	346.3	49.785

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

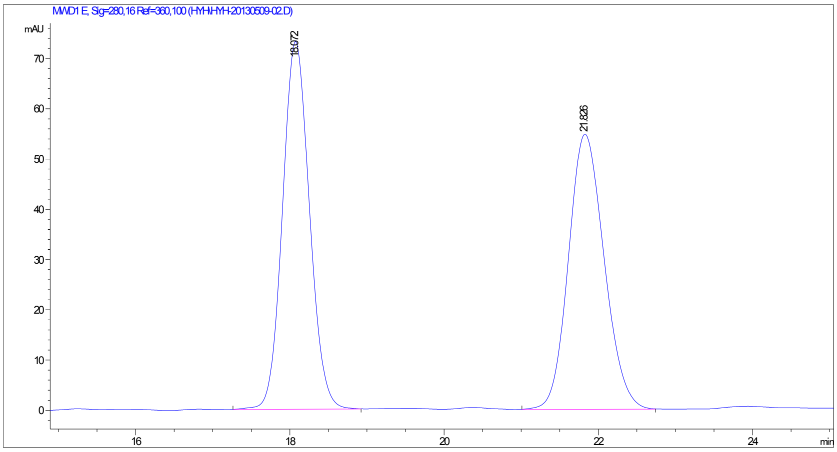


#	Time	Area	Height	Area%
1	28.162	416.8	10.7	2.303
2	30.57	17682.7	385.3	97.697



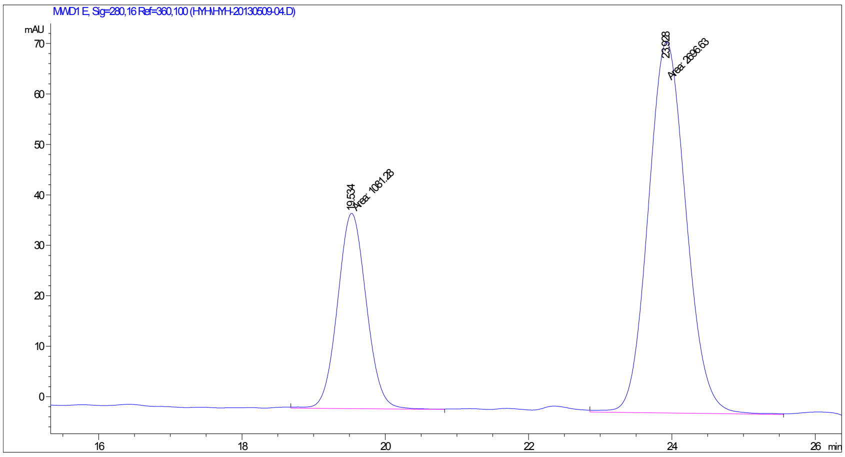
4fm

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

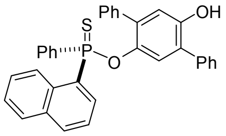


#	Time	Area	Height	Area%
1	18.072	1774.5	73.2	50.181
2	21.826	1761.8	54.8	49.819

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

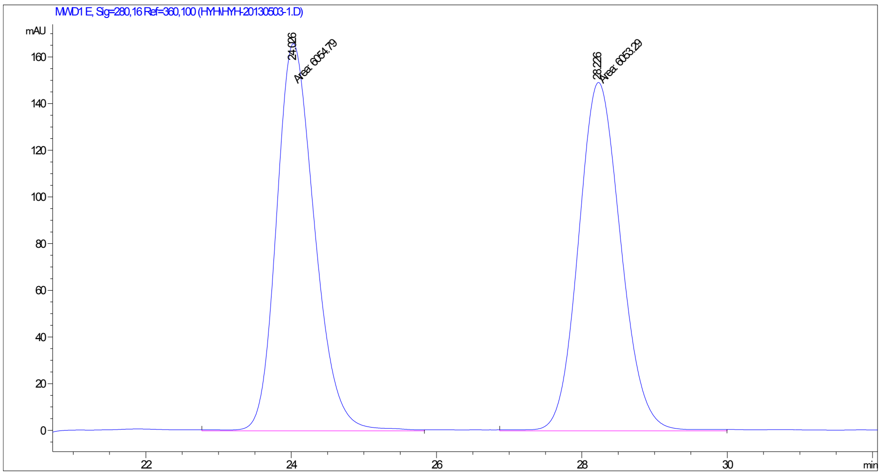


#	Time	Area	Height	Area%
1	19.534	1081.3	38.7	28.621
2	23.928	2696.6	73.5	71.379



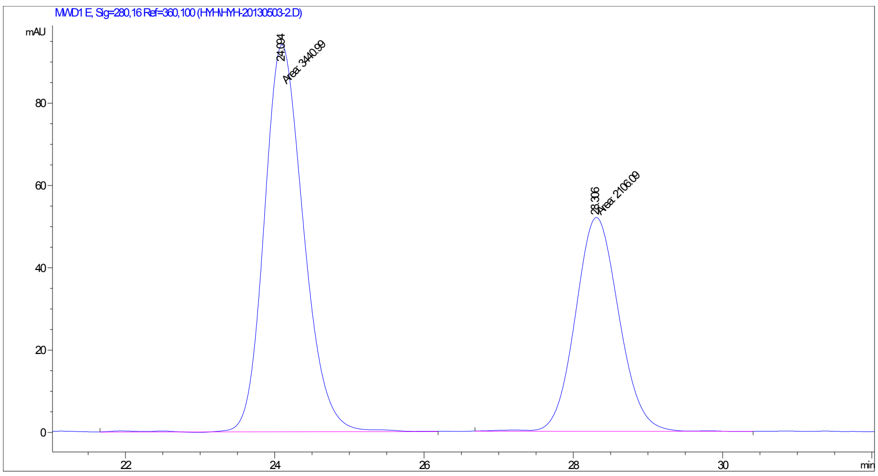
4gm

flow = 0.8 ml/m; IPA = 6%, Hexane = 94%; 280 nm; AD-H

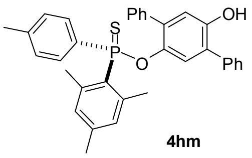


#	Time	Area	Height	Area%
1	24.026	6054.8	165.9	50.006
2	28.226	6053.3	149.3	49.994

flow = 0.8 ml/m; IPA = 6%, Hexane = 94%; 280 nm; AD-H

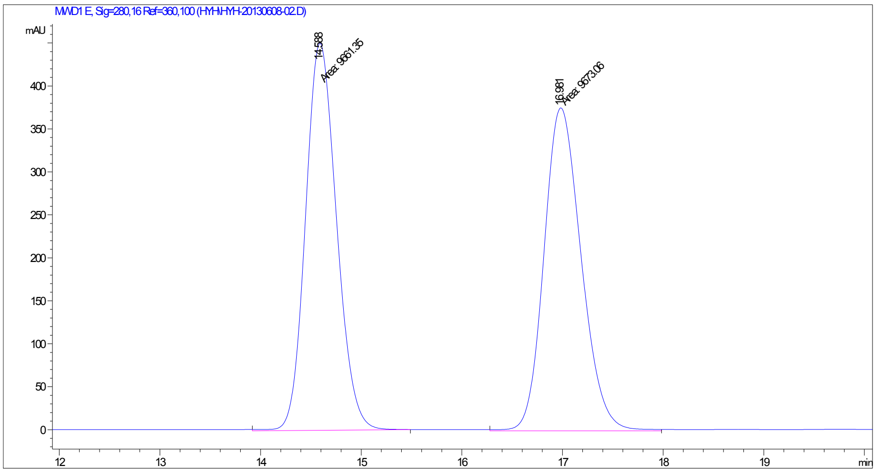


#	Time	Area	Height	Area%
1	24.094	3441	94.1	62.032
2	28.306	2106.1	52	37.968



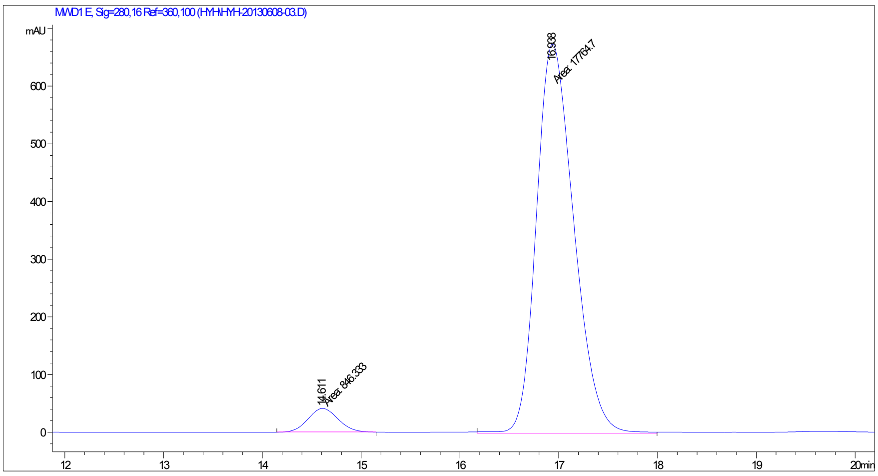
4hm

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

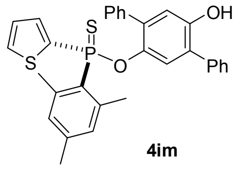


#	Time	Area	Height	Area%
1	14.588	9661.4	450.6	49.970
2	16.981	9673.1	376	50.030

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

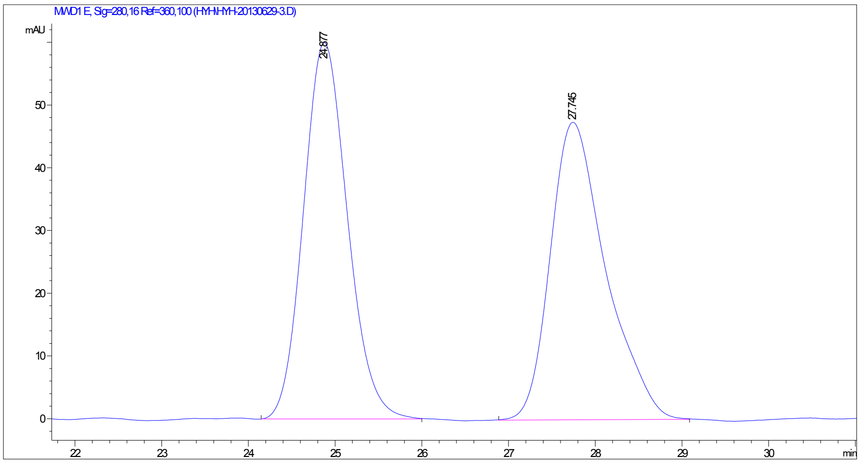


#	Time	Area	Height	Area%
1	14.611	846.3	40.6	4.547
2	16.938	17764.7	674.3	95.453



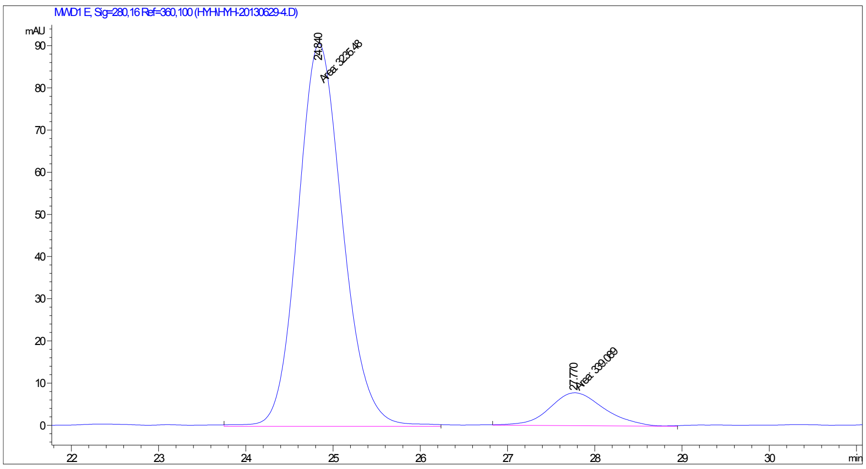
4im

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

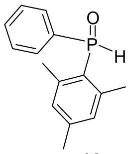


#	Time	Area	Height	Area%
1	24.877	2114.9	60	50.092
2	27.745	2107.1	47.4	49.908

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

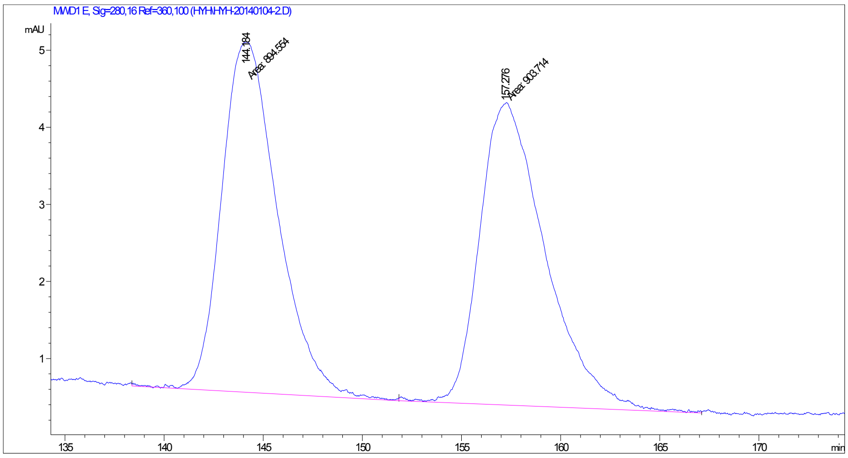


#	Time	Area	Height	Area%
1	24.84	3235.5	90.7	90.514
2	27.77	339.1	7.8	9.486



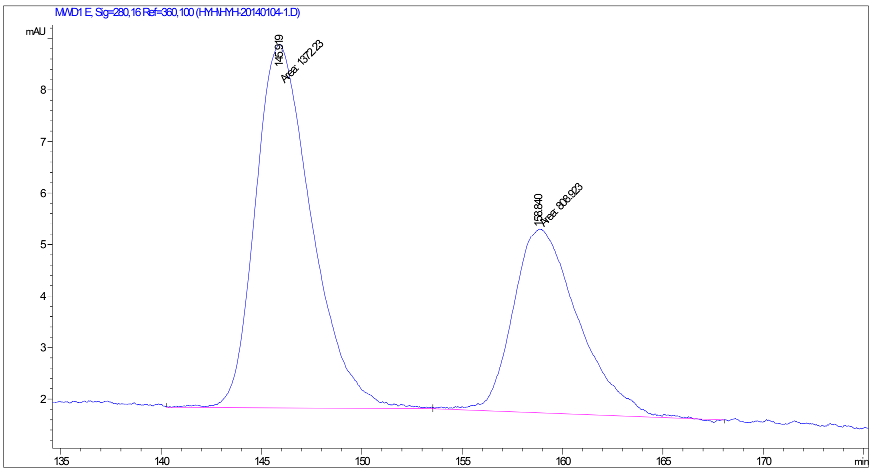
12 (at 63% conversion)

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 280 nm; AD-H , racemic sample

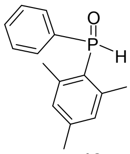


#	Time	Area	Height	Area%
1	144.184	894.6	4.5	49.745
2	157.276	903.7	3.9	50.255

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 280 nm; AD-H

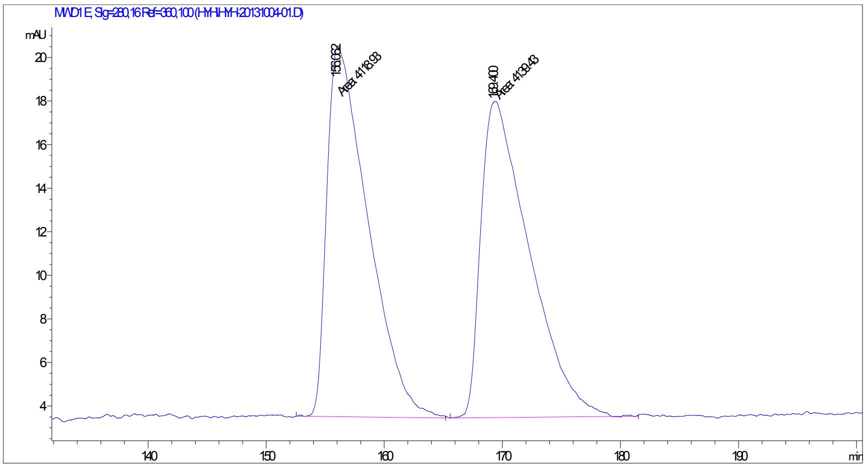


#	Time	Area	Height	Area%
1	145.919	1372.2	7.1	62.913
2	158.84	808.9	3.6	37.087



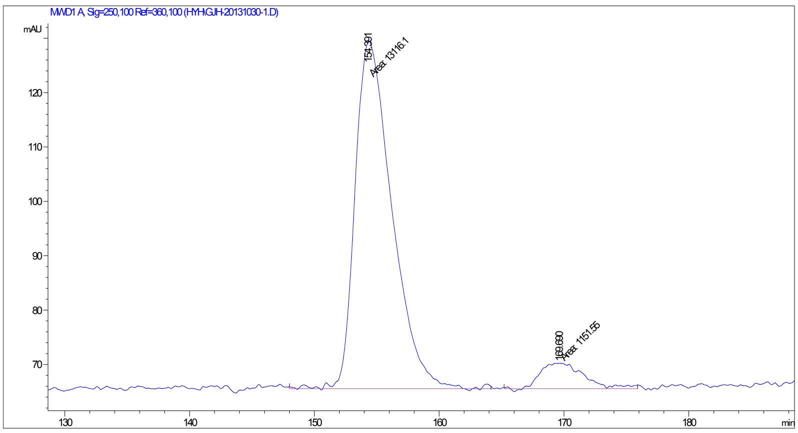
12 (at 97% conversion)

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 280 nm; AD-H, racemic sample

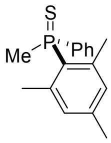


#	Time	Area	Height	Area%
1	156.062	4118.9	17	49.876
2	169.4	4139.4	14.5	50.124

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 250 nm; AD-H

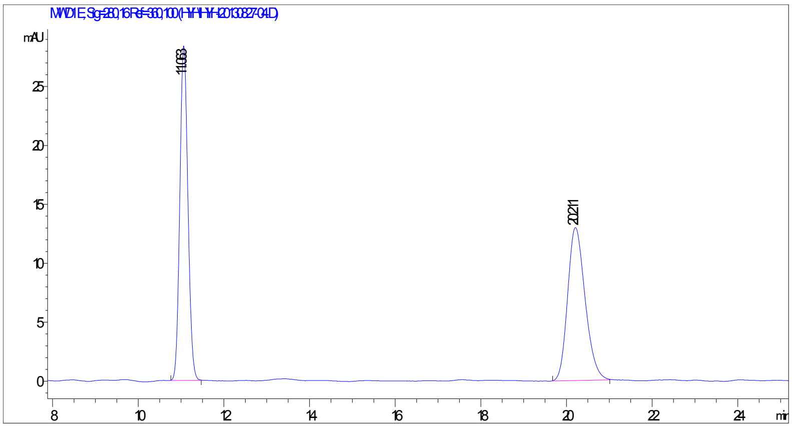


#	Time	Area	Height	Area%
1	154.391	13116.1	63.9	91.929
2	169.69	1151.5	4.7	8.071



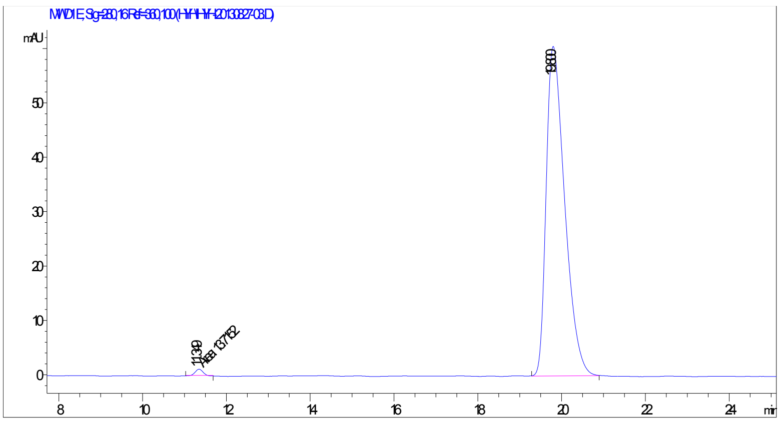
(*S*)-**14a**

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 280 nm; AD-H

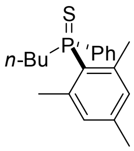


#	Time	Area	Height	Area%
1	11.063	371.1	28.4	50.202
2	20.211	368.1	13	49.798

flow = 1.0 ml/m; IPA = 2%, Hexane = 98%; 280 nm; AD-H

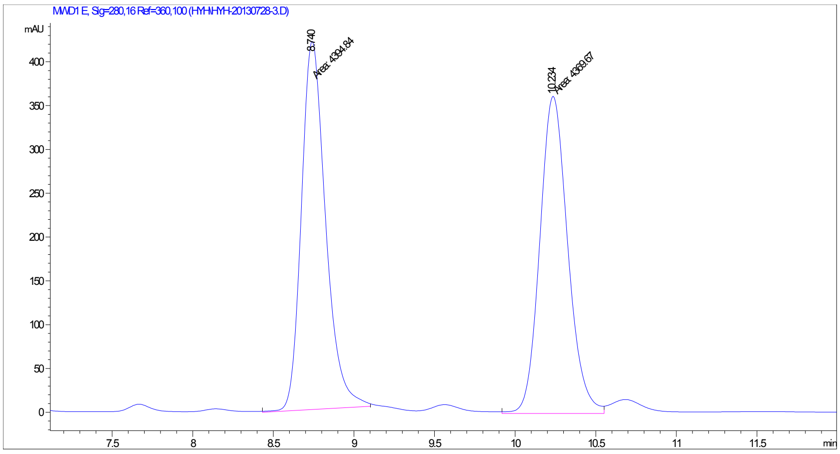


#	Time	Area	Height	Area%
1	11.349	13.7	1.1	0.732
2	19.8	1858.9	60.6	99.268



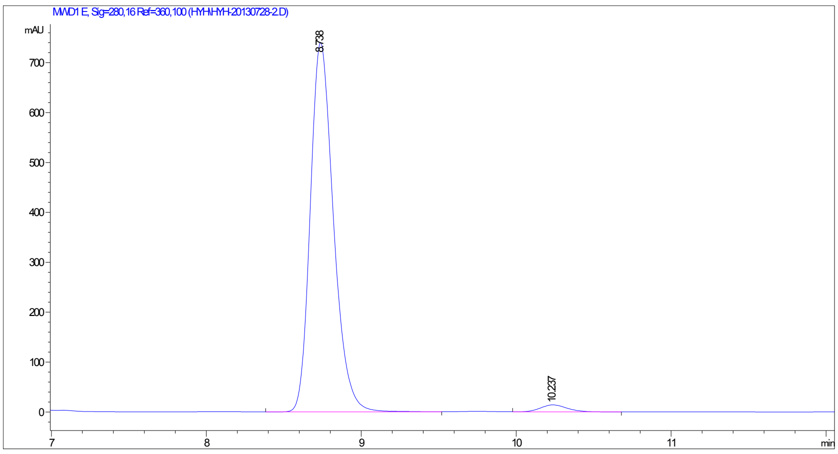
(*S*)-**14b**

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

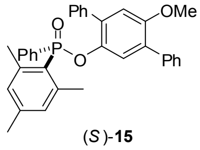


#	Time	Area	Height	Area%
1	8.74	4394.8	420.4	50.144
2	10.234	4369.7	362.1	49.856

flow = 0.8 ml/m; IPA = 5%, Hexane = 95%; 280 nm; AD-H

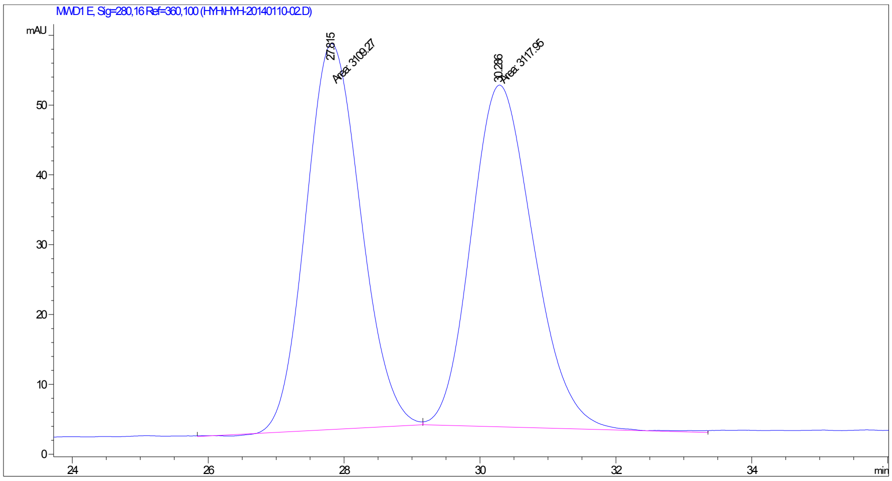


#	Time	Area	Height	Area%
1	8.738	7708.7	740.5	97.807
2	10.237	172.8	14.1	2.193



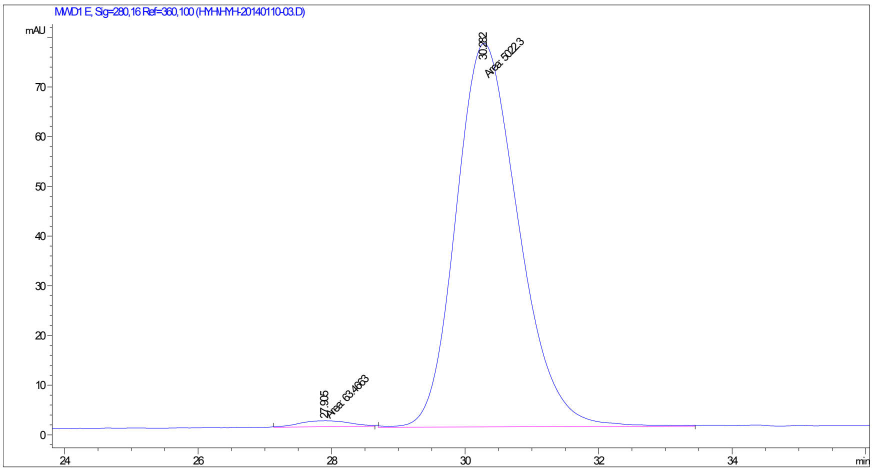
(*S*)-**15**

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC

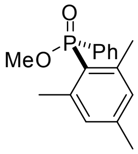


#	Time	Area	Height	Area%
1	27.815	3109.3	55.2	49.930
2	30.286	3117.9	48.9	50.070

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC

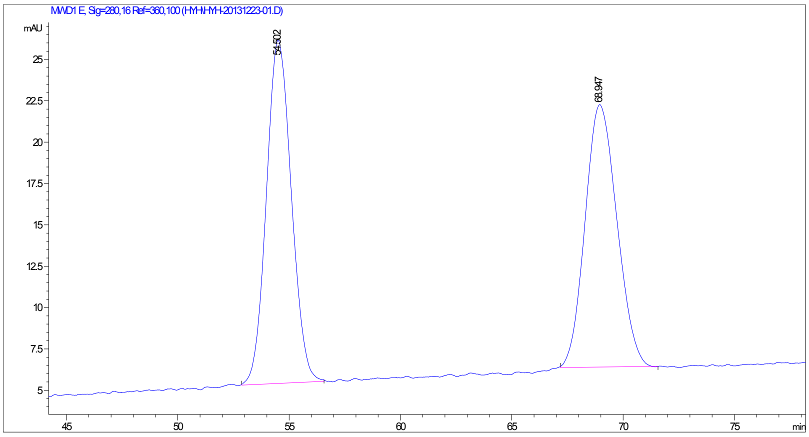


#	Time	Area	Height	Area%
1	27.905	63.5	1.2	1.248
2	30.282	5022.3	77.2	98.752



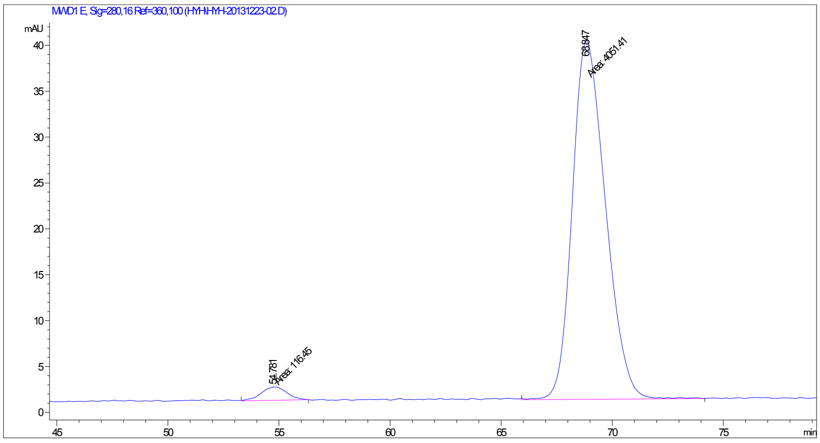
(*R*)-**16**

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC



#	Time	Area	Height	Area%
1	54.502	1618	20.8	50.664
2	68.947	1575.6	15.9	49.336

flow = 1.0 ml/m; IPA = 10%, Hexane = 90%; 280 nm; IC (conv = 92%)



#	Time	Area	Height	Area%
1	54.781	116.4	1.5	2.794
2	68.847	4051.4	39.1	97.206