Electronic Supplementary Material (ESI) for ChemComm.

The Synthesis and Efficient One-Pot Catalytic "Self-Breeding" of Asymmetrical NC(sp^3)E-Hybridised Pincer Complexes

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Supporting Information

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General Information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers. Chemical shifts were reported in ppm and referenced to an internal $SiMe_4$ standard (0 ppm) for ^1H NMR, chloroform-d (77.23 ppm) for ^{13}C NMR, and an external 85% H_3PO_4 for $^{31}P\{^1H\}$ NMR. DCM, DCE, DEE, toluene, acetone, acetonitrile and MeOH were purchased from their respective companies and used as supplied. THF was distilled prior to use. Solvents were degassed when necessary. A Low Temp Pairstirrer PSL-1400 was used for controlling low temperature reactions. Column chromatography was carried out with Silica gel 60 (Merck). Melting points were measured using SRS Optimelt Automated Point System SRS MPA100. Optical rotation were measured with JASCO P-1030 Polarimeter in the specified solvent in a 0.1 dm cell at 22.0°C. The enantioselectivities of the hydrophosphination reactions were determined with Agilent 1200 Series High Performance Liquid Chromatography (HPLC) machine fitted with a Daicel Chiralpak IC column and eluted with a mixture of *n*-hexane/2-propanol.

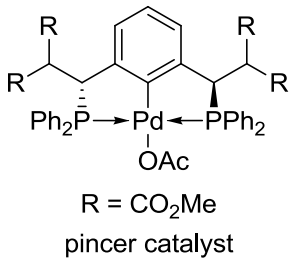


Figure s1. Molecular structure of pincer catalyst.

The pincer catalyst **1**[1] and diene **2**[2] were prepared according to literature methods. $PdCl_2(NCMe)_2$ was prepared by adding $PdCl_2$ portionwise to boiling acetonitrile under vigorous stirring for 30 mins. The yellow suspension was filtered and the yellow residue ($PdCl_2(NCMe)_2$) washed with acetonitrile and dried. All other reactants and reagents were used as supplied without further purification unless stated otherwise.

Synthesis of ligand 3a

To a solution of Ph_2PH (93.1 mg, 0.500 mmol, 1.1 equiv) in acetone (25 mL) was added the pincer catalyst **1** (20.7 mg, 0.023 mmol, 5 mol %) and stirred for 10 minutes before cooling to 0°C. Dienone **2** (107.1 mg, 0.455 mmol, 1.0 equiv) was added and the mixture was stirred at 0°C. Upon completion of the reaction as determined by $^{31}P\{^1H\}$ NMR, the mixture was warmed up to room temperature. S_8 (0.035 g, 0.137 mmol, 0.3 equiv) was added and stirred for 30 min. The crude product was purified by silica gel column chromatography (2 DCM : 1 *n*-hexane) to afford pure white solid of **3a** (181 mg, 0.409 mmol, 90 % yield). $[\alpha]_D$ = -378 (*c* 0.1, DCM). Mp: 95-97°C. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 49.6; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, 1H, ^3J = 4.2 Hz, Ar), 8.13-8.07 (m, 2H, Ar), 7.93-7.89 (m, 3H, Ar), 7.78-7.74 (m, 1H, Ar), 7.50-7.38 (m, 7H, Ar), 7.21-7.12 (m, 5H, Ar), 6.29 (dd, 1H, ^3J = 15.9 Hz, $^4J_{HP}$ = 4.6 Hz, PhC*H*=CH), 6.16 (ddd, 1H, , ^3J = 15.8 Hz, $^3J_{HP}$ = 8.7 Hz, ^3J = 6.5 Hz, PhCH=C*H*), 4.50-4.42 (m, 1H, PC*H*CH_2), 4.11 (ddd, 1H, ^2J = 17.7 Hz, $^3J_{PH}$ = 10.5 Hz, ^3J =

5.6 Hz, O=CCH_2), 3.35 (ddd, 1H, ^2J = 17.6 Hz, $^3J_{PH}$ = 12.5 Hz, ^3J = 2.3 Hz, O=CCH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.9 (d, 1C, $^3J_{PC}$ = 15.1 Hz, *C*=O), 152.9 (1C, Ar), 149.1 (1C, Ar), 136.9-122.0 (23C, Ar + *C*=*C*), 40.5 (d, 1C, $^1J_{PC}$ = 54.9 Hz, P*C*H), 37.5 (1C, O=C*C*H_2). HRMS (+ESI) m/z: $(M + H)^+$ calcd for $C_{28}H_{25}NOPS$, 454.1394; found, 454.1396. Anal. Calcd for $C_{28}H_{24}NOPS$: C, 74.15; H, 5.33; N, 3.09. Found: C, 74.58; H, 5.77; N, 2.66 %. The *ee* was determined on a Daicel Chiralpak IC column with n-hexane/2-propanol = 95/5, flow = 1.0 mL/min, wavelength = 270 nm. Retention times: 23.1 min (major), 28.1 min (minor).

Synthesis of ligand 3b

The preparation is similar to that of compound **3a** but aq. H_2O_2 (31% w/w, 0.2 mL) was used instead of S_8. Purification by silica gel column chromatography (3 DCM : 1 EA) afforded the pure white solid of **3b** (171 mg, 0.391 mmol, 86% yield). $[\alpha]_D$ = -429 (*c* 0.1, DCM). Mp: 191-193^{o}C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 34.2; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.65 (d, 1H, ^3J = 4.2 Hz, Ar), 7.96-7.92 (m, 3H, Ar), 7.84-7.74 (m, 3H, Ar), 7.50-7.41 (m, 7H, Ar), 7.22-7.13 (m, 5H, Ar), 6.35 (dd, 1H, ^3J = 16.0 Hz, $^4J_{HP}$ = 4.3 Hz, PhC*H*=CH), 6.12 (ddd, 1H, , ^3J = 15.9 Hz, $^3J_{HP}$ = 8.8 Hz, ^3J = 5.9 Hz, PhCH=C*H*), 4.19-4.13 (m, 1H, PC*H*CH_2), 4.03 (ddd, 1H, ^2J = 17.6 Hz, $^3J_{HP}$ = 10.7 Hz, ^3J = 5.2 Hz, O=CCH_2), 3.47 (ddd, 1H, ^2J = 17.4 Hz, $^3J_{HP}$ = 10.9 Hz, ^3J = 2.4 Hz, O=CCH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 198.9 (d, 1C, $^3J_{PC}$ = 13.2 Hz, *C*=O), 152.9 (1C, Ar), 149.0 (1C, Ar), 136.8-121.9 (23C, Ar + *C*=*C*), 39.6 (d, 1C, $^1J_{PC}$ = 69.6 Hz, P*C*H), 36.4 (1C, O=C*C*H_2). HRMS (+ESI) m/z: $(M + H)^+$ calcd for $C_{28}H_{25}NO_2P$, 438.1623; found, 438.1625. Anal. Calcd for $C_{28}H_{24}NO_2P$: C, 76.87; H, 5.53; N, 3.20. Found: C, 76.37; H, 5.89; N, 2.79 %. The *ee* was determined on a Daicel Chiralpak IC column with n-hexane/2-propanol = 85/15, flow = 1.0 mL/min, wavelength = 260 nm. Retention times: 70.5 min (major), 79.3 min (minor).

Synthesis of pincer complex 4a

A mixture of $PdCl_2$ (3.90 mg, 22.0 μmol, 1.0 equiv) and LiCl (3.73 mg, 88.0 μmol, 4.0 equiv) in MeOH (10 mL) was stirred for 30 mins. The ligand **3a** (9.99 mg, 22.0 μmol, 1.0 equiv.) was added to the mixture and stirred. Monitoring of the reaction completion was done by thin-layer chromatography (DCM) and confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The crude product was purified by silica gel column chromatography (2 EA : 1 *n*-hexane) to afford white solid of complex **4a** (9.80 mg, 16.9 μmol, 77% yield). $[\alpha]_D$ = -180 (*c* 0.1, DCM). Mp: 226-228^{o}C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ 67.2; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.16 (d, 1H, ^3J = 5.1 Hz, Ar), 8.17-8.11 (m, 2H, Ar), 7.95 (td, 1H, ^3J = 7.7 Hz, ^4J = 1.4 Hz, Ar), 7.84-7.78 (m, 2H, Ar), 7.71-7.47 (m, 8H, Ar), 7.26-7.17 (m, 5H, Ar), 6.49 (dd, 1H, ^3J = 16.0 Hz, $^4J_{HP}$ = 5.0 Hz, PhC*H*=CH), 5.87 (ddd, 1H, ^3J = 15.9, 5.7 Hz, $^3J_{HP}$ = 8.7 Hz, PhCH=C*H*), 4.87-4.76 (m, 1H, PC*H*), 4.45 (dd, 1H, $^3J_{HP}$ = 9.9 Hz, ^3J = 4.9 Hz, PdC*H*); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 192.9 (d, 1C, $^3J_{PC}$ = 17.7 Hz, *C*=O), 155.9 (1C, Ar), 148.8 (1C, Ar), 139.6-122.3 (23C, Ar + *C*=*C*), 55.2 (1C, Pd*C*H), 50.7 (d, 1C, $^1J_{PC}$ = 62.6 Hz, P*C*H). HRMS (+ESI) m/z: $(M - Cl)^+$ calcd for $C_{28}H_{23}NOPPdS$, 558.0273; found, 558.0274. Anal. Calcd for $C_{28}H_{23}ClNOPPdS$: C, 56.58; H, 3.90; N, 2.36. Found: C, 56.96; H, 3.46; N, 2.57 %.

Synthesis of pincer complex 4b

A mixture of $PdCl_2(NCMe)_2$ (5.71 mg, 22.0 μmol, 1.0 equiv), NaOAc (1.81 mg, 22.0 μmol, 1.0 equiv) and ligand **3b** (9.62 mg, 22.0 μmol, 1.0 equiv.) in DCM (10 mL) was stirred in a one-neck RBF. Monitoring of the reaction completion was done by thin-layer chromatography (1 DCM : 1 EA) and confirmed by $^{31}P\{^1H\}$ NMR spectroscopy. The crude product was purified by silica gel column chromatography (10 DCM : 1 EA to 8 DCM : 1 EA) to afford pure yellow solid of **4b** (10.8 mg, 18.7 μmol, 85% yield). $[\alpha]_D$ = -446 (*c* 0.1, DCM). Mp: 170-171°C (dec.). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 74.9; ^1H NMR ($CDCl_3$, 400 MHz): δ 9.07 (d, 1H, ^3J = 5.1 Hz, Ar), 8.12-8.08 (m, 2H, Ar), 7.95 (td, 1H, ^3J = 7.8 Hz, ^4J = 1.4 Hz, Ar), 7.86-7.81 (m, 2H, Ar), 7.70-7.58 (m, 5H, Ar), 7.54-7.49 (m, 2H, Ar), 7.45-7-42 (m, 1H, Ar), 7.30-7.20 (m, 5H, Ar), 6.59 (dd, 1H, ^3J = 15.8 Hz, $^4J_{HP}$ = 4.5 Hz, PhC*H*=CH), 5.85 (ddd, 1H, ^3J = 15.8, 5.6 Hz, $^3J_{HP}$ = 8.5 Hz, PhCH=C*H*), 4.76 (dd, 1H, $^3J_{HP}$ = 10.4 Hz, ^3J = 2.2 Hz, PdC*H*), 4.71-4.62 (m, 1H, PC*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.0 (d, 1C, $^3J_{PC}$ = 15.5 Hz, *C*=O), 157.4 (1C, Ar), 151.5 (1C, Ar), 139.6-121.6 (23C, Ar + *C*=*C*), 55.6 (1C, Pd*C*H), 46.3 (d, 1C, $^1J_{PC}$ = 75.6 Hz, P*C*H). HRMS (+ESI) m/z: $(M - Cl)^+$ calcd for $C_{28}H_{23}NO_2PPd$, 542.0501; found, 542.0500. Anal. Calcd for $C_{28}H_{23}ClNO_2PPd$: C, 58.15; H, 4.01; N, 2.42. Found: C, 58.39; H, 3.84; N, 2.16 %.

General procedure for the asymmetric hydrophosphination reaction

A Schlenk tube was charged with $HPPh_2$ (12.1 mg, 65.0 μmol, 1.5 equiv), complex **4a/b** (2.2 μmol, 5 mol%), base (8.7 μmol, 20 mol%) and diene **2** (10.2 mg, 43.3 μmol, 1.0 equiv) in the stated solvent (2.5 mL) and where specified, H_2O (0.25 mL) was added and stirred at RT for 24h. Subsequently, aq. H_2O_2 (31% w/w, 0.1 mL) or S_8 (3.33 mg, 13.0 μmol, 0.3 equiv.) was introduced to the mixture. The volatiles were removed and the crude product loaded directly onto silica gel column (3 DCM : 1 EA or 2 DCM : 1 *n*-hexane) to afford pure white solid of **3b** or **3a** respectively.

General procedure for recycling of pincer complex 4a

A Schlenk tube was charged with $HPPh_2$ (37.2 mg, 200 μmol, 1.5 equiv), complex **4a** (7.91 mg, 13.3 μmol, 10 mol%), KOAc (5.22 mg, 53.2 μmol, 40 mol%) and diene **2** (31.3 mg, 133 μmol, 1.0 equiv) in THF/H_2O (8 mL/0.8 mL). The mixture was stirred at RT for 24h. LiCl (56.4 mg, 1.33 mmol, 10.0 equiv.) was introduced to the mixture and stirred for 6 h at RT. Subsequently, the mixture was treated with aq. H_2O_2 (31% w/w, 0.3 mL), the volatiles were removed and the residue loaded directly onto silica gel column (1 *n*-hexane : 1 EA to 1 *n*-hexane : 2 EA) to afford pure white solid of **3b** and **4a**. The *ee* of compound **3b** was determined on a Daicel Chiralpak IC column with n-hexane/2-propanol = 85/15, flow = 1.0 mL/min, wavelength = 260 nm. Retention times: 70.5 min (major), 79.3 min (minor). The recovered complex **4a** was used in the second run in 10 mol% loading with the same procedure as above [**4a** (4.11 mg, 6.92 μmol, 10 mol%), KOAc (2.72 mg, 27.7 μmol, 40 mol%), $HPPh_2$ (19.3 mg, 104 μmol, 1.5 equiv), diene **2** (16.3 mg, 69.2 μmol, 1.0 equiv), THF (4 mL), H_2O (0.4 mL), LiCl (29.3 mg, 692 μmol, 10.0 equiv), aq. H_2O_2 (31% w/w, 0.2 mL)]. The recovered complex **4a** was again reused in the third run in 10 mol% loading [**4a** (1.85

mg, 3.11 μmol, 10 mol%), KOAc (1.22 mg, 12.4 μmol, 40 mol%), $HPPh_2$ (8.69 mg, 46.7 μmol, 1.5 equiv), diene **2** (7.32 mg, 31.1 μmol, 1.0 equiv), THF (2 mL), H_2O (0.2 mL), LiCl (13.2 mg, 311 μmol, 10.0 equiv), aq. H_2O_2 (31% w/w, 0.1 mL)].

Reference

[1] X.-Y. Yang, J. H. Gan, Y. Li, S. A. Pullarkat and P.-H. Leung, *Dalton Trans.* **2015**, *44*, 1258.

[2] a) X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics* **2015**, *34*, 5196; b) N. Molleti, N. K. Rana and V. K. Singh, *Org. Lett.* **2012,** *14,* 4322.

[3] J. L. Bookham and W. McFarlane, *J. Chem. Soc., Chem. Commun.* **1993**, 1352.

NMR Spectra

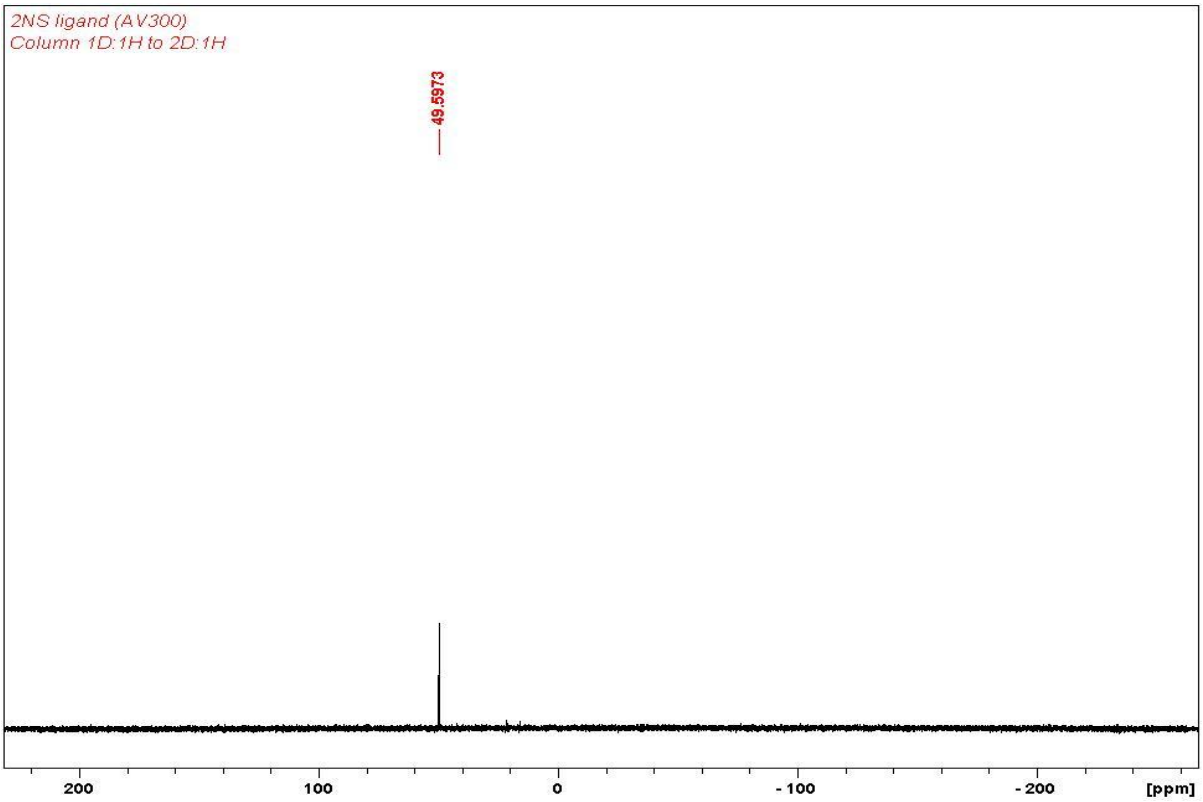


Figure s2. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3a**.

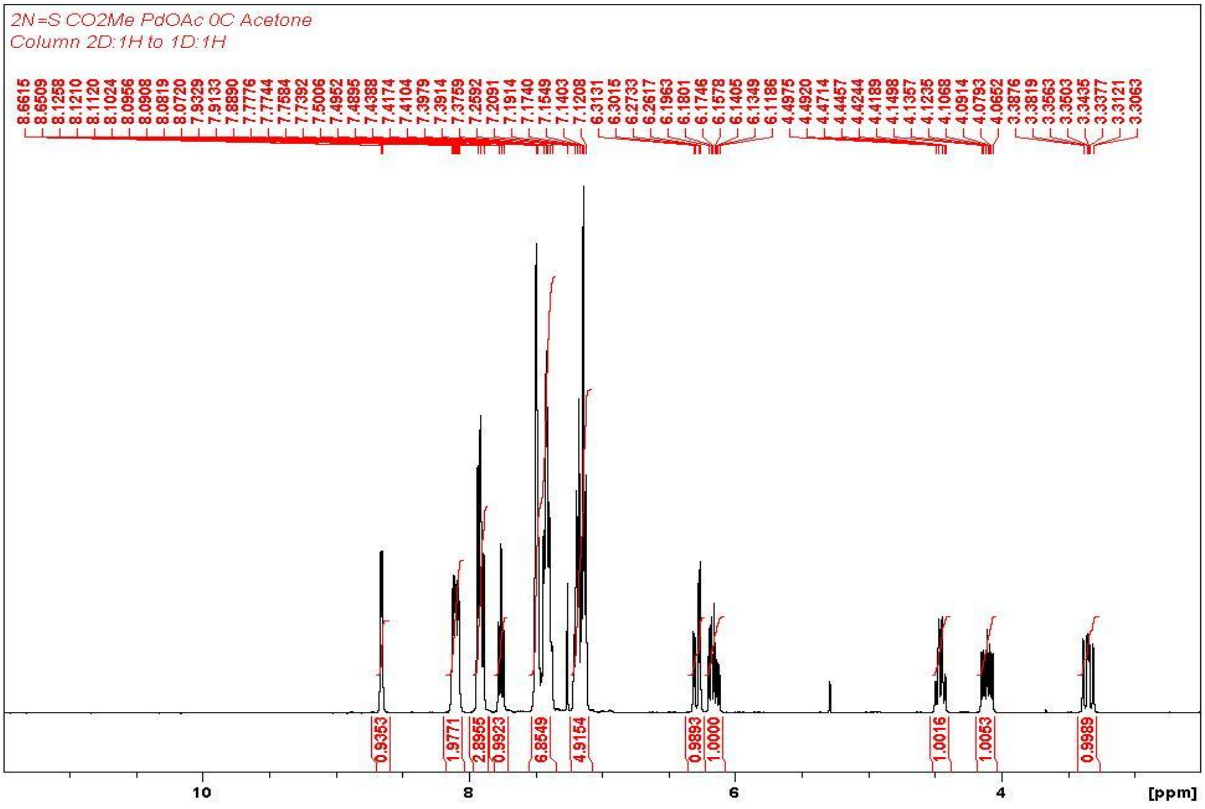


Figure s3. ^{1}H NMR spectrum of compound **3a**.

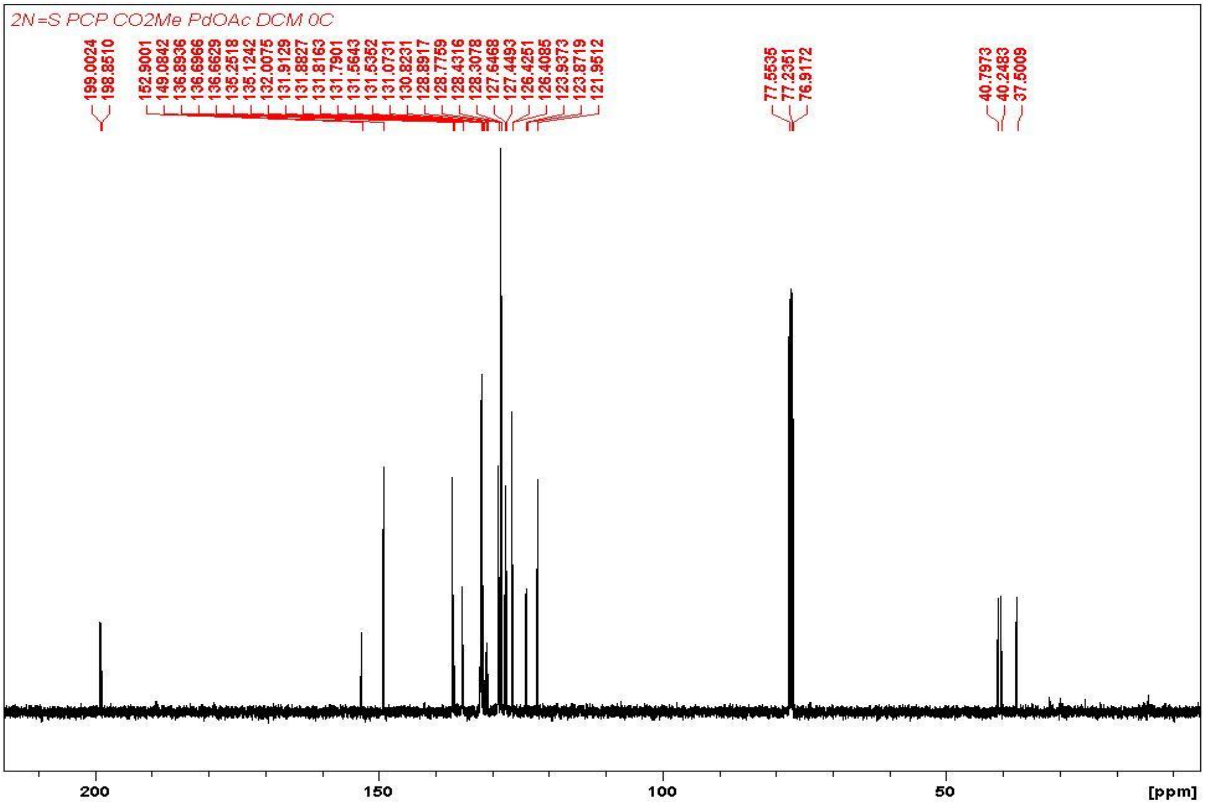


Figure s4. ^{13}C NMR spectrum of compound **3a**.

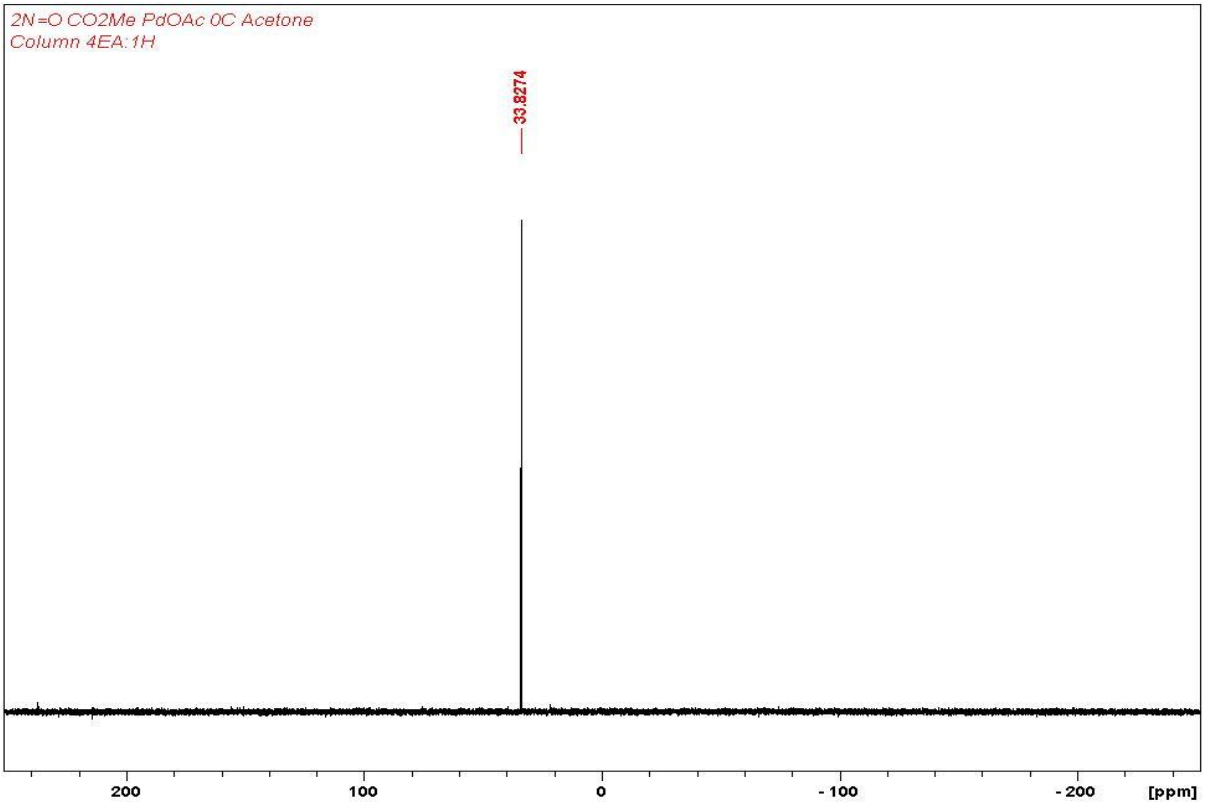


Figure s5. $^{31}P\{^{1}H\}$ NMR spectrum of compound **3b**.

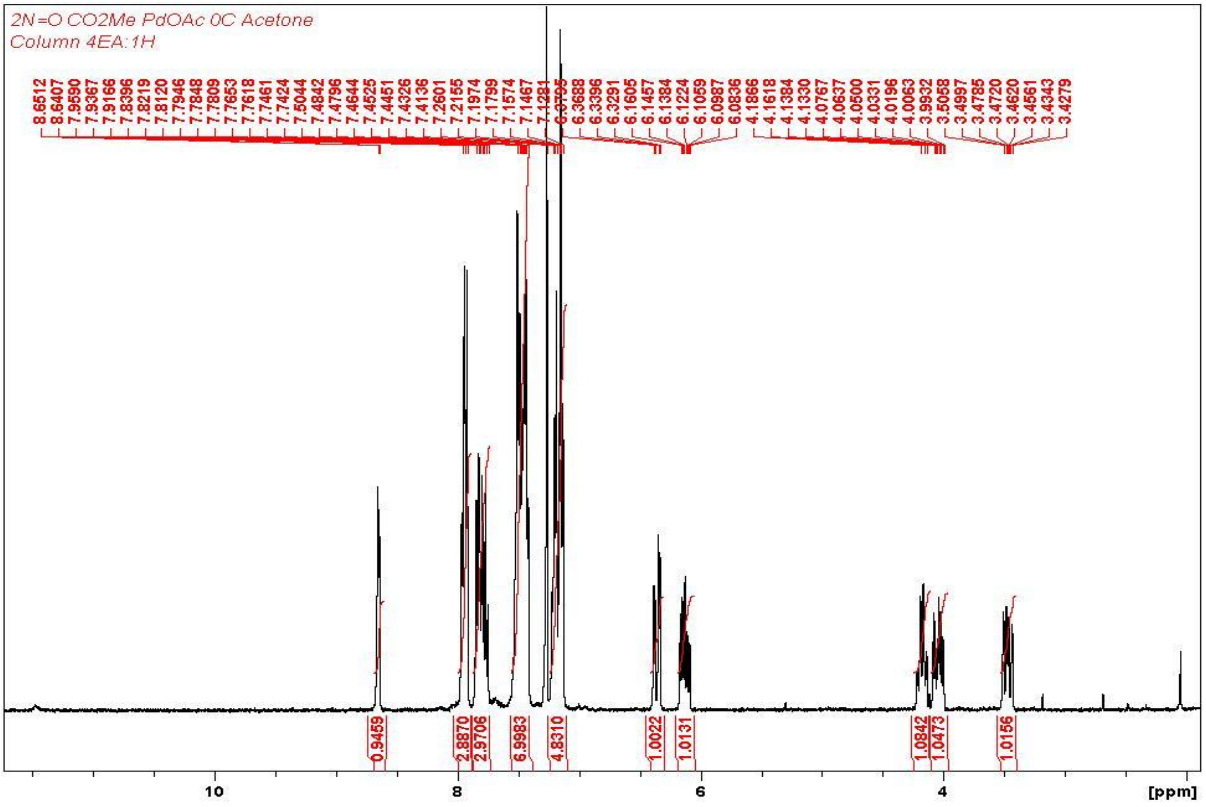


Figure s6. ^{1}H NMR spectrum of compound **3b**.

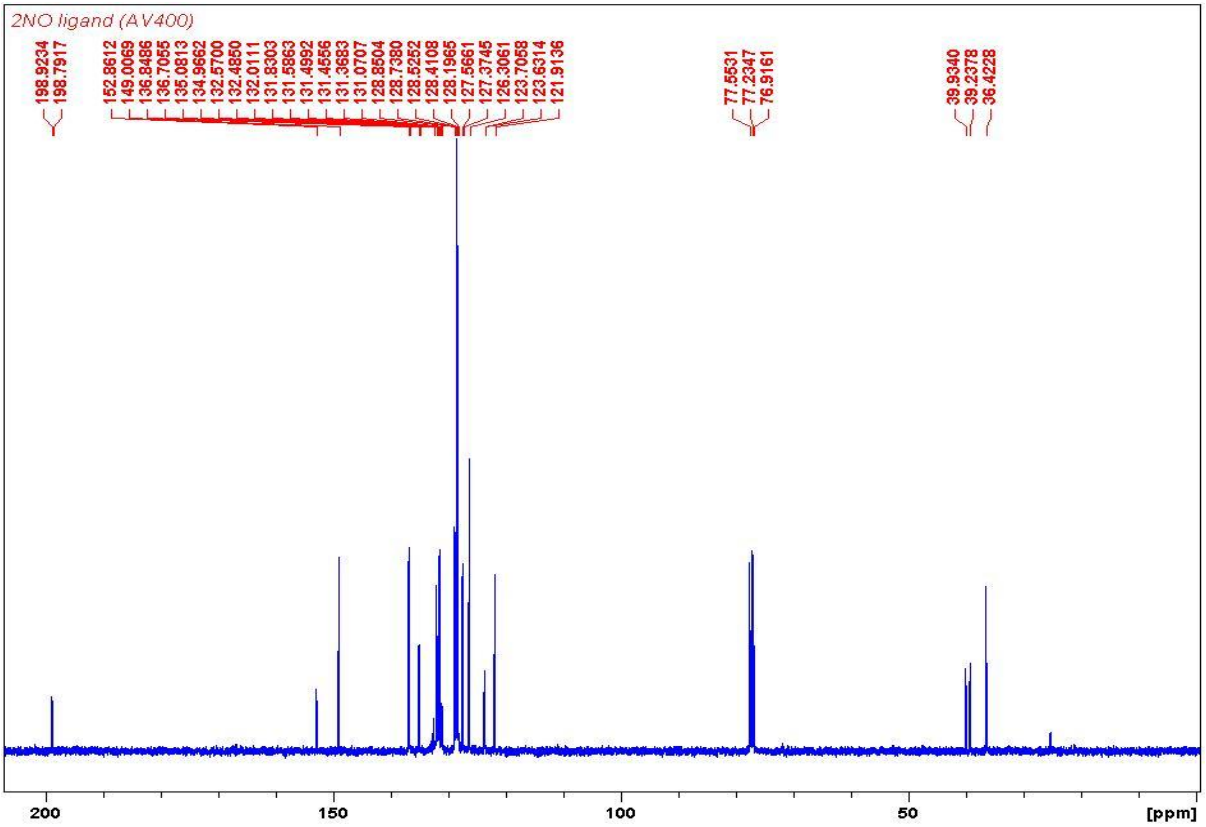


Figure s7. ^{13}C NMR spectrum of compound **3b**.

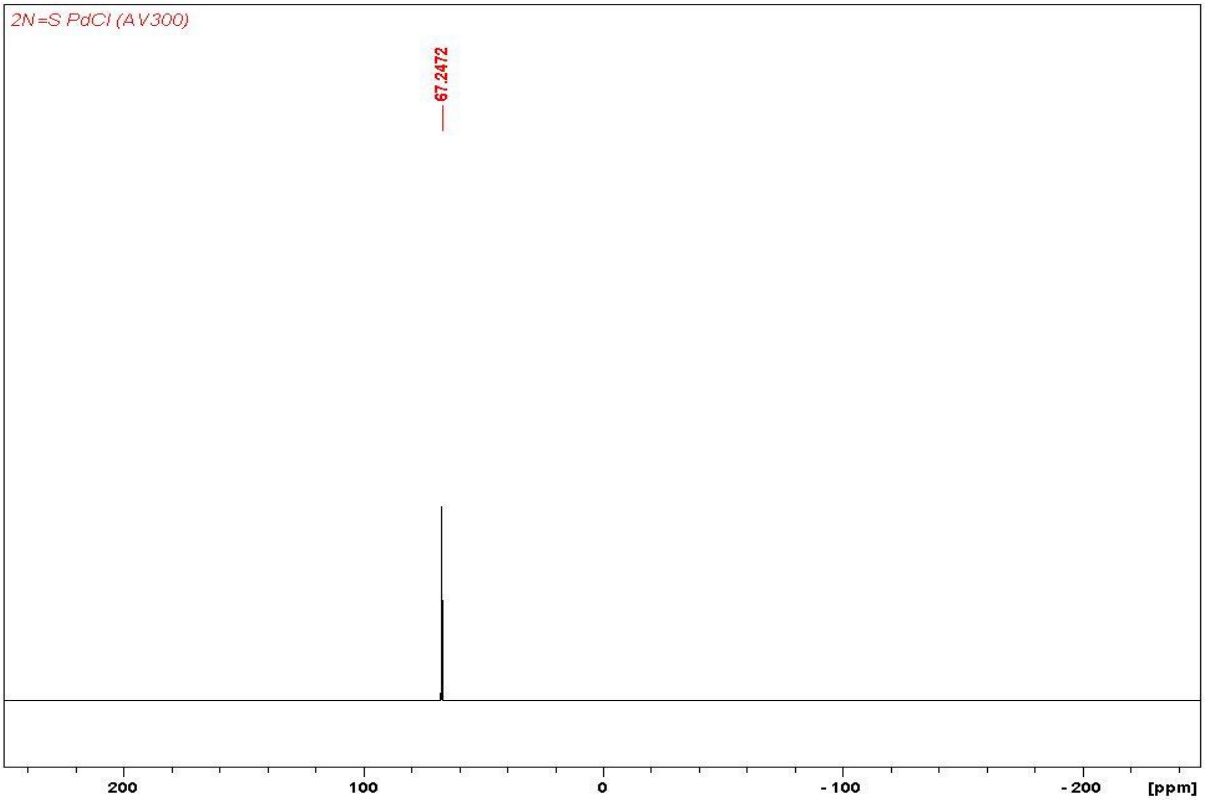


Figure s8. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4a**.

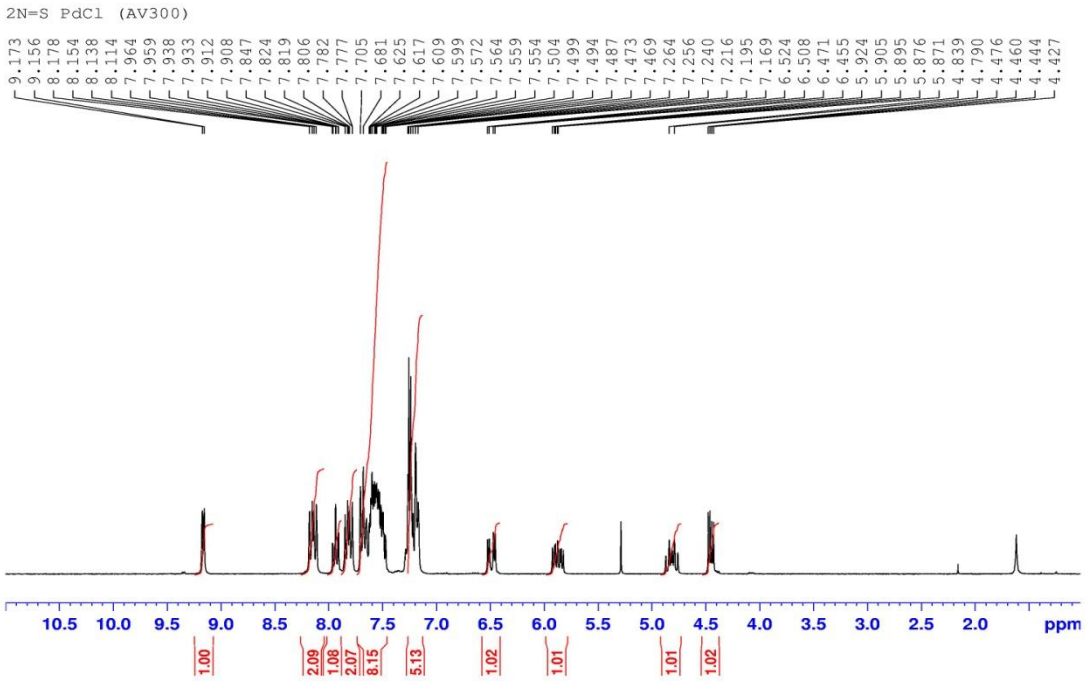


Figure s9. ^{1}H NMR spectrum of compound **4a**.

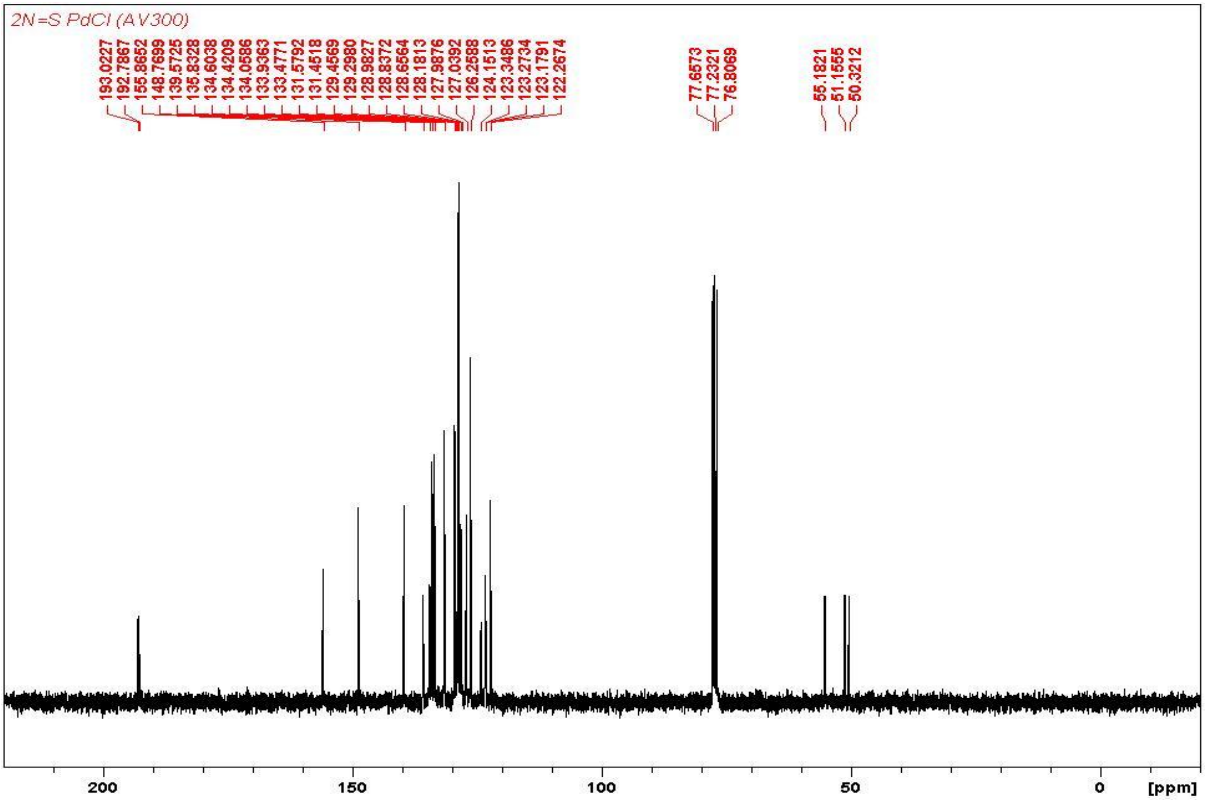


Figure s10. ^{13}C NMR spectrum of compound **4a**.

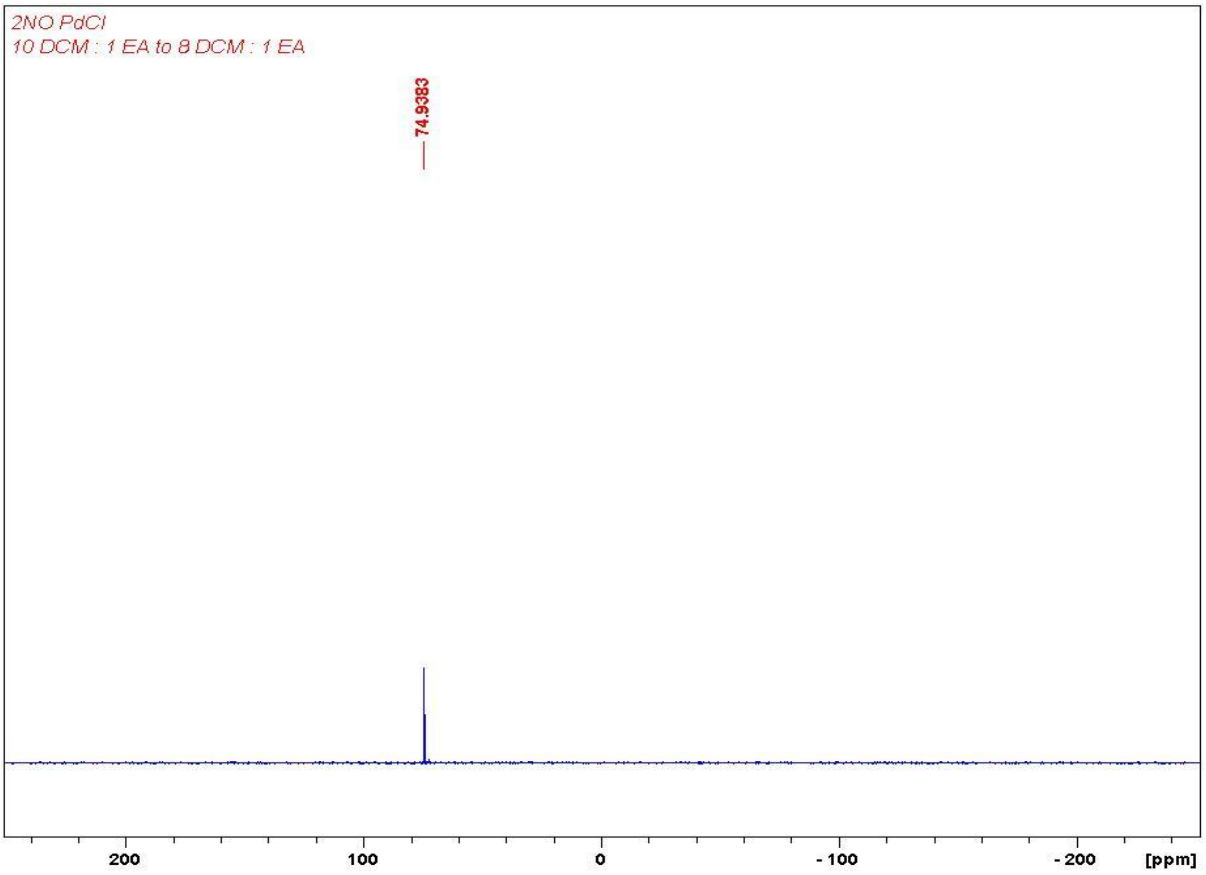


Figure s11. $^{31}P\{^{1}H\}$ NMR spectrum of compound **4b**.

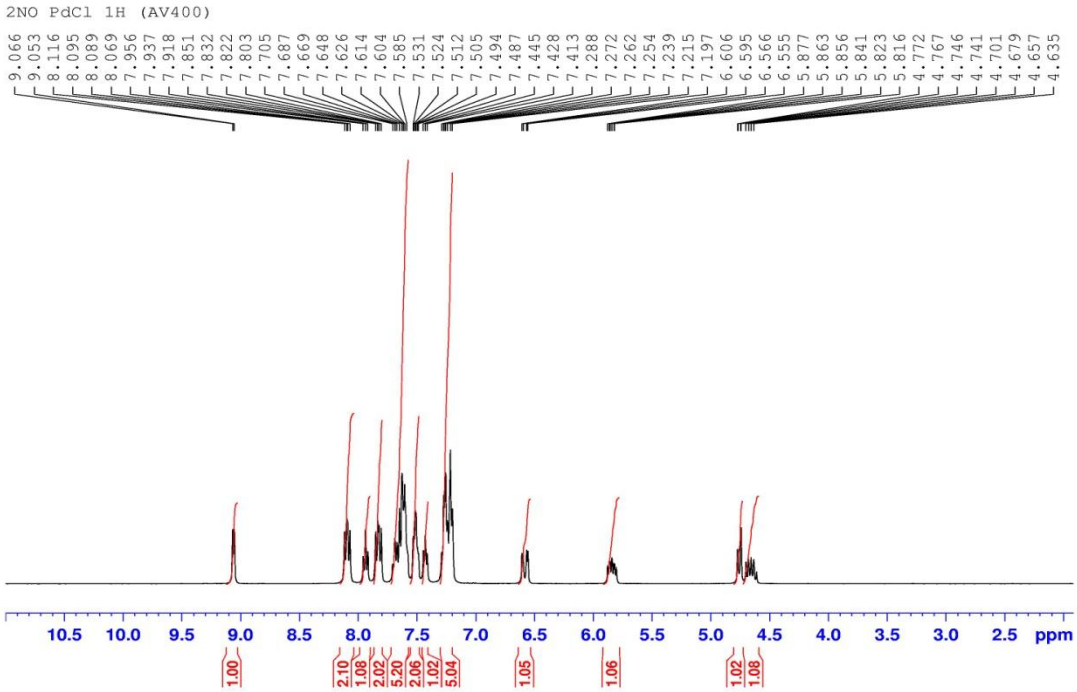


Figure s12. ^{1}H NMR spectrum of compound **4b**.

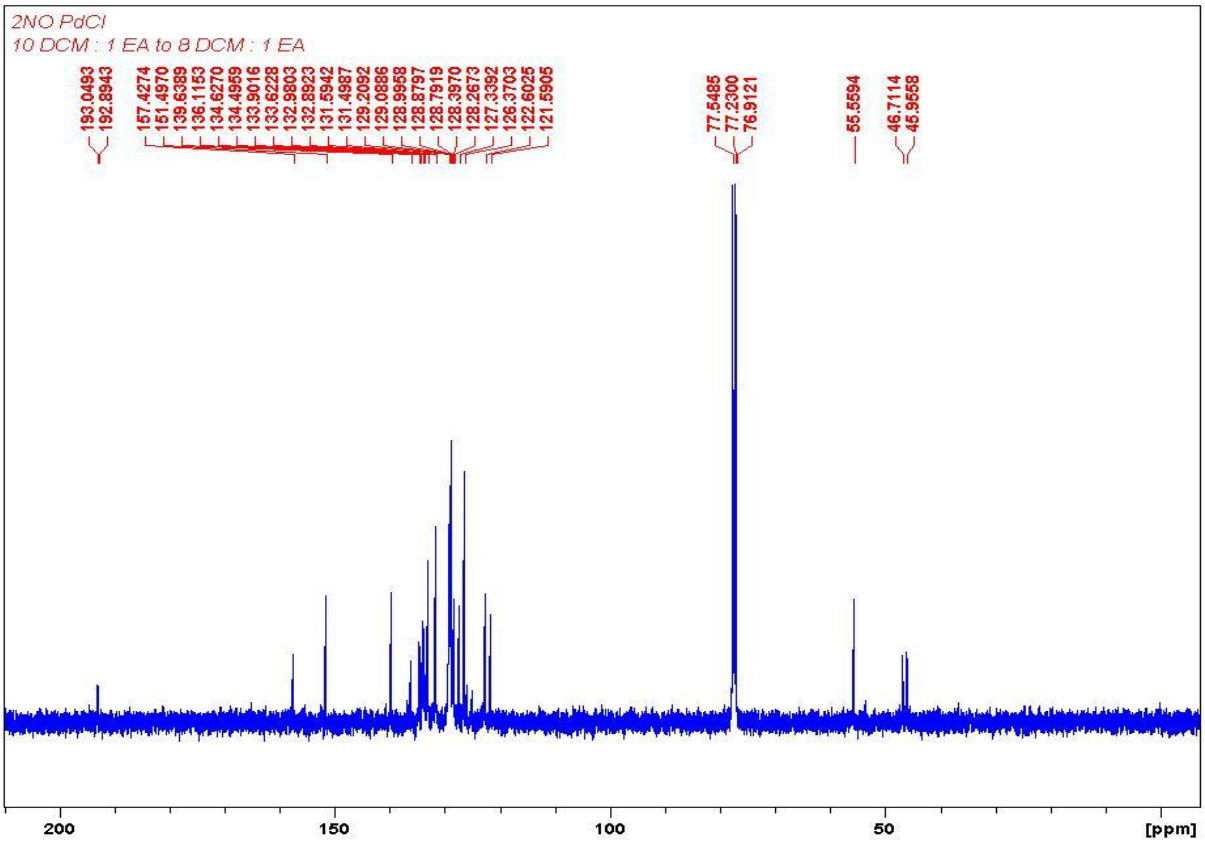


Figure s13. ^{13}C NMR spectrum of compound **4b**.

2D ^{1}H-^{1}H NOESY NMR Spectrum of Complex 4

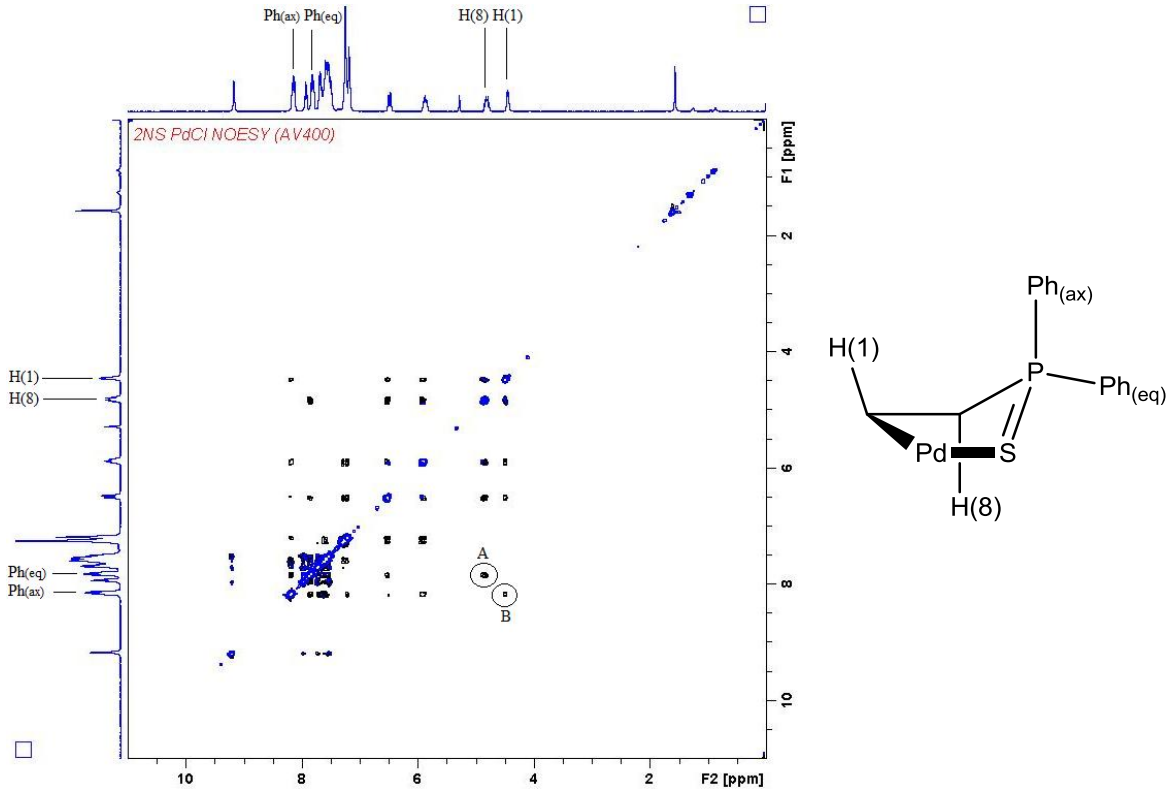


Figure s14. 2D ^{1}H-^{1}H NOESY NMR spectrum of complex **4a**.

A detailed analysis of the ^{1}H-^{1}H NOESY NMR spectrum of complex **4a** revealed the presence of the expected H(8)-Ph$_{(eq)}$ (A) and H(1)-Ph$_{(ax)}$ (B) NOE interactions arising from the S-P-C-C-Pd chelate ring with the δ-conformation, as observed in the solid state. If this chiral five-membered ring undergoes a facile δ-λ dynamic transformation, the H(8)-Ph$_{(ax)}$ and H(1)-Ph$_{(eq)}$ NOE interactions would be observed.[3] The absence of these NOE signals in the 2-D NMR spectrum indicated that the S-P-C-C-Pd chelate ring is locked in the δ-conformation in solution.

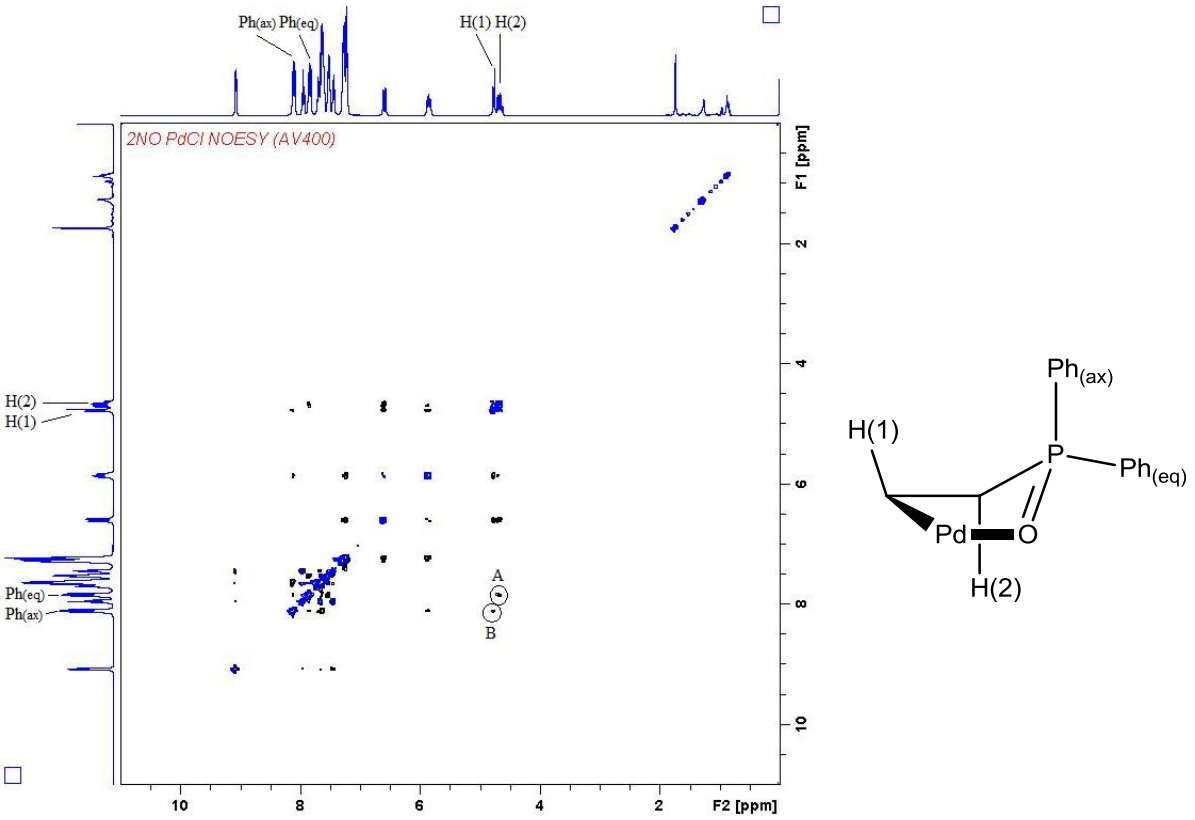
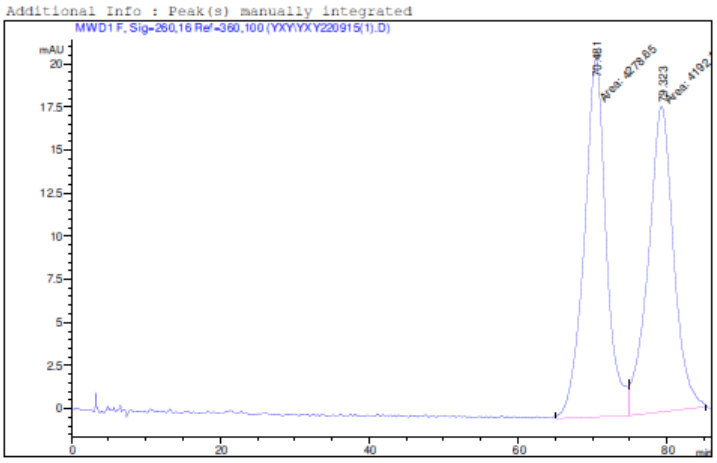


Figure s15. 2D ^{1}H-^{1}H NOESY NMR spectrum of complex **4b**.

From the spectrum, NOE interactions of H(2)-$Ph_{(eq)}$ (A) and H(1)-$Ph_{(ax)}$ (B) were observed. In conjunction with the absence of NOE signals arising from H(2)-$Ph_{(ax)}$ and H(1)-$Ph_{(eq)}$, this conclusively imply that the O-P-C-C-Pd chelate ring is locked in the δ-conformation in solution.

HPLC Spectra

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Use Multiplier & Dilution Factor with ISTDs


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Figure s16. HPLC spectra of racemic **3b**.

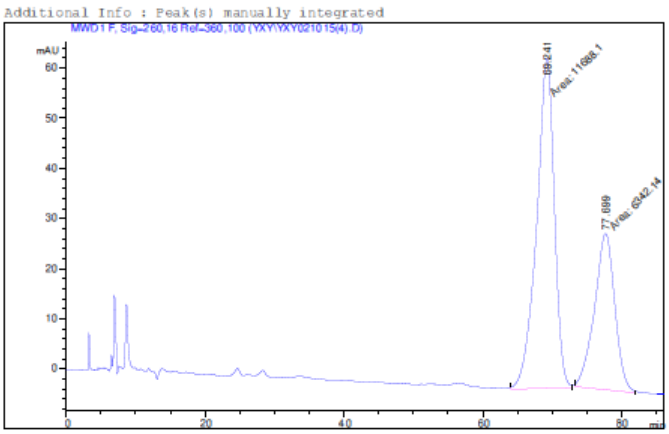


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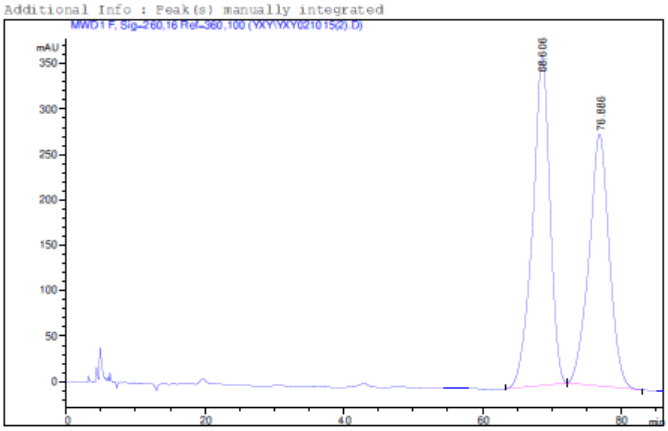
Figure s17. HPLC spectra of chiral **3b** in Table 3 Entry 1.

Additional Info : Peak(s) manually integrated

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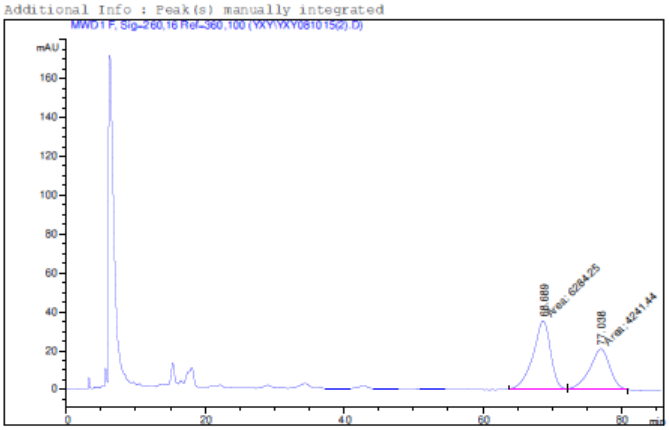
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.606 BB    2.4941 6.28704e4   363.45331  52.7967
   2  76.886 BB    2.8167 5.62099e4   277.08539  47.2033
```

Figure s18. HPLC spectra of chiral **3b** in Table 3 Entry 2.

Additional Info : Peak(s) manually integrated

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                    Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.689 MM    2.9584 6284.25049   35.40379  59.7039
   2  77.038 MM    3.3732 4241.43701   20.95658  40.2961
```
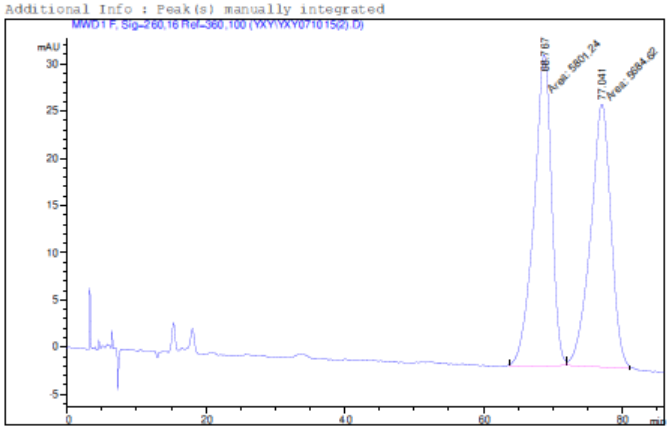

Figure s19. HPLC spectra of chiral **3b** in Table 3 Entry 3.

Additional Info : Peak(s) manually integrated




```
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                    Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.767 MM    2.9363 5801.23779   32.92863  50.5077
   2  77.041 MM    3.4051 5684.62158   27.82411  49.4923
```
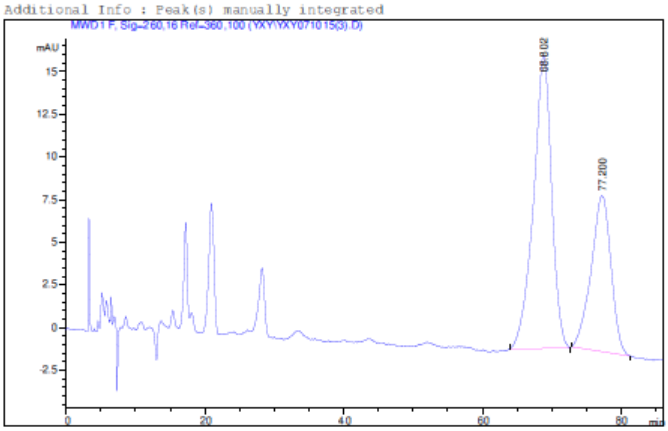

Figure s20. HPLC spectra of chiral **3b** in Table 3 Entry 4.

Additional Info : Peak(s) manually integrated




```
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                    Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.802 BB    2.1389 3126.46387   17.16551  63.2547
   2  77.200 BB    2.3280 1816.19788    9.13300  36.7453
```
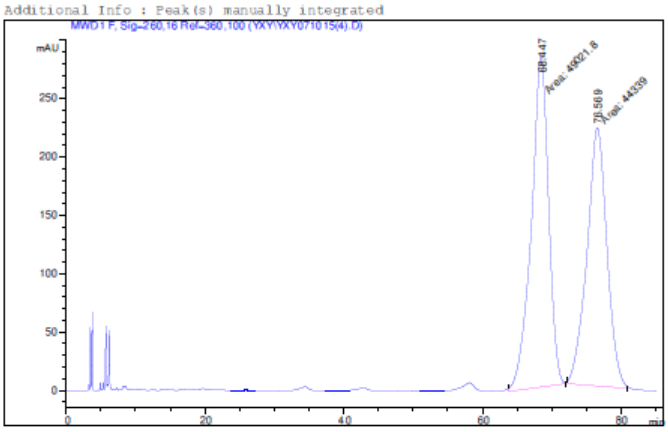

Figure s21. HPLC spectra of chiral **3b** in Table 3 Entry 5.

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                    Area Percent Report
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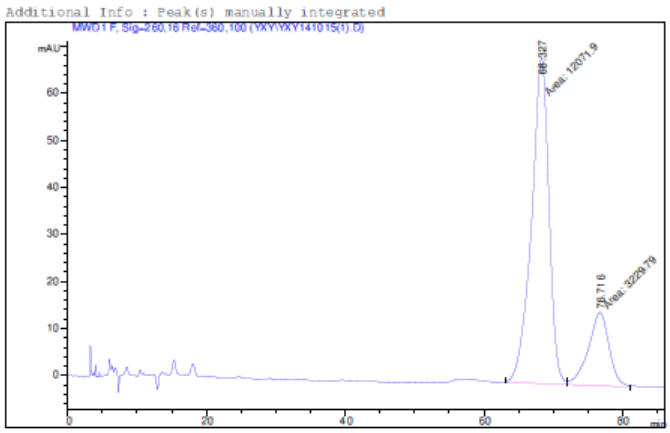
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.447 MM    2.8781 4.90218e4   283.87424  52.5079
   2  76.569 MM    3.3376 4.43390e4   221.41270  47.4921
```

Figure s22. HPLC spectra of chiral **3b** in Table 3 Entry 6.




```
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                    Area Percent Report
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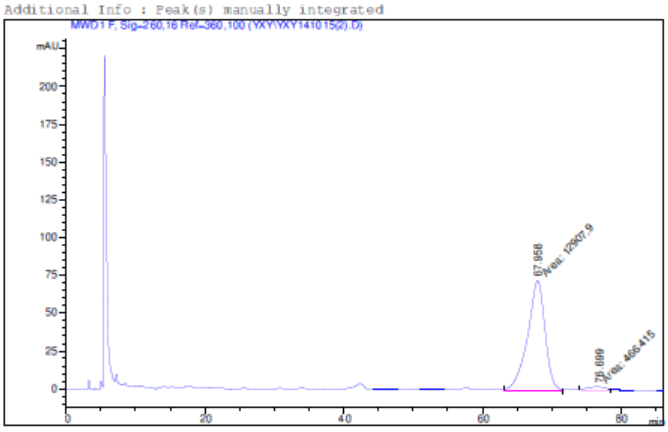
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.327 MF    2.9033 1.20719e4   69.30078  78.8926
   2  76.716 FM    3.4548 3229.78809  15.58112  21.1074
```

Figure s23. HPLC spectra of chiral **3b** in Table 3 Entry 7.

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  67.958 MM    2.9465 1.29079e4    73.01295  96.5126
   2  76.699 MM    3.0162  466.41479    2.57730   3.4874
```
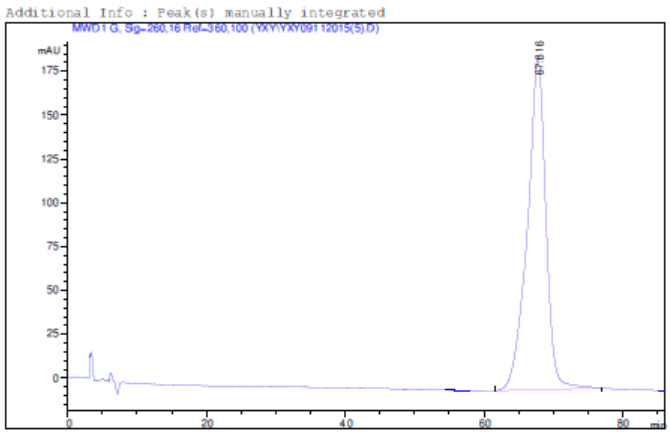

Figure s24. HPLC spectra of chiral **3b** in Table 3 Entry 8.

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                        Area Percent Report
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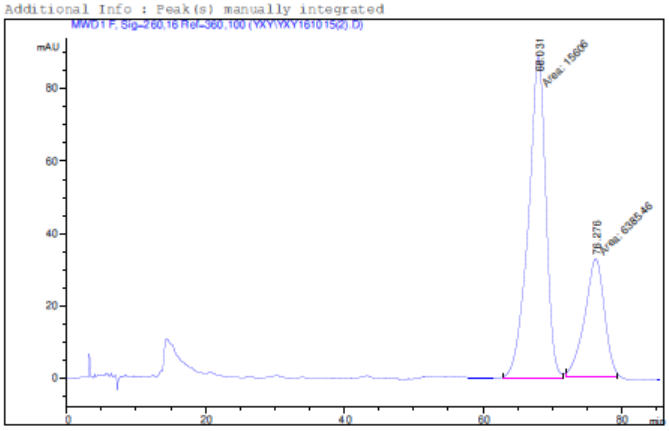
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  67.816 BB    2.6035 3.51101e4   188.80940 100.0000
```

Figure s25. HPLC spectra of chiral **3b** in Table 3 Entry 8 after a single recrystallization.

Additional Info : Peak(s) manually integrated




```
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                    Area Percent Report
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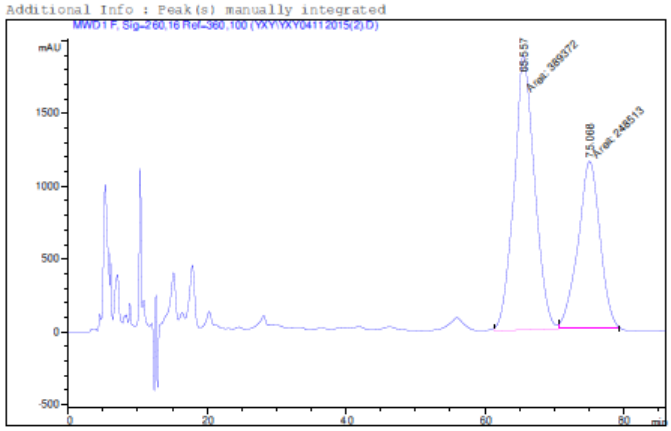
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  68.031 MM    2.9129 1.56060e4   89.29166  70.9639
   2  76.276 MM    3.2661 6385.45703   32.58500  29.0361
```

Figure s26. HPLC spectra of chiral **3b** in Table 3 Entry 9.

Additional Info : Peak(s) manually integrated

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                    Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  65.557 MM    3.4416 3.89372e5  1885.61292  61.0411
   2  75.068 MM    3.6295 2.48513e5  1141.17688  38.9589
```
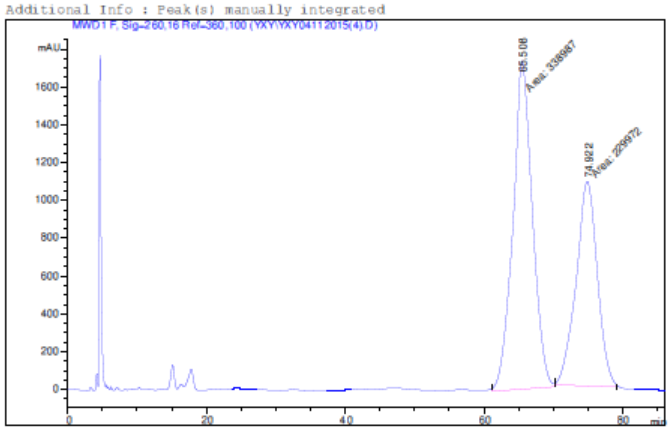

Figure s27. HPLC spectra of chiral **3b** in Table 3 Entry 10.

Additional Info : Peak(s) manually integrated

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                      Area Percent Report
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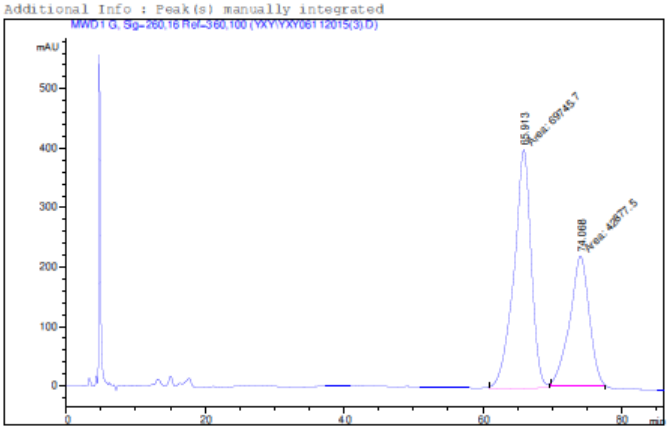
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 F, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  65.508 MM    3.2509 3.38987e5  1737.90320  59.5803
   2  74.922 MM    3.5412 2.29972e5  1082.36047  40.4197
```

Figure s28. HPLC spectra of chiral **3b** in Table 3 Entry 11.

Additional Info : Peak(s) manually integrated




```
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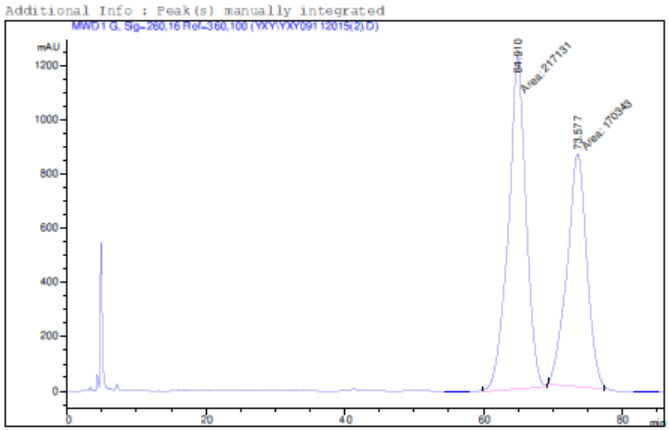
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  65.913 MM    2.8940 6.97457e4   401.67319  61.9284
   2  74.068 MM    3.2684 4.28775e4   218.64529  38.0716
```

Figure s29. HPLC spectra of chiral **3b** in Table 3 Entry 12.




```
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                        Area Percent Report
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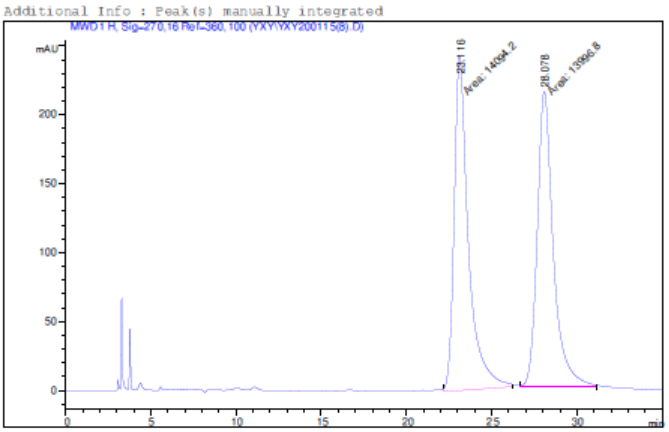
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  64.910 MM    2.9507 2.17131e5  1226.45667  56.0376
   2  73.577 MM    3.3052 1.70343e5   858.95428  43.9624
```

Figure s30. HPLC spectra of chiral **3b** in Table 3 Entry 13.




```
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                        Area Percent Report
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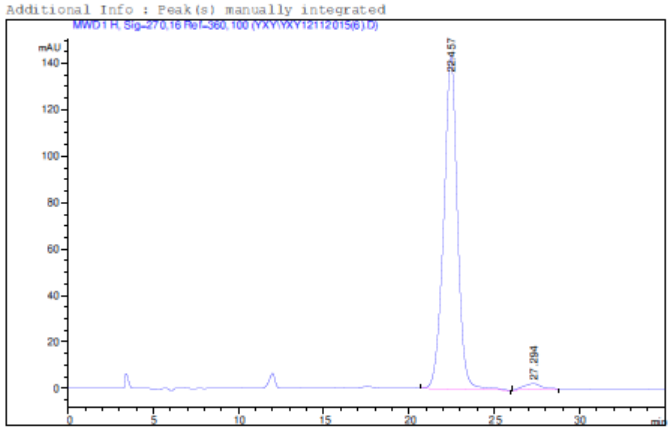
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 H, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]      %
----|-------|----|-------|----------|----------|--------|
   1  23.116 MM    0.9709 1.40942e4   241.94119  50.1733
   2  28.078 MM    1.0891 1.39968e4   214.18726  49.8267
```

Figure s31. HPLC spectra of racemic **3a**.

Additional Info : Peak(s) manually integrated




```
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                        Area Percent Report
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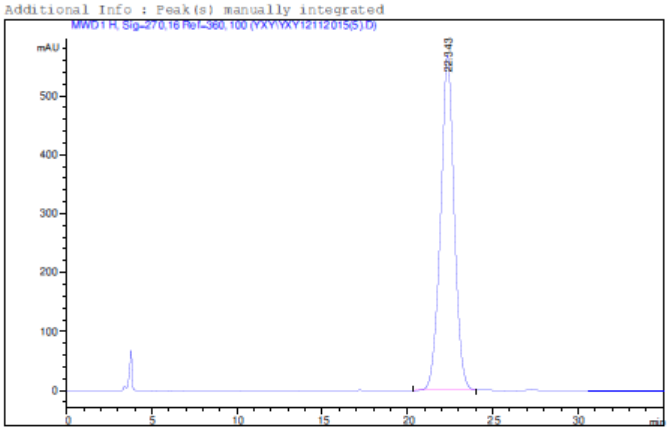
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 H, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.457 BB    0.8279 8023.23096  143.58231  97.8933
   2  27.294 BB    0.8114  172.66145    2.50121   2.1067
```

Figure s32. HPLC spectra of chiral **3a** in Table 3 Entry 14.

Additional Info : Peak(s) manually integrated




```
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                        Area Percent Report
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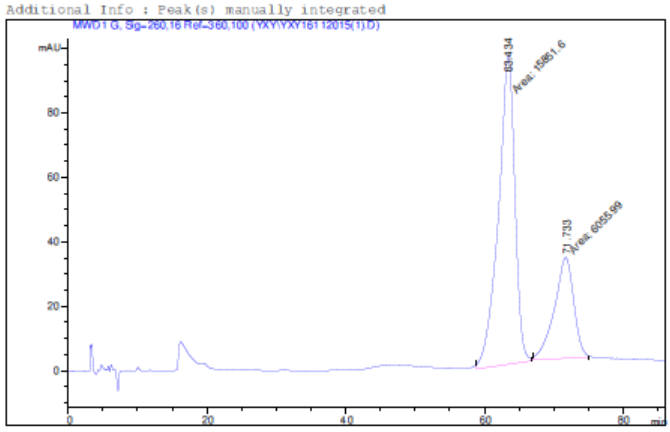
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 H, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  22.343 BB    0.8270 3.16957e4   568.04395 100.0000
```

Figure s33. HPLC spectra of chiral **3a** in Table 3 Entry 14 after a single recrystallization.

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                      Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  63.434 MM    2.7562 1.58516e4    95.85513  72.3566
   2  71.733 MM    3.2209 6055.98926   31.33655  27.6434
```
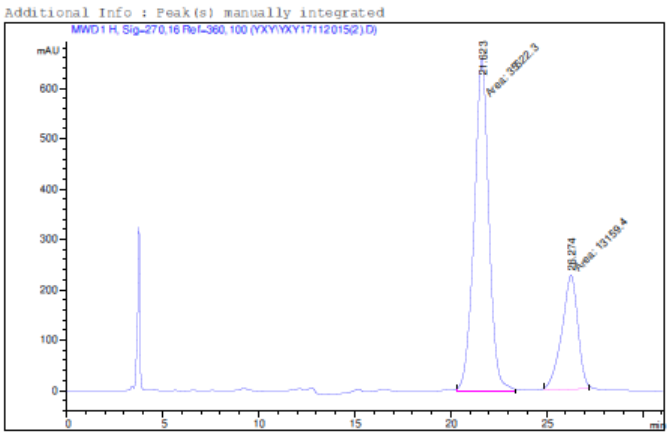

Figure s34. HPLC spectra of chiral **3b** in Table 3 Entry 15.




```
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                      Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 H, Sig=270,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  21.623 MM    0.8951 3.55223e4   661.45160  72.9685
   2  26.274 MM    0.9711 1.31594e4   225.85184  27.0315

Totals :                  4.86816e4   887.30344
```
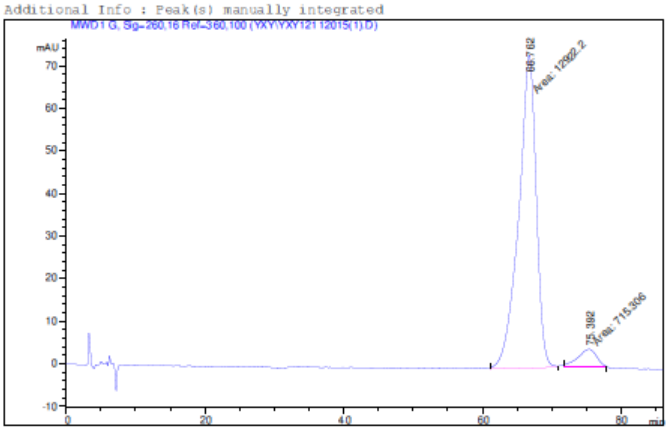

Figure s35. HPLC spectra of chiral **3a** in Table 3 Entry 16.

Additional Info : Peak(s) manually integrated




```
================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  66.762 MM    2.9360 1.29222e4    73.35397  94.7549
   2  75.392 MM    2.9861  715.30579    3.99245   5.2451
```
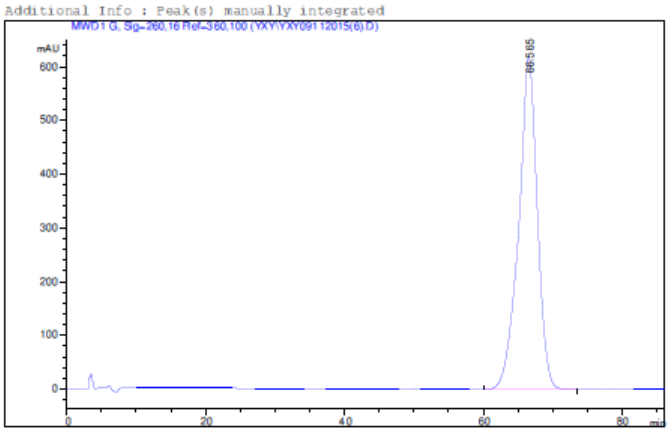

Figure s36. HPLC spectra of chiral **3b** in Table 4 Entry 1.

Additional Info : Peak(s) manually integrated




```
================================================================
                        Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  66.565 BB    2.6396 1.15237e5   619.65637 100.0000
```
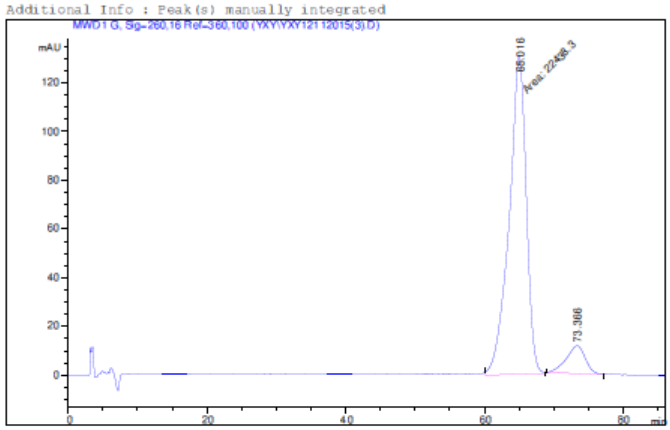

Figure s37. HPLC spectra of chiral **3b** in Table 4 Entry 1 after a single recrystallization.

Additional Info : Peak(s) manually integrated

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                    Area Percent Report
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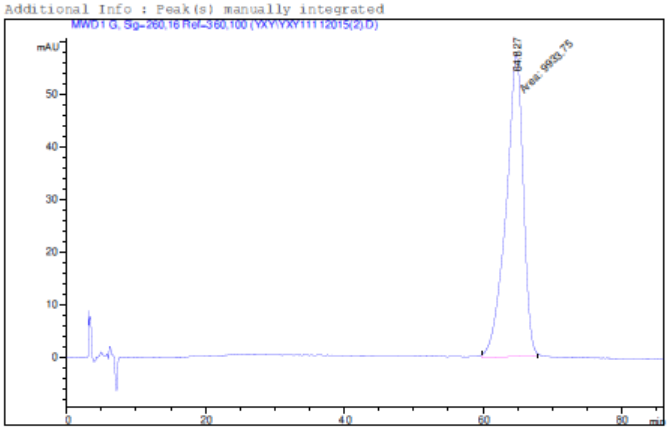
Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  65.016 MM    2.8566 2.24383e4   130.91524  91.2076
   2  73.366 BB    2.2201 2163.03955   11.41831   8.7924
```

Figure s38. HPLC spectra of chiral **3b** in Table 4 Entry 2.

Additional Info : Peak(s) manually integrated

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                    Area Percent Report
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Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]    [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  64.827 MM    2.8880 9933.74512   57.32833 100.0000
```
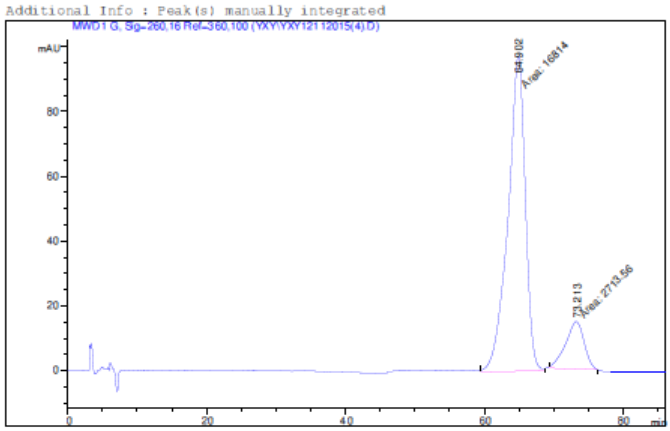
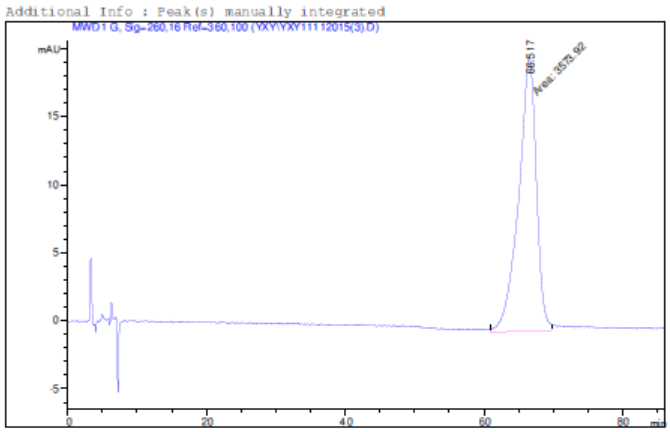

Figure s39. HPLC spectra of chiral **3b** in Table 4 Entry 2 after a single recrystallization.




```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1  64.902 MM    2.8845 1.68140e4    97.15002  86.1039
   2  73.213 MM    3.0849 2713.56299   14.66041  13.8961
```

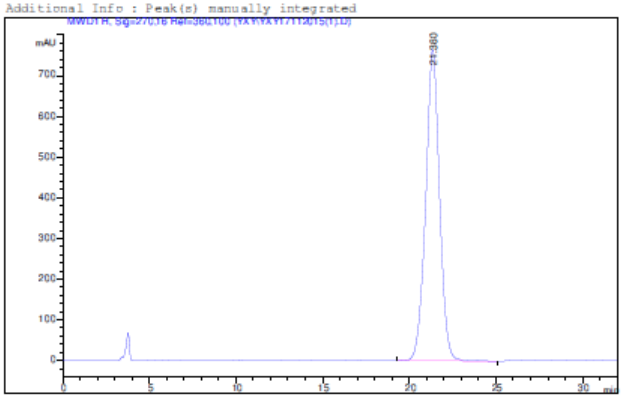
Figure s40. HPLC spectra of chiral **3b** in Table 4 Entry 3.




```
================================================================
                      Area Percent Report
================================================================

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:                :      1.00000  [ng/ul]    (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 G, Sig=260,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|---------|--------|
   1  66.517 MM    2.9589 3573.92017   20.13099 100.0000
```

Figure s41. HPLC spectra of chiral **3b** in Table 4 Entry 3 after a single recrystallization.

Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1.00000 [ng/ul] (not used in calc.)
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 H, Sig=270,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.360	BB	0.8256	4.25477e4	764.13892	100.0000
Totals :				4.25477e4	764.13892	

Figure s42. HPLC spectra of chiral **3a** (after recrystallization) from catalytic "self-breeding" of complex **4a**.

Crystallographic Data

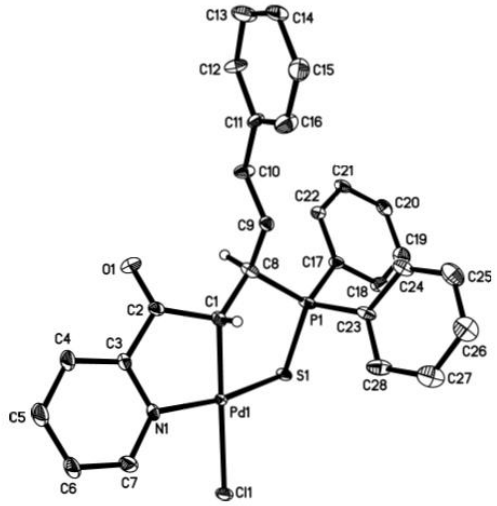


Figure s43. Single crystal X-ray structure of NC(sp^3)S PdCl complex **4a**.

Table s1. Crystallographic data of NC(sp^3)S PdCl complex **4a**.

Chemical formula	$C_{28}H_{23}ClNOPPdS$	
Formula weight	594.35 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.400 x 0.410 x 0.420 mm	
Crystal habit	yellow block	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.3737(3) Å	α = 90°
	b = 12.3461(4) Å	β = 90°
	c = 23.8575(7) Å	γ = 90°
Volume	2466.45(14) $Å^3$	
Z	4	
Density (calculated)	1.601 g/cm^3	
Absorption coefficient	1.033 mm^{-1}	
F(000)	1200	
Theta range for data collection	2.94 to 37.90°	
Index ranges	-14<=h<=14, -21<=k<=14, -40<=l<=40	
Reflections collected	36512	
Independent reflections	13283 [R(int) = 0.0435]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6830 and 0.6710	
Refinement method	Full-matrix least-squares on F^2	

Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	13283 / 651 / 419	
Goodness-of-fit on F^2	1.250	
Δ/σ_{max}	0.001	
Final R indices	12637 data; I>2σ(I)	R1 = 0.0520, wR2 = 0.0992
	all data	R1 = 0.0555, wR2 = 0.1002
Weighting scheme	$w=1/[\sigma^2(F_o^2)+4.5090P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(0)	
Largest diff. peak and hole	1.144 and -2.716 eÅ^{-3}	
R.M.S. deviation from mean	0.149 eÅ^{-3}	

Table s2. Bond lengths (Å) for NC(sp^3)S PdCl complex **4a**.

Pd1-C1	2.049(4)	C18-C19	1.391(5)	C11-C12	1.387(12)
Pd1-S1	2.2884(9)	C20-C21	1.389(7)	C12-C13	1.365(14)
C1-C2	1.497(6)	C23-C24	1.403(12)	C14-C15	1.392(17)
C1-C8A	1.548(14)	C23-P1	1.851(11)	C8A-C9A	1.560(17)
C2-C3	1.512(5)	C25-C26	1.365(16)	C9A-C10A	1.302(13)
C3-C4	1.385(6)	C27-C28	1.393(16)	C11A-C12A	1.39
C5-C6	1.383(7)	C23A-C28A	1.39	C12A-C13A	1.39
C7-N1	1.339(5)	C24A-C25A	1.39	C14A-C15A	1.39
C8-P1	1.811(14)	C26A-C27A	1.39	C17-C22	1.389(5)
C10-C11	1.479(11)	P1-S1	2.0098(13)	C17-P1	1.795(3)
C11-C16	1.415(13)	Pd1-N1	2.051(3)	C19-C20	1.388(6)
C13-C14	1.398(18)	Pd1-Cl1	2.3900(10)	C21-C22	1.385(5)
C15-C16	1.391(15)	C1-C8	1.535(14)	C23-C28	1.410(15)
C8A-P1	1.831(14)	C2-O1	1.211(5)	C24-C25	1.384(16)
C10A-C11A	1.500(10)	C3-N1	1.344(5)	C26-C27	1.366(15)
C11A-C16A	1.39	C4-C5	1.388(6)	C23A-C24A	1.39
C13A-C14A	1.39	C6-C7	1.392(6)	C23A-P1	1.755(10)
C15A-C16A	1.39	C8-C9	1.483(17)	C25A-C26A	1.39
C17-C18	1.398(5)	C9-C10	1.326(11)	C27A-C28A	1.39

Table s3. Bond angles (°) for NC(sp^3)S PdCl complex **4a**.

C1-Pd1-N1	81.84(14)	C1-Pd1-S1	91.97(11)
N1-Pd1-S1	170.95(10)	C1-Pd1-Cl1	174.66(12)
N1-Pd1-Cl1	95.24(10)	S1-Pd1-Cl1	91.43(3)
C2-C1-C8	114.9(7)	C2-C1-C8A	110.5(7)
C2-C1-Pd1	103.3(2)	C8-C1-Pd1	122.8(6)

C8A-C1-Pd1	117.3(6)	O1-C2-C1	125.7(4)
O1-C2-C3	121.4(4)	C1-C2-C3	112.8(3)
N1-C3-C4	122.2(3)	N1-C3-C2	114.2(3)
C4-C3-C2	123.6(4)	C3-C4-C5	118.6(4)
C6-C5-C4	118.9(4)	C5-C6-C7	119.6(4)
N1-C7-C6	121.0(4)	C9-C8-C1	111.5(10)
C9-C8-P1	113.7(10)	C1-C8-P1	104.6(9)
C10-C9-C8	122.7(10)	C9-C10-C11	125.7(8)
C12-C11-C16	117.1(8)	C12-C11-C10	119.5(8)
C16-C11-C10	123.3(8)	C13-C12-C11	122.5(10)
C12-C13-C14	120.2(11)	C15-C14-C13	119.2(12)
C16-C15-C14	119.8(12)	C15-C16-C11	121.0(10)
C1-C8A-C9A	113.8(10)	C1-C8A-P1	103.1(8)
C9A-C8A-P1	116.9(10)	C10A-C9A-C8A	125.1(10)
C9A-C10A-C11A	126.4(8)	C12A-C11A-C16A	120.0
C12A-C11A-C10A	122.1(6)	C16A-C11A-C10A	117.9(6)
C13A-C12A-C11A	120.0	C12A-C13A-C14A	120.0
C15A-C14A-C13A	120.0	C14A-C15A-C16A	120.0
C15A-C16A-C11A	120.0	C22-C17-C18	120.3(3)
C22-C17-P1	123.3(3)	C18-C17-P1	116.4(3)
C19-C18-C17	119.2(4)	C20-C19-C18	120.3(4)
C19-C20-C21	120.1(4)	C22-C21-C20	120.0(4)
C21-C22-C17	120.0(4)	C24-C23-C28	117.0(10)
C24-C23-P1	120.5(10)	C28-C23-P1	122.5(10)
C25-C24-C23	121.6(10)	C26-C25-C24	119.5(10)
C25-C26-C27	121.3(10)	C26-C27-C28	119.7(11)
C27-C28-C23	120.7(10)	C24A-C23A-C28A	120.0
C24A-C23A-P1	120.1(9)	C28A-C23A-P1	119.5(8)
C23A-C24A-C25A	120.0	C26A-C25A-C24A	120.0
C27A-C26A-C25A	120.0	C26A-C27A-C28A	120.0
C27A-C28A-C23A	120.0	C7-N1-C3	119.6(4)
C7-N1-Pd1	127.0(3)	C3-N1-Pd1	112.2(2)
C23A-P1-C17	105.7(6)	C17-P1-C8	114.4(5)
C23A-P1-C8A	108.5(8)	C17-P1-C8A	112.2(5)
C17-P1-C23	103.5(6)	C8-P1-C23	108.1(8)
C23A-P1-S1	115.9(5)	C17-P1-S1	110.68(15)
C8-P1-S1	110.0(5)	C8A-P1-S1	104.0(5)
C23-P1-S1	109.9(5)	P1-S1-Pd1	96.87(5)

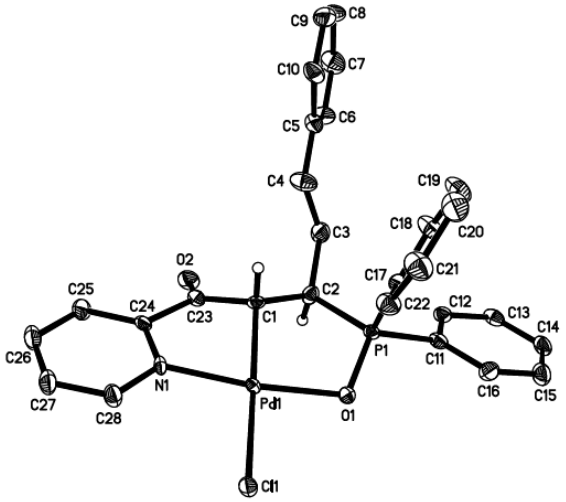


Figure s44. Single crystal X-ray structure of NC(sp^3)S PdCl complex **4b**.

Table s4. Crystallographic data of NC(sp^3)S PdCl complex **4b**.

Chemical formula	$C_{28}H_{23}ClNO_2PPd$	
Formula weight	578.29 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.320 x 0.400 x 0.420 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.4079(4) Å	α = 90°
	b = 12.0255(6) Å	β = 90.682(3)°
	c = 23.7756(12) Å	γ = 90°
Volume	2403.8(2) $Å^3$	
Z	4	
Density (calculated)	1.598 g/cm^3	
Absorption coefficient	0.977 mm^{-1}	
F(000)	1168	
Theta range for data collection	2.41 to 33.84°	
Index ranges	-13<=h<=13, -18<=k<=18, -36<=l<=37	
Reflections collected	74249	
Independent reflections	18919 [R(int) = 0.1015]	
Coverage of independent reflections	99.1%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.7450 and 0.6840	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/4	

Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	18919 / 1 / 613
Goodness-of-fit on F^2	1.074
Δ/σ_{max}	0.001
Final R indices	16986 data; $I>2\sigma(I)$ R1 = 0.0582, wR2 = 0.1223
	all data R1 = 0.0661, wR2 = 0.1257
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0284P)^2+4.7783P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.0(0)
Largest diff. peak and hole	2.079 and -2.125 eÅ^{-3}
R.M.S. deviation from mean	0.154 eÅ^{-3}

Table s5. Bond lengths (Å) for NC(sp^3)S PdCl complex **4b**.

Pd1-N1	2.002(5)	Pd1-C1	2.031(6)	C26-C27	1.384(10)	C27-C28	1.381(9)
Pd1-O1	2.073(4)	Pd1-Cl1	2.4050(15)	C28-N1	1.358(8)	C29-C51	1.489(8)
Pd1-P1	2.9546(15)	Pd2-C29	2.023(5)	C29-C30	1.541(8)	C30-C31	1.508(8)
Pd2-N2	2.024(5)	Pd2-O3	2.068(4)	C30-P2	1.822(6)	C31-C32	1.320(9)
Pd2-Cl2	2.4057(14)	C1-C23	1.485(9)	C32-C33	1.476(9)	C33-C34	1.395(10)
C1-C2	1.536(9)	C2-C3	1.520(9)	C33-C38	1.408(10)	C34-C35	1.370(10)
C2-P1	1.830(6)	C3-C4	1.326(10)	C35-C36	1.395(12)	C36-C37	1.399(11)
C4-C5	1.462(9)	C5-C10	1.386(10)	C37-C38	1.400(9)	C39-C40	1.389(8)
C5-C6	1.403(10)	C6-C7	1.394(11)	C39-C44	1.401(8)	C39-P2	1.797(6)
C7-C8	1.387(11)	C8-C9	1.387(11)	C40-C41	1.396(8)	C41-C42	1.377(9)
C9-C10	1.377(9)	C11-C16	1.392(9)	C42-C43	1.392(9)	C43-C44	1.394(9)
C11-C12	1.395(9)	C11-P1	1.797(6)	C45-C50	1.390(9)	C45-C46	1.403(9)
C12-C13	1.397(8)	C13-C14	1.382(10)	C45-P2	1.797(6)	C46-C47	1.393(10)
C14-C15	1.390(10)	C15-C16	1.385(9)	C47-C48	1.382(11)	C48-C49	1.382(11)
C17-C18	1.384(9)	C17-C22	1.409(9)	C49-C50	1.403(10)	C51-O4	1.209(7)
C17-P1	1.799(6)	C18-C19	1.381(10)	C51-C52	1.497(8)	C52-N2	1.365(8)
C19-C20	1.358(12)	C20-C21	1.413(11)	C52-C53	1.388(9)	C53-C54	1.381(9)
C21-C22	1.399(10)	C23-O2	1.225(7)	C54-C55	1.369(10)	C55-C56	1.384(9)
C23-C24	1.512(8)	C24-N1	1.344(8)	C56-N2	1.337(8)	O1-P1	1.528(4)
C24-C25	1.391(9)	C25-C26	1.391(10)	O3-P2	1.531(4)		

Table s6. Bond angles (°) for NC(sp^3)S PdCl complex **4b**.

N1-Pd1-C1	82.4(2)	C46-C45-P2	121.3(5)	C19-C18-C17	120.2(7)
C1-Pd1-O1	87.5(2)	C48-C47-C46	120.0(7)	C19-C20-C21	120.9(7)

C1-Pd1-Cl1	174.65(17)	C48-C49-C50	120.2(7)	C21-C22-C17	118.6(6)
N1-Pd1-P1	141.68(15)	O4-C51-C29	126.5(5)	O2-C23-C24	121.2(6)
O1-Pd1-P1	29.22(12)	C29-C51-C52	112.0(5)	N1-C24-C25	122.7(6)
C29-Pd2-N2	82.4(2)	N2-C52-C51	113.7(5)	C25-C24-C23	124.0(6)
N2-Pd2-O3	168.21(18)	C54-C53-C52	118.9(6)	C27-C26-C25	118.4(6)
N2-Pd2-Cl2	95.67(15)	C54-C55-C56	119.7(6)	N1-C28-C27	121.5(6)
C23-C1-C2	115.5(5)	C24-N1-C28	118.4(5)	C51-C29-Pd2	104.3(4)
C2-C1-Pd1	114.6(4)	C28-N1-Pd1	126.8(4)	C31-C30-C29	110.5(5)
C3-C2-P1	118.4(5)	C56-N2-Pd2	126.8(4)	C29-C30-P2	102.6(4)
C4-C3-C2	125.7(6)	P1-O1-Pd1	109.3(2)	C31-C32-C33	126.3(6)
C10-C5-C6	117.9(6)	O1-P1-C11	111.6(3)	C34-C33-C32	118.7(6)
C6-C5-C4	123.7(6)	C11-P1-C17	103.3(3)	C35-C34-C33	121.5(7)
C8-C7-C6	119.1(7)	C11-P1-C2	113.7(3)	C35-C36-C37	120.4(6)
C10-C9-C8	121.0(7)	O1-P1-Pd1	41.47(16)	C37-C38-C33	120.9(6)
C16-C11-C12	119.6(6)	C17-P1-Pd1	100.9(2)	C40-C39-P2	121.9(5)
C12-C11-P1	122.4(5)	O3-P2-C39	112.5(2)	C39-C40-C41	119.2(6)
C14-C13-C12	120.0(6)	C39-P2-C45	104.7(3)	C41-C42-C43	121.0(6)
C16-C15-C14	120.1(7)	C39-P2-C30	112.1(3)	C43-C44-C39	119.3(6)
C18-C17-C22	120.5(6)	N1-Pd1-O1	168.63(19)	C50-C45-P2	120.0(5)
C22-C17-P1	118.7(5)	N1-Pd1-Cl1	96.01(15)	C47-C46-C45	120.8(7)
C20-C19-C18	120.4(7)	O1-Pd1-Cl1	94.52(12)	C49-C48-C47	120.0(7)
C22-C21-C20	119.3(7)	C1-Pd1-P1	59.40(17)	C45-C50-C49	120.5(6)
O2-C23-C1	126.5(6)	Cl1-Pd1-P1	121.71(5)	O4-C51-C52	121.5(6)
C1-C23-C24	112.2(5)	C29-Pd2-O3	87.29(19)	N2-C52-C53	120.5(6)
N1-C24-C23	113.2(5)	C29-Pd2-Cl2	174.04(16)	C53-C52-C51	125.7(6)
C24-C25-C26	118.7(6)	O3-Pd2-Cl2	95.13(12)	C55-C54-C53	119.9(6)
C28-C27-C26	120.3(7)	C23-C1-Pd1	104.7(4)	N2-C56-C55	120.9(6)
C51-C29-C30	115.7(5)	C3-C2-C1	115.0(5)	C24-N1-Pd1	114.4(4)
C30-C29-Pd2	116.0(4)	C1-C2-P1	100.7(4)	C56-N2-C52	120.1(5)
C31-C30-P2	115.4(4)	C3-C4-C5	125.9(7)	C52-N2-Pd2	112.6(4)
C32-C31-C30	125.3(6)	C10-C5-C4	118.4(6)	P2-O3-Pd2	111.2(2)
C34-C33-C38	118.3(6)	C7-C6-C5	121.5(7)	O1-P1-C17	111.3(3)
C38-C33-C32	122.9(6)	C7-C8-C9	119.5(6)	O1-P1-C2	107.3(3)
C34-C35-C36	120.0(8)	C9-C10-C5	120.8(7)	C17-P1-C2	109.7(3)
C36-C37-C38	118.9(7)	C16-C11-P1	117.7(5)	C11-P1-Pd1	149.8(2)
C40-C39-C44	120.8(6)	C11-C12-C13	120.0(6)	C2-P1-Pd1	73.9(2)
C44-C39-P2	117.2(4)	C13-C14-C15	120.1(6)	O3-P2-C45	111.0(3)
C42-C41-C40	120.1(6)	C15-C16-C11	120.2(6)	O3-P2-C30	107.8(2)
C42-C43-C44	119.5(6)	C18-C17-P1	120.5(5)	C45-P2-C30	108.7(3)
C50-C45-C46	118.5(6)				

Selected Bond Lengths and Angles of Complex 4

Table s7. Selected bond lengths (Å) and angles (º) of complex **4**.

	(*R*,*R*)-**4a**	(*R*,*R*)-**4b**
Pd←N	2.051(3)	2.002(5)
Pd←E (E = S, O)	2.288(1)	2.073(4)
Pd-Cl	2.390(1)	2.405(2)
Pd-C(sp^3)	2.049(4)	2.031(6)
C-Pd←E	91.97(11)	87.50(20)
C-Pd←N	81.84(14)	82.40(20)
C-Pd-Cl	174.66(12)	174.65(17)
Cl-Pd←E	91.43(3)	94.52(12)
Cl-Pd←N	95.24(10)	96.01(15)
N→Pd←E	170.95(10)	168.63(19)