Nickel Catalyzed Enantioselective Hydroarsination of Nitrostyrene

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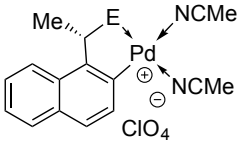
Electronic Supporting Information

General Information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. Solvents were purchased from their respective companies (ACN, MeOH, DCM: VWR Chemicals, DEE: Merck, toluene, n-hexane Avantor, Acetone: Sigma-Aldrich, THF: Tedia) and used as supplied. DCM and THF were dried and distilled. Where necessary, solvents were degassed prior to use. A Low Temp Pairstirrer PSL-1400 was used for controlling low temperature reactions. Column chromatography was done on 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. 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.

The catalysts (*S*)-**1a/b**[1] were prepared according to literature methods. Conversion of M-Cl complexes **5** to M-OAc complexes **2** were performed as described in literature.[2] All other reactants and reagents were used as a supplied.

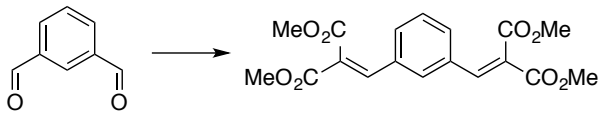


(*S*)-**1a** E = PPh_2
(*S*)-**1b** E = NMe_2

Figure s1. Catalysts involved in this work.

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

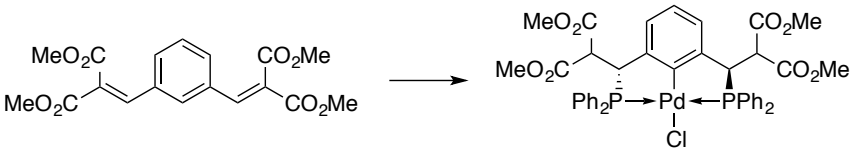
General Procedure for the Synthesis of Complexes (*R*,*R*)-5



A **B**

Scheme s1. Synthesis of ligand precursor.

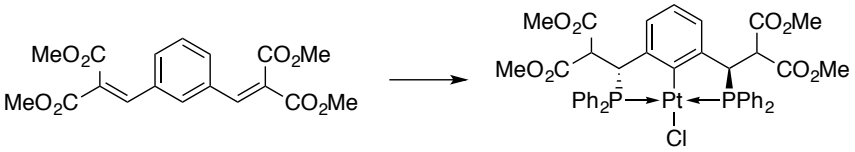
To a solution of dimethyl malonate (5.40g, 14.91 mmol, 2.0 equiv) and piperidine (6.34g, 1.49 mmol, 0.2 equiv) in *n*-heptane (5 mL), isophthaldehyde **A** (1.00g, 7.45 mmol, 1.0 equiv) and glacial AcOH (89.47 mg,1.49 mmol, 0.2 equiv.) were added sequentially. The mixture was refluxed at 140ºC under Dean-Stark conditions for 24 h. The mixture was cooled to RT and volatiles were removed under reduced pressure. The mixture was extracted with DCM (3 X 30 mL) and the organic layer was washed with saturated $NaHCO_3$ (1 X 30 mL) and water (3 X 30 mL), dried over $MgSO_4$, filtered and concentrated. The crude product was purified by silica gel chromatography (2 *n*-hexanes : 1 EA) to afford compound **B** as a pale yellow solid in 80% yield. The spectroscopic data obtained is consistent with literature.[3]



B (*R*,*R*)-**5a**

Scheme s2. Synthesis of complex (*R*,*R*)-5a.

Catalyst (*S*)-**1a** (38.29 mg, 0.061 mmol, 5 mol %) was added to a solution of $HPPh_2$ (0.25 g, 1.33 mmol, 2.3 equiv.) in DCM (10 mL) and stirred for 10 minutes at room temperature before cooling to -80ºC. Compound **B** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the addition of NEt_3 (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL) dropwise. After stirring at -80ºC for 3 days, the solution was warmed up to RT. $PdCl_2(CH_3CN)_2$ (0.15 g, 0.578 mmol, 1.0 equiv.) was added and the solution was stirred overnight at RT. Volatiles were removed and the crude product was purified *via* silica gel chromatography (DCM) to afford complex (*R*,*R*)-**5a** as a white solid in 86% yield. The spectroscopic data obtained is consistent with literature.[3]

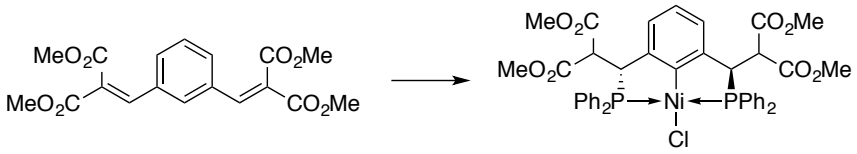


B (*R*,*R*)-**5b**

Scheme s3. Synthesis of complex (*R*,*R*)-5b.

Catalyst (*S*)-**1a** (38.29 mg, 0.061 mmol, 5 mol %) was added to a solution of $HPPh_2$ (0.25 g, 1.33 mmol, 2.3 equiv.) in DCM (10 mL) and stirred for 10 minutes at room temperature before cooling to 80ºC. Compound **B** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the addition of NEt_3 (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL) dropwise. After stirring at -80ºC for 3 days, the solution was warmed up to RT. Volatiles were removed and the residue was redissolved in toluene. $PtCl_2(CH_3CN)_2$ (0.20 g, 0.578 mmol, 1.0 equiv.) was added and the solution was heated at 100ºC for 4h. Upon cooling to RT, volatiles were removed and the crude product was purified *via* silica gel chromatography (19 DCM : 1 EA)

to afford complex (*R*,*R*)-**5b** as a white solid. The spectroscopic data obtained is consistent with literature.[3]



B (*R*,*R*)-**5c**

Scheme s4. Synthesis of complex (*R*,*R*)-5c.

Catalyst (*S*)-**1a** (38.29 mg, 0.061 mmol, 5 mol %) was added to a solution of $HPPh_2$ (0.25 g, 1.22 mmol, 2.1 equiv.) in DCM (10 mL) and stirred for 10 minutes at room temperature before cooling to -80ºC. Compound **B** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the addition of NEt_3 (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL) dropwise. After stirring at -80ºC for 3 days, the solution was warmed up to RT. Volatiles were removed and the residue was redissolved in EtOH. $NiCl_2(CH_3CN)_2$ (0.12 g, 0.578 mmol, 1.0 equiv.) in H_2O (1 mL) was added and the mixture heated at 60ºC for 4 h. Subsequently, $NEt_2{}^iPr$ (74.70 mg, 0.578 mmol, 1.0 equiv.) was added and the mixture was refluxed at 80ºC for 1 h. Upon cooling to RT, volatiles were removed and the crude product was purified *via* silica gel chromatography (19 DCM : 1 EA) to afford complex (*R*,*R*)-**5c** as a yellow solid in 68% yield. The spectroscopic data obtained is consistent with literature.[3]

General Procedure for Catalytic Hydroarsination Reaction

3 **4**

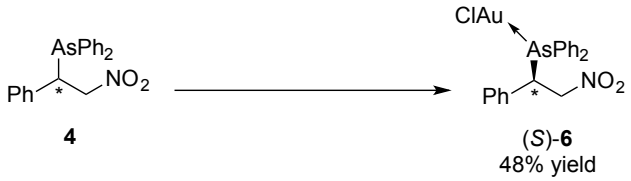
Scheme s5. Catalytic asymmetric hydroarsination reaction.

A stock solution of the catalyst in MeOH (1.00 mM, 5 mL, 5 mol %) was added to a solution of diphenylarsine (2.76 mg, 12.00 μmol, 1.2 equiv.) in the stated solvent (1 mL) and brought to the desired temperature. Nitrostyrene **3** (1.49 mg, 10.0 μmol, 1.0 equiv.) was subsequently added and washed down with the stated solvent to make 2 mL. The reaction was stirred at the indicated temperature and checked every 15 mins by TLC to monitor the consumption of nitrostyrene. Upon completion of the reaction, two drops of the crude reaction mixture was withdrawn from the flask and diluted with hexane (1 mL) to prepare the HPLC sample. The arsine adduct could be crystallized from a mixture of DCM/MeOH to afford the pure product **4** as white crystalline needles. The *ee* was determined on a Daicel Chiralpak ID column with *n*-hexane/2-propanol = 99/1, flow = 0.8 mL/min, wavelength = 254 nm. Retention times: 8.7 min (minor, *R* isomer), 9.5 min (major, *S* isomer). $[\alpha]_D$ = -45.2 (*c* 2.75, MeOH) (measured for Table 3 Entry 9). Mp: 88-90°C. ^{1}H NMR (CD_3CN, 400 MHz): δ 7.68-7.65 (m, 2H, Ar), 7.48-7.47 (m, 2H, Ar), 7.29-7.27 (m, 3H, Ar), 7.25-7.21 (m, 6H, Ar), 7.19-7.16 (m, 1H, Ar), 4.99 (dd, 1H, $^3J_{HH}$ = 13.0 Hz, $^3J_{HH}$ = 12.8 Hz, AsC*H*), 4.60 (dd, 1H, $^3J_{HH}$ = 13.0 Hz, $^2J_{HH}$ = 4.0 Hz, NC*H*), (dd, 1H, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 4.0 Hz, NC*H*); ^{13}C NMR (CD_3CN, 100 MHz): δ 134.5-128.1 (15C, Ar), 79.7 (s, 1C, As*C*), 43.8 (s, 1C, N*C*). HRMS (+ESI) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}NO_2As$, 380.0632; found, 380.0625. Anal. Calcd for $C_{20}H_{18}NO_2As$: C, 63.33; H, 4.78; N, 3.69. Found: C, 63.34; H, 5.09; N, 3.95 %.

Additional Notes: The arsine adduct **4** can be selectively precipitated from the crude reaction mixture by removing the reaction solvent, redissolving the residue in a minimal

amount of DCM and topping up with MeOH (2 mL). Upon stirring under reduced pressure, a white solid precipitates from the DCM/MeOH mixture.

General Procedure for Synthesis of Complex (*S*)-6



Scheme s6. Synthesis of complex (*S*)-6.

To a solution of adduct **4** (10.10 mg, 29.00 µmol, 1.0equiv.) in DCM (3 mL) was added $AuCl(SMe_2)$ (10.25 mg, 34.80 µmol, 1.2 equiv.). The mixture was stirred in the dark overnight at RT and subsequently washed with H_2O (3 X 10 mL) and dried over $MgSO_4$. The crude complex **6** could be recrystallized from ACN to afford pure complex (*S*)-**6** as colourless crystals in 48% yield. $[\alpha]_D$ = -84.4 (*c* 1.58, ACN). Mp: 130-131°C (*dec.)*. ^{1}H NMR (CD_3CN, 400 MHz): δ 7.94-7.91 (m, 2H, Ar), 7.66-7.46 (m, 3H, Ar), 7.40-7.37 (m, 3H, Ar), 7.35-7.35 (m, 2H, Ar), 7.34-7.33 (m, 2H, Ar), 7.27-7.24 (m, 3H, Ar), 5.27 (dd, 1H, $^3J_{HH}$ = 13.88 Hz, $^3J_{HH}$ =11.96 Hz, AsC*H*), 5.00 (dd, 1H, $^3J_{HH}$ = 11.90 Hz, $^2J_{HH}$ = 4.18 Hz, NC*H*), 4.85 (dd, 1H $^3J_{HH}$ = 13.92 Hz, $^2J_{HH}$ = 4.2 Hz, NC*H*); ^{13}C NMR (CD_3CN, 100 MHz): δ 134.5-128.1 (15C, Ar), 76.9 (s, 1C, As*C*), 43.8 (s, 1C, N*C*). HRMS (+ESI) m/z: $(M + H)^+$ calcd for $C_{20}H_{19}NO_2AsAuCl$, 613.9956; found, 613.9951. Anal. Calcd for $C_{20}H_{18}NO_2AsAuCl$: C, 39.27; H, 2.97; N, 2.29. Found: C, 39.73; H, 3.36; N, 2.27 %.

NMR Spectra

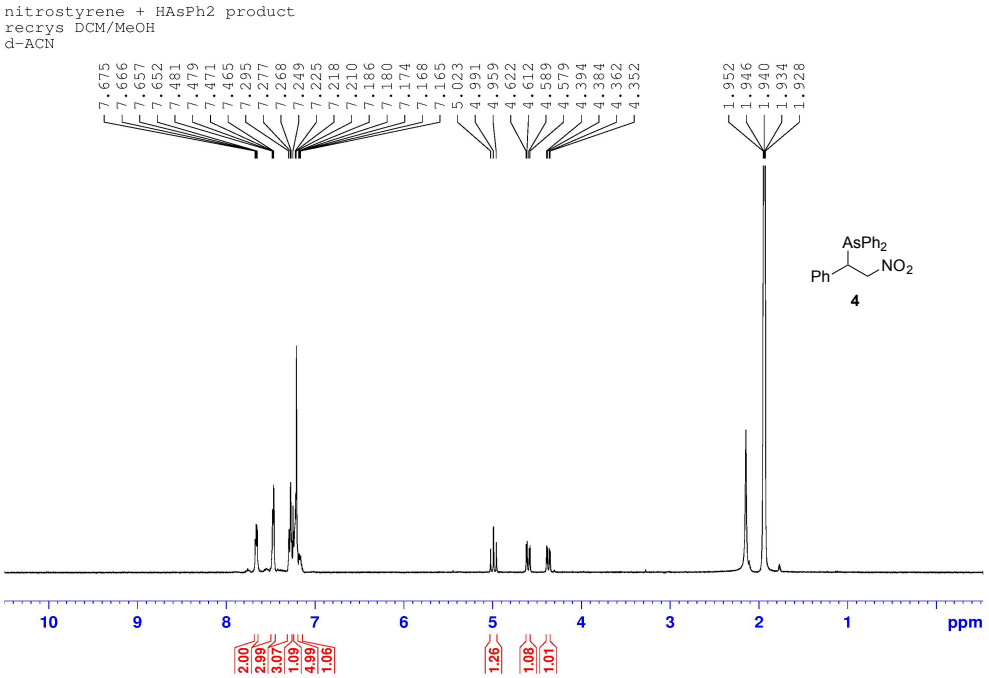


Figure s2. ^{1}H NMR spectrum of adduct 4 in CD_3CN, 400MHz.

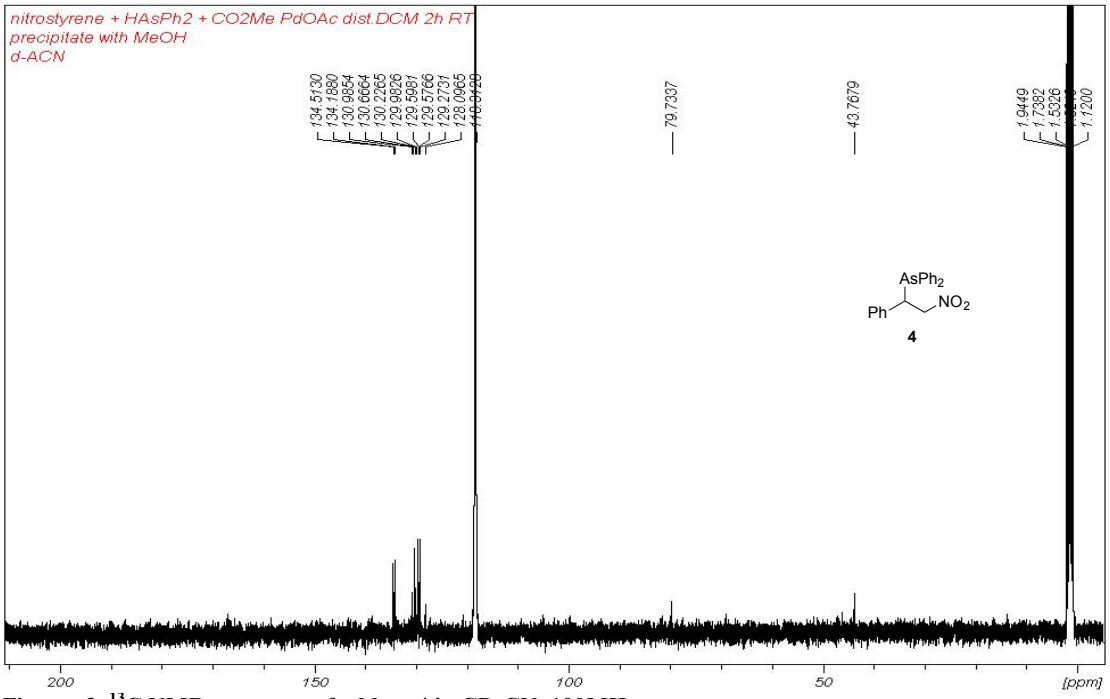


Figure s3. ^{13}C NMR spectrum of adduct 4 in CD_3CN, 100MHz.

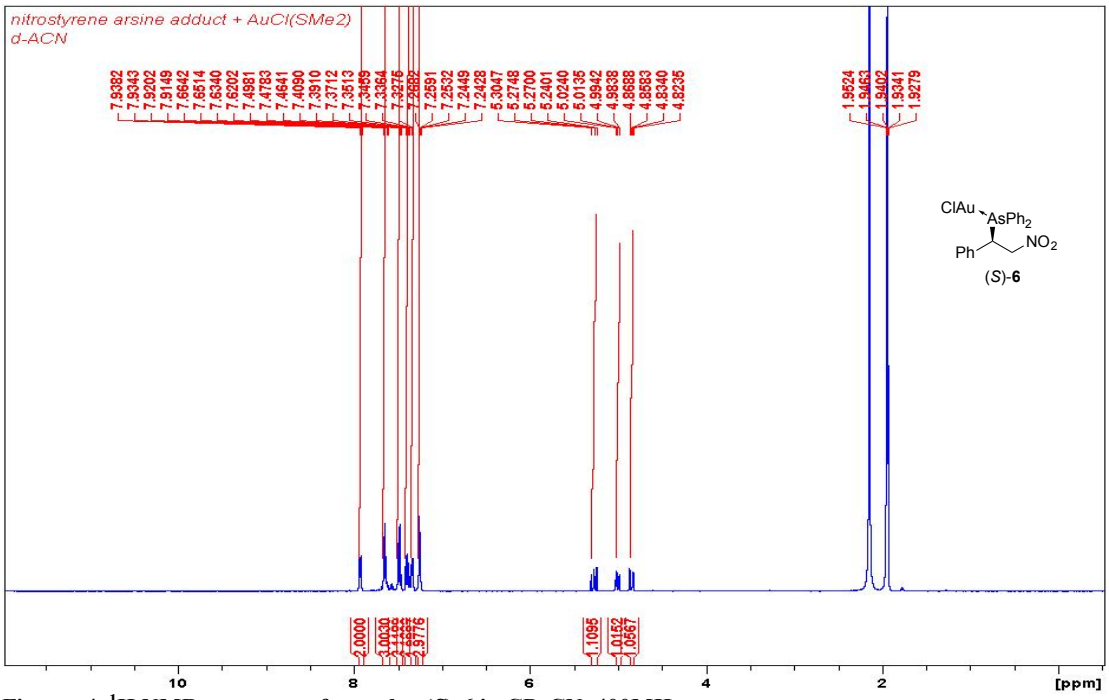


Figure s4. ^{1}H NMR spectrum of complex (*S*)-6 in CD_3CN, 400MHz.

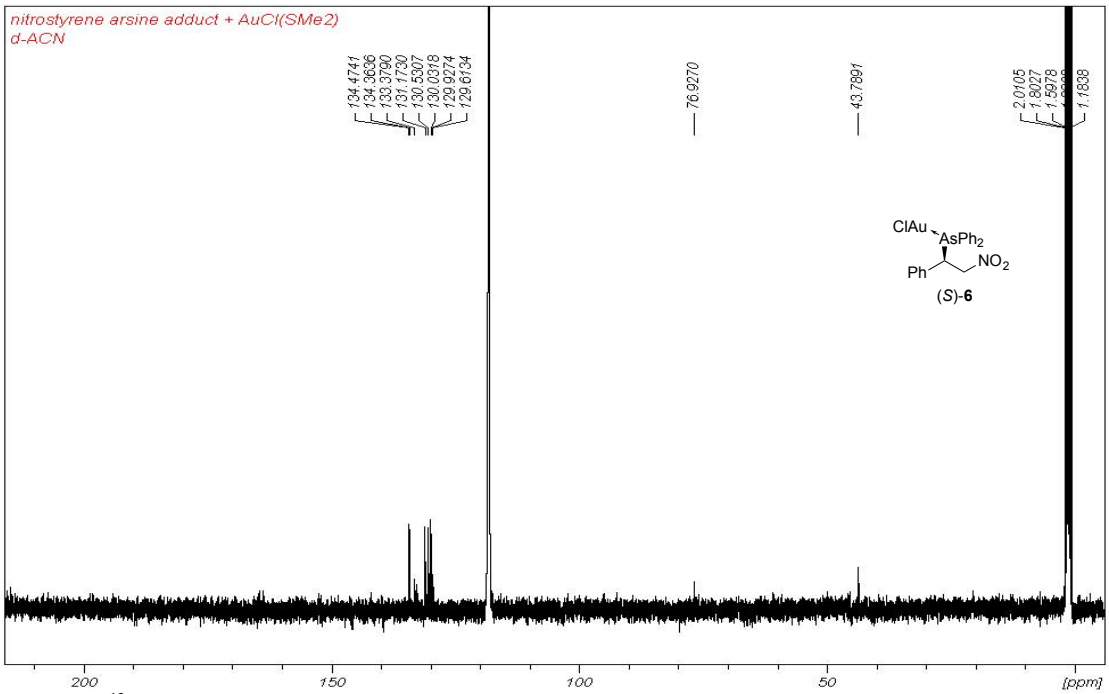


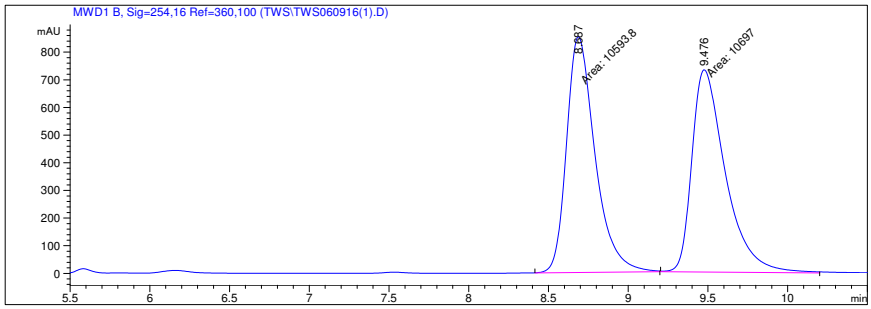
Figure s5. ^{13}C NMR spectrum of complex (*S*)-6 in CD_3CN, 100MHz.

References

[1] a) Y. Huang, R. J. Chew, Y.; Li, S. A. Pullarkat and P.-H. Leung, *Org. Lett.*, 2011, **13**, 5862; b) Y. Huang, S. A. Pullarkat, Y. Li and P.-H. Leung, *Chem. Commun*, 2010, **46**, 6950.
[2] X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics*, 2015, **34**, 5196.
[3] X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics*, 2015, **34**, 1582.

HPLC Spectra

Racemic adduct **4**

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   1   8.687 MM    0.2068 1.05938e4   853.82373  49.7577
   2   9.476 MM    0.2437 1.06970e4   731.61487  50.2423

Totals :                  2.12908e4  1585.43860
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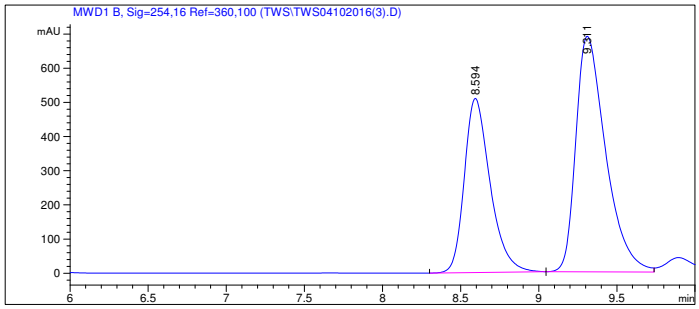
Figure s6. HPLC spectrum of racemic adduct 4.

Table 1 Entry 3

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Peak RetTime Type  Width     Area      Height     Area
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   1   8.594 BB    0.1760 5853.19580  509.77792  39.0131
   2   9.311 BV    0.2008 9149.96484  689.64508  60.9869

Totals :                  1.50032e4  1199.42300
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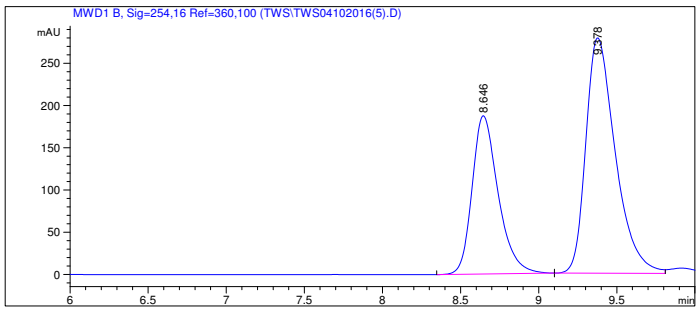
Figure s7. HPLC spectrum of chiral adduct 4 in Table 1 Entry 3.

Table 2 Entry 1

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Do not use Multiplier & Dilution Factor with ISTDs


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Peak RetTime Type  Width     Area      Height     Area
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   1   8.646 BB    0.1751 2169.89209  187.37817  37.2030
   2   9.378 BV    0.1993 3662.68677  278.71609  62.7970

Totals :                  5832.57886  466.09427
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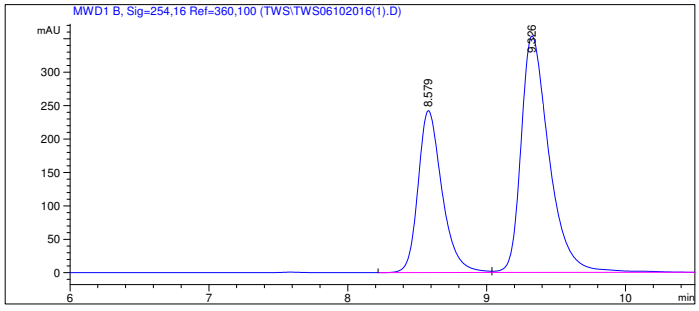
Figure s8. HPLC spectrum of chiral adduct 4 in Table 2 Entry 1.

Table 2 Entry 2

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Sample Amount:                :      1.00000  [ng/ul]   (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.579 BV    0.1817 2903.06812  242.37688  36.8709
   2   9.326 VB    0.2118 4970.54199  353.94751  63.1291

Totals :                  7873.61011  596.32439
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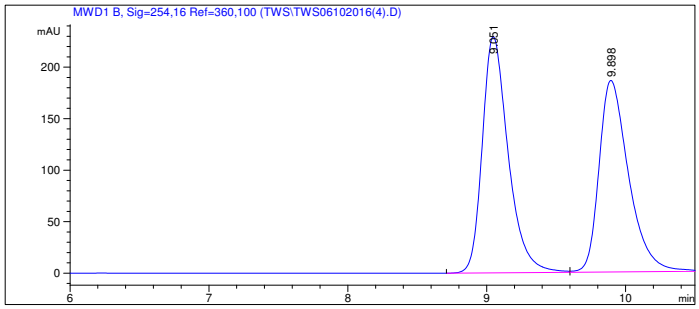
Figure s9. HPLC spectrum of chiral adduct 4 in Table 2 Entry 2.

Table 2 Entry 3

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Peak RetTime Type  Width     Area      Height     Area
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   1   9.051 BV    0.1974 2977.60376  229.50180  51.9359
   2   9.898 VB    0.2247 2755.62207  186.15942  48.0641

Totals :                  5733.22583  415.66122
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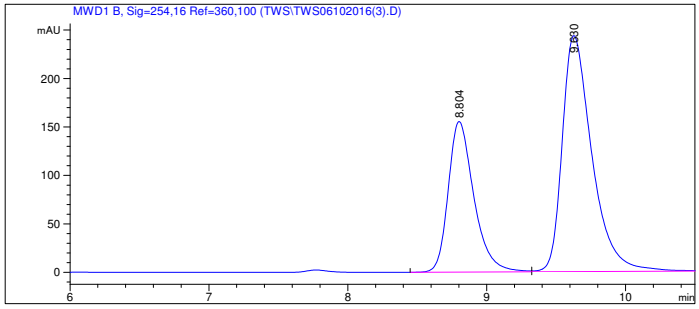
Figure s10. HPLC spectrum of chiral adduct 4 in Table 2 Entry 3.

Table 2 Entry 4

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Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.804 BV    0.1935 1990.90710  155.41502  35.4565
   2   9.630 VBA   0.2256 3624.16748  243.54282  64.5435

Totals :                  5615.07458  398.95784
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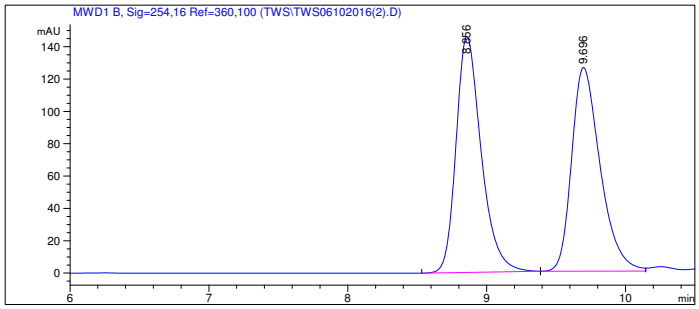
Figure s11. HPLC spectrum of chiral adduct 4 in Table 2 Entry 4.

Table 2 Entry 5

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Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.856 BB    0.1907 1835.72241  146.02344  50.4926
   2   9.696 BV    0.2166 1799.90637  126.03658  49.5074

Totals :                  3635.62878  272.06001
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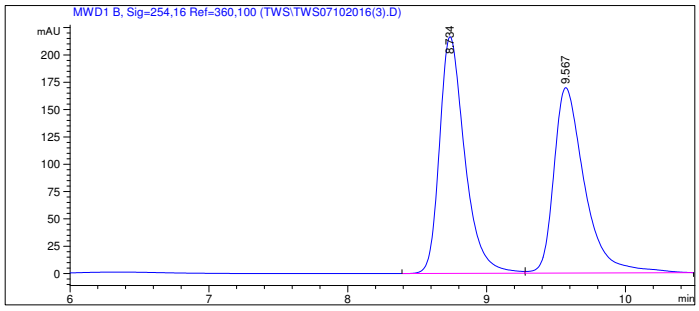
Figure s12. HPLC spectrum of chiral adduct 4 in Table 2 Entry 5.

Table 2 Entry 6

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Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.734 BV    0.1912 2732.97363  216.62737  51.1868
   2   9.567 VBA   0.2313 2606.24512  169.61288  48.8132

Totals :                  5339.21875  386.24025
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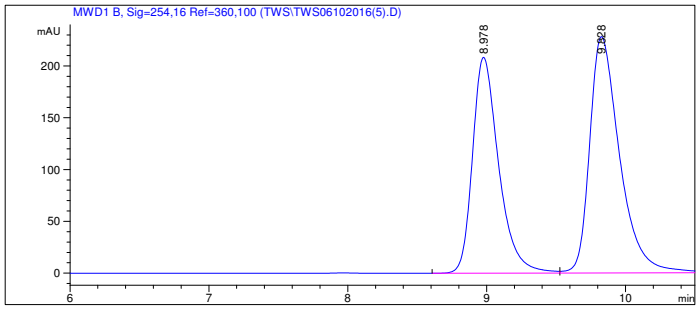
Figure s13. HPLC spectrum of chiral adduct 4 in Table 2 Entry 6.

Table 2 Entry 7

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Do not use Multiplier & Dilution Factor with ISTDs

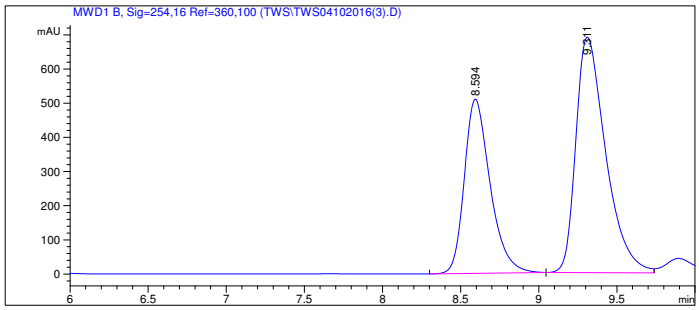

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.978 BV    0.1990 2734.94482  208.51024  44.2359
   2   9.828 VB    0.2282 3447.68896  228.31659  55.7641

Totals :                  6182.63379  436.82683
```

Figure s14. HPLC spectrum of chiral adduct 4 in Table 2 Entry 7.

Table 2 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.)
Do not use Multiplier & Dilution Factor with ISTDs

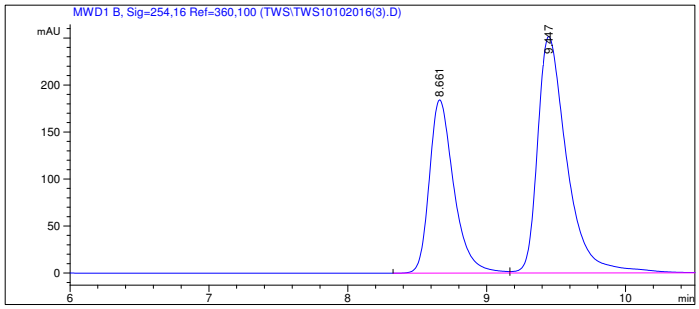

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.594 BB    0.1760 5853.19580  509.77792  39.0131
   2   9.311 BV    0.2008 9149.96484  689.64508  60.9869

Totals :                  1.50032e4  1199.42300
```

Figure s15. HPLC spectrum of chiral adduct 4 in Table 2 Entry 8.

Table 2 Entry 9

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

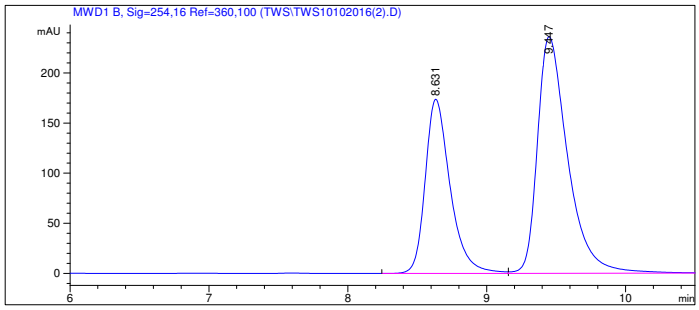

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.661 BV    0.1850 2260.53589  184.42827  38.0587
   2   9.447 VBA   0.2186 3679.06055  251.60297  61.9413

Totals :                  5939.59644  436.03123
```

Figure s16. HPLC spectrum of chiral adduct 4 in Table 2 Entry 9.

Table 2 Entry 10

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

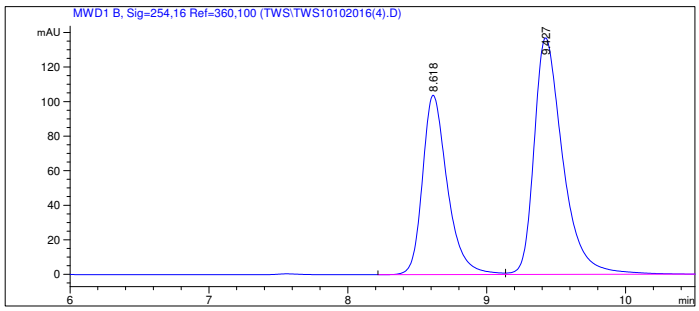

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.631 BV    0.1878 2172.72510  173.88896  37.7082
   2   9.447 VB    0.2292 3589.21753  236.32446  62.2918

Totals :                  5761.94263  410.21342
```

Figure s17. HPLC spectrum of chiral adduct 4 in Table 2 Entry 10.

Table 2 Entry 11

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

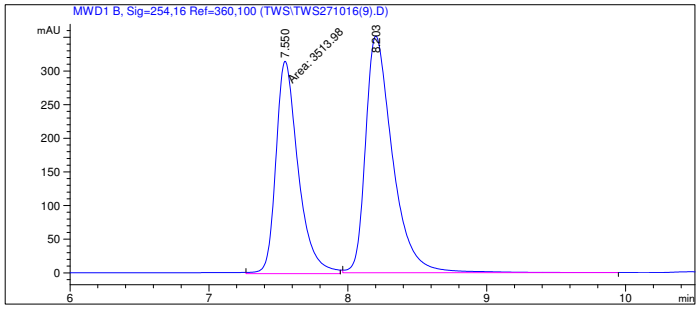

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.618 BV    0.1872 1292.54565  103.88760  39.6951
   2   9.427 VBA   0.2173 1963.64270  136.95599  60.3049

Totals :                  3256.18835  240.84359
```

Figure s18. HPLC spectrum of chiral adduct 4 in Table 2 Entry 11.

Table 3 Entry 1




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

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

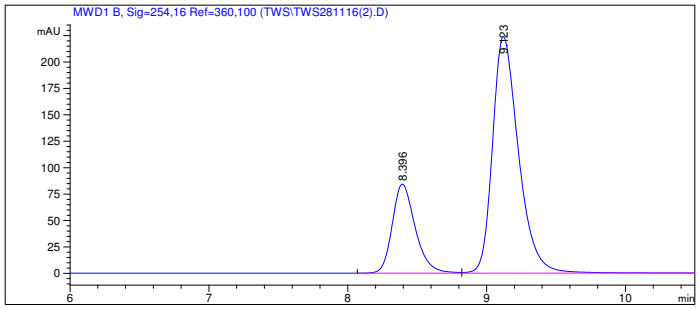

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.550 MM    0.1853 3513.97583  316.01166  42.4614
   2   8.203 VB    0.2039 4761.72852  351.82452  57.5386

Totals :                  8275.70435  667.83618
```

Figure s19. HPLC spectrum of chiral adduct 4 in Table 3 Entry 1.

Table 3 Entry 2




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

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

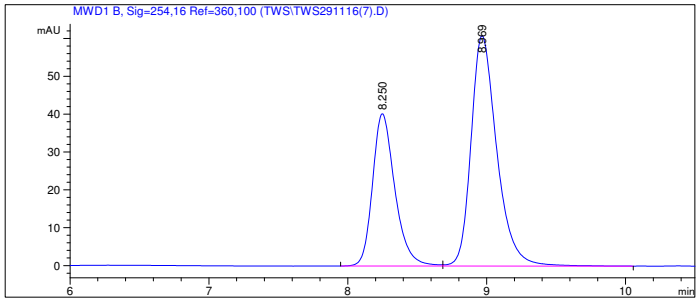

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.396 BV    0.1763  970.70715   84.32536  24.9808
   2   9.123 VB    0.1979 2915.10889  223.93932  75.0192

Totals :                  3885.81604  308.26468
```

Figure s20. HPLC spectrum of chiral adduct 4 in Table 3 Entry 2.

Table 3 Entry 3




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

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

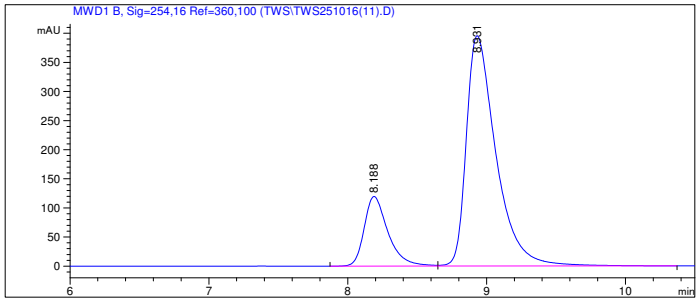

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.250 BV    0.1705  450.32977   40.26073  36.4450
   2   8.969 VB    0.1965  785.31091   60.88341  63.5550

Totals :                  1235.64069  101.14415
```

Figure s21. HPLC spectrum of chiral adduct 4 in Table 3 Entry 3.

Table 3 Entry 4

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

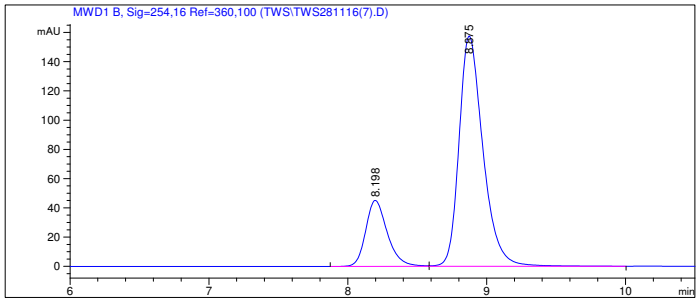

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.188 BV    0.1788 1425.04724  119.77242  19.5273
   2   8.931 VB    0.2231 5872.66162  395.74384  80.4727

Totals :                   7297.70886  515.51626
```

Figure s22. HPLC spectrum of chiral adduct 4 in Table 3 Entry 4.

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.)
Do not use Multiplier & Dilution Factor with ISTDs

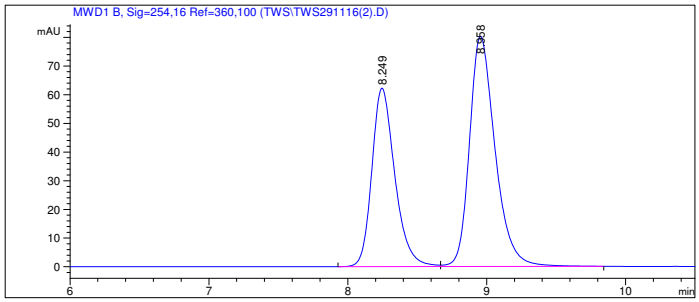

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.198 BV    0.1640  488.04959   45.18439  20.5814
   2   8.875 VB    0.1814 1883.26697  157.62961  79.4186

Totals :                   2371.31656  202.81400
```

Figure s23. HPLC spectrum of chiral adduct 4 in Table 3 Entry 5.

Table 3 Entry 6

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

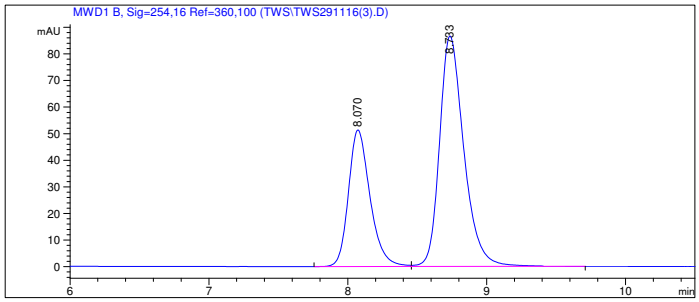

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.249 BV    0.1741  715.68628   62.24938  41.0504
   2   8.958 VB    0.1932 1027.74866   80.34298  58.9496

Totals :                  1743.43494  142.59236
```

Figure s24. HPLC spectrum of chiral adduct 4 in Table 3 Entry 6.

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.)
Do not use Multiplier & Dilution Factor with ISTDs

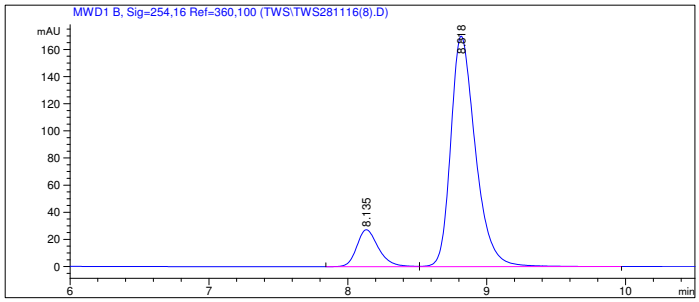

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.070 BV    0.1639  554.80365   51.39540  34.5046
   2   8.733 VB    0.1858 1053.10840   86.66793  65.4954

Totals :                  1607.91205  138.06333
```

Figure s25. HPLC spectrum of chiral adduct 4 in Table 3 Entry 7.

Table 3 Entry 8

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

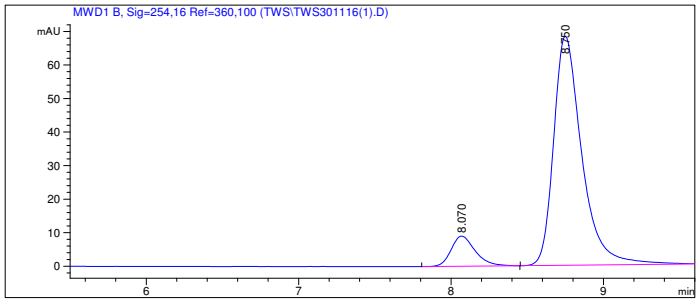

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.135 BV    0.1648  296.04175   27.22886  12.3763
   2   8.818 VB    0.1878 2095.97266  170.00188  87.6237

Totals :                  2392.01440  197.23074
```

Figure s26. HPLC spectrum of chiral adduct 4 in Table 3 Entry 8.

Table 3 Entry 9

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

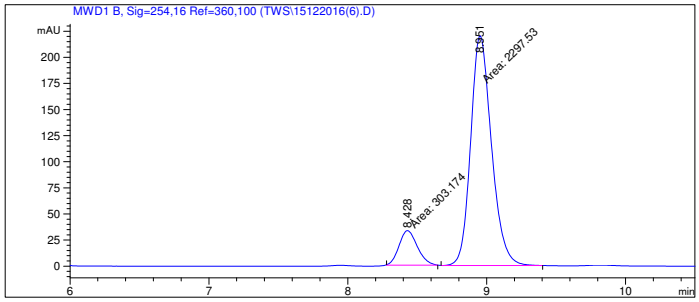

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.070 BB    0.1659   98.58515    8.99597  10.0781
   2   8.750 BBA   0.1940  879.62396   68.40292  89.9219

Totals :                   978.20911   77.39889
```

Figure s27. HPLC spectrum of chiral adduct 4 in Table 3 Entry 9.

Table 3 Entry 10

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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.)
Do not use Multiplier & Dilution Factor with ISTDs

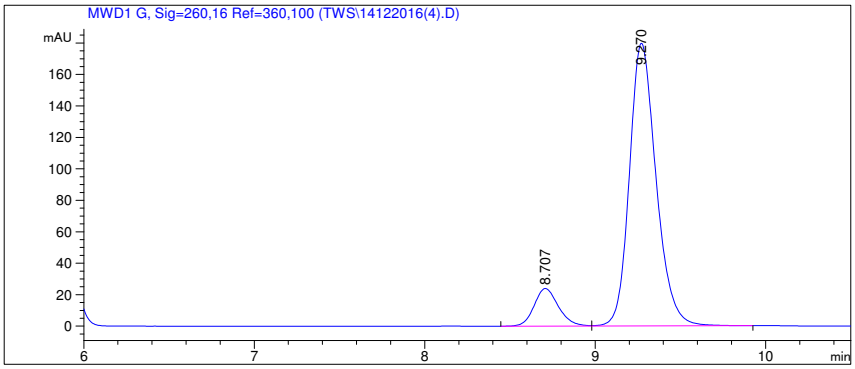

Signal 1: MWD1 B, Sig=254,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]    [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   8.428 MM    0.1526  303.17361   33.10900  11.6574
   2   8.951 MM    0.1738 2297.53027  220.30220  88.3426

Totals :                  2600.70389  253.41120
```

Figure s28. HPLC spectrum of chiral adduct 4 in Table 3 Entry 10.

Table 3 Entry 11

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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.)
Do not 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   8.707 BV    0.1517  237.57396   23.95535  10.8312
   2   9.270 VB    0.1669 1955.83997  179.82191  89.1688

Totals :                  2193.41393  203.77727
```

Figure s29. HPLC spectrum of chiral adduct 4 in Table 3 Entry 11.

Investigation of possible interactions between complex 5c and reagent(s)

We wish to examine whether complex **5c** interacts with (1) both nitrostyrene **3** and diphenylarsine or only (2) either one of the reagents. This was done by a combination of ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. To ensure that any transient interaction(s) between complex **5c** and reagent(s) were detected, a series of variable temperature (VT) NMR experiments (-60^{o}C to 25^{o}C) were conducted.

Control **A**: Nitrostyrene **3** (5.00 mg, 33.50 μmol) was stirred in MeOD (0.5 mL) for 10 mins at RT.

Control **B**: Complex **5c** (8.80 mg, 10.70 μmol) was stirred in MeOD (0.5 mL) for 10 mins at RT.

Sample **C**: Nitrostyrene **3** (2.00 mg, 13.40 μmol, 1.0 equiv.) and complex **5c** (1.10 mg, 1.34 μmol, 0.1 equiv.) were stirred in MeOD (0.5 mL) for 10 mins at RT.

Sample **D**: Diphenylarsine (5.20 mg, 22.60 μmol, 1.0 equiv.) and complex **5c** (1.88 mg, 2.25 μmol, 0.1 equiv.) were stirred in MeOD (0.5 mL) for 10 mins at RT.

Control A (^{1}H NMR spectra of nitrostyrene 3)

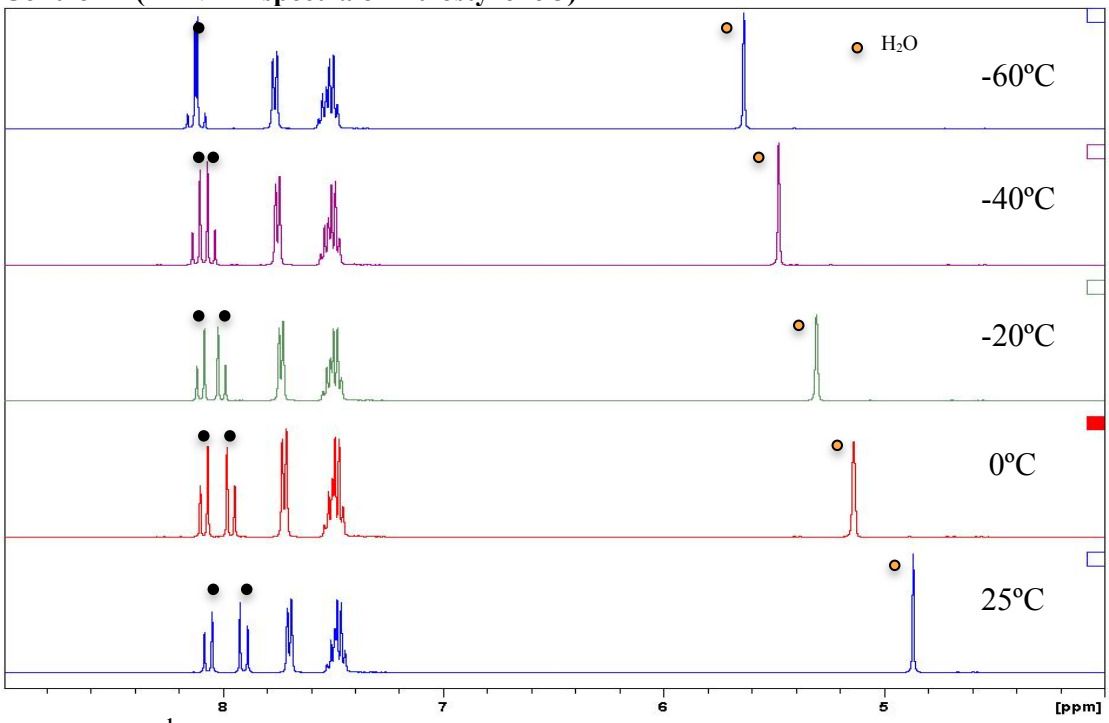


Figure s30. VT ^{1}H NMR spectra of control A (nitrostyrene 3). Signals corresponding to vinylic protons of nitrostyrene 3 labeled with a black dot.

The vinylic proton signals of nitrostyrene **3** (labeled with a black dot) were observed to symmetrically converge towards 8.15 ppm as the temperature was lowered (Figure s30).

Control B (^{31}P{^{1}H} NMR spectra of complex 5c)

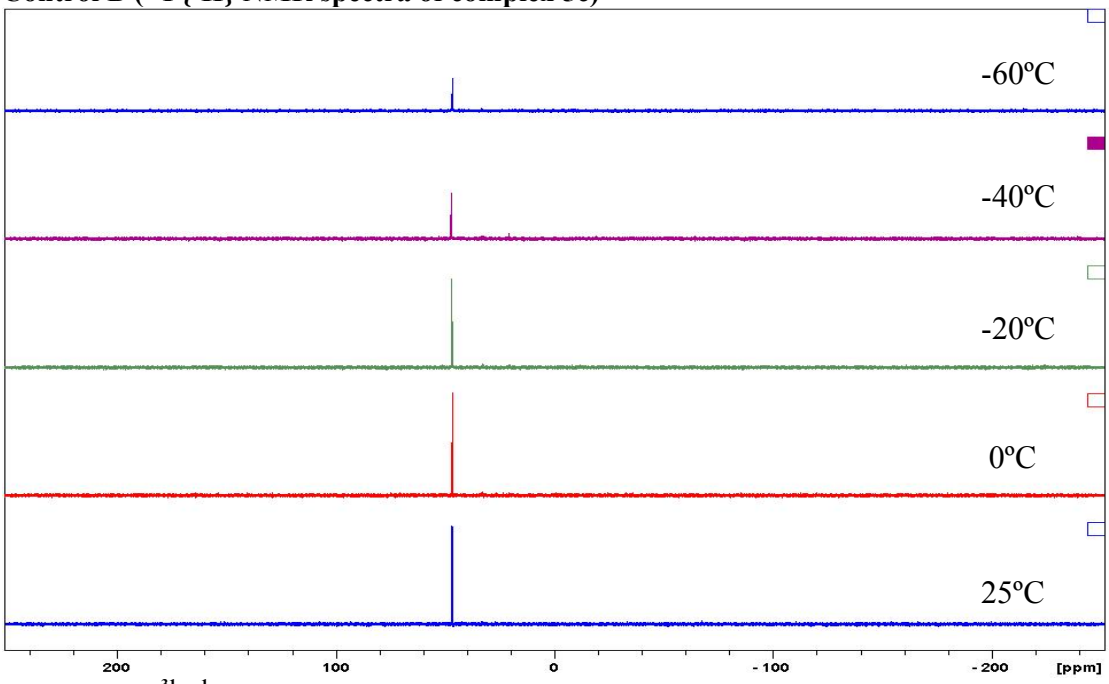


Figure s31. VT ^{31}P{^{1}H} NMR spectra of control B (complex 5c).

The ^{31}P{^{1}H} of complex **5c** remained unchanged as temperature was lowered (Figure s31).

Sample C (^{1}H NMR spectra of nitrostyrene 3 with complex 5c)

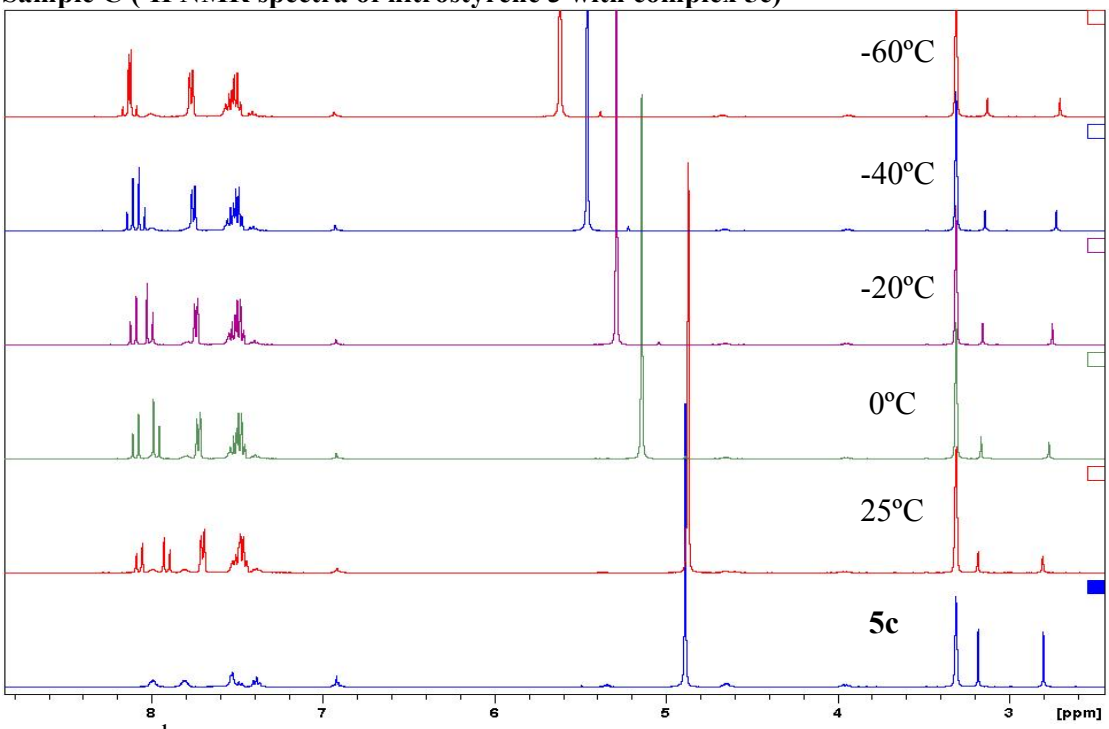


Figure s32. VT ^{1}H NMR spectra of sample C (nitrostyrene 3 with complex 5c).

Sample C (^{31}P{^{1}H} NMR spectra of nitrostyrene 3 with complex 5c)

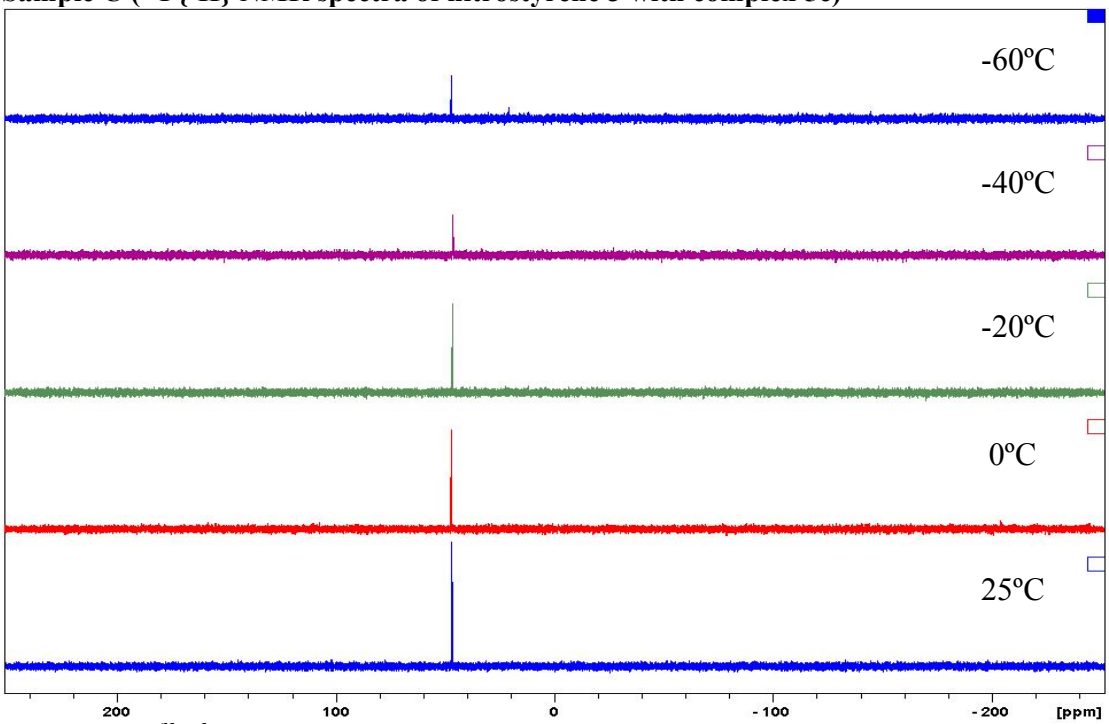


Figure s33. VT ^{31}P{^{1}H} NMR spectra of sample C (nitrostyrene 3 with complex 5c).

By comparing the NMR spectra of sample **C** (Figures s32 and s33) to controls **A** and **B** (Figures s30 and s31), it is clear that there were no interactions between nitrostyrene **3** and complex **5c**.

Sample D ($^{31}P\{^{1}H\}$ NMR spectra of diphenylarsine with complex 5c)

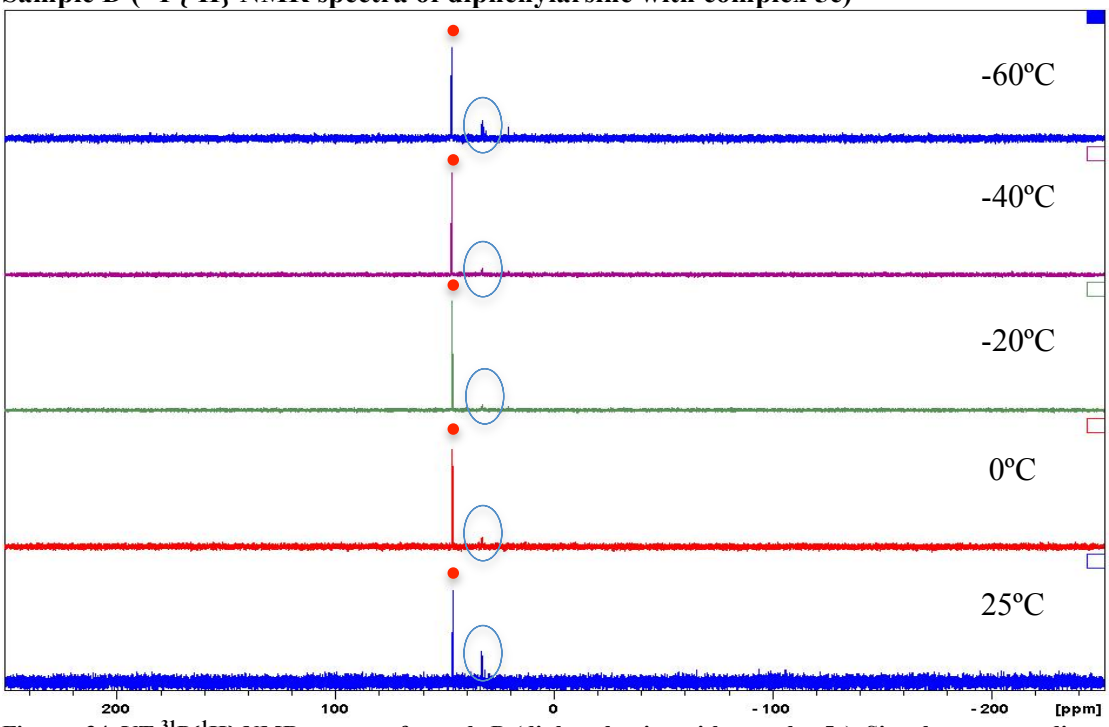


Figure s34. VT $^{31}P\{^{1}H\}$ NMR spectra of sample D (diphenylarsine with complex 5c). Signals corresponding to ester functionalities of catalyst 5c labeled with a red dot.

By comparison of the $^{31}P\{^{1}H\}$ NMR spectra of sample **D** (Figure s34) with control **B** (Figure s31), we observed the appearance of a new signal at 33.1 ppm (see circles on Figure s34). While we are unable to identify the species corresponding to the minor signal at 33.1 ppm, it may be concluded that the appearance of this signal is attributed to some interaction of complex **5c** with diphenylarsine.

Conducting of catalysis in MeOD

Sample **E**: Nitrostyrene **3** (5.60 mg, 36.55 µmol, 1.0 equiv.), diphenylarsine (10.30 mg, 44.76 µmol, 1.2 equiv.) and complex **5c** (2.50 mg, 3.02 µmol, 0.08 equiv.) were stirred in CD_3OD (1 mL) for 5.5 h at RT.

Sample **F**: Nitrostyrene **3** (5.60 mg, 36.55 µmol, 1.0 equiv.), diphenylarsine (10.30 mg, 44.76 µmol, 1.2 equiv.) and complex **5c** (2.50 mg, 3.02 µmol, 0.08 equiv.) were stirred in CD_3OD (1 mL) for 0.5 h at RT.

Sample **G**: Nitrostyrene **3** (5.60 mg, 36.55 µmol, 1.0 equiv.), diphenylarsine (10.30 mg, 44.76 µmol, 1.2 equiv.) and complex **5c** (2.50 mg, 3.02 µmol, 0.08 equiv.) were stirred in CH_3OH (1 mL) for 0.5 h at RT.

Samples E, F, G (^{1}H NMR spectra of nitrostyrene 3, diphenylarsine and complex 5c)

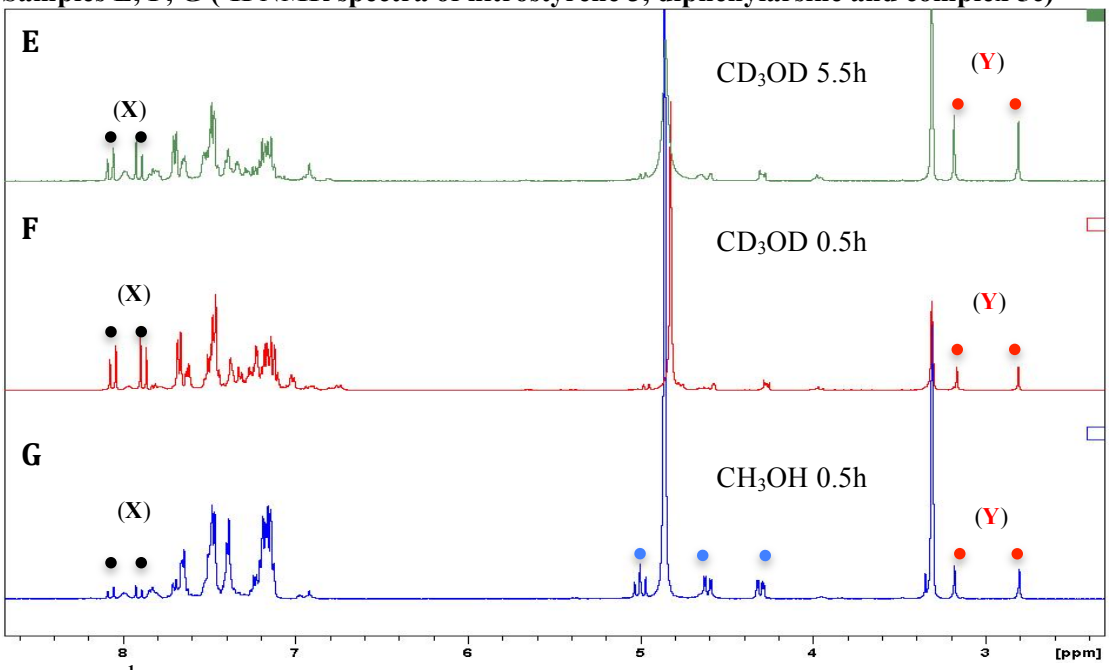


Figure s35. ^{1}H NMR spectra of AHAs reaction in CH_3OH and CD_3OD. Signals corresponding to vinylic protons of nitrostyrene 3 labelled with a black dot, aliphatic protons of adduct 4 with a blue dot and ester functionalities of catalyst 5c with a red dot.

Table s1. Ratios of signals X:Y.

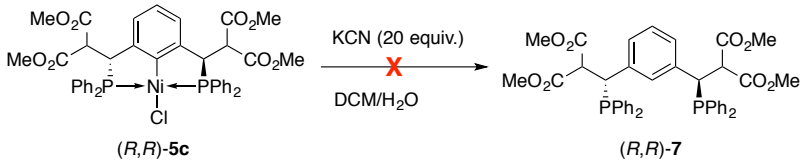
Sample	Ratio of X:Y[a]
E	0.7966 : 1
F	0.8347 : 1
G	0.5695 : 1

[a] Ratio of X:Y was determined by integration of the respective signals. Cat. **5c** signals indicated by red dots were taken as internal standard.

The integrals of vinylic protons on nitrostyrene **3** (black dots on Figure s35) were taken with respect to catalyst -CO_2Me signals (red dots on Figure s35, taken as internal standard) in the ratio of X:Y (Table s1). It was observed that the X:Y ratio of Sample **E** (0.7966 : 1) was still higher than that of sample **G** (0.5695 : 1), reflecting a slower rate of consumption of nitrostyrene **3** when the reaction was conducted in CD_3OD.

Investigation of Complex 5c

To examine the structural integrity of the tridentate PCP ligand on complex **5c**, complex **5c** (8.80 mg, 10.70 µmol, 1.0 equiv.) in DCM (2 mL) was treated with 10 mM aqueous KCN (2.00 mL, 0.21 mmol, 20.0 equiv.) and stirred overnight (Figure s36, Spectrum **I**). Based on previous experience, decomplexation of the ligand from the metal should occur (Scheme s7). However, we did not observe the appearance of the free phosphine peak (Figure s36, Spectrum **H**) even after stirring for three days. Therefore we are convinced that the PCP ligand does not dissociate.



Scheme s7. Attempted decomplexation of catalyst 5c.

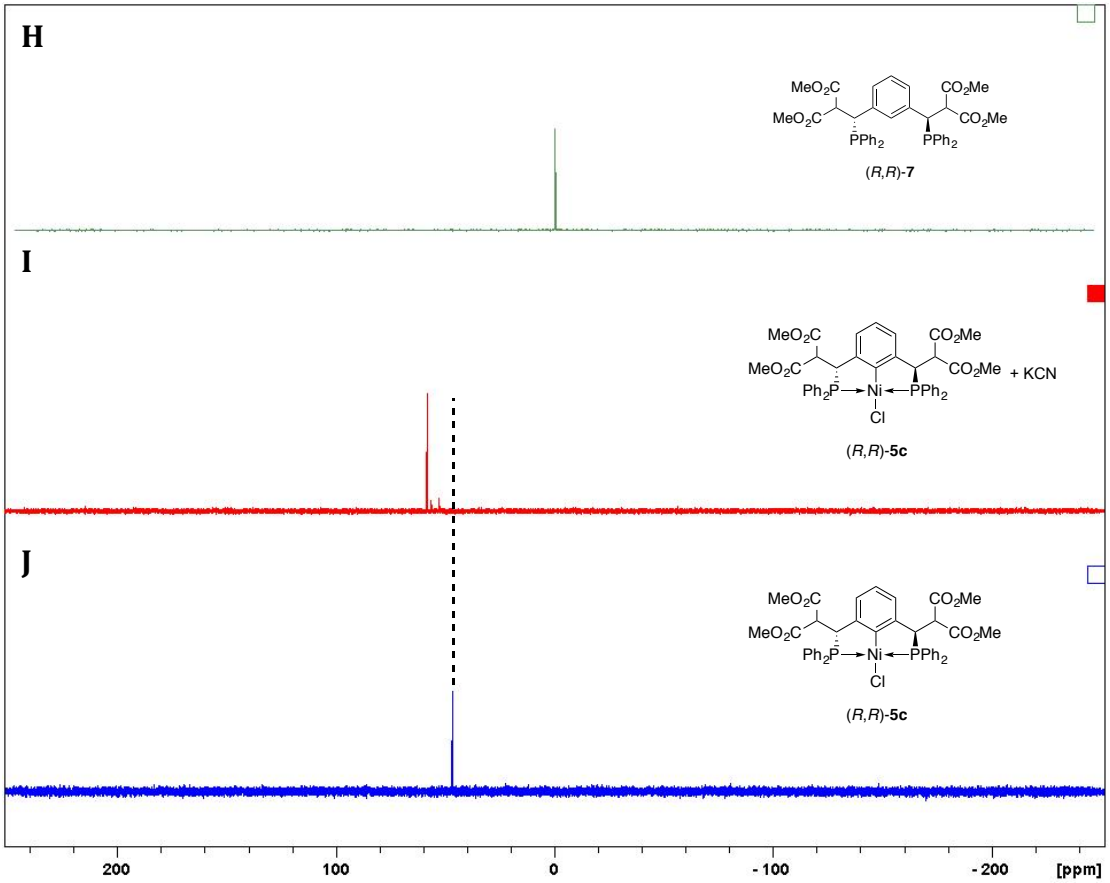
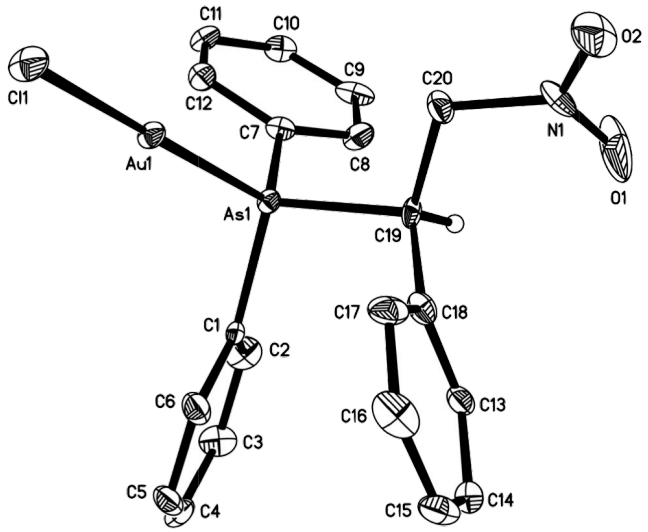


Figure s36. Attempted decomplexation of complex 5c with aq. KCN.

X-Ray Structure of Complex (*S*)-6



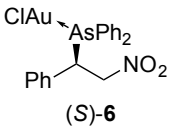


Figure s37. ORTEP of arsine-gold adduct (*S*)-6.

Crystallographic Data for Complex (*S*)-6

Chemical formula	$C_{20}H_{18}AsAuClNO_2$	
Formula weight	611.69 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.120 x 0.360 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 9.8186(5) Å	α = 90°
	b = 9.2688(5) Å	β = 99.2433(18)°
	c = 10.8223(5) Å	γ = 90°
Volume	972.11(9) $Å^3$	
Z	2	
Density (calculated)	2.090 g/cm^3	
Absorption coefficient	9.407 mm^{-1}	
F(000)	580	
Theta range for data collection	1.91 to 27.99°	
Index ranges	-12<=h<=12, -6<=k<=12, -14<=l<=14	
Reflections collected	14442	
Independent reflections	3710 [R(int) = 0.0664]	
Coverage of independent reflections	100.0%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.4530 and 0.1330	

Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
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	3710 / 1 / 235	
Goodness-of-fit on F^2	1.029	
Final R indices	3401 data; I>2σ(I)	R1 = 0.0348, wR2 = 0.0675
	all data	R1 = 0.0421, wR2 = 0.0706
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0198P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.005(13)	
Largest diff. peak and hole	2.361 and -2.019 eÅ^{-3}	
R.M.S. deviation from mean	0.181 eÅ^{-3}	

Table s2. Bond lengths (Å) of complex (*S*)-6.

As1-C7	1.913(9)	As1-C1	1.923(9)
As1-C19	1.979(9)	As1-Au1	2.3309(11)
Au1-Cl1	2.279(3)	C1-C2	1.379(14)
C1-C6	1.410(12)	C2-C3	1.400(14)
C2-H2	0.95	C3-C4	1.392(14)
C3-H3	0.95	C4-C5	1.377(16)
C4-H4	0.95	C5-C6	1.377(13)
C5-H5	0.95	C6-H6	0.95
C7-C12	1.395(13)	C7-C8	1.398(14)
C8-C9	1.397(12)	C8-H8	0.95
C9-C10	1.372(16)	C9-H9	0.95
C10-C11	1.376(14)	C10-H10	0.95
C11-C12	1.388(12)	C11-H11	0.95
C12-H12	0.95	C13-C14	1.375(12)
C13-C18	1.394(13)	C13-H13	0.95
C14-C15	1.387(15)	C14-H14	0.95
C15-C16	1.391(15)	C15-H15	0.95
C16-C17	1.416(13)	C16-H16	0.95
C17-C18	1.402(14)	C17-H17	0.95
C18-C19	1.504(12)	C19-C20	1.508(13)
C19-H19	1.0	C20-N1	1.495(13)
C20-H20A	0.99	C20-H20B	0.99
N1-O1	1.205(14)	N1-O2	1.218(12)

Table s3. Bond angles (°) of complex (*S*)-6.

C7-As1-C1	104.9(4)	C7-As1-C19	105.3(4)
C1-As1-C19	105.2(4)	C7-As1-Au1	117.1(3)
C1-As1-Au1	112.8(3)	C19-As1-Au1	110.7(3)
Cl1-Au1-As1	176.63(7)	C2-C1-C6	119.6(9)
C2-C1-As1	121.1(7)	C6-C1-As1	119.3(7)
C1-C2-C3	119.9(9)	C1-C2-H2	120.0
C3-C2-H2	120.0	C4-C3-C2	119.5(10)
C4-C3-H3	120.3	C2-C3-H3	120.3
C5-C4-C3	120.8(10)	C5-C4-H4	119.6
C3-C4-H4	119.6	C4-C5-C6	119.8(10)
C4-C5-H5	120.1	C6-C5-H5	120.1
C5-C6-C1	120.3(10)	C5-C6-H6	119.8
C1-C6-H6	119.8	C12-C7-C8	119.5(8)
C12-C7-As1	117.7(7)	C8-C7-As1	122.5(7)
C9-C8-C7	119.2(10)	C9-C8-H8	120.4
C7-C8-H8	120.4	C10-C9-C8	120.5(12)
C10-C9-H9	119.8	C8-C9-H9	119.8
C9-C10-C11	120.5(10)	C9-C10-H10	119.7
C11-C10-H10	119.7	C10-C11-C12	120.0(9)
C10-C11-H11	120.0	C12-C11-H11	120.0
C11-C12-C7	120.2(9)	C11-C12-H12	119.9
C7-C12-H12	119.9	C14-C13-C18	121.5(9)
C14-C13-H13	119.2	C18-C13-H13	119.2
C13-C14-C15	120.4(9)	C13-C14-H14	119.8
C15-C14-H14	119.8	C14-C15-C16	119.9(9)
C14-C15-H15	120.0	C16-C15-H15	120.0
C15-C16-C17	119.5(10)	C15-C16-H16	120.3
C17-C16-H16	120.3	C18-C17-C16	120.3(10)
C18-C17-H17	119.9	C16-C17-H17	119.9
C13-C18-C17	118.3(9)	C13-C18-C19	119.5(9)
C17-C18-C19	122.1(9)	C18-C19-C20	115.8(8)
C18-C19-As1	108.9(6)	C20-C19-As1	106.7(6)
C18-C19-H19	108.4	C20-C19-H19	108.4
As1-C19-H19	108.4	N1-C20-C19	111.5(8)
N1-C20-H20A	109.3	C19-C20-H20A	109.3
N1-C20-H20B	109.3	C19-C20-H20B	109.3
H20A-C20-H20B	108.0	O1-N1-O2	122.6(11)
O1-N1-C20	119.3(10)	O2-N1-C20	118.1(10)