Investigating palladium pincer complexes in catalytic asymmetric hydrophosphination and hydroarsination

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Electronic Supporting Information

General information

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk techniques. 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 rotations 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 ^{1}H NMR, chloroform-d (77.23 ppm) for ^{13}C NMR, and an external 85% H$_3$PO$_4$ for ^{31}P{^{1}H} NMR.

The complexes (S)-8,[1] (R)-9,[2] (R,R)-10,[3] (R,R,R,R)-11[4] and enones 1c,[5] 1d,[5] 1e[5] were prepared according to literature methods. Conversion of Pd-Cl complex 2a to Pd-OAc complex 2b were performed as described in literature.[6] All other reactants and reagents were used as supplied (1a: Alfa Aesar, 1b: Sigma Aldrich). Due to compound degredation observed under column chromatography conditions, arsine adducts 4b, 4c, 4d, 4e were characterized by ^{1}H NMR, HRMS, HPLC and optical rotation measurements while adduct 4a was characterized fully.
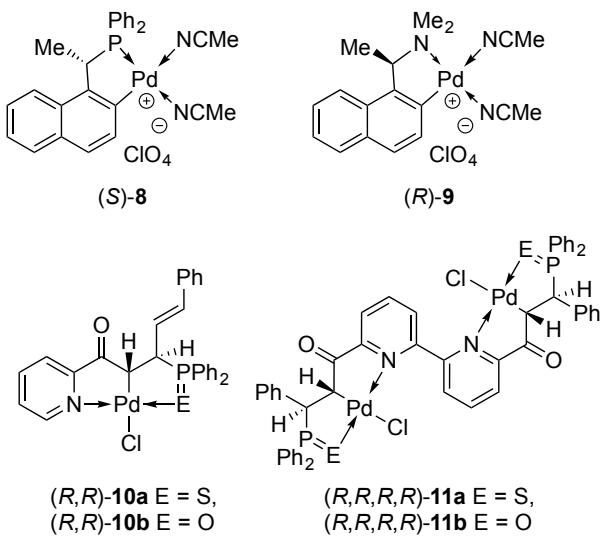
Figure s1. Complex used in this work.

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

Screening of conditions
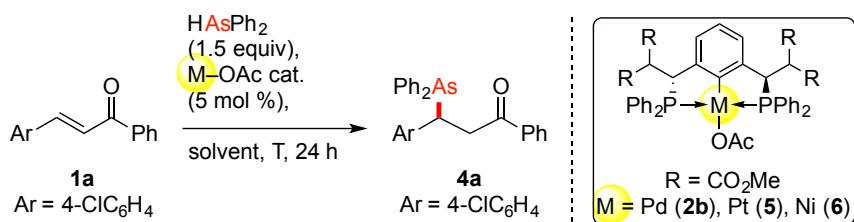
Table s1. *Optimization of hydroarsinatino conditions with M–OAc complexes.*[a]

Entry	Catalyst	Solvent	T (ºC)	Yield[b] (%)	*ee*[c] (%)
1	**2b**	Acetone	25	0	-
2	**2b**	MeOH	25	16	21
3	**2b**	MeOH/H$_2$O (5%)	25	26	32
4	**2b**	MeOH/H$_2$O (10%)	25	33	42
5	**2b**	MeOH/H$_2$O (15%)	25	34	29
6	**2b**	MeOH/H$_2$O (10%)	0	28	49
7	**2b**	MeOH/H$_2$O (10%)	-40	0	-
8	**2b**	MeOH/H$_2$O (10%)	35	16	40
9[d]	**2b**	MeOH/H$_2$O (10%)	25	23	41
10	**2b**	EtOH	25	9	46
11	**2b**	DEE	25	11	16
12	**2b**	MeCN	25	0	-
13	**2b**	DMSO	25	0	-
14	**2b**	MeNO$_2$	25	0	-
15	**2b**	EtOH/H$_2$O(10%)	25	29	31
16	**5**	MeOH	25	0	-
17	**6**	MeOH	25	0	-

[a]Reaction conditions: Enone **1a** (12.1 mg, 0.05 mmol, 1.0 eq.), HAsPh$_2$ (17.26 mg, 0.08 mmol, 1.5 eq.), cat. (5 mol %), solvent (2 mL). [b]^{1}H NMR yield with respect to enone **1**. [c]Determined by chiral HPLC of the crude reaction mixture. [d]Cat. (*R,R*)-**2b** (6.74 mg, 7.50 μmol, 15 mol %) was used instead.

HAsPh$_2$ (1.5 equiv),
Pd-Cl cat. **2a** (5 mol %),
base (1 equiv),

solvent, T, 24 h

1a
Ar = 4-ClC$_6$H$_4$

4a
Ar = 4-ClC$_6$H$_4$
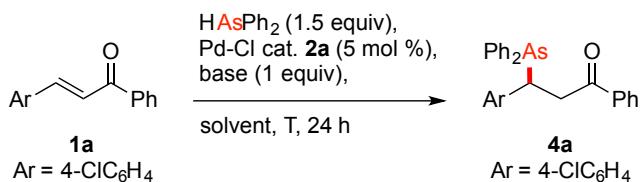
Table s2. *Optimization of conditions for PCP Pd-Cl catalyst **2a**.*[a]

Entry	Solvent	Base	T (ºC)	Yield[b] (%)	*ee*[c] (%)
1	MeOH	-	25	24	13
2	EtOH/H2O(10%)[d]	-	25	33	7
3	MeOH	K$_2$CO$_3$	25	6	4
4	EtOH	K$_3$PO$_4$	25	60	19
5	EtOH	Na$_2$CO$_3$	25	5	44
6	EtOH	NaHCO$_3$	25	28	1
7	EtOH	NaI	25	0	-
8	EtOH	KF[e]	25	24	66
9	EtOH	CsCl[e]	25	36	61
10	EtOH	KCl[e]	25	0	-
11	MeOH	CsF	25	61	44

[a]Reaction conditions: Enone **1a** (12.1 mg, 0.05 mmol, 1.0 eq.), HAsPh₂ (17.26 mg, 0.08 mmol, 1.5 eq.), cat. (*R*,*R*)-**2a** (2.12 mg, 2.50 µmol, 5 mol %), base (0.05 mmol, 1.0 eq.), solvent (2 mL). [b]¹H NMR yield with respect to enone **1**. [c]Determined by chiral HPLC of the crude reaction mixture. [d]H₂O (10 % *v/v*). [e]Base (0.50 mmol, 10 equiv.) was used instead.

Experimental section

General procedure for the preparation of complex 2a, 5, 6
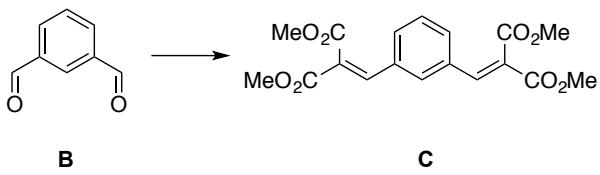
**Scheme s1**. *Synthesis of ligand precursor **C**.*

Dimethyl malonate (5.40 g, 14.91 mmol, 2.0 equiv) and piperidine (6.34g, 1.49 mmol, 0.2 equiv) were dissolved in *n*-heptane (5 mL) to which isophthaldehyde **B** (1.00 g, 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 and cooled to RT before 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 **C** as a pale yellow solid in 80% yield. The spectroscopic data obtained is consistent with literature.[7]
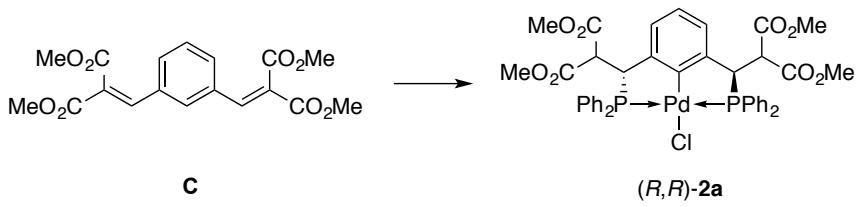
**Scheme s2.** *Synthesis of complex (R,R)-**2a**.*

Catalyst (*S*)-**A** (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 cooled to -80ºC. Compound **C** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the dropwise addition of NEt$_3$ (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL). After stirring at -80ºC for 3 days, the solution was slowly warmed to RT over 3 h. PdCl$_2$(CH$_3$CN)$_2$ (0.15 g, 0.578 mmol, 1.0 equiv.) was added and the solution was stirred overnight at RT and volatiles were removed. The crude product was purified *via* silica gel chromatography (DCM) to afford complex (*R*,*R*)-**2a** as a white solid in 86% yield. The spectroscopic data obtained is consistent with literature.[7]
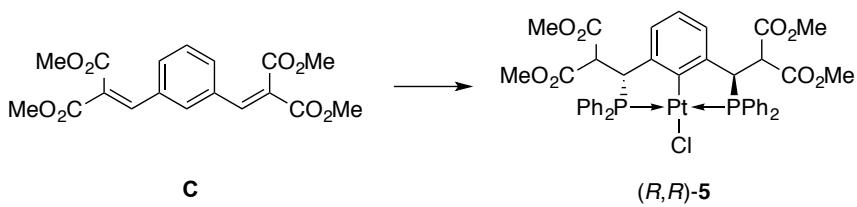
Scheme s3. *Synthesis of complex (R,R)-**5**.*

Catalyst (*S*)-**A** (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 cooled to -80ºC. Compound **C** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the dropwise addition of NEt$_3$ (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL). After stirring at -80ºC for 3 days, the solution was slowly warmed to RT over 3 h. Volatiles were removed and the residue was redissolved in toluene. PtCl$_2$(CH$_3$CN)$_2$ (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*)-**5** as a white solid. The spectroscopic data obtained is consistent with literature.[7]
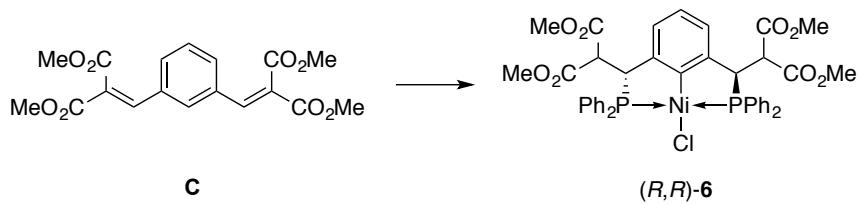
Scheme s4. *Synthesis of complex (R,R)-6.*

Catalyst (*S*)-**A** (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 cooled to -80ºC. Compound **C** (0.21 g, 0.578 mmol, 1.0 equiv.) was added followed by the dropwise addition of NEt_3 (0.12 g, 1.16 mmol, 2.0 equiv.) in DCM (1 mL). After stirring at -80ºC for 3 days, the solution was slowly warmed to RT over 3 h. Volatiles were removed and the residue was redissolved in EtOH. A solution of $NiCl_2(CH_3CN)_2$ (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. $NEt_2{}^iPr$ (74.70 mg, 0.578 mmol, 1.0 equiv.) was then added and the mixture was refluxed at 80ºC for 1 h. After 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*)-**6** as a yellow solid in 68% yield. The spectroscopic data obtained is consistent with literature.[7]

**General procedure for the catalytic asymmetric hydrophosphination reaction**
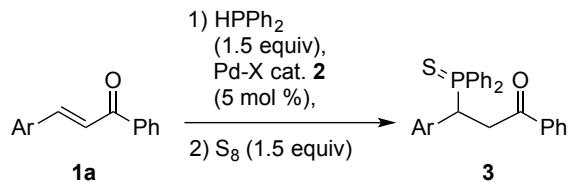
Scheme s5. *Pd-catalyzed asymmetric hydrophosphination reaction.*

$HPPh_2$ (13.96 mg, 0.08 mmol, 1.5 equiv) was charged to a pre-weighed Schlenk vessel under N_2. Catalyst **2** (2.50 µmol, 5 mol %) was added, washed down with the stated solvent (2 mL) and brought to the desired temperature. Enone **1a** (12.1 mg, 0.05 mmol, 1.0 equiv) was subsequently added and the reaction was stirred at the stated temperature. Reaction progress was monitored with $^{31}P\{^1H\}$ NMR spectroscopy and upon complete conversion, S_8 (3.21 mg, 0.10 mmol, 2.0 equiv) was added and the solution was allowed to RT. After stirring for 30 mins at RT, volatiles were removed and the crude product was purified *via* silica gel chromatography (5 Hexane: 1 EA) to afford the pure phosphine sulfide **3** as a white solid. The *ee* was determined on a Daicel Chiralpak IC column with *n*-hexane/2-propanol = 97/3, flow = 0.8 mL/min, wavelength = 220 nm. Retention times: 9.5 min (major, *S* isomer), 12.1 min (minor, *R* isomer). $[\alpha]_D$ = -226.0 (*c* 1.00, DCM). Mp: 117.1-118.2ºC. ^1H NMR (CDCl$_3$, 400 MHz): δ 8.18-8.12 (m, 2H, Ar), 7.86-7.84 (m, 2H, Ar), 7.55-7.50 (m, 6H, Ar), 7.42-7.40 (m, 3H, Ar), 7.28-7.25 (m, 4H, Ar), 7.08-7.06 (m, 2H, Ar), 4.83 (ddd, 1H, $^3J_{PH}$ = 10.2 Hz, $^3J_{HH}$ = 10.2 Hz, $^3J_{HH}$ = 2.4 Hz, PCC*H*), 4.06 (ddd, 1H, $^2J_{PH}$ = 18.3 Hz, $^3J_{HH}$ = 10.5 Hz, $^2J_{HH}$ = 5.24 Hz, PC*H*), 3.30 (ddd, 1H, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 11.6 Hz, $^2J_{HH}$ = 2.4 Hz, PC*H*); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 196.8 (s, 1C, *C*=O), 133.8-128.3 (12C, Ar), 40.8 (s, 1C, C(O)*C*H), 39.8

(d, 1C, $^1J_{PC}$ = 3.9 Hz, P*C*); ^{31}P{^{1}H} NMR (CDCl$_3$, 162 MHz): δ 51.0. HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{27}$H$_{23}$ClOPS, 461.0896; found, 461.0892.

General procedure for the catalytic asymmetric hydroarsination reaction
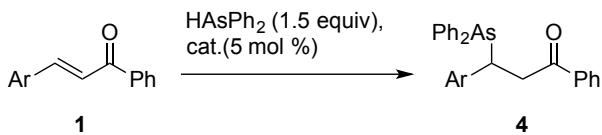
Scheme s6. *Catalytic asymmetric hydroarsination reaction.*

HAsPh$_2$ (17.26 mg, 0.08 mmol, 1.5 equiv) was charged to a pre-weighed Schlenk vessel under N$_2$. Catalyst (2.50 µmol, 5 mol %) and base (0.50 mmol, 10.0 equiv) was added, washed down with the stated solvent (2 mL) and brought to the desired temperature. Enone **1** (0.05 mmol, 1.0 equiv) was subsequently added and the reaction was stirred at the stated temperature. After 24 h, volatiles were removed and two drops of the crude reaction mixture was withdrawn from the flask and diluted with IPA (1 mL) to prepare the HPLC sample. Arsine adduct **4a** could be crystallized from DEE to afford the pure product **4a** as white crystalline needles.

4a White solid. 72% yield. The *ee* was determined on a Daicel Chiralpak IF column with *n*-hexane/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 230 nm. Retention times: 10.2 min (major), 11.2 min (minor). [α]$_D$ = -171.8 (*c* 4.70, DEE) (measured for Table 4 Entry 1). Mp: 137.2-138.2°C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.76-7.73 (m, 2H, Ar), 7.63-7.61 (m, 2H, Ar), 7.52-7.48 (m, 1H, Ar), 7.42-7.35 (m, 5H, Ar), 7.23-7.15 (m, 3H, Ar), 7.11-7.08 (m, 4H, Ar), 7.06-7.02 (m, 2H, Ar), 4.19 (dd, 1H, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*), 3.67 (dd, 1H, $^3J_{HH}$ = 17.2 Hz, $^3J_{HH}$ = 11.2 Hz, AsC*H*), 3.22 (dd, 1H, $^3J_{HH}$ = 17.2 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 198.2 (s, 1C, *C*=O), 134.1-128.2 (12C, Ar), 42.2 (s, 1C, As*C*), 40.2 (s, 1C, C(O)*C*H). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{27}$H$_{23}$AsClO, 473.0653; found, 473.0648.

4b White solid. The *ee* was determined on a Daicel Chiralpak IF column with *n*-hexane/2-propanol = 99/1, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 18.5 min (major), 20.1 min (minor). [α]$_D$ = -38.6 (*c* 4.90, DEE) (measured for Table 4 Entry 2). Mp: 126.3-127.2°C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.75-7.73 (m, 2H, Ar), 7.65-7.63 (m, 2H, Ar), 7.50-7.46 (m, 1H, Ar), 7.41-7.34 (m, 5H, Ar), 7.22-7.18 (m, 1H, Ar), 7.15-7.12 (m, 6H, Ar), 7.08-7.05 (m, 3H, Ar), 4.23 (dd, 1H, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*), 3.73 (dd, 1H, $^3J_{HH}$ = 17.2 Hz, $^3J_{HH}$ = 11.2 Hz, AsC*H*), 3.21 (dd, 1H, $^3J_{HH}$ = 16.8 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*); ^{13}C NMR (CDCl$_3$, 100 MHz): δ 198.5 (s, 1C, *C*=O), 135.3-126.3 (12C, Ar), 42.4 (s, 1C, As*C*), 40.9 (s, 1C, C(O)*C*H). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{27}$H$_{24}$AsO, 439.1043; found, 439.1043.

4c White solid. The *ee* was determined on a Daicel Chiralpak IF column with *n*-hexane/2-propanol = 97/3, flow = 1.0 mL/min, wavelength = 254 nm. Retention times: 15.5 min (major), 17.8 min (minor). [α]$_D$ = -23.7 (*c* 3.80, DEE) (measured for Table 4 Entry 3). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.74-7.72 (m, 2H, Ar), 7.64-7.62 (m, 2H, Ar), 7.50-7.46 (m, 1H, Ar), 7.42-7.33 (m, 5H, Ar), 7.20-7.13 (m, 3H, Ar), 7.09-7.04 (m, 4H, Ar), 6.70-6.68 (m, 2H, Ar), 4.18 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^2J_{HH}$ = 3.0 Hz, AsCC*H*), 3.67 (dd, 1H, $^3J_{HH}$ = 16.9 Hz, $^3J_{HH}$ = 11.3 Hz,

AsC*H*), 3.17 (dd, 1H, $^3J_{HH}$ = 17.0 Hz, $^2J_{HH}$ = 3.1 Hz, AsCC*H*). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{28}$H$_{26}$AsO$_2$, 469.1149; found, 469.1148.

4d White solid. The *ee* was determined on a Daicel Chiralpak IF column with *n*-hexane/2-propanol = 98/2, flow = 1.0 mL/min, wavelength = 254 nm. Retention times: 11.9 min (major), 13.4 min (minor). [α]$_D$ = -48.8 (*c* 3.70, DEE) (measured for Table 4 Entry 4). ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.80-7.78 (m, 2H, Ar), 7.66-7.63 (m, 3H, Ar), 7.49-7.38 (m, 6H, Ar), 7.16-7.12 (m, 6H, Ar), 7.07-7.05 (m, 2H, Ar), 4.22 (dd, 1H, $^3J_{HH}$ = 11.1 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*), 3.70 (dd, 1H, $^3J_{HH}$ = 17.0 Hz, $^3J_{HH}$ = 11.1 Hz, AsC*H*), 3.18 (dd, 1H, $^3J_{HH}$ = 16.9 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*), 2.35 (s, 3H, C*H*$_3$). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{28}$H$_{26}$AsO, 453.1200; found, 453.1198.

4e White solid. The *ee* was determined on a Daicel Chiralpak IF column with *n*-hexane/2-propanol = 99/1, flow = 0.8 mL/min, wavelength = 260 nm. Retention times: 14.8 min (major), 16.2 min (minor). [α]$_D$ = -56.6 (*c* 6.80, DEE) (measured for Table 4 Entry 5). ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* 7.80-7.76 (m, 3H, Ar), 7.64-7.62 (m, 2H, Ar), 7.58-7.47 (m, 4H, Ar), 7.42-7.36 (m, 6H, Ar), 7.21-7.14 (m, 3H, Ar), 7.01-7.05 (m, 1H, Ar), 4.28 (dd, 1H, $^3J_{HH}$ = 11.2 Hz, $^2J_{HH}$ = 3.2 Hz, AsCC*H*), 3.75 (dd, 1H, $^3J_{HH}$ = 17.4 Hz, $^3J_{HH}$ = 11.2 Hz, AsC*H*), 3.29 (dd, 1H, $^3J_{HH}$ = 17.5 Hz, $^2J_{HH}$ = 3.3 Hz, AsCC*H*); ^{19}F NMR (CDCl$_3$, 377 MHz): *δ* -62.4 (s). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C$_{28}$H$_{23}$AsF$_3$O, 507.0917; found, 507.0911.

NMR spectra
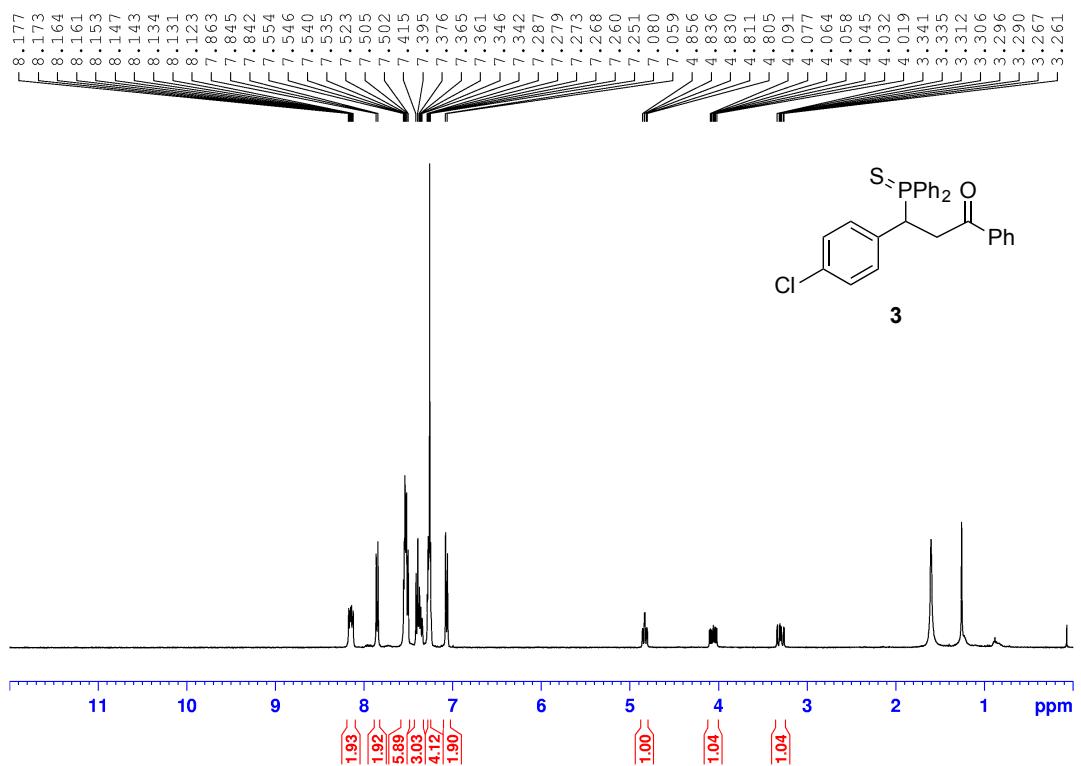
Figure s2. ^1H NMR spectrum of phosphine sulfide 3 in CDCl₃.
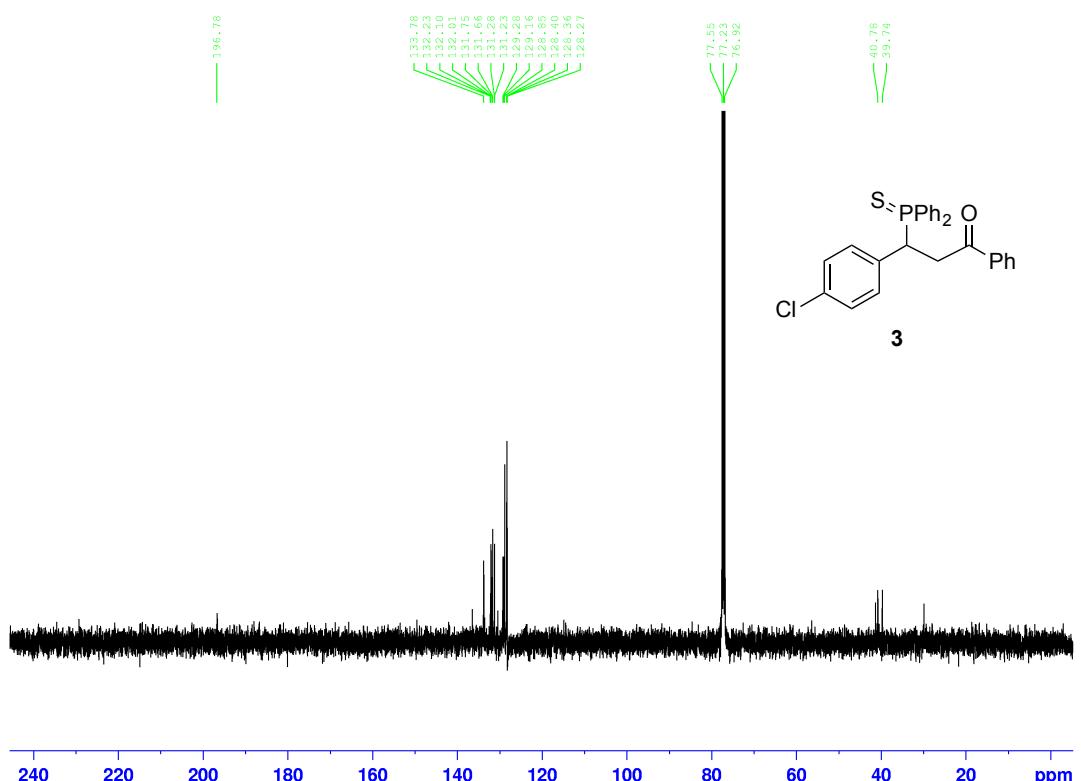
Figure s3. ^{13}C NMR spectrum of phosphine sulfide 3 in CDCl₃.

9
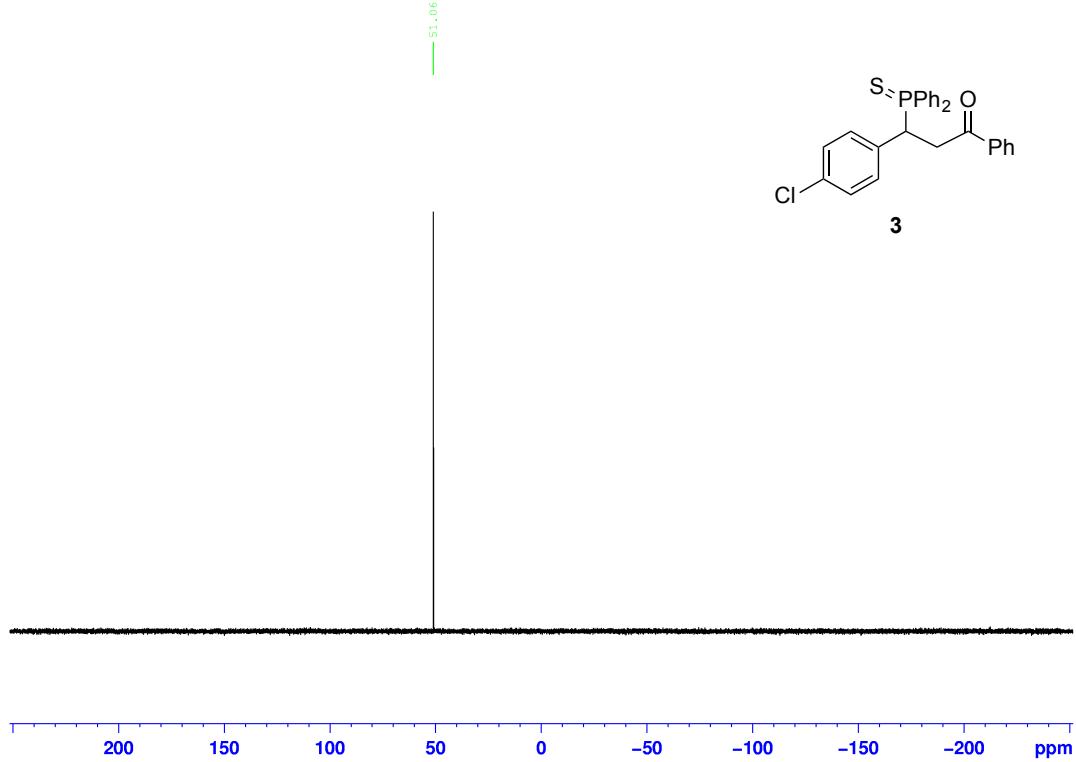
Figure s4. *$^{31}P\{^{1}H\}$ NMR spectrum of phosphine sulfide **3** in CDCl₃.*
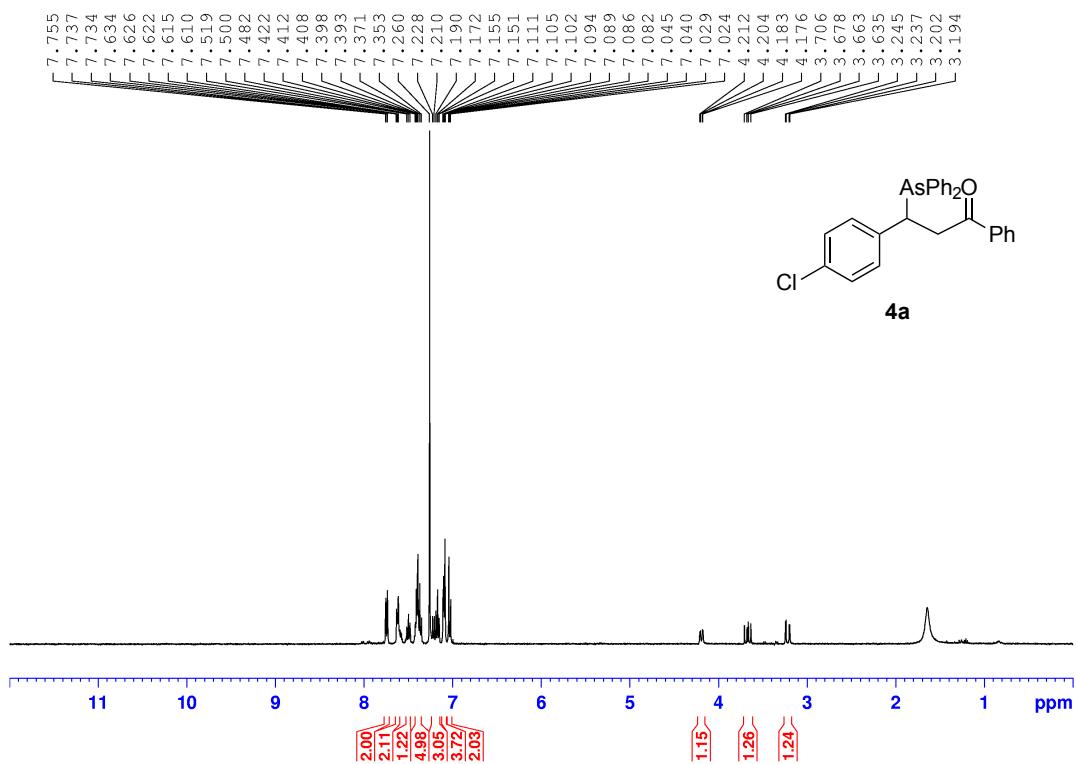
Figure s5. *^{1}H NMR spectrum of arsine **4a** in CDCl₃.*
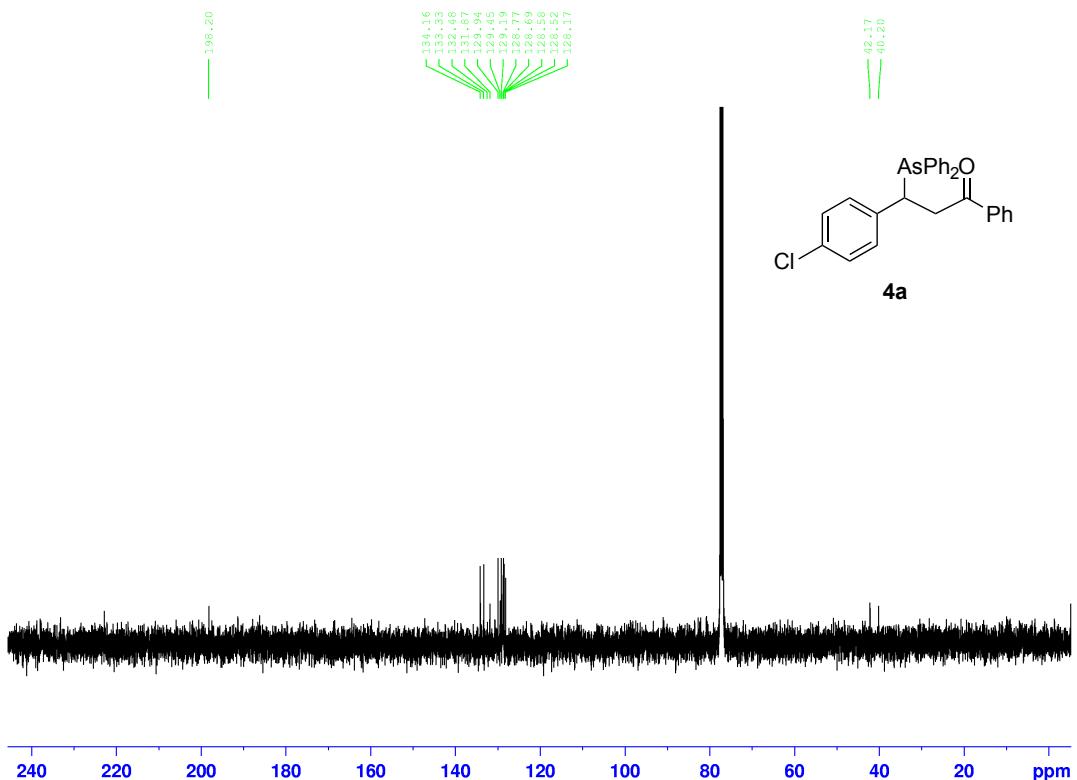
Figure s6. ^{13}C NMR spectrum of arsine **4a** in CDCl$_3$.
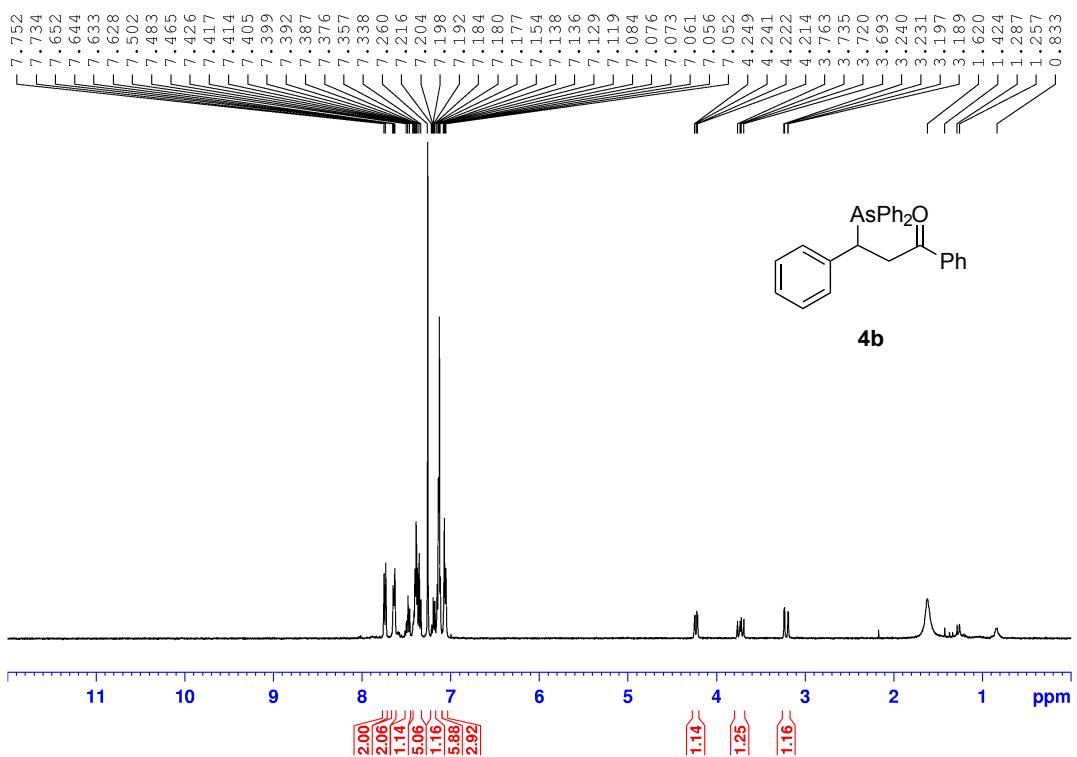
Figure s7. ^{1}H NMR spectrum of arsine **4b** in CDCl$_3$.
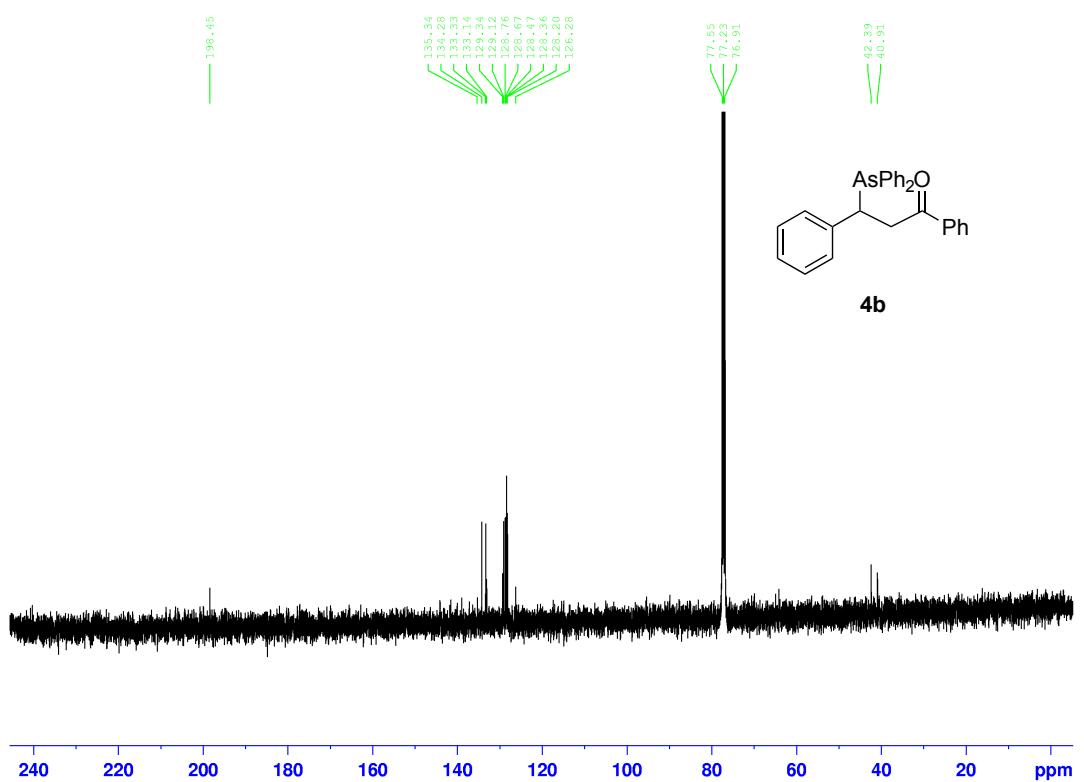
Figure s8. *13C NMR spectrum of arsine **4b** in CDCl3.*
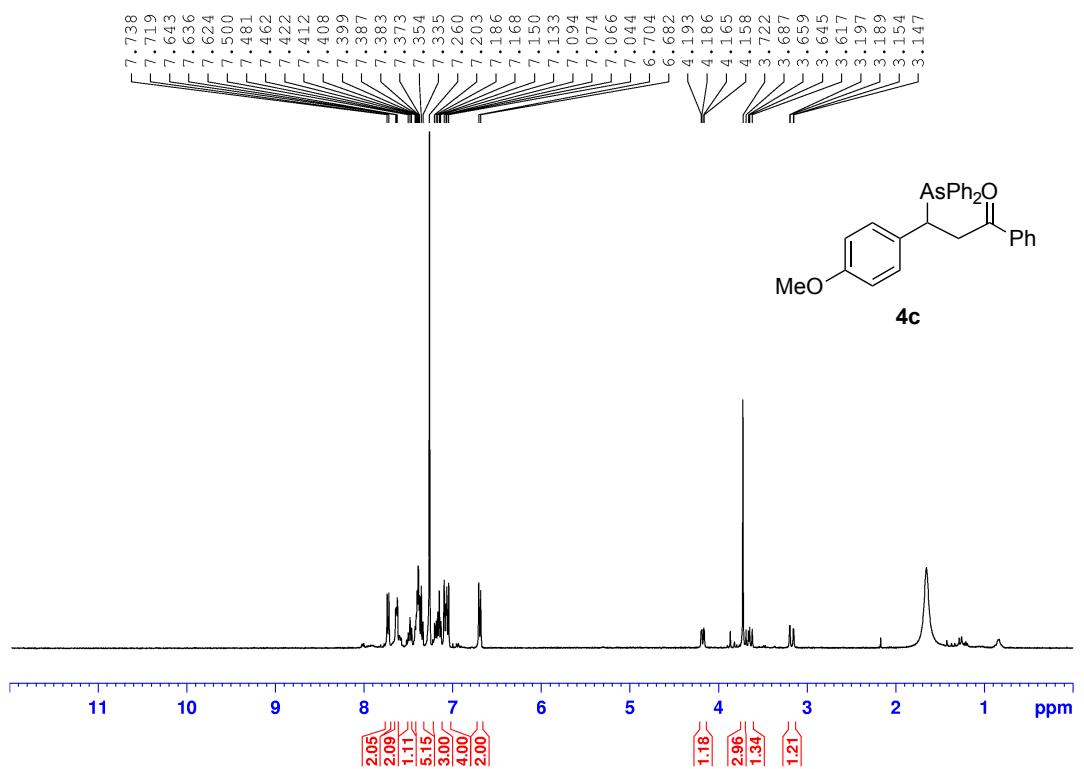
*Figure s9. 1H NMR spectrum of arsine **4c** in CDCl3.*
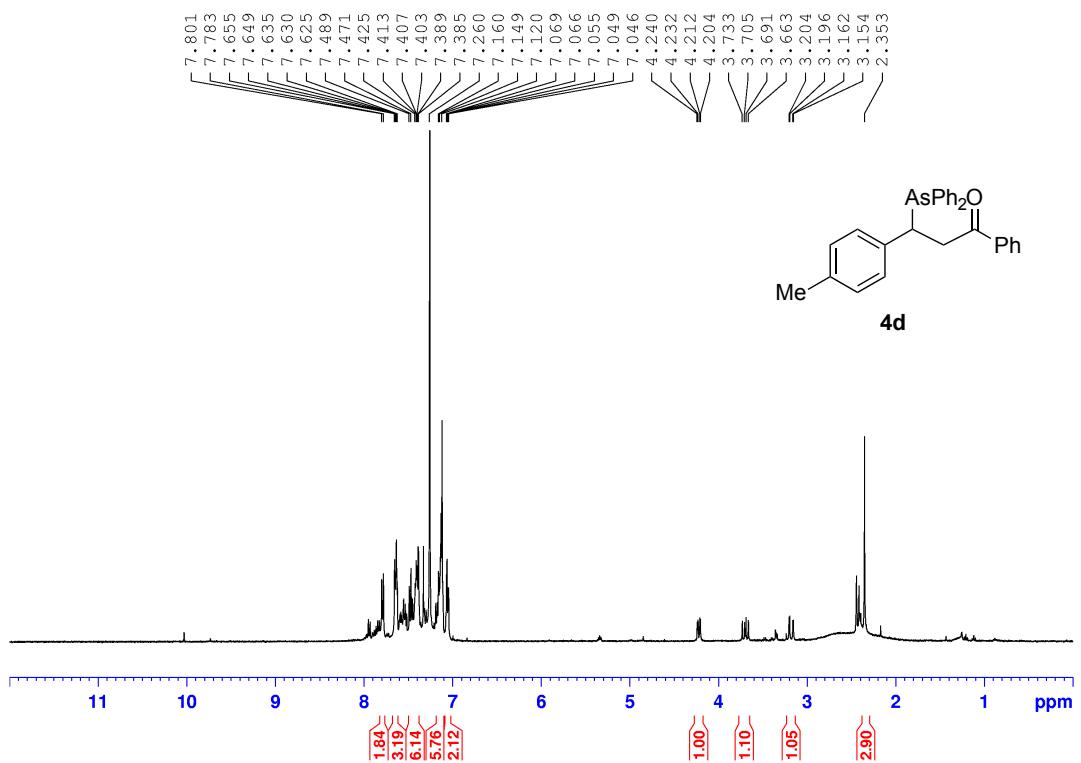
Figure s10. *¹H NMR spectrum of arsine **4d** in CDCl₃.*
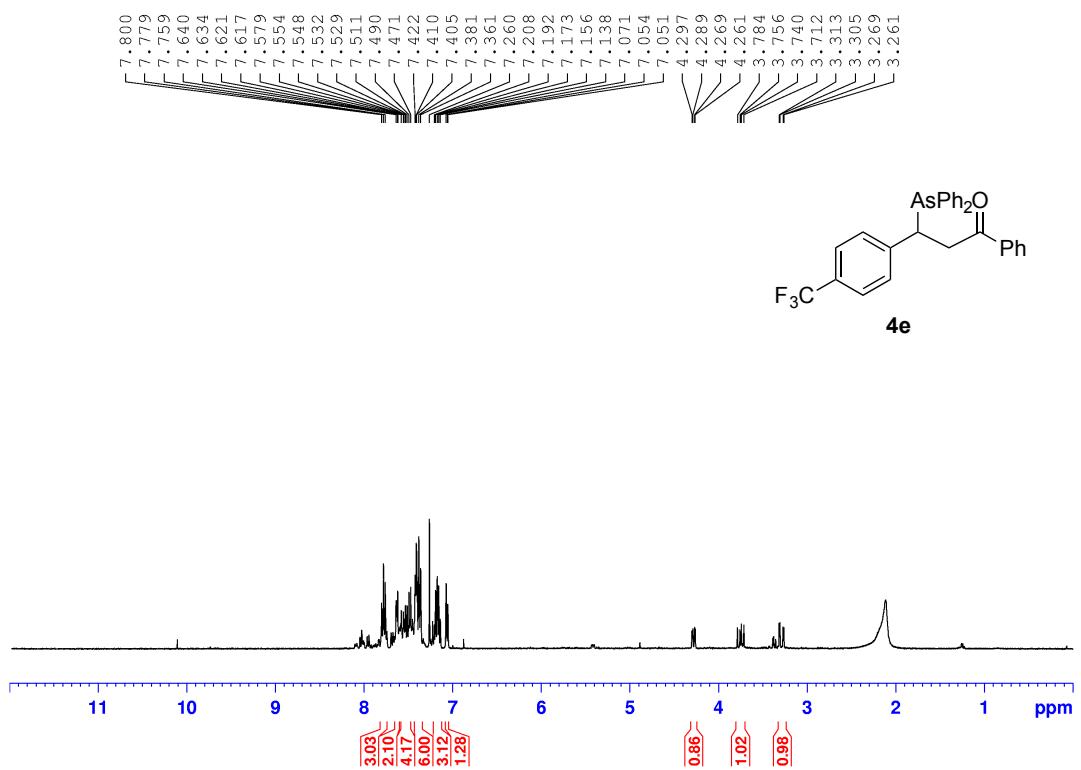
**Figure s11.** *¹H NMR spectrum of arsine **4e** in CDCl₃.*
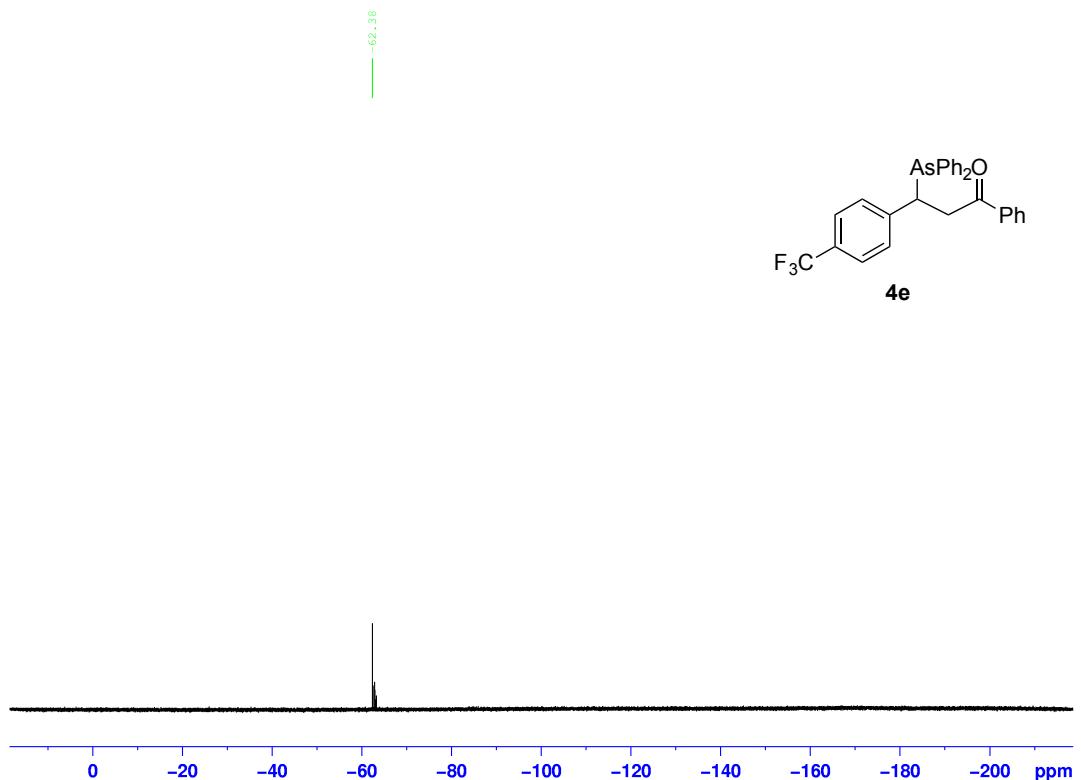
Figure s12. *^{19}F NMR spectrum of arsine **4e** in CDCl$_3$.*

HPLC spectra

Racemic phosphine sulfide **3**
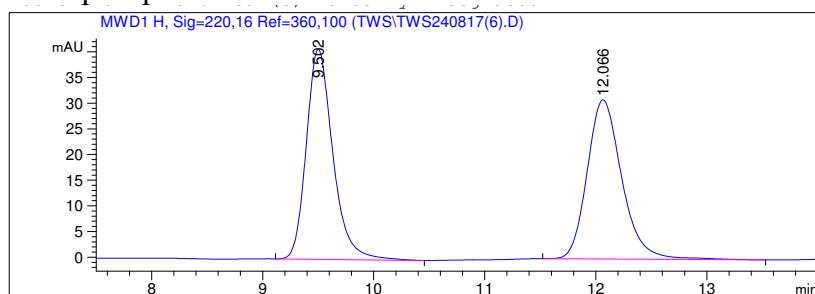

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                    Area Percent Report
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Sorted By              :        Signal
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Dilution:                       :        1.0000
Sample Amount: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


Signal 1: MWD1 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1   9.502 BB   0.2539   680.07605   40.90984  50.2851
  2  12.066 BB   0.3331   672.36462   30.99307  49.7149
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Figure s13. *HPLC spectrum of racemic phosphine sulfide* ***3***.

Table 1 Entry 2
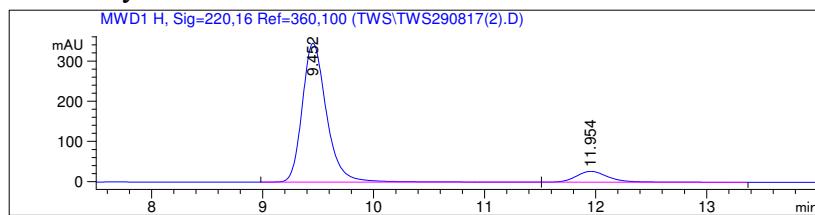

```
==================================================================
                    Area Percent Report
==================================================================

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 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]         %
----|-------|----|-------|----------|----------|--------|
  1   9.452 BV   0.2309  5236.42090  345.41492  90.4579
  2  11.954 VB   0.3099   552.37445   27.08693   9.5421
```

Figure s14. *HPLC spectrum of chiral phosphine sulfide* ***3*** *in Table 1 Entry 2.*

Table 1 Entry 3
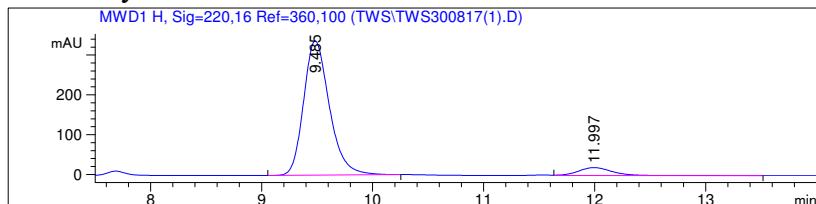

```
========================================================================
                        Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :       1.0000
Dilution:                     :       1.0000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


Signal 1: MWD1 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.485 BB    0.2481 5438.37256  337.35065  92.7534
  2  11.997 VB    0.3276  424.88461   19.85819   7.2466
```

Figure s15. *HPLC spectrum of chiral phosphine sulfide **3** in Table 1 Entry 3.*

Table 1 Entry 4
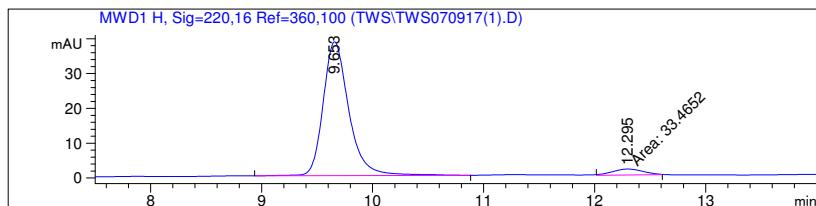

```
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                        Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :       1.0000
Dilution:                     :       1.0000
Sample Amount:     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


Signal 1: MWD1 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.653 BB    0.2438  618.54633   38.43235  94.8674
  2  12.295 MM    0.3246   33.46520    1.71854   5.1326
```

Figure s16. *HPLC spectrum of chiral phosphine sulfide **3** in Table 1 Entry 4.*

Table 1 Entry 4 (after a single recrystallization)
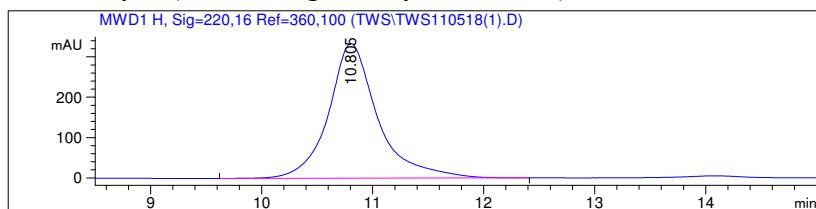

```
=================================================================
                     Area Percent Report
=================================================================

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


Signal 1: MWD1 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
 #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.805 BB   0.4475 1.02788e4   333.54575 100.0000
```

Figure s17. *HPLC spectrum of chiral phosphine sulfide **3** in Table 1 Entry 4 (after a single recrystallization).*

Table 1 Entry 5
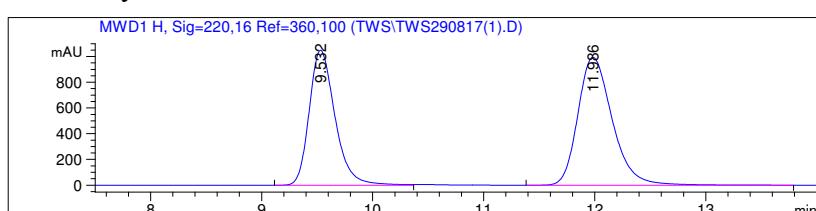

```
=================================================================
                     Area Percent Report
=================================================================

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 H, Sig=220,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
 #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.532 BV   0.2487 1.69641e4  1048.82837  44.2442
   2  11.986 BB   0.3308 2.13779e4   994.43610  55.7558
```

Figure s18. *HPLC spectrum of chiral phosphine sulfide **3** in Table 1 Entry 5.*

Racemic arsine **4a**


```
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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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.233 MM   0.2404  359.60214   24.92695   49.6776
  2  11.218 MM   0.2654  364.27005   22.87154   50.3224
```
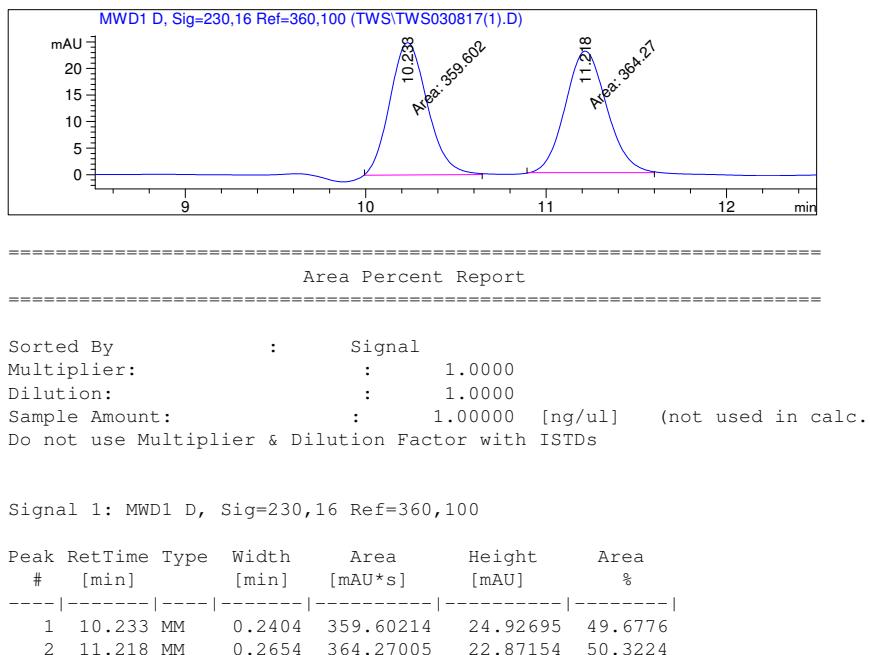
Figure s19. *HPLC spectrum of racemic arsine* ***4a****.*

Table 2 Entry 2


```
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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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.226 BB   0.2571  180.68637   10.91400   60.6518
  2  11.208 BB   0.2896  117.22154    6.22750   39.3482
```
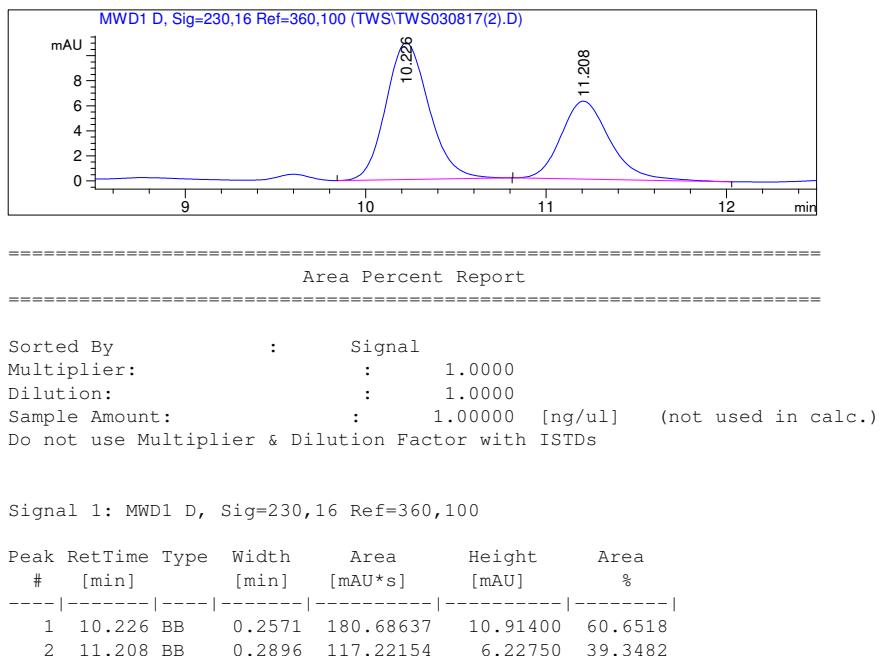
Figure s20. *HPLC spectrum of chiral arsine* ***4a*** *in Table 2 Entry 2.*

Table 2 Entry 3
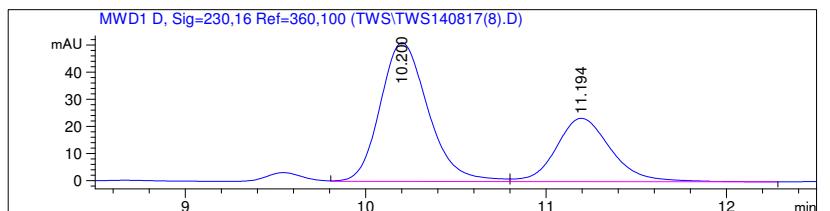

```
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                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :        1.0000
Dilution:                       :        1.0000
Sample Amount: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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]    [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.200 VV   0.2851   944.58893   51.22661   65.7096
  2  11.194 VB   0.3219   492.93210   23.38595   34.2904
```

***Figure s21.** HPLC spectrum of chiral arsine **4a** in Table 2 Entry 3.*

Table 2 Entry 4
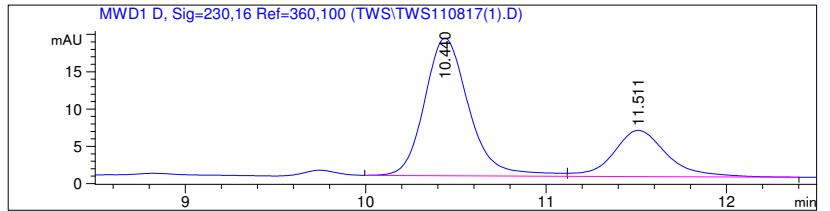

```
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                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :        1.0000
Dilution:                       :        1.0000
Sample Amount: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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]    [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.440 BV   0.2609   314.42728   18.44017   71.1585
  2  11.511 VB   0.3102   127.44170    6.18952   28.8415
```

***Figure s22.** HPLC spectrum of chiral arsine **4a** in Table 2 Entry 4.*

Table 2 Entry 5
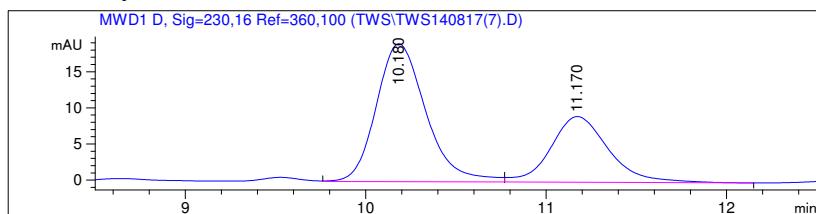

```
=================================================================
                     Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.180 VV   0.2949   364.68622   19.08482   64.3233
  2  11.170 VB   0.3399   202.27214    9.08043   35.6767
```

Figure s23. *HPLC spectrum of chiral arsine **4a** in Table 2 Entry 5.*

Table 2 Entry 6
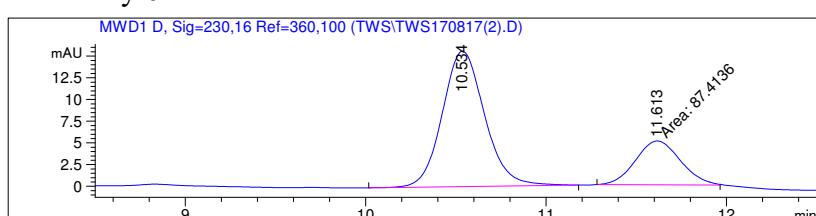

```
=================================================================
                     Area Percent Report
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Sorted By             :        Signal
Multiplier:                    :        1.0000
Dilution:                      :        1.0000
Sample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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.534 BB   0.2501   254.41805   15.61631   74.4279
  2  11.613 MM   0.2883    87.41356    5.05314   25.5721
```

Figure s24. *HPLC spectrum of chiral arsine **4a** in Table 2 Entry 6.*

Table 2 Entry 8
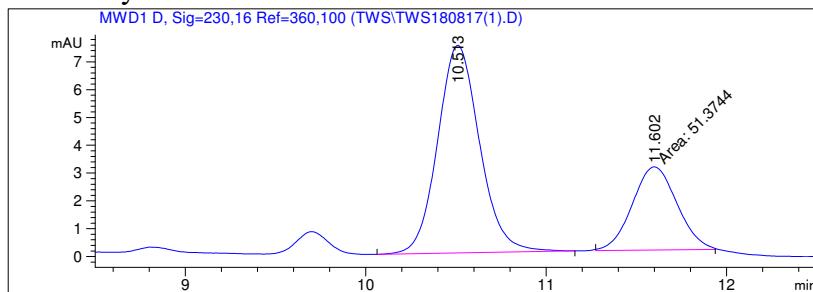

```
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                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :      1.0000
Dilution:                       :      1.0000
Sample Amount: 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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.513 BB    0.2486  120.61105    7.46136   70.1286
  2  11.602 MM    0.2864   51.37437    2.98978   29.8714
```

Figure s25. *HPLC spectrum of chiral arsine **4a** in Table 2 Entry 8.*

Table 2 Entry 9
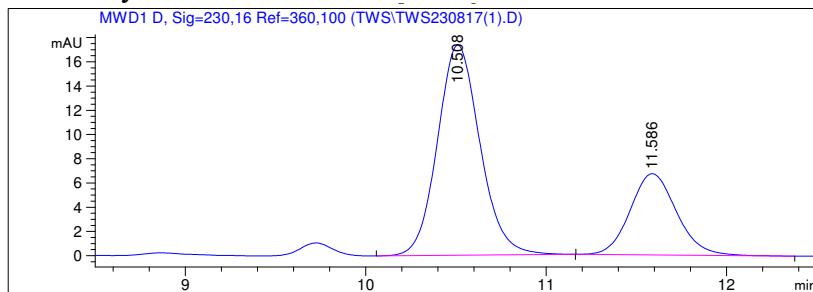

```
===================================================================
                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :      1.0000
Dilution:                       :      1.0000
Sample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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.508 BB    0.2511  284.18588   17.35073   70.2801
  2  11.586 BB    0.2749  120.17574    6.71121   29.7199
```

Figure s26. *HPLC spectrum of chiral arsine **4a** in Table 2 Entry 9.*

Table 3 Entry 2
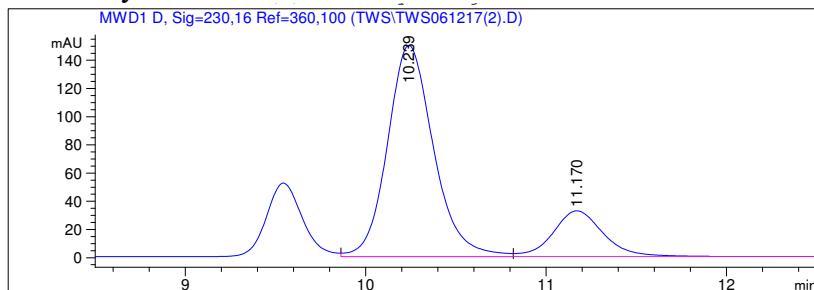

```
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                         Area Percent Report
========================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area         Height      Area
  #   [min]         [min]    [mAU*s]        [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.239 VV    0.2710 2657.53101  149.78130   80.7220
   2  11.170 VB    0.2959  634.67090   32.48362   19.2780
```

Figure s27. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 2*

Table 3 Entry 3
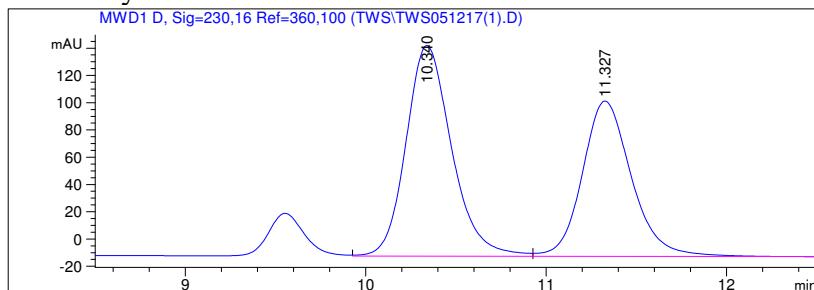

```
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                         Area Percent Report
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Sorted By                  :        Signal
Multiplier:                     :        1.0000
Dilution:                       :        1.0000
Sample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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area         Height      Area
  #   [min]         [min]    [mAU*s]        [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.340 VV    0.2690 2715.93335  154.54321   55.6559
   2  11.327 VBA   0.2874 2163.93628  114.02063   44.3441
```

Figure s28. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 3*

Table 3 Entry 4
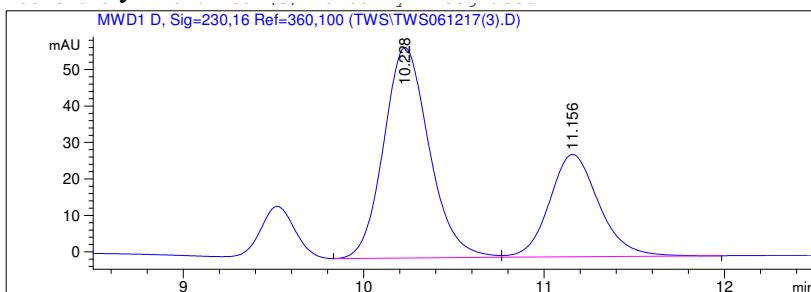

```
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                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :       1.0000
Dilution:                       :       1.0000
Sample Amount: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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.228 BV   0.2682 1011.07990   57.77390  65.3677
  2  11.156 VB   0.2904  535.67664   28.09463  34.6323
```

Figure s29. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 4.*

Table 3 Entry 5
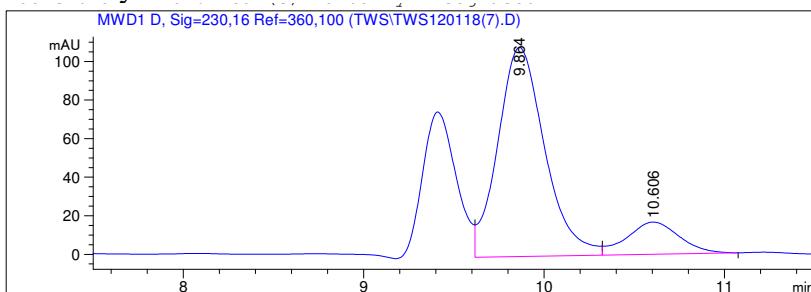

```
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                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :       1.0000
Dilution:                       :       1.0000
Sample Amount: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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.864 VV   0.2744 1955.56848  108.45296  85.3456
  2  10.606 VB   0.3028  335.78290   16.68306  14.6544
```

Figure s30. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 5.*

Table 3 Entry 6
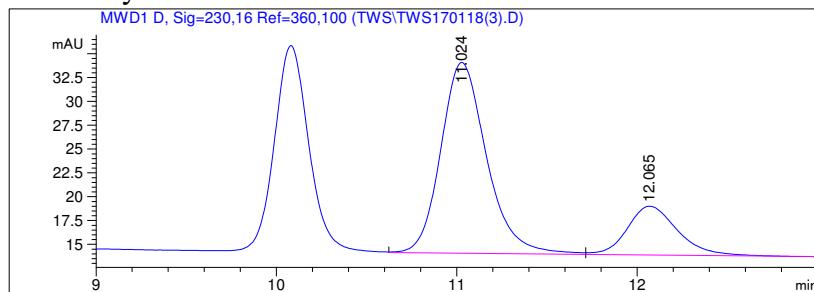

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                        Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:           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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  11.024 VV    0.2674  352.33932   20.01755  77.8769
  2  12.065 VBA   0.2936  100.09152    5.12976  22.1231
```

Figure s31. *HPLC spectrum of chiral arsine 4a in Table 3 Entry 6.*

Table 3 Entry 7
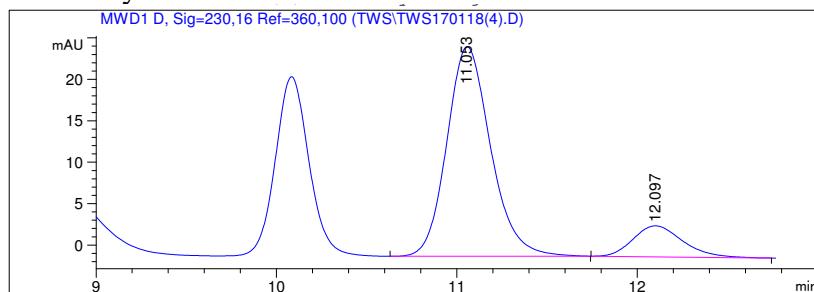

```
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                        Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Sample Amount:       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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  11.053 BB    0.2609  426.58368   25.27765  85.6682
  2  12.097 BBA   0.2907   71.36488    3.73946  14.3318
```

Figure s32. *HPLC spectrum of chiral arsine 4a in Table 3 Entry 7.*

Table 3 Entry 8
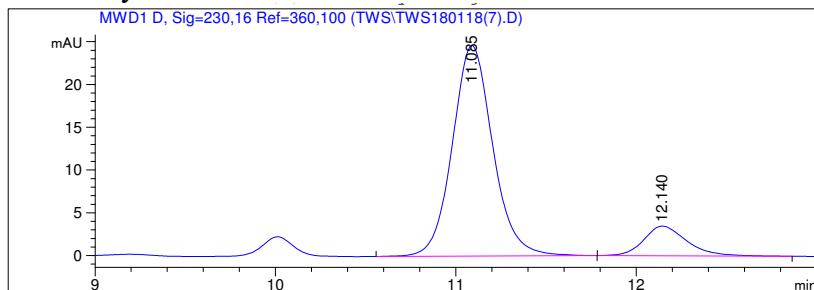

```
=================================================================
                        Area Percent Report
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Sorted By                 :         Signal
Multiplier:                       :        1.0000
Dilution:                         :     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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.085 BB   0.2377   383.45328   24.62228   86.9083
  2  12.140 BB   0.2437    57.76253    3.47867   13.0917
```

Figure s33. HPLC spectrum of chiral arsine 4a in Table 3 Entry 8.

Table 3 Entry 9
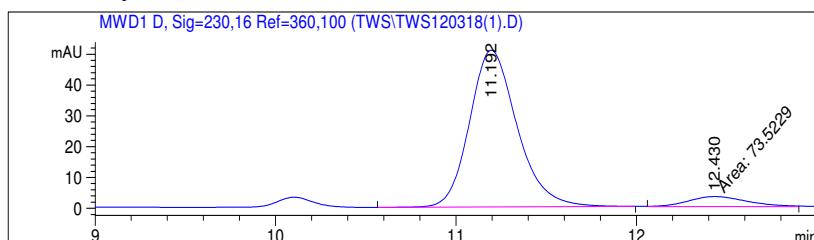

```
=================================================================
                        Area Percent Report
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Sorted By                 :         Signal
Multiplier:                       :        1.0000
Dilution:                         :     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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.192 BB   0.2795   930.84247   50.85662   92.6797
  2  12.430 MM   0.3760    73.52291    3.25937    7.3203
```

Figure s34. HPLC spectrum of chiral arsine 4a in Table 3 Entry 9.

Table 3 Entry 10
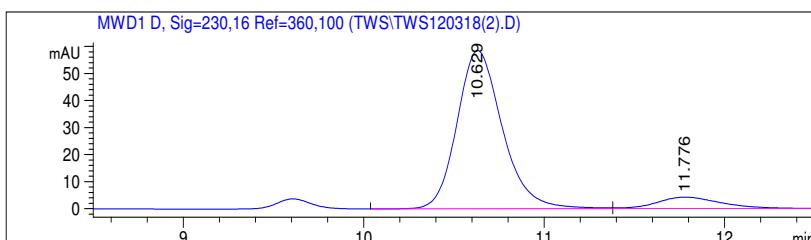

```
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                     Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :       1.0000
Dilution:                     :       1.0000
Sample Amount:        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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.629 BV    0.2681  1024.78076   58.58186  90.6031
  2  11.776 VB    0.3648   106.28550    4.26389   9.3969
```

Figure s35. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 10.*

Table 3 Entry 11
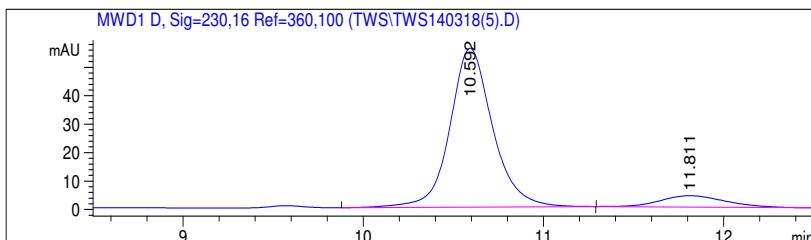

```
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                     Area Percent Report
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Sorted By            :        Signal
Multiplier:                   :       1.0000
Dilution:                     :       1.0000
Sample Amount:        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


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.592 BB    0.2481   920.29401   55.89064  90.1559
  2  11.811 BB    0.3817   100.48656    3.99135   9.8441
```

Figure s36. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 11.*

Table 3 Entry 12
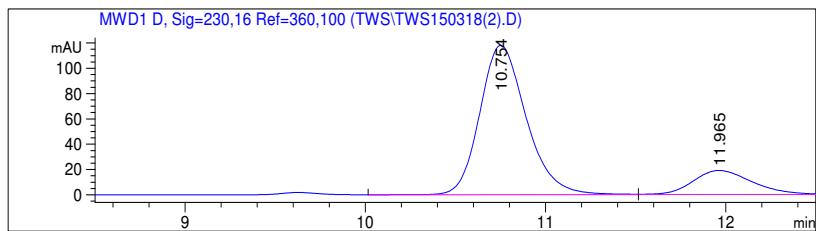
```
===================================================================
                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :        1.0000
Dilution:                       :        1.0000
Sample Amount:                  :        1.00000  [ng/ul]   (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: MWD1 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.754 BV    0.2728 2113.70630  118.08288  82.5503
  2  11.965 VB    0.3562  446.80212   19.15246  17.4497
```

Figure s37. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 12.*

Table 3 Entry 13
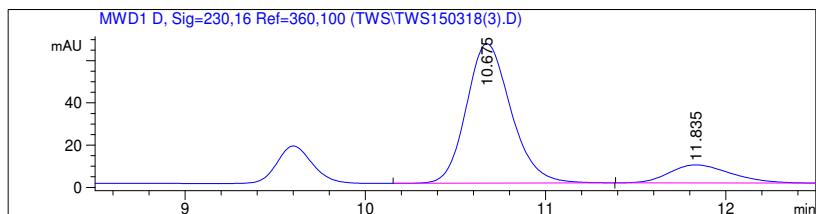

```
===================================================================
                        Area Percent Report
===================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.675 BB    0.2640 1132.96399   66.09711  84.7020
  2  11.835 BB    0.3667  204.62436    8.56656  15.2980
```

Figure s38. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 13.*

Table 3 Entry 14
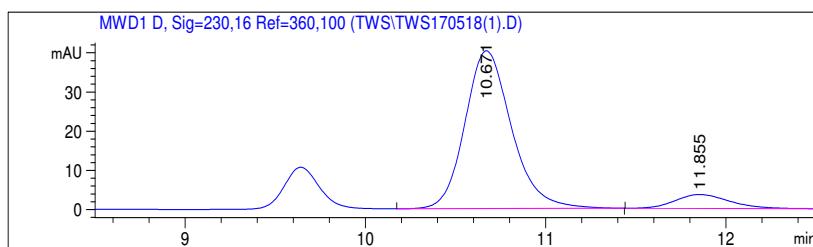

```
================================================================
                    Area Percent Report
================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]         [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.671 BB   0.2736   723.66382   40.27212   90.5503
  2  11.855 BB   0.3182    75.52071    3.54993    9.4497
```

Figure s39. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 14.*

Table 3 Entry 15
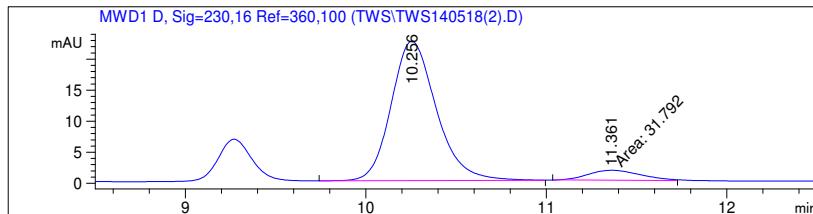

```
================================================================
                    Area Percent Report
================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]         [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.256 BB   0.2663   390.04480   22.49098   92.4634
  2  11.361 MM   0.3342    31.79202    1.58542    7.5366
```

Figure s40. *HPLC spectrum of chiral arsine **4a** in Table 3 Entry 15.*

Table 4 Entry 1
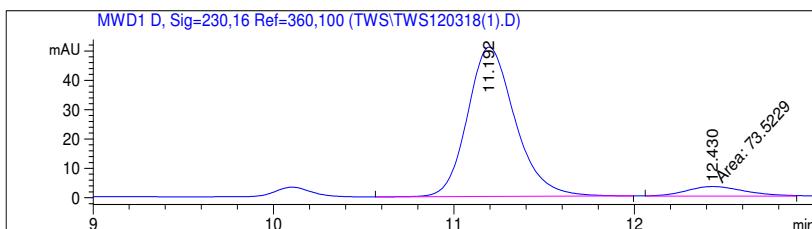

```
================================================================
                      Area Percent Report
================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  11.192 BB   0.2795  930.84247   50.85662  92.6797
  2  12.430 MM   0.3760   73.52291    3.25937   7.3203
```

*Figure s41. HPLC spectrum of chiral arsine **4a** in Table 4 Entry 1.*

Racemic arsine **4b**
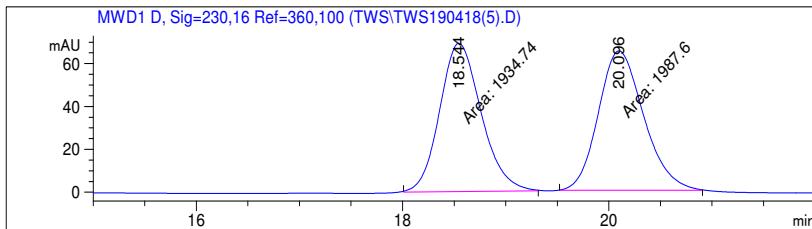

```
================================================================
                      Area Percent Report
================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  18.544 MM   0.4662 1934.73596   69.16474  49.3261
  2  20.096 MM   0.5096 1987.59875   65.00404  50.6739
```

*Figure s42. HPLC spectrum of racemic arsine **4b**.*

Table 4 Entry 2
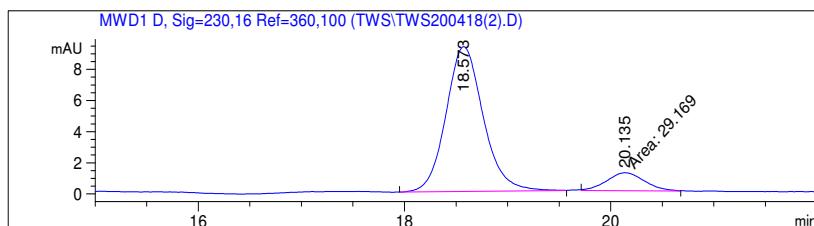

```
========================================================================
                          Area Percent Report
========================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area       Height      Area
  #   [min]        [min]    [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  18.573 BB    0.3805  233.31445    9.30440   88.8873
  2  20.135 MM    0.4230   29.16898    1.14929   11.1127
```

Figure s43. *HPLC spectrum of chiral arsine* ***4b*** *in Table 4 Entry 2.*

Racemic arsine **4c**
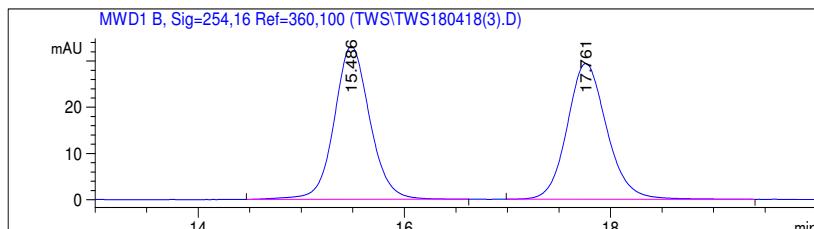

```
================================================================
                          Area Percent Report
================================================================

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  15.486 BB    0.3658  793.76508   33.10006   50.3075
  2  17.761 BB    0.4054  784.06049   29.37558   49.6925
```

Figure s44. *HPLC spectrum of racemic arsine* ***4c****.*

Table 4 Entry 3
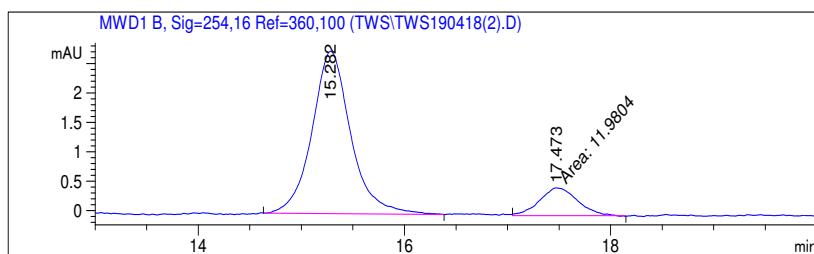

```
===================================================================
                     Area Percent Report
===================================================================

Sorted By              :        Signal
Multiplier:                     :      1.0000
Dilution:                       :      1.0000
Sample Amount:                  :      1.00000  [ng/ul]   (not used in calc.)
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  15.282 BB   0.3804   72.08023    2.76236   85.7479
  2  17.473 MM   0.4258   11.98039  4.68937e-1  14.2521
```

Figure s45. HPLC spectrum of chiral arsine 4c in Table 4 Entry 3.

Racemic arsine **4d**
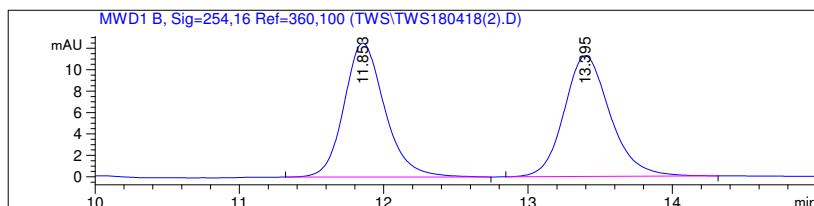

```
===================================================================
                     Area Percent Report
===================================================================

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  11.853 BB   0.2989   245.60713   12.51644  49.5914
  2  13.395 BB   0.3383   249.65414   11.27784  50.4086
```

Figure s46. HPLC spectrum of racemic arsine 4d.

Table 4 Entry 4
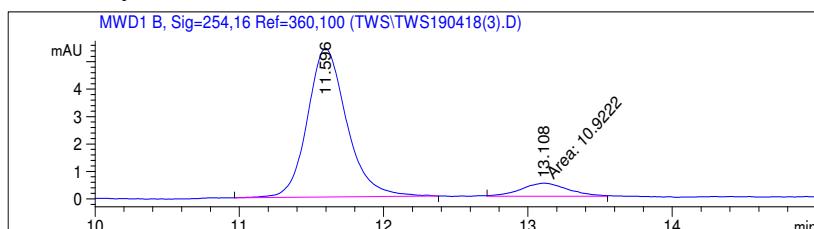

```
===================================================================
                       Area Percent Report
===================================================================

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  11.596 BB    0.2868  102.58904    5.41991  90.3779
  2  13.108 MM    0.3793   10.92220  4.79910e-1  9.6221
```

Figure s47. *HPLC spectrum of chiral arsine* ***4d*** *in Table 4 Entry 4.*

Racemic arsine **4e**
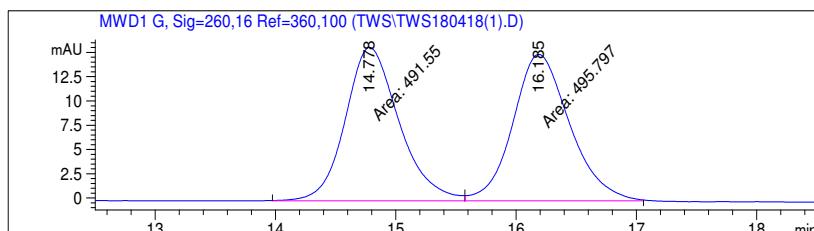

```
===================================================================
                       Area Percent Report
===================================================================

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  14.778 MF    0.5186  491.55026   15.79876  49.7849
  2  16.185 FM    0.5477  495.79736   15.08859  50.2151
```

Figure s48. *HPLC spectrum of racemic arsine* ***4e***.

Table 4 Entry 5
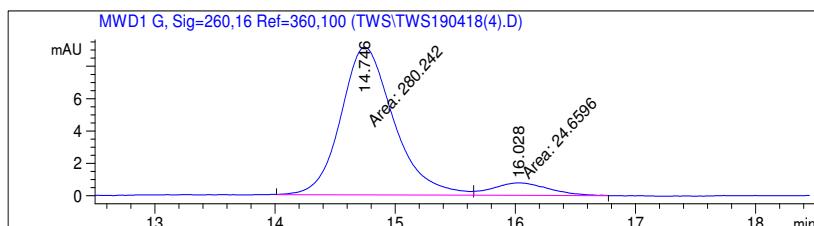

```
========================================================================
                        Area Percent Report
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Sorted By              :        Signal
Multiplier:                     :       1.0000
Dilution:                       :       1.0000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


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

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]    [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.746 MF   0.5115  280.24222    9.13157   91.9123
   2  16.028 FM   0.5370   24.65956  7.65356e-1   8.0877
```

Figure s49. *HPLC spectrum of chiral arsine **4e** in Table 4 Entry 5.*

Table s1 Entry 10
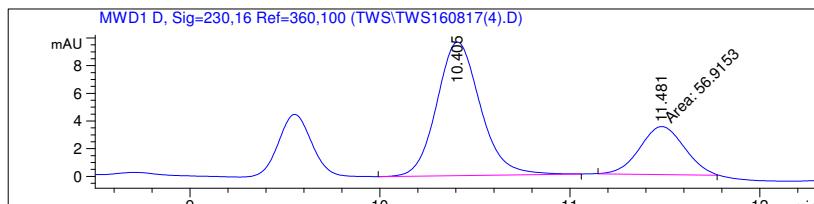

```
========================================================================
                        Area Percent Report
========================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]    [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.405 BB   0.2435  153.55287    9.65874   72.9577
   2  11.481 MM   0.2728   56.91534    3.47676   27.0423
```

Figure s50. *HPLC spectrum of chiral arsine **4a** in Table s1 Entry 10.*

Table s1 Entry 11
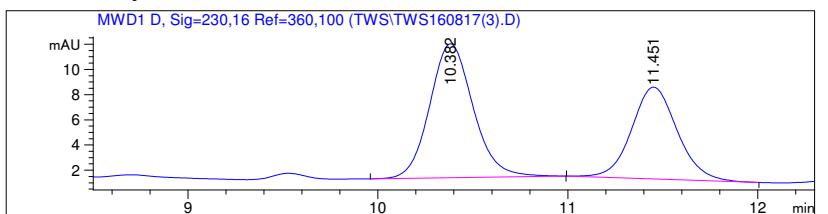

```
=================================================================
                       Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.382 BB    0.2432  168.84918   10.63442  57.9949
  2  11.451 BB    0.2555  122.29566    7.29812  42.0051
```

Figure s51. *HPLC spectrum of chiral arsine **4a** in Table s1 Entry 11.*

Table s1 Entry 15
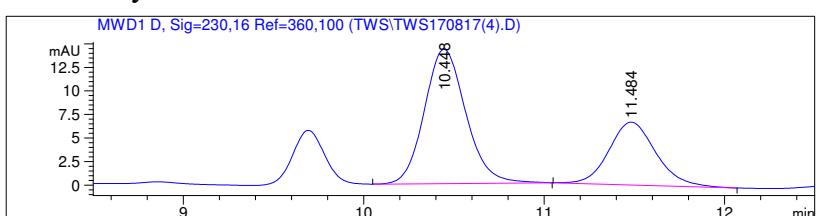

```
=================================================================
                       Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.448 BB    0.2459  227.12941   14.25611  65.2678
  2  11.484 BB    0.2772  120.86658    6.67528  34.7322
```

Figure s52. *HPLC spectrum of chiral arsine **4a** in Table s1 Entry 15*

Table s2 Entry 1
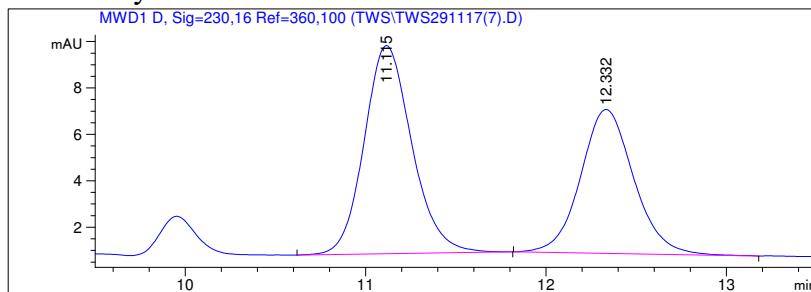

```
=====================================================================
                      Area Percent Report
=====================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.115 BB    0.2802  164.69316    8.97036   56.4613
  2  12.332 BB    0.3109  126.99919    6.20227   43.5387
```

Figure s53. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 1.*

Table s2 Entry 2
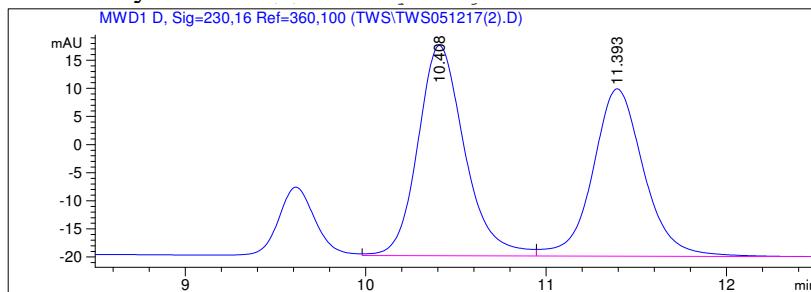

```
=====================================================================
                      Area Percent Report
=====================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width      Area        Height      Area
  #   [min]        [min]    [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.408 VV    0.2737  672.43286   37.40774   53.3875
  2  11.393 VB    0.2980  587.09839   29.77983   46.6125
```

Figure s54. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 2*

Table s2 Entry 3
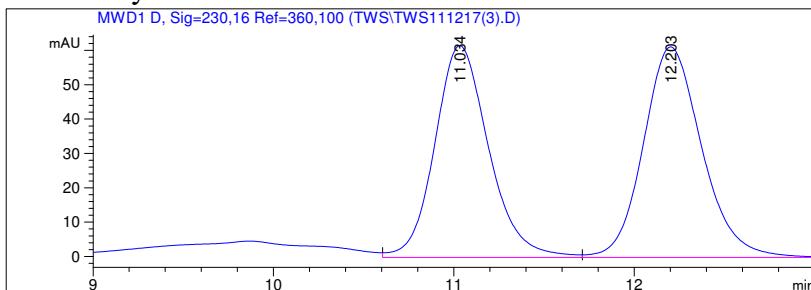

```
=====================================================================
                      Area Percent Report
=====================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  11.034 VV   0.3159 1279.54993   61.70493  48.1300
  2  12.203 VB   0.3445 1378.97729   61.27803  51.8700
```

Figure s55. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 3*

Table s2 Entry 4
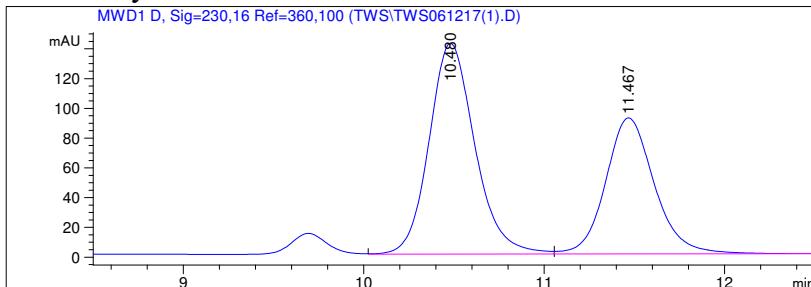

```
=====================================================================
                      Area Percent Report
=====================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.480 VV   0.2697 2500.72485  141.81233  59.1991
  2  11.467 VB   0.2857 1723.53760   91.52664  40.8009
```

Figure s56. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 4*

Table s2 Entry 5
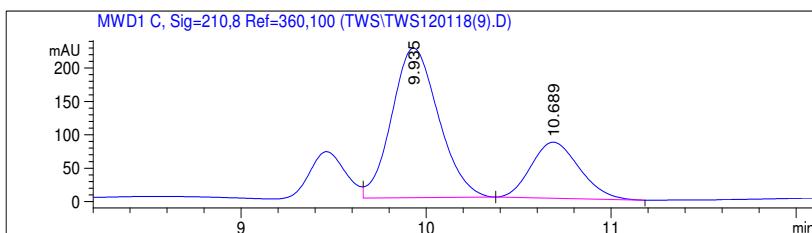

```
=================================================================
                     Area Percent Report
=================================================================

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 C, Sig=210,8 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1   9.935 VB    0.2706 3931.81372  224.24200  72.0836
  2  10.689 BB    0.2817 1522.70618   83.90736  27.9164
```

Figure s57. *HPLC spectrum of chiral arsine* **4a** *in Table s2 Entry 5*

Table s2 Entry 6
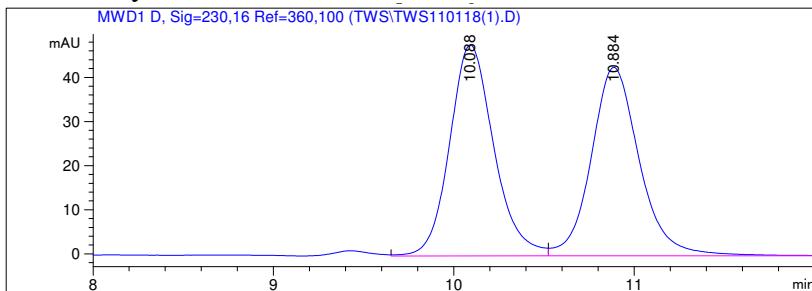

```
=================================================================
                     Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height      Area
  #   [min]        [min]   [mAU*s]      [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.088 VV    0.2584  814.27881   47.87659  50.5448
  2  10.884 VB    0.2834  796.72626   42.75217  49.4552
```

Figure s58. *HPLC spectrum of chiral arsine* **4a** *in Table s2 Entry 6.*

Table s2 Entry 8
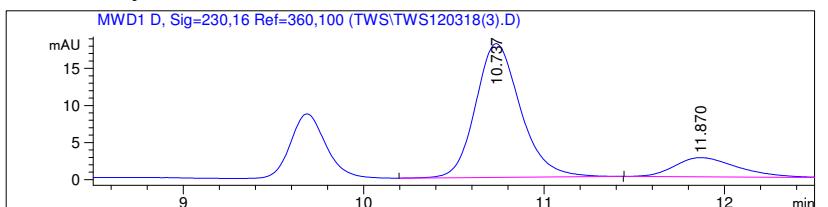

```
=================================================================
                    Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.737 BB   0.2635  311.71494   18.04808   82.9013
  2  11.870 BB   0.3642   64.29214    2.60262   17.0987
```

Figure s59. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 8.*

Table s2 Entry 9
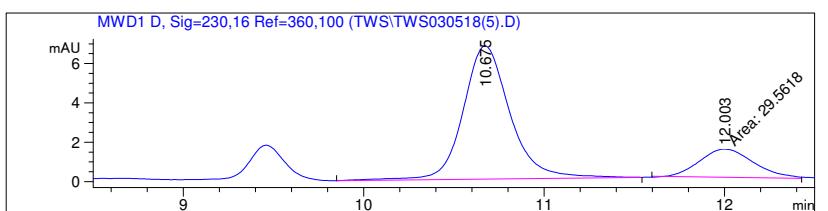

```
=================================================================
                    Area Percent Report
=================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area       Height     Area
  #   [min]        [min]   [mAU*s]      [mAU]       %
----|-------|----|-------|----------|----------|--------|
  1  10.675 BB   0.2708  122.36729    6.77104   80.5424
  2  12.003 MM   0.3447   29.56179    1.42917   19.4576
```

Figure s60. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 9.*

Table s2 Entry 11
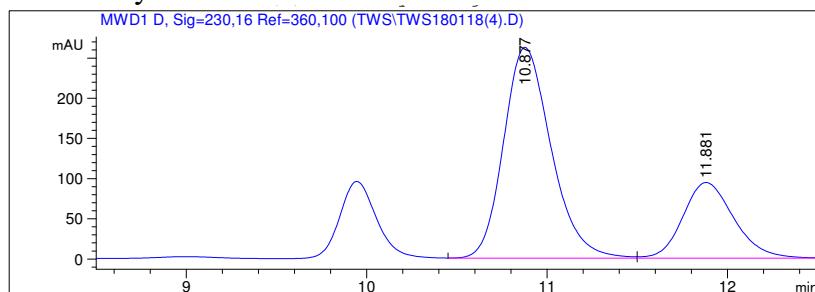

```
========================================================================
                       Area Percent Report
========================================================================

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 D, Sig=230,16 Ref=360,100

Peak RetTime Type  Width     Area        Height     Area
  #   [min]        [min]   [mAU*s]       [mAU]        %
----|-------|----|-------|----------|----------|--------|
  1  10.877 BV    0.2814 4796.88330  262.20886   72.0980
  2  11.881 VB    0.3020 1856.39807   94.17924   27.9020
```

Figure s61. *HPLC spectrum of chiral arsine **4a** in Table s2 Entry 11.*

Investigating interactions between Pd catalysts and HAsPh₂
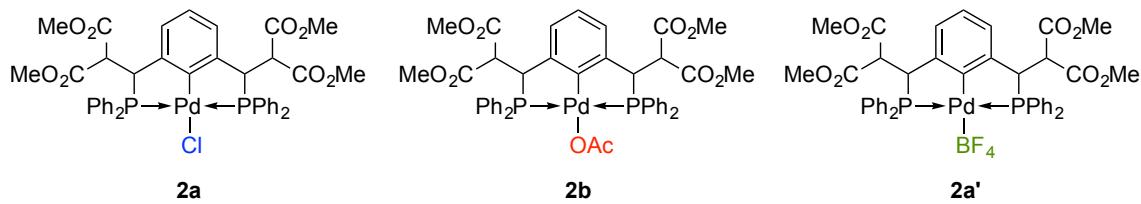
***Figure s62**. Pd(II)-pincer complexes for investigation.*

To investigate interactions between Pd-pincer complexes **2** with HAsPh₂, a series of experiments were carried out and signals were monitored with $^{31}P\{^1H\}$ NMR spectroscopy (Table s3).

Experimental procedure

Preparation of complex **2a'**: Pd complex **2a** (43.78 mg, 0.05 mmol, 1.0 equiv) and AgBF₄ (11.68 mg, 0.06 mmol, 1.2 equiv) was stirred in DCM (2 mL) for 1 h. The crude mixture was passed through a short plug of silica and dried prior to use.

Without base: HAsPh₂ (11.51 mg, 0.05 mmol, 1.0 equiv) and Pd complex **2** (5.00 μmol, 10 mol %) were stirred in CD₃OD (1.2 mL) for 5 mins at RT.

With base: HAsPh₂ (11.51 mg, 0.05 mmol, 1.0 equiv) and Pd complex **2** (5.00 μmol, 10 mol %) were stirred in CD₃OD (1.2 mL) for 5 mins at RT. Subsequently, DIPEA (9.58 μL, 0.06 mmol, 1.1 equiv) was added and the solution was stirred for another 5 mins at RT.

***Table s3.** Interactions between Pd pincer complexes **2** and reagents.*

Entry	Complex	HEPh₂	Base	$^{31}P\{^1H\}$ δ (ppm)	
1	Pd–BF₄ **2a'**	-	-	48.9	(complex **2a'**)
2	Pd–OAc **2b**	-	-	49.4	(complex **2b**)
3	Pd–Cl **2a**	-	-	48.3	(complex **2a**)
4[d]	Pd–BF₄ **2a'**	HAsPh₂	-	48.6	(complex **2a'**)
				51.8	(intermediate **B**)
5[b,d]	Pd–BF₄ **2a'**	HAsPh₂	DIPEA	53.7	(intermediate **A**)
6[c]	Pd–OAc **2b**	HAsPh₂	-	53.5	(intermediate **A**)
7[b,c]	Pd–OAc **2b**	HAsPh₂	DIPEA	53.7	(intermediate **A**)
8[a]	Pd–Cl **2a**	HAsPh₂	-	48.4	(complex **2a**)
				53.3	(intermediate **A**)
9[a,b]	Pd–Cl **2a**	HAsPh₂	DIPEA	53.7	(intermediate **A**)

[a]Reaction conditions: HAsPh₂ (11.51 mg, 0.05 mmol, 1.0 eq.), cat. **2a** (4.38 mg, 5.00 μmol, 10 mol %), CD₃OD (1.2 mL). [b]DIPEA (9.58 μL, 0.06 mmol, 1.1 eq.) was added. [c]Reaction conditions: HAsPh₂ (11.51 mg, 0.05 mmol, 1.0 eq.), cat. **2b** (4.49 mg, 5.0 0μmol, 10 mol %), CD₃OD (1.2 mL). [d]Reaction conditions: HAsPh₂ (11.51 mg, 0.05 mmol, 1.0 eq.), cat. **2a'** (4.63 mg, 5.00 μmol, 10 mol %), CD₃OD (1.2 mL).

Discussion
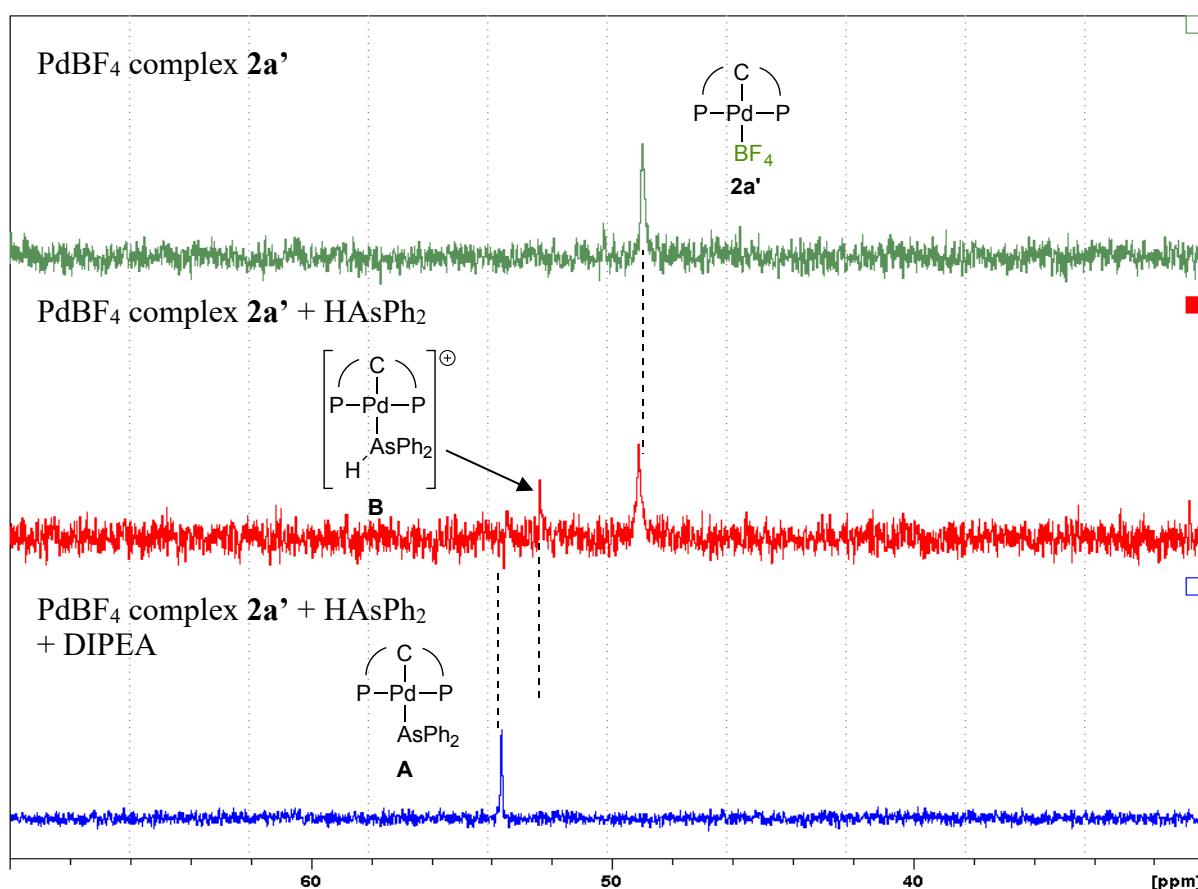
Figure s63. *$^{31}P\{^1H\}$ NMR spectra of PdBF$_4$ complex **2a'** with reagents.*

PdBF$_4$-complex **2a'** was specially prepared for the weakly-coordinating and non-basic properties of the $^-$BF$_4$ anion. Signals corresponding to intermediates **A** and **B** can be clearly observed (Figure s63).

In the absence of DIPEA, interaction between PdBF$_4$-complex **2a'** and HAsPh$_2$ generated a new signal at 51.8 ppm (intermediate **B**) (Entry 8, Figure s63). As expected, this signal could be cleanly converted to 53.7 ppm (intermediate **A**) upon deprotonation with DIPEA (Entry 9, Figure s63).

These spectra serve as a reference for the signals of intermediates **A** and **B**.
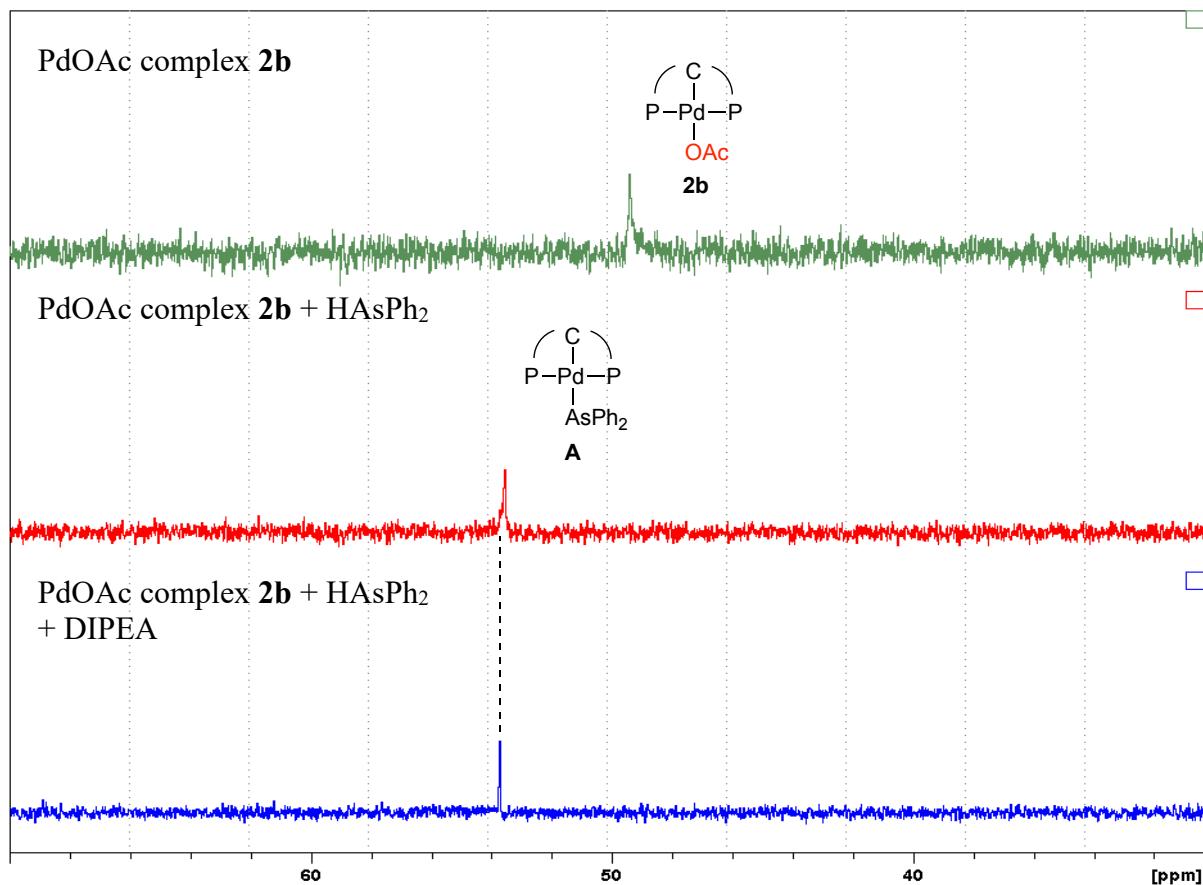
Figure s64. *$^{31}P\{^{1}H\}$ NMR spectra of PdOAc complex **2b** with reagents.*

When PdOAc-complex **2b** was employed, signal 53.5 ppm (intermediate **A**) was observed even without the addition of DIPEA (Entry 6, Figure s64). No further changes were observed when DIPEA was added (Entry 7, Figure s64), indicating that the PdOAc-complex **2b** counteranion functioned as an internal base.
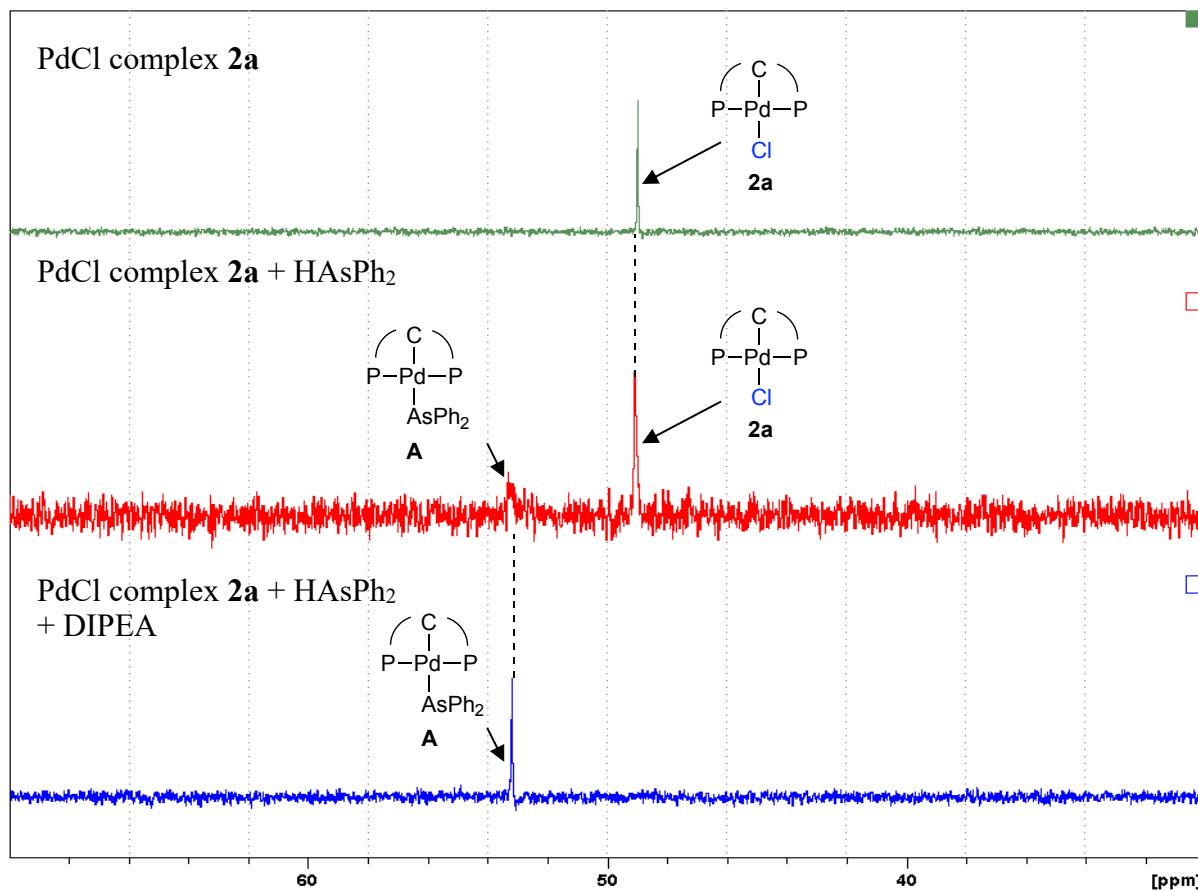
Figure s65. *$^{31}P\{^1H\}$ NMR spectra of PdCl complex **2a** with reagents.*

When PdCl-complex **2a** and $HAsPh_2$ were stirred, the original signal at 48.3 ppm remained unchanged and a minor signal at 53.3 ppm (intermediate **A**) was observed (Entry 4, Figure s65). The addition of DIPEA converted the signal at 48.3 ppm to 53.7 ppm (intermediate **A**) (Entry 5, Figure s65). No signal corresponding to intermediate **B** was observed on the NMR timescale.

The minor signal corresponding to signal **A** observed even in the absence of DIPEA may have arisen *via* 3 distinct mechanisms:

1. $HAsPh_2$ displaces the chloride anion to generate intermediate **B**, which is immediately deprotonated to generate intermediate **A**
2. Transient axial interactions with $HAsPh_2$ acidify the H–As bond to generate $^-AsPh_2$, which replaces the chloride anion to generate intermediate **A**[8]
3. An equilibrium dissociation of $HAsPh_2$ occurs in MeOD to generate $^-AsPh_2$, which displaces the chloride anion to generate intermediate **A**[9]

Pathway (3) is the least likely due to the relatively high pKa of $HAsPh_2$ (pKa = 20.3).[10] Trace ionization of $HAsPh_2$ is insufficient to completely account for the observed $^{31}P\{^1H\}$ NMR signal of intermediate **A**.

Both pathways (1) and (2) suggest that the Pd-catalyzed hydroarsination reaction proceeds *via* a similar mechanism as the corresponding hydrophosphination reaction. Interaction with Pd acidifies the H–As bond, allowing deprotonation to generate the reactive arsenide intermediate **A**. Addition of DIPEA as a proton scavenger drives the deprotonation equilibrium forward, thus cleanly generating intermediate **A** as observed in Figure s65.

Investigating deprotonation of HAsPh$_2$ in MeOH by weak bases

Hydroarsination reactions catalyzed by Pd-complexes **2** only exhibited good reactivities in alcoholic solvents such as MeOH. The high pKa of HAsPh$_2$ (pKa = 20.3)[10] in THF suggests that strong bases were required to deprotonate HAsPh$_2$. However, no pKa values of HAsPh$_2$ were available in MeOH to the best of our knowledge.

According to pKa values, it should be even harder to deprotonate HPPh$_2$: pKa (HAsPh$_2$) = 20.3, pKa (HPPh$_2$) = 21.7.[10] Thus with HPPh$_2$ being the less acidic reagent, ^{31}P{^{1}H} NMR spectroscopy was used as a convenient tool to monitor the effect of DIPEA on the H/D exchange of HPPh$_2$ in MeOD.

Experimental procedure

Without base: HPPh$_2$ (9.30 mg, 0.05 mmol, 1.0 equiv) was stirred in CD$_3$OD (1.2 mL) for 30 mins at RT.

With base: HPPh$_2$ (9.30 mg, 0.05 mmol, 1.0 equiv) was stirred in CD$_3$OD (1.2 mL) for 5 mins at RT. Subsequently, DIPEA (9.58 µL, 0.06 mmol, 1.1 equiv) was added and the solution was stirred for the stated time at RT.

Discussion
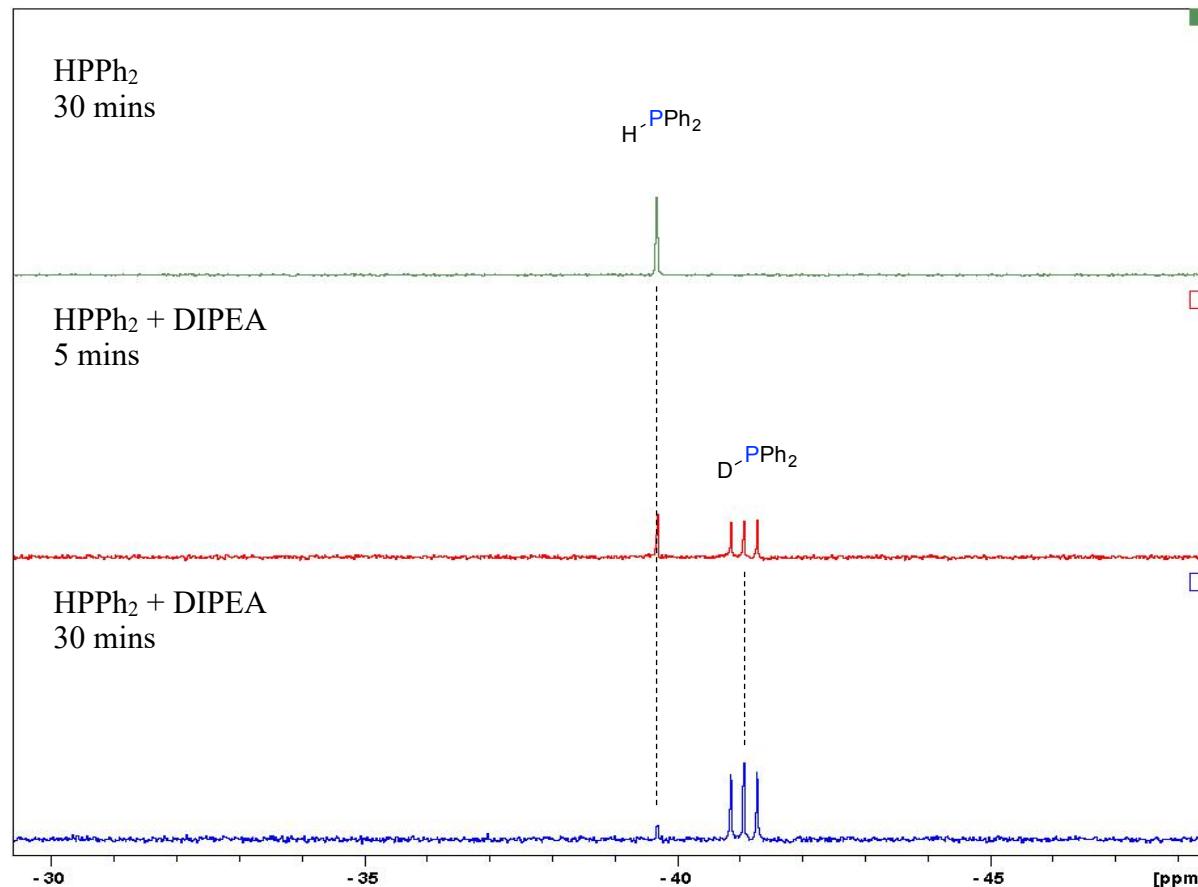
Figure s66. ^{31}P{^{1}H} NMR spectra of HPPh$_2$ with DIPEA in MeOD.

Even after 30 mins, only a single singlet was observed for HPPh$_2$ in the absence of DIPEA. No H/D exchange was observed for HPPh$_2$ in MeOD.

In the presence of DIPEA, the appearance of a characteristic 1:1:1 triplet corresponding to D–PPh$_2$ was observed at 5 minutes. Almost complete conversion of H–PPh$_2$ to D–PPh$_2$ was observed by 30 mins.

Although rate of base-assisted H/D exchange of HPPh$_2$ in MeOD is relatively slow, this suggests that DIPEA was able to deprotonate HPPh$_2$. With a lower pKa value of HAsPh$_2$ (in THF), DIPEA may similarly facilitate the deprotonation of HAsPh$_2$. Further controlled studies are required to determine accurate pKa values of HPPh$_2$ and HAsPh$_2$ in MeOH. Nevertheless, this indicatees that the base-assisted ionization of HAsPh$_2$ under optimized reaction conditions cannot be completely eliminated.

Investigating interactions between Pd catalyst 2a and HPPh$_2$
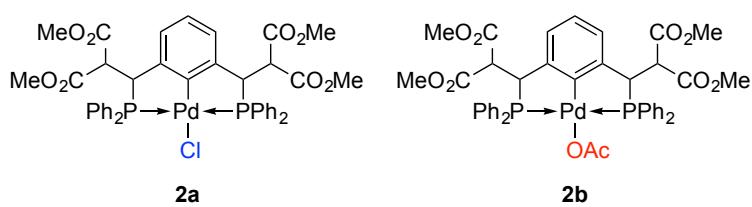
*Figure s67. Pd(II)-pincer complexes for investigation.*

Interactions between PdOAc catalyst **2b** and HPPh$_2$ have been well-established independently by the groups of Duan[11] and Leung.[12] To investigate interactions between PdCl complex **2a** with HPPh$_2$, a series of experiments were carried out and monitored by ^{31}P{^{1}H} NMR spectroscopy (Table s4).

Experimental procedure

Without base: HPPh$_2$ (9.30 mg, 0.05 mmol, 1.0 equiv) and Pd complex **2a** (4.38 mg, 5.00 μmol, 10 mol %) were stirred in the stated solvent (1.2 mL) for 5 mins at RT.

With base: HPPh$_2$ (9.30 mg, 0.05 mmol, 1.0 equiv) and Pd complex **2a** (4.38 mg, 5.00 μmol, 10 mol %) were stirred in the stated solvent (1.2 mL) for 5 mins at RT. Subsequently, DIPEA (9.58 μL, 0.06 mmol, 1.1 equiv) was added and the solution was stirred for another 5 mins at RT.

Table s4. *Interactions between Pd-pincer 2a and reagents.*

Entry	Species	^{31}P{^{1}H} δ (ppm)	J (Hz)	Multiplicity
1	H–PPh$_2$	-41.0	-	Singlet
2	Pd–Cl **2a**	48.3	-	Singlet
3	D–PPh$_2$	-42.4	33.9	1:1:1 triplet
4	**c**	-8.2	35.6	1:2:1 triplet
5	H–P(O)Ph$_2$	24.2	-	Singlet
6	**c**	52.5	35.9	Doublet
7	**B**	ND	ND ($^2J_{P-P}$, $^1J_{P-D}$)	ND (multiplet)
8	**B**	ND	ND ($^2J_{P-P}$, $^3J_{P-D}$)	ND (multiplet)
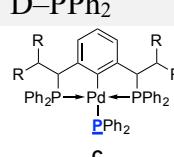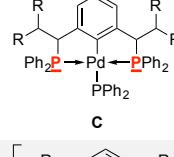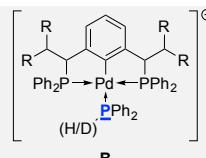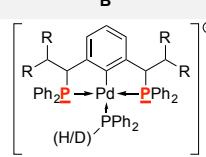
46

Discussion
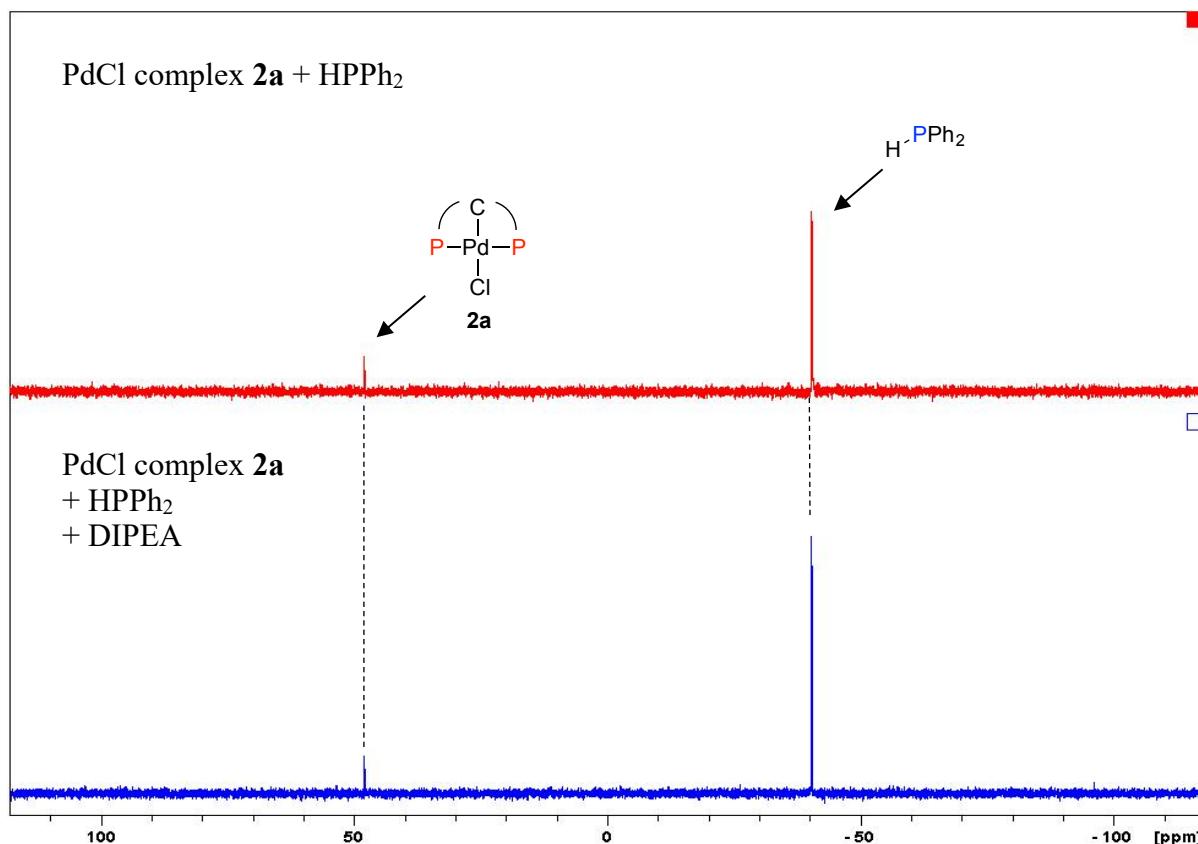
CDCl$_3$:

***Figure s68***. *$^{31}P\{^1H\}$ NMR spectra of PdCl complex **2a** with reagents in CDCl$_3$.*

No changes to the signals of catalyst **2a** and HPPh$_2$ were observed in CDCl$_3$, with and without the addition of DIPEA (Figure s68). This supports the observation that HPPh$_2$ cannot displace the Pd–Cl bond of catalyst **2a** to generate intermediates **B** and/or **C**, even in the presence of DIPEA.

MeOD:
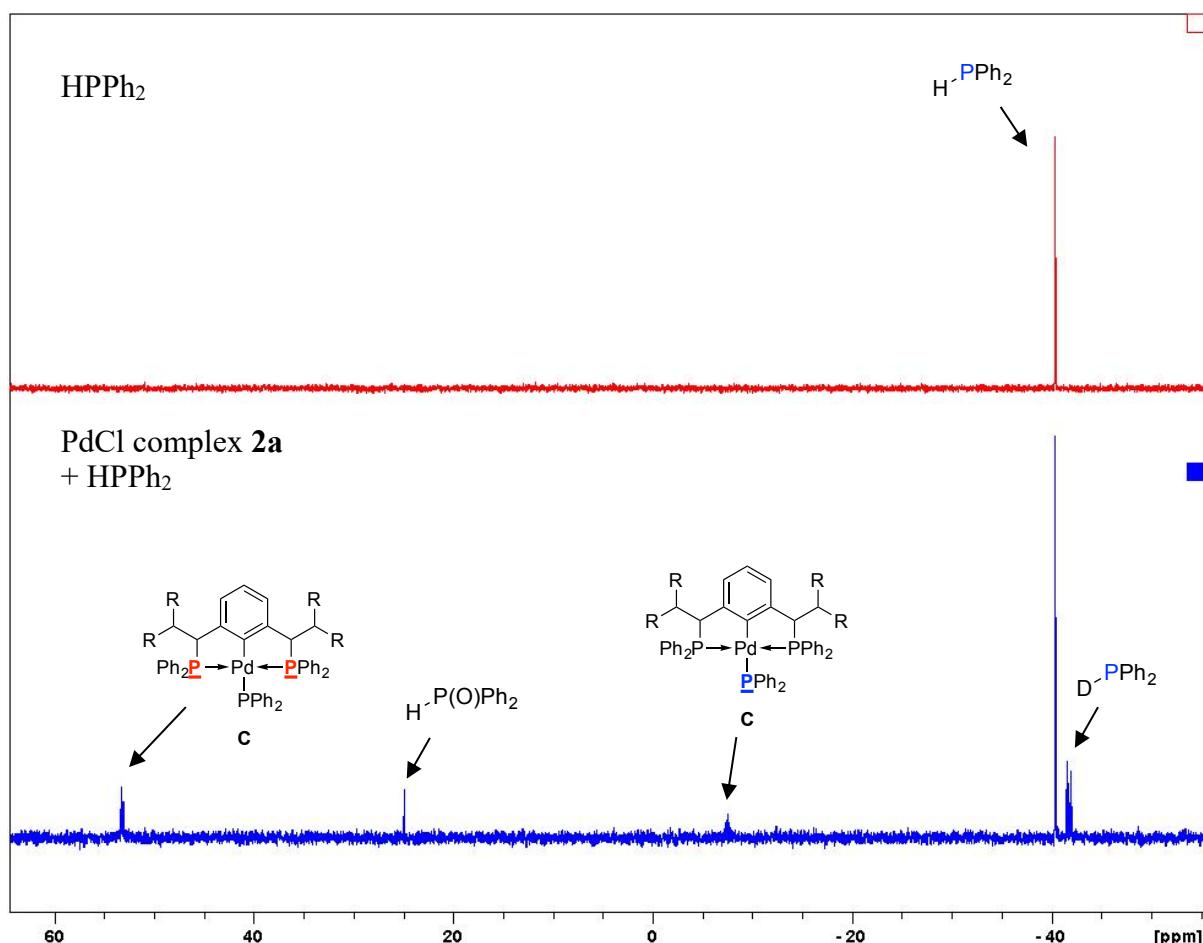
***Figure s69***. *$^{31}P\{^1H\}$ NMR spectra of PdCl complex **2a** with reagents in CD$_3$OD.*

As opposed to the study performed in CDCl$_3$ (Figure s68), two notable observations were made upon addition of catalyst **2a** to HPPh$_2$ in MeOD : 1) appearance of a triplet at -42.4 ppm and 2) a change of chemical shift and splitting patterns of the signal corresponding to catalyst **2a**. This indicates that the choice of solvent has a direct influence in the reaction.

Firstly, it was observed that a H/D exchange of (H/D)–PPh$_2$ occurred only in the presence of catalyst **2a**. Clearly, interaction between catalyst **2a** and HPPh$_2$ is required to weaken the H–PPh$_2$ bond. As the exchange occurred without the appearance of a free phosphine signal belonging to the dissociated PCP ligand, it remains possible that weak axial interactions between Pd and (H/D)–PPh$_2$ were involved.[8] This weakening of the H–PPh$_2$ bond consequently resulted in the clean conversion of catalyst **2a** to intermediate **C** (Table s4, Entries 4 and 6). The further addition of DIPEA did not result in changes to the signal of intermediate **C**.

This differs from experimental observations between catalyst **2a** and HAsPh$_2$ (Figure s65).
With HPPh$_2$: catalyst **2a** is cleanly converted to intermediate **C**
With HAsPh$_2$: catalyst **2a** remains as the major signal. This is partially supported by the lower pKa values of HAsPh$_2$ which suggest that deprotonation of H–As is relatively more challenging.[10] It must be noted that catalyst **2** may acidify the H–P and H–As bonds to different extents.[13] DIPEA was required to generate intermediate **A** cleanly.

References

[1] Y. Huang, R. J. Chew, Y., Li, S. A. Pullarkat and P.-H. Leung, *Org. Lett.*, 2011, **13**, 5862.

[2] Y. Huang, S. A. Pullarkat, Y. Li and P.-H. Leung, *Chem. Commun*, 2010, **46**, 6950.

[3] X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Chem. Commun.* 2016, **52**, 4211.

[4] W. S. Tay, X.-Y. Yang, Y. Li, S. A. Pullarkat and P.-H. Leung, *RSC Advances* 2016, **6**, 75951.

[5] M. Duan, Y. Liu, J. Ao, L. Xue, S. Luo, Y. Tan, W. Qin, C. E. Song and H. Yan, *Org. Lett.* 2017, **19**, 2298.

[6] X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics*, 2015, **34**, 5196.

[7] X.-Y. Yang, W. S. Tay, Y. Li, S. A. Pullarkat and P.-H. Leung, *Organometallics*, 2015, **34**, 1582.

[8] a) L. Maresca and G. Natile, *Comments Inorg. Chem.* 1993, **14**, 349; b) P.-H. Leung, G. M. McLaughlin, J. W. L. Martin, S. B. Wild, *Inorg. Chem.* 1986, **25**, 3392; c) J. K.-P. Ng, G.-K. Tan, J. J. Vittal and P.-H. Leung, *Inorg. Chem.* 2003, **42**, 7674; d) Y. L. Cheow, S. A. Pullarkat, Y. Li and P.-H. Leung, *J. Organomet. Chem.* 2012, **696**, 4215; e) G. Salem and S. B. Wild, *Inorg. Chem.* 1992, **31**, 581.

[9] The extent of ionization of secondary arsines was investigated in (a) V. K. Gupta, L. K. Krannich and C. L. Watkins, *Inorg. Chim. Acta.* 1987, **134**, 197, (b) W. R. Cullen, W. R. Leeder, *Can. J. Chem.* 1970, **48**, 3757.

[10] a) K. Issleib, and R. Kümmel, R. *J. Organomet. Chem.* 1965, **3**, 84; b) J.-N. Li, L. Liu, Y. F and Q.-X. Guo, *Tetrahedron*, 2006, **62**, 4453.

[11] J.-J. Feng, X.-F. Chen, M. Shi and W.-L. Duan, *J. Am. Chem. Soc.* 2010, **132**, 5562.

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

[13] G. M. Bodner, M. P. May and L. E. McKinney, *Inorg. Chem.* 1980, **19**, 1951.

## X-ray structure and crystallographic data for compound 3
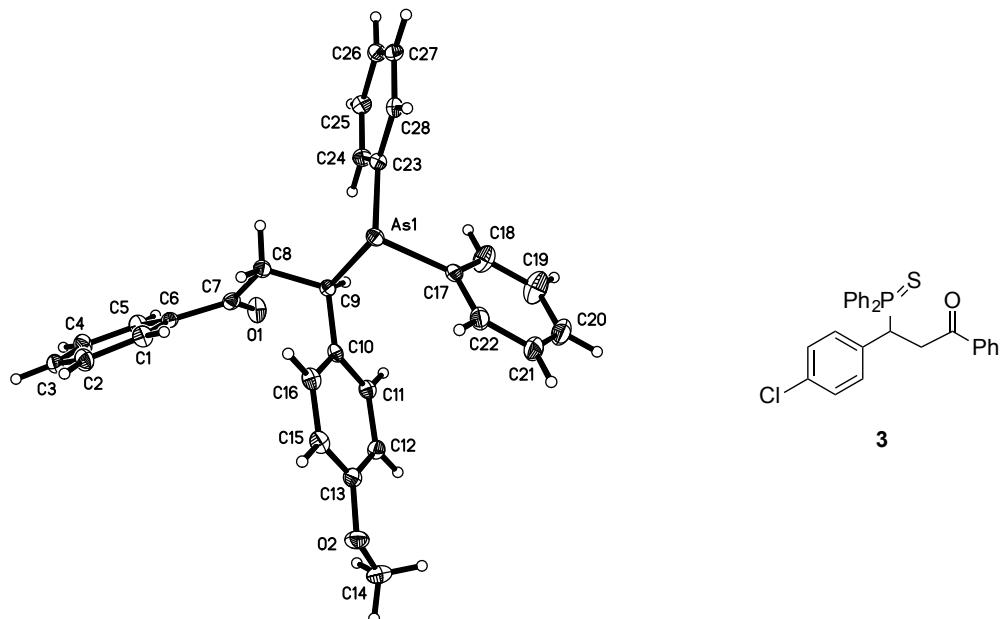
Figure s70. Molecular structure of phosphine sulfide 3.

Crystallographic data for phosphine sulfide 3

Identification code	leung1078m
Chemical formula	$C_{27}H_{22}ClOPS$
Formula weight	460.92 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.200 x 0.220 x 0.240 mm
Crystal habit	colorless block
Crystal system	orthorhombic
Space group	P 21 21 21
Unit cell dimensions	a = 6.4374(2) Å $\alpha = 90°$
	b = 17.2220(7) Å $\beta = 90°$
	c = 21.0699(9) Å $\gamma = 90°$
Volume	2335.91(16) Å^3
Z	4
Density (calculated)	1.311 g/cm^3
Absorption coefficient	0.338 mm^{-1}
F(000)	960
Theta range for data collection	2.27 to 30.02°
Index ranges	-8<=h<=9, -23<=k<=24, -29<=l<=15
Reflections collected	18546
Independent reflections	6539 [R(int) = 0.0623]
Coverage of independent reflections	99.6%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9350 and 0.9230

Structure solution technique	direct methods		
Structure solution program	XT, VERSION 2014/5		
Refinement method	Full-matrix least-squares on F2		
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)		
Function minimized	Σ w(Fo2 - Fc2)2		
Data / restraints / parameters	6539 / 0 / 280		
Goodness-of-fit on F2	1.018		
Final R indices	4855 data; R1 = 0.0537, wR2 = 0.1042 I>2σ(I)		
	all data R1 = 0.0864, wR2 = 0.1224		
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0458P)^2+0.8281P]$ where $P=(F_o^2+2F_c^2)/3$		
Absolute structure parameter	0.03(5)		
Largest diff. peak and hole	0.333 and -0.569 eÅ^{-3}		
R.M.S. deviation from mean	0.075 eÅ^{-3}		

Table s5. *Bond lengths (Å) of phosphine sulfide 3.*

C1-C6	1.388(5)	C1-C2	1.386(5)
C1-H1	0.95	C2-C3	1.375(6)
C2-H2	0.95	C3-C4	1.385(6)
C3-Cl1	1.742(4)	C4-C5	1.397(5)
C4-H4	0.95	C5-C6	1.386(5)
C5-H5	0.95	C6-C7	1.520(5)
C7-C8	1.531(5)	C7-P1	1.852(4)
C7-H7	1.0	C8-C9	1.518(5)
C8-H8A	0.99	C8-H8B	0.99
C9-O1	1.224(4)	C9-C10	1.487(5)
C10-C11	1.389(6)	C10-C15	1.396(5)
C11-C12	1.392(5)	C11-H11	0.95
C12-C13	1.380(6)	C12-H12	0.95
C13-C14	1.382(6)	C13-H13	0.95
C14-C15	1.388(6)	C14-H14	0.95
C15-H15	0.95	C16-C17	1.395(5)
C16-C21	1.399(5)	C16-P1	1.822(4)
C17-C18	1.389(5)	C17-H17	0.95
C18-C19	1.383(6)	C18-H18	0.95
C19-C20	1.377(5)	C19-H19	0.95
C20-C21	1.393(5)	C20-H20	0.95
C21-H21	0.95	C22-C23	1.386(5)
C22-C27	1.399(5)	C22-P1	1.815(4)
C23-C24	1.384(6)	C23-H23	0.95
C24-C25	1.373(6)	C24-H24	0.95
C25-C26	1.368(6)	C25-H25	0.95

C26-C27	1.380(6)	C26-H26	0.95
C27-H27	0.95	P1-S1	1.9535(13)

Table s6. *Bond angles (°) of phosphine sulfide* **3**.

C6-C1-C2	121.5(4)	C6-C1-H1	119.3
C2-C1-H1	119.3	C3-C2-C1	118.9(4)
C3-C2-H2	120.5	C1-C2-H2	120.5
C2-C3-C4	121.5(4)	C2-C3-Cl1	118.8(3)
C4-C3-Cl1	119.7(3)	C3-C4-C5	118.6(4)
C3-C4-H4	120.7	C5-C4-H4	120.7
C6-C5-C4	121.1(4)	C6-C5-H5	119.4
C4-C5-H5	119.4	C1-C6-C5	118.4(4)
C1-C6-C7	119.5(3)	C5-C6-C7	122.0(3)
C6-C7-C8	113.0(3)	C6-C7-P1	111.1(3)
C8-C7-P1	108.6(2)	C6-C7-H7	108.0
C8-C7-H7	108.0	P1-C7-H7	108.0
C9-C8-C7	112.5(3)	C9-C8-H8A	109.1
C7-C8-H8A	109.1	C9-C8-H8B	109.1
C7-C8-H8B	109.1	H8A-C8-H8B	107.8
O1-C9-C10	120.8(4)	O1-C9-C8	119.5(4)
C10-C9-C8	119.6(3)	C11-C10-C15	118.8(4)
C11-C10-C9	122.2(3)	C15-C10-C9	119.0(4)
C10-C11-C12	120.4(4)	C10-C11-H11	119.8
C12-C11-H11	119.8	C13-C12-C11	120.2(4)
C13-C12-H12	119.9	C11-C12-H12	119.9
C12-C13-C14	120.1(4)	C12-C13-H13	120.0
C14-C13-H13	120.0	C13-C14-C15	120.0(4)
C13-C14-H14	120.0	C15-C14-H14	120.0
C14-C15-C10	120.6(4)	C14-C15-H15	119.7
C10-C15-H15	119.7	C17-C16-C21	119.5(3)
C17-C16-P1	118.0(3)	C21-C16-P1	122.4(3)
C18-C17-C16	120.2(3)	C18-C17-H17	119.9
C16-C17-H17	119.9	C19-C18-C17	119.8(3)
C19-C18-H18	120.1	C17-C18-H18	120.1
C20-C19-C18	120.4(4)	C20-C19-H19	119.8
C18-C19-H19	119.8	C19-C20-C21	120.4(4)
C19-C20-H20	119.8	C21-C20-H20	119.8
C20-C21-C16	119.5(3)	C20-C21-H21	120.2
C16-C21-H21	120.2	C23-C22-C27	119.3(4)
C23-C22-P1	122.6(3)	C27-C22-P1	118.1(3)
C24-C23-C22	119.9(4)	C24-C23-H23	120.1
C22-C23-H23	120.1	C25-C24-C23	120.2(4)
C25-C24-H24	119.9	C23-C24-H24	119.9
C26-C25-C24	120.5(4)	C26-C25-H25	119.7

C24-C25-H25	119.7	C25-C26-C27	120.3(4)
C25-C26-H26	119.9	C27-C26-H26	119.9
C26-C27-C22	119.8(4)	C26-C27-H27	120.1
C22-C27-H27	120.1	C22-P1-C16	108.76(17)
C22-P1-C7	106.08(17)	C16-P1-C7	104.83(17)
C22-P1-S1	112.10(13)	C16-P1-S1	112.36(12)
C7-P1-S1	112.25(13)		

X-ray structure and crystallographic data for compound 7
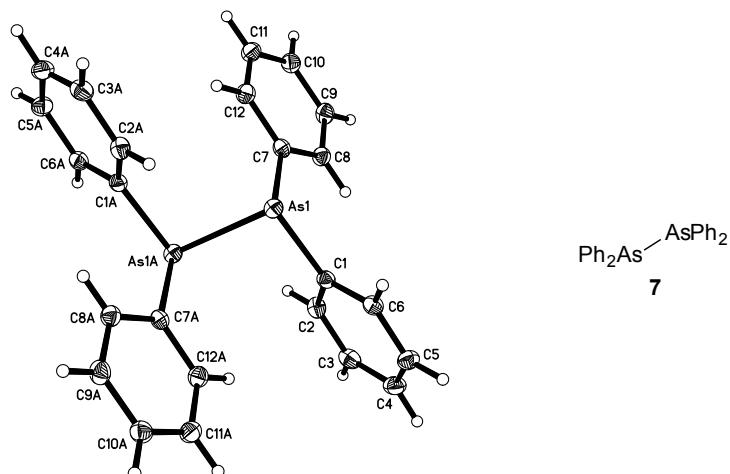
Figure s71. Molecular structure of tetraphenyldiarsine 7.

Crystallographic data for tetraphenyldiarsine 7

Identification code	leung1028m
Chemical formula	$C_{24}H_{20}As_2$
Formula weight	458.24 g/mol
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.040 x 0.200 x 0.220 mm
Crystal habit	colorless plate
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 6.1992(2) Å $\quad$ α = 90°
	b = 7.3524(2) Å $\quad$ β = 90.9970(10)°
	c = 21.2601(5) Å $\quad$ γ = 90°
Volume	968.87(5) Å^3
Z	2
Density (calculated)	1.571 g/cm^3
Absorption coefficient	3.453 mm^{-1}
F(000)	460
Theta range for data collection	2.93 to 35.01°
Index ranges	-9<=h<=10, -11<=k<=11, -34<=l<=34
Reflections collected	21465
Independent reflections	4263 [R(int) = 0.0650]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8740 and 0.5170
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5

Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2016/6 (Sheldrick, 2016)
Function minimized	$\Sigma\ w(Fo2 - Fc2)2$
Data / restraints / parameters	4263 / 0 / 118
Goodness-of-fit on F2	1.021
Δ/σmax	0.001
Final R indices	3075 data; I>2σ(I) R1 = 0.0376, wR2 = 0.0641
	all data R1 = 0.0669, wR2 = 0.0742
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0193P)^2+0.8255P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.731 and -0.593 eÅ^{-3}
R.M.S. deviation from mean	0.126 eÅ^{-3}

Table s7. *Bond lengths (Å) of tetraphenyldiarsine 7.*

As1-C1	1.9545(19)	As1-C7	1.9606(19)
As1-As1	2.4603(4)	C1-C6	1.390(3)
C1-C2	1.398(3)	C2-C3	1.389(3)
C2-H2	0.95	C3-C4	1.387(3)
C3-H3	0.95	C4-C5	1.381(3)
C4-H4	0.95	C5-C6	1.396(3)
C5-H5	0.95	C6-H6	0.95
C7-C8	1.394(3)	C7-C12	1.403(3)
C8-C9	1.394(3)	C8-H8	0.95
C9-C10	1.387(3)	C9-H9	0.95
C10-C11	1.386(3)	C10-H10	0.95
C11-C12	1.390(3)	C11-H11	0.95
C12-H12	0.95		

Table s8. *Bond angles (°) of tetraphenyldiarsine 7.*

C1-As1-C7	102.54(8)	C1-As1-As1	95.03(6)
C7-As1-As1	95.46(6)	C6-C1-C2	118.97(18)
C6-C1-As1	115.80(14)	C2-C1-As1	124.99(15)
C3-C2-C1	120.79(19)	C3-C2-H2	119.6
C1-C2-H2	119.6	C4-C3-C2	119.53(19)
C4-C3-H3	120.2	C2-C3-H3	120.2
C5-C4-C3	120.38(19)	C5-C4-H4	119.8
C3-C4-H4	119.8	C4-C5-C6	120.0(2)
C4-C5-H5	120.0	C6-C5-H5	120.0
C1-C6-C5	120.28(19)	C1-C6-H6	119.9
C5-C6-H6	119.9	C8-C7-C12	119.18(18)
C8-C7-As1	124.13(15)	C12-C7-As1	116.60(14)
C7-C8-C9	120.27(19)	C7-C8-H8	119.9
C9-C8-H8	119.9	C10-C9-C8	120.15(19)

C10-C9-H9	119.9	C8-C9-H9	119.9
C11-C10-C9	119.95(19)	C11-C10-H10	120.0
C9-C10-H10	120.0	C10-C11-C12	120.40(19)
C10-C11-H11	119.8	C12-C11-H11	119.8
C11-C12-C7	120.03(19)	C11-C12-H12	120.0
C7-C12-H12	120.0		