Synthesis, Structures and Photophysical Properties of π-Extended Arsaborins

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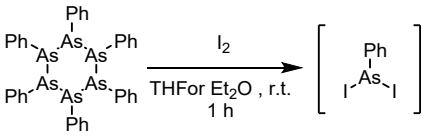
Contents:

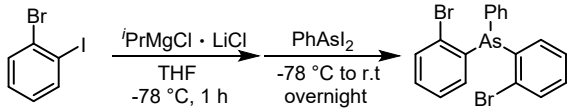
1. Synthesis

Diiodophenylarsine ($PhAsI_2$)



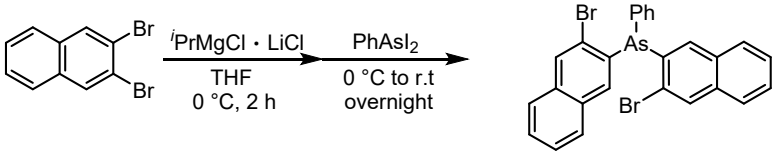
I_2 (6.0 eq.) was directly added to the mixture of As_6Ph_6 (1.0 eq.) in ethereal solution and stirred for 1 h at room temperature. Without isolation, the ethereal solution was used for the next reactions.

Bis(*o*-bromophenyl)phenylarsine (**2a**)



To a solution of 1-bromo-2-iodobenzene (3.91 g, 13.9 mmol) in THF (30 mL) was added ^{i}PrMgCl·LiCl (1.0 M in THF, 13.5 mL, 13.5 mmol) at −78 °C and the mixture was stirred for 1 h at the same temperature. Then, separately prepared $PhAsI_2$ (1.10 mmol) in THF (6.6 mL) was added into the mixture at the same temperature, and the mixture was warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with *sat.* NH_4Cl *aq.* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in *vacuo*. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 100/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **2a** as colorless solids (2.48 g, 82%).^{1}H-NMR ($CDCl_3$, 400 MHz): 7.59 (m, 2H), 7.45-7.27 (m, 5H), 7.25-7.15 (m, 4H), 6.88-6.77 (m, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): 141.3, 138.2, 135.0, 134.1, 132.9, 130.5, 130.3, 129.1, 127.8 ppm. HR-FAB-MASS (m/z): calculated for $C_{18}H_{13}Br_2As$ $[M]^+$; 461.8600, observed; 461.8589.

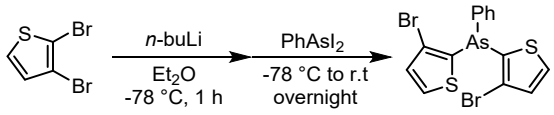
Bis(2-bromonaphthyl)phenylarsine (**2b**)



To a solution of 2,3-dibromonaphthalene (1.48 g, 5.18 mmol) in THF (10 mL) was added ^{i}PrMgCl·LiCl (1.0 M in THF, 5.40 mL, 5.40 mmol) at 0 °C and the mixture was stirred for 2 h at the same temperature. Then, separately prepared $PhAsI_2$ (2.48 mmol) in THF (2.5 mL) was added into the mixture at the same temperature, and the mixture was warmed to room temperature. After stirring at

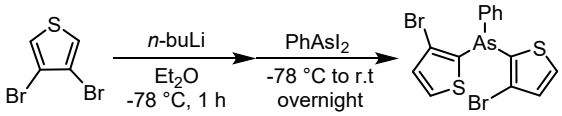
room temperature overnight, the mixture was quenched with *sat.* NH_4Cl *aq.* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **2b** as colorless solids (0.952 g, 68%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.13 (s, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.55-7.49 (m, 4H), 7.44-7.33 (m, 7H), 7.26 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 139.2, 138.3, 135.3, 134.6, 134.2, 132.3, 131.0, 129.1, 128.0, 127.3, 126.7, 126, 126.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{26}H_{17}Br_2As$ $[M]^+$; 561.8913, observed; 561.8902.

Bis(2-bromothienyl)phenylarsine (**2c**)



To a solution of 2,3-dibromothiophene (4.89 g, 20.2 mmol) in ether (40 mL) was added *n*-BuLi (1.6 M in *n*-hexane, 12.3 mL, 19.7 mmol) at -78 °C and the mixture was stirred for 1 h at the same temperature. Then, separately prepared $PhAsI_2$ (9.87 mmol) in ether (10 mL) was added into the mixture at the same temperature, and the mixture was warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with water and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on neutral alumina (eluent: *n*-hexane/EtOAc = 50/1). The solvents were removed in vacuo, and the residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **2c** as colorless solids (2.54 g, 57%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.34 (m, 7H), 7.09 (d, J = 8.0 Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 137.3, 134.1, 133.1, 132.0, 131.7, 129.7, 129.0, 118.4 ppm. HR-FAB-MASS (m/z): calculated for $C_{14}H_9Br_2S_2As$ $[M]^+$; 473.7728, observed; 473.7725.

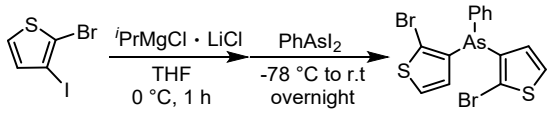
Bis(3-bromothienyl)phenylarsine (**2d**)



To a solution of 3,4-dibromothiophene (3.34 g, 13.8 mmol) in ether (30 mL) was added *n*-BuLi (1.6 M in *n*-hexane, 9.00 mL, 14.4 mmol) at -78 °C and the mixture was stirred for 1 h at the same temperature. Then, separately prepared $PhAsI_2$ (6.60 mmol) in ether (6.6 mL) was added into the mixture at the same temperature, and the mixture was warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with water and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo.

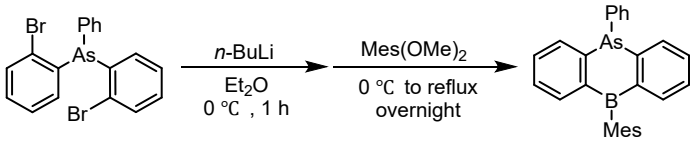
The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **2d** as colorless solids (2.04 g, 65%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.47-7.32 (m, 7H), 6.73 (d, J = 0.6 Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 138.4, 137.6, 133.4, 131.2, 129.1, 129.0, 124.2, 115.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{14}H_9Br_2S_2As$ $[M]^+$; 473.7728, observed; 473.7725.

Bis(4-bromothienyl)phenylarsine (**2e**)



To a solution of 2-bromo-3-iodothiophene (0.496 g, 1.72 mmol) in THF (3.5 mL) was added ^{i}PrMgCl·LiCl (1.0 M in THF, 1.80 mL, 1.80 mmol) at -78 °C and the mixture was stirred for 30 min at the same temperature. Then, separately prepared $PhAsI_2$ (0.865 mmol) in THF (1.7 mL) was added into the mixture at the same temperature, and the mixture was warmed to room temperature. After stirring at room temperature overnight, the mixture was quenched with water and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on neutral alumina (eluent: *n*-hexane). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **2e** as colorless solids (0.409g, 66%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.37-7.34 (m, 5H), 7.23-7.21 (d, J = 8.0 Hz, 2H), 6.41-6.40 (d, J = 4.0 Hz, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 138.4, 138.2, 133.0, 131.9, 128.9, 128.8, 126.9, 118.1 ppm. HR-FAB-MASS (m/z): calculated for $C_{14}H_9Br_2S_2As$ $[M]^+$; 473.7728, observed; 473.7716.

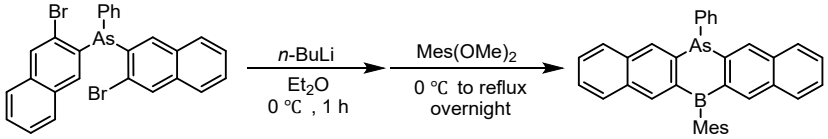
Dibenzoarsaborine (**3a**)



To a solution of **2a** (0.504 g, 1.08 mmol) in ether (17 mL) was added *n*-BuLi (1.6 M in hexane, 1.40 mL, 0.880 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, a solution of $MesB(OMe)_2$ (0.221 g, 1.15 mmol) in ether (4.4 mL) was added into the mixture at the same temperature and the resultant suspension was refluxed overnight. The mixture was quenched with *sat.* NH_4Cl *aq* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **3a** as colorless solids (0.377 g, 80%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, J = 8.0 Hz, 2H) , 7.71 (d, J = 8.0 Hz, 2H) , 7.46 (t, J = 8.0, 8.0 Hz, 2H) , 7.38-7.28 (m, 4H) , 7.24-7.16

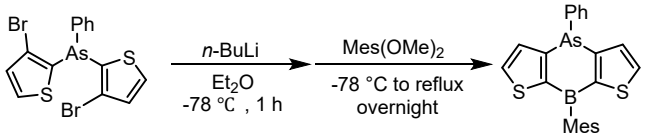
(m, 3H) , 6.92 (s, 2H) , 2.40 (s, 3H) , 2.00 (s, 3H) , 1.96 (s, 3H) ppm; ^{11}B-NMR ($CDCl_3$, 128 MHz): δ 68.0 ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 151.7, 143.0, 141.1, 140.1, 138.1, 137.9, 136.7, 133.6, 133.4, 132.5, 128.7, 128.4, 128.2, 127.0, 22.7, 21.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{27}H_{24}BAs$ $[M]^+$; 434.1187, observed; 434.1176.

Dinaphthoarsaborin (**3b**)



To a solution of **2b** (0.500 g, 0.900 mmol) in ether (20 mL) was added *n*-BuLi (1.6 M in hexane, 1.20 mL, 0.750 mmol) at 0 °C. The mixture was stirred for 1 h at 0 °C. Then, a solution of $MesB(OMe)_2$ (0.182 g, 0.95 mmol) in ether (2.0 mL) was added into the mixture at the same temperature and the resultant suspension was refluxed overnight. The mixture was quenched with *sat.* NH_4Cl *aq* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 100/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **3b** as pale yellow solids (0.295 g, 61%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.33 (d, J = 4.0 Hz, 4H) , 7.86 (d, J = 8.0 Hz, 2H) , 7.81 (d, J = 4.0 Hz, 2H) , 7.57 (t, J = 8.0, 8.0 Hz, 2H) , 7. 46 (t, J = 4.0, 4.0 Hz, 2H) , 7.20-7.14 (m, 2H) , 7.12-7.02 (m, 3H) , 7.00 (s, 1H) , 6.90 (s, 1H) , 2.45 (s, 3H) , 2.08 (s, 3H) , 1.72 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 144.9, 144.2, 143.8, 142.0, 138.6, 138.4, 138.0, 136.7,135.4, 133.9, 133.2, 132.3, 129.9, 128.8, 128.4, 127.7, 127.5,127.2, 127.1, 126.4, 23.1, 22.4, 21.4 ppm. HR-FAB-MASS (m/z): calculated for $C_{35}H_{28}BAs$ $[M]^+$; 534.1500, observed; 534.1492.

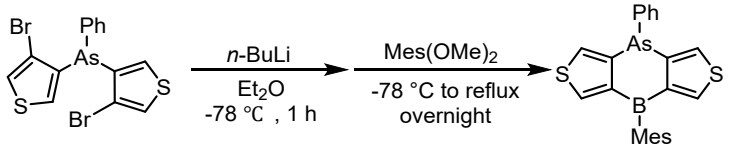
2-Thienoarsaborin (**3c**)



To a solution of **2c** (0.251 g, 0.528 mmol) in ether (10 mL) was added *n*-BuLi (1.6 M in hexane, 0.69 mL, 1.1 mmol) at -78 °C. The mixture was stirred for 1 h at -78 °C. Then, a solution of $MesB(OMe)_2$ (0.106 g, 0.552 mmol) in ether (1.1 mL) was added into the mixture at the same temperature and the resultant suspension was refluxed overnight. The mixture was quenched with *sat.* NH_4Cl *aq.* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **3c** as colorless solids (0.147 g, 63%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.52 (d, J = 4.0

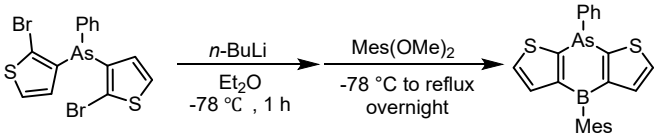
Hz, 2H) , 7.39-7.33 (m, 2H) , 7.28 (d, J = 4.0 Hz, 2H) , 7.29-7.22 (m, 3H) , 6.91 (s, 1H), 6.89 (s, 1H), 2.37 (s, 3H) , 2.08 (s, 3H) , 2.02 (s, 3H) ppm; ^{11}B-NMR ($CDCl_3$, 128 MHz): δ 58.3 ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 156.4, 146.7, 142.4, 141.7, 137.7, 136.7, 135.8, 132.0, 129.3, 129.2, 129.1, 129.0, 127.0, 127.0, 22.2, 22.5, 21.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{23}H_{20}S_2BAs$ $[M]^+$;446.0315, observed; 446.0309.

3-Thienoarsaborin (**3d**)



To a solution of **2d** (0.501 g, 1.05 mmol) in ether (20 mL) was added *n*-BuLi (1.6 M in hexane, 1.40 mL, 0.880 mmol) at -78 °C. The mixture was stirred for 1 h at -78 °C. Then, a solution of $MesB(OMe)_2$ (0.222 g, 1.14 mmol) in ether (3.0 mL) was added into the mixture at the same temperature and the resultant suspension was refluxed overnight. The mixture was quenched with *sat.* NH_4Cl *aq.* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **3d** as colorless solids (0.243 g, 53%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.01 (d, J = 4.0 Hz, 2H) , 7.67 (d, J = 4.0 Hz, 2H) , 7.25-7.10 (m, 5H) , 6.89 (s, 1H) , 6.84 (s, 1H) , 2.35 (s, 3H) , 2.06 (s, 3H) , 1.87 (s, 3H) ppm; ^{11}B-NMR ($CDCl_3$, 128 MHz): δ 52.7 ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 145.2, 144.9, 144.3, 142.1, 130.7, 140.3, 138.5, 138.1, 136.8, 131.5, 129.9, 128.5, 127.9, 127.0, 127.0, 22.9, 22.5, 21.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{23}H_{20}S_2BAs$ $[M]^+$; 446.0315, observed; 446.0322.

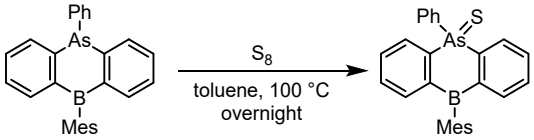
4-Thienoarsaborin (**3e**)



To a solution of **2e** (0.807 g, 1.68 mmol) in ether (30 mL) was added *n*-BuLi (1.6 M in hexane, 2.20 mL, 3.52 mmol) at -78 °C. The mixture was stirred for 1 h at -78 °C. Then, a solution of $MesB(OMe)_2$ (0.342 g, 1.76 mmol) in ether (4.0 mL) was added into the mixture at the same temperature and the resultant suspension was refluxed overnight. The mixture was quenched with *sat.* NH_4Cl *aq.* and extracted with DCM. The extracts were dried over anhydrous Na_2SO_4 and after filtration, the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 50/1). The residue was further purified by recrystallization (DCM/*n*-

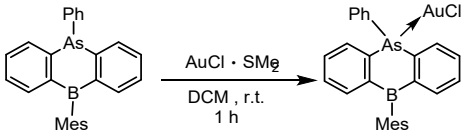
hexane) to obtain **3e** as colorless solids (0.602 g, 63%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 4.0 Hz, 2H) , 7.48 (d, J = 0.4 Hz, 2H) , 7.35-7.20 (m, 5H) , 6.91 (s, 1H) , 2.38 (s, 3H) , 2.18 (s, 3H) , 2.12 (s, 3H) ppm; ^{11}B-NMR ($CDCl_3$, 128 MHz): δ 51.0 ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 153.0, 144.9, 140.2, 139.5, 138.5, 138.4, 137.4, 137.3, 133.0, 129.1, 128.9, 128.8, 127.1, 22.8, 22.7, 21.4 ppm. HR-FAB-MASS (m/z): calculated for $C_{23}H_{20}S_2BAs$ $[M]^+$; 446.0315, observed; 446.0317.

Dibenzoarsaborin sulfide (**3a-S**)



A toluene solution (2.0 mL) of **3a** (0.402 g, 0.92 mmol) and S_8 (0.147 g, 4.68 mmol) was stirred overnight under N_2 atmosphere at 100 °C. The residual S_8 was filtered off, and the volatiles were removed in vacuo. The crude product was purified by column chromatography on silica gel (eluent: *n*-hexane/EtOAc = 2/1). The residue was further purified by recrystallization (DCM/*n*-hexane) to obtain **3a-S** as a pale yellow solids (0.182 g, 43%).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.21 (d, J = 4.0 Hz, 2H) , 7.77 (d, J = 4.0 Hz, 2H) , 7.73 (t, J = 8.0, 8.0 Hz, 2H) , 7.70 (d, J = 8.0 Hz, 2H) , 7.63 (t, J = 8.0, 0.4 Hz, 3H) , 6.94 (d, J = 16.0 Hz, 2H) , 2.40 (s, 3H) , 1.99 (s, 3H) , 1.98 (s, 3H) ppm; ^{11}B-NMR ($CDCl_3$, 128 MHz): δ 60.3 ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 151.7, 143.1, 141.0, 140.1, 138.3, 137.6, 135.0, 133.5, 133.4, 132.5, 131.9, 131.5, 131.0, 130.0,129.1, 128.7, 128.2, 127.4, 22.9, 22.7, 21.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{27}H_{25}SBAs$ $[M+H]^+$; 467.0980, observed; 467.0995.

Dibenzoarsaborin gold(I) chloride complex (**3a-AuCl**)



A DCM solution (1.0 mL) of **3a** (50.3 mg, 0.12 mmol) and AuCl-SMe_2 (35.6 mg, 0.12 mmol) was stirred for 1 h under N_2 atmosphere at room temperature. Insoluble impurities were removed by filtration, and the volatiles were removed from the filtrate in vacuo. The residue was subjected to recrystallization (DCM/hexane) to obtain **3a-AuCl** as a colorless solid (51.4 mg, 67 %).^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.90 (dd, J = 8.0, 0.4 Hz, 2H) , 7.83 (dd, J = 8.0, 0.4 Hz, 2H) , 7.67 (td, J = 8.0, 0.4 Hz, 2H), 7.53-7.49 (m, 4H) , 7.47-7.35 (m, 3H) , 6.96 (s, 1H), 6.92 (s, 1H), 2.40 (s, 3H) , 2.00 (s, 3H) , 1.94 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 141.7, 140.3, 138.1, 137.6, 137.5, 134.7, 134.2, 133.7, 132.5, 131.4, 131.2, 129.6, 127.4, 127.3, 22.9, 22.6, 21.3 ppm. HR-FAB-MASS (m/z): calculated for $C_{27}H_{24}BAsAu$ $[M-Cl]^+$; 631.0857, observed; 631.0855.

2. X-ray crystallographic data for single crystalline products

Table S1. Crystallographic Data of **3a-c**.

	3a	**3b**	**3c**
Crystal data			
Empirical Formula	$C_{27}H_{24}BAs$	$C_{35}H_{28}BAsB$, $+0.5(CH_2Cl_2)$	$C_{23}H_{20}S_2BAs$
Formula Weight	434.19	576.77	446.24
Crystal Dimension, mm^3	0.69 × 0.44 × 0.12	0.91 × 0.15 × 0.05	0.52 × 0.11 × 0.085
Crystal System	triclinic	Triclinic	triclinic
Space Group	*P*-1	*P*-1	*P*-1
a, Å	9.0332 (9)	11.0750(5)	10.0361(6)
b, Å	11.559 (2)	16.3776(7)	12.8683(8)
c, Å	12.589 (2)	16.4079(8)	17.689(1)
α, deg	114.40 (2)	86.788(4)	108.955(6)
β, deg	91.53 (1)	75.613(4)	91.163(5)
γ, deg	112.13 (1)	74.804(4)	104.195(5)
Volume, $Å^3$	1082.7 (3)	2781.84	2082.1(2)
D_{calcd}, g cm^{-3}	1.332	1.377	1.424
Z	2	4	4
F(000)	448.0	1188	912.0
Data Collection			
Temperature, K	93	100	100
2θmax, deg	52.8	52.7	52.7
Tmin/Tmax	0/1.00	0.930/0.993	0.877/0.969
Refinement			
No. of Observed Data	5914	11366	8505
No. of Parameters	266	707	493
R1[a], wR2[b]	0.0420, 0.0789	0.0495, 0.1438	0.0639, 0.1102
Goodness of Fit Indictor	0.881	1.043	1.031

[a]$R1 = \Sigma \, | |Fo| - |Fc| | / \Sigma \, |Fo|$ [b]$wR2 = [\Sigma \, w ((Fo^2-Fc^2)^2 / \Sigma \, w (Fo^2)^2]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

Table S2 Crystallographic Data of **3d-e**, **3a-S**.

	3d	**3e** (100K)	**3e** (173K)
Crystal data			
Empirical Formula	$C_{23}H_{20}S_2BAs$	$C_{23}H_{20}S_2BAs$	$C_{23}H_{20}S_2BAs$
Formula Weight	446.24	446.24	446.24
Crystal Dimension, mm^3	0.30 × 0.25 × 0.21	1.00 × 0.59 × 0.2	0.58 × 0.44 × 0.28
Crystal System	triclinic	monoclinic	triclinic
Space Group	*P*-1	$P2_1/c$	$P2_1/c$
a, Å	12.0647(5)	12.969(2)	13.0015(8)
b, Å	12.4943(7)	20.036(2)	20.047(1)
c, Å	16.6968(8)	8.407(2)	8.4791(6)
α, deg	93.998(4)	90	90
β, deg	110.602(4)	106.28(2)	106.771(7)
γ, deg	114.323(5)	90	90
Volume, $Å^3$	2077.7(2)	2096.9(6)	2116.0(2)
D_{calcd}, g cm^{-3}	1.427	1.414	1.401
Z	4	4	4
F(000)	912.0	912.0	912.0
Data Collection			
Temperature, K	100	100	173
2θmax, deg	53.7	52.7	52.7
Tmin/Tmax	0.916/0.942	0.779/0.939	0.402/0.599
Refinement			
No. of Observed Data	8492	4280	4327
No. of Parameters	493	247	247
R1[a], wR2[b]	0.0759, 0.0677	0.1181, 0.0914	0.0306, 0.0712
Goodness of Fit Indictor	1.013	1.051	1.031

[a] $R1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ [b] $wR2 = [\, \Sigma \, w \, ((Fo^2-Fc^2)^2 \, / \, \Sigma \, w \, (Fo^2)^2 \,]^{1/2}$ $w = [\, \sigma^2(Fo^2) \,]^{-1}$

Table S3 Crystallographic Data of **3a-AuCl**, **6**, triphenylarsine.

	3e (200K)	**3e** (273K)	**3e** (298K)
Crystal data			
Empirical Formula	$C_{23}H_{20}S_2BAs$	$C_{23}H_{20}AsBS_2$	$C_{23}H_{20}AsBS_2$
Formula Weight	446.24	446.24	446.24
Crystal Dimension, mm^3	0.58 × 0.46 × 0.23	0.52 × 0.44 × 0.22	0.52 × 0.42 × 0.25
Crystal System	monoclinic	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	13.0268(9)	13.013(1)	13.041(2)
b, Å	20.063(1)	20.092(2)	20.112(2)
c, Å	8.5129(6)	8.6030(8)	8.6242(9)
α, deg	90	90	90
β, deg	106.887(8)	107.07(1)	107.16(1)
γ, deg	90	90	90
Volume, $Å^3$	2096.9(6)	2150.1(4)	2161(4)
D_{calcd}, g cm^{-3}	1.392	1.379	1.371
Z	4	4	4
F(000)	912.0	912.0	912
Data Collection			
Temperature, K	200	273	298
2θmax, deg	52.7	52.746	52.732
Tmin/Tmax	0.384/0.658	0.413/0.671	0.414/0.643
Refinement			
No. of Observed Data	4353	4308	4409
No. of Parameters	247	247	247
R1[a], wR2[b]	0.00304, 0.0738	0.0579, 0.1534	0.0363, 0.0722
Goodness of Fit Indictor	1.021	0.966	0.968

[a]$R1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ [b]$wR2 = [\, \Sigma \, w \, ((Fo^2-Fc^2)^2 \, / \, \Sigma \, w \, (Fo^2)^2 \,]^{1/2}$ $w = [\, \sigma^2(Fo^2) \,]^{-1}$ **Table**.

Table S4 Crystallographic Data of **3a-AuCl**, **6**, triphenylarsine.

	3a-S (methanol)	**3a-S** (hexane)	**3a-AuCl**
Crystal data			
Empirical Formula	$C_{27}H_{24}AsBS$ + 0.5 (CH_3OH)	$C_{27}H_{24}AsBS$	$C_{55}H_{50}As_2Au_2B_2Cl_4$
Formula Weight	482.27	466.25	1418.14
Crystal Dimension, mm^3	0.76 × 0.36 × 0.12	0.51 × 0.32 × 0.18	0.37 × 0.28 × 0.17
Crystal System	triclinic	triclinic	triclinic
Space Group	*P*-1	*P*-1	*P*-1
a, Å	9.3729(6)	9.5976(7)	9.0967(3)
b, Å	14.908(1)	11.9622(6)	15.1687(7)
c, Å	17.5035(8)	20.811(1)	20.2163(5)
α, deg	86.683(4)	89.766(4)	68.133(3)
β, deg	81.031(4)	78.127(5)	88.064(2)
γ, deg	75.640(5)	77.208(5)	83.955(3)
Volume, $Å^3$	2340.0(2)	2278.0(2)	2574.4(2)
D_{calcd}, g cm^{-3}	1.369	1.360	1.829
Z	4	4	2
F(000)	996.0	960.0	1364.0
Data Collection			
Temperature, K	100	100	100
2θmax, deg	52.7	52.742	52.7
Tmin/Tmax	0.831/0.955	0.546/0.761	0.819/0.891
Refinement			
No. of Observed Data	10513	9271	10513
No. of Parameters	592	547	592
R1[a], wR2[b]	0.0651, 0.0419	0.0579, 0.1534	0.0651, 0.0419
Goodness of Fit Indictor	0.993	1.017	0.993

[a]$R1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ [b]$wR2 = [\, \Sigma \, w \, ((Fo^2-Fc^2)^2 \, / \, \Sigma \, w \, (Fo^2)^2 \,]^{1/2}$ $w = [\, \sigma^2(Fo^2) \,]^{-1}$

Table S5. Crystallographic Data of **3a-AuCl**, **6**, triphenylarsine.

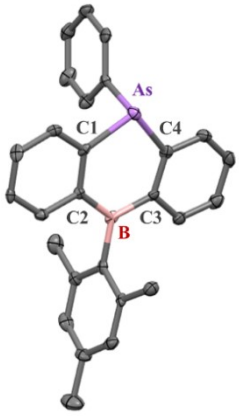
	6	Triphenylarsine
Crystal data		
Empirical Formula	$C_{27}H_{24}AsBS$	$C_{18}H_{15}As$
Formula Weight	466.25	306.22
Crystal Dimension, mm^3	0.51 × 0.32 × 0.18	1.00 × 0.68 × 0.30
Crystal System	triclinic	triclinic
Space Group	*P*-1	*P*-1
a, Å	9.5976(7)	10.9773(3)
b, Å	11.9622(6)	15.1163(5)
c, Å	20.811(1)	17.7332(7)
α, deg	89.766(4)	84.333(3)
β, deg	78.127(5)	80.134(3)
γ, deg	77.208(5)	87.199(3)
Volume, $Å^3$	2278.0(2)	2883.4(2)
D_{calcd}, g cm^{-3}	1.360	1.411
Z	4	8
F(000)	960.0	1248.0
Data Collection		
Temperature, K	100.00	93.15
2θmax, deg	52.7	52.7
Tmin/Tmax	0.546,0.761	0.711,0.869
Refinement		
No. of Observed Data	9271	11776
No. of Parameters	547	685
R1[a], wR2[b]	0.0579, 0.1534	0.0379, 0.0950
Goodness of Fit Indictor	1.017	1.044

[a]$R1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ [b]$wR2 = [\, \Sigma \, w \, ((Fo^2-Fc^2)^2 \, / \, \Sigma \, w \, (Fo^2)^2 \,]^{1/2}$ $w = [\, \sigma^2(Fo^2) \,]^{-1}$

Table S6. Crystal lattice constant of **3e** (298, 273, 200, 173, 100 K).

	298 K	273 K	200K	173K	100K
a-axis (Å)	13.041(2)	13.013(1)	13.0268(9)	13.0015(8)	12.969(2)
b-axis (Å)	20.112(2)	20.092(2)	20.063(1)	20.047(1)	20.036(2)
c-axis (Å)	8.6242(9)	8.6030(8)	8.5129(6)	8.4791(6)	8.407(2)
stacking distance (Å)	3.422(3)	3.407(3)	3.370(3)	3.360(3)	3.344(6)

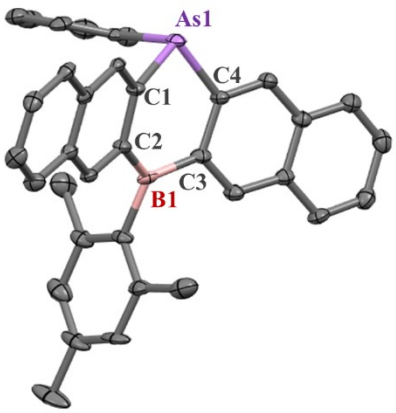
Table S7. ORTEP drawing and selected bond lengths and angles of **3a**.

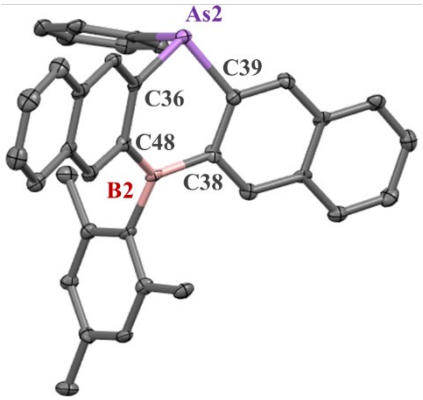


distances (Å)		angles (°)	
As(1)-C(1)	1.955(4)	C(4)-As(1)-C(1)	100.7(2)
As(1)-C(4)	1.939(5)	As(1)-C(1)-C(2)	123.6(3)
B(1)-C(2)	1.552(8)	C(1)-C(2)-B(1)	124.9(4)
B(1)-C(3)	1.556(8)	C(2)-B(1)-C(3)	122.5(4)

		B(1)-C(3)-C(4)	123.5(4)
		C(3)-C(4)-As(1)	124.7(3)

Table S8 ORTEP drawing and selected bond lengths and angles of **3b**.

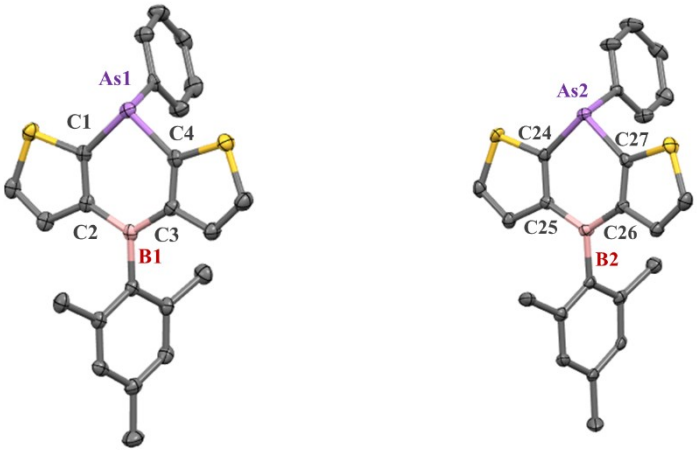




distances (Å)		angles (°)	
As(1)-C(1)	1.944(4)	C(4)-As(1)-C(1)	98.8(1)
As(1)-C(4)	1.933(3)	As(1)-C(1)-C(2)	122.1(2)
B(1)-C(2)	1.537(5)	C(1)-C(2)-B(1)	122.6(3)

B(1)-C(3)	1.539(7)	C(2)-B(1)-C(3)	121.6(3)
As(2)-C(36)	1.948(3)	B(1)-C(3)-C(4)	123.4(3)
As(2)-C(39)	1.947(3)	C(3)-C(4)-As(1)	121.7(3)
B(2)-C(48)	1.540(5)	C(39)-As(2)-C(36)	98.1(1)
B(2)-C(38)	1.556(6)	As(2)-C(36)-C(48)	121.5(2)
		C(36)-C(48)-B(2)	123.3(3)
		C(48)-B(2)-C(38)	120.0(3)
		B(2)-C(38)-C(39)	124.0(3)
		C(38)-C(29)-As(2)	120.3(2)

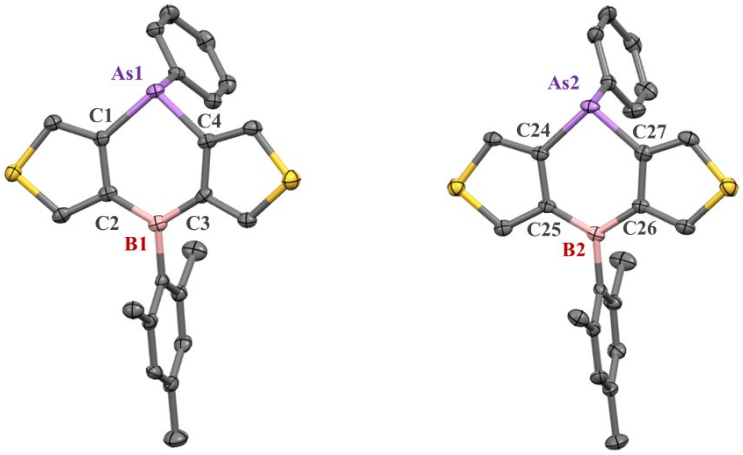
Table S9. ORTEP drawing and selected bond lengths and angles of **3c**.



distances (Å)		angles (°)	
As(1)-C(1)	1.945(4)	C(4)-As(1)-C(1)	94.8(2)
As(1)-C(4)	1.942(4)	As(1)-C(1)-C(2)	129.1(3)
B(1)-C(2)	1.547(6)	C(1)-C(2)-B(1)	123.4(3)
B(1)-C(3)	1.535(5)	C(2)-B(1)-C(3)	119.7(3)
As(2)—C(24)	1.948(3)	B(1)-C(3)-C(4)	123.8(3)
As(2)—C(27)	1.947(3)	C(3)-C(4)-As(1)	128.5(3)
B(2)—C(25)	1.540(5)	C(27)—As(2)—C(24)	94.8(2)
B(2)—C(26)	1.556(6)	As(2)—C(24)—C(25)	129.1(3)
		C(24)—C(25)—B(2)	123.4(3)

C(25)—B(2)—C(26)	119.7(3)
B(2)—C(26)—C(27)	123.8(3)
C(26)—C(27)—As(2)	128.5(3)

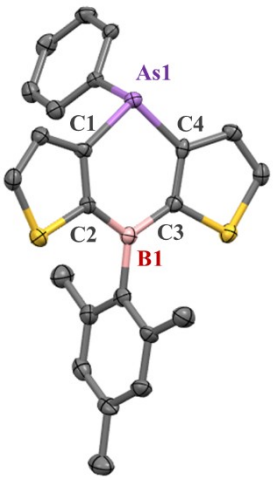
Table S10 . ORTEP drawing and selected bond lengths and angles of **3d**.



distances (Å)		angles (°)	
As(1)-C(1)	1.958(3)	C(4)-As(1)-C(1)	97.2(1)
As(1)-C(4)	1.952(4)	As(1)-C(1)-C(2)	125.4(3)
B(1)-C(2)	1.550(5)	C(1)-C(2)-B(1)	125.9(3)
B(1)-C(3)	1.547(5)	C(2)-B(1)-C(3)	118.3(3)
As(2)-C(24)	1.955(3)	B(1)-C(3)-C(4)	126.2(3)

As(2)-C(27)	1.954(4)	C(3)-C(4)-As(1)	125.6(3)
B(2)-C(25)	1.539(5)	C(27)-As(2)-C(24)	97.4(1)
B(2)-C(26)	1.539(4)	As(2)-C(24)-C(25)	125.5(3)
		C(24)-C(25)-B(2)	126.4(3)
		C(25)-B(2)-C(26)	118.7(3)
		B(2)-C(26)-C(27)	126.1(3)
		C(26)-C(27)-As(2)	125.7(3)

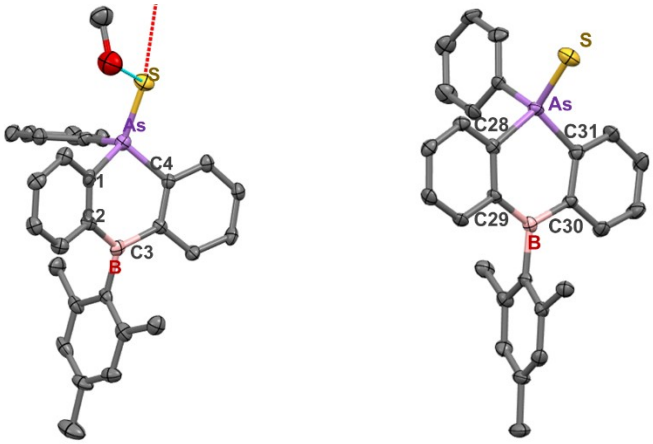
Table S11. ORTEP drawing and selected bond lengths and angles of **3e**.



distances (Å)		angles (°)	
As(1)-C(1)	1.922(5)	C(4)-As(1)-C(1)	98.3(2)

As(1)-C(4)	1.941(5)	As(1)-C(1)-C(2)	123.8(4)
B(1)-C(2)	1.547(8)	C(1)-C(2)-B(1)	129.0(4)
B(1)-C(3)	1.521(9)	C(2)-B(1)-C(3)	115.5(5)
		B(1)-C(3)-C(4)	128.5(5)
		C(3)-C(4)-As(1)	124.2(4)

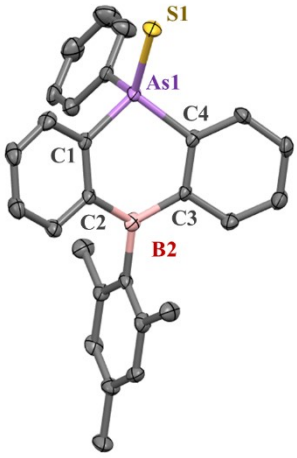
Table S12. ORTEP drawing and selected bond lengths and angles of **3a-S** from methanol.

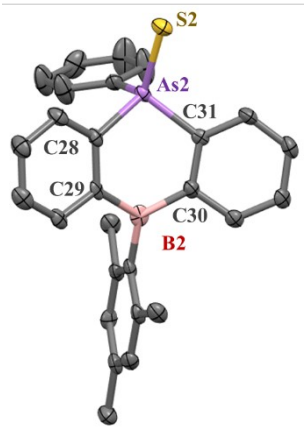


distances (Å)		angles (°)	
As(1)—C(1)	1.941(5)	C(4)—As(1)—C(1)	103.6(2)
As(1)—C(4)	1.927(4)	As(1)—C(1)—C(2)	118.1(3)
B(1)—C(2)	1.571(8)	C(1)—C(2)—B(1)	124.7(4)
B(1)—C(3)	1.582(8)	C(2)—B(1)—C(3)	121.2(4)

As(1)—S(1)	2.063(1)	B(1)—C(3)—C(4)	123.9(4)
As(2)—C(28)	1.935(5)	C(3)—C(4)—As(1)	118.8(3)
As(2)—C(31)	1.922(5)	C(31)—As(2)—C(28)	105.3(2)
B(2)—C(29)	1.567(8)	As(2)—C(28)—C(29)	120.3(3)
B(2)—C(30)	1.579(8)	C(28)—C(29)—B(2)	125.0(4)
As(2)—S(2)	2.071(1)	C(29)—B(2)—C(30)	123.7(4)
		B(2)—C(30)—C(31)	123.0(4)
		C(30)—C(31)—As(2)	122.4(3)

Table S13. ORTEP drawing and selected bond lengths and angles of **3a-S** from hexane.

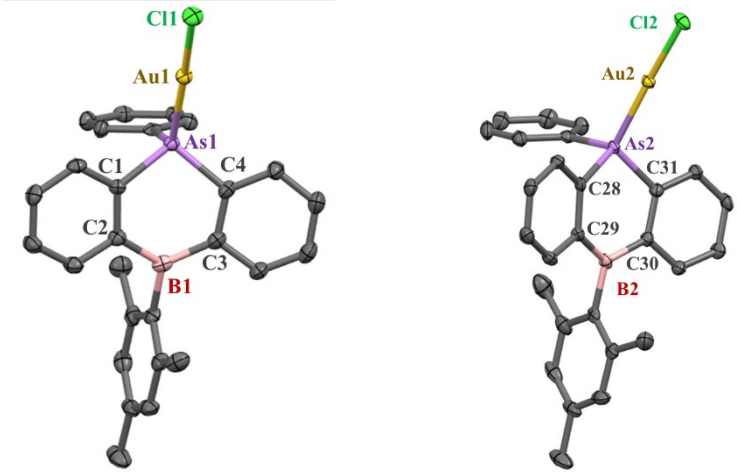




distances (Å)	angles (°)

As(1)-C(1)	1.918(4)	C(4)-As(1)-C(1)	102.9(2)
As(1)-C(4)	1.933(5)	As(1)-C(1)-C(2)	120.1(3)
B(1)-C(2)	1.577(7)	C(1)-C(2)-B(1)	124.1(4)
B(1)-C(3)	1.561(6)	C(2)-B(1)-C(3)	121.1(4)
As(2)-C(28)	1.929(5)	B(1)-C(3)-C(4)	123.7(4)
As(2)-C(31)	1.929(4)	C(3)-C(4)-As(1)	120.0(3)
B(2)-C(29)	1.588(7)	C(31)-As(2)-C(28)	102.7(2)
B(2)-C(30)	1.563(8)	As(2)-C(28)-C(29)	119.4(3)
		C(28)-C(29)-B(2)	123.2(4)
		C(29)-B(2)-C(30)	119.8(5)
		B(2)-C(30)-C(31)	125.2(4)
		C(30)-C(31)-As(2)	118.4(3)

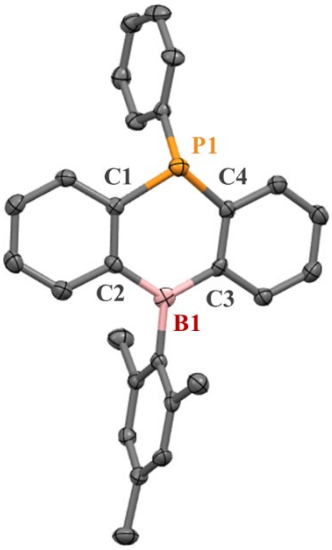
Table S14 . ORTEP drawing and selected bond lengths and angles of **3a-AuCl**.



distances (Å)		angles (°)	
As(1)-C(1)	1.931(6)	C(4)-As(1)-C(1)	103.3(2)
As(1)-C(4)	1.933(4)	As(1)-C(1)-C(2)	119.0(4)
B(1)-C(2)	1.574(7)	C(1)-C(2)-B(1)	124.3(5)
B(1)-C(3)	1.569(9)	C(2)-B(1)-C(3)	121.2(5)
As(2)-C(28)	1.919(5)	B(1)-C(3)-C(4)	124.3(5)
As(2)-C(31)	1.924(4)	C(3)-C(4)-As(1)	119.0(4)
B(2)-C(29)	1.556(7)	C(31)-As(2)-C(28)	104.1(2)
B(2)-C(30)	1.566(7)	As(2)-C(28)-C(29)	119.4(4)
		C(28)-C(29)-B(2)	124.1(5)

C(29)-B(2)-C(30)	122.3(5)
B(2)-C(30)-C(31)	124.1(5)
C(30)-C(31)-As(2)	119.8(4)

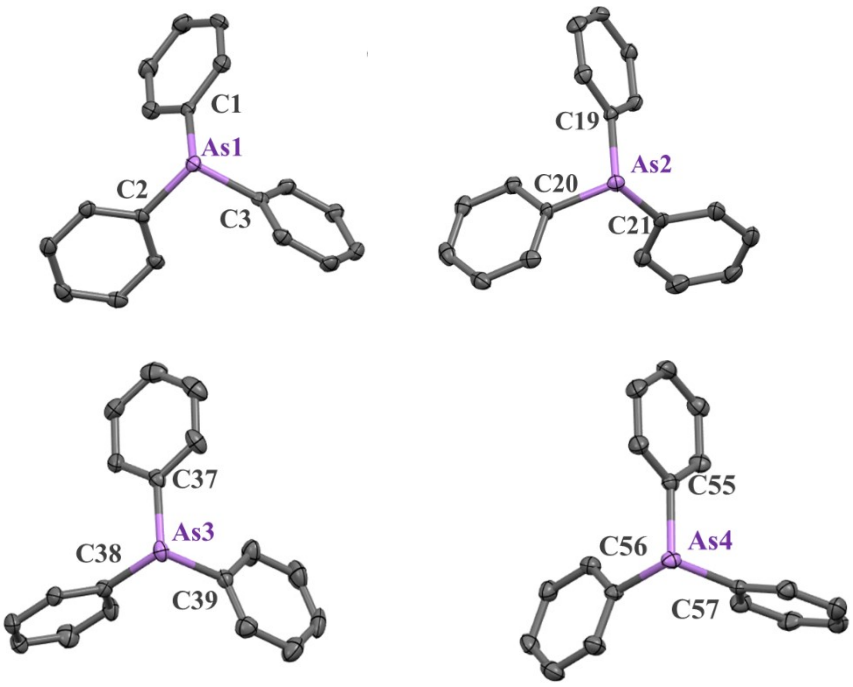
Table S15. ORTEP drawing and selected bond lengths and angles of **5.**



distances (Å)		angles (°)	
P(1)-C(1)	1.811(3)	C(4)-P(1)-C(1)	103.2(1)
P(1)-C(4)	1.818(3)	P(1)-C(1)-C(2)	123.0(2)
B(1)-C(2)	1.553(5)	C(1)-C(2)-B(1)	123.1(3)
B(1)-C(3)	1.553(5)	C(2)-B(1)-C(3)	119.9(3)

		B(1)-C(3)-C(4)	123.2(3)
		C(3)-C(4)-P(1)	123.0(2)

Table S16. ORTEP drawing and selected bond lengths and angles of **tripehnyarsine at 100 K.**



distances (Å)		angles (°)	
As(1)-C(1)	1.951(3)	C(1)-As(1)-C(2)	100.2(1)
As(1)-C(2)	1.955(3)	C(2)-As(1)-C(3)	99.4(1)
As(1)-C(3)	1.948(3)	C(3)-As(1)-B(1)	99.4(1)
As(2)-C(19)	1.946(3)	C(19)-As(2)-C(20)	98.2(1)

As(2)-C(20)	1.953(3)	C(20)-As(2)-C(21)	99.3(1)
As(2)-C(21)	1.950(3)	C(21)-As(2)-B(19)	100.1(1)
As(3)-C(37)	1.954(3)	C(37)-As(3)-C(38)	100.2(1)
As(3)-C(38)	1.953(3)	C(38)-As(3)-C(39)	99.6(1)
As(3)-C(39)	1.955(3)	C(39)-As(3)-B(37)	99.1(1)
As(4)-C(55)	1.960(3)	C(55)-As(4)-C(56)	100.2(1)
As(4)-C(56)	1.952(3)	C(56)-As(4)-C(57)	99.6(1)
As(4)-C(57)	1.964(3)	C(57)-As(4)-B(55)	99.6(1)

3. Photophysical data

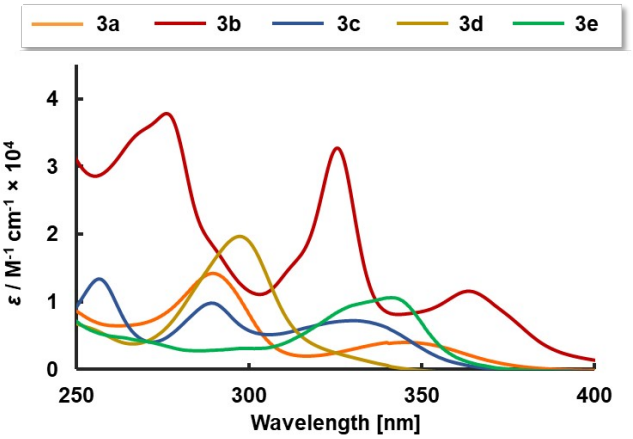


Figure S1. UV-vis spectra of **3a-e** in 2-MeTHF (1.0×10^{-5} mol/L).

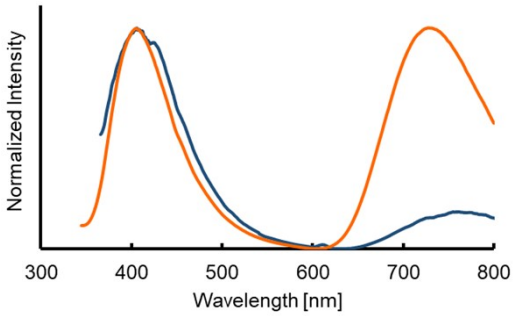


Figure S2. Emission spectra of **3a** in 2Me-THF at 77 K, excitation at 346 nm, (orange) 1.0×10^{-4} mol/L, (blue) 1.0×10^{-5} mol/L.

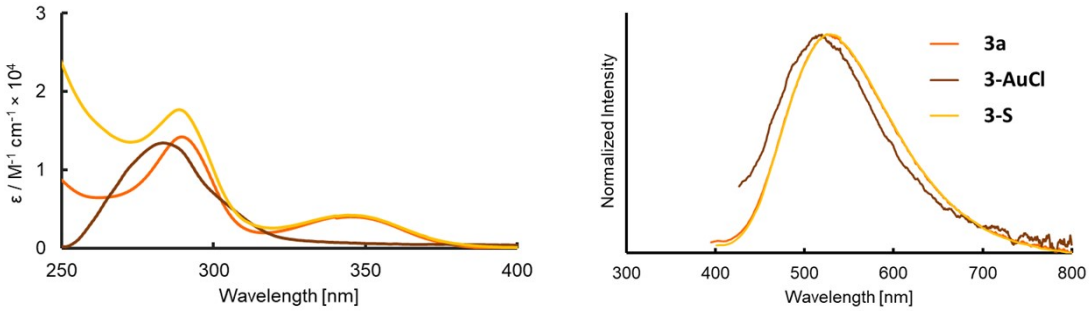


Figure S3. (Left) UV-vis absorption and (right) emission spectra of **3a**, **3a-AuCl**, **3a-S** at 298K (1.0×10^{-5} mol/L in 2Me-THF).

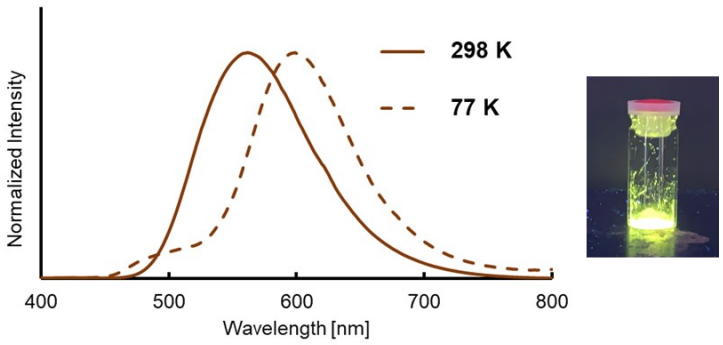


Figure S4. Emission spectra of **3a-AuCl** in solid state and photographs of luminescence at 298 K.

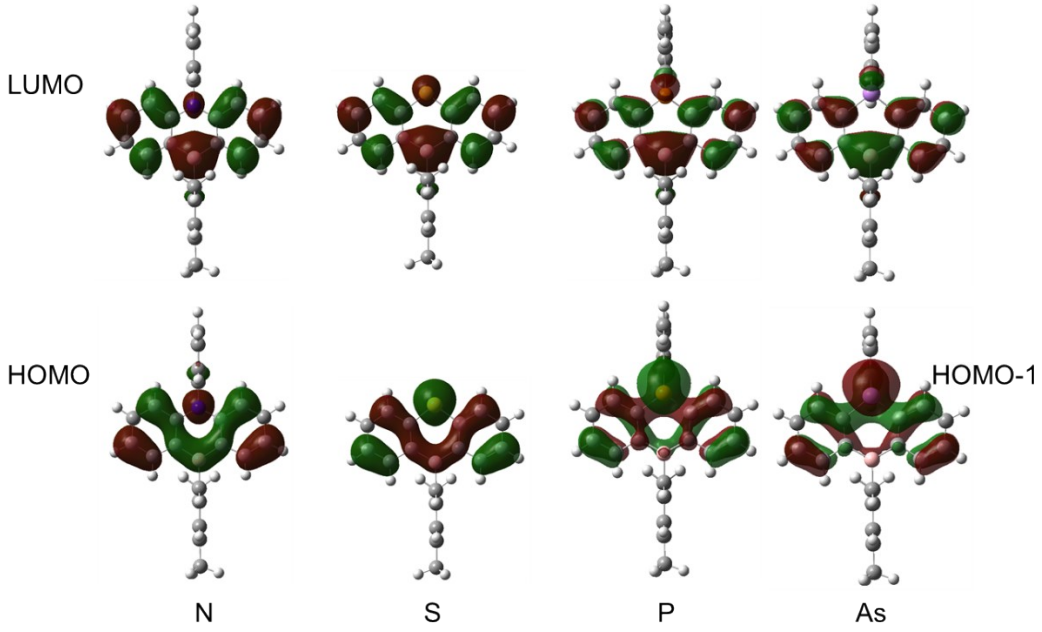


Figure S5 Frontier orbitals of dibenzoheteroborins (N, S, P, and As).

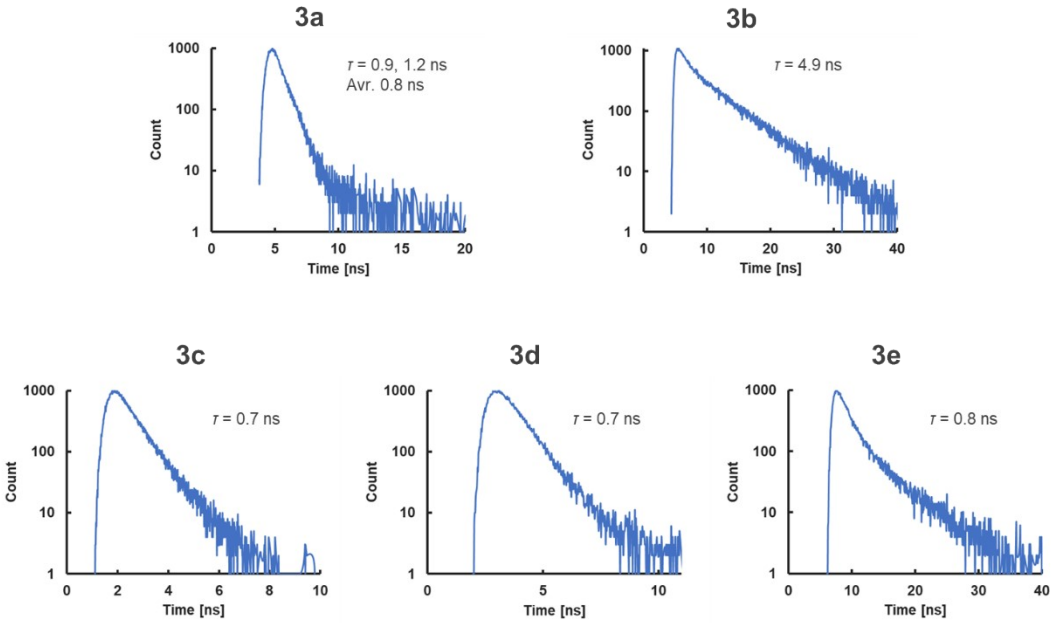


Figure S6. The emission decay kinetics of **3a-e** in the solution at 298 K.

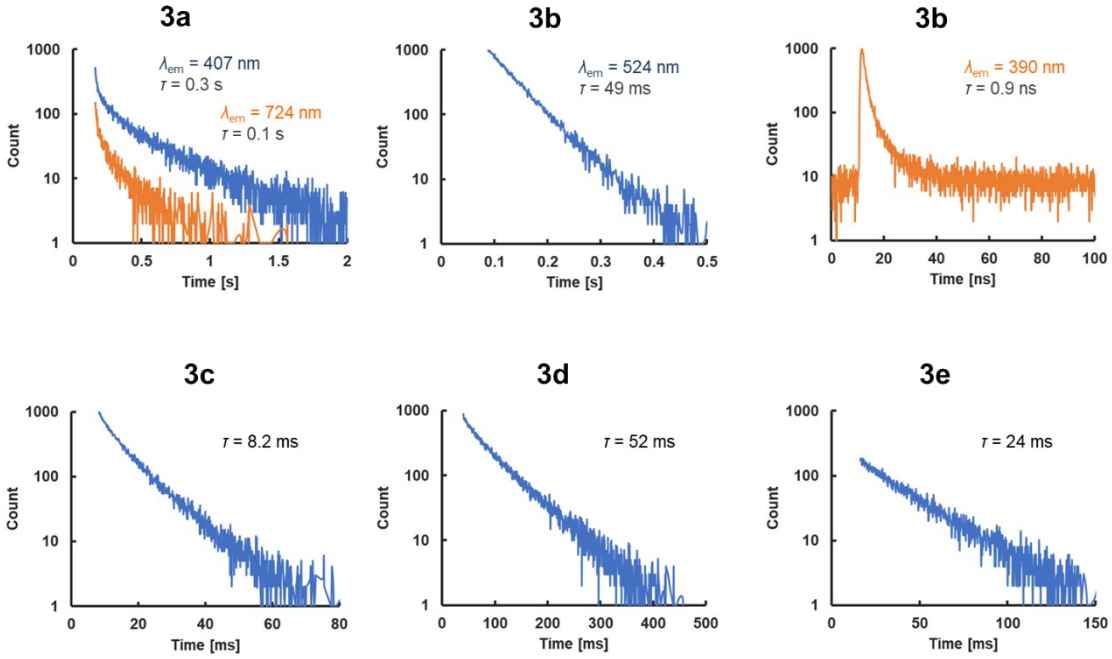


Figure S7. The emission decay kinetics of **3a-e** in the solution at 77 K.

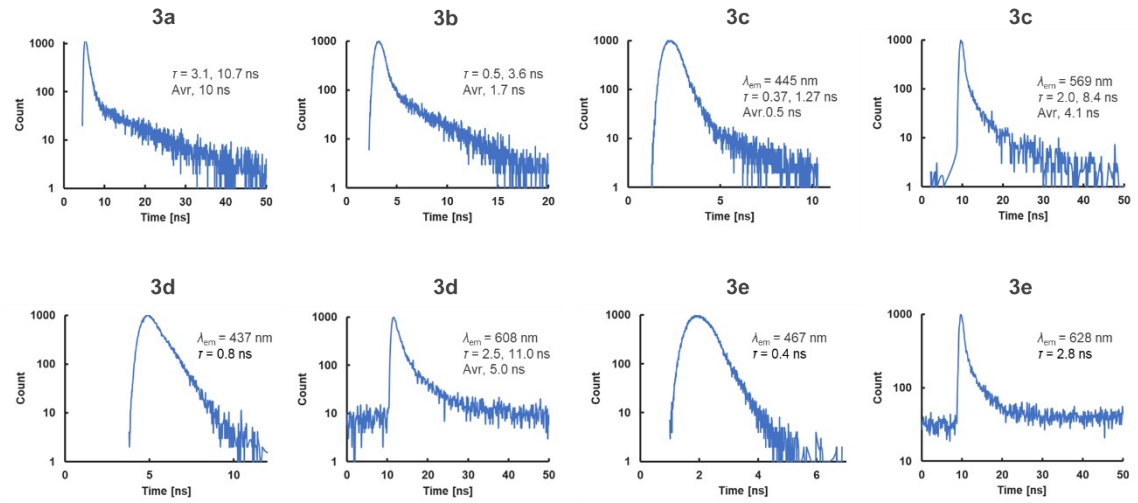


Figure S8. The emission decay kinetics of **3a-e** in the solid states at 298 K.

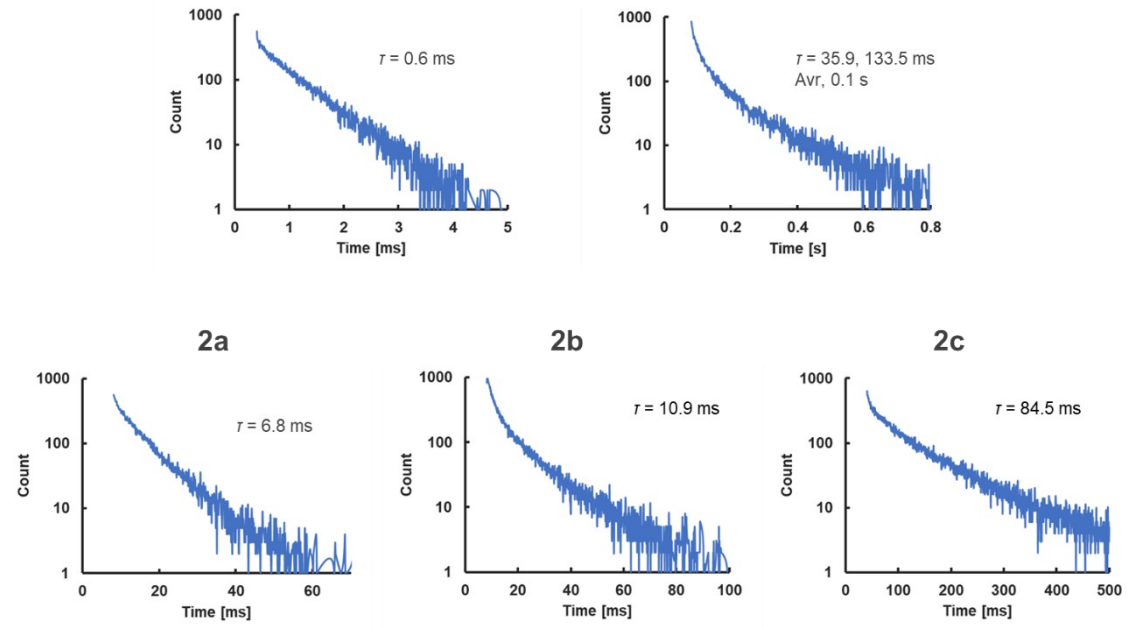


Figure S9. The emission decay kinetics of **3a-e** in the solid states at 77 K.

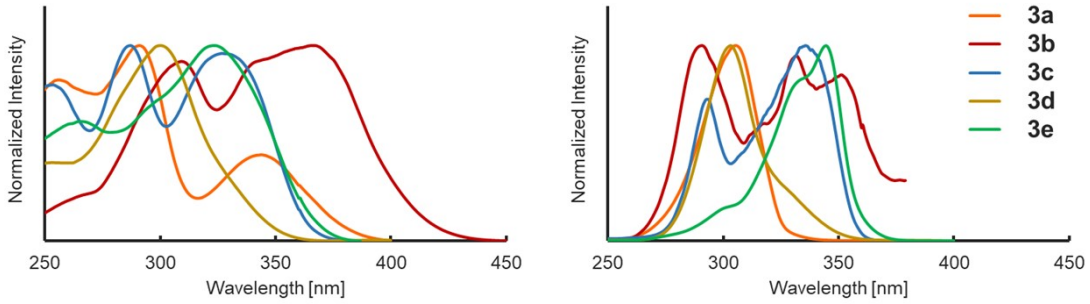


Figure S10. Excitation spectra of **3a-e** in solutions at (left) 298 K and (right) 77 K (1.0×10^{-5} mol/L in 2Me-THF).

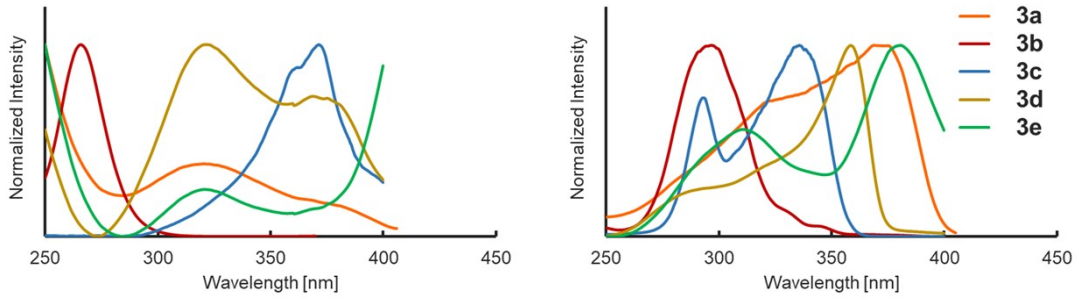


Figure S11. Excitation spectra of **3a-e** in solid states at (a) 298 K and (b) 77 K

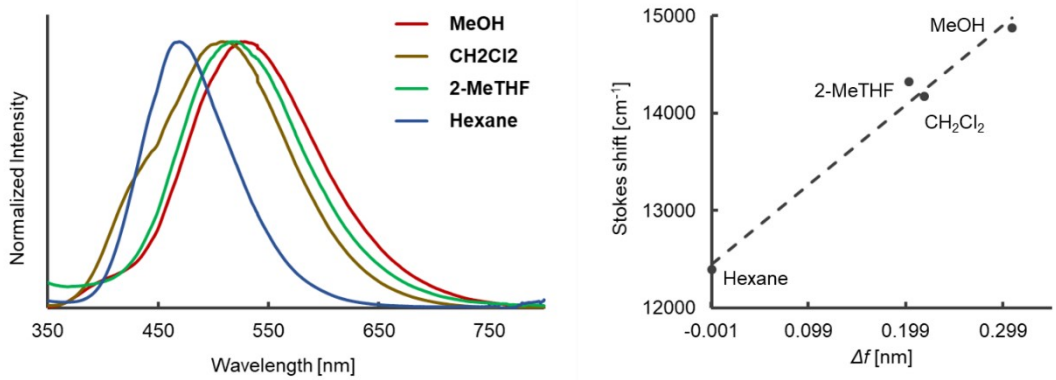


Figure S12. Emission spectrum of **3d** in different solvents and Lippert-Mataga-plots (Δf = [(ε-1)/(2ε+1)]–[(n^2–1)/(2n^2+1)]; ε : permittivity, n: refractive index).

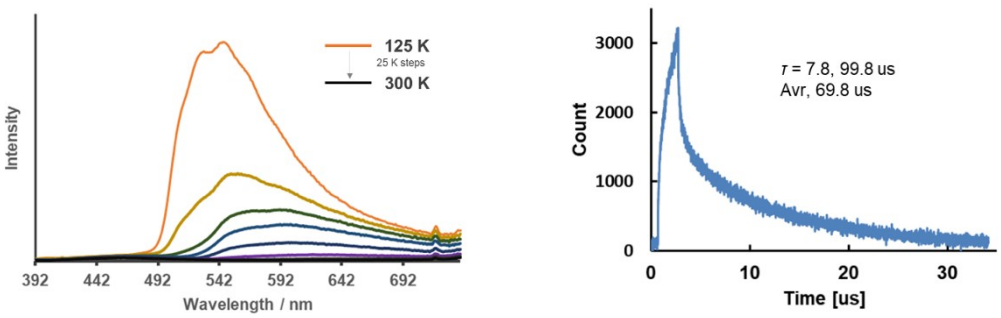


Figure S13. The temperature-dependent emission of **3e** in solid states at 125 K to 300 K and the emission decay kinetics of **3e** in the solid state at 150 K (excitation at 595 nm).

4. DFT calculations

Cartesian coordinates in the structures optimized by DFT calculations

Tabel S17. 3a (S_0): B3LYP/6-31G+(d, p) = -3302.104354

Number	Atom	X	Y	Z
1	C	0.988025	1.50127	-0.66073
2	C	1.59062	2.76576	-0.72452
3	H	2.636992	2.855222	-1.00752
4	C	0.867179	3.918303	-0.42291
5	H	1.353185	4.889519	-0.46331
6	C	-0.48412	3.818144	-0.07326
7	H	-1.05893	4.711478	0.154124
8	C	-1.0898	2.566071	-0.0335
9	H	-2.14201	2.495023	0.226023
10	C	-0.37961	1.37195	-0.31351
11	B	-1.12221	-0.0009	-0.18824
12	C	-0.37819	-1.37322	-0.31093
13	C	-1.08724	-2.56751	-0.02873
14	H	-2.13956	-2.49713	0.230579
15	C	-0.4803	-3.81904	-0.06606
16	H	-1.05426	-4.7125	0.162969
17	C	0.871095	-3.91853	-0.41554
18	H	1.358059	-4.88934	-0.45409
19	C	1.59341	-2.76585	-0.71933
20	H	2.639862	-2.85482	-1.00218
21	C	0.989561	-1.50184	-0.65795
22	C	3.45782	0.001798	0.155716
23	C	4.800502	0.002515	-0.23989
24	H	5.050993	0.00186	-1.29776
25	C	5.825588	0.004042	0.713381
26	H	6.863598	0.004574	0.392541
27	C	5.510806	0.004878	2.073488
28	H	6.303824	0.006063	2.815974
29	C	4.170774	0.004176	2.4786
30	H	3.921153	0.004814	3.536064

31	C	3.153932	0.002646	1.5232
32	H	2.116869	0.002094	1.846881
33	C	-2.68115	-0.00127	0.104732
34	C	-3.18114	-0.00131	1.427443
35	C	-4.564	-0.00528	1.653824
36	H	-4.93003	-0.00913	2.679075
37	C	-5.48384	-0.00667	0.600138
38	C	-4.98096	-0.01055	-0.70559
39	H	-5.67621	-0.01861	-1.54335
40	C	-3.60509	-0.00646	-0.9665
41	C	-2.23374	-0.00156	2.61069
42	H	-2.7821	0.000421	3.557284
43	H	-1.5802	0.879148	2.603348
44	H	-1.58263	-0.8841	2.605519
45	C	-6.97242	0.022592	0.862735
46	H	-7.21643	-0.42615	1.830867
47	H	-7.52597	-0.51921	0.088911
48	H	-7.35293	1.052163	0.874487
49	C	-3.11778	-0.01162	-2.40167
50	H	-3.95559	-0.017	-3.10505
51	H	-2.4999	-0.89264	-2.61415
52	H	-2.50523	0.871307	-2.62161
53	As	2.083907	-0.00028	-1.25256

Tabel S18. 3a (S_1): B3LYP/6-31G+(d, p) = -3301.993638

Number	Atom	X	Y	Z
1	C	1.049442	1.502441	-0.96777
2	C	1.585798	2.758766	-1.25485
3	H	2.611983	2.830011	-1.61072
4	C	0.84284	3.934374	-1.08984
5	H	1.284889	4.902092	-1.30723
6	C	-0.47907	3.832694	-0.63481
7	H	-1.07797	4.729511	-0.49384
8	C	-1.03436	2.585661	-0.37905
9	H	-2.06916	2.554223	-0.04347
10	C	-0.31026	1.36104	-0.53739

11	B	-0.96499	-0.00404	-0.29186
12	C	-0.30498	-1.3708	-0.51501
13	C	-1.02615	-2.59485	-0.34053
14	H	-2.06135	-2.56154	-0.00617
15	C	-0.46716	-3.84389	-0.57794
16	H	-1.06369	-4.74025	-0.42465
17	C	0.854862	-3.94817	-1.032
18	H	1.299483	-4.9176	-1.23616
19	C	1.594459	-2.773	-1.21392
20	H	2.620555	-2.84632	-1.56963
21	C	1.054906	-1.51432	-0.94342
22	C	3.219198	0.007838	0.467872
23	C	4.618299	0.016605	0.435435
24	H	5.13137	0.016522	-0.52356
25	C	5.368003	0.025994	1.617745
26	H	6.453882	0.033277	1.571551
27	C	4.718124	0.024899	2.853363
28	H	5.295299	0.031438	3.77405
29	C	3.319108	0.014752	2.900173
30	H	2.808123	0.013493	3.859779
31	C	2.581407	0.007029	1.715066
32	H	1.496305	-0.00086	1.756959
33	C	-2.50713	-0.00615	0.15582
34	C	-2.88769	0.011129	1.560604
35	C	-4.22048	0.016039	1.914651
36	H	-4.50423	0.029872	2.963261
37	C	-5.24737	0.001926	0.932315
38	C	-4.89047	-0.02278	-0.44217
39	H	-5.68265	-0.03982	-1.18549
40	C	-3.57026	-0.02801	-0.84074
41	C	-1.81388	0.02631	2.60996
42	H	-2.23965	0.031717	3.616544
43	H	-1.1744	0.906306	2.487558
44	H	-1.16209	-0.84647	2.501847
45	C	-6.68385	0.044258	1.339029
46	H	-6.83813	-0.37659	2.335867

47	H	-7.32409	-0.47384	0.619692
48	H	-7.02302	1.090661	1.373005
49	C	-3.20575	-0.0587	-2.2963
50	H	-4.0956	-0.07588	-2.93056
51	H	-2.59015	-0.93666	-2.51637
52	H	-2.59698	0.813656	-2.55458
53	As	2.253964	-0.00646	-1.26109

Tabel S19. 3b (S_0): B3LYP/6-31G+(d, p) = -3609.407121

Number	Atom	X	Y	Z
1	C	-1.50333	1.028928	-0.71212
2	C	-2.74981	1.607688	-0.8464
3	H	-2.83936	2.649613	-1.14986
4	C	-2.55314	-1.06698	-0.11307
5	H	-2.48686	-2.11744	0.158613
6	C	-1.37412	-0.35532	-0.34605
7	B	-0.00552	-1.09588	-0.18258
8	C	1.370654	-0.369	-0.34394
9	C	2.542198	-1.09259	-0.10998
10	H	2.465175	-2.14214	0.162445
11	C	2.766699	1.579157	-0.846
12	H	2.867064	2.619801	-1.15047
13	C	1.514268	1.013446	-0.71144
14	C	0.017095	3.365653	0.38311
15	C	0.022223	4.744512	0.142854
16	H	0.023176	5.112894	-0.88008
17	C	0.026206	5.655644	1.205577
18	H	0.030166	6.723304	1.003881
19	C	0.025114	5.189625	2.521459
20	H	0.028215	5.893347	3.349081
21	C	0.020052	3.812202	2.77172
22	H	0.01922	3.444552	3.794222
23	C	0.016069	2.909428	1.707487
24	H	0.012196	1.842591	1.912887
25	C	-0.01362	-2.64562	0.160545
26	C	-0.0143	-3.10171	1.498941

27	C	-0.01766	-4.47639	1.771444
28	H	-0.01427	-4.80803	2.80833
29	C	-0.02301	-5.43081	0.749054
30	C	-0.01848	-4.9717	-0.57285
31	H	-0.01566	-5.69443	-1.38708
32	C	-0.01537	-3.60518	-0.87951
33	C	-0.00696	-2.11563	2.650119
34	H	-0.01227	-2.63205	3.614484
35	H	-0.8832	-1.45677	2.620859
36	H	0.88011	-1.47131	2.622688
37	C	-0.05908	-6.90976	1.060787
38	H	0.369424	-7.1211	2.04556
39	H	0.498021	-7.48918	0.317279
40	H	-1.08894	-7.28963	1.063823
41	C	-0.00973	-3.16643	-2.33036
42	H	-0.012	-4.02733	-3.00525
43	H	0.874611	-2.56168	-2.56497
44	H	-0.88779	-2.55412	-2.56891
45	As	0.011523	2.171272	-1.18416
46	C	-3.84152	-0.48912	-0.21132
47	C	-3.94511	0.889406	-0.58419
48	C	-5.23467	1.478828	-0.68945
49	H	-5.31352	2.525578	-0.97134
50	C	-6.36825	0.733617	-0.44447
51	H	-7.3487	1.193408	-0.5301
52	C	-6.26722	-0.63347	-0.07515
53	H	-7.17011	-1.20593	0.11594
54	C	-5.03099	-1.23089	0.036869
55	H	-4.94622	-2.27745	0.318003
56	C	3.836501	-0.52819	-0.20855
57	C	5.018171	-1.28206	0.040487
58	H	4.922479	-2.32744	0.322507
59	C	3.954448	0.848791	-0.58287
60	C	5.250046	1.424852	-0.688
61	H	5.339788	2.470495	-0.97073
62	C	6.26053	-0.69752	-0.07165

63	H	7.157396	-1.27913	0.120118
64	C	6.375783	0.668136	-0.44212
65	H	7.360957	1.117711	-0.52778

Tabel S20. 3b (S_1): B3LYP/6-31G+(d, p) = -3609.312352

Number	Atom	X	Y	Z
1	C	-0.91804	-1.54421	-0.3927
2	C	-1.5646	-2.75828	-0.33829
3	H	-2.63556	-2.82789	-0.51649
4	C	1.191373	-2.5626	0.068751
5	H	2.261281	-2.50922	0.251287
6	C	0.503128	-1.3728	-0.21057
7	B	1.232327	0.004624	-0.21984
8	C	0.492826	1.37666	-0.21006
9	C	1.172356	2.571344	0.069492
10	H	2.242675	2.525861	0.251798
11	C	-1.58507	2.746885	-0.33707
12	H	-2.65653	2.808669	-0.51514
13	C	-0.92957	1.537594	-0.39199
14	C	-3.66224	-0.01358	-0.11411
15	C	-4.80027	-0.01739	-0.92714
16	H	-4.70013	-0.01665	-2.0087
17	C	-6.07198	-0.02218	-0.34625
18	H	-6.9548	-0.02515	-0.97845
19	C	-6.20229	-0.02308	1.044456
20	H	-7.18982	-0.02677	1.496227
21	C	-5.06359	-0.01925	1.857577
22	H	-5.16408	-0.01995	2.938809
23	C	-3.79306	-0.01452	1.280619
24	H	-2.9122	-0.01156	1.915151
25	C	2.820458	0.010483	-0.07929
26	C	3.441426	0.012961	1.193379
27	C	4.839563	0.021808	1.300542
28	H	5.293807	0.027556	2.290297
29	C	5.664502	0.025607	0.171469
30	C	5.048797	0.026976	-1.08486

31	H	5.668891	0.036857	-1.98009
32	C	3.654452	0.018372	-1.22331
33	C	2.606119	0.010397	2.458654
34	H	3.240047	0.012613	3.35094
35	H	1.957552	-0.87222	2.50969
36	H	1.951136	0.888282	2.509722
37	C	7.170899	0.00117	0.302694
38	H	7.495809	0.428168	1.257027
39	H	7.652332	0.566566	-0.50232
40	H	7.558477	-1.02496	0.255274
41	C	3.052078	0.021561	-2.61402
42	H	3.831065	0.028401	-3.38308
43	H	2.4152	0.899993	-2.77244
44	H	2.423862	-0.86179	-2.77958
45	As	-1.90534	-0.00683	-0.92834
46	C	0.572648	-3.84298	0.150649
47	C	-0.84262	-3.95866	-0.04846
48	C	-1.46436	-5.22191	0.026514
49	H	-2.53848	-5.29194	-0.12803
50	C	-0.71922	-6.36435	0.296714
51	H	-1.20526	-7.33318	0.356959
52	C	0.671842	-6.25762	0.49653
53	H	1.253613	-7.15019	0.709584
54	C	1.306165	-5.02539	0.425628
55	H	2.379357	-4.95258	0.5801
56	C	0.544211	3.847125	0.15183
57	C	1.269104	5.034772	0.426995
58	H	2.342836	4.969785	0.581184
59	C	-0.8719	3.952409	-0.04695
60	C	-1.50291	5.211063	0.028568
61	H	-2.57756	5.273251	-0.1257
62	C	0.625758	6.262285	0.498357
63	H	1.201004	7.159057	0.711501
64	C	-0.76611	6.358829	0.298904
65	H	-1.25924	7.324053	0.35953

Tabel S21. 3c (S_0): B3LYP/6-31G+(d, p) = -3943.617077

Number	Atom	X	Y	Z
1	C	-0.89453	-1.44252	-0.63937
2	C	0.461708	-1.34426	-0.34315
3	B	1.223918	0.000405	-0.19294
4	C	0.461106	1.344456	-0.34615
5	C	-0.89526	1.441674	-0.6422
6	As	-2.06605	-0.00121	-1.20775
7	C	1.041727	2.652285	-0.15589
8	C	0.160498	3.679945	-0.32532
9	S	-1.42563	3.092791	-0.73412
10	S	-1.42438	-3.09398	-0.72784
11	C	0.161875	-3.67981	-0.3176
12	C	1.04272	-2.6515	-0.15013
13	C	-3.37211	-0.00069	0.261033
14	C	3.230571	0.008081	1.470872
15	C	4.60603	0.012195	1.735956
16	C	5.554773	0.006988	0.707818
17	C	5.089897	0.003855	-0.61207
18	C	3.721729	-0.00071	-0.91137
19	C	2.770153	0.000942	0.134601
20	C	3.269264	-0.00294	-2.35806
21	C	2.246241	0.015741	2.623476
22	C	7.034967	-0.02165	1.014239
23	C	-4.7318	-0.00752	-0.06846
24	C	-5.70546	-0.00803	0.936947
25	C	-5.32007	-0.0017	2.278741
26	C	-3.96121	0.0052	2.615171
27	C	-2.99513	0.005682	1.609049
28	H	2.085174	2.799144	0.100941
29	H	0.333298	4.743415	-0.22749
30	H	0.334994	-4.74302	-0.2176
31	H	2.086141	-2.79736	0.10732
32	H	4.943634	0.021661	2.770904
33	H	5.808683	0.006719	-1.42973
34	H	4.123356	-0.00402	-3.04161

35	H	2.658618	-0.8849	-2.58695
36	H	2.658189	0.877908	-2.59015
37	H	1.593169	-0.86517	2.600381
38	H	2.764376	0.019167	3.586995
39	H	1.596514	0.898873	2.592131
40	H	7.253004	0.451179	1.977137
41	H	7.409828	-1.05217	1.064145
42	H	7.613449	0.49735	0.243103
43	H	-5.03664	-0.01235	-1.11197
44	H	-6.75849	-0.01333	0.670351
45	H	-6.07387	-0.00206	3.060913
46	H	-3.65732	0.01018	3.658167
47	H	-1.9421	0.011104	1.87571

Tabel S22. 3c (S_1): B3LYP/6-31G+(d, p) = -3943.501671

Number	Atom	X	Y	Z
1	C	0.913772	1.423565	-0.76239
2	C	-0.44149	1.325734	-0.38959
3	B	-1.15548	-0.00482	-0.17535
4	C	-0.43668	-1.333	-0.38872
5	C	0.919488	-1.42641	-0.75977
6	As	2.142517	0.000453	-1.20209
7	C	-1.01418	-2.65947	-0.28319
8	C	-0.16301	-3.6803	-0.58473
9	S	1.416366	-3.08838	-1.0179
10	S	1.4048	3.086902	-1.02229
11	C	-0.17633	3.673787	-0.58868
12	C	-1.02368	2.650264	-0.28549
13	C	3.312376	0.004272	0.421327
14	C	-3.16224	-0.01004	1.577236
15	C	-4.51139	-0.00748	1.861563
16	C	-5.48713	-0.0041	0.827383
17	C	-5.06129	-0.00689	-0.52706
18	C	-3.7221	-0.00892	-0.8573
19	C	-2.71059	-0.00823	0.193565
20	C	-3.28187	-0.01261	-2.29207

21	C	-2.14297	-0.01575	2.679793
22	C	-6.94151	0.035293	1.163994
23	C	4.697693	0.025397	0.234965
24	C	5.569373	0.029747	1.330727
25	C	5.053669	0.012291	2.628371
26	C	3.667597	-0.00961	2.825973
27	C	2.807833	-0.01343	1.726059
28	H	-2.04523	-2.84193	0.00732
29	H	-0.36189	-4.74391	-0.5744
30	H	-0.37895	4.7367	-0.57944
31	H	-2.05517	2.829278	0.005632
32	H	-4.8499	-0.0097	2.89391
33	H	-5.81487	-0.00867	-1.30963
34	H	-4.13686	-0.01541	-2.97277
35	H	-2.65651	0.861292	-2.50072
36	H	-2.6543	-0.88601	-2.49603
37	H	-1.48684	0.856304	2.596818
38	H	-2.61912	-0.01492	3.663613
39	H	-1.49446	-0.89336	2.594907
40	H	-7.1475	-0.42354	2.134487
41	H	-7.27327	1.082912	1.22574
42	H	-7.54999	-0.44663	0.394073
43	H	5.103248	0.038497	-0.7749
44	H	6.64438	0.046379	1.170658
45	H	5.726037	0.015331	3.482115
46	H	3.262782	-0.02367	3.834918
47	H	1.732102	-0.0309	1.880755

Tabel S23. 3d (S_0): B3LYP/6-31G+(d, p) = -3943.615879

Number	Atom	X	Y	Z
1	C	-1.08496	1.468463	-0.95071
2	C	0.303238	1.332402	-0.55686
3	B	1.058078	4.8E-06	-0.31293
4	C	0.303229	-1.33238	-0.55691
5	C	-1.08497	-1.46841	-0.95078
6	As	-2.3318	3.59E-05	-1.26274

7	C	0.900882	-2.57592	-0.44039
8	S	-0.16077	-3.87721	-0.82329
9	C	-1.46049	-2.76764	-1.15374
10	C	-1.46047	2.7677	-1.15365
11	S	-0.16074	3.877248	-0.82314
12	C	0.9009	2.575933	-0.44028
13	C	-3.25395	2.5E-06	0.476916
14	C	2.895702	-8.5E-05	1.531191
15	C	4.236146	-0.00011	1.931928
16	C	5.283942	-0.00006	1.002501
17	C	4.952713	2.2E-06	-0.35529
18	C	3.619699	3.07E-05	-0.79141
19	C	2.569253	-1.1E-05	0.153294
20	C	3.320693	9.71E-05	-2.27757
21	C	1.802398	-0.00015	2.581434
22	C	6.724494	2.06E-05	1.461598
23	C	-4.65351	-9E-06	0.473587
24	C	-5.37453	-3.4E-05	1.673447
25	C	-4.69527	-5E-05	2.892998
26	C	-3.29568	-4.2E-05	2.909277
27	C	-2.58631	-1.6E-05	1.70776
28	H	1.926366	-2.78015	-0.15946
29	H	-2.42399	-3.15179	-1.46316
30	H	-2.42396	3.15187	-1.46306
31	H	1.926386	2.780141	-0.15935
32	H	4.468591	-0.00019	2.99567
33	H	5.749414	0.000024	-1.09681
34	H	2.737233	-0.88053	-2.5714
35	H	4.242034	0.000132	-2.86724
36	H	2.737221	0.880742	-2.57132
37	H	1.157099	0.8819	2.490174
38	H	1.157062	-0.88216	2.490033
39	H	2.223714	-0.00024	3.590936
40	H	7.413183	-0.00103	0.611598
41	H	6.948277	-0.88137	2.074333
42	H	6.948749	0.882576	2.072491

43	H	-5.18964	1.7E-06	-0.47261
44	H	-6.46077	-4.1E-05	1.652319
45	H	-5.25108	-7E-05	3.82642
46	H	-2.7613	-5.5E-05	3.85532
47	H	-1.50024	-9.5E-06	1.732888

Tabel S24. 3d (S_1): B3LYP/6-31G+(d, p) = -3943.499605

Number	Atom	X	Y	Z
1	C	-1.06884	1.471982	-0.94884
2	C	0.316646	1.337874	-0.53844
3	B	1.030833	-7.2E-06	-0.29367
4	C	0.316631	-1.33788	-0.53846
5	C	-1.06885	-1.47196	-0.94886
6	As	-2.30437	1.88E-05	-1.26561
7	C	0.89301	-2.61148	-0.41922
8	S	-0.18705	-3.91172	-0.82812
9	C	-1.4547	-2.76504	-1.16553
10	C	-1.45467	2.765065	-1.16549
11	S	-0.187	3.91173	-0.82808
12	C	0.893041	2.611468	-0.41919
13	C	-3.23803	1.06E-05	0.471903
14	C	2.89666	-5.2E-05	1.57416
15	C	4.224313	-6.8E-05	1.950176
16	C	5.269496	-4.3E-05	0.979902
17	C	4.942119	-1.9E-05	-0.39726
18	C	3.62214	-3.9E-06	-0.81207
19	C	2.55056	-0.00002	0.168172
20	C	3.295911	2.42E-05	-2.27559
21	C	1.81843	-7.4E-05	2.621014
22	C	6.696026	4.76E-05	1.42601
23	C	-4.63758	1.35E-05	0.468128
24	C	-5.36231	8.4E-06	1.666374
25	C	-4.68634	1.6E-06	2.887665
26	C	-3.28658	-6E-07	2.905249
27	C	-2.57451	3.5E-06	1.704629
28	H	1.907085	-2.84903	-0.12864

29	H	-2.42188	-3.12694	-1.48977
30	H	-2.42184	3.126983	-1.48974
31	H	1.907121	2.848999	-0.12862
32	H	4.479091	-0.0001	3.00657
33	H	5.736909	-1.6E-05	-1.13743
34	H	2.693654	-0.87766	-2.53164
35	H	4.202869	4.16E-05	-2.88701
36	H	2.693644	0.877716	-2.53161
37	H	1.176504	0.879108	2.509708
38	H	1.176465	-0.87922	2.509635
39	H	2.24478	-0.00012	3.628556
40	H	7.387188	-0.00099	0.580302
41	H	6.902312	-0.8798	2.047984
42	H	6.902724	0.881165	2.046064
43	H	-5.17111	1.92E-05	-0.4796
44	H	-6.44881	1.03E-05	1.643057
45	H	-5.24435	-1.8E-06	3.820133
46	H	-2.75458	-5.9E-06	3.853114
47	H	-1.48813	1.4E-06	1.725096

Tabel S25. 3e (S_0): B3LYP/6-31G+(d, p) = -3943.628696

Number	Atom	X	Y	Z
1	C	-0.26512	1.310549	-0.42055
2	C	1.080314	1.468705	-0.7395
3	C	1.078399	-1.46924	-0.73887
4	C	-0.26701	-1.30916	-0.42079
5	B	-1.05808	0.001229	-0.23851
6	C	1.4922	-2.82984	-0.814
7	C	0.475323	-3.7053	-0.51862
8	S	-1.00499	-2.8879	-0.18151
9	S	-1.00057	2.890346	-0.18044
10	C	0.480739	3.705617	-0.51831
11	C	1.496232	2.828689	-0.8141
12	C	-2.59552	0.001823	0.124451
13	C	-3.56977	0.003565	-0.90153
14	C	-4.93036	0.007621	-0.57169

15	C	-5.36556	0.006949	0.757938
16	C	-4.39524	0.008874	1.765407
17	C	-3.0262	0.005151	1.47152
18	As	2.23324	-0.00108	-1.26668
19	C	3.51981	-0.0018	0.22039
20	C	4.881104	-0.00563	-0.10477
21	C	5.853648	-0.00672	0.901509
22	C	5.466446	-0.00404	2.242843
23	C	4.106799	-0.00022	2.575926
24	C	3.140899	0.000863	1.568522
25	C	-3.15329	0.005003	-2.3587
26	C	-2.02056	0.008839	2.605239
27	C	-6.83846	-0.02279	1.096553
28	H	2.498221	-3.14957	-1.06384
29	H	0.524391	-4.78626	-0.49118
30	H	0.531393	4.786503	-0.49069
31	H	2.502634	3.146925	-1.0643
32	H	-5.66719	0.013059	-1.37293
33	H	-4.71067	0.015349	2.807197
34	H	5.187267	-0.00766	-1.14788
35	H	6.907199	-0.00966	0.636442
36	H	6.218466	-0.00488	3.026743
37	H	3.801393	0.001885	3.618582
38	H	2.087679	0.003839	1.834592
39	H	-2.55087	-0.87749	-2.60559
40	H	-4.02509	0.006996	-3.01939
41	H	-2.54805	0.886071	-2.60376
42	H	-2.52186	0.009107	3.577526
43	H	-1.36918	-0.87251	2.567469
44	H	-1.37236	0.892435	2.565218
45	H	-7.43434	0.492391	0.336254
46	H	-7.20942	-1.05407	1.158112
47	H	-7.03618	0.452912	2.062396

Tabel S26. 3e (S_1): B3LYP/6-31G+(d, p) = -3943.519127

Number	Atom	X	Y	Z

1	C	0.232939	-1.30783	-0.49487
2	C	-1.10375	-1.46526	-0.90541
3	C	-1.09575	1.464791	-0.90743
4	C	0.240725	1.300292	-0.49884
5	B	0.96928	-0.00552	-0.25397
6	C	-1.46625	2.819566	-1.12567
7	C	-0.47081	3.724187	-0.85363
8	S	0.986696	2.910351	-0.3467
9	S	0.968886	-2.92188	-0.33718
10	C	-0.49308	-3.72831	-0.84296
11	C	-1.48269	-2.81848	-1.11889
12	C	2.510283	-0.00974	0.174028
13	C	3.558148	-0.01188	-0.83712
14	C	4.882507	-0.01046	-0.4536
15	C	5.253894	-0.00653	0.916792
16	C	4.238076	-0.0087	1.911583
17	C	2.90186	-0.01064	1.573744
18	As	-2.31001	0.002729	-1.28891
19	C	-3.40662	0.006781	0.371011
20	C	-4.79788	0.015087	0.226359
21	C	-5.63769	0.018674	1.346459
22	C	-5.08504	0.013793	2.628687
23	C	-3.69375	0.005237	2.785459
24	C	-2.86452	0.001823	1.661928
25	C	3.172451	-0.0163	-2.28725
26	C	1.836915	-0.0144	2.63211
27	C	6.693153	0.033877	1.310476
28	H	-2.45282	3.123059	-1.46272
29	H	-0.5012	4.802568	-0.92314
30	H	-0.53004	-4.80671	-0.90891
31	H	-2.47083	-3.11689	-1.45584
32	H	5.666524	-0.01342	-1.20565
33	H	4.534842	-0.01023	2.95668
34	H	-5.23276	0.018741	-0.77086
35	H	-6.71689	0.025162	1.217008
36	H	-5.73201	0.016468	3.501744

37	H	-3.25996	0.00125	3.782303
38	H	-1.7853	-0.00501	1.787656
39	H	2.558568	0.859926	-2.51954
40	H	4.052787	-0.01909	-2.93454
41	H	2.556872	-0.89273	-2.51422
42	H	2.271408	-0.0135	3.634839
43	H	1.188611	0.860763	2.522461
44	H	1.194023	-0.89354	2.521937
45	H	7.332317	-0.44774	0.565667
46	H	7.02063	1.082391	1.383843
47	H	6.861096	-0.42299	2.289164

5. NMR Spectra

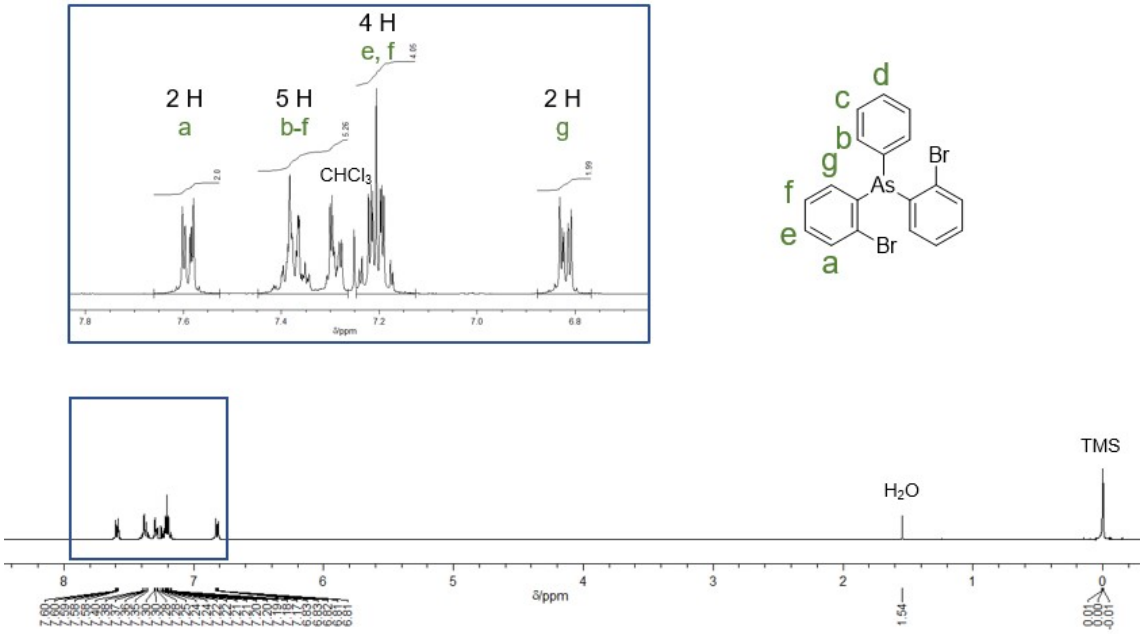


Figure S14. ^{1}H-NMR spectrum (400 MHz) of **2a** in $CDCl_3$

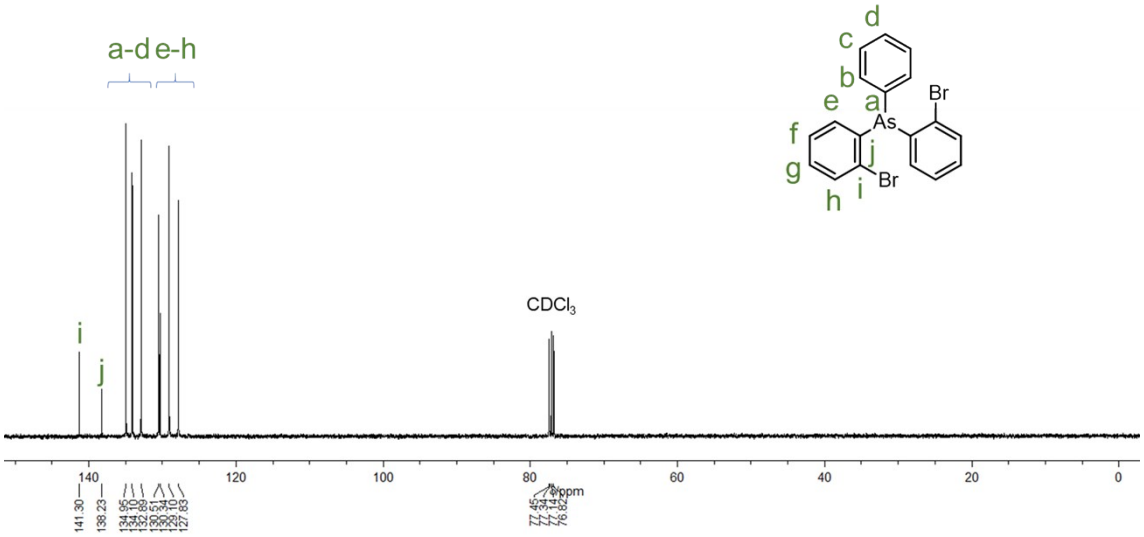


Figure S15. ^{13}C-NMR spectrum (100 MHz) of **2a** in $CDCl_3$.

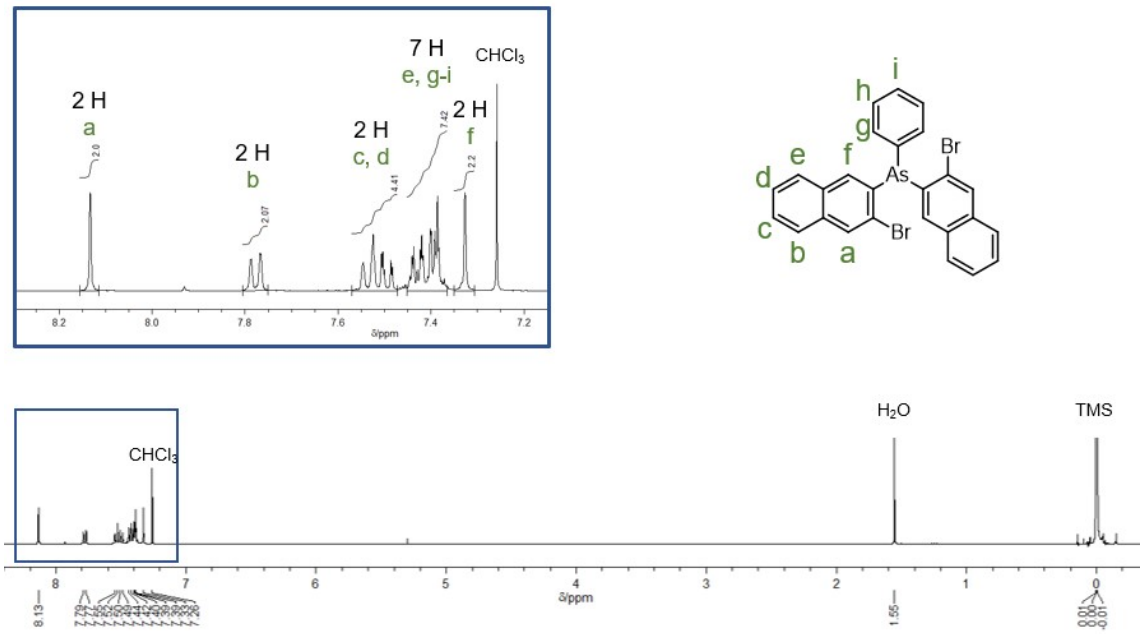


Figure S16. ^{1}H-NMR spectrum (400 MHz) of **2b** in $CDCl_3$.

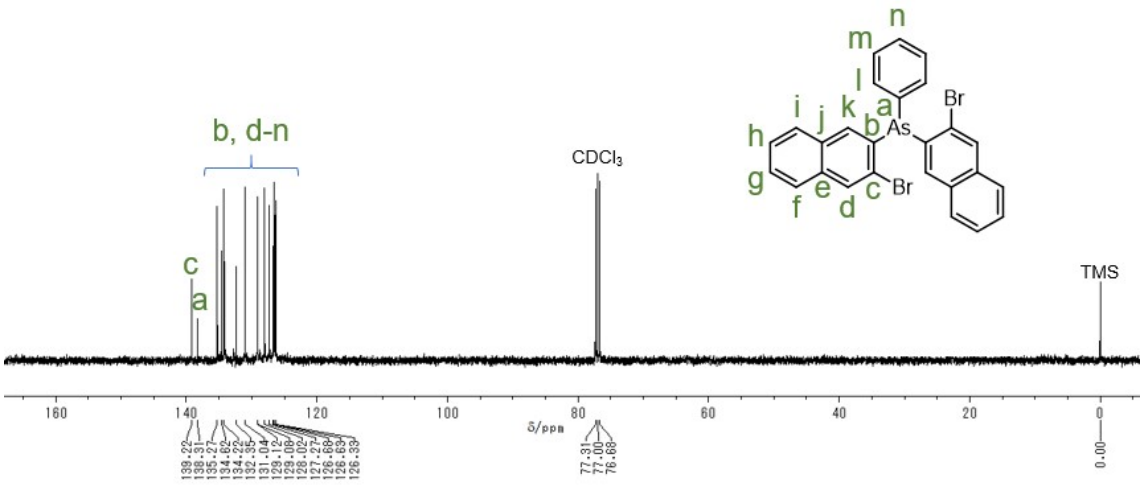


Figure S17. ^{13}C-NMR spectrum (100 MHz) of **2b** in $CDCl_3$.

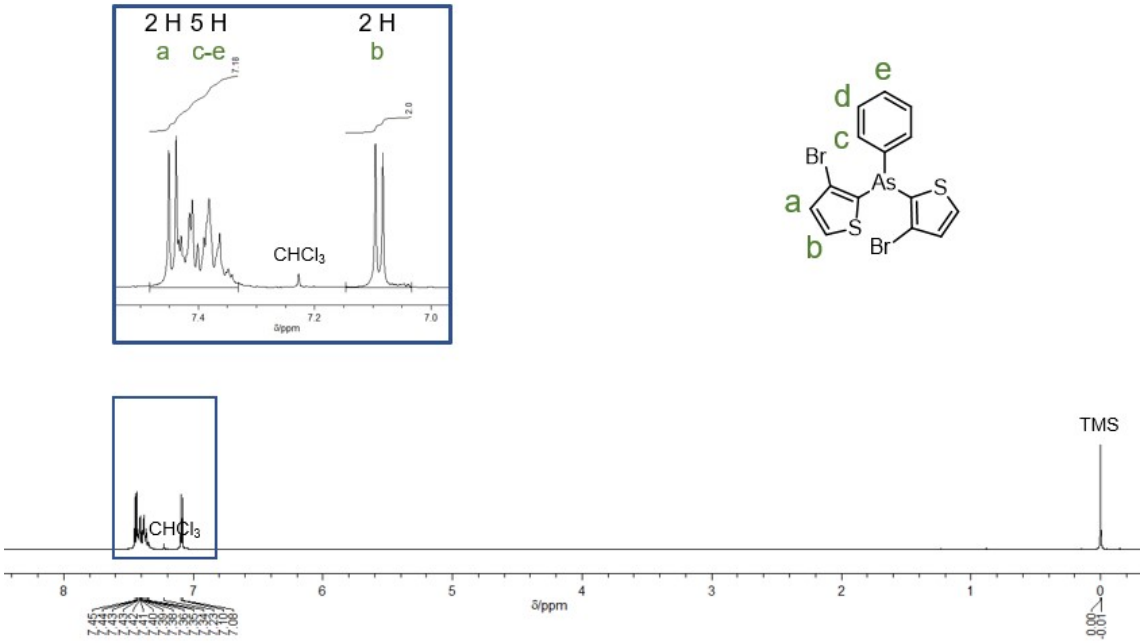


Figure S18. ^{1}H-NMR spectrum (400 MHz) of **2c** in $CDCl_3$.

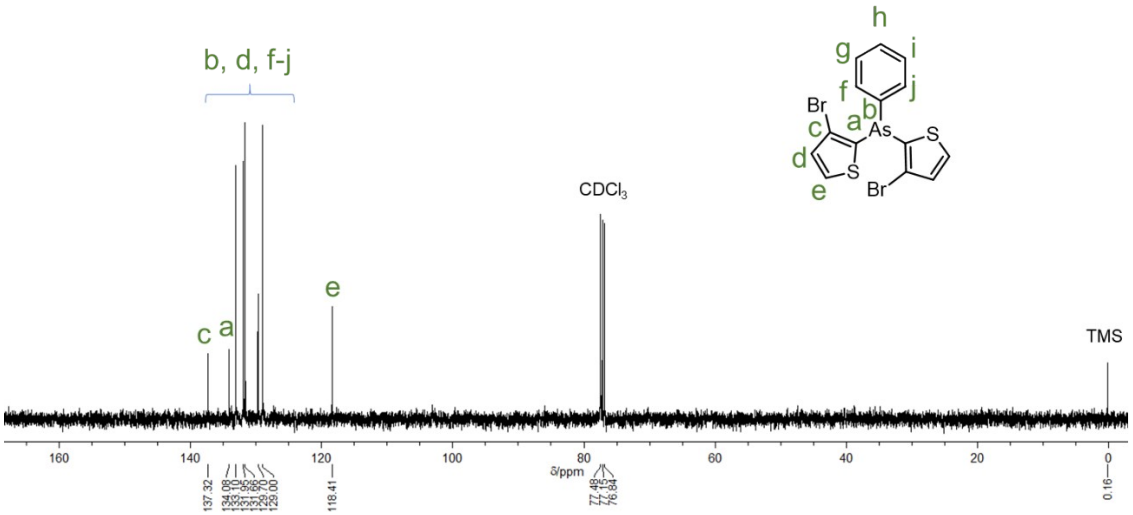


Figure S19. ^{13}C-NMR spectrum (100 MHz) of **2c** in $CDCl_3$.

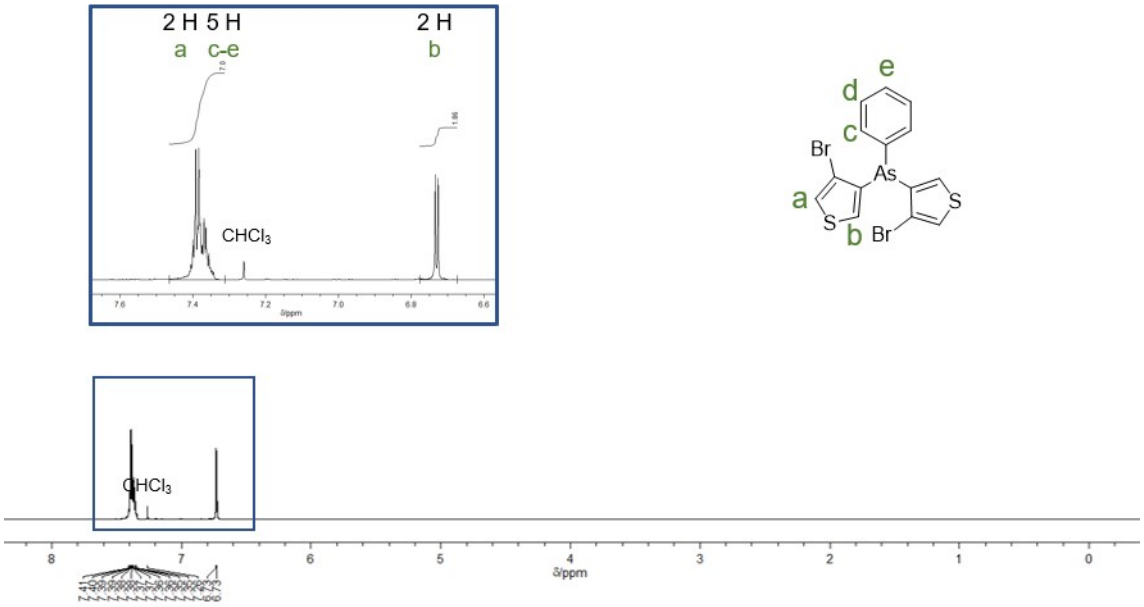


Figure S20. ^{1}H-NMR spectrum (400 MHz) of **2d** in $CDCl_3$.

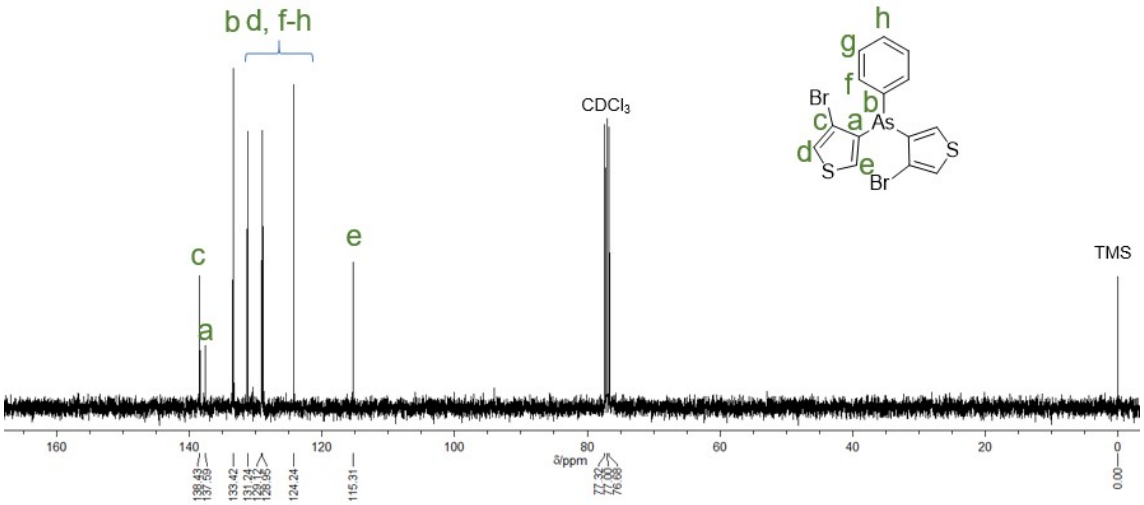


Figure S21. ^{13}C-NMR spectrum (100 MHz) of **2d** in $CDCl_3$.

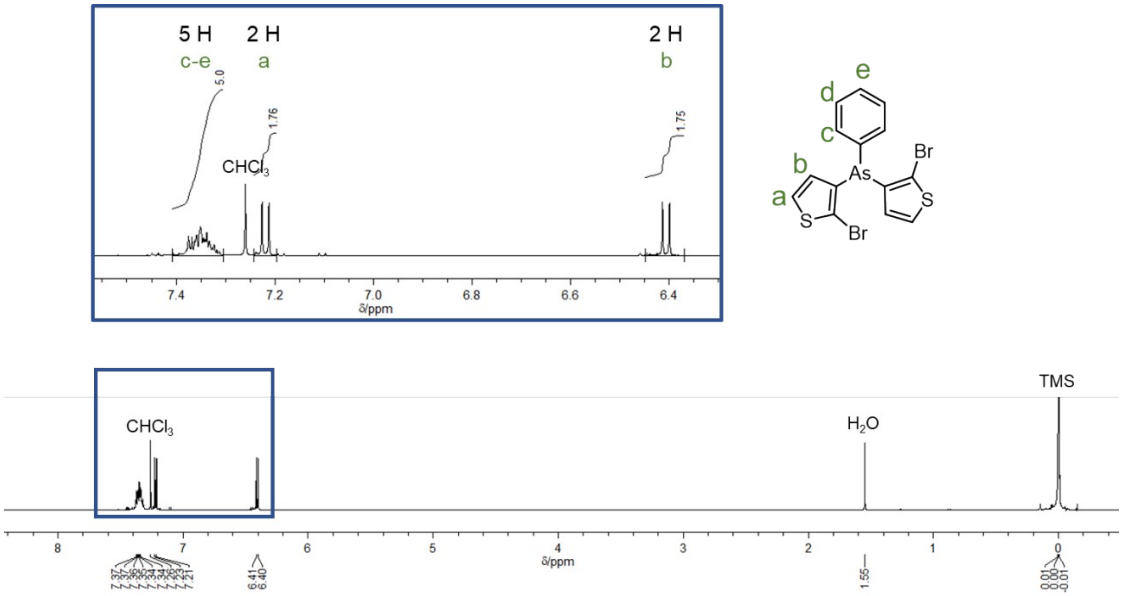


Figure S22. ^{1}H-NMR spectrum (400 MHz) of **2e** in $CDCl_3$.

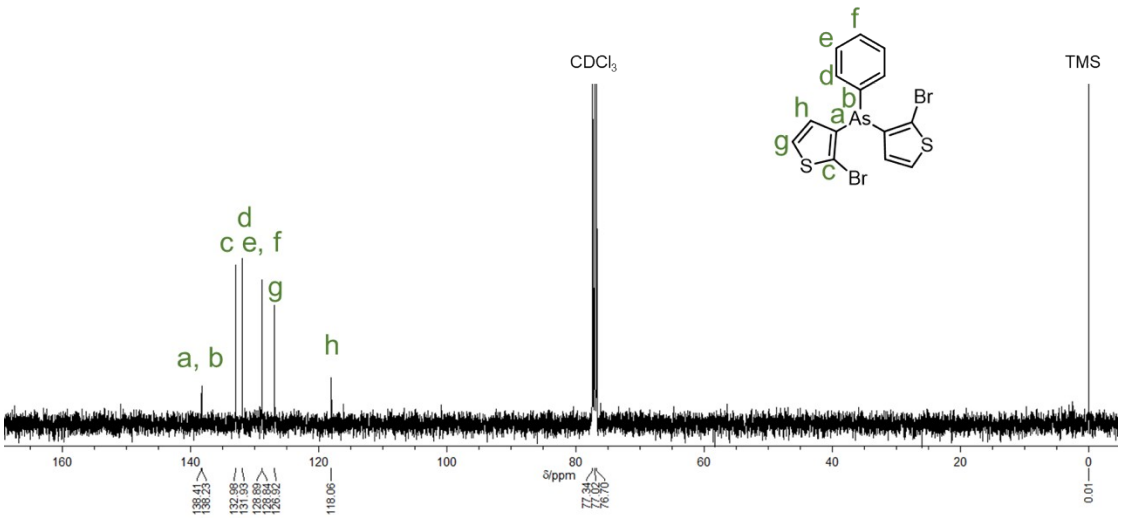


Figure S23. ^{13}C-NMR spectrum (100 MHz) of **2e** in $CDCl_3$.

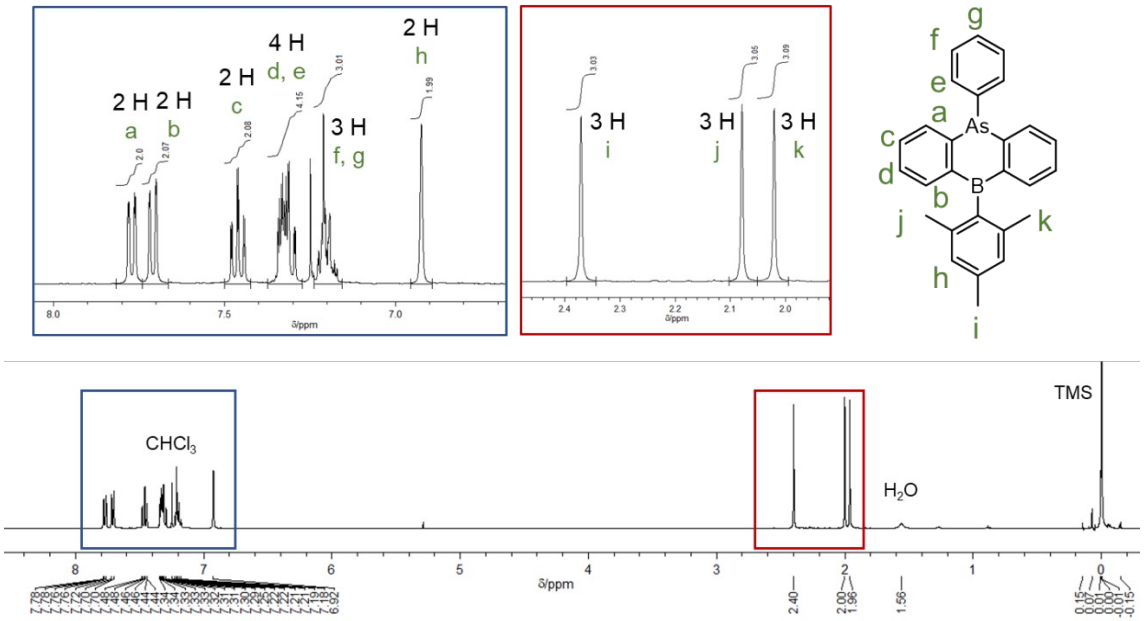


Figure S24. ^{1}H-NMR spectrum (400 MHz) of **3a** in $CDCl_3$.

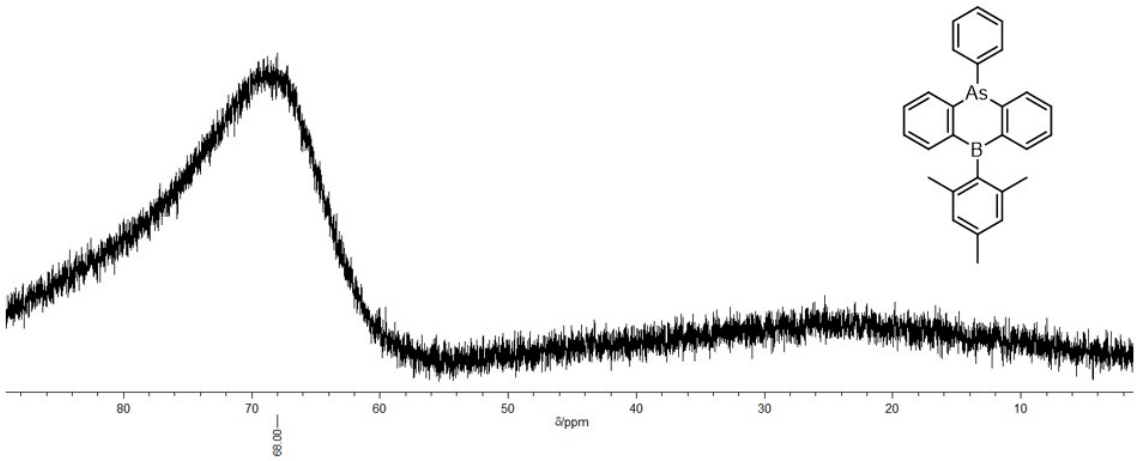


Figure S25. ^{11}B-NMR spectrum (128 MHz) of **3a** in $CDCl_3$.

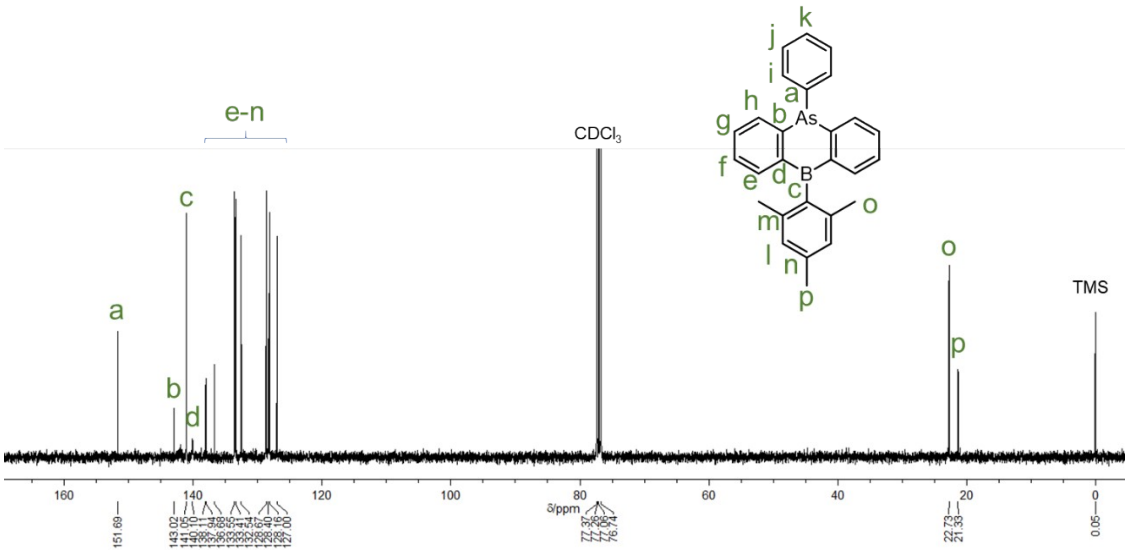


Figure S26. ^{13}C-NMR spectrum (100 MHz) of **2e** in $CDCl_3$.

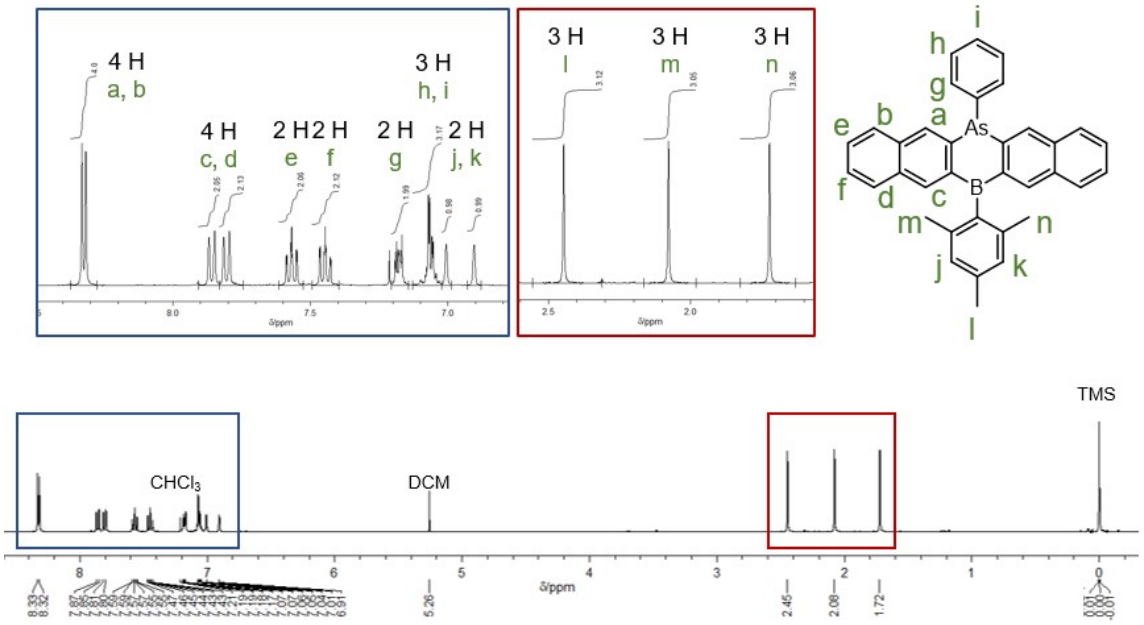


Figure S27. ^{1}H-NMR spectrum (400 MHz) of **3b** in $CDCl_3$.

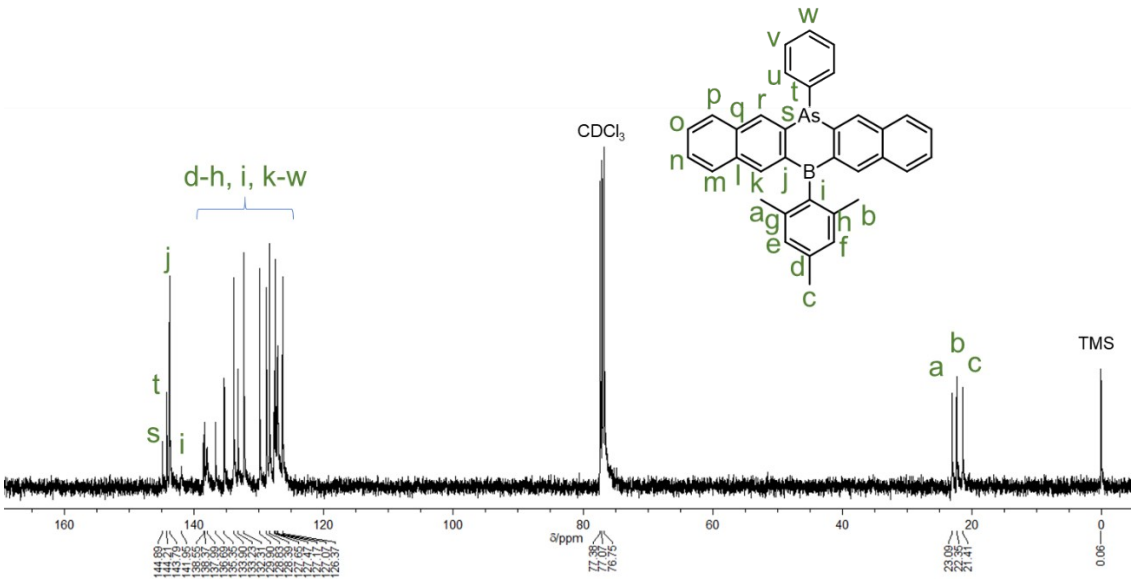


Figure S28. ^{13}C-NMR spectrum (100 MHz) of **3b** in $CDCl_3$.

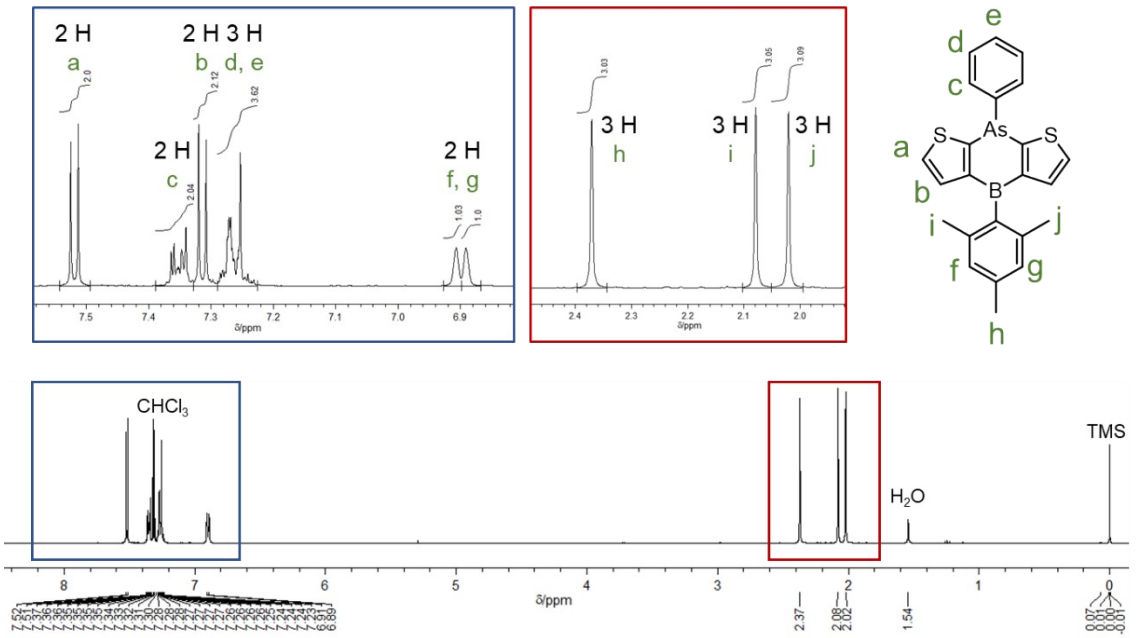


Figure S29. ^{1}H-NMR spectrum (400 MHz) of **3c** in $CDCl_3$.

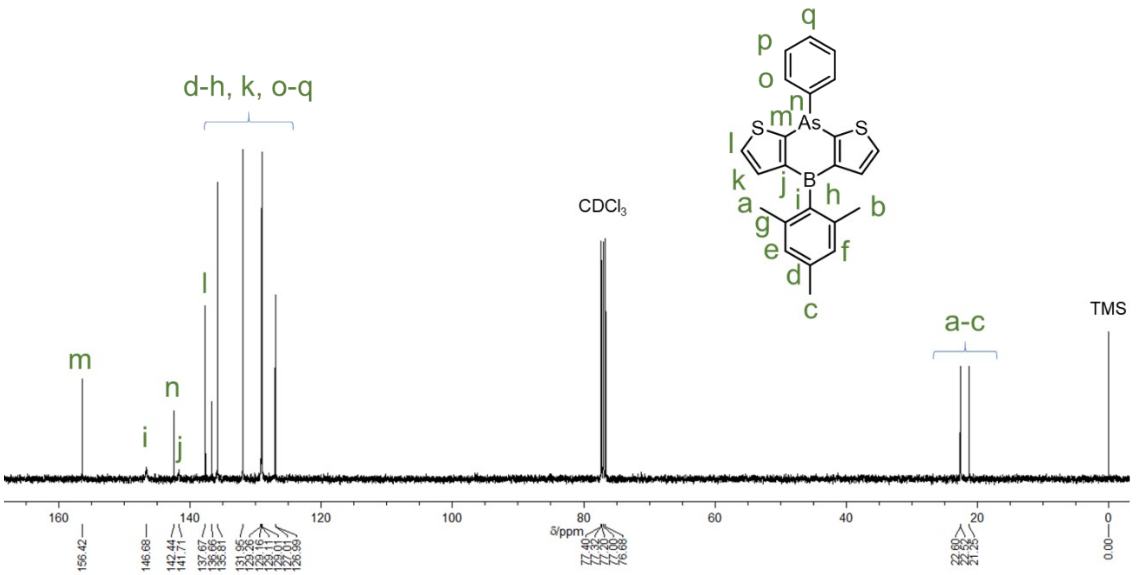


Figure S30. ^{13}C-NMR spectrum (100 MHz) of **3c** in $CDCl_3$

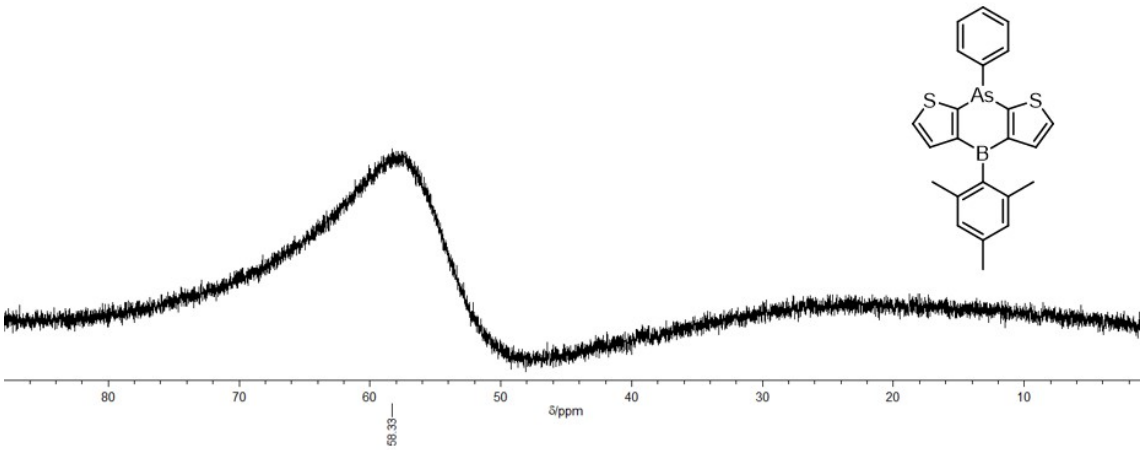


Figure S31. ^{11}B-NMR spectrum (128 MHz) of **3c** in $CDCl_3$**.**

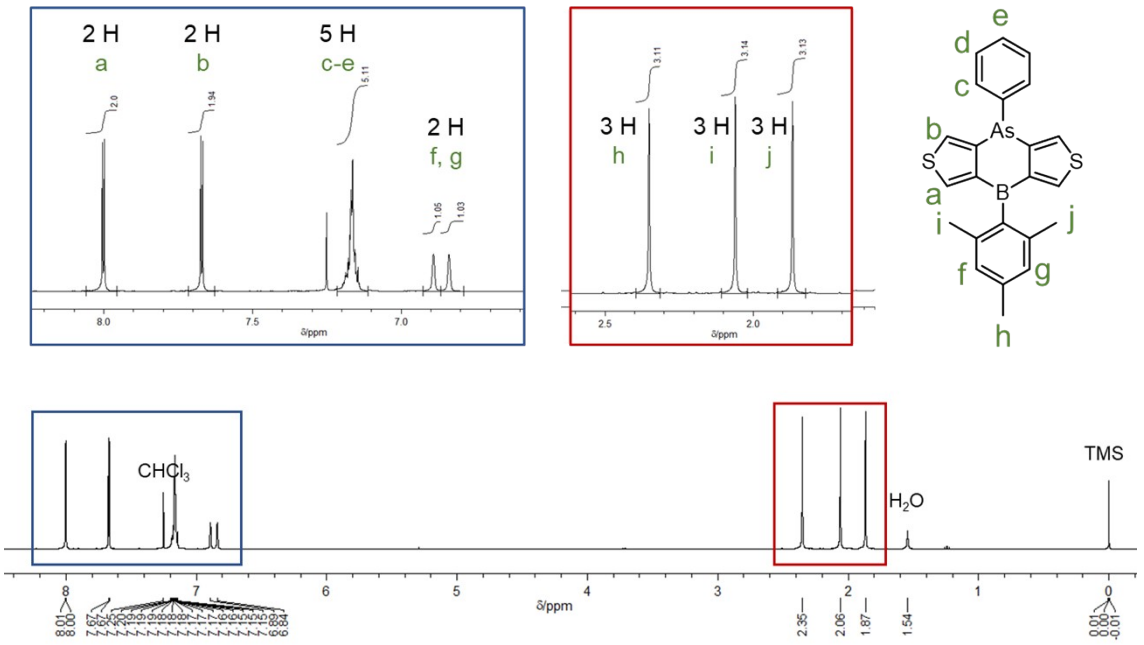


Figure S32. ^{1}H-NMR spectrum (400 MHz) of **3d** in $CDCl_3$**.**

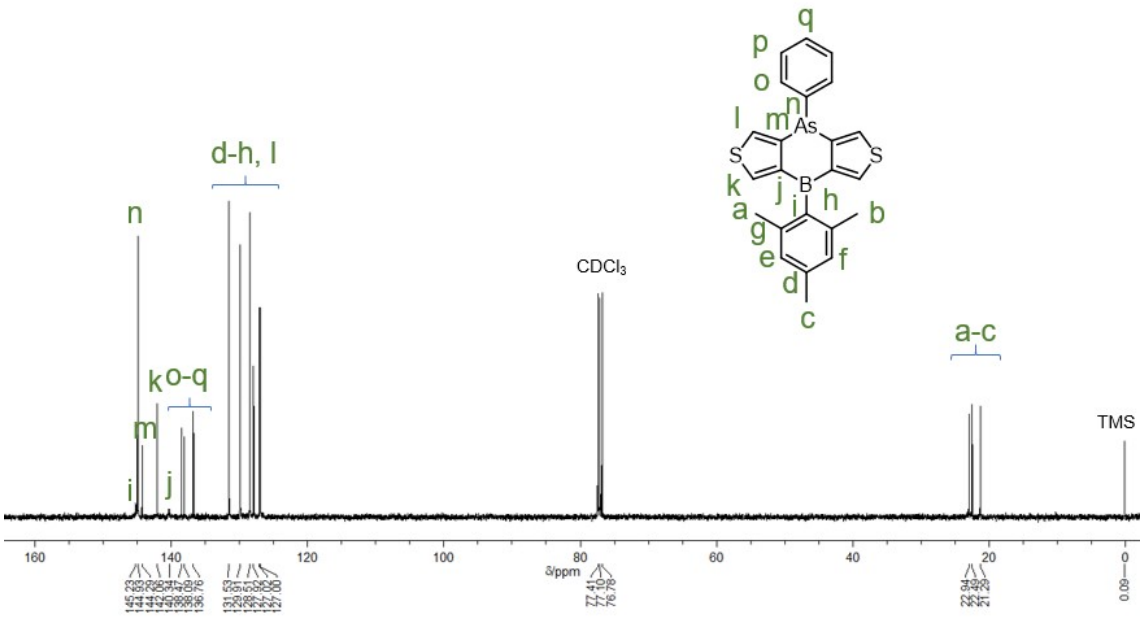


Figure S33. ^{13}C-NMR spectrum (100 MHz) of **3d** in $CDCl_3$**.**

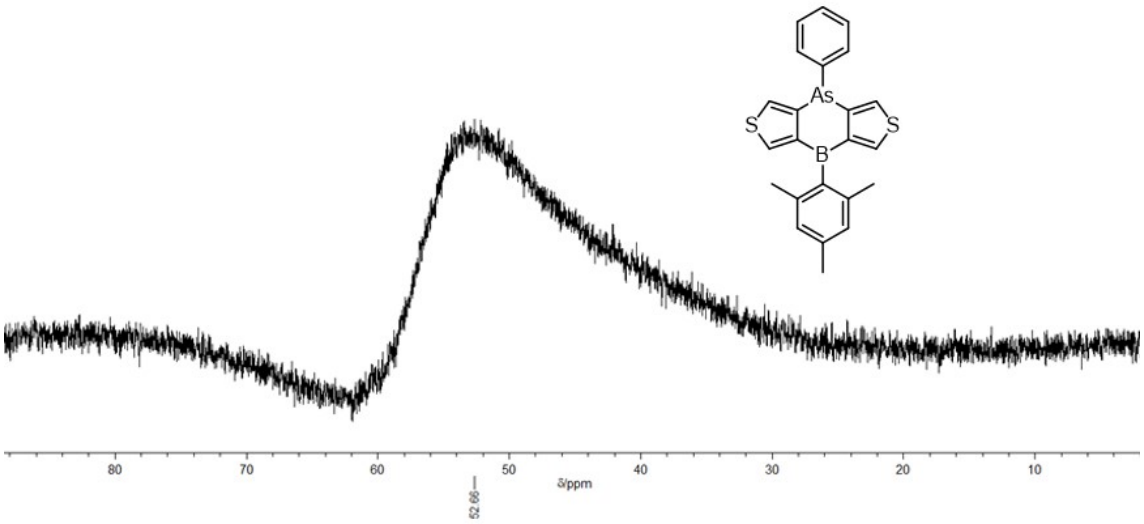


Figure S34. ^{11}B-NMR spectrum (128 MHz) of **3d** in $CDCl_3$**.**

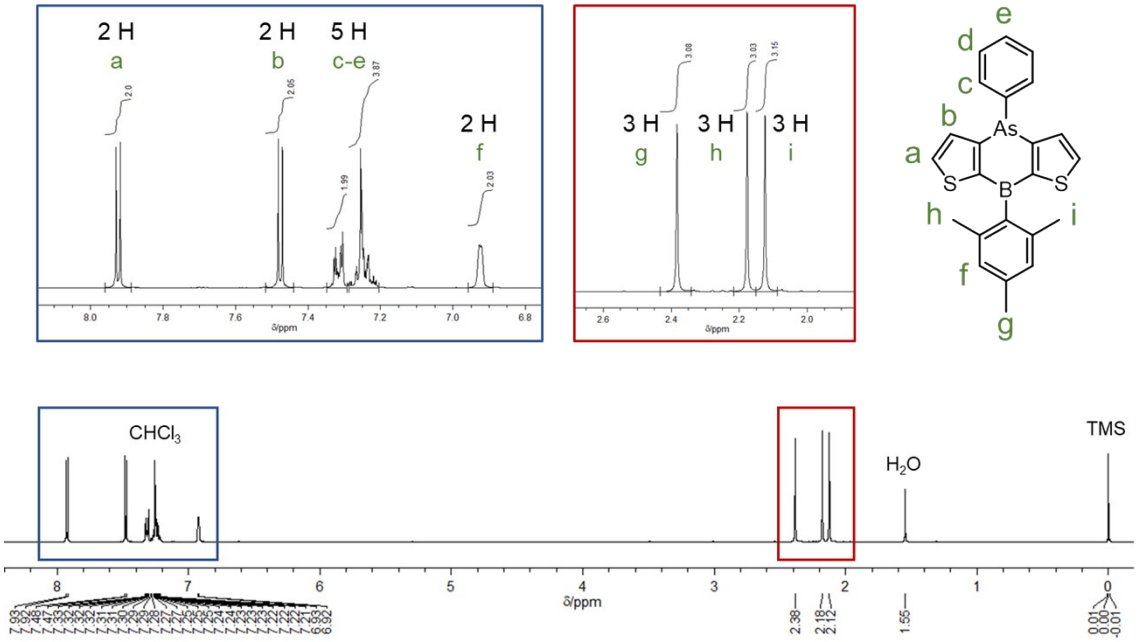


Figure S35. ^{1}H-NMR spectrum (400 MHz) of **3e** in $CDCl_3$**.**

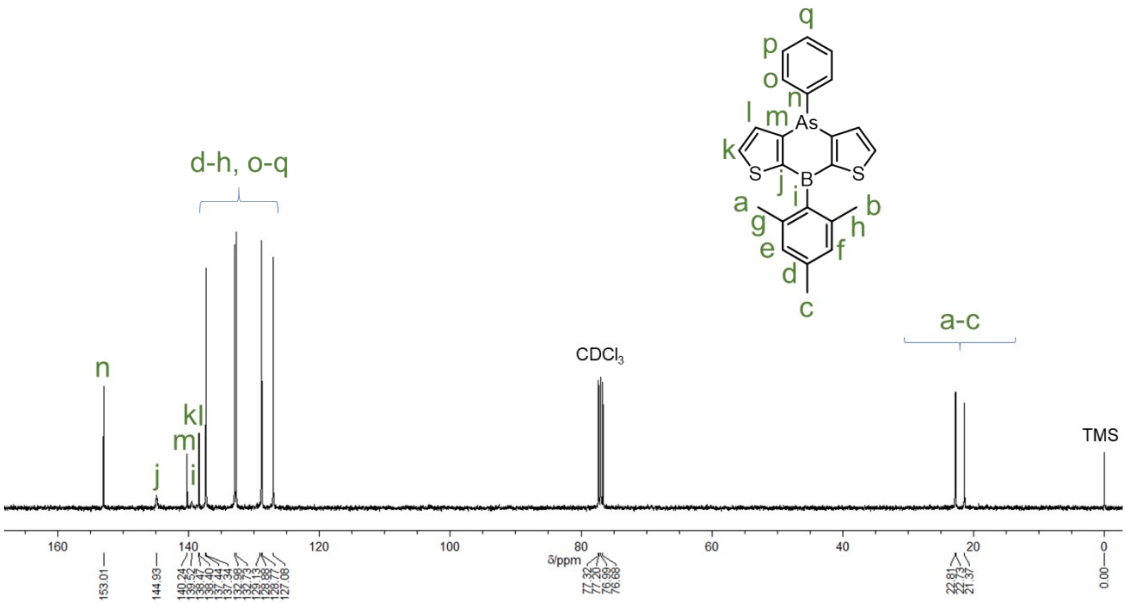


Figure S36. ^{13}C-NMR spectrum (100 MHz) of **3e** in $CDCl_3$**.**

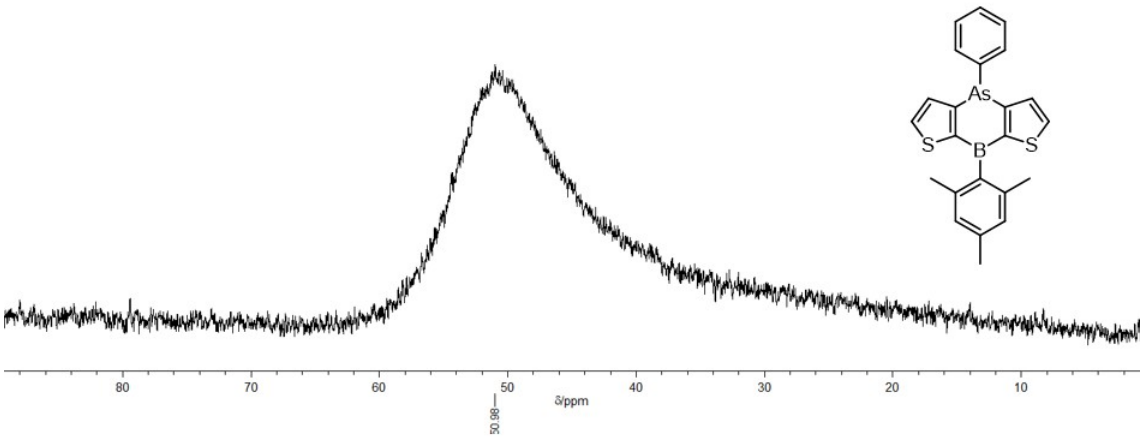


Figure S37. ^{11}B-NMR spectrum (128 MHz) of **3e** in $CDCl_3$**.**

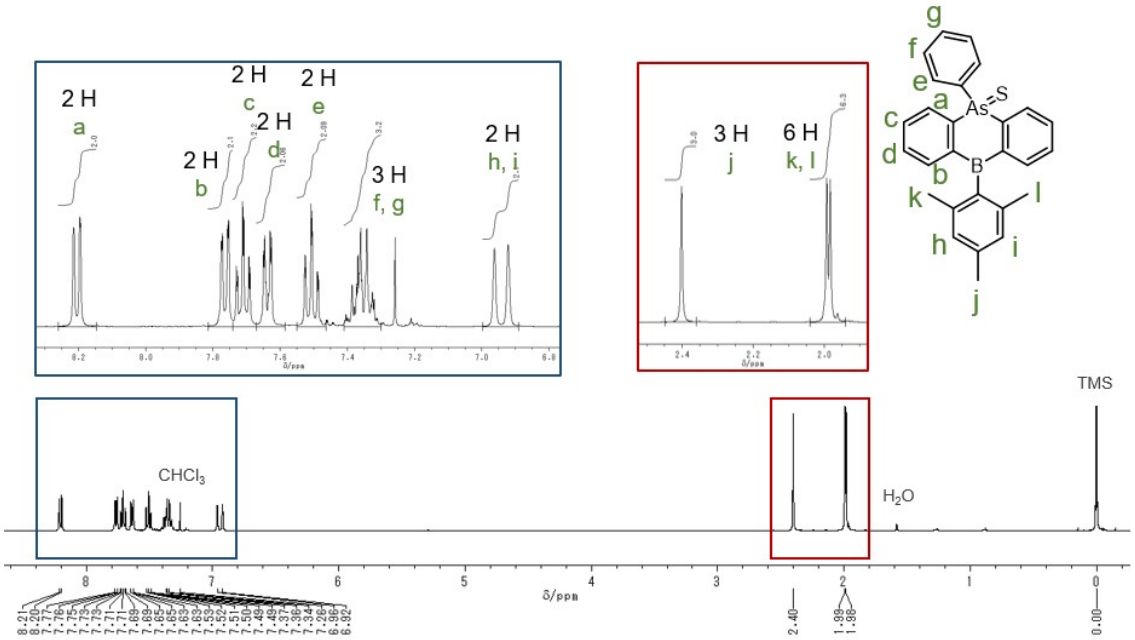


Figure S38. ^{1}H-NMR spectrum (400 MHz) of **3a-S** in $CDCl_3$.

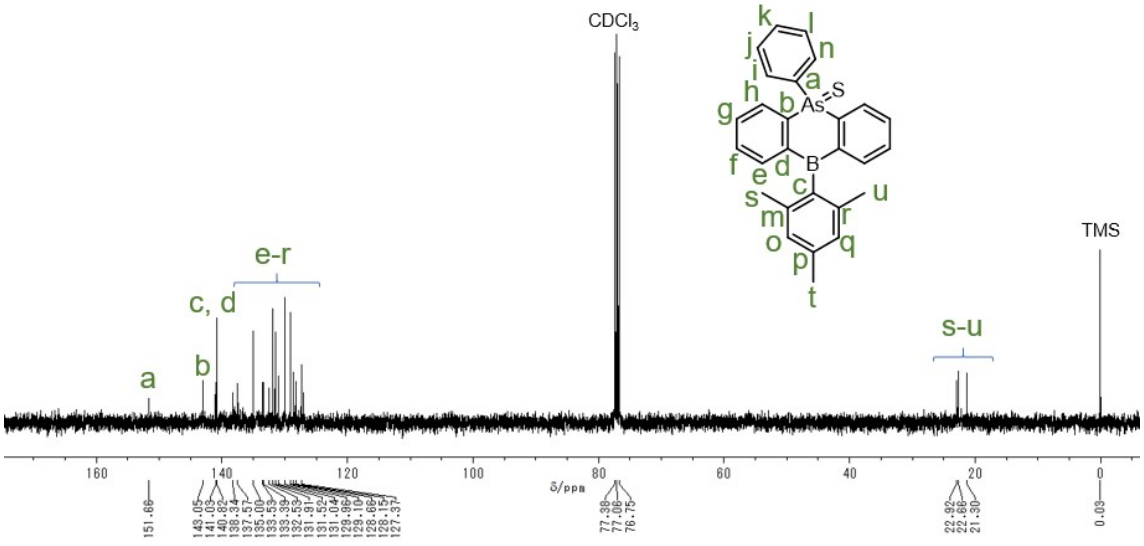


Figure S39. ^{13}C-NMR spectrum (100 MHz) of **3a-S** in $CDCl_3$.

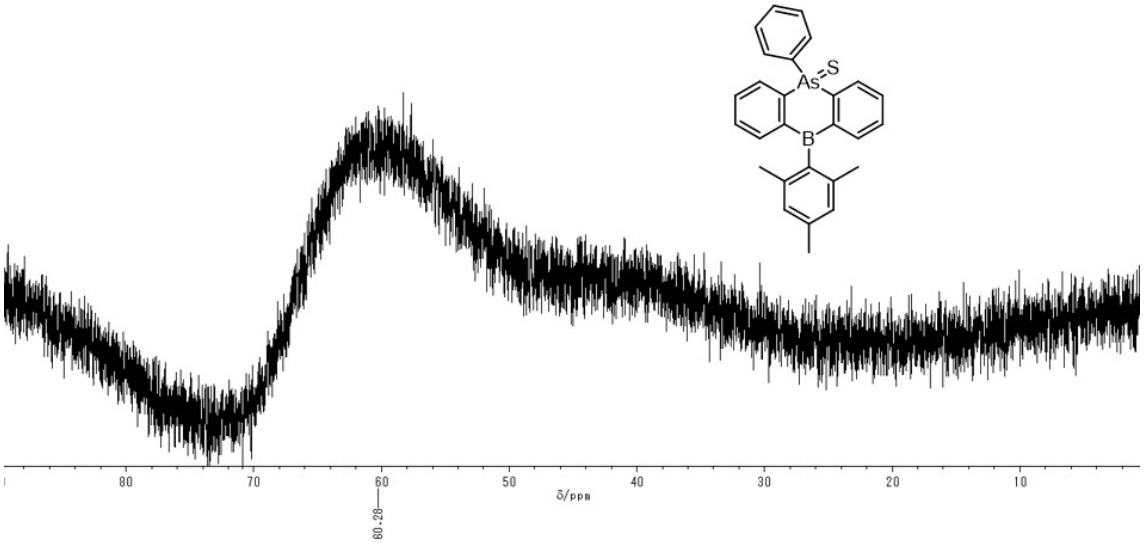


Figure S40. ^{11}B-NMR spectrum (128 MHz) of **3a-S** in $CDCl_3$**.**

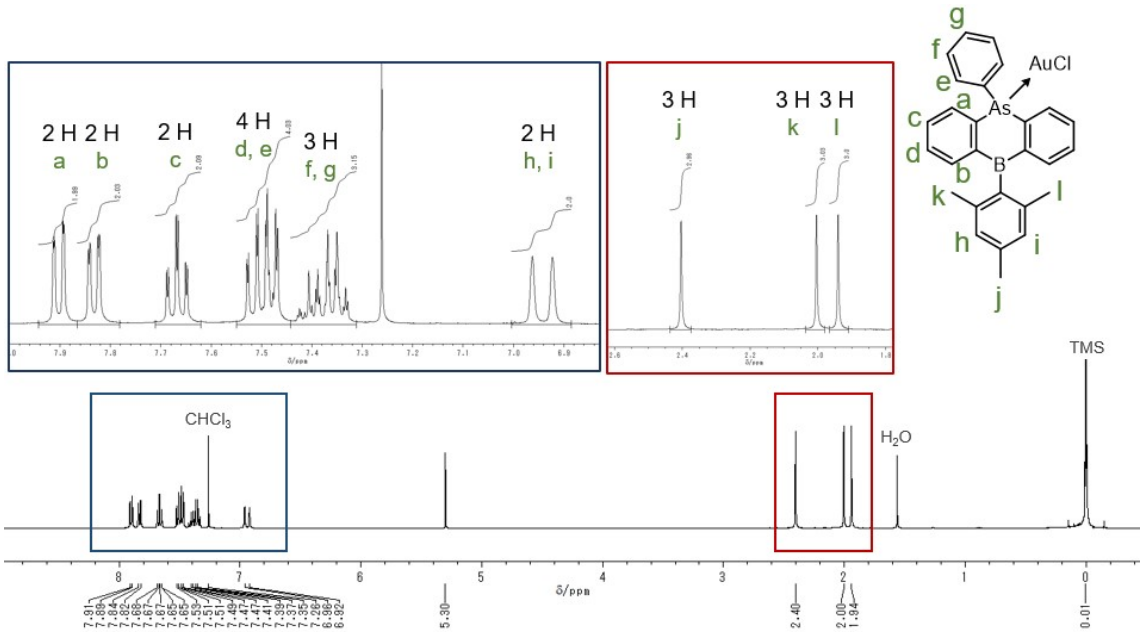


Figure S41. ^{1}H-NMR spectrum (400 MHz) of **3a-AuCl** in $CDCl_3$**.**

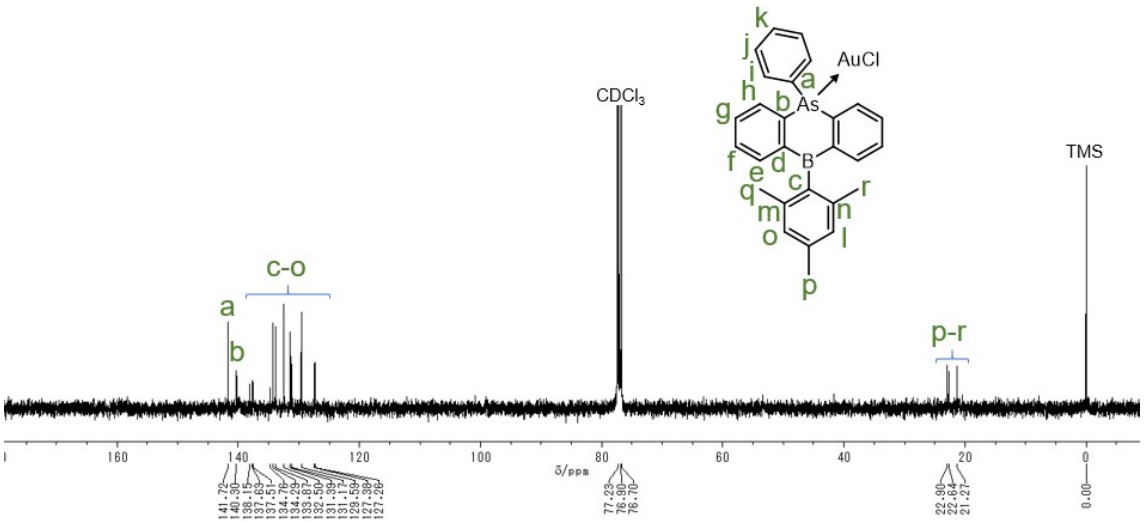


Figure S42. ^{13}C-NMR spectrum (100 MHz) of **3a-AuCl** in $CDCl_3$**.**