Supporting Information

N-Heterocyclic carbene-stabilised arsinidene (AsH)

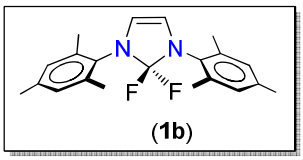
Adinarayana Doddi,[a] Michael Weinhart,[b] Alexander Hinz,[c] Dirk Bockfeld,[a]
Jose M. Goicoechea,*[c] Manfred Scheer*[b] and Matthias Tamm*[a]

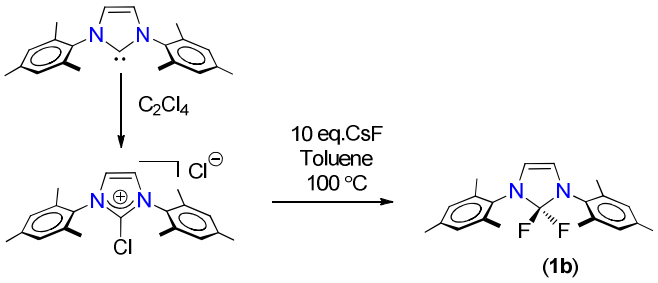
1. Experimental Section

Materials and methods: Due to the high sensitivity (to oxygen and moisture) of all the compounds reported in this study, all manipulations were performed under a strictly dry argon atmosphere using standard Schlenk line techniques and dry argon-filled glove boxes. All solvents were dried using an MBraun solvent purification system. Fluorobenzene was dried by passing through a column filled with well dried neutral Al_2O_3. ^{1}H, ^{13}C and ^{31}P NMR spectra were measured on spectrometers (Bruker AV 300 (300 MHz), Bruker DRX 400 (400 MHz) devices). The chemical shifts are given in parts per million (δ; ppm) relative to residual solvent peaks (δ; 7.15 (C_6D_6), 1.96 (CD_3CN), 5.34 (CD_2Cl_2), 7.24 ($CDCl_3$), 3.58 (THF-d_8) ppm),[1] Coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as s (singlet), d (doublet), t (triplet), m (multiplet), sept (septet) and br (broad). All the spectra were measured at room temperature unless otherwise stated. Mass spectra were recorded on Finnigan MAT 95 (EI) and Finnigan MAT 95 XL (ESI) systems. Elemental analyses were carried out on a Vario Micro Cube System. The starting materials Phenofluor27, $As(SiMe_3)_3$, [2] [IPrH]Cl[3], [IMesH]Cl[3], [IAr*H]Cl[3], [IMesCl]Cl (1,3-bis(2,4,6-trimethylphenyl)-2-chloroimidazolium chloride) [4] were prepared according to the literature procedures.

1.1.Synthesis of the compounds reported

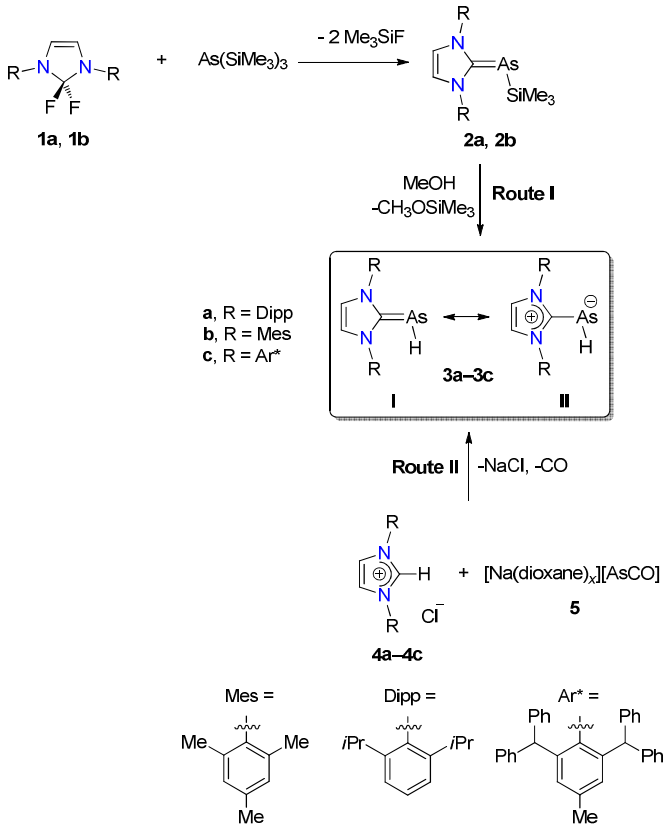
1.1.1 Synthesis of (1,3-Bis(2,4,6-trimethylphenyl)-2,2-difluoroimidazoline) (IMes)F_2 (1b)





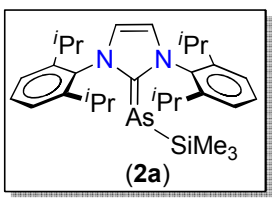
Commercially available Caesium fluoride (CsF) was dried at 170 °C for 15 h and was finely ground prior to use. [IMesCl]Cl was finely ground using a mortar and dried under vacuum at 70 °C for 5 h. To a Schlenk tube containing [IMesCl]Cl (4.46 g, 11.81 mmol) and CsF (17.94 g, 118.19 mmol) was added toluene (200 mL). The Schlenk tube was sonicated for 30 min, and then stirred vigorously at 100 °C for 4 days. Formation of a brown solution was observed during the reaction. The reaction mixture was brought to room temperature, filtered through a pad of Celite and the residue washed with toluene (10 mL × 5). The filtrate was concentrated

and dried under vacuum, washed with cold *n*-hexane followed by CH_3CN (–10 °C) and dried under vacuum to afford **1b** as a pale brown solid. Yield: 3.23 g (80 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 6.75–6.74 (m, 4H, *m*-Ar-H), 5.45 (t, 2H, $^3J_{(H,F)}$ = 1.54 Hz, NC*H*), 2.42 (s, 12H, *p*-CH_3), 2.08 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz); δ = 140.2 (N-*C*(Mes)), 138.6 (*o*-*C*(Mes)), 132.8 (*p*-*C*(Mes)), 129.9 (*m*-*C*(Mes)), 127.4 (t, $^1J_{(C,F)}$= 233.4 Hz, CF_2), 111.8 (N*C*H), 21.3 (*p*-*C*H_3), 18.9 (t, $J_{(C,F)}$ =2.9 Hz, *o*-*C*H_3) ppm. ^{19}F NMR (C_6D_6, 282.5 Hz): δ = –34.8 ppm. Anal. calcd (%) for $C_{21}H_{24}N_2F_2$ (342.425 g/mol): C 73.66, H 7.06, and N 8.18; Found: C 73.39, H 6.97 and N 8.39. HRMS-ESI (*m/z*, CH_3OH) calcd for $C_{21}H_{24}N_2F$ $[M–F]^+$, 323.19180; found, 323.19229. EI-MS (m/z): 342.2 $[M]^{+\cdot}$ (calcd 342.190 g/mol) (60 %), 303.2 $[M–2F]^{+\cdot}$ (30 %).



Scheme S1: Synthesis of carbene-parent arsinidene adducts.

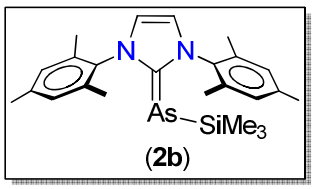
1.1.2. Synthesis of [(IPr)AsSiMe$_3$] (2a)



To a Schlenk tube containing (IPr)F_2 (0.300 g, 0.704 mmol) in fluorobenzene (10 mL) was added As(SiMe$_3$)$_3$ (0.210 g, 0.713 mmol) in dropwise manner at room temperature. The resulting dark orange reaction mixture was stirred at room temperature for two

days. The black precipitate formed was filtered off and the solvent removed under reduced pressure. The brown oily mass obtained was triturated with *n*-pentane until it became a yellow solid and then washed with cold (– 90 °C) *n*-pentane (1 mL × 3). This solid was then extracted with *n*-pentane and the solvent removed under reduced pressure affording 2a as yellow solid. Yield: 0.201 g (52 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 7.29–7.15 (6H, Ar–*H*), 6.31 (s, 2H, NC*H*), 3.07 (sept, 4H, $^{3}J_{(H,H)}$ = 6.6 Hz, C*H*(CH_3)$_2$), 1.48 (d, $^{3}J_{(H,H)}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.09 (d, $^{3}J_{(H,H)}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 0.11 (s, 9H, As-SiMe$_3$) ppm. ^{13}C NMR (C_6D_6, 75.4 MHz): δ = 176.8 (N*C*N), 147.1 (N*C*(Dipp)), 136.3 (*o*-*C*(Dipp)), 130.6 (*p*-*C*(Dipp)), 125.4 (*m*-*C*(Dipp)), 122.4 (N*C*H), 29.5 (*C*H(C*H*$_3$)$_2$), 25.3 (CH(C*H*$_3$)$_2$), 23.9 (CH(C*H*$_3$)$_2$), 5.42 (As–SiMe$_3$) ppm. Anal. Calcd (%) for $C_{30}H_{45}AsN_2Si$ (536.257 g/mol): C 67.14, H 8.45 and N 5.22; Found: C 68.09, H 7.59 and N 5.41. EI-MS (*m/z*): 536.2 (calcd 536.257 g/mol) $[M]^{+\cdot}$ (75 %), 521.2 [M–CH_3] (8 %), 493.2 [M–^{i}Pr] (100 %), 463.2 [M–$SiMe_3$] (25 %) and 387.3 [M–As($SiMe_3$)] (40 %).

1.1.3. Synthesis of [(IMes)AsSiMe$_3$] (2b)



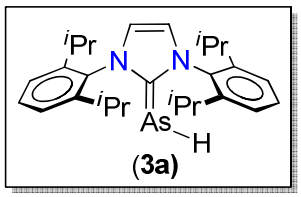
(**2b**)

To a stirred solution of (IMes)F_2 (0.536 g, 1.566 mmol) in fluorobenzene (20 mL), was added As($SiMe_3$)$_3$ (0.461 g, 1.566 mmol) in a drop wise manner. The resulting clear red reaction mixture was stirred for 3.5 h at room temperature. The black precipitate formed was filtered off, and volatiles were then removed *in vacuo*. The residue obtained was quickly washed with *n*-pentane (2 mL × 4) and dried under vacuum to obtain compound **2b** as a pale yellow-brown solid. Yield; 0.401 g (56 % based on (IMes)F_2). ^{1}H NMR (C_6D_6, 300.13 MHz): δ = 6.76 (br, 4H, *m*-Ar-H), 5.89 (s, 2H, NC*H*), 2.19 (s, 12H, *o*-C*H*$_3$), 2.09 (6H, *p*-CH_3), 0.15 (s, As–SiMe$_3$) ppm. ^{13}C {^{1}H} NMR (C_6D_6, 75.47 MHz): δ = 173.6 (N*C*N), 140.3 (N-*C*(Mes)), 137.5 (*o*-*C*(Mes)), 136.8 (*p*-*C*(Mes)), 131.2 (*m*-*C*(Mes)), 121.5 (N*C*H), 22.4 (*p*-*C*H_3), 19.9 (*o*-*C*H_3), 6.3 (As-SiMe$_3$) ppm. ^{29}Si NMR (C_6D_6, 79.5 MHz): δ= – 5.25 (s) ppm. Anal. Calcd (%) for $C_{24}H_{33}N_2AsSi$ (452.593 g/mol): C 63.70, H 7.35, and N 6.19; Found: C 64.95, H 7.29 and N 6.50. EI-MS (*m/z*): 452.1 (calcd 452.162 g/mol) $[M]^{+\cdot}$ (10 %), 437.1 $[M–CH_3]^{+\cdot}$ (4 %), 379.1 $[M–SiMe_3]^{+\cdot}$ (5 %), 303.2 [M–As($SiMe_3$)]$^{+\cdot}$(100 %). *Note:* The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. The solid can be stored at low-temperatures, but slowly decomposes even under inert conditions to a black solid when stored for hours at room temperature. Furthermore, over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid.

1.1.4. Synthesis of [Na(dioxane)$_x$][AsCO][5]

Sodium (6.900 g, 300 mmol; in small pieces), arsenic (7.500 g, 100 mmol; powder), and naphthalene (250 mg, 1.95 mmol) were combined in a Schlenk flask. Then, 200 ml of dimethoxyethane (DME) were added, immediately forming a green solution. The mixture was stirred with a glass-covered stirrer bar at 70 °C for three days, forming a dark greenish solution and black microcrystalline precipitate. To the suspension, *tert*-butanol (14.820 g, 200 mmol) was added via syringe. The suspension was stirred for six hours. When all solid had dissolved, the solution had turned greenish-yellow. Diethylcarbonate (11.810 g, 100 mmol) was added via syringe and the suspension was stirred overnight. The initially greenish-yellow suspension turned orange-yellow during this process. All volatiles were removed *in vacuo* at ambient temperature. To the pale yellowish residue 300 ml of THF were added, resulting in the formation of a dark yellow suspension. After vigorous stirring for 1 hour, the mixture was left to settle overnight. The mixture was filtered over a Celite-padded sinter, affording a clear yellow solution, which was then concentrated to approximately half of the original volume. Then an approximate four-fold amount of 1,4-dioxane was added to precipitate the crude product. The solution was filtered off and the yellow solid was redissolved in THF. After filtration, the solution was concentrated and an approximate four-fold amount of 1,4-dioxane was added to precipitate the product. Drying of the bulk sample at ambient temperature under vacuum for an hour afforded an off-white solid (3.31 molecules of dioxane per Na(AsCO) 23.520 g, 56.3 mmol, 56%). The dioxane content was determined via ^{1}H NMR of a sample dissolved in THF-d_8 vs cyclohexane as internal standard. The product, [Na(dioxane)$_{3.31}$][AsCO], is not stable for prolonged storage at ambient temperature in a brown-glass bottle under an argon atmosphere, in coincidence with solvent loss. Also, thorough drying *in vacuo* causes off-white [Na(dioxane)$_{3.31}$][AsCO] to decompose to a black solid. Thus, storage in a freezer is recommended. Anal. Calcd (%) for $C_{14.24}H_{26.48}O_{7.62}NaAs$: C 40.96, H 6.39, N 0.00; no satisfactory analysis could be obtained. ^{1}H NMR (400 MHz, THF-d_8): δ = 3.56 (s, dioxane) ppm. ^{13}C {^{1}H} NMR (100.6 MHz, THF-d_8): δ = 67.63 (s, dioxane), 178.38 (s, As*C*O) ppm. IR (nujol mull, cm^{-1}): 1748 (CO)).

1.1.5. Synthesis of [(IPr)AsH] (3a)

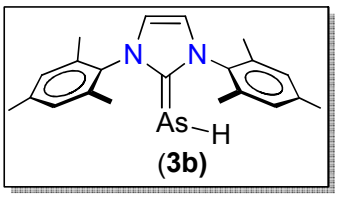


(3a)

Route-I: To a Schlenk tube containing [(IPr)AsSiMe$_3$] (0.050 g, 0.093 mmol) in toluene (5 mL) was added CH_3OH (0.4 mL) at room temperature. The resulting reaction mixture was stirred for 1 h at the same temperature. All the volatiles were removed under reduced pressure, washed the residue with cold (–80° C) *n*-pentane (1 mL × 3) and dried under vacuum affording **3a** as pale yellow solid. Yield: 0.025 g (58 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 7.27–7.19 (m, 4H, Ar-H), 7.13 (m, 2H, Ar-H), 6.31 (s, 2H, NC*H*), 3.01 (sept, 4H, $^3J_{(H,H)}$ = 7.0 Hz, C*H*(CH$_3$)$_2$), 1.49 (d, 12H, $^3J_{(H,H)}$ = 6.8 Hz, CH(C*H*$_3$)$_2$), 1.43 (s, 1H, As-*H*), 1.14 (d, 12H, $^3J_{(H,H)}$ = 6.9 Hz, CH(C*H*$_3$)$_2$) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 184.5 (N*C*N), 147.5 (N*C*(Dipp)), 135.5 (*o*-*C*(Dipp)), 130.6 (*p*-*C*(Dipp)), 125.3 (*m*-*C*(Dipp)), 121.1 (N*C*H), 29.4 (*C*H(CH$_3$)$_2$), 24.9 (CH(C*H*$_3$)$_2$), 24.3 (CH(C*H*$_3$)$_2$) ppm. EI-MS (*m/z*): 464.2 (calcd 464.217 g/mol) $[M]^{+\cdot}$ (100 %), 421.1 [M–^{i}Pr] (55 %), 387.3 [M–AsH] (90 %).

Route-II: The reaction procedure was carried out under rigorous exclusion of light: 0.110 g (0.24 mmol, 1 eq.) of [IPr-H][Cl] and 0.150 g (0.36 mmol, 1.5 eq.) of [Na(dioxane)$_{3.31}$][AsCO] were suspended in ca. 10 mL THF. The grey suspension was stirred at room temperature overnight. After removal of the solvent *in vacuo* the brownish solid was suspended in hexane and filtered over Celite. The volume of the obtained yellow solution was reduced to 3 mL and stored at –30 °C. After 2 days, the product was isolated as yellow crystalline solid. Yield: 14 mg (13 %). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I. Anal. Calcd (%) for $C_{27}H_{37}N_2As$ (464.217 g/mol): C 69.81, H 8.03 and N 6.03; Found: C 68.49, H 7.73 and N 6.65. IR (nujol mull, cm^{-1}): 2080 (As–H).

1.1.6. Synthesis of [(IMes)AsH] (3b)



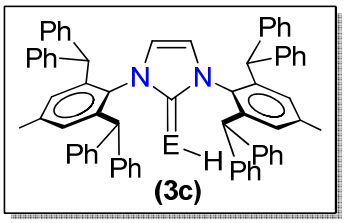
(3b)

***Route-I*:** To a stirred solution of [(IMes)AsSiMe$_3$] (0.230 g, 0.508 mmol) in toluene (15 mL), excess dry CH_3OH (0.652 mL, 20.349 mmol) was added at room temperature. The resulting solution was stirred for 5 h at 45 °C. All volatiles were then removed *in vacuo*, extracted with toluene and the solvent removed under vacuum. The residue obtained was quickly washed with *n*-pentane (1 mL × 7) and dried to afford compound **3b** as a pale yellow to white solid. Yield; 0.123 g (64 %). ^{1}H NMR (C_6D_6, 300.1 MHz): δ = 6.76–6.74 (m, 4H, *m*-Ar-*H*), 6.00 (d, 2H, $^5J_{(H,H)}$ = 0.45 Hz, NC*H*), 2.19 (s, 12H, *o*-C*H*$_3$), 2.07 (6H, *p*-C*H*$_3$), 1.47 (t, $^5J_{(H,H)}$ = 0.45 Hz, As–*H*) ppm. ^{13}C {^{1}H} NMR (C_6D_6, 75.47

MHz): δ = 179.4 (N*C*N), 139.3 (N-*C*(Mes)), 136.5 (*o*-*C*(Mes)), 135.4 (*p*-*C*(Mes)), 130.1 (*m*-*C*(Mes)), 119.5 (N*C*H), 21.4 (*p*-*C*H_3), 18.6 (*o*-*C*H_3) ppm. Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.123 g/mol): C 66.31, H 6.62 and N 7.37; Found: C 66.86, H 6.57 and N 7.59. EI-MS (*m/z*): 380.1 (calcd 380.1233) $[M]^{+\cdot}$ (60%), 365.1[M–CH_3] (8%), [M–AsH] (100 %). ***Note:*** The reaction was performed under the exclusion of light and the solid obtained was stored at –30 °C. Over a period of time, NMR samples in C_6D_6 always showed the formation of a black insoluble solid at room temperature.

***Route-II*:** A grey suspension of 0.200 g (0.59 mmol, 1 eq.) [(IMes)H][Cl] and 0.290 g (0.70 mmol, 1.2 eq.) [Na(dioxane)$_{3.31}$][AsCO] in 10 mL THF was stirred at room temperature for 2 h. After removal of the solvent *in vacuo*, the brownish solid was suspended in toluene and filtrated over Celite. The resulting yellow solution was concentrated to a volume of 5 mL and stored at –30 °C. After 2 days the yellow blocks formed were filtered and dried under vacuum to obtain **3b**. Yield: 30 mg (15%). The ^{1}H and ^{13}C NMR spectra are similar to the reported for route I. Anal. Calcd (%) for $C_{21}H_{25}N_2As$ (380.358 g/mol): C 66.31, H 6.62 and N 7.37; found: C 66.89, H 6.70 and N 7.38. IR (nujol mull, cm^{-1}): 2059 (As–H).

1.1.7. Synthesis of [(IAr*)AsH] (3c)



Route II: The reaction procedure was carried out under rigorous exclusion of light. A light brown suspension of 0.200 g (0.21 mmol, 1 eq.) [(IAr*)H]Cl and 0.110 g (0.27 mmol, 1.3 eq.) [Na(dioxane)$_{3.31}$][AsCO] in *ca*. 10 mL THF was stirred at room temperature overnight. After the removal of the solvent under vacuum, the brown solid was suspended in toluene and filtered over Celite. The volume of the brownish solution was reduced to 3 mL and stored at –30 °C. After 5 days, the product was obtained as light yellow crystalline solid. Yield: 18 mg (9 %). ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.85 (d, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *o*-CH_{Ph}), 7.20 (t, $^3J_{(H,H)}$ = 7.6 Hz, 8 H, *m*-CH_{Ph}),7.10 (s, 4 H, *p*-CH_{Ph}), 6.96 (s, 20 H, CH_{Ph}), 5.96 (s, 4 H, *m*-C*H*), 5.19 (s, 2 H, NC*H*), 2.26 (s, 1 H, As*H*), 1.72 (s, 6 H, CH_3), ppm. ^{13}C{^{1}H} NMR (C_6D_6, 100.6 MHz); δ = 180.9 (N*C*N), 143.6 (s, *C*), 144.4 (s, *C*), 143.0 (s, *C*), 140.2 (s, *C*), 134.7 (s, *C*), 131.1 (s, *C*H), 130.8 (s, *C*H), 130.0 (s, *C*H), 128.7 (s, *C*H), 128.4 (s, *C*H), 127.0 (s, *C*H), 126.5 (s, *C*H), 120.9 (s, *C*H), 52.3 (s, Ph_2*C*H), 21.4 (s, *C*H_3) ppm. Anal. Calcd (%) for $C_{69}H_{57}N_2As$ (988.373 g/mol): C 83.78, H 5.81 and N 2.83; Found: C 83.44, H 5.82 and N 2.89. IR (nujol mull, cm^{-1}): 2090 (As–H).

Note: The low yields for **3a-3c** by route-II are due to the fractional crystallization in order to obtain product free of carbene as the crude extract always contained 20–30 % of the respective free carbene.

2. NMR and other spectra of the reported compounds

2.1. [(IMes)Cl]Cl

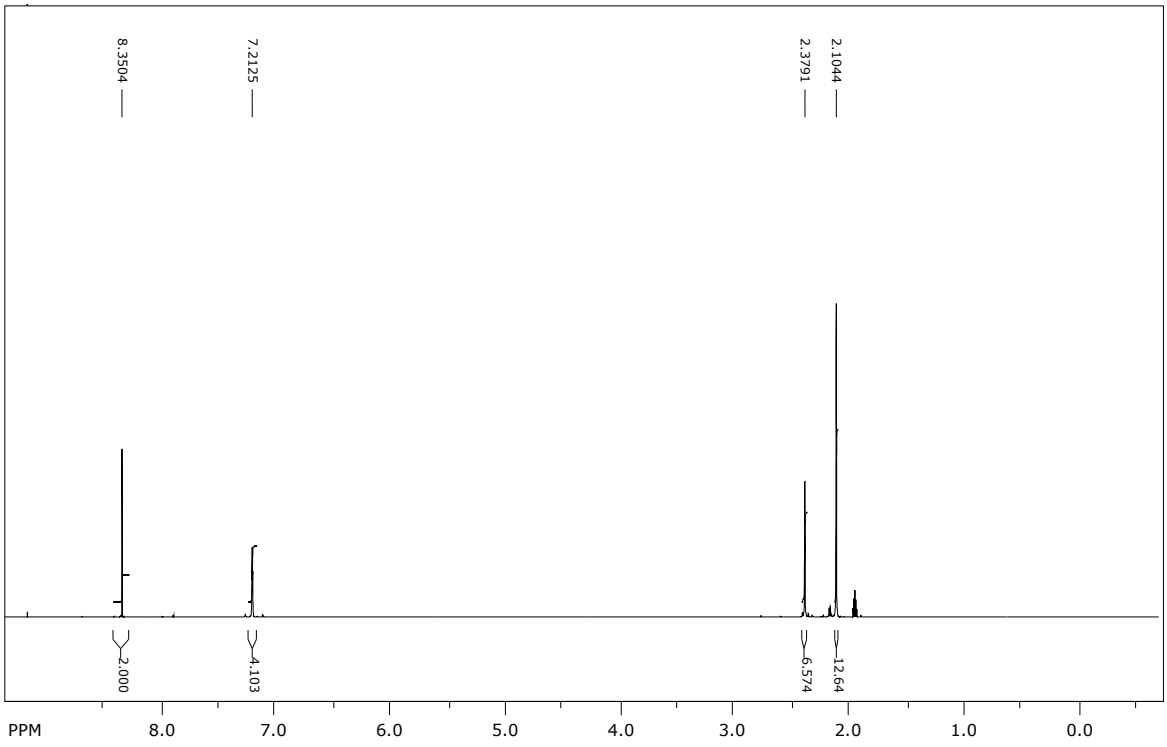


Figure S1. ^{1}H NMR spectrum of chloro-imidazolium chloride [(IMes)Cl]Cl in CD_3CN at room temperature.

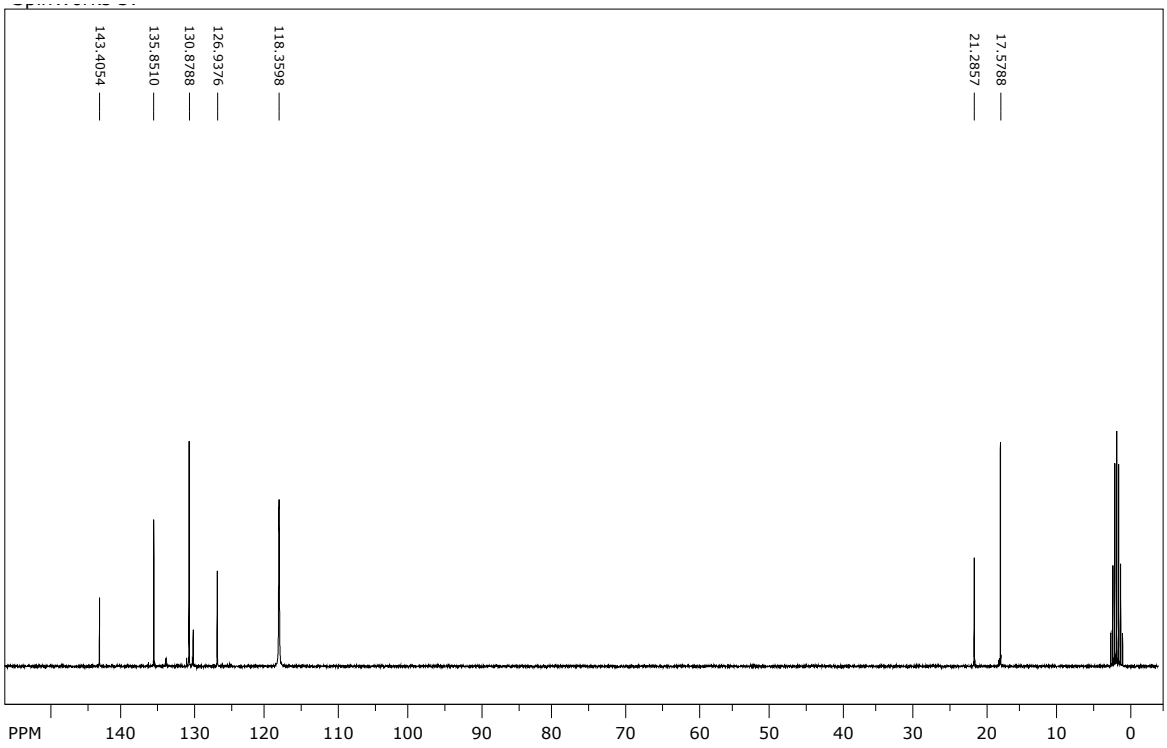


Figure S2. ^{13}C NMR spectrum of [(IMes)Cl]Cl in CD_3CN at room temperature.

2.2. [(IMes)F_2

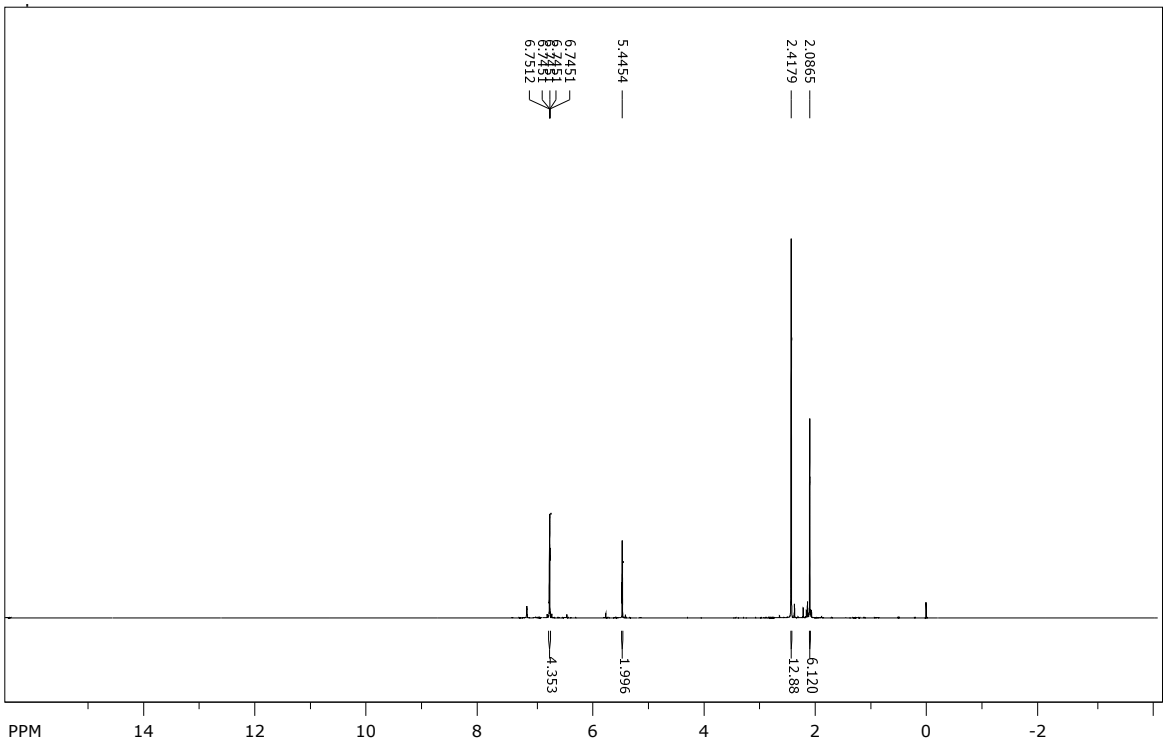


Figure S3. ^{1}H NMR spectrum of $(IMes)F_2$ (**1b**) in C_6D_6 at room temperature.

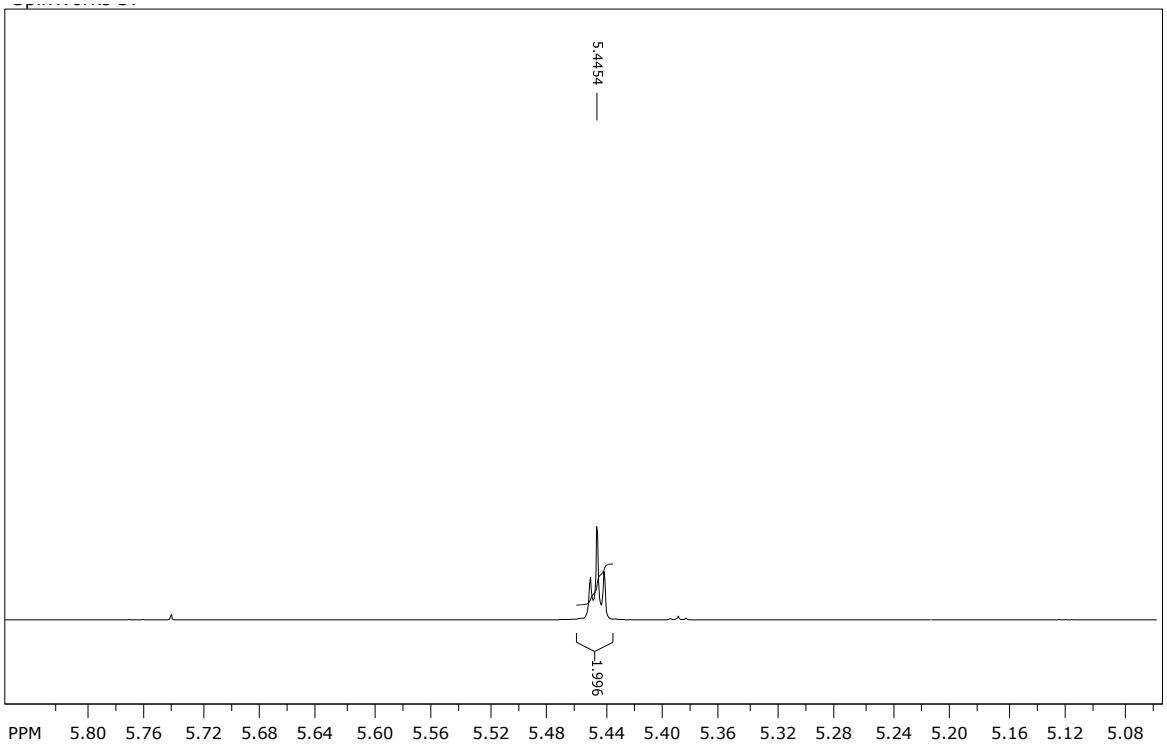


Figure S4. ^{1}H NMR spectrum (expanded) of (IMes)F_2 (**1a**) in C_6D_6 at room temperature.

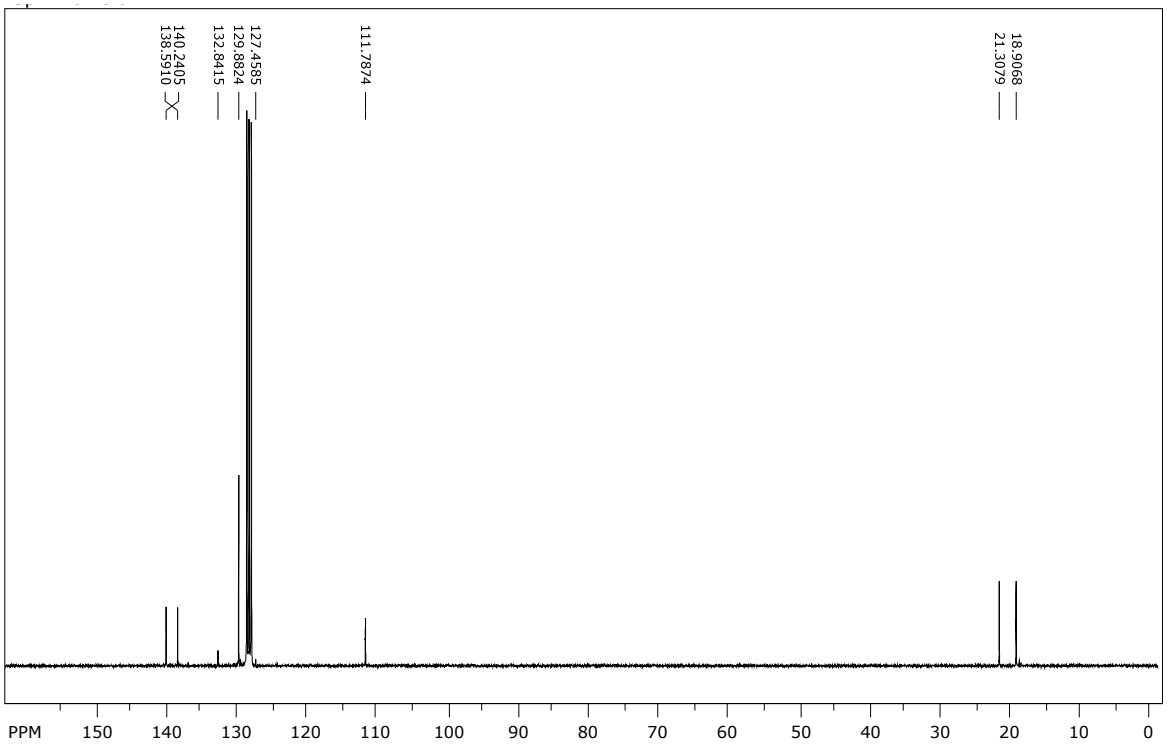


Figure S5. ^{13}C NMR spectrum of (IMes)F_2 (**1b**) at room temperature.

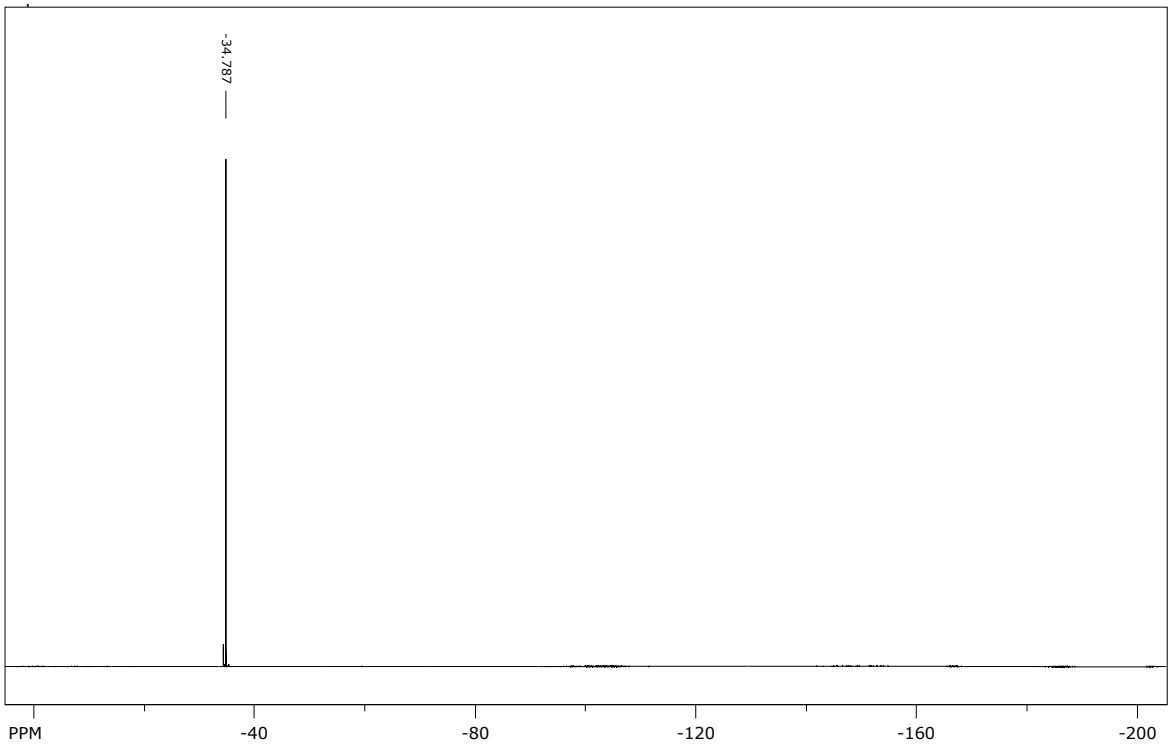


Figure S6. ^{19}F NMR spectrum of (IMes)F_2 (**1b**) at room temperature.

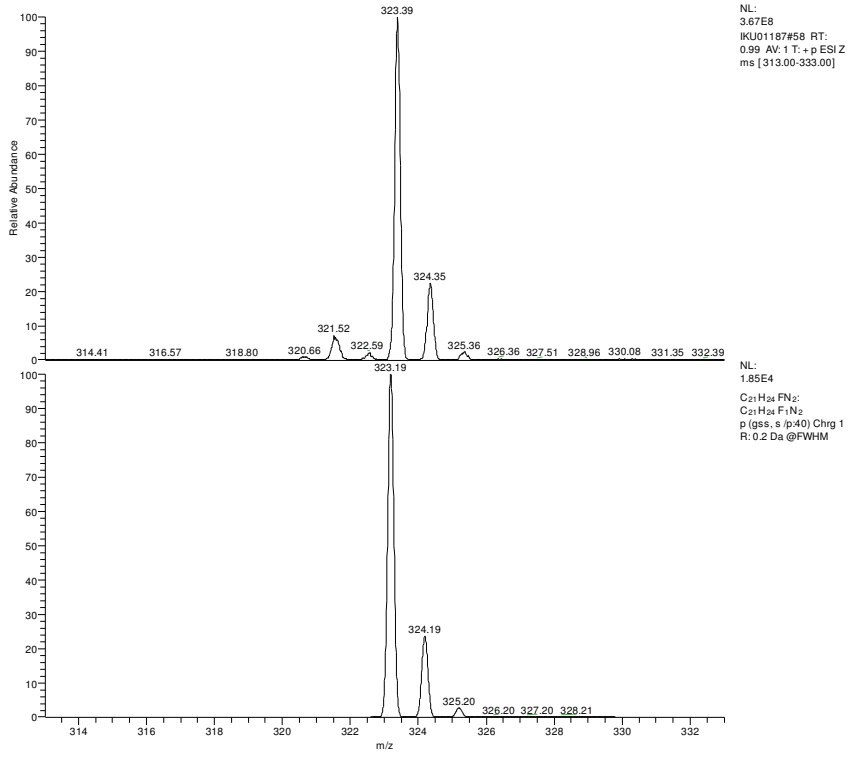


Figure S7. ESI-MS of (IMes)F_2 (in acetonitrile) (**1b**). Isotopic pattern of the experimental sample and calculated.

2.3. [(IPr)AsSi(CH$_3$)$_3$]

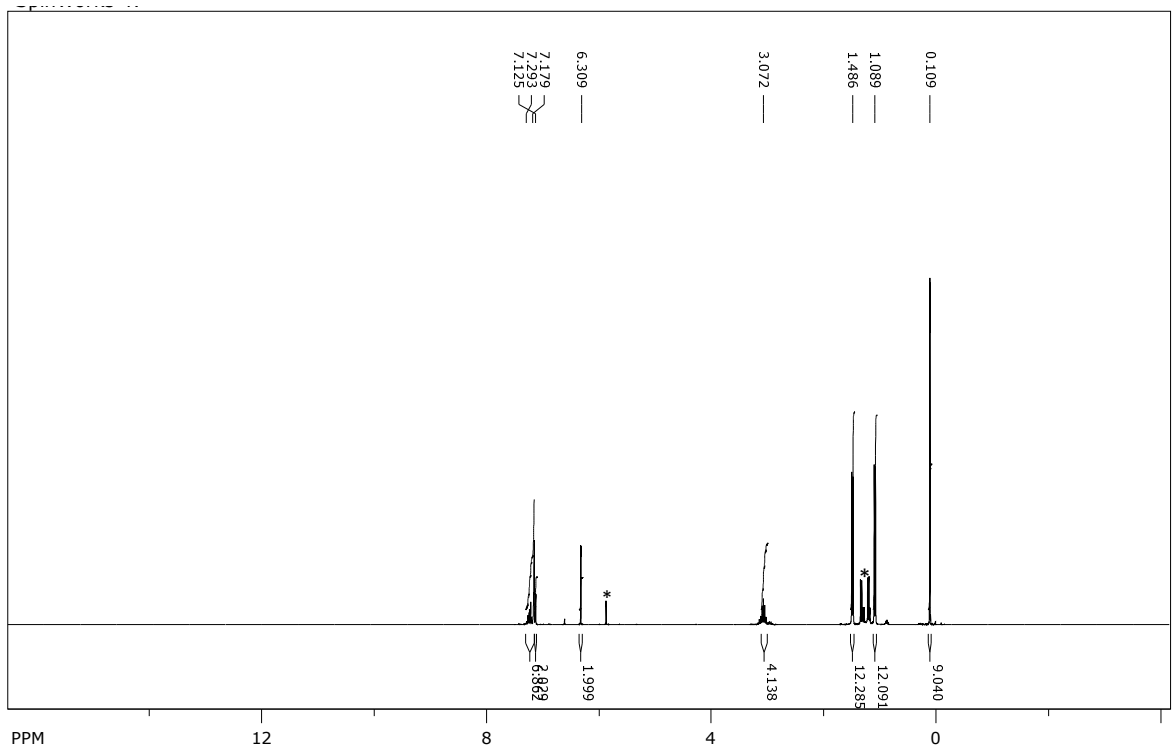


Figure S8. ^{1}H NMR spectrum of [(IPr)AsSi(CH$_3$)$_3$] (**2a**) in C_6D_6 (* Despite many attempts, other impurities could not be removed).

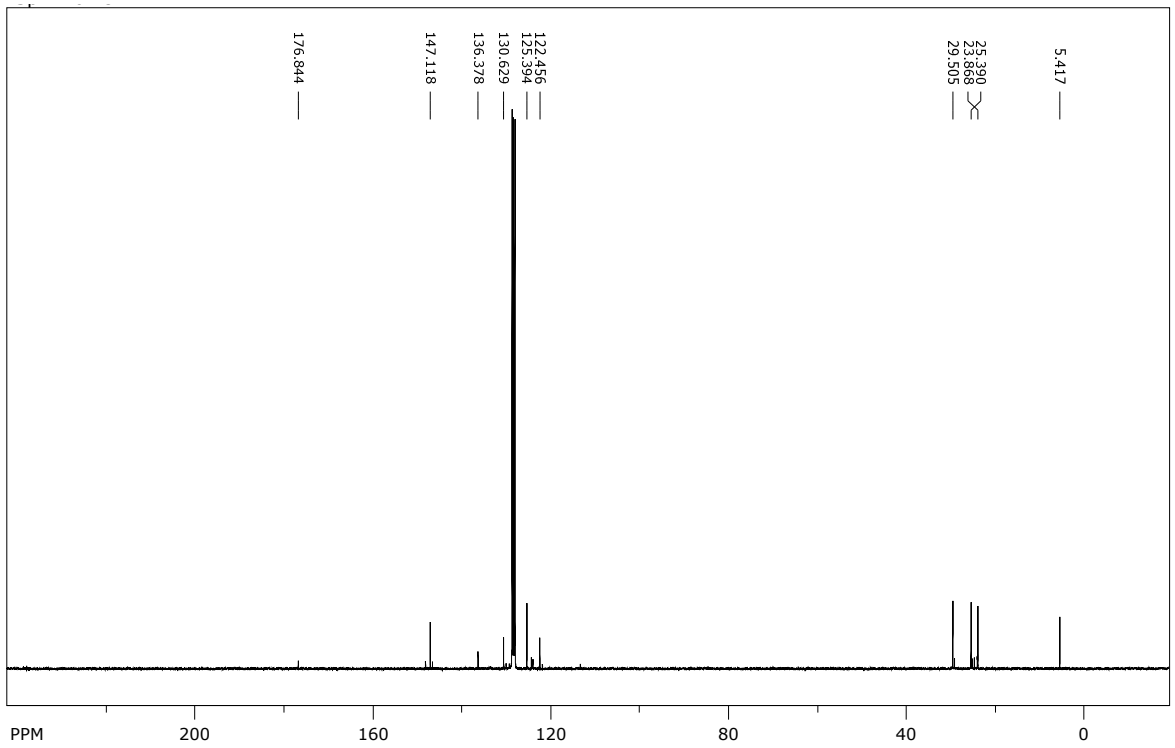


Figure S9. ^{13}C NMR spectrum of [(IPr)AsSi(CH$_3$)$_3$] (**2a**) in C_6D_6.

2.4. [(IMes)AsSi(CH$_3$)$_3$]

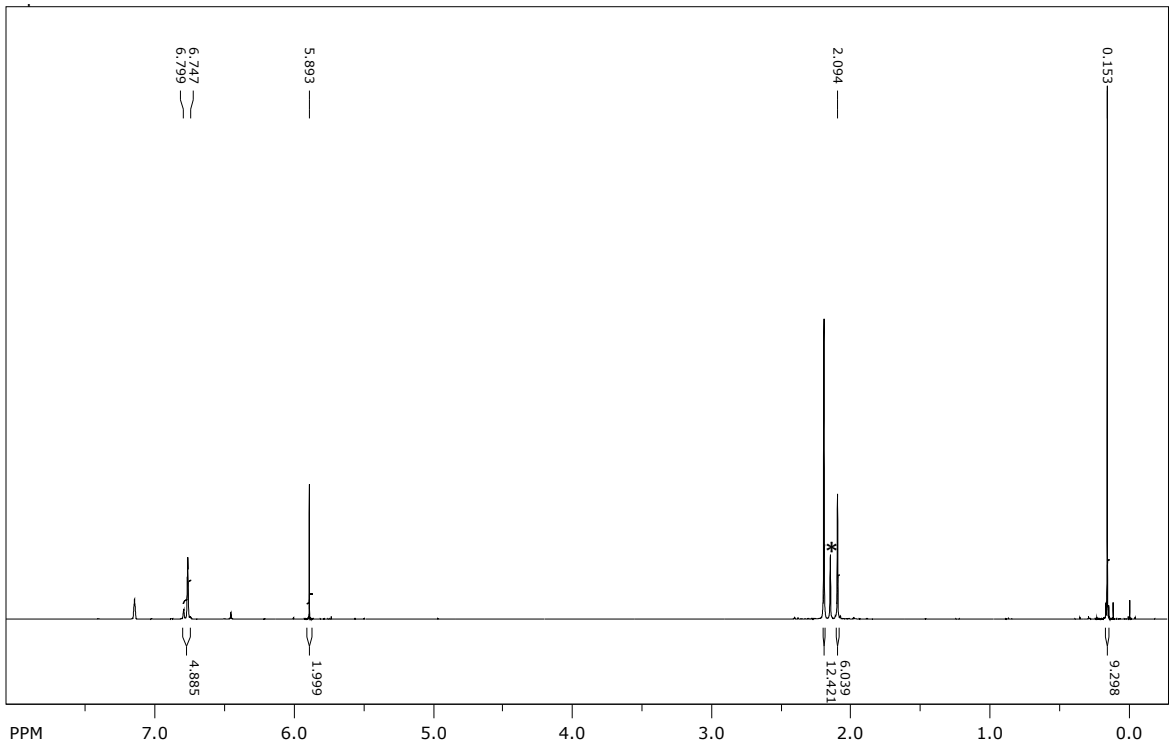


Figure S10. ^{1}H NMR spectrum of [(IMes)AsSi(CH$_3$)$_3$] (**2b**) in C_6D_6 at room temperature (*impurity).

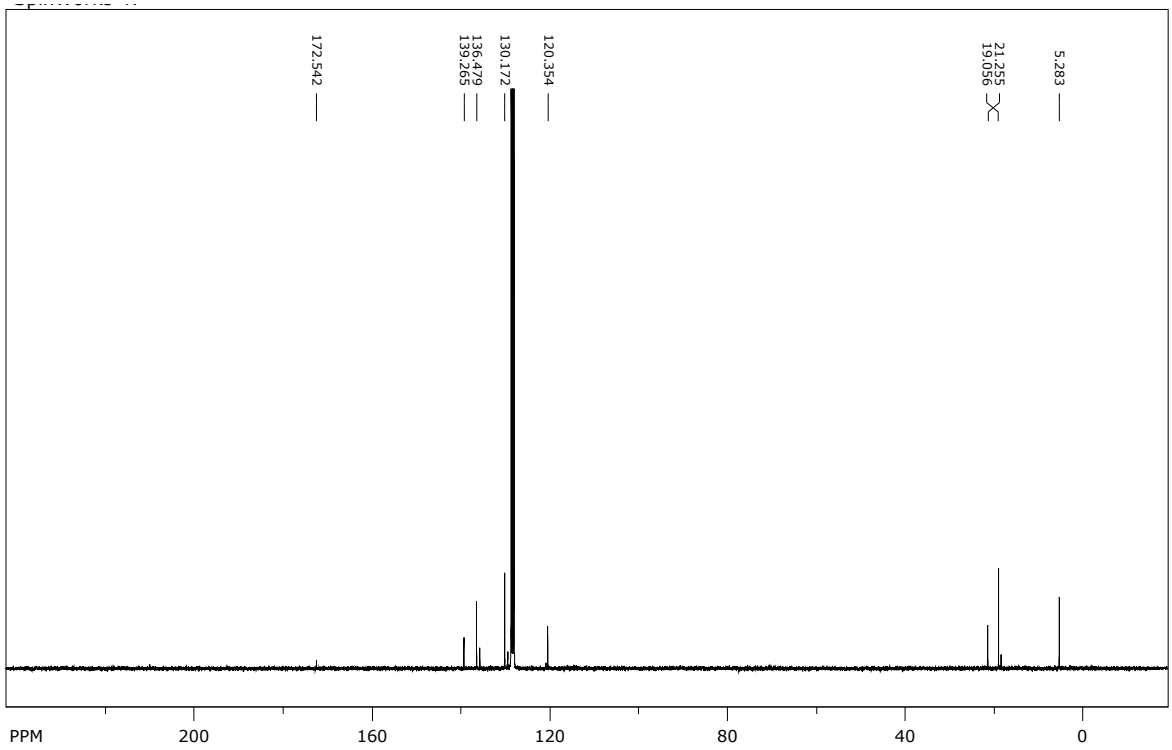


Figure S11. ^{13}C NMR spectrum of [(IMes)AsSi(CH$_3$)$_3$] (**2b**) in C_6D_6 at room temperature.

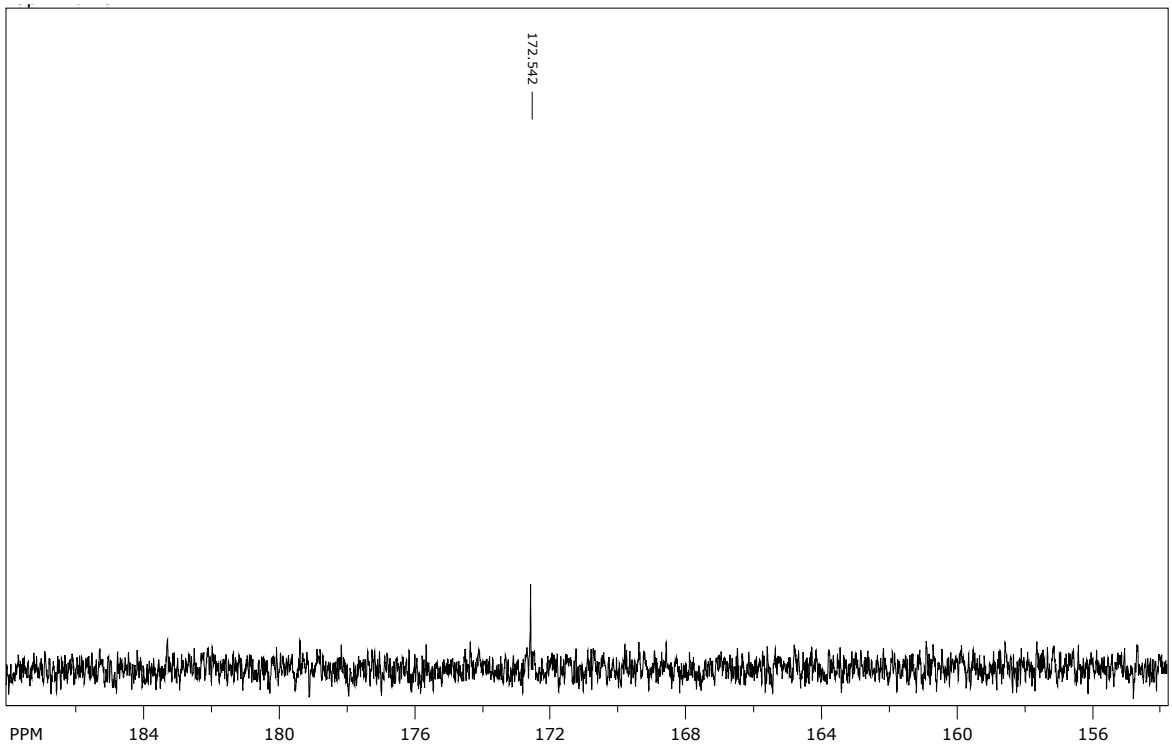


Figure S12. ^{13}C NMR spectrum of [(IMes)AsSi$(CH_3)_3$] (**2b**) in C_6D_6 (expanded).

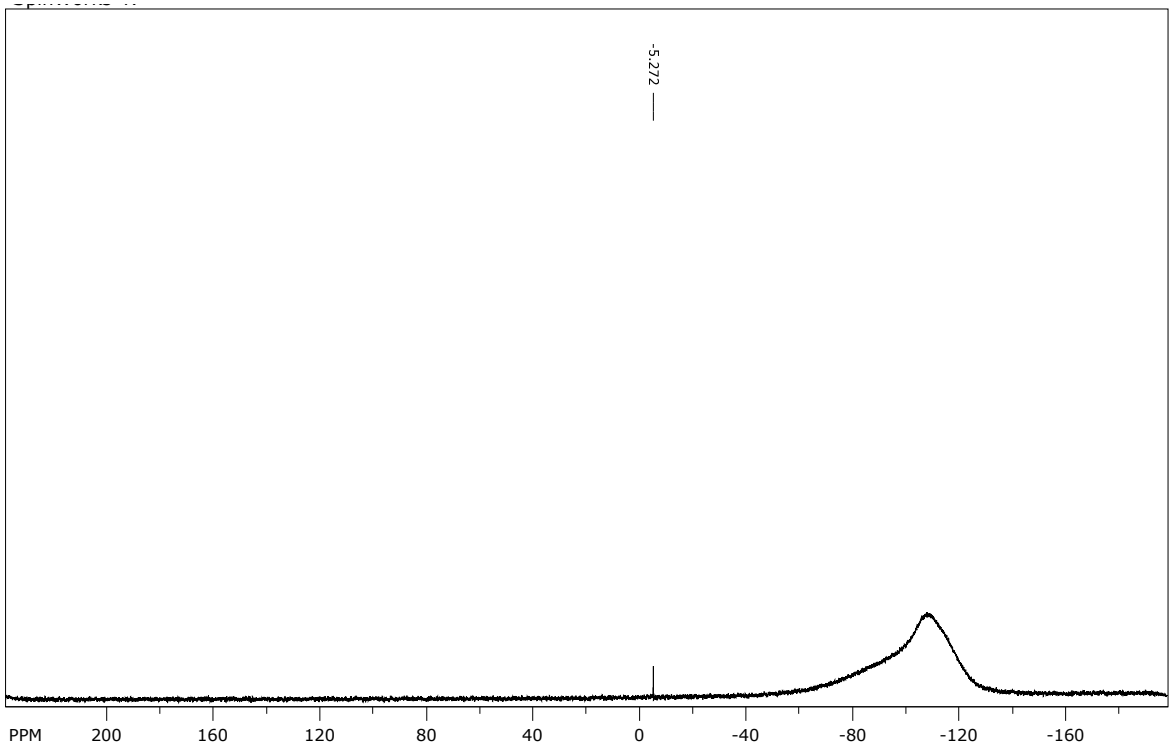


Figure S13. ^{29}Si NMR spectrum of [(IMes)AsSi$(CH_3)_3$] (**2b**) in C_6D_6 at room temperature.

2.5. [(IPr)AsH]

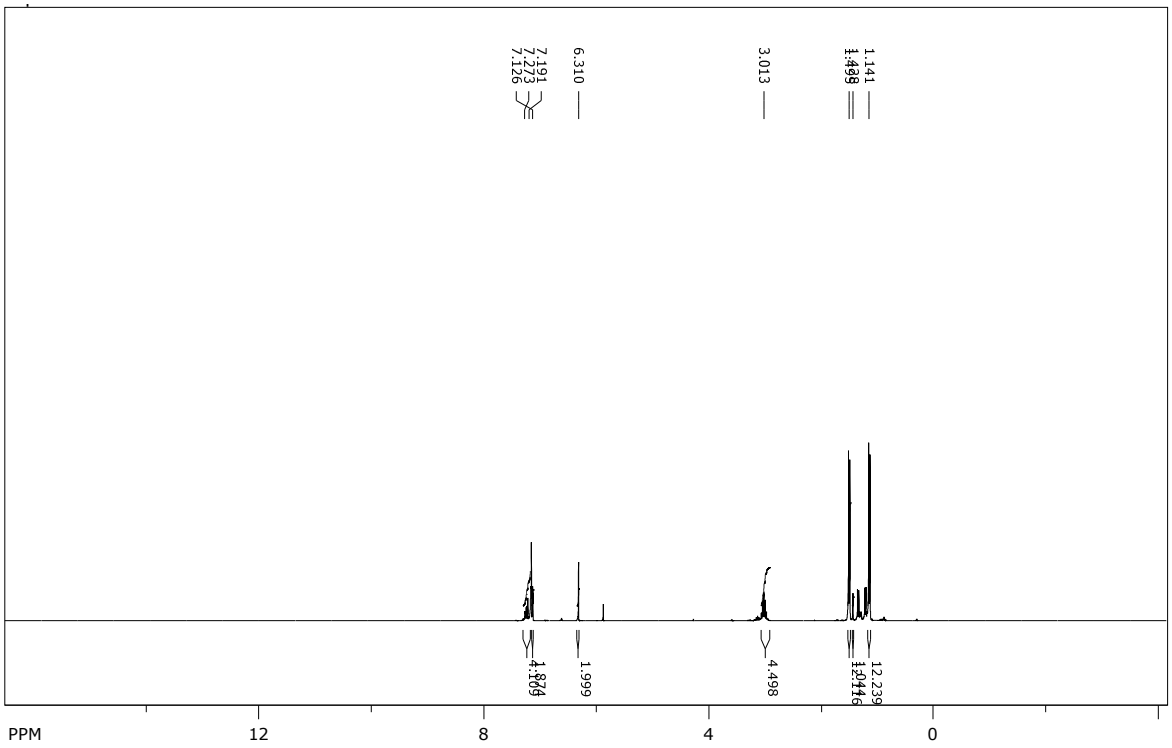


Figure S14. ^{1}H NMR spectrum of [(IPr)AsH] (**3a**) in C_6D_6 at RT route-I.

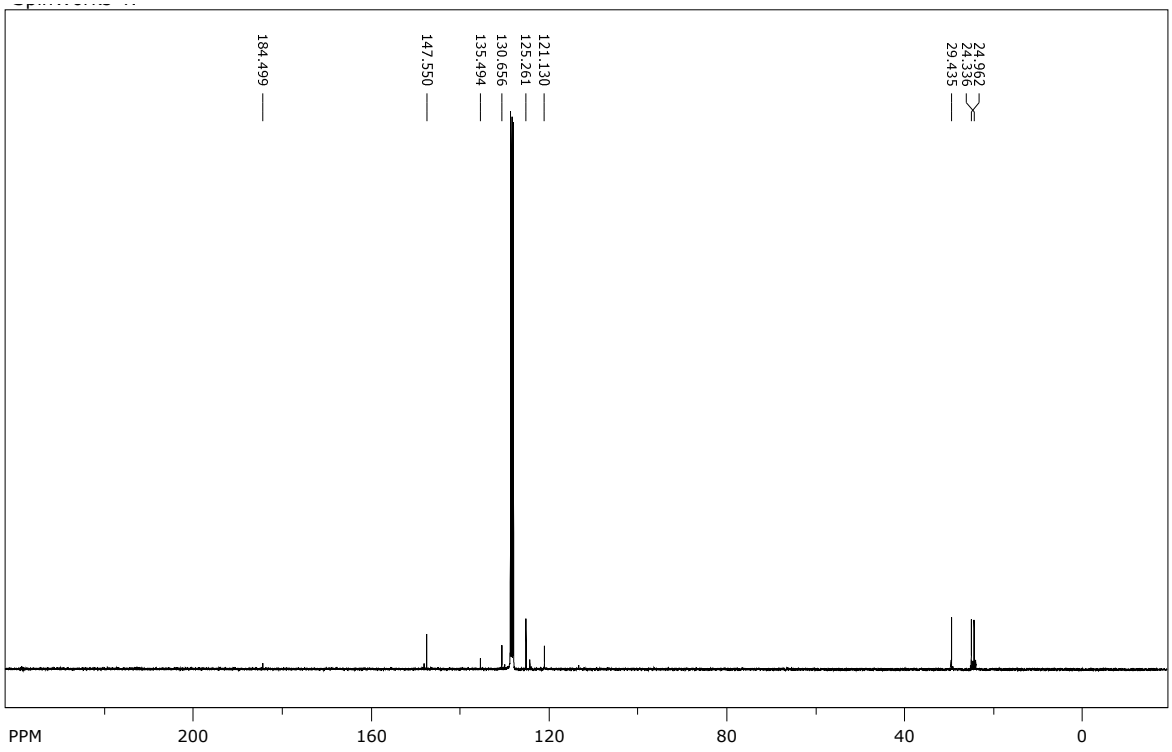


Figure S15. ^{13}C NMR spectrum of [(IPr)AsH] (**3a**) in C_6D_6 at RT route-I.

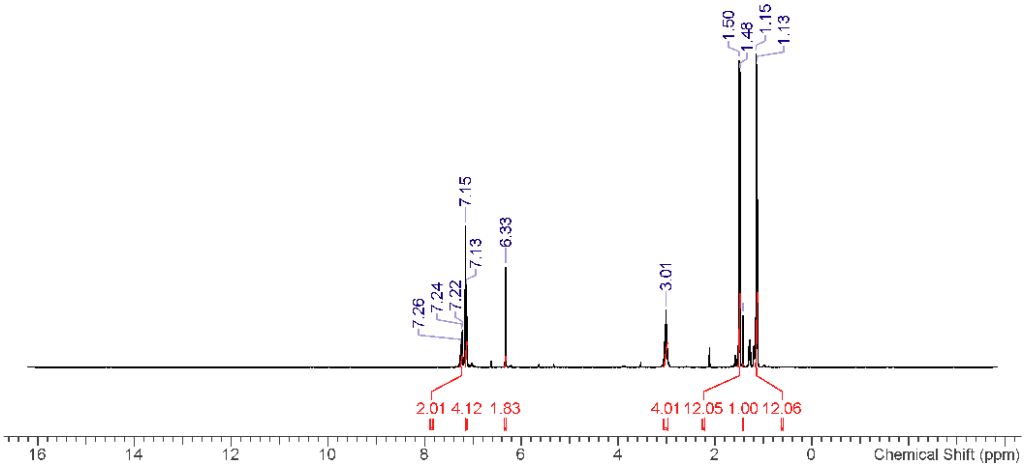


Figure S16. ^{1}H NMR spectrum of [(IPr)AsH] (**3a**) by route-II.

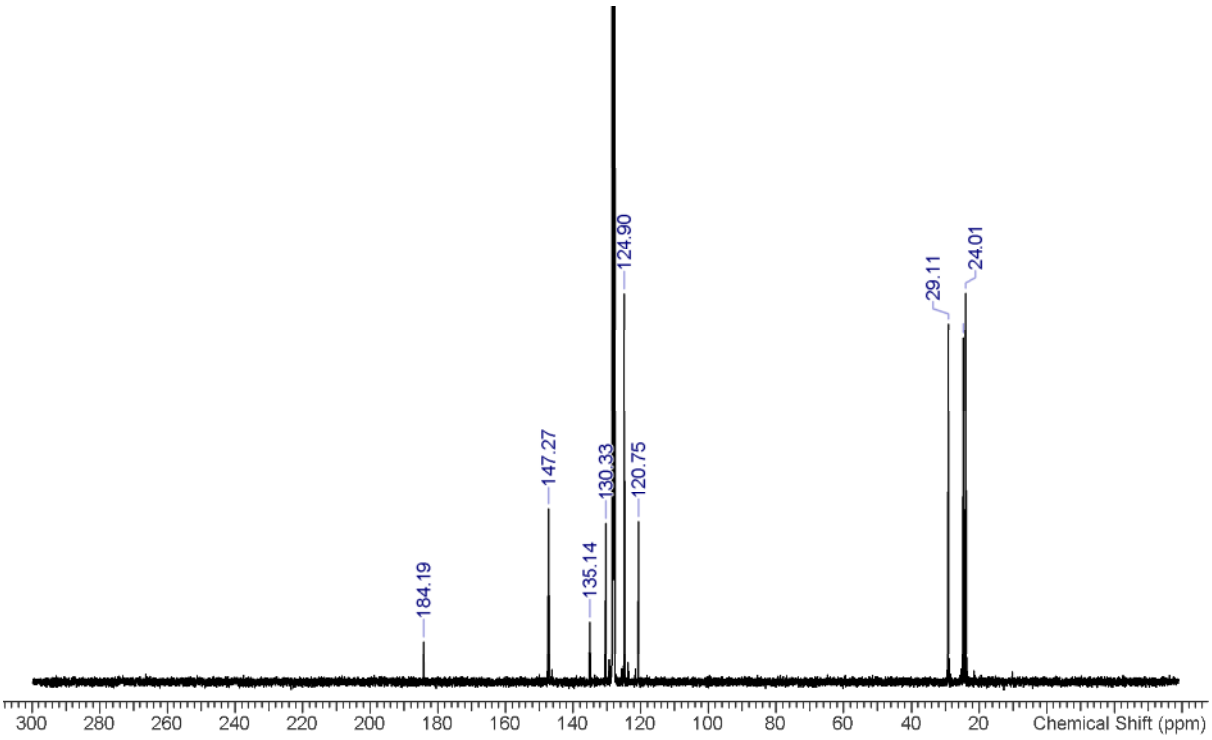


Figure S17. ^{13}C{^{1}H} NMR spectrum of [(IPr)AsH] (**3a**) by route-II.

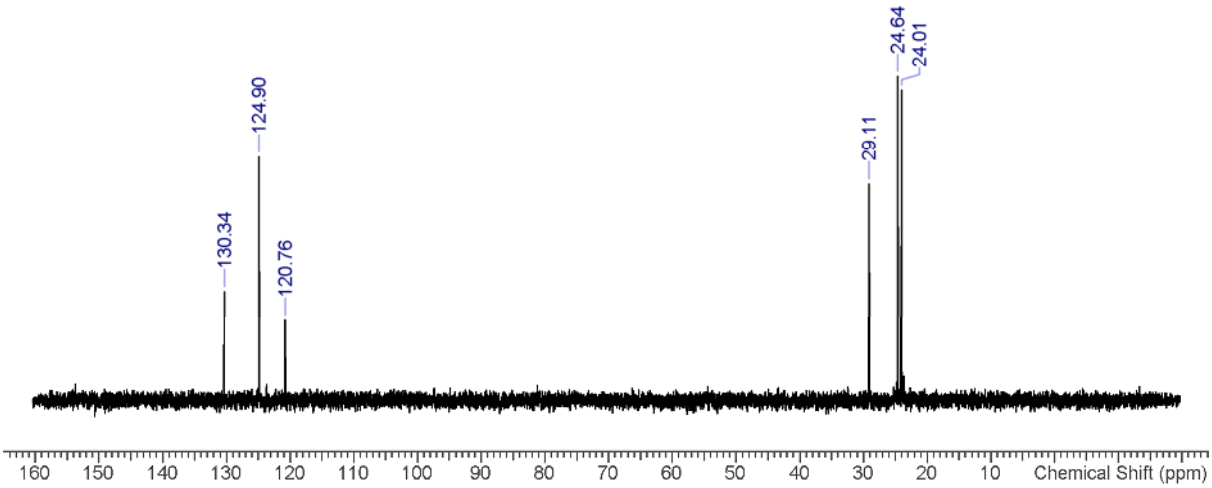


Figure S18. ^{13}C DEPT NMR spectrum of [(IPr)AsH] (**3a**) by route-II.

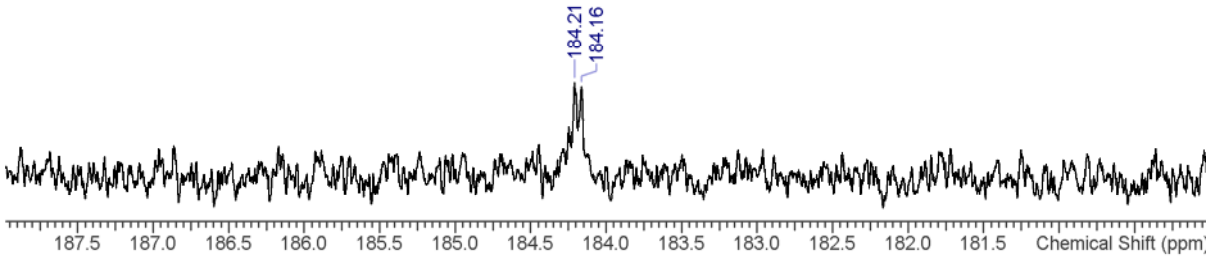


Figure S19. ^{13}C NMR spectrum of [(IPr)AsH] (**3a**) by route-II.

2.6. [(IMes)AsH]

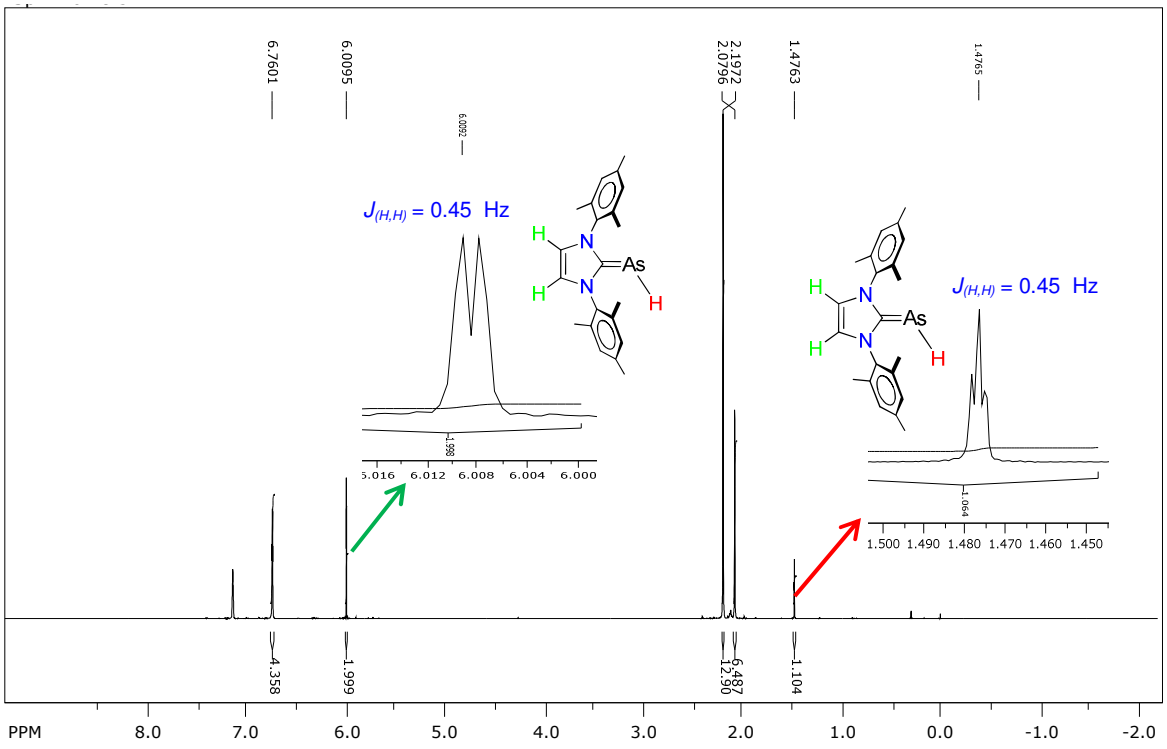


Figure S20. ^{1}H NMR spectrum of [(IMes)AsH] (**3b**) in C_6D_6 at RT route-1.

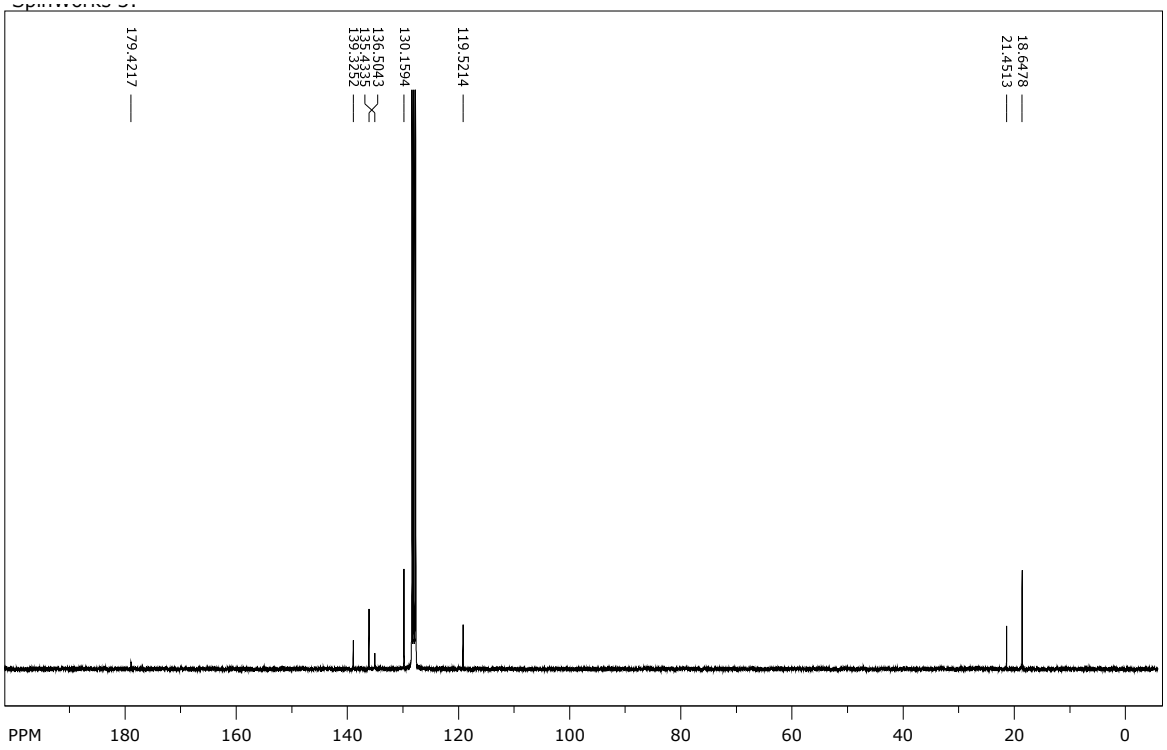


Figure S21. ^{13}C NMR spectrum of [(IMes)AsH] (**3b**) in C_6D_6 at RT.

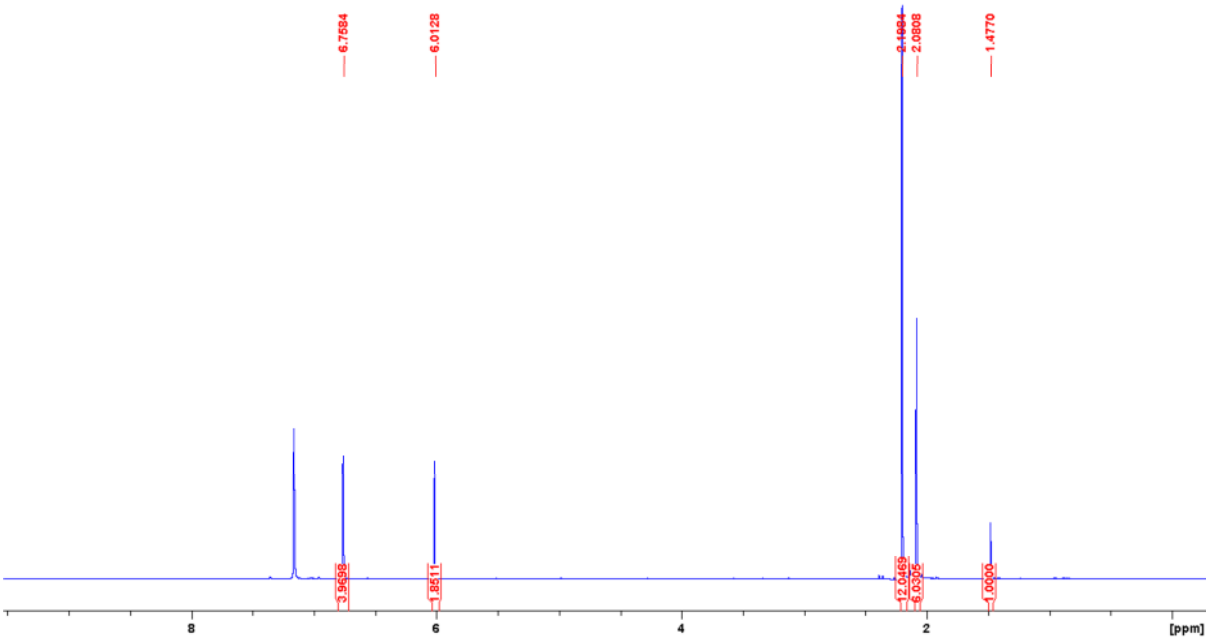


Figure S22. ^{1}H NMR spectrum of [(IMes)AsH] (**3b**) by route-II**.**

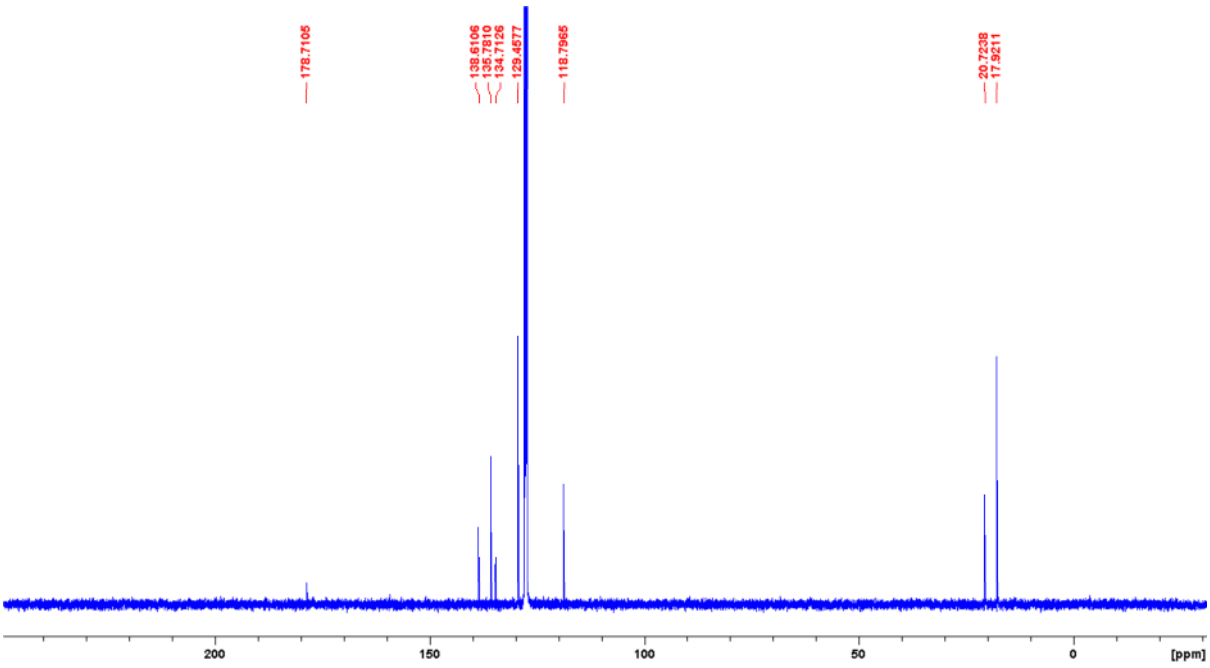


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of [(IMes)AsH] (**3b**) by route-II**.**

.

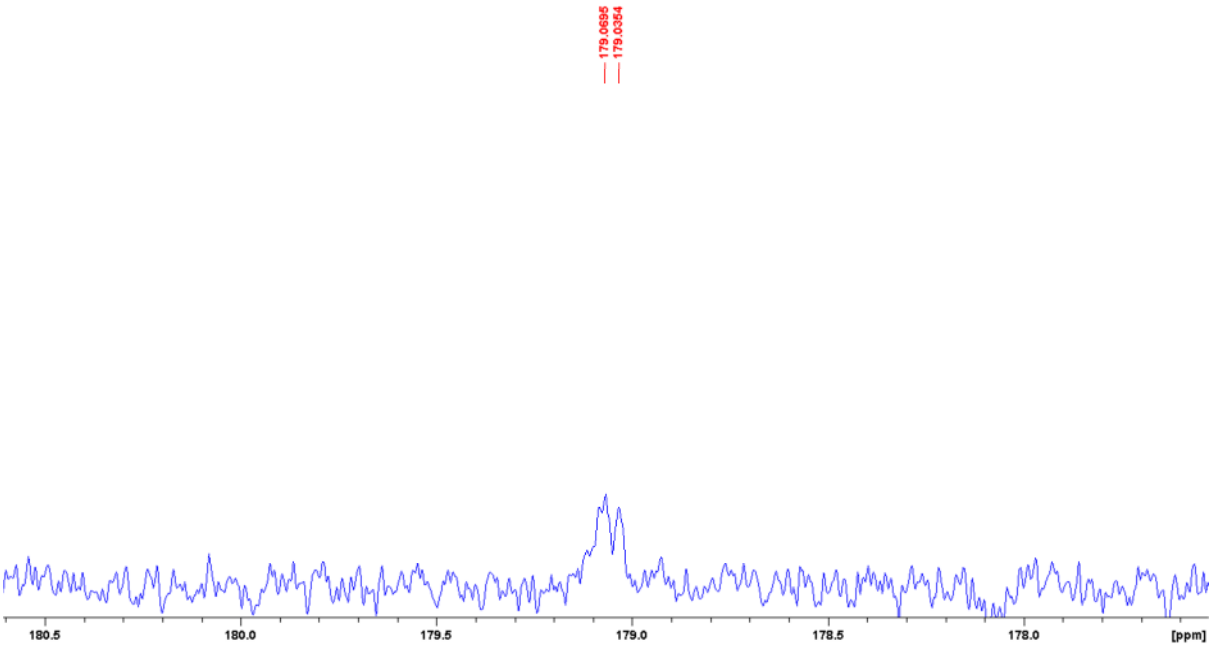


Figure S24. ^{13}C NMR spectrum of [(IMes)AsH] (**3b**) by route-II.

2.7. [(IAr*)AsH]

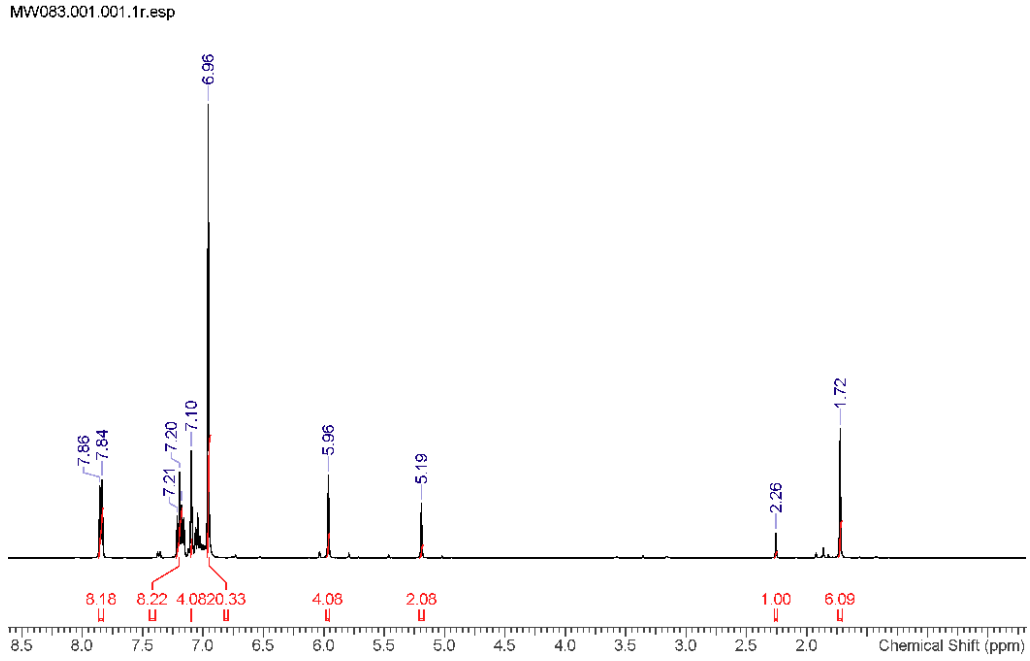


Figure S25. ^{1}H NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6 .

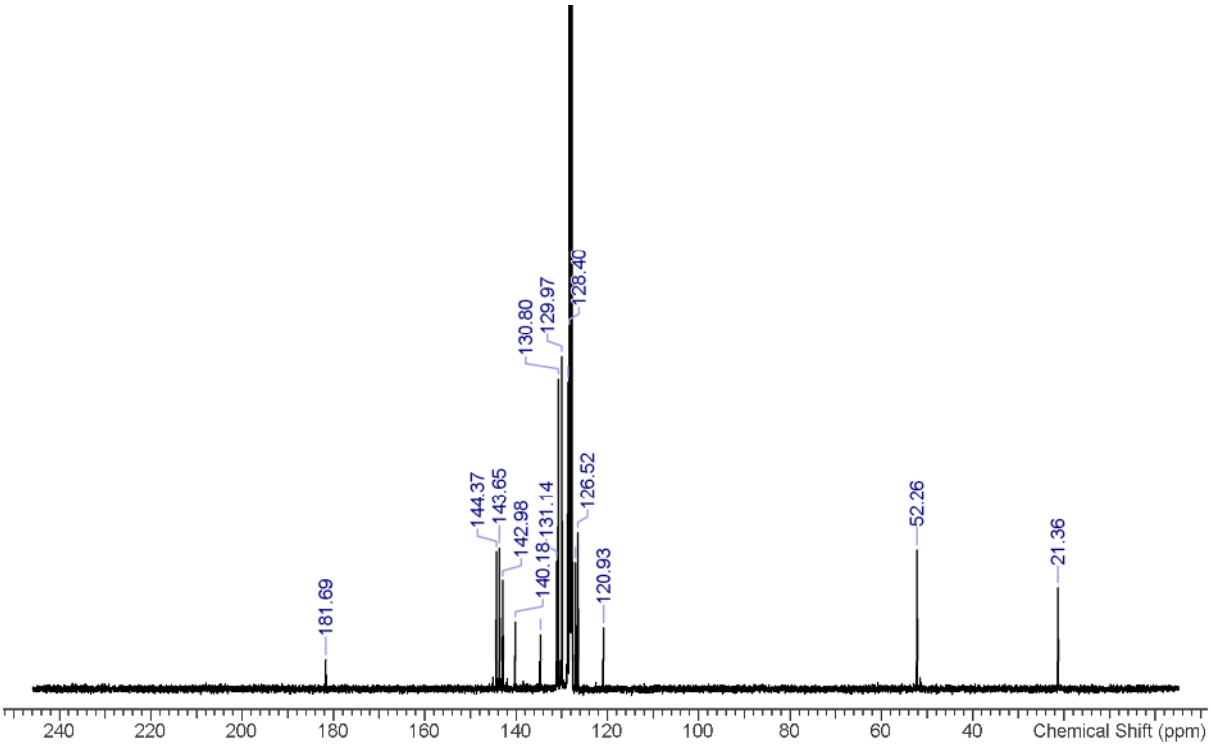


Figure S26. ^{13}C{^{1}H} NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6 .

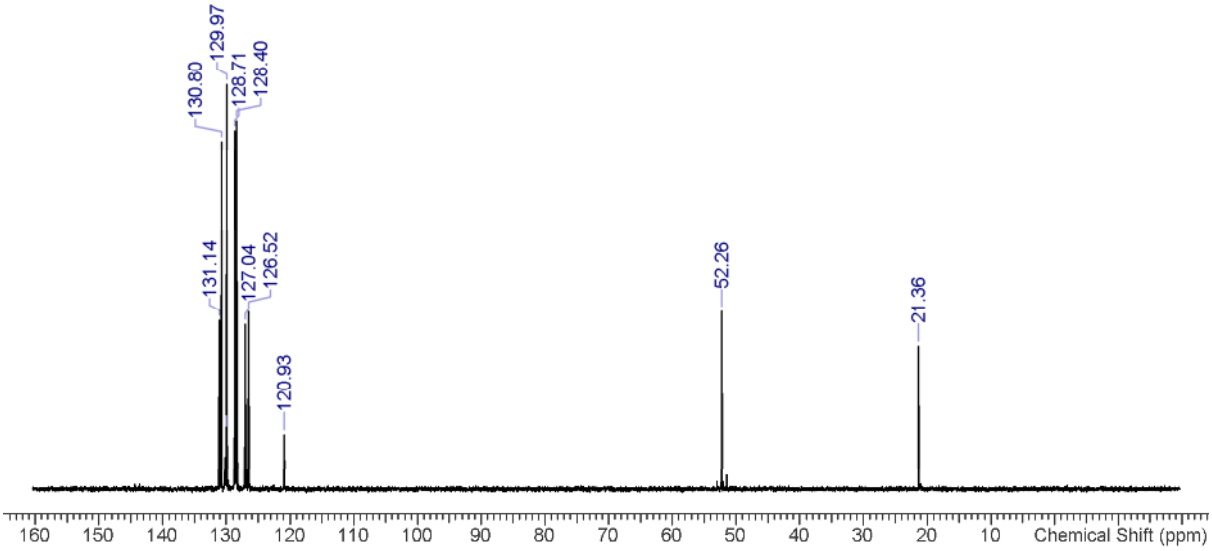


Figure S27. ^{13}C DEPT NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6.

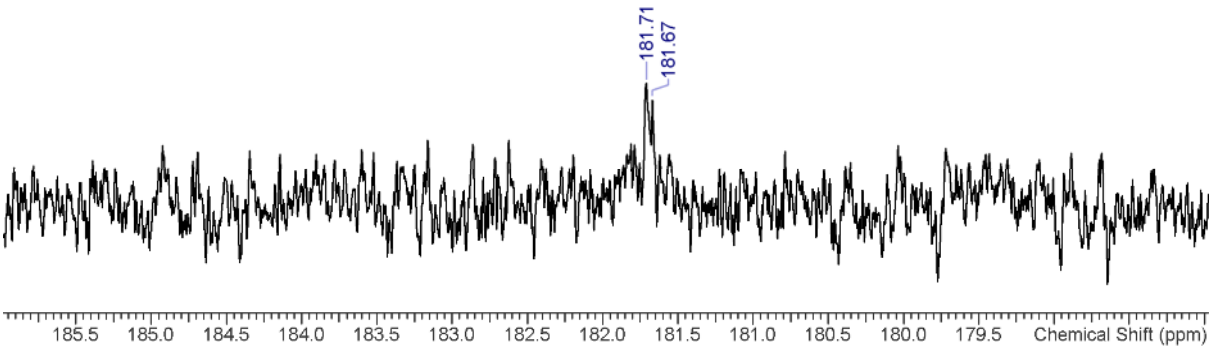


Figure S28. ^{13}C NMR spectrum of [(IAr*)AsH] (**3c**) in C_6D_6.

2.8. [Na(dioxane)$_x$][AsCO]

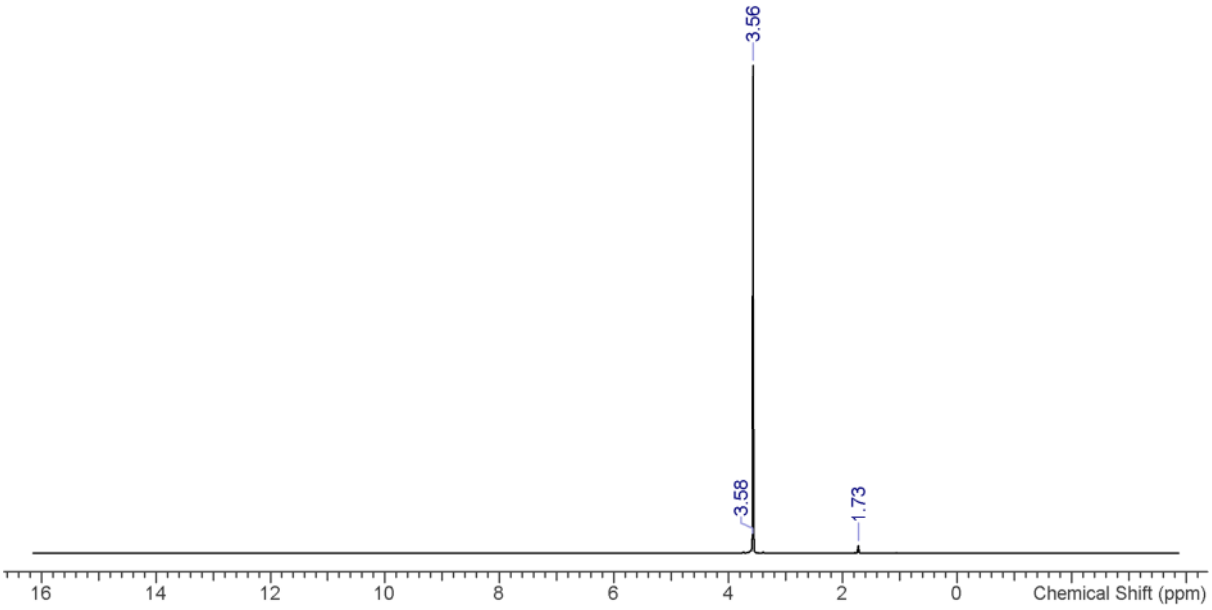


Figure S29. ^{1}H NMR spectrum of [Na(dioxane)$_x$][AsCO] in THF-d$_8$.

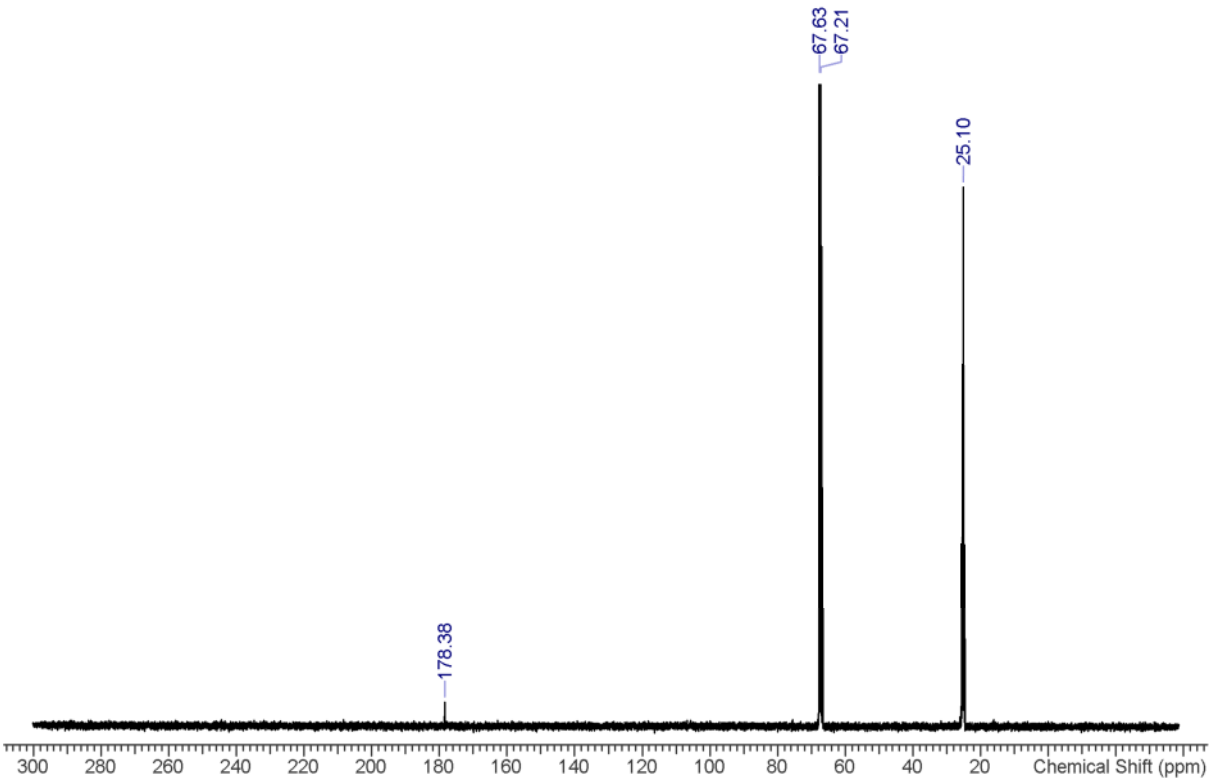


Figure S30. ^{13}C {^{1}H} NMR spectrum of [Na(dioxane)$_x$][AsCO] in THF-d$_8$.

2.9. VT NMR (Variable temperature NMR spectra) of the NHC-parent arsinidene adduct [(IMes)AsH] (3b)

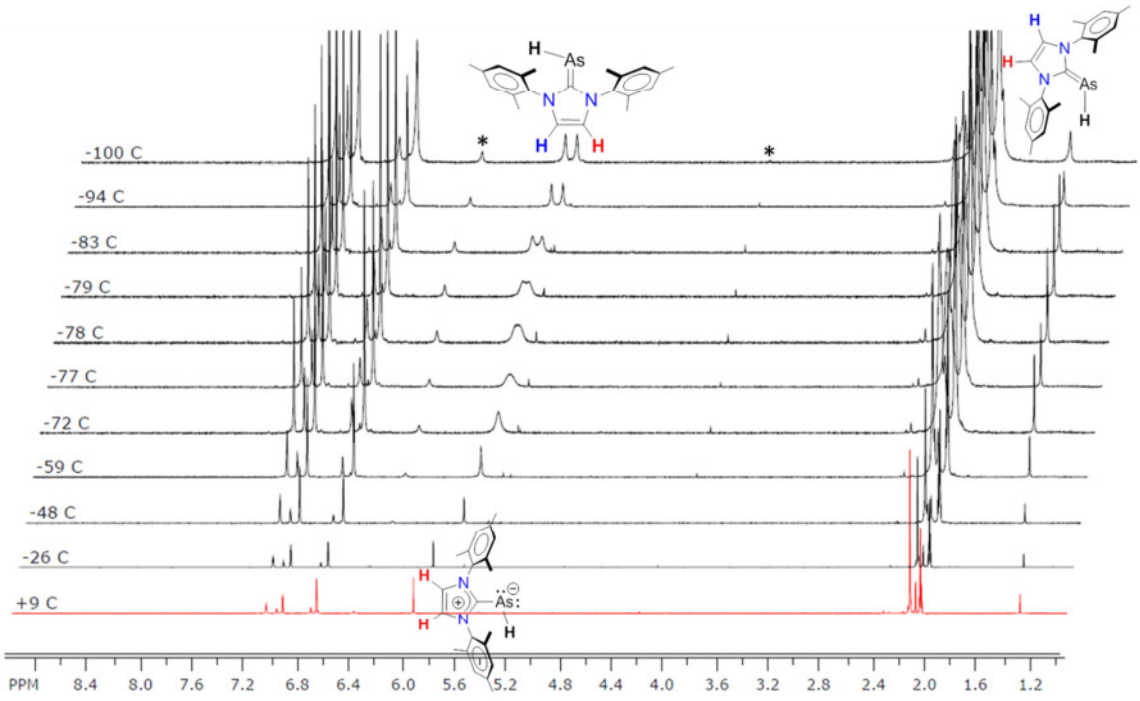


Figure S31. ^{1}H NMR spectrum of the carbene-parent arsinidene adduct [(IMes)AsH] (**3b**) at different temperatures in toluene-d_8 (* impurities).

Calculation of barrier of rotation around the As–C bond in 3b

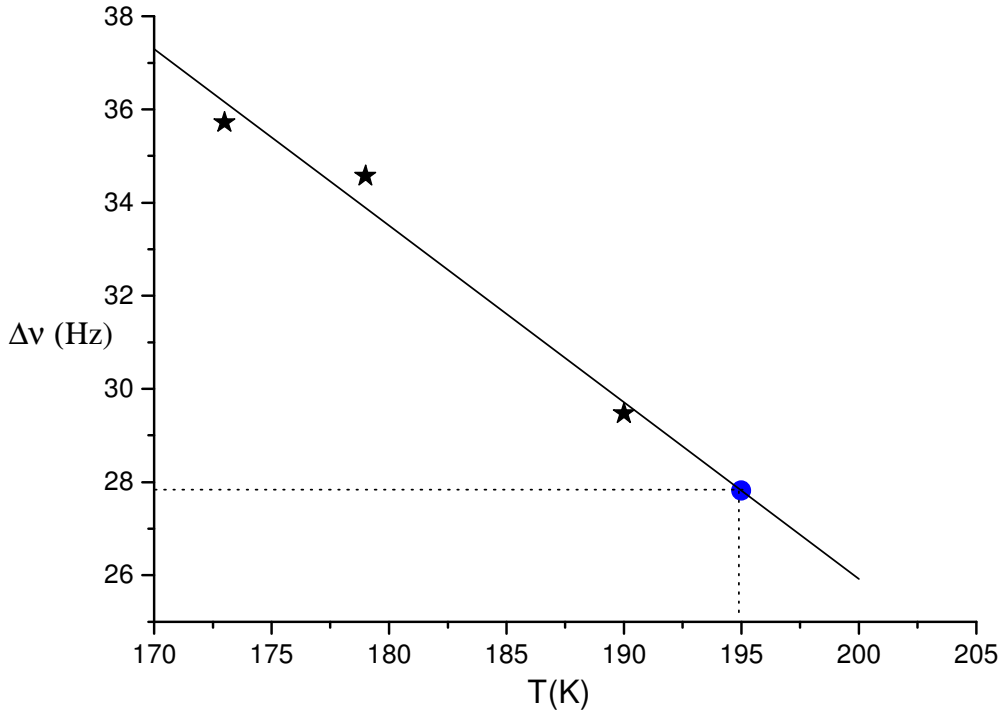


Figure S32: A linear fit of the data points obtained by variable temperature NMR (blue: Δν = separation in Hz between the two signals (27.815 Hz) at the coalescence temperature; *Tc* = 195 K).

Rate constant at the coalescence temperature, $k_C = \frac{\pi \Delta \nu}{\sqrt{2}}$

The following approximate equation was used to calculate the barrier of rotation around the As–C bond.[6]

$$\Delta G_C^{\#} = 4.58\, T_C \left[10.32 + log\left(\frac{T_C}{k_C}\right)\right] cal/mol$$

3. Crystallographic data

Single crystal X-ray structure determination: Single-crystal X-ray diffraction data were collected using Oxford Diffraction diffractometers equipped with a 135 mm Atlas or 165 mm Titan S2 CCD area detector. Crystals were selected under inert oil and mounted on micromount loops (**2b**·0.5(C_6H_{12}), **3a-c**) glass needles (**2a**) or a human hair (**2b**) and quench-cooled using an Oxford Cryosystems open flow N_2 cooling device. Data were collected using mirror monochromated Cu K_α radiation (λ = 1.5418 Å). Data collected on the Oxford Diffraction Supernova (**3a**, **3c**), Nova (**2a**, **2b**) and Agilent GV1000 (**2b**·0.5(C_6H_{12}), **3b**) diffractometers were processed using the CrysAlisPro package, including unit cell parameter refinement and inter-frame scaling (which was carried out using SCALE3 ABSPACK within CrysAlisPro.[7a] Equivalent reflections were merged and diffraction patterns processed with the CrysAlisPro suite. Absorption correction based on face indexation was applied to the datasets for **2b, 2b**·0.5(C_6H_{12}), **3a** and **3b**. Structures were subsequently solved using direct methods and refined on F^2 using ShelXL.[7b] Hydrogen atoms were included by using a riding model or rigid methyl groups. The position of hydrogen H1 in **3a** and **3b** was refined freely, whereas the P-H distance in **3c** was restrained. The crystallographic data are listed in Tables S1 to S6.

Table S1. Crystal data and structure refinement of **2a**

CCDC	1534685	
Empirical formula	$C_{30}H_{45}AsN_2Si$	
Formula weight	536.69	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Oxford Diffraction Xcalibur, Atlas, Nova (ω scan)	
Crystal system	monoclinic	
Space group	*P* $2_1/n$	
Unit cell dimensions	a = 20.0991(4) Å	α = 90°
	b = 14.6635(2) Å	β = 107.342(2)°
	c = 21.6679(4) Å	γ = 90°
Volume	6095.7(2) Å^3	
Z	8	
Density (calculated)	1.170 Mg/m^3	
Absorption coefficient	2.012 mm^{-1}	
F(000)	2288	
Crystal habitus	prism (yellow)	
Crystal size	0.190 x 0.170 x 0.020 mm^3	
Theta range for data collection	3.579 to 76.276°	
Index ranges	-25<=h<=23, -18<=k<=13, -26<=l<=27	
Reflections collected	86050	
Independent reflections	12722 [R(int) = 0.0584]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.87897	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12722 / 0 / 635	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0321, wR2 = 0.0801	
R indices (all data)	R1 = 0.0371, wR2 = 0.0837	
Largest diff. peak and hole	0.303 and -0.701 e.Å^{-3}	
Crystallisation Details:	Fluorobenzene solution layered with *n*-hexane	

Table S2. Crystal data and structure refinement of **2b**

CCDC	1534686	
Empirical formula	$C_{24}H_{33}AsN_2Si$	
Formula weight	452.53	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Oxford Diffraction Xcalibur, Atlas, Nova (ω scan)	
Crystal system	monoclinic	
Space group	*P* $2_1/n$	
Unit cell dimensions	a = 19.0082(3) Å	α = 90°
	b = 9.1958(2) Å	β = 95.759(2)°
	c = 28.5266(5) Å	γ = 90°
Volume	4961.16(16) Å^3	
Z	8	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	2.384 mm^{-1}	
F(000)	1904	
Crystal habitus	irregular (yellow)	
Crystal size	0.220 x 0.150 x 0.100 mm^3	
Theta range for data collection	3.114 to 76.128°	
Index ranges	-21<=h<=23, -11<=k<=11, -35<=l<=35	
Reflections collected	51994	
Independent reflections	10317 [R(int) = 0.0368]	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.75644	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10317 / 0 / 523	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0359, wR2 = 0.0917	
R indices (all data)	R1 = 0.0409, wR2 = 0.0956	
Largest diff. peak and hole	0.484 and -0.700 e.Å^{-3}	
Crystallisation Details:	Fluorobenzene solution layered with *n*-Hexane	

Table S3. Crystal data and structure refinement of **2b**·0.5(C_6H_{12})

CCDC	1534687	
Empirical formula	$C_{25.50}H_{36}AsN_2Si$	
Formula weight	473.57	
Temperature	123(1) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Agilent GV1000, TitanS2 (ω scans)	
Crystal system	monoclinic	
Space group	*C* 2/*c*	
Unit cell dimensions	a = 15.8764(6) Å	α= 90°
	b = 9.1798(3) Å	β= 101.949(4)°
	c = 38.5234(13) Å	γ = 90°
Volume	5492.8(3) Å^3	
Z	8	
Density (calculated)	1.145 Mg/m^3	
Absorption coefficient	2.173 mm^{-1}	
F(000)	2000	
Crystal habitus	block (yellow)	
Crystal size	0.106 x 0.067 x 0.048 mm^3	
Theta range for data collection	2.345 to 74.642°	
Index ranges	-19<=h<=19, -11<=k<=11, -45<=l<=47	
Reflections collected	29510	
Independent reflections	5569 [R(int) = 0.0683]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.925 and 0.852	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5569 / 0 / 289	
Goodness-of-fit on F^2	1.044	
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1731	
R indices (all data)	R1 = 0.0662, wR2 = 0.1853	
Largest diff. peak and hole	0.941 and -0.994 e.Å^{-3}	
Crystallisation Details:	from saturated *n*-hexane solution	

Table S4. Crystal data and structure refinement **3a**

CCDC	1534688	
Empirical formula	$C_{27}H_{37}As_1N_2$	
Formula weight	464.51	
Temperature	150.01(10) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas (ω scans)	
Crystal system	monoclinic	
Space group	*C* 2/*c*	
Unit cell dimensions	a = 20.0571(5) Å	α= 90°
	b = 7.0854(2) Å	β= 107.303(3)°
	c = 39.0742(10) Å	γ = 90°
Volume	5301.6(3) Å^3	
Z	8	
Density (calculated)	1.164 Mg/m^3	
Absorption coefficient	1.824 mm^{-1}	
F(000)	1968	
Crystal habitus	block (yellow)	
Crystal size	0.3 x 0.16 x 0.1 mm^3	
Theta range for data collection	4.618 to 76.340°	
Index ranges	-23<=h<=24, -8<=k<=8, -48<=l<=45	
Reflections collected	15093	
Independent reflections	5494 [R(int) = 0.0267]	
Completeness to theta = 67.684°	99.81 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.74227	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5494 / 0 / 283	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0502, wR2 = 0.1425	
R indices (all data)	R1 = 0.0541, wR2 = 0.1472	
Largest diff. peak and hole	0.715 and -0.587 e.Å^{-3}	
Crystallisation Details:	crystallisation from a saturated *n*-hexane solution	

Table S5. Crystal data and structure refinement of **3b**

CCDC	1534689	
Empirical formula	$C_{21}H_{25}AsN_2$	
Formula weight	380.35	
Temperature	123(1) K	
Wavelength	1.54184 Å	
Instrument (scan mode)	Agilent GV1000, TitanS2 (ω scans)	
Crystal system	monoclinic	
Space group	*P* $2_1/c$	
Unit cell dimensions	a = 8.2857(2) Å	α= 90°
	b = 14.8334(2) Å	β= 102.690(2)°
	c = 16.1781(4) Å	γ = 90°
Volume	1939.80(7) $Å^3$	
Z	4	
Density (calculated)	1.302 Mg/m^3	
Absorption coefficient	2.380 mm^{-1}	
F(000)	792	
Crystal habitus	block (colourless)	
Crystal size	0.182 x 0.081 x 0.055 mm^3	
Theta range for data collection	4.090 to 73.896°	
Index ranges	-10<=h<=8, -17<=k<=18, -18<=l<=19	
Reflections collected	11051	
Independent reflections	3778 [R(int) = 0.0216]	
Completeness to theta = 67.684°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.885 and 0.714	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3778 / 0 / 226	
Goodness-of-fit on F^2	1.063	
Final R indices [I>2sigma(I)]	R1 = 0.0448, wR2 = 0.1269	
R indices (all data)	R1 = 0.0484, wR2 = 0.1304	
Largest diff. peak and hole	0.699 and -1.152 $e.Å^{-3}$	
Crystallisation Details:	from saturated hexanes solution	

Table S6. Crystal data and structure refinement of **3c**

CCDC	1534690	
Empirical formula	$C_{76}H_{65}AsN_2$	
Formula weight	1081.22	
Temperature	150(2) K	
Wavelength	1.54178 Å	
Instrument (scan mode)	Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas (ω scans)	
Crystal system	orthorhombic	
Space group	*P n a* 2_1	
Unit cell dimensions	a = 19.3683(2) Å	α = 90°
	b = 14.8549(2) Å	β = 90°
	c = 20.2018(3) Å	γ = 90°
Volume	5812.34(13) Å^3	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	1.136 mm^{-1}	
F(000)	2272	
Crystal habitus	block (colourless)	
Crystal size	0.230 x 0.140 x 0.080 mm^3	
Theta range for data collection	3.693 to 76.113°	
Index ranges	-14<=h<=24, -16<=k<=18, -25<=l<=25	
Reflections collected	21416	
Independent reflections	9425 [R(int) = 0.0306]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.92908	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9425 / 38 / 719	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1267	
R indices (all data)	R1 = 0.0527, wR2 = 0.1530	
Absolute structure parameter	-0.035(19)	
Largest diff. peak and hole	0.325 and -0.854 e.Å^{-3}	
Crystallisation Details:	crystallisation in a saturated *n*-hexane solution	

3.1. Molecular structures of compounds 2b and 2b·0.5(C_6H_{12})

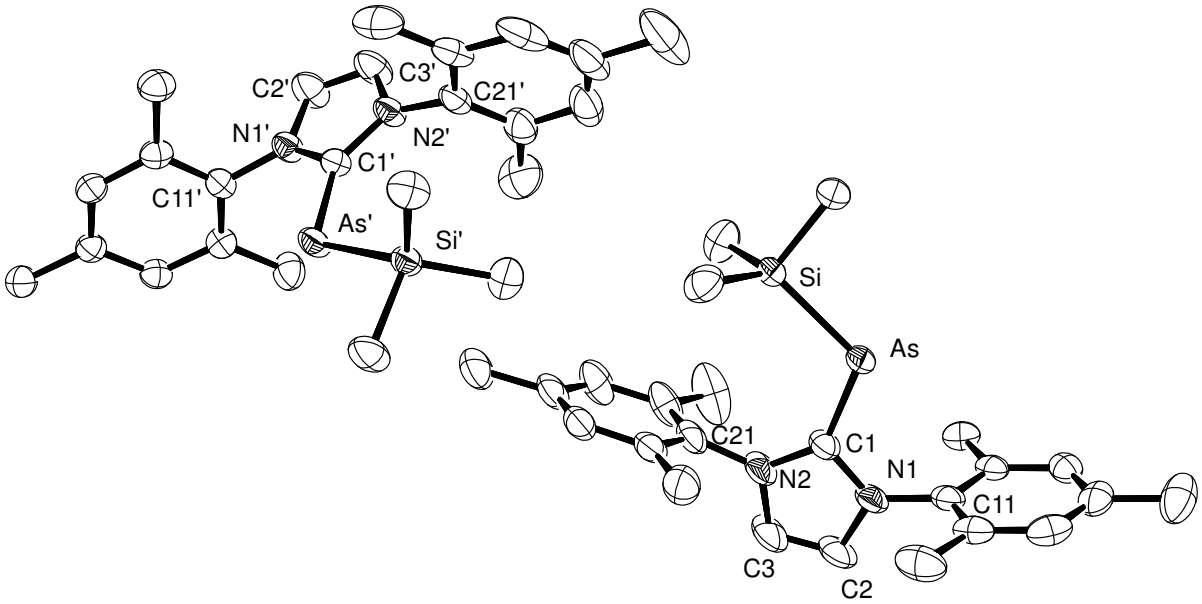


Figure S33. ORTEP diagram of **2b** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [º] of molecule 1/molecule 2: As-Si 2.3234(6)/2.3243(6), C1-As 1.906(2)/1.899(2), C1-N1 1.369(3)/1.373(3), C1-N2 1.371(3), C2-C3 1.336(4)/1.343(3), N1-C1-N2 104.56(18)/103.84(17), C1-As-Si 112.73(7)/112.89(6).

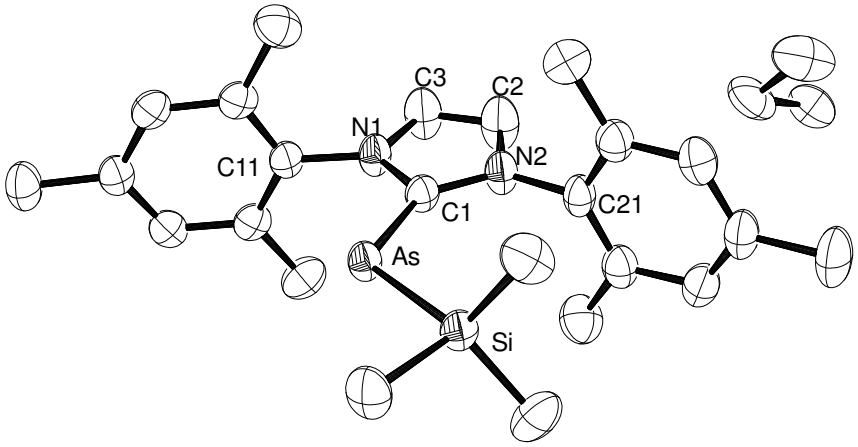


Figure S34. ORTEP diagram of **2b**·0.5(C_6H_{12}) with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [º]: As-Si 2.3209(8), C1-As 1.907(3), C1-N1 1.368(4), C1-N2 1.356(4), C2-C3 1.328(6), N1-C1-N2 104.4(3), C1-As-Si 114.03(9).

3.2. Molecular structures of 3b and 3c

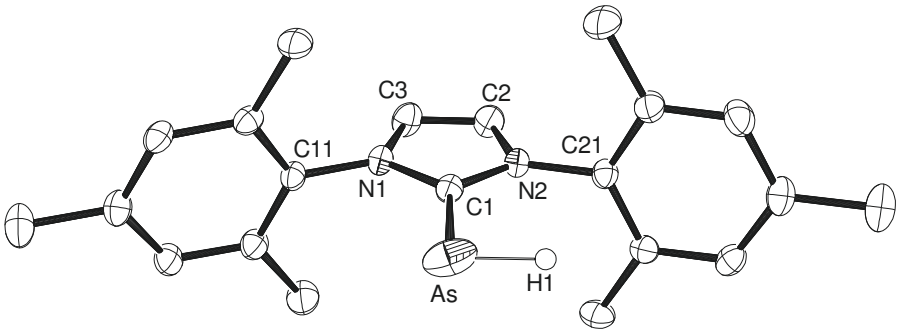


Figure S35. ORTEP diagram of the **3b** with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: C1-As 1.896(2), C1-N1 1.367(3), C1-N2 1.363(3), C2-C3 1.347(3), N1-C1-N2 105.2(2), N2-C1-As1 128.05(16), N1-C1-As1 126.72(16), C1-N1-C11 124.78(19), C1-N2-C21 124.75(19), C1-As-H1 97.75.

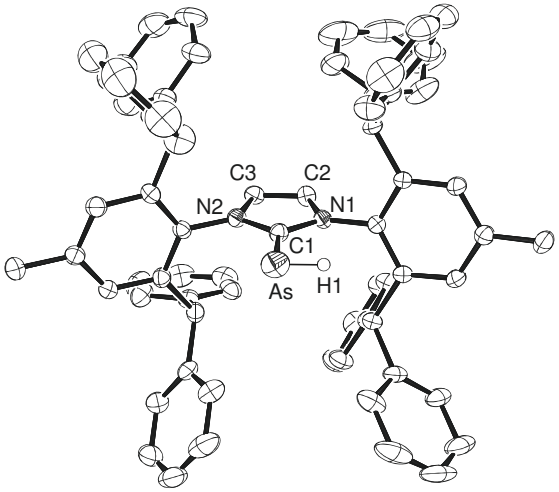


Figure S36: ORTEP diagram of the **3c** in the solid state with thermal displacement parameters drawn at 50% probability level. Selected bond length [Å] and angles [°]: C1-As 1.886(4), C1-N1 1.366(5), C1-N2 1.383(5), C2-C3 1.346(5), N1-C1-N2 104.5(3), N2-C1-As1 129.2(3), N1-C1-As1 126.3(3), C1-As-H1 89.79.

4. Computational data

Computational details: All computations were performed using Gaussian09[8] utilizing the PBE1PBE level of theory and 6-31G(d,p) basis sets. No solvent corrections were applied. Natural Bond Orbital and Natural Resonance Theory were applied to study the electronic states.[9–11]

Table S7. Summary of computational data (d in Å, angle in °, q in e, δ in ppm, ν in cm^{-1}, E in a.u.).

property	H_2CAsH	Ph_2CAsH	$^{Me2}NHCAsH$	(IMes)AsH	(IDipp)AsH	(IAr*)AsH	H_3CAsH_2
C–As	1.766	1.803	1.860	1.851	1.853	1.855	1.961
C–As X-ray				1.879(3)	1.885(2)	1.884(4)	
As–H	1.519	1.515	1.509	1.515	1.515	1.514	1.516
C–As–H	96.13	95.69	93.11	91.96	92.84	92.95	95.22
q C	–0.866	–0.371	+0.079	+0.091	+0.094	+0.094	–1.034
q As	+0.436	+0.399	–0.066	–0.058	–0.045	–0.073	+0.333
q H	–0.070	–0.064	–0.059	–0.046	–0.039	–0.033	–0.042
WBI CAs	1.9345	1.6206	1.2748	1.2704	1.2556	1.2191	0.9662
WBI AsH	0.9727	0.9687	0.9658	0.9620	0.9608	0.9599	0.9813
WBI CH							
ellipticity	0.285	0.277	0.320	0.310	0.315	0.296	0.048
CAs							
ellipticity	0.010	0.014	0.106	0.106	0.108	0.107	0.011
AsH							
δ(^{13}C)	199.66	230.46	178.13	175.75	183.65	177.46	0.28
δ(^{1}H)	6.68	6.05	2.09	1.69	1.80	2.78	2.70
ν(AsH)	2156	2157	2180	2159	2167	2170	2153, 2167
total energy	-	-	-	-	-	-	-
	2273.24504778	2734.84018414	2538.51684754	3157.19274463	3392.79279759	5003.48000979	2274.49032386

4.1. Optimised geometries

4.1.1. (IMes)AsH

```
0 1
 As                  0.15743000   -0.00267400   -1.70489900
 H                  -1.34531000   -0.00008600   -1.89419100
 N                  -1.11020700    0.00060700    0.95369900
 N                   1.06060700    0.00089200    0.99003400
 C                  -0.01113200   -0.00021600    0.13863500
 C                  -0.71823300    0.00230300    2.28822700
 H                  -1.44292200    0.00316200    3.08652300
 C                   0.63135000    0.00235800    2.30934300
 H                   1.33063200    0.00330600    3.12998700
 C                  -2.46604800    0.00048100    0.51036600
 C                  -3.10279100   -1.22449000    0.28514000
 C                  -4.44158100   -1.19969300   -0.10057500
 H                  -4.95278500   -2.14249400   -0.28277100
 C                  -5.13242800    0.00041000   -0.27765500
 C                  -4.44298300    1.20023800   -0.09687200
 H                  -4.95520900    2.14304700   -0.27582400
 C                  -3.10365000    1.22512100    0.28849400
 C                  -2.32228700   -2.50311900    0.36578500
 H                  -1.51150500   -2.46896300   -0.37343400
 H                  -2.95644600   -3.36671800    0.15337300
 H                  -1.86232500   -2.64509700    1.34939400
 C                  -6.58661000   -0.00105200   -0.65706000
 H                  -6.83467800   -0.86088400   -1.28578600
 H                  -6.85913800    0.90783200   -1.20038900
 H                  -7.22418100   -0.05386300    0.23354900
 C                  -2.32426800    2.50428900    0.37188900
 H                  -1.51289900    2.47198000   -0.36671600
 H                  -1.86521800    2.64527500    1.35606500
 H                  -2.95893800    3.36769400    0.16022300
 C                   2.42025600    0.00046100    0.55463000
 C                   3.05698500    1.22598300    0.32575900
 C                   4.39153500    1.19959800   -0.07326500
 H                   4.90258600    2.14241400   -0.25560100
 C                   5.07953000   -0.00026300   -0.26016700
 C                   4.39348700   -1.19923000   -0.06591100
 H                   4.90597500   -2.14237000   -0.24194100
 C                   3.05811300   -1.22498100    0.33281700
 C                   2.29495400    2.51333800    0.43859700
 H                   1.81350200    2.62327000    1.41581800
 H                   1.50458800    2.52705600   -0.32261500
 H                   2.95026500    3.37244400    0.27842700
 C                   6.52903000    0.00162500   -0.65693300
 H                   7.17690200    0.08721900    0.22365900
 H                   6.76167900    0.84412500   -1.31445200
 H                   6.80257800   -0.92080900   -1.17617600
 C                   2.29785400   -2.51280800    0.45224100
 H                   2.95406600   -3.37179400    0.29517300
 H                   1.50676400   -2.53096100   -0.30808200
 H                   1.81751700   -2.61915200    1.43040600
```

4.1.2. (IDipp)AsH

```
0 1
 As                 0.14866200    0.07417300   -1.85069200
 H                 -1.35127700    0.09089500   -2.06374300
 N                  1.06119600   -0.05486900    0.83246800
 C                  0.64686400   -0.11824400    2.15452700
 H                  1.35608300   -0.13514400    2.96635700
 N                 -1.11020900   -0.10330600    0.82014800
 C                  2.42098300    0.03432600    0.39864600
 C                 -0.70178600   -0.15157000    2.14869500
 H                 -1.41676200   -0.20603600    2.95371600
 C                  2.93803400    1.29749300    0.06763300
 C                  4.27996700    1.36390200   -0.31151500
 H                  4.71185800    2.32731800   -0.56680700
 C                  5.06805000    0.22257200   -0.36181200
 H                  6.11065000    0.29679700   -0.65806400
 C                  4.52692100   -1.01616000   -0.04173900
 H                  5.15055700   -1.90299400   -0.09799600
 C                  3.19156100   -1.14016200    0.34344300
 C                  2.10450300    2.56249400    0.14013700
 H                  1.06656600    2.27025700    0.32327500
 C                  2.56264100    3.44578200    1.30426700
 H                  1.93155100    4.33774900    1.37915100
 H                  3.59685700    3.77971300    1.16588200
 H                  2.51038500    2.91163700    2.25857600
 C                  2.11792300    3.32392200   -1.18629100
 H                  1.73375800    2.67904800   -1.98151100
 H                  3.12324500    3.66621700   -1.45475500
 H                  1.47403600    4.20720300   -1.11911400
 C                  2.58252700   -2.50473900    0.60580700
 H                  1.67890900   -2.35807800    1.20808000
 C                  3.50349700   -3.43930600    1.38935900
 H                  3.84725200   -2.98299800    2.32308600
 H                  4.38683700   -3.72545700    0.80885300
 H                  2.97197100   -4.36339500    1.63783300
 C                  2.14824300   -3.12699200   -0.72680400
 H                  1.61575500   -4.07007400   -0.56136700
 H                  3.02045400   -3.33385800   -1.35724700
 H                  1.49338500   -2.43635100   -1.26775200
 C                 -2.47308400   -0.08961300    0.39278200
 C                 -3.09487900   -1.31063500    0.08507700
 C                 -4.42108100   -1.26583200   -0.34897100
 H                 -4.92847400   -2.19055100   -0.60783400
 C                 -5.09832800   -0.05879700   -0.45643700
 H                 -6.12932500   -0.04570500   -0.79877700
 C                 -4.46557300    1.13236600   -0.12383700
 H                 -5.00970500    2.06809600   -0.20636100
 C                 -3.13990600    1.14559000    0.31225600
 C                 -2.35856700   -2.63443000    0.17581600
 H                 -1.43859300   -2.46391800    0.74585700
 C                 -3.16663400   -3.69848800    0.92057600
 H                 -4.06752900   -3.98700300    0.36884300
 H                 -3.47694300   -3.35171600    1.91131000
 H                 -2.56409500   -4.60337600    1.04932100
 C                 -1.94584700   -3.11450300   -1.21970100
 H                 -2.82419400   -3.28145800   -1.85344700
```

H	-1.39002900	-4.05609300	-1.15387000
H	-1.30593300	-2.36407400	-1.69338700
C	-3.33117600	3.41501300	1.43245500
H	-4.16719300	3.78873800	0.83195200
H	-2.74838100	4.28677000	1.74640600
H	-3.74514200	2.94131800	2.32816000
C	-2.44318100	2.45433300	0.64058100
H	-1.57812900	2.21919000	1.27172700
C	-1.90913400	3.11478700	-0.63622600
H	-2.73072300	3.36620100	-1.31662400
H	-1.22188900	2.44077600	-1.15845600
H	-1.37563700	4.04070200	-0.39363500
C	-0.02135600	-0.04325200	-0.00924500

4.1.3. (IAr*)AsH

0 1

As	0.05493700	-0.06246800	-2.19782400
H	-0.19261800	1.42120100	-2.36874100
N	0.03404800	-1.05519200	0.46620500
N	-0.04531700	1.11833400	0.49706800
C	0.00299200	0.04482000	-0.34660300
C	0.00456300	-0.66463800	1.79965000
H	0.03247000	-1.38668100	2.59903700
C	-0.05168800	0.68311100	1.82002700
H	-0.10497300	1.38029900	2.64004700
C	0.25788700	-2.37758000	-0.03308500
C	-0.80524000	-3.09258600	-0.61463000
C	-0.53526900	-4.35813100	-1.12424000
H	-1.34530400	-4.91716500	-1.58395000
C	0.74673500	-4.91364700	-1.08839100
C	1.77312700	-4.17576300	-0.50908300
H	2.78543600	-4.57263200	-0.50664000
C	1.54926400	-2.91095100	0.04062800
C	-2.20667600	-2.50027900	-0.65851800
H	-2.07251200	-1.43861500	-0.90674300
C	-2.92845400	-2.56720900	0.67921100
C	-4.07052700	-1.77731400	0.86093500
H	-4.39886500	-1.12379800	0.05575200
C	-4.79383300	-1.83194700	2.04717800
H	-5.67985100	-1.21384700	2.16422500
C	-4.38301800	-2.67217300	3.08156900
H	-4.94691700	-2.71540500	4.00901400
C	-3.24897000	-3.45828400	2.91257600
H	-2.92091400	-4.12001500	3.70956900
C	-2.52942700	-3.40889600	1.71871400
H	-1.64939000	-4.03358500	1.59418300
C	-3.04627500	-3.08172900	-1.78988100
C	-3.95551100	-4.12154500	-1.58428200
H	-4.10003100	-4.51680000	-0.58253200
C	-4.68743800	-4.64447100	-2.64824100
H	-5.39219500	-5.45216600	-2.47045600
C	-4.52391800	-4.13035300	-3.93065000
H	-5.09942500	-4.53376500	-4.75906500
C	-3.62032800	-3.09149800	-4.14346500
H	-3.48726800	-2.68111000	-5.14083100
C	-2.88517400	-2.57340100	-3.08280800
H	-2.17345200	-1.76557500	-3.24272500

C	1.00607900	-6.26356800	-1.69479900
H	0.26093600	-6.99591500	-1.36849800
H	1.99604300	-6.64055100	-1.42622400
H	0.95296000	-6.21495900	-2.78819500
C	2.68592300	-2.13845700	0.68726300
H	2.37401300	-1.08962200	0.73786700
C	3.92190800	-2.14131500	-0.20580600
C	3.80128200	-1.55053100	-1.47049200
H	2.83369500	-1.14707500	-1.77053000
C	4.89433800	-1.48852900	-2.32462500
H	4.78823200	-1.01721500	-3.29765600
C	6.12172200	-2.02402900	-1.93301300
H	6.97692500	-1.97472800	-2.60098700
C	6.24379800	-2.61869600	-0.68270600
H	7.19603700	-3.03847900	-0.37005000
C	5.14909400	-2.67518800	0.18094200
H	5.25406400	-3.12896500	1.16212200
C	2.94510200	-2.56096400	2.12791200
C	2.85016200	-3.88578300	2.56255600
H	2.54815900	-4.66244800	1.86688900
C	3.12186300	-4.22381100	3.88631100
H	3.04041200	-5.26017500	4.20229200
C	3.48870800	-3.24243000	4.80172900
H	3.69665300	-3.50674300	5.83460500
C	3.57926400	-1.91785600	4.38257800
H	3.85688000	-1.13870600	5.08713700
C	3.30865800	-1.58248700	3.05986100
H	3.37821700	-0.54531400	2.74237000
C	-0.24883600	2.46267200	0.05859000
C	0.82524500	3.18352100	-0.49350300
C	0.57541900	4.47378100	-0.94828400
H	1.39104700	5.03723000	-1.39248100
C	-0.70023300	5.04384500	-0.89465800
C	-1.74393300	4.28778900	-0.37155600
H	-2.75485500	4.68833600	-0.38200500
C	-1.53918700	2.99857400	0.12667400
C	2.19833000	2.53713200	-0.61426000
H	2.00596700	1.49811900	-0.91618400
C	2.96985200	2.50276700	0.69537900
C	4.06794900	1.64035700	0.80073600
H	4.32826500	1.00273300	-0.04102500
C	4.83638500	1.60353500	1.95859400
H	5.68430100	0.92673000	2.01693000
C	4.51616400	2.42425200	3.03986500
H	5.11647800	2.39661800	3.94482800
C	3.42434000	3.28027700	2.94767300
H	3.16609600	3.92614200	3.78249800
C	2.65815600	3.32031100	1.78299800
H	1.81016500	3.99660700	1.71881900
C	3.03052000	3.12955600	-1.74370300
C	3.90685000	4.19813900	-1.53958300
H	4.02997300	4.60544300	-0.53942400
C	4.63356900	4.73094200	-2.60130400
H	5.31216700	5.56130800	-2.42633400
C	4.50012000	4.19622400	-3.87952000
H	5.07219600	4.60759200	-4.70634400

C	3.63579400	3.12453600	-4.08925000
H	3.53175600	2.69417400	-5.08152300
C	2.90532800	2.59632700	-3.02985600
H	2.23151700	1.75559300	-3.18333300
C	-0.93181600	6.43772800	-1.40571200
H	-1.99739500	6.64446100	-1.53339600
H	-0.43618700	6.59411200	-2.36857700
H	-0.52896900	7.18343700	-0.71044200
C	-2.69629300	2.18624800	0.68124900
H	-2.35411200	1.14856100	0.74512700
C	-3.85954200	2.15334800	-0.30539900
C	-3.66666800	1.47809500	-1.51864600
H	-2.69426300	1.03572300	-1.73954100
C	-4.69807400	1.39288500	-2.44541700
H	-4.53815600	0.85457700	-3.37537000
C	-5.93247800	1.98587500	-2.18116900
H	-6.73836600	1.91587800	-2.90612200
C	-6.12518900	2.66365400	-0.98310300
H	-7.08370800	3.12805300	-0.76789900
C	-5.09481300	2.74387000	-0.04619100
H	-5.25752800	3.25794800	0.89681000
C	-3.08435500	2.57237500	2.10324600
C	-2.99077400	3.87400300	2.60192200
H	-2.59416600	4.66604100	1.97475800
C	-3.38425600	4.16884900	3.90586500
H	-3.30153200	5.18828400	4.27253900
C	-3.87246000	3.16638200	4.73711800
H	-4.17499600	3.39680300	5.75460800
C	-3.96059900	1.86289300	4.25469100
H	-4.32931600	1.06614600	4.89489300
C	-3.56899700	1.57130400	2.95296400
H	-3.63529400	0.54972200	2.58754900

4.1.4. H_2CAsH

0 1

As	0.35828400	-0.04902200	-0.00002000
H	0.58120300	1.45349500	0.00028900
C	-1.40656200	0.02213400	0.00024200
H	-1.99134700	0.93634300	-0.00078800
H	-1.97385500	-0.90493200	-0.00027800

4.1.5. ^{Me2}NHCAsH

0 1

As	-1.68834200	-0.10063100	-0.00003400
H	-1.70779400	-1.60961400	0.00101000
N	1.13363100	-0.99226000	0.00008600
N	0.85677700	1.15753400	0.00000100
C	0.16970400	-0.02376500	0.00003700
C	2.39238000	-0.41421700	0.00001300
H	3.29252100	-1.00776600	0.00002100
C	2.21864500	0.92545200	-0.00002700
H	2.93641700	1.72998800	-0.00004700
C	0.18727400	2.43054500	0.00002000
H	-0.45210800	2.51422500	-0.88672300
H	-0.45287800	2.51367200	0.88626200
H	0.92734700	3.23154400	0.00057900
C	0.85026200	-2.40278900	-0.00007300

H	0.26944000	−2.67288600	0.88784200
H	0.26838400	−2.67234100	−0.88746100
H	1.79150600	−2.95425500	−0.00078800

4.1.6. Ph_2CAsH

0 1

As	0.14193300	0.18971500	0.34471500
C	−1.64584300	0.13508400	0.11658900
C	−2.51824200	1.31781900	0.15744300
C	−2.33538800	2.33154500	1.11068400
C	−3.56449600	1.46039100	−0.76985100
C	−3.15005400	3.45661100	1.12121500
H	−1.55929600	2.20934700	1.86064200
C	−4.36932400	2.59248600	−0.76635100
H	−3.72461500	0.68286400	−1.51088400
C	−4.16630400	3.59514800	0.17913500
H	−2.99715400	4.22362800	1.87491400
H	−5.15981600	2.69193000	−1.50470200
H	−4.80279000	4.47514600	0.18744400
C	−2.27339200	−1.17961500	−0.08946200
C	−3.52671600	−1.47002400	0.47824800
C	−1.63123000	−2.19013700	−0.82516700
C	−4.09678500	−2.72848700	0.34097500
H	−4.03863500	−0.70271500	1.05077900
C	−2.20389700	−3.44826300	−0.96101000
H	−0.68805100	−1.96377800	−1.31519000
C	−3.43744100	−3.72406800	−0.37685600
H	−5.05981300	−2.93477300	0.79914700
H	−1.69245700	−4.21156900	−1.54014700
H	−3.88813200	−4.70579300	−0.48958000
H	0.25136200	1.70074000	0.31231000

4.1.7. H_3CAsH_2

0 1

As	−0.41739000	0.00000100	−0.06499600
H	−0.60200900	−1.07936000	0.98317100
C	1.54215500	−0.00002200	0.02200100
H	1.90961100	−0.88401200	−0.50245200
H	1.90942400	0.88545600	−0.50007300
H	−0.60182600	1.07935000	0.98321800
H	1.90573300	−0.00135000	1.04900300

4.2. Analyses of the electronic structure

The electronic structure was analysed with the program MULTIWFN 3.3.9,[12] thereby CDA,[13] ELF,[14] and bond ellipticities/AIM[15] were studied.

4.2.1. Molecular orbitals of [(IMes)AsH]

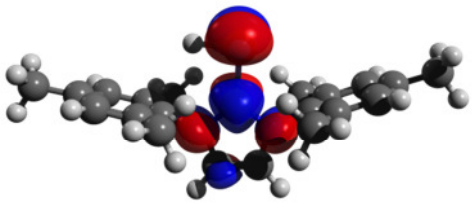


Figure S37. LUMO+4 of ^{Mes}NHCAsH.

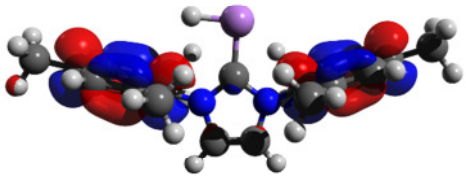


Figure S38. LUMO of ^{Mes}NHCAsH.

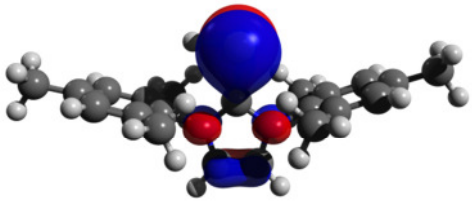


Figure S39. HOMO of ^{Mes}NHCAsH.

Figure S41. HOMO–1 of ^{Mes}NHCAsH.

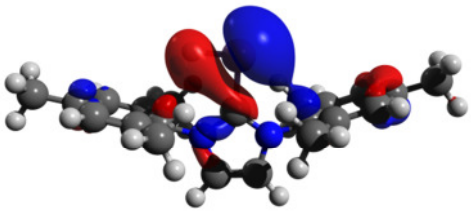


Figure S42. HOMO–5 of ^{Mes}NHCAsH.

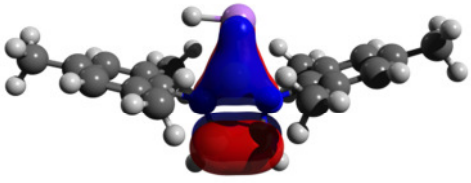


Figure S43. HOMO–6 of ^{Mes}NHCAsH.

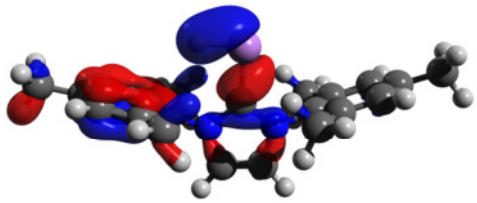


Figure S44. HOMO–8 of ^{Mes}NHCAsH.

4.2.2. Selected NBO data

H_2CAsH

```
    1. (1.98361) BD ( 1)As   1 - H   2
               ( 46.28%)   0.6803*As   1 s( 11.80%)p 7.42( 87.59%)d 0.05(  0.61%)
                                          0.0000  0.0000  0.0001  0.3408 -0.0428
                                          0.0090  0.0000  0.0000  0.0000  0.0000
                                         -0.1741 -0.0350  0.0000 -0.0002  0.9183
                                          0.0337  0.0000  0.0000 -0.0001  0.0000
                                         -0.0007 -0.0144  0.0000  0.0000  0.0000
                                          0.0000  0.0000 -0.0656  0.0000 -0.0396
               ( 53.72%)   0.7329* H   2 s( 99.91%)p 0.00(  0.09%)
                                          0.9996  0.0017  0.0031 -0.0296  0.0000
    2. (1.99969) BD ( 1)As   1 - C   3
               ( 47.19%)   0.6869*As   1 s(  0.00%)p 1.00( 99.42%)d 0.01(  0.58%)
                                          0.0000  0.0000  0.0000 -0.0004  0.0001
                                          0.0000  0.0000  0.0000  0.0000  0.0000
                                         -0.0010 -0.0001  0.0000  0.0000  0.0001
                                          0.0000  0.0000  0.0000  0.9962 -0.0407
                                          0.0000  0.0000  0.0000  0.0727  0.0000
                                          0.0234  0.0000 -0.0001  0.0000  0.0000
               ( 52.81%)   0.7267* C   3 s(  0.00%)p 1.00( 99.94%)d 0.00(  0.06%)
                                          0.0000 -0.0011  0.0000  0.0000  0.0006
                                          0.0000 -0.0002  0.0000  0.9988 -0.0418
                                          0.0000 -0.0247 -0.0013  0.0000  0.0000
    3. (1.99727) BD ( 2)As   1 - C   3
               ( 35.46%)   0.5954*As   1 s( 18.32%)p 4.44( 81.30%)d 0.02(  0.39%)
                                          0.0000  0.0001  0.0000  0.4174 -0.0944
                                         -0.0062 -0.0001  0.0000  0.0000  0.0000
                                          0.8993  0.0591  0.0000  0.0001  0.0175
                                         -0.0220  0.0000  0.0000  0.0011 -0.0001
                                          0.0000  0.0202  0.0000  0.0001  0.0000
                                          0.0000  0.0000  0.0542  0.0000 -0.0228
               ( 64.54%)   0.8034* C   3 s( 36.54%)p 1.74( 63.42%)d 0.00(  0.04%)
                                          0.0001  0.6045  0.0069 -0.0007 -0.7963
                                         -0.0030 -0.0078 -0.0009  0.0012 -0.0001
                                          0.0011  0.0000  0.0000  0.0167 -0.0106
```

^{Ar*}NHC=AsH

```
    2. (1.97326) BD ( 1)As   1 - C   5
               ( 30.42%)   0.5516*As   1 s( 14.00%)p 6.11( 85.57%)d 0.03(  0.43%)
                                          0.0000 -0.0002  0.0004 -0.3690  0.0617
                                         -0.0032 -0.0014  0.0000  0.0000  0.0000
                                          0.0252 -0.0010  0.0000 -0.0001 -0.0204
                                          0.0130  0.0000 -0.0005 -0.9225 -0.0588
                                          0.0000 -0.0020  0.0000  0.0053 -0.0001
                                         -0.0185  0.0000 -0.0058 -0.0002 -0.0628
               ( 69.58%)   0.8341* C   5 s( 42.60%)p 1.35( 57.39%)d 0.00(  0.01%)
                                          0.0003 -0.6520 -0.0310  0.0004 -0.0092
                                          0.0016  0.0030 -0.0027  0.7554 -0.0566
                                          0.0005  0.0007 -0.0024  0.0011 -0.0089
  256. (1.96567) LP ( 1)As   1           s( 73.45%)p 0.36( 26.53%)d 0.00(  0.02%)
```

```
                                        0.0000 -0.0001 -0.0001  0.8569  0.0151
                                        0.0002  0.0002  0.0000  0.0000  0.0000
                                        0.0528  0.0017  0.0000  0.0001 -0.3906
                                        0.0059 -0.0001 -0.0005 -0.3314  0.0047
                                        0.0000  0.0026 -0.0001  0.0016  0.0006
                                       -0.0099  0.0001  0.0068 -0.0001 -0.0042
   257. (1.55393) LP ( 2)As   1           s(  0.03%)p99.99( 99.80%)d 4.78(  0.17%)
                                        0.0000  0.0000 -0.0001  0.0186 -0.0005
                                       -0.0008  0.0001  0.0000  0.0003  0.0018
                                        0.9849 -0.0441  0.0001  0.0003  0.1600
                                       -0.0106  0.0000  0.0000  0.0159 -0.0012
                                        0.0000  0.0210 -0.0034  0.0336 -0.0003
                                        0.0025  0.0001 -0.0082 -0.0001  0.0015

258. LP (   1) N   3               /260. LP*(   1) C   5                 126.80    0.13
0.134
259. LP (   1) N   4               /260. LP*(   1) C   5                 126.92
```

^{Mes}NHC=AsH

```
     1. (1.96837) BD ( 1)As   1 - H   2
                ( 47.10%)   0.6863*As   1 s( 12.82%)p 6.76( 86.69%)d 0.04(  0.49%)
                                        0.0000  0.0000  0.0003  0.3559 -0.0390
                                       -0.0049 -0.0006 -0.0001  0.0000  0.0002
                                       -0.9103 -0.0535  0.0000  0.0000  0.0015
                                        0.0001  0.0000  0.0001 -0.1853 -0.0310
                                        0.0000 -0.0002  0.0012  0.0070  0.0000
                                        0.0000  0.0001  0.0614  0.0000 -0.0332
                ( 52.90%)   0.7273* H   2 s( 99.92%)p 0.00(  0.08%)
                                        0.9996  0.0006  0.0287 -0.0001  0.0035
     2. (1.97472) BD ( 1)As   1 - C   5
                ( 30.14%)   0.5490*As   1 s( 13.97%)p 6.12( 85.56%)d 0.03(  0.47%)
                                        0.0000 -0.0001  0.0004 -0.3663  0.0744
                                       -0.0048 -0.0006 -0.0001  0.0000  0.0001
                                        0.0468 -0.0103  0.0000  0.0000 -0.0012
                                        0.0000  0.0001 -0.0005 -0.9217 -0.0607
                                        0.0000  0.0000  0.0001  0.0232  0.0000
                                       -0.0002  0.0001  0.0058 -0.0002 -0.0641
                ( 69.86%)   0.8358* C   5 s( 42.78%)p 1.34( 57.21%)d 0.00(  0.01%)
                                        0.0003 -0.6534 -0.0309  0.0005 -0.0276
                                        0.0053  0.0009 -0.0001  0.7538 -0.0559
                                        0.0000  0.0030  0.0000 -0.0014 -0.0090
    96. (1.97197) LP ( 1)As   1           s( 73.78%)p 0.36( 26.20%)d 0.00(  0.02%)
                                        0.0000 -0.0001  0.0001  0.8588  0.0191
                                        0.0004  0.0001  0.0000  0.0000 -0.0001
                                        0.3999 -0.0079  0.0000  0.0000 -0.0008
                                        0.0000  0.0000 -0.0005 -0.3193  0.0070
                                        0.0000  0.0000 -0.0006  0.0110  0.0000
                                        0.0000 -0.0001 -0.0068 -0.0002 -0.0034
    97. (1.55176) LP ( 2)As   1           s(  0.00%)p 1.00( 99.79%)d 0.00(  0.21%)
                                        0.0000  0.0000  0.0000  0.0003  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                       -0.0018  0.0001 -0.0002 -0.0019 -0.9979
                                        0.0449  0.0000  0.0000  0.0011  0.0000
                                       -0.0002  0.0268  0.0000  0.0000  0.0037
                                       -0.0377  0.0000  0.0001  0.0000  0.0001
```

^{Me2}NHC=AsH

```
     2. (1.98423) BD ( 1)As   1 - C   5
                ( 69.76%)   0.8352*As   1 s(  0.00%)p 1.00( 99.73%)d 0.00(  0.27%)
                                        0.0000  0.0000  0.0000  0.0001  0.0000
                                        0.0000  0.0000  0.0000  0.0000  0.0000
                                       -0.0002  0.0000  0.0000  0.0000 -0.0006
                                        0.0000  0.0000  0.0001  0.9980 -0.0374
                                        0.0000  0.0000  0.0000 -0.0479  0.0000
                                       -0.0196  0.0000  0.0000  0.0000  0.0000
                ( 30.24%)   0.5499* C   5 s(  0.00%)p 1.00( 99.94%)d 0.00(  0.06%)
                                        0.0000  0.0001  0.0000  0.0000  0.0001
                                        0.0000 -0.0002  0.0001  0.9983 -0.0535
                                        0.0000  0.0242 -0.0001  0.0000  0.0000
     3. (1.97588) BD ( 2)As   1 - C   5
                ( 30.55%)   0.5527*As   1 s( 13.92%)p 6.15( 85.60%)d 0.03(  0.48%)
                                        0.0000  0.0001 -0.0004  0.3642 -0.0809
                                        0.0055 -0.0001  0.0000  0.0001 -0.0004
                                       -0.9205 -0.0612  0.0000  0.0000  0.0679
```

```
                                      0.0171  0.0000  0.0000 -0.0002  0.0000
                                      0.0001  0.0083  0.0000  0.0000  0.0000
                                      0.0000  0.0002  0.0623  0.0000 -0.0290
              ( 69.45%)   0.8334* C   5 s( 42.07%)p 1.38( 57.92%)d 0.00(  0.01%)
                                     -0.0003  0.6478  0.0322 -0.0005  0.7543
                                     -0.0623 -0.0799  0.0021 -0.0001  0.0000
                                      0.0012  0.0000  0.0000  0.0075 -0.0065
    41. (1.97346) LP ( 1)As   1           s( 73.55%)p 0.36( 26.43%)d 0.00(  0.02%)
                                      0.0000 -0.0001  0.0002  0.8573  0.0217
                                      0.0004  0.0000  0.0000  0.0000  0.0004
                                      0.3639 -0.0079  0.0000 -0.0002  0.3629
                                     -0.0093  0.0000  0.0000  0.0002  0.0000
                                      0.0006 -0.0113  0.0000  0.0000  0.0000
                                      0.0000  0.0001 -0.0028  0.0002  0.0054

 42. LP (   1) N   3               /163. BD*(   1)As   1 - C   5           71.59
   42. LP (   1) N   3               /173. BD*(   2) C   6 - C   8           35.48
   43. LP (   1) N   4               /163. BD*(   1)As   1 - C   5           70.81    0.22
0.116
  43. LP (   1) N   4               /173. BD*(   2) C   6 - C   8           36.16
```

4.2.3. NRT analysis

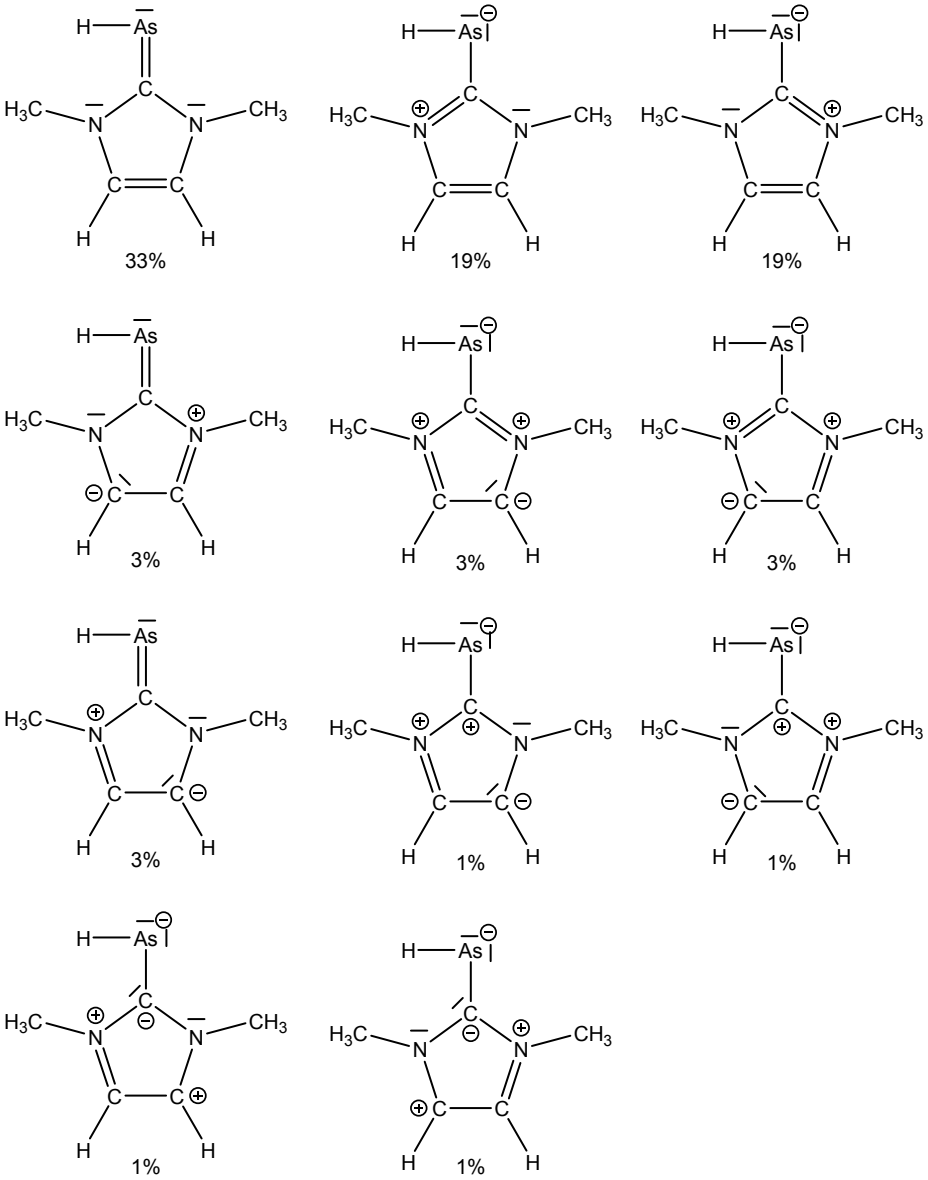


Figure S45. NRT weighting scheme for ^{Me2}NHCAsH.

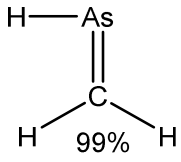


Figure S46. NRT weighting scheme for H_2CAsH.

4.2.4. ELF calculations

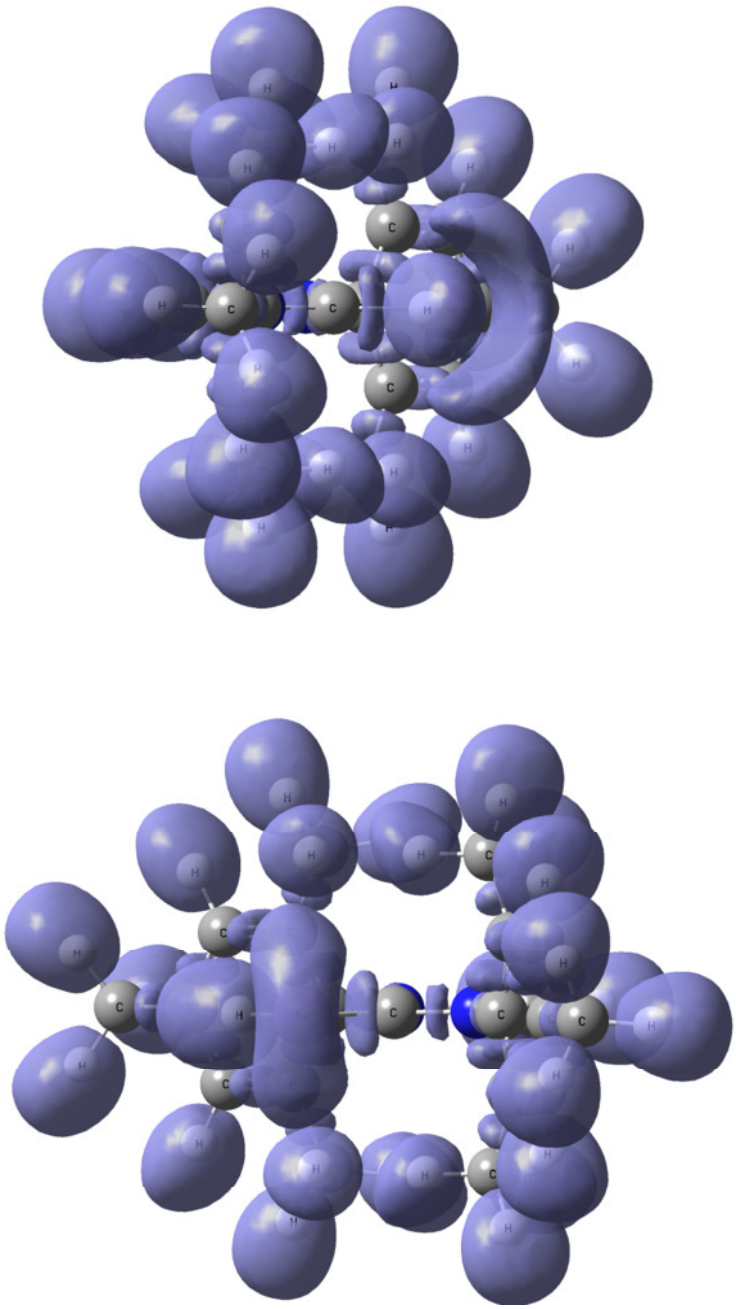


Figure S47. Depiction of the ELF of ^{Mes}NHCAsH at isovalue of 0.85.

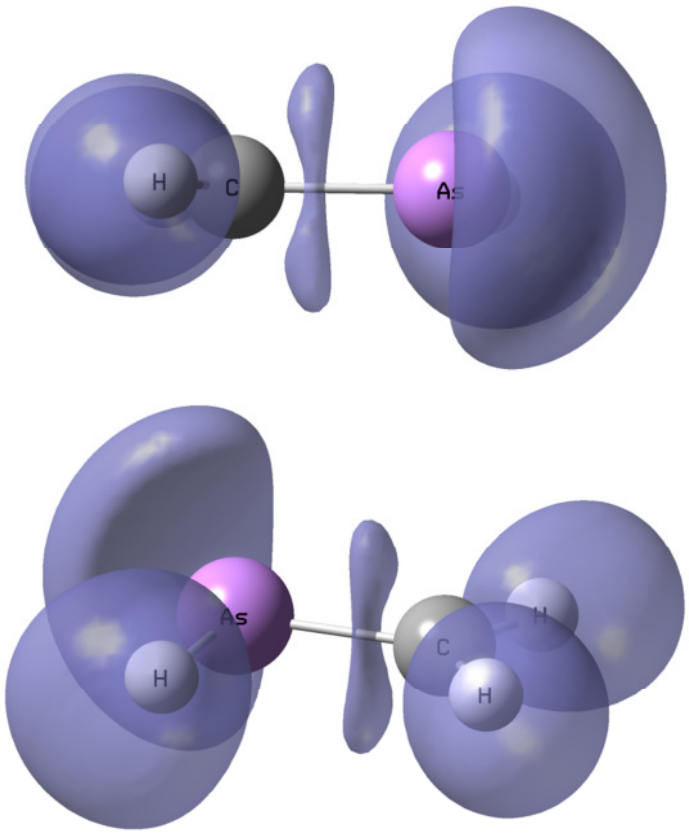


Figure S48. Depiction of the ELF of H_2CAsH at isovalue of 0.85.

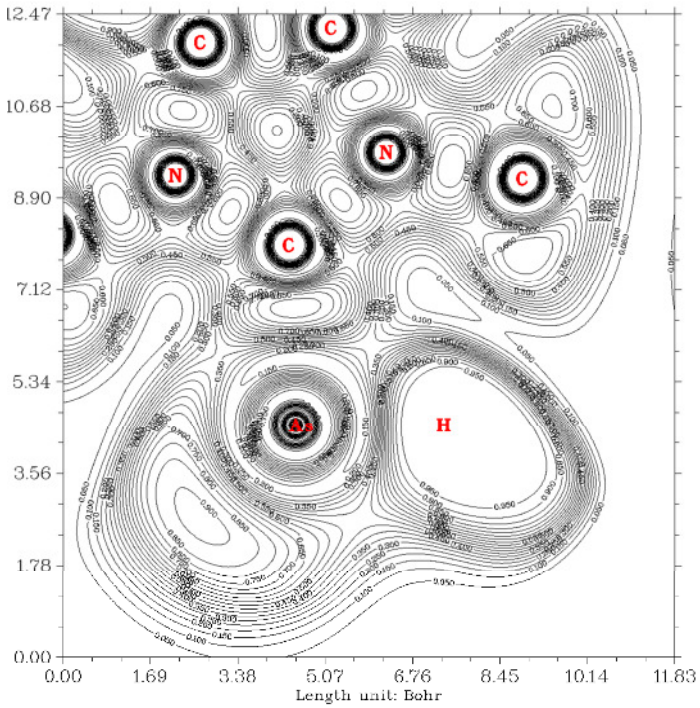


Figure S49. Contour plot of the ELF of ^{Mes}NHCAsH in the CAsH plane.

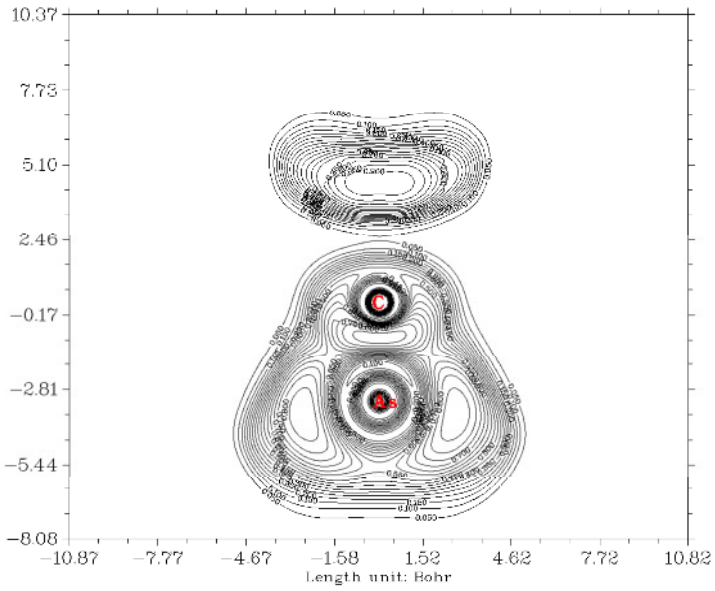


Figure S50. Contour plot of the ELF of ^{Mes}NHCAsH perpendicular to the CAsH plane.

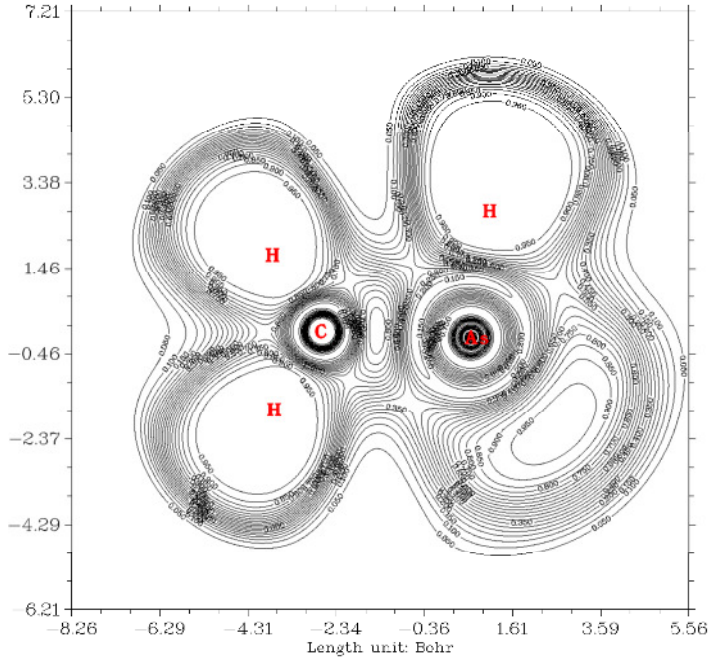


Figure S51. Contour plot of the ELF of H_2CAsH in the CAsH plane.

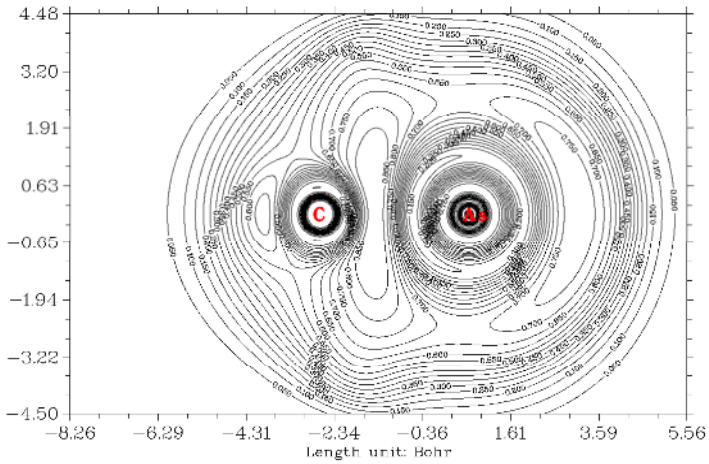


Figure S52. Contour plot of the ELF of H_2CAsH perpendicular to the CAsH plane.

4.2.5. Bond ellipticities at BCP

The ellipticity of 0 means rotational symmetry around the bonding path, while values >0 imply anisotropic distribution of the electron density as it would be expected for a π bond.

As–H and C–As bond values listed, C–As in bold.

Index	X/Y/Z Coordinate (Bohr)			Dist.	Value
^{Mes}NHC=AsH					
63	**0.15894152**	**−0.00295246**	**−1.61704218**	**1.8600**	**0.30972862E+00**
56	−1.38096693	−0.00224921	−3.45184338	1.6500	0.10579991E+00
H_2CAsH					
52	**−0.88865861**	**−0.02823631**	**0.00010787**	**1.5300**	**0.28525157E+00**
38	0.94637638	1.58247993	0.00026892	1.1100	0.99418700E−02
H_3CAsH_2					
38	**−1.00552385**	**−1.22008465**	**1.03104700**	**1.1100**	**0.48347821E−01**
24	3.34260348	1.04948698	−0.57722675	0.6900	0.10842457E−01
^{Dipp}NHC=AsH					
63	**0.13818626**	**0.03964248**	**−1.89421777**	**1.8600**	**0.31453519E+00**
56	−1.39434289	0.15929085	−3.75290267	1.6500	0.10817843E+00
^{Me2}NHC=AsH					
56	−3.22849610	−1.87694305	0.00108695	1.6500	0.10608733E+00
63	**−1.57384251**	**−0.11738765**	**−0.00000729**	**1.8600**	**0.32010277E+00**
Ar*NHC=AsH					
63	**0.06139118**	**−0.03079967**	**−2.54206971**	**1.8600**	**0.29559946E+00**
38	−0.16748481	1.54092343	−4.36062104	1.1100	0.10719466E+00
Ph_2CAsH					
53	**−1.31182345**	**0.31320053**	**0.45143586**	**1.5600**	**0.27723919E+00**
38	0.40716312	2.04680570	0.62034951	1.1100	0.13706356E−01

4.2.6. Laplacian of electron density

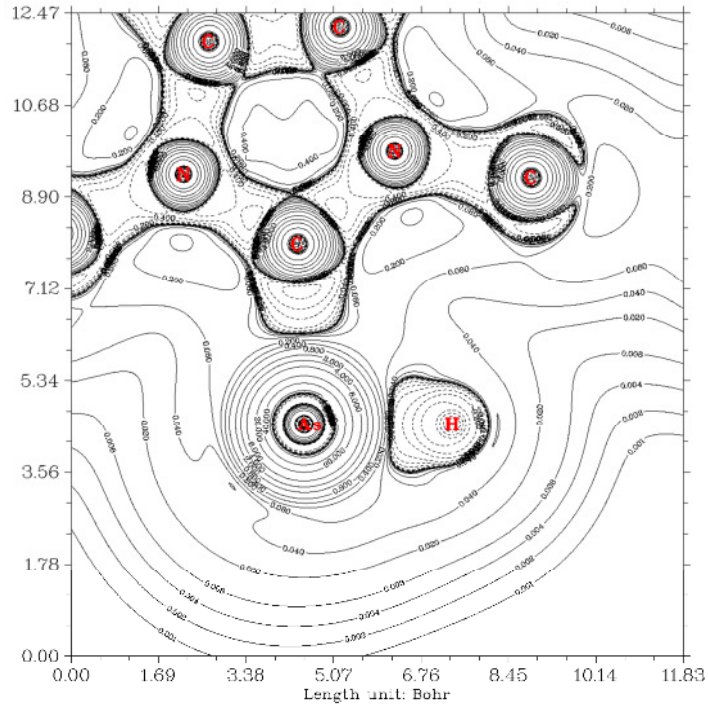


Figure S53. Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH in the CAsH plane.

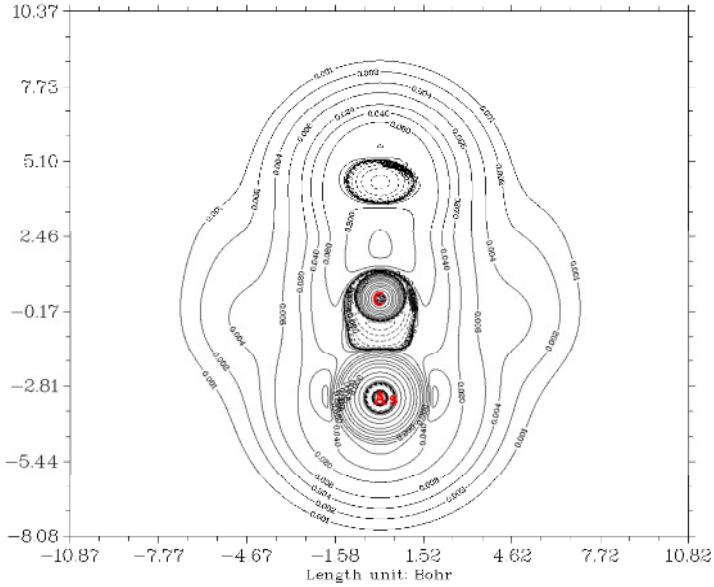


Figure S54. Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH perpendicular to the CAsH plane.

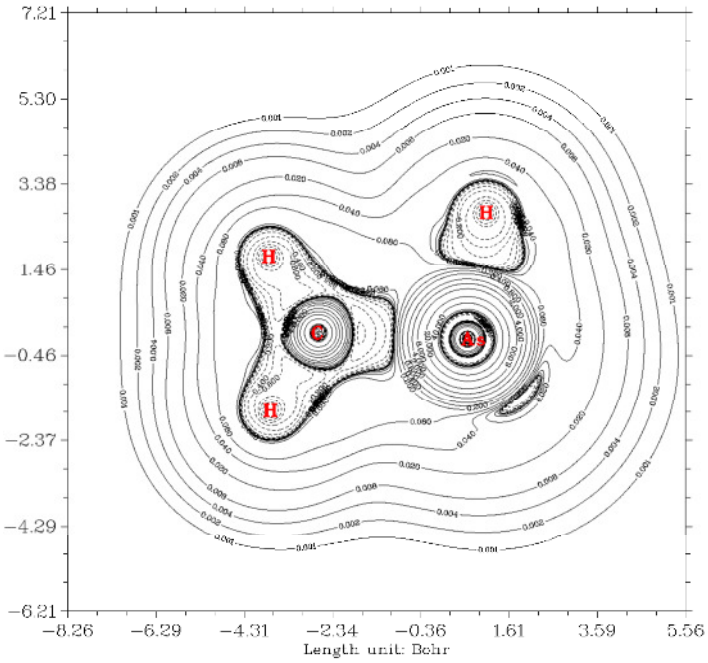


Figure S55. Contour plot of the Laplacian of the electron density of H_2CAsH in the CAsH plane.

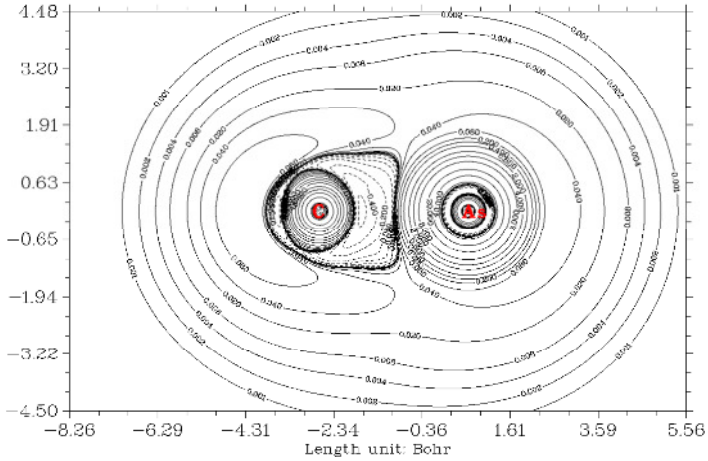


Figure S56. Contour plot of the Laplacian of the electron density of H_2CAsH perpendicular to the CAsH plane.

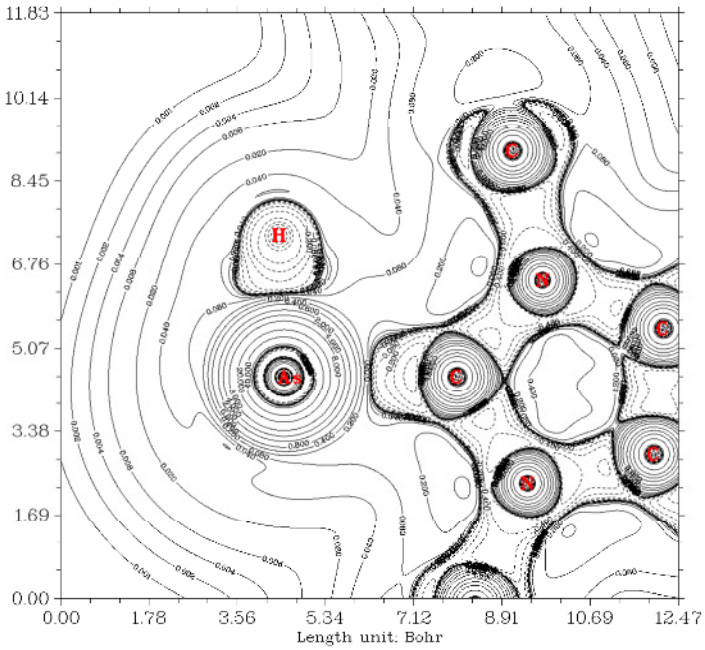


Figure S57. Contour plot of the Laplacian of the electron density of ^{Mes}NHCAsH in the CAsH plane.

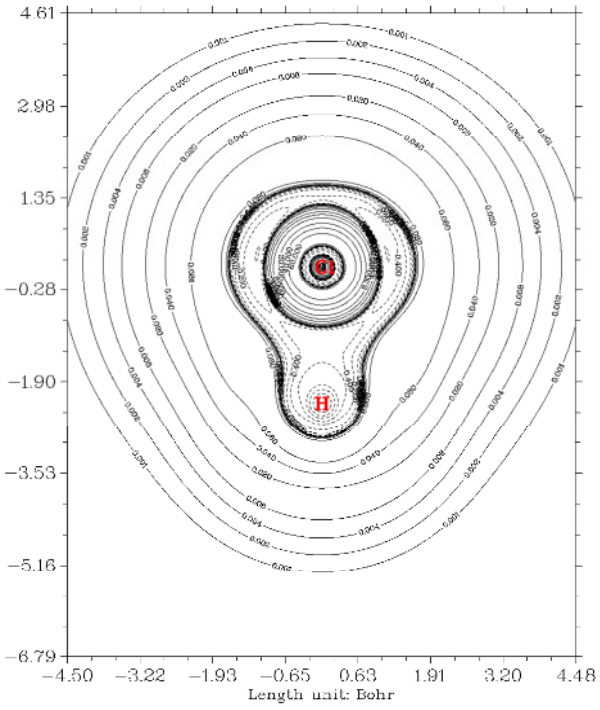


Figure S58. Contour plot of the Laplacian of the electron density of HCl.

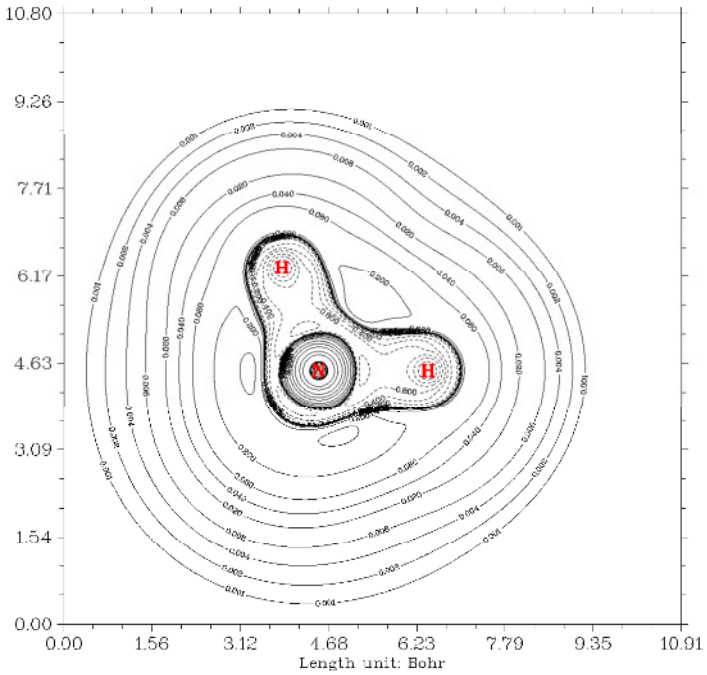


Figure S59. Contour plot of the Laplacian of the electron density of NH_4^+.

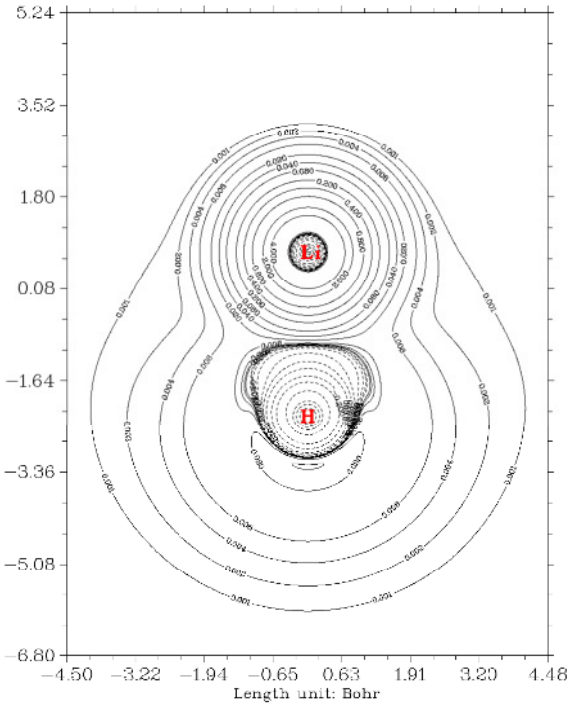


Figure S60. Contour plot of the Laplacian of the electron density of LiH.

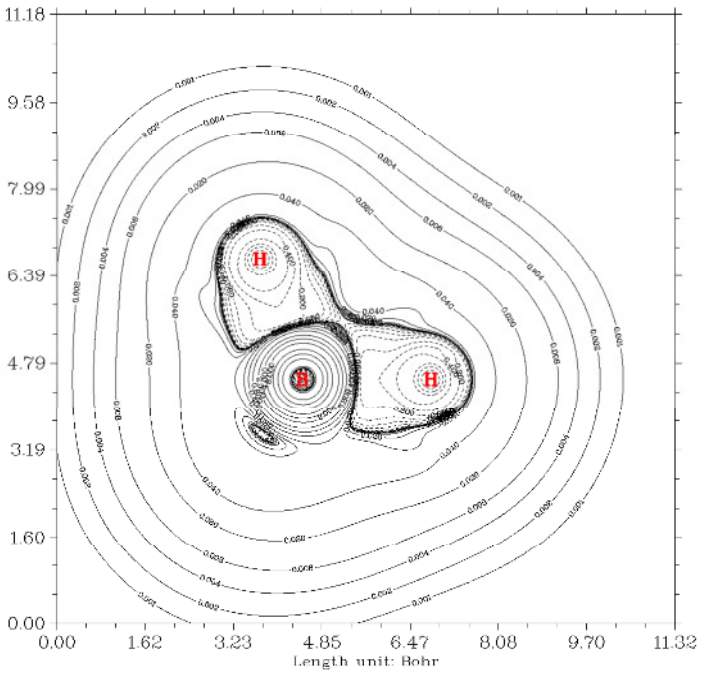


Figure S61. Contour plot of the Laplacian of the electron density of BH_4^-.

Table S8. E–H bond character, ρ and $\nabla^2\rho$ at the BCP.

molecule	$\rho(r_c)$	$\nabla^2\rho(r_c)$
GaH_3	0.1103893575	0.1361723698
GeH_4	0.1290480255	0.07569410550
IMes=AsH	**0.1417169466**	**-0.02743252112**
AsH_3	0.1450980079	-0.05453278431
AsH_4^+	0.1640913825	-0.1638143282
SeH_2	0.1731443529	-0.1877223664
BrH	0.1989594987	-0.3326934586
LiH	0.03479502518	0.1539985379
BH_4^-	0.1444078202	-0.01014669296
NH_4^+	0.3328411735	-1.1864811273

4.2.7. Electron density

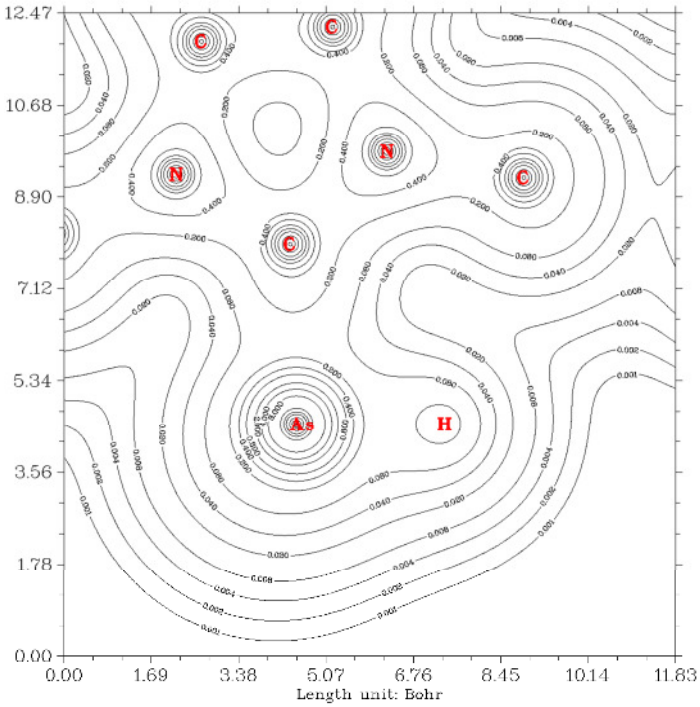


Figure S62. Contour plot of the electron density of ^{Mes}NHCAsH in the CAsH plane.

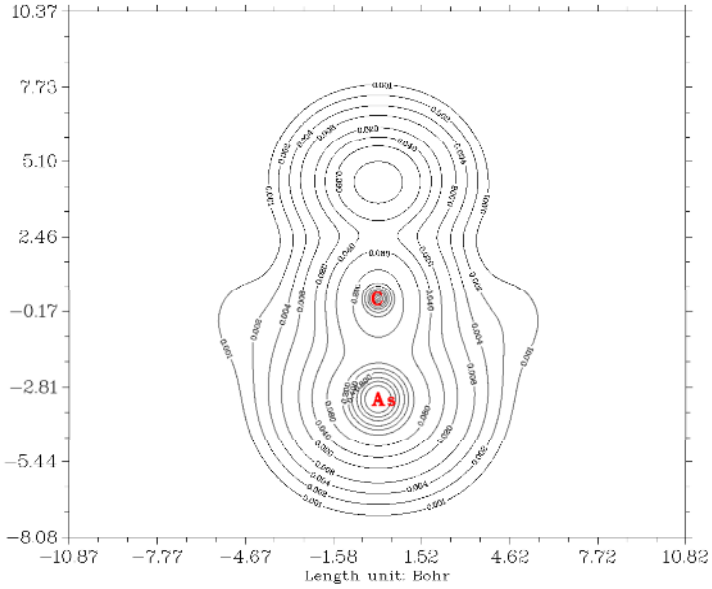


Figure S63. Contour plot of the electron density of ^{Mes}NHCAsH perpendicular to the CAsH plane.

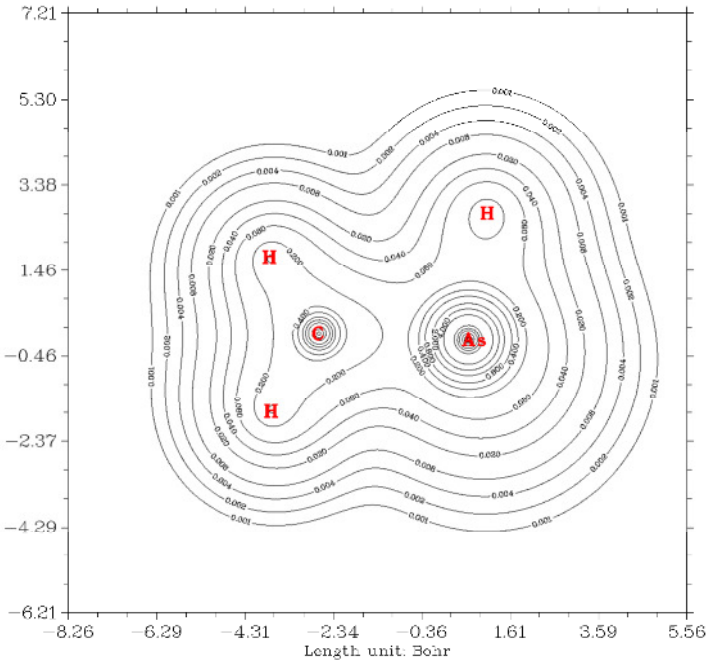


Figure S64. Contour plot of the electron density of H_2CAsH in the CAsH plane.

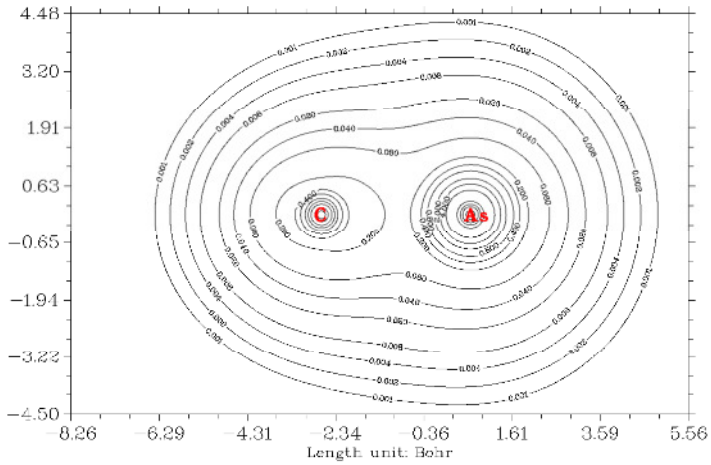


Figure S65. Contour plot of the electron density of H_2CAsH perpendicular to the CAsH plane.

4.2.8. Charge decomposition analysis

[(IMes)AsH]

singlet state of fragments

```
d     +0.185
b     +0.325
d–b   –0.140
r     –0.315
total       –0.354 e As→C
```

HOMO main As→C donor

HOMO-1, HOMO-2 main C→As back donors

triplet state of fragments

```
      a           b           total
d     –0.016      –0.214      –0.231
b     –0.220      –0.007      –0.227
d–b   +0.204      –0.207      –0.004
r     +0.106      +0.139      +0.245
total +1.177      –0.823      +0.354
```

H_2CAsH

singlet state of fragments

```
d     +0.196
b     +0.316
d–b   –0.120
r     –0.176
total       +0.04 e As→C
```

HOMO main As→C donor

HOMO-1, HOMO-2 main C→As back donors

triplet state of fragments

```
      a           b           total
d     +0.230      –0.006      +0.223
b     +0.009      +0.274      +0.283
d–b   +0.221      –0.280      –0.060
r     –0.099      –0.089      –0.188
total +1.020      –0.980      –+0.040
```

4.3. Transition states for rotation around the C–As bond

	IMes	IDipp
E [a.u.]	-3157.19274463	-3392.79279759
$E^{\#}$ [a.u.]	-3157.16837886	-3392.76412058
ΔE [a.u.]	0.02436577	0.02867701
ΔE [kJ mol^{-1}]	64.0	75.3

4.3.1. (IPr)AsH

```
0 1
 As                 0.00000400   -0.32170100   -1.91963800
 H                 -0.00018100   -1.82595300   -1.71202300
 N                 -1.07587500    0.02609900    0.80140400
 C                 -0.67781000    0.19280500    2.11233200
 H                 -1.39015600    0.29728100    2.91511500
 N                  1.07578500    0.02639800    0.80139600
 C                 -2.46033000    0.04450800    0.40558500
 C                  0.67768900    0.19302200    2.11232200
 H                  1.39001100    0.29771100    2.91509700
 C                 -3.15124500   -1.16722800    0.27926400
 C                 -4.52596700   -1.10091700    0.04404300
 H                 -5.08977900   -2.02351300   -0.05921600
 C                 -5.17762400    0.11865300   -0.07054100
 H                 -6.24847200    0.14718100   -0.25068700
 C                 -4.45850800    1.30311900    0.02212000
 H                 -4.97044500    2.25227600   -0.10254600
 C                 -3.08438400    1.29444600    0.26253700
 C                 -2.45867200   -2.51386600    0.32196300
 H                 -1.38846200   -2.33960600    0.47300600
 C                 -2.96152800   -3.38414600    1.47517700
 H                 -2.42622900   -4.33916500    1.49340800
 H                 -4.02923800   -3.60649100    1.37316600
 H                 -2.81480500   -2.89419800    2.44323400
 C                 -2.61116500   -3.21058200   -1.03342400
 H                 -2.25851500   -2.54229300   -1.82440300
 H                 -3.65538000   -3.47540900   -1.23216000
 H                 -2.02030800   -4.13228600   -1.06044200
 C                 -2.29436700    2.58882000    0.24033900
 H                 -1.31906400    2.40131300    0.70334400
 C                 -2.95650400    3.71978400    1.02663400
 H                 -3.15241400    3.43172600    2.06438800
 H                 -3.90684200    4.02708300    0.57813000
 H                 -2.30623200    4.60032600    1.03479100
 C                 -2.04281600    2.98537800   -1.21995000
 H                 -1.38556000    3.85981100   -1.27795200
 H                 -2.98639200    3.23585900   -1.71749800
 H                 -1.58309800    2.15551100   -1.76776500
 C                  2.46025300    0.04505100    0.40562000
 C                  3.08370500    1.29509600    0.26108300
 C                  4.45786300    1.30414000    0.02085200
 H                  4.96932300    2.25340700   -0.10499500
 C                  5.17758000    0.11992200   -0.07021400
 H                  6.24843800    0.14874900   -0.25024800
 C                  4.52649400   -1.09983200    0.04575600
 H                  5.09075100   -2.02228400   -0.05637500
```

C	3.15177700	-1.16650700	0.28086600
C	2.29315900	2.58910500	0.23708000
H	1.31713100	2.40131400	0.69842600
C	2.95349800	3.72053500	1.02422400
H	3.90499000	4.02740400	0.57787600
H	3.14683100	3.43311800	2.06263900
H	2.30331500	4.60116400	1.03022900
C	2.04397000	2.98501600	-1.22377800
H	2.98831300	3.23536600	-1.71993400
H	1.38671100	3.85934600	-1.28322500
H	1.58515800	2.15481800	-1.77184900
C	2.96385400	-3.38329000	1.47752700
H	4.03140000	-3.60585400	1.37430900
H	2.42844900	-4.33822900	1.49672300
H	2.81836800	-2.89299300	2.44559400
C	2.45970700	-2.51336100	0.32462100
H	1.38957400	-2.33945200	0.47664700
C	2.61128400	-3.21022700	-1.03080200
H	3.65544700	-3.47470500	-1.23028900
H	2.25782900	-2.54212300	-1.82158300
H	2.02070300	-4.13212800	-1.05725200
C	-0.00002700	-0.09034800	-0.01910800

4.3.2. (IMes)AsH

0 1

As	0.00000300	0.55604700	-1.72679900
H	-0.00008200	-0.88447400	-2.21380600
N	1.07487300	-0.20401200	0.90080500
N	-1.07487000	-0.20400200	0.90081400
C	0.00000000	-0.02422100	0.09375800
C	0.67851700	-0.49841500	2.18976900
H	1.38995300	-0.67537900	2.98093100
C	-0.67850500	-0.49841900	2.18977200
H	-1.38993600	-0.67538200	2.98093900
C	2.44499800	-0.12185800	0.47846600
C	3.08709200	1.11927700	0.50223700
C	4.43993300	1.15179200	0.17096800
H	4.95536200	2.10955100	0.17446500
C	5.14159900	-0.00197800	-0.17916700
C	4.45106200	-1.21336400	-0.21966100
H	4.97499100	-2.11725300	-0.52234400
C	3.09822800	-1.29857400	0.10263500
C	2.31985200	2.37616100	0.77837300
H	1.62451600	2.54948100	-0.05348300
H	2.98860200	3.23592800	0.85945000
H	1.72924600	2.31104700	1.69806300
C	6.60916500	0.05731100	-0.49698900
H	6.88492200	1.02262600	-0.93046900
H	6.89672100	-0.72666300	-1.20299700
H	7.21377600	-0.07941600	0.40768300
C	2.34270800	-2.58792100	-0.02539300
H	1.58406800	-2.48654900	-0.81047500
H	1.82351300	-2.86151600	0.89922500
H	3.01164600	-3.40790600	-0.29576200
C	-2.44499800	-0.12185200	0.47848300
C	-3.09819400	-1.29855300	0.10250600
C	-4.45101800	-1.21334900	-0.21979000

H	-4.97491600	-2.11721900	-0.52258700
C	-5.14159800	-0.00197800	-0.17916400
C	-4.43998100	1.15176100	0.17112200
H	-4.95544200	2.10950100	0.17473800
C	-3.08713100	1.11924800	0.50240500
C	-2.34264000	-2.58787300	-0.02559900
H	-1.82383400	-2.86174600	0.89915800
H	-1.58368900	-2.48630700	-0.81035200
H	-3.01149400	-3.40776300	-0.29646700
C	-6.60914500	0.05724500	-0.49706700
H	-7.21382200	-0.08222200	0.40714300
H	-6.89609800	-0.72510300	-1.20513000
H	-6.88542900	1.02349100	-0.92811600
C	-2.31994700	2.37613100	0.77869200
H	-2.98874300	3.23584000	0.86001300
H	-1.62472200	2.54964700	-0.05321300
H	-1.72922200	2.31088100	1.69829400

4. References

1. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
2. G. Becker, G. Gutekunst and H. J. Wessely, *Z. Anorg. Allg. Chem.*, 1980, **462**, 113-129.
3. M. Hans, J. Lorkowski, A. Demonceau and L. Delaude, *Beilstein J. Org. Chem.*, 2015, **11**, 2318-2325.
4. M. L. Cole, C. Jones and P. C. Junk, *New J. Chem.*, 2002, **26**, 1296-1303.
5. D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 831–840.
6. H. Friebolin; *Basic One and Two-Dimensional NMR Spectroscopy*, Wiley-VCH Verlag, GmbH, Third Revised Edition, Germany, **1998**; P.307-309.
7. a) *CrysAlisPRO;* Oxford Diffraction /Agilent Technologies UK Ltd, Yarnton, England. b) G. M. Sheldrick, *Acta Crystallogr, Sect. A: Found. Crystallogr.* **2008**, *64*(1), 112–122.
8. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09 Rev. D.01*, Gaussian Inc., Wallingford CT, **2009**.
9. E. D. Glendening, C. R. Landis, F. Weinhold, *J. Comput. Chem.* **2013**, *34*, 1429–1437.
10. E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 593–609.
11. E. D. Glendening, F. Weinhold, *J. Comput. Chem.* **1998**, *19*, 610–627.
12. T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.
13. S. Dapprich, G. Frenking, *J. Phys. Chem.* **1995**, *99*, 9352–9362.
14. A. D. Becke, K. E. Edgecombe, *J. Chem. Phys.* **1990**, *92*, 5397–5403.
15. a) R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928; b) R. F. W. Bader, H. Essén, *J. Chem. Phys.* **1984**, *80*, 1943.