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SUPPORTING INFORMATION

A Strained Intramolecular P/Al-FLP and its Reactivity toward Allene

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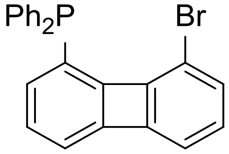
Experimental Section

General Remarks

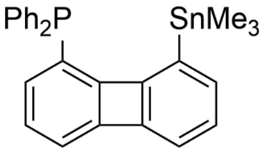
All experiments were carried out in a dry argon or nitrogen atmosphere using an MBraun glovebox, GS Glovebox Systemtechnik glovebox and/or standard Schlenk techniques. Solvents were purified employing an MBraun Solvent Purification System SPS. Elemental analyses were performed with a HEKA Euro 3000EA elemental analyzer. NMR Spectra were recorded on Bruker NMR spectrometers (Avance DPX 300 MHz, Avance 400 MHz, Avance III 500 MHz). Chemical shifts are referenced to the signal of residual protonated solvent. IR spectra were recorded on a Bruker ALPHA spectrometer with an ATR sampling unit. All materials were obtained from commercial vendors as ACS reagent-grade or better and used as received, if not stated otherwise. 1,8-Dibromobiphenylene and [8-Bromo-1-biphenylenyl]bis-2,4,6-trimethylphenylphosphine were prepared as described in literature.[S1, S2]

[8-Bromo-1-biphenylenyl]diphenylphosphine



[1-(Bromo)biphenylen-8-yl]diphenylphosphine was synthesized according to a modified literature procedure. 1,8-Dibromobiphenylene (865 mg, 2.79 mmol, 1.00 eq) was dissolved in Et_2O (50 ml) and cooled to –78 °C. *n*-Butyllithium (2.5 M in hexanes, 1.12 ml, 2.79 mmol, 1.00 eq) was added dropwise to the suspension and subsequently stirred for 2 hours at –78 °C. Chlorodiphenylphosphine (600 µl, 3.35 mmol, 1.20 eq) was added slowly and the resulting mixture was stirred for 1 hour at –78 °C. The cooling bath was removed and the reaction mixture stirred for 3 hours at room temperature. The solvent was removed *in vacuo*. Water (40 ml) and DCM (40 ml) were added. The aqueous phase was extracted with DCM (2x40 ml). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness. Column chromatography (silica, hexane 4:1 DCM) yielded the product as a bright yellow microcrystalline solid (1.06 g, 2.55 mmol, 91%). Analytical data match those reported.[S3]

[8-Trimethylstannyl-1-biphenylenyl]diphenylphosphine, 1-Ph



[1-(Bromo)biphenylen-8-yl]diphenylphosphine (800 mg, 1.93 mmol, 1.00 eq) was dissolved in dry THF (30 ml) and cooled to –78 °C. *n*-Butyllithium (925 µl, 2.31 mmol, 1.20 eq) was added slowly. The green solution was stirred for 1 hour at –78 °C. Trimethyltin chloride (460 mg, 2.31 mmol, 1.20 eq) dissolved in dry THF (5 ml) was added slowly and the mixture was allowed to warm to room temperature overnight. The solvent was removed *in vacuo*. Water (30 ml) and DCM (30 ml) was added. The aqueous phase was extracted with DCM (3x30 ml). The combined organic phases were washed with water and dried over $MgSO_4$. After evaporation, the residue was recrystallized from hot EtOH to give the product (839 mg, 1.68 mmol, 87%) as yellow crystals in two crops.

^{1}H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.43-7.37 (m, 4H, ^{Ar}H), 7.09-7.00 (m, 7H, ^{Ar}H), 6.63-6.58 (m, 1H, ^{Ar}H), 6.55 (ddd, *J* = 8.3 Hz, *J* = 4.1 Hz, *J* = 1.0 Hz, 1H, ^{Ar}H), 6.52-6.48 (m, 1H, ^{Ar}H), 6.39-6.31 (m, 2H, ^{Ar}H), 0.39 (d, *J* = 1.7 Hz, 9H, Me_3Sn).

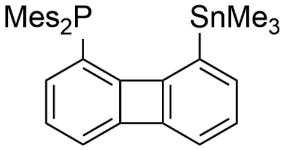
^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 298 K): δ [ppm] = 162.1 (d, *J* = 35.2 Hz), 160.5, 160.4, 151.8 (d, *J* = 13.1 Hz), 137.5 (d, *J* = 10.8 Hz), 136.6, 133.7, 133.4 (d, *J* = 18.0 Hz), 133.2 (d, *J* = 3.2 Hz), 129.0, 128.9, 128.8, 125.1 (d, *J* = 14.7 Hz), 117.7, 117.3, –6.9 (d, *J* = 12.5 Hz).

^{31}P{^{1}H} NMR (202 MHz, C_6D_6, 298 K): δ [ppm] = –21.4.

^{119}Sn{^{1}H} NMR (187 MHz, C_6D_6, 298 K): δ [ppm] = –40.6 (d, *J* = 6.4 Hz).

Elemental analysis: $C_{27}H_{25}PSn$	calculated:	C 64.97% H 5.05%
	found:	C 64.41% H 5.10%

[8-Trimethylstannyl-1-biphenylenyl]bis-2,4,6-trimethylphenylphosphine, 1-Mes



[1-(Bromo)biphenylen-8-yl]bis-2,4,6-trimethylphenylphosphine[Erker] (225 mg, 451 µmol, 1.00 eq) was dissolved in dry THF (30 ml) and cooled to –78 °C. *n*-Butyllithium (340 µl, 541 µmol, 1.20 eq) was added slowly. The dark green solution was stirred for 1 hour at –78 °C. Trimethyltin chloride (108 mg, 541 µmol, 1.20 eq) dissolved in dry THF (5 ml) was added slowly. The mixture was stirred at –78 °C for 1 hour and subsequently refluxed overnight. The solvent was removed *in vacuo*. Water (30 ml) and DCM (30 ml) was added. The aqueous phase was extracted with DCM (2x30 ml). The combined organic phases were washed with water and dried over $MgSO_4$. After evaporation, the residue was recrystallized from hot EtOH to give the product (177 mg, 303 µmol, 67%) as yellow crystals.

^1H NMR (500 MHz, C_6D_6, 296 K): δ [ppm] = 7.00 (dd, J = 8.0 Hz, J = 1.1 Hz, 1H, ^{Ar}H), 6.79 (ddd, J = 6.9 Hz, J = 4.0 Hz, J = 2.2 Hz, 1H, ^{Ar}H), 6.70 (d, J = 3.0 Hz, 4H, ^{Mes}H), 6.58 (dd, J = 8.1 Hz, J = 6.9 Hz, 1H, ^{Ar}H), 6.48 (dd, J = 6.9 Hz, J = 1.0 Hz, 1H, ^{Ar}H), 6.33-6.29 (m, 2H, ^{Ar}H), 2.31 (s, 12H, *o*-CH_3), 2.07 (s, 6H, *p*-CH_3), 0.20 (d, J = 1.0 Hz, 9H, Me_3Sn).

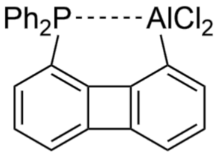
$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 296 K): δ [ppm] = 162.1 (d, J = 36.2 Hz), 160.9 (d, J = 4.0 Hz), 152.2, 151.9, 151.8, 142.5 (d, J = 15.1 Hz), 138.1, 136.7, 133.6, 133.7, 131.5, 131.4, 130.7 (d, J = 3.2 Hz), 127.4 (d, J = 17.2 Hz), 117.2, 116.7, 23.6 (d, J = 14.5 Hz), 20.9, –7.6 (d, J = 8.4 Hz).

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 296 K): δ [ppm] = –32.6 (s).

$^{119}Sn\{^1H\}$ NMR (187 MHz, C_6D_6, 296 K): δ [ppm] = –34.9 (s).

Elemental analysis: $C_{33}H_{37}PSn$	calculated:	C 67.95% H 6.39%
	found:	C 67.96% H 6.42%

[8-diphenylphosphino-1-biphenylenyl]aluminum dichloride, 2-Ph



A 1.0 M solution of methylaluminum dichloride was freshly prepared by stirring a suspension of trimethylaluminum (2 M in toluene, 500 µl, 1.00 mmol, 1.00 eq) and aluminum chloride (267 mg, 2.00 mmol, 2.00 eq) in 2.5 ml toluene for 1.5 hours. $MeAlCl_2$ thus obtained (1.0 M in toluene, 50 µl, 49.1 µmol, 1.00 eq) was added at room temperature to a pale yellow solution of $Biph(PPh_2)(SnMe_3)$, **1-Ph** (24.5 mg, 49.1 µmol, 1.00 eq), in C_6D_6 (0.6 ml); the solution turned intense yellow immediately. After 15 minutes at room temperature the solvent was removed *in vacuo* and the residue freed from Me_4Sn by drying in high vacuum for 30 minutes to quantitatively yield the bright yellow compound $Biph(PPh_2)(AlCl_2)$, **2-Ph**, with satisfactory purity. Single crystals were grown by vapor diffusion of hexane into a saturated solution of **2-Ph** in toluene.

^1H NMR (500 MHz, C_6D_6, 298 K): δ [ppm] = 7.50-7.44 (m, 4H, ^{Ar}H), 7.11 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H, ^{Ar}H), 6.99-6.96 (m, 2H, ^{Ar}H), 6.96-6.91 (m, 4H, ^{Ar}H), 6.51 (ddd, J = 7.9 Hz, J = 7.0 Hz, J = 1.7 Hz, 1H, ^{Ar}H), 6.42 (dd, J = 7.0 Hz, J = 0.7 Hz, 1H, ^{Ar}H), 6.22-6.17 (m, 3H, ^{Ar}H).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 299 K): δ [ppm] = 163.8 (d, J = 20.6 Hz), 157.9 (d, J = 9.6 Hz), 152.4 (d, J = 16.5 Hz), 150.3, 136.6 (d, J = 3.6 Hz), 133.6 (d, J = 11.2 Hz), 131.6 (d, J = 2.7 Hz), 130.4 (d, J = 2.4 Hz), 130.1 (d, J = 4.9 Hz), 129.4 (d, J = 10.3 Hz), 126.2, 125.8, 121.1 (d, J = 2.4 Hz), 120.8, 112.4, 112.1.

An ^{27}Al NMR signal could not be detected.

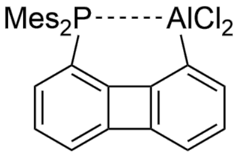
$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 299 K): δ [ppm] = –19.1 (bs).

ATR-IR (solid obtained from DCM-d_2 solution): ν [cm^{-1}] = 3057 (w), 1665 (w), 1483 (w), 1437 (m), 1373 (s), 1269 (m), 1207 (m), 1147 (w), 1096 (m), 1065 (w), 1000 (w), 951 (m), 902 (w), 833 (m), 761 (m), 742 (vs), 710 (vs), 690 (vs), 629 (m), 585 (m), 502 (vs), 480 (vs), 441 (s).

Elemental analysis: $C_{24}H_{16}AlCl_2P$	calculated:	C 66.54% H 3.72%
	found:	C 64.90% H 3.92%

(The carbon value was reproducibly below the range usually considered as acceptable, regardless of whether crystals or the oil obtained after evaporation of the reaction mixture was used.)

[8-bis(2,4,6-trimethylphenyl)phosphino-1-biphenylenyl]aluminum dichloride, 2-Mes



$MeAlCl_2$ (1.0 M in toluene, 40 µl, 39.6 µmol, 1.00 eq) was added at room temperature to a pale yellow solution of Biph($PMes_2$)($SnMe_3$), **1-Mes** (23.1 mg, 39.6 µmol, 1.00 eq), in C_6D_6 (0.6 ml). After 30 minutes at room temperature the solvent was removed *in vacuo* and the residue freed from Me_4Sn by drying in high vacuum for 30 minutes to quantitatively yield the bright yellow compound Biph($PMes_2$)($AlCl_2$), **2-Mes**, with satisfactory purity.

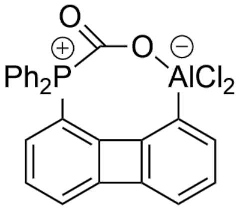
^1H NMR (500 MHz, C_6D_6, 296 K): δ [ppm] = 7.24 (d, J = 8.0 Hz, ^{Ar}H), 6.64-6.59 (m, 2H, ^{Ar}H+^{Mes}H), 6.58-6.54 (m, 2H, ^{Ar}H+^{Mes}H), 6.48 (bs, 1H, ^{Mes}H),6.46 (dd, J = 7.0 Hz, J = 0.7 Hz, 1H, ^{Ar}H), 6.40 (d, J = 3.9 Hz, ^{Mes}H), 6.16-6.14 (m, 2H, ^{Ar}H), 2.69 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.84 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 296 K): δ [ppm] = 160.6 (d, J = 19.9 Hz), 158.0 (d, J = 8.3 Hz), 151.8 (d, J = 16.5 Hz), 149.9, 142.3, 142.1, 142.0, 141.9, 141.4 (d, J = 3.1 Hz), 140.9, 140.7, 136.5 (d, J = 3.6 Hz), 132.0 (d, J = 8.2 Hz), 131.3 (d, J = 6.8 Hz), 131.2 (d, J = 10.0 Hz), 131.0 (d, J = 8.8 Hz), 130.2 (d, J = 2.5 Hz), 129.9 (d, J = 4.1 Hz), 129.8 (d, J = 4.7 Hz), 125.8 (d, J = 44.8 Hz), 122.4 (d, J = 37.6 Hz), 120.3, 120.0 (d, J = 2.7 Hz),117.6, 117.3, 25.6, 24.5 (d, J = 14.5 Hz), 24.2, 23.8 (d, J = 11.3 Hz), 20.9, 20.7.

An ^{27}Al NMR signal could not be detected.

$^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6, 296 K): δ [ppm] = –23.9 (bs).

Carbon dioxide adduct, 3-Ph



A solution of [8-diphenylphosphino-1-biphenylenyl]aluminum dichloride in DCM-d_2 was subjected to three cycles of freeze-pump-thaw degassing. $^{13}CO_2$ was added (2 bar) and the vessel was shaken a few times leading to an intense yellow solution of the compound Biph($PPh_2CO_2AlCl_2$), **3-Ph**.

^{1}H NMR (500 MHz, DCM-d_2, 298 K): δ [ppm] = 7.85 (td, J = 7.3 Hz, J = 1.8 Hz, 2H, ^{Ar}H), 7.78-7.67 (m, 8H, ^{Ar}H), 7.15 (dd, J = 7.9 Hz, J = 1.0 Hz, 1H, ^{Ar}H), 6.87-6.80 (m, 3H, ^{Ar}H), 6.77 (dd, J = 7.0 Hz, J = 1.0 Hz, 1H, ^{Ar}H), 6.30 (dd, J = 11.3 Hz, J = 8.1 Hz, 1H, ^{Ar}H).

^{13}C{^{1}H} NMR (126 MHz, DCM-d_2, 299 K): δ [ppm] = 164.4 (d, J = 8.8 Hz), 159.5 (bs, P–$^{13}CO_2$), 156.9 (d, J = 4.1 Hz), 154.2, 154.1 (m), 150.2, 138.7, 135.7, 134.9, 134.8, 134.2 (d, J = 17.9 Hz), 130.7, 130.6, 130.0, 129.9, 120.8 (d, J = 3.0 Hz), 118.9.

^{27}Al NMR (104 MHz, DCM-d_2, 298 K): δ [ppm] = 103.7 (s)

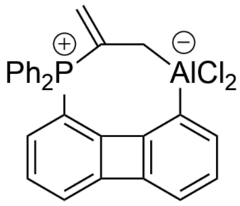
^{31}P{^{1}H} NMR (202 MHz, DCM-d_2, 299 K): δ [ppm] = 3.4 (bs).

ATR-IR (solid obtained from DCM-d_2 solution): ν [cm^{-1}] = 3057 (w), 2924 (w), 2853 (w), 1680 (m), 1598 (m), 1540 (w), 1482 (w), 1439 (m), 1371 (m), 1261 (m), 1241 (m), 1212 (w), 1108 (m), 1098 (m), 1075 (w), 1016 (w), 998 (w), 967 (w), 953 (m), 863 (m), 802 (m), 767 (m), 745 (s), 731 (s), 706 (s), 684 (s), 618 (m), 584 (m), 563 (m), 500 (vs), 447 (m), 424 (w).

For the $^{12}CO_2$ adduct: ν [cm^{-1}] = 3059 (w), 2924 (w), 2853 (w), 1720 (m), 1643 (m), 1586 (w), 1482 (w), 1439 (m), 1408 (w), 1373 (m), 1261 (s), 1212 (w), 1110 (m), 1075(w), 1024 (w), 998 (w), 967 (m), 953 (m), 863 (m), 812 (m), 767 (m), 745 (s), 731 (s), 706 (s), 686 (s), 620 (m), 586 (m), 563 (m), 502 (vs), 406 (w)

Elemental analysis: $C_{24}H_{16}AlCl_2P$	calculated:	C 62.92% H 3.38%
	found:	C 62.94% H 3.43%

Allene adduct, 4-Ph

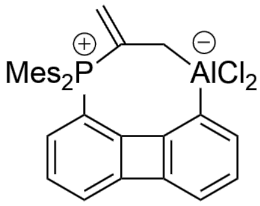


A solution of [8-diphenylphosphino-1-biphenylenyl]aluminum dichloride in C_6D_6 (prepared from 27.4 mg (54.8 µmol) **1-Ph**) was subjected to three cycles of freeze-pump-thaw degassing. Propadiene was added (1.6 bar) and the NMR tube was shaken a few times. After 3 days at 70 °C the solvent was removed *in vacuo* to obtain a crude sample of **4-Ph** as a yellow oil in a yield of ~90% determined by integration of its $^{31}P\{^1H\}$-NMR spectrum. Attempts to develop a reliable work-up procedure to isolate the product in pure form were unsuccessful.

^1H NMR (300 MHz, DCM-d_2, 293 K): δ [ppm] = 7.84-7.74 (m, 2H, ^{Ar}H), 7.70-7.61 (m, 7H, ^{Ar}H), 7.23 (dd, J = 7.8 Hz, J = 1.2 Hz, 1H, ^{Ar}H), 6.86-6.70 (m, 4H, ^{Ar}H), 6.52 (d, J = 52.3 Hz, 1H, $^{Allene}CH$), 6.38 (ddd, J = 10.8 Hz, J = 7.4 Hz, J = 2.0 Hz, 1H, ^{Ar}H), 5.42 (d, J = 24.2 Hz, 1H, $^{Allene}CH$), 1.49 (dd, J = 19.7 Hz, J = 1.3 Hz, 2H, $^{Allene}CH$).

$^{31}P\{^1H\}$ NMR (121 MHz, DCM-d_2, 293 K): δ [ppm] = 23.4 (s).

Allene adduct, 4-Mes



A solution of [8-bis(2,4,6-trimethylphenyl)phosphino-1-biphenylenyl]aluminum dichloride in C_6D_6 (prepared from 20.0 mg (34.3 µmol) **1-Mes**) was subjected to three cycles of freeze-pump-thaw degassing. Propadiene was added (1.6 bar) and the NMR tube was shaken a few times. After 16 h at room temperature the precipitate was collected, washed with toluene (2x0.5 ml) and dried *in vacuo*. This yielded the pure allene adduct **4-Mes** in form of a pale yellow solid (13.6 mg, 24.4 µmol, 71%).

^{1}H NMR (500 MHz, DCM-d_2, 298 K): δ [ppm] = 7.25 (dd, J = 7.9 Hz, J = 1.1 Hz, 1H, $^{\mathrm{Ar}}$H), 7.04 (d, J = 4.3 Hz, 4H, $^{\mathrm{Mes}}$H), 6.82 (dd, J = 7.9 Hz, J = 7.0 Hz, 1H, $^{\mathrm{Ar}}$H), 6.70-6.63 (m, 3H, $^{\mathrm{Ar}}$H), 6.49 (ddd, J = 12.7 Hz, J = 7.8 Hz, J = 1.8 Hz, 1H, $^{\mathrm{Ar}}$H), 6.47 (dd, J = 51.0 Hz, J = 1.5 Hz, 1H, $^{\mathrm{Allene}}$CH), 5.77 (d, J = 22.4 Hz, 1H, $^{\mathrm{Allene}}$CH), 2.34 (s, 6H, p-CH_3), 2.27 (s, 12H, o-CH_3), 1.19 (dd, J = 18.0 Hz, J = 1.4 Hz, 2H, $^{\mathrm{Allene}}CH_2$).

^{13}C{^{1}H} NMR (126 MHz, DCM-d_2, 298 K): δ [ppm] = 162.7 ($^{\mathrm{quart}}$C), 157.6 (d, J = 3.8 Hz, $^{\mathrm{quart}}$C), 153.7 (d, J = 14.1 Hz, $^{\mathrm{quart}}$C), 149.6 ($^{\mathrm{quart}}$C), 144.7 (d, J = 2.9 Hz, $^{\mathrm{quart}}$C), 144.2 (d, J = 9.4 Hz, $^{\mathrm{quart}}$C), 139.3 (CH), 133.3 (d, J = 11.4 Hz, CH), 133.0 (d, J = 10.1 Hz, $^{\mathrm{Allene}}CH_2$), 131.5 (d, J = 12.3 Hz, CH), 129.8 (d, J = 56.9 Hz, $^{\mathrm{Allene}}$C), 129.3 (CH), 129.2 (CH), 128.6 ($^{\mathrm{quart}}$C), 118.4 (d, J = 2.9 Hz, CH), 118.2 (d, J = 81.2 Hz, $^{\mathrm{quart}}$C), 117.4 (CH), 115.8 (d, J = 79.4 Hz, $^{\mathrm{quart}}$C), 25.0 (d, J = 4.7 Hz, o-CH_3), 21.2 (p-CH_3), 19.7 (very broad, $^{\mathrm{Allene}}CH_2$–Al).

^{27}Al NMR signal could not be detected.

^{31}P{^{1}H} NMR (202 MHz, DCM-d_2, 298 K): δ [ppm] = 13.3 (s).

ATR-IR (solid obtained from DCM-d_2 solution): ν [cm^{-1}] = 2990 (w), 2918 (w), 1602 (w), 1555 (w), 1447 (m), 1369 (m), 1286 (w), 1208 (m), 1049 (w), 1000 (w), 963 (m), 936 (m), 914 (m), 855 (s), 778 (m), 761 (s), 708 (s), 688 (m), 651 (s), 622 (s), 598 (s), 573 (s), 547 (m), 514 (m), 473 (vs), 441 (m), 429 (s).

Elemental analysis: $C_{33}H_{32}AlCl_2P$	calculated:	C 71.10% H 5.79%
	found:	C 71.11% H 6.10%

NMR Spectra

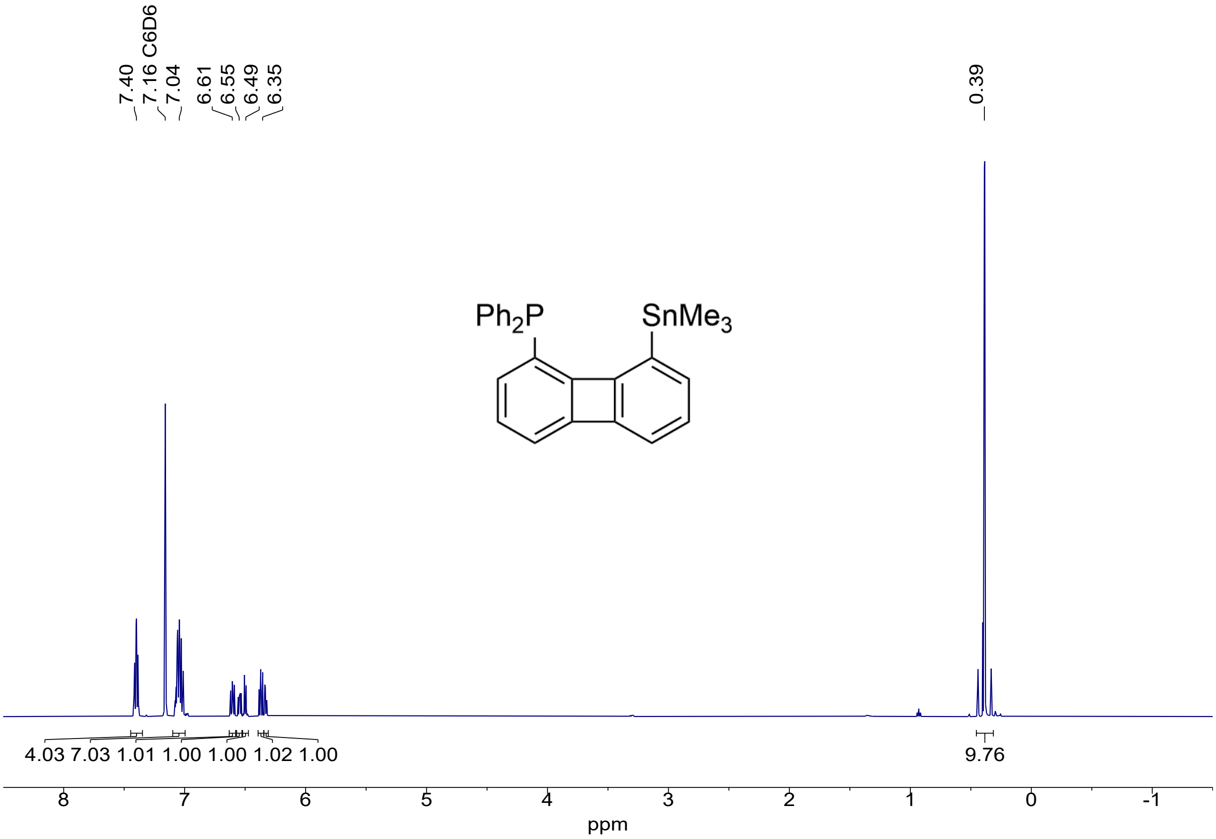


Figure S1. ^{1}H NMR spectrum of **1-Ph** (500 MHz, C_6D_6, 298 K).

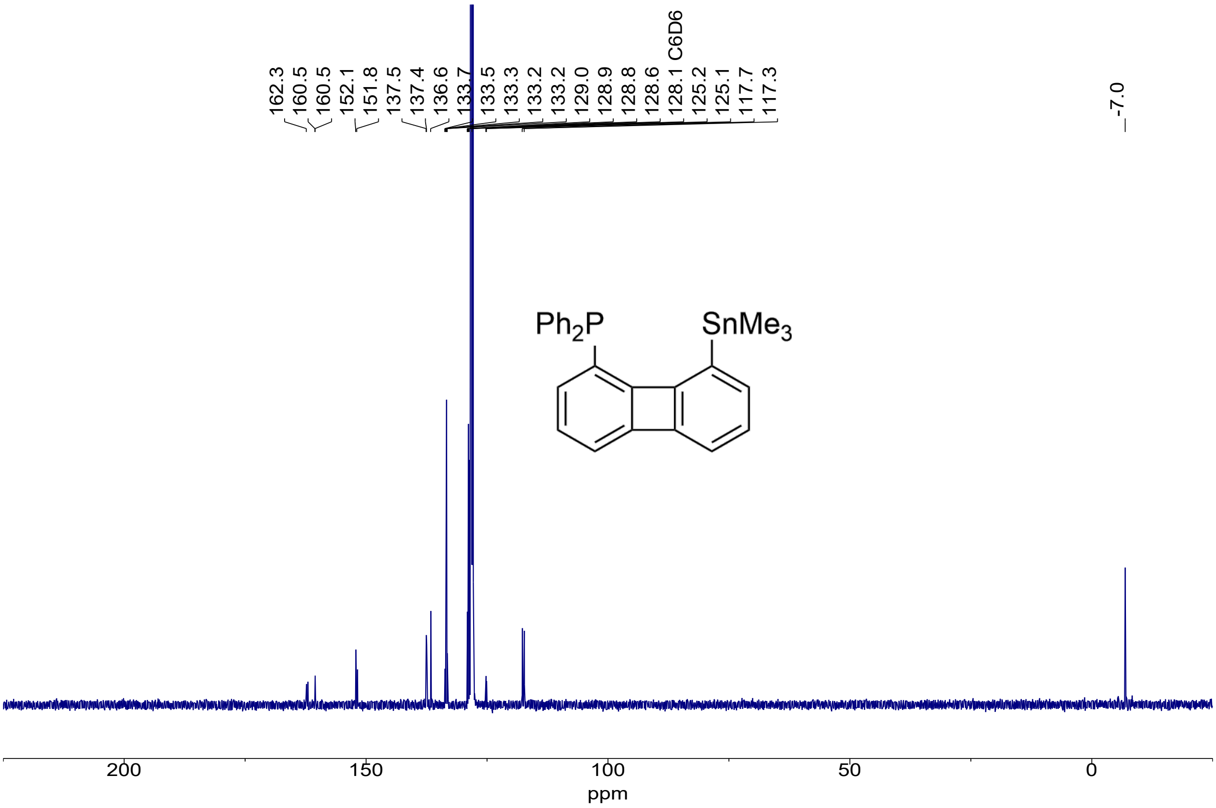


Figure S2. $^{13}C\{^1H\}$ NMR spectrum of **1-Ph** (126 MHz, C_6D_6, 298 K).

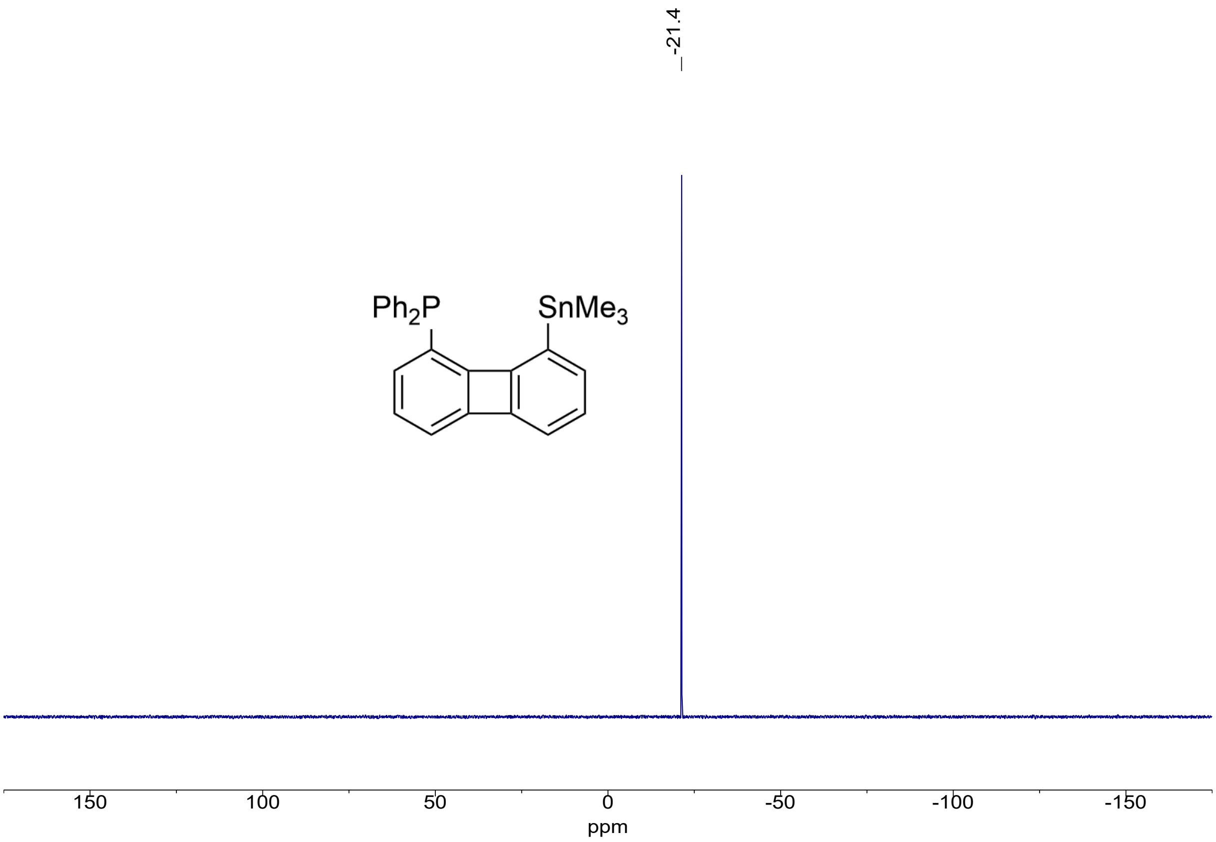


Figure S3. $^{31}P\{^1H\}$ NMR spectrum of **1-Ph** (202 MHz, C_6D_6, 298 K).

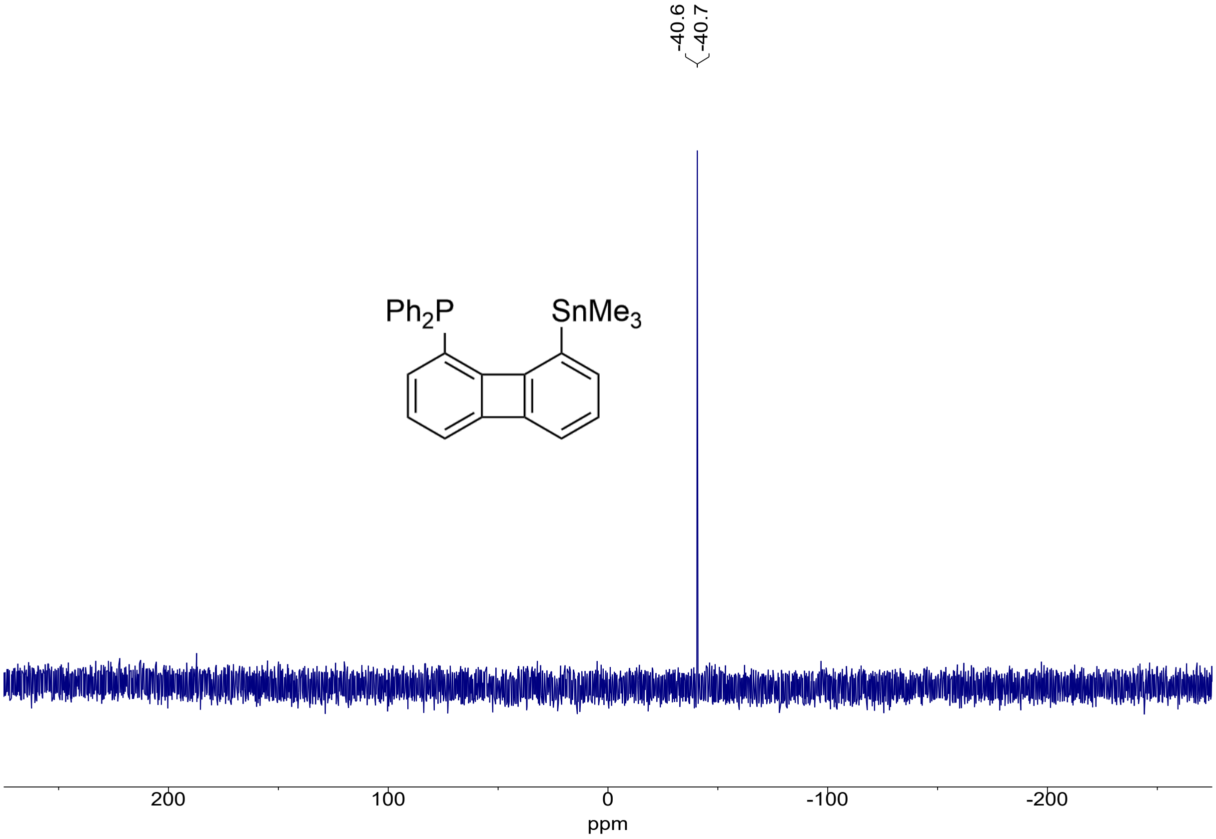


Figure S4. $^{119}Sn\{^1H\}$ NMR spectrum of **1-Ph** (187 MHz, C_6D_6, 298 K).

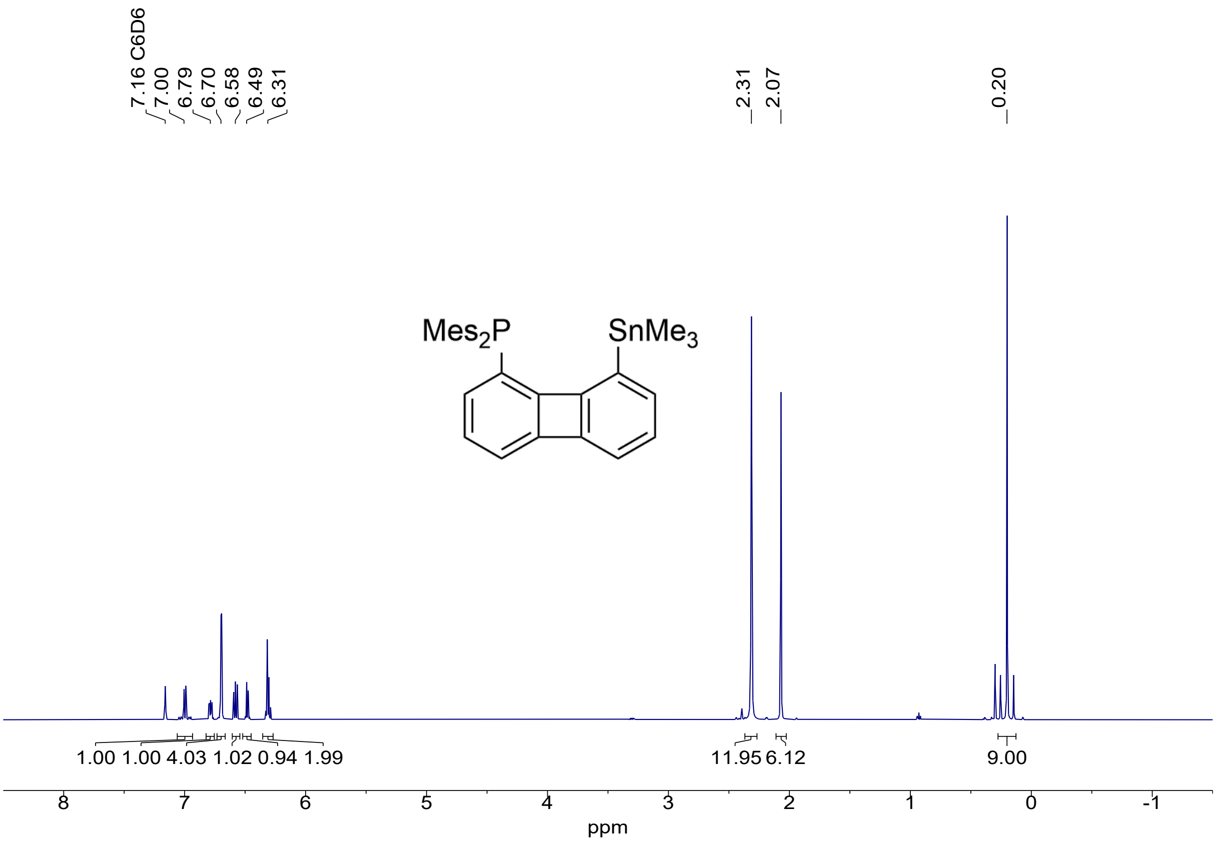


Figure S5. ^{1}H NMR spectrum of **1-Mes** (500 MHz, C_6D_6, 296 K).

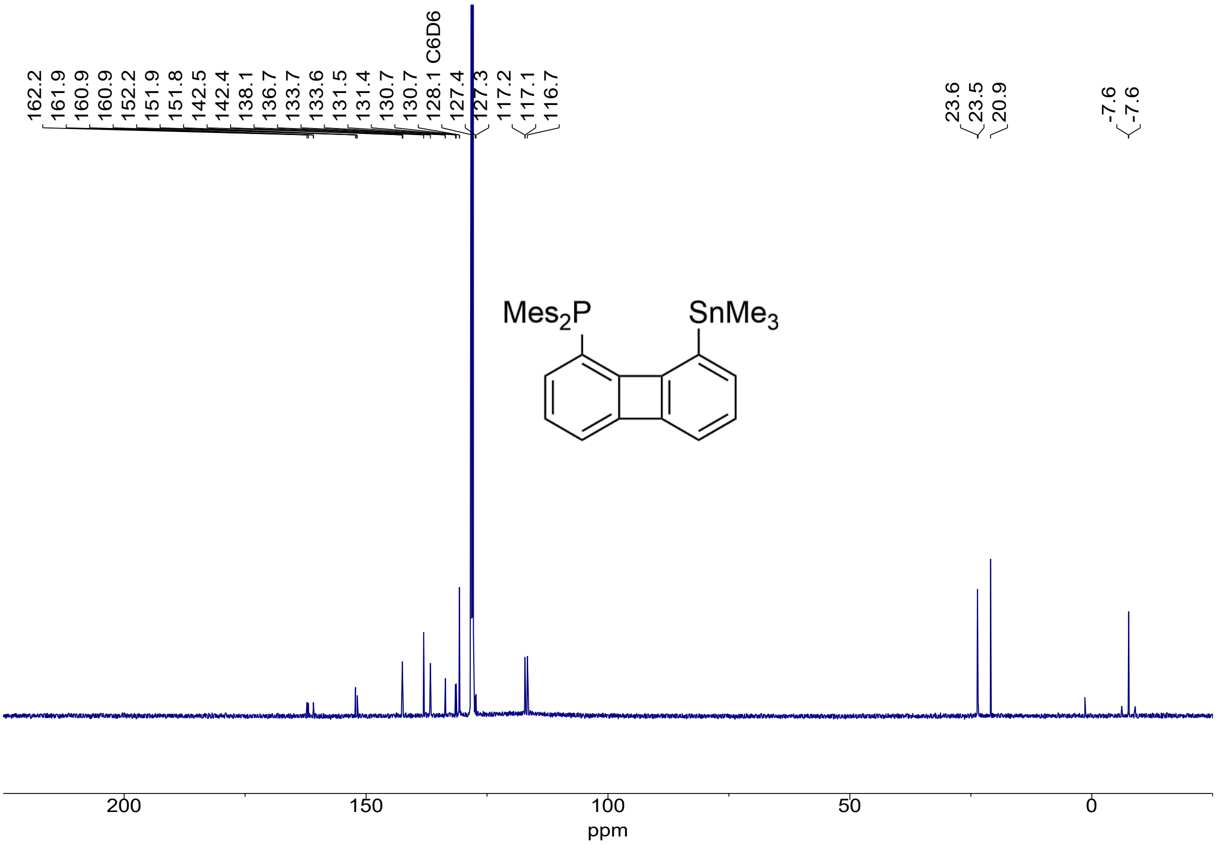


Figure S6. $^{13}C\{^1H\}$ NMR spectrum of **1-Mes** (126 MHz, C_6D_6, 296 K).

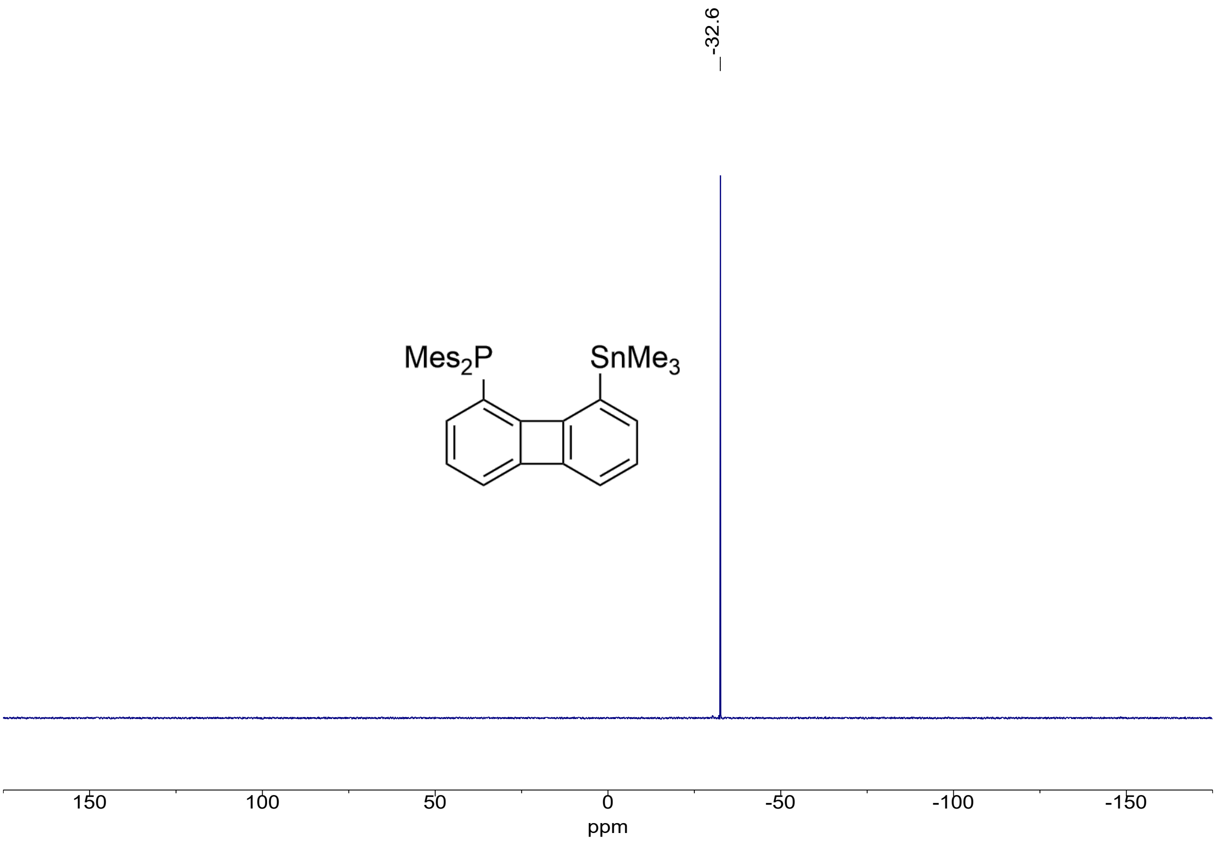


Figure S7. $^{31}P\{^1H\}$ NMR spectrum of **1-Mes** (202 MHz, C_6D_6, 296 K).

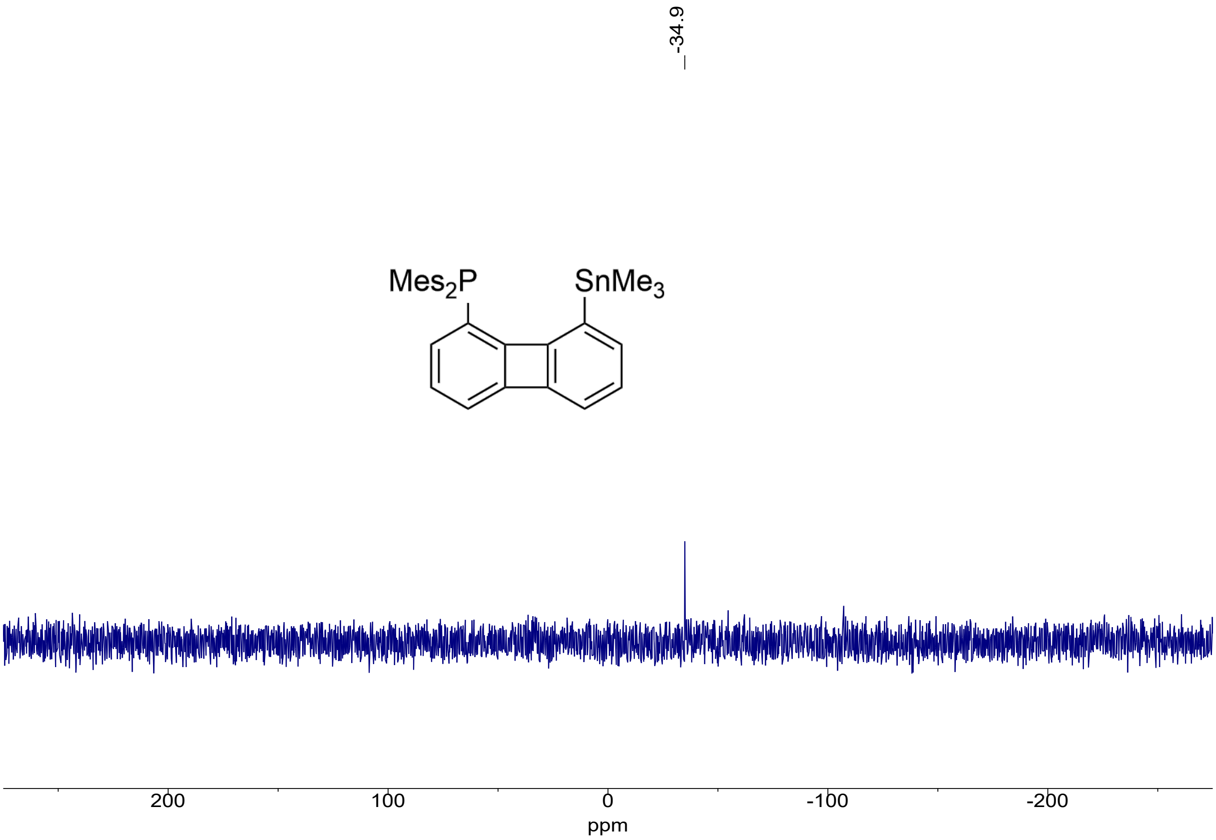


Figure S8. $^{119}Sn\{^1H\}$ NMR spectrum of **1-Mes** (187 MHz, C_6D_6, 296 K).

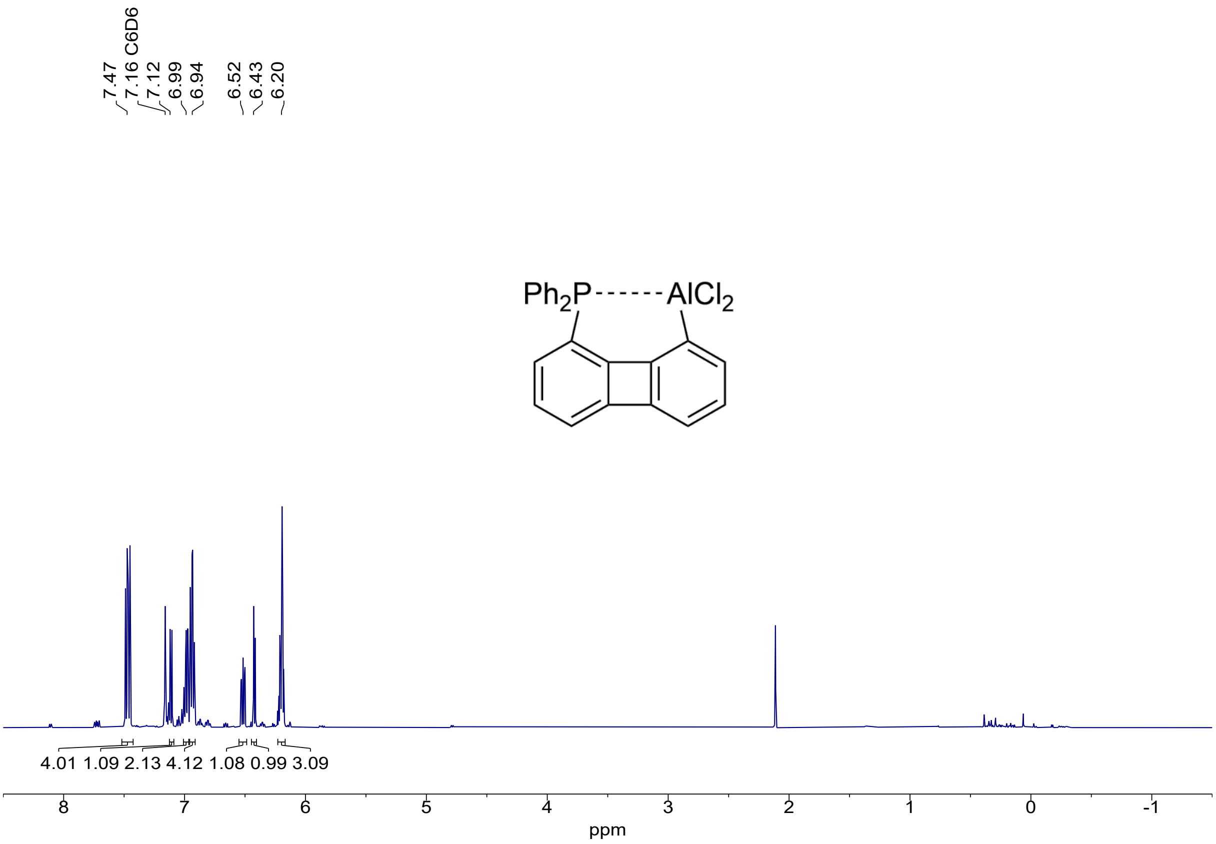


Figure S9. ^{1}H NMR spectrum of **2-Ph** (500 MHz, C_6D_6, 298 K).

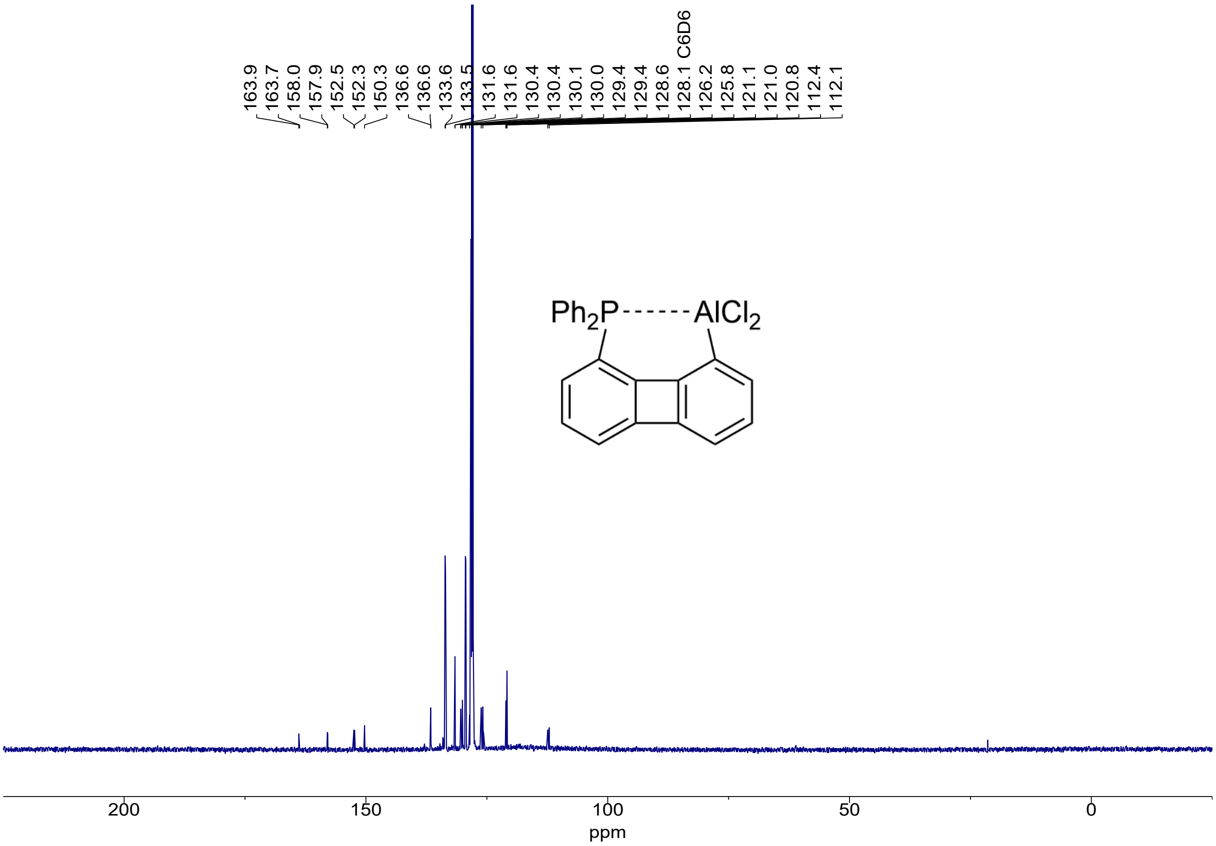


Figure S10. $^{13}C\{^1H\}$ NMR spectrum of **2-Ph** (126 MHz, C_6D_6, 299 K).

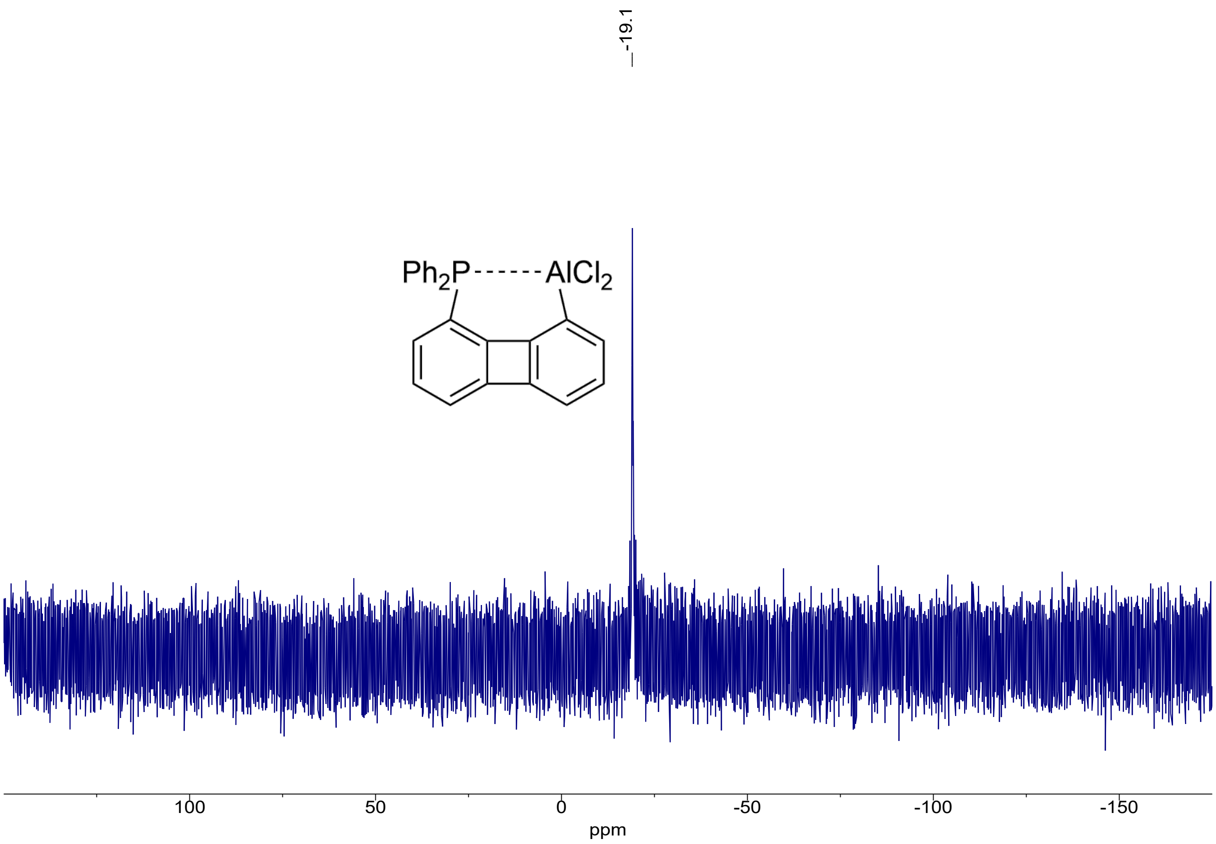


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **2-Ph** (202 MHz, C_6D_6, 299 K).

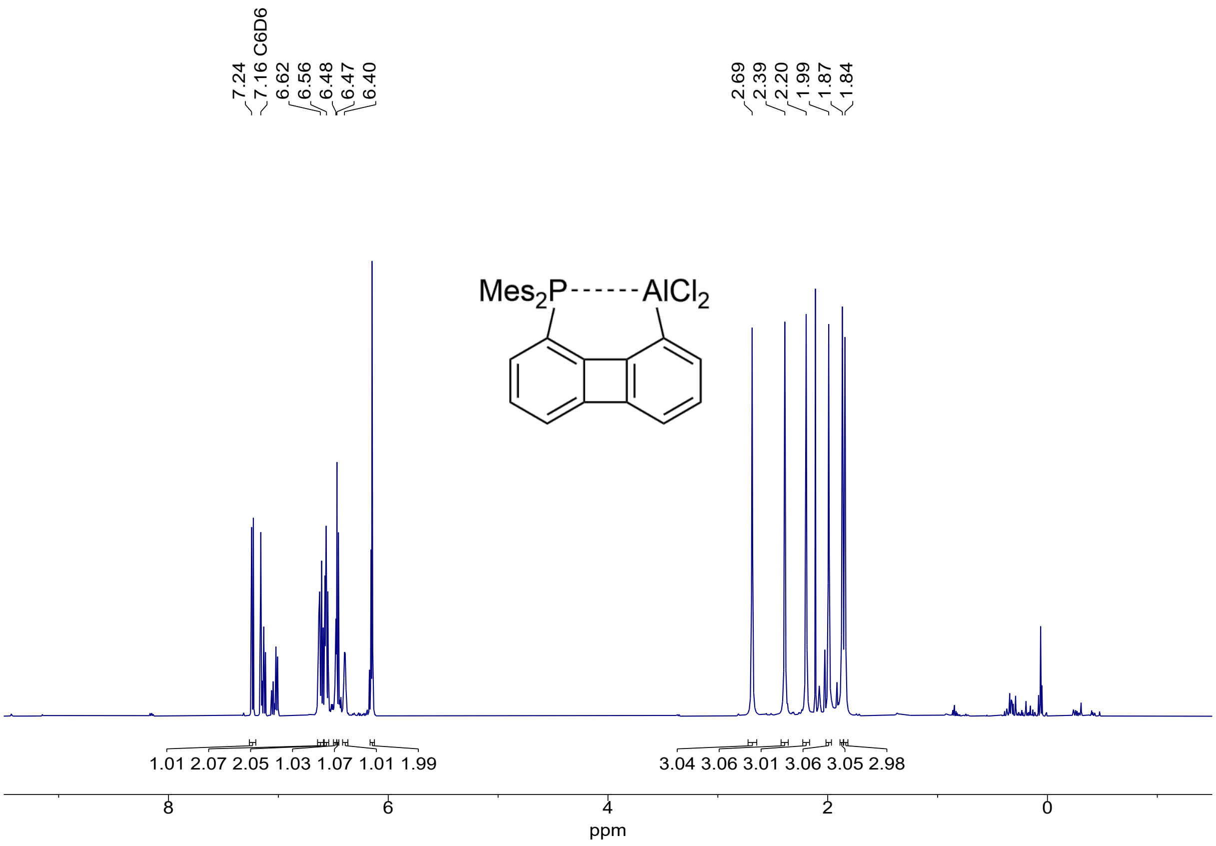


Figure S12. ^{1}H NMR spectrum of **2-Mes** (500 MHz, C_6D_6, 296 K).

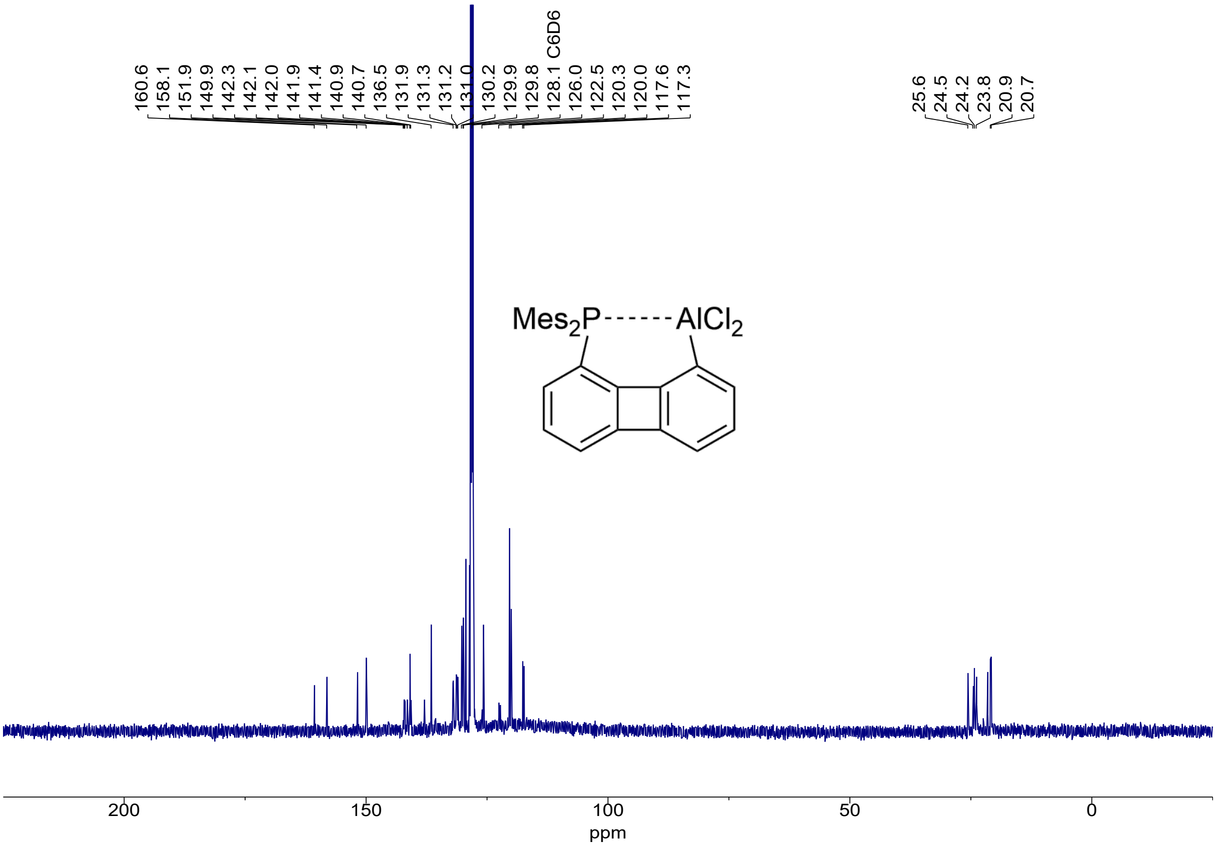


Figure S13. $^{13}C\{^1H\}$ NMR spectrum of **2-Mes** (126 MHz, C_6D_6, 296 K).

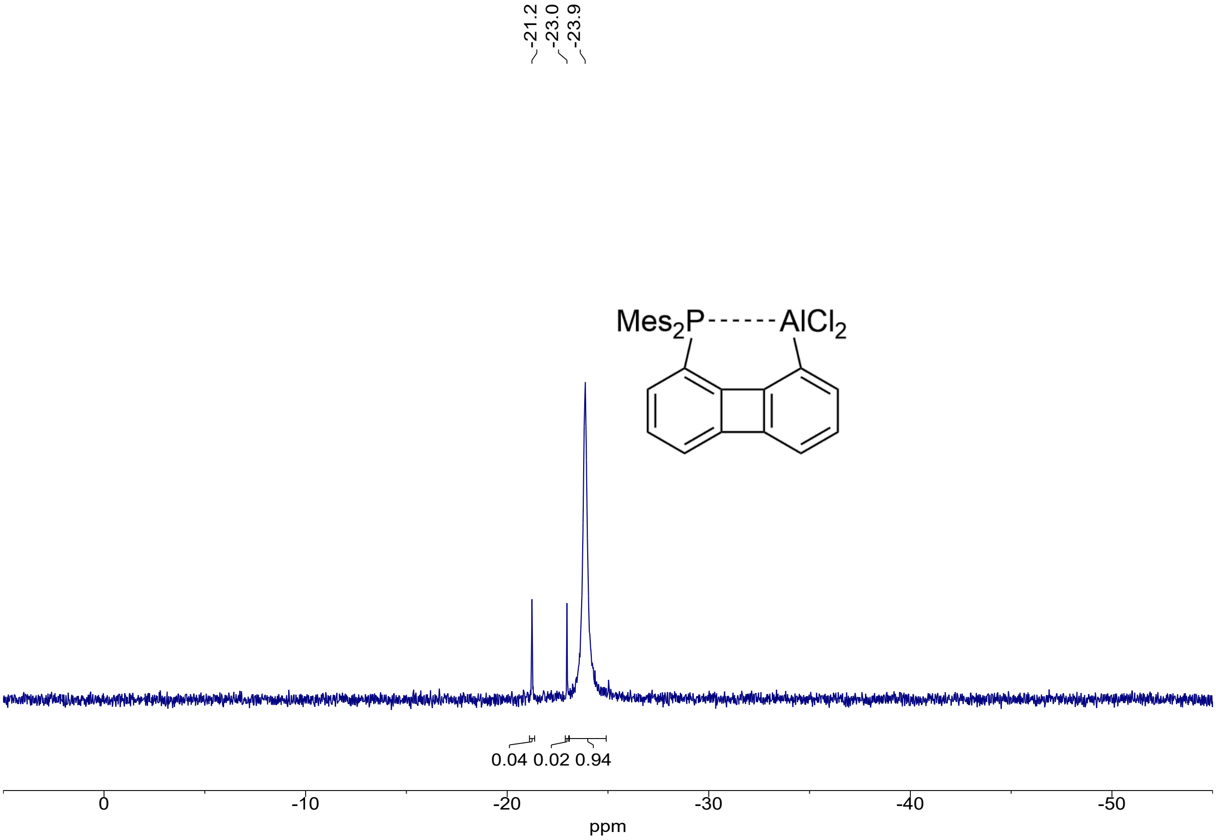


Figure S14. $^{31}P\{^1H\}$ NMR spectrum (202 MHz, C_6D_6, 296 K) of **2-Mes** (minor impurities result from hydrolysis of the Al–C bond).

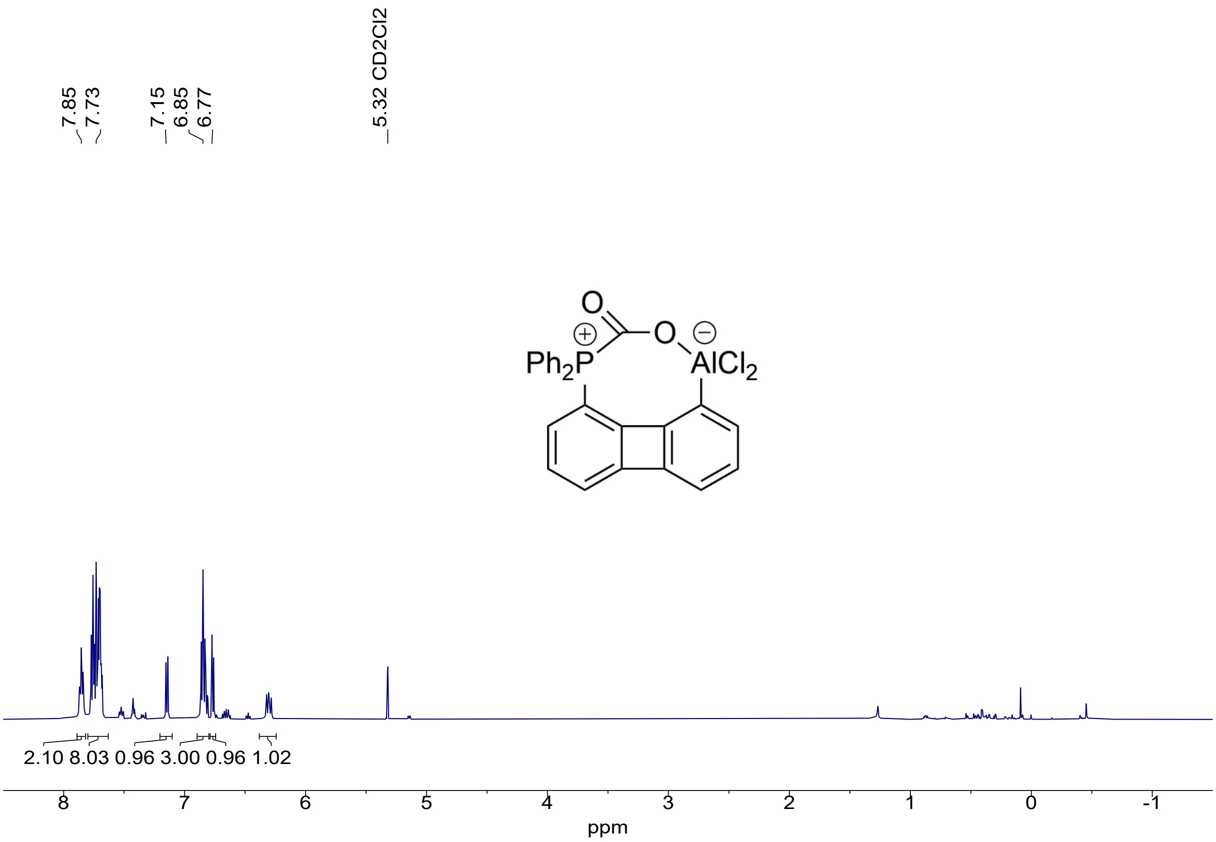


Figure S15. ^{1}H NMR spectrum of **3-Ph** (500 MHz, DCM-*d*$_2$, 298 K).

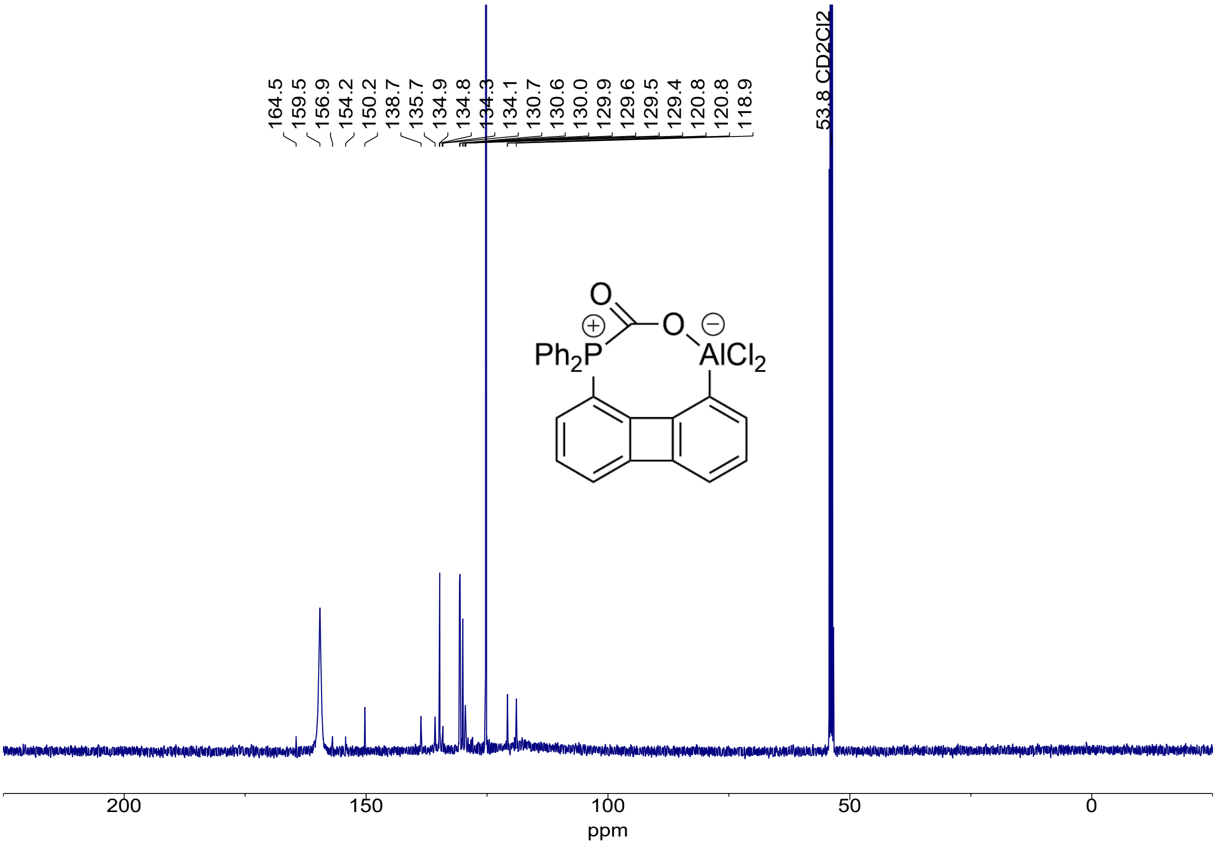


Figure S16. ^{13}C{^{1}H} NMR spectrum of **3-Ph** (126 MHz, DCM-*d*$_2$, 299 K).

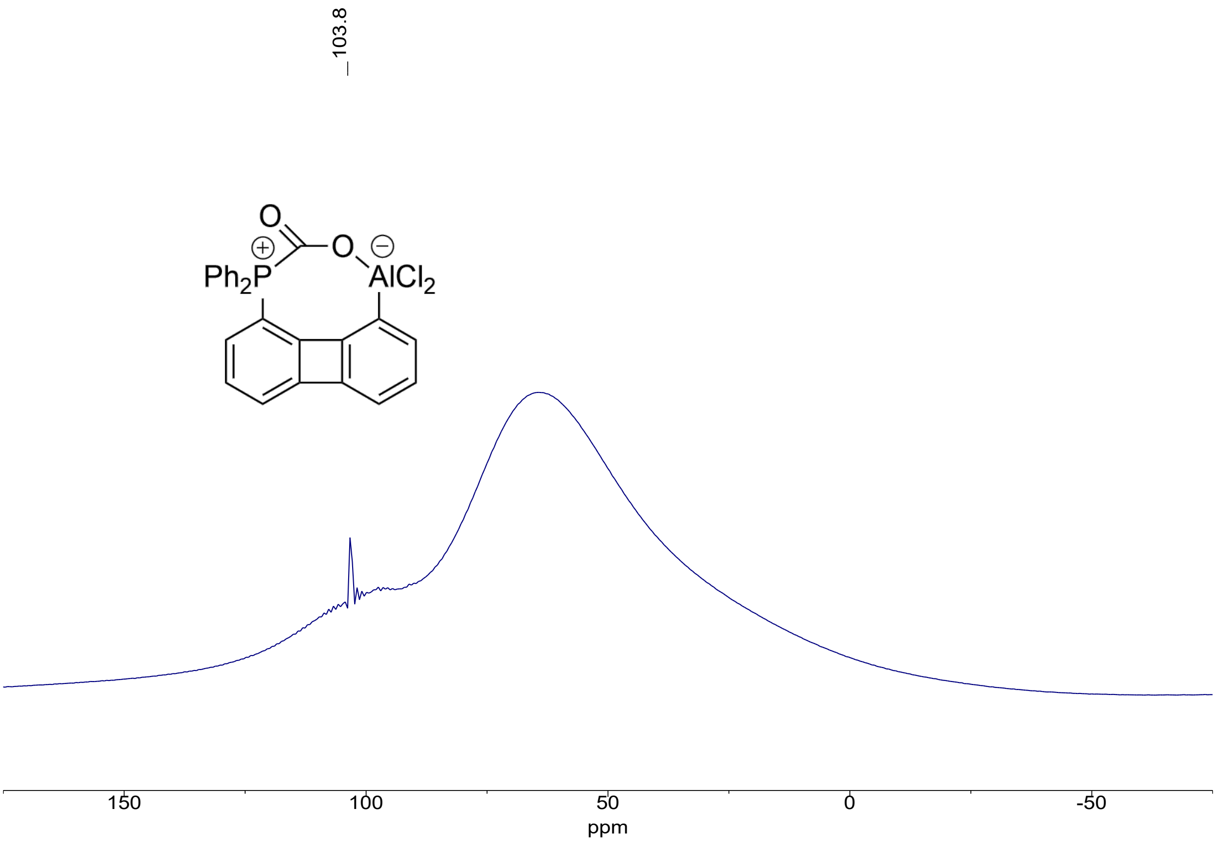


Figure S17. ^{27}Al NMR spectrum of **3-Ph** (104 MHz, DCM-d_2, 298 K).

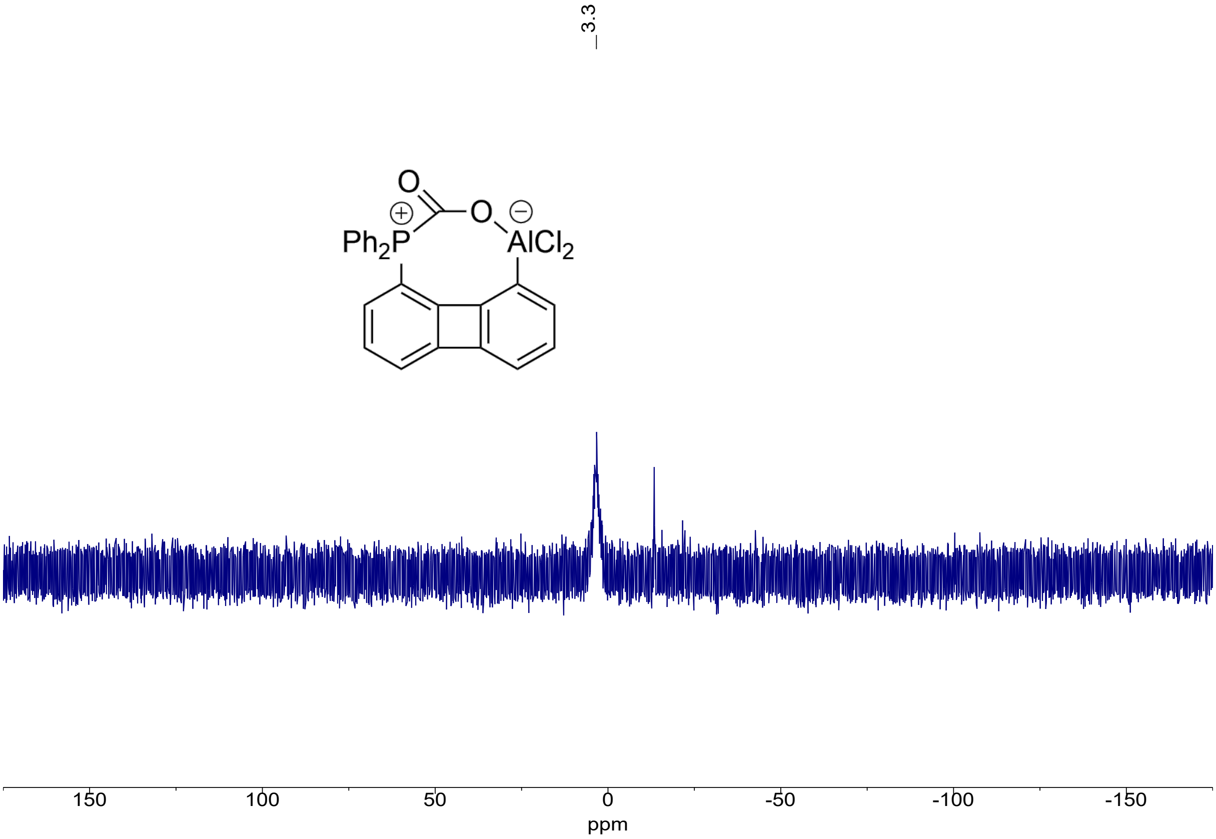


Figure S18. ^{31}P{^{1}H} NMR spectrum of **3-Ph** (202 MHz, DCM-d_2, 299 K).

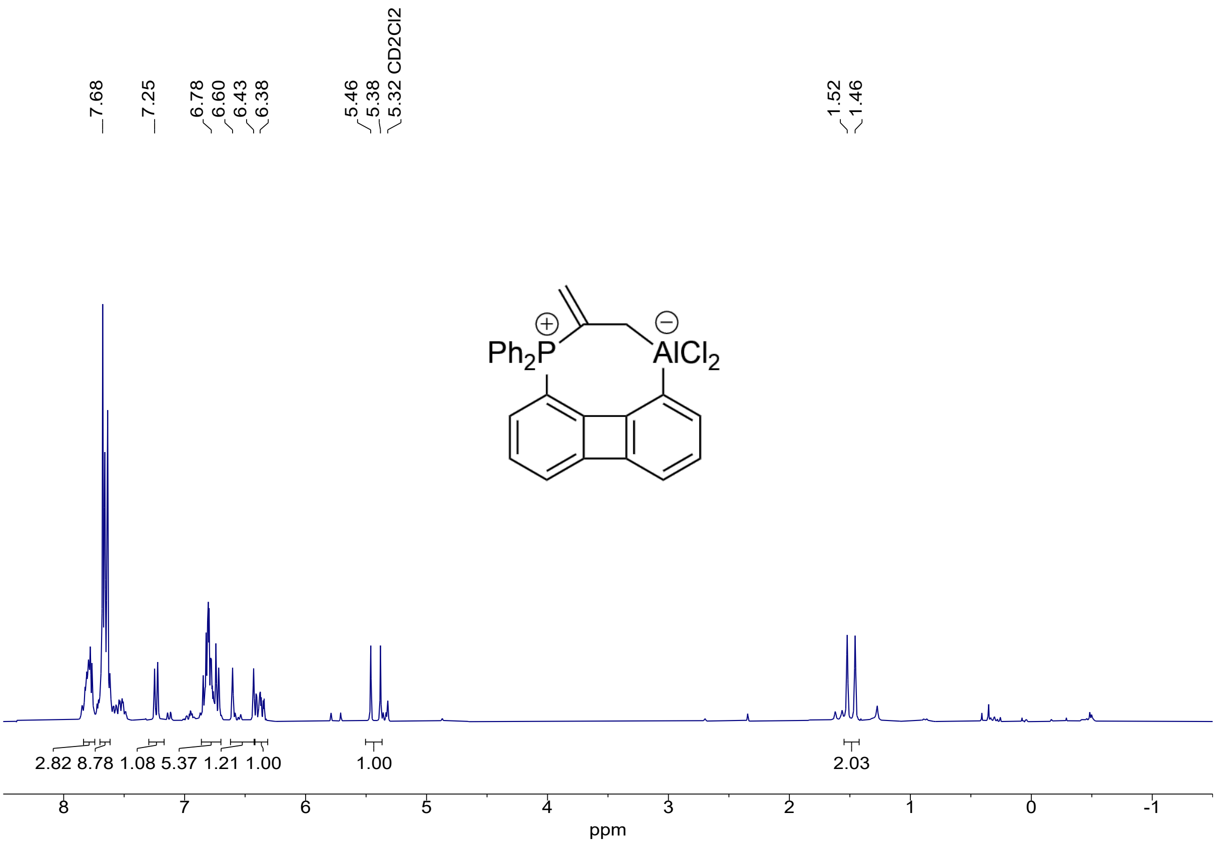


Figure S19. ^{1}H NMR spectrum of a crude sample of **4-Ph** (300 MHz, DCM-d_2, 293 K).

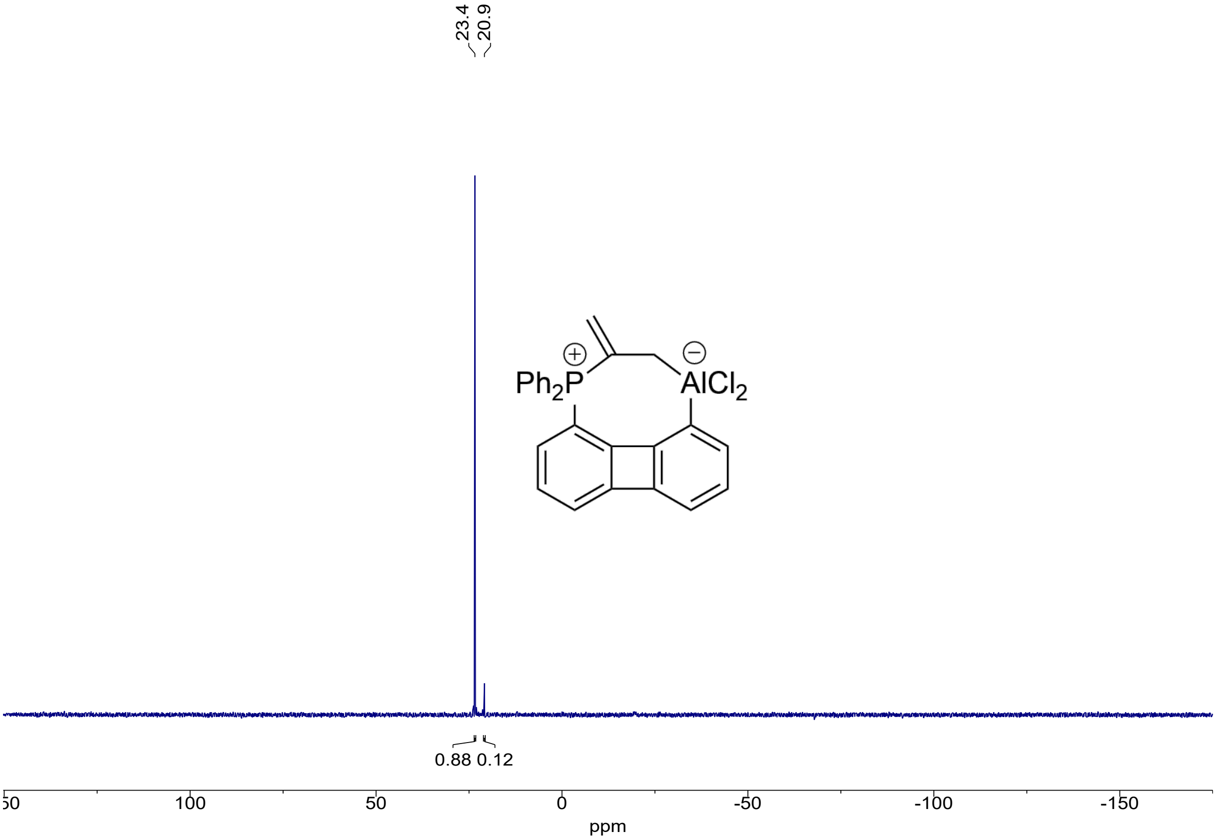


Figure S20. ^{31}P{^{1}H} NMR spectrum of a crude sample of **4-Ph** (121 MHz, DCM-d_2, 293 K).

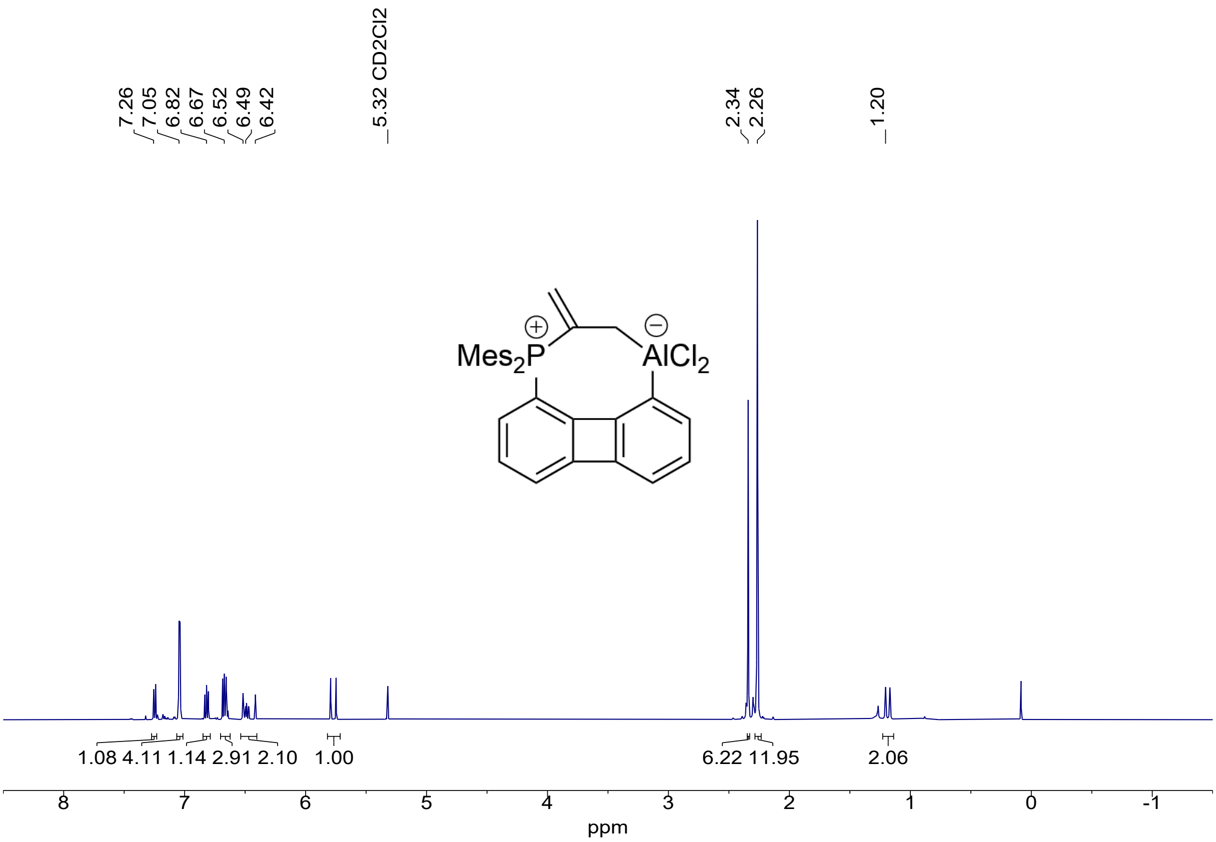


Figure S21. ^{1}H NMR spectrum of **4-Mes** (500 MHz, DCM-d_2, 298 K).

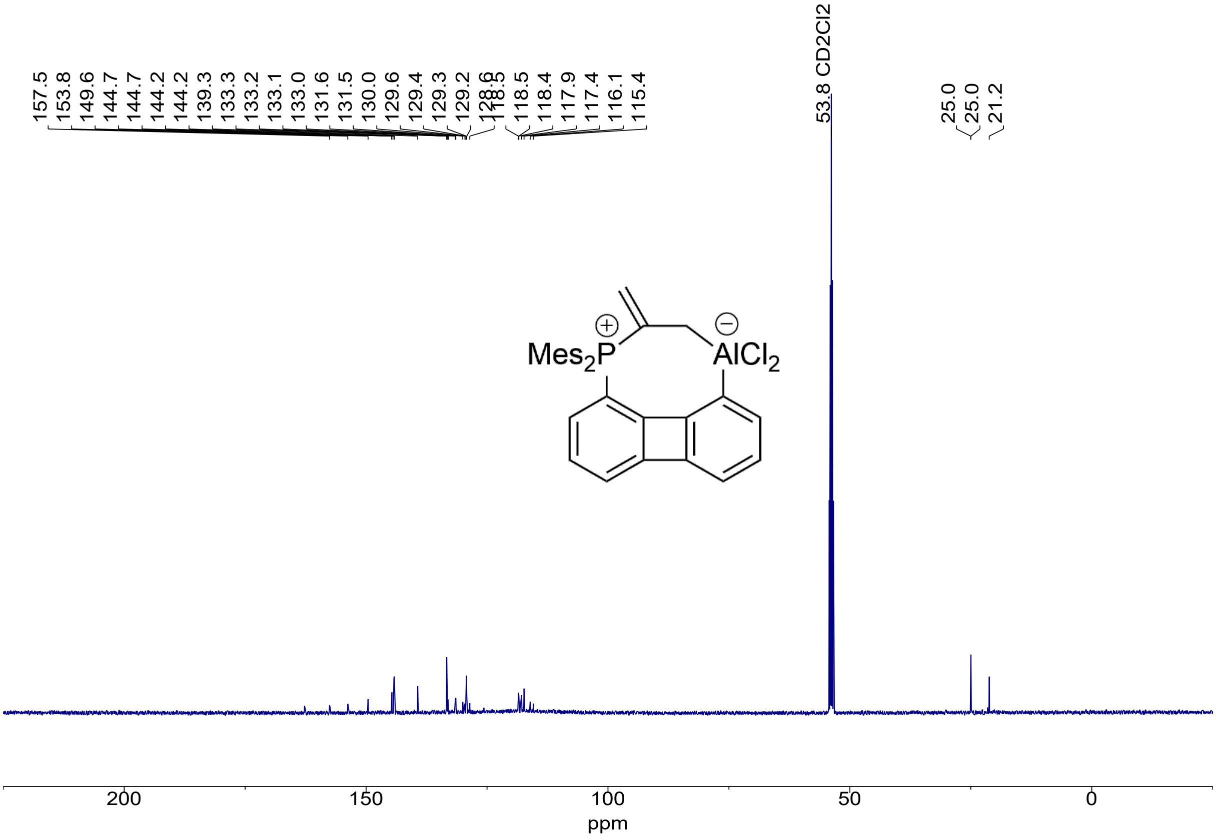


Figure S22. $^{13}C\{^1H\}$ NMR spectrum of **4-Mes** (126 MHz, DCM-d_2, 298 K).

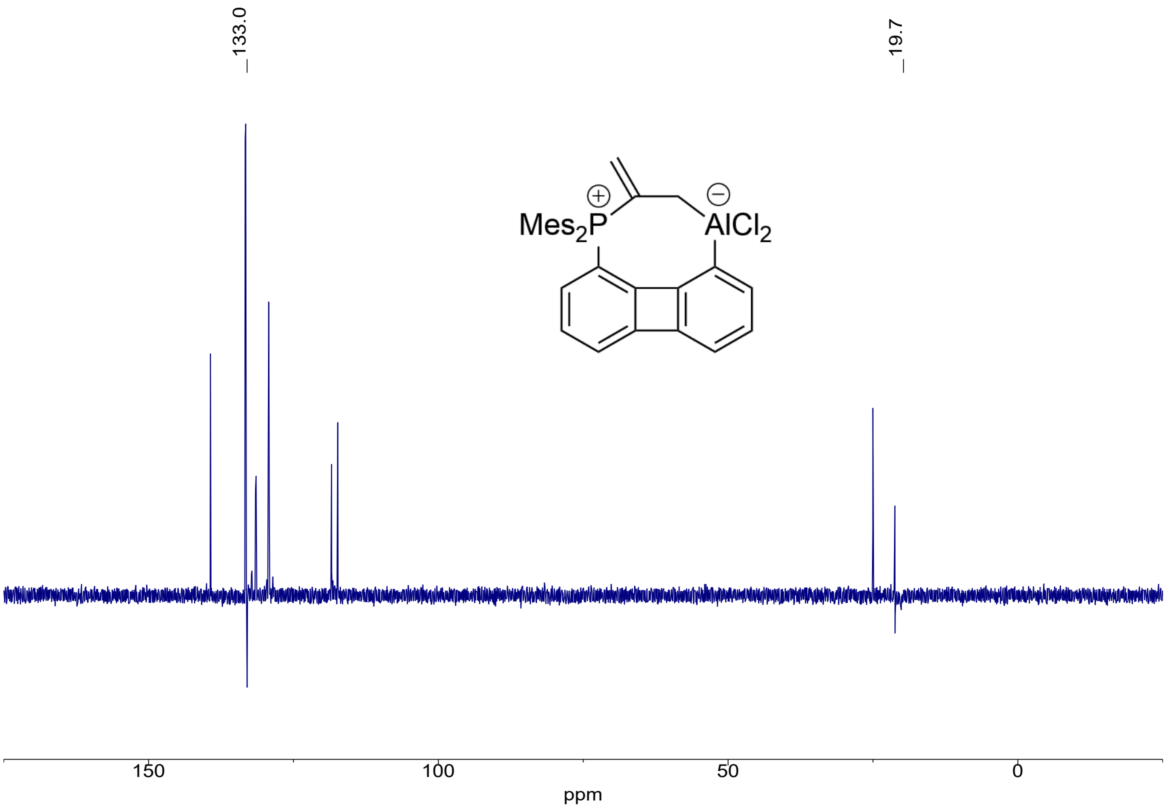


Figure S23. DEPT135 spectrum of **4-Mes** (126 MHz, DCM-d_2, 298 K). Resonances with negative intensity belonging to methylene units have been labeled with their chemical shifts.

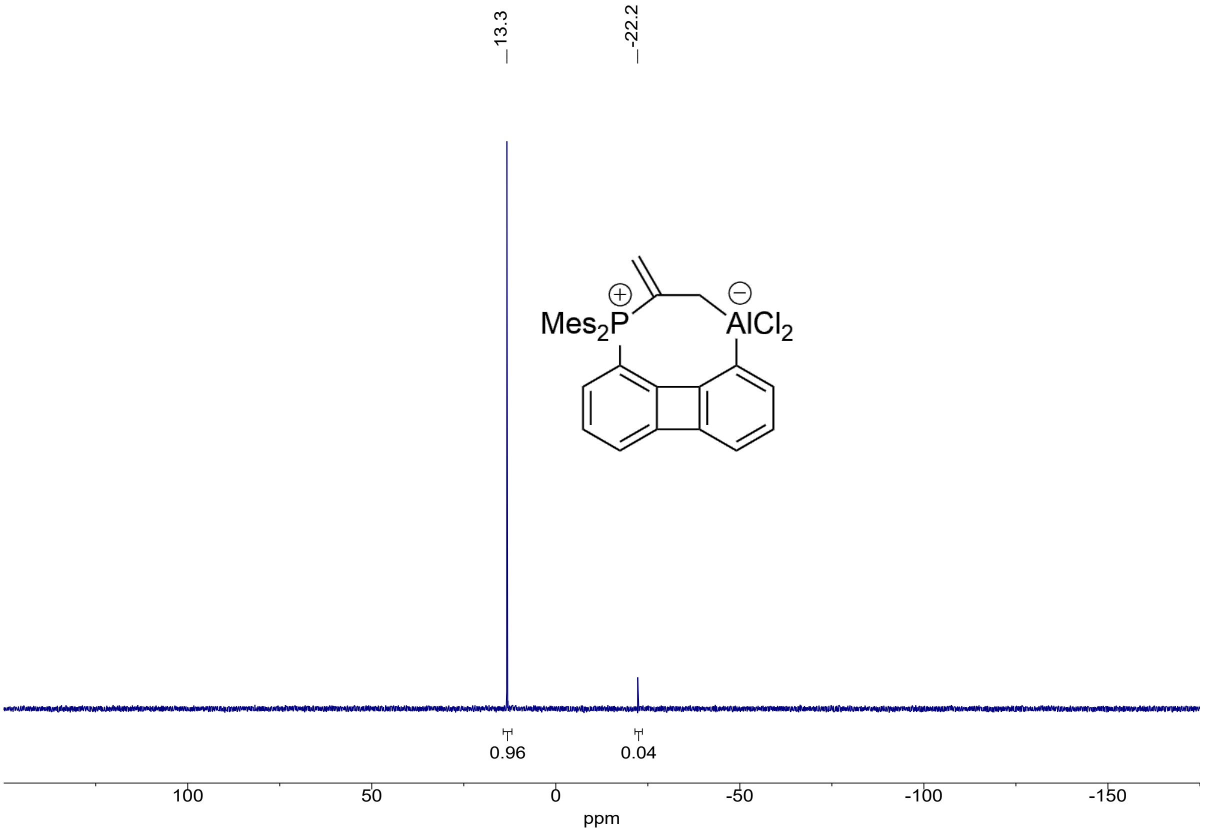


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum (202 MHz, DCM-d_2, 298 K) of **4-Mes** (minor impurity results from hydrolysis of the Al–C bond).

IR Spectra

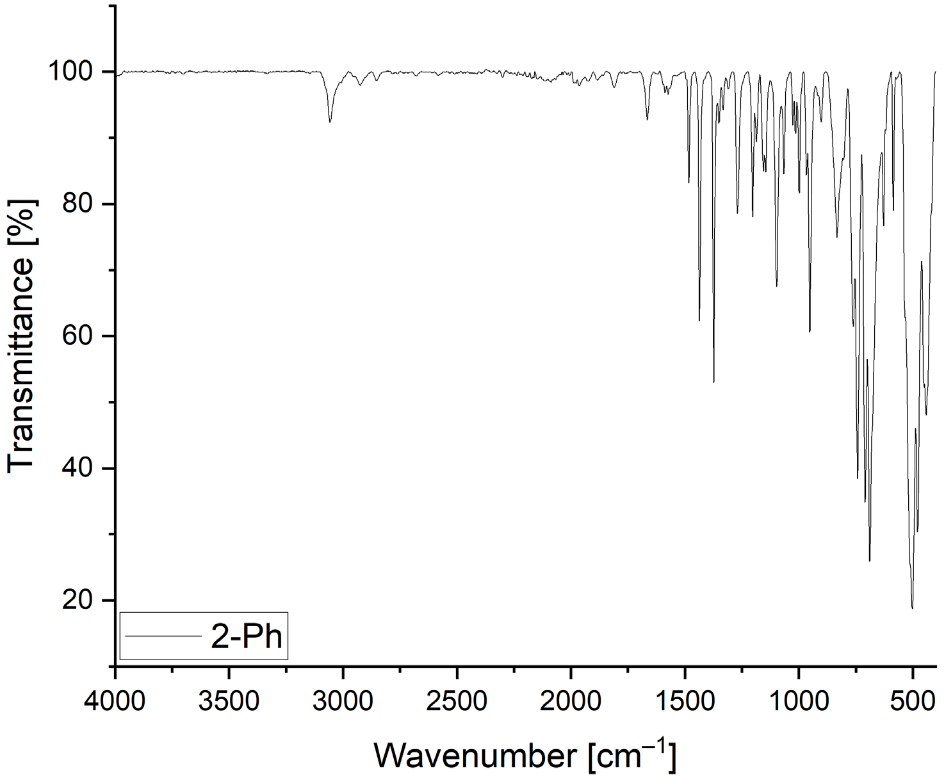


Figure S25. ATR-IR spectrum of the FLP **2-Ph** obtained as solid from a DCM-d_2 solution.

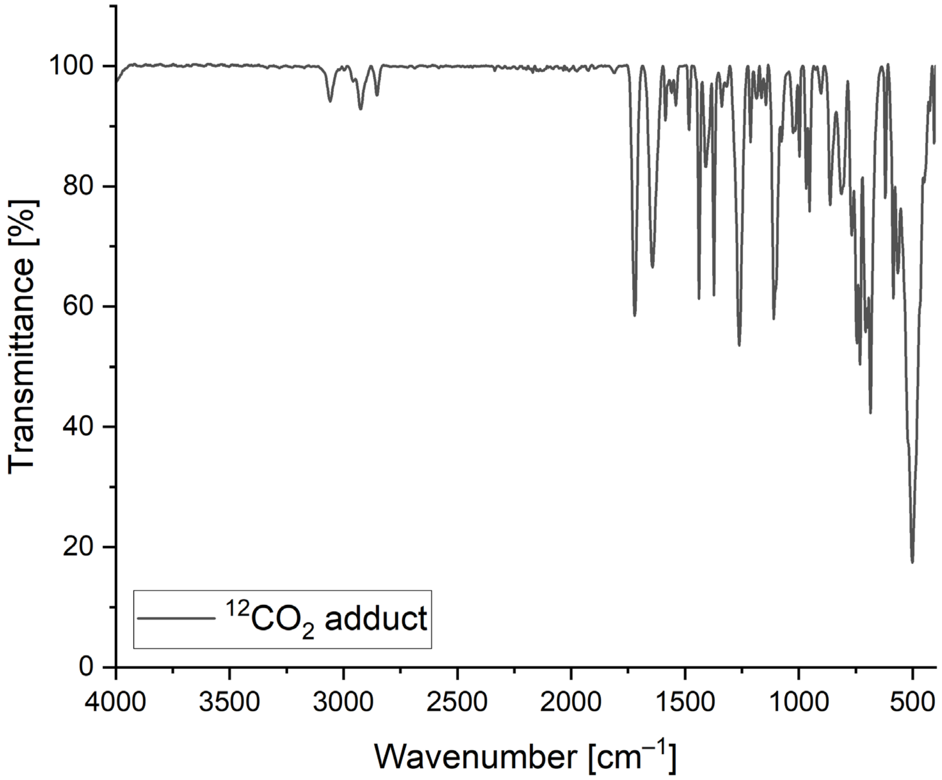


Figure S26. ATR-IR spectrum of the $^{12}CO_2$ adduct **3-Ph** obtained as solid from a DCM-d_2 solution.

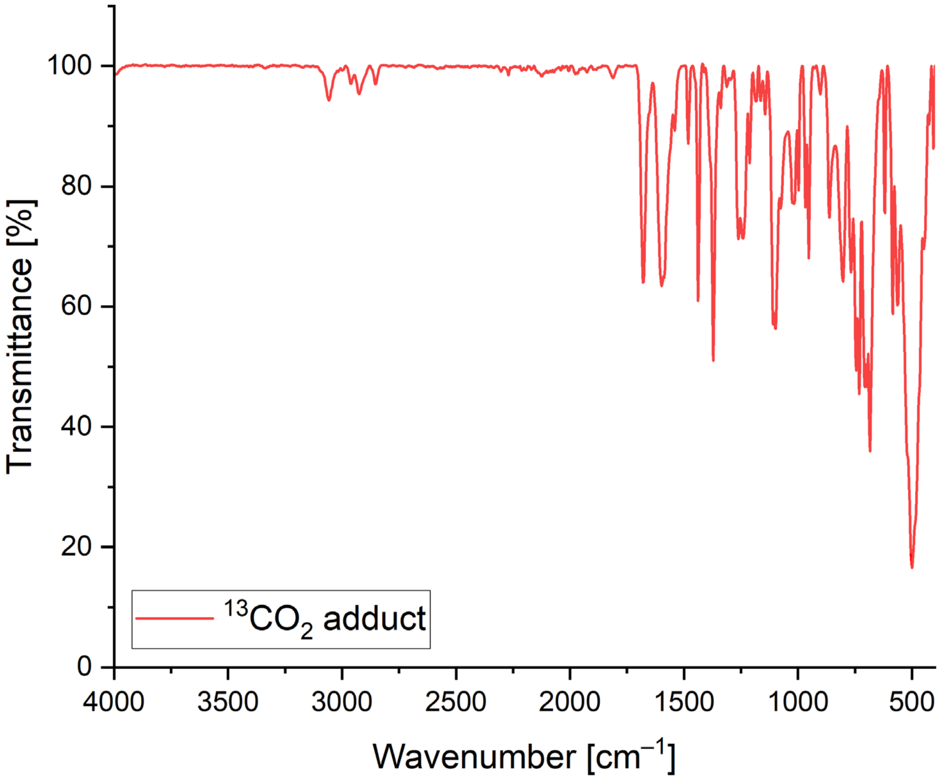


Figure S27. ATR-IR spectrum of the $^{13}CO_2$ adduct **3-Ph** obtained as solid from a DCM-d_2 solution.

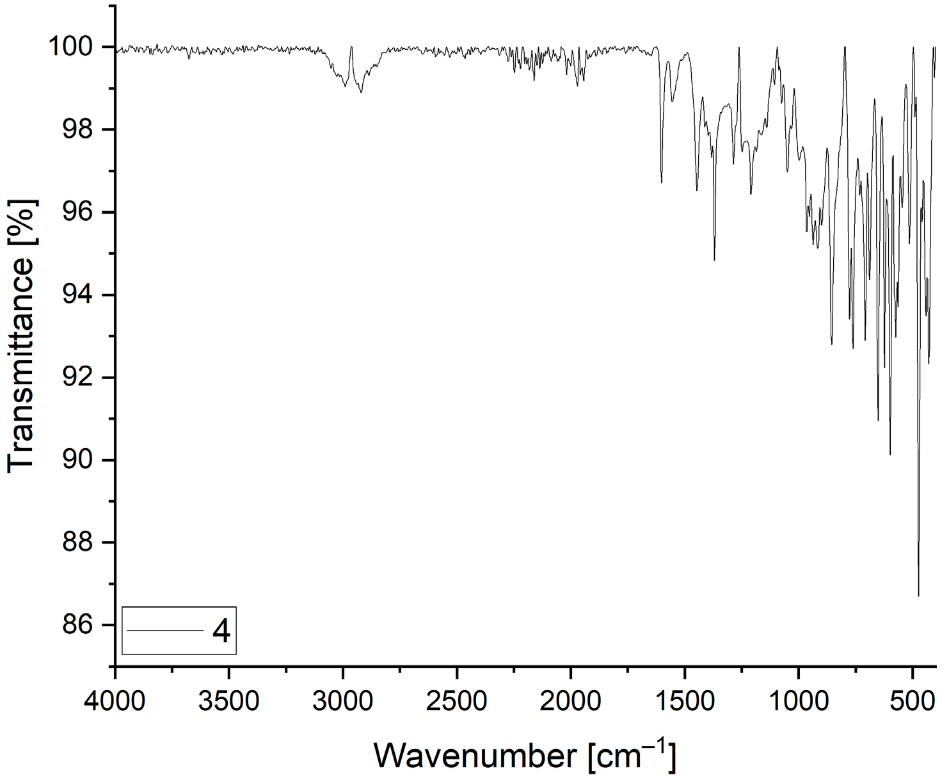


Figure S28. ATR-IR spectrum of the allene adduct **4-Mes** obtained as solid from a DCM-d_2 solution.

Acceptor Number by Gutmann-Beckett

FLP **2-Ph** was prepared by addition of $MeAlCl_2$ (1 M in toluene, 70 µl, 70.5 µmol, 4.00 eq) to a solution of BiphPSn (35.2 mg, 70.5 µmol, 1.00 eq) in toluene. After 1 hour at room temperature the solvent and Me_4Sn were evaporated and the residue dried for 30 minutes *in vacuo*. The residue was dissolved in DCM-d_2 and a capillary filled with 10% triphenylphosphine in C_6D_6 was added as a reference (δ = 5.2 ppm). Triethylphosphine oxide (2.4 mg, 17.6 µmol, 1.00 eq) in DCM-d_2 was added and a $^{31}P\{^1H\}$ NMR spectrum was recorded. From the chemical shift of the Et_3PO adduct (δ = 78.1 ppm) the acceptor number (AN) was calculated using the formula:

$$AN = 2.21 \times (\delta(^{31}P) - 41) = 82$$

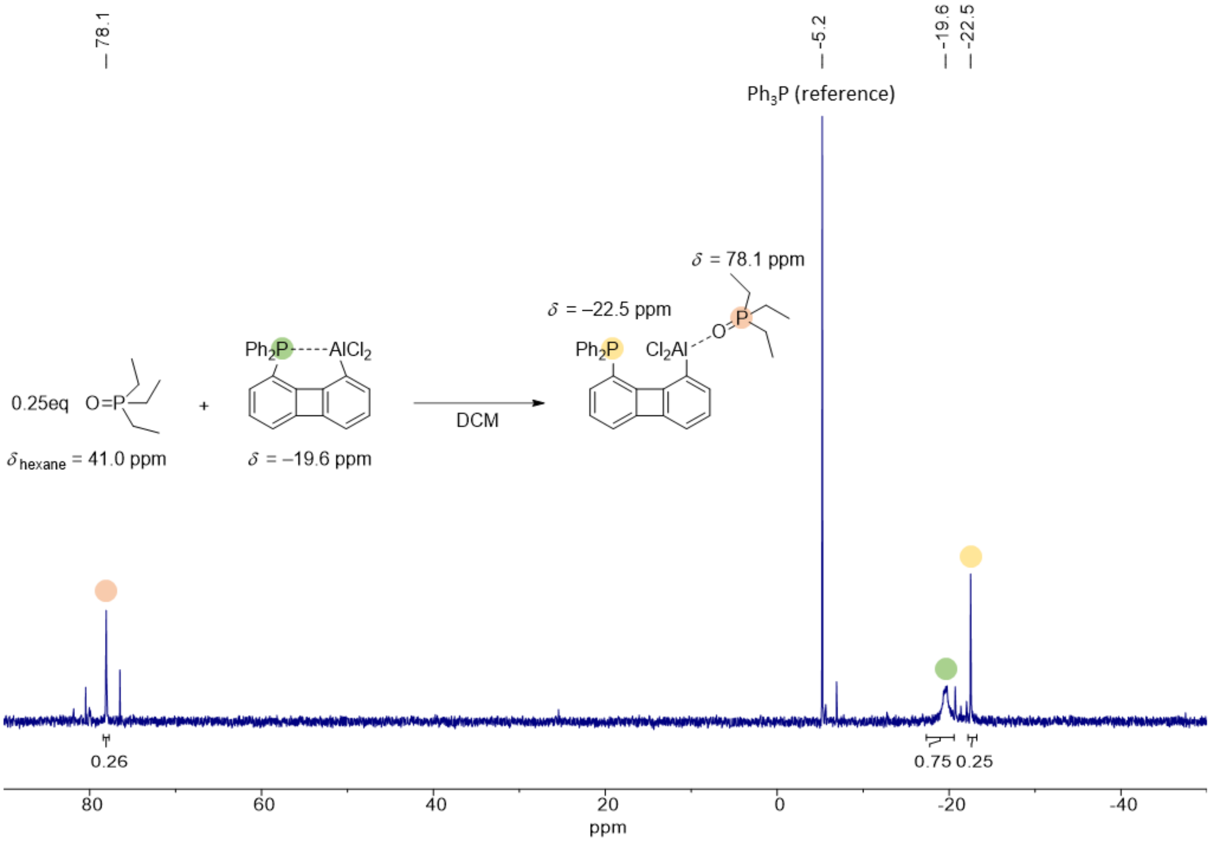
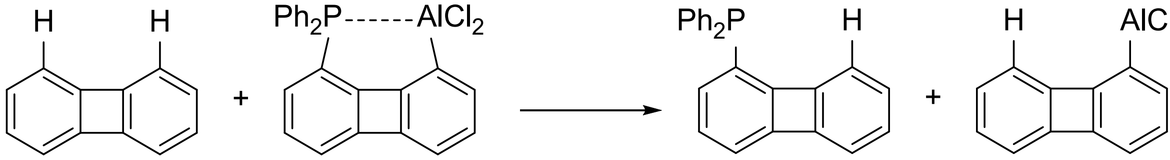


Figure S29. $^{31}P\{^1H\}$ NMR spectrum (DCM-d_2, 121 MHz, 294 K) of the Gutmann-Beckett experiment to quantify the acceptor number of FLP **2-Ph**.

Computational Details

Peri-Interaction Energies

To quantify the energy of the P→Al interaction, the *peri*-interaction energy in Biph(PPh_2)($AlCl_2$), **2-Ph**, was calculated as reaction energy of the isodesmic reaction shown in Scheme S1.[S4] The structures of all four reactants were optimized in redundant internal coordinates without symmetry restrictions using the Gaussian16 software package.[S5] The B3PW91 functional was employed amended by the D3BJ version of Grimme's dispersion, together with the 6-311+G(2df,p) basis set as implemented in Gaussian16. Very tight convergence criteria were chosen for the SCF procedure and a pruned (99.590) "ultrafine" integration grid was used for numerical integrations. Vibrational frequency calculations were performed to ensure the absence of imaginary frequencies.



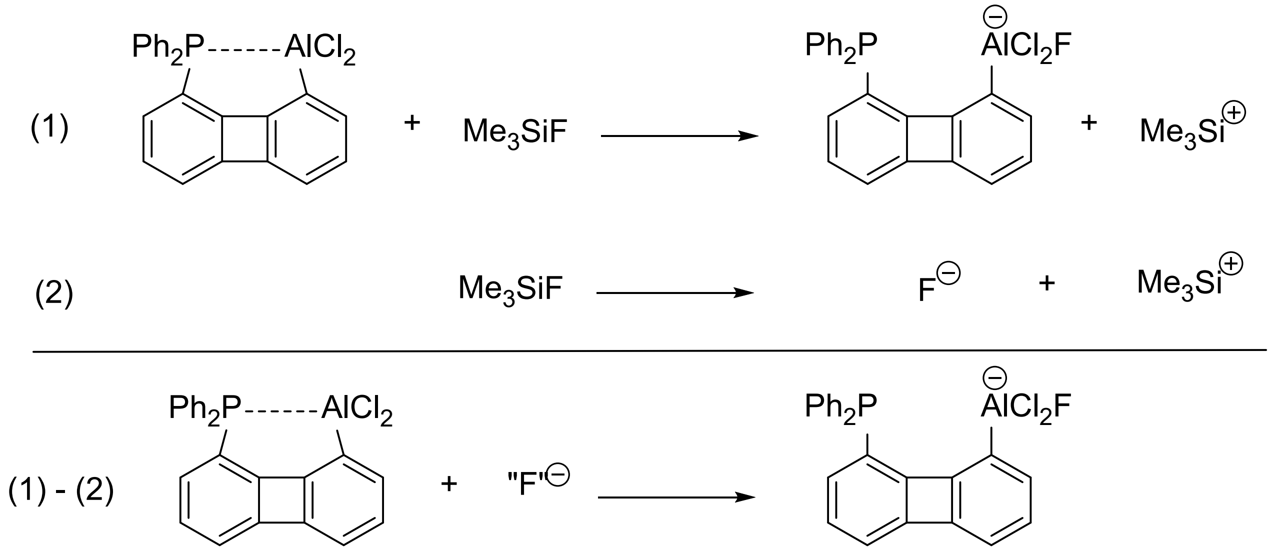
Scheme S1. Isodesmic reaction for the determination of the *α*-*peri*-interaction energy in **2-Ph**.

The α-PIE value in Biph(PPh_2)($AlCl_2$), **2-Ph**, thus calculated is –84.9 kJ/mol.

The α-PIE in Ace(PPh_2)($AlCl_2$) was calculated analogously to be –106.5 kJ/mol.

Fluoride Ion Affinity

The Fluoride Ion Affinity (FIA) of **2-Ph** was calculated using the procedure published by Greb *et al.*[S6] For that, the ORCA[S7] software package (Version 4.1.2) was used. At first, structures of all reaction partners of equation (1) in Scheme S2 were optimized employing the PBEh-3c/def2-mSVP method (which includes dispersion) with Grid6, TightOPT and VeryTightSCF settings,[S8] followed by calculation of vibrational frequencies and the ZPE/thermal corrections (298 K). Second, single point energies for all species were calculated at the DLPNO-CCSD(T)/(aug)-cc-pVQZ level of theory. The electronic energies thus obtained were combined with the thermal corrections of the first step to calculate the reaction enthalpy of eq. (1) (Table S1). For equation (2) the calculated high-level FIA value of Me_3Si^+ of 952.5 kJ/mol (CCSD(T)/CBS) was taken from literature.[S6] Subtraction of eq. (2) from (1) gives the FIA of **2-Ph** with a value of 411.8 kJ/mol.



Scheme S2. Isodesmic reaction for the calculation of the FIA of **2-Ph**.

Table S1. Calculated thermal/ZPE corrections and single point energies for equation (1) in kJ/mol.

	2-Ph	Me_3SiF	[(**2-Ph**)F]$^-$	Me_3Si^+
thermal/ZPE correction at 298.15 K (PBEh-3c/def2-mSVP)	937.042145	321.40150	943.45023	300.19542
Single Point Energy (DLPNO-CCSD(T)/ (aug)-cc-pVQZ)	−6367507.4540	−1335055.5764	−6629861.3087	−1072146.2101

Crystallographic Data

The data collections were performed with a BRUKER D8 VENTURE area detector with Mo-*K*α radiation (λ = 0.71073 Å) at 100 K. Multi-scan absorption corrections implemented in SADABS[S9] were applied to the data. The structures were solved by intrinsic phasing method (SHELXT-2013)[S10] and refined by full matrix least square procedures based on *F*2 with all measured reflections (SHELXL-2014 in the graphical user interface SHELXle)[S11] with anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were added geometrically and refined by using a riding model. data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

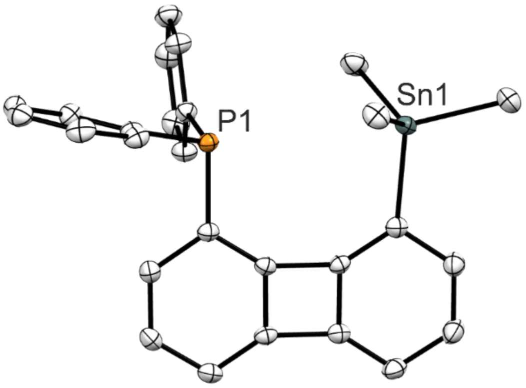


Figure S30. Molecular structure determined for **1-Ph**. H atoms omitted for clarity; thermal ellipsoids drawn at the 50% probability level.

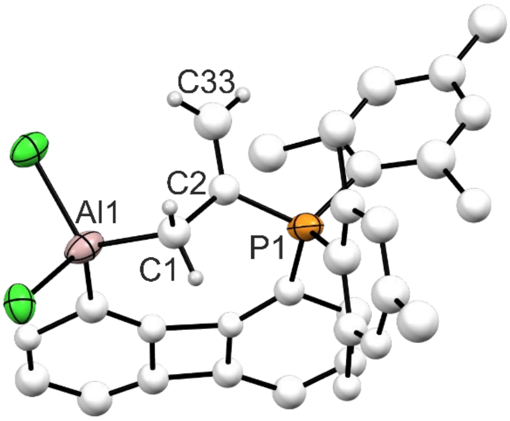


Figure S31. Molecular structure of **4-Mes** as determined by X-ray diffraction analysis. Atoms that could not be refined as ellipsoids are depicted as balls.

Crystal data and structure refinement for 1-Ph

CCDC deposition number	2179789
Empirical formula	$C_{27}H_{25}PSn$
Formula weight/g·mol^{-1}	499.13
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.8677(4)
b/Å	12.9432(5)
c/Å	18.0733(8)
α/°	90
β/°	94.123(2)
γ/°	90
V/Å^3	2302.34(16)
Z	4
$\rho_{\mathrm{calculated}}$/g·cm^{-3}	1.440
μ(MoK$_\alpha$)/mm^{-1}	1.189
F(000)	1008
Crystal size/mm	0.340 x 0.320 x 0.280
Crystal color / shape	light yellow block
2Θ range/°	1.937 to 28.295
Reflections collected	51161
Independent reflections	5555
R_{int}	0.0232
R indices [I>2σ(I)]	R_1 = 0.0185, wR_2 = 0.0451
R indices (all data)	R_1 = 0.0190, wR_2 = 0.0453
GooF (all data)	1.076
Largest diff. peak and hole/ eÅ^{-3}	0.369 / –0.377

Crystal data and structure refinement for 2-Ph

CCDC deposition number	2179788
Empirical formula	$C_{24}H_{16}AlCl_2P$
Formula weight/g·mol^{-1}	433.22
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	11.3572(10)
b/Å	12.4085(11)
c/Å	14.7374(9)
α/°	90
β/°	97.645(2)
γ/°	90
V/Å^3	2058.4(3)
Z	4
$\rho_{\text{calculated}}$/g·cm^{-3}	1.398
μ(MoK$_\alpha$)/mm^{-1}	0.443
F(000)	888
Crystal size/mm	0.430 x 0.250 x 0.180
Crystal color / shape	yellow block
2Θ range/°	2.132 to 25.372
Reflections collected	95869
Independent reflections	3775
R_{int}	0.0332
R indices [I>2σ(I)]	R_1 = 0.0237, wR_2 = 0.0623
R indices (all data)	R_1 = 0.0248, wR_2 = 0.0632
GooF (all data)	1.025
Largest diff. peak and hole/ eÅ^{-3}	0.349 / –0.232

Crystal data and structure refinement for 3-Ph

CCDC deposition number	2179785
Empirical formula	$4\cdot C_{25}H_{16}AlCl_2O_2P$
Formula weight/g·mol^{-1}	1908.91
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	12.083(3)
b/Å	13.097(3)
c/Å	13.743(3)
α/°	88.302(7)
β/°	86.483(8)
γ/°	87.468(8)
V/Å^3	2167.9(8)
Z	1
$\rho_{\text{calculated}}$/g·cm^{-3}	1.462
μ(MoK$_\alpha$)/mm^{-1}	0.435
F(000)	976
Crystal size/mm	0.430 x 0.310 x 0.210
Crystal color / shape	yellow fragment
2Θ range/°	2.123 to 28.425
Reflections collected	10812
Independent reflections	10812
R_{int}	0
R indices [$I>2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.1029$
R indices (all data)	$R_1 = 0.0709$, $wR_2 = 0.1148$
GooF (all data)	1.026
Largest diff. peak and hole/ eÅ^{-3}	0.518 / –0.415

Crystal data and structure refinement for 4-Ph

CCDC deposition number	2179787
Empirical formula	$C_{27}H_{20}AlCl_2P$
Formula weight/g·mol^{-1}	473.28
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	10.0145(10)
b/Å	14.1044(13)
c/Å	16.1893(13)
α/°	90
β/°	90
γ/°	90
V/Å^3	2286.7(4)
Z	4
$\rho_{\text{calculated}}$/g·cm^{-3}	1.375
μ(MoK$_\alpha$)/mm^{-1}	0.405
F(000)	976
Crystal size/mm	0.250 x 0.230 x 0.170
Crystal color / shape	yellow fragment
2Θ range/°	2.391 to 28.327
Reflections collected	46321
Independent reflections	5661
R_{int}	0.0334
R indices [I>2σ(I)]	R_1 = 0.0225, wR_2 = 0.0609
R indices (all data)	R_1 = 0.0229, wR_2 = 0.0613
GooF (all data)	1.042
Largest diff. peak and hole/ eÅ^{-3}	0.311 / –0.159

Due to the low crystal quality for compound **4-Mes**, the data do not permit a discussion of metric parameters, we were only able to provide a connectivity set for the molecular structure. Carbon atoms were refined isotropically and hydrogen atoms were added geometrically. The SQUEEZE function implemented in PLATON was used.[S12] Cell parameters for **4-Mes** (Deposition number 2179786):

$C_{33}H_{32}AlCl_2P$, tetragonal, $I4_1/a$, colorless needle, 0.210 x 0.010 x 0.010 mm, a = 35.029(18) Å, b = 35.029(18) Å, c = 10.984(8) Å, α = 90°, β = 90°, γ = 90°, V = 13478(17) Å^3.

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