Supporting Information for:

Phosphonium-stibonium and bis-stibonium cations as pnictogen-bonding catalysts for the transfer hydrogenation of quinolines

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Experimental Section
Computational Details
Crystallographic Details

1 Experimental Section

General considerations. All syntheses involving organolithium derivatives and methylation reagents were carried out using standard glovebox or Schlenk techniques in the absence of oxygen and moisture. All glassware was dried in an oven and cooled under vacuum before use. 1,2-Dibromo benzene and iodomethane were purchased from Oakwood Chemical, 1-bromo-2-iodobenzene from ArkPharm, tetrakis(triphenylphosphine)palladium from Strem Chemicals, trimethylamine from TCI America, *n*-n-Butyllithium (2.2 M in hexanes) and iodomethane from Alfa Aesar, sodium tetrafluoroborate, triphenyl antimony, and triphenylphosphine from Millipore, antimony trichloride from Acros, tetraphenylantimony(V) bromide from Sigma-Aldrich, trimethyloxonium tetrafluoroborate from BeanTown Chemical, and Silver trifluoromethanesulfonate from Matrix scientific. All commercially available chemicals were used as received. Ph_2SbCl,[1] Ph_3SbBr_2,[2] (2-bromophenyl)diphenylphosphine,[3] [**6**][BF_4]$_2$[4], *o*-(Ph_2P)$C_6H_4SbPh_2$,[5] were synthesized according to reported procedures. The known complexes [**1**][BF_4][6] was synthesized by treating PPh_3 with Me_3OBF_4, and [**2**][BF_4][7] was synthesized by treating Ph_4SbBr with AgOTf. Solvents were dried by passing through an alumina column (*n*-pentane and CH_2Cl_2), heating to reflux under N_2 over Na/K (Et_2O, hexanes, and THF), or over CaH_2 (1,2-dichloroethane). All other solvents were used as received. Deuterated solvents were bought from Cambridge Isotope. NMR spectra were recorded on a Varian Unity Inova 400 FT NMR (399.52 MHz for ^1H, 375.92 MHz for ^{19}F, 161.74 MHz for ^{31}P, 100.46 MHz for ^{13}C) or Varian Unity Inova 500 FT NMR (499.42 MHz for ^1H, 469.86 MHz for ^{19}F, 202.18MHz for ^{31}P, 125.60 MHz for ^{13}C) at ambient temperature. Chemical shifts (δ) are given in ppm and are referenced against residual solvent signals (^1H, ^{13}C) or external standards ($BF_3 \cdot Et_2O$ for ^{19}F (-153 ppm), and 85% H_3PO_4 for ^{31}P (0 ppm)). Elemental analyses were performed at Atlantic Microlab (Norcross, GA).

Synthesis of [*o*-($MePPh_2$)$C_6H_4SbPh_2$]I (3-I). Methyl iodide (0.05 mL, 0.80 mmol) was added to a solution of *o*-(Ph_2P)$C_6H_4SbPh_2$ (210 mg, 0.4 mmol) in CH_2Cl_2 (10 mL). After stirring under N_2 at room temperature overnight, the solution was concentrated to a volume of 3 mL. Et_2O (20 mL) was then added, resulting in a white precipitate, which was collected by filtration and washed with Et_2O (2 × 5 mL) to afford **3**-I as an off-white solid (220 mg, 83% yield). The product was judged to be spectroscopically pure and used as synthesized. ^1H NMR (499 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 4H), 7.73 – 7.59 (m, 6H), 7.58 – 7.43 (m, 4H), 7.39 – 7.23 (m, 6H), 7.12 (d, J = 6.7 Hz, 4H), 3.41 (d, $J_{P\text{-}H}$ = 12.7 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.64 (d, $J_{C\text{-}P}$ = 17.7 Hz, Sb-bound *o*-phenylene quaternary), 141.13 (d, $J_{C\text{-}P}$ = 15.1 Hz, *o*-phenylene), 136.80 (d, $J_{C\text{-}P}$ = 15.2 Hz, , *o*-phenylene, overlapping with Sb*Ph* quaternary), 136.74 (s, Sb*Ph* quaternary, overlapping with *o*-phenylene), 135.96 (s, *o*-Sb*Ph*), 135.17 (d, $J_{C\text{-}P}$ = 3.0 Hz, *p*-P*Ph*), 134.92 (d, $J_{C\text{-}P}$ = 3.3 Hz, *o*-phenylene), 133.80 (d, $J_{C\text{-}P}$ = 10.5 Hz, *m*-P*Ph*), 130.62 (d, $J_{C\text{-}P}$ = 12.8 Hz, *o*-P*Ph*), 130.45 (d, $J_{C\text{-}P}$ = 12.9 Hz, *o*-phenylene), 129.58 (s, *p*-Sb*Ph*), 129.47 (s, *m*-Sb*Ph*), 126.92 (d, $J_{C\text{-}P}$ = 91.0 Hz, P-bound *o*-phenylene quaternary), 119.71 (d, $J_{C\text{-}P}$ = 87.1 Hz, P*Ph* quaternary), 14.11 (d, $J_{C\text{-}P}$ = 56.5 Hz PCH_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.9 (s).

Synthesis of [*o*-($MePPh_2$)$C_6H_4SbPh_2$][BF_4] ([3][BF_4]). A solution of $NaBF_4$ (650 mg, 5.93 mmol) in mixed solvents (15 mL, water: MeOH = 1: 1) was added to a MeOH (20 mL) solution of [o-($MePPh_2$)$C_6H_4SbPh_2$]I (500 mg, 0.74 mmol). The mixture was stirred for 4h, after which a white precipitate formed. The precipitate was collected by filtration then dissolved into 20 mL of CH_2Cl_2 and passed through a celite plug. The final product was crashed out with Et_2O and dried *in vacuo* to afford [**3**][BF_4] as a white powder (400 mg, 85% yield). Single crystals of [**3**][BF_4] were obtained as colorless blocks by diffusing hexanes into a $CDCl_3$ solution. ^1H NMR (499 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 7H), 7.64 – 7.55 (m, 3H), 7.55 – 7.49 (m, 4H), 7.38 – 7.32 (m, 2H), 7.32 – 7.27 (m, 4H), 7.11 (dd, J = 8.0, 1.3 Hz, 1H), 3.14 (d, $J_{P\text{-}H}$ = 13.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 145.64 (d, $J_{C\text{-}P}$ =18.0, Sb-bound *o*-phenylene quaternary), 141.13 (d, $J_{C\text{-}P}$ =15.1, *o*-phenylene), 136.78 (s, Sb*Ph* quaternary), 136.55 (d, $J_{C\text{-}P}$ =14.9, *o*-phenylene), 135.95 (s, *o*-Sb*Ph*), 135.17 (d, $J_{C\text{-}P}$ =3.0, *p*-P*Ph*), 134.91 (d, $J_{C\text{-}P}$ =3.4, *o*-phenylene), 133.53 (d, $J_{C\text{-}P}$ =10.3, *m*-P*Ph*), 130.62 (d, $J_{C\text{-}P}$ =12.8, *o*-P*Ph*), 130.41 (d, $J_{C\text{-}P}$ =12.9, *o*-phenylene), 129.59 (s, *p*-Sb*Ph*), 129.48 (s, *m*-Sb*Ph*), 126.99 (d,

$J_{C\text{-}P}$ =91.1, P-bound *o*-phenylene quaternary), 119.81 (d, $J_{C\text{-}P}$ =86.9, P*Ph* quaternary), 12.05 (d, $J_{C\text{-}P}$ =57.3, P*C*H$_3$). ^{19}F NMR (470 MHz, CDCl$_3$) δ = -152.41 (s, 1F) -152.46 (s, 4F). ^{31}P NMR (202 MHz, CDCl$_3$) δ = 23.6 (s). Elemental analysis calculated (%) for $C_{31}H_{27}BF_4PSb$: C, 58.26; H, 4.26; found C, 58.14; H, 4.40.

Synthesis of *o*-(PPh$_2$)C$_6$H$_4$SbPh$_3$Br (4-Br). Using a 50 mL Schlenk flask as a reaction vessel, *n*-butyllithium (2.2 M) in hexanes (0.8 mL, 1.8 mmol) was slowly added to a Et$_2$O solution (10 mL) of (2-bromophenyl)diphenylphosphine (0.613 g, 1.8 mmol) at -78 °C. After stirring for 1 h, the corresponding lithium salt formed as a white precipitate. The solvent was decanted off using a cannula fitted with a filter tip and the residue was washed with two portions of Et$_2$O (5 mL each). The lithium salt was then suspended in Et$_2$O (20 mL) and cooled down to -78 °C. This mixture was slowly transferred to a solution of Ph$_3$SbBr$_2$ in THF (5 mL) via cannula. After stirring at room temperature for 3 h, an off-white solid precipitated out of solution. The solid was collected by filtration and washed with two portions of Et$_2$O (5 mL each) to afford **4**-Br (0.848 g, 68 % yield). The product was judged to be spectroscopically pure and was used as synthesized. This stibonium bromide salt is highly soluble in CHCl$_3$, CH$_2$Cl$_2$, THF, MeOH, and MeCN and insoluble in Et$_2$O, pentane, and hexanes. ^{1}H NMR (399 MHz, CDCl$_3$) δ = 7.81 (d, *J*=7.1, 6H, *o*-Sb*Ph*), 7.70 – 7.61 (m, 1H, *o*-phenylene), 7.58 – 7.45 (m, 3H), 7.46 – 7.39 (m, 3H), 7.36 (pseudo t, 6H), 7.30 – 7.25 (m, 2H, *o*-phenylene), 7.24 – 7.18 (m, 4H), 7.17 – 7.10 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.96 (d, $J_{C\text{-}P}$ = 83.7 Hz, P*Ph* quaternary), 136.91 (d, $J_{C\text{-}P}$ = 6.6 Hz, Sb*Ph* quaternary), 135.97 (d, $J_{C\text{-}P}$ = 1.6 Hz, *o*-phenylene), 135.52 (d, $J_{C\text{-}P}$ = 2.8 Hz, *o*-Sb*Ph*), 134.27 (d, $J_{C\text{-}P}$ = 1.5 Hz, *o*-phenylene), 133.10 (d, $J_{C\text{-}P}$ = 16.4 Hz, *o*-P*Ph*), 132.77 (d, $J_{C\text{-}P}$ = 11.1 Hz, Sb-bound *o*-phenylene quaternary), 132.54 (d, $J_{C\text{-}P}$ = 22.2 Hz, P-bound *o*-phenylene quaternary), 132.16 (s, *o*-phenylene), 131.37 (d, $J_{C\text{-}P}$ = 1.5 Hz, *o*-phenylene), 130.88 (s, *p*-Sb*Ph*), 129.51 (s, *m*-Sb*Ph*), 129.24 (s, *p*-P*Ph*), 128.67 (d, $J_{C\text{-}P}$ = 7.4 Hz, *m*-P*Ph*). ^{31}P NMR (161.720 MHz, CDCl$_3$): δ 19.6. Elemental analysis calculated (%) for $C_{36}H_{29}BrPSb$: C, 62.28; H, 4.21; found C, 62.39; H, 4.24.

Synthesis of [*o*-(PPh$_2$)C$_6$H$_4$SbPh$_3$][BF$_4$] ([4][BF$_4$]). In the glove box, AgBF$_4$ (100 mg, 0.51 mmol) was added to a CH$_2$Cl$_2$ solution of *o*-(PPh$_2$)C$_6$H$_4$SbPh$_3$Br (340 mg, 0.49 mol). The reaction was stirred in the absence of light for 3 h, at which time it was filtered through Celite. All volatiles were removed from the filtrate under vacuum to give a sticky, colorless oil, which was triturated with two portions of Et$_2$O (3 mL each) to afford [**4**][BF$_4$] as a white powder (252 mg, 65% yield). Single crystals of [**4**][BF$_4$] were obtained as colorless blocks by diffusing hexanes into a CDCl$_3$ solution. ^{1}H NMR (499 MHz, CDCl$_3$) δ 7.82 – 7.76 (m, 2H), 7.75 – 7.70 (m, 1H), 7.71 – 7.66 (m, 6H), 7.67 – 7.59 (m, 4H), 7.59 – 7.53 (m, 6H), 7.36 – 7.30 (m, 2H), 7.27 – 7.22 (m, 3H), 6.98 – 6.90 (m, 4H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 142.59 (d, $J_{C\text{-}P}$ = 2.8 Hz, Sb-bound *o*-phenylene quaternary), 137.22 (d, $J_{C\text{-}P}$ = 1.1 Hz, *o*-phenylene), 137.09 (d, $J_{C\text{-}P}$ = 19.5 Hz, P-bound *o*-phenylene quaternary), 135.29 (d, $J_{C\text{-}P}$ = 2.3 Hz, *o*-Sb*Ph*), 134.72 (d, $J_{C\text{-}P}$ = 1.1 Hz, *o*-phenylene), 133.63 (s, *o*-phenylene), 133.48 (s, *p*-Sb*Ph*), 132.83 (d, $J_{C\text{-}P}$ = 16.7 Hz, *o*-P*Ph*), 132.81 (s, *o*-phenylene), 131.25 (s, *m*-Sb*Ph*), 129.98 (s, *p*-P*Ph*), 129.18 (d, $J_{C\text{-}P}$ = 7.7 Hz, *m*-Sb*Ph*), 124.67 (d, $J_{C\text{-}P}$ = 11.8 Hz, Sb*Ph* quaternary). ^{19}F NMR (470 MHz, CDCl$_3$) δ -152.95 (s, 1F), -153.00 (s, 4F). ^{31}P NMR (202 MHz, CDCl$_3$) δ 11.4 (s). Elemental analysis calculated (%) for $C_{36}H_{29}BF_4PSb$: C, 61.67; H, 4.17; found C, 61.55; H, 4.20.

Synthesis of [*o*-(MePPh$_2$)C$_6$H$_4$SbPh$_3$][BF$_4$]$_2$ ([5][BF$_4$]$_2$) In a 25 mL Schlenk tube, Me$_3$OBF$_4$ (105 mg, 0.71 mol) was added to a solution of [*o*-(PPh$_2$)C$_6$H$_4$SbPh$_3$][BF$_4$] (470 mg, 0.67 mmol) in toluene (2 mL) / 1,2-dichloroethane (1 mL). The Schlenk tube was sealed under N$_2$ atmosphere and the mixture was left to stir in a 90 °C bath for 12 h, during which time a white precipitate formed. The solid was filtered, washed with three portions of Et$_2$O (5 mL each), and dried *in vacuo* to afford [**5**][BF$_4$]$_2$ as a white powder (460 mg, 85 % yield). Single crystals of [**5**][BF$_4$]$_2$ were obtained as colorless blocks by diffusing pentane into a CH$_2$Cl$_2$ solution. ^{1}H NMR (399 MHz, CD$_2$Cl$_2$) δ 8.05 – 7.96 (m, 2H), 7.94 – 7.87 (m, 1H), 7.81 – 7.73 (m, 5H), 7.65 (t, *J* = 7.8 Hz, 6H), 7.58 – 7.40 (m, 15H), 2.50 (d, $J_{P\text{-}H}$ = 13.3 Hz, 3H). ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ 142.10 (d, $J_{C\text{-}P}$ = 12.9 Hz, *o*-phenylene), 140.36 (d, $J_{C\text{-}P}$ = 11.0 Hz, *o*-phenylene), 136.56 (d, $J_{C\text{-}P}$ = 2.9 Hz, *p*-P*Ph*), 136.22 (s, *o*-Sb*Ph*), 135.41 (s, *o*-phenylene), 134.81 (s, br, *p*-Sb*Ph*), 134.28 (d, $J_{C\text{-}P}$ = 12.2 Hz, *o*-phenylene), 133.97 (d, $J_{C\text{-}P}$ = 10.7 Hz, *m*-P*Ph*), 131.98 (s, br, *m*-Sb*Ph*), 131.42 (d, $J_{C\text{-}P}$ = 12.9 Hz, *o*-P*Ph*), 129.83

(s, br, Sb-bound *o*-phenylene quaternary), 125.42 (d, $J_{C\text{-}P}$ = 91.0 Hz, P-bound *o*-phenylene quaternary), 123.21 (s, br, Sb*Ph* quaternary), 118.33 (d, $J_{C\text{-}P}$ = 88.3 Hz, P*Ph* quaternary), 10.11 (d, $J_{C\text{-}P}$ = 56.1 Hz, P*C*H$_3$). ^{19}F NMR (470 MHz, CD_2Cl_2) δ -149.96 (s, 1F), -150.02 (s, 4F). ^{31}P NMR (202 MHz, CD_2Cl_2) δ 26.5 (s). Elemental analysis calculated (%) for $C_{37}H_{32}B_2F_8PSb$: C, 55.34; H, 4.02; found C, 54.85; H, 4.04.

Hydrogenation reaction of quinolines with Hantzsch ester. An NMR tube was charged with a dry $CDCl_3$ solution (0.7 mL) of the antimony catalyst (0.004 mmol), Hantzsch-ester (50 mg, 0.20 mmol), and 2-phenylquinoline or 3-bromoquinoline (0.08 mmol). The tube was then sealed and the formation of the products was monitored by ^{1}H NMR *in situ*. For 2-phenylquinoline, the yield of the product was calculated based on the integration of two resonances: 6.6 ppm (d, 1H) and 6.7 ppm (t, 1H). The amount of the unreacted substrate was calculated based on the integration of two resonances: 7.8 ppm (d, 1H) and 7.9 ppm (d, 1H). For 3-bromoquinoline, the yield of the product was calculated based on the integration of two resonances: 6.5 ppm (d, 1H) and 6.7 ppm (t, 1H). The amount of the unreacted substrate was calculated based on the integration of two resonances: 8.1 ppm (d, 1H) and 8.3 ppm (d, 1H).

Crystallographic measurements.

All crystallographic measurements were performed at 110(2) K using a Bruker SMART APEX II diffractometer or a Brucker D8 QUEST diffractometer (graphite monochromated Mo-Kα radiation, λ = 0.71073 Å) at 110 K. In each case, a specimen of suitable size and quality was selected and mounted onto a nylon loop. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[8] The semiempirical method SADABS was applied for absorption correction. The structures were solved by direct methods (ShelXS)[9] and refined by the full-matrix least-squares technique against F^2 with anisotropic temperature parameters for all non-hydrogen atoms (ShelXL)[9] using Olex2[10] interface. All H-atoms were geometrically placed and refined using a riding model approximation. Diamond[11] was employed for the final data presentation and structure plots.

Computational details

All computations were carried out using density functional theory (DFT) methods as implemented in the Gaussian 09 program.[12] All optimization and frequency calculations were carried out with the M06-2X[13] functional and mixed basis sets (cc-pVTZ-PP[14] with CRENBL ECP[15] for Sb, cc-pVTZ for P, 6-31g(d') for H, C, N, F, 6-311g* for S, Cl) starting from the crystal structure geometries if available. No imaginary frequencies were found for the optimized structures, confirming that a local minimum on the potential energy hypersurface had in all cases been reached. The optimized structures were also subjected to natural bond orbital (NBO)[16] analysis. The molecular orbitals and NBOs were visualized and plotted using the Jimp2 program.[17] The electrostatic potential maps of [**5**]$^{2+}$ and [**6**]$^{2+}$ are based on the single-point calculations of these dications whose coordinates are from the optimization of their quinoline adduct.

1.1 NMR spectrum of 3-I

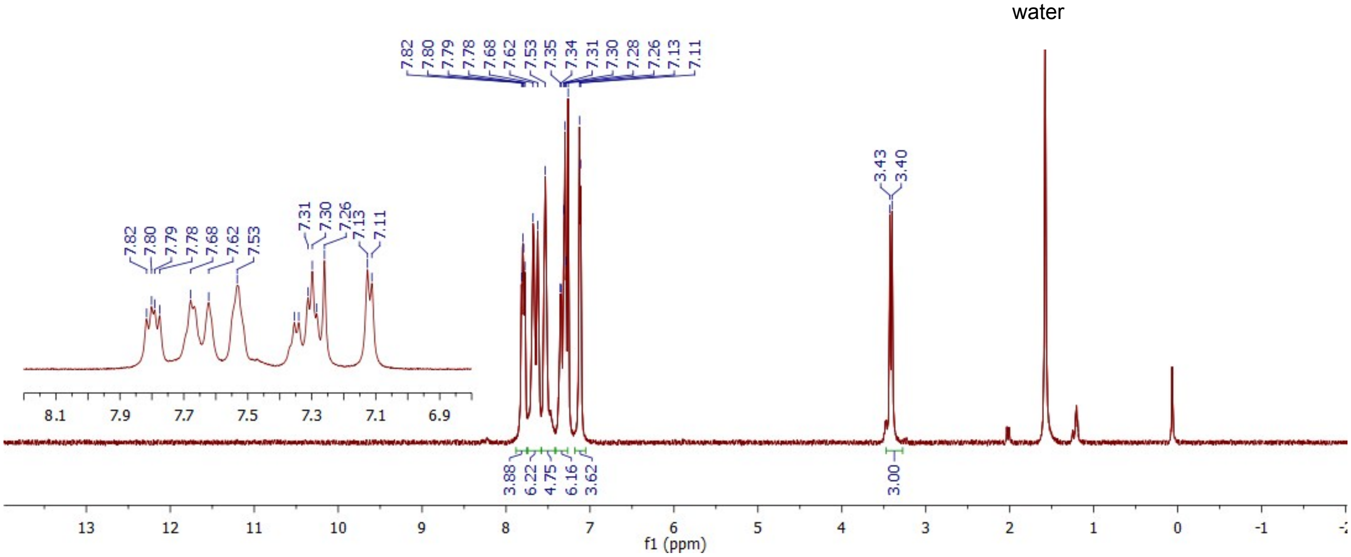


Figure S1. ^{1}H NMR of **3**-I in $CDCl_3$.

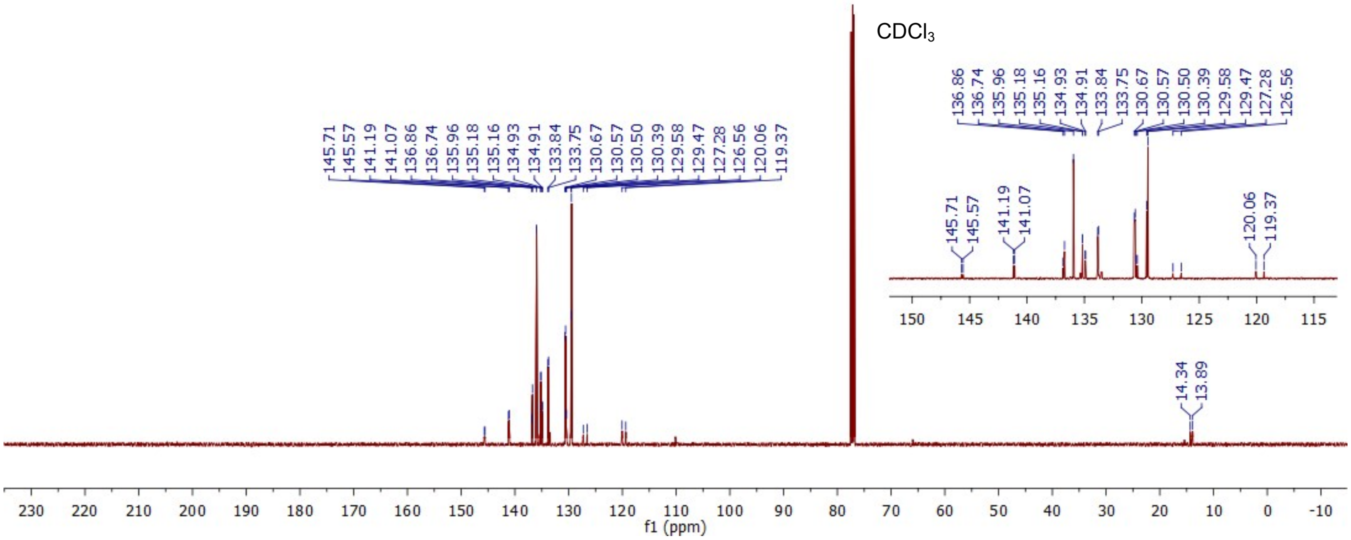


Figure S2. $^{13}C\{^1H\}$ NMR of **3**-I in $CDCl_3$.

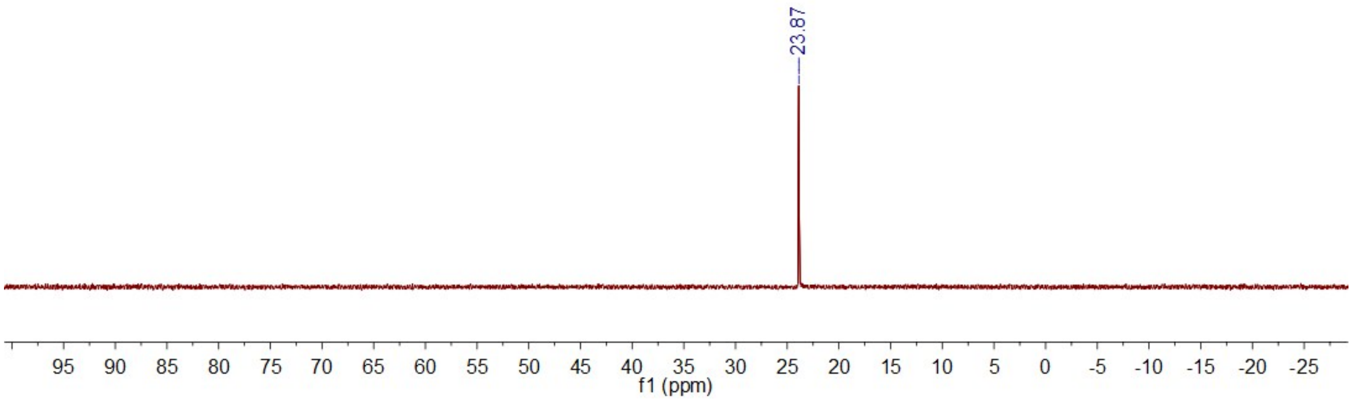


Figure S3. $^{31}P\{^{1}H\}$ NMR of **3**-I in $CDCl_3$.

1.2 NMR spectrum of [3][BF$_4$]

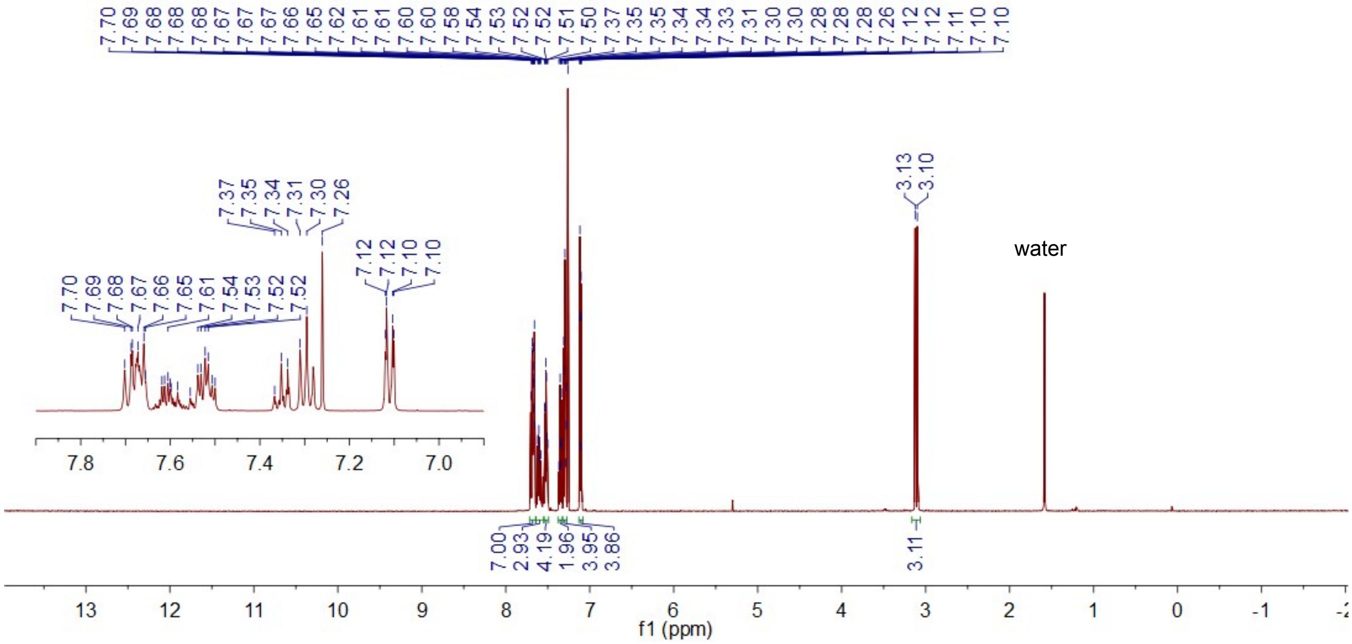


Figure S4. ^{1}H NMR of [**3**][BF$_4$] in $CDCl_3$.

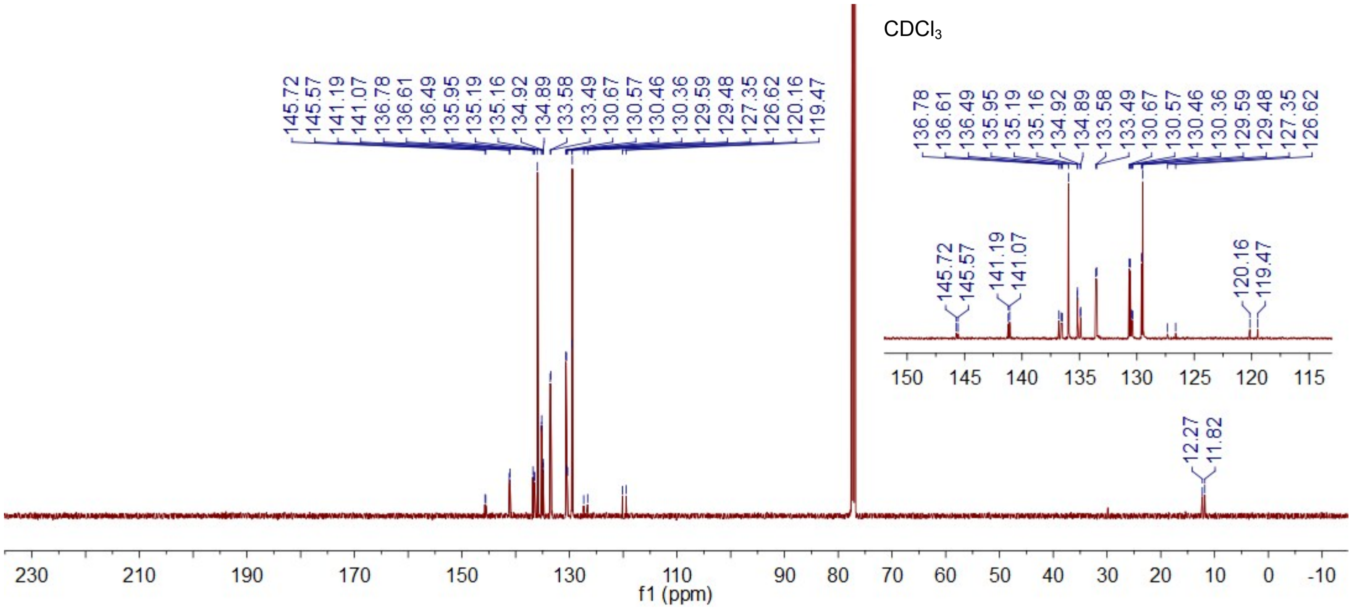


Figure S5. $^{13}C\{^{1}H\}$ NMR of [**3**][BF_4] in $CDCl_3$.

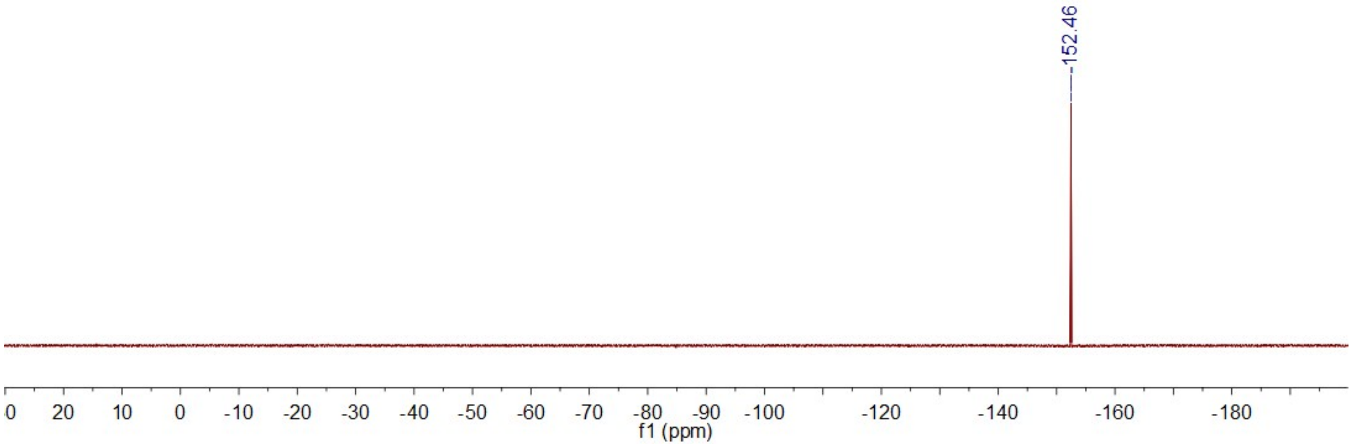


Figure S6. ^{19}F NMR of [**3**][BF_4] in $CDCl_3$.

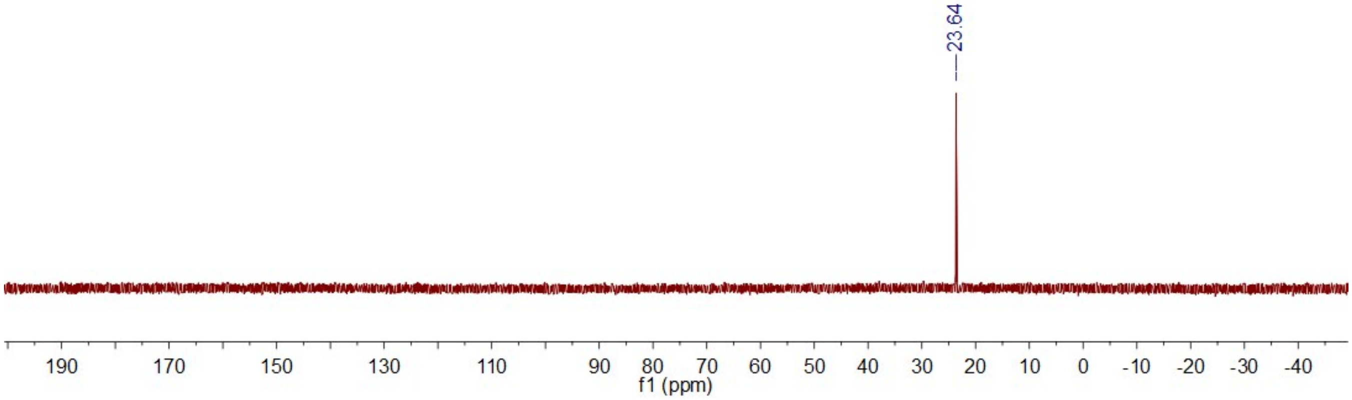


Figure S7. $^{31}P\{^1H\}$ NMR of [**3**][BF_4] in $CDCl_3$.

1.3 NMR spectrum of 4-Br

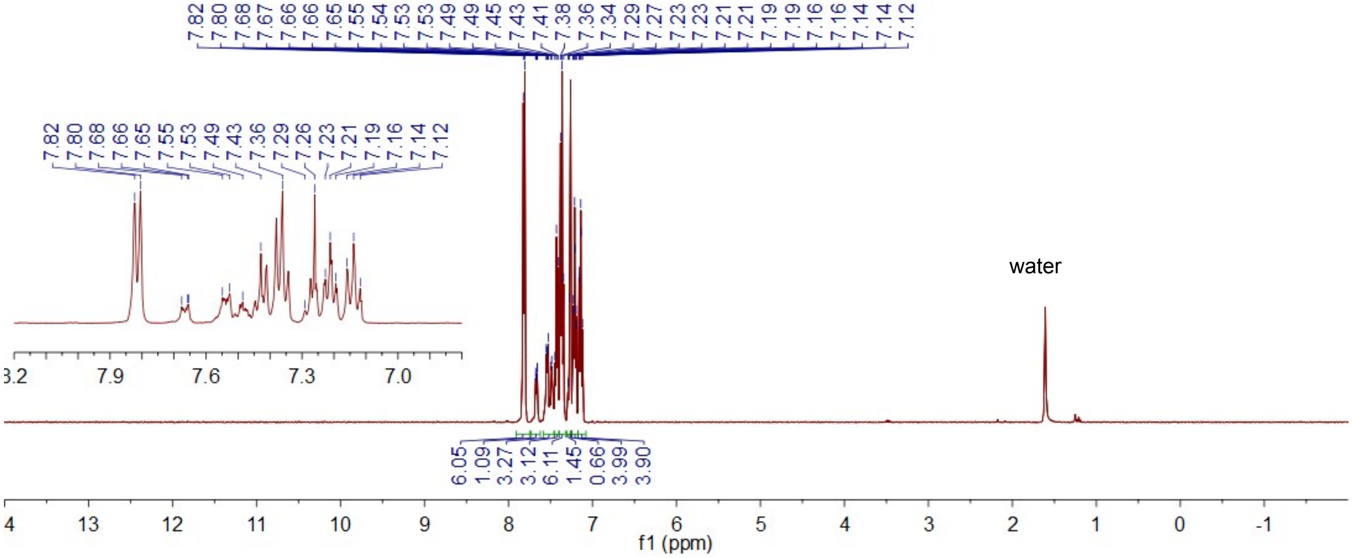


Figure S8. ^1H NMR of **4**-Br in $CDCl_3$.

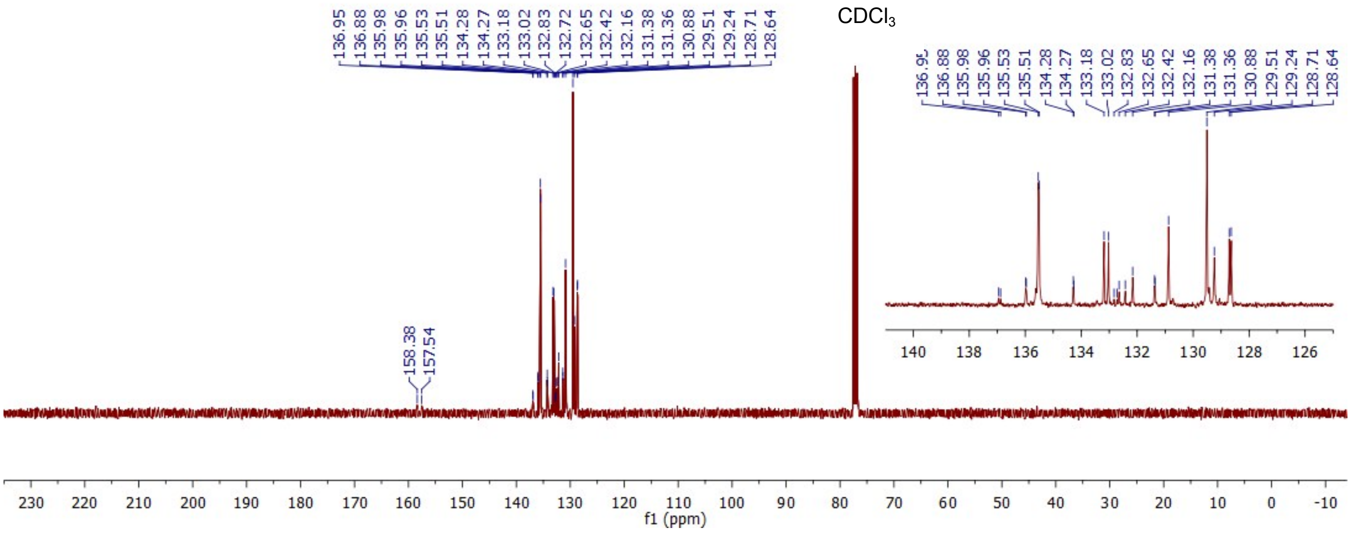


Figure S9. $^{13}C\{^{1}H\}$ NMR of **4**-Br in CDCl$_3$.

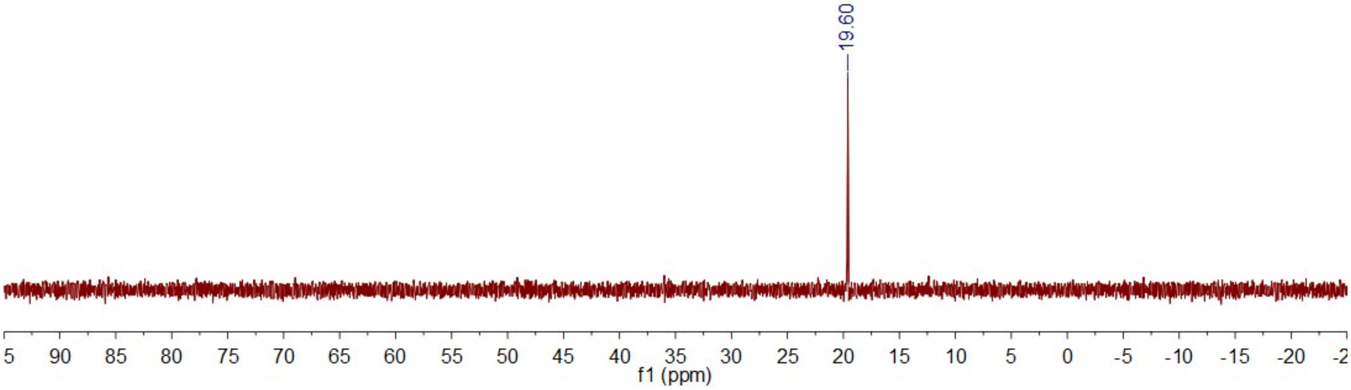


Figure S10. $^{31}P\{^{1}H\}$ NMR of **4**-Br in CDCl$_3$.

1.4 NMR spectrum of [4][BF$_4$]

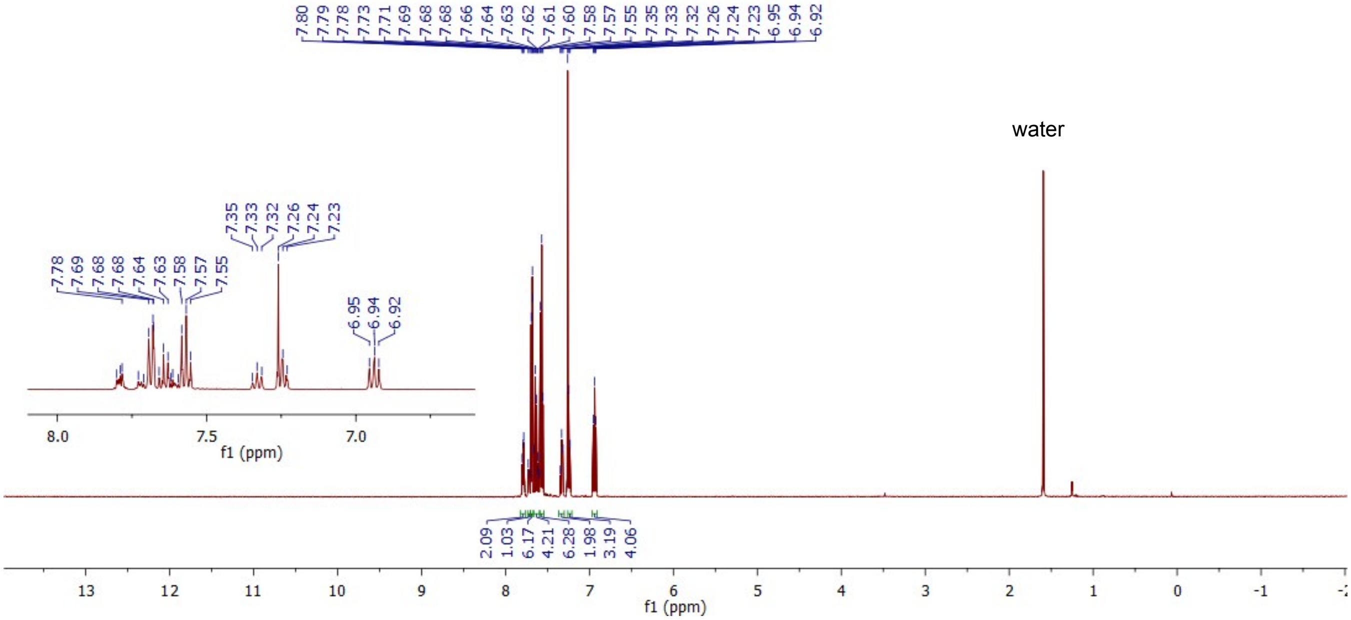


Figure S11. ^{1}H NMR of [**4**][BF$_4$] in CDCl$_3$.

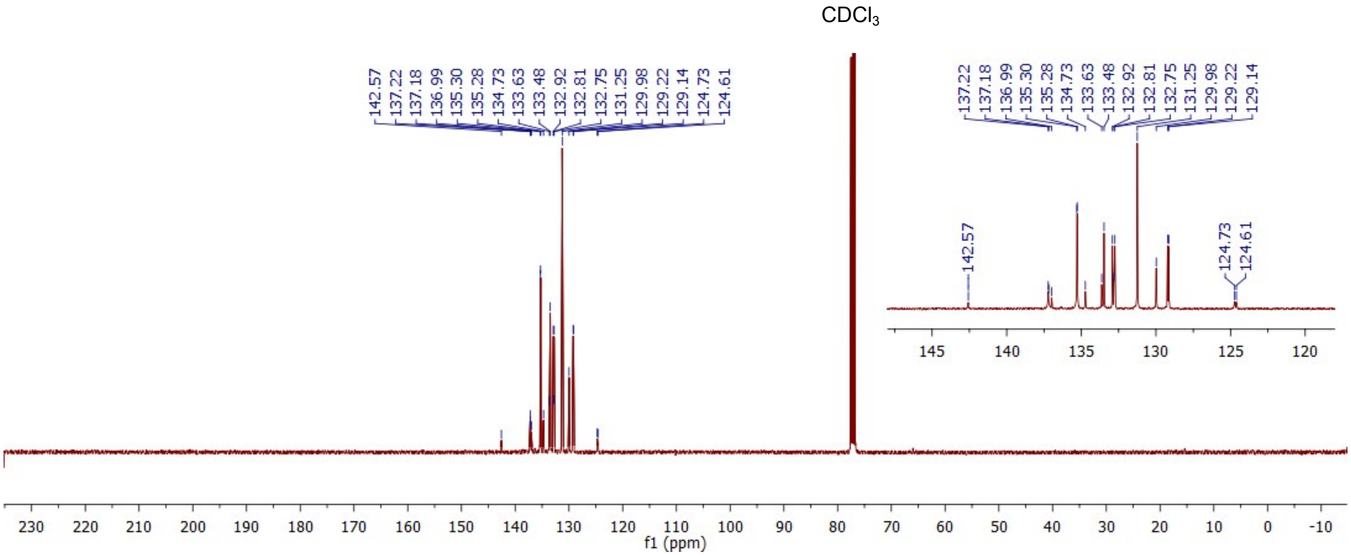


Figure S12. ^{13}C{^{1}H} NMR of [**4**][BF$_4$] in CDCl$_3$.

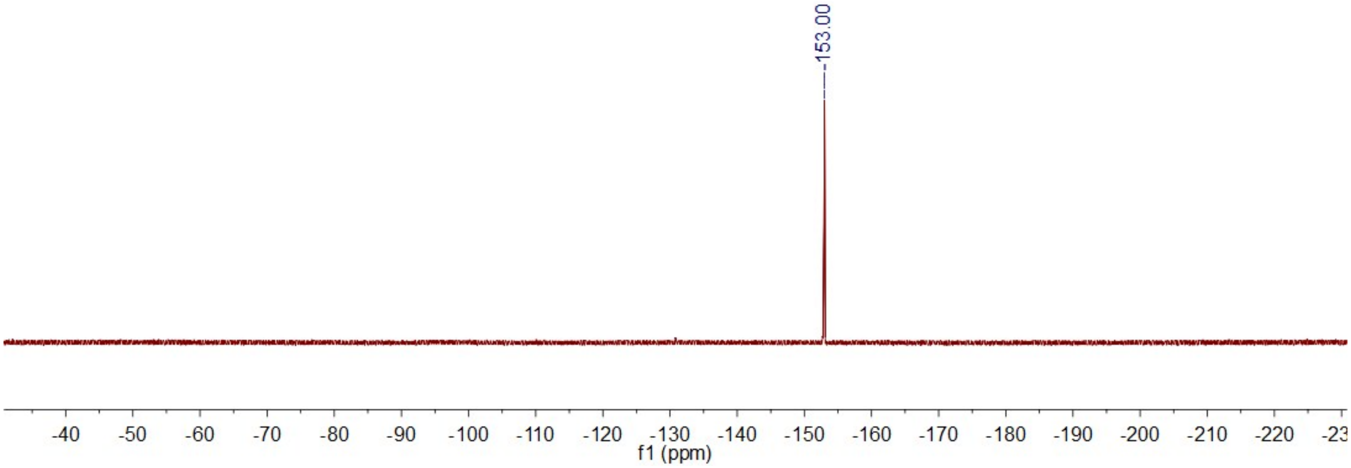


Figure S13. ^{19}F NMR of [**4**][BF$_4$] in CDCl$_3$.

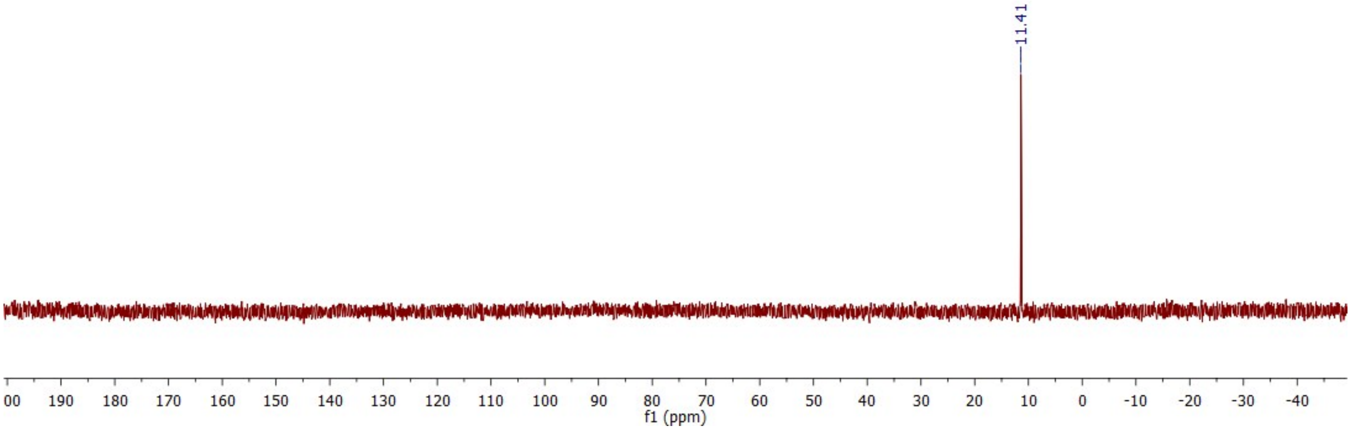


Figure S14. ^{31}P{^{1}H} NMR of [**4**][BF$_4$] in CDCl$_3$.

1.5 NMR spectrum of $[\mathbf{5}][BF_4]_2$

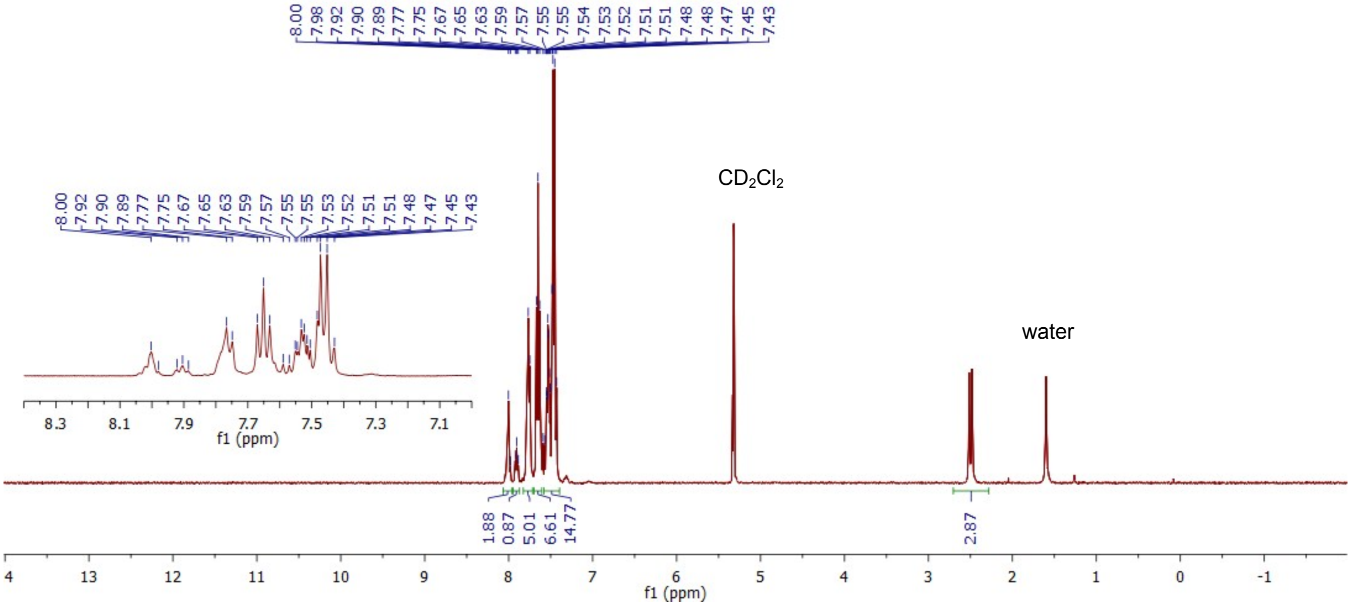


Figure S15. ^{1}H NMR of $[\mathbf{5}][BF_4]_2$ in CD_2Cl_2 .

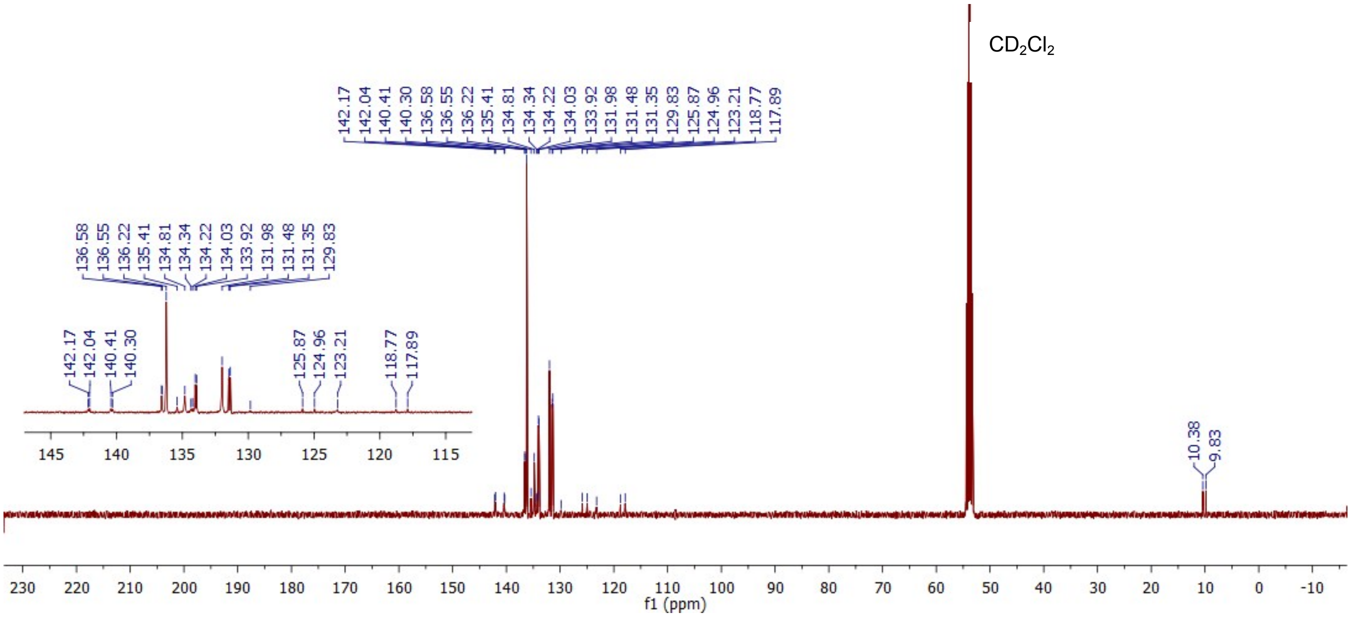


Figure S16. $^{13}C\{^1H\}$ NMR of $[\mathbf{5}][BF_4]_2$ in CD_2Cl_2 .

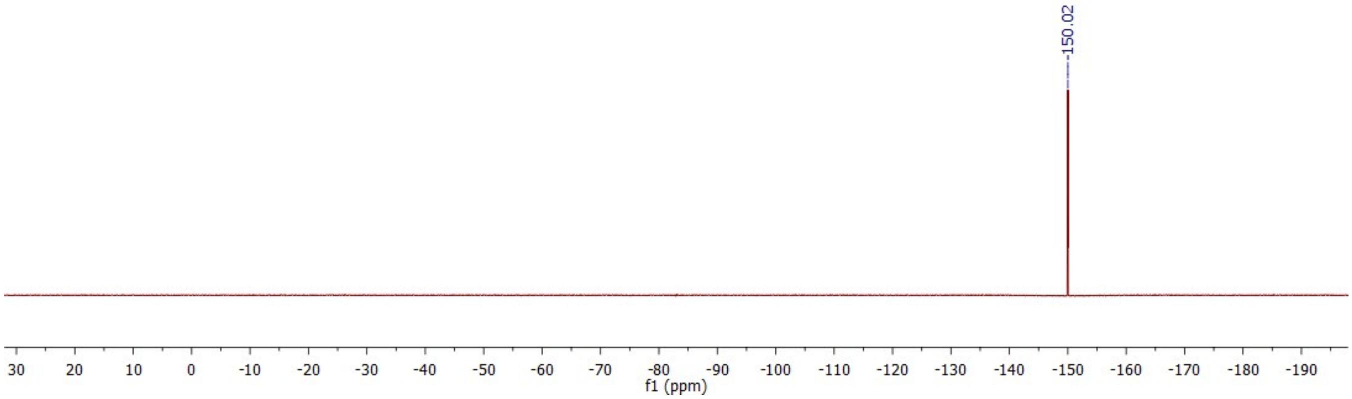


Figure S17. ^{19}F NMR of [**5**][BF_4]$_2$ in CD_2Cl_2 .

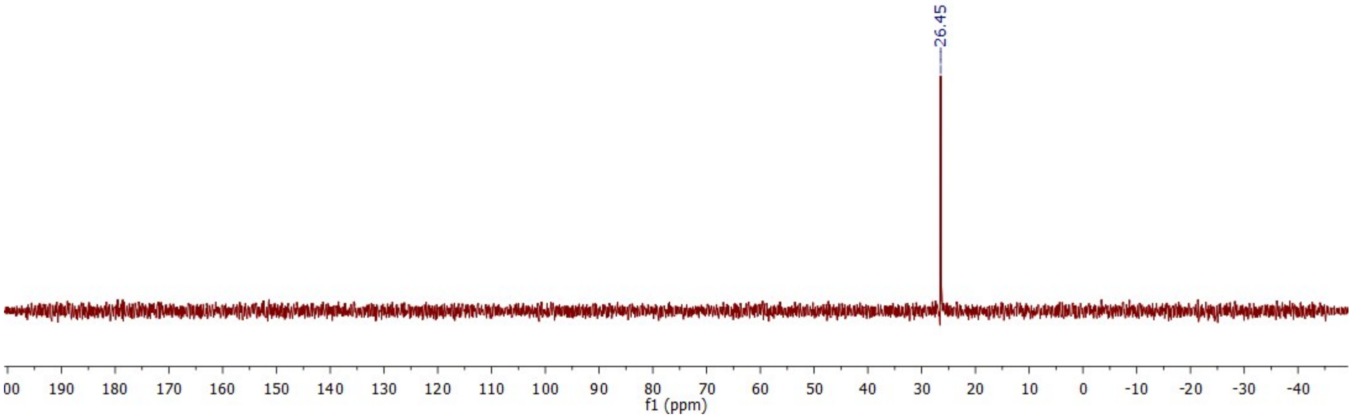


Figure S18. ^{31}P{^{1}H} NMR of [**5**][BF_4]$_2$ in CD_2Cl_2 .

1.6 Transfer hydrogenation

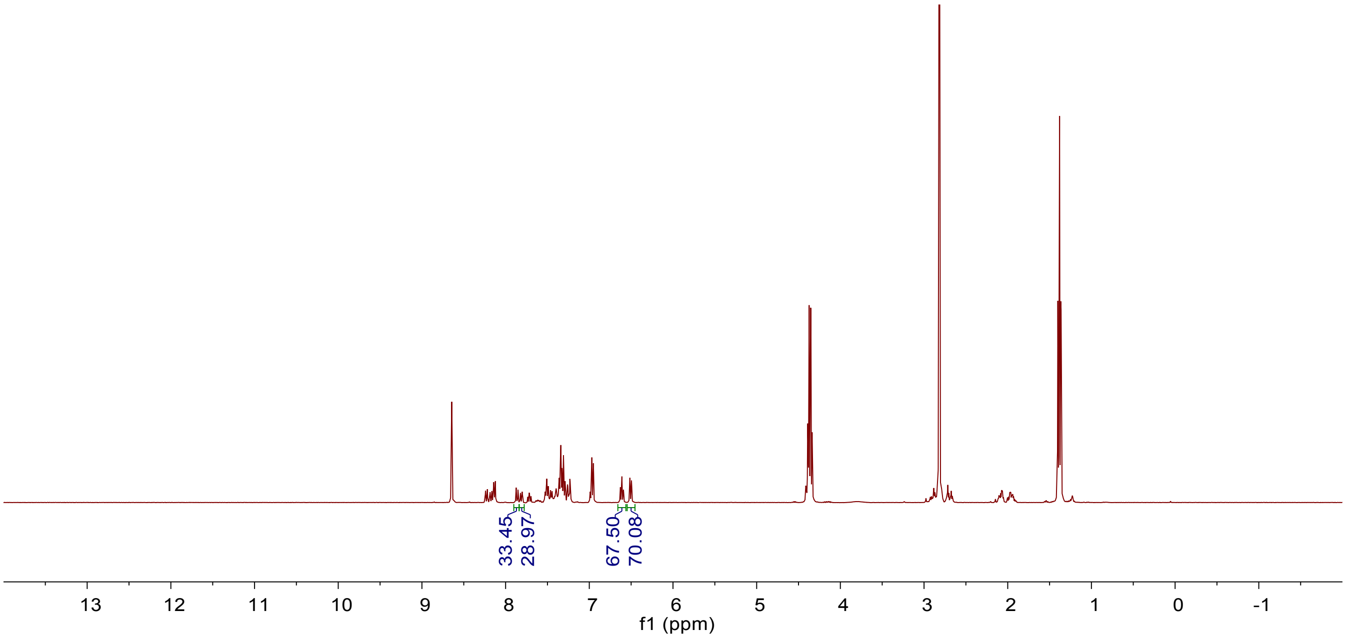


Figure S19. Representative ^{1}H NMR spectrum collected during the transfer hydrogenation reaction involving 2-phenylquinoline and Hantzsch ester with [**5**][BF$_4$]$_2$ as a catalyst.

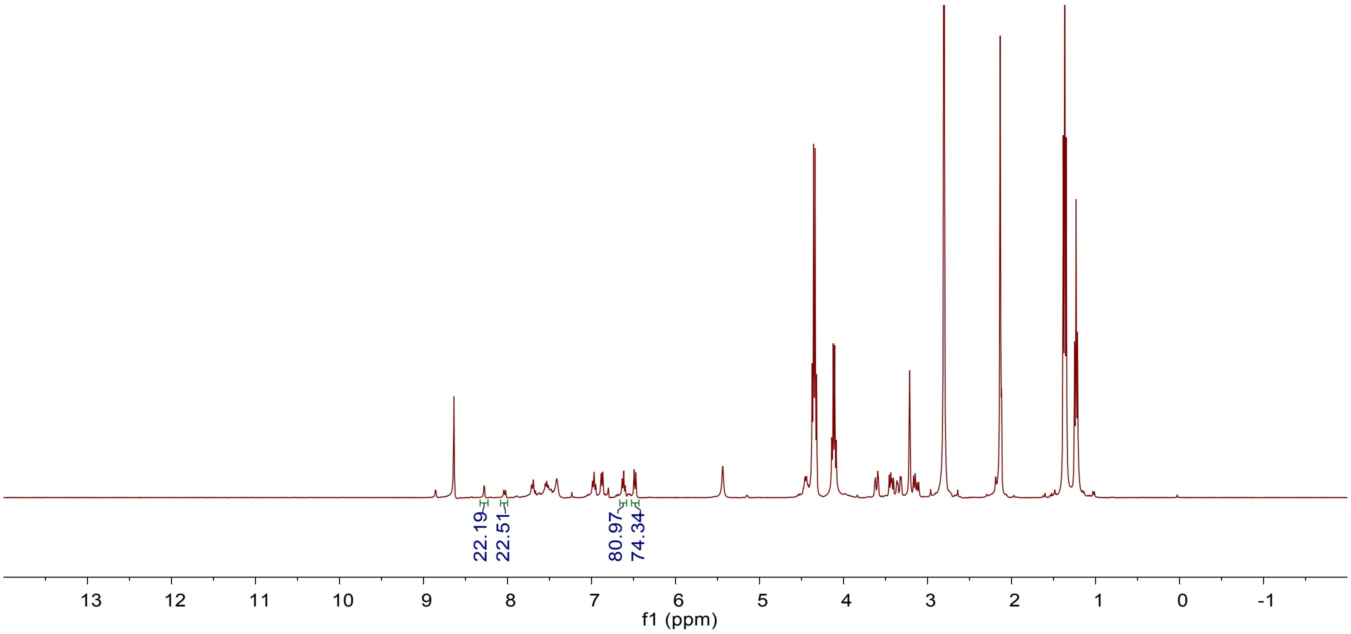
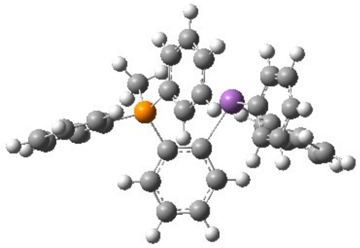


Figure S20. Representative ^{1}H NMR spectrum collected during the transfer hydrogenation reaction involving 3-bromoquinoline and Hantzsch ester with [**5**][BF$_4$]$_2$ as a catalyst.

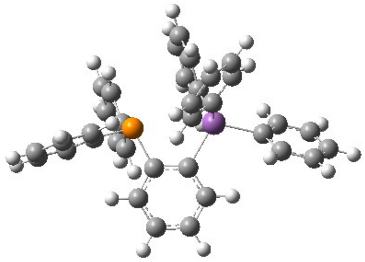
2 Computational Details

Table S1. XYZ coordinates of the optimized geometry of [**3**]$^{+}$.



Sb	1.464054	-0.133354	-0.966718
P	-2.135792	-0.524358	-0.601000
C	-1.083802	-1.397194	0.581053
C	-1.721649	-2.148369	1.577068
H	-2.805972	-2.188835	1.628810
C	-0.967241	-2.846155	2.516724
H	-1.466210	-3.425446	3.288044
C	0.419497	-2.789932	2.455317
H	1.020165	-3.332679	3.180681
C	1.051243	-2.032135	1.466017
H	2.138731	-2.004100	1.445378
C	0.327038	-1.308802	0.512005
C	-1.908353	-1.164466	-2.279812
H	-1.978831	-2.255592	-2.246706
H	-0.927234	-0.879899	-2.668494
H	-2.702198	-0.771420	-2.922261
C	-1.762106	1.226872	-0.547805
C	-1.546063	1.820897	0.703090
H	-1.534495	1.212204	1.605903
C	-1.322650	3.191216	0.783561
H	-1.141234	3.653013	1.749403
C	-1.298593	3.959532	-0.379657
H	-1.108326	5.027522	-0.315213
C	-1.500171	3.366324	-1.626172
H	-1.473313	3.968440	-2.529599
C	-1.738127	1.998212	-1.716033
H	-1.892866	1.539862	-2.689936
C	-3.873250	-0.775542	-0.199826
C	-4.633442	0.260247	0.351308
H	-4.186351	1.232875	0.538310
C	-5.977436	0.044520	0.648980
H	-6.569057	0.850039	1.074071
C	-6.558898	-1.195554	0.397557
H	-7.607579	-1.359648	0.629255
C	-5.801116	-2.230165	-0.153764
H	-6.255899	-3.196795	-0.349688
C	-4.459972	-2.024212	-0.455436
H	-3.874661	-2.839305	-0.877349
C	1.711757	1.605771	0.260487
C	1.666167	1.564561	1.660454
H	1.507659	0.617837	2.175766
C	1.823111	2.730369	2.407505
H	1.792465	2.686358	3.493412
C	2.027635	3.951255	1.762578
H	2.156279	4.859765	2.345448
C	2.077880	4.002401	0.371662
H	2.245060	4.950313	-0.133861
C	1.917688	2.834133	-0.375411
H	1.951795	2.891961	-1.462943
C	3.339136	-1.073151	-0.557661
C	4.270619	-0.547955	0.345810
H	4.061524	0.380594	0.873574
C	5.475625	-1.211616	0.576040
H	6.194695	-0.796345	1.277235
C	5.758593	-2.401590	-0.091519
H	6.698848	-2.915425	0.089276
C	4.838812	-2.929023	-0.996800
H	5.059766	-3.853237	-1.523994
C	3.637260	-2.264244	-1.231846
H	2.932192	-2.682868	-1.949751

Table S2. XYZ coordinates of the optimized geometry of [**4**]$^+$.



Sb	-1.441602	-0.139501	-0.028308
P	1.882559	-0.268939	-0.141548
C	-0.237719	-0.548354	1.653283
C	-0.861496	-0.767374	2.884399
H	-1.940312	-0.665271	2.988920
C	-0.090218	-1.130373	3.988129
H	-0.568777	-1.308061	4.946931
C	1.288816	-1.272906	3.853321
H	1.889071	-1.564332	4.711004
C	1.909265	-1.036812	2.625851
H	2.988341	-1.140617	2.532604
C	1.157657	-0.660073	1.509716
C	3.500249	-1.113229	-0.091142
C	4.656274	-0.526436	0.436756
H	4.620851	0.488899	0.826288
C	5.852720	-1.239917	0.455896
H	6.748996	-0.779792	0.862999
C	5.902138	-2.538697	-0.049027
H	6.837650	-3.091229	-0.035347
C	4.755796	-3.125653	-0.582162
H	4.796814	-4.133101	-0.987134
C	3.560444	-2.412214	-0.610263
H	2.669888	-2.859458	-1.050201
C	2.305684	1.503022	0.057708
C	2.264978	2.193656	1.273867
H	1.995304	1.675184	2.191092
C	2.576114	3.552402	1.320019
H	2.545514	4.079739	2.270010
C	2.938971	4.228075	0.156715
H	3.189987	5.284808	0.196468
C	2.982554	3.545292	-1.058578
H	3.261160	4.068964	-1.969500
C	2.656289	2.193096	-1.110090
H	2.668515	1.668115	-2.064363
C	-1.469311	-1.811631	-1.286772
C	-2.379623	-1.860817	-2.347898
H	-3.072447	-1.040119	-2.530513
C	-2.402964	-2.979269	-3.179518
H	-3.103271	-3.020692	-4.008850
C	-1.533532	-4.042604	-2.941682
H	-1.556547	-4.914302	-3.589697
C	-0.639267	-3.997606	-1.872439
H	0.028756	-4.833333	-1.683132
C	-0.602066	-2.880437	-1.042088
H	0.096369	-2.847646	-0.207044
C	-3.402803	0.111810	0.675706
C	-4.094712	-0.997092	1.179612
H	-3.630237	-1.982827	1.196854
C	-5.394439	-0.840985	1.654716
H	-5.934316	-1.699350	2.044615
C	-6.001169	0.414539	1.622282
H	-7.015652	0.533254	1.992683
C	-5.316046	1.515632	1.112512
H	-5.795063	2.490193	1.080698
C	-4.014038	1.368638	0.637033
H	-3.488615	2.230163	0.228739
C	-0.925597	1.610543	-1.051385
C	-0.777341	2.807755	-0.342147
H	-0.924963	2.843063	0.736719
C	-0.411532	3.965347	-1.024490
H	-0.281563	4.895413	-0.478549
C	-0.198141	3.922844	-2.402066
H	0.087896	4.827766	-2.931537
C	-0.338239	2.726339	-3.102934
H	-0.163736	2.697188	-4.174853
C	-0.697911	1.560825	-2.428745
H	-0.785011	0.621990	-2.973574

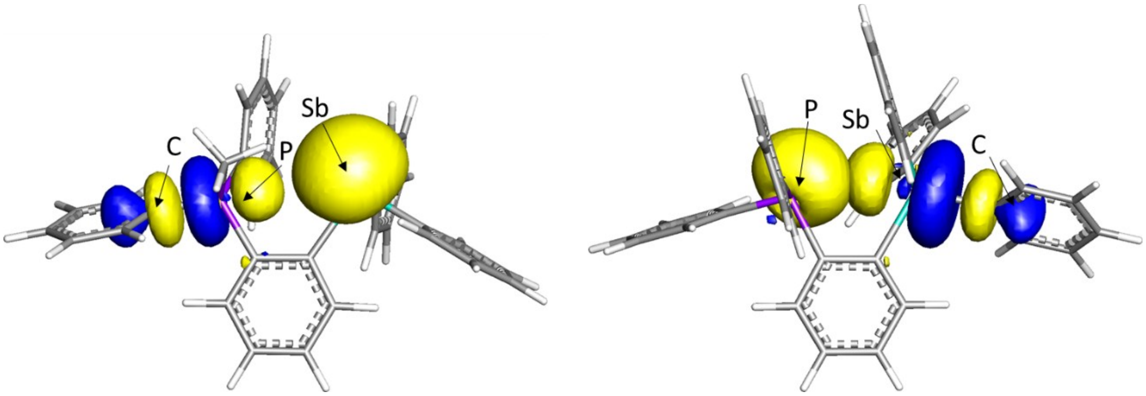
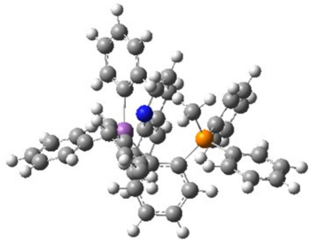
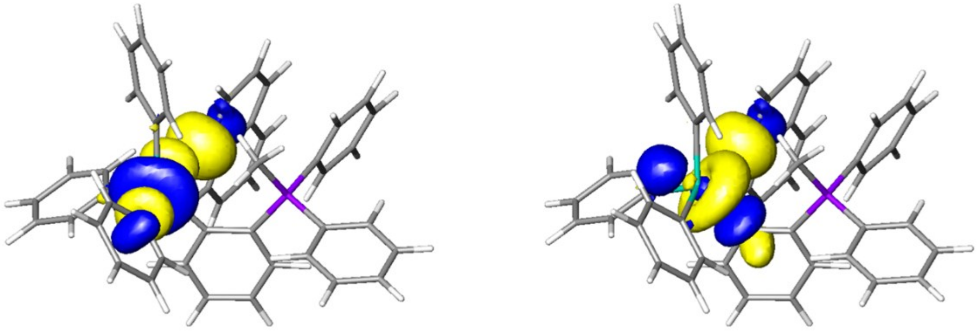


Figure S21. Principle donor-acceptor interactions (isovalue=0.05) present in [**3**]$^+$ (left) and [**4**]$^+$ (right). A lp → σ* donor-acceptor interaction contributes E_{del} = 1.0 kcal/mol and E_{del} = 8.3 kcal/mol to the stability of the cations [**3**]$^+$ and [**4**]$^+$, respectively.

Table S3. XYZ coordinates of the optimized geometry of [**5**]$^{2+}$ - quinoline.

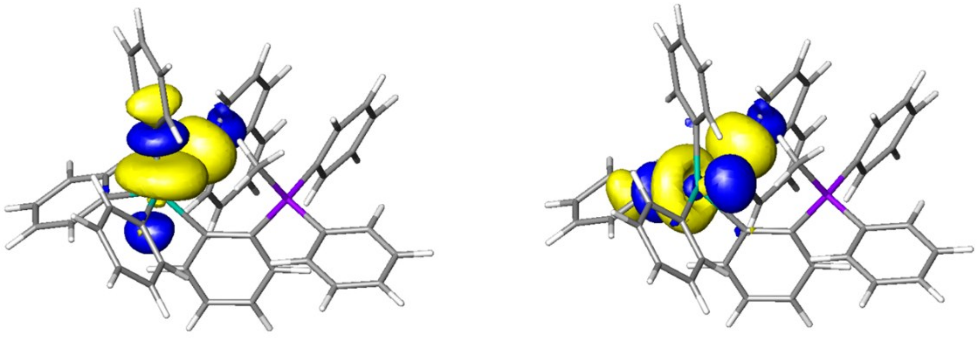


Sb	1.817730	0.216676	0.049832
C	-1.149806	0.796509	-1.278611
C	0.223369	0.501808	-1.374323
C	0.781781	0.387316	-2.656006
H	1.844195	0.179803	-2.777349
C	0.008010	0.502269	-3.810724
H	0.479696	0.399962	-4.784076
C	-1.355527	0.746904	-3.707965
H	-1.974007	0.834768	-4.596228
C	-1.918991	0.916916	-2.448057
H	-2.974520	1.173938	-2.373204
C	-3.237353	-0.135244	0.663891
C	-3.803516	-0.099769	1.947936
H	-3.468950	0.625414	2.686883
C	-4.822843	-0.986433	2.274326
H	-5.265660	-0.958011	3.265748
C	-5.284169	-1.897885	1.321792
H	-6.093367	-2.577888	1.574327
C	-4.715708	-1.936978	0.050735
H	-5.067310	-2.654529	-0.685588
C	-3.686026	-1.059271	-0.285532
H	-3.234503	-1.109073	-1.274378
C	-1.006844	1.552792	1.598240
C	3.134607	-1.106929	-0.903262
C	4.292941	-0.566387	-1.475564
H	4.485241	0.504917	-1.445496
C	5.215196	-1.414024	-2.088057
H	6.115752	-0.998703	-2.531105
C	4.982885	-2.787426	-2.125643
H	5.704964	-3.445246	-2.601290
C	3.829916	-3.323095	-1.551310
H	3.653344	-4.394559	-1.579570
C	2.900279	-2.487722	-0.936687
H	2.002315	-2.912525	-0.493505
C	-0.851837	-2.847447	-0.411923
C	-1.863942	-3.788385	-0.070011
C	-2.281313	-3.864102	1.281753
H	-3.054609	-4.576515	1.563503
C	-1.708059	-3.032856	2.206386
H	-1.997486	-3.049432	3.252193
C	-0.701044	-2.140300	1.773193
H	-0.222123	-1.499475	2.512952
N	-0.268457	-2.032795	0.531510
C	-2.450249	-4.591459	-1.081758
C	-0.446273	-2.756331	-1.768725
C	-1.038513	-3.538994	-2.730943
H	-0.716475	-3.456596	-3.765637
H	0.348015	-2.067829	-2.035241
C	-2.054202	-4.464425	-2.389535
H	-3.217962	-5.308980	-0.799506
H	-2.505522	-5.080057	-3.162150
C	1.946759	-0.218723	2.106606
C	1.857917	0.803595	3.058513
C	2.337209	-1.508092	2.486104
C	2.119348	0.521429	4.398212
H	1.611939	1.823262	2.767135
C	2.604193	-1.777957	3.826637
H	2.429036	-2.303523	1.750653
C	2.487654	-0.767909	4.781022
H	2.048822	1.313007	5.138796
H	2.908921	-2.777614	4.122719
H	2.698376	-0.982827	5.824926
P	-2.098133	1.172463	0.215400
C	2.661817	2.146392	-0.023794
C	3.782210	2.425267	0.772926
C	2.128375	3.141744	-0.852298
C	4.362603	3.690720	0.734403
H	4.206645	1.663156	1.425678
C	2.710432	4.407973	-0.879686
H	1.271025	2.935045	-1.490874
C	3.825135	4.680637	-0.088715
H	5.233938	3.904620	1.346777
H	2.299214	5.178333	-1.526025
H	4.279798	5.667090	-0.115984
C	-3.033512	2.666920	-0.131227
C	-2.320612	3.827531	-0.468145
C	-4.429709	2.684154	-0.055280
C	-3.010613	5.006346	-0.719473
H	-1.233531	3.811224	-0.543095
C	-5.111741	3.872416	-0.313969
H	-4.983262	1.784484	0.201284
C	-4.405495	5.027198	-0.641551
H	-2.465025	5.908837	-0.978428
H	-6.196052	3.892613	-0.257986
H	-4.942070	5.950550	-0.840896
H	-0.235541	2.260055	1.267249
H	-1.595609	2.041152	2.381106
H	-0.559135	0.641138	1.999273



lp(N) → σ^*(Sb-C) 7.23 kcal/mol

lp(N) → σ^*(Sb-C) 3.12 kcal/mol

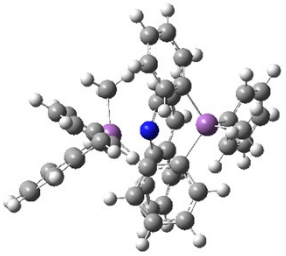


lp(N) → σ^*(Sb-C) 2.37 kcal/mol

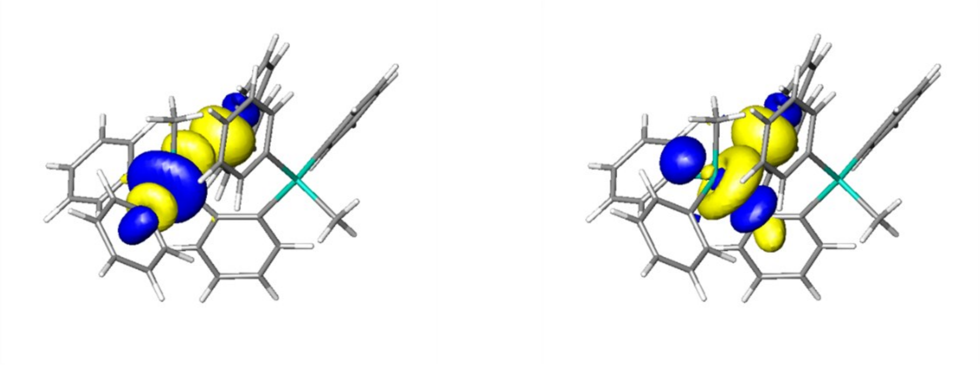
lp(N) → σ^*(Sb-C) 0.51 kcal/mol

Figure S22. Natural Bond Orbital (NBO) plots of the donor-acceptor interactions in [**5**]$^{2+}$ - quinoline (isodensity value 0.05) with the corresponding second order energies.

Table S4. XYZ coordinates of the optimized geometry of [**6**]$^{2+}$ - quinoline.

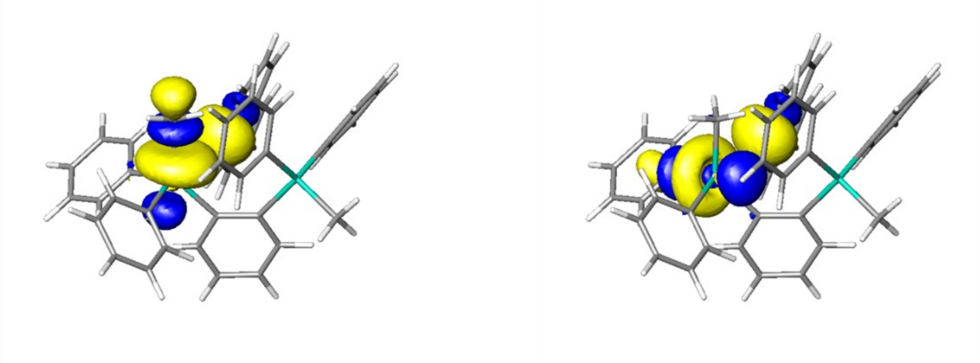


Sb	1.572569	-1.823592	-0.826057
Sb	-1.860402	0.304221	0.399755
C	0.409966	-0.409329	-1.867294
C	-0.786471	0.204131	-1.457066
C	-1.479485	0.992504	-2.386890
H	-2.414156	1.480440	-2.110776
C	-0.989483	1.210218	-3.675396
H	-1.552383	1.832458	-4.365401
C	0.214662	0.636841	-4.061322
H	0.618331	0.806065	-5.055293
C	0.896194	-0.181979	-3.162826
H	1.823172	-0.650338	-3.493685
C	3.441895	-1.104277	-0.249624
C	4.266142	-1.913907	0.543946
H	3.933598	-2.890360	0.893722
C	5.542460	-1.467989	0.875319
H	6.187227	-2.087401	1.492026
C	5.995378	-0.236379	0.399855
H	6.996932	0.101517	0.651380
C	5.178804	0.553474	-0.407898
H	5.537278	1.508325	-0.783265
C	3.892518	0.126516	-0.735071
H	3.255270	0.757415	-1.353809
C	0.439691	-2.697627	0.698204
C	-0.868206	-3.078743	0.367781
H	-1.275940	-2.894971	-0.627559
C	-1.671950	-3.701191	1.322587
H	-2.692552	-3.977227	1.069531
C	-1.155093	-3.974631	2.589352
H	-1.774112	-4.473002	3.330297
C	0.156855	-3.618716	2.910206
H	0.556172	-3.842718	3.895558
C	0.957708	-2.970505	1.969748
H	1.972017	-2.677919	2.235665
C	1.897497	-3.370648	-2.227787
H	0.935250	-3.752381	-2.579023
H	2.451065	-4.173643	-1.732886
H	2.482366	-2.998838	-3.072801
C	-2.483133	2.296857	0.574472
C	-3.706573	2.676429	0.007454
H	-4.322609	1.954916	-0.527981
C	-4.151645	3.989075	0.149964
H	-5.101104	4.287760	-0.285195
C	-3.383695	4.911915	0.858607
H	-3.736171	5.933444	0.970873
C	-2.171493	4.529266	1.432497
H	-1.580618	5.249481	1.991153
C	-1.715916	3.220346	1.294587
H	-0.768595	2.929170	1.744509
C	1.710991	2.286984	0.479789
C	2.947688	2.794960	0.970027
C	3.560968	2.130029	2.059761
H	4.506895	2.501649	2.448750
C	2.955451	1.025435	2.599687
H	3.391341	0.481711	3.431700
C	1.722734	0.604536	2.052079
H	1.228609	-0.264907	2.486165
C	-1.399990	-0.278951	2.371688
H	-0.919524	0.562347	2.873741
H	-0.786737	-1.176984	2.423045
H	-2.375399	-0.478611	2.827139
C	-5.777315	-1.591037	0.559560
C	-4.639697	-0.833642	0.832012
C	-3.679385	-1.522127	-1.284899
C	-4.818042	-2.280814	-1.550604
H	-6.597094	-1.610571	1.272082
H	-4.595355	-0.260870	1.758196
H	-2.875891	-1.490136	-2.019695
H	-4.892290	-2.837234	-2.480770
C	-5.862968	-2.317154	-0.628284
H	-6.750879	-2.906303	-0.839880
N	1.103626	1.188521	1.041466
C	-3.584469	-0.801472	-0.088975
C	3.542609	3.921355	0.345216
C	1.098493	2.938677	-0.621678
C	1.700840	4.023430	-1.212593
H	1.220842	4.513960	-2.054939
H	0.142659	2.575631	-0.983842
C	2.936595	4.520681	-0.730303
H	4.485008	4.299451	0.735131
H	3.394685	5.381667	-1.208041



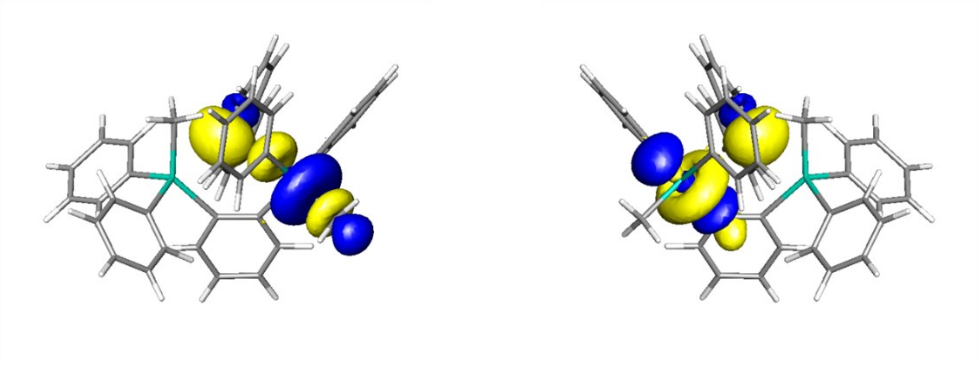
lp(N) → σ*(Sb-C) 6.21 kcal/mol

lp(N) → σ*(Sb-C) 2.29 kcal/mol



lp(N) → σ*(Sb-C) 1.72 kcal/mol

lp(N) → σ*(Sb-C) 0.33 kcal/mol



lp(N) → σ*(Sb-C) 0.61 kcal/mol

lp(N) → σ*(Sb-C) 0.12 kcal/mol

Figure S23. Natural Bond Orbital (NBO) plots of the donor-acceptor interactions in [**6**]$^{2+}$ - quinoline (isodensity value 0.05) with the corresponding second order energies.

References

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