Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

for

Crystallographic evidence for continuum and reversal of roles in primary-secondary interactions in antimony Lewis acids: Applications in carbonyl activation

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1. General Methods

Synthesis: All the reaction procedures were carried out in argon atmosphere using standard glovebox and Schlenk line techniques. [1] All the glassware were dried at 200 °C before use. Dichloromethane, *n*-pentane, C_6D_5-Br and CD_2Cl_2 were dried over CaH_2. Na/Ph_2CO was used as a drying agent for toluene, diethyl ether (Et_2O) and tetrahydrofuran (THF).[2] The solvents were then distilled, degassed and stored over $LiAlH_4$ (toluene, *n*-pentane, THF), CaH_2 (CH_2Cl_2, CD_2Cl_2) and 3 Å molecular sieves(C_6D_5-Br) at least a day prior to the use. Thereafter, the solvents were directly condensed into the reaction flask at -196 °C. Anhydrous $SbCl_3$, Et_3PO, $AgPF_6$ and AgOTf were purchased from Sigma-Aldrich. Et_3PO, $AgPF_6$ and AgOTf were directly taken into glovebox and used in experiments without any further purification. $SbCl_3$ was purified by sublimation and stored in glovebox. (mesityl)Li[3], $[(NMe_2)CH_2C_6H_4Li]$[4], $[(NMe_2)C_6H_4Li]$[4], $((NMe_2)CH_2C_6H_4)SbCl_2$[5], $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$[6] and $[Ag(CH_3CN)_2][B(C_6H_3Cl_2)_4]$[7] were prepared according to the reported literature procedures. 2-Bromomesitylene, N, N-dimethylphenylamine and N, N-dimethylbenzylamine were procured from Sigma-Aldrich. They were dried over CaH_2 and stored over 3 Å molecular sieves before use.[2] Percentage yields are reported for the crystallized products.

Characterization: ^1H, $^{13}C\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker Avance III 500 MHz spectrometer at ambient temperature. The chemical shifts (δ ppm) in ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual signals of the deuterated solvents. ^{19}F and $^{31}P\{^1H\}$ NMR spectra were referenced to $CFCl_3$ and H_3PO_4 (85%) respectively. Abbreviations for NMR spectra: s (singlet), br (broad), m (multiplet). Elemental analyses were performed on samples, well dried at 1×10^{-3} mbar at ambient temperature, on Elemental Vario Micro Cube instrument.

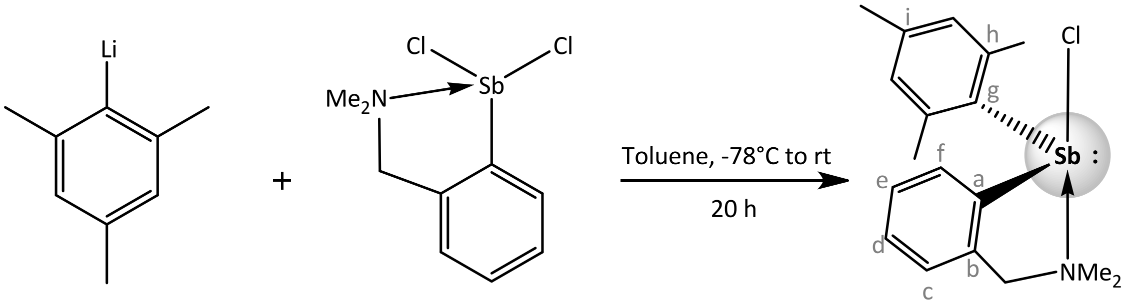
2. Experimental Procedures

2.1 Synthesis and Characterization

Synthesis and characterization of 1A:

A 30 mL toluene solution of (mesityl)Li (0.077 g, 0.611 mmol) was added dropwise to a 20 mL toluene solution of $((NMe_2)CH_2C_6H_4)SbCl_2$ (0.200 g, 0.611 mmol) at -78 ^{o}C. The reaction was allowed to attain ambient temperature and stirred for 20 h. The reaction mixture was filtered and toluene was distilled off. The white powder was dissolved in 2 mL dichloromethane layered with *n*-pentane. Colorless crystals of **1A** were obtained after one day at -30 ^{o}C.

Yield: 0.19 g, 76%



Scheme S1

Elemental analysis for $C_{18}H_{23}NSbCl$: C, 52.65; H, 5.65; N, 3.41. Found: C, 52.62; H, 5.57; N, 3.38

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.96 (s, br, 3H, *o*-CH_3), 2.10 (s, 3H, NMe_2), 2.24 (s, 3H, *p*-CH_3), 2.35 (s, 3H, NMe_2), 2.69 (3H, s, br, *o*-CH_3), AB spin system with A at 3.46, 3.48 (d, 1H, CH_2, $^3J_{HH}$ = 14.0 Hz) and B at 3.69, 3.71 (d, 1H, CH_2, $^3J_{HH}$ = 14.0 Hz), 6.85 (s, br, 2H, *m*-H(C_6H_{11})), 7.21 (d, 1H, *o*-C_6H_4 ,$^3J_{HH}$ = 7.4 Hz), 7.34 (*t*, 1H, C_6H_4, $^3J_{HH}$ = 7.4 Hz), 7.40 (*t*, 1H, C_6H_4, $^3J_{HH}$ = 7.3 Hz), 8.41 (d, 1H, *m*-C_6H_4,$^3J_{HH}$ = 7.3 Hz)

^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 20.7 (*p*-CH_3), 25.2 (*o*-CH_3), 45.4 (NMe_2), 66.3 (*CH_2*NMe_2), 126.2 (c, C_6H_4), 128.4 (d, C_6H_4), 128.8 (*m*-CH, C_9H_{11}), 129.0 (e, C_6H_4), 136.2 (g, C_9H_{11}), 139.2 (i, C_6H_{11}), 141.5 (b, C_6H_4), 142.9 (f, C_6H_4), 145.8 (a, C_6H_4, h, C_6H_{11})

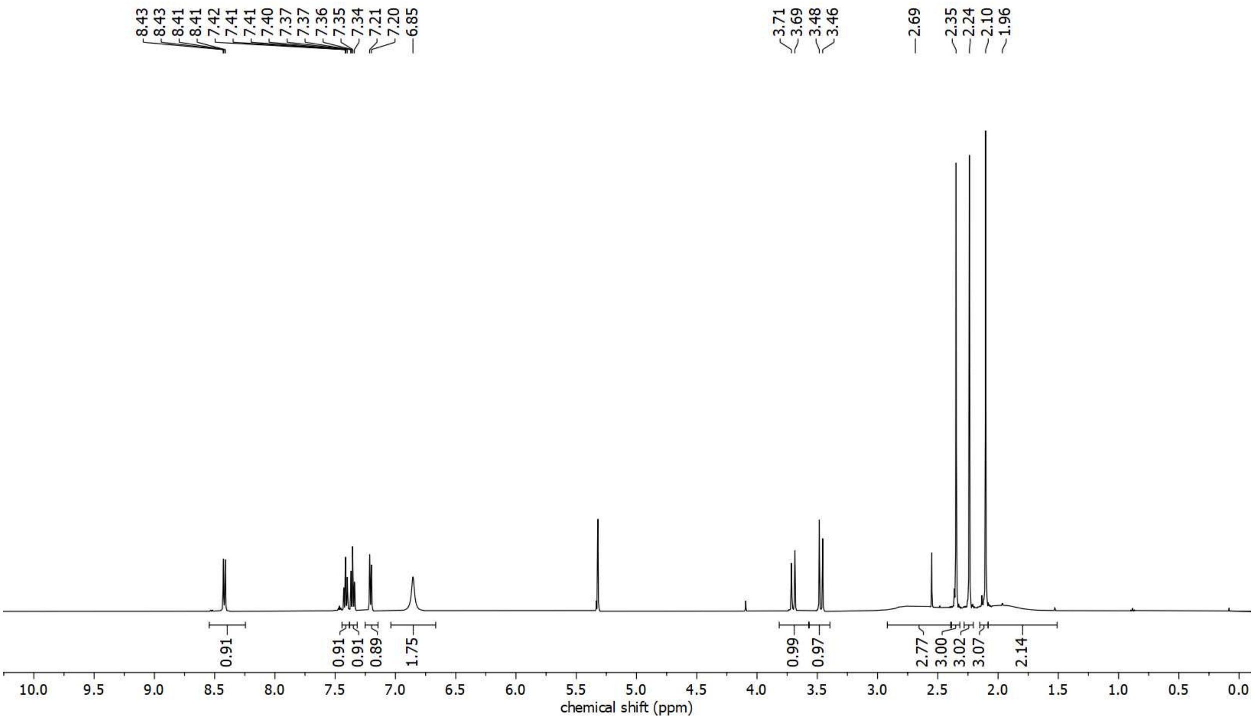


Figure S1: ^1H NMR spectrum of **1A** recorded in CD_2Cl_2.

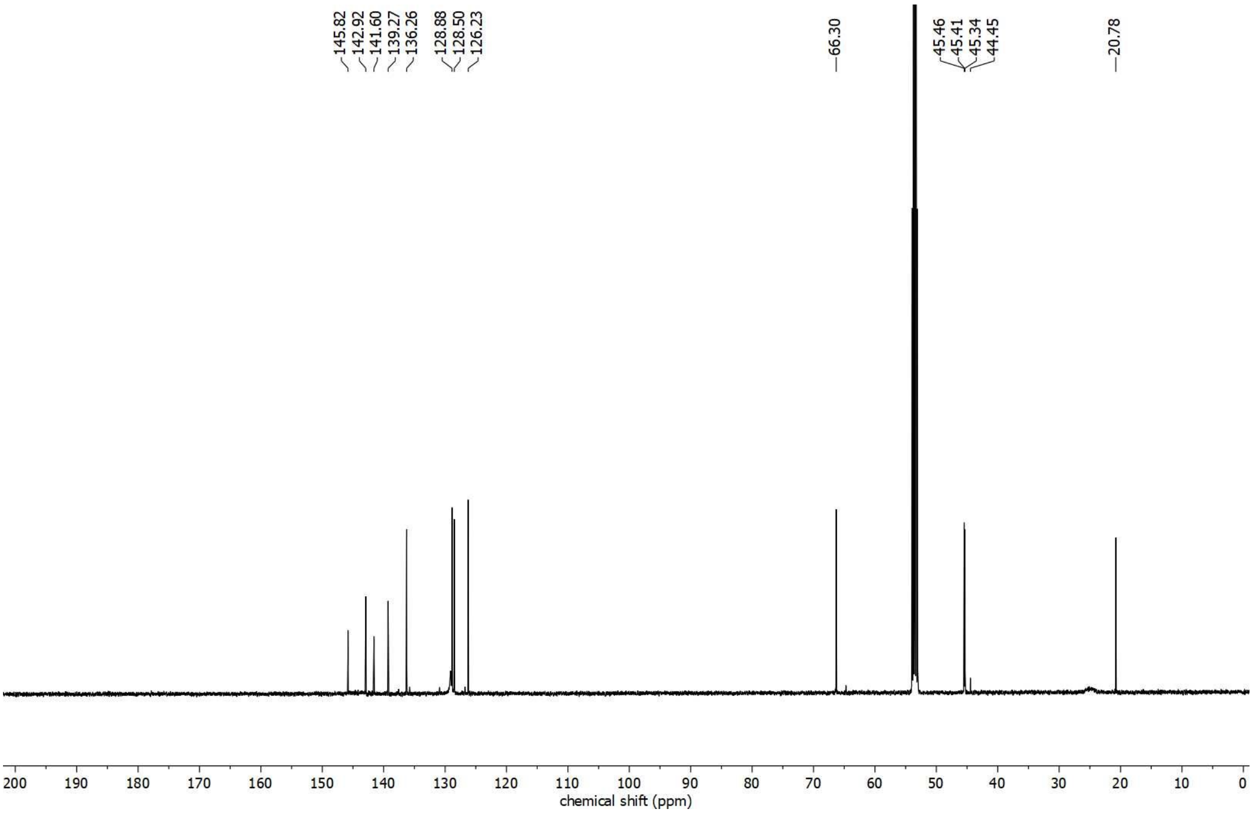
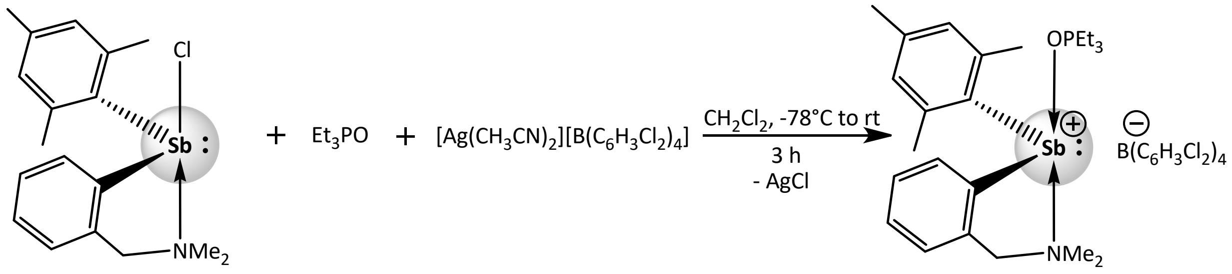


Figure S2: $^{13}C\{^1H\}$ NMR spectrum of **1A** recorded in CD_2Cl_2.

Synthesis and characterization of 2A:

1A (0.035 g, 0.085 mmol), $O{=}PEt_3$ (0.011 g, 0.085 mmol) and $[Ag(CH_3CN)_2][B(C_6H_3Cl_2)_4]$ (0.070 g, 0.085 mmol) were loaded into a Schlenk flask. Dichloromethane (5 mL) was condensed on to the mixture at -78 °C. The reaction mixture was allowed to attain room temperature and stirred for 3 h. Thereafter, filtration of the reaction mixture gave a colorless solution. The solution was concentrated to 1.5 mL, layered with *n*-pentane and stored at -30 °C to obtain colorless crystals of **2A**.

Yield: 0.087 g, 61%



Scheme S2

Elemental analysis for $C_{48}H_{50}BNOPCl_8Sb$: C, 55.22; H, 4.56; N, 1.27. Found: C, 55.18; H, 4.46; N, 1.29

^1H NMR (CD_2Cl_2, 500 MHz): δ 1.03 (m, 9H, Et_3PO, CH_3), 1.68 (m, 6H, Et_3PO, CH_2), δ 1.82 (s, br, 3H, *o*-CH_3), 2.25 (s, 3H, *p*-CH_3), 2.29 (s, 3H, NMe_2), 2.49 (s, 3H, NMe_2), 2.75 (3H, s, br, *o*-CH_3), AB spin system with A at 3.65, 3.68 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz) and B at 3.84, 3.87 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz), 6.84 (s, br, 2H, *m*-H(C_6H_{11})), 7.29 (d, 1H, *o*-C_6H_4 ,$^3J_{HH}$ = 7.1 Hz), 7.44 (m, 2H, C_6H_4, $^3J_{HH}$ = 7.4 Hz), 7.94 (d, 1H, *m*-C_6H_4,$^3J_{HH}$ = 7.1 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 5.2 ($OPEt_3$, CH_3), 18.8 (s, $OPEt_3$, CH_2), δ 20.8 (*p*-CH_3), 25.6 (*o*-CH_3), 45.9 (NMe_2), 67.4 (*CH_2*NMe_2), 126.6 (c, C_6H_4), 129.1 (d, C_6H_4), 129.6 (*m*-CH, C_9H_{11}) 130.0 (e, C_6H_4), 134.7 (g, C_9H_{11}), 141.0 (i, C_9H_{11}), 142.5 (b, C_6H_4), 143.1 (f, C_6H_4), 145.2 (a, C_6H_4, h, C_9H_{11}), 133.1 (*m*-CH, $BAr^{Cl2}{}_4$), 132.9 (q, $^3J_{BC}$ = 4.5 Hz, $BAr^{Cl2}{}_4$), 123.0 (*p*-CH, $BAr^{Cl2}{}_4$), 164.1 (q, $^1J_{BC}$ = 49.2 Hz, $BAr^{Cl2}{}_4$)

^{11}B NMR (CD_2Cl_2, 160 MHz): δ -6.9 (s, $B(C_6H_3Cl_2)_4$)

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 71.4 (s, $OPEt_3$)

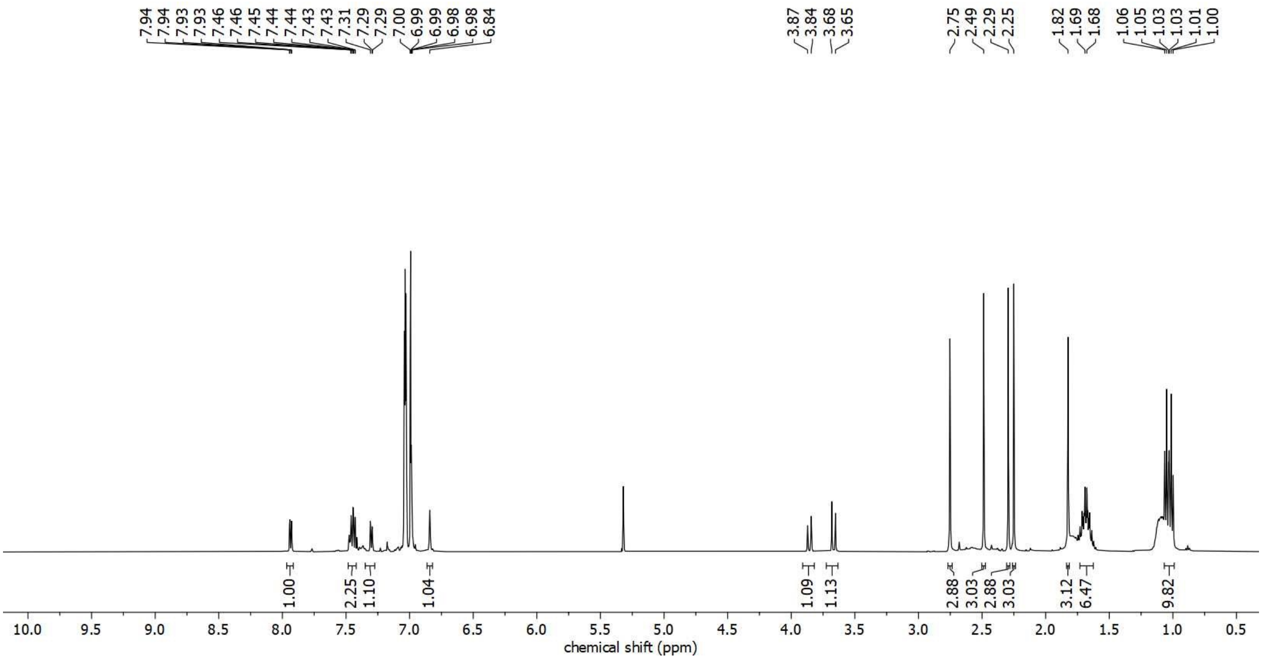


Figure S3: ^{1}H NMR spectrum of **2A** recorded in CD_2Cl_2.

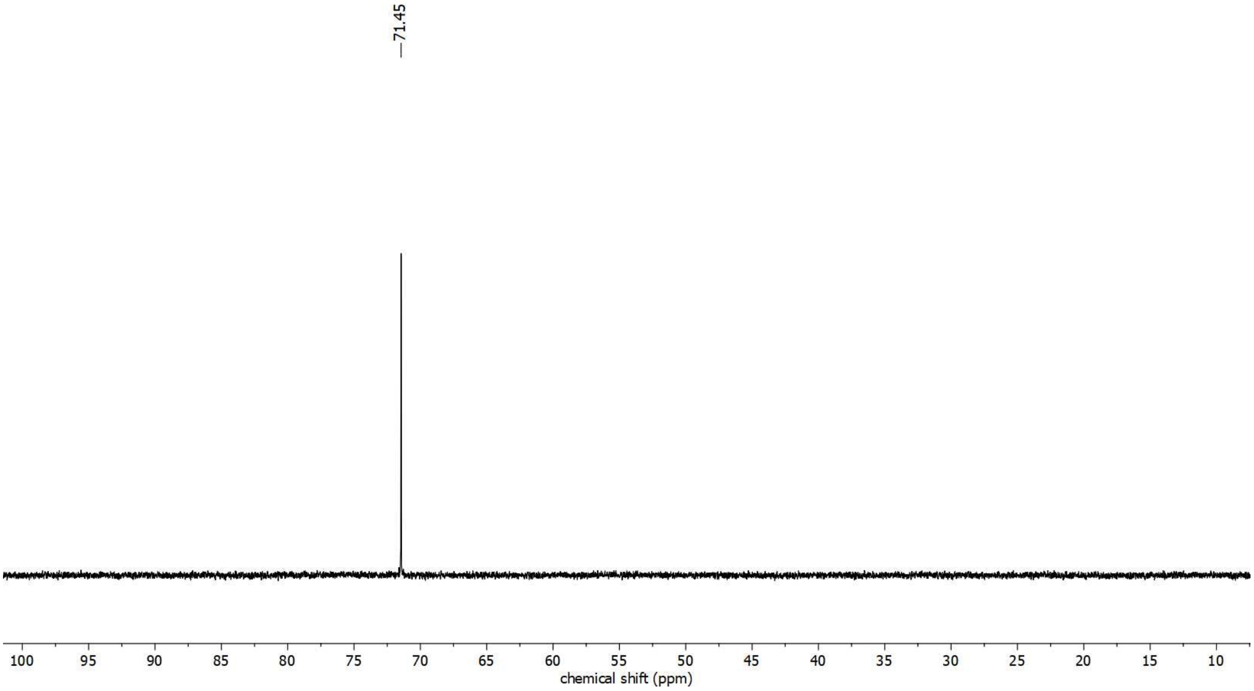


Figure S4: $^{31}P\{^1H\}$ NMR spectrum of **2A** recorded in CD_2Cl_2.

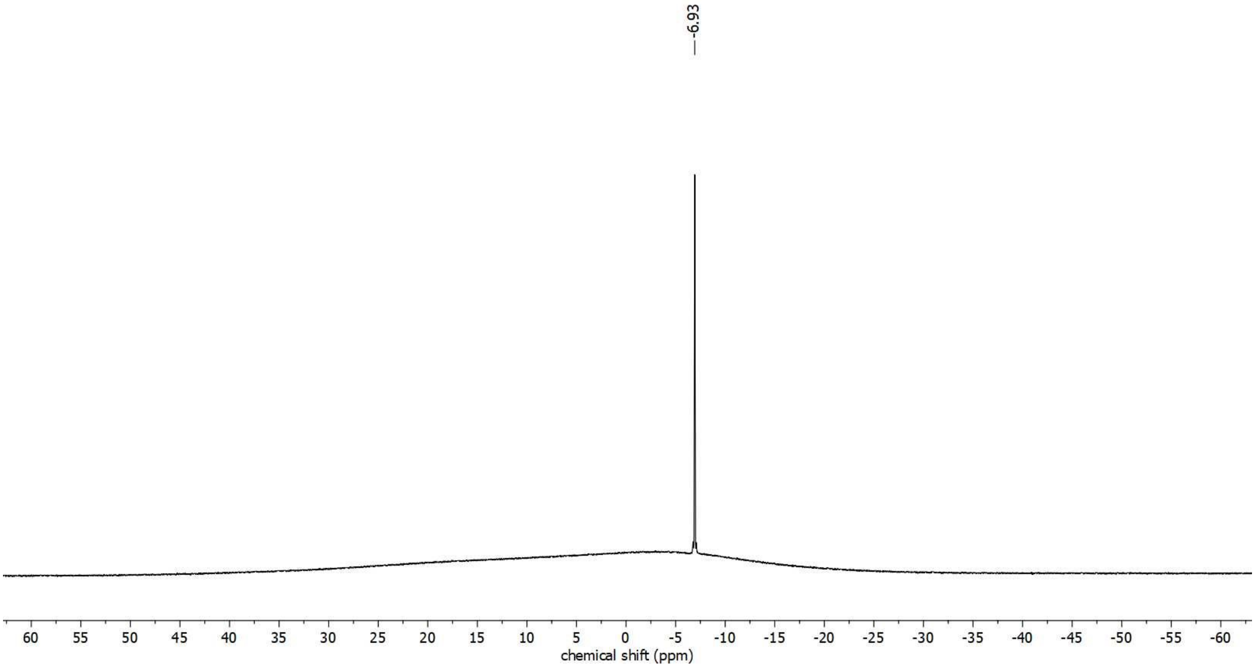


Figure S5: ^{11}B NMR spectrum of **2A** recorded in CD_2Cl_2.

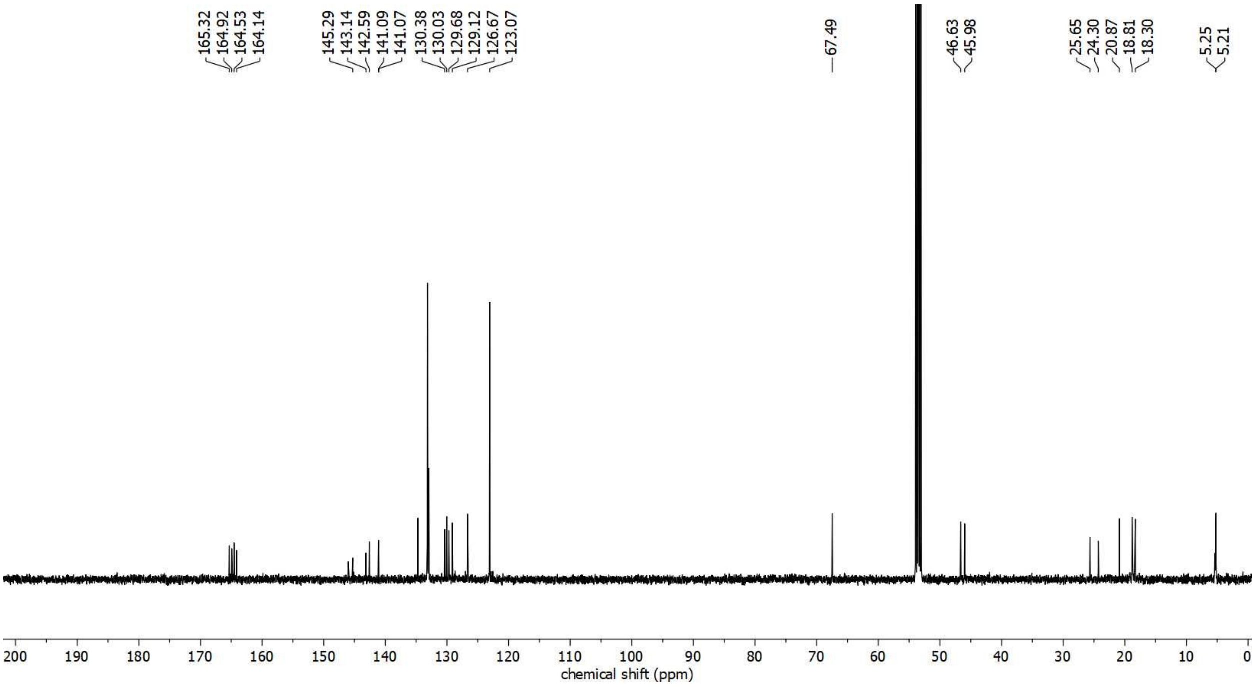
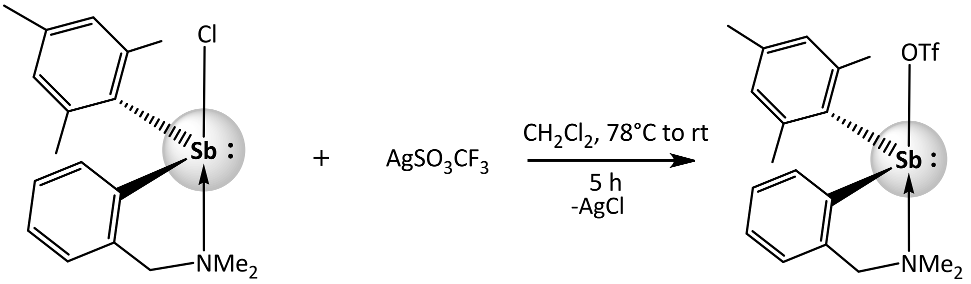


Figure S6: $^{13}C\{^1H\}$ NMR spectrum of **2A** recorded in CD_2Cl_2.

Synthesis and characterization of 3A:

1A (0.100 g, 0.243 mmol) and AgOTf (0.063 g, 0.243 mmol) were loaded into a Schlenk flask. Dichloromethane (5 mL) was condensed on to the mixture at -78 °C. The reaction mixture was allowed to attain room temperature and stirred for 5 h. Thereafter, filtration of the reaction mixture gave a colorless solution. The solution was concentrated to 1 mL, layered with *n*-pentane and stored at -30 °C to receive colorless crystals of **3A**.

Yield: 0.092 g, 72%



Scheme S3

Elemental analysis for $C_{19}H_{23}NO_3SF_3Sb$: C, 43.53; H, 4.42; N, 2.67. Found: C, 43.47; H, 4.38; N, 2.59

^1H NMR(CD_2Cl_2, 500 MHz): δ 1.83 (s, br, 3H, *o*-CH_3), 2.26 (s, 3H, *p*-CH_3), 2.38 (s, 3H, NMe_2), 2.62 (s, 3H, NMe_2), 2.82 (3H, s, br, *o*-CH_3), AB spin system with A at 3.74, 3.77 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz) and B at 3.94, 3.97 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz), 6.86, 6.98 (d, br, 2H, *m*-H (C_6H_{11}), $^3J_{HH}$ = 63.5 Hz), 7.32 (d, 1H, *o*-C_6H_4 ,$^3J_{HH}$ = 7.1 Hz), 7.46(dt, 2H, C_6H_4, $^3J_{HH}$ = 7.4 Hz), 8.18 (d, 1H, *m*-C_6H_4,$^3J_{HH}$ = 7.3 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 20.8 (*p*-CH_3), 24.2 (*o*-CH_3), 47.2 (NMe_2), 68.4 (*CH_2*NMe_2), 126.1 (c, C_6H_4), 129.3 (d, C_6H_4), 129.8 (*m*-CH, C_9H_{11}), 129.3 (e, C_6H_4), 136.1 (g, C_9H_{11}), 139.2 (i, C_9H_{11}), 140.8 (b, C_6H_4), 142.6 (f, C_6H_4), 146.9 (a, C_6H_4, h, C_6H_{11})

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -78.6 (s, OSO_2CF_3)

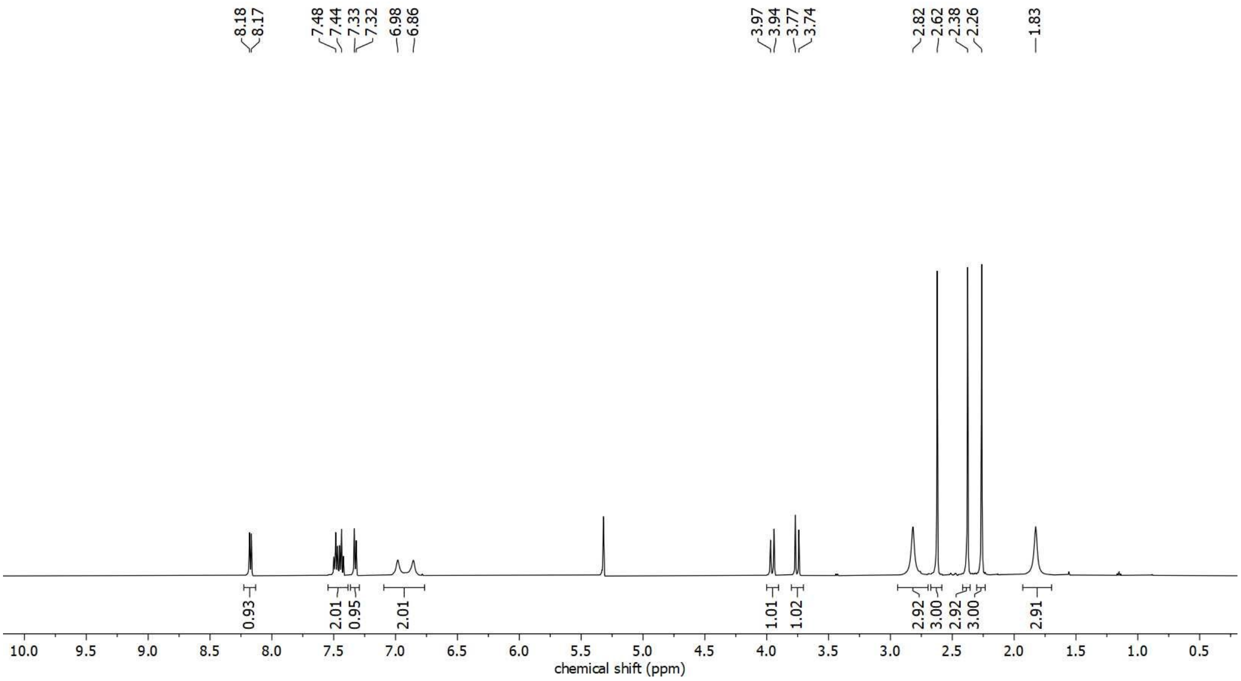


Figure S7: ^{1}H NMR spectrum of **3A** recorded in CD_2Cl_2.

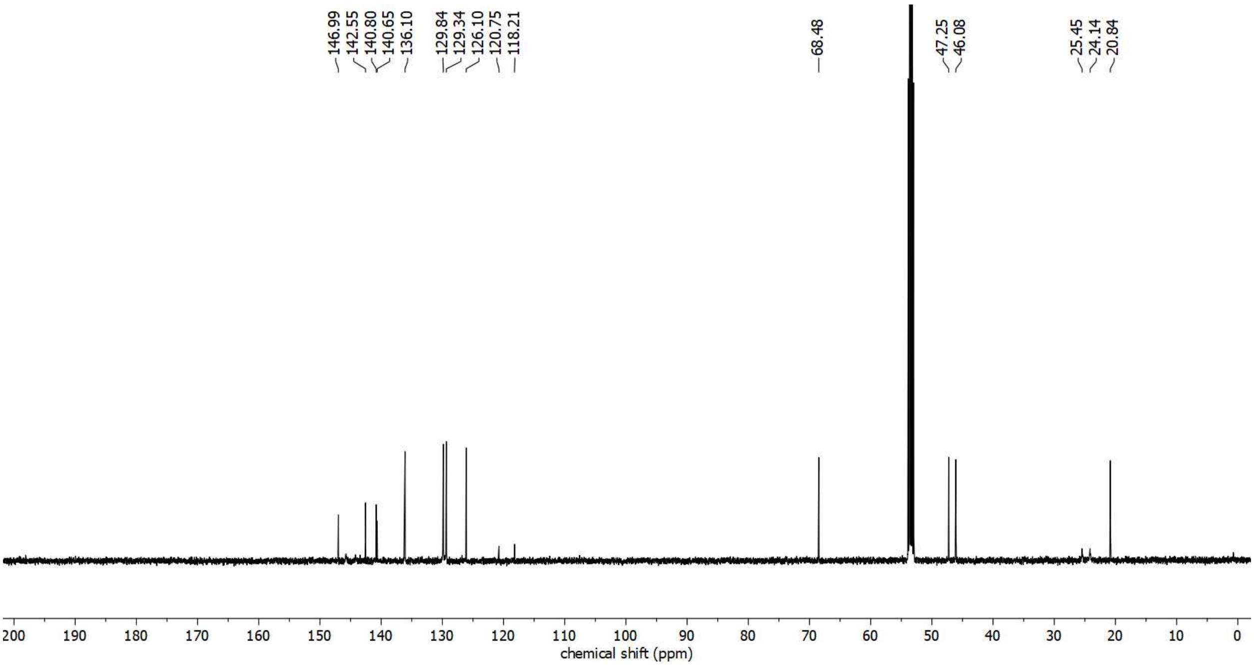


Figure S8: $^{13}C\{^1H\}$ NMR spectrum of **3A** recorded in CD_2Cl_2.

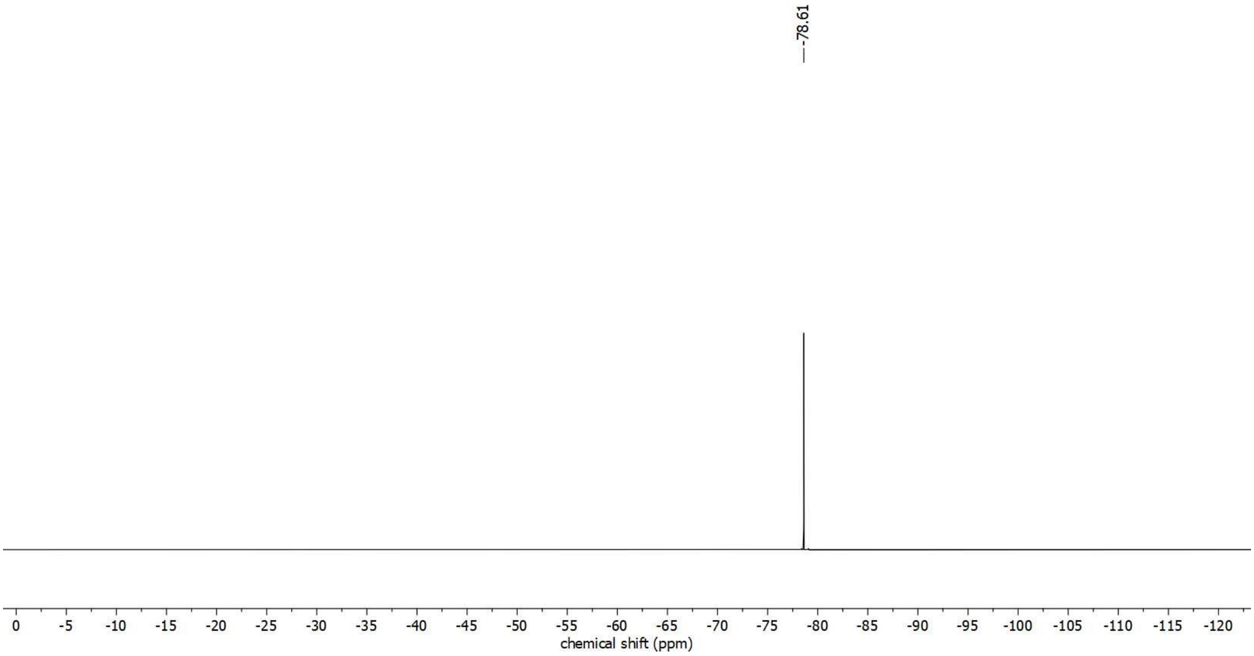
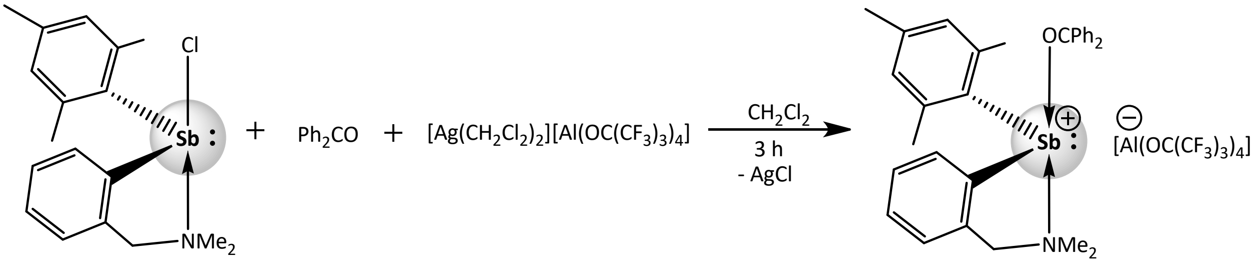


Figure S9: ^{19}F NMR spectrum of **3A** recorded in CD_2Cl_2.

Synthesis and characterization of 4A:

1A (0.1 g, 0.243 mmol), Ph_2CO (0.044 g, 0.085 mmol) and $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.303 g, 0.243 mmol) were loaded into a vial in glovebox. Dichloromethane (5 mL) was added on to the mixture at room temperature. The reaction mixture was stirred for 3 h. Thereafter, filtration of the reaction mixture resulted in a pale-yellow solution. The solution was concentrated to 1.5 mL, layered with *n*-pentane and stored at -30 °C to obtain yellow crystals of **4A** after four days.

Yield: 0.196 g, 47%



Scheme S4

Elemental analysis for $C_{47}H_{33}NO_5F_{36}AlSb$: C, 37.03; H, 2.18; N, 0.92. Found: C, 37.13; H, 2.13; N, 0.90

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.17 (s, br, 6H, *o*-CH_3), 2.25 (s, 3H, *p*-CH_3), 2.60 (s, 3H, NMe_2), 2.85 (s, 3H, NMe_2), AB spin system with A at 4.03, 4.06 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz) and B at 4.22, 4.25 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz), 6.91 (s, br, 2H, *m*-H (C_6H_{11})), 7.52 (t, 4H, *m*-CH,Ph_2CO,

$^3J_{HH}$ = 7.6 Hz), 7.60 (t, 1H, *p*-CH, Ph_2CO, 1H, t, C_6H_4, , $^3J_{HH}$ = 3.4 Hz), 7.66 (d, 1H, *o*-CH, Ph_2CO,$^3J_{HH}$ = 8.9 Hz), 7.71 (*t*, 2H, $C_6H_{4,}$ $^3J_{HH}$ = 7.7 Hz), 8.21 (d, 1H, C_6H_4)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 20.9 (*p*-CH_3), 24.9 (*o*-CH_3), 47.2, 48.7 (NMe_2), 70.7 (CH_2NMe_2), 120.1, 122.5 ($Al(OC(CF_3)_3)_4$, J_{CF} =292.8 Hz), 126.2 (c, C_6H_4), 127.0 (d, C_6H_4), 128.7 (*m*-CH, C_9H_{11}), 130.6 (e, C_6H_4), 136.5 (g, C_9H_{11}), 139.2 (i, C_6H_{11}), 142.9 (b, C_6H_4), 143.0 (f,), 145.2 (h, C_9H_{11}), 146.7 (a, C_6H_4), 202.7 (Ph_2*CO*)

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -75.7 (s, $Al(OC(CF_3)_3)_4$)

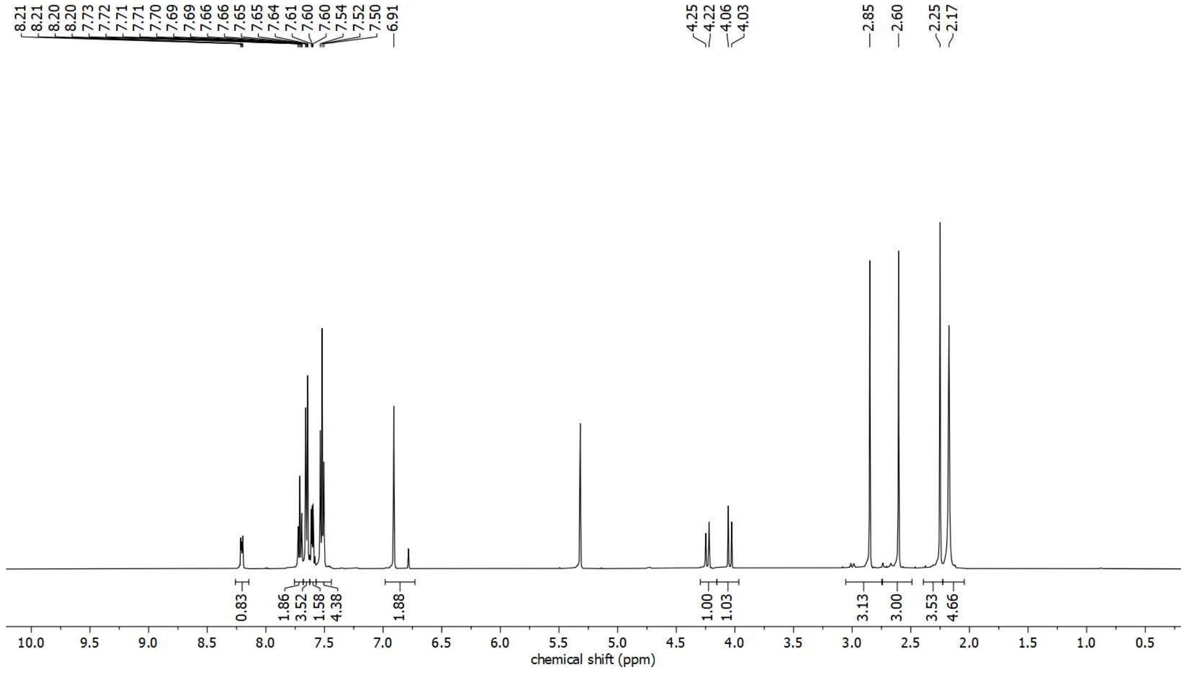


Figure S10: ^1H NMR spectrum of **4A** recorded in CD_2Cl_2.

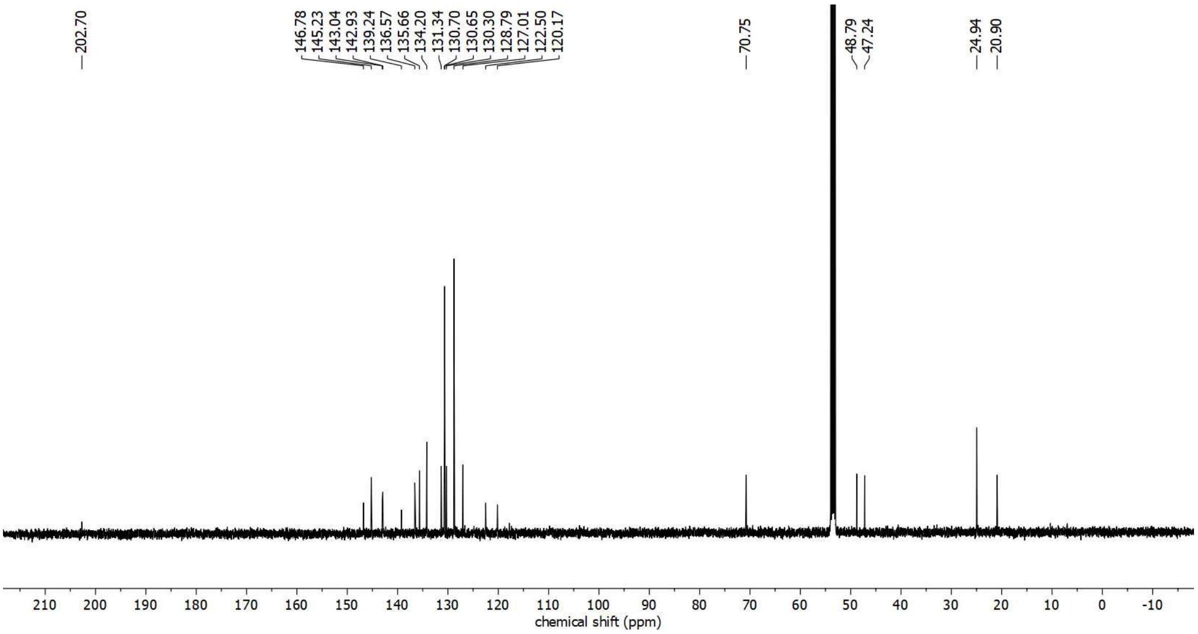


Figure S11: $^{13}C\{^1H\}$ NMR spectrum of **4A** recorded in CD_2Cl_2.

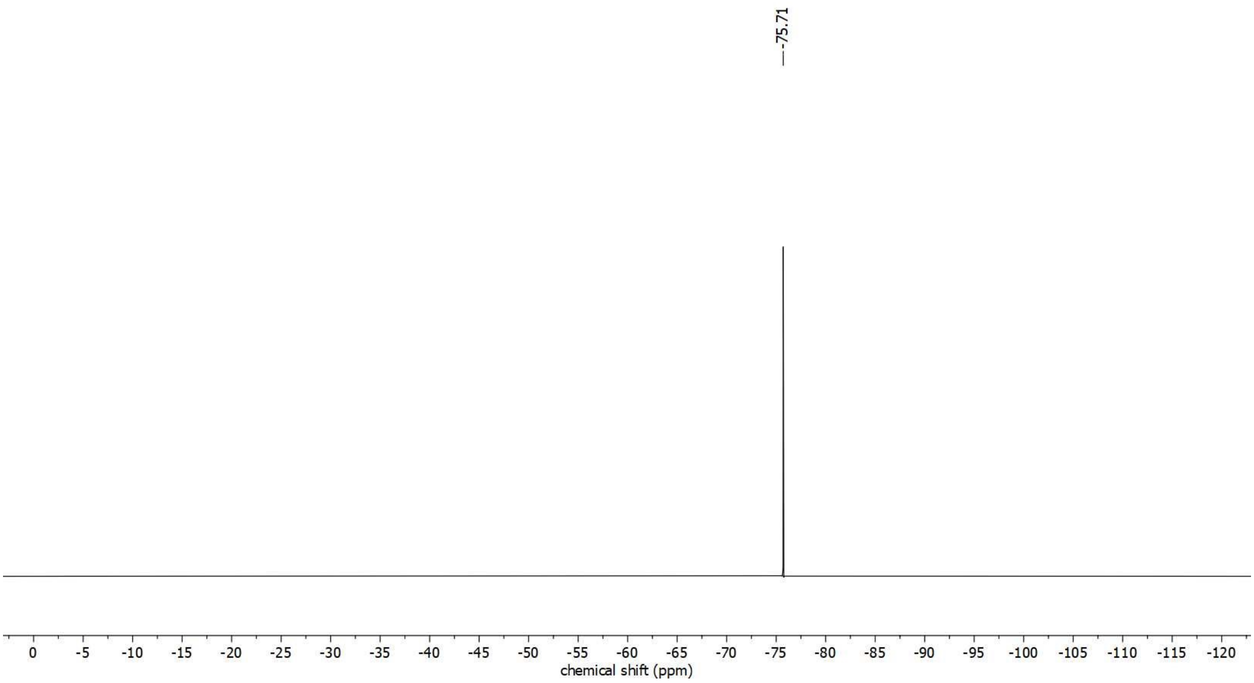
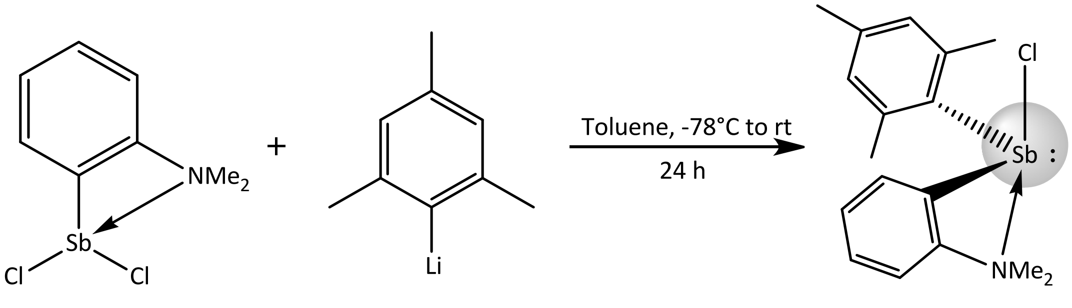


Figure S12: ^{19}F NMR spectrum of **4A** recorded in CD_2Cl_2.

Synthesis and characterization of 1B:

A 30 mL toluene solution of (mesityl)Li (0.323 g, 2.56 mmol) was added dropwise to a 20 mL toluene solution of $((NMe_2)C_6H_4)SbCl_2$ (0.800 g, 2.56 mmol) at -78 °C. The reaction was allowed to attain ambient temperature and stirred for 24 h. The reaction mixture was filtered and toluene was distilled off. The white powder was dissolved in 2 mL dichloromethane layered with *n*-pentane. Colorless crystals of **1B** were obtained after 1 day at -30 °C.

Yield: 0.70 g, 69 %



Scheme S5

Elemental analysis for $C_{17}H_{21}NSbCl$: C, 51.49; H, 5.34; N, 3.53. Found: C, 51.36; H, 5.38; N, 3.52.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.22 (s, 3H, *p*-CH_3), 2.44 (s, br, 6H, NMe_2, 6H, *o*-CH_3), 6.84 (s, br, 2H, *m*-H), 7.21 (d, 1H, *o*-C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.45 (t, 2H, *m*-C_6H_4, $^3J_{HH}$ = 3.5 Hz), 8.01 (d, 1H, *m*-C_6H_4, $^3J_{HH}$ = 5.6 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 20.8 (*p*-CH_3), 24.1 (*o*- CH_3), 46.4 (NMe_2), 120.9 (c, C_6H_4), 129.0 (i, C_9H_{11}), 129.1 (d, C_6H_4), 130.5 (e, C_6H_4), 134.7 (C_9H_{11}, *m*- CH), 139.6 (f, C_6H_4), 142.1 (h, C_9H_{11}), 142.4 (b, C_6H_4), 144.47 (g, C_9H_{11}), 156.1 (a, C_6H_4)

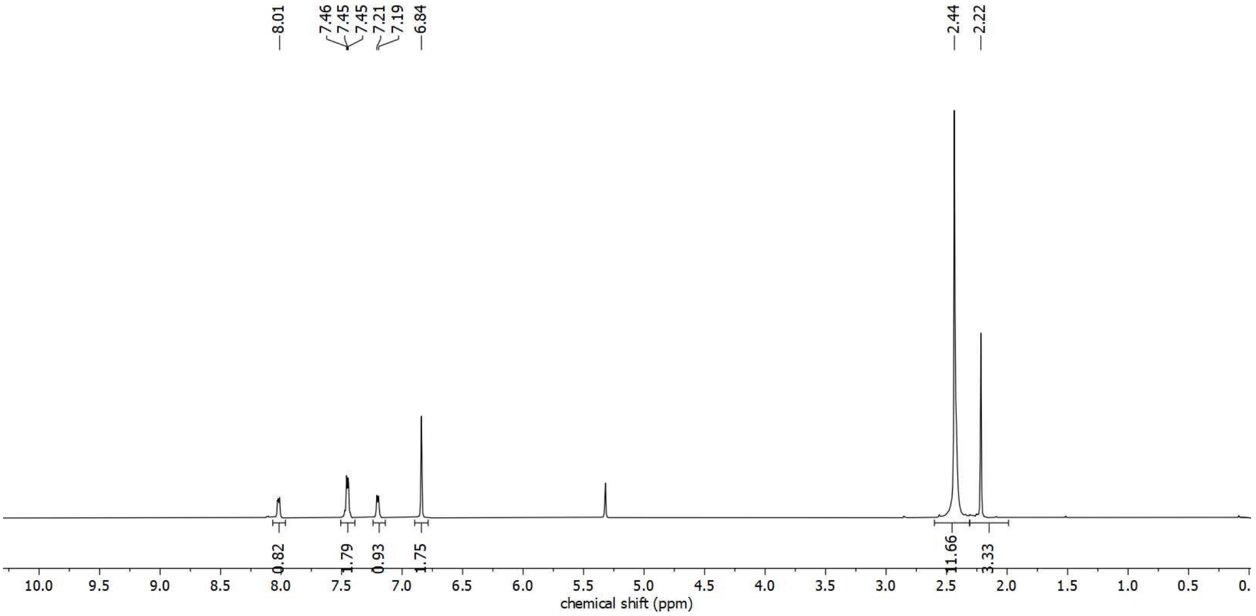


Figure S13: ^1H NMR spectrum of **1B** recorded in CD_2Cl_2.

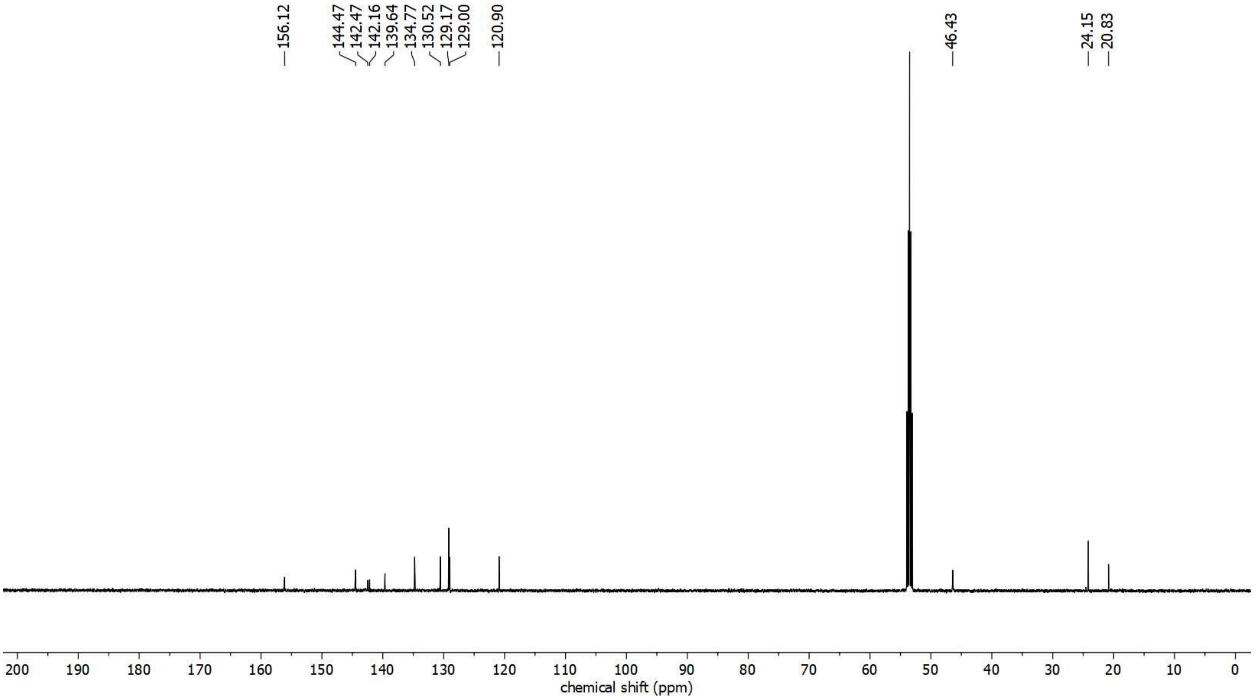
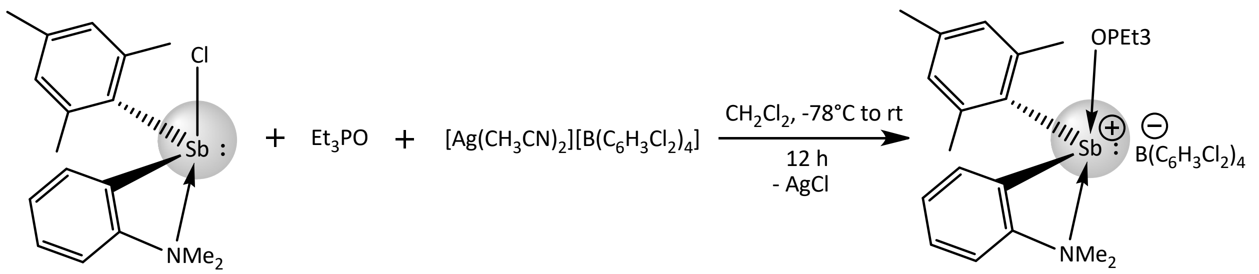


Figure S14: $^{13}C\{^1H\}$ NMR spectrum of **1B** recorded in CD_2Cl_2.

Synthesis and characterization of 2B:

1B (0.050 g, 0.126 mmol), O=PEt_3 (0.017 g, 0.126 mmol) and $[Ag(CH_3CN)_2][B(C_6H_3Cl_2)_4]$ (0.104 g, 0.126 mmol) were loaded into a Schlenk flask. Dichloromethane (5 mL) was condensed on to the mixture at -78 °C. The reaction mixture was allowed to attain room temperature and stirred overnight. Thereafter, filtration of reaction mixture gave a colorless solution. The solution was concentrated to 1.5 mL, layered with *n*-pentane and stored at -30 °C to obtain colorless crystals of **2B**.

Yield: 0.102 g, 66%



Scheme S6

Elemental analysis for $C_{47}H_{48}BNOPCl_8Sb$: C, 51.79; H, 4.44; N, 1.28. Found: C, 51.82; H, 4.38; N, 1.29.

^1H NMR (CD_2Cl_2, 500 MHz): δ 1.12 (m, 9H, Et_3PO, CH_3), 1.92 (m, 6H, Et_3PO, CH_2), 2.11 (s, br, 3H, *o*-CH_3), 2.18 (s, 3H, *p*-CH_3), 2.21 (s, br, 3H, *o*-CH_3) 2.60 (s, 3H, NMe_2), 2.87 (s, 3H, NMe_2), 6.84, 6.91 (d, 2H, *m*-H, $^3J_{HH}$ = 34 Hz), 7.24 (d, 1H, m-C_6H_4, $^3J_{HH}$ = 7.7 Hz), 7.52 (m, 2H, *o*-C_6H_4, $^3J_{HH}$ = 7.5 Hz), 7.70 (d, 1H, *m*-C_6H_4, $^3J_{HH}$ = 7.5 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 5.2 ($OPEt_3$, CH_3), 18.1 ($OPEt_3$, CH_2), 18.6 (*o*-CH_3), 20.9 (*p*-CH_3), 46.8 (3H, NMe_2), 121.0 (c, C_6H_4), 123.0 (i, C_6H_4), 129.9 (C_9H_{11}, *m*-CH), 132.9 (d, C_6H_4), 133.1 (e, C_6H_4), 134.0 (f, C_9H_{11}), 140.7 (h, C_9H_{11}), 141.3 (b, C_6H_4), 143.5 (g, C_9H_{11}), 155.4 (a, C_6H_4), 164.7 (q, $^1J_{BC}$ = 49.2 Hz, $BAr^{Cl2}{}_4$)

^{11}B NMR (CD_2Cl_2, 160 MHz): δ -6.9 (s, $B(C_6H_3Cl_2)_4$)

$^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): δ 77.8 (s, $OPEt_3$)

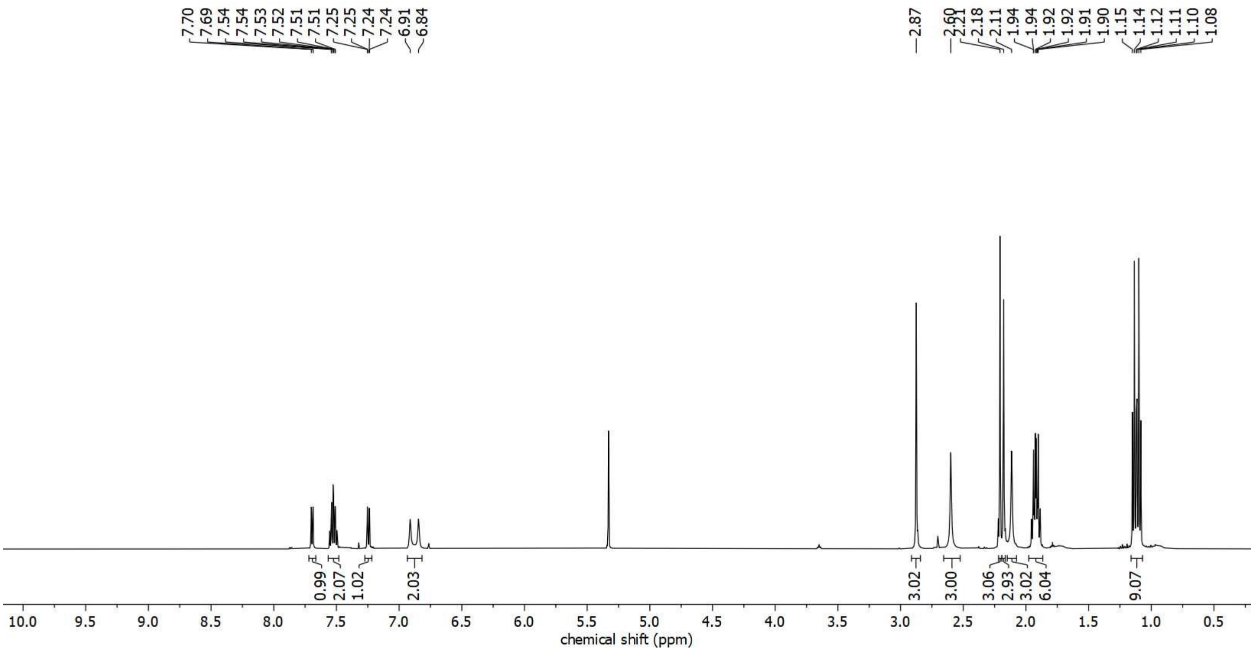


Figure S15: ^{1}H NMR spectrum of **2B** recorded in CD_2Cl_2.

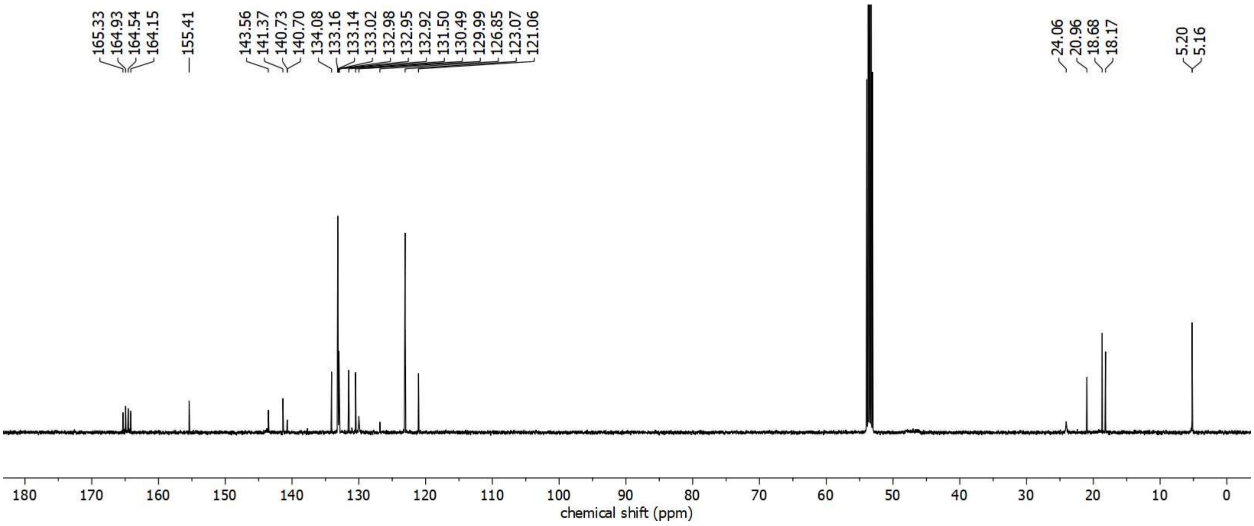


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum of **2B** recorded in CD_2Cl_2.

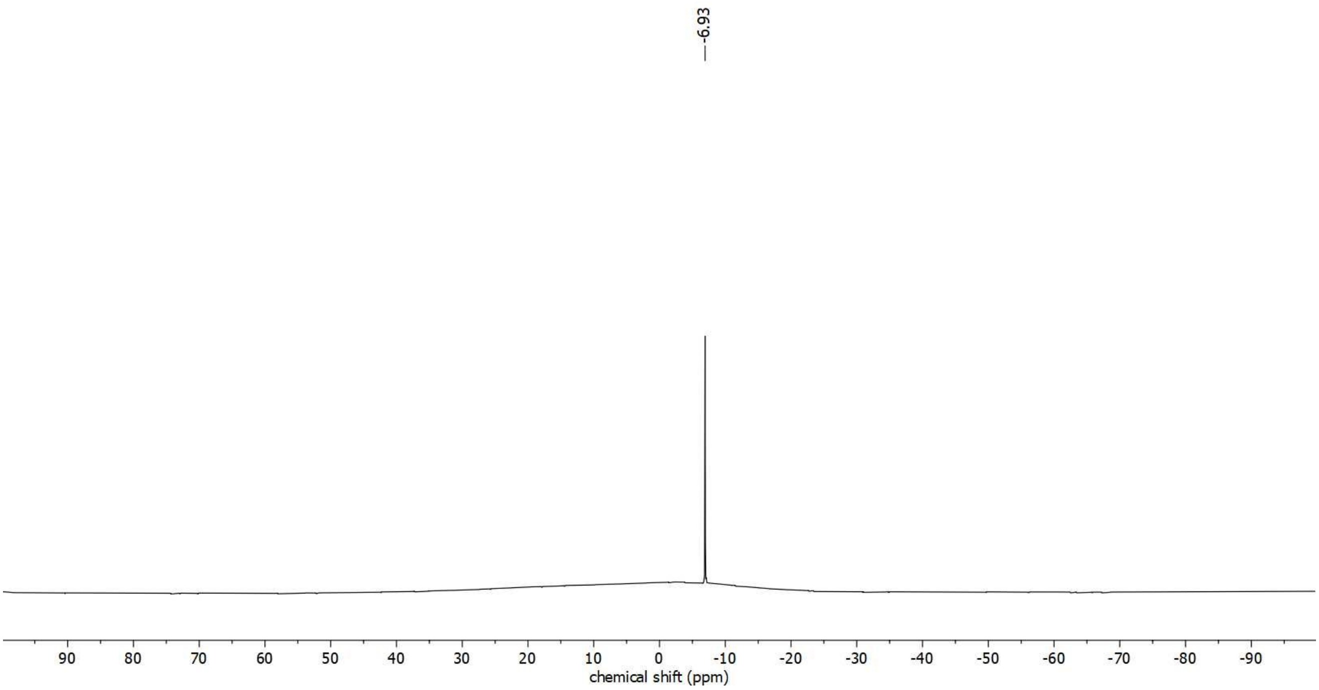


Figure S17: ^{11}B NMR spectrum of **2B** recorded in CD_2Cl_2.

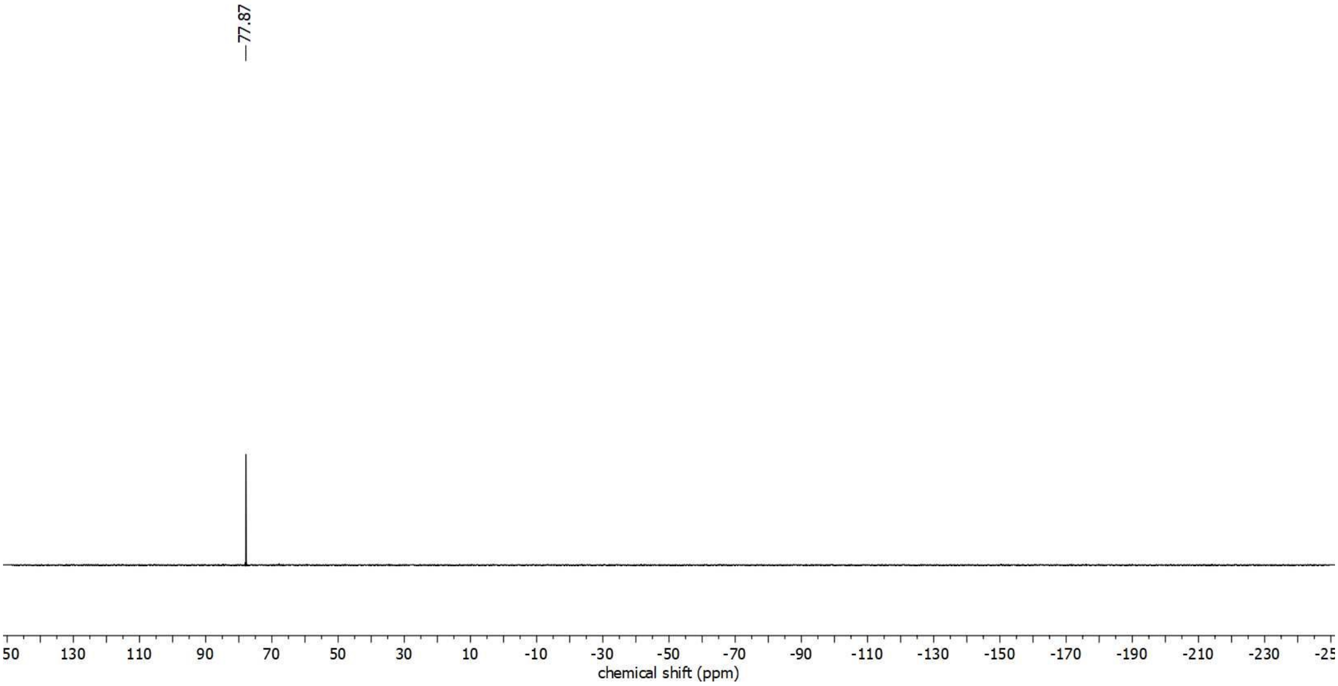
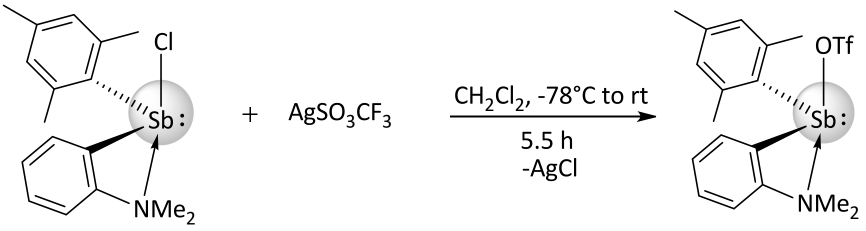


Figure S18: $^{31}P\{^1H\}$ NMR spectrum of **2B** recorded in CD_2Cl_2.

Synthesis and characterization of 3B:

1B (0.100 g, 0.252 mmol), and AgOTf (0.065 g, 0.252 mmol) were loaded into a Schlenk flask. Dichloromethane (5 mL) was condensed on to the mixture at -78 ºC. The reaction mixture was allowed to attain room temperature and stirred for 5.5 h. Thereafter, filtration of the reaction mixture gave a colorless solution. The solution was concentrated to 1 mL, layered with *n*-pentane and stored at -30 ºC to receive colorless crystals of **3B**.

Yield: 0.1 g, 78%



Scheme S7

Elemental analysis for $C_{18}H_{21}NO_3SF_3Sb$: C, 42.38; H, 4.15; N, 2.75. Found: C, 42.41; H, 4.17; N, 2.78

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.12 (s, 3H, *p*-CH_3), 2.20 (s, 3H, *o*-CH_3), 2.27 (s, 3H, *o*-CH_3) 2.61 (s, 3H, NMe_2), 2.95 (s, 3H, NMe_2), 6.87 (d, 2H, *m*-H, $^3J_{HH}$ = 22.4 Hz), 7.19 (d, 1H, *m*-C_6H_4, $^3J_{HH}$ = 8.4 Hz), 7.52 (m, 2H, *p*-C_6H_4, $^3J_{HH}$ = 8 Hz), 7.93 (d, 2H, *m*-C_6H_4, $^3J_{HH}$ = 8.3 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 20.8 (*p*-CH_3), 23.9 (*o*-CH_3), 47.1 (NMe_2), 120.3 (c, C_6H_4), 129.7 (i, C_6H_4), 130.6 (C_9H_{11}, *m*-CH), 131.1 (d, C_6H_4), 131.5 (e, C_6H_4), 135.3 (f, C_6H_4), 140.5 (h, C_9H_{11}), 141.0 (b, C_9H_{11}), 144.3 (g, C_9H_{11}), 155.2 (a, C_6H_4)

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -78.1 (s, OSO_2CF_3)

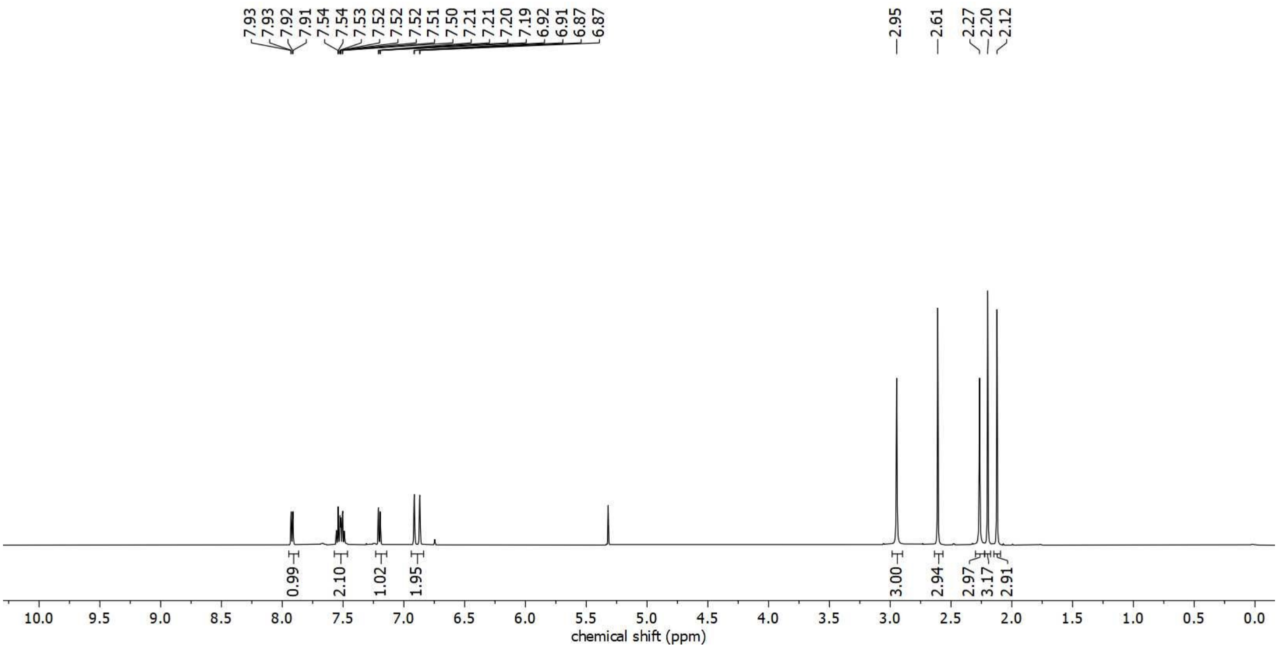


Figure S19: ^{1}H NMR spectrum of **3B** recorded in CD_2Cl_2.

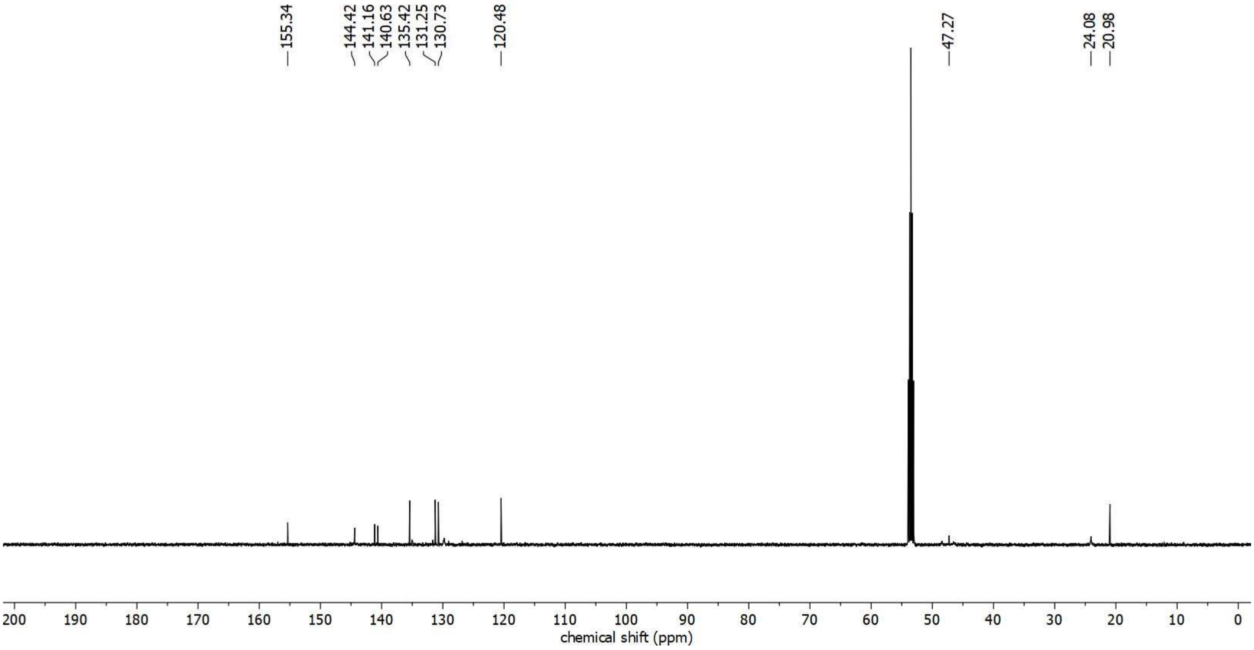


Figure S20: $^{13}C\{^1H\}$ NMR spectrum of **3B** recorded in CD_2Cl_2.

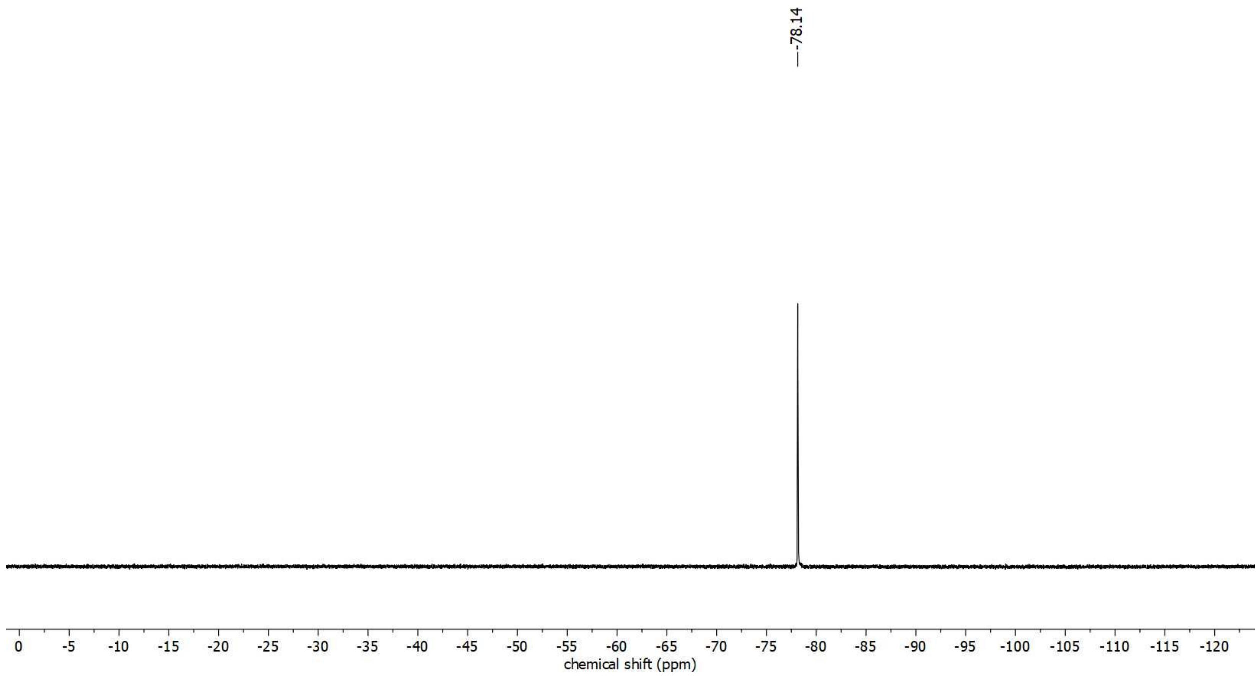
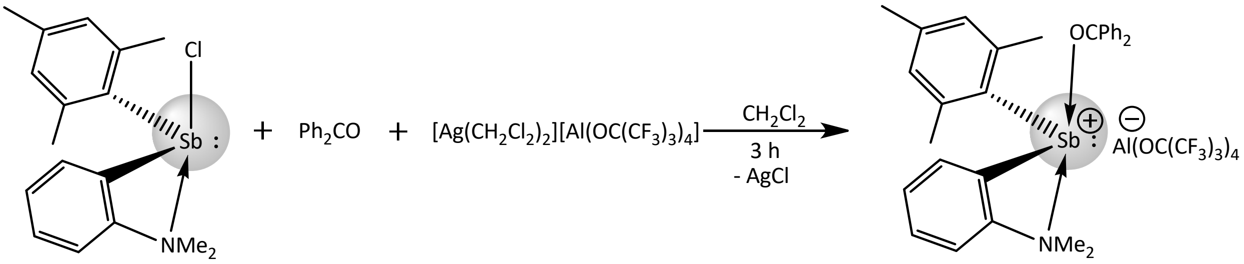


Figure S21: ^{19}F NMR spectrum of **3B** recorded in CD_2Cl_2.

Synthesis and characterization of 4B:

1B (0.040 g, 0.1 mmol), benzophenone (0.018 g, 0.1 mmol) and $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.126 g, 0.1 mmol) were loaded into a vial inside glovebox. Dichloromethane (3 mL) was added on to the mixture at room temperature. The reaction mixture was stirred for 3 h. Thereafter, filtration of the reaction mixture gave a yellow solution. The solution was concentrated to 1.5 mL, layered with *n*-pentane and stored at -30 °C to obtain yellow crystals of **4B**.

Yield: 0.073 g, 43%



Scheme S8

Elemental analysis for $C_{46}H_{31}NO_5F_{36}AlSb$: C, 36.58; H, 2.07; N, 0.93. Found: C, 36.60; H, 2.12; N, 0.91

^1H NMR (CD_2Cl_2, 500 MHz): δ 2.26 (s, 3H, *o*-CH_3), 2.32 (s, br, 3H, *p*-CH_3, 3H, *o*-CH_3), 2.47 (s, 3H, NMe_2), 3.04 (s, 3H, NMe_2), 6.94 (s, br, 2H, *m*-H (C_6H_{11})), 7.30 (d, 1H, Ph_2CO, $^3J_{HH}$ = 8.8 Hz), 7.58 (t, 4H, *m*-CH, Ph_2CO, $^3J_{HH}$ = 7.8 Hz), 7.68 (t, 4H, *p*-CH, Ph_2CO, 1H, t, C_6H_4, , $^3J_{HH}$ = 7.6 Hz), 7.74 (t, C_6H_4, $^3J_{HH}$ = 7.6 Hz), 7.82 (t, 2H, C_6H_4, $^3J_{HH}$ = 7.3 Hz), 8.22 (d, 1H, C_6H_4, $^3J_{HH}$ = 7.5 Hz)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 20.9 (*p*-CH_3), 24.3 (*o*-CH_3), 47.4 (NMe_2), 49.2 (NMe_2), 120.9 ($Al(OC(CF_3)_3)_4$, J_{CF} = 292.8 Hz), 124.8 (c, C_6H_4), 129.4 (Ph_2CO), 126.8 (i, C_6H_4), 130.4 (C_9H_{11}, *m*-CH), 131.4 (Ph_2CO), 131.8 (d, C_9H_{11}), 132.2 (e, C_6H_4), 134.9 (Ph_2CO), 137.7 (f, C_6H_4), 138.4 (h, C_9H_{11}), 142.6 (b, C_6H_4), 144.3 (g, C_9H_{11}), 155.6 (a, C_6H_4), 208.6 (Ph_2CO)

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -75.7 (s, $Al(OC(CF_3)_3)_4$)

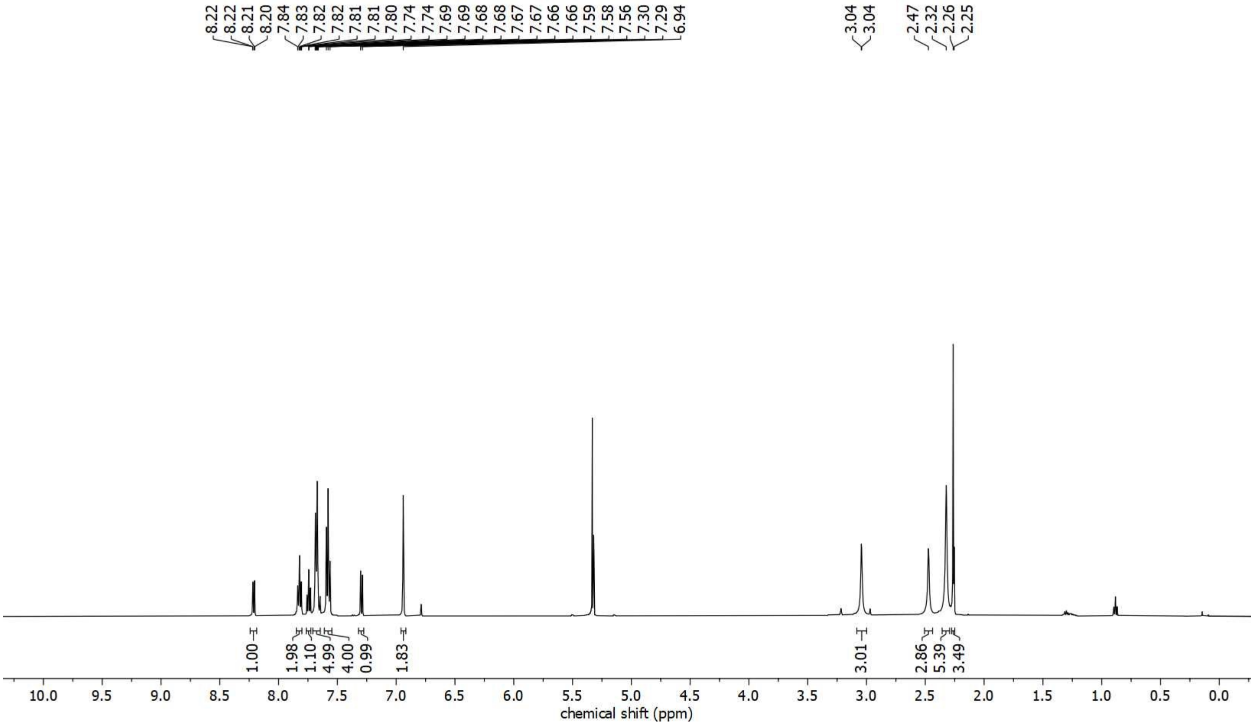


Figure S22: ^1H NMR spectrum of **4B** recorded in CD_2Cl_2.

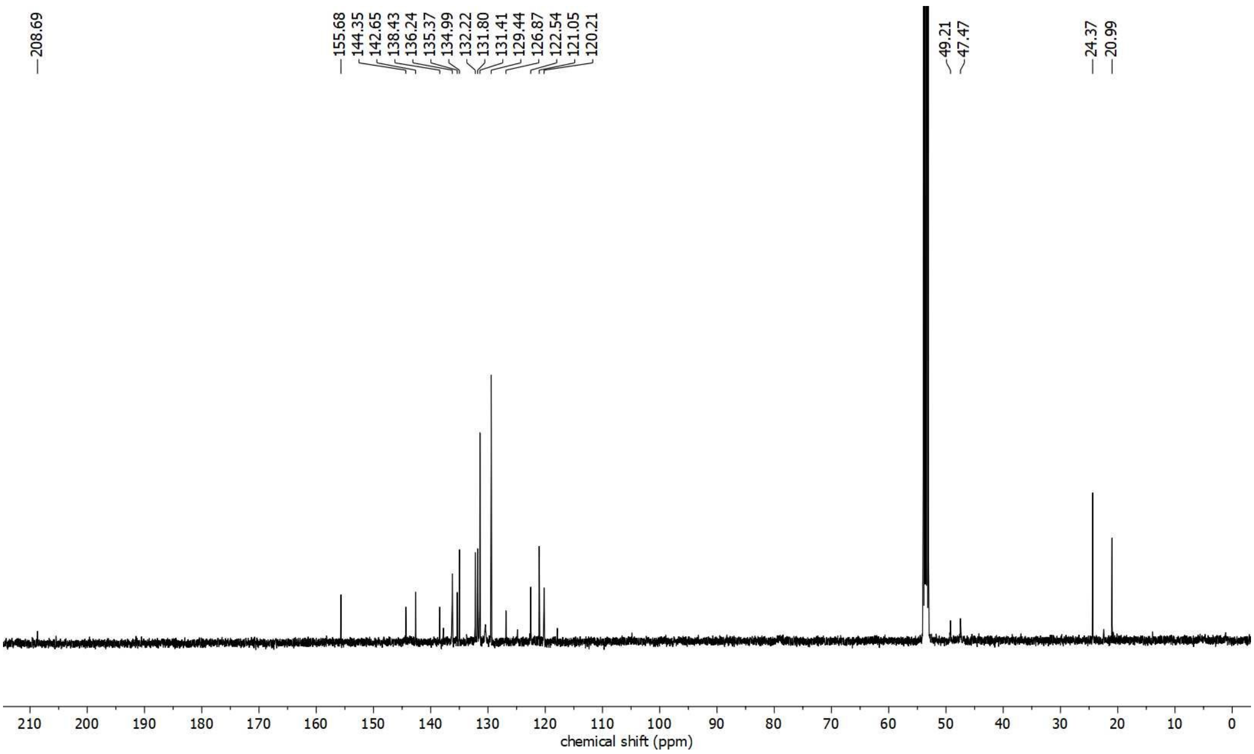


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum of **4B** recorded in CD_2Cl_2.

Figure S24: ^{19}F NMR spectrum of **4B** recorded in CD_2Cl_2.

2.2 Solution NMR Studies for Carbonyl Activation

Experimental Procedure

All the manipulations were carried out in argon atmosphere using Schlenk techniques and glovebox. J Young NMR tubes were oven dried at 200 °C before use. Ph_2CO and PhCHO were dried before use.

$[(NMe_2CH_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ or $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ were generated in situ by reacting equimolar amounts of **1A** or **1B**, PhCHO and $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ in 0.6 mL CD_2Cl_2 in a J Young NMR tube. Reaction completion was monitored via NMR spectroscopy.

Table S1

Compound	$^{13}C\{^1H\}$ NMR chemical shift for CO δ (ppm)
PhCHO	192.6
$SbCl_3$+PhCHO	193.5
$B(C_6F_5)_3$+PhCHO	199.7
$[(NMe_2CH_2C_6H_4)(mesityl)Sb][Al\{O(C(CF_3)_3\}_4]$+PhCHO	196.3
$[(NMe_2C_6H_4)(mesityl)Sb][Al\{O(C(CF_3)_3\}_4]$+ PhCHO	199.5
Ph_2CO	196.4
4A	202.7
4B	208.6

$SbCl_3$+PhCHO (1:1):

$SbCl_3$ (0.01 g, 0.043 mmol), PhCHO (4.46 µL, 0.043 mmol)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 129.4 (*m*-C_6H_5), 130.2 (*o*-C_6H_5), 135.1 (*p*-C_6H_5), 136.6 (*i*-C_6H_5), 193.48 (*C*HO)

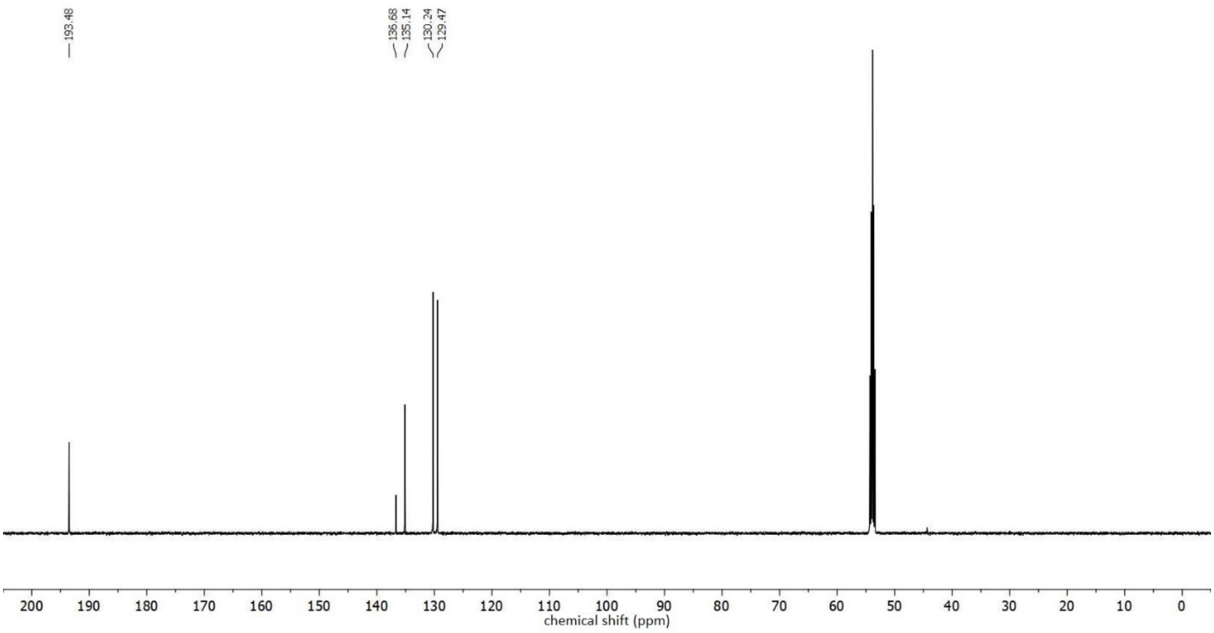


Figure S25: $^{13}C\{^{1}H\}$ NMR spectra of $SbCl_3$+PhCHO recorded in CD_2Cl_2.

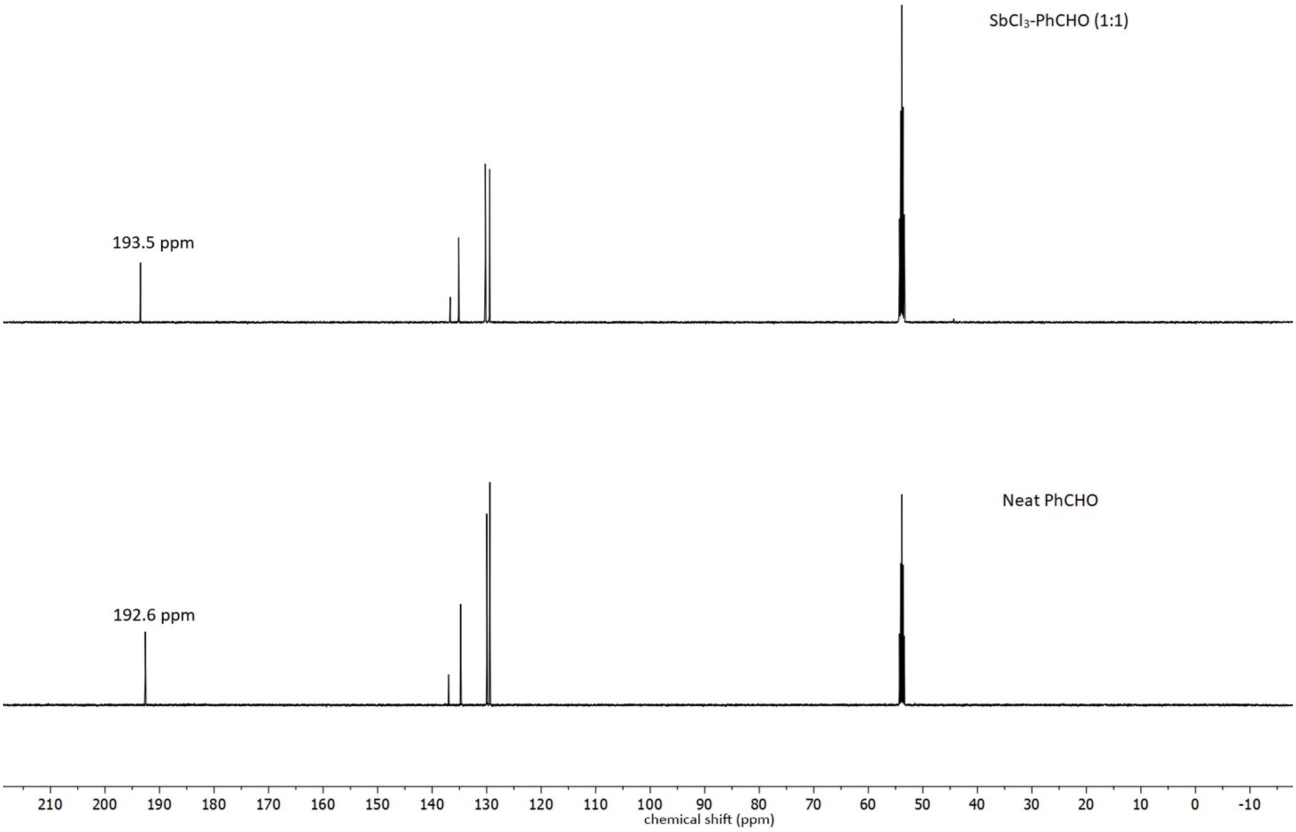


Figure S26: Stacked $^{13}C\{^{1}H\}$ NMR spectra of neat PhCHO vs $SbCl_3$+PhCHO recorded in CD_2Cl_2.

<u>B(C_6F_5)$_3$+PhCHO (1:1)</u>:

B(C_6F_5)$_3$ (0.05 g, 0.098 mmol), PhCHO (10 µL, 0.098 mmol)

^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 115.9 (*i*-C_6F_5), 130.9 (*i*-C_6H_5), 131.6 (*p*-C_6H_5), 136.8 (*o*-C_6H_5), 138.8 (*m*-C_6F_5), 142.7 (*m*-C_6H_5), 147.6 (*p*-C_6F_5), 149.5 (*o*-C_6F_5), 200.0 (CHO)

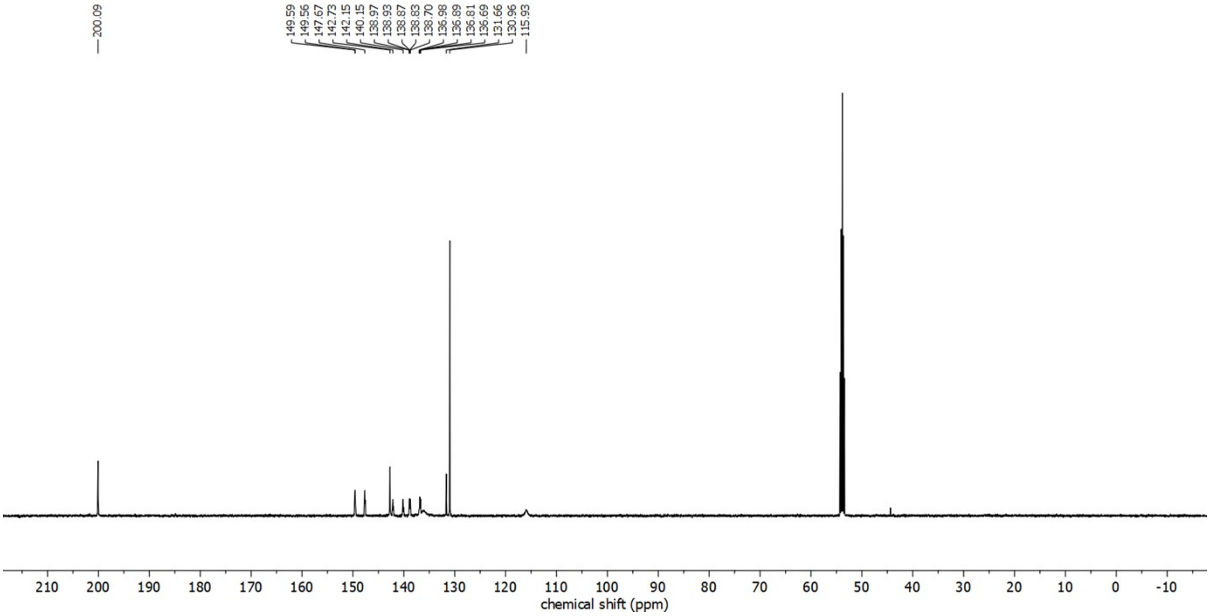


Figure S27: ^{13}C{^{1}H} NMR spectra of B(C_6F_5)$_3$+PhCHO recorded in CD_2Cl_2.

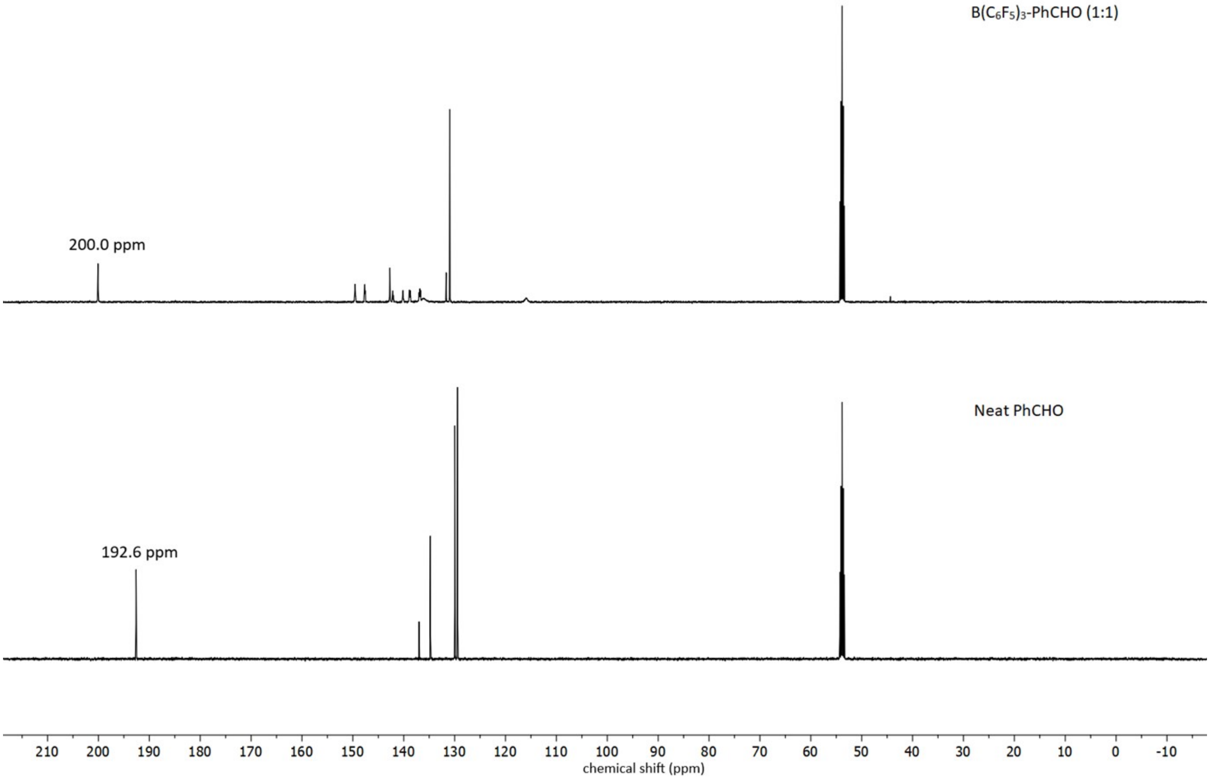


Figure S28: Stacked ^{13}C{^{1}H} NMR spectra of Neat PhCHO vs B(C_6F_5)$_3$+PhCHO recorded in CD_2Cl_2.

[($NMe_2CH_2C_6H_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF_3)$_3$}$_4$]:

1A (0.004 g, 009 mmol), PhCHO (0.99 µL, 0.009 mmol), [Ag(CH_2Cl_2)$_2$][Al(OC(CF_3)$_3$)$_4$] (0.012 g, 0.009 mmol)

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.29 (s, br, 6H, *o*-CH_3), 2.33 (s, 3H, *p*-CH_3), 2.67 (s, 3H, NMe_2), 2.90 (s, 3H, NMe_2), AB spin system with A at 4.06, 4.09 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz) and B at 4.24, 4.27 (d, 1H, CH_2, $^3J_{HH}$ = 14.3 Hz), 7.02 (s, 2H, *m*-H (C_6H_{11})), 7.51 (t, 4H, *m*-CH, PhCHO, $^3J_{HH}$ = 7.9 Hz), 7.58 (t, 1H, *p*-CH, PhCHO, 1H, t, C_6H_4, , $^3J_{HH}$ = 3.4 Hz), 7.60 (d, 1H, *o*-CH, PhCHO,$^3J_{HH}$ = 7.9 Hz), 7.77 (*t*, 2H, C_6H_4, $^3J_{HH}$ = 7.7 Hz), 8.0 (d, 1H, C_6H_4), 9.72 (s, 1H, C*H*O)

^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 20.9 (*p*-CH_3), 25.1 (*o*-CH_3), 47.2 (NMe_2), 48.8 (NMe_2), 70.7 (CH_2NMe_2), 120.1, 122.5 (Al(OC(CF_3)$_3$)$_4$, J_{CF} =292.8 Hz), 127.0 (c, C_6H_4), 129.5 (d, C_6H_4), 130.3 (*o*-C_6H_5 PhCHO), 130.9 (*i*-C_6H_5 PhCHO), 131.1 (*m*-CH, C_9H_{11}), 131.4(e, C_6H_4), 135.2 (*m*-C_6H_5 PhCHO), 135.4 (*p*-C_6H_5 PhCHO), 136.7 (g, C_9H_{11}), 138.4 (i, C_6H_{11}), 142.8 (b, C_6H_4), 143.4 (f,), 145.4 (h, C_9H_{11}), 146.0 (a, C_6H_4), 196.3 (*C*H*O*)

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -75.7 (s, Al(OC(CF_3)$_3$)$_4$)

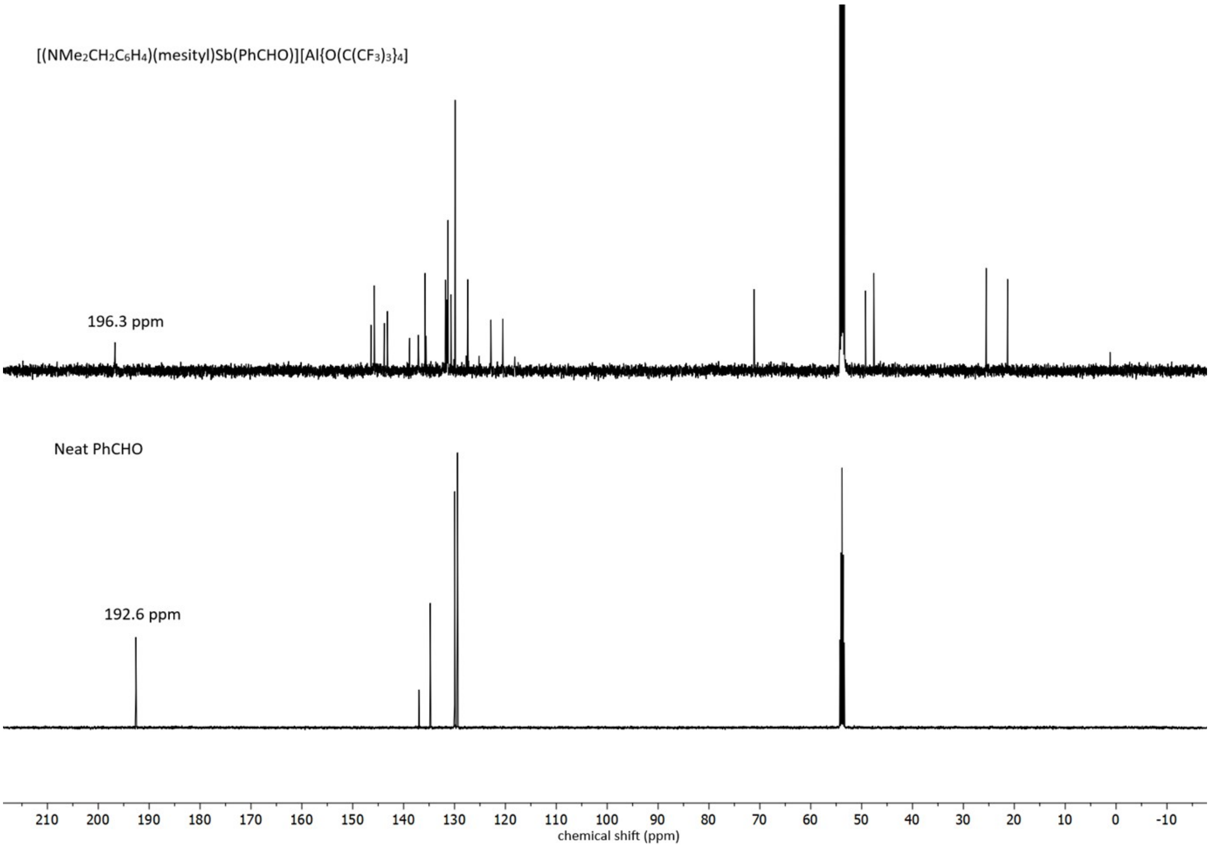


Figure S29: Stacked ^{13}C{^{1}H} NMR spectra of neat PhCHO vs [($NMe_2CH_2C_6H_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF_3)$_3$}$_4$] recorded in CD_2Cl_2.

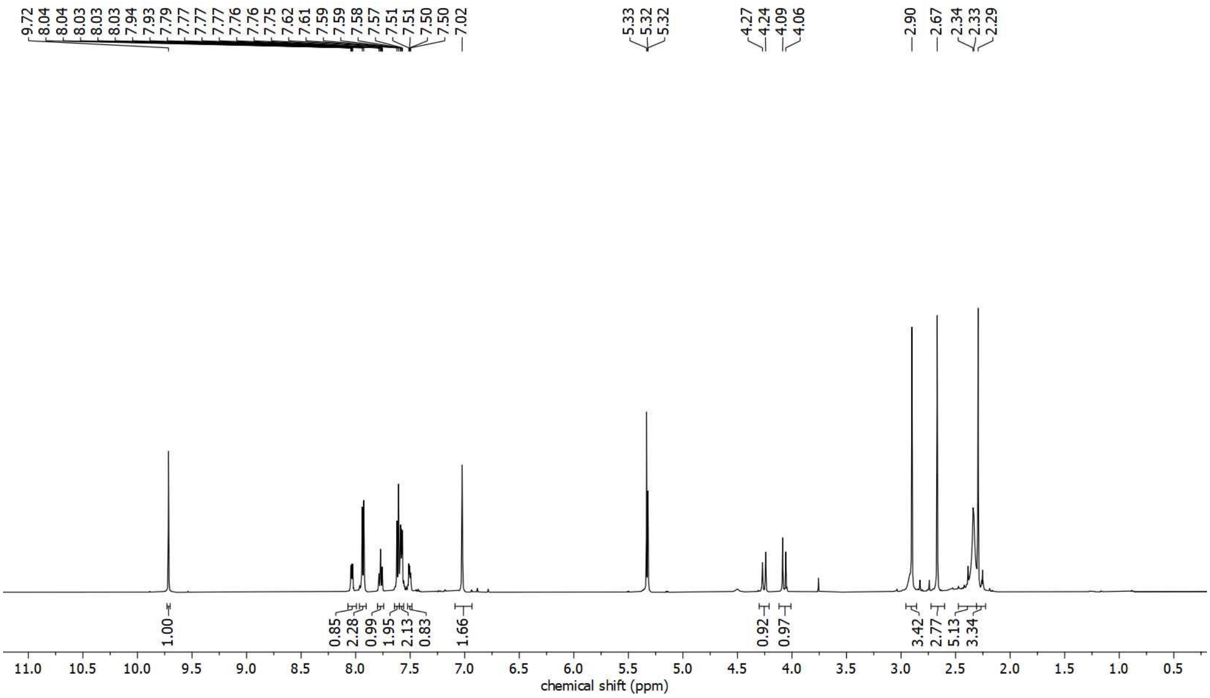


Figure S30: ^{1}H NMR spectrum of [(NMe$_2$CH$_2$C$_6$H$_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF$_3$)$_3$}$_4$] recorded in CD$_2$Cl$_2$.

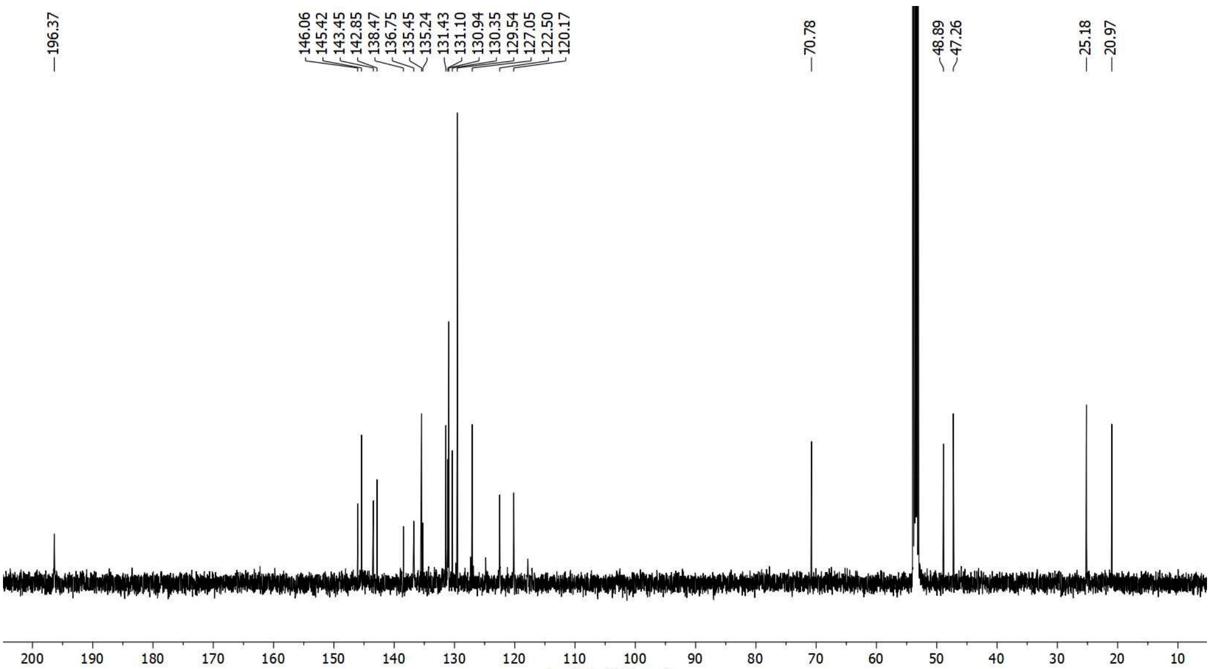


Figure S31: ^{13}C{^{1}H} NMR spectrum of [(NMe$_2$CH$_2$C$_6$H$_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF$_3$)$_3$}$_4$] recorded in CD$_2$Cl$_2$.

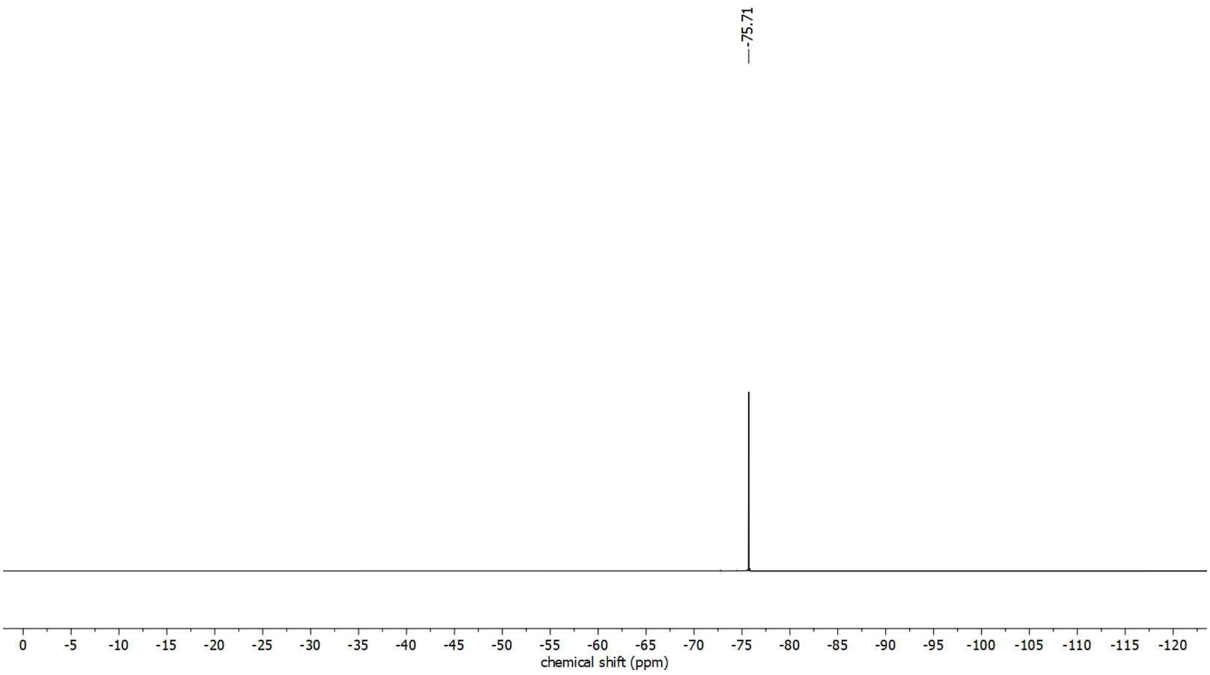


Figure S32: ^{19}F NMR spectrum of [($NMe_2CH_2C_6H_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF_3)$_3$}$_4$] recorded in CD_2Cl_2.

[($NMe_2C_6H_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF_3)$_3$}$_4$]:

1B (0.004 g, 0.01 mmol), PhCHO (1.03 µL, 0.01 mmol), [Ag(CH_2Cl_2)$_2$][Al(OC(CF_3)$_3$)$_4$] (0.012 g, 0.01 mmol)

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 2.27 (s, 3H, *p*-CH_3), 2.36 (s, 3H, *o*-CH_3), 2.43 (s, 3H, *o*-CH_3) 2.78 (s, 3H, NMe_2), 3.21 (s, 3H, NMe_2), 6.99 (s, 2H, *m*-H (C_6H_{11})), 7.31 (t, 1H, t, C_6H_4 ,$^3J_{HH}$ = 6.4 Hz), 7.62 (m, 4H, *o*-CH, PhCHO,$^3J_{HH}$ = 7.8 Hz), 7.79 (*t*, 2H, C_6H_4, $^3J_{HH}$ = 6.9 Hz), 7.96 (m, 1H, C_6H_4, 1H, *p*-CH, PhCHO, $^3J_{HH}$ = 7.5 Hz), 9.87 (s, 1H, C*H*O)

^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ 21.0 (*p*-CH_3), 23.9 (*o*-CH_3), 46.6 (NMe_2), 120.1, 122.9 (Al(OC(CF_3)$_3$)$_4$, J_{CF} =292.8 Hz), 122.4 (c, C_6H_4), 126.8 (d, C_6H_4), 129.9 (*o*-C_6H_5 PhCHO), 131.8 (*i*-C_6H_5 PhCHO), 132.2 (*m*-CH, C_9H_{11}), 132.3 (e, C_6H_4), 134.6 (*m*-C_6H_5 PhCHO), 134.3 (*p*-C_6H_5 PhCHO), 134.6 (g, C_9H_{11}), 137.5 (i, C_6H_{11}), 138.6 (b, C_6H_4), 142.9 (f, C_9H_{11}), 143.0 (h, C_9H_{11}), 155.4 (a, C_6H_4), 199.5 (*CHO*)

^{19}F NMR (CD_2Cl_2, 471 MHz): δ -75.9 (s, Al(OC(CF_3)$_3$)$_4$)

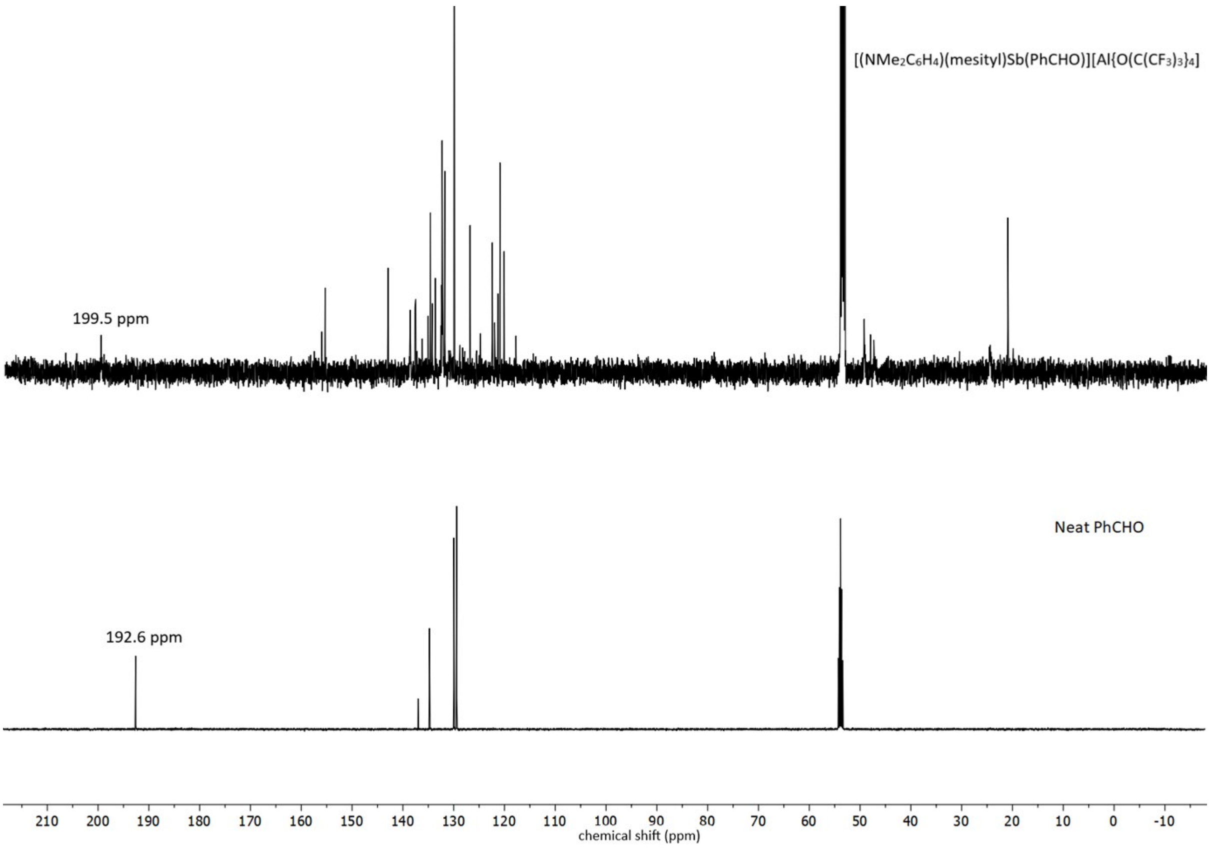


Figure S33: Stacked $^{13}C\{^1H\}$ NMR spectra of Neat PhCHO vs $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2.

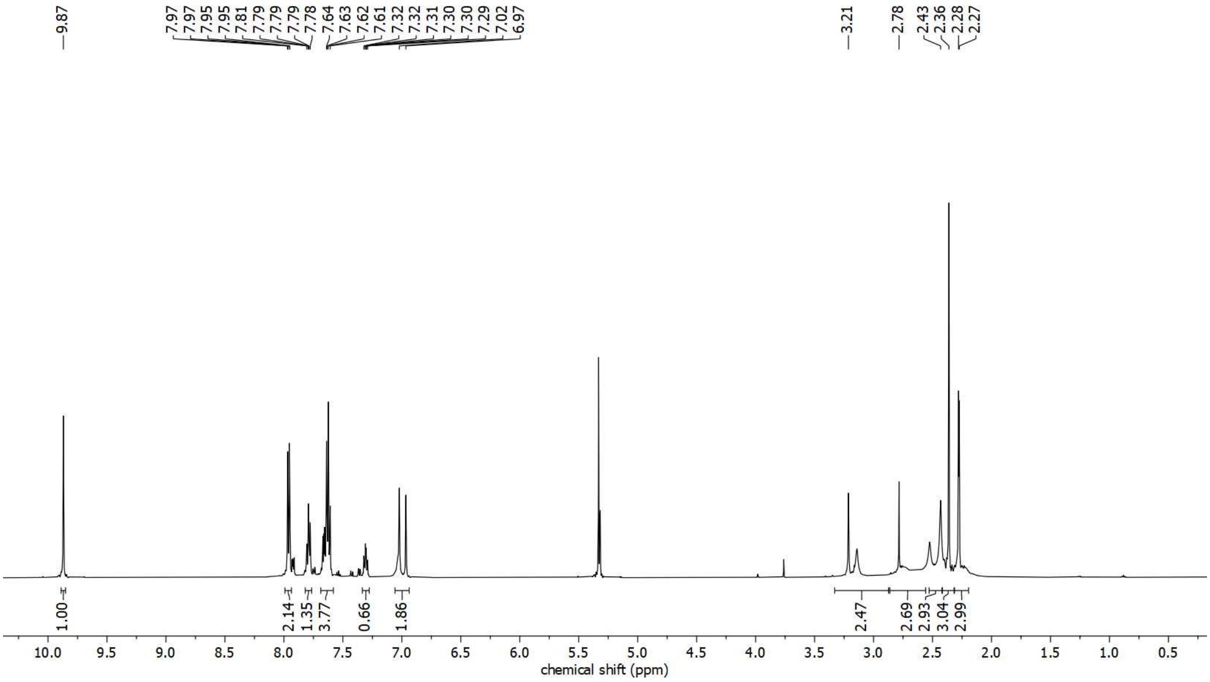


Figure S34: ^1H NMR spectrum of $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2.

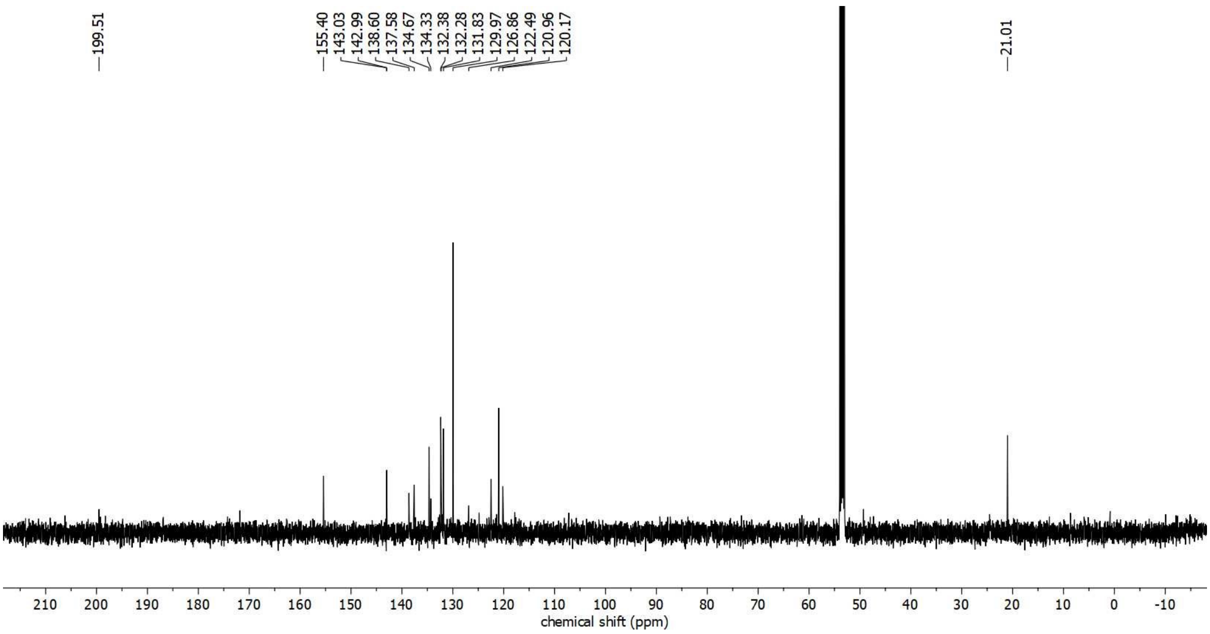


Figure S35: $^{13}C\{^1H\}$ NMR spectrum of $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2.

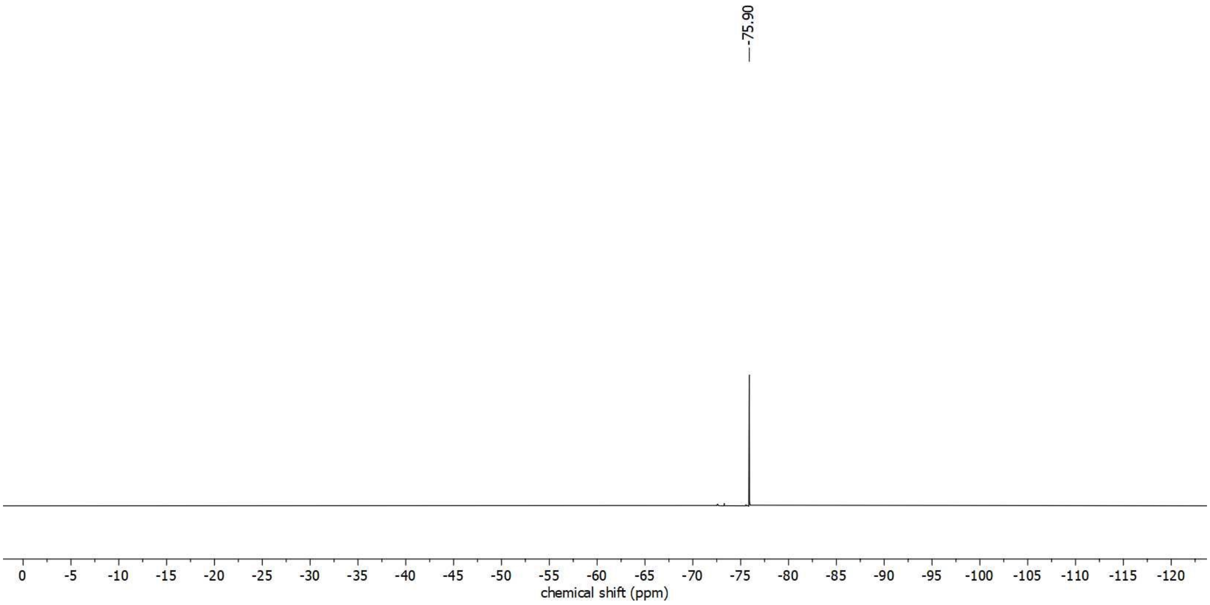


Figure S36: ^{19}F NMR spectrum of $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2.

4A:

1A (0.1 g, 0.243 mmol), Ph_2CO (0.044 g, 0.085 mmol) and $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.303 g, 0.243 mmol)

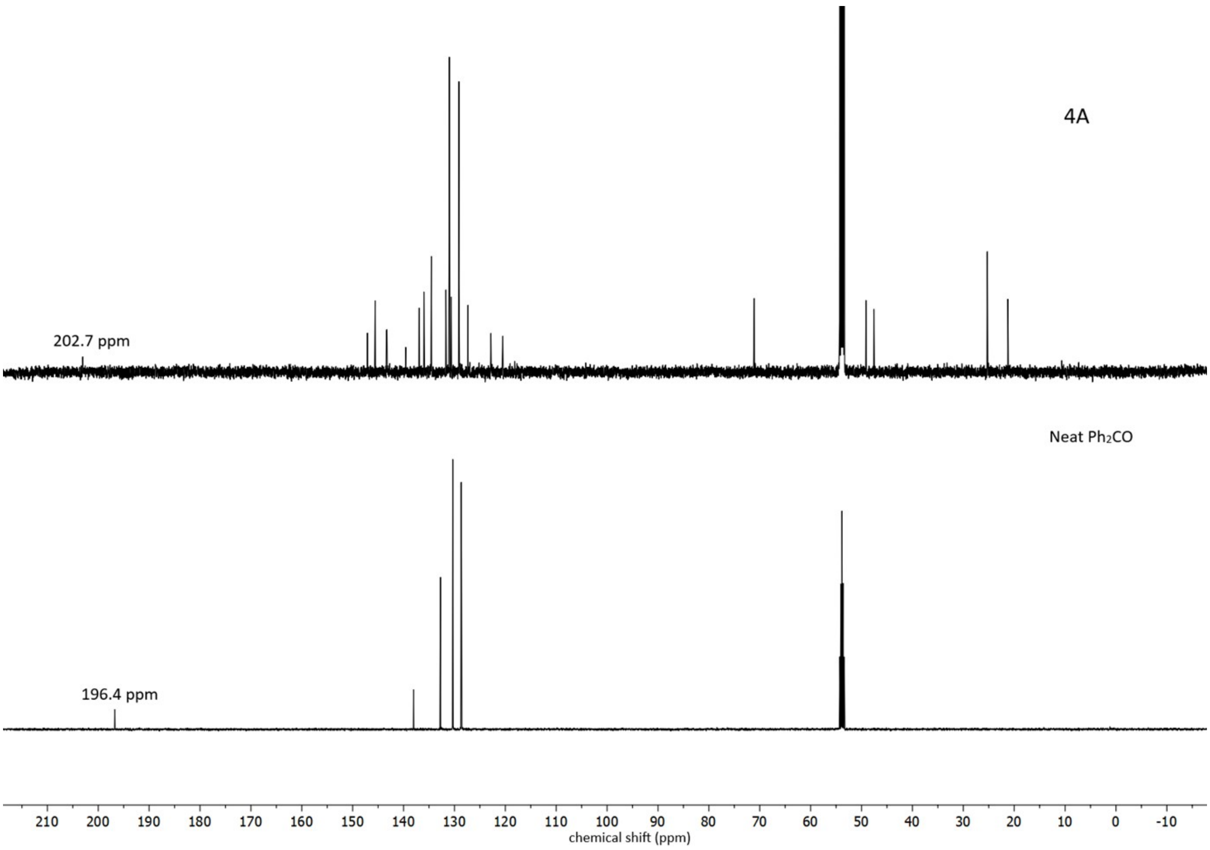


Figure S37: Stacked $^{13}C\{^1H\}$ NMR spectra of Neat Ph_2CO vs **4A** recorded in CD_2Cl_2.

4B:

1B (0.040 g, 0.1 mmol), Ph_2CO (0.018 g, 0.1 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4$ (0.126 g, 0.1 mmol)

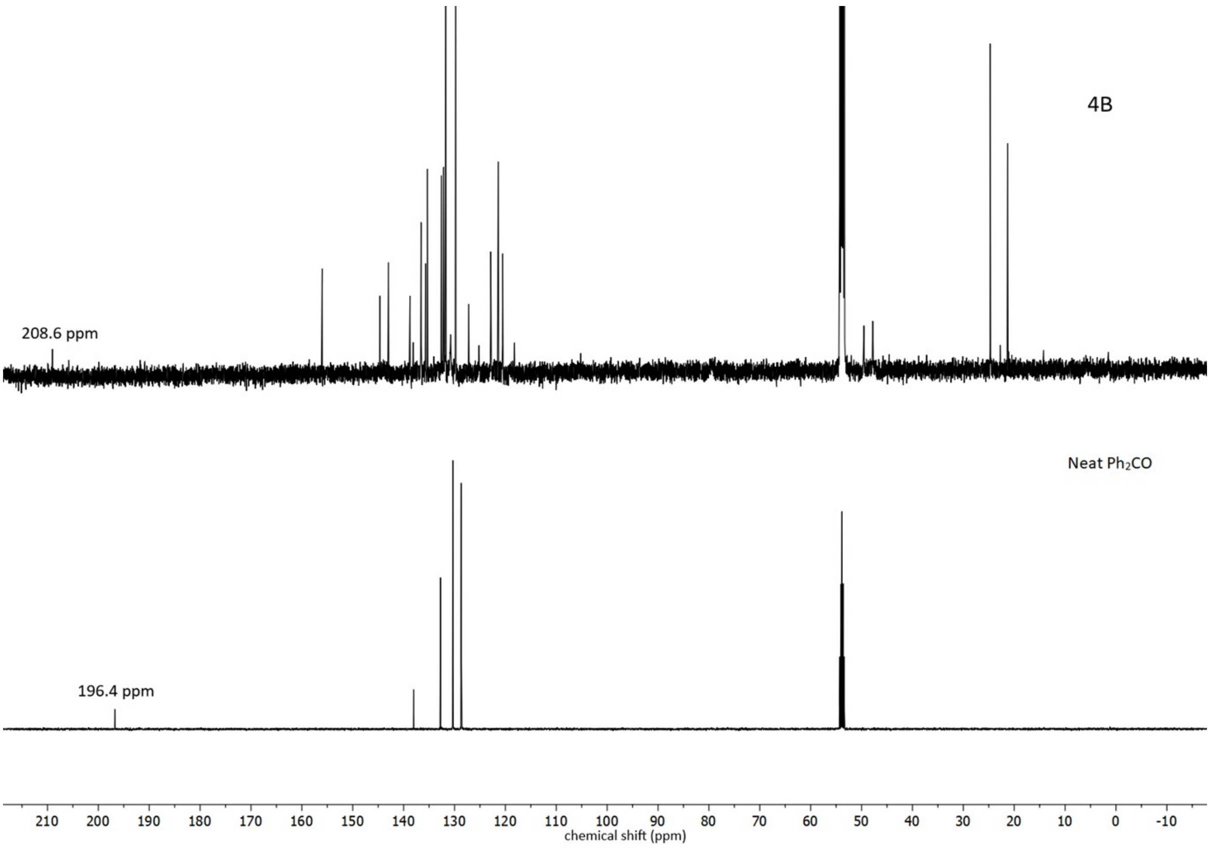


Figure S38: Stacked $^{13}C\{^1H\}$ NMR spectra of neat Ph_2CO vs **4B** recorded in CD_2Cl_2.

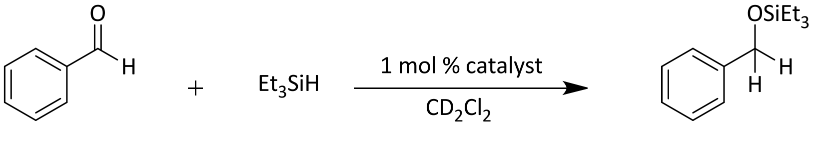
2.3 Reactivities Studies

Catalytic Hydrosilylation of Benzaldehyde

Experimental Procedure

All the manipulations were carried out in argon atmosphere using Schlenk techniques and glovebox. J Young NMR tubes were oven dried at 200 °C before use. Ph_2CO, PhCHO and Et_3SiH were dried before use.

1 mol % of $[(NMe_2CH_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ or $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ was generated in situ with **1A** or **1B** in presence of PhCHO using $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ in 0.6 mL CD_2Cl_2 in a J Young NMR tube. Reaction completion was monitored via NMR spectroscopy. AgCl was removed from the solution by filtration to another J Young NMR tube after 2 h. PhCHO was then loaded into NMR tube and 0.9 equivalent of Et_3SiH with respect to PhCHO was added to the reaction mixture inside glovebox. NMR tube was then sealed and reaction was monitored by ^1H NMR until the hydrosilylation reaction reached completion.



Scheme S9

Using **1A**:

PhCHO (24.85 µL, 0.243 mmol), **1A** (0.001 g, 0.002 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.003 g, 0.002 mmol), Et_3SiH (35.01 µL, 0.219 mmol)

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.6 (q, 6H, $OSiCH_2CH_3$), 0.99 (t, 9H, $OSiCH_2CH_3$), 4.59 (s, 2H, O*CH_2*$SiEt_3$), 7.33 (m, 1H, p-C_6H_4), 7.40 (m, 4H, o, m-C_6H_4)

^{13}C{1H} NMR (CD_2Cl_2, 126 MHz): δ 4.5 (s, $OSiCH_2CH_3$), 6.7 (s, $OSiCH_2CH_3$), 64.7 (s, O*CH_2*), 127.1 (s, o-C_6H_5),128.2 (p-C_6H_5), 129.1 (s, m- C_6H_5), 138.6 (s, i-C_6H_5)

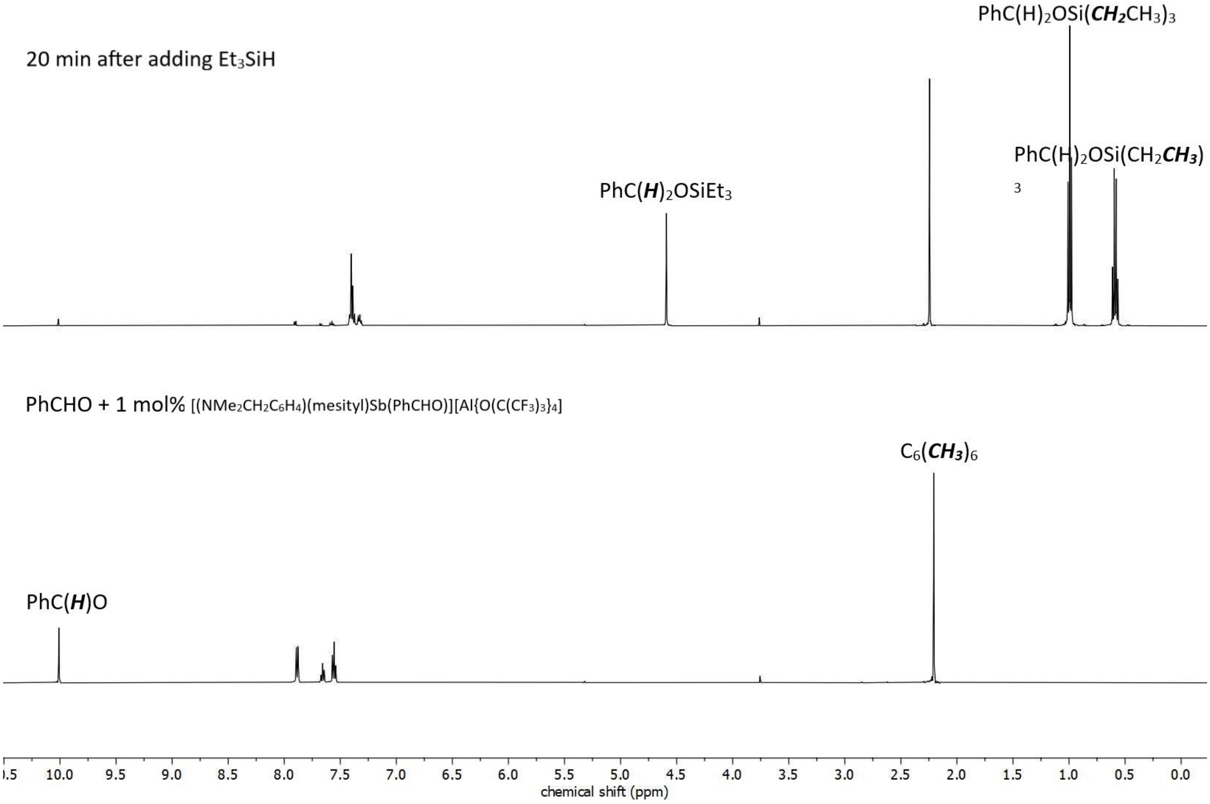


Figure S39: Stacked ^{1}H NMR spectra for hydrosilylation of PhCHO using 1 mol % $[(NMe_2CH_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >98% conversion to $PhC(H)_2OSiEt_3$. Hexamethylbenzene was used as internal reference.

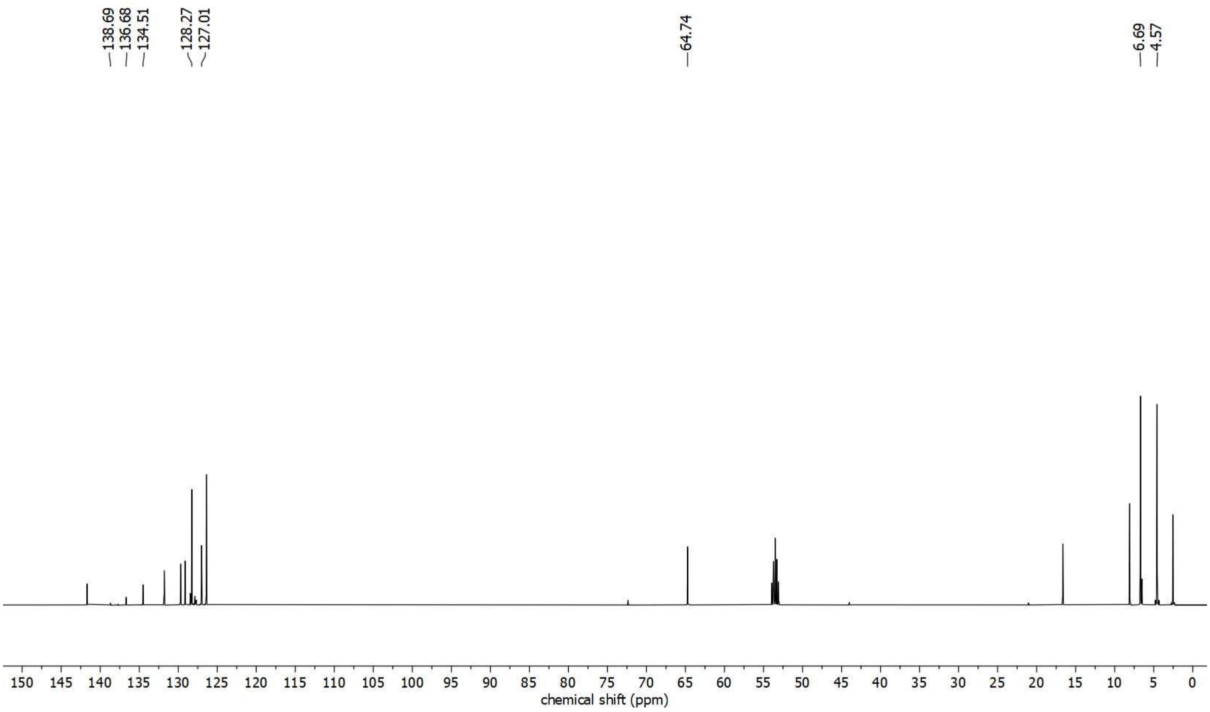


Figure S40: ^{13}C{^{1}H} NMR spectra for hydrosilylation of PhCHO using 1 mol % [(NMe$_2$CH$_2$C$_6$H$_4$)(mesityl)Sb(PhCHO)][Al{O(C(CF$_3$)$_3$}$_4$] recorded in CD$_2$Cl$_2$.

Using **1B**:

PhCHO (25.73 µL, 0.252 mmol), **1A** (0.001 g, 0.002 mmol), [Ag(CH$_2$Cl$_2$)$_2$][Al(OC(CF$_3$)$_3$)$_4$] (0.003 g, 0.002 mmol), Et$_3$SiH (36.25 µL, 0.226 mmol)

^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ 0.6 (q, 6H, OSiCH$_2$CH$_3$), 0.99 (t, 9H, OSiCH$_2$CH$_3$), 4.59 (s, 2H, OCH_2SiEt$_3$), 7.33 (m, 1H, p-C$_6$H$_4$), 7.40 (m, 4H, o, m-C$_6$H$_4$)

^{13}C{1H} NMR (CD$_2$Cl$_2$, 126 MHz): δ 5.3 (s, OSiCH$_2$CH$_3$), 7.4 (s, OSiCH$_2$CH$_3$), 65.4 (s, OCH$_2$), 127.1 (s, o-C$_6$H$_5$),128.5 (p-C$_6$H$_5$), 129.1 (s, m- C$_6$H$_5$), 138.4 (s, i-C$_6$H$_5$)

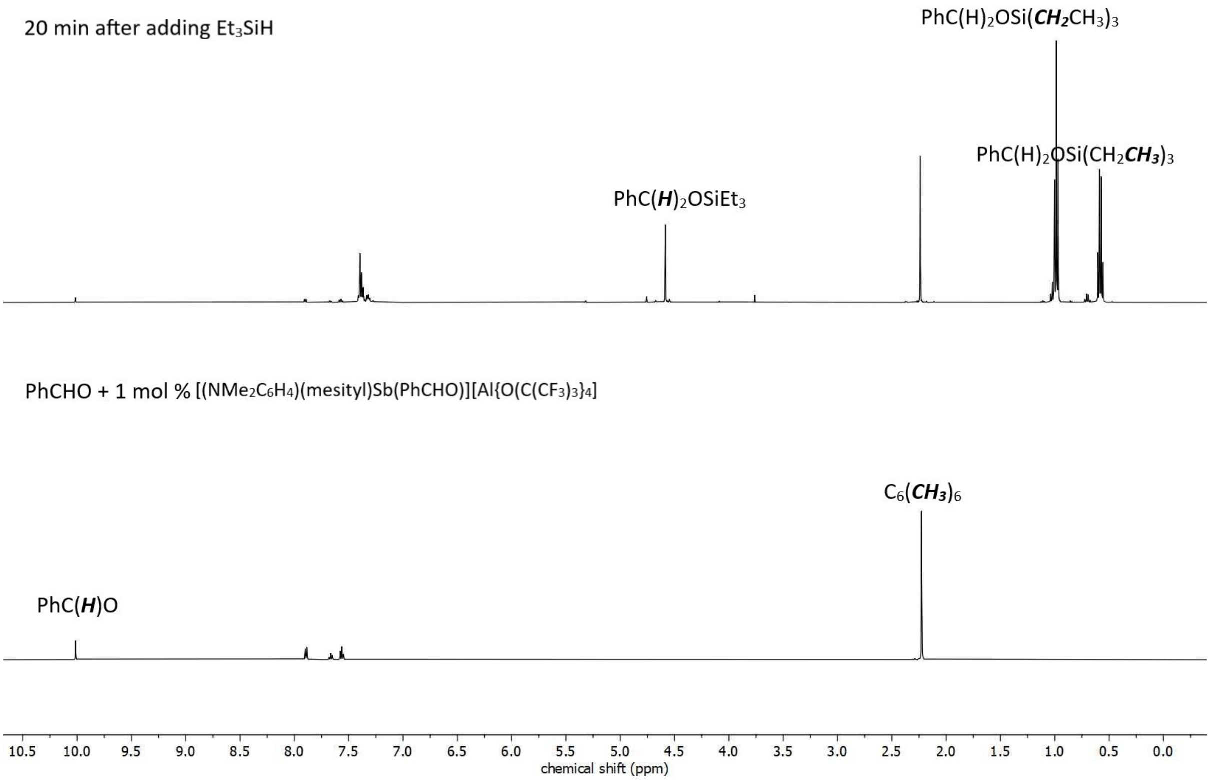


Figure S41: Stacked ^1H NMR spectra for hydrosilylation of PhCHO using 1 mol % $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >98% conversion to $PhC(H)_2OSiEt_3$. Hexamethylbenzene was used as internal reference.

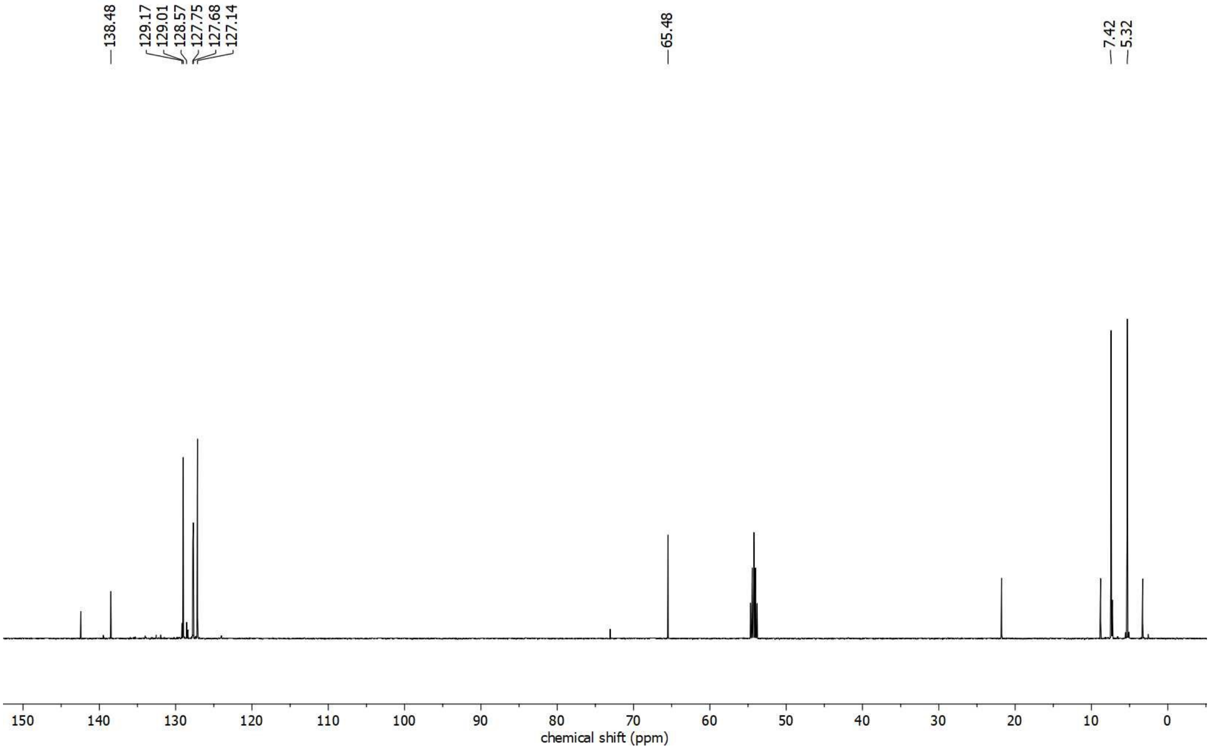
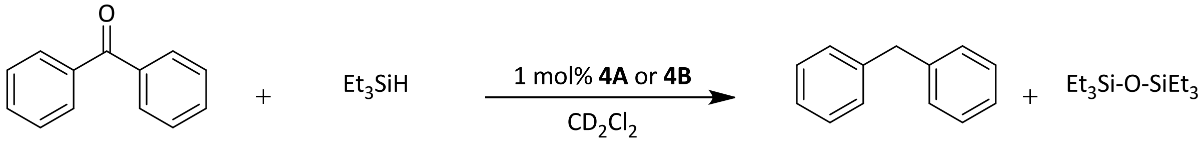


Figure S42: $^{13}C\{^1H\}$ NMR spectrum for hydrosilylation of PhCHO using 1 mol % $[(NMe_2C_6H_4)(mesityl)Sb(PhCHO)][Al\{O(C(CF_3)_3\}_4]$ recorded in CD_2Cl_2.

Catalytic Deoxygenation of Benzophenone

Experimental procedure

1 mol % of **4A** or **4B** and Ph_2CO were loaded into J Young NMR tube. 0.5 mL CD_2Cl_2 was condensed over the reaction mixture. 0.9 equivalent of Et_3SiH with respect to Ph_2CO was added to the reaction mixture inside glovebox. NMR tube was then sealed and reaction was monitored by ^1H NMR until the reaction reached completion.



Scheme S10

Using **4A**:

Ph_2CO (0.012 g, 0.065 mmol), **4A** (0.001 g, 0.0006 mmol), Et_3SiH (9.42 µL, 0.059 mmol)

^1H NMR (CD_2Cl_2, 500 MHz): δ 4.01 (s, 2H, Ph_2CH_2), 7.23 (m, 6H, o,p-C_6H_5), 7.32 (m, 4H, m-C_6H_4)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 42.0 (Ph_2CH_2), 126.1 (*p*-C_6H_5), 128.5 (*o*- C_6H_5), 128.9 (*m*-C_6H_5), 141.5 (*i*- C_6H_5)

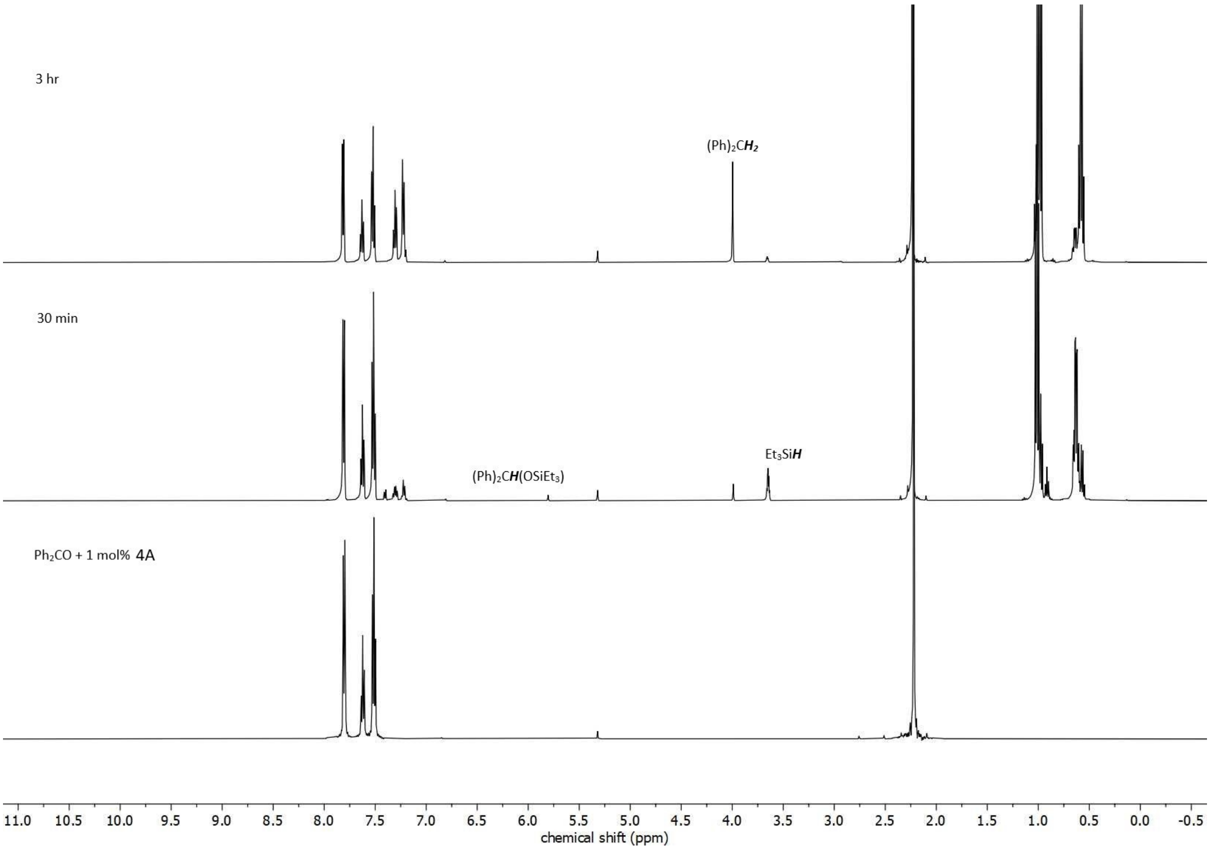


Figure S43: Stacked ^1H NMR spectra for deoxygenation of Ph_2CO using 1 mol % **4A** recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >99% conversion to $(Ph)_2CH_2$ (yield w.r.t Et_3SiH). Hexamethylbenzene was used as an internal standard.

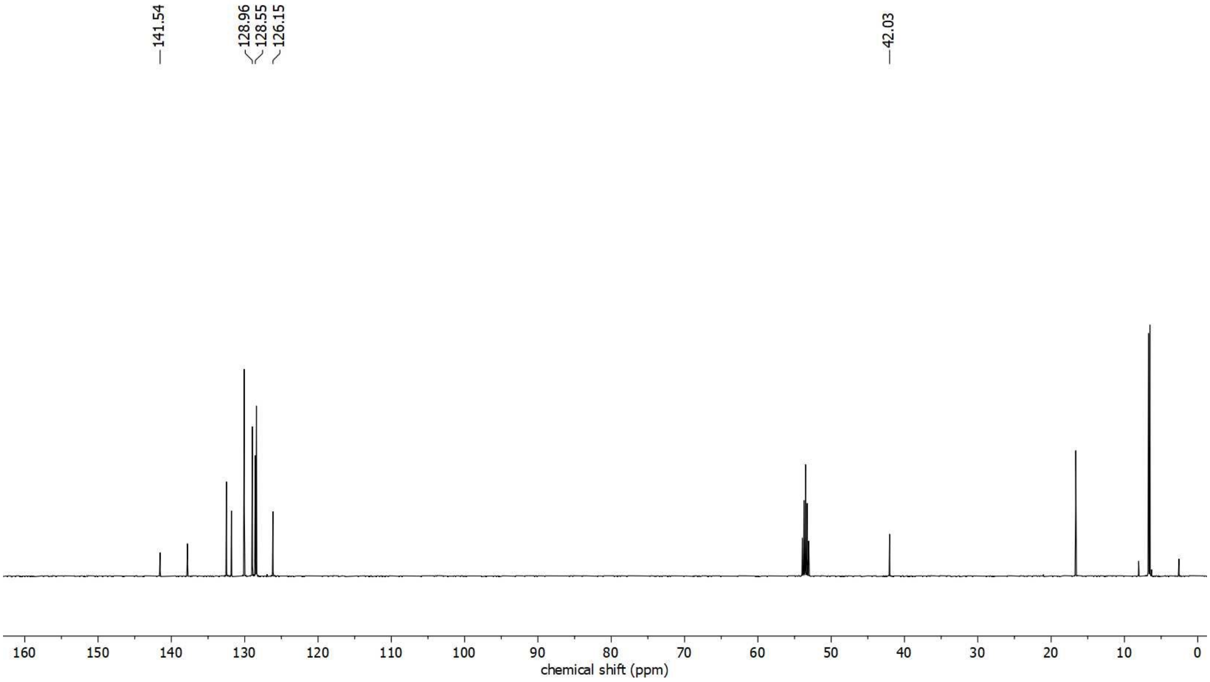


Figure S44: $^{13}C\{^1H\}$ NMR spectrum for deoxygenation of Ph_2CO using 1 mol % 4A recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >99% conversion to $(Ph)_2CH_2$ (yield w.r.t Et_3SiH).

Using **4B**:

Ph_2CO (0.012 g, 0.066 mmol), **4B** (0.001 g, 0.0006 mmol), Et_3SiH (9.51 µL, 0.060 mmol)

^1H NMR (CD_2Cl_2, 500 MHz): δ 4.02 (s, 2H, $Ph_2C\textit{H}_2$), 7.22 (m, 6H, o,p-C_6H_5), 7.33 (m, 4H, m-C_6H_4)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 41.9 (Ph_2CH_2), 126.0 (*p*-C_6H_5), 128.4 (*o*- C_6H_5), 128.8 (*m*-C_6H_5), 141.4 (*i*- C_6H_5)

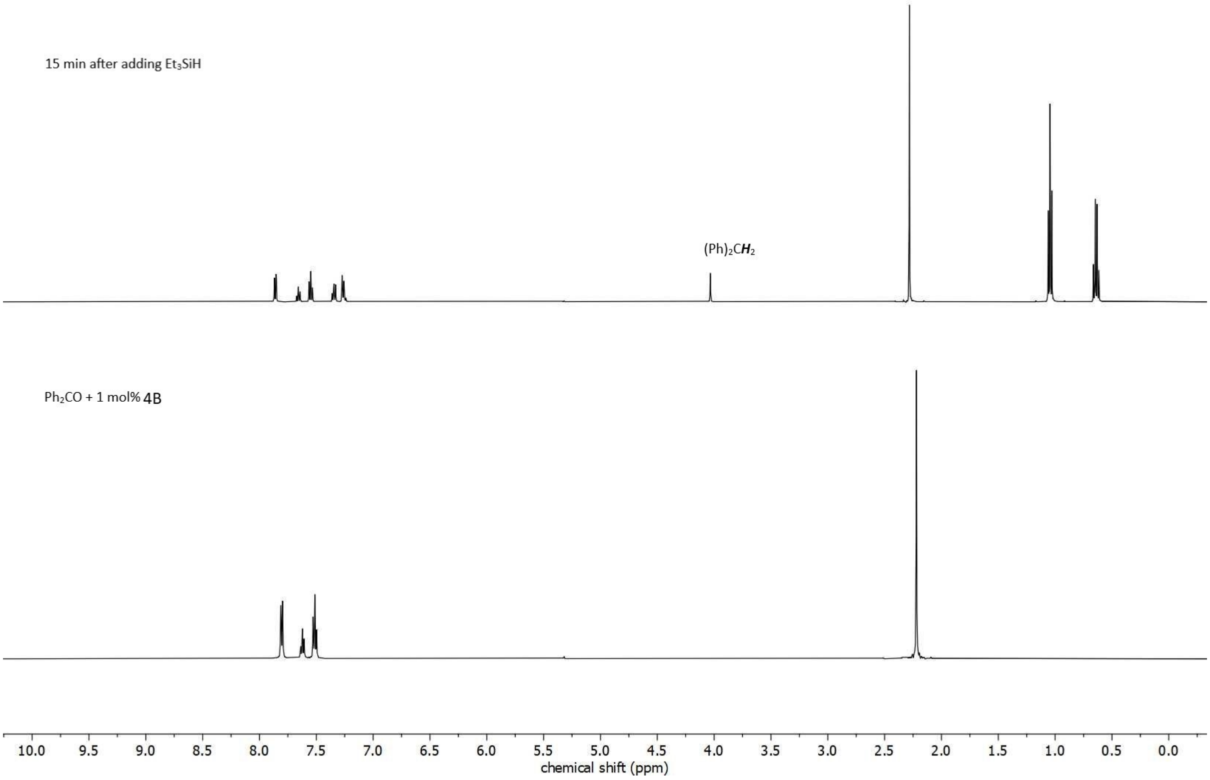


Figure S45: Stacked ^1H NMR spectra for deoxygenation of Ph_2CO using 1 mol % **4B** recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >99% conversion to $(Ph)_2CH_2$ (yield w.r.t Et_3SiH)

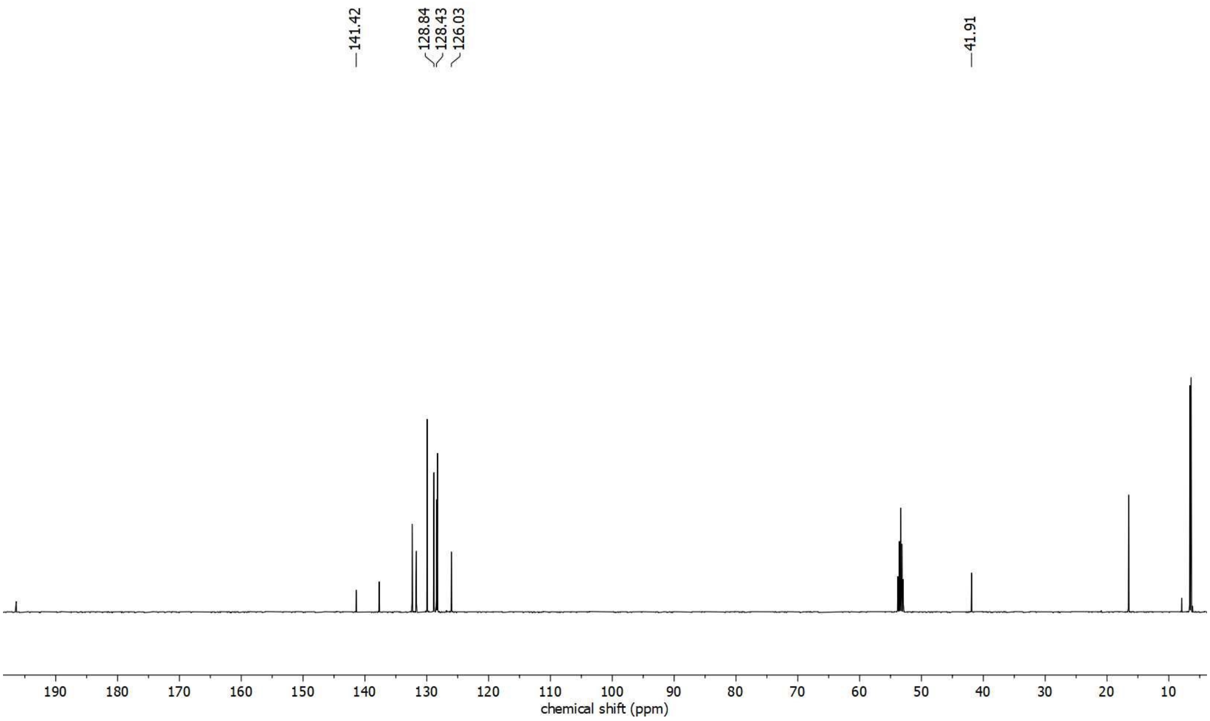


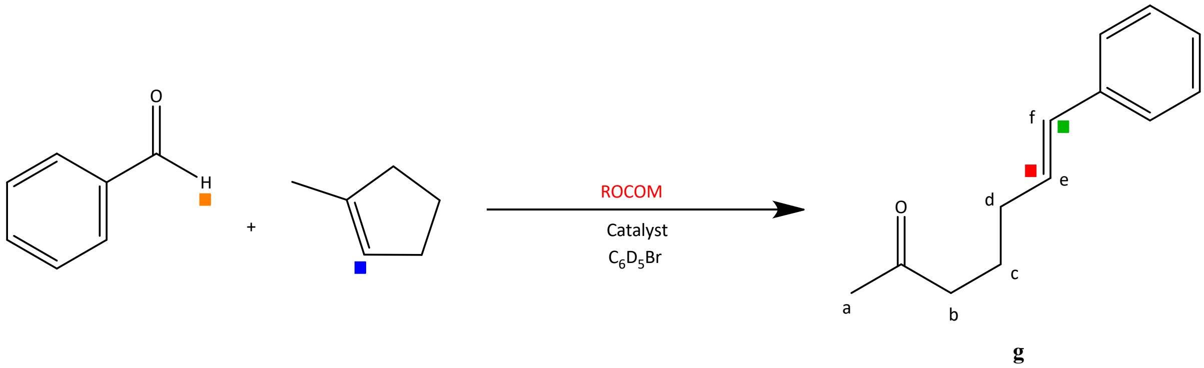
Figure S46: $^{13}C\{^{1}H\}$ NMR spectrum for deoxygenation of Ph_2CO using 1 mol % 4A recorded in CD_2Cl_2. Complete consumption of Et_3SiH resulted in >99% conversion to $(Ph)_2CH_2$ (yield w.r.t Et_3SiH).

Carbonyl olefin Metatheses

Ring Opening Carbonyl Olefin Metathesis (ROCOM)

Experimental procedure

10 mol % $[NMe_2C_6H_4(mesityl)Sb(PhCHO)][Al(OC(CF_3)_3)_4]$/ $[NMe_2CH_2C_6H_4(mesityl)Sb(PhCHO)][Al(OC(CF_3)_3)_4]$ was generated in situ with **1A**/**1B**, $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ and PhCHO in C_6D_5-Br (0.6 mL) in a J Young NMR tube. The solution was filtered to another J Young NMR tube to give a pale-yellow solution. To this, 1-methylcyclopentene was added to the solution giving instant light pink color to the solution. NMR tube was then sealed and reaction was monitored for 24 h at room temperature. Thereafter, the reaction was quenched by passing through a silica plug and eluted using dichloromethane. The volatiles were removed under reduced pressure and the metathesis product was isolated from the crude mixture by flash column (9:1 hexanes/EtOAc) to give **g** as yellow oil.



g

Scheme S11

<u>Using 10 mol % of **$[NMe_2CH_2C_6H_4(mesityl)Sb(PhCHO)][Al(OC(CF_3)_3)_4]$**</u>

1A (0.003 g, 0.007 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.009 g, 0.007 mmol), PhCHO (7.71 µl, 0.0756 mmol), 1-methylcyclopentene (7.96 µl, 0.0756 mmol)

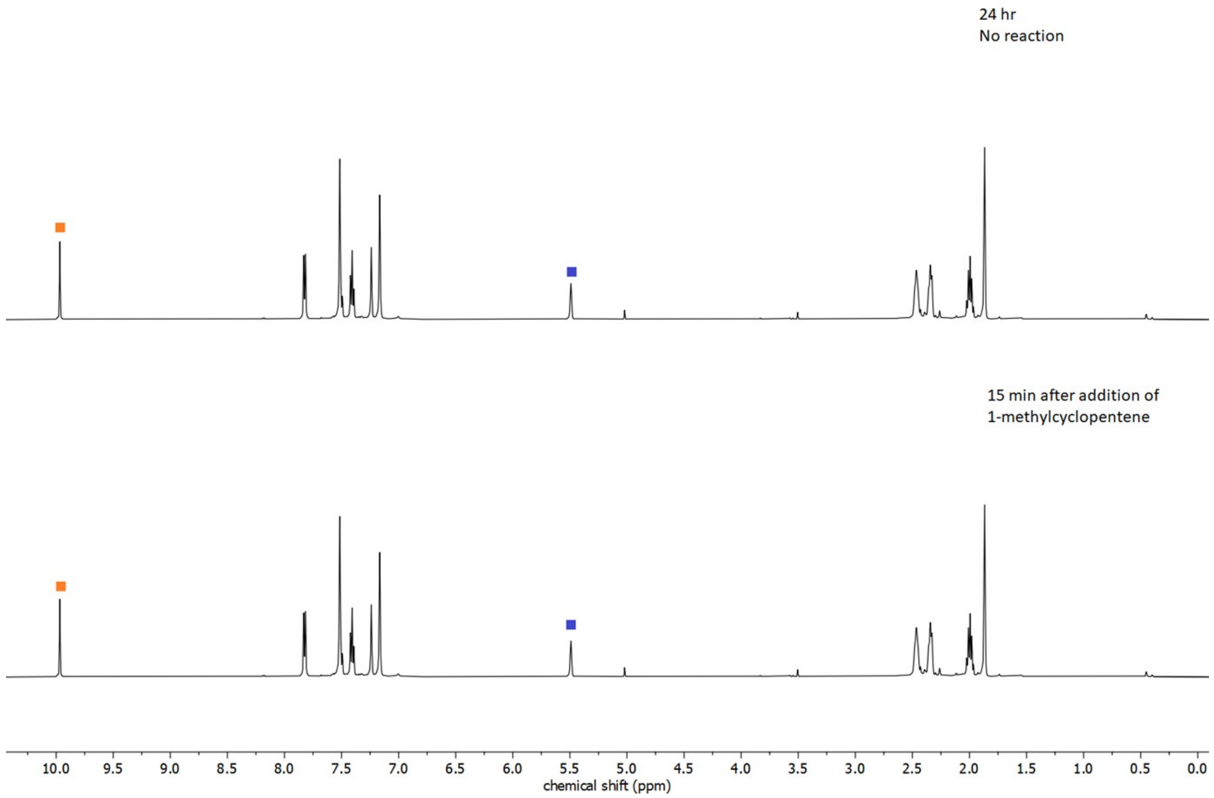


Figure S47: Stacked ^{1}H NMR spectra of ROCOM using 10 mol % [$NMe_2CH_2C_6H_4$(mesityl)Sb(PhCHO)][$Al(OC(CF_3)_3)_4$]: Neat vs reaction after 24 h recorded in C_6D_5-Br.

Using 10 mol % of **[$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][$Al(OC(CF_3)_3)_4$]**

1B (0.003 g, 0.007 mmol), [$Ag(CH_2Cl_2)_2$][$Al(OC(CF_3)_3)_4$] (0.009 g, 0.007 mmol), PhCHO (7.71 µl, 0.0756 mmol), 1-methylcyclopentene (7.96 µl, 0.0756 mmol)

Yield of g = 0.005 g (35%).

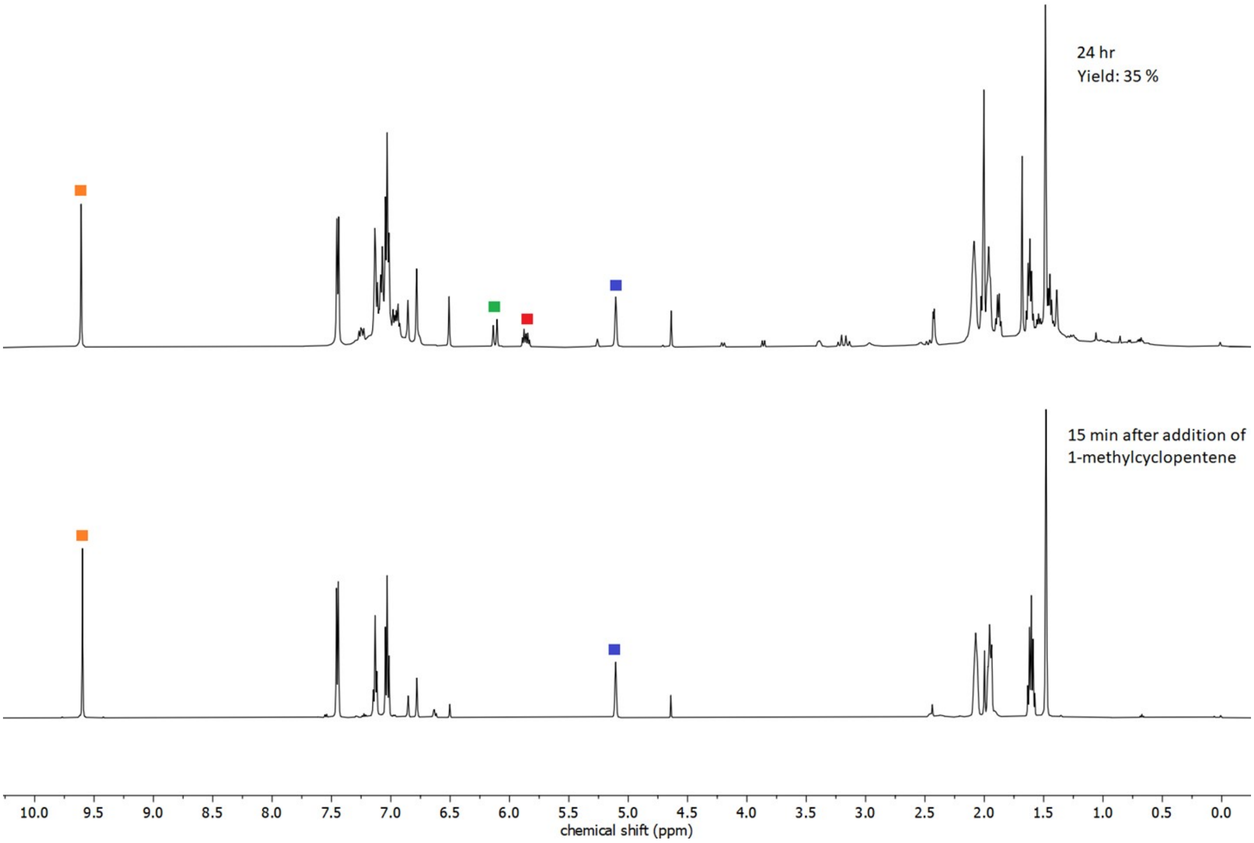


Figure S48: Stacked ^{1}H NMR spectra of ROCOM using 10 mol % [$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][$Al(OC(CF_3)_3)_4$]: Neat vs reaction after 24 h recorded in C_6D_5-Br.

Isolated metathesis product **g**

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.71-1.77 (m, 2H, c-CH_2), 2.10 (s, 3H, a-CH_3), 2.20-2.25 (m, 2H, d-CH_2), 2.47 (t, 2H, b-CH_2), 6.18-6.24 (dt, 1H, e-CH), 6.40 (d, 1H, f-CH), 7.20 (t, 1H, *p*-C_6H_5), 7.29 (t, 2H, *m*-C_6H_5), 7.35 (d, 2H, *o*-C_6H_5)

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): δ 23.7 (c-CH_2), 30.1 (a-CH_3), 32.7 (d-CH_2), 43.1 (b-CH_2), 126.3 (*p*-C_6H_4), 127.3 (*m*-C_6H_4), 128.9 (*o*-C_6H_4), 130.5 (*i*-C_6H_4), 130.8 (e-CH), 138.1 (f-CH), 208.7 (CO)

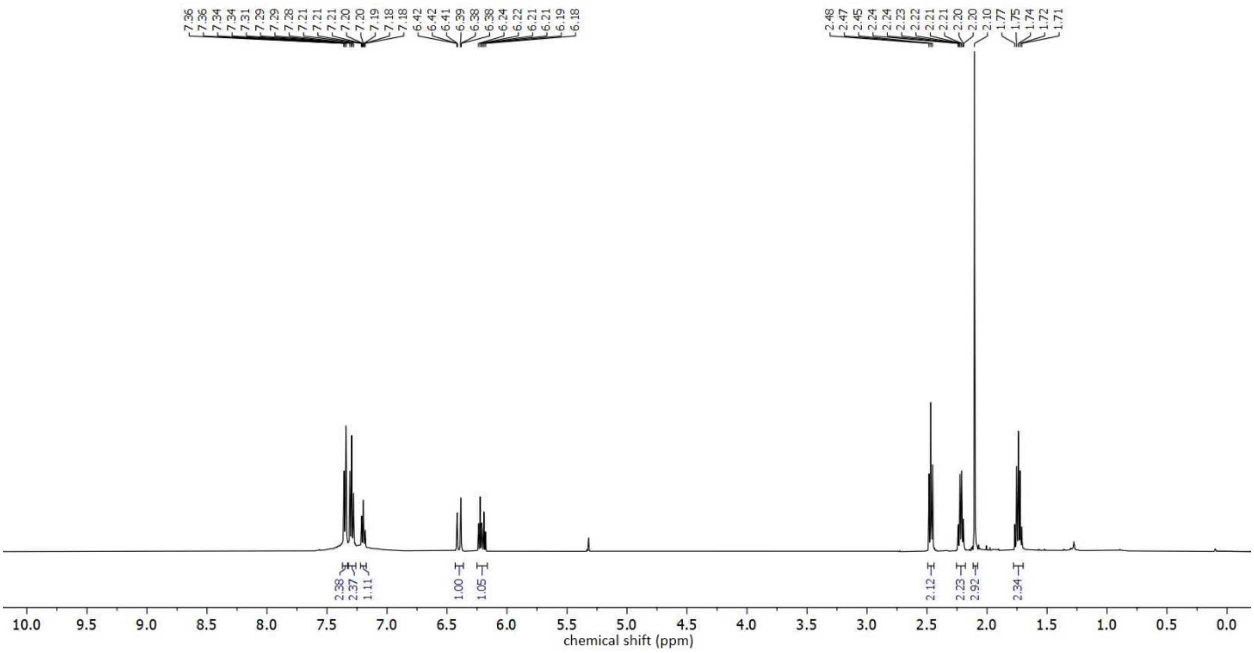


Figure S49: ^{1}H NMR spectrum of **g** recorded in CD_2Cl_2.

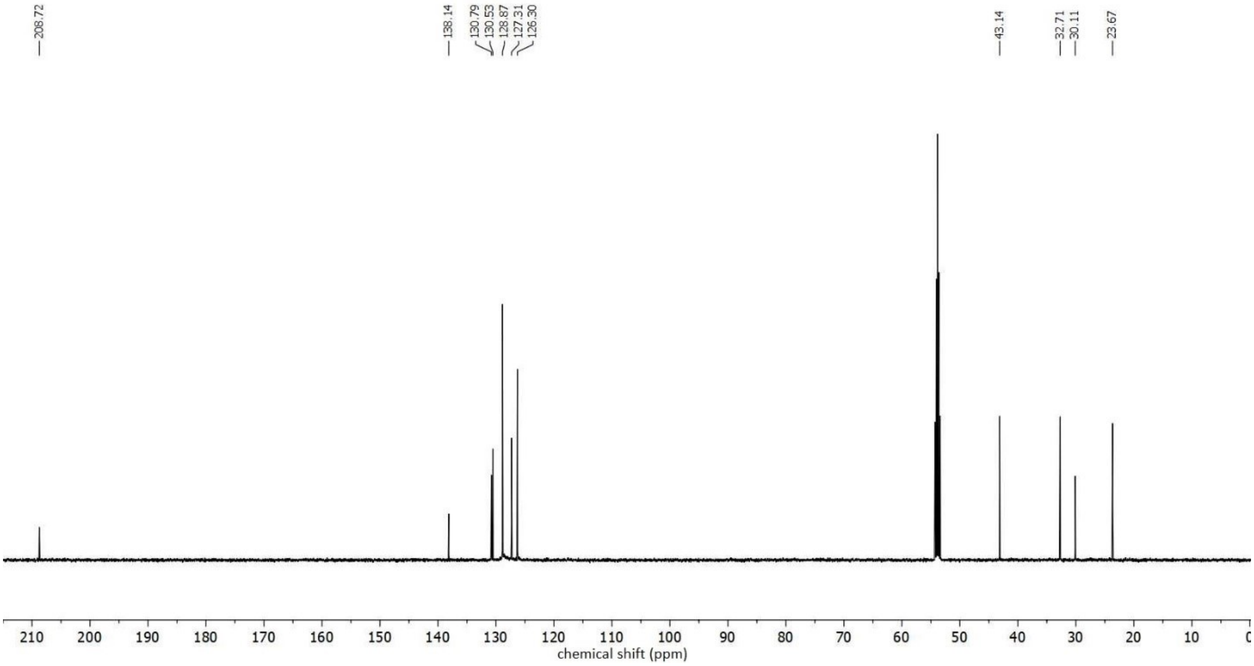


Figure S50: $^{13}C\{^1H\}$ NMR spectrum of **g** recorded in CD_2Cl_2.

Using 5 mol % of **[$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][Al($OC(CF_3)_3)_4$]**

1B (0.002 g, 0.005 mmol), [$Ag(CH_2Cl_2)_2$][Al[O{$C(CF_3)_3$}$_4$] (0.006 g, 0.00), PhCHO (14.7 µL, 0.1 mmol), 1-methylcyclopentene (10.63 µL ,0.1 mmol)

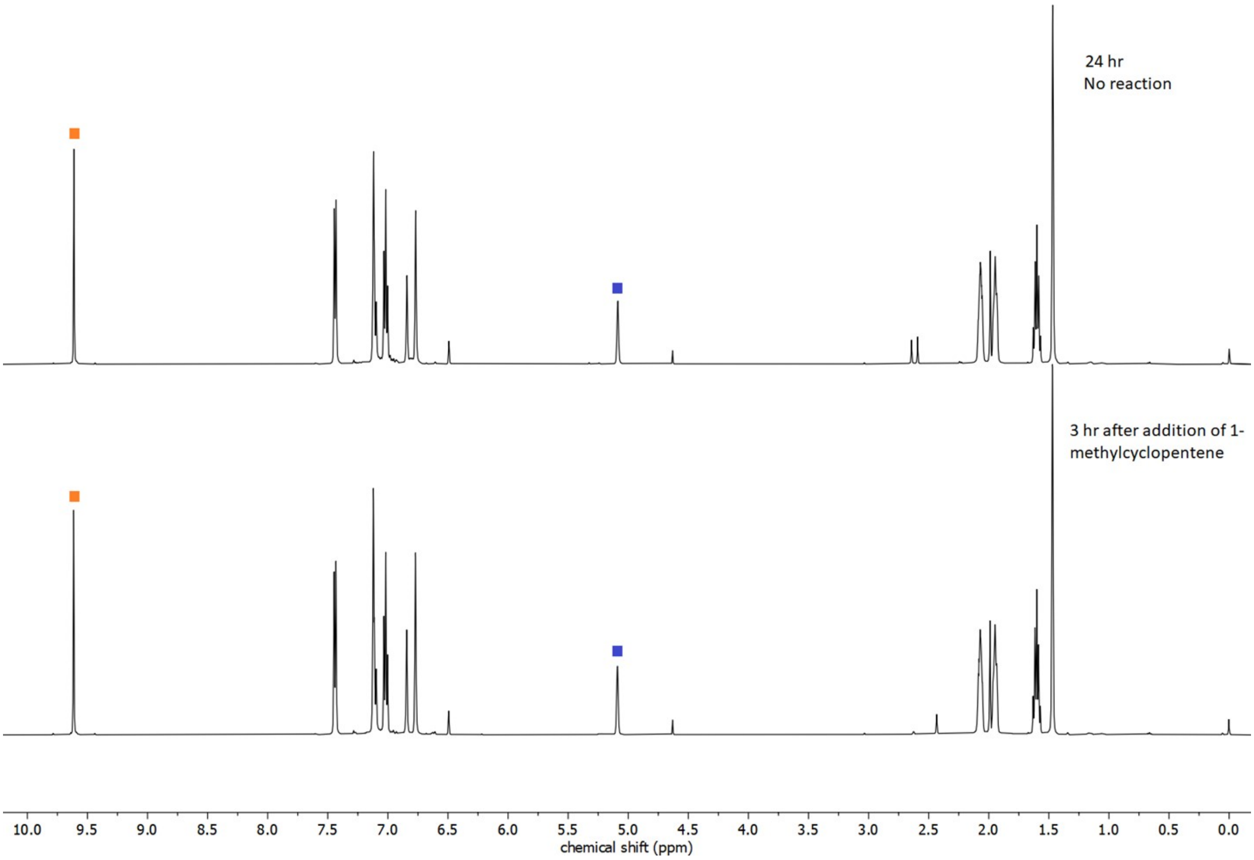


Figure S51: Stacked ^{1}H NMR spectra of ROCOM using 5 mol % [$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][Al($OC(CF_3)_3)_4$] : Neat vs reaction after 24 h recorded in C_6D_5-Br.

Using 20 mol % **$[NMe_2C_6H_4(mesityl)Sb(PhCHO)][Al(OC(CF_3)_3)_4]$**

1B (0.002 g, 0.005 mmol), $[Ag(CH_2Cl_2)_2][Al[O\{C(CF_3)_3\}_4]$ (0.006 g, 0.005), PhCHO (2.71 µL, 0.0252 mmol), 1-methylcyclopentene (2.65 µL ,0.0252 mmol)

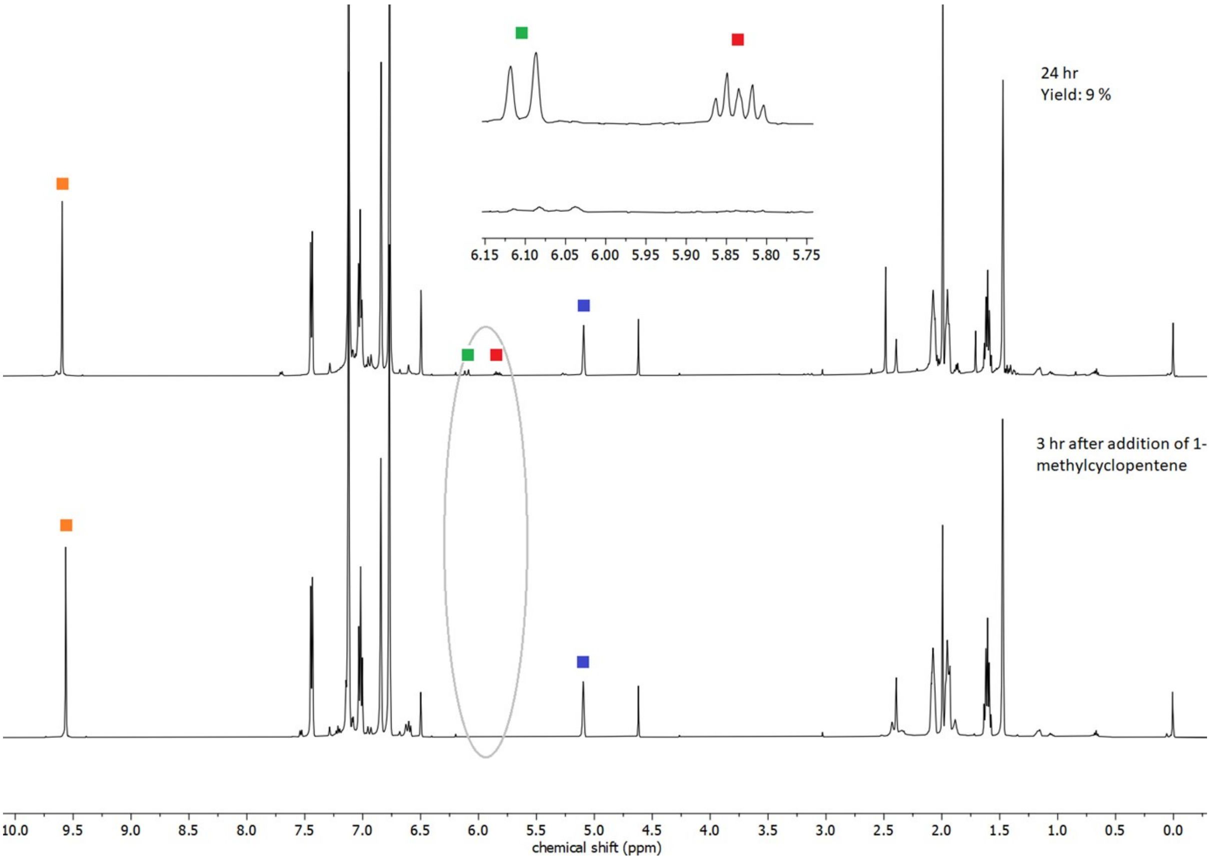


Figure S52: Stacked ^1H NMR spectra of ROCOM using 20 mol % $[NMe_2C_6H_4(mesityl)Sb(PhCHO)][Al(OC(CF_3)_3)_4]$: Neat vs reaction after 24 h recorded in C_6D_5-Br.

Using 10 mol % $SbCl_3$:

$SbCl_3$ (0.002 g, 0.008 mmol), PhCHO (8.94 µL, 0.087 mmol) and 1-methylcyclopentene (9.25 µL ,0.087 mmol)

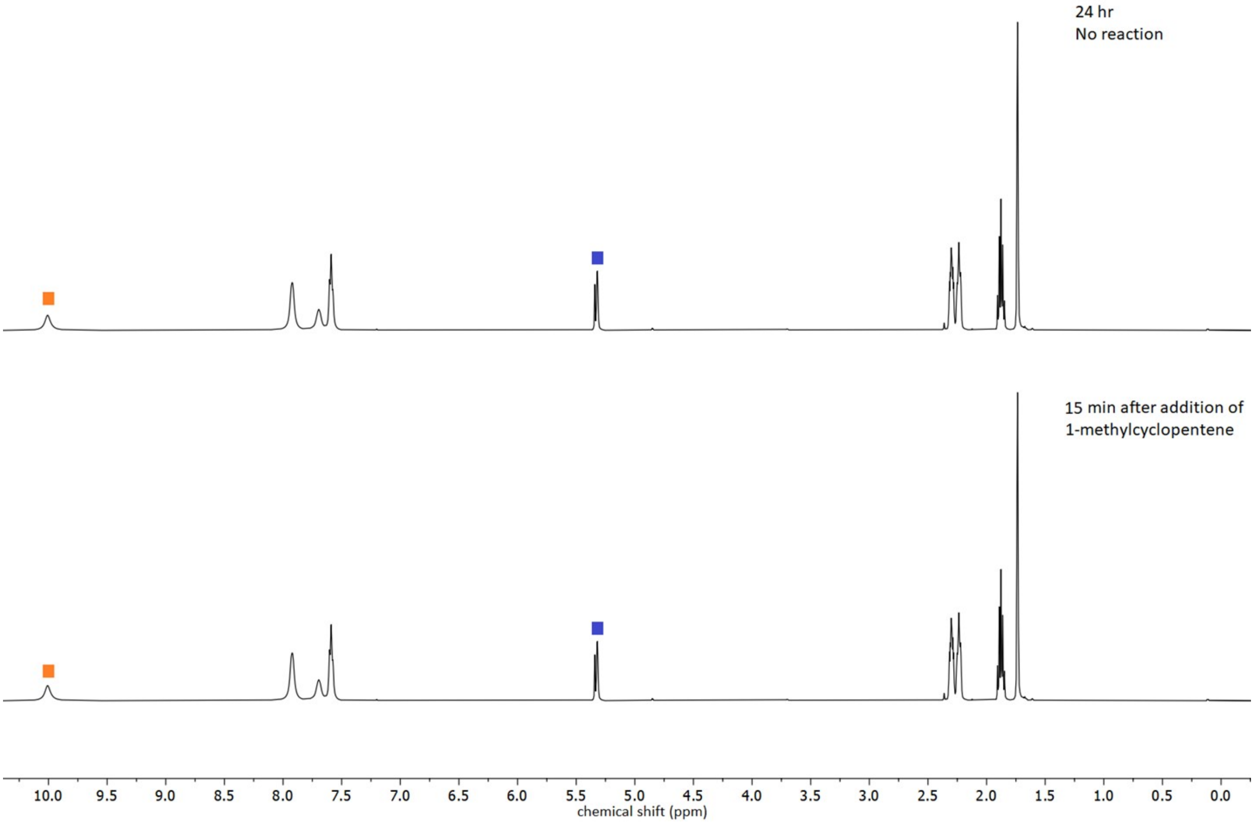


Figure S53: Stacked ^1H NMR spectra of ROCOM using 10 mol % $SbCl_3$: Neat vs reaction after 24 h recorded in CD_2Cl_2.

Using 10 mol % $B(C_6F_5)_3$:

$B(C_6F_5)_3$ (0.002 g, 0.0039 mmol), PhCHO (3.94 µL, 0.039 mmol), 1-methylcyclopentene (4.1 µL, 0.039 mmol)

Figure S54: Stacked ^{1}H NMR spectra of ROCOM using 10 mol % $B(C_6F_5)_3$: Neat vs reaction after 24 h recorded in CD_2Cl_2.

Using 10 mol % $[Ag(CH_2Cl_2)_2][Al[O\{C(CF_3)_3\}_4]$

$[Ag(CH_2Cl_2)_2][Al[O\{C(CF_3)_3\}_4]$ (0.002 g, 0.0039 mmol), PhCHO (3.94 µL, 0.039 mmol), 1-methylcyclopentene (4.1 µL, 0.039 mmol)

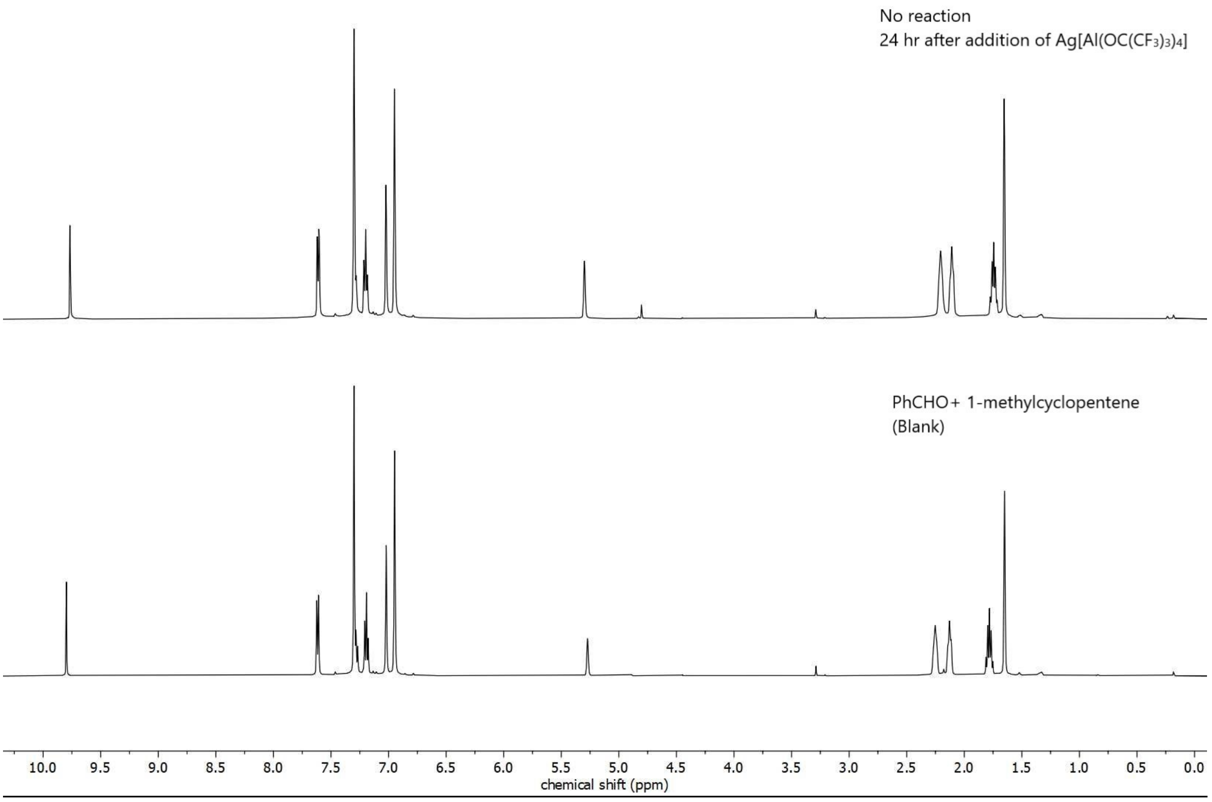


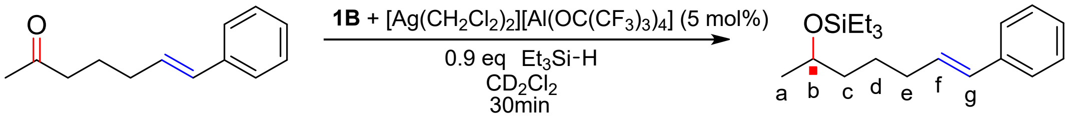
Figure S55: Stacked ^{1}H NMR spectra of ROCOM using 10 mol % [Ag(CH_2Cl_2)$_2$][Al[O{C(CF_3)$_3$}$_4$]: Neat vs reaction after 24 h recorded in CD_2Cl_2.

Table S2

Catalyst (mol%)	**Product**	**Time** (h)	**Yield** (%)
[$NMe_2CH_2C_6H_4$(mesityl)Sb(PhCHO)][Al(OC(CF_3)$_3$)$_4$] (10%	No reaction	24	-
[$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][Al(OC(CF_3)$_3$)$_4$] (5%)	No reaction	24	-
[$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][Al(OC(CF_3)$_3$)$_4$] (10%)	g	24	35
[$NMe_2C_6H_4$(mesityl)Sb(PhCHO)][Al(OC(CF_3)$_3$)$_4$] (20%)	g	24	9
$SbCl_3$ (10%)	No reaction	24	-
B(C_6F_5)$_3$ (10%)	No reaction	24	-
[Ag(CH_2Cl_2)$_2$][Al[O{C(CF_3)$_3$}$_4$] (10%)	No reaction	24	-

Hydrosilylation of metathesis product **g** using Et_3SiH

1B (0.002 g, 0.005 mmol), **g** (0.019 g, 0.1 mmol) and [Ag(CH_2Cl_2)$_2$][Al[O{C(CF_3)$_3$}$_4$] (0.006 g, 0.005 mmol) were loaded into a J Young NMR tube with 0.6 mL CD_2Cl_2. The reaction mixture was filtered into another J Young NMR tube. Et_3SiH (14.49 µL, 0.09 mmol) was added to the solution. NMR tube was then sealed and reaction was monitored by ^{1}H NMR until the reaction reached completion.



Scheme S12

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 0.58-0.69 (m, 9H, $OSiCH_2\mathit{CH_3}$), 0.96-1.04 (q, 6H, $OSiCH_2CH_3$), 1.15 (d, 3H, a-CH_3), 1.41-1.59 (m, 4H, c, d-CH_2), 1.72-1.74 (q, 2H, e-CH_2), 3.82-3.84 (q, 1H, b-CH), 6.21-6.24 (m, 1H, f-CH), 6.38, 6.40 (d, 1H, g-CH), 7.18, 7.20 (d, 2H, *o*-C_6H_5), 7.23-7.38 (m, 3H, *m*, *p*-C_6H_5)

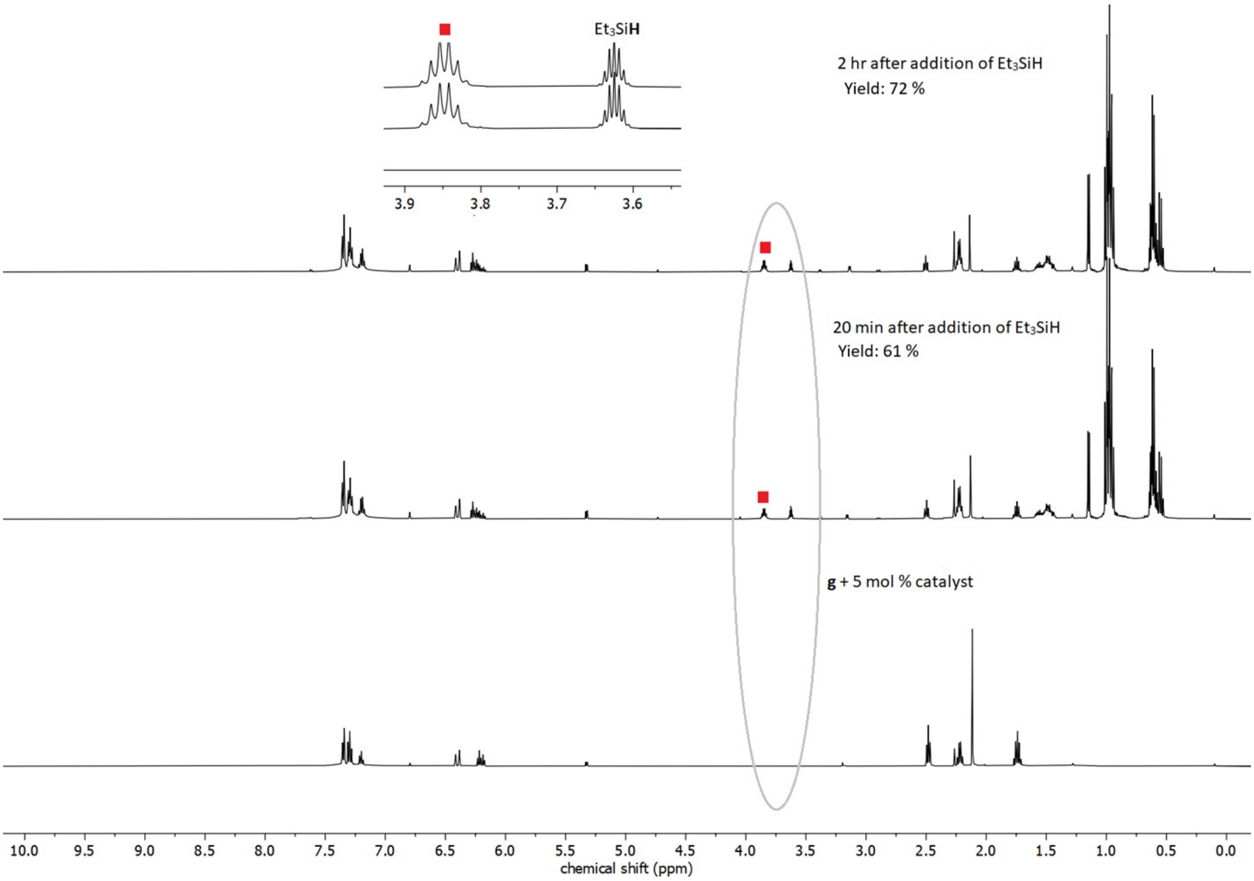
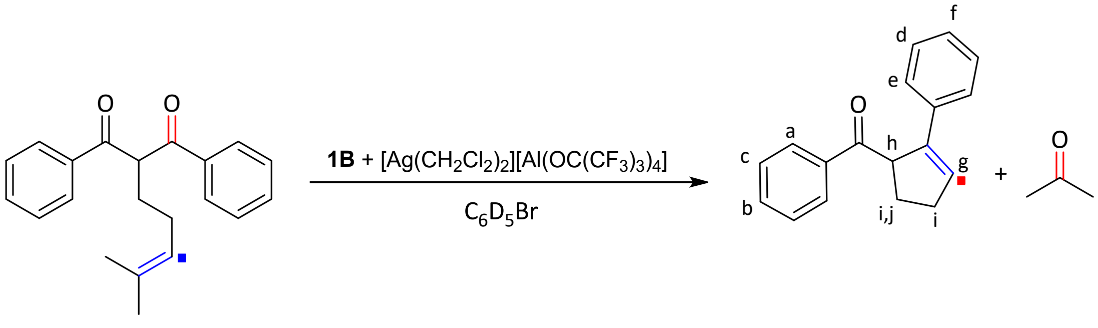


Figure S56: Stacked ^{1}H NMR spectra of hydrosilylation of **g** using 5 mol % **4B**: Neat (**g** + 5 mol% catalyst) vs reaction 2 h after adding Et_3SiH recorded in CD_2Cl_2.

Ring Closing Carbonyl Olefin Metathesis (RCCOM)

Experimental Procedure:

Substrate **d** was synthesized according to literature procedure.[8] **1A**/**1B** and **d** were loaded in 0.6 mL C_6D_5-Br in a J Young NMR tube. $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ was added to the reaction mixture. The precipitated AgCl was removed from the solution by filtration to another J Young NMR tube within five minutes. NMR tube was then sealed and the reaction was monitored by ^{1}H NMR until the reaction reached completion.



d **e**

Scheme S13

Using **1A**

1A (0.004 g, 0.01 mmol), **d** (0.003 g, 0.01 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.012 g, 0.01 mmol)

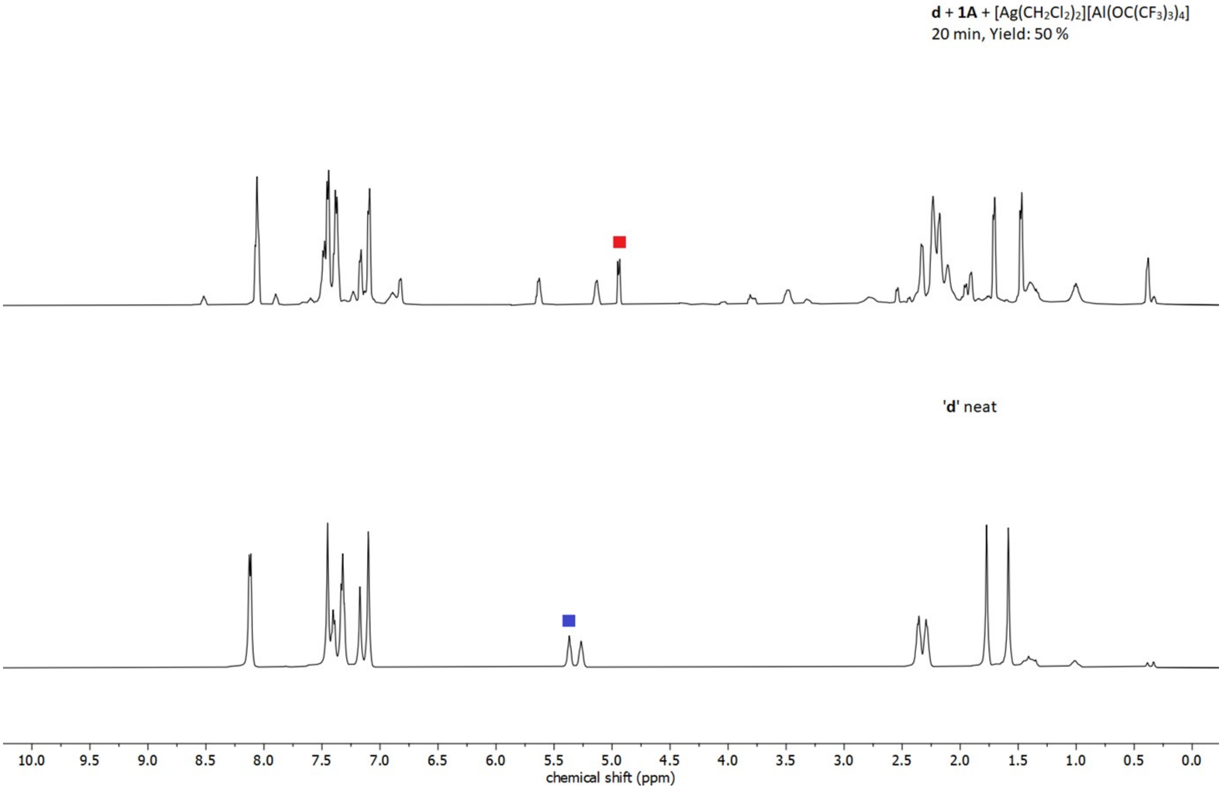


Figure S57: Stacked ^{1}H NMR spectra of RCCOM: Neat **d** vs reaction using **1A** after 20 min recorded in C_6D_5-Br.

Using **1B**

1B (0.004 g, 0.01 mmol), **d** (0.003 g, 0.01 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.012 g, 0.01 mmol)

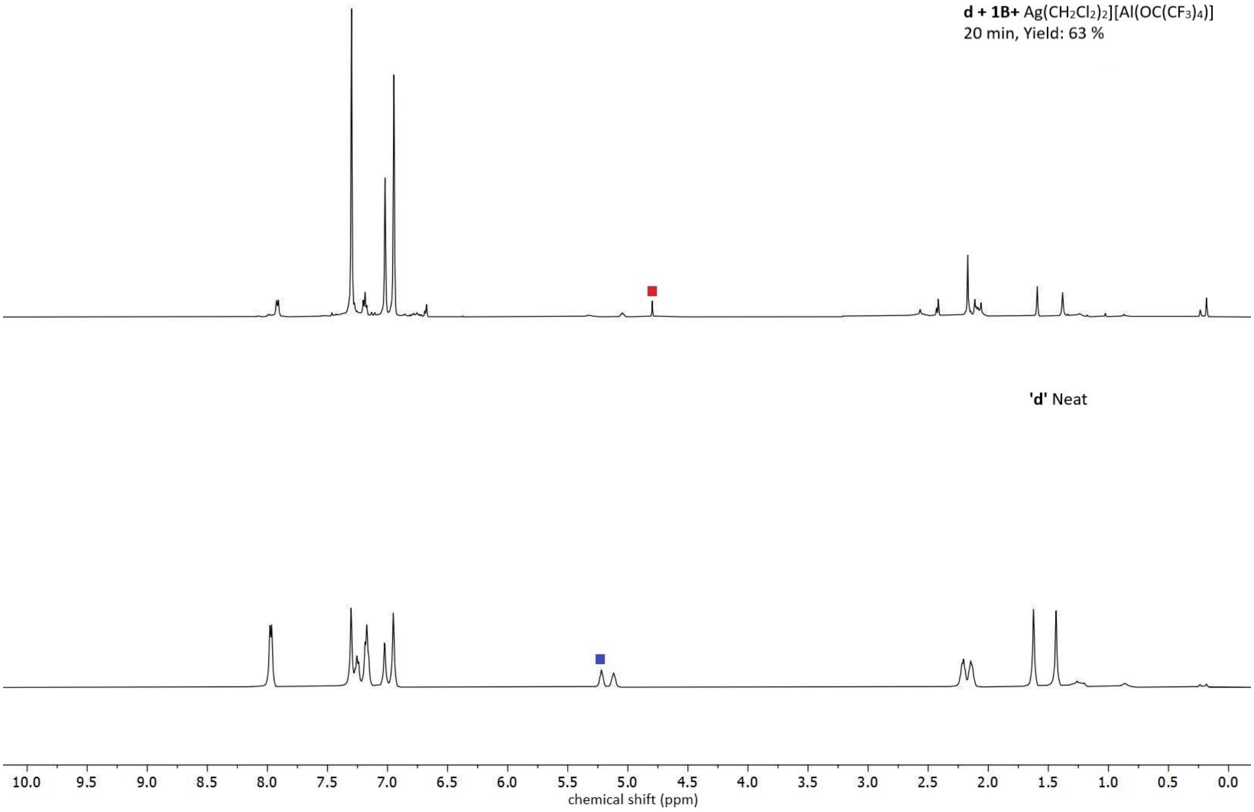


Figure S58: Stacked ^1H NMR spectra of RCCOM: Neat **d** vs reaction after 20 min recorded in C_6D_5-Br.

Metathesis Product (**e**)

^1H NMR (CD_2Cl_2, 500 MHz): δ 2.26 (m, 1H, j-CH_2), 2.58 (m, 3H, i-CH_2), 4.95 (ddd, 1H, h-CH), 6.83 (m, 1H, g-CH), 6.94 (m, 1H, f-C_6H_5), 7.33-7.38 (m, 9H, a,b,c,d,e-C_6H_4)

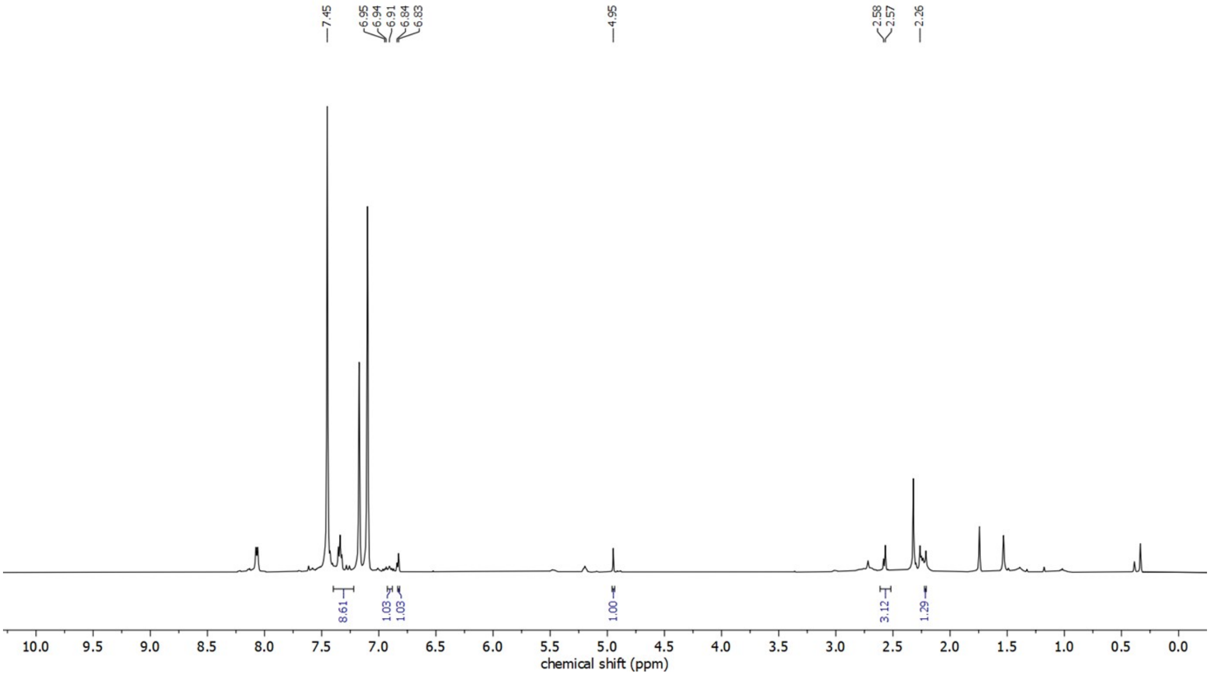
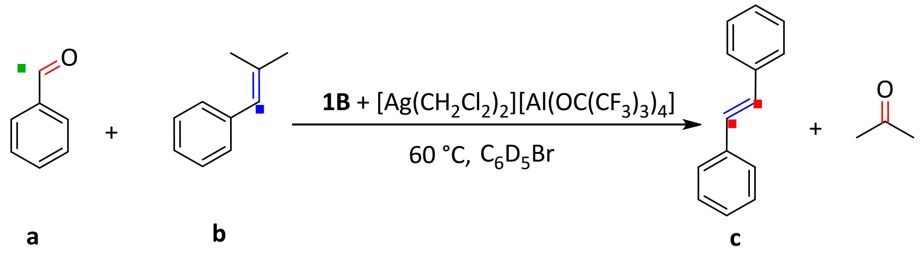


Figure S59: Stacked ^{1}H NMR spectra of RCCOM reaction using **1B** after 20 min recorded in C_6D_5-Br.

Cross Carbonyl Olefin Metathesis (CCOM)

Experimental procedure:

1A/1B and PhCHO were loaded into a J Young NMR tube. 0.6 mL C_6D_5-Br was condensed over the mixture. $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ was added to the reaction mixture. Thereafter, the precipitated AgCl was removed from the solution by filtration to another J Young NMR tube after 1 h. To this pale-yellow solution, **b** was added. NMR tube was then sealed and the reaction was kept at 60 °C in an oil bath. Reaction was monitored by ^{1}H NMR for 12 h.



Scheme S14

Using **1A**

1A (0.004 g, 0.01 mmol), PhCHO (1.47 µL, 0.01 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.012 g, 0.01 mmol), **b** (1.02 µL, 0.01 mmol)

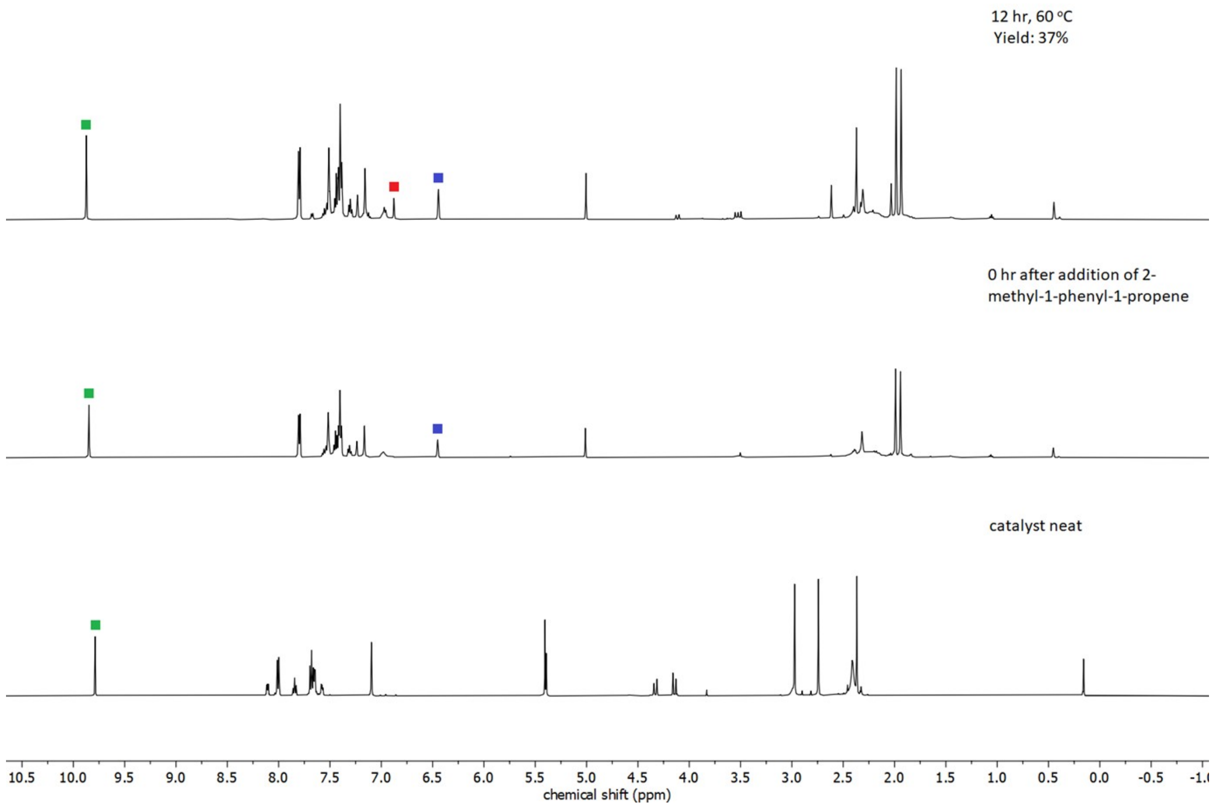


Figure S60: Stacked ^{1}H NMR spectra of CCOM: Neat catalyst vs reaction after 12 h at 60 ºC recorded in C_6D_5-Br.

<u>Using **1B**</u>

1B (0.004 g, 0.01 mmol), PhCHO (1.47 µL, 0.01 mmol), $[Ag(CH_2Cl_2)_2][Al(OC(CF_3)_3)_4]$ (0.012 g, 0.01 mmol), **b** (1.02 µL, 0.01 mmol)

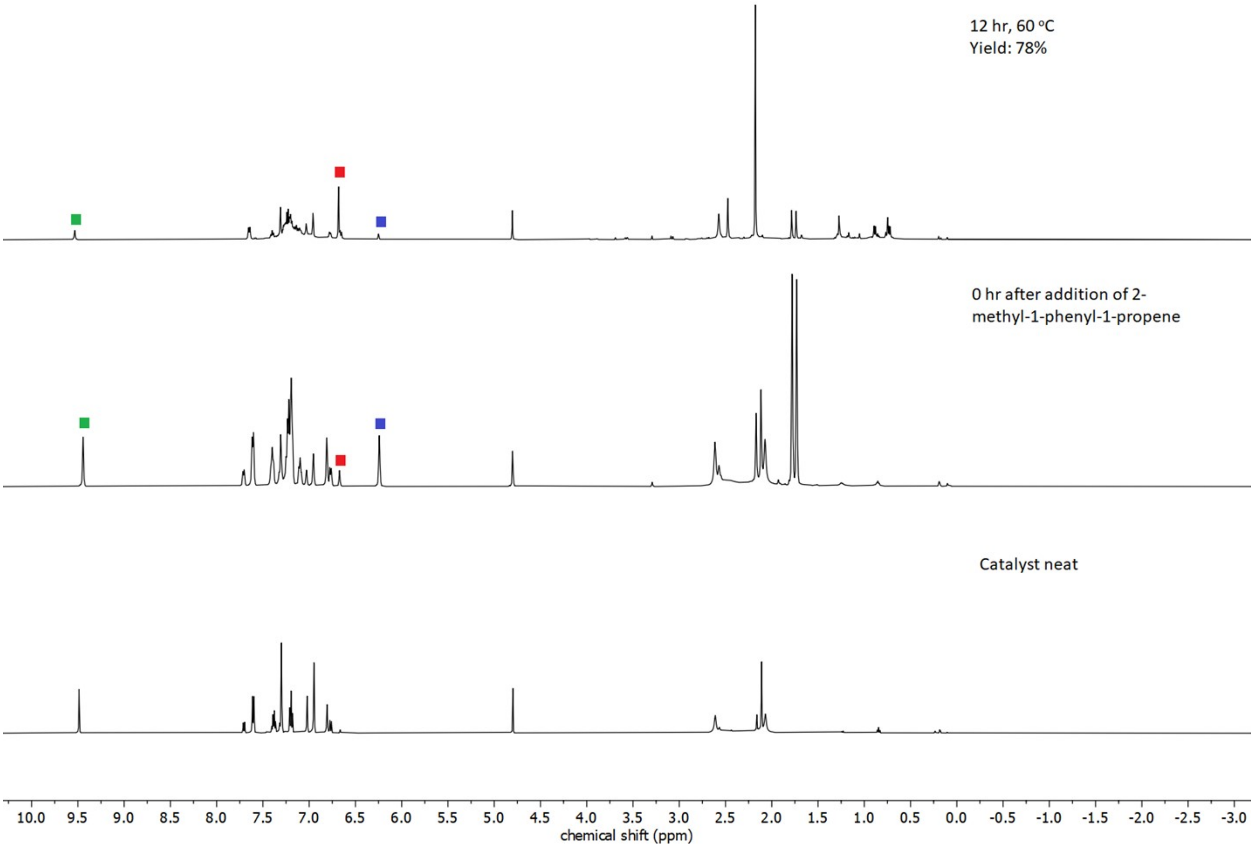


Figure S61: Stacked ^{1}H NMR spectra of CCOM: Neat catalyst vs reaction after 12 h at 60 ºC recorded in C_6D_5-Br.

Metathesis product (**c**):

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 6.82 (s, 2H, CH), 7.33-7.38 (m, 10H, C_6H_5)

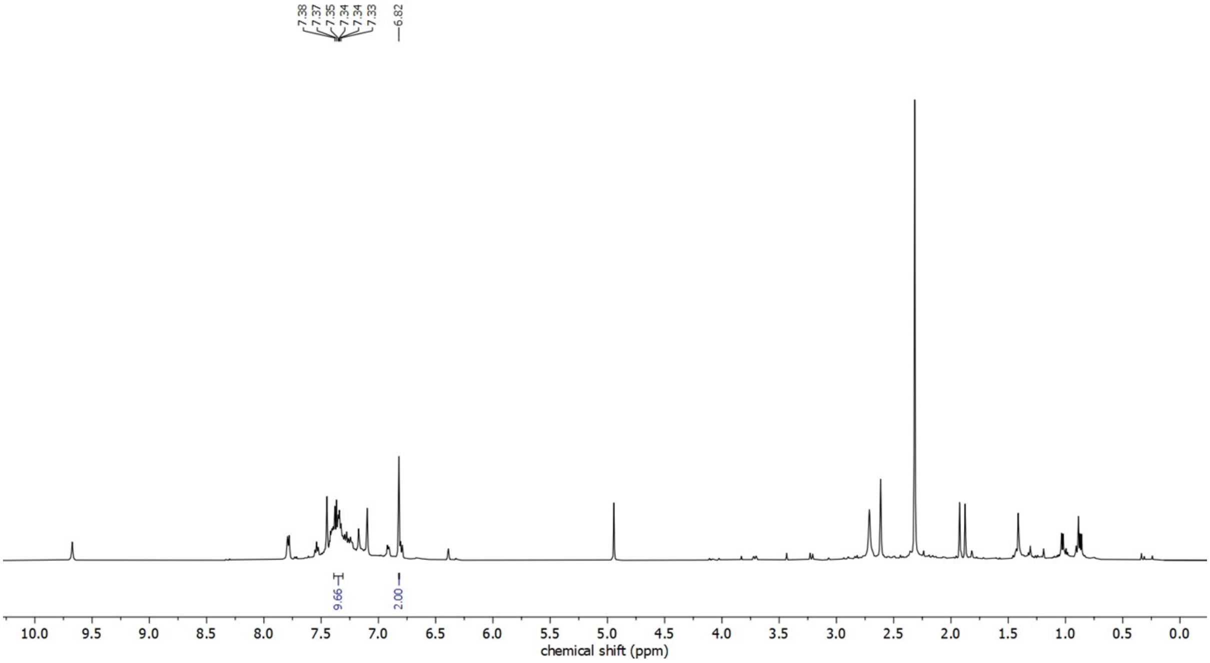


Figure S62: ^{1}H NMR spectra of CCOM reaction using **1B** after 12 h at 60 ºC recorded in C_6D_5-Br.

3. Crystallographic Data

Crystals were layered with paratone oil before mounting on diffractometer. Single-crystal X-ray crystallography for structural analysis was performed on a Bruker Kappa APEX II CCD Diffractometer, using Mo-Kα radiation, having a wavelength of 0.71073 Å, equipped with a CCD detector by using the APEX software package.[9] A matrix scan was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects and background using SAINT.[10] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[11] Space group assignments were based upon systematic absences, E statistics, and successful refinement of the structures. The structures were solved by SHELXT (version 2018/2) and refined by SHELXTL (version 2018/3) software package installed in the platform WinGX.[12,13] All non-hydrogen atoms, including those in disordered molecules, were refined anisotropically. Hydrogen atoms are placed at calculated positions and refined using a riding model. The structures of **1(A,B), 3(A,B)** and the cations of **2(A,B)** and **4(A,B)** is shown in the figure below.

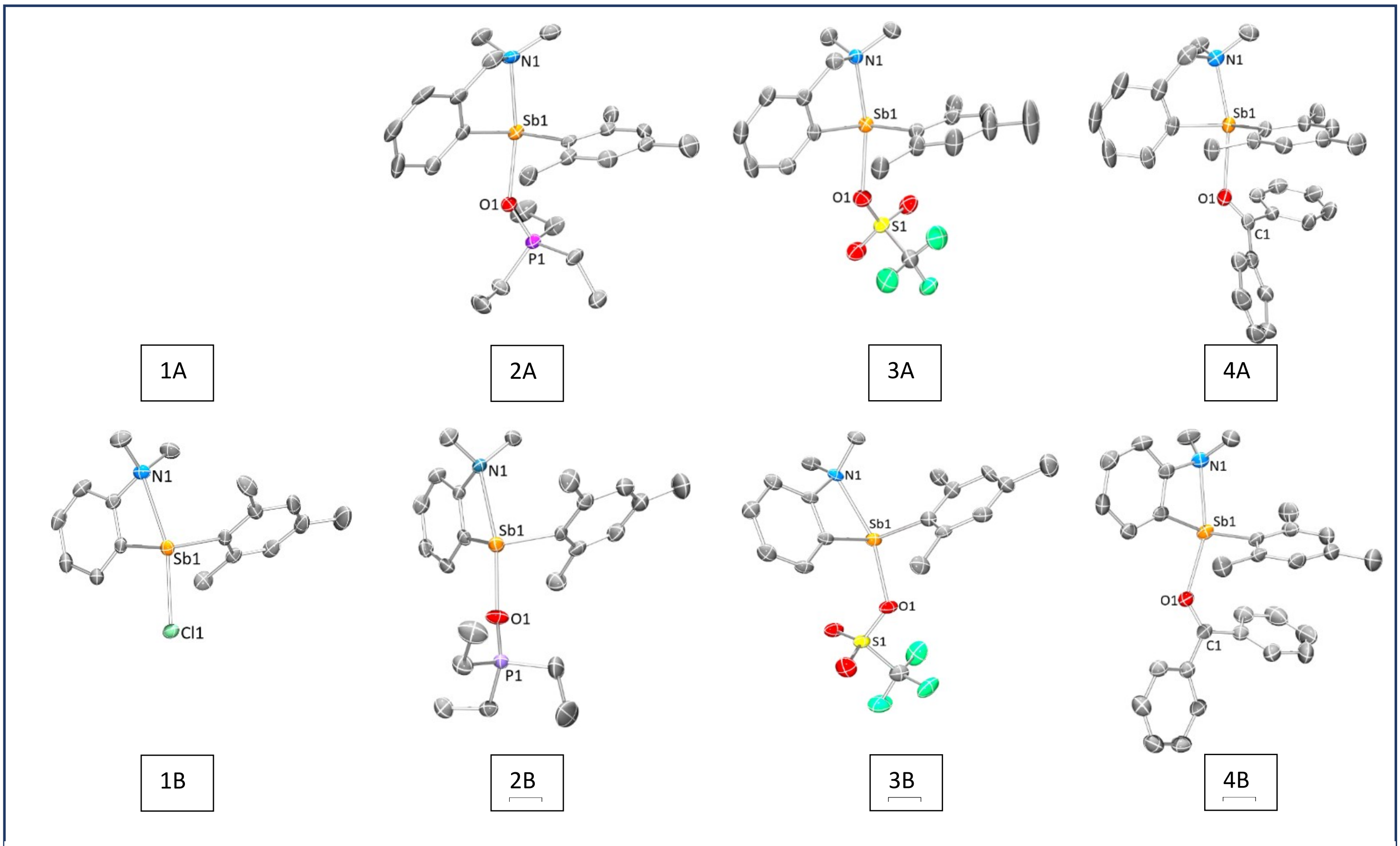


Figure S63: Solid-state structures of the complexes **1A-4A** (top, left to right) and **1B-4B** (below, left to right). Ellipsoids are at 35% probability level. Counter anions in **2(A,B)** and **4(A,B)**, and H-atoms in all the structures are omitted for clarity.

Table S3. Sb-N and Sb-X bond lengths (Å) and their deviation from the corresponding average covalent bond distances (Å) ($\sum_{cov}$(Sb—N)=2.10 Å, $\sum_{cov}$(Sb—Cl)=2.41 Å and $\sum_{cov}$(Sb—O)=2.05 Å).

	Sb-N	Sb-X	Sb-N — $\sum_{cov}$(Sb-N)	Sb-X — $\sum_{cov}$(Sb-X)
1A	2.480(2)	2.565(7)	0.380	0.155
2A	2.407(6)	2.220(5)	0.307	0.170
3A	2.334(3)	2.379(2)	0.234	0.329
4A	2.312(2)	2.465(2)	0.212	0.415
1B	2.619(3)	2.469(6)	0.519	0.059
2B	2.557(3)	2.154(2)	0.457	0.104
3B	2.451(7)	2.291(6)	0.351	0.241
4B	2.423(4)	2.340(3)	0.323	0.290

Estimated standard deviations (esd) in bond lengths do not have implications on our studies in determining primary and secondary interactions while calculating Sb-N and Sb-X bond lengths (Å) deviation from their corresponding average covalent bond distances. This is demonstrated below:

1A: Sb-N=2.480(2) Å, Sb-Cl= 2.565(7) Å

Sb-N, 2.478-2.10= 0.380 Å

Sb-N, esd (+2) 2.482-2.10= 0.382 Å

esd (-2) 2.478-2.10= 0.378 Å

Sb-Cl, 2.565-2.41=0.155 Å

Sb-Cl, esd (+7) 2.572-2.41= 0.162 Å

esd (-7) 2.558-2.41= 0.148 Å

2A: Sb-N=2.407(6) Å, Sb-O= 2.220(5) Å

Sb-N, 2.407-2.10= 0.307 Å

Sb-N, esd (+6) 2.413-2.10= 0.313 Å

esd (-6) 2.401-2.10= 0.301 Å

Sb-O, 2.220-2.05=0.170 Å

Sb-O, esd (+5) 2.225-2.05= 0.175 Å

esd (-5) 2.215-2.05= 0.165 Å

As Deviation$_{(Sb-O)}$< Deviation$_{(Sb-N)}$, Sb-O is the primary interaction.

3A: Sb-N=2.334(3) Å, Sb-O= 2.379(2) Å

Sb-N, 2.334-2.10= 0.234 Å   Sb-O, 2.379-2.05=0.329 Å

Sb-N, esd (+3) 2.337-2.10= 0.237 Å   Sb-O, esd (+2) 2.381-2.05= 0.331 Å

esd (-3) 2.331-2.10= 0.231 Å   esd (-2) 2.377-2.05= 0.327 Å

2B: Sb-N=2.557(3) Å, Sb-O= 2.154(2) Å

Sb-N, 2.557-2.10= 0.457 Å   Sb-O, 2.154-2.05=0.104 Å

Sb-N, esd (+3) 2.56-2.10= 0.460 Å   Sb-O, esd (+2) 2.156-2.05= 0.106 Å

esd (-3) 2.554-2.10= 0.454 Å   esd (-2) 2.152-2.05= 0.102 Å

3B: Sb-N= 2.451(7) Å, Sb-O= 2.291(6) Å

Sb-N, 2.451-2.10= 0.351 Å   Sb-O, 2.291-2.05=0.241 Å

Sb-N, esd (+7) 2.458-2.10= 0.358 Å   Sb-O, esd (+6) 2.297-2.05= 0.247 Å

esd (-7) 2.444-2.10= 0.344 Å   esd (-6) 2.285-2.05= 0.235 Å

Table S4. Crystal data and structure refinement for **1A**.

Identification code	1A	
CCDC Number	2164736	
Empirical formula	$C_{18}H_{23}ClNSb$	
Formula weight	410.57	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.7795(16) Å	α = 90°
	b = 9.5084(15) Å	β = 99.156(6)°
	c = 20.932(4) Å	γ = 90°
Volume	1725.1(5) $Å^3$	
Z	4	
Density (calculated)	1.581 Mg/m^3	
Absorption coefficient	1.748 mm^{-1}	
F(000)	824	
Crystal size	0.086 x 0.068 x 0.038 mm^3	
Theta range for data collection	1.971 to 27.998°	
Index ranges	-11<=h<=11, -12<=k<=12, -27<=l<=27	
Reflections collected	31810	
Independent reflections	4165 [$R_{(int)}$ = 0.0423]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.997 and 0.994	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4165 / 0 / 195	
Goodness-of-fit on F2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0252, wR2 = 0.0566	
R indices (all data)	R1 = 0.0325, wR2 = 0.0594	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.760 and -0.478 e.$Å^{-3}$	

Table S5. Crystal data and structure refinement for **2A**.

Identification code	2A	
CCDC Number	2164737	
Empirical formula	$C_{49}H_{52}BNOPCl_{10}Sb$	
Formula weight	1188.94	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 20.4940(18) Å	α = 90°
	b = 12.5955(11) Å	β = 100.742(2)°
	c = 20.8355(18) Å	γ = 90°
Volume	5284.1(8) $Å^3$	
Z	4	
Density (calculated)	1.495 Mg/m^3	
Absorption coefficient	1.095 mm^{-1}	
F(000)	2408	
Crystal size	0.096 x 0.075 x 0.048 mm^3	
Theta range for data collection	0.995 to 25.000°.	
Index ranges	-24<=h<=24, -14<=k<=14, -23<=l<=24	
Reflections collected	54028	
Independent reflections	18591 [$R_{(int)}$ = 0.0537]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.949 and 0.902	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18591 / 2 / 1169	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0854	
R indices (all data)	R1 = 0.0614, wR2 = 0.0920	
Absolute structure parameter	-0.027(9)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.819 and -0.610 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for **3A**.

Identification code	3A	
CCDC Number	2164738	
Empirical formula	$C_{19}H_{23}NO_3F_3SSb$	
Formula weight	524.19	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.0671(18) Å	α= 90°
	b = 9.5855(11) Å	β= 110.010(5)°
	c = 17.307(3) Å	γ = 90°
Volume	2192.8(5) Å^3	
Z	4	
Density (calculated)	1.588 mg/m^3	
Absorption coefficient	1.397 mm^{-1}	
F(000)	1048	
Crystal size	0.068 x 0.038 x 0.028 mm^3	
Theta range for data collection	2.466 to 24.997°	
Index ranges	-16<=h<=16, -11<=k<=11, -20<=l<=20	
Reflections collected	23704	
Independent reflections	3874 [$R_{(int)}$ = 0.0610]	
Completeness to theta = 24.997°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.962 and 0.911	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3874 / 0 / 258	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R_1 = 0.0304, wR_2 = 0.0645	
R indices (all data)	R_1 = 0.0458, wR_2 = 0.0709	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.655 and -0.407 e.Å^{-3}	

Table S7. Crystal data and structure refinement for **4A**.

Identification code	4A	
CCDC Number	2164742	
Empirical formula	$C_{47}H_{33}AlF_{36}NO_5Sb$	
Formula weight	1524.47	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 13.7542(11) Å	α = 97.575(3)°
	b = 14.4647(12) Å	β = 112.199(2)°
	c = 15.6531(13) Å	γ = 98.467(3)°
Volume	2791.5(4) $Å^3$	
Z	2	
Density (calculated)	1.814 Mg/m^3	
Absorption coefficient	0.677 mm^{-1}	
F(000)	1500	
Crystal size	0.075 x 0.045 x 0.038 mm^3	
Theta range for data collection	1.435 to 24.998°	
Index ranges	-16<=h<=16, -17<=k<=17, -18<=l<=18	
Reflections collected	69803	
Independent reflections	9825 [$R_{(int)}$ = 0.0423]	
Completeness to theta = 24.998°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.975 and 0.951	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9825 / 82 / 1024	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0312, wR2 = 0.0693	
R indices (all data)	R1 = 0.0397, wR2 = 0.0747	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.567 and -0.512 e.$Å^{-3}$	

Table S8. Crystal data and structure refinement for **1B**.

Identification code	1B	
CCDC Number	2164735	
Empirical formula	$C_{17}H_{21}ClNSb$	
Formula weight	396.55	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.6015(6) Å	α = 90°
	b = 12.9734(9) Å	β = 103.132(2)°
	c = 15.5648(10) Å	γ = 90°
Volume	1691.5(2) Å^3	
Z	4	
Density (calculated)	1.557 Mg/m^3	
Absorption coefficient	1.780 mm^{-1}	
F(000)	792	
Crystal size	0.125 x 0.085 x 0.045 mm^3	
Theta range for data collection	2.431 to 28.000°	
Index ranges	-11<=h<=11, -17<=k<=17, -20<=l<=20	
Reflections collected	23276	
Independent reflections	4095 [$R_{(int)}$ = 0.0366]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.924 and 0.808	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4095 / 0 / 186	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0235, wR2 = 0.0563	
R indices (all data)	R1 = 0.0297, wR2 = 0.0592	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.596 and -0.488 e.Å^{-3}	

Table S9. Crystal data and structure refinement for **2B**.

Identification code	2B	
CCDC Number	2164740	
Empirical formula	$C_{47}H_{48}BNOPCl_8Sb$	
Formula weight	1089.99	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 12.3460(7) Å	α = 90°
	b = 22.8428(13) Å	β = 103.197(2)°
	c = 17.8648(10) Å	γ = 90°
Volume	4905.1(5) $Å^3$	
Z	4	
Density (calculated)	1.476 mg/m^3	
Absorption coefficient	1.067 mm^{-1}	
F(000)	2208	
Crystal size	0.076 x 0.054 x 0.037 mm^3	
Theta range for data collection	2.133 to 24.999°.	
Index ranges	-14<=h<=14, -27<=k<=27, -20<=l<=21	
Reflections collected	68011	
Independent reflections	8637 [R_{int} = 0.0600]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.962 and 0.923	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8637 / 0 / 549	
Goodness-of-fit on F^2	1.049	
Final R indices [I>2sigma(I)]	R_1 = 0.0362, wR_2 = 0.0841	
R indices (all data)	R_1 = 0.0511, wR_2 = 0.0927	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.206 and -0.890 e.$Å^{-3}$	

Table S10. Crystal data and structure refinement for **3B**.

Identification code	3B	
CCDC Number	2164739	
Empirical formula	$C_{18}H_{21}F_3NO_3SSb$	
Formula weight	510.17	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.401(5) Å	α = 90°
	b = 9.453(6) Å	β = 96.737(13)°
	c = 25.467(16) Å	γ = 90°
Volume	2009(2) $Å^3$	
Z	4	
Density (calculated)	1.687 Mg/m^3	
Absorption coefficient	1.522 mm^{-1}	
F(000)	1016	
Crystal size	0.250 x 0.150 x 0.020 mm^3	
Theta range for data collection	1.610 to 24.999°.	
Index ranges	-9<=h<=9, -11<=k<=11, -30<=l<=30	
Reflections collected	34625	
Independent reflections	3518 [$R_{(int)}$ = 0.1101]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.970 and 0.702	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3518 / 0 / 249	
Goodness-of-fit on F^2	1.166	
Final R indices [I>2sigma(I)]	R1 = 0.0624, wR2 = 0.1376	
R indices (all data)	R1 = 0.0789, wR2 = 0.1454	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.403 and -2.479 e.$Å^{-3}$	

Table S11. Crystal data and structure refinement for **4B**.

Identification code	4B	
CCDC Number	2164741	
Empirical formula	$C_{47}H_{33}AlCl_2F_{36}NO_5Sb$	
Formula weight	1595.37	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.3903(18) Å	α = 99.484(5)°
	b = 15.266(2) Å	β = 109.810(5)°
	c = 17.646(3) Å	γ = 106.208(4)°
Volume	2888.4(7) $Å^3$	
Z	2	
Density (calculated)	1.834 Mg/m^3	
Absorption coefficient	0.748 mm^{-1}	
F(000)	1568	
Crystal size	0.075 x 0.065 x 0.045 mm^3	
Theta range for data collection	1.789 to 24.999°	
Index ranges	-14<=h<=14, -18<=k<=18, -20<=l<=20	
Reflections collected	71280	
Independent reflections	10155 [$R_{(int)}$ = 0.0827]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.967 and 0.946	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10155 / 558 / 1280	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1135	
R indices (all data)	R1 = 0.0809, wR2 = 0.1319	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.637 and -0.712 e.$Å^{-3}$	

4. Computational Details

Theoretical calculations were performed to provide additional insight into the bonding at the Sb(III) center of complexes **1(A,B), 3(A,B)** and the cations of **2(A,B)** and **4(A,B)**. The structures have been optimized using density functional theory with the B3LYP[14] functional corrected by Grimme's D3[15] dispersion (B3LYP-D3) using the Gaussian 16 program package, revision c.[16] Def2-TZVP[17] basis set was used to describe all atoms in the molecules. The effect of solvents was accounted for by applying the polarizable continuum model (PCM) for the respective solvents. The vibrational frequencies for the optimized geometries were calculated at the same level of theory. The absence of any imaginary frequencies allowed us to characterize them as true minima on their respective potential energy hypersurfaces. The results from DFT calculations and structural data from XRD analysis is presented below.

Table S12: A comparison of the XRD and calculated bond lengths of isolated molecules. There is reasonable parity between the two except in the case of molecule **1A** and **1B**.

Compound	XRD		DFT	
	Sb—N (Å)	**Sb—X (Å)**	**Sb-N**	**Sb-X**
1A	2.480	2.565	2.692	2.504
2A	2.407	2.220	2.485	2.254
3A	2.334	2.379	2.445	2.368
4A	2.312	2.465	2.388	2.529
1B	2.619	2.469	2.795	2.465
2B	2.557	2.154	2.601	2.176
3B	2.451	2.291	2.553	2.268
4B	2.423	2.340	2.486	2.358

To understand the large deviation observed in the Sb-N distance in **1A**, between the computed and the X-ray value, preliminary investigations were performed on the solid state crystal structure of **1A** in our set of compounds using the Vienna Ab initio Simulation Package[18] (VASP) with PBE[19] functional and plane wave basis set was used to model the atoms (vide infra). The energy cut-off for the plane wave basis set was chosen to be 450 eV and the electronic energy convergence threshold was set at 10^{-7} eV while that for force is 10^{-3} eV/Å. This brought the Sb-N distance closer to that obtained from the X-Ray analysis. To eliminate the possibility that this change in the computed value arose from the new functional, the structure of **1A** was again optimized using VASP at the same level by removing all atoms aside from those belonging to a single molecule of complex **1A** from the unit cell and introducing a separation of 20 Å between each molecule – essentially isolating the single molecule. This Sb-N distance is closer to that calculated for the isolated molecule calculated at B3LYP-D3/Def2-TZVP level. If these structures are compared, it is clear that the short Sb-N bond observed in the X-ray analysis of **1A** is the result of intermolecular interactions/packing forces in the solid state which are particularly large for Cl substituent. It is reasonable to assume that effective Sb-N distance in solution is significantly longer than that observed in the solid state. The Sb-Cl bond shows a corresponding shrinking. This indicates a possible interaction between Cl atom and its several neighboring H atoms in the crystal.

Table S13: A comparison of the XRD and calculated bond lengths (Å) for **1A** and **1B**.

Molecule	**XRD Data**		**G16 Optimisation (PCM)**		**Solid State Optimisation (VASP)**			
					Crystal		**Single Molecule**	
	Sb-N	**Sb-Cl**	**Sb-N**	**Sb-Cl**	**Sb-N**	**Sb-Cl**	**Sb-N**	**Sb-Cl**
1A	2.480	2.565	2.692	2.504	2.518	2.584	2.717	2.480
1B	2.619	2.469	2.795	2.465	2.629	2.501	2.802	2.453

In the following step, population analyses of these optimized geometries were performed using the NBO6 package[20] in conjunction with Gaussian09 revision d.[21] Donor acceptor interactions between vacant and occupied natural bond orbitals (NBO) was evaluated using second order perturbation theory, implemented along with NBO analysis. The relative energetic importance of the interaction between the unoccupied Lewis vacant orbital on Sb and the lone pairs on N and X have been evaluated for complexes **1(A,B), 3(A,B)** and the cations of **2(A,B)** and **4(A,B)** through this well-established method. To this end, the Lewis structure where a Lewis vacant orbital on Sb and lone pairs on N and X of appropriate symmetry were chosen or was explicitly selected using the $CHOOSE functionality in NBO analysis when that was not the default Lewis structure chosen by the program. The analysis shows that the donor strength of nucleophilic substrate follows the order: Cl^- >> $OPEt_3$ > TfO^- > Ph_2CO and the Sb-N interaction shows a corresponding progressive weakening. The effect of substrates as diverse as the set chosen in this study can be normalized by looking at the effect they have on the trans Sb-N bond. Therefore, the Sb-N bond strength has been chosen as the x-axis in figure 1 of the article.

Table S14: Energy of interaction between Sb and N (*lp*(N)→*p*(Sb)) and that between Sb and X (*lp*(X)→*p*(Sb)) as calcualted by second order perturbation analysis implemented in the NBO package

Compound	*lp*(N)→*p*(Sb) **(kcal/mol)**	*lp*(X)→*p*(Sb) **(kcal/mol)**
1A	29.95	158.19
2A	48.52	66.24
3A	53.21	56.59
4A	66.25	31.72
1B	19.08	167.75
2B	32.68	81.37
3B	37.06	70.87
4B	48.43	51.64

Finally, The extent of activation of carbonyl compounds relative to their free state have been further investigated theoretically by studying the benzaldehyde and phenyl benzoate adducts of $[(NMe_2CH_2C_6H_4)(mesityl)Sb]^+$ and $[(NMe_2C_6H_4)(mesityl)Sb]^+$ and comparing the results with **4A** and **4B**. The C=O bond length and the natural charges on the carbonyl C and O obtained from natural population analysis have been noted. In each case, the extent of activation by cation $[(NMe_2C_6H_4)(mesityl)Sb]^+$ is found to be greater.

Table S15: Natural charges on the carbonyl C and O atoms using DFT at B3LYP-D3/Def2-TZVP level:

Compound	Computed C=O bond length (Å)	NBO Charges on C=O	
		C	O
Ph_2CO	1.223	0.528	-0.526
4A	1.241	0.589	-0.621
4B	1.249	0.600	-0.628
PhCHO	1.214	0.405	-0.509
$[(NMe_2CH_2C_6H_4)(mesityl)(PhCHO)Sb]^+$	1.227	0.453	-0.593
$[(NMe_2C_6H_4)(mesityl)(PhCHO)Sb]^+$	1.233	0.452	-0.607
$PhCH_2OC(O)Ph$	1.213	0.751	-0.588
$[(NMe_2CH_2C_6H_4)(mesityl)(PhCO(O)Ph)Sb]^+$	1.230	0.803	-0.667
$[(NMe_2C_6H_4)(mesityl)(PhCO(O)Ph)Sb]^+$	1.238	0.813	-0.672

DFT optimized structural Coordinates:

The coordinates of the optimized geometries of neutral complexes **1(A,B)**, **3(A,B)** and cationic complexes **2(A, B)**, **4(A, B)** as well as complexes of cation **A** and **B** with PHCHO and PhC(O)OPh are provided below.

1A

Sum of electronic and zero-point energies = -1455.091123 a.u.

C	1.975334	-0.1907	0.310064
C	2.936952	-1.17609	0.520553
H	2.870388	-2.11731	-0.00957
C	3.971638	-0.97732	1.430199
H	4.707875	-1.75597	1.586942
C	4.05755	0.218407	2.132803
H	4.861093	0.380716	2.84015
C	3.11052	1.213139	1.916827
H	3.179402	2.150089	2.457997
C	2.069733	1.017658	1.011741
C	1.014061	2.077519	0.830492
H	1.36726	3.046203	1.210426
H	0.127595	1.807682	1.411497
C	1.65525	2.755891	-1.41373
H	1.895581	3.785277	-1.11618
H	2.557613	2.152635	-1.32898
H	1.333563	2.757355	-2.4547
C	-0.62682	3.004123	-0.67952
H	-0.46625	4.016281	-0.28449
H	-0.92113	3.089344	-1.72448
H	-1.43501	2.531081	-0.12502
C	-1.40794	-0.33488	-0.0069
C	-1.51073	-0.68841	1.351644
C	-2.73488	-0.52083	2.004472
H	-2.80666	-0.79624	3.051342
C	-3.86402	-0.03336	1.357948
C	-3.7578	0.259379	0.002278
C	-2.55775	0.109293	-0.69119
C	-0.37374	-1.27443	2.151931
H	-0.757	-1.75871	3.05025
H	0.181612	-2.01461	1.57874
H	0.337809	-0.5105	2.468742
C	-5.15823	0.173968	2.098209
H	-5.24238	-0.50124	2.950746
H	-5.22538	1.196223	2.482159
N	0.590175	2.194156	-0.5731
Sb	0.425542	-0.41799	-1.20196
Cl	0.506121	-2.91893	-1.10756

H	-6.01938	0.013639	1.44768
H	-4.63583	0.601512	-0.53497
C	-2.56839	0.388929	-2.1779
H	-3.53632	0.782676	-2.48774
H	-1.81075	1.113481	-2.47824
H	-2.38619	-0.52329	-2.75169

1B

Sum of electronic and zero-point
energies = -1415.784429 a.u.

C	-1.90801	0.022461	0.359556
C	-1.94043	-1.33529	0.06841
C	-2.81496	-2.18679	0.737949
H	-2.83101	-3.24694	0.516421
C	-3.66961	-1.65578	1.698866
C	-3.65146	-0.29075	1.981278
H	-4.32306	0.113147	2.728746
C	-2.77114	0.553386	1.310774
H	-2.74461	1.612139	1.537995
C	0.003497	-2.70218	-0.46926
H	0.487708	-2.28591	0.411214
H	0.760936	-2.84398	-1.24086
H	-0.42407	-3.68088	-0.21557
C	-1.68469	-2.27311	-2.16216
H	-2.20629	-3.22181	-1.98074
H	-0.94217	-2.43233	-2.94509
H	-2.40986	-1.53991	-2.51342
C	1.377564	0.327127	-0.00725
C	2.379738	-0.10491	-0.89849
C	3.586595	-0.58752	-0.39486
H	4.350426	-0.92054	-1.08937
C	3.837736	-0.65342	0.971549
C	2.836692	-0.22676	1.836155
H	3.010577	-0.27421	2.905917
C	1.609858	0.260211	1.379189
C	2.199246	-0.09161	-2.40046
H	3.096947	-0.45826	-2.89789
H	2.0013	0.912942	-2.781
H	1.368411	-0.72779	-2.71628
C	5.162601	-1.13986	1.494869
H	5.061207	-1.58447	2.485878
C	0.587917	0.655787	2.414529
H	-0.20598	-0.09013	2.483838
H	0.114958	1.607279	2.180649
H	1.052279	0.738577	3.397222

Cl	-0.66747	3.170835	0.159927
Sb	-0.48509	0.977662	-0.9496
N	-1.01463	-1.76679	-0.9596
H	-4.3537	-2.30731	2.227943
H	5.606315	-1.88175	0.82915
H	5.871738	-0.31127	1.579213

2A

Sum of electronic and zero-point energies = -1648.978383 a.u.

C	-1.92321	-1.34874	0.332712
C	-1.57724	-2.65514	0.668254
H	-0.65348	-3.08147	0.301025
C	-2.4051	-3.40851	1.495245
H	-2.12896	-4.42242	1.756334
C	-3.58826	-2.86035	1.980222
H	-4.23661	-3.44522	2.620014
C	-3.94552	-1.56173	1.633753
H	-4.87058	-1.13681	2.005249
C	-3.11693	-0.80259	0.811678
C	-3.4488	0.627453	0.478624
H	-4.52196	0.822518	0.575504
H	-2.93473	1.295777	1.174221
C	-3.85117	0.353112	-1.90856
H	-4.87143	0.742513	-1.83937
H	-3.87801	-0.72516	-1.76305
H	-3.45442	0.568829	-2.89898
C	-2.98539	2.445391	-1.05963
H	-3.98148	2.855796	-0.86606
H	-2.70589	2.689213	-2.08218
H	-2.27245	2.897118	-0.3734
C	0.067867	1.453007	0.182589
C	0.576326	2.554524	-0.53968
C	1.190582	3.602425	0.145065
H	1.581298	4.44062	-0.42089
C	1.325346	3.598271	1.52948
C	0.839694	2.496055	2.223586
H	0.957096	2.460819	3.301022
C	0.218108	1.421498	1.583538
C	0.51841	2.651839	-2.04906
H	-0.5012	2.614167	-2.4333
H	1.072966	1.846006	-2.53439
H	0.954484	3.591054	-2.38673
C	1.962182	4.754148	2.251676
H	2.72905	5.231989	1.640689

H	2.415927	4.435949	3.190904
H	1.214197	5.515457	2.490623
C	-0.22771	0.271101	2.451837
H	-1.30931	0.262992	2.591019
H	0.228172	0.344584	3.438684
H	0.043713	-0.69131	2.024834
C	3.237306	-2.94535	-0.67983
C	2.752178	-4.05331	0.260413
H	3.046661	-3.86371	1.293316
H	3.184523	-5.00808	-0.03856
H	1.666763	-4.14969	0.228074
C	3.243672	-0.1149	-1.44702
C	2.963955	-0.37563	-2.93059
H	3.441472	-1.2937	-3.27323
H	3.355943	0.446314	-3.52964
H	1.895354	-0.45716	-3.13265
C	2.972622	-0.84344	1.362155
C	4.470815	-0.87042	1.680013
H	4.891214	-1.87087	1.57421
H	4.629206	-0.55355	2.710953
H	5.035331	-0.19409	1.037544
N	-2.98852	0.981055	-0.88445
O	0.991715	-1.4149	-0.46575
Sb	-0.77993	-0.14745	-1.04302
P	2.511566	-1.32828	-0.32005
H	2.850768	0.856109	-1.13412
H	4.318243	-0.0971	-1.25353
H	2.973608	-3.17474	-1.71445
H	4.323997	-2.83807	-0.64276
H	2.560701	0.157373	1.506606
H	2.420122	-1.50843	2.029393

2B

Sum of electronic and zero-point energies = -1609.665838 a.u.

C	1.605227	1.594771	-0.56963
C	3.977257	1.89061	-0.95264
H	5.006556	1.656531	-0.71239
C	2.924626	1.306925	-0.25753
C	3.67674	-0.91351	0.430635
H	3.148046	-1.31639	-0.42974
H	3.602105	-1.62601	1.2515
H	4.732664	-0.77859	0.175099
C	3.737115	0.933181	2.01642
H	4.792034	1.141564	1.811336

H	3.674121	0.225437	2.842298
H	3.245432	1.860646	2.306084
C	0.400893	-1.49003	0.040236
C	0.274514	-1.78633	-1.33032
C	0.187332	-3.12271	-1.72447
H	0.089225	-3.34793	-2.78082
C	0.227657	-4.17255	-0.81281
C	0.363433	-3.85907	0.536156
H	0.402116	-4.66152	1.264454
C	0.44615	-2.54023	0.978471
C	0.252208	-0.73532	-2.41145
H	-0.42726	0.080595	-2.17555
H	-0.05367	-1.17201	-3.36179
H	1.242086	-0.29704	-2.55043
C	0.099101	-5.60102	-1.26781
H	-0.94885	-5.91423	-1.25902
H	0.646802	-6.27846	-0.61148
H	0.469984	-5.72988	-2.28528
C	0.568723	-2.29733	2.465909
H	0.628467	-3.2414	3.006012
H	-0.29341	-1.75079	2.857484
H	1.462435	-1.72302	2.720085
N	3.05881	0.360511	0.839469
O	-1.339	1.074892	-0.20188
Sb	0.462593	0.513706	0.881575
P	-2.86464	1.057857	-0.02885
C	-3.61403	0.722545	-1.63856
C	-5.14449	0.646623	-1.64717
C	-3.40939	-0.20623	1.149252
C	-3.44588	2.666786	0.555534
C	-2.84174	3.098399	1.895961
H	-4.53581	2.627159	0.610981
H	-3.18984	3.378977	-0.23324
H	-3.12132	2.419925	2.70268
H	-3.20454	4.092173	2.157832
H	-1.75347	3.142493	1.845338
H	-3.25297	1.507594	-2.30724
H	-3.1699	-0.21381	-1.98434
H	-5.51592	-0.13008	-0.97805
H	-5.59753	1.593525	-1.35324
H	-5.49173	0.410992	-2.65291
H	-2.83211	-0.04049	2.062508
H	-4.45138	0.012064	1.395337
C	-3.25228	-1.65075	0.659872
H	-3.90184	-1.85774	-0.19063
H	-3.52609	-2.3373	1.460773
H	-2.22691	-1.87091	0.366702

C	3.673855	2.787495	-1.97327
H	4.476044	3.253715	-2.53071
C	2.347706	3.092282	-2.28334
H	2.13187	3.794588	-3.07872
C	1.303384	2.498133	-1.57993
H	0.273626	2.723921	-1.82684

3A

Sum of electronic and zero-point energies = -1956.602365 a.u.

C	2.006898	-1.23481	0.415217
C	3.121584	-0.53496	0.886596
C	4.006846	-1.14876	1.76815
H	4.870218	-0.60405	2.131805
C	3.78337	-2.45717	2.183553
H	4.473507	-2.92999	2.870596
C	2.680765	-3.15869	1.706824
H	2.509058	-4.18016	2.022315
C	1.797416	-2.55093	0.819101
H	0.937288	-3.10004	0.460623
C	-0.22061	1.337054	0.076527
C	-1.01761	2.468082	2.055719
H	-1.1392	2.487098	3.133221
C	-0.78642	2.334637	-2.22044
H	0.215364	2.287704	-2.65008
H	-1.34376	1.469054	-2.58602
C	0.048945	0.255024	2.396145
H	-0.42825	0.369684	3.369026
H	-0.22505	-0.72043	1.998562
H	1.127219	0.24611	2.559499
C	3.302135	0.899779	0.469813
H	4.342179	1.223585	0.576961
H	2.690821	1.547435	1.103263
C	3.808402	0.504044	-1.88343
H	3.933193	-0.55477	-1.66584
H	3.430209	0.617842	-2.89753
C	2.703775	2.549831	-1.21099
H	2.419813	2.691112	-2.25135
H	1.937158	2.974874	-0.5676
H	3.651153	3.067956	-1.03557
C	-3.3454	-1.33158	0.516288
C	-0.38016	1.369665	1.474713
F	-3.13007	-0.06445	0.883398
F	-4.63607	-1.46056	0.179947
F	-3.10274	-2.12317	1.570142

N	2.850582	1.107805	-0.92889
O	-2.53262	-0.80546	-1.93482
O	-0.90381	-1.69355	-0.3325
O	-2.6378	-3.16919	-1.21754
S	-2.26354	-1.80698	-0.92744
Sb	0.800903	-0.21822	-1.05641
H	4.781655	0.997221	-1.80585
C	-0.78103	2.367166	-0.70834
C	-1.41131	3.440508	-0.08199
H	-1.8402	4.226555	-0.69359
C	-1.52229	3.521435	1.302627
H	-1.26304	3.229255	-2.61982
C	-2.17061	4.709897	1.959463
H	-2.98655	5.103931	1.351752
H	-2.565	4.455926	2.943926
H	-1.4457	5.518015	2.093992

3B

Sum of electronic and zero-point energies = -1917.288750 a.u.

C	0.406315	1.983658	0.414246
C	1.583377	2.521703	-0.08049
C	2.120949	3.696576	0.430235
H	3.044698	4.10813	0.044026
C	1.435377	4.334818	1.459944
H	1.831902	5.250825	1.878609
C	0.241772	3.807703	1.955095
H	-0.27925	4.320668	2.753608
C	-0.28276	2.628592	1.432916
H	-1.2046	2.222006	1.82872
C	2.211333	2.459608	-2.44365
H	1.228673	2.866267	-2.67651
C	3.465226	1.145893	-0.81906
H	4.231626	1.922749	-0.73822
H	3.391345	0.613719	0.125836
C	1.321128	-1.23388	0.059949
C	2.799418	-3.10233	-0.3689
H	3.283278	-3.76738	-1.07564
C	1.950072	-2.10761	-0.85006
C	0.948464	-0.48227	2.490366
H	1.10426	-0.90047	3.484457
H	-0.12065	-0.34473	2.343496
H	1.407929	0.507387	2.471431
C	1.752896	-2.00981	-2.34698
H	2.092492	-1.05132	-2.74761

H	0.704331	-2.12857	-2.62962
C	-3.92207	-1.26522	-0.34216
N	2.154299	1.728825	-1.16235
O	-1.62227	-0.37398	0.502006
O	-3.20058	1.271033	-0.3988
O	-3.59117	0.219915	1.809162
F	-5.22053	-0.97258	-0.46845
F	-3.80423	-2.38747	0.374397
F	-3.41383	-1.48464	-1.56182
S	-3.02834	0.145223	0.486924
Sb	0.07007	0.286982	-0.85491
H	3.758822	0.441319	-1.59609
C	1.553998	-1.38026	1.441206
C	2.407997	-2.3964	1.874061
H	2.584568	-2.50809	2.938278
C	3.040195	-3.26593	0.991592
H	2.318049	-2.7874	-2.85945
C	3.929432	-4.37066	1.494829
H	3.346364	-5.27677	1.68296
H	4.700722	-4.62445	0.766493
H	4.415253	-4.09541	2.431805
H	2.933305	3.280595	-2.40171
H	2.507453	1.770695	-3.23373

4A

Sum of electronic and zero-point energies = -1571.358986 a.u.

Sb	1.377012	-0.30648	-1.06603
O	-0.67687	1.166309	-1.16411
N	3.463426	-1.08195	-0.20153
C	-0.8442	-3.33156	1.201502
H	-1.1528	-4.34425	0.96817
C	0.307324	-1.302	0.550519
C	2.246141	1.453109	-0.17766
C	-0.09416	-0.70651	1.763766
C	0.227944	0.713104	2.15927
H	1.273283	0.828438	2.448564
H	-0.38134	1.014838	3.010138
H	0.044248	1.415849	1.351536
C	-2.51932	-0.30796	-1.0239
C	-2.26175	-1.05008	-2.18052
H	-1.62688	-0.63128	-2.95037
C	-3.34093	-0.84165	-0.02691

H	-3.5218	-0.28125	0.879583
C	-0.85381	-1.45489	2.663991
H	-1.16529	-0.98896	3.592115
C	-0.08959	-2.62768	0.265436
C	-1.23908	-2.76521	2.406679
C	0.253564	-3.35015	-1.01802
H	-0.39896	-4.21191	-1.15019
H	1.27994	-3.7211	-1.01549
H	0.131891	-2.72262	-1.90054
C	3.700103	-0.20519	0.980302
H	4.741485	-0.2964	1.300628
H	3.072894	-0.58576	1.78995
C	4.49033	-0.83792	-1.24636
H	4.269949	-1.44818	-2.11965
H	5.479752	-1.10054	-0.86457
H	4.488879	0.212157	-1.52993
C	3.334783	1.218984	0.666622
C	-2.10953	-3.52629	3.367804
H	-2.03848	-3.12388	4.378518
H	-1.84223	-4.58364	3.395596
H	-3.15759	-3.46468	3.059934
C	-2.8351	-2.30149	-2.34555
H	-2.64819	-2.86518	-3.24998
C	3.498328	-2.50348	0.208395
H	2.685909	-2.70637	0.901966
H	4.451544	-2.72653	0.69395
H	3.398736	-3.13707	-0.66912
C	-3.88035	-2.11038	-0.17992
H	-4.48666	-2.53441	0.609409
C	-3.63721	-2.8365	-1.34136
H	-4.06859	-3.82171	-1.46249
C	-1.86969	1.012329	-0.8602
C	-2.63585	2.162934	-0.34116
C	-1.94242	3.253987	0.202336
C	-4.03444	2.208264	-0.41388
C	-2.63349	4.352444	0.683738
H	-0.86379	3.225232	0.250409
C	-4.72253	3.318571	0.055033
H	-4.58076	1.387935	-0.85668
C	-4.02536	4.386779	0.610116
H	-2.09219	5.183811	1.115734
H	-5.80166	3.351416	-0.01488
H	-4.56443	5.248513	0.982298
C	1.880224	2.759646	-0.48918
H	1.052994	2.94955	-1.15899
C	2.56995	3.829218	0.074581
H	2.277372	4.843919	-0.16396

C	3.63806	3.59471	0.934466
H	4.177875	4.42587	1.369458
C	4.027948	2.290572	1.221013
H	4.872717	2.107474	1.874189

4B
Sum of electronic and zero-point energies = -1532.044861 a.u.

C	-1.86146	1.024824	-0.77143
C	-2.7392	2.078264	-0.24936
C	-2.17106	3.219197	0.338789
C	-4.94123	2.999897	0.132513
H	-6.01648	2.923833	0.042499
C	-4.13487	1.980644	-0.35126
H	-4.58471	1.121209	-0.82686
C	-2.38821	-0.32936	-1.04287
C	-2.09196	-0.94888	-2.26141
H	-1.53777	-0.4093	-3.01829
C	-2.53839	-2.23866	-2.50801
H	-2.32671	-2.70837	-3.45935
C	-3.24675	-2.92907	-1.52867
H	-3.57499	-3.94334	-1.71466
C	-3.53161	-2.31991	-0.31067
H	-4.06687	-2.86246	0.456914
C	-3.12481	-1.01557	-0.07309
H	-3.33645	-0.54417	0.876386
C	0.400693	-1.26142	0.544191
C	0.190286	-2.62794	0.269091
C	-0.44942	-3.42338	1.216921
C	-0.00815	-0.72786	1.781082
C	0.640988	-3.28544	-1.01501
H	0.234017	-2.78802	-1.89694
H	1.729695	-3.29233	-1.10933
H	0.309098	-4.32217	-1.05077
C	3.689393	-1.42483	0.901113
H	3.541437	-2.45347	0.576076
C	4.525265	-0.82869	-1.31077
H	4.375046	-1.85197	-1.65163
H	4.390264	-0.14851	-2.1496
H	5.545071	-0.72642	-0.93071
N	3.533146	-0.52173	-0.25794
O	-0.65791	1.286853	-0.97894
Sb	1.231316	-0.1178	-1.10478
C	-4.36692	4.118551	0.728171
H	-4.99871	4.909793	1.110676
C	-2.98023	4.227008	0.830959
H	-2.53705	5.097721	1.295456
C	-0.89477	-2.90798	2.428758
C	-0.65201	-1.56428	2.693491

H	-0.97537	-1.14858	3.641265
H	-0.61761	-4.47084	0.993885
C	0.233587	0.701278	2.197521
H	1.293977	0.883364	2.381601
H	-0.08018	1.415076	1.440501
H	-0.3069	0.928502	3.115407
C	-1.64962	-3.76899	3.403639
H	-1.29517	-4.80037	3.382595
H	-1.56101	-3.39254	4.423102
H	-2.7138	-3.78532	3.150051
C	2.294974	1.485908	-0.16009
C	3.513711	0.889029	0.11814
C	4.566051	1.595038	0.684851
H	5.511916	1.118601	0.907938
C	4.366625	2.945036	0.960343
H	5.166697	3.522693	1.404568
C	3.150306	3.562226	0.663843
H	3.019904	4.615585	0.877163
C	2.105918	2.837072	0.096595
H	1.165808	3.320361	-0.13352
H	4.689076	-1.3277	1.332798
H	2.945785	-1.18301	1.655718
H	-1.09669	3.296967	0.413342

$[(NMe_2CH_2C_6H_4)(mesityl)(PhCHO)Sb]^+$
Sum of electronic and zero-point energies = -1340.281551 a.u.

Sb	-0.9376	0.213319	-1.02618
O	0.330033	-2.11658	-0.99184
N	-2.37869	1.918156	-0.32282
C	2.622541	1.693038	1.049222
H	3.40202	2.388705	0.758888
C	0.506529	0.616843	0.553685
C	-2.52255	-0.88044	-0.07471
C	0.616528	-0.10823	1.764105
C	-0.40084	-1.11308	2.24491
H	-1.37102	-0.65384	2.433051
H	-0.06718	-1.56896	3.175962
H	-0.56372	-1.9112	1.52189
C	2.679105	-1.70934	-0.82582
C	2.788032	-0.81974	-1.90229
H	1.943358	-0.6782	-2.56318
C	3.774919	-1.92339	0.0174
H	3.685959	-2.61583	0.845469
C	1.735425	0.090992	2.567727
H	1.819971	-0.47356	3.489362
C	1.520558	1.532571	0.20646

C	2.758445	0.973184	2.224754
C	1.508834	2.399909	-1.03124
H	2.499184	2.423587	-1.48628
H	1.244616	3.427614	-0.77282
H	0.811451	2.071642	-1.80093
C	-3.06019	1.3562	0.881628
H	-3.9431	1.958023	1.110221
H	-2.36543	1.459316	1.718418
C	-3.36226	2.144729	-1.41537
H	-2.84319	2.495239	-2.30462
H	-4.09147	2.895287	-1.10424
H	-3.88279	1.216683	-1.6416
C	-3.40227	-0.09352	0.673909
C	3.989896	1.096793	3.077388
H	3.762945	0.943187	4.133056
H	4.461295	2.072981	2.960958
H	4.72486	0.340216	2.786628
C	3.976491	-0.14722	-2.12214
H	4.068035	0.533103	-2.95833
C	-1.70138	3.192415	0.016472
H	-0.93542	3.010659	0.766234
H	-2.4313	3.903866	0.4084
H	-1.24433	3.610461	-0.877
C	4.95652	-1.2279	-0.1908
H	5.797987	-1.37586	0.472585
C	5.056125	-0.34272	-1.26009
H	5.980645	0.194588	-1.42826
C	1.431948	-2.40572	-0.53689
C	-2.78097	-2.23557	-0.25706
H	-2.1024	-2.84853	-0.83521
C	-3.90325	-2.81097	0.331569
H	-4.1007	-3.86673	0.196328
C	-4.77347	-2.0304	1.086376
H	-5.64918	-2.47749	1.538768
C	-4.52833	-0.67114	1.251997
H	-5.21185	-0.06239	1.831533
H	1.510622	-3.25015	0.167181

$[(NMe_2C_6H_4)(mesityl)(PhCHO)Sb]^+$
Sum of electronic and zero-point energies = -1300.966403 a.u.

C	1.204953	-2.64646	-0.76568
C	2.512856	-2.03965	-0.62243
C	2.848378	-0.83005	-1.24664
H	2.147163	-0.36231	-1.92066
C	4.082725	-0.25424	-1.01395
H	4.34207	0.680467	-1.49151

C	4.988676	-0.87583	-0.15412
H	5.949616	-0.41492	0.034884
C	4.673783	-2.08879	0.453082
H	5.386304	-2.56948	1.109555
C	3.444532	-2.67958	0.207759
H	3.188553	-3.62335	0.673197
C	0.471632	0.889365	0.116113
C	1.141615	2.002593	-0.43348
C	2.217105	2.560184	0.253294
C	0.883027	0.37483	1.362805
C	0.754223	2.62451	-1.75656
H	0.900037	1.936299	-2.59337
H	-0.28903	2.946793	-1.7761
H	1.362904	3.505172	-1.95643
C	-2.42768	2.343036	0.836404
H	-1.99446	3.192441	0.310935
C	-3.82315	1.845348	-1.10365
H	-3.3905	2.68935	-1.63836
H	-4.09774	1.069479	-1.81554
H	-4.72046	2.178146	-0.57685
N	-2.82289	1.312959	-0.14967
O	0.17937	-2.09728	-1.17553
Sb	-1.03167	0.015738	-1.18195
C	2.663446	2.0412	1.463837
C	1.973407	0.961109	2.00376
H	2.296079	0.555176	2.955719
H	2.728579	3.413712	-0.17686
C	0.199288	-0.76934	2.066415
H	-0.80822	-0.49497	2.382927
H	0.097334	-1.65094	1.437131
H	0.760207	-1.05904	2.953672
C	3.875426	2.604807	2.151573
H	4.035078	3.650849	1.888818
H	3.791361	2.527336	3.236194
H	4.769618	2.049691	1.85316
C	-2.37346	-0.98037	0.15696
C	-3.23747	0.054758	0.471468
C	-4.35264	-0.13301	1.275302
H	-5.02023	0.682573	1.52082
C	-4.58666	-1.41711	1.759859
H	-5.44564	-1.5994	2.392279
C	-3.73157	-2.4721	1.435446
H	-3.93915	-3.46321	1.818291
C	-2.61824	-2.26318	0.625875
H	-1.95562	-3.08206	0.377574
H	-3.29736	2.67993	1.405385
H	-1.68748	1.932603	1.517668

H	1.126361	-3.69774	-0.45178

$[(NMe_2CH_2C_6H_4)(mesityl)(PhC(O)OPh)Sb]^+$
Sum of electronic and zero-point energies = -1685.923516 a.u.

Sb	-1.92962	-0.32352	-0.92857
O	0.558817	-0.16148	-1.69322
N	-3.79079	-1.05941	0.312496
C	-1.19807	3.245427	1.507539
H	-1.54467	4.269298	1.428145
C	-1.23889	0.963173	0.691093
C	-1.37045	-2.31817	-0.352
C	-0.28368	0.61845	1.672253
C	0.29204	-0.76392	1.848291
H	-0.44032	-1.46392	2.251244
H	1.132575	-0.73641	2.540035
H	0.64276	-1.18547	0.910469
C	1.260107	2.101727	-1.32828
C	0.312264	2.685219	-2.17131
H	-0.25822	2.06066	-2.84577
C	2.012076	2.899123	-0.46268
H	2.737263	2.440874	0.194214
C	0.18227	1.606052	2.539338
H	0.923836	1.335682	3.282458
C	-1.69542	2.298353	0.614277
C	-0.25262	2.924874	2.471883
C	-2.71897	2.785627	-0.38601
H	-2.64128	3.864811	-0.50919
H	-3.73613	2.570655	-0.05233
H	-2.59712	2.343808	-1.37466
C	-3.21884	-2.02871	1.292619
H	-4.02576	-2.62418	1.726839
H	-2.77455	-1.44097	2.098938
C	-4.7078	-1.75414	-0.62971
H	-5.07326	-1.04491	-1.36909
H	-5.55496	-2.16964	-0.07986
H	-4.18141	-2.5626	-1.13232
C	-2.17278	-2.88939	0.63959
C	0.326307	3.981716	3.369993
H	0.678113	3.55941	4.311695
H	-0.40254	4.762779	3.589376
H	1.181568	4.46043	2.883732
C	0.119788	4.05814	-2.1509
H	-0.60903	4.510111	-2.81038
C	-4.52294	0.015527	1.020972
H	-3.83427	0.574689	1.649894
H	-5.31006	-0.41912	1.641131

H	-4.97804	0.681861	0.292652
C	1.799043	4.269215	-0.43031
H	2.364892	4.885061	0.256052
C	0.857019	4.849508	-1.27484
H	0.696132	5.91958	-1.24906
C	1.434825	0.634767	-1.35952
C	-0.38362	-3.07905	-0.97203
H	0.227204	-2.64816	-1.75342
C	-0.16911	-4.39523	-0.57346
H	0.604831	-4.98294	-1.05046
C	-0.95353	-4.95676	0.429134
H	-0.79032	-5.98185	0.735561
C	-1.96216	-4.20872	1.027752
H	-2.5843	-4.65222	1.795758
O	2.644597	0.242294	-0.99535
C	2.93821	-1.19299	-1.00796
H	2.127294	-1.71874	-0.5105
H	2.971678	-1.50912	-2.05032
C	4.245163	-1.3918	-0.30845
C	4.273937	-1.66067	1.059858
C	5.446705	-1.2867	-1.00872
C	5.486632	-1.8191	1.720768
H	3.343843	-1.7493	1.607883
C	6.660558	-1.44395	-0.35002
H	5.430441	-1.08213	-2.0726
C	6.681657	-1.70942	1.016208
H	5.499313	-2.03059	2.782318
H	7.588367	-1.36286	-0.90166
H	7.626666	-1.83488	1.529204

[(NMe$_2$C$_6$H$_4$)(mesityl)(PhC(O)OPh)Sb]$^+$
Sum of electronic and zero-point energies = -1646.606768 a.u.

C	1.455963	0.428606	-1.30693
C	1.294741	1.894404	-1.33301
C	0.42034	2.468635	-2.25789
H	-0.09839	1.840602	-2.97005
C	0.241387	3.843689	-2.27514
H	-0.42618	4.290785	-2.99949
C	0.913526	4.642994	-1.35518
H	0.75908	5.714172	-1.35806
C	1.783429	4.07038	-0.43157
H	2.297861	4.693142	0.288009
C	1.989819	2.699253	-0.42774
H	2.659543	2.245839	0.288952
C	-1.25707	0.995025	0.652439
C	-1.77752	2.30518	0.600645

C	-1.36309	3.239902	1.545633
C	-0.36069	0.641606	1.678985
C	-2.7792	2.750901	-0.44046
H	-2.3742	2.686788	-1.45248
H	-3.69718	2.158788	-0.41199
H	-3.06291	3.789481	-0.27566
C	-3.95213	-0.69368	1.562696
H	-4.41705	0.284223	1.449628
C	-4.90586	-1.41428	-0.56478
H	-5.37829	-0.44021	-0.68211
H	-4.6656	-1.81926	-1.54588
H	-5.60059	-2.09028	-0.06099
N	-3.66347	-1.25118	0.223254
O	0.551806	-0.38187	-1.54868
Sb	-1.8131	-0.26008	-1.02891
C	-0.44622	2.922116	2.541825
C	0.027598	1.616109	2.598588
H	0.727835	1.343928	3.380269
H	-1.75783	4.248071	1.492989
C	0.195581	-0.74748	1.860365
H	-0.57797	-1.44748	2.18156
H	0.612225	-1.14931	0.940748
H	0.980627	-0.75049	2.615138
C	0.043131	3.97069	3.501503
H	-0.7456	4.681407	3.751908
H	0.416638	3.526996	4.424667
H	0.862948	4.53966	3.052946
C	-1.60831	-2.26981	-0.3166
C	-2.84682	-2.46346	0.271928
C	-3.22087	-3.68114	0.821743
H	-4.18761	-3.82079	1.287508
C	-2.30364	-4.72658	0.75459
H	-2.56125	-5.6894	1.176072
C	-1.06069	-4.55005	0.143991
H	-0.36824	-5.38071	0.094279
C	-0.7046	-3.31971	-0.40201
H	0.258335	-3.18895	-0.87776
H	-4.62938	-1.35176	2.112733
H	-3.02595	-0.582	2.119525
O	2.671061	0.036992	-0.99564
C	2.951116	-1.40374	-0.90924
H	2.155595	-1.87168	-0.33505
H	2.934861	-1.79727	-1.9245
C	4.283359	-1.56151	-0.25029
C	4.371083	-1.62667	1.140712
C	5.449258	-1.61968	-1.01267
C	5.60854	-1.74518	1.761737

H	3.467902	-1.58634	1.737799
C	6.688108	-1.73933	-0.39317
H	5.386455	-1.57278	-2.09324
C	6.768792	-1.80098	0.994657
H	5.668098	-1.79774	2.841248
H	7.588428	-1.78679	-0.99213
H	7.73304	-1.89651	1.477342

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