Influence of the catalyst structure in the cycloaddition of oxiranes and isocyanates promoted by tetraarylstibonium cations

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1 Experimental Section

1.1 Synthesis of 1-Naphthyltriphenylstibonium triflate (2[OTf])

2[OTf] has been previously described.[1] As part of the current study, it was prepared as follows. A 100 mL Schlenk flask was charged with 1-bromonaphthalene (600 mg, 2.4 mmol, 1 eq) and 15 mL THF. The solution was cooled to -78 ºC and treated with ^{n}BuLi (2.65 M in hexanes, 1.0 mL, 2.6 mmol, 1.1 eq) which was added drop-wise. The resulting bright yellow solution was stirred at -78 ºC for 1 h. Next, the solution was transferred drop wise to a Ph_3SbBr_2 (1.20g, 2.4 mmol, 1 eq) solution in mixed solvents (6 mL THF, 30 mL Et_2O) at -78 ºC. The reaction mixture, which turned dark yellow, was allowed to warm to room temperature overnight, resulting in a pale-yellow solution. The solvent was removed *in vacuo* to afford an oily solid, which was dissolved in CH_2Cl_2 and passed through a short plug of Celite in air. After removing CH_2Cl_2 *in vacuo*, the solid was extracted with methanol and passed through a second plug of Celite in air. Removal of the solvent *in vacuo* afforded a pale-yellow solid which was used without further purification. This solid was dissolved in CH_2Cl_2 (15 mL) and treated with solid AgOTf (380 mg, 1.5 mmol, 0.6 eq) under N_2 atmosphere. The resulting yellow suspension was allowed to stir at room temperature in the dark for 2 h. The suspension was then filtered over Celite, and the filtrate was reduced and purified by flash chromatography over silica gel (100% ethyl acetate). The second major fraction was collected and washed with hexanes to yield **2**[OTf] as air- and moisture- stable white powder (551 mg, 37% yield based on Ph_3SbBr_2).

2[OTf]: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.33 – 8.24 (m, 1H), 8.14 – 8.05 (m, 1H), 7.86 – 7.55 (m, 19H), 7.55 – 7.45 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 137.75 (s, naphthyl), 135.72 (s, *o*-Ph), 134.77 (s, naphthyl), 133.92 (s, *p*-Ph), 131.47 (s, *m*-Ph), 130.28 (s, naphthyl), 129.00 (s, naphthyl), 127.80 (s, naphthyl), 126.94 (s, naphthyl), 126.81 (s, naphthyl), 123.17 (s, quaternary, Ph), 120.72 (q, $J_{C\text{-}F}$ = 324.8, OTf). ^{19}F NMR (470 MHz, $CDCl_3$) δ = -78.74 (s, OTf). Spectral data are in accord with the previous report.[1] Single crystals suitable for X-ray diffraction were obtained by slow evaporation of hexanes into a $CDCl_3$ solution in air.

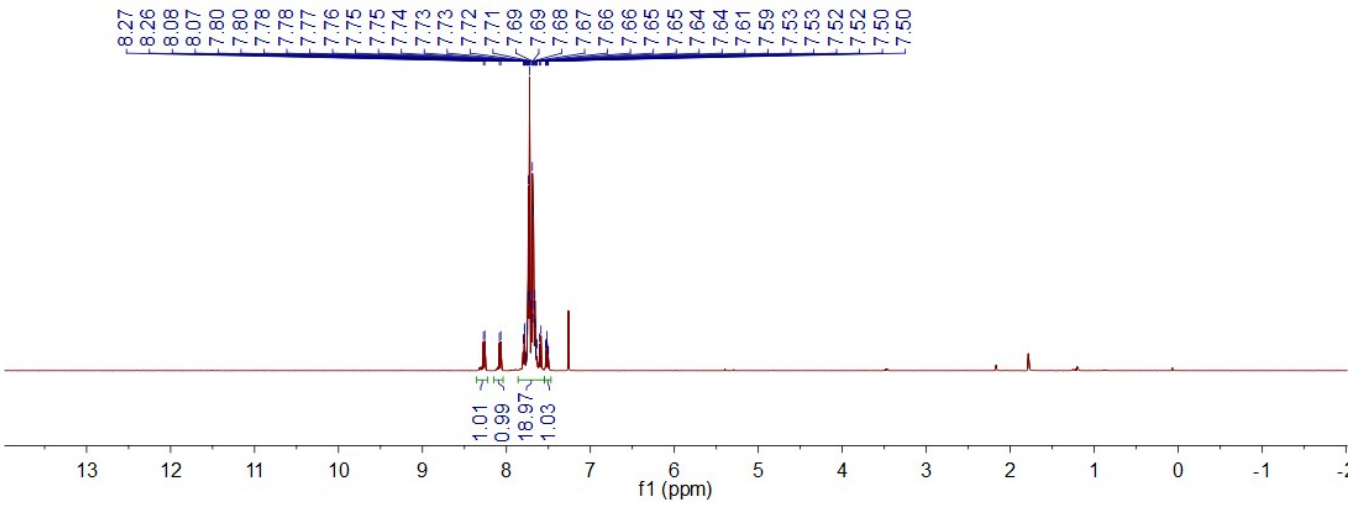


Figure S1. ^{1}H NMR of **2**[OTf] in $CDCl_3$.

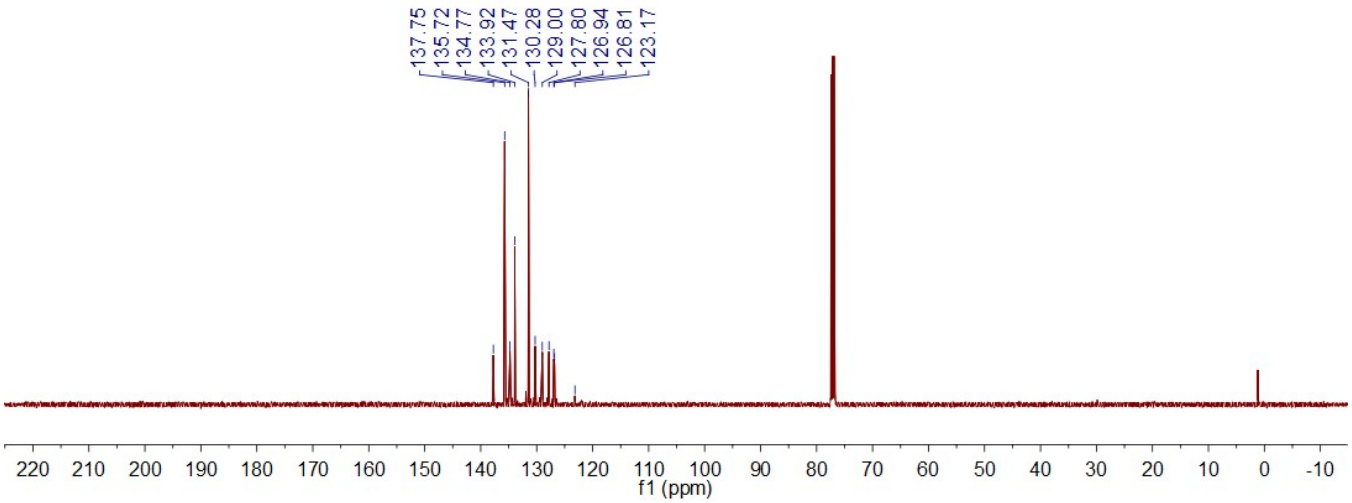


Figure S2. ^{13}C NMR of **2**[OTf] in $CDCl_3$.

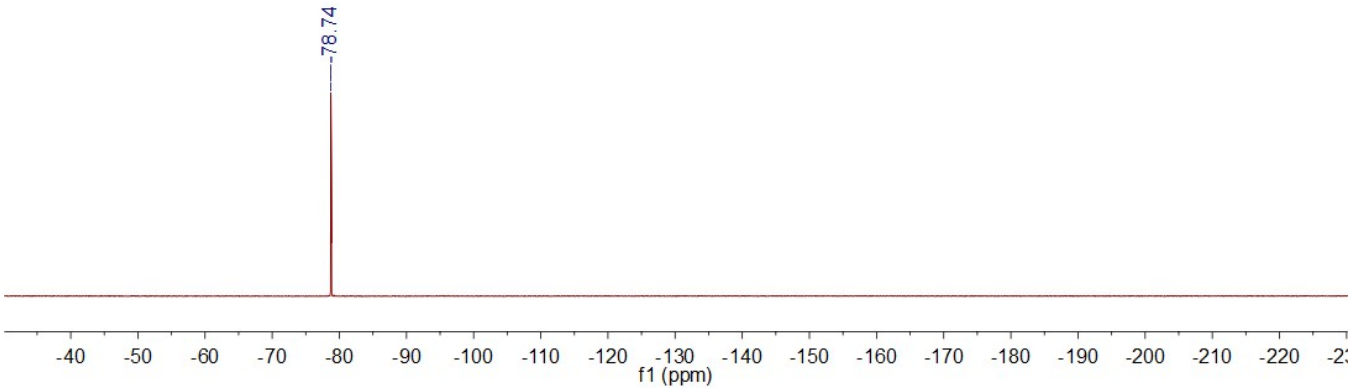


Figure S3. ^{19}F NMR of **2**[OTf] in $CDCl_3$.

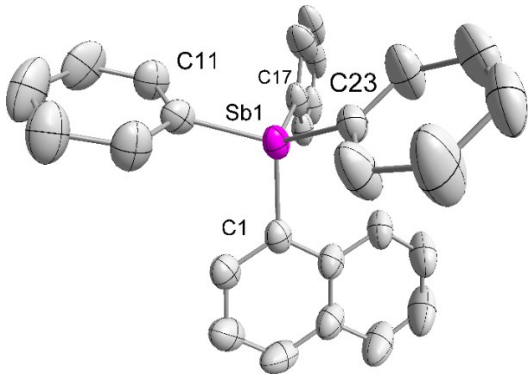


Figure S4. Crystal structure of $\mathbf{2}^+$ in **2**[OTf].
Ellipsoids are drawn at a 50% probability level. The triflate counteranion and the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (º): Sb1-C1 = 2.086(4), Sb1-C11 = 2.085(4), Sb1-C17 = 2.098(4), Sb1-C23 = 2.091(4), ∠C1-Sb1-C11 = 107.0(2), ∠C1-Sb1-C17 = 112.1(2), ∠C1-Sb1-C23 = 104.2(2), ∠C11-Sb1-C17 = 108.1(2), ∠C11-Sb1-C23 = 114.1(2), ∠C17-Sb1-C23 = 111.3(2).

1.2 NMR spectra of 4-6[OTf], 7[$SbCl_6$]

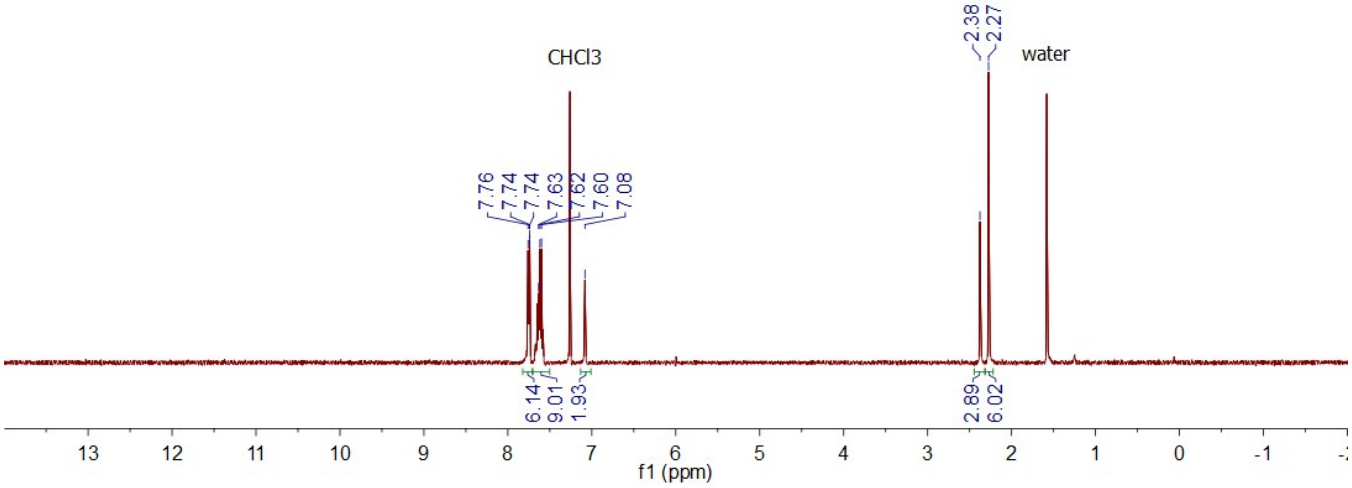


Figure S5. ^{1}H NMR of **4**[OTf] in $CDCl_3$.

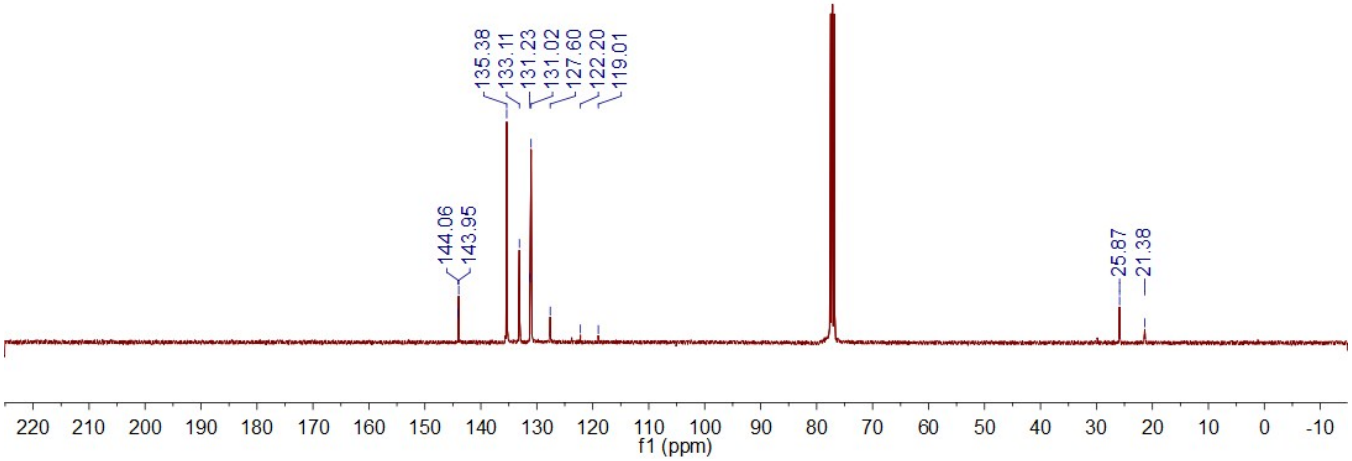


Figure S6. ^{13}C NMR of **4**[OTf] in $CDCl_3$.

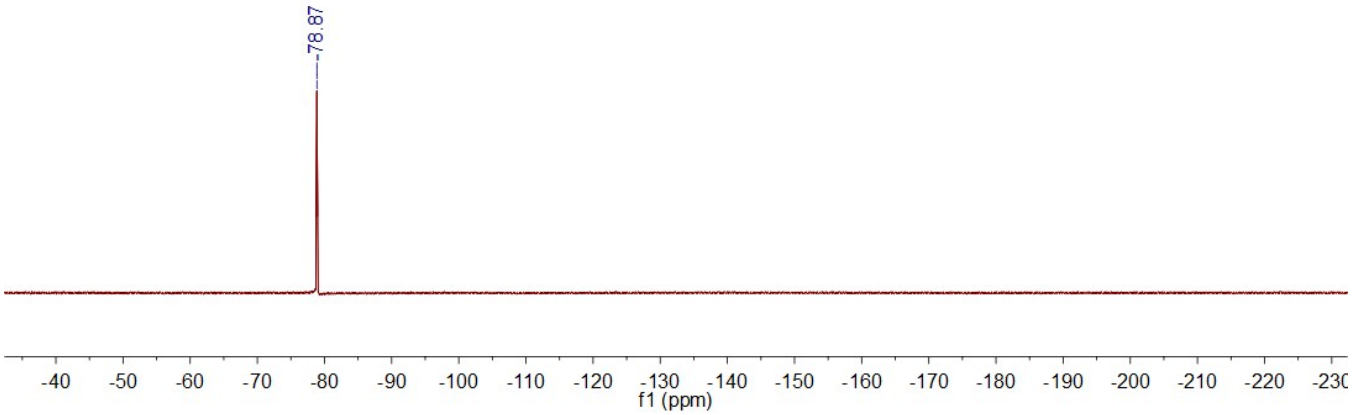


Figure S7. ^{19}F NMR of **4**[OTf] in $CDCl_3$.

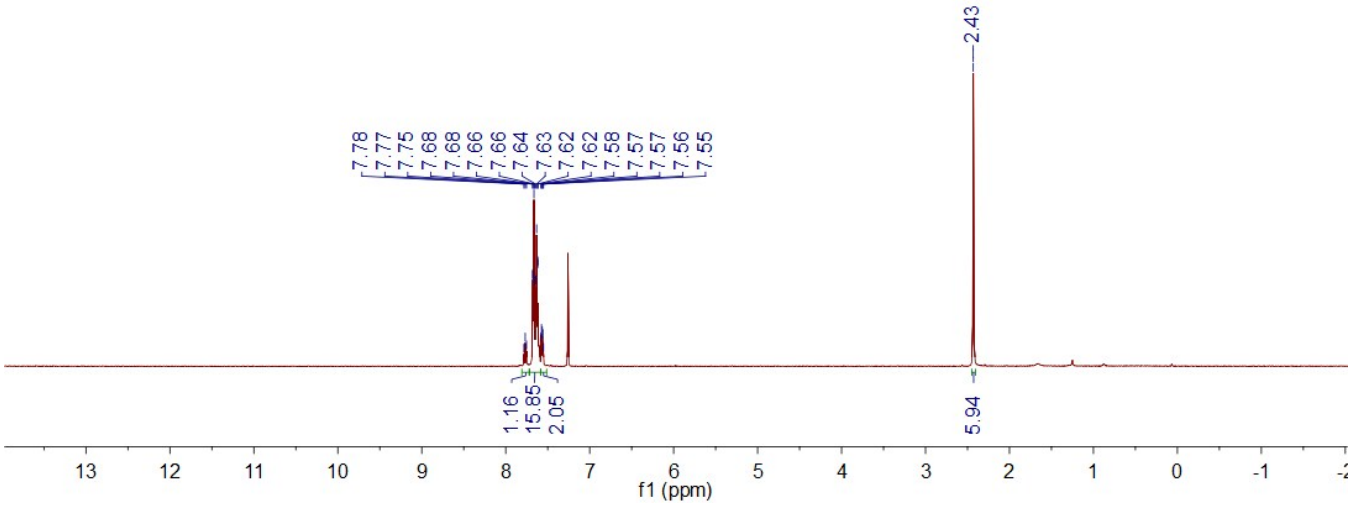


Figure S8. ^{1}H NMR of **5**[OTf] in $CDCl_3$.

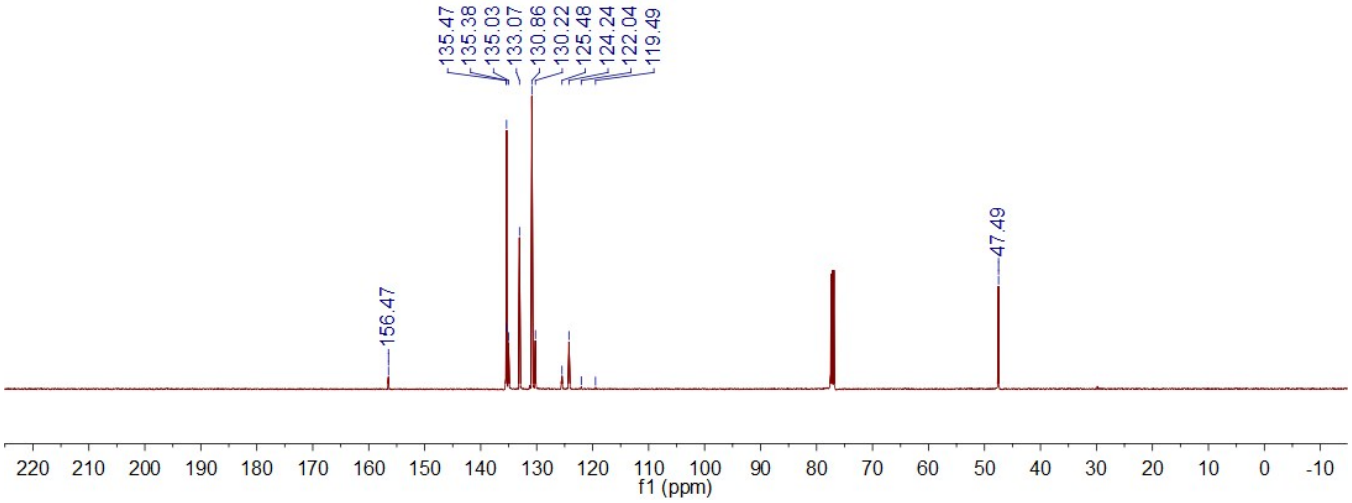


Figure S9. ^{13}C NMR of **5**[OTf] in $CDCl_3$.

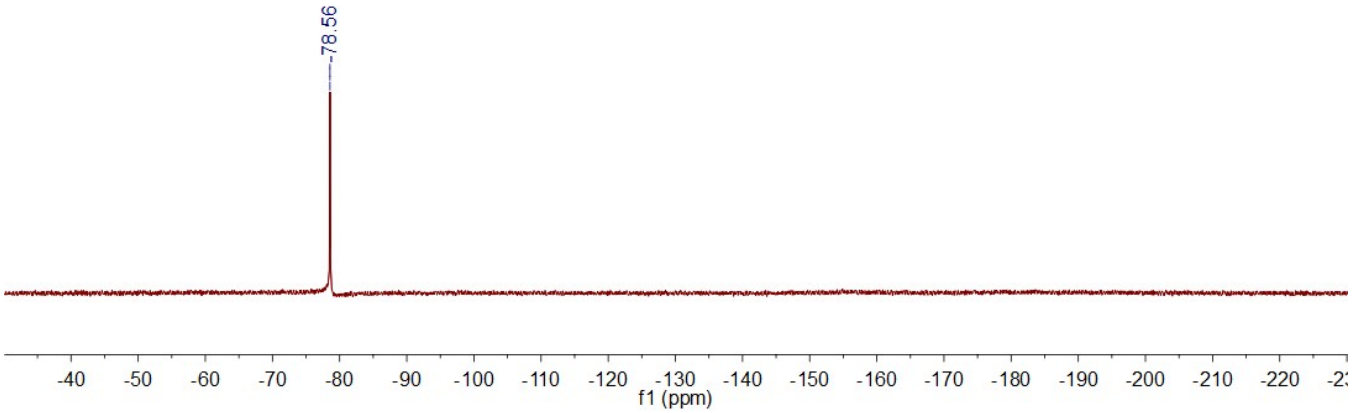


Figure S10. ^{19}F NMR of **5**[OTf] in $CDCl_3$.

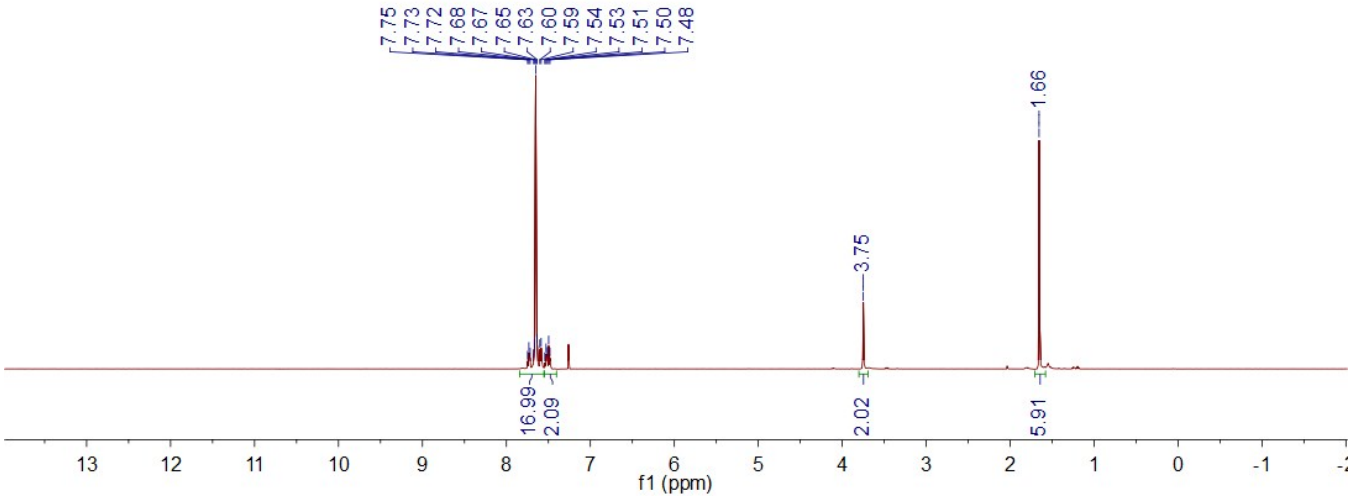


Figure S11. ^{1}H NMR of **6**[OTf] in $CDCl_3$.

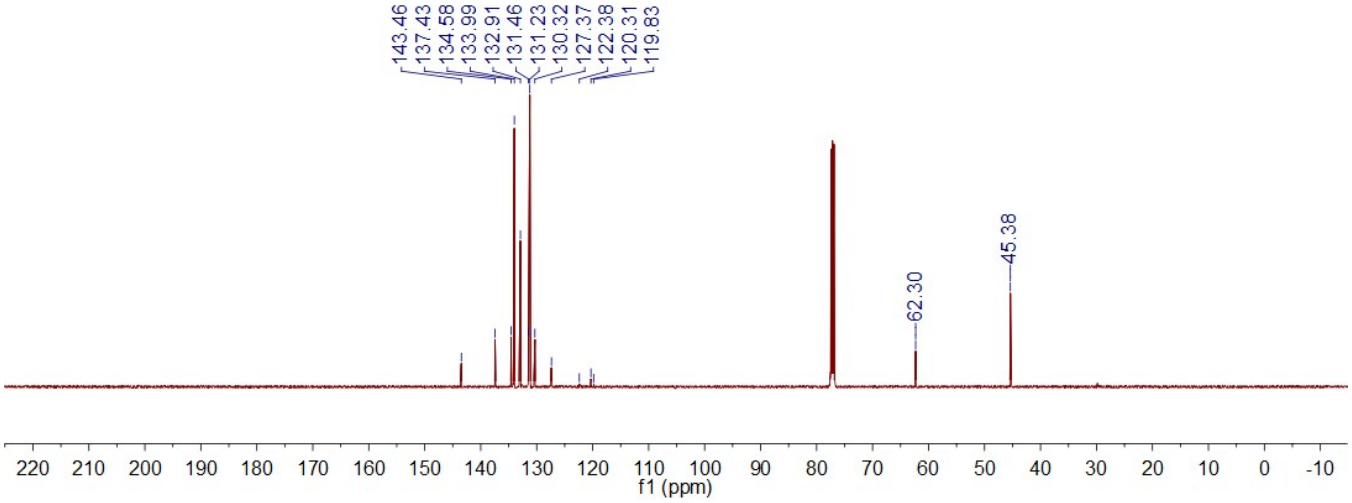


Figure S12. ^{13}C NMR of **6**[OTf] in $CDCl_3$.

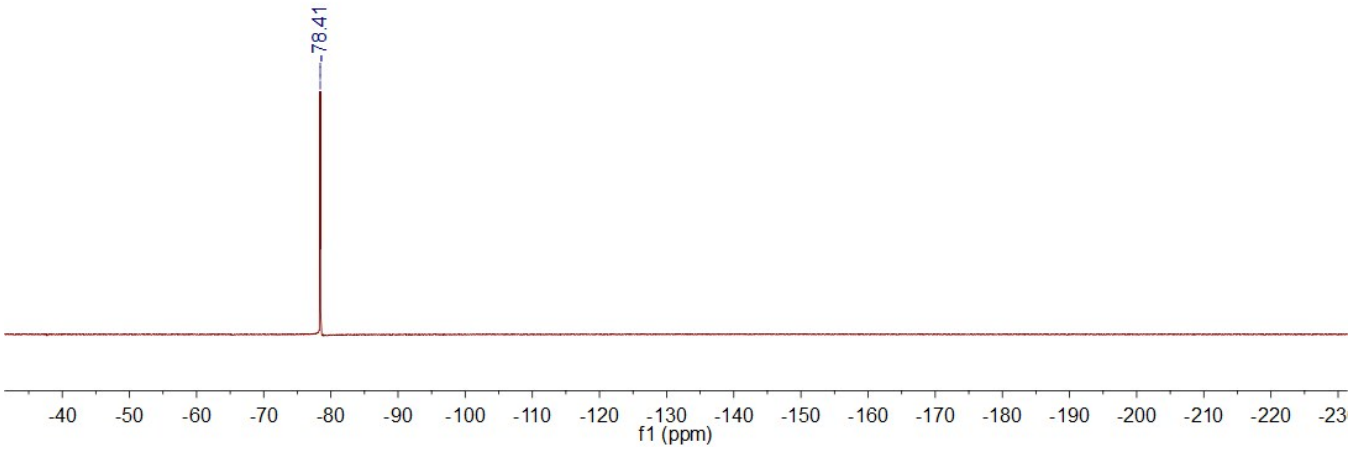


Figure S13. ^{19}F NMR of **6**[OTf] in $CDCl_3$.

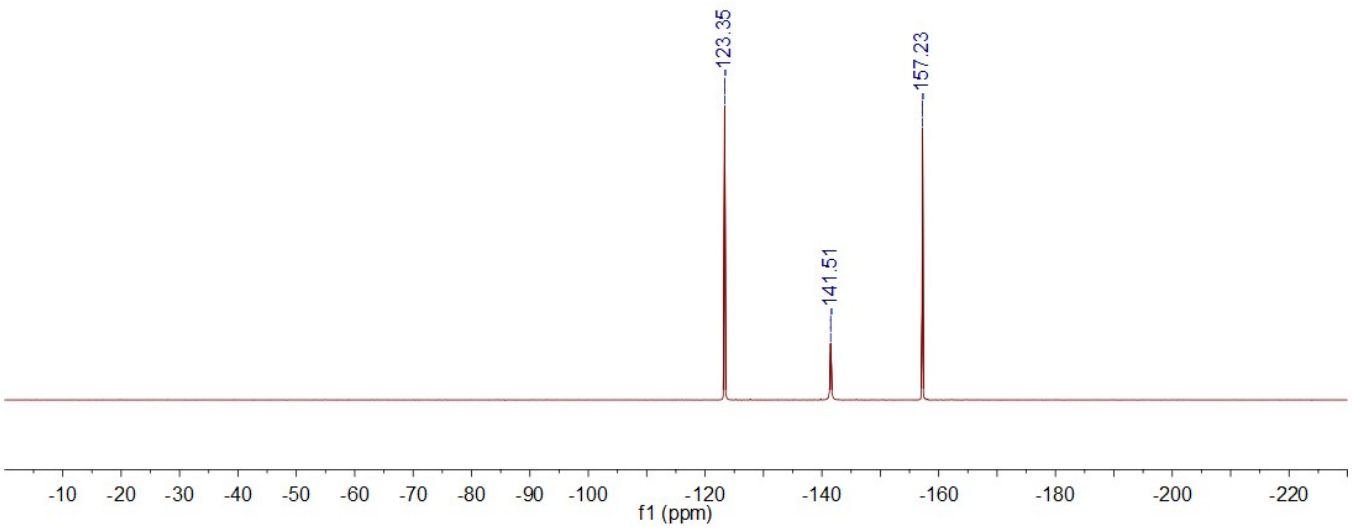


Figure S14. ^{19}F NMR of **7**[$SbCl_6$] in CD_3CN.

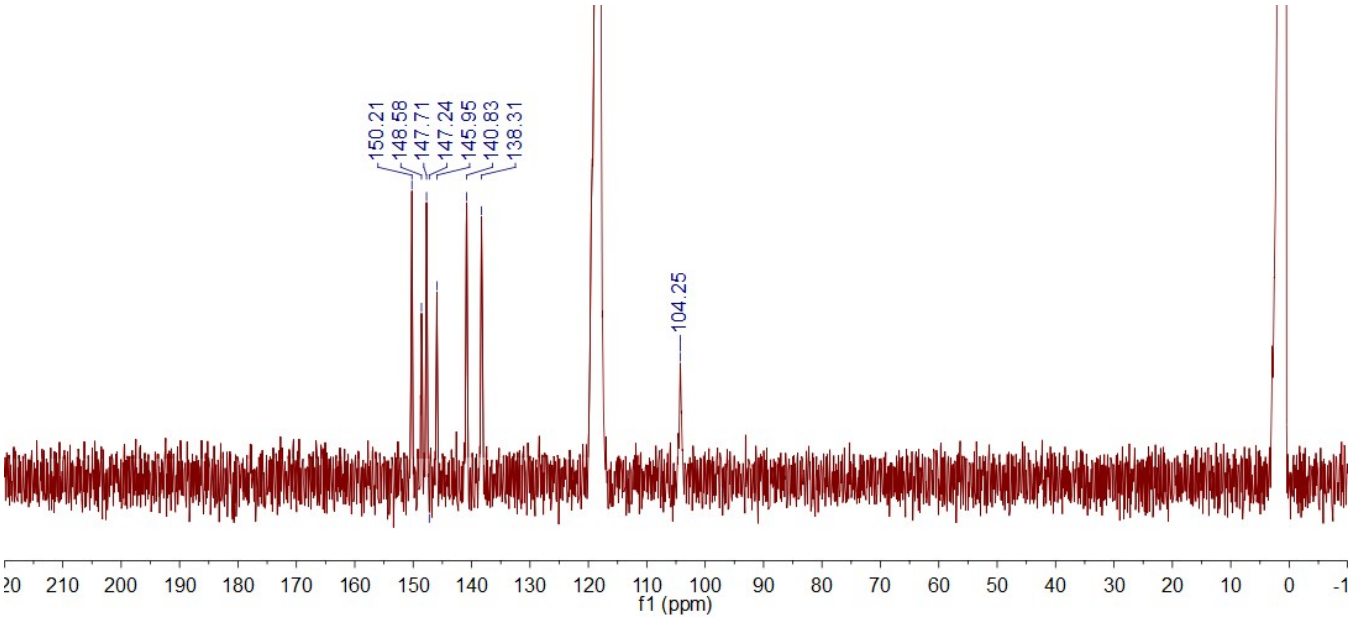
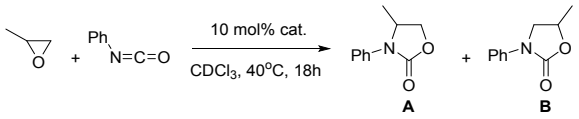


Figure S15. ^{13}C NMR of **7**[$SbCl_6$] in CD_3CN.

1.3 Catalytic cycloaddition of oxiranes and isocyanates in NMR scale.

For each entry in Table s 1-2, the yield and selectivity are reported as the average result across multiple data points, only one representative ^{1}H NMR spectrum for each entry is shown below.

1.3.1 *In situ* NMR spectra collected during the experiments presented in Table 1.



The formation of the products was monitored by ^{1}H NMR *in situ*. The integration of the resonance at 3.0 ppm (m, 12H) of the tetrabutylammonium cation was used as a standard. The yield of the major isomer A was calculated based on the integration of two resonances: 4.4 ppm (m, 2H) and 3.8 ppm (m, 1H). The yield of the minor isomer B was calculated based on the integration of three resonances: 4.6 ppm (m, 1H), 4.0 ppm (t, 1H), and 3.5 ppm (dd, 1H). An impurity in the reaction mixture gives three resonances in the 2.5 – 5.0 ppm region, two of which overlap with isomer A: 4.7 ppm (1H), 4.4 ppm (1H) and 3.8 ppm (1H).

Additionally, no reaction took place when catalysts **5**[OTf] and **6**[OTf] were mixed with a stoichiometric amount of propylene oxide in $CDCl_3$ over the course of 12 hours at 40℃. Spectra of these two stoichiometric experiments are provided below as well.

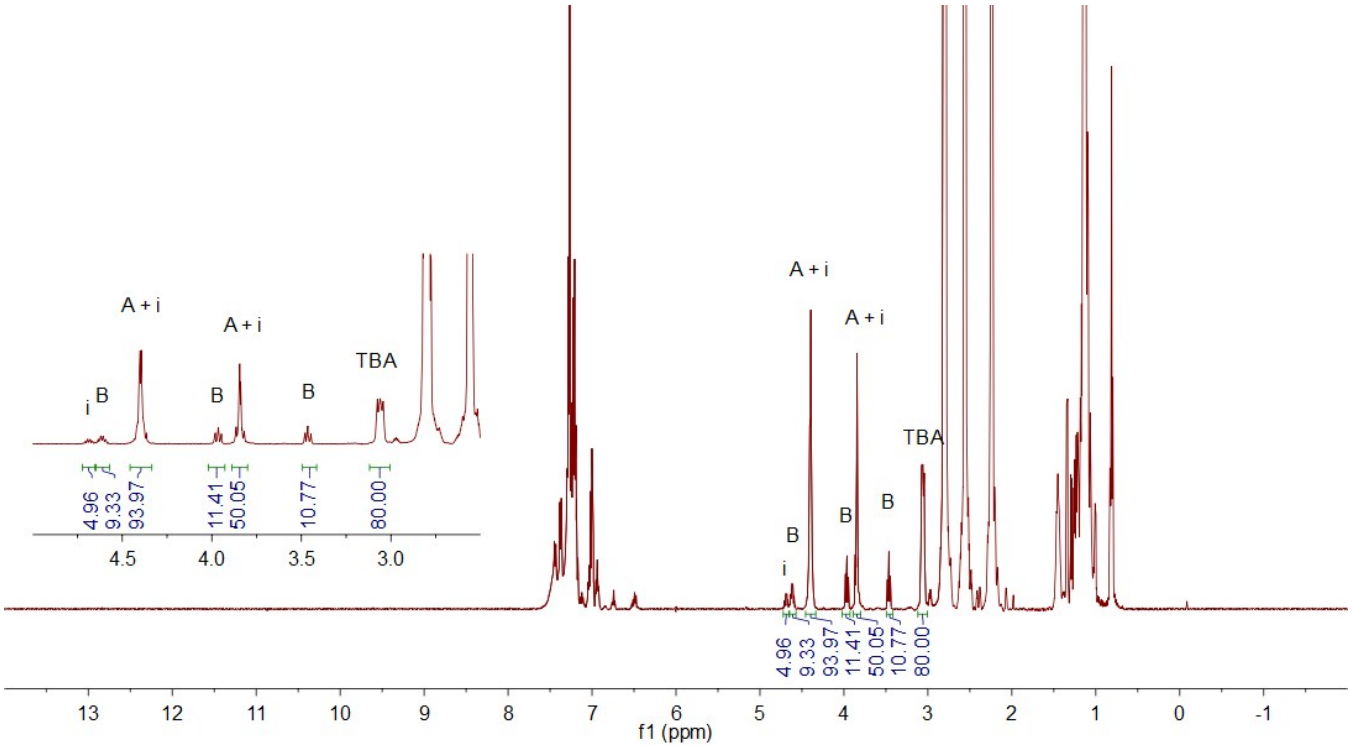


Figure S16. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 1.

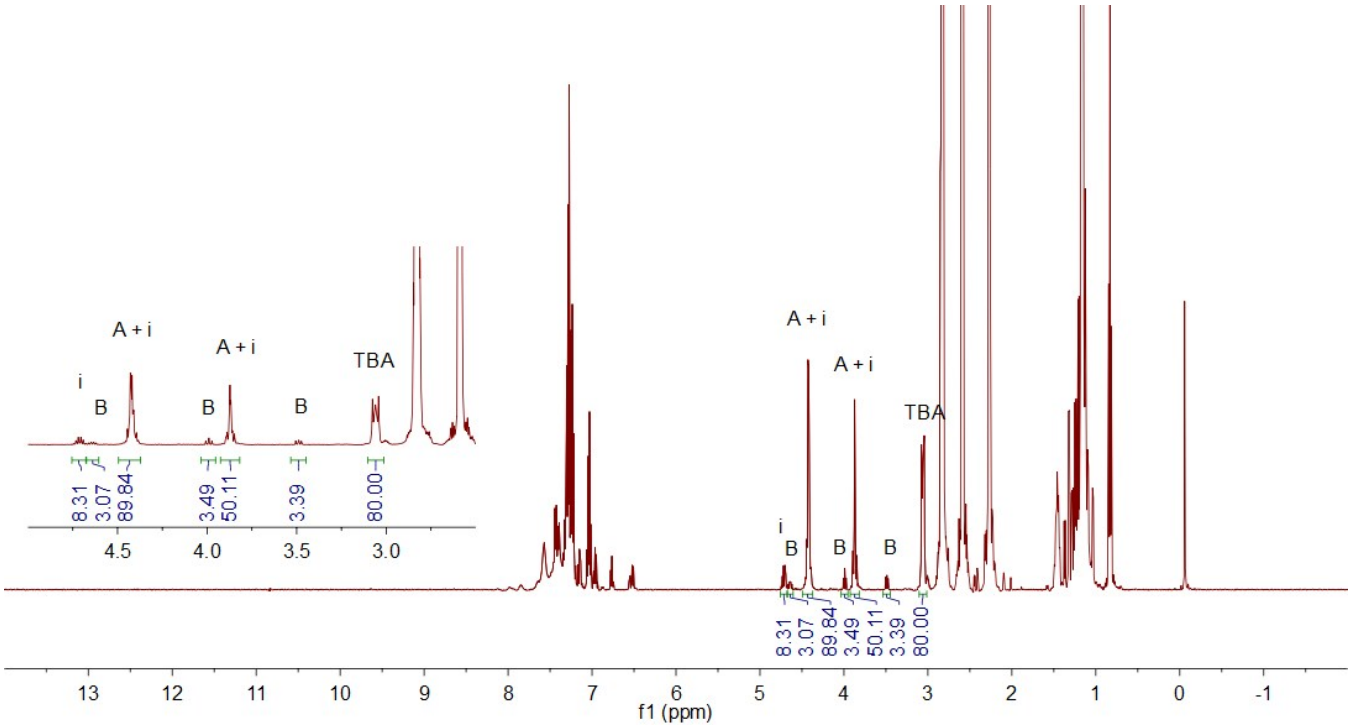


Figure S17. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 2.

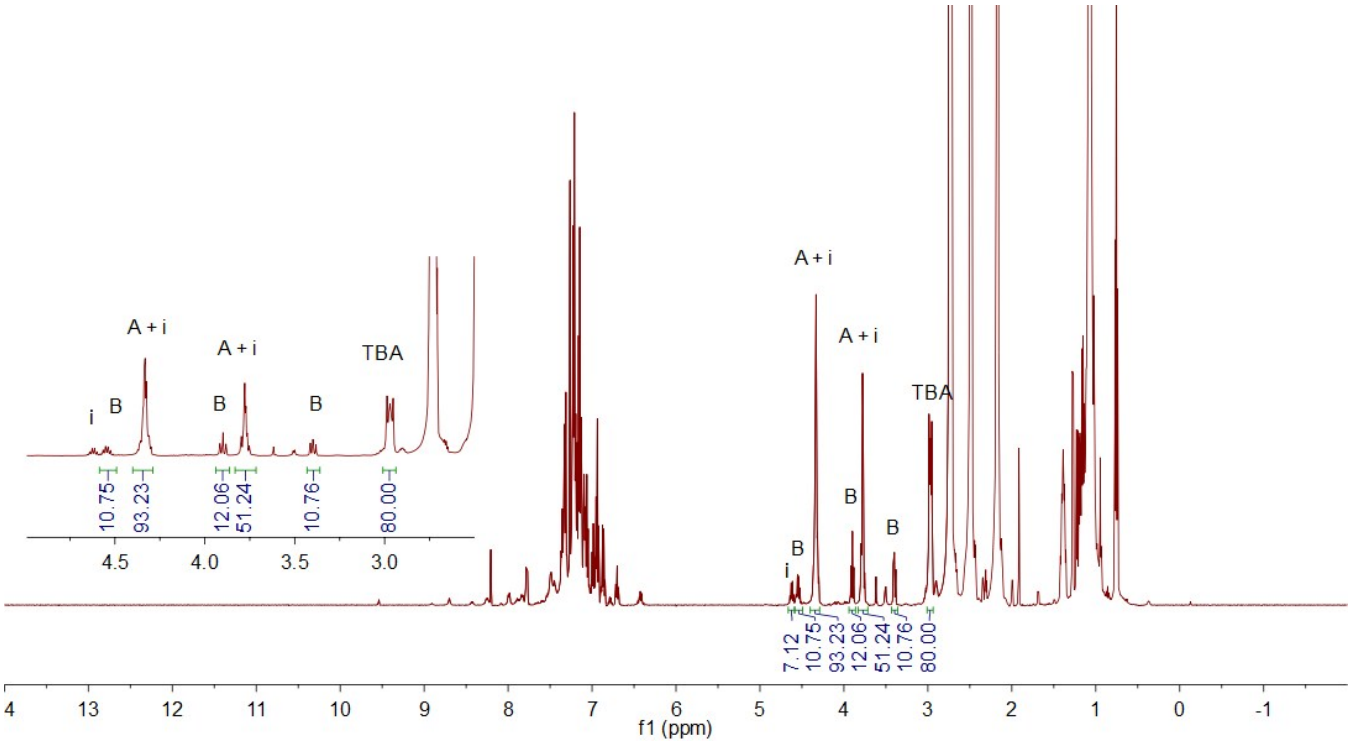


Figure S18. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 3.

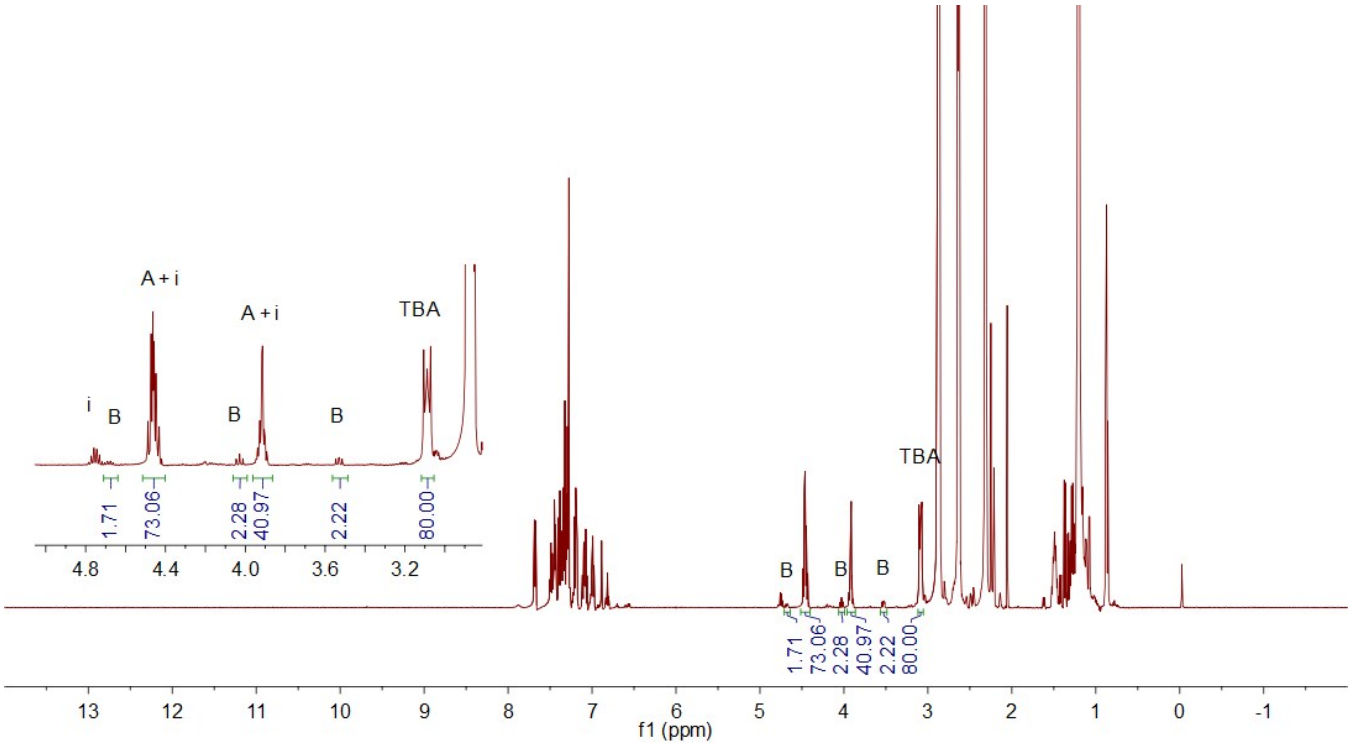


Figure S19. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 4.

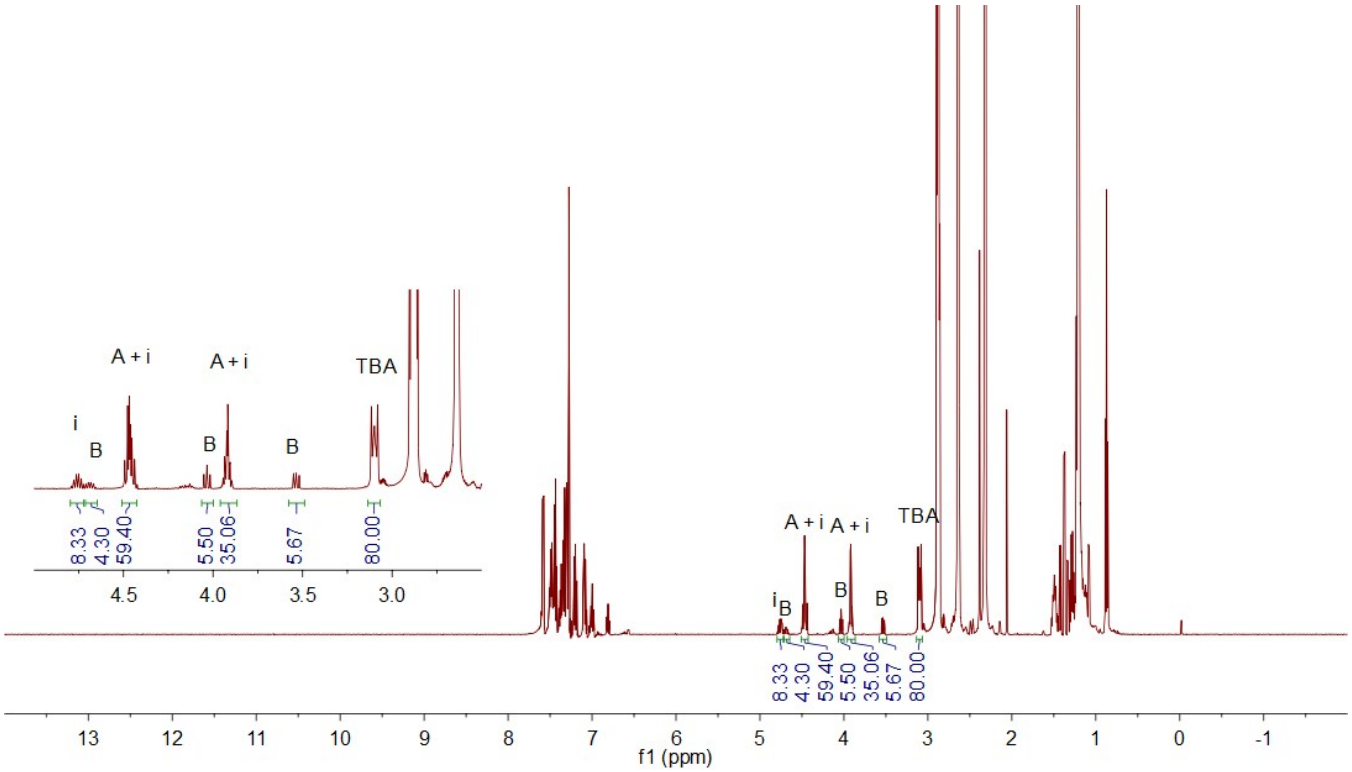


Figure S20. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 5.

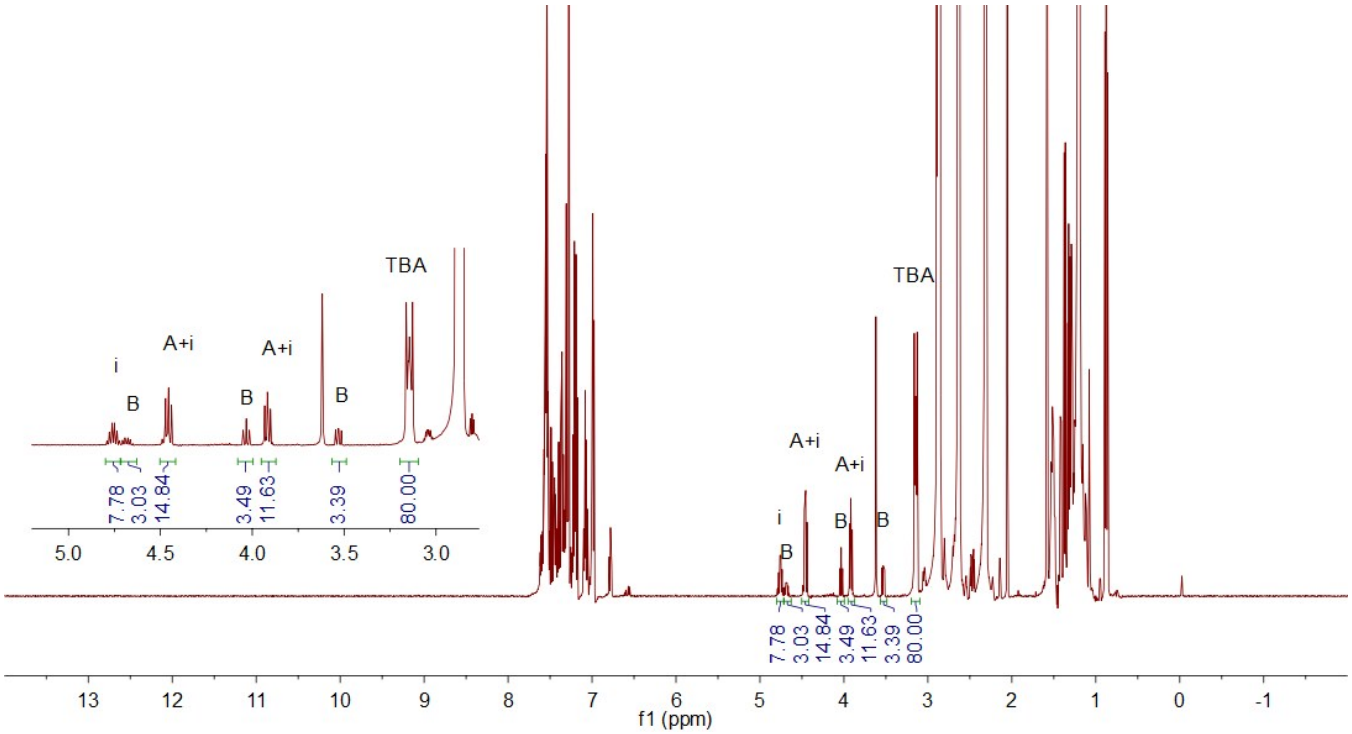


Figure S21. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 6.

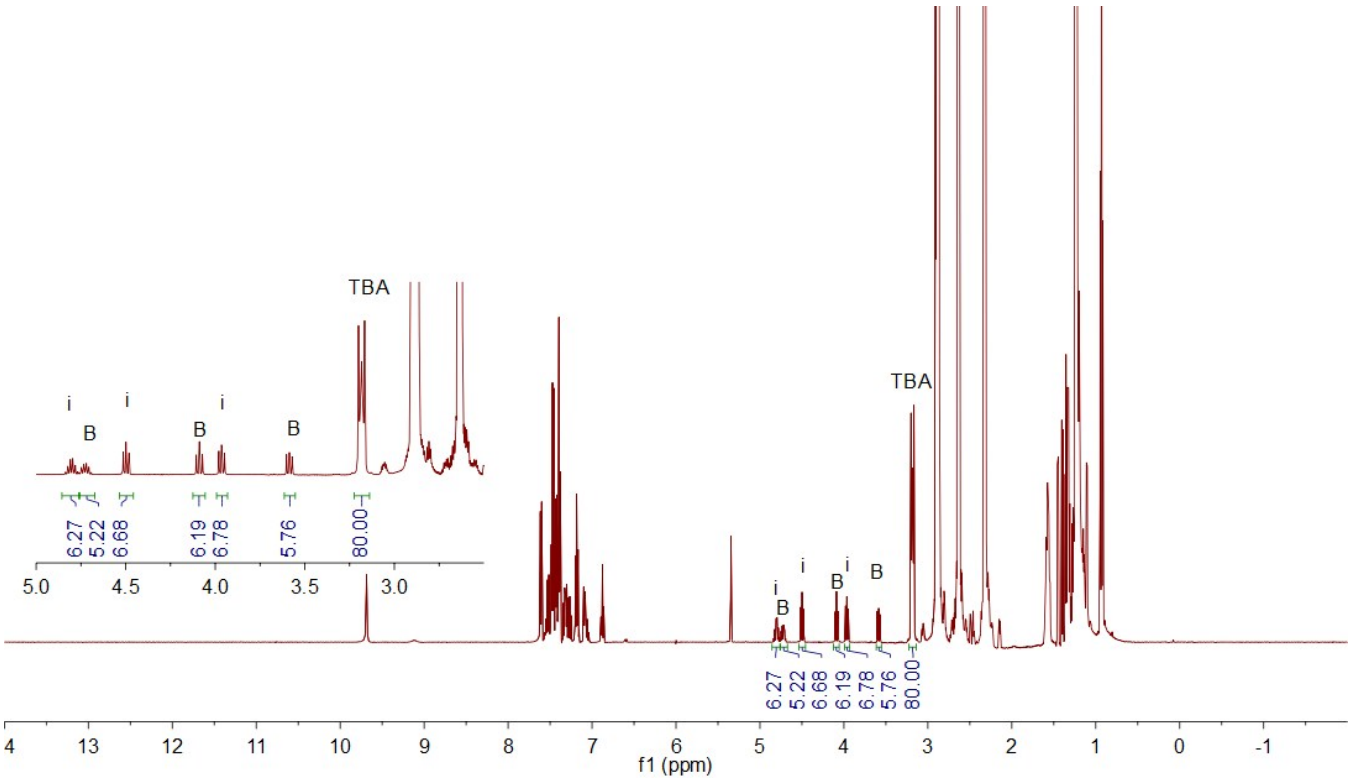


Figure S22. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 7.

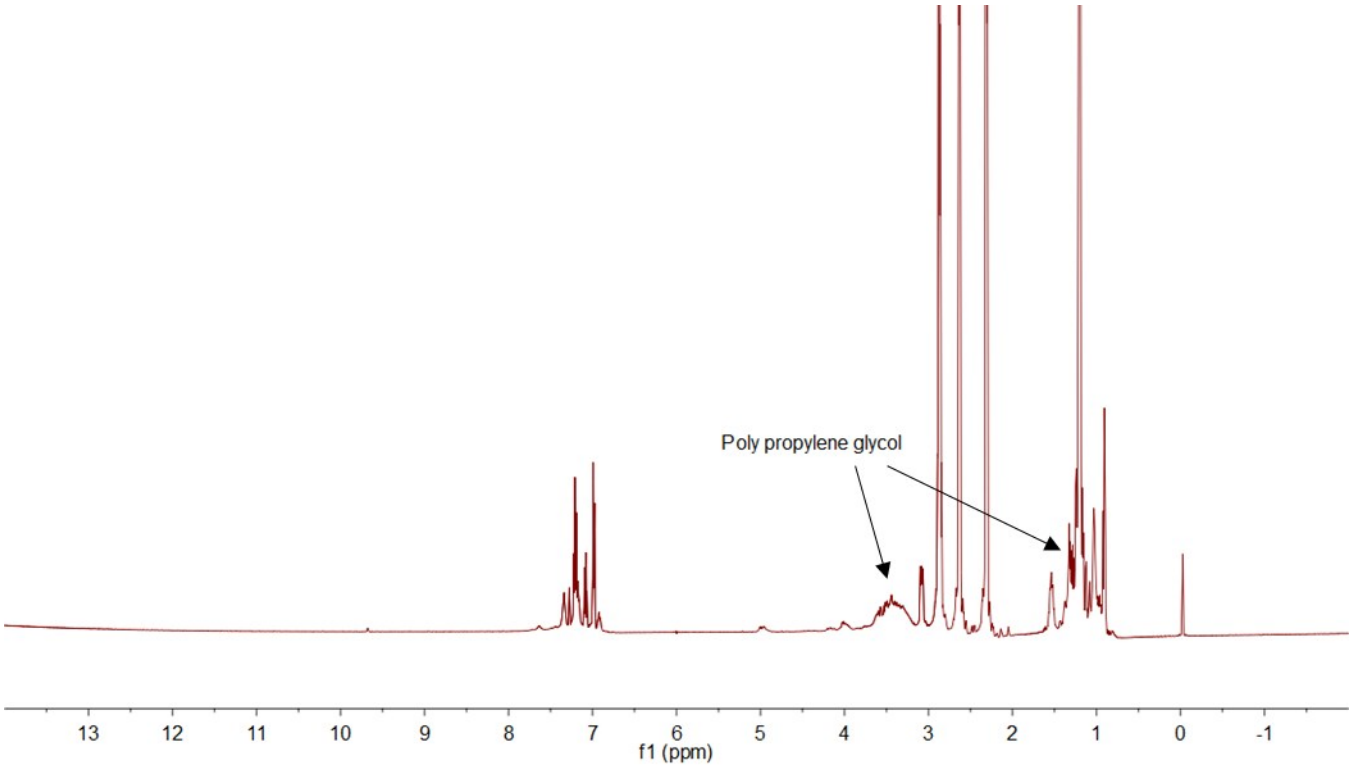


Figure S23. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 1, Entry 8.

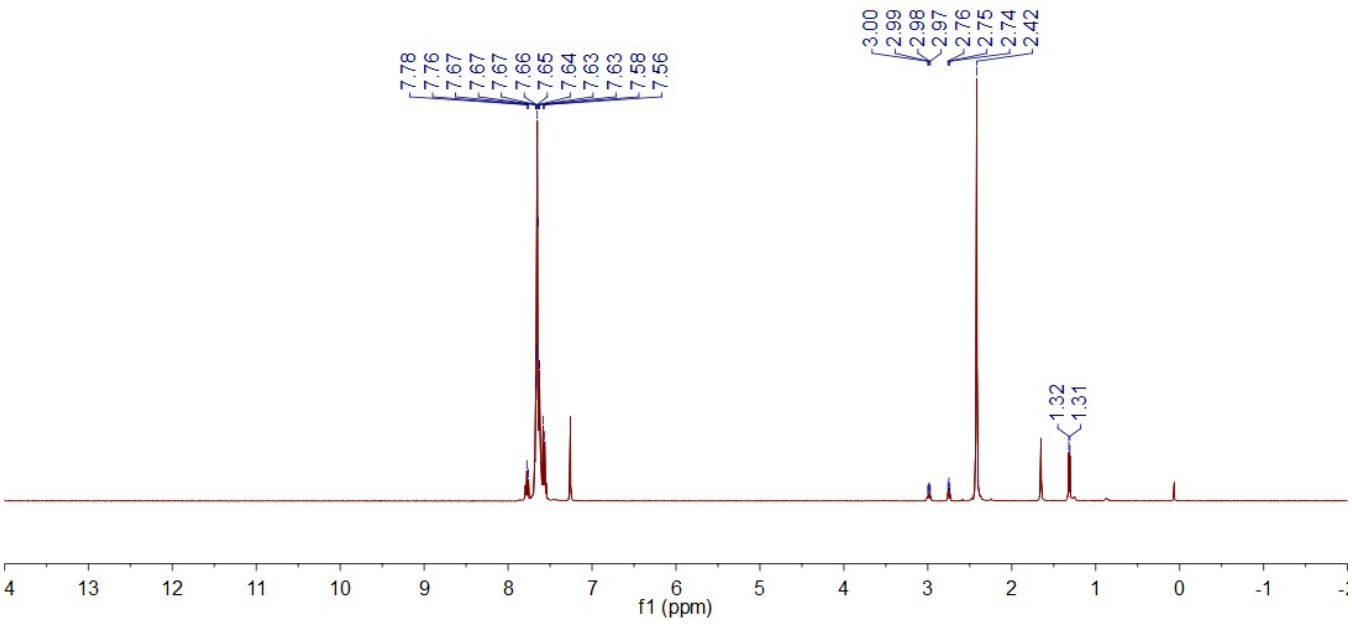


Figure S24. ^{1}H NMR of the stoichiometric reaction of **5**[OTf] and propylene oxide.

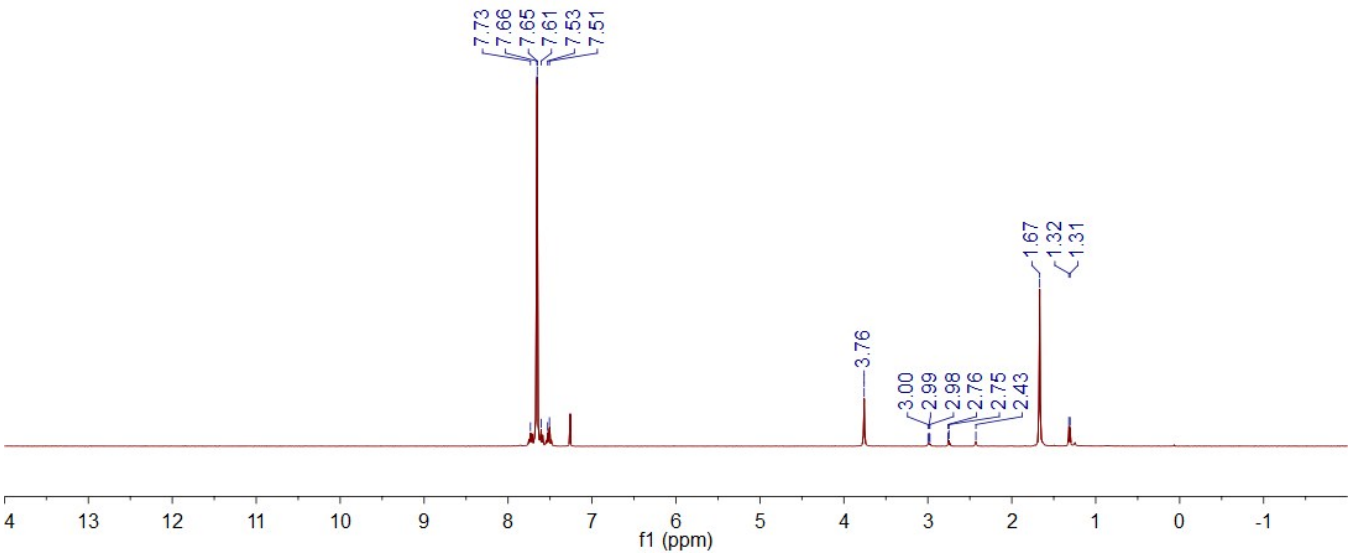
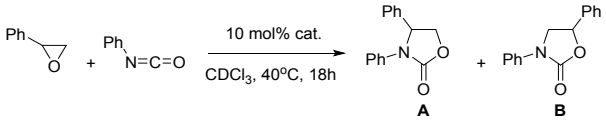


Figure S25. ^{1}H NMR of the stoichiometric reaction of **6**[OTf] and propylene oxide.

1.3.2 *In situ* NMR spectra collected during the experiments presented in Table 1.

1.3.2.1 *In situ* NMR spectrum of Table 2, Entries 1-2



The formation of the products was monitored by ^{1}H NMR *in situ*. The integration of the resonance at 1.5 ppm (m, 12H) of the tetrabutylammonium cation was used as a standard. The yield of the major isomer A was calculated based on the integration of three resonances: 5.4 ppm (dd, 1H), 4.7 ppm (t, 1H), and 4.2 ppm (dd, 1H). The yield of the minor isomer B was calculated based on the integration of three resonances: 5.6 ppm (dd, 1H), 4.7 ppm (t, 1H), and 4.3 ppm (dd, 1H).

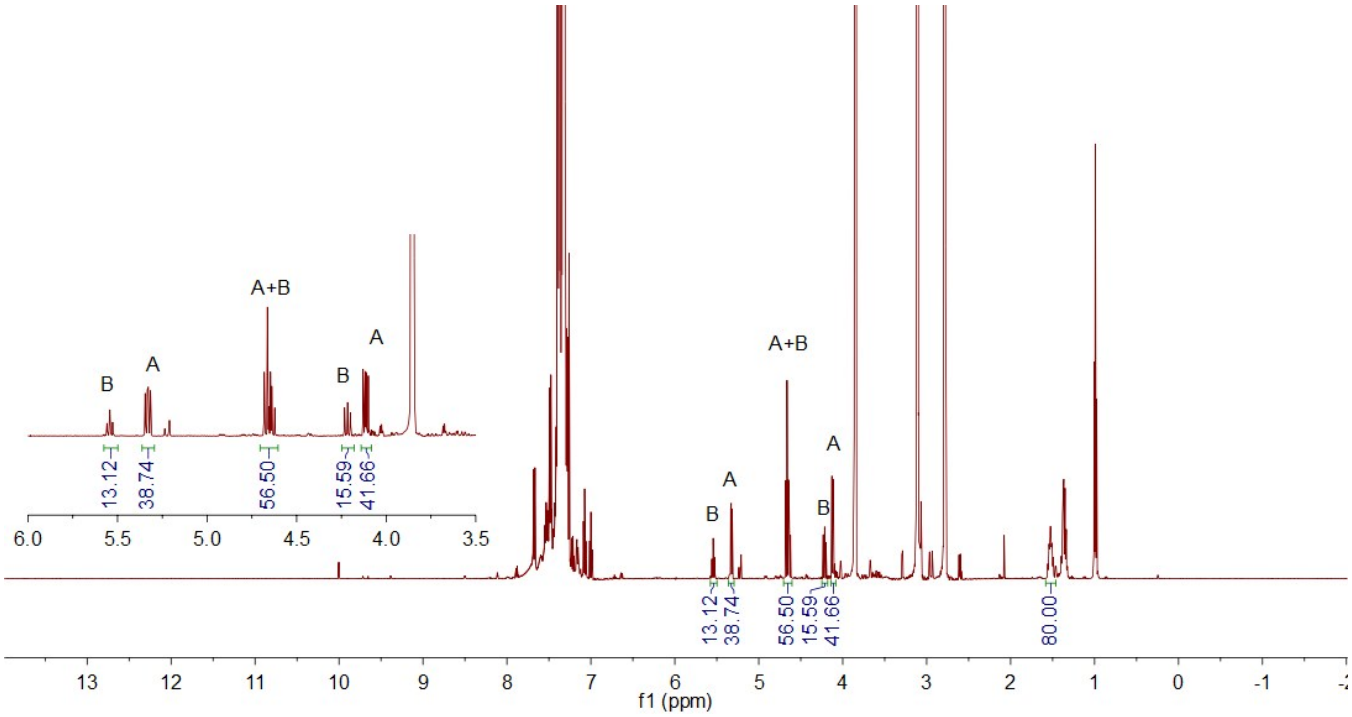


Figure S26. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 1.

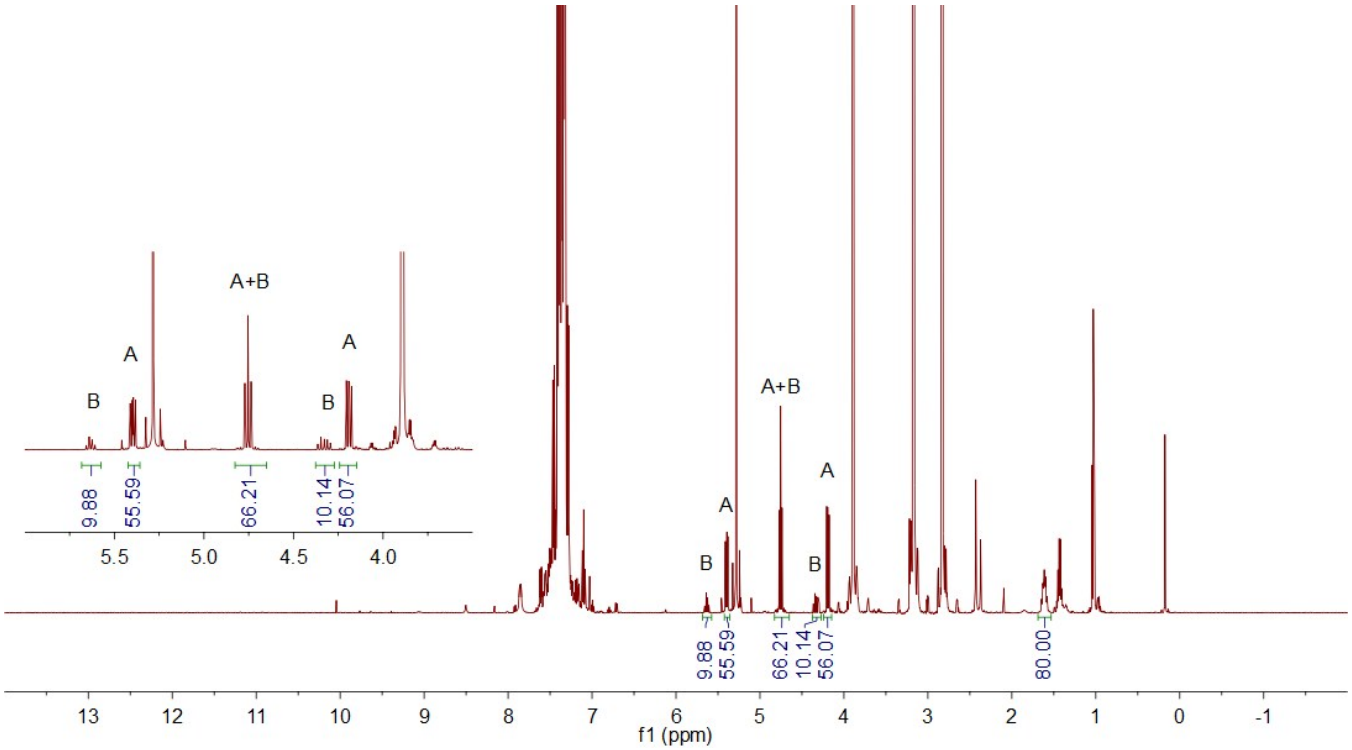
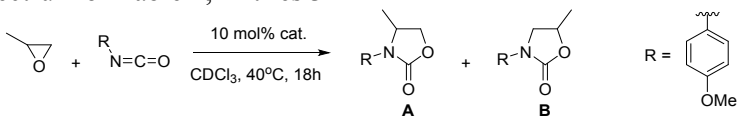


Figure S27. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 2.

1.3.2.2 *In situ* NMR spectrum of Table 2, Entries 3-4



The formation of the products was monitored by ^{1}H NMR *in situ*. The integration of the resonance at 3.0 ppm (m, 12H) of the tetrabutylammonium cation was used as a standard. The yield of the major isomer A was calculated based on the integration of three resonances: 4.5 ppm (t, 1H), 4.4 ppm (m, 1H), and 3.9 ppm (dd, 1H). The yield of the minor isomer B was calculated based on the integration of three resonances: 4.7 ppm (m, 1H), 4.0 ppm (t, 1H), and 3.5 ppm (dd, 1H). An impurity in the reaction mixture gives three resonances in the 2.5 – 5.0 ppm region, one of which overlaps with isomer A: 4.8 ppm (m, 1H), 4.5 ppm (t, 1H) and 3.9 ppm (dd, 1H).

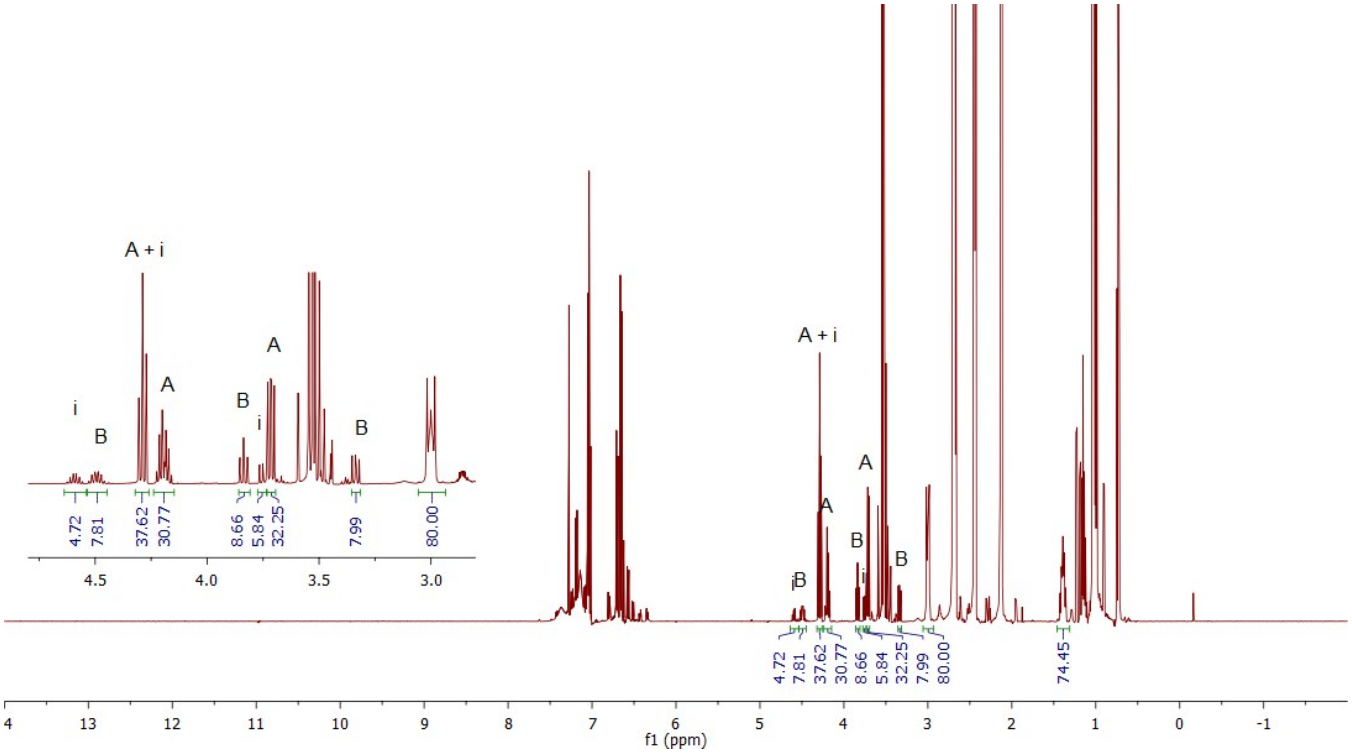


Figure S28. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 3.

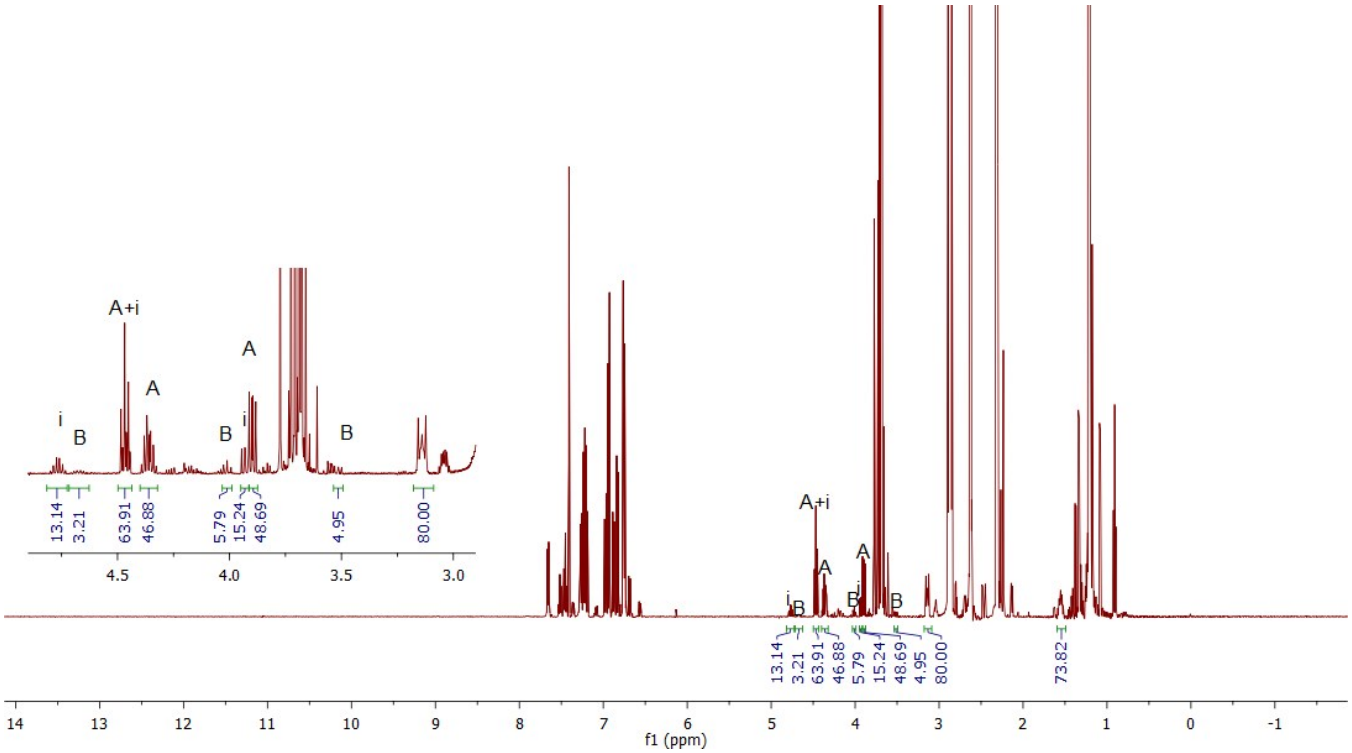
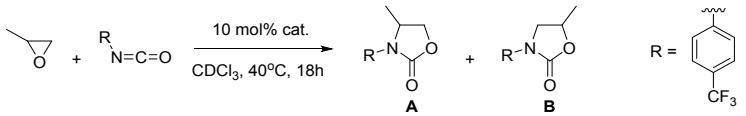


Figure S29. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 4.

1.3.2.3 *In situ* NMR spectrum of Table 2, Entries 5-6



The formation of the products was monitored by ^{1}H NMR *in situ*. The integration of the resonance at 3.0 ppm (m, 12H) of the tetrabutylammonium cation was used as a standard. The yield of the major isomer A was calculated based on the integration of three resonances: 4.4 ppm (m, 1H), 4.3 ppm (t, 1H), and 3.8 ppm (dd, 1H). The yield of the minor isomer B was calculated based on the integration of three resonances: 4.6 ppm (m, 1H), 4.0 ppm (t, 1H), and 3.4 ppm (dd, 1H).

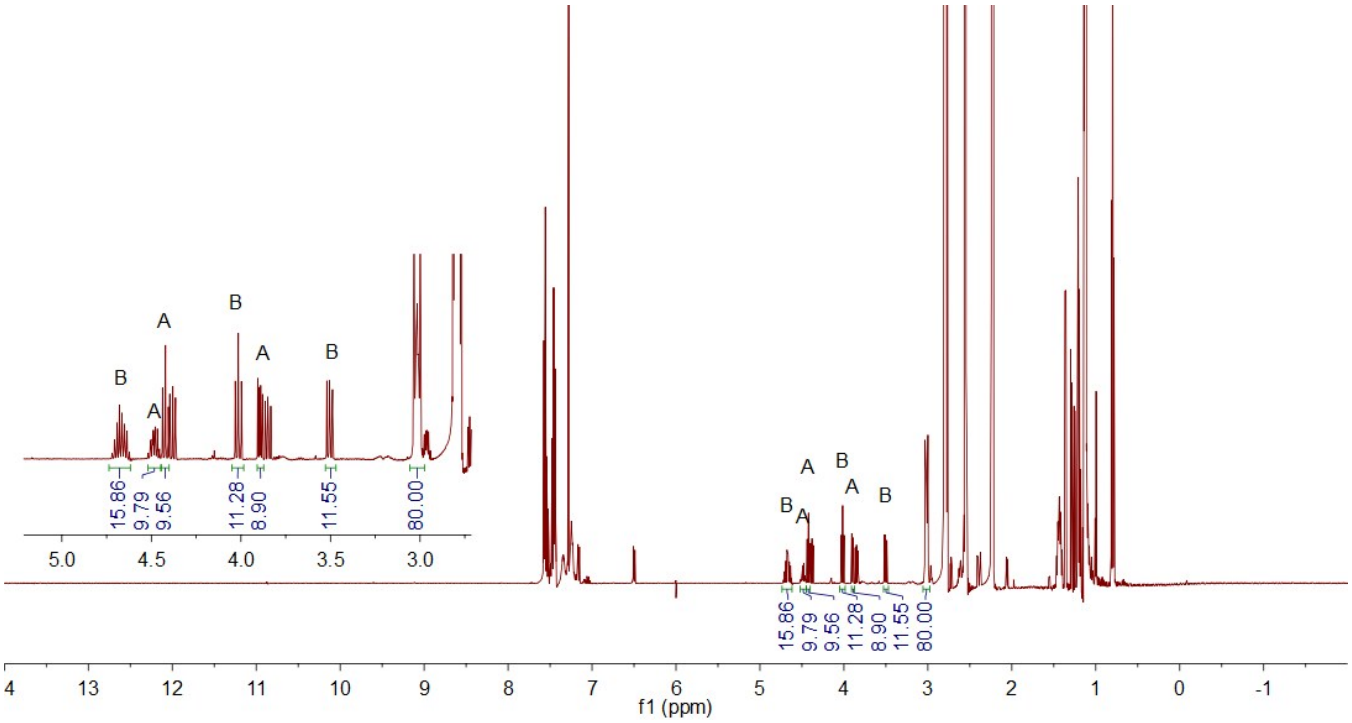


Figure S30. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 5.

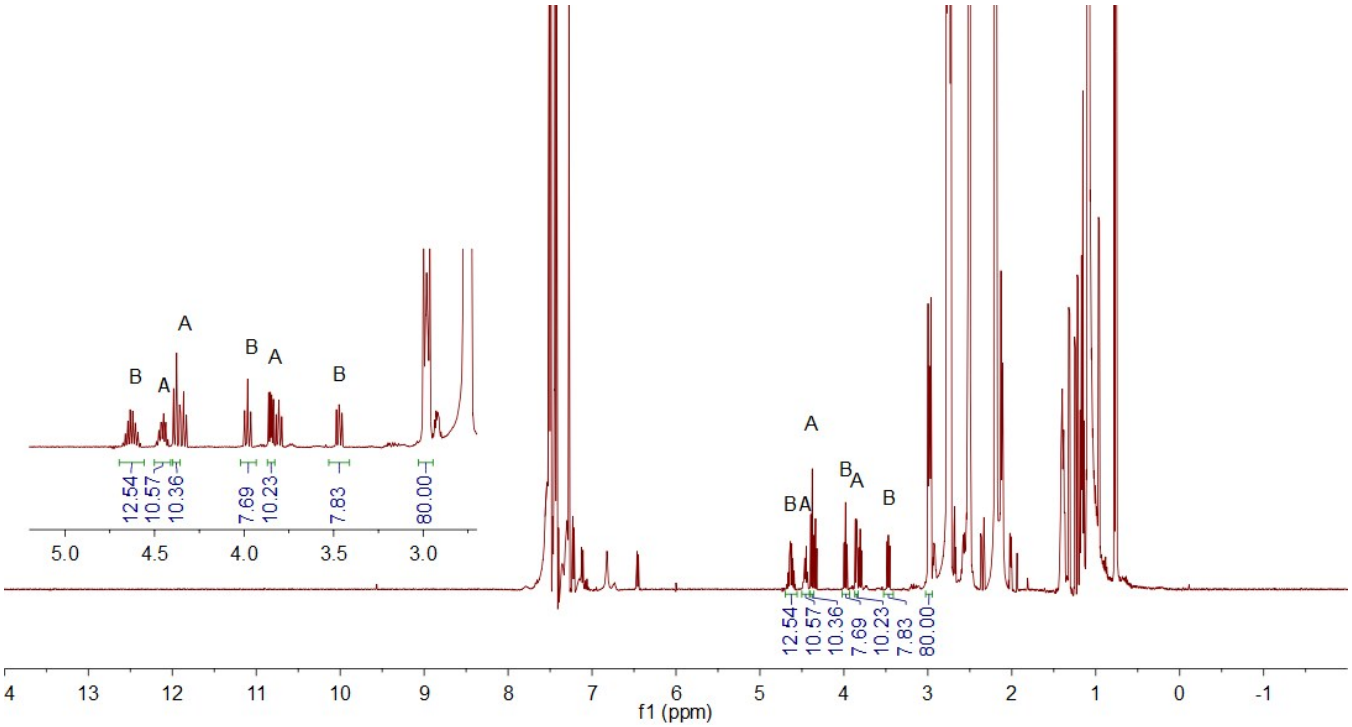
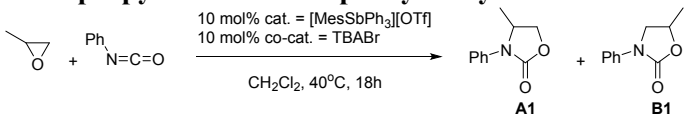


Figure S31. Representative ^{1}H NMR spectrum collected during the experiment presented in Table 2, Entry 6.

1.4 Catalytic cycloaddition of propylene oxide and phenyl isocyanate



To a stirred solution containing [$MesSbPh_3$][OTf] (150 mg, 0.24 mmol, 0.1 eq) and TBABrr (77 mg, 0.24 mmol, 0.1 eq) in CH_2Cl_2 (5 mL), was added propylene oxide (2.5 mL, 36 mmol, 15 eq) and phenyl isocyanate (286 mg, 2.4 mmol, 1 eq). The reaction was stirred in a 40 °C bath for 18 h under N_2. An aliquot was taken from the reaction mixture and the yield of the two regioisomeric oxazolidinones was determined by ^{1}H NMR spectroscopy. The crude reaction mixture was subjected to flash chromatography over silica gel (3% ethyl acetate in hexanes). The third major fraction (very close to the second one) was collected washed with diethyl ether to afford product 5-methyl-3-phenyl-2-oxazolidinone (**B1**) as white powder (16 mg, 4%), and the fourth major fraction was collected to afford product 4-methyl-3-phenyl-2-oxazolidinone (**A1**) as colorless oil (170 mg, 40%).

4-methyl-3-phenyl-2-oxazolidinone (**A1**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 4H), 7.20 – 7.15 (m, 1H), 4.59 – 4.45 (m, 2H), 4.00 (dd, *J* = 7.8, 5.3, 1H), 1.30 (d, *J* = 5.9, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.82 (s), 136.60 (s), 129.27 (s), 125.32 (s), 122.04 (s), 68.76 (s), 52.42 (s), 18.54 (s). Spectral data are in accord with the previous report.[2]

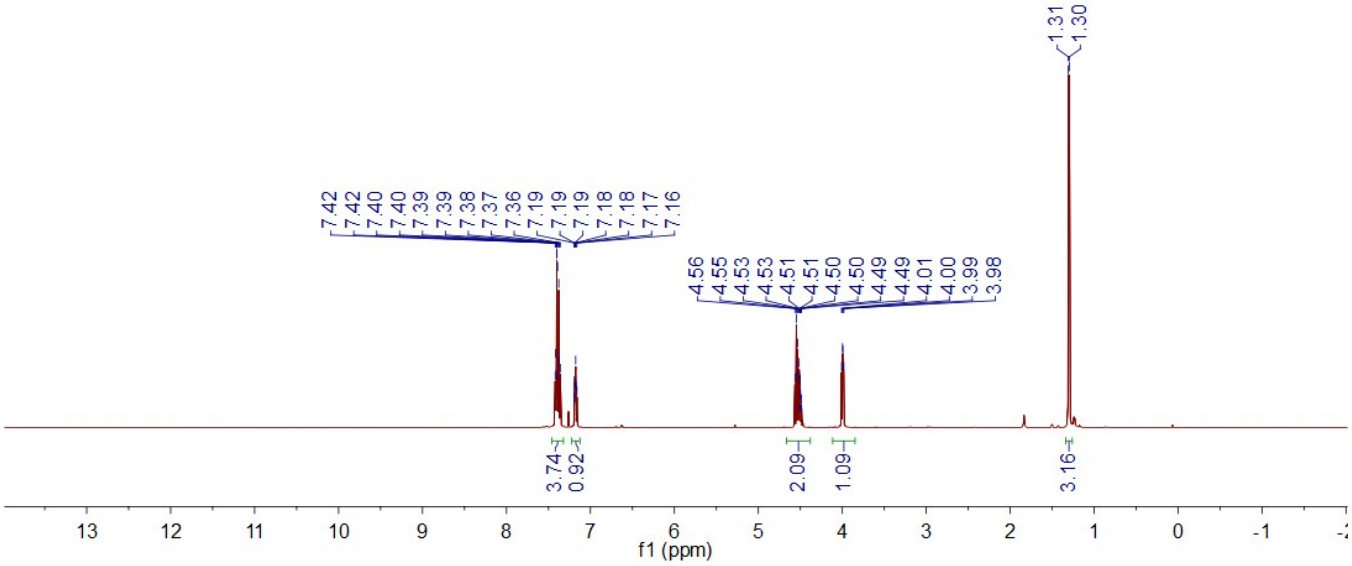


Figure S32. ^{1}H NMR of 4-methyl-3-phenyl-2-oxazolidinone (**A1**) in $CDCl_3$.

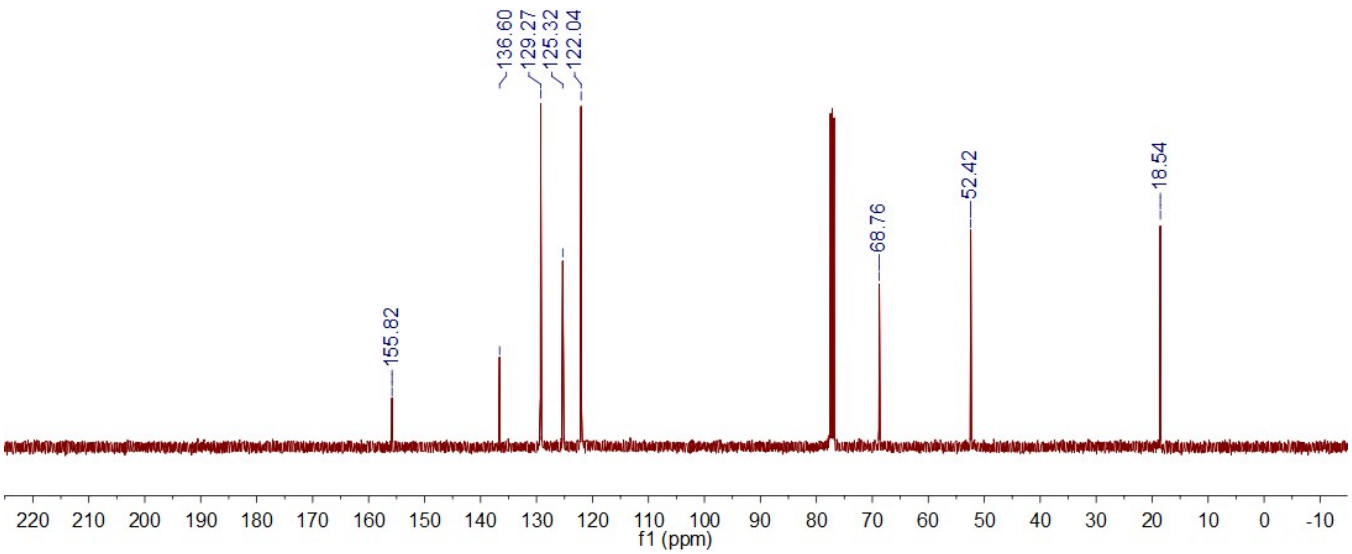


Figure S33. ^{13}C NMR of 4-methyl-3-phenyl-2-oxazolidinone (**A1**) in $CDCl_3$.

5-methyl-3-phenyl-2-oxazolidinone (**B1**): ^1H NMR (500 MHz, $CDCl_3$) δ = 7.57 – 7.50 (m, 2H), 7.41 – 7.35 (m, 2H), 7.17 – 7.11 (m, 1H), 4.85 – 4.74 (m, 1H), 4.12 (t, *J* = 8.4, 1H), 3.63 (dd, *J* = 8.6, 7.1, 1H), 1.54 (d, *J* = 6.3, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 155.01 (s), 138.51 (s), 129.18 (s), 124.09 (s), 118.31 (s), 69.66 (s), 52.03 (s), 20.87 (s). Spectral data are in accord with the previous report.[2]

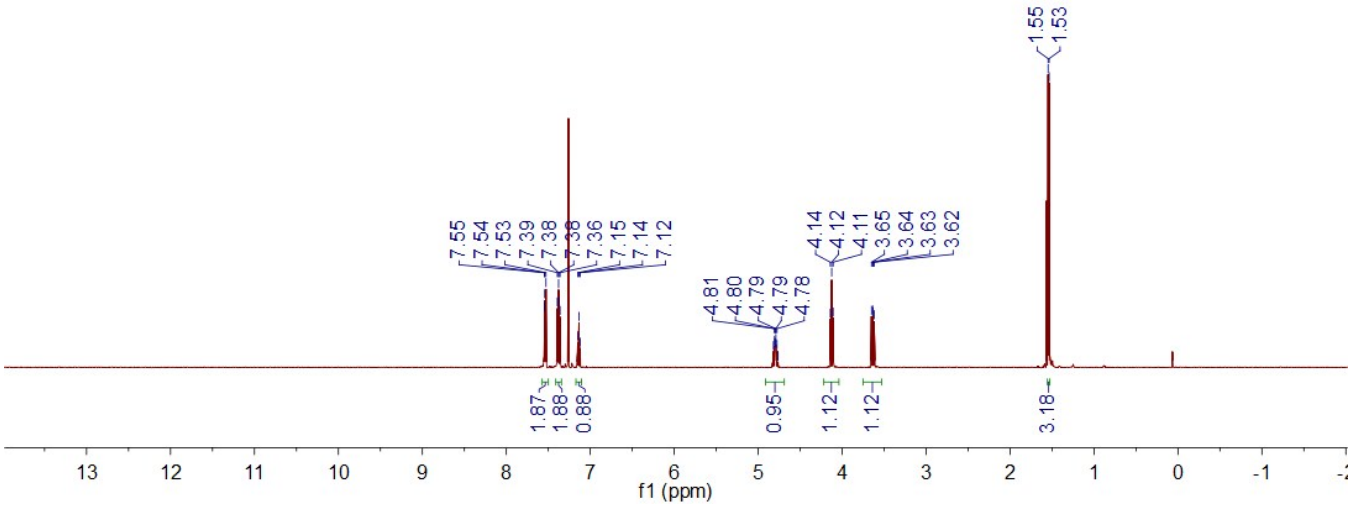


Figure S34. ^1H NMR of 5-methyl-3-phenyl-2-oxazolidinone (**B1**) in $CDCl_3$.

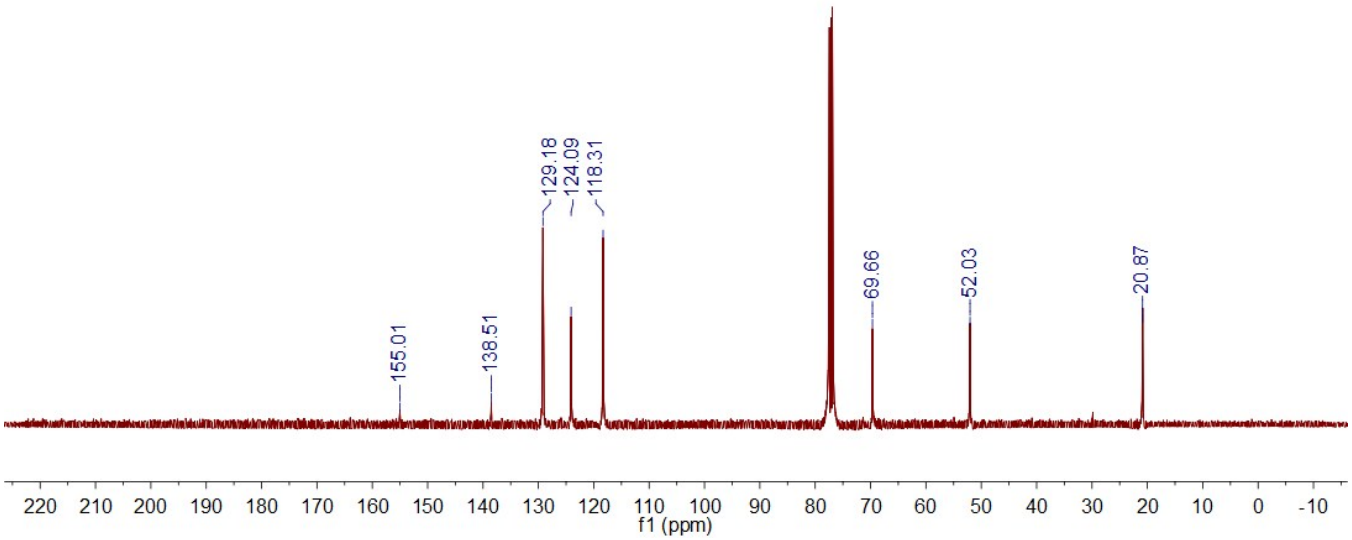
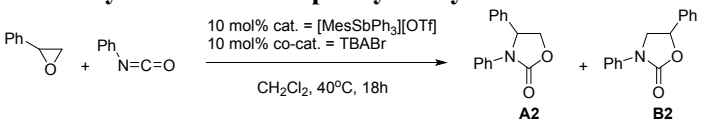


Figure S35. ^{13}C NMR of 5-methyl-3-phenyl-2-oxazolidinone (**B1**) in $CDCl_3$.

1.5 Catalytic cycloaddition of styrene oxide and phenyl isocyanate



To a stirred solution of catalyst [$MesSbPh_3$][OTf] (125 mg, 0.20 mmol, 0.1 eq), co-catalyst TBABr (65 mg, 0.20 mmol, 0.1 eq) in CH_2Cl_2 (5 mL) was added styrene oxide (3.5 mL, 30 mmol, 15 eq) and phenyl isocyanate (243 mg, 2.0 mmol, 1 eq). The reaction was stirred in a 40 °C bath for 18 h under N_2. An aliquot was taken from the reaction mixture and the yield of two regioisomeric oxazolidinones was determined by ^{1}H NMR spectroscopy. The reaction mixture was treated to flash chromatography over silica gel (gradient 0-50% ethyl acetate in hexanes) and the third major fraction was collected and treated again to flash chromatography over silica gel (gradient 5-20% ethyl acetate in hexanes). The third major fraction was collected and recrystallized with diethyl ether to afford product 3,5-diphenyl-2-oxazolidinone (**B2**) as white powder (16 mg, 3%), and the fourth major fraction was collected and washed with hexanes to afford product 3,4-diphenyl-2-oxazolidinone (**A2**) as white powder (210 mg, 43%).

3,4-diphenyl-2-oxazolidinone (**A2**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 – 7.35 (m, 4H), 7.35 – 7.30 (m, 3H), 7.30 – 7.25 (m, 2H), 7.11 – 7.06 (m, 1H), 5.42 (dd, *J* = 8.7, 6.0, 1H), 4.80 (t, *J* = 8.7, 1H), 4.22 (dd, *J* = 8.7, 6.0, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 156.08 (s), 138.37 (s), 137.13 (s), 129.52 (s), 129.04 (s), 128.97 (s), 126.37 (s), 124.83 (s), 120.98 (s), 69.95 (s), 60.85 (s). Spectral data are in accord with the previous report.[2]

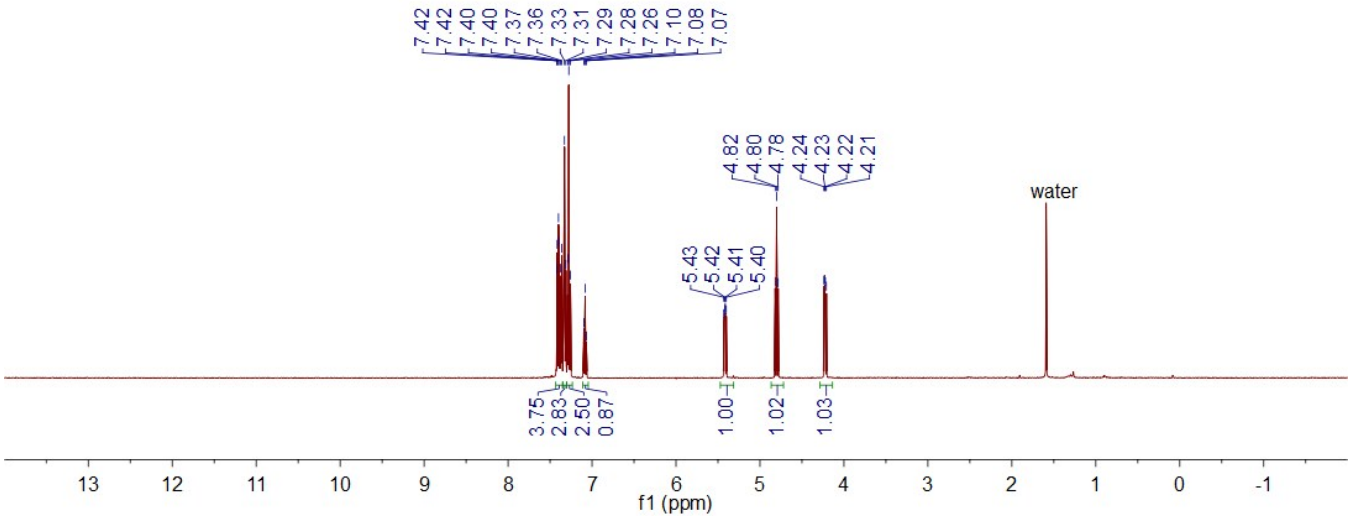


Figure S36. ^{1}H NMR of 3,4-diphenyl-2-oxazolidinone (**A2**) in $CDCl_3$.

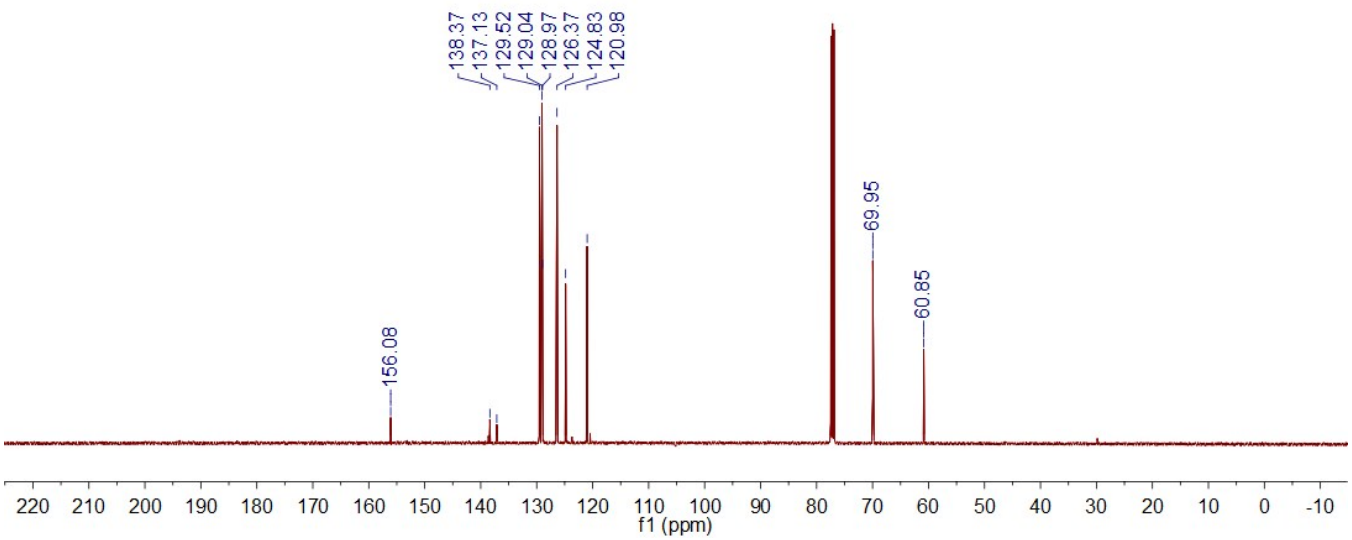


Figure S37. ^{13}C NMR of 3,4-diphenyl-2-oxazolidinone (**A2**) in $CDCl_3$.

3,5-diphenyl-2-oxazolidinone (**B2**): ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 – 7.52 (m, 2H), 7.48 – 7.36 (m, 7H), 7.19 – 7.12 (m, 1H), 5.65 (dd, *J* = 8.8, 7.5, 1H), 4.39 (t, *J* = 8.8, 1H), 3.98 (dd, *J* = 8.8, 7.5, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 154.85 (s), 138.27 (s), 138.24 (s), 129.28 (s), 129.27 (s), 129.20 (s), 125.83 (s), 124.35 (s), 118.45 (s), 74.19 (s), 52.88 (s). Spectral data are in accord with the previous report.[2]

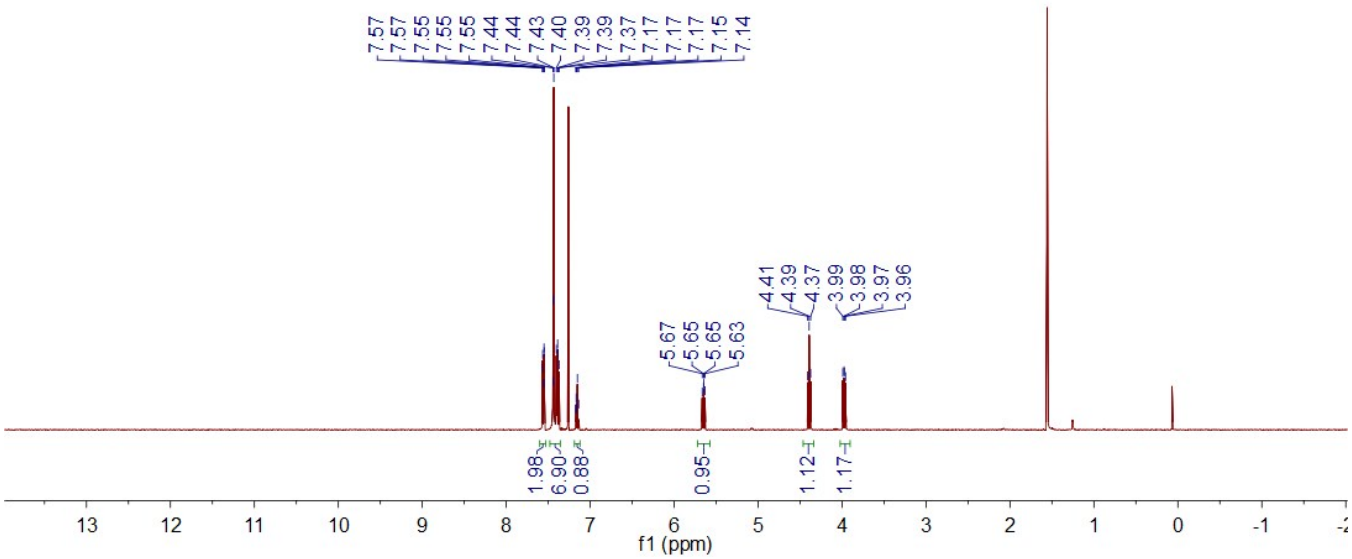


Figure S38. ^{1}H NMR of 3,5-diphenyl-2-oxazolidinone (**B2**) in $CDCl_3$.

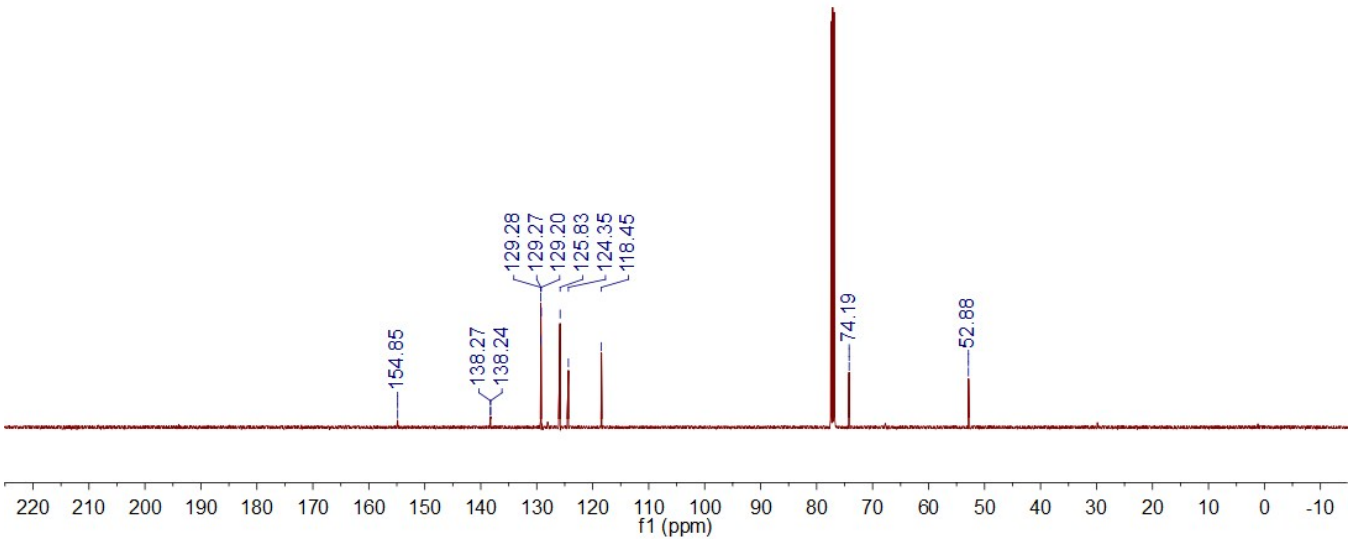


Figure S39. ^{13}C NMR of 3,5-diphenyl-2-oxazolidinone (**B2**) in $CDCl_3$.

2 Crystallographic measurements.

2.1 1-Naphthyltriphenylstibonium triflate (2[OTf])

Table S1. Crystal data, data collection, and structure refinement for **2**[OTf]

Empirical formula	C_{29} H_{22} F_3 O_3 S Sb
Formula weight	629.27
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*C* 1 2/*c* 1
Unit cell dimensions	a = 14.848(7) Å
	b = 14.208(7) Å
	c = 24.673(17) Å
	α = 90°.
	β = 102.698(9)°.
	γ = 90°.
Volume	5078(5) Å^3
Z	8
Density (calculated)	1.646 Mg/m^3
Absorption coefficient	1.221 mm^{-1}
F(000)	2512
Crystal size	0.42 x 0.3 x 0.1 mm^3
Theta range for data collection	2.296 to 27.447°.
Index ranges	-18< = h< = 18, -18< = k< = 18, -31< = l< = 31
Reflections collected	78867
Independent reflections	5413 [R(int) = 0.0800]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.5966
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5413 / 121 / 437
Goodness-of-fit on F2	1.025
Final R indices [I>2sigma(I)]	R1[a] = 0.0400, wR2[b] = 0.0761
R indices (all data)	R1 = 0.0769, wR2 = 0.0904
Extinction coefficient	n/a
Largest diff. peak and hole	0.575 and -0.538 e.Å-3

[a] $R1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. [b] $wR2$ $([w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with a = 0.02430 and b = 20.4903.

2.2 [MesSbPh$_3$][OTf] (4[OTf])

Table S2. Crystal data, data collection, and structure refinement for **4**[OTf]

Empirical formula	C_{28} H_{26} F_3 O_3 S Sb
Formula weight	621.30
Temperature	110 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 1 2_1/*n* 1
Unit cell dimensions	a = 11.4672(4) Å
	b = 19.4493(8) Å
	c = 11.7980(5) Å
	α = 90°.
	β = 95.029(2)°.
	γ = 90°.
Volume	2621.17(18) Å^3
Z	4
Density (calculated)	1.574 Mg/m^3
Absorption coefficient	1.181 mm^{-1}
F(000)	1248
Crystal size	0.36 x 0.29 x 0.1 mm^3
Theta range for data collection	2.025 to 27.900°.
Index ranges	-15< = h< = 15, -25< = k< = 25, -15< = l< = 15
Reflections collected	96586
Independent reflections	6238 [R(int) = 0.0997]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6324
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6238 / 0 / 328
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1[a] = 0.0352, wR2[b] = 0.0756
R indices (all data)	R1 = 0.0648, wR2 = 0.0885
Extinction coefficient	n/a
Largest diff. peak and hole	0.742 and -1.319 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. [b] $wR2\ ([w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with a = 0.0370 and b = 4.2008.

2.3 [(*o*-(Me$_2$N)C$_6$H$_4$)SbPh$_3$][OTf] (5 [OTf])

Table S3. Crystal data, data collection, and structure refinement for **5**[OTf]

Empirical formula	C_{27} H_{25} F_3 N O_3 S Sb
Formula weight	622.29
Temperature	110.0 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 18.642(2) Å
	b = 14.0067(18) Å
	c = 19.752(2) Å
	α = 90°.
	β = 90°.
	γ = 90°.
Volume	5157.5(10) Å^3
Z	8
Density (calculated)	1.603 Mg/m^3
Absorption coefficient	1.202 mm^{-1}
F(000)	2496
Crystal size	0.45 x 0.05 x 0.04 mm^3
Theta range for data collection	2.062 to 27.974°.
Index ranges	-24<=h<=24, -18<=k<=18, -25<=l<=25
Reflections collected	114700
Independent reflections	6139 [R(int) = 0.1617]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5849
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6139 / 0 / 328
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1[a] = 0.0448, wR2 [b] = 0.1024
R indices (all data)	R1 = 0.0722, wR2 = 0.1220
Extinction coefficient	0.00058(14)
Largest diff. peak and hole	1.445 and -1.334 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. [b] $wR2\ ([w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with a = 0.00313 and b = 14.5167.

2.4 [(*o*-(Me_2NCH_2)C_6H_4)$SbPh_3$][OTf] (6[OTf])

Table S4. Crystal data, data collection, and structure refinement for **6**[OTf]

Empirical formula	C_{28} H_{27} F_3 N O_3 S Sb
Formula weight	636.31
Temperature	110.0 K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* 1 2_1/c 1
Unit cell dimensions	a = 9.9453(7) Å
	b = 11.0052(8) Å
	c = 25.4792(17) Å
	α = 90°.
	β = 101.217(4)°.
	γ = 90°.
Volume	2735.4(3) Å^3
Z	4
Density (calculated)	1.545 Mg/m^3
Absorption coefficient	1.135 mm^{-1}
F(000)	1280
Crystal size	0.55 x 0.1 x 0.1 mm^3
Theta range for data collection	1.630 to 27.696°.
Index ranges	-12<= h<= 12, -14<= k<= 14, -33<= l<= 33
Reflections collected	87657
Independent reflections	6349 [R(int) = 0.1112]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.5519
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6349 / 205 / 392
Goodness-of-fit on F2	1.171
Final R indices [I>2sigma(I)]	R1[a] = 0.0991, wR2[b] = 0.1890
R indices (all data)	R1 = 0.1296, wR2 = 0.2027
Extinction coefficient	0.0014(3)
Largest diff. peak and hole	1.332 and -1.787 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. [b] $wR2$ $([w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with a = 0.0001 and b = 35.9234.

2.5 $[Sb(C_6F_5)_4][SbCl_6]$ (7[$SbCl_6$])

Table S5. Crystal data, data collection, and structure refinement for **7**[$SbCl_6$]

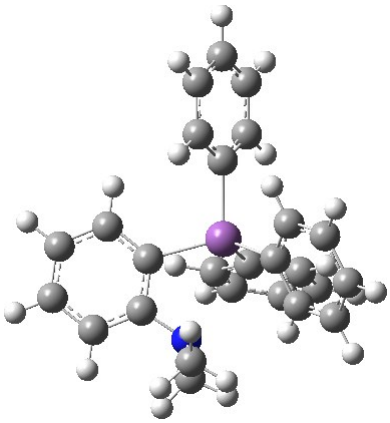
Empirical formula	C_{24} Cl_6 F_{20} Sb_2
Formula weight	1124.44
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 1 2_1 1
Unit cell dimensions	a = 17.482(4) Å
	b = 21.716(5) Å
	c = 19.115(4) Å
	a = 90°.
	b = 116.456(6)°.
	g = 90°.
Volume	6497(3) Å^3
Z	8
Density (calculated)	2.299 Mg/m^3
Absorption coefficient	2.292 mm^{-1}
F(000)	4224
Crystal size	0.426 x 0.186 x 0.092 mm^3
Theta range for data collection	1.19 to 30.66°.
Index ranges	-25< = h< = 24, -30< = k< = 31, -27< = l< = 27
Reflections collected	159165
Independent reflections	39702 [R(int) = 0.1041]
Completeness to theta = 30.66°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.82 and 0.66
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	39702 / 1 / 1874
Goodness-of-fit on F2	1.005
Final R indices [I>2sigma(I)]	R1[a] = 0.0472, wR2[b] = 0.0922
R indices (all data)	R1 = 0.0823, wR2 = 0.1167
Absolute structure parameter	0.143(16)
Largest diff. peak and hole	1.079 and -1.346 e.Å^{-3}

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2$ $([w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2])^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$ with a = 0.0407 and b = 0.00.

3 Computational Details

3.1 [(*o*-(Me_2N)C_6H_4)$SbPh_3$]$^+$ (5^+)

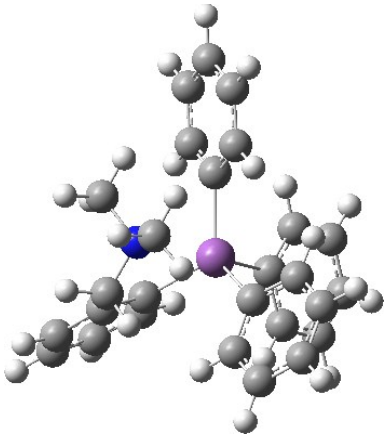
Table S6. XYZ coordinates of the optimized geometry of 5^+



Sb	0.254890	-0.029084	-0.006581	C	-0.483066	4.133824	-1.060417
N	-2.547314	0.205567	-0.761231	H	-1.241479	4.878500	-0.832194
C	2.219894	-0.780900	-0.026817	C	0.610896	4.469802	-1.861306
C	0.379618	1.889671	-0.844290	H	0.700165	5.476862	-2.260300
C	-0.880363	-1.524261	-0.933158	C	1.593822	3.522298	-2.143528
C	-0.355350	0.137937	1.987810	H	2.449785	3.788554	-2.757650
C	2.972294	-0.826269	1.152339	C	1.487490	2.229875	-1.627788
H	2.545561	-0.490193	2.096662	H	2.273501	1.504385	-1.830839
C	4.279939	-1.312685	1.121446	C	-0.959341	-0.960008	2.612355
H	4.863959	-1.349192	2.037216	H	-1.134413	-1.886417	2.065078
C	4.834473	-1.750590	-0.080989	C	-1.348834	-0.862689	3.947840
H	5.853303	-2.128646	-0.101513	H	-1.818982	-1.711677	4.437111
C	4.086165	-1.707094	-1.259013	C	-1.135159	0.323286	4.652427
H	4.518493	-2.051205	-2.195025	H	-1.441428	0.395698	5.692839
C	2.778997	-1.223376	-1.234223	C	-0.530032	1.415131	4.029120
H	2.202089	-1.200253	-2.159649	H	-0.362471	2.336525	4.580594
C	-0.432736	-2.810753	-1.242615	C	-0.136152	1.326155	2.693366
H	0.604368	-3.097398	-1.077313	H	0.335900	2.181797	2.211904
C	-1.344568	-3.731314	-1.758952	C	-2.905316	0.993952	-1.949132
H	-1.017089	-4.737079	-2.007404	H	-2.078465	0.977696	-2.667131
C	-2.678106	-3.362043	-1.952562	H	-3.087885	2.031558	-1.651146
H	-3.383193	-4.084754	-2.354946	H	-3.812516	0.607205	-2.439633
C	-3.118399	-2.076603	-1.634983	C	-3.604797	0.278086	0.255097
H	-4.159781	-1.801130	-1.789629	H	-4.578732	-0.066211	-0.127153
C	-2.211609	-1.149427	-1.119073	H	-3.710701	1.319416	0.579329
C	-0.603618	2.841870	-0.552243	H	-3.327226	-0.329859	1.121517
H	-1.457812	2.576882	0.069296				

3.2 $[(o\text{-}(Me_2NCH_2)C_6H_4)SbPh_3]^+$ (6^+)

Table S7. XYZ coordinates of the optimized geometry of 6^+



Sb	0.191784	0.031428	0.031696	H	2.812543	1.823920	-0.286460
C	-0.317577	-0.808203	1.885290	C	-0.481837	-1.152035	-1.576870
C	-0.830813	-2.109822	1.919697	C	0.453505	-1.608879	-2.512308
H	-0.965639	-2.679765	1.000225	H	1.506646	-1.351349	-2.412967
N	-2.511747	0.321955	-0.176014	C	0.038213	-2.404677	-3.580466
C	-1.158943	-2.693852	3.143546	H	0.764056	-2.755299	-4.309007
H	-1.554611	-3.705877	3.170654	C	-1.307516	-2.742479	-3.706797
C	-0.971701	-1.981721	4.328650	H	-1.637578	-3.359500	-4.538492
H	-1.231182	-2.436859	5.280941	C	-2.238355	-2.282264	-2.774352
C	-0.434041	-0.694809	4.296391	H	-3.290091	-2.540585	-2.884933
H	-0.266937	-0.149728	5.221731	C	-1.839652	-1.485225	-1.701147
C	-0.098919	-0.107262	3.076325	C	-2.852135	-1.011580	-0.681049
H	0.346188	0.886558	3.069391	H	-3.864584	-1.020675	-1.119279
C	0.033282	2.117201	-0.135574	H	-2.872111	-1.701395	0.173243
C	-0.460847	2.904060	0.909299	C	-3.253192	0.608786	1.057005
H	-0.757744	2.457508	1.856487	H	-3.001758	1.615841	1.405480
C	-0.591398	4.282425	0.735067	H	-2.983186	-0.114243	1.834221
H	-0.971601	4.895627	1.548090	H	-4.341256	0.563594	0.887351
C	-0.236658	4.870360	-0.479682	C	-2.828939	1.333490	-1.195091
H	-0.343998	5.943560	-0.614143	H	-2.589318	2.331040	-0.815721
C	0.257833	4.084987	-1.521564	H	-3.898596	1.299161	-1.457313
H	0.534705	4.542680	-2.467793	H	-2.240221	1.152108	-2.101355
C	0.397897	2.707327	-1.350686	C	4.558041	0.571103	-0.191111
H	0.781913	2.102831	-2.173289	H	5.246893	1.404604	-0.301755
C	2.789026	-1.567904	0.106972	C	5.046918	-0.726347	-0.049179
H	2.109286	-2.412202	0.230353	H	6.119049	-0.905435	-0.051708
C	2.291179	-0.265455	-0.042406	C	4.163247	-1.797342	0.101645
C	3.180904	0.804379	-0.186049	H	4.545235	-2.808216	0.218298

4 References

1. Arias Ugarte, R.; Devarajan, D.; Mushinski, R. M.; Hudnall, T. W., Antimony(v) cations for the selective catalytic transformation of aldehydes into symmetric ethers, α,β-unsaturated aldehydes, and 1,3,5-trioxanes. *Dalton Transactions* **2016,** *45* (27), 11150-11161.

2. Fujiwara, M.; Baba, A.; Matsuda, H., Selective α-cleavage cycloaddition of oxiranes with heterocumulenes catalyzed by tetraphenylstibonium iodide. *J. Heterocycl. Chem.* **1988,** *25* (5), 1351-1357.