Highly Enantioselective Ruthenium/PNNP-Catalyzed Imine Aziridination: Evidence of Carbene Transfer from a Diazoester Complex

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SUPPORTING INFORMATION

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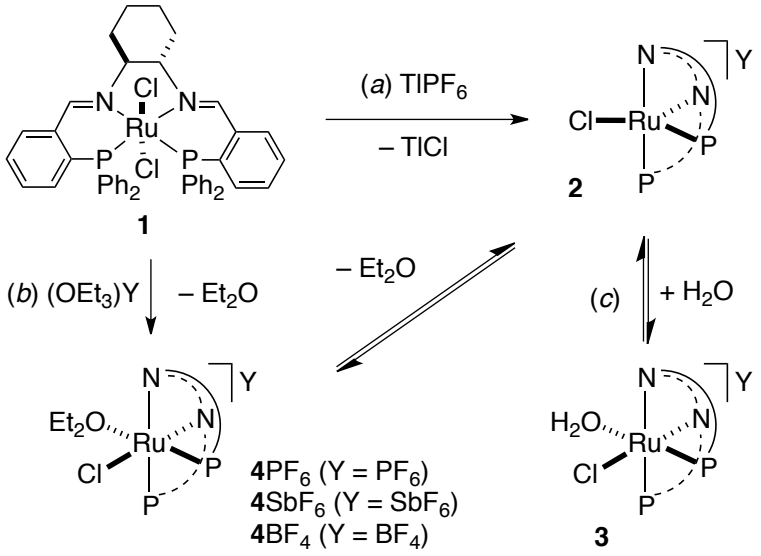
Low-Temperature NMR Spectra of [RuCl(OEt$_2$)(PNNP)]Y (Y = PF$_6$, BF$_4$, or SbF$_6$). As previously reported, [RuCl(OEt$_2$)(PNNP)]PF$_6$ (**4**PF$_6$) gives a broad ^{31}P NMR signal at δ 41 at room temperature, which decoalesces upon cooling and eventually gives a sharp AX system (δ 55.5 and 36.9) at low temperature.[1] This behavior has been explained with the dissociation of [RuCl(OEt$_2$)(PNNP)]$^+$ to give OEt$_2$ and the 16-electron species [RuCl(PNNP)]$^+$ (**2**), which is a fast equilibrium on the NMR time scale at room temperature and is frozen out at –40 °C (Scheme 3 of main paper):



The low-temperature ^{31}P NMR spectra of the BF_4^- and SbF_6^- salts of **4** contain an additional, broad signal at ca. δ 49, which is nearly indistinguishable in the spectrum of **4**PF$_6$. Interestingly, the nature of the counterion affects the temperature at which this signal appears (–80, –60, and –20 °C for **4**PF$_6$, **4**BF$_4$, and **4**SbF$_6$, respectively), as well as its intensity at –80 °C (5, 26, and 45% of the total integrated intensity, see Figures S1-S4). The chemical shift of this signal (δ 49) is indicative of an octahedral complex of the type *trans*-[RuCl(Y)(PNNP)],[1] in which the counterion Y (Y = BF_4^- or SbF_6^-) is associated with the 16-electron complex

[RuCl(PNNP)]$^+$ in the low-polar CD_2Cl_2 solvent. We have previously suggested[1] that the inequivalent phosphines of complexes of the type *trans*-[RuCl(Y)(PNNP)] resonate in a δ region centered at about δ 48, which is the chemical shift of *trans*-[$RuCl_2$(PNNP)],[2] because they are *trans* to the same donor type, that is, imine. Therefore, these complexes typically give relatively tight AB spin systems. An example thereof is the alkyl complex *trans*-[RuCl(CH_2COOEt)(PNNP)] (**11**) (see Figure S6 below). In contrast, in *cis*-β complexes such as [RuCl(OEt_2)(PNNP)]$^+$ (**4**), one of the phosphines resonates at a much higher frequency (*ca*. δ 63) than the other one (*ca*. δ 45). This indicates that these P donors are *trans* to ligands with a largely different *trans* influence, such as aqua and imine.[1] The same pattern has been observed for the ^{31}P NMR chemical shifts in [Ru(OH_2)$_2$(PNNP)]$^{2+}$.[3]

As the signal at δ 49 observed in the low-temperature spectra of [RuCl(OEt_2)(PNNP)]Y is broad even at –80 °C, which prevents further studies by 2D NMR spectroscopy, the formulation of the corresponding species as *trans*-[RuCl(Y)(PNNP)] remains tentative. Furthermore, the low-temperature ^{19}F NMR spectra show the essentially unperturbed signals of the free anions at δ –73 (PF_6^-) and –152 (BF_4^-) (unsurprisingly, no signal was observed for SbF_6^-).[4] Overall, the low-temperature NMR spectra suggest that the dissociation of the Et_2O adduct **4** into five-coordinate **2** and Et_2O is the main dynamic process in solution and fail to give conclusive evidence of the cation/anion interactions evoked by the counterion effect observed in catalysis.

Figure S1. Effect of the counterion Y on the NMR spectra of [RuCl(OEt$_2$)(PNNP)]Y (Y = PF_6, **4**PF_6; BF_4, **4**BF_4; or SbF_6, **4**SbF_6) at –80 °C (202 MHz, CD_2Cl_2). In the spectra of **4**BF_4 and **4**SbF_6, "A" denotes the unknown signal at δ 49. The signals of the aqua complex *trans*-[RuCl(OH$_2$)(PNNP)]$^+$ (present in traces in **4**PF_6 and **4**SbF_6) are marked "*". The other signals belong to unknown impurities.

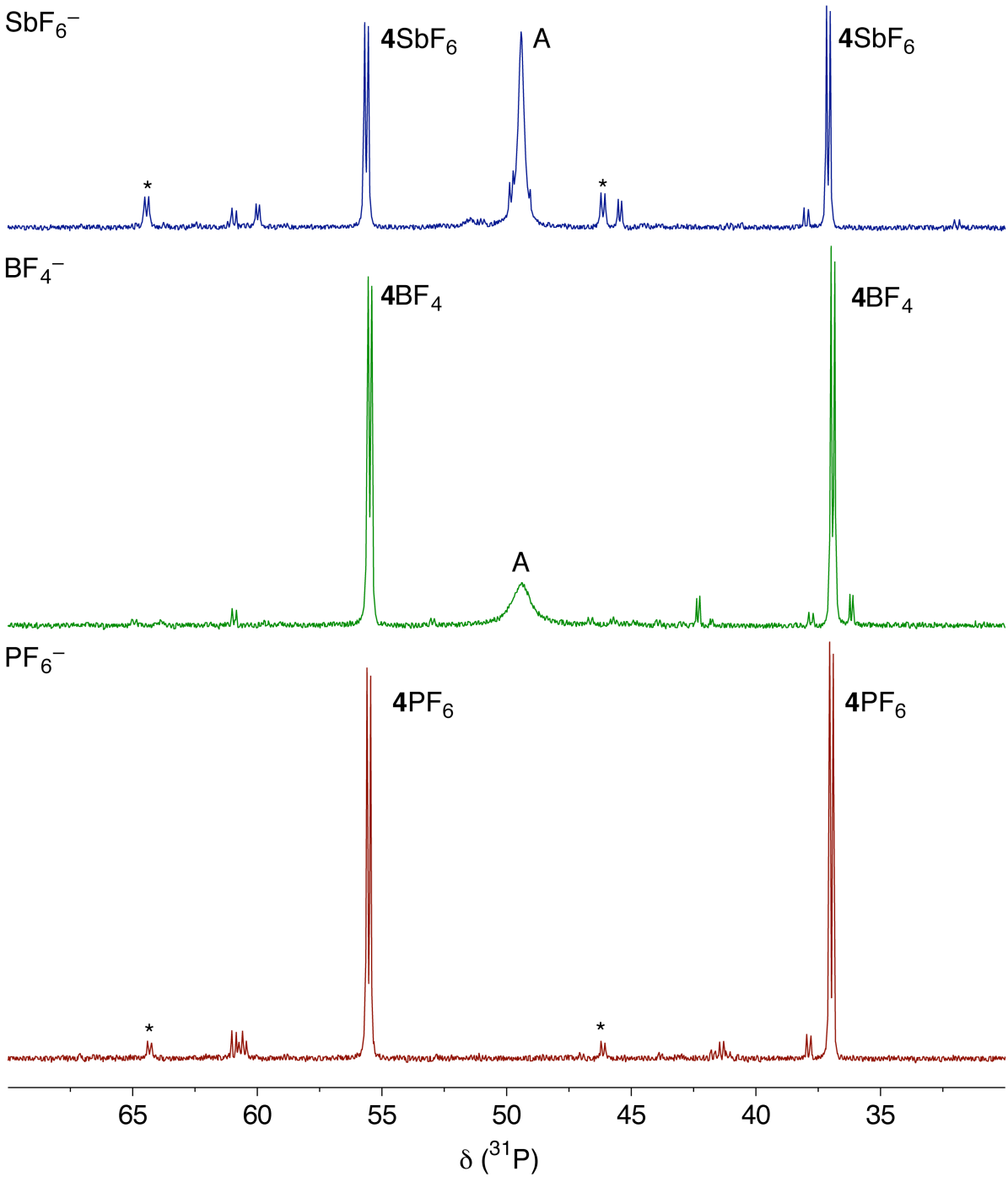


Figure S2. ^{31}P NMR spectra of [RuCl(OEt_2)(PNNP)]PF_6 (**4**PF_6) at different temperatures (202 MHz, CD_2Cl_2). The signals of the aqua complex *trans*-[RuCl(OH_2)(PNNP)]$^+$ (traces) are marked "*". The other signals belong to unknown impurities.

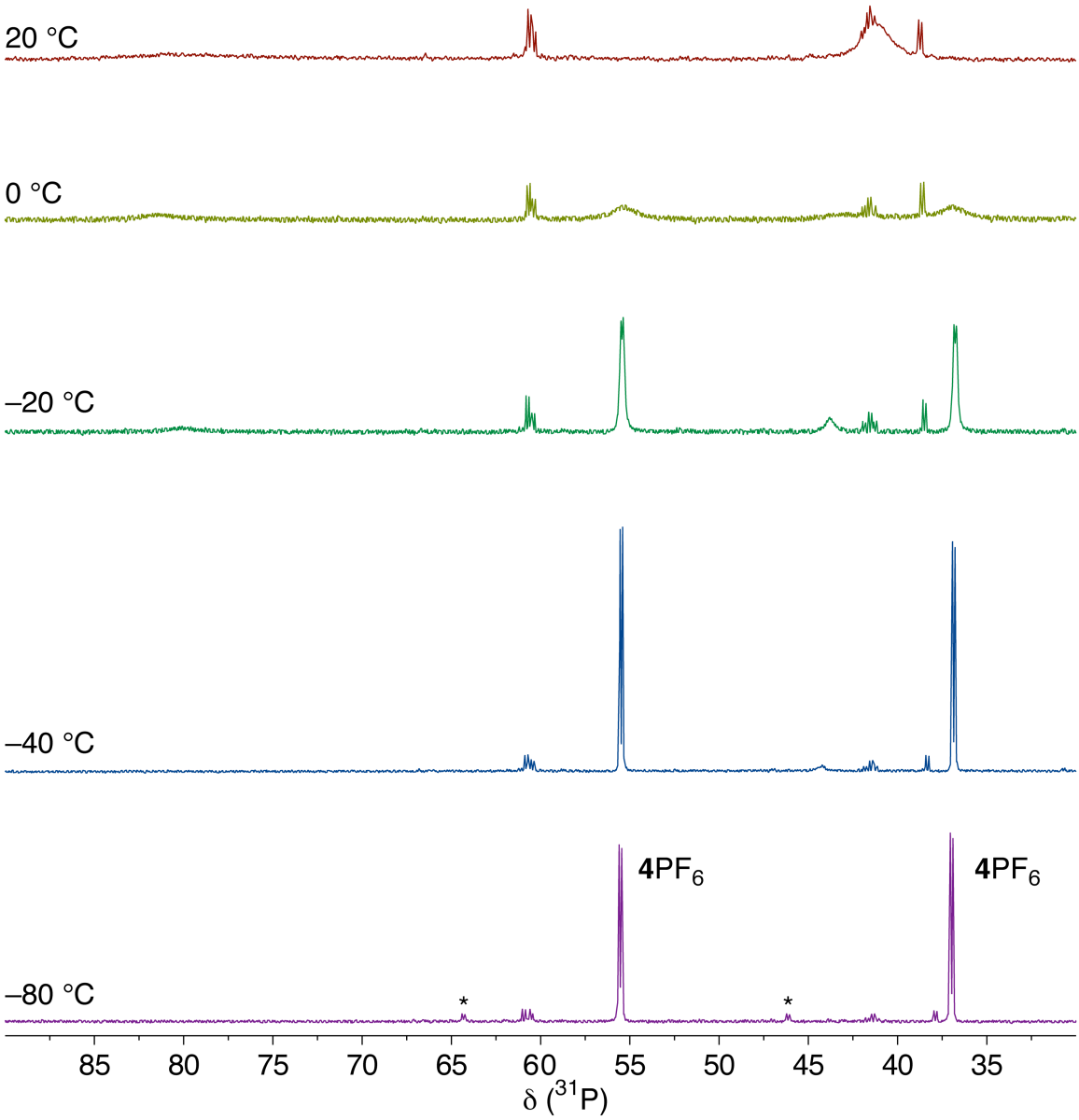


Figure S3. ^{31}P NMR spectra of $[RuCl(OEt_2)(PNNP)]BF_4$ (**4**BF_4) at different temperatures (202 MHz, CD_2Cl_2). "A" denotes the unknown signal at δ 49. The other signals belong to unknown impurities.

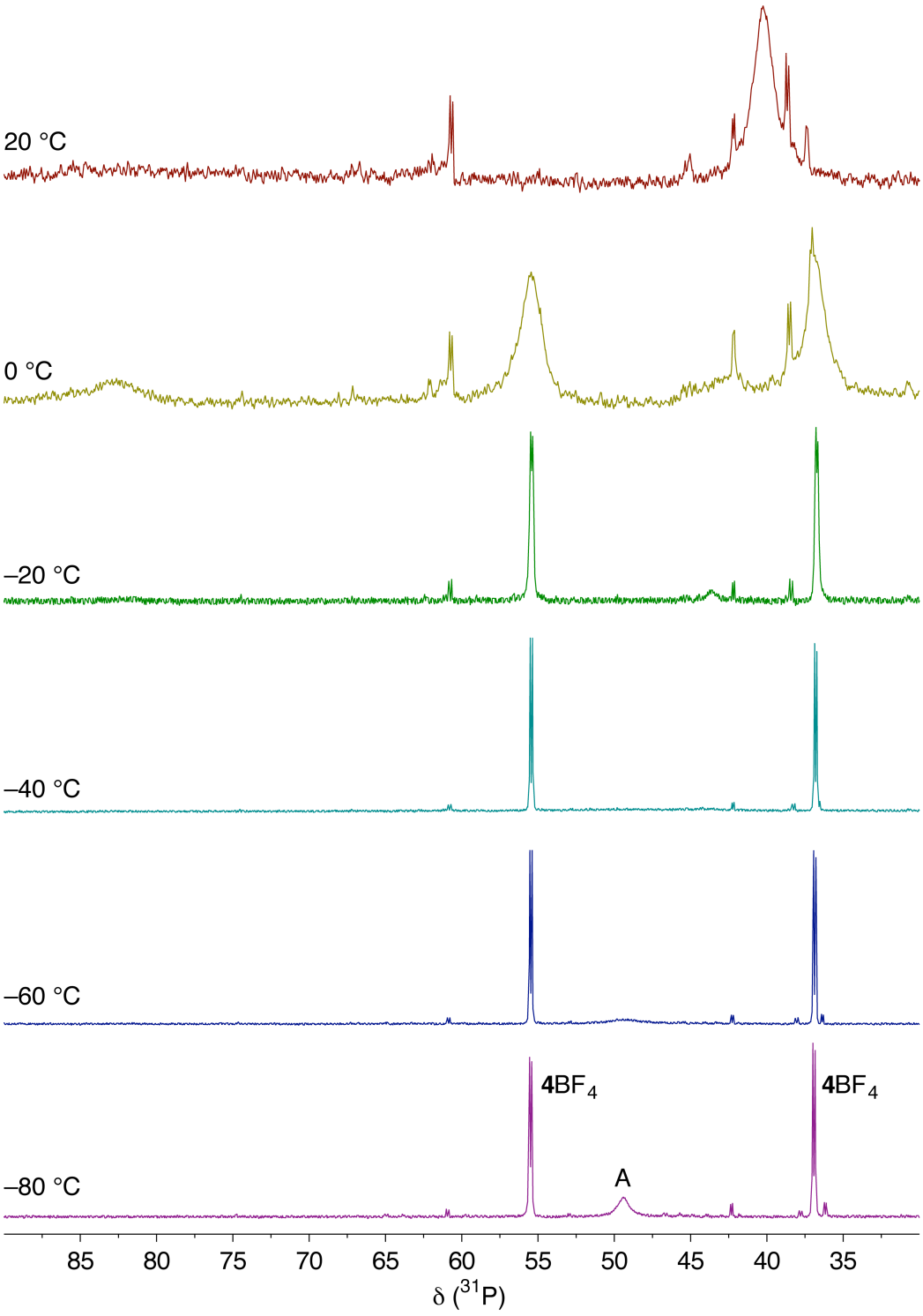
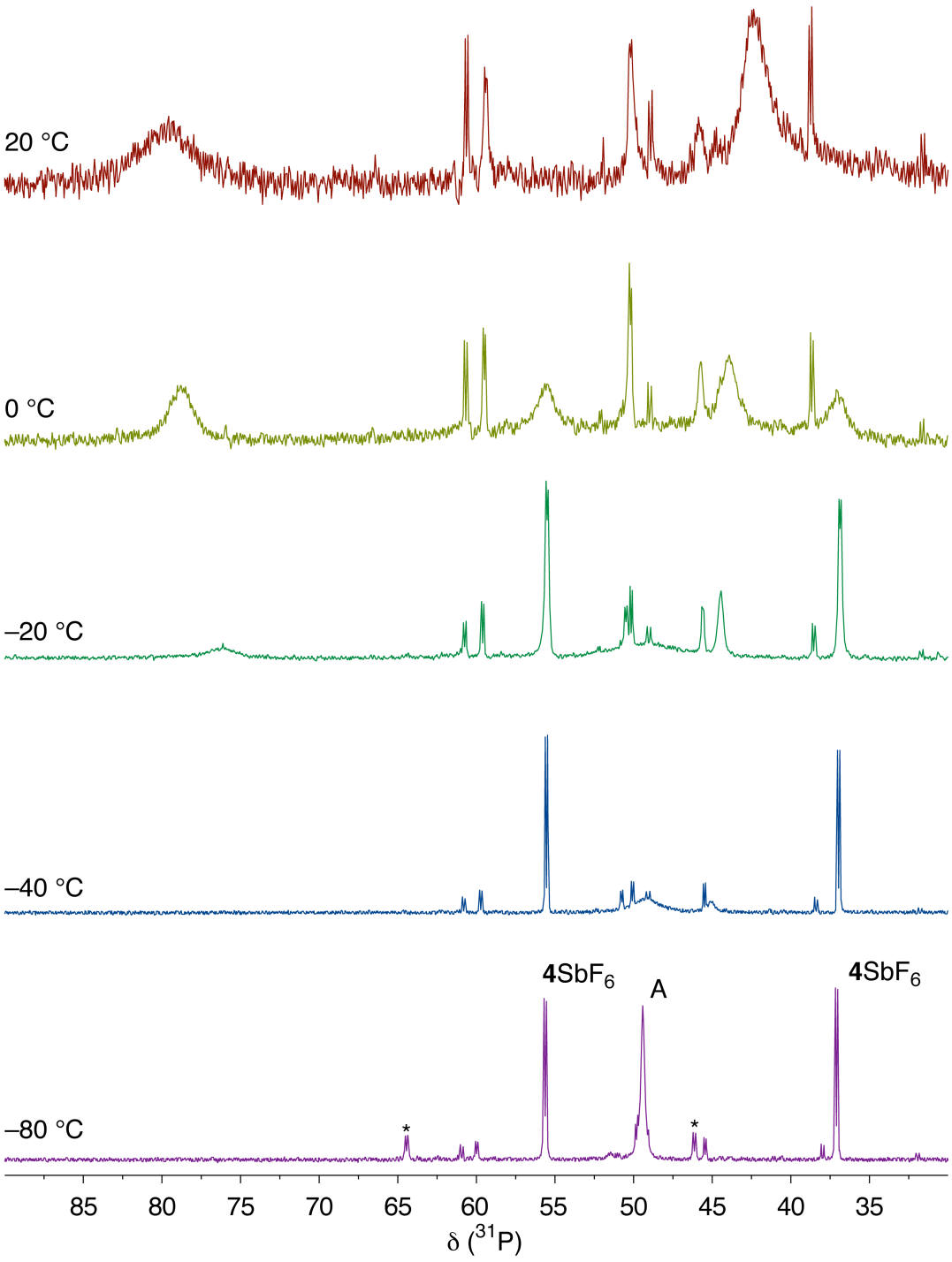


Figure S4. ^{31}P NMR spectra of $[RuCl(OEt_2)(PNNP)]SbF_6$ (**4**SbF_6) at different temperatures (202 MHz, CD_2Cl_2). "A" denotes the unknown signal at δ 49. The signals of the aqua complex *trans*-$[RuCl(OH_2)(PNNP)]^+$ (traces) are marked "*". The other signals belong to unknown impurities.



Synthesis of ^{13}C- and ^{15}N-Labeled EDA

Ethyl 2-^{13}C-Glycine Hydrochloride.[5] 2-^{13}C-glycine (98% 2-^{13}C, 0.50 g, 4.85 mmol) was suspended in ethanol, and the mixture cooled down to –20 °C (ice-salt bath). $SOCl_2$ (0.58 mL, 8.00 mmol) was added, the temperature raised to room temperature, and another equivalent of solid 2-^{13}C-glycine (0.50 g, 4.85 mmol) was slowly added. The mixture was refluxed for 2 h. After cooling the colorless solution to room temperature, the solvent was evaporated under reduced pressure. The resulting white solid was dried in high vacuum for 2 h and recrystallized from ethanol. Yield: 1.10 g, 95 %. m.p. = 145–147 °C.

Synthesis of $N_2{}^{13}CHCO_2Et$ (^{13}C-EDA).[6] Ethyl 2-^{13}C-glycine hydrochloride (1.00 g, 7.1 mmol) was mixed with H_2O (2 mL) and CH_2Cl_2 (4 mL) in a two-necked flask equipped with septum, argon inlet, and internal thermometer. The colorless mixture was cooled down to –5 °C, and an ice-cold solution of $NaNO_2$ (0.59 g, 8.5 mmol) in H_2O (2 mL) was added. The resulting mixture was cooled to –9 °C, and a 5% (w/w) H_2SO_4 solution (0.679 g) was slowly added. As higher temperature might decrease the yield, the temperature was never let to above +1 °C during the addition. Thereafter, the mixture was stirred for 20 min between –9 °C and +1 °C, and then poured into an ice-cold separating funnel. The yellow organic layer was recovered, and the water phase was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic phase was washed with a 5% ice-cold $NaHCO_3$ solution (6 mL), the organic phase was separated, and the water phase was extracted with CH_2Cl_2 (2 × 3 mL). The combined organic phase was dried over Na_2SO_4, filtered, and the solvent was removed under reduced pressure. The resulting yellow oil was dried in vacuum for 15 min, and the product distilled with cold distillation under high vacuum. Yield: g (0.74 g, 81%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 4.80 (*d*, 1H, $^1J_{C,H}$ = 205 Hz, $N_2{}^{13}CH$), 4.23

(q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 1.30 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3). C NMR (126 MHz, CD_2Cl_2, 25 °C): δ 46.3 (s, N_2*C*H). Low-temperature data: ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ 5.01 (d, 1H, $^1J_{C,H}$ = 205 Hz, $N_2{}^{13}$C*H*), 4.72 (d, 1H, $^1J_{C,H}$ = 205 Hz, $N_2{}^{13}$C*H*), 4.20 (q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 4.17 (q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 1.29 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3), 1.25 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3). ^{13}C NMR (126 MHz, CD_2Cl_2, –78 °C): δ 47.5 (s, N_2*C*H), 46.5 (s, N_2*C*H).

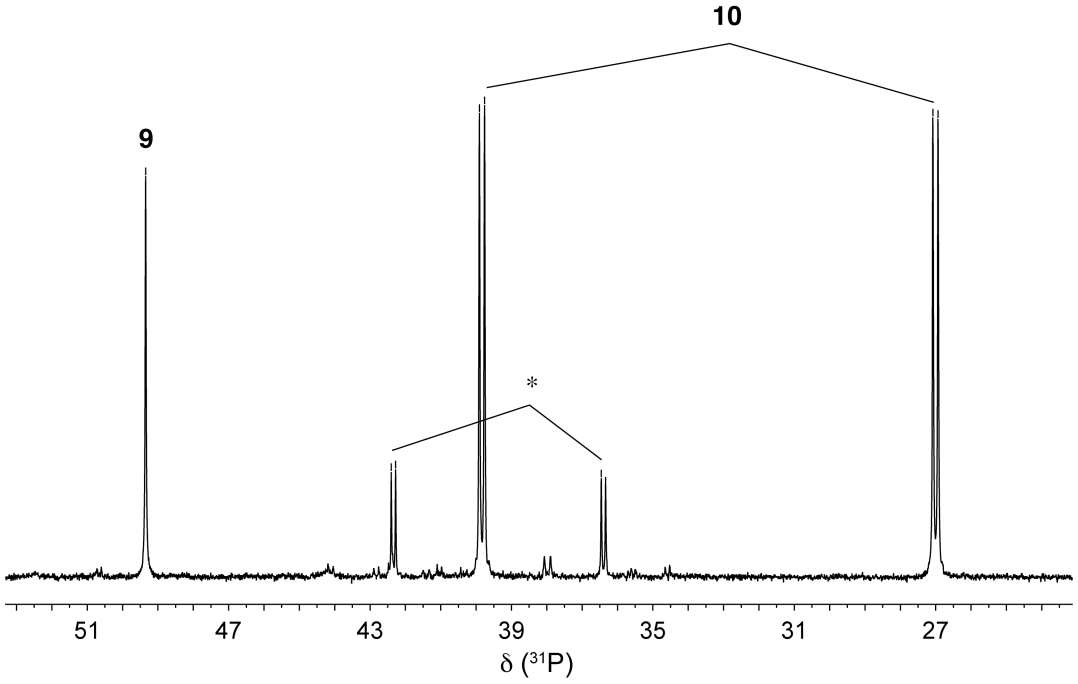
Synthesis of ^{15}*N*NCHCO$_2$Et. (^{15}N-EDA).[6] Terminally ^{15}N-labeled ^{15}N-EDA was prepared analogously to ^{13}C-EDA from ethyl glycine hydrochloride (1.00 g, 7.1 mmol) and Na$^{15}NO_2$ (98% ^{15}N, 0.60 g, 8.5 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 4.80 (*br s*, 1H, N_2C*H*), 4.23 (q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 1.30 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3). ^{15}N NMR (50.7 MHz, CD_2Cl_2, 25 °C): δ 4.05 (*br s*, 1N, ^{15}*N*NC). Low-temperature data: ^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ 5.04 (s, 1H, N_2C*H*), 4.74 (s, 1H, N_2C*H*), 4.20 (q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 4.17 (q, $^2J_{H,H'}$ = 7.1, 2H, OCH_2CH$_3$), 1.29 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3), 1.25 (t, $^2J_{H,H'}$ = 7.1, 3H, OCH$_2$CH_3). ^{15}N NMR (50.7 MHz, CD_2Cl_2, –78 °C): δ 7.6 (s, 1N, ^{15}*N*NC), –1.29 (s, 1N, ^{15}*N*NC).

NMR Spectroscopic Studies: General. The reactions described below were run under argon in NMR tubes fitted with serum septa and were monitored by NMR spectroscopy as detailed below. Additions of reagents were performed by microsyringe. A 2-PrOH bath at the appropriate temperature was used to keep the sample temperature at the values indicated below during all manipulations and transfers from and to the spectrometer.

Experiment 1: [RuCl(OEt$_2$)(PNNP)]PF$_6$ (4PF$_6$) + EDA, then imine 5a (1:1:1). Complex **4**PF$_6$ was prepared by treating [RuCl$_2$(PNNP)] (**1**) (28.0 mg, 0.034 mmol) with (Et$_3$O)PF$_6$ (8.4 mg, 0.034 mmol) in CD_2Cl_2 (0.5 mL). After stirring the solution at room temperature overnight, the formation of **4**PF$_6$ was confirmed by the ^{31}P and ^{1}H NMR spectra at 298 and –78 °C. Then, EDA (3.7 μL, 0.034 mmol) was added at –78 °C, and quantitative

conversion of **4**PF_6 to give the carbene complex *trans*-[RuCl(CHCOOEt)(PNNP)]$^+$ (**10**) (71%, δ: 39.8 and 27.0, $^2J_{P,P'}$ = 29.8 Hz)),[7] dinitrogen complex **9** (15%, δ 49.2, see below), and the AB pattern (marked "*") of an unkown impurity (14%, δ 42.3 and 36.3 (*d*, $^2J_{P,P'}$ = 24.8 Hz)) was observed (Figure S5).

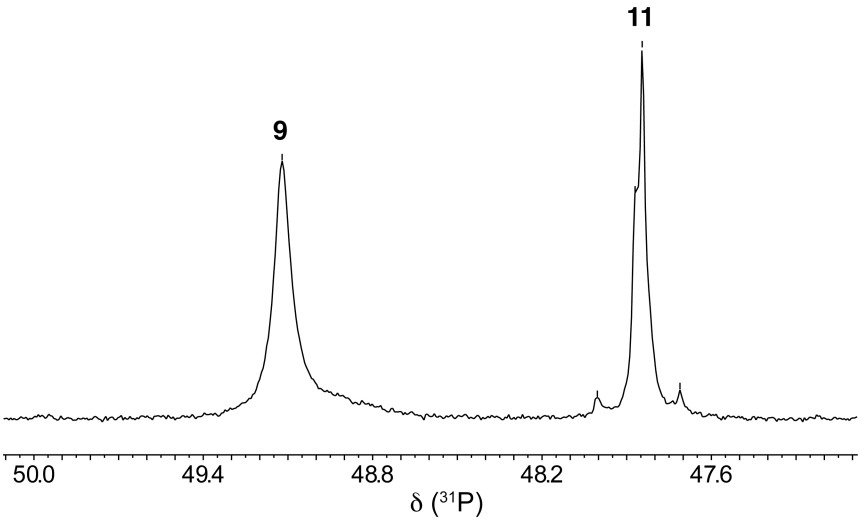
Figure S5. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2, –78 °C) immediately after the addition of EDA (1 equiv) to **4**PF_6 at –78 °C, showing carbene complex **10** (71%) along with dinitrogen complex **9** (15%) and an unknown species (14%) whose signals are marked "*".



After adding imine **5a** (0.0091 g, 0.034 mmol) to this solution at –78 °C, the ^{31}P NMR spectrum remained unchanged in the temperature range between –78 °C and room temperature. After 4 h at room temperature, a (^{13}C,^{1}H)-HMQC experiment showed that no aziridine had formed. The ^{31}P NMR spectrum of the reaction solution shows no signals attributable to the

carbene complex **10** (Figure S6). The newly appeared tight AB pattern at δ 47.9 (*d*, *J* = 28.2 Hz) and 47.8 (*d*, *J* = 28.2 Hz) (202 MHz, CD_2Cl_2, 25 °C) was assigned to the alkyl complex *trans*-[RuCl(CH_2COOEt)(PNNP)] (**11**) on the basis of the ^{1}H NMR signals of the RuCH_2COOEt moiety, which were identified by means of (^{31}P,^{1}H)-HMQC and (^{13}C,^{1}H)-HMQC experiments: ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 3.79 (*d*, 1H, *J* = 11.2 Hz, RuC*H*H'COOEt), 3.36 (*d*, 1H, *J* = 11.2 Hz, RuCH*H'*COOEt.

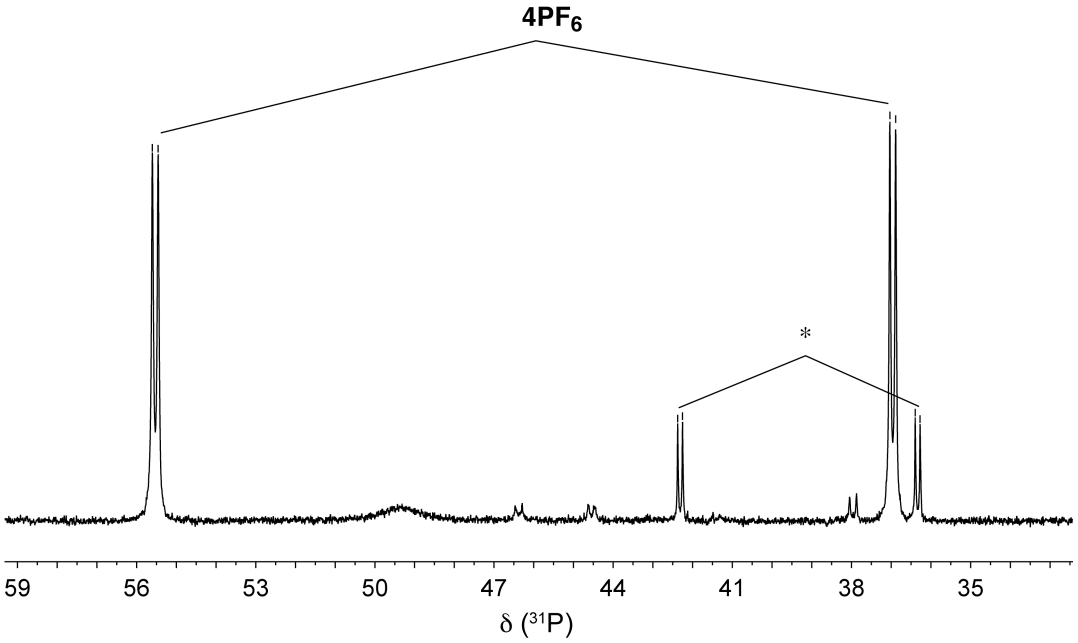
Figure S6. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2, 25 °C) of the same reaction solution after 4 h at 25 °C showing the signals of *trans*-[RuCl(CH_2COOEt)(PNNP)] (**11**), the decay product of 10, and of the N_2 complex **9**.



Experiment 2: [RuCl(OEt_2)(PNNP)]PF_6 (4PF_6) + imine 5a, then EDA (1:1:1). Complex **4PF_6** was prepared by treating [$RuCl_2$(PNNP)] (**1**) (30.0 mg, 0.036 mmol) with (Et_3O)PF_6 (9.0 mg, 0.036 mmol) in CD_2Cl_2 (0.5 mL). After stirring the solution at room temperature overnight, the formation of **4PF_6** was confirmed by the ^{31}P and ^{1}H NMR spectra at 298 and –78 °C. Imine **5a** (9.8 mg, 0.036 mmol) was added to the mixture at room temperature,

and the ^{31}P and ^{1}H NMR spectra were recorded at 25 °C and at –78 °C. Along with unreacted **4PF$_6$**, the signals (marked "*") of the unknown product described above were observed (Figure S7). This species is not an imine complex, as confirmed by (^{1}H,^{1}H)-NOESY analysis and by the observation that it is formed in small amounts also in the reaction of **4PF$_6$** with EDA, that is, in the absence of imine (see Experiment 1, Figure S5). After extracting the sample from the NMR spectrometer, EDA (9.0 mL, 0.036 mmol) was added by microsyringe to the solution at –78 °C. The sample was transferred immediately to the precooled NMR spectrometer (–78 °C) and the ^{31}P and ^{1}H NMR spectra were recorded.

Figure S7. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2, –78 °C) of the reaction solution of **4PF$_6$** with imine **5a** (1 equiv). Unreacted **4PF$_6$** is the main species in solution, along with the unknown species marked "*".

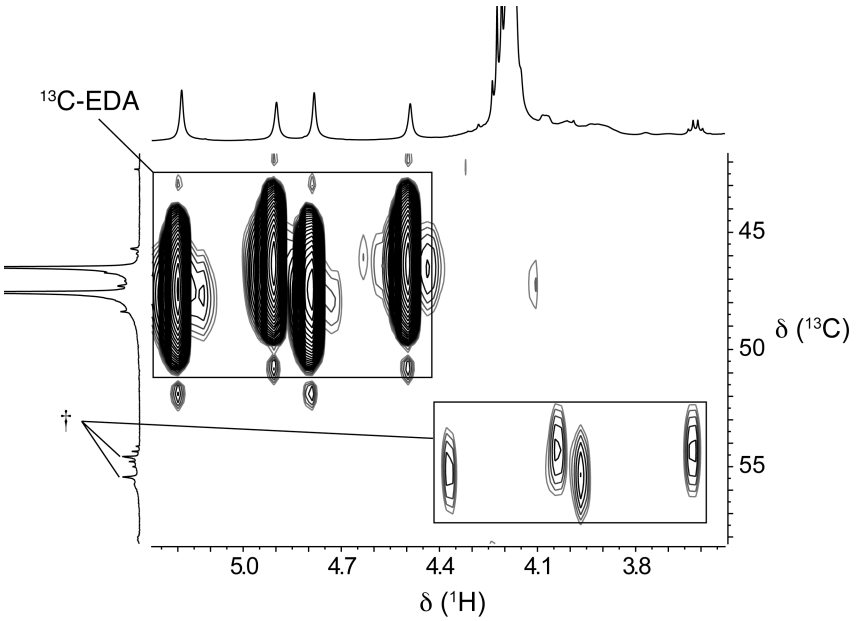


The ^{31}P NMR spectrum of the reaction solution (not shown) indicates that **4PF$_6$** was quantitatively converted to the carbene complex *trans*-[RuCl(CHCOOEt)(PNNP)]$^+$ (**10**) (74%)[7] and to the dinitrogen complex **9** (15%). Upon warming to room temperature in 20 °C steps, the composition of the solution did not change, and no aziridine was formed, as indicated by (^{13}C,^{1}H)-HMQC experiments. The signals of impurity (signal "*", 11%) remained unchanged up to room temperature and disappeared within 4 h time. After 4 h at room temperature, all the species had converted to dinitrogen complex **9** (60%) and to the alkyl complex [RuCl(CH$_2$COOEt)(PNNP)] (**11**, 40%, δ 47.8, AB system) already observed in Experiment 1.

Experiment 3: [RuCl(OEt$_2$)(PNNP)]PF$_6$ (4PF$_6$) + imine 5a, then ^{13}C-EDA (1:1:10). Complex **4PF$_6$** was prepared by treating [RuCl$_2$(PNNP)] (**1**) (24.3 mg, 0.029 mmol) with (Et$_3$O)PF$_6$ (7.3 mg, 0.029 mmol) in CD$_2$Cl$_2$ (0.5 mL). After stirring the solution at room temperature overnight, the formation of **4PF$_6$** was confirmed by the ^{31}P and ^{1}H NMR spectra at 25 °C and –78 °C. Then, imine **5a** (7.9 mg, 0.029 mmol) was added to the solution, which was cooled again. EDA (32.2 μL, 0.293 mmol) was added at –78 °C, and the ^{13}C, ^{1}H, and ^{31}P NMR spectra were run at the same temperature, as well as a (^{13}C,^{1}H)-HMQC experiment. The (^{13}C,^{1}H)-HMQC correlation showed the signals of unreacted ^{13}C-EDA as major product (Figure S8).

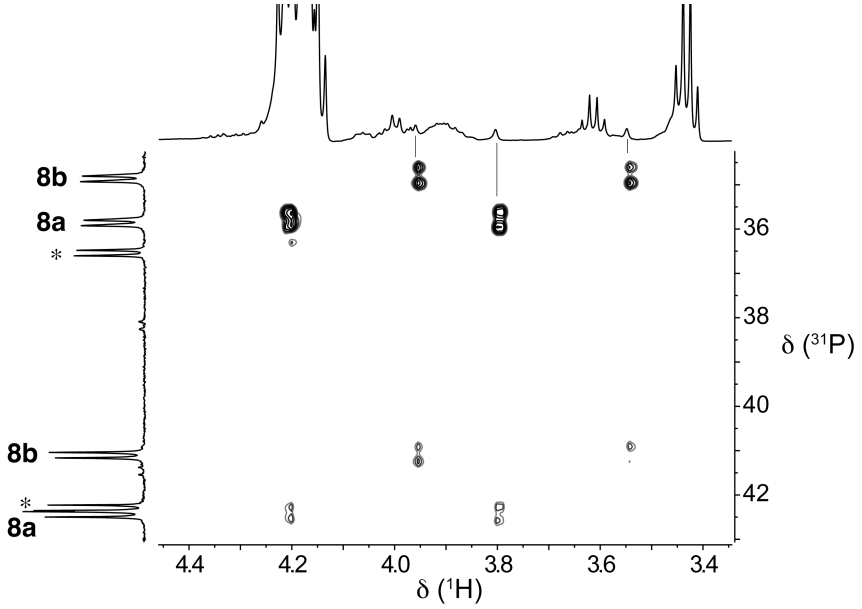
The signal (marked "†") of an additional ^{13}C-containing species with a $J_{C,H}$ comparable to that of ^{13}C-EDA was present, but disappeared after heating to –20 °C. As this signal has never been observed at temperatures higher than –20 °C, we deem it immaterial for the further discussion. The ^{31}P NMR spectrum showed the quantitative conversion of the Et$_2$O adduct **4PF$_6$** to several unknown species. Outside the spectral range shown in Figure S8, traces of *trans*-[RuCl(^{13}CHCOOEt)(PNNP)]$^+$ (**10**) and of ^{13}C-labeled dietyl maleate (**7**) were detected.

Figure S8. Section of a (^{13}C,^{1}H)-HMQC experiment after EDA addition (10 equiv) to a solution containing complex **4PF$_6$** and imine **5a** (1 equiv) at –78 °C (500 MHz (^{1}H), CD_2Cl_2). The signal marked "†" belongs to an unknown species (see footnote 25 of paper).



As no aziridine **6a** was observed at –80 °C, the sample was carefully warmed up to –20 °C. At this temperature, a (^{13}C,^{1}H)-HMQC correlation experiment indicated that a small amount of ^{13}C-aziridine had formed. To slow down the reaction, the sample was cooled to –60 °C, at which temperature a (^{13}C,^{1}H)-HMQC experiment revealed new signals that we assign to coordinated ^{13}C-EDA in [RuCl(^{13}C-EDA)(PNNP)]PF_6 (**8**) (see Figure 2 of main paper). At the same temperature, the ^{31}P NMR spectrum shows the signals of the dinitrogen complex **9** (31%) and the same AB system observed in Experiment 2 upon addition of imine to the Et_2O adduct **4PF$_6$** (signal marked "*", 9%) (see Figure 3 of main paper). The main feature of the spectrum consists of two AB patterns in equal ratio, **8a** (31%) and **8b** (31%) (δ(**8a**) 42.4 (*d*, $^{2}J_{P,P'}$ = 25.3 Hz) and 35.8 (*d*, $^{2}J_{P,P'}$ = 25.2 Hz); δ(**8b**) 41.1 (*d*, $^{2}J_{P,P'}$ = 25.3 Hz), 34.8 (*d*, $^{2}J_{P,P'}$ = 25.4 Hz)), which we assign to the diazoester complex *trans*-[RuCl($N_2{}^{13}$CHCOOEt)(**1a**)]$^{+}$ (^{13}C-**8**).

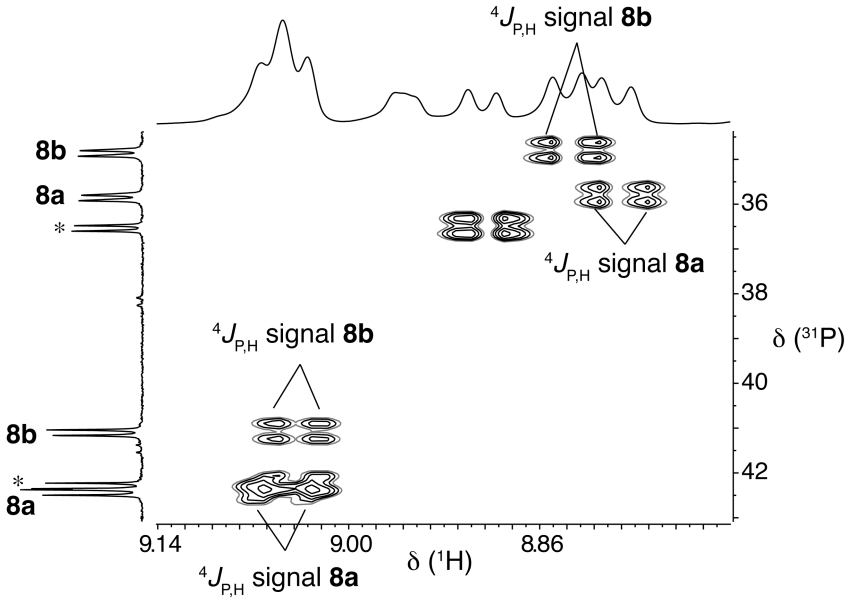
Figure S9. Section of (^{31}P,^{1}H)-HMQC NMR spectrum of EDA complex ^{13}C-**8** (500 MHz (^{1}H), CD_2Cl_2, –60 °C). The signals of ^{13}C-**8** are labeled "**8a**" and "**8b**", those marked with "*" belong to the impurity seen in Figures S5 and S7.



Despite the fact that no NOESY contacts were detected between the sp^2 diazoester proton ($N_2{}^{13}C$-*H*) and any other signal of the PNNP ligand, the diazoester complex **8** was identified unambiguously by (^{31}P,^{1}H)-HMQC and by the use of ^{15}N labeled EDA (see Experiment 4 below). The (^{31}P,^{1}H)-HMQC spectrum showed cross peaks between the ^{31}P signals and the $N_2{}^{13}C$-*H* proton of the coordinated diazoester in **8a** and **8b**, which had been previously identified by the (^{13}C,^{1}H)-HMQC spectrum of **8** at –60 °C (Figure S9). Additionally, this spectrum shows a $^{4}J_{P,H}$ coupling constant of about 18 Hz for both imine H atoms (despite their signals are overlapped with those of the other Ru/PNNP complexes in solution (Figure S10). This is diagnostic of two *trans*-P–Ru–N moieties and hence of the *trans* configuration.[1] Finally, (^{1}H-^{1}H)-NOESY and (^{31}P,^{1}H)-HMQC experiments indicate that the species giving signals **8a** and **8b** are exchanging

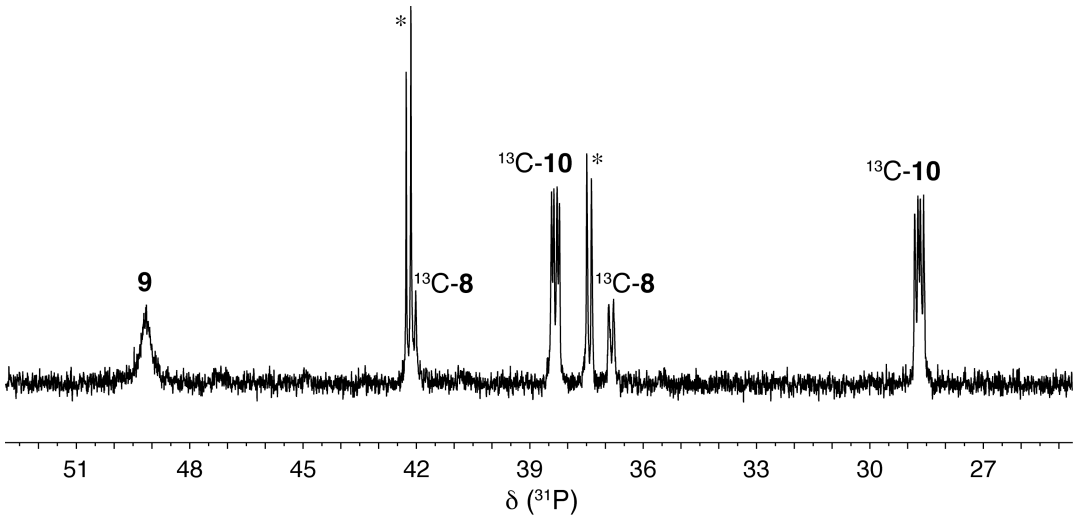
with each other even at –40 °C. Again, we attribute this observation to the interconversion between the *s-cis* and *s-trans* isomers of the CHCOOEt moiety of complex **8** (see above).

Figure S10. Section of the (^{31}P,^{1}H)-HMQC spectrum of *trans*-[RuCl(EDA)(PNNP)]$^{+}$ (**8**) (500 MHz, CD_2Cl_2, –60 °C) showing coupling of both imine H atoms to phosphorus.



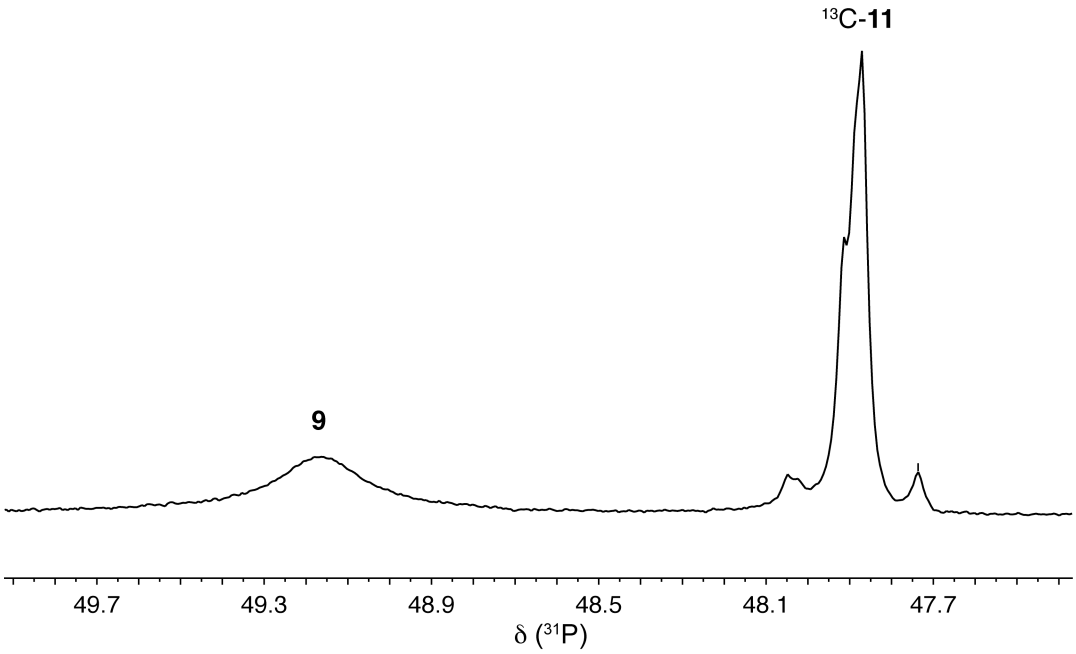
Upon raising the temperature in 20 °C-steps, the ^{31}P NMR signals of the rotamers of the EDA complex **8** coalesced at –20 °C to give the a single well-resolved AB system at 20 °C (**8**, δ 42.1 (*d*, $^{2}J_{P,P'}$ = 24.2 Hz), 36.9 (*d*, $^{2}J_{P,P'}$ = 24.2 Hz)) (see Figure 4 of paper). In the temperature interval between 253 and 20 °C, imine **5a** was fully converted to aziridine **6a**, and the signals of free ^{13}C-EDA disappeared from the ^{1}H and ^{13}C NMR spectra. After few minutes at 20 °C, the ^{13}C-EDA complex **8** was converted to the carbene complex *trans*-[RuCl(^{13}CHCOOEt)(PNNP)]$^{+}$ (^{13}C-**10**) (Figure S11).

Figure S11. ^{31}P NMR spectrum of the reaction solution of **4PF$_6$** with imine **5a** (1 equiv) and ^{13}C-EDA (10 equiv) after few minutes at room temperature (202 MHz, CD_2Cl_2, 25 °C). The main species in solution is the carbene complex ^{13}C-**10**. The other signals belong to the EDA complex ^{13}C-**8** (in the fast exchange regime), dinitrogen complex **9**, and to the unknown impurity "*" (see Figures S5 and S7).



The ^{31}P and ^{13}C NMR spectra indicated that the conversion of **8** to **10** begins after the disappearance of free ^{13}C-EDA from the reaction solution and is quantitative after 15 min. Then, the *trans*-carbene complex **10** decomposes within 4 h to the alkyl derivative [RuCl($^{13}CH_2COOEt$)(PNNP)] (**11**). The main signals in the ^{31}P NMR spectrum after 10 h at 20 °C are those of the dinitrogen complex **9** (55%) at δ 49.2 and of alkyl complex **11** at ca. δ 47.9 (45%, AB part of an ABX system, where X is ^{13}C) (Figure S12). As previously observed in Experiment 1, the alkyl complex **10** was detected as the main product after 3 days at 25 °C. At present, we have no explanation for its formation from *trans*-carbene **9**.

Figure S12. ^{31}P NMR spectrum of the reaction solution in Figure S11 after 4 h at room temperature (202 MHz, CD_2Cl_2, 25 °C) showing the signals of alkyl complex **11** and of the N_2 complex **12**.



Experiment 3 was repeated three times with essentially the same results. In the last run, the ^{13}C NMR signals of the coordinated diazoester of the EDA adduct **8** at δ 58.0 were irradiated at 0 °C, which left the intensity of the signal of free $N_2{}^{13}CHCOOEt$ unchanged, indicating that the exchange between free and coordinated EDA is slow on the NMR time scale at this temperature.

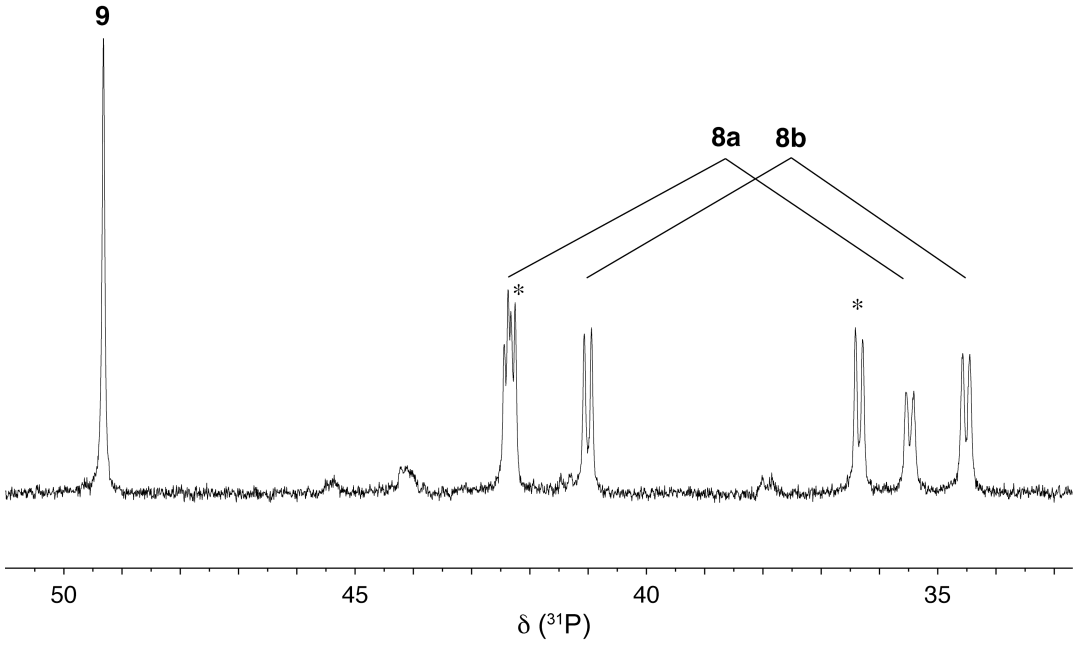
Experiment 4: [RuCl(OEt$_2$)(PNNP)]PF$_6$ (4PF$_6$) + imine 5a, then ^{15}N-EDA (1:1:10). To prove the coordination of EDA to ruthenium, the former experiment was repeated with ^{15}N-labeled EDA (10 equiv) instead of ^{13}C-EDA. The Ru:imine:^{15}N-EDA ratio was 1:1:10. [$RuCl_2$(PNNP)] (**1**) (21.5 mg, 0.026 mmol) and (Et_3O)PF_6 (6.4 mg, 0.026 mmol) were dissolved in CD_2Cl_2 (0.5 mL) and stirred overnight at room temperature, and ^{31}P and ^{1}H NMR spectra were recorded at 25 °C and –78 °C. Imine **5a** (7.0 mg, 0.026 mmol) was added to the solution at room

temperature. Then, after cooling the sample to –78 °C, ^{15}N-EDA (28.4 μL, 0.259 mmol) was added at –78 °C, and the sample was transferred to the precooled NMR spectrometer.

After warming to –20 °C for 15 min to ensure aziridine formation, the sample was cooled at –60 °C. A (^{13}C,^{1}H)-HMQC experiment confirmed the formation of the aziridine. The ^{31}P NMR spectrum at the same temperature (–60 °C) showed that the Et_2O adduct **4PF$_6$** was quantitatively converted to the diazoester complex **8** (signals **8a**+**8b**), the unknown impurity at δ 42.3 and 36.3, and to the dinitrogen complex **9** with the same pattern observed in Experiment 3. As no P,N coupling was detected, the sample was further cooled down to –80 °C. At this temperature, the high-frequency ^{31}P NMR signals of *trans*-[RuCl($^{15}N_2$CHCOOEt)(PNNP)]$^+$ (^{15}N-**8**) showed coupling to ^{15}N (δ 42.4 and 41.1, $^2J_{P,P'}$ = 25.3, $^2J_{P,N}$ = 2.4 Hz for both) (see Figure 5 of paper). Additionally, the ^{15}N NMR spectrum at –60 °C showed two broad signals corresponding to the two isomers of ^{15}N-**8** along with free ^{15}N-EDA, ^{15}NN, and coordinated ^{15}NN (see Figure 6 of paper).

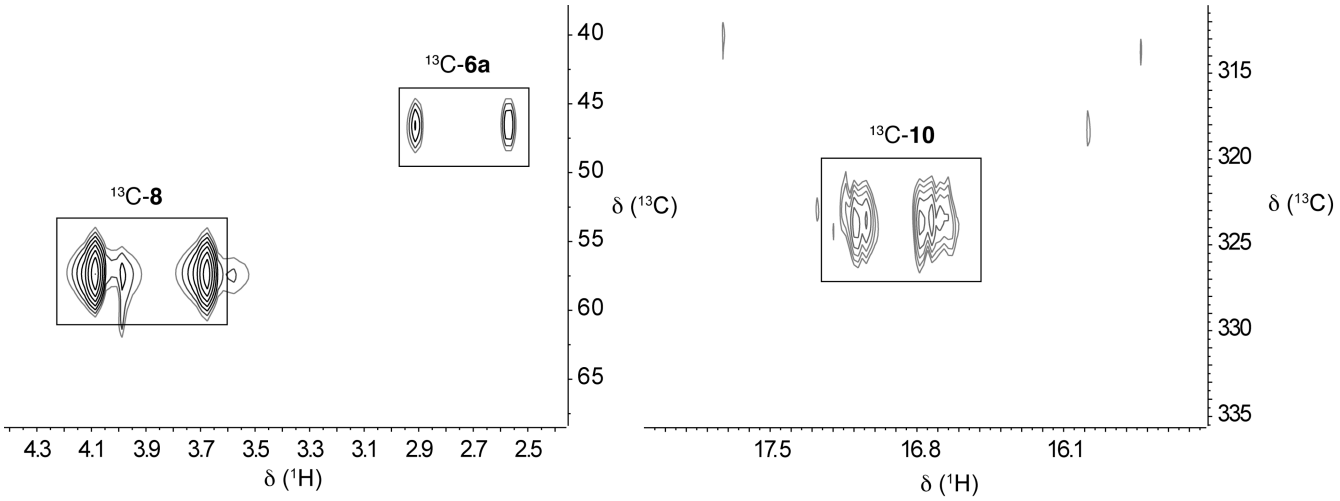
Experiment 5: [RuCl(OEt$_2$)(PNNP)]PF$_6$ (4PF$_6$) + ^{13}C-EDA, then 5a (1:10:1). The goal of this experiment was to check whether aziridine **5a** is formed in the presence of the diazoester complex **8** *after quantitative consumption of EDA*. [$RuCl_2$(PNNP)] (**1**) (21.8 mg, 0.026 mmol) and (Et_3O)PF_6 (6.5 mg, 0.026 mmol) were dissolved in CD_2Cl_2 (0.5 mL) and stirred at room temperature overnight. The formation of **4PF$_6$** was confirmed by ^{31}P and ^{1}H NMR spectroscopy at 25 °C and –78 °C. Then, ^{13}C-EDA (28.8 μL, 0.262 mmol) was added at –78 °C, and the mixture was warmed to 0 °C. After 30 min, the ^{1}H and ^{13}C NMR signals of free EDA had disappeared. Then, the mixture was cooled to –78 °C, and ^{31}P NMR spectrum showed the signals of the EDA adduct **8** (**8a**+**8b**), N_2 complex **9**, and of the unknown impurity (marked "*") (Figure S13), with the same pattern observed in the presence of imine **5a** (see Experiment 2).

Figure S13. ^{31}P NMR spectrum (202 MHz, CD_2Cl_2, –78 °C) recorded just after the addition of ^{13}C-EDA (10 equiv) to **4PF$_6$** showing the signals of the EDA complex ^{13}C-**8** (**8a** and **8b**). The other signals are those of the dinitrogen complex **9** and of the unknown impurity (marked "*", see Figure S5).



Then, imine **5a** (7.1 mg, 0.026 mmol) was added to the solution at –78 °C. The sample temperature was increased in 20 °C-steps. At –20 °C, a (^{13}C,^{1}H)-HMQC experiment (Figure S14) indicated the formation of aziridine **6a** and the decomposition of the diazoester complex **8** to the carbene complex **10** as usually observed after the consumption of free EDA.

Figure S14. Section of the (^{13}C,^{1}H)-HMQC experiment after addition of imine **5a** (1 equiv) to a solution containing the EDA adduct **8** at –78 °C (500 MHz (^{1}H), CD_2Cl_2).

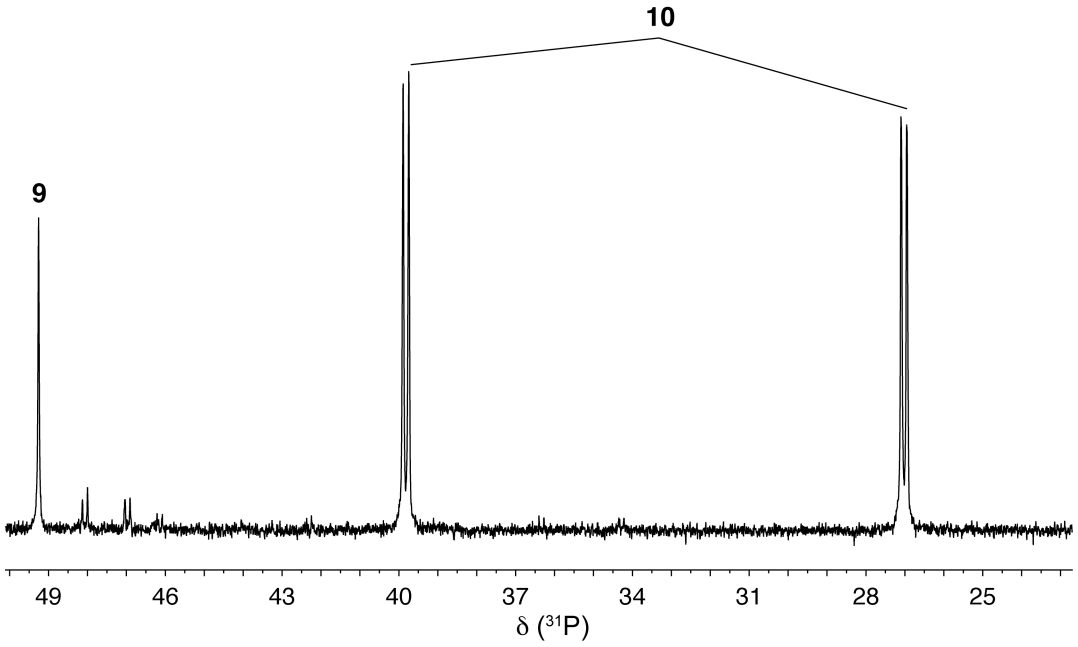


Experiment 6: Non-labeled [RuCl(CHOOEt)(PNNP)]$^{+}$ (10) + ^{13}C-EDA (1:2). [$RuCl_2$(PNNP)] (**1**) (19.8 mg, 0.024 mmol) and $TlPF_6$ (8.3 mg, 0.024 mmol) were dissolved in CD_2Cl_2 (0.5 mL) and stirred overnight at room temperature, The ^{31}P and ^{1}H NMR spectra at 25 °C showed the formation of the five-coordinate complex [RuCl(PNNP)]PF_6 (**2**). Then, EDA (5.2 μL, 0.024 mmol) was added at room temperature, and the mixture was cooled down to –78 °C. The ^{31}P and ^{1}H NMR spectra showed full conversion of [RuCl(PNNP)]PF_6 (**2**) to [RuCl(CHCOOEt)(**1a**)]$^{+}$ (**10**) (85%) and to the dinitrogen complex **9** (15%) (Figure S15).

Upon addition of ^{13}C-EDA (10.4 μL, 0.048 mmol) at –78 °C, the (^{13}C,^{1}H)-HMQC and ^{1}H NMR spectra showed the signals of the diazoester complex [RuCl($N_2{}^{13}$CHCOOEt)(PNNP)]$^{+}$ (**8**), traces of [RuCl(^{13}CHCOOEt)(PNNP)]$^{+}$ (^{13}C-**10**), and the signals of different isotopomers of diethyl maleate. The isotopic distribution, as determined by integration of the ^{1}H NMR spectrum, was 41% diethyl 2-(^{13}C)-maleate, 52% diethyl 2,3-bis(^{13}C)-maleate, and 7% diethyl maleate.

Upon increasing the temperature, the ratio between labeled [RuCl(^{13}CHCOOEt)(PNNP)]PF_6 (^{13}C-**10**) and the nonlabeled analogue [RuCl(CHCOOEt)(PNNP)]PF_6 (**10**) gradually increased.

Figure S15. ^{31}P NMR spectrum of the reaction solution of [RuCl(PNNP)]PF_6 (**2**) with EDA (1 equiv) at room temperature (202 MHz, CD_2Cl_2, –78 °C). The products are the carbene complex **10** (84%) and the dinitrogen complex **9** (16%).



Summary of NMR Spectroscopic Data

***cis*-β-[RuCl(OEt$_2$)(PNNP)]$^+$ (4PF$_6$):**

^{31}P NMR (202 MHz, CD_2Cl_2, –78 °C): δ 55.5 (*d*, $^2J_{P,P'}$ = 29.5 Hz), 36.9 (*d*, $^2J_{P,P'}$= 29.5 Hz).

Diethylmaleate (7):

^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ 6.29 (*s*, 2H).

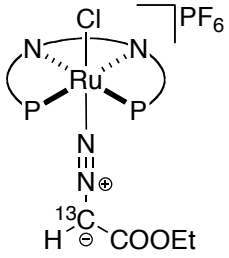
2-^{13}C-diethylmaleate:

^{1}H NMR data (500 MHz, CD_2Cl_2, –78 °C): δ 6.29 (*dd*, 1H, $^2J_{C,H}$ = 2.0 Hz, $^2J_{H,H'}$ = 11.9 Hz, *H*C), 6.29 (*dd*, 1H, $^1J_{C,H}$ = 167 Hz, $^2J_{H,H'}$ = 11.9 Hz, *H*^{13}C).

2,3-bis(^{13}C)-diethylmaleate

^{1}H NMR data (500 MHz, CD_2Cl_2, –78 °C): δ 6.29 (AA' of an AA'XX' system, 2H, $^1J_{C,H}$ = 166 Hz, $^2J_{C,H}$ = 16.7 Hz, $^3J_{C,H}$ = 6.81).

***trans*-[RuCl(N$_2$^{13}CHCOOEt)(PNNP)]$^+$ (^{13}C-8):**



^{31}P NMR (202 MHz, CD_2Cl_2, –60 °C): δ 42.4 (*d*, $^2J_{P,P'}$ = 25.3 Hz), 41.1 (*d*, $^2J_{P,P'}$ = 25.3 Hz), 35.8 (*d*, $^2J_{P,P'}$ = 25.2 Hz), 34.8 (*d*, $^2J_{P,P'}$ = 25.4 Hz).

25 °C: δ 42.1 (*d*, $^2J_{P,P'}$ = 24.2 Hz), 36.9 (*d*, $^2J_{P,P'}$ = 24.2 Hz).

^{1}H NMR (500 MHz, CD_2Cl_2, –60 °C): δ 3.97 (*d*, 1H, $^1J_{C,H}$ = 203 Hz, $RuN_2CHCOOEt$) 3.72 (*d*, 1H, $^1J_{C,H}$ = 205 Hz, $RuN_2CHCOOEt$).

^{13}C NMR (126 MHz, CD_2Cl_2, –60 °C): δ 58.1 (*s*, $RuN_2CHCOOEt$), 58.0 (*s*, $RuN_2CHCOOEt$).

***trans*-[RuCl(^{15}NNCHCOOEt)(PNNP)]$^+$ (^{15}N-8):**

^{15}N NMR (50.7 MHz, CD_2Cl_2, –60 °C): δ –24.9 (*s*, 1N, ^{15}*N*NC), –25.3 (*s*, 1N, ^{15}*N*NC).

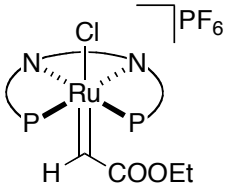
^{31}P NMR (202 MHz, CD_2Cl_2, –80 °C): δ 42.4 (*dd*, $^2J_{P,P'}$ = 25.3 Hz, $^2J_{P,N}$ = 2.4 Hz), 41.1 ($^2J_{P,P'}$ = 25.3 Hz, $^2J_{P,N}$ = 2.4 Hz), 35.8 (*d*, $^2J_{P,P'}$ = 25.2 Hz), 34.8 (*d*, $^2J_{P,P'}$ = 25.4 Hz).

Dinitrogen Complex [RuCl(N$_2$)(PNNP)] (9):

^{31}P NMR (202 MHz, CD_2Cl_2, –78 °C): δ 49.2 (*s*). 20 °C: δ 49.2 (*br s*).

^{15}N NMR (50.7 MHz, CD_2Cl_2, –60 °C): δ –89.9 (*bt*, 1N, Ru–^{15}*N*N), –40.2 (*s*, 1N, Ru–N^{15}*N*).

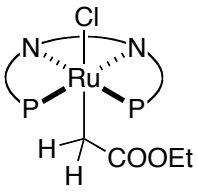
***trans*-[RuCl(¹³CHCOOEt)(PNNP)]⁺ (¹³C-10):**



^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C): 38.3 (*dd*, $^2J_{P,C}$ = 13.9 Hz, $^2J_{P,P'}$ = 30.4 Hz), 28.7 (*dd*, $^2J_{P,C}$ = 13.9 Hz, $^2J_{P,P'}$ = 30.4 Hz).

***trans*-[RuCl(CH_2COOEt)(PNNP)] (11):**

^{31}P NMR (202 MHz, CD_2Cl_2, 25 °C): 47.9 (*d*, $^2J_{P,P'}$ = 28.2 Hz), 47.8 (*d*, $^2J_{P,P'}$ = 28.2 Hz).



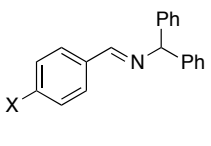
^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 3.79 (*d*, 1H, $^2J_{H,H'}$ = 11.2 Hz, RuC*H*H'COOEt), 3.36 (*d*, 1H, $^2J_{H,H'}$ = 11.2 Hz, RuCH*H'*COOEt).

(¹³C-Labeled) Unknown Species containing a X=C(H)Y moiety observed below –20 °C (see Figure S8 and footnote 25 of main paper):

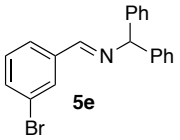
^{1}H NMR (500 MHz, CD_2Cl_2, –78 °C): δ 4.21 (*d*, 1H, $^1J_{C,H}$ = 206 Hz), 4.21 (*d*, 1H, $^1J_{C,H}$ = 213 Hz).

^{13}C NMR (126 MHz, CD_2Cl_2, –78 °C): δ 55.4 (*s*), 54.6 (s).

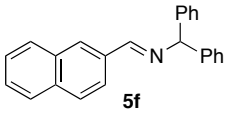
Table S1. Optimization of the Asymmetric Aziridination with Selected Imines and Catalysts.[a]



X = H (**5a**)
Cl (**5b**)
F (**5c**)
CO_2Me (**5d**)
2-Pr (**5g**)
or Me (**5h**)



5e



5f

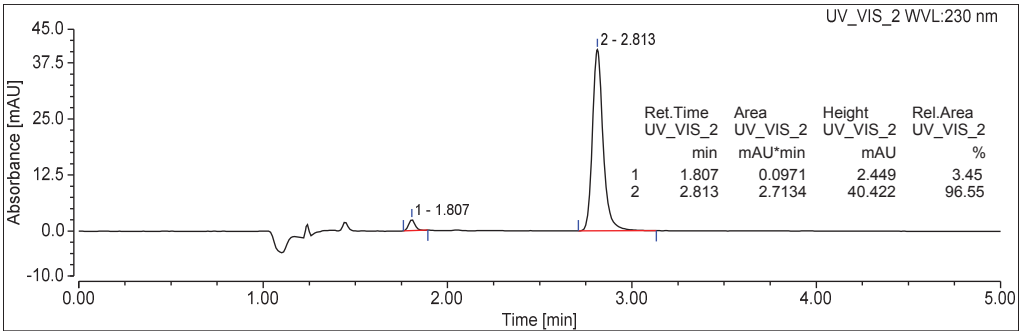
entry	Y	imine	EDA (equiv)	crude **6** [b] yield (%)	*cis*:*trans*	isolated *cis*-**6** yield (%) [c]	ee (%) [d]
1	PF_6	**5a**	1	22	77:23	13	80
2	PF_6	**5a**	4	35	79:21	30	53 [e]
3	BF_4	**5a**	1	32	78:22	24	78
4	BF_4	**5a**	4	53	81:19	20	78
5	SbF_6	**5a**	1	32	85:15	24	93
6	SbF_6	**5a**	4	58	78:22	40	67
7	BF_4	**5b**	1	36	86:14	23	70
8	BF_4	**5b**	4	50	74:26	33	25
9	SbF_6	**5b**	1	18	85:15	14	91
10	BF_4	**5c**	1	24	79:21	16	68
11	BF_4	**5c**	4	20	65:35	20	17
12	SbF_6	**5c**	1	16	84:16	9	75
13	SbF_6	**5d**	1	30	*cis* only	24	79
14	SbF_6	**5e**	1	46	93:7	34	83
15	BF_4	**5f**	1	32	81:19	24	70
16	BF_4	**5f**	4	53	77:23	38	60
17	SbF_6	**5f**	1	40	90:10	33	93
18	SbF_6	**5g**	1	11	*cis* only	4	57
19	SbF_6	**5h**	1	25	90:10	17	63

[a] Reaction conditions: EDA (0.48 mmol, 1 equiv, or 1.92 mmol, 4 equiv, neat) was added in one portion to a CH_2Cl_2 solution (3 mL) containing the imine (0.48 mmol) and the catalyst (10 mol%) prepared by activation of [$RuCl_2$(PNNP)] (**1**) (0.048 mmol) with (Et_3O)Y (0.048 mmol). The total reaction time was 24 h at 0 °C. [b] Based on the imine, determined by ^{1}H NMR spectroscopy. [c] Isolated yield. [d] The absolute configuration of **6b-6h** was not assigned. [e] The isolated aziridine was contaminated with variable amounts of diethyl maleate.

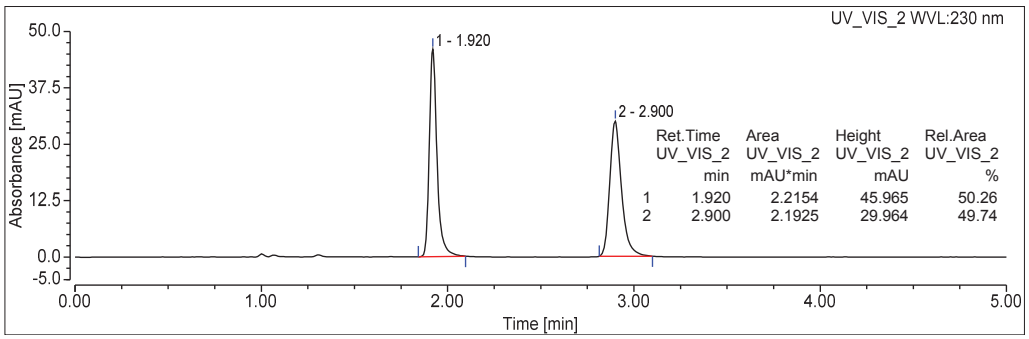
(2*R*,3*R*)-Ethyl 1-Benzhydryl-3-phenylaziridine-2-carboxylate (6a). The reaction of **5a** and EDA gave aziridine **6a** as a white solid after workup (see above). ^{1}H NMR and ^{13}C NMR spectroscopic data are in agreement with published values.[8] ^{1}H NMR ($CDCl_3$, 300.2 MHz): δ 1.00 (*t*, 3H, *J*= 7.11 Hz, C*H*$_3$), 2.71 (*d*, 1H, *J*= 6.84 Hz, NC*H*Ph), 3.25 (*d*, 1H, *J*= 6.84 Hz, NC*H*COOEt), 3.96 (*q*, 2H, *J*= 7.14 Hz, COOC*H*$_2$), 3.99 (*s*, 1H, C*H*Ph$_2$), 7.18 – 7.64 (*m*, 14H, H$_{arom}$). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.0, 46.5, 48.1, 60.6, 77.8, 127.3 – 128.6, 135.1, 134.0, 142.5, 142.6, 167.8. Chiral HPLC: IB column, 3 μm, eluent: hexane/2-propanol (95:5), flow rate 2.0 mL/min, R_t (min) = 1.8 (minor, (2*S*,3*S*)-**6a**), 2.8 (major, (2*R*,3*R*)-**6a**). $[\alpha]_D^{20}$ = 22.9 ± 1 (c = 1.5, $CHCl_3$) @ 93% ee (Table S1, entry 5). Absolute configuration assigned on the basis of the sign of the reported optical rotation.[8] HRMS (MALDI): Calcd. for $C_{24}H_{24}NO_2$ *m/z* 358.1802 found *m/z* 358.1801**.**

Figure S16. HPLC traces of **6a**.

Catalysis Product



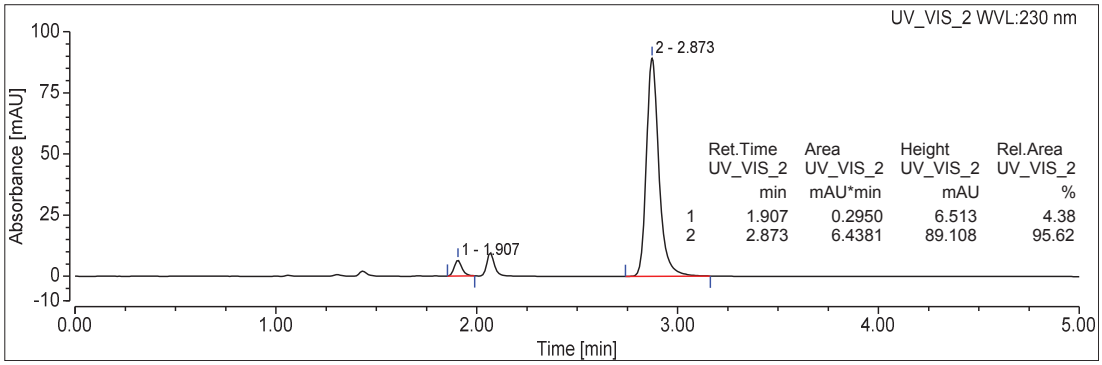
Racemate



Ethyl 1-Benzhydryl-3-(4-chlorophenyl)aziridine-2-carboxylate (6b). The reaction of **5b** and EDA gave **6b** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 1.06 (*t*, 3H, *J*= 6.95 Hz, H13), 2.72 (*d*, 1H, *J*= 6.35 Hz, H1), 3.20 (*d*, 1H, *J*= 6.45 Hz, H2), 3.97 (*s*, 1H, H15), 3.99 (*q*, 2H, *J*= 6.55 Hz, H12), 3.97 (*s*, 1H, H15), 7.22 – 7.62 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.4, 46.9, 47.7, 61.1, 78.1, 127.6 – 129.6, 133.6, 134.0, 142.6, 142.8, 167.9. Chiral HPLC: IB column, 3 μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 1.9 (minor), 2.8 (major), 91% ee (Table S1, entry 9). $[\alpha]_D^{20}$ = 21.4 ± 0.1 @ 91% ee (c = 0.368, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{24}H_{23}ClNO_2$ *m/z* 392.1412 found *m/z* 392.1412.

Figure S17. HPLC traces of **6b**.

Catalysis Product



Racemate

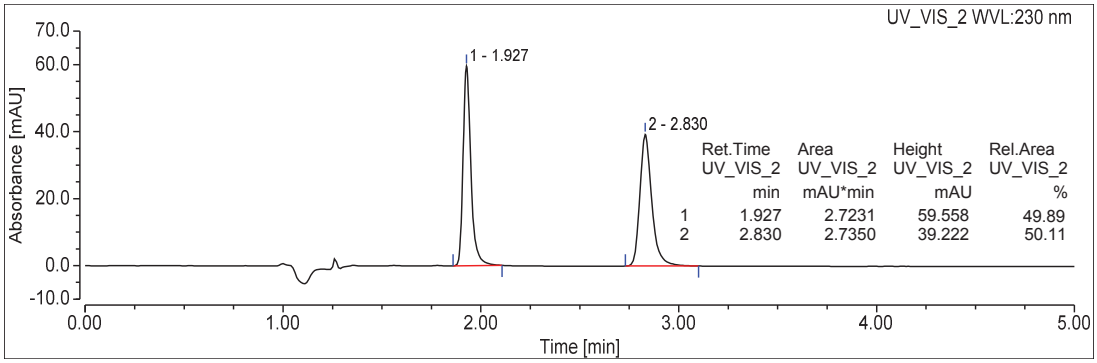


Figure S18. ^{1}H NMR Spectrum of **6b** (500.2 MHz, $CDCl_3$).

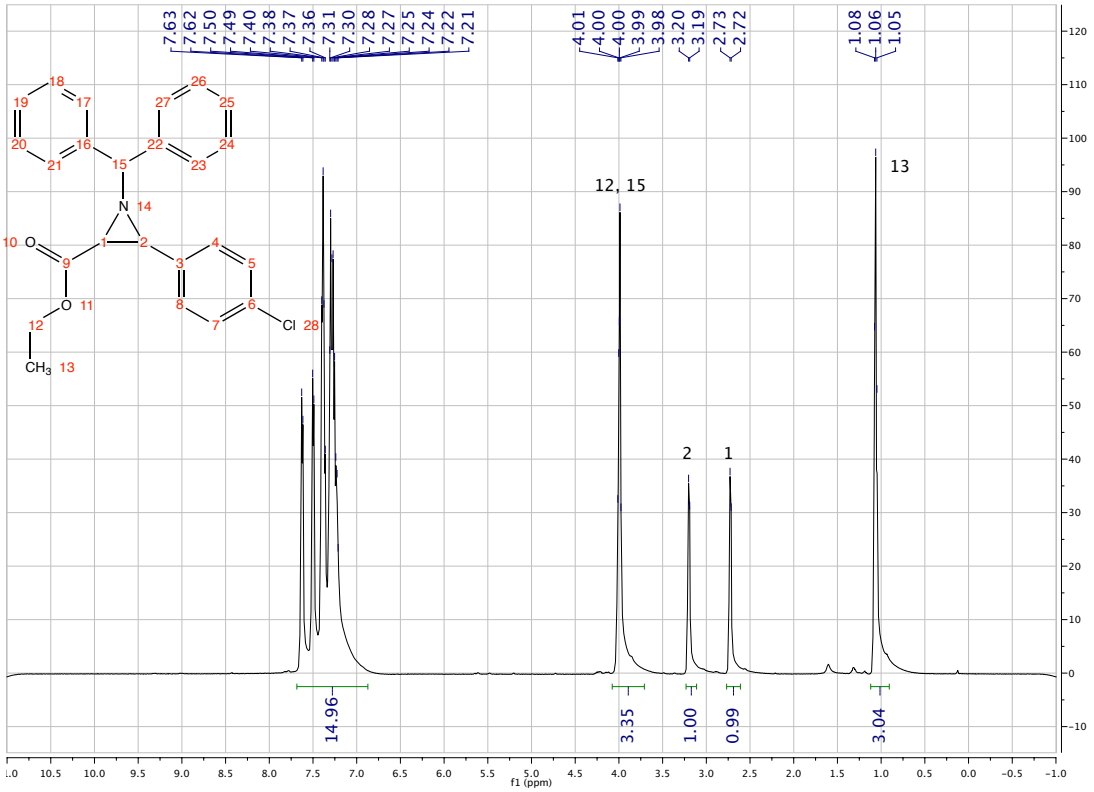
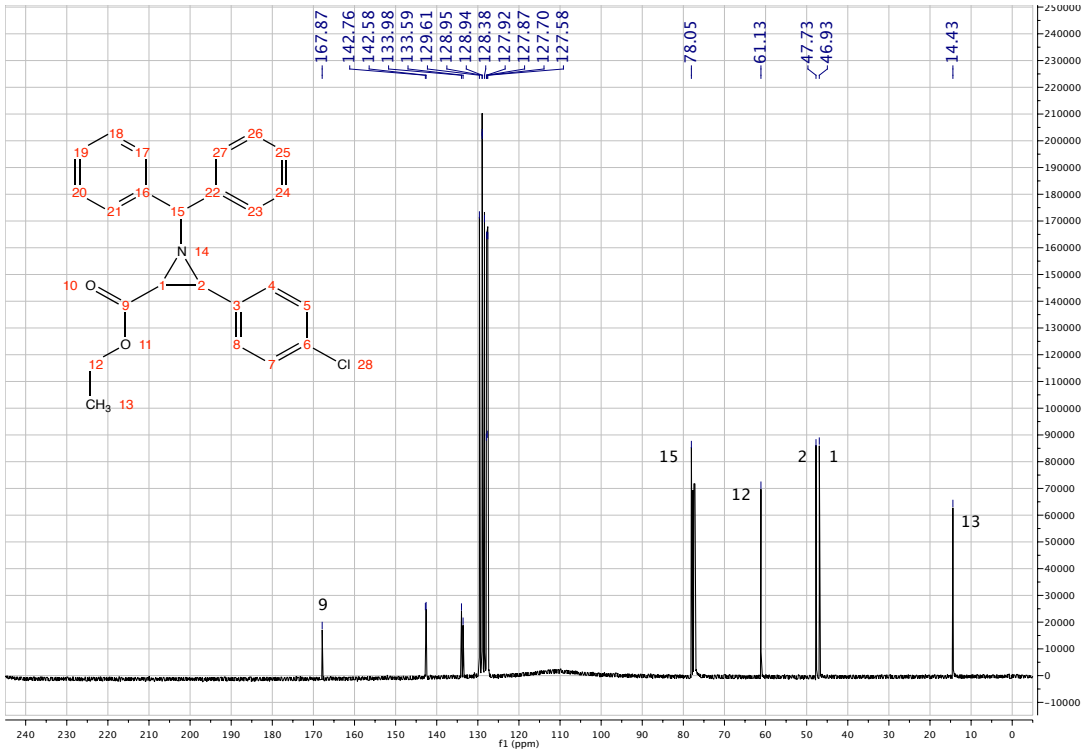


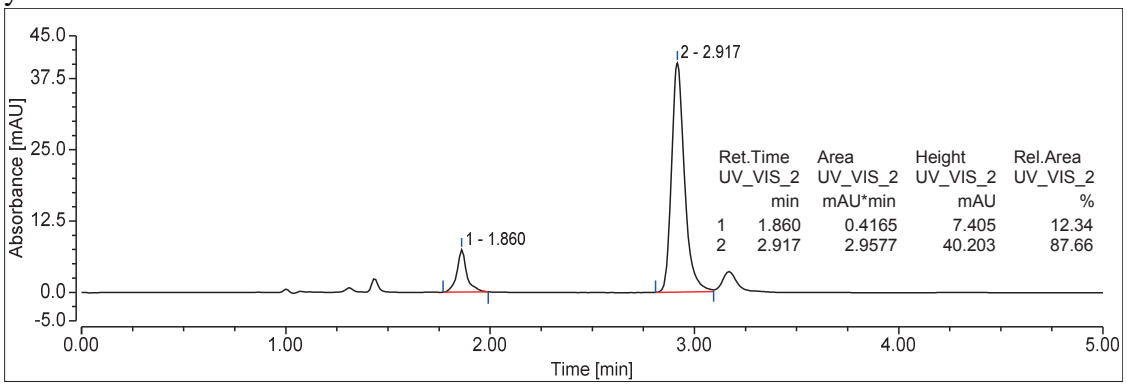
Figure S19. ^{13}C NMR Spectrum of **6b** (125.8 MHz, $CDCl_3$).



Ethyl 1-Benzhydryl-3-(4-fluorophenyl)aziridine-2-carboxylate (6c). The reaction of **5c** and EDA gave **6c** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 1.05 (*t*, 3H, *J*= 7.10 Hz, H13), 2.71 (*d*, 1H, *J*= 6.80 Hz, H1), 3.22 (*d*, 1H, *J*= 6.85 Hz, H2), 3.97 (*s*, 1H, H15), 3.99 (*q*, 2H, *J*= 6.60 Hz, H12), 6.96 – 7.64 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.4, 46.8, 47.7, 61.1, 78.1, 115.0, 115.2, 127.9 – 129.0, 142.7, 142.9, 161.7, 163.6, 168.0. Chiral HPLC: IB column, 3 μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 1.8 (minor); 2.9 (major), 75% ee (Table S1, entry 12). $[\alpha]_D^{20}$ = 39 ± 0.1 @ 75% ee (c = 0.232, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{24}H_{23}FNO_2$ *m/z* 376.1707 found *m/z* 376.1707.

Figure S20. HPLC traces of **6c**.

Catalysis Product



Racemate

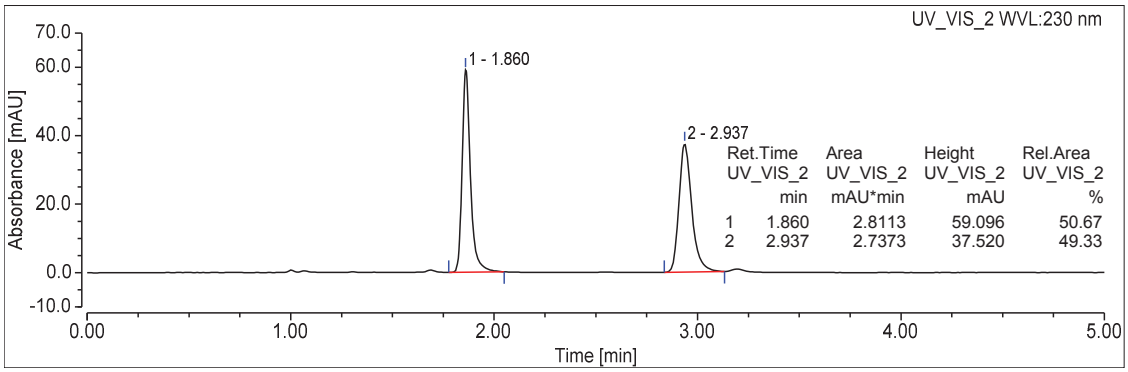


Figure S21. ^{1}H NMR Spectrum of **6c** (500.2 MHz, $CDCl_3$).

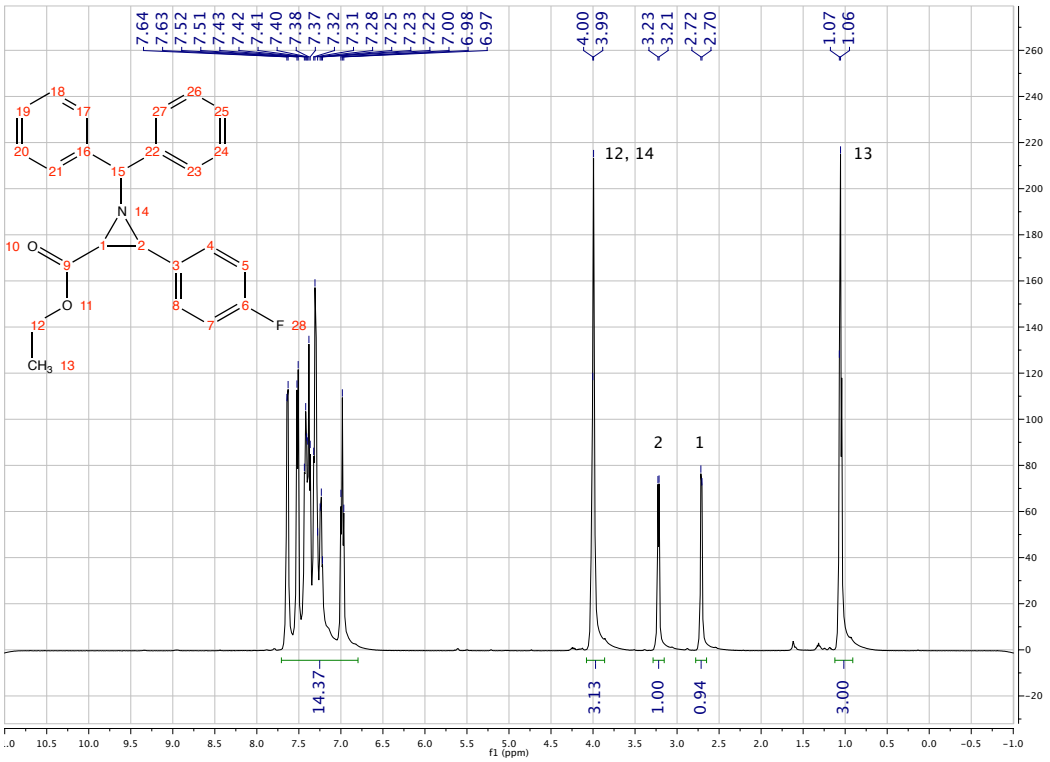
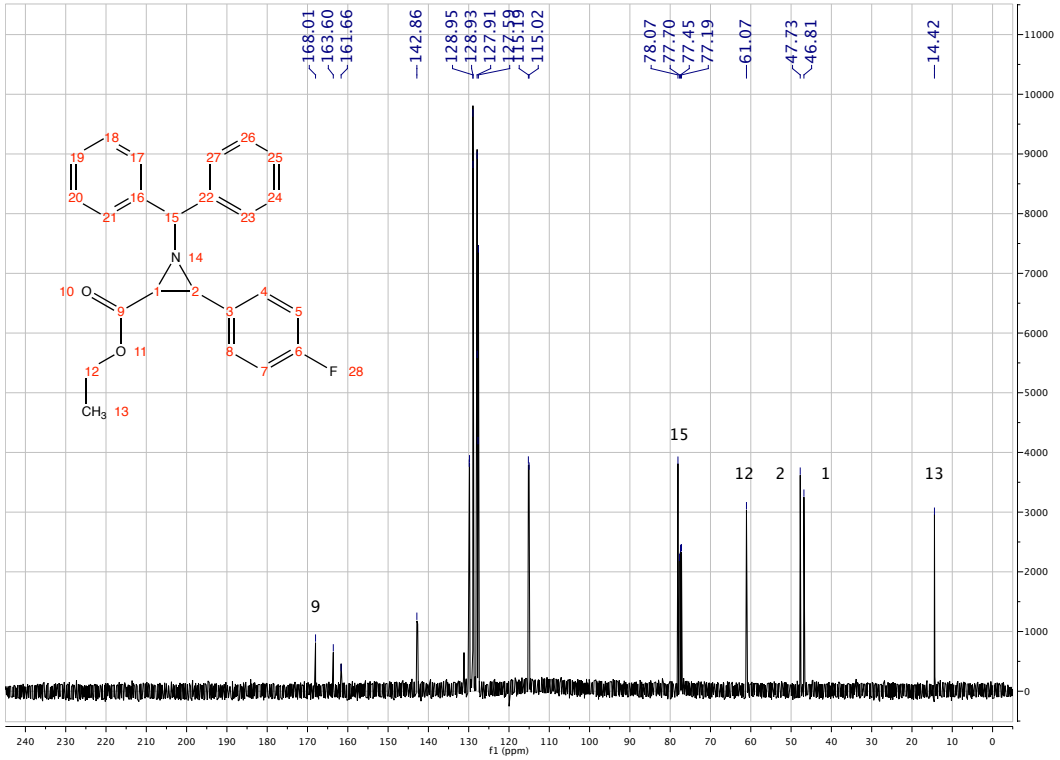


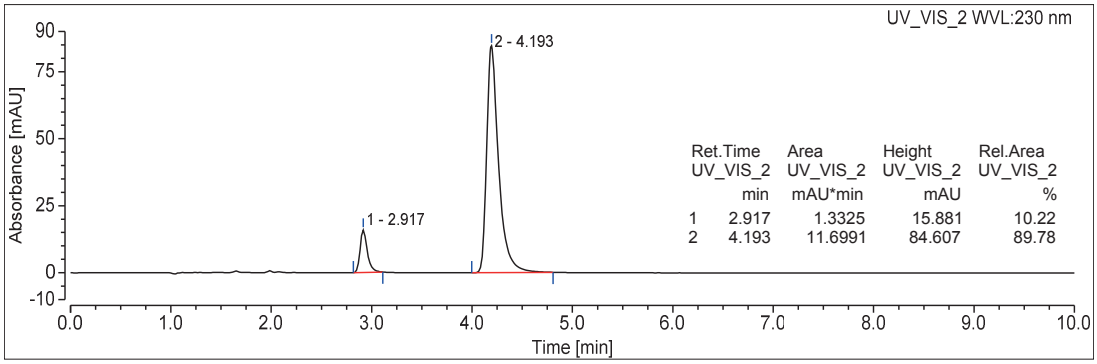
Figure S22. ^{13}C NMR Spectrum of **6c** (125.8 MHz, $CDCl_3$).



Ethyl 1-Benzhydryl-3-(4-(methoxycarbonyl)phenyl)aziridine-2-carboxylate (6d). The reaction of **5d** and EDA gave **6d** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.02 (*t*, *J*= 7.2 Hz, 3H, H17), 2.77 (*d*, *J*= 6.8 Hz, 1H, H1), 3.26 (*d*, *J*= 6.8 Hz, 1H, H2), 3.91 (*s*, 3H, H10), 3.96 (*qd*-like, AB part of ABX_3 system, 2H, ^{3}J= 7.2, 2H, H16), 4.00 (*s*, 1H, H19), 7.18 – 7.64 (*m*, 12H, H_{arom}), 7.97 (*m*, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 14.02, 46.72 47.62, 52.02, 60.76, 77.62, 127.17, 127.34, 127.44, 127.53, 127.89, 128.56, 129.12, 129.23, 140.31, 142.15, 142.30, 166.96, 167.32. Chiral HPLC: IB column, 3 μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 2.9 (minor); 4.2 (major), 79% ee (Table S1, entry 13). $[\alpha]_D^{20}$ = 7.7 ± 0.1 @ 79% ee (c = 1.16, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{26}H_{26}NO_4$ *m/z* 416.1856 found *m/z* 416.1857.

Figure S23. HPLC traces of **6d**.

Catalysis Product



Racemate

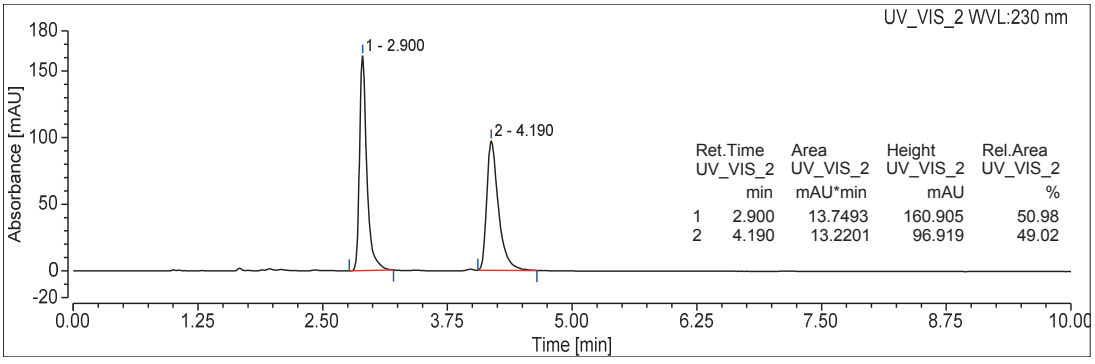


Figure S24. ^{1}H NMR Spectrum of **6d** (400 MHz, $CDCl_3$).

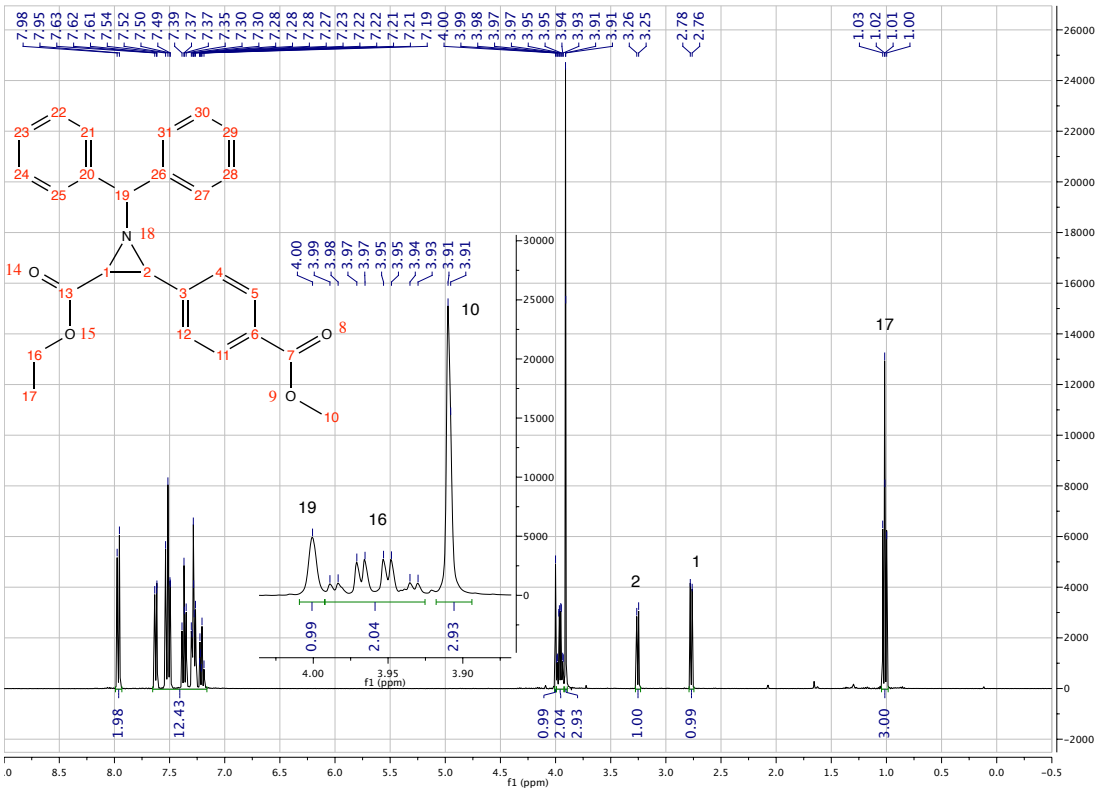
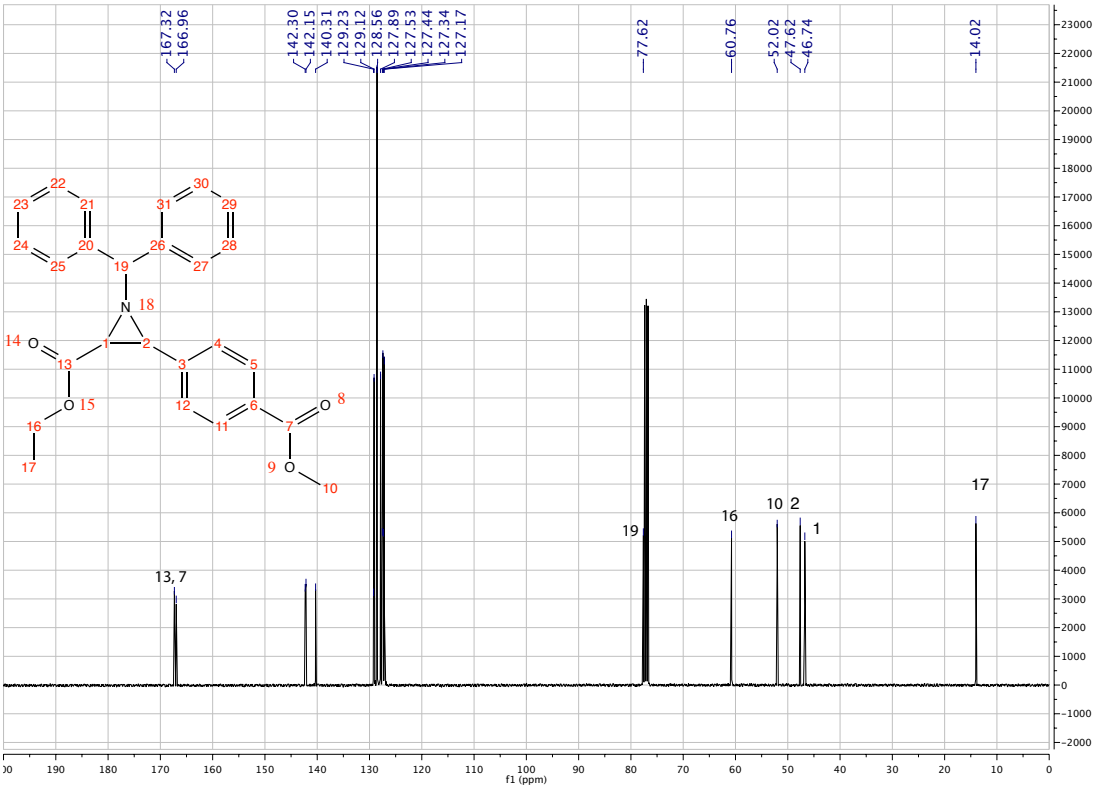


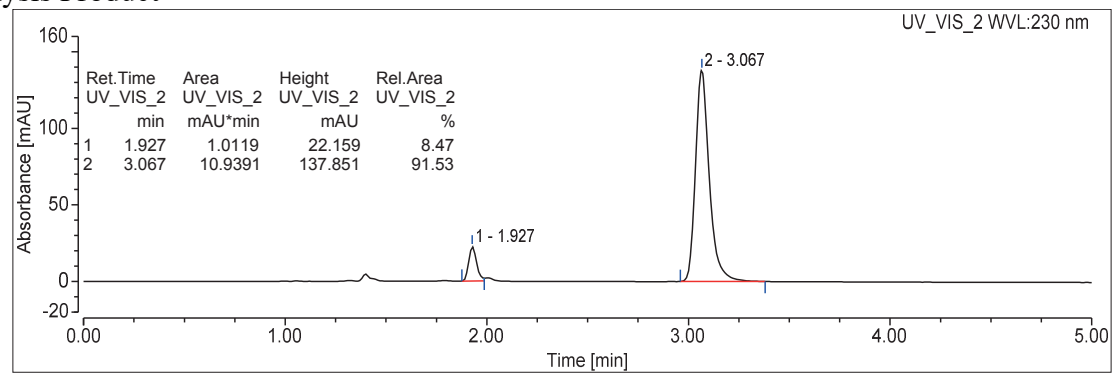
Figure S25. ^{13}C NMR Spectrum of **6d** (101 MHz, $CDCl_3$).



Ethyl 1-Benzhydryl-3-(3-bromophenyl)aziridine-2-carboxylate (6e). The reaction of **5e** and EDA gave **6e** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 1.08 (*t*, 3H, *J*= 7.1 Hz, H14), 2.75 (*d*, 1H, *J*= 6.8 Hz, H1), 3.20 (*d*, 1H, *J*= 6.8 Hz, H2), 4.0 (s, 1H, H1), 4.02 (*qd* like, AB part of ABX_3 system, 2H, ^{3}J= 7 Hz, H13), 7.14 – 7.66 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.05, 46.63, 47.20, 60.80, 77.66, 121.91, 126.59, 127.21, 127.35, 127.51, 127.58, 128.57, 128.61, 129.42, 130.54, 130.90, 137.51, 142.16, 142.33, 167.45. Chiral HPLC: IB column, 3μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 1.9 (minor); 3.1 (major), 83% ee (Table S1, entry 14). $[\alpha]_D^{20}$ = 30.4 ± 0.2 @ 83% ee (c = 1.44, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{24}H_{23}BrNO_2$ *m/z* 436.0907 found *m/z* 436.0906.

Figure S26. HPLC traces of **6e**.

Catalysis Product



Racemate

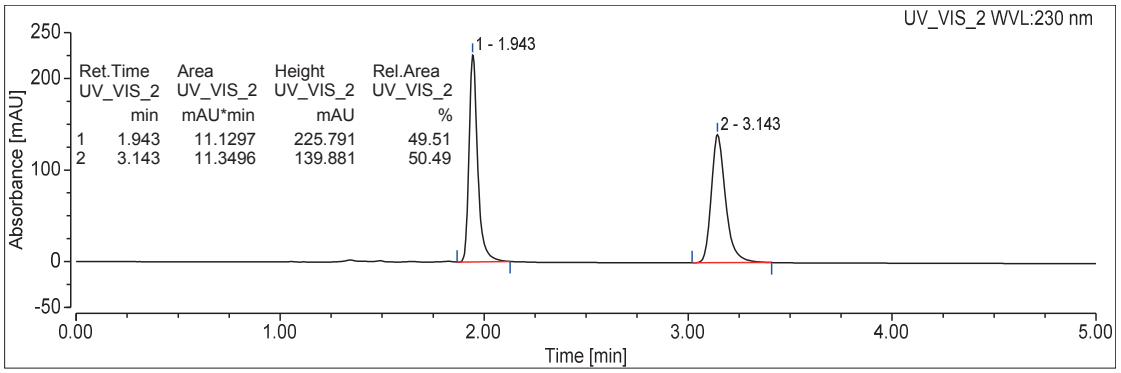


Figure S27. ^{1}H NMR Spectrum of **6e** (500.2 MHz, $CDCl_3$).

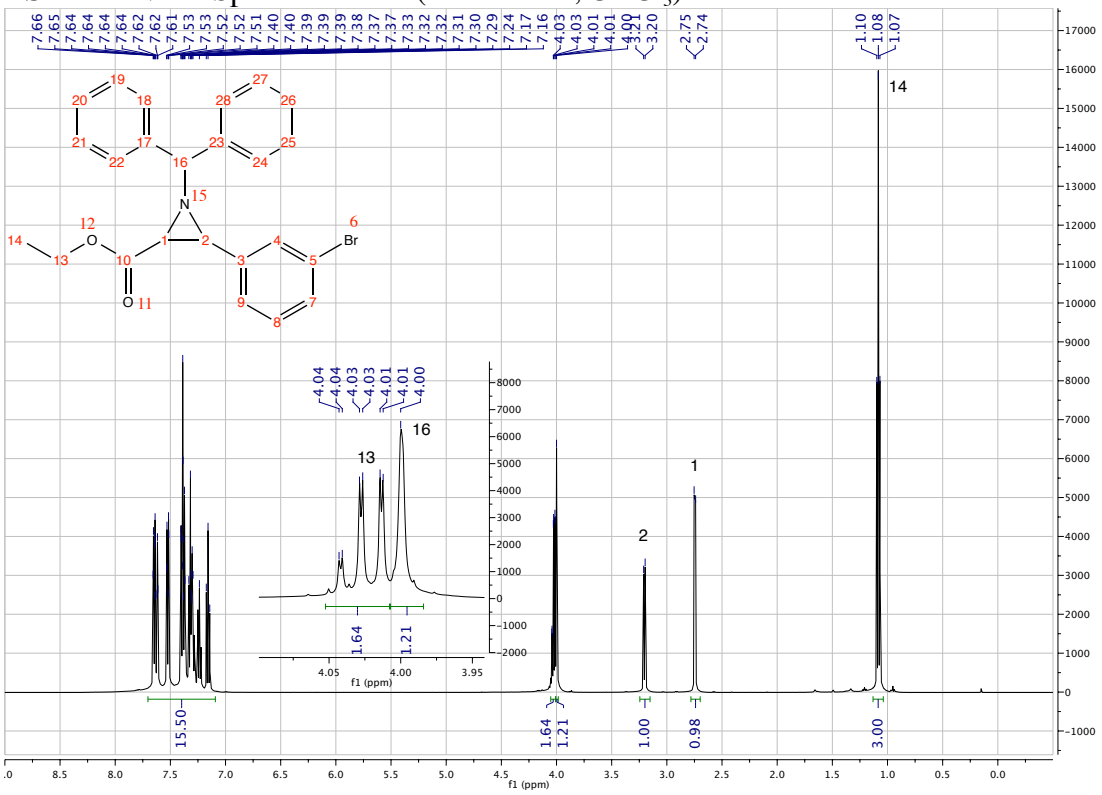
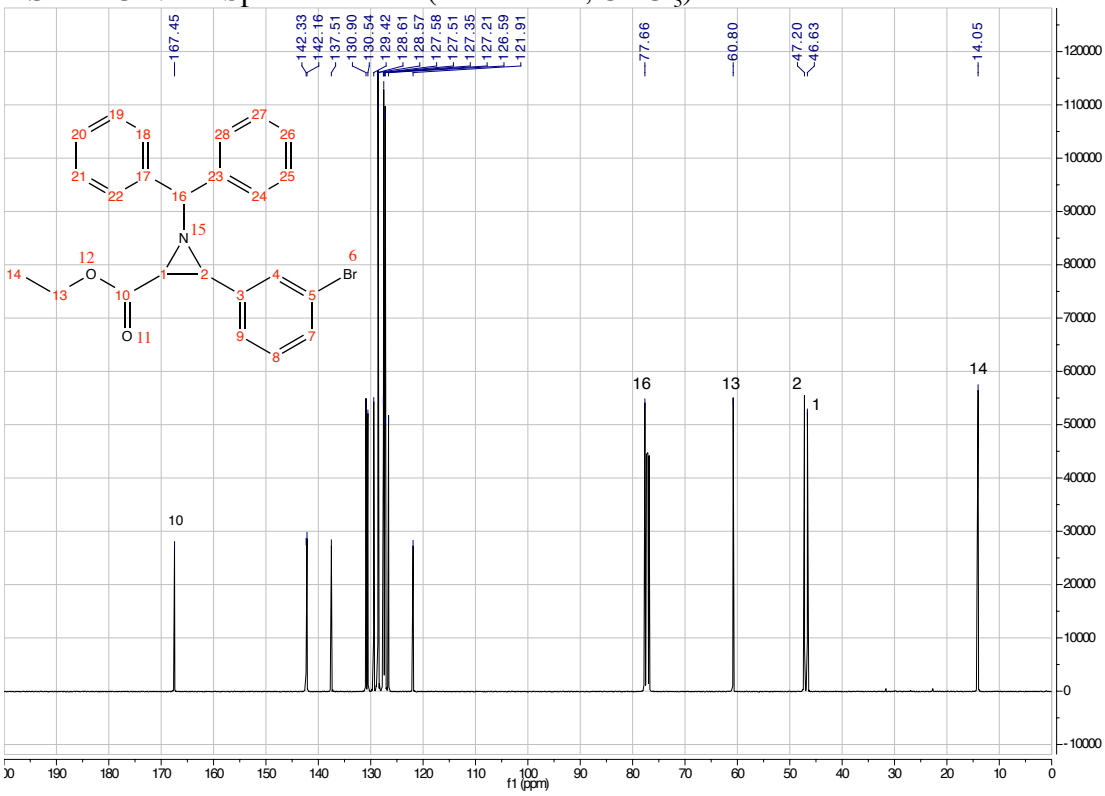


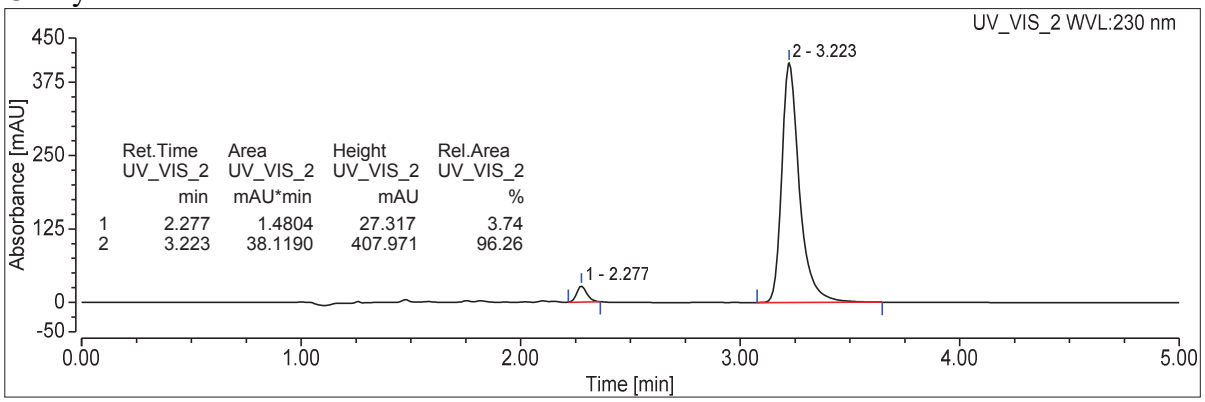
Figure S28. ^{13}C NMR Spectrum of **6e** (125.8 MHz, $CDCl_3$).



Ethyl 1-Benzhydryl-3-(2-naphthalene-2-yl)aziridine-2-carboxylate (6f). The reaction of **5f** and EDA gave **6f** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 0.98 (*t*, 3H, *J*= 7.4 Hz, H13), 2.80 (*d*, 1H, *J*= 6.85 Hz, H1), 3.40 (*d*, 1H, *J*= 6.80 Hz, H2), 3.94 (*q*, 2H, *J*= 7.50 Hz, H12), 4.06 (*s*, H15) 7.19 – 7.92 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.1, 46.9, 48.4, 60.8, 77.9, 125.8 – 128.7, 132.8, 133.0, 133.1, 142.5, 142.6, 167.9. Chiral HPLC: IB column, 3μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 2.7 (minor), 3.2; (major), 93% ee (Table S1, entry 17). $[\alpha]_D^{20}$ = 10.0 ± 0.3 @ 93% ee (c = 0.81, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{28}H_{26}NO_2$ *m/z* 408.1958 found *m/z* 408.1958.

Figure S29. HPLC traces of **6f**.

Catalysis Product



Racemate

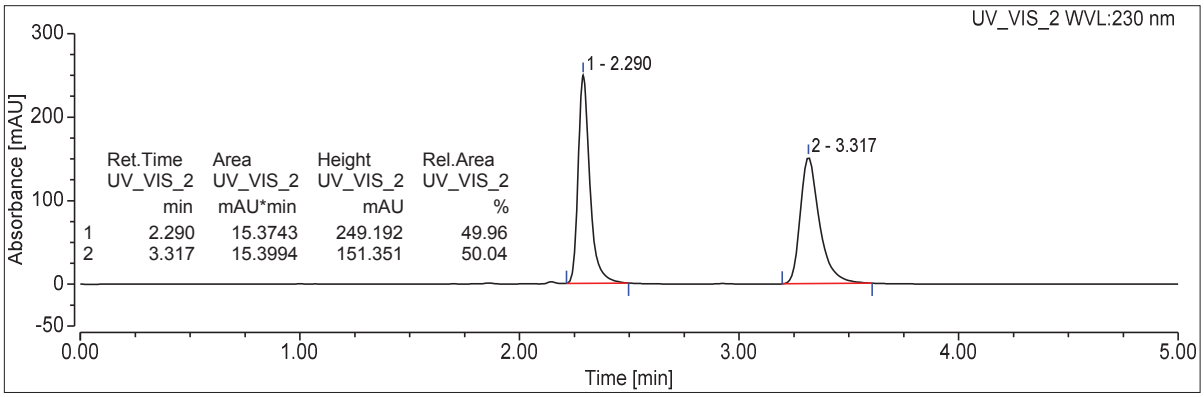


Figure S30. ^{1}H NMR Spectrum of **6f** (500.2 MHz, $CDCl_3$).

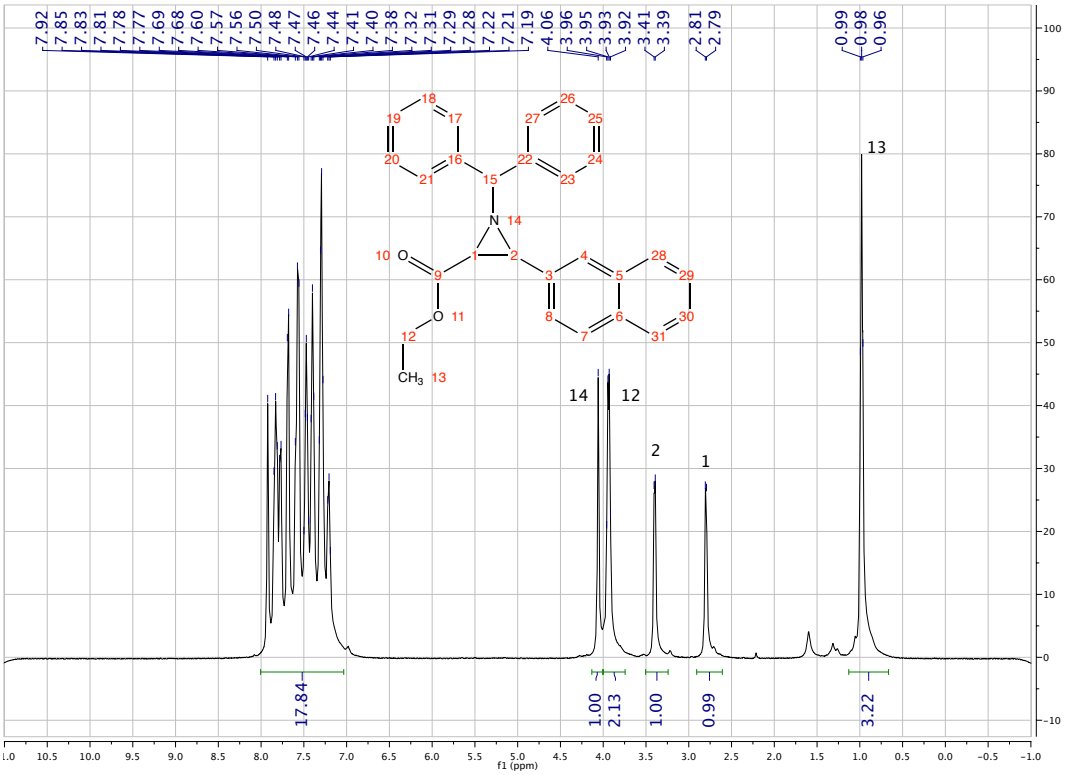
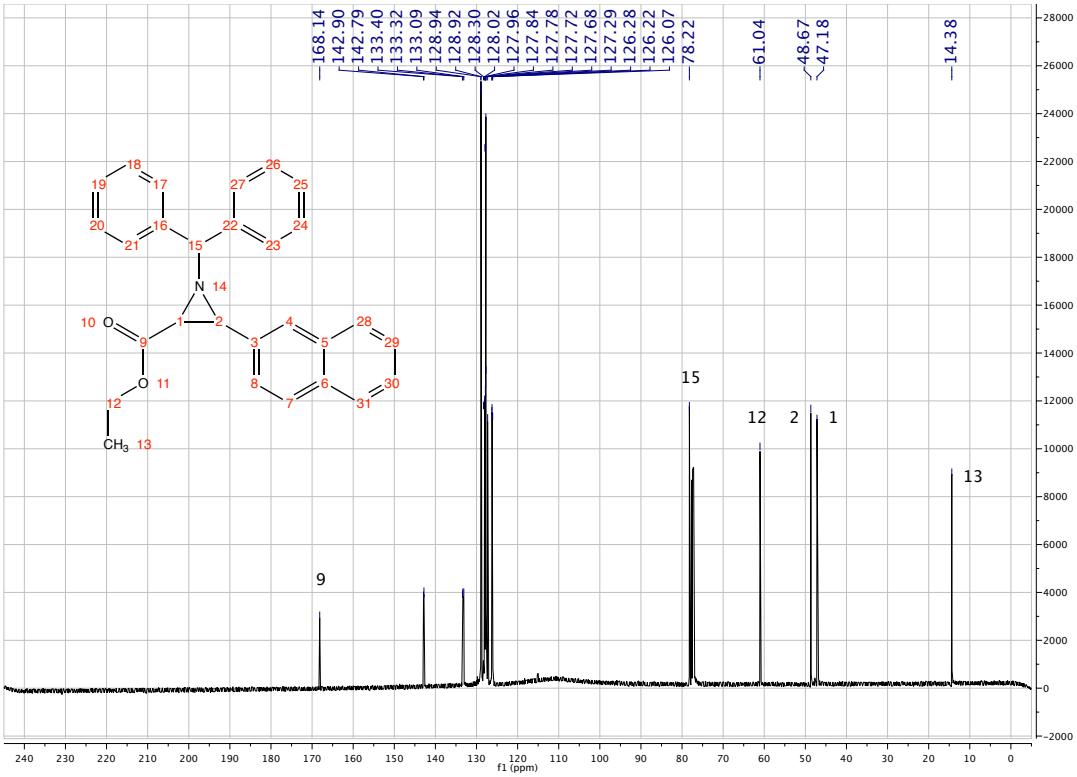


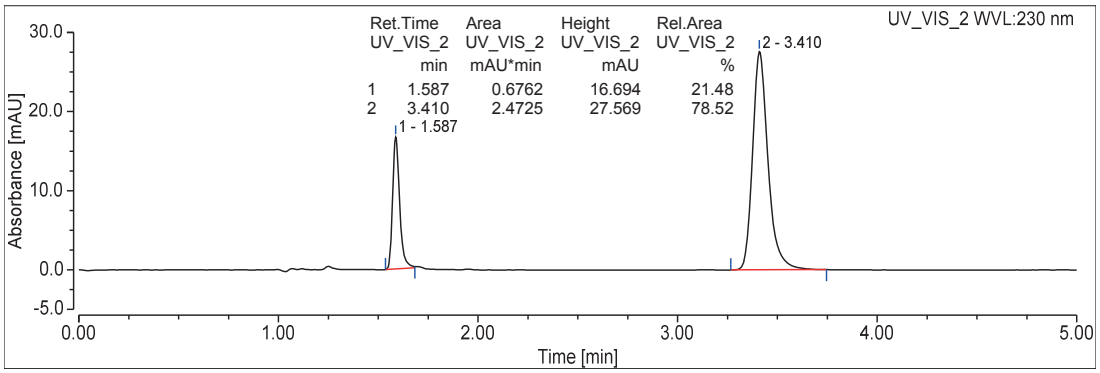
Figure S31. ^{13}C NMR Spectrum of **6f** (125.8 MHz, $CDCl_3$).



Ethyl 1-Benzhydryl-3-(4-isopropylphenyl)aziridine-2-carboxylate (6g). The reaction of **5g** and EDA gave **6g** as a white solid after workup (see above). ^{1}H NMR ($CDCl_3$, 500.2 MHz): δ 0.99 (*t*, 3H, *J*= 6.95 Hz, H13), 1.24 (*d*, 6H, *J*= 6.95 Hz, H29 and H30), 2.67 (*d*, 1H, *J*= 6.75 Hz, H1), 2.88 (*sep*, 1H, *J*= 6.90 Hz, H28), 3.23 (*d*, 1H, *J*= 6.85 Hz, H2), 3.99 (*q*, 2H, *J*= 7.3 Hz, H12), 3.97 (*s*, 1H, H15), 7.13 – 7.64 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 14.30, 24.3, 24.4, 34.2, 46.7, 48.4, 60.9, 77.9, 126.3 - 128.9, 132.8, 143.0, 148.3, 168.3. Chiral HPLC: IB column, 3μm; eluent: hexane/2-propanol (95:5); flow rate: 2.0 mL/min; R_t (min) = 1.6 (minor); 3.4 (major), 57% ee (Table S1, entry 18). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{27}H_{30}NO_2$ *m/z* 400.2271 found *m/z* 400.2271.

Figure S32. HPLC traces of **6g**.

Catalysis Product



Racemate

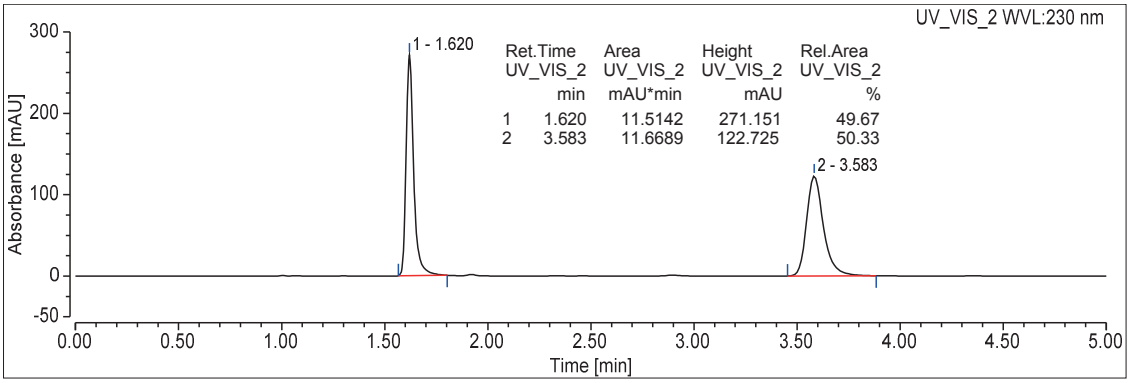


Figure S33. ^{1}H NMR Spectrum of **6g** (500.2 MHz, $CDCl_3$).

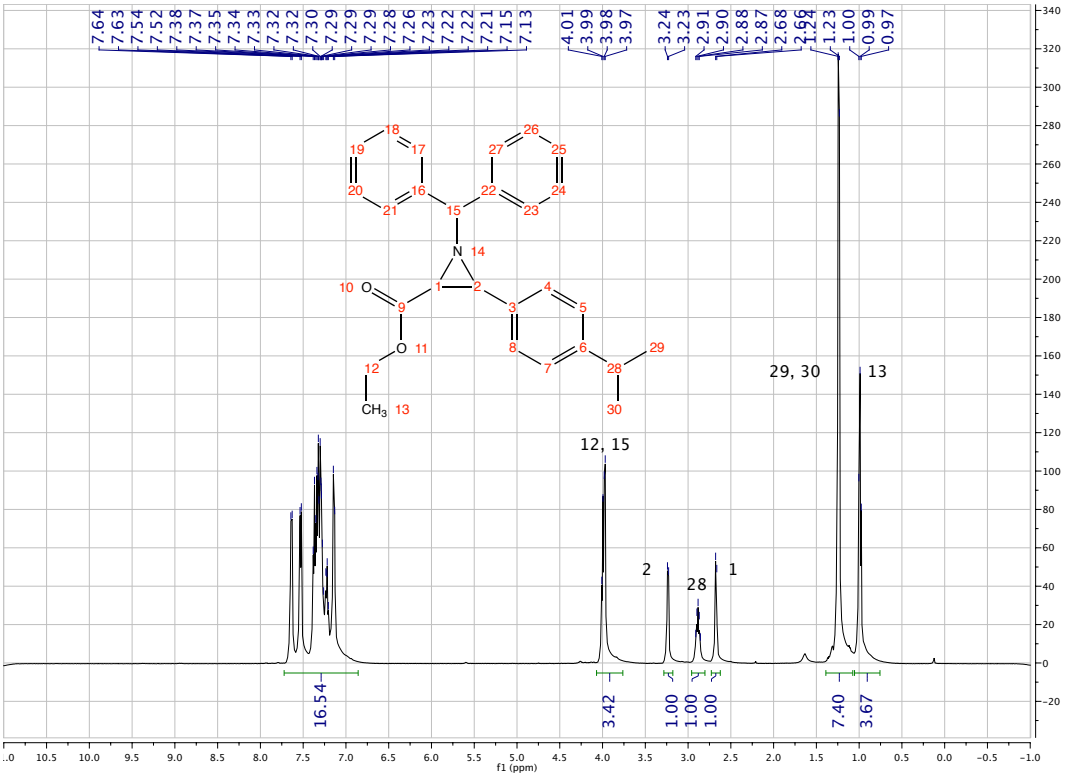
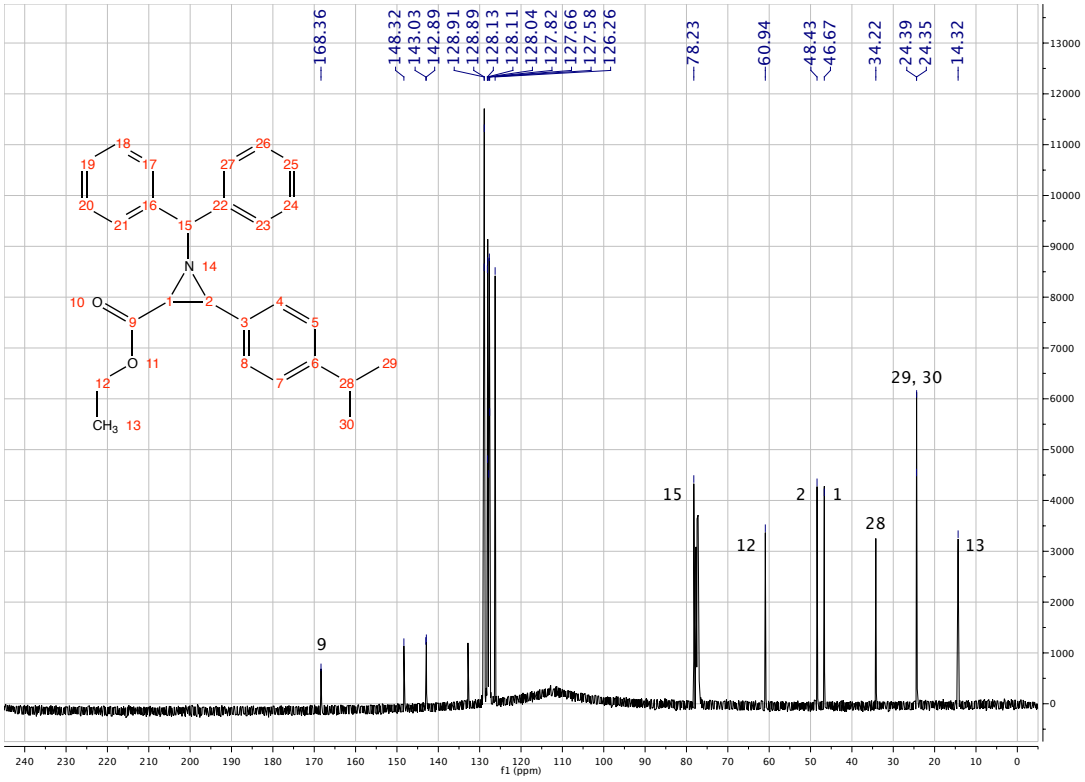


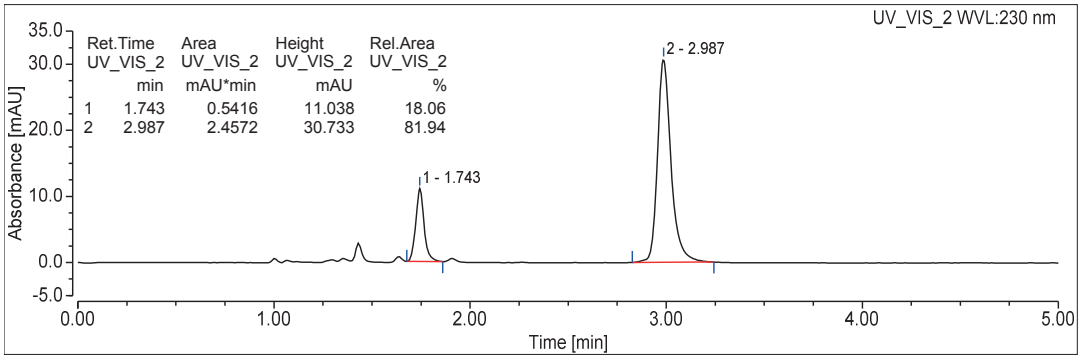
Figure S34. ^{13}C NMR Spectrum of **6g** (125.8 MHz, $CDCl_3$).



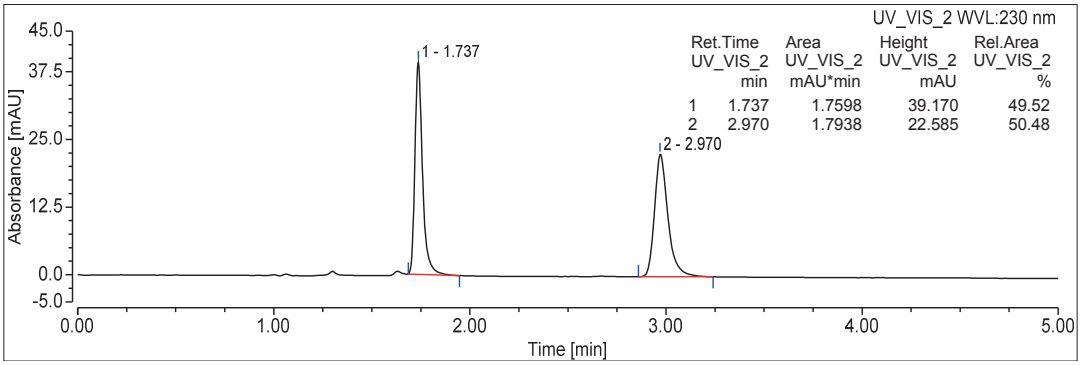
Ethyl 1-Benzhydryl-3-(*p*-tolyl)aziridine-2-carboxylate (6h). The reaction of **5g** and EDA gave **6g** as a white solid after workup (see above). ^{1}H NMR and ^{13}C NMR spectroscopic data are in agreement with published values.[9] ^{1}H NMR ($CDCl_3$, 300.2 MHz): δ 1.00 (*t*, 3H, *J*= 7.1 Hz, $COOCH_2CH_3$), 2.27 (*s*, 3H, $PhCH_3$), 2.63 (*d*, 1H, *J*= 6.8 Hz, NC*H*Ph), 3.17 (*d*, 1H, *J*= 6.84 Hz, NC*H*COOEt), 3.93 (*s*, 1H, C*H*Ph_2), 3.94 (*q*, *J*= 7.1 Hz, $COOCH_2CH_3$), 7.03 – 7.60 (*m*, 14H, H_{arom}). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.06, 21.20, 46.42, 48.11, 60.59, 77.83, 127.23, 127.30, 127.42, 127.60, 127.73, 128.52, 132.06, 136.96, 142.51, 142.62, 167.88. Chiral HPLC: IB column, 3 μm, eluent: hexane/2-propanol (95:5), flow rate 2.0 mL/min, R_t (min) = 1.7 (minor), 3.0 (major), 63 % ee (Table S1, entry 19). $[\alpha]_D^{20}$ = 23.6 ± 0.3 @ 63% ee (c = 0.364, $CHCl_3$). The absolute configuration was not assigned. HRMS (MALDI): Calcd. for $C_{25}H_{26}NO_2$ *m/z* 372.1958 found *m/z* 372.1958.

Figure S35. HPLC traces of **6h**.

Catalysis Product

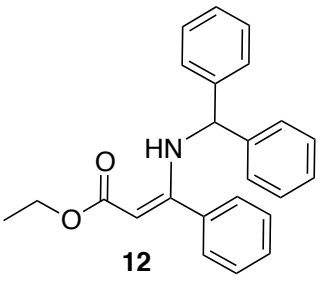


Racemate



Synthesis of Racemic Aziridines 6a-6h. The racemic aziridines **6a-6h** were prepared according to a published procedure[10] and used as references for the chiral HPLC determination of the enantiomeric purity of the catalysis products. The corresponding HPLC traces are shown above. Boron trifluoride ethyl etherate (0.11 mmol, 0.1 equiv) was added to a CH_2Cl_2 solution (10 ml) of the imine **5a-5h** (1.1 mmol, 1 equiv) and EDA (1 equiv), and the mixture was stirred for 2 h. The solvent was evaporated under reduced pressure, and the oily residue was subject to flash chromatography on silica (hexane/ethyl acetate 95:5) and cystallized from hexane. Yields were in the range 70–90%.

(*Z*)-Ethyl 3-(Benzhydrylamino)-3-phenylacrylate (12). The title compound was prepared as authentic sample to rule out its formation in imine aziridination with catalyst **4**PF_4 following a published procedure.[11] Diphenylmethaneamine (7.5 mL, 43.2 mmol, 5 equiv), ethyl 3-oxo3-phenylpropanoate (1.5 mL, 8.6 mmol, 1 equiv) and glacial acetic acid (2.5 mmol, 43.2 mmol, 5 equiv) were mixed at room temperature. Immediately, a light yellow precipitate formed. The identity of **12** was confirmed by the ^{1}H NMR spectrum, which showed the diagnostic broad doublet of the N*H* group. ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 5.61 (*d*, 1H, *J*= 10.06 Hz, C*H*Ph_2), 9.42 (*bd*, 1H, *J*= 10.08 Hz, N*H*).



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