**Transition Metal Catalyzed Synthesis and Reactivity of N-Alkenyl
Aziridines**

Shadi Dalili and Andrei K. Yudin*

*Department of Chemistry, University of Toronto, 80 St.
George Street, Toronto, Ontario M5S 3H6, Canada*

Supporting Information

Table of Contents:

General information	S2
Preparation of starting materials	S3-S7
Experimental procedures for N-alkenyl aziridines	S8-S14
Application of N-alkenyl aziridines	S15-S17
References	S18

General: In experiments requiring anhydrous solvents: ether, toluene, acetonitrile, and dichloromethane were purified using the method described by Grubbs (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518). Tetrahydrofuran (THF) was distilled over sodium-benzophenone ketyl under argon. Unless otherwise stated, all reactions were performed under nitrogen or argon atmosphere using flame-dried glassware.

Nuclear magnetic resonance spectra: ^1H and ^{13}C NMR spectra were recorded on either Mercury 300, Varian Gemini 300, or VRX-S (Unity) 400 spectrometer. ^1H NMR spectra were referenced to residual CDCl_3 (δ 7.27 ppm) and ^{13}C NMR spectra were referenced to CDCl_3 (δ 77.23 ppm). Peak multiplicities are designated by the following abbreviations: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets; dt, doublet of triplets; br, broad; and J , coupling constant in Hz.

Chromatography: Analytical thin layer chromatography (TLC) was performed on Macherey Nagel pre-coated glass-backed TLC plates (SIL G/UV₂₅₄, 0.25mm) purchased from Rose Scientific Limited and visualized by UV lamp (254 nm) or iodine. Solvent ratios for R_f values are reported as v/v. Column chromatography was carried out using aluminum oxide.

(3-But-3-enyl-*trans*-aziridin-2-yl)-phenylmethanone^{1,2} (5)

To a mixture of ethyl 4-pentenoate (10 g, 78 mmol) and toluene (100 mL), 1.5M DIBAL in toluene (57 mL, 86 mmol) was slowly added at -78°C , and the mixture was stirred for 1 hour at -78°C . To this reaction mixture, THF (240 mL), boron trifluoride diethyl ether (11 mL, 86 mmol), and 1-phenyl-1-trimethylsilyloxyethylene (16.5 g, 86 mmol) were successively added at -78°C , and the reaction mixture was allowed to warm up to around 0°C with stirring. After completion judged by TLC, 1N HCl (240 g), cooled in the ice bath, was added into the reaction mixture and separated to two layers and the water layer was extracted with toluene (50 mL). The combined organic layers were washed with water (150 mL) and dried over sodium sulfate. The solvent was removed in vacuo and the aldol product was obtained as crude yellow oil (16.2 g).

A mixture of this aldol (18.0 g), *p*-toluenesulfonic acid hydrate (16.7 g, 88 mmol), and toluene (200 mL) was heated to 40°C for 4 hours. After completion judged by TLC, sodium sulfate was added to the reaction mixture and filtered, and the solid residue was washed by toluene (40 mL). The solvent was removed from the filtrate in vacuo and α,β -unsaturated ketone was obtained as crude yellow oil (15.5 g).

A mixture of the unsaturated ketone (15.5 g), 12% NH_2OMe in ethanol (33 g, 84 mmol), and ethanol (100 mL) was heated to gentle reflux for 4 hours. After completion judged by TLC, the solvent was removed in vacuo. The residue was added to DMF (100 mL), and this solution was added to the mixture of sodium methoxide (9.3g, 172 mmol) and DMF (250 mL) at room temperature and the reaction mixture was stirred for 1 hour. Dichloromethane (1000 mL) and water (670 mL) was added to the reaction mixture, separated to two layers, and the water layer was extracted with dichloromethane (670 mL). The combined organic layers were washed with water (330 mL) and dried over sodium sulfate. The solvent was removed in vacuo and the residue was purified on a silica gel column (hexane/ethyl acetate = 7/3), to give 9.2 g of (3-but-3-enyl-*trans*-aziridin-2-yl)-phenylmethanone (**5**, total yield: 53% vs. ethyl 4-pentenoate).

^1H NMR (CDCl_3 , 300MHz): δ 8.00-8.03 (m, 2H), 7.58-7.64 (m, 1H), 7.48-7.53 (m, 2H), 5.76-5.90 (m, 1H), 4.95-5.06 (m, 2H), 3.27 (br, 1H), 2.11-2.29 (m, 4H), 1.65-1.72 (m, 2H); ^{13}C NMR (CDCl_3 , 75MHz): δ 197.3 137.7, 136.3, 133.9, 129.0, 128.4, 115.6, 42.9, 40.0, 32.8, 31.5.

Synthesis of (2*S*,3*R*)-2-phenyl-3-methyl-1-aziridine (**4**)³

To 76 mL of dry CHCl_3 , added 20 mmol of (1*S*,2*R*)-(+)-norephedrine and 26 mmol of PCl_5 . The mixture was stirred and refluxed for 1 h. The reaction was allowed to stand at room temperature for an additional hour and then the excess PCl_5 was decomposed with 16 mL of MeOH. Finally the solvent was removed *in vacuo* and the hydrochloride, (1*R*,2*R*)-(-)-1-chloro-1-phenyl-2-propylamine hydrochloride was obtained as a sticky

yellow solid. (65% yield). To a solution of 91 mL of NaOH (20%) was added 21.8 mmol of the hydrochloride salt, and the reaction was stirred at 80 °C for 2 h. The reaction was extracted with CHCl₃ (3 × 150 mL), the organic layers were dried over anhydrous sodium sulfate, filtered, and the solvent removed *in vacuo*. The viscous yellow oil was purified by silica gel column (1:1 hexanes:ethyl acetate), to obtain the product as a crystalline white solid. Yield: 50%. ¹H NMR (CDCl₃, 300 MHz): δ 7.31-7.33 (m, 5H), 3.26 (d, *J*=6.3 Hz, 1H), 2.40-2.44 (m, 1H), 0.92 (d, *J*=5.7 Hz, 3H); ¹³C NMR (CDCl₃, 167 MHz): δ 137.7, 127.9, 127.8, 126.6, 37.1, 32.2, 13.7; m.p. 65-66°C (Lit.³ 68°C)

Synthesis of 2-Bromo-1-decene⁴

To a flame-dried 2-neck, 250 mL flask added B-Br-9-BBN (3.62 g, 18 mmol) under N₂ flow. 100 mL of dichloromethane was added, after which the flask was cooled to 0 °C. To the well-stirred solution 1-decyne (2.7 mL, 15 mmol) was added dropwise, and the reaction mixture was stirred at 0 °C for 3 hrs. Acetic acid (10 mL) was added for protonation and the mixture stirred an additional 1 h. This was followed by the addition of 120 mL of 3M NaOH and 20 mL of 30% hydrogen peroxide. The mixture was stirred for 30 minutes at room temperature and the product was extracted 3 times with pure hexanes and the combined organic layers were washed with water, aqueous NaHCO₃, and then dried over MgSO₄. The organic layer was concentrated in *vacuo* and purified by column chromatography (silica gel, pure hexanes) to give 3.28 g of 2-bromo-1-decyne (71% yield) as a clear oil. ¹H NMR (CDCl₃, 300 MHz): δ 5.55 (s, 1H), 5.38 (s, 1H), 2.41 (t, *J*=7.5 Hz, 2H), 1.54-1.56 (m, 2H), 1.26-1.28 (m, 10H), 0.88 (t, *J*=5.7 Hz,

3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 135.2, 116.4, 41.6, 32.1, 29.5, 29.4, 28.6, 28.1, 22.9, 14.3.

Synthesis of *N,N*-Dibenzyl-(2-bromoallyl) amine⁵

To a solution of dibenzylamine (23.8 mL, 120 mmol) in dry ether (100 mL), added 2,3-dibromopropene (4.9 mL, 40 mmol) at room temperature. The reaction was stirred for 16 hrs. The white solid which precipitated was filtered and the filtrate concentrated in vacuo. The filtrate was purified by silica gel column (pure hexanes) to give the product as a yellowish oil (50% yield). ^1H NMR (CDCl_3 , 400 MHz): δ 7.22-7.42 (m, 10H), 5.95 (s, 1H), 5.60 (s, 1H), 3.62 (s, 4H), 3.26 (s, 2H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 138.9, 132.3, 128.8, 128.4, 127.2, 118.6, 61.6, 57.5.

Synthesis of 2,4,6-Trivinylcyclotriboroxane-Pyridine Complex⁶

A solution of trimethyl borate (5 mL, 44.6 mmol) in dry THF (37.5 mL) was cooled to -78 °C under N_2 in a dry ice-acetone bath. Vinylmagnesium bromide (25 mL of a 1.0 M solution in THF, 25 mmol) was added dropwise over 1h and the reaction stirred for a further 1h. Hydrochloric acid (1M, 12.5 mL) was added over 5 min and the solution removed from the cooling bath and allowed to warm to room temperature. Brine (10 mL) was added, the solution was extracted with diethyl ether (4×25 mL), and the

combined extracts were washed with water (25 mL) and brine (25 mL), dried over sodium sulfate, and concentrated under reduced pressure. The diethyl ether solution was treated with pyridine (5 mL) and stirred at r.t. for 4h. The solvents were evaporated under reduced pressure to give pale yellow oil. Distillation under reduced pressure (75-85°C, 0.1 Torr) gave the product as a white solid, 1.2 g, 75% yield. ^1H NMR (CDCl_3 , 400 MHz): δ 8.83-8.85 (m, 2H), 8.03-8.07 (m, 1H), 7.62-7.66 (m, 2H), 6.00-6.03 (m, 6H), 5.80-5.84 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 144.0, 141.0, 138.0 (broad), 131.5, 125.6; m.p. 48-49 °C (Lit.⁶ m.p. 46-48°C)

Synthesis of 7-azabicyclo[4.1.0]heptane

A mixture of cyclohexene oxide (30.1 g, 306 mmol) and NaN_3 (50.4 g, 775 mmol) in H_2O /acetone (1:1) was heated to reflux for 17 hrs. Acetone was removed by rotavapor vacuum, and the residue was extracted with *tert*-butyl methyl ether (3×160 mL) and dichloromethane (3×160 mL). The combined organic phases were washed with water, and dried over MgSO_4 . The solvent was removed in vacuo and the azido alcohol was obtained as an almost pure yellow oil (40 g, 283 mmol, 93%), which was reacted without further purification. PPh_3 (57.7 g, 220 mmol) was added to a solution of azido-cyclohexanol (31.1 g, 220 mmol) in *tert*-butyl methyl ether (250 mL). N_2 evolved from the mixture, and after heating to reflux for 16 hr, the solvent was removed through distillation at 760 mmHg. Continued distillation under reduced pressure yielded compound **1b** (16.8 g, 173 mmol, 79%) as a colorless liquid, which solidified at 0°C. ^1H NMR (CDCl_3 , 400 MHz): δ 3.21 (d, 1H, $J=2$ Hz), 2.17 (s, 2H), 1.80 (s, 4H), 1.34-1.16 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 29.5, 24.8, 20.4

Typical procedure for the Pd-catalyzed synthesis of N-alkenyl aziridines (Table 1,

Entry 1):

A flame-dried Schlenk flask under argon atmosphere was charged with (±)-BINAP (6 mol%), $\text{Pd}_2(\text{dba})_3$ (2 mol%), NaO^tBu (1.4 eq.) and dry, degassed toluene (4 mL for every 1 mmol of alkenyl bromide). After stirring at room temperature about 10 min, the alkenyl bromide (1 eq.) and the aziridine (1.1 eq.) were added under argon and the flask was immersed in an oil bath and heated to 90 °C with stirring until the starting alkenyl bromide had been completely consumed as judged by GC and TLC analysis. All reactions were generally completed after 24 hrs unless otherwise stated. The mixture was then allowed to cool to room temperature, and diluted with hexanes (15 mL for every 1 mmol of alkenyl bromide), and filtered through Celite®. The solvent were evaporated *in vacuo*, and the residue redissolved in hexanes (15 mL for every 1 mmol of alkenyl bromide), filtered again through celite and concentrated under reduced pressure and dried under high vacuum to remove any excess aziridine. This afforded a residue which consisted of the essentially pure N-alkenyl aziridine, which could be purified further by Kugelrohr distillation under high vacuum (dependent on the boiling point and amount of product obtained in case of very small scale reaction).

2-Methyl-1-(1-phenylvinyl) aziridine (2a)

Obtained in 75% yield as a light yellow oil after Kugelrohr distillation (150 °C). ^1H

NMR (CDCl₃, 300 MHz): δ 7.61-7.65 (m, 2H), 7.30-7.37 (m, 3H), 4.89 (s, 1H), 4.49 (s, 1H), 1.87-1.92 (m, 3H), 1.30 (d, $J=5.0$ Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 157.6, 138.6, 128.3, 128.2, 126.2, 95.4, 35.1, 34.8, 18.2; HR-MS (EI) m/z : calcd. for C₁₁H₁₃N 159.2309, found 159.1045.

***Trans*-2-Methyl-1-styryl aziridine [(*E*)-2b]**

Obtained in 67% yield as a light yellow oil after column chromatography on aluminum oxide (hexanes/ethyl acetate = 8/2). ¹H NMR (CDCl₃, 400 MHz): δ 7.12-7.26 (m, 5H), 6.83 (d, $J=14$ Hz, 1H), 5.98 (d, $J=14$ Hz, 1H), 1.96-1.99 (m, 1H), 1.89-1.93 (m, 1H), 1.83-1.85 (m, 1H), 1.29 (d, $J=5.6$ Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ 142.3, 137.1, 128.7, 126.2, 125.4, 116.7, 35.3, 35.1, 18.0; HR-MS (EI) m/z : calcd. for C₁₁H₁₃N 159.2309, found 159.1050.

7-(1-Phenylvinyl)-7-azabicyclo[4.1.0]heptane (1a)

Obtained in 69% yield as a light yellow oil after Kugelrohr distillation (180 °C). ¹H NMR (CDCl₃, 400 MHz): δ 7.59-7.63 (m, 2H), 7.31-7.35 (m, 3H), 4.85 (s, 1H), 4.48 (s, 1H), 1.98-2.04 (m, 4H), 1.77-1.82 (m, 2H), 1.61-1.65 (m, 2H), 1.35-1.38 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 158.5, 138.8, 128.2, 128.1, 126.4, 94.7, 38.5, 24.5, 20.6; HR-MS (EI) m/z : calcd. for C₁₄H₁₇N 199.2957, found 200.1439 (M+H⁺).

***Trans*-7-Styryl-7-azabicyclo[4.1.0]heptane [(*E*)-1b]**

Obtained in 65% yield as a light yellow oil after Kugelrohr distillation (200°C). ¹H NMR (CDCl₃, 400 MHz): δ 7.21-7.25 (m, 4H), 7.10-7.12 (m, 1H), 6.84 (d, *J*=14Hz, 1H), 5.96 (d, *J*=14Hz, 1H), 2.09-2.10 (m, 2H), 1.90-1.97 (m, 2H), 1.82-1.84 (m, 2H), 1.40-1.45 (m, 2H), 1.24-1.27 (m, 2H); ¹³C NMR (CDCl₃, 100 MHz): δ 143.1, 137.3, 128.7, 125.9, 125.3, 115.9, 39.1, 24.5, 20.5; HR-MS (EI) *m/z*: calcd. for C₁₄H₁₇N 199.2957, found 199.1358.

1-(1-Phenylvinyl) aziridine-2-carboxylic acid methyl ester (3a)

Obtained in 65% yield as a light yellow oil after Kugelrohr distillation (192°C). ¹H NMR (CDCl₃, 400 MHz): δ 7.57 (d, *J*=7.2 Hz, 2H), 7.32 (d, *J*=6.4 Hz, 3H), 4.96 (s, 1H), 4.58 (s, 1H), 3.74 (s, 3H), 2.56 (s, 1H), 2.48 (s, 1H), 2.16 (d, *J*=6.4 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ 170.5, 155.4, 137.2, 128.6, 128.4, 125.9, 96.8, 52.4, 37.2, 34.2; HR-MS (EI) *m/z*: calcd. for C₁₂H₁₃NO₂ 203.2408, found 203.0952.

***Trans*-1-Styrylaziridine-2-carboxylic acid methyl ester [(*E*)-3b]**

Obtained in 60% yield as a light yellow oil after column chromatography on aluminum oxide (hexanes/ethyl acetate = 8/2). ¹H NMR (CDCl₃, 400 MHz): δ 7.17-7.29 (m, 5H),

6.78 (d, $J=14\text{Hz}$, 1H), 6.08 (d, $J=14\text{Hz}$, 1H), 3.79 (s, 3H), 2.59 (dd, $J_1=6\text{Hz}$, $J_2=2.8\text{ Hz}$, 1H), 2.51 (dd, $J_1=3.2\text{ Hz}$, $J_2=1.6\text{ Hz}$, 1H), 2.17 (d, $J=6.4\text{Hz}$, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 170.4, 139.7, 136.1, 128.8, 126.9, 125.7, 118.4, 52.6, 37.3, 34.4; HR-MS (FAB) m/z : calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2$ 203.2408, found 203.0946.

3-Methyl-1-(1-methylpropenyl)-2-phenyl aziridine (4e)

Obtained in 85% yield as a light yellow oil after work-up of reaction mixture. ^1H NMR (CDCl_3 , 300 MHz): δ 7.25-7.39 (m, 5H), 4.61-4.66 (m, 1H), 3.08 (d, $J=6.3\text{Hz}$, 1H), 2.32-2.37 (m, 1H), 1.79 (s, 3H), 1.60 (d, $J=6.5\text{ Hz}$, 3H), 1.02 (d, $J=5.7\text{ Hz}$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 145.2, 136.9, 127.5, 127.3, 126.3, 104.7, 45.3, 41.0, 19.9, 12.9, 11.9; HR-MS (EI) m/z : calcd. for $\text{C}_{13}\text{H}_{17}\text{N}$ 187.2847, found 187.1358.

3-Methyl-2-phenyl-1-(1-phenylvinyl) aziridine (4a)

Obtained in 64% yield as a light yellow oil after work-up of reaction mixture. ^1H NMR (CDCl_3 , 500 MHz): δ 7.09-7.28 (m, 10H), 4.79 (s, 1H), 4.48 (s, 1H), 2.91 (d, $J=7\text{Hz}$, 1H), 2.09-2.11 (m, 1H), 0.95 (d, $J=6\text{Hz}$, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 158.0, 138.1, 136.9, 128.2, 128.19, 128.09, 127.8, 126.9, 126.3, 95.1, 46.1, 42.1, 13.0; HR-MS (EI) m/z : calcd. for $\text{C}_{17}\text{H}_{17}\text{N}$ 235.3287, found 236.1434 $[\text{M}+\text{H}]^+$.

Trans-3-Methyl-2-phenyl-1-propenyl aziridine [(E)-4d]

Obtained in 65% yield (reaction heated for 48 hrs) as a light yellow oil after column chromatography on aluminum oxide (hexanes). ^1H NMR (CDCl_3 , 300 MHz): δ 7.14-7.23 (m, 5H), 6.06 (d, $J=13.5$ Hz, 1H), 4.99-5.10 (m, 1H), 2.81 (d, $J=6.3$ Hz, 1H), 2.04-2.10 (m, 1H), 1.53 (dd, $J_1=1.35$ Hz, $J_2=6.6$ Hz, 3H), 0.89 (d, $J=5.7$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 142.5, 137.1, 128.0, 127.8, 126.8, 110.4, 46.1, 41.9, 14.7, 13.1; HR-MS (EI) m/z : calcd. for $\text{C}_{12}\text{H}_{15}\text{N}$ 173.2578, found 173.1208.

Trans-3-Methyl-2-phenyl-1-styryl aziridine [(E)-4b]

Obtained in 68% yield as a light yellow oil after work-up of reaction mixture. ^1H NMR (CDCl_3 , 300 MHz): δ 7.24-7.36 (m, 10H), 7.0 (d, $J=13.8$ Hz, 1H), 6.08 (d, $J=13.8$ Hz, 1H), 3.11 (d, $J=6.6$ Hz, 1H), 2.32-2.40 (m, 1H), 1.06 (d, $J=5.7$ Hz, 3H); ^{13}C NMR (CDCl_3 , 75 MHz): δ 142.3, 136.9, 136.7, 128.8, 128.3, 127.9, 127.2, 126.3, 125.4, 116.1, 46.5, 42.4, 13.1; HR-MS (EI) m/z : calcd. for $\text{C}_{17}\text{H}_{17}\text{N}$ 235.3287, found 235.1362.

3-Methyl-1-(2-methylpropenyl)-2-phenyl aziridine (4c)

Obtained in 70% yield as a light yellow oil after column chromatography on aluminum

oxide (hexanes/ethyl acetate = 9/1). ^1H NMR (CDCl_3 , 300 MHz): δ 7.13-7.30 (m, 5H), 5.56 (s, 1H), 2.82 (d, $J=6.6$ Hz, 1H), 2.04-2.12 (m, 1H), 1.64 (s, 3H), 1.54 (s, 3H), 0.91 (d, $J=5.4$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 137.4, 136.9, 128.0, 127.8, 126.8, 121.9, 48.1, 43.8, 22.3, 17.4, 13.1; HR-MS (EI) m/z : calcd. for $\text{C}_{13}\text{H}_{17}\text{N}$ 187.2847, found 187.1366.

Typical procedure for the Cu-catalyzed synthesis of N-alkenyl aziridines (Table 2, Entry 1):

To the mixture of alkenylboronic acid (3 mmol), $\text{Cu}(\text{OAc})_2$ (0.2 mmol), and myristic acid (0.4 mmol) were successively added toluene (4 mL), 2,6-lutidine (2 mmol), and the respective aziridine (2 mmol). The reaction mixture was stirred at room temperature for 24 hrs, diluted with ethyl acetate (20 mL), filtered through a plug of silica gel, and then purified on an aluminum oxide column or on aluminum oxide prep TLC plate.

1-Hex-1-enyl-3-methyl-2-phenyl aziridine (4f)

Obtained in 50% yield as a light yellow oil after purification by chromatography on aluminum oxide prep TLC plate (hexanes/ethyl acetate = 9/1). ^1H NMR (CDCl_3 , 500 MHz): δ 7.18-7.31 (m, 5H), 6.13 (d, $J=13$ Hz, 1H), 5.07-5.13 (m, 1H), 2.86 (d, $J=6.5$ Hz, 1H), 2.10-2.13 (m, 1H), 1.93-1.96 (m, 2H), 1.29-1.31 (m, 4H), 0.97 (d, $J=6$ Hz, 3H), 0.87-0.89 (m, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 141.7, 137.1, 128.0, 127.8,

126.8, 116.0, 46.2, 41.9, 32.5, 29.3, 22.2, 14.1, 13.1; HR-MS (EI) m/z : calcd. for $C_{15}H_{21}N$ 215.3385, found 215.1670.

7-(2-*p*-Tolylvinyl)-7-azabicyclo[4.1.0]heptane (1c)

Obtained in 40% yield as a white solid after purification by chromatography on aluminum oxide prep TLC plate (hexanes). 1H NMR ($CDCl_3$, 400 MHz): δ 7.12 (d, $J=8.4$ Hz, 2H), 7.05 (d, $J=8.4$ Hz, 2H), 6.79 (d, $J=14$ Hz, 1H), 5.95 (d, $J=14$ Hz, 1H), 2.29 (s, 3H), 1.83-1.95 (m, 5H), 1.24-1.43 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.3, 135.7, 134.5, 129.4, 125.2, 115.9, 39.1, 24.5, 21.3, 20.5; HR-MS (EI) m/z : calcd. for $C_{15}H_{19}N$ 213.3226, found 213.1514. m.p. 54-55°C.

3-Methyl-2-phenyl-1-vinyl aziridine (4g)

Obtained by using 2,4,6-trivinylcyclotriboroxane pyridine complex as source of vinyl moiety gave product in 30% yield as a clear oil after purification by column chromatography on aluminum oxide (hexanes). 1H NMR ($CDCl_3$, 500 MHz): δ 7.31-7.32 (m, 5H), 6.48 (dd, $J_1=15$ Hz, $J_2=7.5$ Hz, 1H), 4.57 (d, $J=15$ Hz, 1H), 4.43 (d, $J=7.5$ Hz, 1H), 2.96 (d, $J=6.5$ Hz, 1H), 2.19-2.23 (m, 1H), 0.99 (d, $J=5.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.4, 136.9, 128.1, 127.8, 127.0, 98.4, 45.7, 41.5, 13.1; HR-MS (EI) m/z : calcd. for $C_{11}H_{13}N$ 159.2309, found $[M+H]^+$ 160.1123.

General procedure for reaction of N-alkenyl aziridines with DMAD:

Method A⁷: To a flame-dried sealed tube under argon, added N-alkenyl aziridine (0.63

mmol) and degassed toluene (3 mL). Then $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was added (0.03 mmol, 5 mol%) under argon and the mixture was heated to 60°C in an oil bath. A solution of DMAD (1.26 mmol) in 3 mL of toluene was taken up in a syringe and added slowly via syringe pump to the reaction mixture (rate of flow: 0.85 mL/1 h). The reaction was heated at 60°C for 24 hrs until no more N-alkenyl aziridine was observed by GC analysis. The reaction mixture was cooled to room temperature and concentrated *in vacuo* and purified by column chromatography.

Method B: The procedure is same as Method A, except $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was eliminated from the reaction mixture (i.e. no metal catalyst).

Method C: The procedure is same as Method B, except the ratio of N-alkenyl aziridine to DMAD is 1:1, not 1:2 as is the case in Method B.

4-Methyl-1-(1-phenylvinyl)-4,5-dihydro-1H-pyrrole-2,3-dicarboxylic acid dimethyl ester and 5-Methyl-1-(1-phenylvinyl)-4,5-dihydro-1H-pyrrole-2,3-dicarboxylic acid dimethyl ester

All three procedures gave the product in 80% yield as an inseparable mixture of diastereomers (yellowish/orange oil) after purification by column chromatography on aluminum oxide (hexanes/ethyl acetate = 6/4). ^1H NMR (CDCl_3 , 400 MHz): δ 7.21-7.38 (m, 10H), 6.59 (d, $J=1.6$ Hz, 1H), 6.03 (d, $J=1.6$ Hz, 1H), 5.94 (d, $J=1.6$ Hz, 1H), 5.26 (d, $J=1.6$ Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H), 3.44 (s, 3H), 2.24-2.28 (m, 1H), 2.21 (d, $J=4$ Hz, 1H), 2.16-2.19 (m, 1H), 2.14 (d, $J=6$ Hz, 1H), 1.89 (d, $J=6.4$ Hz,

1H), 1.87 (d, $J=3.6$ Hz, 1H), 1.25 (d, $J=5.6$ Hz, 3H), 1.10 (d, $J=5.6$ Hz, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 168.1, 168.0, 167.0, 166.2, 164.4, 164.1, 139.1, 138.8, 138.4, 136.7, 129.8, 128.4, 128.27, 128.26, 128.1, 128.0, 127.9, 111.8, 111.1, 52.4, 52.2, 51.7, 51.4, 39.7, 39.2, 38.3, 36.9, 18.3, 18.1; HR-MS (EI) m/z : calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_4$ 301.3422, found 301.2656.

1-(1-Phenylvinyl)-4,5-dihydro-1H-pyrrole-2,3,4-tricarboxylic acid trimethyl ester and 1-(1-Phenylvinyl)-4,5-dihydro-1H-pyrrole-2,3,5-tricarboxylic acid trimethyl ester

All three procedures gave the product in 65% yield as an inseparable mixture of diastereomers (yellowish/orange oil) after purification by column chromatography on aluminum oxide (hexanes/ethyl acetate = 6/4). ^1H NMR (CDCl_3 , 500 MHz): δ 7.24-7.40 (m, 10H), 6.56 (d, $J=1$ Hz, 1H), 6.06 (d, $J=1$ Hz, 1H), 5.97 (d, $J=1\text{Hz}$, 1H), 5.26 (d, $J=1\text{Hz}$, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.71 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H), 3.45 (s, 3H), 3.09 (dd, $J_1=5.75$ Hz, $J_2=2.5$ Hz, 1H), 2.81 (dd, $J_1=5.75$ Hz, $J_2=2.5$ Hz, 1H), 2.53 (d, $J=3$ Hz, 1H), 2.42 (d, $J=3$ Hz, 1H), 2.27 (d, $J=6$ Hz, 1H), 2.18 (d, $J=6$ Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 169.8, 169.4, 167.6, 167.5, 166.4, 165.8, 161.1, 160.5, 138.0, 137.9, 137.5, 136.0, 130.4, 130.3, 128.8, 128.5, 128.1, 128.09, 126.9, 114.0, 113.6, 113.2, 52.6, 52.5, 52.2, 51.9, 51.7, 42.4, 39.9, 36.6, 35.5, 29.9; HR-MS (EI) m/z : calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_6$ 345.3520, found 345.1204.

General procedure for thermal rearrangement of N-alkenyl aziridines:

A solution of N-alkenyl aziridine (0.3 mmol) and thiophene or furan (0.5 mmol) in xylenes (1 mL) was heated in a sealed tube to 135°C for 24 hrs. The reaction went to full conversion after overnight heating as determined by GC analysis. The solvent was evaporated under high vacuum, and product was obtained in quantitative yield. ¹H NMR (CDCl₃, 300 MHz): δ 7.79-7.82 (m, 2H), 7.37-7.39 (m, 3H), 6.06-6.18 (m, 1H), 5.25 (dd, *J*₁ = 17.1 Hz, *J*₂ = 2.1 Hz, 1H), 5.15 (dd, *J*₁ = 10.5 Hz, *J*₂ = 1.8 Hz, 1H), 4.18 (d, *J* = 6 Hz, 2H), 2.25 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ 15.9, 54.8, 115.4, 126.8, 128.4, 128.5, 129.8, 136.2, 166.1.

¹ Seko, S.; Tani, N. *Tetrahedron Lett.* **1998**, 39, 8117.

² Sasaki, M.; Yudin, A. K. *Synlett* **2004**, 2443.

³ Galindo, A.; Orea, L.F.; Gnecco, D.; Enriquez, R.G.; Toscano, R.A.; Reynolds, W.F. *Tetrahedron: Asymm.* **1997**, 8, 2877.

⁴ Hara, S.; Dojo, H.; Takinami, S.; Suzuki, A. *Tetrahedron Lett.* **1983**, 24, 731.

⁵ Barluenga, J.; Canteli, R.M.; Florez, J.; Garcia-Granda, S.; Rodriguez, A.G.; Martin, E. *J. Am. Chem. Soc.* **1998**, 120, 2514.

⁶ Kerins, F.; O'Shea, D.F. *J. Org. Chem.* **2002**, 67, 4968.

⁷ Wender, P.A.; Pederson, T.M.; Scanio, M.J.C. *J. Am. Chem. Soc.* **2002**, 124, 15154